Supporting Information for

Phosphinoboration of Carbodiimides, Isocyanates, Isothiocyanates and CO_2

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General Conditions and Methods

All reagents and solvents, unless otherwise noted, were purchased from commercial sources and used without further purification. Solvents were distilled over appropriate drying agents under dinitrogen: CH_2Cl_2 over CaH_2; hexane, benzene and toluene over freshly wired sodium. $CDCl_3$ was purchased from Cambridge Isotope Laboratories, degassed by three freeze-pump-thaw cycles and stored in a dark place over oven-activated 4Å molecular sieves. Ph_2PBpin was prepared as previously reported.

NMR spectra were recorded on Bruker AvanceIII-400 MHz (^{1}H: 400 MHz; ^{11}B: 128 MHz and ^{13}C: 100 MHz) and Agilent DD2-500 MHz (^{13}C: 126 MHz and ^{31}P: 202 MHz), or JEOL JNM-GSX400 (^{1}H: 400 MHz; ^{11}B: 128 MHz; ^{13}C: 100 MHz and ^{31}P: 162 MHz) spectrometers. Chemical shifts (δ) are reported in ppm [relative to residual solvent peaks (^{1}H and ^{13}C), external $BF_3{\cdot}OEt_2$ (^{11}B) or H_3PO_4 (^{31}P)]. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint), multiplet (m), overlapping (ov), and broad (br). Melting points were measured uncorrected with a Stuart SMP30 apparatus. All manipulations were performed under an atmosphere of dinitrogen using standard Schlenk techniques or in an MBraun LabMaster glovebox. Elemental Analysis was performed at the University of Windsor using a Perkin Elmer 2400 combustion CHN analyser.

*General Procedure: Preparation of Compounds **1a-12a***

Phosphinoboration of Carbodiimides, Isocyanates and Isothiocyanates. A mixture of Ph_2PBpin (100 mg, 0.320 mmol) and substrate (0.32 mmol for **1a-7a** and **9a-11a**; 0.64 mmol for **8a** and **12a**) in toluene (5 mL) was stirred for the prescribed time at room temperature. The solvent was removed under vacuum and the residue was either washed with hexane (method A) - or recrystallized from hexane (method B).

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*Synthesis of 1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-N,N'-di-p-tolylphosphinecarboximidamide (**1a**)*

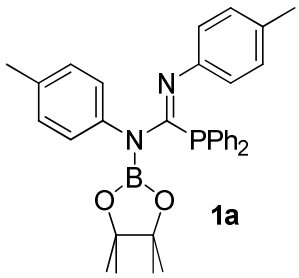
This mixture was allowed to stir for 18 h and the product was isolated using method A. Colourless crystalline solid. Yield: 82% (140 mg); mp: 117-120°C; Anal. Calcd. For $C_{33}H_{36}BN_2O_2P$: (534.44): C, 74.16; H, 6.79; N, 5.24. Found: C, 74.33; H, 6.96; N, 5.09.

^{1}H NMR ($CDCl_3$): δ: 7.59 (t, *J* = 7.8 Hz, 4H, Ar), 7.29-7.23 (ov m, 6H, Ar), 7.01-6.97 (ov m, 6H, Ar), 6.78 (d, *J* = 7.0 Hz, 2H, Ar), 2.30 (s, 3H, Me), 2.23 (s, 3H, Me), 0.88 (s, 12H, pin).

$^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 21.8 (s).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 164.2, 146.6 (d, J_{CP} = 5.7 Hz), 139.2, 135.5 (d, J_{CP} = 5.6 Hz), 135.3 (d, J_{CP} = 21.1 Hz), 133.7, 133.6, 129.3 (d, J_{CP} = 14.4 Hz), 128.9, 128.0 (d, J_{CP} = 7.7 Hz), 124.3, 120.8, 83.3, 24.2, 21.0.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 2.2 (s).



1a

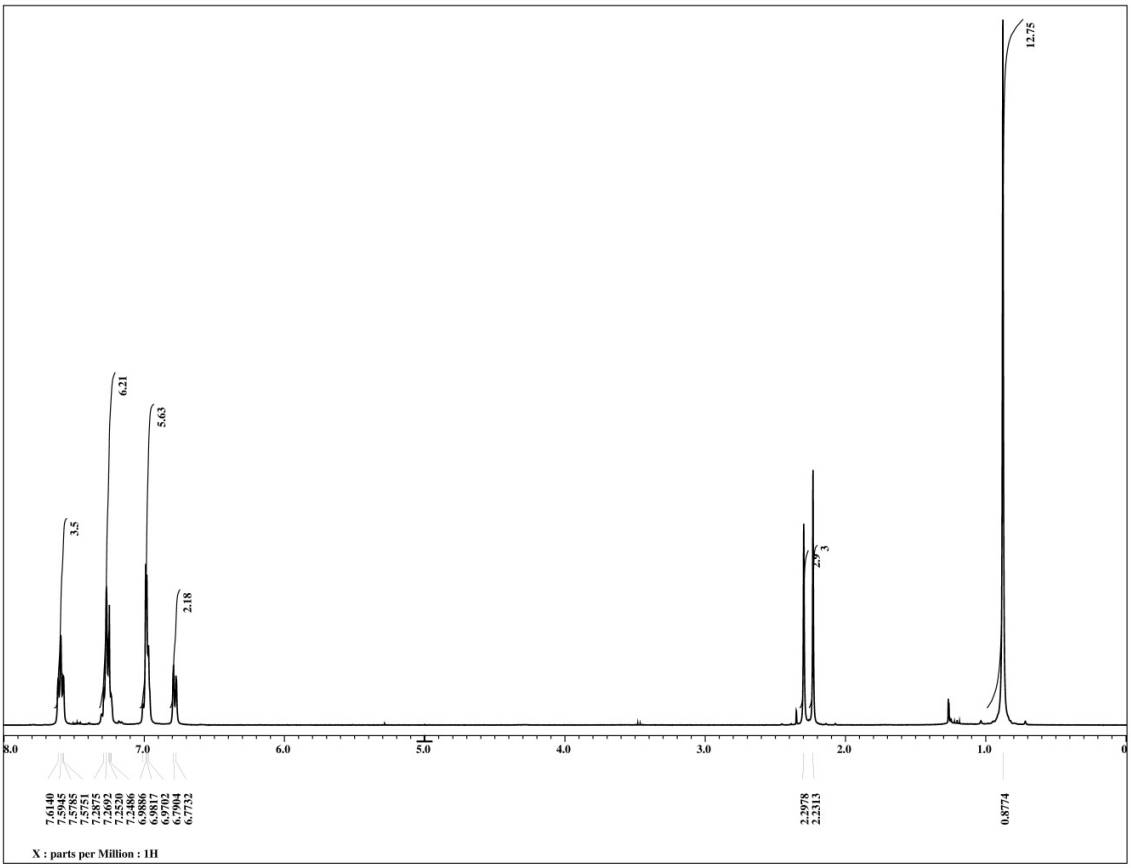


Figure S1. ^1H NMR spectrum of **1a** in $CDCl_3$ at 293 K.

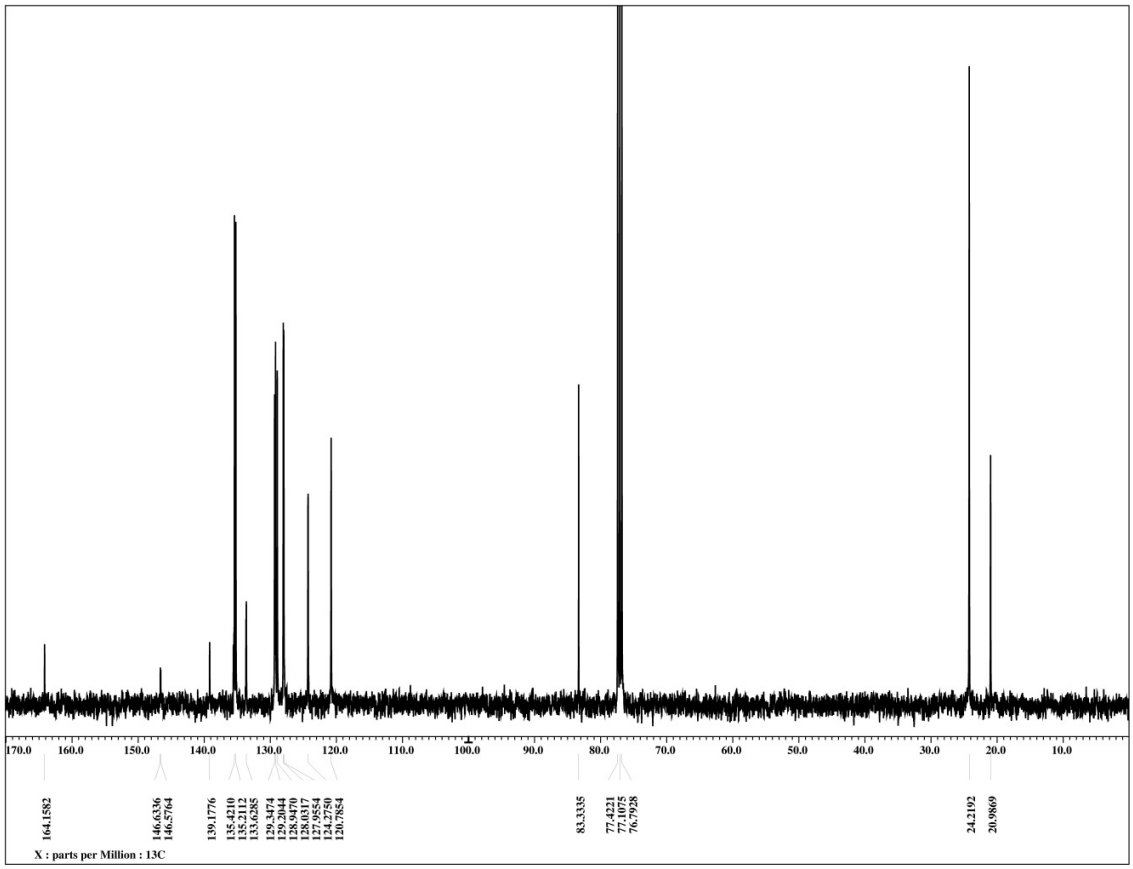


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **1a** in $CDCl_3$ at 293 K.

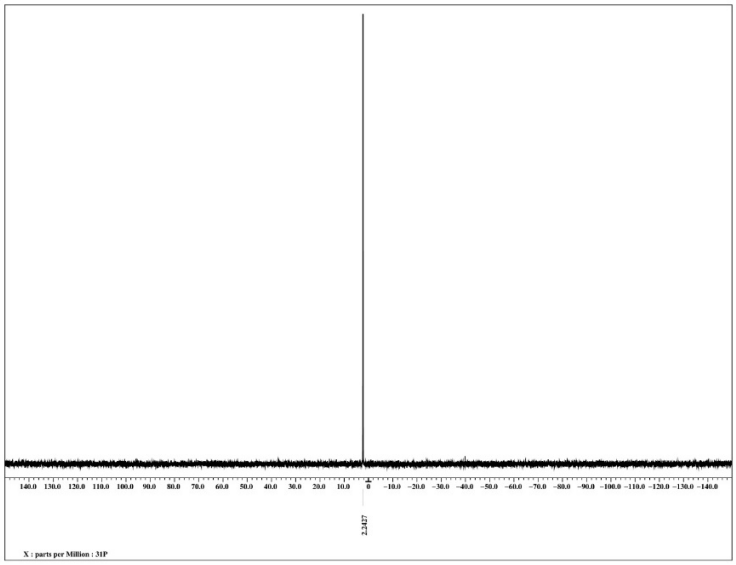


Figure S3. $^{31}P\{^{1}H\}$ NMR spectrum of **1a** in $CDCl_3$ at 293 K.

*Synthesis of N,N'-diisopropyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboximidamide (**2a**)*

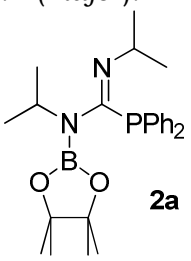
This mixture was allowed to stir for 18 h and the product was isolated using method B. Colourless crystalline solid. Yield: 74% (123 mg); mp: 83.5-84.5°C; Anal. Calcd. For $C_{25}H_{36}BN_2O_2P$: (438.36): C, 68.50; H, 8.28; N, 6.39. Found: C, 68.12; H, 8.00; N, 6.47.

^{1}H NMR ($CDCl_3$): δ 7.58 (br, 4H, Ar), 7.27-7.18 (m, 6H, Ar), 3.92 (sept, *J* = 6.2 Hz, *major*, 1H, NC*H*), 3.65 (d q, *J* = 2.6 Hz, *minor*, NC*H*), 3.38 (d q, *J* = 2.6 Hz, *major*, 1H, NC*H*), 1.10 (s, 12H, pin), 1.09-0.97 (ov m, 12H, CH(CH_3)$_2$).

$^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 21.6.

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 161.2 (d, J_{CP} = 7.7 Hz), 136.6, 135.0 (d, J_{CP} = 17.2 Hz), 134.4 (d, J_{CP} = 19.2 Hz), 128.5, 128.1 (d, J_{CP} = Hz), 127.9 (d, J_{CP} = 7.7 Hz), 82.2, 51.3 (d, J_{CP} = 14.4 Hz, *minor*), 50.7 (d, J_{CP} = 4.8 Hz), 49.0 (d, J_{CP} = 8.6 Hz), 24.7, 24.5, 23.7, 22.8, 22.7.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 0.6 (*minor*), -0.7 (*major*).



2a

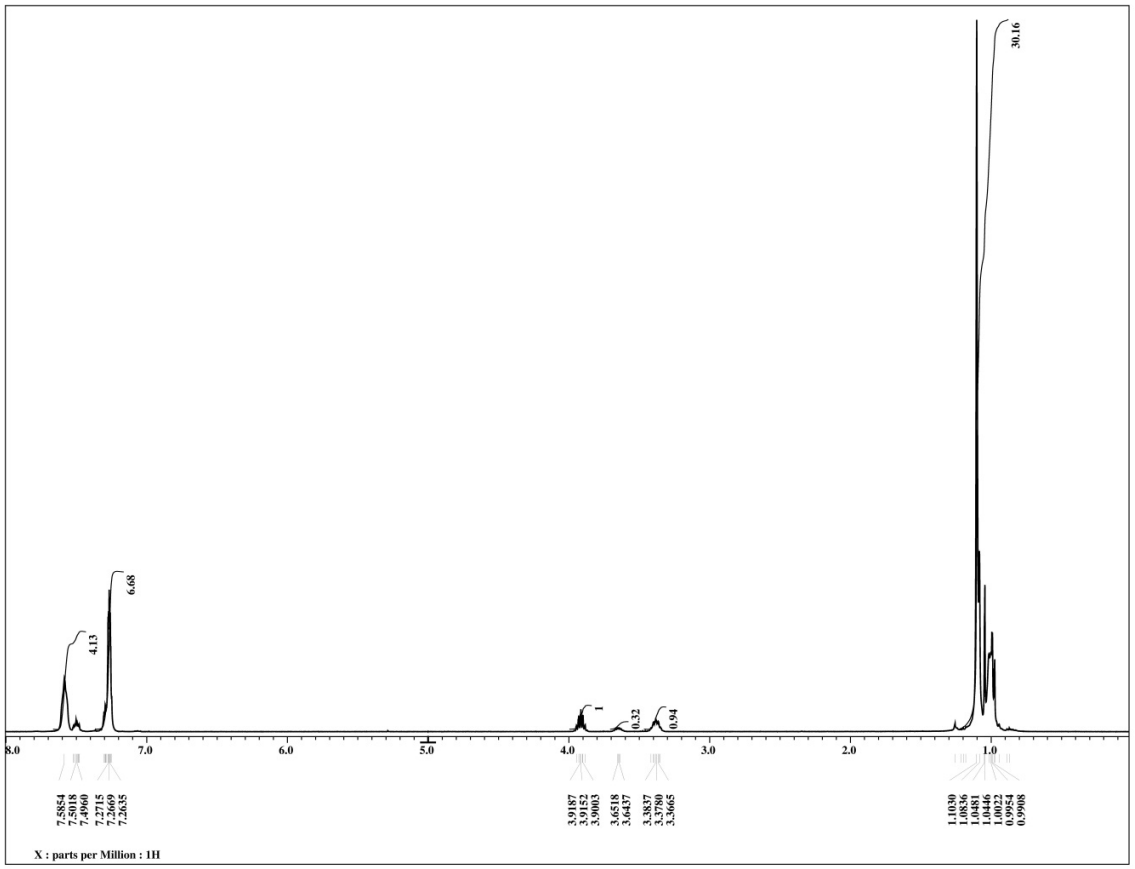


Figure S4. ^{1}H NMR spectrum of **2a** in $CDCl_3$ at 293 K.

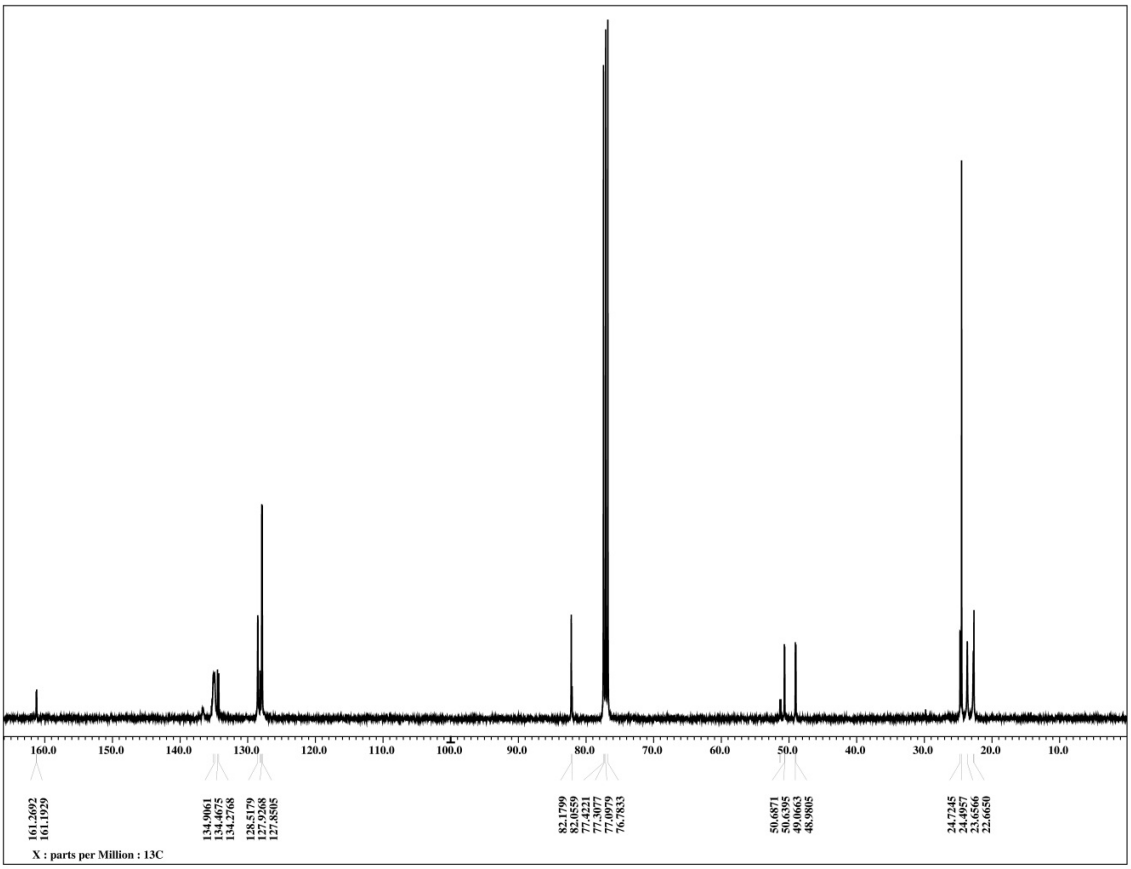


Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in $CDCl_3$ at 293 K.

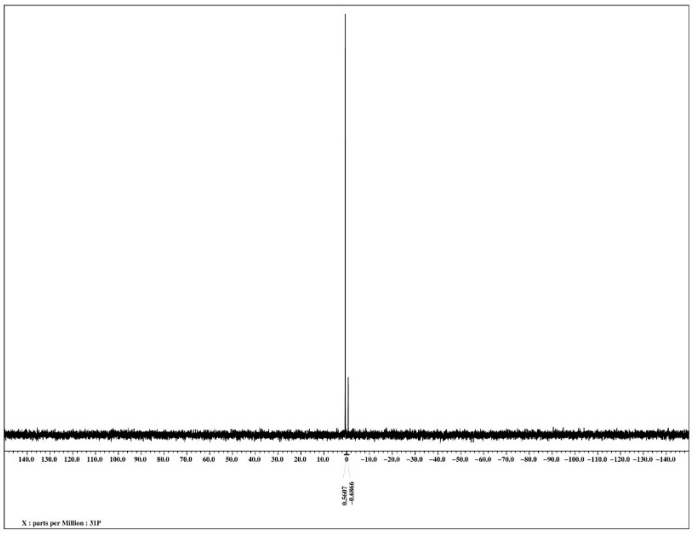


Figure S6. $^{31}P\{^{1}H\}$ NMR spectrum of **2a** in $CDCl_3$ at 293 K.

*Synthesis of N,N'-dicyclohexyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboximidamide (**3a**)*

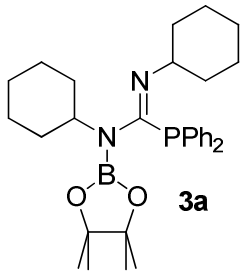
This mixture was allowed to stir for 18 h and the product was isolated using method B. White solid. Yield: 123 mg (74%); mp: 90.5-93.5°C; Anal. Calcd. For $C_{31}H_{44}BN_2O_2P$: (518.49): C, 71.81; H, 8.55; N, 5.40. Found: C, 71.58; H, 8.76; N, 5.30.

