Supporting Information

Isomeric Dithienophosphepines: The Impact of Ring Fusion on Electronic and Structural Properties

Kevin Padberg,[b] Johannes D. R. Ascherl,[a] Frank Hampel,[b] and Milan Kivala*[a]

c chem_201905429_sm_m miscellaneous_information.pdf
Table of Contents

1. Experimental Details 2
2. Experimental Procedures 3
3. Nuclear Magnetic Resonance Spectra 8
4. X-ray Crystallographic Analysis 23
5. UV-Vis Spectroscopy 27
6. Cyclic Voltammetry 28
7. Theoretical Calculations 29
8. Cartesian (XYZ) Coordinates 30
9. References 34
SUPPORTING INFORMATION

1. Experimental Details

Reagents were purchased at reagent grade from commercial suppliers and used without further purification. THF and EtOAc were dried over KOH and subsequently distilled over sodium metal. Complete dryness was indicated by the dark blue benzophenone ketyl radical anion. CH2Cl2 was dried over CaCl2 and subsequently distilled over NaH. Toluene was dried over molecular sieve (4 Å) and subsequently distilled over sodium metal. MgSO4 was used as the drying agent after aqueous workup.

(Z)-1,2-Bis(2-bromothiophene-3-yl)ethene (2) and (Z)-1,2-bis(3-bromothiophene-2-yl)ethene (3) were prepared according to a literature-known procedure.[1]

All reactions involving oxygen- or moisture-sensitive compounds were carried out in a dry reaction vessel under an inert atmosphere of nitrogen or argon using anhydrous solvents and standard Schlenk techniques. All oxygen- and moisture-sensitive liquids and anhydrous solvents were transferred via syringe or stainless steel cannula. Analytical TLC analysis was performed on aluminum plates coated with 0.20 mm silica gel containing a fluorescent indicator (Macherey-Nagel, ALUGRAM® SIL G/UV254) or on aluminum plates coated with 0.20 mm aluminum oxide containing a fluorescent indicator (Macherey-Nagel, ALUGRAM® ALOX N/UV254). TLC plates were visualized by exposure to UV light (λ = 254 nm and 366 nm). Column chromatography was performed on silica gel (Macherey-Nagel, M-N Silica Gel 60A, 230-400 mesh) or aluminum oxide (Macherey-Nagel, M-N Aluminum oxide neutral, 90A, 50-200 mesh).

Melting points were determined using a Büchi M-560 melting point apparatus in open capillaries. “Decomp.” refers to decomposition.

1H, 13C, and 31P NMR spectra were recorded on a Bruker Avance 400 (400 MHz for 1H, 101 MHz for 13C, and 162 MHz for 31P) and a Bruker Avance 300 (300 MHz for 1H, 75 MHz for 13C, and 121 MHz for 31P) spectrometer. Chemical shifts (δ) are reported in ppm and were referenced to the residual solvent signal as an internal reference (CD2Cl2: 5.32 ppm for 1H, 53.8 ppm for 13C; CDCl3: 7.24 ppm for 1H, 77.2 ppm for 13C). Chemical shifts (δ) in 31P NMR spectra are reported as observed. 13C NMR spectra of phosphorus compounds were acquired with 31P decoupling. Coupling constants (J) are given in Hz and the apparent resonance multiplicity is reported as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet) or m (multiplet). Signals of solvents and impurities are assigned according to literature.[2] All spectra were recorded at ambient probe temperature.

IR spectra were recorded on a Varian 660-IR spectrometer in ATR mode and characteristic IR absorptions are reported in cm⁻¹ and labelled as strong (s), medium (m), weak (w), and very weak (vw).

Mass spectra were recorded on a Bruker MicroTOF II (HR ESI and APPI) or a Bruker UltraflexTOF/TOF (HR MALDI) mass spectrometer at the Institute of Organic Chemistry, University of Erlangen-Nürnberg.

UV-Vis absorption measurements were carried out on a Varian Cary 5000 UV-Vis-NIR spectrophotometer. Emission measurements were acquired on a JASCO FP-8500 spectrofluorometer. Spectra were recorded in 10 mm quartz cuvettes at rt. Fluorescence quantum yields (ΦF) were determined from the direct and indirect excitation spectra and the incident light spectra using a JASCO FP-8500 spectrofluorometer with a JASCO ILF-835 100mm integrating sphere. Absorption (λmax) and emission maxima (λem) are reported in nm with the extinction coefficient given in M⁻¹ cm⁻¹.

