Supporting Information

**Straightforward Access to Multifunctional π-Conjugated P-Heterocycles Featuring an Internal Ylidic Bond**

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Supporting information

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Experimental section.

All experiments were performed under argon atmosphere using standard Schlenk techniques. Commercially available reagents were used as received without further purification. Solvents were freshly purified using MBRAUN SPS-800 drying columns. Separations were performed by gravity column chromatography on basic alumina (Aldrich, Type 5016A, 150 mesh, 58 Å) or silica gel (Merck Geduran 60, 0.063-0.200 mm). \(^1\)H, \(^13\)C, and \(^{31}\)P NMR spectra were recorded on Bruker AV III 300 and 400 MHz NMR spectrometers equipped with BBO or BBFO probe heads. Assignment of proton and carbon atoms is based on COSY, NOESY, edited-HSQC and HMBC experiments. Special \(^{31}\)P decoupled experiments (\({^{31}\text{P}}\)\(^1\)H, \({^{31}\text{P}}\)\(^{1\text{H}}\)\(^{13}\)C, \({^{31}\text{P}}\)-HSQC, HMBC, COSY, NOESY) were performed on a Bruker Av III HD 500 MHz fitted with a triple inverse probehead (\({^{1\text{H}}}\)\(^{31}\text{P}-\)\(\text{X}\)). These \(^{31}\)P decoupled experiments have been performed using 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 residual solvent signal as reference. High-resolution mass spectra were obtained on a Varian MAT 311 or ZabSpec TOF Micromass instrument at CRMPO (Scanmat, UMS 2001). UV-Visible spectra were recorded rt on a VARIAN Cary 5000 spectrophotometer. The UV-Vis emission and excitation spectra measurements were recorded on a FL 920 Edinburgh Instrument equipped with a Hamamatsu R5509-73 photomultiplier for the NIR domain (300-1700 nm) and corrected for the response of the photomultiplier. The absolute quantum yields were measured with a C9920-03 Hamamatsu. 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 potential 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 DCM and 0.2 M tetrabutylammoniumhexafluorophosphate. \(1a, 6a\) and \(15\) were prepared according to the literature.\(^1\)

\(^1\) a) J. Beckmann, T. G. Do, S. Grabowsky, E. Hupf, E. Lork and S. Mebs, Z. anorg. allg. Chem., 2013, 639, 2233–2249; b) H. Brunner and M. Janura, Synthesis, 1998, 1998, 45–55; c) K. J. Brown, M. S. Berry, K. C. Waterman, D. Lingenfelter and J. R. Murdoch, J. Am. Chem. Soc., 1984, 106, 4717–4723
1b: **(General method A)** 1,8-dibromonaphthalene (1 g, 3.5 mmol, 1 eq) is dissolved in 50 mL of dry Et₂O. The solution is cooled down to -80°C and t-BuLi (1 eq) is added dropwise and the solution is stirred for 30 mn at -80°C and 30 mn at rt. The solution is again cooled down to -80°C and Cy₂PCL (0.7 mL, 3.5 mmol, 1 eq) is added dropwise and the mixture is stirred at RT overnight. Then the solution is quenched with water, the solution is extracted with water and evaporated. The crude mixture was purified by silica gel chromatography (C₆/DCM: 9/1) to afford 1b as a white powder (720 mg, η = 57 %). ¹H NMR (300 MHz, CD₂Cl₂) δ 7.87 (dd, J = 7.4, 1.3 Hz, 1H, H₂), 7.85 – 7.79 (m, 3H, H₆, H₅, H₃), 7.47 (t, J = 7.6 Hz, 1H, H₃), 7.25 (t, J = 7.7 Hz, 1H, H₂), 2.10 – 1.94 (m, 4H, H₆_O), 1.84 – 1.73 (m, 2H, H₇_O), 1.68 – 1.54 (m, 6H, H₈-O), 1.38 – 1.09 (m, 10H, H₉). ¹³C NMR (75 MHz, CD₂Cl₂) δ 137.0 (d, J_c-p = 3.8 Hz, C₆), 136.2 (d, J_c-p = 18.7 Hz, C₁₀), 135.4 (d, J_c-p = 38.4 Hz, C₁), 135.0 (d, J_c-p = 1.8 Hz, C₃), 134.7 (C₈), 130.5 (C₆), 130.0 (d, J_c-p = 1.6 Hz, C₄), 126.0 (C₃), 125.5 (C₁), 120.9 (d, J_c-p = 3.1 Hz, C₂), 37.4 (d, J_c-p = 20.0 Hz, Cᵥ), 31.0 (Cᵥ), 30.8 (Cᵥ), 30.4 (Cᵥ), 30.2 (Cᵥ), 27.9 (d, J = 10.5 Hz, Cᵥ), 27.7 (d, J_c-p = 11.0 Hz, Cᵥ), 26.9 (d, J = 1.3 Hz, Cᵥ). ³¹P NMR (121 MHz, CD₂Cl₂) δ -8.4. HRMS (ESI, CH₃OH/CH₃Cl₂ : 9/1) [M+H]+ (C₂₂H₂₃BrP) : m/z Theoretical : 403.1185, m/z Found : 403.1185.

5a: **(General method B)** 1a (0.391 mg, 1.00 mmol, 1 eq) and 2-Bromoacetophenone (219 mg, 1.10 mmol, 1.1 eq) were dissolved in 5 mL of toluene. The mixture was heated at 90°C for 3 h. Then, BuOK (168 mg, 1.50 mmol, 1.5 eq) was added at room temperature (r.t.) and the mixture stirred for 30 min allowing the obtention of the phosphonium ylides. The reaction was then heated to reflux for 4 h. After evaporation of the solvent, the crude product was purified through silica gel column chromatography (DCM/Acetone: 9/1). A yellow-orange powder was obtained. (244 mg, η = 57 %). ¹H NMR (400 MHz, CD₂Cl₂) δ 8.03 (d, J = 8.1 Hz, 1H, H₄), 7.95 (dd, J = 13.7, 7.2 Hz, 4H, Hortho), 7.81 (dd, J = 8.8, 7.1 Hz, 1H, H₃), 7.72 – 7.62 (m, 5H, H₈₁₅,para), 7.60 – 7.53 (m, 4H, Hmeta), 7.51 – 7.46 (m, 3H, H₁₄₁₆), 7.28 – 7.20 (m, 2H, H₆₅), 6.68 (d, J = 6.9, 1.3 Hz, 1H, H₈), 13C NMR (101 MHz, CD₂Cl₂) δ 185.7 (d, J_c-p = 8.1 Hz, Cᵥ), 143.4 (d, J_c-p = 12.9 Hz, Cᵥ), 140.1 (d, J_c-p = 25.7 Hz, Cᵥ), 135.8 (d, J_c-p = 23.7 Hz, Cᵥ), 133.6 (d, J_c-p = 11.4 Hz, Cortho), 132.9 (d, J_c-p = 3.1 Hz, Cpara), 132.8 (d, J_c-p = 9.7 Hz, Cᵥ), 132.1 (d, J_c-p = 2.7 Hz, C₄), 129.6 (d, J_c-p = 2.2 Hz, C₁), 129.3 (d, J_c-p = 13.2 Hz, Cmeta), 129.3 (C₁₀), 128.6 (C₁₄), 128.4 (d, J_c-p = 6.4 Hz, Cᵥ), 127.7 (s, C₁₅), 127.0 (d, J_c-p = 11.2 Hz, Cᵥ), 125.9 (d, J_c-p = 9.3 Hz, Cortho), 124.1 (d, J_c-p = 87.5 Hz, Cᵥ), 117.6 (s, C₆), 115.5 (d, J_c-p = 14.1 Hz, Cᵥ), 77.8 (d, J_c-p = 107.2 Hz, C₁₁). ³¹P NMR (162 MHz, CD₂Cl₂) δ +22.8. HRMS (ESI, CH₃OH/CH₃Cl₂ : 9/1) [M+Na]+ (C₆₀H₄₂ONaP) : m/z Theoretical : 451.1222, m/z Found : 451.1222.
5b: General method B was used with 1a (391 mg, 1.00 mmol, 1 eq), 4-Nitrophenacyl bromide (268 mg, 1.10 mmol, 1.1 eq), BuOK (168 mg, 1.50 mmol, 1.5 eq) in 5 mL of toluene. The product was purified through silica gel column chromatography (DCM/Acetone: 9/1). A dark red powder was obtained (290 mg, η = 70%). 1H NMR (400 MHz, CD2Cl2) δ 8.30 (d, J = 8.6 Hz, 2H, H15), 8.03 (d, J = 8.2 Hz, 1H, H3), 7.96 – 7.87 (m, 4H, Hortho), 7.85 – 7.78 (m, 3H, H3,14a), 7.70 – 7.60 (m, 3H, H3,para), 7.58 – 7.51 (m, 4H, Hmeta), 7.28 (d, J = 8.2 Hz, 1H, H6), 7.23 – 7.17 (m, 1H, H1), 6.54 (d, J = 7.3 Hz, 1H, H8). 13C NMR (101 MHz, CD2Cl2) δ 182.6 (d, J, C6P = 8.6 Hz, C12), 123.1 (m, C11), 127.4 (d, J, C6P = 11.4 Hz, C11), 115.4 (d, J, C6P = 91.2 Hz, Cipso), 124.2 (s, C15), 123.6 (d, J, C6P = 88.3 Hz, C1i), 118.4 (s, C6i), 115.5 (d, J, C6P = 17.3 Hz, C6a), 78.9 (d, J, C6P = 107.8 Hz, C11). 31P NMR (162 MHz, CD2Cl2) δ +23.6. HRMS (ESI, CH3OH/CH2Cl2 : 9/1) [M+Na]+ (C30H20NO3NaP) : m/z Theoretical : 565.1153, m/z Found : 565.1153.

5c: General method B was used with 1a (391 mg, 1.00 mmol, 1 eq), 3′,5′-Bis(trifluoromethyl)-2-bromoacetophenone (369 mg, 1.10 mmol, 1.1 eq), BuOK (168 mg, 1.50 mmol, 1.5 eq) in 5 mL of toluene. The product was purified through silica gel column chromatography (DCM/Acetone: 98/2). A yellow powder was obtained (337 mg, η = 60 %). 1H NMR (400 MHz, CD2Cl2) δ 8.22 (d, J = 1.7 Hz, 2H, H4a), 8.07 – 8.02 (m, 1H, H16), 8.01 – 7.98 (m, 1H, H18), 7.92 (dd, J = 13.8, 8.4, 1.4 Hz, 4H, Hortho), 7.85 – 7.80 (m, 1H, , H4), 7.70 – 7.60 (m, 3H, H3,para), 7.58 – 7.52 (m, 4H, Hmeta), 7.33 – 7.29 (m, 1H, H4), 7.27 – 7.20 (m, 1H, H1), 6.61 (d, J = 7.3 Hz, 1H, H8), 13C NMR (101 MHz, CD2Cl2) δ 181.1 (d, J, C6P = 9.0 Hz, C12), 145.3 (d, J, C6P = 13.8 Hz, Cq), 139.3 (d, J, C6P = 24.8 Hz, Cq), 136.0 (d, J, C6P = 23.4 Hz, Cq), 133.7 (d, J, C6P = 11.5 Hz, Cortho), 133.2 (d, J, C6P = 3.1 Hz, Cpara), 133.0 (d, J, C6P = 9.7 Hz, Cq), 132.5 (d, J, C6P = 2.7 Hz, C16), 131.8 (d, J, C6P = 33.3 Hz, Cq), 129.5 (d, J, C6P = 13.3 Hz, Cmeta), 129.5 (d, J, C6P = 2.3 Hz, C1i), 128.8 (d, J, C6P = 3.6 Hz, C14), 128.7 (d, J, C6P = 6.6 Hz, C4i), 127.4 (d, J, C6P = 11.3 Hz, C3i), 125.3 (d, J, C6P = 91.2 Hz, C1i), 124.8 (d, J, C6P = 125.9 Hz, Cipso), 123.0 (d, J, C6P = 58.3 Hz, C2i), 123.1 – 122.9 (m, C15s), 118.7 (s, C6i), 115.4 (d, J, C6P = 13.8 Hz, C6a), 78.9 (d, J, C6P = 108.4 Hz, C11). 31P NMR (376 MHz, CD2Cl2) δ -63.1. 31P NMR (162 MHz, CD2Cl2) δ +24.2. HRMS (ESI, CH3OH/CH2Cl2 : 9/1) [M+H]+ (C30H20F6OP) : m/z Theoretical : 565.1151, m/z Found : 565.1153.
5f: General method B was used with 1b (0.350 mg, 0.87 mmol, 1 eq), 2-bromoacetophenone (191 mg, 0.96 mmol, 1.1 eq), 'BuOK (147 mg, 1.50 mmol, 1.5 eq) in 5 mL of toluene. After evaporation of the solvent, the crude product was purified through silica gel column chromatography (DCM/AcOEt : 95/5). A yellow-orange powder was obtained (180 mg, η = 47 %). 1H NMR (400 MHz, CD2Cl2) δ 7.93 (dd, J = 8.3 Hz, 1H, H5), 7.57 (t, J = 7.2 Hz, 1H, H6), 7.48 – 7.53 (m, 3H, H12), 7.40 – 7.47 (m, 3H, H14, 15), 7.16 – 7.03 (m, 2H, H16,17), 6.38 (d, 1H, H2), 2.94 – 2.80 (m, 2H, H3), 1.21 – 2.07 (m, 2H, H5), 1.88 – 1.76 (m, 6H, H4, H6), 1.74 – 1.66 (m, 2H, H10), 1.63 – 1.50 (m, 2H, H6), 1.45 – 1.30 (m, 6H, H7, H8), 1.25 – 1.09 (m, 2H, H8), 13C NMR (101 MHz, CD2Cl2) δ 185.5 (d, Jc= = 12.8 Hz, C12), 141.9 (d, Jc= = 20.0 Hz, Cq), 132.7 (d, Jc= = 19.0 Hz, Cq), 134.0 (s, Cq), 132.5 (d, Jc= = 8.6 Hz, Cq), 131.6 (d, Jc= = 2.6 Hz, Cq), 129.2 (d, Jc= = 2.1 Hz, Cq), 128.9 (s, C16), 128.7 (s, C14), 128.0 (d, Jc= = 5.8 Hz, Cq), 127.5 (s, C15), 126.4 (d, Jc= = 10.4 Hz, Cq), 121.2 (d, Jc= = 76.0 Hz, Cq), 116.7 (s, Cq), 114.7 (d, Jc= = 11.7 Hz, Cq), 74.8 (d, Jc= = 97.5 Hz, C11), 33.7 (d, Jc= = 48.2 Hz, Cq), 27.3 (d, Jc= = 2.5 Hz, Cq), 27.0 (d, Jc= = 13.8 Hz, Cq), 26.9 (d, Jc= = 13.1 Hz, Cq), 26.4 (s, Cq), 26.2 (d, Jc= = 1.8 Hz, Cq). 31P NMR (162 MHz, CD2Cl2) δ + 41.6. HRMS (ESI, CH3Cl2/CH3OH: 9:1) [M+H]+ (C10H13OP): m/z Theoretical : 441.2342, m/z Found : 441.2340.

