Electronic Supplementary Information

Ruthenium-catalyzed ring-closing metathesis accelerated by long-range steric effect

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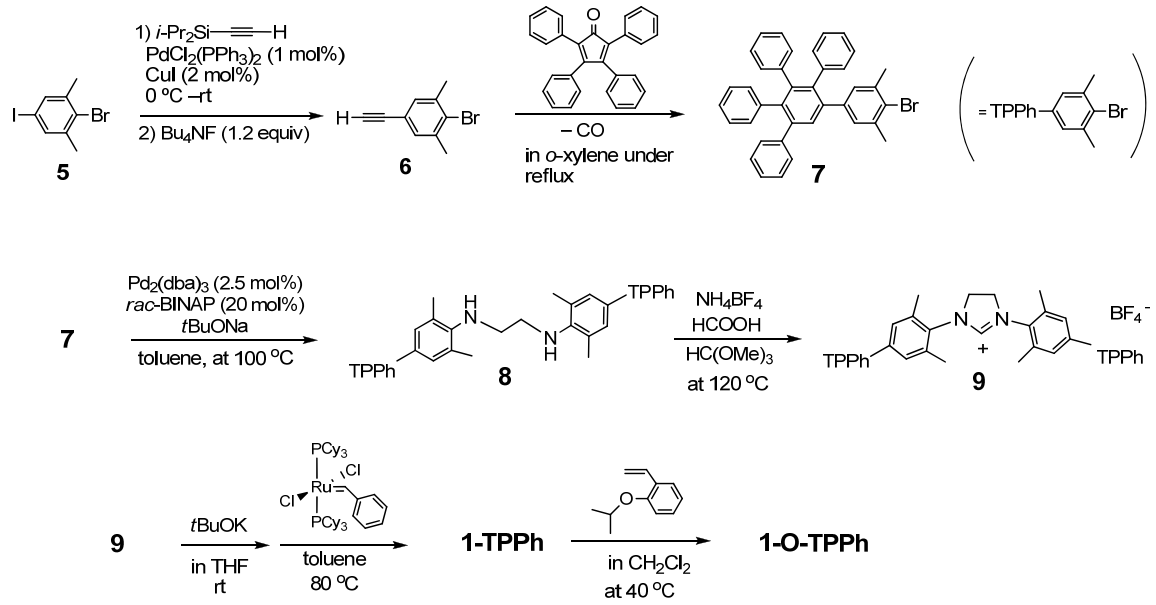
1. Experimental

General procedures and materials

All manipulations were performed under an argon atmosphere using standard Schlenk-type glasswares on a dual-manifold Schlenk line. Reagents and solvents were dried and purified before use by usual procedures.[1] ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were measured with a JEOL ECX-400P spectrometer. The ^{1}H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm) or residual protiated solvent (7.26 ppm) in $CDCl_3$. The ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm). ^{31}P{^{1}H} NMR spectra were also recorded at a JEOL ECX-400P spectrometer using 85% H_3PO_4 as an external standard. MALDI-TOF mass spectra were recorded on a Bruker Autoflex. Elemental analysis was carried out at Center for Organic Elemental Microanalysis, Graduate School of Pharmaceutical Science, Kyoto University. Column chromatography was carried out on silica gel (Kanto N60, spherical, neutral, 63-210 μm) or Alumina (Merck, neutral, Act I). GC analysis was carried out using a Shimadzu GC-17A equipped with an integrator (C-R8A) with a capillary column (CBP-5, 0.25 mm i.d. × 25 m). The Grubbs first-generation catalyst, $(PCy_3)_2(Cl)_2Ru$=CHPh (**2**), was purchased from Aldrich.

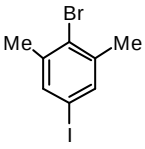
2. Synthesis of Catalysts

A synthetic route of **1-TPPh** and **1-O-TPPh** was shown in Scheme S1.



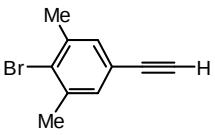
Scheme S1 Synthesis of **1-TPPh** and **1-O-TPPh.**

Synthesis of 2-bromo-5-iodo-*m*-xylene (5)[2]



To a solution of 4-bromo-3,5-dimethylaniline[3] (5.0 g, 25 mmol) in aqueous H_2SO_4 (225 mL, 6.0 M) at –10 °C, a solution of $NaNO_2$ (3.5 g, 50 mmol) in H_2O (20 mL) was added dropwise over a period of 10 min. The resulting mixture was stirred at –10 °C for an additional 15 min. Then, a solution of KI (8.33 g, 50.2 mmol) in H_2O (20 mL) was slowly added to the mixture over a period of 5 min. The reaction mixture was stirred at –10 °C for 15 min, then stirred at 0 °C for 2 h. After the mixture was stirred overnight at room temperature, the resulting mixture was neutralized by adding Na_2CO_3. The mixture was subsequently extracted with Et_2O (100 mL × 4). The combined organic layers were washed with H_2O (200 mL), aqueous Na_2SO_3 (1 M, 50 mL × 2), aqueous NaOH (2.5 M, 50 mL × 2) and H_2O (100 mL), and were dried over $MgSO_4$. After filtration, the filtrate was evaporated to dryness. The residue was purified by silica gel column chromatography using hexane as an eluent. Remove of all volatiles gave colorless oil. Yield 5.0 g (64%). ^{1}H NMR (400 MHz, $CDCl_3$): δ7.40 (s, 2H), 2.35 (s, 6H).