Electrochemical measurements were carried out at room temperature in THF, containing 0.1 M n-Bu4NPF₆ in a standard three-electrode cell. The supporting electrolyte n-Bu4NPF6 was purchased in electrochemical grade from commercial suppliers and used as received. The working electrode was a Pt electrode (3 mm in diameter), the auxiliary electrode was a Pt wire, and the reference electrode was a Ag/AgNO₃ electrode. All potentials are referenced against the ferrocene/ferrocinium (Fc/Fc⁺) couple, used as internal standard, and are uncorrected from ohmic drop. The cell was connected to BAS CV 50 W version 2.

Single crystals suitable for X-ray crystallographic analysis were mounted on a loop on a SuperNova, Dual, Cu at zero, Atlas diffractometer. Structures were solved with the ShelX structure solution program using direct methods and refined with the ShelXL refinement package using least squares minimization. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed according to a riding model refinement routine. CCDC 1961144-1961149 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif).
All compounds were named in accordance with IUPAC standards, except for thiophene-fused phosphepines, which are referred to as dithienophosphepines rather than phosphepinodithiophenes, to highlight the central phosphepine as the main focus of this work.

2. Experimental Procedures

\[ \text{4α} \rightarrow \text{1α} \]

\[ \text{4β} \rightarrow \text{1β} \]

\[ \text{5α} \rightarrow \text{5β} \]

\[ \text{6α} \rightarrow \text{6β} \]

\[ \text{P-Phenyldithieno[2,3-b:3',2'-f]phosphepine (1a).} \]
To a stirred solution of 4α (428 mg, 1.37 mmol) in toluene (30 mL) was added DABCO (769 mg, 6.85 mmol). After completion (TLC, 1 h), the reaction was quenched via addition of aq. HCl (5 wt. %, 20 mL) and extracted with CH₂Cl₂ (2 x 30 mL). The combined organic phases were dried (MgSO₄), filtered, and the solvent was removed under reduced pressure to give 1α (394 mg, 96%) as a colorless solid.

m.p. 137–139 °C; Rᵣ = 0.59 (SiO₂, hexanes/CH₂Cl₂ 2:1); \(^{1}H\) NMR (300 MHz, CDCl₃) \(\delta\) 7.49 (dd, \(J = 6.2, 5.1\) Hz, 2H), 7.16 (d, \(J = 5.0\) Hz, 2H), 7.13–7.11 (m, 3H), 6.95–6.89 (m, 2H), 6.75 (s, 2H) ppm; \(^{31}P\) \(^{1}H\) NMR (101 MHz, CDCl₃) \(\delta\) 144.9, 138.0, 132.3, 131.0, 130.5, 130.2, 128.1, 127.9, 125.5 ppm; \(^{31}P\) NMR (121 MHz, CDCl₃) \(\delta\) –55.6 ppm; IR (ATR) \(\tilde{\nu}\) 3094 (vw), 3061 (vw), 2920 (vw), 2851 (vw), 1518 (w), 1498 (w), 1475 (m), 1429 (m), 1396 (m), 1338 (w), 1029 (m), 1026 (m) cm\(^{-1}\); UV-Vis (CH₂Cl₂) \(\lambda_{\text{max}} (\epsilon)\) 306 (4900) nm; APPI HRMS (toluene) \(m/z\) calcd. for C₁₆H₁₂PS₂ [M+H]\(^{+}\) 299.0113, found 299.0110.
**P-Phenyldithieno[3,2-b:2',3'-f]phosphepine (1β).** To a stirred solution of 4β (210 mg, 0.673 mmol) in toluene (15 mL) was added DABCO (377 mg, 3.36 mmol). After completion (TLC, 4 h), the reaction was quenched via addition of aq. HCl (5 wt. %, 20 mL) and extracted with CH₂Cl₂ (2 x 20 mL). The combined organic phases were dried (MgSO₄), filtered, and the solvent was removed under reduced pressure. The residue was dissolved in minimal amount of CH₂Cl₂, filtered through a short pad of SiO₂, and eluted with CH₂Cl₂ (80 mL). Solvent removal afforded 1β (183 mg, 91%) as a yellow solid.

