Electronic Supplementary Material (ESI) for Dalton Transactions.

Direct P-Functionalization of Azobenzene by a Cationic Phosphidozirconocene Compound†

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Supporting Information

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1. General procedures

All reactions were carried out under Ar using conventional Schlenk techniques or in a glovebox with an Ar atmosphere. Toluene, CH_2Cl_2, Et_2O, pentane and THF were dried using a Grubbs-type solvent purification system with alumina spheres as the drying agent. Deuterated solvents were dried by passage through a short column of activated neutral alumina (Brockman grade I) and stored over activated 3Å molecular sieves in the glovebox, either at room temperature (C_6D_5Br) or at -35°C (CD_2Cl_2). Alumina and molecular sieves were activated by heating 6 hours above 180°C *in vacuo*. Compounds **I** ($[Cp_2Zr(Me)(PCy_2)]$) and **II** ($[Cp_2Zr(PCy_2)][MeB(C_6F_5)_3]$) were synthesized according to previously reported procedures.[1] Tris(pentafluorophenyl)borane was obtained from Boulder Scientific Company and purified by extraction from pentane followed by precipitation. Azobenzene was recrystallized from warm EtOH. Sodium tetrakis[pentafluorophenyl]borate ($NaB(C_6F_5)_4$) was dried over P_2O_5 at 6.10^{-3} mbar and 120 °C for 14 hours.[2] All other reagents were commercially available and used as received. Analyses were performed using analytical equipement of the Organisch-Chemisches Institut der Westfalischen-Wilhelms Üniversitat Münster, or of the "Plateforme d'Analyses Chimiques et de Synthèse Moléculaire de l'Université de Bourgogne". The identity and purity of the compounds were unambiguously established using elemental analysis, high-resolution mass spectrometry, X-ray diffraction analysis, NMR and IR spectroscopy. NMR spectra (^1H, ^{11}B, ^{13}C, ^{19}F, ^{31}P) were recorded on a DD2600 MHz (Agilent), a Bruker AV500, and a VNMRS500 MHz (Agilent). NMR spectroscopy chemical shifts are quoted in parts per million (δ) relative to TMS (for ^1H and ^{13}C), $BF_3.Et_2O$ (for ^{19}F) or H_3PO_4 (for ^{31}P). For ^1H and ^{13}C spectra, values were determined by using solvent residual signals (*e.g.* $CDHCl_2$ in CD_2Cl_2) as internal standards.[3] The ^{31}P, ^{19}F and ^{11}B NMR spectra were referenced according to IUPAC recommendations (absolute referencing).

X-Ray diffraction: For compound **2'** data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (R. W. W. Hooft, Bruker AXS, 2008, Delft, The Netherlands); data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods Enzymol.* **1997**, *276*, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Crystallogr*. **2003**, *A59*, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr*. **1990**, *A46*, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr*. **2008**, *A64*, 112-122) and graphics, XP (BrukerAXS, 2000). For compound **3** data sets were collected with a D8 Venture Dual Source 100 CMOS diffractometer. Programs used: data collection: APEX2 V2014.5-0 (Bruker AXS Inc., 2014); cell refinement: SAINT V8.34A (Bruker AXS Inc., 2013); data reduction: SAINT V8.34A (Bruker AXS Inc., 2013); absorption correction, SADABS V2014/2 (Bruker AXS Inc., 2014); structure solution SHELXT-2014 (Sheldrick, 2014); structure refinement SHELXL-2014 (Sheldrick, 2014) and graphics, XP (Bruker AXS Inc., 2014). *R*-values are given for observed reflections, and wR^2 values are given for all reflections.

Exceptions and special features: For compound **2'** one C_6F_5 group was found disordered over two positions. The hydrogen atom at N2 was refined freely. For compound **3** one cyclohexyl group was found disordered over two positions. Several restraints (SADI, SAME, ISOR and SIMU) were used in

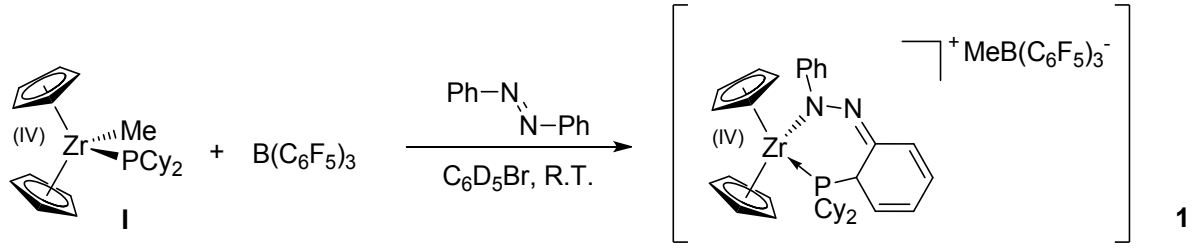
[1] A. T. Normand, C. G. Daniliuc, B. Wibbeling, G. Kehr, P. Le Gendre and G. Erker, *J. Am. Chem. Soc.*, 2015, **137**, 10796.
[2] Yakelis, N. A.; Bergman, R. G. *Organometallics* 2005, **24**, 3579.
[3] Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., *Organometallics* 2010, **29**, 2176.

order to improve refinement stability of both compounds. Compound **3** was refined as a 2-component inversion twin.

2. Experimental Part

2.1. Synthesis of compounds

***In situ* generation of compound 1**



I **1**

A red-orange solution of compound **II** was prepared by mixing compound **I** (43.4 mg, 0.1 mmol) and tris(pentafluorophenyl)borane (51.2 mg, 0.1 mmol) in C_6D_5Br (1 mL). Azobenzene (18.2 mg, 0.1 mmol) was added to the reaction mixture, which turned to a deep purple color instantly. This solution was placed in a flame-sealed NMR tube and compound **1** was characterized by ^{1}H NMR spectroscopy at 273 K (Figure S1). Small amounts of residual azobenzene were observed, along with growing quantities of compound **2** when the sample was warmed up from 273 to 300 K. Heteronuclear and 2D NMR spectroscopy were better performed at 300 K due to the disappearance of important cross peaks at lower temperatures, hence the experiment was repeated and the spectra measured directly at 300 K (Figures S2-S6).

^{1}H NMR (500 MHz, C_6D_5Br, 273 K): δ = 7.27 (m, 2H, *m*-Ph), 6.93 (m, 1H, *p*-Ph), 6.68 (m, 2H, *o*-Ph), 6.11-6.05 (m, 1H, =C*H*), 5.97 (s, 5H, Cp), 5.95-5.94 (m, 2H, two overlapping =C*H*), 5.87-5.82 (m, 1H, =C*H*), 5.45 (s, 5H, Cp), 3.86 (dm, $^2J_{PH}$ = 12.5 Hz, 1H, PC*H*CN), 2.25 (m, 1H, C*H* of Cy), 2.06-1.95 (m, 1H, C*H* of Cy), 1.88-1.44 (m, 8H, overlapping CH_2 of Cy), 1.44-0.93 (m, 12H, CH_2 of Cy overlapping with CH_3-B), 1.18 (bs, 3H, CH_3-B overlapping with CH_2 of Cy).

^{13}C{^{1}H} NMR (126 MHz, C_6D_5Br, 300 K): δ = 149.9 (s, *i*-Ph), 148.6 (dm, $^1J_{FC}$ ~ 235 Hz, Ar*C*-F), 142.4 (bs, *C*=N), 137.4 (dm, $^1J_{FC}$ ~ 245 Hz, Ar*C*-F overlapping with ArC-F), 136.5 (dm, $^1J_{FC}$ ~ 250 Hz, Ar*C*-F overlapping with ArC-F), n.o (*m*-Ph, overlapping with C_6D_5Br signal), 128.9 (d, J_{PC} = 3.8 Hz, =*C*H), 128.5 (d, J_{PC} = 10.6 Hz, =*C*H), 125.3 (d, J_{PC} = 5.0 Hz, =*C*H), 123.2 (s, *p*-Ph), 118.5 (d, J_{PC} = 4.3 Hz, =*C*H), 116.8 (s, *o*-Ph), 110.0 (s, Cp), 108.9 (s, Cp), 46.2 (d, $^1J_{PC}$ = 13.3 Hz, P*C*HCN), 37.5 (d, $^1J_{PC}$ = 2.6 Hz, *C*H of Cy), 34.9 (d, $^1J_{PC}$ = 5.7 Hz, *C*H of Cy), 30.0 (bs, *C*H_2 of Cy), 29.8 (bs, *C*H_2 of Cy), 28.2 (s, *C*H_2 of Cy), 27.9 (d, J_{PC} = 4.8 Hz, *C*H_2 of Cy), 27.1 (d, J_{PC} = 10.1 Hz, *C*H_2 of Cy), 27.0 (d, J_{PC} = 7.0 Hz, *C*H_2 of Cy), 26.8 (d, J_{PC} = 10.2 Hz, *C*H_2 of Cy), 26.4 (d, J_{PC} = 10.4 Hz, *C*H_2 of Cy), 25.5 (m, two overlapping *C*H_2 of Cy), 11.0 (br s, *C*H_3-B).

^{1}H, ^{1}H gCOSY (500 MHz / 500 MHz, C_6D_5Br, 300 K)[selected traces]: δ^{1}H / δ^{1}H = 7.27 / 6.93, 6.68 (*m*-Ph / *p*-Ph, *o*-Ph), 3.93 / 5.92-5.85 (PC*H*CN, =C*H*).

^{1}H, ^{13}C gHMBC (500 MHz / 126 MHz, C_6D_5Br, 300 K)[selected traces]: δ ^{1}H / δ ^{13}C = 7.27 / 149.9, 116.8 (*m*-Ph / *i*-Ph, *o*-Ph), 6.68 / 149.9 (*o*-Ph / *i*-Ph), 5.95-5.94 / 142.4 (=C*H* / *C*=N) 3.93 / 142.4, 128.5, 125.3, 37.5 (PC*H*CN / *C*=N, =*C*H, =*C*H, *C*H of Cy).

^{11}B{^{1}H} NMR (160 MHz, C_6D_5Br, 300 K): δ = -14.2 ($\nu_{1/2}$ ~ 77 Hz)

^{19}F{^{1}H} NMR (470 MHz, C_6D_5Br, 300 K): δ = -131.4 (m, 2F, *o*-Ar*F*), -163.6 (m, 1F, *p*-Ar*F*), -166.1 (m, 2F, *m*-Ar*F*). $\Delta\delta^{mp}$ = 2.5 ppm.

^{31}P{^{1}H} NMR (202 MHz, C_6D_5Br, 300 K): δ = 78.0 ($\nu_{1/2}$ ~ 7 Hz).

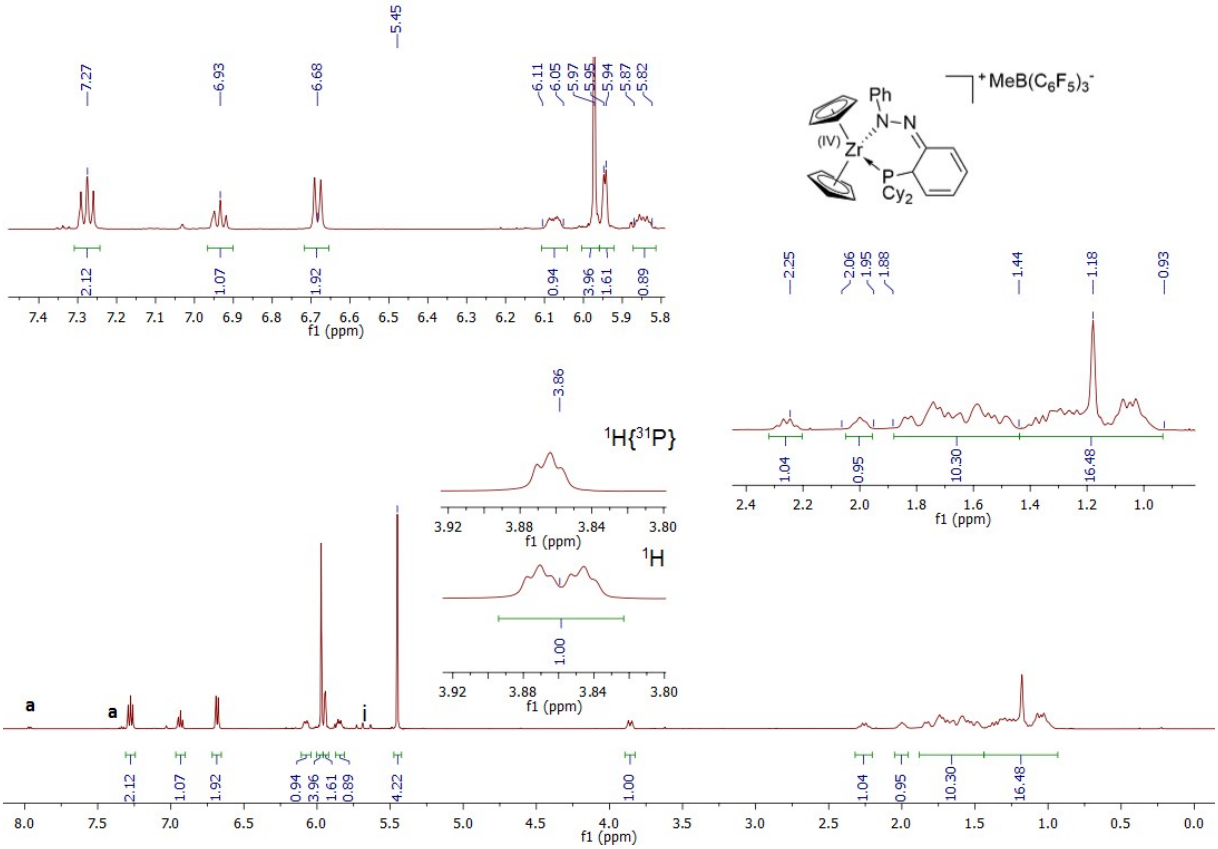


Figure S1. ^{1}H NMR (500 MHz, C_6D_5Br, 273 K)(a: azobenzene; i: impurity)

