Electronic Supplementary Information

Zirconium-catalyzed intermolecular hydrophosphination using a chiral, air-stable primary phosphine

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Experimental considerations

General methods

All air-sensitive manipulations were performed under a positive pressure of nitrogen using standard Schlenk line techniques or in an M. Braun glovebox. Diethyl ether was dried over sodium and transferred under vacuum. Benzene-d_6 was degassed and dried over NaK alloy. Celite-454® was purchased and heated to 180˚C under dynamic vacuum for overnight before use. Compound **1**[1] and (*R*)-MeO-MOPH_2[2, 3] were prepared according to literature procedures. All other chemicals were obtained from commercial suppliers and dried by appropriate means. NMR spectra were collected on a Bruker AXR 500 MHz spectrometer in benzene-d_6 solution unless otherwise noted and are reported with reference to residual solvent signals (benzene-d_6, δ 7.16 and 128.0) or to an external standard of 85% H_3PO_4 (δ 0.0) for ^{31}P NMR spectra. Infrared spectra were collected on a Bruker Alpha FT-IR spectrometer with an ATR head. ESI-mass spectra were collected on an Applied Biosystems 4000QTrap Pro.

General procedure for hydrophosphination reactions targeting secondary phosphine products

A Teflon-sealed reaction vial was charged with 0.18 mmol of the unsaturated substrate, dissolved in Et_2O, and equipped with a magnetic stir bar. The reaction vessel was charged with 0.18 mmol of (*R*)-MeO-MOPH_2 and 0.009 mmol (5 mol %) of **1**. The reactions were stirred at ambient temperature for either 24 h or 48 h. Products **2a** and **2e** were isolated by removal of the volatiles and recrystallization in hexanes. Products **2a** and **2h** were isolated by sublimation of the unreacted (*R*)-MeO-MOPH_2 at 120 ºC under vacuum and recrystallization from hexanes.

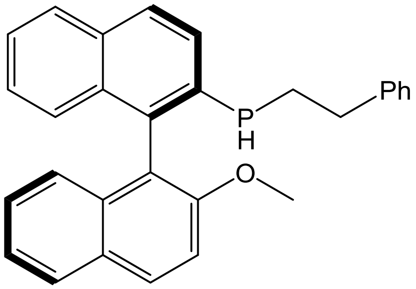
General procedure for hydrophosphination reactions targeting tertiary phosphine formation

A Teflon-sealed reaction vial was charged with 0.18 mmol of unsaturated substrate, dissolved in Et_2O, and equipped with a magnetic stir bar. The reaction vessel was charged with 0.90 mmol of (*R*)-MeO-$MOPH_2$ and 0.0045 mmol (5 mol %) of **1**. The reactions were stirred at ambient temperature for 48 h. The crude reaction mixture was filtered through Celite to remove **1**. Concentration of the filtrate afforded **3a** and **3b** as pale yellow solids.

General procedure for assessing air-stability of 2f and 2h[4]

Adapted from [2]: The secondary phosphine was placed in an uncapped NMR tube and dissolved in benzene-d_6. The NMR tube was exposed to air and periodically monitored by ^{31}P NMR for formation of any new products, presumed to be the result of air oxidation. Both samples do not show new product formation after 7 d.

NMR chemical shifts for hydrophosphination products



(2'-methoxy-[1,1'-binaphthalen]-2-yl)(phenethyl)phosphine (2a)

^{1}H: δ 7.79-7.65 (m, CH_{Ar}, 6 H), 7.61-7.59 (m, CH_{Ar}, 1 H), 7.42-7.34 (m, CH_{Ar}, 1 H), 7.27–7.17 (m, CH_{Ar}, 4 H), 7.11–6.89 (m, CH_{Ar}, 5 H), 4.02 (ddd, J_{PH} = 208 Hz, $^2J_{PH}$ = 9.1 Hz, $^3J_{PH}$ = 5.7 Hz, 1 H, minor isomer), 3.91 (ddd, J_{PH} = 210 Hz, $^2J_{PH}$ = 9.0 Hz, $^3J_{PH}$ = 5.8 Hz, 1 H, major isomer), 3.23 (s, CH_3, 3 H), 2.68–2.64 (m, CH_2, 1 H), 2.44–2.34 (m, CH_2, 1 H), 1.90–1.87 (m, CH_2, 1 H), 1.74-1.69 (m, CH_2, 1 H). ^{31}P{^{1}H}: δ –54.1 (s, minor product), –56.5 (s, major product). MS calcd for $C_{29}H_{25}OP$: m/z 420.2. Found: 417.3. Mixture of diastereomers formed in a 1: 1.16 ratio with 55% conversion as determined by NMR spectroscopy. Isolated 40% yield as a yellow solid.

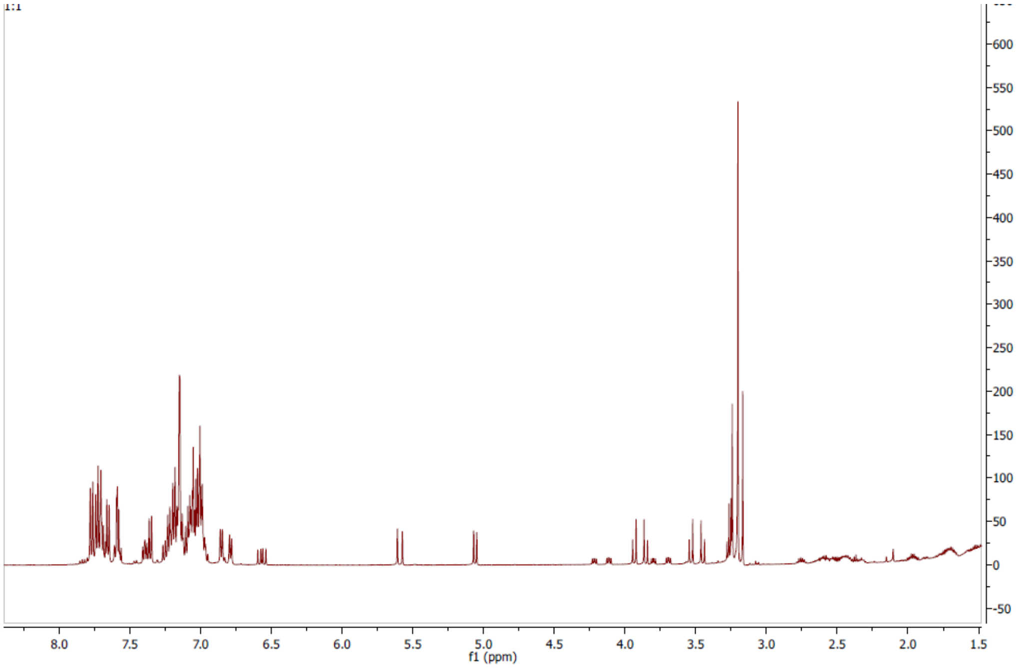


Figure S1: ^{1}H NMR spectrum of crude 2a

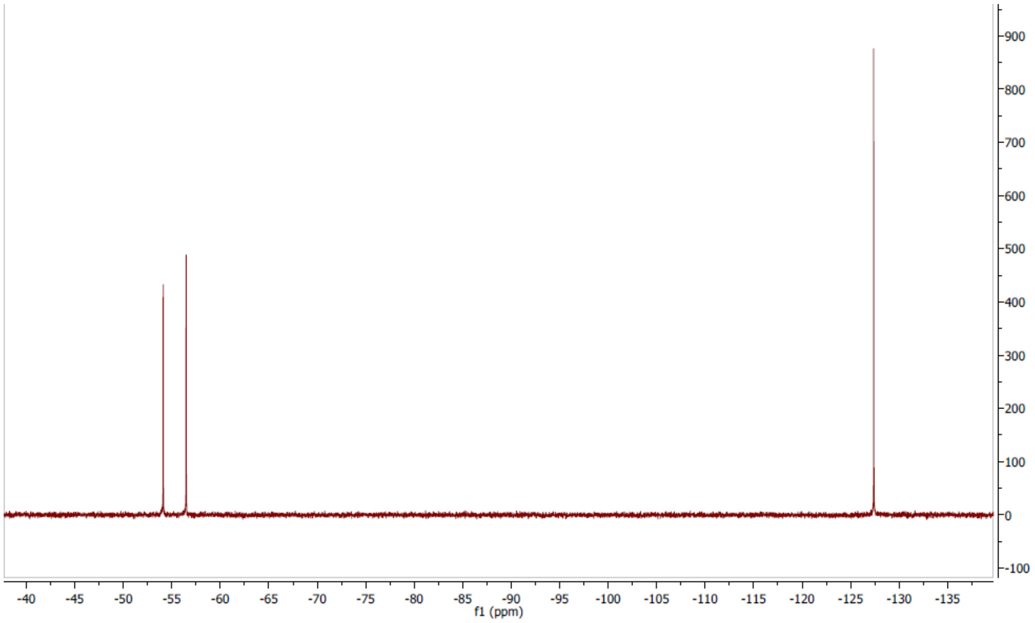
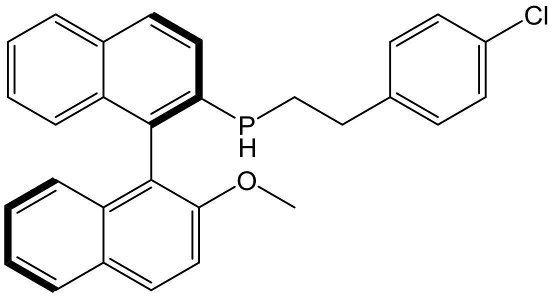


Figure S2: $^{31}P\{^{1}H\}$ NMR spectrum of crude 2a



(4-chlorophenethyl)(2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphine (2b)

^{31}P: δ –53.9 (s, minor product), –57.1 (s, major product). MS calcd for $C_{29}H_{25}OPCl$: m/z 454.1. Found: 455.7. Mixture of diastereomers in a 1: 1.30 ratio with 58% conversion as determined by NMR spectroscopy.

