

Facile Formation of Five-membered N-heterocyclic Zirconacycloalleneoids

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[§] X-ray crystal structure analyses.

Supporting Information

Experimental work in Münster:

General remarks: All manipulations were performed in oven- or flame-dried glassware under an argon atmosphere in a glovebox or by standard Schlenk techniques unless specified otherwise. Solvents were dried according to the reported methods (A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics* 1996, **15**, 1518-1520) or, particularly deuterated solvents, were distilled from appropriate drying agents and stored over molecular sieves (4Å) under argon. Compounds such as, (η^5 -C₅H₅)₂ZrCl₂ (J. J. Eisch, F. A. Owuor, P. O. Otieno, *Organometallics* 2001, **20**, 4132-4134), (η^5 -C₅H₅)₂ZrHCl (S. L. Buchwald, S. J. LaMaire, R. B. Nielsen, B. T. Watson, S. M. King, *Tetrahedron Lett.* 1987, **28**, 3895-3898) and LiC≡CSi(CH₃)₃ (C. Raminelli, J. Gargalaka, Jr., C. C. Silveirab, J. V. Comasseto, *Tetrahedron*, 2007, **63**, 8801-8809) were prepared according to published procedures and fully characterized by HRMS, NMR, and IR spectroscopy. Purchased starting materials and other chemicals or reagents (Aldrich, Fluka, ABCR, Merck and Acros) were used without further purification. NMR spectra were recorded on a Bruker AC 200 P-FT (¹H: 200.1 MHz, ¹³C: 50.3 MHz), on a Bruker AV 300 (¹H: 300.1 MHz, ¹³C: 75.5 MHz, ²⁹Si: 59.6 MHz), on a Bruker AV 400 (¹H: 400.1 MHz, ¹³C: 100.6 MHz), on a Varian Inova 500 (¹H: 499.9 MHz, ¹³C: 125.7 MHz, ²⁹Si: 99.3 MHz) and on a Varian UnityPlus 600 (¹H: 599.8 MHz, ¹³C: 150.8 MHz, ²⁹Si: 119.2 MHz) spectrometer, respectively, in the indicated solvent and are listed in parts per million (ppm) downfield from tetramethylsilane (TMS) as an internal standard for ¹H and ¹³C. NMR assignments are supported by additional 2D NMR experiments. IR spectra were recorded on Varian 3100 FT-IR (Excalibur Series) spectrometer using ATR technology. Elemental analyses were performed on Elementar Vario El III. Mass spectra were recorded on Triplequad TSQ (Thermo-Finnigan-MAT) spectrometer. X-ray crystal structure analyses: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT (COLLECT data collection software, R. W. W. Hooft, Bruker AXS, Delft, The Netherlands, 2008); data reduction Denzo-SMN (Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1997, **276**, 307-326); absorption correction, Denzo (Z. Otwinowski, D. Borek, W. Majewski and W. Minor, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2003, **59**, 228-234); structure solution SHELXS-97 (G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1990, **46**, 467-473); structure refinement SHELXL-97 (G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112-

122) and graphics, XP (BrukerAXS, 2000). Thermal ellipsoids are shown with 30 and 50% probability, respectively. *R*-values are given for observed reflections, and wR^2 values are given for all reflections. The CCDC reference numbers are 875088, 875089, and 875090. *Exceptions and special features:* The carbon atom C10 in the compound **10c** displayed irregular displacement ellipsoid, which was therefore constrained to be more regular using the program command ISOR. For the compound **11a** the Flack parameter was refined to 0.04 (11).

$(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{CH}=\text{N}^t\text{Bu})\text{Cl}$ (9a**):**

tert-Butyl isocyanide (283 mg, 3.41 mmol, 1 eq) was added dropwise to a suspension of $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrHCl}$ (800 mg, 3.10 mmol) in abs. benzene (10 mL). The reaction mixture was stirred at room temperature for 1 h and after this time solvent was removed in *vacuum* and the resultant residue was washed with abs. pentane (5 mL). The pure compound **9a** was isolated as yellow solid (82%, 870 mg, 2.55 mmol). Crystals suitable for an X-ray crystal structure analysis were obtained by crystallization of a saturated pentane solution of **9a** at $-35\text{ }^\circ\text{C}$. ^1H NMR (500 MHz, C_6D_6 , 298 K): δ 10.14 (s, 1H, CH=N), 5.62 (s, 10H, Cp), 1.13 (s, 9H, ^tBu); $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 , 298 K): δ 220.3 (CH=N), 109.4 (Cp), 60.4 (^tBu), 28.4 (^tBu); $^1\text{H},^{13}\text{C}$ GHSQC (500 MHz / 126 MHz, C_6D_6 , 298 K): $\delta^1\text{H} / \delta^{13}\text{C}$: 5.62 / 109.4 (Cp), 10.14 / 220.3 (CH=N), 1.13 / 28.4 (^tBu); $^1\text{H},^{13}\text{C}$ GHMBC (500 MHz / 126 MHz, C_6D_6 , 298 K): $\delta^1\text{H} / \delta^{13}\text{C}$: 5.62 / 109.4 (Cp / Cp), 1.14 / 60.4, 28.4 ($^t\text{Bu} / ^t\text{Bu}$); $^1\text{H}\{^1\text{H}\}$ NOE (500 MHz, C_6D_6 , 298 K): $\delta^1\text{H}_{\text{irr}} / \delta^1\text{H}_{\text{res}}$: 10.14 / 5.62, 1.13 (CH=N / Cp, ^tBu), 1.13 / 10.14 ($^t\text{Bu} / \text{CH}=\text{N}$); IR (KBr): 3457 (w), 3105 (w), 2966 (s), 2931 (w), 1825 (w), 1734 (w), 1638 (m), 1602 (s), 1458 (m), 1338 (m), 1363 (s), 1324 (w), 1294 (w), 1249 (s), 1203 (s), 1164 (s), 1111 (w), 1063 (w), 1013 (s), 915 (w), 889 (m), 803 (vs), 579 (w), 524 (m), 501 (m), 440 (w) cm^{-1} ; Anal. Calcd for $\text{C}_{15}\text{H}_{20}\text{ZrNCl}$: C, 52.83; H, 5.91; N, 4.11; Found: C, 52.35; H, 5.87; N, 4.37.

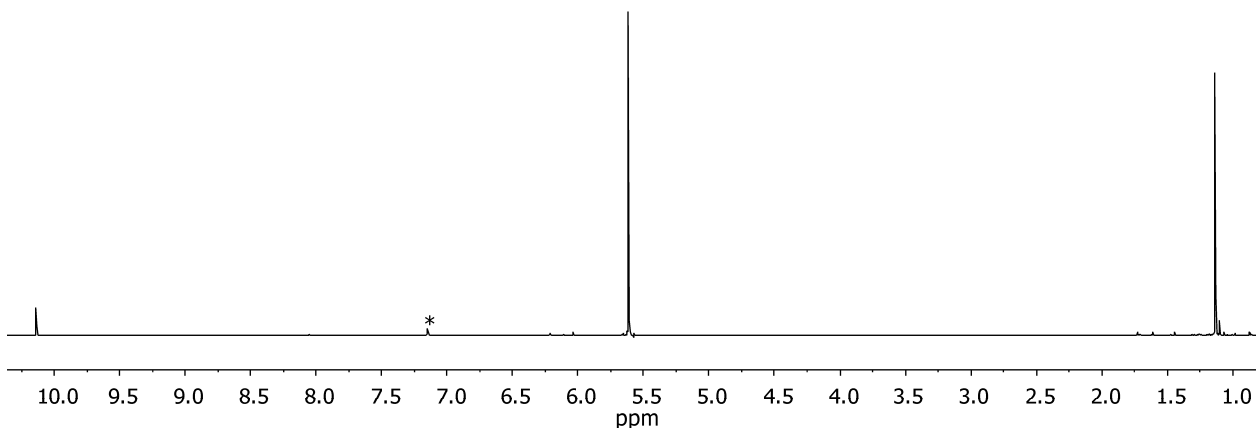


Figure S1. ^1H NMR (500 MHz, C_6D_6 (*), 298 K) spectrum of **9a**.

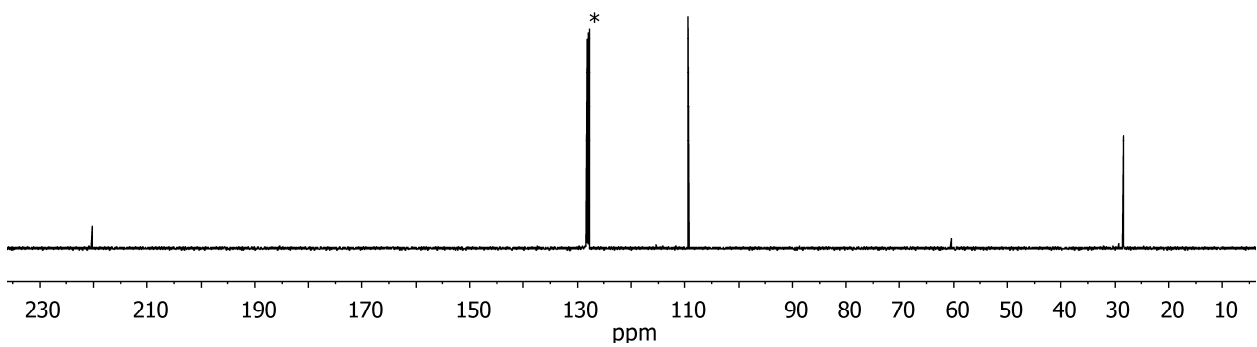


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, C_6D_6 (*), 298 K) spectrum of **9a**.