^{1}H NMR ($CDCl_3$): δ 7.63-7.55 (ov, m, 4H, Ar), 7.27 (m, 6H, Ar), 3.62 (br, 1H, NCH), 2.85 (br, 1H, NCH), 1.67-1.17 (ov, m, 20H, Cy), 1.11 (s, 12H, pin).

$^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 22.4 (s).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 161.1 (d, J_{CP} = 7.7 Hz), 136.8, 135.0, 134.4 (d, J_{CP} = 20.1 Hz), 128.5, 128.1 (d, J_{CP} = 7.7 Hz), 127.8 (d, J_{CP} = 6.7 Hz), 82.1, 59.6 (d, J_{CP} = 12.5 Hz, *minor*), 59.1 (d, J_{CP} = 5.8 Hz), 57.4 (d, J_{CP} = 6.7 Hz), 33.3, 32.9, 32.7, 26.7, 26.0, 25.8, 25.6, 25.5, 24.7, 24.5.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 0.0 (*minor*), -0.7 (*major*).



3a

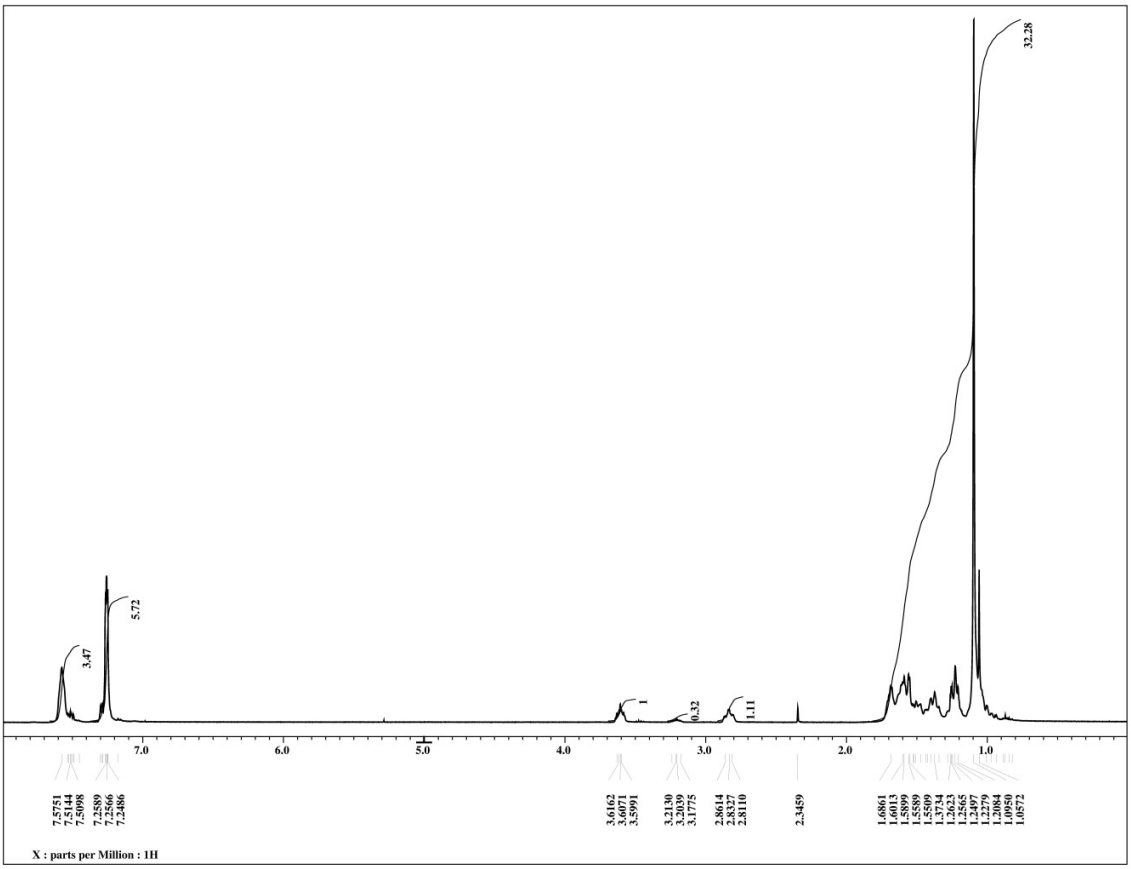


Figure S7. ^{1}H NMR spectrum of **3a** in $CDCl_3$ at 293 K.

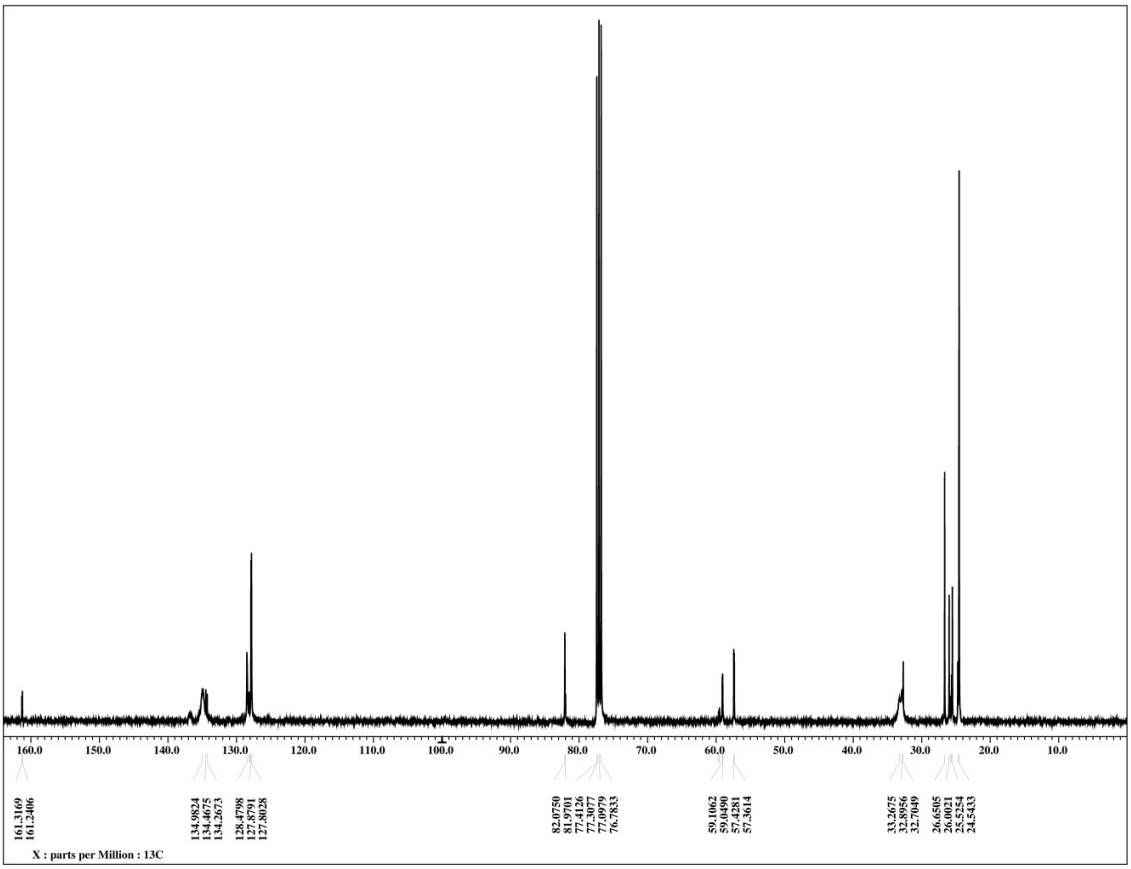


Figure S8. $^{13}C\{^{1}H\}$ NMR of **3a** in $CDCl_3$ at 293 K.

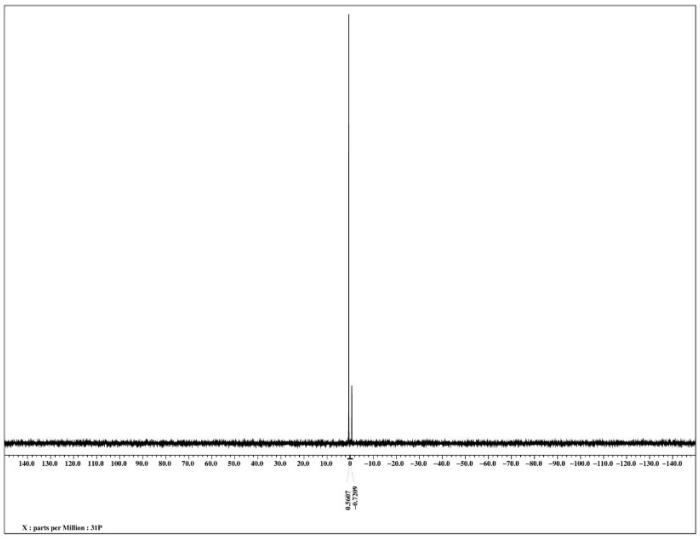


Figure S9. $^{31}P\{^{1}H\}$ NMR spectrum of **3a** in $CDCl_3$ at 293 K.

*Synthesis of N-1,1-triphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboxamide (**4a**)*

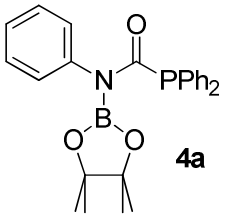
This mixture was allowed to stir for 6 h and the product was isolated using method A. White solid. Yield: 110 mg (80%); mp: 123-125°C; Anal. Calcd. For $C_{25}H_{27}BNO_3P$: (431.28): C, 69.62; H, 6.31; N, 3.25. Found: C, 69.80; H, 6.45; N, 3.29.

^{1}H NMR ($CDCl_3$): δ 7.40 (m, 4H, Ar), 7.33-7.30 (ov m, 6H, Ar), 7.25-7.20 (ov m, 3H, Ar), 7.01 (d, J = 6.9 Hz, 2H, Ar), 1.06 (s, 12H, pin).

$^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 25.2 (s).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 184.6, 139.5 (d, J_{CP} = 2.9 Hz), 134.8 (d, J_{CP} = 20.1 Hz), 134.7, 129.2, 128.9, 128.6, 128.4 (d, J_{CP} = 5.7 Hz), 127.1, 84.4, 24.2.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 9.5 (s).



4a

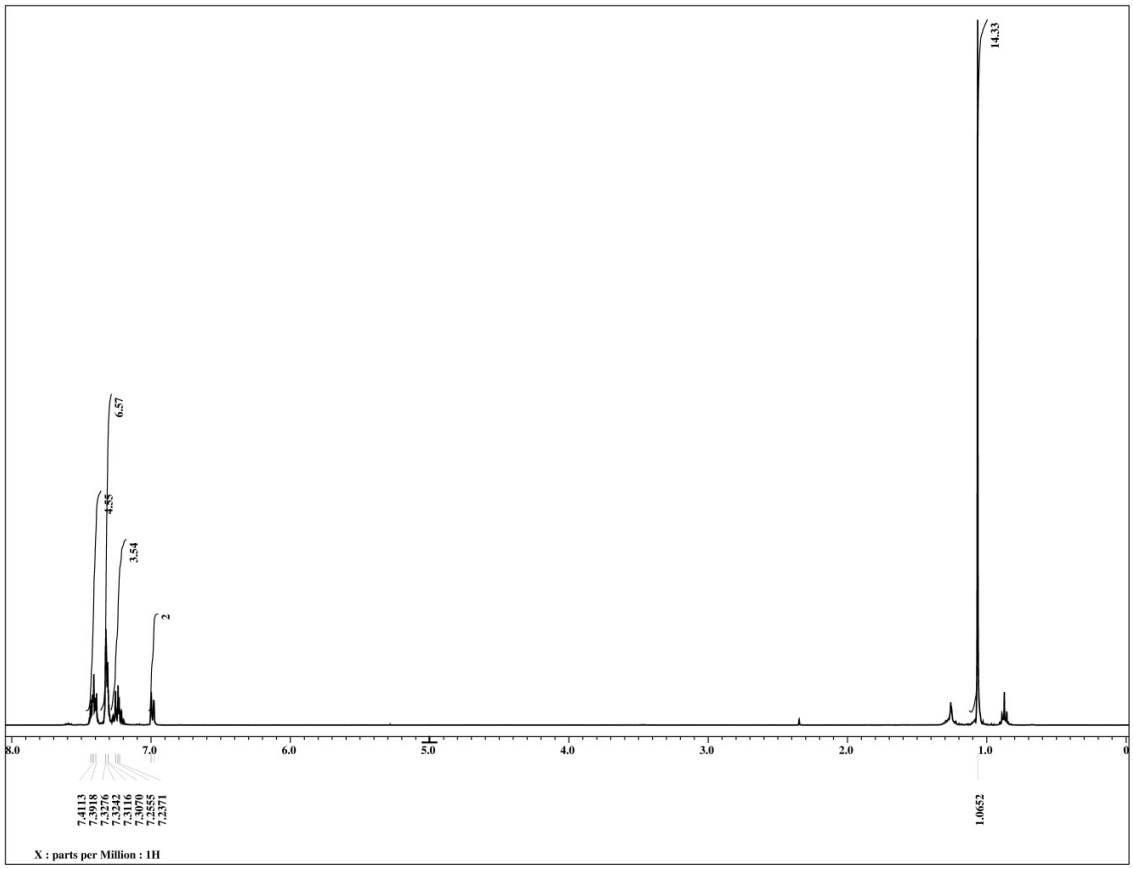


Figure S10. ^{1}H NMR spectrum of **4a** in $CDCl_3$ at 293 K.

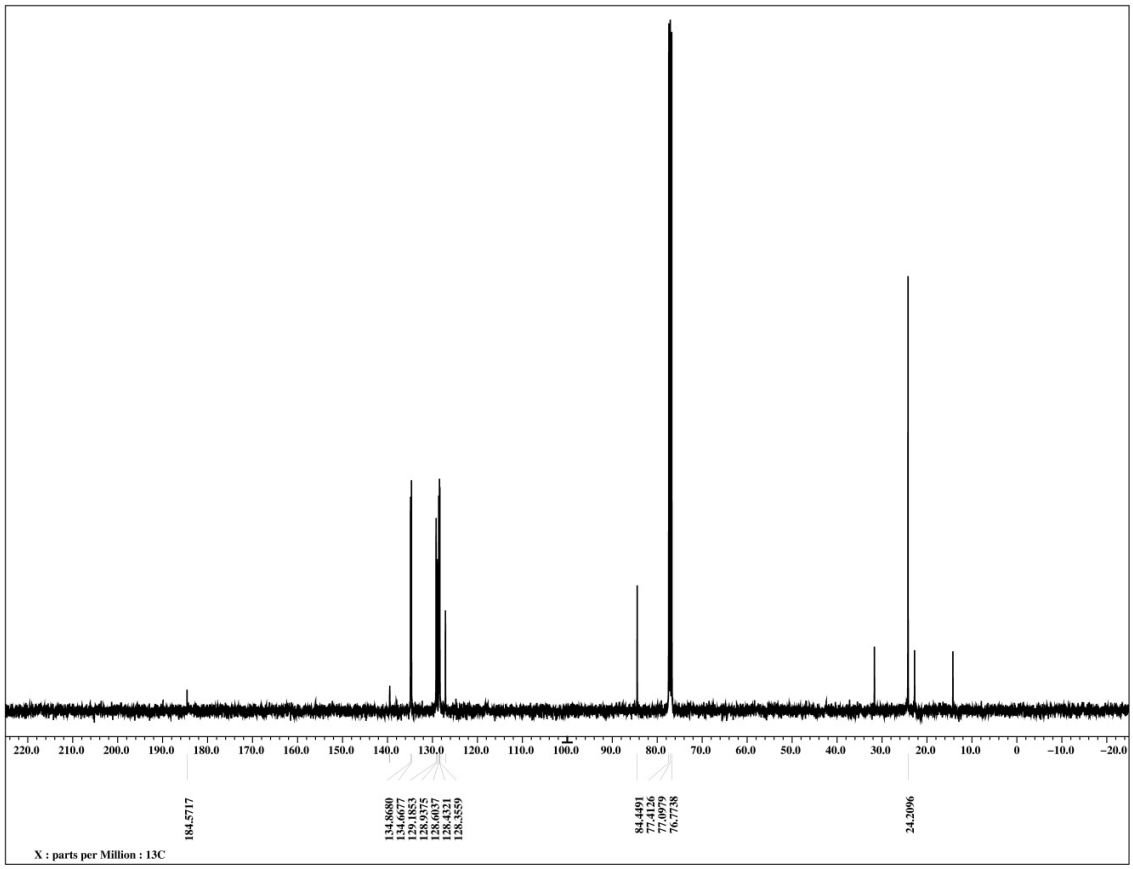


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **4a** in $CDCl_3$ at 293 K.

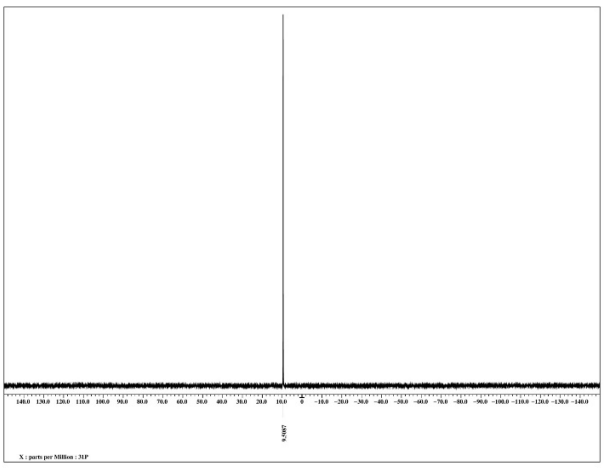


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of **4a** in $CDCl_3$ at 293 K.

*Synthesis of N-(4-nitrophenyl)-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboxamide (**5a**)*

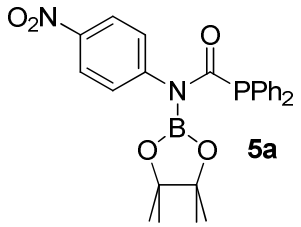
This mixture was allowed to stir for 6 h and the product was isolated using method A. Yellow solid. Yield: 130 mg (85%); mp: 94-95°C; Anal. Calcd. For $C_{25}H_{26}BN_2O_5P$: (476.28): C, 63.05; H, 5.50; N, 5.88. Found: C, 62.67; H, 5.74; N, 5.87.

^{1}H NMR ($CDCl_3$): δ 8.14 (d, *J* = 8.8 Hz, 2H, Ar), 7.41 (m, 4H, Ar), 7.38-7.33 (ov m, 6H, Ar), 7.19 (d, *J* = 8.7 Hz, 2H, Ar), 1.05 (s, 12H, pin).

$^{11}B\{^1H\}$ NMR ($CDCl_3$): δ: 23.9 (s).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 184.6 (d, J_{CP} = 34.5 Hz), 146.5, 145.8 (d, J_{CP} = 1.9 Hz), 134.7 (d, J_{CP} = 20.1 Hz), 134.1 (d, J_{CP} = 7.7 Hz), 129.7 (d, J_{CP} = 21.1 Hz), 128.6 (d, J_{CP} = 7.7 Hz), 124.0, 85.1, 24.2.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 10.8 (s).



5a

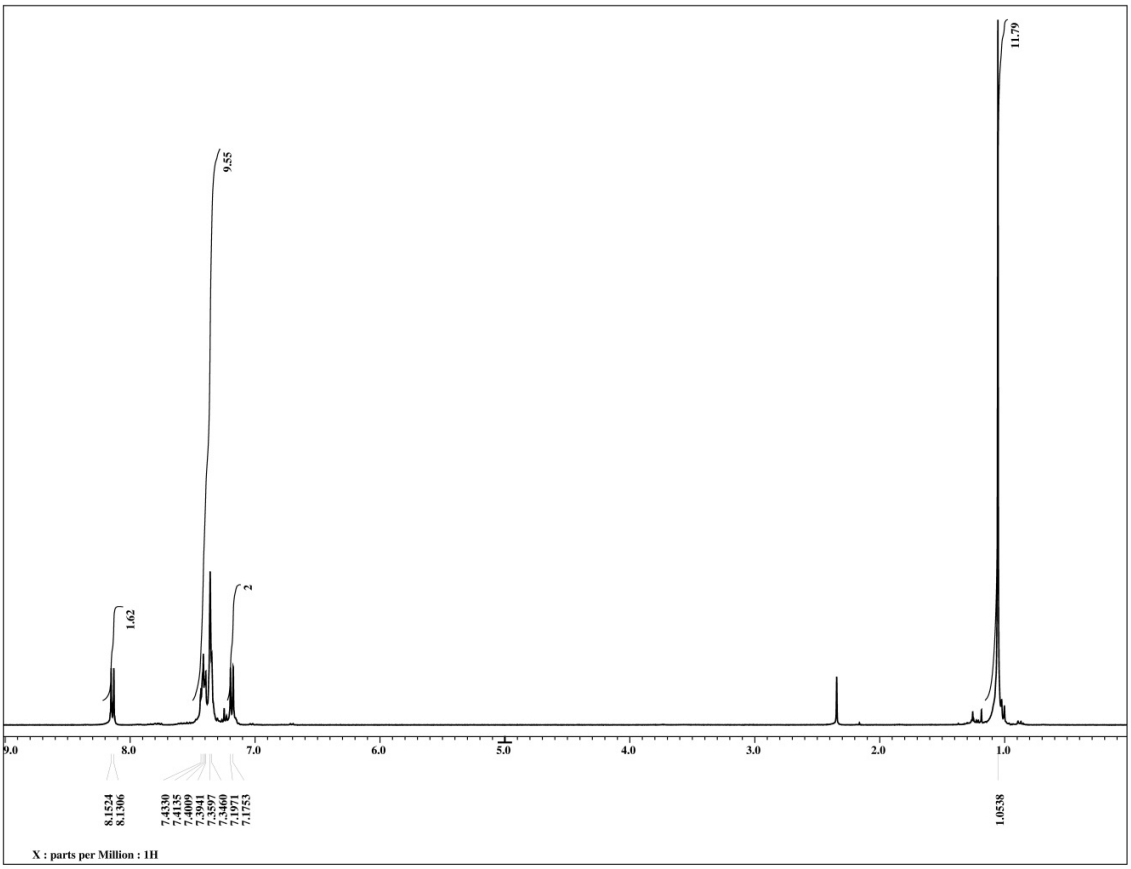


Figure S13. ^{1}H NMR spectrum of **5a** in $CDCl_3$ at 293 K.

