Supporting Information

S1: Synthetic details

S2: X-Ray diffraction studies

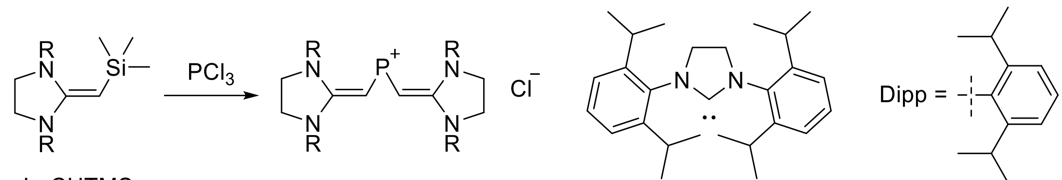
S3: Theoretical details

S4: References

S1: Synthetic details

General: All manipulations were performed under an inert atmosphere of dry nitrogen, using standard Schlenk techniques. Dry, oxygen-free solvents were employed unless otherwise mentioned. The compounds L=CH_2 (L = 1,3-Bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene), L=CHTMS, [LC(Ph)]PCl_2, MesPCl_2 4,5-dimethyl-1,3-diisopropylimidazol-2-ylidene (^{Me}ipr) were prepared following literature procedures,[1] while all other starting materials were purchased from commercial sources. NMR spectra were recorded on Bruker Avance 400 MHz spectrometers (^{1}H, 400.1 MHz; ^{13}C, 100.5 MHz; ^{31}P, 161.9 MHz) or Bruker Avance 600 MHz spectrometers (^{1}H, 600.2 MHz; ^{13}C, 150.8 MHz; ^{31}P, 242.9 MHz). The chemical shifts (δ) were measured according to IUPAC and expressed in ppm relative to $SiMe_4$ (^{1}H, ^{13}C), and 85% H_3PO_4 (^{31}P). Coupling constants *J* are reported in Hertz [Hz] as absolute values. Because of high sensitivity of these compounds or the contamination of solvents, the elemental analyses gave unsatisfying results. The high purity of these isolated compounds has been proved mainly by NMR spectra. ESI-MS spectra were measured on Bruker ESI-Q-TOF maxis 4G. UV/vis spectra were measured on Shimadzu UV/vis/NIR UV-3600-spectrometer. Melting point (M. p.) were measured on Jiahang JH30 apparatus.

Synthesis of 1a:



L=CHTMS, R= Dipp

1a, R = Dipp

L

PCl$_3$ (685 mg, 5 mmol) in toluene (5 mL) was added to a stirred solution of **L=CHTMS** (5.2 g, 11 mmol) in toluene (40 mL) at room temperature. After stirring at 130 °C for 24 h, the reaction mixture was allowed to cool slowly to room temperature. The resulting precipitates were collected via filtration, then washed with hexane (2×5 mL) and dried *in vacuo* to afford **1a** (4.0 g, yield = 92 %) as an orange powder. M. p. > 250.0 °C. ^{1}H NMR (600.2 MHz, CD$_3$CN): δ = 7.39 (t, J_{HH} = 7.6 Hz, 4 H, C_{Ar}), 7.14 (d, J_{HH} = 7.6 Hz, 8 H, C_{Ar}), 4.88 (d, $^2J_{PH}$ = 13.5 Hz, 2 H, C*H*P), 3.95 (s, 8 H, NC*H*$_2$), 2.83 (m, 8 H, C*H*(CH$_3$)$_2$), 1.19 (d, *J* = 7.0 Hz, 12 H, CH(C*H*$_3$)$_2$), 0.90 (d, *J* = 7.0 Hz, 12 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (150.8 MHz, CD$_3$CN): δ = 166.3 (d, $^2J_{PC}$ = 20.9 Hz, N*C*N), 147.8 (C_{Ar}), 133.4 (C_{Ar}), 131.4 (C_{Ar}), 129.9 (C_{Ar}), 129.2 (C_{Ar}), 126.2 (C_{Ar}), 107.2 (d, $^1J_{PC}$ = 45.0 Hz, *C*H-P), 51.9 (N*C*H$_2$), 29.4, 24.9, 24.5. ^{31}P{^{1}H} NMR (242.9 MHz, CD$_3$CN): δ = 331.8. ^{31}P NMR (242.9 MHz, CD$_3$CN): δ = 331.7 (t, $^2J_{PH}$ = 13.5 Hz). UV/Vis (acetonitrile, λ (nm) ε (M^{-1}cm^{-1})): 332 (8125), 473.5 (43599). HRMS (ESI, m/z) calc. for: $C_{56}H_{78}N_4P^+$: 837.5959 [M]$^+$; found: 837.5888. IR (ATR, cm^{-1}): 3395, 2961, 2927, 2866, 1425, 1313, 905.

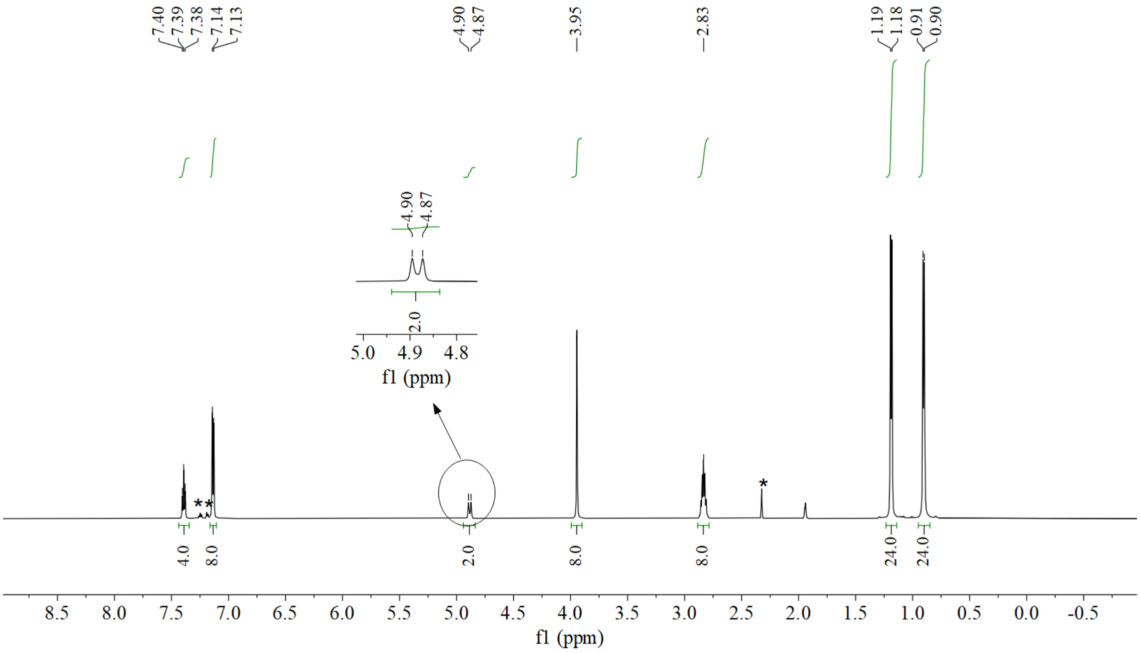


Figure S1. ^{1}H NMR of **1a** in CD_3CN. *Toluene.

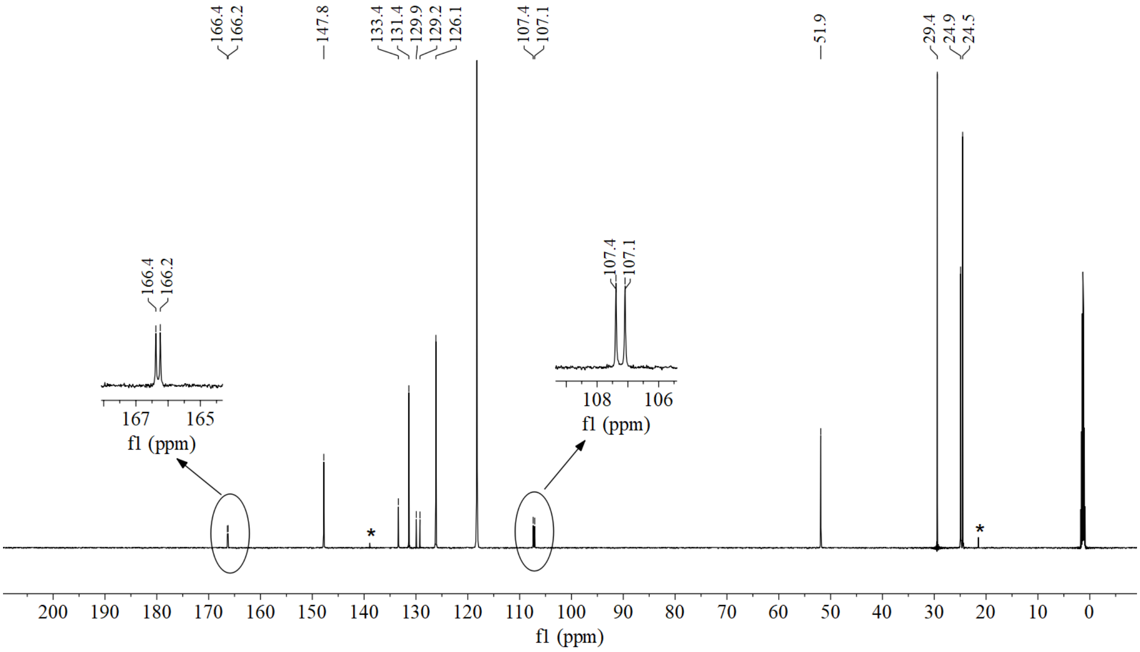


Figure S2. $^{13}C\{^{1}H\}$ NMR of **1a** in CD_3CN. *Toluene.

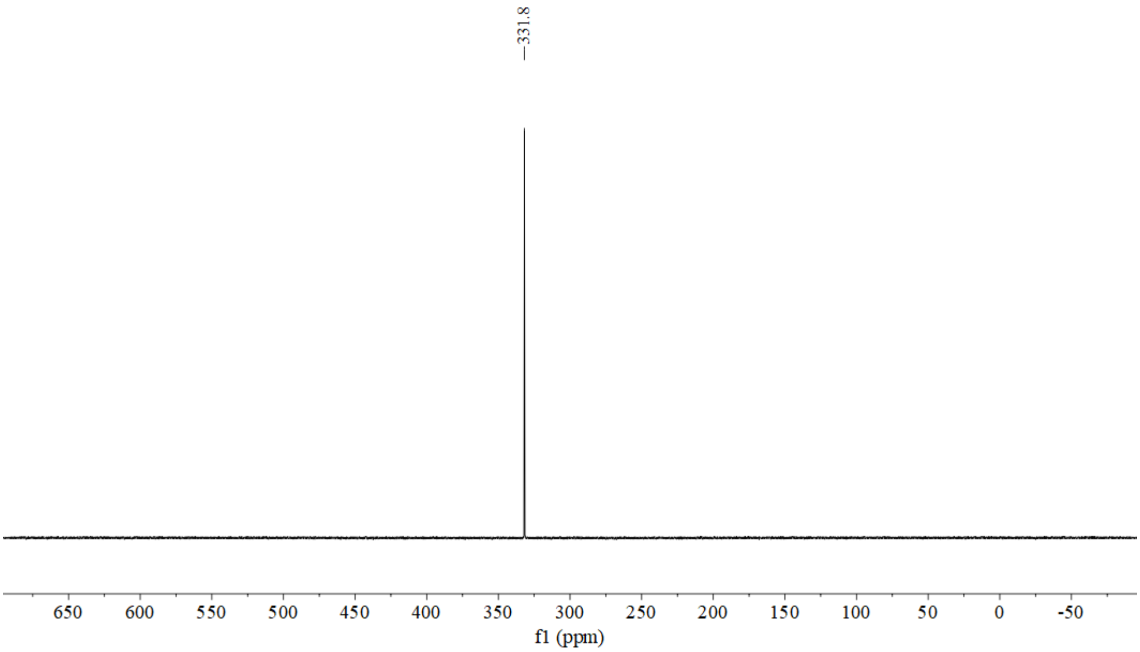


Figure S3. $^{31}P\{^{1}H\}$ NMR of **1a** in CD_3CN.

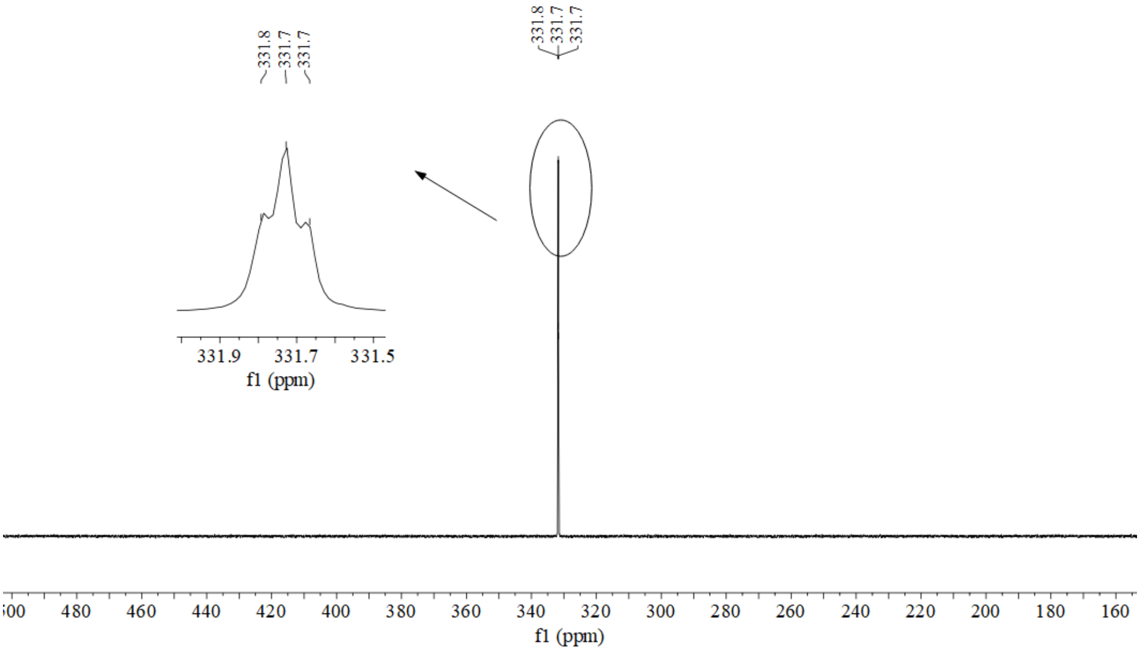


Figure S4. ^{31}P NMR of **1a** in CD_3CN.

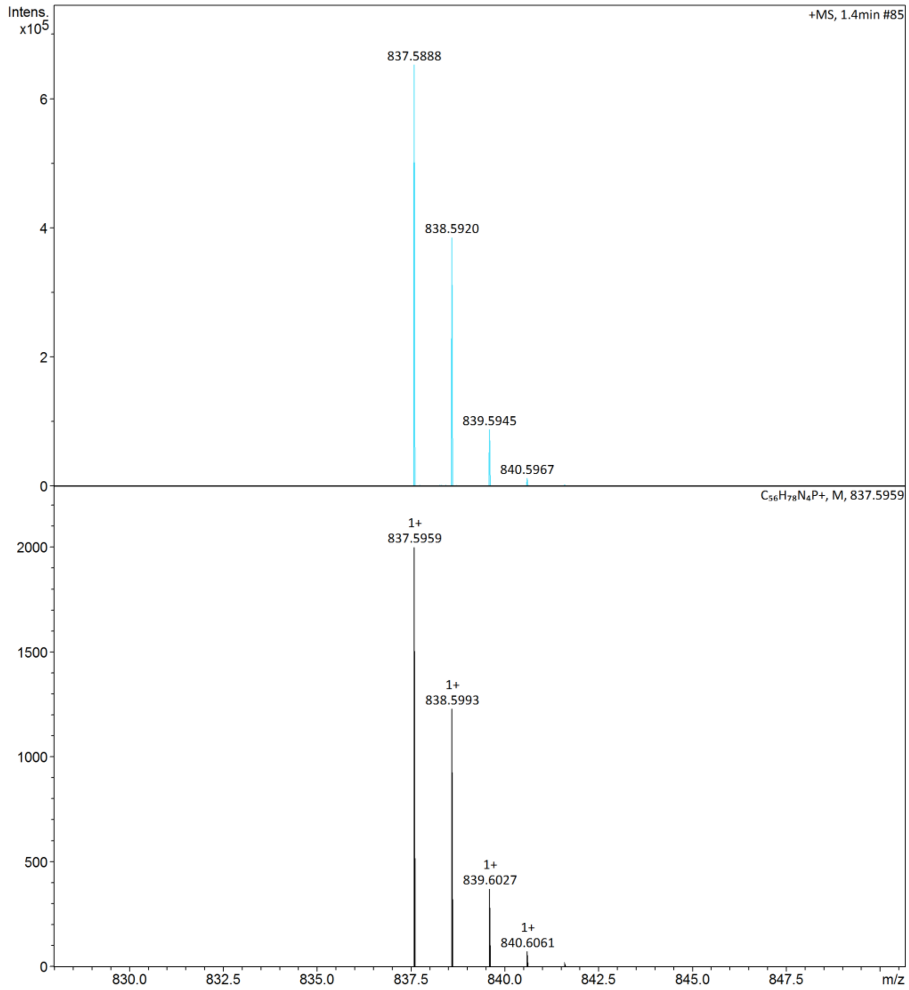


Figure S5. HRMS of **1a**.

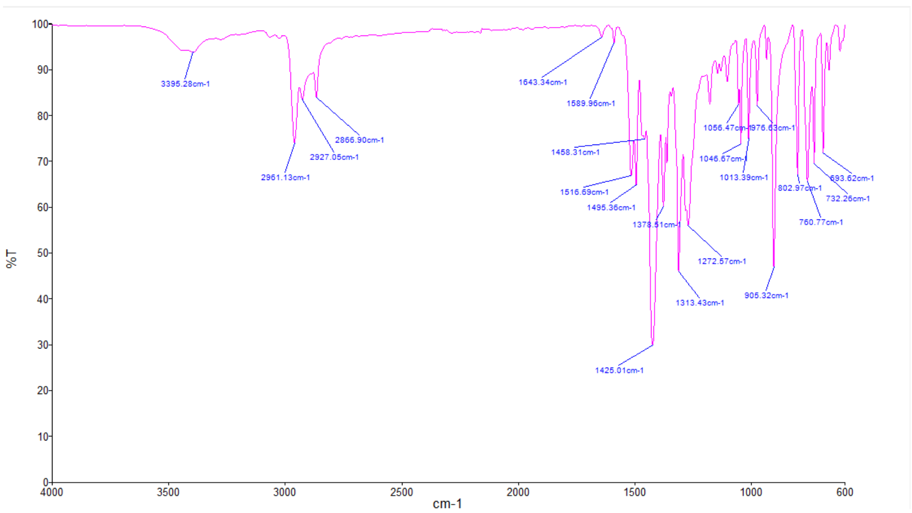
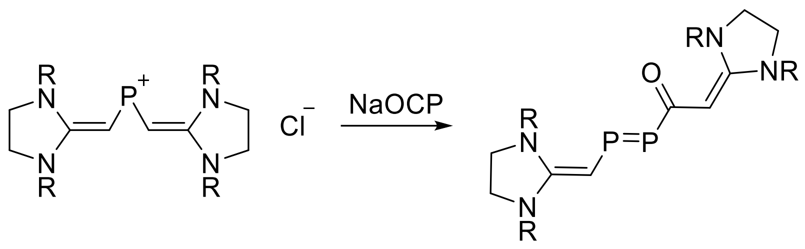


Figure S6. IR spectrum of **1a**.

Synthesis of 3a:



1a, R = Dipp   **3a**, R = Dipp

NaOCP (151 mg, 0.5 mmol) in tetrahydrofuran (10 mL) was added dropwise to a stirred solution of **1a** (450 mg, 0.5 mmol) in a mixed solvent of acetonitrile (1 mL) and tetrahydrofuran (20 mL). After stirring for 20 minutes, the solvent was removed under reduced pressure. The remaining solid was extracted with a mixed solvent of hexane (20 mL) and diethyl ether (10 mL). The mixture was then filtered and concentrated to approximately 5 mL with a concomitant precipitation. The precipitates were collected, washed with a minimum amount of cold hexane (2×1 mL) and dried *in vacuo* to afford **3a** (340 mg, 76 %) as a red powder. Red crystals of **3a** were obtained from a saturated hexane solution stored at -30 °C for 1 day. M. p. = 134.3 °C. ^{1}H NMR (600.2 MHz, C_6D_6): δ = 7.29 (t, J_{HH} = 7.8Hz, 1 H, C_{Ar}), 7.15 (m, 2 H, C_{Ar}), 7.08 ~ 7.00 (br., 7 H, C_{Ar}), 6.96 (d, J_{HH} = 7.8 Hz, 2 H, C_{Ar}), 5.77 (br., 1 H, P-C*H*), 4.77 (s, 1 H, C(O)C*H*), 3.42 (br., 2 H, C*H*(CH_3)$_2$), 3.34 (m, 4 H, NC*H*$_2$), 3.27 (m, 4 H, NC*H*$_2$), 3.17 (m, 2 H, C*H*(CH_3)$_2$), 3.10 (br., 2 H, C*H*(CH_3)$_2$), 3.02 (m, 2 H, C*H*(CH_3)$_2$), 1.41 (br., 6 H, CH(C*H*$_3$)$_2$), 1.27 (br., 6 H, CH(C*H*$_3$)$_2$), 1.23 ~ 1.19 (m, 24 H, CH(C*H*$_3$)$_2$), 1.12 (d, J_{HH} = 7.4 Hz, 6 H, CH(C*H*$_3$)$_2$), 1.11 (d, J_{HH} = 6.8 Hz, 6 H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (150.8 MHz, C_6D_6): δ = 198.9 (m, *C*O), 159.0 (N*C*N), 157.2 (N*C*N), 148.4 (C_{Ar}), 148.2 (C_{Ar}), 147.7 (C_{Ar}), 145.8 (C_{Ar}), 139.2 (C_{Ar}), 136.6 (C_{Ar}), 135.0 (C_{Ar}), 134.6 (C_{Ar}), 129.6 (C_{Ar}), 129.5 (C_{Ar}), 129.2 (C_{Ar}), 128.4 (C_{Ar}), 125.0 (C_{Ar}), 124.6 (C_{Ar}), 124.7 (C_{Ar}), 123.9 (C_{Ar}), 89.4 (br., *C*HP), 84.6 (d, $^{2}J_{PC}$ = 48.7 Hz, *C*HCO), 53.6 (N*C*H$_2$), 52.0 (N*C*H$_2$), 50.4 (N*C*H$_2$), 49.9 (N*C*H$_2$), 29.1, 29.0, 25.4, 25.3, 24.9, 24.5, 24.3, 24.0. ^{31}P{^{1}H} NMR (242.9 MHz, C_6D_6): δ = 487.5 (d, $^{1}J_{PP}$ = 529.5 Hz, CH-*P*=P-CO), 385.0 (d, $^{1}J_{PP}$ = 529.5 Hz, CH-P=*P*-CO). UV/Vis (toluene, λ (nm) ε ($M^{-1}cm^{-1}$)): 368 (15262), 488.0 (49678). HRMS (ESI, m/z) calc. for: $C_{57}H_{78}N_4OP_2$: 897.5724 [M+H]$^{+}$;

found: 897.5707. IR (ATR, cm^{-1}): 2960, 2927, 2868, 1502, 1494, 1445, 1434, 1323, 1054, 1042, 803.

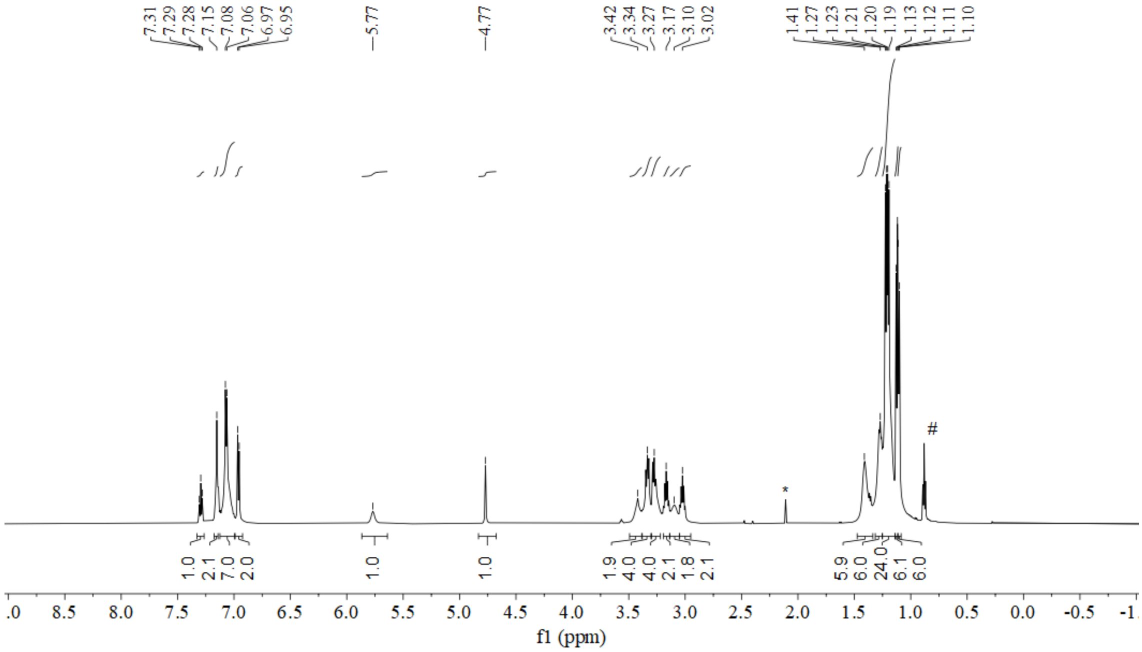


Figure S7. ^{1}H NMR of **3a** in C_6D_6. *Toluene, #hexane.

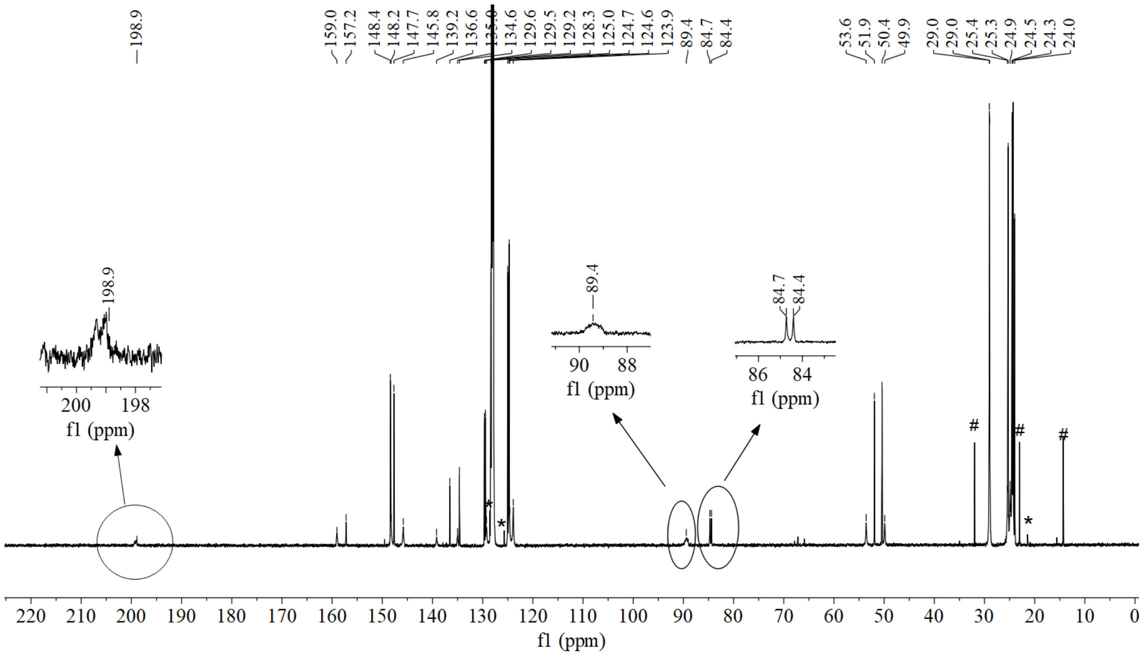


Figure S8. $^{13}C\{^{1}H\}$ NMR of **3a** in C_6D_6. *Toluene, #hexane.

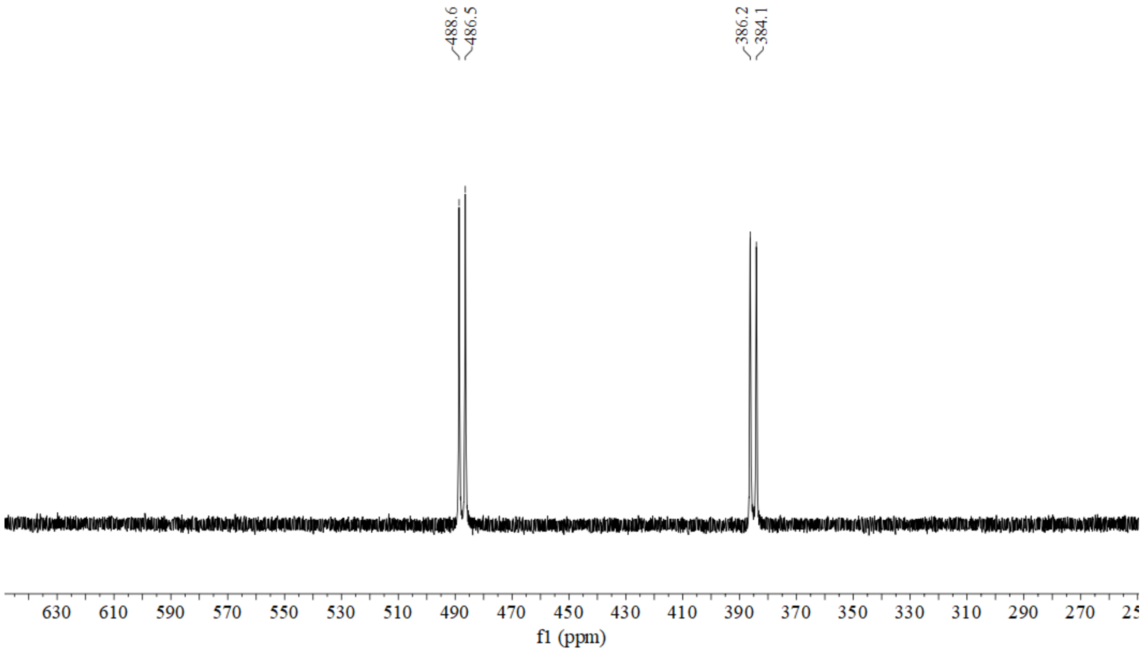


Figure S9. ${}^{31}P\{{}^{1}H\}$ NMR of **3a** in C_6D_6.

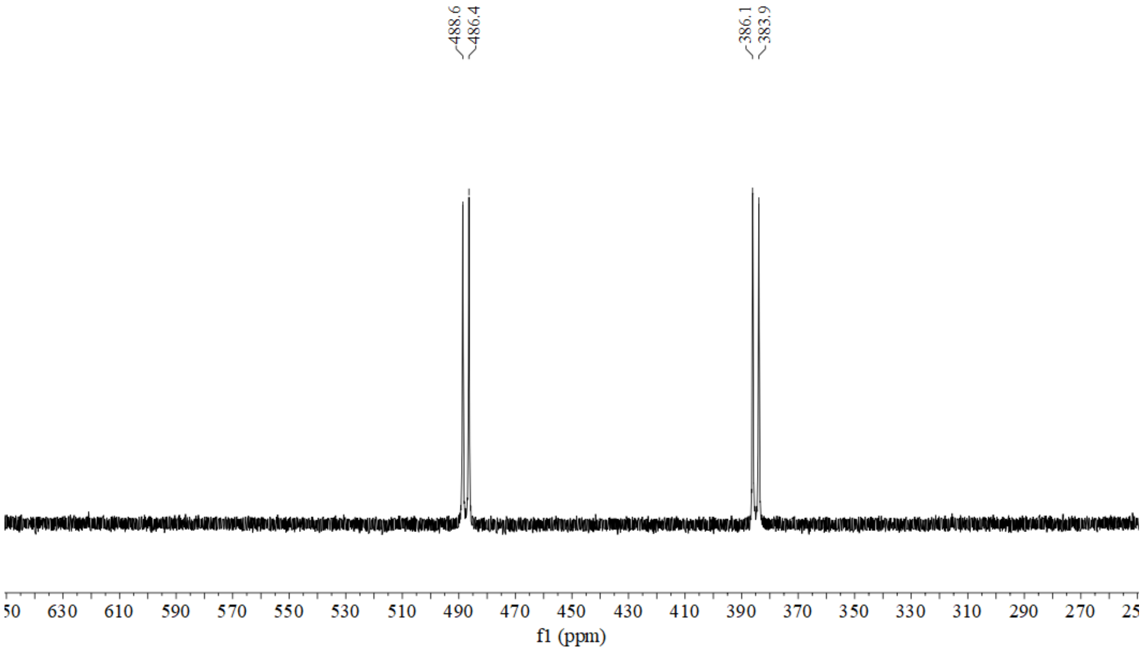
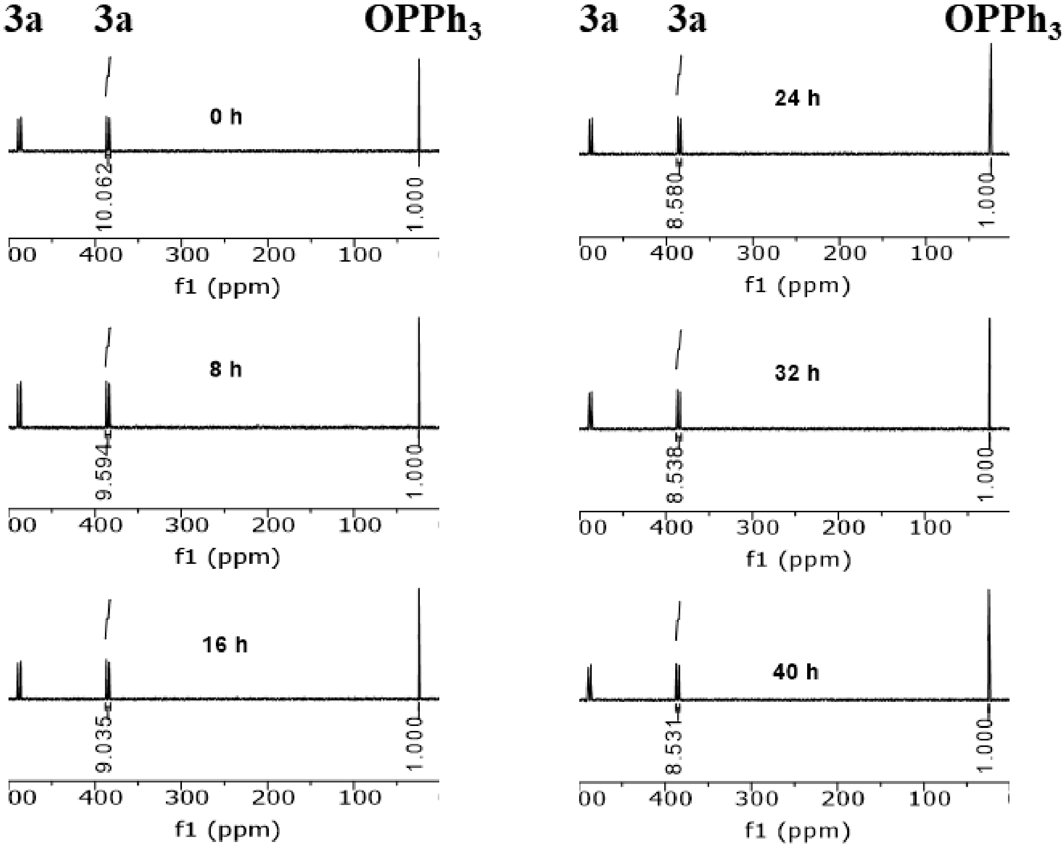


Figure S10. ${}^{31}P$ NMR of **3a** in C_6D_6.

(a)



(b)

T (h)	$\int_{3a}$	[3a] ($mol*L^{-1}$)
0	10.062	0.072
8	9.594	0.069
16	9.035	0.065
24	8.580	0.062
32	8.538	0.061
40	8.531	0.061

(c)

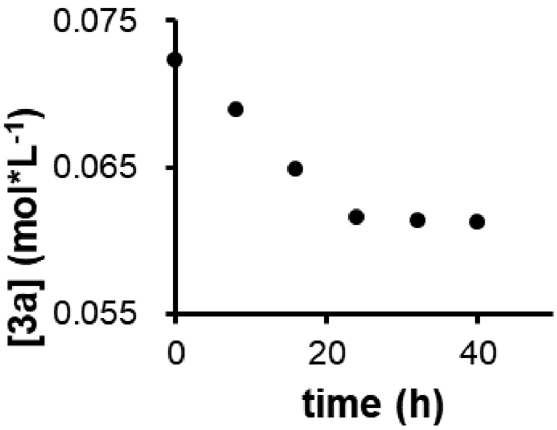


Figure S11. (a) $^{31}P\{^1H\}$ NMR spectra of **3a** (internal standard $OPPh_3$) over a period of 40 h in C_6D_6. (b) Table of the concentration of **3a** over a period of 40 h in C_6D_6. (c) Plot of concentration of **3a** against time in C_6D_6.

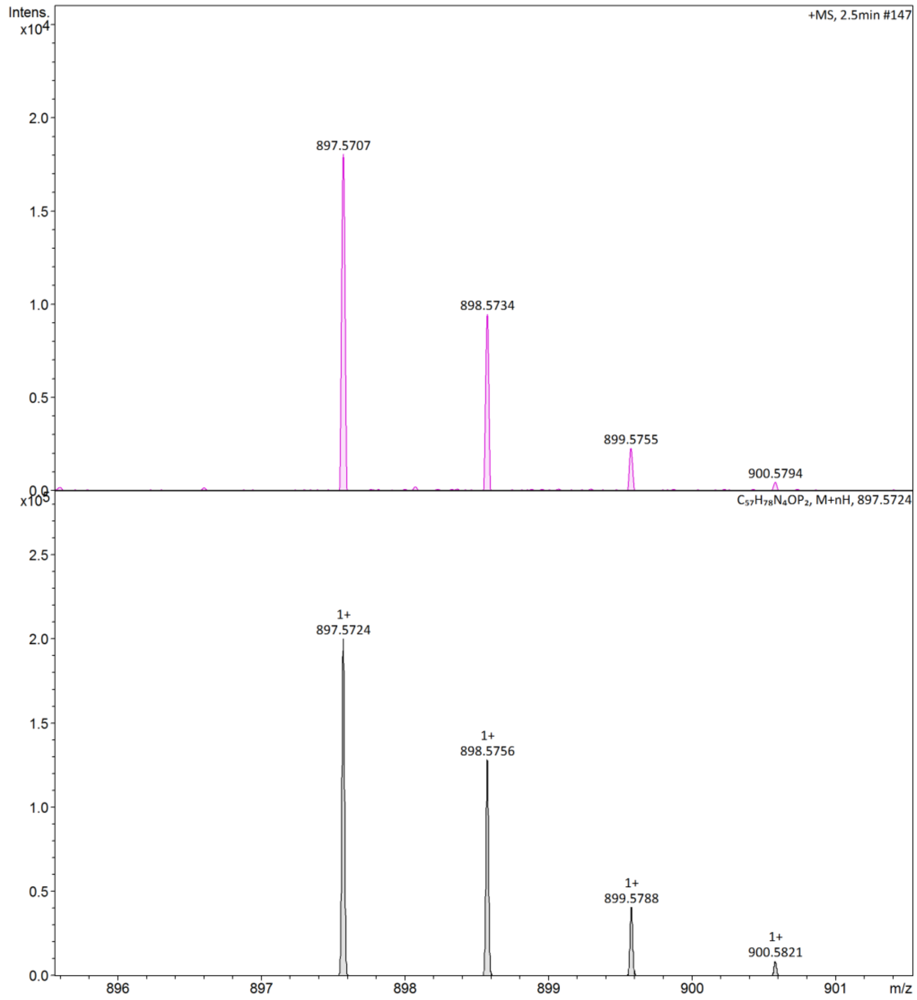


Figure S12. HRMS of **3a**.

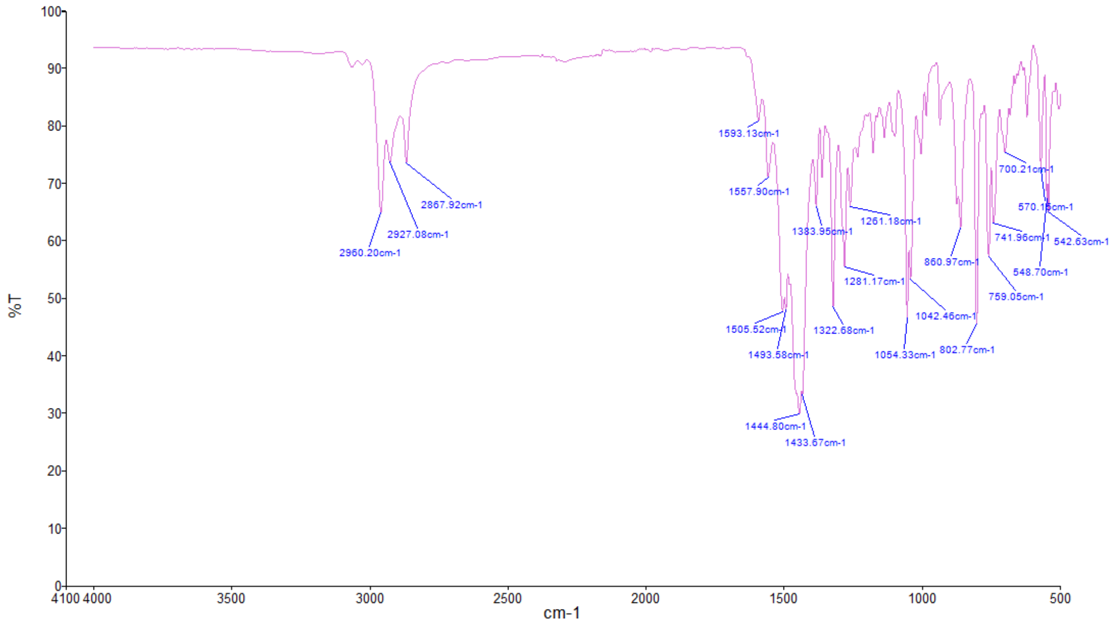
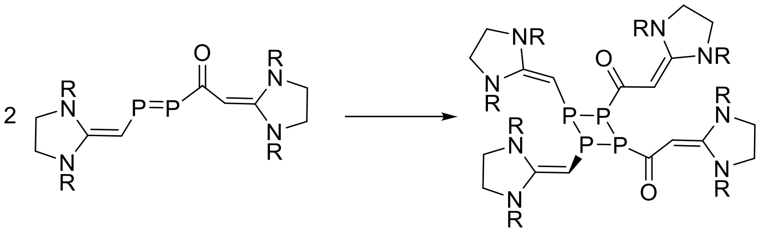


Figure S13**.** IR spectrum of **3a**.

Synthesis of 3a-dimer:



3a, R = Dipp   **3a-dimer**, R = Dipp

3a (200 mg, 0.2 mmol) in hexane (20 mL) was allowed to evaporate slowly at room temperature for 1 week. Yellow crystals were then formed and collected to afford **3a-dimer** (122 mg, yield = 61 %) as yellow crystalline materials. M. p. = 193.1 °C (Decomposition). ^{1}H NMR (600.2 MHz, C_6D_6): δ = 7.45 (d, *J* = 7.7 Hz, 2 H, $C_{Ar}H$), 7.41 (t, *J* = 7.5 Hz, 2 H, $C_{Ar}H$), 7.37 (t, *J* = 7.7 Hz, 2 H, $C_{Ar}H$), 7.30 (d, *J* = 7.7 Hz, 2 H, $C_{Ar}H$), 7.26 (t, *J* = 7.5 Hz, 4 H, $C_{Ar}H$), 7.21 (t, *J* = 7.7 Hz, 2 H, $C_{Ar}H$), 7.14 (d, *J* = 7.5 Hz, 2 H, $C_{Ar}H$), 7.11~7.08 (m, 2 H, $C_{Ar}H$), 4.81 (s, 2 H, C*H*C(O)PP), 3.80 (m, 6 H, NCH_2), 3.61 (m, 2 H, NCH_2), 3.28 (m, 8 H, NCH_2), 3.18 (m, 6 H, $CH(CH_3)_2$), 3.13 (m, 4 H, $CH(CH_3)_2$), 3.07 (m, 6 H, $CH(CH_3)_2$), 2.83 (m, 2 H, C*H*PP), 1.86 (d, *J* = 6.6 Hz, 6 H, $CH(CH_3)_2$), 1.46 (d, *J* = 6.6 Hz, 6 H, $CH(CH_3)_2$), 1.44 (d, *J* = 7.1 Hz, 6 H, $CH(CH_3)_2$), 1.39~1.37 (m, 12 H, $CH(CH_3)_2$), 1.36 (d, *J* = 6.6 Hz, 6 H, $CH(CH_3)_2$), 1.34 (d, *J* = 6.6 Hz, 12 H, $CH(CH_3)_2$), 1.28 (d, *J* = 6.9 Hz, 6 H, $CH(CH_3)_2$), 1.26 (d, *J* = 6.8 Hz, 6 H, $CH(CH_3)_2$), 1.22 (m, 12 H, $CH(CH_3)_2$), 1.18 (d, *J* = 6.9 Hz, 6 H, $CH(CH_3)_2$), 1.06 (d, *J* = 6.6 Hz, 6 H, $CH(CH_3)_2$), 0.62 (d, *J* = 6.6 Hz, 6 H, $CH(CH_3)_2$), 0.56 (d, *J* = 6.6 Hz, 6 H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (150.8 MHz, C_6D_6): δ = 201.8 (m, *C*=O), 159.4 (N*C*N), 156.8 (m, N*C*N), 150.6 (C_{Ar}), 150.0 (C_{Ar}), 150.0 (C_{Ar}), 148.7 (C_{Ar}), 147.8 (C_{Ar}), 146.8 (C_{Ar}), 145.6 (C_{Ar}), 143.8 (C_{Ar}), 141.7 (C_{Ar}), 141.1 (C_{Ar}), 137.2 (C_{Ar}), 133.8 (C_{Ar}), 128.8 (C_{Ar}), 128.5 (C_{Ar}), 127.4 (C_{Ar}), 127.3 (C_{Ar}), 127.0 (C_{Ar}), 125.7 (C_{Ar}), 125.2 (C_{Ar}), 124.6 (C_{Ar}), 124.5 (C_{Ar}), 123.9 (C_{Ar}), 123.9 (C_{Ar}), 123.7 (C_{Ar}), 80.2 (t, $^{1}J_{PC}$ ~$^{2}J_{PC}$ = 10.3 Hz, *C*HPP), 71.3 (m, *C*HC(O)P), 54.0 (N*C*H_2), 51.9 (N*C*H_2), 50.4 (N*C*H_2), 50.3 (N*C*H_2), 29.6, 28.7, 28.5, 28.4, 28.3, 28.2, 27.9, 27.9, 26.2, 26.1, 26.1, 26.0, 25.9, 25.8, 25.6, 25.4, 25.3, 24.8, 24.7, 24.6, 24.1, 23.9, 23.8, 15.6. ^{31}P{^{1}H} NMR (242.9 MHz, C_6D_6): δ = -30.9 (br., C(H)-*P*P-C(O)), -43.7 (br., C(H)-P*P*-C(O)). UV/Vis (toluene, λ (nm) ε ($M^{-1}cm^{-1}$)): 373.0 (27134), 486.0 (1872). HRMS (ESI, m/z) calc. for:

$C_{114}H_{156}N_8O_2P_4$: 1794.1374 [M+H]$^+$; found: 1794.1267. IR (ATR, cm^{-1}): 2960, 2925, 2864, 1503, 1472, 1447, 1325, 1054, 1043, 803, 760.

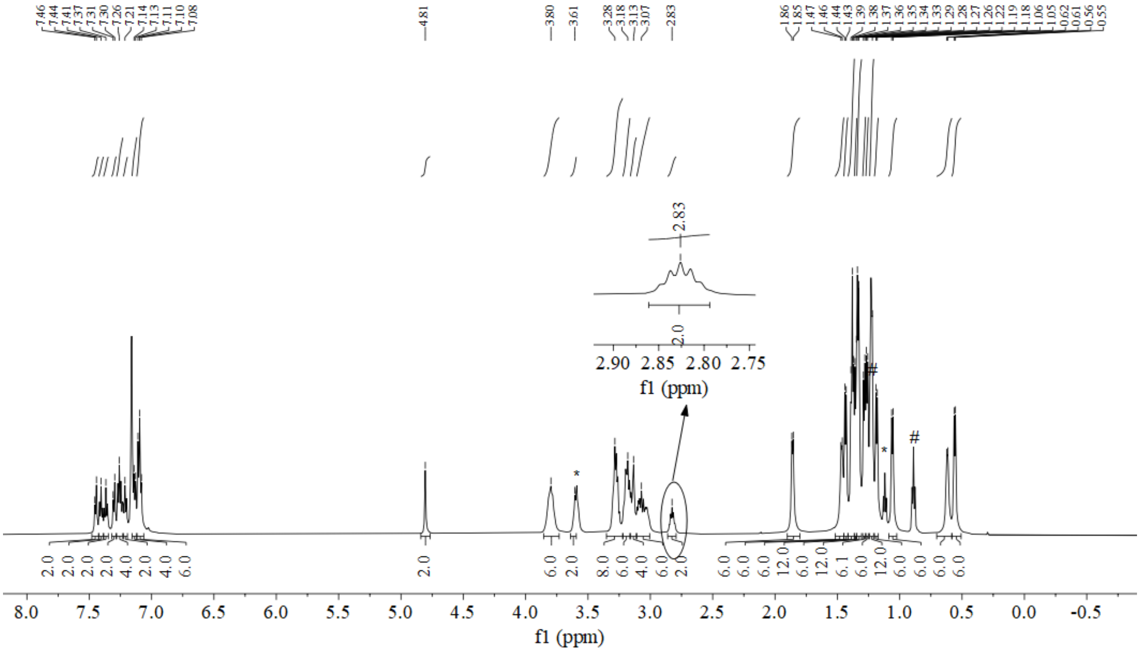


Figure S14. ^{1}H NMR of **3a-dimer** in C_6D_6. #Hexane, *tetrahydrofuran.

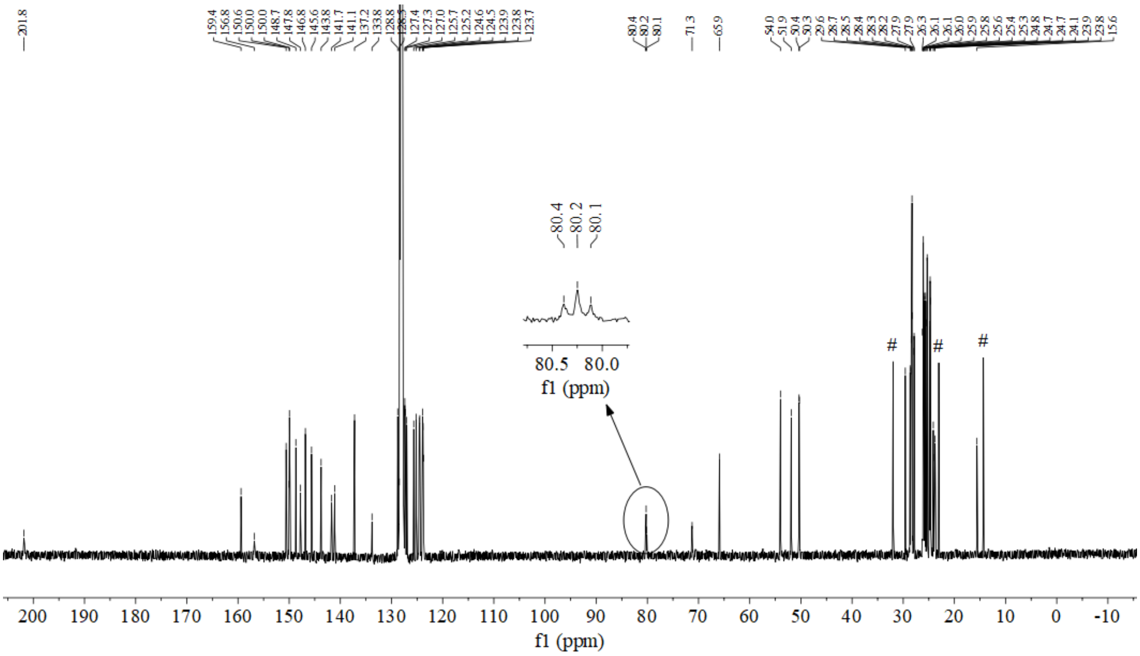


Figure S15. $^{13}C\{^1H\}$ NMR of **3a-dimer** in C_6D_6. #Hexane.

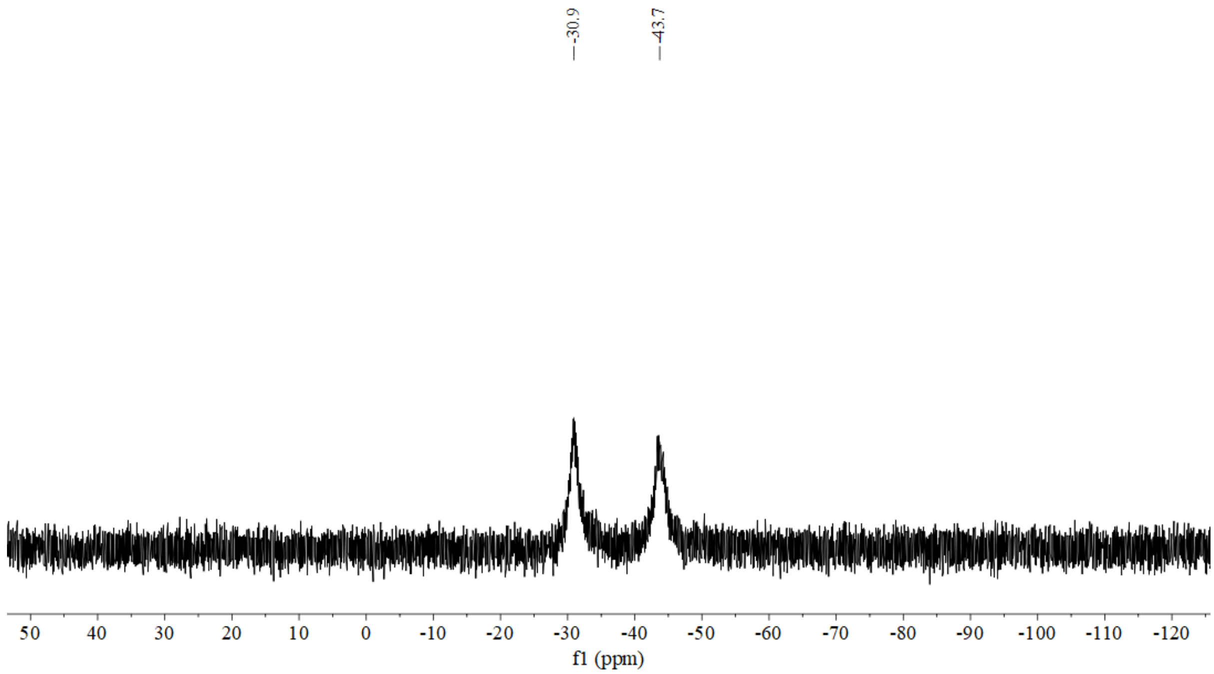


Figure 16. $^{31}P\{^{1}H\}$ NMR of **3a-dimer** in C_6D_6.