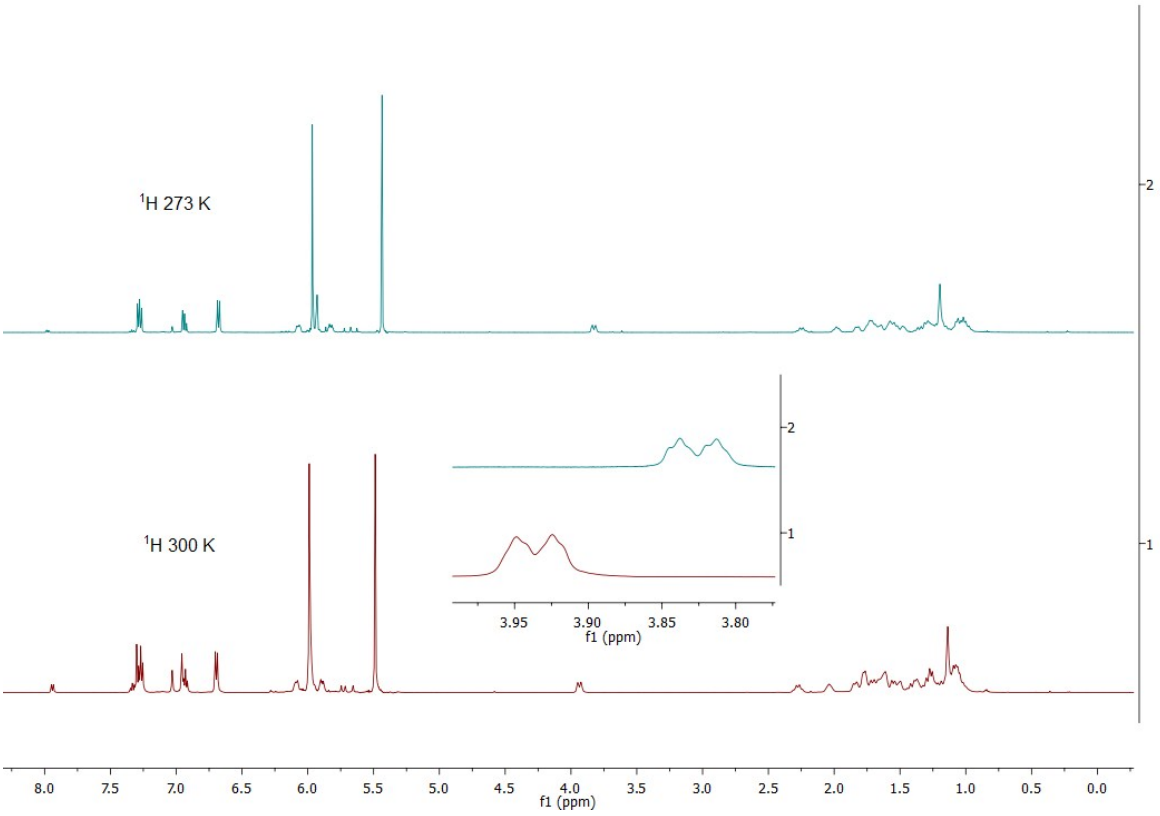


Figure S2. ^{1}H NMR (500 MHz, C_6D_5Br, 273 K and 300 K, different samples)

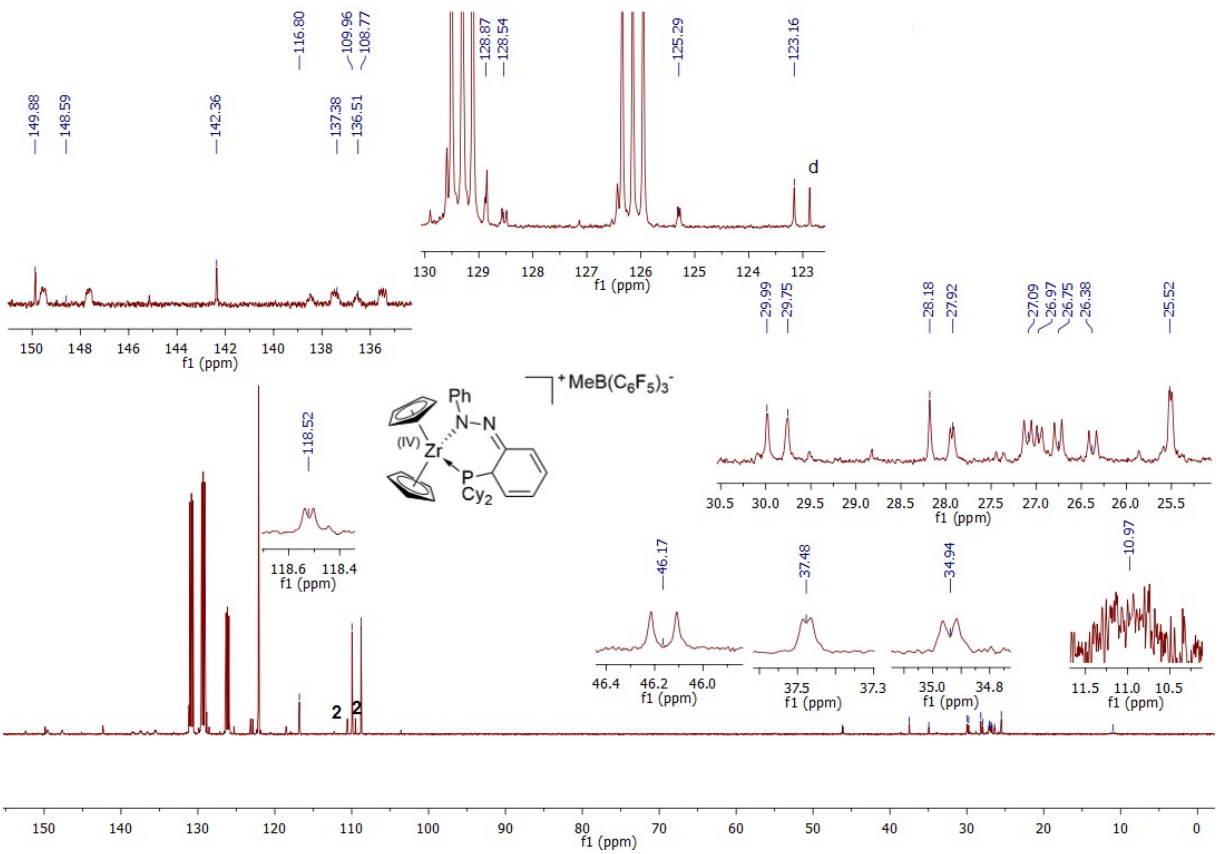


Figure S3. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_5Br, 300 K)

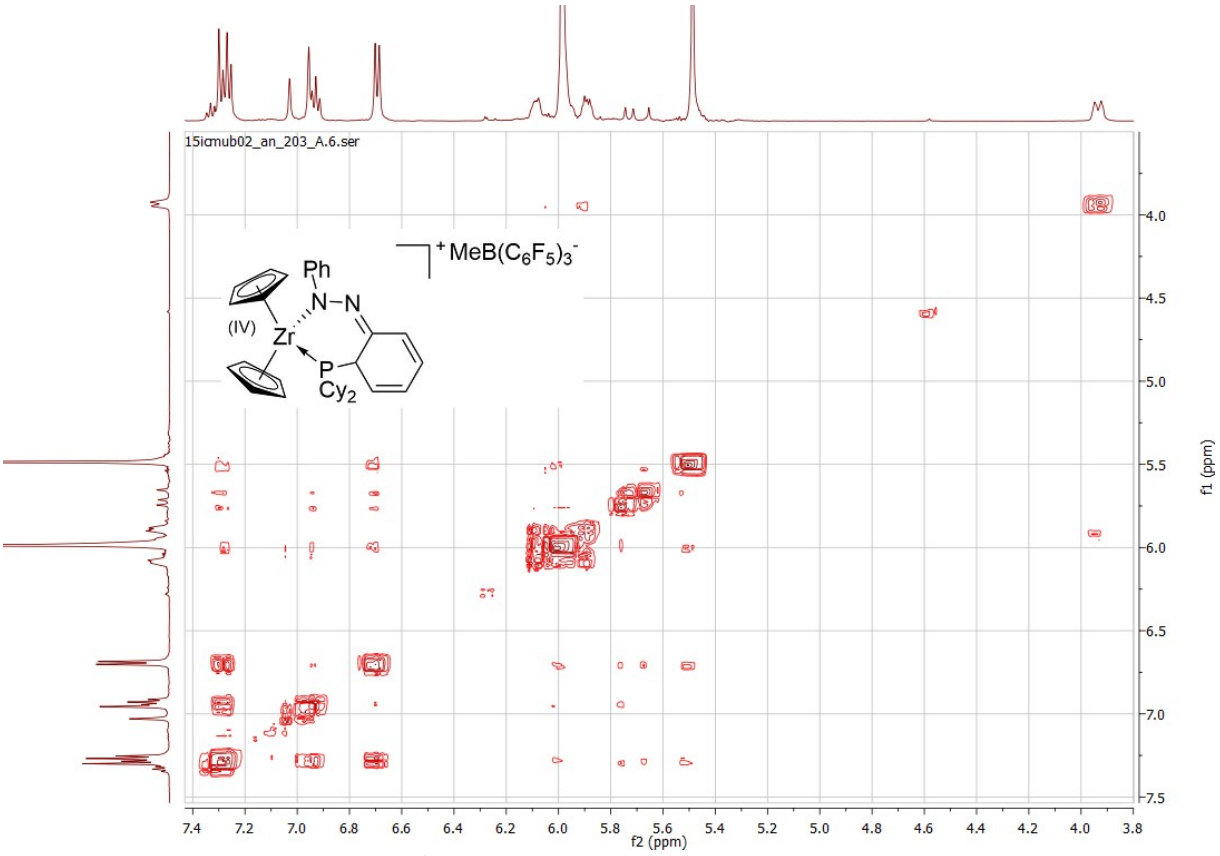


Figure S4. ^{1}H, ^{1}H gCOSY (500 MHz / 500 MHz, C_6D_5Br, 300 K)

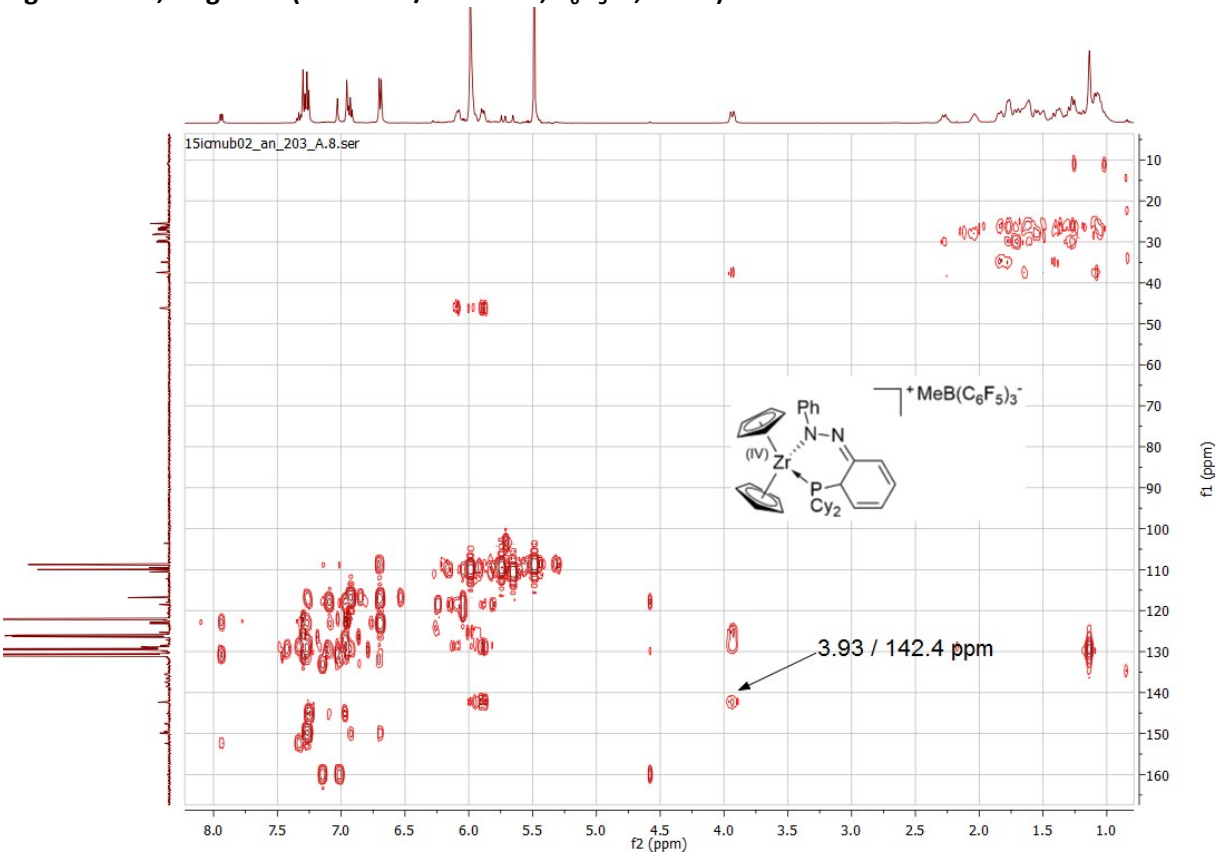


Figure S5. ^{1}H, ^{13}C gHMBC (500 MHz / 126 MHz, C_6D_5Br, 300 K)

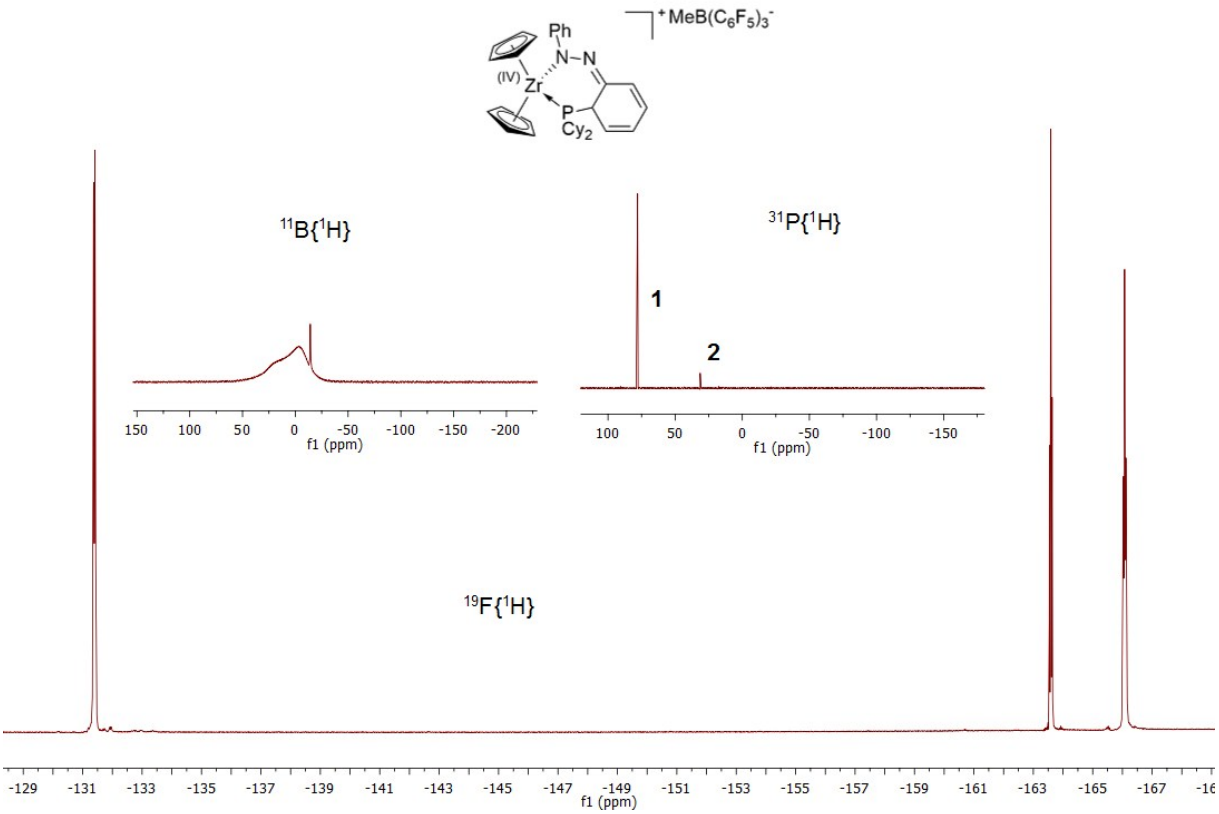


Figure S6. $^{11}B\{^1H\}$ NMR (160 MHz), $^{19}F\{^1H\}$ NMR (470 MHz), $^{31}P\{^1H\}$ NMR (202 MHz)(C_6D_5Br, 300 K)

Attempted isolation of compound 1

Crude mixtures of **1** and **2** could be obtained in the following way ; in a glovebox with an Ar atmosphere, compound **I** (434 mg, 1.0 mmol) and tris(pentafluorophenyl)borane (512 mg, 1 mmol) were mixed in toluene (4.5 mL) for 1 min, followed by addition of azobenzene (182 mg, 1.0 mmol). A purple viscous oil precipitated out. The supernatant solution was removed and the oil was added to 50 mL of pentane under vigorous agitation. The resulting oil was rinsed twice with pentane (5 mL) and dried *in vacuo*. Analysis by ^1H NMR spectroscopy in C_6D_5Br (acquisition performed within 5 min of sample preparation) revealed a 98:2 mixture of compounds **1** and **2** with 66 mol % of toluene. This material was used for the preparation of compound **2'** (*vide infra*).