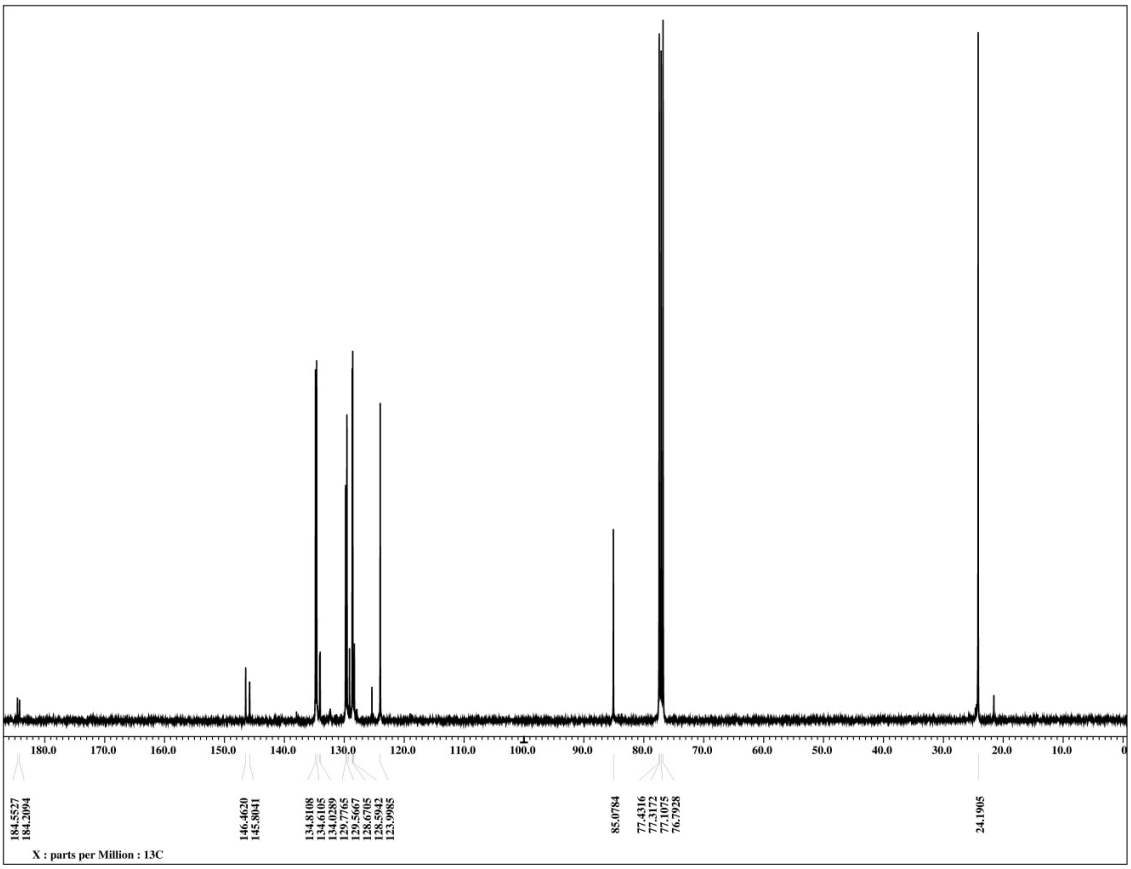


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **5a** in $CDCl_3$ at 293 K.

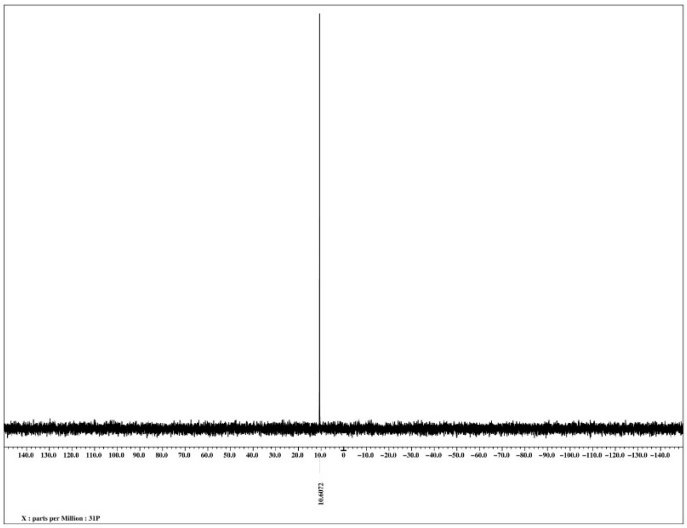


Figure S15. $^{31}P\{^{1}H\}$ NMR spectrum of **5a** in $CDCl_3$ at 293 K.

*Synthesis of N-ethyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboxamide (**6a**)*

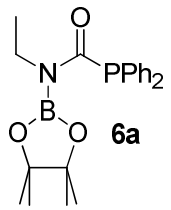
This mixture was allowed to stir for 18 h and the product was isolated using method B. White solid. Yield: 93 mg (76%); mp: 79.4-80.4°C; Anal. Calcd. For $C_{21}H_{27}BNO_3P$: (383.23): C, 65.82; H, 7.10; N, 3.65. Found: C, 65.40; H, 7.42; N, 3.58.

^1H NMR ($CDCl_3$): δ 7.36 (m, 4H, Ar), 7.34-7.31 (ov m, 6H, Ar), 3.53 (q, J = 6.9 Hz, 2H, CH_2), 1.11 (t, J = 6.9 Hz, 3H, CH_3), 1.00 (s, 12H, pin).

$^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 24.5 (s).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 183.4 (d, J_{CP} = 30.7 Hz), 135.9 (d, J_{CP} = 6.7 Hz), 134.5 (d, J_{CP} = 20.1 Hz), 129.0, 128.4 (d, J_{CP} = 7.7 Hz), 84.3, 38.9, 15.4.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 10.9 (s).



6a

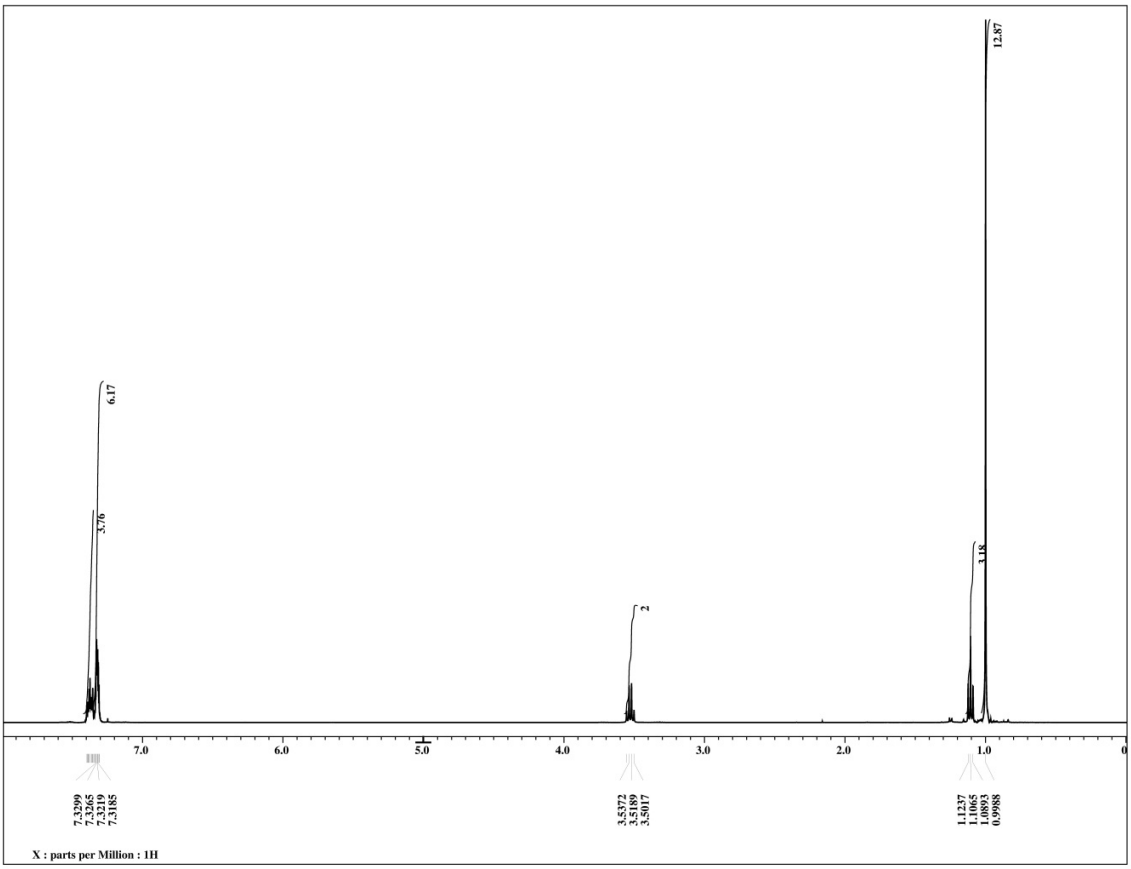


Figure S16. ^{1}H NMR spectrum of **6a** in $CDCl_3$ at 293 K.

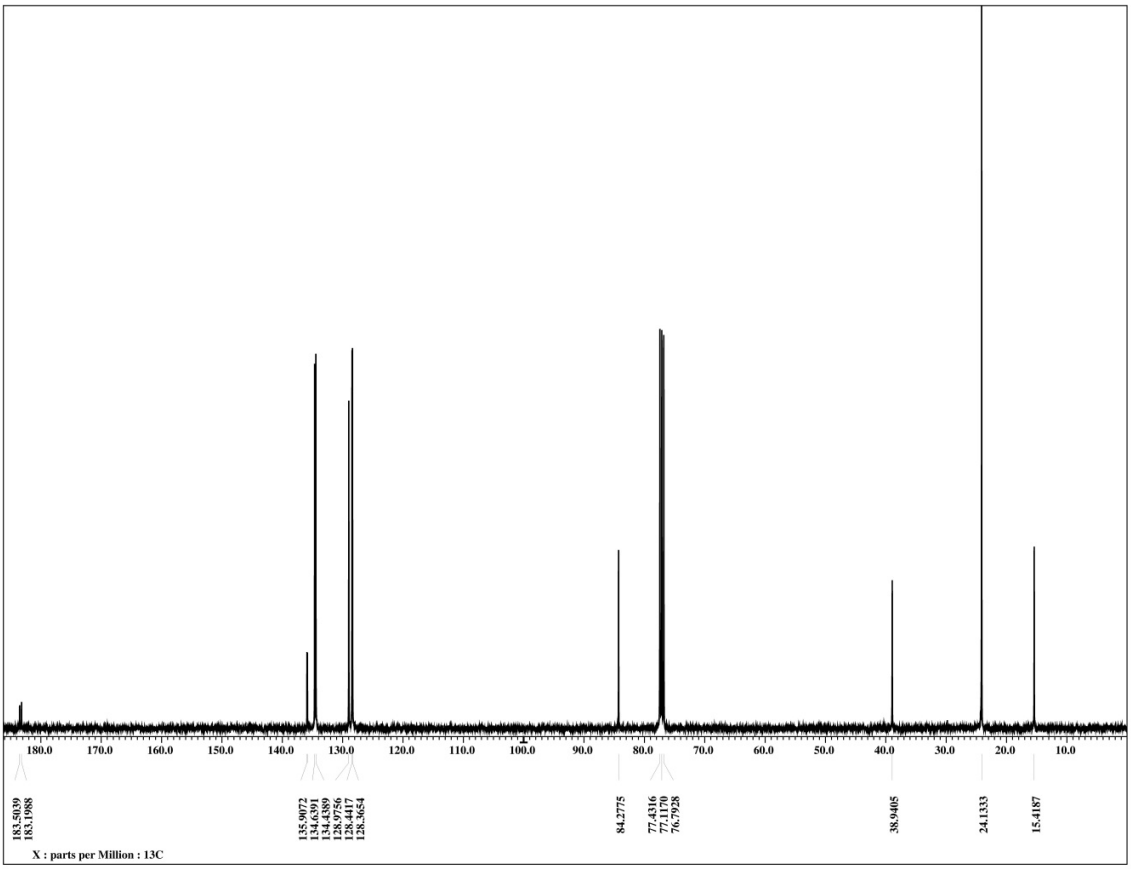


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **6a** in $CDCl_3$ at 293 K.

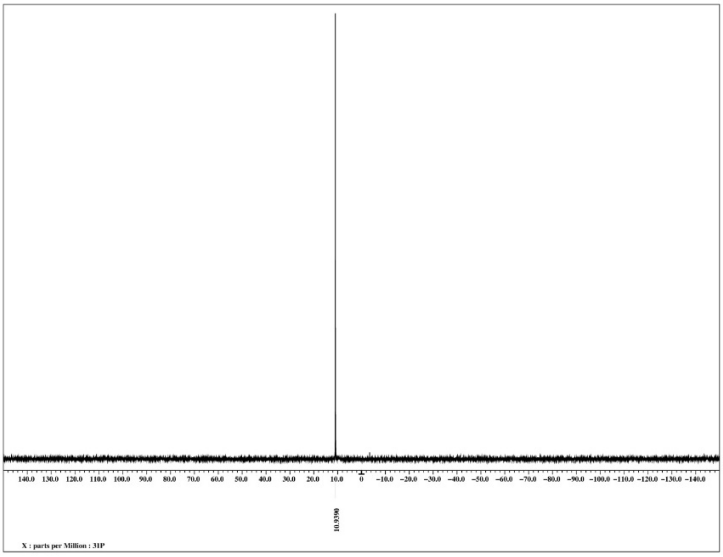


Figure S18. $^{31}P\{^{1}H\}$ NMR spectrum of **6a** in $CDCl_3$ at 293 K.

*Synthesis of N-cyclohexyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboxamide (**7a**)*

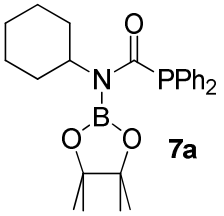
This mixture was allowed to stir for 18 h where the product was isolated using method A. White solid. Yield: 110 mg (78%); mp: 128.5-131.5°C; Anal. Calcd. For $C_{25}H_{33}BNO_3P$: (437.33): C, 68.66; H, 7.61; N, 3.20. Found: C, 68.49; H, 7.97; N, 3.31.

^{1}H NMR ($CDCl_3$): δ 7.39 (m, 4H, Ar), 7.33-7.30 (ov m, 6H, Ar), 4.24 (tt, *J* = 3.0 Hz, *J* = 0.9 Hz, 2H, C*H*), 1.89 (m, 2H, Cy), 1.72 (m, 2H, Cy), 1.62-1.54 (ov m, 3H, Cy), 1.26 (m, 2H, Cy), 1.11 (m, 1H, Cy), 1.02 (s, 12H, pin).

$^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 24.7 (s).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 183.4 (d, J_{CP} = 29.6 Hz), 136.2 (d, J_{CP} = 8.1 Hz), 134.5 (d, J_{CP} = 20.1 Hz), 128.9, 128.3 (d, J_{CP} = 8.1 Hz), 84.0, 54.3, 31.4, 26.5, 25.5, 24.3.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 11.8 (s).



7a

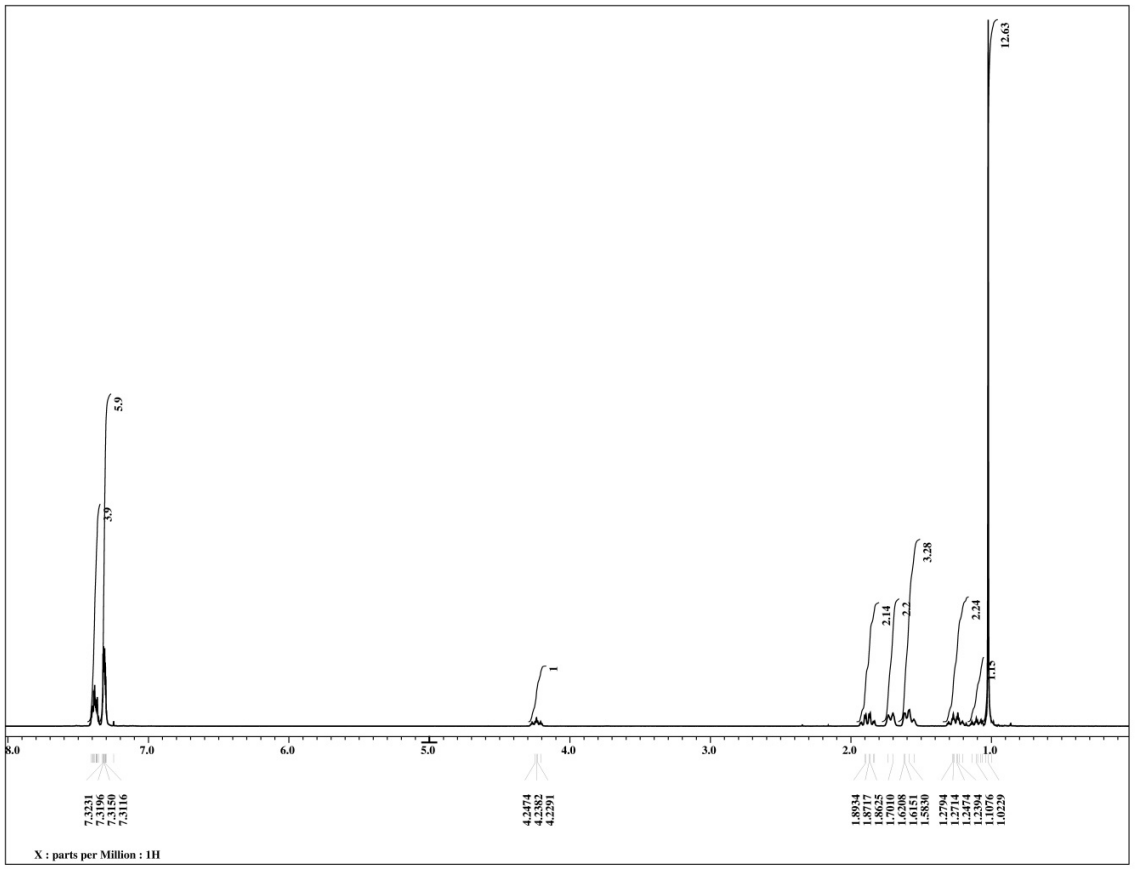


Figure S19. ^{1}H NMR spectrum of **7a** in $CDCl_3$ at 293 K.

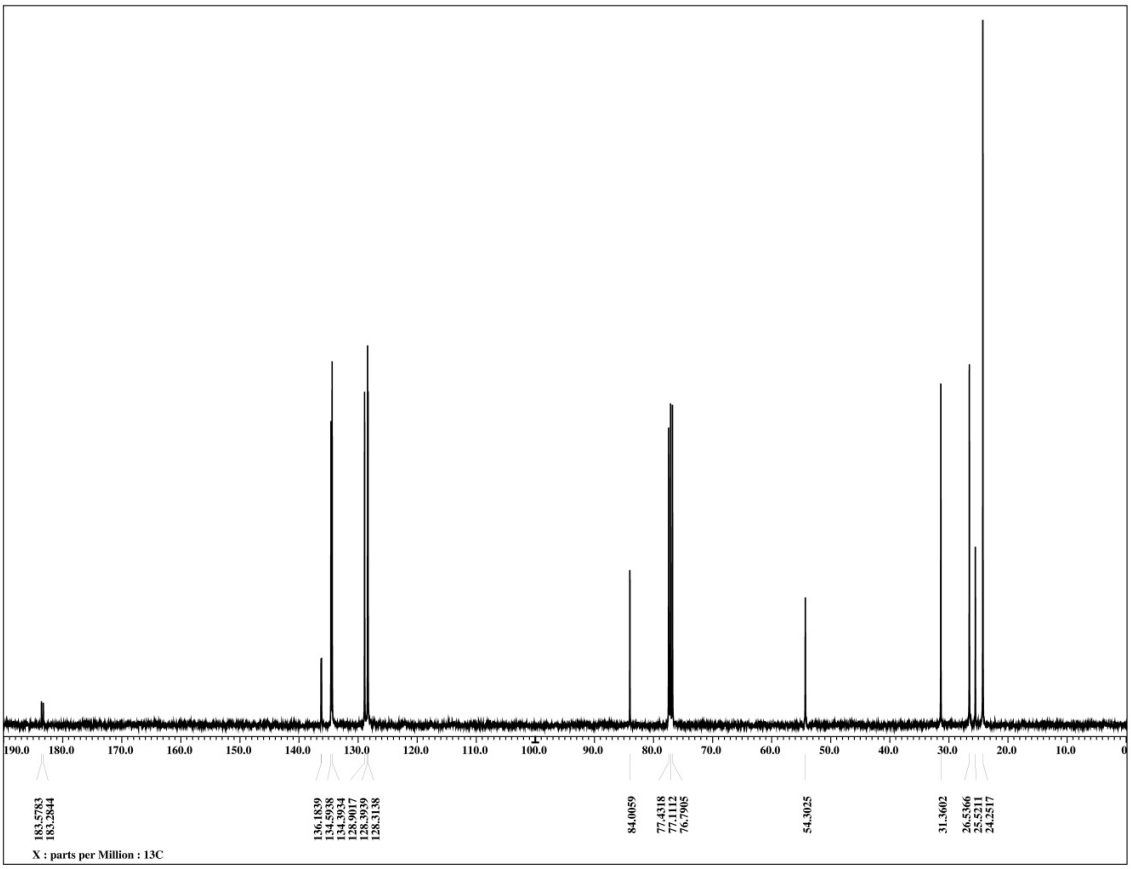


Figure S20. $^{13}C\{^{1}H\}$ NMR spectrum of **7a** in $CDCl_3$ at 293 K.

