Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Lewis acidity enhancement of triarylborane by appended phosphine oxide groups

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Table S1. Crystallographic data and parameters for **3**.

Compound	**3**·4(C_4H_8O)
formula	$C_{76}H_{86}BO_7P_3$
formula weight	1215.17
crystal system	Monoclinic
space group	$P2_1$
a (Å)	8.6329(2)
b (Å)	32.1721(8)
c (Å)	12.9756(3)
α (°)	90.00
β (°)	105.072(2)
γ (°)	90.00
V (Å^3)	3479.85(14)
Z	2
ρ_{calc} (g cm^{-3})	1.160
μ (mm^{-1})	0.137
F(000)	1296
T (K)	296(2)
hkl range	$-10 \rightarrow +10$, $-38 \rightarrow +38$, $-14 \rightarrow +15$
measd reflns	25249
unique reflns [R_{int}]	11390 [0.0476]
reflns used for refinement	11390
refined parameters	791
R1[a] ($I > 2\sigma(I)$)	0.0727
wR2[b] all data	0.1742
GOF on F^2	1.026
ρ_{fin} (max/min) (e Å^{-3})	0.388/–0.362

[a] $R1 = \sum||Fo| - |Fc||/\sum|Fo|$. [b] $wR2 = \{[\sum w(Fo^2 - Fc^2)^2]/[\sum w(Fo^2)^2]\}^{1/2}$.

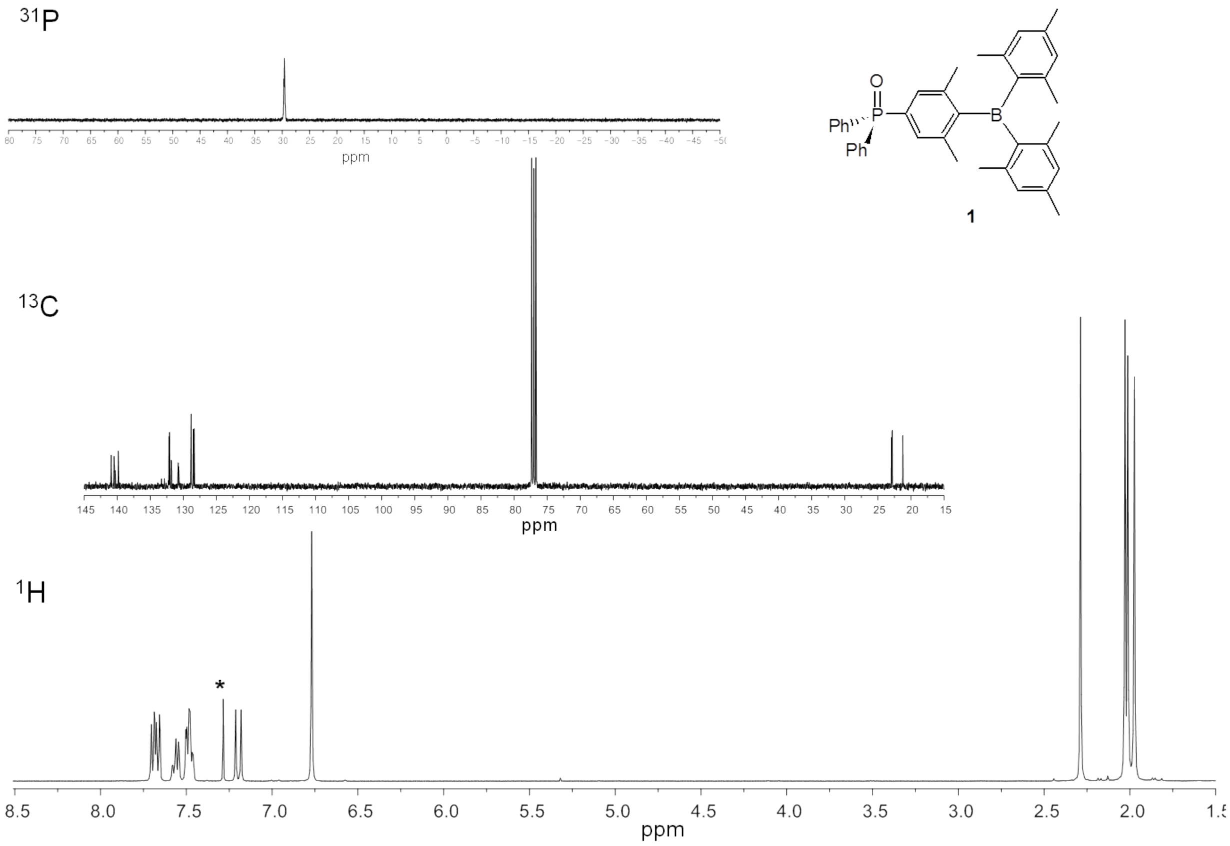


Figure S1. ^{31}P (top), ^{13}C (middle), and ^{1}H (bottom) NMR spectra of **1** ($*$ from residual $CHCl_3$ in $CDCl_3$).