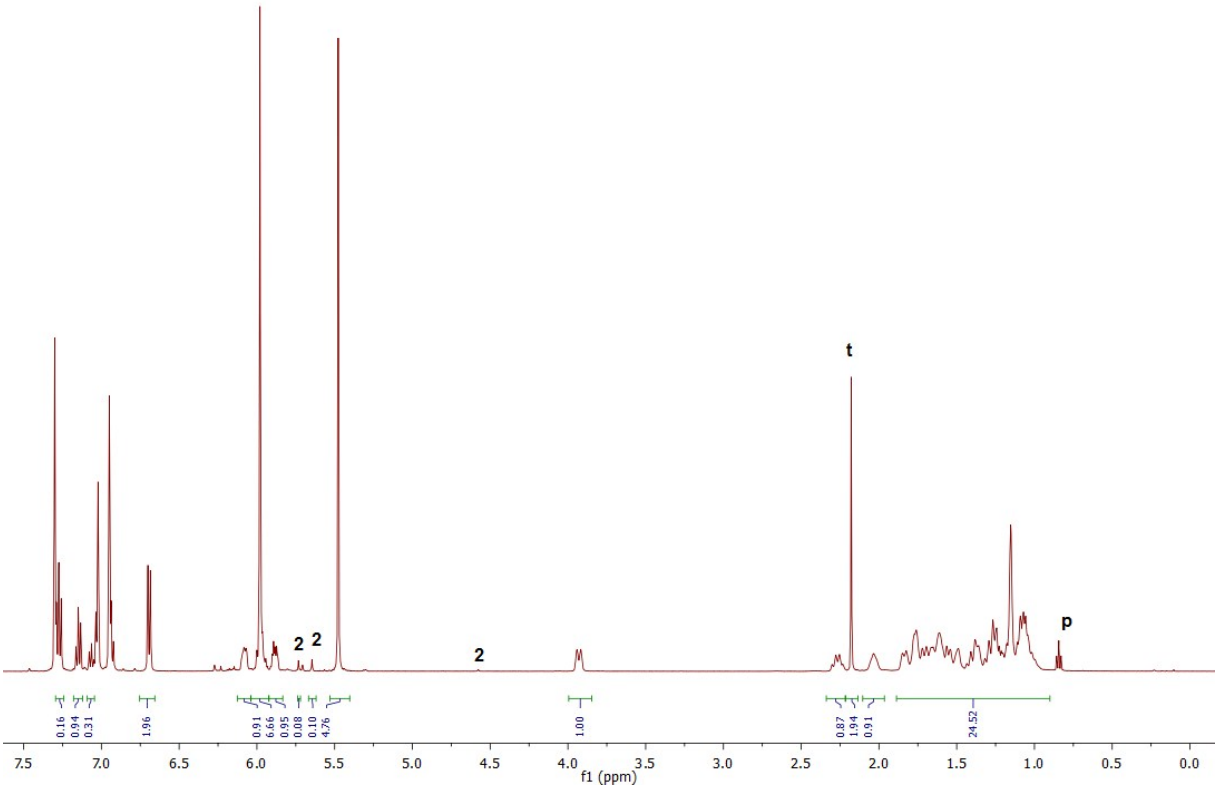
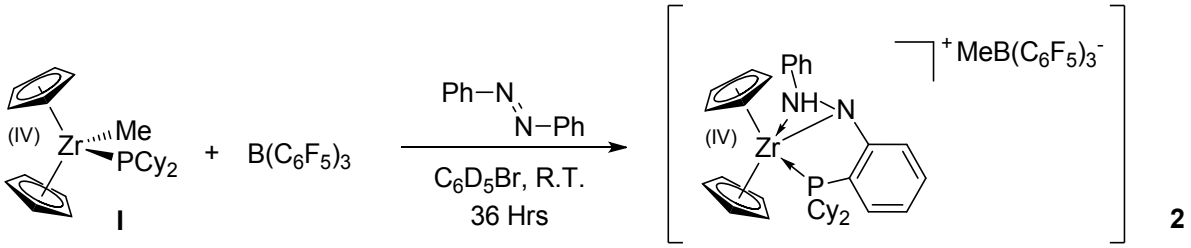


Figure S7. ^{1}H NMR (500 MHz, C_6D_5Br, 300 K)(t: toluene; p:pentane)

***In situ* generation of compound 2**



I **2**

Compound **2** was prepared and characterized *in situ* as described for the preparation of compound **1**. After being stored ca. 36 hours in C_6D_5Br at room temperature in a flame-sealed NMR tube, > 95 % conversion to compound **2** was observed. The ^{1}H and ^{31}P NMR spectra of the cationic part of 2 were essentially similar to that of compound **2'**, therefore the assignment of ^{1}H and ^{13}C NMR signals was made by analogy to compound **2'**.

^{1}H NMR (500 MHz, C_6D_5Br, 299 K)[numbering of positions on the Ar ring attached to P and N: carbon attached to P: 1, carbon attached to N: 2 etc.]: δ = 7.26 (m, 2H, *m*-Ph), 7.17-7.13 (m, 1H, *H*(6)C=), 7.12-7.08 (m, 1H, *p*-Ph), 7.04-6.99 (m, 1H, *H*(5)C= overlapping with C_6D_5Br signal), 6.97 (dm, 2H, *o*-Ph), 6.73-6.68 (m, 1H, *H*(4)C=), 6.05 (dd, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{PH}$ = 4.1 Hz, 1H, *H*(3)C=), 5.74 (d, $^{3}J_{PH}$ = 1.4 Hz, 5H, Cp), 5.65 (d, $^{3}J_{PH}$ = 1.3 Hz, 5H, Cp), 4.58 (bs, 1H, N*H*), 2.42 (apparent q, *J* = 11.6 Hz, 1H, C*H* of Cy), 2.16-2.07 (m, 1H, C*H* of Cy), 2.02-1.89 (m, 2H, CH_2 of Cy), 1.89-1.45 (m, 8H, CH_2 of Cy), 1.45-0.88 (m, 8H, CH_2 of Cy overlapping with CH_3-B), 1.16 (bs, 3H, CH_3-B overlapping with CH_2 of Cy).

^{13}C{^{1}H} NMR (126 MHz, C_6D_5Br, 299 K): δ = 160.1 (d, $^{2}J_{PC}$ = 16.6 Hz, , N*C*=), 148.7 (dm, $^{1}J_{FC}$ ~ 235 Hz, Ar*C*-F), 145.2 (s, *i*-Ph), 137.2 (dm, $^{1}J_{FC}$ ~ 245 Hz, Ar*C*-F overlapping with ArC-F), 136.3 (dm, $^{1}J_{FC}$ ~ 245 Hz, Ar*C*-F overlapping with ArC-F), 133.2 (d, $^{3}J_{PC}$ = 1.2 Hz, H*C(*5)=), 131.6 (d, $^{2}J_{PC}$ = 3.1 Hz, H*C(*6)=),

130.0 (s, *m*-Ph), n.o (B*C*), 127.2 (s, *p*-Ph), 120.6 (d, $^{3}J_{PC}$ = 5.2 Hz, H*C*(4)=), 118.0 (bs, *o*-Ph), 117.7 (d, $^{1}J_{PC}$ = 32.7 Hz, P*C*=), 110.6 (s, Cp), 109.6 (s, Cp), 108.8 (d, $^{3}J_{PC}$ = 6.3 Hz, H*C*(3)= overlapping with Cp signal of compound **1**), 38.7 (d, $^{1}J_{PC}$ = 10.4 Hz, *C*H of Cy), 33.9 (d, $^{1}J_{PC}$ = 12.7 Hz, *C*H of Cy), 30.1 (d, J_{PC} = 3.4 Hz, *C*H_2 of Cy), 29.6 (d, J_{PC} = 0.9 Hz, *C*H_2 of Cy), 28.9 (s, *C*H_2 of Cy), 27.5 (d, J_{PC} = 11.6 Hz, *C*H_2 of Cy), 27.2-27.1 (m, two overlapping *C*H_2 of Cy), 27.0 (d, J_{PC} = 10.9 Hz, *C*H_2 of Cy), 26.8 (d, J_{PC} = 10.6 Hz, *C*H_2 of Cy), 25.9 (s, *C*H_2 of Cy), 25.7 (s, *C*H_2 of Cy), 11.0 (br s, *C*H_3-B).

^{11}B{^{1}H} NMR (160 MHz, C_6D_5Br, 299 K): δ = -14.4 ($\nu_{1/2}$ ~ 95 Hz).

^{19}F NMR (470 MHz, C_6D_5Br, 299 K): δ = -131.4 (m, 2F, *o*-Ar*F*), -163.6 (m , 1F, *p*-Ar*F*), -166.1 (m, 2F, *m*-Ar*F*). $\Delta\delta^{mp}$ = 2.5 ppm.

^{31}P{^{1}H} NMR (202 MHz, C_6D_5Br, 299 K): δ = 31.2 ($\nu_{1/2}$ ~ 2 Hz).

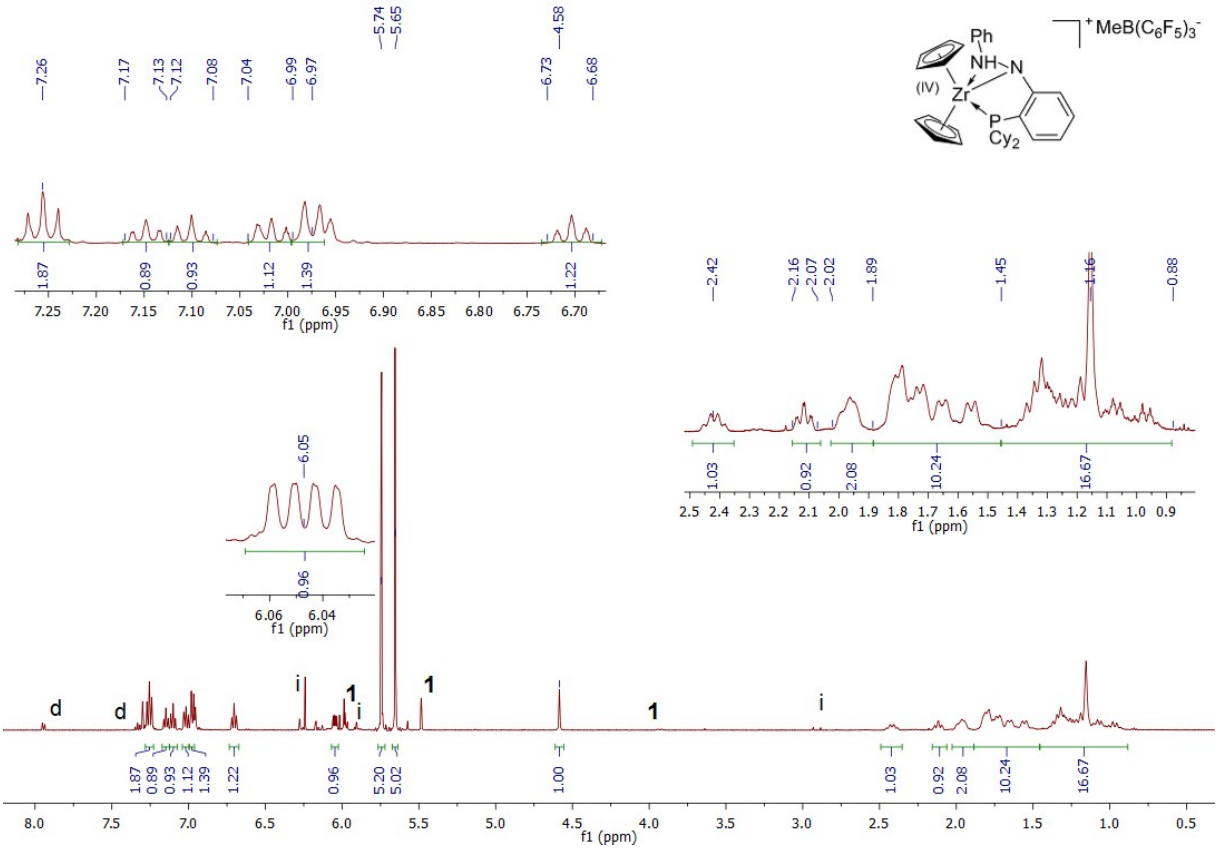


Figure S8. ^{1}H NMR (500 MHz, C_6D_5Br, 299 K)(d: azobenzene; i: impurity)

