Supplementary Information

## **B**-substituted group 1 phosphides: Synthesis and reactivity<sup>†</sup>

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Figure S1. PovRay presentation of molecular structure of **3**. Hydrogen atoms are omitted for clarity.



Figure S2. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500.13 MHz) of 1-BCy<sub>2</sub>-8-PCl<sub>2</sub>-C<sub>10</sub>H<sub>6</sub> (1)



Figure S3.  ${}^{13}C{}^{1H}$  NMR (C<sub>6</sub>D<sub>6</sub>, 125.77 MHz) of 1-BCy<sub>2</sub>-8-PCl<sub>2</sub>-C<sub>10</sub>H<sub>6</sub>(1)



Figure S4. <sup>11</sup>B{<sup>1</sup>H} NMR ( $C_6D_6$ , 160.57 MHz) of 1-BCy<sub>2</sub>-8-PCl<sub>2</sub>- $C_{10}H_6$  (1)



Figure S5. <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 202.49 MHz) of 1-BCy<sub>2</sub>-8-PCl<sub>2</sub>-C<sub>10</sub>H<sub>6</sub> (**1**)



S9



Figure S7.  $^{13}C\{^{1}H\}$  NMR (C\_6D\_6, 125.77 MHz) of 1-BCy\_2-8-PPhCl-C\_{10}H\_6 (**2**)



Figure S8. <sup>11</sup>B{<sup>1</sup>H} NMR ( $C_6D_6$ , 160.57 MHz) of 1-BCy<sub>2</sub>-8-PPhCl- $C_{10}H_6$  (2)



Figure S9.  ${}^{31}P{}^{1}H$  NMR ( $C_6D_6$ , 202.49 MHz) of 1-BCy<sub>2</sub>-8-PPhCl- $C_{10}H_6$  (**2**)



Figure S10. <sup>1</sup>H NMR (THF-d<sub>8</sub>, 500.13 MHz) of {1-BCy-8-PCy-C<sub>10</sub>H<sub>6</sub>}<sub>2</sub> (**3**)

![](_page_13_Figure_0.jpeg)

Figure S11. <sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 125.77 MHz) of {1-BCy-8-PCy-C<sub>10</sub>H<sub>6</sub>}<sub>2</sub> (**3**)

![](_page_14_Figure_0.jpeg)

Figure S12. <sup>11</sup>B{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 160.57 MHz) of {1-BCy-8-PCy-C<sub>10</sub>H<sub>6</sub>}<sub>2</sub> (**3**)

![](_page_15_Figure_0.jpeg)

Figure S13.  ${}^{31}P{}^{1}H{}$  NMR (THF-d<sub>8</sub>, 202.49 MHz) of {1-BCy-8-PCy-C<sub>10</sub>H<sub>6</sub>}<sub>2</sub> (**3**)

![](_page_16_Figure_0.jpeg)

Figure S14. <sup>1</sup>H NMR (THF-d<sub>8</sub>, 500.13 MHz) of {1-BCy<sub>2</sub>-8-PPh-C<sub>10</sub>H<sub>6</sub>}<sub>2</sub> (4)

![](_page_17_Figure_0.jpeg)

Figure S15. <sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 125.77 MHz) of {1-BCy<sub>2</sub>-8-PPh-C<sub>10</sub>H<sub>6</sub>}<sub>2</sub> (4)

![](_page_18_Figure_0.jpeg)

Figure S16. <sup>11</sup>B{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 160.57 MHz) of {1-BCy<sub>2</sub>-8-PPh-C<sub>10</sub>H<sub>6</sub>}<sub>2</sub> (4)

![](_page_19_Figure_0.jpeg)

Figure S17.  ${}^{31}P_{1}^{1}H_{1}^{3}NMR$  (THF-ds, 202.49 MHz) of {1-BCy<sub>2</sub>-8-PPh-C<sub>10</sub>H<sub>6</sub>} (4)

![](_page_20_Figure_0.jpeg)