**P-Phenyldithieno[2,3-b:3',2'-f]phosphepine-P-borane (4α).** To a solution of 2 (853 mg, 2.44 mmol) in dry Et₂O (30 mL) at −78 °C was added dropwise t-BuLi (1.9 m in n-pentane, 3.9 mL, 7.3 mmol) and stirred for 45 min. Dichlorophenylphosphine (436 mg, 0.330 mL, 2.44 mmol) was added and the reaction mixture was stirred for 5.5 h at rt. Borane dimethylsulfide (222 mg, 0.277 mL, 2.92 mmol) was added and the mixture was stirred for 16 h. The reaction was quenched via dropwise addition of H₂O (30 mL) and the phases were separated. The aqueous phase was extracted with CH₂Cl₂ (40 mL) and both organic phases were separately washed with sat. aq. NaCl (40 mL each). The combined organic phases were dried (MgSO₄) and filtered. Solvent removal and purification by column chromatography (SiO₂, hexanes/CH₂Cl₂ 1:1) afforded 4α (350 mg, 46%) as an ivory solid.

**P-Phenyldithieno[3,2-b:2',3'-f]phosphepine-P-borane (4β).** To a solution of 3 (488 mg, 1.39 mmol) in dry Et₂O (15 mL) at −78 °C was added dropwise t-BuLi (1.9 m in n-pentane, 2.2 mL, 4.2 mmol) and stirred for 45 min. Dichlorophenylphosphine (249 mg, 0.190 mL, 1.39 mmol) was added and the reaction mixture was stirred for 6 h at rt. Borane dimethylsulfide (127 mg, 0.160 mL, 1.67 mmol) was added and the mixture was stirred for 16 h. The reaction was quenched via dropwise addition of H₂O (15 mL) and the phases were separated. The aqueous phase was extracted with CH₂Cl₂ (20 mL) and both organic phases were separately washed with sat. aq. NaCl (20 mL each). The combined organic phases were dried (MgSO₄) and filtered. Solvent removal and purification by column chromatography (SiO₂, CH₂Cl₂) afforded 4β (302 mg, 69%) as a yellowish solid.
**SUPPORTING INFORMATION**

**P-Phenyldithieno[2,3-b:3’,2’-f]phosphepine-P-oxide (5a).** To a solution of 1α (342 mg, 1.15 mmol) in CH₂Cl₂ (20 mL) was added aq. H₂O₂ (30 wt. %, 1.17 mL, 11.5 mmol) and stirred for 16 h. The reaction was quenched via addition of H₂O (20 mL), the phases were separated, and the aqueous phase was extracted with CH₂Cl₂ (20 mL). The combined organic phases were washed with H₂O (40 mL), dried (MgSO₄), filtered, and the solvent was removed in vacuo. The crude product was dissolved in CH₂Cl₂ (5 mL) and a solid was precipitated by the addition of hexanes (50 mL) and concentration under reduced pressure. Filtration and washing with hexanes (2 x 20 mL) afforded 5α (294 mg, 82%) as a colorless solid.

m.p. 206–208 °C; Rf = 0.60 (SiO₂, CH₂Cl₂/MeOH 15:1); ¹H NMR (300 MHz, CDCl₃) δ 7.70–7.62 (m, 4H), 7.53–7.48 (m, 1H), 7.44–7.38 (m, 2H), 7.27 (q, J = 2.5 Hz, 2H), 7.06 (s, 2H) ppm; ³¹C(³¹P, ¹H) NMR (101 MHz, CDCl₃) δ 143.1, 133.8, 132.7, 132.1, 131.9, 131.0, 128.9, 128.8, 128.5 ppm; ³¹P NMR (121 MHz, CDCl₃) δ 11.4 ppm; IR (ATR) 3064 (w), 3032 (w), 1502 (w), 1479 (w), 1435 (w), 1406 (m), 1346 (m), 1313 (s), 1113 (s), 801 (s), 720 (s) cm⁻¹; UV-Vis (CH₂Cl₂) λmax (ε) 314 (7800) nm; APPI HRMS (toluene) m/z calcd. for C₁₈H₁₂OPS₂ [M+H⁺] 315.0062, found 315.0064.

**P-Phenyldithieno[3,2-b:2’,3’-f]phosphepine-P-oxide (5β).** To a solution of 1β (100 mg, 0.335 mmol) in CH₂Cl₂ (10 mL) was added aq. H₂O₂ (30 wt. %, 0.340 mL, 3.35 mmol) and stirred for 16 h. The reaction was quenched via addition of H₂O (10 mL), the phases were separated, and the aqueous phase was extracted with CH₂Cl₂ (10 mL). The combined organic phases were washed with H₂O (20 mL), dried (MgSO₄), and filtered. Solvent removal afforded 5β (98.0 mg, 93%) as a yellowish solid.

