Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

***B*-substituted group 1 phosphides: Synthesis and reactivity**†

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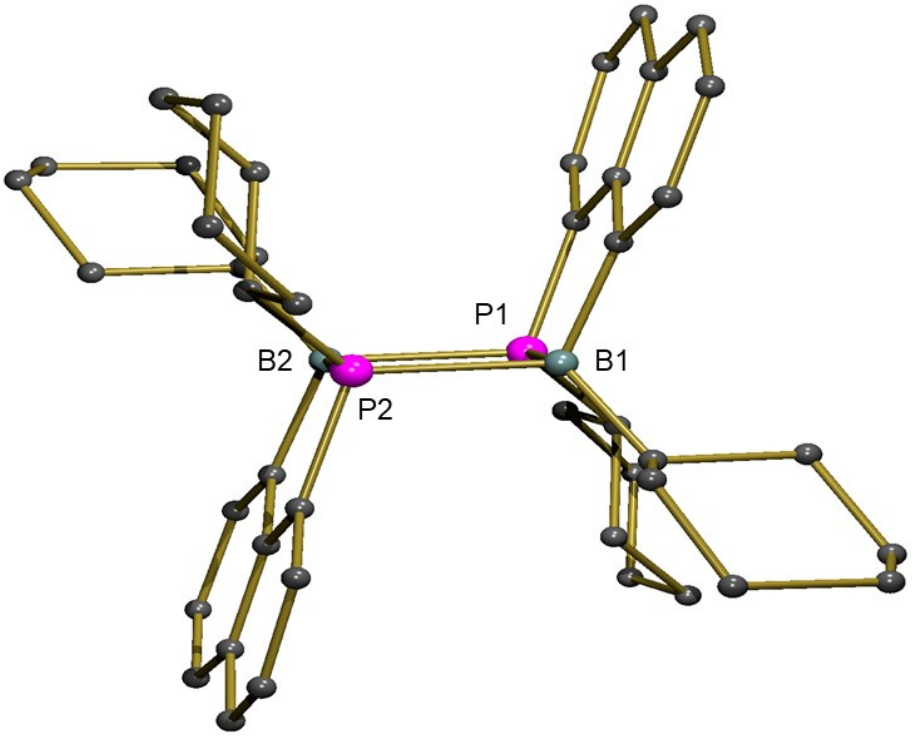

*Figure S1. PovRay presentation of molecular structure of **3**. Hydrogen atoms are omitted for clarity.*

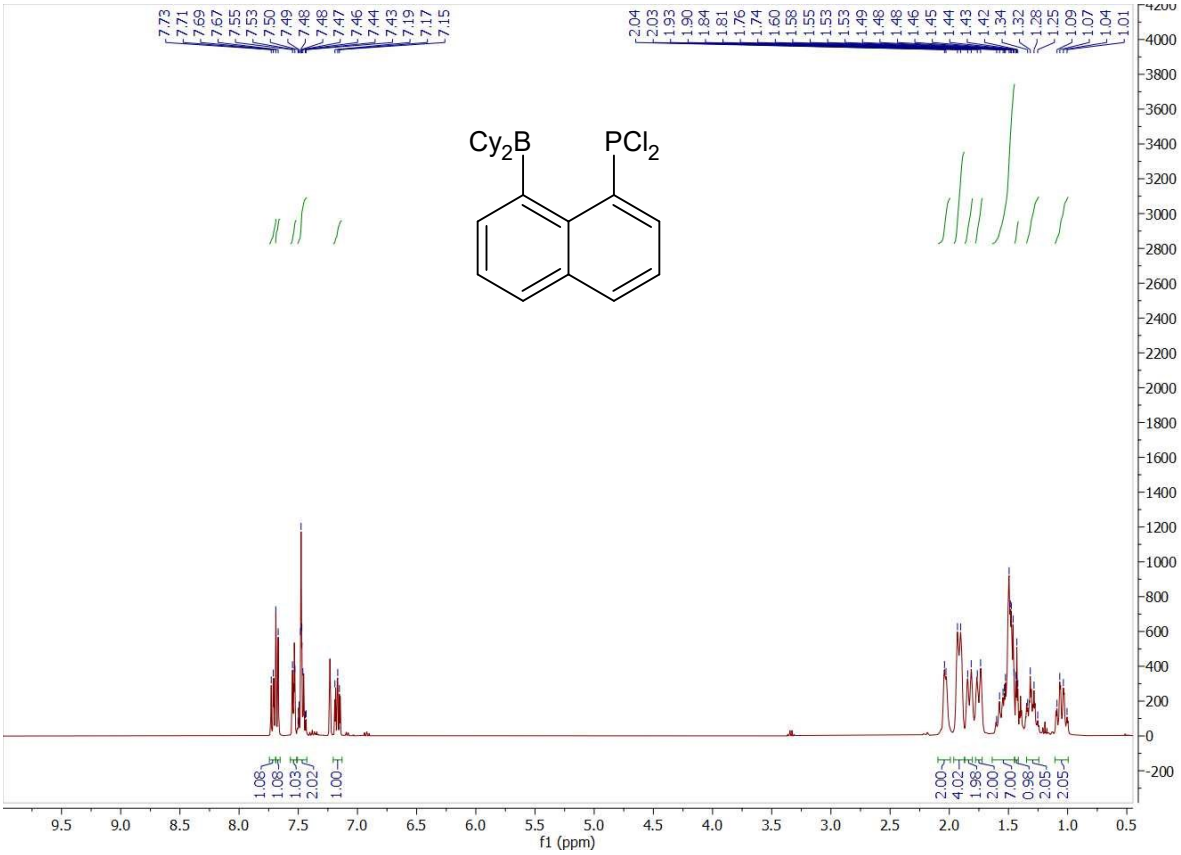

*Figure S2. ^{1}H NMR (C_6D_6, 500.13 MHz) of 1-BCy_2-8-PCl_2-$C_{10}H_6$ (**1**)*

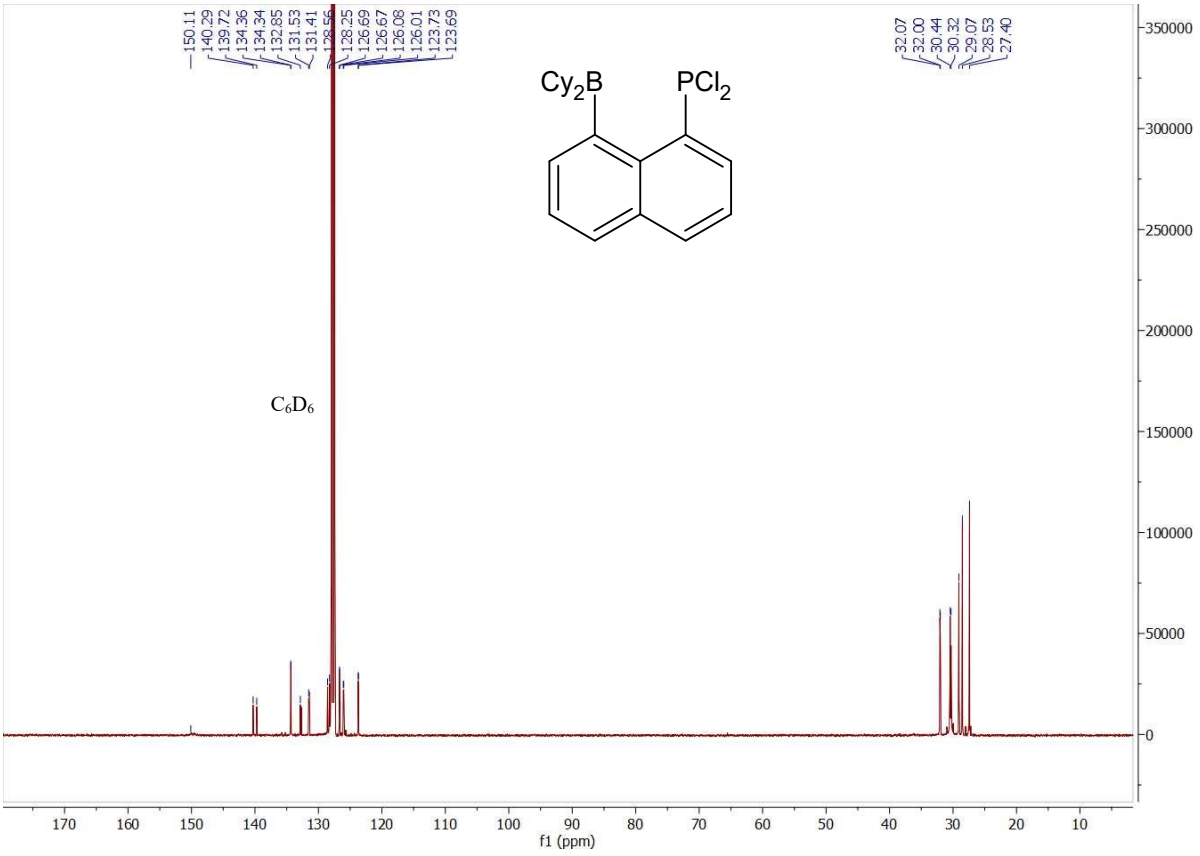

*Figure S3. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125.77 MHz) of 1-BCy_2-8-PCl_2-$C_{10}H_6$ (**1**)*

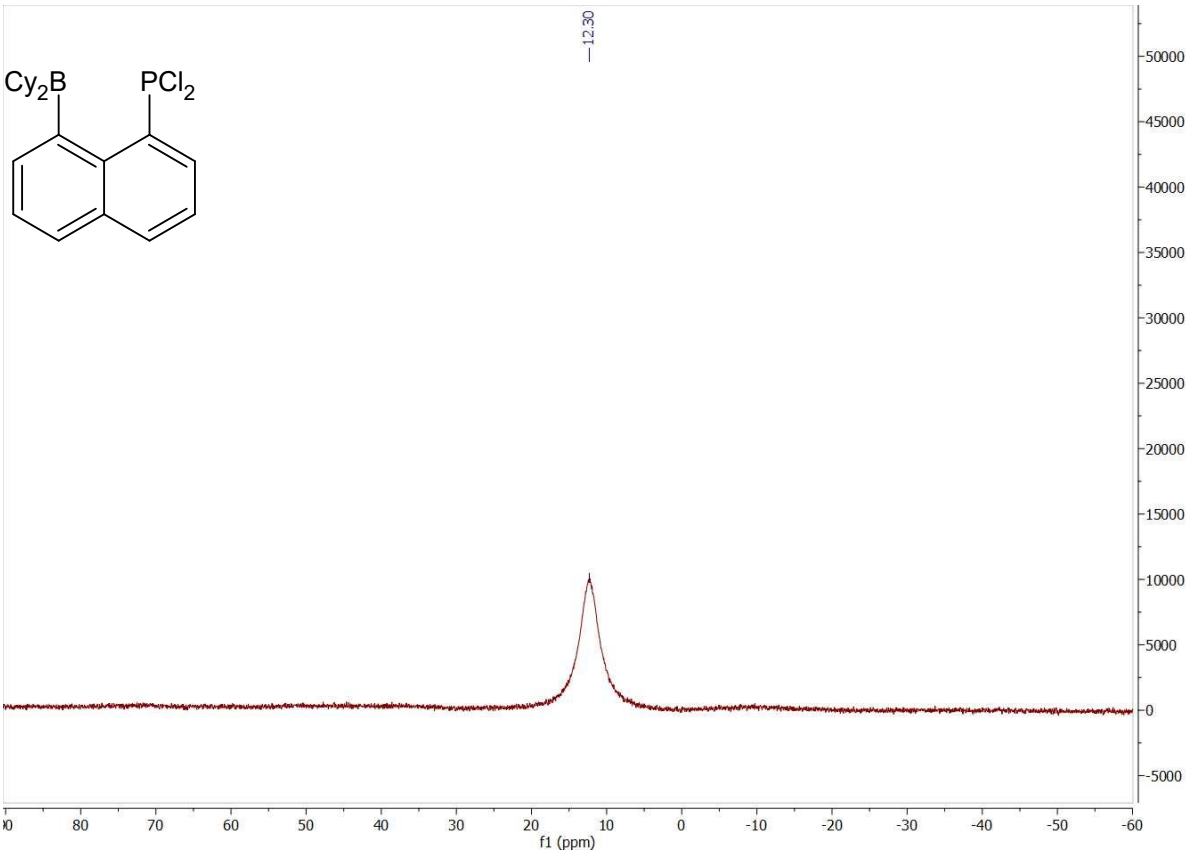

*Figure S4. $^{11}B\{^{1}H\}$ NMR (C_6D_6, 160.57 MHz) of 1-BCy_2-8-PCl_2-$C_{10}H_6$ (**1**)*

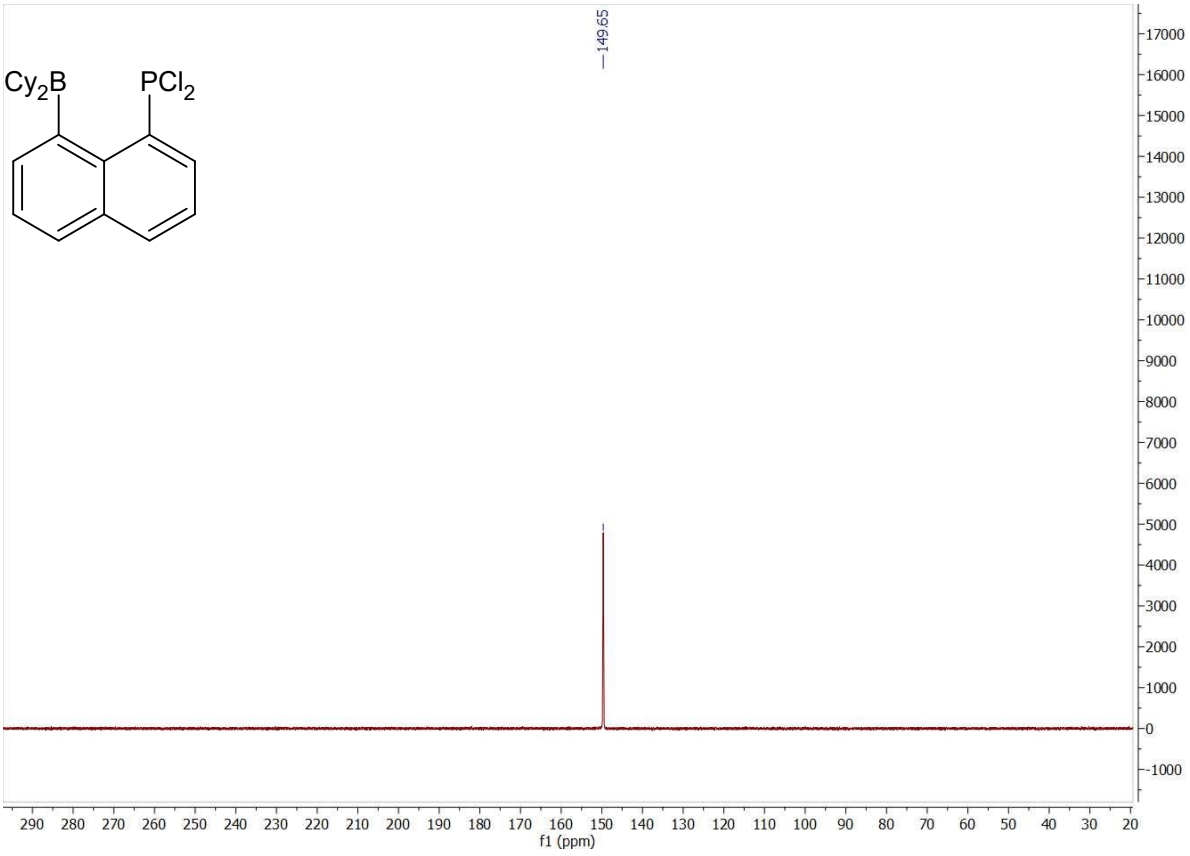

*Figure S5. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 202.49 MHz) of 1-BCy_2-8-PCl_2-$C_{10}H_6$ (**1**)*

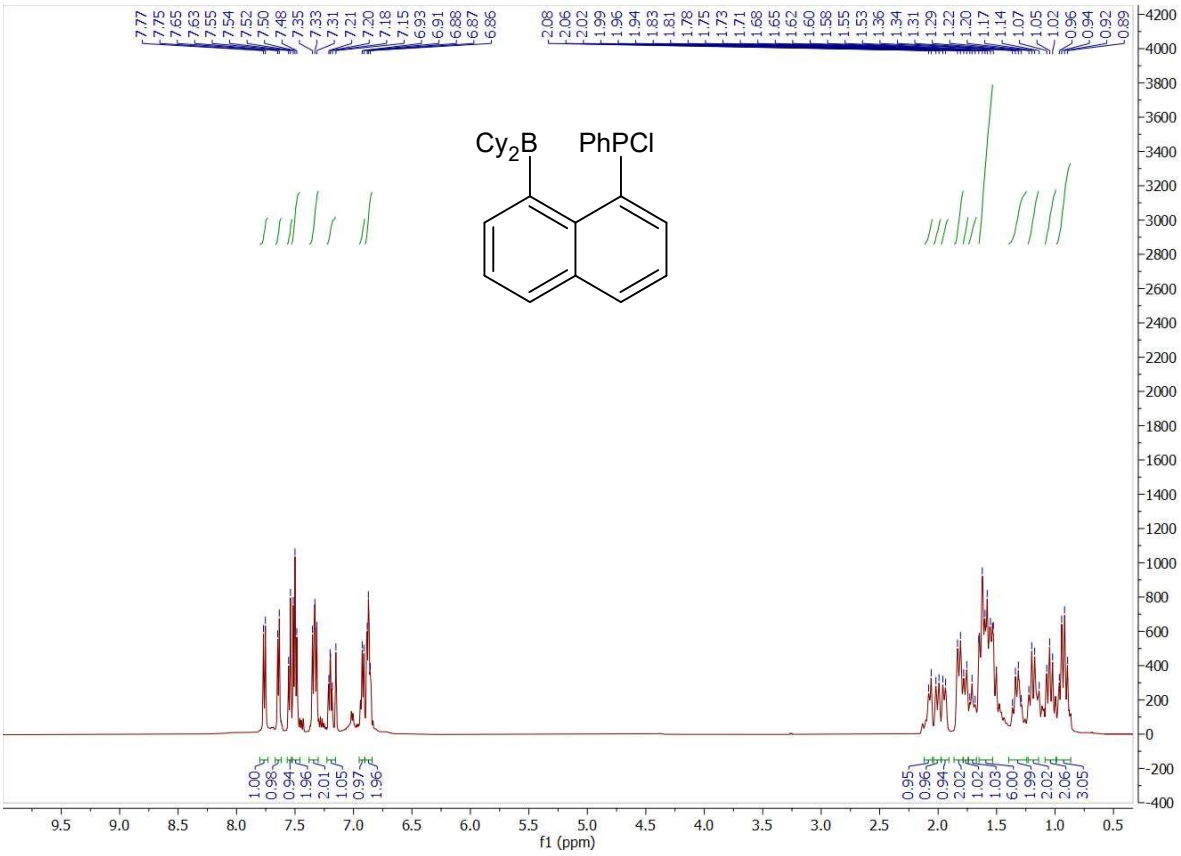

*Figure S6. ^{1}H NMR (C_6D_6, 500.13 MHz) of 1-BCy_2-8-PPhCl-$C_{10}H_6$ (**2**)*

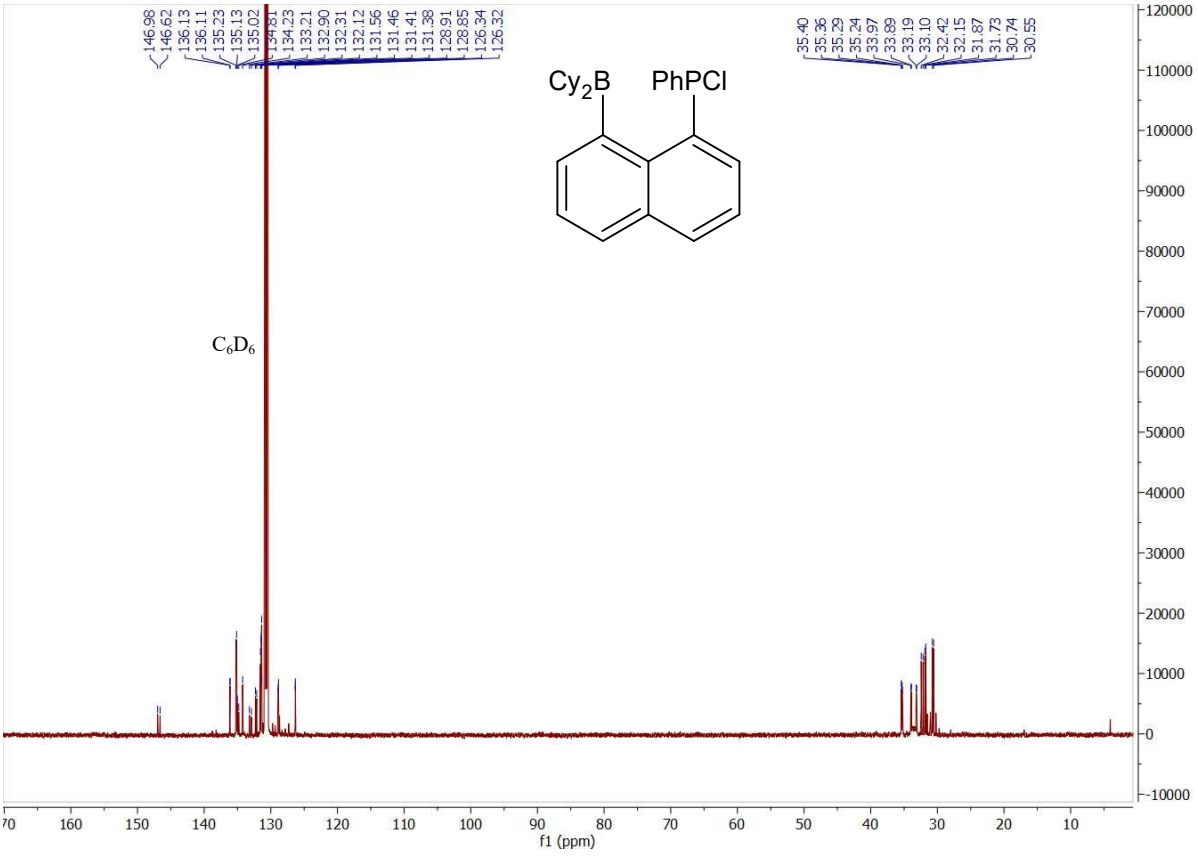

*Figure S7. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125.77 MHz) of 1-BCy_2-8-PPhCl-$C_{10}H_6$ (**2**)*

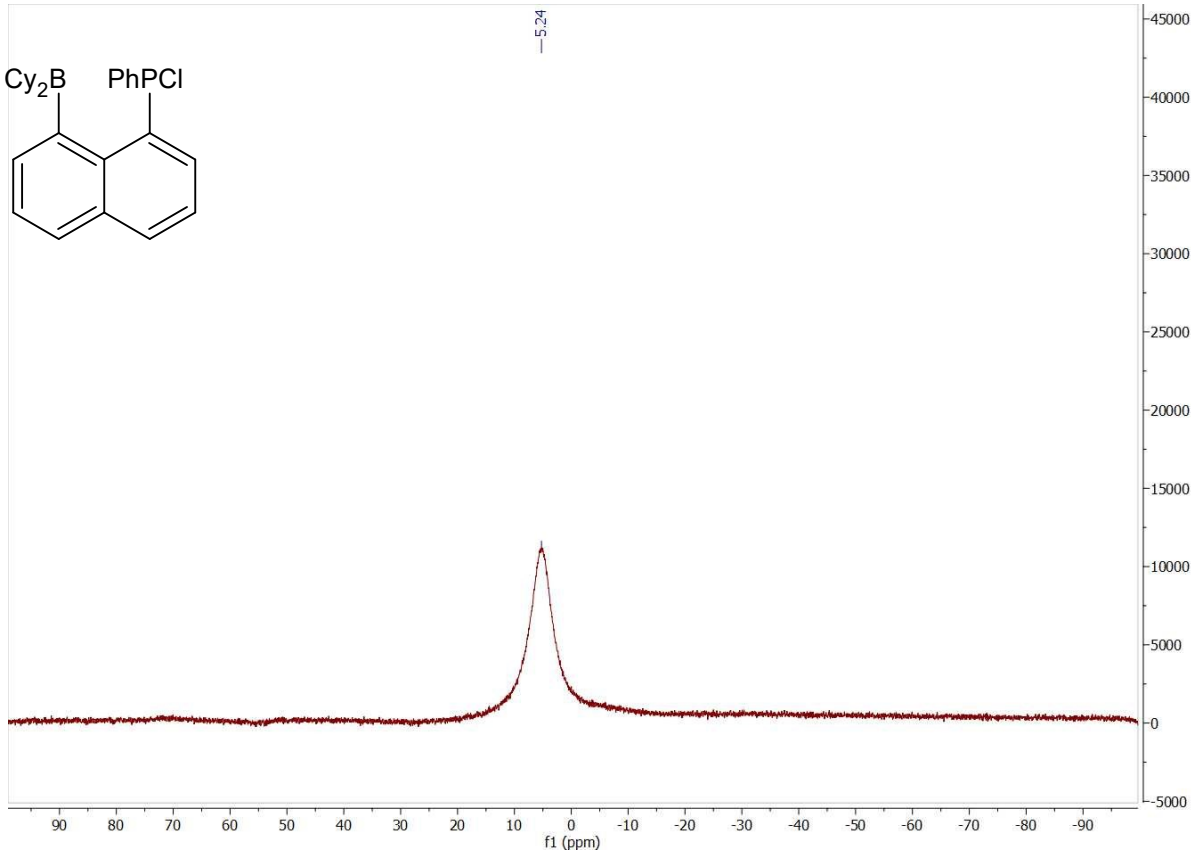

Figure S8. $^{11}B\{^{1}H\}$ NMR (C_6D_6, 160.57 MHz) of 1-BCy_2-8-PPhCl-$C_{10}H_6$ (**2**)