Figure S18. <sup>1</sup>H NMR (THF-d<sub>8</sub>, 500.13 MHz) of [Na(THF)<sub>3</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-PPh-C<sub>10</sub>H<sub>6</sub>]<sup>-</sup> (**5**)

![](_page_21_Figure_0.jpeg)

Figure S19. <sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 125.77 MHz) of [Na(THF)<sub>3</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-PPh-C<sub>10</sub>H<sub>6</sub>]<sup>-</sup> (**5**)

![](_page_22_Figure_0.jpeg)

Figure S20. <sup>11</sup>B{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 160.57 MHz) of [Na(THF)<sub>3</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-PPh-C<sub>10</sub>H<sub>6</sub>]<sup>-</sup> (**5**)

![](_page_23_Figure_0.jpeg)

Figure S21.  ${}^{31}P{}^{1}H{}$  NMR (THF-d<sub>8</sub>, 202.49 MHz) of [Na(THF)<sub>3</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-PPh-C<sub>10</sub>H<sub>6</sub>]<sup>-</sup> (5)

![](_page_24_Figure_0.jpeg)

Figure S22. <sup>1</sup>H NMR (THF-d<sub>8</sub>, 500.13 MHz) of {[K(THF)<sub>2</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-PPh-C<sub>10</sub>H<sub>6</sub>]<sup>-</sup>}<sub>∞</sub> (6)

![](_page_25_Figure_0.jpeg)

Figure S23. <sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 125.77 MHz) of { $[K(THF)_2]^+$  [1-BCy<sub>2</sub>-8-PPh-C<sub>10</sub>H<sub>6</sub>]<sup>-</sup>}<sub>∞</sub> (6)

![](_page_26_Figure_0.jpeg)

Figure S24. <sup>11</sup>B{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 160.57 MHz) of {[K(THF)<sub>2</sub>]+  $[1-BCy_2-8-PPh-C_{10}H_6]^-$ } (6)

![](_page_27_Figure_0.jpeg)

Figure S25. <sup>31</sup>P{<sup>1</sup>H} NMR (THF- $d_8$ , 202.49 MHz) of {[K(THF)<sub>2</sub>]+ [1-BCy<sub>2</sub>-8-PPh- $C_{10}H_6$ ]<sup>-</sup>} $_{\infty}$  (6)

![](_page_28_Figure_0.jpeg)

![](_page_29_Figure_0.jpeg)

Figure S27. <sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 125.77 MHz) of {[Na(THF)<sub>2</sub>]+ [1-BCy<sub>2</sub>-8-P(O)Ph-C<sub>10</sub>H<sub>6</sub>]-}<sub>2</sub> (**7**)

![](_page_30_Figure_0.jpeg)

Figure S28. <sup>11</sup>B{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 160.57 MHz) of {[Na(THF)<sub>2</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-P(O)Ph-C<sub>10</sub>H<sub>6</sub>]<sup>-</sup>}<sub>2</sub> (7)

![](_page_31_Figure_0.jpeg)

Figure S29. <sup>31</sup>P{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 202.49 MHz) of {[Na(THF)<sub>2</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-P(O)Ph-C<sub>10</sub>H<sub>6</sub>]<sup>-</sup>}<sub>2</sub> (7)

![](_page_32_Figure_0.jpeg)

![](_page_33_Figure_0.jpeg)

![](_page_34_Figure_0.jpeg)

![](_page_35_Figure_0.jpeg)

Figure S33. <sup>31</sup>P{<sup>1</sup>H} NMR ( $C_6D_6$ , 202.49 MHz) of {[Na(THF)<sub>2</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-P(S)Ph- $C_{10}H_6$ ]<sup>-</sup>}<sub>2</sub> (**8**)

![](_page_36_Figure_0.jpeg)