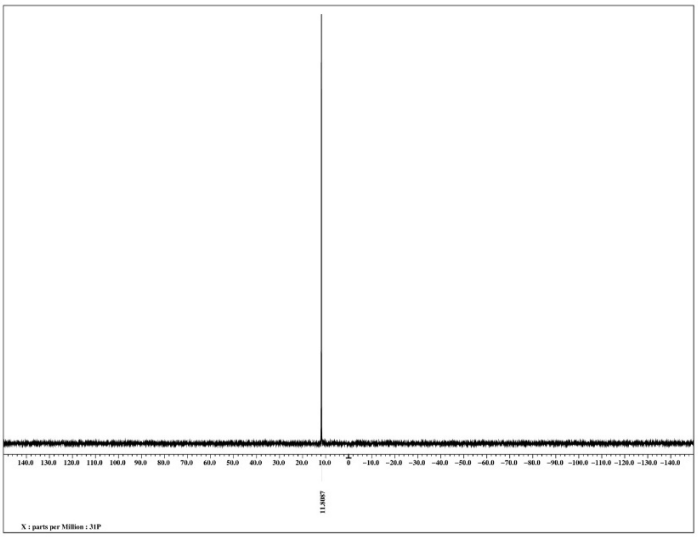


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of **7a** in $CDCl_3$ at 293 K.

*Synthesis of N-tert-butyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarboxamide (**8a**)*

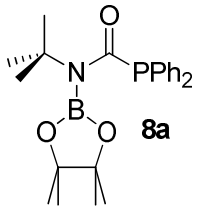
This mixture was allowed to stir for 2 days and the product was isolated using method A. White solid. Yield: 100 mg (76%); mp: 119.1-120.5°C; Anal. Calcd. For $C_{23}H_{31}BNO_3P$: (411.29): C, 67.17; H, 7.60; N, 3.41. Found: C, 67.01; H, 7.21; N, 3.43.

^1H NMR ($CDCl_3$): δ 7.49 (m, 4H, Ar), 7.35-7.31 (ov m, 6H, Ar), 7.19 (d, J = 8.7 Hz, 2H, Ar), 1.43 (s, 9H, tBu), 1.38 (s, 12H, pin).

$^{11}B\{^1H\}$ NMR ($CDCl_3$): δ 25.2 (s).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.4 (d, J_{CP} = 12.5 Hz), 134.6 (d, J_{CP} = 8.6 Hz), 134.0 (d, J_{CP} = 19.2 Hz), 129.1, 128.4 (d, J_{CP} = 6.7 Hz), 84.9, 56.8 (d, J_{CP} = 7.7 Hz), 28.9, 25.4, 25.4.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 3.5 (s).



8a

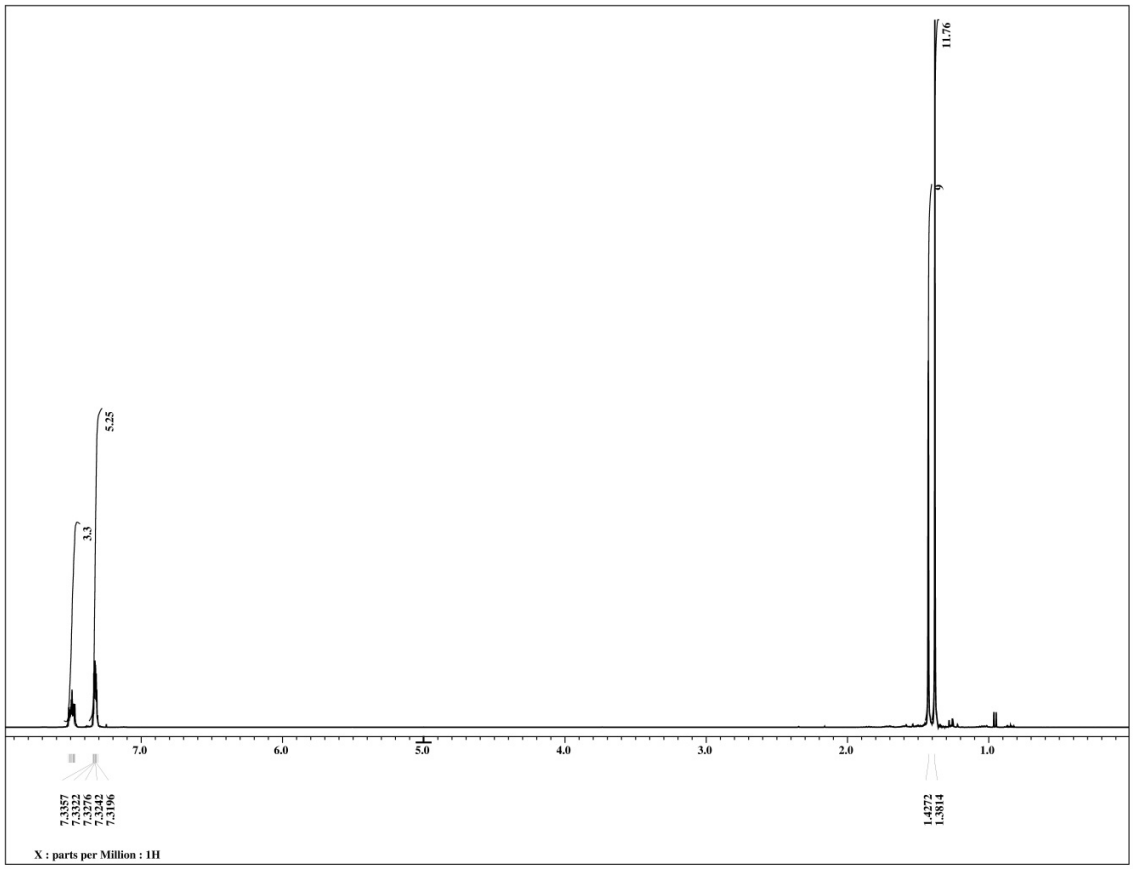


Figure S22. ^{1}H NMR spectrum of **8a** in $CDCl_3$ at 293 K.

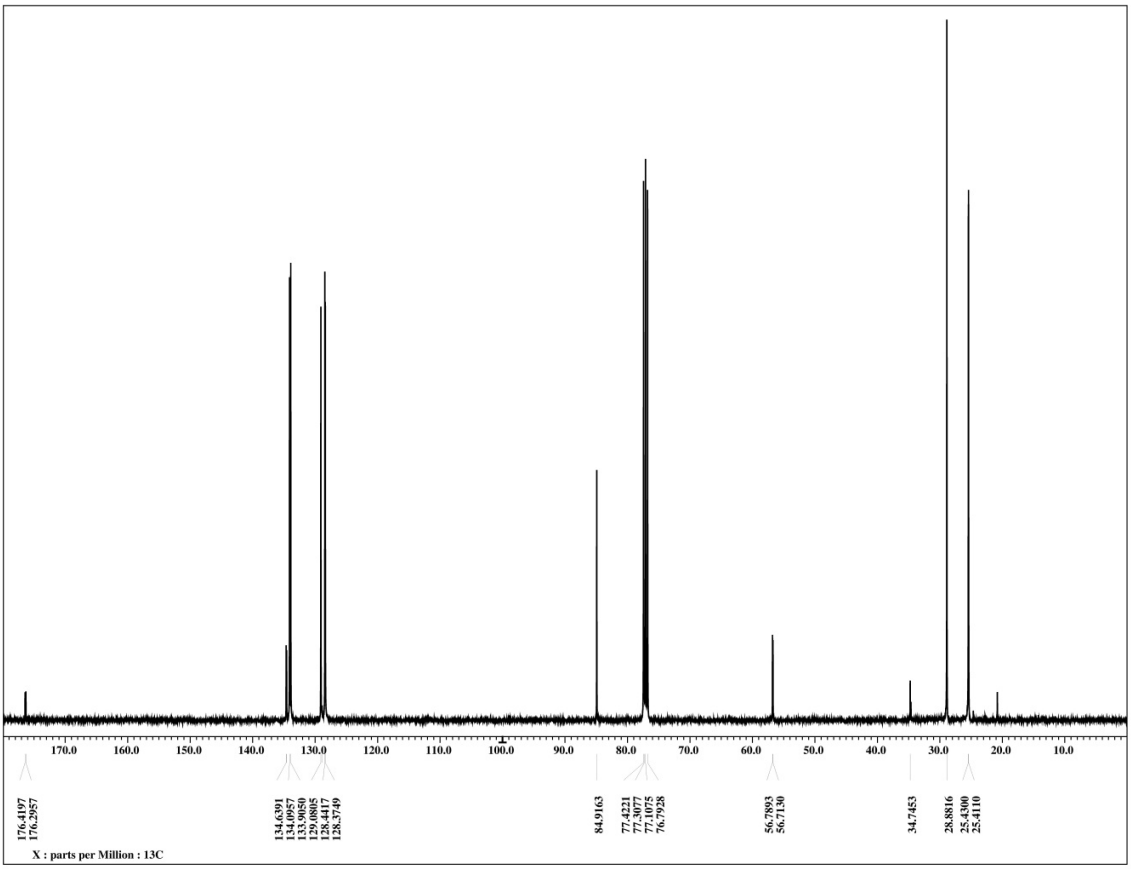


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **8a** in $CDCl_3$ at 293 K.

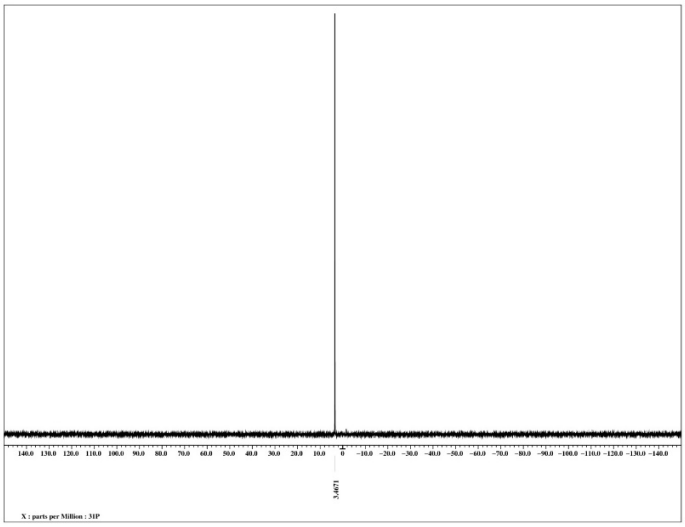


Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum of **8a** in $CDCl_3$ at 293 K.

*Synthesis of N,1,1-triphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarbothioamide (**9a**)*

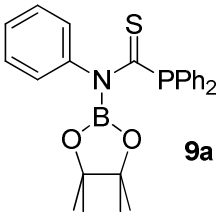
This mixture was allowed to stir for 6 and the product was isolated using method A. Yellow solid. Yield: 112 mg (78%); mp: 147-149°C; Anal. Calcd. For $C_{25}H_{27}BNO_2PS$: (447.34): C, 67.12; H, 6.08; N, 3.13. Found: C, 66.88; H, 5.74; N, 3.07.

^{1}H NMR ($CDCl_3$): δ 7.42 (m, 4H, Ar), 7.34-7.23 (ov m, 9H, Ar), 7.25-7.20 (ov m, 3H, Ar), 7.04 (d, *J* = 7.4 Hz, 2H, Ar), 1.09 (s, 12H, pin).

$^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 24.1 (s).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ: 225.0 (d, J_{CP} = 44 Hz), 143.5 (d, J_{CP} = 3.8 Hz), 136.5 (d, J_{CP} = 6.7 Hz), 134.9 (d, J_{CP} = 21.1 Hz), 129.4, 129.1, 129.0, 128.4 (d, J_{CP} = 7.7 Hz), 127.9, 127.4, 85.1, 24.2.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 26.7 (s).



9a

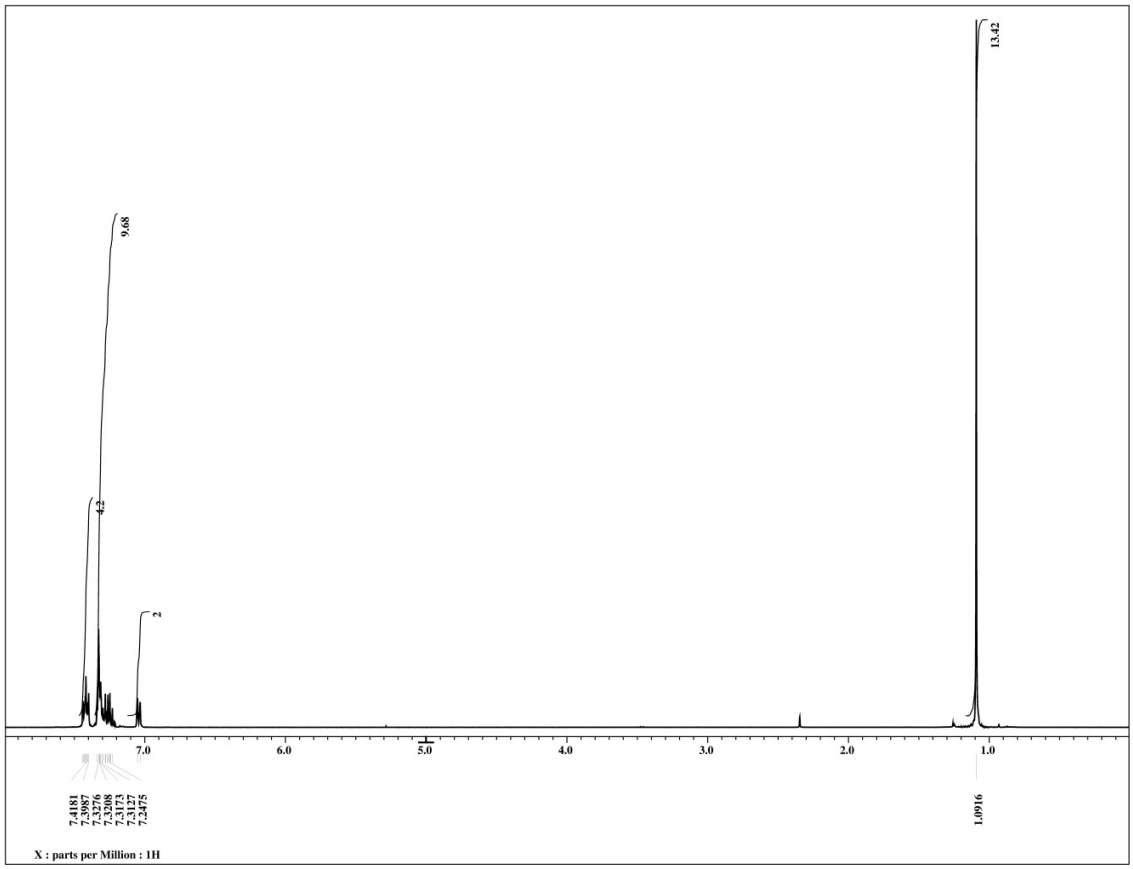


Figure S25. ^{1}H NMR spectrum of **9a** in $CDCl_3$ at 293 K.

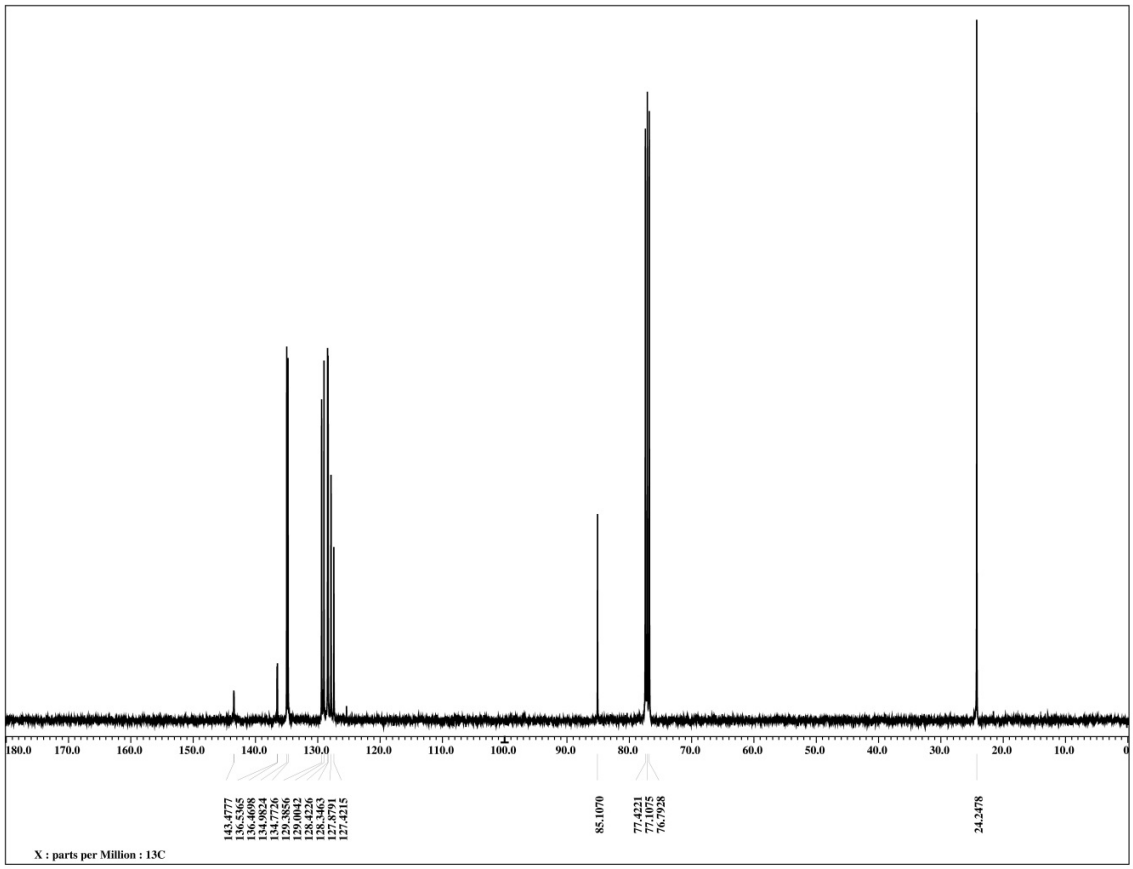


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **9a** in $CDCl_3$ at 293 K.

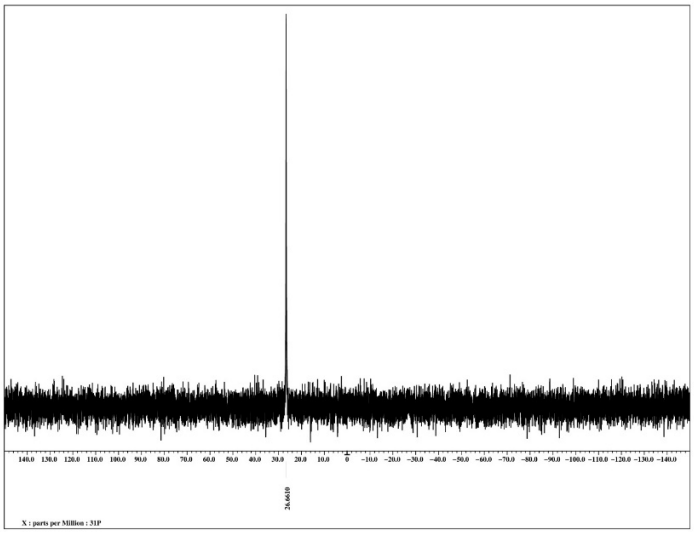


Figure S27. $^{31}P\{^{1}H\}$ NMR spectrum of **9a** in $CDCl_3$ at 293 K.

*Synthesis of N-benzyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarbothioamide (**10a**)*

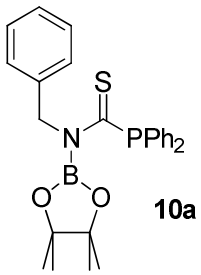
This mixture was allowed to stir for 18 h and the product was isolated using method B. Yellow solid, Method B. Yield: 98 mg (72%); mp: 113-114.5°C; Anal. Calcd. for $C_{26}H_{29}BNO_2PS$: (461.37): C, 67.69; H, 6.34; N, 3.04. Found: C, 67.47; H, 6.14; N, 3.07.

^{1}H NMR ($CDCl_3$): δ 7.33-7.24 (ov m, 15H, Ar), 5.38 (s, 2H, CH_2), 0.98 (s, 12H, pin).

$^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 24.5 (s).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 224.8 (d, J_{CP} = 46 Hz), 138.2, 138.1 (d, J_{CP} = 3.8 Hz), 134.9, 134.7, 129.2, 128.5, 128.4 (d, J_{CP} = 7.7 Hz), 128.1, 127.0, 85.2, 53.8, 24.2.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 31.1 (s).



