

Supplementary Information

B-substituted group 1 phosphides: Synthesis and reactivity[†]

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Table S1. Crystallographic data of compounds **3**, **4**· $(\text{C}_4\text{H}_8\text{O})$, **5**, **6**, **7**, **9**, **10**· $2(\text{C}_4\text{H}_8\text{O})$, **11**, and **12**· $0.5(\text{C}_7\text{H}_8)$ S64

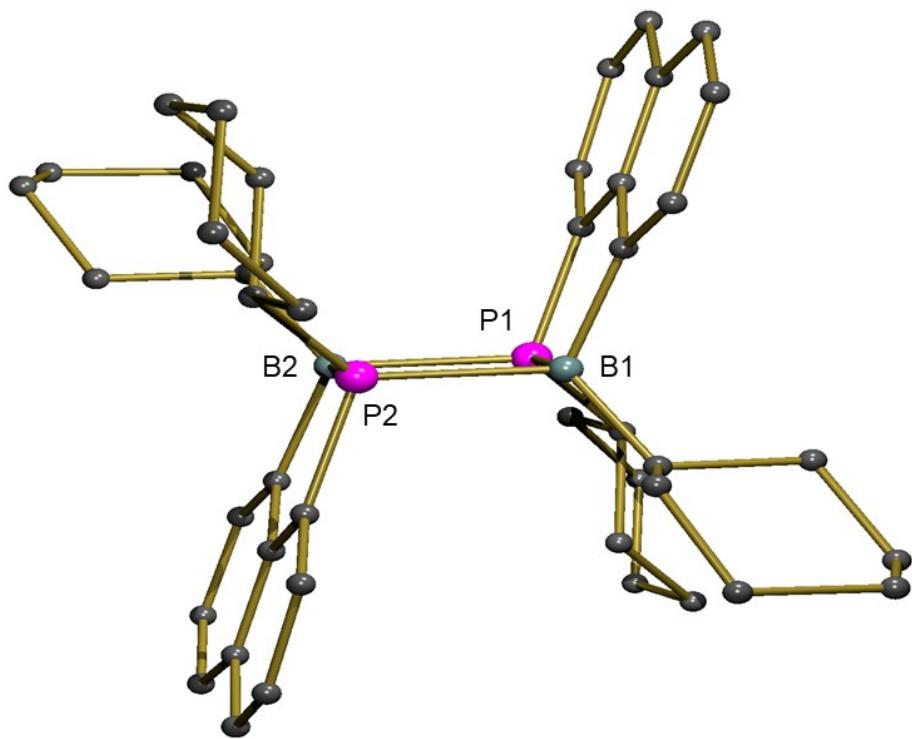
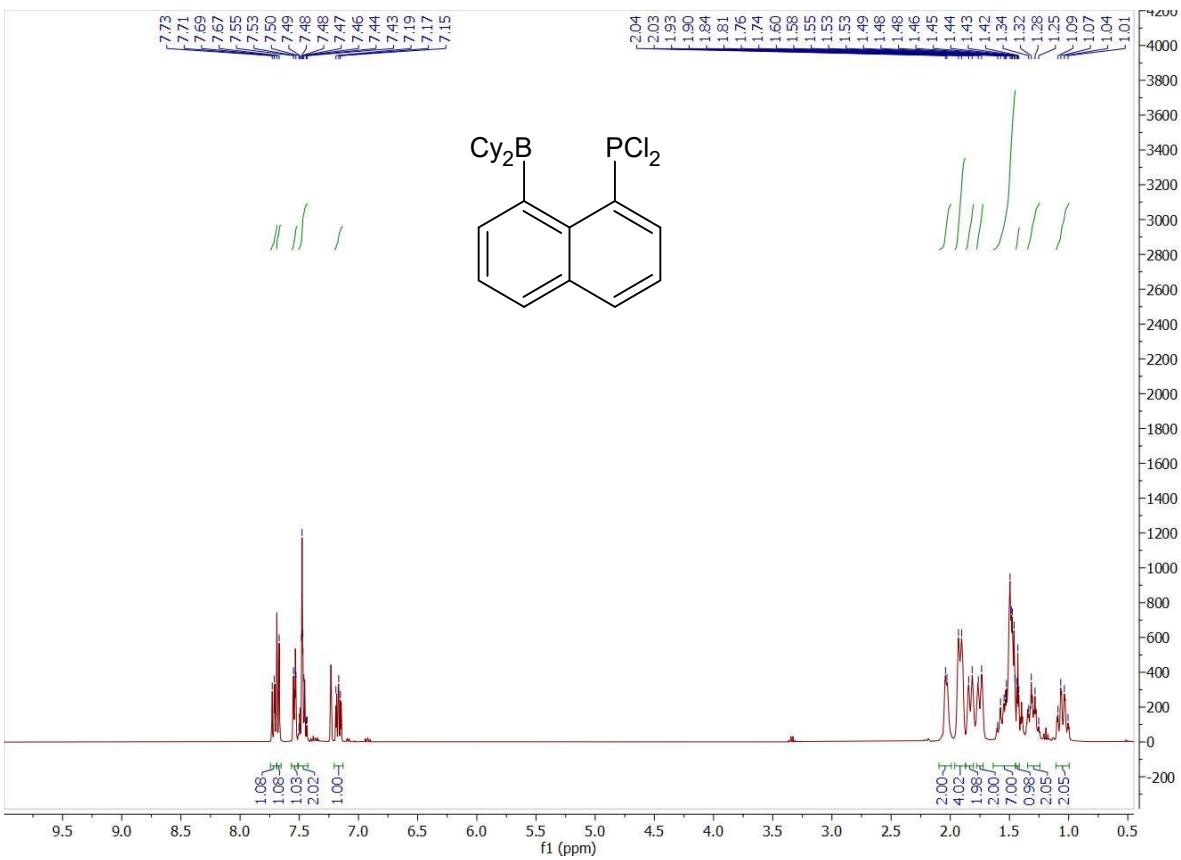


Figure S1. PovRay presentation of molecular structure of **3**. Hydrogen atoms are omitted for clarity.



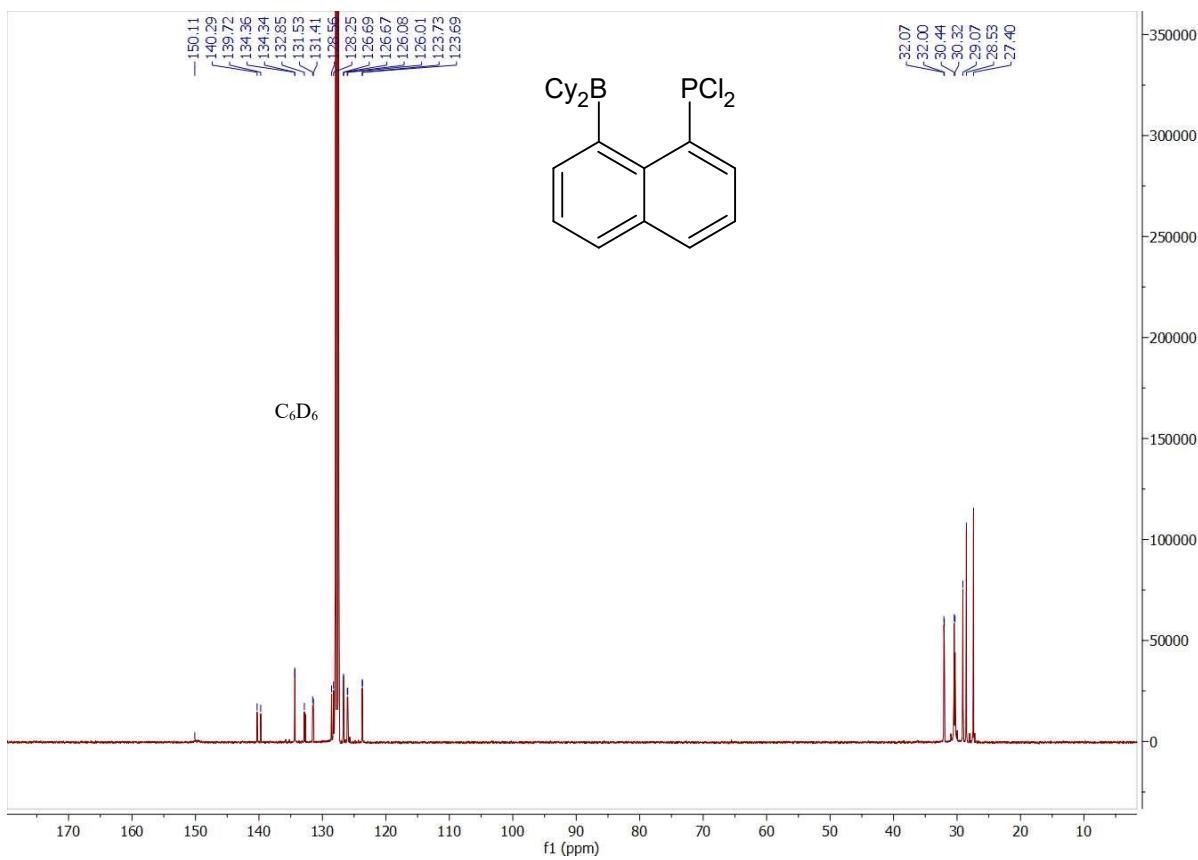


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.77 MHz) of 1-BCy₂-8-PCl₂-C₁₀H₆ (**1**)

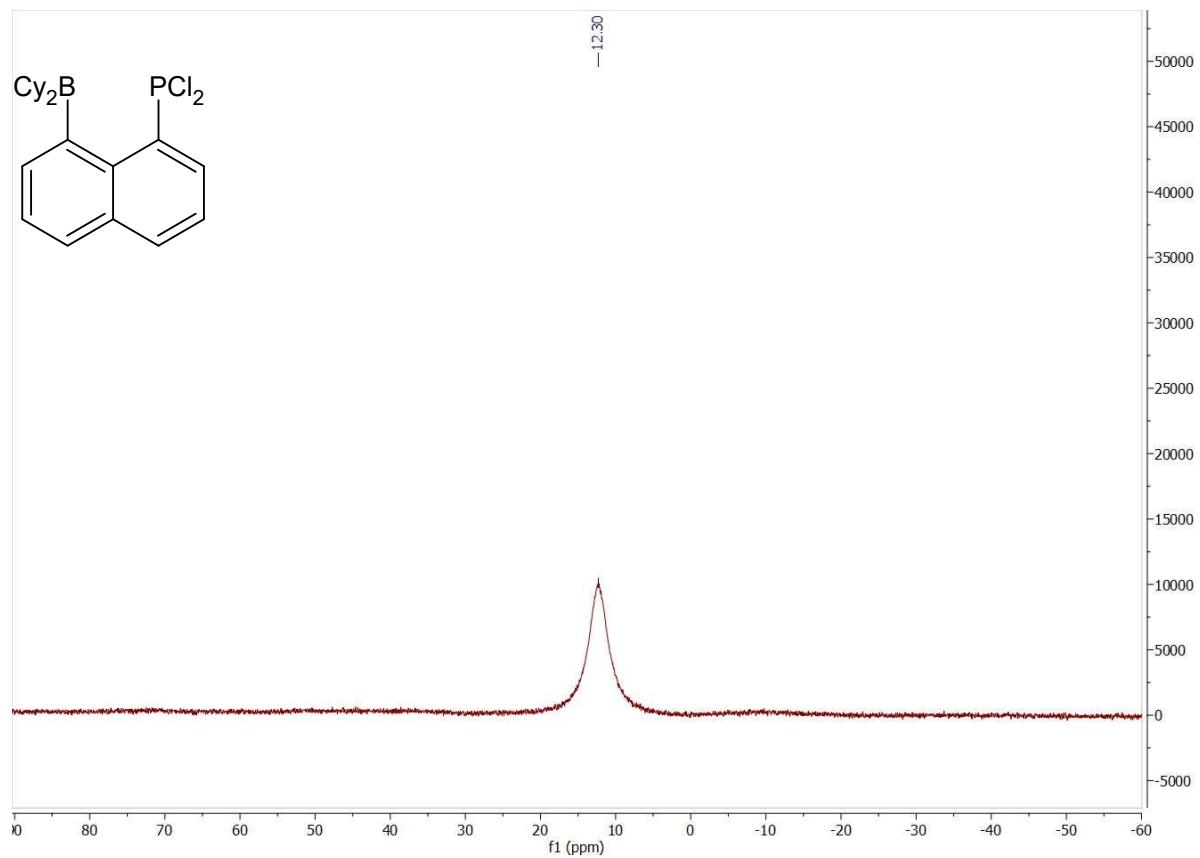


Figure S4. $^{11}\text{B}\{\text{H}\}$ NMR (C_6D_6 , 160.57 MHz) of $1-\text{BCy}_2\text{-8-PCl}_2\text{-C}_{10}\text{H}_6$ (**1**)

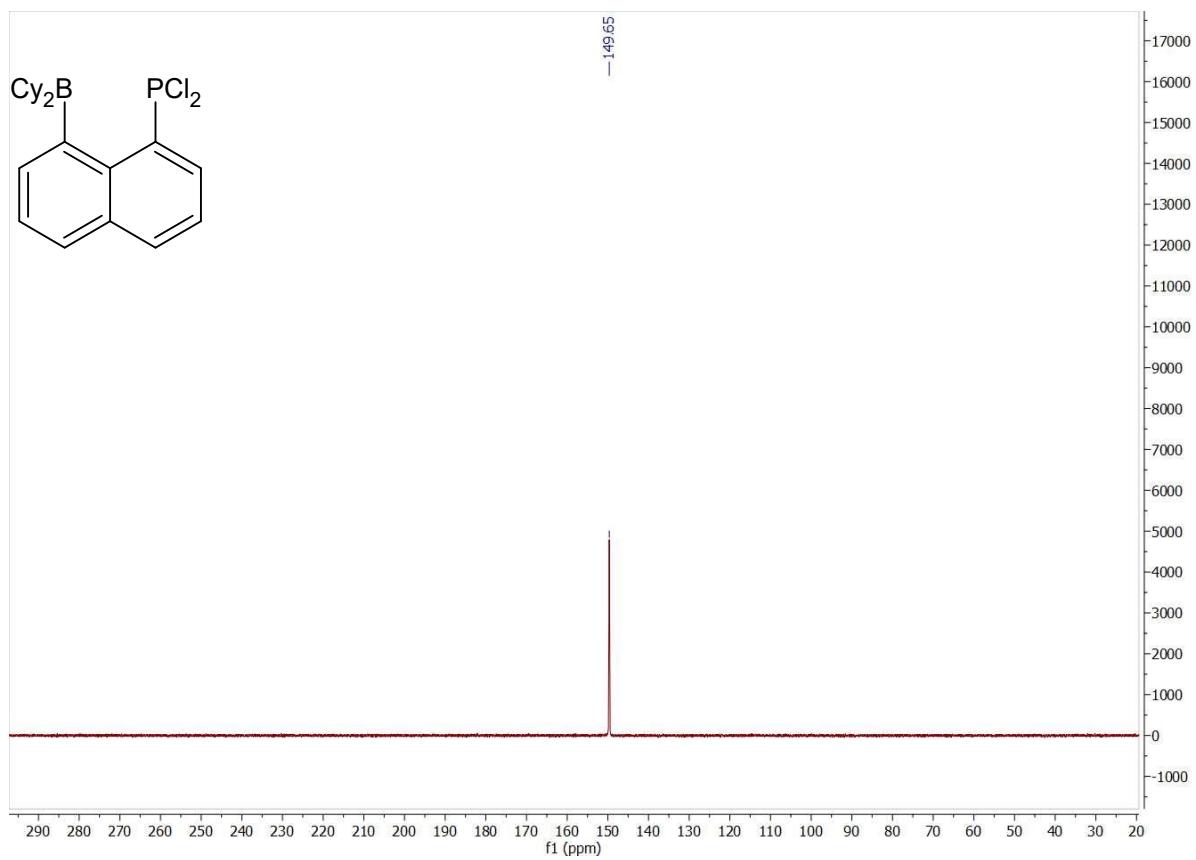


Figure S5. $^{31}\text{P}\{\text{H}\}$ NMR (C_6D_6 , 202.49 MHz) of $1-\text{BCy}_2\text{-}8\text{-PCl}_2\text{-C}_{10}\text{H}_6$ (**1**)

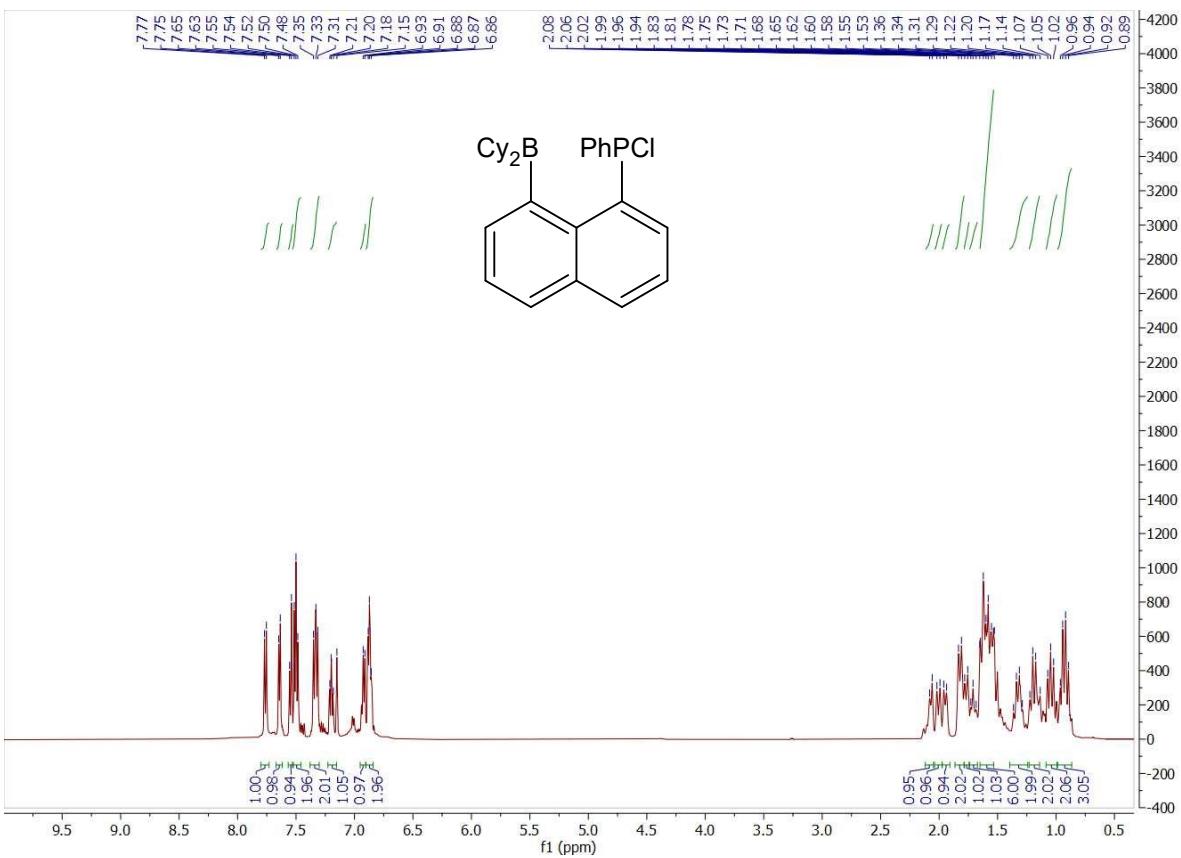


Figure S6. ^1H NMR (C_6D_6 , 500.13 MHz) of $1-\text{BCy}_2\text{-}8\text{-PPhCl-C}_{10}\text{H}_6$ (**2**)

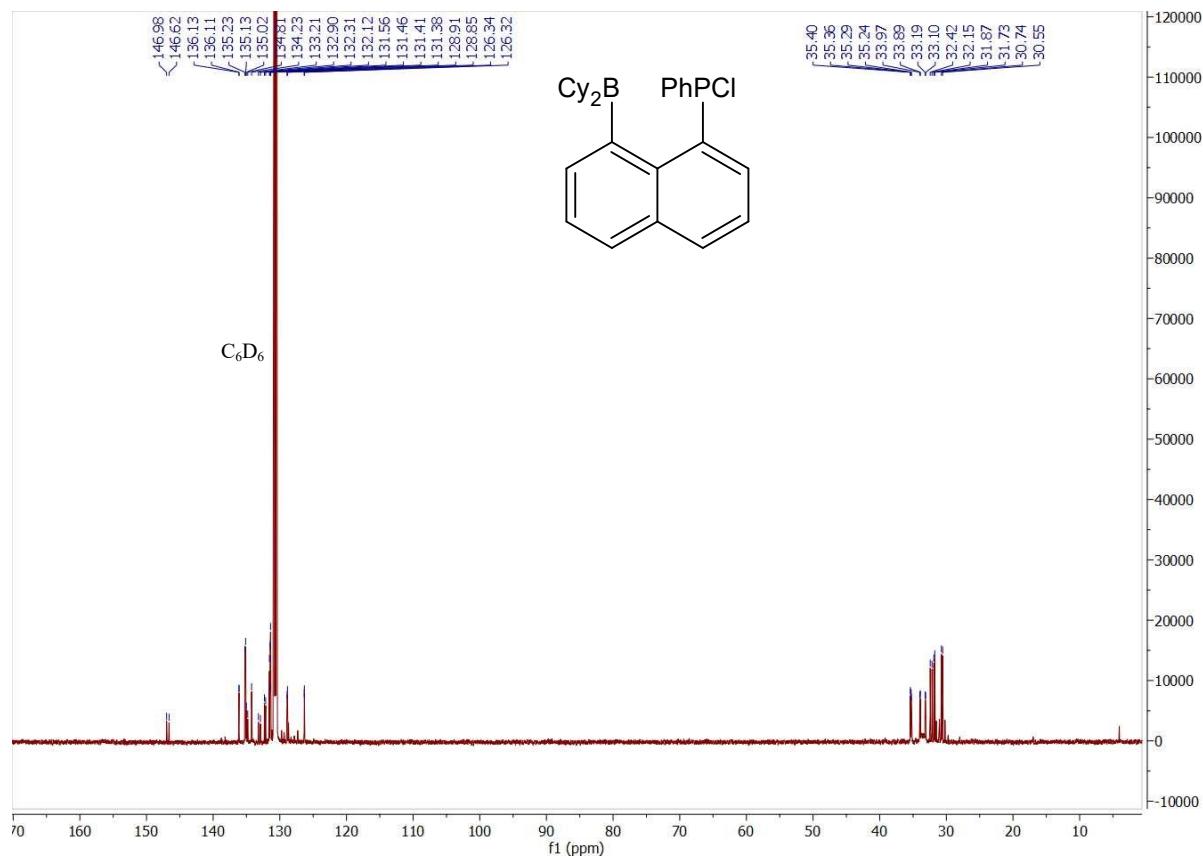


Figure S7. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.77 MHz) of 1- BCy_2 -8- $\text{PPhCl-C}_{10}\text{H}_6$ (**2**)

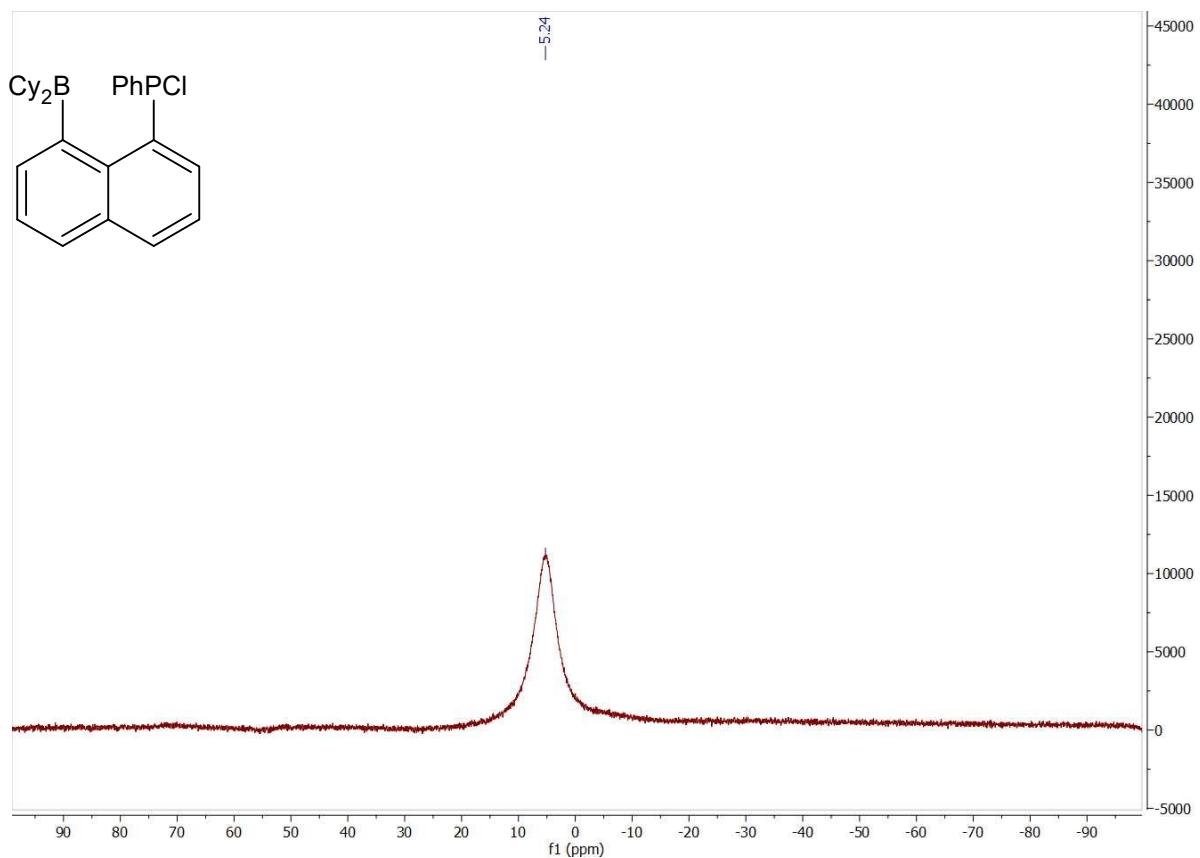


Figure S8. $^{11}\text{B}\{\text{H}\}$ NMR (C_6D_6 , 160.57 MHz) of $1-\text{BCy}_2\text{-}8\text{-PPhCl-C}_{10}\text{H}_6$ (**2**)