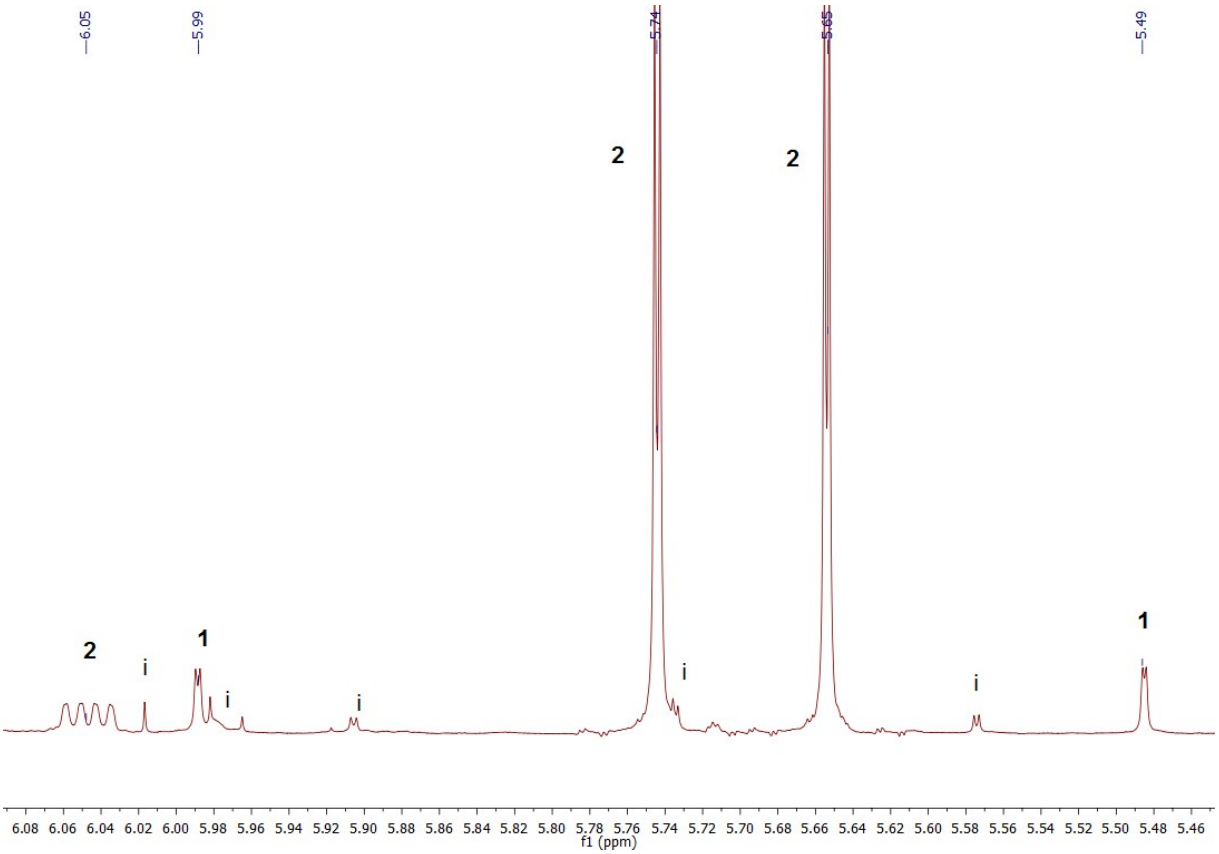


Figure S9. ^{1}H NMR expanded area (500 MHz, C_6D_5Br, 299 K)

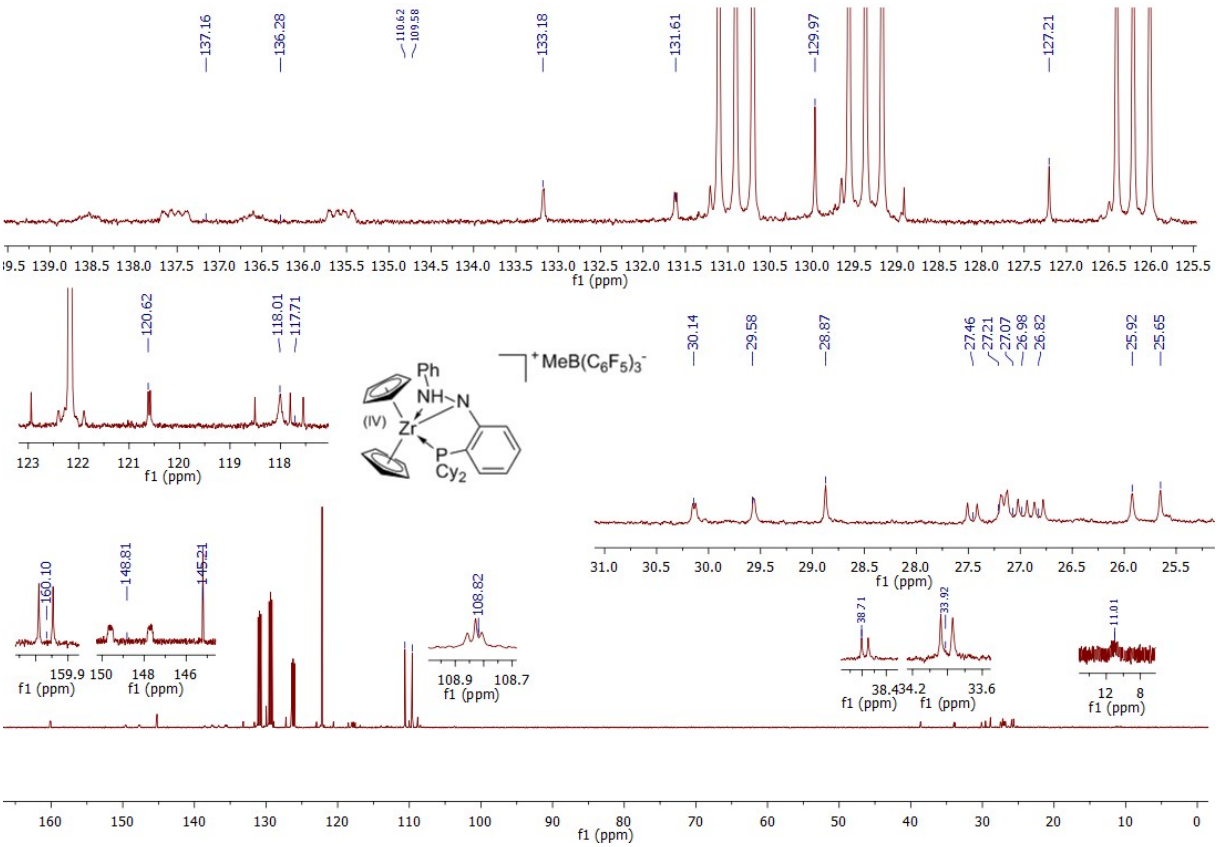


Figure S10. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_5Br, 299 K)

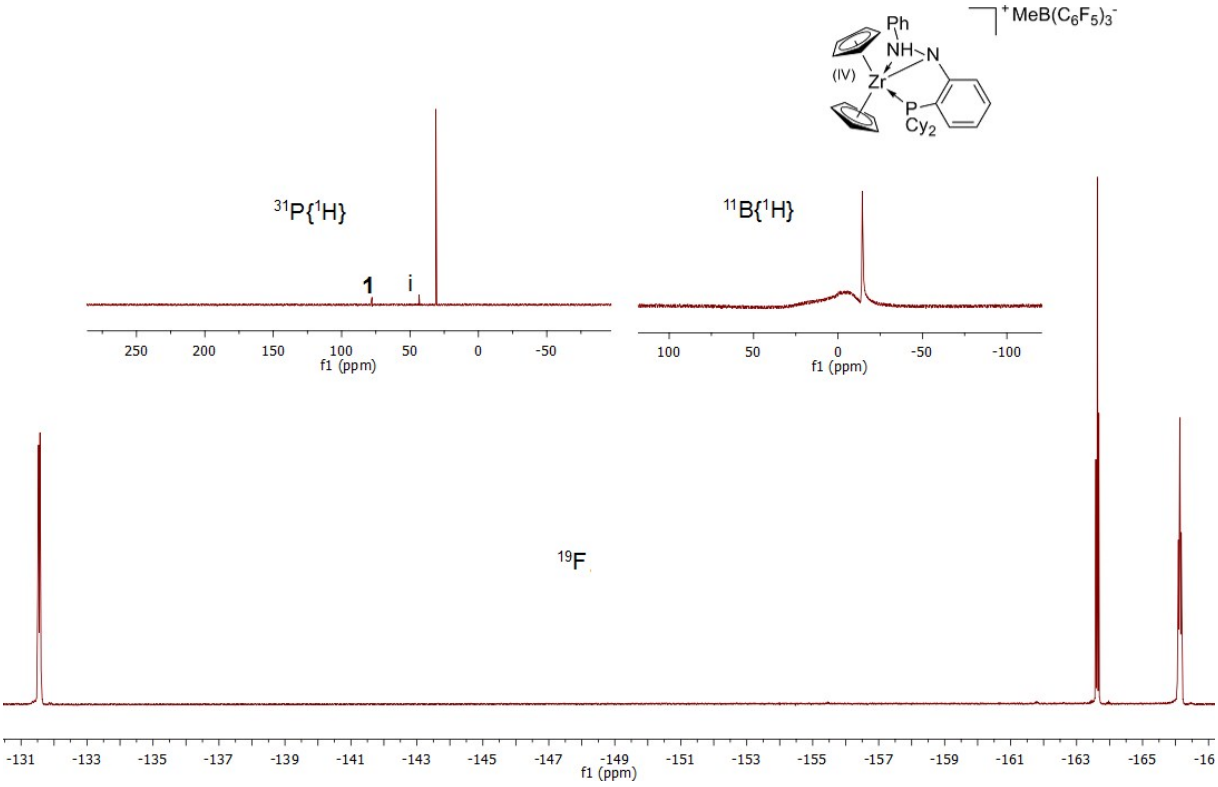
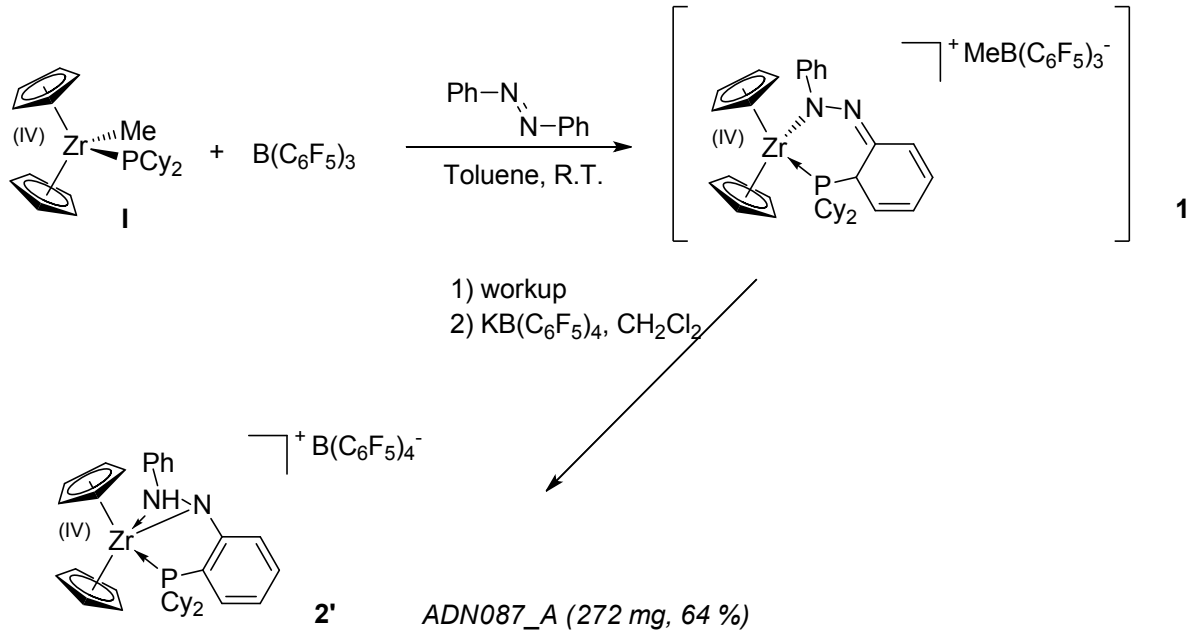


Figure S11. $^{11}B\{^1H\}$ NMR (160 MHz), ^{19}F NMR (470 MHz), $^{31}P\{^1H\}$ NMR (202 MHz)(C_6D_5Br, 299 K)(i: impurity)

Preparation of compound 2'



ADN087_A (272 mg, 64 %)

Compound **2'** was prepared from an isolated mixture of compounds **1** and **2** (*vide supra*). The crude mixture (373 mg, 0.31 mmol) was dissolved in 3 mL of CH_2Cl_2 and potassium tetrakis(pentafluorophenyl)borate (285 mg, 0.40 mmol) was added. The mixture was stirred overnight and turned from red to yellow over a few hours. The resulting suspension was filtered over celite® and the filtrate was precipitated by addition to 50 mL of pentane under vigorous agitation. The resulting solid was rinsed with pentane and dried *in vacuo*. Compound **2'** was obtained as a yellow powder (272 mg, 64 %). Single crystals suitable for X-

ray diffraction analysis were obtained by diffusion of pentane in a CH_2Cl_2 solution of **2'** at -35 °C.

*Note: The isolated material originally contained 150 mol% of pentane, which decreased to 75 mol% after 3 months of storage in the glovebox. Residual $MeB(C_6F_5)_3^-$ anion (10 to 13 %) was also observed by ^1H and $^{19}F\{^1H\}$ NMR (this could come either from $KMeB(C_6F_5)_3$ or from residual compound **2**). Elemental analysis was conducted on this material and although the result would be satisfactory for solventless material, the carbon value is still somewhat low for a solvated sample.*

Elemental Analysis: calcd for $C_{58}H_{42}BF_{20}N_2PZr$: C, 54.43; H, 3.31; N: 2.19. Found: C, 53.93; H, 3.43; N: 2.09.

HRMS (ESI-pos): calcd for $C_{34}H_{42}N_2PZr$ $[M\text{-}B(C_6F_5)_4^-]^+$: 599.21272. Found: 599.21.040 (rel. ab. 100 %, -3.9 ppm). Calcd for $C_{24}H_{34}N_2P$ $[M\text{-}B(C_6F_5)_4^-\text{-}C_{10}H_{10}Zr]^+$: 381.24596. Found: 381.24352 (rel. ab. 5 %, -6.4 ppm).

^{1}H NMR (500 MHz, CD_2Cl_2, 300 K)[numbering of positions on the Ar ring attached to P and N: carbon attached to P: 1, carbon attached to N: 2 etc.]: δ = 7.47 (m, 2H, *m*-Ph), 7.42 (apparent t, $^3J_{HH}$ = 7.2 Hz, $^3J_{PH}$ = 7.2 Hz, 1H, *H*(6*)*C=), 7.35-7.31 (m, 1H, *p*-Ph), 7.29-7.25 (m, 1H, *H*(5*)*C=), 7.17 (m, 2H, *o*-Ph), 6.91-6.86 (m, 1H, *H*(4*)*C=), 6.37 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{PH}$ = 4.1 Hz, 1H, *H*(3*)*C=), 6.13 (d, $^3J_{PH}$ = 1.3 Hz, 5H, Cp), 6.00 (d, $^3J_{PH}$ = 1.1 Hz, 5H, Cp), 4.83 (bs, 1H, N*H*), 2.77-2.66 (m, 1H, C*H* of Cy), 2.46-2.36 (m, 1H, C*H* of Cy), 2.31-2.16 (m, 2H, CH_2 of Cy), 2.10-1.86 (m, 7H, CH_2 of Cy), 1.83-1.74 (m, 1H, CH_2 of Cy), 1.74-1.16 (m, 19H, CH_2 of Cy overlapping with CH_2 of pentane) 0.90 (t, $^3J_{HH}$ = Hz, CH_3 of pentane).