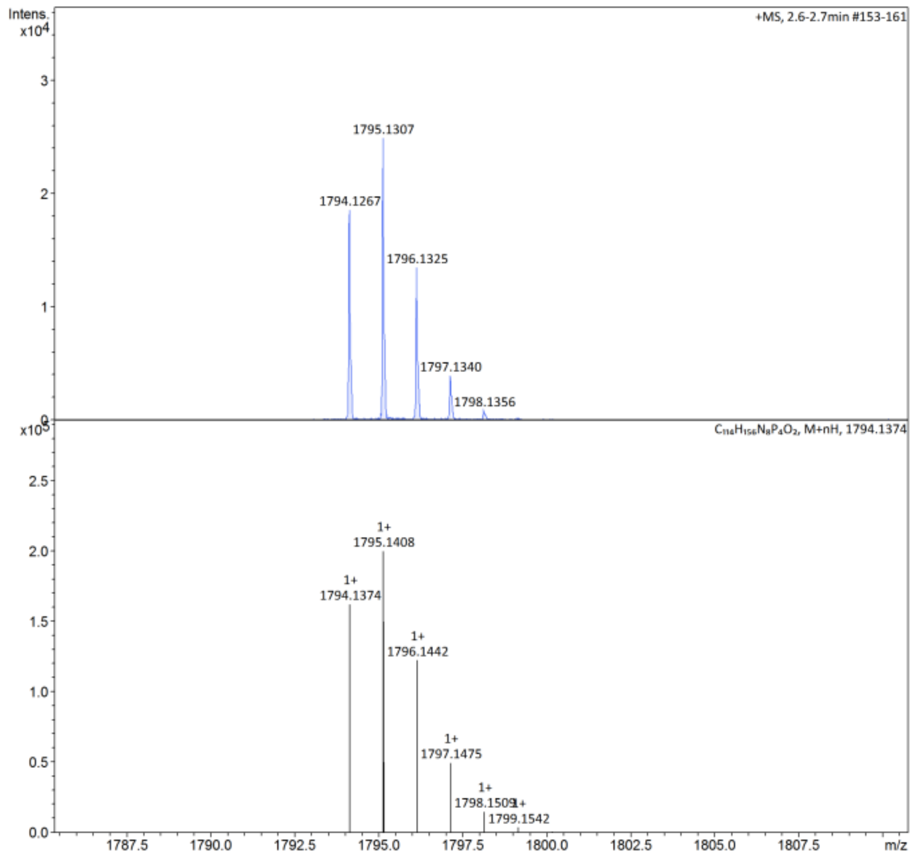


Figure 17. HRMS of **3a-dimer**.

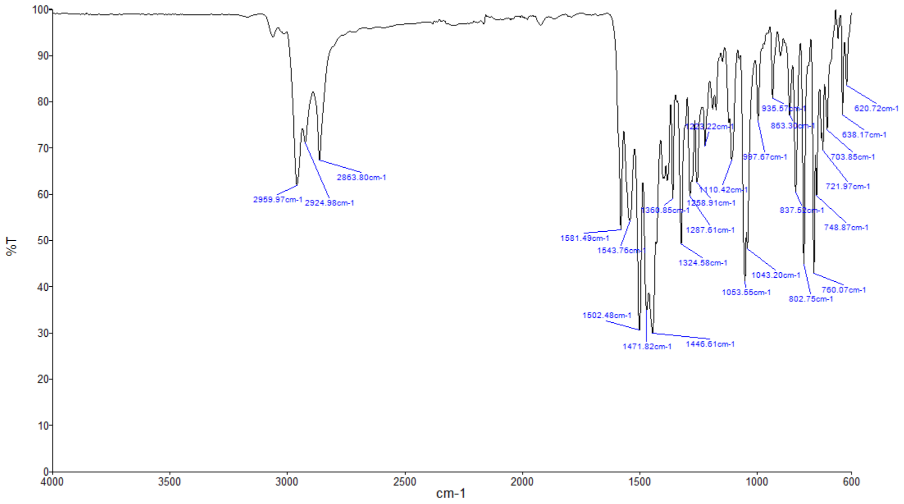
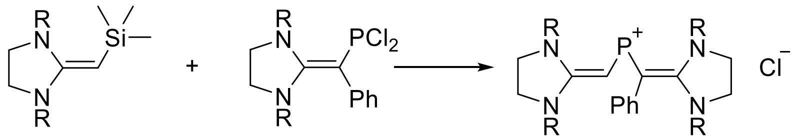


Figure S18. IR spectrum of **3a-dimer**.

Synthesis of 1b:



L=CHTMS, R= Dipp

L=C(Ph)PCl_2, R= Dipp

1b, R = Dipp

L=CHTMS (500 mg, 1.0 mmol) and L=C(Ph)PCl_2 (580 mg, 1.0 mmol) were mixed in toluene (20 mL) at room temperature. After stirring at 110 °C for 24 h, the solution was allowed to cool slowly to room temperature. The resulting precipitates were collected, washed with hexane (2 × 2 mL) and dried *in vacuo* to afford **1b** (721 mg, yield = 76 %) as an orange powder. M. p. > 250.0 °C. ^{1}H NMR (600.2 MHz, CD_3CN): δ = 7.40 (t, J = 7.8 Hz, 2 H, $C_{Ar}H$), 7.32 (t, J = 7.8 Hz, 2 H, $C_{Ar}H$), 7.11 (d, J = 7.8 Hz, 4 H, $C_{Ar}H$), 7.03 (d, J = 7.8 Hz, 4 H, $C_{Ar}H$), 6.50 (t, J = 7.3 Hz, 1 H, $C_{Ar}H$), 6.45 (t, J = 7.3 Hz, 2 H, $C_{Ar}H$), 5.99 (d, J = 7.3 Hz, 2 H, $C_{Ar}H$), 4.63 (d, $^{2}J_{PH}$ = 12.5 Hz, 1 H, C*H*-P), 3.94 (s, 4 H, NCH_2), 3.82 (s, 4 H, NCH_2), 2.93 (m, 4 H, C*H*$(CH_3)_2$), 2.76 (m, 4 H, C*H*$(CH_3)_2$), 1.17 (d, J = 7.2 Hz, 12 H, $CH(CH_3)_2$), 1.14 (d, J = 7.2 Hz, 12 H, $CH(CH_3)_2$), 1.02 (d, J = 6.9 Hz, 12 H, $CH(CH_3)_2$), 0.98 (d, J = 6.9 Hz, 12 H, $CH(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR (150.8 MHz, CD_3CN): δ = 169.3 (d, $^{2}J_{PC}$ = 34.2 Hz, -*C*=CHP), 166.1 (d, $^{2}J_{PC}$ = 25.6 Hz, -*C*=C(Ph)P), 147.1 (C_{Ar}), 146.7 (C_{Ar}), 137.7 (d, $^{2}J_{PH}$ = 5.5 Hz, =CP-C_{Ar}), 136.1 (C_{Ar}), 133.4 (C_{Ar}), 131.4 (C_{Ar}), 130.9 (C_{Ar}), 130.7 (C_{Ar}), 129.2 (C_{Ar}), 127.1 (C_{Ar}), 126.4 (C_{Ar}), 125.9 (C_{Ar}), 121.9 (d, ${}^{1}J_{PC}$ = 52.5 Hz, =*C*HP), 103.0 (d, ${}^{1}J_{PC}$ = 45.0 Hz, =*C*(Ph)P), 53.6 (N*C*H$_2$), 52.1 (N*C*H$_2$), 29.5, 29.4, 26.3, 24.9, 24.8, 23.9. ^{31}P{^{1}H} NMR (242.9 MHz, CD_3CN): δ = 323.3. ^{31}P NMR (242.9 MHz, CD_3CN): δ = 323.2 (d, ${}^{2}J_{PH}$ = 12.5 Hz). UV/Vis (acetonitrile, λ (nm) ε ($M^{-1}cm^{-1}$)): 334.5 (8776), 477.0 (53152). HRMS (ESI, m/z) calc. for: $C_{62}H_{82}N_4P^+$: 913.6272 $[M]^+$; found: 913.6273. IR (ATR, cm^{-1}): 2961, 2923, 2865, 1490, 1455, 1410, 1369, 1359, 1311, 1293, 901, 803, 697.

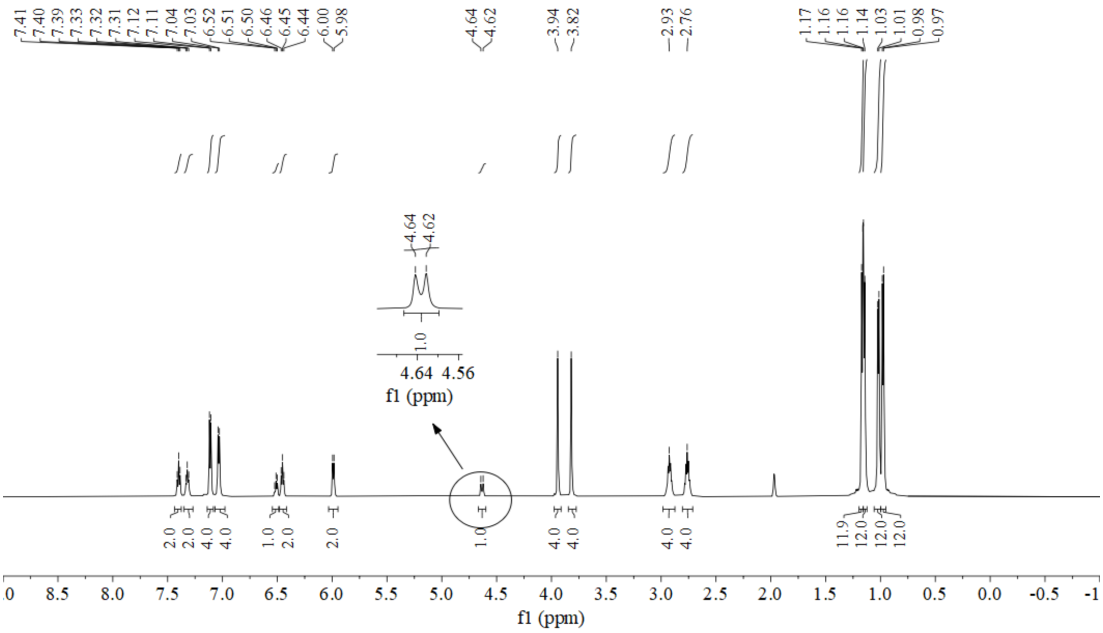


Figure S19. ^{1}H NMR of **1b** in CD_3CN.

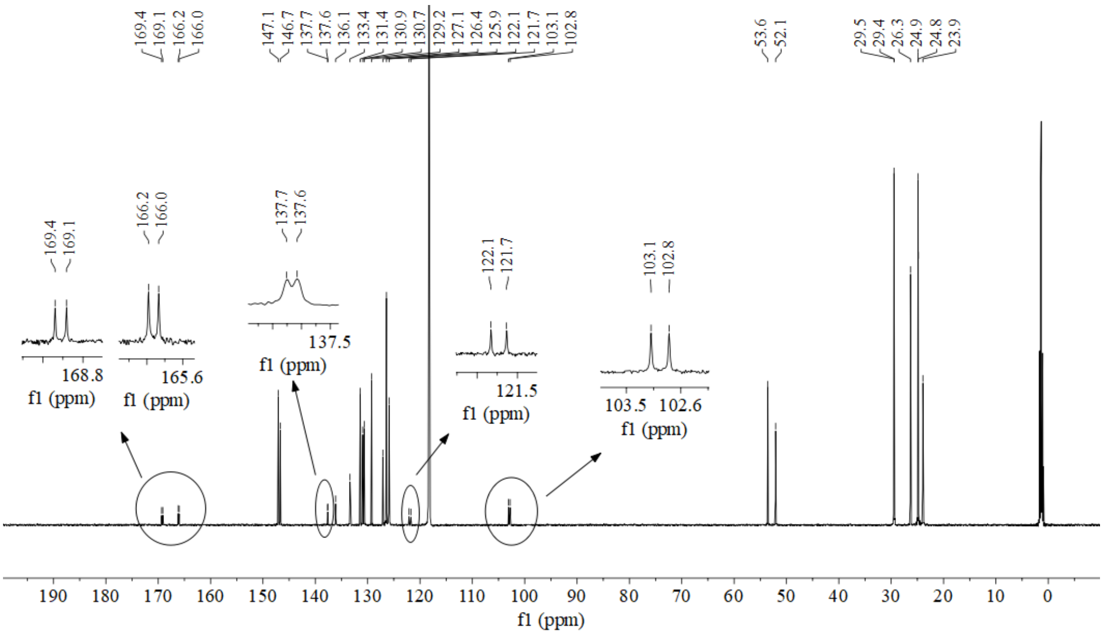


Figure S20. ^{13}C{^{1}H} NMR of **1b** in CD_3CN.

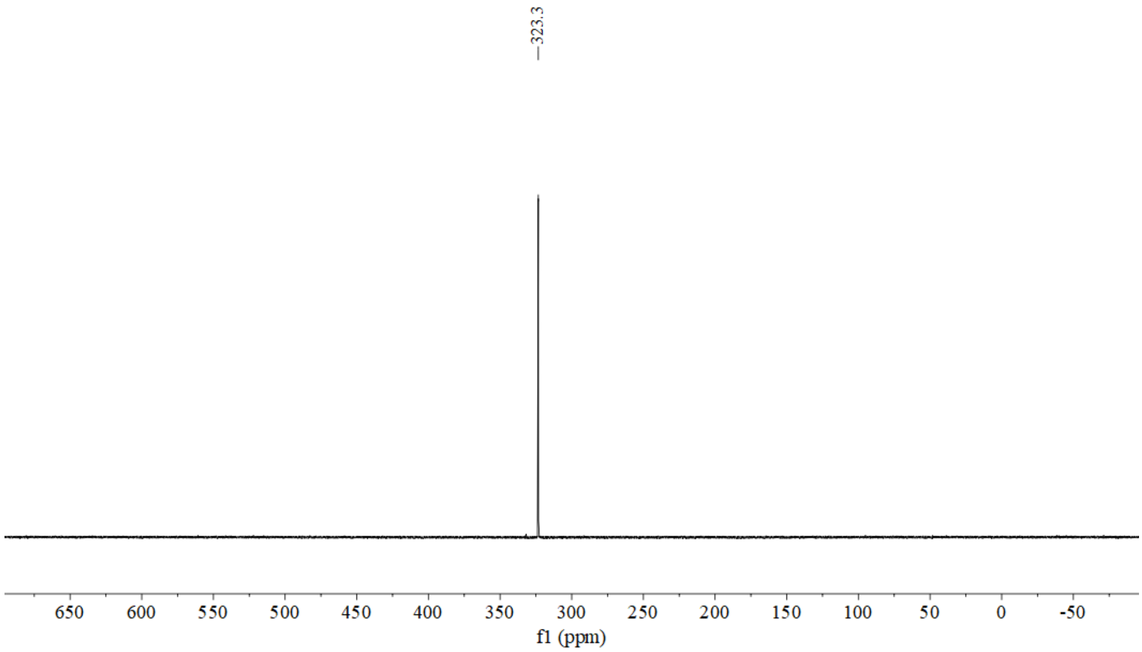


Figure S21. $^{31}P\{^{1}H\}$ NMR of **1b** in CD_3CN.

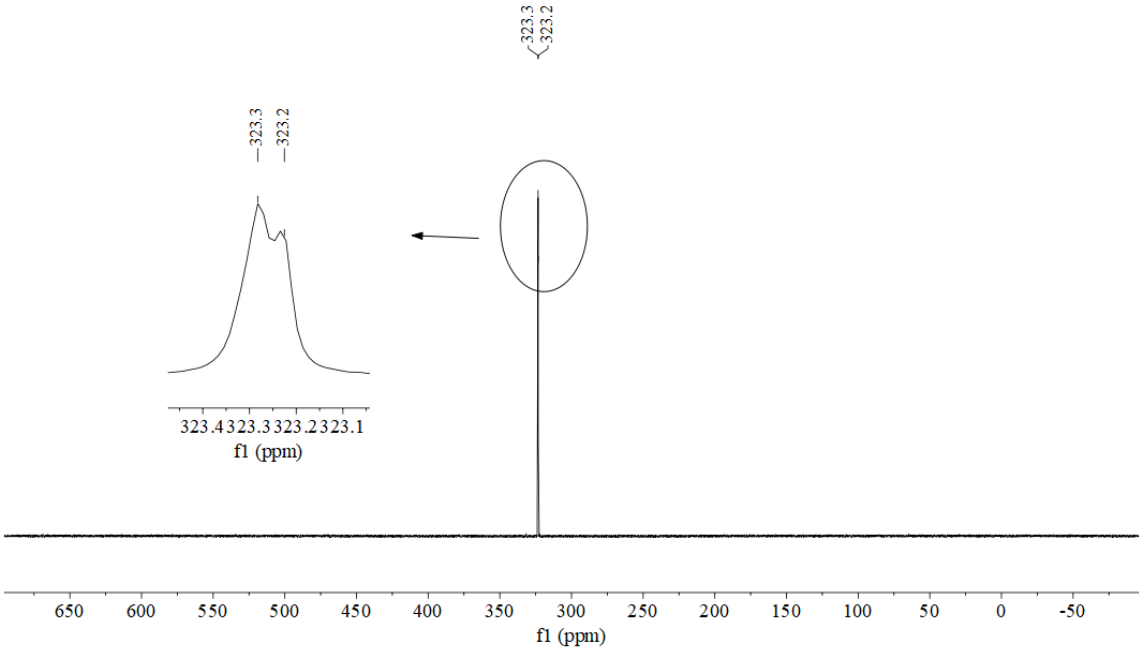


Figure S22. ^{31}P NMR of **1b** in CD_3CN.

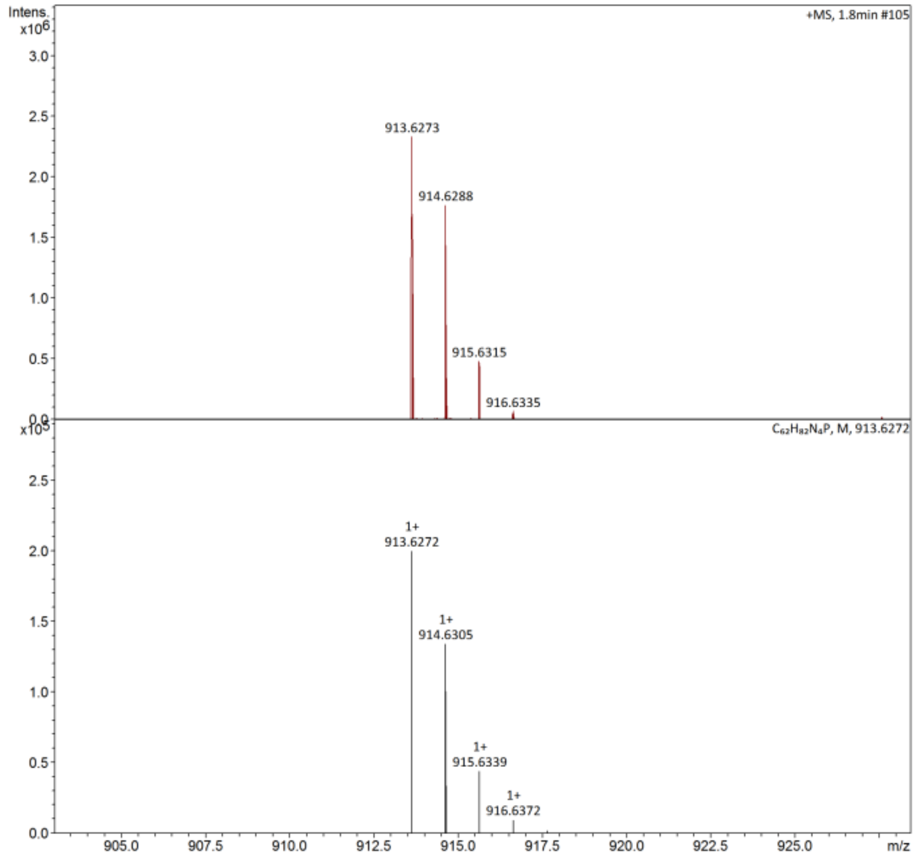


Figure S23. HRMS of **1b**.

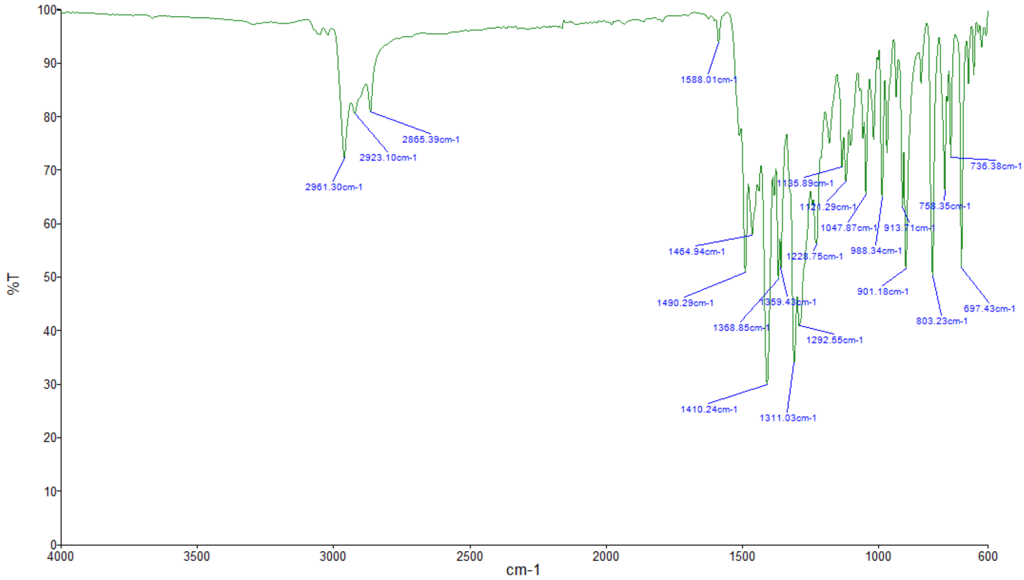
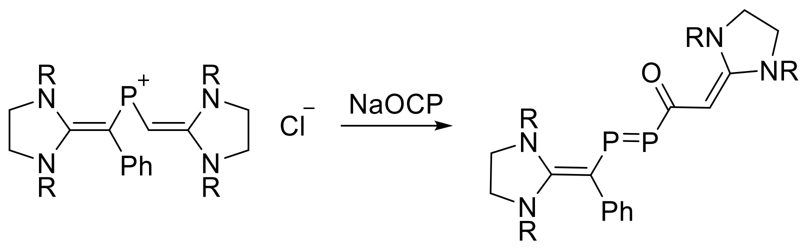


Figure S24. IR spectrum of **1b**.

Synthesis of 3b:



1b, R = Dipp **3b**, R = Dipp

NaOCP (100 mg, 0.3 mmol) in tetrahydrofuran (10 mL) was added dropwise to a solution of **1b** (300 mg, 0.3 mmol) in a mixed solvent of acetonitrile (1 mL) and tetrahydrofuran (15 mL). After stirring for 1 hour, the solvent was removed under reduced pressure. The residue was extracted with hexane (20 mL), washed with a minimum amount of cold hexane (2 × 1 mL), and dried *in vacuo* to afford **3b** (216 mg, 74 %) as a red powder. Red crystals of **3b** were obtained from saturated hexane solution stored at -30 °C for 3 days. M. p. = 148.2 °C. ^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.29 (br., 2 H, $C_{Ar}H$), 7.11 (br., 3 H, $C_{Ar}H$), 7.02 (br., 2 H, $C_{Ar}H$), 6.92 (br., 3 H, $C_{Ar}H$), 6.78 (br., 4 H, $C_{Ar}H$), 6.64 (m., 3 H, $C_{Ar}H$), 4.54 (s, 1 H, =C*H*C(O)), 3.40 (br., 8 H, NCH_2), 3.30 (br., 2 H, $CH(CH_3)_2$), 3.21 (br., 4 H, $CH(CH_3)_2$), 2.99 (br., 2 H, $CH(CH_3)_2$), 1.41 (br., 12 H, $CH(CH_3)_2$), 1.32 (br., 12 H, $CH(CH_3)_2$), 1.20 (br., 3 H, $CH(CH_3)_2$), 1.10 (br., 12 H, $CH(CH_3)_2$), 1.02 (br., 9 H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (150.8 MHz, C_6D_6): δ = 198.3 (m, PP*C*O), 159.6 (m, N*C*N), 157.0 (m, N*C*N), 148.0 (C_{Ar}), 147.2 (C_{Ar}), 145.7 (C_{Ar}), 144.3 (C_{Ar}), 139.2 (m, C_{Ar}-CHPP), 134.8 (C_{Ar}), 130.7 (C_{Ar}), 129.3 (C_{Ar}), 129.0 (C_{Ar}), 124.7 (C_{Ar}), 124.5 (C_{Ar}), 123.9 (C_{Ar}), 110.8 (m, *C*HPP), 86.6 (d, $^{2}J_{PC}$ = 70.8 Hz, PPCO*C*H), 53.6 (NCH_2), 52.5 (NCH_2), 52.0 (NCH_2), 49.8 (NCH_2), 29.3, 29.1, 28.8, 28.6, 26.6, 25.8, 25.4, 24.7, 24.5, 24.4, 23.6, 22.7. ^{31}P NMR (242.9 MHz, C_6D_6): δ = 525.5 (d, $^{1}J_{PP}$ = 515.9 Hz, C(Ph)-*P*), 376.7 (d, $^{1}J_{PP}$ = 515.9 Hz, C(O)-*P*). UV/Vis (toluene, λ (nm) ε ($M^{-1}cm^{-1}$)): 317.5 (17369), 495.5(19943). HRMS (ESI, m/z) calc. for: $C_{57}H_{78}N_4OP_2C_6H_4$: 973.6037 $[M+H]^+$; found: 973.6038. IR (ATR, cm^{-1}): 3063, 2962, 2927, 2868, 1505, 1461, 1058, 800.

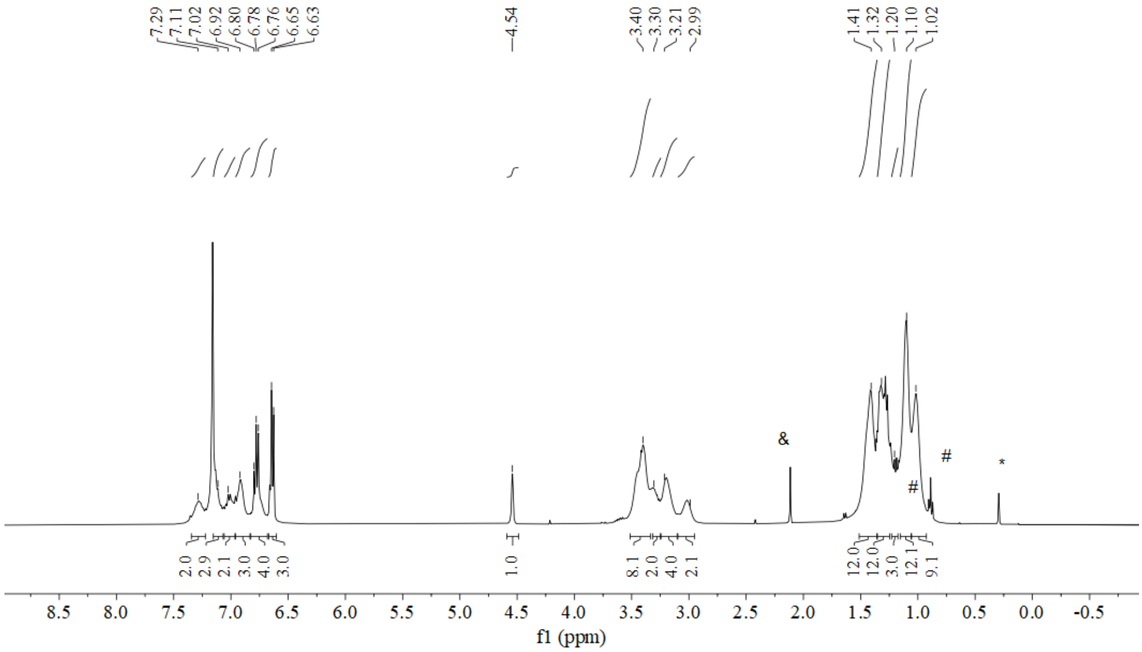


Figure S25. ^{1}H NMR of **3b** in C_6D_6. *Silicone grease, #hexane, &toluene.

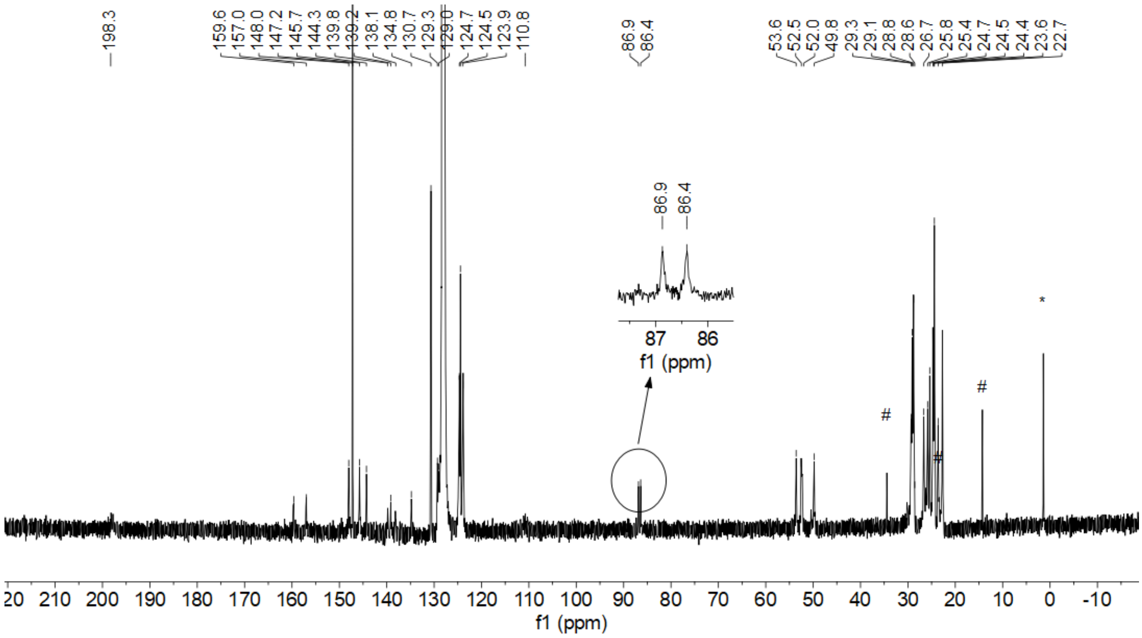


Figure S26. $^{13}C\{^{1}H\}$ NMR of **3b** in C_6D_6. *Silicone grease, #hexane.

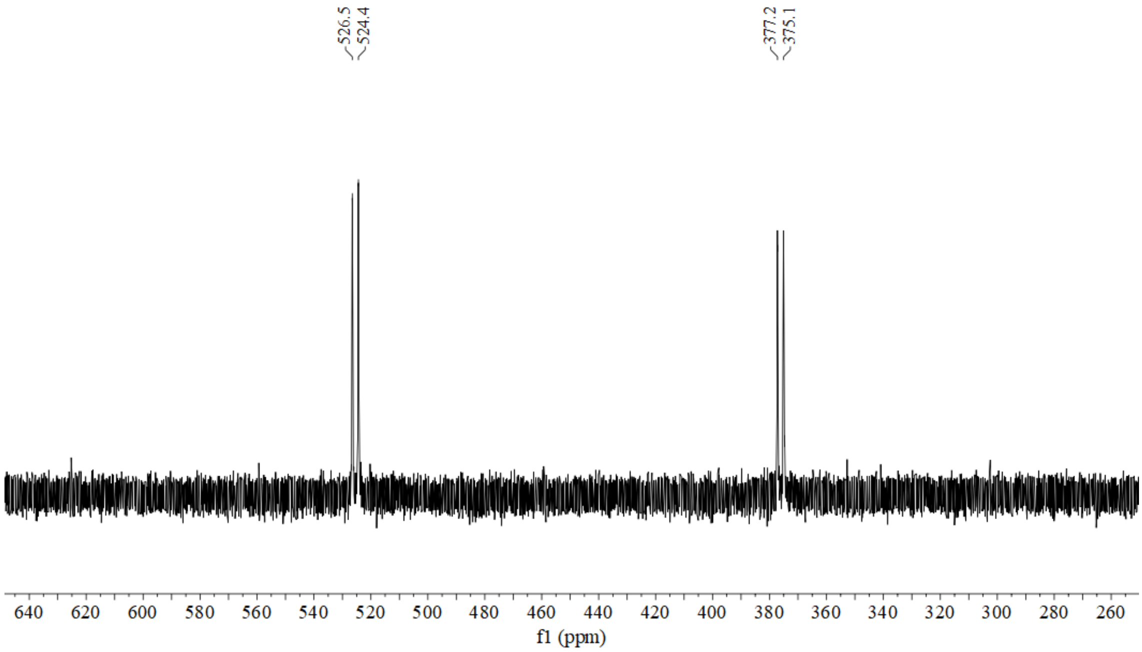


Figure S27. $^{31}P\{^{1}H\}$ NMR of **3b** in C_6D_6.

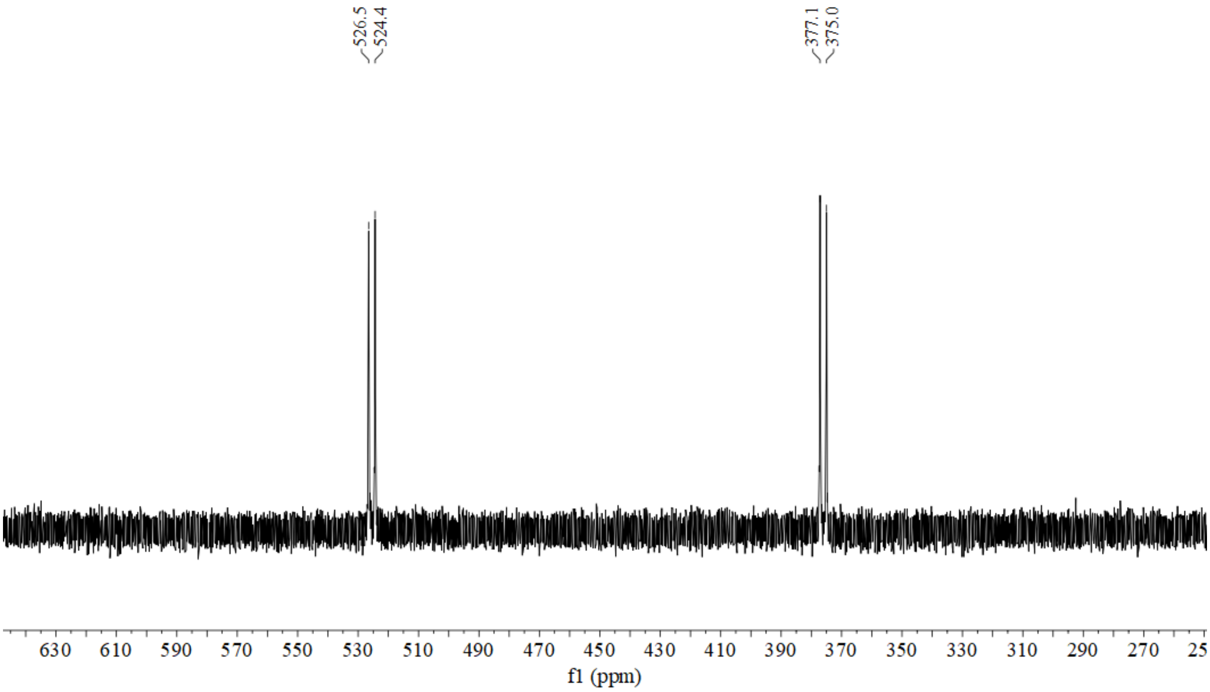


Figure S28. ^{31}P NMR of **3b** in C_6D_6.

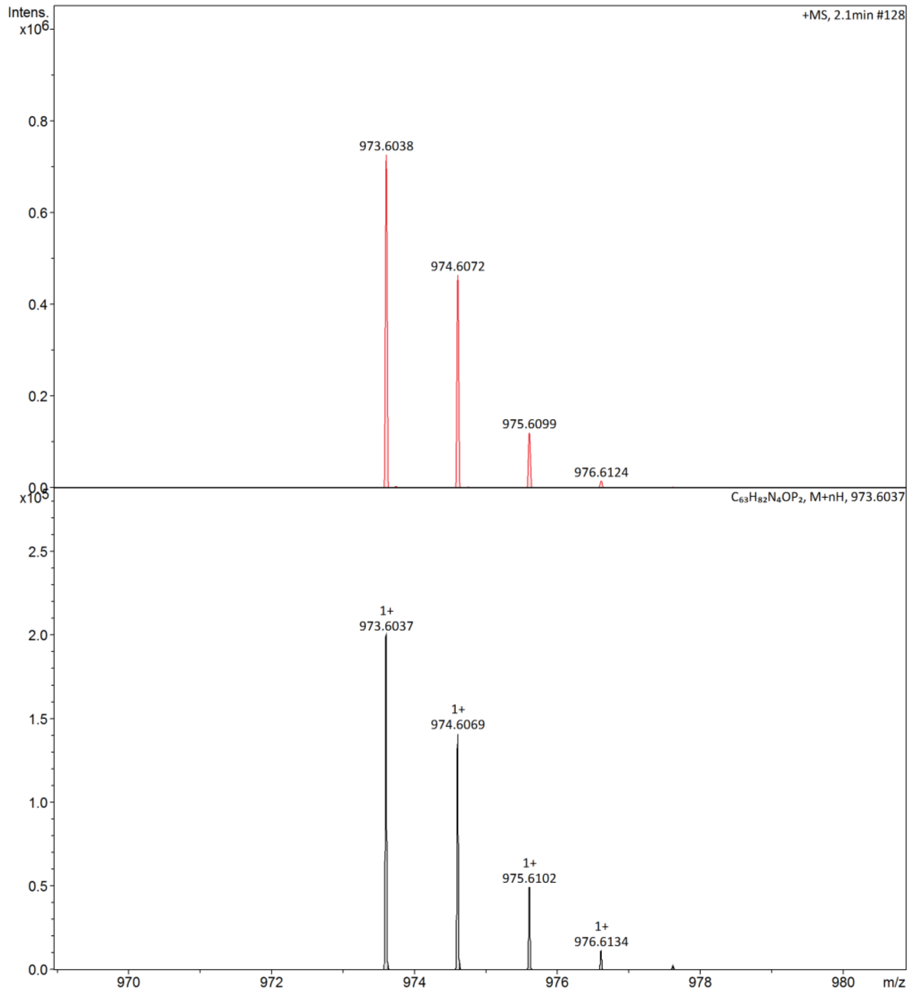


Figure S29. HRMS of **3b**.

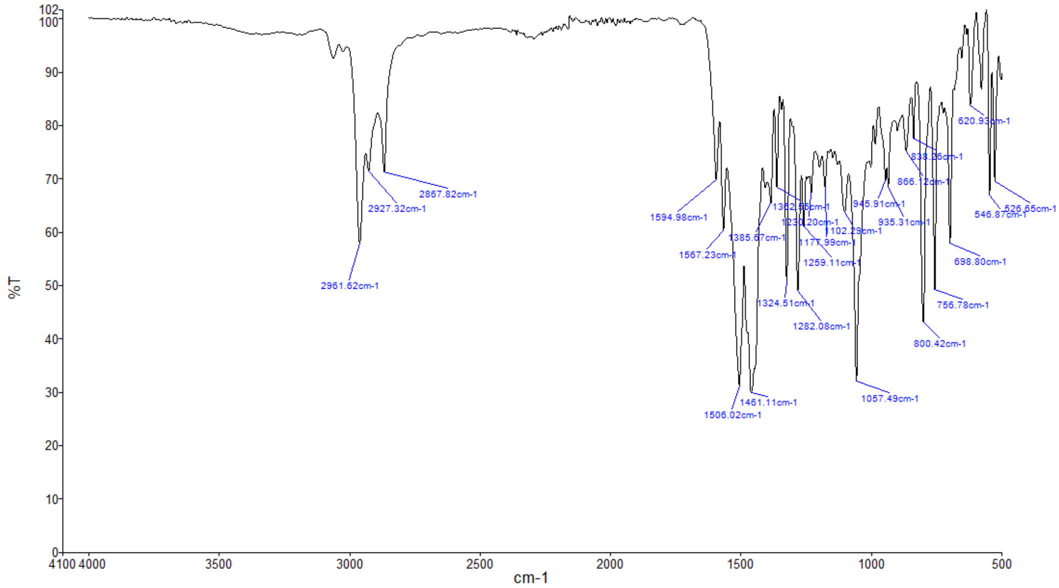
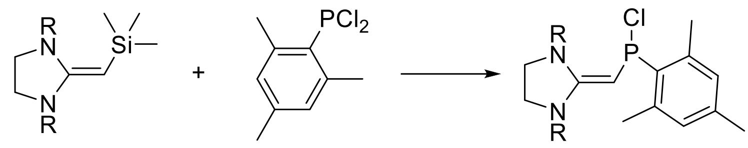


***Figure S30*.** IR spectrum of **3b**.

Synthesis of 4:



L=CHTMS, R= Dipp MesPCl$_2$, **4**, R = Dipp

L=CHTMS (476 mg, 1 mmol) and MesPCl$_2$ (220 mg, 1 mmol) were mixed in tetrahydrofuran (20 mL) at room temperature. After stirring at room temperature overnight, the solvent was removed under reduced pressure. The residue was extracted with hexane (20 mL), washed with a minimum amount of acetonitrile (2 × 1 mL), and dried *in vacuo* to afford **4** (531 mg, 90 %) as a white powder (7 % impurify). M. p. = 132.1 °C. ^{1}H NMR (400.1 MHz, C_6D_6) δ 7.30-7.29 (m, 2 H, $C_{Ar}H$), 7.18 (d, J = 7.4 Hz, 1 H, $C_{Ar}H$), 7.14-7.12 (m, 2 H, $C_{Ar}H$), 7.00 (d, J = 7.1Hz, 1 H, $C_{Ar}H$), 6.53 (s, 2 H, ^{Mes}H), 4.42 (d, $^{2}J_{PH}$ = 3.5 Hz, 1 H, PCH), 3.66 (m, 1 H, CH(CH_3)$_2$), 3.62 (m, 1 H, CH(CH_3)$_2$), 3.33 (m, 4 H, NCH_2), 3.18 (m, 1 H, CH(CH_3)$_2$), 3.01 (m, 1 H, CH(CH_3)$_2$), 2.40 (s, 6 H, $^{m\text{Mes}}CH_3$), 1.89 (s, 3 H, $^{p\text{Mes}}CH_3$), 1.81 (d, J = 6.9 Hz, 3 H, CH(CH_3)$_2$), 1.58 (d, J = 6.7 Hz, 3 H, CH(CH_3)$_2$), 1.28 (d, J = 6.9 Hz, 3 H, CH(CH_3)$_2$), 1.20 (d, J = 6.7 Hz, 3 H, CH(CH_3)$_2$), 1.17-1.14 (m, 6 H, CH(CH_3)$_2$), 1.09 (d, J = 6.9 Hz, CH(CH_3)$_2$), 1.01 (d, J = 6.9 Hz, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (150.8 MHz, C_6D_6): δ = 163.4 (d, $^{2}J_{PC}$ = 36.8 Hz, NCN), 149.0 (d, $^{1}J_{PC}$ = 9.5 Hz, PC_{Ar}), 148.5 (C_{Ar}), 146.6 (C_{Ar}), 138.7 (C_{Ar}), 136.7 (d, $^{1}J_{PC}$ = 38.3 Hz, P-C_{Ar}), 134.4 (C_{Ar}), 130.0 (C_{Ar}), 129.6 (C_{Ar}), 129.3 (C_{Ar}), 125.3 (C_{Ar}), 125.1 (d, $^{1}J_{PC}$ = 12.9 Hz, P-$^{m}C_{Ar}$), 124.6 (C_{Ar}), 66.3 (d, $^{1}J_{PC}$ = 42.6 Hz, PCH), 52.3 (NCH$_2$), 49.9 (NCH$_2$), 29.4, 29.0, 28.8 (d, $^{3}J_{PC}$ = 12.5 Hz, $^{o}C_{Ar}$-CH$_3$), 26.1, 25.7, 25.0, 24.9, 24.7, 24.4, 24.0, 23.4, 22.9, 22.7, 20.9. ^{31}P{^{1}H} NMR (161.9 MHz, C_6D_6): δ = 96.3. HRMS (ESI, m/z) calc. for: $C_{37}H_{50}N_2PCl$: 589.3473 $[M + H]^{+}$; found: 589.3495.

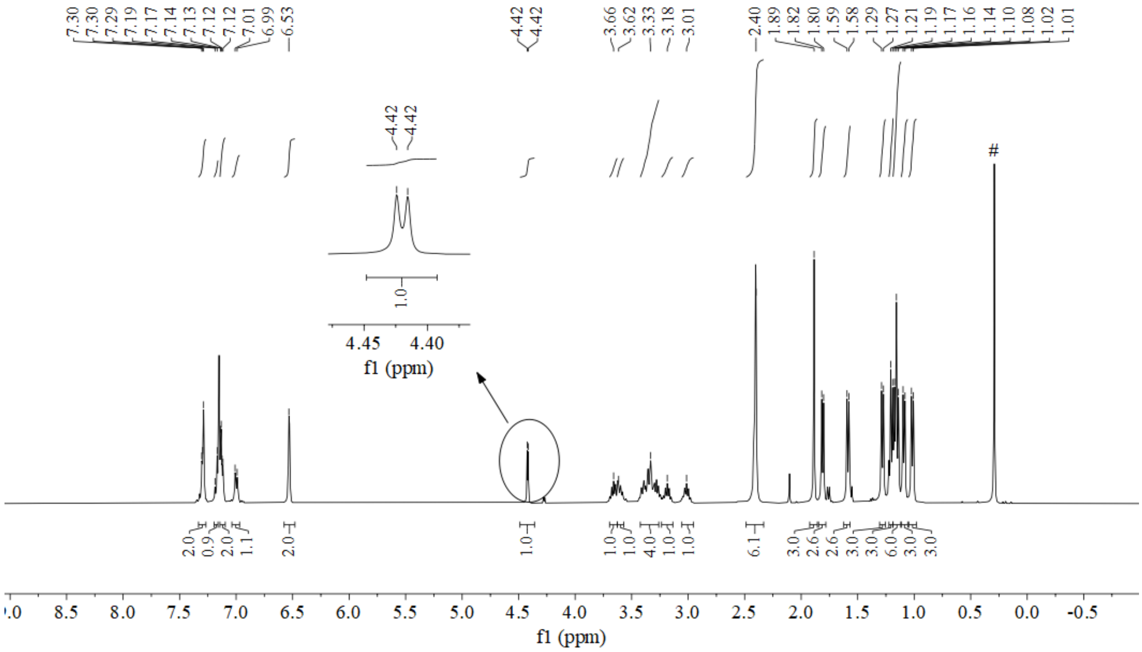


Figure S31. [1]H NMR of **4** in C_6D_6.

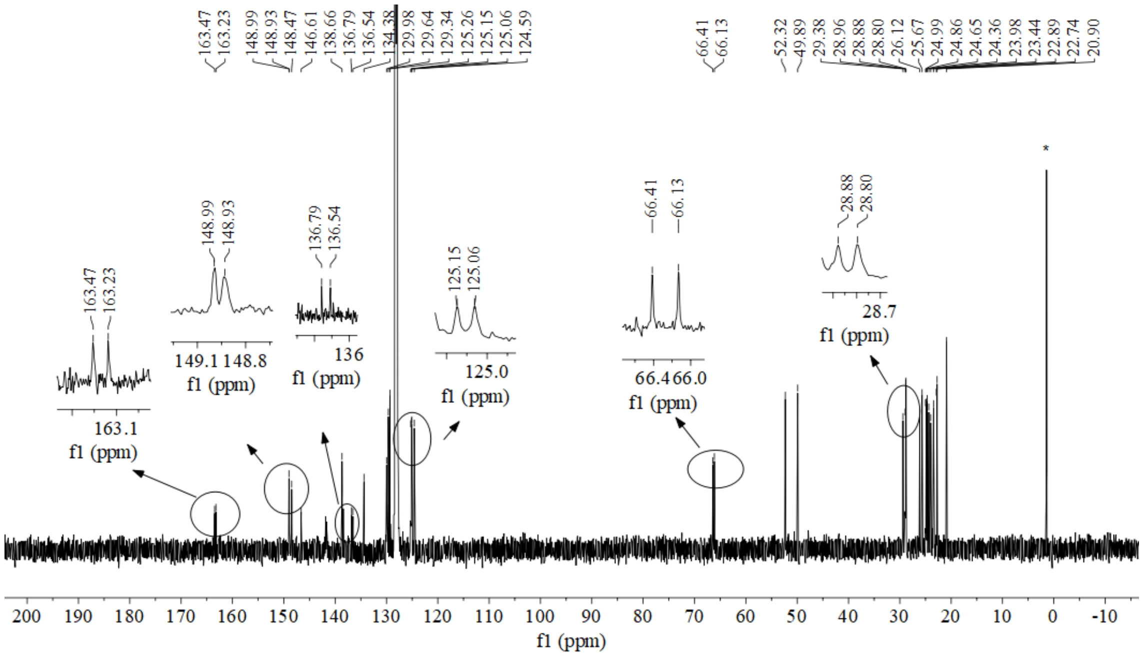


Figure S32 $^{13}C\{^1H\}$ NMR of **4** in C_6D_6.

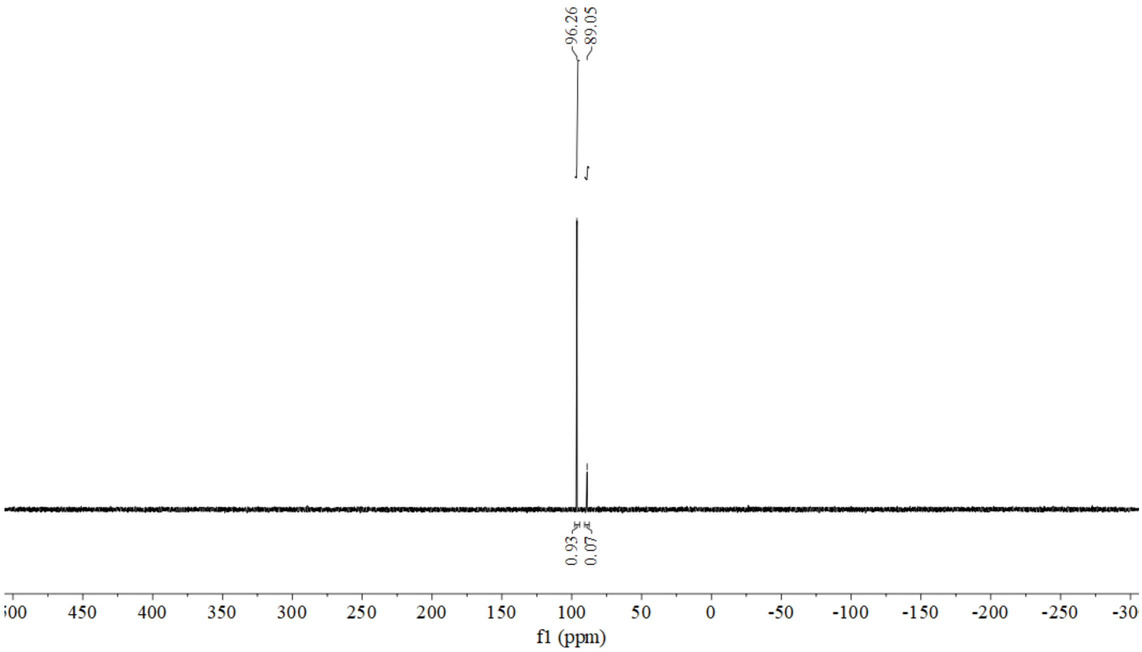


Figure S33. $^{31}P\{^{1}H\}$ NMR of **4** in C_6D_6.

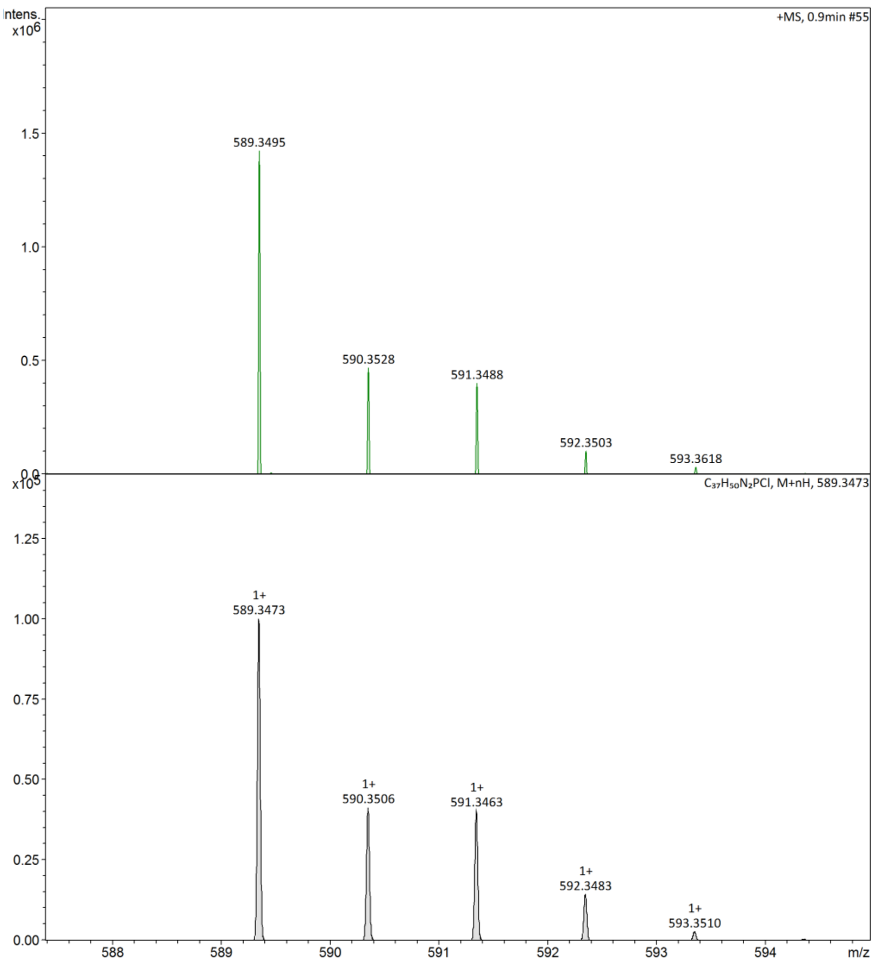
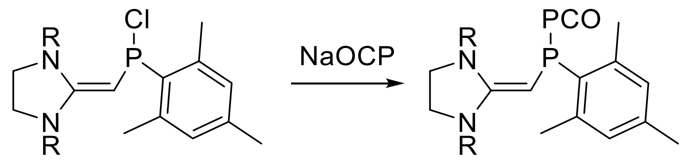


Figure S34. HRMS of **4**.

Synthesis of 5:



4, R = Dipp   **5**, R = Dipp

NaOCP (150 mg, 0.5 mmol) was added in several portions to a toluene (16 mL) solution of **4** (280 mg, 0.5 mmol). After stirred for 1 hour, the remaining precipitate was filtered off and solvent was removed under reduced pressure. The remaining residue was washed with a minimum amount of acetonitrile (1 mL) and dried *in vacuo* to afford **5** (169 mg, 55 %) as a white powder. M. p. = 129.6 °C (Decomposition). ^{1}H NMR (600.2 MHz, C_6D_6): δ = 7.27~7.25 (m, 2 H, $C_{Ar}H$), 7.18 (t, J = 7.7 Hz, 1 H, $C_{Ar}H$), 7.13 (d, J = 7.1 Hz, 1 H, $C_{Ar}H$), 7.06 (d, J = 7.8 Hz, 1 H, $C_{Ar}H$), 7.03 (d, J = 7.1 Hz, 1 H, $C_{Ar}H$), 6.54 (s, 2 H, $^{Mes}C_{Ar}H$), 3.78 (m, 1 H, PC*H*), 3.61 (m, 1 H, C*H*(CH_3)$_2$), 3.57 (m, 1 H, C*H*(CH_3)$_2$), 3.37 (m, 2 H, NCH_2), 3.29 (m, 2 H, NCH_2), 3.22 (m, 1 H, C*H*(CH_3)$_2$), 3.16 (m, 1 H, C*H*(CH_3)$_2$), 2.23 (s, 6 H, $C_{Ar}CH_3$), 1.93(s, 3 H, $C_{Ar}CH_3$), 1.73 (d, J = 6.9 Hz,3 H, CH(CH_3)$_2$), 1.54 (d, J = 6.7 Hz, 3 H, CH(CH_3)$_2$), 1.28 (d, J = 6.9 Hz, 3 H, CH(CH_3)$_2$), 1.20 (d, J = 6.9 Hz, 3 H, CH(CH_3)$_2$), 1.17 (d, J = 6.9 Hz, 3 H, CH(CH_3)$_2$), 1.14 (d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$), 1.11 (d, J = 6.9 Hz, 3 H, CH(CH_3)$_2$), 0.93 (d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (150.8 MHz, C_6D_6): δ = 201.1 (dd, $^{1}J_{PC}$ = 113.8Hz, $^{2}J_{PC}$ = 20.7Hz, *C*(O)), 160.4 (dd, $^{2}J_{PC}$ = 40.4 Hz, $^{3}J_{PC}$ = 3.3Hz, N*C*N), 149.1 (C_{Ar}), 148.9 (C_{Ar}), 148.7 (d, J_{PH} = 3.5 Hz, P-C_{Ar}), 146.9 (C_{Ar}), 142.0 (C_{Ar}), 141.9 (C_{Ar}), 139.2 (d, J_{PH} = 3.6 Hz, P-C_{Ar}), 137.5 (dd, $^{1}J_{PH}$ = 32.6 Hz, $^{2}J_{PH}$ = 11.5 Hz, P-C_{Ar}), 135.3 (C_{Ar}), 129.8 (C_{Ar}), 129.4 (C_{Ar}), 128.9 (C_{Ar}), 128.4 (C_{Ar}), 125.1 (C_{Ar}), 125.0 (C_{Ar}), 124.4 (C_{Ar}), 61.1 (dd, $^{1}J_{PC}$ = 25.7 Hz, $^{2}J_{PC}$ = 13.6 Hz, PP-*C*H=), 52.3 (NCH_2), 49.9 (NCH_2), 29.5, 28.8, 28.6, 25.8, 25.7, 25.1, 24.9, 24.7, 24.2, 23.7, 23.6, 23.6, 23.5, 22.7. ^{31}P{^{1}H} NMR (242.9 MHz, C_6D_6): δ = -41.0 (-*P*PCO, $^{1}J_{PP}$ = 170.9 Hz), -248.6 (-P*P*CO, $^{1}J_{PP}$ = 170.9 Hz). HRMS (ESI, m/z) calc. for: $(C_{38}H_{50}N_2P_2O)_2$: 1225.6870 [M + H]$^{+}$; found: 1225.6834. IR (ATR, cm^{-1}): 2964, 1929 (CO), 1535, 1455, 873, 806, 703.