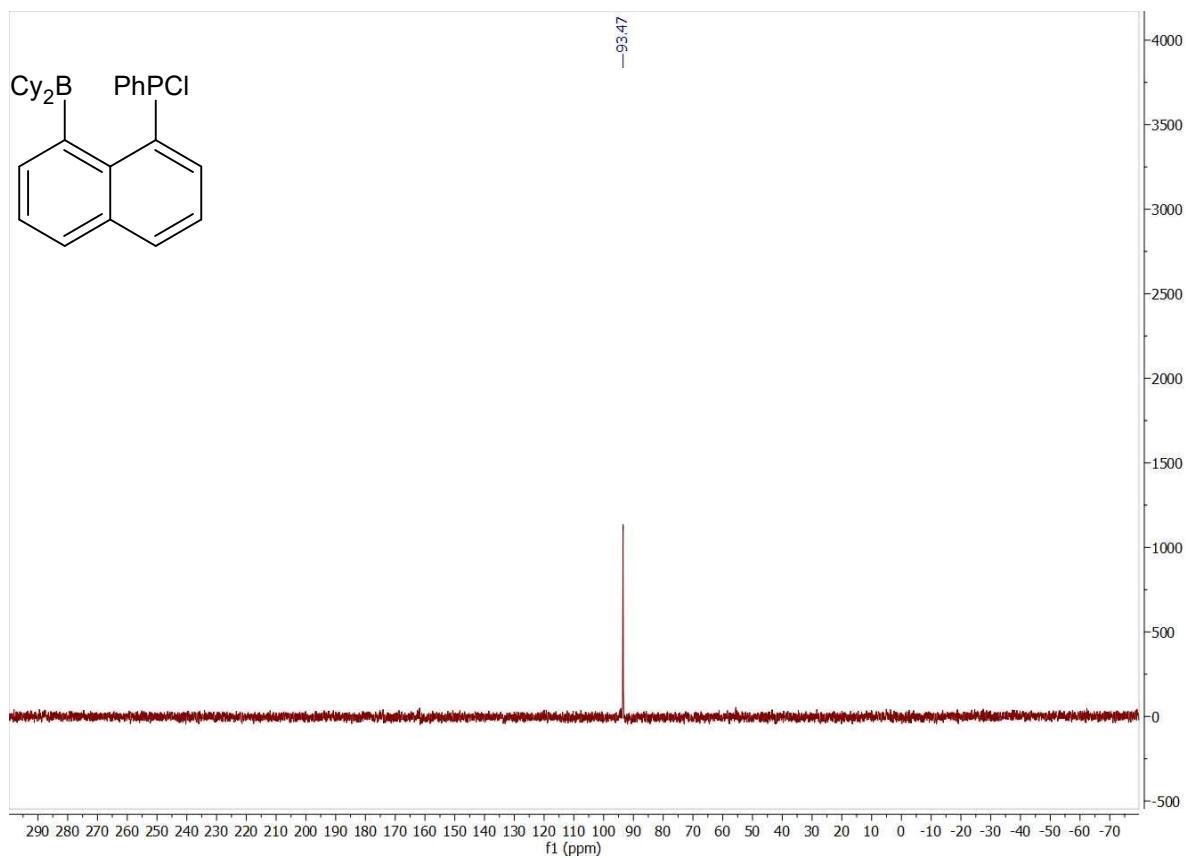


Figure S9. $^{31}\text{P}\{\text{H}\}$ NMR (C_6D_6 , 202.49 MHz) of $1-\text{BCy}_2\text{-}8\text{-PPhCl-C}_{10}\text{H}_6$ (**2**)

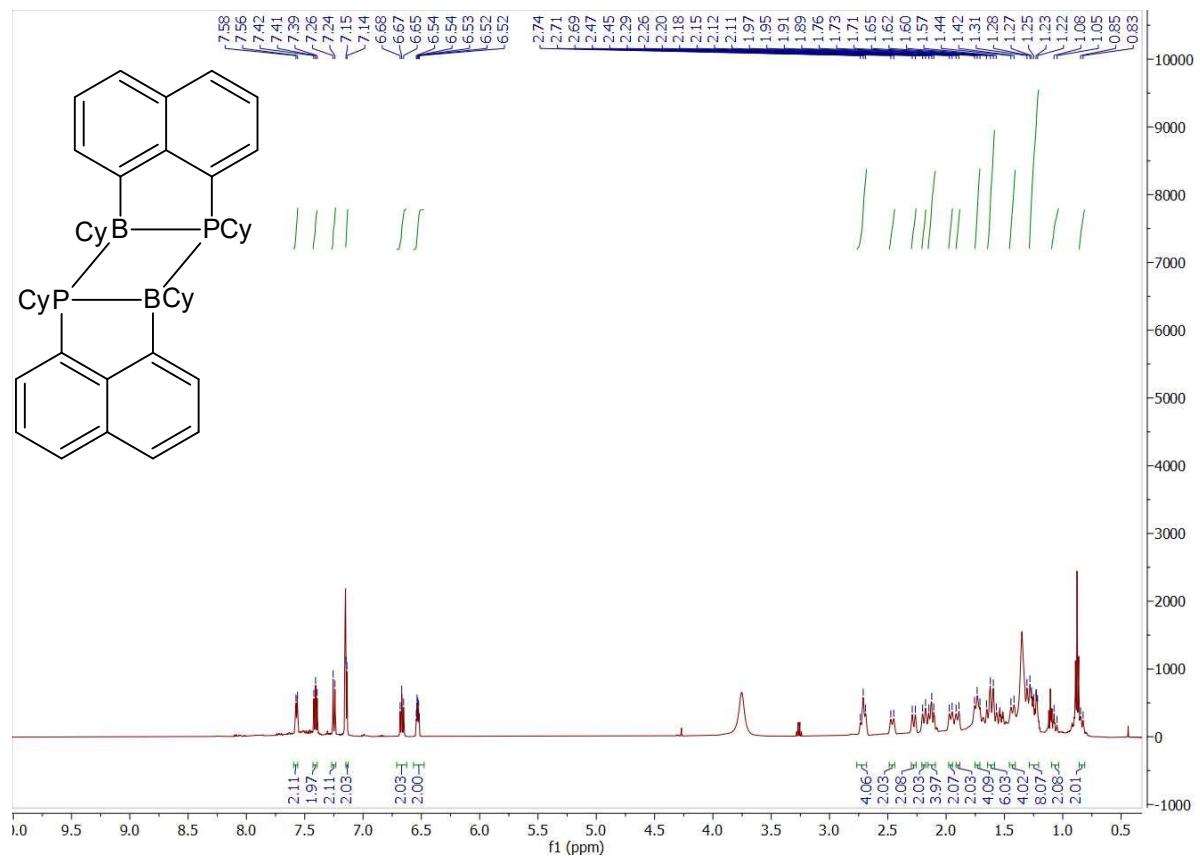


Figure S10. ^1H NMR ($\text{THF}-d_8$, 500.13 MHz) of $\{1-\text{BCy}-8-\text{PCy}-\text{C}_{10}\text{H}_6\}_2$ (**3**)

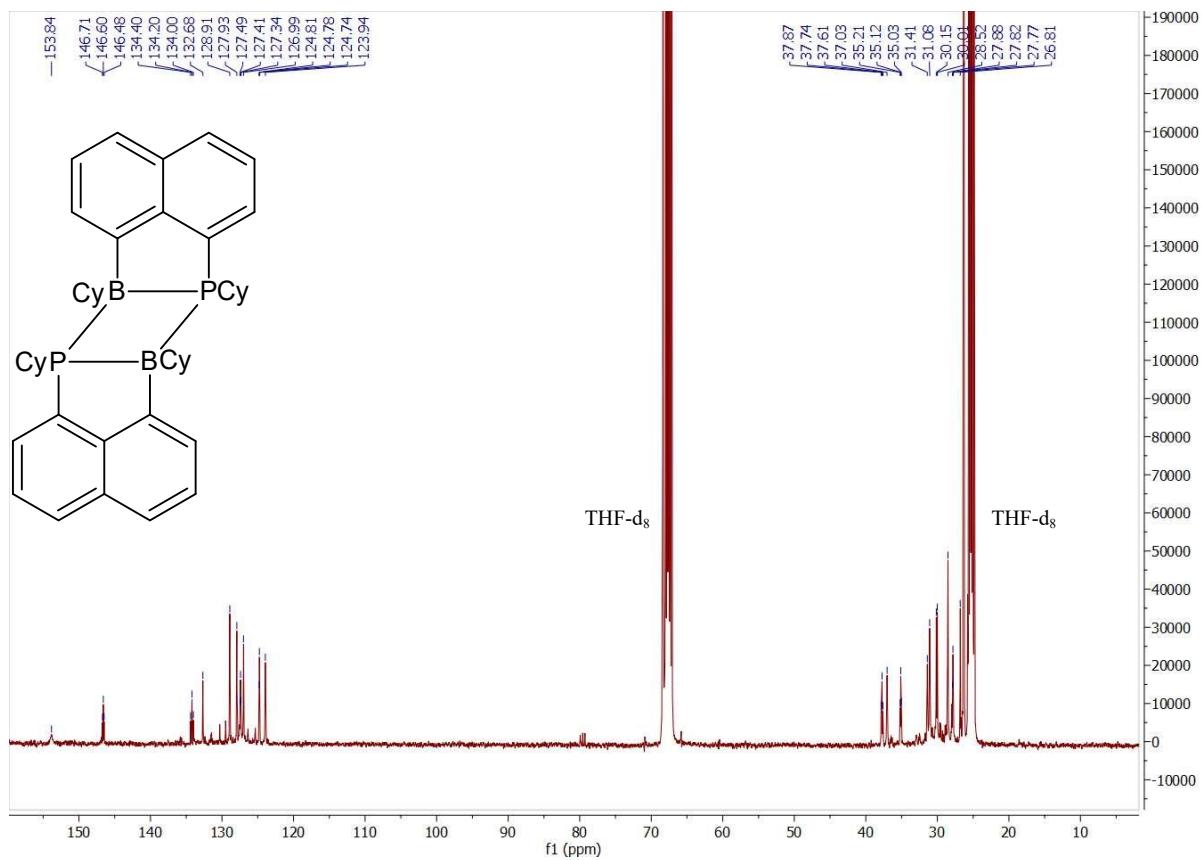


Figure S11. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 125.77 MHz) of $\{1-\text{BCy}-8-\text{PCy}-\text{C}_{10}\text{H}_6\}_2$ (**3**)

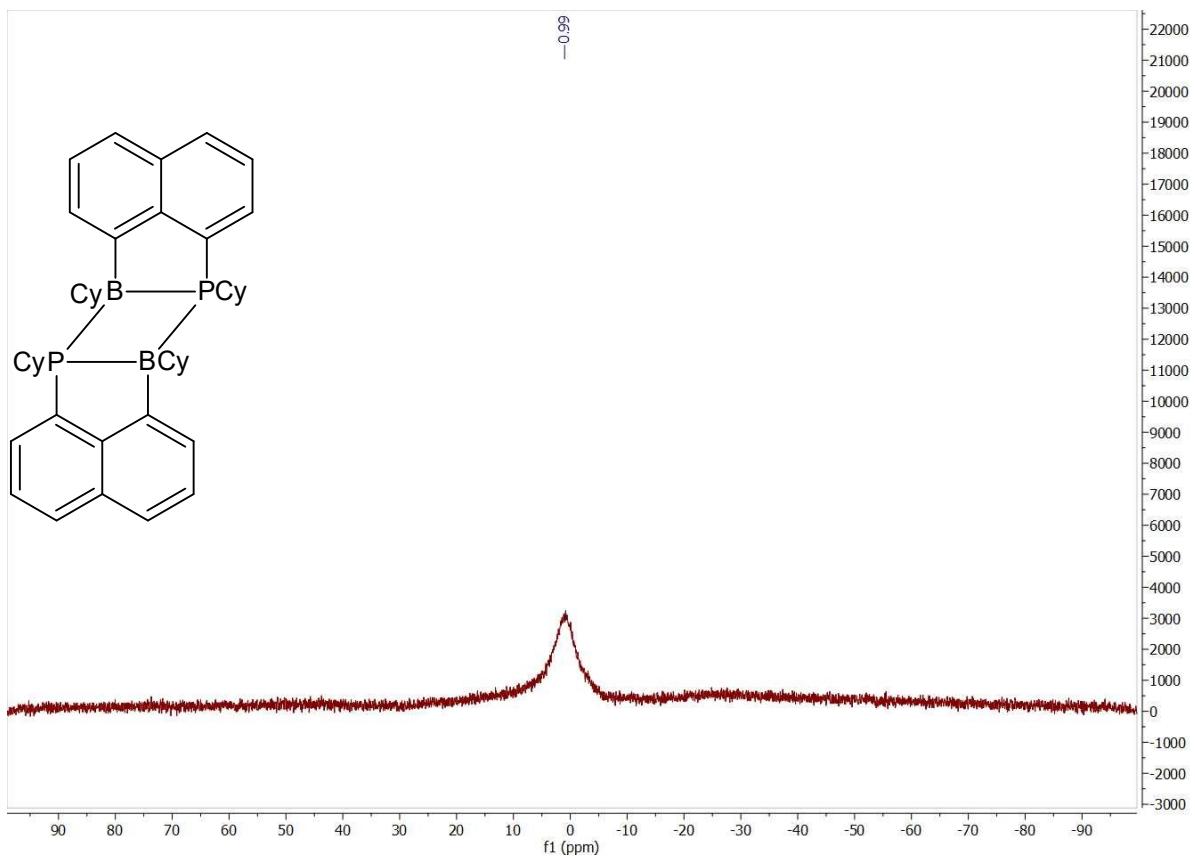


Figure S12. $^{11}\text{B}\{^1\text{H}\}$ NMR (THF- d_8 , 160.57 MHz) of $\{1-\text{BCy}-8-\text{PCy}-\text{C}_{10}\text{H}_6\}_2$ (3)

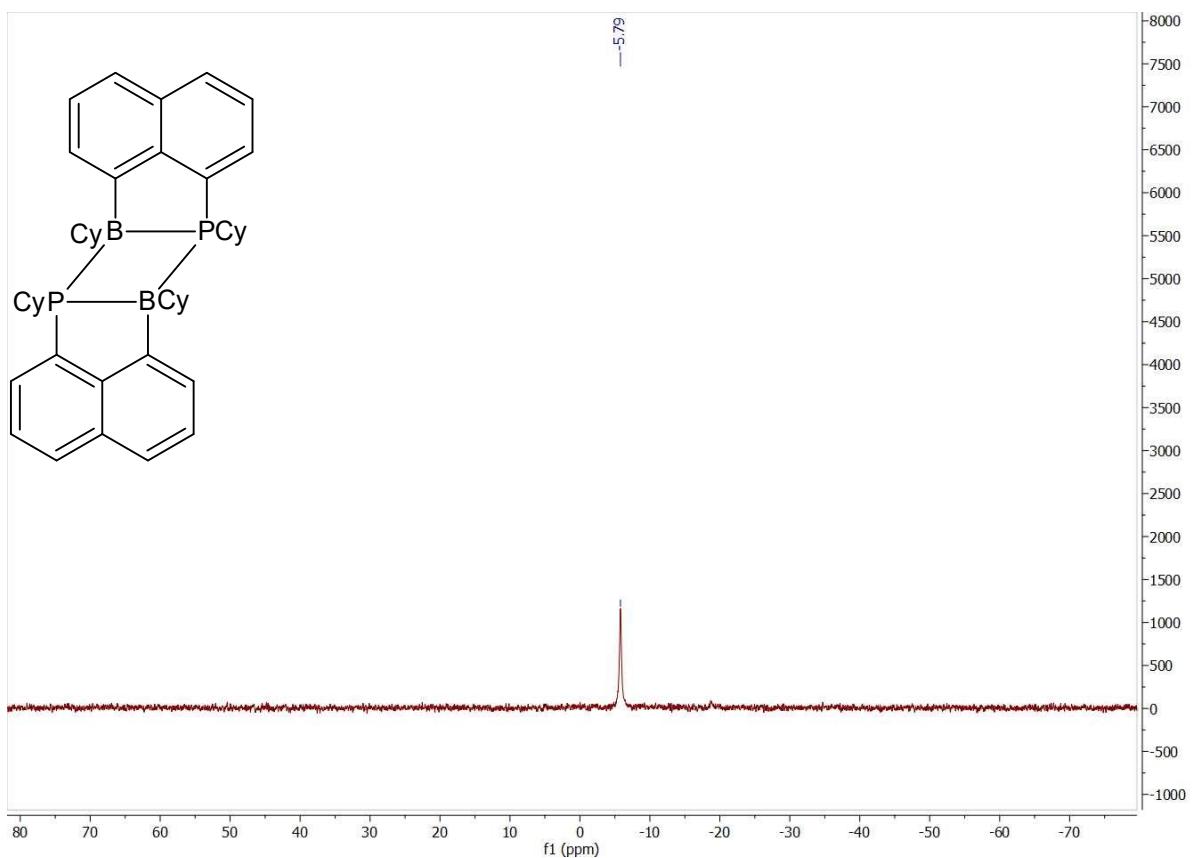


Figure S13. $^{31}\text{P}\{\text{H}\}$ NMR ($\text{THF}-d_8$, 202.49 MHz) of $\{1-\text{BCy}-8-\text{PCy}-\text{C}_{10}\text{H}_6\}_2$ (**3**)

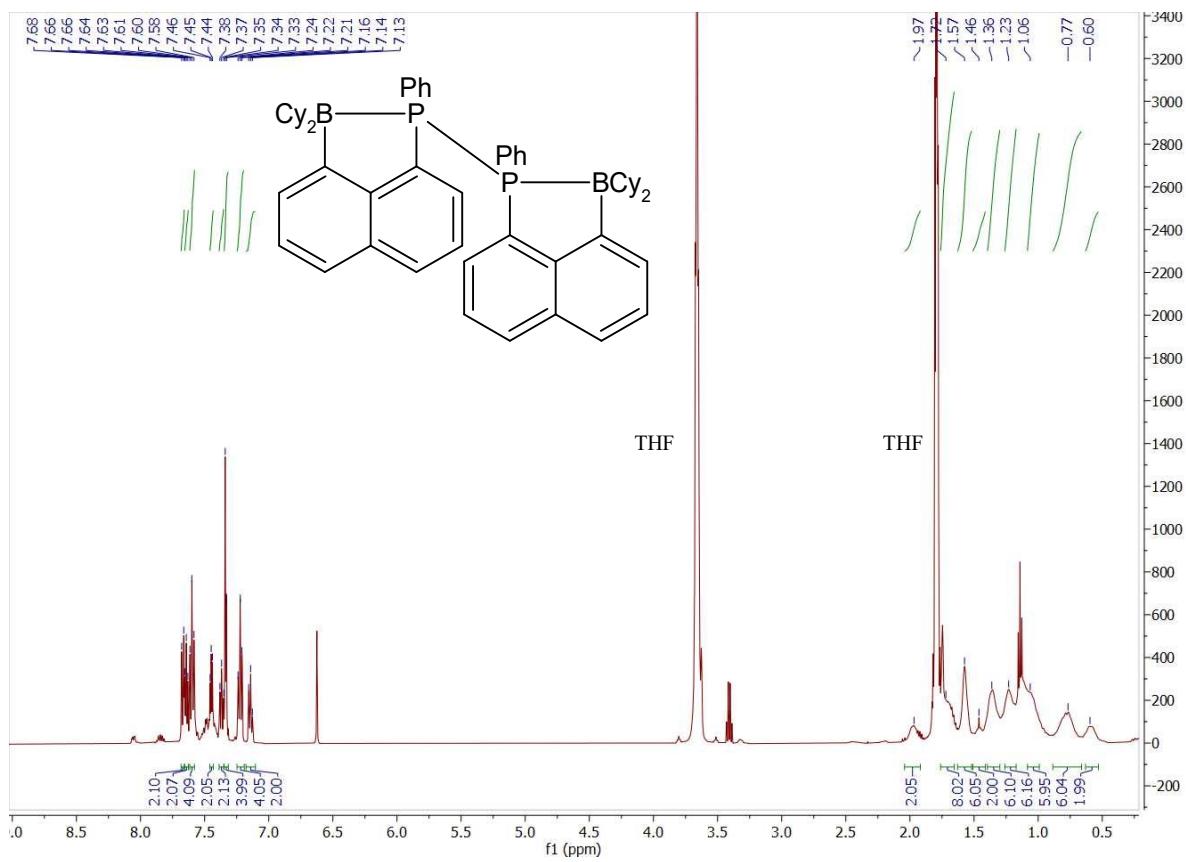


Figure S14. ^1H NMR ($\text{THF}-d_8$, 500.13 MHz) of $\{1-\text{BCy}_2-8-\text{PPh}-C_{10}\text{H}_6\}_2$ (**4**)

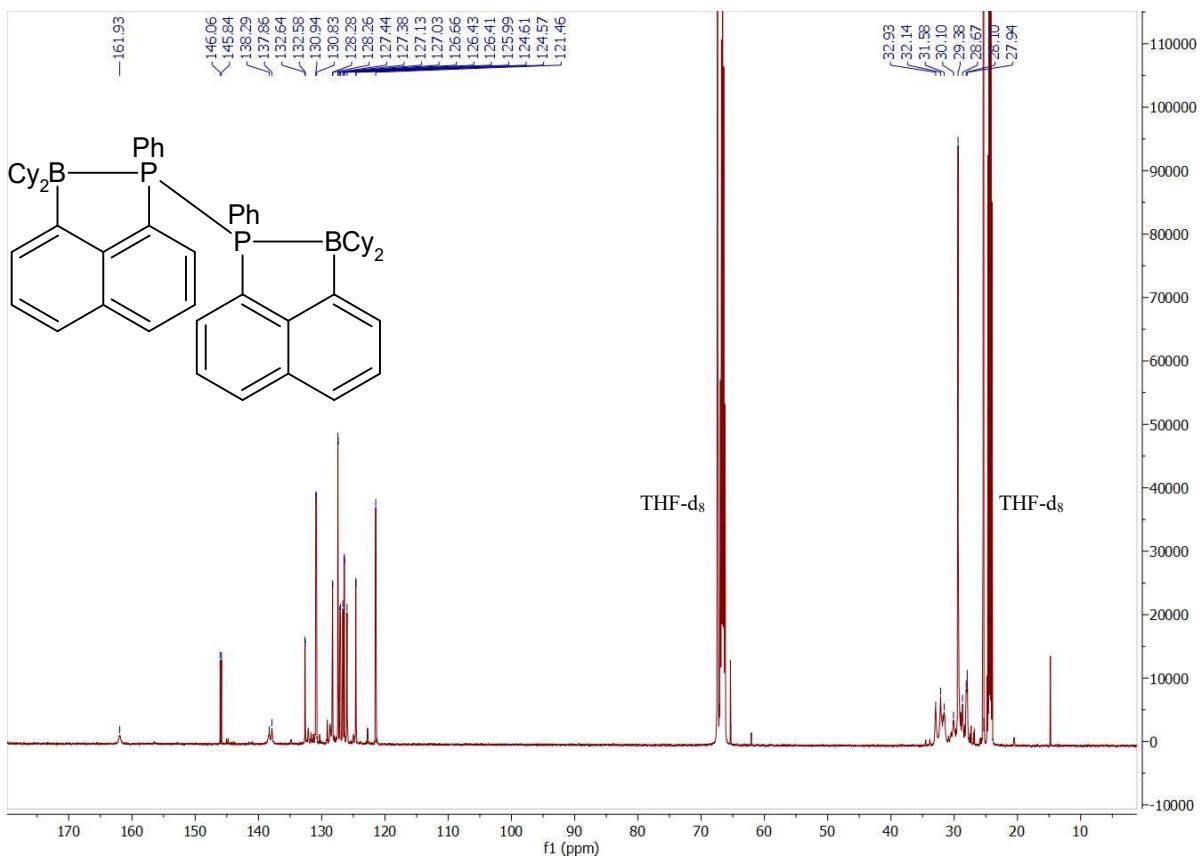


Figure S15. $^{13}\text{C}\{\text{H}\}$ NMR (THF-d_8 , 125.77 MHz) of $\{1-\text{BCy}_2-8-\text{PPh-C}_{10}\text{H}_6\}_2$ (**4**)

