Zirconium and Hafnium Complexes Based on 2-Aryl-8-arylaminoquinoline Ligands: Synthesis, Molecular Structure, and Catalytic Performance in Ethylene Copolymerization

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Supporting Information

1. Preparation of CNN ligands.

2-Phenyl-8-bromquinoline (2). A mixture of 2,8-dibromoquinoline (2.87 g, 10 mmol), phenylboronic acid (1.83 g, 15 mmol), K_2CO_3 (3.9 g, 28 mmol), $Pd(AcO)_2$ (40 mg), tri(*o*-tolyl)phosphine (90 mg), DME (37 mL) and H_2O (12 mL) was refluxed for 4 h under stirring in an argon atmosphere. The mixture was subsequently poured into water and extracted with benzene (3×50 mL). The combined organic phase was washed with water, evaporated, and purified by column chromatography (silica gel 40, 1:1 benzene/petroleum ether) to give 2.2 g (77%) of the product (viscous oil, crystallizes slowly). $C_{15}H_{10}BrN$ (284.15): calcd C 63.40, H 3.55, N 4.93; found C 63.49, H 3.65, N 4.90. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 7.33 (t, 1H), 7.57 (m, 3H), 7.72 (d, 1H), 7.90 (d, 1H), 8.07 (d, 1H), 8.11 (d, 1H), 8.36 (d, 2H).

8-Bromo-2-(1-naphthyl)quinoline (3). A mixture of 2,8-dibromoquinoline (6.0 g, 21 mmol), 1-naphthylboronic acid (4.1 g, 24 mmol), K_2CO_3 (6.6 g, 48 mmol), $Pd(OAc)_2$ (0.1g, 0.4 mmol), P(*o*-Tol)$_3$ (0.25 g, 0.8 mmol), DME (50 mL) and water (15 mL) was refluxed for 6 h under stirring in argon atmosphere. The mixture was subsequently poured into water and extracted with $CHCl_3$ (3×50 mL). The combined organic phase was washed by water, brine, evaporated, and purified by column chromatography (silica gel 40, 1:1 hexane/benzene) to give 4.1 g (57%) of the product (red purple oil). $C_{19}H_{12}BrN$ (334.21): calcd C 68.28, H 3.62, N 4.19; found C 68.38, H 3.70, N 4.14. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 7.99-7.95 (group of signals, 2H), 7.84 (t, 1H), 7.80 (d, 2H), 7.63 (t, 1H), 7.57 (m, 2H), 7.42 (t, 1H). 8.11 (d, 1H), 8.22 (d, 1H), 8.60 (m, 1H).

8-Bromo-2-(4-*tert*-butylphenyl)quinoline (4). A mixture of 2,8-dibromoquinoline (2.87 g, 10 mmol), 4-*tert*-butylphenylboronic acid (2.67 g, 15 mmol), K_2CO_3 (3.9 g, 28 mmol), $Pd(OAc)_2$ (40 mg), P(*o*-Tol)$_3$ (90 mg), DME (37 mL) and water (10 mL) was refluxed for 6 h under stirring in argon atmosphere. The mixture was subsequently poured into water and extracted with

benzene (3×50 mL). The combined organic phase was washed with water, evaporated, and purified by column chromatography (silica gel 40, 1:1 benzene/petroleum ether) to give 3.62 g (71%) of the product. $C_{19}H_{18}BrN$ (340.26): calcd C 67.07, H 5.33, N 4.12; found C 67.17, H 5.40, N 4.08. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 8.22 (m, 2H), 8.15 (d, 1H), 8.05 (dd, 1H), 7.92 (d, 1H), 7.80 (dd, 1H), 7.33 (m, 3H), 1.46 (s, 9H).

8-Bromo-2-(4-methylphenyl)quinoline (5). A solution of $ZnCl_2$ (3.4 g, 25 mmol) in THF (50 mL) was added dropwise to a cooled (0 °C) etheral solution of *p*-tolyl-Li (50 mmol, in 50 mL of Et_2O). The reaction mixture was allowed to warm to room temperature and was subsequently stirred for 20 min. Then, Pd(dba)2 (0.3 g), *N*-[2'-(dicyclohexylphosphino)[1,1'-biphenyl]-2-yl]-*N*,*N*-dimethylamine (0.42 g), and 1 (11.5 g, 40 mmol) were added. After 16 h of stirring, aq. NH_4Cl (50 mL, 10%) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3×30 mL). The combined organic phase was dried over $MgSO_4$ and evaporated; the residue was recrystallized (benzene/EtOH 1:10) to yield 8 g (67%) of the product. $C_{16}H_{12}BrN$ (298.18): calcd C 64.45, H 4.06, N 4.70; found C 64.50, H 4.10, N 4.66. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 8.23 (m, 2H), 8.15 (d, 1H), 8.06 (dd, 1H), 7.94 (d, 1H), 7.76 (dd, 1H), 7.35 (m, 3H), 2.46 (s, 3H).

8-Bromo-2-(4-fluorophenyl)quinoline (6). A solution of $ZnCl_2$ (1.36 g, 10 mmol) in THF (20 mL) was added dropwise to a cooled (0 °C) solution of *p*-fluorophenyl-Li (50 mmol, obtained at -30 °C in 50 mL of Et_2O). The reaction mixture was allowed to warm to room temperature and was subsequently stirred for 1 h. Then, Pd(dba)2 (0.3 g), *N*-[2'-(dicyclohexylphosphino)[1,1'-biphenyl]-2-yl]-*N*,*N*-dimethylamine (0.42 g), and 1 (4.3 g, 15 mmol) were added. After 16 h of stirring, aq. NH_4Cl (50 mL, 10%) was added. The organic layer was separated, and the aqueous layer was extracted with Et_2O (3×30 mL). The combined organic phase was dried over $MgSO_4$ and evaporated. The product (yield 70%, brown oil) was used without purification.

***N*-(2,6-Diisopropylphenyl)-2-phenyl-8-quinolinamine (7).** A mixture of 2 (2.22 g, 7.7 mmol), 2,6-diisopropylaniline (1.5 g, 8.5 mmol), sodium *tert*-butylate (1 g), $Pd(dba)_2$ (90 mg) and *N*-[2'-(dicyclohexylphosphino)[1,1'-biphenyl]-2-yl]-*N*,*N*-dimethylamine (120 mg) in toluene (17 mL) was stirred at 105 °C under an argon atmosphere for 6 h. The reaction mixture was cooled and then treated with water (20 mL). The organic layer was separated, and the water layer was extracted with benzene (3×10 mL). The combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure. The product was purified by column chromatography (silica gel 40, petroleum ether). The yield was 1.64 g (56%). $C_{27}H_{28}N_2$ (380.53): calcd C 85.22, H 7.42, N 7.36; found C 85.24, H 7.48, N 7.28. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 8.26 (m, 2H), 8(d, 1H), 7.97 (d, 1H), 7.88 (br.s., 1H), 7.59 (m, 2H), 7.52 (m, 1H), 7.42 (m, 1H), 7.30 (m, 3H), 7.15 (dd, 1H), 6.38 (dd, 1H), 3.35 (m, 2H), 1.29 (d, 6H), 1.22 (d, 6H).

***N*-(2,6-Dimethylphenyl)-2-(1-naphthyl)-8-quinolinamine (8).** A mixture of 3 (2.03 g, 6 mmol), 2,6-dimethylaniline (0.83 mL, 6.9 mmol), $Pd(dba)_2$ (72 mg, 0.12 mmol), *N*-[2'-(dicyclohexylphosphino)[1,1'-biphenyl]-2-yl]-*N*,*N*-dimethylamine (94 mg, 0.24 mmol), sodium *tert*-butylate (0.72 g, 7.2 mmol) in toluene (15 mL) was stirred at 105 °C under an argon atmosphere for 8 h. The reaction mixture was cooled and then treated with water (20 mL). The organic layer was separated, and the water layer was extracted with benzene (3×10 mL). The combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure. The product was purified by column chromatography (silica gel 40, hexane/toluene 2:1). The yield was 1.59 g (71%). $C_{27}H_{22}N_2$ (374.48): calcd C 86.60, H 5.92, N 7.48; found C 86.62, H 6.01, N 7.37. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 8.47 (d, 1H), 8.27 (d, 1H), 8.00-7.97 (group of signals, 2H), 7.81 (d, 1H), 7.78 (d, 1H), 7.76 (br.s., 1H), 7.64 (m, 1H), 7.57-7.50 (group of signals, 2H), 7.33 (t, 1H), 7.21-7.12 (group of signals, 4H), 6.35 (d, 1H), 2.31 (s, 6H).

***N*-(2,6-Diisopropylphenyl)-2-(1-naphthyl)-8-quinolinamine (9).** A mixture of **3** (2.03 g, 6 mmol), 2,6-diisopropylaniline (1.3 mL, 7 mmol), $Pd(dba)_2$ (72 mg, 0.12 mmol), *N*-[2'-(dicyclohexylphosphino)[1,1'-biphenyl]-2-yl]-*N*,*N*-dimethylamine (94 mg, 0.24 mmol), sodium *tert*-butylate (0.72 g, 7.2 mol) in toluene (15 mL) was stirred at 105 °C under an argon atmosphere for 8 h. The reaction mixture was cooled and then treated with water (20 mL). The organic layer was separated, and the water layer was extracted with benzene (3×10 mL). The combined organic phases were dried over $MgSO_4$ and evaporated under reduced pressure. The product was purified by column chromatography (silica gel 40, hexane/ toluene 2:1). The yield was 1.7 g (66%). $C_{31}H_{30}N_2$ (430.59): calcd C 86.47, H 7.02, N 6.51; found C 86.46, H 7.11, N 6.43. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 8.57 (d, 1H), 8.28 (d, 1H), 8.00-7.98 (group of signals, 2H), 7.83 (dd, 1H), 7.81 (d, 1H), 7.74 (br.s., 1H), 7.67 (dd, 2H), 7.59-7.50 (group of signals, 2H), 7.40-7.30 (group of signals, 3H), 7.19 (dd, 1H), 6.37 (dd, 1H), 3.35 (m, 2H), 1.22 (s, 12H).

***N*-(2,6-Diisopropylphenyl)-2-(4-*tert*-butylphenyl)-8-quinolinamine (10).** The synthesis of **10** was carried out in the same way as that described for **9**, but **4** was used, and the reaction time was 5 h. The product was purified by column chromatography (silica gel 40, hexane). The yield was 68%. $C_{31}H_{36}N_2$ (436.64): calcd C 85.27, H 8.31, N 6.42; found C 85.30, H 8.35, N 6.35. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 8.20 (m, 3H), 7.95 (d, 1H), 7.87 (br.s., 1H), 7.62 (m, 2H), 7.35 (m, 4H), 7.13 (dd, 1H), 6.35 (dd, 1H), 3.34 (m, 2H), 1.45 (s, 9H), 1.28 (d, 6H), 1.21 (d, 6H).

***N*-(2,6-Diisopropylphenyl)-2-(4-methylphenyl)-8-quinolinamine (11).** The synthesis of **10** was carried out in the same way as that described for **9**, but **5** was used, and the reaction time was 5 h. The product was purified by recrystallization (hexane). The yield was 68%. $C_{28}H_{30}N_2$ (394.55): calcd C 85.24, H 7.66, N 7.10; found C 85.23, H 7.69, N 7.08. ^{1}H NMR (400 MHz,

$CDCl_3$, 20 °C): δ 8.19 (m, 3H), 7.95 (d, 1H), 7.88 (br.s., 1H), 7.38 (m, 5H), 7.28 (d, 1H), 6.37 (dd, 1H), 3.35 (m, 1H), 2.50 (s, 3H), 1.29 (d, 6H), 1.22 (d, 6H).

N-(2,6-diisopropylphenyl)-2-(4-fluorophenyl)-8-quinolinamine (12). The synthesis of 10 was carried out in the same way as that described for **9**, but **6** was used, and the reaction time was 10 h. The product was purified by column chromatography (silica gel 40, hexane). The yield was 11.3%. $C_{27}H_{27}FN_2$ (398.52): calcd C 81.37, H 6.83, N 7.03; found C 81.40, H 6.88, N 6.94. ^{1}H NMR (400 MHz, $CDCl_3$, 20 °C): δ 8.15 (m, 3H), 7.92 (d, 1H), 7.88 (br.s., 1H), 7.38 (m, 5H), 7.22 (d, 1H), 6.44 (dd, 1H), 3.40 (m, 1H), 1.33 (d, 6H), 1.28 (d, 6H).

2. Crystal structure determination.

Table S1. Atomic coordinates (Å × 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **15**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Zr(1)	2293(1)	10058(1)	2402(1)	20(1)
N(1)	2089(2)	9362(2)	3557(2)	21(1)
N(2)	2954(2)	10989(2)	3524(2)	22(1)
C(1)	1194(3)	8778(3)	1960(3)	24(1)
C(2)	690(3)	8506(3)	1073(3)	27(1)
C(3)	256(3)	7609(3)	828(3)	29(1)
C(4)	375(3)	6883(3)	1454(3)	27(1)
C(5)	59(3)	5911(3)	1212(3)	35(1)
C(6)	229(3)	5201(3)	1811(3)	39(1)
C(7)	731(3)	5422(3)	2709(3)	35(1)
C(8)	1041(3)	6352(3)	2966(3)	29(1)
C(9)	866(3)	7123(3)	2362(3)	24(1)
C(10)	1203(3)	8113(3)	2585(2)	22(1)
C(11)	1591(3)	8515(3)	3477(3)	23(1)
C(12)	1397(3)	8175(3)	4183(3)	26(1)
C(13)	1719(3)	8693(3)	4944(3)	28(1)
C(14)	2248(3)	9574(3)	5041(2)	25(1)
C(15)	2575(3)	10188(3)	5779(3)	34(1)
C(16)	3051(4)	11040(3)	5771(3)	38(1)
C(17)	3203(3)	11348(3)	5037(3)	30(1)
C(18)	2883(3)	10782(3)	4292(3)	23(1)
C(19)	2410(3)	9881(3)	4308(2)	23(1)
C(21)	3585(3)	9262(3)	2258(3)	28(1)
C(22)	3682(3)	8332(3)	2728(2)	23(1)
C(23)	3270(3)	7456(3)	2304(3)	31(1)
C(24)	3303(3)	6608(3)	2752(3)	37(1)
C(25)	3748(3)	6595(3)	3654(3)	37(1)
C(26)	4169(3)	7439(3)	4092(3)	35(1)
C(27)	4142(3)	8296(3)	3647(3)	30(1)
C(31)	1241(3)	11075(3)	1329(3)	30(1)
C(32)	1975(3)	11008(3)	953(3)	26(1)
C(33)	1856(3)	10408(3)	238(3)	31(1)
C(34)	2634(3)	10261(3)	-11(3)	35(1)
C(35)	3570(3)	10695(4)	441(3)	38(1)
C(36)	3706(3)	11288(3)	1137(3)	36(1)
C(37)	2932(3)	11440(3)	1395(3)	31(1)
C(41)	3341(3)	11940(3)	3465(2)	22(1)
C(42)	4344(3)	12041(3)	3573(2)	24(1)
C(43)	4671(3)	12956(3)	3442(3)	29(1)
C(44)	4036(3)	13753(3)	3217(3)	31(1)
C(45)	3064(3)	13652(3)	3138(3)	29(1)
C(46)	2705(3)	12756(3)	3271(2)	24(1)
C(47)	1651(3)	12684(3)	3222(3)	33(1)
C(48)	5066(3)	11198(3)	3834(3)	35(1)

Table S2. Bond lengths [Å] for **15**.