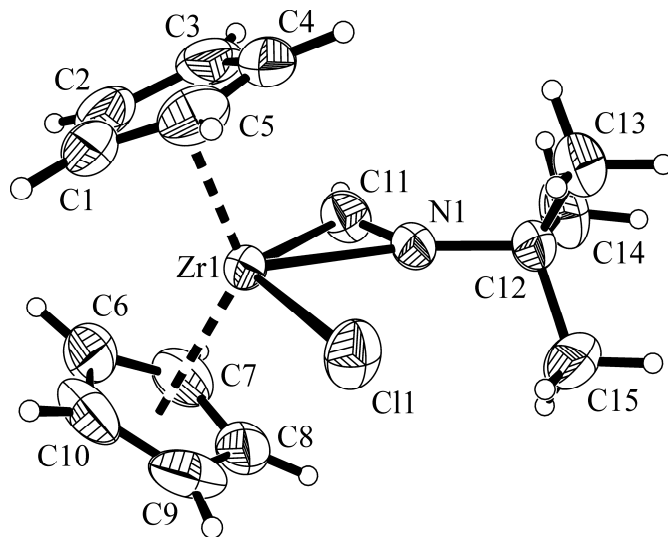


Figure S3. Thermals ellipsoids are shown with 50% probability. X-ray crystal structure analysis of **9a**: formula $C_{15}H_{20}ClNZr$, $M = 340.99$, pale yellow crystal, $0.20 \times 0.17 \times 0.07$ mm, $a = 7.7027(1)$, $b = 16.6435(3)$, $c = 12.4812(2)$ Å, $\beta = 104.966(1)^\circ$, $V = 1545.81(4)$ Å³, $\rho_{\text{calc}} = 1.465$ g cm⁻³, $\mu = 0.868$ mm⁻¹, empirical absorption correction ($0.845 \leq T \leq 0.942$), $Z = 4$, monoclinic, space group $P2_1/c$ (No. 14), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and φ scans, 15492 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å⁻¹, 2693 independent ($R_{\text{int}} = 0.039$) and 2579 observed reflections [$I > 2\sigma(I)$], 166 refined parameters, $R = 0.023$, $wR^2 = 0.057$, max. (min.) residual electron density 0.30 (-0.31) e.Å⁻³, hydrogen atoms calculated and refined as riding atoms.

(η^5 -C₅H₅)₂Zr(CH=NCy)Cl (9b**)**

This compound was prepared from (η^5 -C₅H₅)₂ZrHCl (300 mg, 1.16 mmol) and cyclohexyl isocyanide (139 mg, 1.27 mmol, 1.1 eq) by the same procedure as described for **9a**. The pure product was isolated as light red amorphous solid (84%, 359 mg, 0.979 mmol). ¹H NMR (500 MHz, C₆D₆, 298 K): δ 10.11 (d, ⁴J_{HH} = 1.0 Hz, 1H, CH=N), 5.63 (s, 10H, Cp), 3.30 (sept, 1H, CH^{Cy}), 1.59 / 1.07 (m, each 2H, ^βCH₂^{Cy}), 1.54 / 1.52 (m, each 2H, ^αCH₂^{Cy}), 1.45 / 1.06 (m, each 1H, ^γCH₂^{Cy}), [¹from cosy, ghsqc and ghmbc experiment]; ¹³C{¹H} NMR (126 MHz, C₆D₆, 298 K): δ 225.0 (CH=N), 109.4 (Cp), 65.3 (CH^{Cy}), 32.3 (^αCH₂^{Cy}), 25.6 (^γCH₂^{Cy}), 25.2 (^βCH₂^{Cy}), [¹from cosy, ghsqc and ghmbc experiment]; ¹H, ¹H GCOSY (500 MHz / 500 MHz, C₆D₆, 298 K)[selected traces]: $\delta^1\text{H} / \delta^1\text{H}$: 10.11 / 3.30 (CH=N / CH^{Cy}), 3.30 / 10.11, 1.54 (CH^{Cy} / CH=N, ^αCH₂^{Cy}); ¹H, ¹³C GHSQC (500 MHz / 126 MHz, C₆D₆, 298 K): $\delta^1\text{H} / \delta^{13}\text{C}$: 10.11 / 225.0 (CH=N), 5.63 / 109.4 (Cp), 3.30 / 65.3 (CH^{Cy}), 1.59, 1.07 / 25.2 (^βCH₂^{Cy}), 1.54, 1.52 / 32.3 (^αCH₂^{Cy}), 1.45, 1.06 / 25.6 (^γCH₂^{Cy}); ¹H, ¹³C GHMBC (500 MHz / 126 MHz, C₆D₆, 298 K) [selected traces]: $\delta^1\text{H} / \delta^{13}\text{C}$: 10.11 / 225.0, 65.3 (CH=N / CH=N, CH^{Cy}), 3.30 / 225.0, 32.3, 25.2 (CH^{Cy} / CH=N, ^αCH₂^{Cy}, ^βCH₂^{Cy}); IR (KBr): 3082 (w), 2929 (s), 2851 (m), 2137 (w), 1669 (w), 1604 (s), 1520 (w), 1448 (s), 1363 (m), 1303 (w), 1248 (w), 1169 (m), 1128 (m), 1058 (w), 1013 (s), 955 (w), 891 (w), 797 (vs), 737 (w), 587 (w), 525 (w), 457 (w) cm⁻¹; HRMS (EI) calcd for C₁₇H₂₂ZrNCl, 364.0; found, 364.0; Anal. Calcd for C₁₇H₂₂ZrNCl: C, 55.63; H, 6.04; N, 3.82; Found: C, 56.31; H, 5.98; N, 4.61.

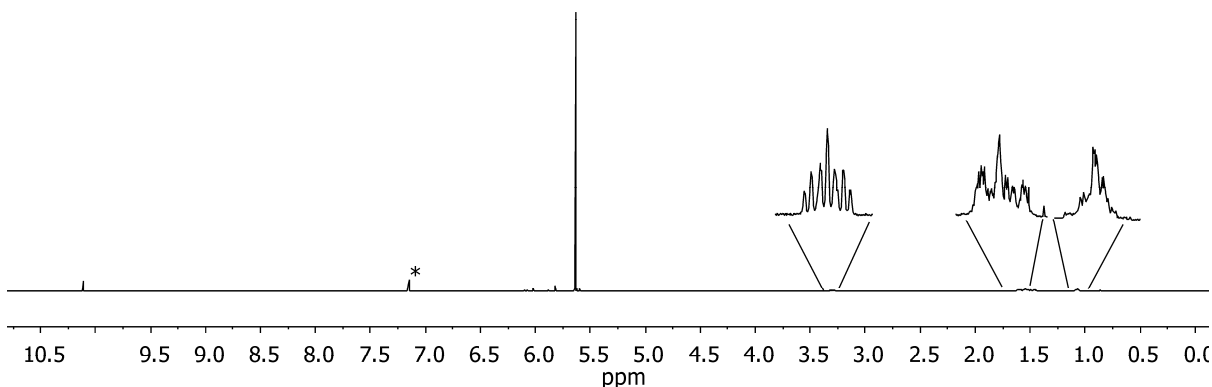


Figure S4. ^1H NMR (500 MHz, C_6D_6 (*), 298 K) spectrum of **9b**.

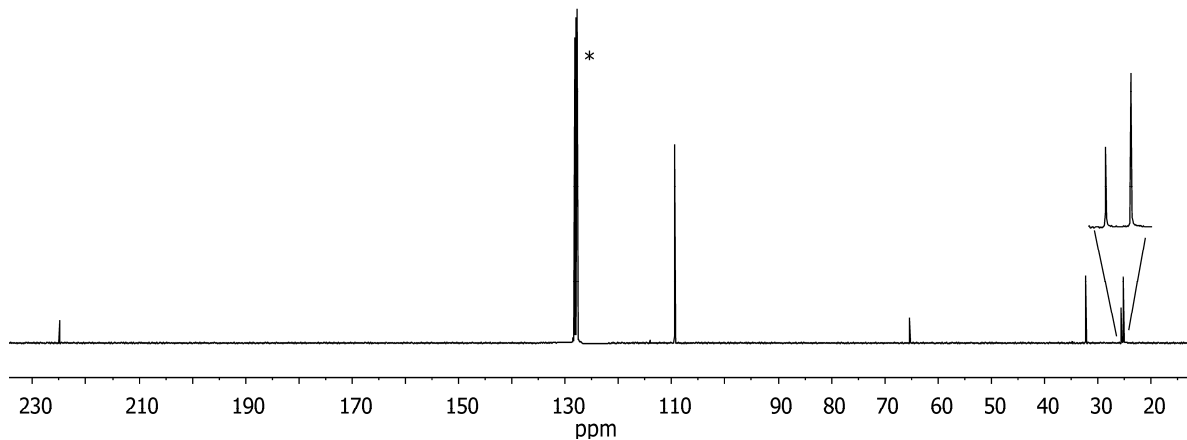


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ NMR (500 MHz, C_6D_6 (*), 298 K) spectrum of **9b**.