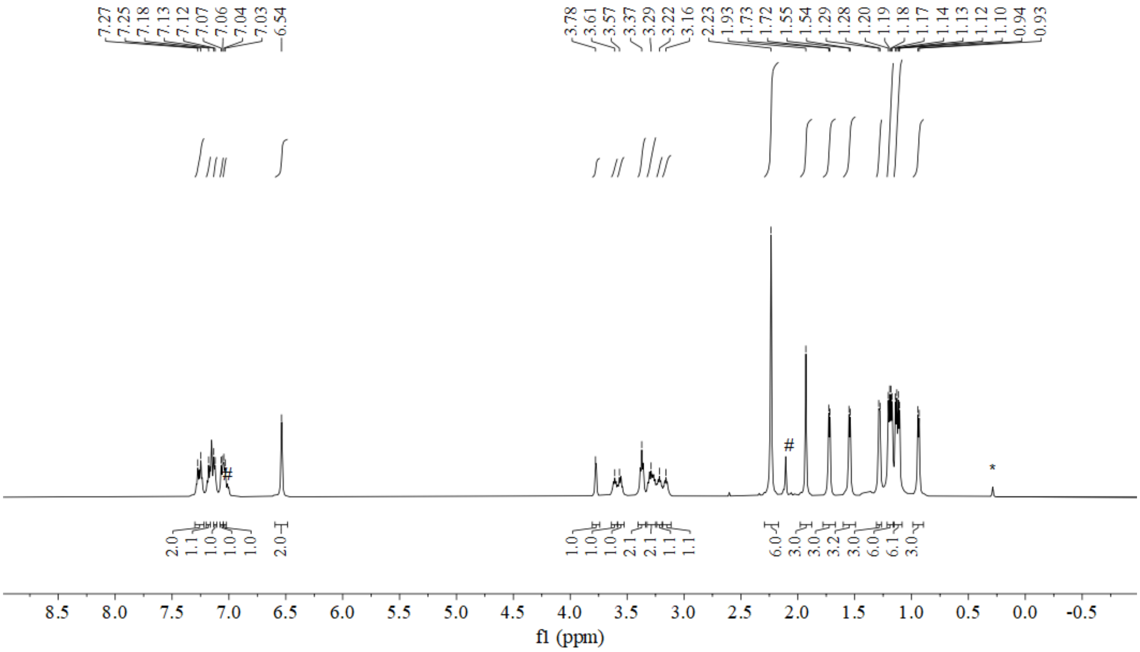


Figure S35. ^1H NMR of **5** in C_6D_6. #Toluene, *silicon grease.

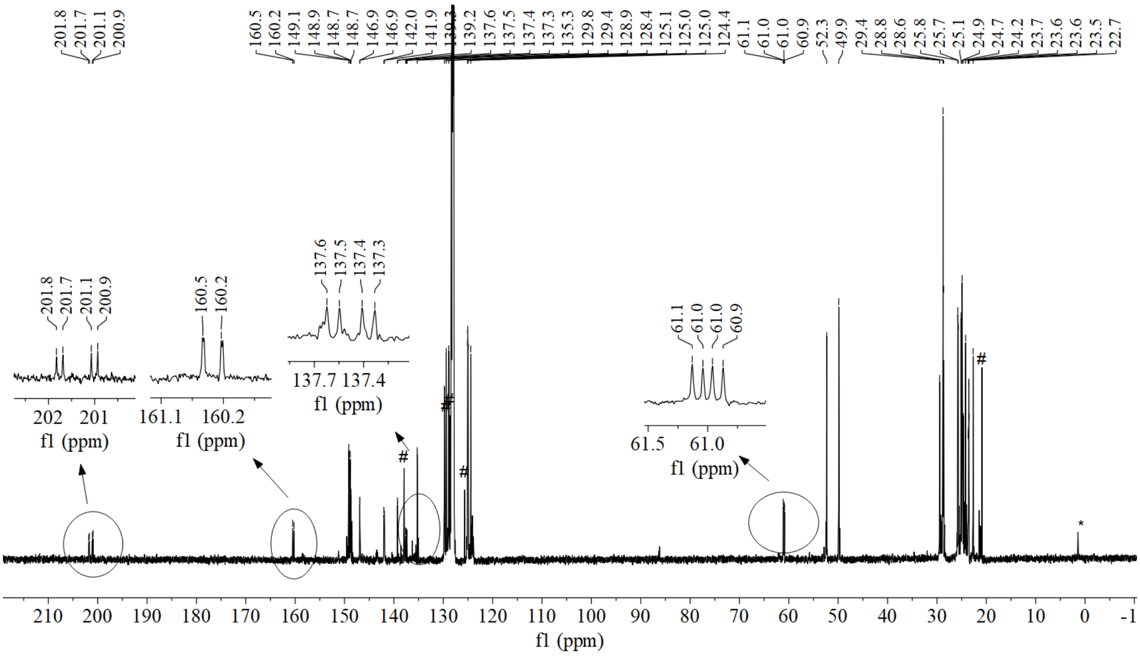


Figure S36. $^{13}C\{^1H\}$ NMR of **5** in C_6D_6. #Toluene, *silicon grease.

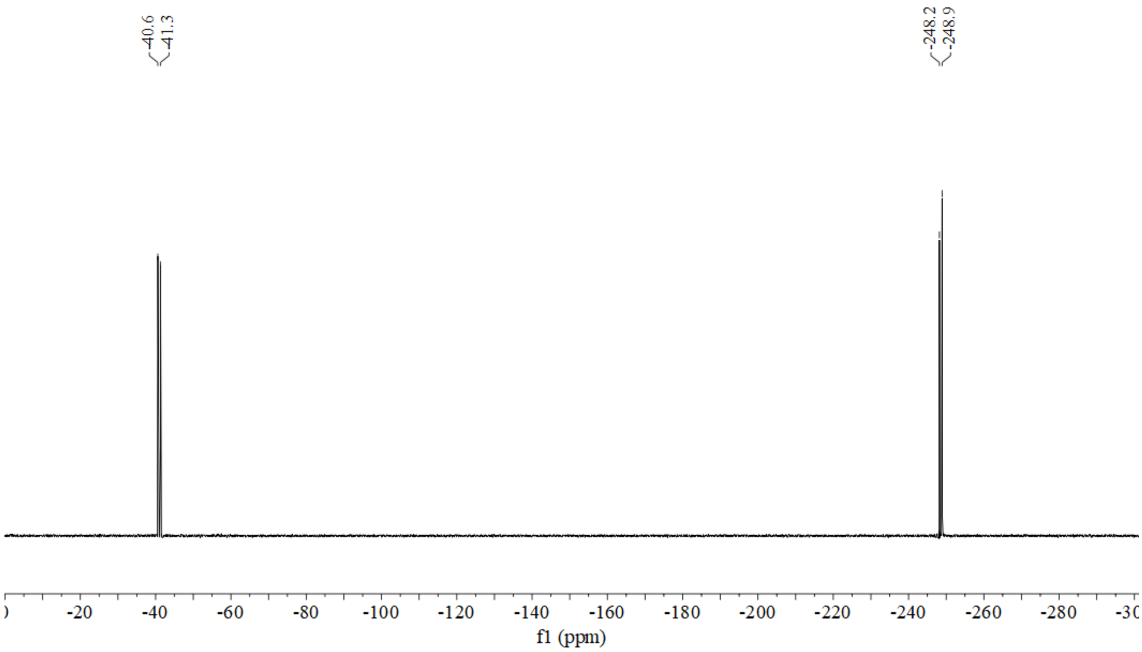


Figure S37. ${}^{31}P\{{}^{1}H\}$ NMR of **5** in C_6D_6.

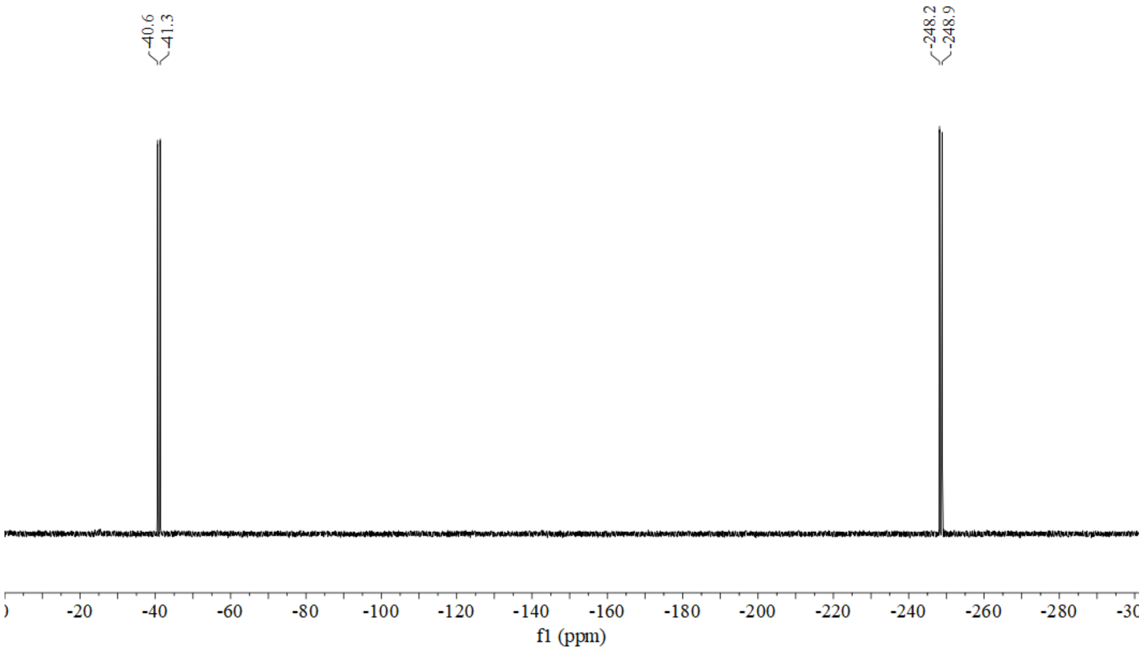


Figure S38 ${}^{31}P$ NMR of **5** in C_6D_6.

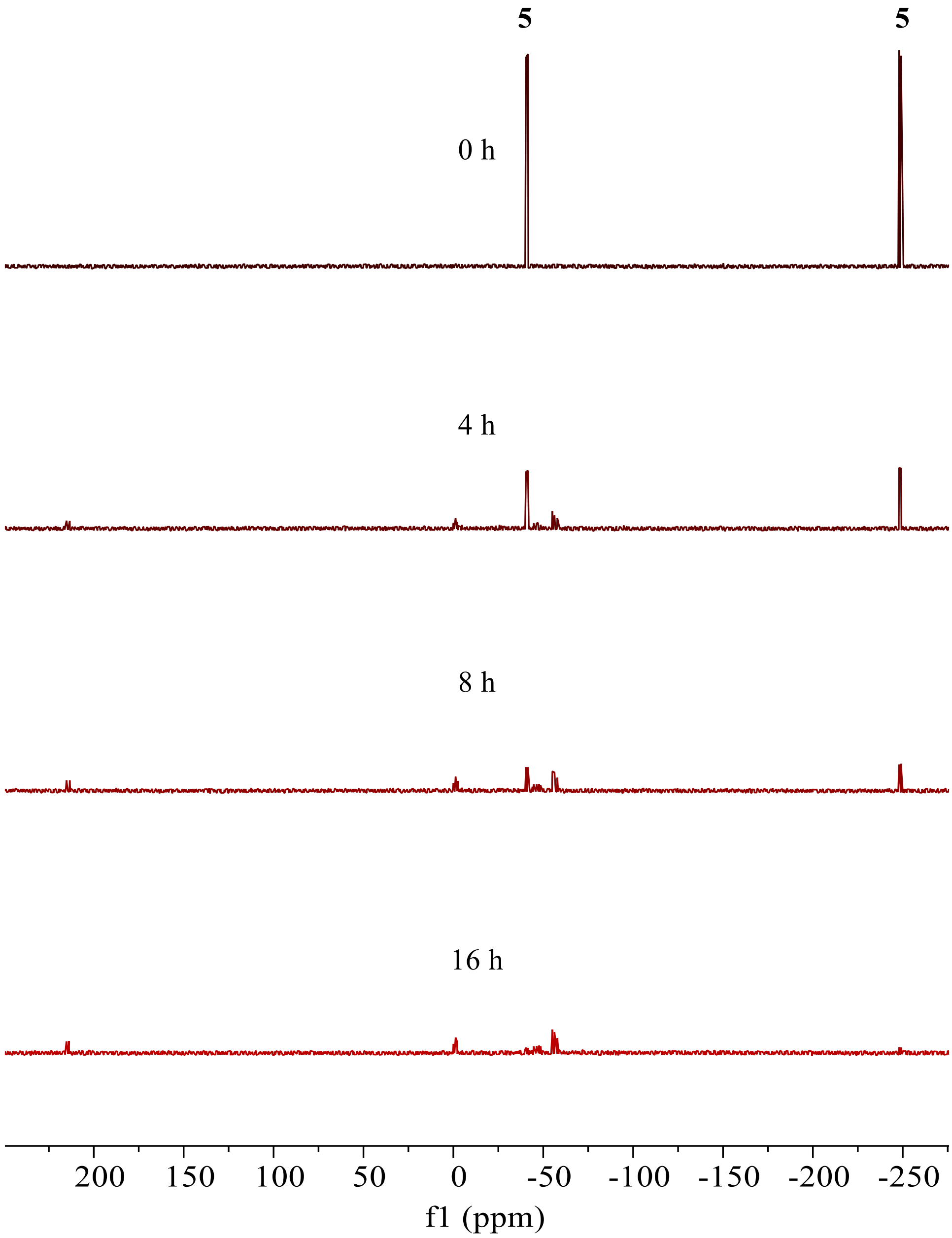


Figure S39. $^{31}P\{^{1}H\}$ NMR spectra of **5** over a period of 16 h in C_6D_6 at room temperature.

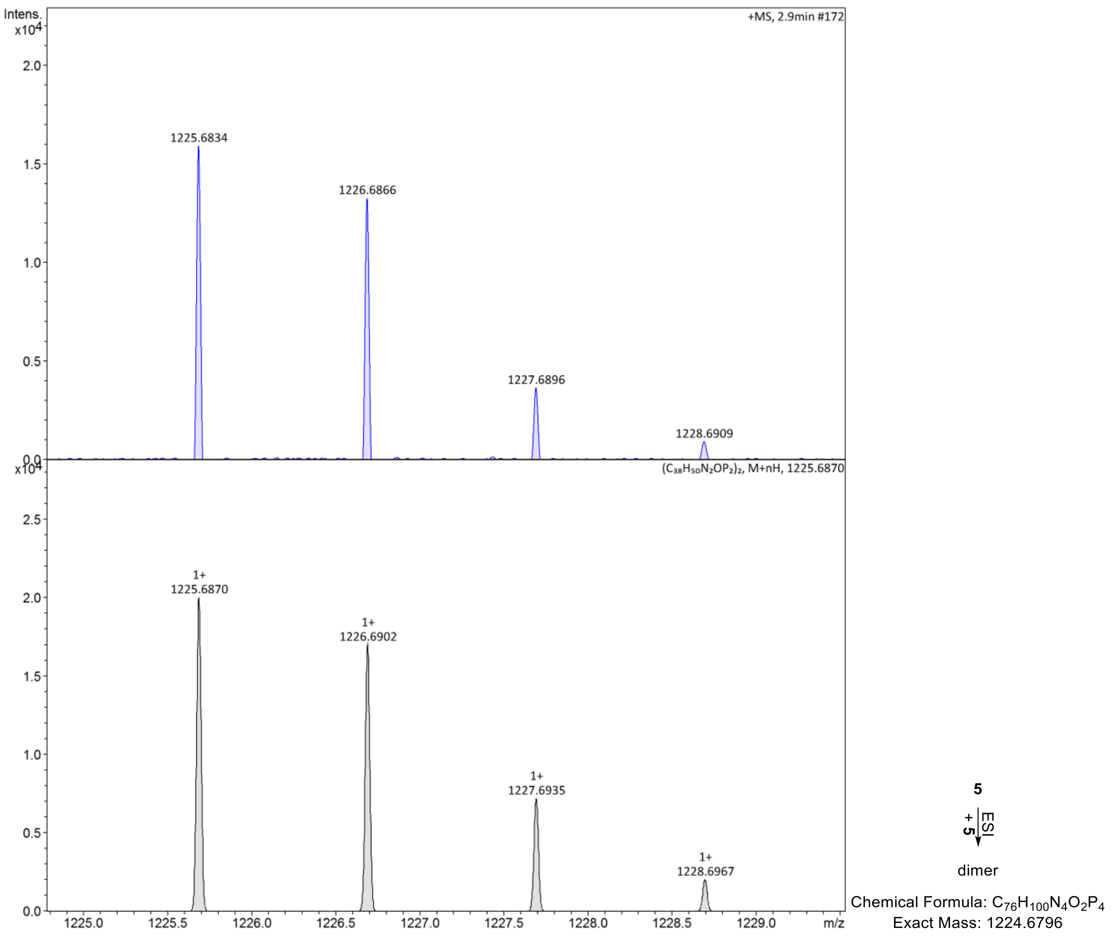


Figure S40. HRMS of **5**.

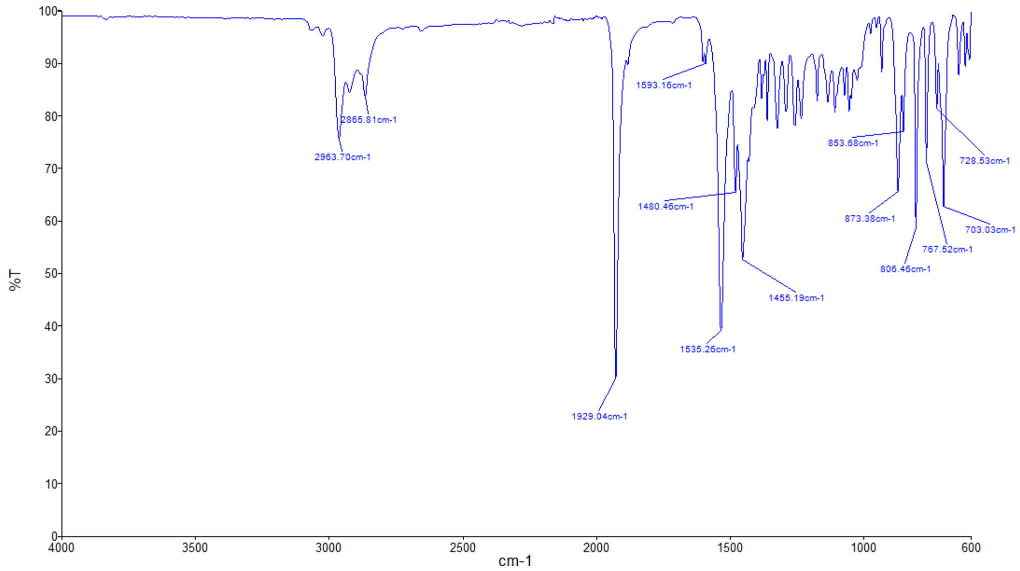
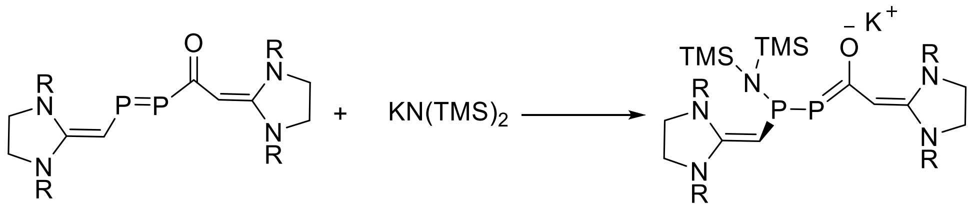


Figure S41. IR spectrum of **5**.

Synthesis of 6a:



3a, R = Dipp **6a**, R = Dipp

Potassium bis(trimethylsilyl)amide (60 mg, 0.3 mmol) in tetrahydrofuran (4 mL) was added to a stirred solution of **3a** (300 mg, 0.3 mmol) in tetrahydrofuran (12 mL) at room temperature. After stirring for 0.5 hour, the solvent was removed under reduced pressure. Then, the residue was washed with hexane (1 mL) and dried *in vacuo* to afford **6a** (311 mg, yield = 95 %) as a yellow powder. Light orange crystals of **6a** were obtained from a saturated fluorobenzene solution layered hexane on top at -30 °C for 6 days. M. p. = 143.5 °C (Decomposition). ^{1}H NMR (600.2 MHz, C_6D_6): δ = 7.14 (t, J = 6.6 Hz, 2 H, $C_{Ar}H$), 7.08 (t, J = 8.1 Hz, 2 H, $C_{Ar}H$), 7.03 (t, J = 6.8 Hz, 2 H, $C_{Ar}H$), 7.00 (t, J = 7.0 Hz, 1 H, $C_{Ar}H$), 6.98~6.90 (m, 4 H, $C_{Ar}H$), 6.86 (d, J = 7.5 Hz, 1 H, $C_{Ar}H$), 4.86 (s, 1 H, =C*H*C(O)), 3.87 (m, 2 H, NCH_2), 3.72 (m, 2 H, NCH_2), 3.58 (m, 3 H, NCH_2 & $CH(CH_3)_2$), 3.45 (m, 2 H, NCH_2), 3.34 (m, 1 H, $CH(CH_3)_2$), 3.27 (m, 3 H, NCH_2 & $CH(CH_3)_2$), 3.18 (m, 1 H, $CH(CH_3)_2$), 3.13 (m, 1 H, $CH(CH_3)_2$), 3.10 (m, 1 H, $CH(CH_3)_2$), 2.88 (t, $^{2}J_{PH} \approx {}^{3}J_{PH}$ = 8.9 Hz, 1 H, =C*H*PP), 1.72 (d, J = 6.6 Hz, 3 H, $CH(CH_3)_2$), 1.54 (d, J = 6.6 Hz, 6 H, $CH(CH_3)_2$), 1.48 (d, J = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.43 (d, J = 6.6 Hz, 3 H, $CH(CH_3)_2$), 1.35 (d, J = 6.6 Hz, 6 H, $CH(CH_3)_2$), 1.30 (d, J = 7.2 Hz, 3 H, $CH(CH_3)_2$), 1.29 (d, J = 7.2 Hz, 3 H, $CH(CH_3)_2$), 1.25 (d, J = 6.9 Hz, 3 H, $CH(CH_3)_2$), 1.21 (m, 9 H, $CH(CH_3)_2$), 1.14~1.10 (m, 9 H, $CH(CH_3)_2$), 0.42 (br. s, 9 H, $-Si(CH_3)_2$)), 0.28 (br. s, 9 H, -$Si(CH_3)_2$)). $^{13}C\{^{1}H\}$ NMR (150.8 MHz, C_6D_6): δ = 217.6 (dd, $^{1}J_{PC}$ = 81.9 Hz, $^{2}J_{PC}$ = 7.5 Hz, *C*O), 152.2 (C_{Ar}), 150.8 (d, $^{2}J_{PC}$ = 25.0 Hz, N*C*NCHC(O)P), 150.4 (C_{Ar}), 150.3 (C_{Ar}), 150.0 (C_{Ar}), 149.8 (dd, $^{3}J_{PC}$ = 30.2 Hz, $^{2}J_{PC}$ = 7.4 Hz, N*C*NCHPP), 148.7 (C_{Ar}), 148.7 (C_{Ar}), 148.3 (C_{Ar}), 146.7 (C_{Ar}), 144.6 (C_{Ar}), 144.4 (C_{Ar}), 136.7 (C_{Ar}), 136.0 (C_{Ar}), 128.9 (C_{Ar}), 128.7 (C_{Ar}), 128.4 (C_{Ar}), 125.5 (C_{Ar}), 125.3 (C_{Ar}), 124.7 (C_{Ar}), 124.6 (C_{Ar}), 124.5 (C_{Ar}), 124.0 (C_{Ar}), 123.6 (C_{Ar}), 123.0 (C_{Ar}), 122.9 (C_{Ar}), 87.4 (dd, $^{1}J_{PC}$ = 74.8 Hz, $^{2}J_{PC}$ = 4.5 Hz, *C*HPP), 74.6 (d, $^{3}J_{PC}$ = 28.2 Hz, *C*HC(O)PP), 53.2 (NCH_2), 53.1 (NCH_2), 49.6 (NCH_2), 49.2 (NCH_2), 29.3, 28.8, 28.7, 28.6, 28.3, 28.2, 26.5, 25.9, 25.9, 25.6, 25.6, 25.5, 25.4, 25.0, 24.8, 24.8, 24.8, 24.7, 24.5, 24.3, 23.8, 23.7, 6.5 (Si(CH_3)$_3$), 4.9 (Si(CH_3)$_3$). ^{31}P{^{1}H} NMR (242.9 MHz, C_6D_6): δ = 61.6 (d, $^1J_{PP}$ = 276.8 Hz, (N(TMS)$_2$)*P*P), 29.7 (d, $^1J_{PP}$ = 276.8 Hz, (N(TMS)$_2$)P*P*). UV/Vis (toluene, λ (nm) ε ($M^{-1}cm^{-1}$)): 314.5 (35226), 428.5 (41434). HRMS (ESI, m/z) calc. for: $C_{63}H_{96}N_5OP_2Si_2^-$: 1056.6634 [M]$^-$; found: not detected. IR (ATR, cm^{-1}): 2959, 2867, 1568, 1505, 1448, 869, 805.

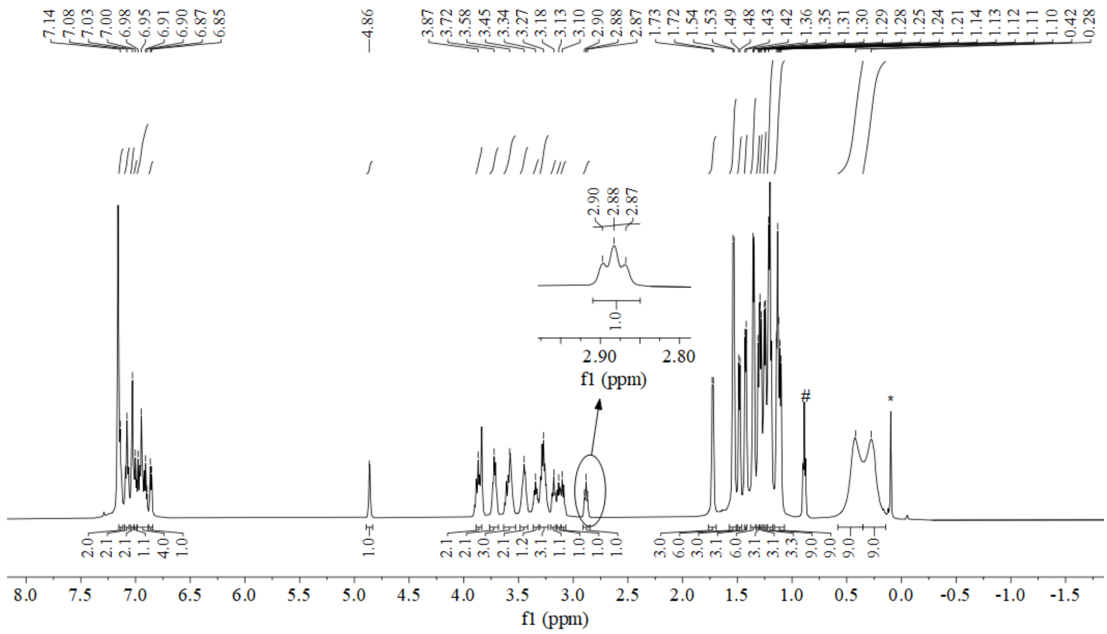


Figure S42. ^{1}H NMR of **6a** in C_6D_6. $^{\#}$Hexane, *silicone grease.

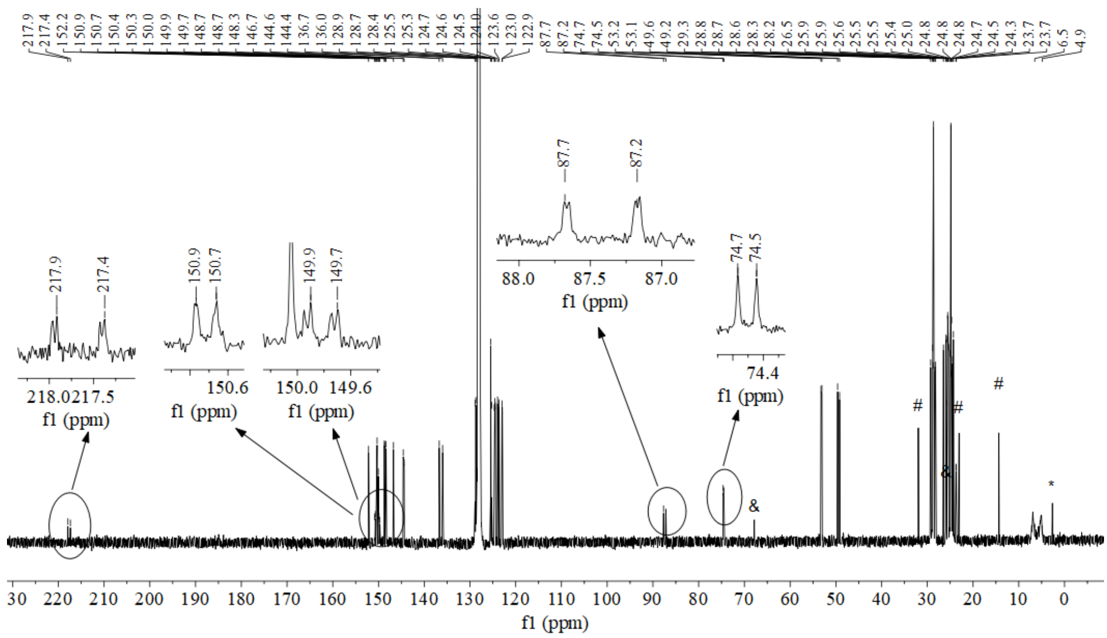


Figure S43. ^{13}C{^{1}H} NMR of **6a** in C_6D_6. $^{\#}$Hexane, *silicone grease, $^{\&}$tetrahydrofuran.

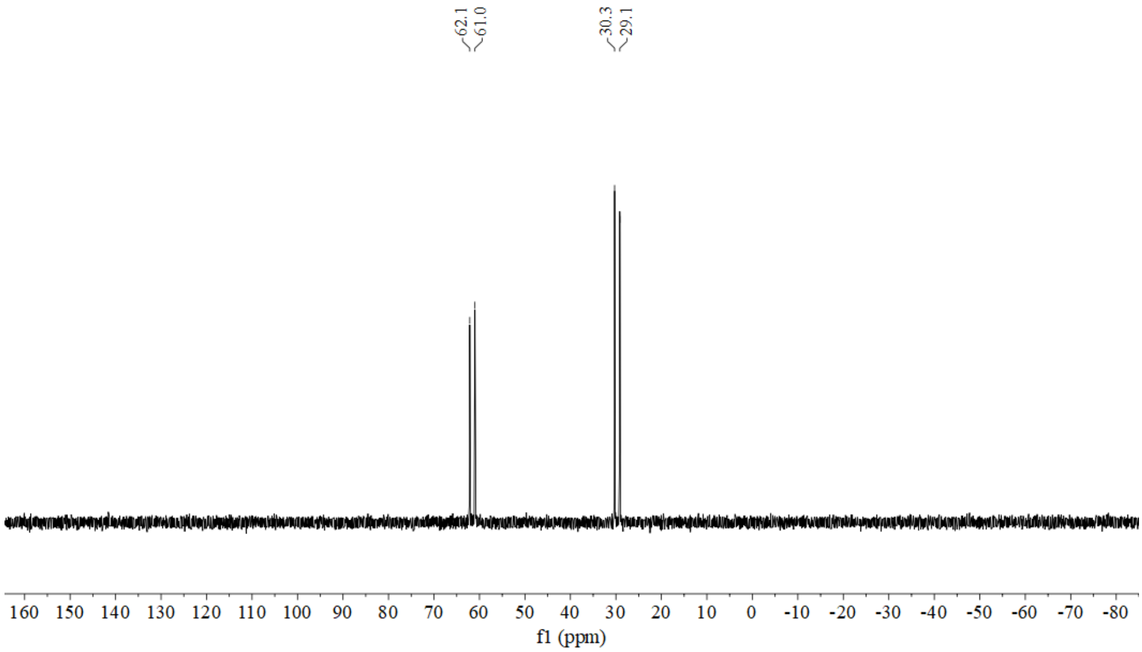


Figure S44. $^{31}P\{^{1}H\}$ NMR of **6a** in C_6D_6.

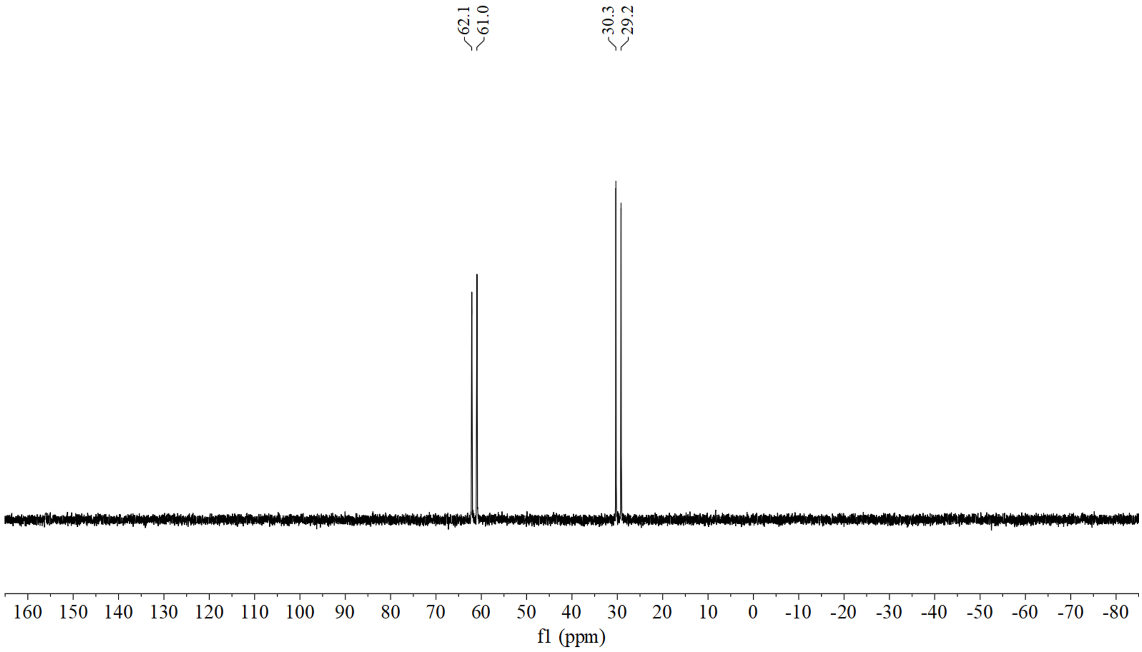


Figure S45. ^{31}P NMR of **6a** in C_6D_6.

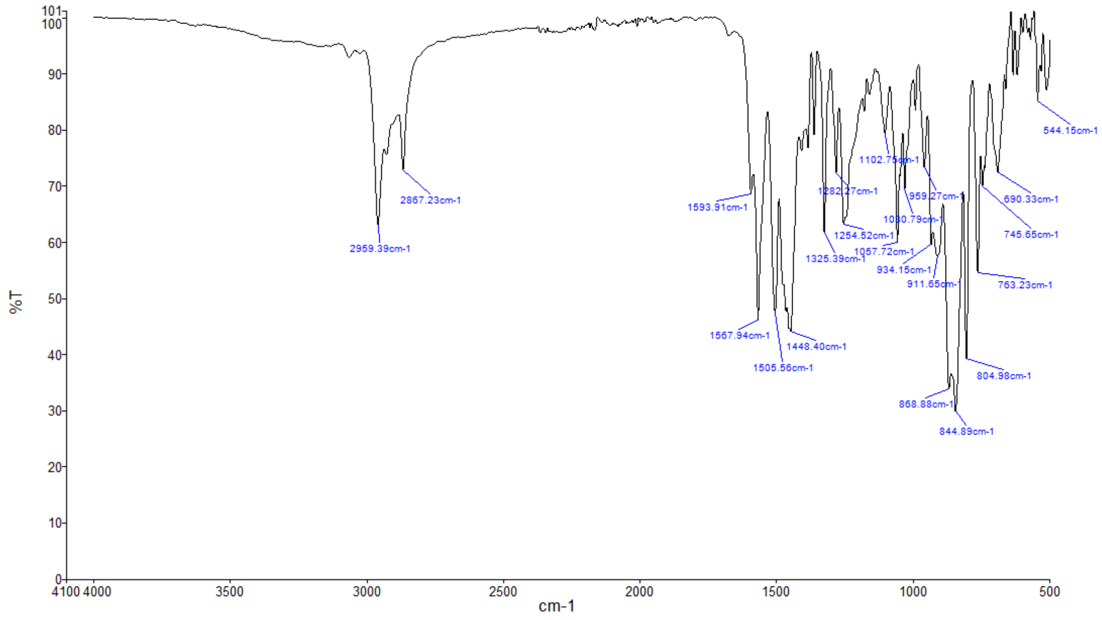
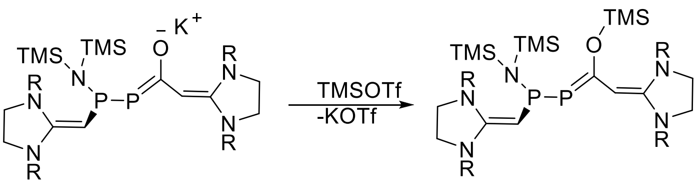


Figure S46. IR spectrum of **6a**.

Synthesis of 7a:



Trimethylsilyl trifluoromethanesulfonate (66 mg, 0.3 mmol) in tetrahydrofuran (4 mL) was added to a stirred solution of **6a** (300 mg, 0.3 mmol) in tetrahydrofuran (20 mL) at room temperature. After stirring for 10 minutes, the solvent was removed under reduced pressure and the residue was extracted with hexane. Then, the solvent was removed under reduced pressure, the residue was washed with acetonitrile (1 mL) and dried *in vacuo* to afford **7a** (121 mg, yield = 36 %) as a yellow powder. M. p. = 183.7 °C (Decomposition). ^{1}H NMR (600.2 MHz, C_6D_6): δ = 7.33 (t, J = 7.7 Hz, 1 H, $C_{Ar}H$), 7.28 (d, J = 7.7 Hz, 1 H, $C_{Ar}H$), 7.24~7.21 (m, 3 H, $C_{Ar}H$), 7.18 (d, J = 7.5 Hz, 2 H, $C_{Ar}H$), 7.14 (d, J = 6.8 Hz, 1 H, $C_{Ar}H$), 7.12 (t, J = 8.0 Hz, 2 H, $C_{Ar}H$), 7.04 (d, J = 7.7 Hz, 1 H, $C_{Ar}H$), 7.02 (d, J = 7.7 Hz, 1 H, $C_{Ar}H$), 4.02 (d, $^2J_{PH}$ = 18.2 Hz, =C*H*PP), 3.82 (d, $^3J_{PH}$ = 9.4 Hz, =C*H*C(OSi(CH_3)$_3$)P), 3.64 (m, 1 H, C*H*(CH_3)$_3$), 3.57 (m, 1 H, C*H*(CH_3)$_3$), 3.52 (m, 1 H, C*H*(CH_3)$_3$), 3.49 (m, 2 H, C*H*(CH_3)$_3$), 3.42 (m, 4 H, NCH_2), 3.35~3.23 (m, 1 H, C*H*(CH_3)$_3$ & 4 H, NCH_2), 3.17 (m, 1 H, C*H*(CH_3)$_3$), 3.05 (m, 1 H, CH(CH$_3$)$_3$), 1.64 (d, J = 6.9 Hz, 3 H, CH(CH_3)$_3$), 1.52 (d, J = 6.9 Hz, 3 H, CH(CH_3)$_3$), 1.49 (d, J = 6.7 Hz, 3 H, CH(CH_3)$_3$), 1.46 (m, 6 H, CH(CH_3)$_3$), 1.37 (m, 6 H, CH(CH_3)$_3$), 1.31 (m, 12 H, CH(CH_3)$_3$), 1.26 (d, J = 3.5 Hz, 3 H, CH(CH_3)$_3$), 1.24 (d, J = 3.8 Hz, 3 H, CH(CH_3)$_3$), 1.18 (m, 6 H, CH(CH_3)$_3$), 1.16 (d, J = 6.9 Hz, 3 H, CH(CH_3)$_3$), 0.24 (s, 9 H, NSi(CH_3)$_3$), 0.10 (s, 9 H, NSi(CH_3)$_3$), 0.01 (s, 9 H, OSi(CH_3)$_3$). ^{13}C{^{1}H} NMR (150.8 MHz, C_6D_6): δ = 193.8 (dd, $^1J_{PC}$ = 85.4 Hz, $^2J_{PC}$ = 13.3 Hz, CO), 154.3 (d, $^3J_{PC}$ = 4.0 Hz, NCN=CH-CO-), 153.5 (dd, $^2J_{PC}$ = 35.6 Hz, $^3J_{PC}$ = 12.7 Hz, NCN-PP), 149.3 (C_{Ar}), 148.9 (C_{Ar}), 148.8 (C_{Ar}), 148.8 (C_{Ar}), 148.7 (C_{Ar}), 148.6 (C_{Ar}), 147.1 (C_{Ar}), 146.0 (C_{Ar}), 146.0 (C_{Ar}), 145.4 (C_{Ar}), 138.7 (C_{Ar}), 138.4 (C_{Ar}), 138.4 (C_{Ar}), 137.5 (C_{Ar}), 136.8 (C_{Ar}), 129.0 (C_{Ar}), 128.4 (C_{Ar}), 125.8 (C_{Ar}), 125.5 (C_{Ar}), 124.8 (C_{Ar}), 124.6 (C_{Ar}), 124.3 (C_{Ar}), 124.1 (C_{Ar}), 123.9 (C_{Ar}), 86.2 (d, $^2J_{PC}$ = 21.0 Hz, =CHC(OTMS)P), 71.1 (dd, $^1J_{PC}$ = 37.4 Hz, $^2J_{PC}$ = 24.1 Hz, =CHPP), 54.9 (NCH$_2$), 52.8 (NCH$_2$), 50.2 (NCH$_2$), 49.5 (NCH$_2$), 29.0, 28.9, 28.8, 28.7, 28.7, 28.6, 28.1, 27.0, 26.5, 26.2, 26.1, 26.0, 25.9, 25.4, 25.2, 24.8, 24.8, 24.4, 24.4, 24.3, 24.0, 23.9, 23.6, 23.5, 7.5 (br., PNSiCH$_3$)$_3$), 5.2 (d, $^3J_{PC}$ = 13.6 Hz, PNSi(CH$_3$)$_3$), 2.45 (COSi(CH$_3$)). ^{31}P{^{1}H} NMR (242.9 MHz, C_6D_6): δ = 140.8 (d, $^1J_{PP}$ = 245.5 Hz, CH-P[N(TMS)$_2$]-P-), 29.9 (d, $^1J_{PP}$ = 245.5 Hz, CH-P[N(TMS)$_2$]-P-). ^{31}P NMR (242.9 MHz, C_6D_6): δ = 140.8 (dq, $^1J_{PP}$ = 245.5 Hz, CH-P[N(TMS)$_2$]-P-), 29.9 (d, $^1J_{PP}$ = 245.5 Hz, CH-P[N(TMS)$_2$]-P-). UV/Vis (toluene, λ (nm) ε ($M^{-1}cm^{-1}$)): 325.5 (37785), 425.0 (5080). HRMS (ESI, m/z) calc. for: $C_{66}H_{105}N_5OP_2Si_3$: 1129.7102 [M]$^+$; found: not detected. IR (ATR, cm^{-1}): 2959, 2866, 1548, 877, 863, 843, 801.

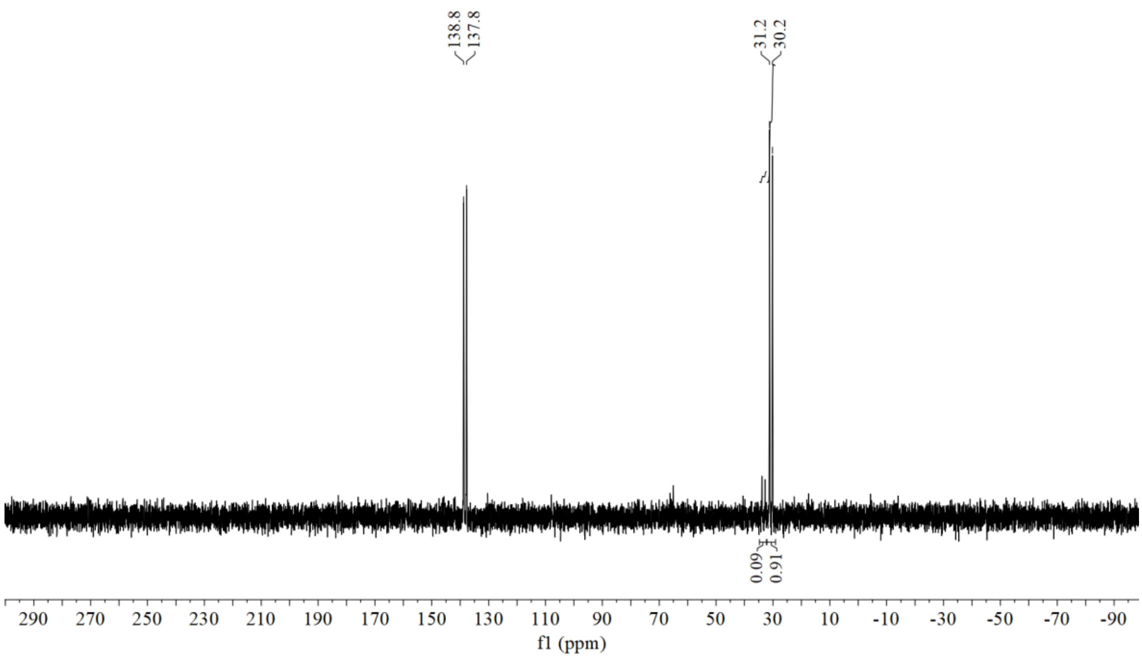


Figure S47. $^{31}P\{^{1}H\}$ NMR of the reaction mixture for the preparation of **7a** in tetrahydrofuran, the NMR spectroscopic yield is about 91%.

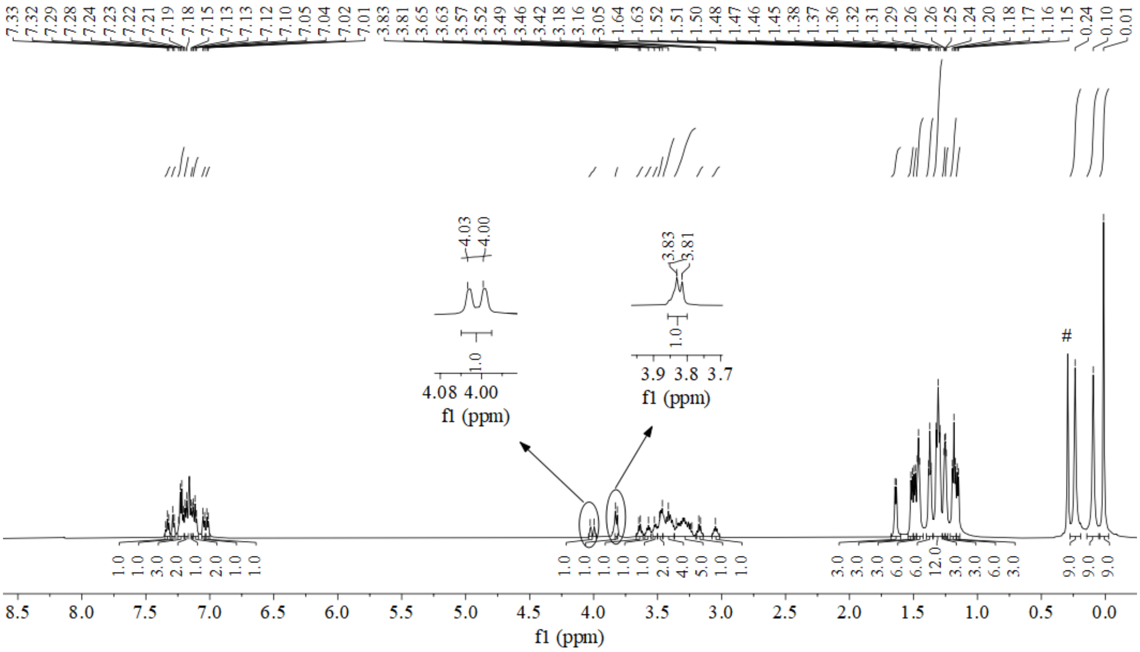


Figure S48. ^{1}H NMR of **7a** in C_6D_6.

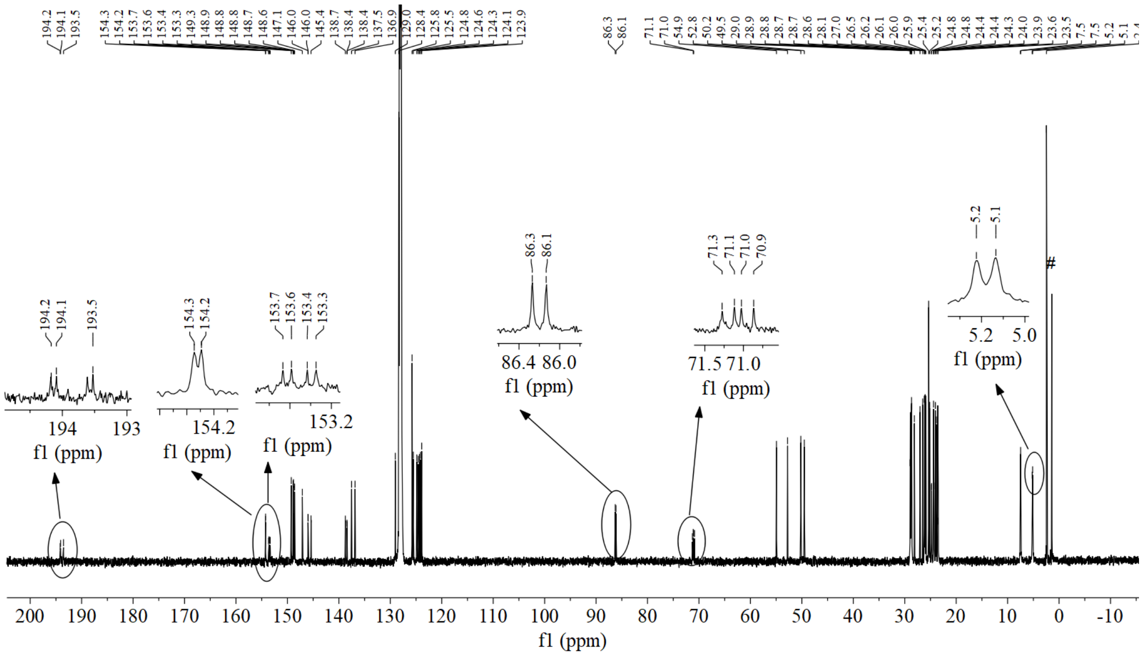


Figure S49. $^{13}C\{^1H\}$ NMR of **7a** in C_6D_6.

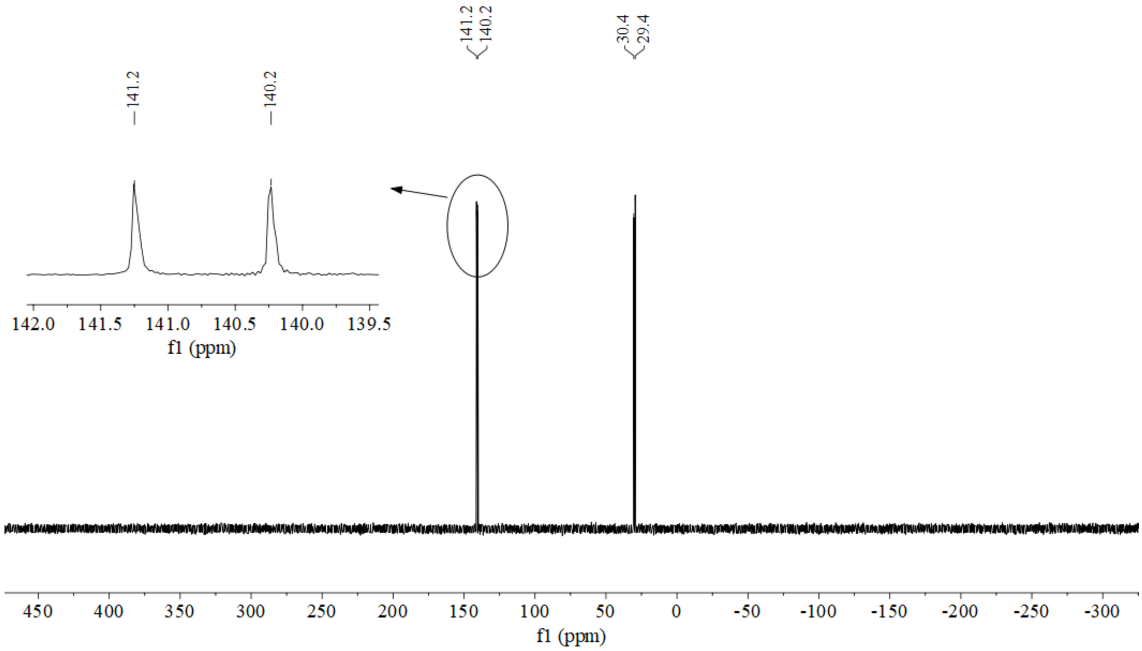


Figure S50. $^{31}P\{^1H\}$ NMR of **7a** in C_6D_6.