m.p. 158–160 °C; Rf = 0.39 (SiO₂, CH₂Cl₂/MeOH 15:1); ¹H NMR (300 MHz, CDCl₃) δ 7.65–7.57 (m, 2H), 7.52–7.38 (m, 5H), 7.29 (t, J = 5.0 Hz, 2H), 7.01 (s, 2H) ppm; ³¹C(³¹P, ¹H) NMR (101 MHz, CDCl₃) δ 145.5, 134.7, 132.2, 131.8, 131.6, 131.0, 128.8, 128.7, 121.6 ppm; ³¹P NMR (121 MHz, CDCl₃) δ 13.0 ppm; IR (ATR) 3090 (w), 2957 (vw), 1488 (w), 1437 (w), 1398 (m), 1259 (m), 1185 (s), 1146 (s), 1124 (s), 720 (s) cm⁻¹; UV-Vis (CH₂Cl₂) λmax (ε) 345 (14500) nm; APPI HRMS (toluene) m/z calcd. for C₁₈H₁₂OPS₂ [M+H⁺] 315.0062, found 315.0061.

**2,2’-Bis(phenylethynyl)-P-phenyldithieno[2,3-b:3’,2’-f]phosphepine-P-oxide (6α).** A microwave vessel under Ar atmosphere was charged with Pd₂(dba)₃ (209 µg, 0.229 µmol), Cs₂CO₃ (62.2 mg, 191 µmol), PivOH (39.0 mg, 382 µmol), Ag₂O (66.4 mg, 286 µmol), and 5α (30.0 mg, 95.4 µmol). Dry DME (1 mL), Et₃N (9.66 mg, 13.3 µL, 95.4 µmol), and phenylacetylene (19.5 mg, 21.0 µL, 191 µmol) were added. The vessel was sealed and heated to 100 °C for 16 h. The reaction mixture was allowed to cool to rt, filtered through a short pad of SiO₂, and eluted
2,2'-Bis(phenylethynyl)-P-phenyldithieno[3,2-b:2',3'-f]phosphepine-P-oxide (6β). A microwave vessel under Ar atmosphere was charged with Pd2(dba)3 (291 µg, 0.319 µmol), Cs2CO3 (20.7 mg, 63.6 µmol), PinOH (13.0 mg, 127 µmol), Ag2O (22.1 mg, 95.4 µmol), and 5β (10.0 mg, 31.8 µmol). Dry DME (0.5 mL), Et3N (3.22 mg, 4.43 µL, 31.8 µmol), and phenylacetylene (8.12 mg, 8.73 µL, 79.5 µmol) were added. The vessel was sealed and heated to 100 °C for 19 h. The reaction mixture was allowed to cool to rt, filtered through a short pad of SiO2, and eluted with EtOAc (80 mL). Purification by column chromatography (SiO2, hexanes/EtOAc 1:1) afforded 6β (7.3 mg, 45%) as an orange oil.

2,2'-Dibromo-P-phenyldithieno[3,2-b:2',3'-f]phosphepine-P-borane (S1). To a solution of 4β (100 mg, 320 µmol) in dry EtOAc (20 mL) at -78 °C was added dropwise t-BuLi (1.9 M in n-pentane, 506 µL, 961 µmol) and stirred for 45 min. Br2 (156 mg, 5.00 µL, 961 µmol) was added and the reaction mixture was stirred for 16 h with gradual warming to rt. The reaction was quenched via dropwise addition of sat. aq. Na2S2O3 (20 mL) and extracted with CH2Cl2 (40 mL). The organic phase was dried (MgSO4), filtered, and the solvent removed in vacuo. The crude product was dissolved in CH2Cl2 (2 mL) and a solid was precipitated by the addition of hexanes (30 mL) and concentration under reduced pressure. Filtration and washing with cold hexanes (2 x 20 mL) afforded S1 (100 mg, 66%) as an orange solid.
P-Phenylidithieno[3,2-b:2',3'-f]phosphepine-P-borane-2,2'-dicarbaldehyde (S2). To a solution of 4β (100 mg, 320 µmol) in dry Et₂O (20 mL) at −78 °C was added dropwise t-BuLi (1.9 M in n-pentane, 506 µL, 961 µmol) and stirred for 45 min. DMF (93.6 mg, 98.6 µL, 1.28 mmol) was added and the reaction mixture was stirred for 16 h with gradual warming to rt. The reaction was quenched with sat. aq. NaCl (20 mL) and extracted with CH₂Cl₂ (5 x 20 mL). The combined organic phases were dried (MgSO₄), filtered, and the solvent was removed in vacuo. Purification by column chromatography (SiO₂, hexanes/CH₂Cl₂ 1:1 → CH₂Cl₂) afforded S2 (68.0 mg, 58%) as a yellow solid.