$(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrCH}=\text{N}(2,6(\text{Me})_2\text{C}_6\text{H}_3)\text{Cl}$ (9c**)**

Benzene (7 mL) was added to a mixture of 2,6-dimethylphenyl isocyanide (277 mg, 2.11 mmol, 1.09 eq) and $(\eta^5\text{-C}_5\text{H}_5)_2\text{ZrHCl}$ (500 mg, 1.94 mmol). The reaction mixture was stirred at 50 °C for 3 h. After this time solvent was removed in *vacuum* and the resultant material was washed with abs. pentane (5 mL). Diethyl ether (3 mL) was added to the remaining residue and the solution was stored at -35 °C for 12 h. After this time, the solvent was decanted and the residue was dried in *vacuum*. The pure compound **9c** was isolated as isolated gray red powder (66%, 495 mg, 1.28 mmol). ^1H NMR (600 MHz, CD_2Cl_2 , 299 K): δ 11.10 (s, 1H, CH=N), 7.04 (m, 2H, *m*-Ar)¹, 7.01 (m, 1H, *p*-Ar)¹, 6.01 (s, 10H, Cp), 2.19 (s, 6H, Me),

[¹from ghsqc experiment]; ¹³C{¹H} NMR (151 MHz, CD₂Cl₂, 299 K): δ 241.0 (CH=N), 146.1 (*i*-Ar), 130.2 (*o*-Ar), 129.1 (*m*-Ar), 126.1 (*p*-Ar), 110.3 (Cp), 19.1 (Me); ¹H, ¹³C GHSQC (600 MHz / 151 MHz, CD₂Cl₂, 299 K): δ¹H / δ¹³C: 11.10 / 241.0 (CH=N), 7.04 / 129.1 (*m*-Ar), 7.01 / 126.1 (*p*-Ar), 6.01 / 110.3 (Cp), 2.19 / 19.1 (Me); ¹H, ¹³C GHMBC (600 MHz / 151 MHz, CD₂Cl₂, 299 K)[selected traces]: δ¹H / δ¹³C: 11.10 / 146.1 (CH=N / *i*-Ar), 7.04 / 146.1, 129.1, 19.1 (*m*-Ar / *i*-Ar, *m*-Ar, Me), 7.01 / 130.2 (*p*-Ar / *o*-Ar), 2.19 / 146.1, 130.2, 129.1 (Me / *i*-Ar, *o*-Ar, *m*-Ar); IR (KBr): 3107 (w), 3080 (w), 2962 (w), 2916 (w), 1934 (w), 1838 (w), 1734 (w), 1624 (m), 1590 (s), 1569 (s), 1471 (s), 1442 (s), 1376 (m), 1277 (m), 1175 (vs), 1090 (s), 1015 (vs), 906 (m), 842 (s), 736 (m), 682 (m), 586 (m), 505 (w) cm⁻¹; HRMS (EI) calcd for C₁₉H₂₀ZrNCl, 387.0; found, 387.1; Anal. Calcd for C₁₉H₂₀ZrNCl: C, 58.66; H, 5.18; N, 3.60; Found: C, 58.46; H, 5.08; N, 3.65.

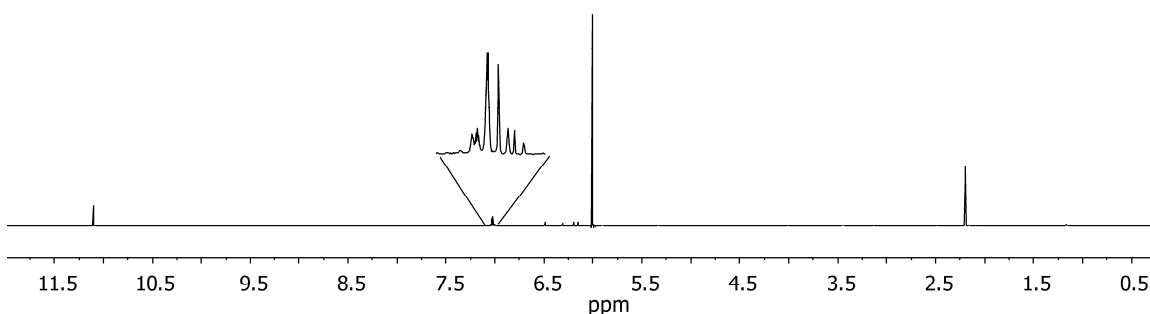


Figure S6. ¹H NMR (600 MHz, CD₂Cl₂, 298 K) spectrum of **9c**.

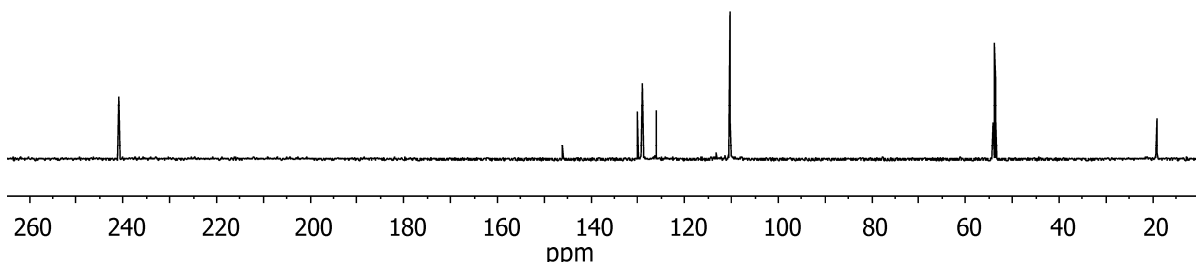


Figure S7. ¹³C{¹H} NMR (151 MHz, 298 K, CD₂Cl₂) spectrum of **9c**.

Preparation of compound **11a**

In exclusion of light diethyl ether (5 mL) was added to a mixture of trimethylsilylethynyllithium (109 mg, 1.05 mmol, 1.2 eq) and η^2 -iminozirconocene chloride complex **9a** (300 mg, 0.879 mmol). The obtained reaction mixture was stirred at room temperature for 12 h. After this time, solvent was removed in *vacuum* and the resulting dark red material was dissolved in abs. pentane (5 mL). Lithium chloride was filtered-off through a short pad of celite and the dark red colored filtrate was collected. Solvent was removed under reduced pressure and the pure compound **11a** was isolated as dark red amorphous solid (82%, 290 mg, 0.720 mmol). Crystals suitable for an X-ray crystal structure analysis were obtained by crystallization of a saturated pentane solution of **11a** at -35 °C. ^1H NMR (600 MHz, C_6D_6 , 299 K): δ 5.58 (s, 5H, Cp^{A}), 5.22 (s, 5H, Cp^{B}), 5.20 (s, 1H, NCH), 1.21 (s, 9H, ^tBu), 0.35 (s, $^2J_{\text{SiH}} = 6.7$ Hz, 9H, SiMe_3); $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 , 299 K): δ 134.6 ($=\text{C}^{\text{Zr}}$), 122.5 ($=\text{C}=\text{}$), 106.2 ($^1J_{\text{CH}} \sim 171$ Hz, $^1\text{Cp}^{\text{A}}$), 101.4 ($^1J_{\text{CH}} \sim 172$ Hz, $^1\text{Cp}^{\text{B}}$), 97.6 ($^1J_{\text{CH}} \sim 177$ Hz, ^1NCH), 56.4 (^tBu), 31.1 ($^1J_{\text{CH}} \sim 126$ Hz, $^1^t\text{Bu}$), 1.6 ($^1J_{\text{SiC}} = 53.9$ Hz, $^1J_{\text{CH}} \sim 120$ Hz, $^1\text{SiMe}_3$), [1 from ghmbc experiment]; $^{29}\text{Si}\{\text{DEPT}\}$ NMR (119 MHz, C_6D_6 , 299 K): δ -8.2; ^1H , ^{13}C GHSQC (600 MHz / 151 MHz, C_6D_6 , 299 K): $\delta^1\text{H} / \delta^{13}\text{C}$: 5.58 / 106.2 (Cp^{A}), 5.22 / 101.4 (Cp^{B}), 5.20 / 97.6 (NCH), 1.21 / 31.1 (^tBu), 0.35 / 1.6 (SiMe_3); ^1H , ^{13}C GHMBC (600 MHz / 151 MHz, C_6D_6 , 299 K)[selected traces]: $\delta^1\text{H} / \delta^{13}\text{C}$: 5.20 / 134.6, 122.5, 56.4 (NCH / $=\text{C}^{\text{Zr}}$, $=\text{C}=\text{}$, ^tBu), 1.21 / 56.4, 31.1 (^tBu), 0.35 / 134.6, 1.6 ($\text{SiMe}_3 / =\text{C}^{\text{Zr}}$, SiMe_3); IR (KBr): 3086 (w), 2960 (w), 2123 (w), 1800 (s), 1684 (w), 1456 (m), 1380 (s), 1356 (s), 1245 (vs), 1216 (s), 1132 (s), 1011 (s), 938 (m), 853 (s), 786 (s), 753 (m), 692 (w), 558 (w), 485 (w) cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{29}\text{ZrNSi}$, 401.1; found, 401.1; Anal. Calcd for $\text{C}_{20}\text{H}_{29}\text{ZrNSi}$: C, 59.64; H, 7.26; N, 3.48; Found: C, 59.12; H, 7.12; N, 3.73.

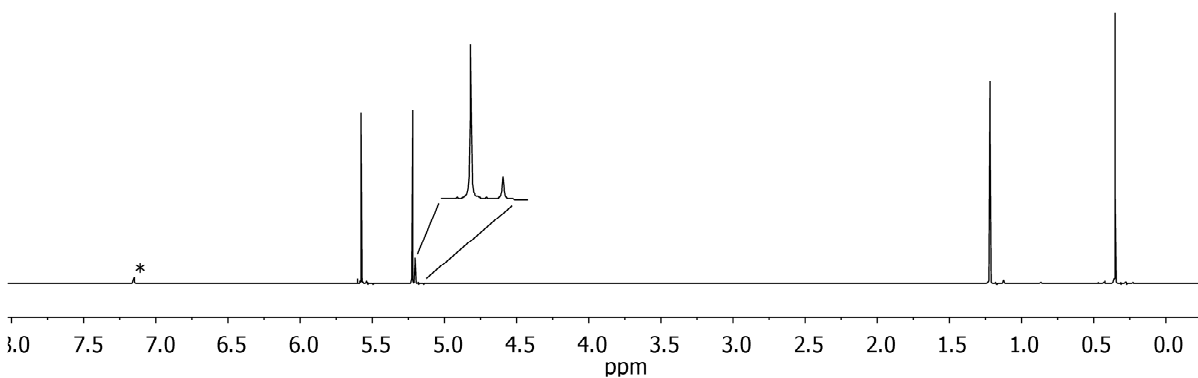


Figure S8. ^1H NMR (600 MHz, C_6D_6 (*), 298 K) spectrum of **11a**.