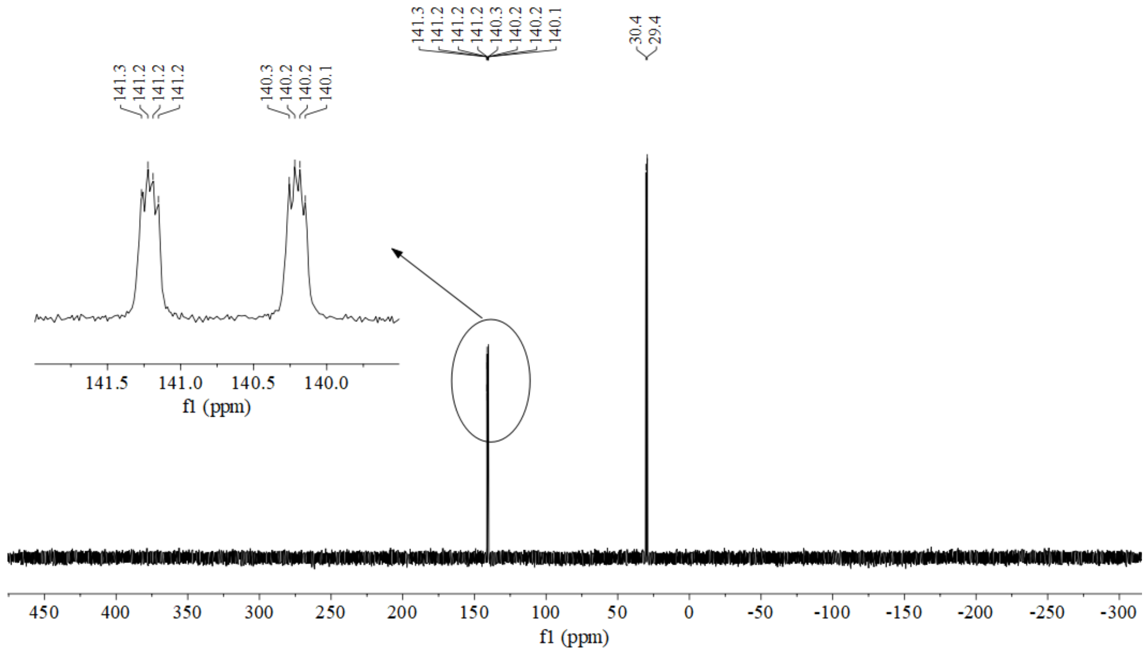


Figure S51. ^{31}P NMR of **7a** in C_6D_6.

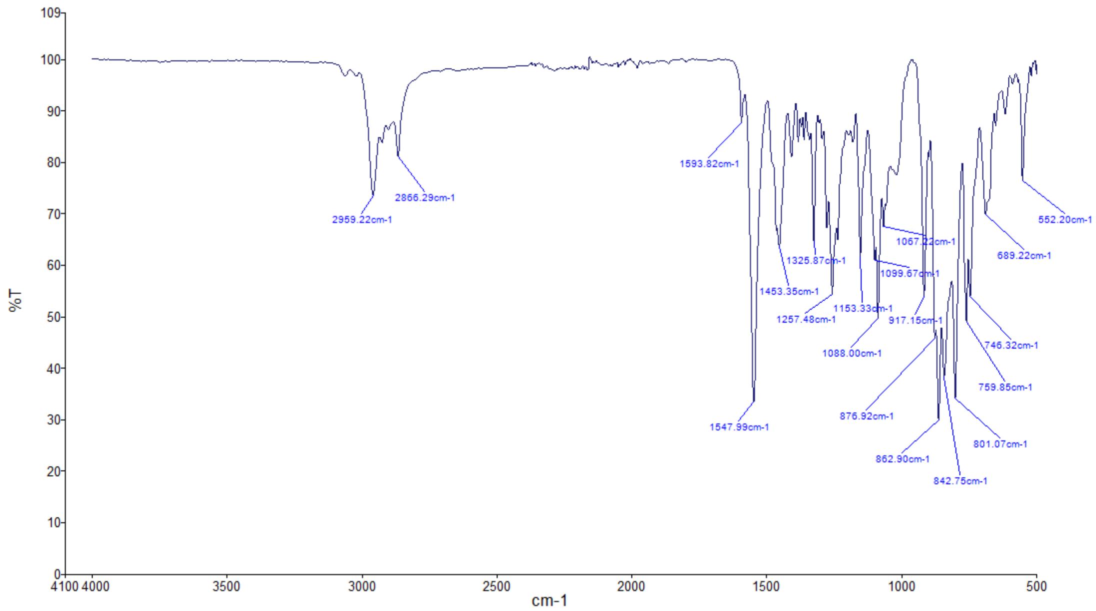
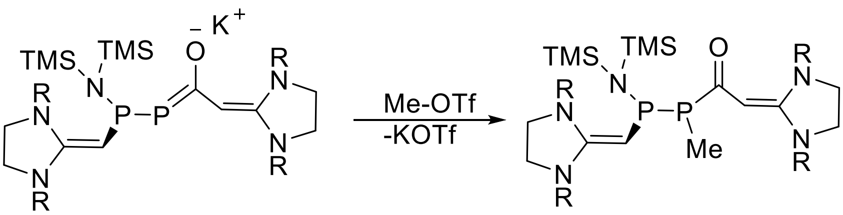


Figure S52. IR spectrum of **7a**.

Synthesis of 8a:



6a, R = Dipp **8a**, R = Dipp

Methyl trifluoromethanesulfonate (49 mg, 0.3 mmol) in tetrahydrofuran (4 mL) was added to a stirred solution of **6a** (300 mg, 0.3 mmol) in tetrahydrofuran (20 mL) at room temperature. After stirring for 0.5 hour, the solvent was removed under reduced pressure and the residue was extracted with hexane (20 mL). Then, the residue was washed with acetonitrile (1 mL) and dried *in vacuo* to afford **8a** (167 mg, yield = 49 %) as a light yellow powder. Light yellow crystals of **8a** were obtained from a saturated acetonitrile solution stored at -30 °C for 5 days. M. p. = 162.1 °C (Decomposition). ^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.26~7.17 (m, 6 H, $C_{Ar}H$), 7.13~7.08 (m, 5 H, $C_{Ar}H$), 7.00 (d, J = 7.2 Hz, 1 H, $C_{Ar}H$), 4.41 (s, 1 H, PC(O)C*H*=), 3.65 (d, $^{2}J_{PH}$ = 8.8 Hz, 1 H, PPC*H*=), 3.56 (m, 3 H, C*H*(CH_3)$_2$), 3.41 (m, 4 H, NCH_2), 3.36 (m, 1 H, C*H*(CH_3)$_2$), 3.26 (m, 4 H, NCH_2), 3.15 (m, 3 H, C*H*(CH_3)$_2$), 3.01 (m, 1 H, C*H*(CH_3)$_2$), 1.54 (d, J_{HH} = 6.7 Hz, 3 H, CH(CH_3)$_2$), 1.51~1.47 (m, 6 H, CH(CH_3)$_2$), 1.44~1.39 (m, 12 H, CH(CH_3)$_2$), 1.31~1.28 (m, 6 H, CH(CH_3)$_2$), 1.24~1.16 (m, 21 H, CH(CH_3)$_2$), 1.01 (d, J = 6.7 Hz, 3 H, P(CH_3)), 0.17 (s, 9 H, Si(CH_3)$_3$), 0.05 (s, 9 H, Si(CH_3)$_3$). ^{13}C{^{1}H} NMR (150.8 MHz, C_6D_6): δ = 201.7 (dd, $^{1}J_{PC}$ = 32.9 Hz, $^{2}J_{PC}$ = 10.4 Hz, *C*O), 157.9 (dd, $^{2}J_{PC}$ = 38.6 Hz, $^{3}J_{PC}$ = 9.1 Hz, (N*C*N)=CHPP-), 155.9 (d, $^{3}J_{PC}$ = 9.5 Hz, (N*C*N)=CHC(O)PP-), 149.2 (C_{Ar}), 148.8 (C_{Ar}), 148.8 (C_{Ar}), 148.6 (C_{Ar}), 148.5 (C_{Ar}), 146.3 (C_{Ar}), 145.8 (C_{Ar}), 145.7 (C_{Ar}), 140.6 (C_{Ar}), 140.6 (C_{Ar}), 138.4 (C_{Ar}), 135.7 (C_{Ar}), 135.2 (C_{Ar}), 129.4 (C_{Ar}), 128.8 (C_{Ar}), 128.4 (C_{Ar}), 128.0 (C_{Ar}), 125.6 (C_{Ar}), 124.9 (C_{Ar}), 124.8 (C_{Ar}), 124.7 (C_{Ar}), 124.5 (C_{Ar}), 124.2 (C_{Ar}), 124.0 (C_{Ar}), 81.7 (d, $^{1}J_{PC}$ = 45.9 Hz, =*C*H-PP-), 69.4 (dd, $^{2}J_{PC}$ = 29.2 Hz, $^{3}J_{PC}$ = 24.5 Hz, =*C*HC(O)P), 53.1 (N*C*H_2), 53.0 (N*C*H_2), 49.9 (N*C*H_2), 49.5 (N*C*H_2), 29.3, 29.2, 29.0, 28.9, 28.9, 28.6, 28.5, 28.4, 26.5, 25.9, 25.9, 25.6, 25.4, 25.3, 25.1, 24.9, 24.7, 24.5, 24.2, 24.1, 24.1, 24.1, 24.0, 23.6, 8.7 (t, $^{1}J_{PC} \approx {}^{2}J_{PC}$ = 24.2 Hz, -PP(*C*H_3)-), 6.7 (d, $^{3}J_{PC}$ = 6.7 Hz, -PNSi(*C*H_3)$_2$), 5.2 (d, $^{3}J_{PC}$ = 15.0 Hz, -PNSi(*C*H_3)$_2$). ^{31}P{^{1}H} NMR (242.9 MHz, C_6D_6): δ = 40.3 (d, $^{1}J_{PP}$ = 170.5 Hz, -C(O)-P(CH_3)-*P*-), -20.4 (d, $^{1}J_{PP}$ = 170.5 Hz, -C(O)-*P*(CH_3)-P-). ^{31}P NMR (242.9 MHz, C_6D_6): δ = 40.3 (d, $^{1}J_{PP}$ = 170.5 Hz, -C(O)-P(CH_3)-*P*-), -20.4 (d, $^{1}J_{PP}$ = 170.5 Hz, -C(O)-*P*(CH_3)-P-). UV/Vis (toluene, λ (nm) ε ($M^{-1}cm^{-1}$)): 304.5 (32237), 335.0 (34665), 379.5 (12458). HRMS (ESI, m/z) calc. for: $C_{64}H_{99}N_5OP_2Si_2$: 1110.6495 [M+K]$^{+}$; found: 1110.6481. IR (ATR, cm^{-1}): 2960, 2927, 2868, 1515, 1053, 882, 850, 840, 800, 760.

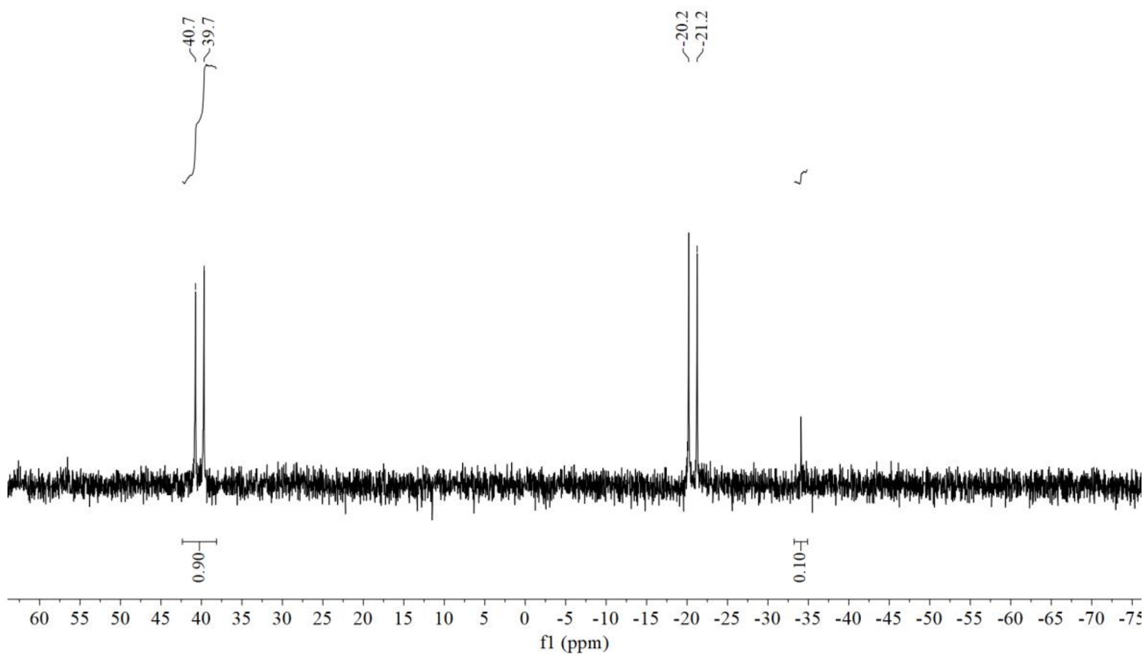


Figure S53. $^{31}P\{^{1}H\}$ NMR of the reaction mixture for the preparation of **8a** in tetrahydrofuran, the NMR spectroscopic yield is about 90%.

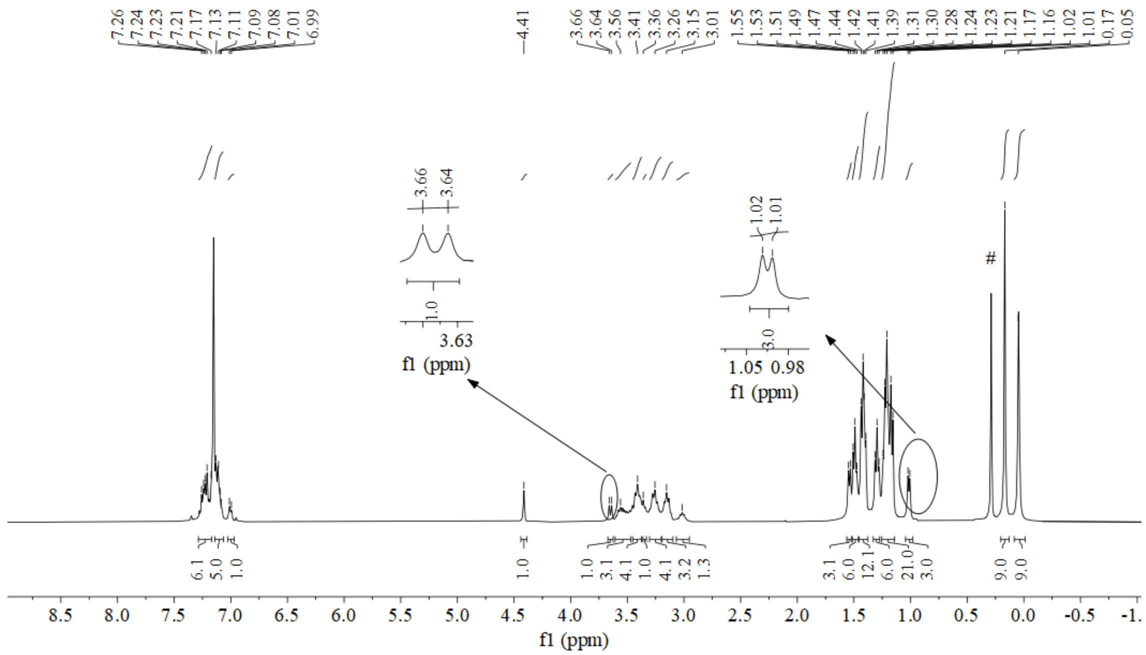


Figure S54. ^{1}H NMR of **8a** in C_6D_6. # silicon grease.

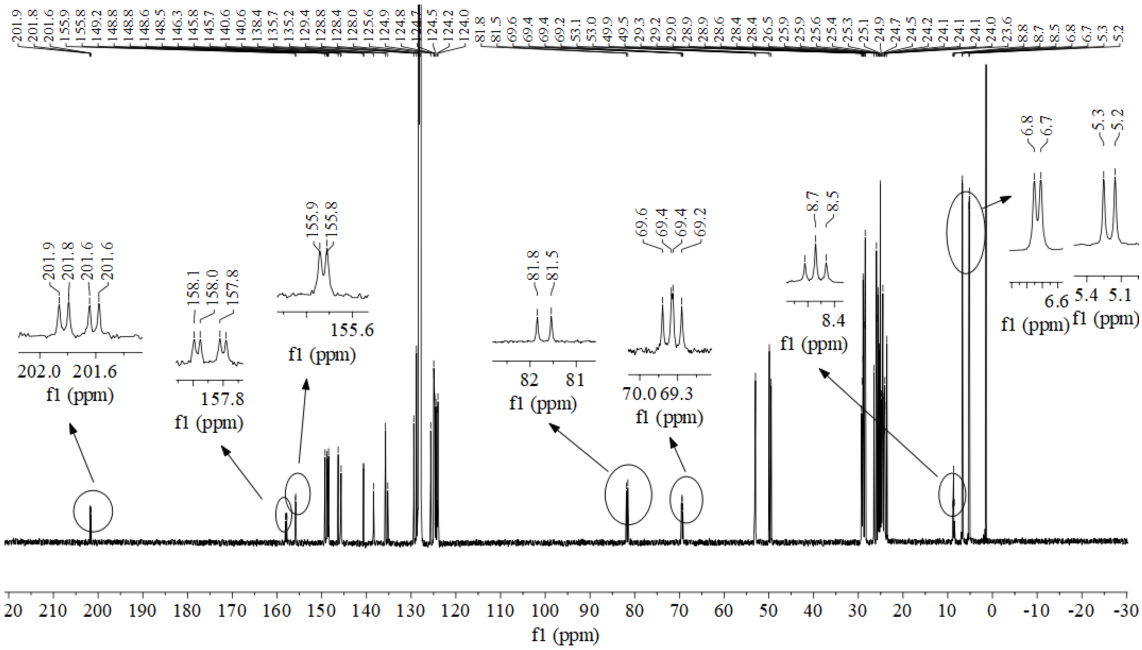


Figure S55. $^{13}C\{^1H\}$ NMR of **8a** in C_6D_6.

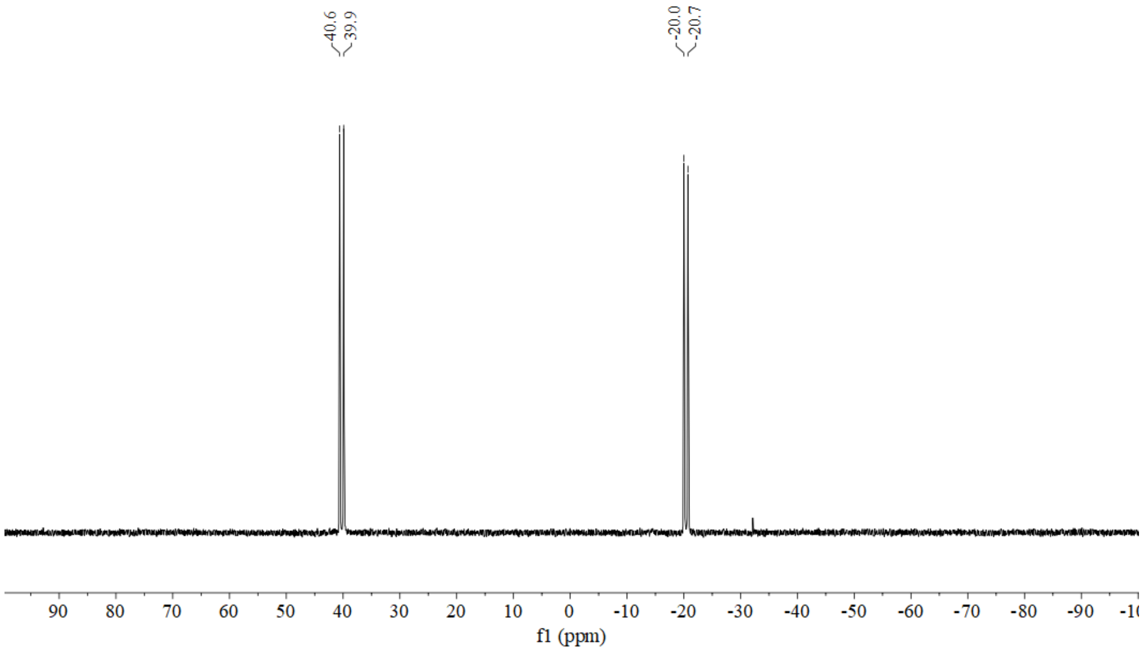


Figure S56. $^{31}P\{^1H\}$ NMR of **8a** in C_6D_6.

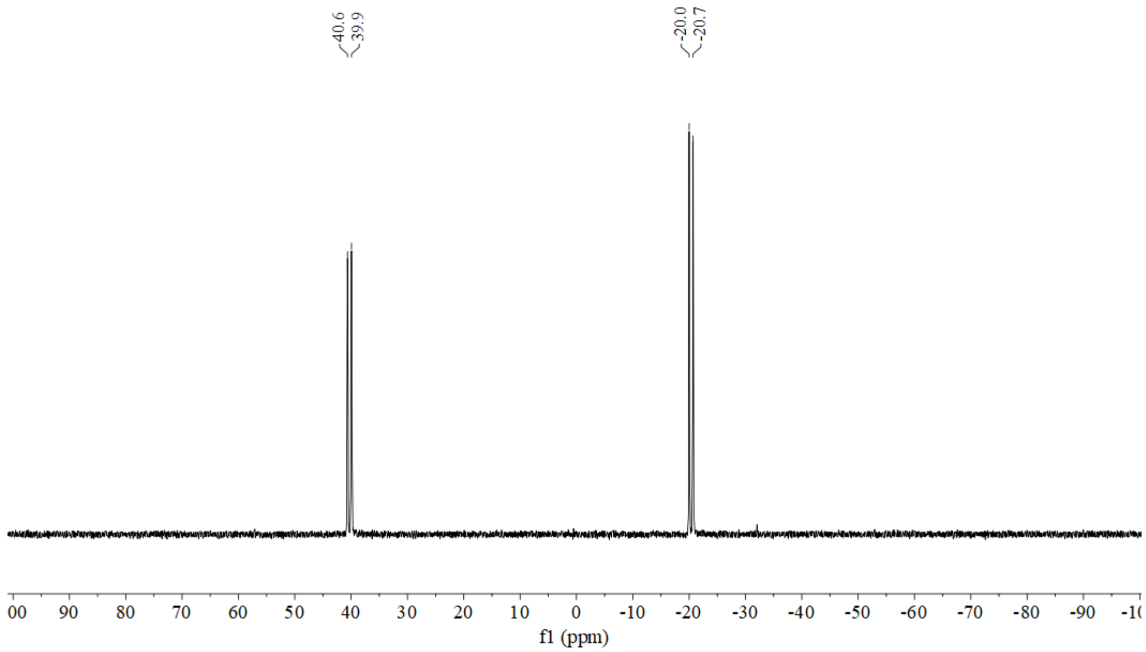


Figure S57. ^{31}P NMR of **8a** in C_6D_6.

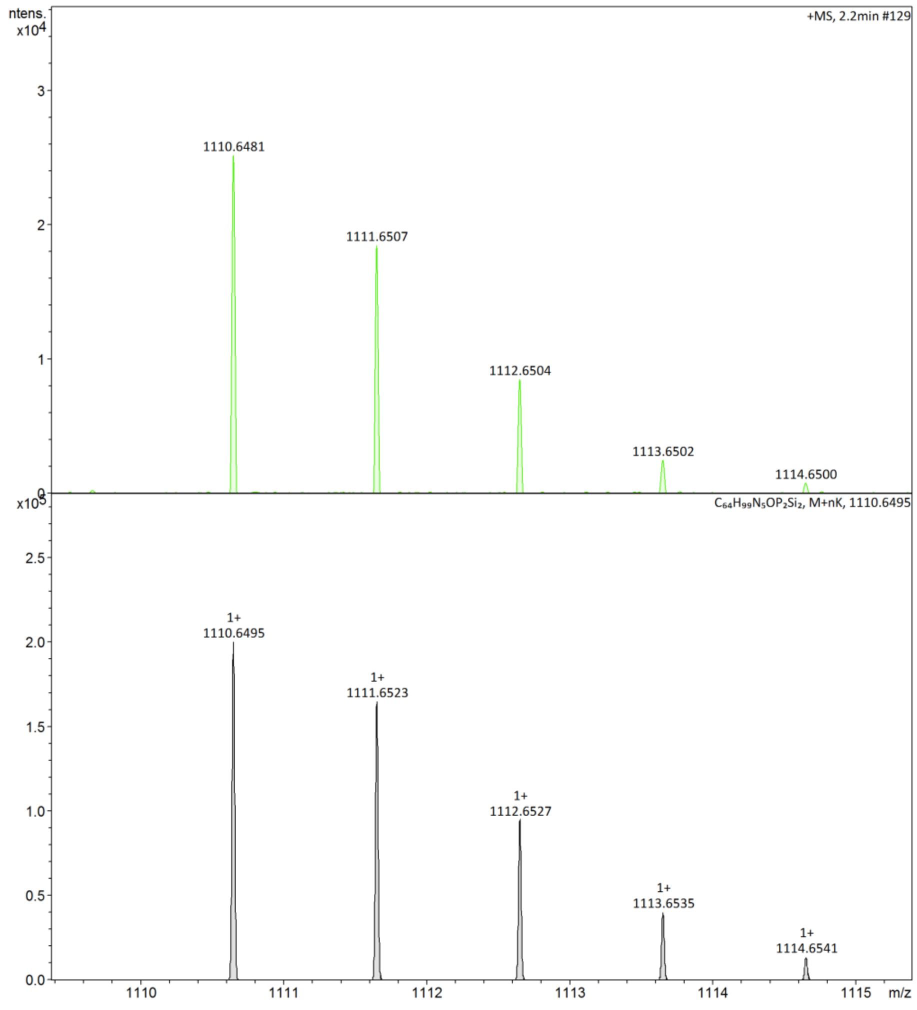


Figure S58. HRMS of **8a**.

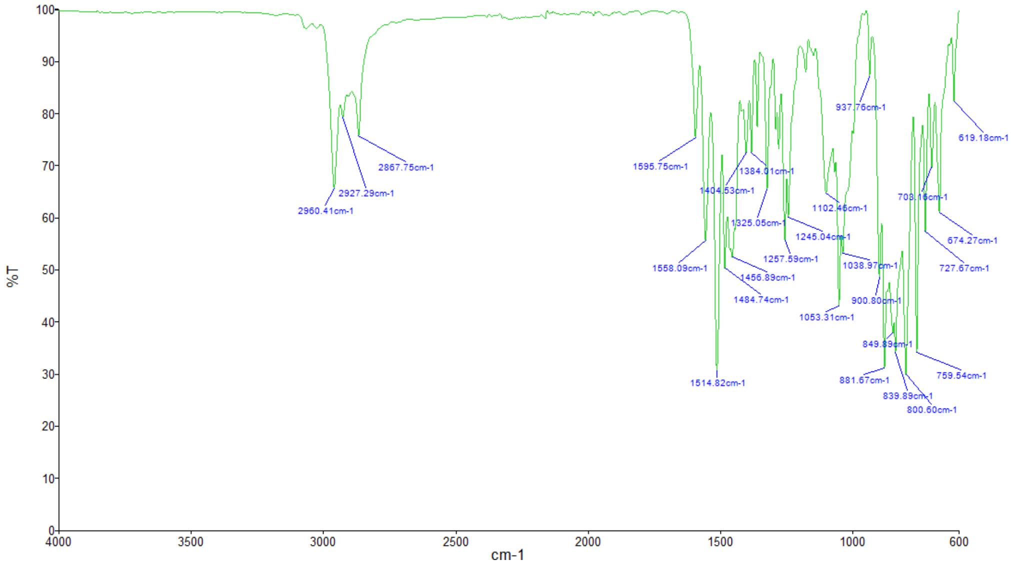
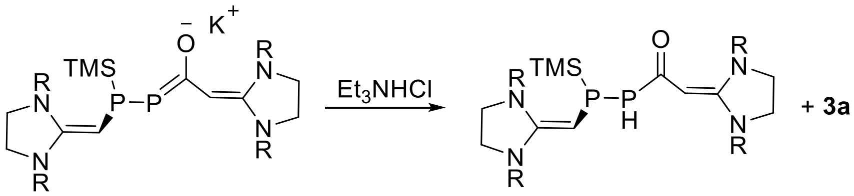


Figure S59. IR spectrum of **8a**.

Synthesis of S1:



6a, R = Dipp **S1**, R = Dipp

Triethylamine hydrochloride (Et_3NHCl) (2 mg) was added slowly to a stirred solution of **6a** (20 mg) in tetrahydrofuran (0.5 mL) at room temperature. After stirring for 0.5 h, monitor the solution $^{31}P\{^1H\}$ and ^{31}P NMR signal. $^{31}P\{^1H\}$ NMR (242.9 MHz, tetrahydrofuran): δ = 485.4 (d, $^1J_{PP}$ = 530.6 Hz), 381.63 (d, $^1J_{PP}$ = 530.6 Hz), 35.8 (d, $^1J_{PP}$ = 158.2 Hz, (TMS)*P*-PH), -39.1 (d, $^1J_{PP}$ = 158.2 Hz, (TMS)P-*P*H). ^{31}P NMR (242.9 MHz, tetrahydrofuran): δ = 35.8 (d, $^1J_{PP}$ = 158.2 Hz, (TMS)*P*-PH), -39.1 (d, $^1J_{PP}$ = 158.2 Hz, $^1J_{PH}$ = 202.8 Hz, (TMS)P-*P*H).

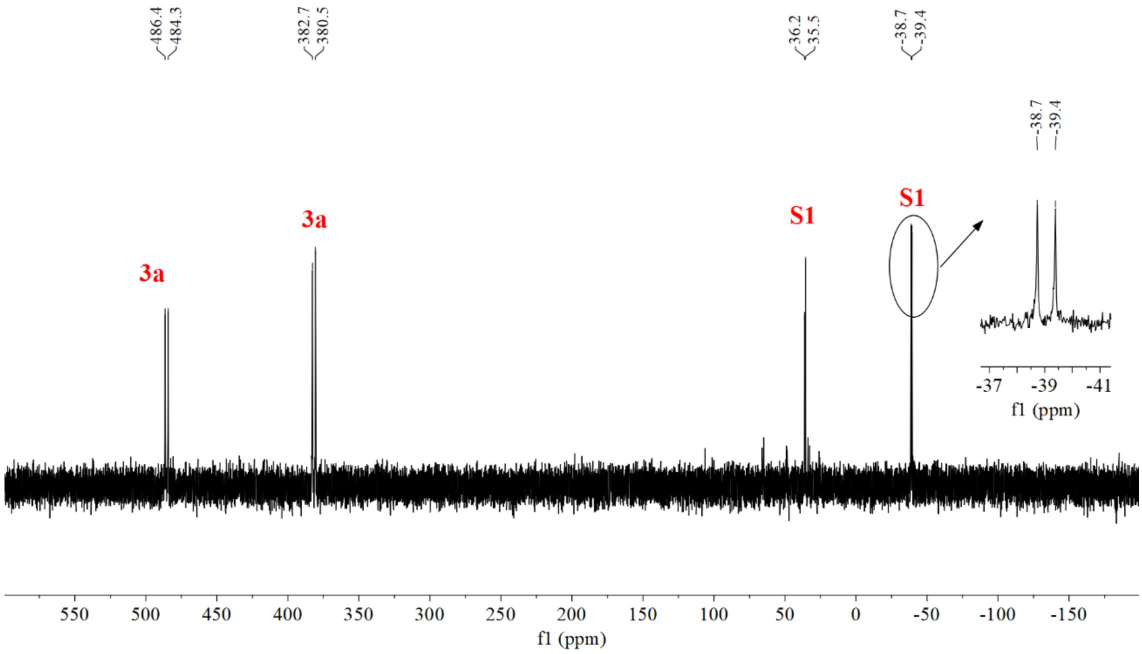


Figure S60. $^{31}P\{^{1}H\}$ NMR of the reaction between **6a** and Et_3NHCl in tetrahydrofuran.

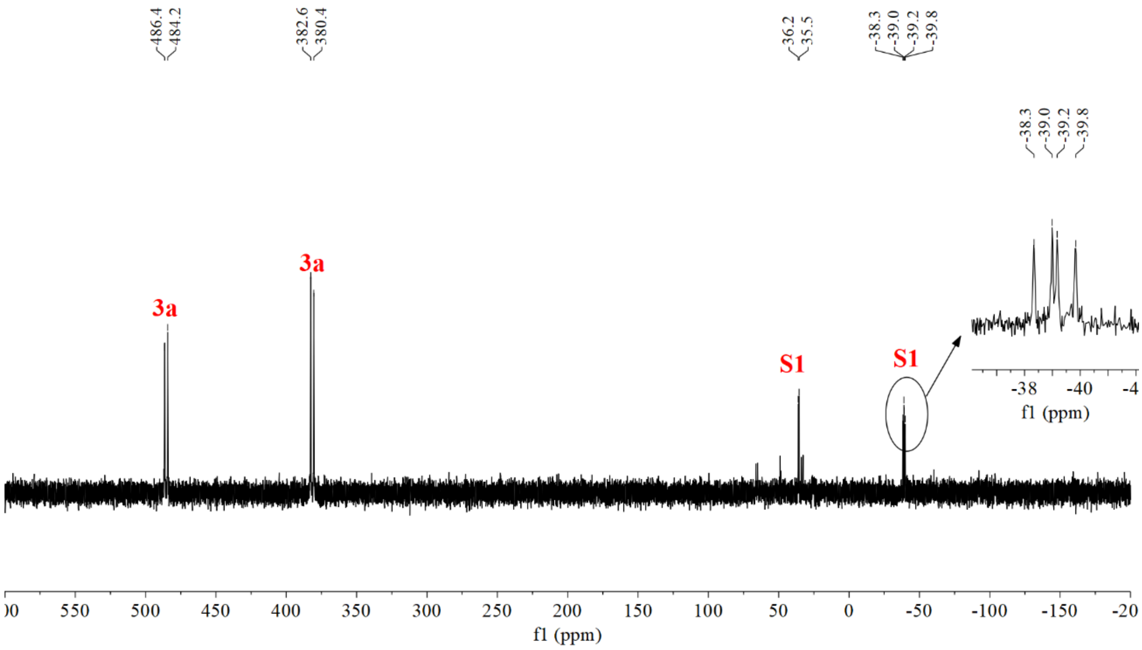
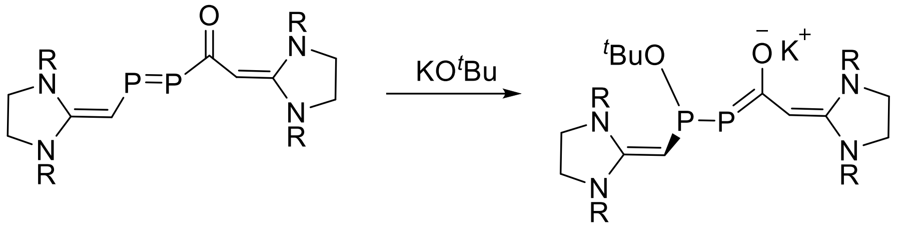


Figure S61. ^{31}P NMR of the reaction between **6a** and Et_3NHCl in tetrahydrofuran.

Synthesis of 6b:



3a, R = Dipp **6b**, R = Dipp

Potassium *tert*-butoxide (^{t}BuOK) (37 mg, 0.3 mmol) in tetrahydrofuran (4 mL) was added to a stirred solution of **3a** (300 mg, 0.3 mmol) in tetrahydrofuran (12 mL) at room temperature. After stirring for 0.5 hour, the solvent was removed under reduced pressure. Then, the residue was washed with hexane (2 × 2 mL) and dried *in vacuo* to afford **6b** (314 mg, yield = 93 %) as a yellow powder. M. p. = 113.6 °C (Decomposition). ^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.14~7.11 (3 H, $C_{Ar}H$), 7.08~7.03 (4 H, $C_{Ar}H$), 6.98~6.89 (3 H, $C_{Ar}H$), 6.88~6.86 (2 H, $C_{Ar}H$), 4.90 (s, 1 H, =C*H*C(O)-), 4.02 (br., 1 H, =C*H*PP-), 3.69 (m, 2 H, NCH_2), 3.64 (m, 1 H, C*H*(CH_3)$_3$), 3.50 (m, 4 H, C*H*(CH_3)$_3$), 3.39~3.28 (m, 3 H, C*H*(CH_3)$_3$ & 4 H, NCH_2), 3.17 (m, 2 H, NCH_2), 1.51 (d, J = 6.7 Hz, 3 H, CH(CH_3)$_2$), 1.49~1.43 (m, 9 H, CH(CH_3)$_2$), 1.41~1.38 (m, 6 H, CH(CH_3)$_2$), 1.36~1.32 (m, 6 H, CH(CH_3)$_2$ & 9 H, -OC(CH_3)$_3$), 1.31 (d, J = 6.9 Hz, 3 H, CH(CH_3)$_2$), 1.27~1.22 (m, 18 H, CH(CH_3)$_2$), 1.20~1.17 (m, 6 H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (150.8 MHz, C_6D_6): δ = 219.1 (m, PP*C*O$^-$), 151.7 (br., PPC(O$^-$)CH=*C*), 150.8 (br., PPCH=*C*), 150.1 (C_{Ar}), 149.5 (C_{Ar}), 148.7 (C_{Ar}), 148.3 (C_{Ar}), 147.5 (C_{Ar}), 144.6 (C_{Ar}), 143.4 (C_{Ar}), 136.6 (C_{Ar}), 125.2 (C_{Ar}), 124.7 (C_{Ar}), 124.4 (C_{Ar}), 124.3 (O*C*(CH_3)$_3$), 123.0 (C_{Ar}), 88.3 (d (br.), $^2J_{PC}$ = 69.8 Hz, PPC(O$^-$)*C*H=), 74.8 (br., PP*C*H=), 53.5 (N*C*H_2), 52.4 (N*C*H_2), 50.0 (N*C*H_2), 49.9 (N*C*H_2), 31.7, 31.6, 29.1, 29.0, 28.9, 28.8, 28.7, 28.7, 28.6, 28.5, 25.8, 25.4, 25.3, 25.2, 25.2, 25.1, 25.0, 25.0, 24.9, 24.6, 24.6, 24.5, 24.5, 24.4, 24.3. ^{31}P{^{1}H} NMR (242.9 MHz, C_6D_6): δ = 104.9 (d, $^1J_{PP}$ = 301.8 Hz, *P*PC(O$^-$)), 82.1 (br., P*P*C(O$^-$)). ^{31}P{^{1}H} NMR (242.9 MHz, tetrahydrofuran): δ = 107.6 (d, $^1J_{PP}$ = 301.8 Hz, *P*PC(O$^-$)), 82.1 (d, $^1J_{PP}$ = 301.8 Hz, P*P*C(O$^-$)). UV/Vis (toluene, λ (nm) ε ($M^{-1}cm^{-1}$)): 327.5 (14384), 423.5 (15269), 515.0 (3582). HRMS (ESI, m/z) calc. for: $C_{61}H_{87}N_4O_2P_2^-$: 969.6310 [M]$^-$; found: not detected. IR (ATR, cm^{-1}): 2961, 2928, 2868, 1504, 1455, 1324, 805.

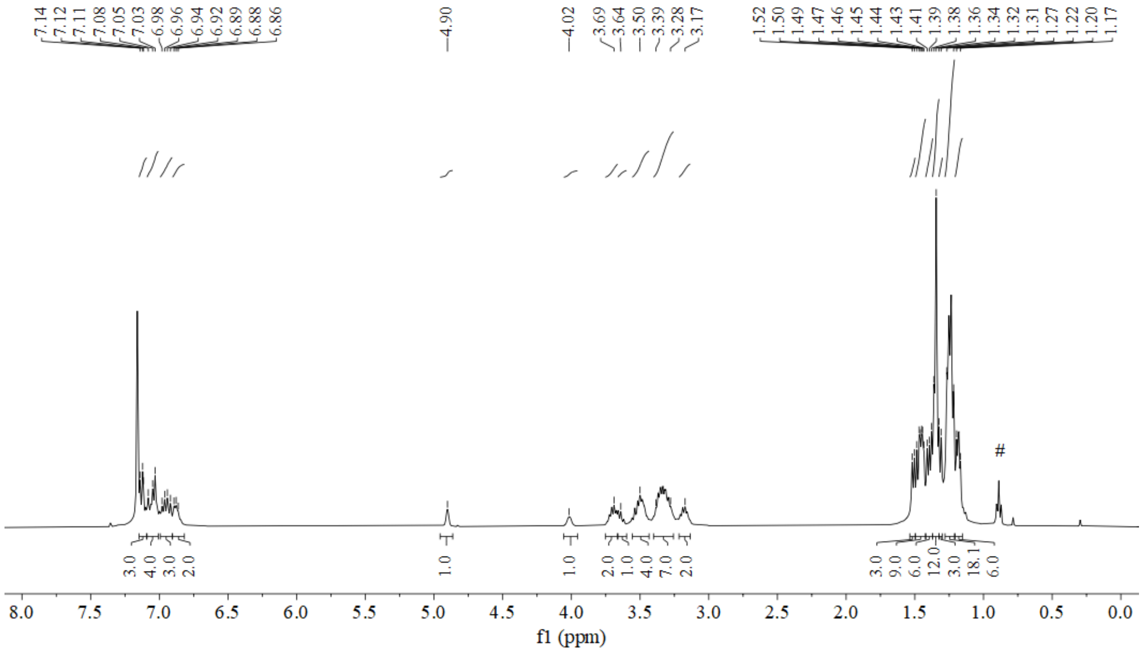


Figure S62. ^{1}H NMR of **6b** in C_6D_6. #Hexane.

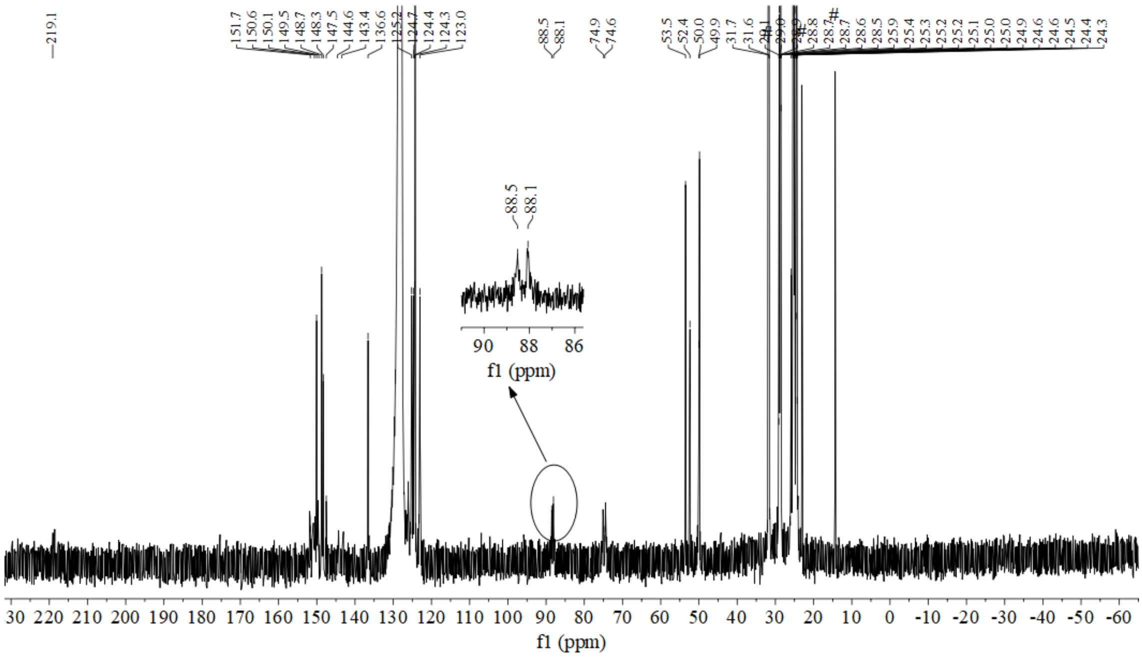


Figure S63. $^{13}C\{^{1}H\}$ NMR of **6b** in C_6D_6. #Hexane.

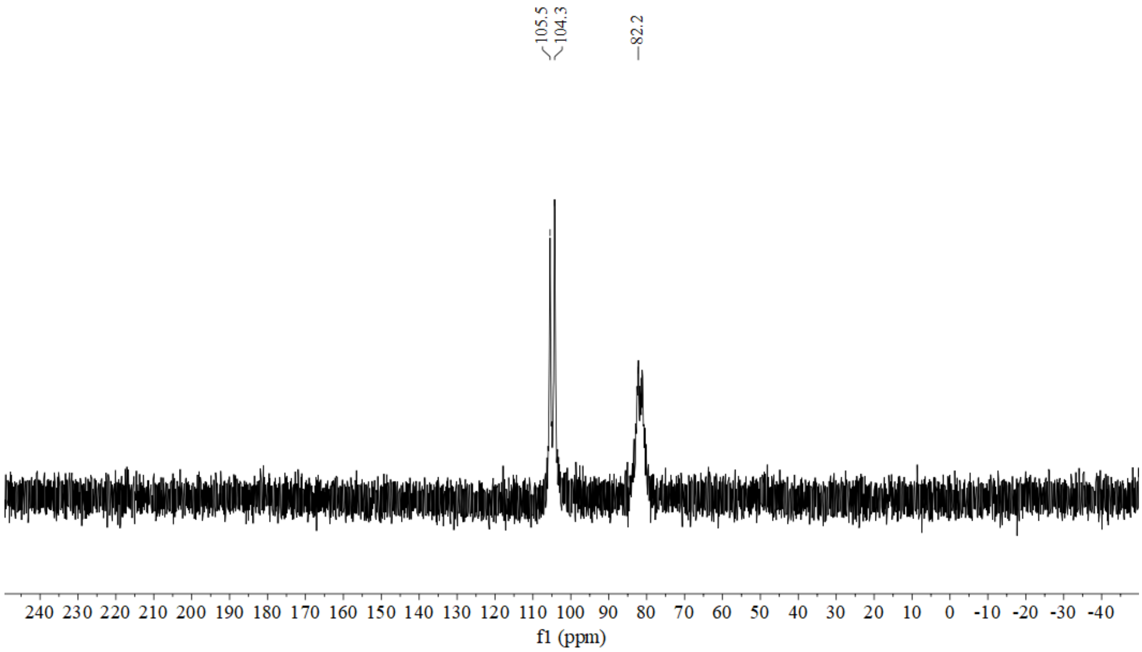


Figure S64. $^{31}P\{^{1}H\}$ NMR of **6b** in C_6D_6.

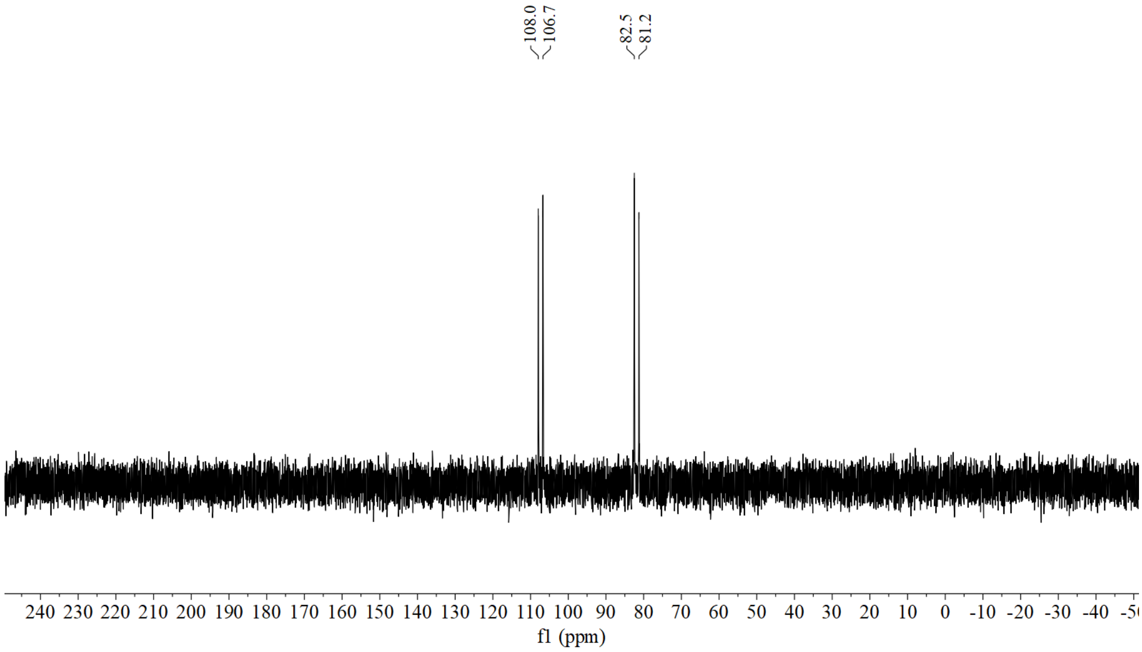


Figure S65. $^{31}P\{^{1}H\}$ NMR of **6b** in tetrahydrofuran.

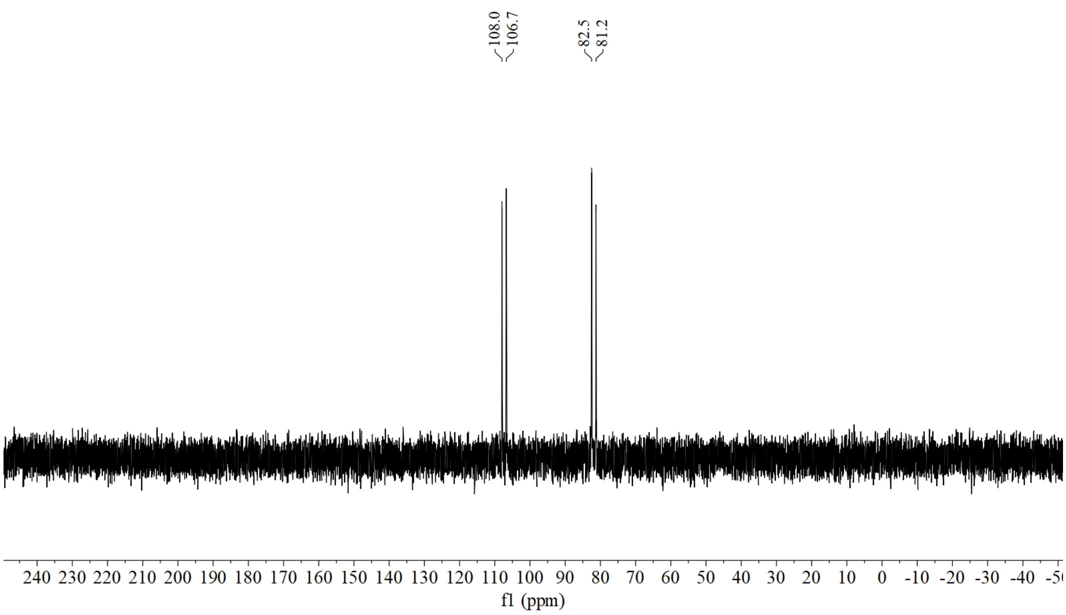


Figure S66. ^{31}P NMR of **6b** in tetrahydrofuran.

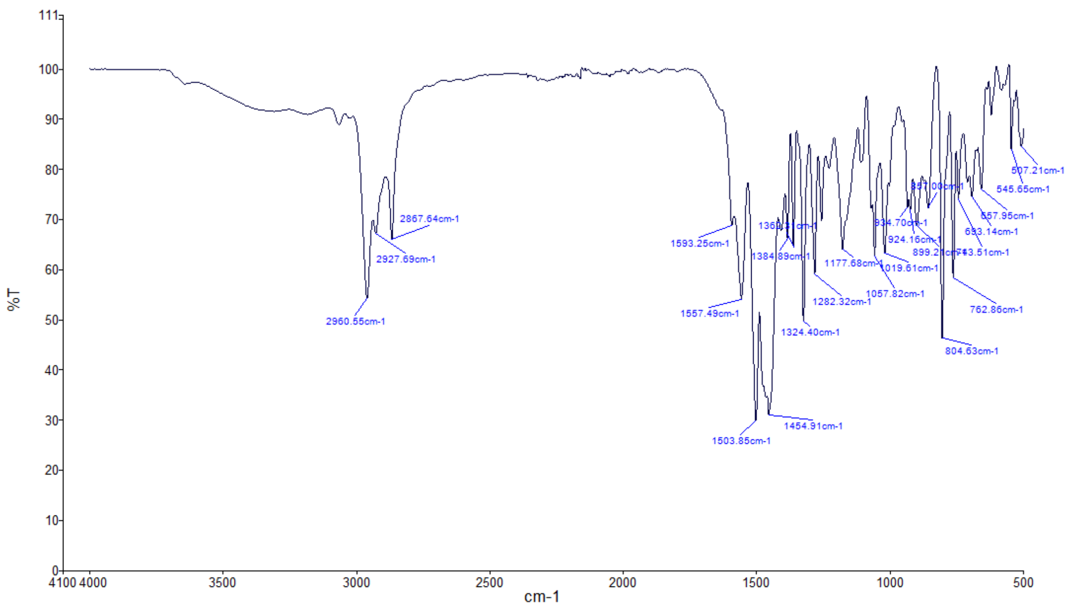
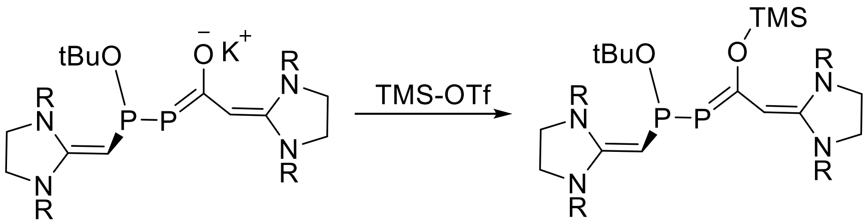


Figure S67. IR spectrum of **6a**.

Synthesis of 7b:



6b, R = Dipp **7b**, R = Dipp

Trimethylsilyl trifluoromethanesulfonate (TMS-OTf) (66 mg, 0.3 mmol) in tetrahydrofuran (4 mL) was added to the solution of **6b** (300 mg, 0.3 mmol) in tetrahydrofuran (12 mL) at room temperature. After stirring for 0.5 h, the solvent was removed under reduced pressure, and the residue was extracted with hexane (20 mL). Then, the residue was washed with acetonitrile (1 mL) and dried *in vacuo* to afford **7b** (156 mg, yield = 52 %) as an orange powder. Orange crystals of **7b** were obtained from a saturated acetonitrile solution stored at -30 °C for 5 days. M. p. = 154.3 °C (Decomposition). ^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.38 (t, J = 7.6 Hz, 1 H, $C_{Ar}H$), 7.28 (d, J = 7.8 Hz, 2 H, $C_{Ar}H$), 7.20~7.19 (m, 4 H, $C_{Ar}H$), 7.12~7.08 (m, 4 H, $C_{Ar}H$), 6.98 (t, J = 7.4 Hz, $C_{Ar}H$), 3.84 (s, 1 H, P=C-C*H*=), 3.76 (m, 1 H, PP-C*H*=), 3.53 (m, 4 H, NCH_2), 3.40 (m, 8 H, NCH_2 & $CH(CH_3)_2$), 3.25 (m, 2 H, $CH(CH_3)_2$), 3.16 (m, 1 H, $CH(CH_3)_2$), 3.07 (m, 1 H, $CH(CH_3)_2$), 1.59~1.55 (m, 9 H, $CH(CH_3)_2$), 1.44~1.40 (m, 6 H, $CH(CH_3)_2$), 1.37~1.25 (m, 24 H, $CH(CH_3)_2$), 1.22~1.17 (m, 9 H, $CH(CH_3)_2$), 1.03 (s, 9 H, $-OC(CH_3)_3$), 0.02 (s, 9 H, $-Si(CH_3)_3$). ^{13}C{^{1}H} NMR (100.5 MHz, C_6D_6): δ = 196.1 (dd, $^{1}J_{PC}$ = 77.9 Hz, $^{2}J_{PC}$ = 11.8 Hz, P-P=*C*(O)-), 157.00 (d, $^{3}J_{PC}$ = 3.2 Hz, N*C*N), 156.0 (dd, $^{2}J_{PC}$ = 32.1 Hz, $^{3}J_{PC}$ = 16.2 Hz, N*C*N), 149.9 (C_{Ar}), 149.2 (C_{Ar}), 148.7 (C_{Ar}), 148.6 (C_{Ar}), 148.4 (C_{Ar}), 148.4 (C_{Ar}), 147.9 (C_{Ar}), 147.7 (C_{Ar}), 145.5 (C_{Ar}), 139.9 (C_{Ar}), 139.9 (C_{Ar}), 139.0 (C_{Ar}), 136.9 (C_{Ar}), 136.5 (C_{Ar}), 128.9 (C_{Ar}), 128.6 (C_{Ar}), 128.1 (C_{Ar}), 127.9 (C_{Ar}), 125.2 (C_{Ar}), 124.9 (C_{Ar}), 124.8 (C_{Ar}), 124.7 (C_{Ar}), 124.5 (C_{Ar}), 124.2 (C_{Ar}), 86.4 (d, $^{2}J_{PC}$ = 20.1 Hz, $-P-O-C(CH_3)_3$), 73.3 (d, $^{2}J_{PC}$ = 4.2 Hz, $-P-O-C(CH_3)_3$), 72.5 (dd, $^{1}J_{PC}$ = 43.5 Hz, $^{2}J_{PC}$ = 13.8 Hz, =*C*H-PP), 54.6(NCH_2), 52.5 (NCH_2), 50.0 (NCH_2), 49.3 (NCH_2), 30.8 (d, $^{3}J_{PC}$ = 7.6 Hz, $-OC(CH_3)_3$), 29.0, 29.0, 28.9, 28.8, 28.7, 28.7, 28.6, 28.2, 26.7, 26.1, 25.9, 25.7, 25.7, 25.5, 25.4, 25.1, 25.0, 24.8, 24.7, 24.7, 24.6, 24.6, 24.5, 23.5, 1.3 ($-Si(CH_3)_3$). ^{31}P{^{1}H} NMR (242.9 MHz, C_6D_6): δ = 148.2 (d, $^{1}J_{PP}$ = 247.2 Hz, *P*P-C(OTMS)), 87.6 (d, $^{1}J_{PP}$ = 247.2 Hz, P*P*-C(OTMS)). ^{31}P NMR (242.9 MHz, C_6D_6): δ = 148.2 (d, $^{1}J_{PP}$ = 247.2 Hz, *P*P-C(OTMS)), 87.6 (d, $^{1}J_{PP}$ = 247.2 Hz, P*P*-C(OTMS)). UV/Vis (toluene, λ (nm) ε ($M^{-1}cm^{-1}$)): 331.0 (6804), 432.0 (8996). HRMS (ESI, m/z) calc. for: $C_{61}H_{87}N_4O_2P_2SiC_3H_9$: 1043.6851 $[M + H]^+$; found: 1043.6777. IR (ATR, cm^{-1}): 2961, 2928, 2868, 1504, 1455, 805.

