Electronic Supplementary Material (ESI) for Dalton Transactions


# Addition of a Phosphine Ligand Switches an *N*-Heterocyclic Carbene-Zirconium Catalyst from Oligomerization to Polymerization of 1-Hexene

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## *Contents*

## *1. Experimental details:*

All experiments were performed using conventional vacuum line and Schlenk tube techniques or in a glovebox under nitrogen atmosphere. Solvents were dried by the method of Grubbs.[1] *N,N'*-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine,[2] and $ZrBn_4$[3] were prepared according to published procedure. Potassium hexamethyldisilazane were purchased from Sigma Aldrich and used as received. Benzene-$d_6$ was degassed and passed through a plug of activated alumina prior to use. NMR spectra were recorded on Varian Mercury 300, Varian INOVA 500 or Varian INOVA 600 spectrometers and referenced to the solvent residual peak. Elemental analyses were performed by Robertson Microlit Laboratories, Inc., Ledgewood, NJ 07852.

**1,3-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1*H*-benzo[*d*]imidazol-3-ium chloride (1):** To a solution of phenylenediamine (6 g, 11.61 mmol) in triethyl orthoformate (120 mL) was added a solution of $HCl_{conc}$ (0.67 mL) and 12 drops of acetic acid. After one hour at 60 °C, the white precipitate was collected and washed several times with hexane yielding the desired benzimidazolium **1** as a white powder (4.8 g, 8.52 mmol, 74 %). $^1$H NMR (400 MHz, $CDCl_3$): δ 9.29 (s, 2H, OH), 9.04 (s, 1H, NCHN), 7.62 (s, 2H, CH), 7.68-7.59 (m, 4H, CH), 7.56 (d, $J$ = 2.3 Hz, 2H, CH), 7.16 (d, $J$ = 2.3 Hz, 2H, CH), 1.48 (s, 18H, *t*Bu), 1.34 (s, 18H, *t*Bu). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 149.1 (C), 143.0 (C), 141.5 (NCHN), 141.4 (C), 132.2 (C), 127.7 (CH), 126.7 (CH), 121.0 (C), 120.7 (CH), 114.4 (CH), 35.7 ($C_{t\mathrm{Bu}}$), 34.5 ($C_{t\mathrm{Bu}}$), 31.4 ($CH_{t\mathrm{Bu}}$), 29.6 ($CH_{t\mathrm{Bu}}$). Anal. Calcd. for $C_{35}H_{47}ClN_2O_2$: C, 74.64; H, 8.41; N, 4.97. Found: C, 74.68; H, 8.27; N, 4.68.

**(OCO)$ZrBn_2$ (2)**: A solution of benzimidazolium chloride salt **1** (0.1 g, 0.18 mmol) in toluene (4 mL) and a solution of KHMDS (35.4 mg, 0.18 mmol) in toluene (1 mL) were mixed and stirred for 30 minutes at room temperature. Then a solution of $ZrBn_4$ (77 mg, 0.17 mmol) in toluene (5 mL) was added and the mixture was stirred for an extra hour. After evaporation, the residue was solubilized in pentane and filtered through a pad of Celite. A yellow powder was obtained after evaporation affording the desired complex (0.123 g, 88 %). Further purification can be carried out by precipitation of the complex in a pentane solution at low temperature (-35 °C). $^1$H NMR

[1] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518-1520.
[2] Blackmore, K. J.; Lal, N.; Ziller, J. W.; Heyduck, A. F. *Eur. J. Inorg. Chem.* **2009**, 735-743.
[3] Zucchini, U.; Albizzati, E.; Giannini, U. *J. Organomet. Chem.* **1971**, *26*, 357-372.

(400 MHz, $C_6D_6$): δ 7.77 (m, 2H, CH), 7.75 (d, *J* = 2.4 Hz, 2H, CH), 7.62 (d, *J* = 2.4 Hz, 2H, CH), 6.99 (d, *J* = 7.8 Hz, 4H, CH), 6.88 (m, 2H, CH), 6.79 (pt, *J* = 7.7 Hz, 4H, CH), 6.50 (pt, *J* = 7.3 Hz, 2H, CH), 2.45 (s, 4H, $CH_2Ph$), 1.82 (s, 18H, *t*Bu), 1.40 (s, 18H, *t*Bu). $^{13}C$ NMR (100 MHz, $C_6D_6$): δ 199.9 (NCN), 150.9 (C), 140.0 (C), 139.2 (C), 138.6 (C), 133.9 (C), 129.8 (CH), 129.1 (CH), 128.2 (C), 127.9 (C), 124.8 (CH), 122.4 (CH), 122.2 (CH), 118.2 (CH), 114.7 (CH), 57.6 ($CH_2PH$), 36.2 ($C_{tBu}$), 34.7 ($C_{tBu}$), 31.8 ($CH_{tBu}$), 30.5 ($CH_{tBu}$). Anal. Calcd. for $C_{49}H_{59}N_2O_2Zr$: C, 73.64; H, 7.44; N, 3.51. Found: C, 70,20; H, 7.41; N, 3.59. (This compound is air- and moisture-sensitive, and despite repeated attempts satisfactory %C analysis could not be obtained.)

**Generation of [(OCO)ZrBn][B($C_6F_5$)$_4$] (3):** A solution of zirconium complex **2** (20 mg, 0.025 mmol) in chlorobenzene-d5 (0.6 mL) was added to [$Ph_3C$][B($C_6F_5$)$_4$] (23 mg, 0.025 mmol) powder at room temperature. The dark yellow solution was transferred to a J-Young NMR tube and NMR analysis confirmed the quantitative formation of complex **3**. $^1H$ NMR (500 MHz, $C_6D_5Cl$, 0 ºC): δ 7.77 (m, 2H, aryl), 7.70 (d, *J* = 2.3 Hz, 2H, aryl), 7.58 (d, *J* = 2.3 Hz, 2H, aryl), 7.24 (m, 2H, aryl), 6.56 (br, 2H, Bn), 6.41 (br, 1H, Bn), 6.19 (br, 2H, Bn), 2.95 (s, 2H, C*H*$_2$Ph), 1.54 (s, 18H, *t*Bu), 1.41 (s, 18H, *t*Bu). $^1H$ NMR (300 MHz, $C_6D_5Cl$, rt): δ 7.78 (m, 2H, aryl), 7.68 (d, *J* = 2.3 Hz, 2H, aryl), 7.57 (d, *J* = 2.3 Hz, 1H, aryl), 7.24 (m, 2H, aryl), 6.57 (t, *J* = 7.4 Hz, 2H, Bn), 6.42 (t, *J* = 7.4 Hz, 1H, Bn), 6.17 (d, *J* = 7.4 Hz, 1H, Bn), 2.94 (s, 2H, C*H*$_2$Ph), 1.53 (s, 18H, *t*Bu), 1.40 (s, 18H, *t*Bu). $^{13}C$ NMR (125 MHz, $C_6D_5Cl$, 0 ºC): δ 196.0 (NCN), 148.9 (d, $^1J_{CF}$ = 240.0 Hz, $C_6F_5$), 148.6 (C), 143.8 (C), 138.9 (d, $^1J_{CF}$ = 240.0 Hz, $C_6F_5$), 136.8 (d, $^1J_{CF}$ = 240.0 Hz, $C_6F_5$), 133.2 (C), 133.1 (C), 131.9 (C), 126.6 (CH), 123.8 (CH), 118.7 (CH), 114.3 (CH), 71.5 ($^1J_{CH}$ = 142 Hz, $CH_2Ph$), 35.9 ($C_{tBu}$), 34.9 ($C_{tBu}$), 31.5 ($CH_{tBu}$), 30.0 ($CH_{tBu}$). Broad peaks for the aromatic benzyl signals were observed at 0 °C, indicating the fluxionality of the benzyl group. Some aryl and benzyl signals overlapped with those of the chlorobenzene-$d_5$ and the 1,1,1,2-tetraphenylethane generated by abstraction of the benzyl group. $^{19}F$ NMR (282.09 MHz, $C_6D_5Cl$, rt): δ -131.8 (br, 6F, o-$C_6F_5$), -162.6 (t, *J* = 20.6 Hz, 3F, p-$C_6F_5$), -166.3 (br, 6F, m-$C_6F_5$).

**Generation of [(OCO)ZrBn($PMe_3$)][B($C_6F_5$)$_4$] (4):** In the J-Young NMR tube, one equivalent of trimethylphosphine was added to the solution of complex **3** in chlorobenzene-$d_5$ affording

quantitative formation of the cationic phosphine zirconium complex **4** as a light yellow solution. $^{1}$H NMR (500 MHz, $C_6D_5Cl$, 0 ºC): δ 7.72 (br s, 4H, aryl), 7.55 (br s, 2H, aryl), 7.39 (br, 3H, aryl), 7.32-7.23 (br peaks, 4H, aryl), 3.00 (d, $J_{HP}$ = 6.5 Hz, C*H*$_2$Ph), 1.55 (s, 18H, *t*Bu), 1.36 (s, 18H, *t*Bu), 0.52 (d, $J_{HP}$ = 7.9 Hz, 9H, $PMe_3$). $^{13}$C NMR (125 MHz, $C_6D_5Cl$, 0 ºC): δ 196.4 (NCN), 149.1 (C), 148.9 (d, $^{1}J_{CF}$ = 241.0 Hz, $C_6F_5$), 143.7 (C), 138.9 (d, $^{1}J_{CF}$ = 240.0 Hz, $C_6F_5$), 138.2 (C), 136.8 (d, $^{1}J_{CF}$ = 240.0 Hz, $C_6F_5$), 133.6 (C), 133.3 (CH), 132.0 (C), 129.9 (CH), 126.2 (CH), 123.6 (CH), 124.7 (CH), 118.3 (CH), 114.5 (CH), 63.2 (br, $CH_2Ph$), 35.8 ($C_{tBu}$), 34.9 ($C_{tBu}$), 31.4 ($CH_{tBu}$), 29.6 ($CH_{tBu}$), 12.7 (d, $J_{CP}$ = 20.6 Hz, $PMe_3$). Signals for two quaternary carbons are missing, probably overlapping with those of the chlorobenzene-$d_5$ and the 1,1,1,2-tetraphenylethane generated by abstraction of the benzyl group. $^{31}$P NMR (202.34 MHz, $C_6D_5Cl$, 0 ºC): δ -20.2. $^{19}$F NMR (282.09 MHz, $C_6D_5Cl$, rt): δ –131.7 (br, 2F, o-$C_6F_5$), -162.4 (t, $J$ = 20.6 Hz, 1F, p-$C_6F_5$), -166.2 (br, 2F, m-$C_6F_5$).

**Generation of [(OCO)ZrBn(PMe$_3$)$_2$][B(C$_6$F$_5$)$_4$] (5):** In the J-Young NMR tube, one equivalent of trimethylphosphine was added to the solution of complex **4** in chlorobenzene-$d_5$ affording quantitative formation of the cationic bisphosphine zirconium complex **5** as a light yellow solution. $^{1}$H NMR (500 MHz, $C_6D_5Cl$, 0 ºC): δ 8.13 (m, 2H, aryl), 7.91 (d, $J$ = 2.4 Hz, 2H, aryl), 7.73 (d, $J$ = 2.4 Hz, 1H, aryl), 7.55 (d, $J$ = 2.4 Hz, 2H, aryl), 7.39 (m, 5H, aryl), 7.28 (d, $J$ = 2.4 Hz, 1H), 2.77 (t, $J$ = 4.1 Hz, 2H, C*H*$_2$Ph), 1.48 (s, 18H, *t*Bu), 1.39 (s, 18H, *t*Bu), 0.45 (br, 9H, $PMe_3$), -0.10 (br, 9H, $PMe_3$). $^{13}$C NMR (125 MHz, $C_6D_5Cl$, 0 ºC): δ 199.6 (NCN), 149.6 (C), 148.9 (d, $^{1}J_{CF}$ = 241.0 Hz, $C_6F_5$), 144.8 (C), 140.2 (C), 138.9 (d, $^{1}J_{CF}$ = 240.0 Hz, $C_6F_5$), 138.5 (C), 137.0 (C), 136.8 (d, $^{1}J_{CF}$ = 240.0 Hz, $C_6F_5$), 132.7 (CH), 131.3 (C), 130.2 (CH), 127.2 (CH), 123.8 (CH), 118.2 (CH), 114.6 (CH), 61.2 (br, $CH_2Ph$), 35.8 ($C_{tBu}$), 34.9 ($C_{tBu}$), 31.5 ($CH_{tBu}$), 29.5 ($CH_{tBu}$), 12.8 (br, $PMe_3$), 11.7 (br, $PMe_3$). Signals for two carbons are missing, probably overlapping with those of the chlorobenzene-$d_5$ and the 1,1,1,2-tetraphenylethane generated by abstraction of the benzyl group.$^{31}$P NMR (202.34 MHz, $C_6D_5Cl$, 0 ºC): δ -27.96 and -32.65 (ABq, 2P, $J_{PP}$ = 99.8 Hz, $PMe_3$). $^{19}$F NMR (282.09 MHz, $C_6D_5Cl$, rt): δ –131.7 (br, 2F, o-$C_6F_5$), -162.4 (t, $J$ = 20.6 Hz, 1F, p-$C_6F_5$), -166.2 (br, 2F, m-$C_6F_5$).