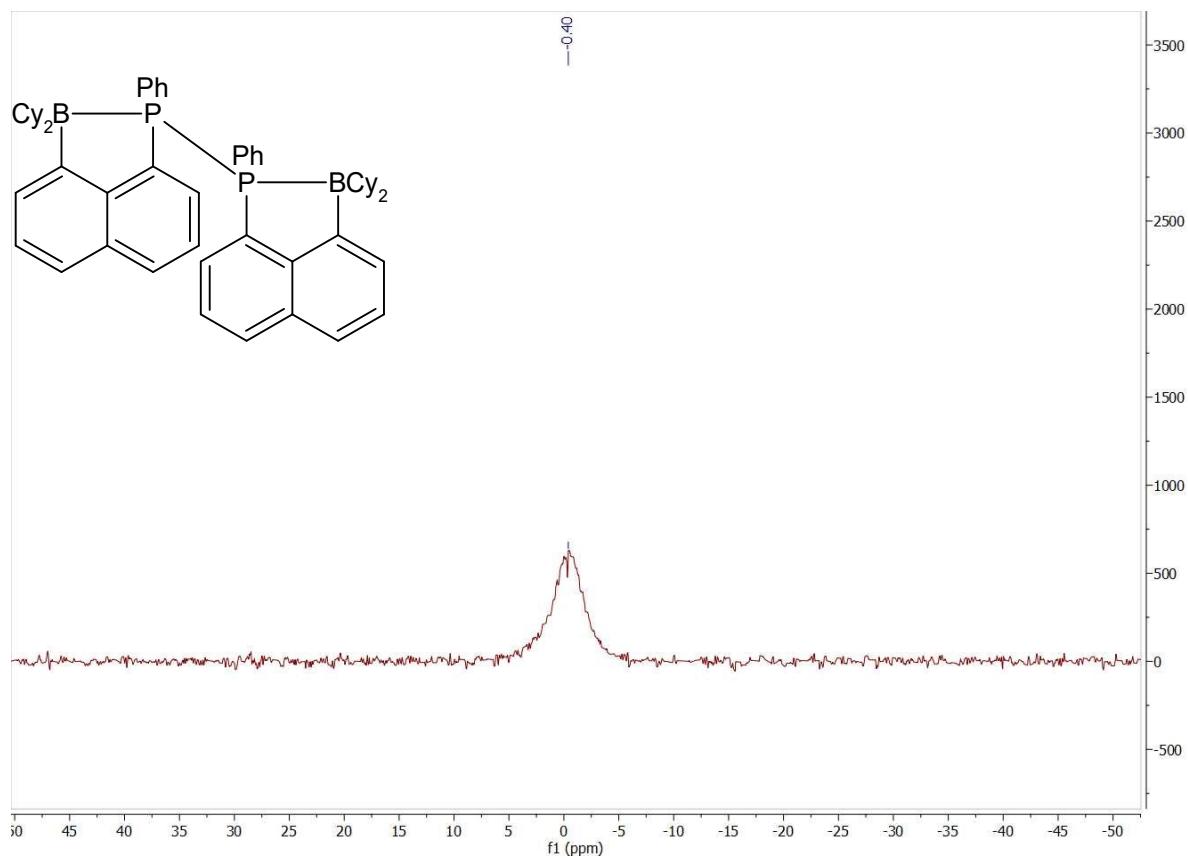


Figure S16. ¹¹B{¹H} NMR (THF-d₈, 160.57 MHz) of {1-BCy₂-8-PPh-C₁₀H₆}₂ (**4**)

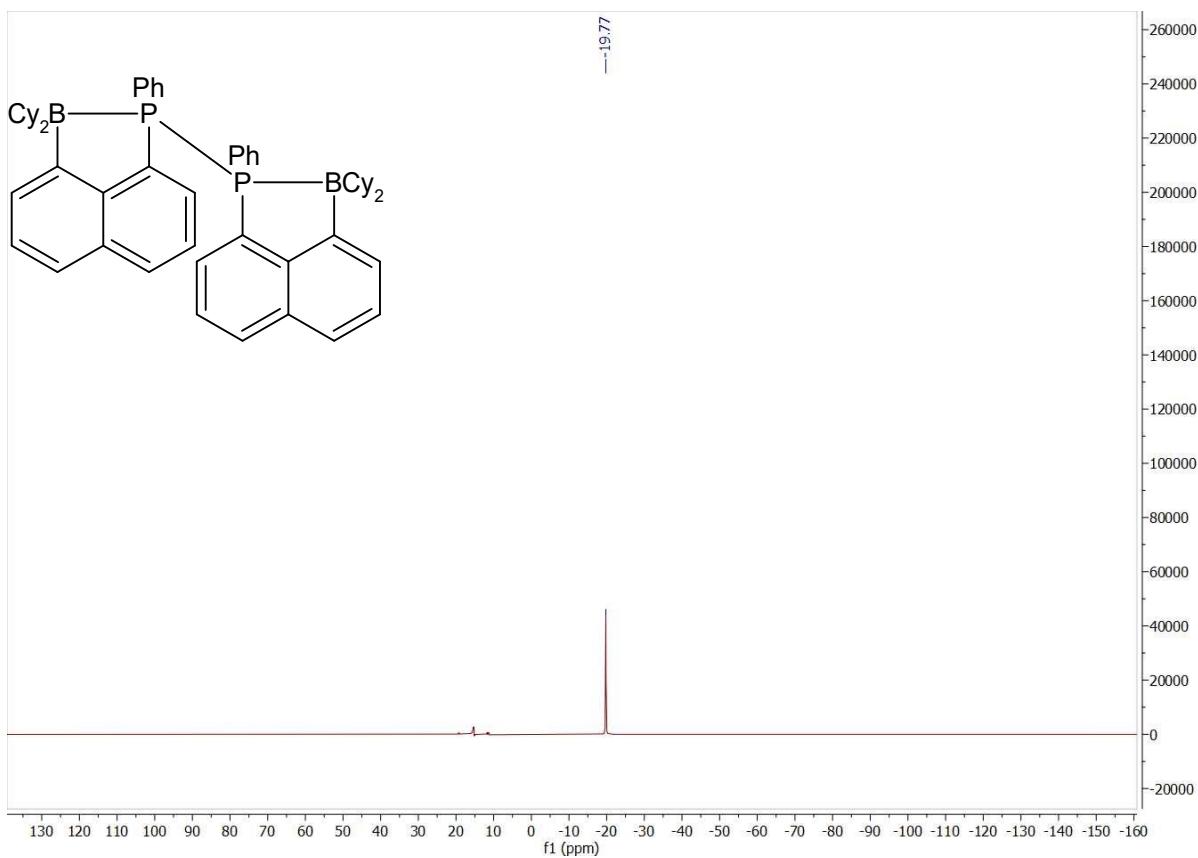


Figure S17. $^{31}P\{^1H\}$ NMR (THF- d_8 , 202.49 MHz) of $\{1-BCy_2-8-PPh-C_{10}H_6\}_2$ (4)

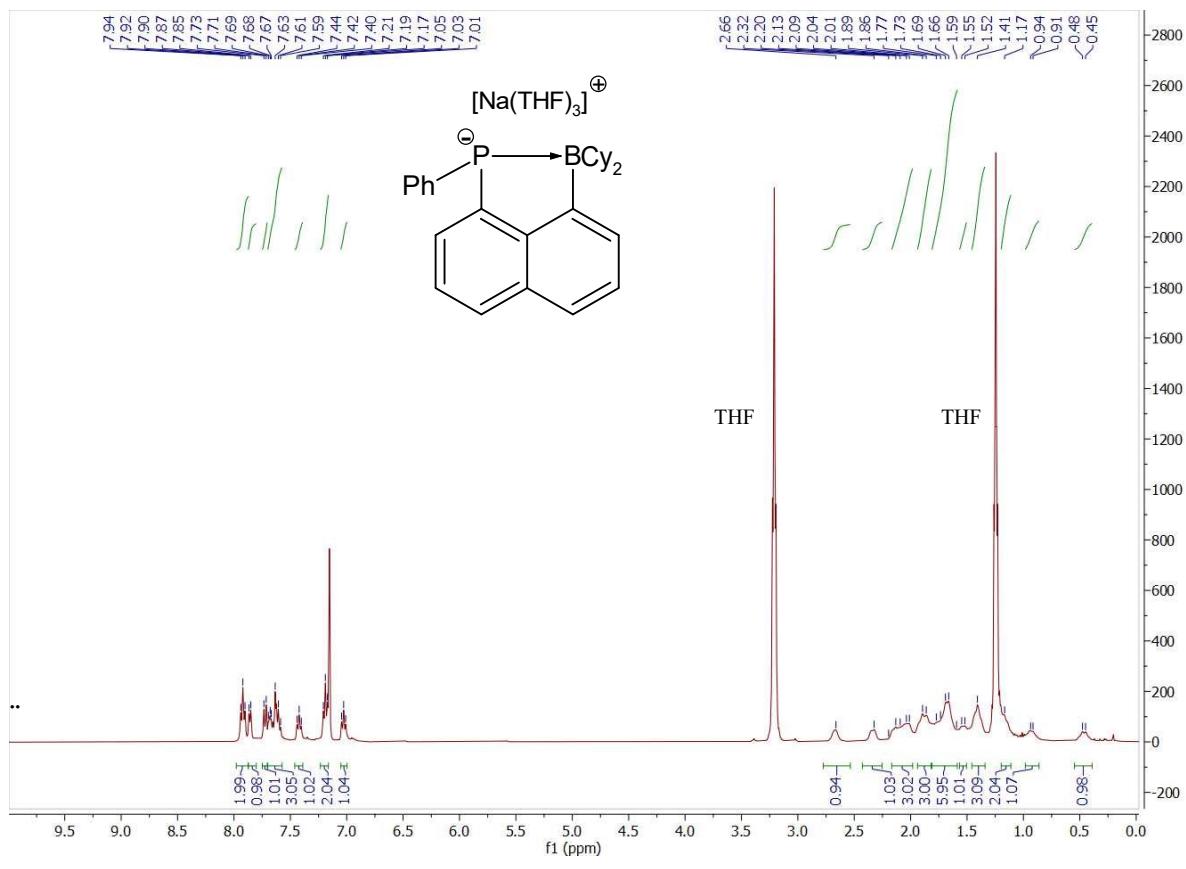


Figure S18. ^1H NMR ($\text{THF}-d_8$, 500.13 MHz) of $[\text{Na}(\text{THF})_3]^+ [1-\text{BCy}_2-8-\text{PPh}-\text{C}_{10}\text{H}_6]^-$ (5)

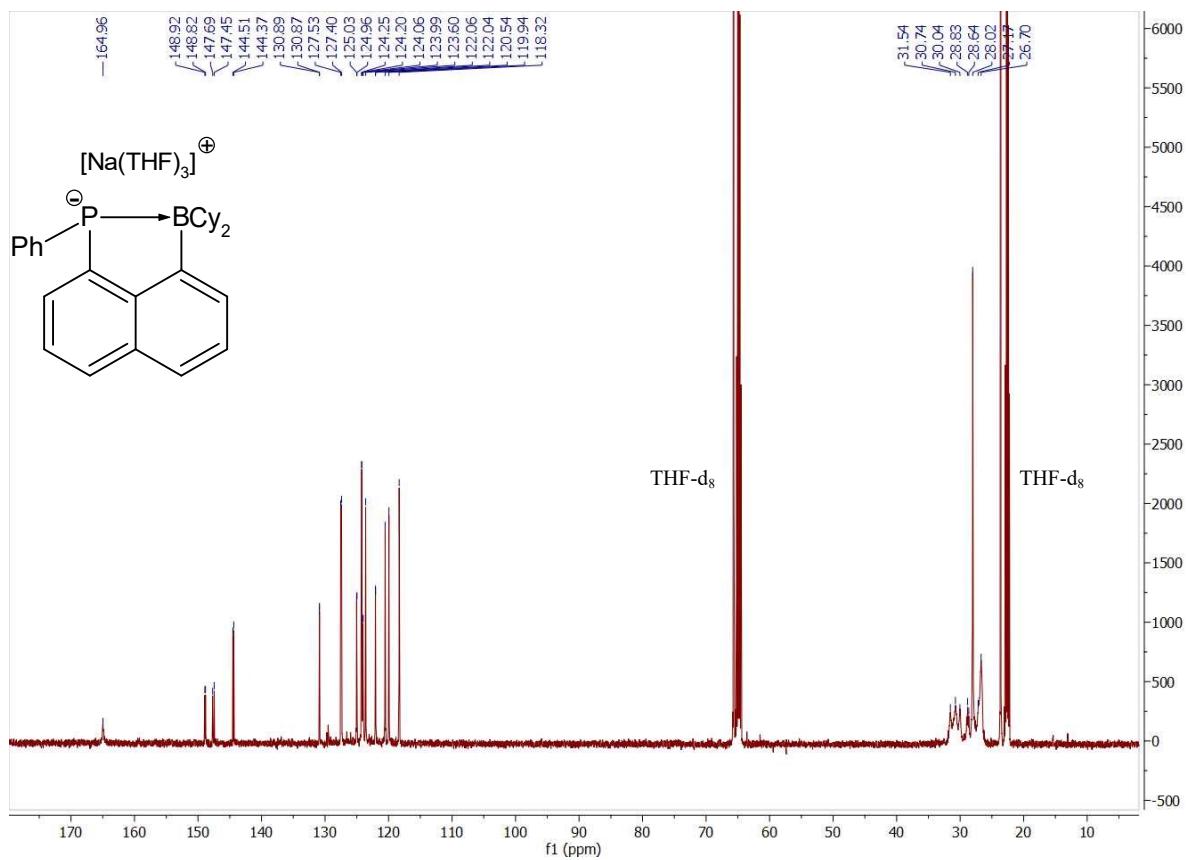


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-d₈, 125.77 MHz) of $[\text{Na}(\text{THF})_3]^+ [1-\text{BCy}_2-8-\text{PPh}-\text{C}_{10}\text{H}_6]^-$ (5)

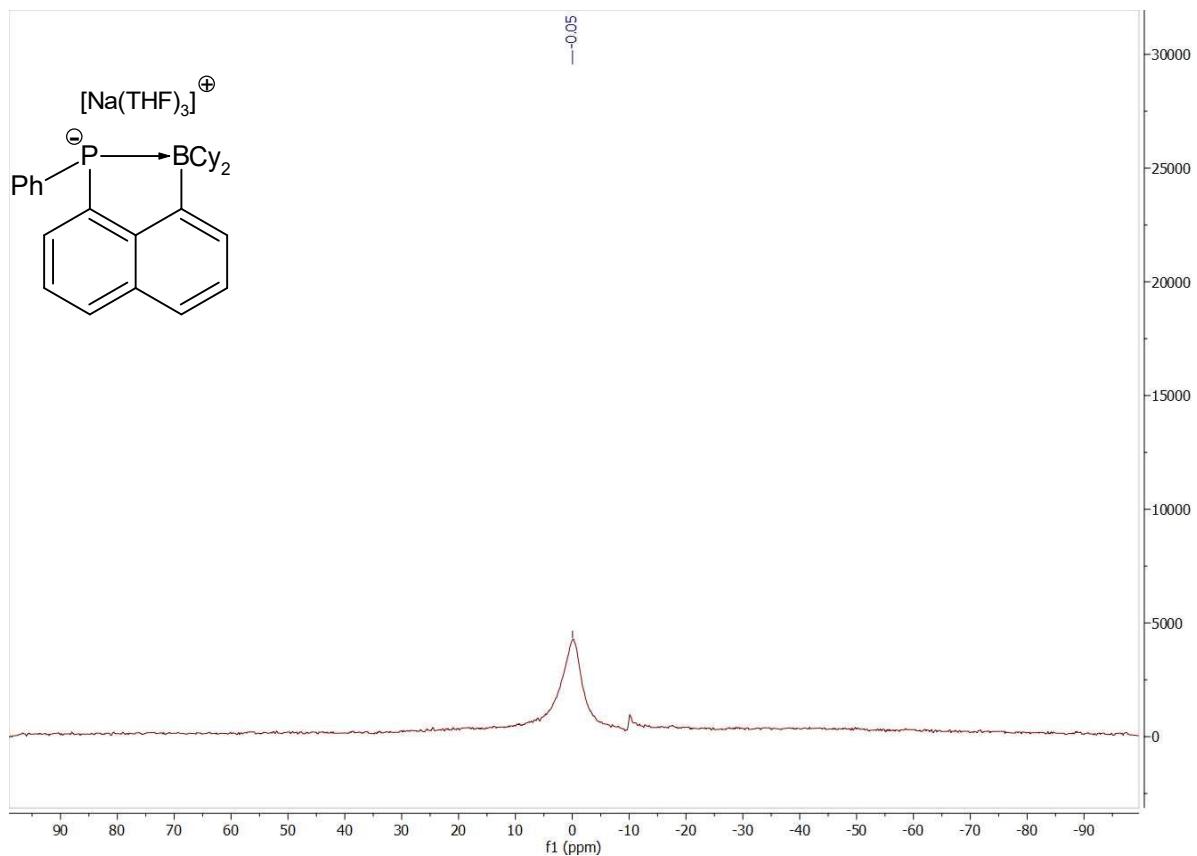


Figure S20. $^{11}B\{^1H\}$ NMR ($THF-d_8$, 160.57 MHz) of $[Na(THF)_3]^+ [1-BCy_2-8-PPh-C_{10}H_6]^-$ (5)

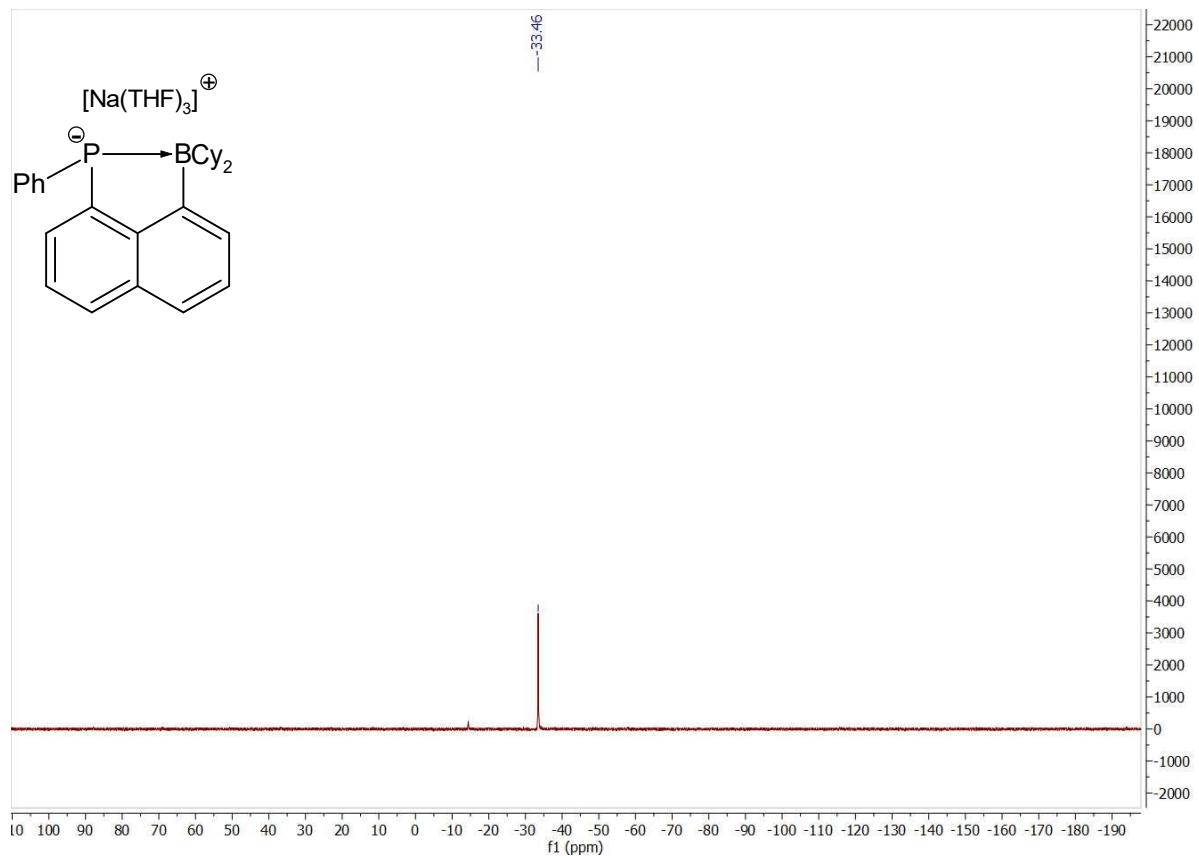


Figure S21. $^{31}\text{P}\{\text{H}\}$ NMR ($\text{THF}-d_8$, 202.49 MHz) of $[\text{Na}(\text{THF})_3]^+ [1-\text{BCy}_2-8-\text{PPh}-\text{C}_{10}\text{H}_6]^-$ (5)

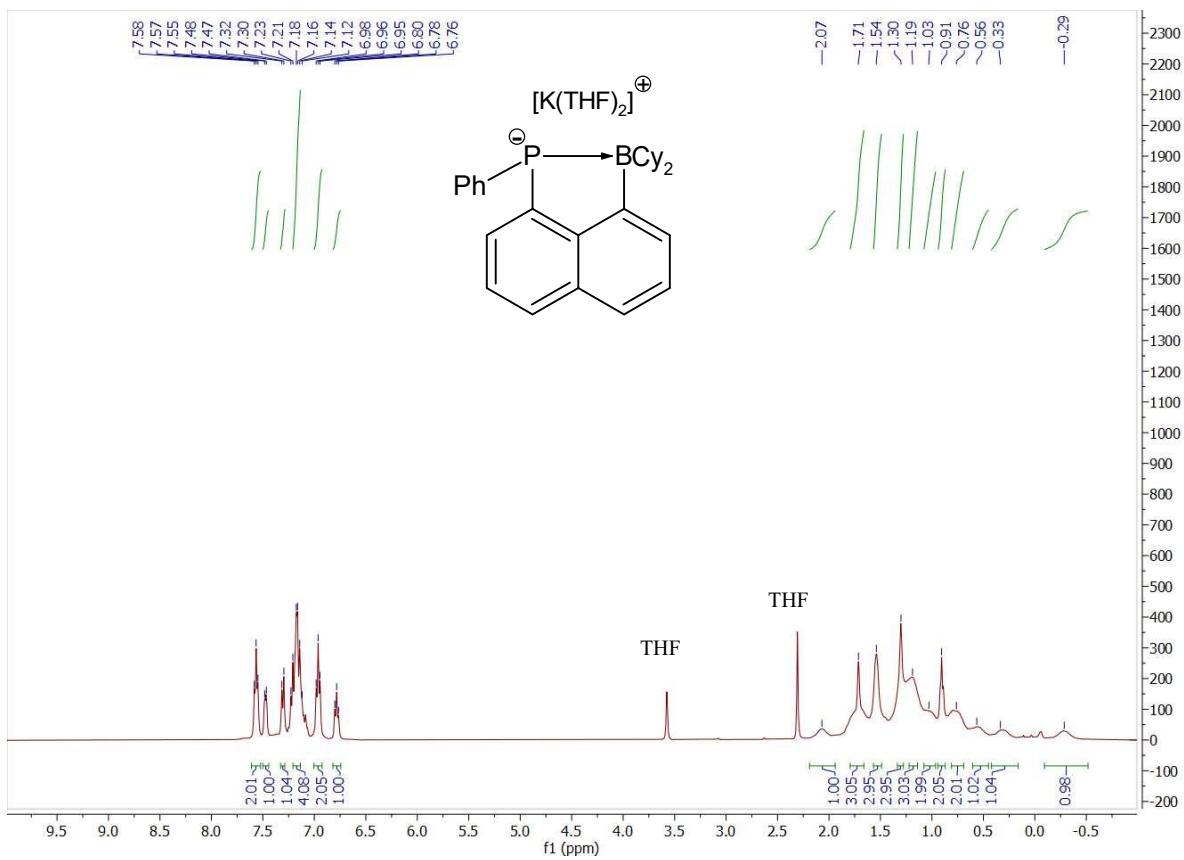


Figure S22. ^1H NMR ($\text{THF}-d_8$, 500.13 MHz) of $\{[\text{K}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{PPh-C}_{10}\text{H}_6]\}_\infty$ (6)

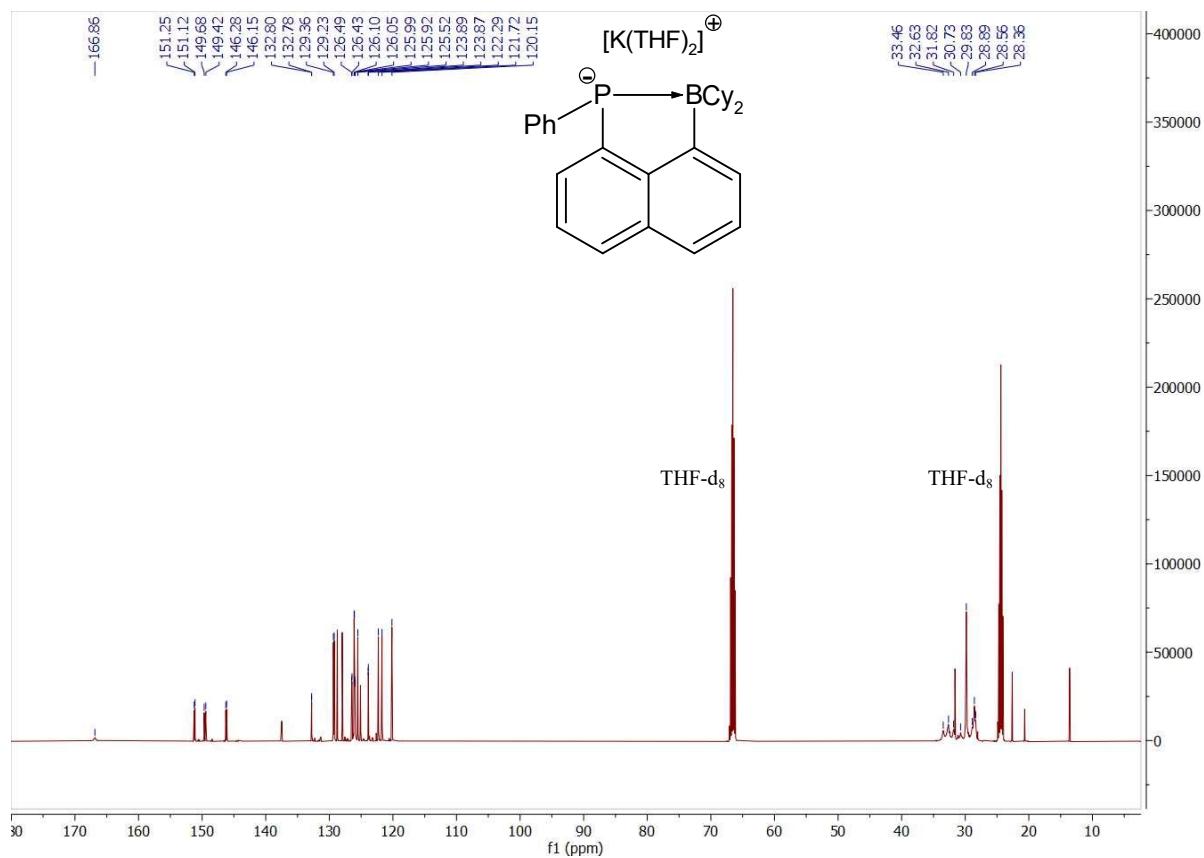


Figure S23. $^{13}\text{C}^{\{1\text{H}\}}$ NMR (THF-d_8 , 125.77 MHz) of $\{[\text{K}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{PPh}-\text{C}_{10}\text{H}_6]\}_\infty$ (6)