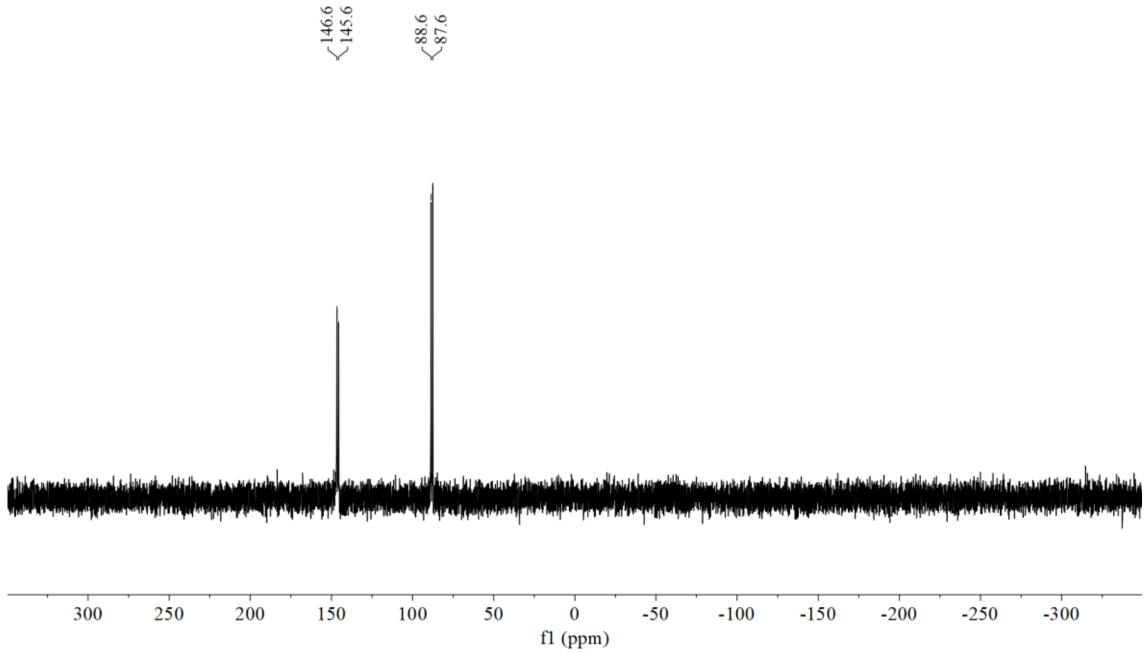


Figure S68. $^{31}P\{^{1}H\}$ NMR of the reaction mixture for the preparation of **7b** in tetrahydrofuran, the NMR spectroscopic yield is nearly quantitative.

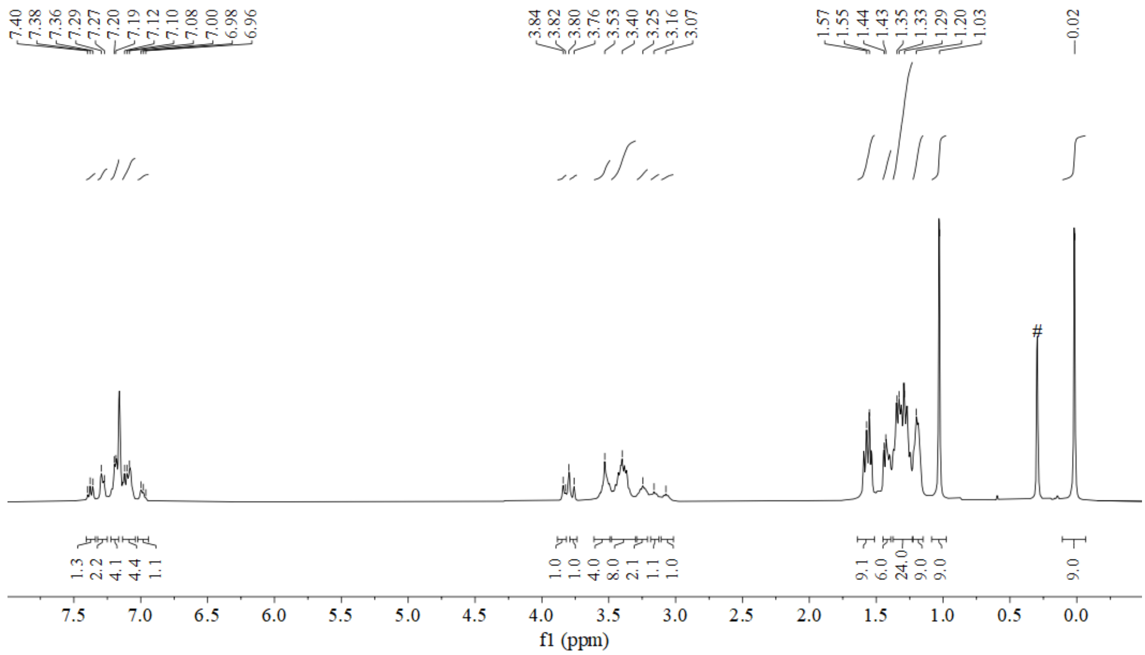


Figure S69. ^{1}H NMR of **7b** in C_6D_6. #Silicone grease.

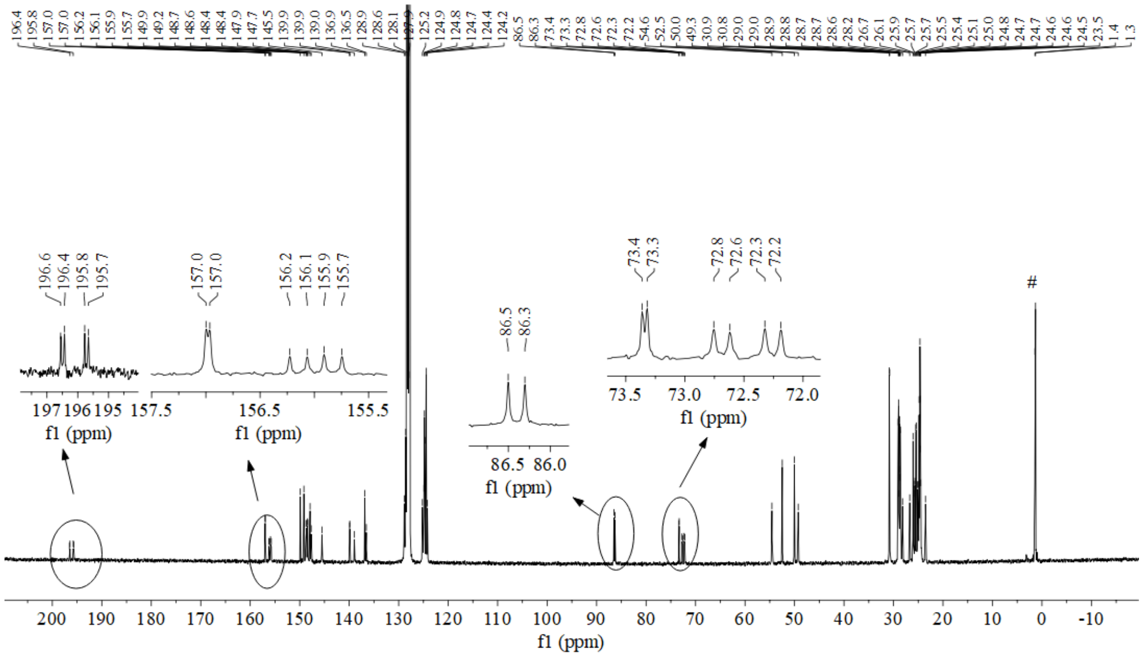


Figure S70. $^{13}C\{^{1}H\}$ NMR of **7b** in C_6D_6. #Silicone grease.

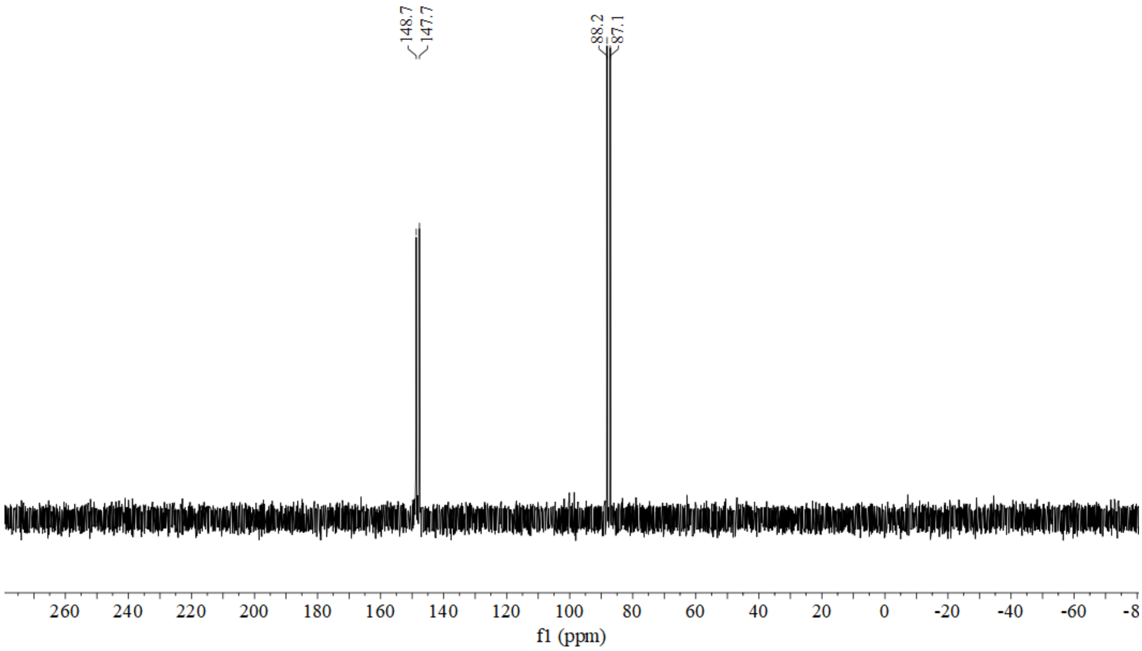


Figure S71. $^{31}P\{^{1}H\}$ NMR of **7b** in C_6D_6.

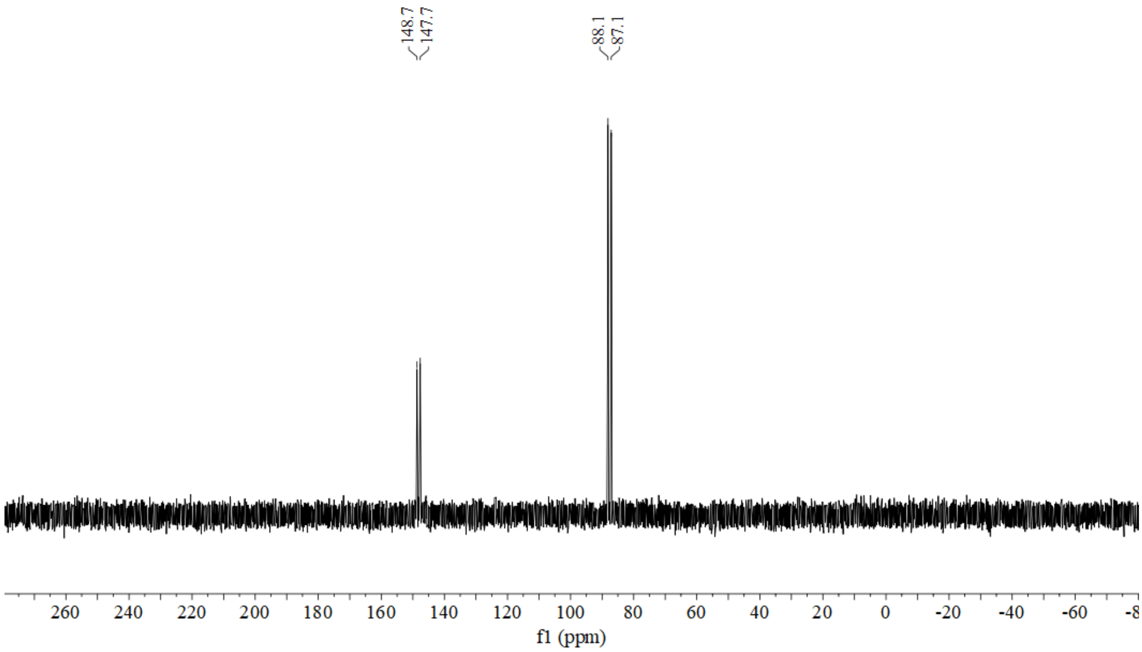


Figure S72. ^{31}P NMR of **7b** in C_6D_6.

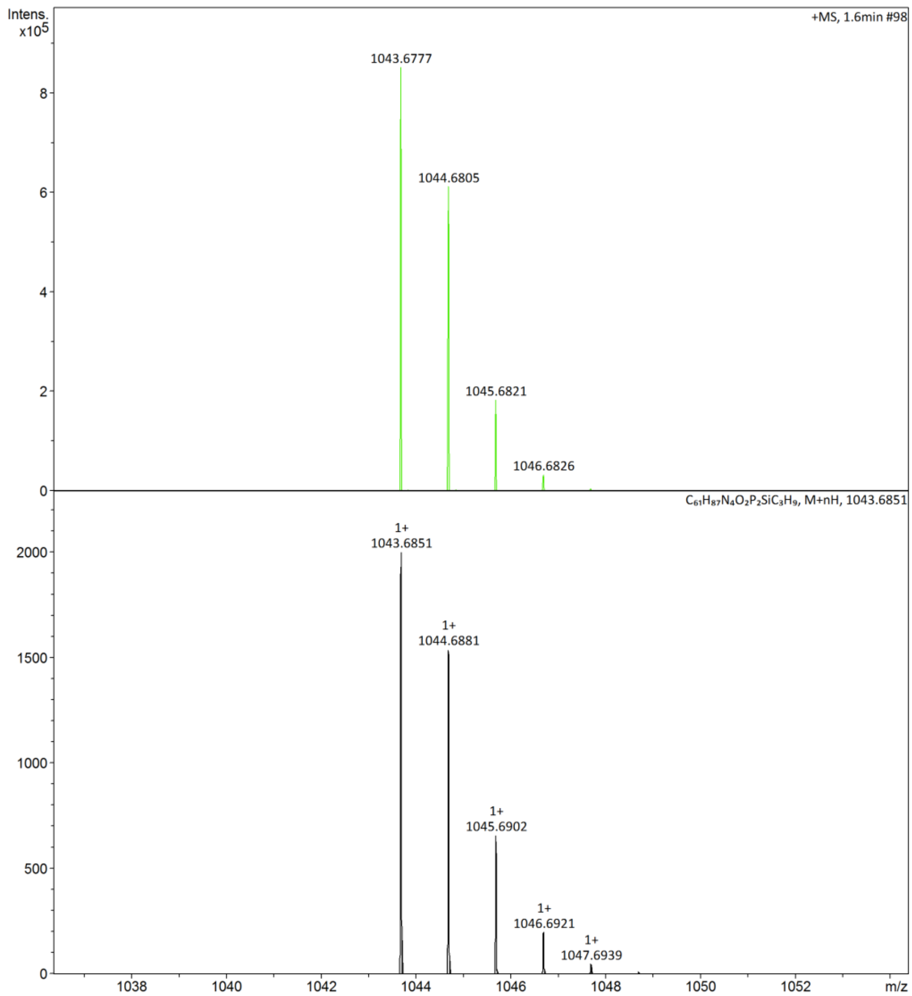


Figure S73. HRMS of **7b**.

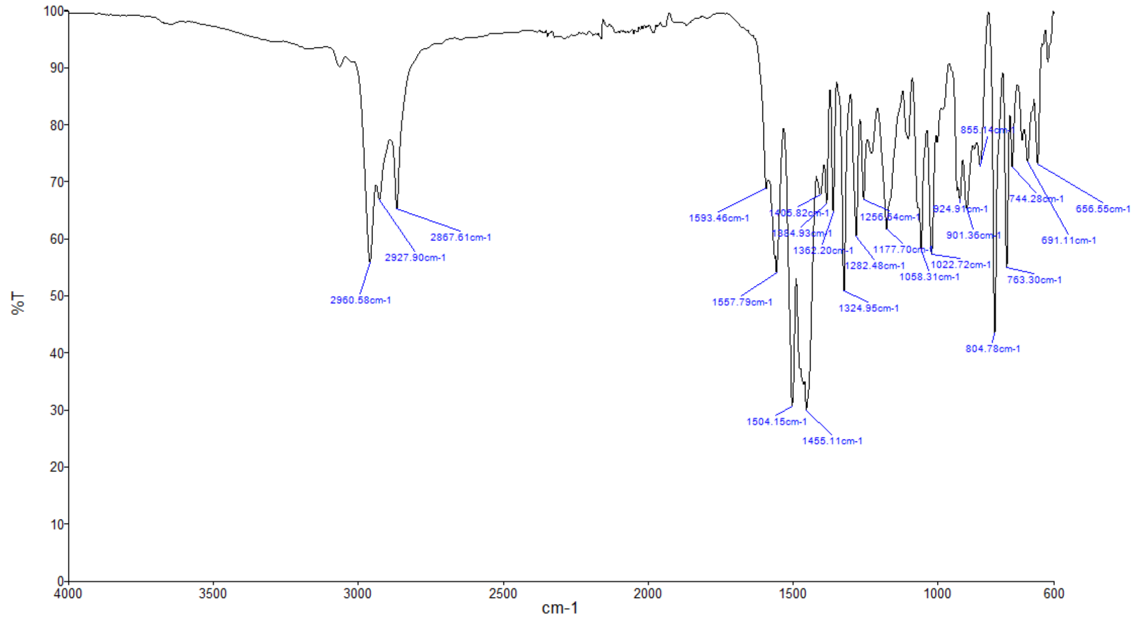
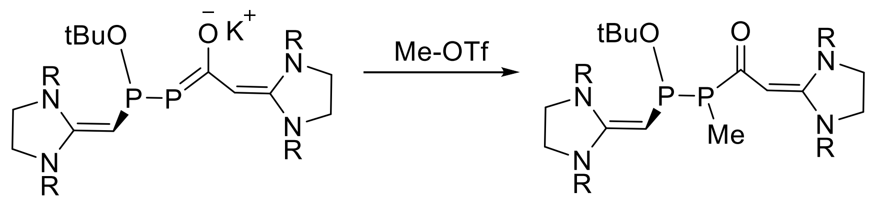


Figure S74. IR spectrum of **7b**.

Synthesis of 8b:



6b, R = Dipp **8b**, R = Dipp

Methyl trifluoromethanesulfonate (Me-OTf) (49 mg, 0.3 mmol) in tetrahydrofuran (4 mL) was added to a stirred solution of **6b** (300 mg, 0.3 mmol) in tetrahydrofuran (12 mL) at room temperature. After stirring for 0.5 h, the solvent was removed under reduced pressure. Then, the residue was extracted with hexane (20 mL), washed with acetonitrile (1 mL) and dried *in vacuo* to afford **8b** (167 mg, yield = 56 %) as a yellow powder. M. p. = 133.5 °C (Decomposition). ^{1}H NMR (400.1 MHz, C_6D_6): δ = 7.22 (t, J = 7.7 Hz, 3 H, $C_{Ar}H$), 7.14~7.08 (m, 6 H, $C_{Ar}H$), 7.04 (d, J = 7.3 Hz, 3 H, $C_{Ar}H$), 4.52 (s, 1 H, C(O)C*H*=), 3.57 (m, 2 H, NCH_2), 3.38 (m, 6 H, NCH_2), 3.26 (m, 8 H, $CH_2(CH_3)_2$), 3.10 (br., 1 H, =C*H*PP), 1.50 (d, J = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.44 (br., 6 H, $CH(CH_3)_2$), 1.34 (m, 9 H, $CH(CH_3)_2$), 1.27 (br., 15 H, $CH(CH_3)_2$), 1.21~1.18 (m, 12 H, $CH(CH_3)_2$), 1.16 (d, J = 6.9 Hz, 3 H, $CH(CH_3)_2$), 1.05 (s, 9 H, $C(CH_3)_3$), 0.96 (m, 3 H, $P(CH_3)$). $^{13}C\{^{1}H\}$ NMR (150.8 MHz, C_6D_6): δ = 197.8 (d, $^{1}J_{PC}$ = 34.1 Hz, P*C*(O)), 155.6 (d, $^{3}J_{PC}$ = 15.6 Hz, PC(O)CH=*C*), 153.6 (m, *C*=CHP(O^{t}Bu)P), 149.2

(C_{Ar}), 149.0 (C_{Ar}), 148.4 (C_{Ar}), 148.1 (C_{Ar}), 145.9 (C_{Ar}), 145.3 (C_{Ar}), 139.6 (C_{Ar}), 138.8 (C_{Ar}), 136.0 (C_{Ar}), 135.1 (C_{Ar}), 129.4 (C_{Ar}), 125.0 (C_{Ar}), 124.7 (C_{Ar}), 124.6 (C_{Ar}), 124.5 (C_{Ar}), 124.0 (C_{Ar}), 123.9 (C_{Ar}), 123.6 (C_{Ar}), 83.5 (d, $^2J_{PC}$ = 64.4 Hz, =*C*HC(O)P), 73.3 (m, =*C*HPP), 66.9 (m, PP(O*C*(CH_3)$_3$), 53.5 (N*C*H_2), 52.0 (N*C*H_2), 49.9 (N*C*H_2), 49.9 (N*C*H_2), 30.8 (d, $^3J_{PC}$ = 8.1 Hz, P(OC(*C*H_3)$_3$)), 29.3, 29.0, 28.8, 28.7, 28.7, 28.5, 26.4, 25.6, 25.2, 25.0, 24.8, 24.6, 24.5, 23.8, -1.5 (d, $^1J_{PC}$ = 25.9 Hz, P(*C*H_3)). ^{31}P NMR (242.9 MHz, C_6D_6): δ = 90.1 (d, $^1J_{PP}$ = 311.0 Hz, *P*P(CH_3)C(O)), 5.3 (d, $^1J_{PP}$ = 311.0 Hz, P*P*(CH_3)C(O)). ^{31}P{^{1}H} NMR (242.9 MHz, C_6D_6): δ = 90.1 (d, $^1J_{PP}$ = 311.0 Hz, *P*P(CH_3)C(O)), 5.3 (d, $^1J_{PP}$ = 311.0 Hz, P*P*(CH_3)C(O)). UV/Vis (toluene, λ (nm) ε ($M^{-1}cm^{-1}$)): 332.5 (77091.0). HRMS (ESI, m/z) calc. for: $C_{62}H_{90}N_4O_2P_2$: 985.6621 [M + H]$^+$; found: 985.6621. IR (ATR, cm^{-1}): 2961, 2926, 2866, 1510, 1054, 805, 764, 795.

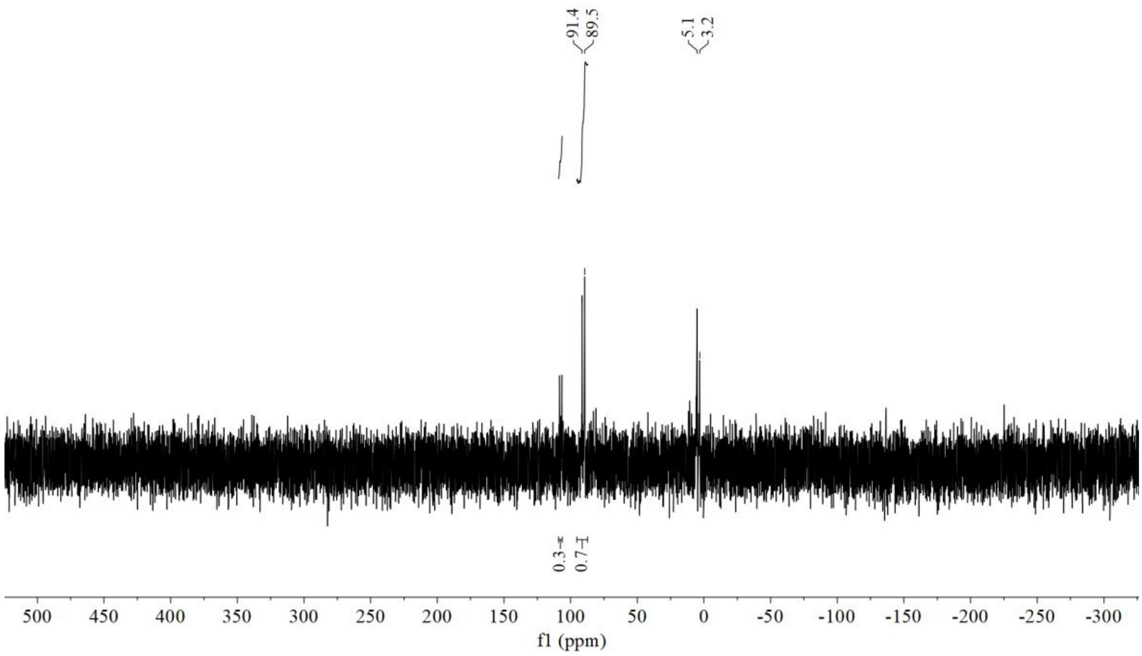


Figure S75. ^{31}P{^{1}H} NMR of the reaction mixture for the preparation of **8b** in THF, the NMR spectroscopic yield is about 70%.

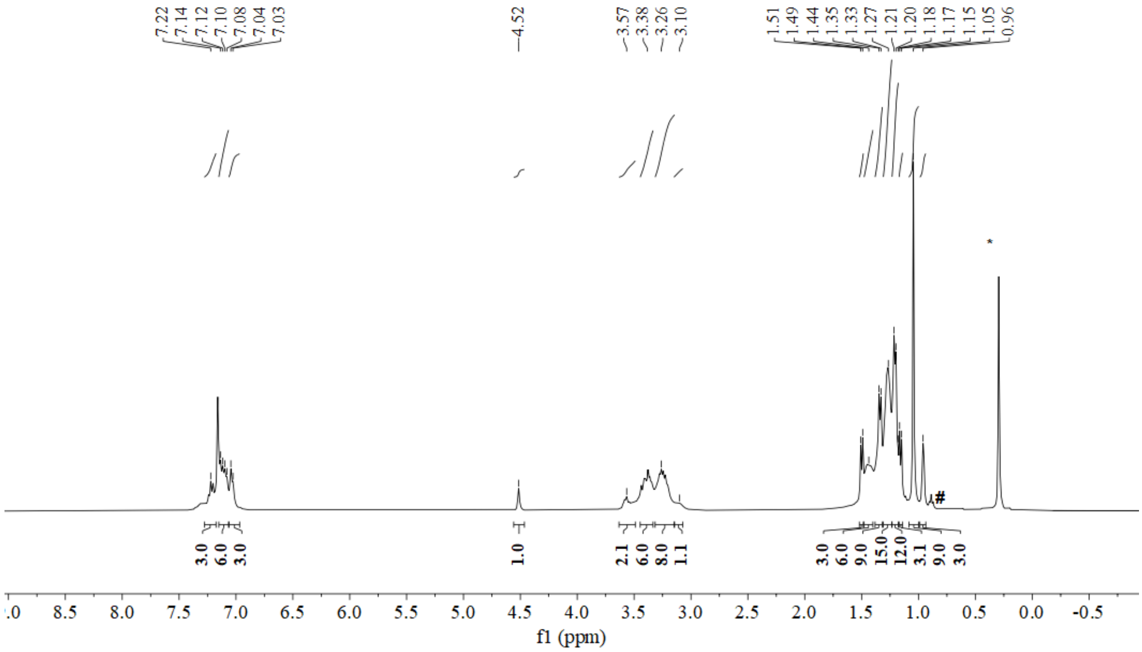


Figure S76. ^{1}H NMR of **8b** in C_6D_6. #Hexane, *silicone grease.

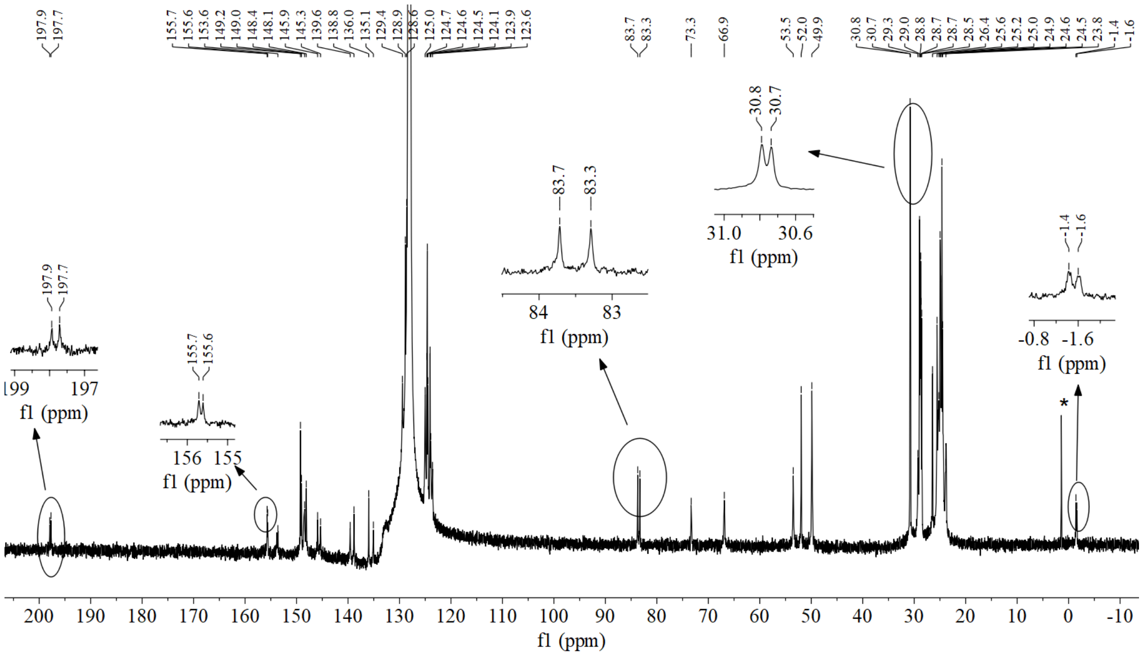


Figure S77. $^{13}C\{^{1}H\}$ NMR of **8b** in C_6D_6. *Silicone grease.

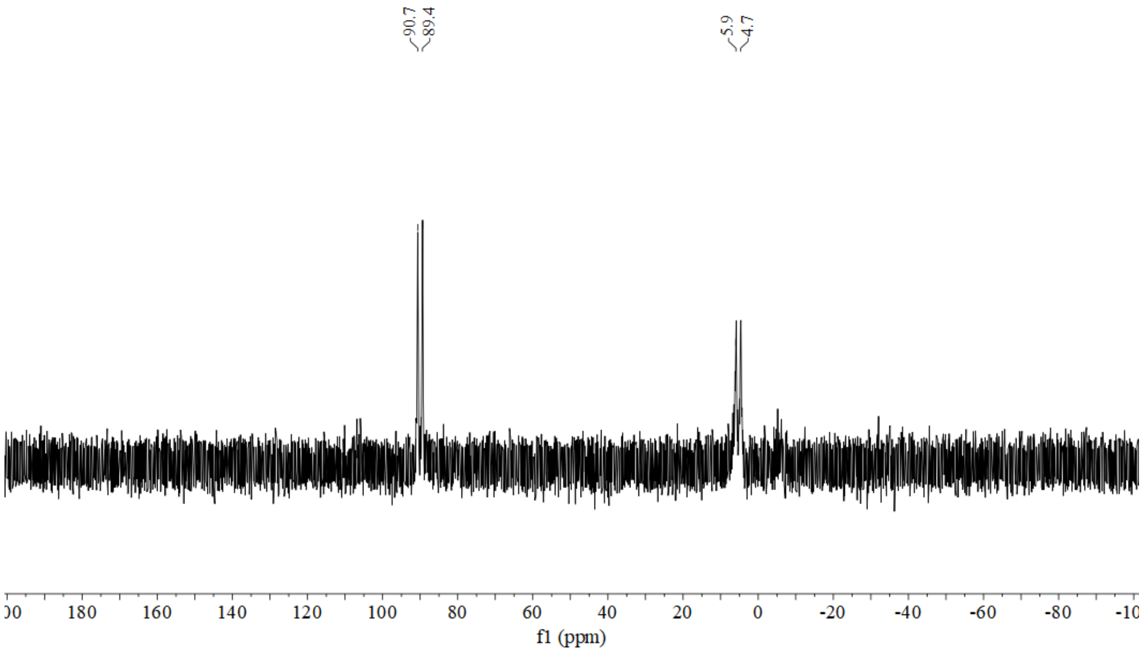


Figure S78. $^{31}P\{^1H\}$ NMR of **8b** in C_6D_6.

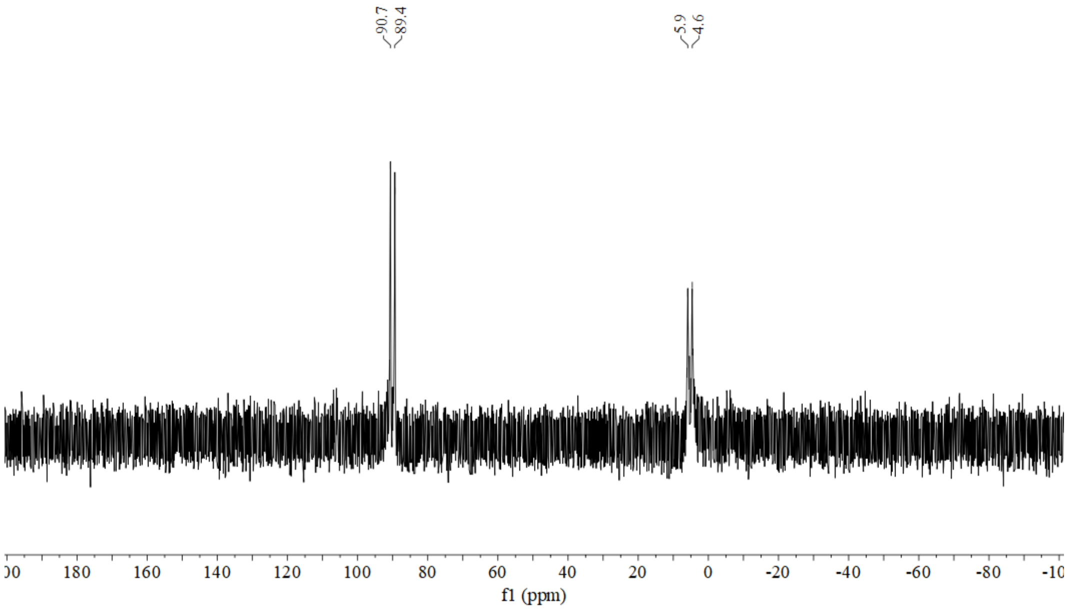


Figure S79. $^{31}P\{^1H\}$ NMR of **8b** in C_6D_6.

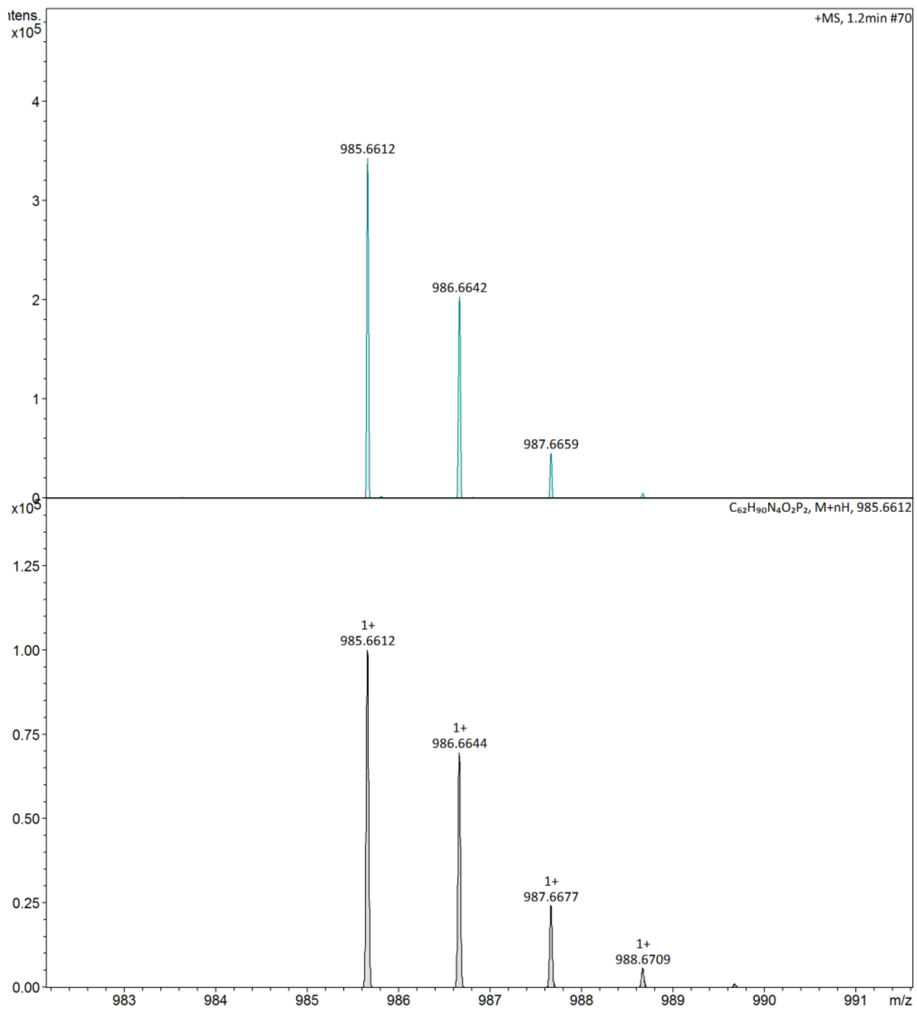


Figure S80. HRMS of **8b**.

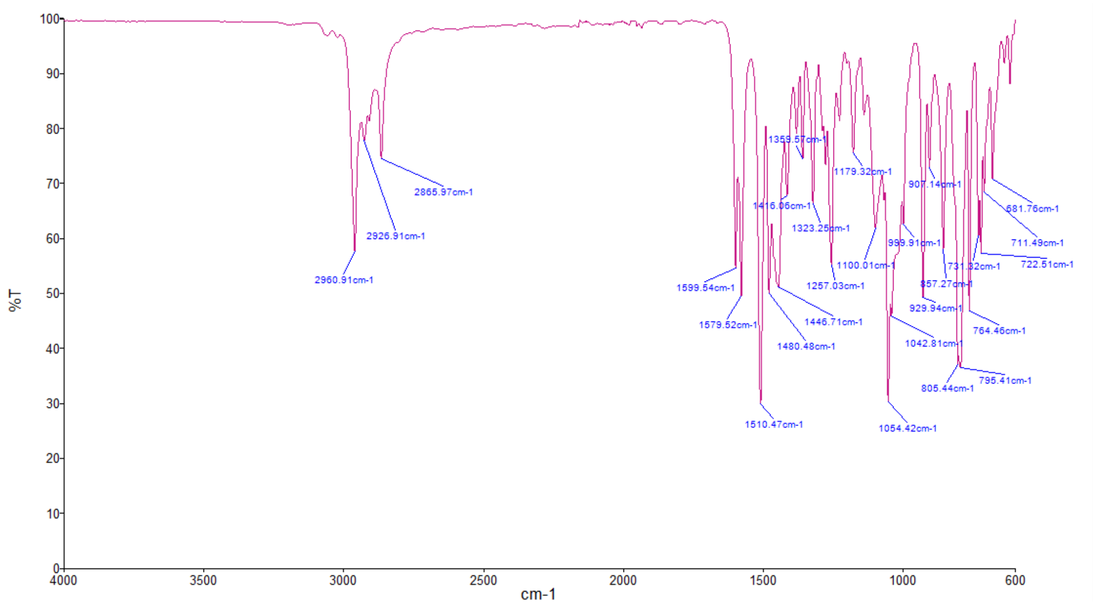
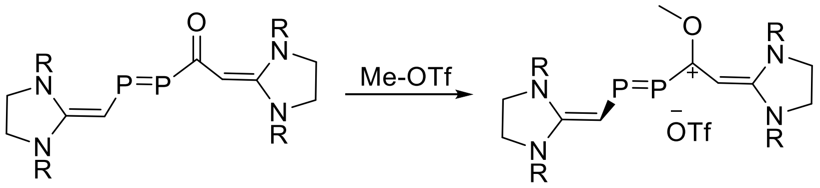


Figure S81. IR spectrum of **8b**.

Synthesis of 9a:



3a, R = Dipp **9a**, R = Dipp

Methyl trifluoromethanesulfonate (Me-OTf) (18 mg, 0.1 mmol) in hexane (10 mL) was added to a stirred solution of **3a** (100 mg, 0.1 mmol) in hexane (30 mL) at room temperature. After stirring at room temperature for 0.5 h, the resulting precipitates were collected via filtration, then washed with hexane (2 × 1 mL) and dried *in vacuo* to afford **9a** (103 mg, yield = 99 %) as a purple powder. M. p. 115 °C (Decomposition). ^{1}H NMR (400.1 MHz, CD_3CN): δ = 7.46-7.41(m, 4 H, $C_{Ar}H$), 7.30 (d, J = 7.8 Hz, 4 H, $C_{Ar}H$), 7.24 (d, J = 7.8 Hz, 4 H, $C_{Ar}H$), 6.11 (t, $^2J_{PH} \approx {}^3J_{PH}$ = 14.1 Hz, 1 H, C*H*PP), 4.85 (s, 1 H, C*H*CO), 4.05 (s, 4 H, NCH_2), 3.97 (s, 4 H, NCH_2), 3.01 (m, 4 H, $CH(CH_3)_2$), 2.93 (m, 4 H, $CH(CH_3)_2$), 2.82 (s, 3 H, $PCO(CH_3)$)), 1.27 (d, J = 6.8 Hz, 24 H, $CH(CH_3)_2$), 1.08 (d, J = 6.8 Hz, 12 H, $CH(CH_3)_2$), 1.01 (d, J = 6.8 Hz, 12 H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (150.8 MHz, CD_3CN): δ = 195.0 (d, $^1J_{PC}$ = 84.6 Hz, $^2J_{PC}$ = 18.5 Hz, -PP(O)C^+), 162.7 (m, N*C*N), 161.6 (N*C*N), 148.3 (C_{Ar}), 146.6 (C_{Ar}), 134.4 (C_{Ar}), 133.8 (C_{Ar}), 131.4 (C_{Ar}), 130.9 (C_{Ar}), 126.1 (CF_3), 126.0 (C_{Ar}), 103.9 (t, $^1J_{PC} \approx {}^2J_{PC}$ = 54.3 Hz, *C*HPP), 87.9 (d, $^2J_{PC}$ = 15.8 Hz, *C*HC(OCH_3)P), 59.6 (d, $^3J_{PC}$ = 24.4 Hz, (CH_3O)CP), 53.4 (NCH_2), 52.2 (NCH_2), 29.7, 29.6, 25.1, 24.8, 24.5, 24.4. ^{31}P{^{1}H} NMR (242.9 MHz, CD_3CN): δ = 471.3 (d, $^1J_{PP}$ = 500.6 Hz, -*P*=P-C^+-), 229.7 (d, $^1J_{PP}$ = 500.6 Hz, -P=*P*-C^+-). ^{31}P NMR (242.9 MHz, CD_3CN): δ = 471.3 (d, $^1J_{PP}$ = 500.6 Hz, -*P*=P-C^+-), 229.7 (d, $^1J_{PP}$ = 500.6 Hz, -P=*P*-C^+-). ^{19}F{^{1}H} NMR (376 MHz, CD_3CN): δ = -79.3. UV/Vis (acetonitrile, λ (nm) ε ($M^{-1}cm^{-1}$)): 569.0(21688). HRMS (ESI, m/z) calc. for: $C_{58}H_{81}N_4OP_2^+$: 911.5880 [M]; found: 911.5881. IR (ATR, cm^{-1}): 2963, 2929, 2870, 1435, 1263, 1030, 805, 637, 539.

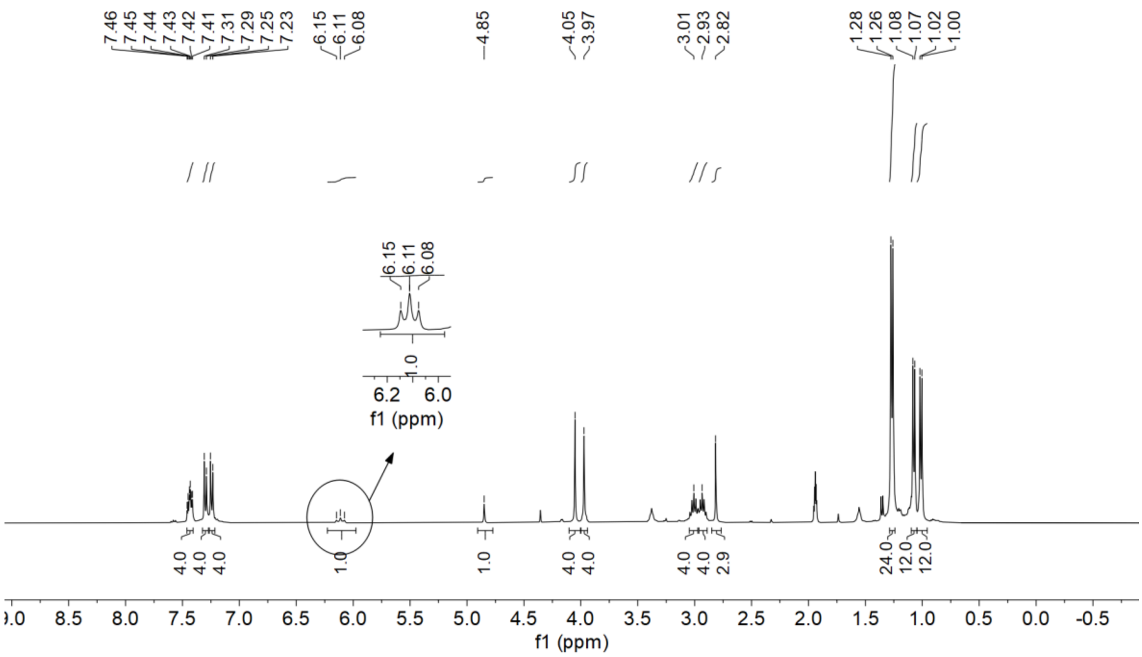


Figure S82. ^{1}H NMR of **9a** in CD_3CN.

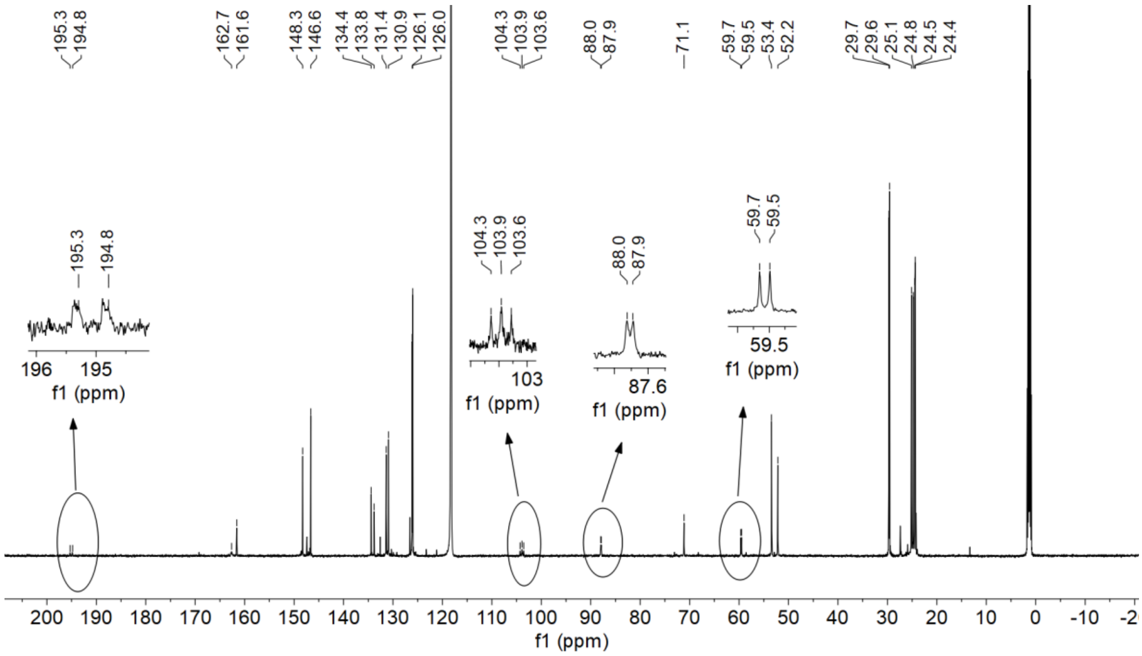


Figure S83. $^{13}C\{^{1}H\}$ NMR of **9a** in CD_3CN.

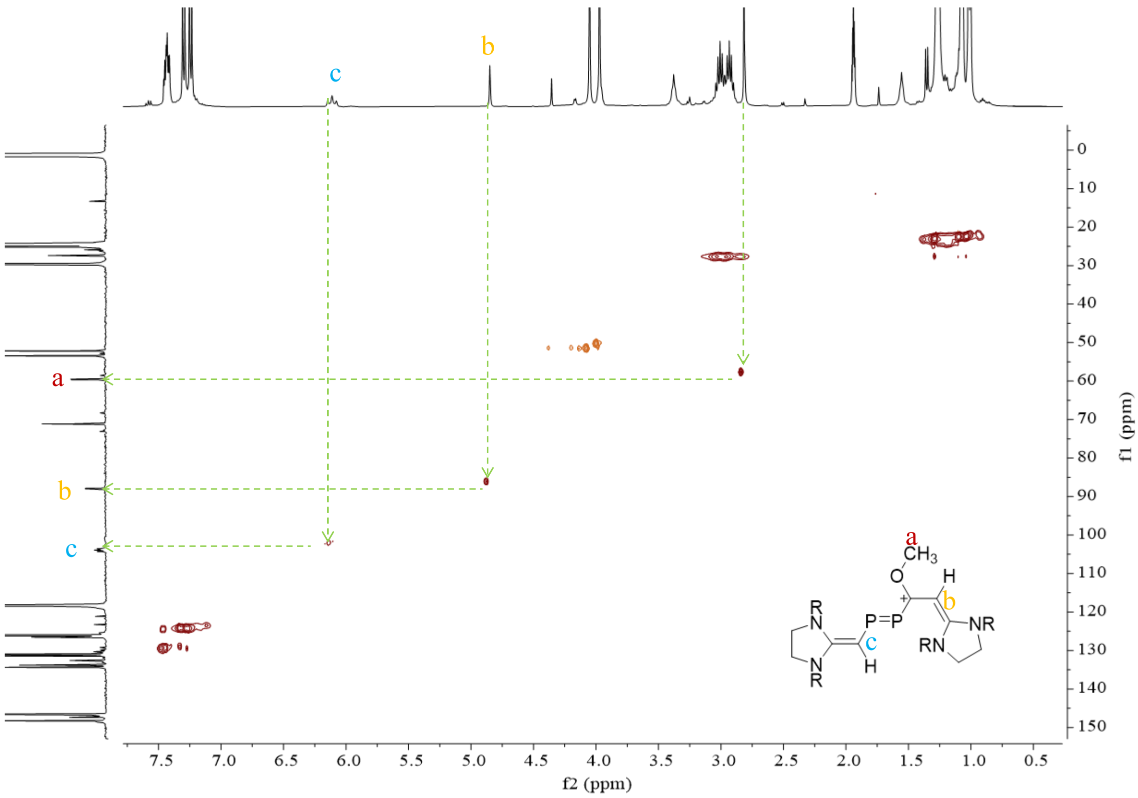


Figure S84. ^{1}H-^{13}C HSQC NMR of **9a** in CD_3CN.

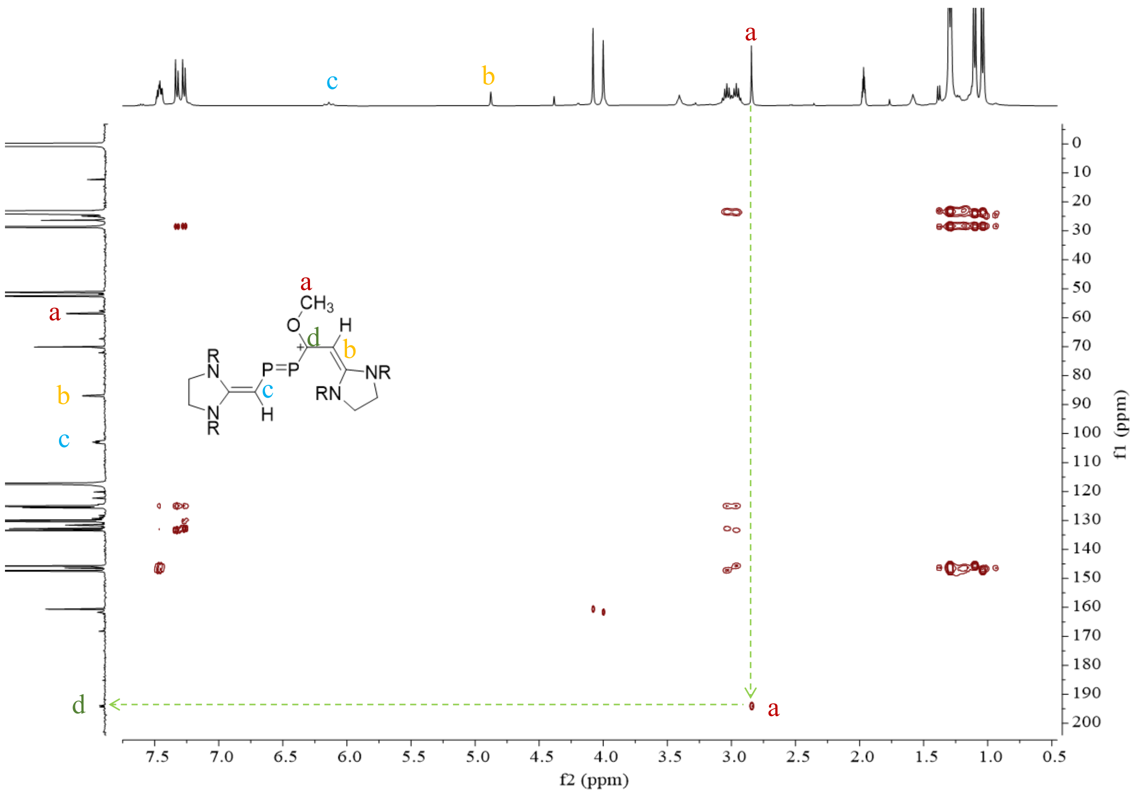


Figure S85. ^{1}H-^{13}C HMBC NMR of **9a** in CD_3CN.