***2. Oligomerization/polymerization of 1-hexene:***

In a vial, a solution of complex **2** (5 mg, 0.0063 mmol) in chlorobenzene (0.7 mL) was added to $[Ph_3C][B(C_6F_5)_4]$ powder. After 10 minutes at room temperature, the solution was added to a mixture of 1-hexene (0.53 g, 0.63 mmol) and additive (none, phosphine or amine) and then stored in a 10 mL-Strauss flask. After stirring during 14 hours, the reaction was quenched with 0.1 mL of methanol and one drop of hydrochloric acid. In the case of oligomerization, biphenyl (50 mg) was added to get an internal reference for the GC, and then the mixture was filtered through a plug of silica.

**Table S1.** Oligomerization/polymerization of 1-hexene using complex **2**.[a]

| Entry | Additives | Conv. (%) | C12 (%) | C18 (%) | C24 (%) | C30 (%) | C36 (%) | C42 (%) | Higher oligomers | Polymer (g, Mn[b]) |
|---|---|---|---|---|---|---|---|---|---|---|
| **1** | None | 89 | 7 | 7 | 15 | 13 | 11 | 5 | 31 | <0.02 |
| **2** | None[c] | 68 | 7 | 6 | 12 | 10 | 8 | 5 | 20 | <0.02 |
| **3** | $[HNMe_2Ph][B(C_6F_5)_4]$[d] | 5 | 4 | 1 | - | - | - | - | - | - |
| **4** | 2.6-lutidine | 0 | - | - | - | - | - | - | - | - |
| **5** | $PPh_3$ | 96 | 7 | 6 | 16 | 15 | 13 | 6 | 33 | <0.02 |
| **6** | $PEt_3$ | 99 | 0 | 0 | 0 | 0 | 2 | 6 | nd | 0.48, 2965 |
| **7** | $PEt_3$[e] | 0 | - | - | - | - | - | - | - | - |
| **8** | $PMe_3$ | 99 | 0 | 0 | 0 | 0 | 0 | 0 | nd | 0.49, 10545 |
| **9** | $PCy_3$ | 0 | - | - | - | - | - | - | - | - |

[a] Conditions: [**2**] = $[Ph_3C][B(C_6F_5)_4]$ = 0.006 mmol; 1-hexene (0.53 g, 6.3 mmol); additive (1 equiv., 0.006 mmol), room temperature; reaction time: 14h, the oligomers obtained were analyzed by GC. [b] Calculated by $^1H$ NMR spectroscopy. [c] A second aliquot of 1000 equivalents of 1-hexene was added after 14 hours (so total 1-hexene at the end of reaction is 2000 equivalents). [d] The anilinium was used as activator. [e] 2 equivalents of $PEt_3$.

**a) GC trace:**

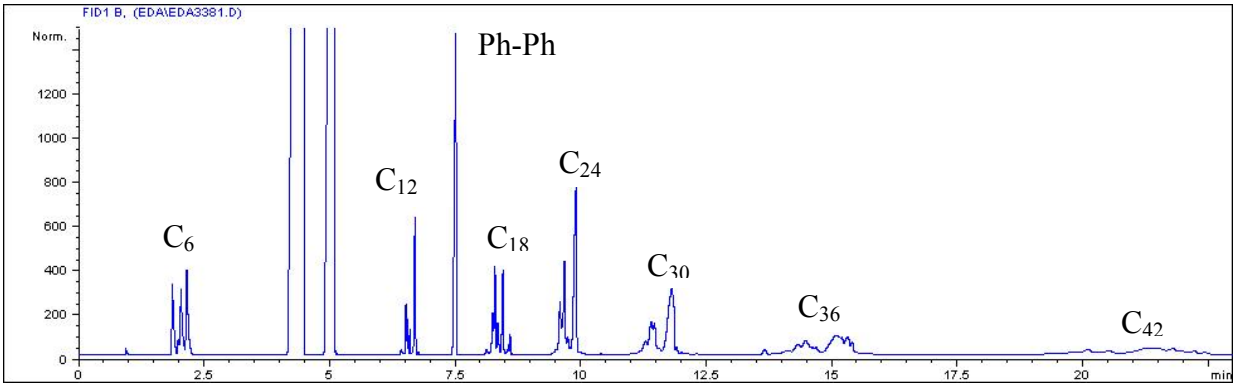



**Figure S1.** GC analysis of oligo(1-hexene)s obtained using **2**/[$Ph_3C$][$B(C_6F_5)_4$] (Table S1, entry 1).

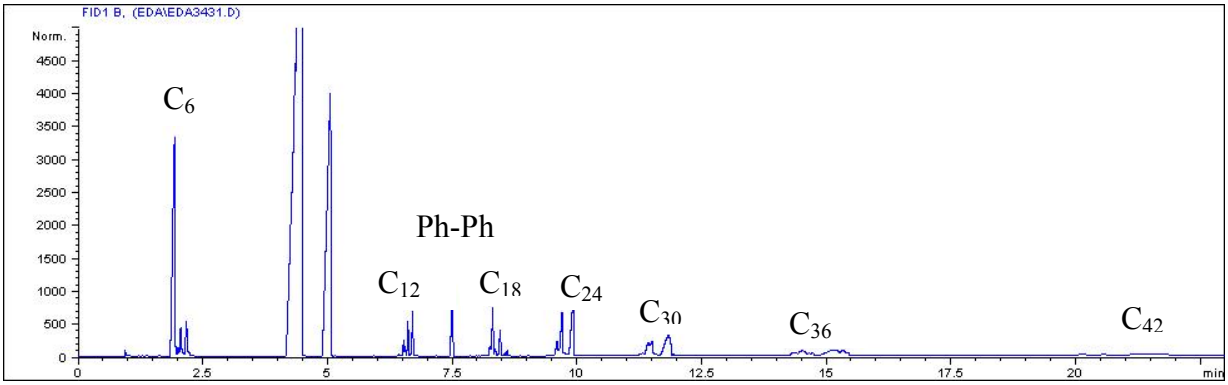



**Figure S2.** GC analysis of oligo(1-hexene)s obtained after addition of a total of 2000 equivalents of 1-hexene to **2**/[$Ph_3C$][$B(C_6F_5)_4$] (Table S1, entry 2). Conditions: **2**/[$Ph_3C$][$B(C_6F_5)_4$] was added to 1000 equivalents of 1-hexene; after 14 hours another 1000 equivalents of 1-hexene were added. The mixture was stirred an extra 14 hours before quenching.

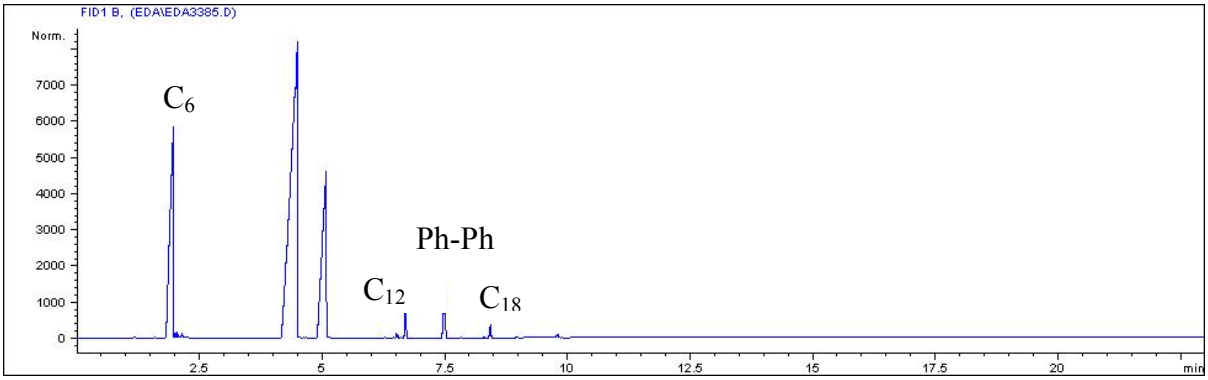



**Figure S3:** GC analysis of oligo(1-hexene)s obtained using **2**/[$HNMe_2Ph$][$B(C_6F_5)_4$] (Table S1, entry 3).

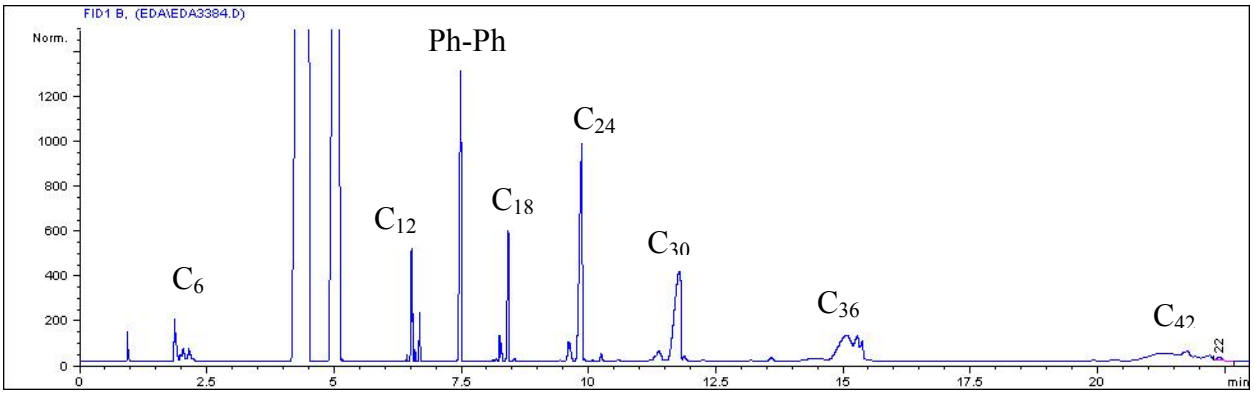



**Figure S4.** GC analysis of oligo(1-hexene)s obtained using **2**/[$Ph_3C$][$B(C_6F_5)_4$ with one equivalent of triphenylphosphine (Table S1, entry 5).

**b) Analysis of oligo(1-hexene)s obtained using 2/[$Ph_3C$][$B(C_6F_5)_4$] (Table S1, entry 1):**

***MALDI-TOF mass spectrometry:***

The mass spectrum was acquired with a Voyager DE-PRO™ MALDI-TOF mass spectrometer (Applied BioSystems) that uses a 20 Hz nitrogen laser (337 nm). The mass spectrometer was operated in reflectron mode for higher resolution and mass accuracy. The mass axis was calibrated superficially with the Sequazyme Kit™ provided by the manufacturer. The method settings were: Accelerating voltage 20kV, Grid voltage 75%, Mirror voltage ratio 1.12, Guide wire 0.005%, Extraction delay time 100 nsec.

Oligo(1-hexene) was prepared at 10 mg/mL in THF, dithranol matrix at 20 mg/mL and AgTFA at 10 mg/mL. The oligo(1-hexene) was mixed with dithranol and AgTFA in a 1:2:1 ratio and spotted on a stainless steel MALDI target for analysis.

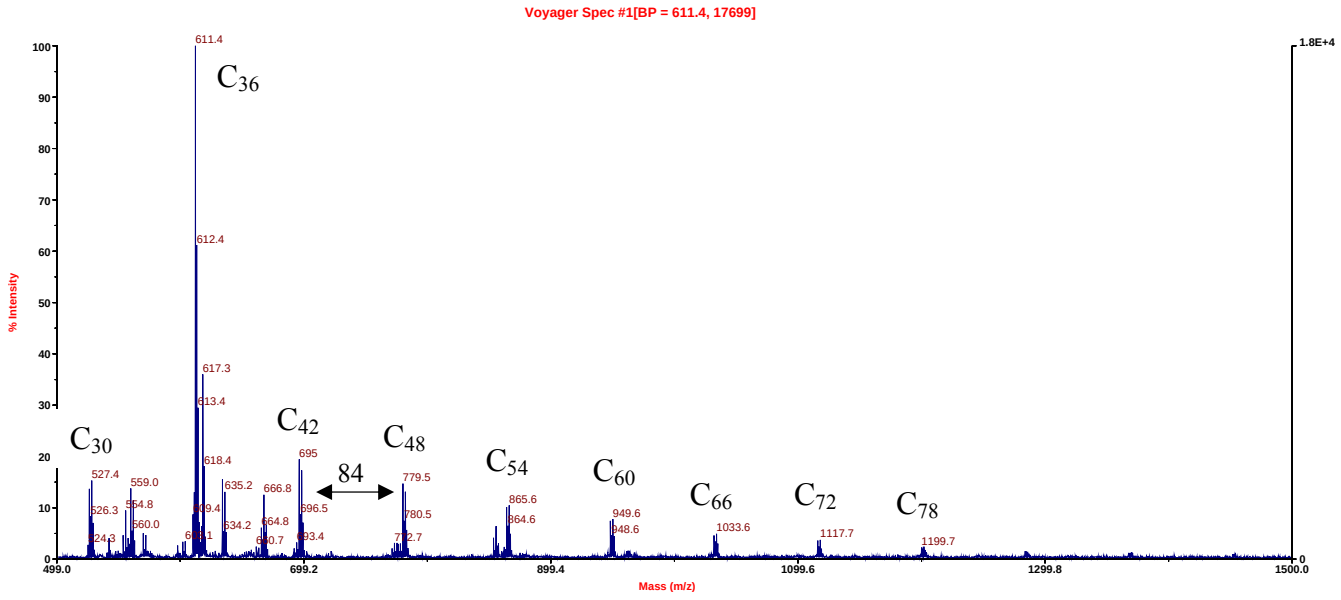



**Figure S5.** MALDI-TOF of oligo(1-hexene) obtained using **2**/[$Ph_3C$][$B(C_6F_5)_4$] (Table S1, entry 1). Peaks correspond to the silver adduct.