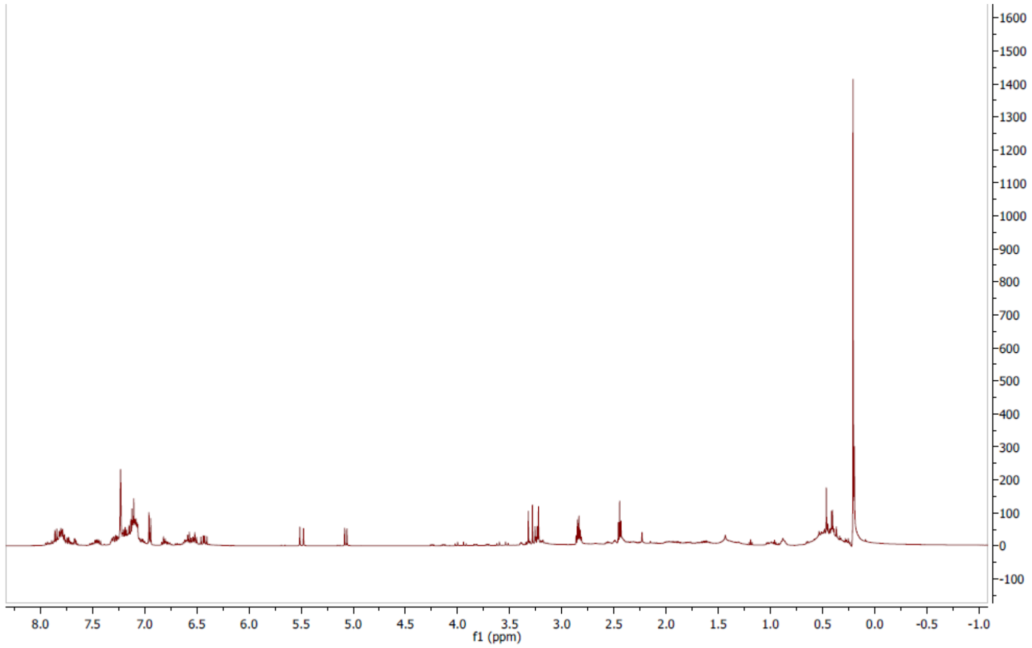


Figure S3: ^{1}H NMR spectrum of crude 2b

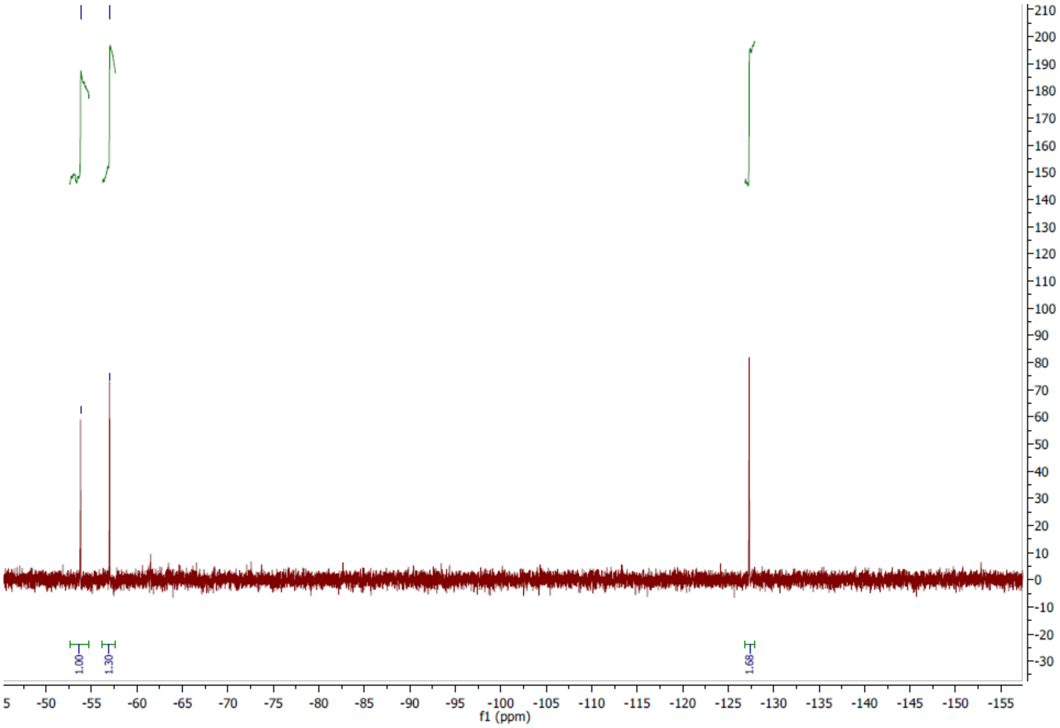


Figure S4: ^{31}P{^{1}H} NMR spectrum of crude 2b

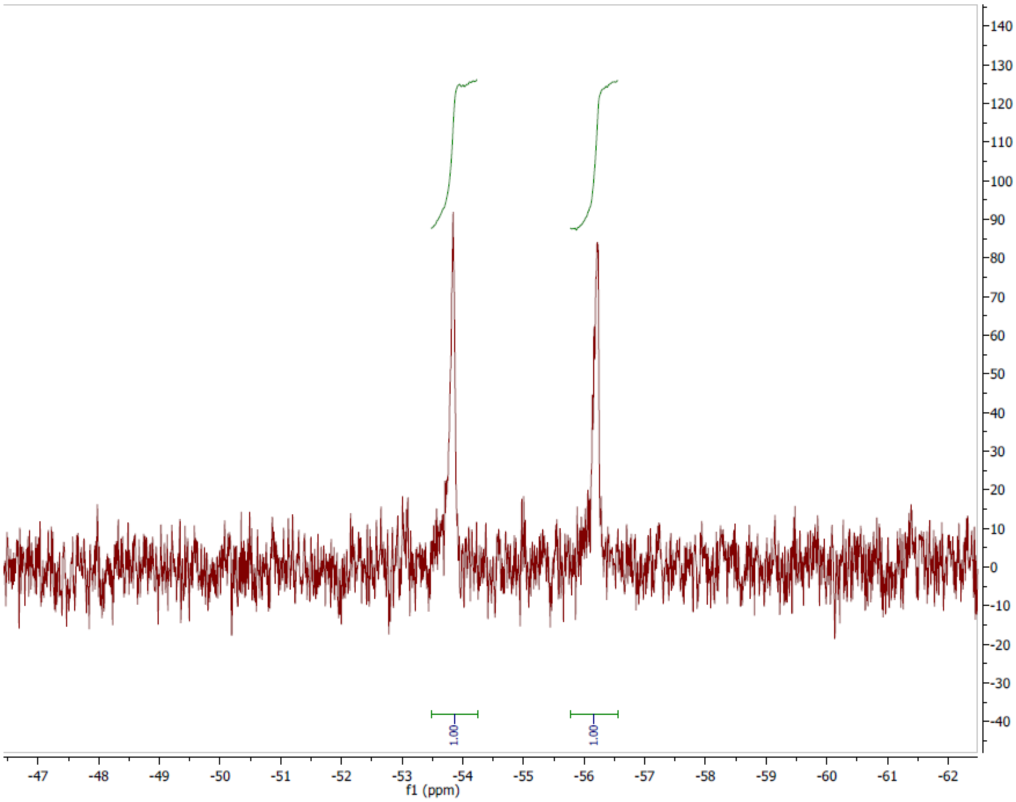
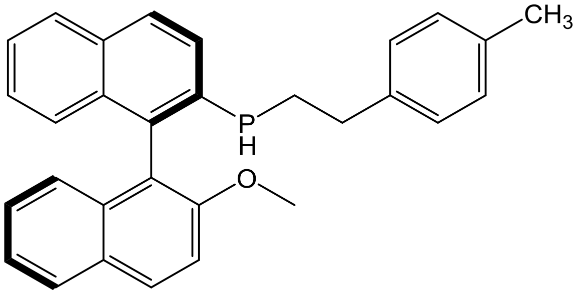


Figure S5: $^{31}P\{^{1}H\}$ NMR spectrum of racemized 2b after heating to 120 °C



(2'-methoxy-[1,1'-binaphthalen]-2-yl)(4-methylphenethyl)phosphine (2c)

^{1}H: δ 7.80-7.65 (m, CH_{Ar}, 4 H), 7.60 (m, CH_{Ar}, 1 H), 7.39 (m, CH_{Ar}, 1 H), 7.39 (m, CH_{Ar}, 1 H), 7.26 (m, CH_{Ar}, 1 H), 7.09–6.98 (m, CH_{Ar}, 9 H), 4.02 (ddd, J_{PH} = 208.5 Hz, $^{2}J_{PH}$ = 9.1 Hz, $^{3}J_{PH}$ = 5.8 Hz, 1 H, major product), 3.95 (ddd, J_{PH} = 210.3 Hz, $^{2}J_{PH}$ = 9.1 Hz, $^{3}J_{PH}$ = 5.8 Hz, 1 H, minor product), 3.25 (s, CH_3, 3 H), 3.21 (s, CH_3, 3 H), 3.18 (s, CH_3, 3 H), 2.55 (m, CH_2, 2 H), 1.70 (m, CH_2, 2 H). ^{31}P{^{1}H}: δ –54.1 (s, minor product), –56.5 (s, major product). MS calcd for $C_{30}H_{27}OP$: m/z 434.5. Found: 432.1. Mixture of diastereomers formed in a 1:1.33 ratio with 63% conversion as determined by NMR spectroscopy.

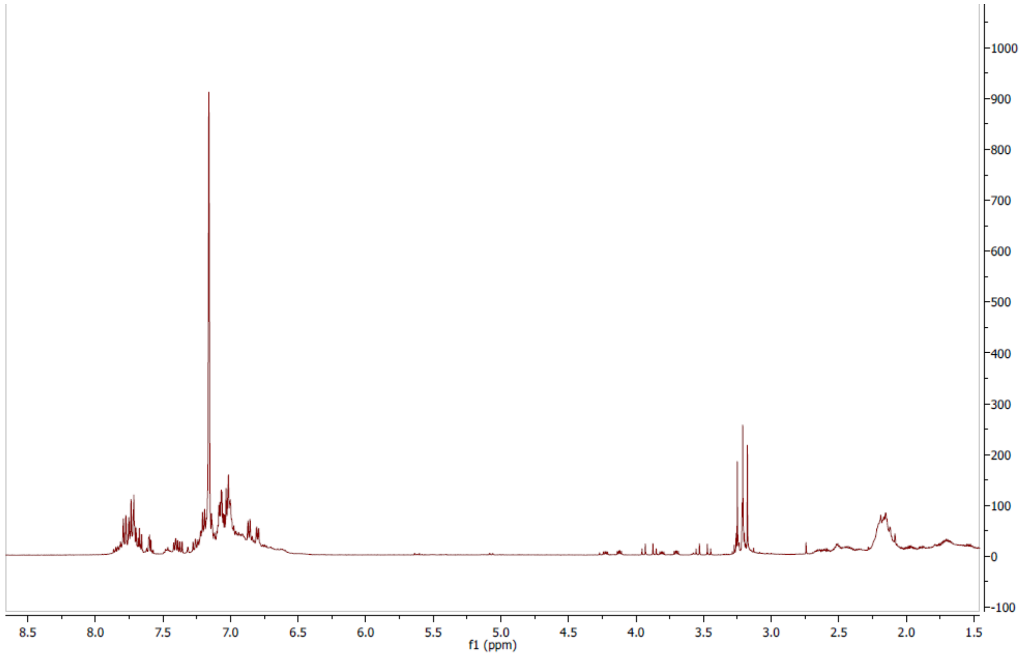


Figure S6: ^{1}H NMR spectrum of crude 2c

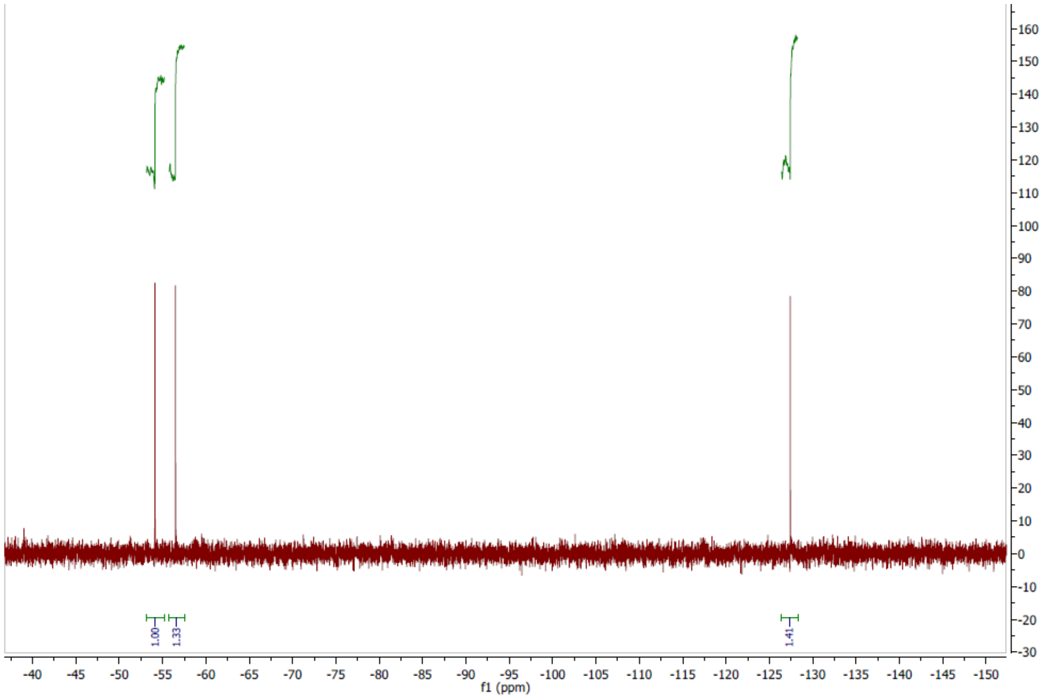
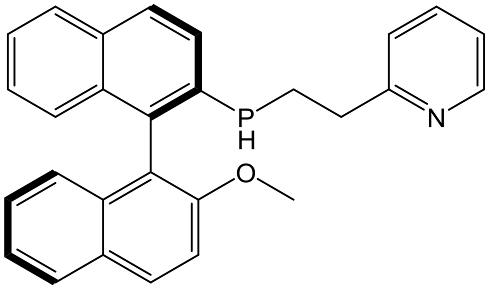