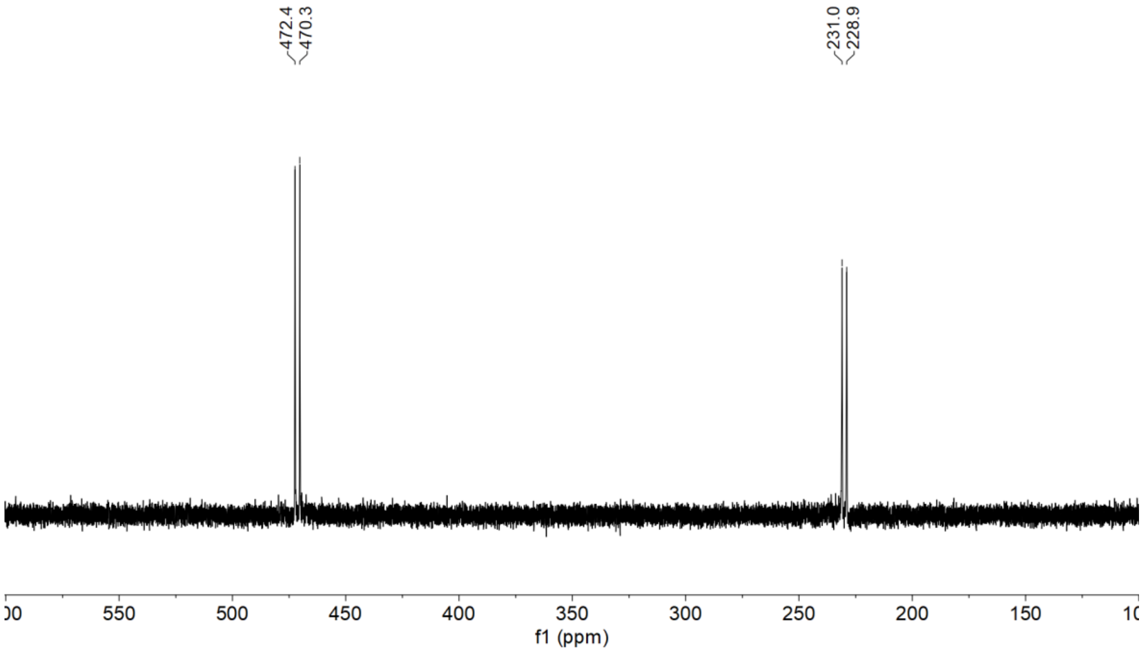


Figure S86. $^{31}P\{^{1}H\}$ NMR of **9a** in CD_3CN.

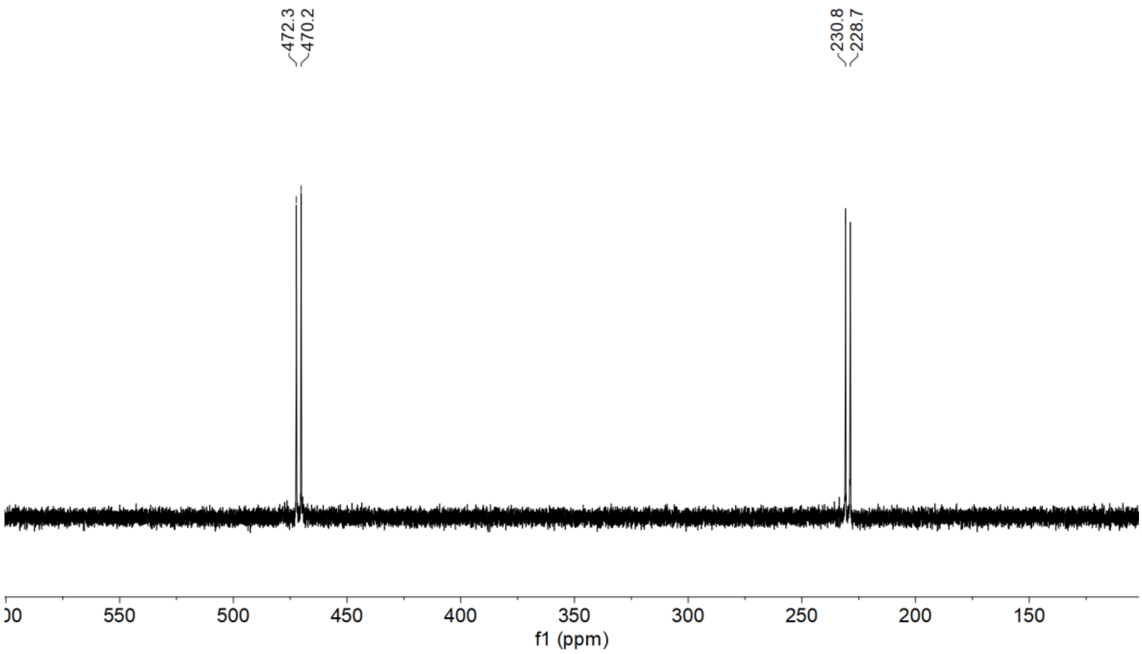


Figure S87. ^{31}P NMR of **9a** in CD_3CN.

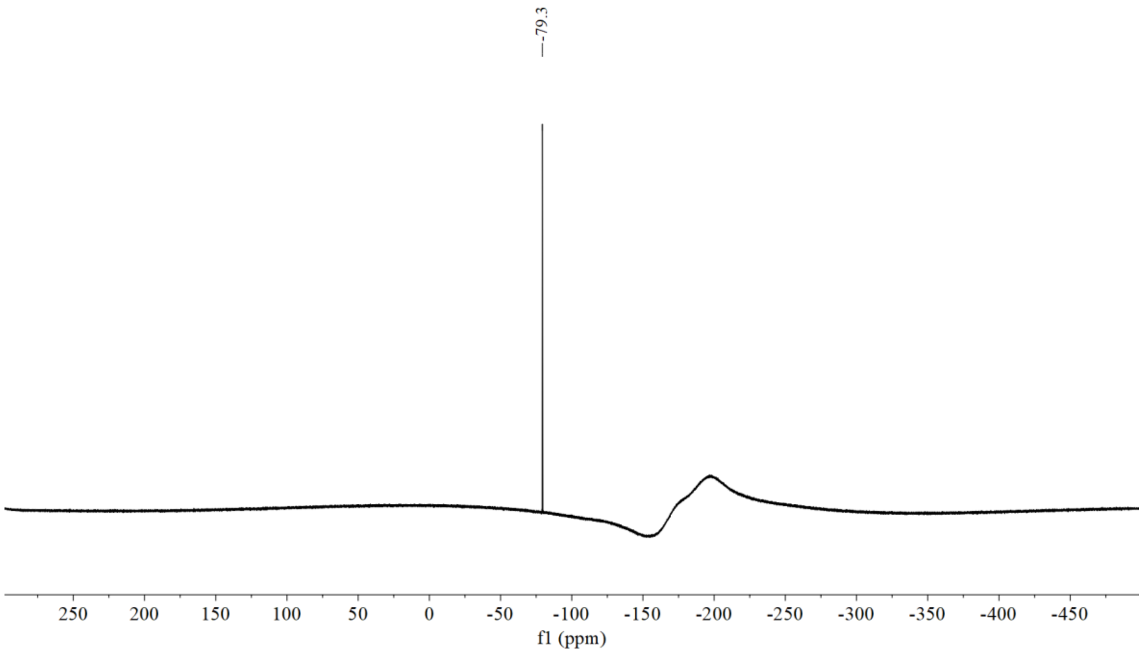


Figure S88. $^{19}F\{^{1}H\}$ NMR of **9a** in CD_3CN.

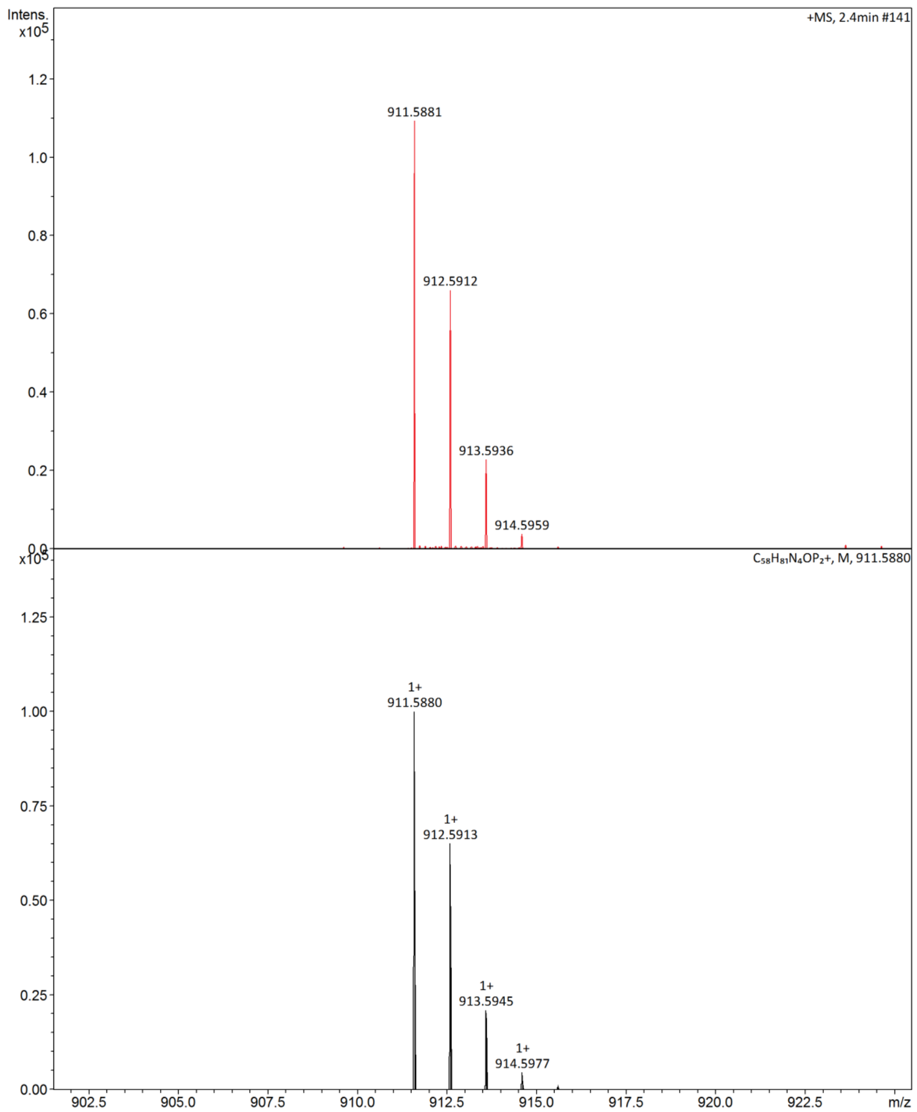


Figure S89. HRMS of **9a**.

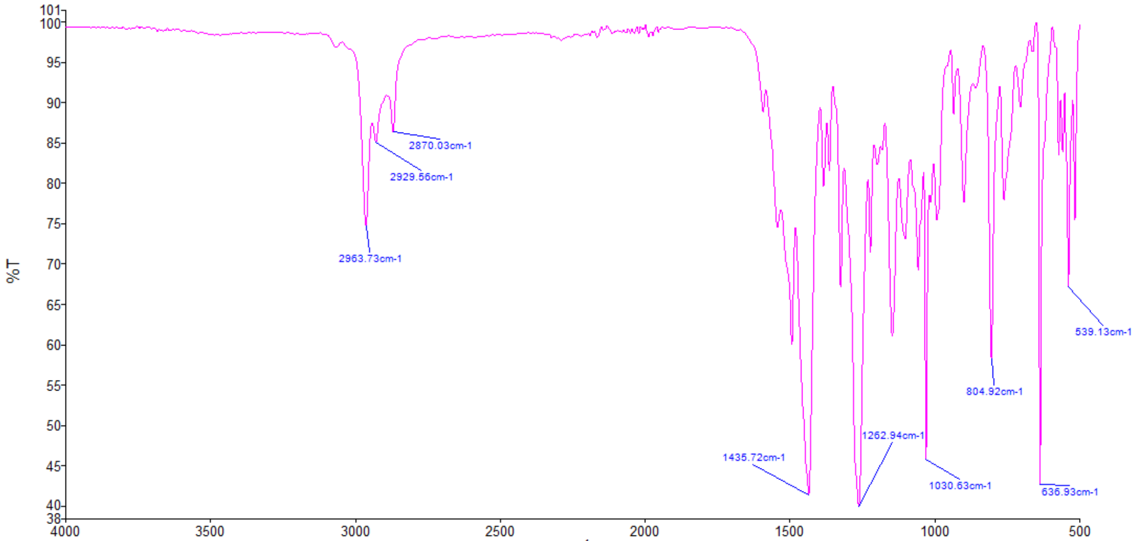
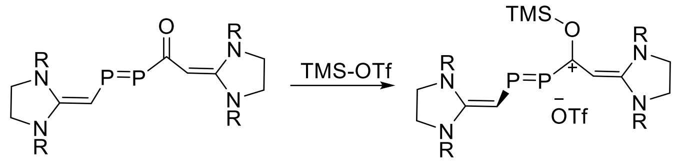


Figure S90. IR spectrum of **9a**.

Synthesis of 9b:



3a, R = Dipp **9b**, R = Dipp

Trimethylsilyl trifluoromethanesulfonate (TMS-OTf) (24 mg, 0.1 mmol) in hexane (10 mL) was added to a stirred solution of **3a** (100 mg, 0.1 mmol) in hexane (30 mL) at room temperature. After stirring at room temperature for 0.5 h, the resulting precipitates were collected via filtration, then washed with hexane (2 × 1 mL) and dried *in vacuo* to afford **9b** (98 mg, yield = 90 %) as a purple powder. ^{1}H NMR (600.2 MHz, CD_3CN): δ = 7.41 (t, J = 7.1 Hz, 2 H, $C_{Ar}H$), 7.33 (t, J = 7.8 Hz, 2 H, $C_{Ar}H$), 7.28 (d, J = 7.1 Hz, 4 H, $C_{Ar}H$), 7.20(d, J = 7.8 Hz, 4 H, $C_{Ar}H$), 6.06 (t, $^{2}J_{PH} \sim {}^{3}J_{PH}$ = 11.0 Hz, 1 H, C*H*-PP), 4.70 (d, $^{3}J_{PH}$ = 19.5 Hz, 1 H, C*H*-C(O)-P), 4.18 (s, 4 H, NCH_2), 3.98 (s, 4 H, NCH_2), 3.07 (m, 4 H, $CH(CH_3)_2$), 2.89 (m, 4 H, $CH(CH_3)_2$), 1.28 (d, J = 7.0 Hz, 12 H, $CH(CH_3)_2$), 1.20 (d, J = 6.8 Hz, 12 H, $CH(CH_3)_2$), 1.11~1.09 (m, 24 H, $CH(CH_3)_2$), -0.34 (s, 9 H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (150.8 MHz, CD_3CN): δ = 188.1(m, ^{+}C-O-), 167.7 (N*C*N), 163.1 (N*C*N), 148.5 (C_{Ar}), 147.3 (C_{Ar}), 134.5 (C_{Ar}), 133.2 (C_{Ar}), 131.4 (C_{Ar}), 131.1 (C_{Ar}), 126.1 (CF_3), 126.0 (C_{Ar}), 101.0 (t, $^{1}J_{PC} = {}^{2}J_{PC}$ = 51.7 Hz, =*C*HPP), 98.8 (d, $^{2}J_{PC}$ = 22.2 Hz, =*C*HC(OTMS)P), 53.3 (NCH_2), 52.2 (NCH_2), 29.7, 29.6, 26.1, 24.9, 24.5, 23.9, 0.2 ($Si(CH_3)_3$). ^{31}P{^{1}H} NMR (242.9 MHz, CD_3CN): δ = 477.5 (d, 493.4 Hz, CH*P*P), 252.0 (d, 493.4 Hz, CHP*P*). ^{31}P NMR (242.9 MHz, CD_3CN): δ = 477.5 (d, 493.4 Hz, CH*P*P), 252.0 (d, 493.4 Hz, CHP*P*). ^{19}F{^{1}H} NMR (565 MHz, CD_3CN): δ = -79.3. UV/Vis (acetronitrile, λ (nm) ε ($M^{-1}cm^{-1}$)): 426.5 (11963), 555.0 (21071). HRMS (ESI, m/z) calc. for: $C_{60}H_{87}N_4SiOP_2^{+}$: 969.6119 [M]; found: 969.6115. IR (ATR, cm^{-1}): 2962, 2928, 2869, 1508, 1499, 1459, 1273, 1148, 1031, 804, 637.

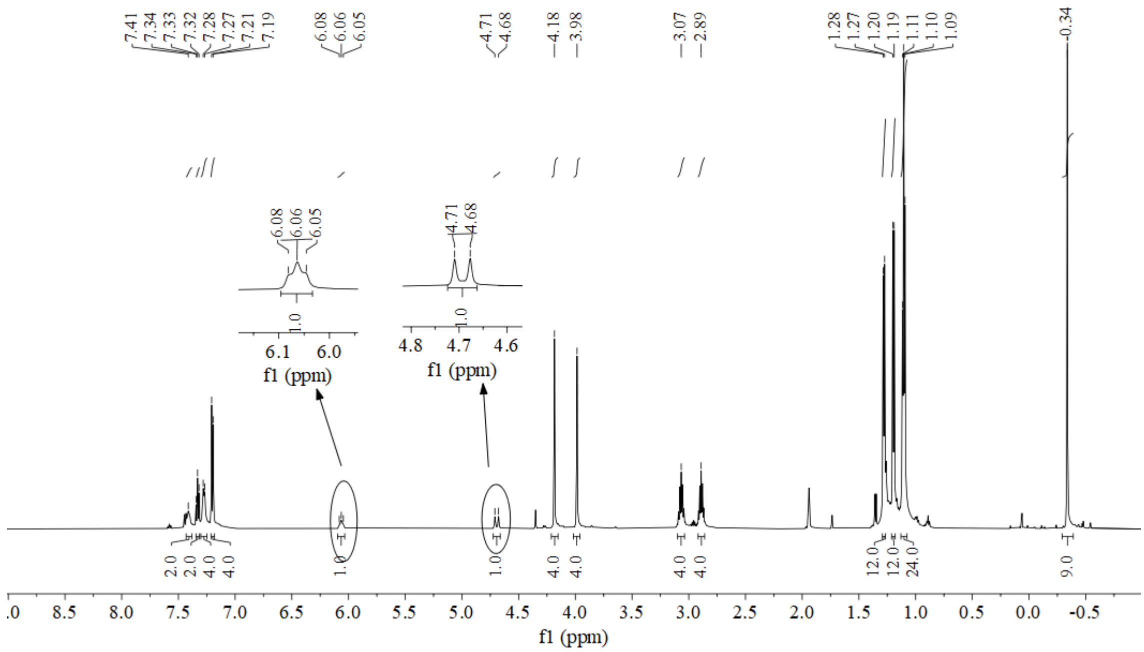


Figure S91. [1]H NMR of **9b** in CD_3CN.

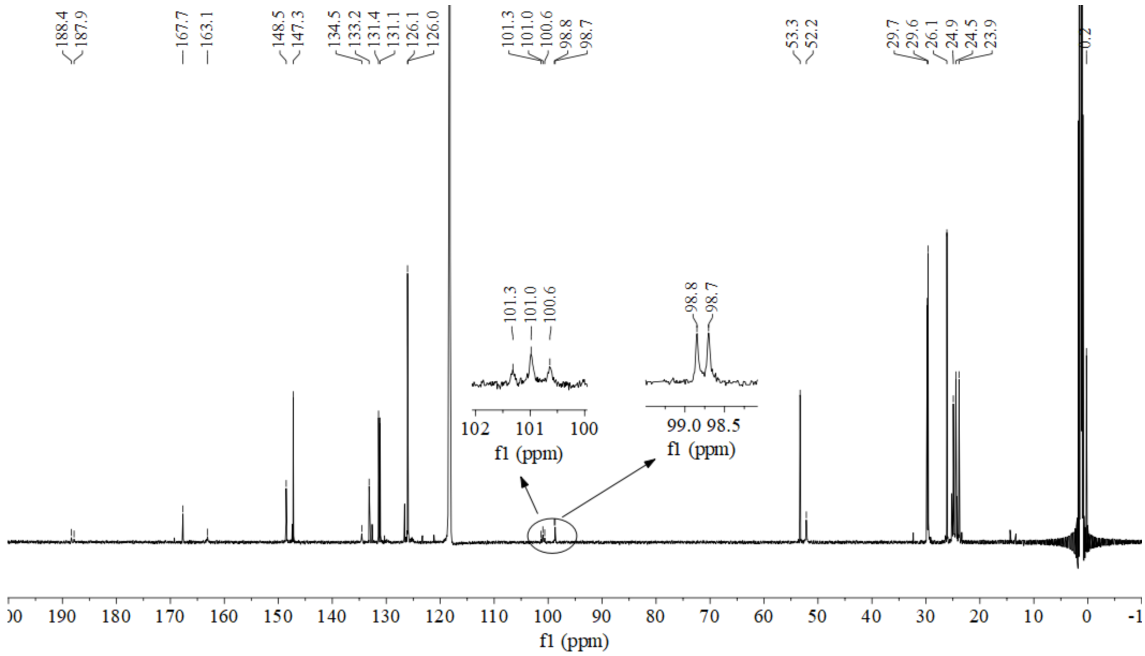


Figure S92. $^{13}C\{^1H\}$ NMR of **9b** in CD_3CN.

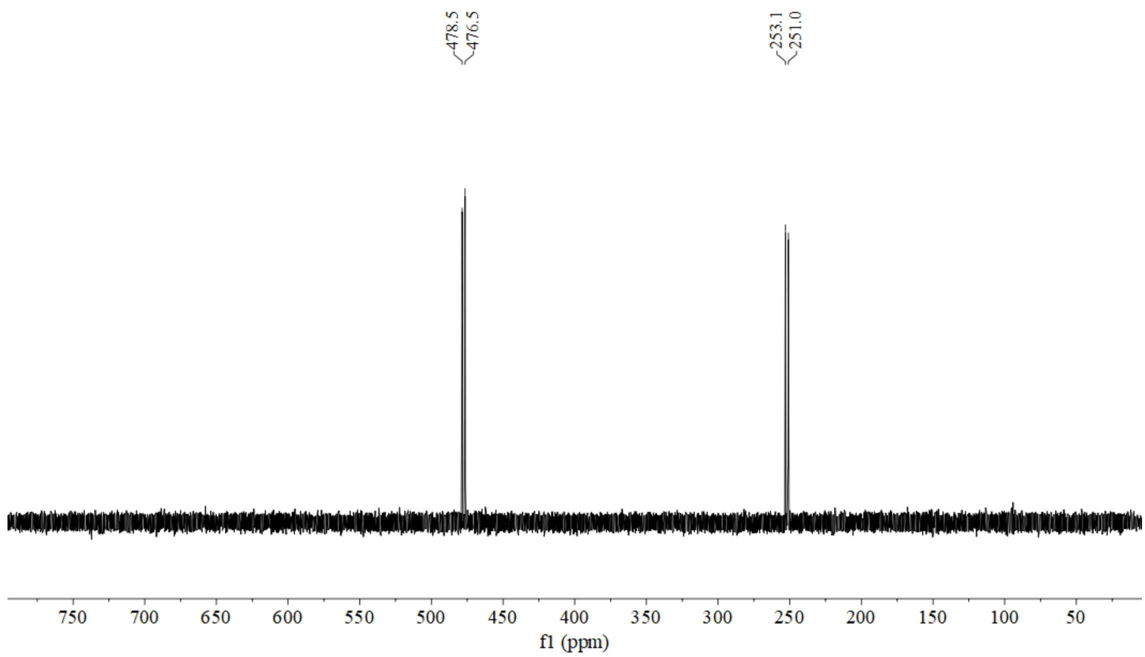


Figure S93. $^{35}P\{^{1}H\}$ NMR of **9b** in CD_3CN.

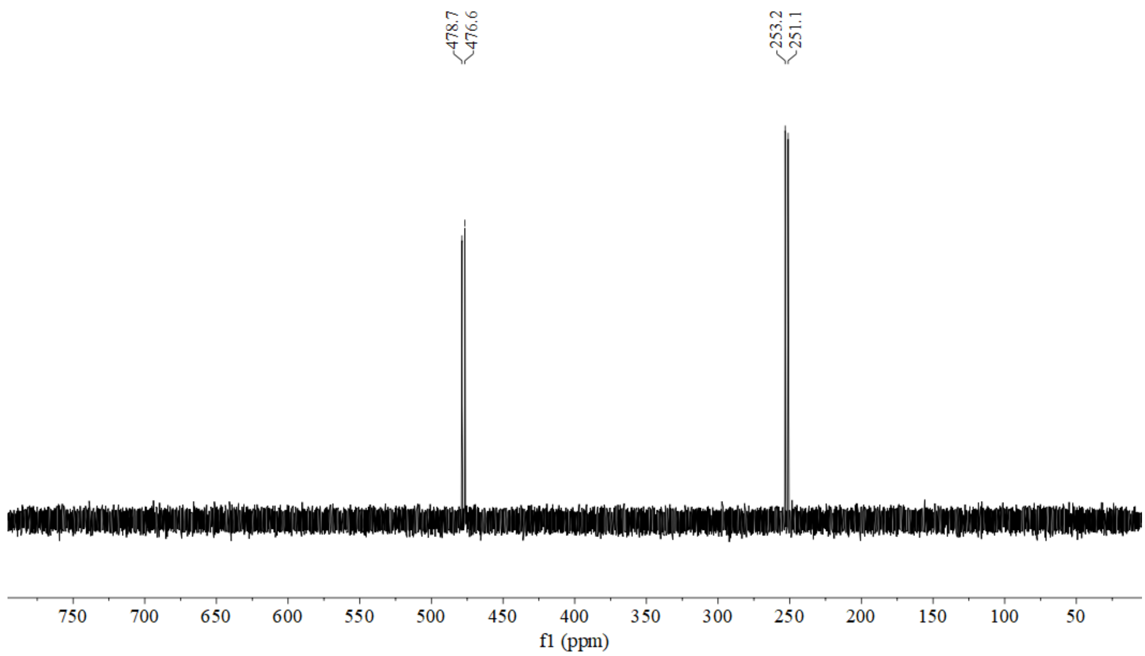


Figure S94. $^{35}P\{^{1}H\}$ NMR of **9b** in CD_3CN.

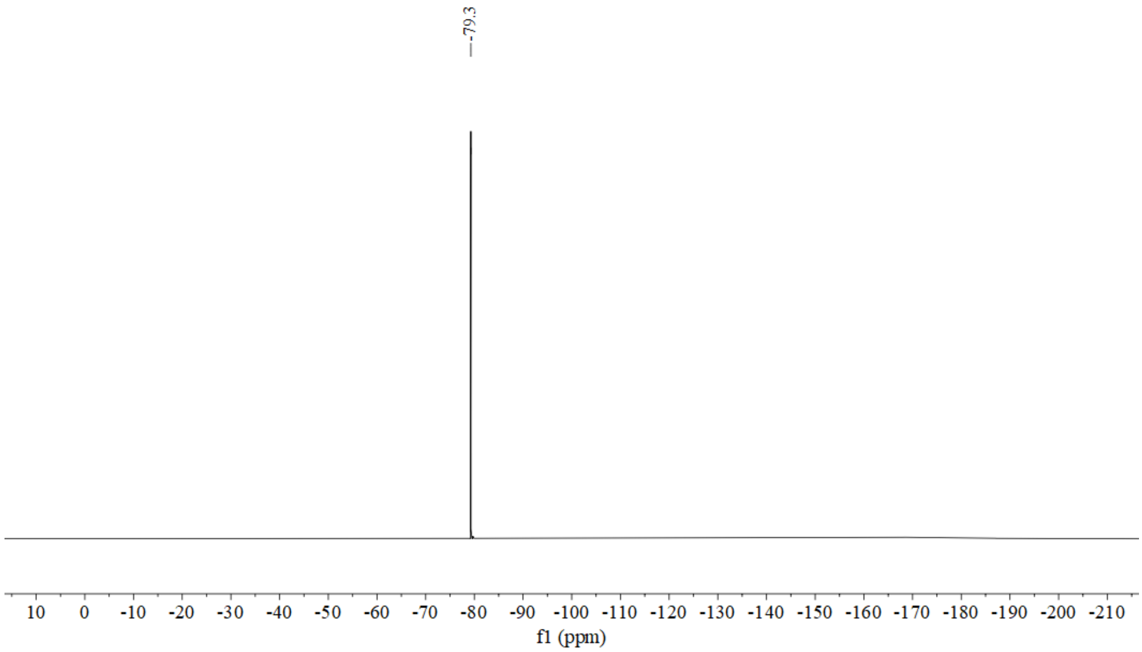


Figure S95. $^{19}F\{^{1}H\}$ NMR of **9b** in CD_3CN.

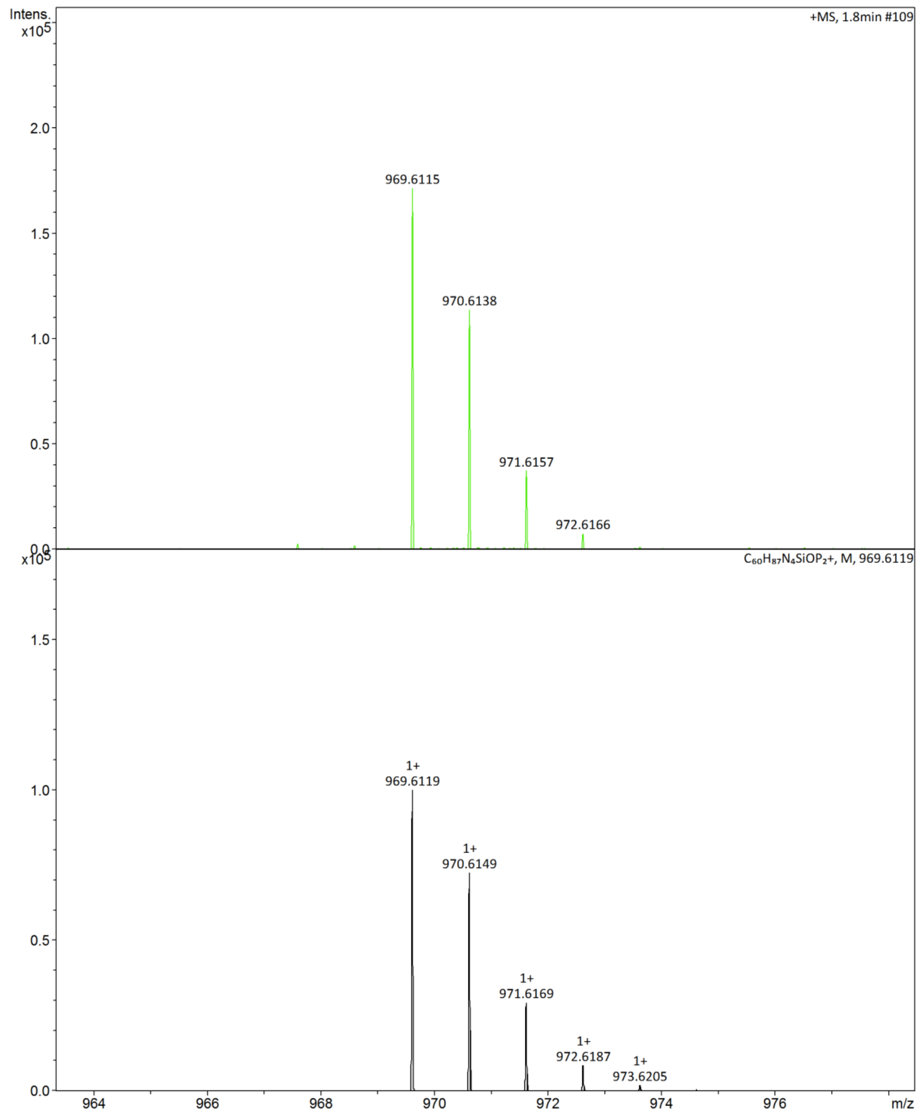


Figure S96. HRMS of **9b**.

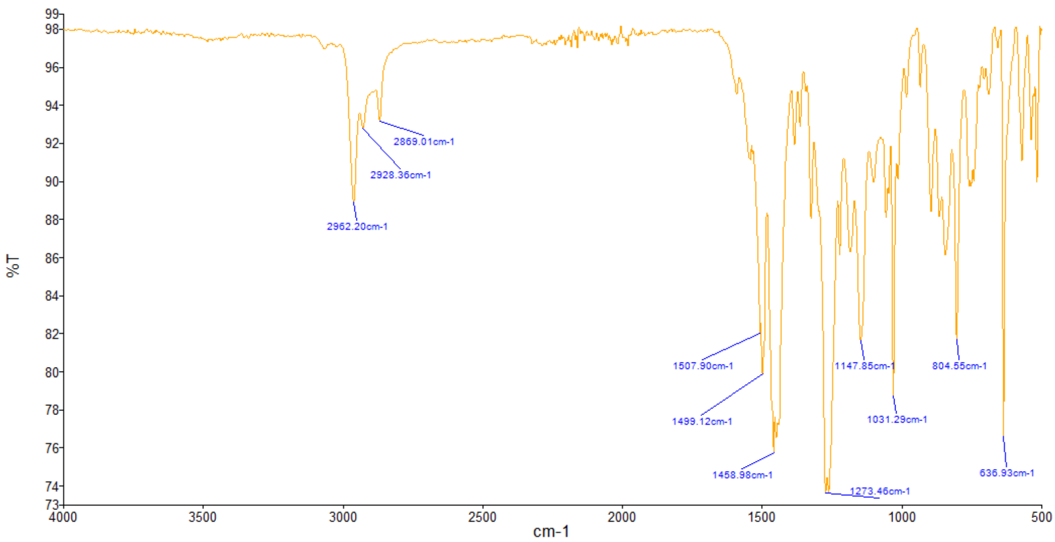
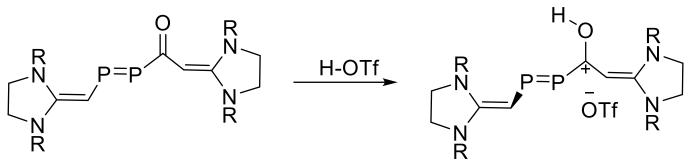


Figure S97. IR spectrum of **9b**.

Synthesis of S2:



3a, R = Dipp   **S2**, R = Dipp

Trifluoromethanesulfonic acid (H-OTf) (3 mg, 0.02 mmol) in acetonitrile (0.1 mL) was added slowly to a stirred solution of **3a** (18 mg, 0.02 mmol) in tetrahydrofuran (1 mL) at room temperature. The reaction mixture was monitored with NMR spectroscopy revealing that **S2** was too unstable to be isolated. $^{31}P\{^{1}H\}$ NMR (161.9 MHz): δ = 509.2 (d, $^{1}J_{PP}$ = 503.6 Hz), 267.9 (d, $^{1}J_{PP}$ = 503.6 Hz). ^{31}P NMR (161.9 MHz): δ = 509.2 (d, $^{1}J_{PP}$ = 503.6 Hz), 267.9 (d, $^{1}J_{PP}$ = 503.6 Hz).

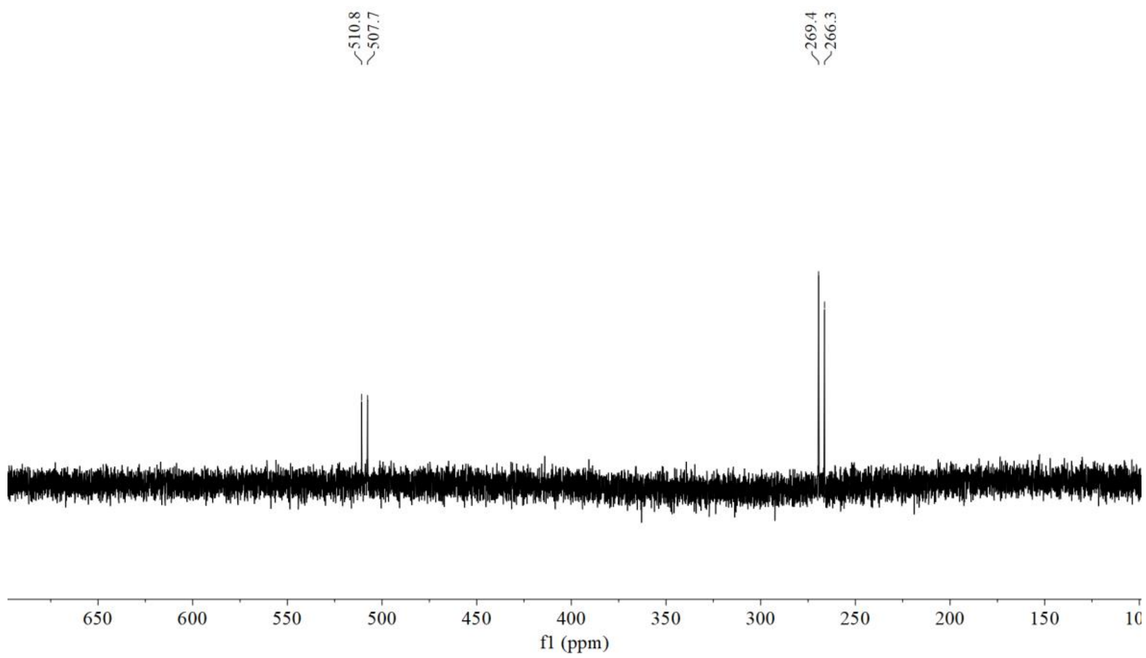


Figure S98. $^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture.

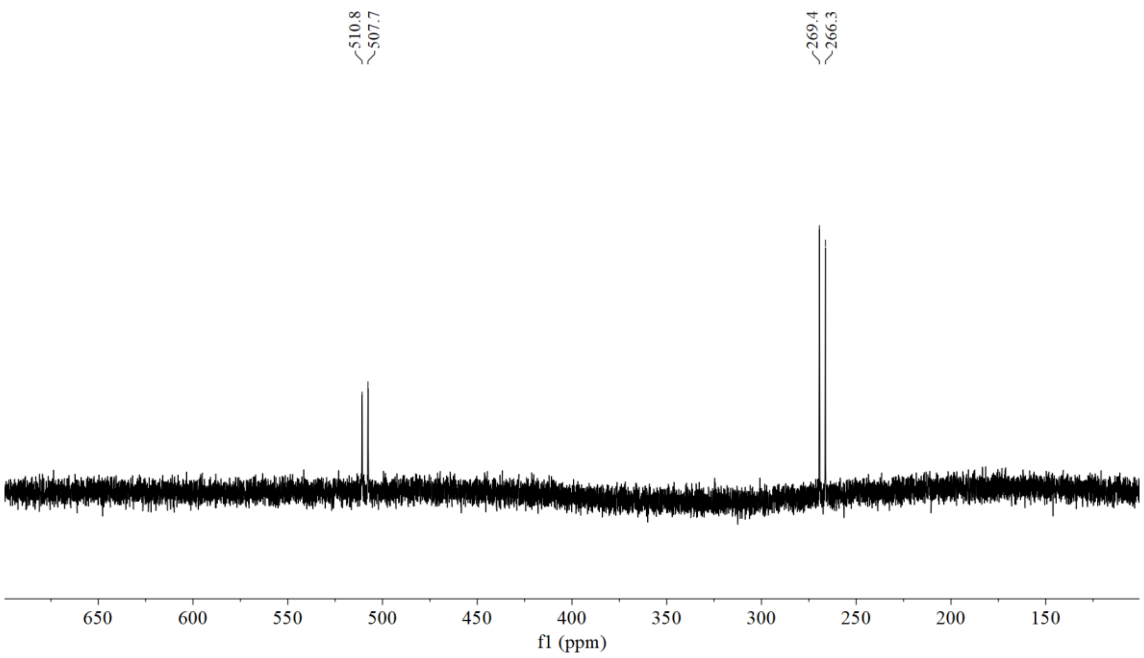


Figure S99. ^{31}P NMR spectrum of the reaction mixture.

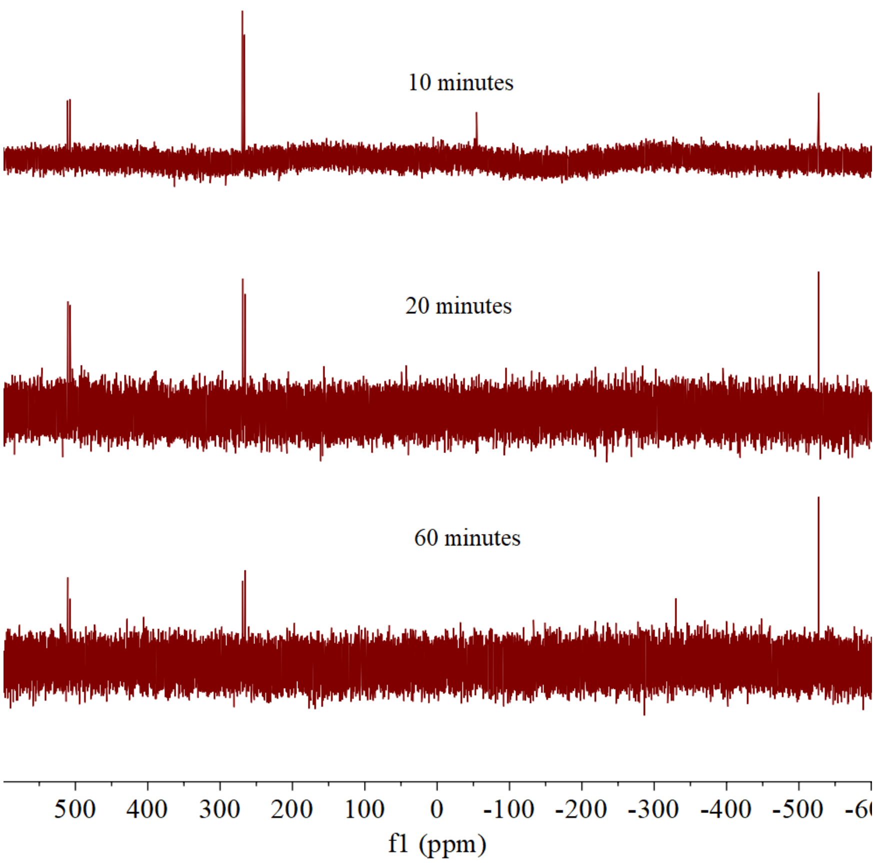
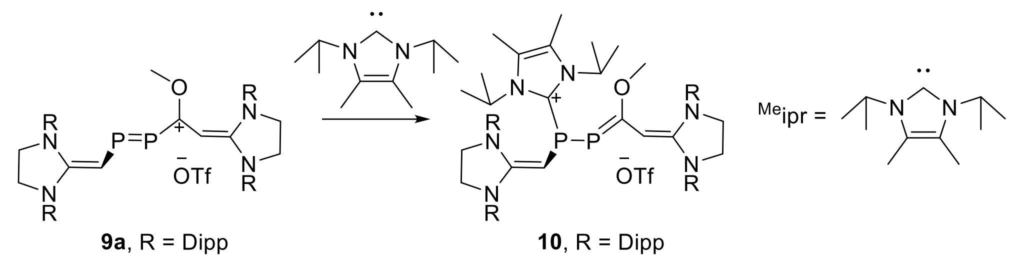


Figure S100 ^{31}P{^{1}H} NMR spectra the reaction mixture within one hour.

Synthesis of 10:



4,5-Dimethyl-1,3-diisopropylimidazol-2-ylidene (^{Me}ipr, 16 mg, 0.1 mmol) in tetrahydrofuran (4 mL) was added to a stirred solution of **9a** (100 mg, 0.1 mmol) in tetrahydrofuran (20 mL) at room temperature. After stirring at room temperature for 0.5 h, the solvent was removed *in vacuo*, the residue was dispersed in hexane (6 mL). The resulting precipitates were collected via filtration, and then washed with hexane (2 × 1 mL) and dried *in vacuo* to afford **10** (102 mg, yield = 88 %) as a dark red powder. M. p. 102 °C (decompose). ^{1}H NMR (600.2 MHz, CD_2Cl_2): δ = 7.36 (t, *J* = 7.7 Hz, 2 H, $C_{Ar}H$), 7.30 (t, *J* = 7.7 Hz, 1 H, $C_{Ar}H$), 7.27 – 7.23 (m, 2 H, $C_{Ar}H$), 7.21 (d, *J* = 8.0 Hz, 3 H, $C_{Ar}H$), 7.13 (m, 2 H, $C_{Ar}H$), 7.08 (d, *J* = 7.5 Hz, 1 H, $C_{Ar}H$), 7.02 (d, *J* = 7.6 Hz, 1 H, $C_{Ar}H$), 5.15 (br., 1 H, =C(CH_3)), 4.98 (br., 1 H, =C(CH_3)), 4.51 (m, 1 H, $CH(CH_3)_2$), 4.40 (d, $^{1}J_{PC}$ = 7.4 Hz, 1 H, =CHPP), 3.99 (m, 1 H, $CH(CH_3)_2$ or/and NCH_2), 3.88 (m, 3 H, $CH(CH_3)_2$ or/and NCH_2), 3.75 (m, 2 H, $CH(CH_3)_2$ or/and NCH_2), 3.60 (m, 1 H, $CH(CH_3)_2$ or/and NCH_2), 3.55 (m, 1 H, $CH(CH_3)_2$ or/and NCH_2), 3.36 (m, 1 H, $CH(CH_3)_2$ or/and NCH_2), 3.20 (m, 1 H, $CH(CH_3)_2$ or/and NCH_2), 3.11 (m, 3 H, $CH(CH_3)_2$ or/and NCH_2), 2.88 (m, 3 H, $CH(CH_3)_2$ or/and NCH_2), 2.54 (d, $^{2}J_{PC}$ = 4.5 Hz, 1 H, =CHC(OCH_3)PP), 2.42 (s, 2 H, =C(CH_3)), 2.30 (s, 2 H, =C(CH_3)), 2.14 (br., 4 H, -PCO(CH_3) & $CH(CH_3)_2$), 1.63 (d, *J* = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.35 – 1.18 (m, 48 H, $CH(CH_3)_2$), 1.01 (m, 6 H, $CH(CH_3)_2$), 0.72 (d, *J* = 6.9 Hz, 3 H, $CH(CH_3)_2$). $^{13}C\{^{1}H\}$ NMR (150.8 MHz, CD_2Cl_2): δ = 205.8 (dd, $^{1}J_{PC}$ = 97.5, $^{2}J_{PC}$ = 9.5 Hz, *C*(OCH_3)), 160.5 (d, $^{2}J_{PC}$ = 39.3 Hz, N*C*N), 156.2 (d, $^{3}J_{PC}$ = 18.0 Hz, N*C*N), 152.8 (d, $^{1}J_{PP}$ = 80.8 Hz, NCN), 149.5 (C_{Ar}), 149.2 (C_{Ar}), 148.0 (C_{Ar}), 147.9 (C_{Ar}), 147.0 (C_{Ar}), 146.8 (C_{Ar}), 146.2 (C_{Ar}), 138.6 (C_{Ar}), 134.9 (C_{Ar}), 128.9 (C_{Ar}), 128.6 (C_{Ar}), 128.1 (C_{Ar}), 126.3 (CF_3), 124.9 (C_{Ar}), 124.8 (C_{Ar}), 124.6 (C_{Ar}), 124.5 (C_{Ar}), 124.0 (C_{Ar}), 123.4 (C_{Ar}), 81.4 (dd, $^{1}J_{PC}$ = 52.2, $^{2}J_{PC}$ = 9.3 Hz, =*C*HPP), 60.6 (d, $^{1}J_{PC}$ = 24.3 Hz, =*C*HC(OCH_3)PP), 52.2 (NCH_2), 51.6 (NCH_2), 51.0 (NCH_2), 50.7 (d, $^{3}J_{PC}$ = 5.6 Hz, N*C*(CH_3)), 50.5 (d, $^{3}J_{PC}$ = 5.6 Hz, N*C*(CH_3)), 49.5 (N*C*H_2), 28.7, 28.5, 28.4, 28.3, 28.2, 25.6, 25.5, 24.9, 24.5, 24.4, 24.3, 24.1, 24.1, 23.8, 23.4, 23.3, 22.7, 22.6, 22.6, 22.2, 8.4. $^{31}P\{^1H\}$ NMR (242.9 MHz, CD_2Cl_2): δ = 35.0 (d, $^1J_{PP}$ = 265.2 Hz, =CH*P*PC(OCH_3)), -54.1 (d, $^1J_{PP}$ = 265.2 Hz, =CHP*P*C(OCH_3)). ^{31}P NMR (242.9 MHz, CD_2Cl_2): δ = 35.0 (d, *J* = 265.2 Hz, =CH*P*PC(OCH_3)), -54.1 (d, *J* = 265.2 Hz, =CH*P*PC(OCH_3)). $^{19}F\{^1H\}$ NMR (565 MHz, CD_2Cl_2): δ = -79.3. UV/Vis (acetonitrile, λ (nm) ε ($M^{-1}cm^{-1}$)): 390.5 (3322), 464.0 (4546). HRMS (ESI, m/z) calc. for: $C_{69}H_{101}N_6OP_2^+$: 1091.7507 [M]; found: 1091.7501. IR (ATR, cm^{-1}): 2962, 2930, 2868, 1507, 1480, 1456, 1262, 1146, 1031, 805, 637.

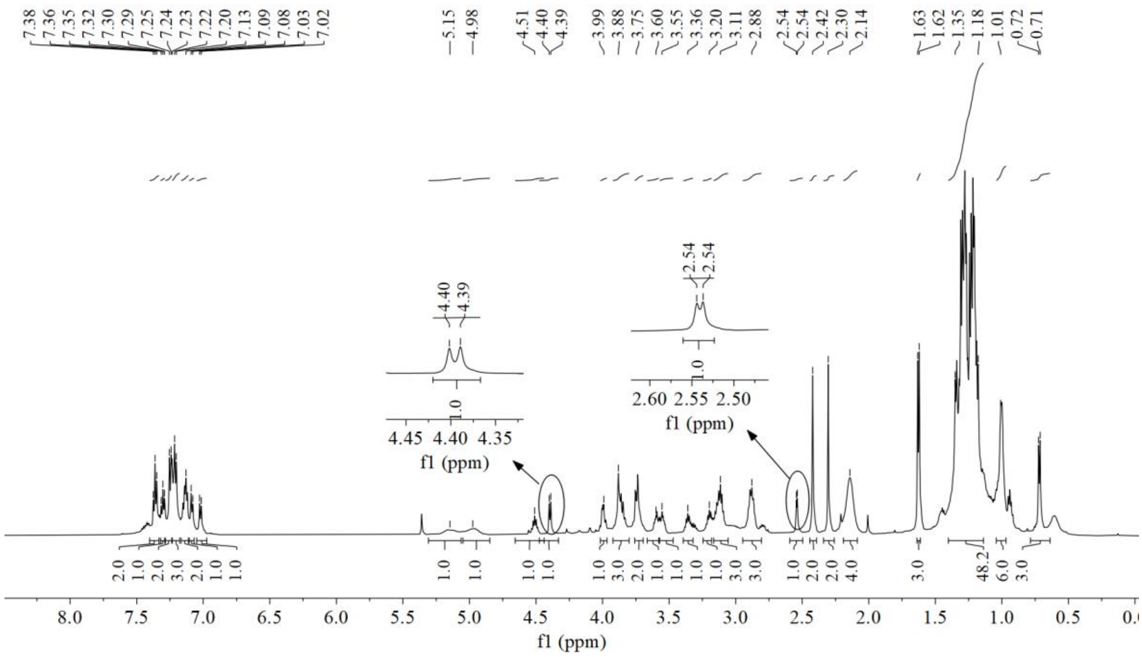


Figure S101. ^1H NMR of **10** in CD_2Cl_2.

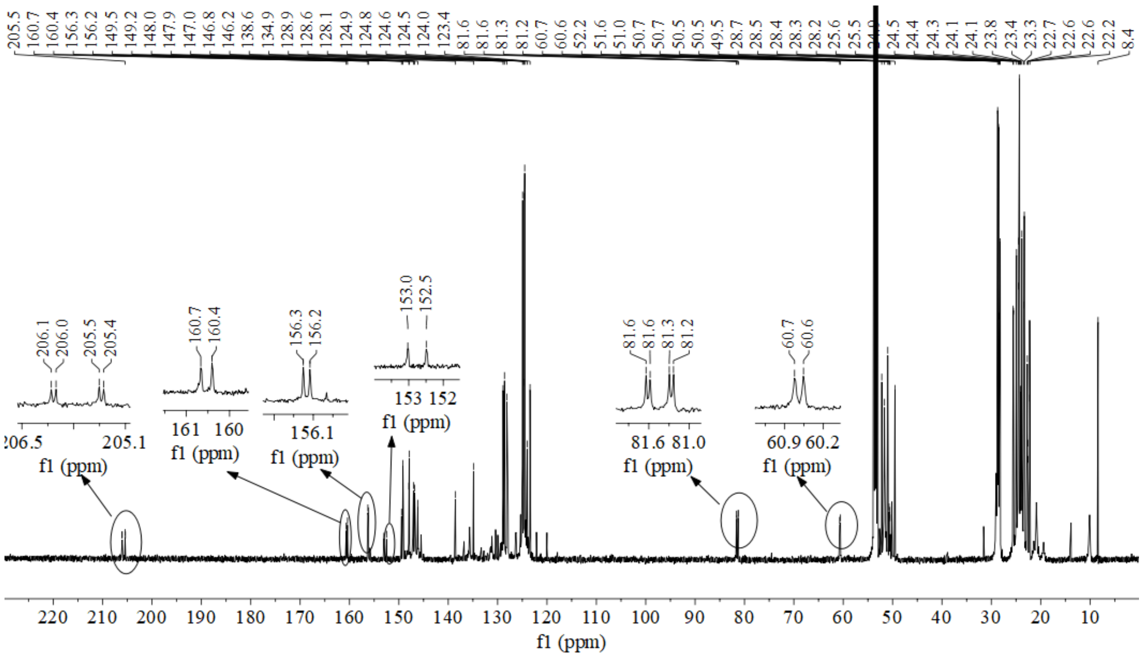


Figure S102. $^{13}C\{^1H\}$ NMR of **10** in CD_2Cl_2.

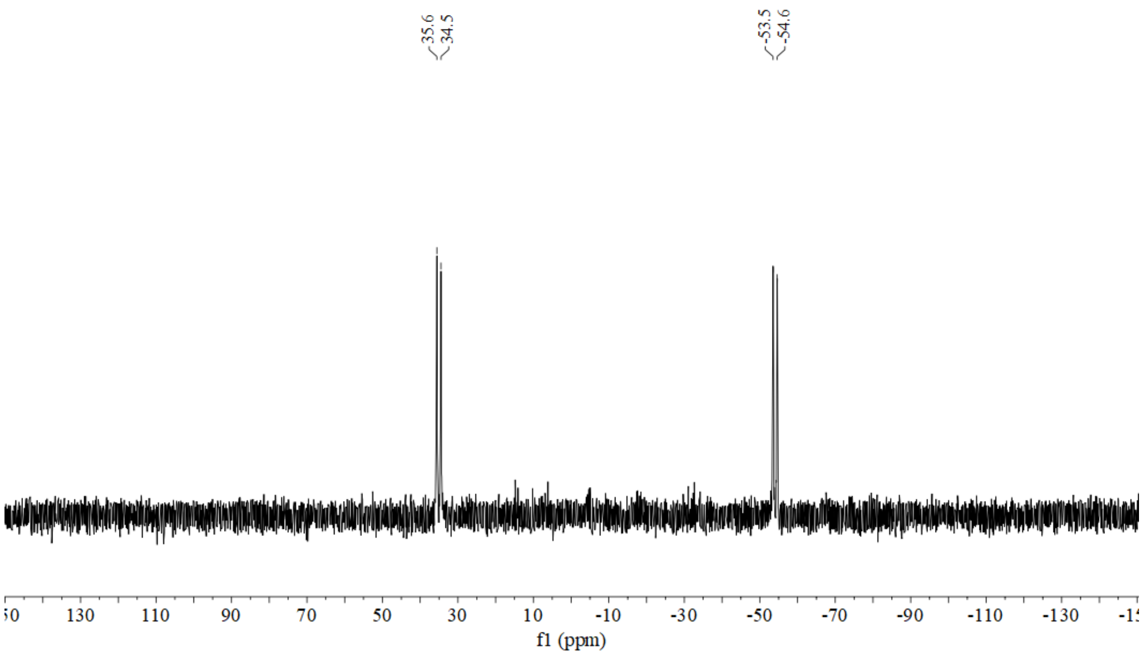


Figure S103. $^{31}P\{^1H\}$ NMR of **10** in CD_2Cl_2.