Bond	Length [Å]	Bond	Length [Å]	Bond	Length [Å]
Zr(1)-N(2)	2.163(3)	C(12)-C(13)	1.374(6)	C(31)-H(31B)	0.9900
Zr(1)-C(21)	2.285(4)	C(12)-H(12A)	0.9500	C(32)-C(33)	1.415(6)
Zr(1)-C(1)	2.295(4)	C(13)-C(14)	1.414(6)	C(32)-C(37)	1.420(6)
Zr(1)-N(1)	2.305(3)	C(13)-H(13A)	0.9500	C(33)-C(34)	1.383(6)
Zr(1)-C(31)	2.309(4)	C(14)-C(15)	1.419(6)	C(33)-H(33A)	0.9500
Zr(1)-C(32)	2.646(4)	C(14)-C(19)	1.420(5)	C(34)-C(35)	1.400(6)
Zr(1)-C(22)	3.029(4)	C(15)-C(16)	1.370(6)	C(34)-H(34A)	0.9500
N(1)-C(11)	1.353(5)	C(15)-H(15A)	0.9500	C(35)-C(36)	1.380(6)
N(1)-C(19)	1.362(5)	C(16)-C(17)	1.414(6)	C(35)-H(35A)	0.9500
N(2)-C(18)	1.376(5)	C(16)-H(16A)	0.9500	C(36)-C(37)	1.390(6)
N(2)-C(41)	1.448(5)	C(17)-C(18)	1.389(6)	C(36)-H(36A)	0.9500
C(1)-C(10)	1.395(5)	C(17)-H(17A)	0.9500	C(37)-H(37A)	0.9500
C(1)-C(2)	1.423(6)	C(18)-C(19)	1.428(5)	C(41)-C(46)	1.410(5)
C(2)-C(3)	1.373(6)	C(21)-C(22)	1.485(6)	C(41)-C(42)	1.412(5)
C(2)-H(2A)	0.9500	C(21)-H(21A)	0.9900	C(42)-C(43)	1.399(6)
C(3)-C(4)	1.415(6)	C(21)-H(21B)	0.9900	C(42)-C(48)	1.509(6)
C(3)-H(3A)	0.9500	C(22)-C(23)	1.407(6)	C(43)-C(44)	1.387(6)
C(4)-C(5)	1.421(6)	C(22)-C(27)	1.418(6)	C(43)-H(43A)	0.9500
C(4)-C(9)	1.441(6)	C(23)-C(24)	1.382(6)	C(44)-C(45)	1.383(6)
C(5)-C(6)	1.356(7)	C(23)-H(23A)	0.9500	C(44)-H(44A)	0.9500
C(5)-H(5A)	0.9500	C(24)-C(25)	1.393(7)	C(45)-C(46)	1.396(5)
C(6)-C(7)	1.422(7)	C(24)-H(24A)	0.9500	C(45)-H(45A)	0.9500
C(6)-H(6A)	0.9500	C(25)-C(26)	1.381(6)	C(46)-C(47)	1.515(5)
C(7)-C(8)	1.369(6)	C(25)-H(25A)	0.9500	C(47)-H(47A)	0.9800
C(7)-H(7A)	0.9500	C(26)-C(27)	1.393(6)	C(47)-H(47B)	0.9800
C(8)-C(9)	1.423(6)	C(26)-H(26A)	0.9500	C(47)-H(47C)	0.9800
C(8)-H(8A)	0.9500	C(27)-H(27A)	0.9500	C(48)-H(48A)	0.9800
C(9)-C(10)	1.447(5)	C(31)-C(32)	1.463(6)	C(48)-H(48B)	0.9800
C(10)-C(11)	1.485(5)	C(31)-H(31A)	0.9900	C(48)-H(48C)	0.9800
C(11)-C(12)	1.417(5)				

Table S3. Bond angles [°] for **15**.

Bonds	angle, °	Bonds	angle, °	Bonds	angle, °
N(2)-Zr(1)-C(21)	106.70(14)	C(9)-C(10)-C(11)	124.3(3)	C(32)-C(31)-H(31A)	114.3
N(2)-Zr(1)-C(1)	137.89(13)	N(1)-C(11)-C(12)	119.3(3)	Zr(1)-C(31)-H(31A)	114.3
C(21)-Zr(1)-C(1)	95.63(14)	N(1)-C(11)-C(10)	112.8(3)	C(32)-C(31)-H(31B)	114.3
N(2)-Zr(1)-N(1)	70.67(11)	C(12)-C(11)-C(10)	127.5(3)	Zr(1)-C(31)-H(31B)	114.3
C(21)-Zr(1)-N(1)	107.09(13)	C(13)-C(12)-C(11)	120.5(4)	H(31A)-C(31)-H(31B)	111.5
C(1)-Zr(1)-N(1)	68.79(12)	C(13)-C(12)-H(12A)	119.8	C(33)-C(32)-C(37)	116.3(4)
N(2)-Zr(1)-C(31)	104.06(14)	C(11)-C(12)-H(12A)	119.8	C(33)-C(32)-C(31)	123.8(4)
C(21)-Zr(1)-C(31)	121.46(14)	C(12)-C(13)-C(14)	121.0(4)	C(37)-C(32)-C(31)	119.2(4)
C(1)-Zr(1)-C(31)	93.31(15)	C(12)-C(13)-H(13A)	119.5	C(33)-C(32)-Zr(1)	114.6(3)
N(1)-Zr(1)-C(31)	129.85(13)	C(14)-C(13)-H(13A)	119.5	C(37)-C(32)-Zr(1)	87.7(2)
N(2)-Zr(1)-C(32)	111.41(12)	C(13)-C(14)-C(15)	125.7(4)	C(31)-C(32)-Zr(1)	60.5(2)
C(21)-Zr(1)-C(32)	88.62(13)	C(13)-C(14)-C(19)	115.8(4)	C(34)-C(33)-C(32)	121.3(4)
C(1)-Zr(1)-C(32)	104.23(13)	C(15)-C(14)-C(19)	118.4(4)	C(34)-C(33)-H(33A)	119.4
N(1)-Zr(1)-C(32)	163.11(11)	C(16)-C(15)-C(14)	119.4(4)	C(32)-C(33)-H(33A)	119.4
C(31)-Zr(1)-C(32)	33.47(13)	C(16)-C(15)-H(15A)	120.3	C(33)-C(34)-C(35)	121.1(4)
N(2)-Zr(1)-C(22)	106.33(11)	C(14)-C(15)-H(15A)	120.3	C(33)-C(34)-H(34A)	119.4
C(21)-Zr(1)-C(22)	28.27(12)	C(15)-C(16)-C(17)	122.1(4)	C(35)-C(34)-H(34A)	119.4
C(1)-Zr(1)-C(22)	77.62(12)	C(15)-C(16)-H(16A)	119.0	C(36)-C(35)-C(34)	118.8(4)
N(1)-Zr(1)-C(22)	80.28(10)	C(17)-C(16)-H(16A)	119.0	C(36)-C(35)-H(35A)	120.6
C(31)-Zr(1)-C(22)	143.24(13)	C(18)-C(17)-C(16)	120.9(4)	C(34)-C(35)-H(35A)	120.6
C(32)-Zr(1)-C(22)	113.96(11)	C(18)-C(17)-H(17A)	119.6	C(35)-C(36)-C(37)	120.6(4)
C(11)-N(1)-C(19)	120.7(3)	C(16)-C(17)-H(17A)	119.6	C(35)-C(36)-H(36A)	119.7
C(11)-N(1)-Zr(1)	121.8(3)	N(2)-C(18)-C(17)	127.8(4)	C(37)-C(36)-H(36A)	119.7
C(19)-N(1)-Zr(1)	117.3(2)	N(2)-C(18)-C(19)	115.1(3)	C(36)-C(37)-C(32)	121.9(4)
C(18)-N(2)-C(41)	115.9(3)	C(17)-C(18)-C(19)	117.1(4)	C(36)-C(37)-H(37A)	119.1
C(18)-N(2)-Zr(1)	121.8(2)	N(1)-C(19)-C(14)	122.8(3)	C(32)-C(37)-H(37A)	119.1
C(41)-N(2)-Zr(1)	121.5(2)	N(1)-C(19)-C(18)	115.0(3)	C(46)-C(41)-C(42)	120.4(3)
C(10)-C(1)-C(2)	117.7(3)	C(14)-C(19)-C(18)	122.2(4)	C(46)-C(41)-N(2)	119.8(3)
C(10)-C(1)-Zr(1)	118.1(3)	C(22)-C(21)-Zr(1)	104.9(2)	C(42)-C(41)-N(2)	119.8(3)
C(2)-C(1)-Zr(1)	122.4(3)	C(22)-C(21)-H(21A)	110.8	C(43)-C(42)-C(41)	118.3(4)
C(3)-C(2)-C(1)	122.1(4)	Zr(1)-C(21)-H(21A)	110.8	C(43)-C(42)-C(48)	119.7(3)
C(3)-C(2)-H(2A)	119.0	C(22)-C(21)-H(21B)	110.8	C(41)-C(42)-C(48)	121.9(4)
C(1)-C(2)-H(2A)	119.0	Zr(1)-C(21)-H(21B)	110.8	C(44)-C(43)-C(42)	121.5(4)
C(2)-C(3)-C(4)	120.7(4)	H(21A)-C(21)-H(21B)	108.8	C(44)-C(43)-H(43A)	119.3
C(2)-C(3)-H(3A)	119.7	C(23)-C(22)-C(27)	116.1(4)	C(42)-C(43)-H(43A)	119.3
C(4)-C(3)-H(3A)	119.7	C(23)-C(22)-C(21)	122.7(4)	C(45)-C(44)-C(43)	119.7(4)
C(3)-C(4)-C(5)	121.7(4)	C(27)-C(22)-C(21)	121.0(4)	C(45)-C(44)-H(44A)	120.2
C(3)-C(4)-C(9)	119.3(4)	C(23)-C(22)-Zr(1)	117.7(2)	C(43)-C(44)-H(44A)	120.2
C(5)-C(4)-C(9)	118.9(4)	C(27)-C(22)-Zr(1)	102.0(2)	C(44)-C(45)-C(46)	121.1(4)
C(6)-C(5)-C(4)	121.8(4)	C(21)-C(22)-Zr(1)	46.81(18)	C(44)-C(45)-H(45A)	119.5
C(6)-C(5)-H(5A)	119.1	C(24)-C(23)-C(22)	122.3(4)	C(46)-C(45)-H(45A)	119.5
C(4)-C(5)-H(5A)	119.1	C(24)-C(23)-H(23A)	118.8	C(45)-C(46)-C(41)	119.0(3)
C(5)-C(6)-C(7)	119.9(4)	C(22)-C(23)-H(23A)	118.8	C(45)-C(46)-C(47)	119.5(4)
C(5)-C(6)-H(6A)	120.0	C(23)-C(24)-C(25)	120.4(4)	C(41)-C(46)-C(47)	121.5(3)
C(7)-C(6)-H(6A)	120.0	C(23)-C(24)-H(24A)	119.8	C(46)-C(47)-H(47A)	109.5
C(8)-C(7)-C(6)	119.9(4)	C(25)-C(24)-H(24A)	119.8	C(46)-C(47)-H(47B)	109.5
C(8)-C(7)-H(7A)	120.1	C(26)-C(25)-C(24)	118.8(4)	H(47A)-C(47)-H(47B)	109.5
C(6)-C(7)-H(7A)	120.1	C(26)-C(25)-H(25A)	120.6	C(46)-C(47)-H(47C)	109.5
C(7)-C(8)-C(9)	122.2(4)	C(24)-C(25)-H(25A)	120.6	H(47A)-C(47)-H(47C)	109.5
C(7)-C(8)-H(8A)	118.9	C(25)-C(26)-C(27)	121.1(4)	H(47B)-C(47)-H(47C)	109.5
C(9)-C(8)-H(8A)	118.9	C(25)-C(26)-H(26A)	119.4	C(42)-C(48)-H(48A)	109.5
C(8)-C(9)-C(4)	117.3(4)	C(27)-C(26)-H(26A)	119.4	C(42)-C(48)-H(48B)	109.5
C(8)-C(9)-C(10)	125.1(4)	C(26)-C(27)-C(22)	121.2(4)	H(48A)-C(48)-H(48B)	109.5
C(4)-C(9)-C(10)	117.5(4)	C(26)-C(27)-H(27A)	119.4	C(42)-C(48)-H(48C)	109.5
C(1)-C(10)-C(9)	121.7(4)	C(22)-C(27)-H(27A)	119.4	H(48A)-C(48)-H(48C)	109.5
C(1)-C(10)-C(11)	114.0(3)	C(32)-C(31)-Zr(1)	86.0(2)	H(48B)-C(48)-H(48C)	109.5

Table S4. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **15**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zr(1)	18(1)	21(1)	20(1)	1(1)	7(1)	0(1)
N(1)	15(2)	22(2)	24(2)	-1(1)	6(1)	1(1)
N(2)	19(2)	21(2)	25(2)	-3(1)	8(1)	-2(1)
C(1)	17(2)	25(2)	27(2)	-2(2)	8(2)	2(1)
C(2)	23(2)	30(2)	26(2)	1(2)	9(2)	1(2)
C(3)	21(2)	36(2)	26(2)	-6(2)	7(2)	-1(2)
C(4)	15(2)	31(2)	36(2)	-5(2)	10(2)	-1(2)
C(5)	23(2)	39(2)	40(3)	-14(2)	11(2)	-9(2)
C(6)	32(2)	26(2)	59(3)	-11(2)	20(2)	-11(2)
C(7)	31(2)	24(2)	50(3)	1(2)	17(2)	-1(2)
C(8)	22(2)	27(2)	37(2)	0(2)	12(2)	0(2)
C(9)	13(2)	25(2)	34(2)	-2(2)	9(2)	1(1)
C(10)	11(2)	25(2)	26(2)	0(2)	5(2)	3(1)
C(11)	16(2)	21(2)	28(2)	2(2)	6(2)	3(1)
C(12)	25(2)	20(2)	33(2)	6(2)	10(2)	3(2)
C(13)	29(2)	30(2)	26(2)	10(2)	12(2)	6(2)
C(14)	24(2)	27(2)	22(2)	6(2)	7(2)	5(2)
C(15)	43(3)	34(2)	25(2)	5(2)	15(2)	3(2)
C(16)	50(3)	35(2)	24(2)	-4(2)	11(2)	-2(2)
C(17)	34(2)	28(2)	25(2)	-1(2)	9(2)	-5(2)
C(18)	16(2)	23(2)	27(2)	1(2)	5(2)	3(1)
C(19)	18(2)	25(2)	22(2)	2(2)	5(2)	5(1)
C(21)	26(2)	32(2)	27(2)	2(2)	12(2)	6(2)
C(22)	12(2)	31(2)	25(2)	-3(2)	6(2)	6(1)
C(23)	21(2)	36(2)	30(2)	-9(2)	5(2)	1(2)
C(24)	28(2)	31(2)	49(3)	-12(2)	14(2)	-4(2)
C(25)	29(2)	34(2)	48(3)	10(2)	17(2)	2(2)
C(26)	30(2)	47(3)	28(2)	1(2)	10(2)	8(2)
C(27)	24(2)	34(2)	28(2)	-7(2)	6(2)	0(2)
C(31)	28(2)	32(2)	26(2)	7(2)	8(2)	7(2)
C(32)	28(2)	26(2)	22(2)	7(2)	8(2)	4(2)
C(33)	28(2)	35(2)	27(2)	3(2)	8(2)	-3(2)
C(34)	38(2)	40(2)	29(2)	-5(2)	16(2)	-4(2)
C(35)	34(2)	48(3)	34(2)	4(2)	17(2)	-3(2)
C(36)	33(2)	43(3)	30(2)	5(2)	10(2)	-9(2)
C(37)	38(2)	30(2)	24(2)	3(2)	13(2)	-4(2)
C(41)	20(2)	26(2)	21(2)	-5(2)	8(2)	-5(2)
C(42)	19(2)	30(2)	20(2)	-3(2)	5(2)	-1(2)
C(43)	21(2)	37(2)	29(2)	-4(2)	11(2)	-11(2)
C(44)	36(2)	26(2)	32(2)	2(2)	15(2)	-8(2)
C(45)	32(2)	24(2)	29(2)	0(2)	12(2)	0(2)
C(46)	23(2)	27(2)	24(2)	-2(2)	10(2)	-2(2)
C(47)	26(2)	29(2)	46(3)	-4(2)	19(2)	1(2)
C(48)	23(2)	34(2)	42(3)	-5(2)	8(2)	-2(2)

Table S5. Hydrogen coordinates ($Å \times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **15**.

