Supporting Information

A biphenyl containing two electron-donating and two accepting moieties: a rigid and small donator-acceptor-donator ladder system

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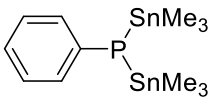
1. General

All moisture- and air-sensitive reactions were performed in oven-dried or heat-gun-dried glassware under an argon atmosphere using standard *Schlenk* techniques. Solvents used for extraction and flash chromatography (FC) were distilled before use. All chemicals were purchased from *Sigma Aldrich*, *Acros Organics*, *ABCR* or *Alfa Aesar* and were used as received. UV-visible absorption spectra were recorded on a *Shimadzu UV-3150* spectrometer with a resolution of 0.5 nm. A *Hitachi F-4500* spectrometer was used to measure the emission spectra of solution samples with a resolution of 1 nm. Fluorescence quantum yields were determined with a *Hamamatsu C9920-02* calibrated integrating sphere system. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a *Bruker DPX 300* or *Bruker AV 400* spectrometer. Chemicals shifts δ are given in ppm and the solvent residual peak ($CDCl_3$: ^{1}H, δ = 7.26, ^{13}C, δ = 77.0; CH_2Cl_2: ^{1}H, δ = 5.32, ^{13}C, δ = 54.0) was used as an internal standard. Peak multiplicities are specified as followed: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. ^{31}P NMR (122 MHz) spectra were recorded on a *Bruker DPX 300* spectrometer. Chemicals shifts δ are given in ppm and referenced to the solvent residual peak.[a] HRMS ESI (*m/z*) spectra were recorded on a *Bruker MicroTof*. Melting points (MP) were measured on a *Stuart SMP10* and are uncorrected. IR spectra were recorded on a *Digilab* Varian 3100 FT-IR Excalibur Series. The resulting IR signals are specified as *w* (weak), *m* (middle), *s* (strong), *br* (broad) in cm^{-1}. *Merck* silica gel 60 F_{254} plates were used for thin layer chromatography (TLC) and detection was achieved by UV light or dipping into a solution of $KMnO_4$ (1.0 g) and $NaHCO_3$ (3.5 g) in H_2O (200 mL) followed by heating. FC was performed with an argon excess pressure of 0.4 – 0.5 bar on *Merck* silica gel 60 (40-63 µm) or on *Acros Organics* silica gel 60 (35-70 µm). 1,3-Dibromo-5-nitrobenzene and 3,5-dibromoaniline were synthesized according to a literature procedure.[b]

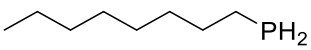
2. Preparative Experiments

Bis(trimethyltin) phenylphosphine (**S1**)



The stannylated phosphine **S1** was synthesized according to a literature procedure[c] and handled with care. Stored under argon in a freezer (-20 °C), bis(trimethyltin) phenylphosphine (**S1**) was stable for a few month.

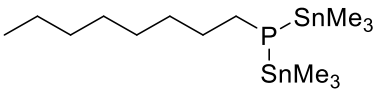
n-Octyl phosphine (**S2**)



In analogy to a literature procedure[d] $LiAlH_4$ (1.73 g, 45.7 mmol, 2.05 eq.) was suspended in distilled tetraethylene glycol dimethyl ether (115 mL) and $AlCl_3$ (15.2 g, 114 mmol, 5.0 eq.) was added portion wise at 0 °C. Then diethyl-*n*-octylphosphonate (5.72 g, 22.9 mmol, 1.0 eq.) was added dropwise and the mixture was stirred at rt for 1 h. At 0 °C H_2O (dist., 100 mL) was added carefully and the organic phase was transferred under argon. The phosphine **S2** was isolated after distillation (85 °C, 16 mbar) and trapped at -78 °C as a colorless oil (2.54 g, 17.4 mmol, 71%).

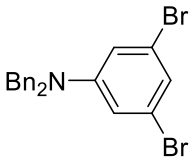
^{1}H NMR (400 MHz, $CDCl_3$, 300 K) δ = 2.72 (*br s*, 2H, PH_2), 1.50-1.47 (*m*, 4H, CH_2), 1.33-1.26 (*m*, 10H, CH_2), 0.87 (*t*, *J* = 6.6 Hz, 3H, CH_3). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K) δ = 33.0 (*d*, *J* = 3.3 Hz, CH_2), 32.0 (CH_2), 30.7 (*d*, *J* = 5.8 Hz, CH_2), 29.30 (CH_2), 29.28 (CH_2), 22.8 (CH_2), 14.2 (CH_3), 13.8 (*d*, *J* = 7.0 Hz, CH_2). **^{31}P NMR** (162 MHz, $CDCl_3$, 300 K) δ = -136.8.

Bis(trimethyltin) *n*-octylphosphine (**S3**)



In analogy to a literature procedure[c] (diemthylamino)trimethyltin (5.08 mL, 31.1 mmol, 2.1 eq.) was placed in a *Schlenk*-tube under argon, phosphine **S2** (2.17 mL, 14.8 mmol, 1.00 eq.) was added dropwise during 30 min and the mixture was stirred at rt for an additional 4 h. All volatile components were removed under high vacuum at rt and then at 70 °C. The bisstannylated phosphine **S3** (6.83 g, 14.5 mmol, 98%) was used for the phosphanylation reactions without any further purification. **^{1}H NMR** (400 MHz, $CDCl_3$, 300 K) δ = 1.77-1.73 (*m*, 2H, CH_2), 1.45-1.25 (*m*, 12H, CH_2), 0.87 (*t*, *J* = 6.6 Hz, 3H, CH_3), 0.31-0.19 (*m*, 18H, CH_2). **^{13}C NMR** (100 MHz, $CDCl_3$, 300 K) δ = 34.3 (*d*, *J* = 12.7 Hz, CH_2), 32.0 (CH_2), 31.9 (CH_2), 31.1 (*d*, *J* = 11.4 Hz, CH_2), 29.3 (*d*, *J* = 6.0 Hz, CH_2), 22.8 (CH_2), 17.0 (*d*, *J* = 26.7 Hz, CH_2), 14.2 (CH_3), -7.0 (*d*, *J* = 7.2 Hz, CH_3). **^{31}P NMR** (162 MHz, $CDCl_3$, 300 K) δ = -166.6.

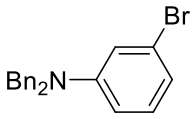
N,*N*-Dibenzyl-3,5-dibromoaniline (**1**)



In analogy to a literature procedure[e] 3,5-dibromoaniline (2.51 g, 10.0 mmol, 1.0 eq.), K_2CO_3 (4.15 g, 30.0 mmol, 3.0 eq.) and benzyl bromide (2.84 mL, 24.0 mmol, 2.4 eq.) were suspended in acetonitrile (10 mL). The reaction mixture was heated at 125 °C for 4 h and then all volatiles were removed *in vacuo*. The residue was dissolved in H_2O (20 mL), extracted with EtOAc and dried over $MgSO_4$. The solvent was removed *in vacuo* and FC (P/EtOAc = 100/1) afforded the desired product **1** as a colorless solid (3.45 g, 8.00 mmol, 80%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K) δ = 7.29-7.24 (*m*, 4H, CH_{arom}), 7.22-7.16 (*m*, 2H, CH_{arom}), 7.10 (*d*, *J* = 6.8 Hz, 4H, CH_{arom}), 6.89 (*t*, *J* = 1.5 Hz, 1H, CH_{arom}), 6.71 (*d*, *J* = 1.5 Hz, 2H, CH_{arom}), 4.50 (*s*, 4H, CH_2). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K) δ = 151.3 (C_q), 137.1 (C_q), 129.0 (CH), 127.5 (CH), 126.7 (CH), 123.8 (C_q), 122.2 (CH), 114.1 (CH), 54.0 (CH_2). **HRMS** (**ESI**) *m/z* = 431.9786 calcd. for $C_{20}H_{17}NBr_2H$ $[M+H]^+$; found: 431.9785. **IR** (ATR): 3087 *w*, 3062 *w*, 3028 *w*, 2919 *w*, 2866 *w*, 1949 *w*, 1860 *w*, 1807 *w*, 1577 *s*, 1537 *s*, 1494 *m*, 1479 *m*, 1449 *s*, 1359 *m*, 1295 *m*, 1233 *m*, 1201 *w*, 1157 *w*, 1104 *m*, 1057 *w*, 1208 *m*. **MP**: 76 °C.

N,*N*-Dibenzyl-3-bromoaniline (**S4**)

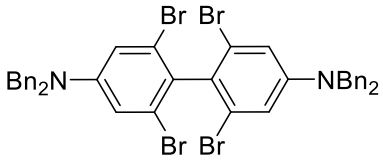


According to a literature procedure[e] 3-bromoaniline (1.53 g, 8.87 mmol, 1.0 eq.), K_2CO_3 (3.68 g, 26.6 mmol, 3.0 eq.) and benzyl bromide (2.55 mL, 21.3 mmol, 2.4 eq.) were suspended in acetonitrile (10 mL). The reaction mixture was heated at 125 °C for 4 h and then all volatiles were removed *in vacuo*. The residue was dissolved in H_2O (20 mL), extracted with EtOAc

and dried over $MgSO_4$. The solvent was removed *in vacuo* and FC (P → P/EtOAc = 100/1) afforded the desired product **S4** as a colorless solid (2.28 g, 6.47 mmol, 73%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K) δ = 7.46-7.37 (*m*, 4H, CH_{arom}), 7.35-7.29 (*m*, 2H, CH_{arom}), 7.29-7.23 (*m*, 4H, CH_{arom}), 7.05 (*t*, *J* = 8.0 Hz, 1H, CH_{arom}), 6.96 (*t*, *J* = 1.9 Hz, 1H, CH_{arom}), 6.88 (*d*, *J* = 8.0 Hz, 1H, CH_{arom}), 6.70 (*dd*, *J* = 8.4 Hz, *J* = 2.4 Hz, 1H, CH_{arom}), 4.68 (*s*, 4H, CH_2). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K) δ = 150.6 (C_q), 137.9 (C_q), 130.6 (CH), 128.9 (CH), 127.2 (CH), 126.7 (CH), 123.7 (C_q), 119.8 (CH), 115.3 (CH), 111.3 (CH), 54.2 (CH_2). **HRMS** (**ESI**) *m/z* = 352.0695 calcd. for $C_{20}H_{18}NBrH$ $[M+H]^+$; found: 352.0684. Spectroscopic data are in agreement with those reported in literature.[5]

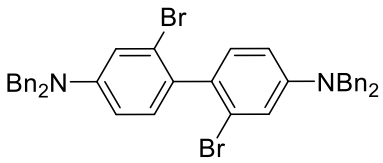
N^4,*N*^{4},*N*$^{4'}$,*N*$^{4'}$-Tetrabenzyl-2,2´-6,6´-tetrabromobiphenyl-4,4´-diamine (**2**)



In analogy to a literature procedure[e] aniline **1** (173 mg, 0.400 mmol, 1.0 eq.) was added to $FeCl_3 \cdot 6\ H_2O$ (270 mg, 1.00 mmol, 2.5 eq.) in toluene (2 mL). The reaction mixture was heated at 85 °C for 24 h. At rt NH_3 (aq., 25%, 10 mL) was added and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were washed with H_2O and brine and dried over $MgSO_4$. FC (P/EtOAc = 100/1) afforded the desired benzidine **2** as a light brown solid (76 mg, 0.088 mmol, 44%).

^{1}H NMR (300 MHz, CD_2Cl_2, 300 K) δ = 7.39-7.36 (*m*, 8H, CH_{arom}), 7.31-7.29 (*m*, 4H, CH_{arom}), 7.27-7.25 (*m*, 8H, CH_{arom}), 6.99 (*s*, 4H, CH_{arom}), 4.66 (*s*, 8H, CH_2). **^{13}C NMR** (75 MHz, CD_2Cl_2, 300 K) δ = 150.9 (C_q), 137.8 (C_q), 130.8 (C_q), 129.3 (CH), 127.8 (CH), 127.1 (CH), 126.5 (C_q), 115.3 (CH), 54.6 (CH_2). **HRMS** (**ESI**) *m/z* = 860.9331 calcd. for $C_{40}H_{32}N_2Br_4H$ $[M+H]^+$; found: 860.9325. **IR** (ATR): 3029 *w*, 2923 *br w*, 1591 *s*, 1516 *s*, 1479 *s*, 1450 *s*, 1359 *m*, 1230 *m*, 1156 *w*, 1076 *w*, 1028 *w*, 960 *m*, 908 *m*, 825 *m*, 731 *s*, 697 *m*, 646 *w*. **Elem. Anal.** calcd. for $C_{40}H_{32}N_2Br_4$: C 55.84, H 3.75, N 3.26; found: C 55.87, H 3.52, N 3.22. **MP**: 196 °C.

N^4,*N*^{4},*N*$^{4'}$,*N*$^{4'}$-Tetrabenzyl-2,2-dibromobiphenyl-4,4´-diamine (**4**)

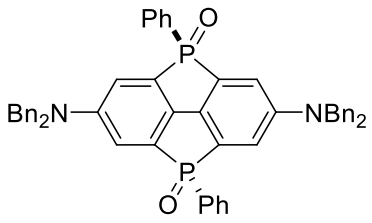


According to a literature procedure[e] aniline **S4** (141 mg, 0.400 mmol, 1.0 eq.) was added to $FeCl_3 \cdot 6\ H_2O$ (270 mg, 1.00 mmol, 2.5 eq.) in toluene (2 mL). The reaction mixture was heated at 85 °C for 5.5 h. NH_3 (aq., 25%, 10 mL) was added at rt and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were washed with H_2O and brine and dried over $MgSO_4$. FC (P/EtOAc = 100/1) afforded the desired benzidine **4** as a colorless solid (132 mg, 0.188 mmol, 94%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K) δ = 7.38-7.30 (*m*, 8H, CH_{arom}), 7.28-7.23 (*m*, 12H, CH_{arom}), 7.02 (*s*, 2H, CH_{arom}), 7.01 (*d*, *J* = 10.5 Hz, 2H, CH_{arom}), 6.67 (*dd*, *J* = 8.6 Hz, *J* = 2.6 Hz, 2H, CH_{arom}), 4.63 (*s*, 8H, CH_2). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K) δ = 149.7 (C_q), 138.1 (C_q), 132.2 (CH), 130.5 (C_q), 128.9 (CH), 127.3 (CH), 126.9 (CH), 125.4 (C_q), 115.7 (CH), 111.3

(CH), 54.2 (CH_2). **HRMS** (**ESI**) *m/z* = 703.1141 calcd. for $C_{40}H_{34}N_2Br_2H$ $[M+H]^+$; found: 703.1121. Spectroscopic data are in agreement with those reported in literature.[e]

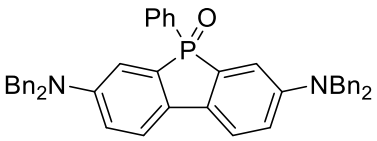
2,6-Bis(dibenzylamino)-4,8-diphenylphosphindolo[4,3,2-*bcd*]phosphindole 4,8-dioxide (**3a**)



Tetrabromide **2** (0.43 g. 0.50 mmol, 1.0 eq.), stannylated phosphine **S1** (654 mg, 1.50 mmol, 3.0 eq.) and 1,1´-azobis(cyclohexanecarbonitrile) (109 mg, 0.250 mmol, 0.5 eq.) were placed under argon in an oven-dried *Schlenk*-tube. Trifluorotoluene (5 mL) was added and the reaction mixture was stirred for 3 d at 125 °C. The reaction mixture was allowed to cool to rt and stirred overnight. The precipitate was collected and washed with trifluorotoluene (2 × 1 mL). Then the solid was dissolved in CH_2Cl_2 (100 mL), H_2O_2 (2 mL) and H_2O (10 mL) were directly added. Rigorous stirring was continued for 3 h and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with $Na_2S_2O_3$ (aq., sat.) and dried over $MgSO_4$. The solvent was removed *in vacuo* to afford the crude product. The residue was purified by FC (CH_2Cl_2/MeOH = 70/1) and product **3a** was isolated as an orange solid (95 mg, 0.12 mmol, 24%).