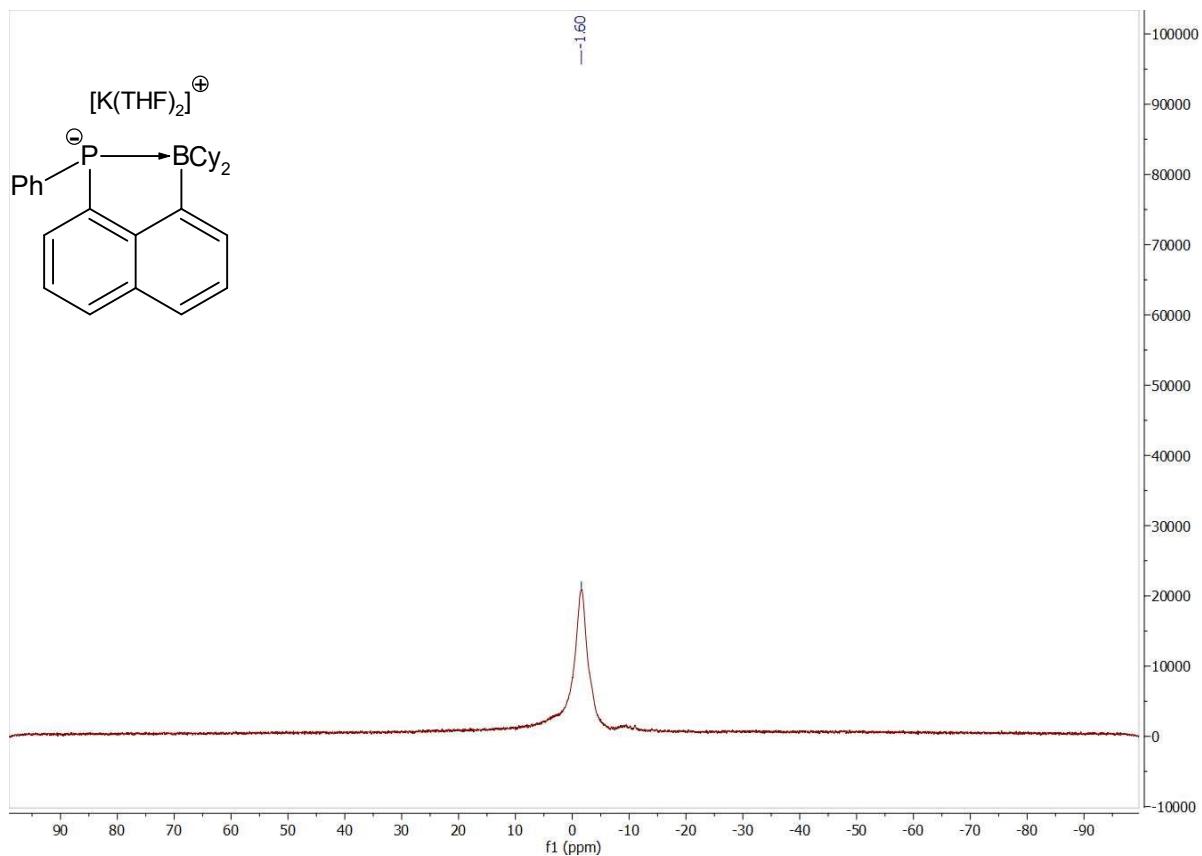


Figure S24. $^{11}\text{B}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$, 160.57 MHz) of $\{[K(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{PPh-C}_{10}\text{H}_6]\}_\infty$ (**6**)

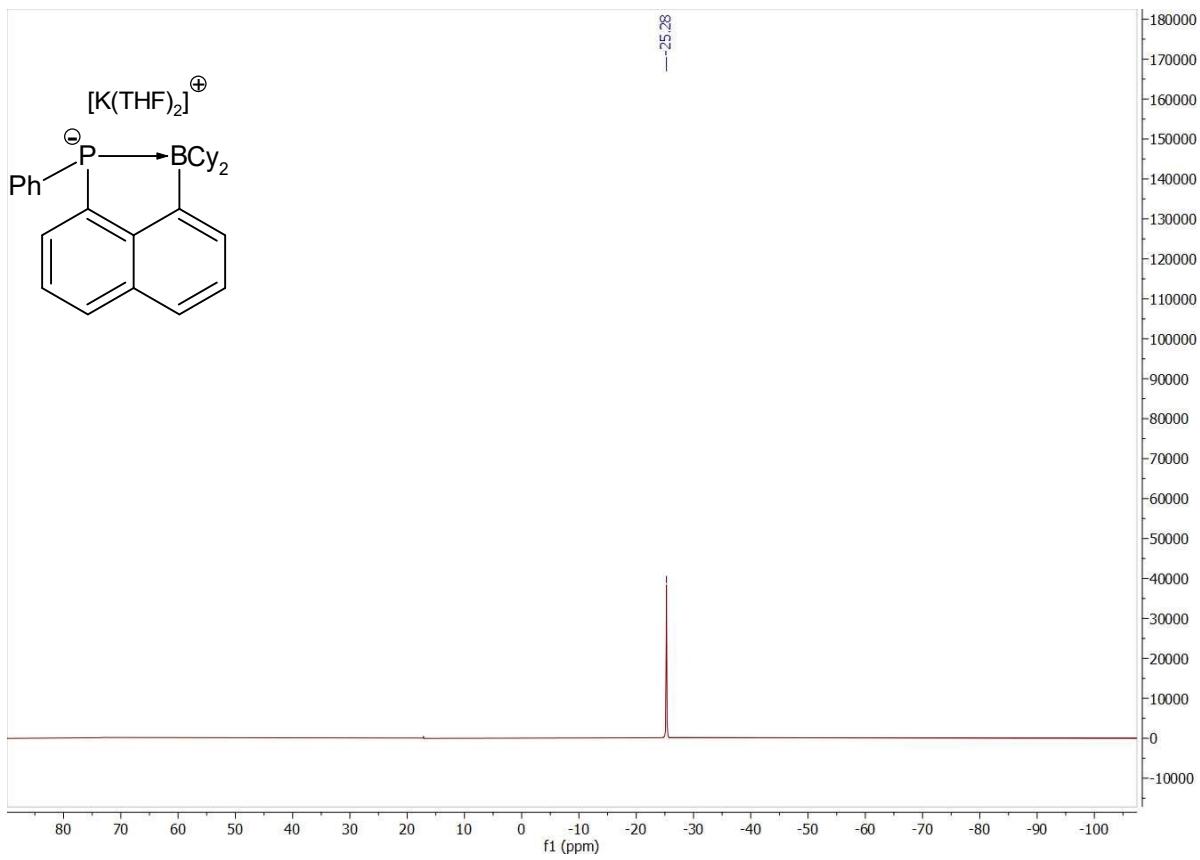


Figure S25. $^{31}\text{P}\{\text{H}\}$ NMR ($\text{THF}-d_8$, 202.49 MHz) of $\{[K(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{PPh}-\text{C}_{10}\text{H}_6]\}_\infty^-$ (6)

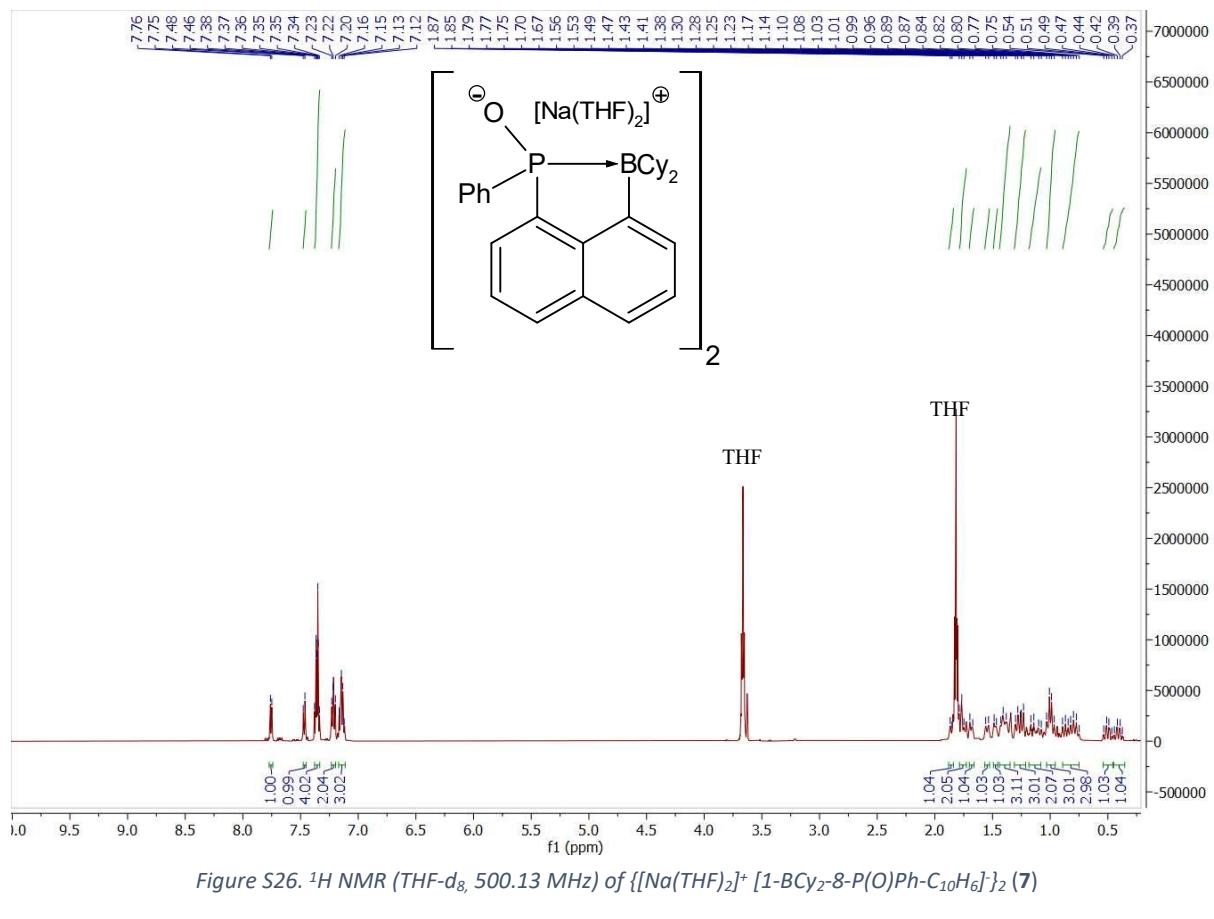


Figure S26. ^1H NMR ($\text{THF}-d_8$, 500.13 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}(\text{O})\text{Ph}-\text{C}_{10}\text{H}_6]\}_2$ (**7**)

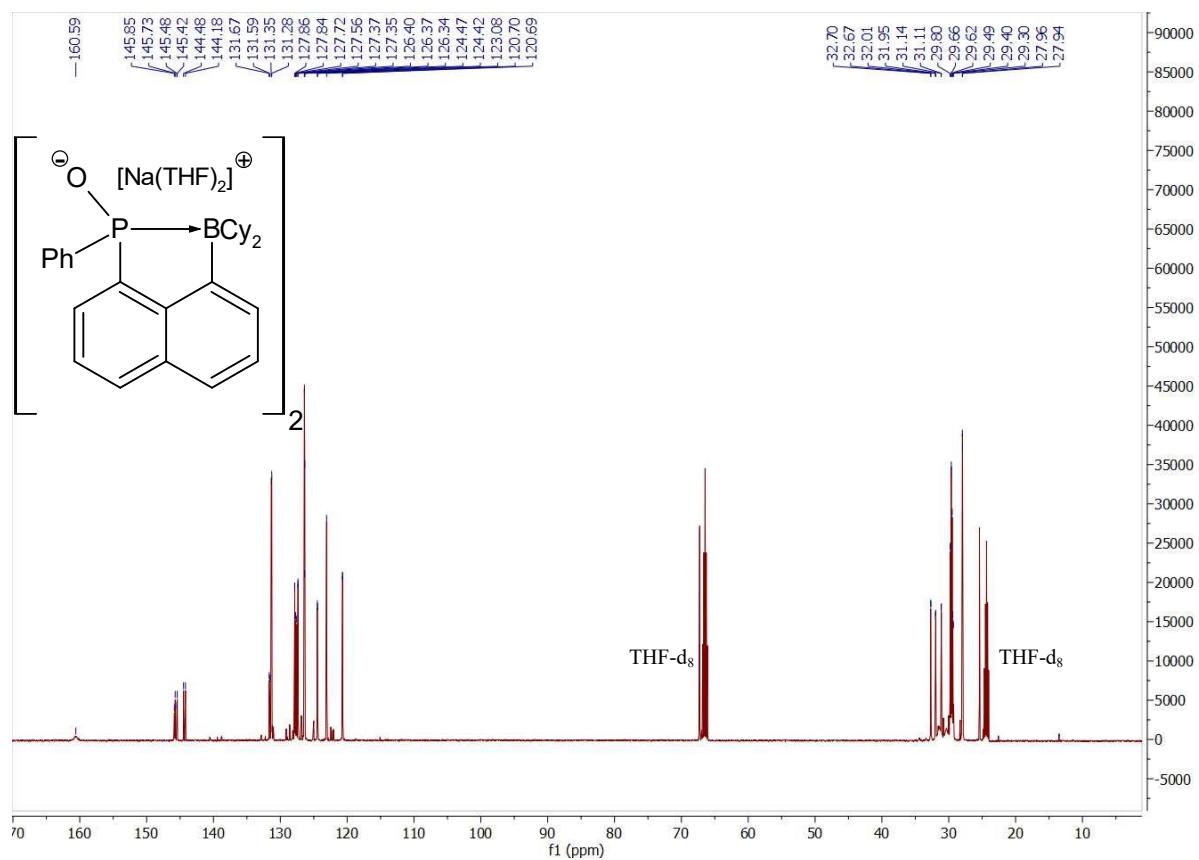


Figure S27. $^{13}\text{C}\{\text{H}\}$ NMR (THF-d₈, 125.77 MHz) of $\{[\text{Na(THF)}_2]^+ [1\text{-BCy}_2\text{-}8\text{-P}(\text{O})\text{Ph-C}_{10}\text{H}_6]\}_2$ (7)

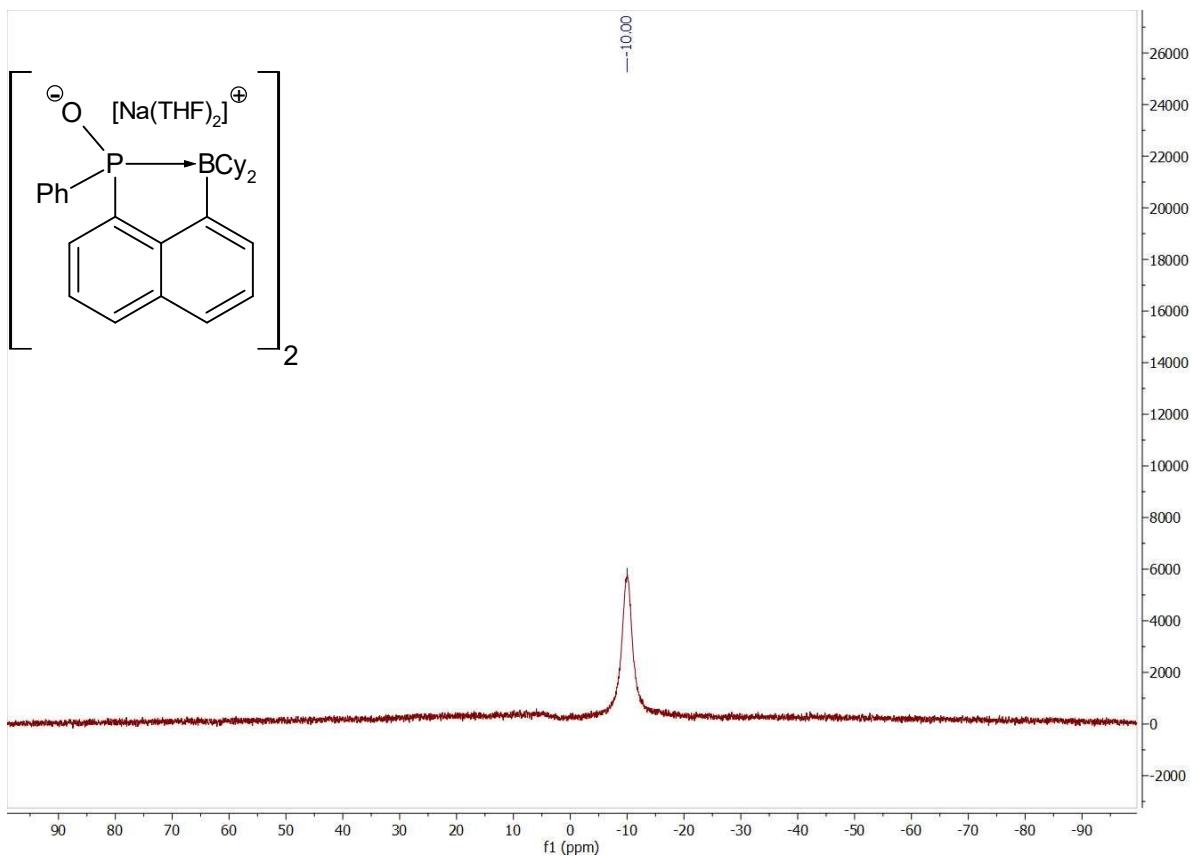


Figure S28. $^{11}\text{B}\{\text{H}\}$ NMR ($\text{THF}-d_8$, 160.57 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}(\text{O})\text{Ph}-\text{C}_{10}\text{H}_6]\}_2$ (7)

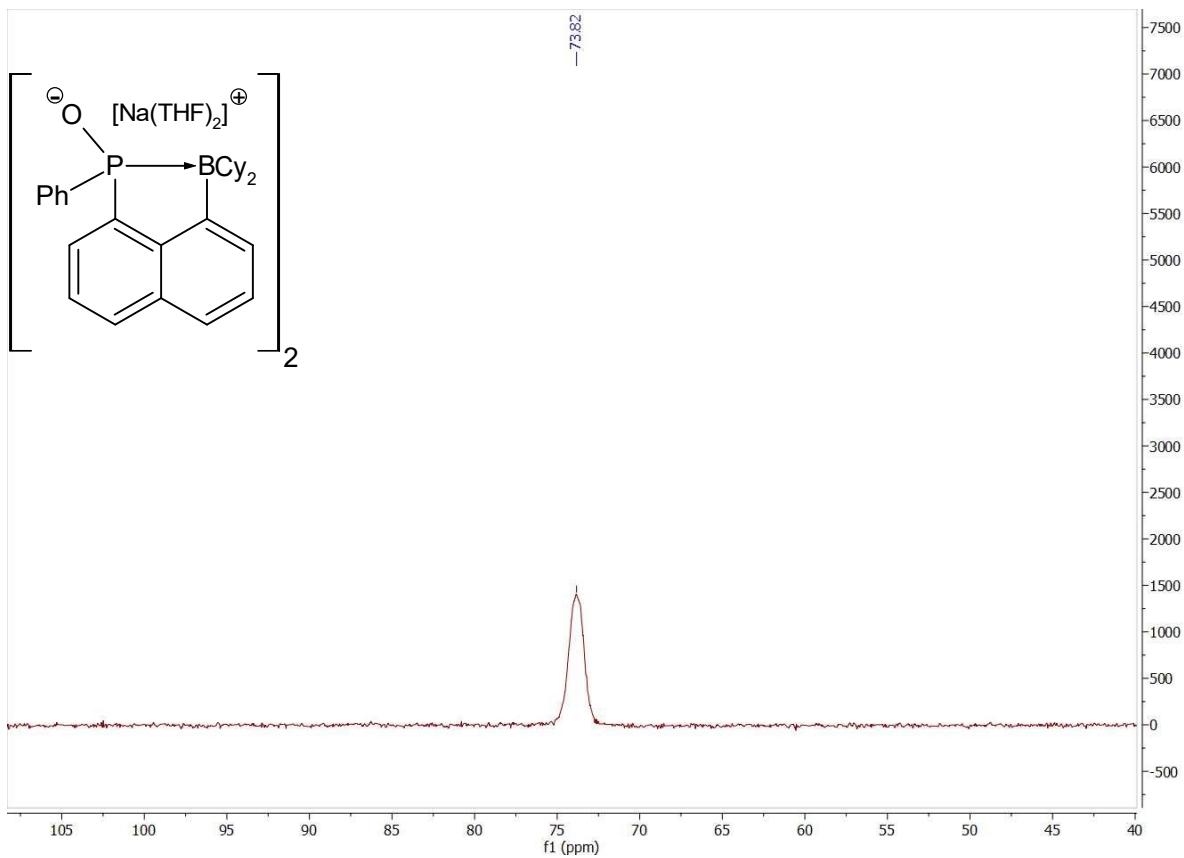


Figure S29. $^{31}\text{P}\{\text{H}\}$ NMR ($\text{THF}-d_8$, 202.49 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}(\text{O})\text{Ph}-\text{C}_{10}\text{H}_6]\}_2$ (7)

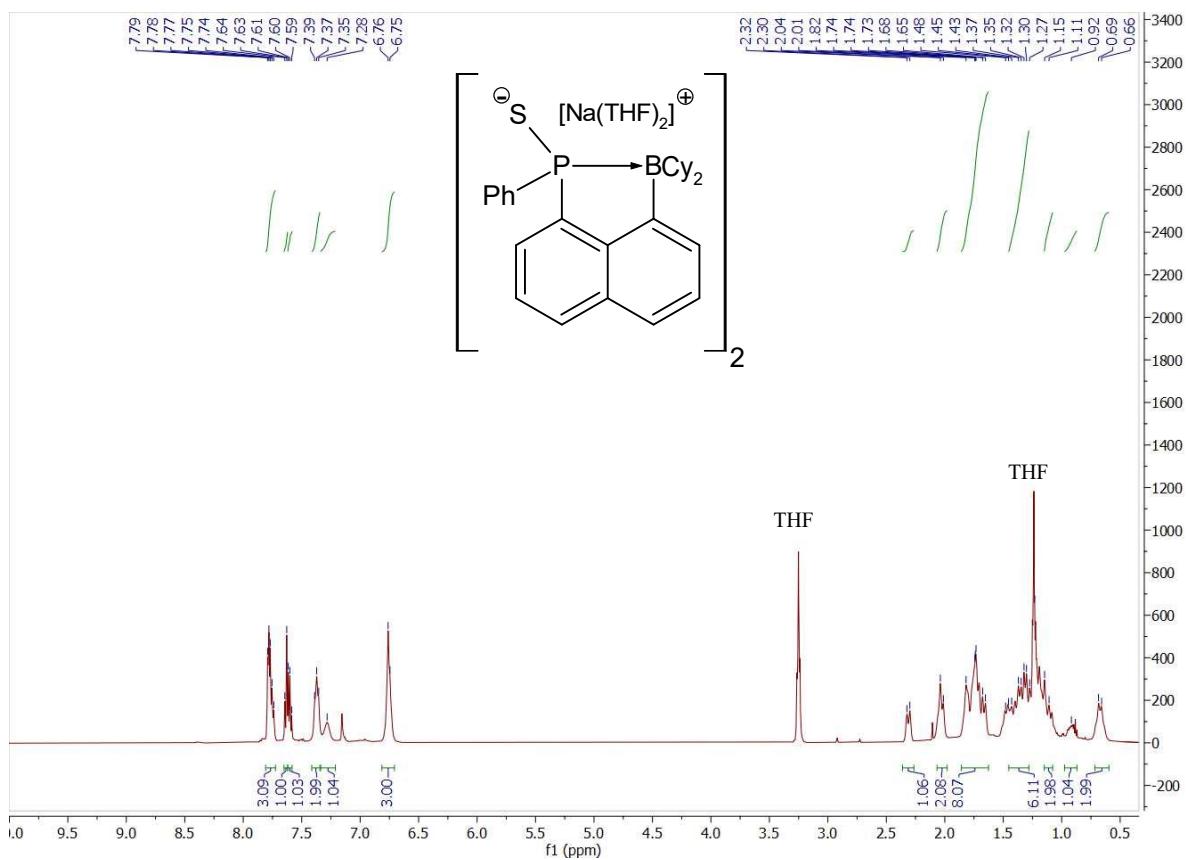


Figure S30. ^1H NMR (C_6D_6 , 500.13 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}(\text{S})\text{Ph}-\text{C}_{10}\text{H}_6]\}_2$ (**8**)