8: General method A was used with 3,3'-Dibromo-2,2'-bithiophène (3.00 g, 9.27 mmol, 1 eq), n-BuLi (4.65 mL, 10.20 mmol, 1.1 eq) and Ph3PCl (2.24 g, 10.20 mmol, 1 eq) in 150 mL of dry Et2O. The crude mixture was purified by silica gel chromatography using C7/DCM (8/2) to afford a yellowish oil (1.73 g, η = 44 %). The compound was used without further purification.

1H NMR (300 MHz, CD2Cl2) δ 7.44 (d, J = 5.2 Hz, 1H, H9), 7.39 – 7.31 (m, 11H, Hphen), 7.06 (d, J = 5.3 Hz, 1H, Hz), 6.79 (d, J = 5.3 Hz, 1H, Hz). 13C NMR (75 MHz, CD2Cl2) δ 139.7 (d, Jc= = 37.2 Hz, Cq), 138.5 (d, Jc= = 22.2 Hz, Cq), 138.3 (d, Jc= = 11.1 Hz, Cq), 133.6 (d, Jc= = 19.5 Hz, Cq), 133.5 (d, Jc= = 19.6 Hz, Cortho), 132.7 (d, Jc= = 1.7 Hz, Cq), 130.9 (s, Cq), 128.9 (d, Jc= = 5.1 Hz, Cmeta), 128.8 (s, Cpara), 128.0 (d, Jc= = 1.3 Hz, Cq), 127.8 (d, Jc= = 2.2 Hz, Cq), 112.9 (s, Cq). 31P NMR (121 MHz, CD2Cl2) δ -25.3.

7a: (General method C) 6 (200 mg, 0.51 mmol, 1 eq), 2-bromoacetophenone (111 mg, 1.10 mmol, 1.1 eq) were dissolved in 2 mL of dry DMF and heated at 100°C during 4h. Then the mixture was cooled down to 0°C and 'BuOK (86 mg, 0.56 mmol, 1.5 eq) was added. After stirring for 30 min, the reaction was heated at 175°C during 1 night. After evaporation of the solvent, the crude product was purified through silica gel column chromatography (DCM/Acetone: 95/5). An orange-brown powder was obtained (114 mg, η = 49 %). 1H NMR (400 MHz, CD2Cl2) δ 8.21 (dd, J = 8.3, 4.9 Hz, 1H, H9), 7.90 – 7.85 (m, 1H, H11), 7.81 – 7.73 (m, 4H, Hortho), 7.72 – 7.67 (m, 3H, H15,16,17), 7.58 – 7.50 (m, 2H, Hpara), 7.50 – 7.43 (m, 4H, Hmeta), 7.39 – 7.23 (m, 5H, H5,6,15,16), 7.04 – 6.99 (m, 1H, Hz), 6.90 – 6.84 (m, 2H, H10). 13C NMR (101 MHz, CD2Cl2) δ 186.9 (d, Jc= = 4.9 Hz, Cq), 142.2 (d, Jc= = 10.4 Hz, Cq), 141.2 (d, Jc= = 5.1 Hz, Cq), 136.8 (d, Jc= = 8.1 Hz, Cq), 133.0 (s, Cq), 132.9 (d, Jc= = 10.6 Hz, Cortho), 132.1 (d, Jc= = 2.3 Hz, Cq), 131.8 (d, Jc= = 3.1 Hz, Cpara), 130.1 (d, Jc= = 10.6 Hz, Cq), 129.6 (s, C9or), 129.3 (s, C12), 128.7 (d, Jc= = 12.8 Hz, Cmeta), 128.0 (s, C16), 127.6 (s, C9or), 127.4 (d, Jc= = 91.9 Hz, Cipso), 126.4 (d, Jc= = 11.4 Hz, C9or), 126.0 (d, Jc= = 2.3 Hz, C10).
7b: General method C was used with 6 (80 mg, 0.20 mmol, 1 eq), 4-Nitrophenacyl bromide (55 mg, 0.22 mmol, 1.1 eq), 14BuOK (34 mg, 0.31 mmol, 1.5 eq) in 1.5 mL of DMF. The product was purified through silica gel column chromatography (DCM/Acetone: 95/5). A yellow powder was obtained. (60 mg, η = 60 %). 1H NMR (300 MHz, CD2Cl2) δ 8.21 (dd, J = 8.3, 4.9 Hz, 1H, Hj), 8.15 – 8.05 (m, 2H, H12), 7.92 – 7.80 (m, 3H, H11,meta), 7.79 – 7.70 (m, 5H, Hortho, 3), 7.60 – 7.51 (m, 2H, Hpara), 7.51 – 7.41 (m, 4H, Hmeta), 7.41 – 7.31 (m, 1H, H4), 7.31 – 7.20 (m, 1H, H5), 6.98 – 6.79 (m, 3H, H8,9,10). 13C NMR (101 MHz, CD2Cl2) δ 184.2 (d, JcP = 5.5 Hz, C14), 148.8 (d, JcP = 10.3 Hz, Cq), 141.6 (d, JcP = 5.1 Hz, Cq), 136.2 (d, JcP = 7.6 Hz, Cq), 133.5 (d, JcP = 7.5 Hz, C5), 133.4 (d, JcP = 10.7 Hz, Cortho), 132.9 (d, JcP = 2.1 Hz, C3), 132.6 (d, JcP = 3.1 Hz, Cpara), 130.9 (d, JcP = 10.3 Hz, Cq), 130.8 (s, C16), 129.3 (d, JcP = 12.9 Hz, Cmeta), 128.4 (s, C10), 127.5 (s, Cq), 127.08 (d, JcP = 11.5 Hz, Cq), 127.04 (d, JcP = 92.0 Hz, Cipsocl), 126.6 (d, JcP = 2.3 Hz, C15), 126.5 (d, JcP = 8.6 Hz, Cq), 126.2 (d, JcP = 8.8 Hz, C2), 123.7 (s, C17), 122.1 (s, C8), 118.6 (d, JcP = 88.3 Hz, C1), 69.5 (d, JcP = 106.0 Hz, C13). 31P NMR (121 MHz, CD2Cl2) δ +2.2. HRMS (ESI, CH3OH/CH2Cl2 : 9/1) - [M+Na]+ (C32H23ONaP) : m/z Theoretical : 477.1379, m/z Found : 477.1374.

9: General method C was used with 8 (1.73 g, 4.05 mmol, 1 eq), 2-bromocetophenone (0.89 g, 4.45 mmol, 1.1 eq) and 14BuOK (0.60 g, 5.38 mmol, 1.5 eq) in 17 mL of dry DMF. After evaporation of the solvent, the crude product was purified through silica gel column chromatography (DCM/Acetone: 95/5). An orange-brown powder was obtained (1.44 g, η = 76 %). 1H NMR (400 MHz, CD2Cl2) δ 7.84 (ddd, J = 13.8, 6.7, 1.6 Hz, 4H, Hortho), 7.60 – 7.46 (m, 8H, H11,meta,para), 7.46 – 7.32 (m, 3H, H12,13); 7.13 (dd, J = 5.3, 2.7 Hz, 1H, H5), 6.93 – 6.88 (m, 2H, H6,7), 6.36 (dd, J = 5.4, 1.1 Hz, 1H, H7). 13C NMR (101 MHz, CD2Cl2) δ 188.9 (d, JcP = 4.3 Hz, Cq), 147.6 (d, JcP = 8.8 Hz, Cq), 142.8 (d, JcP = 10.4 Hz, Cq), 138.1 (d, JcP = 10.1 Hz, Cq), 133.2 (d, JcP = 11.5 Hz, Cortho), 131.9 (d, JcP = 3.2 Hz, Cpara), 129.9 (s, C13), 129.1 (d, JcP = 10.5 Hz, Cq), 128.9 (s, C12), 128.8 (s, C11), 128.6 (d, JcP = 6.9 Hz, Cmeta), 128.4 (d, JcP = 97.7 Hz, Cipsocl), 127.8 (d, JcP = 12.4 Hz, C7), 123.76 (s, C6), 122.38 (d, JcP = 15.1 Hz, C2), 115.0 (d, JcP = 7.3 Hz, Cq), 110.5 (d, JcP = 89.8 Hz, C1), 72.0 (d, JcP = 110.5 Hz, C4). 31P NMR (162 MHz, CD2Cl2) δ +1.6. HRMS (ESI, CH3OH/CH2Cl2 : 90/10) M+ (C28H19O2PS2) : m/z Calculated : 466.0610, m/z Found : 466.0615.
**10: (General method D)** 9 (200 mg, 0.43 mmol, 1 eq), K$_2$CO$_3$ (236 mg, 1.74 mmol, 4 eq), Pd(OAc)$_2$ (10 mg, 0.04 mmol, 0.1 eq), 4-iodonitrobenzene (500 mg, 1.74 mmol, 4 eq), PCY$_3$HBF$_4$ (32 mg, 0.09 mmol, 0.2 eq), PivOH (14 mg, 0.13 mmol, 0.3 eq) were dissolved in 2 mL of DMAc under argon. The mixture was heated at 125°C for 20h. DMAc was then evaporated and the product was purified through silica gel column (CH$_2$Cl$_2$/AcOEt : 95/5) to afford a dark purple solid (m = 158 mg, η = 52 %). $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 8.24 – 8.18 (m, 2H, H$_{13}$), 8.17 – 8.09 (m, 2H, H$_{13}$), 7.90 (ddd, J = 14.0, 6.8, 1.6 Hz, 4H, H$_{ortho}$), 7.69 – 7.64 (m, 2H, H$_5$), 7.64 – 7.50 (m, 9H, H$_{meta,para,20,22}$), 7.46 (dd, J = 8.1, 6.7 Hz, 2H, H$_{21}$), 7.40 – 7.33 (m, 2H, H$_{12}$), 7.29 (d, J = 3.5 Hz, 1H, H$_2$), 6.69 (d, J = 1.1 Hz, 1H, H$_{15}$). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) $\delta$ 189.6 (d, J$_{C-P}$ = 88.5 Hz, C$_{18}$), 147.3 (d, J$_{C-P}$ = 7.6 Hz, C$_{6}$), 147.2 (s, C$_7$), 147.2 (s, C$_{14}$), 142.4 (d, J$_{C-P}$ = 10.2 Hz, C$_{19}$), 140.7 (d, J$_{C-P}$ = 10.4 Hz, C$_8$), 140.2 (s, C$_{11}$), 139.8 (s, C$_{10}$), 139.4 (s, C$_4$), 138.7 (d, J$_{C-P}$ = 14.7 Hz, C$_3$), 133.3 (d, J$_{C-P}$ = 11.6 Hz, H$_{ortho}$), 132.4 (d, J = 3.3 Hz, H$_{para}$), 130.4 (s, C$_{22}$), 129.1 (d, J$_{C-P}$ = 13.4 Hz, C$_{meta}$), 128.9 (s, C$_{21}$), 128.43 (s, C$_{20}$), 127.7 (d, J$_{C-P}$ = 9.7 Hz, C$_{para}$), 127.6 (d, J$_{C-P}$ = 10.3 Hz, C$_{3}$), 126.3 (s, C$_5$), 126.3 (d, J$_{C-P}$ = 12.5 Hz, C$_{12}$), 126.2 (s, C$_{12}$), 124.8 (s, C$_{6}$), 124.7 (s, C$_{13}$), 116.3 (s, C$_{14}$), 113.2 (d, J$_{C-P}$ = 88.5 Hz, C$_3$), 72.5 (d, J$_{C-P}$ = 111.0 Hz, C$_{17}$). $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$) $\delta$ +0.9. HRMS (ESI, CH$_3$OH/CH$_2$Cl$_2$ : 90/10) [M+H]$^+$ (C$_{34}$H$_{26}$NO$_5$P$_2$) : m/z Calculated : 709.1015, m/z Found : 709.1018.