Figure S7: ^{31}P{^{1}H} NMR spectrum of crude 2c



2-(2-((2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphinyl)ethyl)pyridine (2d)

^{1}H: δ 8.48 (m, CH_{Ar}, 1 H), 7.79–7.76 (m, CH_{Ar}, 4 H), 7.61–7.59 (m, CH_{Ar}, 1 H), 7.43–7.40 (m, CH_{Ar}, 1 H), 7.22-7.13 (m, CH_{Ar}, 4 H), 7.12–6.99 (m, CH_{Ar}, 4 H), 6.59–6.49 (m, CH_{Ar}, 1 H), 4.06 (ddd, J_{PH} = 209.6 Hz, $^{2}J_{\mathrm{PH}}$ = 9.2 Hz, $^{3}J_{\mathrm{PH}}$ = 5.8 Hz, 1 H), 3.95 (ddd, J_{PH} = 210.4 Hz, $^{2}J_{\mathrm{PH}}$ = 9.3 Hz, $^{3}J_{\mathrm{PH}}$ = 5.8 Hz, 1 H), 3.23 (s, CH_2, 2 H), 3.27 (s, CH_2, 2 H), 2.92–2.88 (m, CH_2, 1 H), 2.79–2.73 (m, CH_2, 1 H), 2.29–2.24 (m, CH_2, 1 H), 2.12-2.07 (m, CH_2, 1 H). ^{31}P{^{1}H}: δ –54.1 (s, minor product), –56.5 (s, major product). MS calcd for $C_{28}H_{24}NOP$: m/z 421.2. Found: 419.1. Mixture of diastereomers formed in a 1:1.20 ratio with 74% conversion as determined by NMR spectroscopy. Isolated 66% yield as a yellow soild.

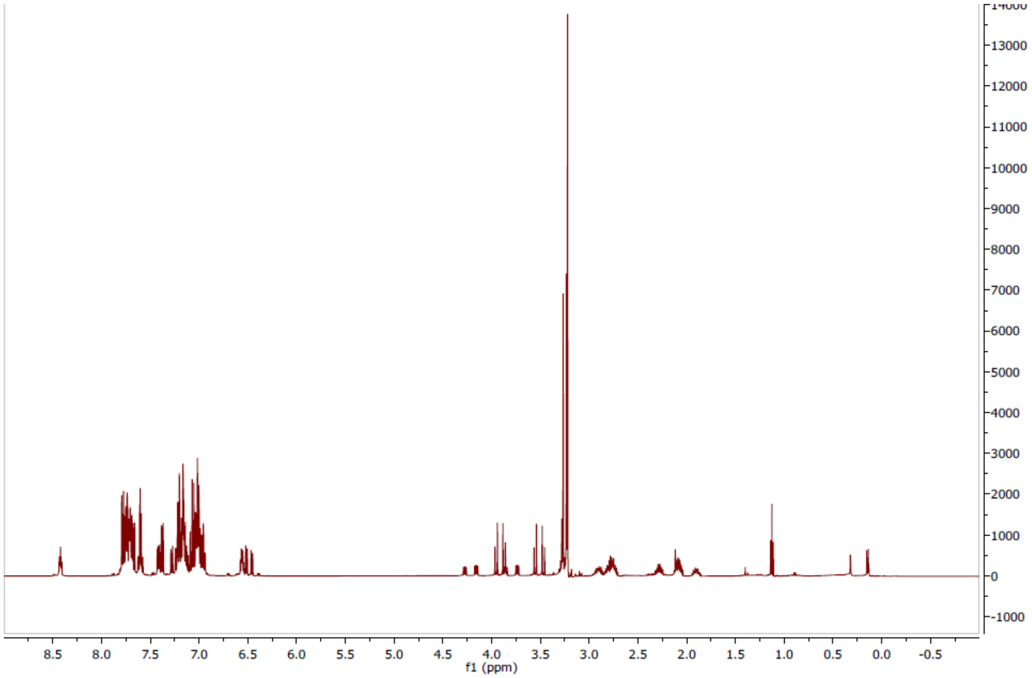


Figure S8: ^{1}H NMR spectrum of crude 2d

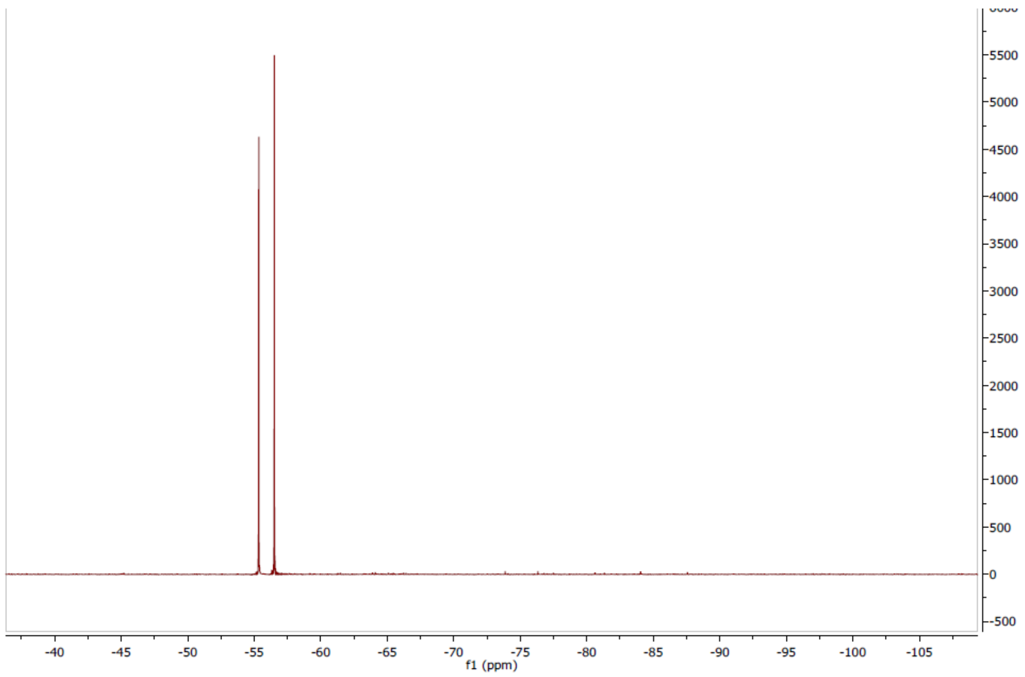
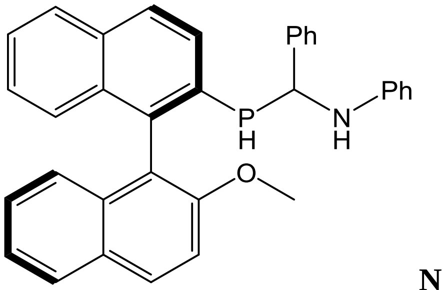


Figure S9: $^{31}P\{^{1}H\}$ NMR spectrum of crude 2d



N-(((2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphinyl)(phenyl)methyl)aniline (2e)

^{1}H: δ 7.78–7.73 (m, C*H*$_{Ar}$, 6 H), 7.70–7.54 (m, C*H*$_{Ar}$, 1 H), 7.38–7.35 (m, C*H*$_{Ar}$, 1 H), 7.26-7.09 (m, C*H*$_{Ar}$, 2 H), 7.09-6.86 (m, C*H*$_{Ar}$, 6 H), 6.72 (m, C*H*$_{Ar}$, 1 H), 6.62 (m, C*H*$_{Ar}$, 2 H), 6.32 (d, *J* = 7.68 Hz, 2 H), 6.22 (d, *J* = 7.64 Hz, 1 H), 5.02 (t, N*H*, minor product, 1 H), 4.57 (t, N*H*, major product, 1 H), 4.51 (m, PC*H*, 1 H), 4.22 (dd, J_{PH} = 221.0 Hz P*H*, minor product, 1 H), 4.07 (dd, J_{PH} = 203.8 Hz P*H*, major product, 1 H), 3.36 (s, OC*H*$_3$, major product, 3 H), 3.16 (s, OC*H*$_3$, minor product, 3 H). $^{31}P\{^{1}H\}$: δ –25.7 (s, minor product), –28.3 (s, major product). MS calcd for $C_{34}H_{28}NOP$: m/z 497.2. Found: 491.2. Mixture of diastereomers in a 1:1.78 ratio formed in 72% conversion as determined by NMR spectroscopy. Isolated 69% yield as a yellow solid.