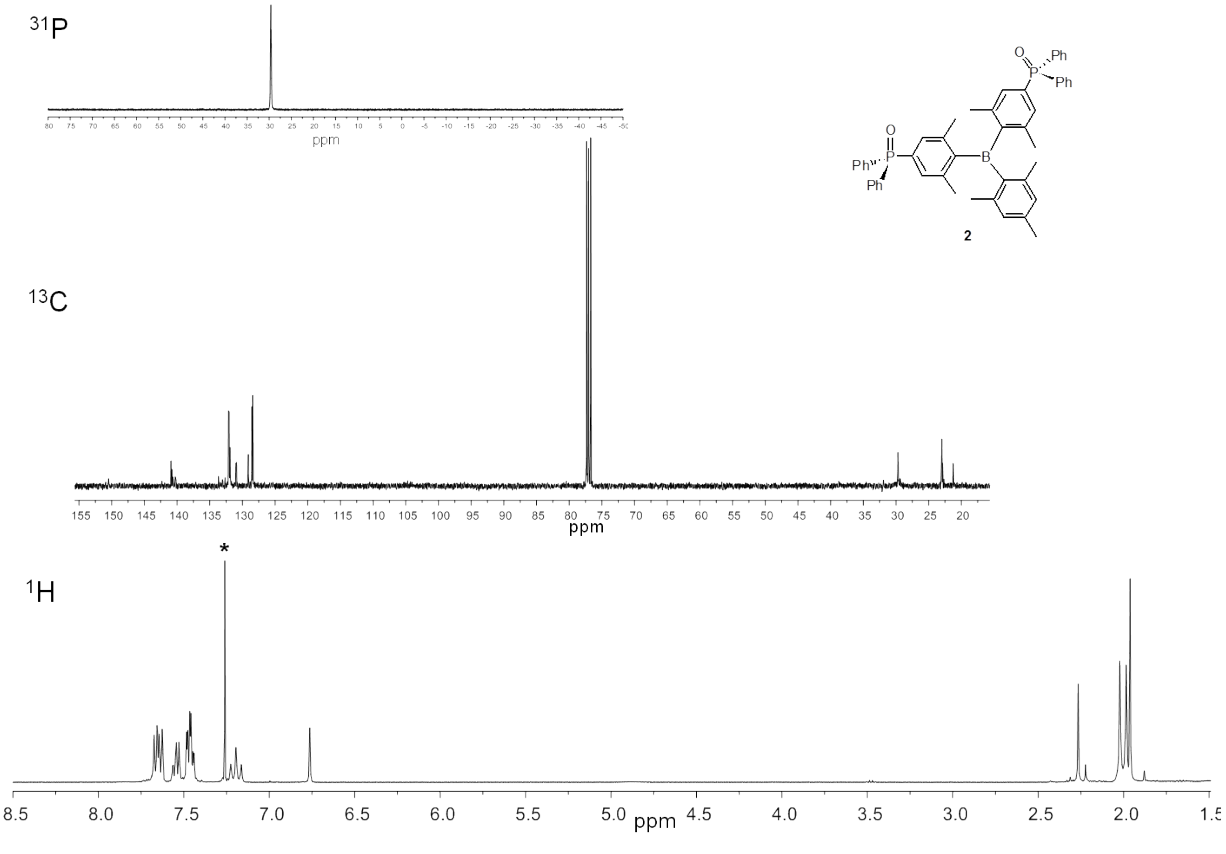


Figure S2. ^{31}P (top), ^{13}C (middle), and ^{1}H (bottom) NMR spectra of **2** (∗ from residual $CHCl_3$ in $CDCl_3$).