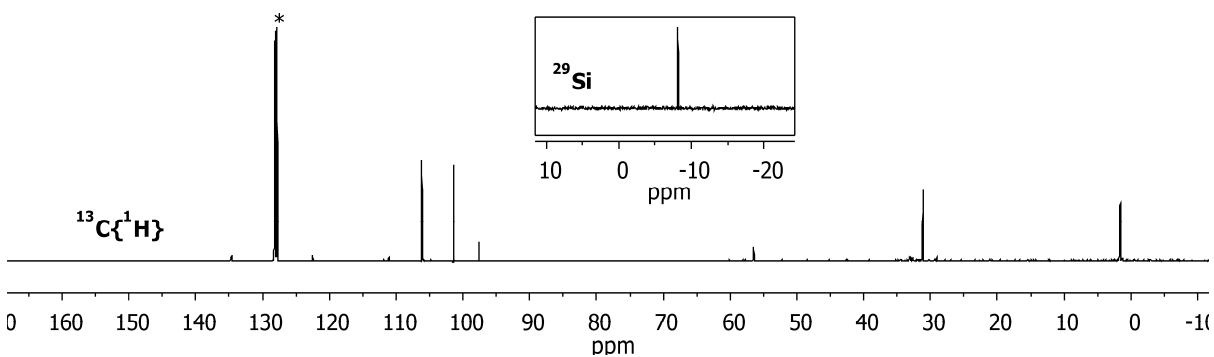


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, C_6D_6 (*), 299 K) and $^{29}\text{Si}\{\text{DEPT}\}$ NMR (119 MHz, C_6D_6 , 299 K) spectra of **11a**.

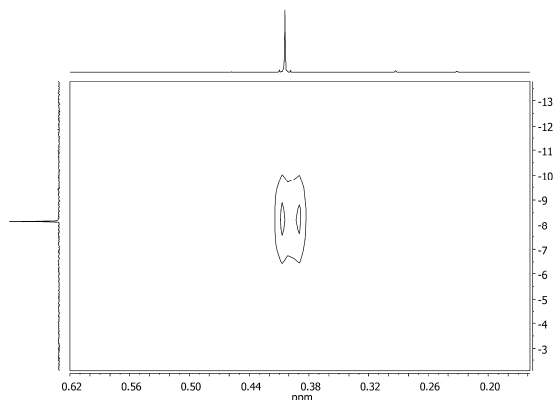


Figure S10. ^1H , ^{29}Si ghmqc (600 MHz / 119 MHz, C_6D_6 , 299 K) spectrum of **11a**.

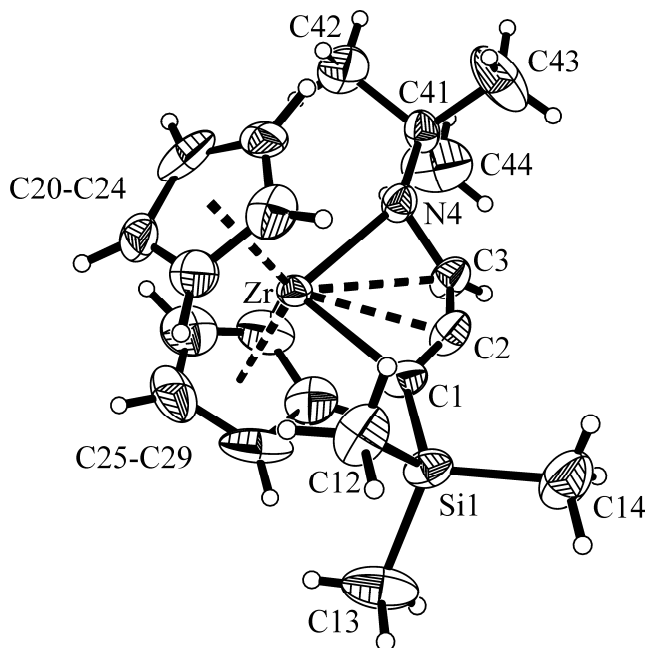


Figure S11. Thermal ellipsoids are shown with 30% probability].

X-ray crystal structure analysis of **11a**: formula $C_{20}H_{29}NSiZr$, $M = 402.75$, red crystal, $0.18 \times 0.17 \times 0.06$ mm, $a = 9.0492(2)$, $b = 14.0508(4)$, $c = 15.8272(5)$ Å, $V = 2012.40(10)$ Å³, $\rho_{\text{calc}} = 1.329$ g cm⁻³, $\mu = 0.606$ mm⁻¹, empirical absorption correction ($0.898 \leq T \leq 0.964$), $Z = 4$, orthorhombic, space group $P2_12_12_1$ (No. 19), $\lambda = 0.71073$ Å, $T = 223(2)$ K, ω and ϕ scans, 16272 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.67$ Å⁻¹, 4975 independent ($R_{\text{int}} = 0.060$) and 4567 observed reflections [$I > 2\sigma(I)$], 214 refined parameters, $R = 0.068$, $wR^2 = 0.182$, max. (min.) residual electron density 1.42 (-0.59) e.Å⁻³, hydrogen atoms calculated and refined as riding atoms.

Preparation of compound **11b**

This compound was prepared from η^2 -iminozirconocene chloride complex **9b** (394 mg, 1.07 mmol) and trimethylsilylethynyllithium (123 mg, 1.18 mmol, 1.1 eq) by the same procedure as described for **11a**. The title compound **11b** was isolated as dark red amorphous solid (82%, 379 mg, 0.884 mmol). The obtained compound was not stable in C_6D_6 solution. It was decomposed during the characterization by NMR: ¹H NMR (600 MHz, C_6D_6 , 299 K) [key resonances]: δ 5.56 (s, 5H, Cp^A), 5.17 (s, 5H, Cp^B), 5.01 (s, 1H, NCH), 2.44 (m, 1H, CH^{Cy}), 0.33 (s, ² $J_{\text{SiH}} = 6.7$ Hz, 9H, SiMe₃); ¹³C{¹H} NMR (151 MHz, C_6D_6 , 299 K) [key resonances]: δ 137.9 (=C^{Zr}), 124.7 (=C=), 106.1 (Cp^A), 104.1 (NCH), 101.5 (Cp^B), 66.5 (CH^{Cy}), 1.5 (SiMe₃); ²⁹Si{DEPT} NMR (119 MHz, C_6D_6 , 299 K): δ -8.3; ¹H, ¹³C GHSQC (600 MHz / 151 MHz, C_6D_6 , 299 K)[selected traces]: $\delta^1\text{H} / \delta^{13}\text{C}$: 5.56 / 106.1 (Cp^A), 5.17 / 101.5 (Cp^B), 5.01 / 104.1 (NCH), 2.44 / 66.5 (CH^{Cy}), 0.33 / 1.5 (SiMe₃); ¹H, ¹³C GHMBC (600 MHz / 151 MHz, C_6D_6 , 299 K)[selected traces]: $\delta^1\text{H} / \delta^{13}\text{C}$: 5.01 / 137.9, 124.7, 66.5 (NCH / =C^{Zr}, =C=, CH^{Cy}), 0.33 / 137.9, 1.5 (SiMe₃ / =C^{Zr}, SiMe₃); IR (KBr): 3100 (w), 2932 (s), 2850 (m), 2117 (s), 2017 (w), 1798 (m), 1616 (m), 1521 (w), 1448 (s), 1356 (w), 1245 (s), 1214 (m), 1130 (w), 1069 (w), 1014 (s), 971 (w), 859 (s), 784 (m), 686 (m), 609 (w), 564 (w), 523 (w), 419 (w) cm⁻¹; Anal. Calcd for $C_{22}H_{31}ZrNSi$: C, 61.62; H, 7.29; N, 3.27; Found: C, 61.65; H, 7.65; N, 3.54.

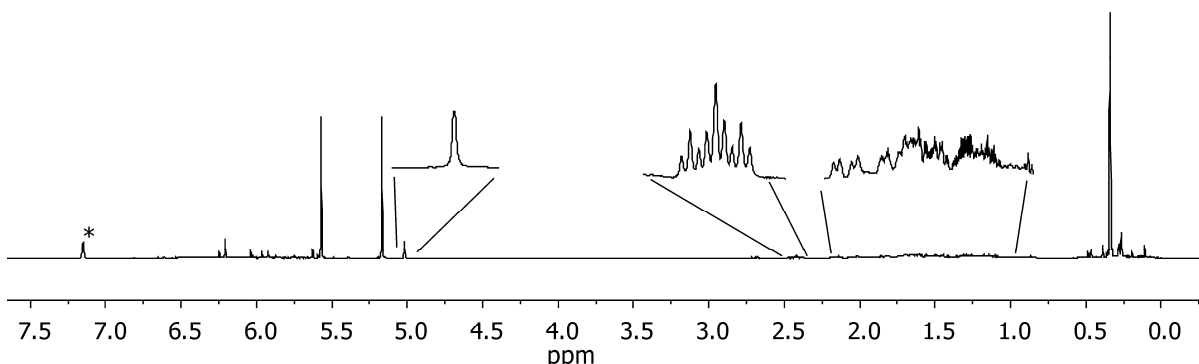


Figure S12. ^1H NMR (300 MHz, C_6D_6 (*), 298 K) spectrum of **11b**.

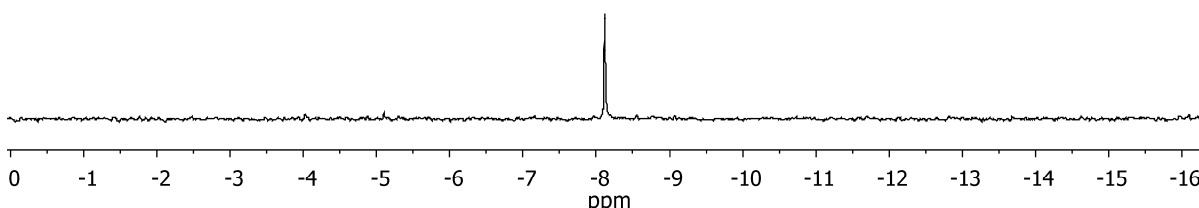


Figure S13. $^{29}\text{Si}\{\text{DEPT}\}$ NMR (59 MHz, C_6D_6 , 298 K) spectrum of **11b**.