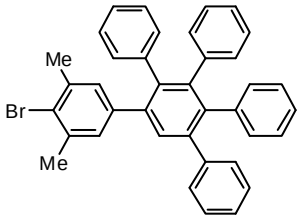
Synthesis of 6



$PdCl_2(PPh_3)_2$ (0.13 g, 0.19 mmol) and CuI (72 mg, 0.38 mmol) were added to a solution of **5** (5.8 g, 19 mmol) and triisopropylsilylacethylene (4.1 g, 22 mmol) in degassed piperidine (30 mL) at 0 °C under an argon atmosphere. The reaction

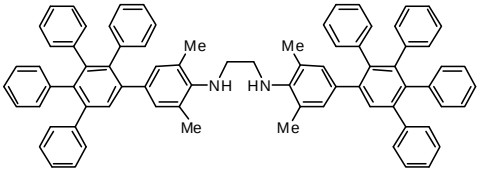
mixture was stirred at 0 °C for 1 h and for an additional 2 h at room temperature. After filtration with Celite, the filtrate was evaporated to dryness. Then, 1 N HCl and Et_2O were added to the residue and the organic layer was washed twice with brine. The combined organic layers were dried over $MgSO_4$. After filtration, the filtrate was evaporated to dryness. The residue was purified by silica gel column chromatography using hexane as an eluent. Removal of all volatiles gave 2-bromo-5-(triisopropylsilyl)ethynyl-*m*-xylene as white needle crystals. Yield 6.7 g (99% based on ^{1}H NMR). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.18 (s, 2H), 2.38 (s, 6H), 1.12 (m, 21H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) δ 138.8, 131.7, 128.3, 122.2, 106.7, 91.3, 23.8, 18.8, 11.7. Anal. calcd for $C_{19}H_{29}BrSi$: C 62.65, H 8.00, found: C 62.36, H 7.97. Tetra(*n*-butyl)ammonium fluoride (1.0 M in THF, 24 mL, 24 mmol) was added to a solution of 2-bromo-5-(triisopropylsilyl)ethynyl-*m*-xylene (7.3 g, 19.9 mmol) in dry THF (25 mL) under an argon atmosphere and the mixture was stirred at room temperature for 1 h under an argon atmosphere. Saturated NH_4Cl aq. (100 mL) and pentane (100 mL) were added to the mixture. The organic layer was washed twice with H_2O and dried over $MgSO_4$. After filtration, the filtrate was evaporated to dryness. Purification by silica gel column chromatography using hexane as an eluent gave colorless oil. Yield 2.8 g (68%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.12 (s, 2H), 3.04 (s, 1H), 2.30 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) δ 139.0, 131.8, 128.8, 120.7, 83.1, 77.3, 23.8. Anal. Calcd for $C_{10}H_9Br$: C 57.44, H 4.34, found: C 57.61, H 4.51.

Synthesis of 7



A solution of tetraphenylcyclopentadienone (4.3 g, 11 mmol) and **6** (2.8 g, 14 mmol) in *o*-xylene (35 mL) was refluxed for 2.5 h under an argon atmosphere. After a color of the reaction mixture changed from dark purple to yellow, all volatiles were removed *in vacuo*. The residue was washed with hexane, and dried *in vacuo*. Yield 13.6 g (99%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.49 (s, 1H), 7.16 (s, 5H), 6.82-6.98 (m, 17H), 2.24 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2) δ 29.8, 111.3, 111.48, 111.53, 111.6, 111.7, 112.1, 112.5, 112.6, 113.1, 114.6, 114.9, 115.0, 115.8, 116.17, 116.19, 116.23, 120.9, 122.4, 122.6, 122.8, 123.06, 123.12, 123.2, 123.4, 123.7, 124.46, 124.53. Anal. Calcd for $C_{38}H_{29}Br$: C 80.70, H 5.17, found: C 80.85, H 5.47.

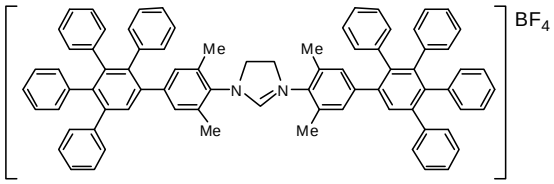
Synthesis of 8



Ethylenediamine (0.14 mL, 2.0 mmol) was added to a mixture of **7** (2.3 g, 4.0 mmol), *t*BuONa (0.58 g, 6.0 mmol), $Pd_2(dba)_3$ (52 mg, 50 μmol) and *rac*-BINAP (0.25 g, 0.40 mmol) in degassed toluene (24 mL) under an argon atmosphere,[4] then the mixture was stirred at 100 °C for 21 h. The mixture was filtrated through Celite and evaporated to dryness. The residue was washed with MeOH and purified by silica gel column chromatography using chloroform as an eluent to give slightly yellow solid. Yield 1.55 g

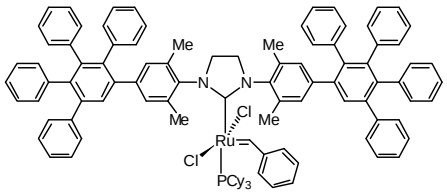
(75%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.48 (s, 2H), 7.16 (s, 10H), 6.81-6.99 (m, 34H), 3.57 (br, 4H), 2.00 (s, 12H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 18.5, 48.7, 125.2, 125.45, 125.49, 126.2, 126.6, 126.9, 127.6, 128.4, 129.0, 130.0, 130.7, 131.3, 131.5, 131.6,, 138.8, 139.1, 140.1, 140.3, 140.4, 140.5, 140.6, 141.6, 141.9.