Atom	x	y	z	U(eq)
H(2A)	653	8959	638	32
H(3A)	-127	7475	231	35
H(5A)	-281	5755	615	42
H(6A)	13	4556	1631	46
H(7A)	851	4925	3129	42
H(8A)	1384	6487	3567	35
H(12A)	1043	7584	4130	32
H(13A)	1584	8455	5411	34
H(15A)	2464	10009	6275	41
H(16A)	3288	11438	6274	45
H(17A)	3528	11949	5054	36
H(21A)	3431	9143	1639	34
H(21B)	4210	9645	2517	34
H(23A)	2957	7447	1689	37
H(24A)	3021	6030	2441	44
H(25A)	3761	6015	3963	44
H(26A)	4482	7435	4708	42
H(27A)	4437	8867	3964	36
H(31A)	581	10788	967	36
H(31B)	1171	11732	1534	36
H(33A)	1230	10101	-78	38
H(34A)	2531	9858	-496	42
H(35A)	4103	10582	270	46
H(36A)	4334	11596	1443	44
H(37A)	3045	11845	1881	37
H(43A)	5342	13034	3508	35
H(44A)	4268	14365	3118	37
H(45A)	2634	14201	2992	34
H(47A)	1404	12019	3070	49
H(47B)	1212	13132	2778	49
H(47C)	1655	12855	3785	49
H(48A)	5744	11436	4182	52
H(48B)	5050	10874	3313	52
H(48C)	4871	10735	4177	52

Table S6. Atomic coordinates (Å × 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **16**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Hf(1)	9178(1)	2474(1)	3863(1)	17(1)
N(1)	10841(3)	2583(1)	3080(1)	18(1)
N(2)	8934(3)	1543(1)	3271(1)	19(1)
C(1)	10821(4)	3443(2)	4066(2)	20(1)
C(2)	10752(4)	3886(2)	4627(2)	23(1)
C(3)	11611(4)	4506(2)	4728(2)	23(1)
C(4)	12678(4)	4711(2)	4287(2)	22(1)
C(5)	13584(4)	5355(2)	4399(2)	28(1)
C(6)	14688(4)	5545(2)	4003(2)	29(1)
C(7)	14992(4)	5097(2)	3492(2)	28(1)
C(8)	14124(4)	4479(2)	3362(2)	24(1)
C(9)	12874(4)	4270(1)	3731(2)	20(1)
C(10)	11845(4)	3649(1)	3620(2)	18(1)
C(11)	11728(4)	3177(2)	3028(2)	18(1)
C(12)	12327(4)	3286(2)	2420(2)	24(1)
C(13)	12194(4)	2781(2)	1934(2)	25(1)
C(14)	11381(4)	2142(2)	2007(2)	22(1)
C(15)	11209(4)	1577(2)	1547(2)	26(1)
C(16)	10290(4)	1001(2)	1660(2)	26(1)
C(17)	9492(4)	957(2)	2224(2)	23(1)
C(18)	9651(4)	1494(2)	2696(2)	19(1)
C(19)	10653(4)	2085(2)	2584(2)	19(1)
C(21)	6760(4)	3065(2)	3514(2)	24(1)
C(22)	7064(4)	3347(2)	2862(2)	20(1)
C(23)	7881(4)	3995(2)	2831(2)	24(1)
C(24)	8302(5)	4229(2)	2233(2)	31(1)
C(25)	7899(5)	3832(2)	1650(2)	33(1)
C(26)	7074(5)	3204(2)	1660(2)	34(1)
C(27)	6656(4)	2965(2)	2256(2)	25(1)
C(31)	9693(4)	2091(2)	4947(2)	22(1)
C(32)	7883(4)	2088(2)	4972(2)	21(1)
C(33)	7008(5)	2710(2)	5066(2)	25(1)
C(34)	5276(5)	2727(2)	4988(2)	31(1)
C(35)	4325(5)	2128(2)	4830(2)	37(1)
C(36)	5143(5)	1504(2)	4751(2)	35(1)
C(37)	6877(4)	1490(2)	4812(2)	26(1)
C(41)	8274(4)	890(2)	3475(2)	19(1)
C(42)	6551(4)	731(2)	3306(2)	24(1)
C(43)	5986(4)	97(2)	3529(2)	27(1)
C(44)	7087(5)	-360(2)	3917(2)	31(1)
C(45)	8792(5)	-198(2)	4084(2)	27(1)
C(46)	9419(4)	420(2)	3864(2)	23(1)
C(47)	11285(4)	580(2)	4041(2)	25(1)
C(48)	5301(4)	1222(2)	2896(2)	30(1)

Table S7. Bond lengths [Å] for **16**.

Bond	Length [Å]	Bond	Length [Å]	Bond	Length [Å]
Hf(1)-N(2)	2.128(2)	C(12)-C(13)	1.363(4)	C(31)-H(31B)	0.9900
Hf(1)-C(21)	2.241(3)	C(12)-H(12)	0.9500	C(32)-C(37)	1.402(4)
Hf(1)-C(31)	2.257(3)	C(13)-C(14)	1.407(4)	C(32)-C(33)	1.413(4)
Hf(1)-C(1)	2.266(3)	C(13)-H(13)	0.9500	C(33)-C(34)	1.373(5)
Hf(1)-N(1)	2.269(2)	C(14)-C(19)	1.404(4)	C(33)-H(33)	0.9500
Hf(1)-C(32)	2.740(3)	C(14)-C(15)	1.411(4)	C(34)-C(35)	1.380(5)
N(1)-C(11)	1.357(4)	C(15)-C(16)	1.371(4)	C(34)-H(34)	0.9500
N(1)-C(19)	1.365(4)	C(15)-H(15)	0.9500	C(35)-C(36)	1.387(5)
N(2)-C(18)	1.394(4)	C(16)-C(17)	1.412(4)	C(35)-H(35)	0.9500
N(2)-C(41)	1.447(4)	C(16)-H(16)	0.9500	C(36)-C(37)	1.378(5)
C(1)-C(10)	1.391(4)	C(17)-C(18)	1.385(4)	C(36)-H(36)	0.9500
C(1)-C(2)	1.420(4)	C(17)-H(17)	0.9500	C(37)-H(37)	0.9500
C(2)-C(3)	1.367(4)	C(18)-C(19)	1.430(4)	C(41)-C(42)	1.395(4)
C(2)-H(2)	0.9500	C(21)-C(22)	1.482(4)	C(41)-C(46)	1.408(4)
C(3)-C(4)	1.407(4)	C(21)-H(21A)	0.9900	C(42)-C(43)	1.398(4)
C(3)-H(3)	0.9500	C(21)-H(21B)	0.9900	C(42)-C(48)	1.499(4)
C(4)-C(5)	1.426(4)	C(22)-C(27)	1.402(4)	C(43)-C(44)	1.374(5)
C(4)-C(9)	1.433(4)	C(22)-C(23)	1.409(4)	C(43)-H(43)	0.9500
C(5)-C(6)	1.355(5)	C(23)-C(24)	1.385(5)	C(44)-C(45)	1.382(5)
C(5)-H(5)	0.9500	C(23)-H(23)	0.9500	C(44)-H(44)	0.9500
C(6)-C(7)	1.396(5)	C(24)-C(25)	1.379(5)	C(45)-C(46)	1.391(4)
C(6)-H(6)	0.9500	C(24)-H(24)	0.9500	C(45)-H(45)	0.9500
C(7)-C(8)	1.371(4)	C(25)-C(26)	1.375(5)	C(46)-C(47)	1.505(4)
C(7)-H(7)	0.9500	C(25)-H(25)	0.9500	C(47)-H(47A)	0.9800
C(8)-C(9)	1.421(4)	C(26)-C(27)	1.384(5)	C(47)-H(47B)	0.9800
C(8)-H(8)	0.9500	C(26)-H(26)	0.9500	C(47)-H(47C)	0.9800
C(9)-C(10)	1.439(4)	C(27)-H(27)	0.9500	C(48)-H(48A)	0.9800
C(10)-C(11)	1.481(4)	C(31)-C(32)	1.469(4)	C(48)-H(48B)	0.9800
C(11)-C(12)	1.415(4)	C(31)-H(31A)	0.9900	C(48)-H(48C)	0.9800

Table S8. Bond angles [°] for **16**.

Bonds	angle, °	Bonds	angle, °	Bonds	angle, °
N(2)-Hf(1)-C(21)	105.58(11)	C(12)-C(11)-C(10)	128.7(3)	Hf(1)-C(31)-H(31B)	113.2
N(2)-Hf(1)-C(31)	104.30(10)	C(13)-C(12)-C(11)	121.5(3)	H(31A)-C(31)-H(31B)	110.6
C(21)-Hf(1)-C(31)	116.63(11)	C(13)-C(12)-H(12)	119.2	C(37)-C(32)-C(33)	115.9(3)
N(2)-Hf(1)-C(1)	140.38(11)	C(11)-C(12)-H(12)	119.2	C(37)-C(32)-C(31)	121.9(3)
C(21)-Hf(1)-C(1)	94.86(11)	C(12)-C(13)-C(14)	120.8(3)	C(33)-C(32)-C(31)	121.7(3)
C(31)-Hf(1)-C(1)	95.85(11)	C(12)-C(13)-H(13)	119.6	C(37)-C(32)-Hf(1)	109.2(2)
N(2)-Hf(1)-N(1)	72.02(9)	C(14)-C(13)-H(13)	119.6	C(33)-C(32)-Hf(1)	99.39(19)
C(21)-Hf(1)-N(1)	109.41(10)	C(19)-C(14)-C(13)	115.7(3)	C(31)-C(32)-Hf(1)	55.37(16)
C(31)-Hf(1)-N(1)	132.68(10)	C(19)-C(14)-C(15)	118.5(3)	C(34)-C(33)-C(32)	121.8(3)
C(1)-Hf(1)-N(1)	69.26(10)	C(13)-C(14)-C(15)	125.7(3)	C(34)-C(33)-H(33)	119.1
N(2)-Hf(1)-C(32)	102.77(9)	C(16)-C(15)-C(14)	119.6(3)	C(32)-C(33)-H(33)	119.1
C(21)-Hf(1)-C(32)	86.74(11)	C(16)-C(15)-H(15)	120.2	C(33)-C(34)-C(35)	120.7(3)
C(31)-Hf(1)-C(32)	32.38(10)	C(14)-C(15)-H(15)	120.2	C(33)-C(34)-H(34)	119.6
C(1)-Hf(1)-C(32)	112.10(10)	C(15)-C(16)-C(17)	121.8(3)	C(35)-C(34)-H(34)	119.6
N(1)-Hf(1)-C(32)	163.76(9)	C(15)-C(16)-H(16)	119.1	C(34)-C(35)-C(36)	119.1(3)
C(11)-N(1)-C(19)	120.8(3)	C(17)-C(16)-H(16)	119.1	C(34)-C(35)-H(35)	120.5
C(11)-N(1)-Hf(1)	121.52(19)	C(18)-C(17)-C(16)	120.7(3)	C(36)-C(35)-H(35)	120.5
C(19)-N(1)-Hf(1)	116.50(19)	C(18)-C(17)-H(17)	119.7	C(37)-C(36)-C(35)	120.2(3)
C(18)-N(2)-C(41)	114.4(2)	C(16)-C(17)-H(17)	119.7	C(37)-C(36)-H(36)	119.9
C(18)-N(2)-Hf(1)	120.78(19)	C(17)-C(18)-N(2)	128.2(3)	C(35)-C(36)-H(36)	119.9
C(41)-N(2)-Hf(1)	124.16(19)	C(17)-C(18)-C(19)	117.2(3)	C(36)-C(37)-C(32)	122.2(3)
C(10)-C(1)-C(2)	117.6(3)	N(2)-C(18)-C(19)	114.6(3)	C(36)-C(37)-H(37)	118.9
C(10)-C(1)-Hf(1)	121.0(2)	N(1)-C(19)-C(14)	122.9(3)	C(32)-C(37)-H(37)	118.9
C(2)-C(1)-Hf(1)	121.2(2)	N(1)-C(19)-C(18)	114.9(3)	C(42)-C(41)-C(46)	120.4(3)
C(3)-C(2)-C(1)	122.5(3)	C(14)-C(19)-C(18)	122.1(3)	C(42)-C(41)-N(2)	121.5(3)
C(3)-C(2)-H(2)	118.8	C(22)-C(21)-Hf(1)	100.1(2)	C(46)-C(41)-N(2)	118.0(3)
C(1)-C(2)-H(2)	118.8	C(22)-C(21)-H(21A)	111.8	C(41)-C(42)-C(43)	118.8(3)
C(2)-C(3)-C(4)	120.2(3)	Hf(1)-C(21)-H(21A)	111.8	C(41)-C(42)-C(48)	121.6(3)
C(2)-C(3)-H(3)	119.9	C(22)-C(21)-H(21B)	111.8	C(43)-C(42)-C(48)	119.5(3)
C(4)-C(3)-H(3)	119.9	Hf(1)-C(21)-H(21B)	111.8	C(44)-C(43)-C(42)	121.2(3)
C(3)-C(4)-C(5)	119.9(3)	H(21A)-C(21)-H(21B)	109.5	C(44)-C(43)-H(43)	119.4
C(3)-C(4)-C(9)	120.2(3)	C(27)-C(22)-C(23)	116.7(3)	C(42)-C(43)-H(43)	119.4
C(5)-C(4)-C(9)	120.0(3)	C(27)-C(22)-C(21)	121.8(3)	C(43)-C(44)-C(45)	119.6(3)
C(6)-C(5)-C(4)	120.9(3)	C(23)-C(22)-C(21)	121.3(3)	C(43)-C(44)-H(44)	120.2
C(6)-C(5)-H(5)	119.6	C(24)-C(23)-C(22)	121.3(3)	C(45)-C(44)-H(44)	120.2
C(4)-C(5)-H(5)	119.6	C(24)-C(23)-H(23)	119.4	C(44)-C(45)-C(46)	121.3(3)
C(5)-C(6)-C(7)	119.9(3)	C(22)-C(23)-H(23)	119.4	C(44)-C(45)-H(45)	119.3
C(5)-C(6)-H(6)	120.1	C(25)-C(24)-C(23)	120.1(3)	C(46)-C(45)-H(45)	119.3
C(7)-C(6)-H(6)	120.1	C(25)-C(24)-H(24)	119.9	C(45)-C(46)-C(41)	118.6(3)
C(8)-C(7)-C(6)	120.8(3)	C(23)-C(24)-H(24)	119.9	C(45)-C(46)-C(47)	120.4(3)
C(8)-C(7)-H(7)	119.6	C(26)-C(25)-C(24)	120.1(3)	C(41)-C(46)-C(47)	121.0(3)
C(6)-C(7)-H(7)	119.6	C(26)-C(25)-H(25)	120.0	C(46)-C(47)-H(47A)	109.5
C(7)-C(8)-C(9)	122.1(3)	C(24)-C(25)-H(25)	120.0	C(46)-C(47)-H(47B)	109.5
C(7)-C(8)-H(8)	119.0	C(25)-C(26)-C(27)	120.1(3)	H(47A)-C(47)-H(47B)	109.5
C(9)-C(8)-H(8)	119.0	C(25)-C(26)-H(26)	119.9	C(46)-C(47)-H(47C)	109.5
C(8)-C(9)-C(4)	116.1(3)	C(27)-C(26)-H(26)	119.9	H(47A)-C(47)-H(47C)	109.5
C(8)-C(9)-C(10)	126.6(3)	C(26)-C(27)-C(22)	121.7(3)	H(47B)-C(47)-H(47C)	109.5
C(4)-C(9)-C(10)	117.2(3)	C(26)-C(27)-H(27)	119.2	C(42)-C(48)-H(48A)	109.5
C(1)-C(10)-C(9)	122.0(3)	C(22)-C(27)-H(27)	119.2	C(42)-C(48)-H(48B)	109.5
C(1)-C(10)-C(11)	113.2(3)	C(32)-C(31)-Hf(1)	92.26(19)	H(48A)-C(48)-H(48B)	109.5
C(9)-C(10)-C(11)	124.8(3)	C(32)-C(31)-H(31A)	113.2	C(42)-C(48)-H(48C)	109.5
N(1)-C(11)-C(12)	117.7(3)	Hf(1)-C(31)-H(31A)	113.2	H(48A)-C(48)-H(48C)	109.5
N(1)-C(11)-C(10)	113.5(3)	C(32)-C(31)-H(31B)	113.2	H(48B)-C(48)-H(48C)	109.5