## c) *$^{1}$H and $^{13}$C NMR spectrum of oligomer/polymer of 1-hexene:*

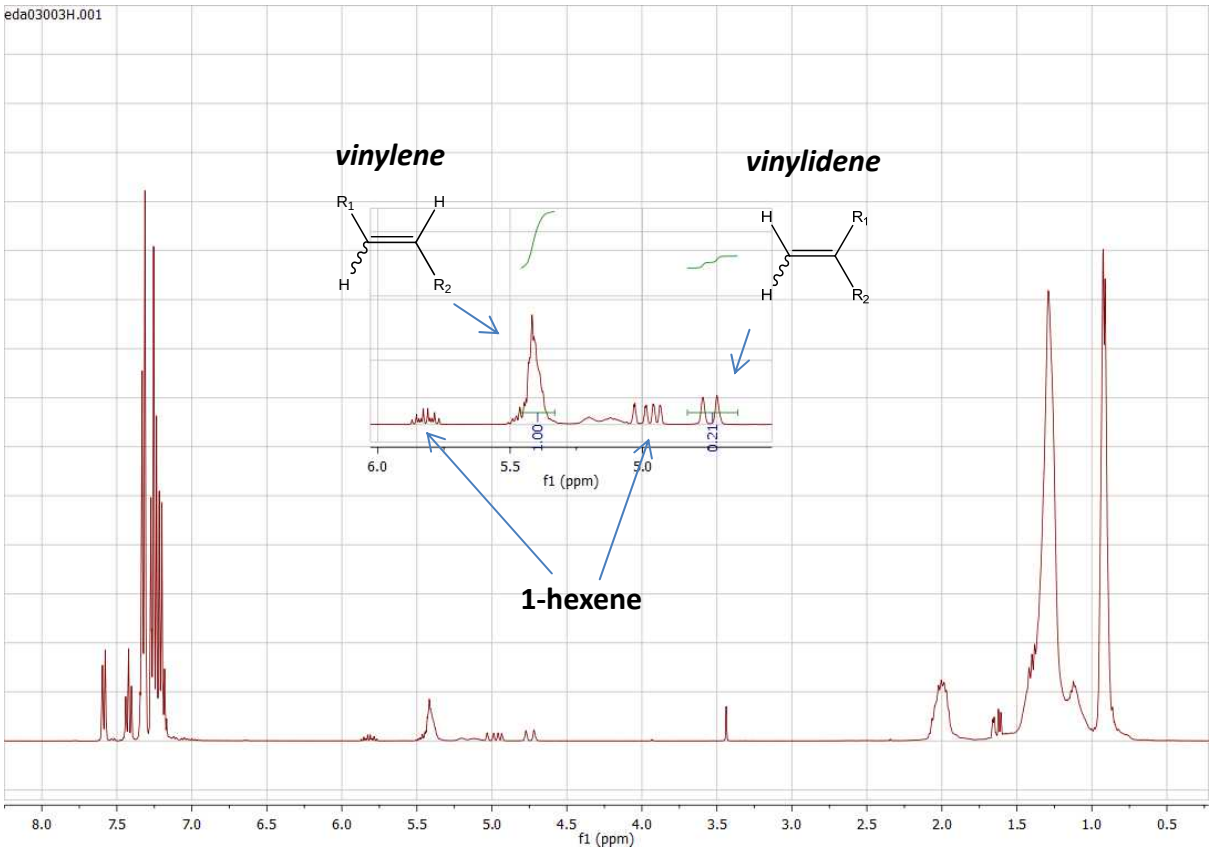



**Figure S6.** $^{1}$H NMR in chloroform-$d_1$ of oligo(1-hexene)s obtained using **2**/$[Ph_3C][B(C_6F_5)_4$ (presence of chlorobenzene and biphenyl) (Table S1, entry 1).

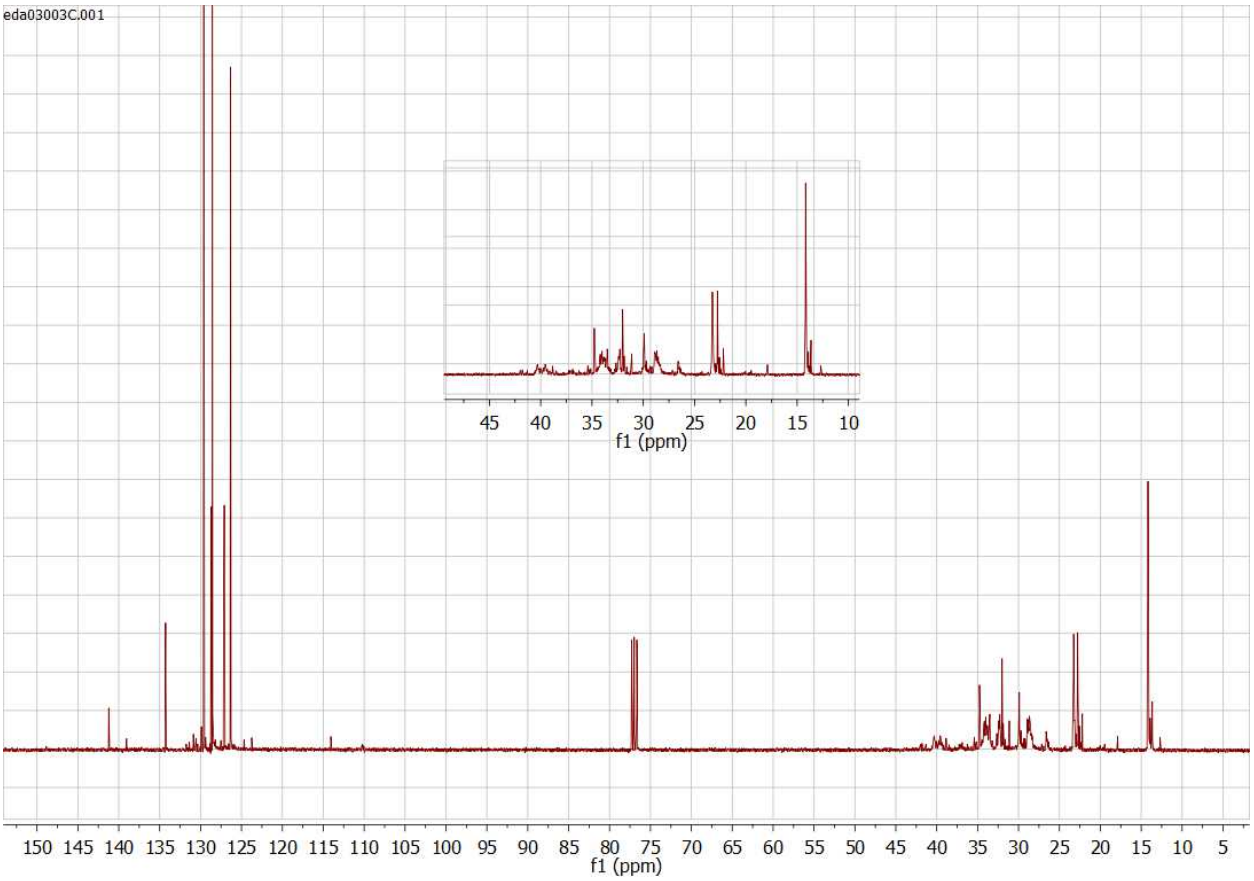



**Figure S7.** $^{13}C$ NMR in chloroform-$d_1$ of oligo(1-hexene)s obtained using **2**/$[Ph_3C][B(C_6F_5)_4$ (presence of chlorobenzene and biphenyl) (Table S1, entry 1).

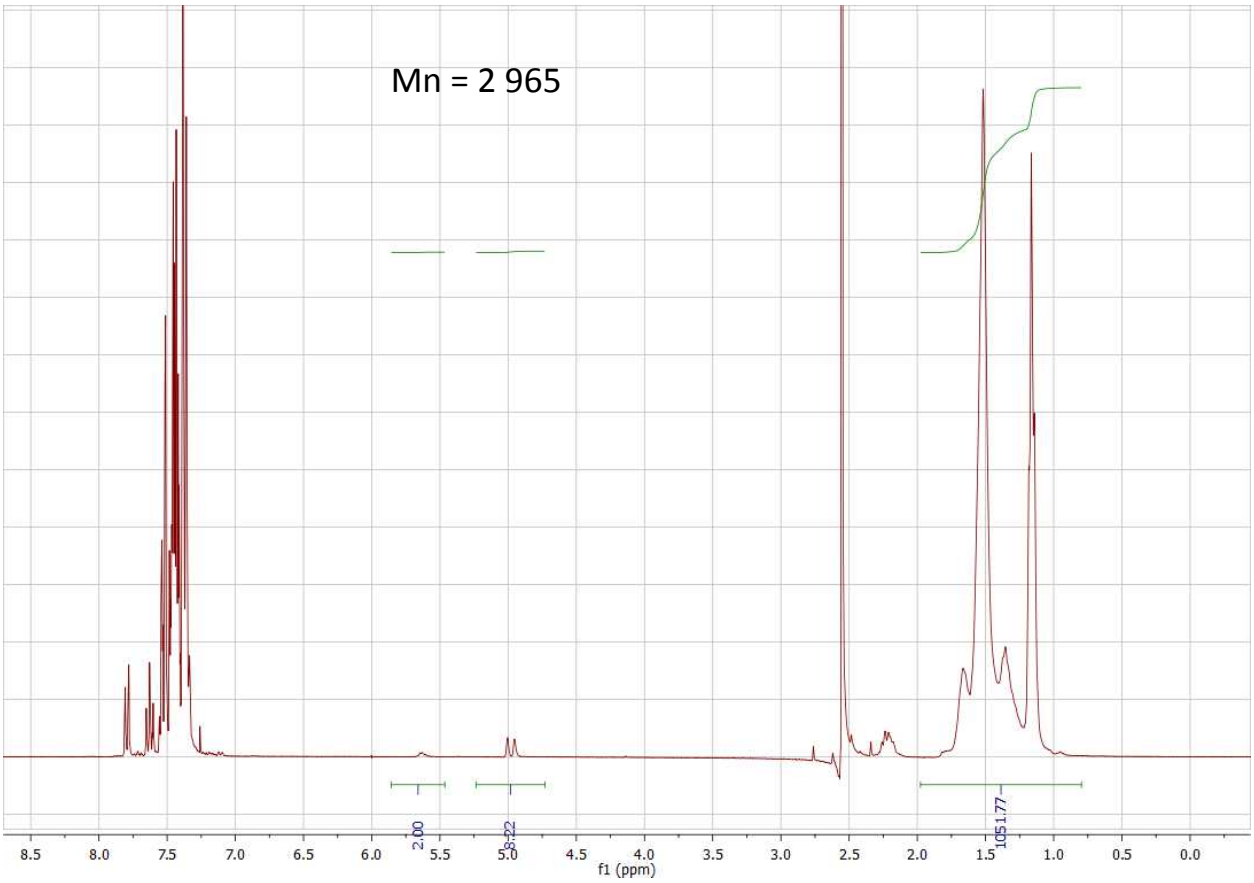



**Figure S8.** $^{1}$H NMR in chloroform-$d_1$ of poly(1-hexene) obtained using **2**/$[Ph_3C][B(C_6F_5)_4$ with one equivalent of triethylphosphine (Mn = 2965) (presence of chlorobenzene and toluene) (Table S1, entry 6).