m.p. 163 °C (decomp.); Rf = 0.82 (SiO₂, CH₂Cl₂); ¹H NMR (400 MHz, CD₂Cl₂) δ 10.0 (s, 2H), 8.32 (d, J = 4.8 Hz, 2H), 7.43–7.38 (m, 1H), 7.33–7.28 (m, 2H), 7.14–7.09 (m, 2H), 7.07 (s, 2H), 1.9–0.7 (br m, 3H) ppm; ¹³C{³¹P,¹H} NMR (101 MHz, CD₂Cl₂) δ 183.0, 153.1, 146.6, 141.4, 131.6, 131.0, 129.1, 128.8, 127.1, 125.7 ppm; ³¹P NMR (121 MHz, CDCl₃) δ −3.3 ppm; IR (ATR) ν 3068 (vw), 2837 (w), 2385 (m), 2348 (m), 1668 (s), 1507 (m), 1222 (m), 1117 (m), 1057 (m) cm⁻¹; APPI HRMS (CH₂Cl₂, MeCN) m/z calcd. for C₁₈H₁₂O₂PS₂ [M−BH₃+H]+ 355.0011, found 355.0017.
3. Nuclear Magnetic Resonance Spectra

Figure S1. $^1$H NMR spectrum of $1\alpha$ measured in CDCl$_3$ (300 MHz).

Figure S2. $^{13}$C($^{31}$P, $^1$H) NMR spectrum of $1\alpha$ measured in CD$_2$Cl$_2$ (101 MHz).
Figure S3. $^{31}$P NMR spectrum of 1α measured in CDCl$_3$ (121 MHz).

Figure S4. $^1$H NMR spectrum of 1β measured in CDCl$_3$ (300 MHz).
Figure S5. $^1$H$^3$C$^31$P NMR spectrum of 1β measured in CD$_2$Cl$_2$ (101 MHz).

Figure S6. $^{31}$P NMR spectrum of 1β measured in CDCl$_3$ (121 MHz).
Figure S7. $^1$H NMR spectrum of 4α measured in CD$_2$Cl$_2$ (400 MHz).

Figure S8. $^{31}$C($^{31}$P,$^1$H) NMR spectrum of 4α measured in CD$_2$Cl$_2$ (101 MHz).
Figure S9. $^{31}$P NMR spectrum of 4a measured in CDCl$_3$ (121 MHz).

Figure S10. $^1$H NMR spectrum of 4b measured in CD$_2$Cl$_2$ (400 MHz).
**Figure S11.** $^{13}$C($^{31}$P,$^1$H) NMR spectrum of 4β measured in CD$_2$Cl$_2$ (101 MHz).

**Figure S12.** $^{31}$P NMR spectrum of 4β measured in CDCl$_3$ (121 MHz).
Figure S13. $^1$H NMR spectrum of 5a measured in CDCl$_3$ (300 MHz).

Figure S14. $^{13}$C($^{31}$P,$^1$H) NMR spectrum of 5a measured in CD$_2$Cl$_2$ (101 MHz).
Figure S15. $^{31}$P NMR spectrum of 5α measured in CDCl$_3$ (121 MHz).

Figure S16. $^1$H NMR spectrum of 5β measured in CDCl$_3$ (300 MHz).
Figure S17. $^{31}\text{C}^{[31}\text{P},^{1}\text{H}]$ NMR spectrum of 5β measured in CD$_2$Cl$_2$ (101 MHz).

Figure S18. $^{31}\text{P}$ NMR spectrum of 5β measured in CDCl$_3$ (121 MHz).
Figure S19. $^1$H NMR spectrum of 6α measured in CD$_2$Cl$_2$ (400 MHz).

Figure S20. $^{13}$C($^{31}$P, $^1$H) NMR spectrum of 6α measured in CD$_2$Cl$_2$ (101 MHz).
Figure S21. $^{31}$P NMR spectrum of 6α measured in CDCl$_3$ (121 MHz).

Figure S22. $^1$H NMR spectrum of 6β measured in CD$_2$Cl$_2$ (400 MHz).
Figure S23. $^{13}$C($^{31}$P,1H) NMR spectrum of 6β measured in CD$_2$Cl$_2$ (101 MHz).

Figure S24. $^{31}$P NMR spectrum of 6β measured in CDCl$_3$ (121 MHz).
Figure S25. $^1$H NMR spectrum of S1 measured in CD$_2$Cl$_2$ (400 MHz).