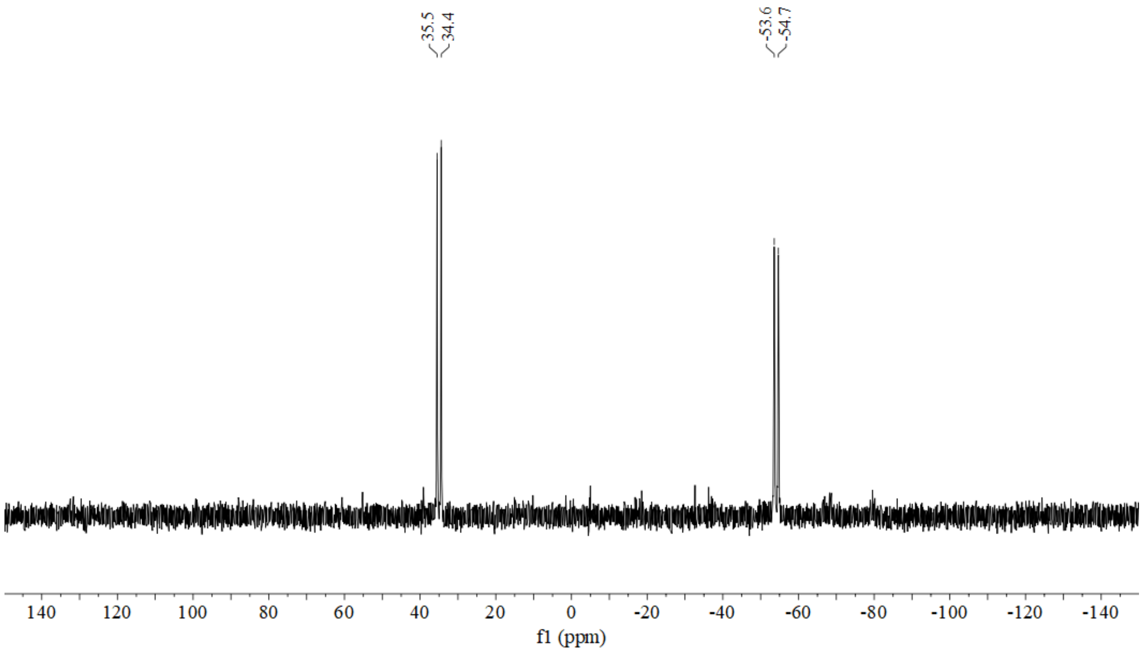


Figure S104. ^{31}P NMR of **10** in CD_2Cl_2.

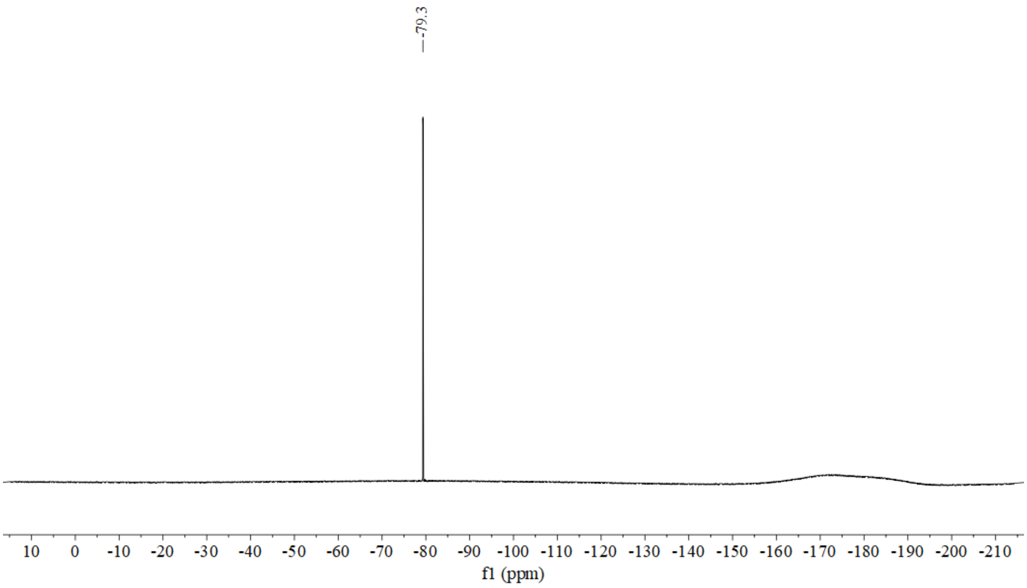


Figure S105. ^{19}F{^{1}H} NMR of **10** in CD_2Cl_2.

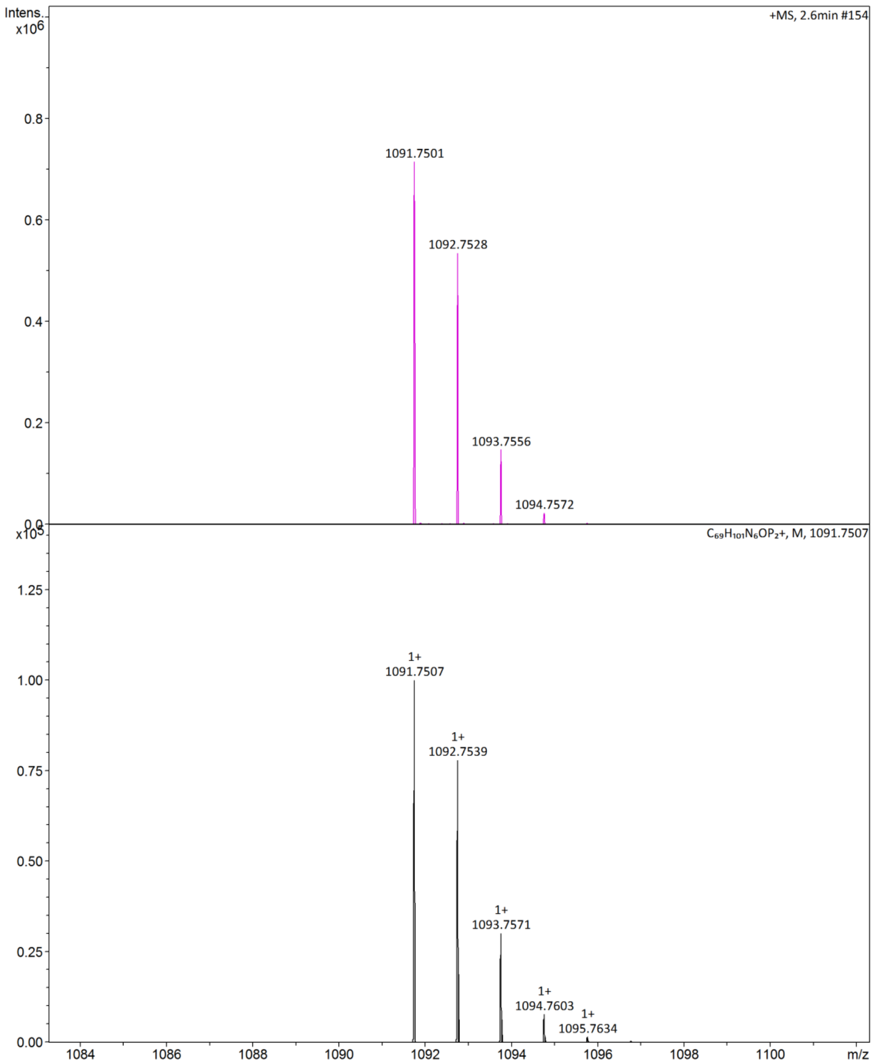


Figure S106. HRMS of **10**.

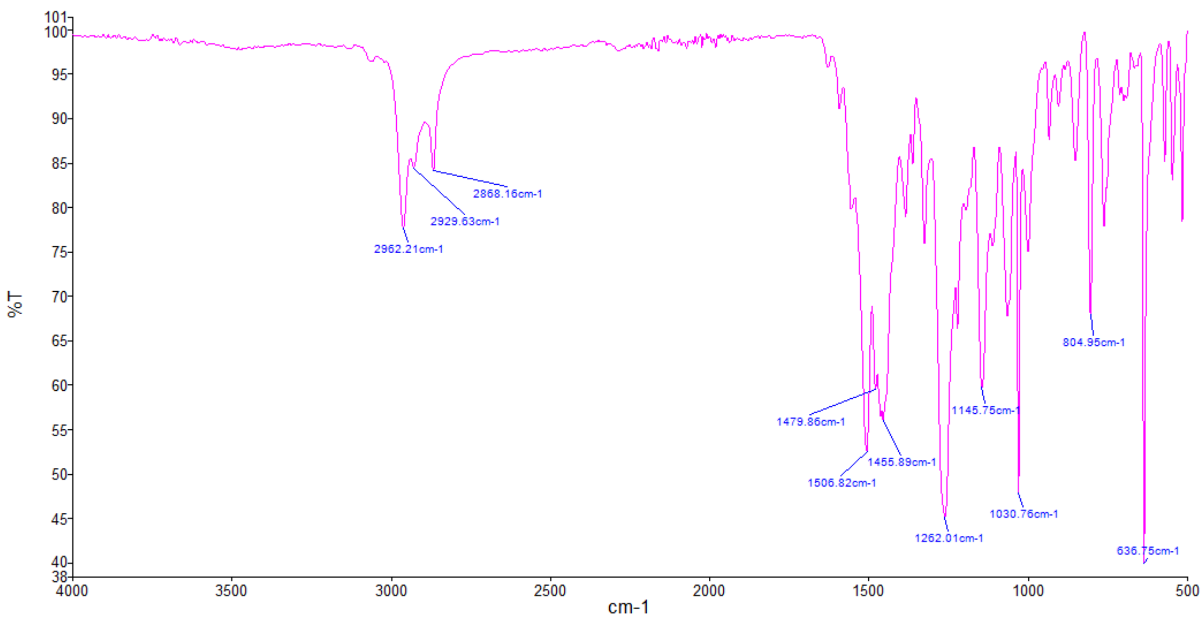
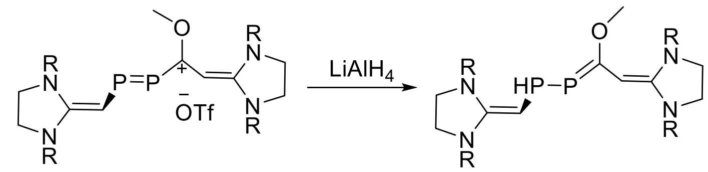


Figure S107**.** IR spectrum of **10**.

Synthesis of 11:



9a, R = Dipp **11**, R = Dipp

Lithium aluminium hydride ($LiAlH_4$, 2 mg, 0.05 mmol) in tetrahydrofuran (1 mL) was added to a stirred solution of **9a** (50 mg, 0.05 mmol) in tetrahydrofuran (10 mL) at room temperature. After stirring for 0.5 hour, the solvent was removed under reduced pressure and the residue was extracted with hexane (20 mL). Then, the solvent was removed under reduced pressure to afford crude product **11** (31 mg, yield = 62 %) as a light yellow oil. ^{1}H NMR (600.2 MHz, C_6D_6): δ = 7.30 (t, J = 7.7 Hz, 1 H, $C_{Ar}H$), 7.26 (t, J = 7.6 Hz, 1 H, $C_{Ar}H$), 7.14 (d, J = 4.6 Hz, 1 H, $C_{Ar}H$), 7.10-7.12 (m, 2 H, $C_{Ar}H$), 7.09-7.04 (m, 4 H, $C_{Ar}H$), 7.00-6.97(m, 2 H, $C_{Ar}H$), 6.94-6.93 (m, 1 H, $C_{Ar}H$), 4.35 (s, 1 H, C(OMe)-C*H*=), 3.77 (d, $^2J_{PH}$ = 6.3 Hz, 1 H, =C*H*-P(H)P), 3.32-3.47 (m, NCH_2 or $CH(CH_3)_2$ or P(*H*), 10 H), 3.23 (m, NCH_2 or $CH(CH_3)_2$ or P(*H*), 3 H), 3.15 (m, NCH_2 or $CH(CH_3)_2$ or P(*H*), 1 H), 3.09 (m, NCH_2 or $CH(CH_3)_2$ or P(*H*), 1 H), 3.04 (m, NCH_2 or $CH(CH_3)_2$ or P(*H*), 2 H), 2.96 (d, $^4J_{PH}$ = 1.7 Hz, 1 H, OCH_3), 1.46 (d, J = 6.8 Hz, 3 H, $CH(CH_3)_2$), 1.40 (t, J = 6.4 Hz, 6 H, $CH(CH_3)_2$), 1.35 (d, J = 6.9 Hz, 3 H, $CH(CH_3)_2$), 1.29 (d, J = 7.0 Hz, 3 H, $CH(CH_3)_2$), 1.26 (m, 6 H, $CH(CH_3)_2$), 1.23 (d, J = 4.8 Hz, 6 H, $CH(CH_3)_2$), 1.21 (d, J = 7.2 Hz, 15 H, $CH(CH_3)_2$), 1.16 (d, J = 6.7 Hz, 3 H, $CH(CH_3)_2$), 1.13 (d, J = 6.9 Hz, 3 H, $CH(CH_3)_2$). ^{13}C{^{1}H} NMR (150.8 MHz, C_6D_6): δ = 205.3 (dd, $^1J_{PC}$ = 72.6, $^2J_{PC}$ = 10.1 Hz, P(H)-P=*C*(OCH_3)), 156.9 (dd, $^2J_{PC}$ = 22.7, $^2J_{PC}$ = 8.9 Hz, *C*=CHP(H)-P=C(OCH_3)), 156.1 (=C(OCH_3)-CH=*C*), 149.2 (C_{Ar}), 148.8 (C_{Ar}), 148.7 (C_{Ar}), 148.6 (C_{Ar}), 148.3 (C_{Ar}), 148.2 (C_{Ar}), 147.8 (C_{Ar}), 146.4 (C_{Ar}), 145.9 (C_{Ar}), 145.9 (C_{Ar}), 140.1 (C_{Ar}), 140.0 (C_{Ar}), 138.8 (C_{Ar}), 138.7 (C_{Ar}), 137.2 (C_{Ar}), 136.7 (C_{Ar}), 135.8 (C_{Ar}), 128.6 (C_{Ar}), 124.6 (C_{Ar}), 124.4 (C_{Ar}), 82.4 (dd, $^1J_{PC}$ = 27.6, $^2J_{PC}$ = 11.3 Hz, P(H)-P-C(OCH_3)-*C*H=). 55.4 (N*C*H_2), 55.1 (N*C*H_2), 53.6 (N*C*H_2), 52.9 (dd, $^2J_{PC}$ = 28.1, $^3J_{PC}$ = 9.2 Hz, =*C*HP(H)-P-), 52.2 (O*C*H_3), 51.9 (N*C*H_2), 50.5 (N*C*H_2), 50.2 (N*C*H_2), 49.9 (N*C*H_2), 49.8 (N*C*H_2), 29.1, 29.0, 29.0, 28.9, 28.9, 28.8, 28.7, 25.7, 25.4, 25.3, 25.2, 24.9, 24.8, 24.6, 24.3, 24.1, 24.0, 23.7. ^{31}P{^{1}H} NMR (243 MHz, C_6D_6): δ = 49.9 (d, $^1J_{PP}$ = 218.9 Hz, HP-*P*-C(OCH_3)), -105.4 (d, $^1J_{PP}$ = 218.9 Hz, H*P*-P-C(OCH_3)). ^{31}P NMR (243 MHz, C_6D_6): δ = 49.9 (d, $^1J_{PP}$ = 218.9 Hz, HP-*P*-C(OCH_3)), -105.4 (d, $^1J_{PP}$ = 218.9 Hz, $^1J_{PH}$ = 179.8

Hz, H*P*-P-C(OCH$_3$)). UV/Vis (toluene, λ (nm) ε($M^{-1}cm^{-1}$)): 308.5 (19707), 433.5 (20806), 504.0 (16207). HRMS (ESI, m/z) calc. for: $C_{58}H_{82}N_4OP_2$: 913.6037 $[M + H]^+$; found: 913.6010.

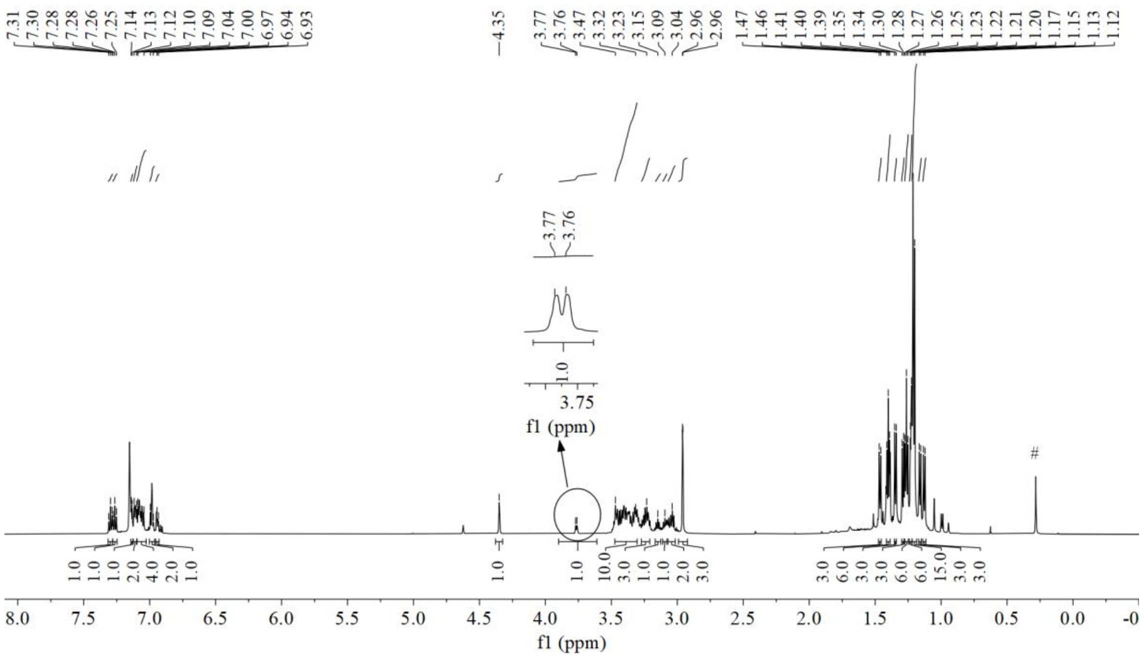


Figure S108. ^{1}H NMR of **11** in C_6D_6. #Silicon grease.

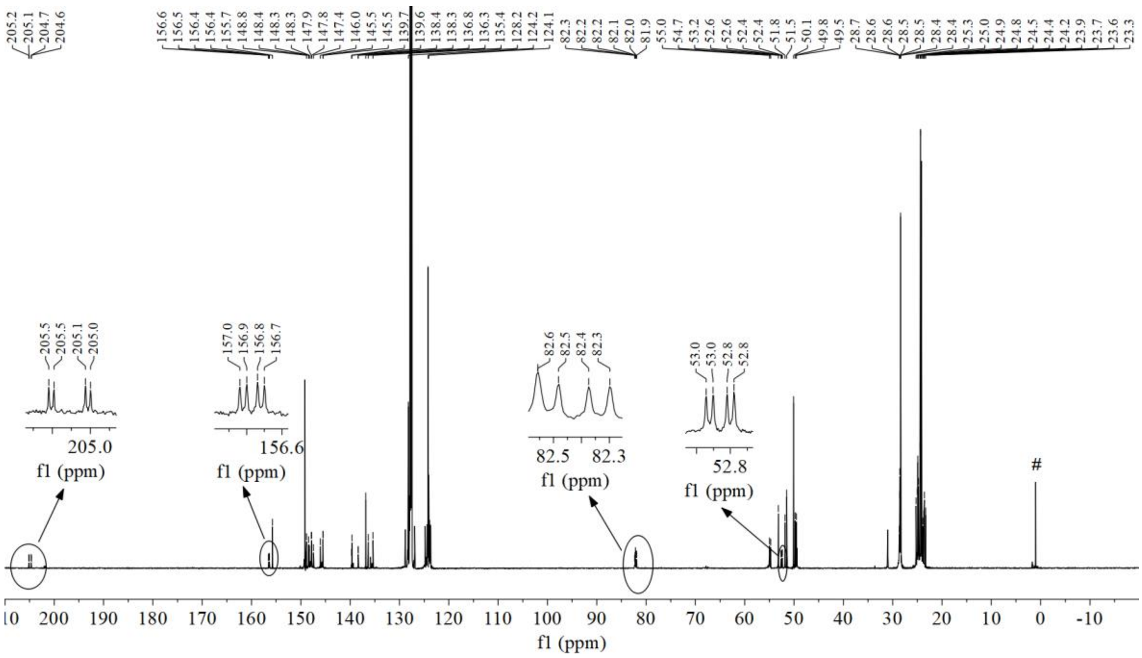


Figure S109. $^{13}C\{^1H\}$ NMR of **11** in C_6D_6. #Silicon grease.

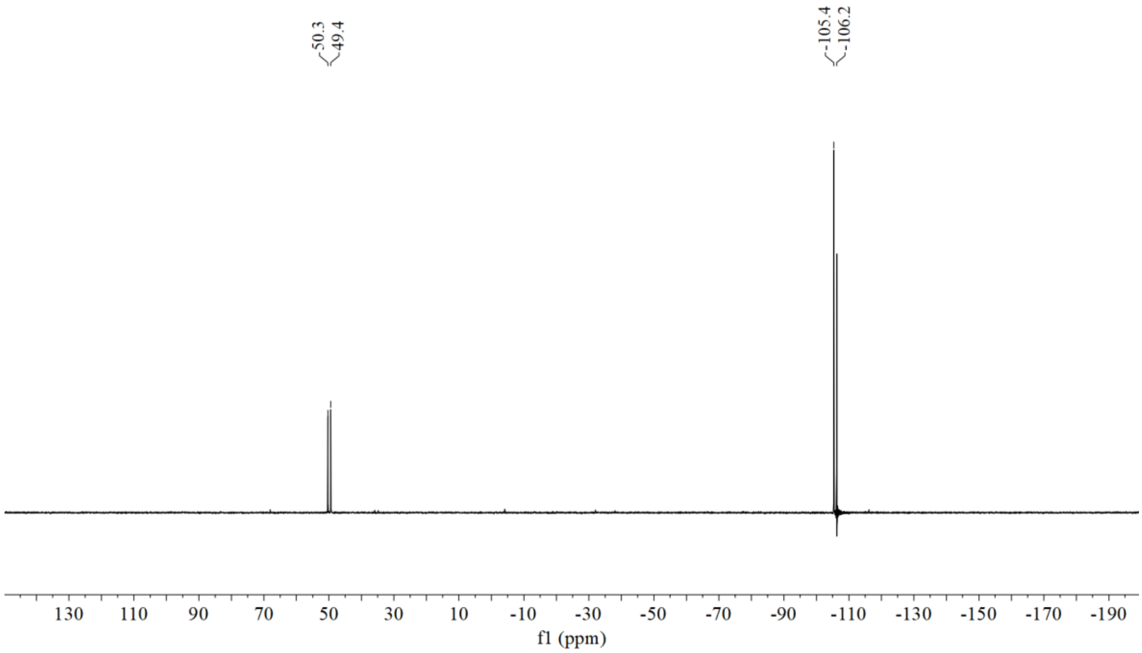


Figure S110. $^{31}P\{^1H\}$ NMR of **11** in C_6D_6.

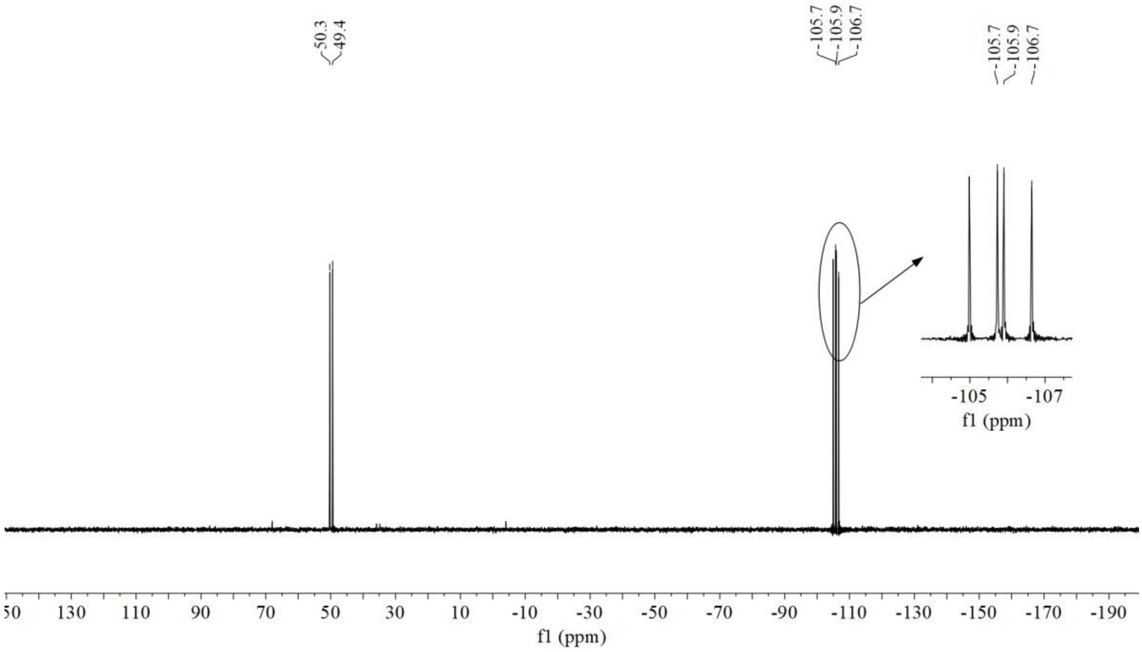


Figure S111. ^{31}P NMR of **11** in C_6D_6.

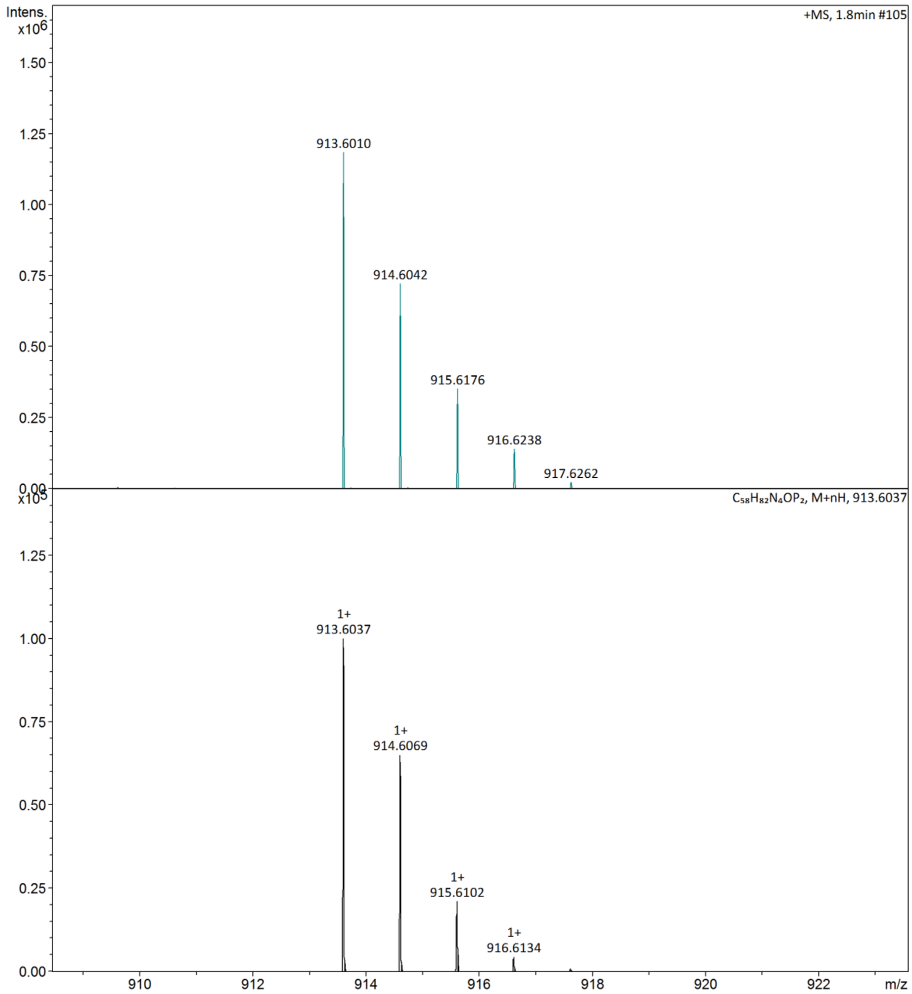
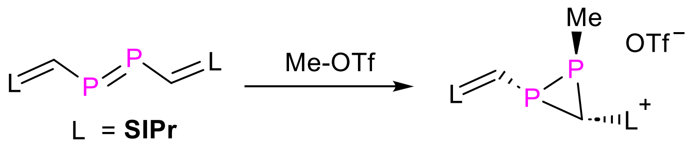


Figure S112. HRMS of **11**.

Synthesis of 14:



Methyl trifluoromethanesulfonate (Me-OTf) (18 mg, 0.1 mmol) in hexane (10 mL) was added to a stirred solution of **12** (100 mg, 0.1 mmol) in hexane (30 mL) at room temperature. After stirring at room temperature for 0.5 h, the resulting precipitates were collected via filtration, then washed with hexane (2 × 2 mL) and dried *in vacuo* to afford **14** (103 mg, yield = 91 %) as a yellow powder. Yellow crystals of **14** were obtained from a saturated solution of fluorobenzene and hexane stored at -30 °C for 7 days. ^{1}H NMR (600.2 MHz, CD_3CN): δ = 7.43 (t, J = 7.7 Hz, 3 H, $C_{Ar}H$), 7.31 (t, J = 7.7 Hz, 3 H, $C_{Ar}H$), 7.11 (d, J = 7.7 Hz, 6 H, $C_{Ar}H$), 4.35

(s, 1 H, C=C*H*), 4.17 (br., 2 H, NCH_2), 4.03 (br., 2 H, NCH_2), 3.73(s, 4 H, NCH_2), 3.65 (m, 1 H, C^+-C*H*), 2.95 (m, 8 H, C*H*(CH_3)$_2$), 2.56 (br., 3 H, PCH_3), 1.27 (d, J = 6.9 Hz, 9 H, CH(CH_3)$_2$), 1.19 (d, J = 6.6 Hz, 9 H, CH(CH_3)$_2$), 1.14 (d, J = 6.7 Hz, 18 H, CH(CH_3)$_2$), 1.09 (br., 3 H, CH(CH_3)$_2$), 0.76 (m, 6 H, CH(CH_3)$_2$), 0.30 (d, J = 6.8 Hz, 3 H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (150.8 MHz, CD_3CN): δ = 172.6 (m, N*C*N^+), 162.30 (d, $^2J_{PC}$ = 15.4 Hz, N*C*N), 147.2 (C_{Ar}), 135.1 (C_{Ar}), 132.2 (C_{Ar}), 131.2 (C_{Ar}), 130.4 (C_{Ar}), 126.2 (CF_3), 53.2 (N*C*H_2), 51.5 (N*C*H_2), 50.1 (dd, $^1J_{PC}$ = 53.6 Hz, $^2J_{PC}$ = 3.9 Hz, C=*C*HPP), 35.3 (dd, $^1J_{PC}$ = 49.6, $^1J_{PC}$ = 38.9 Hz, P*C*HP), 29.6, 29.0, 26.0, 25.2, 24.9, 24.5, 24.2, 6.71 (d, $^1J_{PC}$ = 45.7 Hz,P*C*H_3). ^{31}P{^{1}H} NMR (242.9 MHz, CD_3CN): δ = -120.2 (d, $^1J_{PP}$ = 184.6 Hz, *P*(CH_3)PCH), -124.9 (d, $^1J_{PP}$ = 184.5 Hz, P(CH_3)*P*CH). ^{31}P NMR (242.9 MHz, CD_3CN): δ = -120.2 (d, $^1J_{PP}$ = 184.6 Hz, *P*(CH_3)PCH), -124.9 (dd, $^1J_{PP}$ = 184.5 Hz, $^2J_{PH}$= 5.8Hz, P(CH_3)*P*CH). ^{19}F{^{1}H} NMR (565 MHz, CD_3CN): δ = -79.3. UV/Vis (acetonitrile, λ (nm) ε($M^{-1}cm^{-1}$)): 328.0 (54024.3), 472.0 (5748.5). HRMS (ESI, m/z) calc. for: $C_{57}H_{81}N_4P_2^+$: 883.5931 [M]; found: 883.5927.

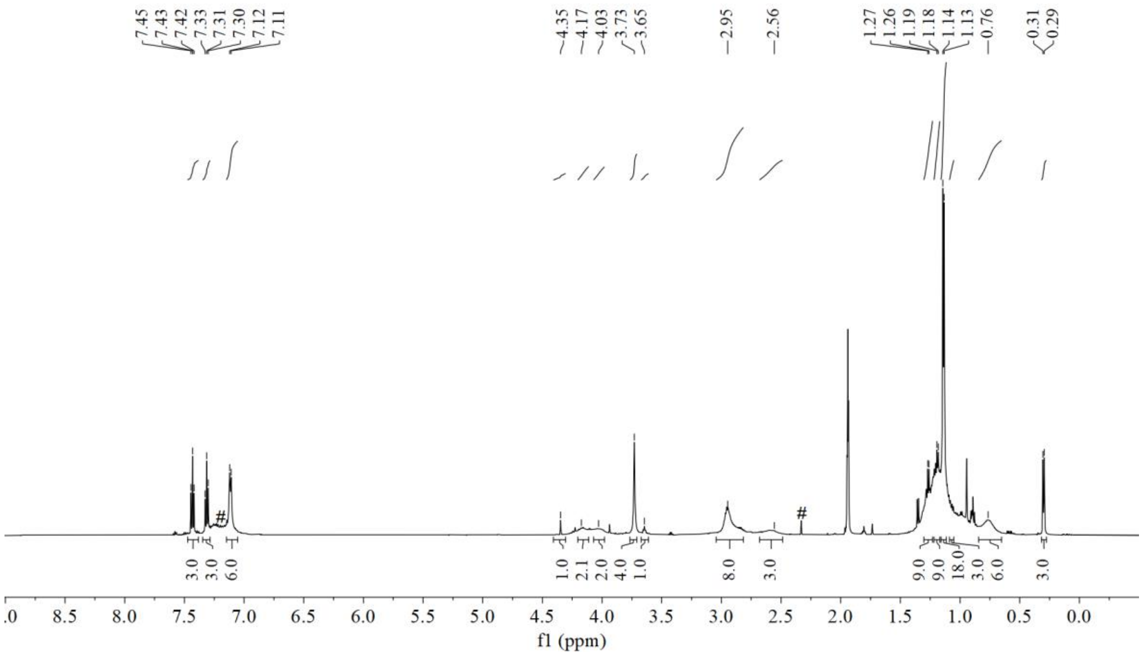


Figure S113. ^{1}H NMR of **14** in CD_3CN. #Toluene.

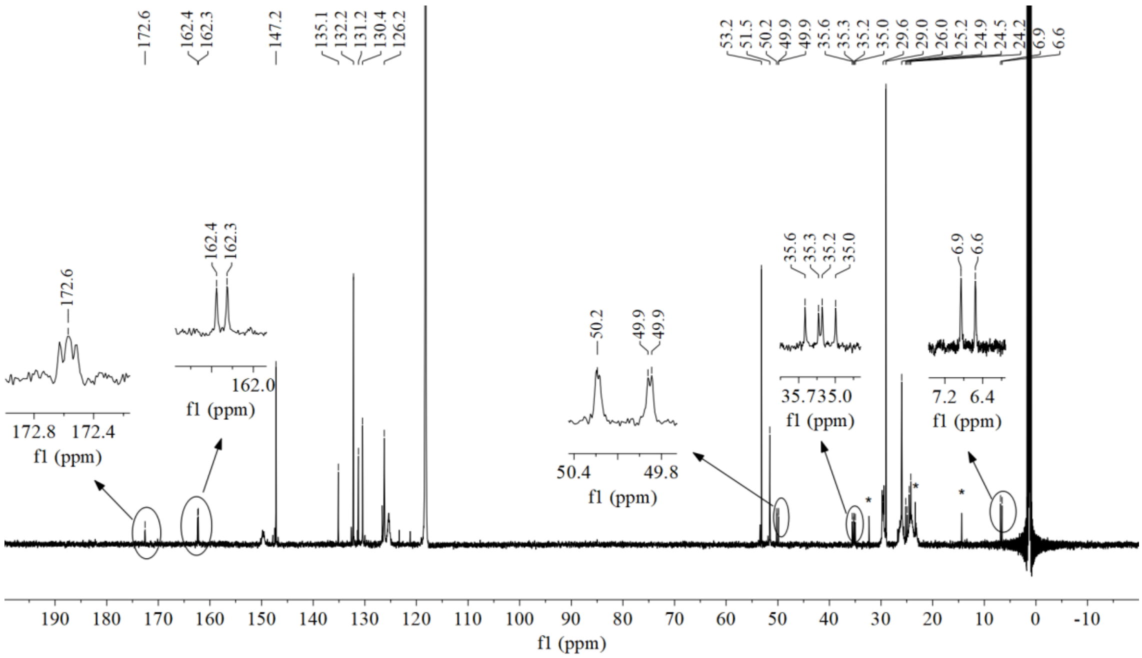


Figure S114. $^{13}C\{^1H\}$ NMR of **14** in CD_3CN. #Hexane.

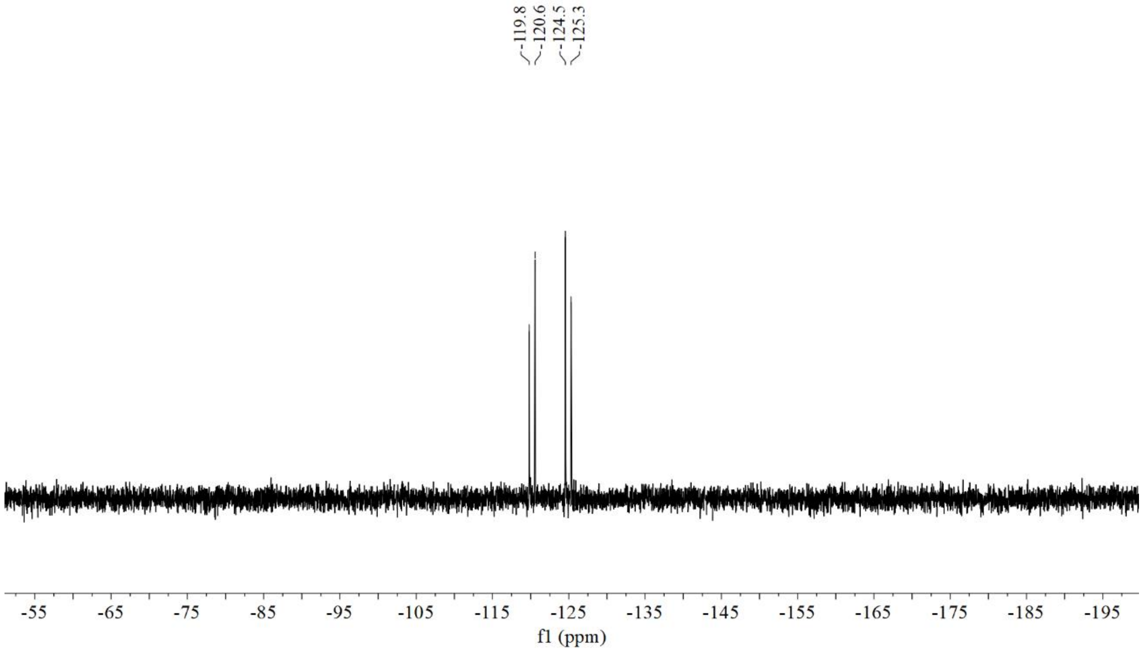


Figure S115. $^{31}P\{^1H\}$ NMR of **14** in CD_3CN.

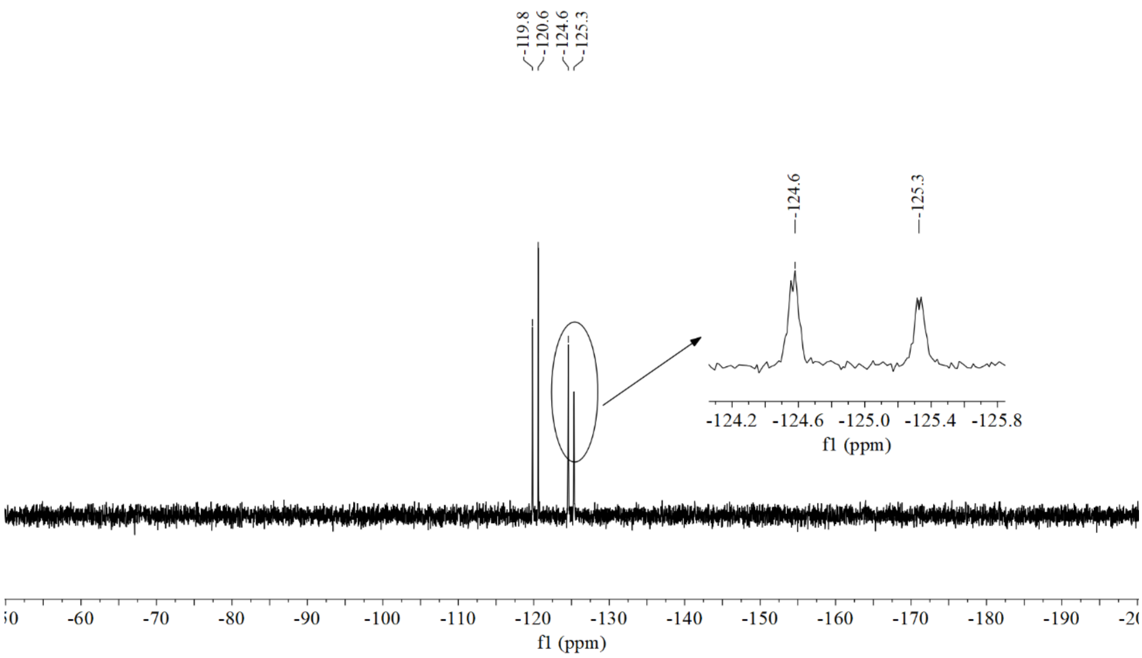


Figure S116. ^{31}P NMR of **14** in CD_3CN.

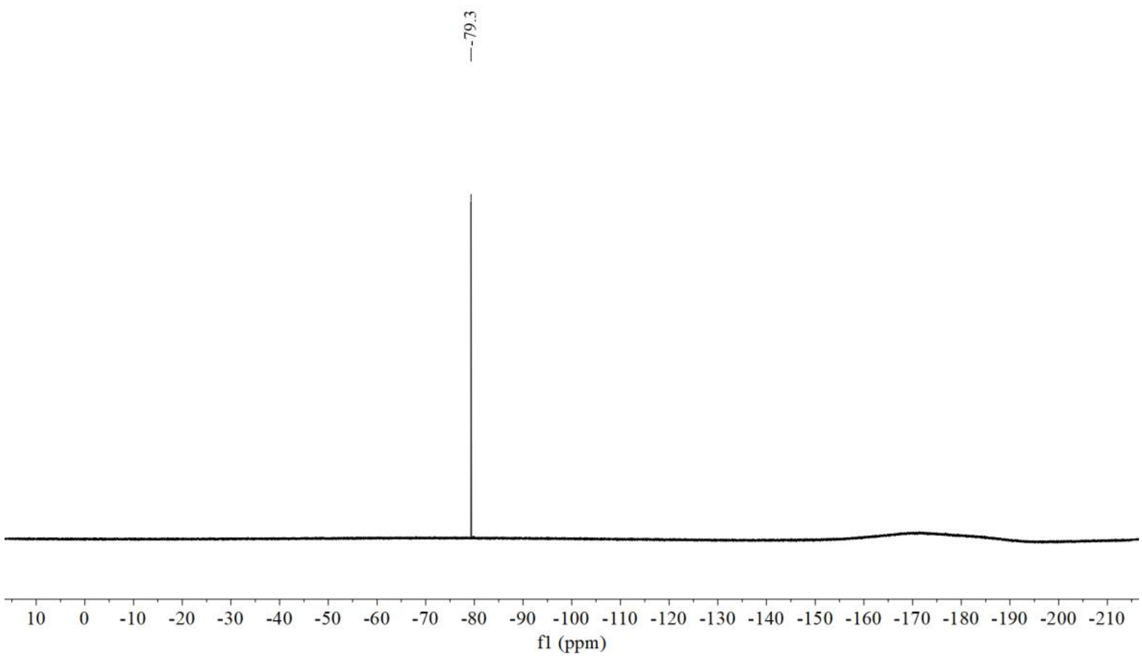


Figure S117. $^{19}F\{^1H\}$ NMR of **14** in CD_3CN.

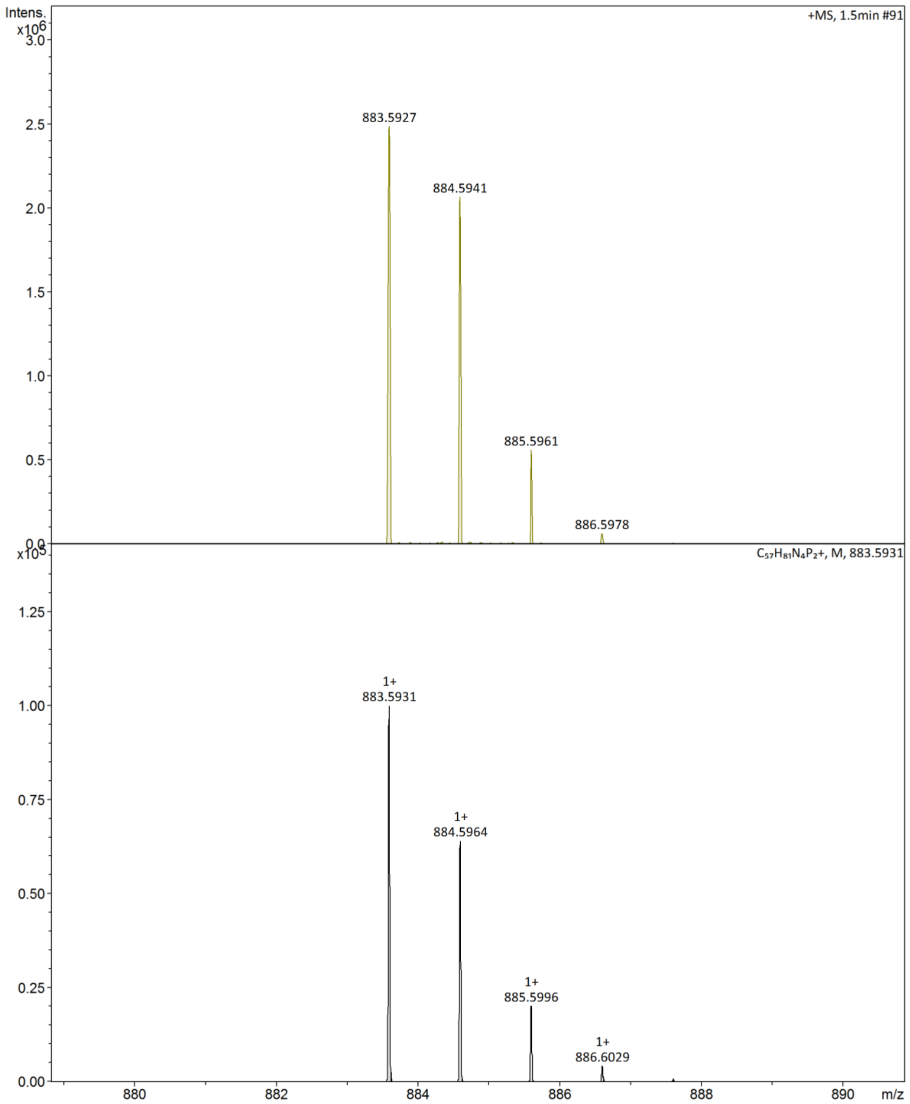


Figure S118. HRMS of **14**.

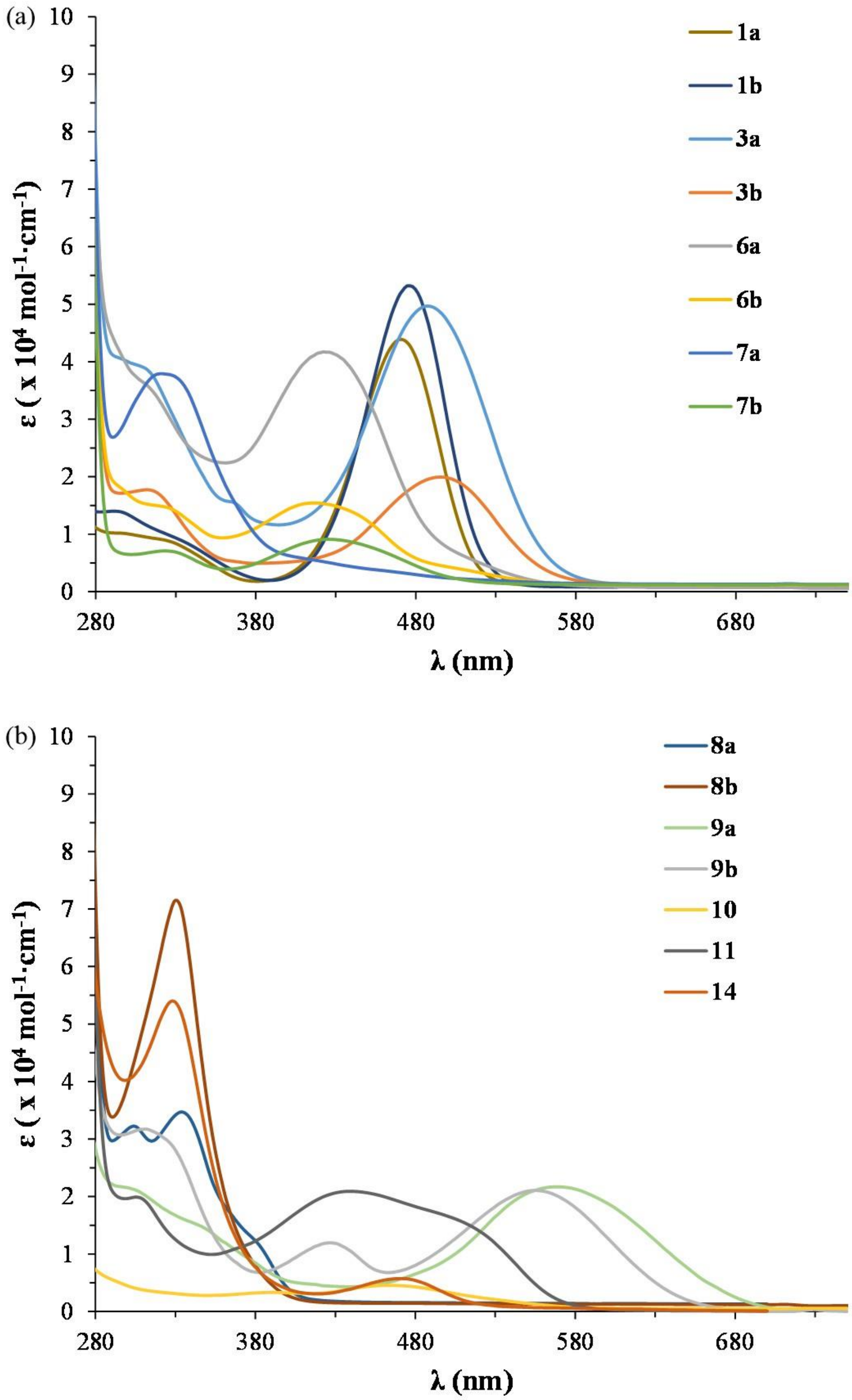


Figure S119. (a) UV-Vis absorption spectra of the acetonitrile solution of **1a**, **1b,** and toluene solution of **3a**, **3b**, **6a, 6b, 7a, 7b**. (b) UV-Vis absorption spectra of the acetonitrile solution of **9a**, **9b**, **10**, **14,** and toluene solution of **11**.

S2. X-Ray diffraction studies

These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/cgi-bin/catreq.cgi, or by emailing data_request@ccdc.cam.ac.uk. The CCDC reference numbers are 2343829, 2343830, 2343833-2343835, 2346470, and 2385608.

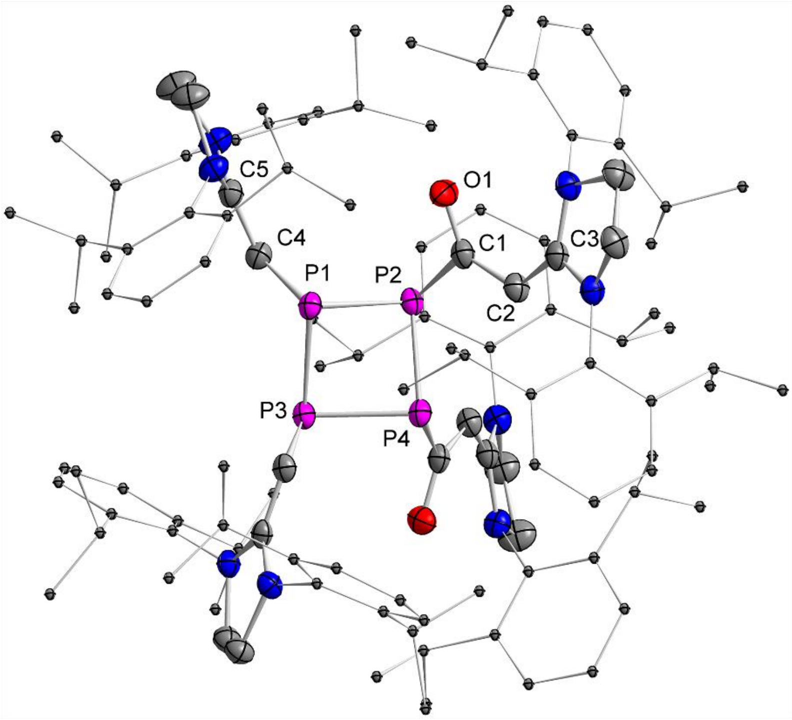


Figure S120. Solid-state structure of **3a_dimer** (Ellipsoids are set to 50% probability; H atoms are omitted for clarity). Selected distances (Å): P1-P2 2.2431(5), P1-P3 2.2563(6), P2-P4 2.2018(6), P3-P4 2.2441(5), P2-C1 1.8811(17), C1-O1 1.238(2), C1-C2 1.426(2), C2-C3 1.376(2), P1-C4 1.7877(17), C4-C5 1.359(2).