Table S9. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **16**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Hf(1)	18(1)	17(1)	18(1)	-1(1)	5(1)	-1(1)
N(1)	16(1)	16(1)	20(1)	0(1)	4(1)	0(1)
N(2)	21(2)	18(1)	20(1)	-2(1)	5(1)	-3(1)
C(1)	19(2)	20(2)	20(2)	3(1)	3(1)	4(1)
C(2)	23(2)	27(2)	21(2)	0(1)	6(1)	-3(1)
C(3)	22(2)	23(2)	23(2)	-4(1)	3(1)	1(1)
C(4)	19(2)	20(2)	24(2)	0(1)	0(1)	2(1)
C(5)	28(2)	21(2)	32(2)	-5(1)	4(2)	0(1)
C(6)	29(2)	18(2)	37(2)	-1(2)	2(2)	-6(1)
C(7)	24(2)	24(2)	37(2)	6(2)	8(2)	-2(1)
C(8)	23(2)	23(2)	25(2)	3(1)	5(2)	3(1)
C(9)	21(2)	13(1)	23(2)	4(1)	3(1)	5(1)
C(10)	17(2)	16(1)	19(2)	1(1)	0(1)	5(1)
C(11)	13(2)	21(2)	20(2)	2(1)	0(1)	2(1)
C(12)	24(2)	24(2)	24(2)	0(1)	6(2)	-7(1)
C(13)	22(2)	34(2)	20(2)	3(1)	8(2)	-2(2)
C(14)	18(2)	25(2)	21(2)	0(1)	3(1)	2(1)
C(15)	25(2)	37(2)	17(2)	-3(1)	6(2)	1(2)
C(16)	28(2)	27(2)	20(2)	-9(1)	2(2)	0(1)
C(17)	25(2)	20(2)	24(2)	-2(1)	2(2)	-1(1)
C(18)	17(2)	20(2)	18(2)	0(1)	-1(1)	2(1)
C(19)	19(2)	22(2)	17(2)	1(1)	2(1)	1(1)
C(21)	29(2)	25(2)	18(2)	2(1)	7(2)	2(1)
C(22)	18(2)	24(2)	19(2)	4(1)	4(1)	9(1)
C(23)	19(2)	28(2)	26(2)	-1(1)	2(1)	6(1)
C(24)	29(2)	29(2)	36(2)	7(2)	3(2)	0(2)
C(25)	29(2)	46(2)	25(2)	8(2)	10(2)	1(2)
C(26)	41(2)	39(2)	24(2)	-4(2)	8(2)	-2(2)
C(27)	26(2)	23(2)	27(2)	3(1)	6(2)	-2(1)
C(31)	21(2)	21(2)	24(2)	0(1)	3(1)	-2(1)
C(32)	25(2)	27(2)	11(2)	3(1)	6(1)	-1(1)
C(33)	33(2)	24(2)	22(2)	2(1)	10(2)	-1(1)
C(34)	33(2)	32(2)	28(2)	1(2)	8(2)	13(2)
C(35)	22(2)	51(2)	38(2)	-9(2)	7(2)	6(2)
C(36)	28(2)	39(2)	39(2)	-10(2)	8(2)	-11(2)
C(37)	30(2)	28(2)	22(2)	-4(1)	9(2)	2(1)
C(41)	23(2)	17(1)	18(2)	-3(1)	7(1)	-2(1)
C(42)	27(2)	24(2)	22(2)	-7(1)	6(2)	-1(1)
C(43)	25(2)	27(2)	29(2)	-8(1)	10(2)	-12(1)
C(44)	40(2)	22(2)	33(2)	-1(2)	15(2)	-9(2)
C(45)	34(2)	21(2)	27(2)	-1(1)	8(2)	4(1)
C(46)	23(2)	24(2)	23(2)	-6(1)	8(2)	0(1)
C(47)	25(2)	23(2)	27(2)	-2(1)	7(2)	5(1)
C(48)	22(2)	31(2)	35(2)	-6(2)	-1(2)	-5(2)

Table S10. Hydrogen coordinates (Å $\times 10^4$) and isotropic displacement parameters (Å^2 $\times 10^3$) for **16**.

Atom	x	y	z	U(eq)
H(2)	10083	3747	4944	28
H(3)	11488	4799	5097	28
H(5)	13412	5655	4757	33
H(6)	15253	5983	4073	35
H(7)	15810	5222	3231	34
H(8)	14367	4181	3015	28
H(12)	12833	3722	2349	29
H(13)	12656	2861	1540	30
H(15)	11727	1595	1162	31
H(16)	10188	620	1350	31
H(17)	8839	556	2281	28
H(21A)	5761	2752	3446	28
H(21B)	6616	3443	3835	28
H(23)	8147	4276	3227	29
H(24)	8869	4664	2224	38
H(25)	8192	3993	1241	39
H(26)	6791	2933	1257	41
H(27)	6077	2532	2254	30
H(31A)	10214	1620	5002	27
H(31B)	10361	2426	5270	27
H(33)	7636	3127	5187	30
H(34)	4726	3157	5044	37
H(35)	3127	2142	4775	44
H(36)	4506	1085	4654	42
H(37)	7409	1059	4743	31
H(43)	4818	-19	3408	32
H(44)	6680	-786	4070	37
H(45)	9549	-515	4354	32
H(47A)	11876	199	4318	37
H(47B)	11464	1019	4297	37
H(47C)	11731	625	3623	37
H(48A)	4193	993	2778	46
H(48B)	5688	1350	2479	46
H(48C)	5205	1645	3162	46

Table S11. Atomic coordinates (Å × 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **18**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
Hf(1)	1473(1)	1424(1)	2215(1)	20(1)
N(1)	1188(4)	664(3)	3237(3)	22(1)
N(2)	2710(4)	1561(3)	3125(3)	24(2)
C(1)	177(5)	563(4)	1858(4)	16(2)
C(2)	-277(5)	484(4)	1083(4)	27(2)
C(3)	-1137(6)	21(4)	905(5)	29(2)
C(4)	-1610(5)	-318(4)	1480(5)	25(2)
C(5)	-2505(6)	-747(5)	1291(5)	36(2)
C(6)	-3018(6)	-1025(5)	1835(5)	36(2)
C(7)	-2628(6)	-862(4)	2613(5)	34(2)
C(8)	-1761(5)	-480(4)	2811(5)	28(2)
C(9)	-1174(5)	-214(4)	2262(4)	22(2)
C(10)	-236(5)	161(4)	2432(4)	20(2)
C(11)	405(5)	170(4)	3185(4)	19(2)
C(12)	326(6))	-322(4)	3836(5)	28(2)
C(13)	976(6)	-249(5)	4501(5)	32(2)
C(14)	1756(6)	288(5)	4574(4)	27(2)
C(15)	2495(6)	406(5)	5229(4)	32(2)
C(16)	3263(6)	919(5)	5187(4)	30(2)
C(17)	3368(6)	1325(4)	4513(4)	29(2)
C(18)	2688(6)	1237(4)	3851(4)	27(2)
C(19)	1863(5)	733(4)	3902(4)	21(2)
C(21)	608(6)	2575(4)	2157(5)	27(2)
C(22)	-246(6)	2331(4)	2519(5)	28(2)
C(23)	-1164(6)	2146(5)	2054(5)	34(2)
C(24)	-1950(7)	1857(5)	2395(6)	44(2)
C(25)	-1842(8)	1740(5)	3166(6)	52(3)
C(26)	-976(8)	1923(5)	3630(5)	45(2)
C(27)	-184(7)	2229(5)	3295(5)	37(2)
C(31)	2260(6)	1149(4)	1223(4)	30(2)
C(32)	2031(5)	1922(4)	836(4)	21(2)
C(33)	2439(6)	2639(5)	1149(4)	32(2)
C(34)	2152(6)	3386(5)	840(5)	39(2)
C(35)	1432(7)	3446(5)	206(5)	45(2)
C(36)	1015(6)	2747(5)	-136(5)	39(2)
C(37)	1284(6)	2004(5)	175(4)	30(2)
C(41)	3635(5)	1930(4)	3024(4)	20(2)
C(42)	3794(5)	2763(4)	3159(4)	22(2)
C(43)	4659(6)	3108(5)	3013(4)	30(2)
C(44)	5394(6)	2650(4)	2759(5)	31(2)
C(45)	5249(6)	1818(5)	2656(5)	29(2)
C(46)	4380(6)	1444(5)	2787(4)	27(2)
C(47)	4294(5)	530(4)	2711(5)	27(2)
C(48)	3053(6)	3292(4)	3501(4)	27(2)
C(49)	4832(7)	115(5)	3434(5)	42(2)
C(50)	4725(6)	191(5)	2014(5)	38(2)
C(51)	2695(6)	4015(4)	2971(5)	33(2)
C(52)	3530(6)	3612(5)	4282(4)	35(2)
C(61)	1024(8)	2514(7)	5656(6)	74(4)
C(62)	1509(8)	3047(8)	5304(7)	85(4)
C(63)	1051(8)	3733(7)	4953(7)	74(4)
C(64)	49(7)	3829(6)	4919(5)	50(3)
C(65)	-456(7)	3267(5)	5280(5)	47(2)
C(66)	12(7)	2613(6)	5642(5)	50(3)

Table S12. Bond lengths [Å] for **18**.

Bond	Length [Å]	Bond	Length [Å]	Bond	Length [Å]
Hf(1)-N(2)	2.148(6)	C(16)-C(17)	1.387(10)	C(43)-C(44)	1.388(11)
Hf(1)-C(21)	2.232(7)	C(16)-H(16A)	0.9500	C(43)-H(43A)	0.9500
Hf(1)-C(31)	2.234(8)	C(17)-C(18)	1.376(10)	C(44)-C(45)	1.394(10)
Hf(1)-N(1)	2.274(6)	C(17)-H(17A)	0.9500	C(44)-H(44A)	0.9500
Hf(1)-C(1)	2.281(6)	C(18)-C(19)	1.416(10)	C(45)-C(46)	1.391(10)
Hf(1)-C(32)	2.777(7)	C(21)-C(22)	1.474(11)	C(45)-H(45A)	0.9500
Hf(1)-C(22)	2.910(8)	C(21)-H(21A)	0.9900	C(46)-C(47)	1.516(10)
N(1)-C(11)	1.337(9)	C(21)-H(21B)	0.9900	C(47)-C(49)	1.524(10)
N(1)-C(19)	1.374(9)	C(22)-C(27)	1.361(11)	C(47)-C(50)	1.546(11)
N(2)-C(18)	1.387(9)	C(22)-C(23)	1.418(11)	C(47)-H(47A)	1.0000
N(2)-C(41)	1.442(9)	C(23)-C(24)	1.397(12)	C(48)-C(52)	1.518(10)
C(1)-C(10)	1.398(10)	C(23)-H(23A)	0.9500	C(48)-C(51)	1.544(10)
C(1)-C(2)	1.409(10)	C(24)-C(25)	1.352(13)	C(48)-H(48A)	1.0000
C(2)-C(3)	1.397(10)	C(24)-H(24A)	0.9500	C(49)-H(49A)	0.9800
C(2)-H(2A)	0.9500	C(25)-C(26)	1.361(13)	C(49)-H(49B)	0.9800
C(3)-C(4)	1.398(10)	C(25)-H(25A)	0.9500	C(49)-H(49C)	0.9800
C(3)-H(3A)	0.9500	C(26)-C(27)	1.407(12)	C(50)-H(50A)	0.9800
C(4)-C(5)	1.409(10)	C(26)-H(26A)	0.9500	C(50)-H(50B)	0.9800
C(4)-C(9)	1.418(10)	C(27)-H(27A)	0.9500	C(50)-H(50C)	0.9800
C(5)-C(6)	1.352(11)	C(31)-C(32)	1.455(10)	C(51)-H(51A)	0.9800
C(5)-H(5A)	0.9500	C(31)-H(31A)	0.9900	C(51)-H(51B)	0.9800
C(6)-C(7)	1.412(11)	C(31)-H(31B)	0.9900	C(51)-H(51C)	0.9800
C(6)-H(6A)	0.9500	C(32)-C(33)	1.384(10)	C(52)-H(52A)	0.9800
C(7)-C(8)	1.340(10)	C(32)-C(37)	1.426(10)	C(52)-H(52B)	0.9800
C(7)-H(7A)	0.9500	C(33)-C(34)	1.378(10)	C(52)-H(52C)	0.9800
C(8)-C(9)	1.419(10)	C(33)-H(33A)	0.9500	C(61)-C(62)	1.315(14)
C(8)-H(8A)	0.9500	C(34)-C(35)	1.369(11)	C(61)-C(66)	1.391(13)
C(9)-C(10)	1.414(10)	C(34)-H(34A)	0.9500	C(61)-H(61A)	0.9500
C(10)-C(11)	1.467(10)	C(35)-C(36)	1.381(11)	C(62)-C(63)	1.389(14)
C(11)-C(12)	1.421(10)	C(35)-H(35A)	0.9500	C(62)-H(62A)	0.9500
C(12)-C(13)	1.356(10)	C(36)-C(37)	1.367(10)	C(63)-C(64)	1.374(13)
C(12)-H(12A)	0.9500	C(36)-H(36A)	0.9500	C(63)-H(63A)	0.9500
C(13)-C(14)	1.377(10)	C(37)-H(37A)	0.9500	C(64)-C(65)	1.371(12)
C(13)-H(13A)	0.9500	C(41)-C(42)	1.404(10)	C(64)-H(64A)	0.9500
C(14)-C(19)	1.417(10)	C(41)-C(46)	1.411(10)	C(65)-C(66)	1.359(12)
C(14)-C(15)	1.420(10)	C(42)-C(43)	1.374(10)	C(65)-H(65A)	0.9500
C(15)-C(16)	1.361(10)	C(42)-C(48)	1.531(10)	C(66)-H(66A)	0.9500
C(15)-H(15A)	0.9500				

Table S13. Bond angles [°] for **18**.