Synthesis of 9



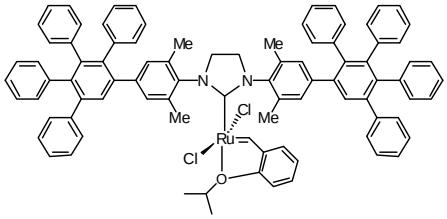
Formic acid (5 drops) was added to a solution of **8** (1.3 g, 1.2 mmol) and NH_4BF_4 (0.19 g, 1.8 mmol) in Ar-bubbled $HC(OMe)_3$ (20 mL). The mixture was refluxed for 4 h. After a removal of all volatiles, the orange solid was suspended in MeOH. The suspension was filtered off and washed with MeOH. The resulting solids were dried *in vacuo* to give white solids. Yield 1.35 g (81%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.78 (s, 1H), 7.51 (s, 2H), 6.83-7.78 (m, 44H), 4.48 (t, 4H), 2.23 (s, 12H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2) δ 17.8, 52.1, 125.8, 126.1, 126.3, 126.8, 127.0, 127.2, 127.5, 128.0, 130.2, 130.9, 131.3, 131.4, 131.8, 134.9, 139.2, 139.6, 140.0, 140.3, 140.4, 140.4, 141.4, 141.9, 142.4, 144.7, 158.5. Anal. for $C_{79}H_{63}BF_4N_2 \cdot CH_3OH$: C 82.89, H 5.83, found: C 82.53, H 5.60. MALDI-TOF-MS (DIT): *m/z* 1625 ($[M\text{-}BF_4]^+$).

Syntheis of 1-TPPh.



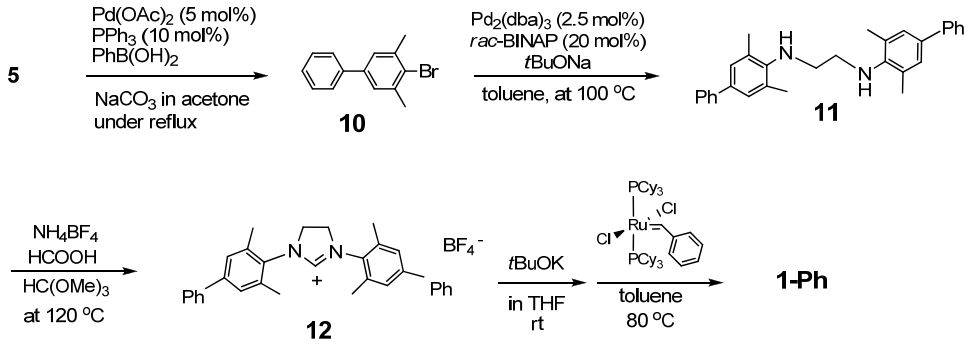
A solution of *t*BuOK in THF (1.0 M, 0.48 mL, 0.48 mmol) was added to a solution of **9** (0.45 g, 0.40 mmol) in degassed THF (9.0 mL) under an argon atmosphere and the resulting mixture was stirred for 1 h at room temperature. After removal of all volatiles under vacuum, a solution of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (**2**: 0.33 g, 0.40 mmol) in degassed toluene (9.0 mL) was added to the residue. The reaction mixture was heated at 80 ^{o}C for 30 min. Then, all volatiles were removed *in vacuo*. Purification was performed with alumina column chromatography using Ar-bubbled toluene as an eluent. Removal of all volatiles gave red solids. The solid was dissolved in a small amount of toluene and re-precipitation by adding pentane to give reddish purple solids. Yield 0.29 g (46%). ^{1}H NMR (400 MHz, CD_2Cl_2, –10 ^{o}C) δ 18.94 (s, 1H), 7.51 (s, 1H), 6.79-7.21 (m, 50H), 3.76 (m, 4H), 0.88-2.47 (m, 45H). ^{31}P{^{1}H} NMR (160 MHz, CD_2Cl_2, –10 ^{o}C) δ 27.97 (s). Anal. Calcd for $C_{104}H_{101}Cl_2N_2PRu$: C 78.96, H 6.44, found: C 79.16, H 6.44. MALDI-TOF-MS (DIT): *m/z* 1582, ($[M]^+$), 1625 ($[M+K]^+$).

Synthesis of 1-O-TPPh



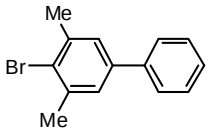
A solution of **1-TPPh** (0.29 g, 0.18 mmol) in CH_2Cl_2 (10 mL) was added to CuCl (79 mg, 0.80 mmol) under an argon atmosphere. Then, isopropoxystylene (69 μL, 0.40 mmol) was added to the mixture and stirred at 40 °C for 1 h.[5] After removal of all volatiles under vacuum, the residue was dissolved in degassed CH_2Cl_2 and purified by alumina column chromatography with Ar-bubbled pentane/CH_2Cl_2 (1:1) as an eluent. Removal of all volatiles gave green solids. The resulting solid was dissolved in a small amount of CH_2Cl_2 and crystallized by adding pentane to afford green crystals. Yield 0.23 g (89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 16.60 (s, 1H), 7.62-6.83 (m, 50H), 4.97 (sept, J = 5.89 Hz, 1H), 4.09 (s, 4H), 2.32 (br, s, 12H), 1.38 (d, J = 5.89 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2,) δ 210.4, 151.7, 144.7, 141.7, 141.5, 140.5, 140.2, 139.8, 139.6, 139.1, 138.8, 131.3, 131.2, 131.1, 129.9, 129.5, 129.2, 127.3, 126.7, 126.5, 126.2, 126.0, 125.4, 125.3, 125.0, 121.94, 121.88, 112.7, 74.8, 51.3, 6,31.2, 22.3, 20.9, 13.6. Anal. Calcd for $C_{89}H_{74}Cl_2N_2ORu \cdot CH_2Cl_2$:$C_{90}H_{76}Cl_4N_2ORu$: C 74.84, H 5.30, N 1.94, found: C 74.25, H 5.19, N 2.04. MALDI-TOF-MS (CSA): *m/z* 1360 ([M]$^+$).