^{1}H NMR (300 MHz, $CDCl_3$, 300 K) δ = 7.52-7.47 (*m*, 6H, CH_{arom}), 7.31 (*td*, *J* = 8.0 Hz, *J* = 2.8 Hz, 4H, CH_{arom}), 7.29-7.27 (*m*, 4H, CH_{arom}), 7.26-7.20 (*m*, 8H, CH_{arom}), 7.15-7.10 (*m*, 8H, CH_{arom}), 7.05 (*d*, *J* = 9.6 Hz, 4H, CH_{arom}), 4.61 (*s*, 8H, CH_2). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K) δ = 151.9 (C_q)*, 137.2 (C_q), 137.1 (C_q), 132.5 (CH), 131.0 (*d*, *J* = 101.0 Hz, C_q), 130.9 (*d*, *J* = 11.4 Hz, CH), 130.9 (CH), 129.8 (*d*, *J* = 100.6 Hz, C_q), 128.9 (CH), 127.4 (CH), 126.7 (CH), 118.2 (*d*, *J* = 9.2 Hz, CH), 55.6 (CH_2). **^{31}P NMR** (122 MHz, $CDCl_3$, 300 K) δ = 47.7. **HRMS** (**ESI**) *m/z* = 811.2614 calcd. for $C_{52}H_{42}N_2O_2P_2Na$ $[M+Na]^+$; found: 811.2610. **IR** (ATR): 3412 *br w*, 2923 *br s*, 2854 *m*, 2363 *m*, 2349 *m*, 1731 *br w*, 1461 *br w*, 1377 *w*, 1262 *m*, 1218 *w*, 1098 *m*, 1020 *m*, 801 *m*. **MP**: >260 °C. * Two signals of this triplet were not distinguishable from the background noise.

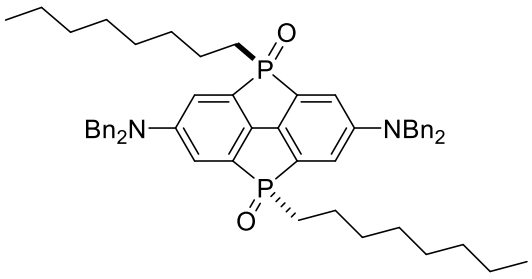
3,7-Bis(dibenzylamino)-5-phenylbenzo[*b*]phosphindole 5-oxide (**5a**)



Bisbromide **4** (210 mg. 0.300 mmol, 1.0 eq.), stannylated phosphine **S1** (196 mg, 0.450 mmol, 1.5 eq.) and 1,1´-azobis(cyclohexanecarbonitrile) (65 mg, 0.15 mmol, 0.5 eq.) were placed under argon in an oven-dried *Schlenk*-tube. Trifluorotoluene (3 mL) was added and the reaction was stirred for 2 d at 125 °C. The reaction mixture was allowed to cool to rt and stirred overnight. The precipitate was collected and washed with trifluorotoluene (2 × 0.5 mL). Then the solid was dissolved in CH_2Cl_2 (80 mL), H_2O_2 (1.5 mL) and H_2O (10 mL) were directly added. Rigorous stirring was continued for 3 h and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were washed with $Na_2S_2O_3$ (aq., sat.) and dried over $MgSO_4$. The solvent was removed *in vacuo* to afford the crude product. The residue was purified by FC (CH_2Cl_2/MeOH = 100/1) and product **5a** was isolated as a yellow solid (68 mg, 0.10 mmol, 34%).

^{1}H NMR (300 MHz, CD_2Cl_2, 300 K) δ = 7.46-7.35 (*m*, 5H, CH_{arom}), 7.31-7.28 (*m*, 5H, CH_{arom}), 7.26-7.18 (*m*, 18H, CH_{arom}), 7.10 (*dd*, *J* = 11.4 Hz, *J* = 2.4 Hz, 2H, CH_{arom}), 6.83 (*dd*, *J* = 8.6 Hz, *J* = 2.4 Hz,, 2H, CH_{arom}), 4.69 (*d*, *J* = 17.5 Hz, 4H, CH_2), 4.58 (*d*, *J* = 17.5 Hz, 4H, CH_2). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K) δ = 148.7 (*d*, *J* = 13.3 Hz, C_q), 137.9 (C_q), 132.8 (*d*, *J* = 107.9 Hz, C_q), 132.5 (*d, J* = 101.4 Hz, C_q), 131.5 (*d*, *J* = 2.8 Hz, CH), 131.2 (C_q), 130.9 (*d*, *J* = 10.7 Hz, CH), 128.7 (CH), 128.5 (*d*, *J* = 12.3 Hz, CH), 127.1 (CH), 126.8 (CH), 121.0 (*d*, *J* = 12.1 Hz, CH), 117.3 (CH), 113.8 (*d*, *J* = 11.4 Hz, CH), 54.7 (CH_2). **^{31}P NMR** (122 MHz, $CDCl_3$, 300 K) δ = 35.2. **HRMS** (**ESI**) *m/z* = 689.2692 calcd. for $C_{46}H_{39}N_2OPNa$ $[M+Na]^+$; found: 689.2694. **IR** (ATR): 3059 *w*, 3029 *w*, 2924 *m*, 2855 *w*, 2347 *w*, 2222 *br w*, 1700 *w*, 1602 *s*, 1568 *m*, 1481 *s*, 1451 *s*, 1386 *w*, 1358 *m*, 1297 *w*, 1228 *s*, 1197 *s*, 1113 *m*, 1075 *w*, 1028 *m*, 992 *m*, 958 *m*, 910 *w*, 844 *m*, 711 *m*, 731 *s*, 695 *s*, 517 *m*. **MP**: 194 °C.

2,6-Bis(dibenzylamino)-4,8-dioctylphosphindolo[4,3,2-*bcd*]phosphindole 4,8-dioxide (**3b**)

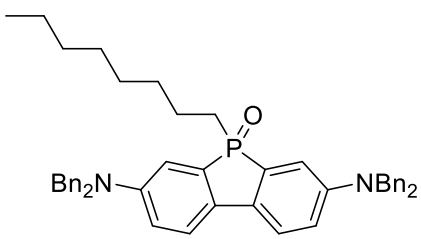


Tetrabromide **2** (1.15 g, 1.34 mmol, 1.0 eq.), stannylated phosphine **S3** (3.1 g, 6.5 mmol, 3.0 eq.) and 1,1´-azobis(cyclohexanecarbonitrile) (164 mg, 0.670 mmol, 0.5 eq.) were placed under argon in an oven-dried *Schlenk*-tube. Trifluorotoluene (13 mL) was added and the reaction mixture was stirred for 3 d at 125 °C. The reaction mixture was allowed to cool to rt and was added to a mixture of CH_2Cl_2 (120 mL), H_2O_2 (6 mL) and H_2O (60 mL). Rigorous stirring was continued for 3 h and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with $Na_2S_2O_3$ (aq., sat.) and dried over $MgSO_4$. The solvent was removed *in vacuo* to afford the crude product. The residue was purified by FC (CH_2Cl_2/MeOH = 100/1 → 70/1) and product **3b** was isolated as an orange solid (208 mg, 0.24 mmol, 18%).

^{1}H NMR (300 MHz, CD_2Cl_2, 300 K) δ = 7.37-7.31 (*m*, 8H, CH_{arom}), 7.29-7.23 (*m*, 12H, CH_{arom}), 7.04 (*dd*, *J* = 9.0 Hz, *J* = 2.5 Hz, 4H, CH_{arom}), 4.77 (*d*, *J* = 17.2 Hz, 4H, CH_2), 4.68 (*d*, *J* = 17.2 Hz, 4H, CH_2), 1.92-1.82 (*m*, 4H, CH_2), 1.37-1.11 (*m*, 24H, CH_2), 0.89 (*t*, *J* = 6.8 Hz,

3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$, 300 K) δ = 151.9 (C_q), 138.2 (CH), 136.8 (C_q), 129.3 (CH), 128.1 (*d*, *J* = 8.1 Hz, C_q), 127.7 (CH), 127.2 (CH), 117.7 (*d*, *J* = 8.9 Hz, C_q), 56.4 (CH_2), 32.4 (CH_2), 31.7 (*d*, *J* = 59.8 Hz, CH_2), 31.3 (*d*, *J* = 15.5 Hz, CH_2), 29.7 (CH_2), 29.5 (CH_2), 23.2 (CH_2), 22.5 (CH_2), 14.5 (CH_3). **^{31}P NMR** (122 MHz, $CDCl_3$, 300 K) δ = 56.8. **HRMS** (**ESI**) *m/z* = 883.4492 calcd. for $C_{56}H_{66}N_2O_2P_2Na$ $[M+Na]^+$; found: 883.4462. **IR** (ATR): 3061 *w*, 3030 *w*, 2926 *m*, 2855 *m*, 1574 *m*, 1494 *m*, 1433 *s*, 1358 *m*, 1296 *w*, 1226 *m*, 1190 *s*, 1075 *w*, 1028 *w*, 989 *m*, 963 *w*, 898 *w*, 844 *w*, 812 *w*. **MP**: 178 °C.

3,7-Bis(dibenzylamino)-5-octylbenzo[*b*]phosphindole 5-oxide (**5b**)



Bisbromide **4** (703 mg. 1.00 mmol, 1.0 eq.), stannylated phosphine **S3** (708 mg, 1.50 mmol, 1.5 eq.) and 1,1´-azobis(cyclohexanecarbonitrile) (122 mg, 0.5 mmol, 0.5 eq.) were placed under argon in an oven-dried *Schlenk*-tube. Trifluorotoluene (10 mL) was added and the reaction was stirred for 3 d at 125 °C. The reaction mixture was allowed to cool to rt and was added to a mixture of CH_2Cl_2 (80 mL), H_2O_2 (4 mL) and H_2O (40 mL). Rigorous stirring was continued for 3 h and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were washed with $Na_2S_2O_3$ (aq., sat.) and dried over $MgSO_4$. The solvent was removed *in vacuo* to afford the crude product. The residue was purified by FC (CH_2Cl_2/MeOH = 100/1) and product **5b** was isolated as a yellow solid (289 mg, 0.411 mmol, 41%).

^{1}H NMR (300 MHz, CD_2Cl_2, 300 K) δ = 7.39-7.33 (*m*, 10H, CH_{arom}), 7.30-7.24 (*m*, 12H, CH_{arom}), 7.05 (*dd*, *J* = 10.8 Hz, *J* = 2.5 Hz, 2H, CH_{arom}), 6.84 (*dd*, *J* = 8.6 Hz, *J* = 2.5 Hz, 2H, CH_{arom}), 4.79 (*d*, *J* = 17.2 Hz, 4H, CH_2), 4.68 (*d*, *J* = 17.2 Hz, 4H, CH_2), 1.80-1.71 (*m*, 2H, CH_2), 1.35-1.13 (m, 12H, CH_2), 0.92 (*t*, *J* = 6.8 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, CD_2Cl_2, 300 K) δ = 148.9 (*d*, *J* = 12.8 Hz, C_q), 138.8 (C_q), 133.2 (*d*, *J* = 101.0 Hz, C_q), 131.1 (*d*, *J* = 20.5 Hz, C_q), 129.2 (CH), 127.6 (C_q), 127.3 (CH), 121.2 (*d*, *J* = 11.2 Hz, CH), 117.3 (*d*, *J* = 1.9 Hz, CH), 113.5 (*d*, *J* = 11.5 Hz, CH), 55.5 (CH_2), 32.4 (CH_2), 31.4 (*d*, *J* = 14.8 Hz, CH_2), 31.1 (*d*, *J* = 56.9 Hz, CH_2), 29.7 (CH_2), 29.4 (CH_2), 23.2 (CH_2), 22.3 (*d*, *J* = 3.5 Hz, CH_2), 14.5 (CH_3). **^{31}P NMR** (122 MHz, CD_2Cl_2, 300 K) δ = 43.6. **HRMS** (**ESI**) *m/z* = 725.3631 calcd. for $C_{48}H_{51}N_2OPNa$ $[M+Na]^+$; found: 725.3614. **IR** (ATR): 3061 *w*, 3029 *w*, 2924 *m*, 2854 *w*, 2361 *w*, 2336 *w*, 1865 *br w*, 1807 *w*, 1735 *br w*, 1602 *s*, 1568 *m*, 1480 *s*, 1451 *s*, 1429 *m*, 1385 *w*, 1358 *m*, 1296 *w*, 1226 *s*, 1197 *s*, 1075 *w*, 1028 *m*, 992 *m*, 958 *m*, 898 *w*, 849 *w*, 808 *m.* **MP**: 167 °C.

References for Synthesis Part:

[a] R. K. Harris, E. D. Becker, S. M. Cabral De Menezes, R. Goodfellow, P. Granger, *Pure Appl. Chem.* **2001**, *73* (11), 1795-1818.

[b] C. Görl, N. Beck, K. Kleiber, H. G. Alt, *J. Mol. Catal. A: Chem.* **2012**, *352*, 110-127.

[c] A. Bruch, A. Fukazawa, E. Yamaguchi, S. Yamaguchi and A. Studer, *Angew. Chem. Int. Ed.*, 2011, **50**, 12094-12098.

[d] M. R. Douglass, C. L. Stern, T. J. Marks, *J. Am. Chem. Soc.* **2001**, *123*, 10221-10238.

