Supplementary Materials: Enantiopure C_1-symmetric *N*-Heterocyclic Carbene Ligands from Desymmetrized *meso*-1,2-Diphenylethylenediamine: Application in Ruthenium-Catalyzed Olefin Metathesis

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1. NMR Spectra and Specific Rotations

For compounds **B**–**D**, **1a** and **1b,** signals of both enantiomers have been found to be coherent with those of the corresponding racemic samples. **1a** and **1b** exist as a mixture of rotational isomers *syn: anti* ~0.4:1 (*syn*: *N*-alkyl group located on the same side as the benzylidene unit) [1]. Representative NMR spectra of (−)-**C**, (−)-**D** and **1b** are reported below. For comparison, NMR analysis of **1a** is also provided.

NMR spectra data are reported as follows: chemical shift (δ ppm), multiplicity, coupling costant in Hertz (Hz) and integration. Multiplicity are abbreviated as follows: singlet (s), doublet (d), triplet (t), multiplet (m), broad (br), overlapped (o).

^{1}H NMR of (−)-**C** (400 MHz, $CDCl_3$) (Figure S1): *δ* 7.25 (br s, 3H); 7.17 (br s, 3H); 7.10 (d, $^{3}J_{HH}$ = 7.32 Hz, 1H); 6.98 (br s, 4H); 6.85 (t, $^{3}J_{HH}$ = 7.62 Hz, 1H); 6.61 (t, $^{3}J_{HH}$ = 7.32 Hz, 1H); 6.24 (d, $^{3}J_{HH}$ = 7.93 Hz, 1H); 5.27 (br s, 1H); 4.56 (br s, 1H); 4.30 (d, $^{3}J_{HH}$ = 4.27 Hz, 1H); 3.01–2.94 (m, 1H); 2.32 (br t, 1H); 1.90 (br t, 1H); 1.70–1.59 (o m, 3H); 1.57–1.47 (o m, 3H); 1.34 (t, $^{3}J_{HH}$ = 6.68 Hz, 3H); 1.28 (t, $^{3}J_{HH}$ = 6.68 Hz, 3H); 1.22–0.98 (o m, 3H).

$[\alpha]_D^{20} = -13.0$ (c = 0.5, CH_2Cl_2).

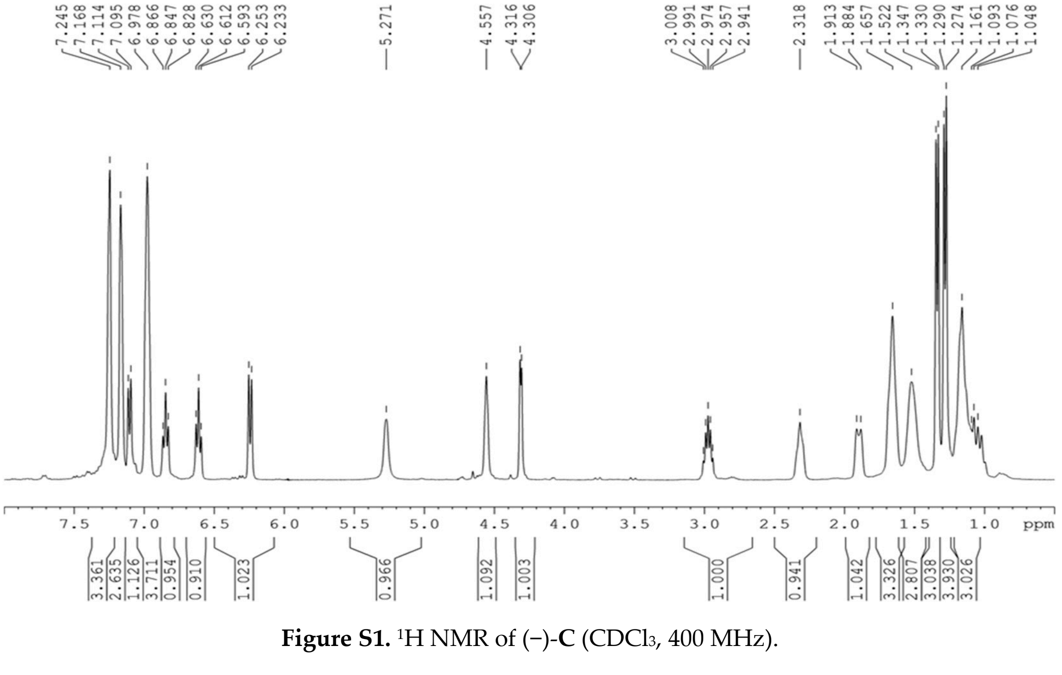

Figure S1. ^{1}H NMR of (−)-**C** ($CDCl_3$, 400 MHz).