Figure S26. $^{13}$C($^{31}$P, $^1$H) NMR spectrum of S1 measured in CD$_2$Cl$_2$ (101 MHz).
**Figure S27.** \(^{31}\text{P}\) NMR spectrum of S1 measured in CDCl\(_3\) (121 MHz).

**Figure S28.** \(^1\text{H}\) NMR spectrum of S2 measured in CD\(_2\)Cl\(_2\) (400 MHz).
Figure S29. $^{13}$C($^{31}$P, $^1$H) NMR spectrum of S2 measured in CD$_2$Cl$_2$ (101 MHz).

Figure S30. $^{31}$P NMR spectrum of S2 measured in CDCl$_3$ (121 MHz).
4. X-ray Crystallographic Analysis

**Compound 1α.** Single crystals of 1α suitable for X-ray crystallographic analysis were obtained by slow liquid phase diffusion of n-pentane into a solution of 1α in CH₂Cl₂ at room temperature (Figure S31). The compound crystallizes in the monoclinic space group P2₁/c with one independent molecule in the asymmetric unit. The crystal data are as follows: Formula C₁₆H₁₁PS₂, formula weight = 298.34, crystal size 0.248 × 0.182 × 0.159 mm³, monoclinic, a = 11.8620(3) Å, b = 10.5407(3) Å, c = 11.1639(3) Å, α = y = 90°, β = 94.772(2)°, V = 1391.03(6) Å³, T = 153.00(10) K, Z = 4, ρcalc 1.425 g·cm⁻³, μ (Cu Kα) = 1.54184 mm⁻¹, 4456 reflections measured, 2644 unique (Rint = 0.0206), which were used in all calculations. The final wR² was 0.0831 (all data) and R₁ was 0.0308 (I > 2 σ (I)). CCDC number: 1961145.

![Figure S31. ORTEP plot of 1α drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.](image)

**Compound 1β.** Single crystals of 1β suitable for X-ray crystallographic analysis were obtained by slow liquid phase diffusion of n-pentane into a solution of 1β in CH₂Cl₂ at room temperature (Figure S32). The compound crystallizes in the monoclinic space group P2₁/c with one independent molecule in the asymmetric unit. The crystal data are as follows: Formula C₁₆H₁₁PS₂, formula weight = 298.34, crystal size 0.353 × 0.266 × 0.206 mm³, monoclinic, a = 8.4888(3) Å, b = 20.6901(6) Å, c = 8.7328(4) Å, α = y = 90°, β = 114.068(5)°, V = 1400.43(10) Å³, T = 153.00(10) K, Z = 4, ρcalc 1.415 g·cm⁻³, μ (Cu Kα) = 1.54184 mm⁻¹, 4497 reflections measured, 2665 unique (Rint = 0.0221), which were used in all calculations. The final wR² was 0.1156 (all data) and R₁ was 0.0427 (I > 2 σ (I)). CCDC number: 1961148.

![Figure S32. ORTEP plot of 1β drawn at the 50% probability level (left). Hydrogen atoms are omitted for clarity. Solid state packing (right).](image)
Compound 4a. Single crystals of 4a suitable for X-ray crystallographic analysis were obtained by slow liquid phase diffusion of n-pentane into a solution of 4a in CH2Cl2 at room temperature (Figure S33). The compound crystallizes in the orthorhombic space group Pna21 with one independent molecule in the asymmetric unit. The crystal data are as follows: Formula C16H14BP2S2, formula weight = 312.17, crystal size 0.233 × 0.155 × 0.136 mm3, orthorhombic, a = 9.7065(3) Å, b = 12.3356(3) Å, c = 12.8781(3) Å, α = β = γ = 90°, V = 1541.97(7) Å3, T = 153.00(10) K, Z = 4, ρ calc 1.345 g·cm−3, μ (Cu Kα) = 1.54184 mm−1, 3272 reflections measured, 2025 unique (Rint = 0.0304), which were used in all calculations. The final wR2 was 0.1210 (all data) and R1 was 0.0448 (I > 2 σ (I)). CCDC number: 1961147.

![Figure S33. ORTEP plot of 4a drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.](image)

Compound 4β. Single crystals of 4β suitable for X-ray crystallographic analysis were obtained by slow liquid phase diffusion of n-pentane into a solution of 4β in CH2Cl2 at room temperature (Figure S34). The compound crystallizes in the orthorhombic space group Pna21 with one independent molecule in the asymmetric unit. The crystal data are as follows: Formula C16H14BP2S2, formula weight = 312.17, crystal size 0.201 × 0.102 × 0.089 mm3, orthorhombic, a = 9.6639(4) Å, b = 12.3217(6) Å, c = 13.0378(5) Å, α = β = γ = 90°, V = 1552.49(12) Å3, T = 153.00(10) K, Z = 4, ρ calc 1.336 g·cm−3, μ (Cu Kα) = 1.54184 mm−1, 3116 reflections measured, 2190 unique (Rint = 0.0377), which were used in all calculations. The final wR2 was 0.1000 (all data) and R1 was 0.0434 (I > 2 σ (I)). CCDC number: 1961146.