[e] X. Ling, Y. Xiong, R. Huang, X. Zhang, S. Zhang, C. Chen, *J. Org. Chem.* **2013**, *78*, 5218-5226.

3. X-ray Crystallographic Data

CCDC numbers for compound **2** 1052539, compound **3a** 1052540, compound **4** 1052541, compound **5a** 1052542 and compound **3b** 1425330 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-Ray diffraction: For the compounds **4**, **5a** and **3b** data sets were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used: data collection: APEX2 V2014.5-0 (Bruker AXS Inc., 2014); cell refinement: SAINT V8.34A (Bruker AXS Inc., 2013); data reduction: SAINT V8.34A (Bruker AXS Inc., 2013); absorption correction, SADABS V2014/2 (Bruker AXS Inc., 2014); structure solution SHELXT-2014 (Sheldrick, 2014); structure refinement SHELXL-2014 (Sheldrick, 2014) and graphics, XP (Bruker AXS Inc., 2014). For the compounds **2** and **3a** data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Exceptions and special features: A badly disordered half dichloromethane molecule was found in the asymmetrical unit of compound **3a** and could not be satisfactorily refined. The program SQUEEZE (A. L. Spek J. Appl. Cryst., 2003, 36, 7-13) was therefore used to remove mathematically the effect of the solvent. The quoted formula and derived parameters are not included the squeezed solvent molecule. One bromine atom in compound **4** and two phenyl groups in compound **5** are disordered over two positions. Several restraints (SADI, SAME, ISOR and SIMU) were used in order to improve refinement stability.

X-ray crystal structure analysis of 2: Formula $C_{40}H_{32}Br_4N_2$, M = 860.32, colourless crystal, 0.23 × 0.05 × 0.02 mm, a = 18.6729(2), b = 11.0827(1), c = 33.8570(4) Å, V = 7006.6(1) Å^3, ρ_{calc} = 1.631 gcm^{-3}, μ = 4.626 mm^{-1}, empirical absorption correction (0.415 ≤ T ≤ 0.913), Z = 8, monoclinic, space group *P*bca (No. 61), λ = 0.71073 Å, T = 223(2) K, ω and φ scans, 49259 reflections collected (±h, ±k, ±l), 8457 independent (R_{int} = 0.065) and 6612 observed reflections [I>2σ(I)], 415 refined parameters, R = 0.049, wR^2 = 0.088, max. (min.) residual electron density 0.49 (-0.48) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

X-ray crystal structure analysis of 3a: Formula $C_{52}H_{42}N_2O_2P_2$, *M* = 788.82, colourless crystal, 0.23 × 0.13 × 0.01 mm, *a* = 28.1262(5), *b* = 8.5442(2), *c* = 20.5029(4) Å, *β* = 109.719(1)°, *V* = 4638.2(2) Å^3, ρ_{calc} = 1.130 gcm^{-3}, μ = 0.134 mm^{-1}, empirical absorption correction (0.969 ≤ T ≤ 0.998), *Z* = 4, monoclinic, space group *C*2/c (No. 15), *λ* = 0.71073 Å, *T* = 223(2) K, *ω* and *φ* scans, 13982 reflections collected (±*h*, ±*k*, ±*l*), 4013 independent (R_{int} = 0.053) and 2997 observed reflections [*I*>2*σ*(*I*)], 262 refined parameters, *R* = 0.076, wR^2 = 0.212, max. (min.) residual electron density 0.48 (-0.27) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

X-ray crystal structure analysis of 4: Formula $C_{40}H_{34}Br_2N_2$, *M* = 702.51, colourless crystal, 0.28 × 0.14 × 0.13 mm, *a* = 11.0372(6), *b* = 12.6734(7), *c* = 13.6066(7) Å, α = 87.925(2), *β* = 67.674(2), *γ* = 66.578(2)°, *V* = 1600.7(2) Å^3, ρ_{calc} = 1.458 gcm^{-3}, *μ* = 3.444 mm^{-1}, empirical absorption correction (0.444 ≤ T ≤ 0.669), *Z* = 2, triclinic, space group $P\bar{1}$ (No. 2), *λ* = 1.54178 Å, *T* = 100(2) K, *ω* and *φ* scans, 45014 reflections collected (±*h*, ±*k*, ±*l*), 5859 independent (R_{int} = 0.032) and 5575 observed reflections [*I*>2*σ*(*I*)], 410 refined parameters, *R* = 0.026, wR^2 = 0.067, max. (min.) residual electron density 1.57 (-0.34) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

X-ray crystal structure analysis of 5a: Formula $C_{46}H_{39}N_2OP$, *M* = 666.76, yellow crystal, 0.26 × 0.13 × 0.01 mm, *a* = 10.7866(1), *b* = 32.1890(3), *c* = 10.4301(1) Å, *β* = 99.194(6)°, *V* = 3574.9(6) Å^3, ρ_{calc} = 1.239 gcm^{-3}, *μ* = 0.972 mm^{-1}, empirical absorption correction (0.785 ≤ T ≤ 0.939), *Z* = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, *T* = 100(2) K, *ω* and *φ* scans, 29470 reflections collected (±*h*, ±*k*, ±*l*), 4911 independent (R_{int} = 0.184) and 3244 observed reflections [*I*>2*σ*(*I*)], 561 refined parameters, *R* = 0.198, wR^2 = 0.408, max. (min.) residual electron density 1.15 (-0.36) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

X-ray crystal structure analysis of 3b: formula $C_{56}H_{66}N_2O_2P_2$, *M* = 861.04, yellow crystal, 0.147 x 0.094 x 0.063 mm, *a* = 29.5733(17), *b* = 8.8680(6), *c* = 20.0015(11) Å, *β* = 109.810(2)°, *V* = 4935.1(5) Å^3, ρ_{calc} = 1.159 gcm^{-3}, μ = 0.130 mm^{-1}, empirical absorption correction (0.981 ≤ T ≤ 0.992), *Z* = 4, monoclinic, space group *C*2/c (No. 15), λ = 0.71073 Å, *T* = 100(2) K, ω and φ scans, 37687 reflections collected (±*h*, ±*k*, ±*l*), 4351 independent (R_{int} = 0.122) and 3206 observed reflections [*I*>2σ(*I*)], 335 refined parameters, *R* = 0.062, wR^2 = 0.162, max. (min.) residual electron density 0.50 (-0.35) e.Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

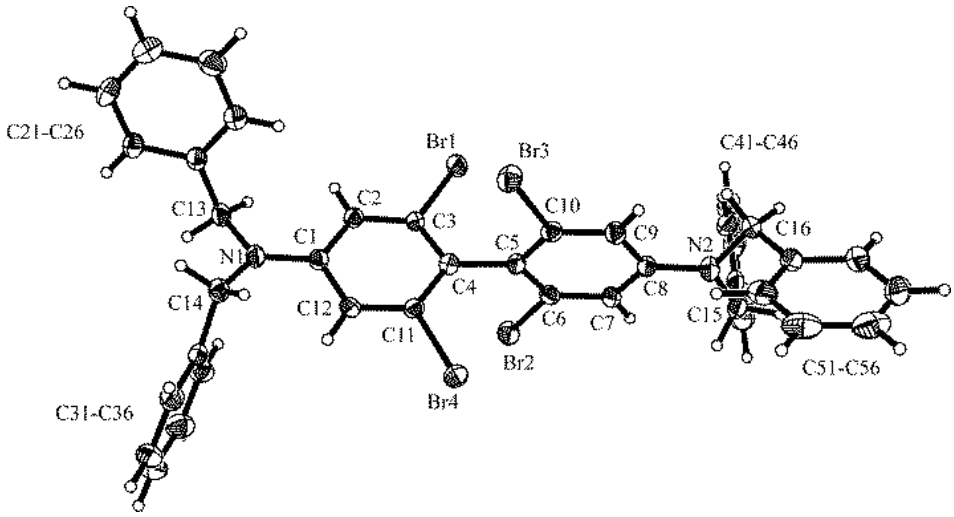


Figure S1. Crystal structure of compound **2**.

(Thermals ellipsoids are shown with 30% probability.)

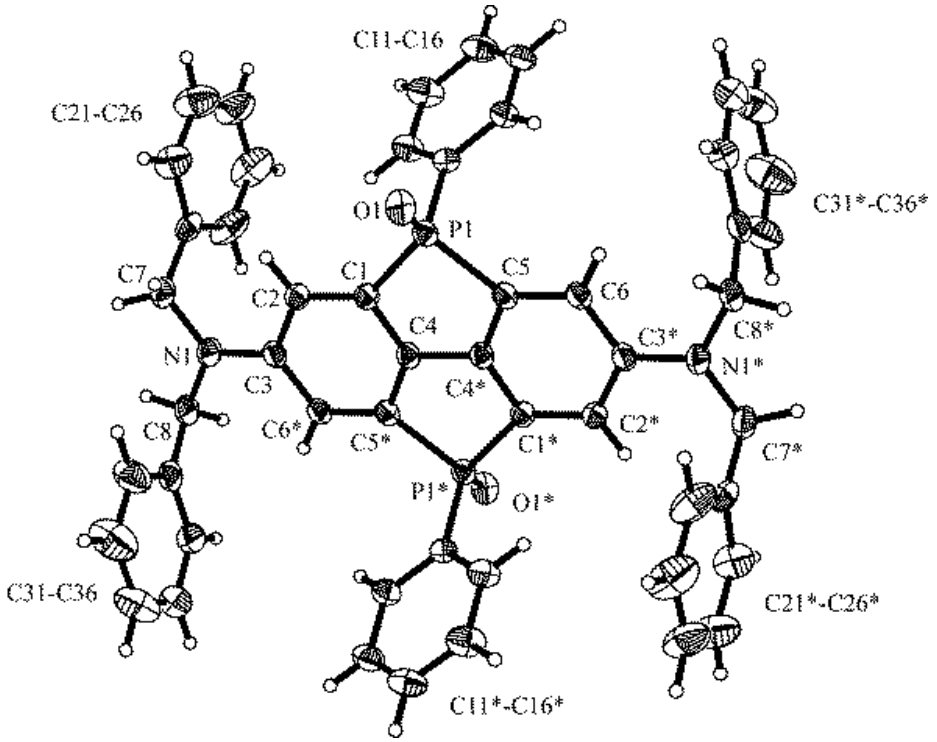


Figure S2. Crystal structure of compound **3a**.

(Thermals ellipsoids are shown with 30% probability.)

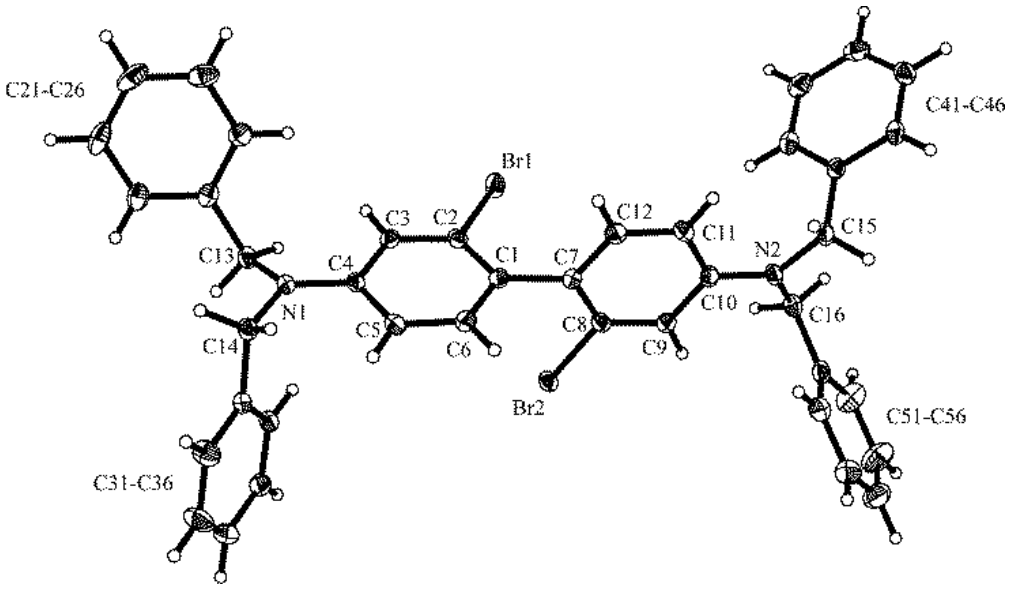


Figure S3. Crystal structure of compound **4**.

(Thermals ellipsoids are shown with 50% probability.)

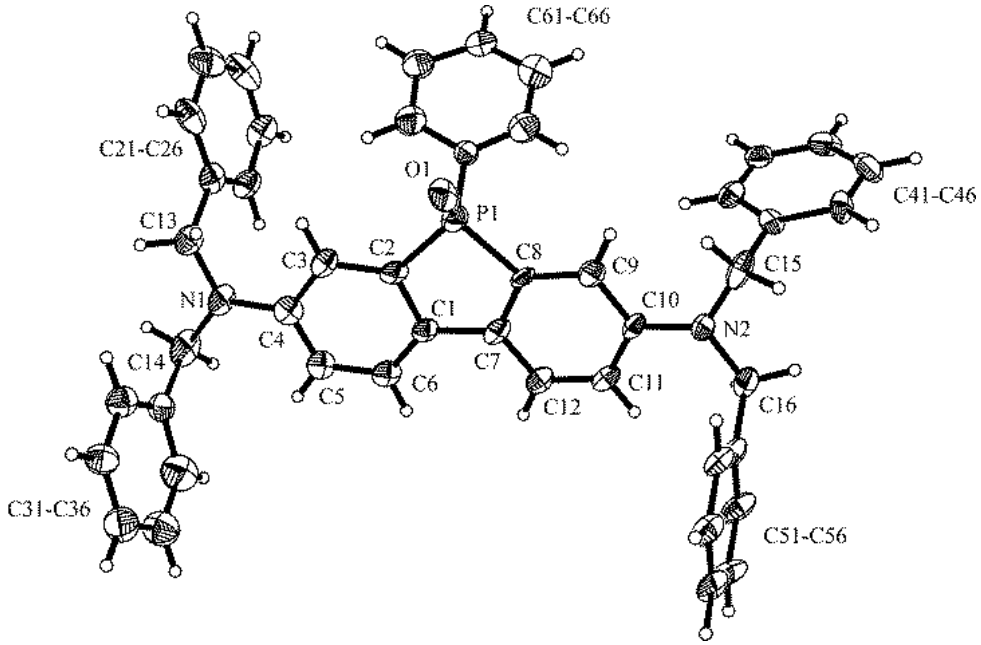


Figure S4. Crystal structure of compound **5a**.

(Thermals ellipsoids are shown with 30% probability.)