^{1}H NMR of (−)-**D** (400 MHz, $CDCl_3$) (Figure S2): *δ* 8.29 (s, 1H); 7.49 (d, $^{3}J_{HH}$ = 8.08 Hz, 1H); 7.30–7.24 (o m, 3H); 7.22–7.15 (o m, 3H); 7.02–6.93 (o m, 5H); 6.86 (d, $^{3}J_{HH}$ = 6.55 Hz, 2H); 6.48 (d, $^{3}J_{HH}$ = 11.81 Hz, 1H); 6.04 (d, $^{3}J_{HH}$ = 11.81 Hz, 1H); 3.46 (m, 1H); 3.19 (m, 1H); 2.26 (br d, 2H); 1.91 (br d, 1H); 1.82–1.69 (o m, 2H); 1.63 (o m, 1H); 1.54 (o m, 1H); 1.34–1.29 (o m, 6H); 1.25–1.13 (o m, 3H).

$[\alpha]_D^{20} = -38.8$ (*c* = 0.5, CH_2Cl_2).

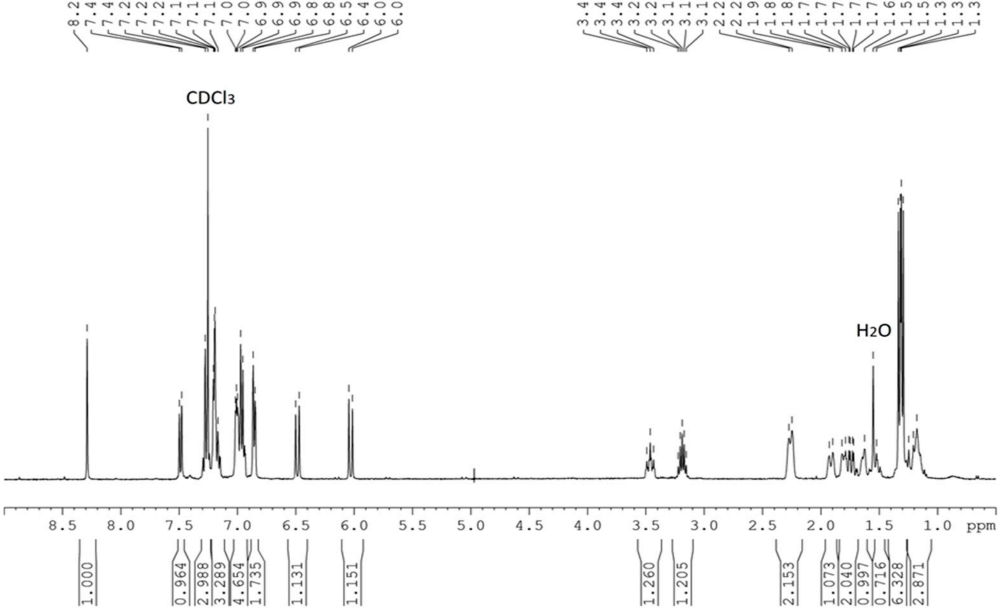

Figure S2. ^{1}H NMR of (−)-**D** ($CDCl_3$, 400 MHz).