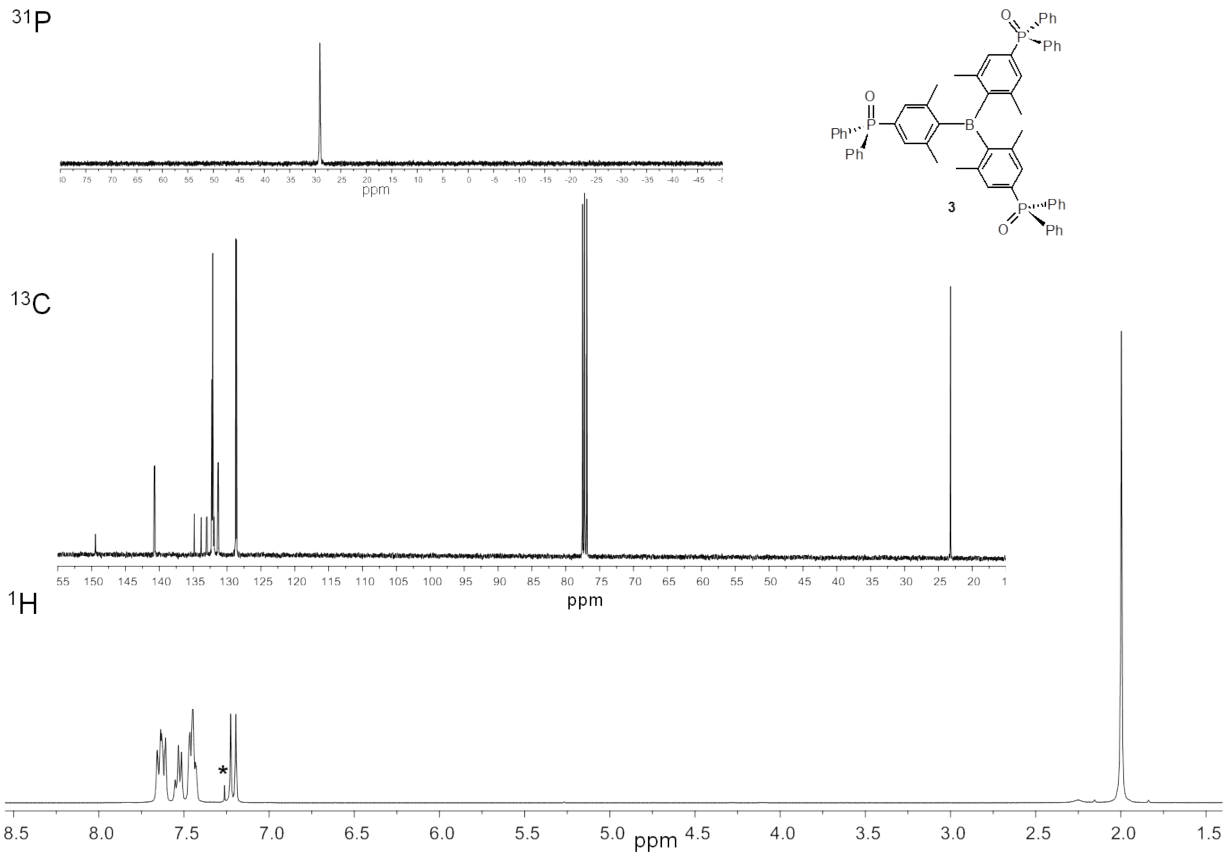
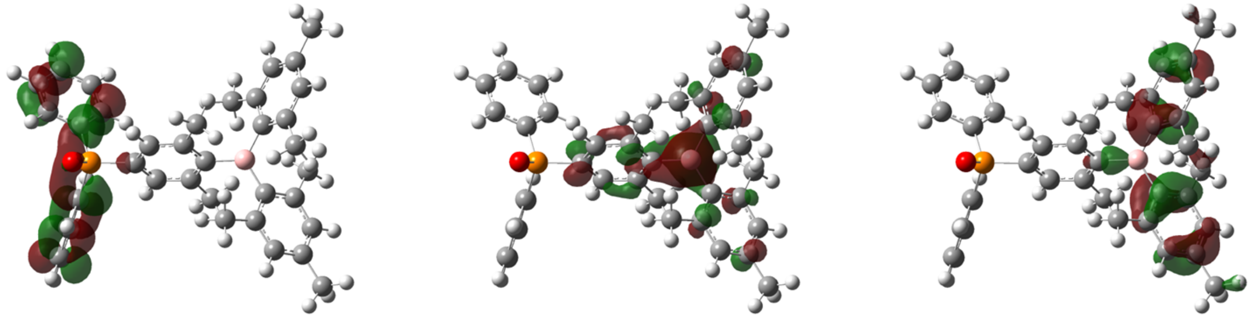
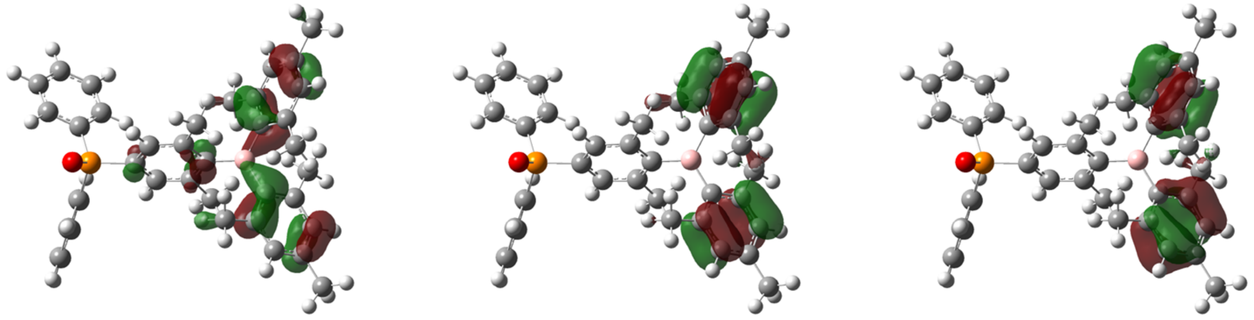


Figure S3. ^{31}P (top), ^{13}C (middle), and ^{1}H (bottom) NMR spectra of **3** (∗ from residual $CHCl_3$ in $CDCl_3$).