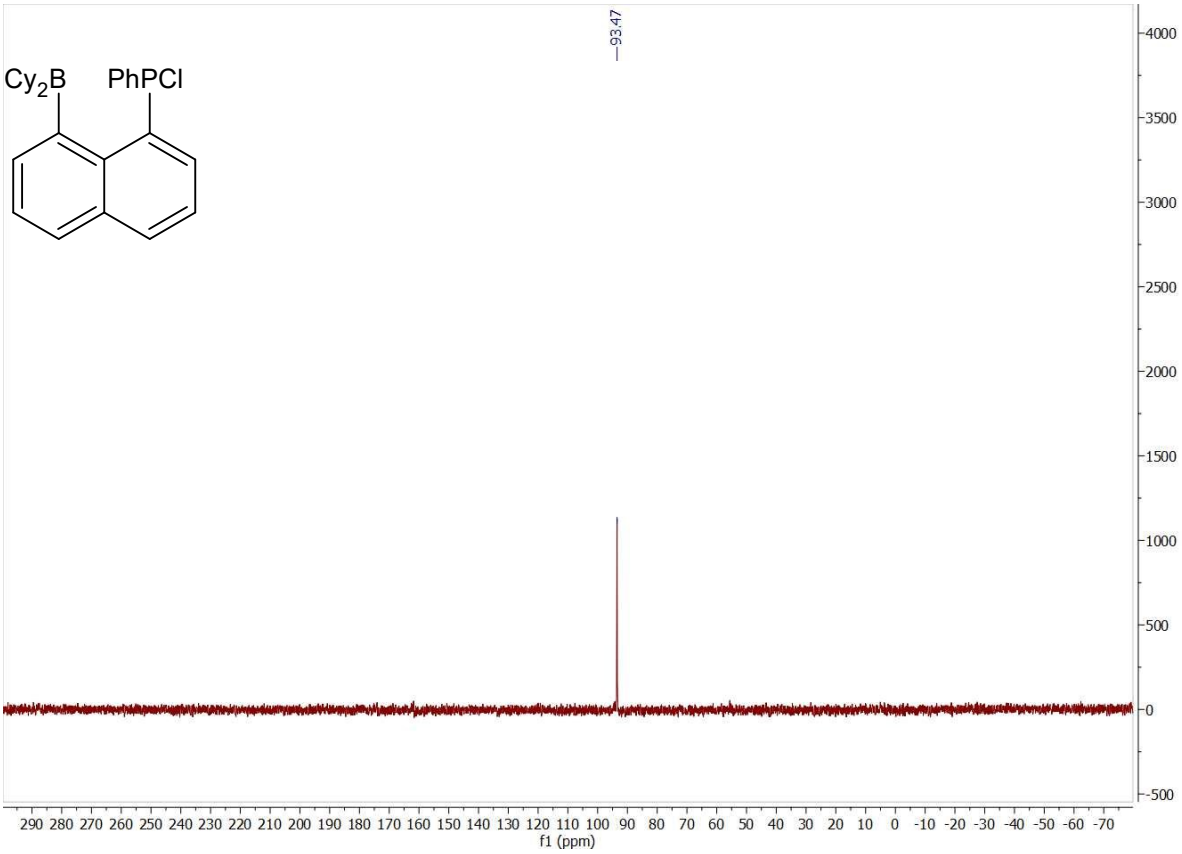

*Figure S9. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 202.49 MHz) of 1-BCy_2-8-PPhCl-$C_{10}H_6$ (**2**)*

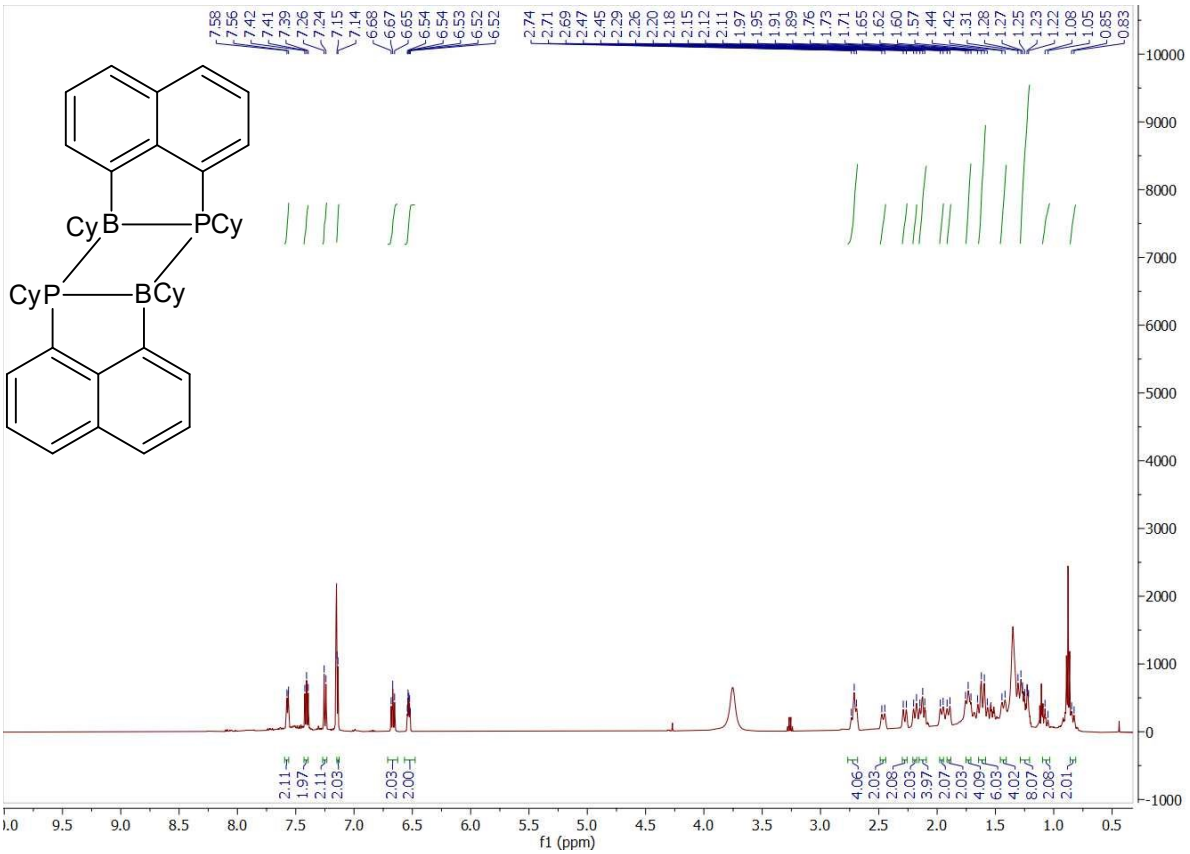

*Figure S10. ^{1}H NMR (THF-d_8, 500.13 MHz) of {1-BCy-8-PCy-$C_{10}H_6$}$_2$ (**3**)*

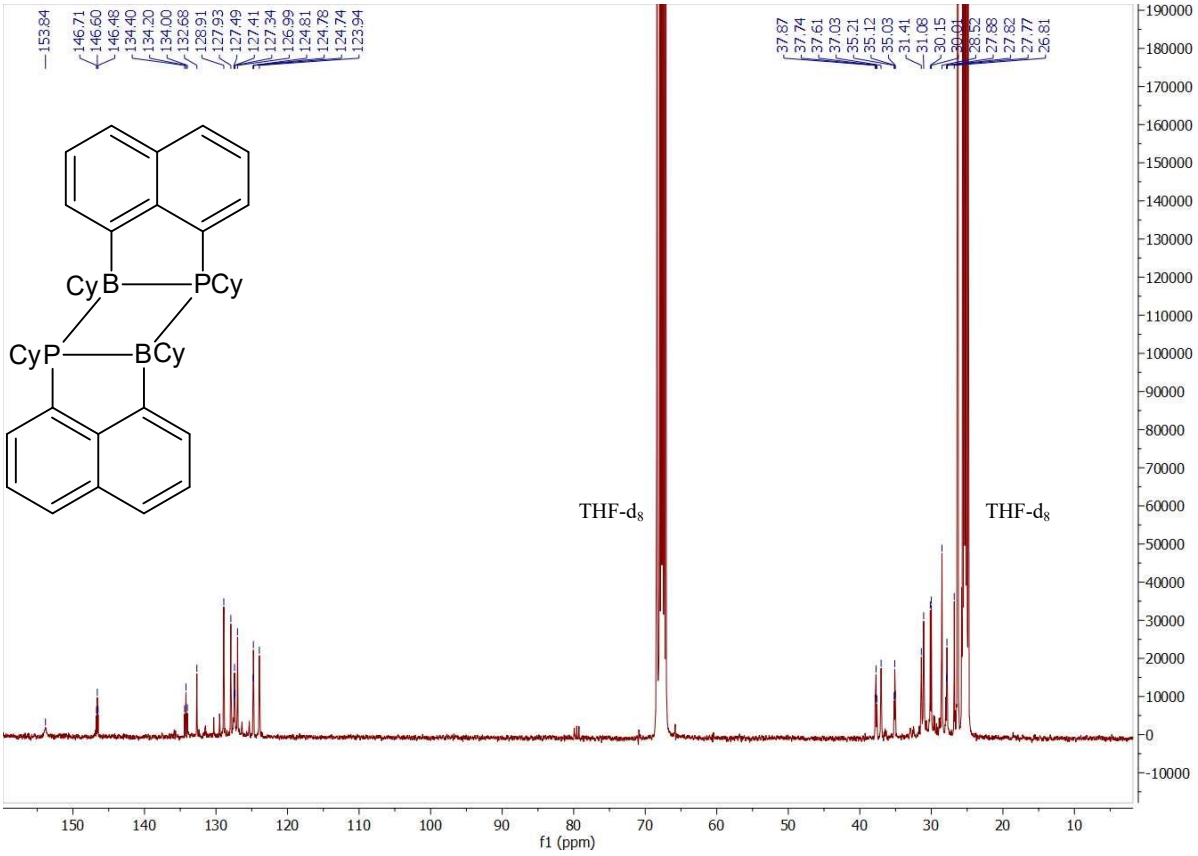

*Figure S11. $^{13}C\{^{1}H\}$ NMR (THF-d_8, 125.77 MHz) of {1-BCy-8-PCy-$C_{10}H_6$}$_2$ (**3**)*

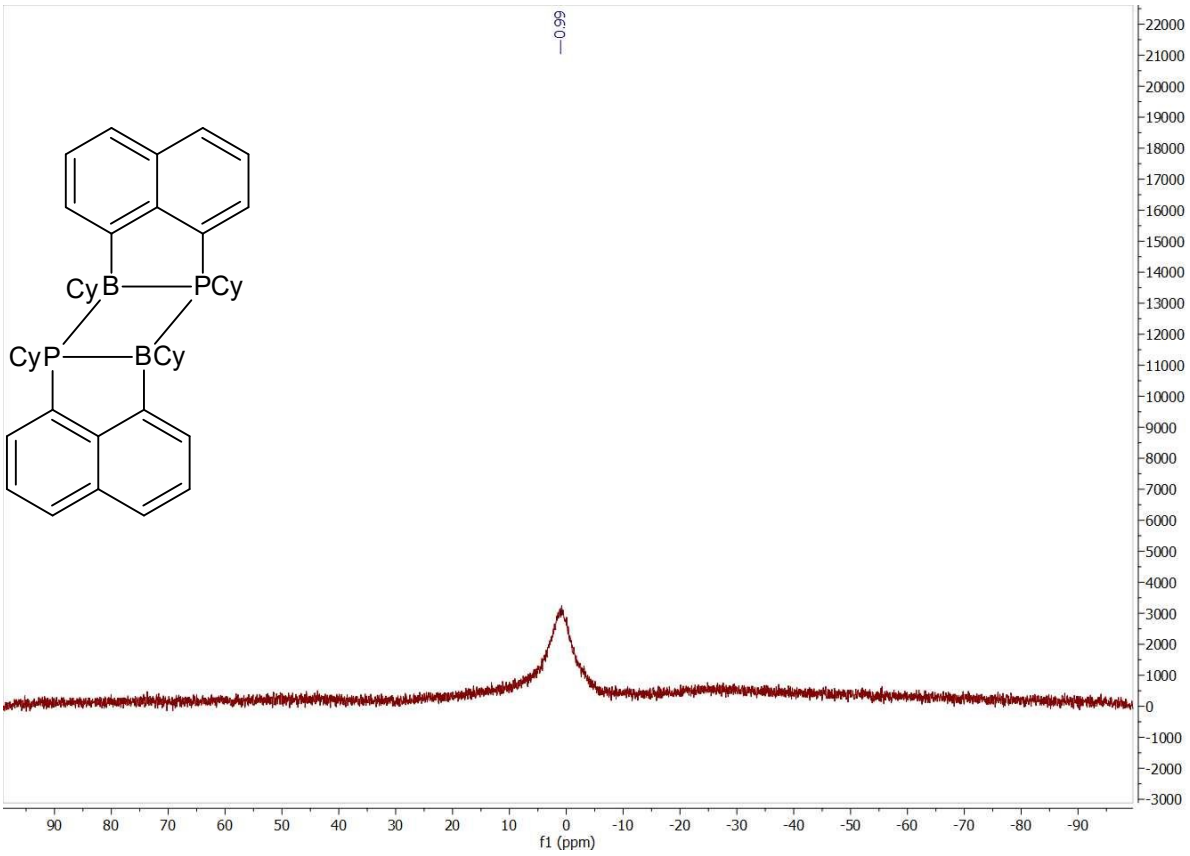

*Figure S12. $^{11}B\{^1H\}$ NMR (THF-d_8, 160.57 MHz) of {1-BCy-8-PCy-$C_{10}H_6$}$_2$ (**3**)*

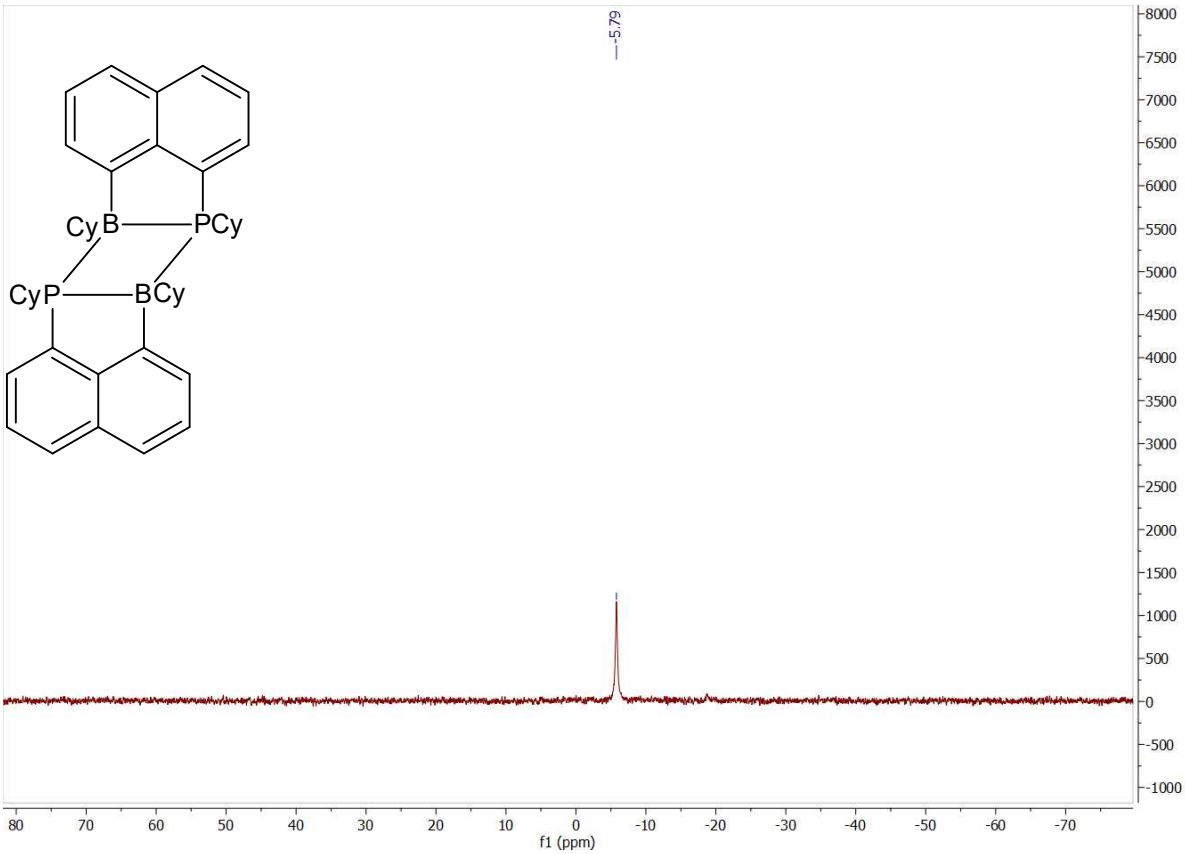

*Figure S13. $^{31}P\{^{1}H\}$ NMR (THF-d_8, 202.49 MHz) of {1-BCy-8-PCy-$C_{10}H_6$}$_2$ (**3**)*

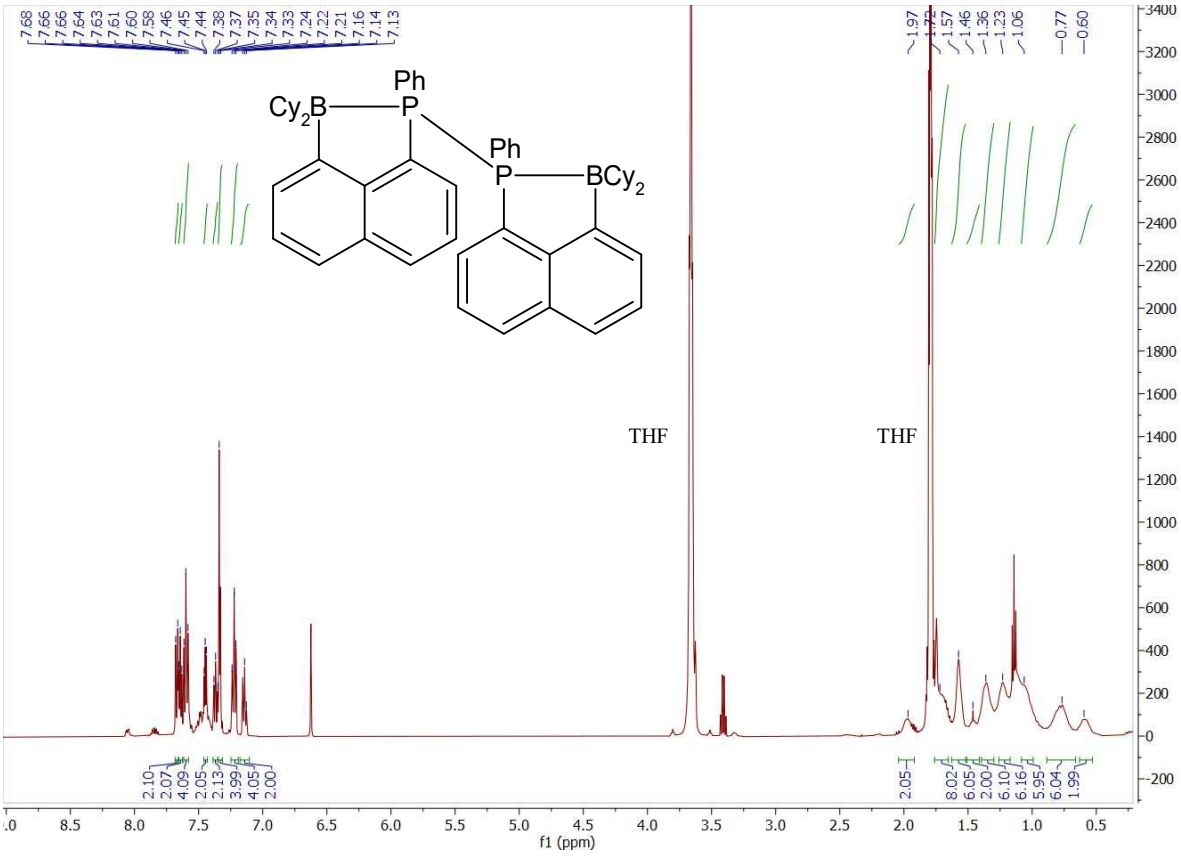

*Figure S14. ^{1}H NMR (THF-d_8, 500.13 MHz) of {1-BCy_2-8-PPh-$C_{10}H_6$}$_2$ (**4**)*

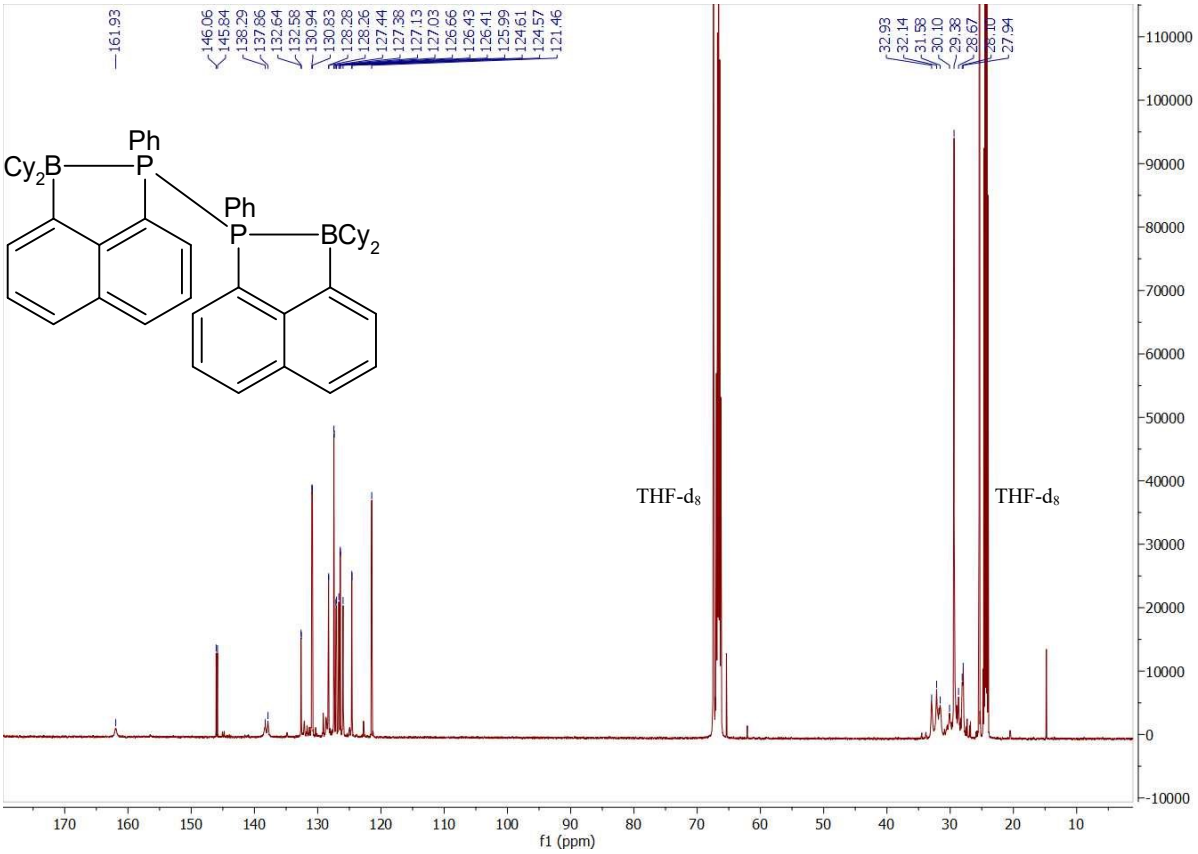

*Figure S15. $^{13}C\{^{1}H\}$ NMR (THF-d_8, 125.77 MHz) of {1-BCy_2-8-PPh-$C_{10}H_6$}$_2$ (**4**)*