Preparation of compound **10c**

A solution of diethyl ether and benzene (5 mL / 5 mL) was added to a mixture of η^2 -iminozirconocene chloride complex **9c** (274 mg, 0.704 mmol) and trimethylsilylethynyl lithium (87 mg, 0.844 mmol, 1.2 eq). The reaction mixture was stirred overnight at room temperature. After this time, solvent was removed in *vacuum* and the resulting dark red material was dissolved in abs. pentane (3 mL). LiCl was filtered-off through a short pad of celite and the dark red colored filtrate was collected. Solvent was removed under reduced pressure and the pure compound **10c** was isolated as dark red solid (80%, 256 mg, 0.567 mmol). Crystals suitable for an X-ray crystal structure analysis were obtained by crystallization of a saturated pentane solution of **10c** at $-35\text{ }^\circ\text{C}$. ^1H NMR (600 MHz, CD_2Cl_2 , 299 K): δ 11.01 (s, 1H, CH=N), 7.01 (m, 2H, *m*-Ar)¹, 6.99 (m, 1H, *p*-Ar)¹, 5.87 (s, 10H, Cp), 2.18 (s, 6H, Me), 0.02 (s, $^2J_{\text{SiH}} = 6.9\text{ Hz}$, 9H, SiMe₃), [¹from ghsqc experiment]; $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_2Cl_2 , 299 K): δ 238.2 (CH=N), 157.8 (ZrC \equiv), 147.1 (*i*-Ar), 130.1 (*o*-Ar), 128.9 (*m*-Ar), 125.7 (*p*-Ar), 124.4 ($\equiv\text{CSi}$), 107.5 (Cp), 19.3 (Me), 1.0 (SiMe₃); $^{29}\text{Si}\{\text{DEPT}\}$ NMR (119 MHz, CD_2Cl_2 , 299 K): δ -26.4; ^1H , ^1H GCOSY (600 MHz / 600 MHz, CD_2Cl_2 , 299 K): $\delta^{1\text{H}} / \delta^{1\text{H}}$: 7.01 / 2.18 (*m*-Ar / Me); ^1H , ^{13}C GHSQC (600 MHz / 151 MHz, CD_2Cl_2 ,

299 K): $\delta^1\text{H} / \delta^{13}\text{C}$: 11.01 / 238.2 (CH=N), 7.01 / 128.9 (*m*-Ar), 6.99 / 125.7 (*p*-Ar), 5.87 / 107.5 (Cp), 2.18 / 19.3 (Me); ^1H , ^{13}C GHMBC (600 MHz / 151 MHz, CD_2Cl_2 , 299 K): $\delta^1\text{H} / \delta^{13}\text{C}$: 11.01 / 157.8, 147.1 (CH=N / ZrC \equiv , *i*-Ar), 7.01 / 147.1, 128.9, 19.3 (*m*-Ar / *i*-Ar, *m*-Ar, Me), 6.99 / 130.1 (*p*-Ar / *o*-Ar), 5.87 / 107.5 (Cp), 2.18 / 147.1, 130.1, 128.9, 19.3 (Me / *i*-Ar, *o*-Ar, *m*-Ar, Me), 0.02 / 124.4, 1.0 (SiMe $_3$ / $\equiv\text{CSi}$, SiMe $_3$); IR (KBr): 3072 (w), 2949 (m), 2024 (s), 1904 (w), 1647 (w), 1571 (s), 1473 (m), 1442 (w), 1376 (w), 1244 (vs), 1163 (vs), 1092 (m), 1018 (vs), 961 (w), 843 (s), 795 (s), 770 (m), 683 (s), 599 (w), 530 (w), 503 (w) cm^{-1} ; HRMS (EI) calcd for $\text{C}_{24}\text{H}_{29}\text{ZrNSi}$, 449.1; found, 449.1; Anal. Calcd for $\text{C}_{24}\text{H}_{29}\text{ZrNSi}$: C, 63.94; H, 6.48; N, 3.11; Found: C, 63.57; H, 6.50; N, 3.03.

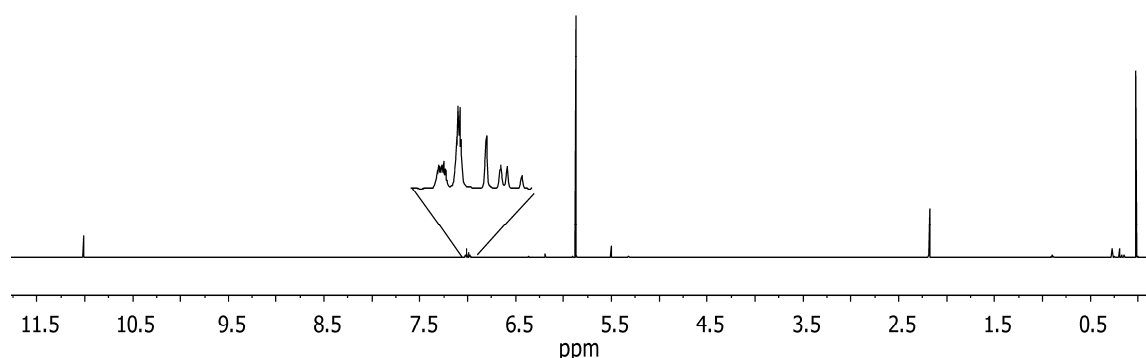


Figure S14. ^1H NMR (600 MHz, CD_2Cl_2 , 299 K) spectrum of **10c**.

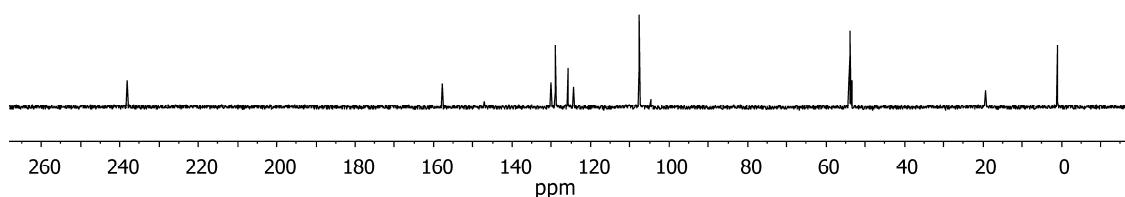


Figure S15. $^{13}\text{C}\{^1\text{H}\}$ NMR (151 MHz, CD_2Cl_2 , 299 K) spectrum of **10c**.

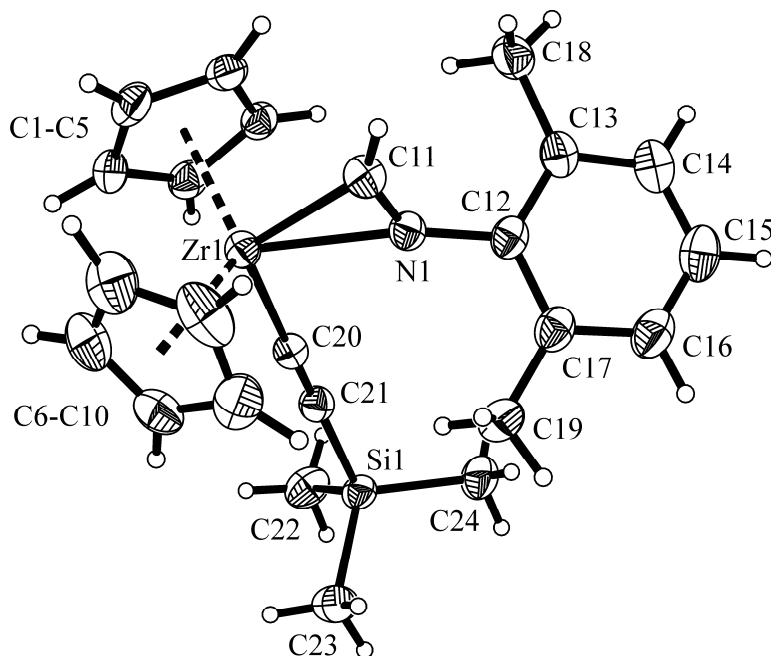


Figure S17. Thermals ellipsoids are shown with 30% probability. X-ray crystal structure analysis of **10c**: formula $C_{24}H_{29}NSiZr$, $M = 450.79$, colourless crystal $0.22 \times 0.10 \times 0.08$ mm, $a = 10.5164(2)$, $b = 11.0732(2)$, $c = 11.1400(3)\text{\AA}$, $\alpha = 93.189(1)$, $\beta = 116.139(1)$, $\gamma = 95.688(1)^\circ$, $V = 1151.67(4)\text{\AA}^3$, $\rho_{\text{calc}} = 1.300\text{ g cm}^{-3}$, $\mu = 0.537\text{ mm}^{-1}$, empirical absorption correction ($0.891 \leq T \leq 0.958$), $Z = 2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda = 0.71073\text{\AA}$, $T = 223(2)\text{ K}$, ω and φ scans, 10328 reflections collected ($\pm h, \pm k, \pm l$), $[(\sin\theta)/\lambda] = 0.59\text{\AA}^{-1}$, 3918 independent ($R_{\text{int}} = 0.049$) and 3629 observed reflections [$I \geq 2\sigma(I)$], 249 refined parameters, $R = 0.040$, $wR^2 = 0.104$, max. (min.) residual electron density 0.63 (-0.44) $e\text{\AA}^{-3}$, hydrogen atoms calculated and refined as riding atoms.

Experimental work in Tokyo:

General remarks: All manipulations involving organometallic compounds were carried out under an inert atmosphere using standard Schlenk technique or a glove box. Anhydrous tetrahydrofuran was purchased from Kanto Chemical Co., Inc. and purified using a Glass-Contour Solvent SystemsTM (SG Water USA) prior to use. *n*-Butyllithium (hexane solution) was purchased from Kanto Chemical Co., Inc. and used as received. Dichlorobis(η^5 -cyclopentadienyl)zirconium was purchased from Sigma-Aldrich Co. LLC and used without

further purification. The alkynylimines **14d-g** were prepared according to the literature. (M. Movassaghi and M. D. Hill, *J. Am. Chem. Soc.* 2006, 128, 4592-4593) NMR spectra were recorded on JEOL ECX 300 and ECA 500 spectrometers, infrared spectra on Shimadzu FT-IR 8300. FAB-MS spectra were collected on the JEOL JMS-700. High resolution mass spectrometry was recorded on a JEOL JMS-T100LC instrument with electrospray ionization using acetonitrile solutions.