^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 300 K): δ = 160.1 (d, $^2J_{PC}$ = 16.5 Hz, N*C*=), 148.7 (dm, $^1J_{FC}$ ~ 239 Hz, Ar*C*-F), 146.0 (s, *i*-Ph), 138.8 (dm, $^1J_{FC}$ ~ 239 Hz, Ar*C*-F overlapping with ArC-F), 137.7 (dm, $^1J_{FC}$ ~ 245 Hz, Ar*C*-F overlapping with ArC-F), 133.3 (d, $^3J_{PC}$ = 1.7 Hz, H*C*(5)=), 132.5 (d, $^2J_{PC}$ = 3.1 Hz, H*C*(6)=), 130.7 (s, *m*-Ph), 127.8 (s, *p*-Ph), 124.6 (bs, B*C*), 121.2 (d, $^3J_{PC}$ = 5.4 Hz, H*C*(4)=), 118.8 (d, $^1J_{PC}$ = 32.8 Hz, P*C*=), 118.6 (bs, *o*-Ph), 111.5 (s, Cp), 110.4 (s, Cp), 109.6 (d, $^3J_{PC}$ = 6.5 Hz, H*C*(3)=), 39.6 (d, $^1J_{PC}$ = 10.7 Hz, *C*H of Cy), 34.9 (d, $^1J_{PC}$ = 13.0 Hz, *C*H of Cy), 34.6 (s, *C*H_2 of pentane), 31.1 (d, J_{PC} = 3.6 Hz, *C*H_2 of Cy), 30.5 (s, *C*H_2 of Cy), 29.7 (s, *C*H_2 of Cy), 28.1 (d, J_{PC} = 11.8 Hz, *C*H_2 of Cy), 28.0 (d, J_{PC} = 4.3 Hz, *C*H_2 of Cy), 27.9 (d, J_{PC} = 8.5 Hz, *C*H_2 of Cy), 27.6 (d, J_{PC} = 10.8 Hz, *C*H_2 of Cy), 27.5 (d, J_{PC} = 10.6 Hz, *C*H_2 of Cy), 26.5 (d, J_{PC} = 1.0 Hz, *C*H_2 of Cy), 26.3 (d, J_{PC} = 0.9 Hz, *C*H_2 of Cy), 22.8 (s, *C*H_2 of pentane), 14.3 (s, *C*H_3 of pentane),

^{1}H, ^{1}H gCOSY (500 MHz / 500 MHz, CD_2Cl_2, 300 K)[selected traces]: δ^{1}H / δ^{1}H = 7.47 / 7.35-7.31, 7.17 (*m*-Ph / *p*-Ph, *o*-Ph), 7.42 / 6.91-6.86 (*H*(6*)*C= / *H*(4*)*C=), 7.29-7.25 / 6.91-6.86, 6.37 (*H*(5*)*C= / *H*(4*)*C=, *H*(3*)*C=).

^{1}H, ^{13}C gHMBC (500 MHz / 126 MHz, CD_2Cl_2, 300 K)[selected traces]: δ ^{1}H / δ ^{13}C = 7.47 / 146.0, 130.7 (*m*-Ph / *i*-Ph, *m*-Ph), 7.42 / 160.1, 133.1 (*H*(6*)*C= / N*C*=, H*C*(5)=), 7.35-7.31 / 118.6 (*p*-Ph / *o*-Ph), 7.29-7.25 / 160.1, 132.5 (*H*(5*)*C= / *NC*=, H*C*(6)=), 7.17 / 127.8, 118.6 (*o*-Ph / *p*-Ph, *o*-Ph), 6.91-6.86 / 118.8, 109.6 (*H*(4*)*C= / P*C*=, H*C*(3)=), 6.37 / 121.2, 118.8 (*H*(3*)*C= / H*C*(4)=, P*C*=), , 4.83 / 160.1, 118.6 (N*H* / *NC*=, *o*-Ph).

^{1}H, ^{1}H NOESY (500 MHz, CD_2Cl_2, 300 K)[selected cross-peaks]: δ^{1}H / δ^{1}H = 7.42 / 2.77-2.66 (*H*(6)C= / C*H* of Cy), 7.42 / 2.31-2.16 (*H*(6)C= / CH_2 of Cy), 7.17 / 4.83 (*o*-Ph / N*H*), 6.37 / 4.83 (*H*(3)C= / N*H*), 6.13 / 4.83 (Cp / N*H*).

^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 300 K): δ = -16.6 ($\nu_{1/2}$ ~ 20 Hz).

^{19}F{^{1}H} NMR (470 MHz, CD_2Cl_2, 300 K): δ = -133.0 (m , 2F, *o*-Ar*F*), -163.6 (m , 1F, *p*-Ar*F*), -167.4 (m, 2F, *m*-Ar*F*). $\Delta\delta^{mp}$ = 3.8 ppm.

^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 300 K): δ = 31.8 ($\nu_{1/2}$ ~ 8 Hz).

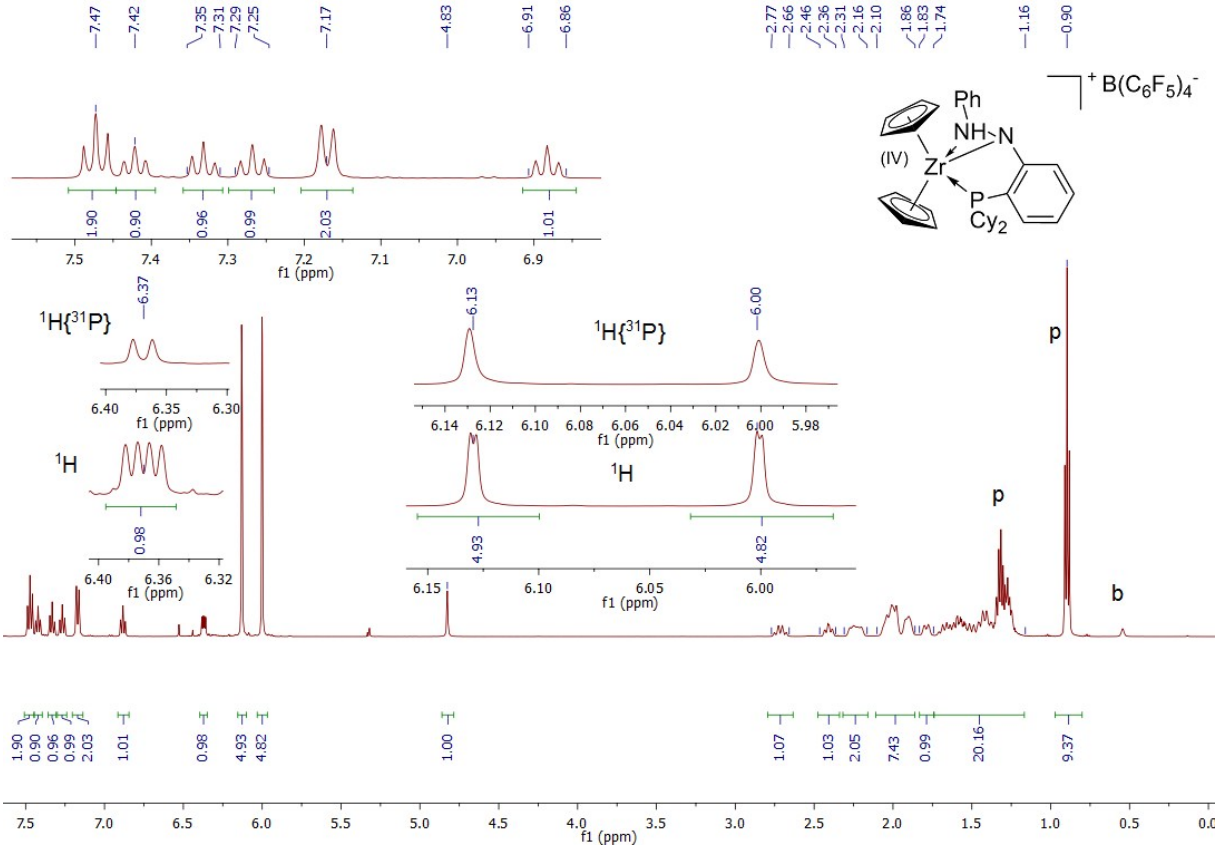


Figure S12. ^{1}H NMR (500 MHz, CD_2Cl_2, 300 K)(p: pentane; b: $MeB(C_6F_5)_3^-$ anion)

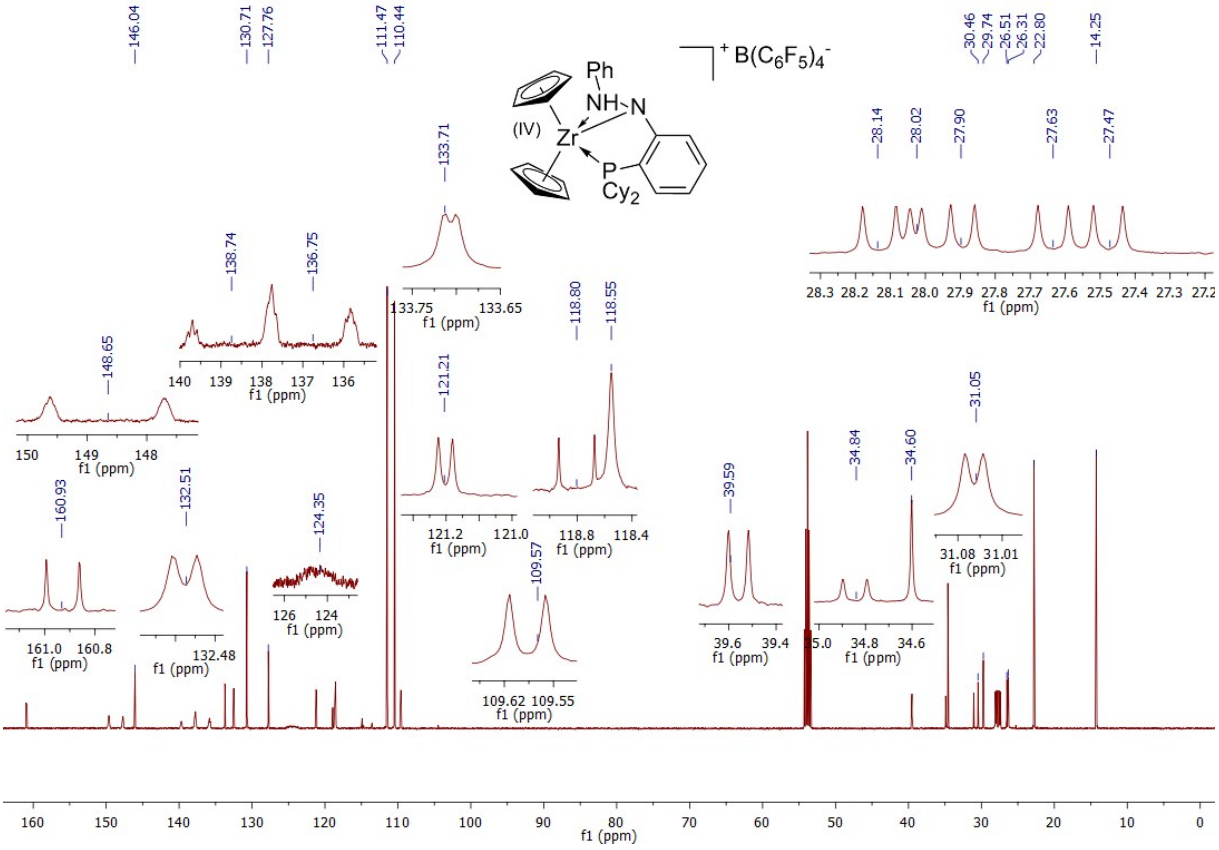


Figure S13. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 300 K)

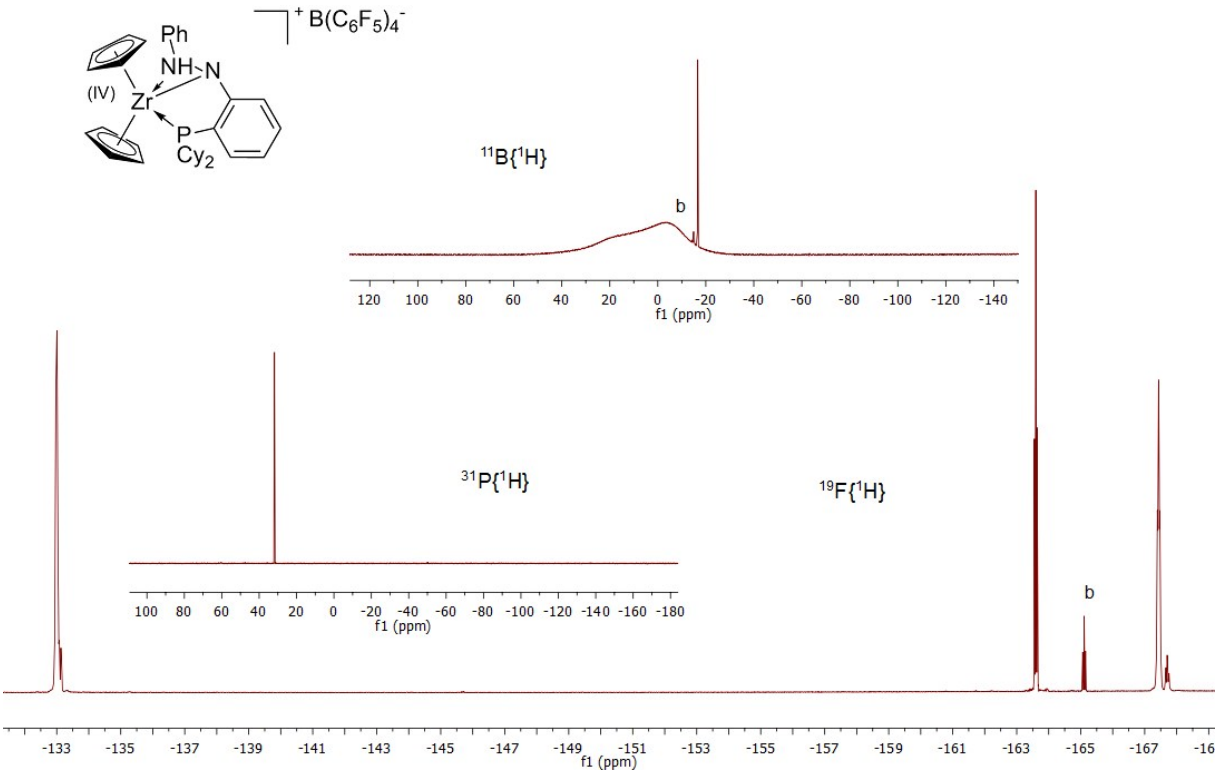


Figure S14. $^{11}B\{^{1}H\}$ NMR (160 MHz), $^{19}F\{^{1}H\}$ NMR (470 MHz), $^{31}P\{^{1}H\}$ NMR (202 MHz)(CD_2Cl_2, 300 K)(b: $MeB(C_6F_5)_3^-$ anion)