NMR analysis of **1a**: ^{1}H NMR (400 MHz, C_6D_6) (Figure S3): δ 21.06 (minor rotational isomer, d, $^3J_{HP}$ = 4.0 Hz, 0.4H); 19.75 (major rotational isomer, s, 1H); (only major isomer signals are reported below) 9.02–6.60 (overlapped signals of both isomers); 6.40 (t, $^3J_{HH}$ = 7.5 Hz, 1H); 6.15 (br t, 2H); 5.89 (d, $^3J_{HH}$ = 10.52 Hz, 1H); 5.30 (br t, 1H); 5.16 (d, $^3J_{HH}$ = 10.52 Hz, 1H); 3.56–3.44 (o m, 2H); 3.23 (br d, 1H); 2.55 (br d, 2H); 2.41–2.38 (o m, 5H); 2.08–0.91 (overlapped signals of both isomers). ^{13}C NMR (C_6D_6, 100 MHz): δ 299.4 (Ru = CHPh); 221.0 (iNCN, $^2J_{C\text{-}P}$ = 79.2 Hz); 152.3; 137.6; 134.4; 134.0; 133.8; 132.2; 130.6; 130.4; 129.8; 129.1; 127.5; 126.3; 125.9; 75.8; 67.5; 61.1; 33.9; 33.7; 33.5; 33.4; 33.0; 30.4; 30.2; 29.9; 29.8; 28.7; 28.6; 27.3; 26.0; 25.9; 25.4; 23.6. ^{31}P NMR (C_6D_6, 161.97 MHz): δ 24.9; 24.6.

Determination of the specific rotation was not possible due to the rapid decomposition of the complex.

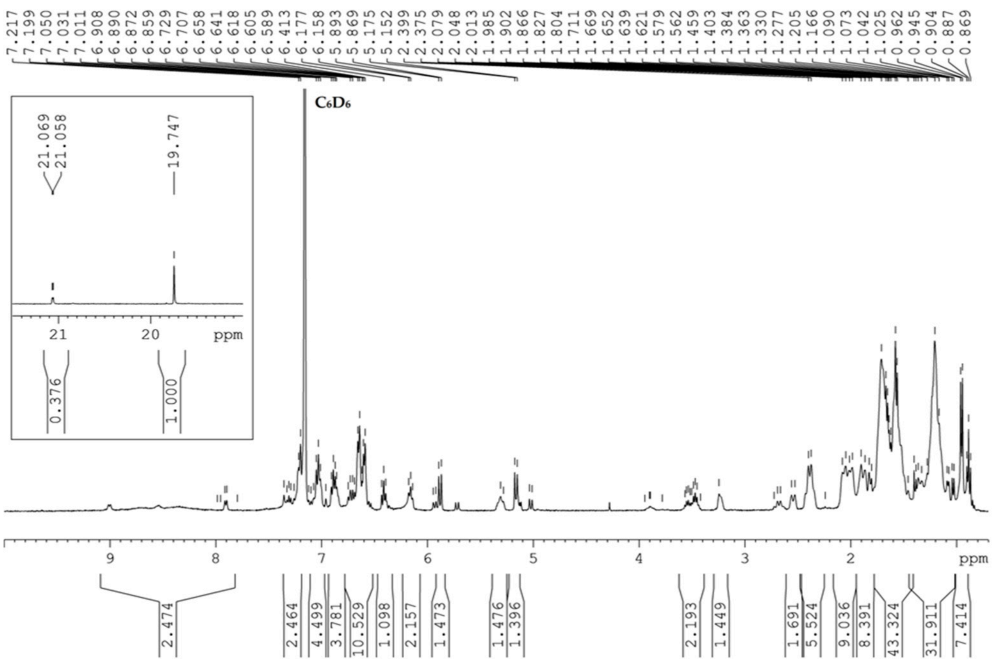

Figure S3. ^{1}H NMR of **1a** (C_6D_6, 400 MHz).

NMR analysis of **1b**: ^{1}H NMR (400 MHz, C_6D_6) (Figure S4): δ 21.06 (minor rotational isomer, d, $^3J_{HP}$ = 4.0 Hz, 0.4H); 19.74 (major rotational isomer, s, 1H); (only major isomer signals are reported below) 9.02–6.57 (overlapped signals of both isomers); 6.41 (t, $^3J_{HH}$ = 7.5 Hz, 1H); 6.15 (br s, 2H); 5.89 (d, $^3J_{HH}$ = 10.52 Hz, 1H); 5.29 (br t, 1H); 5.16 (d, $^3J_{HH}$ = 10.52 Hz, 1H); 3.56–3.44 (o m, 2H); 3.25 (br d, 1H); 2.55 (br d, 1H); 2.41–2.38 (o m, 5H); 2.08–0.91 (overlapped signals of both isomers). ^{13}C NMR (C_6D_6, 100 MHz): δ 299.4 (Ru = CHPh); 221.0 (iNCN, $^2J_{C\text{-}P}$ = 79.2 Hz); 152.3; 137.6; 134.4; 134.0; 133.8; 132.2; 130.6; 130.4; 129.8; 129.1; 127.5; 126.3; 125.9; 75.8; 67.5; 61.1; 33.9; 33.7; 33.5; 33.4; 33.0; 30.4; 30.2; 29.9; 29.8; 28.7; 28.6; 27.3; 26.0; 25.9; 25.4; 23.6. ^{31}P NMR (C_6D_6, 161.97 MHz): δ 24.9; 24.6.