10a

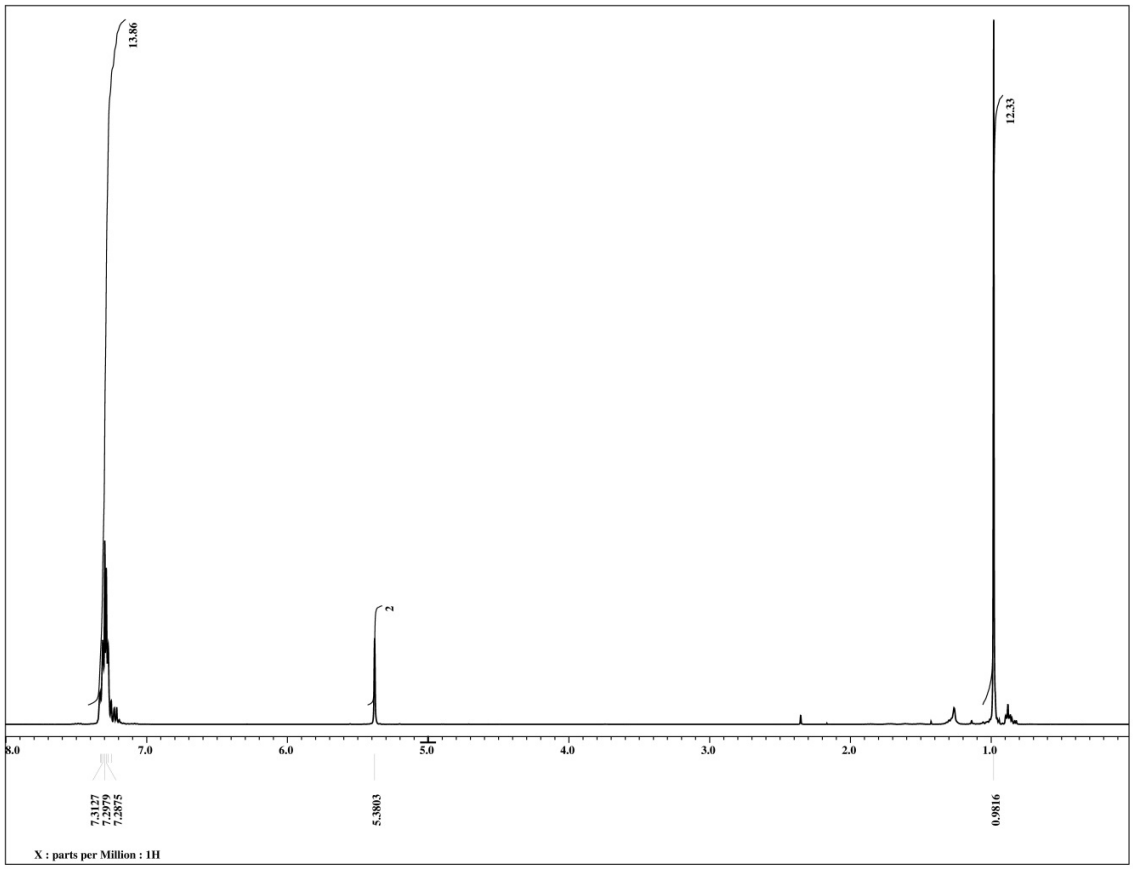


Figure S28. ^{1}H NMR spectrum of **10a** in $CDCl_3$ at 293 K.

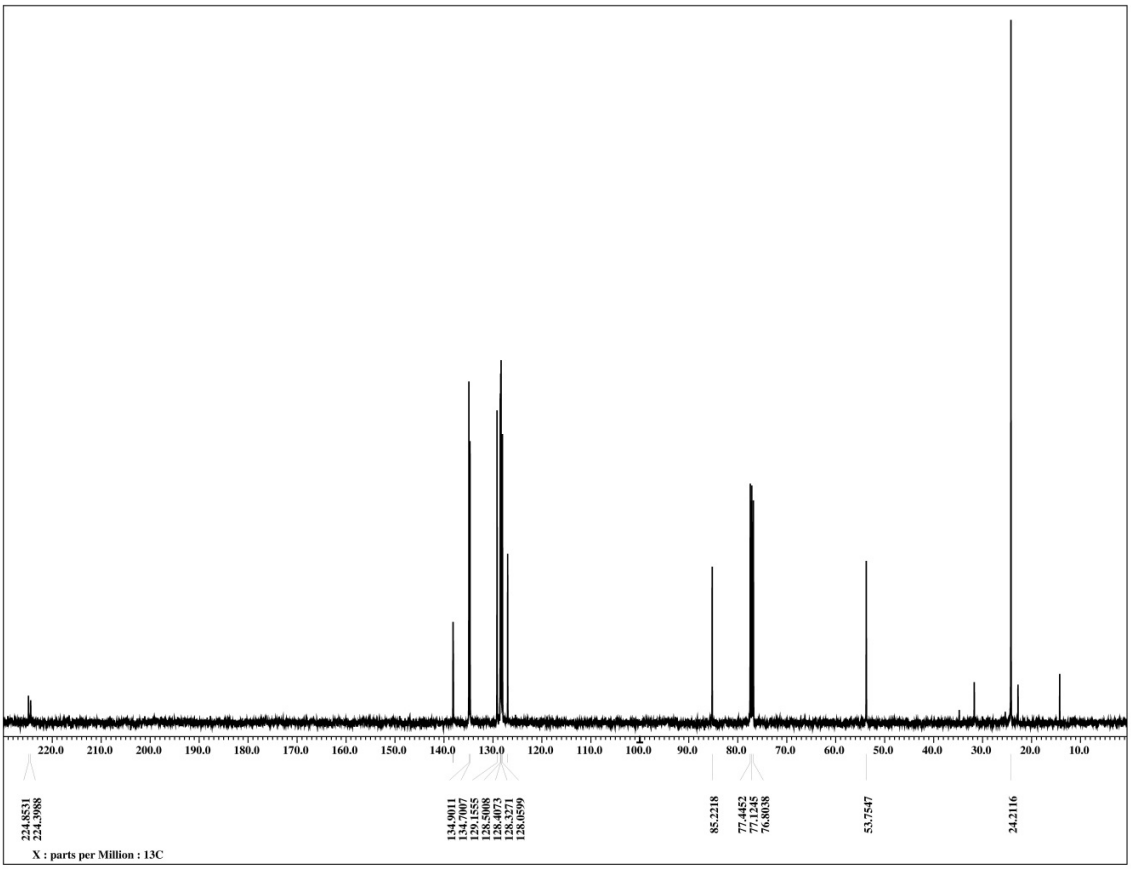


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **10a** in $CDCl_3$ at 293 K.

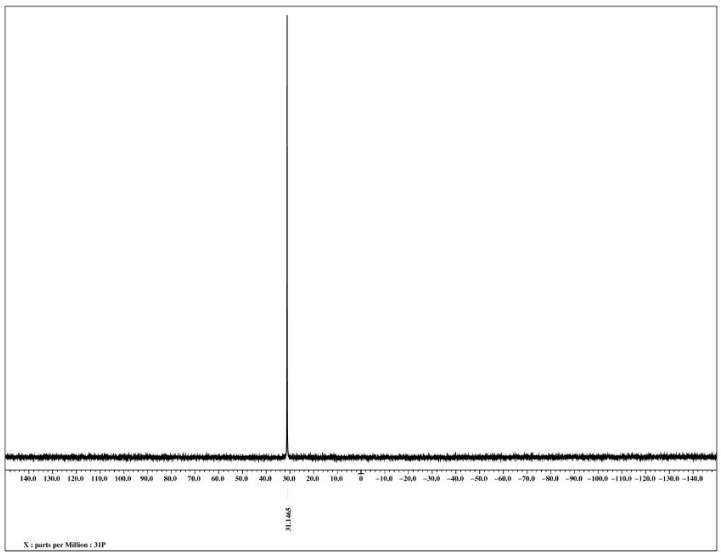


Figure S30. $^{31}P\{^{1}H\}$ NMR spectrum of **10a** in $CDCl_3$ at 293 K.

*Synthesis of N-cyclohexyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarbothioamide (**11a**)*

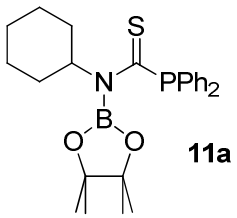
This mixture was allowed to stir for 18 and the product was isolated using method B. Yellow solid. Yield: 98 mg (72%); mp: 137-138°C; Anal. Calcd. For $C_{25}H_{33}BNO_2PS$: (453.39): C, 66.23; H, 7.34; N, 3.09. Found: C, 65.94; H, 7.37; N, 3.16.

^{1}H NMR ($CDCl_3$): δ 7.46 (m, 4H, Ar), 7.36-7.32 (ov m, 6H, Ar), 4.66 (br s, 1H, C*H*), 1.84 (d, *J* = 11.1 Hz, 2H, Cy), 1.70 (d, *J* = 13.1 Hz, 2H, Cy), 1.43 (m, 2H, Cy), 1.32 (s, 12H, pin), 1.19 (m, 2H, Cy), 1.06 (m, 1H, Cy).

^{11}B{^{1}H} NMR ($CDCl_3$): δ 24.4 (s).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 216.2 (d, J_{CP} = 32.2 Hz), 135.2, 134.5 (d, J_{CP} = 20.1 Hz), 129.5, 128.4 (d, J_{CP} = 8.1 Hz), 85.2, 60.8 (d, J_{CP} = 12.1 Hz), 31.4, 25.8, 25.5, 25.1.

^{31}P{^{1}H} NMR ($CDCl_3$): δ 19.3 (br s).



11a

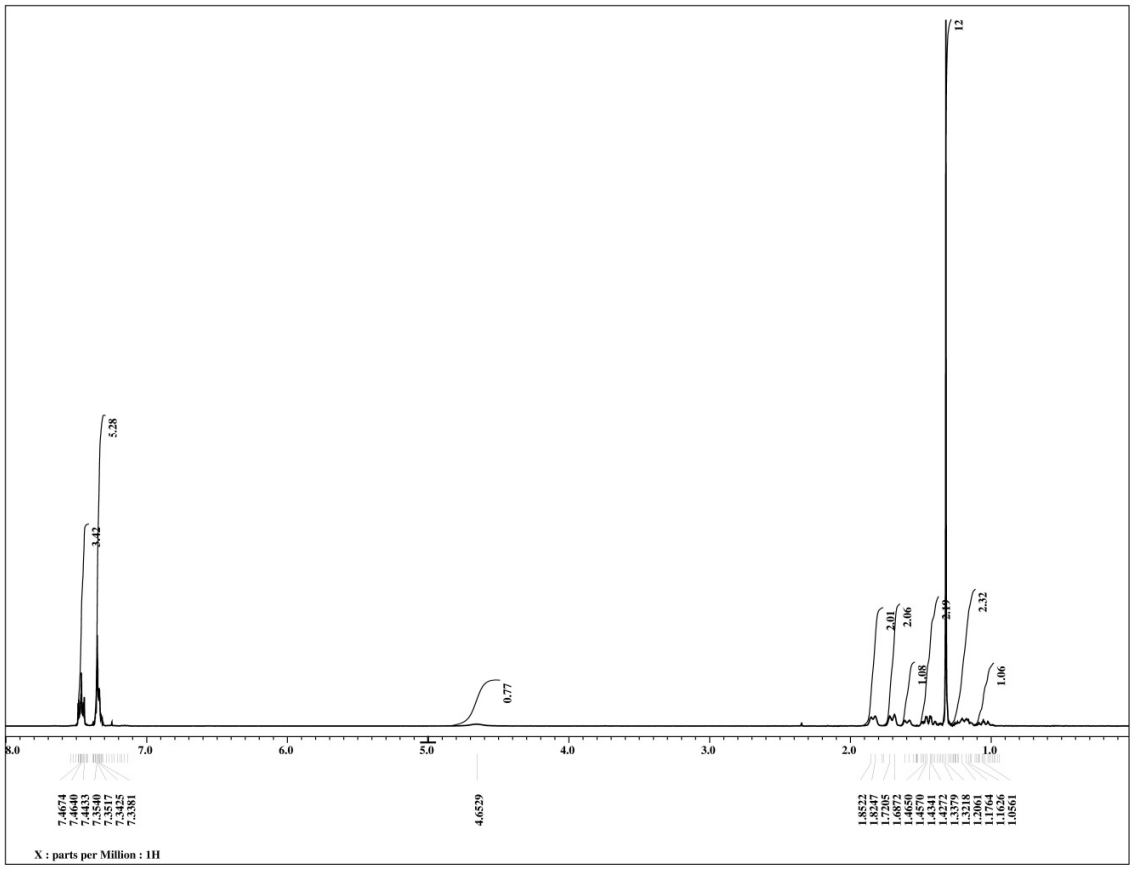


Figure S31. ^{1}H NMR spectrum of **11a** in $CDCl_3$ at 293 K.

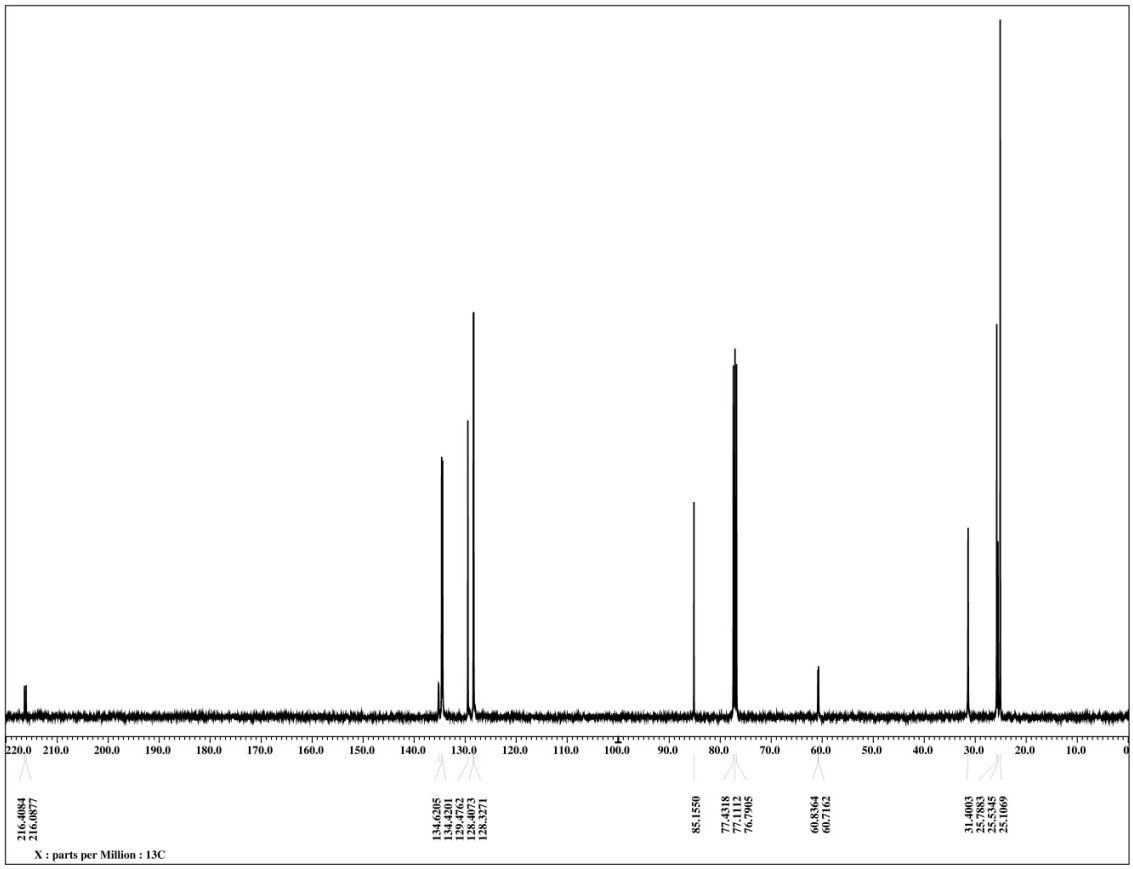


Figure S32. $^{13}C\{^{1}H\}$ NMR spectrum of **11a** in $CDCl_3$ at 293 K.

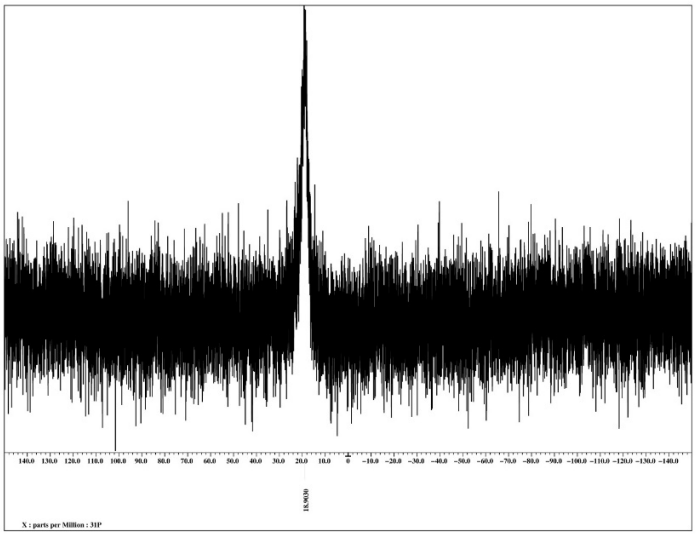


Figure S31. $^{31}P\{^{1}H\}$ NMR spectrum of **11a** in $CDCl_3$ at 293 K.

*Synthesis of N-tert-butyl-1,1-diphenyl-N-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phosphinecarbothioamide (**12a**)*

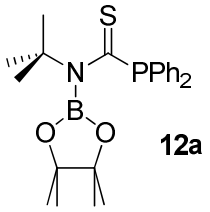
This mixture was allowed to stir for 18 and the product was isolated using method B. Yellow solid. Yield: 98 mg (72%); mp: 118-119°C; Anal. Calcd. For $C_{23}H_{31}BNO_2PS$: (427.35): C, 64.64; H, 7.31; N, 3.28. Found: C, 64.32; H, 7.27; N, 2.77.

^{1}H NMR ($CDCl_3$): δ 7.48 (m, 4H, Ar), 7.38-7.31 (ov m, 6H, Ar), 1.67 (s, 9H, *t-Bu*), 1.09 (s, 12H, pin).

$^{11}B\{^{1}H\}$ NMR ($CDCl_3$): δ 23.4 (s).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 135.1 (d, J_{CP} = 4.0 Hz), 134.0 (d, J_{CP} = 18.8 Hz), 129.3, 128.3 (d, J_{CP} = 8.1 Hz), 85.3, 61.4 (d, J_{CP} = 9.4 Hz), 28.2, 25.8.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 22.3 (s).



12a

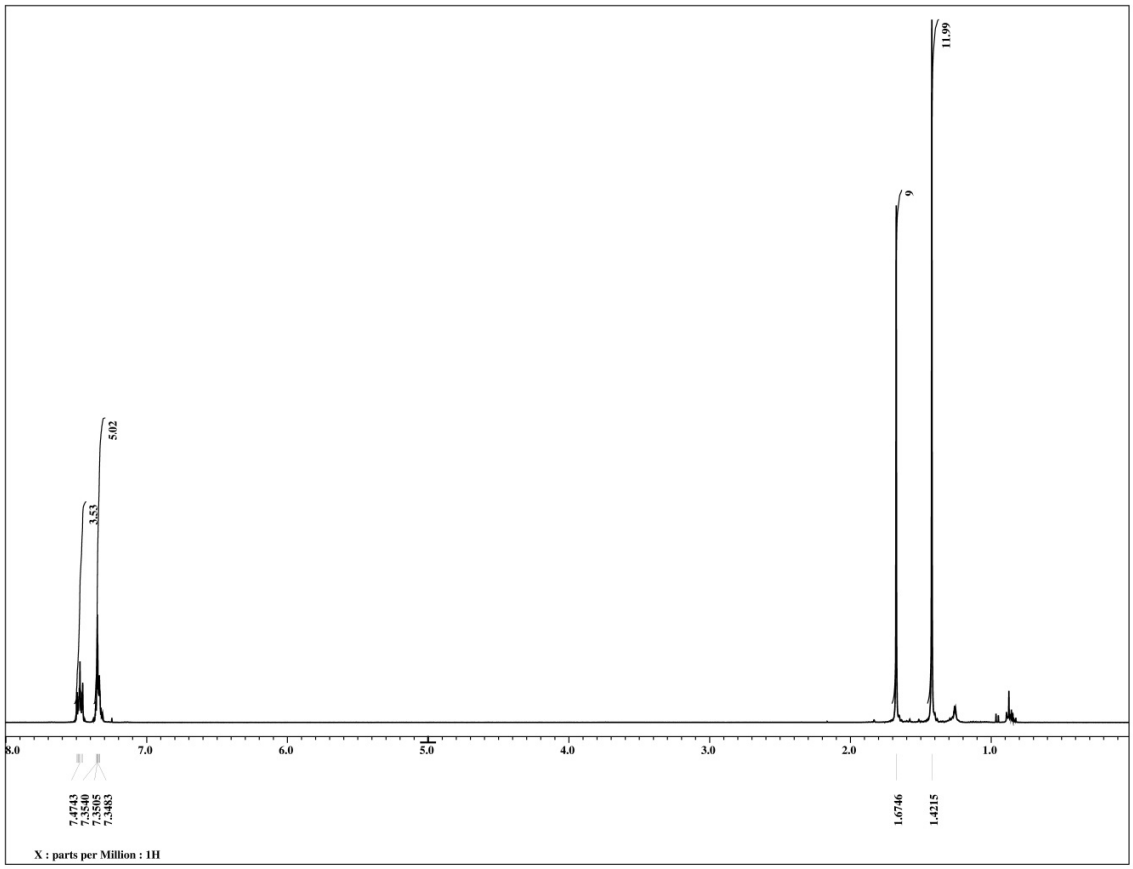


Figure S34. ^{1}H NMR spectrum of **12a** in $CDCl_3$ at 293 K.

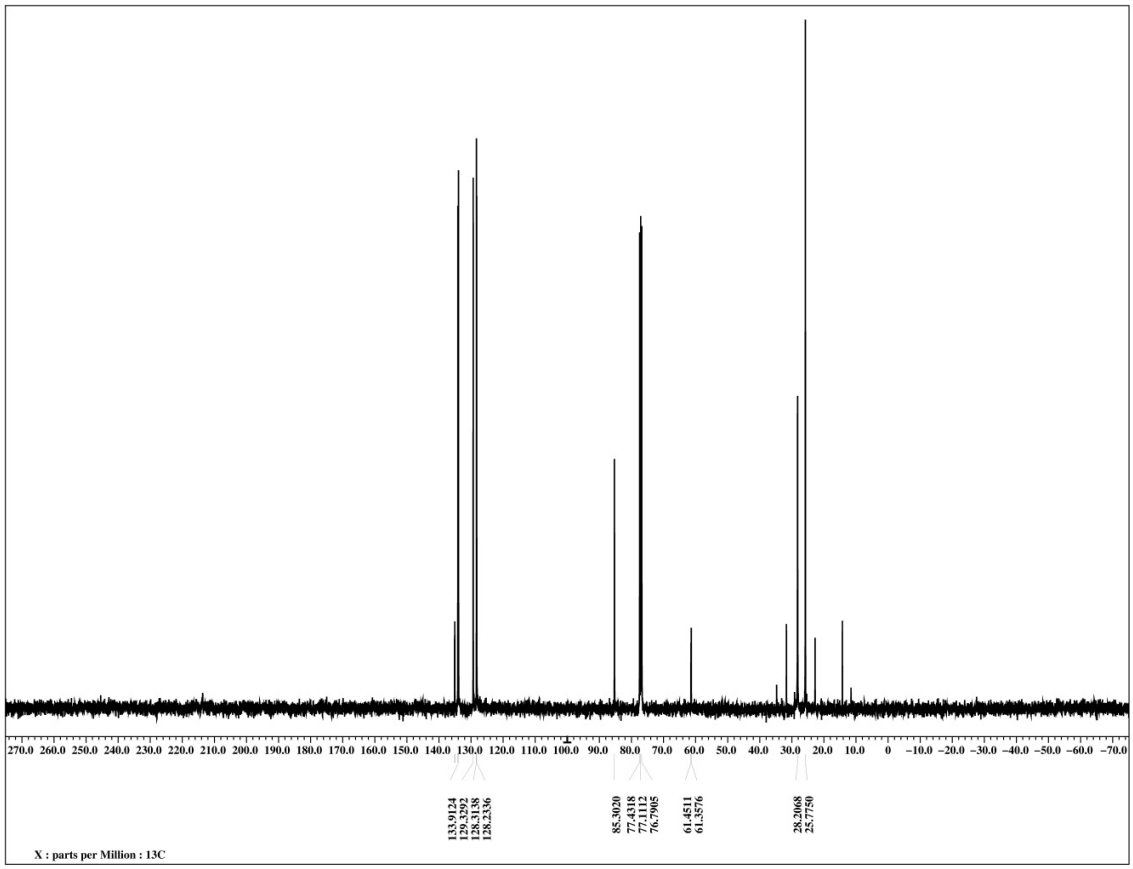


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum of **12a** in $CDCl_3$ at 293 K.