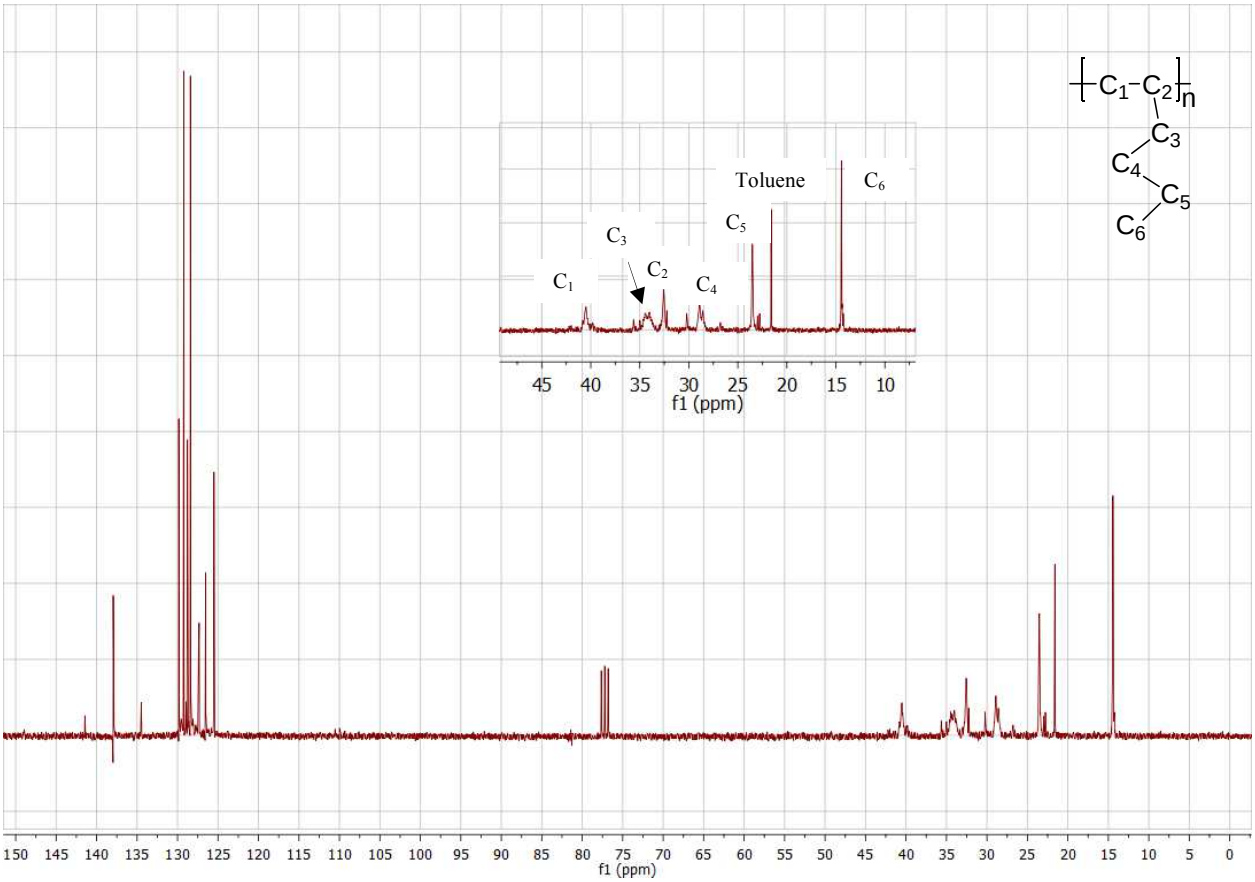



**Figure S9.** $^{13}C$ NMR in chloroform-$d_1$ of poly(1-hexene) obtained using **2**/$[Ph_3C][B(C_6F_5)_4$ with one equivalent of triethylphosphine (Mn = 2965) (presence of chlorobenzene and toluene) (Table S1, entry 6).

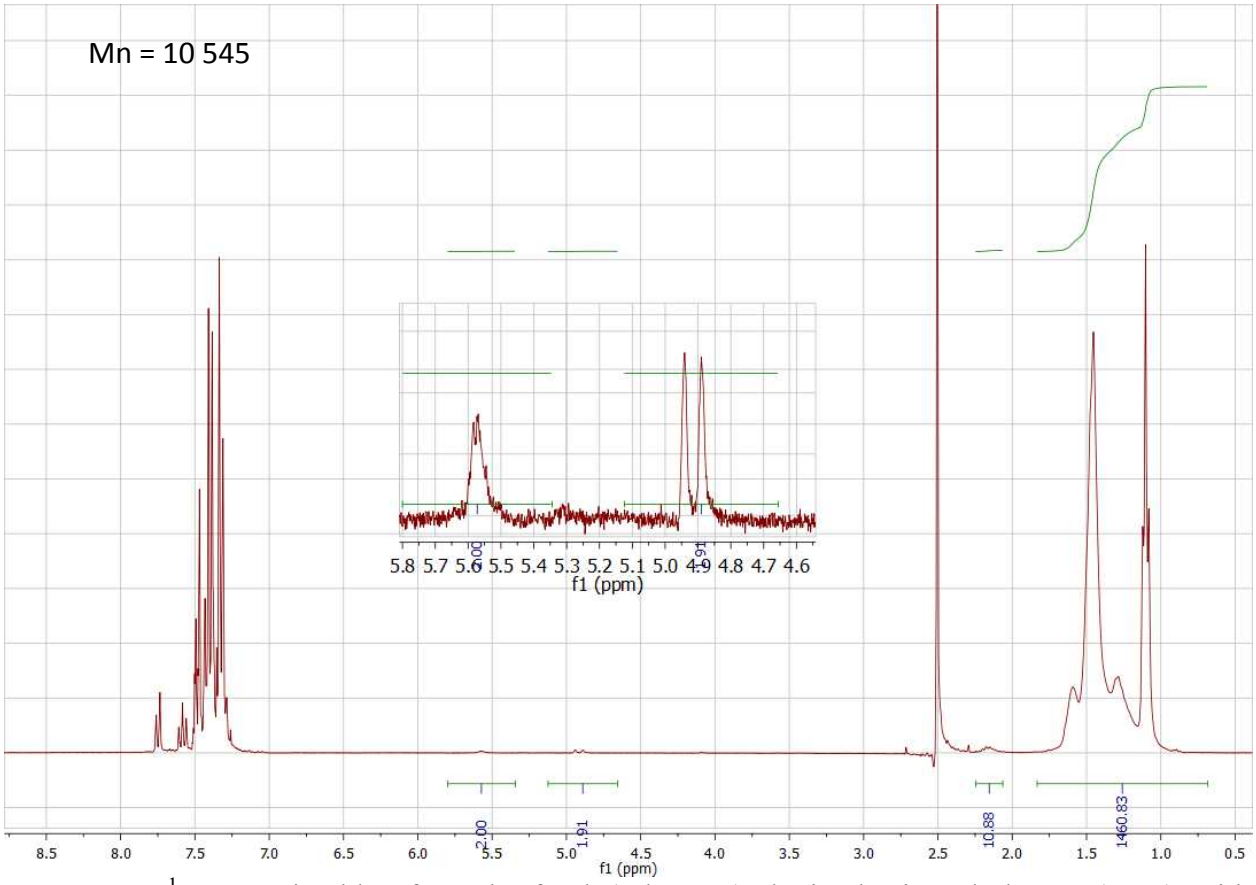



**Figure S10.** $^{1}H$ NMR in chloroform-$d_1$ of poly(1-hexene) obtained using **2**/$[Ph_3C][B(C_6F_5)_4$ with one equivalent of trimethylphosphine (Mn = 10545) (presence of chlorobenzene and toluene) (Table S1, entry 8).

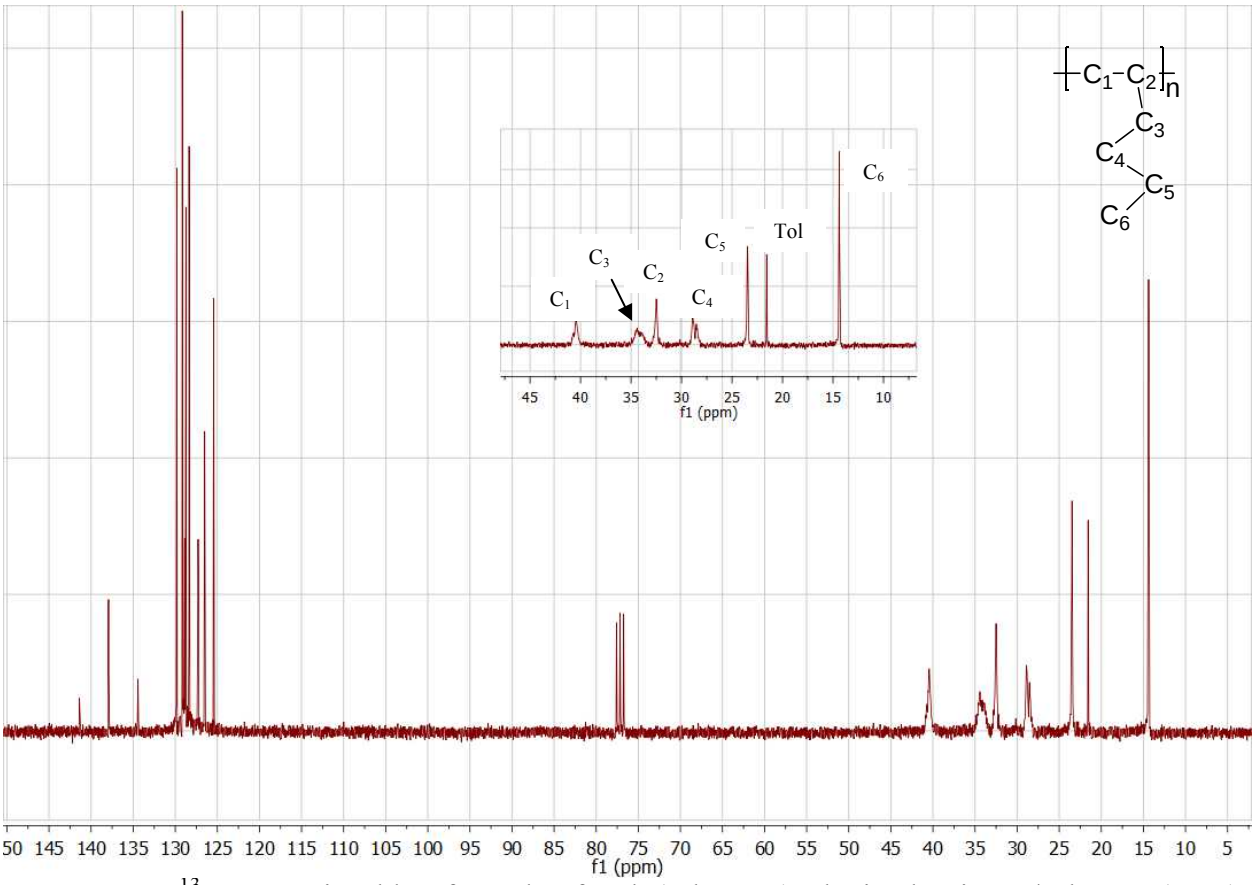



**Figure S11.** $^{13}C$ NMR in chloroform-$d_1$ of poly(1-hexene) obtained using **2**/$[Ph_3C][B(C_6F_5)_4$ with one equivalent of trimethylphosphine (presence of chlorobenzene and toluene) (Table S1, entry 8).

**d) <u>Kinetic Analysis:</u>**

5 reactions were set up in parallel (see general procedure for oligomerization/polymerization of 1-hexene, page 5) and quenched at different times.

| Quenching time (min.) | Conv. (%) |
|---|---|
| 60 | 60 |
| 120 | 78 |
| 240 | 87 |
| 330 | 89 |
| 1550 | 89 |