During the synthesis of 10, a second product was purified through silica gel column (CH$_2$Cl$_2$/AcOEt : 95/5) to afford a dark purple solid (m = 57 mg, η = 23 %). $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 8.22 – 8.15 (m, 2H, H$_6$), 7.86 (dd, J = 14.0, 6.8, 1.6 Hz, 4H, H$_{ortho}$), 7.67 – 7.61 (m, 2H, H$_5$), 7.58 – 7.48 (m, 8H, H$_{meta,para,16}$), 7.43 – 7.35 (m, 3H, H$_{17,18}$), 7.25 (d, J = 3.5 Hz, 1H, H$_2$), 6.96 (dd, J = 5.4, 2.4 Hz, 1H, H$_{11}$), 6.35 (dd, J = 5.4, 1.1 Hz, 1H, H$_{10}$). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) $\delta$ 189.4 (d, J$_{C-P}$ = 4.3 Hz, C$_{14}$), 148.4 (d, J$_{C-P}$ = 8.0 Hz, C$_9$), 147.1 (s, C$_4$), 142.5 (d, J$_{C-P}$ = 10.3 Hz, C$_{13}$), 139.7 (d, J$_{C-P}$ = 9.9 Hz, C$_8$), 139.6 (s, C$_9$), 137.7 (d, J$_{C-P}$ = 14.7 Hz, C$_{15}$), 133.2 (d, J$_{C-P}$ = 11.4 Hz, C$_{ortho}$), 132.2 (d, J$_{C-P}$ = 3.0 Hz, C$_{para}$), 130.1 (s, C$_{18}$), 129.0 (d, J$_{C-P}$ = 13.3 Hz, C$_{meta}$), 128.7 (s, C$_{17}$), 128.50 (s, C$_{16}$), 128.0 (d, J$_{C-P}$ = 97.8 Hz, C$_{ipso}$), 127.8 (d, J$_{C-P}$ = 12.5 Hz, C$_{10}$), 127.5 (d, J$_{C-P}$ = 10.4 Hz, C$_6$), 126.1 (s, C$_5$), 125.2 (s, C$_{11}$), 124.8 (s, C$_4$), 114.5 (d, J$_{C-P}$ = 7.5 Hz, C$_{12}$), 112.1 (d, J$_{C-P}$ = 89.0 Hz, C$_1$), 72.8 (d, J$_{C-P}$ = 109.6 Hz, C$_{13}$). $^{31}$P NMR (162 MHz, CD$_2$Cl$_2$) $\delta$ +1.1. HRMS (ESI, CH$_3$OH/CH$_2$Cl$_2$ : 90/10) [M+H]$^+$ (C$_{34}$H$_{23}$NO$_5$P$_2$) : m/z Calculated : 588.0852, m/z Found : 588.0851.

**11: General method D** was used with 9 (200 mg, 0.43 mmol, 1 eq), K$_2$CO$_3$ (236 mg, 1.74 mmol, 4 eq), Pd(OAc)$_2$ (10 mg, 0.04 mmol, 0.1 eq), 4-bromobenzene (400 mg, 2.54 mmol, 4 eq), PCY$_3$HBF$_4$ (32 mg, 0.09 mmol, 0.2 eq), PivOH (14 mg, 0.13 mmol, 0.3 eq) as starting material to afford an orange solid (m = 225 mg, η = 85 %) after purification on silica gel column (CH$_2$Cl$_2$/AcOEt : 99/1). $^1$H NMR (400 MHz, CD$_2$Cl$_2$) $\delta$ 7.93 (dd, J = 13.9 Hz, J = 6.5 Hz, 4H, H$_{ortho}$), 7.67 – 7.60 (m, 2H, H$_{20}$), 7.58 – 7.50 (m, 8H, H$_{12,13,meta}$), 7.50 – 7.43 (m, 3H, H$_{21,22}$), 7.38 (t, J = 8.3 Hz, 2H, H$_{para}$), 7.33 – 7.21 (m, 6H, H$_{6,6,7,14}$), 7.14 (d, J = 3.4 Hz, 1H, H$_2$),
6.57 (d, J = 1.1 Hz, 1H, H12). 13C NMR (101 MHz, CD2Cl2) δ 189.3 (d, JCP = 4.5 Hz, C18), 146.3 (d, JCP = 7.8 Hz, Cq), 142.8 (d, JCP = 10.3 Hz, Cq), 141.9 (s, Cq), 141.0 (d, JCP = 14.7 Hz, Cq), 139.3 (d, JCP = 10.1 Hz, Cq), 133.8 (d, JCP = 83.0 Hz, Cipso), 133.3 (d, JCP = 11.4 Hz, Cortho), 132.0 (d, JCP = 3.1 Hz, C12), 130.0 (s, C22), 129.4 (d, JCP = 2.8 Hz, Cpara), 129.2 (s, C5), 128.9 (d, JCP = 13.2 Hz, Cmeta), 128.7 (s, C21), 128.6 (s, Cq), 128.5 (s, C20), 128.4 (s, C14a), 128.2 (s, C1), 126.7 (s, Cq), 126.0 (s, C13), 125.8 (s, C6), 124.5 (d, JCP = 10.5 Hz, C5), 123.8 (d, JCP = 12.7 Hz, C15), 114.6 (d, JCP = 7.9 Hz, Cq), 111.3 (d, JCP = 89.6 Hz, C1), 72.4 (d, JCP = 110.6 Hz, C17). 31P NMR (162 MHz, CD2Cl2) δ +0.9. HRMS (ESI, CH3OH/CH2Cl2: 90/10) [M+H]+ (C60H32OP2): m/z Calculated : 619.1314, m/z Found : 619.1315.

12: General method D was used with 9 (200 mg, 0.43 mmol, 1 eq), K2CO3 (236 mg, 1.74 mmol, 4 eq), Pd(OAc)2 (10 mg, 0.04 mmol, 0.1 eq), 4-bromotriphenylamine (565 mg, 1.74 mmol, 4 eq), PCy3HBF4 (32 mg, 0.09 mmol, 0.2 eq), PivOH (14 mg, 0.13 mmol, 0.3 eq) as starting material to afford an orange solid (m = 405 mg, η = 99 %) after purification on silica gel column (CH2Cl2/Acetone: 1:5). 1H NMR (400 MHz, CD2Cl2) δ 7.92 (ddd, J = 13.7 Hz, J = 7.6 Hz, J = 1.6 Hz, 4H, Hortho), 7.65 – 7.58 (m, 2H, H20), 7.58 – 7.47 (m, 6H, Hmeta,para), 7.45 – 7.39 (m, 3H, H21,22), 7.38 – 7.34 (m, 2H, H8), 7.27 (t, J = 7.6 Hz, 8H, HNPh2), 7.12 – 7.04 (m, 15H, H2,13,NPh2), 7.00 (dd, J = 6.3 Hz, J = 2.7 Hz, 2H, H8), 6.95 – 6.90 (m, 2H, H21), 6.46 (d, J = 1.0 Hz, 1H, H15). 13C NMR (101 MHz, CD2Cl2) δ 189.2 (d, JCP = 4.4 Hz, C18), 148.0 (d, JCP = 12.7 Hz, Cq), 147.7 (d, JCP = 6.0 Hz, Cq), 145.6 (d, JCP = 7.9 Hz, Cq), 142.9 (d, JCP = 10.2 Hz, Cq), 141.7 (s, Cq), 140.8 (d, JCP = 15.0 Hz, Cq), 139.1 (d, JCP = 10.2 Hz, Cq), 133.3 (d, JCP = 11.4 Hz, Cortho), 132.0 (d, JCP = 3.1 Hz, Cpara), 130.0 (s, C22), 129.7 (d, JCP = 2.3 Hz, Cipso), 128.9 (d, JCP = 13.2 Hz, Cmeta), 128.7 (s, C21), 128.5 (s, C20), 128.2 (d, JCP = 97.2 Hz, Cipso), 128.0 (s, Cq), 127.13 (s, Cq), 126.73 (s, C6), 126.6 (s, C13), 125.1 (d, JCP = 3.8 Hz, Cipso), 123.8 (d, JCP = 7.2 Hz, C12), 123.5 (d, JCP = 12.8 Hz, C1), 123.3 (d, JCP = 10.5 Hz, C15), 122.7 (d, JCP = 12.6 Hz, C13), 114.1 (d, JCP = 7.9 Hz, Cq), 110.9 (d, JCP = 89.5 Hz, Cipso), 72.4 (d, JCP = 110.2 Hz, C12). 31P NMR (162 MHz, CD2Cl2) δ +0.8. HRMS (ESI, CH3OH/CH2Cl2: 90/10) [M+H]+ (C60H32OP2): m/z Calculated : 953.2784, m/z Found : 953.2783.

13: General method A was used with 3,3′-dibromo-2,2′-bienzo[b]thiophene (600 mg, 1.41 mmol, 1 eq), 50 mL of dry Et2O, BuLi (0.65 mL, 1.56 mmol, 1 eq) and Ph3PCl (326 g, 1.56 mmol, 1 eq). The crude mixture was purified by silica gel chromatography (DCM/AcOEt: 1/1) to afford a white powder (320 mg, η = 43 %). 1H NMR (400 MHz, CD2Cl2) δ 7.86 (d, J = 8.1 Hz, 1H, H3), 7.48 – 7.13 (m, 16H, H6,11,12,13,ortho,meta,para), 7.06 (t, J = 7.7 Hz, 1H, HA). 13C NMR (101 MHz, CD2Cl2) δ 147.2 (d, J = 54.5 Hz, Cq), 141.9 (s, Cq), 140.7 – 140.6 (m, Cq), 136.2 – 135.5 (m, Cq), 133.1 – 132.2 (m, CH), 128.8 – 128.6 (m, CH), 128.4 (s, CH), 126.1 (s, CH), 125.4 (s, CH), 124.7 (s, CH), 122.7 (s, CH). 31P NMR (162 MHz, CD2Cl2) δ = -26.9. HRMS: MALDI TOF: [M+H]+ (C68H19BrPS2): m/z Calculated : 528.9849, m/z Found : 528.854.
14: General method C was used with 13 (320 mg, 0.61 mmol, 1 eq), 2-bromoaacetophenone (130 mg, 0.67 mmol, 1.1 eq), BuOK (102 mg, 1.50 mmol, 1.5 eq) in 4 mL of DMF. After evaporation of the solvent, the crude product was purified through silica gel column chromatography (DCM/Acetone: 99/1). A red powder was obtained. (285 mg, η = 83%). 1H NMR (300 MHz, CD2Cl2) δ 7.97 (ddd, J = 13.8, 6.9, 1.5 Hz, 4H, Hortho), 7.88 (d, J = 8.0 Hz, 1H, Hs), 7.69 – 7.60 (m, 3H, H14,20), 7.57 – 7.49 (m, 2H, Hpar), 7.49 – 7.40 (m, 4H, Hmeta), 7.31 – 7.21 (m, 3H, H4,13,22), 7.19 – 7.07 (m, 4H, H5,11,21), 6.98 (d, J = 8.3 Hz, 1H, His), 6.81 (t, J = 8.3 Hz, 1H, H12). 13C NMR (101 MHz, CD2Cl2) δ 187.0 (d, JC-P = 5.4 Hz, C18), 148.5 (d, JC-P = 8.1 Hz, Cq), 142.8 (d, JC-P = 10.0 Hz, Cq), 140.3 (d, JC-P = 9.6 Hz, Cq), 139.9 (s, Cq), 138.6 (d, JC-P = 13.4 Hz, Cq), 138.3 (d, JC-P = 11.6 Hz, Cq), 136.0 (d, JC-P = 8.4 Hz, Cq), 133.2 (d, JC-P = 11.4 Hz, Cortho), 132.3 (d, JC-P = 3.2 Hz, Cpara), 130.5 (s, C22), 129.5 (s, C20), 129.1 (d, JC-P = 13.1 Hz, Cmeta), 128.3 (s, C21), 127.9 (d, JC-P = 93.5 Hz, Cipso), 127.6 (s, C13), 125.7 (d, JC-P = 4.2 Hz, C2), 124.8 (s, C2), 123.5 (s, C3), 122.9 (s, C3), 122.8 (s, C4), 115.0 (d, JC-P = 8.5 Hz, Cq), 103.7 (d, JC-P = 94.3 Hz, C1), 70.9 (d, JC-P = 110.2 Hz, C17). 31P NMR (162 MHz, CD2Cl2) δ +6.9. HRMS (ESI, CH3OH/CH2Cl2: 90/10) [M+H]+ (C68H60OP2): m/z Calculated : 567.1001, m/z Found : 567.0997.

16a: General method C was used with 15 (200 mg, 0.39 mmol, 1 eq) and 2-Bromoaacetophenone (85 mg, 0.43 mmol, 1.1 eq), BuOK (65 mg, 0.58 mmol, 1.5 eq) in 2 mL of DMF. The product was purified through silica gel column chromatography (DCM/Acetone: 95/5). An orange powder was obtained (133 mg, η = 62%). 1H NMR (500 MHz, CD2Cl2) δ 7.96 – 7.90 (m, 3H, H18,22), 7.87 – 7.81 (m, 3H, H13,24), 7.74 (d, J = 8.7 Hz, 1H, Ha), 7.61 – 7.58 (m, 2H, H6,16), 7.58 – 7.48 (m, 4H, H30,32,34), 7.47 – 7.38 (m, 5H, H26,29,33), 7.38 – 7.28 (m, 5H, H7,18,19,25), 7.20 – 7.14 (m, 3H, H2,13,15), 7.02 – 6.97 (m, 1H, H14). 13C NMR (126 MHz, CD2Cl2) δ 186.0 (d, JC-P = 6.3 Hz, C22), 142.3 (d, JC-P = 10.9 Hz, C23), 141.0 (d, JC-P = 4.6 Hz, C10), 138.1 (d, JC-P = 7.0 Hz, C20), 135.2 (d, JC-P = 2.1 Hz, C4), 133.6 (d, JC-P = 11.3 Hz, C28), 133.6-133.3 (m, C12,32), 132.9 (d, JC-P = 3.0 Hz, C30), 132.2 (d, JC-P = 3.1 Hz, C34), 131.3 (d, JC-P = 9.3 Hz, C10), 130.5 (s, C14), 130.2 (s, C24), 130.1 (s, C30), 130.0 (d, JC-P = 8.3 Hz, C19), 129.7 (s, C27), 129.5 (d, JC-P = 12.4 Hz, C29), 129.1 (d, JC-P = 13.1 Hz, C33), 128.5 (s, C5,25), 128.2 (s, C6), 128.1 (s, C16), 128.1 (s, C18), 127.3 (s, C13), 127.2 (d, JC-P = 12.2 Hz, C1), 127.0 (d, JC-P = 8.7 Hz, C1), 126.5 (d, JC-P = 84.2 Hz, C31), 126.5 (d, JC-P = 94.0 Hz, C27), 126.2 (s, C15), 125.4 (s, C14), 123.5 (s, C15), 120.8 (s, C11), 120.1 (d, JC-P = 95.9 Hz, C1), 71.3 (d, JC-P = 108.6 Hz, C21). 31P NMR (162 MHz, CD2Cl2) δ +3.8. HRMS (ESI, CH3OH/CH2Cl2: 95/5) [M+H]+ (C68H60OP2): m/z Theoretical : 555.1872, m/z Found : 555.1870.