A synthetic route of **1-Ph** was shown in Scheme S2.



Scheme S2 Synthesis of **1-Ph**.

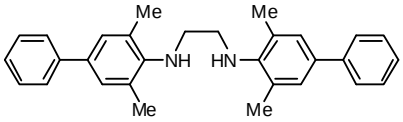
Synthesis of 10



$Pd(OAc)_2$ (95 mg, 0.43 mmol), PPh_3 (0.21 g, 0.81 mmol) and $PhB(OH)_2$ (1.1 g, 8.8 mmol) were suspended in acetone (30 mL). **5** (2.5g, 8.0 mmol) and 2 M Na_2CO_3 aq. (12 mL) were added and the resulting reaction mixture was refluxed for 18 h. After cooling to room temperature, the mixture was poured into water (50 mL) and extracted with Et_2O (100 mL). The organic layer was washed with H_2O and brine, dried over $MgSO_4$. After filtration, the filtrate was evaporated to dryness. Purification was performed by silica gel column chromatography using hexane as an eluent. Removal of all volatiles gave white solids. Yield 1.4 g

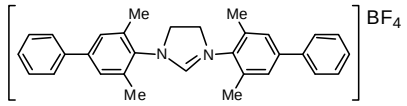
(65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.25 Hz, 2H), 7.43 (dd, *J* = 7.25 Hz, *J* = 7.25 Hz, 2H),. 7.34 (dd, *J* = 6.80 Hz, *J* = 6.80 Hz, 1H), 7.29 (s, 2H).

Synthesis of 11



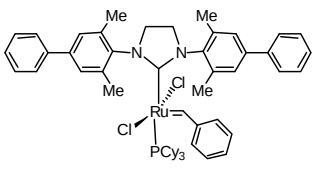
Ethylenediamine (0.14 mL, 2.0 mmol) was added to a mixture of **10** (1.0 g, 4.0 mmol), *t*BuONa (0.58 g, 6.0 mmol), $Pd_2(dba)_3$ (52 mg, 50 μmol) and *rac*-BINAP (0.25 g, 0.40 mol) in degassed toluene (24 mL) under an argon atmosphere,[5] then the mixture was stirred at 100 °C for 44 h. The mixture was filtrated through Celite and the filtrate was evaporated to dryness. Then, the residue was washed with MeOH. The resulted solid was dissolved in $CHCl_3$ and purified by silica gel column chromatography using $CHCl_3$ as an eluent. Removal of all volatiles give pale-yellow solid. Yield 0.62 g (74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.25 Hz, 4H), 7.39 (dd, *J* = 7.25 Hz, *J* = 7.25 Hz, 4H), 7.30-7.22, (m, 6H), 3.46 (br s, 2H), 3.28 (s, 4H), 2.38 (s, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 145.3, 141.0, 134.7, 129.5, 128.5, 127.6, 126.7, 126.5, 48.8, 18.8. Anal. Calcd for $C_{30}H_{32}N_2$: C 85.67, H 7.67, N 6.66, found: C 85.41, H 7.54, N 6.58. MALDI-TOF-MS (DIT): *m/z* 421 ($[M]^+$).

Synthesis of 12



Formic acid (5 drops) was added to a solution of **11** (0.62 g, 1.5 mmol) and NH_4BF_4 (0.23 g, 2.2 mmol) in Ar-bubbled $HC(OMe)_3$ (25 mL). The mixture was refluxed for 6 h. After a removal of volatiles, the orange solid was suspended in MeOH filtered off. The resulting solid was washed with MeOH and dried *in vacuo*. White solids were obtained. Yield 0.66 g (86%). ^{1}H NMR (400 MHz, DMSO-*d*6) δ 9.11 (s, 1H), 7.71 (d, *J* = 7.25 Hz, 4H), 7.61 (s, 4H), 7.50 (dd, *J* = 7.25 Hz, *J* = 7.25 Hz, 4H), 7.42 (dd, *J* = 7.25 Hz, *J* = 7.25 Hz, 2H), 4.55 (s, 4H), 2.50 (s, 12H). ^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*6) δ 145.3, 141.0, 134.7, 129.5, 128.5, 127.6, 126.7, 126.5, 48.8, 18.8. Anal. Calcd for $C_{31}H_{31}BF_4N_2$: C 71.82, H 6.03, N 5.40, found: C 71.62, H 6.03, N 5.45. MALDI-TOF-MS (DIT): *m/z* 431 ($[M\text{-}BF_4]^+$).