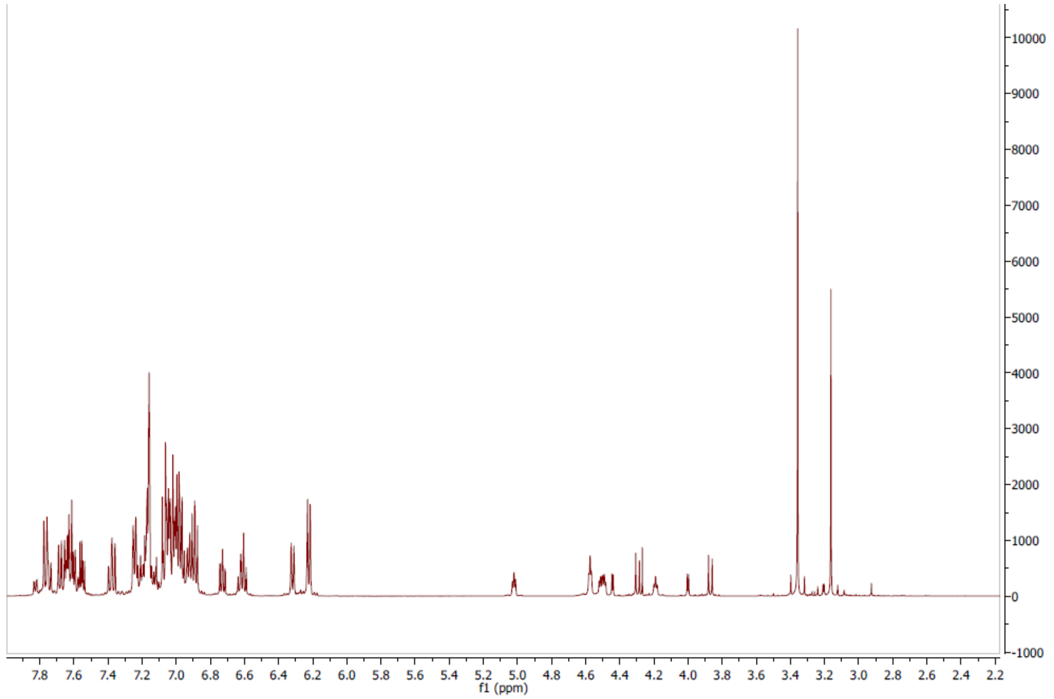


Figure S10: ^{1}H NMR spectrum for isolated 2e

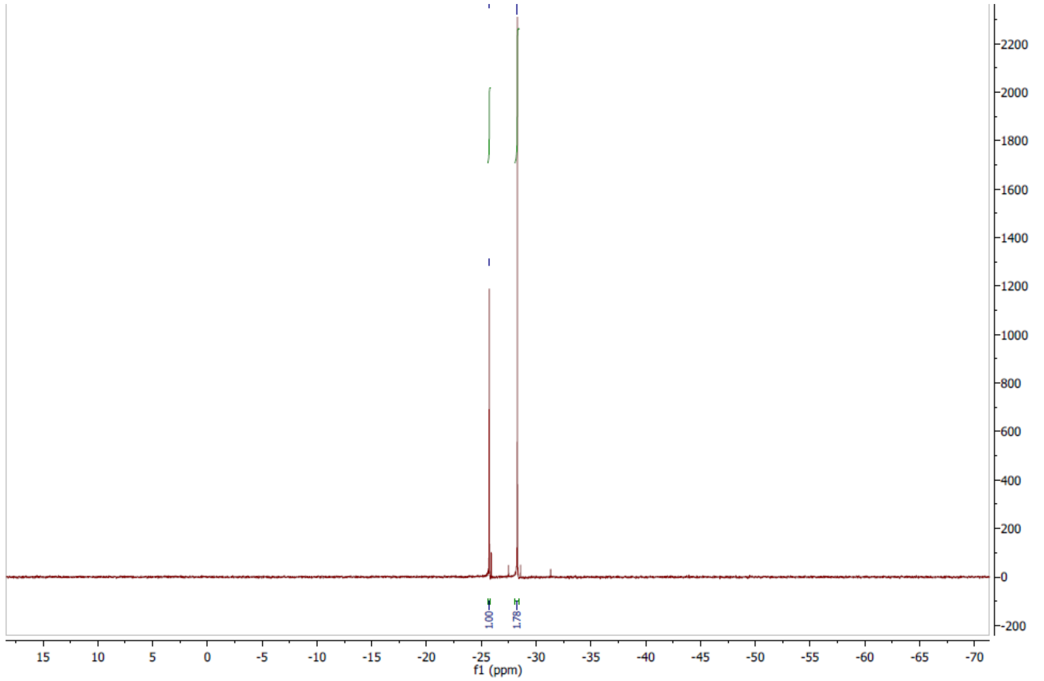


Figure S11: ^{31}P{^{1}H} NMR spectrum for isolated 2e

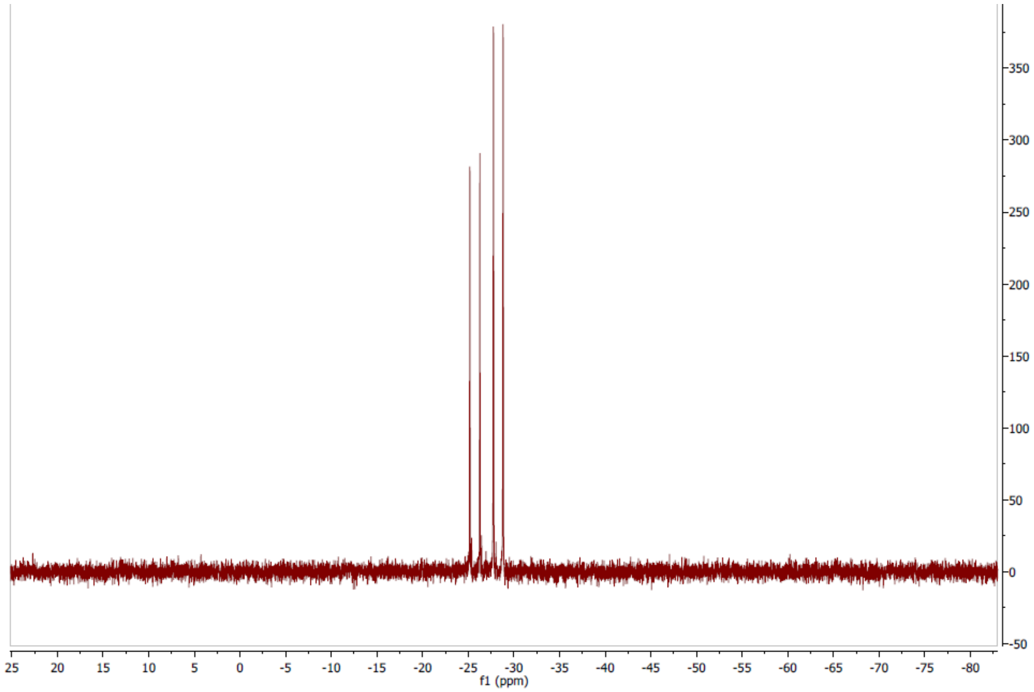
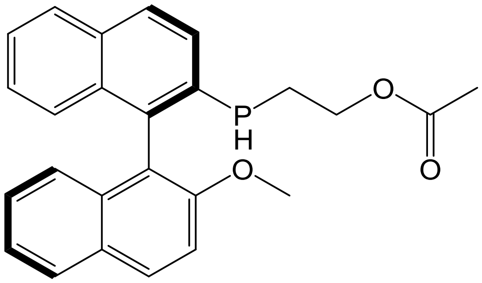


Figure S12: ^{31}P NMR spectrum for isolated 2e



2-((2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphanyl)ethyl acetate (2f)

^{1}H: 7.77 (m, CH_{Ar}, 2 H), 7.70–7.65 (m, CH_{Ar}, 2 H), 7.60 (m, CH_{Ar}, 1 H), 7.36 (m, CH_{Ar}, 1 H), 7.20 (m, CH_{Ar}, 2 H), 7.06–6.95 (m, CH_{Ar}, 3 H), 3.94 (ddd, J_{PH} = 210.64, $^{2}J_{PH}$ = 9.56 Hz, $^{3}J_{PH}$ = 5.29 Hz, PH, 1 H, minor product), 3.84 (ddd, J_{PH} = 210.07, $^{2}J_{PH}$ = 10.09 Hz, $^{3}J_{PH}$ = 5.05 Hz, PH, 1 H, major product), 3.26 (t, CH_3, 3 H), 3.24 (t, CH_3, 3 H), 2.33 (m, CH_2, 1 H), 2.16 (m, CH_2, 1 H), 1.98 (m, CH_2, 1 H), 1.77 (m, CH_2, 1 H). $^{31}P\{^{1}H\}$: δ –54.5 (s, major product), –55.1 (s, minor product). MS calcd for $C_{25}H_{23}O_3P$: m/z 402.1. Found: 401.0. Mixture of diastereomers in a 1:1.32 ratio formed in 87% conversion as determined by NMR spectroscopy. Isolated 82% yield as a yellow solid.

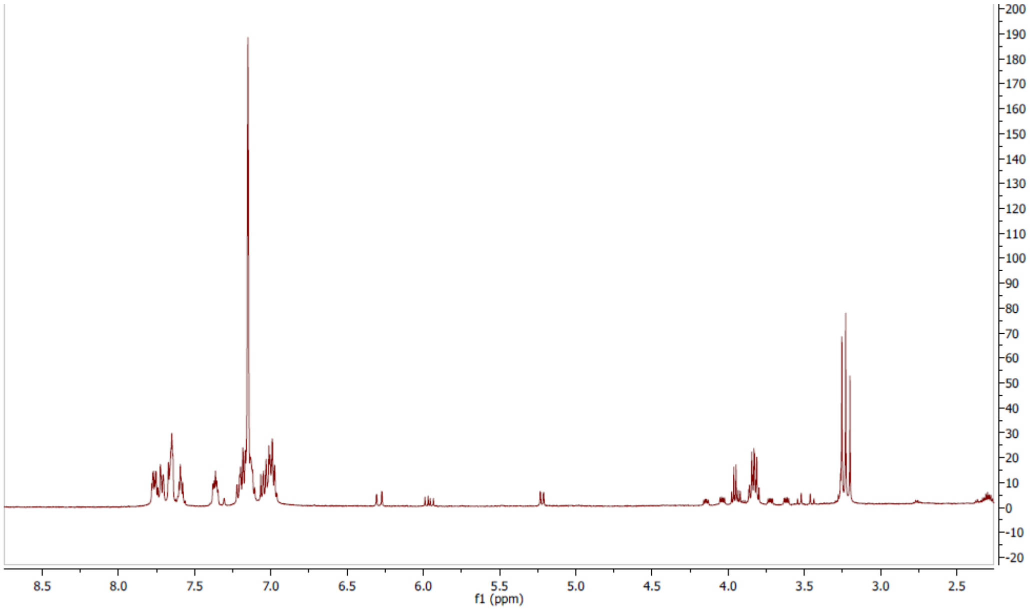


Figure S13: ^{1}H NMR spectrum of crude 2f

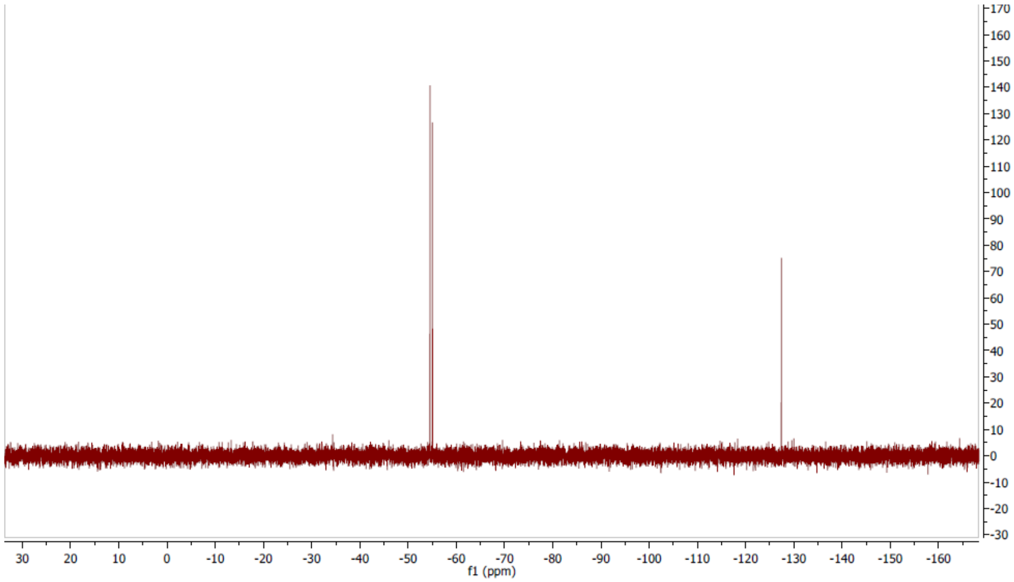
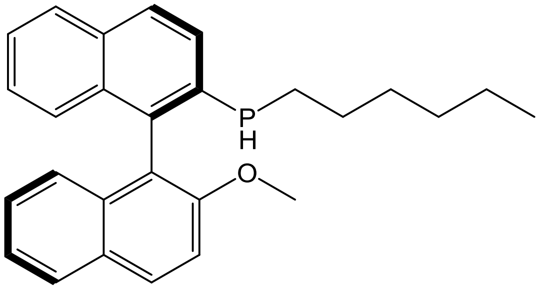


Figure S14: ^{31}P{^{1}H} NMR spectrum of crude 2f



Hexyl(2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphine (2g)

^{31}P: δ –53.58 (s, minor product), –57.7 (s, major product). MS calcd for $C_{27}H_{29}OP$: m/z 400.2. Found: 404.8. Formed as a 1:1.06 ratio of diastereomers in 8 % conversion as determined by NMR spectroscopy.