Bonds	angle, °	Bonds	angle, °	Bonds	angle, °
N(2)-Hf(1)-C(21)	107.1(3)	C(16)-C(15)-H(15A)	120.0	C(46)-C(41)-N(2)	119.1(6)
N(2)-Hf(1)-C(31)	100.4(3)	C(14)-C(15)-H(15A)	120.0	C(43)-C(42)-C(41)	119.2(7)
C(21)-Hf(1)-C(31)	117.1(3)	C(15)-C(16)-C(17)	122.1(7)	C(43)-C(42)-C(48)	118.7(7)
N(2)-Hf(1)-N(1)	71.6(2)	C(15)-C(16)-H(16A)	119.0	C(41)-C(42)-C(48)	121.9(7)
C(21)-Hf(1)-N(1)	110.3(2)	C(17)-C(16)-H(16A)	119.0	C(42)-C(43)-C(44)	121.6(7)
C(31)-Hf(1)-N(1)	132.0(2)	C(18)-C(17)-C(16)	121.4(7)	C(42)-C(43)-H(43A)	119.2
N(2)-Hf(1)-C(1)	139.2(2)	C(18)-C(17)-H(17A)	119.3	C(44)-C(43)-H(43A)	119.2
C(21)-Hf(1)-C(1)	97.6(3)	C(16)-C(17)-H(17A)	119.3	C(43)-C(44)-C(45)	118.8(7)
C(31)-Hf(1)-C(1)	96.3(3)	C(17)-C(18)-N(2)	128.6(7)	C(43)-C(44)-H(44A)	120.6
N(1)-Hf(1)-C(1)	69.5(2)	C(17)-C(18)-C(19)	116.6(7)	C(45)-C(44)-H(44A)	120.6
N(2)-Hf(1)-C(32)	108.9(2)	N(2)-C(18)-C(19)	114.7(7)	C(46)-C(45)-C(44)	121.5(8)
C(21)-Hf(1)-C(32)	85.8(3)	N(1)-C(19)-C(18)	115.5(7)	C(46)-C(45)-H(45A)	119.3
C(31)-Hf(1)-C(32)	31.5(2)	N(1)-C(19)-C(14)	121.3(7)	C(44)-C(45)-H(45A)	119.3
N(1)-Hf(1)-C(32)	163.2(2)	C(18)-C(19)-C(14)	123.1(7)	C(45)-C(46)-C(41)	118.3(7)
C(1)-Hf(1)-C(32)	104.7(2)	C(22)-C(21)-Hf(1)	101.5(5)	C(45)-C(46)-C(47)	118.8(7)
N(2)-Hf(1)-C(22)	112.0(2)	C(22)-C(21)-H(21A)	111.5	C(41)-C(46)-C(47)	122.8(7)
C(21)-Hf(1)-C(22)	29.8(2)	Hf(1)-C(21)-H(21A)	111.5	C(46)-C(47)-C(49)	110.7(6)
C(31)-Hf(1)-C(22)	138.7(3)	C(22)-C(21)-H(21B)	111.5	C(46)-C(47)-C(50)	113.3(7)
N(1)-Hf(1)-C(22)	83.8(2)	Hf(1)-C(21)-H(21B)	111.5	C(49)-C(47)-C(50)	107.6(6)
C(1)-Hf(1)-C(22)	75.7(2)	H(21A)-C(21)-H(21B)	109.3	C(46)-C(47)-H(47A)	108.4
C(32)-Hf(1)-C(22)	110.5(2)	C(27)-C(22)-C(23)	117.4(8)	C(49)-C(47)-H(47A)	108.4
C(11)-N(1)-C(19)	122.2(6)	C(27)-C(22)-C(21)	122.5(8)	C(50)-C(47)-H(47A)	108.4
C(11)-N(1)-Hf(1)	121.2(5)	C(23)-C(22)-C(21)	120.1(8)	C(52)-C(48)-C(42)	109.7(6)
C(19)-N(1)-Hf(1)	116.6(5)	C(27)-C(22)-Hf(1)	101.3(5)	C(52)-C(48)-C(51)	109.0(6)
C(18)-N(2)-C(41)	115.1(6)	C(23)-C(22)-Hf(1)	116.9(5)	C(42)-C(48)-C(51)	111.8(6)
C(18)-N(2)-Hf(1)	120.9(5)	C(21)-C(22)-Hf(1)	48.7(4)	C(52)-C(48)-H(48A)	108.8
C(41)-N(2)-Hf(1)	123.8(4)	C(24)-C(23)-C(22)	119.9(8)	C(42)-C(48)-H(48A)	108.8
C(10)-C(1)-C(2)	119.1(6)	C(24)-C(23)-H(23A)	120.0	C(51)-C(48)-H(48A)	108.8
C(10)-C(1)-Hf(1)	118.9(5)	C(22)-C(23)-H(23A)	120.0	C(47)-C(49)-H(49A)	109.5
C(2)-C(1)-Hf(1)	121.8(5)	C(25)-C(24)-C(23)	120.5(9)	C(47)-C(49)-H(49B)	109.5
C(3)-C(2)-C(1)	119.5(7)	C(25)-C(24)-H(24A)	119.7	H(49A)-C(49)-H(49B)	109.5
C(3)-C(2)-H(2A)	120.2	C(23)-C(24)-H(24A)	119.7	C(47)-C(49)-H(49C)	109.5
C(1)-C(2)-H(2A)	120.2	C(24)-C(25)-C(26)	121.0(10)	H(49A)-C(49)-H(49C)	109.5
C(2)-C(3)-C(4)	121.9(7)	C(24)-C(25)-H(25A)	119.5	H(49B)-C(49)-H(49C)	109.5
C(2)-C(3)-H(3A)	119.1	C(26)-C(25)-H(25A)	119.5	C(47)-C(50)-H(50A)	109.5
C(4)-C(3)-H(3A)	119.1	C(25)-C(26)-C(27)	119.0(9)	C(47)-C(50)-H(50B)	109.5
C(3)-C(4)-C(5)	121.1(8)	C(25)-C(26)-H(26A)	120.5	H(50A)-C(50)-H(50B)	109.5
C(3)-C(4)-C(9)	118.6(7)	C(27)-C(26)-H(26A)	120.5	C(47)-C(50)-H(50C)	109.5
C(5)-C(4)-C(9)	120.3(7)	C(22)-C(27)-C(26)	122.1(8)	H(50A)-C(50)-H(50C)	109.5
C(6)-C(5)-C(4)	122.3(8)	C(22)-C(27)-H(27A)	118.9	H(50B)-C(50)-H(50C)	109.5
C(6)-C(5)-H(5A)	118.8	C(26)-C(27)-H(27A)	118.9	C(48)-C(51)-H(51A)	109.5
C(4)-C(5)-H(5A)	118.8	C(32)-C(31)-Hf(1)	95.3(5)	C(48)-C(51)-H(51B)	109.5
C(5)-C(6)-C(7)	117.4(7)	C(32)-C(31)-H(31A)	112.7	H(51A)-C(51)-H(51B)	109.5
C(5)-C(6)-H(6A)	121.3	Hf(1)-C(31)-H(31A)	112.7	C(48)-C(51)-H(51C)	109.5
C(7)-C(6)-H(6A)	121.3	C(32)-C(31)-H(31B)	112.7	H(51A)-C(51)-H(51C)	109.5
C(8)-C(7)-C(6)	121.6(8)	Hf(1)-C(31)-H(31B)	112.7	H(51B)-C(51)-H(51C)	109.5
C(8)-C(7)-H(7A)	119.2	H(31A)-C(31)-H(31B)	110.2	C(48)-C(52)-H(52A)	109.5
C(6)-C(7)-H(7A)	119.2	C(33)-C(32)-C(37)	115.8(7)	C(48)-C(52)-H(52B)	109.5
C(7)-C(8)-C(9)	122.9(8)	C(33)-C(32)-C(31)	121.3(6)	H(52A)-C(52)-H(52B)	109.5
C(7)-C(8)-H(8A)	118.6	C(37)-C(32)-C(31)	122.5(7)	C(48)-C(52)-H(52C)	109.5
C(9)-C(8)-H(8A)	118.6	C(33)-C(32)-Hf(1)	93.2(5)	H(52A)-C(52)-H(52C)	109.5
C(10)-C(9)-C(4)	119.0(7)	C(37)-C(32)-Hf(1)	118.5(5)	H(52B)-C(52)-H(52C)	109.5
C(10)-C(9)-C(8)	125.8(7)	C(31)-C(32)-Hf(1)	53.2(4)	C(62)-C(61)-C(66)	119.3(10)
C(4)-C(9)-C(8)	115.1(7)	C(34)-C(33)-C(32)	122.4(7)	C(62)-C(61)-H(61A)	120.4
C(1)-C(10)-C(9)	120.9(7)	C(34)-C(33)-H(33A)	118.8	C(66)-C(61)-H(61A)	120.4
C(1)-C(10)-C(11)	113.1(6)	C(32)-C(33)-H(33A)	118.8	C(61)-C(62)-C(63)	121.8(11)
C(9)-C(10)-C(11)	126.1(7)	C(35)-C(34)-C(33)	120.5(8)	C(61)-C(62)-H(62A)	119.1
N(1)-C(11)-C(12)	117.1(6)	C(35)-C(34)-H(34A)	119.7	C(63)-C(62)-H(62A)	119.1

Table S13 (continued). Bond angles [°] for **18**.

Bonds	angle, °	Bonds	angle, °	Bonds	angle, °
N(1)-C(11)-C(10)	115.3(6)	C(33)-C(34)-H(34A)	119.7	C(64)-C(63)-C(62)	119.4(10)
C(12)-C(11)-C(10)	127.5(7)	C(34)-C(35)-C(36)	119.2(7)	C(64)-C(63)-H(63A)	120.3
C(13)-C(12)-C(11)	121.2(7)	C(34)-C(35)-H(35A)	120.4	C(62)-C(63)-H(63A)	120.3
C(13)-C(12)-H(12A)	119.4	C(36)-C(35)-H(35A)	120.4	C(65)-C(64)-C(63)	118.4(9)
C(11)-C(12)-H(12A)	119.4	C(37)-C(36)-C(35)	120.5(8)	C(65)-C(64)-H(64A)	120.8
C(12)-C(13)-C(14)	122.0(7)	C(37)-C(36)-H(36A)	119.7	C(63)-C(64)-H(64A)	120.8
C(12)-C(13)-H(13A)	119.0	C(35)-C(36)-H(36A)	119.7	C(66)-C(65)-C(64)	121.1(9)
C(14)-C(13)-H(13A)	119.0	C(36)-C(37)-C(32)	121.5(7)	C(66)-C(65)-H(65A)	119.4
C(13)-C(14)-C(19)	115.9(7)	C(36)-C(37)-H(37A)	119.2	C(64)-C(65)-H(65A)	119.4
C(13)-C(14)-C(15)	127.3(7)	C(32)-C(37)-H(37A)	119.2	C(65)-C(66)-C(61)	119.8(10)
C(19)-C(14)-C(15)	116.6(7)	C(42)-C(41)-C(46)	120.4(7)	C(65)-C(66)-H(66A)	120.1
C(16)-C(15)-C(14)	120.0(7)	C(42)-C(41)-N(2)	120.5(7)	C(61)-C(66)-H(66A)	120.1

Table S14. Anisotropic displacement parameters ($Å^2 \times 10^3$) for **18**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