Determination of the specific rotation was not possible due to the rapid decomposition of the complex.

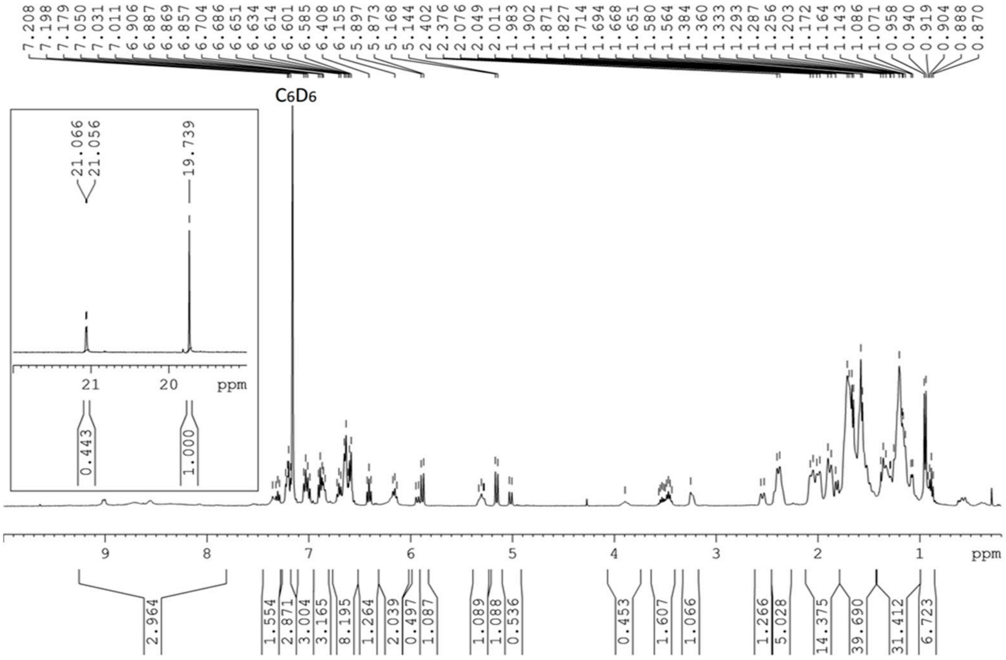

Figure S4. ^{1}H NMR of **1b** (C_6D_6, 400 MHz).

2. GC Data Analysis

2.1. *ARCM of* 5

Chiral Column Supelco β-DEX 120, heating program 60 °C for 60 min, then 5 °C/min up to 100 °C for 10 min. Retention times are 68.7 and 69.0 min (Racemic sample Figure S5, enantioenriched sample Figure S6).

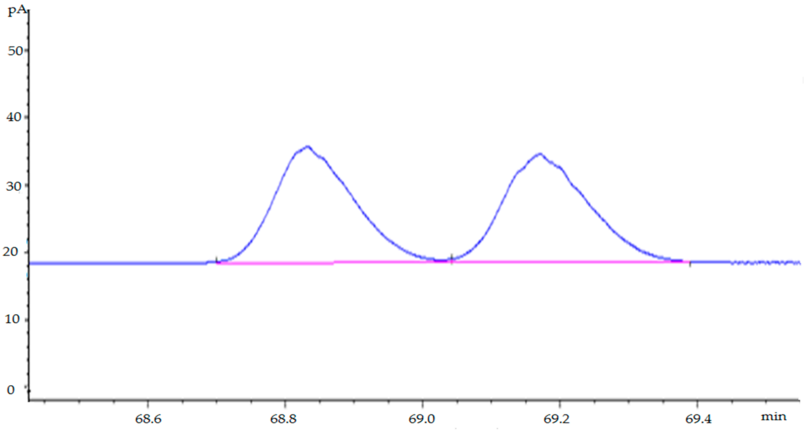

Figure S5.GC analysis of racemic **7**.