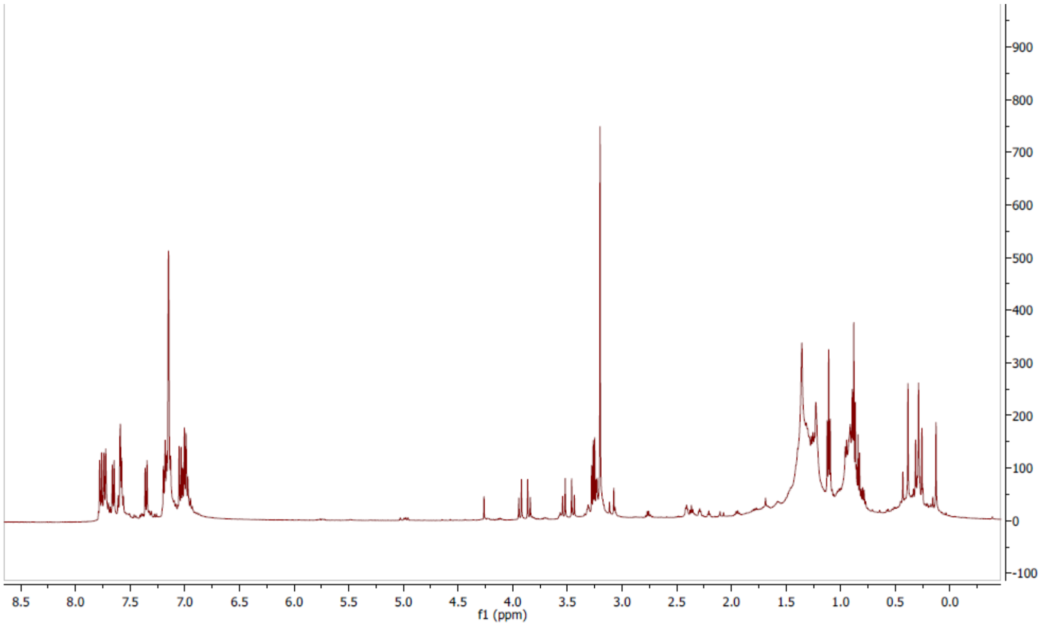


Figure S15: ^{1}H NMR spectrum of crude 2g

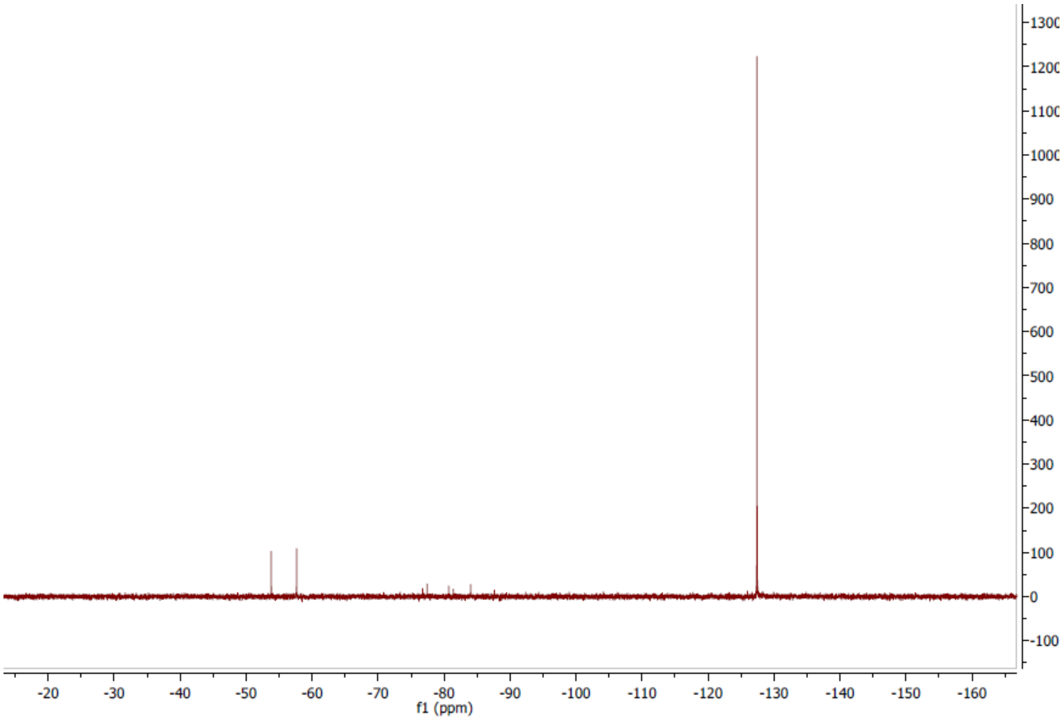
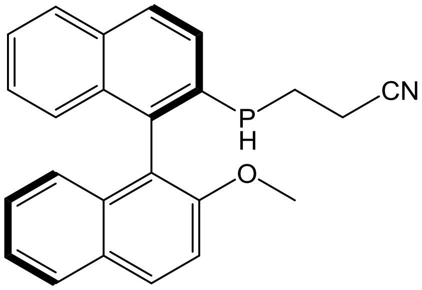


Figure S16: $^{31}P\{^{1}H\}$ NMR spectrum of crude 2g



3-((2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphanyl)propanenitrile (2h)

^{1}H: δ 7.76 (q, CH_{Ar}, 1 H), 7.66 (m, CH_{Ar}, 2 H), 7.45 (dq, CH_{Ar}, 1 H), 7.31 (m, CH_{Ar}, 1 H), 7. 19 (t, CH_{Ar}, 1 H), 7.13 (m, CH_{Ar}, 1 H), 7.05 (d, CH_{Ar}, 1H), 7.02–6.94 (m, CH_{Ar}, 4 H), 3.87 (ddd, J_{PH} = 212.23, $^{2}J_{PH}$ = 10.63 Hz, $^{3}J_{PH}$ = 4.00 Hz, P*H*, 1 H, minor product), 3.69 (ddd, J_{PH} = 210.94, $^{2}J_{PH}$ = 10.95 Hz, $^{3}J_{PH}$ = 3.84 Hz, P–H, 1 H, major product), 3.23 (s, CH_3, 3 H, minor product), 3.15 (s, CH_3, 3 H, major product), 2.15 (m, CH_2, 2 H). 1.78 (m, CH_2, 2 H). ^{31}P{^{1}H}: δ –53.6 (s, major product), –56.5 (s, minor product). MS calcd for $C_{24}H_{20}NOP$: m/z 369.1. Found: 369.1. Mixture of diastereomers in a 1:1.12 ratio formed in 80% conversion as determined by NMR spectroscopy. Isolated 72% yield as a yellow solid.

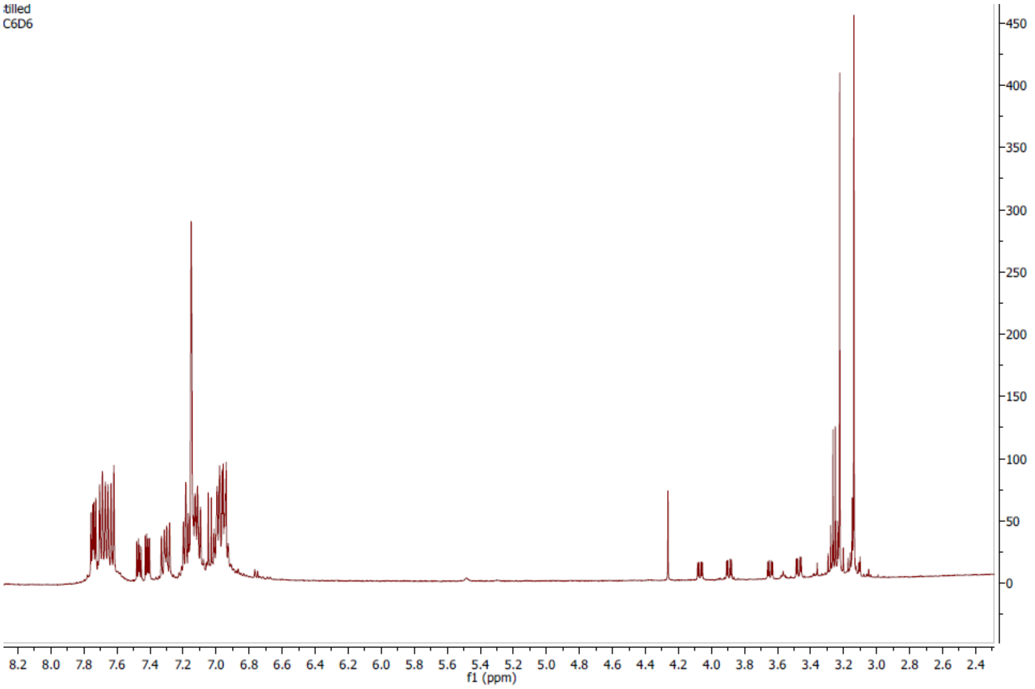


Figure S17: ^{1}H NMR spectrum of crude 2h

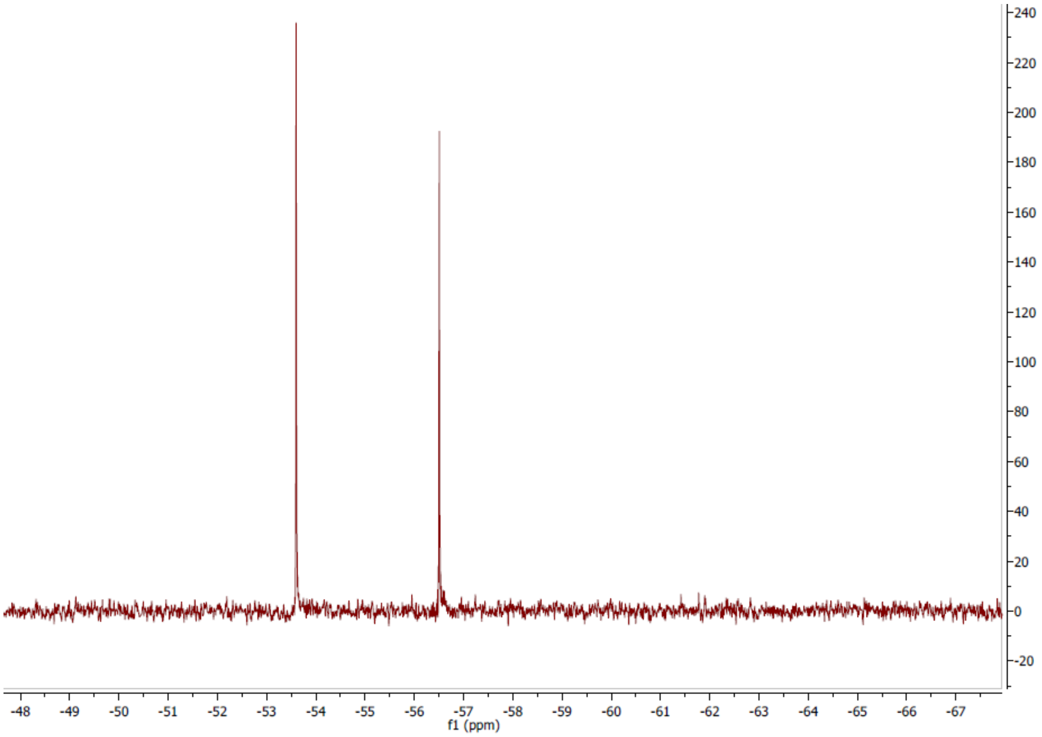
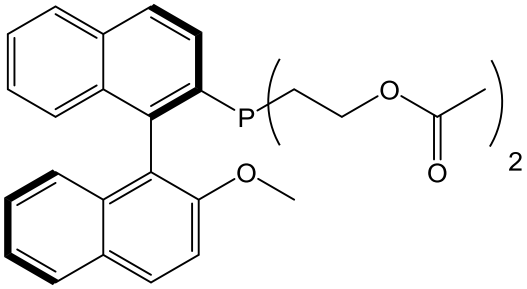


Figure S18: ^{31}P{^{1}H} NMR spectrum of crude 2h



((2'-methoxy-[1,1'-binaphthalen]-2-yl)phosphanediyl)bis(ethane-2,1-diyl) diacetate (3a)

$^{31}P\{^1H\}$ NMR: δ -34.2 (s). MS calcd for $C_{29}H_{29}O_5P$: m/z 488.2. Found: 489.3. Reaction of two equivalents of the substrate to (*R*)-MeO-MOPH$_2$ resulted in 64 % conversion to the tertiary phosphine after 48 h as determined by ^{31}P NMR spectroscopy.