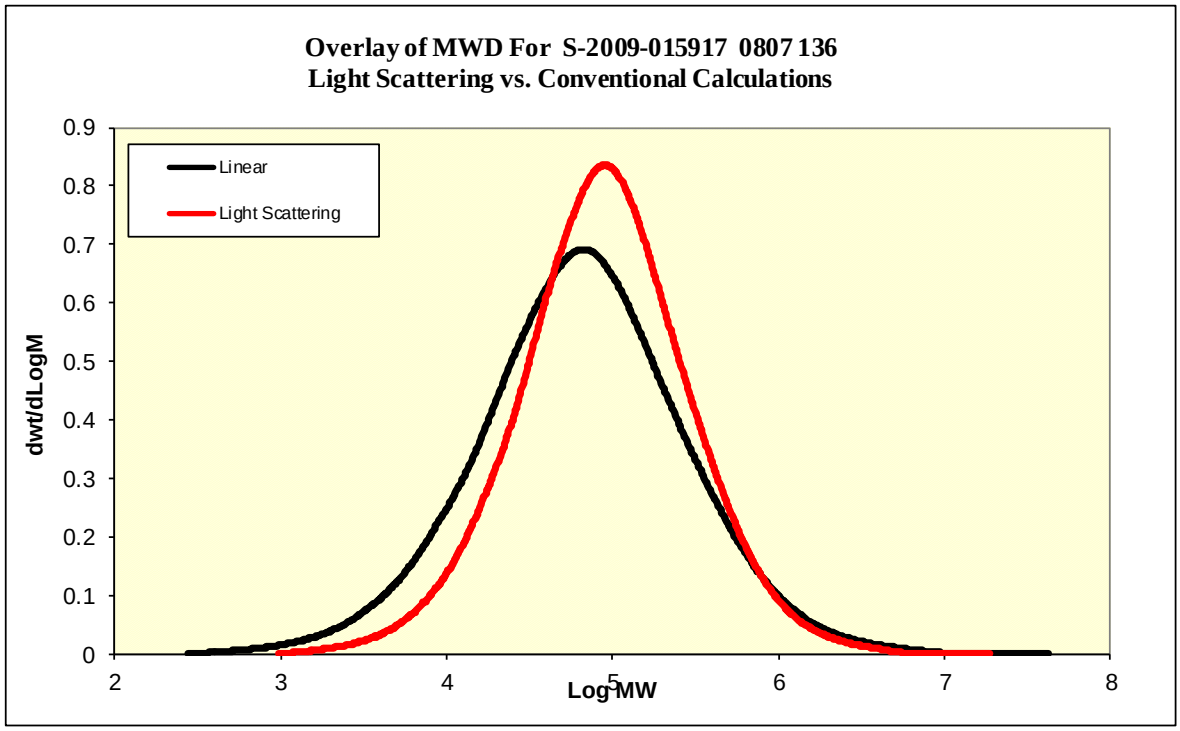
Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Hf(1)	19(1)	19(1)	21(1)	2(1)	-1(1)	-2(1)
N(1)	23(4)	17(3)	27(4)	-2(3)	5(3)	-1(3)
N(2)	23(4)	24(4)	29(4)	4(3)	12(3)	-3(3)
C(1)	15(3)	15(3)	14(3)	-7(3)	-3(3)	-6(3)
C(2)	21(5)	31(5)	28(5)	5(4)	2(4)	-4(4)
C(3)	32(5)	23(4)	28(5)	1(4)	-6(4)	7(4)
C(4)	18(4)	19(4)	39(5)	-3(4)	5(4)	3(3)
C(5)	23(5)	25(4)	56(6)	-10(4)	-4(4)	-9(4)
C(6)	14(5)	29(5)	61(6)	-2(4)	-8(4)	-8(4)
C(7)	27(5)	30(5)	47(6)	1(4)	12(4)	-6(4)
C(8)	11(4)	31(4)	41(5)	-3(4)	3(4)	-4(3)
C(9)	17(4)	14(4)	35(5)	1(3)	4(4)	3(3)
C(10)	20(4)	10(4)	29(5)	-8(3)	3(4)	0(3)
C(11)	15(4)	20(4)	20(4)	-7(3)	1(3)	1(3)
C(12)	26(5)	22(4)	36(5)	3(4)	7(4)	-7(4)
C(13)	37(5)	27(4)	32(5)	12(4)	6(4)	2(4)
C(14)	30(5)	29(4)	21(4)	0(4)	7(4)	4(4)
C(15)	33(5)	42(5)	18(4)	10(4)	-4(4)	3(4)
C(16)	20(5)	38(5)	27(5)	-1(4)	-8(4)	8(4)
C(17)	27(5)	22(4)	36(5)	-3(4)	-1(4)	-9(4)
C(18)	31(5)	17(4)	31(5)	5(3)	1(4)	2(3)
C(19)	19(4)	24(4)	22(4)	-1(3)	4(3)	3(3)
C(21)	22(5)	23(4)	37(5)	-2(4)	4(4)	-6(4)
C(22)	31(5)	16(4)	37(5)	-2(4)	4(4)	6(4)
C(23)	25(5)	29(5)	44(5)	-3(4)	-6(4)	12(4)
C(24)	29(6)	38(5)	65(7)	-6(5)	6(5)	7(4)
C(25)	59(8)	33(5)	72(8)	2(5)	38(7)	4(5)
C(26)	67(8)	33(5)	36(6)	2(4)	17(5)	4(5)
C(27)	44(6)	22(4)	42(6)	-10(4)	-3(5)	8(4)
C(31)	31(5)	27(4)	29(5)	-7(4)	-4(4)	1(4)
C(32)	19(4)	26(4)	15(4)	3(3)	-3(3)	-2(3)
C(33)	30(5)	43(5)	22(4)	10(4)	0(4)	-8(4)
C(34)	43(6)	38(6)	33(5)	3(4)	-2(4)	-15(4)
C(35)	59(6)	22(5)	50(6)	12(4)	-2(5)	-2(4)
C(36)	30(5)	54(6)	28(5)	19(4)	-8(4)	4(4)
C(37)	32(5)	31(5)	29(5)	-2(4)	12(4)	-6(4)
C(41)	21(4)	20(4)	16(4)	5(3)	-3(3)	-10(3)
C(42)	14(4)	33(5)	18(4)	0(3)	-2(3)	3(3)
C(43)	26(5)	26(4)	35(5)	5(4)	-4(4)	-1(4)
C(44)	20(5)	26(5)	47(6)	0(4)	2(4)	-8(4)
C(45)	19(5)	26(4)	42(5)	1(4)	8(4)	7(4)
C(46)	31(5)	23(4)	25(4)	-2(4)	0(3)	3(4)
C(47)	7(4)	23(4)	49(5)	1(4)	-3(4)	2(3)
C(48)	30(5)	23(4)	27(4)	-7(3)	3(4)	-4(3)
C(49)	47(6)	33(5)	43(6)	8(4)	-2(5)	2(4)
C(50)	26(5)	34(5)	54(6)	-8(4)	3(4)	8(4)
C(51)	31(5)	19(4)	46(6)	0(4)	-7(4)	-2(4)
C(52)	40(5)	35(4)	26(4)	-6(4)	-2(4)	1(4)
C(61)	48(7)	102(9)	68(8)	47(7)	-1(6)	20(7)
C(62)	41(7)	140(12)	73(9)	62(8)	12(6)	17(7)
C(63)	39(7)	94(9)	87(9)	40(7)	10(6)	-5(6)
C(64)	52(7)	49(6)	45(6)	1(5)	-2(5)	5(5)
C(65)	40(6)	48(6)	55(6)	-1(5)	13(5)	0(5)
C(66)	46(7)	56(7)	50(6)	9(5)	10(5)	1(5)

Table S15. Hydrogen coordinates (Å × 10^4) and isotropic displacement parameters (Å^2 × 10^3) for **18**.

Atom	x	y	z	U(eq)
H(2A)	1	744	684	32
H(3A)	-1409	-67	380	34
H(5A)	-2756	-846	764	43
H(6A)	-3618	-1317	1699	43
H(7A)	-2989	-1027	3006	41
H(8A)	-1529	-384	3342	33
H(12A)	-193	-709	3806	33
H(13A)	891	-579	4929	38
H(15A)	2453	128	5696	38
H(16A)	3744	1001	5633	35
H(17A)	3921	1672	4507	35
H(21A)	991	3015	2451	33
H(21B)	399	2753	1618	33
H(23A)	-1243	2220	1511	40
H(24A)	-2567	1741	2082	53
H(25A)	-2377	1527	3387	62
H(26A)	-908	1845	4171	53
H(27A)	414	2370	3621	45
H(31A)	2979	1066	1384	36
H(31B)	1969	682	912	36
H(33A)	2935	2615	1593	39
H(34A)	2456	3864	1070	47
H(35A)	1222	3963	2	54
H(36A)	536	2782	-590	47
H(37A)	967	1532	-55	36
H(43A)	4755	3675	3088	35
H(44A)	5986	2899	2657	38
H(45A)	5754	1498	2491	35
H(47A)	3578	380	2650	32
H(48A)	2469	2952	3571	32
H(49A)	4525	273	3879	63
H(49B)	5528	280	3519	63
H(49C)	4788	-475	3367	63
H(50A)	4444	488	1547	57
H(50B)	4558	-386	1948	57
H(50C)	5445	255	2104	57
H(51A)	2358	3812	2473	50
H(51B)	3264	4346	2891	50
H(51C)	2234	4346	3213	50
H(52A)	3774	3157	4618	52
H(52B)	3040	3918	4516	52
H(52C)	4083	3969	4217	52
H(61A)	1360	2066	5918	88
H(62A)	2192	2961	5288	101
H(63A)	1428	4132	4738	88
H(64A)	-287	4274	4651	60
H(65A)	-1146	3336	5278	56
H(66A)	-350	2226	5885	61

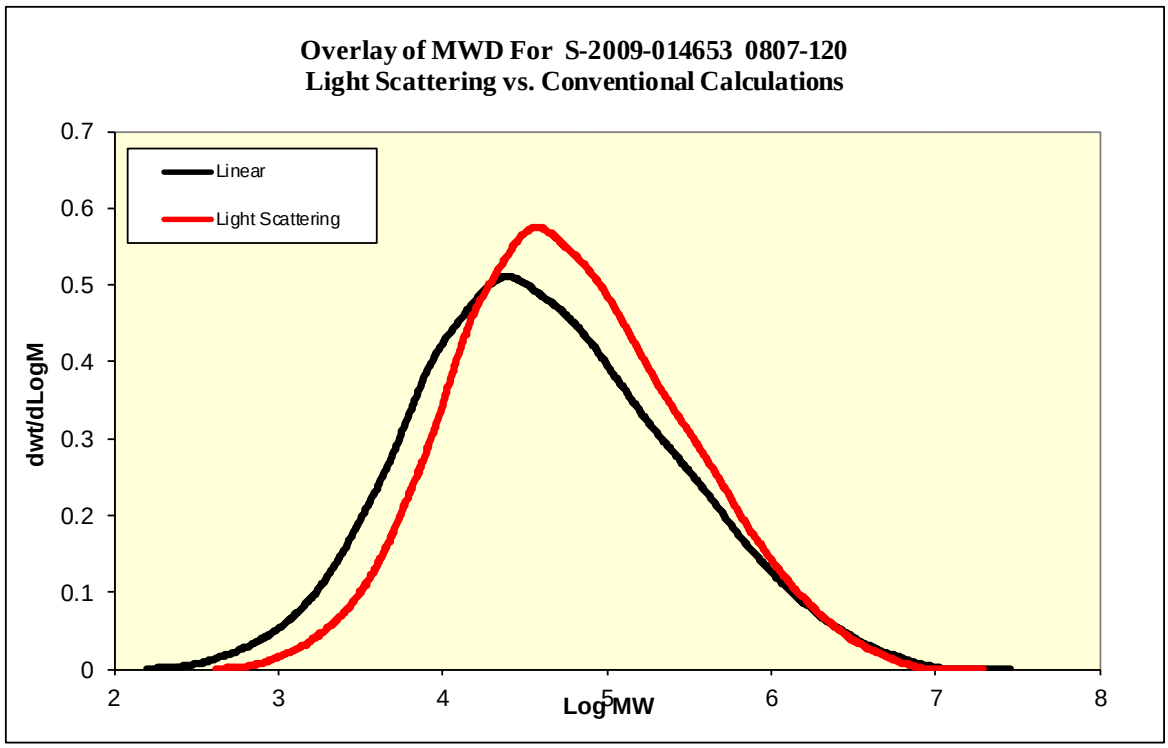
3. GPC traces of selected polymer samples

Run 4:



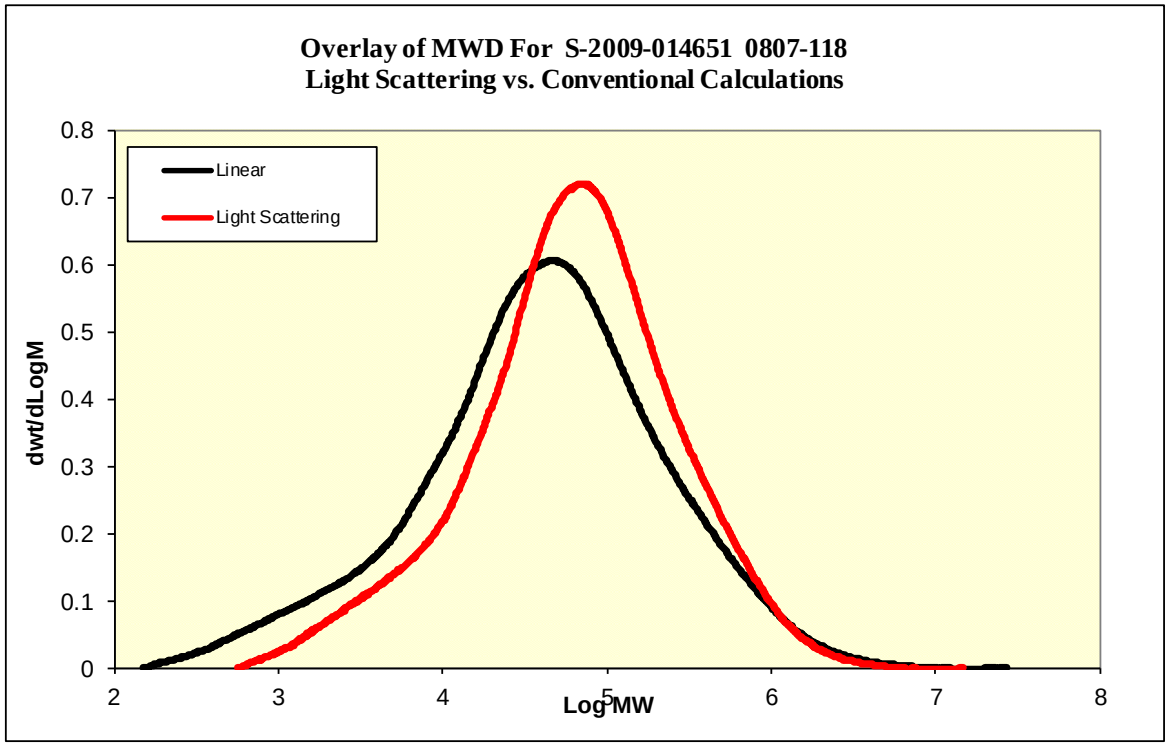
	Mn	Mw	Mz	Mz+1	PD	IV	gpcBR
Conventional	22,035	181,831	1,341,892	5,284,128	8.25	2.05	
3D-G{C	22,035	177,544	735,346	2,210,995	8.06	2.02	0.00

Run 17:



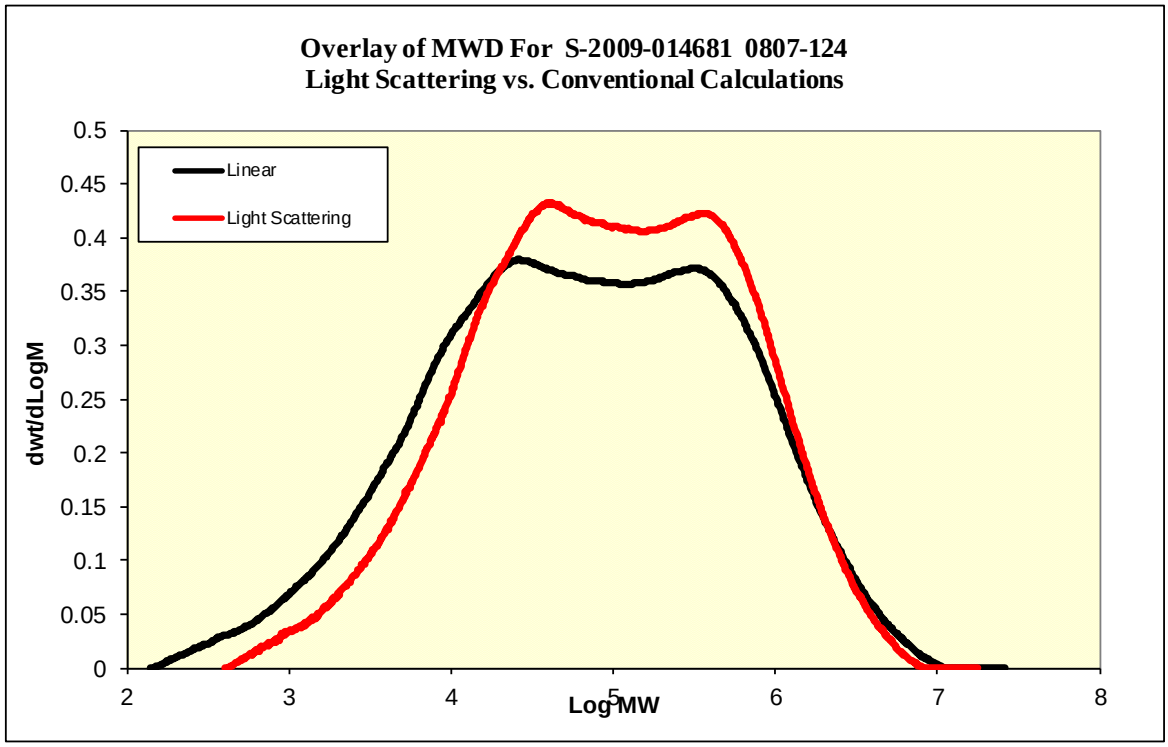
	Mn	Mw	Mz	Mz+1	PD	IV	gpcBR
Conventional	10,041	210,942	1,895,689	4,249,722	21.01	2.08	
3D-G{C	10,041	217,052	1,445,439	3,165,042	21.62	2.02	0.05