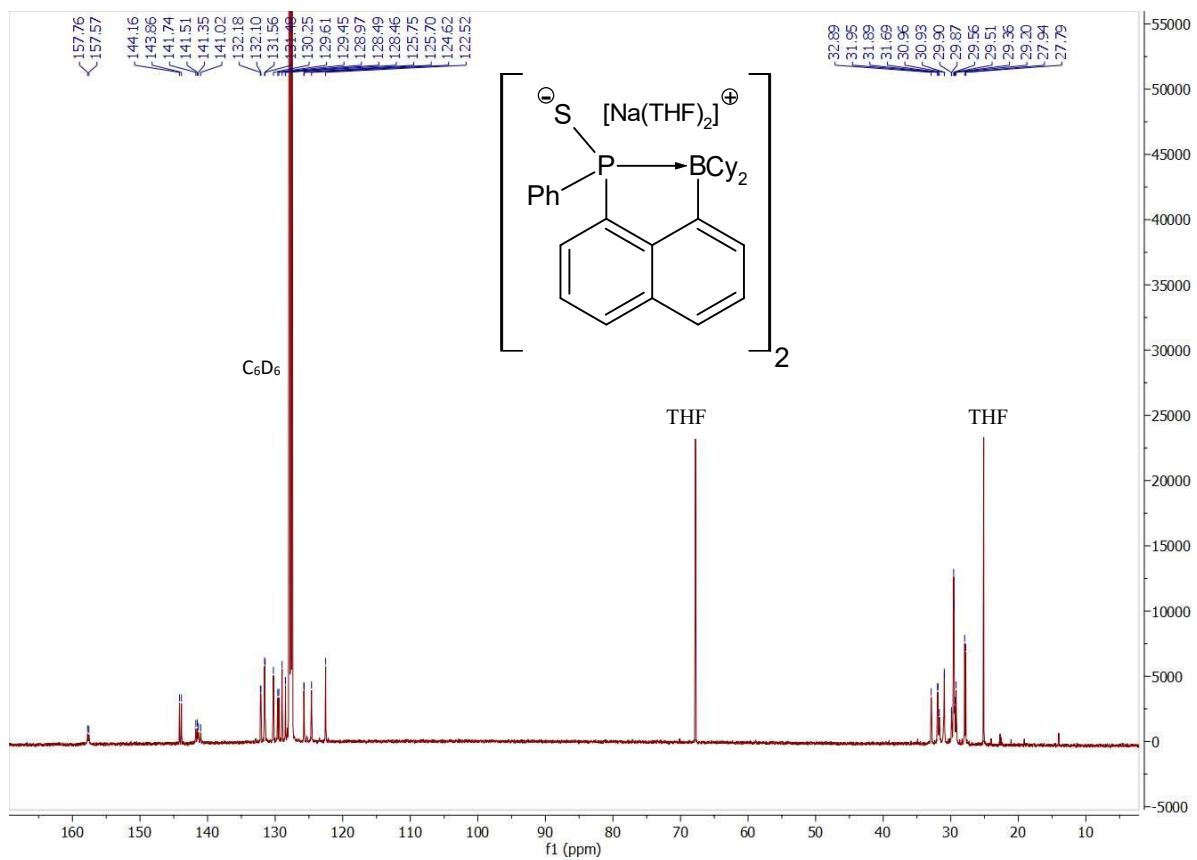


Figure S31. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.77 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}(\text{S})\text{Ph}-\text{C}_{10}\text{H}_6]\}_2$ (**8**)

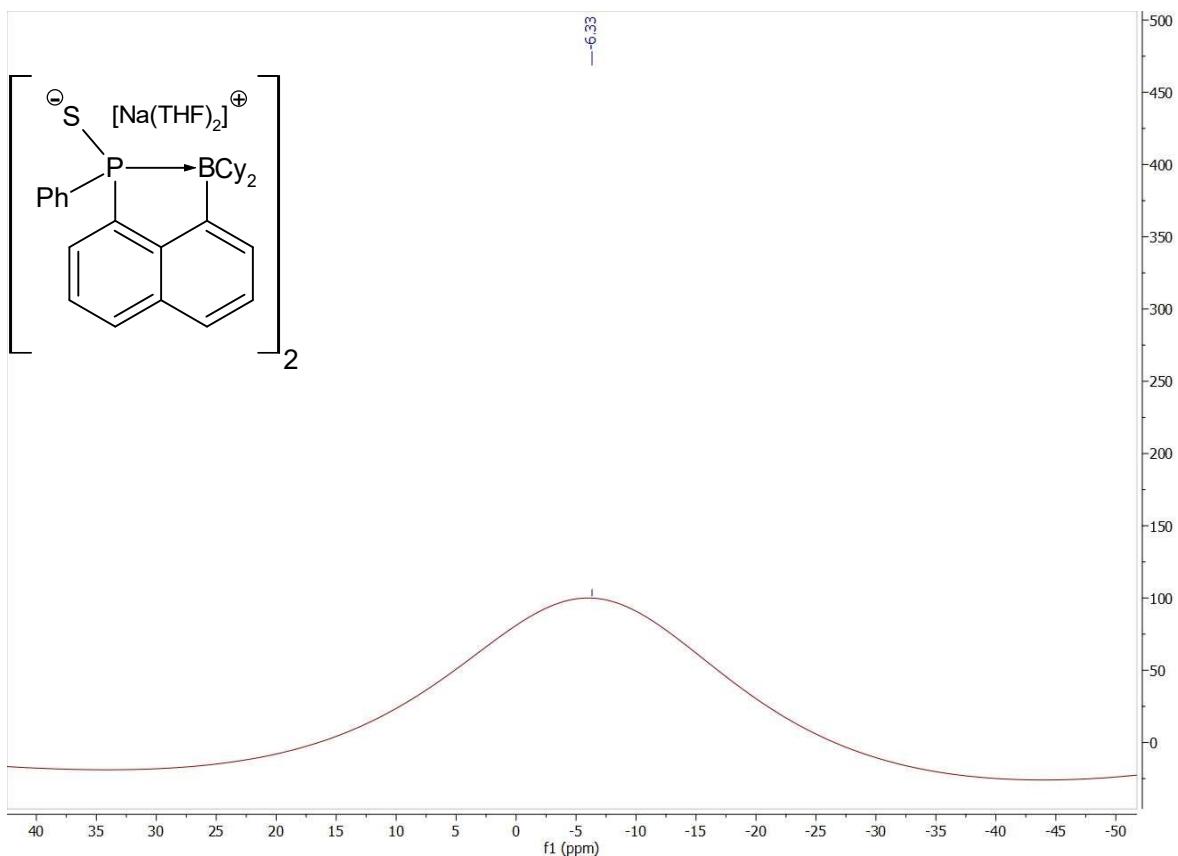


Figure S32. $^{11}\text{B}\{^1\text{H}\}$ NMR (C_6D_6 , 160.57 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}(\text{S})\text{Ph}-\text{C}_{10}\text{H}_6]\}_2$ (**8**)

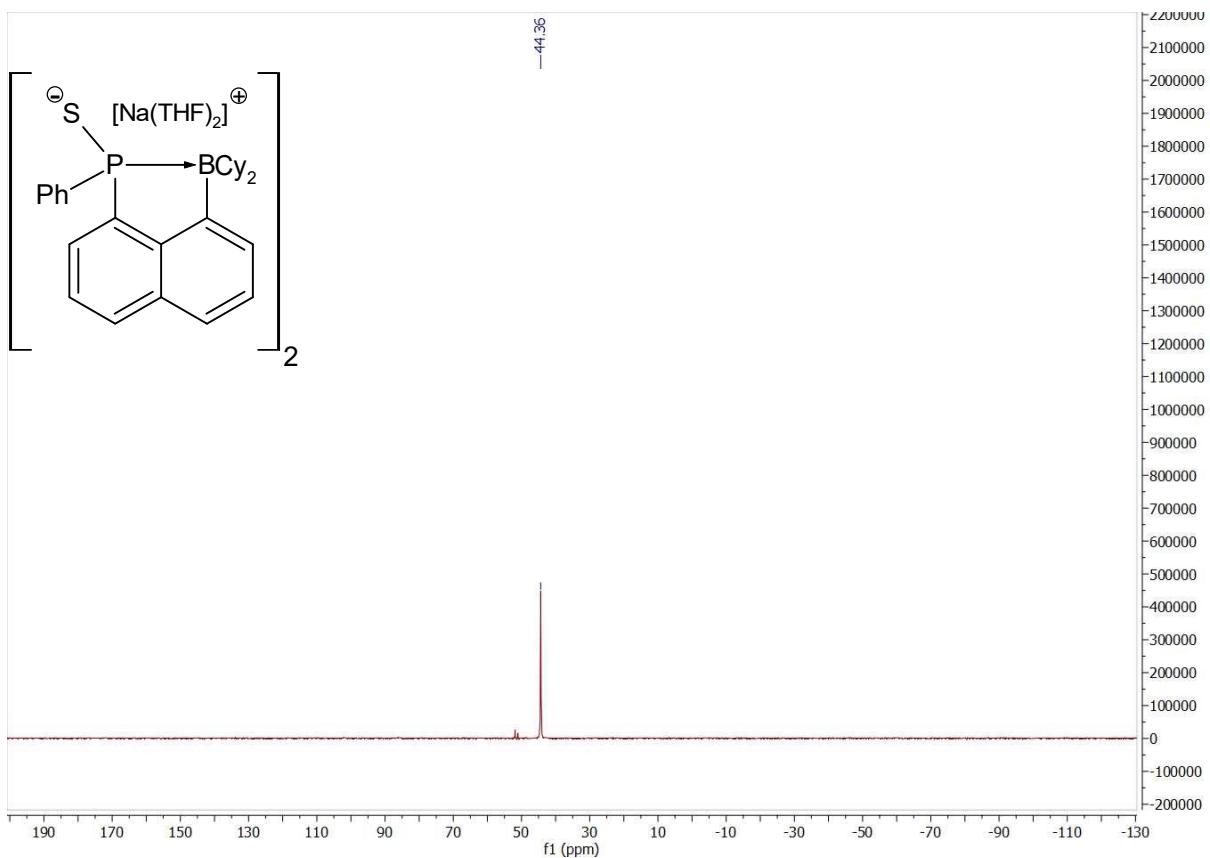


Figure S33. $^{31}\text{P}\{\text{H}\}$ NMR (C_6D_6 , 202.49 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}(\text{S})\text{Ph}-\text{C}_{10}\text{H}_6]\}_2$ (**8**)

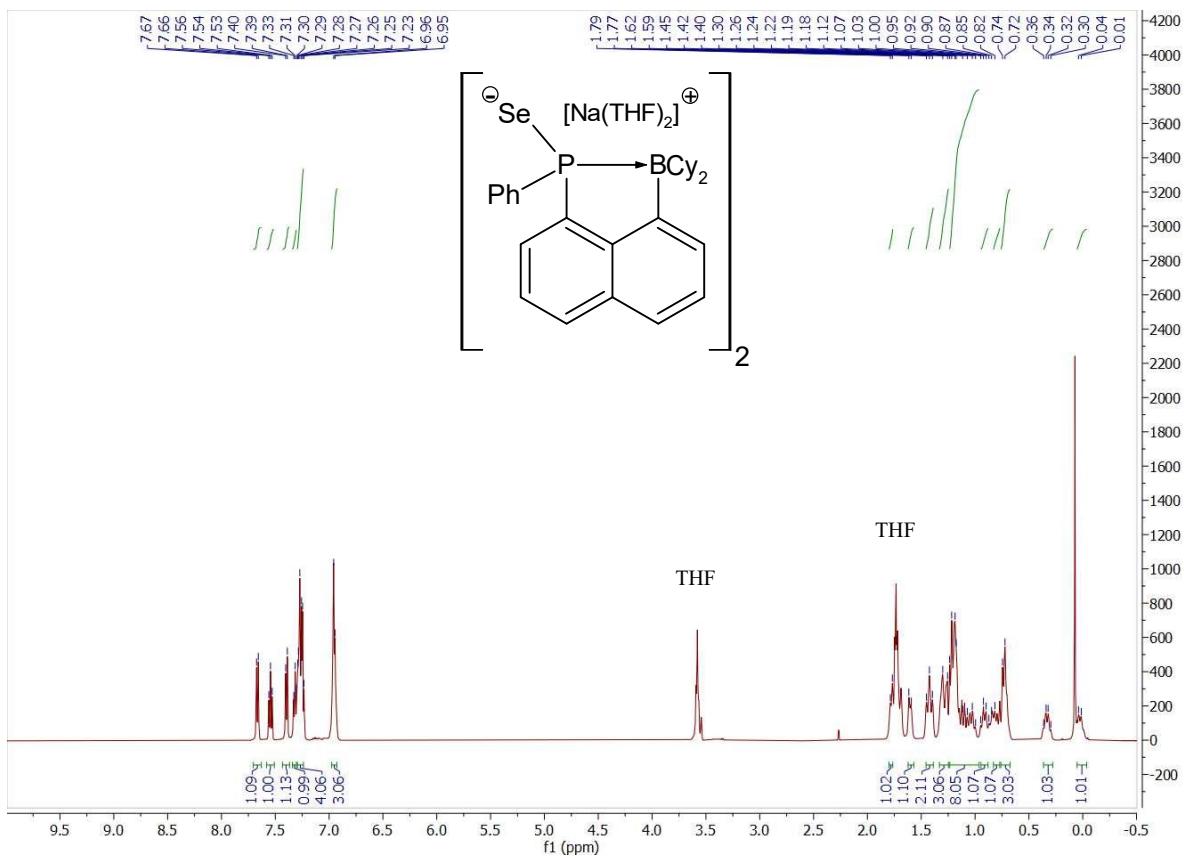


Figure S34. ^1H NMR ($\text{THF}-d_8$, 500.13 MHz) of $\{[\text{Na}(\text{THF})_2]^\oplus [1-\text{BCy}_2-8-\text{P}(\text{Se})\text{Ph}-\text{C}_6\text{H}_4]\}_2$ (**9**)

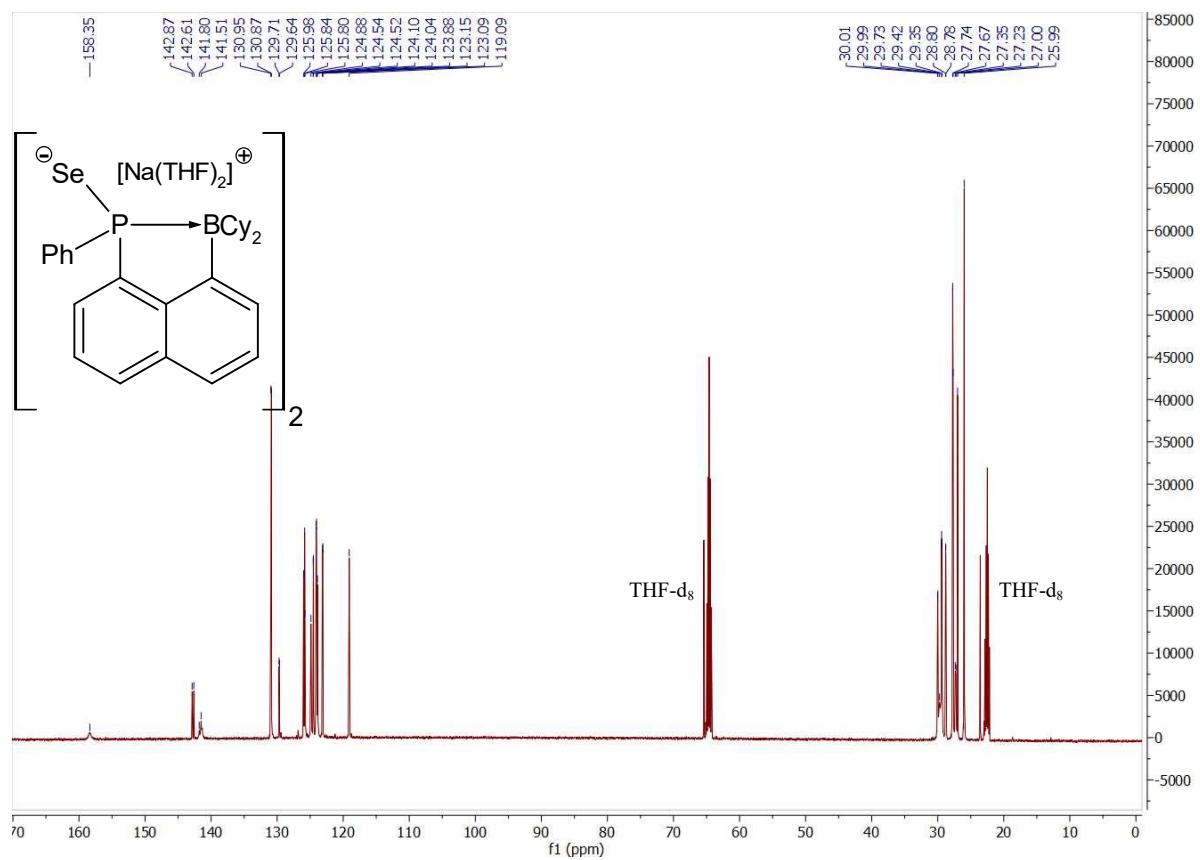


Figure S35. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 125.77 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}(\text{Se})\text{Ph}-\text{C}_{10}\text{H}_6]^- \}_2$ (9)

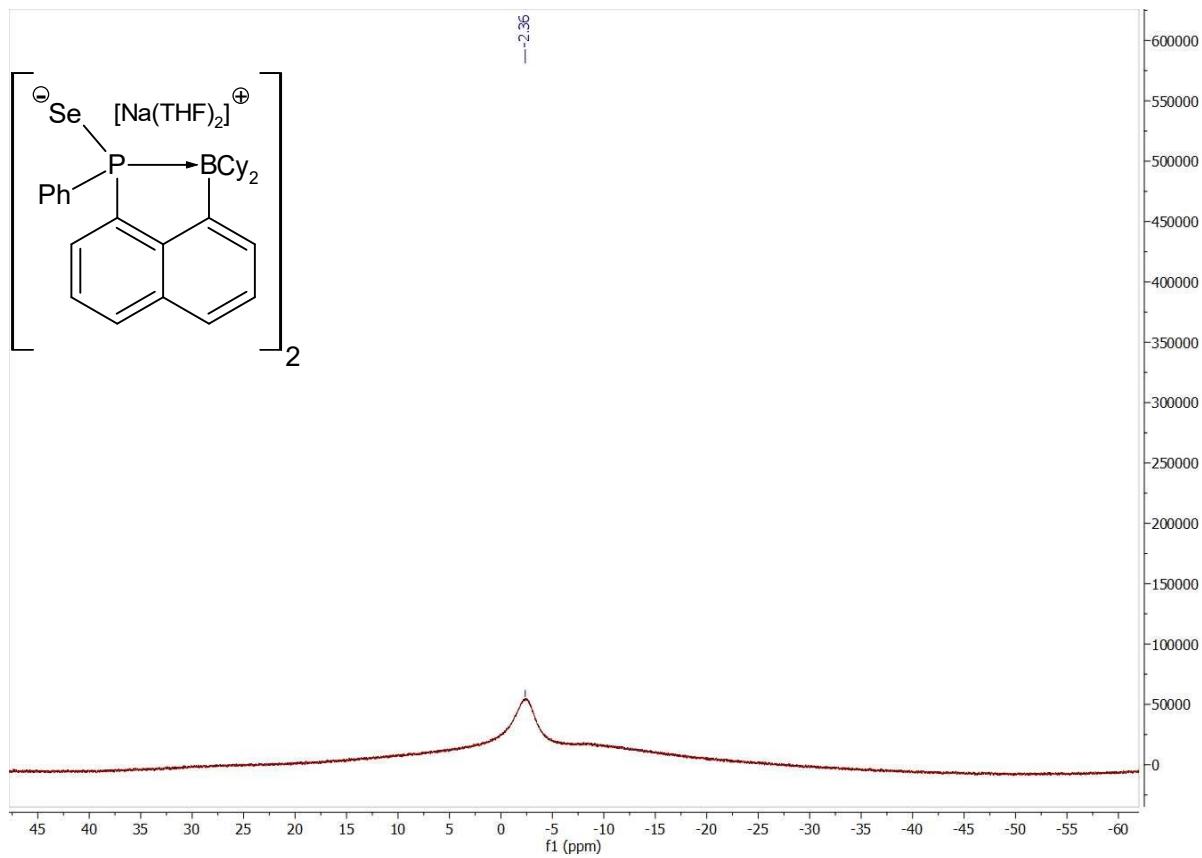


Figure S36. $^{11}\text{B}\{\text{H}\}$ NMR ($\text{THF}-d_8$, 160.57 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}(\text{Se})\text{Ph}-\text{C}_{10}\text{H}_6]^- \}_2$ (**9**)

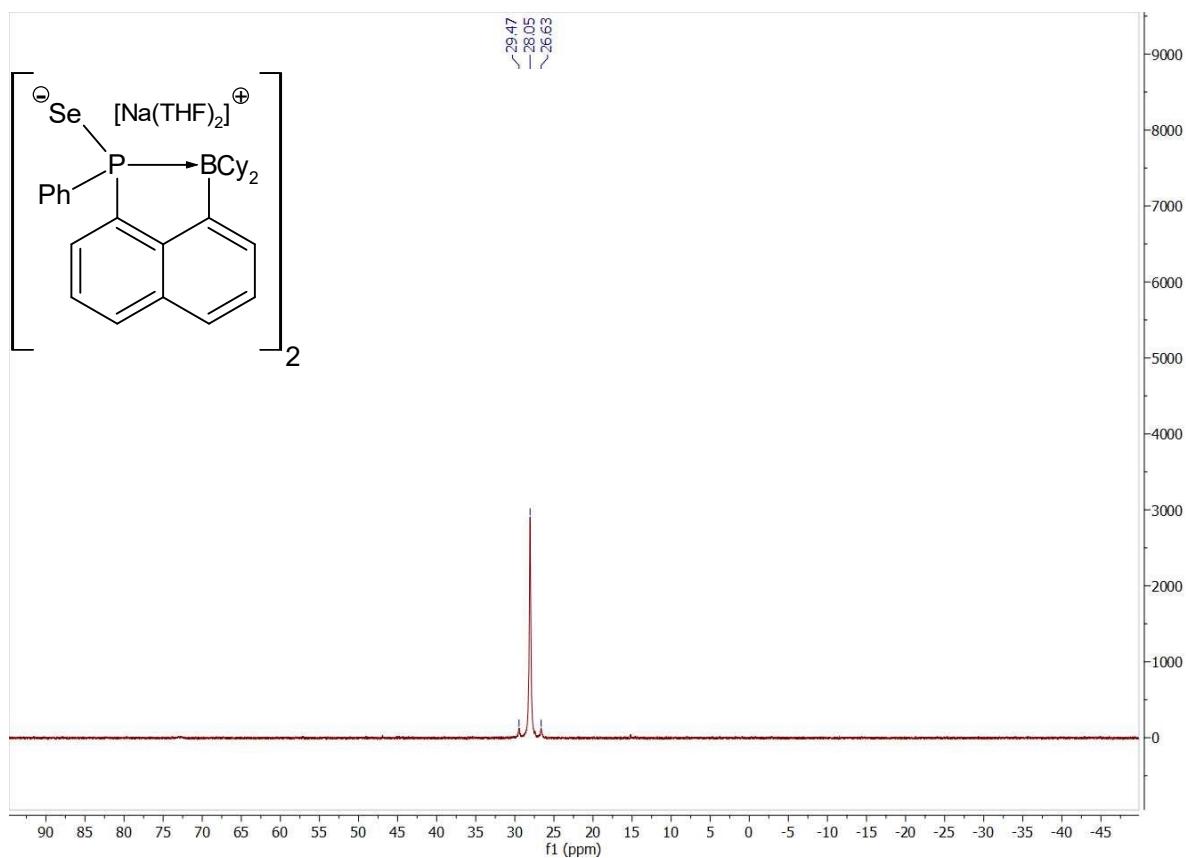


Figure S37. $^{31}\text{P}\{\text{H}\}$ NMR ($\text{THF}-d_8$, 202.49 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}(\text{Se})\text{Ph}-\text{C}_{10}\text{H}_6]\}_2$ (**9**)

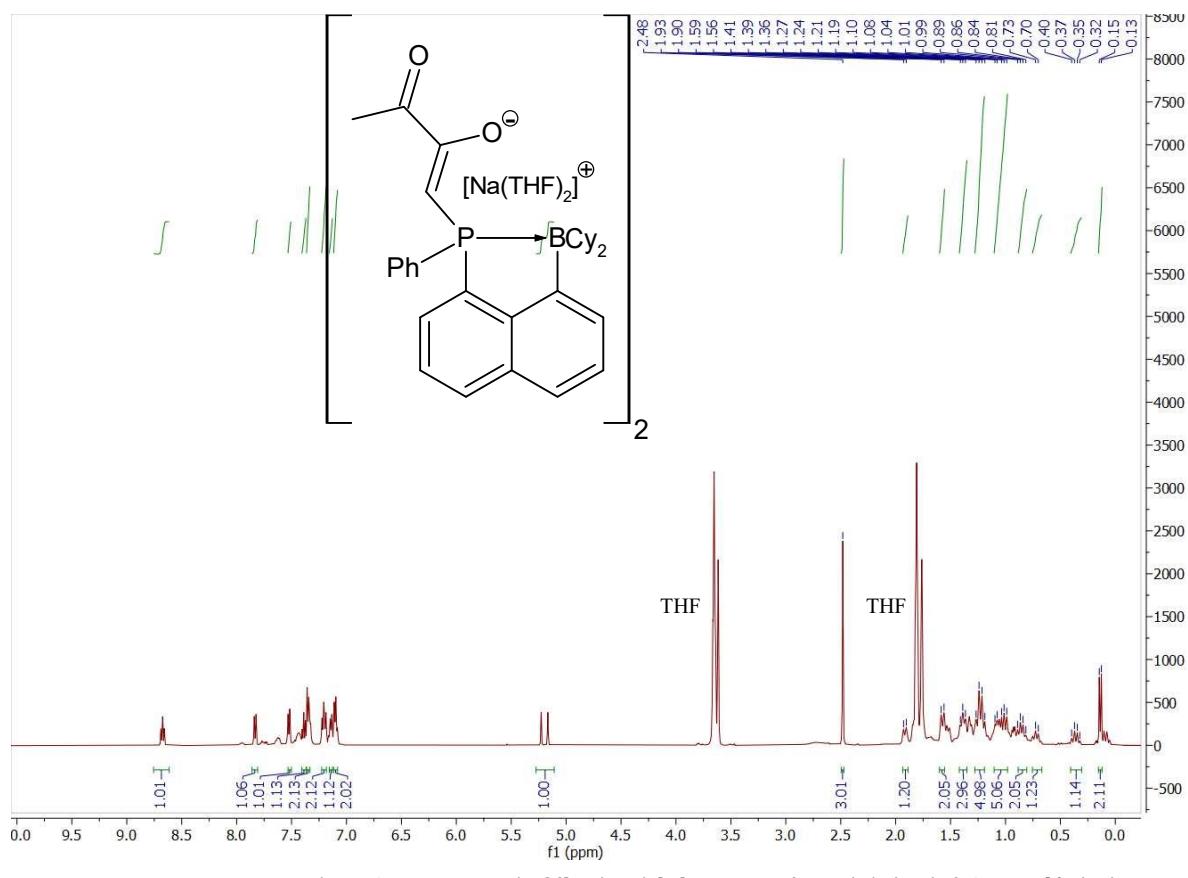


Figure S38. ^1H NMR ($\text{THF}-d_8$, 500.13 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}\{\text{CH}=\text{C}(\text{O})\text{C}(\text{Me})\text{O}\}\text{Ph}-\text{C}_{10}\text{H}_6]\}_2$ (**10**)