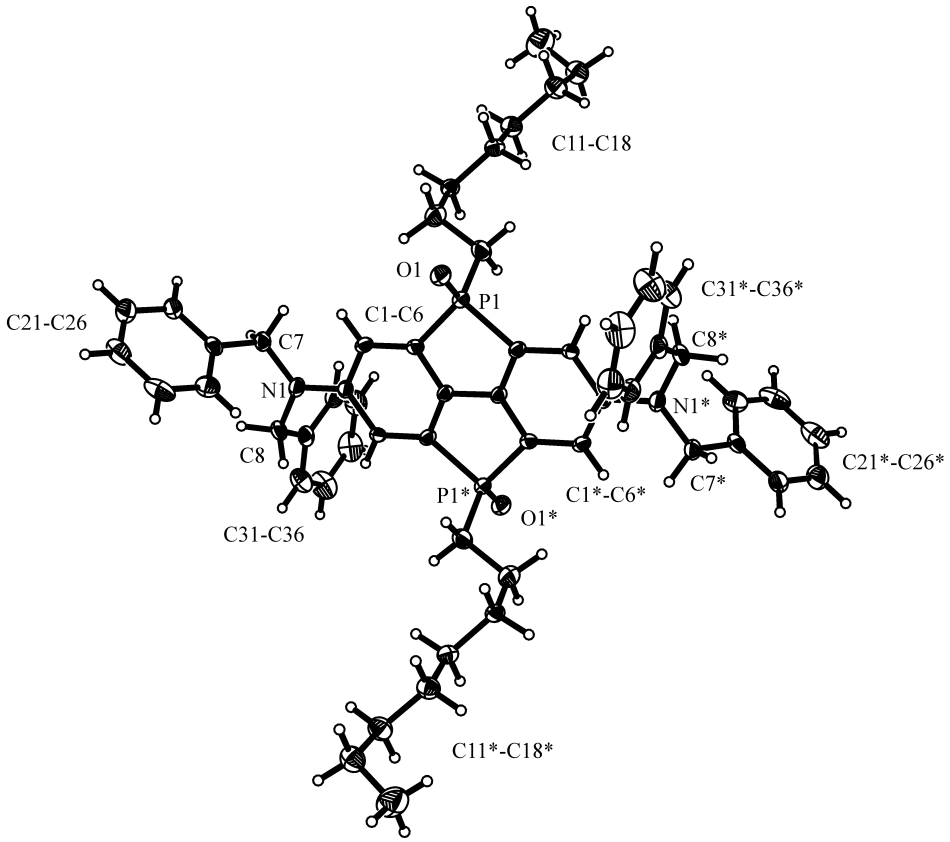


Figure S5. Crystal structure of compound **3b**.

(Thermals ellipsoids are shown with 50% probability.)

References for X-Ray Part:

[a] Bruker (2013). *APEX2*, *SAINT* and *SADABS* Bruker AXS Inc., Madison, Wisconsin, USA.

[b] SHELXT und SHELXL Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

[c] Z. Otwinowski, W. Minor, Methods Enzymol. 1997, 276, 307–326.

[d] Z. Otwinowski, D. Borek, W. Majewski, W. Minor, Acta Crystallogr. Sect. A 2003, 59, 228-234.

[e] G. M. Sheldrick, Acta Crystallogr. Sect. A 1990, 46, 467–473.

4. Theoretical Calculations

Computational methods. The geometry optimizations of compounds **3a**, **5a**, and **7** were performed using the B3LYP functional (A. D. Becke, Phys. Rev. A, 1988, 38, 3098-3100) with the 6-31G(d) basis set (R. Ditchfield, J. Chem. Phys. 1971, 54, 724), implemented in the

Gaussian 09 program (M. J. Frisch Gaussian 09 Revision C.01, Gaussian Inc., Wallingford, CT, 2009). Stationary points were optimized without any symmetry assumptions and characterized by frequency analysis at the same level of theory (the number of imaginary frequencies, NIMAG, was 0). The geometry of **7** was optimized with the restriction that the central biphenyl moiety is fixed in a coplanar fashion. TD-DFT vertical excitation calculations (E. K. U. Gross, In Density Functional Theory; R. F. Nalewajski, Ed.; Springer: Heidelberg, 1996.) of all compounds were performed using the optimized geometry at the B3LYP/6-31G(d) level, implemented in the Gaussian 09 program (M. J. Frisch Gaussian 09 Revision C.01, Gaussian Inc., Wallingford, CT, 2009). Calculation of compound **6** was reported in our previous report (A. Bruch, Angew. Chem. Int. Ed., 2011, 50, 12094-12098).

Table S1. Cartesian Coordinates [**Å**] of the Optimized Structure for **3a** in the Gas Phase in S_0[a]

Atom	X	Y	Z
C	0.895671	0.983391	0.614642
C	2.494599	-0.901657	-0.777605
C	0.373329	-0.030973	-0.171868
C	2.282066	1.074887	0.699158
C	3.096649	0.129834	0.005304
C	1.108142	-0.974962	-0.871942
H	2.749959	1.874252	1.262770
H	3.122137	-1.639757	-1.264428
C	-1.056276	-0.120979	-0.257263
C	-3.762815	-0.329694	-0.368260
C	-1.787210	0.813252	0.464643
C	-1.573137	-1.147786	-1.033324
C	-2.964564	-1.243518	-1.096304
C	-3.175645	0.694220	0.414266
H	-3.441931	-2.016274	-1.690753
H	-3.832315	1.355899	0.968017
P	-0.556621	1.913645	1.332339
P	-0.122555	-2.075008	-1.747089
C	-0.089258	-3.704091	-0.922521
C	-0.012322	-6.249934	0.230274
C	-0.377193	-3.868402	0.440456
C	0.233143	-4.820540	-1.704904
C	0.272063	-6.090725	-1.126911
C	-0.338354	-5.138767	1.013080
H	-0.641141	-3.010575	1.053143
H	0.440344	-4.681644	-2.761917
H	0.521369	-6.954620	-1.737304
H	-0.567634	-5.261667	2.068030
H	0.016171	-7.239582	0.678960
C	-0.611809	3.536745	0.495565
C	-0.683252	6.075810	-0.672840
C	-0.594064	3.669805	-0.900537
C	-0.667827	4.680027	1.302093
C	-0.703692	5.947072	0.716470
C	-0.628935	4.936461	-1.481238
H	-0.554114	2.787775	-1.534545
H	-0.684699	4.562215	2.381548
H	-0.746801	6.831968	1.345880

H	-0.612180	5.035694	-2.563404
H	-0.709278	7.062608	-1.127910
O	-0.636500	2.032008	2.825792
O	-0.006720	-2.180789	-3.239724
N	-5.199820	-0.403571	-0.395636
N	4.485425	0.212015	0.093457
C	-5.814337	0.439250	-1.445437
H	-5.423655	0.180768	-2.445217
H	-6.883267	0.193086	-1.451113
C	-5.767240	-1.760116	-0.376911
H	-5.554377	-2.333466	-1.297479
H	-6.857515	-1.630108	-0.356205
C	5.360655	-0.400033	-0.895749
H	4.819100	-0.465162	-1.846643
H	6.190974	0.294848	-1.079401
C	5.152631	0.918659	1.177289
H	6.027947	0.324855	1.472729
H	4.491442	0.918628	2.051668
C	-5.341910	-2.570058	0.832003
C	-4.641926	-4.102960	3.081380
C	-4.916665	-3.894549	0.688425
C	-5.408802	-2.019150	2.118953
C	-5.060141	-2.778088	3.234621
C	-4.571169	-4.659925	1.804759
H	-4.852947	-4.332928	-0.305272
H	-5.725796	-0.986780	2.235795
H	-5.113657	-2.335599	4.225950
H	-4.240103	-5.686638	1.672645
H	-4.370745	-4.694027	3.952289
C	-5.655933	1.926933	-1.207974
C	-5.395914	4.688700	-0.759522
C	-6.288786	2.535814	-0.114552
C	-4.895757	2.720293	-2.072184
C	-4.764180	4.093709	-1.850874
C	-6.160647	3.905111	0.109828
H	-6.876875	1.924927	0.566329
H	-4.397478	2.258196	-2.921391
H	-4.161533	4.694804	-2.526259
H	-6.657151	4.363041	0.961423
H	-5.292443	5.755997	-0.583545
C	5.606296	2.342949	0.868825
C	6.455939	4.979958	0.392152
C	5.114081	3.061513	-0.224892
C	6.535358	2.959606	1.718263
C	6.955078	4.268114	1.486195
C	5.536624	4.372257	-0.462189
H	4.398141	2.592307	-0.893279
H	6.933298	2.408382	2.568423
H	7.676005	4.730942	2.155094
H	5.143798	4.916815	-1.316846
H	6.784662	5.999076	0.207419
C	5.934532	-1.766257	-0.529855
C	7.019144	-4.292643	0.055731
C	5.405188	-2.544624	0.503916
C	7.018990	-2.266483	-1.263871

C	7.556005	-3.520236	-0.977787
C	5.944554	-3.800475	0.795425
H	4.568162	-2.165270	1.082542
H	7.445947	-1.667124	-2.066041
H	8.396835	-3.892906	-1.556998
H	5.520916	-4.392818	1.602222
H	7.438736	-5.269001	0.282623

[a] Calculated at the B3LYP/6-31G(d) level of theory.

Table S2. Cartesian Coordinates [**Å**] of the Optimized Structure for **5a** in the Gas Phase in S_0[a]

Atom	X	Y	Z
C	-0.937747	0.022775	0.156127
C	-2.722180	1.736806	-1.080984
C	-0.435518	1.051396	-0.666516
C	-2.296634	-0.159795	0.362001
C	-3.230464	0.708087	-0.253624
C	-1.354461	1.900185	-1.287642
H	-2.637233	-0.985004	0.978420
H	-3.403430	2.445522	-1.538752
C	1.039050	1.086081	-0.746012
C	3.864486	0.861574	-0.657059
C	1.672984	0.086939	0.024333
C	1.839992	1.974620	-1.464092
C	3.231022	1.854469	-1.424270
C	3.054776	-0.018337	0.088044
H	3.824837	2.557711	-1.996955
H	3.518778	-0.764485	0.721983
P	0.434017	-0.952089	0.874679
C	0.444642	-2.576733	0.028876
C	0.472886	-5.111366	-1.157364
C	0.420759	-2.702484	-1.367898
C	0.483882	-3.726559	0.826156
C	0.497715	-4.990929	0.232771
C	0.434620	-3.965365	-1.957869
H	0.391913	-1.814628	-1.994465
H	0.506011	-3.614733	1.906141
H	0.526493	-5.880366	0.856838
H	0.414356	-4.057580	-3.040781
H	0.480883	-6.095603	-1.618958
O	0.494719	-1.101900	2.368314
N	5.286499	0.714368	-0.604550
N	-4.599852	0.552636	-0.052960
C	5.795123	-0.504208	-1.277792
H	5.372380	-0.597651	-2.291651
H	6.874527	-0.358128	-1.401931
C	6.079728	1.905318	-0.924889
H	5.958443	2.236447	-1.972996
H	7.130803	1.602907	-0.833558
C	-5.582151	1.148675	-0.943705
H	-5.136168	1.243235	-1.940959

H	-6.405736	0.431347	-1.058509
C	-5.136133	-0.196495	1.074141
H	-5.995798	0.360876	1.469872
H	-4.391992	-0.194055	1.878593
C	5.836199	3.079575	0.006225
C	5.525672	5.278642	1.729167
C	5.885333	4.387523	-0.488868
C	5.627006	2.885288	1.377327
C	5.469526	3.976352	2.231364
C	5.735811	5.481846	0.364987
H	6.042814	4.552198	-1.553287
H	5.575585	1.872700	1.765688
H	5.300347	3.808996	3.291907
H	5.775658	6.490736	-0.037706
H	5.401487	6.127802	2.395981
C	5.574809	-1.797616	-0.517339
C	5.210026	-4.204764	0.884807
C	6.138334	-1.974722	0.754380
C	4.832503	-2.842319	-1.075864
C	4.647256	-4.039778	-0.380195
C	5.957776	-3.167794	1.451159
H	6.707674	-1.163301	1.201257
H	4.381391	-2.713036	-2.056953
H	4.050607	-4.833243	-0.821504
H	6.397423	-3.289942	2.437653
H	5.064129	-5.132645	1.431321
C	-5.573506	-1.627183	0.774430
C	-6.374867	-4.282981	0.317740
C	-5.096474	-2.332972	-0.334653
C	-6.463621	-2.266124	1.648307
C	-6.859187	-3.584222	1.426383
C	-5.494671	-3.652755	-0.561670
H	-4.411552	-1.846174	-1.022622
H	-6.849974	-1.725013	2.510188
H	-7.550215	-4.064178	2.114561
H	-5.113406	-4.187556	-1.427712
H	-6.684603	-5.309454	0.140722
C	-6.158311	2.492975	-0.505189
C	-7.253929	4.978501	0.221161
C	-5.558013	3.271090	0.489413
C	-7.319178	2.972601	-1.127635
C	-7.862159	4.205976	-0.771918
C	-6.102672	4.506365	0.850608
H	-4.662025	2.907267	0.983503
H	-7.802556	2.372366	-1.896614
H	-8.763316	4.562034	-1.264527
H	-5.623807	5.098063	1.626481
H	-7.677940	5.938516	0.503034
H	1.393541	2.762791	-2.065134
H	-1.015102	2.713830	-1.923831

[a] Calculated at the B3LYP/6-31G(d) level of theory.