Table *S1*. The summary of crystal data and structure refinement

Compounds	**3a**	**3b**	**6a**
CCDC	2343829	2346470	2343833
Empirical formula	$C_{57}H_{78}N_4OP_2$	$C_{63}H_{82}N_4OP_2$	$C_{69}H_{100}FKN_5OP_2Si_2$
Formula weight	897.17	973.26	1191.75
Temperature/K	149.99(10)	100.00(10)	150.00
Crystal system	tetragonal	orthorhombic	triclinic
Space group	P-42$_1$c	P2$_1$2$_1$2$_1$	P-1
a/Å	27.95760(10)	10.5100(2)	12.0896(6)
b/Å	27.95760(10)	18.2431(3)	16.0159(8)
c/Å	15.51230(10)	30.1703(7)	21.5597(11)

α/°	90	90	98.712(2)
β/°	90	90	103.862(2)
γ/°	90	90	98.212(2)
Volume/$Å^3$	12124.84(12)	5784.7(2)	3935.8(3)
Z	8	4	2
$\rho_{calc}g/cm^3$	0.983	1.118	1.006
μ/mm^{-1}	0.919	1.001	1.038
F(000)	3888.0	2104.0	1286.0
Crystal size/mm^3	0.18 × 0.16 × 0.16	0.09 × 0.08 × 0.08	0.15 × 0.08 × 0.04
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	GaKα (λ = 1.34138)
2Θ range for data collection/°	6.322 to 148.658	5.662 to 151.826	3.742 to 118.882
Index ranges	$-23 \le h \le 34$, $-34 \le k \le 34$, $-19 \le l \le 12$	$-12 \le h \le 11$, $-22 \le k \le 22$, $-36 \le l \le 36$	$-15 \le h \le 15$, $-20 \le k \le 20$, $-27 \le l \le 27$
Reflections collected	73809	33798	74751
Independent reflections	12206 [R_{int} = 0.0426, R_{sigma} = 0.0268]	11179 [R_{int} = 0.0622, R_{sigma} = 0.0598]	17203 [R_{int} = 0.0569, R_{sigma} = 0.0474]
Data/restraints/parameters	12206/0/593	11179/8/658	17203/42/770
Goodness-of-fit on F^2	1.068	1.049	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0330, wR_2 = 0.0896	R_1 = 0.0708, wR_2 = 0.1789	R_1 = 0.0459, wR_2 = 0.1243
Final R indexes [all data]	R_1 = 0.0342, wR_2 = 0.0904	R_1 = 0.0893, wR_2 = 0.1909	R_1 = 0.0636, wR_2 = 0.1360
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.24	0.83/-0.37	0.39/-0.42
Flack parameter	0.011(5)	0.022(10)	

Compounds	**7b**	**8a**	**14**
CCDC	2343835	2343834	2385608
Empirical formula	$C_{66}H_{99}N_5O_2P_2Si$	$C_{64}H_{99}N_5OP_2Si_2$	$C_{73}H_{93}F_6N_4O_3P_2S$
Formula weight	1084.53	1072.60	1282.51
Temperature/K	100.00(10)	155(8)	149.9(6)
Crystal system	monoclinic	orthorhombic	triclinic
Space group	$P2_1/n$	$P2_12_12_1$	P-1
a/Å	18.5772(2)	15.1737(2)	13.0834(2)
b/Å	16.1173(2)	20.6058(2)	13.3184(2)
c/Å	21.8954(2)	20.9842(3)	20.9406(3)
α/°	90	90	79.7010(10)
β/°	99.6100(10)	90	86.7710(10)

γ/°	90	90	80.6750(10)
Volume/Å^3	6463.80(12)	6561.05(14)	3541.26(9)
Z	4	4	2
ρ_{calc}g/cm^3	1.114	1.086	1.203
μ/mm^{-1}	1.126	1.261	1.352
F(000)	2360.0	2336.0	1366.0
Crystal size/mm^3	0.06 × 0.05 × 0.03	0.18 × 0.16 × 0.15	0.09 × 0.08 × 0.06
Radiation	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.784 to 103.646	7.19 to 144.804	6.828 to 145.374
Index ranges	-18 ≤ h ≤ 18, -16 ≤ k ≤ 16, -22 ≤ l ≤ 22	-16 ≤ h ≤ 18, -22 ≤ k ≤ 25, -23 ≤ l ≤ 25	-16 ≤ h ≤ 16, -16 ≤ k ≤ 15, -25 ≤ l ≤ 25
Reflections collected	67186	21497	63032
Independent reflections	7107 [R_{int} = 0.0337, R_{sigma} = 0.0136]	12465 [R_{int} = 0.0283, R_{sigma} = 0.0347]	13789 [R_{int} = 0.0274, R_{sigma} = 0.0185]
Data/restraints/parameters	7107/0/708	12465/0/690	13789/0/828
Goodness-of-fit on F^2	1.038	1.046	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0319, wR_2 = 0.0794	R_1 = 0.0436, wR_2 = 0.1140	R_1 = 0.0587, wR_2 = 0.1671
Final R indexes [all data]	R_1 = 0.0346, wR_2 = 0.0809	R_1 = 0.0460, wR_2 = 0.1172	R_1 = 0.0652, wR_2 = 0.1743
Largest diff. peak/hole / e Å^{-3}	0.18/-0.25	0.87/-0.24	0.99/-0.65
Flack parameter		0.010(6)	

Compounds	**3a_dimer**
CCDC	2343830
Empirical formula	$C_{114}H_{156}N_8O_2P_4$
Formula weight	1794.34
Temperature/K	149.99(10)
Crystal system	monoclinic
Space group	I2/c
a/Å	27.6579(4)
b/Å	15.0908(2)
c/Å	57.5737(9)
α/°	90
β/°	97.571(2)

$\gamma/°$	90
Volume/$Å^3$	23820.6(6)
Z	8
$\rho_{calc}g/cm^3$	1.001
μ/mm^{-1}	0.936
F(000)	7776.0
Crystal size/mm^3	0.21 × 0.16 × 0.13
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.448 to 150.8
Index ranges	-30 ≤ h ≤ 34, -16 ≤ k ≤ 18, -70 ≤ l ≤ 71
Reflections collected	110629
Independent reflections	23738 [R_{int} = 0.0903, R_{sigma} = 0.0608]
Data/restraints/parameters	23738/0/1185
Goodness-of-fit on F^2	1.078
Final R indexes [I>=2σ (I)]	R_1 = 0.0529, wR_2 = 0.1312
Final R indexes [all data]	R_1 = 0.0652, wR_2 = 0.1423
Largest diff. peak/hole / e $Å^{-3}$	0.59/-0.56

S3: Theoretical details

Geometry optimizations were performed using the Gaussian16 optimizer.[2] All geometry optimizations were computed using the functional M06-2X functional. The Def2-SVP basis set was used for all the atoms. Frequency calculations at the same level of theory were performed to identify the number of imaginary frequencies (zero for local minimum and one for transition states) and provide the thermal corrections of Gibbs free energy. Transition states were submitted to intrinsic reaction coordinate (IRC) calculations to determine two corresponding minima. The single-point energy calculations were performed at the M06-2X/Def2-TZVP level of theory for solution-phase (toluene) for organic compounds. The gas-phase geometry was used for all the solution phase calculations. The SMD method was used with the corresponding solvent, while the Bondi radii were chosen as the atomic radii to define the molecular cavity.[3] The Gibbs energy corrections from frequency calculations were added to the single-point energies to obtain the Gibbs free energies in solution, respectively. All the solution-phase free energies reported in the paper correspond to the reference state of 1 mol/L, 298K. TD-DFT calculations were performed at the PBE0-SMD(toluene)/def2tzvp level of theory. NBO calculations were carried out using NBO 7.0 program[4] at the M06-2X/Def2TZVP//M06-2X/Def2-SVP level of theory.

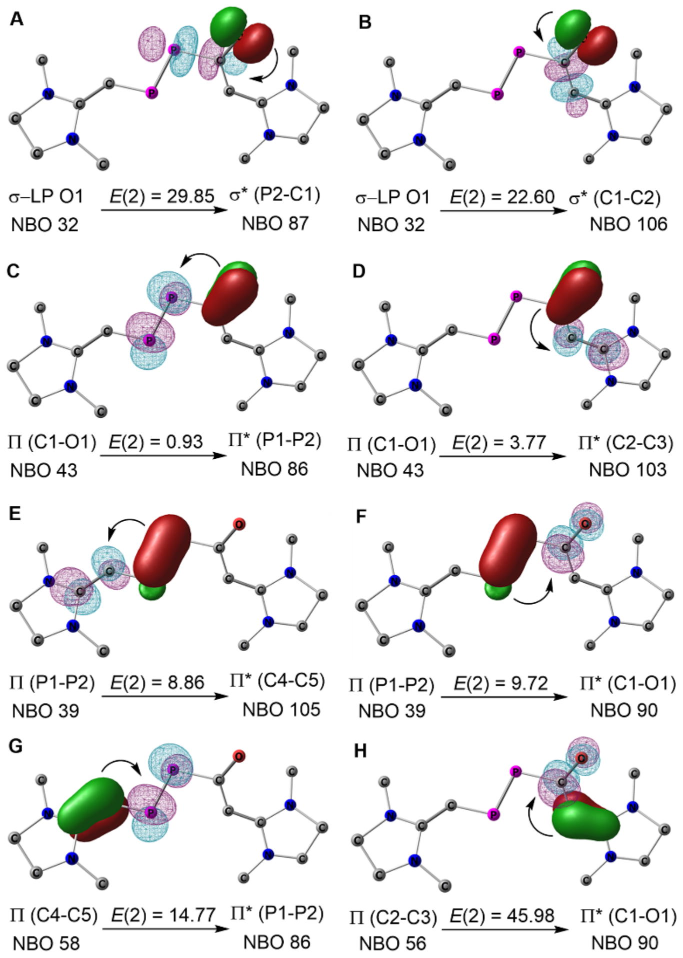


Figure S121. Second order perturbation analysis of **3a**$^{\mathbf{M}}$ at M062X/Def2-TZVP level of theory.

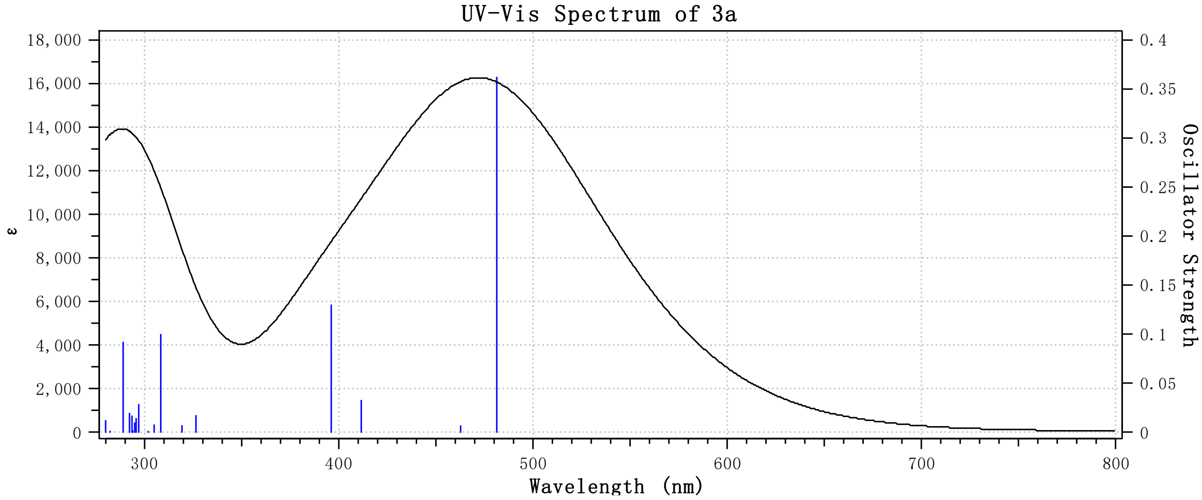


Figure S122. Electronic transitions of **3a** as modeled by TD-DFT.

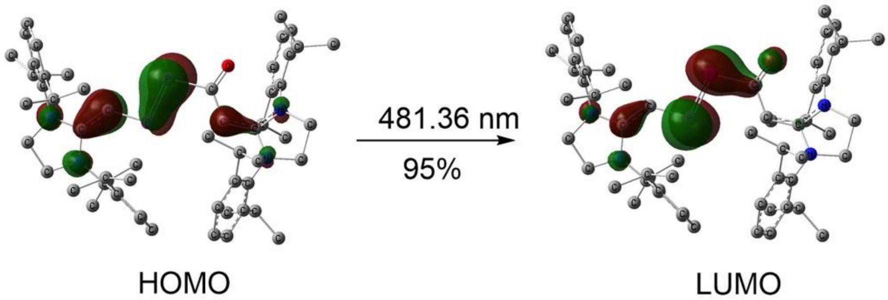


Figure S123. Major Kohn-Sham orbitals of **3a** for transitions at 481 nm from TD-DFT calculations.

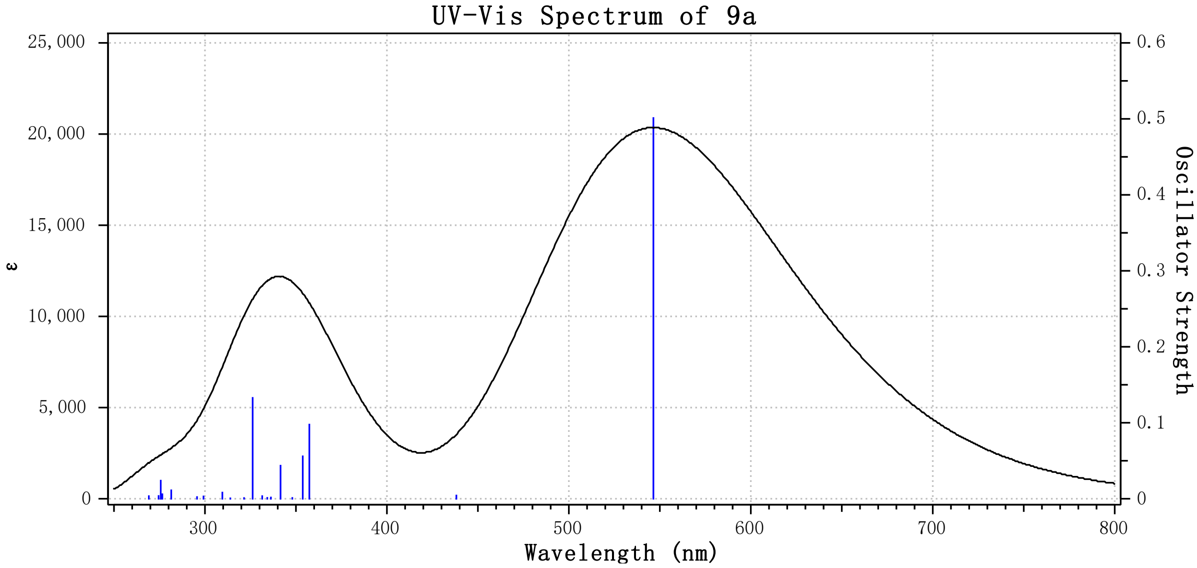


Figure S124. Electronic transitions of **9a** as modeled by TD-DFT.

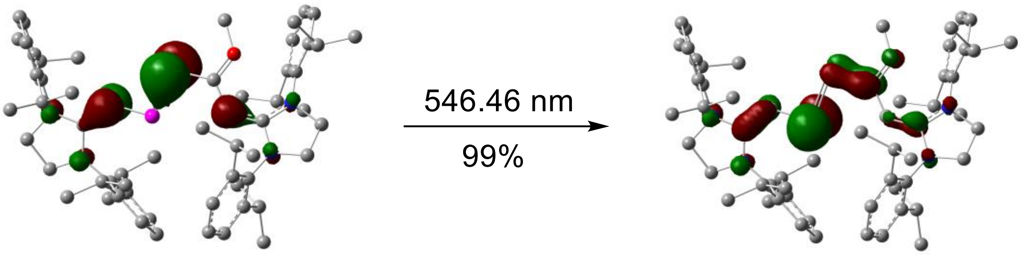


Figure S125. Major Kohn-Sham orbitals of **9a** for transitions at 546 nm from TD-DFT calculations.

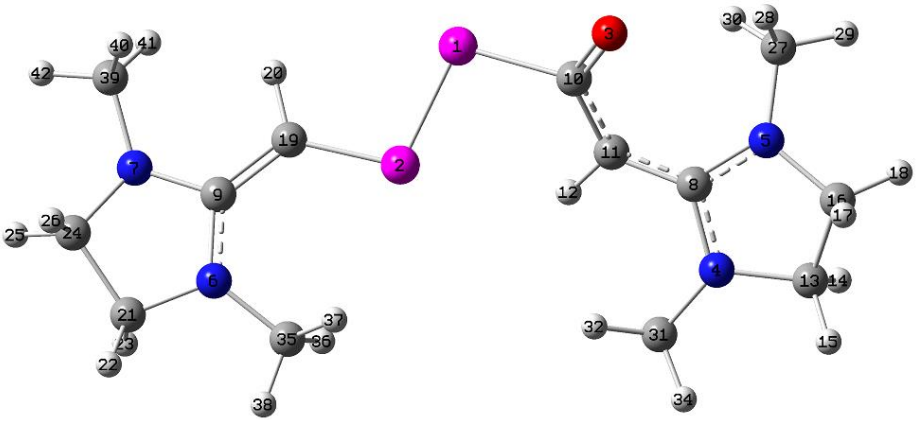


Figure S126. Optimized geometry of **3a$^{\mathbf{M}}$**.

Table *S2*. Calculated ^{1}H and ^{31}P NMR chemical shifts (ppm) of **3a$^{\mathbf{M}}$** at the B97-2/def2TZVP-SMD(benzene)//M062X/Def2SVP level of theory.

Atomic number	Calculated GIAO magnetic shielding tensor	Predicted chemical shifts	Experimental chemical shifts
H12	26.0491	5.5604^{a}	4.77
H20	25.0390	6.5705^{a}	5.77
P1	–112.957	413.9188^{b}	385.0
P2	–210.318	511.2799^{b}	487.5

^{a} Relative to TMS with calculated average GIAO magnetic shielding tensor $^{1}H_{cal.}$ = 31.6095 ppm, $^{13}C_{cal.}$ = 186.9552; ^{b} Relative to PH_3 with calculated GIAO magnetic shielding tensor $^{31}P_{cal.}$ = 567.0622 ppm and experimentally observed $^{31}P_{exp.}$ = –266.1 ppm. The predicted ^{31}P chemical shifts were calculated according to formular: $^{31}P_{pred.}$ (sample) = $^{31}P_{cal.}$ (PH_3) + $^{31}P_{exp.}$ (PH_3) – $^{31}P_{cal.}$ (sample).[4]

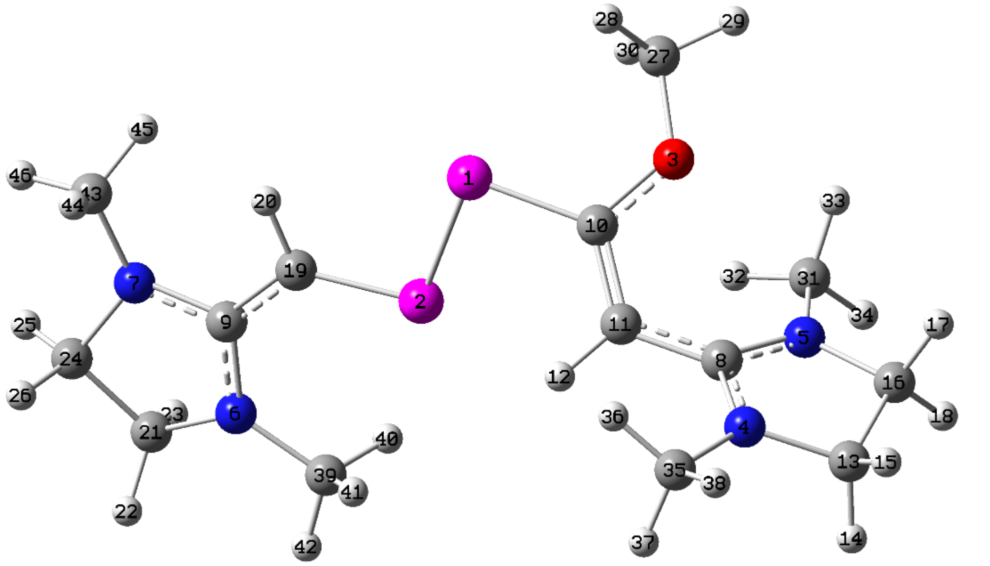


Figure S127. Optimized geometry of **9a^{M}**.

Table *S3*. Calculated ^{1}H and ^{31}P NMR chemical shifts (ppm) of **9a^{M}** at the B97-2/def2TZVP-SMD(benzene)//M062X/Def2SVP level of theory.

Atomic number	Calculated GIAO magnetic shielding tensor	Predicted chemical shifts	Experimental chemical shifts
H28, 29, 30	27.5547	4.0548	2.82
H12	25.9258	5.6837	4.85
H20	24.0929	7.5166	6.11
C27	127.0909	59.8643	59.6
C10	-18.2827	205.2379	195.0
C11	103.0425	83.9127	87.9
C19	74.0868	112.8684	103.9
P1	64.6911	236.2711	229.7
P2	-215.3132	516.2754	471.3

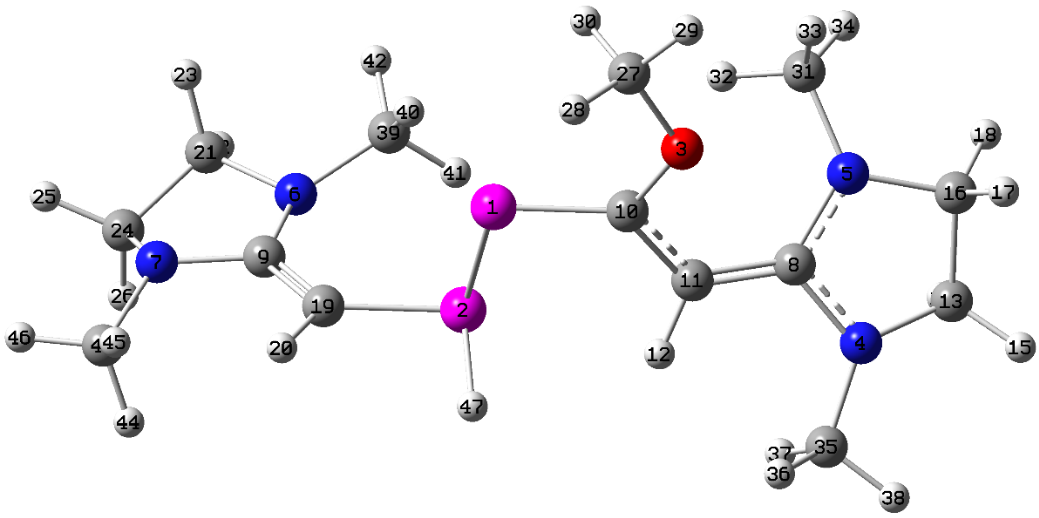
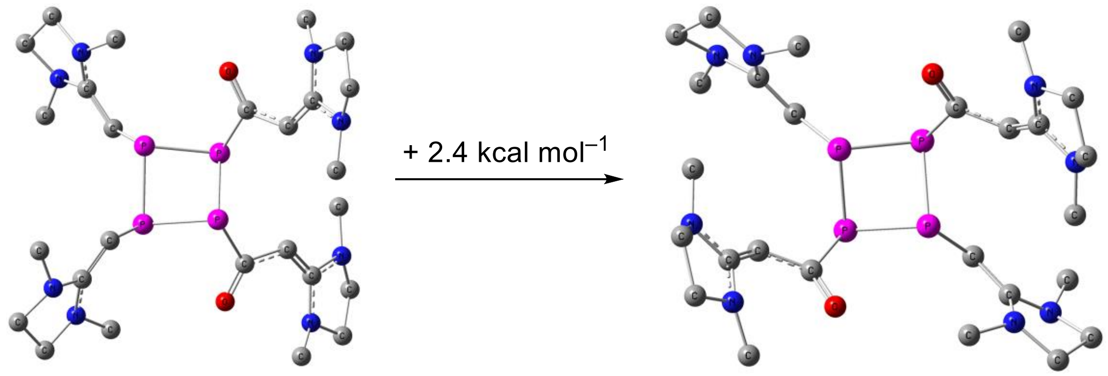


Figure S128. Optimized geometry of **11^{M}**.

Table *S4*. Calculated ^{1}H and ^{31}P NMR chemical shifts (ppm) of **11^{M}** at the B97-2/def2TZVP-SMD(benzene)//M062X/Def2SVP level of theory.

Atomic number	Calculated GIAO magnetic shielding tensor	Predicted chemical shifts	Experimental chemical shifts
C27	131.3167	55.6385	55.2
C10	-26.3173	213.2725	205.3
C11	108.5255	78.4297	82.0
C19	133.9734	52.9818	52.5
P1	264.9559	36.0063	49.6
P2	400.9159	-99.9537	-105.9



3a_dimer^{M} **3a_dimer_iso^{M}**

Figure S129. Optimized geometry of **3a_dimer^{M}** and its regioisomer **3a_dimer_iso^{M}**, and their free energy difference calculated at the M062X/Def2-TZVP-SMD(toluene)//M062X/Def2SVP level of theory.

Cartesian Coordinates:

3a

P 0.19079200 2.05146600 -0.6901610

P 0.95734800 0.27745300 -0.0137120

O -2.31206400 2.65546900 -1.1943810

N -4.17816100 -1.02783400 -0.4318340

N -4.58240900 1.13535000 -0.1538960

N 3.77229200 -1.48433700 0.5232570

N 5.06465200 0.29924500 0.2684850

C -3.59012800 0.21178200 -0.3480850

C 3.74981000 -0.13563700 0.2774930

C -4.43830200 2.35421800 0.5744870

C -1.66423500 1.70619600 -0.7765310

C -3.03487300 -2.46474400 -2.0503870

C 2.63703600 -2.31021800 0.7682490

C -2.23182900 0.42425700 -0.4193360

H -1.58963200 -0.45170000 -0.3276430

C -3.65632400 1.04169700 2.6539540

H -3.79001800 0.19690200 1.9668430

C -3.49125600 -2.23257200 -0.7366180

C -3.31021400 -3.18419400 0.2858700

C -4.01207100 2.32403000 1.9164400

C 2.17192700 -2.47910500 2.0813440

C -5.61769100 -0.97050500 -0.2251580

H -5.90482800 -1.36301700 0.7676110

H -6.13948600 -1.56335600 -0.9895900

C -4.71233600 4.74488700 0.6777590

H -4.97537700 5.69063100 0.2004340

C 5.45845600 1.49847600 -0.3996520

C 5.34353900 1.58821000 -1.7998060

C -3.93374400 3.53816000 2.6086270

H -3.59924000 3.53735200 3.6484150

C -5.89796500 0.53297000 -0.3564350

H	-6.29442000	0.78288100	-1.3555040
H	-6.60429300	0.90274400	0.3984860
C	2.01633200	-2.93415400	-0.3326670
C	-4.77600600	3.56393300	-0.0622660
C	2.67727700	0.69858000	0.0472960
H	2.96266700	1.73181100	-0.1709210
C	-2.41381000	-3.68786500	-2.3226540
H	-2.04979200	-3.88811400	-3.3332210
C	6.36080600	3.72513000	-0.2797930
H	6.76339100	4.56088700	0.2928270
C	-5.19126300	3.59356700	-1.5210640
H	-4.89827000	2.62464600	-1.9496670
C	2.44039900	-2.58556100	-1.7512640
H	2.64851000	-1.50273500	-1.7543790
C	-4.28979200	4.73713400	2.0039340
H	-4.23104500	5.67093800	2.5652930
C	1.12614800	-3.38398100	2.2947480
H	0.74858600	-3.54233200	3.3078720
C	5.73296200	2.78418500	-2.4123500
H	5.64242900	2.88563500	-3.4960010
C	5.10520800	-1.92109400	0.9199560
H	5.31871500	-2.92616600	0.5320710
H	5.20553800	-1.94660300	2.0203470
C	-3.70218800	-2.88826800	1.7239500
H	-4.14673000	-1.88488000	1.7464780
C	0.96464900	-3.81233800	-0.0761860
H	0.44484400	-4.29772000	-0.9017200
C	5.97313400	2.55479200	0.3766460
C	6.23440200	3.84168400	-1.6624560
H	6.53272500	4.76656400	-2.1584690
C	-2.27576700	-4.66097700	-1.3362180
H	-1.81340500	-5.62022000	-1.5774590
C	0.54383200	-4.05800600	1.2293950
H	-0.27209500	-4.75959900	1.4066540
C	5.98047000	-0.83454700	0.3040340
H	6.87304900	-0.60673900	0.9030580
H	6.30663500	-1.10640900	-0.7176580
C	-3.21830400	-1.44725700	-3.1640860
H	-3.73136000	-0.57206800	-2.7431340
C	-2.72108100	-4.40840200	-0.0422330
H	-2.60109800	-5.17054100	0.7317800
C	2.70568300	-1.65168500	3.2385350
H	3.48783600	-0.98292300	2.8493730
C	-2.46580100	-2.83975300	2.6268430
H	-2.00202800	-3.83484900	2.7148220
H	-2.74403800	-2.50868800	3.6394520
H	-1.70868100	-2.14842900	2.2260100
C	6.05011300	2.41906100	1.8892620
H	6.33683800	1.37759000	2.1046950
C	3.32425000	-2.52798400	4.3311050
H	2.56834900	-3.19381100	4.7747370
H	3.73736800	-1.90614500	5.1388650
H	4.13125700	-3.16039300	3.9322970
C	-1.87119700	-0.96535300	-3.7108530
H	-1.24688700	-0.54155400	-2.9105270
H	-2.02631700	-0.18426900	-4.4694120
H	-1.31828300	-1.79152100	-4.1856480
C	-4.59478000	0.80399100	3.8419290
H	-4.48563000	1.59133400	4.6030130
H	-4.36769800	-0.16018400	4.3230820
H	-5.64755600	0.79159800	3.5222590
C	4.82409700	0.44173200	-2.6554550
H	4.59559800	-0.40968700	-1.9977420
C	-4.09989600	-2.01238900	-4.2828960
H	-3.62161300	-2.87681200	-4.7684200
H	-4.27453900	-1.24874500	-5.0549080
H	-5.07522200	-2.34221200	-3.8959680
C	-2.18857400	1.03861900	3.0936150
H	-1.51855400	1.16699800	2.2307590
H	-1.93761000	0.08768400	3.5878850
H	-1.99028600	1.85199900	3.8087430
C	-6.70878700	3.77097700	-1.6525970
H	-7.26298700	2.99265100	-1.1070790
H	-7.01612300	3.73809300	-2.7089150
H	-7.01817400	4.74443200	-1.2406800
C	-4.74326900	-3.87878900	2.2507780
H	-5.64217500	-3.89013200	1.6169550
H	-5.04490000	-3.61355200	3.2749250
H	-4.33909200	-4.90247200	2.2760430
C	-4.44334400	4.67210500	-2.3077530
H	-4.73228200	5.68386500	-1.9837750
H	-4.68419800	4.59069100	-3.3784610
H	-3.36150200	4.54563200	-2.1766870
C	1.59800200	-0.75420000	3.8027980
H	1.16795500	-0.12045700	3.0133740
H	1.99684600	-0.10191400	4.5938400

H 0.78387700 -1.35555600 4.2365580
C 5.89267000 -0.02505300 -3.6504940
H 6.13781900 0.76988700 -4.3709030
H 5.53173100 -0.89342300 -4.2214610
H 6.82357000 -0.30965500 -3.1378910
C 3.72697700 -3.30656700 -2.1652490
H 4.56008300 -3.06618800 -1.4897990
H 4.02179300 -3.00986200 -3.1835620
H 3.58129400 -4.39771300 -2.1552010
C 3.52461800 0.81421000 -3.3774080
H 2.74091600 1.11612400 -2.6678190
H 3.15179500 -0.04716800 -3.9533360
H 3.68883100 1.64275800 -4.0834560
C 4.67076800 2.65229700 2.5192040
H 4.32578600 3.67644700 2.3096790
H 4.71922600 2.52376900 3.6111850
H 3.92106700 1.95506400 2.1199880
C 1.32919000 -2.82852900 -2.7705070
H 1.14409900 -3.90374400 -2.9230510
H 1.61144600 -2.40166100 -3.7441070
H 0.38766000 -2.35956000 -2.4487640
C 7.09414500 3.33357700 2.5271640
H 8.07777000 3.22786600 2.0470250
H 7.20292500 3.09067300 3.5937070
H 6.79401000 4.39045400 2.4647870

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P 0.35449000 -0.82223600 0.0437880
N -2.32254200 -1.63380100 -1.3475120
N -3.54327900 0.01065600 -0.4324410
C -2.24897200 -0.42783800 -0.6818800
C -1.09223000 0.21725000 -0.2691920
C -3.70271300 -1.95336600 -1.6669320
H -3.91500600 -3.02478800 -1.5425300
H -3.92599000 -1.67570800 -2.7146770
C -4.47039700 -1.08388300 -0.6883100
H -5.42610500 -0.72209800 -1.0925980
H -4.67473600 -1.63641300 0.2482600
C -1.29904900 -2.12849300 -2.2450120
H -0.63337700 -1.30784700 -2.5494960
H -0.68206800 -2.91121000 -1.7817680
H -1.78915100 -2.54088900 -3.1401940
C -3.84653100 0.82281400 0.7357140
H -3.25762700 0.49448000 1.6089890
H -3.64557500 1.88711400 0.5628690
H -4.91519100 0.70886800 0.9597600
C 1.68972300 0.36173600 0.0979430
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C 5.03702200 -0.93862000 -0.6128090
C 3.14022000 -2.37209500 0.1597680
C 5.10482000 0.51978900 -1.0420060
C 3.59339300 2.44745900 -0.5831420
H 5.43318300 -1.62595200 -1.3737510
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H 2.59183600 -2.19181000 1.0970900
H 2.47872400 -2.92269500 -0.5240520
H 4.01117300 -3.00397100 0.3865270
H 6.04296500 1.01193900 -0.7498530
H 4.98441600 0.61419000 -2.1397040
H 2.98067500 2.55769700 -1.4974640
H 3.02035400 2.84980100 0.2630300
H 4.50623000 3.04814900 -0.6871040
P 0.01267500 -1.27111000 2.3420630
C -0.44351000 -2.81785200 1.9123630
O -0.75883000 -3.89401200 1.6219960
C -1.13066700 1.66311900 0.0497720
C -0.66837000 2.18856400 1.2688540
C -1.62769700 2.57190700 -0.9010560
C -0.71937000 3.55572700 1.5317820
H -0.27582800 1.50817600 2.0277030
C -1.69181000 3.93812100 -0.6356650
H -1.97820600 2.18377900 -1.8599260
C -1.23592000 4.43970800 0.5836020
H -0.36093900 3.93225600 2.4916620
H -2.09117900 4.61743900 -1.3912200
H -1.27899200 5.50976500 0.7920030

TS1-b

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N -2.73558400 -2.21354700 -0.4093490
N -3.87562600 -0.28220800 -0.2361530
C -2.60302900 -0.85140200 -0.1676470
C -1.44087700 -0.16618400 0.1108920

C	-4.11553500	-2.52852900	-0.7366710
H	-4.43237000	-3.48948200	-0.3060050
H	-4.25048100	-2.58017600	-1.8343860
C	-4.86371600	-1.34653800	-0.1539460
H	-5.77589700	-1.09629300	-0.7134570
H	-5.14284300	-1.53904400	0.9006590
C	-1.71681200	-2.99893200	-1.0782300
H	-1.03002900	-2.34319300	-1.6359000
H	-1.11681900	-3.59577900	-0.3781100
H	-2.21102400	-3.67783900	-1.7901060
C	-4.20399700	0.92547900	0.4977230
H	-3.78551600	0.90417100	1.5197230
H	-3.83362100	1.82640600	-0.0054780
H	-5.29791600	0.99671100	0.5612770
C	1.37532900	-0.05402400	-0.0941290
C	2.62943800	-0.42197600	-0.5682860
H	1.04252700	0.93263000	-0.4225770
N	3.25357700	-1.64079300	-0.5282620
N	3.52495400	0.50437500	-1.0088750
C	4.68988000	-1.44853000	-0.6768960
C	2.76362500	-2.77231200	0.2308250
C	4.75572600	-0.12877200	-1.4403770
C	3.18246100	1.86895600	-1.3230090
H	5.14819700	-2.28455000	-1.2221880
H	5.17611900	-1.35827100	0.3125750
H	2.60415100	-2.52009100	1.2943390
H	1.81406000	-3.13440300	-0.1797780
H	3.50611700	-3.57733300	0.1570660
H	5.63142900	0.47641400	-1.1696270
H	4.76364400	-0.29333300	-2.5342700
H	2.49692300	1.94206700	-2.1850270
H	2.71489700	2.35049000	-0.4533250
H	4.10589200	2.41250100	-1.5578000
P	0.64227300	-0.28055000	2.6573880
C	1.94104300	0.52097100	1.8189970
O	2.93012100	1.15030700	1.8541250
C	-1.37049800	1.30306100	-0.1063620
C	-1.11942200	2.22579900	0.9232520
C	-1.49971000	1.80273200	-1.4144880
C	-1.00550000	3.58922100	0.6522600
H	-1.02548400	1.86495700	1.9473430
C	-1.40223100	3.16667900	-1.6845580
H	-1.68475500	1.09485700	-2.2256070
C	-1.14830100	4.06795100	-0.6501440
H	-0.81442500	4.28507700	1.4712770
H	-1.51818700	3.52674700	-2.7087030
H	-1.06555600	5.13617200	-0.8572060

IN1-b

P	0.01839700	-1.07506500	0.8291950
N	-2.71045100	-2.23198900	-0.3872320
N	-3.84666400	-0.28858300	-0.3386950
C	-2.58114000	-0.86156700	-0.1770870
C	-1.43749200	-0.17337900	0.1560120
C	-4.06481900	-2.54031600	-0.8120060
H	-4.41860500	-3.49492000	-0.3962590
H	-4.12337300	-2.60007000	-1.9164730
C	-4.84207600	-1.34781000	-0.2947940
H	-5.71912900	-1.10507000	-0.9110760
H	-5.18280200	-1.52270400	0.7448390
C	-1.65457500	-3.04004700	-0.9637150
H	-0.96260700	-2.41277500	-1.5485100
H	-1.06331400	-3.56580300	-0.2024980
H	-2.11220000	-3.78271000	-1.6345690
C	-4.21466000	0.93116100	0.3557140
H	-3.85895400	0.92440300	1.4014320
H	-3.81162200	1.82391900	-0.1368800
H	-5.31025500	1.00639900	0.3516000
C	1.41661000	0.03090900	0.2031530
C	2.60254200	-0.42295500	-0.5098320
H	0.99355600	0.90335000	-0.3091710
N	3.25269600	-1.56859200	-0.3169070
N	3.30244700	0.39506500	-1.3046900
C	4.46611200	-1.61027600	-1.1276060
C	2.84541600	-2.67664800	0.5271200
C	4.64602700	-0.13825800	-1.5125100
C	3.03485300	1.82149700	-1.4216750
H	4.31524800	-2.25623000	-2.0088680
H	5.30649600	-2.00618700	-0.5429500
H	2.35755500	-2.29219700	1.4336270
H	2.15820100	-3.35869400	0.0064880
H	3.75144300	-3.22274000	0.8199640
H	5.35151800	0.37855700	-0.8405190
H	4.97391800	-0.00208600	-2.5510800
H	2.02831200	1.99204700	-1.8260320
H	3.12476700	2.30339700	-0.4371500

H 3.76399300 2.24566600 -2.1221480
P 0.69959100 -0.14437600 2.7546180
C 1.92285800 0.52172800 1.6366940
O 2.96795200 1.13847800 1.7461470
C -1.35313000 1.29148100 -0.0720950
C -1.14030400 2.22084600 0.9607620
C -1.40565600 1.77903000 -1.3915890
C -0.98198300 3.57810700 0.6796630
H -1.10187200 1.86777800 1.9910260
C -1.26662900 3.13770700 -1.6708180
H -1.56734300 1.06537600 -2.2031440
C -1.04532800 4.04491800 -0.6330900
H -0.81665400 4.27889800 1.4999550
H -1.32662500 3.48925800 -2.7029300
H -0.92906000 5.10885800 -0.8461860

TS2-b

P 0.14665500 -0.39830300 -0.9888670
N -0.79891100 2.51149800 -0.3788260
N -2.96552600 2.03135200 -0.5315310
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C -1.42966600 0.11483700 -0.3282550
C -1.46100200 3.80477700 -0.4213320
H -0.96075800 4.50035700 -1.1103640
H -1.45717700 4.25953300 0.5863340
C -2.87239800 3.44410000 -0.8700950
H -3.64645700 4.03711800 -0.3634920
H -2.99234600 3.57938900 -1.9604220
C 0.52178200 2.43457100 0.2094040
H 0.59487200 1.55216800 0.8584480
H 1.31306500 2.35179800 -0.5495390
H 0.69127600 3.33907700 0.8152890
C -4.09339800 1.27668600 -1.0499440
H -3.76284000 0.56246100 -1.8195420
H -4.60681300 0.71355900 -0.2595590
H -4.80259300 1.98563900 -1.4967080
C 1.90011800 -1.07389000 0.4269670
C 2.98805400 -0.19447600 0.4750650
H 1.27424700 -1.11296000 1.3187740
N 3.90795000 -0.01411200 -0.4954820
N 3.19690600 0.74195000 1.4663450
C 4.76031300 1.12490800 -0.2018310
C 3.87159400 -0.61786900 -1.8126030
C 4.51968200 1.32350500 1.2927250
C 2.69422400 0.55209000 2.8065980
H 4.44211600 2.00693300 -0.7878280
H 5.81185600 0.91292200 -0.4389780
H 2.83487800 -0.67542800 -2.1762770
H 4.45747200 0.01292900 -2.4935280
H 4.27142700 -1.64116500 -1.7893160
H 5.26783400 0.77078500 1.8921970
H 4.53953100 2.37885300 1.5976410
H 1.60865500 0.39200000 2.7896240
H 3.16813400 -0.30638600 3.3153900
H 2.89073800 1.46288100 3.3874010
P 0.21953700 -2.54103000 -1.1529870
C 1.88906200 -2.31922500 -0.4316010
O 2.87044400 -3.03626600 -0.5461250
C -2.45287000 -0.77882500 0.2653430
C -2.89493400 -1.94709100 -0.3744330
C -3.00209000 -0.47284400 1.5234260
C -3.85163500 -2.77100500 0.2166820
H -2.49752000 -2.19766400 -1.3588870
C -3.96634800 -1.28793200 2.1104070
H -2.66339200 0.42779700 2.0421990
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H -4.17692200 -3.67380800 -0.3028250
H -4.37869300 -1.02469400 3.0863240
H -5.14489100 -3.09073300 1.9180610

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P -0.26916000 0.23554900 -0.2069620
N -2.24491200 2.66863300 0.0443350
N -4.08650600 1.51074500 -0.4743060
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C -2.04808700 0.20020300 -0.0100550
C -3.29989500 3.65953400 -0.0866950
H -2.95929200 4.55304000 -0.6289900
H -3.64905200 3.97559700 0.9143770
C -4.37705100 2.89173100 -0.8315540
H -5.39471000 3.18147100 -0.5354600
H -4.27932100 3.03258000 -1.9248150
C -1.13249400 2.99525600 0.9148630
H -0.96550000 2.18421800 1.6383810
H -0.19762400 3.15313100 0.3606980
H -1.38079400 3.91498400 1.4661960

C	-4.78055900	0.49316700	-1.2447000
H	-4.14686600	0.10602800	-2.0602940
H	-5.09373300	-0.35251100	-0.6209680
H	-5.67843600	0.95306600	-1.6775080
C	2.90218700	-0.31438600	0.3607540
C	4.22189300	0.04983400	0.1720940
H	2.41104900	0.04107100	1.2625380
N	4.98416000	-0.10551000	-0.9480900
N	4.98986500	0.66597900	1.1438800
C	6.31076800	0.45134700	-0.7377220
C	4.44818500	-0.14019600	-2.2949230
C	6.39077200	0.53506400	0.7810720
C	4.62588400	0.58474700	2.5371630
H	6.38263300	1.45421400	-1.1990060
H	7.09430900	-0.18517000	-1.1723620
H	3.42313600	0.25370500	-2.2958290
H	5.07755200	0.50121100	-2.9307360
H	4.41272800	-1.15814900	-2.6990730
H	6.82246200	-0.39145600	1.2068490
H	6.98305000	1.39025100	1.1351420
H	3.66329700	1.08133000	2.7141110
H	4.54964700	-0.46011800	2.8896020
H	5.38677400	1.10984300	3.1289350
P	0.38576300	-1.68395300	0.0024490
C	2.20138000	-1.30131400	-0.4335670
O	2.69358600	-1.99624500	-1.3066090
C	-2.81148600	-1.04889700	0.2583420
C	-2.79790200	-2.13901400	-0.6251780
C	-3.57929700	-1.15565900	1.4270640
C	-3.54747000	-3.28210000	-0.3624900
H	-2.19618000	-2.07600200	-1.5338600
C	-4.33581600	-2.29727700	1.6904870
H	-3.58802300	-0.31858900	2.1287430
C	-4.32436700	-3.36495500	0.7945200
H	-3.52728700	-4.11465100	-1.0677400
H	-4.93205800	-2.35456100	2.6029730
H	-4.91246700	-4.26105500	0.9987500

TS1-c

P	0.17720600	-1.39960200	0.5822040
N	-2.82383100	-1.54771500	-0.8368130
N	-3.17445400	0.63836200	-0.9814460
C	-2.25232700	-0.32038400	-0.6267590
C	-1.04418300	-0.04940800	0.0369740
C	-4.10540900	-1.40993700	-1.5059290
H	-4.82912200	-2.14574000	-1.1296880
H	-3.99594700	-1.55066500	-2.5980150
C	-4.47974500	0.01833600	-1.1610400
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H	-5.05495800	0.06402300	-0.2181330
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C 2.17460000 -3.88267300 -0.756885
H 1.48832500 -4.12871100 -1.579353
H 3.10518200 -4.45094800 -0.857891
H 1.69925100 -4.11153400 0.207827

9a^M

P -0.08343200 -1.99436000 -0.64040800
P -0.96349000 -0.25616600 0.11052600
O 2.55573200 -2.51317400 -0.80935500
N 3.92492600 1.40577600 -0.28151800
N 4.64799400 -0.63279000 0.14921100
N -3.88647400 1.29087200 0.60548700
N -5.01718700 -0.54038500 0.12625000
C 3.56355900 0.10490600 -0.17892100
C -3.77185300 -0.00752100 0.25233400
C 1.68557200 -1.53894800 -0.57042000
C 2.21009100 -0.27310100 -0.36733700
H 1.52268900 0.57090100 -0.39643300
C 5.37959400 1.54713600 -0.24798400
H 5.67878200 2.44412600 0.30941800
H 5.76505400 1.63053700 -1.27920000
C 5.79476300 0.24409500 0.42222700
H 6.71948100 -0.18734500 0.01754300
H 5.90773300 0.35473200 1.51460000
C -2.60942000 -0.76220600 0.00093900
H -2.83067800 -1.78061600 -0.33086200
C -5.27937100 1.62892500 0.91106500
H -5.52549800 2.62766700 0.52893700
H -5.44043800 1.62450600 2.00247400
C -6.03940600 0.50165500 0.21555700
H -6.91192900 0.15131900 0.78191300
H -6.37210700 0.78652900 -0.79860900
C 2.17460000 -3.88267300 -0.75688500
H 1.48832500 -4.12871100 -1.57935300
H 3.10518200 -4.45094800 -0.85789100
H 1.69925100 -4.11153400 0.20782700
C 4.67817856 -1.97292507 0.75255740
H 3.81752377 -2.10341131 1.37476851
H 4.67462654 -2.71240316 -0.02078570
H 5.56435647 -2.07843280 1.34285972
C 3.09342242 2.50211693 -0.79875911
H 2.50711869 2.14786816 -1.62074192
H 2.44509375 2.85424870 -0.02379257
H 3.72281102 3.30225048 -1.12823793
C -2.81725132 2.25947538 0.88739186
H -2.19544444 1.88549826 1.67377428
H -2.22816825 2.40689855 0.00639949
H -3.24986389 3.19106691 1.18719778
C -5.29630846 -1.79021550 -0.59549437
H -4.88809557 -1.73074764 -1.58277640
H -4.84976226 -2.61074114 -0.07373372
H -6.35423754 -1.93889790 -0.65532410

11^M

P -0.1926530 1.5380980 0.8429610

P -1.0247450 -0.5353440 0.8030650
O 2.3947850 2.1641300 0.4383310
N 4.0461430 -1.5856370 0.5694950
N 3.9810500 0.0680550 -0.9039250
N -3.5949630 -0.5951690 -1.2716410
N -5.1081920 -0.0760700 0.2988750
C 3.3155190 -0.4924010 0.1523350
C -3.7439460 -0.2684080 0.0693260
C 1.4911990 1.1713500 0.6334810
C 2.1096530 -0.1252260 0.7126150
H 1.6073720 -0.8819140 1.3101010
C 5.0334630 -1.9398430 -0.4298490
H 4.6428260 -2.6921100 -1.1432820
H 5.9441150 -2.3408010 0.0363160
C 5.2578740 -0.5893240 -1.1121050
H 6.0865060 -0.0339440 -0.6370810
H 5.4748820 -0.6834420 -2.1852600
C -2.7839930 -0.1548990 1.0274740
H -3.1226040 0.1685160 2.0112650
C -4.8794780 -0.5154400 -1.9427320
H -4.9868190 -1.2947140 -2.7111600
H -5.0196960 0.4724330 -2.4241990
C -5.8486170 -0.6919640 -0.7844730
H -6.8136370 -0.1921630 -0.9495890
H -6.0368660 -1.7676180 -0.5907170
C 1.9274110 3.4785290 0.2705120
H 1.4018200 3.8270690 1.1743740
H 2.8085190 4.1054810 0.0877900
H 1.2264830 3.5449580 -0.5787890
C 3.4444980 1.0184150 -1.8415800
H 2.3475930 0.9935210 -1.7972030
H 3.7733850 2.0497930 -1.6418530
H 3.7609290 0.7318070 -2.8565430
C 3.5329640 -2.5540840 1.4982770
H 3.1433190 -2.0422790 2.3888480
H 2.7221530 -3.1715010 1.0686290
H 4.3508310 -3.2156070 1.8130690
C -2.3998500 -0.2770450 -2.0271930
H -1.8915090 0.6085940 -1.6101300
H -1.6791280 -1.1061050 -2.0384200
H -2.6904620 -0.0522620 -3.0640500
C -5.6378850 -0.1671830 1.6333930
H -5.4186020 -1.1421450 2.1100060
H -5.2212890 0.6271620 2.2673090
H -6.7260550 -0.0256730 1.5927110
H -0.7625150 -0.8745300 2.1643010

3a_dimer^{M}

P 1.5240760 -1.1116120 -0.180737
P -0.6211040 -0.7755440 -0.804439
P 1.5238260 1.1116130 0.180346
P -0.6212060 0.7751660 0.804129
O -0.8536160 -3.3674620 -0.133908
O -0.8542300 3.3671280 0.133919
N 3.3844410 -3.5008550 -1.502149
N 4.0276690 -2.2611070 -3.248332
N -3.2994870 -4.3271300 1.365441
N -4.1314860 -2.6449550 2.567860
N 4.0258560 2.2621400 3.248858
N 3.3836320 3.5015940 1.502136
N -3.3002120 4.3264290 -1.365630
N -4.1316010 2.6441350 -2.568303
C -1.3950100 -2.2835350 0.038601
C -2.5972390 -2.0281980 0.790615
H -2.8311390 -0.9866330 1.001163
C -3.2989500 -2.9726590 1.518051
C 2.4468160 -1.2156930 -1.719955
H 2.4332720 -0.3509460 -2.384242
C 3.2207850 -2.2726020 -2.109755
C -1.3953330 2.2830930 -0.038847
C -2.5974560 2.0275890 -0.790960
H -2.8311290 0.9859920 -1.001618
C -3.2993020 2.9719730 -1.518377
C 2.4465100 1.2160790 1.719551
H 2.4329660 0.3514550 2.384005
C 3.2199640 2.2732740 2.109657
C -4.1945640 -4.9427200 2.331979
H -3.7662650 -5.8609070 2.758168
H -5.1569370 -5.2002200 1.850922
C -4.3697710 -3.8360170 3.365535
H -5.3698260 -3.8271890 3.820705
H -3.6173670 -3.9245780 4.172584
C 5.0140340 -3.3166590 -3.126026
H 5.9161120 -2.9674900 -2.583577
H 5.3235930 -3.6966890 -4.109998
C 4.2529540 -4.3434200 -2.300923

H	3.6644630	-5.0187450	-2.952588
H	4.9133980	-4.9587340	-1.672637
C	-4.1955350	4.9418250	-2.332078
H	-3.7675890	5.8602430	-2.758117
H	-5.1580040	5.1988710	-1.850971
C	-4.3703350	3.8352180	-3.365805
H	-5.3703910	3.8261010	-3.820959
H	-3.6179750	3.9241920	-4.172848
C	5.0112200	3.3187670	3.128107
H	5.9143190	2.9708490	2.586566
H	5.3192070	3.6988030	4.112581
C	4.2499070	4.3449550	2.302507
H	3.6596980	5.0191570	2.953775
H	4.9103870	4.9614250	1.675393
C	-4.0179040	1.3634740	-3.228033
H	-2.9868610	1.1626760	-3.569766
H	-4.3172690	0.5510420	-2.552637
H	-4.6980020	1.3526830	-4.089183
C	-3.0570250	5.0041320	-0.107689
H	-3.0908940	4.2802050	0.715061
H	-2.0735460	5.4875310	-0.082322
H	-3.8510420	5.7534150	0.039398
C	4.4273140	-1.0133490	-3.844469
H	4.9603070	-0.3557810	-3.131340
H	5.0852130	-1.2252320	-4.697830
H	3.5517700	-0.4698250	-4.223626
C	2.3987780	-4.1224720	-0.639252
H	2.5880510	-3.9171670	0.424415
H	1.3782000	-3.7765960	-0.864097
H	2.4396050	-5.2107210	-0.797004
C	2.3984670	4.1221960	0.637897
H	1.3775430	3.7776570	0.863406
H	2.4404340	5.2107240	0.793198
H	2.5876170	3.9143280	-0.425270
C	4.4255410	1.0146500	3.845488
H	3.5499910	0.4709990	4.224489
H	4.9589210	0.3569920	3.132738
H	5.0830980	1.2269010	4.699016
C	-3.0560010	-5.0049240	0.107619
H	-2.0725170	-5.4883320	0.082524
H	-3.8499750	-5.7542320	-0.039607
H	-3.0896850	-4.2810640	-0.715190
C	-4.0181080	-1.3642800	3.227607
H	-2.9873520	-1.1636860	3.570343
H	-4.3166400	-0.5518450	2.551863
H	-4.6990510	-1.3532640	4.088089

3a_dimer_iso^{M}

P	-1.3218600	-0.6452360	0.7367780
P	0.6401590	-1.3276660	1.5936120
P	1.3219280	0.6451540	0.7367720
P	-0.6400660	1.3276120	1.5935960
O	0.4313940	-3.1266120	-0.4488840
O	-0.4313040	3.1266160	-0.4488900
N	-3.9998860	-2.3992690	0.2484640
N	-4.8474790	-2.0447040	2.2943500
N	2.9606700	-3.5778050	-2.1417290
N	4.4436390	-1.9806510	-1.6591900
N	4.8475380	2.0447180	2.2943660
N	3.9999170	2.3993260	0.2485010
N	-2.9607730	3.5778110	-2.1416960
N	-4.4438280	1.9807850	-1.6589580
C	1.2279810	-2.4371740	0.1690170
C	2.6439270	-2.2842990	-0.0635390
H	3.1516500	-1.5562600	0.5684240
C	3.3043740	-2.6287960	-1.2271710
C	-2.6129610	-1.1564850	1.8815140
H	-2.5647390	-0.8365610	2.9226920
C	-3.7313710	-1.8339270	1.4855780
C	-1.2278720	2.4371420	0.1689960
C	-2.6438020	2.2842030	-0.0635990
H	-3.1514920	1.5561810	0.5684010
C	-3.3044040	2.6288110	-1.2270950
C	2.6130390	1.1564390	1.8814830
H	2.5648480	0.8364160	2.9226340
C	3.7314450	1.8338880	1.4855580
C	3.9266560	-3.6040380	-3.2270550
H	3.4399890	-3.7252230	-4.2052980
H	4.6344860	-4.4428340	-3.0867590
C	4.6233030	-2.2555190	-3.0756990
H	5.6860930	-2.2878470	-3.3530480
H	4.1234960	-1.4816830	-3.6893710
C	-5.9809320	-2.3451760	1.4414780
H	-6.4922760	-1.4181250	1.1085500
H	-6.7164590	-2.9814590	1.9535110
C	-5.3027630	-3.0389030	0.2701970

H	-5.2041780	-4.1258770	0.4566060
H	-5.8425270	-2.9010620	-0.6785980
C	-3.9269110	3.6041130	-3.2268880
H	-3.4403620	3.7253320	-4.2051840
H	-4.6347170	4.4429050	-3.0864550
C	-4.6235280	2.2555960	-3.0754740
H	-5.6863270	2.2878760	-3.3527970
H	-4.1236990	1.4817570	-3.6891290
C	5.9809550	2.3453500	1.4415090
H	6.4924090	1.4183640	1.1085530
H	6.7164150	2.9816900	1.9535720
C	5.3027380	3.0390500	0.2702320
H	5.2041010	4.1260280	0.4566050
H	5.8425450	2.9012250	-0.6785480
C	2.2277610	-4.7862120	-1.8224460
H	2.1010130	-4.8623130	-0.7374880
H	1.2277130	-4.7916770	-2.2731660
H	2.8056460	-5.6525830	-2.1846430
C	4.7618350	-0.6610260	-1.1556060
H	3.9084350	0.0365430	-1.2422920
H	5.0462370	-0.7064080	-0.0947960
H	5.6193080	-0.2688700	-1.7183610
C	-2.9821960	-2.9543260	-0.6274820
H	-2.0312580	-3.1165840	-0.1002890
H	-3.3383750	-3.9255640	-1.0060580
H	-2.7657860	-2.3017160	-1.4865410
C	-5.0667600	-1.2130950	3.4493170
H	-4.2600800	-1.3502150	4.1810620
H	-5.1187940	-0.1378680	3.1890690
H	-6.0084770	-1.5128620	3.9276490
C	-4.7620050	0.6611400	-1.1554280
H	-5.6198190	0.2692210	-1.7178360
H	-3.9087850	-0.0365920	-1.2425970
H	-5.0459030	0.7064290	-0.0944790
C	-2.2277800	4.7862030	-1.8225090
H	-2.1008750	4.8623090	-0.7375710
H	-1.2277900	4.7916360	-2.2733610
H	-2.8056830	5.6525870	-2.1846400
C	5.0669480	1.2129710	3.4492090
H	6.0085520	1.5129040	3.9276640
H	4.2601870	1.3497620	4.1809230
H	5.1192910	0.1378000	3.1887890
C	2.9821650	2.9541640	-0.6274950
H	2.7655190	2.3012910	-1.4862900
H	2.0313080	3.1166790	-0.1002190
H	3.3383930	3.9252250	-1.0064540

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