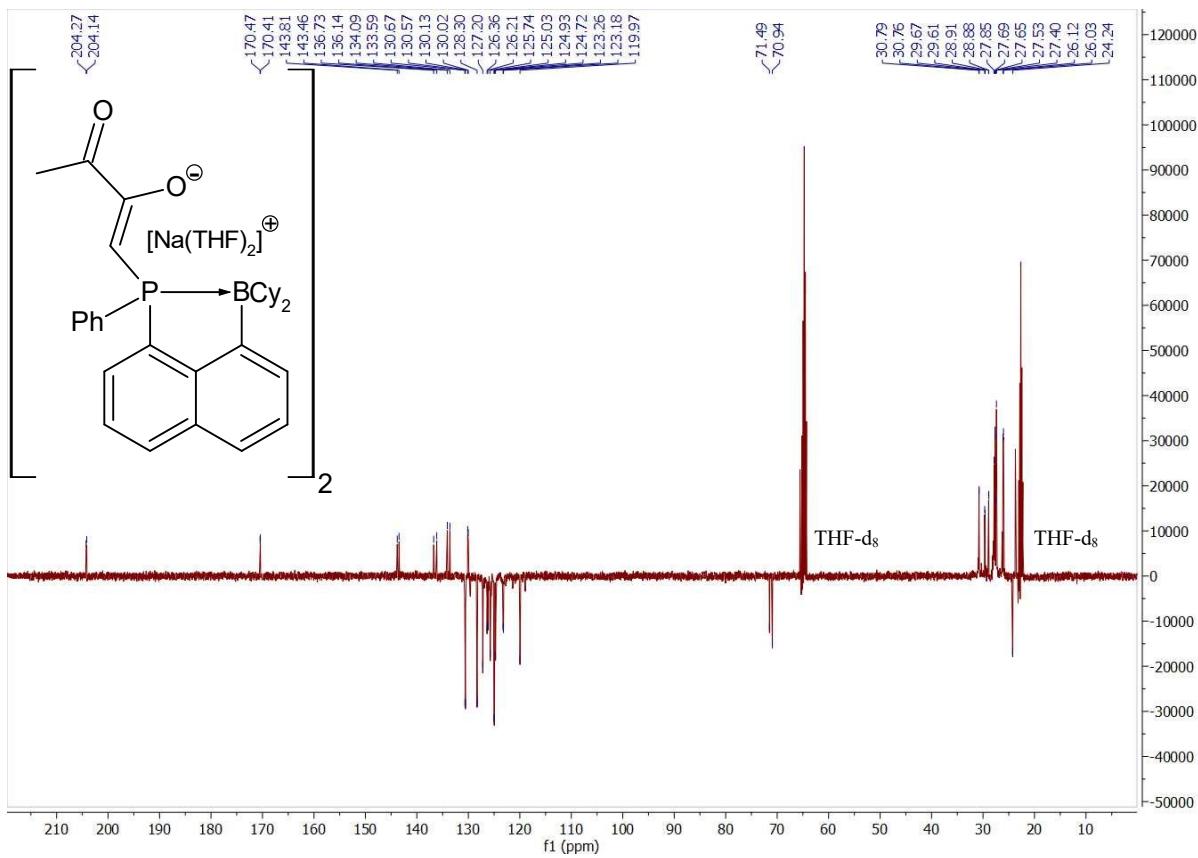


Figure S39. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF-d₈, 125.77 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}\{\text{CH}=\text{C}(\text{O})\text{C}(\text{Me})\text{O}\}\text{Ph}-\text{C}_{10}\text{H}_6]\}_2$ (**10**)

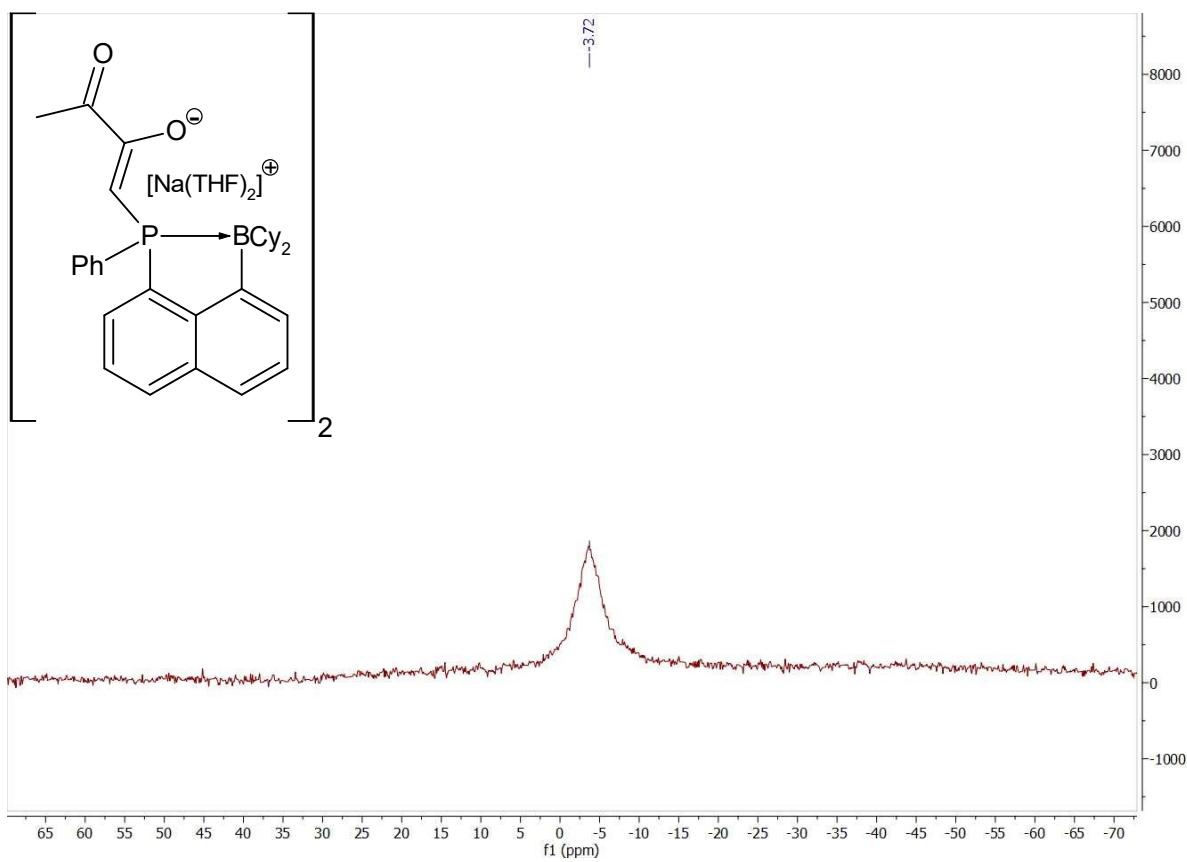


Figure S40. $^{11}\text{B}\{\text{H}\}$ NMR ($\text{THF}-d_8$, 160.57 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}\{\text{CH}=\text{C(O)C(Me)O}\text{Ph}-\text{C}_{10}\text{H}_6\}]_2\}$ (**10**)

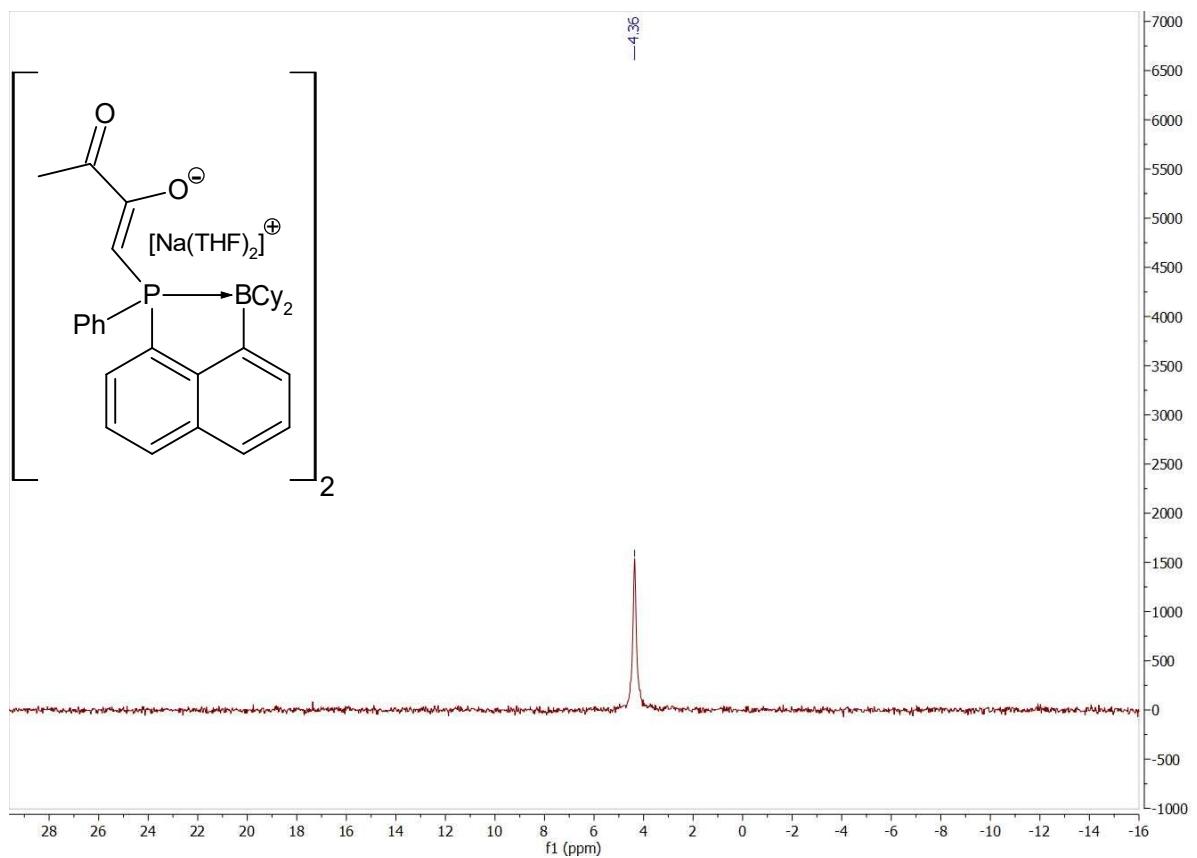


Figure S41. $^{31}\text{P}\{\text{H}\}$ NMR ($\text{THF}-d_8$, 202.49 MHz) of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}\{\text{CH=C(O)C(Me)O}\text{Ph-C}_{10}\text{H}_6\}]_2$ (**10**)

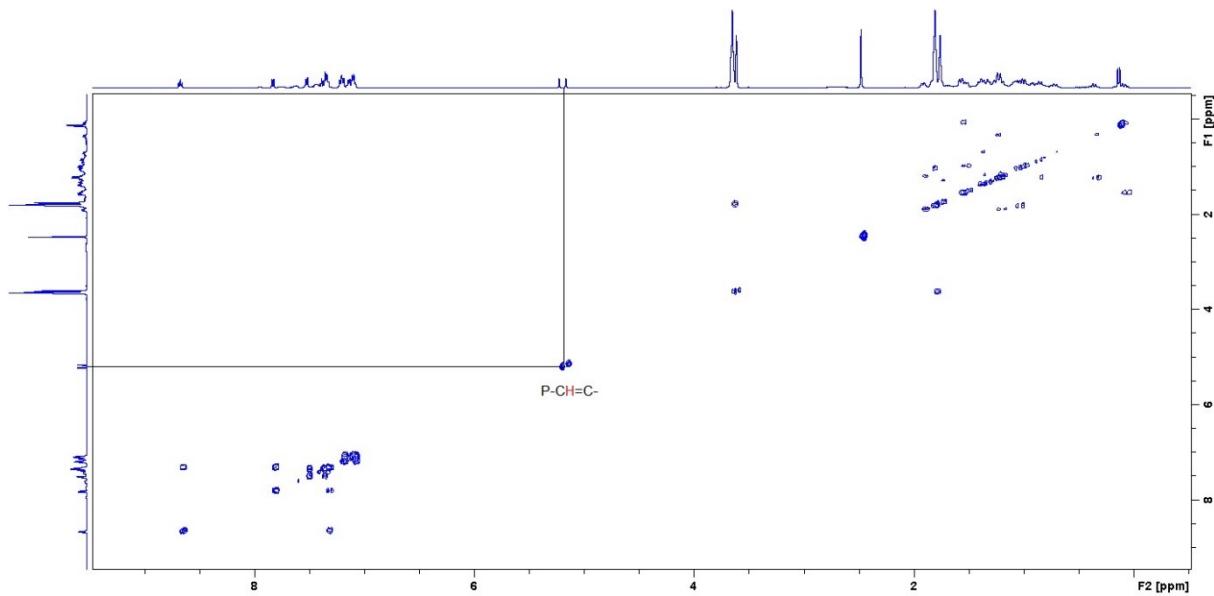


Figure S42. ^1H - ^1H COSY NMR of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}\{\text{CH}=\text{C}(\text{O})\text{C}(\text{Me})\text{O}\}\text{Ph}-\text{C}_{10}\text{H}_6]\}_2$ (**10**)

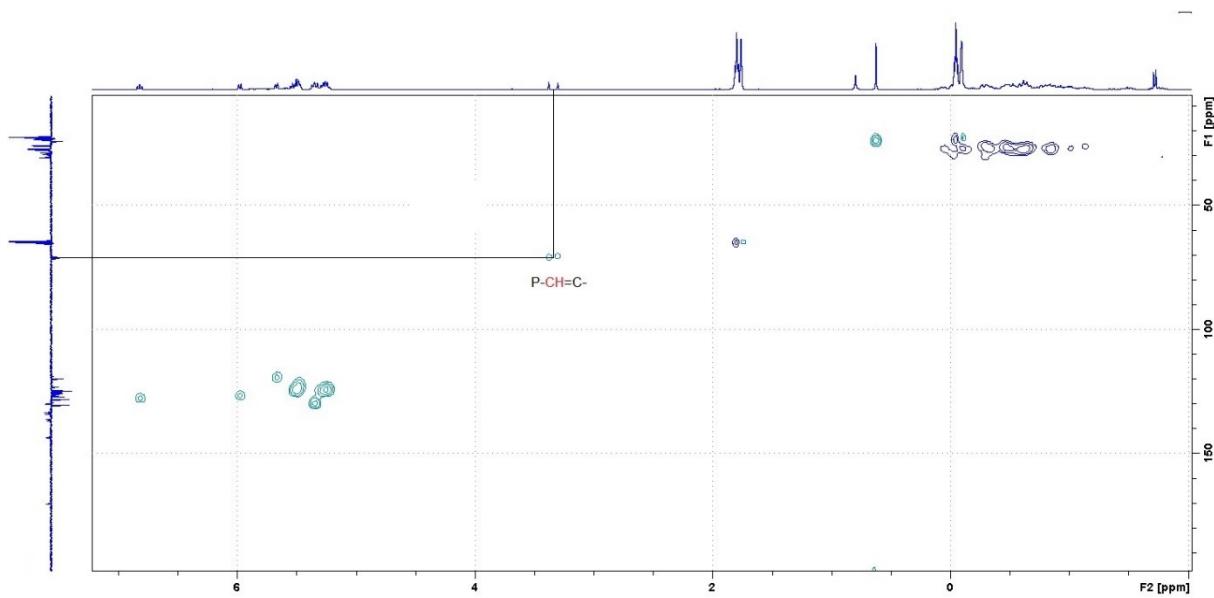


Figure S43. ^1H - ^{13}C HSQC NMR of $\{[\text{Na}(\text{THF})_2]^+ [1-\text{BCy}_2-8-\text{P}\{\text{CH}=\text{C}(\text{O})\text{C}(\text{Me})\text{O}\}\text{Ph}-\text{C}_{10}\text{H}_6]\}_2$ (**10**)

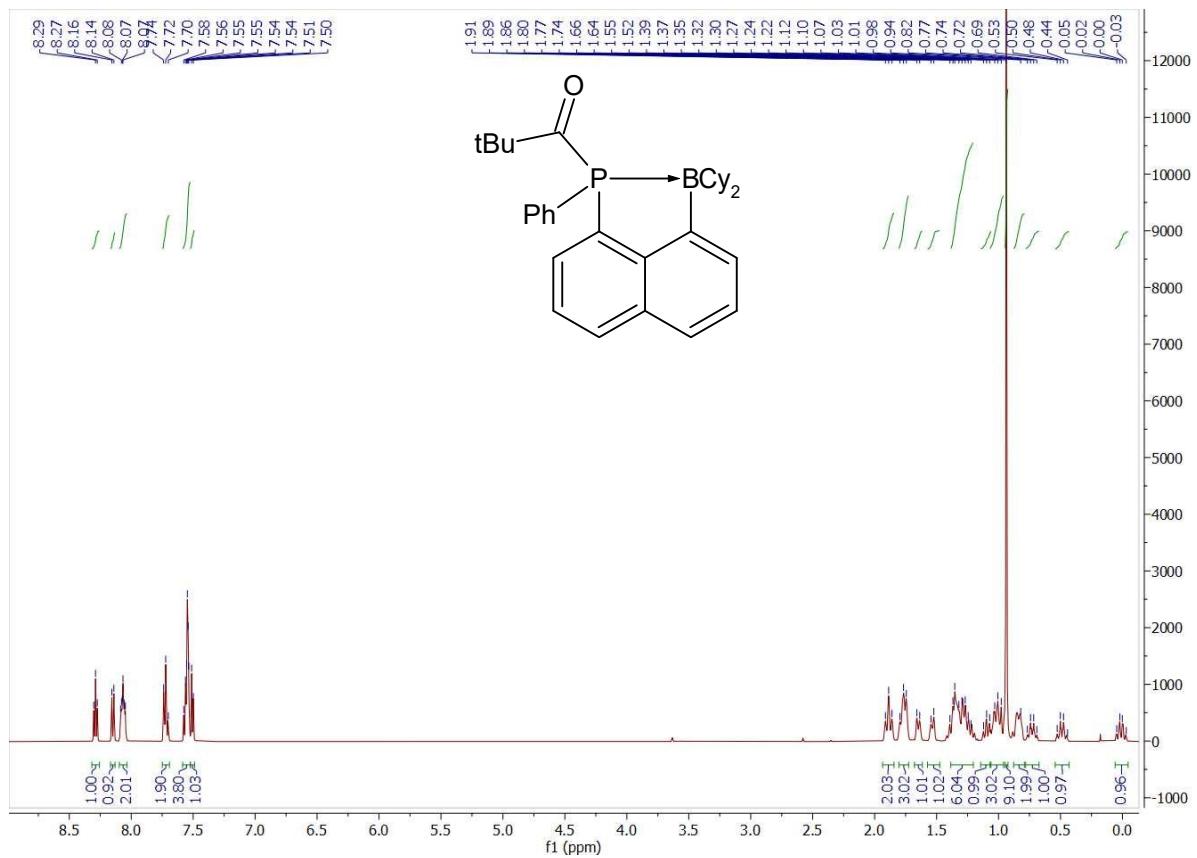


Figure S44. ^1H NMR ($\text{THF}-d_8$, 500.13 MHz) of [1- BCy_2 -8- $P\{\text{C}(O)\text{tBu}\}\text{Ph-C}_{10}\text{H}_6$] (**11**)

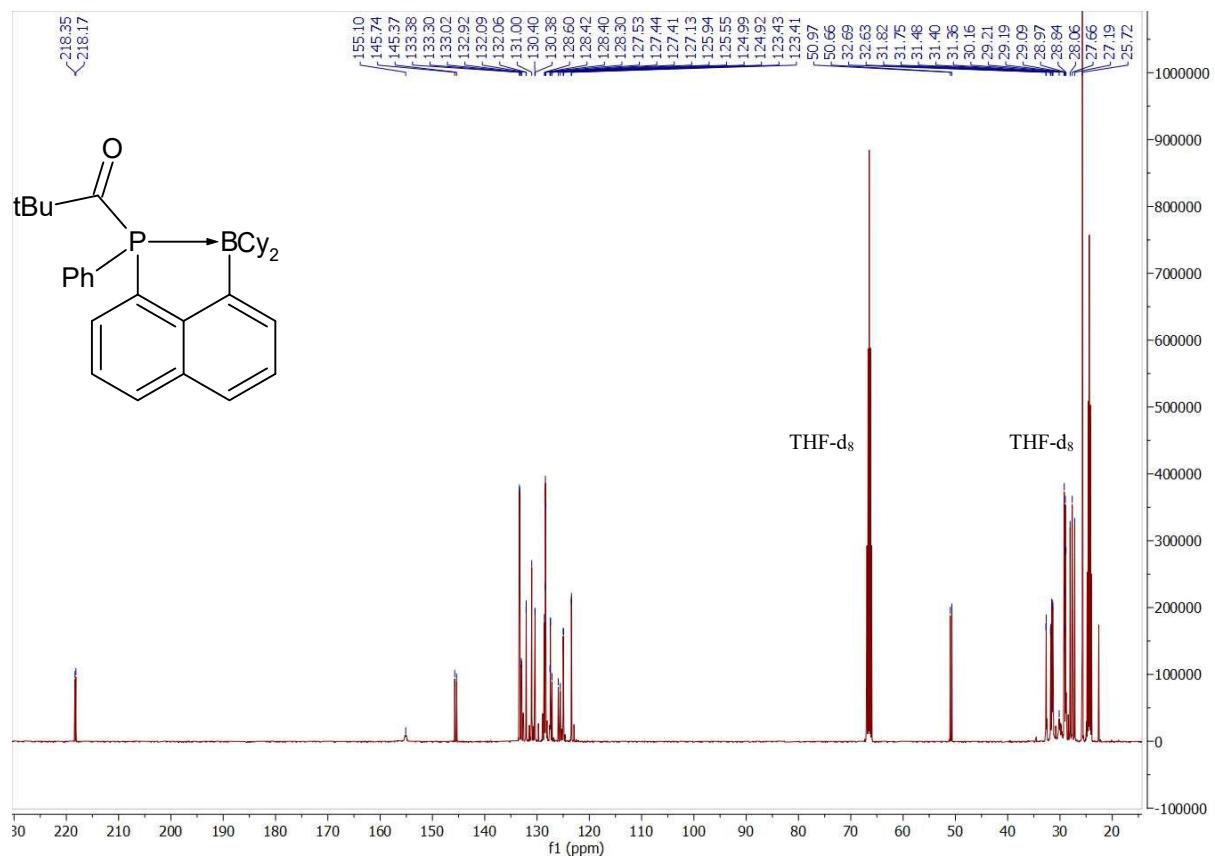


Figure S45. $^{13}\text{C}\{^1\text{H}\}$ NMR (THF- d_8 , 125.77 MHz) of [1-BCy₂-8-P{C(O)tBu}Ph-C₁₀H₆] (**11**)

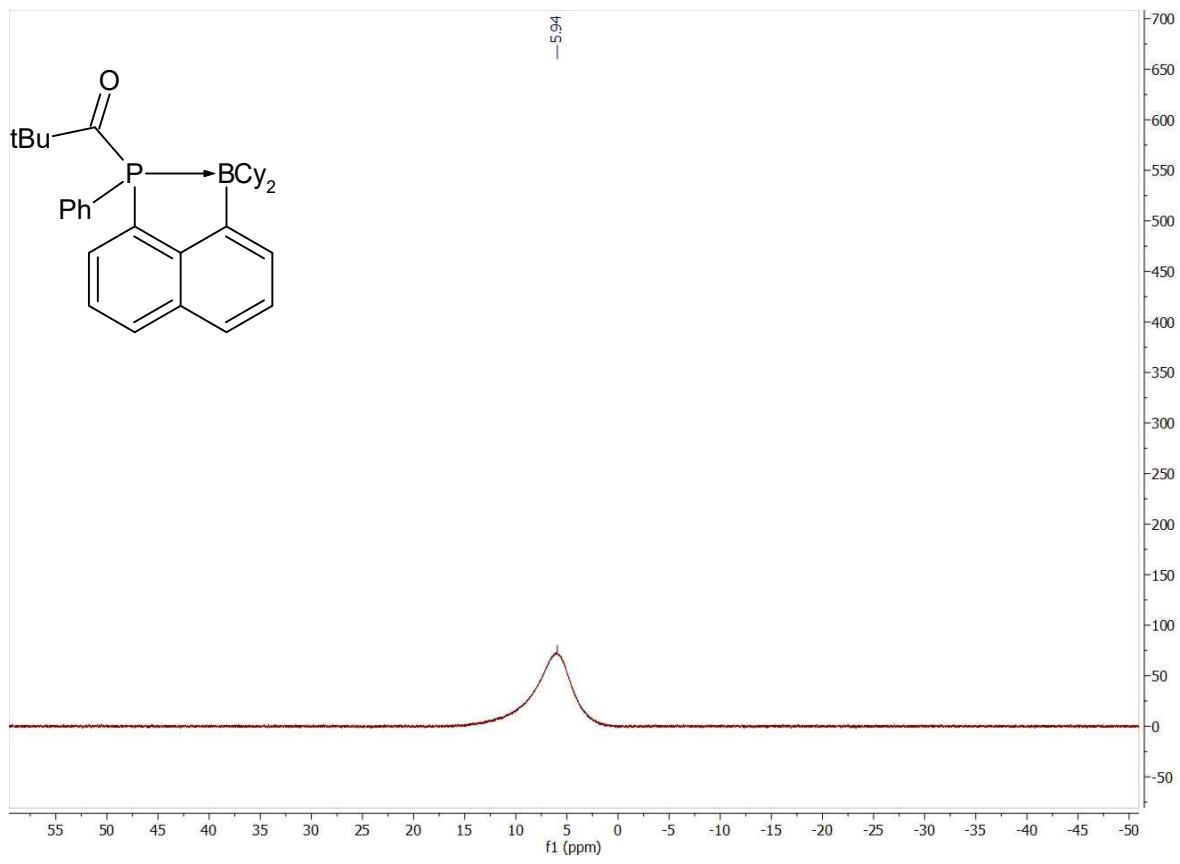


Figure S46. $^{11}\text{B}\{^1\text{H}\}$ NMR ($\text{THF}-d_8$, 160.57 MHz) of $[1-\text{BCy}_2-8-\text{P}\{\text{C}(O)\text{tBu}\}\text{Ph}-\text{C}_{10}\text{H}_6]$ (**11**)