Table S3. Cartesian Coordinates [**Å**] of the Optimized Structure for **7** in the Gas Phase in S_0[a]

Atom	X	Y	Z
C	0.925794	0.627193	0.777584
C	2.456483	-0.755513	-1.063359
C	0.247699	-0.099111	-0.218760
C	2.311834	0.676268	0.858787
C	3.123923	-0.019640	-0.061533
C	1.069328	-0.782103	-1.134171
H	2.763796	1.293782	1.627586
H	3.022475	-1.343679	-1.777786
C	-1.237808	-0.134228	-0.303809
C	-4.089653	-0.211849	-0.459584
C	-2.052635	0.547613	0.620243
C	-1.907119	-0.858070	-1.309903
C	-3.296175	-0.893448	-1.390256
C	-3.441940	0.508840	0.546475
H	-3.761775	-1.462159	-2.191085
H	-4.043075	1.041830	1.275794
N	-5.534022	-0.211266	-0.515922
N	4.515187	0.019353	0.012971
C	-6.064771	0.713819	-1.535623
H	-5.678811	0.478581	-2.543885
H	-7.150104	0.551672	-1.570234
C	-6.135548	-1.548830	-0.617648
H	-5.842223	-2.086776	-1.537452
H	-7.220378	-1.393247	-0.695633
C	5.358226	-0.347522	-1.113144
H	4.790570	-0.186242	-2.036842
H	6.194395	0.363581	-1.155140
C	5.214188	0.422140	1.222764
H	6.072947	-0.249546	1.356692
H	4.558718	0.233008	2.080655
C	-5.848818	-2.425307	0.586347
C	-5.418118	-4.082130	2.816393
C	-5.442408	-3.752967	0.421327
C	-6.033571	-1.934629	1.885853
C	-5.818502	-2.754673	2.992078
C	-5.230967	-4.579734	1.527132
H	-5.287618	-4.143961	-0.582082
H	-6.335974	-0.899809	2.018908
H	-5.963605	-2.358698	3.994132
H	-4.913101	-5.608696	1.379450
H	-5.249916	-4.721237	3.679309
C	-5.795141	2.172055	-1.223148
C	-5.361127	4.891969	-0.660987
C	-6.320448	2.754018	-0.060838
C	-5.049339	2.970154	-2.095112
C	-4.833019	4.322685	-1.819167
C	-6.105763	4.101963	0.219955
H	-6.894970	2.137706	0.626234
H	-4.630307	2.528120	-2.996181
H	-4.248488	4.927652	-2.507491
H	-6.521708	4.539450	1.124123
H	-5.194418	5.943735	-0.443359

C	5.709789	1.865163	1.256617
C	6.627488	4.518792	1.413096
C	5.142540	2.862469	0.456291
C	6.748034	2.213033	2.131169
C	7.202105	3.528678	2.213831
C	5.598852	4.180596	0.533683
H	4.342099	2.604145	-0.230686
H	7.206164	1.444698	2.751546
H	8.009400	3.779874	2.897026
H	5.147705	4.943158	-0.096037
H	6.982823	5.544077	1.472150
C	5.920871	-1.766315	-1.091899
C	6.973748	-4.373534	-1.144300
C	5.334283	-2.785758	-0.334759
C	7.046682	-2.068195	-1.870116
C	7.568148	-3.360799	-1.901239
C	5.857824	-4.080853	-0.360301
H	4.465805	-2.562893	0.277894
H	7.520294	-1.281893	-2.455439
H	8.442614	-3.576305	-2.509895
H	5.390411	-4.861082	0.234970
H	7.381065	-5.380857	-1.163177
H	0.368263	1.195370	1.514368
H	-1.606092	1.119849	1.426040
H	0.628162	-1.377270	-1.926553
H	-1.343112	-1.405972	-2.057081

[a] Calculated at the B3LYP/6-31G(d) level of theory. The geometry was optimized with the restriction that the central biphenyl moiety is fixed in a coplanar fashion.

Table S4. TD-DFT Vertical Excitation Energies and Oscillator Strengths in the Gas Phase[a]

Compound	State	Energy (Wavelength)	Oscillator strength	Contribution
3a	$S_0 \rightarrow S_1$	3.06 eV 405 nm	0.0024	HOMO→LUMO
5a	$S_0 \rightarrow S_1$	3.35 eV 370 nm	0.1498	HOMO→LUMO (0.68992) HOMO→LUMO+1 (–0.11654)
7	$S_0 \rightarrow S_1$	4.01 eV 309 nm	0.9363	HOMO→LUMO (0.67715) HOMO→LUMO+2 (–0.16929)

[a] Calculated at the B3LYP/6-31G(d) level of theory.

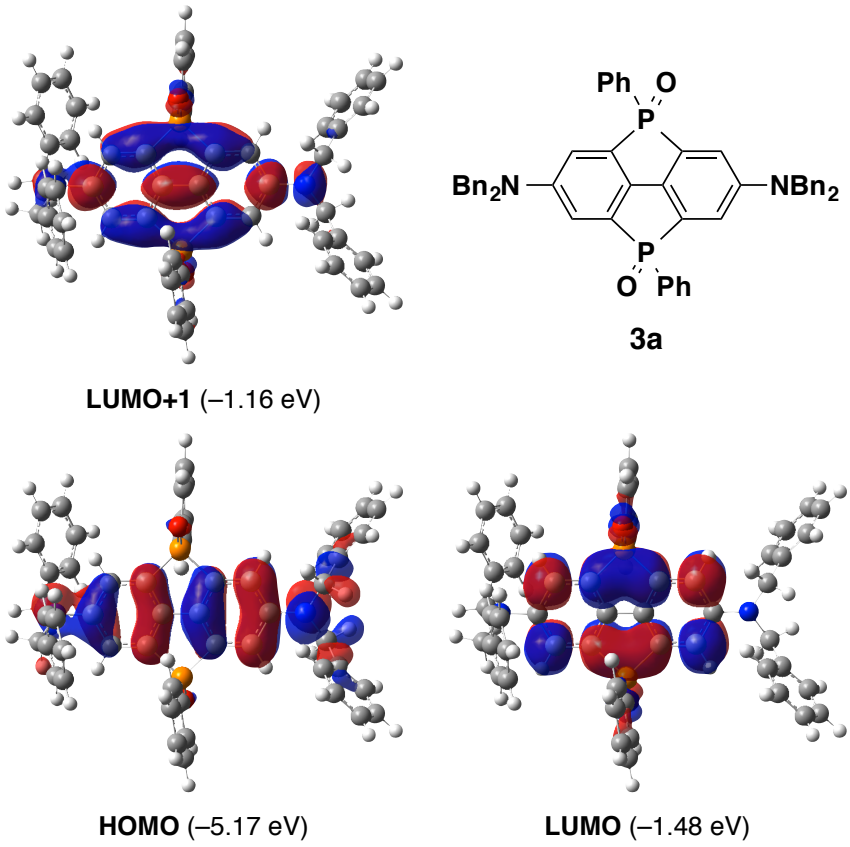


Figure S6. Pictorial representation of molecular orbitals of **3a** in the gas phase in S_0 calculated using the B3LYP functional with the 6-31G(d) basis set.

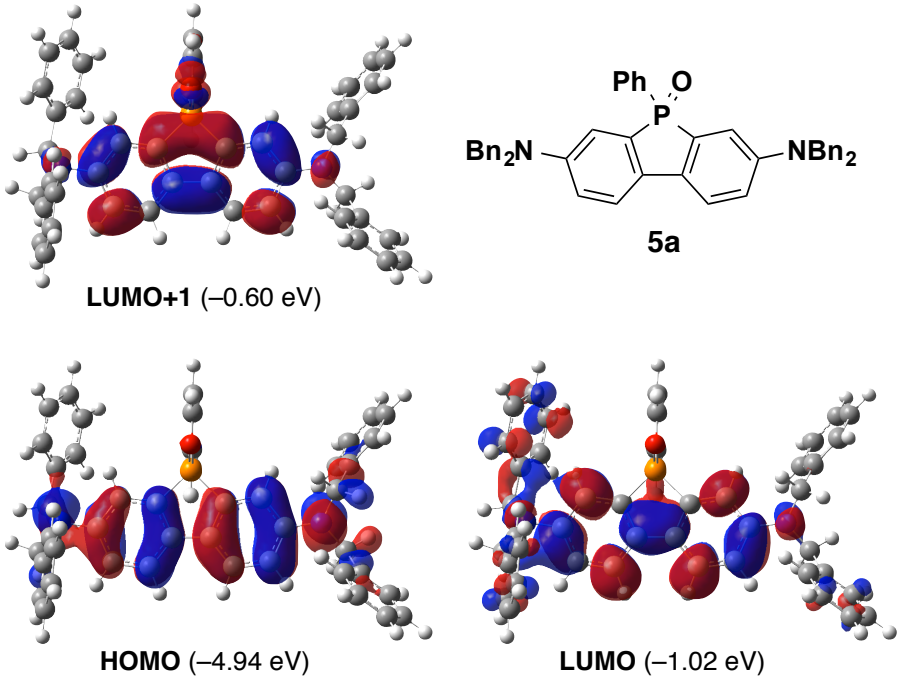


Figure S7. Pictorial representation of molecular orbitals of **5a** in the gas phase in S_0 calculated using the B3LYP functional with the 6-31G(d) basis set.

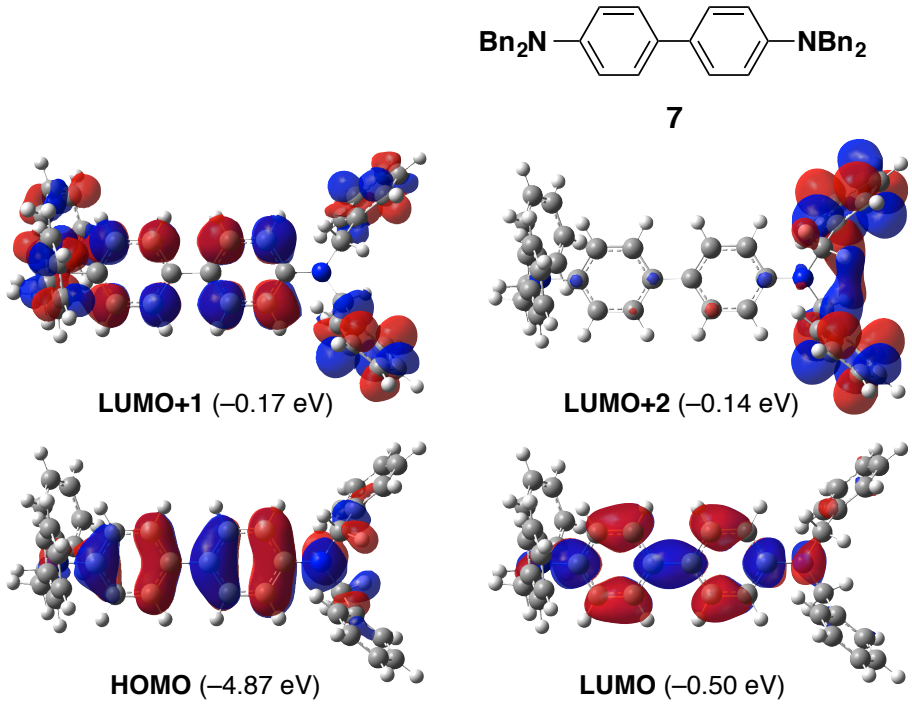


Figure S8. Pictorial representation of molecular orbitals of **7** in the gas phase in S_0 calculated using the B3LYP functional with the 6-31G(d) basis set.

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[d] a) E. K. U. Gross, J. F. Dobson, M. Petersilka, In Density Functional Theory; R. F. Nalewajski, Ed.; Springer: Heidelberg, 1996. b) M. E. Casida, In Recent Advances in Density Functional Methods; D. P. Chong, Ed; World Scientific: Singapole, 1995; Vol. 1, 155-193.

[e] A. Bruch, A. Fukazawa, E. Yamaguchi, S. Yamaguchi and A. Studer, *Angew. Chem. Int. Ed.*, 2011, **50**, 12094-12098.

5. Photophysical Properties

Measurements of the photophysical data: UV-visible absorption spectra were recorded on a *Shimadzu UV-3150* spectrometer with a resolution of 0.5 nm. A *Hitachi F-4500* spectrometer was used to measure the emission spectra of solution samples with a resolution of 1 nm. Fluorescence quantum yields were determined with a *Hamamatsu C9920-02* calibrated integrating sphere system.

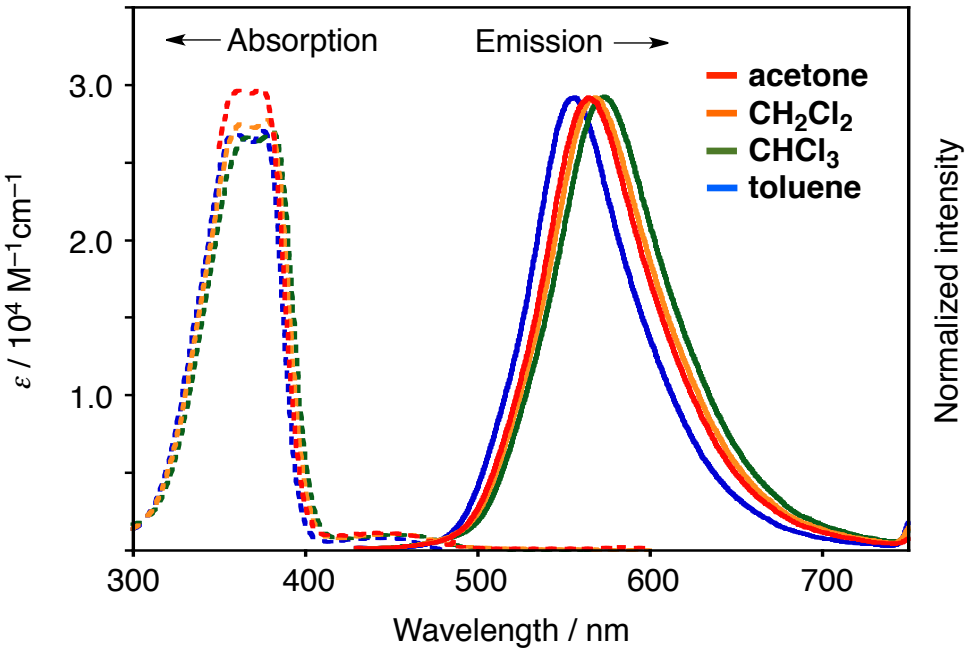


Figure S9. Absorption (dotted line) and emission (solid line) spectra of **3b** in various solvents.

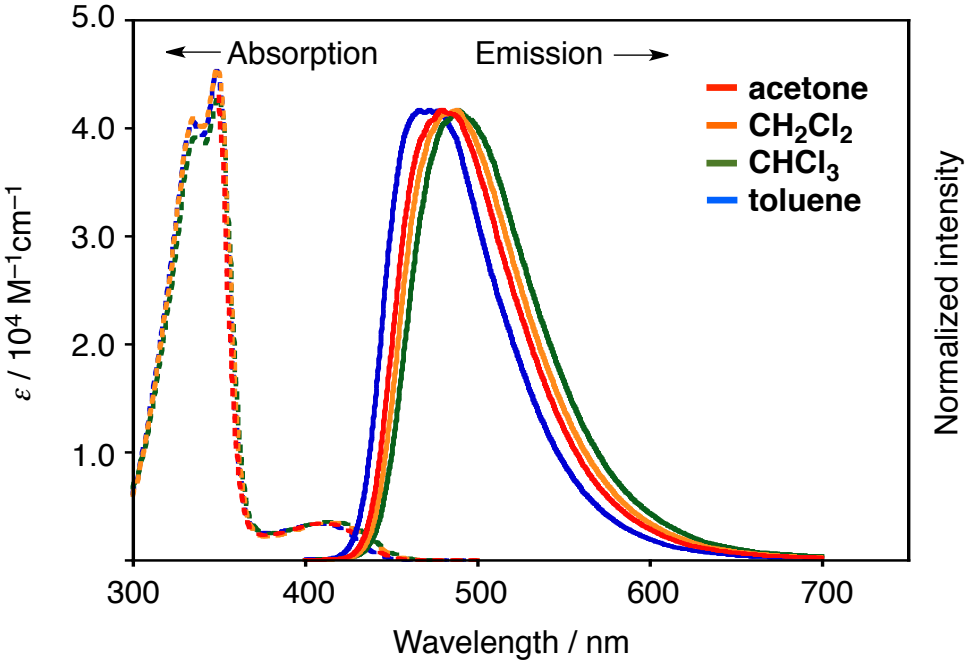


Figure S10. Absorption (dotted line) and emission (solid line) spectra of **5b** in various solvents.