Figure S34. <sup>1</sup>H NMR (THF-d<sub>8</sub>, 500.13 MHz) of {[Na(THF)<sub>2</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-P(Se)Ph-C<sub>10</sub>H<sub>6</sub>]<sup>-</sup>}<sub>2</sub> (**9**)

![](_page_37_Figure_0.jpeg)

Figure S35.  ${}^{13}C{}^{1}H$  NMR (THF-d<sub>8</sub>, 125.77 MHz) of {[Na(THF)<sub>2</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-P(Se)Ph-C<sub>10</sub>H<sub>6</sub>]<sup>-</sup>}<sub>2</sub> (9)

![](_page_38_Figure_0.jpeg)

S39

![](_page_39_Figure_0.jpeg)

Figure S37. <sup>31</sup>P{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 202.49 MHz) of {[Na(THF)<sub>2</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-P(Se)Ph-C<sub>10</sub>H<sub>6</sub>]<sup>-</sup>}<sub>2</sub> (**9**)

![](_page_40_Figure_0.jpeg)

Figure S38. <sup>1</sup>H NMR (THF-d<sub>8</sub>, 500.13 MHz) of {[Na(THF)<sub>2</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-P{CH=C(O)C(Me)O}Ph-C<sub>10</sub>H<sub>6</sub>]<sup>-</sup>}<sub>2</sub> (**10**)

![](_page_41_Figure_0.jpeg)

Figure S39. <sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 125.77 MHz) of {[*Na*(*THF*)<sub>2</sub>]+ [1-BCy<sub>2</sub>-8-P{CH=C(O)C(Me)O}Ph-C<sub>10</sub>H<sub>6</sub>]-}<sub>2</sub> (**10**)

![](_page_42_Figure_0.jpeg)

Figure S40. <sup>11</sup>B{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 160.57 MHz) of {[Na(THF)<sub>2</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-P{CH=C(0)C(Me)O}Ph-C<sub>10</sub>H<sub>6</sub>]<sup>-</sup>}<sub>2</sub> (**10**)

![](_page_43_Figure_0.jpeg)

Figure S41.  ${}^{31}P{}^{1}H$  NMR (THF-d<sub>8</sub>, 202.49 MHz) of {[Na(THF)<sub>2</sub>]+ [1-BCy<sub>2</sub>-8-P{CH=C(O)C(Me)O}Ph-C<sub>10</sub>H<sub>6</sub>]-}<sub>2</sub> (10)

![](_page_44_Figure_0.jpeg)

Figure S42. <sup>1</sup>H-<sup>1</sup>H COSY NMR of  $\{[Na(THF)_2]^+ [1-BCy_2-8-P\{CH=C(O)C(Me)O\}Ph-C_{10}H_6]^-\}_2$  (10)

![](_page_45_Figure_0.jpeg)

Figure S43. <sup>1</sup>H-<sup>13</sup>C HSQC NMR of {[Na(THF)<sub>2</sub>]<sup>+</sup> [1-BCy<sub>2</sub>-8-P{CH=C(O)C(Me)O}Ph-C<sub>10</sub>H<sub>6</sub>]<sup>+</sup>}<sub>2</sub> (**10**)

![](_page_46_Figure_0.jpeg)

![](_page_47_Figure_0.jpeg)

Figure S45. <sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 125.77 MHz) of [1-BCy<sub>2</sub>-8-P{C(O)tBu}Ph-C<sub>10</sub>H<sub>6</sub>] (11)

![](_page_48_Figure_0.jpeg)

![](_page_49_Figure_0.jpeg)

Figure S47. <sup>31</sup>P{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 202.49 MHz) of [1-BCy<sub>2</sub>-8-P{C(O)tBu}Ph-C<sub>10</sub>H<sub>6</sub>] (11)

![](_page_50_Figure_0.jpeg)

Figure S48. <sup>1</sup>H NMR (THF-d<sub>8</sub>, 500.13 MHz) of [1-BCy<sub>2</sub>-8-P(SnL)Ph-C<sub>10</sub>H<sub>6</sub>] (**12**)