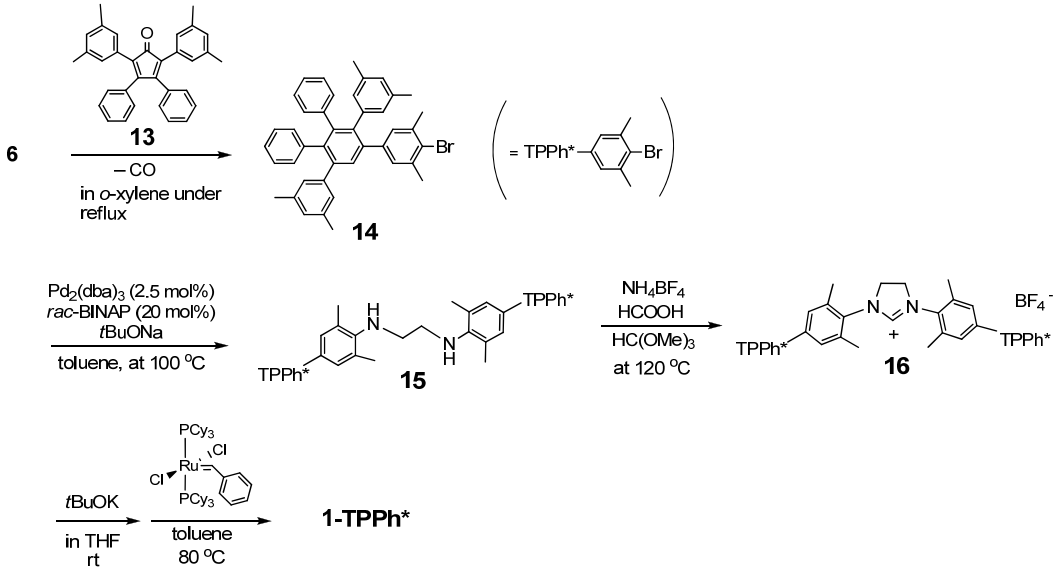
Synthesis of 1-Ph



A solution of *t*BuOK in THF (1.0 M, 1.0 mL, 1.0 mmol) was added to a suspension of **12** (0.42 g, 0.80 mmol) in degassed THF (18 mL) under Ar atmosphere and the resulting mixture was stirred for 1 h at room temperature. After removal of all volatiles under vacuum, a solution of **2** (0.66 g, 0.80 mmol) in degassed toluene (18 mL) was added to the residue. The reaction mixture was heated at 80 °C for 30 min. Then, all volatiles were removed *in vacuo*. Purification was performed with alumina column chromatography using Ar-bubbled toluene as an eluent. Removal of all volatiles gave red solids. The solid was dissolved in a small amount of toluene and precipitated by adding pentane to give reddish purple solids. Yield 0.33 g (44%). ^{1}H NMR (400 MHz, CD_2Cl_2, –10 °C) δ 18.97 (s, 1H),

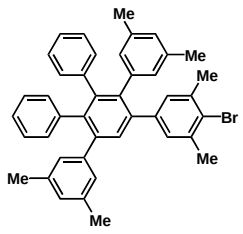
8.91 (d, *J* = 7.70 Hz, 1H), 7.62 (d, *J* = 6.80 Hz, 1H), 7.46-7.10 (m, 14H), 6.84 (d, *J* = 8.16 Hz, 1H), 6.65 (t, *J* = 7.25 Hz, 1H), 6.20 (s, 1H), 4.08-3.74 (m, 4H), 2.82 (s, 3H), 2.62 (s, 3H), 2.59 (s, 3H), 2.05 (s, 3H), 1.39-0.64 (m, 33H). $^{31}P\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, -20 °C) δ 30.56 (s). Anal. Calcd for $C_{56}H_{69}Cl_2N_2PRu$: C 69.12, H 7.15, N 2.79, found: C 69.39, H 7.18, N 2.75. MALDI-TOF-MS (CSA): *m/z* 973 ($[M]^+$).

A synthetic route of **1-TPPh*** was shown in Scheme S3.



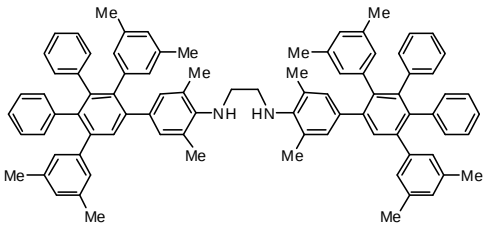
Scheme S3 Synthesis of **1-TPPh***.

Synthesis of 14



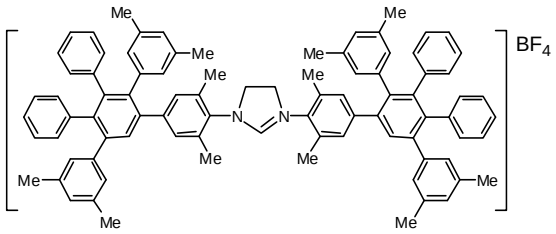
A solution of **13**[6] (5.4 g, 12 mmol) and **6** (2.8 g, 14 mmol) in *o*-xylene (40 mL) was refluxed for 24 h under Ar atmosphere. After a color of the reaction mixture changed from dark purple to yellow, all volatiles were removed *in vacuo*. The residue was washed with hexane, and dried *in vacuo*. Pale-orange solids were obtained. 7.30 g (86%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 1H), 6.94-6.75 (m, 16H), 6.55 (s, 1H), 6.44 (s, 1H), 2.25 (s, 6H) 2.14 (s, 6H), 2.00 (s, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 141.7, 141.5, 140.6, 140.4, 140.3, 140.1, 139.40, 139.36, 139.20, 139.19, 137.1, 136.9, 136.0, 131.44, 131.38, 131.0, 129.8, 129.4, 127.9, 127.8, 127.1, 126.8, 126.4, 125.48, 125.45, 125.2, 23.7, 21.2, 21.0. Anal. Calcd for $C_{42}H_{37}Br$: C 81.15, H 6.00, found: C 81.34, H 5.95. MALDI-TOF-MS (CSA): *m/z* 621 ($[M]^+$).