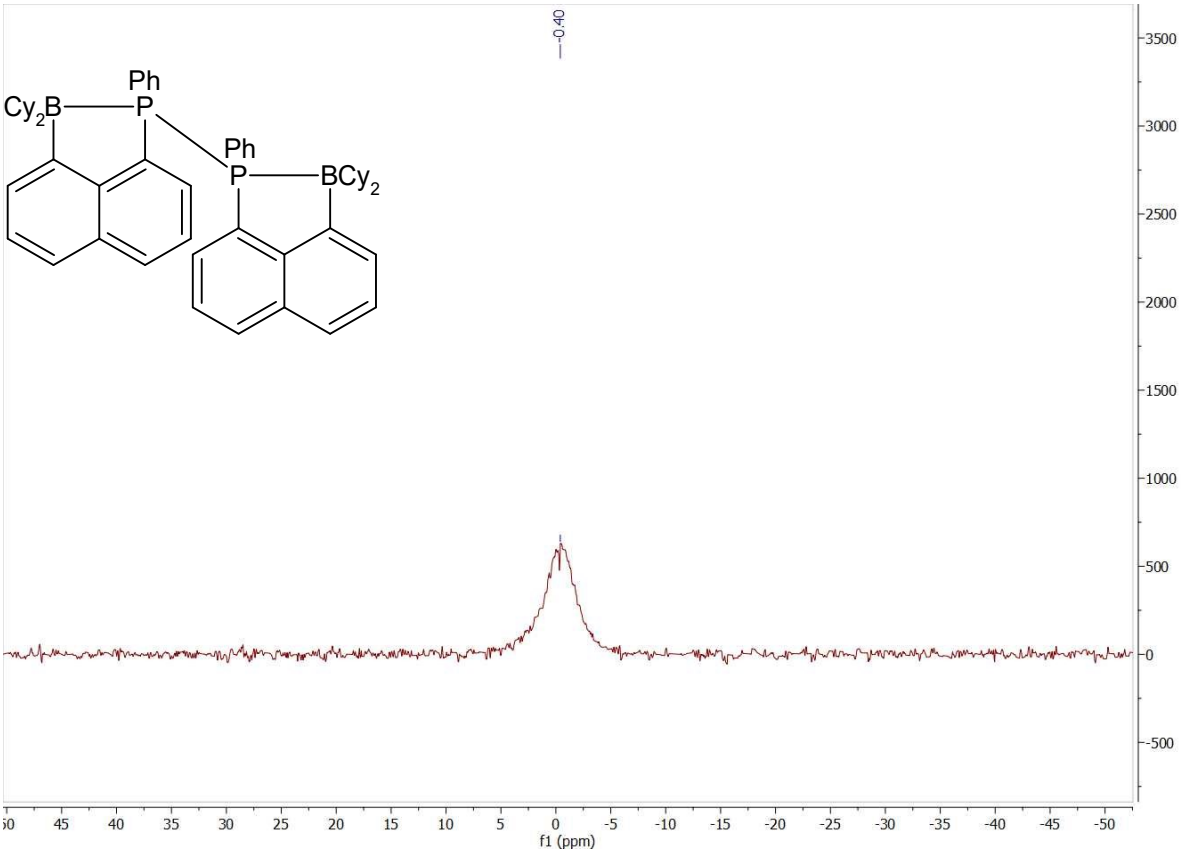

*Figure S16. $^{11}B\{^1H\}$ NMR (THF-d_8, 160.57 MHz) of {1-BCy_2-8-PPh-$C_{10}H_6$}$_2$ (**4**)*

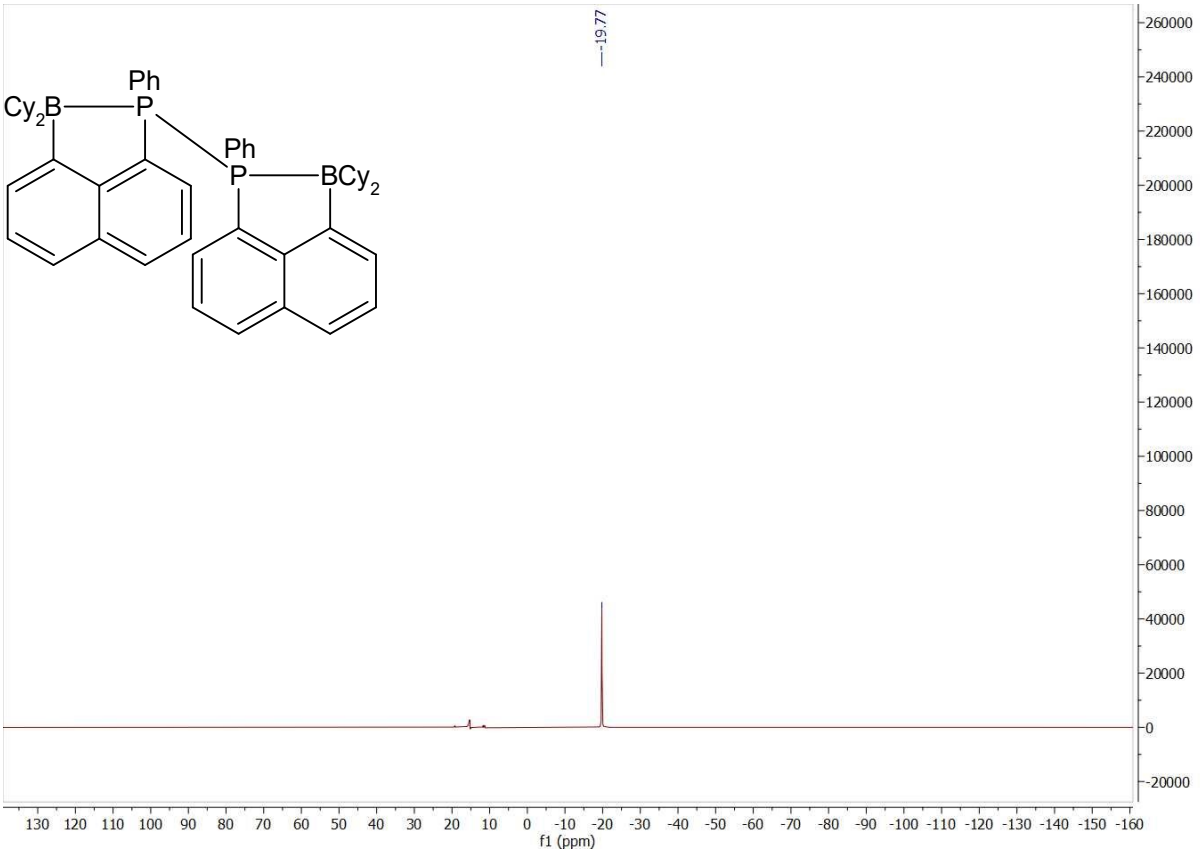

*Figure S17. $^{31}P\{^{1}H\}$NMR (THF-d_8, 202.49 MHz) of {1-BCy_2-8-PPh-$C_{10}H_6$}$_2$ (**4**)*

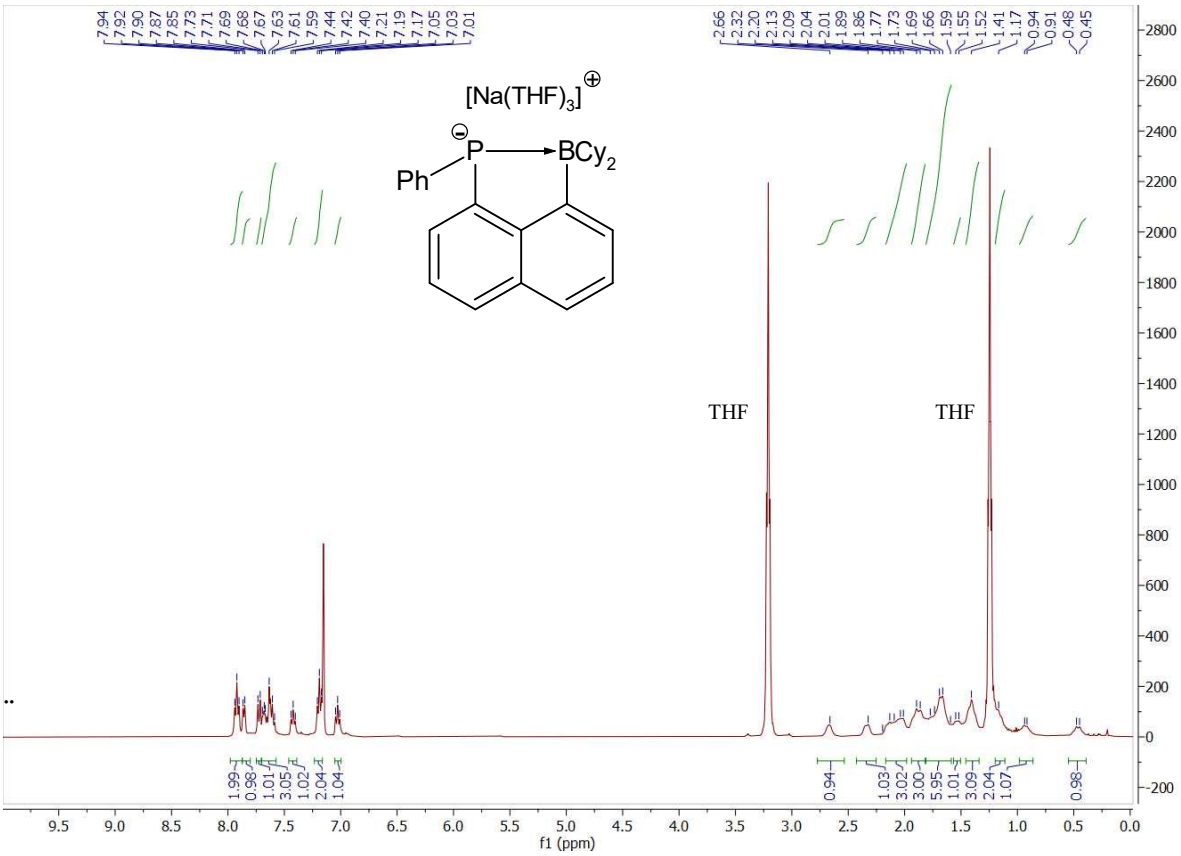

*Figure S18. ^{1}H NMR (THF-d_8, 500.13 MHz) of $[Na(THF)_3]^+$ $[1\text{-}BCy_2\text{-}8\text{-}PPh\text{-}C_{10}H_6]^-$ (**5**)*

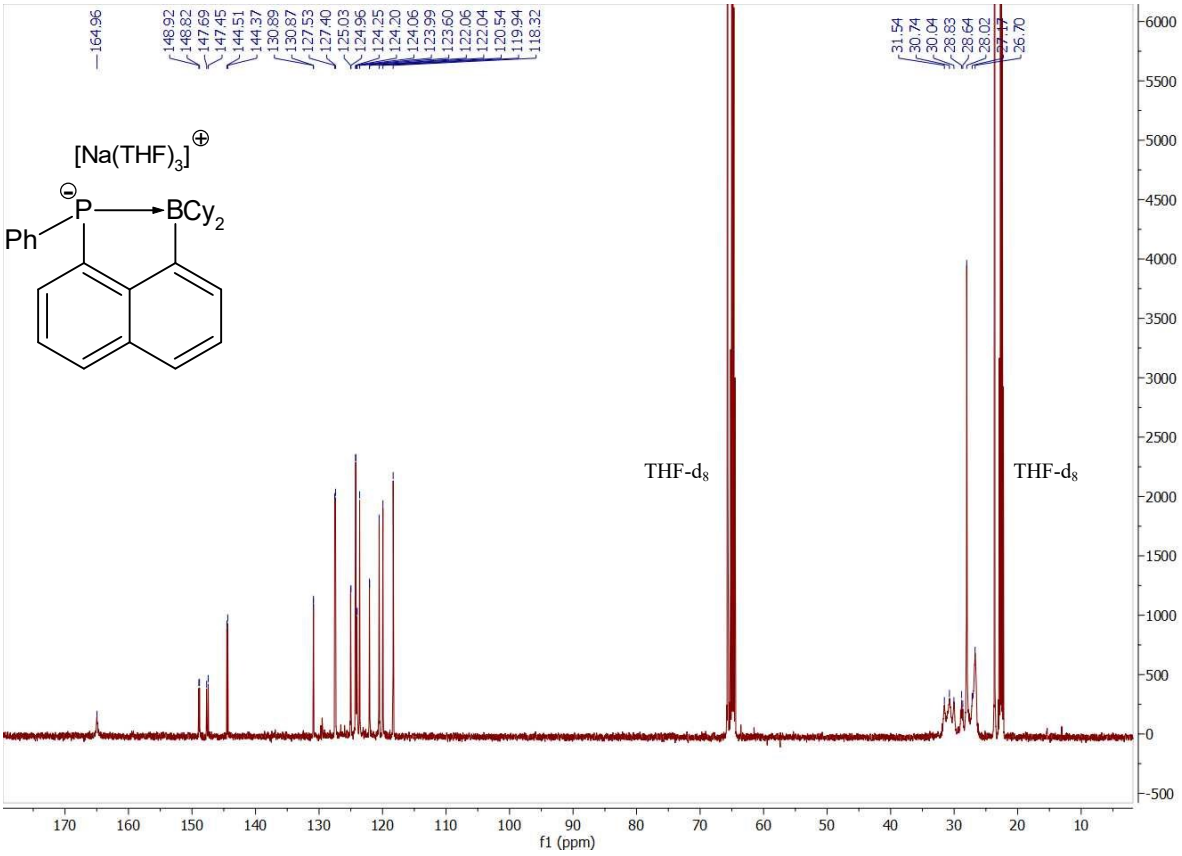

*Figure S19. $^{13}C\{^{1}H\}$ NMR (THF-d_8, 125.77 MHz) of $[Na(THF)_3]^+$ [1-BCy_2-8-PPh-$C_{10}H_6]^-$ (**5**)*

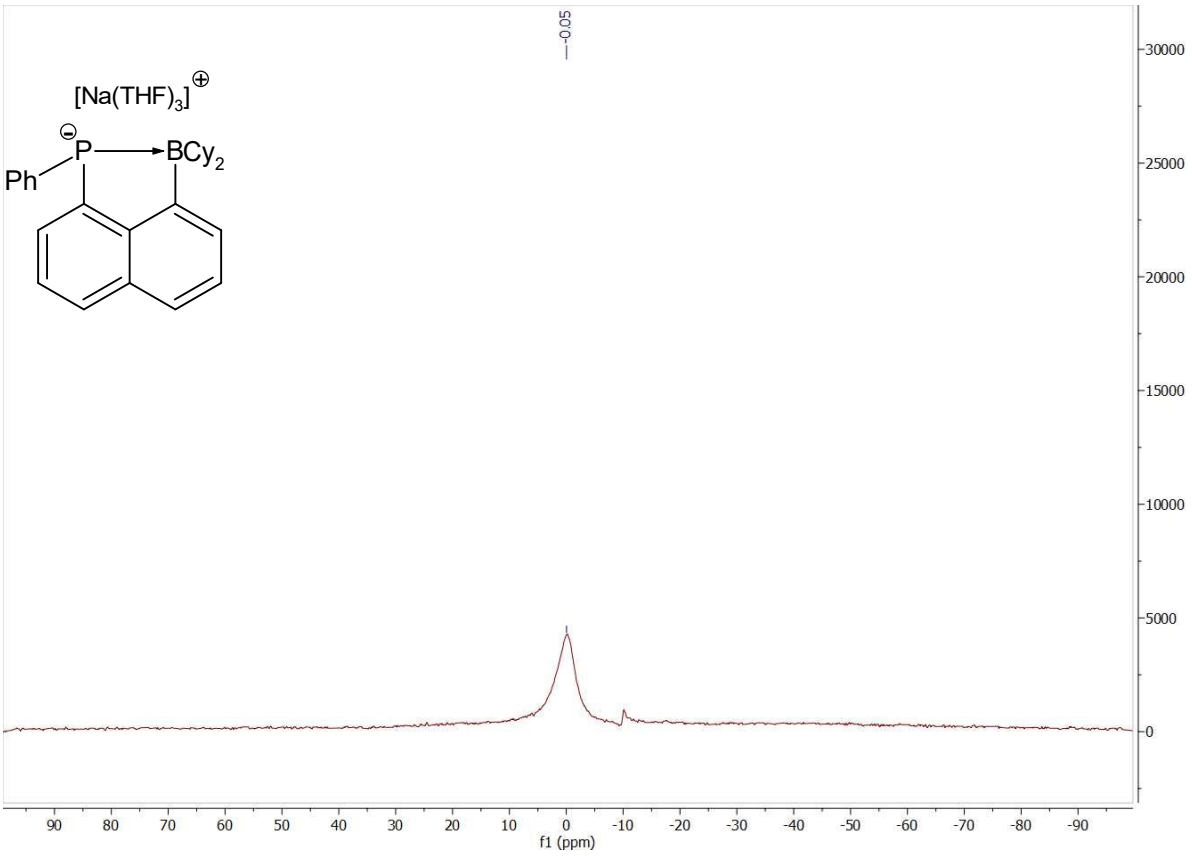

*Figure S20. $^{11}B\{^1H\}$ NMR (THF-d_8, 160.57 MHz) of $[Na(THF)_3]^+$ [1-BCy_2-8-PPh-$C_{10}H_6$]$^-$ (**5**)*

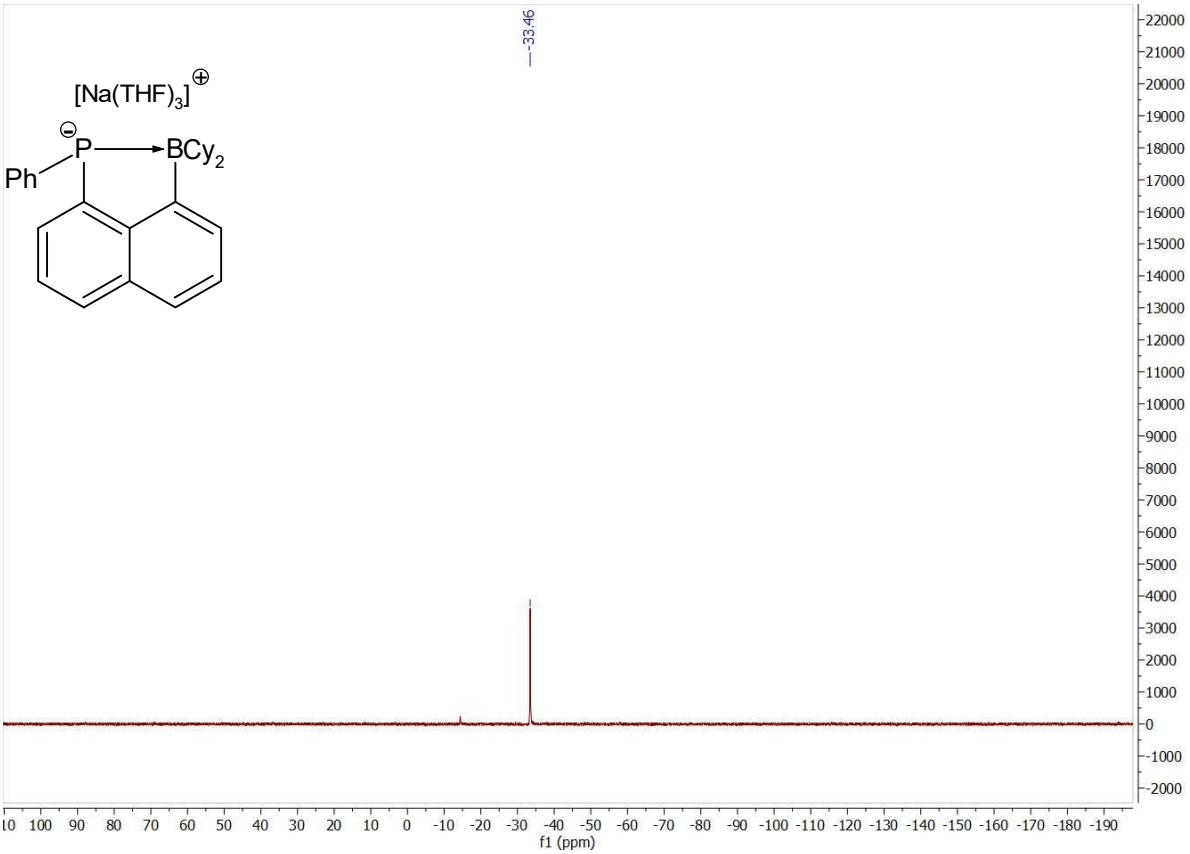

*Figure S21. $^{31}P\{^{1}H\}$ NMR (THF-d_8, 202.49 MHz) of $[Na(THF)_3]^+$ $[1\text{-}BCy_2\text{-}8\text{-}PPh\text{-}C_{10}H_6]^-$ (**5**)*

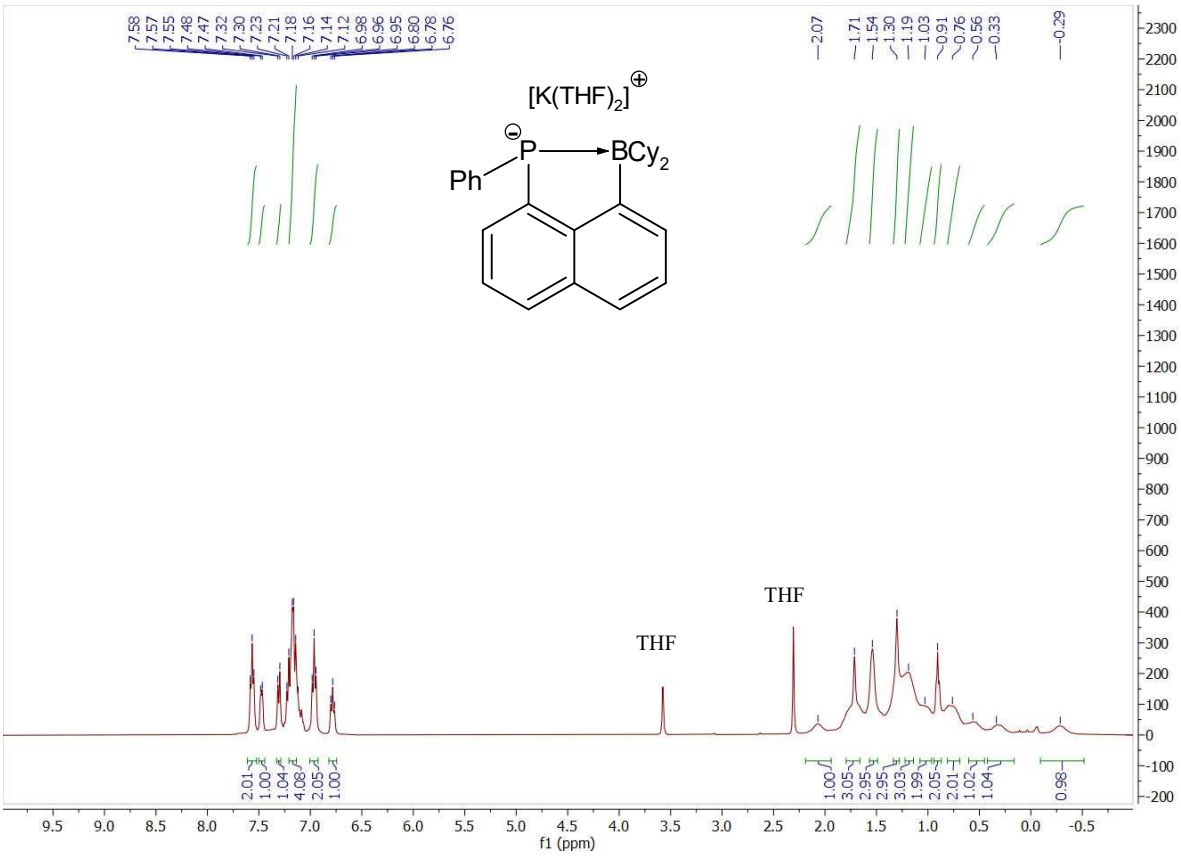

*Figure S22. ^{1}H NMR (THF-d_8, 500.13 MHz) of {[K(THF)$_2$]$^+$ [1-BCy$_2$-8-PPh-C$_{10}$H$_6$]$^-$}$_\infty$ (**6**)*

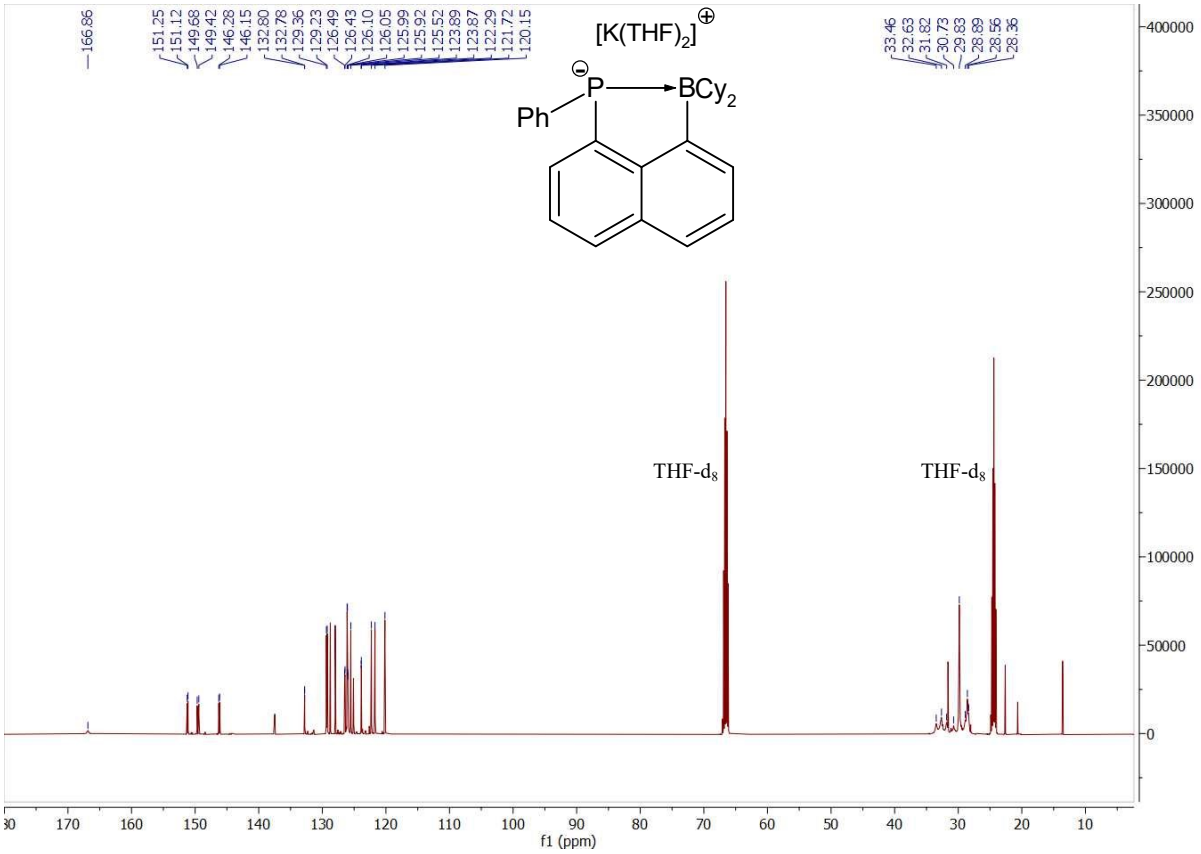

*Figure S23. $^{13}C\{^{1}H\}$ NMR (THF-d_8, 125.77 MHz) of $\{[K(THF)_2]^+ [1\text{-}BCy_2\text{-}8\text{-}PPh\text{-}C_{10}H_6]^-\}_\infty$ (**6**)*