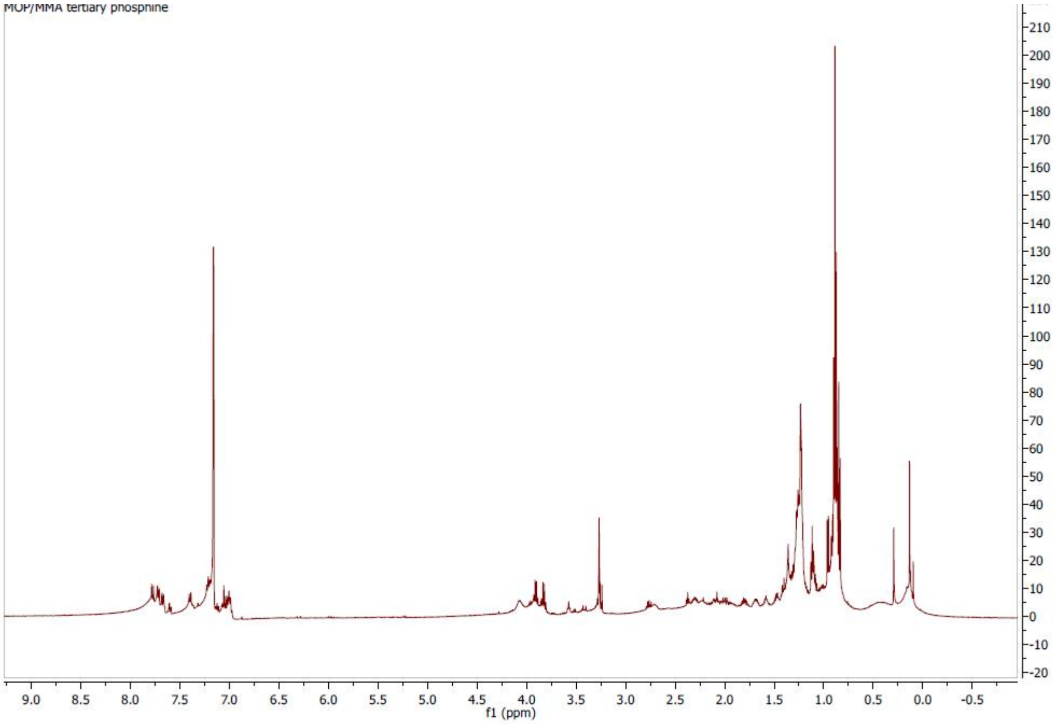


Figure S19: ^1H NMR spectrum of crude 3a

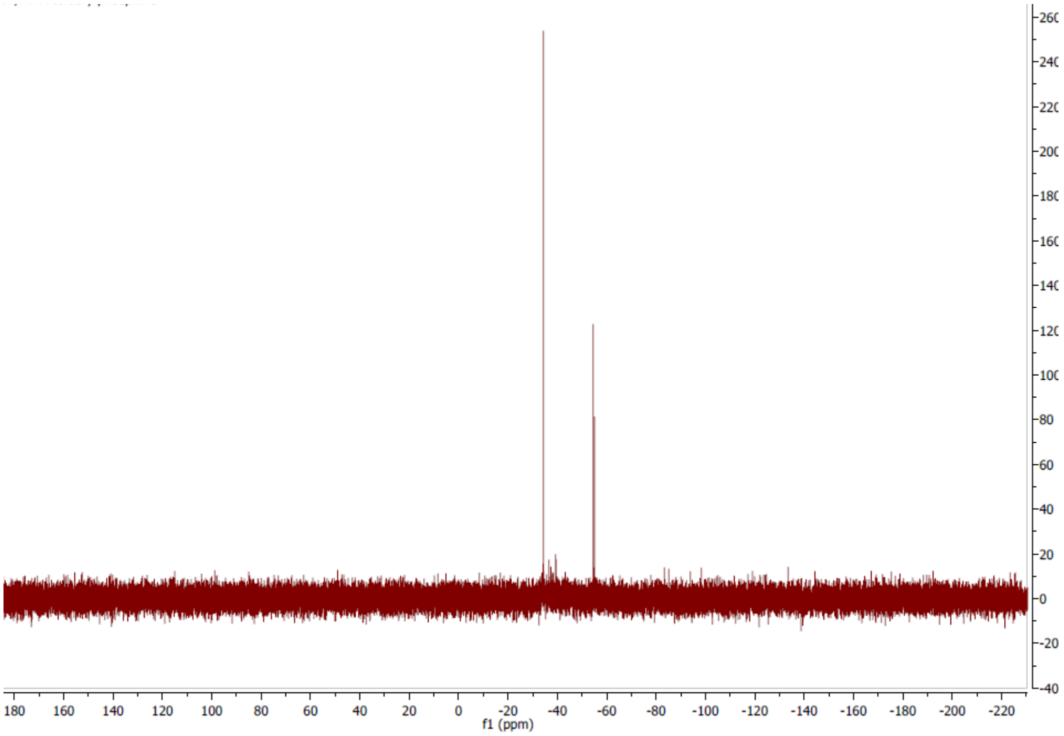
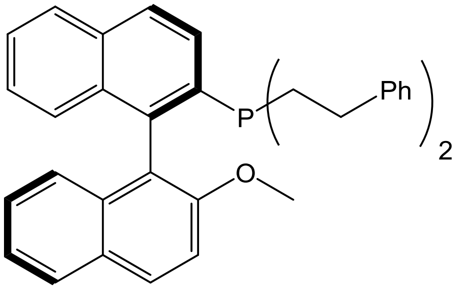


Figure S20: $^{31}P\{^1H\}$ NMR spectrum of crude 3a



(2'-methoxy-[1,1'-binaphthalen]-2-yl)diphenethylphosphine (3b)

$^{31}P\{^1H\}$ NMR: δ -34.3 (s). MS calcd for $C_{37}H_{33}OP$: m/z 524.2. Found: 522.8. Reaction of two equivalents of the substrate to (*R*)-MeO-MOPH_2 resulted in 30 % conversion to the tertiary phosphine after 48 h as determined by ^{31}P NMR spectroscopy.

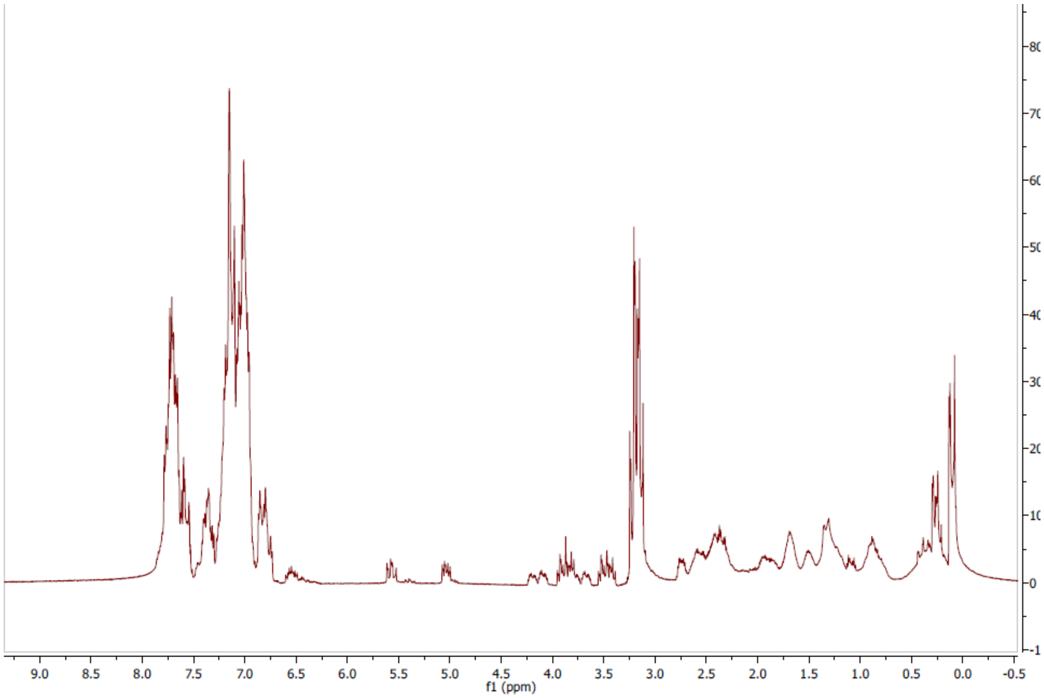


Figure S21: ^{1}H NMR spectrum of crude 3b

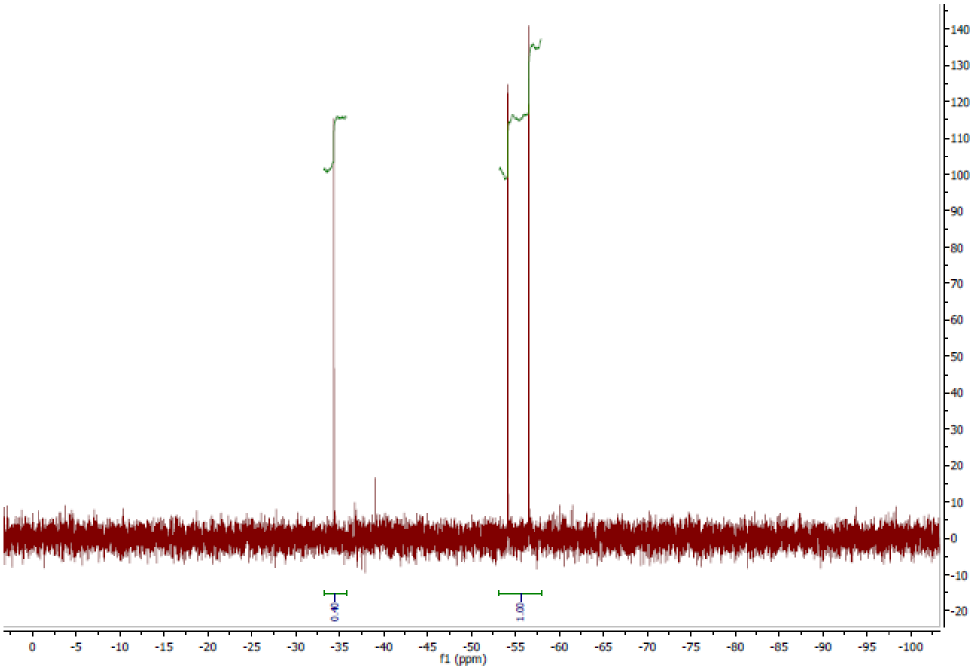


Figure S22: ^{31}P{^{1}H} NMR spectrum of crude 3b

Air-stability of secondary phosphines

Secondary phosphine **2f** showed no oxidation after 7 d in an uncapped NMR tube in benzene-d_6 (Figure S22).