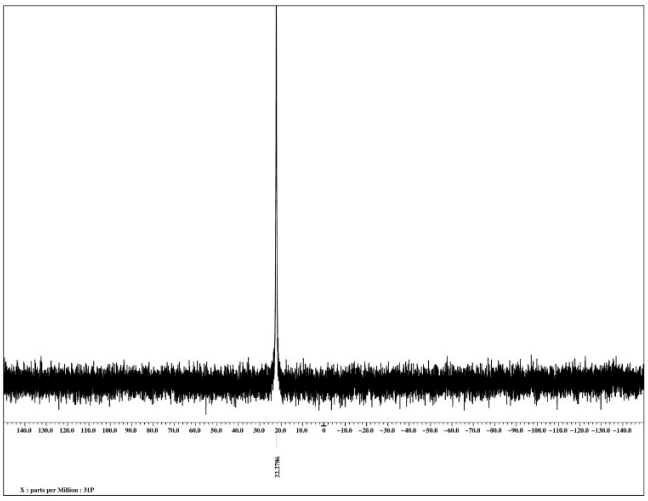


Figure S36. $^{31}P\{^{1}H\}$ NMR spectrum of **12a** in $CDCl_3$ at 293 K.

*Synthesis of 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl diphenylphosphinecarboxylate (**13**)*

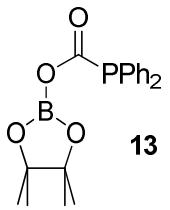
A benzene solution of Ph_2PBpin (100 mg, 0.32 mmol) was subjected to 3 freeze-pump thaw cycles and charged with 1 atmosphere of carbon dioxide. The solution was allowed to stir for 4 days. The solvent was removed under vacuum, leaving a yellow oil, which was recrystallized from pentane, leaving a light yellow solid. Yield: 40 mg (35%); mp: 58-59°C; Anal. Calcd. For $C_{19}H_{22}BO_4P$: (427.35): C, 64.07; H, 6.23. Found: C, 64.27; H, 6.27.

^1H NMR (C_6D_6): δ 7.57 (m, 4H, Ar), 7.00 (m, 6H, Ar), 0.94 (s, 12H, pin).

$^{11}B\{^1H\}$ NMR (C_6D_6): δ 22.7 (s).

$^{13}C\{^1H\}$ NMR (C_6D_6): δ 177.5 (d, J_{CP} = 16 Hz), 135.0 (d, J_{CP} = 20 Hz), 132.8 (d, J_{CP} = 5 Hz), 129.8, 128.9 (d, J_{CP} = 8 Hz), 84.2, 24.5.

$^{31}P\{^1H\}$ NMR (C_6D_6): δ -0.7 (s).



13

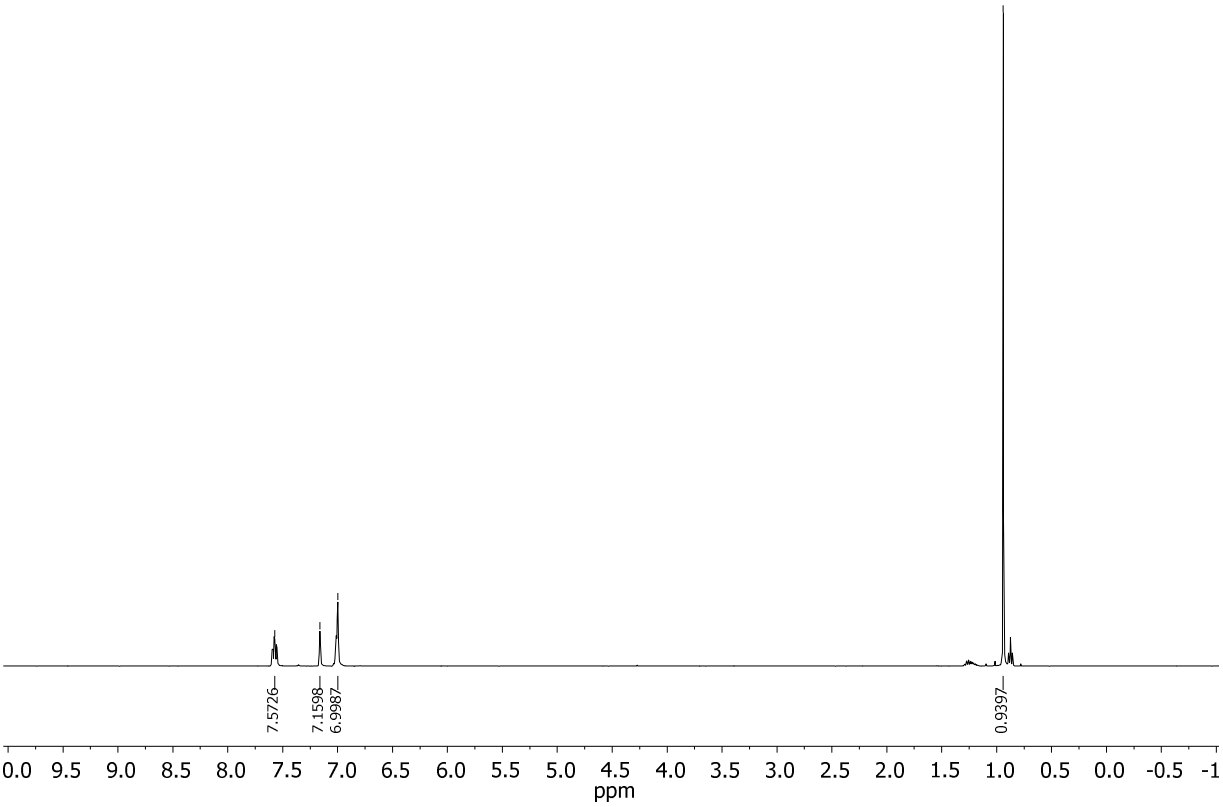


Figure S37. ^{1}H NMR spectrum of **13** in C_6D_6 at 293 K.

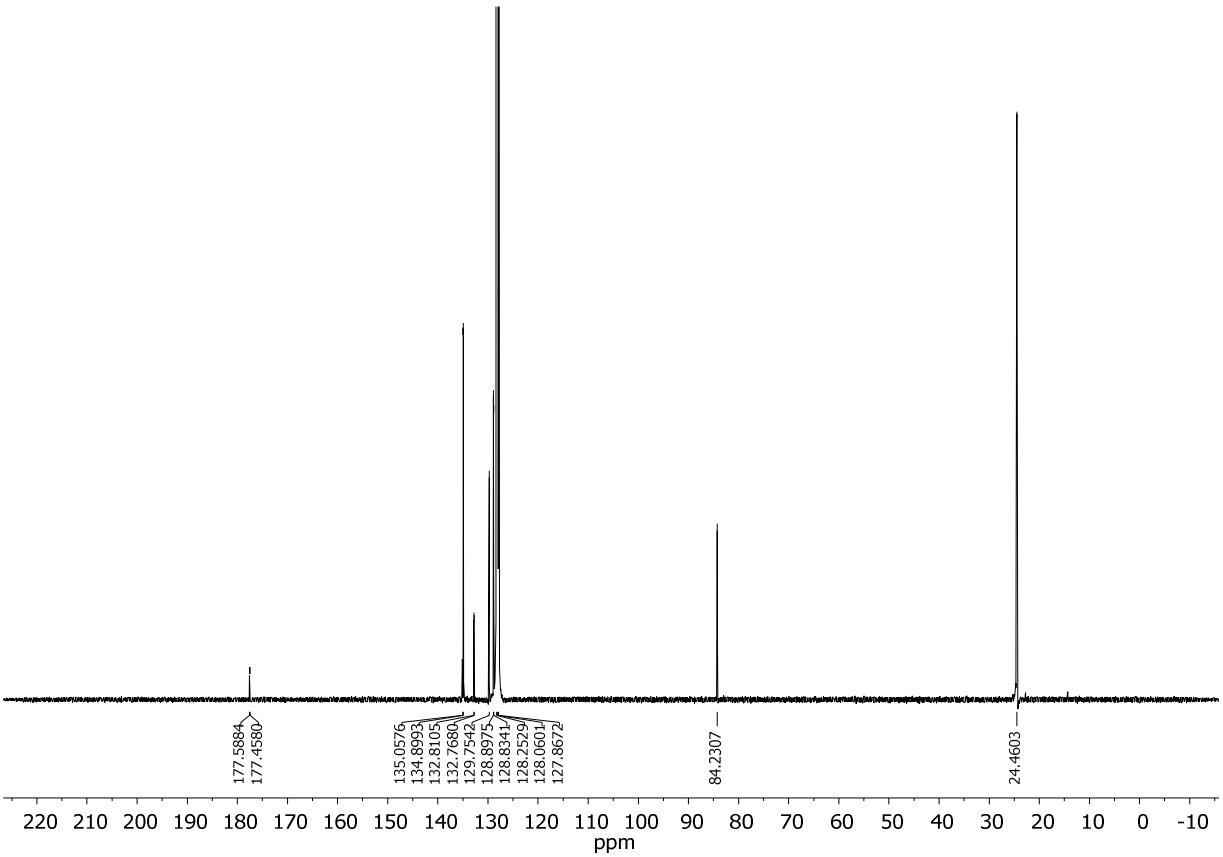


Figure S38. $^{13}C\{^{1}H\}$ NMR spectrum of **13** in C_6D_6 at 293 K.

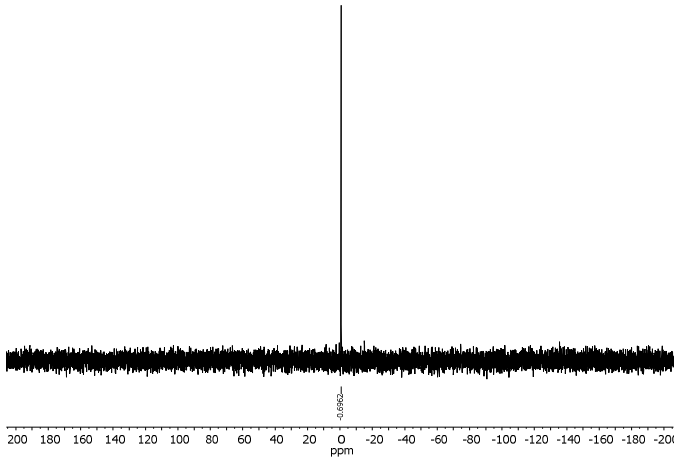


Figure S38. $^{31}P\{^{1}H\}$ NMR spectrum of **13** in C_6D_6 at 293 K.

*General Procedure: Preparation of Compounds **1b-12b***

Phosphinoboration reactions were carried out as described above. Following the prescribed time, methanol (5 drops) was added and the solution was stirred for

an additional 30 minutes. The solvent was removed under vacuum and the residue was either washed with hexane (Method A) or recrystallized from hexane (Method B) or diethyl ether (Method C).

*Synthesis of 1,1-diphenyl-N,N'-di-p-tolylphosphinecarboximidamide (**1b**)*

Method A. White solid. Yield: 91% (119 mg). Analytical data matches that which has been previously published for this compound.[1]

*Synthesis of N,N'-diisopropyl-1,1-diphenylphosphinecarboximidamide (**2b**)*

Method B. Colourless crystalline solid. Yield: 8mg (81%). Analytical data matches that which has been previously published for this compound.[2]

*Synthesis of N,N'-dicyclohexyl-1,1-diphenylphosphinecarboximidamide (**3b**)*

Method B. White solid. Yield: 106 mg (84%). Analytical data matches that which has been previously published for this compound.[2]

*Synthesis of N,1,1-triphenylphosphinecarboxamide (**4b**)*

Method A. White solid. Yield: 78 mg, (80%). Analytical data matches that which has been previously published for this compound.[3]

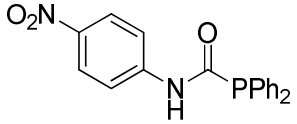
*Synthesis of N-(4-nitrophenyl)-1,1-diphenylphosphinecarboxamide (**5b**)*

Washed with cold diethyl ether (3x5 mL). Yellow solid. Yield: 88 mg (78%); mp: 149.5-151 °C (decomp.). Anal. Calcd. For $C_{19}H_{15}N_2O_3P$: (350.31): C, 65.14; H, 4.32; N, 8.00. Found: C, 65.01; H,4.44 ; N, 8.18.

^{1}H NMR ($CDCl_3$): δ 8.14 (dm, *J* = 9.2 Hz, 2H, Ar), 7.61-7.56 (ov m, 5H, Ar, N*H*), 7.53 (dm, *J* = 9.2 Hz, 2H, Ar), 7.49-7.43 (ov m, 6H, Ar).

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 177.6 (d, J_{CP} = 20.1 Hz), 143.8, 143.0, 134.6 (d, J_{CP} = 20.1 Hz), 132.2 (d, J_{CP} = 9.6 Hz), 130.6, 129.4 (d, J_{CP} = 7.7 Hz), 125.2, 125.2, 119.0.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 1.9 (s).



5b

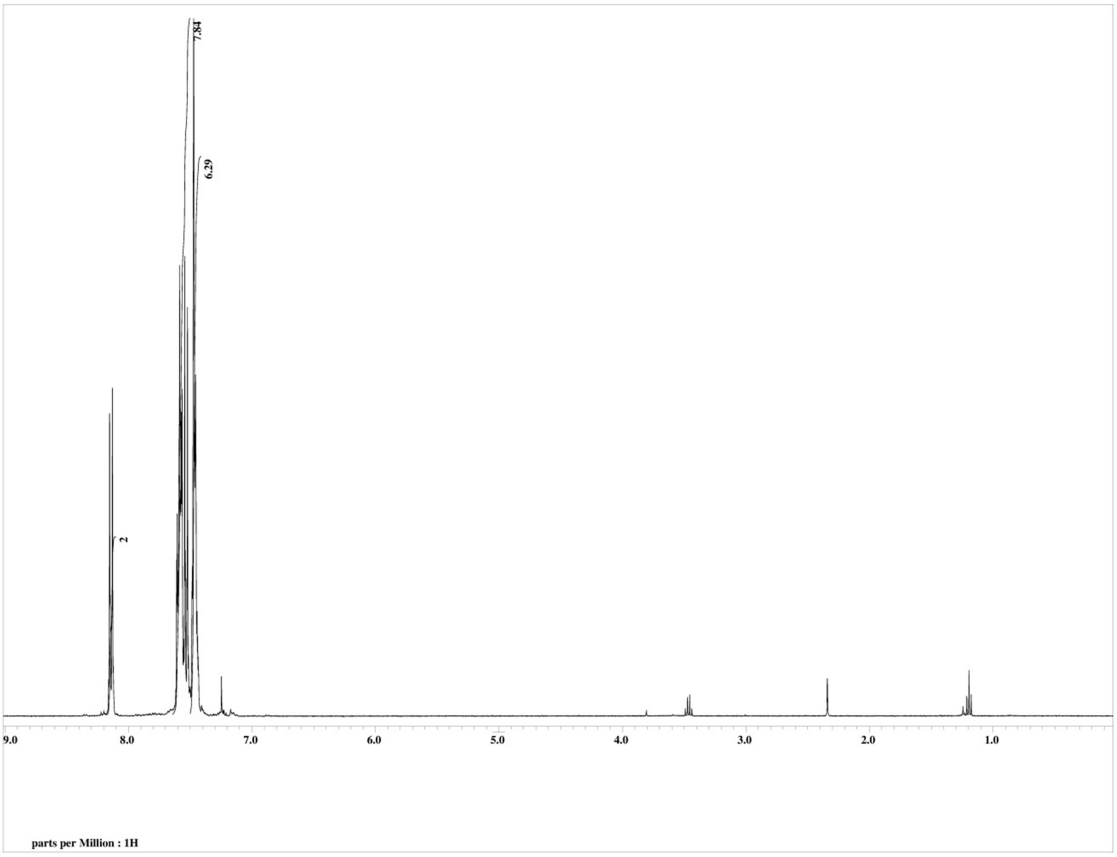


Figure S40. ^{1}H NMR spectrum of **5b** in $CDCl_3$ at 293 K.

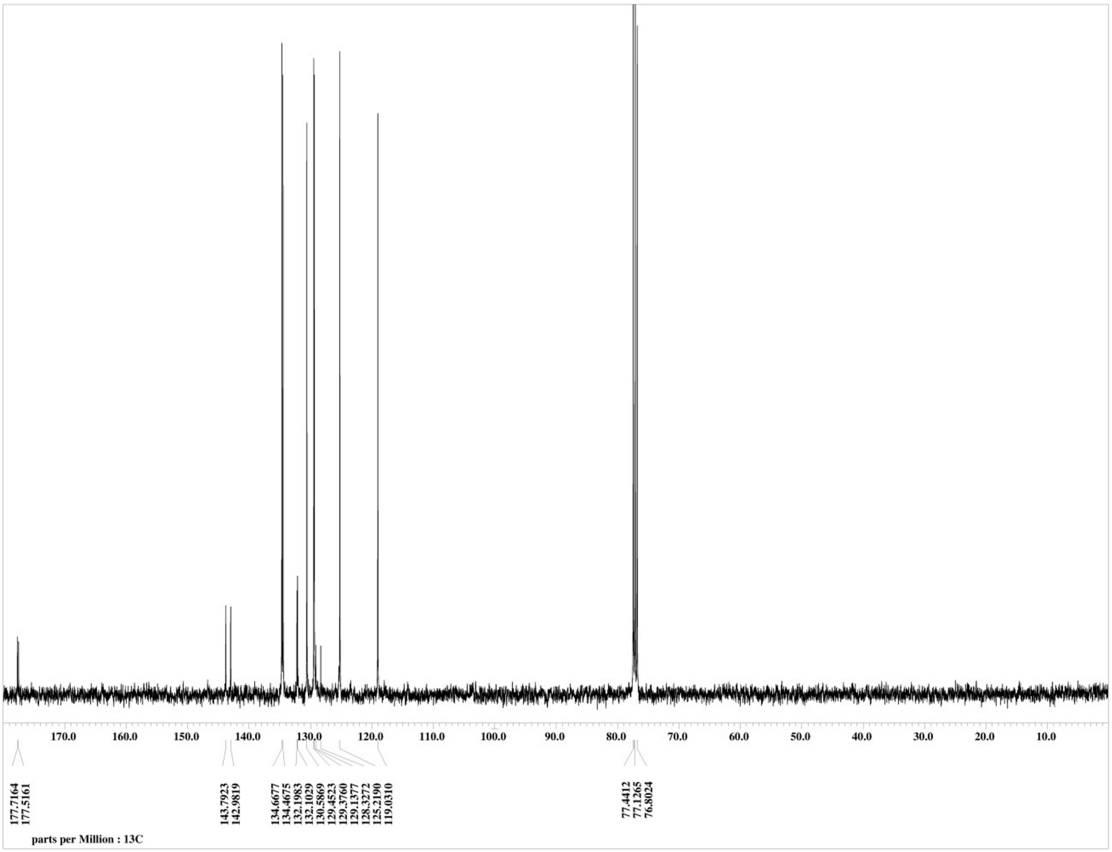


Figure S41. ^{13}C NMR spectrum of **5b** in $CDCl_3$ at 293 K.

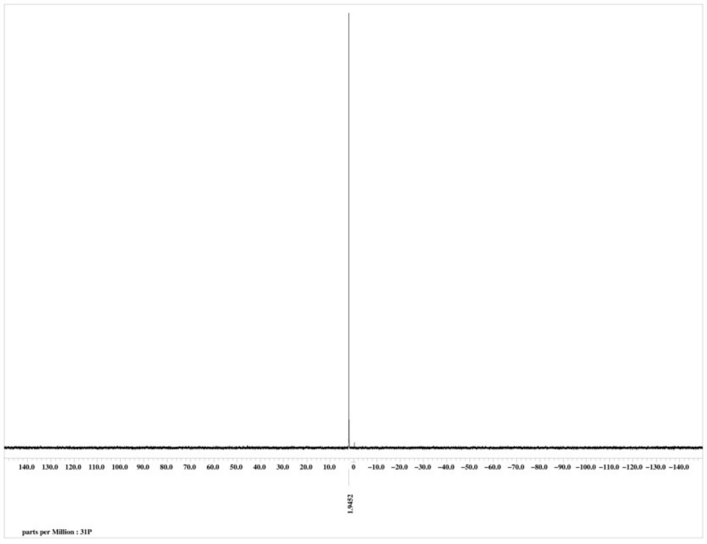


Figure S42. ^{31}P NMR spectrum of **5b** in $CDCl_3$ at 293 K.