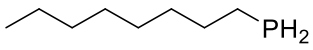
Table S5. Photophysical data for mono- and bisphospholes **3b** and **5b** in various solvents

Compound	solvent	Absorption		Fluorescence	
		λ_{max} / nm	ε / 10^3 cm^{-1}M^{-1}	λ_{em} / nm	Φ_F[a]
3b	toluene	446	0.759	556	0.036
	$CHCl_3$	453	1.00	572	0.022
	CH_2Cl_2	452	1.02	569	0.024
	acetone	442	1.12	565	0.022
5b	toluene	408	3.39	472	0.31
	$CHCl_3$	415	3.55	489	0.30
	CH_2Cl_2	415	3.47	488	0.39
	acetone	411	3.39	480	0.28

[a]Absolute fluorescence quantum yields determined by a calibrated integrating sphere system.

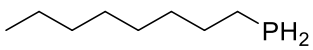
6. ^{1}H, ^{13}C, ^{31}P NMR Spectra of New Compounds

^{1}H NMR: *n*-Octyl phosphine (**S2**)



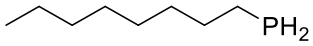
S2

^{13}C NMR: *n*-Octyl phosphine (**S2**)



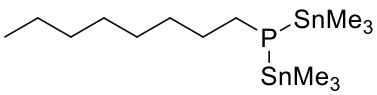
S2

^{31}P NMR: *n*-Octyl phosphine (**S2**)



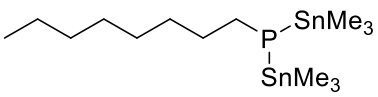
S2

^{1}H NMR: Bis(trimethyltin) *n*-octylphosphine (**S3**)

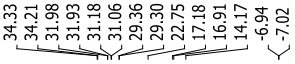


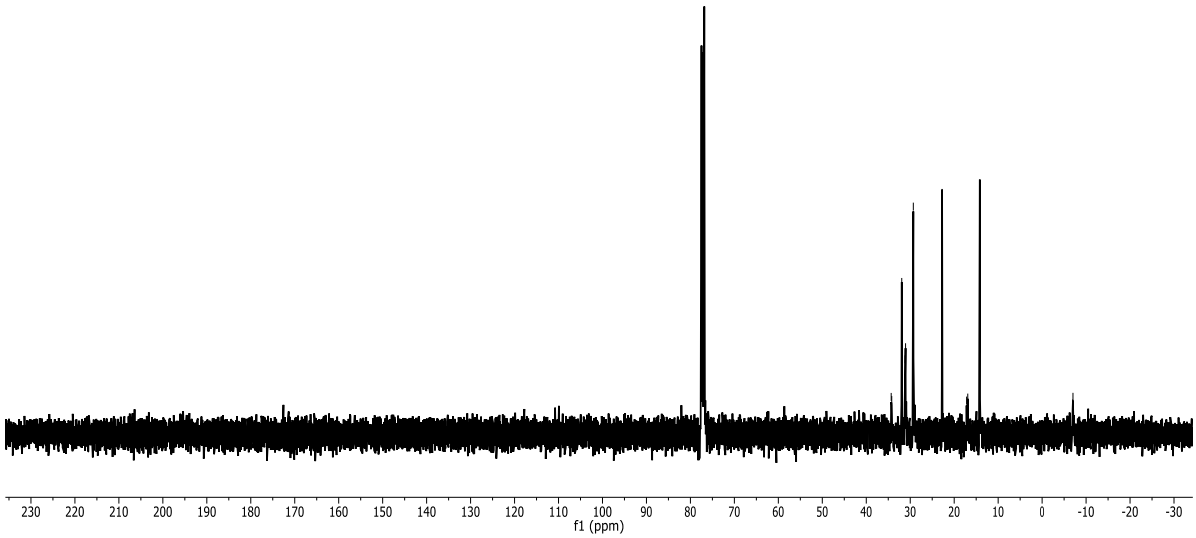
S3

^{13}C NMR: Bis(trimethyltin) *n*-octylphosphine (**S3**)

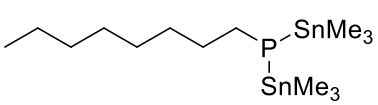


S3

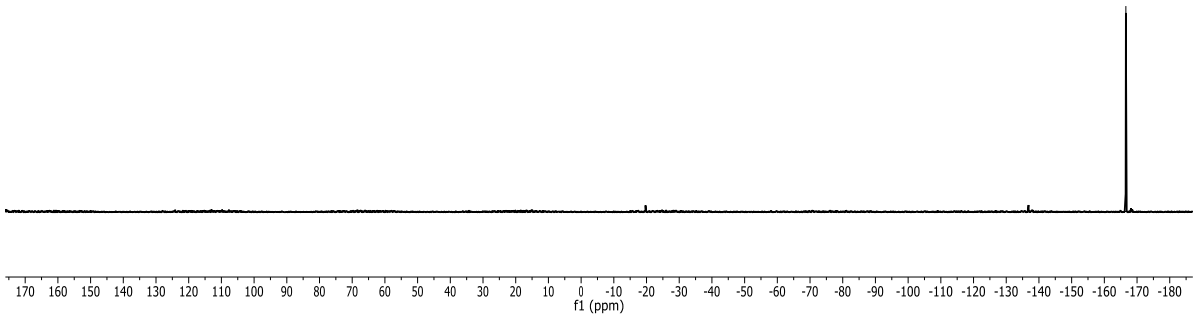




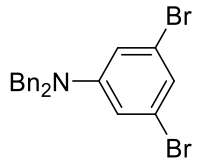
^{31}P NMR: Bis(trimethyltin) *n*-octylphosphine (**S3**)



S3

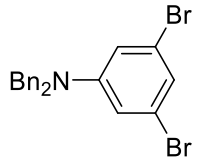


^{1}H NMR: *N*,*N*-Dibenzyl-3,5-dibromoaniline (**1**)



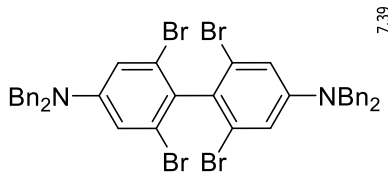
1

^{13}C NMR: *N*,*N*-Dibenzyl-3,5-dibromoaniline (**1**)



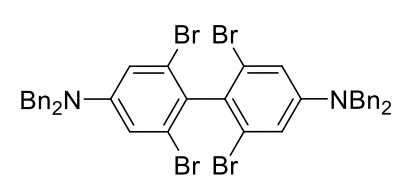
1

^{1}H NMR: N^4,N^4,$N^{4'}$,$N^{4'}$-Tetrabenzyl-2,2′-6,6′-tetrabromobiphenyl-4,4′-diamine (**2**)



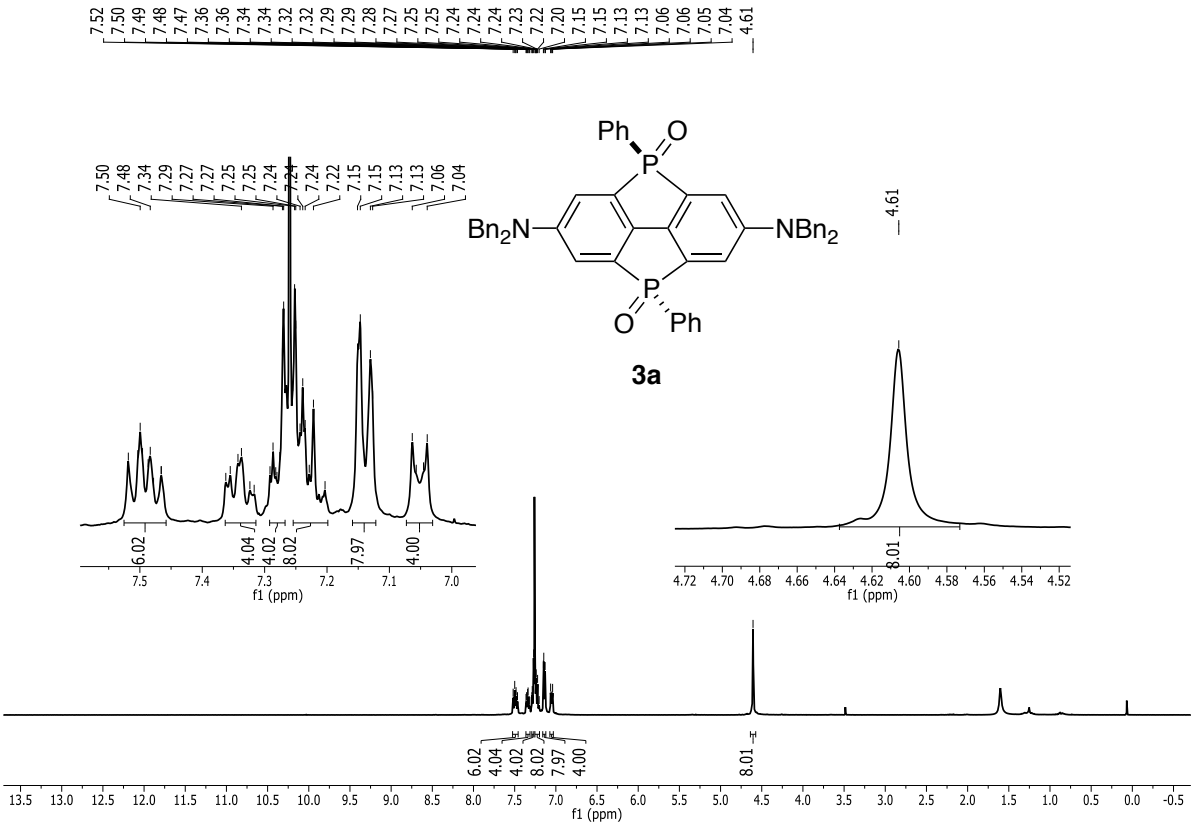
2

^{13}C NMR: N^4,N^4,$N^{4'}$,$N^{4'}$-Tetrabenzyl-2,2′-6,6′-tetrabromobiphenyl-4,4′-diamine (**2**)



2

^{1}H NMR: 2,6-Bis(dibenzylamino)-4,8-diphenylphosphindolo[4,3,2-*bcd*]phosphindole-4,8-dioxide (**3a**)