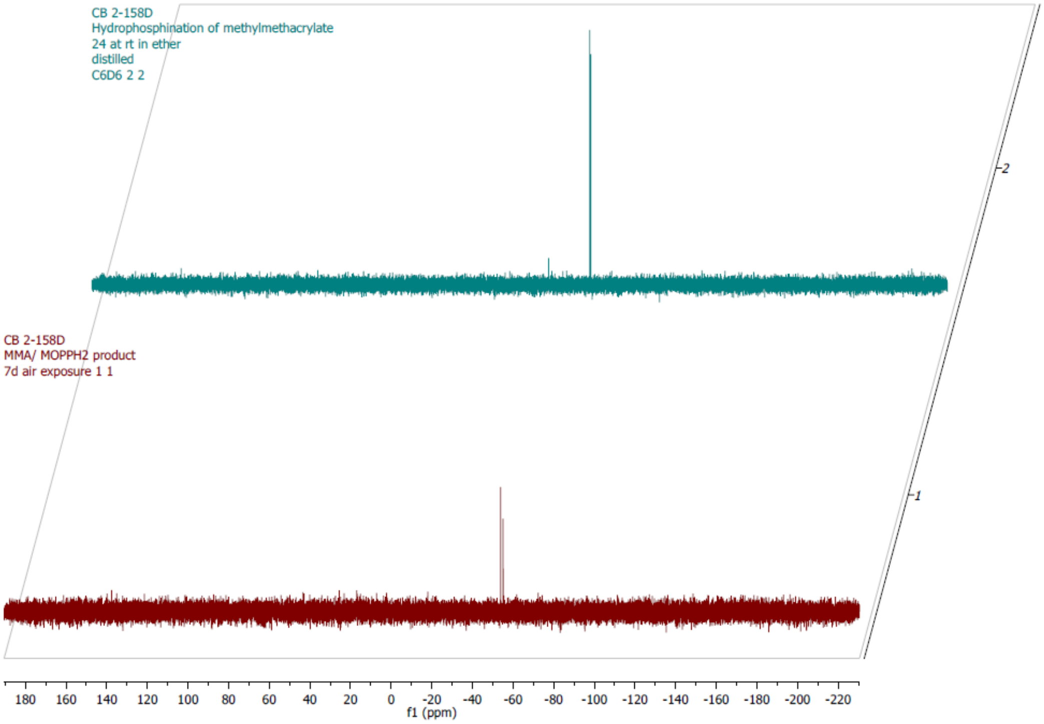
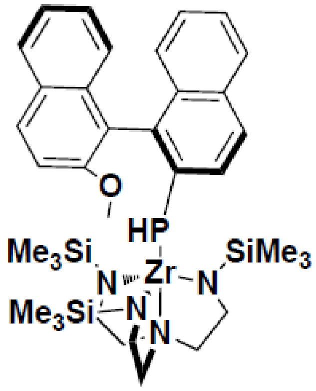


Figure S23: Product phosphine 2f after isolation (top) and 7 d of air exposure in benzene-d_6 (bottom).

Formation of (N$_3$N)Zr(*R*)-MeO-MOPH



(4) (N$_3$N)Zr(*R*)-MeO-MOPH

Synthesis of **2**. A scintillation vial was charged with **1** (198 mg, 0.440 mmol) and 3 mL of benzene. To the solution of **1**, (*R*)-MeO-MOPH$_2$ (139 mg, 0.443 mmol) was added and the resultant red solution was stirred at ambient temperature for 30 minutes, then frozen and lyophilized. The red powder was dissolved in Et$_2$O, filtered through a bed of Celite® and concentrated until incipient crystallization. Gentle warming redissolved the solids, and the solution was cooled to –30 ˚C for ~16 h to afford red crystals (276 mg, 0.361mmol, 82%). ^{1}H NMR: δ 8.16 (t, J = 9.5 Hz, C$_{10}H_6$, 1H), 7.83 (d, J = 7.9 Hz, C$_{10}H_6$, 1H), 7.78 (t, J = 7.9 Hz, C$_{10}H_6$, 2H), 7.51 (d, J = 9.5 Hz, C$_{10}H_6$, 1H), 7.32 (d, J = 7.9 Hz, C$_{10}H_6$, 2H), 7.14–7.10 (m, C$_{10}H_6$, 3H), 7.00 (t, C$_{10}H_6$, 2H), 3.61 (d, J_{PH} = 240 Hz, P*H*, 1H), 3.40 (s, CH_3, 3H), 3.24 (m, C$_2H_2$ 6H), 2.12 (m, C$_2H_2$ 6H), 0.16 (s, CH_3, 27H). ^{13}C{^{1}H} NMR: δ 154.71 (s), 134.36 (d), 133.91 (s), 132.78 (s), 132.17 (s), 131.91 (d), 129.96 (s), 129.73 (s), 128.75 (s), 128.21 (s), 126.32 (m), 126.23 (s), 126.95 (s), 125.85 (d), 125.77 (s), 124.91 (s), 123.73 (s), 123.50 (d), 114.21 (s), 113.33 (s), 63.52 (s), 55.83 (s), 47.37 (s), 0.93 (s). ^{31}P{^{1}H} NMR: δ –36.3 (s). ^{31}P NMR: –36.3 (dd, J = 236 Hz, 9.8 Hz). IR (KBr, Nujol): 2950 m, 2895 w, 2838 w, 2290 w (ν_{PH}), 1621 w, 1592 w, 1509 w, 1460 w, 1398 w, 1347 w, 1332 w, 1244 s, 1147 w, 1081 w, 927 s, 807 s, 723 w, 647 w, 412 w cm^{-1}. Anal. Calcd. for C$_{36}$H$_{55}$N$_4$OSi$_3$PZr: C, 56.42; H, 7.23; N, 7.31. Found: C, 56.71; H, 7.59; N, 7.07.