![](_page_51_Figure_0.jpeg)

Figure S49. <sup>13</sup>C{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 125.77 MHz) of [1-BCy<sub>2</sub>-8-P(SnL)Ph-C<sub>10</sub>H<sub>6</sub>] (12)

![](_page_52_Figure_0.jpeg)

Figure S50. <sup>11</sup>B{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 160.57 MHz) of [1-BCy<sub>2</sub>-8-P(SnL)Ph-C<sub>10</sub>H<sub>6</sub>] (**12**)

![](_page_53_Figure_0.jpeg)

![](_page_54_Figure_0.jpeg)

Figure S52. <sup>119</sup>Sn{<sup>1</sup>H} NMR (THF-d<sub>8</sub>, 186.52 MHz) of [1-BCy<sub>2</sub>-8-P(SnL)Ph-C<sub>10</sub>H<sub>6</sub>] (**12**)

![](_page_55_Figure_0.jpeg)

Figure S53. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 500.13 MHz) of [1-BCy<sub>2</sub>-8-P(PbL)Ph-C<sub>10</sub>H<sub>6</sub>] (**13**)

![](_page_56_Figure_0.jpeg)

Figure S54. <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 125.77 MHz) of [1-BCy<sub>2</sub>-8-P(PbL)Ph-C<sub>10</sub>H<sub>6</sub>] (13)

![](_page_57_Figure_0.jpeg)

Figure S55. <sup>11</sup>B{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 160.57 MHz) of [1-BCy<sub>2</sub>-8-P(PbL)Ph-C<sub>10</sub>H<sub>6</sub>] (**13**)

![](_page_58_Figure_0.jpeg)

S59

![](_page_59_Figure_0.jpeg)

Figure S57. <sup>209</sup>Pb{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 104.64 MHz) of [1-BCy<sub>2</sub>-8-P(PbL)Ph-C<sub>10</sub>H<sub>6</sub>] (**13**)

![](_page_60_Figure_0.jpeg)

S61

![](_page_61_Figure_0.jpeg)

j.10 5.05 5.00 4.95 4.90 4.85 4.80 4.75 4.70 4.65 4.60 4.55 4.50 4.45 4.40 4.35 4.30 4.25 4.20 4.15 4.10 4.05 4.00 3.95 3.90 3.85 f1 (ppm)

Figure S59. <sup>1</sup>H NMR spectrum of  $H_2$  in THF/C<sub>6</sub>D<sub>6</sub>

![](_page_62_Figure_0.jpeg)

Figure S60. Expended part of the <sup>1</sup>H NMR spectrum of the reaction mixture of 5 and 2,3-butanedione in THF/C<sub>6</sub>D<sub>6</sub>.