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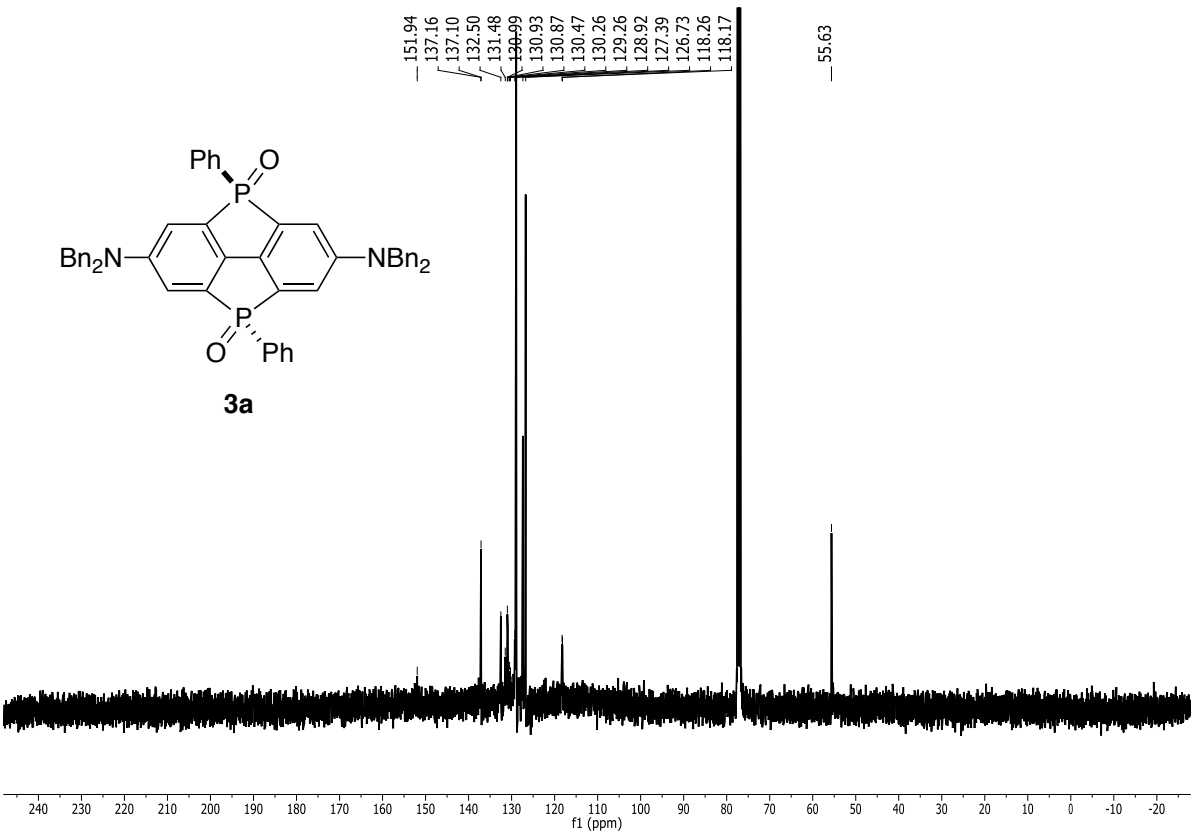
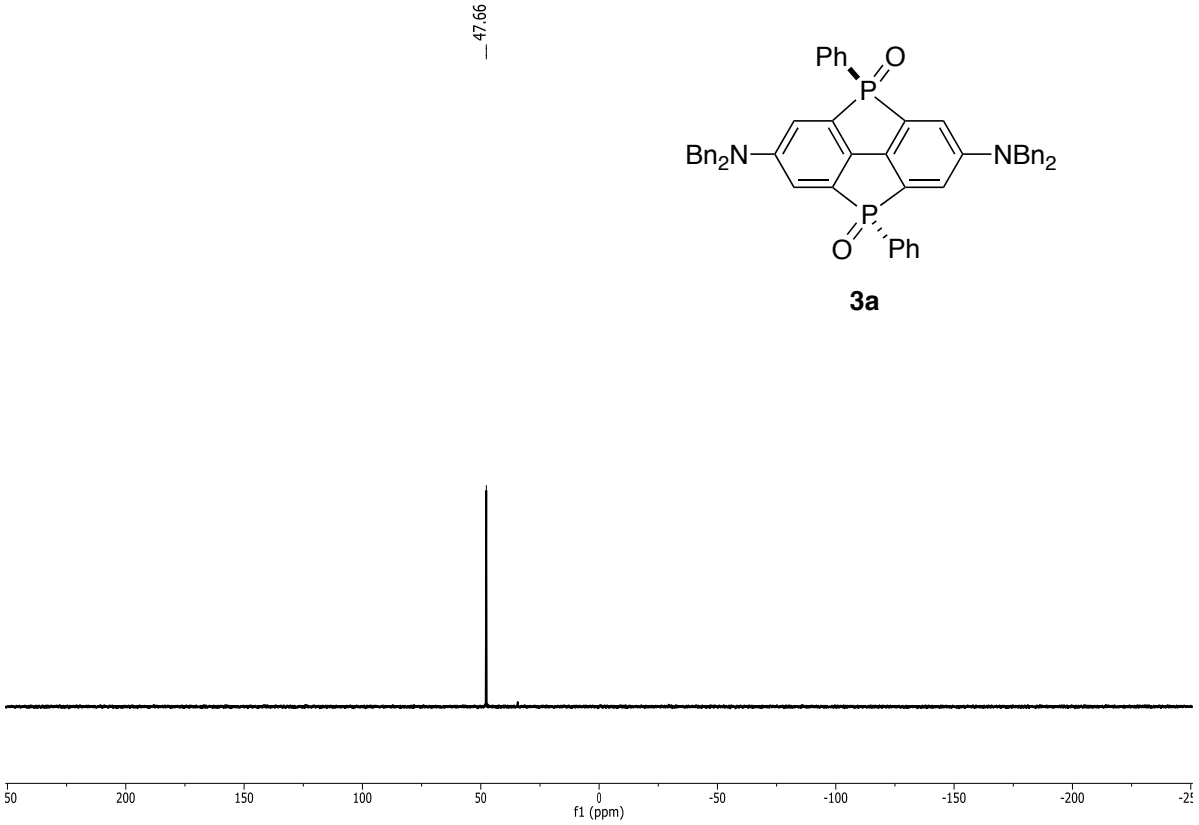
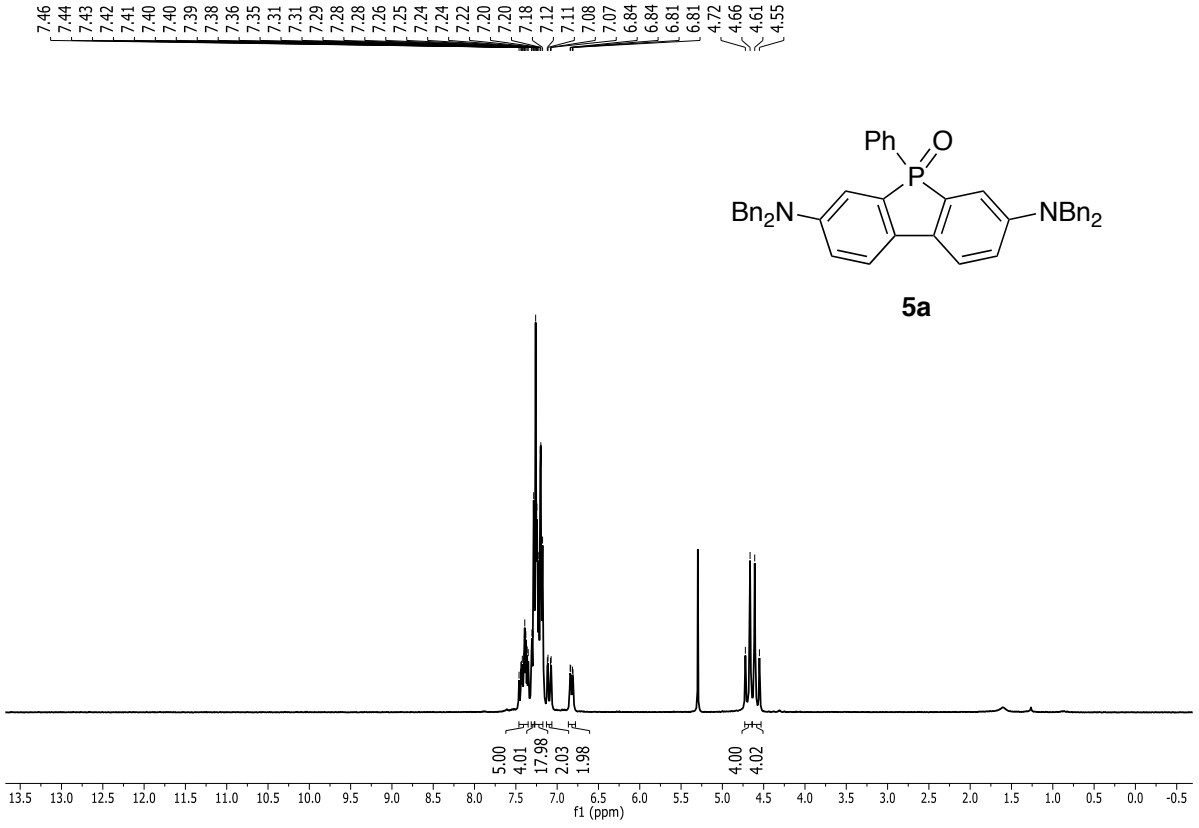


^{31}P NMR: 2,6-Bis(dibenzylamino)-4,8-diphenylphosphindolo[4,3,2-*bcd*]phosphindole-4,8-dioxide (**3a**)



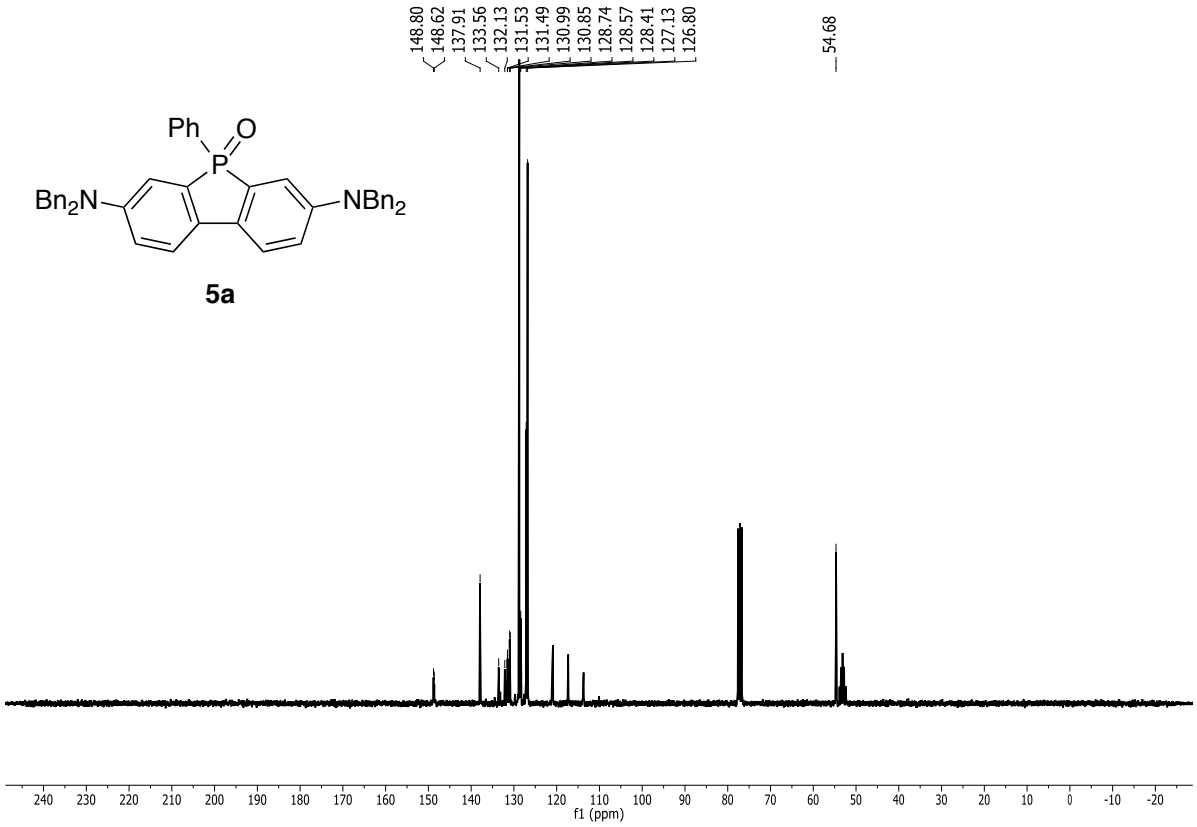
3a

^{1}H NMR: 3,7-Bis(dibenzylamino)-5-phenylbenzo[*b*]phosphindole 5-oxide (**5a**)

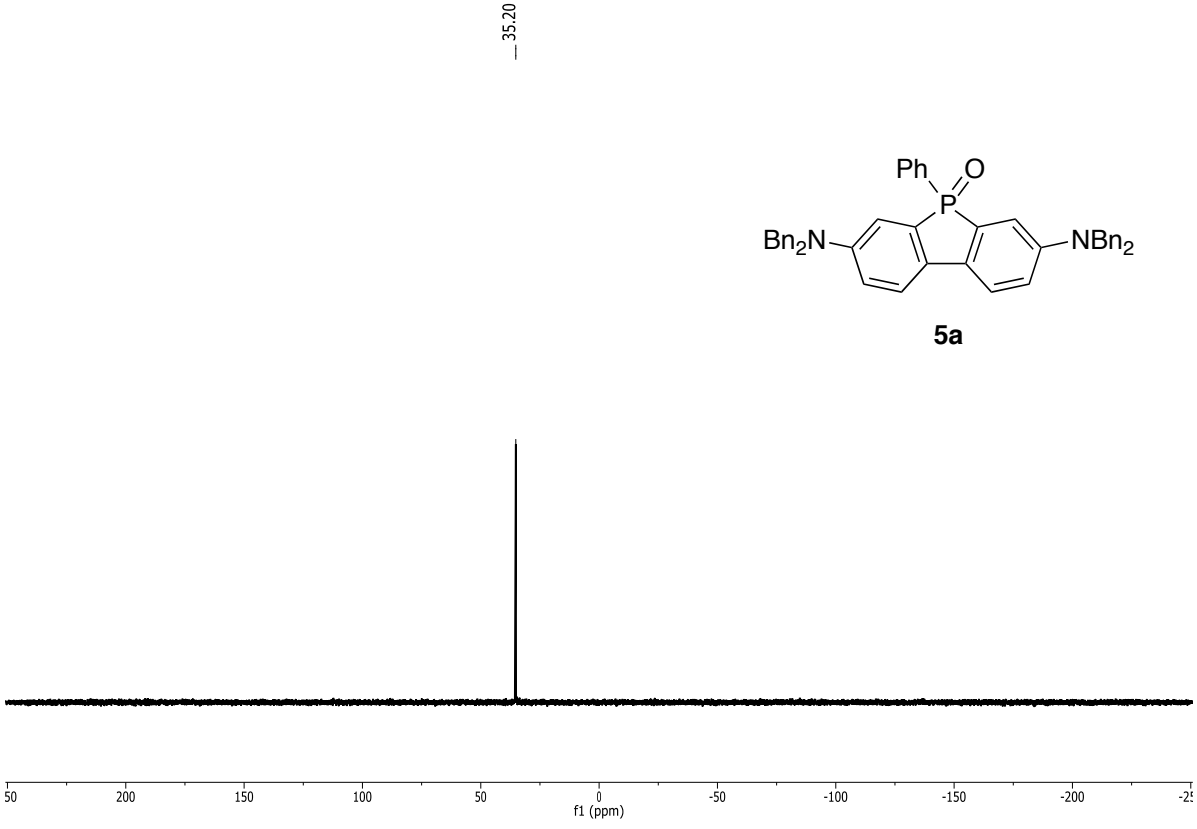


5a

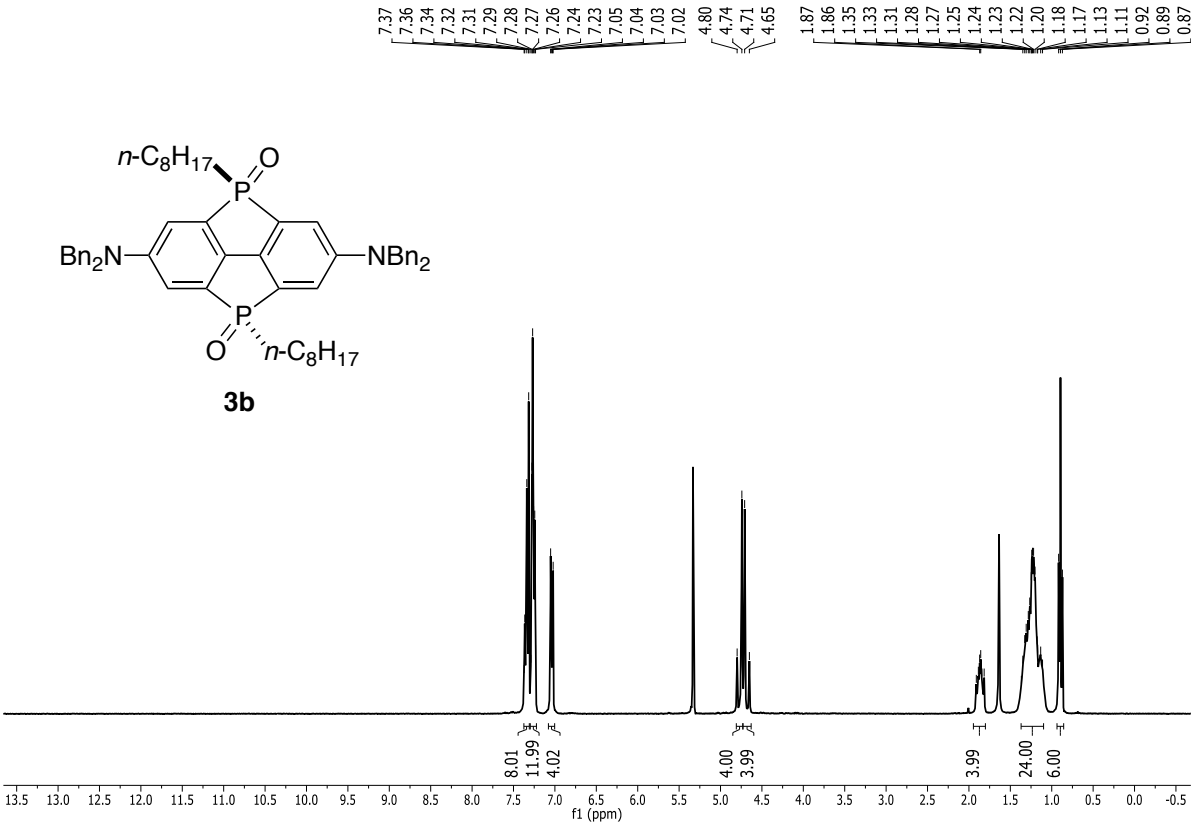
^{13}C NMR: 3,7-Bis(dibenzylamino)-5-phenylbenzo[*b*]phosphindole 5-oxide (**5a**)