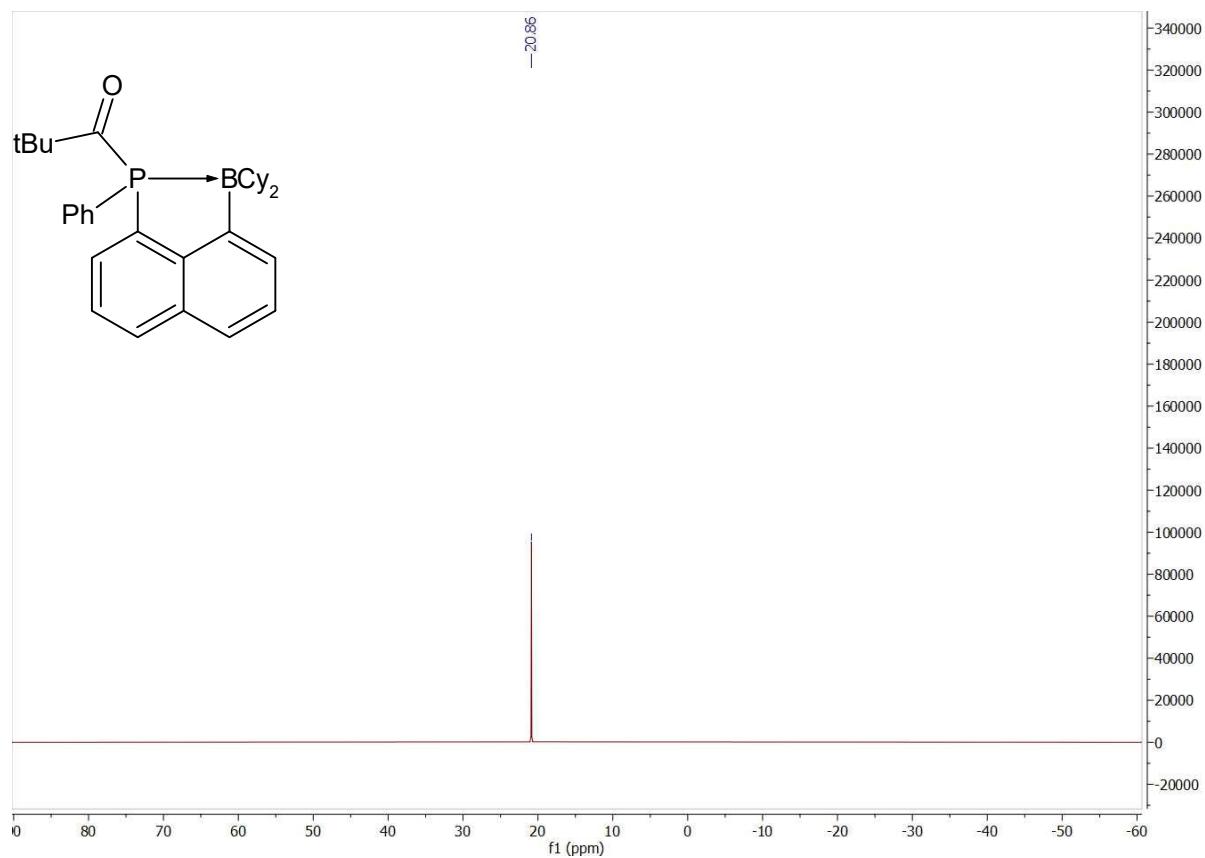


Figure S47. $^{31}\text{P}\{\text{H}\}$ NMR ($\text{THF}-d_8$, 202.49 MHz) of $[1-\text{BCy}_2-8-\text{P}\{\text{C}(=\text{O})\text{tBu}\}\text{Ph}-\text{C}_{10}\text{H}_6]$ (**11**)

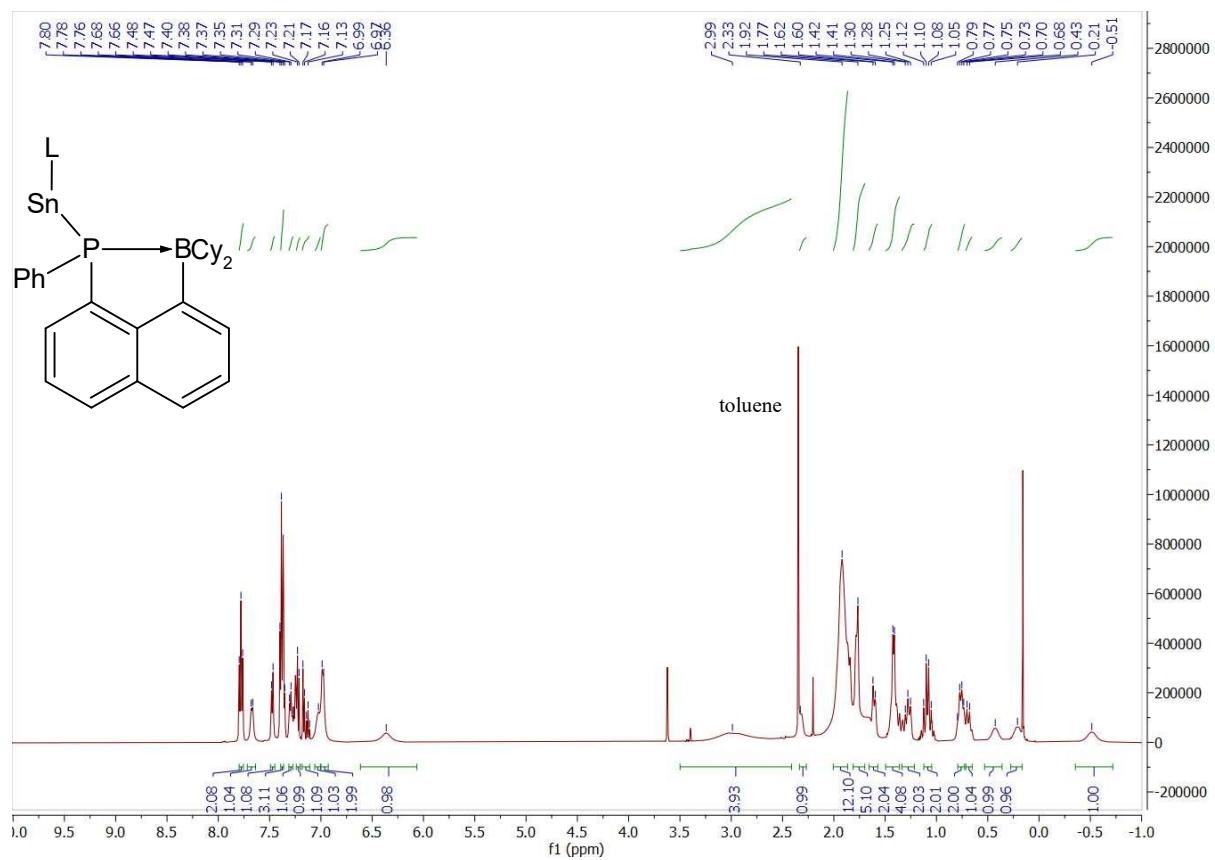


Figure S48. ^1H NMR ($\text{THF}-d_8$, 500.13 MHz) of $[1-\text{BCy}_2-8-\text{P}(\text{SnL})\text{Ph}-\text{C}_{10}\text{H}_6]$ (**12**)

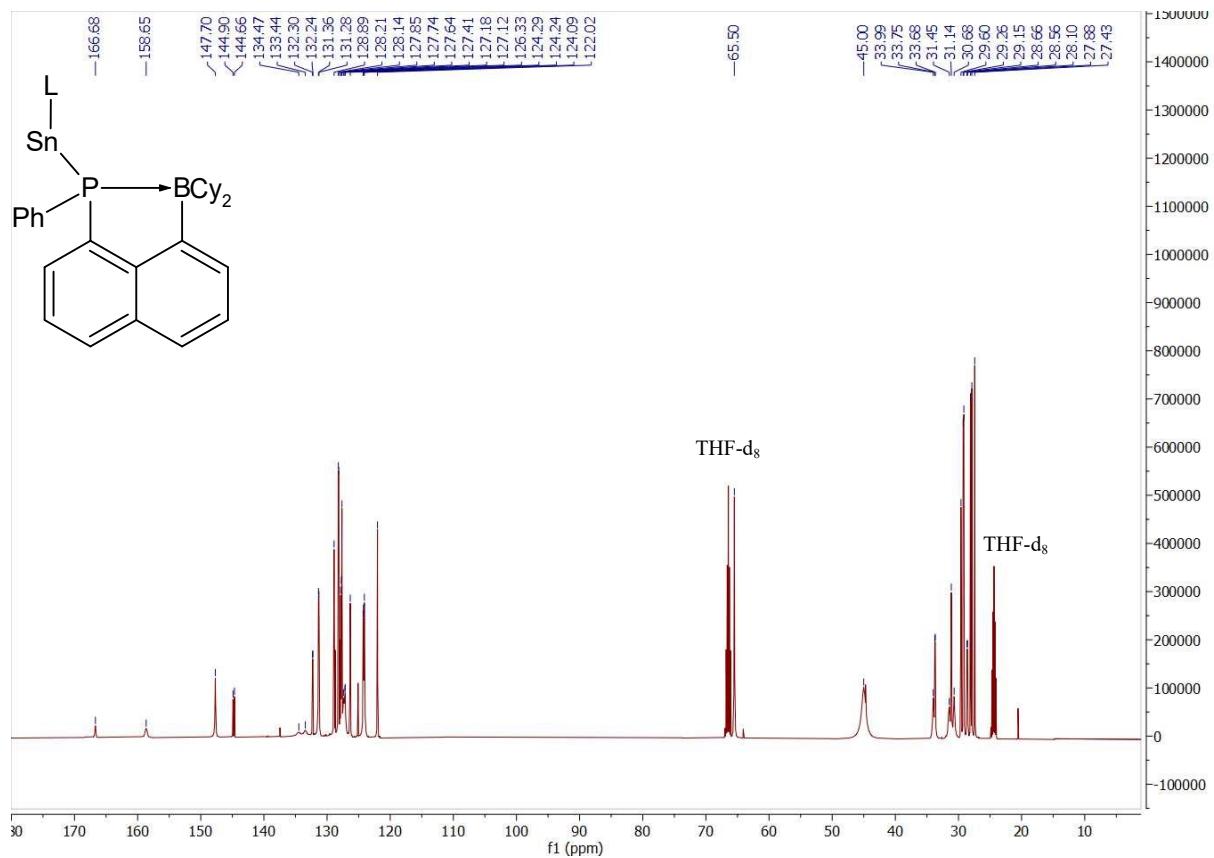


Figure S49. $^{13}\text{C}\{\text{H}\}$ NMR (THF-d_8 , 125.77 MHz) of $[1-\text{BCy}_2-8-\text{P}(\text{SnL})\text{Ph-C}_{10}\text{H}_6]$ (**12**)

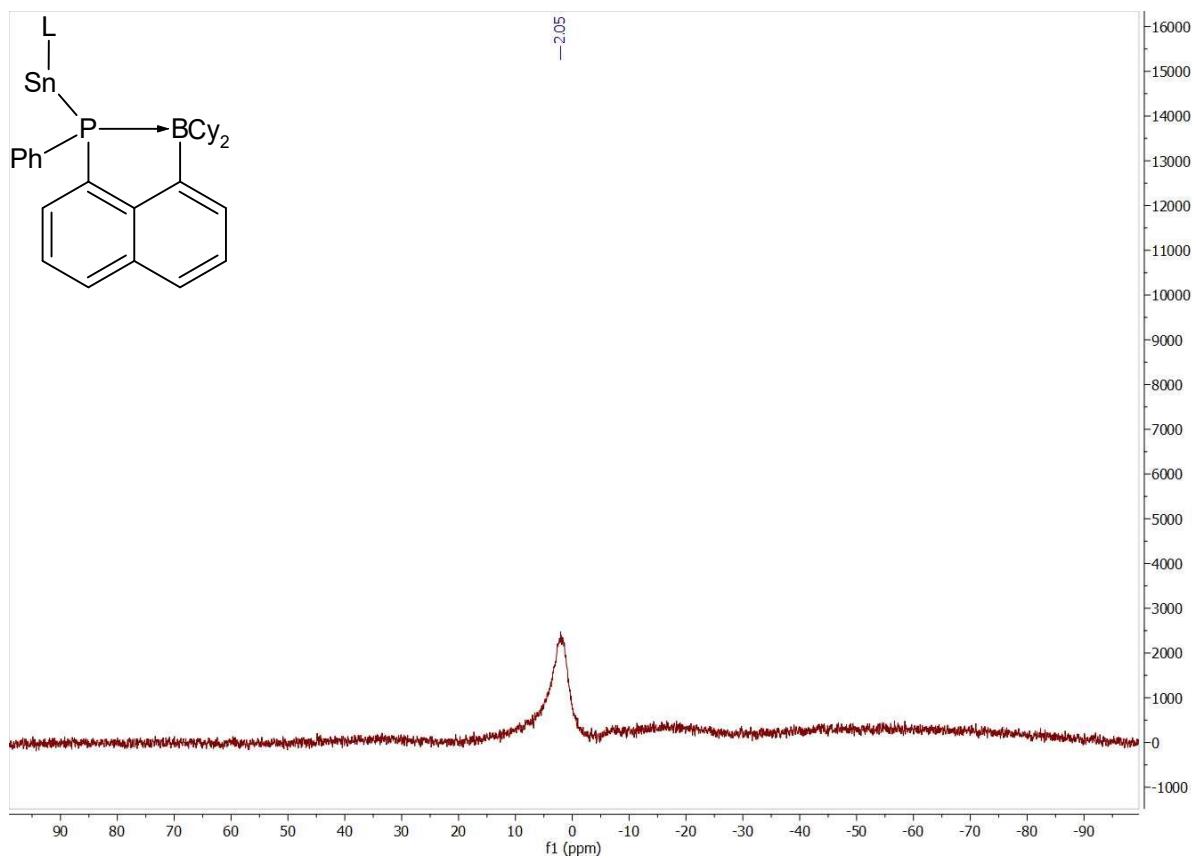


Figure S50. $^{11}\text{B}\{\text{H}\}$ NMR ($\text{THF}-d_8$, 160.57 MHz) of $[1-\text{BCy}_2-8-\text{P}(\text{SnL})\text{Ph}-\text{C}_{10}\text{H}_6]$ (**12**)

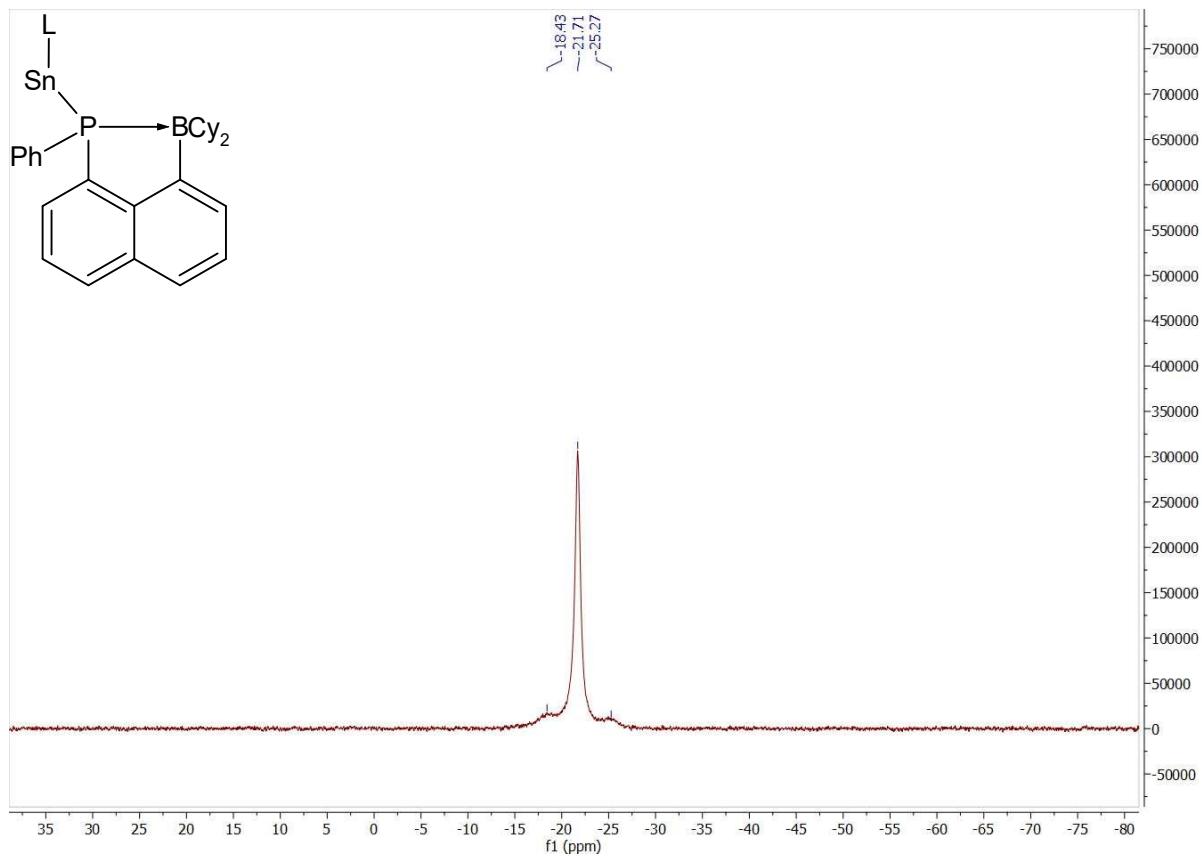


Figure S51. $^{31}\text{P}\{\text{H}\}$ NMR ($\text{THF}-d_8$, 202.49 MHz) of $[1-\text{BCy}_2-8-\text{P}(\text{SnL})\text{Ph}-\text{C}_{10}\text{H}_6]$ (**12**)

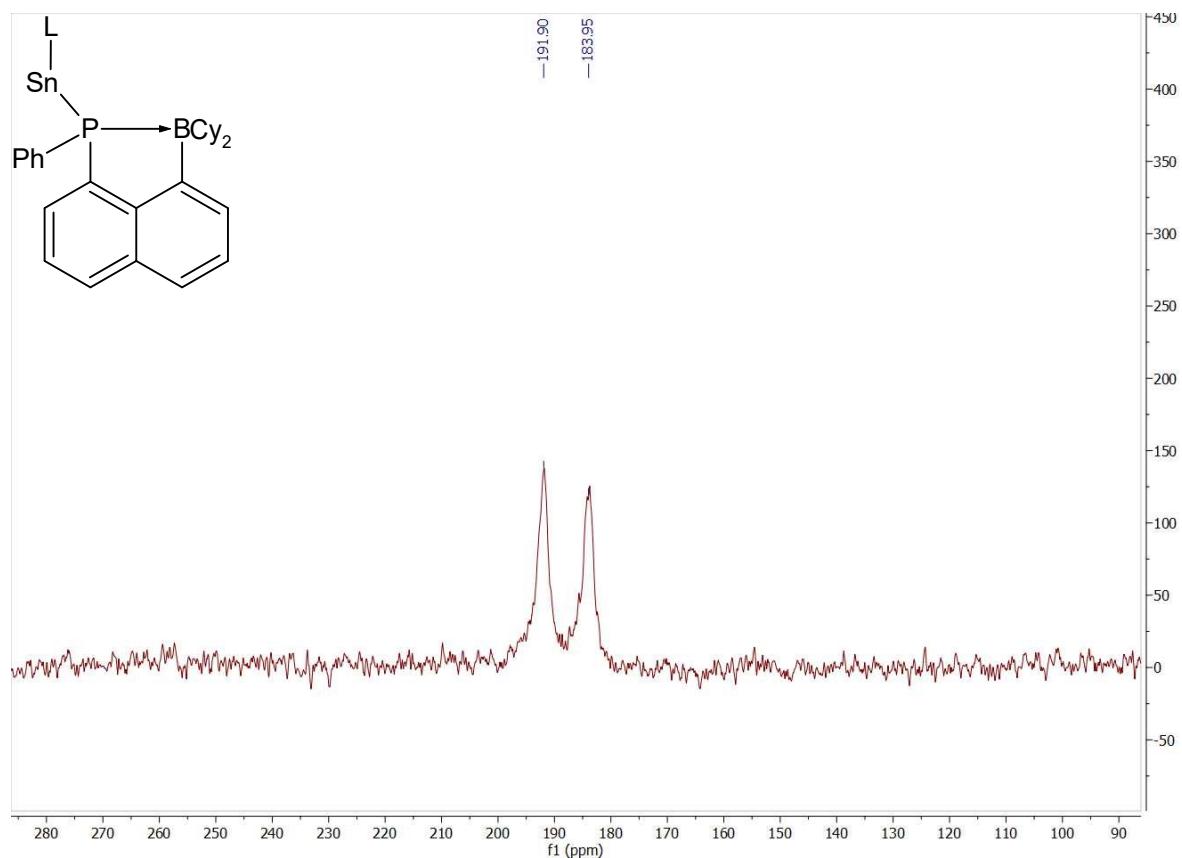


Figure S52. $^{119}\text{Sn}\{\text{H}\}$ NMR (THF-*d*₈, 186.52 MHz) of [1-BCy₂-8-P(SnL)Ph-C₁₀H₆] (**12**)

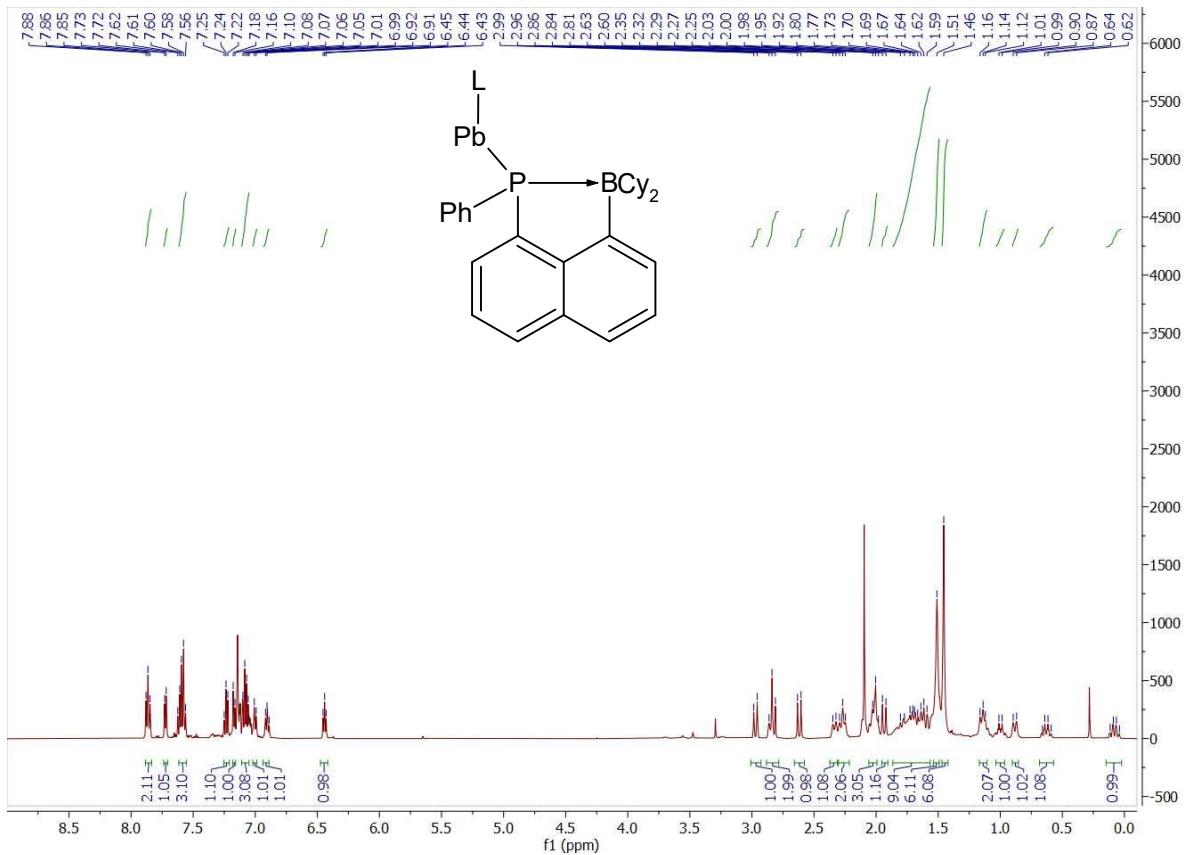


Figure S53. ^1H NMR (C_6D_6 , 500.13 MHz) of [1-BCy₂-8-P(PbL)Ph-C₁₀H₆] (13)