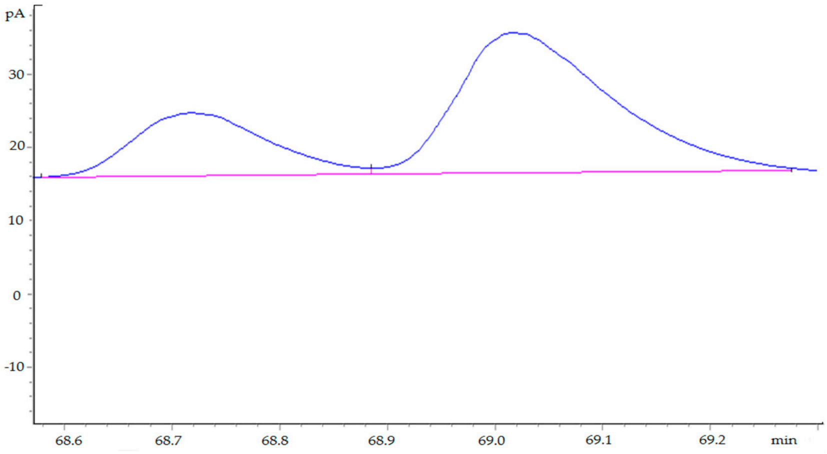

Figure S6. GC analysis of enantioenriched **7** (44 ee %).

2.2. ARCM of ***6***

Column Supelco β-DEX 120, heating program 40 °C for 100 min, then 1 °C/ min up to 50 °C for 120 min, then 1 °C/ min up to 100 °C for 10 min. Retention times are 259.9 and 261.0 min (Racemic sample Figure S7, enantioenriched sample Figure S8).

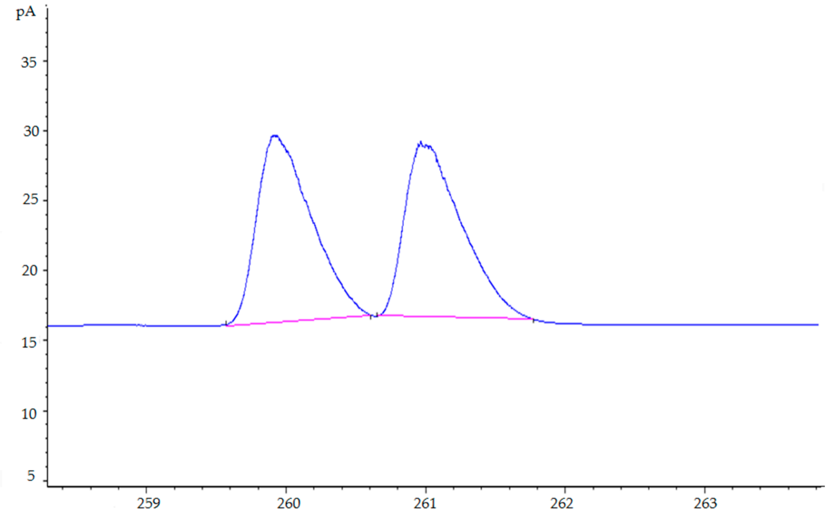

Figure S7. GC analysis of racemic **8**.

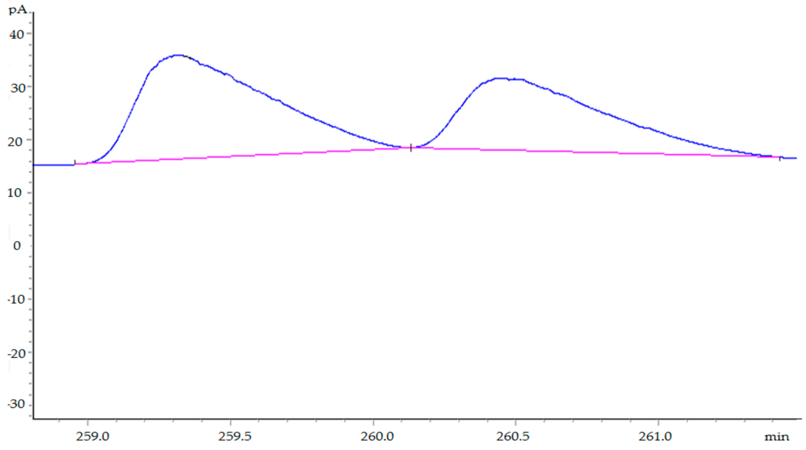

Figure S8. GC analysis of enantioenriched **8** (14 ee %).