P-(+)-16a: [α]D23 = +346 (± 5%) (DCM, 8.2 10−3 mol·L−1).
M-(−)-16a:[α]D23=-350 (± 5%) (DCM, 1.2 10−3 mol·L−1).
16b: General method C was used with 15 (190 mg, 0.37 mmol, 1 eq) and 4-Nitrophenacyl bromide (99 mg, 0.40 mmol, 1.1 eq), 'BuOK (62 mg, 0.55 mmol, 1.5 eq.) in 2 mL of DMF. The product was purified through silica gel column chromatography (DCM/Acetone: 95/5). A dark red powder was obtained (155 mg, η = 70 %).

1H NMR (400 MHz, CD2Cl2) δ 8.14 (d, J = 8.2 Hz, 2H, H25), 8.04 – 7.83 (m, 6H, H3,5,24,28), 7.71 (d, J = 8.7 Hz, 1H, H8), 7.64 – 7.37 (m, 11H, H6,16,18,29,30,32,33,34), 7.36 – 7.29 (m, 1H, H7), 7.23 – 7.10 (m, 4H, H2,13,15,19), 7.04 – 6.97 (m, 1H, H14).

13C NMR (101 MHz, CD2Cl2) δ 182.8 (d, Jc-P = 7.5 Hz, C22), 141.2 (d, Jc-P = 5.2 Hz, C10), 136.9 (d, Jc-P = 5.1 Hz, C2), 135.3 (d, Jc-P = 2.0 Hz, C4), 133.8-133.4 (m, C28,32), 133.2 (d, Jc-P = 2.9 Hz, C30), 132.5 (d, Jc-P = 2.0 Hz, C18), 131.4 (d, Jc-P = 9.6 Hz, C9), 131.1 (s, C24), 130.2 (s, C17), 130.1 (d, Jc-P = 7.9 Hz, C19), 130.0 (s, C8), 129.6 (d, Jc-P = 12.4 Hz, C26), 129.2 (d, Jc-P = 12.2 Hz, C27), 128.6 (s, C18), 128.5 (s, C5), 128.5 (s, C6), 128.3 (s, C10), 127.6 (d, Jc-P = 12.2 Hz, C3), 127.5 (s, C13), 127.0 (d, Jc-P = 7.2 Hz, C2), 126.5 (s, C7), 125.7 (s, C14), 124.0 (s, C15), 123.7 (s, C25), 122.0 (s, C11), 120.3 (d, Jc-P = 98.0 Hz, C1), 72.6 (d, Jc-P = 107.1 Hz, C21).

31P NMR (162 MHz, CD2Cl2) δ +4.06. HRMS (ESI, CH2Cl2/CH3OH : 95/5) - [M+Na]+ (C40H26NO3NaP) : m/z Theoretical : 622.1543, m/z Found : 622.1544.
Figure S1: ^1^H NMR (300 MHz, CD$_2$Cl$_2$, 293K), ^1^3C NMR (75 MHz, CD$_2$Cl$_2$, 293K) and ^3^1P{^1^H} NMR (121 MHz, CD$_2$Cl$_2$, 293K) spectra of compound 1b.
Figure S2: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293K), $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, 293K) and $^{31}$P{${^1}$H} NMR (162 MHz, CD$_2$Cl$_2$, 293K) spectra of compound 5a.
Figure S3: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293K), $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, 293K) and $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, 293K) spectra of compound 5b.
Figure S4: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293K), $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, 293K), $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) and $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, 293K) spectra of compound 5c.
Figure S5: \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\), 293K), \(^{13}\)C NMR (75 MHz, CD\(_2\)Cl\(_2\), 293K) and \(^{31}\)P{\(^1\)H} NMR (162 MHz, CD\(_2\)Cl\(_2\), 293K) spectra of compound 5f.
Figure S6: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 293K), $^{13}$C NMR (75 MHz, CD$_2$Cl$_2$, 293K) and $^{31}$P($^1$H) NMR (121 MHz, CD$_2$Cl$_2$, 293K) spectra of compound 8.
Figure S7: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293K), $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, 293K) and $^{31}$P($^1$H) NMR (121 MHz, CD$_2$Cl$_2$, 293K) spectra of compound 7a.
Figure S8: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 293K), $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, 293K) and $^{31}$P{$^1$H} NMR (121 MHz, CD$_2$Cl$_2$, 293K) spectra of compound 7b.
Figure S10: 1H NMR (400 MHz, CDCl$_3$, 293K), 13C NMR (101 MHz, CDCl$_3$, 293K) and 31P{1H} NMR (162 MHz, CDCl$_3$, 293K) spectra of compound 9.
Figure S11: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293K), $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 293K) and $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, 293K) spectra of 10°.
Figure S12: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293K), $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$, 293K) and $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, 293K) spectra of 10.
Figure S13: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293K), $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, 293K) and $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, 293K) spectra of compound 11.
Figure S14: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293K), $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, 293K) and $^{31}$P{$^1$H} NMR (121 MHz, CD$_2$Cl$_2$, 293K) spectra of compound 12.
Figure S15: $^1$H NMR (400 MHz, CDCl$_3$, 293K), $^{13}$C NMR (101 MHz, CDCl$_3$, 293K) and $^{31}$P{ $^1$H} NMR (162 MHz, CDCl$_3$, 293K) spectra of compound 13.
Figure S16: $^1$H NMR (300 MHz, CD$_2$Cl$_2$, 293K), $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, 293K) and $^{31}$P{$^1$H} NMR (121 MHz, CD$_2$Cl$_2$, 293K) spectra of compound 14.
Figure S17: $^1$H NMR (500 MHz, CD$_2$Cl$_2$, 293K), $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, 293K) and $^{31}$P{$^1$H} NMR (162 MHz, CD$_2$Cl$_2$, 293K) spectra of compound 16a.
Figure S18: $^1$H NMR (400 MHz, CD$_2$Cl$_2$, 293K), $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$, 293K) and $^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$, 293K) spectra of compound 16b.
X-ray crystallography

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 rt. Single crystal data collection were performed at 150 K with an D8 Venture Bruker-AXS diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by dual-space algorithm using the SHELXT program, and then refined with full-matrix least-squares methods based on F^2(SHELXL). 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.
| Compound | 5a | 5b | 5f | 7a |
|----------|----|----|----|----|
| CCDC     | 2143639 | 2143642 | 2143643 | 2143644 |
| Formula  | C30 H21 O P | C30 H20 N O3 P | C30 H33 O P | C32 H23 O P |
| MW       | 428.44 | 473.44 | 440.53 | 454.47 |
| a (Å)    | 12.0964(11) | 10.8566(16) | 12.5560(11) | 10.1144(8) |
| b (Å)    | 11.0843(13) | 15.166(2) | 13.9341(10) | 14.5902(12) |
| c (Å)    | 19.243(2) | 17.859(3) | 13.9603(12) | 17.2815(12) |
| α (°)    | 90 | 79.317(5) | 82.137(3) | 90.342 |
| β (°)    | 104.733(4) | 75.424(5) | 86.710(3) | 97.270(3) |
| γ (°)    | 90 | 70.381(5) | 89.314(3) | 103.927(3) |
| V (Å³)   | 2495.3(5) | 2664.2(7) | 2415.5(3) | 2453.6(3) |
| Z        | 4 | 4 | 4 | 4 |
| Dc (g.cm⁻³) | 1.140 | 1.180 | 1.211 | 1.230 |
| Crystal system | monoclinic | triclinic | triclinic | triclinic |
| Space group | P 21/n | P -1 | P -1 | P -1 |
| T (K) | 150 | 150 | 150 | 150 |
| WavelengthMo-Kα (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| μ (mm⁻¹) | 0.128 | 0.133 | 0.134 | 0.134 |
| F (000) | 896 | 984 | 944 | 952 |
| θ limit (°) | 2.139 to 27.523 | 2.371 to 27.666 | 2.132 to 27.521 | 2.267 to 27.566 |
| Index ranges hkl | -15 ≤ h ≥ 15 | -13 ≤ h ≥ 14 | -16 ≤ h ≥ 16 | -13 ≤ h ≥ 13 |
| | -14 ≤ k ≥ 14 | -19 ≤ k ≥ 19 | -18 ≤ k ≥ 15 | -18 ≤ k ≥ 18 |
| | -24 ≤ l ≥ 25 | 0 ≤ l ≥ 23 | -18 ≤ l ≥ 18 | -21 ≤ l ≥ 22 |
| Reflectionscollected | 28373 | 11965 | 45844 | 42583 |
| Independantreflections | 5671 | 11965 | 11020 | 11188 |
| Reflections [l>2σ(l)] | 4139 | 8631 | 8858 | 8699 |
| Data / restraints / parameters | 5671 / 0 / 290 | 11965 / 0 / 632 | 11020 / 0 / 577 | 11188 / 0 / 613 |
| Goodness-of-fit on F² | 1.025 | 1.085 | 0.993 | 1.030 |
| Final R indices [l>2σ(l)] | R1 = 0.0636 | R1 = 0.0927 | R1 = 0.0431 | R1 = 0.0521 |
| wR2 = 0.1646 | wR2 = 0.2478 | wR2 = 0.1064 | wR2 = 0.1182 |
| R indices (all data) | R1 = 0.0902 | R1 = 0.1283 | R1 = 0.0588 | R1 = 0.0723 |
| wR2 = 0.1860 | wR2 = 0.2738 | wR2 = 0.1178 | wR2 = 0.1288 |
| Larg. Diff. peak / hole (e Å⁻³) | 0.590 and -0.544 | 0.722 and -0.676 | 0.317 and -0.336 | 0.363 and -0.387 |
| Compound | 9 | 10' | 10 | 14 |
|----------|---|-----|----|----|
| CCDC     | 2143645 | 2143649 | 2143648 | 2143650 |
| Formula  | C28H19OPS2 | C71H50Cl6N2O6P2S4 | C41H27Cl2N2O5 PS2 | C36H23OPS2 |
| MW       | 466.52 | 1430.01 | 793.63 | 566.63 |
| a (Å)    | 9.9301(8) | 9.3695(11) | 16.921(2) | 8.3232(7) |
| b (Å)    | 12.6533(13) | 11.2239(15) | 13.9828(13) | 14.8898(14) |
| c (Å)    | 18.2991(16) | 15.7853(19) | 15.5120(18) | 22.077(2) |
| α (°)    | 90 | 92.323(5) | 90 | 90 |
| β (°)    | 100.319(3) | 91.708(5) | 97.303(4) | 100.327 |
| γ (°)    | 90 | 104.146(4) | 90 | 90 |
| V (Å³)   | 2262.1(4) | 1607.0(3) | 3640.4(7) | 2691.7(4) |
| Z        | 4 | 1 | 4 | 4 |
| Dc (g.cm⁻³) | 1.370 | 1.478 | 1.448 | 1.398 |
| Crystal system | monoclinic | triclinic | monoclinic | monoclinic |
| Space group | P 21/c | P -1 | P 21/c | P 21/c |
| T (K)    | 150 | 150 | 150 | 150 |
| WavelengthMo-Kα (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| μ (mm⁻¹) | 0.325 | 0.504 | 0.387 | 0.288 |
| F (000)  | 968 | 734 | 1632 | 1176 |
| θ limit (°) | 2.634 to 27.502 | 2.223 to 27.497 | 2.222 to 25.680 | 2.321 to 27.503 |
| Index ranges hkl | -12 ≤ h ≥ 12 | -12 ≤ h ≥ 11 | -20 ≤ h ≥ 20 | -7 ≤ h ≥ 10 |
| | -14 ≤ k ≥ 16 | -14 ≤ k ≥ 14 | -17 ≤ k ≥ 16 | -19 ≤ k ≥ 19 |
| | -23 ≤ l ≥ 23 | -20 ≤ l ≥ 20 | -18 ≤ l ≥ 18 | -28 ≤ l ≥ 28 |
| Reflectionscollected | 23959 | 22210 | 40352 | 22710 |
| Independantreflections | 5168 | 7299 | 6902 | 6159 |
| Reflections [l>2σ(l)] | 4307 | 5660 | 5614 | 4901 |
| Data / restraints / parameters | 5168 / 0 / 289 | 7299 / 0 / 424 | 6902 / 55 / 535 | 6159 / 0 / 361 |
| Goodness-of-fit on $F^2$ | 1.053 | 1.018 | 1.192 | 1.026 |
|-------------------------|-------|-------|-------|-------|
| Final $R$ indices [$>2\sigma(I)$] | $R_1 = 0.0494$ | $R_1 = 0.0915$ | $R_1 = 0.1184$ | $R_1 = 0.0491$ |
| $wR_2 = 0.1257$ | $wR_2 = 0.2353$ | $wR_2 = 0.3043$ | $wR_2 = 0.1222$ |
| $R_1 = 0.0606,$ | $R_1 = 0.1135$ | $R_1 = 0.1388$ | $R_1 = 0.0672$ |
| $wR_2 = 0.1351$ | $wR_2 = 0.2576$ | $wR_2 = 0.3263$ | $wR_2 = 0.1338$ |
| Larg. diff peak / hole (e Å$^{-3}$) | 0.945 and -0.562 | 1.361 and -1.126 | 1.610 and -1.193 | 0.460 and -0.538 |
Table S2. Distances and angles