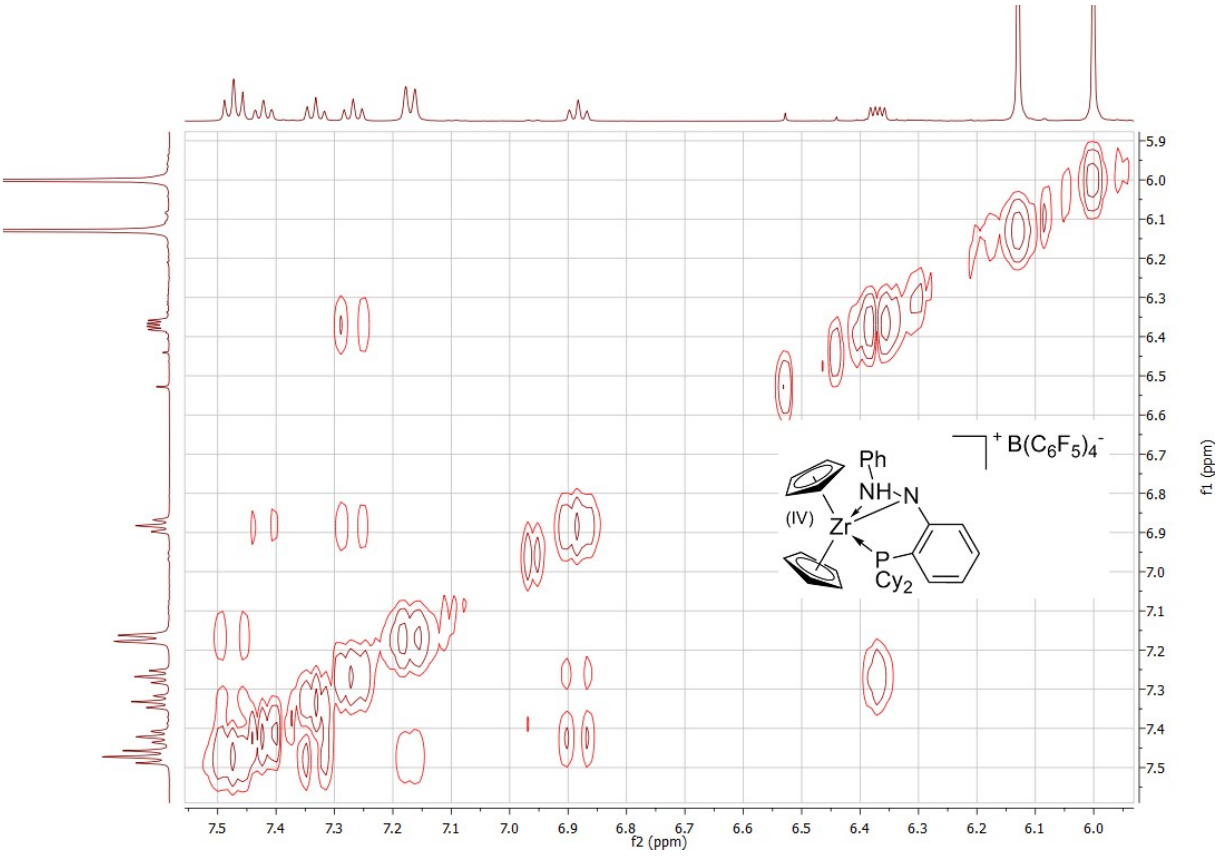


Figure S15. ^{1}H, ^{1}H gCOSY(500 MHz / 500 MHz, CD_2Cl_2, 300 K)

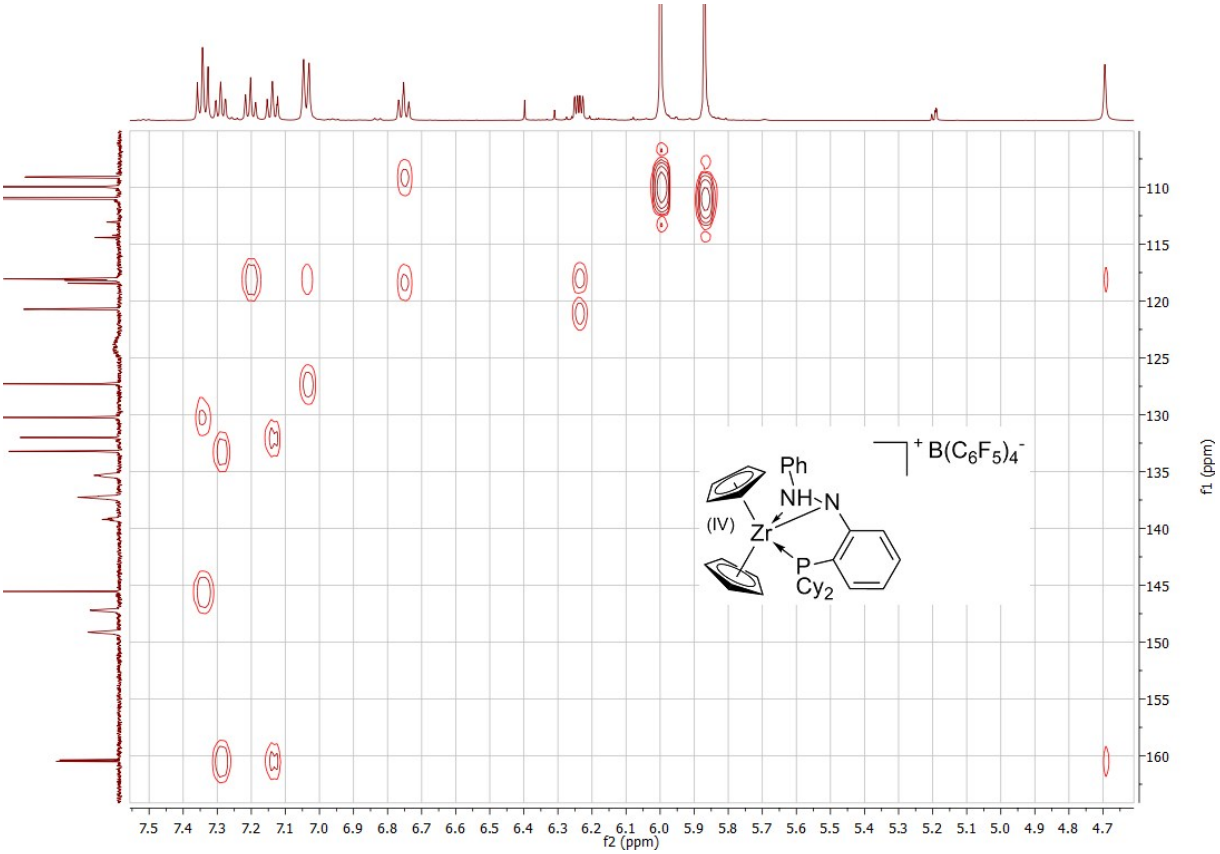


Figure S16. ^{1}H, ^{13}C gHMBC (500 MHz / 126 MHz, CD_2Cl_2, 300 K)

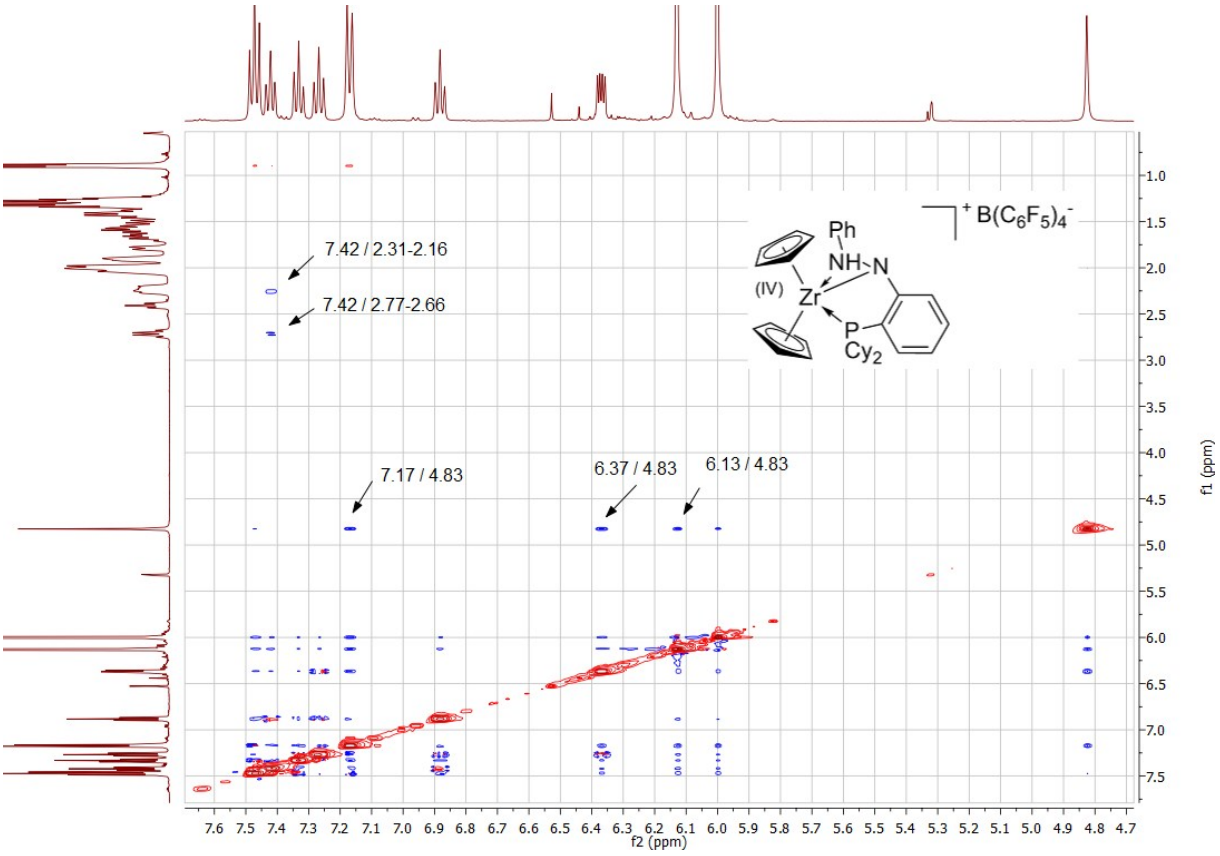


Figure S17. ^{1}H, ^{1}H NOESY (500 MHz, CD_2Cl_2, 300 K)

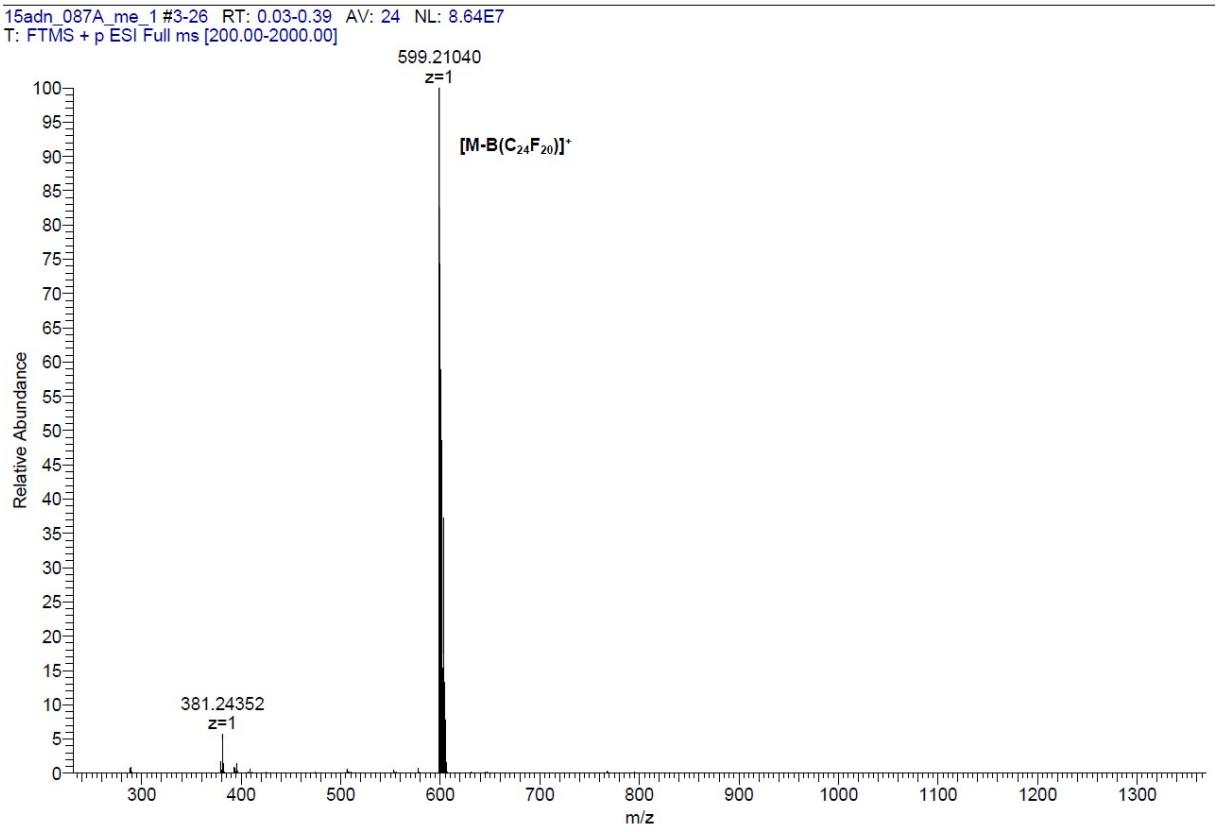
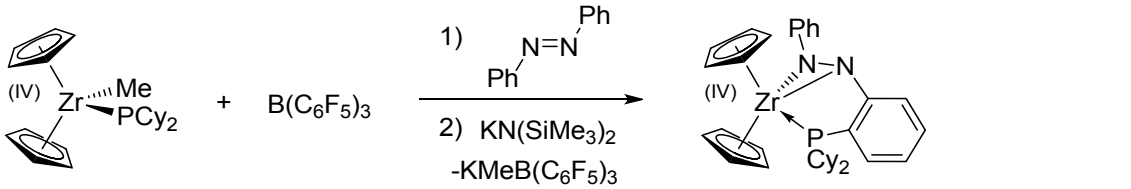


Figure S18. HRMS (ESI-pos)

Preparation of compound 3



3 *ADN699_A (0.42 g, 70 %)*

In a glovebox with an Ar atmosphere, compound **I** (434 mg, 1.0 mmol) and tris(pentafluorophenyl)borane (512 mg, 1.0 mmol) were mixed in toluene (6 mL). After 1 min, azobenzene was added (182 mg, 1.0 mmol), followed by potassium bis(trimethylsilyl)amide (200 mg, 1.0 mmol). The solution turned from purple to yellow and a precipitate slowly formed. After 30 min, 30 mL of pentane was added and the mixture was filtered over Celite®. The clear filtrate was evaporated to ~2 mL, to which 50 mL of pentane was added, causing the precipitation of a yellow solid. The collected solid was washed twice with 5 mL of pentane and dried *in vacuo*. Compound **3** was obtained a yellow powder (0.42 g, 70 %). Single crystals suitable for X-ray diffraction analysis were obtained by diffusion of pentane into a toluene solution of **3** at -35 °C.