Synthesis of 15



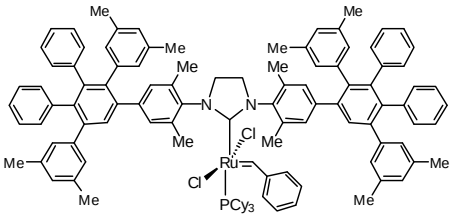
Ethylenediamine (0.14 mL, 2.0 mmol) was added to a solution of **14** (2.3 g, 4.0 mmol), *t*BuONa (0.870 g, 9.1 mmol), $Pd_2(dba)_3$ (78 mg, 75 μmol) and *rac*-BINAP (0.37 g, 0.60 mmol) in degassed toluene (36 mL) under an argon atmosphere,[4] then the mixture was stirred at 100 °C for 2 days. The mixture was filtrated through Celite and evaporated to dryness. The residue was washed with MeOH and purified by silica gel column chromatography using chloroform as an eluent. Pale-yellow solids were obtained. 2.7 g (78%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 2H), 6.93-6.75 (m, 30H), 6.52 (s, 2H), 6.44 (s, 4H), 3.27 (br s, 2H), 3.11 (s, 4H), 2.14 (s, 12H) 2.12 (s, 12H), 1.97 (s, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$,) δ 143.9, 141.7, 141.5, 140.7, 140.4, 140.3, 140.2, 139.8, 139.2, 138.5, 136.8, 135.7, 135.3, 131.53, 131.45, 131.1, 130.6, 129.5, 128.1, 127.9, 127.6, 126.8, 126.7, 126.3, 125.3, 125.0, 48.8, 21.2, 21.0, 18.5. Anal. Calcd for $C_{86}H_{80}N_2$: C 90.48, H 7.06, N 2.45, found: C 90.21, H 7.04, N 2.46.

Synthesis of 16



Formic acid (7 drops) was added to a solution of **15** (2.3 g, 2.0 mmol) and NH_4BF_4 (0.32 g, 3.0 mmol) in Ar-bubbled $HC(OMe)_3$ (32 mL). The mixture was refluxed for 5 h. After a removal of all volatiles, the orange solid was suspended in MeOH. The suspension was filtered off and washed with MeOH. The resulting solids were dried *in vacuo* to give white solids. 2.0 g (81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.47 (s, 2H), 7.02 (s, 4H), 6.94-6.75 (m, 24H), 6.58 (s, 2H), 6.45 (s, 4H), 4.57 (s, 4H), 2.25 (s, 12H), 2.15 (s, 12H), 2.01 (s, 12H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$,) δ 157.5, 144.7, 142.0, 141.2, 140.8, 140.1, 139.91, 139.87, 139.2, 139.1, 138.3, 137.0, 134.2, 131.34, 131.26, 131.1, 130.9, 130.3, 129.2, 127.9, 127.8, 127.5, 126.8, 126.5, 125.6, 125.3, 51.9, 21.2, 21.1, 17.6. Anal. Calcd for $C_{87}H_{79}BF_4N_2$: C 84.31, H 6.42, N 2.26, found: C 84.09, H 6.49, N 2.20. MALDI-TOF-MS (DIT): *m/z* 1152 ([M-BF_4]$^+$).

Synthesis of 1-TPPh*



A solution of *t*BuOK in THF (1.0 M, 0.48 mL, 0.48 mmol) was added to a solution of **16** (0.50 g, 0.40 mmol) in degassed THF (9.0 mL) under Ar atmosphere and the resulting mixture was stirred for 1 h at room temperature. After removal of all volatiles under vacuum, a solution of $(PCy_3)_2(Cl)_2Ru{=}CHPh$ (0.33 g, 0.40 mmol) in degassed toluene (9.0 mL) was added to the residue. The reaction mixture was heated at 80 °C for 30 min. Then, all volatiles were removed *in vacuo*. Purification was performed with alumina column chromatography using Ar-bubbled toluene as an eluent. Removal of all volatiles gave red solids. The solid was dissolved in a small amount of toluene and reprecipitation by adding pentane. Reddish purple solid, 0.35 g (52%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 18.93 (s, 1H), 8.85 (d, J = 6.80, 1H), 7.49 (s, 1H), 7.19-6.73 (m, 31H), 6.67 (s, 2H), 6.57 (s, 1H), 6.48 (s, 2H), 6.41 (s, 2H) 6.34 (s, 1H), 6.15 (s, 1H), 5.91 (s, 1H), 3.73 (m, 4H), 2.53-0.74 (m, 69H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$,) δ 219.6 (d, J_{CP} = 76.3 Hz), 151.5, 141.7, 141.6, 141.5, 141.4, 141.2, 140.8, 140.54, 140.53, 140.43, 140.41, 140.38, 139.97, 139.95, 139.8, 139.5, 139.4, 139.12, 139.10, 138.9, 138.0, 137.1, 137.0, 136.12, 136.09, 135.9, 131.5, 130.8, 130.7, 130.6, 128.1, 127.91, 127.87, 127.78, 127.0, 126.9, 126.83, 126.79, 126.50, 126.47, 125.65, 125.61, 125.4, 125.3, 52.4, 51.3, 31.1, 30.9, 27.8, 27.7, 26.4, 22.6, 21.2, 21.1, 20.9, 20.8, 20.8, 19.7, 14.1. Anal. Calcd for $C_{112}H_{117}Cl_2N_2PRu$: C 79.41, H 6.96, N 1.65, found: C 79.23, H 6.99, N 1.66. MALDI-TOF-MS (CSA): *m/z* 1694 ($[M]^+$).