![Chemical structure](image)

|       | 5a          | 5b          | 5f          |
|-------|-------------|-------------|-------------|
| P-C₁ (Å) | 1,794(2)   | 1,795(6)/1,791(5) | 1,801(2)/1,799(2) |
| P-C₄ (Å) | 1,751(2)   | 1,745(4)/1,763(6) | 1,763(2)/1,756(2) |
| C₁-C₂(Å) | 1,416(3)   | 1,412(6)/1,414(9) | 1,417(2)/1,416(2) |
| C₂-C₃(Å) | 1,441(3)   | 1,430(8)/1,438(6) | 1,438(2)/1,435(2) |
| C₃-C₄(Å) | 1,462(3)   | 1,464(6)/1,472(8) | 1,460(2)/1,463(2) |
| C₄-C₅(Å) | 1,416(3)   | 1,403(5)/1,396(7) | 1,404(2)/1,400(2) |
| C₅=O (Å) | 1,257(3)   | 1,254(5)/1,263(7) | 1,260(2)/1,264(2) |
| C₁-P-C₄(°) | 94,8(1)    | 93,8(2)/94,6(2) | 94,17(7)/94,30(7) |
| P- - - O (Å) | 2,905       | 2,945/2,901 | 2,907/2,882 |

|       | 7a²          | 9          |
|-------|-------------|-------------|
| P-C₁ (Å) | 1,807(2)/1,795(2) | 1.7773(19) |
| P-C₄ (Å) | 1,729(2)/1,728(2) | 1.758(2) |
| C₁-C₂(Å) | 1,412(6)/1,410(2) | 1.388(3) |
| C₂-C₃(Å) | 1,480(3)/1,483(3) | 1.425(3) |
| C₃-C₄(Å) | 1,422(3)/1,425(3) | 1.396(3) |
| C₄-C₅(Å) | 1,457(3)/1,459(3) | 1.461(3) |
| C₅-C₆(Å) | 1,432(3)/1,438(3) | 1.426(3) |
| C₆=O (Å) | 1,245(3)/1,249(2) | 1.257(2) |
| C₁-P-C₄(°) | 103,2(1)/103,9 | 105.01(9) |
| P- - - O (Å) | 2,906/2,869 | 2.741 |

² Two independent molecules of 7a are present in the unit cell
Figure S19: ORTEP representation of 5a with 50% probability ellipsoids

Figure S20: ORTEP representation of 5b with 50% probability ellipsoids
Figure S21: ORTEP representation of 5f with 50% probability ellipsoids

Figure S22: ORTEP representation of 7a with 50% probability ellipsoids
Figure S23: ORTEP representation of 9 with 50% probability ellipsoids

Figure S24: ORTEP representation of 10 with 50% probability ellipsoids
Figure S25: ORTEP representation of 10' with 50% probability ellipsoids

Figure S26: ORTEP representation of 14 with 50% probability ellipsoids
Optical data

Figure S27: UV-vis absorption of 5a-5c in diluted DCM ($c=10^{-5}$ M)

Figure S28: UV-vis absorption of 5a in various solvents ($c=10^{-5}$ M)
Figure S29: Solid state luminescence of 5a, 7a and 9

Figure S30: UV-vis absorption of 10 (purple), 11 (blue) and 12 (red) in DCM (solid line) and C5 (dashed line) (c = 10^{-5} M)
Figure S31: Normalized absorption (red), normalized emission (green) in diluted C5 (10^{-5} \text{ M}) and normalized emission in powder of $14$ (purple).

**Nonlinear optical experiments**

All solvent used for photophysical measurements were of spectrometric grade. The absolute quantum yields were measured with a C9920–03 Hamamatsu system. Emission spectra by two photon (2PE) absorption were recorded using a femtosecond laser chain (Ti-Sapphire Chameleon ultra II Coherent + pulse picker + SHG module when needed, pulse duration: 100-130 fs; pulse frequency: 5 MHz) and an Ocean optics QEPro CCD detector with integrating times ranging from 1 to 20s. The excitation beam crossed a lens before arriving on the sample and a short-pass 750 nm filter after the sample to remove the excitation signal and prevent damages on the CCD detector. The power of the beam was measured with a PMD100 console and a S142C integrating sphere sensor from Thorlabs. For emission intensity vs excitation power measurements, a $\lambda/2$ waveplate and a polarizer were used to vary the laser power. The 2PE was recorded in solution, perpendicularly to the beam using an optical fiber connected to a CCD detector.

To validate the experimental set-up, the quadraticity (I vs $P^2$) was first verified on a Rhodamine B solution at 8.25. $10^{-5}$ \text{ M} in MeOH. Two-photon absorption cross-section values were evaluated using Rhodamine B as standard ([RhB] = 8.25 $10^{-5}$ \text{ M} in MeOH using $\sigma_2$ reference values from Makarov et al.\(^3\)).

In order to maximize the detection, hexane was chosen has the compounds display better luminescence in apolar solvent, and hexane has a higher boiling point than pentane. Finally, $12$ was chosen as it displays both good luminescence and solubility in hexane. ([12] = 6.1 $10^{-5}$ \text{ M} in n-C\textsubscript{6}H\textsubscript{14})

\(^3\) Makarov, N. S.; Drobizhev, M.; Rebane, A., Two-photon absorption standards in the 550–1600 nm excitation wavelength range. *Opt. Express* 2008, *16* (6), 4029-4047
Figure S32. 2PE spectra vs irradiation power of 12 in hexane; inset: quadratic relationship of the observed two-photon emission intensity with the excitation laser power at 810 nm.

Figure S33. two photon absorption cross section values vs excitation wavelength (1GM = 10^{-50} cm^4 s photon^{-1}) of 12; error on calculated values is estimated as ±15%.
Electrochemical data

Figure S34: Cyclic voltammograms of 5a-5f (c = 10^{-3} M) recorded in DCM (Bu_{4}NPF_{6} (0.2 M), 200 mVs^{-1}, potentials vs Fc^{+}/Fc).

Figure S35: Cyclic voltammograms of 5a (up), 7a (middle), 9 (down) (c = 10^{-3} M) recorded in DCM (Bu_{4}NPF_{6} (0.2 M), 200 mVs^{-1}, potentials vs Fc^{+}/Fc).
Figure S36: Cyclic voltammograms of 9, 10' and 10 (c = 10^{-3} M) recorded in DCM (Bu$_4$NPF$_6$ (0.2 M), 200 mV\text{s}^{-1}, potentials vs Fc$^+$/Fc).

Figure S37: Cyclic voltammograms of 9 and 14 (c = 10^{-3} M) recorded in DCM (Bu$_4$NPF$_6$ (0.2 M), 200 mV\text{s}^{-1}, potentials vs Fc$^+$/Fc).
Analytical chiral HPLC separation

• 16a is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

| Column      | Mobile Phase                                          | t1     | k1  | t2     | k2  | α   | Rs  |
|-------------|-------------------------------------------------------|--------|-----|--------|-----|-----|-----|
| (S,S)-Whelk-O1 | Heptane / 2-PrOH / dichloromethane (50/20/30)       | 4.05 (+)| 0.37| 7.13 (-)| 1.42| 3.81| 10  |

| RT [min] | Area | Area% | Capacity Factor | Enantioselectivity | Resolution (USP) |
|----------|------|-------|-----------------|--------------------|------------------|
| 4.05     | 1533 | 54.77 | 0.37            |                    |                  |
| 7.13     | 1266 | 45.23 | 1.42            | 3.81               | 10.00            |
| Sum      | 2799 | 100.00|                 |                    |                  |
Preparative separation for compound **DT565**:

- **Sample preparation**: About 40 mg of compound **DT565** are dissolved in 8 mL of a mixture of dichloromethane/hexane (50/50).

- **Chromatographic conditions**: (S,S)-Whelk-O1 (250 x 10 mm), Hexane / 2-PrOH / dichloromethane (50/20/30) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.

- **Injections (stacked)**: 20 times 400 µL, every 8 minutes.

- **First fraction**: 17 mg of the first eluted enantiomer with ee > 99.5%

  | RT [min] | Area  | Area% |
  |----------|-------|-------|
  | 4.06     | 785   | 100.00|
  | Sum      | 785   | 100.00|

- **Second fraction**: 14 mg of the second eluted enantiomer with ee > 99.5 %

  | RT [min] | Area  | Area% |
  |----------|-------|-------|
  | 7.16     | 1137  | 100.00|
  | Sum      | 1137  | 100.00|
- Third fraction: 14 mg of intermediate

Kinetic of enantiomerization of **16a** in chlorobenzene
About 0.3 mg of the second eluted enantiomer of **16a** is heated in about 15 mL of chlorobenzene at 132°C. 20 µL are taken and then injected on (S,S)-Whelk-O1 (50:20:30 heptane / 2-PrOH / dichloromethane, 1 mL/min, UV 290 nm). The percentage decrease of the second eluted enantiomer of DT565 is monitored.

| Time (min) | % second eluted enantiomer | ln ((%t-50%)/(%t=0-50%)) |
|------------|---------------------------|--------------------------|
| 0          | 95.59                     | 0                        |
| 5          | 93.74                     | -0.041425379             |
| 10         | 91.73                     | -0.0884681               |
| 15         | 90.06                     | -0.129310064             |
| 20         | 88.41                     | -0.171370552             |
| 25         | 86.81                     | -0.213918847             |
| 30         | 84.92                     | -0.266628663             |
| 35         | 83.65                     | -0.303675338             |
| 40         | 81.83                     | -0.359279153             |
| 45         | 80.33                     | -0.407551073             |
| 50         | 78.77                     | -0.460355217             |
| 55         | 77.72                     | -0.49753422              |
Fig S38: Kinetic of enantiomerization of 16a in chlorobenzene

\[ k_{\text{enantiomerisation}} = 7.62 \times 10^{-5} \text{ s}^{-1} \ (132^\circ \text{C}, \ \text{chlorobenzene}) \]

\[ \Delta G^\circ = 132.2 \text{ kJ.mol}^{-1} \ (132^\circ \text{C}, \ \text{chlorobenzene}) \]

\[ t_{1/2} = 76 \text{ minutes} \ (132^\circ \text{C}, \ \text{chlorobenzene}) \]
Theory

Methods

We have performed the DFT and TD-DFT calculations with Gaussian 16.\textsuperscript{[1]} Default Gaussian 16 thresholds and algorithms were used but for an improved optimization threshold (10\textsuperscript{-5} au on average residual forces), a stricter self-consistent field convergence criterion (10\textsuperscript{-10} a.u.) and the use of the ultrafine DFT integration grid. Firstly, the $S_0$ geometries have been optimized with DFT and the vibrational frequencies have been analytically determined, using the M06-2X meta-GGA hybrid exchange-correlation functional.\textsuperscript{[2]} These calculations were performed with the 6-31G(d) atomic basis set and account for solvent effects through the linear-response PCM approach considering DCM as solvent.\textsuperscript{[3]} Secondly, starting from the optimal ground-state geometries, we have used TD-DFT with the same functional and basis set to optimize the $S_1$ geometry and compute the vibrational frequencies. All optimized structures correspond to true minima of the potential energy surface. Thirdly, the vertical transition energies were determined with TD-DFT and the same functional, but a larger basis set, namely 6-311+G(2d,p), in gas-phase as well as in solution using the cL2\textsuperscript{2} variant of the PCM,\textsuperscript{[4]} in its non-equilibrium limit. The selection of M06-2X for computing the lowest energy excited state is justified by numerous benchmarks on organic derivatives demonstrating that this functional offers one of the best compromise with high-correlations and rather low average deviations with respect to trustworthy experiments.\textsuperscript{[5]} We use Le Bahers’ $d_{CT}$ model\textsuperscript{[6]} on the so-called relaxed TD-M06-2X densities to quantify CT. The full UV/Vis and ECD spectra have been modelled with LR-PCM-B3LYP/6-311+G(2d,p), using a convoluting Gaussian of HWHM of 0.2 eV. The selection of B3LYP rather than M06-2X in this context is explained by the fact that the shape of ECD spectra depends on numerous excited states and that B3LYP globally provides a good balance for this task.\textsuperscript{[7]} Ref. 7 concludes: “Overall for ECD and OR, ‘traditional’ GHs seem to provide the best choice”. The TPA cross-sections have been obtained using QR-TD-DFT, with the CAM-B3LYP\textsuperscript{[8]} range-separated hybrid functional and the 6-31G atomic basis set, with the Dalton code,\textsuperscript{[9]} under its 2016 version. Default Dalton parameters were used to obtain the cross sections. Using a range-separate hybrid is typically necessary for modelling non-linear optical properties, and CAM-B3LYP is a typical choice for TPA.\textsuperscript{[7]} Eventually, NICS(0) and NICS(1) values have been computed at the usual reference B3LYP/6-311+G(d,p)\textsuperscript{[10]} level on the PCM-M06-2X/6-31G(d) geometries.

\[1\] M. J. Frisch, et al. Gaussian 16, revision A.03; Gaussian Inc.: Wallingford, CT, 2016.
\[2\] Y. Zhao, D. G. Truhlar, Theor. Chem. Acc. 2008, 120, 215–241.
\[3\] J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev. 2005, 105, 2999–3094.
\[4\] C. A. Guido, A. Chrayeh, G. Sclamani, B. Mennucci, D. Jacquemin J. Chem. Theory Comput. 2021, 17, 5155–5164.
\[5\] See for instance: a) S. S. Leang, F. Zahariev, M. S. Gordon, J. Chem. Phys. 2012, 136, 10401; b) D. Jacquemin, A. Planchat, C. Adamo, B. Mennucci, , J. Chem. Theory Comput. 2012, 8, 2350–2372; c) M. Isegawa, R. Peverati, D. G. Truhlar, J. Chem. Phys. 2012, 137, 244204.
\[6\] T. Le Bahers, C. Adamo, I. Ciofini, J. Chem. Theory Comput. 2011, 7, 2498–2506.
\[7\] Previous TD-DFT benchmarks and a summary of their conclusions can be found in: A. D. Laurent, D. Jacquemin, Int. J. Quantum Chem. 2013, 113, 2019-2039.
\[8\] T. Yanai, D. P. Tew, N. C. Handy, Chem. Phys. Lett. 2004, 393, 51–57.
\[9\] K. Aidas, et al. WIREs Comput. Mol. Sci. 2014, 4, 269–284.
\[10\] Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. von Ragué Schleyer Chem. Rev. 2005, 105, 3842–3888.
Structures of 5a and 7a

Figure S39: Top and side views of 5a (top) and 7a (bottom), as obtained by PCM-M06-2X/6-311+G(2d,p) on PCM-M06-2X/6-31G(d) geometries. Representation of the frontier MOs for these two compounds at the same level of theory.