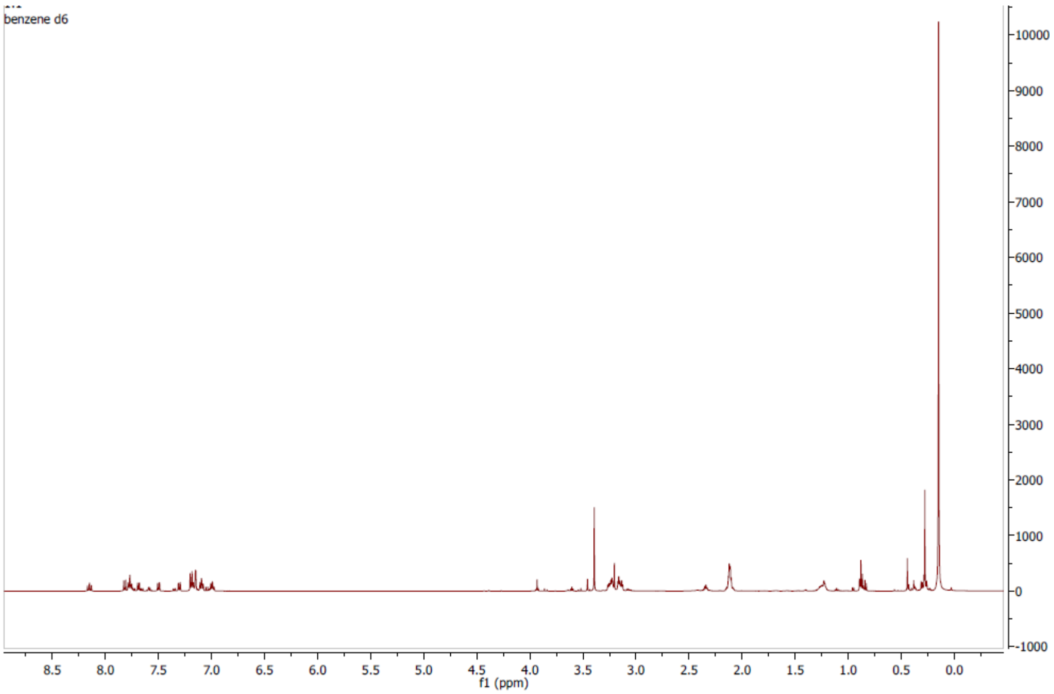


Figure S24: Full ^{1}H NMR spectrum of isolated 4

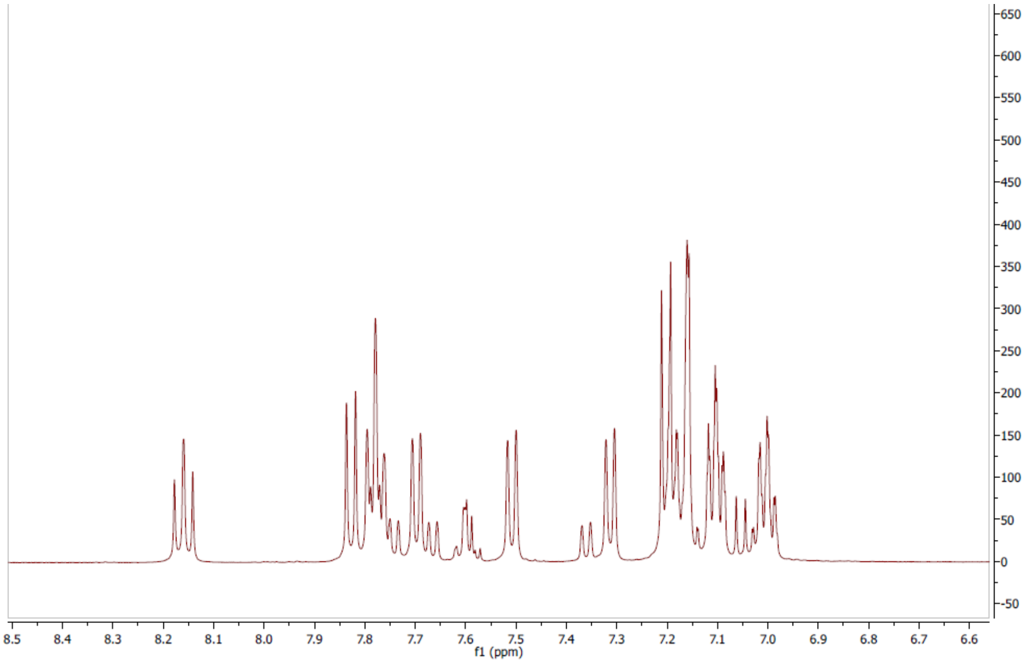


Figure S25: ^{1}H NMR spectrum of isolated 4, 6.6-8.5 ppm

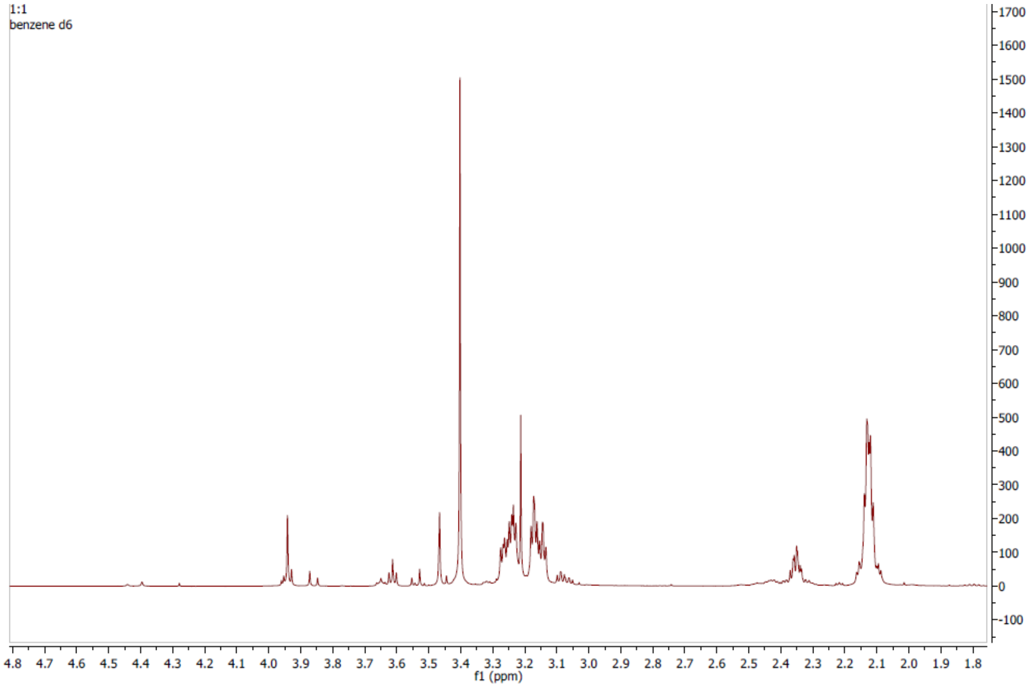


Figure S26: ^{1}H NMR spectrum of isolated 4, 1.8 – 4.8 ppm

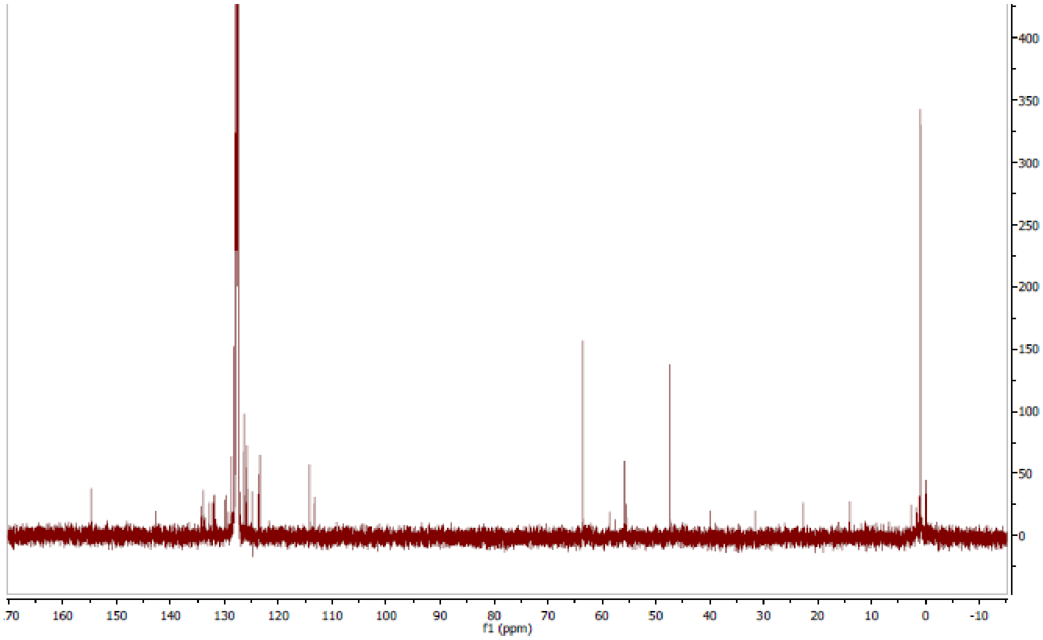


Figure S27: ^{13}C NMR spectrum of isolated 4

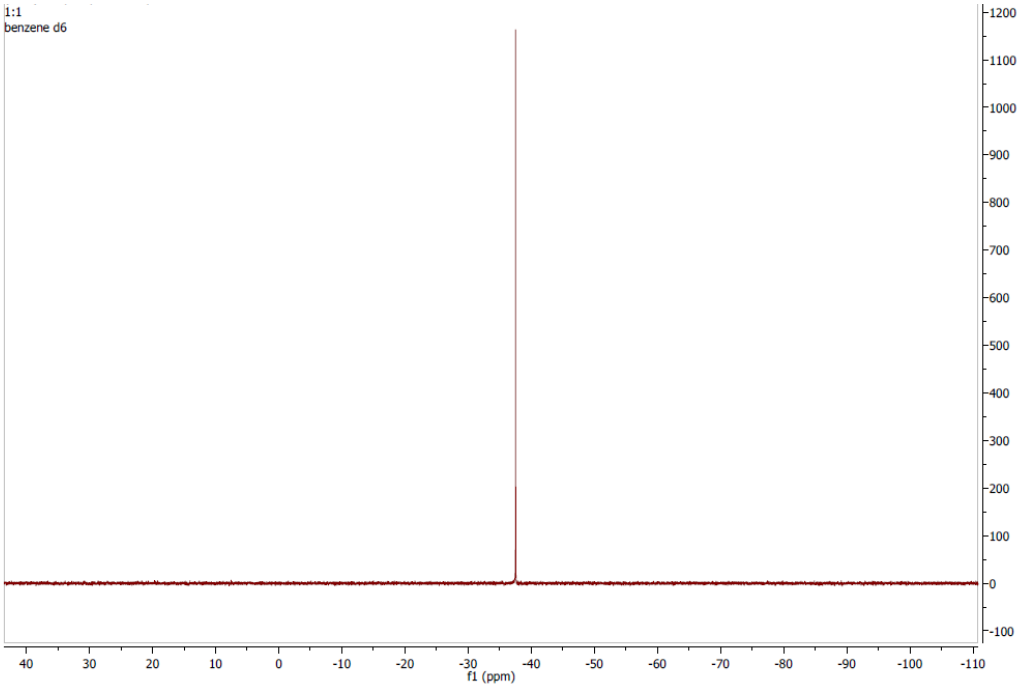


Figure S28: ^{31}P{^{1}H} NMR spectrum of isolated 4

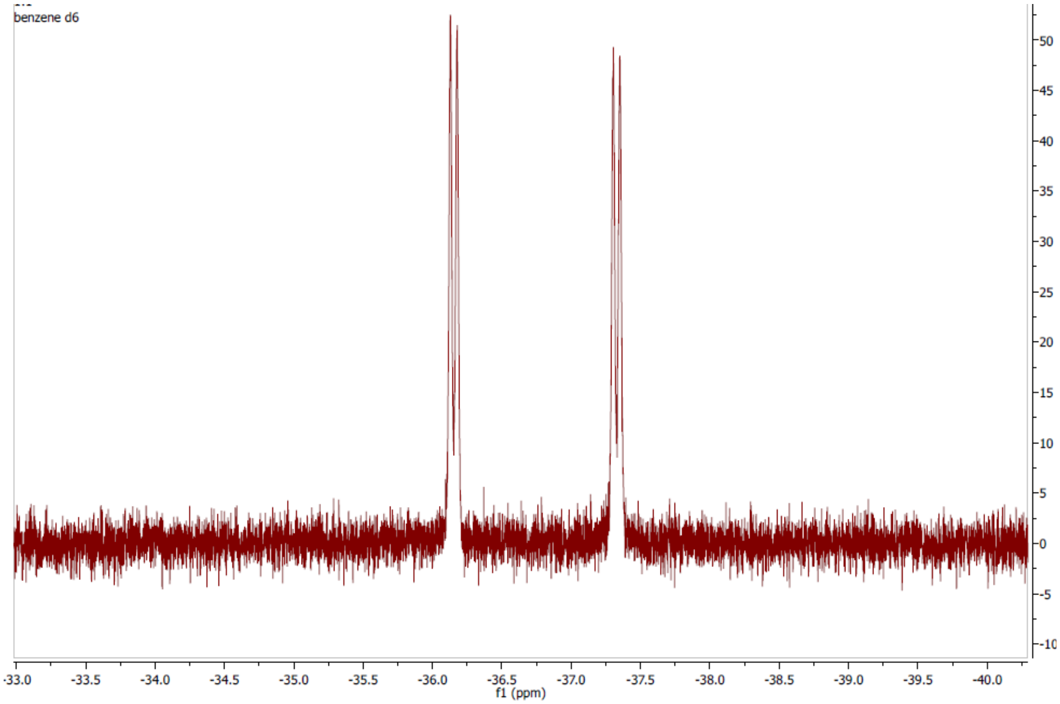


Figure S29: ^{31}P NMR spectrum of isolated 4

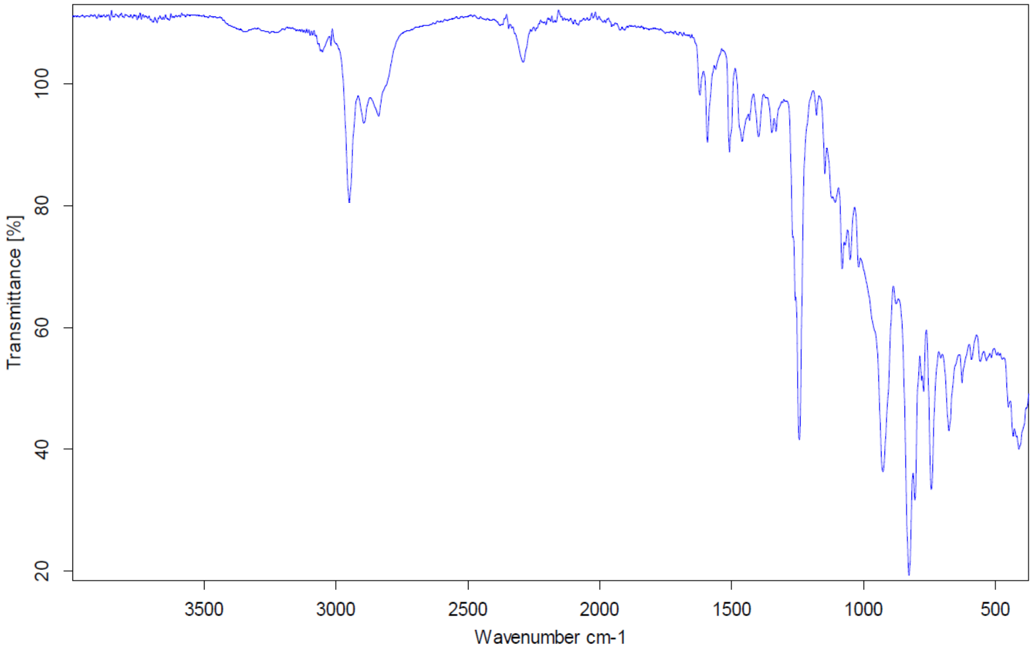


Figure S30: IR spectrum of 4

Crystal data and structure refinement parameters for compound 4.

X-ray quality crystals were obtained from concentrated Et_2O solution cooled in a –30℃ freezer in a glovebox for 2 d. X-Ray diffraction data were collected at 128 K on a Bruker APEX 2 CCD platform diffractometer (MoKα, λ = 0.71073 Å). Crystals were selected and mounted under Paratone-N cryoprotectant oil on to a nylon loop. The structure was solved by direct methods and standard difference map techniques, the refinement was completed with full-matrix least squares procedures on F^2 with SHELXTL (version 6.14).[5] All non-hydrogen atoms were refined anisotropically, in calculated positions, using a riding model. The hydrogen atoms on the phosphorus atoms, H(1) and H(2), were refined freely after location in the Fourier difference map. Crystal data and refinement details are presented in Table S1. Two solvent molecules were included in the unit cell. Both were refined isotopically, but no additional modeling was made for the observed disorder.

Table S1. Crystal data and structure refinement parameters for **4**.

formula	$C_{72}H_{110}N_8O_2P_2Si_6Zr_2$
M	1532.59
crystal system	triclinic
color	yellow
a/Å	10.843(2)
b/Å	12.324(2)
c/Å	18.699(3)
α/°	77.714(2)
β/°	81.478(2)
γ/°	71.588(2)
unit cell vol./$Å^3$	2307.7(7)
space group	P 1
Z	1
θ range/°	1.92–21.89
μ/mm^{-1}	0.385
N	16718
N_{ind}	10948
R_{int}	0.0332
R_1[a] ($I > 2\sigma(I)$)	0.0485
wR_2[b] ($I > 2\sigma(I)$)	0.1255
$\Delta\rho_{max}$; $\Delta\rho_{min}$/e $Å^3$	0.525; –0.400
GoF on R_1	1.056

[a] $R_1 = ||F_o| - |F_c|| / \Sigma|F_o|$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}s^{1/2}$.

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