3. General Procedure for the reaction in Table 1.

In a 20 mL Schlenk-type glassware, **1** (2.5 μmol, 1.0 mol%) and bibenzyl (18 mg, 0.10 mmol as an internal standard) were dissolved in toluene (5.0 mL) under an argon atmosphere and the resulting solution was cooled to 0 °C. Diolefin **3** (0.25 mmol) was added to the solution via gas-tight syringe and the reaction mixture was stirred at 0 °C under an argon atmosphere. After the reaction was terminated by adding ethyl vinyl ether (3.0 mL), the yield of the product was determined by GC analysis relative to the internal standard.

4. General Procedure for the reaction in Table 2.

In a 20 mL Schlenk-type glassware, **1** (2.5 μmol, 1.0 mol%), PCy_3 (0.25 μmol or 0.50 μmol) and bibenzyl (18 mg, 0.10 mmol as an internal standard) were dissolved in toluene (5.0 mL) under an argon atmosphere. and the resulting solution was cooled to 0 °C. **3a** (0.25 mmol) was added to the solution via gas-tight syringe and the reaction mixture was stirred at 0 °C under an argon atmosphere. After the reaction was terminated by adding ethyl vinyl ether (3.0 mL), the yield of the product was determined by GC analysis relative to the internal standard.

5. General Procedure for the reaction in Table 3

In a 20 mL Schlenk-type glassware, **1** (2.5 μmol, 1.0 mol%), CuCl (0.99 mg, 0.010 mmol), bibenzyl (18 mg, 0.10 mmol as an internal standard) were suspended in THF (2.0 mL) under an argon atmosphere. The resulting solution was cooled to reaction temperature and stirred for 5 min. (in the case of room temperature) or 10 min (in the case of 10 °C or 0 °C). Diolefin **3** (0.25 mmol) was added to the solution via gas-tight syringe and the reaction mixture was stirred under an argon atmosphere. After the reaction was terminated by adding ethyl vinyl ether (3.0 mL), the yield of the product was determined by GC analysis relative to the internal standard.

6. Time-dependent changes of the reaction of 3f (Fig. S1)

In a 20 mL Schlenk-type glassware, **1** (2.5 μmol), CuCl (0.99 mg, 0.010 mmol), bibenzyl (18 mg, 0.010 mmol as an internal standard) were suspended in THF (2.0 mL) under an argon atmosphere and the resulting mixture was stirred for 10 min. **3f** (0.25 mmol) was added to the mixture via gas-tight syringe and the reaction mixture was stirred under an argon atmosphere. The yield of **4f** at each reaction time was determined by GC analysis relative to the internal standard.

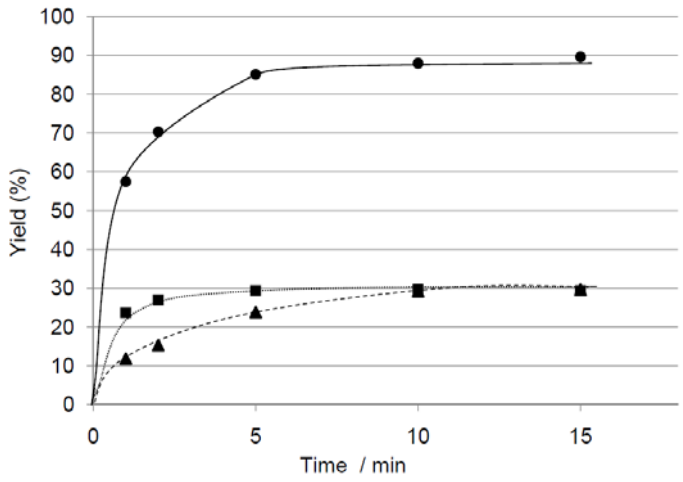


Fig. S1 Time-dependent changes of the reaction of **3f** with **1-TPPh*** (●; entry 6 in Table 3), **1-TPPh** (■; entry 7) and **1-Me** (▲; entry 8) as catalysts.

7. Crystal Structure Refinement

Data were collected on a Rigaku/Saturn70 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) at 153 K, and processed using CrystalClear[7] (Rigaku). Single crystals of **1-O-TPPh** for X-ray diffraction study were obtained by diffusion of pentane into **1-O-TPPh** in CH_2Cl_2. The structures was solved by direct methods (SHELX97[8]) and refined by full-matrix least-square refinement on F^2. The non-hydrogen atoms except for disordered solvents were refined anisotropically. All hydrogen atoms were located on the calculated positions and not refined. All calculations were performed using the CrystalStructure[9] crystallographic software package. *Crystal data for* **1-O-TPPh**: $C_{92}H_{80}Cl_8N_2ORu$, M = 1614.35, T = 153 K, triclinic, space group $P\bar{1}$ (No. 2), a = 12.7107(2) Å, b = 14.1983(1) Å, c = 24.5773(13) Å, α = 86.648(8) º, β = 89.389(8) º, γ = 63.635(6) º, U = 3966.7(2) Å^3, Z = 2, μ (Mo Kα) = 5.16 cm^{-1}, Unique reflections 16946 (R_{int} = 0.065), $R1(I > 2\sigma(I))$, $wR2$ = 0.0857, 0.1643. GOF = 1.321. CCDC 825592 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