Density differences plots of 5a, 7a, and 9

Figure S40: Density difference plots of 5a, 7a, and 9 obtained at the PCM-M06-2X/6-311+G(2d,p) level of theory for the lowest excited-transition ($S_0$-$S_1$). The blue and red lobes correspond to regions of decrease and increase of electron density upon excitation (absorption), respectively. Contour threshold: $15 \times 10^{-4}$. 
**Fig. S41**: Representation of the frontier MOs for 9-12, as obtained by PCM-M06-2X/6-311+G(2d,p) on PCM-M06-2X/6-31G(d) geometries.
Figure S42: Density difference plots of 14, 16a, and 16b obtained at the PCM-M06-2X/6-311+G(2d,p) level of theory for the lowest excited-transition ($S_0$-$S_1$). The blue and red lobes correspond to regions of decrease and increase of electron density upon excitation (absorption), respectively. Contour threshold: $1 \times 10^{-3}$.

Figure S43: Density difference plots 11 obtained at the PCM-M06-2X/6-311+G(2d,p) level of theory for the lowest excited-transition ($S_0$-$S_1$). The blue and red lobes correspond to regions of decrease and increase of electron density upon excitation (absorption), respectively. Contour threshold: $1 \times 10^{-3}$. 
**Fig. S44:** Representation of the frontier MOs for 14-16a, as obtained by PCM-M06-2X/6-311+G(2d,p) on PCM-M06-2X/6-31G(d) geometries.

**TD-DFT values**

**Table S3:** TD-DFT data determined for selected dyes. We report the vertical absorption and emission, together with the associated oscillator strength. The transition energies are obtained at the cLR^2(neq)-PCM(DCM)-TD-M06-2X/6-311+G(2d,p) level, the oscillator strength at the correspond LR(neq)-values. In the rightmost column, we provide the CT distance (for absorption) as given by Le Bahers’ model.

| Dye | Vert abs (nm) | f abs | Vert fl (nm) | f fl | d^CT (Å) |
|-----|---------------|-------|--------------|------|----------|
| 5a  | 407           | 0.15  | 577          | 0.13 | 1.97     |
| 7a  | 372           | 0.24  | 952^a        | 0.02^a| 0.86     |
| 9   | 401           | 0.30  | 550          | 0.24 | 0.90     |
| 10  | 491           | 0.76  | 635          | 0.88 | 2.20     |
| 11  | 439           | 0.57  | 545          | 0.60 | 1.23     |
| 12  | 451           | 1.03  | 563          | 1.11 | 0.63     |
Values indicating a likely dark state quenching and a strong relaxation of the excited-state geometry.

**Modeling of the UV/Vis and ECD spectra of 16a**

**Figure S45**: UV/Vis and ECD spectra modelled for 16a. The stick (vertical) contributions computed at LR-PCM-B3LYP/6-311+G(2d,p) level have been convoluted with a Gaussian of HWHM of 0.2 eV.

**Two-photon spectra of 12**

**Table S4**: One and two-photon excitation obtained with (QR-)TD-DFT (CAM-B3LYP/6-31G) for dye 12. We report the (one-photon) transition energy, the corresponding oscillator strength as well as the TPA cross section.
Figure S46: Density difference plots (CAM-B3LYP/6-31G) of 12: two lowest excited-state. The blue and red lobes correspond to regions of decrease and increase of electron density upon excitation (absorption), respectively. Contour threshold: $10 \times 10^{-4}$. Note that for the lowest one, the topology is totally similar to the one reported in the main text with the M06-2X functional and a much larger basis set.

NICS Calculations.

Fig. S47: NICS(0) aromaticity pattern of 5a, 7a and 9 at the B3LYP/6-311+G(d,p) level on the PCM-M06-2X/6-31G(d) geometries.

Fig. S48: NICS(1) aromaticity pattern of 5a, 7a and 9 at the B3LYP/6-311+G(d,p) level on the PCM-M06-2X/6-31G(d) geometries.
Fig. S48: NICS(0) aromaticity pattern of 10, 11 and 12 at the B3LYP/6-311+G(d,p) level on the PCM-M06-2X/6-31G(d) geometries.

Fig. S49: NICS(1) aromaticity pattern of 10, 11 and 12 at the B3LYP/6-311+G(d,p) level on the PCM-M06-2X/6-31G(d) geometries.
Fig. S50: NICS(0) aromaticity pattern of 14 and 16a at the B3LYP/6-311+G(d,p) level on the PCM-M06-2X/6-31G(d) geometries.

Fig. S51: NICS(0) aromaticity pattern of 14 and 16a at the B3LYP/6-311+G(d,p) level on the PCM-M06-2X/6-31G(d) geometries.
**Cartesian coordinates (ground state in Å)**

| Atom | X      | Y      | Z     |
|------|--------|--------|-------|
| P    | 0.9540180 | -0.1081680 | 0.0457130 |
| O    | -0.8731120 | -2.1825120 | -0.5969640 |
| C    | 1.9799670 | -0.6555990 | -1.3486250 |
| C    | 2.6604500 | 0.2790460  | -2.1344580 |
| H    | 2.6038200 | 1.3376190  | -1.8997590 |
| C    | 3.4173540 | -0.1512990 | -3.2221870 |
| H    | 3.9472940 | 0.5751940  | -3.8295210 |
| C    | 3.4943770 | -1.5080930 | -3.5244840 |
| H    | 4.0856680 | -1.8414320 | -4.3715690 |
| C    | 2.8122840 | -2.4406420 | -2.7424530 |
| H    | 2.8703020 | -3.4976330 | -2.9813940 |
| C    | 2.0530100 | -2.0206130 | -1.6560580 |
| H    | 1.5041490 | -2.7370830 | -1.0537130 |
| C    | 1.4083240 | -1.1462220 | 1.4592000 |
| C    | 2.7316400 | -1.5626160 | 1.6346350 |
| H    | 3.4869240 | -1.3205050 | 0.8915520 |
| C    | 3.0786910 | -2.2993890 | 2.7636840 |
| H    | 4.1052870 | -2.6225640 | 2.9019040 |
| C    | 2.1073570 | -2.6265240 | 3.7080930 |
| H    | 2.3792310 | -3.2065140 | 4.5843570 |
| C    | 0.7876240 | -2.2145200 | 3.5296310 |
| H    | 0.0313240 | -2.4752300 | 4.2627630 |
| C    | 0.4354850 | -1.4707580 | 2.4076680 |
| H    | -0.5900280 | -1.1437600 | 2.2593320 |

S65
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | 1.267496  | 1.639289  | 0.372411  |
| C    | 2.421120  | 2.307434  | 0.712670  |
| H    | 3.359624  | 1.778576  | 0.855315  |
| C    | 2.365908  | 3.712517  | 0.868850  |
| H    | 3.267871  | 4.250992  | 1.140678  |
| C    | 1.188918  | 4.402920  | 0.670612  |
| H    | 1.170188  | 5.483839  | 0.783085  |
| C    | -0.010748 | 3.732842  | 0.314502  |
| C    | -1.254538 | 4.376836  | 0.065462  |
| H    | -1.330163 | 5.456148  | 0.155731  |
| C    | -2.336246 | 3.614726  | -0.302699 |
| H    | -3.284101 | 4.102201  | -0.512591 |
| C    | -2.274541 | 2.201356  | -0.423325 |
| H    | -3.166717 | 1.665696  | -0.726018 |
| C    | -1.098185 | 1.523468  | -0.155382 |
| C    | 0.045052  | 2.329528  | 0.185302  |
| C    | -0.772170 | 0.100168  | -0.190538 |
| C    | -1.483630 | -1.105876 | -0.420961 |
| C    | -2.985572 | -1.149897 | -0.394565 |
| C    | -3.720130 | -0.463290 | 0.575277  |
| H    | -3.201001 | 0.168518  | 1.291496  |
| C    | -5.106049 | -0.592759 | 0.628254  |
| H    | -5.669953 | -0.064171 | 1.390678  |
| C    | -5.766070 | -1.403091 | -0.293848 |
| H    | -6.847001 | -1.498304 | -0.257366 |
| C    | -5.036134 | -2.099201 | -1.257336 |
| H    | -5.547936 | -2.737082 | -1.971404 |
|  | X          | Y          | Z          |
|---|------------|------------|------------|
| C | -3.6501750 | -1.9848150 | -1.2962750 |
| H | -3.0653670 | -2.5414660 | -2.0220940 |

### 7a

|  | X          | Y          | Z          |
|---|------------|------------|------------|
| P | 0.9445480  | -0.1889150 | 0.0478520  |
| C | 1.9892760  | -0.2453810 | 1.5370680  |
| C | 3.0578360  | 0.6376630  | 1.7105110  |
| H | 3.2970730  | 1.3663640  | 0.9415140  |
| C | 3.8177080  | 0.5832460  | 2.8778490  |
| H | 4.6474800  | 1.2695460  | 3.0126440  |
| C | 3.5100210  | -0.3468420 | 3.8669380  |
| H | 4.1030730  | -0.3867840 | 4.7752730  |
| C | 2.4386520  | -1.2249760 | 3.6964970  |
| H | 2.1980350  | -1.9459320 | 4.4712460  |
| C | 1.6737290  | -1.1770270 | 2.5365480  |
| H | 0.8297740  | -1.8464940 | 2.3916470  |
| C | 1.2649810  | -1.7180400 | -0.8761900 |
| C | 0.3937720  | -2.0669330 | -1.9130270 |
| H | -0.4891820 | -1.4615690 | -2.1022790 |
| C | 0.6535000  | -3.1924290 | -2.6853670 |
| H | -0.0275460 | -3.4664620 | -3.4845130 |
| C | 1.7848800  | -3.9688070 | -2.4314620 |
| H | 1.9861220  | -4.8470190 | -3.0367570 |
| C | 2.6541130  | -3.6199340 | -1.4022390 |
| H | 3.5332470  | -4.2235270 | -1.2012850 |
| C | 1.5063480  | 1.1624200  | -1.0031400 |
| C | 2.6571290  | 0.9805320  | -1.7823000 |
H  3.2230730  0.0562510  -1.6964680
C  2.3959330 -2.4947810  -0.6199100
H  3.0726250 -2.2295850   0.1872300
C  3.0704950  1.9619630  -2.6693810
H  3.9648530  1.8195400  -3.2662920
C  2.3012310  3.1189400  -2.8026270
H  2.5878860  3.8825190  -3.5189210
C  1.1570700  3.2967420  -2.0400650
H  0.5599120  4.1870190  -2.1998920
C  0.7379420  2.3404200  -1.0957190
C  -0.4597370  2.5798030  -0.2588880
C  -0.8908100  3.9020590  -0.0531890
H  -0.3075760  4.7191820  -0.4641730
C  -2.0194650  4.2028630   0.6893500
H  -2.3216400  5.2351700   0.8310050
C  -2.7365790  3.1590630   1.2782500
H  -3.6107680  3.3686110   1.8875790
C  -2.3074170  1.8528730   1.1286790
H  -2.8408060  1.0611690   1.6429700
C  -1.1770250  1.5141980   0.3510190
C  -0.7510540  0.1184810   0.2621090
C  -1.5284090  1.0485900   0.5661040
O  -1.0090780  2.1032200   0.9773150
C  -3.0063150  1.0748670   0.2739850
C  -3.5633050  0.3642820  -0.7936870
H  -2.9255460  0.2681640  -1.4049470
C  -4.9215730  0.4744740  -1.0756800
|   | X Coordinate  | Y Coordinate  | Z Coordinate  |
|---|--------------|--------------|--------------|
| H | -5.3459600   | 0.0715090    | -1.9125940   |
| C | -5.7357600   | -1.2862310   | -0.2861260   |
| H | -6.7966150   | -1.3662300   | -0.5031140   |
| C | -5.1848870   | -1.9998090   | 0.7772780    |
| H | -5.8156080   | -2.6362620   | 1.3904000    |
| C | -3.8230020   | -1.9026170   | 1.0476540    |
| H | -3.3731610   | -2.4671640   | 1.8583700    |

|   | X Coordinate  | Y Coordinate  | Z Coordinate  |
|---|--------------|--------------|--------------|
| 9 | 1.6487760    | 1.1746540    | -0.6135220   |
| C | 2.9578210    | 1.3102140    | -1.1835550   |
| H | 3.6533900    | 0.4865760    | -1.3032840   |
| C | 3.2318320    | 2.5859030    | -1.5582740   |
| H | 4.1340600    | 2.9729560    | -2.0104600   |
| C | 0.9482920    | 2.3690250    | -0.5733250   |
| C | -0.3728440   | 2.5318750    | -0.0522710   |
| C | -1.1749970   | 1.4672700    | 0.3497350    |
| C | -2.4148450   | 1.9603540    | 0.9041370    |
| H | -3.1831940   | 1.3225940    | 1.3202110    |
| C | -2.5218570   | 3.3129640    | 0.8757740    |
| H | -3.3456850   | 3.9165200    | 1.2312420    |
| C | -0.7653570   | 0.0810340    | 0.2660580    |
| C | -1.5529150   | -1.0940890   | 0.5053760    |
| O | -1.0062680   | -2.1818890   | 0.7658750    |
| C | -3.0466650   | -1.0861980   | 0.3433750    |
| C | -3.6679180   | -0.3844230   | -0.6940060   |
| H | -3.0670840   | 0.2254160    | -1.3637220   |