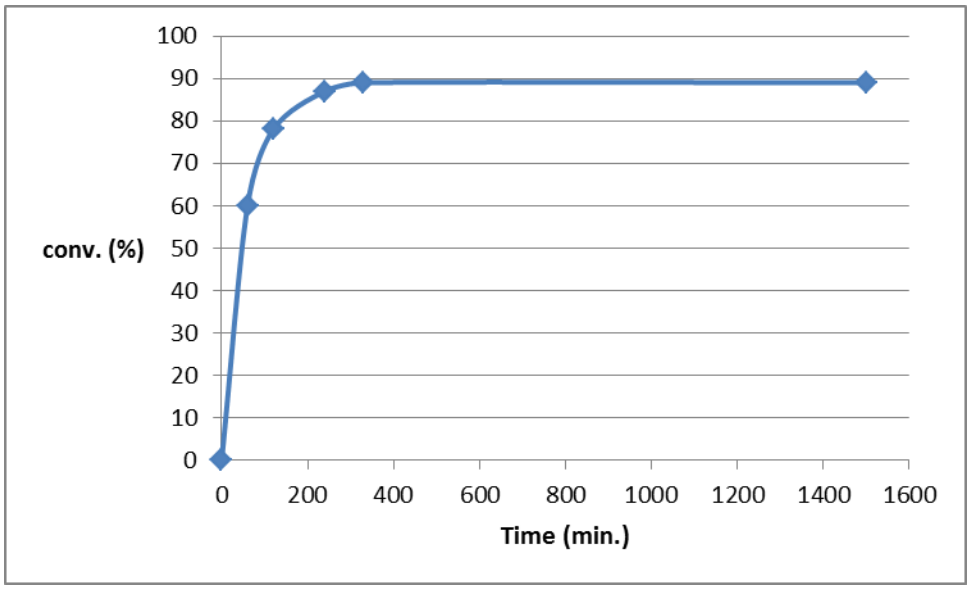
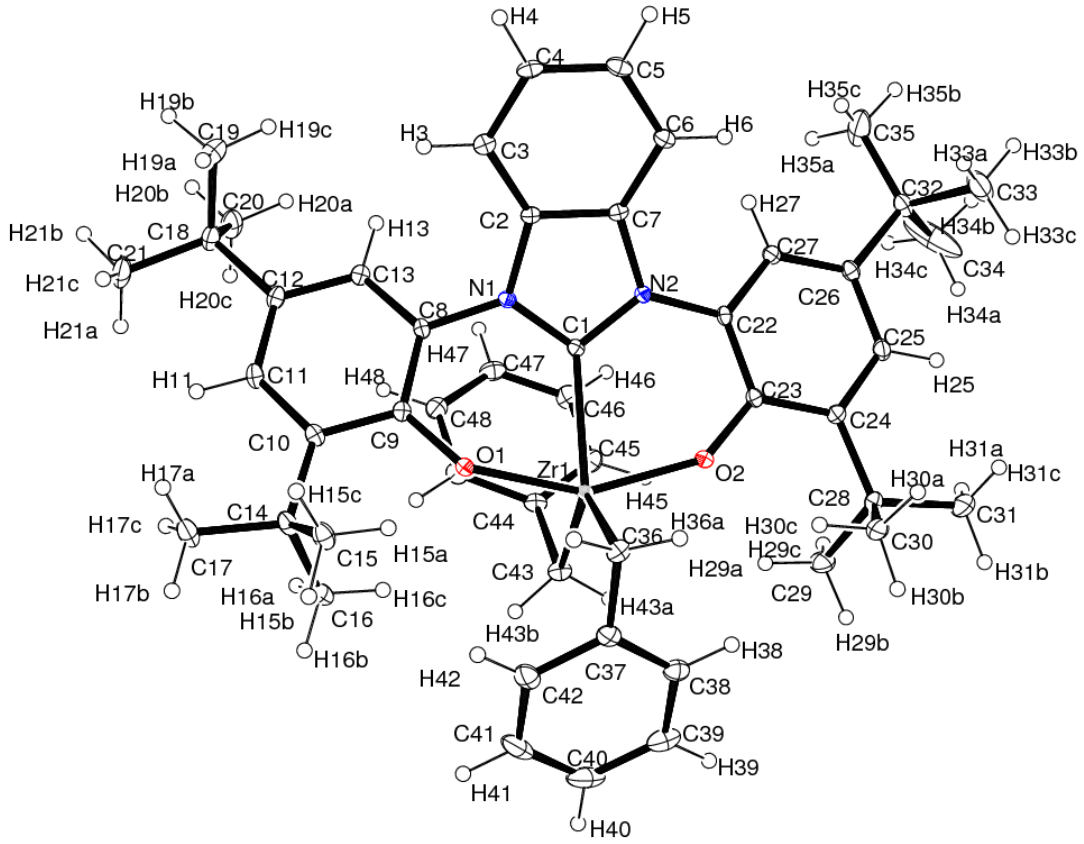
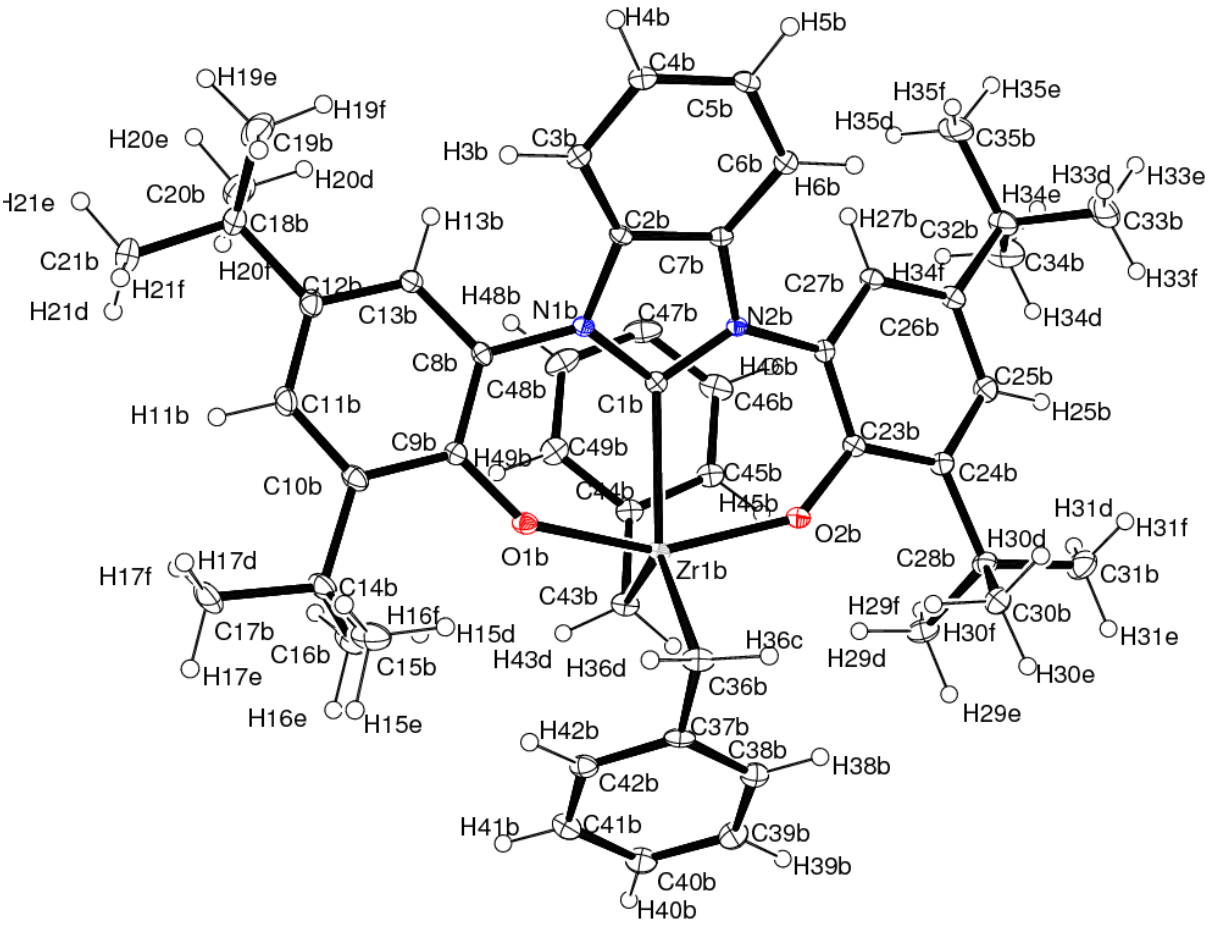



**Figure S12.** Kinetic analysis using **2**/[$Ph_3C$][$B(C_6F_5)_4$].

***3. Crystallographic data for complex 2 (CCDC 942447):***

Two independent molecules are observed in the cell:





| | |
|---|---|
| Empirical formula | C53 H68 N2 O3 Zr |
| Formula weight | 872.31 |
| Crystallization solvent | ether |
| Crystal shape | lump |
| Crystal color | yellow |
| Crystal size | 0.11 x 0.13 x 0.21 mm |

## Data Collection

| | | |
|---|---|---|
| Preliminary photograph(s) | rotation | |
| Type of diffractometer | Bruker APEX-II CCD | |
| Wavelength | 0.71073 Å MoK | |
| Data collection temperature | 100 K | |
| Theta range for 9041 reflections used in lattice determination | 2.25 to 30.38° | |
| Unit cell dimensions | a = 21.4874(19) Å<br>b = 21.1068(18) Å<br>c = 22.3719(18) Å | α= 90°<br>β= 111.269(2)°<br>γ = 90° |
| Volume | 9455.2(14) $Å^3$ | |
| Z | 8 | |
| Crystal system | monoclinic | |
| Space group | P 1 21/n 1 (# 14) | |
| Density (calculated) | 1.226 $g/cm^3$ | |
| F(000) | 3712 | |
| Theta range for data collection | 1.6 to 32.8° | |
| Completeness to theta = 25.000° | 100.0% | |
| Index ranges | -32 ≤ h ≤ 32, -30 ≤ k ≤ 31, -33 ≤ l ≤ 33 | |
| Data collection scan type | and scans | |
| Reflections collected | 238757 | |
| Independent reflections | 33053 [$R_{int}$= 0.0941] | |
| Reflections > 2□(I) | 21641 | |
| Average □(I)/(net I) | 0.0802 | |
| Absorption coefficient | 0.28 $mm^{-1}$ | |
| Absorption correction | Semi-empirical from equivalents | |
| Max. and min. transmission | 1.0000 and 0.8905 | |

## Structure Solution and Refinement

| | |
|---|---|
| Primary solution method | ? |
| Secondary solution method | ? |
| Hydrogen placement | geom |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 33053 / 0 / 1091 |
| Treatment of hydrogen atoms | constr |
| Goodness-of-fit on $F^2$ | 1.13 |
| Final R indices [I>2σ(I), 21641 reflections] | R1 = 0.0479, wR2 = 0.0924 |
| R indices (all data) | R1 = 0.0980, wR2 = 0.1049 |
| Type of weighting scheme used | calc |
| Weighting scheme used | |
| Max shift/error | 0.002 |
| Average shift/error | 0.000 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.01 and -0.73 e·Å$^{-3}$ |

## Programs Used

| | |
|---|---|
| Cell refinement | SAINT V8.27B (Bruker-AXS, 2007) |
| Data collection | APEX2 2013.2-0 (Bruker-AXS, 2007) |
| Data reduction | SAINT V8.27B (Bruker-AXS, 2007) |
| Structure solution | SHELXT (Sheldrick, 2012) |
| Structure refinement | SHELXL-2013/2 (Sheldrick, 2013) |
| Graphics | DIAMOND 3 (Crystal Impact, 1999) |

## Bond lengths [Å] and angles [°] for complex 2:

| | | | |
|---|---|---|---|
| Zr(1)-O(1) | 1.9957(12) | N(2)-C(1) | 1.370(2) |
| Zr(1)-O(2) | 1.9953(11) | N(2)-C(7) | 1.408(2) |
| Zr(1)-C(1) | 2.3358(17) | N(2)-C(22) | 1.431(2) |
| Zr(1)-C(36) | 2.3038(17) | C(2)-C(3) | 1.388(2) |
| Zr(1)-C(37) | 2.6406(17) | C(2)-C(7) | 1.391(2) |
| Zr(1)-C(43) | 2.2737(18) | C(3)-H(3) | 0.9500 |
| Zr(1)-C(44) | 2.8246(16) | C(3)-C(4) | 1.384(2) |
| O(1)-C(9) | 1.341(2) | C(4)-H(4) | 0.9500 |
| O(2)-C(23) | 1.3430(19) | C(4)-C(5) | 1.390(3) |
| N(1)-C(1) | 1.360(2) | C(5)-H(5) | 0.9500 |
| N(1)-C(2) | 1.405(2) | C(5)-C(6) | 1.378(3) |
| N(1)-C(8) | 1.432(2) | C(6)-H(6) | 0.9500 |

| | | | |
|---|---|---|---|
| C(6)-C(7) | 1.396(2) | C(31)-H(31A) | 0.9800 |
| C(8)-C(9) | 1.403(2) | C(31)-H(31B) | 0.9800 |
| C(8)-C(13) | 1.384(2) | C(31)-H(31C) | 0.9800 |
| C(9)-C(10) | 1.411(2) | C(32)-C(33) | 1.524(3) |
| C(10)-C(11) | 1.397(3) | C(32)-C(34) | 1.510(3) |
| C(10)-C(14) | 1.532(2) | C(32)-C(35) | 1.492(3) |
| C(11)-H(11) | 0.9500 | C(33)-H(33A) | 0.9800 |
| C(11)-C(12) | 1.385(2) | C(33)-H(33B) | 0.9800 |
| C(12)-C(13) | 1.391(2) | C(33)-H(33C) | 0.9800 |
| C(12)-C(18) | 1.532(3) | C(34)-H(34A) | 0.9800 |
| C(13)-H(13) | 0.9500 | C(34)-H(34B) | 0.9800 |
| C(14)-C(15) | 1.540(2) | C(34)-H(34C) | 0.9800 |
| C(14)-C(16) | 1.538(3) | C(35)-H(35A) | 0.9800 |
| C(14)-C(17) | 1.535(3) | C(35)-H(35B) | 0.9800 |
| C(15)-H(15A) | 0.9800 | C(35)-H(35C) | 0.9800 |
| C(15)-H(15B) | 0.9800 | C(36)-H(36A) | 0.9900 |
| C(15)-H(15C) | 0.9800 | C(36)-H(36B) | 0.9900 |
| C(16)-H(16A) | 0.9800 | C(36)-C(37) | 1.465(3) |
| C(16)-H(16B) | 0.9800 | C(37)-C(38) | 1.405(3) |
| C(16)-H(16C) | 0.9800 | C(37)-C(42) | 1.408(3) |
| C(17)-H(17A) | 0.9800 | C(38)-H(38) | 0.9500 |
| C(17)-H(17B) | 0.9800 | C(38)-C(39) | 1.381(3) |
| C(17)-H(17C) | 0.9800 | C(39)-H(39) | 0.9500 |
| C(18)-C(19) | 1.537(3) | C(39)-C(40) | 1.373(3) |
| C(18)-C(20) | 1.538(3) | C(40)-H(40) | 0.9500 |
| C(18)-C(21) | 1.530(3) | C(40)-C(41) | 1.381(4) |
| C(19)-H(19A) | 0.9800 | C(41)-H(41) | 0.9500 |
| C(19)-H(19B) | 0.9800 | C(41)-C(42) | 1.382(3) |
| C(19)-H(19C) | 0.9800 | C(42)-H(42) | 0.9500 |
| C(20)-H(20A) | 0.9800 | C(43)-H(43A) | 0.9900 |
| C(20)-H(20B) | 0.9800 | C(43)-H(43B) | 0.9900 |
| C(20)-H(20C) | 0.9800 | C(43)-C(44) | 1.473(2) |
| C(21)-H(21A) | 0.9800 | C(44)-C(45) | 1.402(2) |
| C(21)-H(21B) | 0.9800 | C(44)-C(49) | 1.397(3) |
| C(21)-H(21C) | 0.9800 | C(45)-H(45) | 0.9500 |
| C(22)-C(23) | 1.403(2) | C(45)-C(46) | 1.388(3) |
| C(22)-C(27) | 1.398(2) | C(46)-H(46) | 0.9500 |
| C(23)-C(24) | 1.410(2) | C(46)-C(47) | 1.383(3) |
| C(24)-C(25) | 1.388(2) | C(47)-H(47) | 0.9500 |
| C(24)-C(28) | 1.536(3) | C(47)-C(48) | 1.379(3) |
| C(25)-H(25) | 0.9500 | C(48)-H(48) | 0.9500 |
| C(25)-C(26) | 1.395(3) | C(48)-C(49) | 1.383(3) |
| C(26)-C(27) | 1.379(2) | C(49)-H(49) | 0.9500 |
| C(26)-C(32) | 1.541(2) | Zr(1B)-O(1B) | 1.9945(12) |
| C(27)-H(27) | 0.9500 | Zr(1B)-O(2B) | 2.0045(12) |
| C(28)-C(29) | 1.544(3) | Zr(1B)-C(1B) | 2.3335(17) |
| C(28)-C(30) | 1.531(3) | Zr(1B)-C(36B) | 2.3033(17) |
| C(28)-C(31) | 1.530(3) | Zr(1B)-C(37B) | 2.6583(16) |
| C(29)-H(29A) | 0.9800 | Zr(1B)-C(43B) | 2.2784(18) |
| C(29)-H(29B) | 0.9800 | Zr(1B)-C(44B) | 2.7608(17) |
| C(29)-H(29C) | 0.9800 | O(1B)-C(9B) | 1.345(2) |
| C(30)-H(30A) | 0.9800 | O(2B)-C(23B) | 1.342(2) |
| C(30)-H(30B) | 0.9800 | N(1B)-C(1B) | 1.364(2) |
| C(30)-H(30C) | 0.9800 | N(1B)-C(2B) | 1.406(2) |