DFT Computational Results



LUMO+1 LUMO HOMO



HOMO-1 HOMO-2 HOMO-3

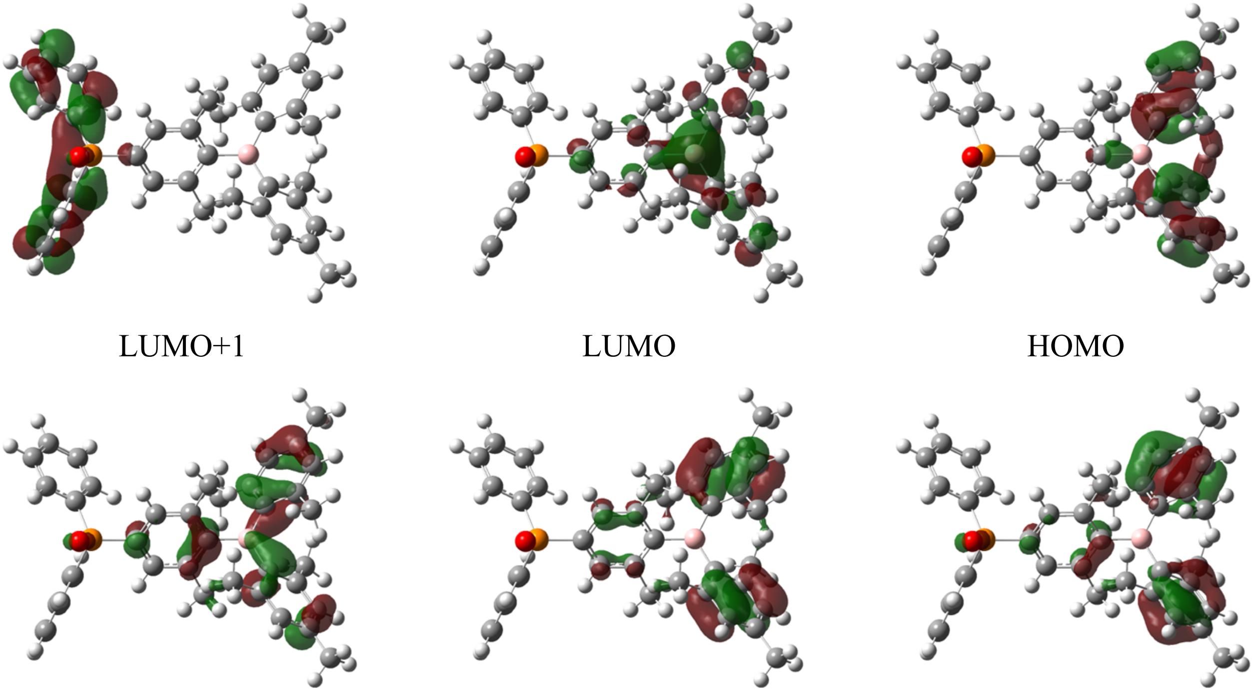
Figure S4. Frontier molecular orbitals of **1** from B3LYP/6-31G(d) calculations (Isovalue = 0.04) with PCM in THF at the ground state (S_0) optimized geometries.

Table S2. Molecular orbital energies (in eV) and distributions (in %) of **1** at the ground state (S_0) optimized geometries.

MO	Energy	Boron	Phenylene_1	Phosphine oxide_1	Mesityl_2	Mesityl_3
LUMO+2	–0.70	1.8	25.5	56.1	8.6	8.0
LUMO+1	–0.81	0.07	9.7	90.0	0.2	0.08
LUMO	–1.87	27.6	27.1	4.0	20.8	20.6
HOMO	–6.12	1.2	9.6	0.2	42.3	46.7
HOMO-1	–6.27	2.3	14.0	1.6	40.3	41.8
HOMO-2	–6.34	0.5	1.1	0.05	53.1	45.2
HOMO-3	–6.41	0.4	1.1	0.1	48.7	49.6

Table S3. Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **1** from TD-B3LYP/6-31G(d) calculations with PCM in THF at the ground state (S_0) optimized geometries.

state	$\lambda_{calc.}$/ nm	$f_{calc.}$	major contribution
S1	356.9	0.1543	HOMO→LUMO (99%)
S2	342.8	0.1354	HOMO-1→LUMO (94%)
S3	329.6	0.0269	HOMO-2→LUMO (99%)
S4	323.2	0.0733	HOMO-3→LUMO (98%)