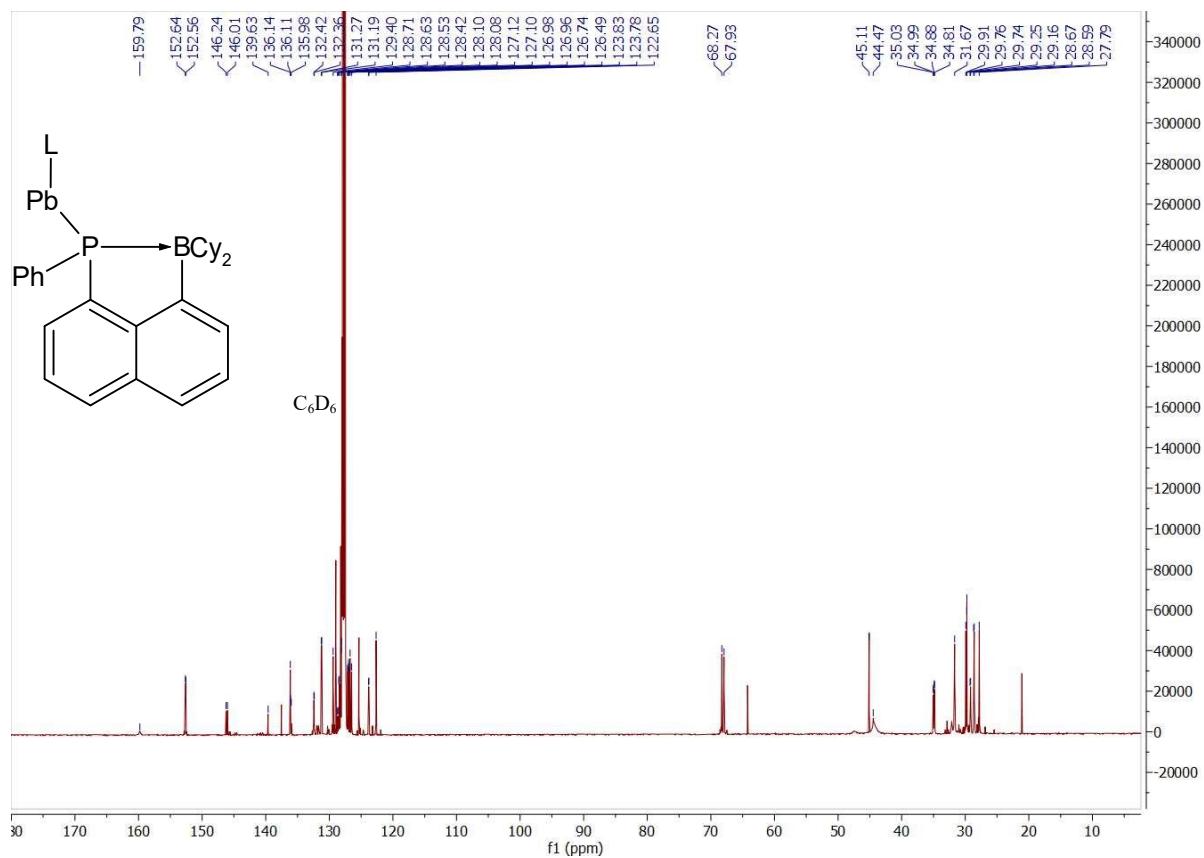


Figure S54. $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 125.77 MHz) of $[1-\text{BCy}_2-8-\text{P}(\text{PbL})\text{Ph}-\text{C}_{10}\text{H}_6]$ (**13**)

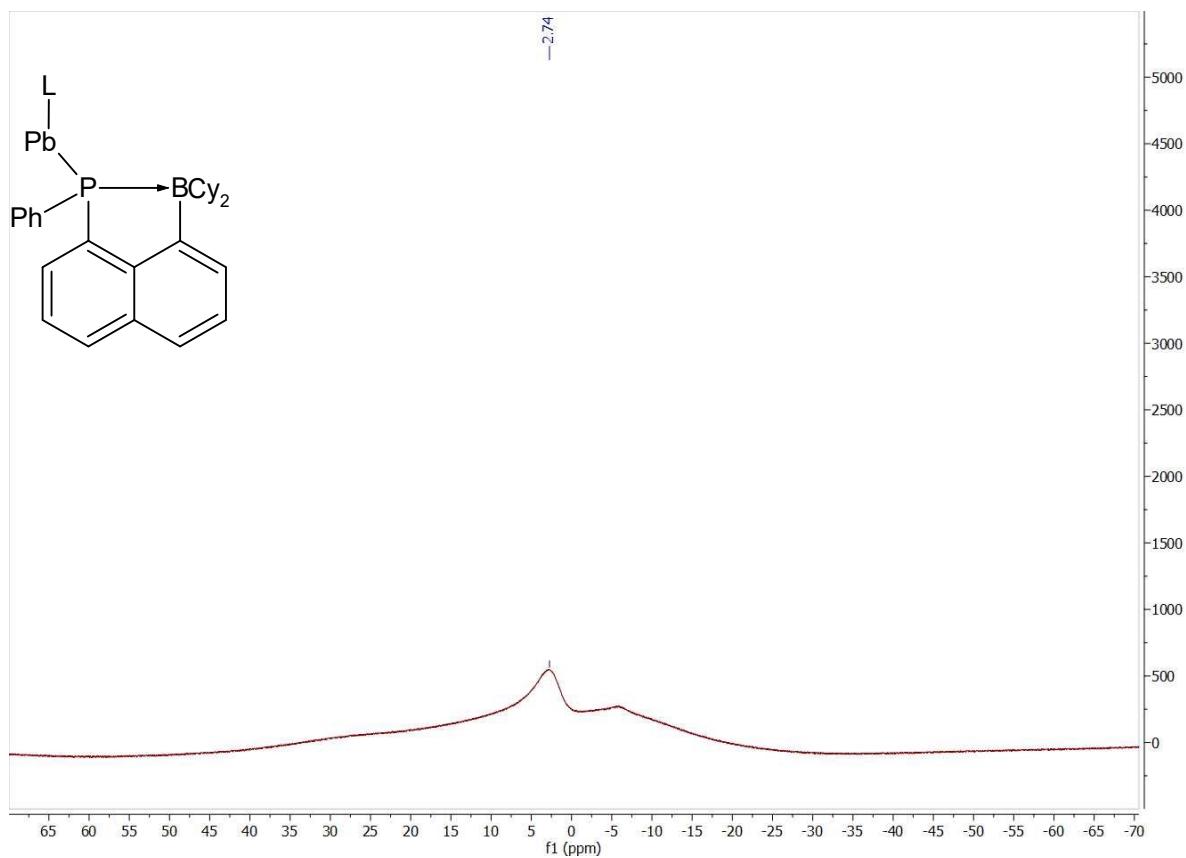


Figure S55. $^{11}\text{B}\{\text{H}\}$ NMR (C_6D_6 , 160.57 MHz) of $[1-\text{BCy}_2-8-\text{P}(\text{PbL})\text{Ph}-\text{C}_{10}\text{H}_6]$ (**13**)

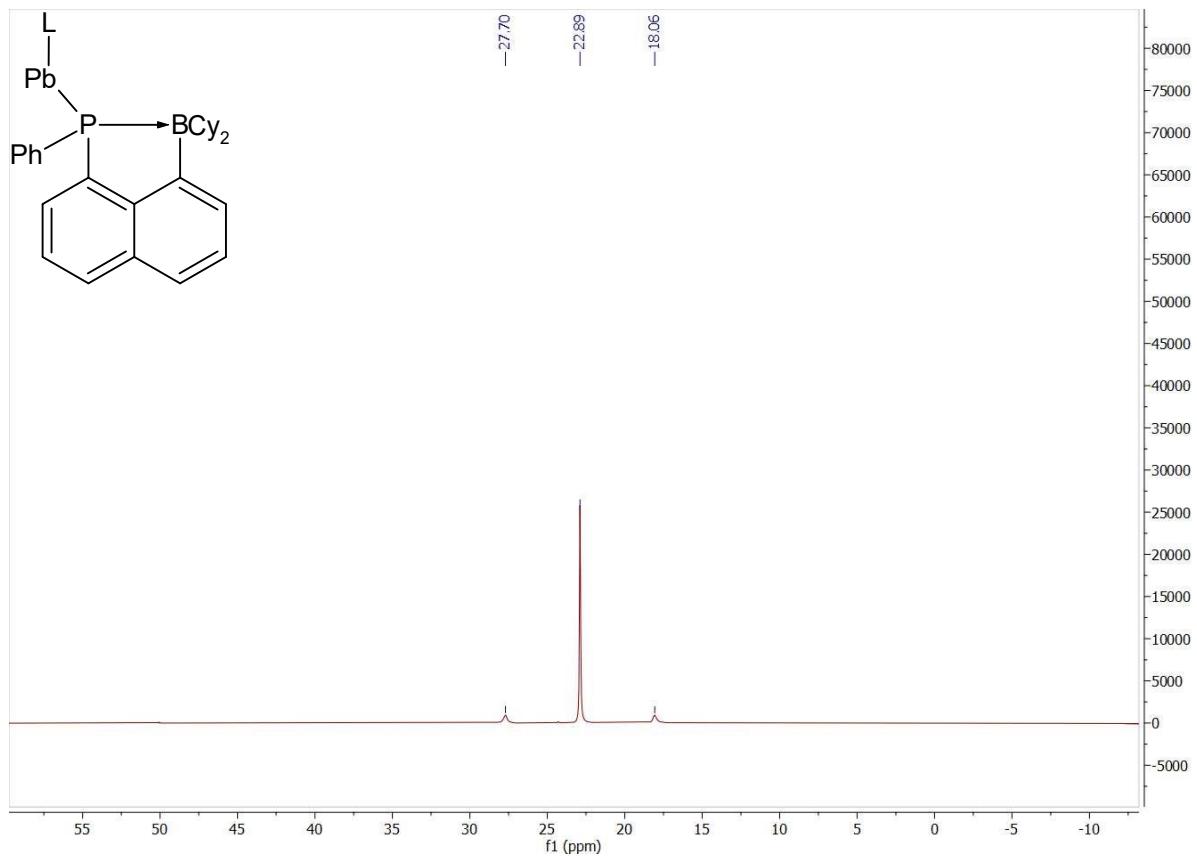


Figure S56. $^{31}\text{P}\{\text{H}\}$ NMR (C_6D_6 , 202.49 MHz) of $[1-\text{BCy}_2-8-\text{P}(\text{PbL})\text{Ph}-\text{C}_{10}\text{H}_6]$ (**13**)

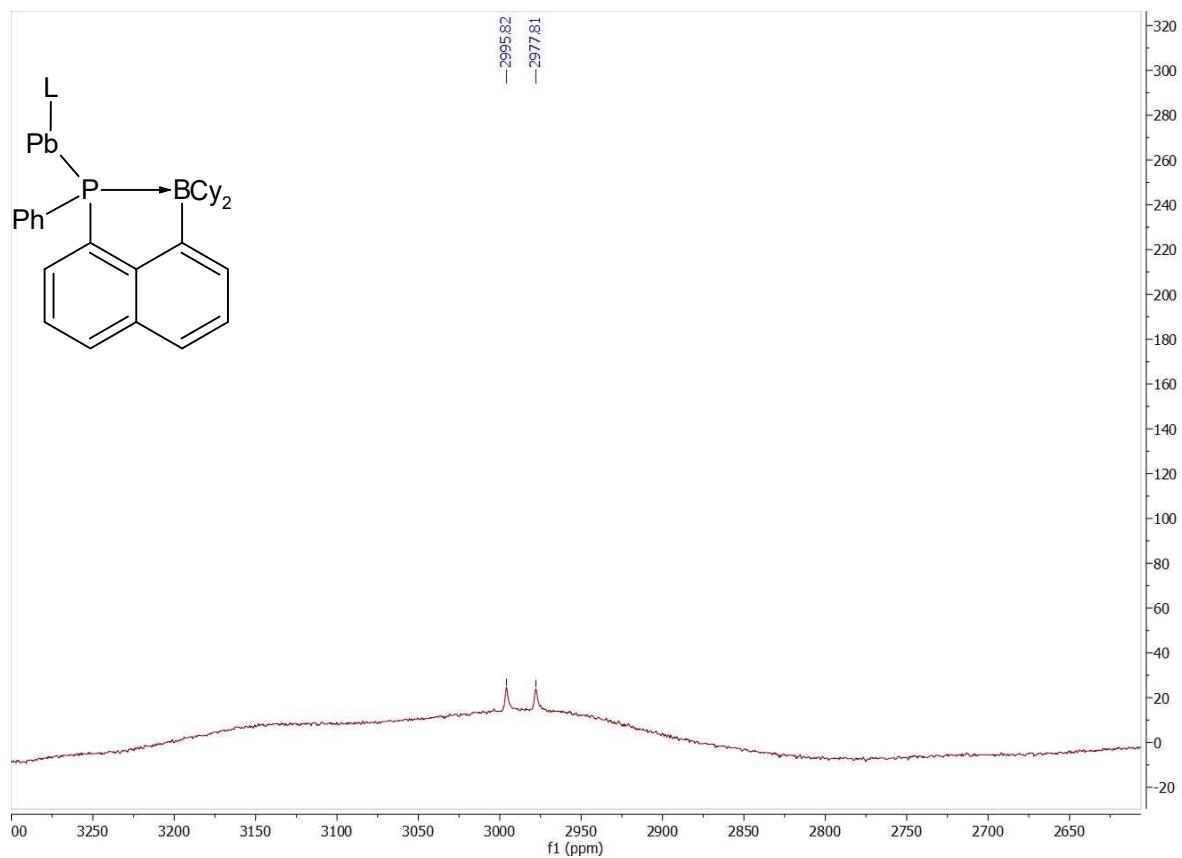


Figure S57. $^{209}\text{Pb}\{\text{H}\}$ NMR (C_6D_6 , 104.64 MHz) of [1- BCy_2 -8- $\text{P}(\text{PbL})\text{Ph-C}_{10}\text{H}_6$] (**13**)

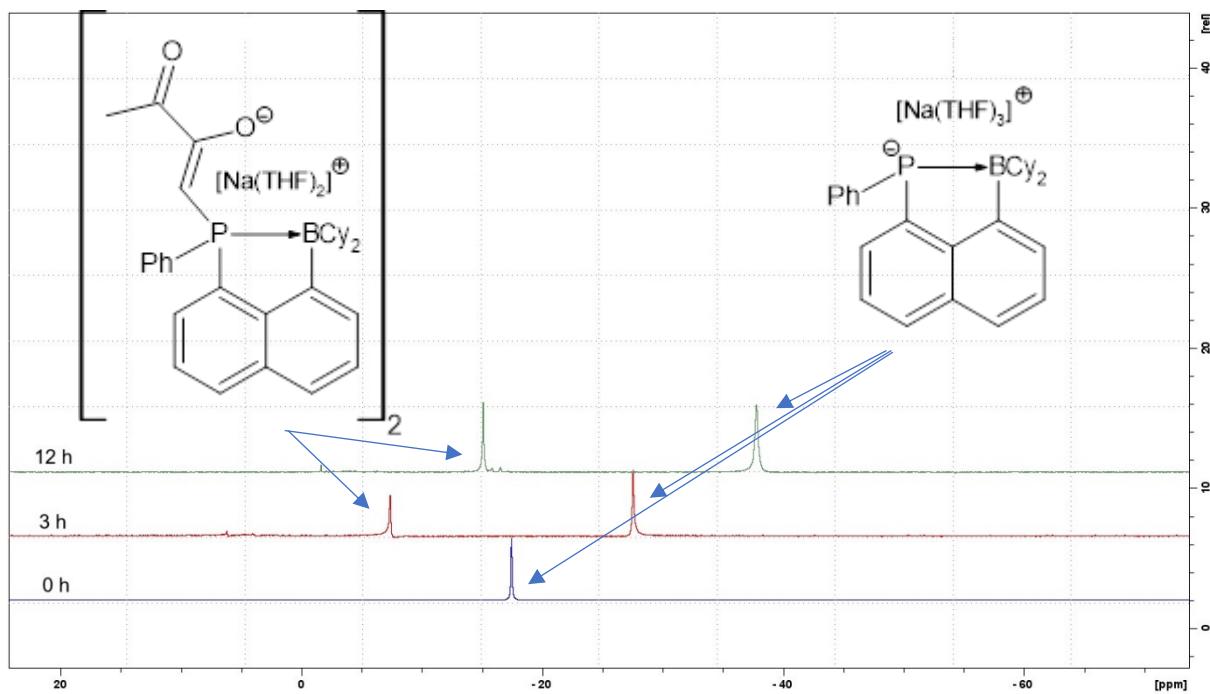


Figure S58. The $^{31}\text{P}\{\text{H}\}$ NMR spectra of the reaction mixture of **5** and 2,3-butanedione

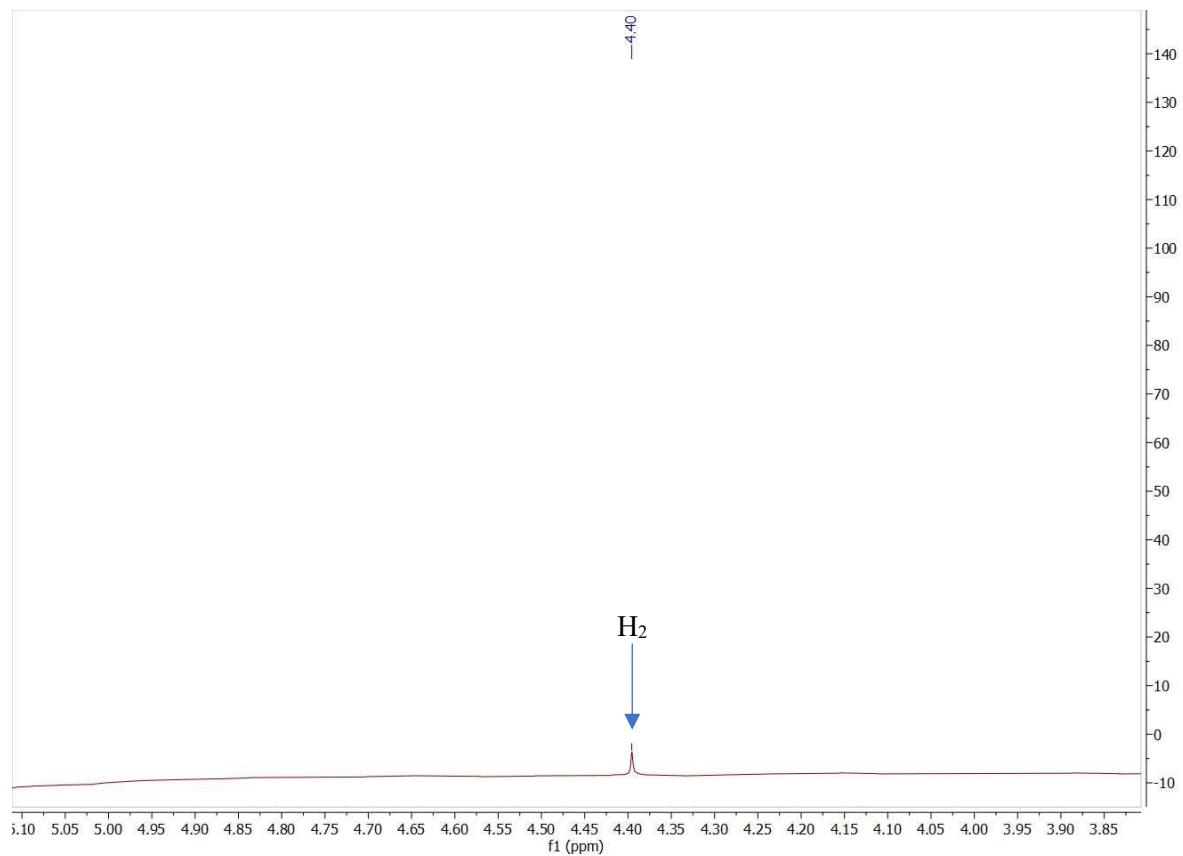


Figure S59. ^1H NMR spectrum of H_2 in $\text{THF}/\text{C}_6\text{D}_6$

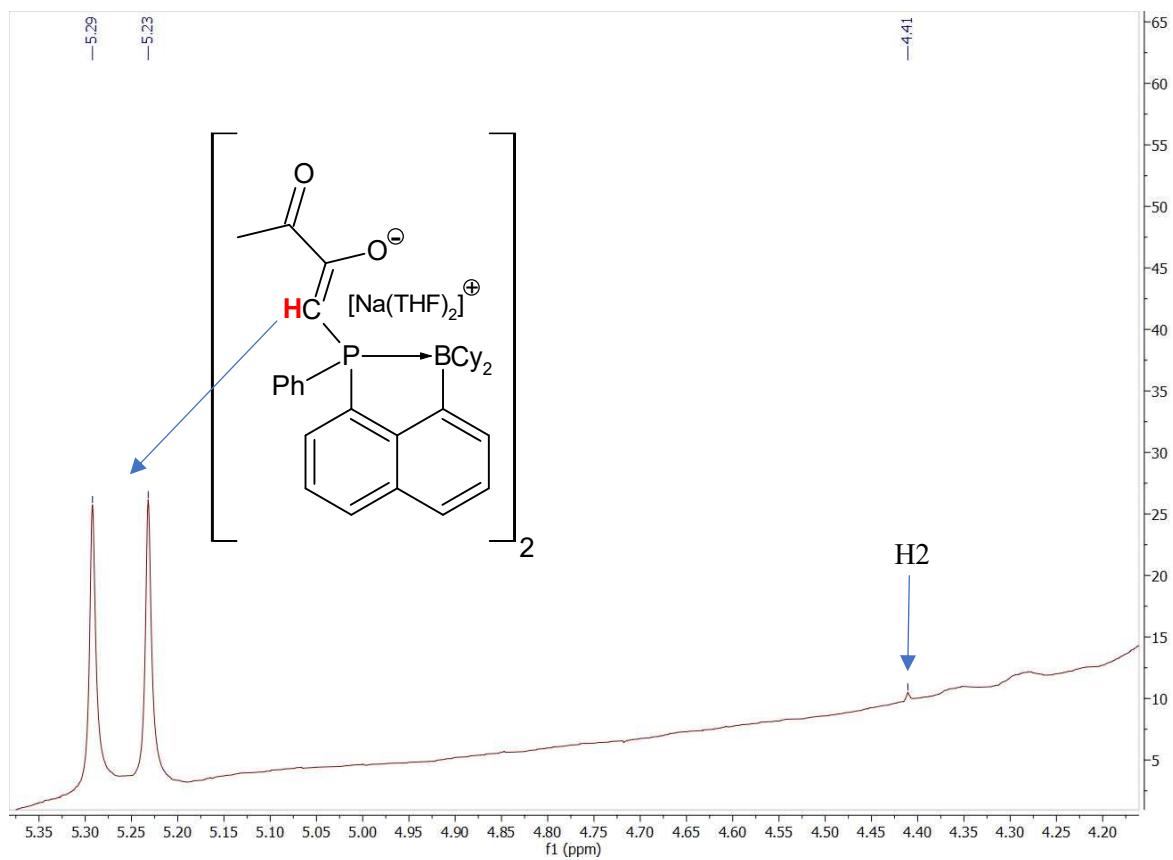


Figure S60. Expanded part of the ^1H NMR spectrum of the reaction mixture of 5 and 2,3-butanedione in $\text{THF}/\text{C}_6\text{D}_5$.

Table S1: Crystallographic data of compounds **3**, **4**·(C₄H₈O), **5**, **6**, **7**, **9**, **10**·2(C₄H₈O), **11**, and **12**·0.5(C₇H₈)

Compound	3	4 ·(C ₄ H ₈ O)	5	6	7	9	10 ·2(C ₄ H ₈ O)	11	12 ·0.5(C ₇ H ₈)
Empirical formula	C ₄₄ H ₅₆ B ₂ P ₂	C ₅₆ H ₆₆ B ₂ P ₂ ·(C ₄ H ₈ O)	C ₄₀ H ₅₇ BNaO ₃ P	C ₃₆ H ₄₉ BKO ₂ P	C ₇₂ H ₉₈ B ₂ Na ₂ O ₆ P ₂	C ₇₂ H ₉₈ B ₂ Na ₂ O ₄ Se ₂ P ₂	C ₈₀ H ₁₀₆ B ₂ Na ₂ O ₈ P ₂ , 2(C ₄ H ₈ O)	C ₃₃ H ₄₂ BOP	C ₄₀ H ₅₂ BNP Sn, 0.5(C ₇ H ₈)
Crystal system	Triclinic	Triclinic	orthorhombic	monoclinic	monoclinic	Triclinic	Triclinic	orthorhombic	monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>Pna</i> 2 ₁	<i>P2</i> ₁ /n	<i>P2</i> ₁ /n	<i>P</i> -1	<i>P</i> -1	<i>P</i> - <i>b</i> - <i>c</i> - <i>a</i>	<i>P</i> 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 $R_{int} = \sum |F_o|^2 - |F_c|^2| / \sum |F_o|^2$, ^b $GOF = [\sum (w(F_o^2 - F_c^2)^2) / (N_{differ} - N_{params})]^{1/2}$, ^cWeighting scheme: $w = [\sigma^2(F_o^2) + (w_1 P)^2 + w_2 P]^{-1}$, where $P = [\max(F_o^2) + 2F_c^2]$, $R(F) = \sum |F_o| - |F_c| / \sum |F_o|$, $wR(F^2) = [\sum (w(F_o^2 - F_c^2)^2) / (\sum w(F_o^2)^2)]^{1/2}$