Preparation of 1-aza-2-zirconacylopenta-3,4-diene compounds **11d-g**.

Typically, to a solution of dichlorobis(η^5 -cyclopentadienyl)zirconium (146 mg, 0.5 mmol) in tetrahydrofuran (THF, 2 mL) was added dropwise *n*-butyllithium (1.6 M hexane solution, 1.0 mmol) at -78 °C. The mixture was stirred for 1h, and then **14d** (110 mg, 0.4 mmol) was added and the mixture was allowed to warm up to room temperature, then stirred for 1 h. ^1H NMR spectroscopy of the solution showed the formation of **11d**, and the yield was estimated using toluene as an internal standard (88%). The volatiles were removed in vacuo and the residue was dissolved in hexane and filtered. Evaporation of the solvent left yellow oil that may contain unreacted starting materials and unidentified byproducts (91 mg, 46% crude). Despite our attempt to purify **11** by recrystallization, we have not succeeded to obtain solid products.

11d: ^1H NMR (500 MHz, C_6D_6 , 298 K): δ 6.81-7.20 (m, 10H), 5.50 (s, 5H), 5.15 (s, 5H), 0.26 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 298 K): δ 136.44 (q, $J_{\text{Si-C}} = 59$ Hz), 129.28, 128.70, 128.52, 127.28, 126.06 (q, N-C(Ph)=), 123.49 (ipso), 121.22, 120.84, 106.61, 104.97, (Cp \times 2), 100.45 (q, =C=), 1.67. MS (FAB) 497 (M^+). IR (KBr): 2957 (s), 2862 (w), 2168 (w), 1593 (s), 1490 (s), 1340 (s), 1248 (m), 1018 (s), 843 (s), 796 (m), 694 (m). High resolution mass spectrometry, calcd. for $^{12}\text{C}_{30}^{1}\text{H}_{33}^{14}\text{N}_2^{28}\text{Si}_1^{90}\text{Zr}_1$ ($[\text{M}+\text{CH}_3\text{CN}]^+$) = 539.14600, found = 539.14563.

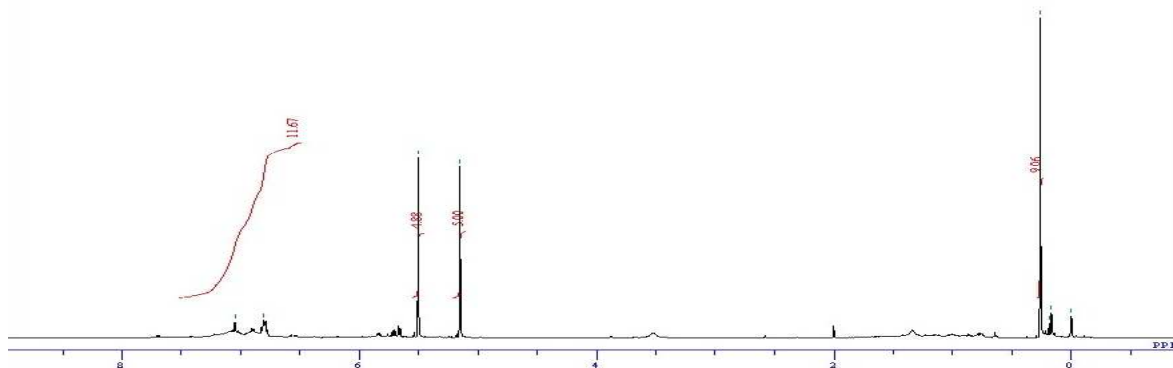


Figure S18. ^1H NMR (500 MHz, C_6D_6 , 298 K) spectrum of **11d**.

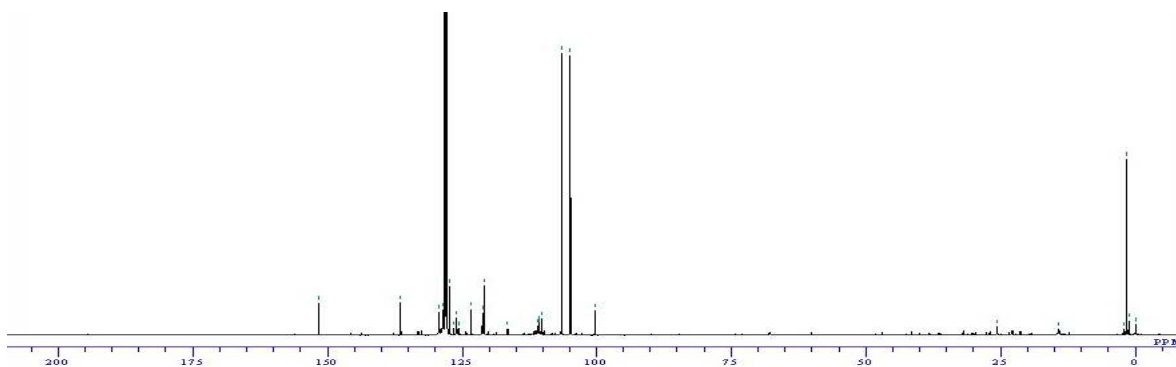


Figure S19. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 298 K) spectrum of **11d**.

11e: Complex **11e** was prepared in a similar manner to **11d** using 234 mg (0.8 mmol) of Cp_2ZrCl_2 and 206 mg (0.8 mmol) of **14e**. The volatiles were removed in vacuo and the residue was dissolved in toluene and filtered. Evaporation of the solvent gave orange oil as a crude product that may contain unreacted starting materials and unidentified byproducts. Yield 82% crude, 74% by ^1H NMR. ^1H NMR (500 MHz, C_6D_6 , 333 K): δ 7.25 (m, 2H), 7.09 (d, 7 Hz, 2H), 6.97 (t, 7 Hz, 1H), 5.54 (s, 5H), 5.42 (s, 5H), 1.17 (s, 9H), 0.41 (s, 9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 333 K): δ 153.82 (ipso), 132.31 (q, $^1J_{\text{Si-C}} = 70$ Hz), 128.64, 125.87 (q, =C=), 123.69, 122.02, 114.34 (q, N-C(*t*-Bu)=), 106.55, 104.14 ($\text{Cp} \times 2$), 36.92 (q), 30.68, 1.85. MS (FAB) 412 ($\text{M}^+ - \text{Cp}$). IR (KBr) 2963 (s), 2168 (w), 1596 (s), 1365 (m), 1250 (s), 1111 (w), 1018 (s), 961 (m), 849(s), 795 (s). High resolution mass spectrometry, calcd. for $^{12}\text{C}_{28}^{1}\text{H}_{37}^{14}\text{N}_2^{28}\text{Si}_1^{90}\text{Zr}_1$ ($[\text{M} + \text{CH}_3\text{CN}]^+$) = 519.17730, found = 519.17983.

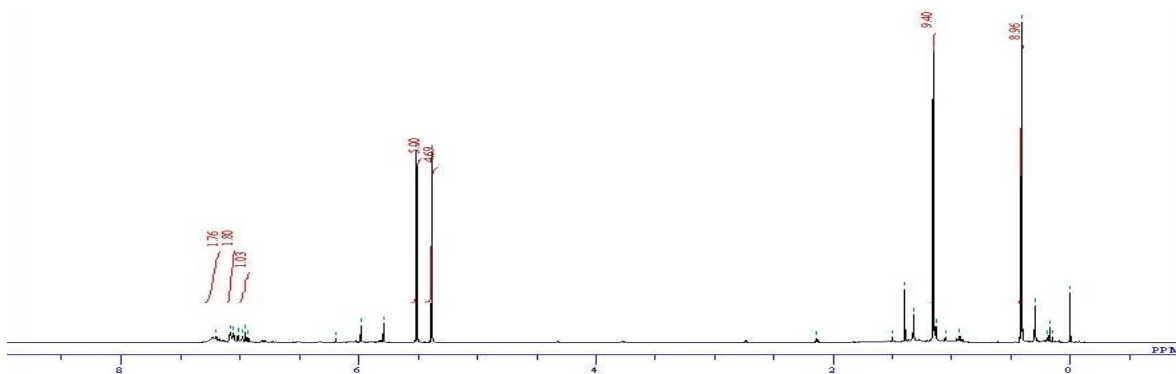


Figure S20. ^1H NMR (500 MHz, C_6D_6 , 333 K) spectrum of **11e**.

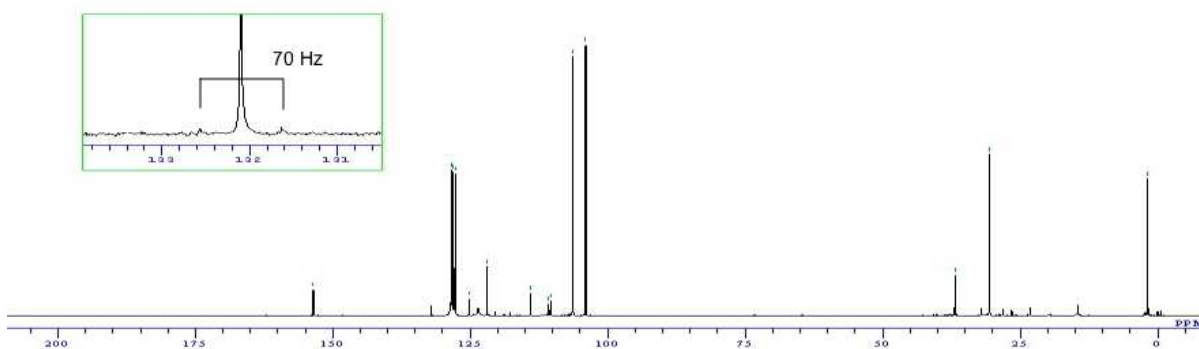


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 333 K) spectrum of **11e**.