LUMO+1 LUMO HOMO

HOMO-1 HOMO-2 HOMO-3

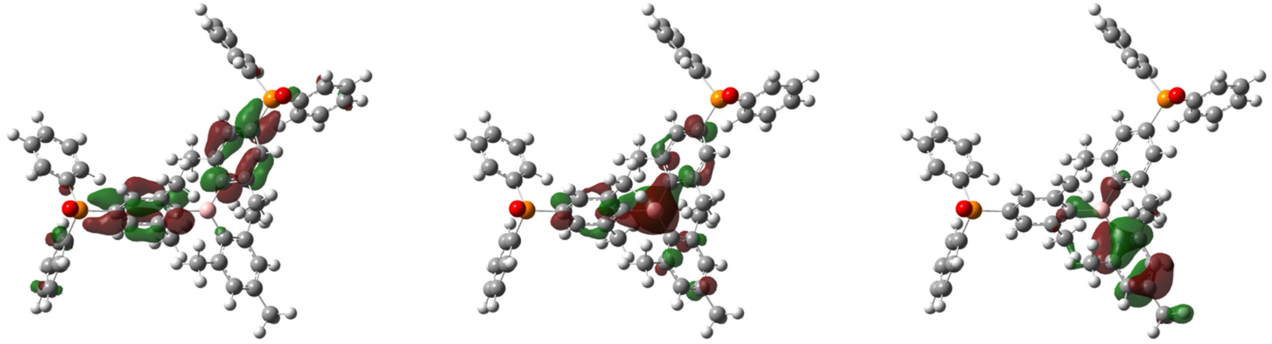
Figure S5. Frontier molecular orbitals of **1** from B3LYP/6-31G(d) calculations (Isovalue = 0.04) with PCM in THF at the first excited state (S_1) optimized geometries obtained from CIS/3-21G with PCM in THF calculations.

Table S4. Molecular orbital energies (in eV) and distributions (in %) of **1** at the first excited state (S_1) optimized geometries.

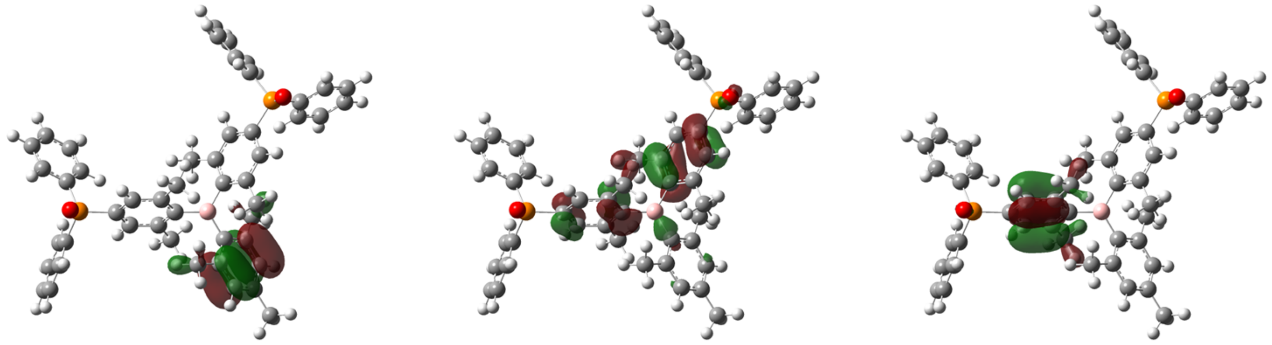
MO	Energy	Boron	Phenylene_1	Phosphine oxide_1	Mesityl_2	Mesityl_3
LUMO+2	–0.65	1.1	46.9	27.9	12.3	11.8
LUMO+1	–0.79	0.1	10.2	89.1	0.4	0.3
LUMO	–2.00	24.7	21.7	3.3	24.6	25.7
HOMO	–5.86	1.2	9.4	0.2	42.1	47.1
HOMO-1	–6.31	2.7	20.2	3.4	38.1	35.6
HOMO-2	–6.42	0.7	13.2	0.6	45.6	39.9
HOMO-3	–6.55	1.1	13.4	4.2	46.9	34.5

Table S5. Computed emission wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **1** from TD-B3LYP/6-31G(d) calculations with PCM in THF at the first excited state (S_1) optimized geometries.

state	$\lambda_{calc.}$/ nm	$f_{calc.}$	major contribution
S1	399.9	0.1519	HOMO→LUMO (99%)
S2	345.7	0.1621	HOMO-1→LUMO (91%)
S3	334.4	0.0385	HOMO-2→LUMO (98%)
S4	320.7	0.0475	HOMO-3→LUMO (81%) HOMO-4→LUMO (10%)