![Figure S34. ORTEP plot of 4β drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.](image)
Compound 5α. Single crystals of 5α suitable for X-ray crystallographic analysis were obtained by slow liquid phase diffusion of n-pentane into a solution of 5α in CH₂Cl₂ at room temperature (Figure S35). The compound crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit. The crystal data are as follows: Formula C₁₆H₁₁OPS₂, formula weight = 314.34, crystal size 0.219 × 0.198 × 0.112 mm³, triclinic, $a = 8.1239(4)$ Å, $b = 12.9728(8)$ Å, $c = 13.8900(8)$ Å, $\alpha = 92.868(5)^\circ$, $\beta = 94.306(4)^\circ$, $\gamma = 91.887(5)^\circ$, $V = 1456.92(14)$ Å³, $T = 153.1(4)$ K, $Z = 4$, $\rho$ calc. 1.433 g cm⁻³, $\mu$ (Cu Kα) = 1.54184 mm⁻¹, 8572 reflections measured, 5491 unique ($R_{int} = 0.0319$), which were used in all calculations. The final $wR_2$ was 0.1044 (all data) and $R_1$ was 0.0380 ($I > 2\sigma(I)$). CCDC number: 1961149.

Figure S35. ORTEP plot of 5α drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Compound 5β. Single crystals of 5β suitable for X-ray crystallographic analysis were obtained by slow liquid phase diffusion of n-pentane into a solution of 5β in CH₂Cl₂ at room temperature (Figure S36). The compound crystallizes in the monoclinic space group $P2_1/c$ with one independent molecule in the asymmetric unit. The crystal data are as follows: Formula C₁₆H₁₁OPS₂, formula weight = 314.34, crystal size 0.290 × 0.192 × 0.187 mm³, monoclinic, $a = 8.30400(13)$ Å, $b = 17.6092(3)$ Å, $c = 9.78573(16)$ Å, $\alpha = \gamma = 90^\circ$, $\beta = 101.9041(15)^\circ$, $V = 1400.16(4)$ Å³, $T = 153.05(10)$ K, $Z = 4$, $\rho$ calc. 1.491 g cm⁻³, $\mu$ (Cu Kα) = 1.54184 mm⁻¹, 5235 reflections measured, 2698 unique ($R_{int} = 0.0239$), which were used in all calculations. The final $wR_2$ was 0.0838 (all data) and $R_1$ was 0.0311 ($I > 2\sigma(I)$). CCDC number: 1961144.

Figure S36. ORTEP plot of 5β drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.
Table S1. Selected bond lengths given in Å as well as selected bond angles given in ° as obtained from the crystal structures of DTPs 1, 4, and 5.

|       | 1α     | 1β     | 4α     | 4β     | 5α     | 5β     |
|-------|--------|--------|--------|--------|--------|--------|
| P1-C1 | 1.7974(18) | 1.814(2) | 1.777(5) | 1.795(5) | 1.772(2) | 1.7843(18) |
| C1-C2 | 1.379(3)  | 1.384(3) | 1.398(7) | 1.381(8) | 1.387(3) | 1.386(2)  |
| C2-C3 | 1.455(3)  | 1.446(3) | 1.449(7) | 1.450(8) | 1.456(3) | 1.442(3)  |
| C3-C4 | 1.346(3)  | 1.349(3) | 1.348(7) | 1.347(7) | 1.338(4) | 1.346(3)  |
| C4-C5 | 1.453(3)  | 1.443(3) | 1.452(7) | 1.447(8) | 1.450(4) | 1.440(2)  |
| C5-C6 | 1.381(3)  | 1.376(3) | 1.390(7) | 1.376(7) | 1.388(3) | 1.390(2)  |
| C6-P1 | 1.8005(18)| 1.820(2) | 1.770(5) | 1.783(5) | 1.768(2) | 1.7823(17)|
| P1-C7 | 1.8341(18) | 1.839(2) | 1.817(5) | 1.804(5) | 1.802(3) | 1.8029(17)|
| P1-E1 | -       | -       | 1.908(6) (E = B) | 1.913(7) (E = B) | 1.4856(18) (E = O) | 1.4917(12) (E = O) |
| C1-P1-C6 | 100.91(8) | 101.66(9) | 104.6(2) | 106.4(2) | 103.83(11) | 107.01(8) |
| C1-P1-C7 | 103.90(8) | 101.59(9) | 106.6(2) | 104.8(2) | 109.23(12) | 104.60(8) |
| C6-P1-C7 | 100.67(8) | 100.67(9) | 106.5(2) | 106.1(2) | 106.04(11) | 105.54(8) |
5. UV-Vis spectroscopy