S69
C  -5.0464280  -0.4679940  -0.8680370
H  -5.5223750  0.0710760  -1.6811750
C  -5.8134620  -1.2430750  0.0007600
H  -6.8896560  -1.3009730  -0.1302290
C  -5.1975460  -1.9496790  1.0331940
H  -5.7930080  -2.5578960  1.7069780
C  -3.8168780  -1.8829880  1.1935900
H  -3.3189110  -2.4458140  1.9770580
C  1.9103950  -0.8645500  1.4415810
C  2.7041230  0.0752190  2.1058100
H  2.7568810  1.0981950  1.7429260
C  3.4321060  -0.3006390  3.2327750
H  4.0492110  0.4308440  3.7443640
C  3.3679060  -1.6118250  3.6964680
H  3.9363440  -1.9046710  4.5737100
C  2.5734120  -2.5501810  3.0369380
H  2.5226010  -3.5713830  3.4009500
C  1.8412970  -2.1818060  1.9133710
H  1.2087440  -2.9011630  1.4040400
C  1.1428620  -1.6090810  -1.2678140
C  2.3429690  -2.3192820  -1.3578000
H  3.1229550  -2.1776960  -0.6147620
C  2.5373900  -3.2237550  -2.3999580
H  3.4701440  -3.7742910  -2.4670390
C  1.5354960  -3.4237570  -3.3459190
H  1.6864890  -4.1325060  -4.1539830
C  0.3378930  -2.7148370  -3.2559940
H  -0.4451540  -2.8719920  -3.9906620
C   0.1426240  -1.8041900  -2.2233200
H  -0.7872840  -1.2461380  -2.1520820
P   0.9210940  -0.3280910   0.0055860
S   1.9058300   3.6568970  -1.2382110
S  -1.1268070   4.0805940   0.2084760

10
S  -1.8140660   2.2660620  -0.1647810
S   1.5436920   2.3482920   0.0262930
P  -0.8488720  -1.8994790   0.2598990
O   1.0425160  -3.9212990   0.2281500
O  -9.3791540   3.1135190  -0.0331600
O  -9.3160620   4.8417240  -0.9222590
O   8.1957250   5.0796660   0.7578960
O   9.0926590   3.3066530  -0.0760310
N  -8.4305860   3.7373920  -0.4121080
N   8.1309150   3.9438590   0.3189560
C  -1.6344760  -2.9943690  -0.9588960
C  -1.7632230  -4.3669870  -0.7219800
H  -1.3979150  -4.7904500   0.2074640
C  -2.3457770  -5.1814590  -1.6877520
H  -2.4451380  -6.2462940  -1.5042660
C  -2.7949800  -4.6330930  -2.8883690
H  -3.2490530  -5.2725640  -3.6387850
C  -2.6613380  -3.2673930  -3.1284870
H  -3.0099990  -2.8394090  -4.0625820
C  -2.0812660  -2.4461480  -2.1655490
H   -1.9782430  -1.3806570  -2.3527560
C   -1.2806180  -2.5560730   1.9011270
C    -0.3110140  -2.5335060   2.9047580
H     0.6939350  -2.1912890   2.6713460
C    -0.6353660  -2.9571610   4.1905300
H     0.1199680  -2.9459440   4.9695450
C   -1.9266340  -3.3978800   4.4736860
H    -2.1782990  -3.7279570   5.4765930
C    -2.8961120  -3.4206950   3.4718460
H    -3.8998840  -3.7694920   3.6916540
C   -2.5755310  -3.0022700   2.1837780
H    -3.3293790  -3.0397880   1.4012730
C     0.8630650  -1.6116770   0.0065280
C     1.3965530  -0.2708270   0.0179380
C     0.6072730   0.8806930  -0.0041510
C    -0.8163700   0.8529580  -0.0276970
C    -1.5977060  -0.2909510   0.0707390
C     2.7858220   0.0891710   0.1076530
H     3.5834770  -0.6332590   0.2175070
C     3.0213620   1.4337660   0.1020370
C    -2.9954810  -0.0130130   0.0331450
H    -3.7604490  -0.7821180   0.0605460
C    -3.2817330   1.3182770  -0.0926660
C     1.5793680  -2.8530840  -0.1111690
C     2.9568130  -2.9073020  -0.7060090
C     3.9120260  -3.7385400  -0.1180380
|   |   |   |   |   |
|---|---|---|---|---|
| H | 3.6424190 | -4.3065700 | 0.7671820 |
| C | 5.1923990 | -3.8248610 | -0.6579990 |
| H | 5.9377280 | -4.4579790 | -0.1869470 |
| C | 5.5136350 | -3.1035980 | -1.8070570 |
| H | 6.5100120 | -3.1752410 | -2.2320830 |
| C | 4.5519500 | -2.2976680 | -2.4172940 |
| H | 4.7949130 | -1.7504790 | -3.328550 |
| C | 3.2784700 | -2.1947780 | -1.8649910 |
| H | 2.5278830 | -1.5604920 | -2.3289450 |
| C | -4.5985380 | 1.9537020 | -0.1731600 |
| C | -5.7264920 | 1.2938350 | 0.3432710 |
| H | -5.6138870 | 0.3321520 | 0.8317930 |
| C | -6.9842330 | 1.8684670 | 0.2615220 |
| H | -7.8593730 | 1.3690530 | 0.6578680 |
| C | -7.1059000 | 3.1211640 | -0.3295440 |
| C | -6.0129430 | 3.8099650 | -0.8398880 |
| H | -6.1491200 | 4.7830770 | -1.2946380 |
| C | -4.7616610 | 3.2178180 | -0.7614340 |
| H | -3.9059230 | 3.7394720 | -1.1789900 |
| C | 4.3279230 | 2.0959150 | 0.1580950 |
| C | 5.4699000 | 1.4137770 | -0.2937690 |
| H | 5.3719550 | 0.4170150 | -0.7126320 |
| C | 6.7192830 | 2.0106570 | -0.2368610 |
| H | 7.6070820 | 1.4963930 | -0.5828520 |
| C | 6.8149860 | 3.3044970 | 0.2629990 |
| C | 5.7063160 | 4.0148590 | 0.7063370 |
| H | 5.8243140 | 5.0204620 | 1.0898530 |
C  4.4638350  3.4015030  0.6534580
H  3.5927490  3.9375950  1.0176440

11
S  1.7956160 -1.8114670  -0.1069380
S -1.5738410 -1.8800510   0.0220280
P  0.8328210  2.3520610  0.2893960
O -1.0486740  4.3880490  0.1875810
C  1.6587970  3.4488980  0.9023540
C  1.7913420  4.8192210 -0.6553300
H  1.4020370  5.2409650  0.2651150
C  2.4074980  5.6340920 -1.5998070
H  2.5092810  6.6973560 -1.4083340
C  2.8873290  5.0881370 -2.7896400
H  3.3677690  5.7277310 -3.5234310
C  2.7506860  3.7245660 -3.0399410
H  3.1236990  3.2981300 -3.9653520
C  2.1368280  2.9033130 -2.0980170
H  2.0325350  1.8390940 -2.2917290
C  1.2224330  3.0121730  1.9413000
C  0.2171830  3.0304920  2.9089790
H -0.7884860  2.7164770  2.6414120
C  0.5076340  3.4584900  4.2016090
H -0.2754330  3.4790550  4.9526260
C  1.8007700  3.8626060  4.5275010
H  2.0260800  4.1957580  5.5356860
C  2.8062560  3.8444180  3.5615340
| H     | C    | C     | H    |
|-------|------|-------|------|
| 3.8119620 | 4.1640340 | 3.8146860 |     |
| 2.5193050 | 3.4218010 | 2.2670030 |     |
| 3.3016260 | 3.4266480 | 1.5118690 |     |
| -0.8721000 | 2.0751660 | -0.0142370 |     |
| -1.4136980 | 0.7347610 | -0.0069770 |     |
| -0.6276670 | -0.4168840 | -0.0024010 |     |
| 0.7973460 | -0.3943920 | 0.0078500 |     |
| 1.5819020 | 0.7442120 | 0.1197350 |     |
| -2.8070140 | 0.3825900 | 0.0584630 |     |
| -3.6040520 | 1.1095170 | 0.1422000 |     |
| -3.0515980 | -0.9600880 | 0.0624780 |     |
| 2.9822480 | 0.4614570 | 0.1049790 |     |
| 3.7506880 | 1.2268230 | 0.1413810 |     |
| 3.2673700 | -0.8690730 | -0.0137600 |     |
| -1.5763130 | 3.3181380 | -0.1647190 |     |
| -2.9288770 | 3.3769940 | -0.8154400 |     |
| -3.8928120 | 4.2395690 | -0.2899380 |     |
| -3.6503730 | 4.8246180 | 0.5920190 |     |
| -5.1467130 | 4.3366570 | -0.8870590 |     |
| -5.8991080 | 4.9948450 | -0.4638510 |     |
| -5.4321730 | 3.5939530 | -2.0318720 |     |
| -6.4075720 | 3.6738500 | -2.5018390 |     |
| -4.4610080 | 2.7555410 | -2.5798190 |     |
| -4.6752870 | 2.1903150 | -3.4815610 |     |
| -3.2148900 | 2.6426570 | -1.9700750 |     |
| -2.4574880 | 1.9837620 | -2.3859380 |     |
| 4.5830910 | -1.5148110 | -0.0678990 |     |
C  5.6968950  -0.8928020  0.5144200
H  5.5719210  0.0456330  1.0461100
C  6.9517810  -1.4806580  0.4497180
H  7.7935300  -0.9902890  1.0461100
C  7.1409540  -2.7160950  -0.1844190
C  6.0245230  -3.3413770  -0.7528830
H  6.1454030  -4.2872590  -1.2726800
C  4.7685850  -2.7515200  -0.6995010
H  3.9284660  -3.2469870  -1.1789950
C  -4.3608790  -1.6214200  0.0952470
C  -5.4894810  -0.9607060  -0.4110790
H  -5.3779370  0.0206830  -0.8640920
C  -6.7387900  -1.5631760  -0.3726160
H  -7.5936730  -1.0420600  -0.7936840
C  -6.9058870  -2.8492870  0.1586370
C  -5.7744040  -3.5109250  0.6519340
H  -5.8795270  -4.4980040  1.0924910
C  -4.5238910  -2.9081730  0.6238550
H  -3.6690000  -3.4331250  1.0419400
C  -8.2423170  -3.4916940  0.1937850
C  -8.3820270  -4.8682870  -0.0247680
C  -9.3930490  -2.7340500  0.4469360
C  -9.6362800  -5.4699990  0.0092390
H  -7.5032030  -5.4671360  -0.2466740
C  -10.6475210  -3.3352290  0.4801870
H  -9.3006000  -1.6695430  0.6429790
C  -10.7738930  -4.7056850  0.2615630
H  -9.7256330  -6.5369860  -0.1700930
H  -11.5270840  -2.7328490  0.6854300
H  -11.7523180  -5.1749240  0.2876630
C   8.4838070  -3.3423380  -0.2489790
C   8.6330480  -4.7312700  -0.1452130
C   9.6312360  -2.5564290  -0.4165040
C   9.8934980  -5.3175170  -0.2076660
H   7.7564360  -5.3538990  0.0097960
C  10.8918740  -3.1422080  -0.4780460
H   9.5318160  -1.4799030  -0.5234850
C  11.0277340  -4.5251900  -0.3740860
H   9.9902490  -6.3950780  -0.1177730
H  11.7689650  -2.5174920  -0.4223520

S   -1.7739540   1.0545620  -0.0735960
S   1.5971440  1.1179260   0.0108210
P  -0.8122290  -3.1106570  0.2871120
O   1.0655320  -5.1500860  0.1546340
C  -1.6540760  -4.2032460  -0.8979440
C  -1.7841470  -5.5744910  -0.6548030
H  -1.3834510  -5.9999760  0.2590190
C  -2.4125140  -6.3854520  -1.5946340
H  -2.5122770  -7.4494500  -1.4060980
C  -2.9071090  -5.8346760  -2.7761590
H  -3.3969590  -6.4712110  -3.5063980