LUMO+1 LUMO HOMO



HOMO-1 HOMO-2 HOMO-3

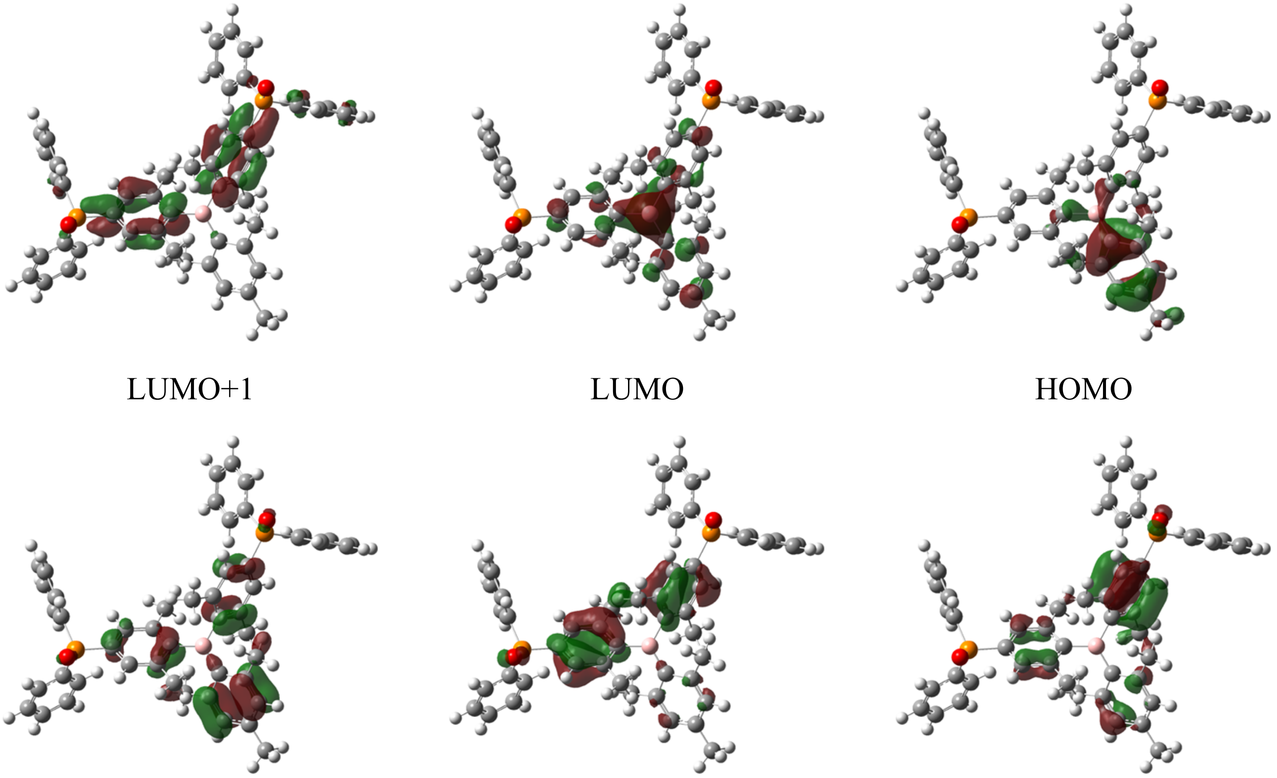
Figure S6. Frontier molecular orbitals of **2** from B3LYP/6-31G(d) calculations (Isovalue = 0.04) with PCM in THF at the ground state (S_0) optimized geometries.

Table S6. Molecular orbital energies (in eV) and distributions (in %) of **2** at the ground state (S_0) optimized geometries.

MO	Energy	Boron	Phenylene_1	Phosphine oxide_1	Phenylene_2	Phosphine oxide_2	Mesityl_3
LUMO+2	–0.83	0.08	0.9	5.8	9.7	83.3	0.2
LUMO+1	–0.91	1.5	30.1	18.6	29.3	15.5	5.0
LUMO	–2.07	27.3	23.7	3.2	23.8	3.3	18.7
HOMO	–6.27	1.8	11.1	0.6	10.2	0.6	75.8
HOMO-1	–6.42	0.4	2.4	0.2	2.8	0.3	94.0
HOMO-2	–6.56	1.5	32.0	4.7	45.2	6.2	10.3
HOMO-3	–6.64	0.2	89.8	4.0	3.3	0.1	2.5

Table S7. Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **2** from TD-B3LYP/6-31G(d) calculations with PCM in THF at the ground state (S_0) optimized geometries.

state	$\lambda_{calc.}$/ nm	$f_{calc.}$	major contribution
S1	362.0	0.1388	HOMO→LUMO (97%)
S2	343.5	0.0403	HOMO-1→LUMO (82%) HOMO-2→LUMO (15%)
S3	334.7	0.1629	HOMO-2→LUMO (79%) HOMO-1→LUMO (16%)
S4	321.0	0.0286	HOMO-3→LUMO (97%)



LUMO+1 LUMO HOMO

HOMO-1 HOMO-2 HOMO-3

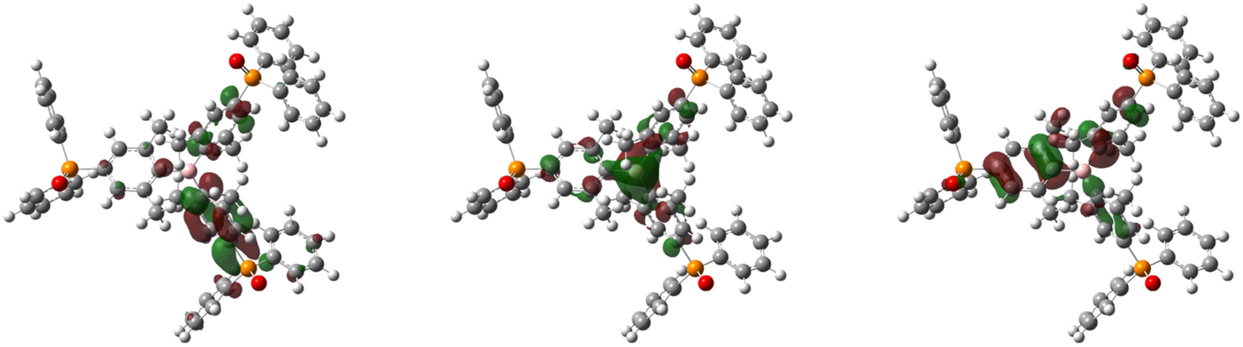
Figure S7. Frontier molecular orbitals of **2** from B3LYP/6-31G(d) calculations (Isovalue = 0.04) with PCM in THF at the first excited state (S_1) optimized geometries obtained from CIS/3-21G with PCM in THF calculations.