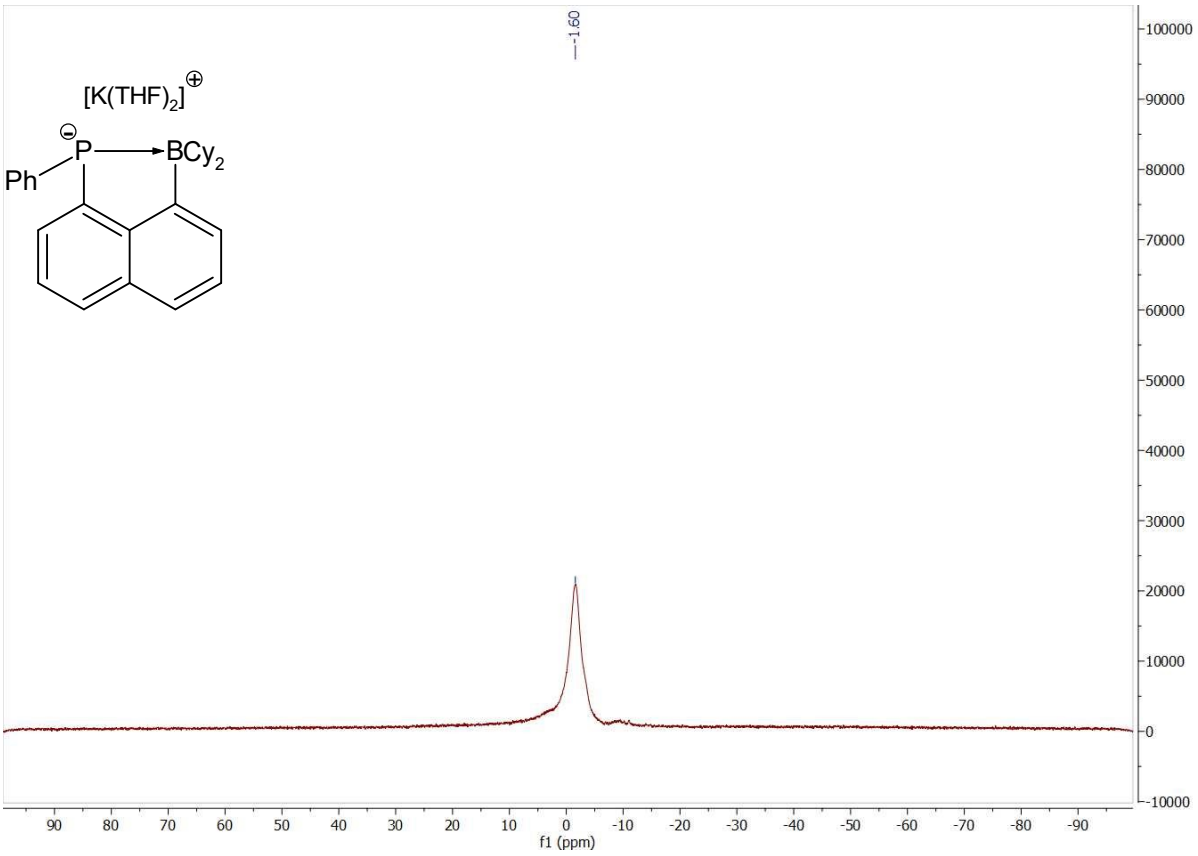

*Figure S24. $^{11}B\{^1H\}$ NMR (THF-d_8, 160.57 MHz) of $\{[K(THF)_2]^+ [1\text{-}BCy_2\text{-}8\text{-}PPh\text{-}C_{10}H_6]^-\}_\infty$ (**6**)*

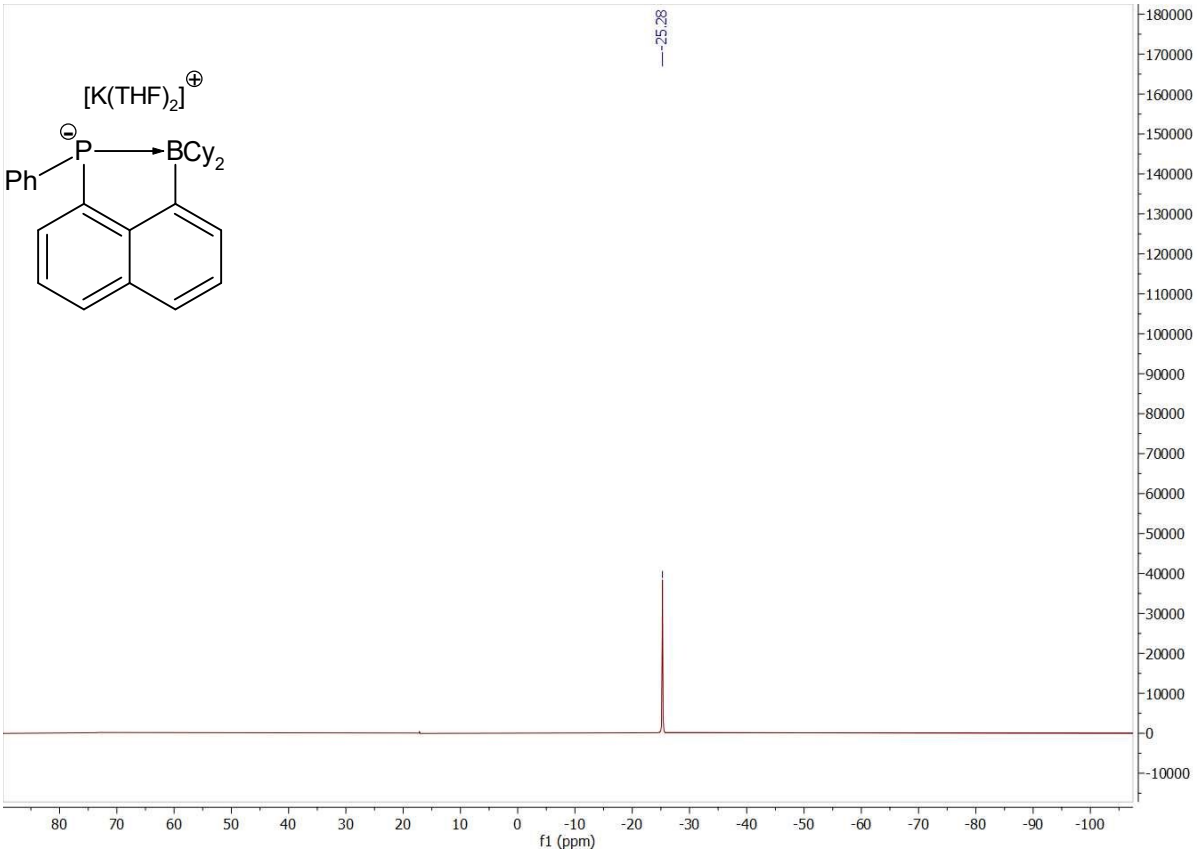

*Figure S25. $^{31}P\{^{1}H\}$ NMR (THF-d_8, 202.49 MHz) of $\{[K(THF)_2]^+ [1\text{-}BCy_2\text{-}8\text{-}PPh\text{-}C_{10}H_6]^-\}_\infty$ (**6**)*

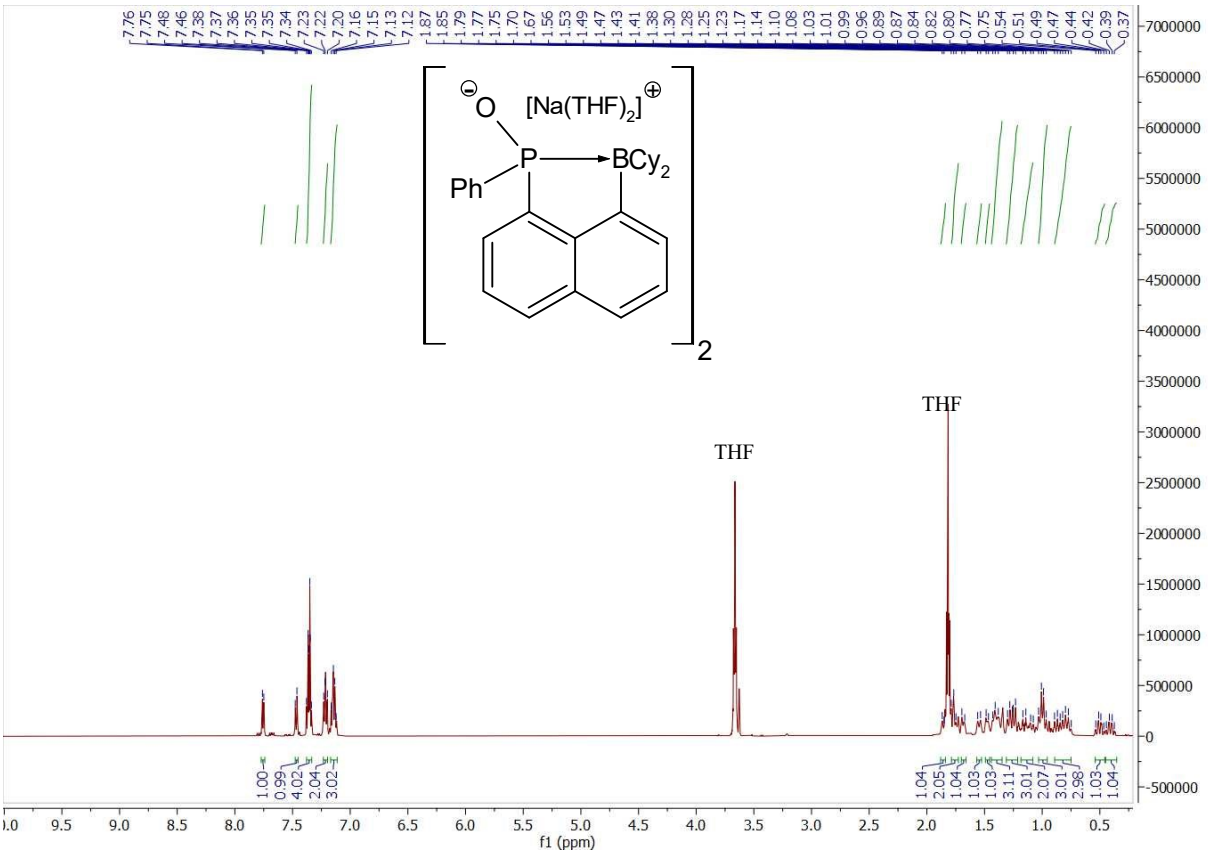

Figure S26. ^{1}H NMR (THF-d_8, 500.13 MHz) of {[Na(THF)$_2$]$^+$ [1-BCy$_2$-8-P(O)Ph-C$_{10}$H$_6$]$^-$}$_2$ (**7**)

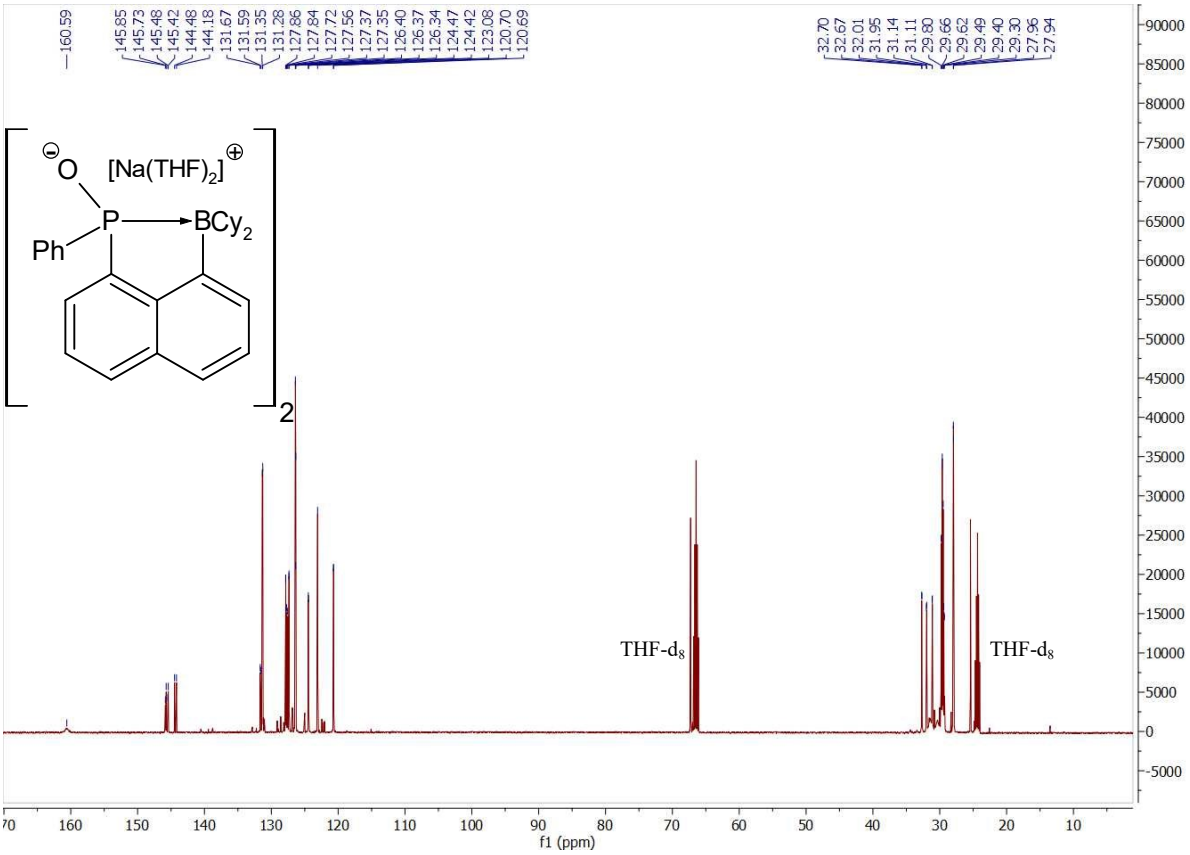

*Figure S27. $^{13}C\{^{1}H\}$ NMR (THF-d_8, 125.77 MHz) of $\{[Na(THF)_2]^+ [1\text{-}BCy_2\text{-}8\text{-}P(O)Ph\text{-}C_{10}H_6]^-\}_2$ (**7**)*

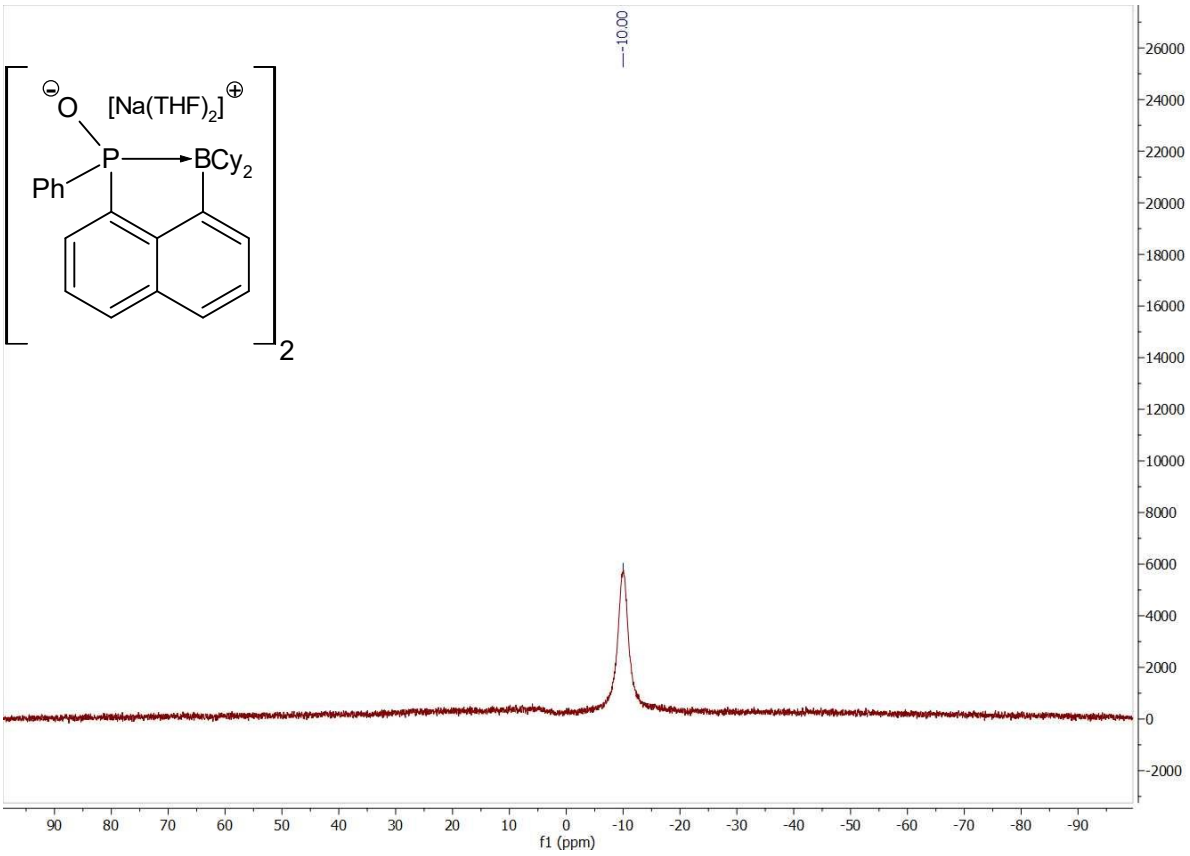

*Figure S28. $^{11}B\{^1H\}$ NMR (THF-d_8, 160.57 MHz) of $\{[Na(THF)_2]^+ [1\text{-}BCy_2\text{-}8\text{-}P(O)Ph\text{-}C_{10}H_6]^-\}_2$ (**7**)*

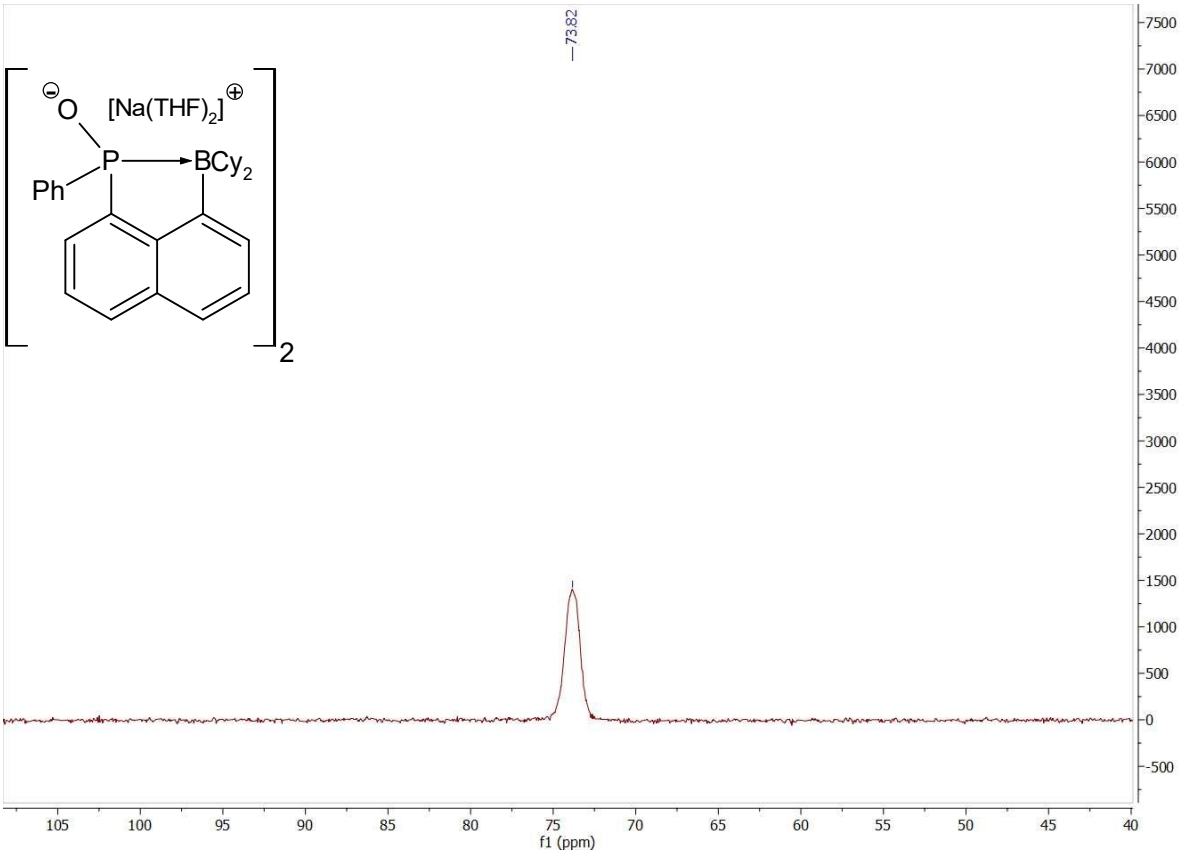

*Figure S29. $^{31}P\{^{1}H\}$ NMR (THF-d_8, 202.49 MHz) of $\{[Na(THF)_2]^+ [1\text{-}BCy_2\text{-}8\text{-}P(O)Ph\text{-}C_{10}H_6]^-\}_2$ (**7**)*

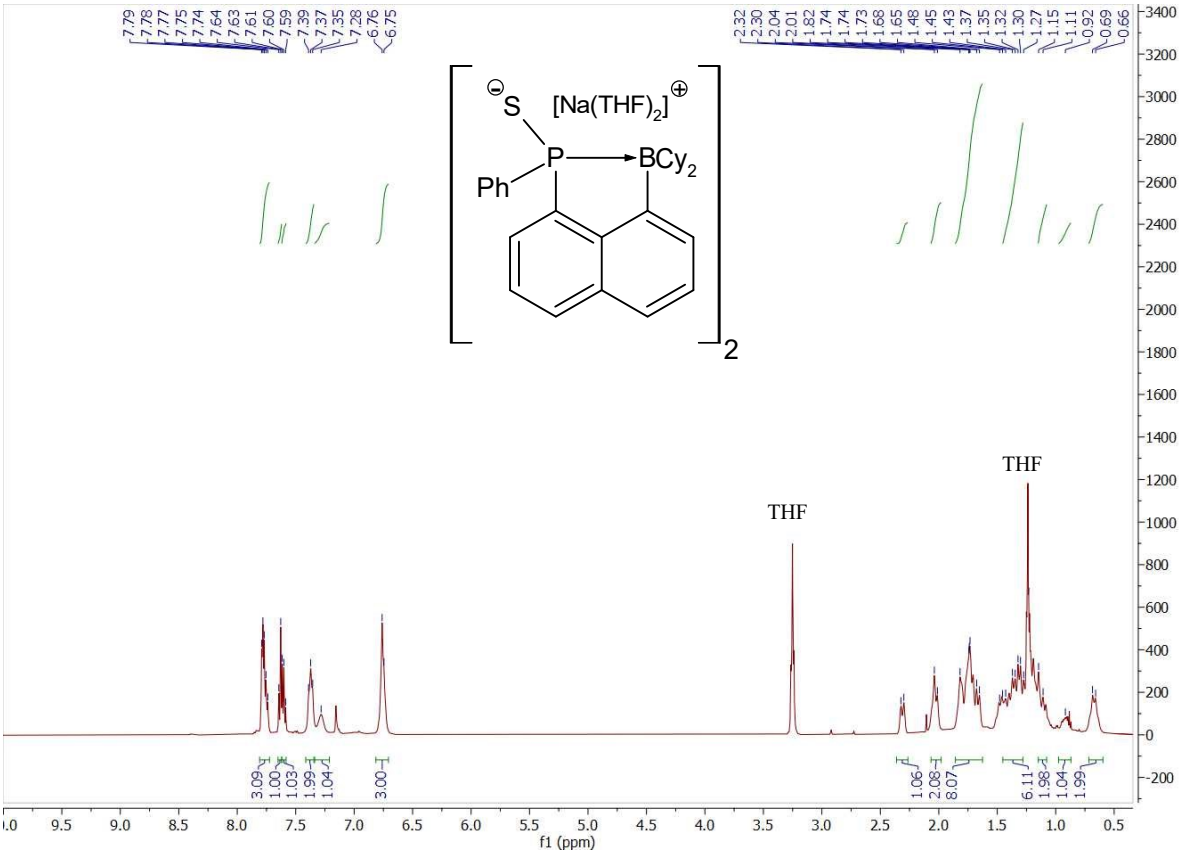

*Figure S30. ^{1}H NMR (C_6D_6, 500.13 MHz) of {[Na(THF)$_2$]$^+$ [1-BCy$_2$-8-P(S)Ph-$C_{10}H_6$]$^-$}$_2$ (**8**)*