^{31}P NMR: 3,7-Bis(dibenzylamino)-5-phenylbenzo[*b*]phosphindole 5-oxide (**5a**)

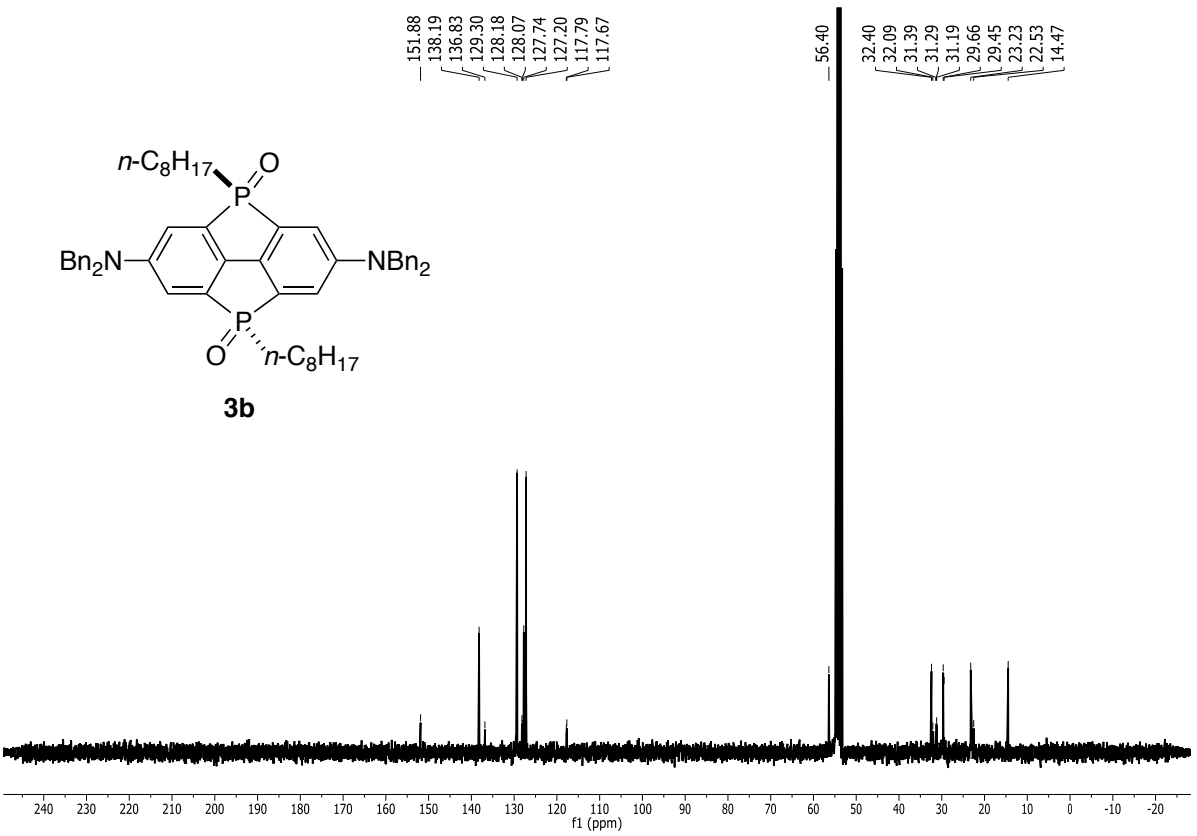


^{1}H NMR: 2,6-Bis(dibenzylamino)-4,8-dioctylphosphindolo[4,3,2-*bcd*]phosphindole 4,8-dioxide (**3b**)



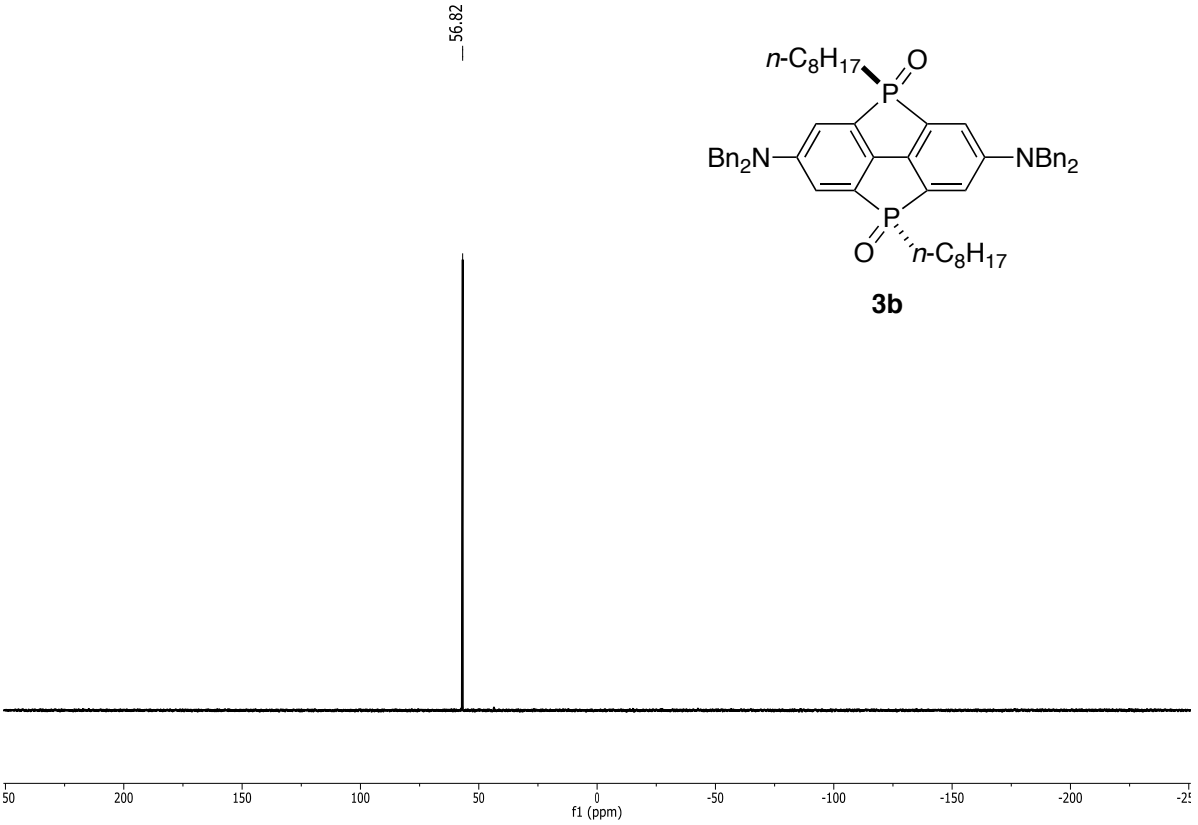
3b

^{13}C NMR: 2,6-Bis(dibenzylamino)-4,8-dioctylphosphindolo[4,3,2-*bcd*]phosphindole 4,8-dioxide (**3b**)



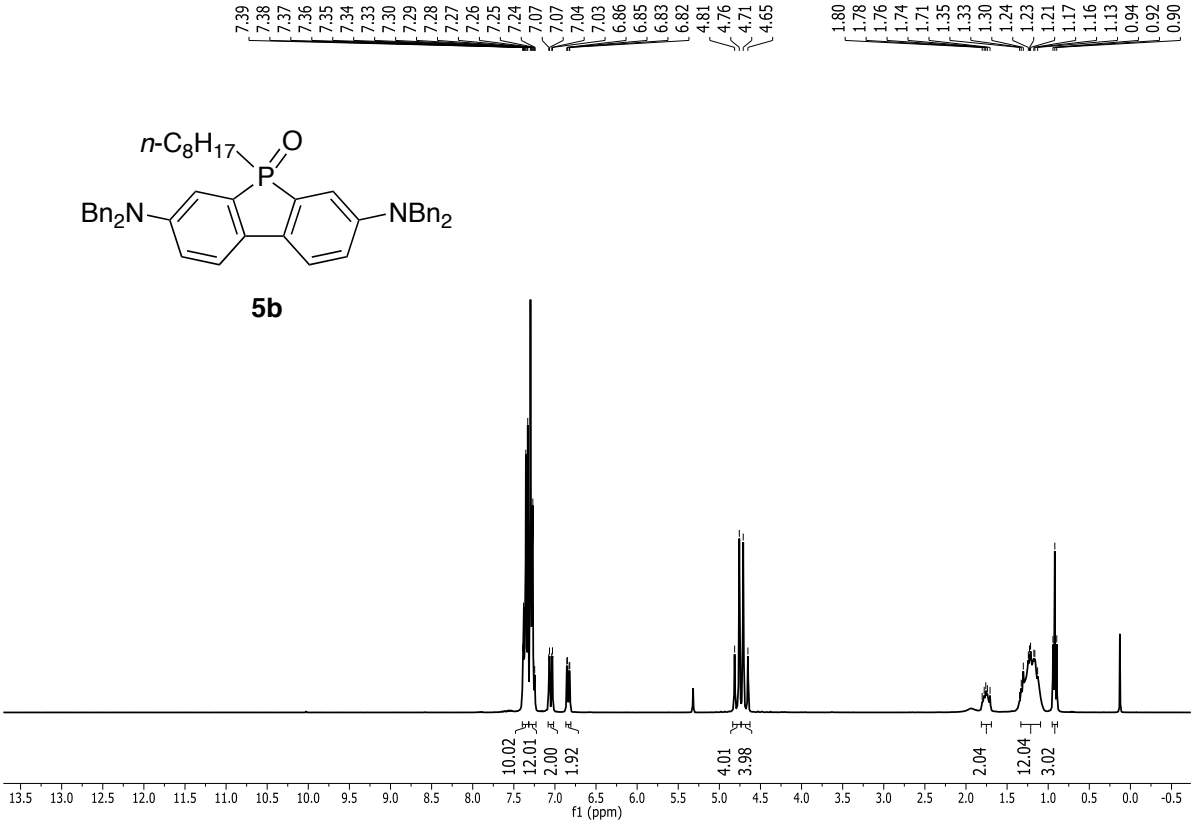
3b

^{31}P NMR: 2,6-Bis(dibenzylamino)-4,8-dioctylphosphindolo[4,3,2-*bcd*]phosphindole 4,8-dioxide (**3b**)



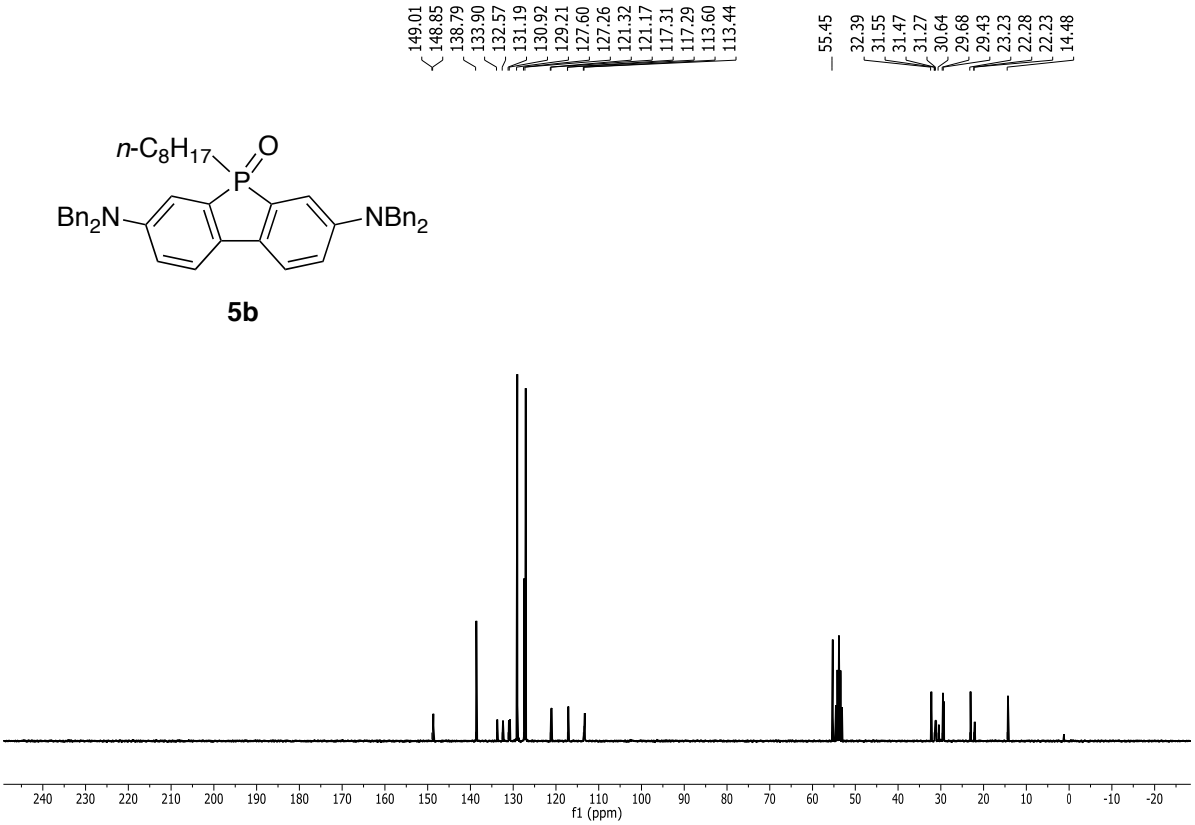
3b

^{1}H NMR: 3,7-Bis(dibenzylamino)-5-octylbenzo[*b*]phosphindole 5-oxide (**5b**)



5b

^{13}C NMR: 3,7-Bis(dibenzylamino)-5-octylbenzo[*b*]phosphindole 5-oxide (**5b**)



^{31}P NMR: 3,7-Bis(dibenzylamino)-5-octylbenzo[*b*]phosphindole 5-oxide (**5b**)