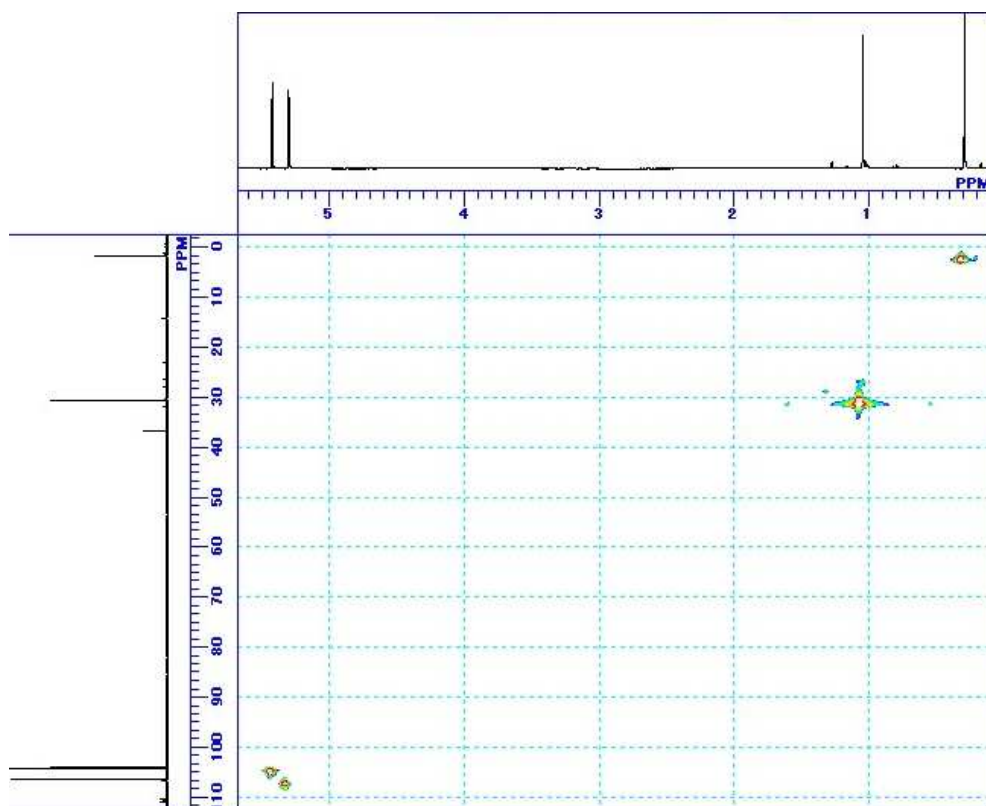


Figure S22. ^1H , ^{13}C hmqc (500 MHz, C_6D_6 , 299 K) spectrum of **11e**.

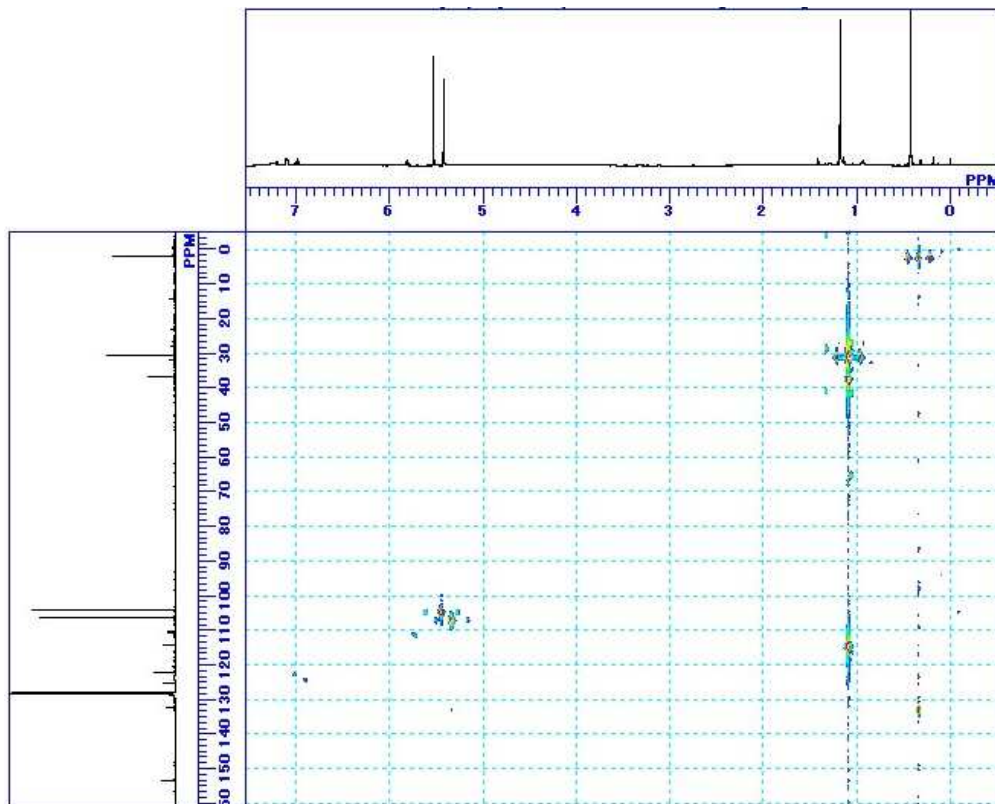


Figure S23. ^1H , ^{13}C ghmhc (500 MHz, C_6D_6 , 299 K) spectrum of **11e**.

11f: Complex **11f** was prepared similarly to **11d** using 146 mg (0.5 mmol) of Cp_2ZrCl_2 and 141 mg (0.5 mmol) of **14f**. The volatiles were removed in vacuo and the residue was dissolved in toluene and filtered. Evaporation of the solvent left a orange oil as a crude product that may contain unreacted starting materials and unidentified byproducts, yield 95% crude, 93% by ^1H NMR; ^1H NMR (300 MHz, C_6D_6 , 298 K): δ 7.76-6.86 (m, 15H), 5.55 (s, 5H), 5.36 (s, 5H). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 298 K): δ 151.09 (q), 142.44 (q), 136.65 (q), 135.81 (q), 133.45, 129.37, 128.78, 128.59, 128.50, 128.14, 127.31, 121.26, 121.00, 118.40 (q, N-C(Ph)=), 111.17 (q, =C=), 107.20, 105.05 (Cp \times 2). MS (FAB) 502 (M^+). IR (KBr): 3057 (w), 2928(w), 2023 (m), 1591 (s), 1487 (s), 1449 (M), 1348 (s), 1234 (m), 1169 (m), 1016 (s), 799 (m), 758, (m), 694 (m). High resolution mass spectrometry, calcd. for $^{12}\text{C}_{31}^{1}\text{H}_{26}^{14}\text{N}_1^{90}\text{Zr}_1$ ($\text{M}+\text{H}^+$) = 502.11123, found = 502.11019.

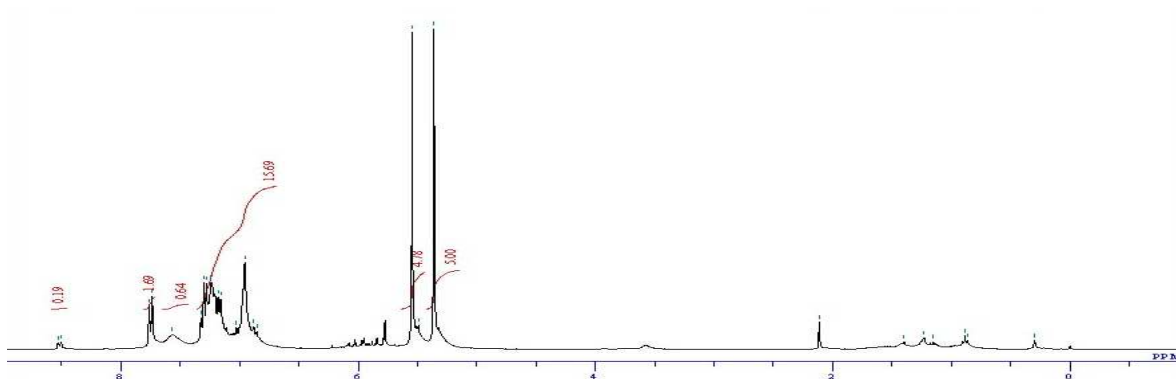


Figure S24. ^1H NMR (300 MHz, C_6D_6 , 298 K) spectrum of **11f**.

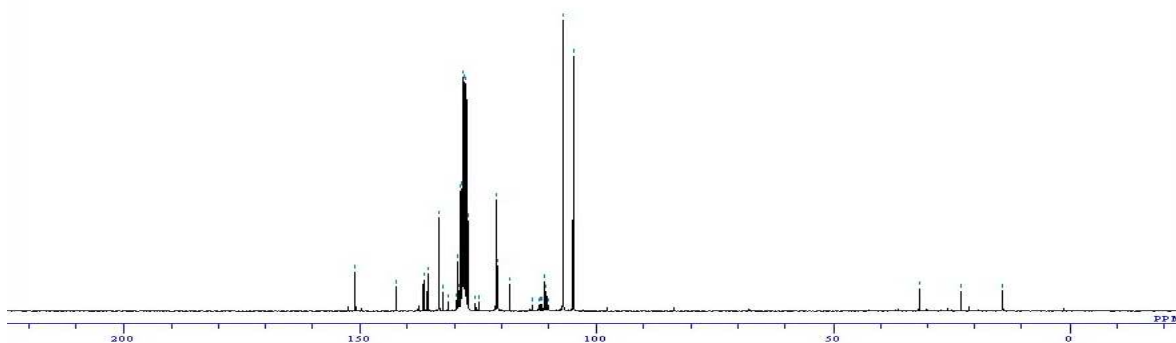


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6 , 298 K) spectrum of **11f**.