S77
| C          | -2.7732240 | -4.4701240 | -3.0226160 |
| H          | -3.1578350 | -4.0398680 | -3.9415070 |
| C          | -2.1472000 | -3.6528590 | -2.0852170 |
| H          | -2.0451830 | -2.5878020 | -2.2755420 |
| C          | -1.1816350 | -3.7783740 |  1.9410240 |
| C          | -0.1631170 | -3.8065130 |  2.8944460 |
| H          |  0.8401630 | -3.4959350 |  2.6141820 |
| C          | -0.4374680 | -4.2398440 |  4.1888480 |
| H          |  0.3559330 | -4.2680280 |  4.9287180 |
| C          | -1.7278480 | -4.6395040 |  4.5308380 |
| H          | -1.9406380 | -4.9768050 |  5.5403740 |
| C          | -2.7466540 | -4.6114650 |  3.5791510 |
| H          | -3.7503050 | -4.9274370 |  3.8448110 |
| C          | -2.4757490 | -4.1834490 |  2.2829150 |
| H          | -3.2686780 | -4.1801450 |  1.5389020 |
| C          |  0.8893120 | -2.8357960 | -0.0371110 |
| C          |  1.4338610 | -1.4958620 | -0.0309130 |
| C          |  0.6483890 | -0.3443920 | -0.0100920 |
| C          | -0.7761950 | -0.3653160 |  0.0197480 |
| C          | -1.5621850 | -1.5022930 |  0.1341490 |
| C          |  2.8283760 | -1.1459710 |  0.0203220 |
| H          |  3.6257880 | -1.8739470 |  0.0908520 |
| C          |  3.0755200 |  0.1966470 |  0.0301560 |
| C          | -2.9629580 | -1.2173370 |  0.1358190 |
| H          | -3.7321270 | -1.9818710 |  0.1746990 |
| C          | -3.2477440 |  0.1144010 |  0.0284560 |
| C          |  1.5893820 | -4.0789730 | -0.2006750 |
|  |  |  |  |
|---|---|---|---|
| C | 2.933400 | -4.137068 | -0.869273 |
| C | 3.903421 | -5.002432 | -0.359844 |
| H | 3.672148 | -5.590367 | 0.523207 |
| C | 5.149151 | -5.098781 | -0.974011 |
| H | 5.906513 | -5.759077 | -0.563088 |
| C | 5.420061 | -4.352515 | -2.120028 |
| H | 6.389059 | -4.431680 | -2.603188 |
| C | 4.442448 | -3.511361 | -2.652024 |
| H | 4.645232 | -2.943223 | -3.554612 |
| C | 3.204809 | -3.399157 | -2.025105 |
| H | 2.442664 | -2.737858 | -2.428219 |
| C | -4.559601 | 0.766455 | -0.002668 |
| C | -5.670789 | 0.150673 | 0.591923 |
| H | -5.546077 | -0.792829 | 1.115038 |
| C | -6.922159 | 0.745166 | 0.562285 |
| H | -7.764302 | 0.257725 | 1.042696 |
| C | -7.108728 | 1.984362 | -0.068046 |
| C | -6.002316 | 2.607706 | -0.660554 |
| H | -6.129524 | 3.562275 | -1.160554 |
| C | -4.752077 | 2.008415 | -0.622359 |
| H | -3.918410 | 2.504506 | -1.112643 |
| C | 4.383170 | 0.857905 | 0.047841 |
| C | 5.504747 | 0.209885 | -0.490483 |
| H | 5.387400 | -0.765116 | -0.956130 |
| C | 6.753659 | 0.810429 | -0.478558 |
| H | 7.604727 | 0.298290 | -0.915500 |
| C | 6.926355 | 2.086256 | 0.078812 |

S79
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | 5.8087010| 2.7408630| 0.6151570|
| H    | 5.9259240| 3.7240360| 1.0589020|
| C    | 4.5608150| 2.1362400| 0.5926790|
| H    | 3.7158400| 2.6562880| 1.0366310|
| N    | -8.3801830| 2.5906430| -0.0996290|
| N    | 8.1952350| 2.6981070| 0.0943870|
| C    | -8.5029470| 4.0011290| -0.0096970|
| C    | -7.7134160| 4.7253840| 0.8906050|
| C    | -9.4221130| 4.6806950| -0.8166270|
| C    | -7.8359230| 6.1086050| 0.9700330|
| H    | -7.0055710| 4.1983070| 1.5229910|
| C    | -9.5510030| 6.0620800| -0.7167090|
| H    | -10.0328060| 4.1193480| -1.5170570|
| C    | -8.7568180| 6.7847760| 0.1717580|
| H    | -7.2160810| 6.6578500| 1.6719720|
| H    | -10.2690090| 6.5762110| -1.3481790|
| H    | -8.8550060| 7.8630730| 0.2418400|
| C    | -9.5485570| 1.7951120| -0.2188430|
| C    | -9.5788880| 0.7077880| -1.0994020|
| C    | -10.6855320| 2.0954670| 0.5395150|
| C    | -10.7260480| -0.0713620| -1.2069980|
| H    | -8.7001650| 0.4791350| -1.6946650|
| C    | -11.8344400| 1.3220170| 0.4113380|
| H    | -10.6614880| 2.9373090| 1.2246290|
| C    | -11.8610390| 0.2322780| -0.4572090|
| H    | -10.7351270| -0.9125640| -1.8932750|
| H    | -12.7096040| 1.5671550| 1.0051420|
H  -12.7567690  -0.3730680  -0.5495160
C   8.3152060   4.1033570  -0.0610690
C   9.2178910   4.8235770   0.7289970
C   7.5409650   4.7810430  -1.0094590
C   9.3459480   6.1989160   0.5652280
H   9.8166870   4.2980740   1.4665560
C   7.6621140   6.1592580  -1.1530530
H   6.8458570   4.2218440  -1.6282590
C   8.5668460   6.7563400  -0.3714500
H  10.0511930   6.7449710   1.1841490
H   7.0541760   6.6724210  -1.8917560
H   8.6640700   7.9496080  -0.4916490
C   9.3663210   1.9155620   0.2640790
C  10.5095200   2.1869220  -0.4958830
C   9.3940420   0.8718940   1.1959790
C  11.6619950   1.4286360  -0.3187510
H  10.4874870   2.9949310  -1.2206470
C  10.5449310   0.1066110   1.3525140
H  8.5105010   0.6655730   1.7922600
C  11.6859970   0.3816820   0.6008880
H  12.5418940   1.6512020  -0.9144680
H  10.5517480  -0.7009930   2.0780310
H  12.5843520  -0.2126840   0.7312940

S   -1.5152150   3.3908720  -1.1803070
S   1.6219120   3.5429210  -0.1201210

S81
P   -0.9073290  -0.5780960  0.3964370
O   1.0086860  -2.7042660  0.6400000
C   -0.6951610  2.0223140  -0.4604250
C   -1.5423710  0.9489180  -0.2680010
C   -2.8962240  1.2110940  -0.7097940
C   -4.0312970  0.3839800  -0.6690570
H   -3.9615250  -0.6229420  -0.2685030
C   -5.2422770  0.8625800  -1.1428550
H   -6.1180120  0.2226820  -1.1119710
C   -5.3524840  2.1616700  -1.6605280
H   -6.3098080  2.5171750  -2.0269910
C   -4.2478760  3.0004430  -1.7058700
H   -4.3272060  4.0079230  -2.1011740
C   -3.0306380  2.5154310  -1.2282330
C   0.6875950  2.0561000  -0.1173750
C   1.4044140  0.9314040  0.2638560
C   2.7612600  1.3069450  0.6584900
C   3.7605920  0.5235290  1.2609670
H   3.5707070  -0.5182240  1.4908680
C   4.9852600  1.0859010  1.5752730
H   5.7517400  0.4742640  2.0397290
C   5.2430300  2.4403210  1.3097590
H   6.2112580  2.8645400  1.5555040
C   4.2608170  3.2489470  0.7615730
H   4.4396100  4.3048830  0.5857650
C   3.0236900  2.6759790  0.4557710
C   -1.6467070  -0.8697890  2.0349950
| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| C    | -1.2456860   | -1.9861350   | 2.7823760    |
| H    | -0.5108540   | -2.6694390   | 2.3660040    |
| C    | -1.7849870   | -2.1959780   | 4.0471070    |
| H    | -1.4766650   | -3.0599820   | 4.6270060    |
| C    | -2.7149710   | -1.2977060   | 4.5712920    |
| H    | -3.1319080   | -1.4651840   | 5.5594370    |
| C    | -3.1036420   | -0.1824940   | 3.8337890    |
| H    | -3.8208060   | 0.5209990    | 4.2440570    |
| C    | -2.5683960   | 0.0367140    | 2.5660510    |
| H    | -2.8657480   | 0.9133060    | 1.9976900    |
| C    | -1.4788300   | -1.9204940   | -0.6935510   |
| C    | -1.0022320   | -1.9270120   | -2.0079730   |
| H    | -0.2837100   | -1.1761890   | -2.3282270   |
| C    | -1.4402340   | -2.8995960   | -2.8999390   |
| H    | -1.0653070   | -2.9051360   | -3.9181950   |
| C    | -2.3594040   | -3.8629220   | -2.4853160   |
| H    | -2.7020210   | -4.6205540   | -3.1829070   |
| C    | -2.8384420   | -3.8534400   | -1.1780120   |
| H    | -3.5526700   | -4.6029450   | -0.8529240   |
| C    | -2.3995560   | -2.8838070   | -0.2784720   |
| H    | -2.7745070   | -2.8829370   | 0.7405990    |
| C    | 0.8365310    | -0.3940190   | 0.3006900    |
| C    | 1.5201000    | -1.6614380   | 0.2009110    |
| C    | 2.8044470    | -1.7814570   | -0.5723090   |
| C    | 3.1103490    | -0.9379390   | -1.6435730   |
| H    | 2.4215400    | -0.1445950   | -1.9198080   |
| C    | 4.2905900    | -1.1173460   | -2.3599230   |

S83
H  4.5197660  -0.4629800  -3.1951390
C  5.1746230  -2.1349760  -2.0065790
H  6.0987100  -2.2681410  -2.5607450
C  4.8680070  -2.9873230  -0.9456470
H  5.5521710  -3.7849710  -0.6732090
C  3.6815990  -2.8179350  -0.2404850
H  3.4196140  -3.4794610  0.5795170

16a
P  1.1386030  -0.8968340  0.3068720
O  3.2342960  1.1388640  0.3864210
C  -1.4794010  -0.7527790  -0.5074690
C  -0.3568510  -1.5723180  -0.4374500
C  -1.5646290  0.4932890  0.2867080
C  -0.4216400  1.2954100  0.4571160
C  1.3431100  -1.5423140  1.9906010
C  2.3849290  -1.0306750  2.7762110
H  3.0441460  -0.2726670  2.3596220
C  2.5563220  -1.4987100  4.0739310
H  3.3622920  -1.1082240  4.6868790
C  1.6913730  -2.4659530  4.5889550
H  1.8275610  -2.8265610  5.6037030
C  0.6517120  -2.9666370  3.8095980
H  -0.0229780  -3.7139520  4.2143510
C  0.4734570  -2.5050450  2.5064980
H  -0.3395050  -2.8899000  1.8966540
C  2.5148280  -1.5329110  -0.6854440

S84
C  2.7356700  -0.9855270  -1.9537440
H  2.1292270  -0.1501590  -2.2947020
C  3.7373120  -1.5048800  -2.7646130
H  3.9134760  -1.0752340  -3.7453550
C  4.5151280  -2.5739320  -2.3174240
H  5.2962140  -2.9781090  -2.9535440
C  4.2910800  -3.1214680  -1.0577330
H  4.8966120  -3.9517170  -0.7077430
C  3.2915040  -2.6020220  -0.2368910
H  3.1230600  -3.0289800  0.7477360
C  0.9195760  0.8217140  0.1425730
C  2.1272820  1.5943160  0.0491340
C  2.0920770  2.9658480  -0.5715560
C  1.1472150  3.3185870  -1.5403840
H  0.3897930  2.5982310  -1.8362690
C  1.1852100  4.5792010  -2.1292320
H  0.4545460  4.8440090  -2.8872060
C  2.1620780  5.4987000  -1.7489700
H  2.1874230  6.4836760  -2.2050990
C  3.1099270  5.1502880  -0.7872830
H  3.8737660  5.8634840  -0.4929840
C  3.0798560  3.8851760  -0.2089260
H  3.8192660  3.5898960  0.5288570
C  -2.7947240  0.8594300  0.9484250
C  -3.8880970  -0.0373450  1.1126990
C  -2.9187140  2.1470450  1.5385260
C  -5.0428640  0.3488010  1.7500510

S85
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | -3.8032230 | -1.0537180 | 0.7453520 |
| C    | -4.1278560 | 2.5300260  | 2.1702250 |
| C    | -5.1814210 | 1.6556490  | 2.2679080 |
| H    | -5.8531980 | -0.3645610 | 1.8659890 |
| H    | -4.1935880 | 3.5286010  | 2.5949560 |
| H    | -6.1022390 | 1.9524050  | 2.7596790 |
| C    | -2.5131530 | -1.1332910 | -1.4439450 |
| C    | -2.4665170 | -2.4169230 | -2.0598270 |
| C    | -3.5477310 | -0.2424380 | -1.8456690 |
| C    | -3.4975150 | -2.8040740 | -2.9569870 |
| C    | -4.5118940 | -0.6303440 | -2.7415880 |
| H    | -3.5598290 | 0.7659370  | -1.4499570 |
| C    | -4.5055120 | -1.9359970 | -3.2860890 |
| H    | -3.4541270 | -3.7970770 | -3.3958700 |
| H    | -5.2820780 | 0.0733450  | -3.0408730 |
| H    | -5.2831130 | -2.2362280 | -3.9812080 |
| C    | -1.3598680 | -3.2765390 | -1.8243020 |
| C    | -0.3010440 | -2.8364240 | -1.0834240 |
| H    | -1.3432590 | -4.2567530 | -2.2916940 |
| H    | 0.5892320  | -3.4502460 | -0.9779940 |
| C    | -1.7869110 | 3.0093520  | 1.5420100 |
| C    | -0.5831870 | 2.5808180  | 1.0735550 |
| H    | -1.8784500 | 3.9916760  | 1.9985030 |
| H    | 0.2898740  | 3.2129160  | 1.1891180 |

**16b**

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| P    | -0.8709050 | 1.5619770 | -0.1843530 |
| Element | X  | Y  | Z  | Energy |
|---------|----|----|----|---------|
| H       | -1.1911260 | -3.5102080 | 1.2585990 |
| C       | -3.5516340 | -3.2915600 | 3.6972450 |
| H       | -4.6580380 | -1.5316210 | 4.2066270 |
| H       | -2.2230920 | -4.8628870 | 3.0139870 |
| H       | -4.0118090 | -3.9063820 | 4.4641350 |
| C       | -3.6019670 | 0.2283480  | 2.4989550 |
| C       | -2.9039980 | 1.0350340  | 1.6466360 |
| H       | -4.3389530 | 0.6439620  | 3.1798270 |
| H       | -3.0534490 | 2.1110740  | 1.6612850 |
| C       | 0.8952120  | -2.6873340 | -2.2247400|
| C       | 1.1752450  | -1.4630580 | -1.6989920|
| H       | 1.5999430  | -3.1686570 | -2.8979130|
| H       | 2.0893920  | -0.9563120 | -1.9880000|
| N       | 6.7898100  | -1.2693550 | 0.6721050 |
| O       | 6.7930490  | -2.2121660 | 1.4447930 |
| O       | 7.7883060  | -0.8209090 | 0.1356740 |