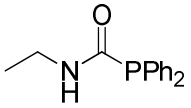
*Synthesis of N-ethyl-1,1-diphenylphosphinecarboxamide (**6b**)*

Method A. White solid. Yield: 78 mg (94%); mp: 81.3-82.8 °C; Anal. Calcd. For $C_{15}H_{16}NOP$: (257.27): C, 70.01; H, 6.30; N, 5.43. Found: C, 69.79; H, 6.39; N, 5.57.

^{1}H NMR ($CDCl_3$): δ 7.54-7.48 (m, 4H, Ar), 7.40-7.37 (ov m, 6H, Ar), 5.66 (br s, N*H*), 3.32 (qd, J = 6.9 Hz, J_{HP} = 5.5 Hz, 2H, CH_2), 1.05 (t, J = 6.9 Hz, 3H, CH_3).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 177.0 (d, J_{CP} = 12.7 Hz), 134.4 (d, J_{CP} = 18.5 Hz), 133.7 (d, J_{CP} = 11.6 Hz), 129.8, 129.0 (d, J_{CP} = 8.1 Hz), 35.0, 15.0.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -3.4 (s).



6b

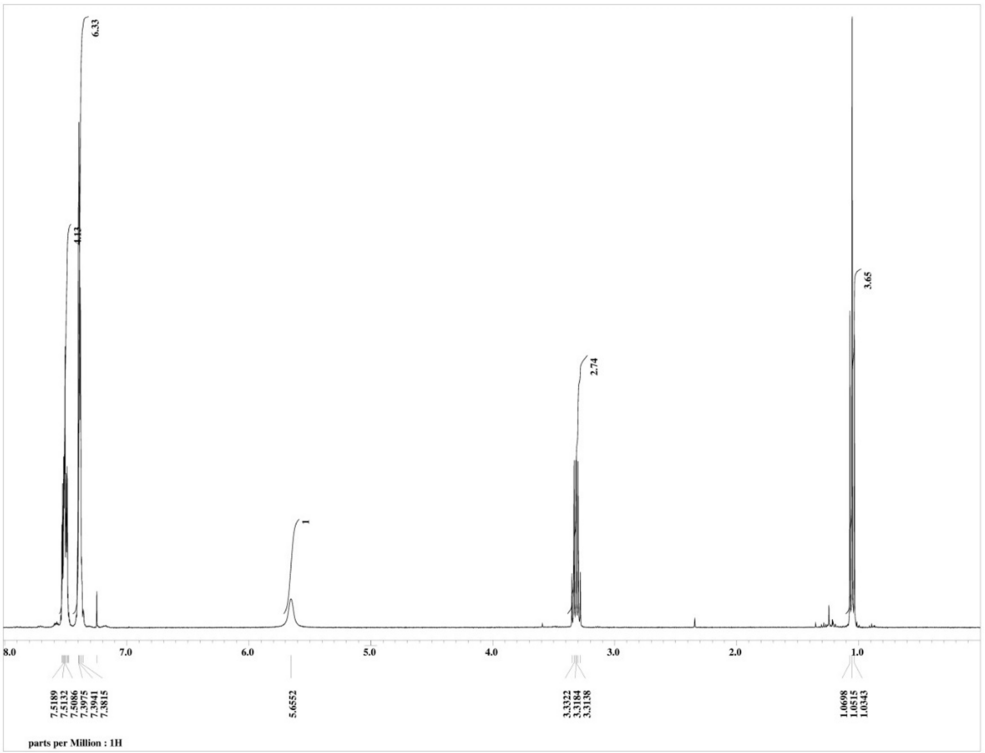


Figure S43. ^{1}H NMR spectrum of **6b** in $CDCl_3$ at 293 K.

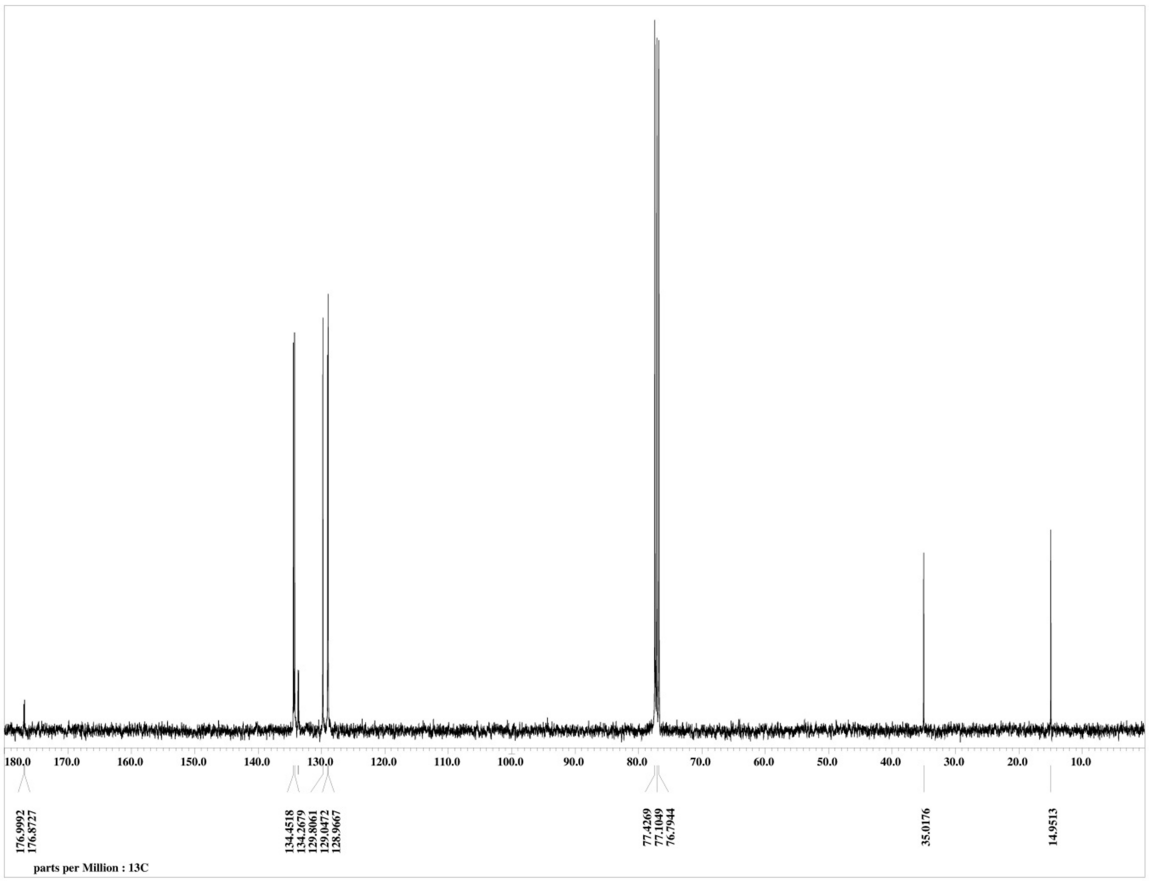


Figure S44. ^{13}C NMR spectrum of **6b** in $CDCl_3$ at 293 K.

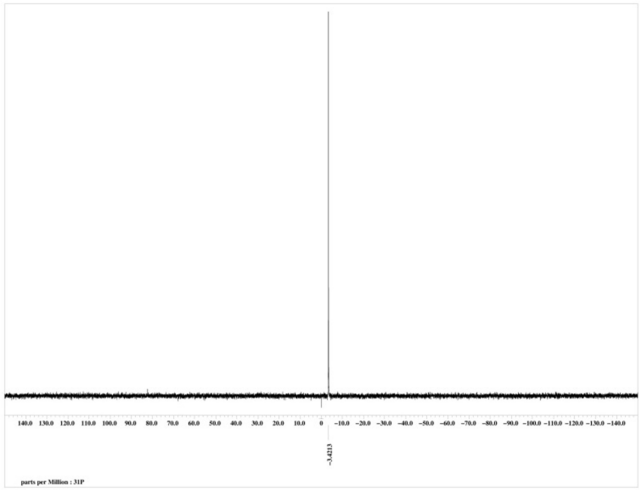


Figure S45. ^{31}P NMR spectrum of **6b** in $CDCl_3$ at 293 K.

*Synthesis of N-cyclohexyl-1,1-diphenylphosphinecarboxamide (**7b**)*

Method A. White solid. Yield: 86mg (86%). Analytical data matches that which has been previously reported for this compound.[3,4]

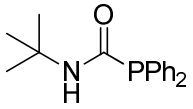
*Synthesis of N-tert-butyl-1,1-diphenylphosphinecarboxamide (**8b**)*

Method A. White solid. Spectroscopic data matches that which has been previously reported,[5] however since full spectroscopic details have not been reported for this compound, they are presented here. Yield: 83 mg (91%); mp: 119.2-120.8 °C; Anal. Calcd. For $C_{17}H_{20}NOP$: (285.33): C, 71.56; H, 7.07; N, 4.91. Found: C, 71.77; H, 7.17; N, 5.01.

^{1}H NMR ($CDCl_3$): δ 7.52-7.47 (m, 4H, Ar), 7.40-7.35 (ov m, 6H, Ar), 5.51 (br s, N*H*), 1.28 (s, 9H, *t-Bu*).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 176.1 (d, J_{CP} = 13.4 Hz), 134.2 (d, J_{CP} = 19.2 Hz), 134.2, 129.7, 128.9 (d, J_{CP} = 6.7 Hz), 52.9, 28.8.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ -1.6 (s).



8b

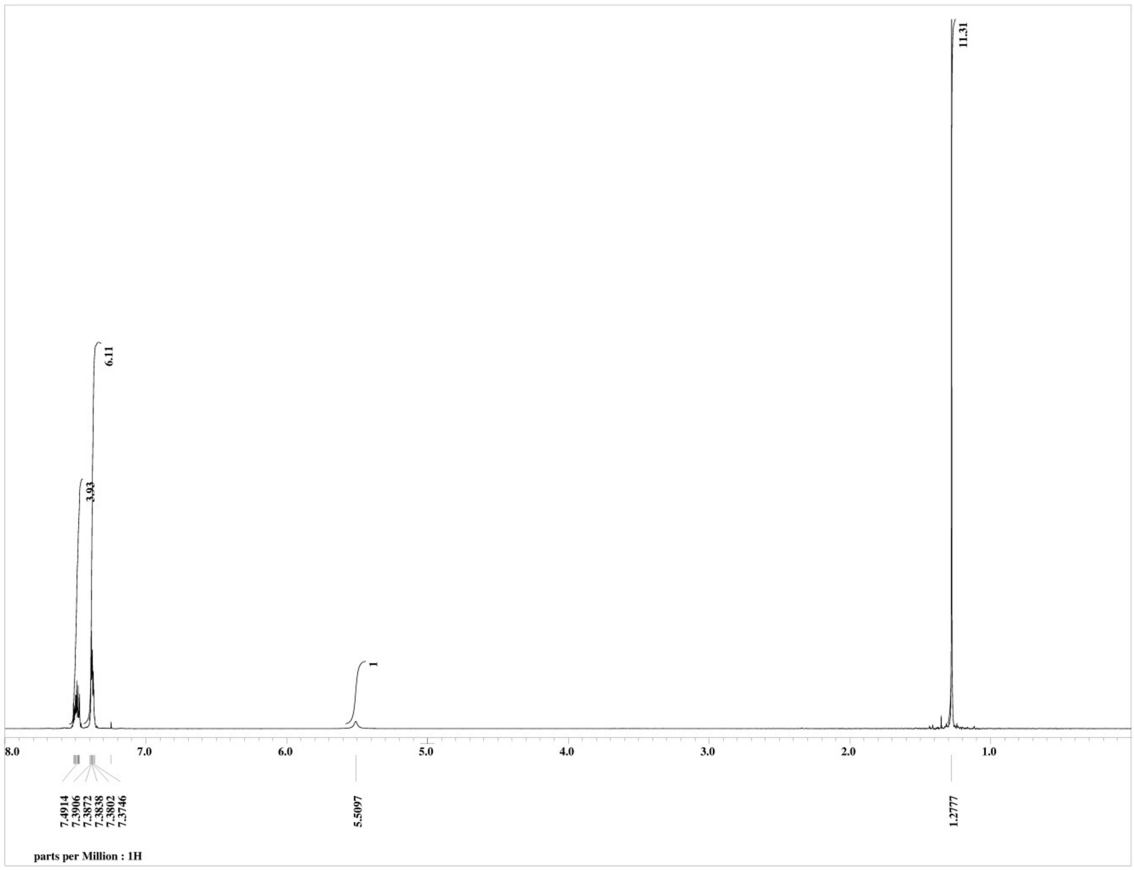


Figure S46. ^{1}H NMR spectrum of **8b** in $CDCl_3$ at 293 K.

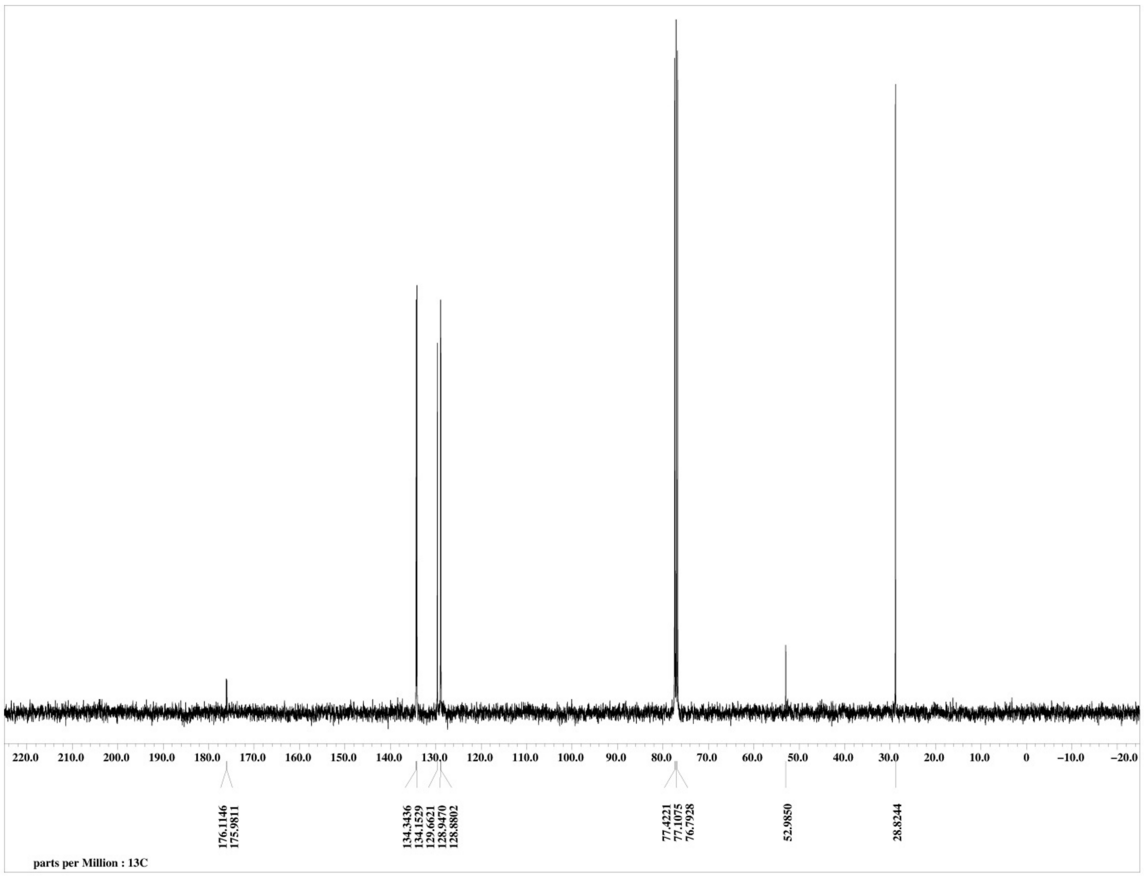


Figure S47. ^{13}C NMR spectrum of **8b** in $CDCl_3$ at 293 K.

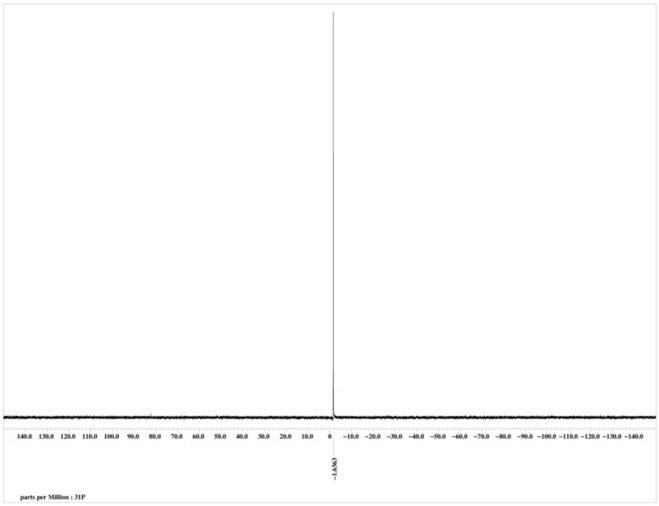


Figure S48. ^{31}P NMR spectrum of **8b** in $CDCl_3$ at 293 K.

*Synthesis of N,1,1-triphenylphosphinecarbothioamide (**9b**)*

Method A. Yellow solid. Yield: 86% (88 mg). Analytical data matches that which has been previously reported for this compound.[3-7]

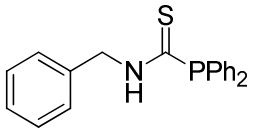
*Synthesis of N-benzyl-1,1-diphenylphosphinecarbothioamide (**10b**)*

Method A. Yellow solid. Yield: 86 mg (84%); mp: 80.9-82.1°C; Anal. Calcd. For $C_{20}H_{18}NPS$: (319.34): C, 71.62; H, 5.41; N, 4.18. Found: C, 71.55; H, 5.51; N, 4.26.

^{1}H NMR ($CDCl_3$): δ 7.50-7.44 (m, 5H), 7.41-7.36 (ov m, 6H, Ar), 7.32-7.26 (m, 3H), 7.14 (dd, J = 7.8 Hz, J = 2.3 Hz, 2H, Ar), 4.89 (d, J_{HP} = 5.0 Hz, 2H, CH_2).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 208.1 (d, J_{CP} = 39.0 Hz), 135.9, 134.4 (d, J_{CP} = 21.5 Hz), 134.1, 130.2, 129.2 (d, J_{CP} = 6.7 Hz), 129.0, 128.1, 127.7, 50.2.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 16.2 (s).



10b

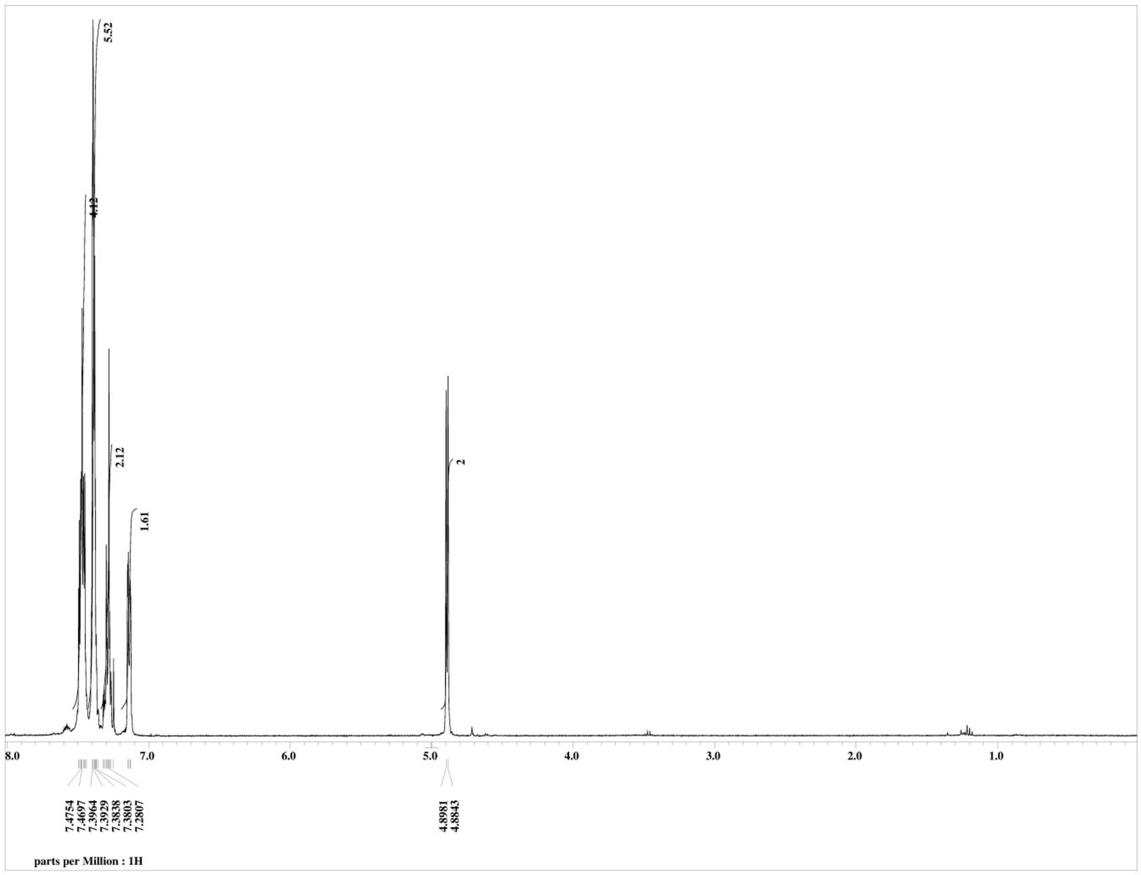


Figure S49. ^{1}H NMR spectrum of **10b** in $CDCl_3$ at 293 K.