Run 18:



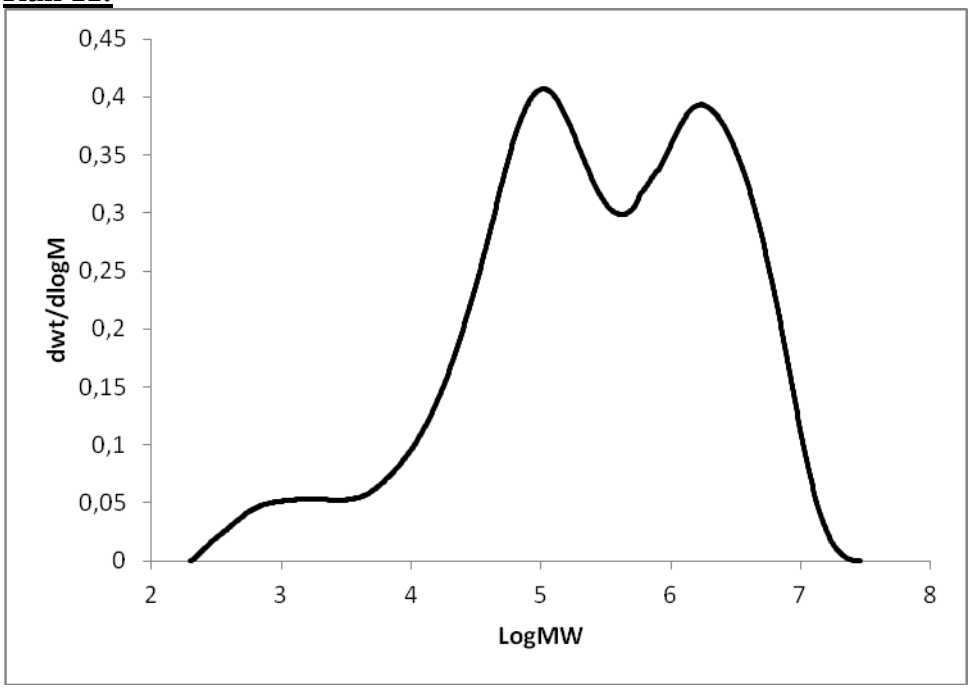
	Mn	Mw	Mz	Mz+1	PD	IV	gpcBR
Conventional	7,975	142,711	986,272	2,595,498	17.89	1.67	
3D-G{C	7,975	154,795	683,755	1,635,090	19.41	1.52	0.17

Run 19:

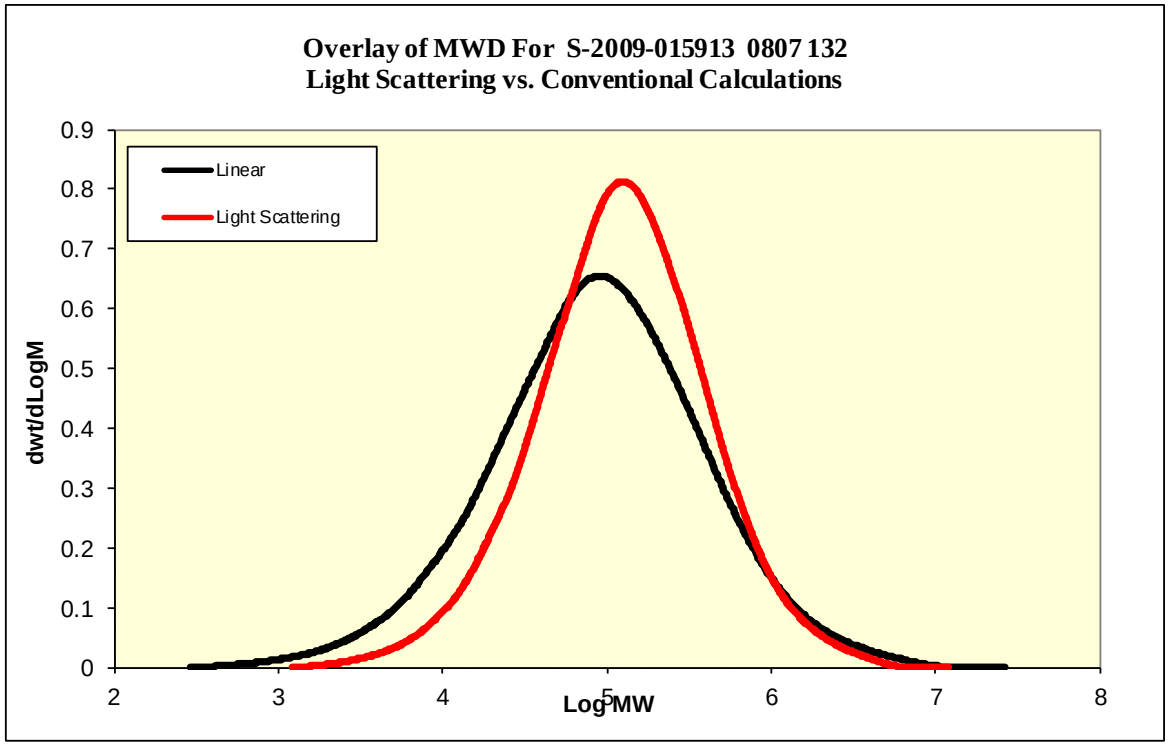


	Mn	Mw	Mz	Mz+1	PD	IV	gpcBR
Conventional	8,427	356,512	2,060,373	4,062,077	42.30	3.18	
3D-G{C	8,427	350,250	1,585,353	2,968,111	41.56	3.21	-0.02

Run 11:



Run 29:



	Mn	Mw	Mz	Mz+1	PD	IV	gpcBR
Conventional	26,705	255,093	1,590,292	4,114,463	9.55	2.62	
3D-G{C	26,705	244,820	884,151	2,056,774	9.17	2.65	-0.04

4. DFT calculations

Table S16. Calculated energies of optimized structures and reactivity indexes derived based on these values.

Spartan '06; B3LYP/6-31G**; full optimization						
				Et=	-78.5934	a.u.
Ligands	ZrMe2	ZrMe+	Delta Estab	ZrMe+/Et=	Dela Epi	LUMO
	a.u.	a.u.	kcal/mol	a.u		kJ/mol
Cp2	-513.5493	-473.4038	0	-552.0291	-20.01725	-675.015
Ind2	-820.8251	-780.696	-10.291	-859.3101	-12.98925	-629.324
Flu2	-1128.096	-1087.984	-21.02125	-1166.587	-6.024	
PhN-Qui-Ph	-1044.6959	-1004.5618	-7.1535	-1083.1833	-17.63275	-564.109
PhN-CH2-Py-Ph	-930.3493	-890.2242	-12.801	-968.8414	-14.9345	-549.757
PhN-Qui-CH2CH2-Ph	-1123.3038	-1083.2003	-26.355	-1161.8046	-6.83975	-528.514
iPrPhN-iPr-Qui-Ph	-1240.0634	-1199.9291	-7.028	-1278.553	-19.13875	-566.653
PhN-MeQui-Ph_1	-1044.6404	-1004.4968	-1.19225	-1083.1298	-24.849	-585.259
PhN-MeQui-Ph_2	-1044.6552	-1004.5077	1.255	-1083.1471	-28.865	-608.498
PhN-MeQui-CH2CH2-Ph_1	-1123.2808	-1083.1439	-5.3965	-1161.7658	-17.88375	-537.588
PhN-MeQui-CH2CH2-Ph_2	-1123.2936	-1083.165	-10.60475	-1161.787	-17.9465	-542.806

Table S17. Optimized geometry of cationic models.

Cp_2ZrMe^+

Zr	0.004465	0.240504	0.325934
H	2.436913	1.451642	-1.391025
C	2.246862	0.557775	-0.813774
C	1.666951	-0.648440	-1.302056
H	2.983133	1.108743	1.218952
H	1.382390	-0.844843	-2.327509
C	1.639006	-1.591682	-0.229438
H	1.288394	-2.613129	-0.290709
C	2.163558	-0.957096	0.919754
H	2.285770	-1.410447	1.897164
C	2.529255	0.376207	0.562506
H	-2.118627	0.852764	-2.026042
C	-2.075667	0.225686	-1.145381
C	-2.538697	0.575839	0.145298
H	-1.184552	-1.677089	-1.918896
H	-2.995791	1.516691	0.420629
C	-2.313586	-0.531078	1.011156
H	-2.585308	-0.583833	2.059676
C	-1.717273	-1.574262	0.251265
H	-1.463556	-2.562826	0.611608
C	-1.562515	-1.102816	-1.083975
C	-0.036256	2.441419	-0.116101
H	-0.279484	2.722391	-1.147178
H	0.903746	2.935300	0.149401
H	-0.841452	2.855190	0.511033
Lig	2.049126	-0.452647	-0.172602
Lig	-2.041548	-0.481326	-0.164327

Ind_2ZrMe^+

Zr	0.595842	-0.586277	0.429506
H	2.865698	-0.400734	-1.825374
C	1.820497	-0.684632	-1.798674
C	0.720354	0.209061	-1.944525
H	1.942161	-2.856247	-1.330936
C	-0.488278	-0.585997	-1.915194
C	-0.102671	-1.942107	-1.589410
C	1.338730	-1.977928	-1.515675
C	-0.820075	1.478765	1.046791
C	0.377452	1.495115	1.862939
H	-2.516142	-0.006959	0.983890
C	0.334448	0.342293	2.726196
H	1.054137	0.099385	3.494188
C	-0.875419	-0.344102	2.465247
C	-1.558600	0.286850	1.392361
H	0.784139	1.256578	-2.208800
H	-1.205501	-1.243754	2.972497
C	1.353228	2.510737	1.669586
H	2.258949	2.521006	2.267794
C	1.089395	3.517085	0.759443
H	1.806232	4.321362	0.629257
C	-0.113633	3.537215	0.004436
H	-0.292214	4.362228	-0.677596
C	-1.050814	2.531005	0.118882
H	-1.967348	2.555367	-0.461872
C	-1.098941	-2.924050	-1.340996
H	-0.818588	-3.941991	-1.087207
C	-2.428976	-2.574973	-1.514165
H	-3.200795	-3.323803	-1.368406
C	-2.803427	-1.265846	-1.906452
H	-3.853825	-1.043600	-2.064431
C	-1.859651	-0.270189	-2.083763
H	-2.156114	0.730699	-2.380450
C	2.449082	-1.378468	1.420159
H	3.114645	-0.502982	1.526652
H	2.991420	-2.112481	0.817060
H	2.314600	-1.787632	2.427043
Lig	0.657726	-0.996321	-1.752696
Lig	-0.508439	0.651784	1.898707

Flu_2ZrMe^+

Zr	0.639907	-0.514469	0.451822
C	1.980741	-0.561660	-1.674903
C	0.870819	0.310156	-1.999084
H	2.058764	-2.747341	-1.164885
C	-0.336039	-0.507147	-2.003607
C	0.053358	-1.851360	-1.642480
C	1.467173	-1.867214	-1.371894
C	-0.931492	1.490913	1.163048
C	0.276920	1.492520	1.958390
C	0.338305	0.266899	2.711379
H	1.072313	0.027191	3.466583
C	-0.877933	-0.453244	2.464215
C	-1.653010	0.262640	1.474042
C	1.210693	2.548358	1.798571
H	2.134560	2.552149	2.368512
C	0.885536	3.608905	0.966659
H	1.574006	4.442557	0.873225
C	-0.339740	3.643904	0.260298
H	-0.572655	4.508012	-0.353465
C	-1.236992	2.592585	0.334488
H	-2.172518	2.624130	-0.215242
C	-0.942958	-2.854614	-1.520037
H	-0.668755	-3.864313	-1.229961
C	-2.250549	-2.540660	-1.850229
H	-3.011717	-3.312937	-1.803707
C	-2.611936	-1.241736	-2.283056
H	-3.640697	-1.045969	-2.567784
C	-1.677437	-0.223974	-2.345072
H	-1.962148	0.770013	-2.676311
C	2.337054	-1.544018	1.532419
H	2.927751	-0.812486	2.100451
H	3.022657	-2.118220	0.905534
H	1.902687	-2.232010	2.274301
C	1.105168	1.669608	-2.326308
H	0.283557	2.314149	-2.619443
C	2.396116	2.155688	-2.279519
H	2.592846	3.189279	-2.544042
C	3.477772	1.320737	-1.895323
H	4.478964	1.738476	-1.859122
C	3.287727	-0.011939	-1.580636
H	4.125875	-0.645724	-1.309911
C	-2.907255	-0.238351	1.054007
H	-3.517172	0.323723	0.355124
C	-3.344484	-1.451371	1.551177
H	-4.310232	-1.841868	1.248377
C	-2.548982	-2.197430	2.456282
H	-2.915288	-3.154309	2.814933
C	-1.326596	-1.727219	2.905002
H	-0.744688	-2.291008	3.627181
Lig	0.807210	-0.895445	-1.738393
Lig	-0.569442	0.611946	1.954214

[PhN-CH_2-Py-Ph]ZrMe$^+$

N	0.956670	-1.196917	-0.036564
C	2.519978	-3.455864	0.040407
C	2.313769	-1.054311	0.014695
C	0.374354	-2.413358	-0.119801
C	1.135113	-3.576450	-0.079625
C	3.115614	-2.196270	0.075104
H	0.657828	-4.547247	-0.151551
H	4.193294	-2.104207	0.124489
H	3.139587	-4.346172	0.079688
C	-1.127930	-2.378008	-0.285268
H	-1.608545	-2.722130	0.644000
H	-1.434583	-3.072655	-1.079019
C	2.780852	0.342942	-0.060747
C	3.527612	3.029552	-0.267338
C	1.772853	1.326338	-0.252943
C	4.129820	0.702226	0.034028
C	4.497171	2.045184	-0.074307
C	2.177503	2.667060	-0.346222
H	4.902822	-0.043085	0.194131
H	5.544271	2.322202	-0.004835
H	1.443665	3.461538	-0.490696
H	3.821146	4.071292	-0.353532
N	-1.470037	-1.006801	-0.605976
C	-2.714811	-0.430459	-0.472198
C	-4.919970	1.256637	0.052939
C	-2.779487	0.893022	-1.013513
C	-3.809423	-0.907757	0.283840
C	-4.888640	-0.070077	0.524860
C	-3.879829	1.729900	-0.730699
H	-2.151233	1.128910	-1.880168
H	-3.805278	-1.919357	0.675481
H	-5.727598	-0.446073	1.102832
H	-3.931194	2.719344	-1.174772
H	-5.776957	1.886028	0.265840
Zr	-0.348201	0.667243	-0.007102
C	-0.734823	0.807670	2.157791
H	0.165387	0.580210	2.743315
H	-1.550605	0.157204	2.492871
H	-1.015134	1.850300	2.382943