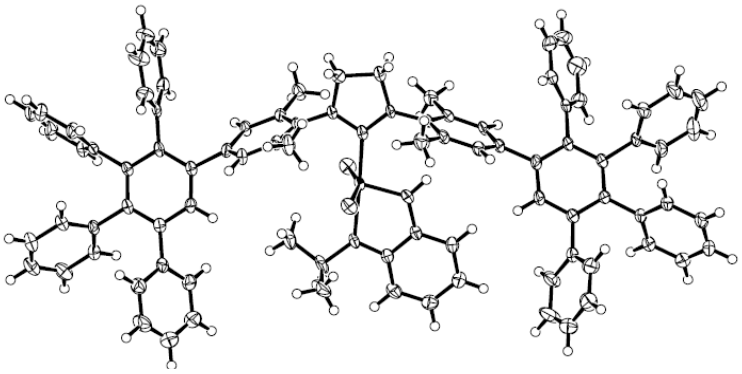


Fig. S2 Molecular structure of **1-O-TPPh** with thermal ellipsoids at 50% probability levels.

A single crystal for **1-TPPh** was obtained by diffusion of pentane into **1-TPPh** in CH_2Cl_2 in a refrigerator (–20 ^{o}C) and data were collected on a Rigaku/Saturn70 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71070 Å) at 153 K, and processed using CrystalClear[7] (Rigaku). However, the structure was not completely solved due to disorder of cyclohexyl groups on PCy_3 and solvated CH_2Cl_2. Fig. S2 showed one of molecular structures of **1-TPPh**. *Crystal data for* **1-TPPh**: $C_{104}H_{101}Cl_2N_2PRu{\cdot}nCH_2Cl_2$, T = 153 K, triclinic, space group $P\bar{1}$ (No. 2), a = 11.049(2) Å, b = 27.744(6) Å, c = 36.361(7) Å, α = 36.361(7) º, β = 98.794(3) º, γ = 101.472(4) º, U = 10780(4) Å^3, Z = 4, Unique reflections 48578 (R_{int} = 0.051), $R1$ ($I > 2\sigma$ (I)), $wR2$ (all data) = 0.154, 0.440.

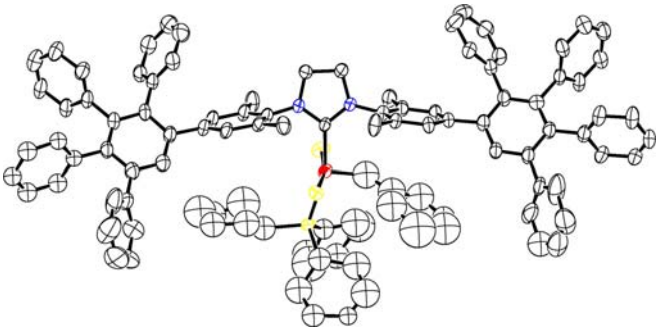


Fig. S3 A molecular structure of **1-TPPh**. Disordered atoms were omitted for clarity.

8. Optimization of structures for 1-TPPh and 1-TPPh*

An initial structure of **1-TPPh** was obtained by a preliminary crystallographic result (Fig. S3). The structure of **1-TPPh** was optimized by B3LYP[10]/LANL2DZ[11] calculation (Fig. S4). The structure of **1-TPPh*** was also optimized by B3LYP[10]/LANL2DZ[11] calculation (Fig. S5). All calculations were performed with the Gaussian 03 program[12] on a HIT HPC-IA642/SS 1.3/3D-4G.

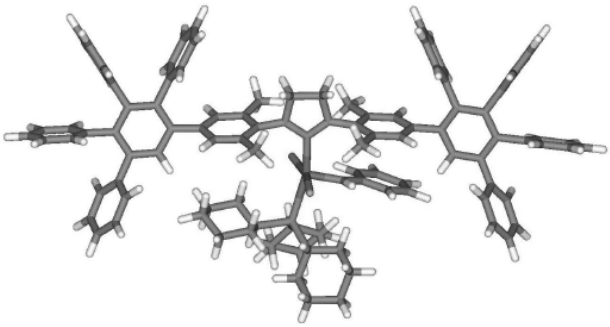


Fig. S4 An optimized structure of **1-TPPh** calculated by B3LYP/LANL2DZ.

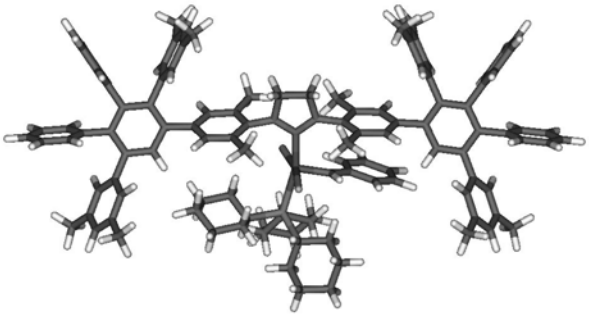


Fig. S5 An optimized structure of **1-TPPh*** calculated by B3LYP/LANL2DZ.

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