Table S8. Molecular orbital energies (in eV) and distributions (in %) of **2** at the first excited state (S_1) optimized geometries.

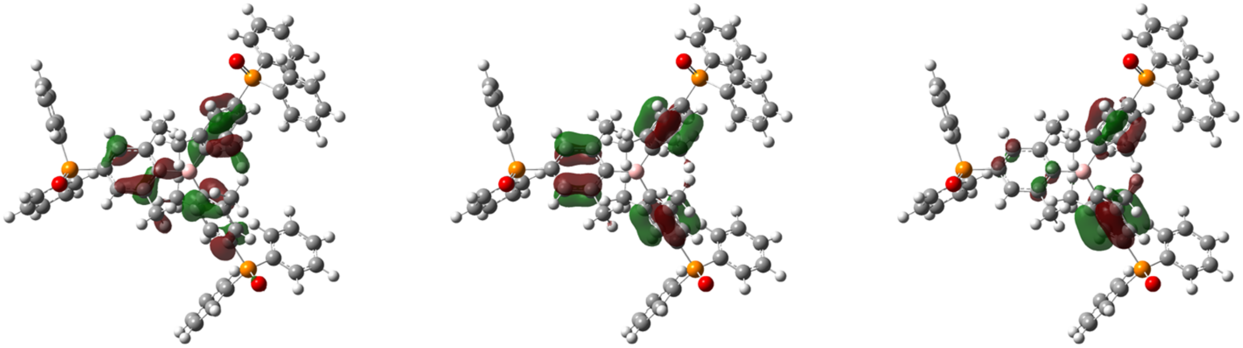
MO	Energy	Boron	Phenylene_1	Phosphine oxide_1	Phenylene_2	Phosphine oxide_2	Mesityl_3
LUMO+2	–0.75	0.05	0.6	2.6	9.9	85.9	0.8
LUMO+1	–0.82	1.2	29.9	14.6	31.8	18.0	4.5
LUMO	–2.20	24.5	21.9	3.0	22.0	3.0	25.6
HOMO	–6.00	2.0	11.7	0.5	12.1	0.7	72.9
HOMO-1	–6.54	0.9	19.7	2.9	25.7	3.8	47.0
HOMO-2	–6.59	0.8	48.6	6.6	32.9	2.0	9.1
HOMO-3	–6.72	0.3	15.6	1.1	59.4	7.5	16.1

Table S9. Computed emission wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **2** from TD-B3LYP/6-31G(d) calculations with PCM in THF at the first excited state (S_1) optimized geometries.

state	$\lambda_{calc.}$/ nm	$f_{calc.}$	major contribution
S1	404.0	0.1671	HOMO→LUMO (98%)
S2	347.7	0.1241	HOMO-1→LUMO (86%) HOMO-2→LUMO (11%)
S3	336.8	0.0403	HOMO-2→LUMO (85%) HOMO-1→LUMO (12%)
S4	322.4	0.0583	HOMO-3→LUMO (92%)



LUMO+1 LUMO HOMO



HOMO-1 HOMO-2 HOMO-3

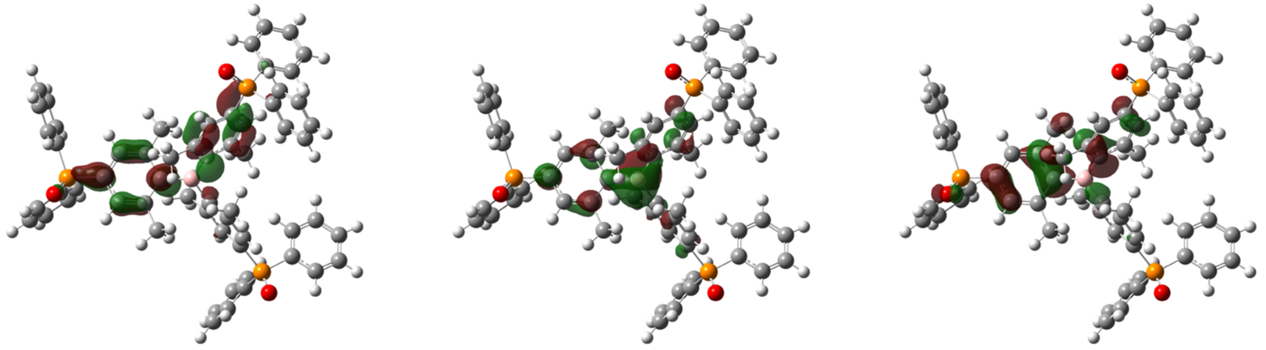
Figure S8. Frontier molecular orbitals of **3** from B3LYP/6-31G(d) calculations (Isovalue = 0.04) with PCM in THF at the ground state (S_0) optimized geometries.