Note: Assignment of the ^{1}H and $^{13}C\{^{1}H\}$ NMR signals of the Ph ring (o, m, p) is incomplete due to the ABCDE spin system and the overlap with the signal of HC(3)=.

Elemental Analysis: calcd for $C_{34}H_{41}N_2PZr$: C, 68.07; H, 6.89; N, 4.67. Found: C, 68.29; H, 6.82; N, 4.55.

^{1}H NMR (500 MHz, C_6D_5Br, 299 K)[numbering of positions on the Ar ring attached to P and N: carbon attached to P: 1, carbon attached to N: 2 etc.] : δ = 7.36-7.31 (m, 1H, Ph overlapping with bromobenzene signal), 7.23 (m, 1H, Ph), 7.09 (apparent t, $^{3}J_{HH}$ = 6.7 Hz, $^{3}J_{PH}$ = 6.7 Hz, 1H, *H(*6)C=), 7.06-7.02 (m, 2H, Ph overlapping with *H(*4)C=), 6.78 (m, 1H, Ph), 6.71 (m, 1H, Ph), 6.49 (t, $^{3}J_{HH}$ = 7.0 Hz, 1H, *H(*5)C=), 6.36 (dd, $^{3}J_{HH}$ = 8.1 Hz, $^{4}J_{PH}$ = 4.0 Hz, 1H, *H(*3)C=), 5.76 (s, 5H, Cp), 5.74 (s, 5H, Cp), 2.42-2.23 (m, 3H, CH_2 of Cy overlapping with C*H* of Cy), 2.16-2.07 (m, 1H, CH_2 of Cy), 2.06-1.93 (m, 2H, CH_2 of Cy), 1.90-1.72 (m, 4H, CH_2 of Cy), 1.69-0.96 (m, 12H, CH_2 of Cy).

$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_5Br, 299 K): δ = 168.0 (d, $^{2}J_{PC}$ = 19.4 Hz, N*C*=), 164.2 (s, *i*-Ph), 131.8 (s, H*C(*4)=), 129.3 (m, Ph and H*C(*6)= overlapping with bromobenzene signal), 125.0 (s, Ph), 119.7 (d, $^{1}J_{PC}$ =35.4 Hz, P*C*=), 117.7 (s, Ph), 115.8-115.4 (m, Ph and H*C(*5)=), 113.1-112.8 (m, Ph and H*C(*3)=), 108.8 (s, Cp), 107.7 (s, Cp), 38.5 (d, $^{1}J_{PC}$ = 7.7 Hz, *C*H of Cy), 34.0 (d, $^{1}J_{PC}$ = 8.6 Hz, *C*H of Cy), 30.8 (d, J_{PC} = 6.4 Hz, *C*H_2 of Cy), 30.3 (s, *C*H_2 of Cy), 29.4 (s, *C*H_2 of Cy), 28.0 (s, *C*H_2 of Cy), 27.9 (d, J_{PC} = 11.8 Hz, *C*H_2 of Cy), 27.7 (d, J_{PC} = 8.7 Hz, *C*H_2 of Cy), 27.5 (d, J_{PC} = 10.4 Hz, *C*H_2 of Cy), 27.3 (d, J_{PC} = 8.7 Hz, *C*H_2 of Cy), 26.4 (s, *C*H_2 of Cy), 26.2 (s, *C*H_2 of Cy).

^{1}H, ^{1}H gCOSY (500 MHz / 500 MHz, C_6D_5Br, 299 K)[selected traces]: δ^{1}H / δ^{1}H = 7.36-7.31 / 7.06-7.02, 6.71 (Ph / Ph, Ph), 7.23 / 6.78, 6.71 (Ph / Ph, Ph), 7.09 / 6.49 (*H*(6)C= / *H*(5)C=), 7.06-7.02 / 6.49, 6.36 (*H*(4)C= / *H*(5)C=, *H*(3)C=).

^{1}H, ^{13}C gHMBC (500 MHz / 126 MHz, C_6D_5Br, 299 K)[selected traces]: δ ^{1}H / δ ^{13}C = 7.36-7.31 / 164.2, 129.3 (Ph / *i*-Ph, Ph), 7.23 / 164.2, 129.3 (Ph / *i*-Ph, Ph), 7.09 / 168.0, 131.8, 113.1-112.8 (*H(*6)C= / N*C*=, H*C*(4)=, H*C(*3)=), 7.06-7.02 / 168.0, 129.3 (*H(*4)C= / N*C*=, H*C*(6)=), 6.71 / 117.7, 113.1-112.8 (Ph / Ph, Ph), 6.49 / 131.8, 129.3, 119.7, 113-112.8 (*H(*5)C= / H*C*(4)=, H*C*(6)=, P*C*=, H*C*(3)=), , 6.36 / 119.7, 115.7-115.5 (*H(*3)C= / P*C*=, H*C*(5)=).

$^{31}P\{^{1}H\}$ NMR (202 MHz, C_6D_5Br, 299 K): δ = 29.1 ($\nu_{1/2}$ ~ 8 Hz).

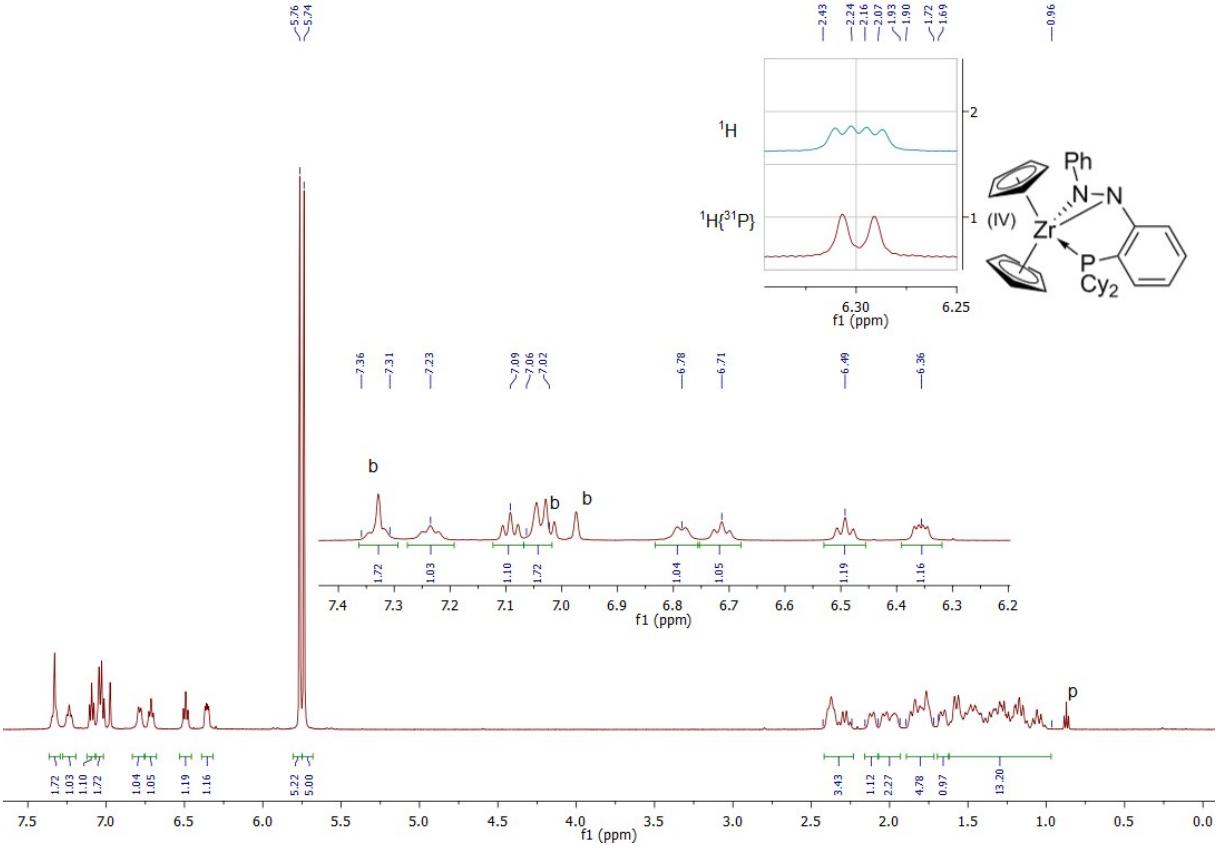


Figure S19. ^{1}H NMR (500 MHz, C_6D_5Br, 299 K)(p: pentane)

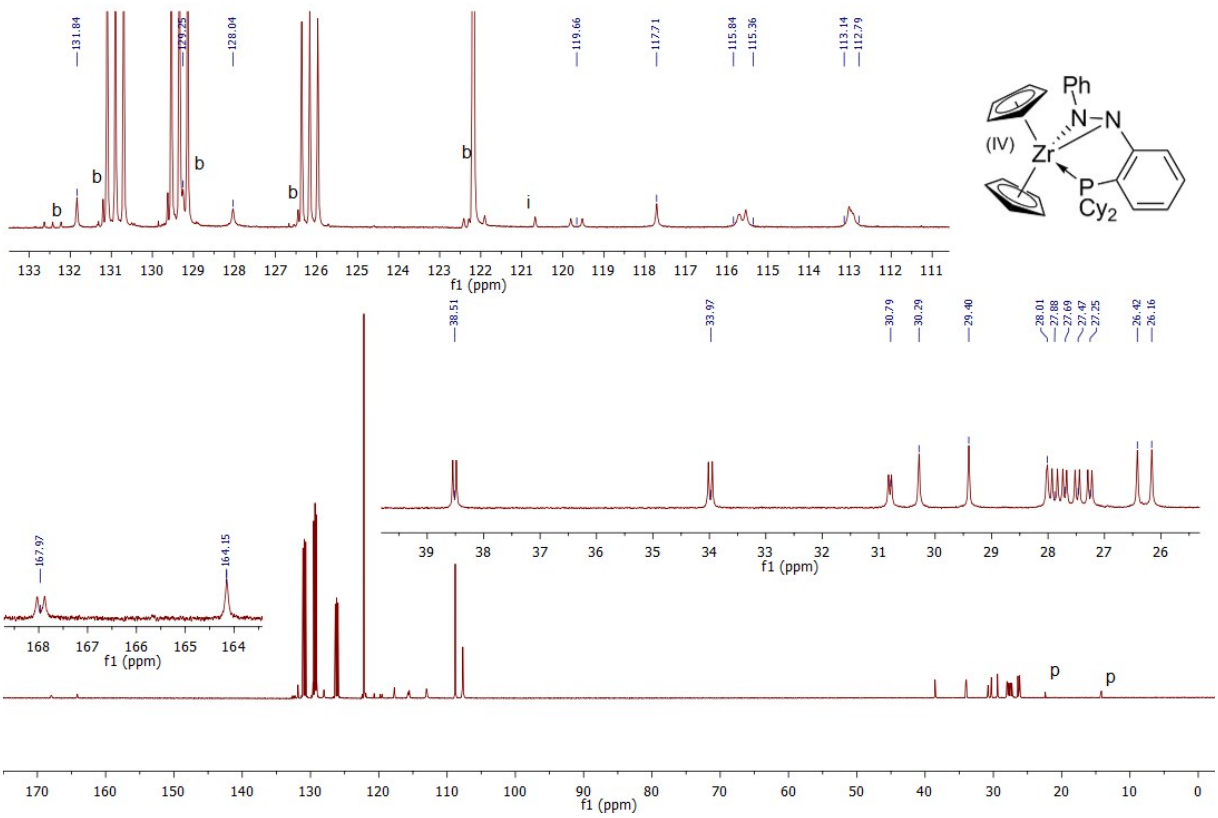


Figure S20. $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_5Br, 299 K)(p: pentane; b: bromobenzene; i: impurity)

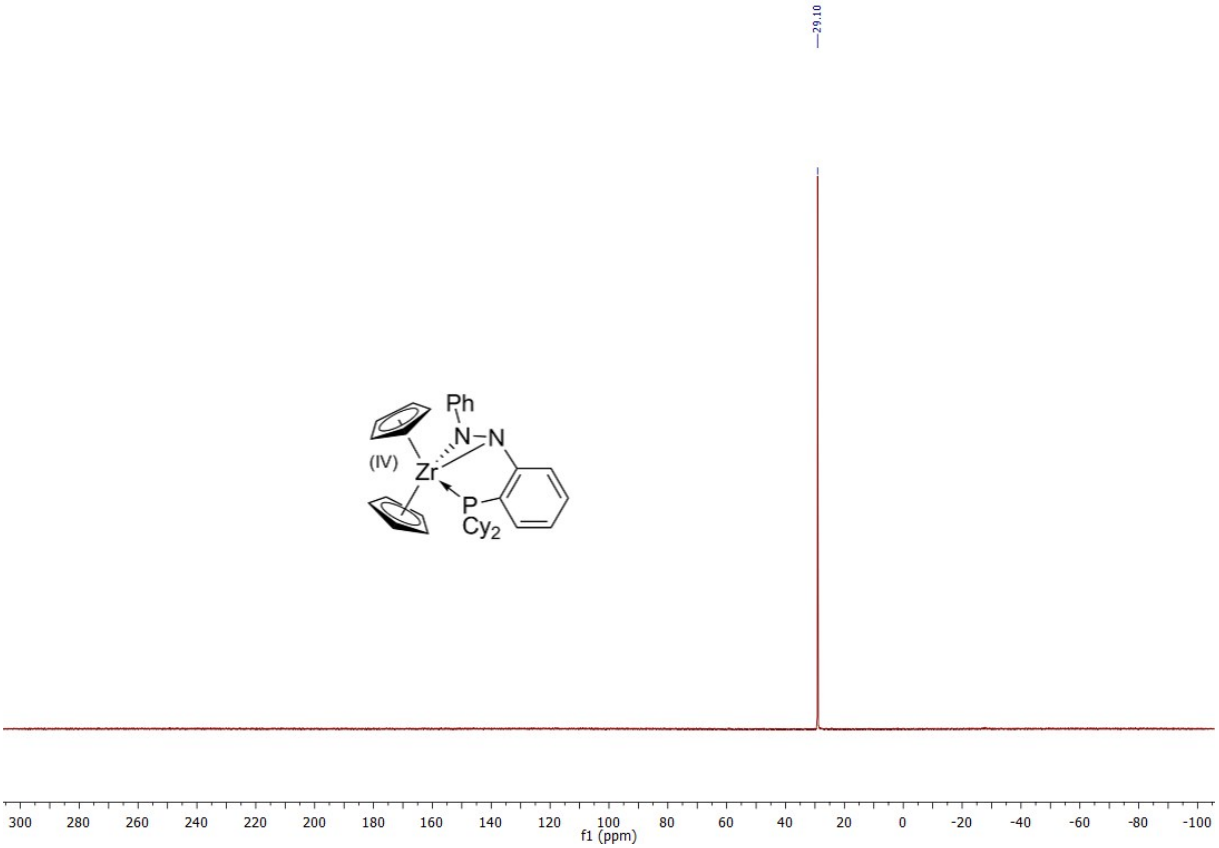


Figure S21. $^{31}P\{^{1}H\}$ NMR (202 MHz)(C_6D_5Br, 299 K)