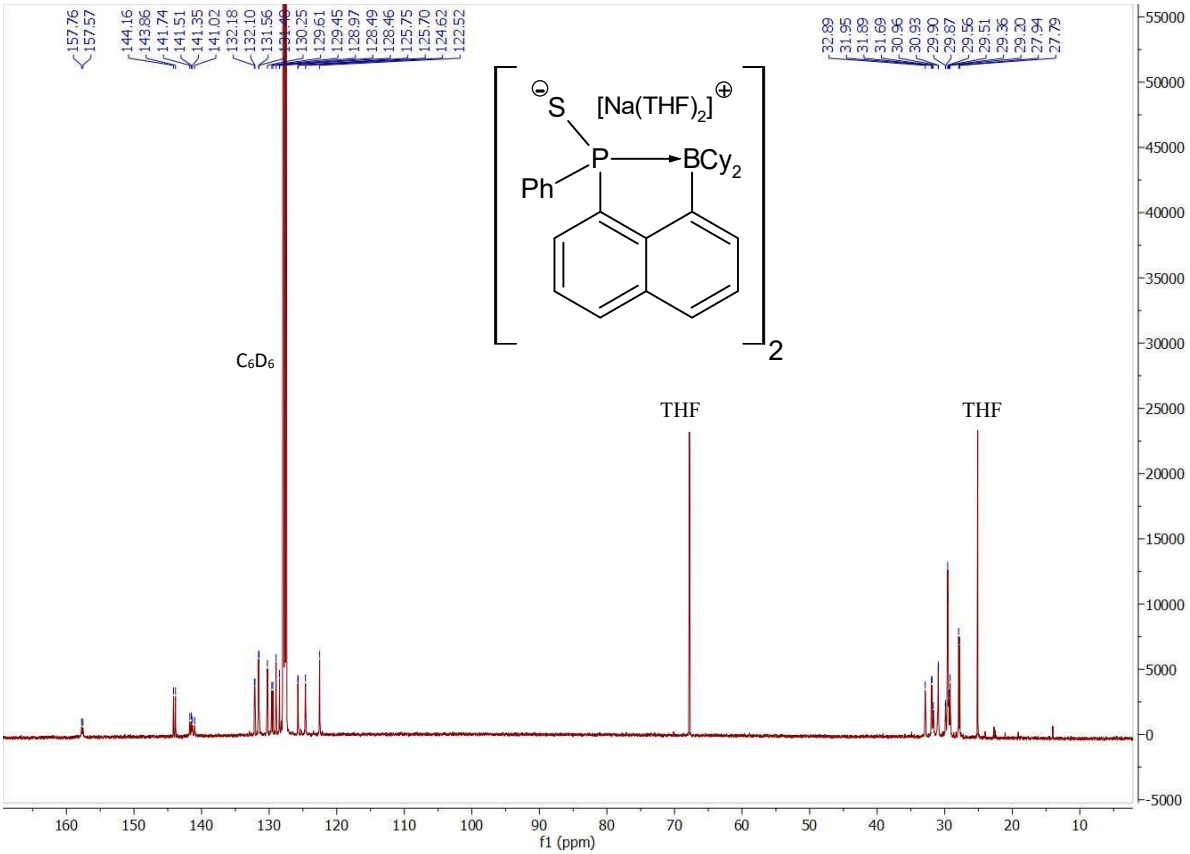

*Figure S31. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125.77 MHz) of $\{[Na(THF)_2]^+$ [1-BCy_2-8-P(S)Ph-$C_{10}H_6]^-\}_2$ (**8**)*

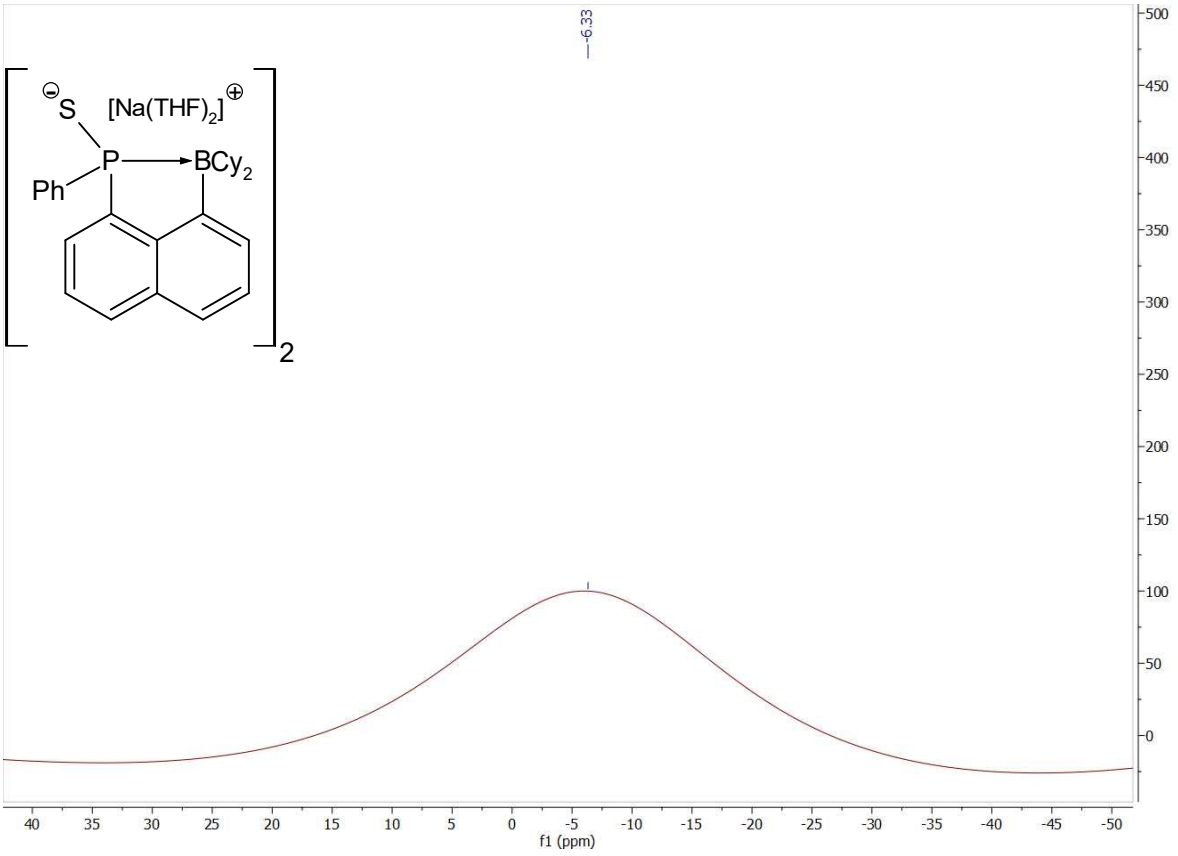

*Figure S32. $^{11}B\{^{1}H\}$ NMR (C_6D_6, 160.57 MHz) of $\{[Na(THF)_2]^+$ [1-BCy_2-8-P(S)Ph-$C_{10}H_6]^-\}_2$ (**8**)*

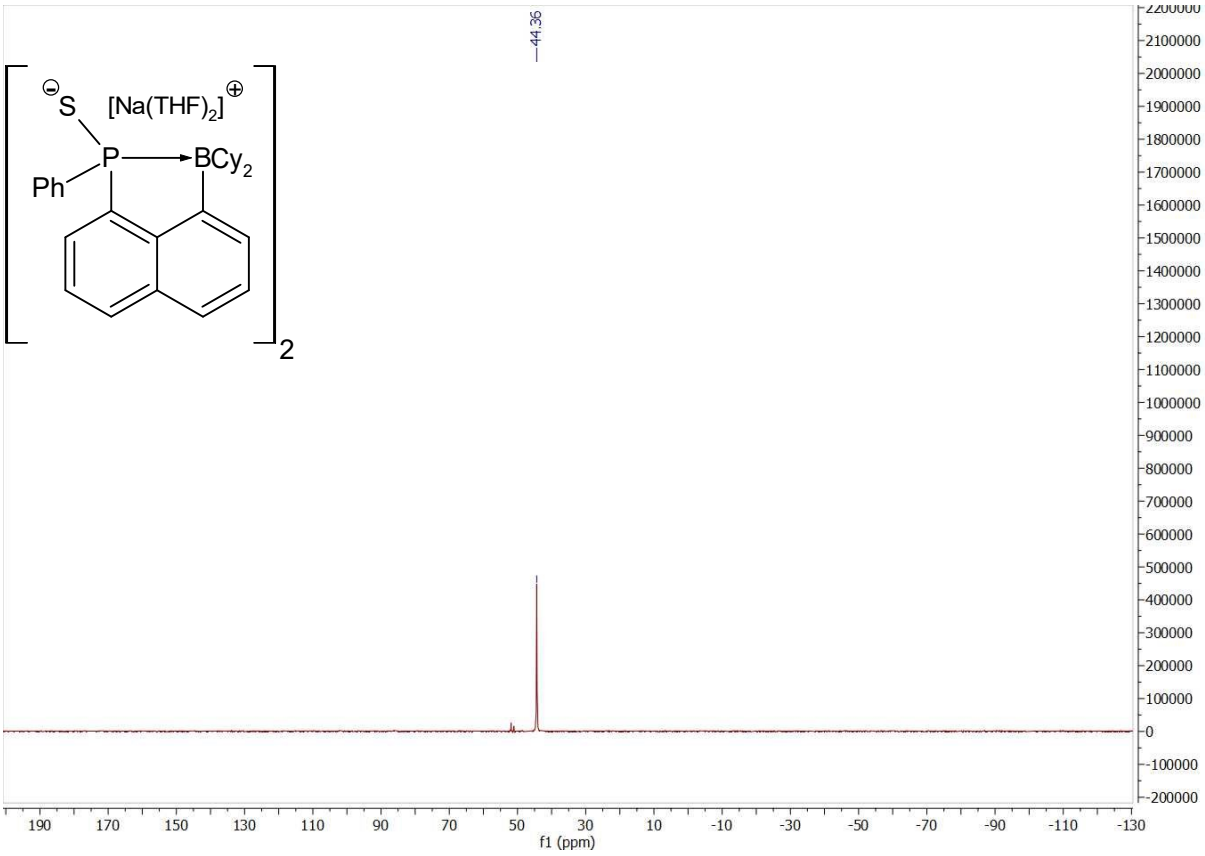

*Figure S33. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 202.49 MHz) of $\{[Na(THF)_2]^+$ [1-BCy_2-8-P(S)Ph-$C_{10}H_6]^-\}_2$ (**8**)*

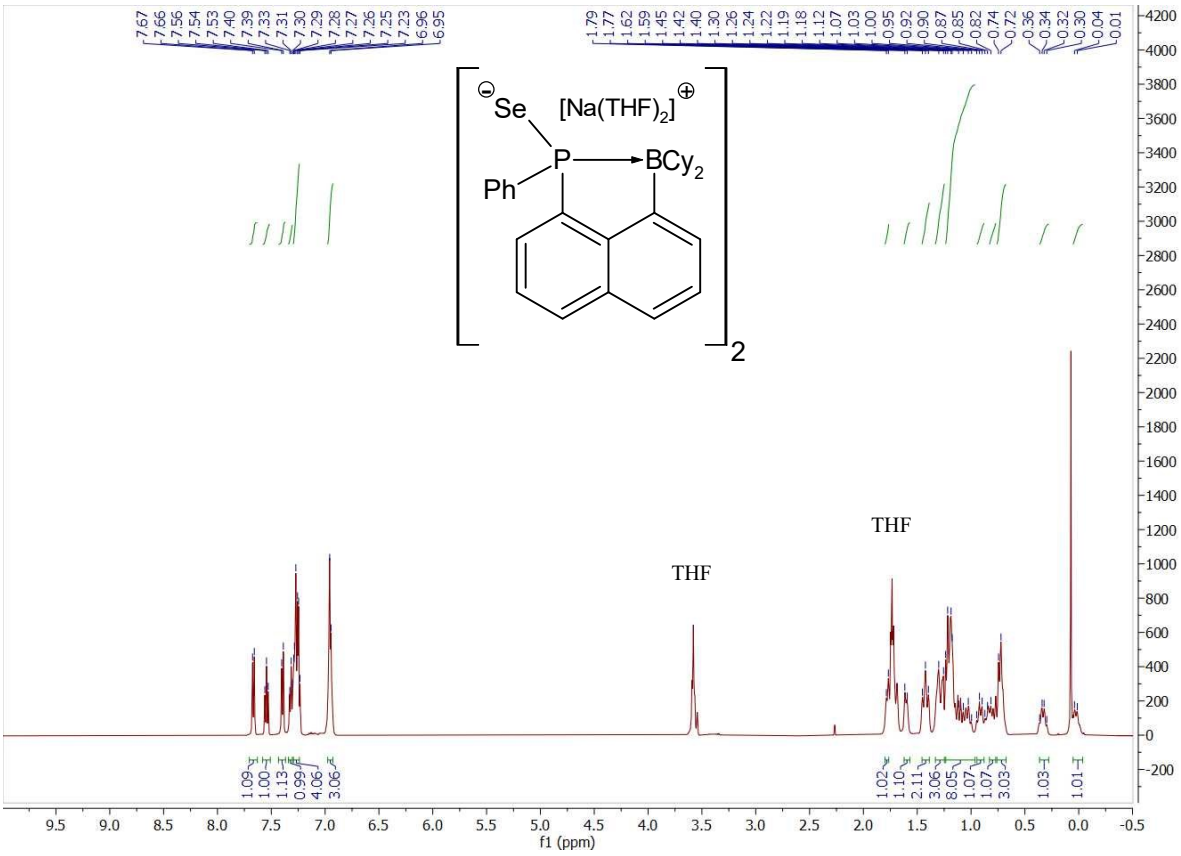

*Figure S34. ^{1}H NMR (THF-d_8, 500.13 MHz) of {[Na(THF)$_2$]$^+$ [1-BCy$_2$-8-P(Se)Ph-C$_{10}$H$_6$]$^-$}$_2$ (**9**)*

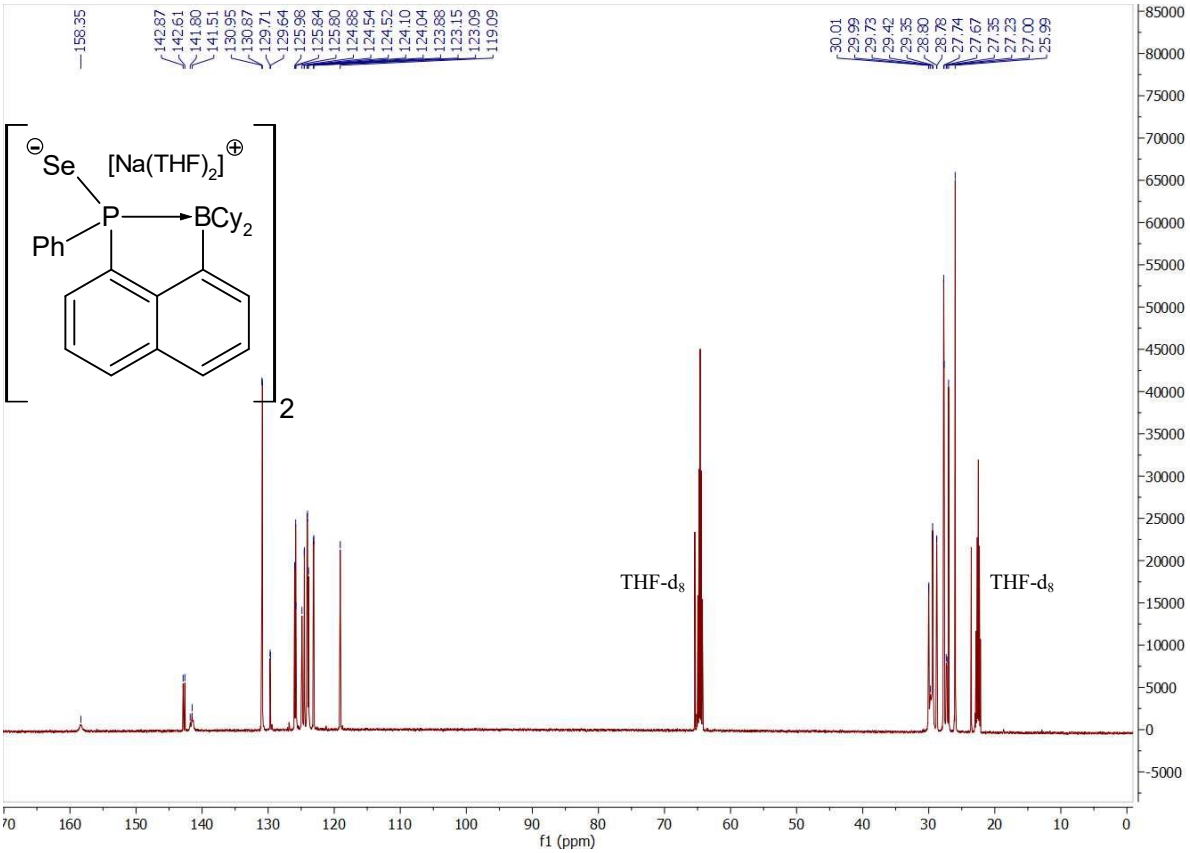

*Figure S35. $^{13}C\{^{1}H\}$ NMR (THF-d_8, 125.77 MHz) of $\{[Na(THF)_2]^+ [1\text{-}BCy_2\text{-}8\text{-}P(Se)Ph\text{-}C_{10}H_6]^-\}_2$ (**9**)*

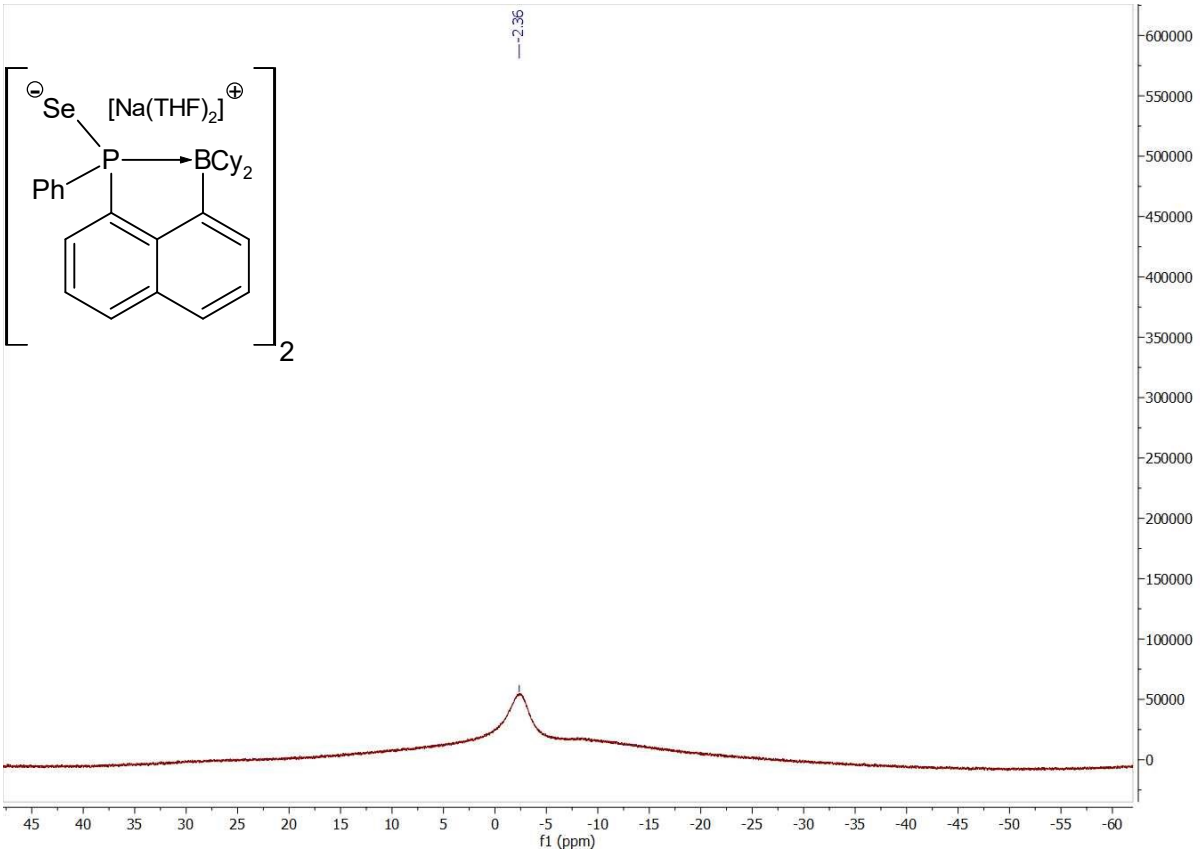

*Figure S36. $^{11}B\{^1H\}$ NMR (THF-d_8, 160.57 MHz) of $\{[Na(THF)_2]^+ [1\text{-}BCy_2\text{-}8\text{-}P(Se)Ph\text{-}C_{10}H_6]^-\}_2$ (**9**)*

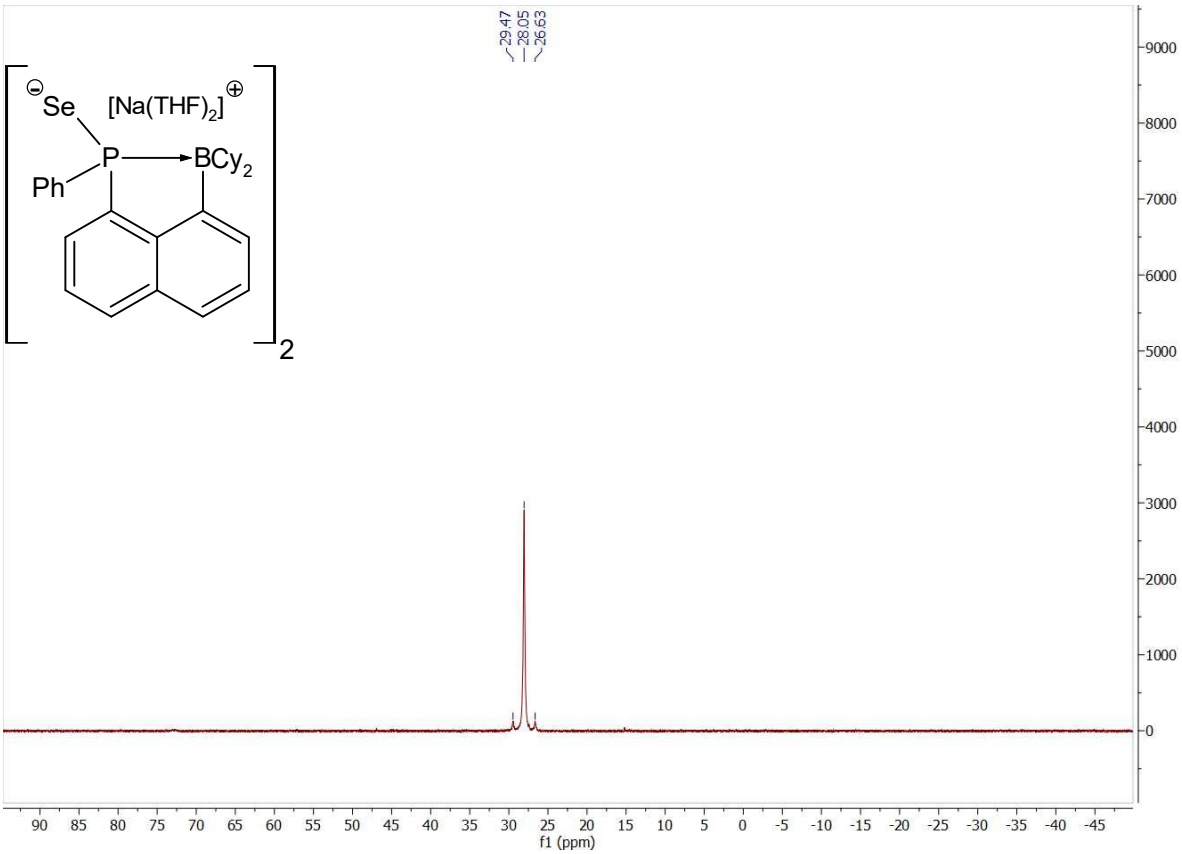

*Figure S37. $^{31}P\{^{1}H\}$ NMR (THF-d_8, 202.49 MHz) of $\{[Na(THF)_2]^+ [1\text{-}BCy_2\text{-}8\text{-}P(Se)Ph\text{-}C_{10}H_6]^-\}_2$ (**9**)*