| | | | |
|---|---|---|---|
| N(1B)-C(8B) | 1.434(2) | C(25B)-C(26B) | 1.398(2) |
| N(2B)-C(1B) | 1.356(2) | C(26B)-C(27B) | 1.381(2) |
| N(2B)-C(7B) | 1.400(2) | C(26B)-C(32B) | 1.530(3) |
| N(2B)-C(22B) | 1.439(2) | C(27B)-H(27B) | 0.9500 |
| C(2B)-C(3B) | 1.393(2) | C(28B)-C(29B) | 1.534(3) |
| C(2B)-C(7B) | 1.393(2) | C(28B)-C(30B) | 1.541(3) |
| C(3B)-H(3B) | 0.9500 | C(28B)-C(31B) | 1.534(3) |
| C(3B)-C(4B) | 1.379(2) | C(29B)-H(29D) | 0.9800 |
| C(4B)-H(4B) | 0.9500 | C(29B)-H(29E) | 0.9800 |
| C(4B)-C(5B) | 1.403(2) | C(29B)-H(29F) | 0.9800 |
| C(5B)-H(5B) | 0.9500 | C(30B)-H(30D) | 0.9800 |
| C(5B)-C(6B) | 1.384(2) | C(30B)-H(30E) | 0.9800 |
| C(6B)-H(6B) | 0.9500 | C(30B)-H(30F) | 0.9800 |
| C(6B)-C(7B) | 1.388(2) | C(31B)-H(31D) | 0.9800 |
| C(8B)-C(9B) | 1.403(2) | C(31B)-H(31E) | 0.9800 |
| C(8B)-C(13B) | 1.388(2) | C(31B)-H(31F) | 0.9800 |
| C(9B)-C(10B) | 1.406(2) | C(32B)-C(33B) | 1.534(3) |
| C(10B)-C(11B) | 1.401(3) | C(32B)-C(34B) | 1.537(3) |
| C(10B)-C(14B) | 1.530(3) | C(32B)-C(35B) | 1.532(3) |
| C(11B)-H(11B) | 0.9500 | C(33B)-H(33D) | 0.9800 |
| C(11B)-C(12B) | 1.386(3) | C(33B)-H(33E) | 0.9800 |
| C(12B)-C(13B) | 1.393(2) | C(33B)-H(33F) | 0.9800 |
| C(12B)-C(18B) | 1.539(3) | C(34B)-H(34D) | 0.9800 |
| C(13B)-H(13B) | 0.9500 | C(34B)-H(34E) | 0.9800 |
| C(14B)-C(15B) | 1.541(3) | C(34B)-H(34F) | 0.9800 |
| C(14B)-C(16B) | 1.535(3) | C(35B)-H(35D) | 0.9800 |
| C(14B)-C(17B) | 1.533(3) | C(35B)-H(35E) | 0.9800 |
| C(15B)-H(15D) | 0.9800 | C(35B)-H(35F) | 0.9800 |
| C(15B)-H(15E) | 0.9800 | C(36B)-H(36C) | 0.9900 |
| C(15B)-H(15F) | 0.9800 | C(36B)-H(36D) | 0.9900 |
| C(16B)-H(16D) | 0.9800 | C(36B)-C(37B) | 1.462(2) |
| C(16B)-H(16E) | 0.9800 | C(37B)-C(38B) | 1.415(3) |
| C(16B)-H(16F) | 0.9800 | C(37B)-C(42B) | 1.404(3) |
| C(17B)-H(17D) | 0.9800 | C(38B)-H(38B) | 0.9500 |
| C(17B)-H(17E) | 0.9800 | C(38B)-C(39B) | 1.380(3) |
| C(17B)-H(17F) | 0.9800 | C(39B)-H(39B) | 0.9500 |
| C(18B)-C(19B) | 1.526(3) | C(39B)-C(40B) | 1.381(3) |
| C(18B)-C(20B) | 1.533(3) | C(40B)-H(40B) | 0.9500 |
| C(18B)-C(21B) | 1.537(3) | C(40B)-C(41B) | 1.383(3) |
| C(19B)-H(19D) | 0.9800 | C(41B)-H(41B) | 0.9500 |
| C(19B)-H(19E) | 0.9800 | C(41B)-C(42B) | 1.378(3) |
| C(19B)-H(19F) | 0.9800 | C(42B)-H(42B) | 0.9500 |
| C(20B)-H(20D) | 0.9800 | C(43B)-H(43C) | 0.9900 |
| C(20B)-H(20E) | 0.9800 | C(43B)-H(43D) | 0.9900 |
| C(20B)-H(20F) | 0.9800 | C(43B)-C(44B) | 1.470(2) |
| C(21B)-H(21D) | 0.9800 | C(44B)-C(45B) | 1.401(3) |
| C(21B)-H(21E) | 0.9800 | C(44B)-C(49B) | 1.407(2) |
| C(21B)-H(21F) | 0.9800 | C(45B)-H(45B) | 0.9500 |
| C(22B)-C(23B) | 1.394(2) | C(45B)-C(46B) | 1.379(3) |
| C(22B)-C(27B) | 1.389(2) | C(46B)-H(46B) | 0.9500 |
| C(23B)-C(24B) | 1.419(2) | C(46B)-C(47B) | 1.378(3) |
| C(24B)-C(25B) | 1.383(2) | C(47B)-H(47B) | 0.9500 |
| C(24B)-C(28B) | 1.539(2) | C(47B)-C(48B) | 1.380(3) |
| C(25B)-H(25B) | 0.9500 | C(48B)-H(48B) | 0.9500 |

| | | | |
|---|---|---|---|
| C(48B)-C(49B) | 1.383(3) | C(1)-N(1)-C(2) | 111.02(13) |
| C(49B)-H(49B) | 0.9500 | C(1)-N(1)-C(8) | 125.33(14) |
| O(3)-C(51) | 1.418(3) | C(2)-N(1)-C(8) | 123.62(14) |
| O(3)-C(52) | 1.422(3) | C(1)-N(2)-C(7) | 110.47(14) |
| C(50)-H(50A) | 0.9800 | C(1)-N(2)-C(22) | 124.82(14) |
| C(50)-H(50B) | 0.9800 | C(7)-N(2)-C(22) | 124.55(13) |
| C(50)-H(50C) | 0.9800 | N(1)-C(1)-Zr(1) | 124.19(11) |
| C(50)-C(51) | 1.486(4) | N(1)-C(1)-N(2) | 105.76(14) |
| C(51)-H(51A) | 0.9900 | N(2)-C(1)-Zr(1) | 123.94(12) |
| C(51)-H(51B) | 0.9900 | C(3)-C(2)-N(1) | 132.04(16) |
| C(52)-H(52A) | 0.9900 | C(3)-C(2)-C(7) | 121.52(16) |
| C(52)-H(52B) | 0.9900 | C(7)-C(2)-N(1) | 106.15(14) |
| C(52)-C(53) | 1.491(4) | C(2)-C(3)-H(3) | 121.3 |
| C(53)-H(53A) | 0.9800 | C(4)-C(3)-C(2) | 117.31(17) |
| C(53)-H(53B) | 0.9800 | C(4)-C(3)-H(3) | 121.3 |
| C(53)-H(53C) | 0.9800 | C(3)-C(4)-H(4) | 119.3 |
| O(3B)-C(51B) | 1.431(2) | C(3)-C(4)-C(5) | 121.32(17) |
| O(3B)-C(52B) | 1.396(2) | C(5)-C(4)-H(4) | 119.3 |
| C(50B)-H(50D) | 0.9800 | C(4)-C(5)-H(5) | 119.2 |
| C(50B)-H(50E) | 0.9800 | C(6)-C(5)-C(4) | 121.56(17) |
| C(50B)-H(50F) | 0.9800 | C(6)-C(5)-H(5) | 119.2 |
| C(50B)-C(51B) | 1.493(3) | C(5)-C(6)-H(6) | 121.3 |
| C(51B)-H(51C) | 0.9900 | C(5)-C(6)-C(7) | 117.48(17) |
| C(51B)-H(51D) | 0.9900 | C(7)-C(6)-H(6) | 121.3 |
| C(52B)-H(52C) | 0.9900 | C(2)-C(7)-N(2) | 106.31(14) |
| C(52B)-H(52D) | 0.9900 | C(2)-C(7)-C(6) | 120.77(16) |
| C(52B)-C(53B) | 1.500(3) | C(6)-C(7)-N(2) | 132.49(16) |
| C(53B)-H(53D) | 0.9800 | C(9)-C(8)-N(1) | 120.20(15) |
| C(53B)-H(53E) | 0.9800 | C(13)-C(8)-N(1) | 118.58(15) |
| C(53B)-H(53F) | 0.9800 | C(13)-C(8)-C(9) | 121.21(15) |
| | | O(1)-C(9)-C(8) | 119.83(15) |
| O(1)-Zr(1)-C(1) | 77.55(5) | O(1)-C(9)-C(10) | 121.49(15) |
| O(1)-Zr(1)-C(36) | 92.86(6) | C(8)-C(9)-C(10) | 118.67(16) |
| O(1)-Zr(1)-C(37) | 98.87(5) | C(9)-C(10)-C(14) | 120.89(16) |
| O(1)-Zr(1)-C(43) | 98.50(6) | C(11)-C(10)-C(9) | 117.71(16) |
| O(1)-Zr(1)-C(44) | 88.98(5) | C(11)-C(10)-C(14) | 121.37(15) |
| O(2)-Zr(1)-O(1) | 152.65(5) | C(10)-C(11)-H(11) | 118.1 |
| O(2)-Zr(1)-C(1) | 76.96(5) | C(12)-C(11)-C(10) | 123.82(16) |
| O(2)-Zr(1)-C(36) | 92.44(6) | C(12)-C(11)-H(11) | 118.1 |
| O(2)-Zr(1)-C(37) | 100.34(5) | C(11)-C(12)-C(13) | 117.35(16) |
| O(2)-Zr(1)-C(43) | 101.08(6) | C(11)-C(12)-C(18) | 122.82(16) |
| O(2)-Zr(1)-C(44) | 97.96(5) | C(13)-C(12)-C(18) | 119.82(16) |
| C(1)-Zr(1)-C(37) | 155.93(6) | C(8)-C(13)-C(12) | 120.78(16) |
| C(1)-Zr(1)-C(44) | 83.83(5) | C(8)-C(13)-H(13) | 119.6 |
| C(36)-Zr(1)-C(1) | 122.34(6) | C(12)-C(13)-H(13) | 119.6 |
| C(36)-Zr(1)-C(37) | 33.60(6) | C(10)-C(14)-C(15) | 108.72(14) |
| C(36)-Zr(1)-C(44) | 153.53(6) | C(10)-C(14)-C(16) | 110.78(14) |
| C(37)-Zr(1)-C(44) | 120.10(5) | C(10)-C(14)-C(17) | 111.86(16) |
| C(43)-Zr(1)-C(1) | 114.92(6) | C(16)-C(14)-C(15) | 110.79(16) |
| C(43)-Zr(1)-C(36) | 122.73(6) | C(17)-C(14)-C(15) | 107.26(15) |
| C(43)-Zr(1)-C(37) | 89.13(6) | C(17)-C(14)-C(16) | 107.39(15) |
| C(43)-Zr(1)-C(44) | 31.26(6) | C(14)-C(15)-H(15A) | 109.5 |
| C(9)-O(1)-Zr(1) | 142.92(10) | C(14)-C(15)-H(15B) | 109.5 |
| C(23)-O(2)-Zr(1) | 145.47(11) | C(14)-C(15)-H(15C) | 109.5 |