[PhN-Qui-Ph]ZrMe^{+}

N	0.947202	0.872810	-0.002475
C	2.147510	3.361562	-0.175995
C	2.292105	0.942970	-0.066789
C	0.181845	2.000947	0.059054
C	0.736143	3.299051	-0.034844
C	2.911670	2.211846	-0.175370
H	3.990302	2.277947	-0.246415
H	2.630678	4.330851	-0.260744
C	2.962296	-0.362077	0.033607
C	4.075472	-2.911725	0.274212
C	2.096126	-1.477402	0.215279
C	4.350634	-0.524101	-0.027311
C	4.901585	-1.801058	0.098173
C	2.685252	-2.745812	0.323780
H	5.010751	0.326046	-0.168766
H	5.978573	-1.927958	0.055949
H	2.070403	-3.637196	0.458525
H	4.510911	-3.901529	0.372031
N	-1.478437	0.429887	0.438403
C	-2.667673	-0.282394	0.351596
C	-4.689496	-2.210144	-0.021778
C	-2.631132	-1.527466	1.041693
C	-3.756777	-0.006335	-0.501071
C	-4.753064	-0.960231	-0.663530
C	-3.635740	-2.491220	0.836772
H	-1.967481	-1.624751	1.907546
H	-3.797098	0.932092	-1.042947
H	-5.591136	-0.741089	-1.318227
H	-3.608046	-3.426206	1.387652
H	-5.478117	-2.938271	-0.176583
C	-1.207239	1.783343	0.274434
C	-2.042332	2.885708	0.363695
H	-3.102284	2.762472	0.557836
C	-1.499370	4.187697	0.227864
H	-2.172812	5.036053	0.292516
C	-0.148649	4.405903	0.037576
H	0.244117	5.413712	-0.046831
Zr	-0.108028	-1.121427	0.013964
C	-0.480093	-1.502741	-2.122274
H	0.460983	-1.575943	-2.681653
H	-1.119954	-0.750048	-2.595286
H	-0.994456	-2.475902	-2.197279

[PhN-Qui-CH_2CH_2-Ph]ZrMe$^+$

N	0.762436	-1.107457	0.000729
C	1.651428	-3.715724	0.208762
C	2.071268	-1.340111	0.147121
C	-0.142198	-2.129160	-0.066809
C	0.260535	-3.484851	0.046976
C	2.548726	-2.663921	0.256810
H	3.612458	-2.842111	0.363832
H	2.012742	-4.737042	0.290209
C	2.889672	-0.102904	0.240777
C	4.176729	2.344773	0.723519
C	2.721995	0.969034	-0.685358
C	3.732850	0.059083	1.352558
C	4.376424	1.269432	1.592180
C	3.366804	2.187882	-0.397362
H	3.851059	-0.763456	2.051372
H	5.018122	1.377703	2.460410
H	3.264523	3.010391	-1.099778
H	4.668749	3.294431	0.906714
N	-1.666591	-0.373958	-0.418669
C	-2.771254	0.417903	-0.077666
C	-4.608511	2.391139	0.719104
C	-2.873604	1.639359	-0.786023
C	-3.627742	0.184228	1.019901
C	-4.541576	1.159556	1.393273
C	-3.775861	2.629642	-0.366021
H	-2.342861	1.750135	-1.731499
H	-3.554101	-0.744486	1.575737
H	-5.202609	0.973572	2.234397
H	-3.846488	3.560517	-0.919494
H	-5.324220	3.142477	1.035366
Zr	-0.065285	0.995395	-0.241578
C	-0.069520	2.427257	1.449515
H	0.763850	2.175062	2.125530
H	-0.990977	2.437084	2.043992
C	-1.504467	-1.745466	-0.245726
C	-2.459095	-2.751229	-0.280648
H	-3.505954	-2.505794	-0.423057
C	-2.066021	-4.106778	-0.152647
H	-2.836542	-4.870344	-0.186246
C	-0.746615	-4.483390	0.001040
H	-0.472419	-5.528976	0.091462
C	2.020106	0.848480	-2.055796
H	2.746091	1.184802	-2.805624
H	1.820441	-0.201527	-2.285842
C	0.711618	1.696953	-2.186656
H	0.156535	1.417268	-3.087170
H	0.944195	2.767647	-2.238466
H	0.107771	3.449646	1.081910

[iPr_2PhN-Qui-Ph]ZrMe$^+$

N	1.477469	1.009212	-0.195776
C	2.661657	3.430311	-0.849807
C	2.804141	1.159638	-0.015507
C	0.707128	2.047803	-0.626870
C	1.252130	3.311581	-0.963753
C	3.422726	2.380849	-0.378112
H	4.492600	2.496693	-0.255814
H	3.138931	4.370590	-1.111117
C	3.450447	0.005252	0.622429
C	4.498304	-2.250481	1.886820
C	2.560777	-1.024772	1.034373
C	4.829956	-0.093569	0.836367
C	5.347844	-1.223135	1.472025
C	3.120498	-2.150486	1.659715
H	5.508011	0.689772	0.511508
H	6.417198	-1.303036	1.639539
H	2.489145	-2.978295	1.984458
H	4.908524	-3.126819	2.379691
N	-0.984786	0.492703	-0.279752
C	-2.242142	-0.146305	-0.137818
C	-4.515728	-1.753778	0.221763
C	-2.498706	-0.757850	1.129499
C	-3.131514	-0.357703	-1.229464
C	-4.265957	-1.138833	-1.006178
C	-3.631273	-1.574878	1.274356
H	-4.961875	-1.300109	-1.823457
H	-3.839600	-2.043677	2.231328
H	-5.399785	-2.369894	0.350789
C	-0.694626	1.795938	-0.653751
C	-1.541644	2.845131	-0.983160
H	-2.616585	2.705826	-0.969854
C	-1.000906	4.105192	-1.334673
H	-1.685774	4.903718	-1.601264
C	0.359463	4.346074	-1.341796
H	0.750440	5.321242	-1.612331
Zr	0.403590	-0.911666	0.410815
C	0.369213	-2.487848	-1.137191
H	0.892246	-3.388670	-0.785824
H	0.908535	-2.121187	-2.023316
H	-0.644410	-2.766408	-1.449197
C	-2.866661	0.180197	-2.633146
H	-1.965618	0.795862	-2.601858
C	-1.634192	-0.503116	2.374967
H	-0.844872	0.229729	2.118695
C	-2.596974	-0.968363	-3.626407
H	-2.367040	-0.561482	-4.616066
H	-3.468494	-1.622890	-3.731819
H	-1.750256	-1.584908	-3.311058
C	-4.021095	1.067097	-3.139411
H	-3.775325	1.477454	-4.123343
H	-4.224514	1.905082	-2.465588
H	-4.949637	0.497478	-3.244344
C	-0.989164	-1.799546	2.929784
H	-0.427711	-2.412058	2.192452
H	-1.763484	-2.485742	3.281888
H	-0.310224	-1.590420	3.760352
C	-2.424521	0.202787	3.498118
H	-2.871415	1.128316	3.127899
H	-1.769840	0.446492	4.340078
H	-3.227840	-0.441030	3.866258

[PhN-MeQui-Ph]ZrMe^{+}_1

N	-0.687283	0.614172	0.688128
C	-2.424522	2.854282	0.440588
C	-0.278371	1.778752	0.031854
C	-1.059707	2.935305	-0.065582
C	-2.933499	1.692680	0.877864
H	-3.963299	1.641929	1.218914
H	-3.043120	3.746581	0.412097
C	-2.591760	-0.739684	0.059841
C	-3.290719	-2.946909	-1.527723
C	-1.571425	-1.613790	-0.419761
C	-3.930611	-0.988632	-0.239995
C	-4.274031	-2.083232	-1.038619
C	-1.951838	-2.714072	-1.215786
H	-4.713390	-0.329533	0.122976
H	-5.316796	-2.258365	-1.285085
H	-1.200214	-3.393849	-1.614894
H	-3.568727	-3.791141	-2.150852
N	1.437210	0.355514	-0.581836
C	2.713442	-0.143575	-0.376085
C	5.009964	-1.561833	0.432016
C	2.835498	-1.541326	-0.628783
C	3.775784	0.537667	0.262960
C	4.904578	-0.171880	0.642107
C	3.986878	-2.241205	-0.209010
H	2.178233	-1.998238	-1.374292
H	3.690091	1.600698	0.459550
H	5.721272	0.355613	1.125728
H	4.085085	-3.297893	-0.437169
H	5.905822	-2.088099	0.742775
Zr	0.379121	-1.106412	0.443548
C	0.971795	1.683296	-0.603944
C	1.523173	2.792751	-1.242225
H	2.480628	2.723918	-1.747905
C	0.785153	3.984556	-1.259779
H	1.200445	4.857488	-1.751911
C	-0.493924	4.050772	-0.703284
H	-1.068912	4.968746	-0.777923
C	-2.135220	0.407321	1.000143
C	-2.238490	-0.079553	2.469239
H	-3.272039	-0.323020	2.729872
H	-1.866045	0.684605	3.155689
H	-1.652890	-1.002546	2.618533

[PhN-MeQui-Ph]ZrMe^{+}_2

N	0.797005	-0.357624	0.374237
C	2.192500	-0.089446	0.366969
C	0.410791	-1.668690	0.034356
C	1.256558	-2.771391	0.134075
C	3.071978	-1.102673	0.494817
H	4.135532	-0.888210	0.460673
C	2.470892	1.338585	0.104251
C	2.850908	4.056453	-0.512352
C	1.349105	2.147809	-0.257356
C	3.747690	1.909315	0.186993
C	3.932180	3.253761	-0.127917
C	1.572091	3.506826	-0.567821
H	4.601378	1.310937	0.489852
H	4.927544	3.683560	-0.072119
H	0.743941	4.149300	-0.866600
H	3.010434	5.101307	-0.759816
N	-1.478828	-0.479441	-0.606298
C	-2.785986	-0.104245	-0.336708
C	-5.173932	1.129157	0.525773
C	-3.098168	1.235168	-0.713278
C	-3.704534	-0.819109	0.469233
C	-4.880601	-0.203678	0.872619
C	-4.290972	1.842362	-0.270493
H	-2.547615	1.684278	-1.544793
H	-3.477098	-1.836268	0.767992
H	-5.585258	-0.762297	1.481265
H	-4.533763	2.848535	-0.597540
H	-6.101850	1.582610	0.856433
Zr	-0.549170	1.187446	0.254481
C	-0.892473	-1.755150	-0.490251
C	-1.400892	-2.988992	-0.886885
H	-2.391718	-3.072455	-1.320669
C	-0.579377	-4.114523	-0.746349
H	-0.957584	-5.086286	-1.046046
C	0.725451	-4.009658	-0.257633
H	1.333180	-4.904808	-0.186405
C	2.668656	-2.552631	0.666999
H	2.655711	-2.765677	1.750902
C	3.717886	-3.490383	0.039583
H	4.709484	-3.269658	0.445478
H	3.756187	-3.368513	-1.046744
H	3.502535	-4.537948	0.261607

[PhN-MeQui-CH_2CH_2-Ph]ZrMe$^+$_1

N	0.350104	0.866274	-0.333173
C	1.251472	3.524227	-0.244482
C	-0.551544	1.895622	-0.114316
C	-0.183545	3.248946	-0.146723
C	2.137723	2.546473	-0.517251
H	3.206654	2.736412	-0.537028
H	1.597477	4.531491	-0.028868
C	2.535961	-0.046420	-0.618567
C	3.959559	-2.446520	-0.082939
C	2.676261	-0.514635	0.725476
C	3.159128	-0.788639	-1.642589
C	3.866955	-1.961130	-1.387493
C	3.370462	-1.724189	0.950376
H	3.094140	-0.442886	-2.665957
H	4.338057	-2.493238	-2.207719
H	3.481645	-2.069711	1.975101
H	4.503110	-3.361327	0.130647
N	-1.811889	0.097214	0.621628
C	-2.599671	-0.925057	0.128132
C	-3.652214	-3.295790	-0.981832
C	-2.334440	-2.196485	0.727938
C	-3.435631	-0.863007	-1.014757
C	-3.954154	-2.033781	-1.539441
C	-2.862006	-3.375457	0.150736
H	-1.989204	-2.221245	1.764727
H	-3.648599	0.100012	-1.466048
H	-4.598101	-1.981076	-2.412258
H	-2.687642	-4.331456	0.634833
H	-4.074229	-4.193601	-1.419978
Zr	-0.014775	-0.989607	0.456424
C	-1.825190	1.471244	0.303155
C	-2.832298	2.416082	0.495632
H	-3.826414	2.113757	0.808654
C	-2.511165	3.773876	0.342351
H	-3.284258	4.518673	0.498145
C	-1.204508	4.189186	0.068969
H	-0.971355	5.249507	0.041190
C	2.132815	0.197318	1.973252
H	2.895734	0.108554	2.756362
H	1.990466	1.259239	1.772994
C	0.791328	-0.426080	2.442158
H	0.188532	0.268061	3.030504
H	0.964829	-1.333903	3.042109
C	1.644458	1.177017	-0.975655
C	1.398475	1.287504	-2.503343
H	2.309516	1.579741	-3.033413
H	0.652198	2.064162	-2.676371
H	1.021994	0.348053	-2.921165

[PhN-MeQui-CH_2CH_2-Ph]ZrMe$^+$_2

N	0.853399	-0.388873	0.013699
C	2.097307	0.129408	0.415045
C	0.691492	-1.778348	0.000531
C	1.707304	-2.682318	0.310085
C	3.138201	-0.661266	0.730598
H	4.065282	-0.202362	1.062880
C	1.996952	1.612339	0.551560
C	1.393389	4.333836	0.962618
C	1.511417	2.400384	-0.534568
C	2.215266	2.220503	1.800069
C	1.930472	3.568735	2.002701
C	1.196052	3.755265	-0.289572
H	2.591519	1.611824	2.616228
H	2.109025	4.018464	2.974192
H	0.851552	4.371968	-1.116382
H	1.159618	5.382105	1.118493
N	-1.431487	-1.084138	-0.669037
C	-2.658959	-0.756259	-0.121064
C	-4.903626	0.469948	1.082866
C	-3.257685	0.409559	-0.693058
C	-3.223839	-1.303896	1.059787
C	-4.331907	-0.699791	1.628309
C	-4.376773	1.014094	-0.074643
H	-3.026461	0.654657	-1.733367
H	-2.780412	-2.188808	1.502387
H	-4.764866	-1.132251	2.525500
H	-4.845342	1.873712	-0.543908
H	-5.772844	0.916340	1.553249
Zr	-0.703060	0.884851	-0.488891
C	-0.616823	-2.184115	-0.320270
C	-0.944328	-3.537049	-0.314526
H	-1.943472	-3.869420	-0.576454
C	0.058539	-4.457706	0.016840
H	-0.177126	-5.516720	0.027628
C	1.357656	-4.040118	0.318634
H	2.109136	-4.783949	0.567436
C	1.459005	1.872995	-1.985451
H	1.860798	2.670372	-2.621192
H	2.132198	1.017139	-2.065328
C	0.041890	1.461900	-2.476024
H	0.080538	0.710781	-3.266713
H	-0.522101	2.332953	-2.846630
C	3.110898	-2.171018	0.614675
H	3.426778	-2.587300	1.583621
C	4.142218	-2.653603	-0.435444
H	5.143565	-2.287333	-0.188417
H	3.878933	-2.289603	-1.432919
H	4.181547	-3.745764	-0.468902