Table S10. Molecular orbital energies (in eV) and distributions (in %) of **3** at the ground state (S_0) optimized geometries.

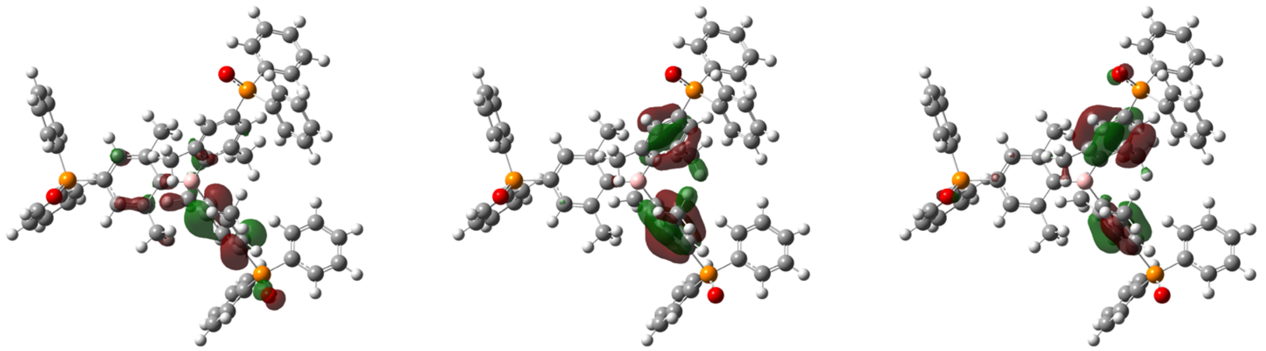
MO	Energy	Boron	Phenylene_1	Phosphine oxide_1	Phenylene_2	Phosphine oxide_2	Phenylene_3	Phosphine oxide_3
LUMO+2	–0.96	1.4	32.9	17.2	26.9	13.9	6.2	1.5
LUMO+1	–0.98	1.5	9.9	3.1	17.6	8.2	37.3	22.2
LUMO	–2.26	27.5	21.4	2.7	21.3	2.9	21.5	2.7
HOMO	–6.61	1.3	40.7	6.0	31.0	4.5	15.7	0.9
HOMO-1	–6.62	1.1	26.1	2.0	28.2	2.6	34.2	5.7
HOMO-2	–6.68	0.6	33.0	1.5	32.2	1.6	29.8	1.3
HOMO-3	–6.72	0.3	11.8	1.9	23.5	1.9	57.5	3.1

Table S11. Computed absorption wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **3** from TD-B3LYP/6-31G(d) calculations with PCM in THF at the ground state (S_0) optimized geometries.

state	$\lambda_{calc.}$/ nm	$f_{calc.}$	major contribution
S1	349.3	0.1668	HOMO→LUMO (95%)
S2	348.5	0.1319	HOMO-1→LUMO (92%)
S3	333.7	0.0205	HOMO-2→LUMO (97%)
S4	329.7	0.0625	HOMO-3→LUMO (81%) HOMO-4→LUMO (14%)



LUMO+1 LUMO HOMO



HOMO-1 HOMO-2 HOMO-3

Figure S9. Frontier molecular orbitals of **3** from B3LYP/6-31G(d) calculations (Isovalue = 0.04) with PCM in THF at the first excited state (S_1) optimized geometries obtained from CIS/3-21G with PCM in THF calculations.

Table S12. Molecular orbital energies (in eV) and distributions (in %) of **3** at the first excited state (S_1) optimized geometries.

MO	Energy	Boron	Phenylene_1	Phosphine oxide_1	Phenylene_2	Phosphine oxide_2	Phenylene_3	Phosphine oxide_3
LUMO+2	–0.86	1.4	5.7	0.8	21.6	12.9	38.6	19.1
LUMO+1	–0.99	1.6	37.4	13.1	25.2	8.5	11.3	2.9
LUMO	–2.38	25.2	29.8	4.4	20.3	2.7	16.0	1.7
HOMO	–6.37	1.5	47.6	6.3	28.9	2.9	12.2	0.7
HOMO-1	–6.62	0.6	14.1	0.6	13.5	0.8	64.8	5.6
HOMO-2	–6.65	0.9	5.6	0.3	39.2	3.4	44.6	6.1
HOMO-3	–6.74	0.2	5.5	1.1	53.4	2.3	35.0	2.5

Table S13. Computed emission wavelengths (λ_{calc} in nm) and oscillator strengths ($f_{calc.}$) for **3** from TD-B3LYP/6-31G(d) calculations with PCM in THF at the first excited state (S_1) optimized geometries.

state	$\lambda_{calc.}$/ nm	$f_{calc.}$	major contribution
S1	384.7	0.2189	HOMO→LUMO (98%)
S2	355.3	0.1245	HOMO-2→LUMO (59%) HOMO-1→LUMO (37%)
S3	347.2	0.0150	HOMO-1→LUMO (60%) HOMO-2→LUMO (38%)
S4	336.9	0.0753	HOMO-3→LUMO (97%)