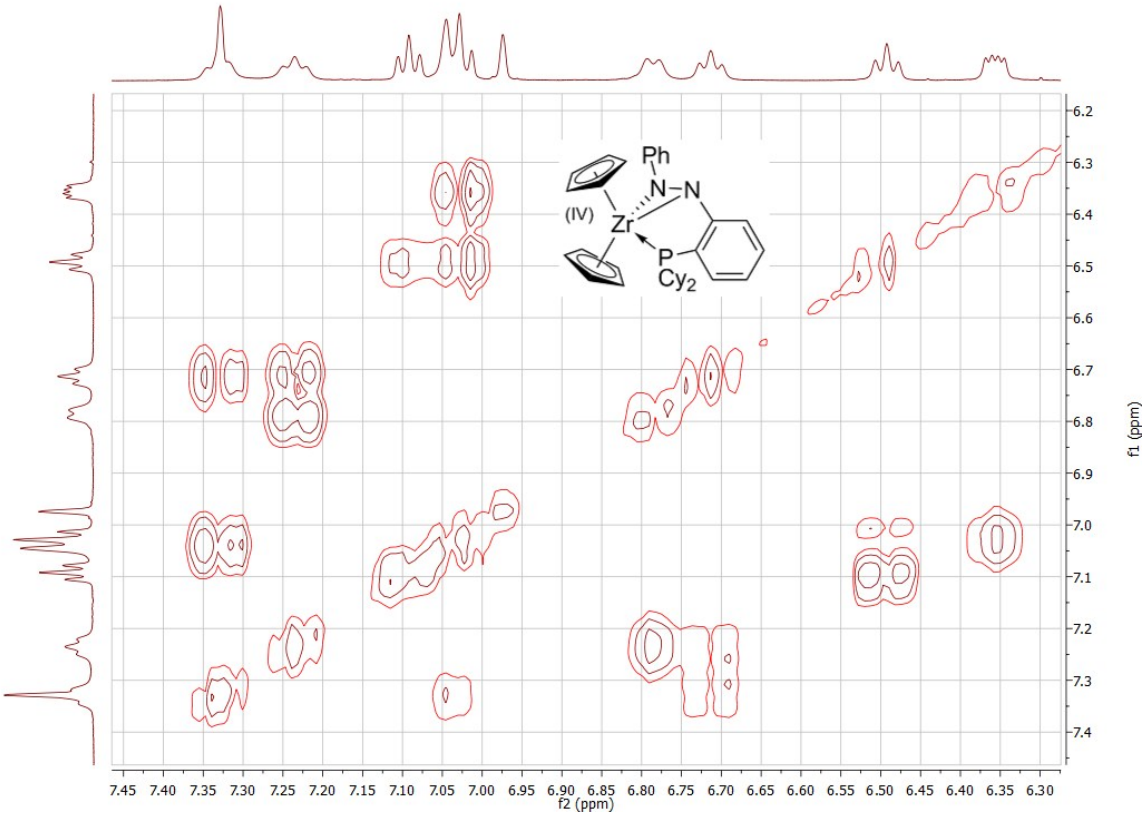


Figure S22. ^{1}H, ^{1}H gCOSY(500 MHz / 500 MHz, C_6D_5Br, 299 K)

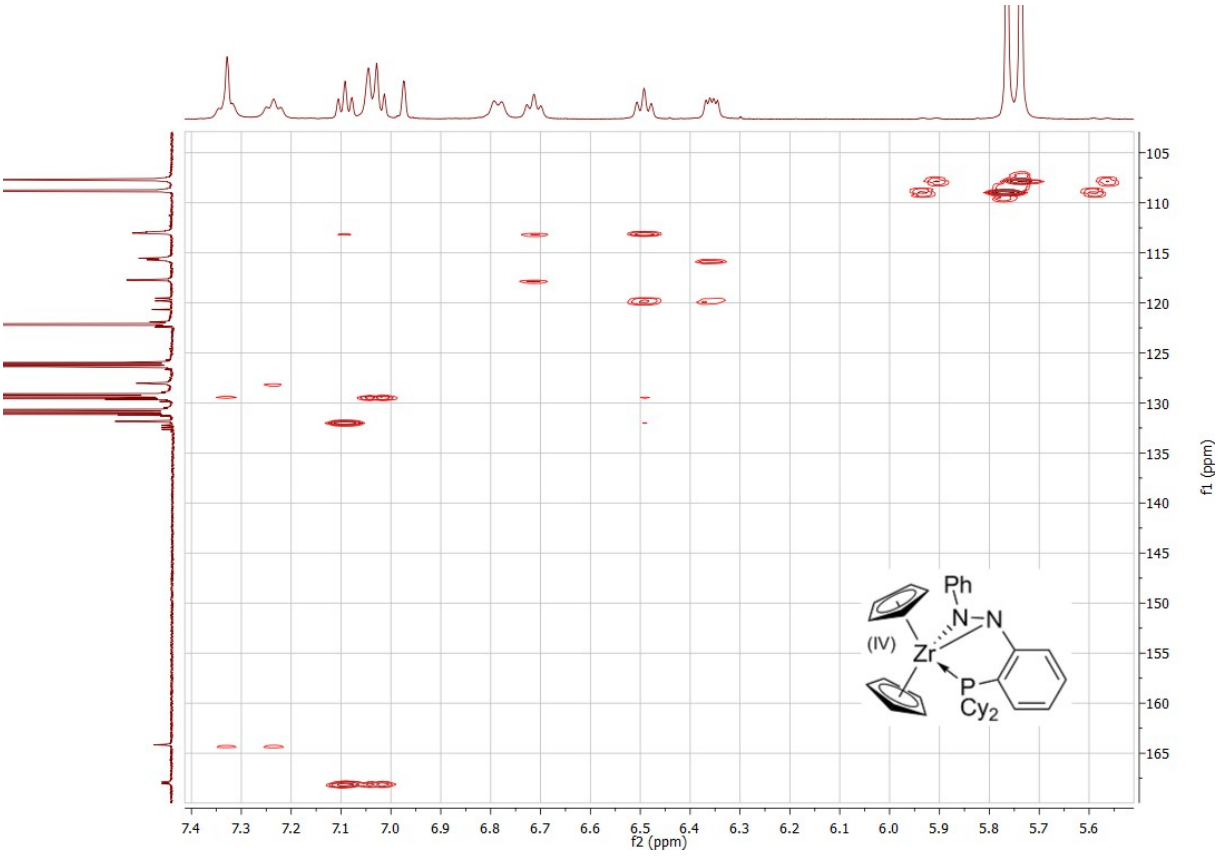


Figure S23. ^{1}H, ^{13}C gHMBC (500 MHz / 126 MHz, C_6D_5Br, 299 K)

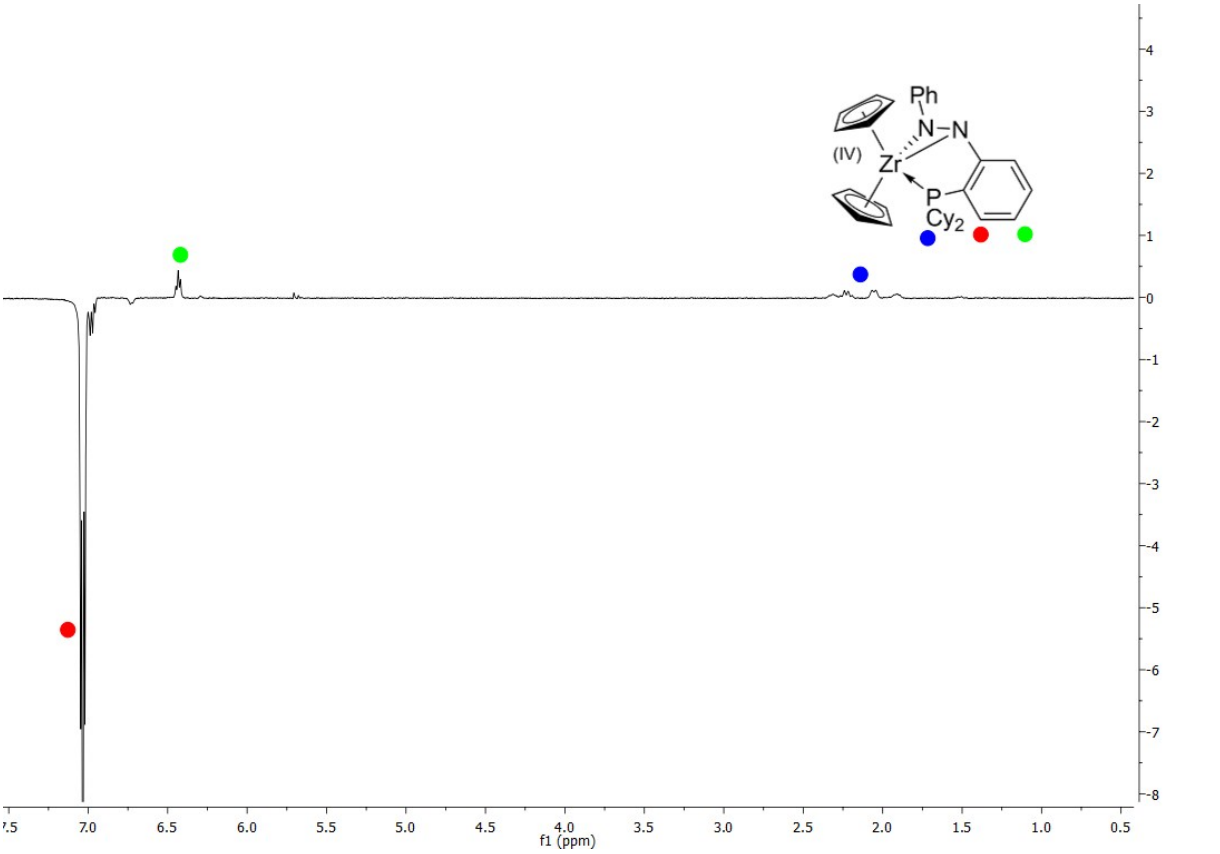


Figure S24. $^{1}\{H\}^{1}\{H\}$ 1D NOESY (500 MHz, C_6D_5Br, 299 K)

3. Crystallographic studies

X-ray crystal structure analysis of 2': formula $C_{58}H_{42}BF_{20}N_2PZr$, M = 1279.94, yellow crystal, 0.18 x 0.10 x 0.03 mm, a = 16.6678(2), b = 19.1180(2), c = 17.7773(3) Å, β = 111.521(1)°, V = 5269.9(1) Å^3, ρ_{calc} = 1.613 gcm^{-3}, μ = 0.353 mm^{-1}, empirical absorption correction (0.939 ≤ T ≤ 0.989), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 0.71073 Å, T = 223(2) K, ω and ϕ scans, 26444 reflections collected (±h, ±k, ±l), 9102 independent (R_{int} = 0.069) and 7033 observed reflections [I>2σ(I)], 852 refined parameters, R = 0.074, wR^2 = 0.154, max. (min.) residual electron density 0.45 (-0.54) e.Å^{-3}, hydrogen atom at N2 was refined freely; others were calculated and refined as riding atoms.

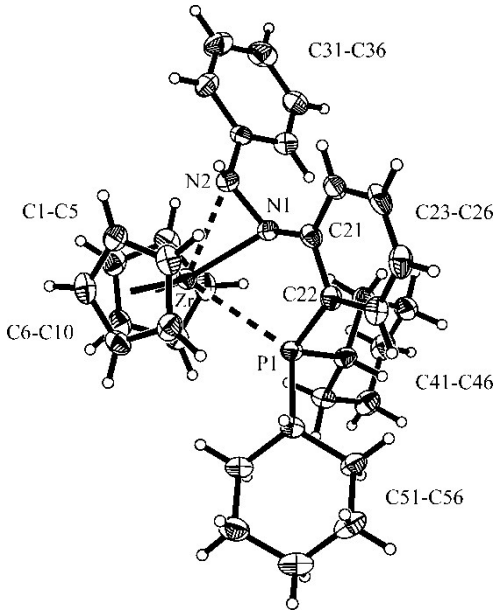


Figure S25. Crystal structure of compound 2'.
(Thermals ellipsoids are shown with 30% probability.)

X-ray crystal structure analysis of 3: formula $C_{34}H_{41}N_2PZr$, M = 599.88, yellow crystal, 0.18 x 0.12 x 0.06 mm, a = 8.7851(3), b = 19.9807(8), c = 16.4334(5) Å, β = 93.982(1)°, V = 2877.6(2) Å^3, ρ_{calc} = 1.385 gcm^{-3}, μ = 0.464 mm^{-1}, empirical absorption correction (0.921 ≤ T ≤ 0.973), Z = 4, monoclinic, space group Cc (No. 9), λ = 0.71073 Å, T = 100(2) K, ω and ϕ scans, 49032 reflections collected (±h, ±k, ±l), 6369 independent (R_{int} = 0.054) and 6133 observed reflections [I>2σ(I)], 399 refined parameters, R = 0.021, wR^2 = 0.048, max. (min.) residual electron density 0.20 (-0.22) e.Å^{-3}, hydrogen atoms were calculated and refined as riding atoms.

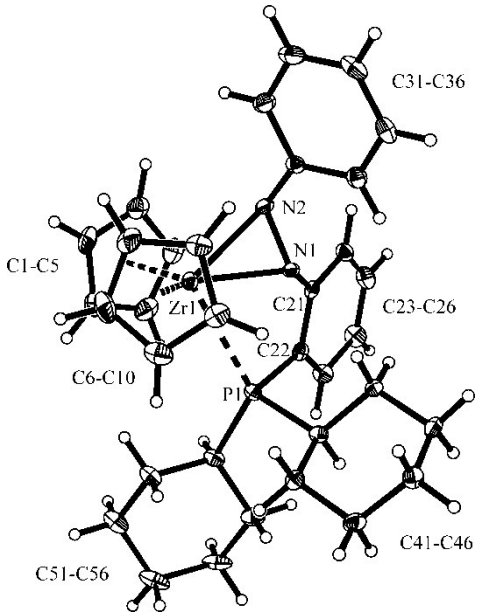


Figure S26. Crystal structure of compound 3.
(Thermals ellipsoids are shown with 50% probability.)