| | | | |
|---|---|---|---|
| H(15A)-C(15)-H(15B) | 109.5 | C(22)-C(27)-H(27) | 119.6 |
| H(15A)-C(15)-H(15C) | 109.5 | C(26)-C(27)-C(22) | 120.86(16) |
| H(15B)-C(15)-H(15C) | 109.5 | C(26)-C(27)-H(27) | 119.6 |
| C(14)-C(16)-H(16A) | 109.5 | C(24)-C(28)-C(29) | 109.99(16) |
| C(14)-C(16)-H(16B) | 109.5 | C(30)-C(28)-C(24) | 109.47(16) |
| C(14)-C(16)-H(16C) | 109.5 | C(30)-C(28)-C(29) | 110.96(15) |
| H(16A)-C(16)-H(16B) | 109.5 | C(31)-C(28)-C(24) | 112.32(15) |
| H(16A)-C(16)-H(16C) | 109.5 | C(31)-C(28)-C(29) | 107.36(17) |
| H(16B)-C(16)-H(16C) | 109.5 | C(31)-C(28)-C(30) | 106.70(17) |
| C(14)-C(17)-H(17A) | 109.5 | C(28)-C(29)-H(29A) | 109.5 |
| C(14)-C(17)-H(17B) | 109.5 | C(28)-C(29)-H(29B) | 109.5 |
| C(14)-C(17)-H(17C) | 109.5 | C(28)-C(29)-H(29C) | 109.5 |
| H(17A)-C(17)-H(17B) | 109.5 | H(29A)-C(29)-H(29B) | 109.5 |
| H(17A)-C(17)-H(17C) | 109.5 | H(29A)-C(29)-H(29C) | 109.5 |
| H(17B)-C(17)-H(17C) | 109.5 | H(29B)-C(29)-H(29C) | 109.5 |
| C(12)-C(18)-C(19) | 109.60(16) | C(28)-C(30)-H(30A) | 109.5 |
| C(12)-C(18)-C(20) | 109.33(16) | C(28)-C(30)-H(30B) | 109.5 |
| C(19)-C(18)-C(20) | 109.13(16) | C(28)-C(30)-H(30C) | 109.5 |
| C(21)-C(18)-C(12) | 112.24(15) | H(30A)-C(30)-H(30B) | 109.5 |
| C(21)-C(18)-C(19) | 108.44(17) | H(30A)-C(30)-H(30C) | 109.5 |
| C(21)-C(18)-C(20) | 108.05(16) | H(30B)-C(30)-H(30C) | 109.5 |
| C(18)-C(19)-H(19A) | 109.5 | C(28)-C(31)-H(31A) | 109.5 |
| C(18)-C(19)-H(19B) | 109.5 | C(28)-C(31)-H(31B) | 109.5 |
| C(18)-C(19)-H(19C) | 109.5 | C(28)-C(31)-H(31C) | 109.5 |
| H(19A)-C(19)-H(19B) | 109.5 | H(31A)-C(31)-H(31B) | 109.5 |
| H(19A)-C(19)-H(19C) | 109.5 | H(31A)-C(31)-H(31C) | 109.5 |
| H(19B)-C(19)-H(19C) | 109.5 | H(31B)-C(31)-H(31C) | 109.5 |
| C(18)-C(20)-H(20A) | 109.5 | C(33)-C(32)-C(26) | 109.54(15) |
| C(18)-C(20)-H(20B) | 109.5 | C(34)-C(32)-C(26) | 109.88(17) |
| C(18)-C(20)-H(20C) | 109.5 | C(34)-C(32)-C(33) | 106.7(2) |
| H(20A)-C(20)-H(20B) | 109.5 | C(35)-C(32)-C(26) | 112.43(17) |
| H(20A)-C(20)-H(20C) | 109.5 | C(35)-C(32)-C(33) | 107.1(2) |
| H(20B)-C(20)-H(20C) | 109.5 | C(35)-C(32)-C(34) | 111.0(2) |
| C(18)-C(21)-H(21A) | 109.5 | C(32)-C(33)-H(33A) | 109.5 |
| C(18)-C(21)-H(21B) | 109.5 | C(32)-C(33)-H(33B) | 109.5 |
| C(18)-C(21)-H(21C) | 109.5 | C(32)-C(33)-H(33C) | 109.5 |
| H(21A)-C(21)-H(21B) | 109.5 | H(33A)-C(33)-H(33B) | 109.5 |
| H(21A)-C(21)-H(21C) | 109.5 | H(33A)-C(33)-H(33C) | 109.5 |
| H(21B)-C(21)-H(21C) | 109.5 | H(33B)-C(33)-H(33C) | 109.5 |
| C(23)-C(22)-N(2) | 120.61(14) | C(32)-C(34)-H(34A) | 109.5 |
| C(27)-C(22)-N(2) | 118.73(15) | C(32)-C(34)-H(34B) | 109.5 |
| C(27)-C(22)-C(23) | 120.65(16) | C(32)-C(34)-H(34C) | 109.5 |
| O(2)-C(23)-C(22) | 119.78(15) | H(34A)-C(34)-H(34B) | 109.5 |
| O(2)-C(23)-C(24) | 121.25(15) | H(34A)-C(34)-H(34C) | 109.5 |
| C(22)-C(23)-C(24) | 118.96(15) | H(34B)-C(34)-H(34C) | 109.5 |
| C(23)-C(24)-C(28) | 120.30(15) | C(32)-C(35)-H(35A) | 109.5 |
| C(25)-C(24)-C(23) | 118.11(16) | C(32)-C(35)-H(35B) | 109.5 |
| C(25)-C(24)-C(28) | 121.54(16) | C(32)-C(35)-H(35C) | 109.5 |
| C(24)-C(25)-H(25) | 118.3 | H(35A)-C(35)-H(35B) | 109.5 |
| C(24)-C(25)-C(26) | 123.45(17) | H(35A)-C(35)-H(35C) | 109.5 |
| C(26)-C(25)-H(25) | 118.3 | H(35B)-C(35)-H(35C) | 109.5 |
| C(25)-C(26)-C(32) | 120.29(16) | Zr(1)-C(36)-H(36A) | 114.3 |
| C(27)-C(26)-C(25) | 117.65(15) | Zr(1)-C(36)-H(36B) | 114.3 |
| C(27)-C(26)-C(32) | 122.06(16) | H(36A)-C(36)-H(36B) | 111.5 |

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| C(37)-C(36)-Zr(1) | 85.91(10) | O(1B)-Zr(1B)-C(37B) | 100.03(5) |
| C(37)-C(36)-H(36A) | 114.3 | O(1B)-Zr(1B)-C(43B) | 101.55(6) |
| C(37)-C(36)-H(36B) | 114.3 | O(1B)-Zr(1B)-C(44B) | 99.55(5) |
| C(36)-C(37)-Zr(1) | 60.49(9) | O(2B)-Zr(1B)-C(1B) | 77.85(5) |
| C(38)-C(37)-Zr(1) | 99.35(11) | O(2B)-Zr(1B)-C(36B) | 90.30(6) |
| C(38)-C(37)-C(36) | 121.25(17) | O(2B)-Zr(1B)-C(37B) | 98.60(5) |
| C(38)-C(37)-C(42) | 116.61(18) | O(2B)-Zr(1B)-C(43B) | 100.89(6) |
| C(42)-C(37)-Zr(1) | 102.31(12) | O(2B)-Zr(1B)-C(44B) | 89.98(5) |
| C(42)-C(37)-C(36) | 121.36(19) | C(1B)-Zr(1B)-C(37B) | 158.19(6) |
| C(37)-C(38)-H(38) | 119.2 | C(1B)-Zr(1B)-C(44B) | 81.87(5) |
| C(39)-C(38)-C(37) | 121.7(2) | C(36B)-Zr(1B)-C(1B) | 124.89(6) |
| C(39)-C(38)-H(38) | 119.2 | C(36B)-Zr(1B)-C(37B) | 33.30(6) |
| C(38)-C(39)-H(39) | 119.8 | C(36B)-Zr(1B)-C(44B) | 152.58(6) |
| C(40)-C(39)-C(38) | 120.4(2) | C(37B)-Zr(1B)-C(44B) | 119.83(5) |
| C(40)-C(39)-H(39) | 119.8 | C(43B)-Zr(1B)-C(1B) | 113.64(6) |
| C(39)-C(40)-H(40) | 120.2 | C(43B)-Zr(1B)-C(36B) | 121.45(6) |
| C(39)-C(40)-C(41) | 119.5(2) | C(43B)-Zr(1B)-C(37B) | 88.17(6) |
| C(41)-C(40)-H(40) | 120.2 | C(43B)-Zr(1B)-C(44B) | 32.13(6) |
| C(40)-C(41)-H(41) | 119.7 | C(9B)-O(1B)-Zr(1B) | 144.80(11) |
| C(40)-C(41)-C(42) | 120.6(2) | C(23B)-O(2B)-Zr(1B) | 141.55(10) |
| C(42)-C(41)-H(41) | 119.7 | C(1B)-N(1B)-C(2B) | 110.60(14) |
| C(37)-C(42)-H(42) | 119.4 | C(1B)-N(1B)-C(8B) | 125.05(15) |
| C(41)-C(42)-C(37) | 121.1(2) | C(2B)-N(1B)-C(8B) | 124.35(14) |
| C(41)-C(42)-H(42) | 119.4 | C(1B)-N(2B)-C(7B) | 111.15(14) |
| Zr(1)-C(43)-H(43A) | 112.6 | C(1B)-N(2B)-C(22B) | 124.57(14) |
| Zr(1)-C(43)-H(43B) | 112.6 | C(7B)-N(2B)-C(22B) | 124.14(14) |
| H(43A)-C(43)-H(43B) | 110.1 | N(1B)-C(1B)-Zr(1B) | 125.58(12) |
| C(44)-C(43)-Zr(1) | 95.49(11) | N(2B)-C(1B)-Zr(1B) | 123.82(11) |
| C(44)-C(43)-H(43A) | 112.6 | N(2B)-C(1B)-N(1B) | 105.81(14) |
| C(44)-C(43)-H(43B) | 112.6 | C(3B)-C(2B)-N(1B) | 132.31(16) |
| C(43)-C(44)-Zr(1) | 53.25(9) | C(7B)-C(2B)-N(1B) | 106.09(14) |
| C(45)-C(44)-Zr(1) | 107.35(12) | C(7B)-C(2B)-C(3B) | 121.14(16) |
| C(45)-C(44)-C(43) | 121.11(17) | C(2B)-C(3B)-H(3B) | 121.4 |
| C(49)-C(44)-Zr(1) | 104.14(11) | C(4B)-C(3B)-C(2B) | 117.11(16) |
| C(49)-C(44)-C(43) | 121.45(16) | C(4B)-C(3B)-H(3B) | 121.4 |
| C(49)-C(44)-C(45) | 117.13(16) | C(3B)-C(4B)-H(4B) | 119.2 |
| C(44)-C(45)-H(45) | 119.7 | C(3B)-C(4B)-C(5B) | 121.66(16) |
| C(46)-C(45)-C(44) | 120.68(18) | C(5B)-C(4B)-H(4B) | 119.2 |
| C(46)-C(45)-H(45) | 119.7 | C(4B)-C(5B)-H(5B) | 119.4 |
| C(45)-C(46)-H(46) | 119.5 | C(6B)-C(5B)-C(4B) | 121.22(17) |
| C(47)-C(46)-C(45) | 120.92(18) | C(6B)-C(5B)-H(5B) | 119.4 |
| C(47)-C(46)-H(46) | 119.5 | C(5B)-C(6B)-H(6B) | 121.5 |
| C(46)-C(47)-H(47) | 120.4 | C(5B)-C(6B)-C(7B) | 117.05(16) |
| C(48)-C(47)-C(46) | 119.14(18) | C(7B)-C(6B)-H(6B) | 121.5 |
| C(48)-C(47)-H(47) | 120.4 | C(2B)-C(7B)-N(2B) | 106.05(15) |
| C(47)-C(48)-H(48) | 119.9 | C(6B)-C(7B)-N(2B) | 131.67(16) |
| C(47)-C(48)-C(49) | 120.22(19) | C(6B)-C(7B)-C(2B) | 121.77(16) |
| C(49)-C(48)-H(48) | 119.9 | C(9B)-C(8B)-N(1B) | 119.99(15) |
| C(44)-C(49)-H(49) | 119.1 | C(13B)-C(8B)-N(1B) | 118.91(15) |
| C(48)-C(49)-C(44) | 121.87(17) | C(13B)-C(8B)-C(9B) | 121.11(16) |
| C(48)-C(49)-H(49) | 119.1 | O(1B)-C(9B)-C(8B) | 119.94(15) |
| O(1B)-Zr(1B)-O(2B) | 151.13(5) | O(1B)-C(9B)-C(10B) | 121.14(16) |
| O(1B)-Zr(1B)-C(1B) | 76.65(5) | C(8B)-C(9B)-C(10B) | 118.90(16) |
| O(1B)-Zr(1B)-C(36B) | 93.28(6) | C(9B)-C(10B)-C(14B) | 120.82(16) |