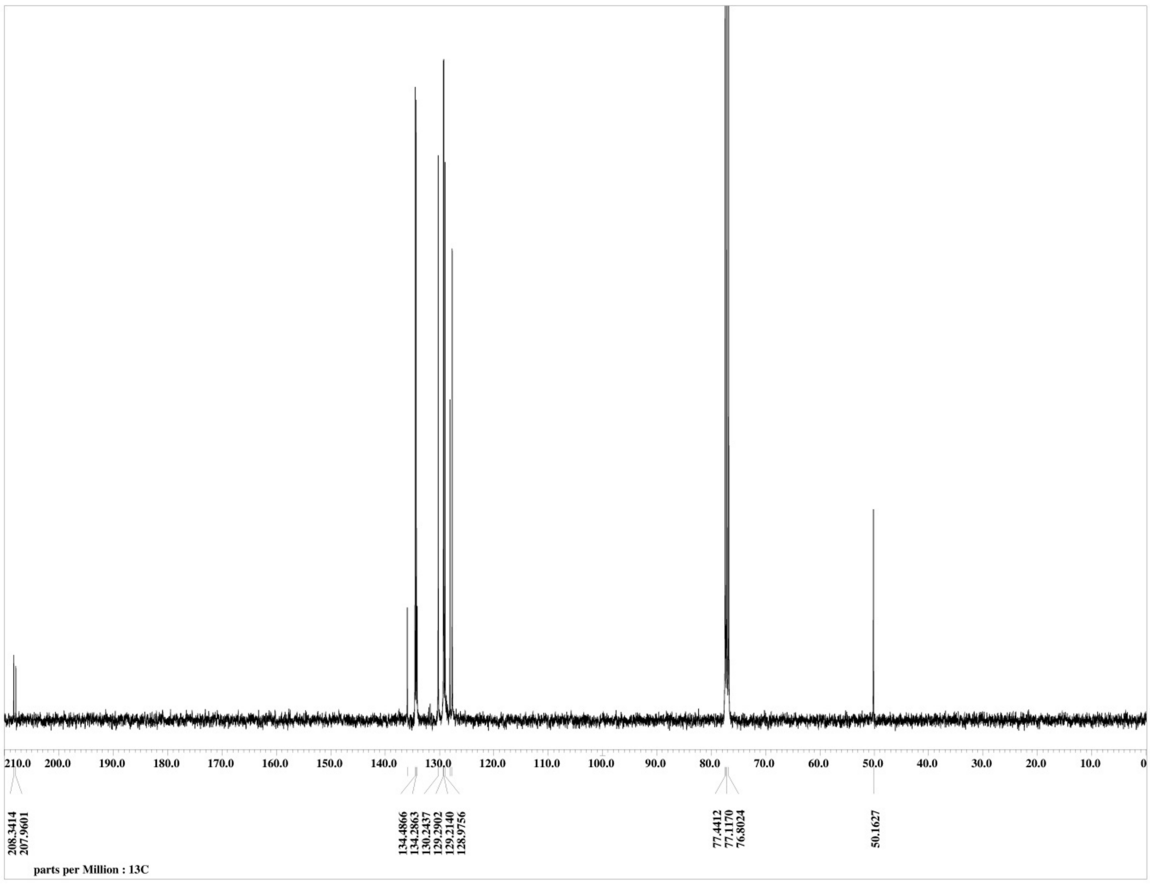


Figure S50. ^{13}C NMR spectrum of **10b** in $CDCl_3$ at 293 K.

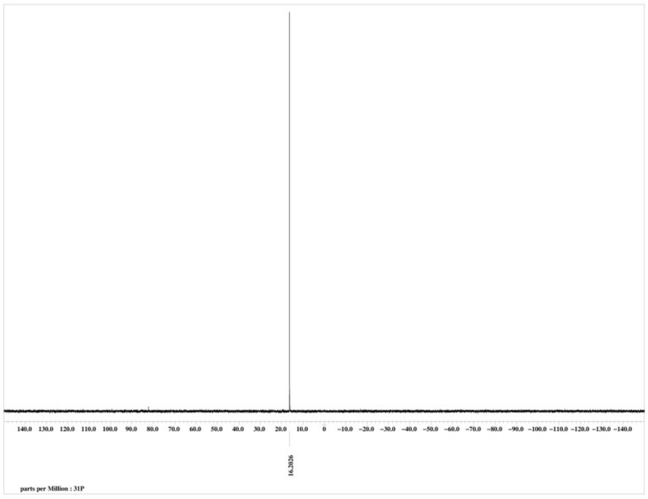


Figure S51. ^{31}P NMR spectrum of **10b** in $CDCl_3$ at 293 K.

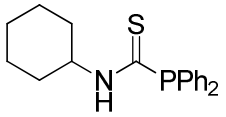
*Synthesis of N-cyclohexyl-1,1-diphenylphosphinecarbothioamide (**11b**)*

Method A. Yellow solid. Yield: 91 mg (87%); mp: 94.0-95.4 °C; Anal. Calcd. For $C_{19}H_{22}NPS$: (327.43): C, 69.70; H, 6.77; N, 4.28. Found: C, 69.17; H, 7.02; N, 3.91.

^{1}H NMR ($CDCl_3$): δ 7.48-7.38 (ov m, 10H, Ar), 4.51 (m, 1H, C*H*), 1.91 (m, 2H, *Cy*), 1.54-1.34 (ov m, 5H, *Cy*), 1.19-1.05 (ov m, 3H, *Cy*).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 205.7 (d, J_{CP} = 39.0 Hz), 134.5 (d, J_{CP} = 14.8 Hz), 134.3 (d, J_{CP} = 20.1 Hz), 130.1, 129.2 (d, J_{CP} = 6.7 Hz), 53.6, 31.2, 25.3, 24.0.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 14.5 (s).



11b

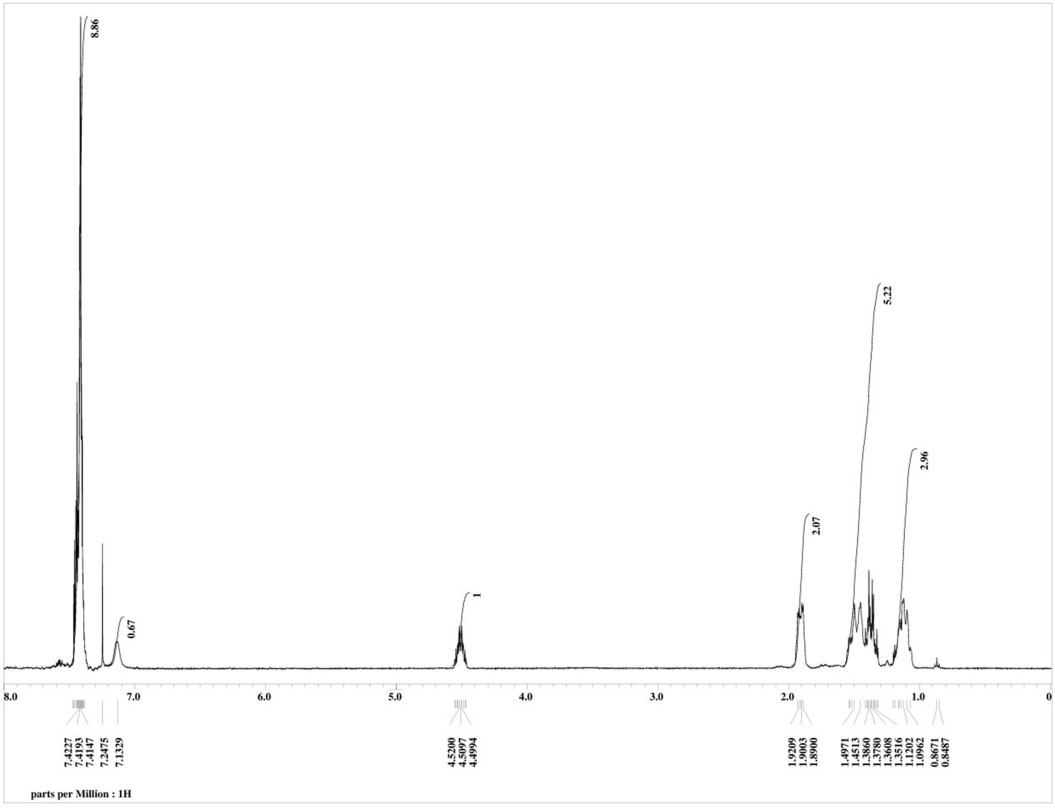


Figure S52. ^{1}H NMR spectrum of **11b** in $CDCl_3$ at 293 K.

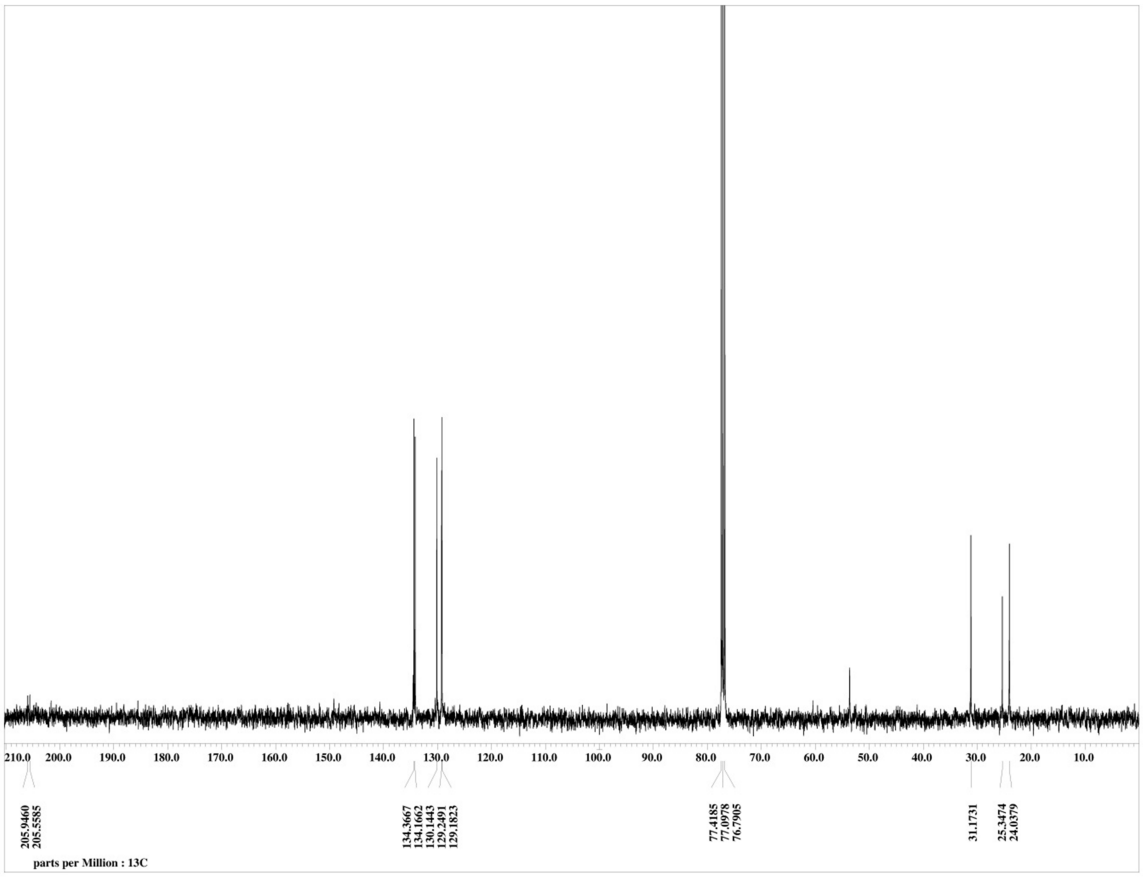


Figure S53. ^{13}C NMR spectrum of **11b** in $CDCl_3$ at 293 K.

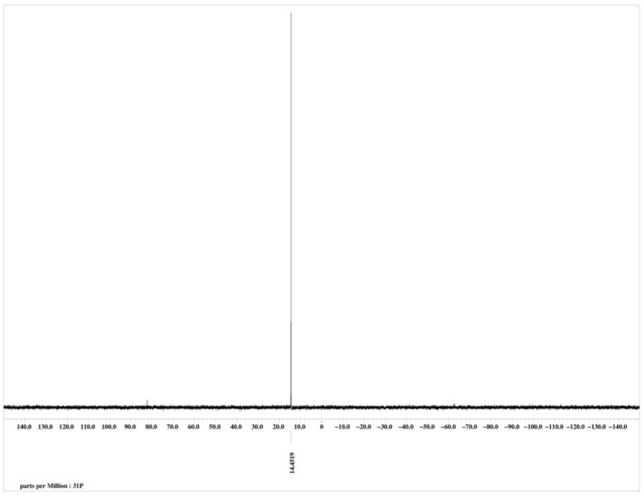


Figure S54. ^{31}P NMR spectrum of **11b** in $CDCl_3$ at 293 K.

*Synthesis of N-tert-butyl-1,1-diphenylphosphinecarbothioamide (**12b**)*

Method A. Yellow solid. Yield: 87 mg (90%); mp: 121.9-122.5°C; Anal. Calcd. For $C_{17}H_{20}NPS$: (301.39): C, 67.75; H, 6.69; N, 4.65. Found: C, 67.99; H, 6.66; N, 4.76.

^{1}H NMR ($CDCl_3$): δ 7.46-7.39 (ov m, 10H, Ar), 7.07 (br s, 1H, N*H*), 1.43 (s, 9H, *t-Bu*).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 206.3 (d, J_{CP} = 40.3 Hz), 135.2 (d, J_{CP} = 17.5 Hz), 134.2 (d, J_{CP} = 20.2 Hz), 130.1, 129.2 (d, J_{CP} = 8.1 Hz), 57.6, 27.7.

$^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 17.4 (s).

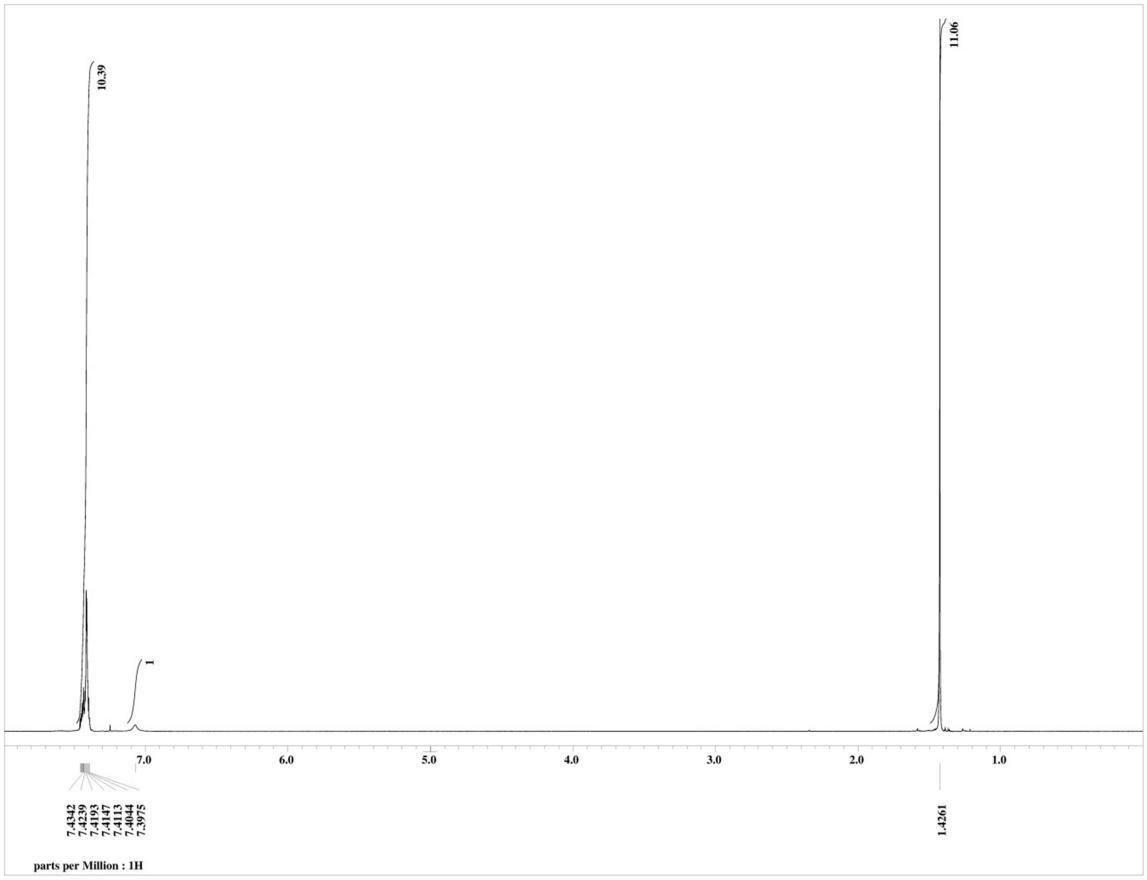


Figure S55. ^{1}H NMR spectrum of **12b** in $CDCl_3$ at 293 K.

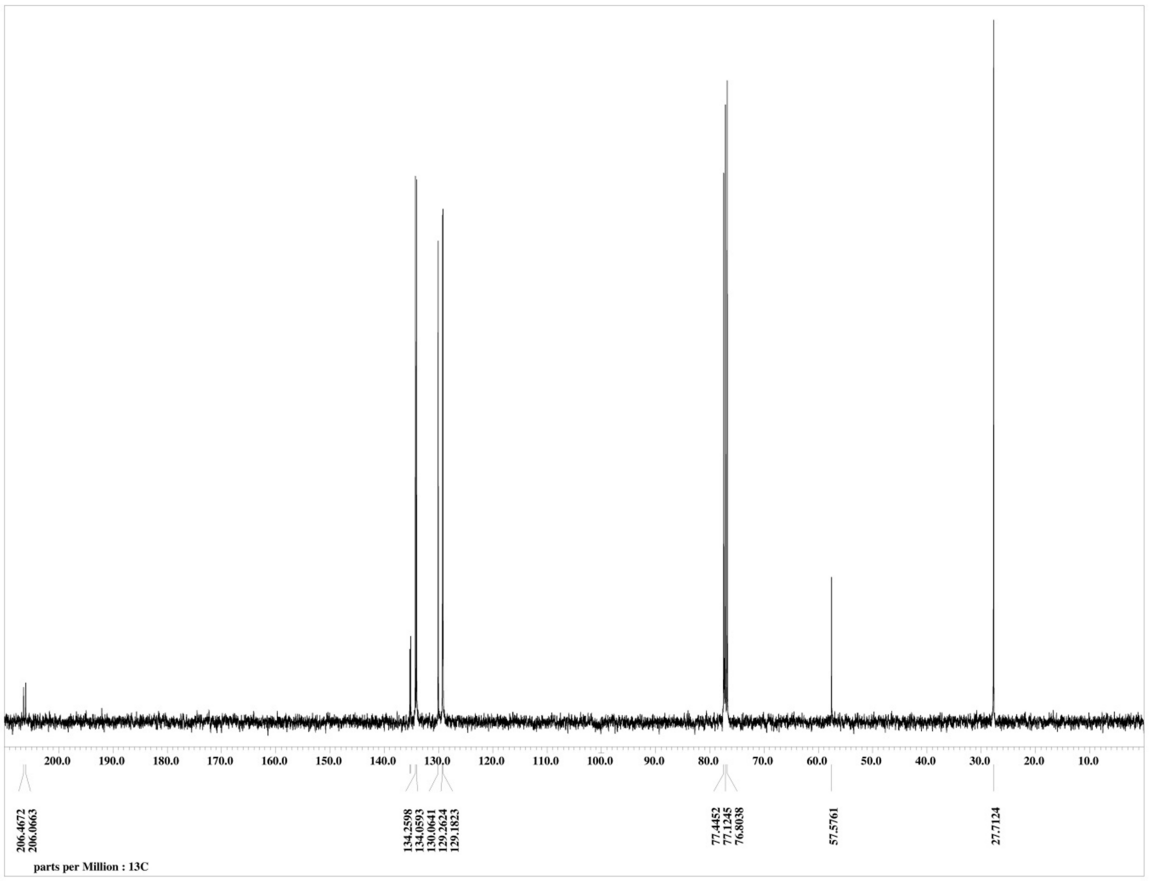


Figure S56. ^{13}C NMR spectrum of **12b** in $CDCl_3$ at 293 K.

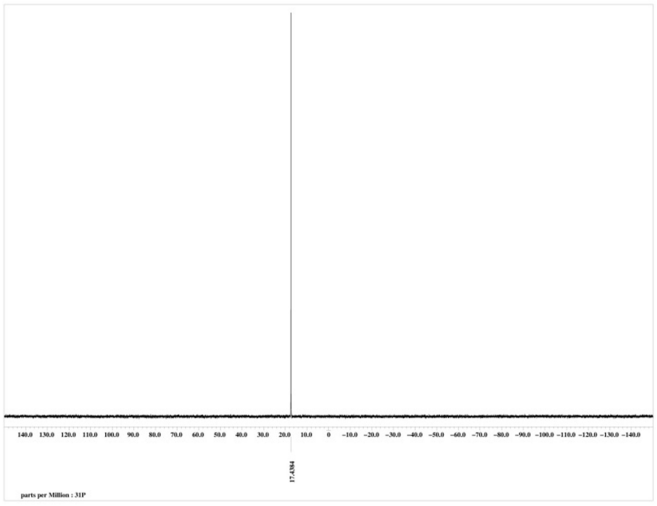


Figure S57. ^{31}P NMR spectrum of **12b** in $CDCl_3$ at 293 K.

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X-ray Diffraction Data

Crystals for investigation were covered in Nujol®, mounted into a goniometer head, and then rapidly cooled under a stream of cold N_2 of the low-temperature apparatus (Oxford Cryostream) attached to the diffractometer. The data were then collected using the APEXIII software suite[1] on a Bruker Photon 100 CMOS diffractometer using a graphite monochromator with Mo-Kα radiation (λ = 0.71073 Å). For each sample, data were collected at low temperature. APEX-III software was used for data collection and reduction and SADABS[2] was used for absorption corrections (multi-scan; semi-empirical from equivalents). XPREP was used to determine the space group and the structures were solved and refined using the SHELX[3] software suite as implemented in the WinGX[4] program suites. Validation of the structures was conducted using PLATON.[5] Crystallographic information has also been deposited with the Cambridge Crystallographic Data Centre (CCDC 1549899-1549904). Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: + 44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

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