Figure S37. UV-Vis absorption (solid lines) and fluorescence spectra (dashed lines) of a) 1α and 5α, b) 1β and 5β, c) 6α, and d) 6β recorded in CH$_2$Cl$_2$ at rt. Excitation wavelengths: 1α: 300 nm, 5α: 310 nm, 1β and 5β: 340 nm, 6α: 345 nm, 6β: 405 nm.
6. Cyclic Voltammetry

Figure S38. Cyclic voltammograms of a) 1α and 5α, b) 1β and 5β, c) 6α, and d) 6β recorded in 0.1 m solutions of n-Bu4NPF6 in THF at a scan rate of 0.1 V s⁻¹. Half wave potentials are given in V against the Fc/Fc⁺ couple.
7. Theoretical calculations

All calculations were performed using the Turbomole quantum chemistry suite. Geometries were optimized adopting the B3-LYP functional together with the triple zeta def2-TZVPD Gaussian basis set. All calculations were done applying the semi-empirical D3 dispersion correction according to Grimme et al. Frequency calculations were carried out to characterize ground state as well as transition state geometries. All energies contain ZPVE and thermal corrections at 298.15 K (within the ideal gas / rigid rotor / harmonic oscillator approximations) unless otherwise noted. Isosurfaces of molecular orbitals were visualized with the software ChemCraft.

Figure S39. B3LYP-D3/def2-TZVPD geometries of a) 1α, b) 5α, c) 1β, and d) 5β. Energies are given relative to the more stable conformation in each pair and in kcal mol⁻¹.
8. Cartesian (XYZ) coordinates

**1α (syn)**

\[ E_{\text{total}} = -1753.804461 \text{ H} \]
\[ \mu = 0.7377576 \text{ H} \]
\[ E_{\text{corr}} = -1753.066704 \text{ H} \]

**1α (anti)**

\[ E_{\text{total}} = -1753.799695 \text{ H} \]
\[ \mu = 0.7420922 \text{ H} \]
\[ E_{\text{corr}} = -1753.057602 \text{ H} \]
$E_{\text{total}} = -1753.804297 \text{ H}$
$\mu = 0.7396503 \text{ H}$
$E_{\text{corr}} = -1753.064707 \text{ H}$

$E_{\text{total}} = -1753.799996 \text{ H}$
$\mu = 0.7410086 \text{ H}$
$E_{\text{corr}} = -1753.058987 \text{ H}$
Supporting Information

5α (syn)

\[ E_{\text{total}} = -1829.075644 \, \text{H} \]
\[ \mu = 0.7533271 \, \text{H} \]
\[ E_{\text{corr}} = -1828.322317 \, \text{H} \]

5α (anti)

\[ E_{\text{total}} = -1829.076357 \, \text{H} \]
\[ \mu = 0.7537255 \, \text{H} \]
\[ E_{\text{corr}} = -1828.322632 \, \text{H} \]
### SUPPORTING INFORMATION

#### 5B (syn)

\[
E_{\text{tot}} = -1829.077794 \text{ H}
\]
\[
\mu = 0.7544588 \text{ H}
\]

#### 5B (anti)

\[
E_{\text{tot}} = -1829.077323 \text{ H}
\]
\[
\mu = 0.7548888 \text{ H}
\]
9. References

[1] H.-G. Imrich, J. Conrad, U. Beifuss, Eur. J. Org. Chem. 2015, 7718-7734.
[2] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, Organometallics 2010, 29, 2176-2179.
[3] Turbomole 6.5, a development of the University of Karlsruhe and Forschungszentrum Karlsruhe GmbH, 1989-2007, Turbomole GmbH, since 2007; available from www.turbomole.com.
[4] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.
[5] F. Weigend, R. Ahlrichs, Phys. Chem. Chem. Phys. 2005, 7, 3297-3305.
[6] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys. 2010, 132, 154104.
[7] ChemCraft, version 1.8; available from www.chemcraftprog.com.