Compound	3	<b>4</b> ⋅(C <sub>4</sub> H <sub>8</sub> O)	5	6	7	9	10·2(C <sub>4</sub> H <sub>8</sub> O)	11	12·0.5(C <sub>7</sub> H <sub>8</sub> )
Empirical formula	C44H56B2P2	C56H66B2P2 ·(C4H8O)	C40H57BNaO3P	C36H49BKO2P	C72H98B2Na2O6P2	C72H98B2Na2O4Se2P2	C <sub>80</sub> H <sub>106</sub> B <sub>2</sub> Na <sub>2</sub> O <sub>8</sub> P <sub>2</sub> , 2(C <sub>4</sub> H <sub>8</sub> O)	C33H42BOP	C <sub>40</sub> H <sub>52</sub> BNP Sn, 0.5(C <sub>7</sub> H <sub>8</sub> )
Crystal system	Triclinic	Triclinic	orthorhombic	monoclinic	monoclinic	Triclinic	Triclinic	orthorhombic	monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	Pna21	$P2_1/n$	P21/n	<i>P</i> -1	<i>P</i> -1	P-b-c-a	<i>P</i> 2 <sub>1</sub> /n
a (Å)	11.682(3)	12.7391(4)	18.0350(18)	11.7259(5)	12.4520 (5)	10.3398(6)	11.2912(16)	12.4512(11)	10.6741(4)
b (Å)	13.1359(19	13.6807(5)	10.8962(10)	13.9936(5)	21.9900 (7)	11.6405(7)	12.339(2)	18.8303(14)	23.3192(9)
c (Å)	13.467(2))	16.2189(5)	19.662(4)	20.7353(8)	12.6888 (5)	14.3578(9)	15.225(3)	24.5695(19)	15.7863(6)
α (°)	73.078(5)	65.293(2)	90	90	90	93.217(2)	79.661(5)	90	90
β (°)	79.266(9)	80.363(2)	90	104.2330(10)	106.105 (2)	93.157(2)	79.404(6)	90	100.784(2)
γ (°)	71.317(9)	77.830(2)	90	90	90	102.117(2)	88.828(5)	90	90
Ζ	2	2	4	4	2	1	1	8	4
V (Å <sup>3</sup> )	1863.1(6)	2500.14(15)	3863.9(9)	3298.0(2)	3338.1(2)	1682.99(18)	2051.1(6)	5760.6(8)	3860.0(3)
D <sub>c</sub> (g cm <sup>-3</sup> )	1.192	1.189	1.118	1.198	1.183	1.297	1.190	1.145	1.320
$\mu$ (mm <sup>-1</sup> )	0.148	0.128	0.117	0.240	0.129	1.206	0.121	0.119	0.740
Reflections measured	48821	61236	34880	97874	110937	67540	65674	25448	87950
independent (R <sub>int</sub> ) <sup>a)</sup>	41237 (0.0700)	11528 (0.1014)	8653 (0.0577)	7585 (0.0408)	7689 (0.0214)	6572 (0.0234)	9469 (0.0341)	4958 (0.0483)	8886 (0.0275)

## **Table S1:** Crystallographic data of compounds **3**, **4**·(C<sub>4</sub>H<sub>8</sub>O), **5**, **6**, **7**, 9, **10**·2(C<sub>4</sub>H<sub>8</sub>O), **11**, and **12**·0.5(C<sub>7</sub>H<sub>8</sub>)

- observed [I>2σ(I)]	6207	7125	6656	5573	6481	6315	7330	4039	7437
Parameters refined	421	578	454	370	379	405	535	328	410
R <sup>c)</sup> / wR <sup>c)</sup>	0.0706 / 0.1307	0.0651 / 0.1508	0.0649 / 0.1652	0.0547 / 0.1509	0.0493 / 0.1205	0.0830 / 0.2510	0.0589 / 0.1672	0.0715 / 0.1435	0.0305 / 0.0678

 ${}^{a}R_{\text{int}} = \sum \left| F_{o}^{2} - F_{o,\text{mean}}^{2} \right| / \Sigma F_{o}^{2}, {}^{b}GOF = \left[ \sum (w(F_{o}^{2} - F_{c}^{2})^{2}) / (N_{\text{diffrs}} - N_{\text{params}}) \right]^{\frac{1}{2}}, {}^{c}\text{Weighting scheme: } w = \left[ \sigma^{2}(F_{o}^{2}) + (w_{1}P)^{2} + w_{2}P \right]^{-1}, \text{ where } P = \left[ \max(F_{o}^{2}) + 2F_{c}^{2} \right], R(F) = \sum \left| F_{o} \right| - \left| F_{c} \right| \left| \Sigma \right| \left| F_{o} \right|, wR(F^{2}) = \left[ \sum (w(F_{o}^{2} - F_{c}^{2})^{2}) / (\Sigma w(F_{o}^{2})^{2} - F_{c}^{2})^{2} \right] / \left[ \Sigma (w(F_{o}^{2} - F_{c}^{2})^{2}) / (\Sigma w(F_{o}^{2})^{2} - F_{c}^{2})^{2} \right] \right|^{\frac{1}{2}}$