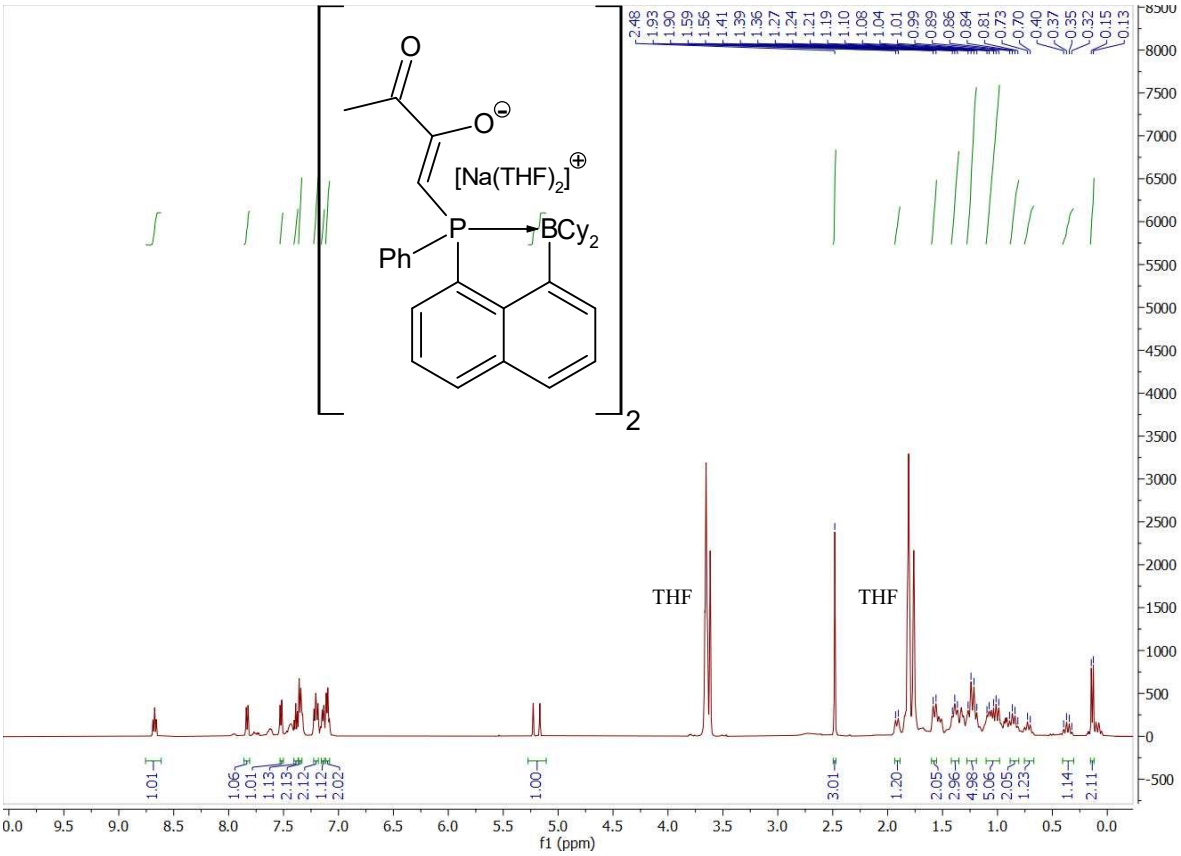

*Figure S38. ^{1}H NMR (THF-d_8, 500.13 MHz) of {[Na(THF)$_2$]$^+$ [1-BCy$_2$-8-P{CH=C(O)C(Me)O}Ph-C$_{10}$H$_6$]$^-$}$_2$ (**10**)*

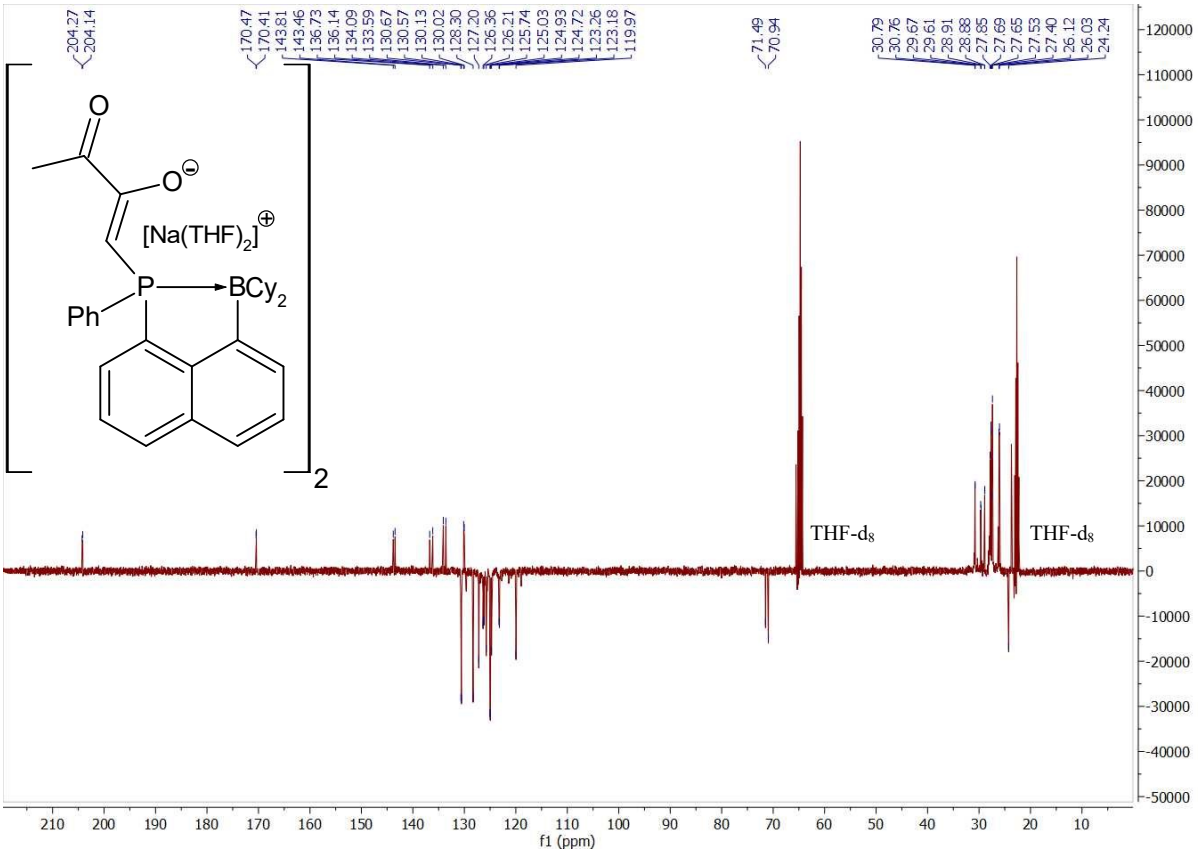

Figure S39. $^{13}C\{^{1}H\}$ NMR (THF-d_8, 125.77 MHz) of *{[Na(THF)$_2$]$^+$ [1-BCy$_2$-8-P{CH=C(O)C(Me)O}Ph-C$_{10}$H$_6$]$^-$}$_2$* (***10***)

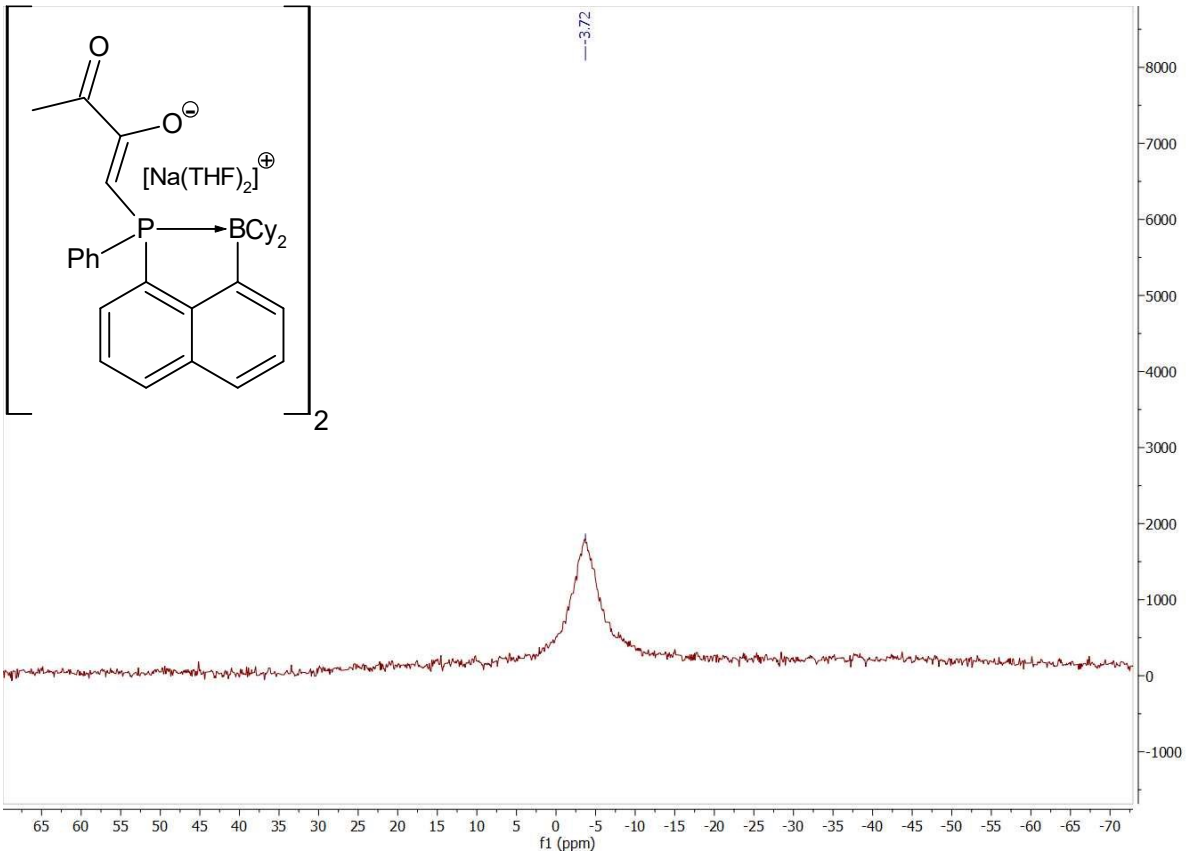

*Figure S40. $^{11}B\{^1H\}$ NMR (THF-d_8, 160.57 MHz) of $\{[Na(THF)_2]^+$ [1-BCy_2-8-P{CH=C(O)C(Me)O}Ph-$C_{10}H_6]^-\}_2$ (**10**)*

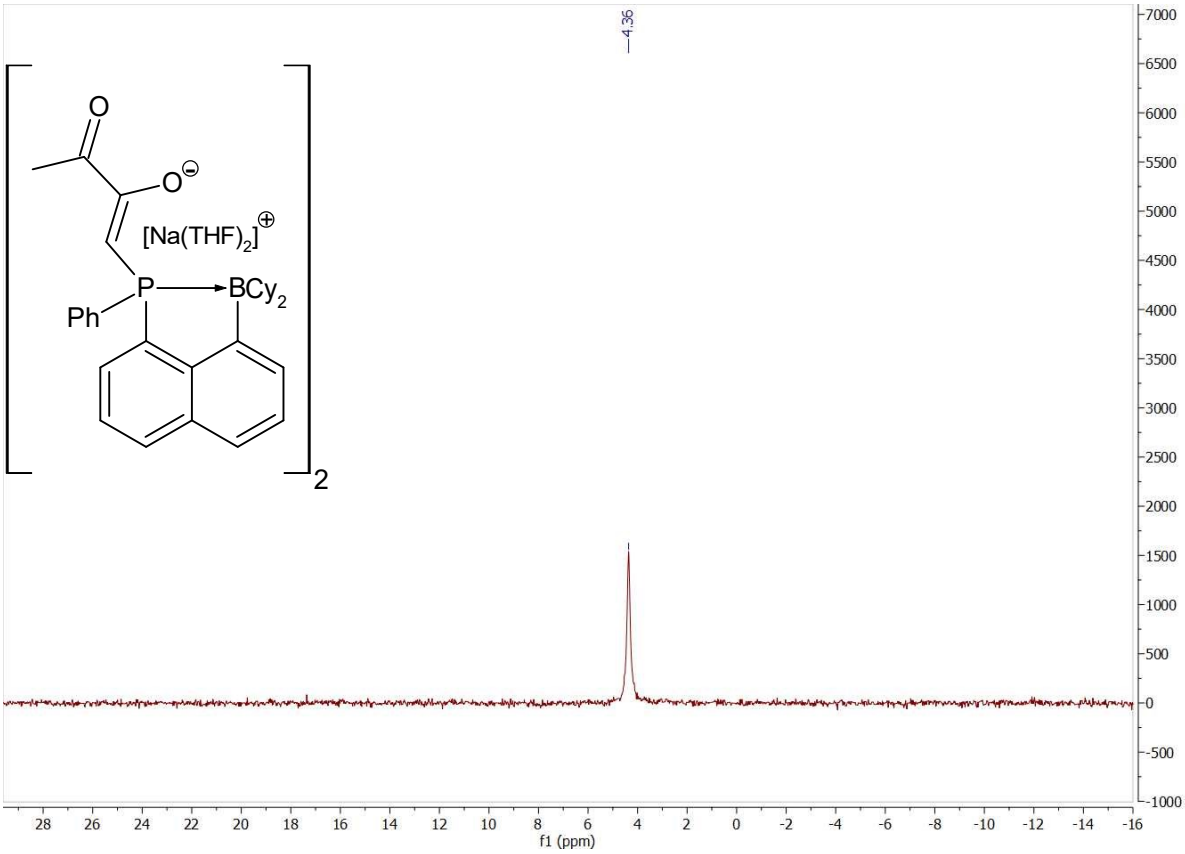

*Figure S41. $^{31}P\{^{1}H\}$ NMR (THF-d_8, 202.49 MHz) of $\{[Na(THF)_2]^+$ [1-BCy_2-8-P{CH=C(O)C(Me)O}Ph-$C_{10}H_6]^-\}_2$ (**10**)*

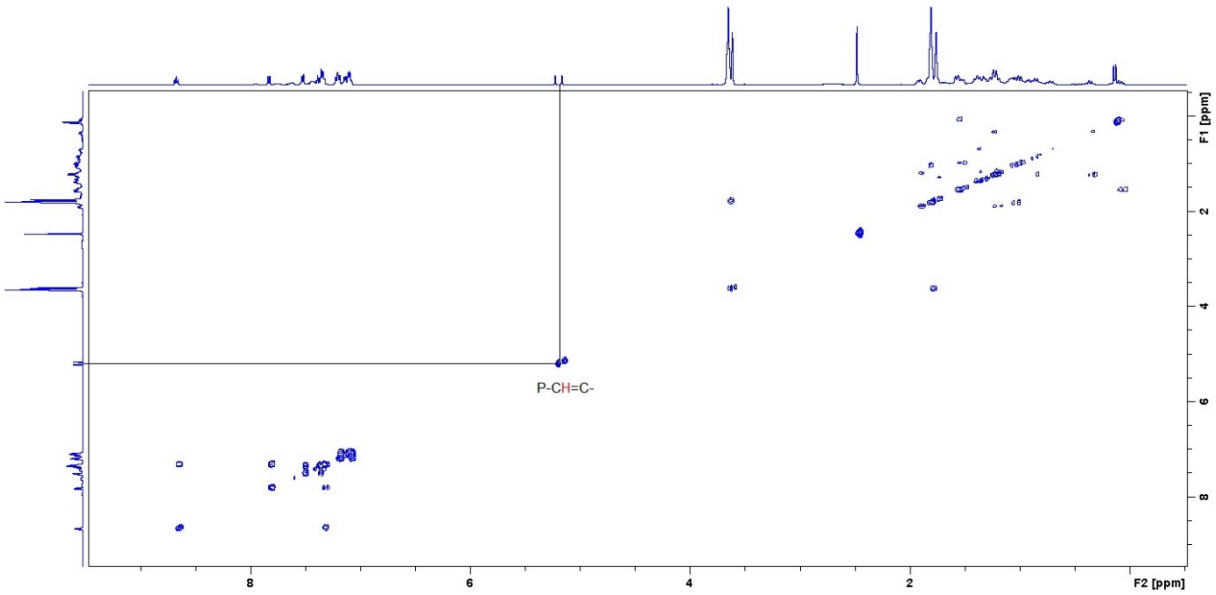

*Figure S42. ^{1}H-^{1}H COSY NMR of $\{[Na(THF)_2]^+$ [1-BCy_2-8-P{CH=C(O)C(Me)O}Ph-$C_{10}H_6]^-\}_2$ (**10**)*

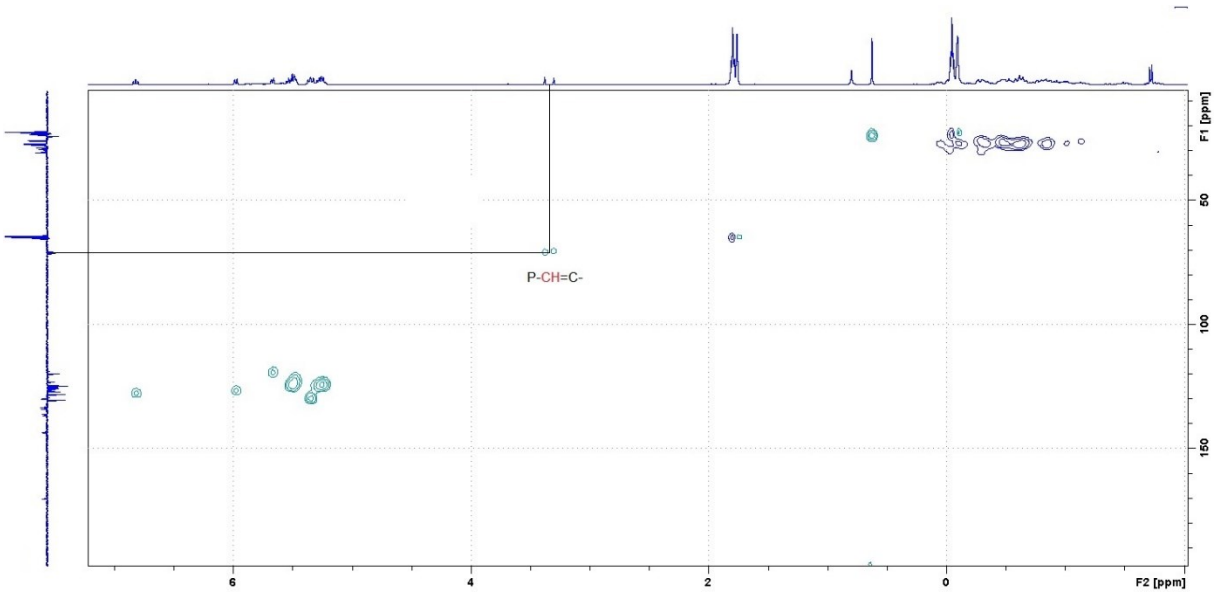

*Figure S43. ^{1}H-^{13}C HSQC NMR of {[Na(THF)$_2$]$^+$ [1-BCy$_2$-8-P{CH=C(O)C(Me)O}Ph-C$_{10}$H$_6$]$^-$}$_2$ (**10**)*

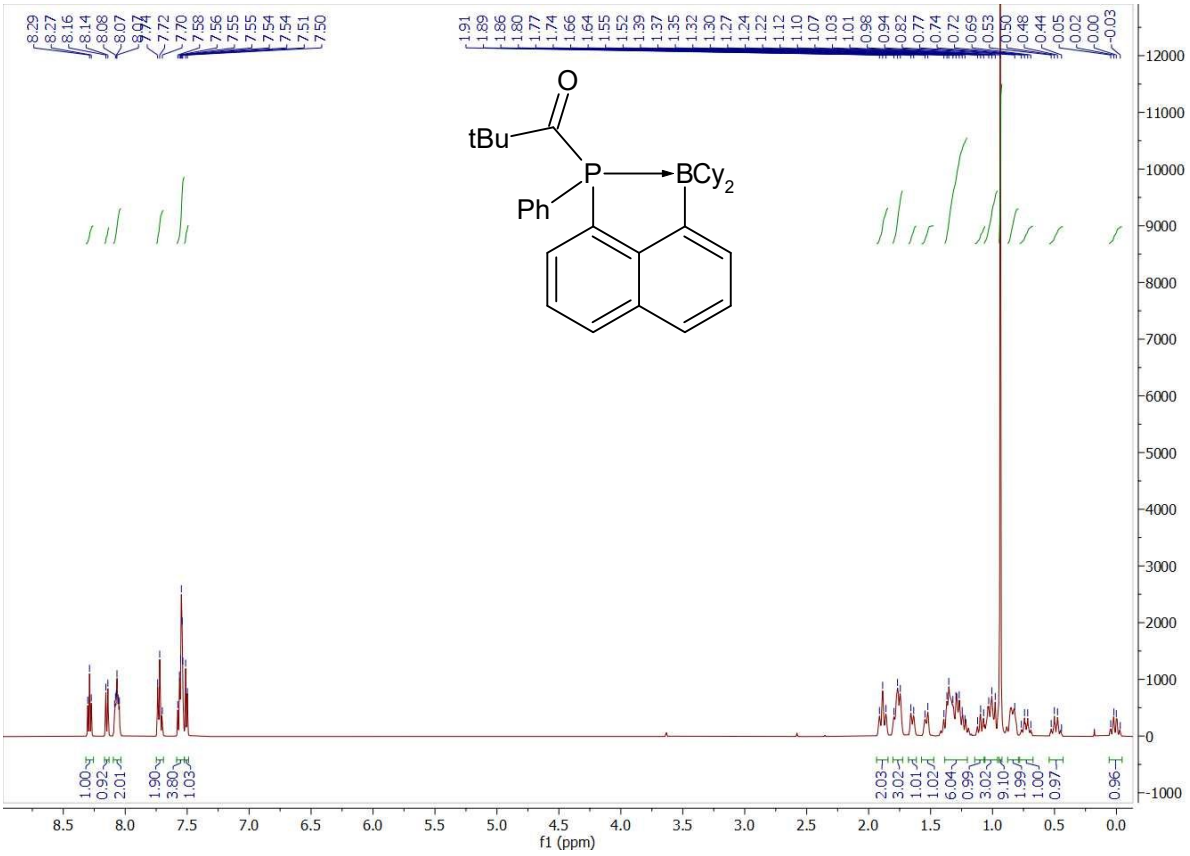

*Figure S44. ^{1}H NMR (THF-d_8, 500.13 MHz) of [1-BCy_2-8-P{C(O)tBu}Ph-$C_{10}H_6$] (**11**)*

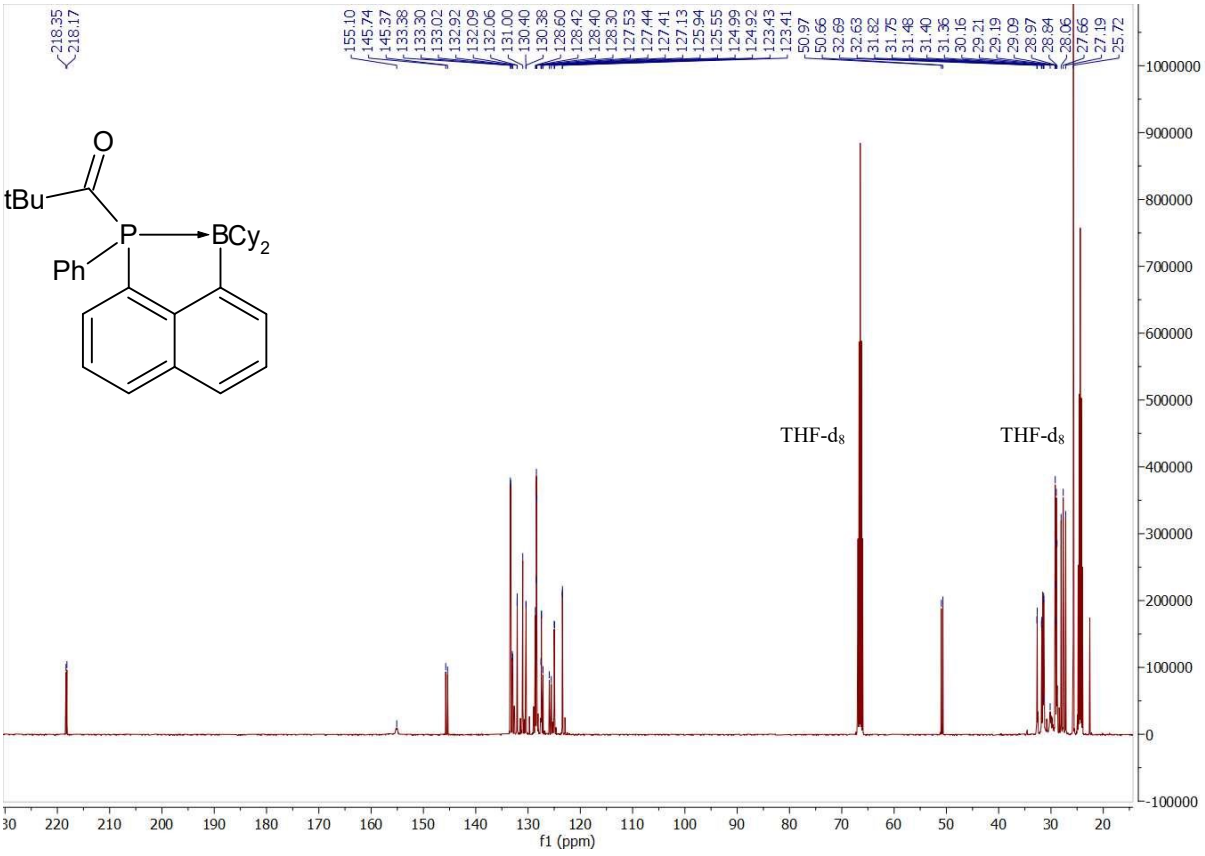

*Figure S45. $^{13}C\{^{1}H\}$ NMR (THF-d_8, 125.77 MHz) of [1-BCy_2-8-P{C(O)tBu}Ph-$C_{10}H_6$] (**11**)*