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| C(11B)-C(10B)-C(9B) | 117.78(17) | C(18B)-C(21B)-H(21E) | 109.5 |
| C(11B)-C(10B)-C(14B) | 121.39(17) | C(18B)-C(21B)-H(21F) | 109.5 |
| C(10B)-C(11B)-H(11B) | 118.2 | H(21D)-C(21B)-H(21E) | 109.5 |
| C(12B)-C(11B)-C(10B) | 123.69(18) | H(21D)-C(21B)-H(21F) | 109.5 |
| C(12B)-C(11B)-H(11B) | 118.2 | H(21E)-C(21B)-H(21F) | 109.5 |
| C(11B)-C(12B)-C(13B) | 117.33(17) | C(23B)-C(22B)-N(2B) | 120.44(15) |
| C(11B)-C(12B)-C(18B) | 123.18(17) | C(27B)-C(22B)-N(2B) | 117.98(15) |
| C(13B)-C(12B)-C(18B) | 119.49(17) | C(27B)-C(22B)-C(23B) | 121.50(16) |
| C(8B)-C(13B)-C(12B) | 120.73(17) | O(2B)-C(23B)-C(22B) | 120.09(15) |
| C(8B)-C(13B)-H(13B) | 119.6 | O(2B)-C(23B)-C(24B) | 121.54(15) |
| C(12B)-C(13B)-H(13B) | 119.6 | C(22B)-C(23B)-C(24B) | 118.35(16) |
| C(10B)-C(14B)-C(15B) | 110.12(17) | C(23B)-C(24B)-C(28B) | 119.99(15) |
| C(10B)-C(14B)-C(16B) | 109.60(16) | C(25B)-C(24B)-C(23B) | 117.67(16) |
| C(10B)-C(14B)-C(17B) | 112.17(17) | C(25B)-C(24B)-C(28B) | 122.31(16) |
| C(16B)-C(14B)-C(15B) | 111.37(17) | C(24B)-C(25B)-H(25B) | 117.9 |
| C(17B)-C(14B)-C(15B) | 106.61(18) | C(24B)-C(25B)-C(26B) | 124.11(17) |
| C(17B)-C(14B)-C(16B) | 106.92(18) | C(26B)-C(25B)-H(25B) | 117.9 |
| C(14B)-C(15B)-H(15D) | 109.5 | C(25B)-C(26B)-C(32B) | 120.56(16) |
| C(14B)-C(15B)-H(15E) | 109.5 | C(27B)-C(26B)-C(25B) | 116.87(16) |
| C(14B)-C(15B)-H(15F) | 109.5 | C(27B)-C(26B)-C(32B) | 122.56(16) |
| H(15D)-C(15B)-H(15E) | 109.5 | C(22B)-C(27B)-H(27B) | 119.5 |
| H(15D)-C(15B)-H(15F) | 109.5 | C(26B)-C(27B)-C(22B) | 120.96(16) |
| H(15E)-C(15B)-H(15F) | 109.5 | C(26B)-C(27B)-H(27B) | 119.5 |
| C(14B)-C(16B)-H(16D) | 109.5 | C(24B)-C(28B)-C(30B) | 108.93(15) |
| C(14B)-C(16B)-H(16E) | 109.5 | C(29B)-C(28B)-C(24B) | 111.19(15) |
| C(14B)-C(16B)-H(16F) | 109.5 | C(29B)-C(28B)-C(30B) | 109.86(15) |
| H(16D)-C(16B)-H(16E) | 109.5 | C(29B)-C(28B)-C(31B) | 107.00(16) |
| H(16D)-C(16B)-H(16F) | 109.5 | C(31B)-C(28B)-C(24B) | 111.92(16) |
| H(16E)-C(16B)-H(16F) | 109.5 | C(31B)-C(28B)-C(30B) | 107.88(16) |
| C(14B)-C(17B)-H(17D) | 109.5 | C(28B)-C(29B)-H(29D) | 109.5 |
| C(14B)-C(17B)-H(17E) | 109.5 | C(28B)-C(29B)-H(29E) | 109.5 |
| C(14B)-C(17B)-H(17F) | 109.5 | C(28B)-C(29B)-H(29F) | 109.5 |
| H(17D)-C(17B)-H(17E) | 109.5 | H(29D)-C(29B)-H(29E) | 109.5 |
| H(17D)-C(17B)-H(17F) | 109.5 | H(29D)-C(29B)-H(29F) | 109.5 |
| H(17E)-C(17B)-H(17F) | 109.5 | H(29E)-C(29B)-H(29F) | 109.5 |
| C(19B)-C(18B)-C(12B) | 109.95(16) | C(28B)-C(30B)-H(30D) | 109.5 |
| C(19B)-C(18B)-C(20B) | 108.89(19) | C(28B)-C(30B)-H(30E) | 109.5 |
| C(19B)-C(18B)-C(21B) | 108.94(19) | C(28B)-C(30B)-H(30F) | 109.5 |
| C(20B)-C(18B)-C(12B) | 109.18(16) | H(30D)-C(30B)-H(30E) | 109.5 |
| C(20B)-C(18B)-C(21B) | 108.17(19) | H(30D)-C(30B)-H(30F) | 109.5 |
| C(21B)-C(18B)-C(12B) | 111.65(17) | H(30E)-C(30B)-H(30F) | 109.5 |
| C(18B)-C(19B)-H(19D) | 109.5 | C(28B)-C(31B)-H(31D) | 109.5 |
| C(18B)-C(19B)-H(19E) | 109.5 | C(28B)-C(31B)-H(31E) | 109.5 |
| C(18B)-C(19B)-H(19F) | 109.5 | C(28B)-C(31B)-H(31F) | 109.5 |
| H(19D)-C(19B)-H(19E) | 109.5 | H(31D)-C(31B)-H(31E) | 109.5 |
| H(19D)-C(19B)-H(19F) | 109.5 | H(31D)-C(31B)-H(31F) | 109.5 |
| H(19E)-C(19B)-H(19F) | 109.5 | H(31E)-C(31B)-H(31F) | 109.5 |
| C(18B)-C(20B)-H(20D) | 109.5 | C(26B)-C(32B)-C(33B) | 109.51(16) |
| C(18B)-C(20B)-H(20E) | 109.5 | C(26B)-C(32B)-C(34B) | 109.16(17) |
| C(18B)-C(20B)-H(20F) | 109.5 | C(26B)-C(32B)-C(35B) | 111.94(16) |
| H(20D)-C(20B)-H(20E) | 109.5 | C(33B)-C(32B)-C(34B) | 110.16(18) |
| H(20D)-C(20B)-H(20F) | 109.5 | C(35B)-C(32B)-C(33B) | 107.76(18) |
| H(20E)-C(20B)-H(20F) | 109.5 | C(35B)-C(32B)-C(34B) | 108.29(17) |
| C(18B)-C(21B)-H(21D) | 109.5 | C(32B)-C(33B)-H(33D) | 109.5 |

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| C(32B)-C(33B)-H(33E) | 109.5 | C(49B)-C(44B)-Zr(1B) | 100.28(11) |
| C(32B)-C(33B)-H(33F) | 109.5 | C(49B)-C(44B)-C(43B) | 120.72(17) |
| H(33D)-C(33B)-H(33E) | 109.5 | C(44B)-C(45B)-H(45B) | 119.0 |
| H(33D)-C(33B)-H(33F) | 109.5 | C(46B)-C(45B)-C(44B) | 121.93(18) |
| H(33E)-C(33B)-H(33F) | 109.5 | C(46B)-C(45B)-H(45B) | 119.0 |
| C(32B)-C(34B)-H(34D) | 109.5 | C(45B)-C(46B)-H(46B) | 120.0 |
| C(32B)-C(34B)-H(34E) | 109.5 | C(47B)-C(46B)-C(45B) | 120.0(2) |
| C(32B)-C(34B)-H(34F) | 109.5 | C(47B)-C(46B)-H(46B) | 120.0 |
| H(34D)-C(34B)-H(34E) | 109.5 | C(46B)-C(47B)-H(47B) | 120.2 |
| H(34D)-C(34B)-H(34F) | 109.5 | C(46B)-C(47B)-C(48B) | 119.56(19) |
| H(34E)-C(34B)-H(34F) | 109.5 | C(48B)-C(47B)-H(47B) | 120.2 |
| C(32B)-C(35B)-H(35D) | 109.5 | C(47B)-C(48B)-H(48B) | 119.6 |
| C(32B)-C(35B)-H(35E) | 109.5 | C(47B)-C(48B)-C(49B) | 120.80(19) |
| C(32B)-C(35B)-H(35F) | 109.5 | C(49B)-C(48B)-H(48B) | 119.6 |
| H(35D)-C(35B)-H(35E) | 109.5 | C(44B)-C(49B)-H(49B) | 119.6 |
| H(35D)-C(35B)-H(35F) | 109.5 | C(48B)-C(49B)-C(44B) | 120.78(19) |
| H(35E)-C(35B)-H(35F) | 109.5 | C(48B)-C(49B)-H(49B) | 119.6 |
| Zr(1B)-C(36B)-H(36C) | 114.2 | C(51)-O(3)-C(52) | 112.4(2) |
| Zr(1B)-C(36B)-H(36D) | 114.2 | H(50A)-C(50)-H(50B) | 109.5 |
| H(36C)-C(36B)-H(36D) | 111.3 | H(50A)-C(50)-H(50C) | 109.5 |
| C(37B)-C(36B)-Zr(1B) | 86.80(10) | H(50B)-C(50)-H(50C) | 109.5 |
| C(37B)-C(36B)-H(36C) | 114.2 | C(51)-C(50)-H(50A) | 109.5 |
| C(37B)-C(36B)-H(36D) | 114.2 | C(51)-C(50)-H(50B) | 109.5 |
| C(36B)-C(37B)-Zr(1B) | 59.90(9) | C(51)-C(50)-H(50C) | 109.5 |
| C(38B)-C(37B)-Zr(1B) | 106.87(11) | O(3)-C(51)-C(50) | 108.4(2) |
| C(38B)-C(37B)-C(36B) | 122.19(18) | O(3)-C(51)-H(51A) | 110.0 |
| C(42B)-C(37B)-Zr(1B) | 96.38(11) | O(3)-C(51)-H(51B) | 110.0 |
| C(42B)-C(37B)-C(36B) | 120.77(17) | C(50)-C(51)-H(51A) | 110.0 |
| C(42B)-C(37B)-C(38B) | 116.40(17) | C(50)-C(51)-H(51B) | 110.0 |
| C(37B)-C(38B)-H(38B) | 119.4 | H(51A)-C(51)-H(51B) | 108.4 |
| C(39B)-C(38B)-C(37B) | 121.16(18) | O(3)-C(52)-H(52A) | 109.8 |
| C(39B)-C(38B)-H(38B) | 119.4 | O(3)-C(52)-H(52B) | 109.8 |
| C(38B)-C(39B)-H(39B) | 119.6 | O(3)-C(52)-C(53) | 109.4(2) |
| C(38B)-C(39B)-C(40B) | 120.84(18) | H(52A)-C(52)-H(52B) | 108.2 |
| C(40B)-C(39B)-H(39B) | 119.6 | C(53)-C(52)-H(52A) | 109.8 |
| C(39B)-C(40B)-H(40B) | 120.4 | C(53)-C(52)-H(52B) | 109.8 |
| C(39B)-C(40B)-C(41B) | 119.26(18) | C(52)-C(53)-H(53A) | 109.5 |
| C(41B)-C(40B)-H(40B) | 120.4 | C(52)-C(53)-H(53B) | 109.5 |
| C(40B)-C(41B)-H(41B) | 119.8 | C(52)-C(53)-H(53C) | 109.5 |
| C(42B)-C(41B)-C(40B) | 120.35(19) | H(53A)-C(53)-H(53B) | 109.5 |
| C(42B)-C(41B)-H(41B) | 119.8 | H(53A)-C(53)-H(53C) | 109.5 |
| C(37B)-C(42B)-H(42B) | 119.0 | H(53B)-C(53)-H(53C) | 109.5 |
| C(41B)-C(42B)-C(37B) | 121.97(18) | C(52B)-O(3B)-C(51B) | 111.13(16) |
| C(41B)-C(42B)-H(42B) | 119.0 | H(50D)-C(50B)-H(50E) | 109.5 |
| Zr(1B)-C(43B)-H(43C) | 113.2 | H(50D)-C(50B)-H(50F) | 109.5 |
| Zr(1B)-C(43B)-H(43D) | 113.2 | H(50E)-C(50B)-H(50F) | 109.5 |
| H(43C)-C(43B)-H(43D) | 110.6 | C(51B)-C(50B)-H(50D) | 109.5 |
| C(44B)-C(43B)-Zr(1B) | 92.32(11) | C(51B)-C(50B)-H(50E) | 109.5 |
| C(44B)-C(43B)-H(43C) | 113.2 | C(51B)-C(50B)-H(50F) | 109.5 |
| C(44B)-C(43B)-H(43D) | 113.2 | O(3B)-C(51B)-C(50B) | 107.48(18) |
| C(43B)-C(44B)-Zr(1B) | 55.55(9) | O(3B)-C(51B)-H(51C) | 110.2 |
| C(45B)-C(44B)-Zr(1B) | 107.78(11) | O(3B)-C(51B)-H(51D) | 110.2 |
| C(45B)-C(44B)-C(43B) | 121.89(16) | C(50B)-C(51B)-H(51C) | 110.2 |
| C(45B)-C(44B)-C(49B) | 116.89(17) | C(50B)-C(51B)-H(51D) | 110.2 |

| | | | |
|---|---|---|---|
| H(51C)-C(51B)-H(51D) | 108.5 | C(52B)-C(53B)-H(53D) | 109.5 |
| O(3B)-C(52B)-H(52C) | 109.8 | C(52B)-C(53B)-H(53E) | 109.5 |
| O(3B)-C(52B)-H(52D) | 109.8 | C(52B)-C(53B)-H(53F) | 109.5 |
| O(3B)-C(52B)-C(53B) | 109.48(16) | H(53D)-C(53B)-H(53E) | 109.5 |
| H(52C)-C(52B)-H(52D) | 108.2 | H(53D)-C(53B)-H(53F) | 109.5 |
| C(53B)-C(52B)-H(52C) | 109.8 | H(53E)-C(53B)-H(53F) | 109.5 |
| C(53B)-C(52B)-H(52D) | 109.8 | | |