11g: Complex **11g** was prepared in a similar manner to **11d** using 146 mg (0.5 mmol) of Cp_2ZrCl_2 and 131 mg (0.5 mmol) of **14g** (yellow oil). Yield 53% crude, 68% by ^1H NMR. ^1H NMR (500 MHz, C_6D_6 , 298 K): δ 7.22-7.30 (m, 5H), 6.97-7.10 (m, 5H), 5.60 (s, 5H), 5.33 (s, 5H), 2.82 (ddd, 16, 8, 7 Hz, 1H), 2.65 (ddd, 16, 8, 6 Hz, 1H), 1.92 (m, 1H), 1.83 (m, 1H), 1.60 (m, 2H), 1.07 (t, 7 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 298 K): δ 151.46 (ipso), 140.84 (q), 136.45 (ipso), 129.32, 128.1, 127.93, 127.03 (q, N-C(Ph)=), 121.00, 120.95, 120.57, 110.61 (q, =C=), 106.82, 104.86 ($\text{Cp} \times 2$), 35.12, 32.32, 22.92, 14.26. MS (FAB) 416 ($\text{M}^+ - \text{Cp}$). IR (KBr): 2959 (s), 2869 (s), 2233 (w), 1593 (s), 1489 (s), 1447 (m), 1346 (s), 1261 (m), 1018 (s), 799 (s), 694 (m). High resolution mass spectrometry, calcd. for $^{12}\text{C}_{29}\text{H}_{30}^{14}\text{N}_1^{90}\text{Zr}_1$ ($\text{M}+\text{H}^+$) = 482.14253, found = 482.14487.

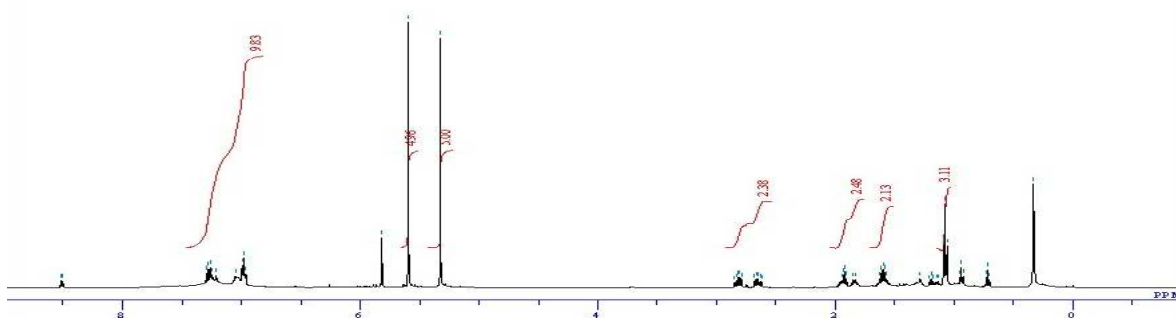


Figure S26. ^1H NMR (500 MHz, C_6D_6 , 298 K) spectrum of **11g**.

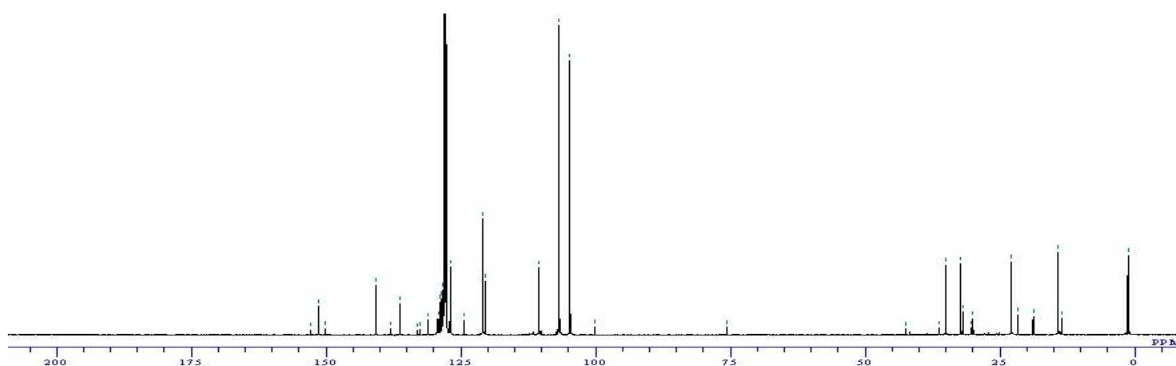


Figure S27. $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, C_6D_6 , 298 K) spectrum of **11g**.

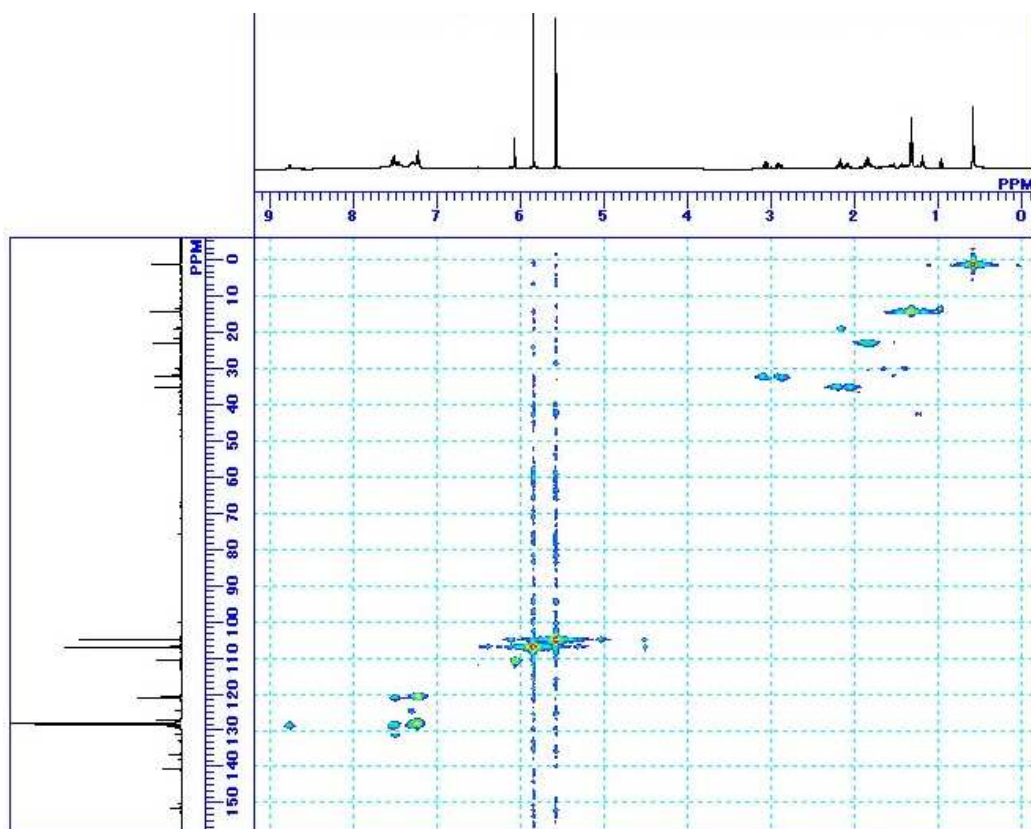


Figure S28. ^1H , ^{13}C hmqc (500 MHz, C_6D_6 , 299 K) spectrum of **11g**.

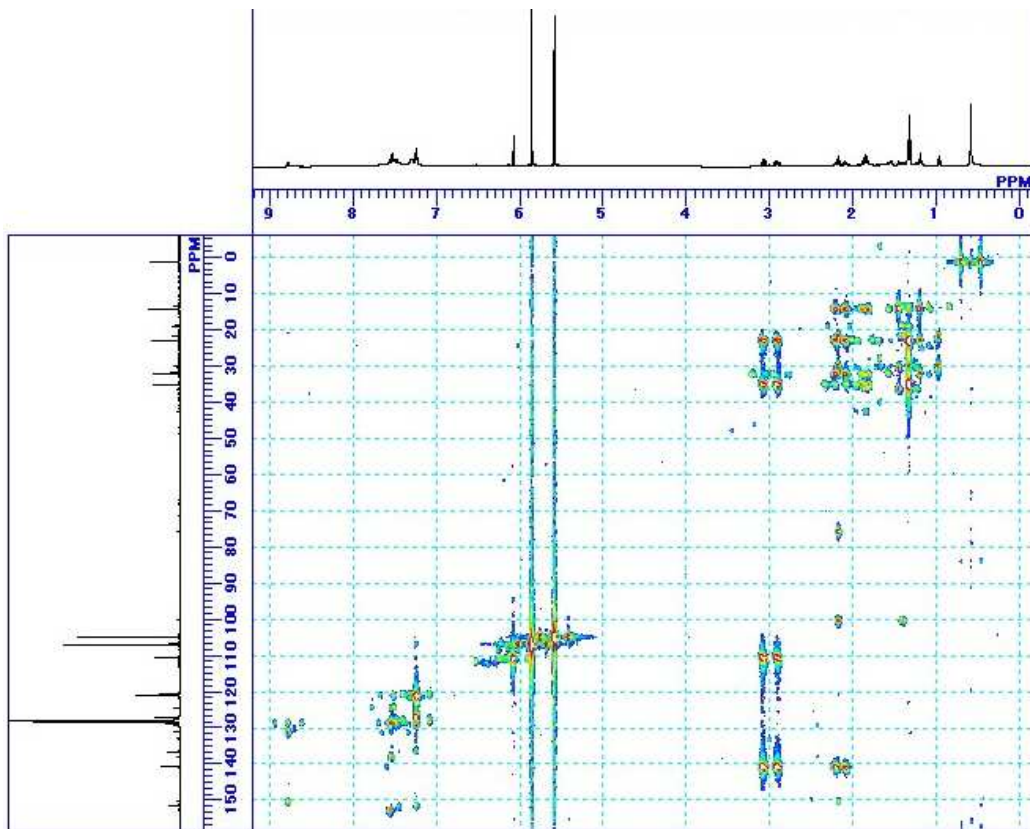


Figure S29. ^1H , ^{13}C ghmhc (500 MHz, C_6D_6 , 299 K) spectrum of **11g**.