3. HPLC Data Analysis

AROCM of **9** *with Styrene*

Column Chiralpak AS-H, Hexane:2-propanol 98:2, 1 mL/min. Retention times are 77.0 and 81.1 min (Racemic sample Figure S9, enantioenriched sample Figure S10).

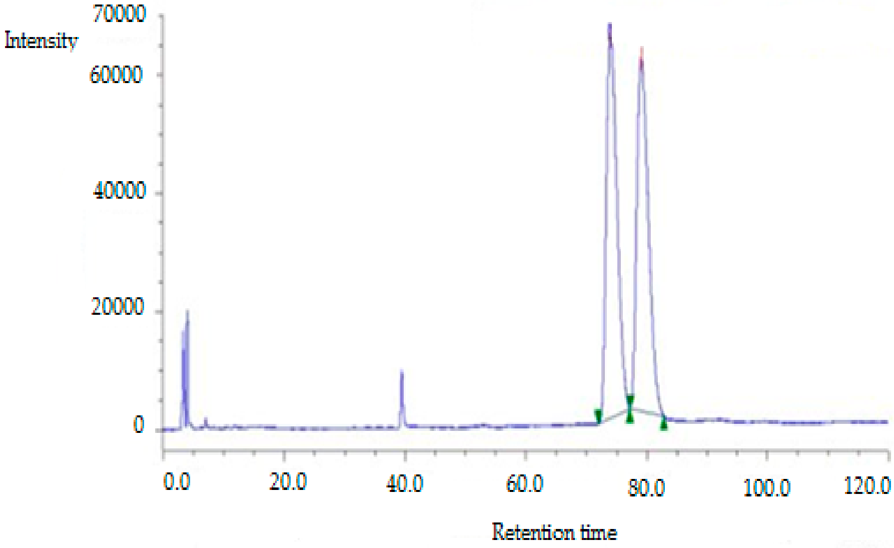

Figure S9. HPLC analysis of racemic **10**.

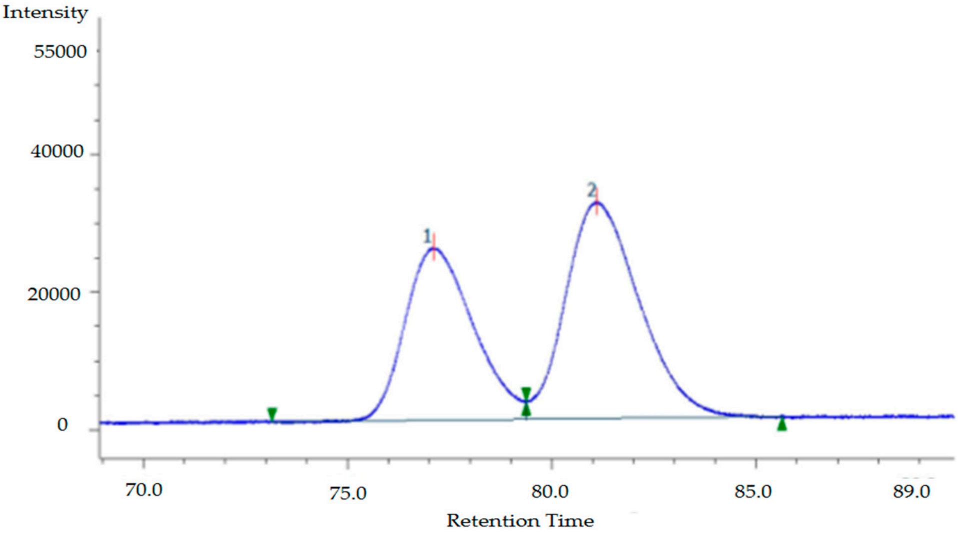

Figure S10. HPLC analysis of enantioenriched **10** (15 ee %).

Reference

1. Paradiso, V.; Bertolasi, V.; Grisi, F. Novel Olefin Metathesis Ruthenium Catalysts Bearing Backbone-Substituted Unsymmetrical NHC Ligands. *Organometallics* **2014**, *33*, 5932–5935.