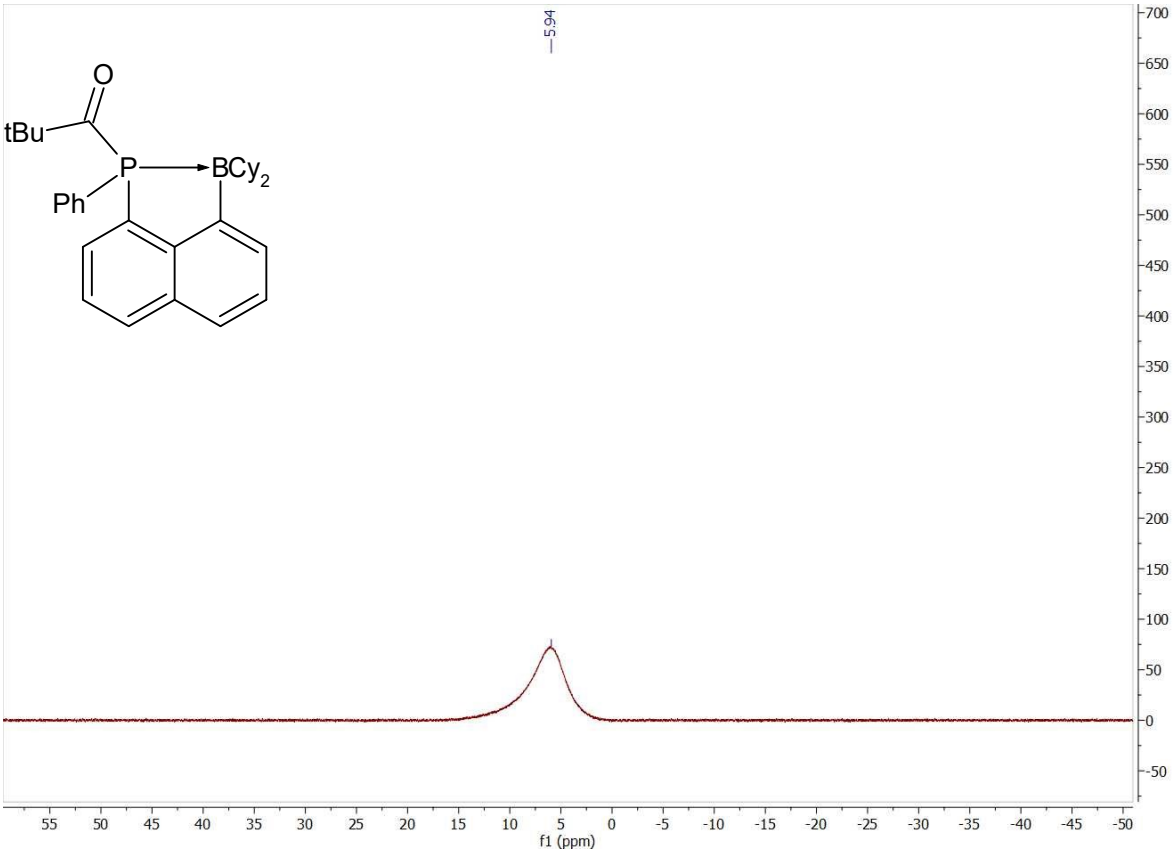

*Figure S46. $^{11}B\{^{1}H\}$ NMR (THF-d_8, 160.57 MHz) of [1-BCy_2-8-P{C(O)tBu}Ph-$C_{10}H_6$] (**11**)*

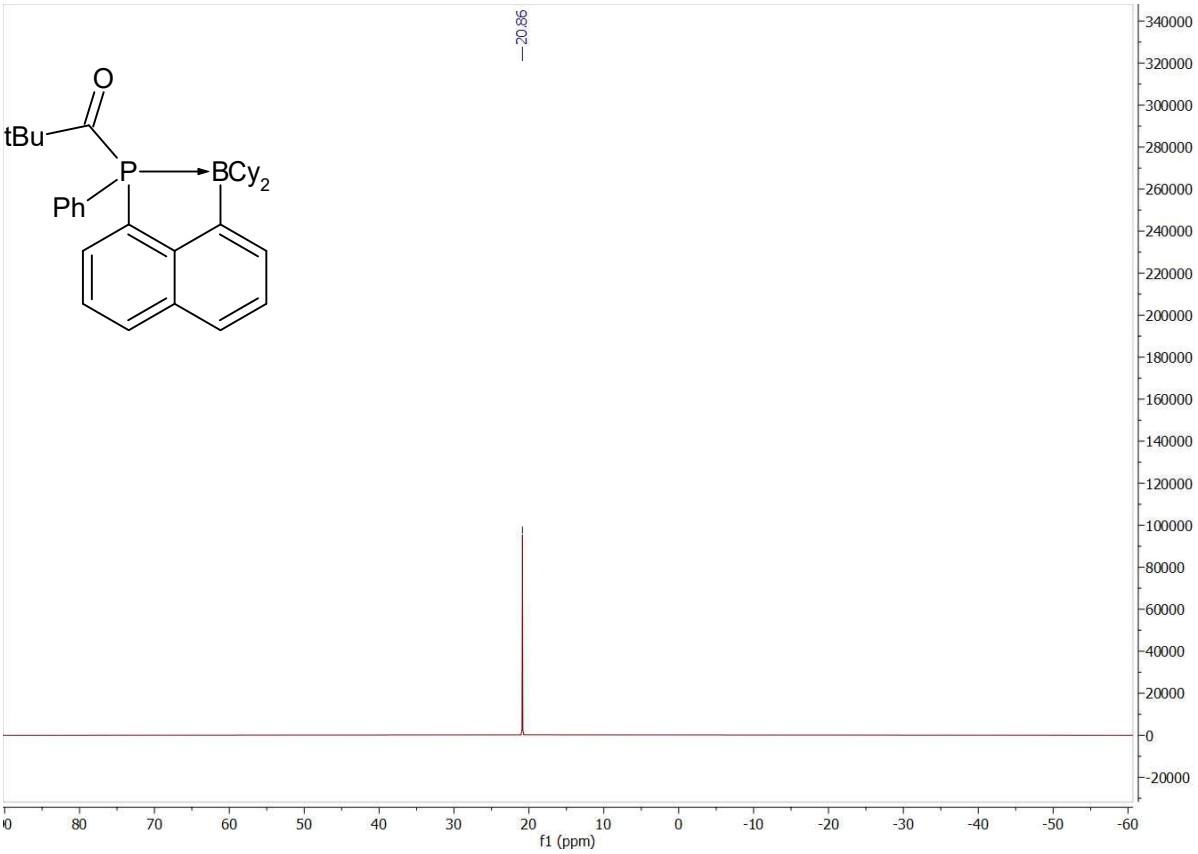

*Figure S47. $^{31}P\{^{1}H\}$ NMR (THF-d_8, 202.49 MHz) of [1-BCy_2-8-P{C(O)tBu}Ph-$C_{10}H_6$] (**11**)*

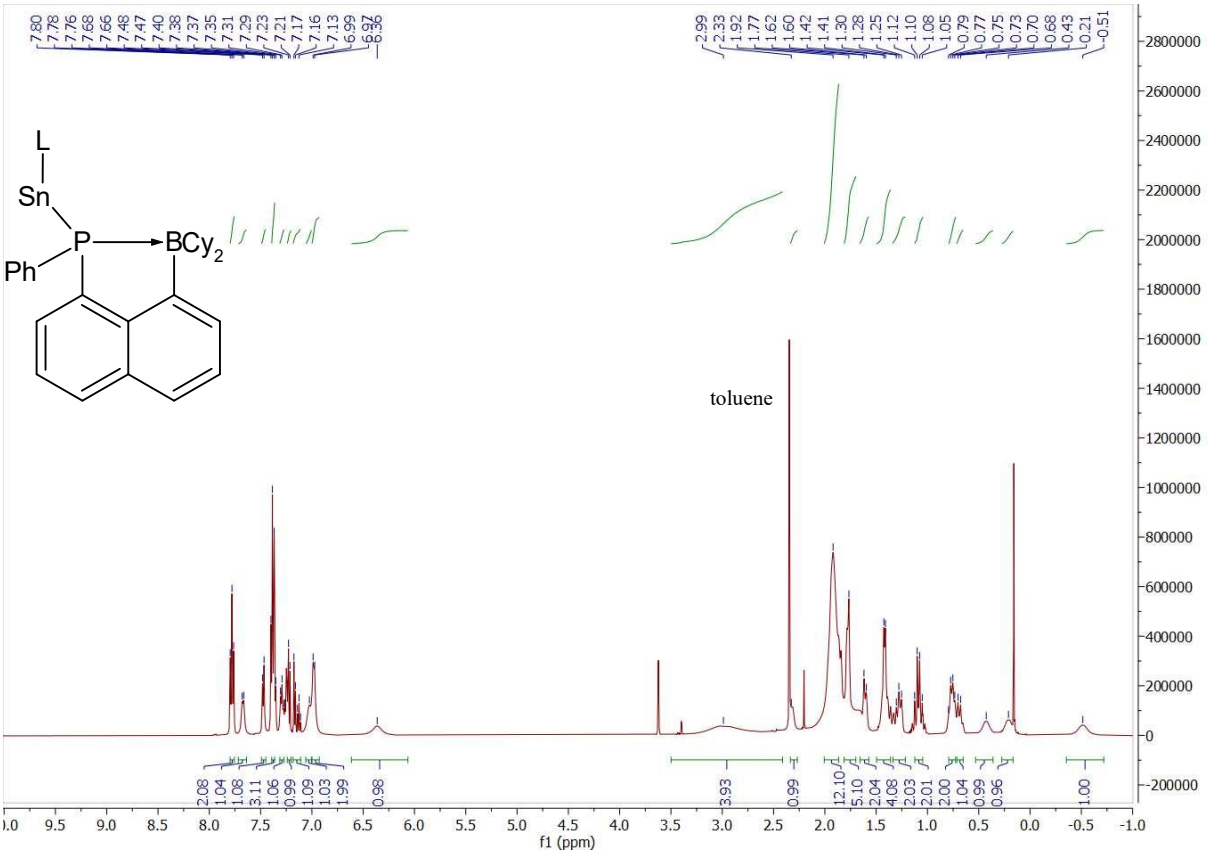

*Figure S48. ^{1}H NMR (THF-d_8, 500.13 MHz) of [1-BCy_2-8-P(SnL)Ph-$C_{10}H_6$] (**12**)*

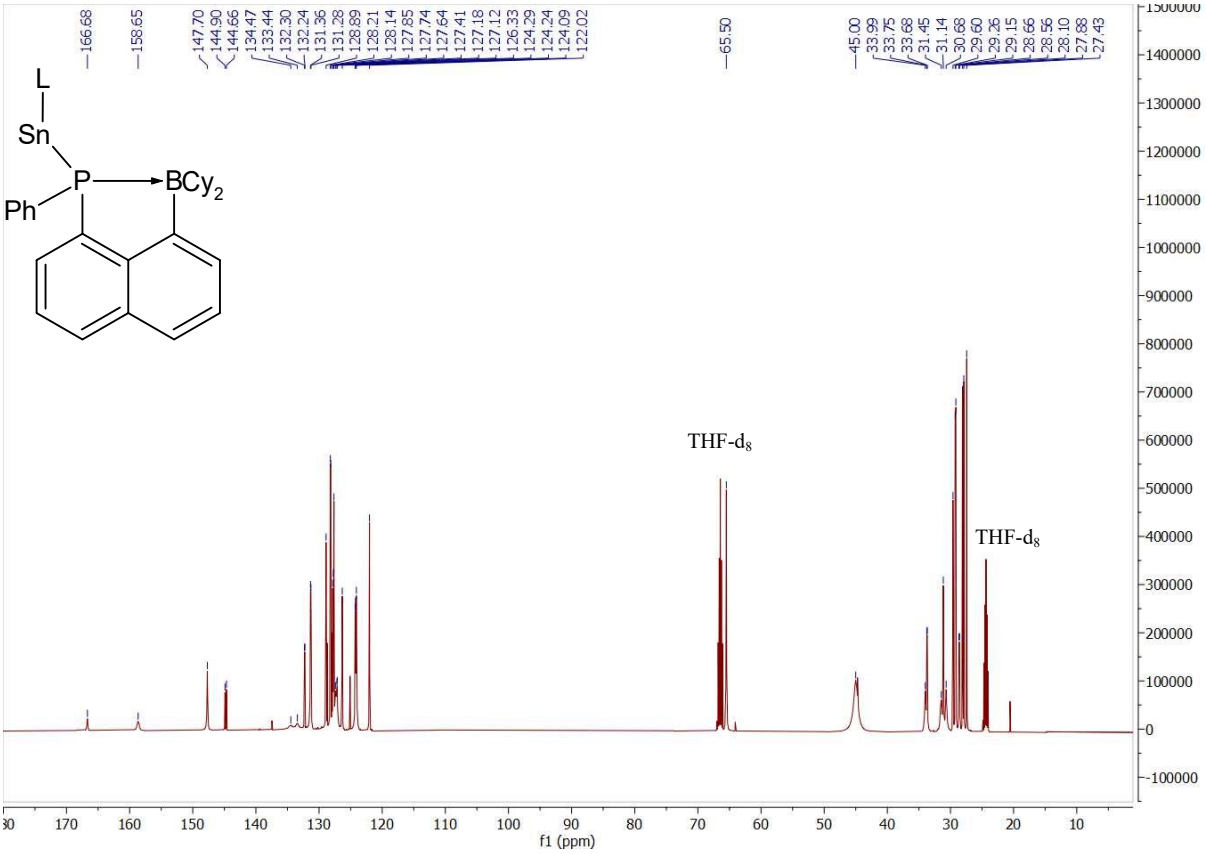

Figure S49. $^{13}C\{^{1}H\}$ NMR (THF-d_8, 125.77 MHz) of *[1-BCy_2-8-P(SnL)Ph-$C_{10}H_6$]* (***12***)

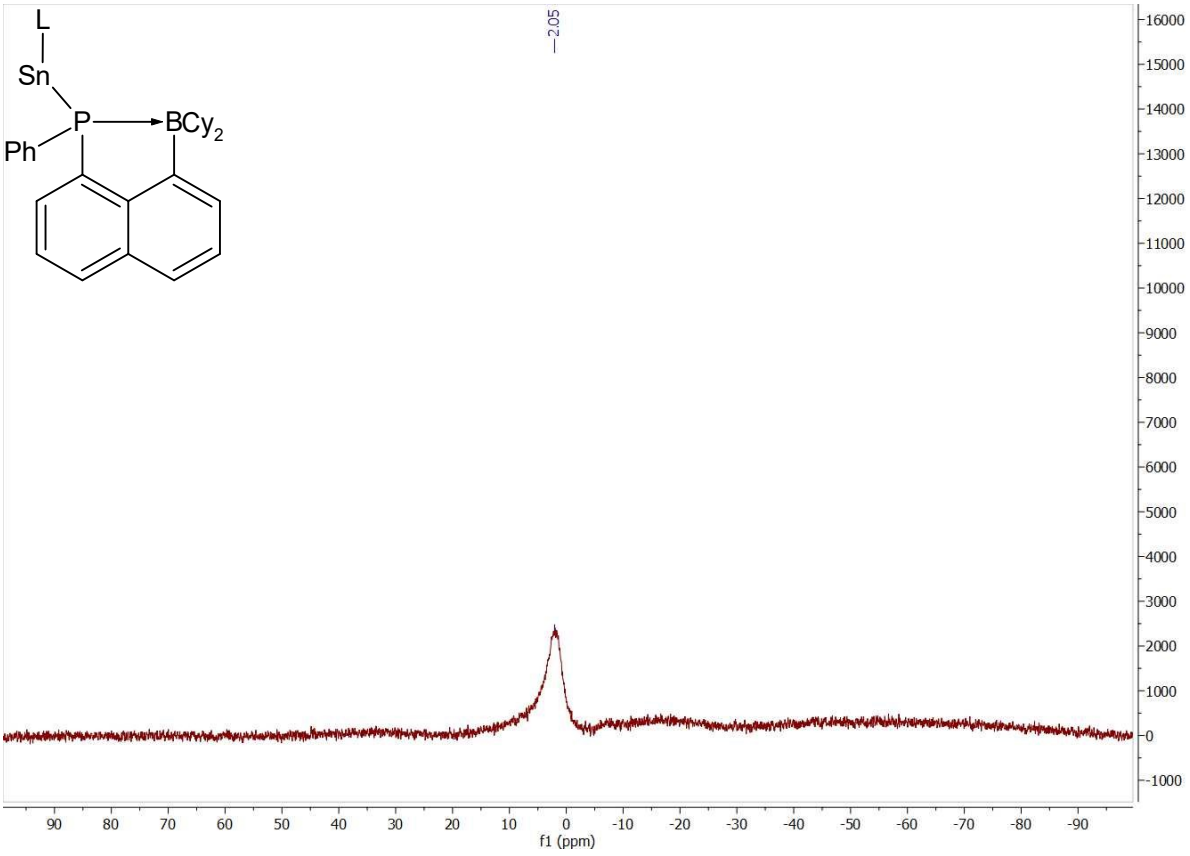

*Figure S50. $^{11}B\{^{1}H\}$ NMR (THF-d_8, 160.57 MHz) of [1-BCy_2-8-P(SnL)Ph-$C_{10}H_6$] (**12**)*

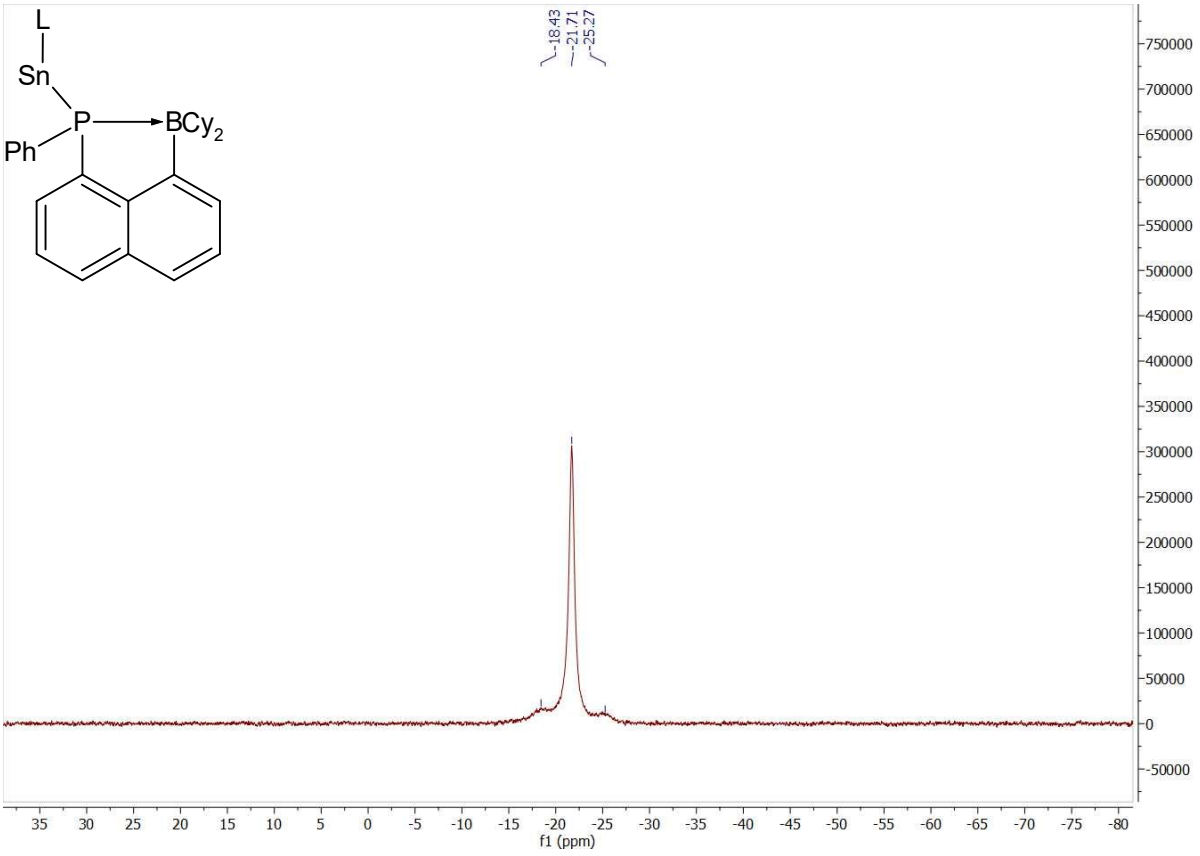

*Figure S51. $^{31}P\{^{1}H\}$ NMR (THF-d_8, 202.49 MHz) of [1-BCy_2-8-P(SnL)Ph-$C_{10}H_6$] (**12**)*

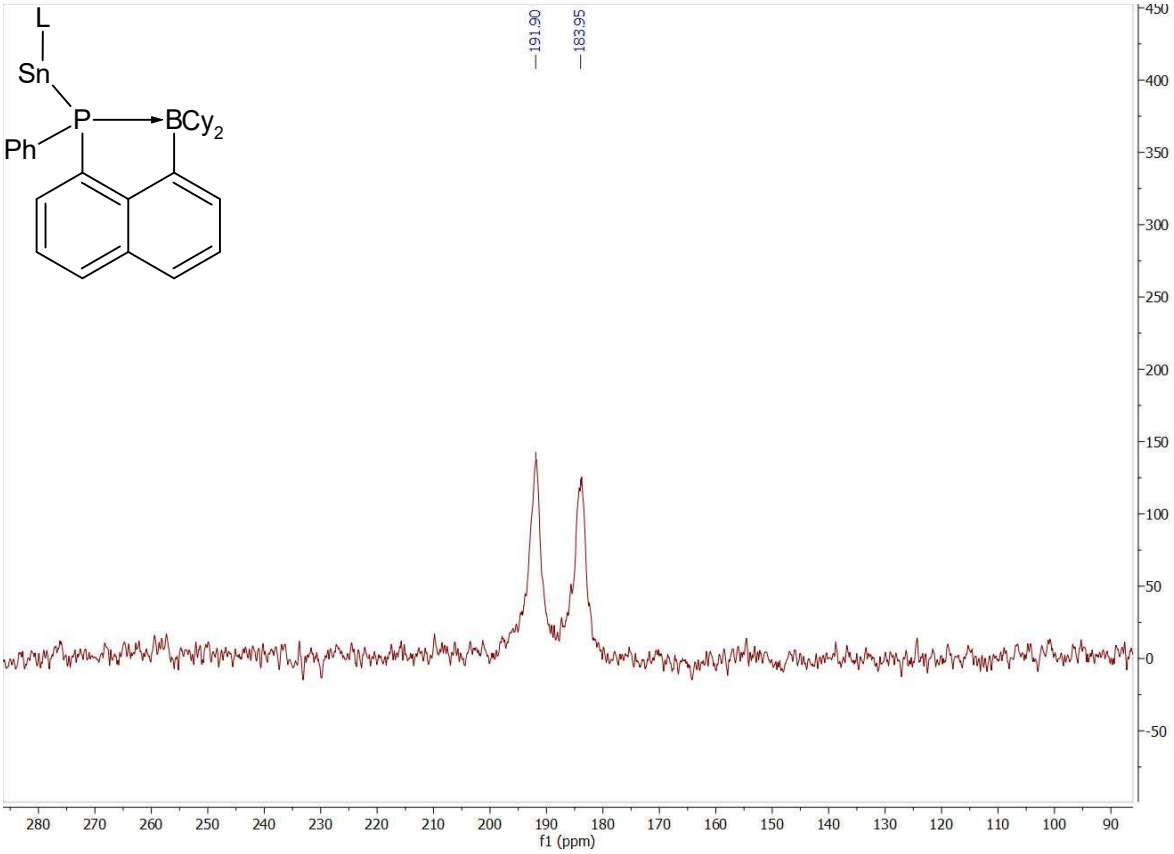

*Figure S52. $^{119}Sn\{^{1}H\}$ NMR (THF-d_8, 186.52 MHz) of [1-BCy_2-8-P(SnL)Ph-$C_{10}H_6$] (**12**)*

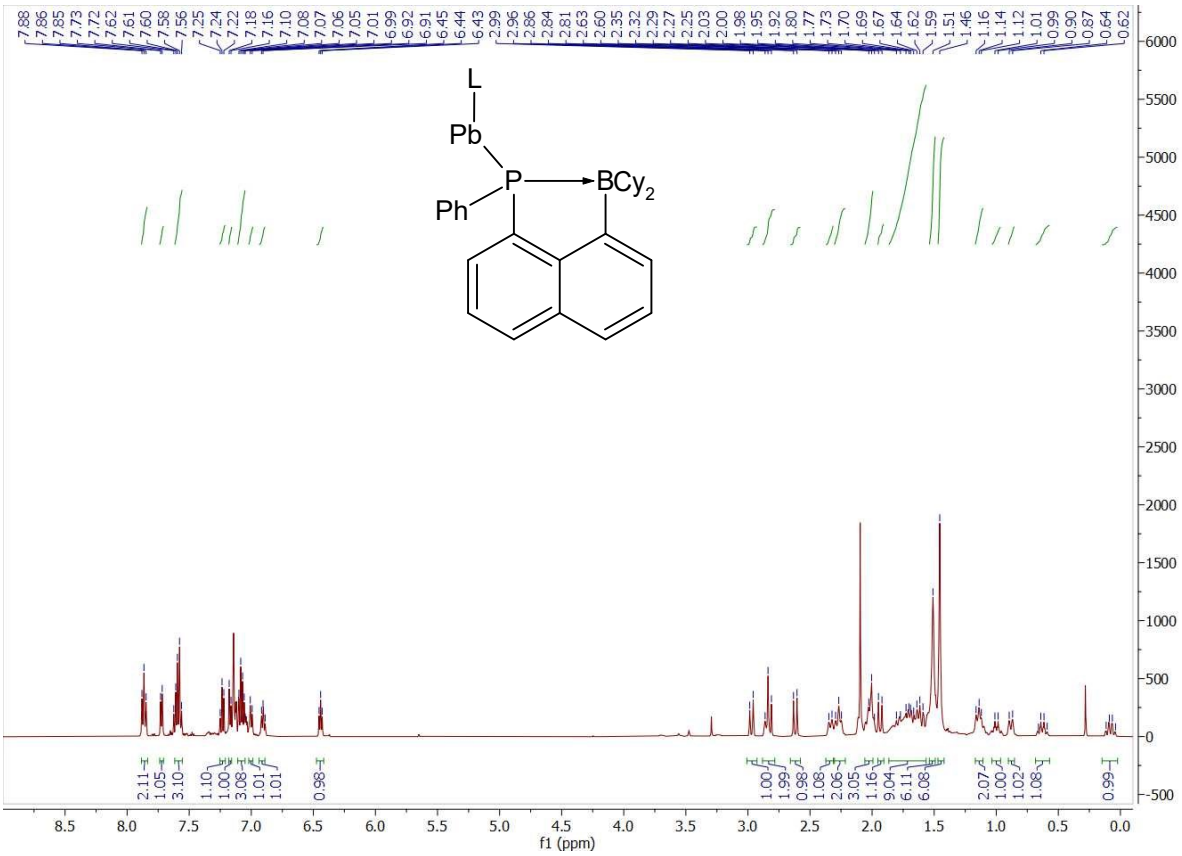

*Figure S53. ^{1}H NMR (C_6D_6, 500.13 MHz) of [1-BCy_2-8-P(PbL)Ph-$C_{10}H_6$] (**13**)*

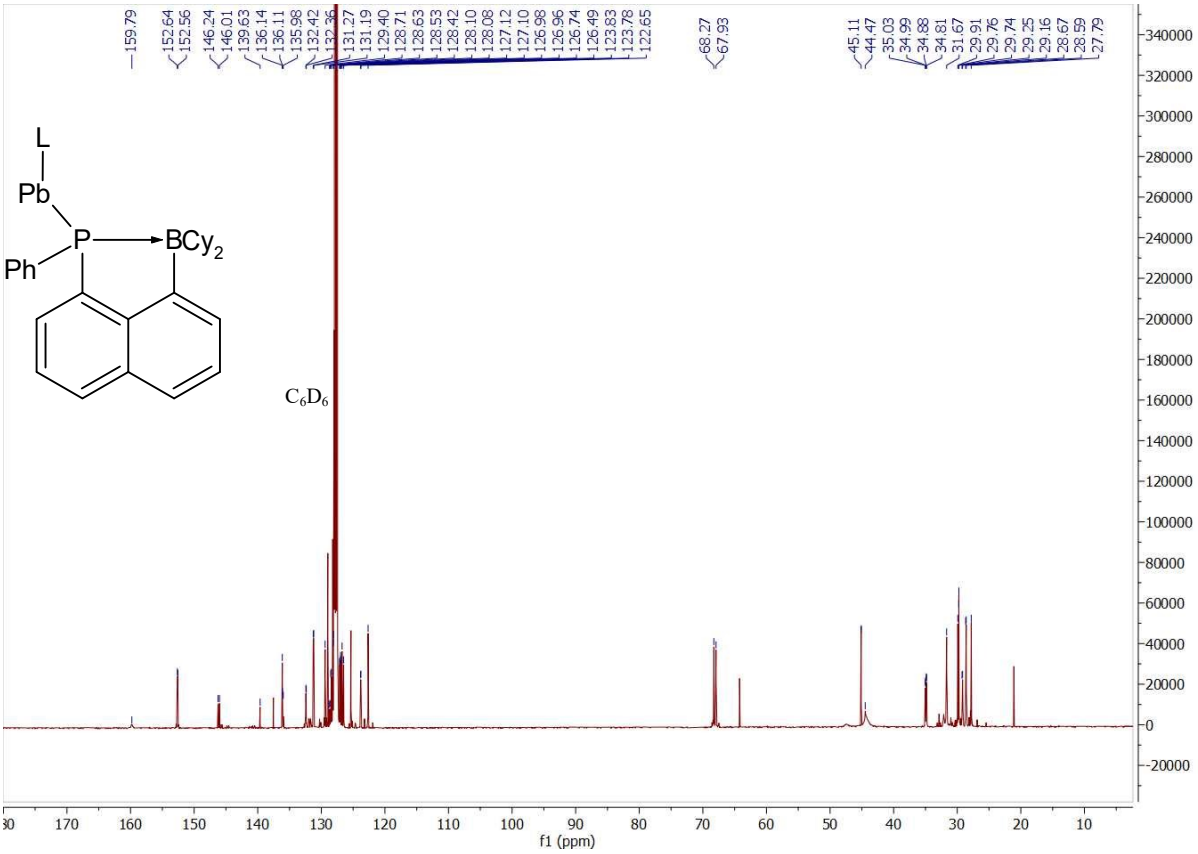

*Figure S54. $^{13}C\{^{1}H\}$ NMR (C_6D_6, 125.77 MHz) of [1-BCy_2-8-P(PbL)Ph-$C_{10}H_6$] (**13**)*

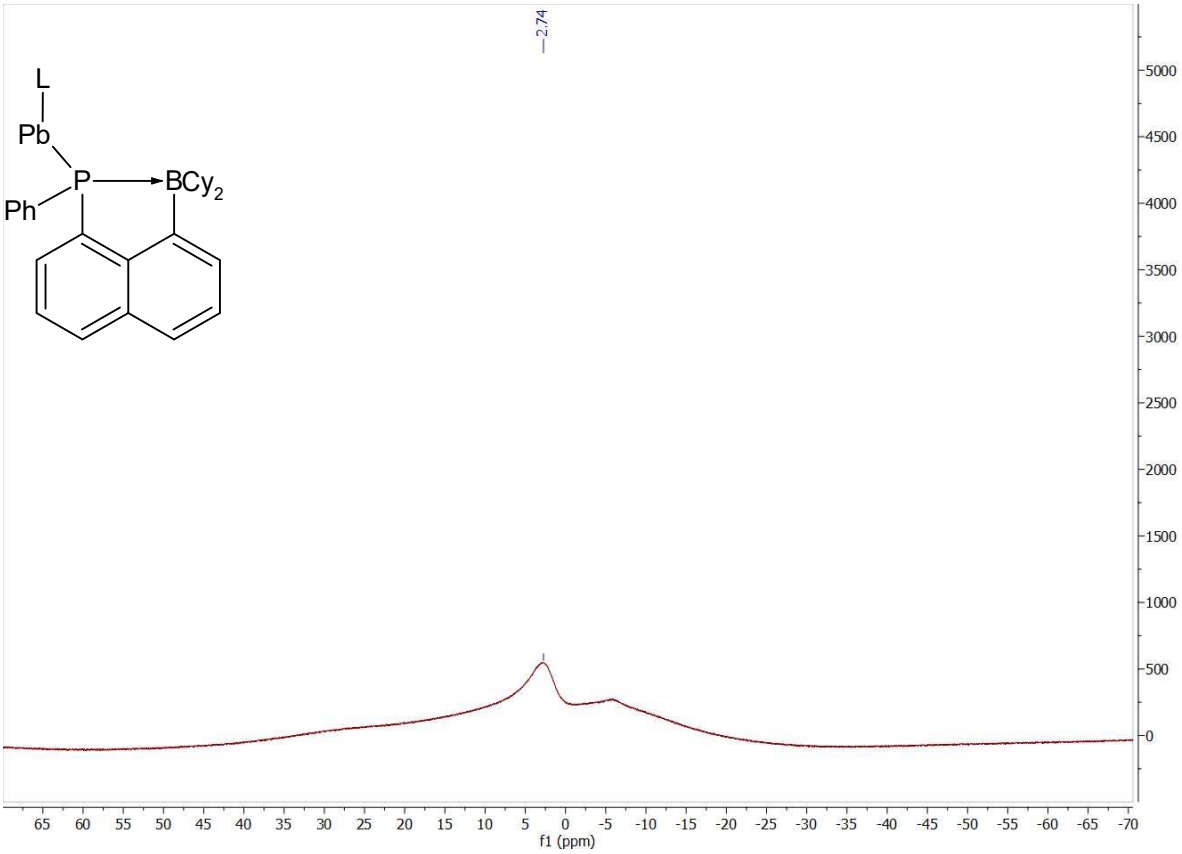

*Figure S55. $^{11}B\{^1H\}$ NMR (C_6D_6, 160.57 MHz) of [1-BCy_2-8-P(PbL)Ph-$C_{10}H_6$] (**13**)*

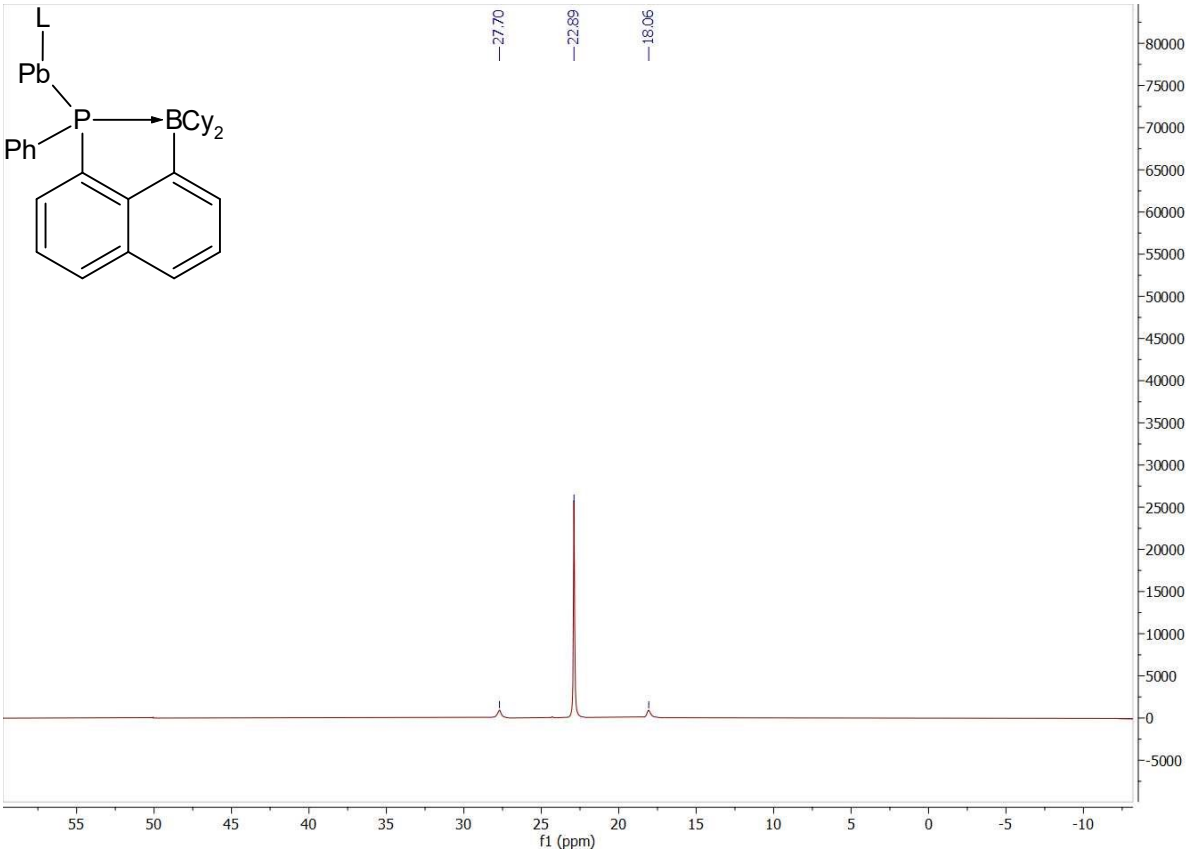

*Figure S56. $^{31}P\{^{1}H\}$ NMR (C_6D_6, 202.49 MHz) of [1-BCy_2-8-P(PbL)Ph-$C_{10}H_6$] (**13**)*

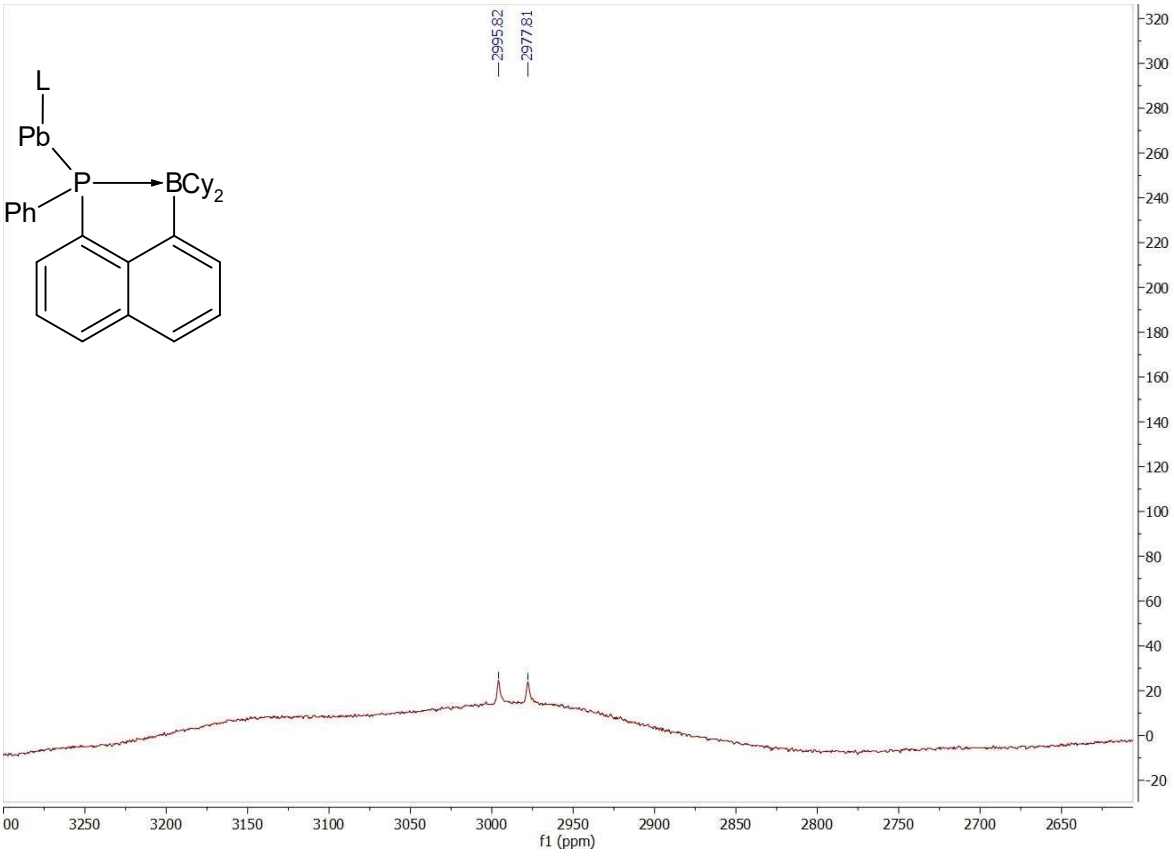

*Figure S57. $^{209}Pb\{^{1}H\}$ NMR (C_6D_6, 104.64 MHz) of [1-BCy_2-8-P(PbL)Ph-$C_{10}H_6$] (**13**)*

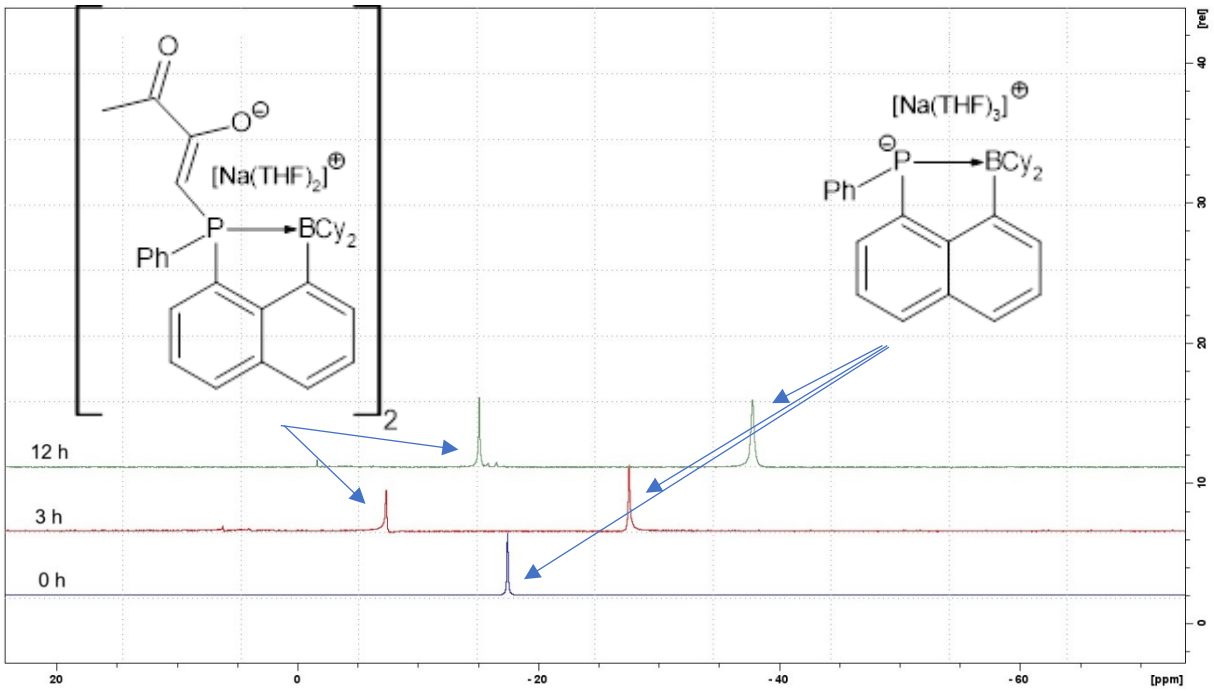

*Figure S58. The $^{31}P\{^{1}H\}$ NMR spectra of the reaction mixture of **5** and 2,3-butanedione*

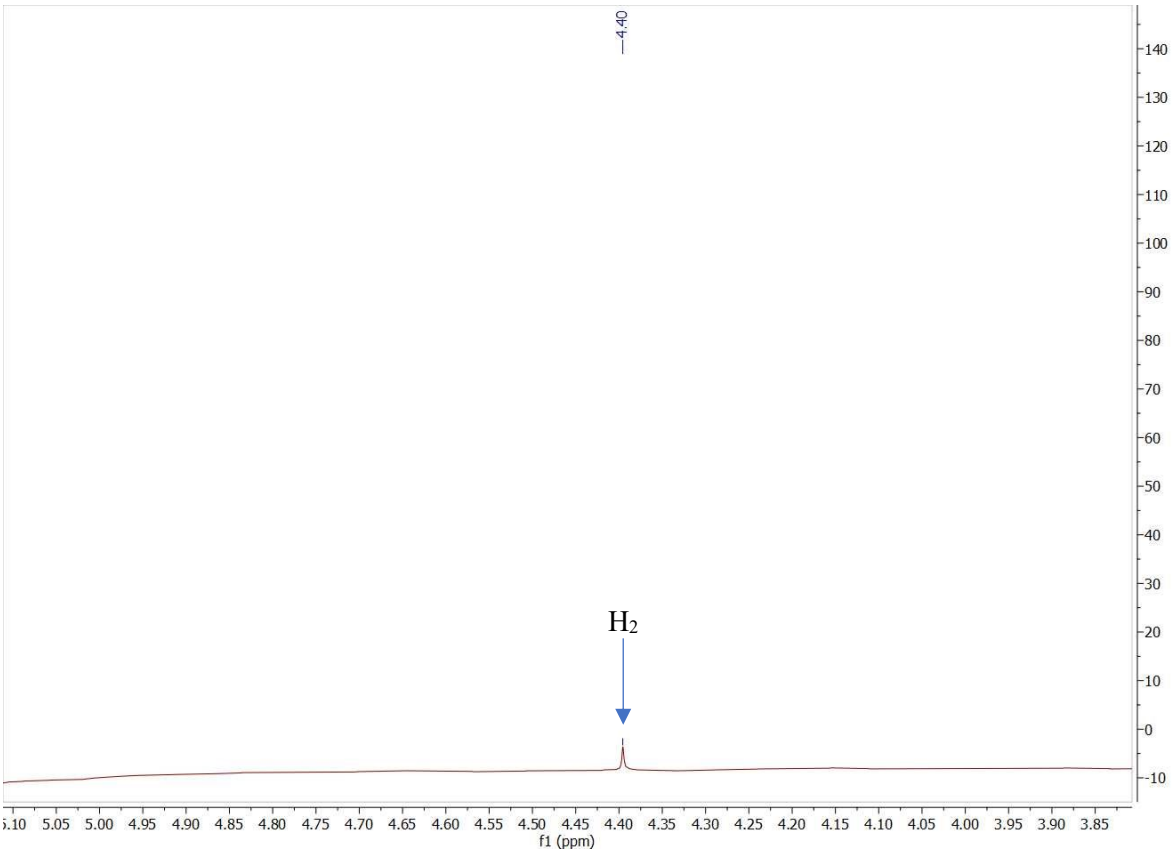

Figure S59. ^{1}H NMR spectrum of H_2 in THF/C_6D_6

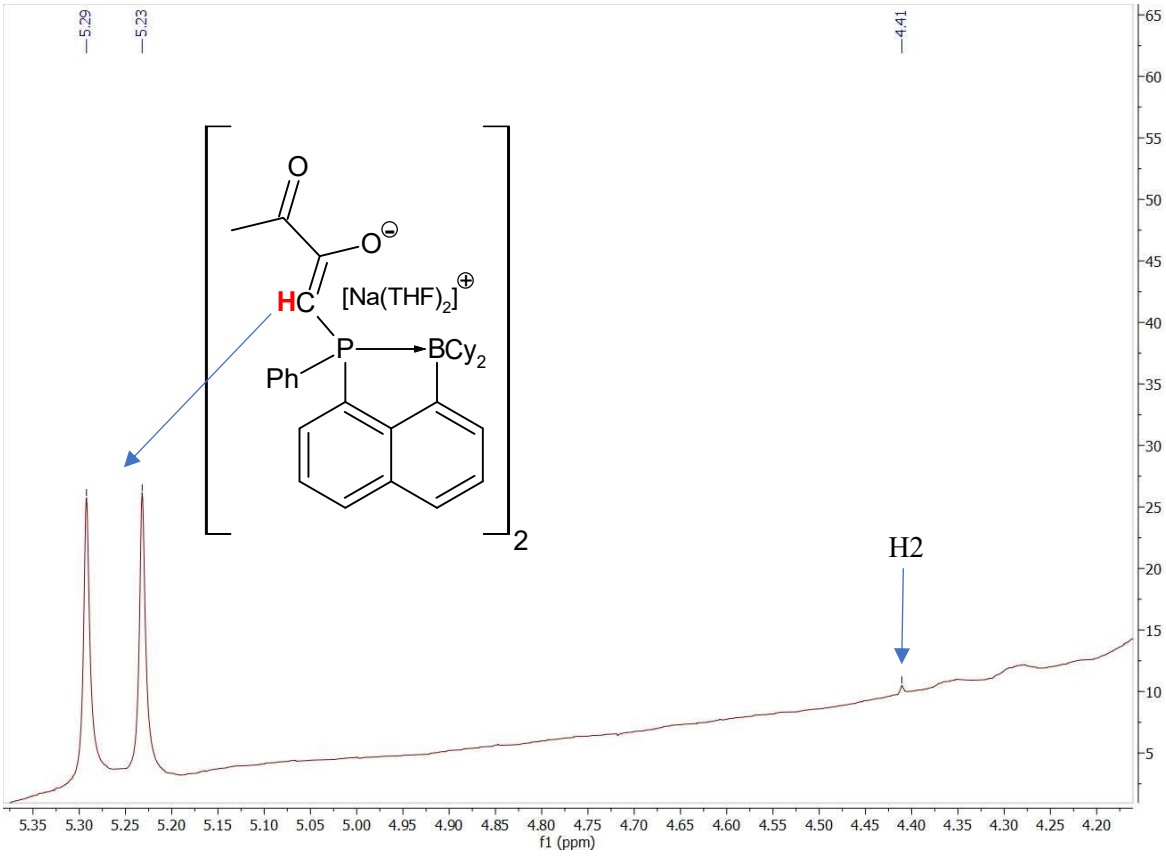

Figure S60. Expended part of the ^1H NMR spectrum of the reaction mixture of 5 and 2,3-butanedione in THF/C_6D_6.

Table S1: Crystallographic data of compounds **3**, **4**·(C_4H_8O)**, 5, 6**, **7**, 9, **10**·2(C_4H_8O), **11**, and **12**·0.5(C_7H_8)

Compound	**3**	**4**·(C_4H_8O)	**5**	**6**	**7**	**9**	**10**·2(C_4H_8O)	**11**	**12**·0.5(C_7H_8)
Empirical formula	$C_{44}H_{56}B_2P_2$	$C_{56}H_{66}B_2P_2$ ·(C_4H_8O)	$C_{40}H_{57}BNaO_3P$	$C_{36}H_{49}BKO_2P$	$C_{72}H_{98}B_2Na_2O_6P_2$	$C_{72}H_{98}B_2Na_2O_4Se_2P_2$	$C_{80}H_{106}B_2Na_2O_8P_2$, 2($C_4H_8O$)	$C_{33}H_{42}BOP$	$C_{40}H_{52}BNP$ Sn, 0.5(C_7H_8)
Crystal system	Triclinic	Triclinic	orthorhombic	monoclinic	monoclinic	Triclinic	Triclinic	orthorhombic	monoclinic
Space group	*P*-1	*P*-1	*P*na2$_1$	*P*2$_1$/n	*P*2$_1$/n	*P*-1	*P*-1	*P-b-c-a*	*P* 2$_1$/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
Z	2	2	4	4	2	1	1	8	4
V (Å^3)	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_c (g cm^{-3})	1.192	1.189	1.118	1.198	1.183	1.297	1.190	1.145	1.320
μ (mm^{-1})	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_{int})[a)]	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)

- 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[c] / wR[c]	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] $R_{int} = \Sigma \left| F_o^2 - F_{o,mean}^2 \right| / \Sigma F_o^2$, [b] $GOF = [\Sigma(w(F_o^2 - F_c^2)^2)/(N_{diffrs} - N_{params})]^{½}$, [c] Weighting scheme: $w = [\sigma^2(F_o^2) + (w_1P)^2 + w_2P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \Sigma \left| \left| F_o \right| - \left| F_c \right| \right| / \Sigma \left| F_o \right|$, $wR(F^2) = [\Sigma(w(F_o^2 - F_c^2)^2)/(\Sigma w(F_o^2)^2)]^{½}$