Oxidative Coupling with Zr(IV) Supported by a Non-Innocent Anthracene-Based Ligand: Application to the Catalytic Cotrimerization of Alkynes and Nitriles to Pyrimidines

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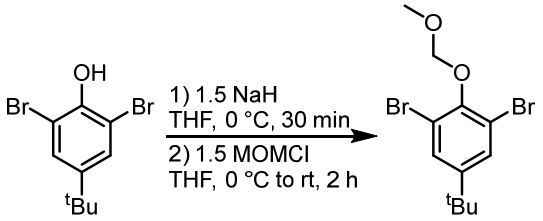
Supporting Information

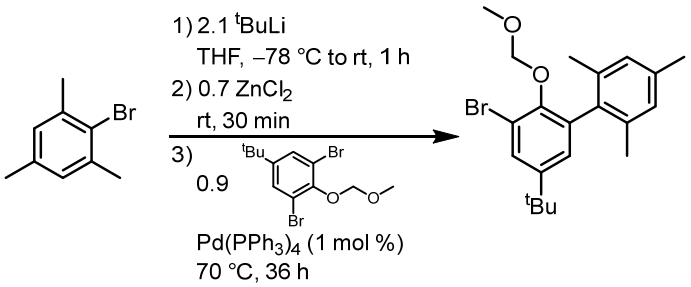
Contents

General Considerations. Unless otherwise specified, all operations involving air- or water-sensitive reagents were carried out in an MBraun drybox under a nitrogen atmosphere or using standard Schlenk and vacuum line techniques. Solvents for air- and moisture-sensitive reactions were dried by the method of Grubbs.[1] Deuterated solvents were purchased from Cambridge Isotope Laboratories and C_6D_6 vacuum transferred from sodium benzophenone ketyl before use. All solvents, once dried and degassed, were stored under a nitrogen atmosphere over 4 Å molecular sieves. Sodium hydride dispersion in oil was washed with multiple times with hexanes and dried *in vacuo* before used. 4-*tert*-butyl-2,6-dibromophenol,[2] chloromethyl methyl ether solution,[3] tetrabenzylzirconium,[4] and $Mg(THF)_3(C_{14}H_{10})$[5] were prepared according to literature procedures. Alkynes and nitriles used were either sublimed under reduced pressure or distilled from calcium hydride before use. All other reagents were used as received. ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra were recorded on Varian Mercury 300 MHz or Varian 400 MHz spectrometers at ambient temperatures, unless otherwise denoted. ^1H and $^{13}C\{^1H\}$ NMR spectra are reported referenced internally to residual solvent peaks reported relative to tetramethylsilane. ^{19}F NMR chemical shifts are referenced to external standard of C_6F_6 (-164.9 ppm). Fast atom bombardment-mass spectrometry (FAB-MS) analyses were performed with a JEOL JMS-600H high resolution mass spectrometer. Gas chromatography-mass spectrometry (GC-MS) were performed with on an Agilent 6890A instrument using a HP-5MS column (30 m length, 0.25 mm diameter, 0.50 μm film) and an Agilent 5973N mass-selective EI detector. Photolyses were conducted using an Oriel Instruments arc lamp housing and a Osram 75 W Xe arc lamp set to a current of 5.4 A.

Experimental

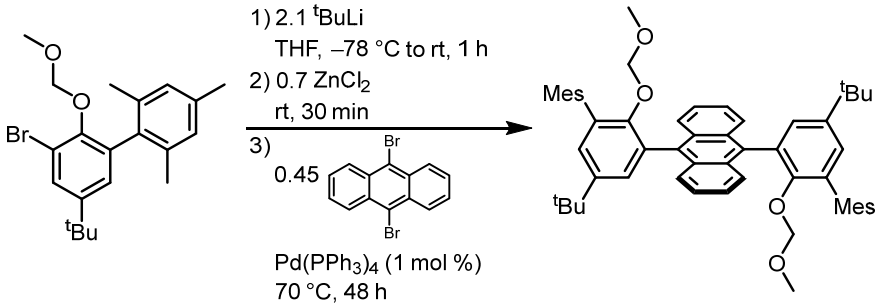


1,3-dibromo-5-(*tert*-butyl)-2-(methoxymethoxy)benzene. To a solution of 2,6-dibromo-4-(*tert*-butyl)phenol (100 g, 325 mmol) in THF (500 mL) at 0 °C was added portion-wise NaH (11.7 g, 487 mmol) slowly (caution: effervescence). After stirring for an additional 30 min, a toluene solution of chloromethyl methyl ether (232 mL, 487 mmol, 2.1 M) was added slowly at 0 °C. After complete addition, the reaction was allowed to warm up to room temperature and stirred an additional 2 h. The reaction was quenched by the slow addition of water (50 mL) and was then concentrated to *ca.* 200 mL under vacuum. The remaining suspension was partitioned between water (300 mL) and CH_2Cl_2 (200 mL). The organic layer was separated and the aqueous layer extracted with CH_2Cl_2 (2 × 200 mL). The combined organic extracts was then dried over $MgSO_4$, filtered and concentrated *in vacuo* to provide a pale yellow oil (106.8 g, 98.4%). The product was further dried by stirring over calcium hydride and filtering before using in the next step. ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (s, 2H, Ar*H*), 5.15 (s, 2H, CH_2), 3.72 (s, 3H, OCH_3), 1.28 (s, 9H, C(CH_3)$_3$); $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 150.28 (aryl-*C*), 149.13 (aryl-*C*), 130.20 (aryl-*C*), 118.02 (aryl-*C*), 99.66 (*C*H_2), 58.58 (O*C*H$_3$), 34.72 (*C*(CH$_3$)$_3$), 31.26 (C(*C*H$_3$)$_3$); HRMS (FAB+) m/z Calcd. for $C_{12}H_{16}Br_2O_2$ $[(M + H) - H_2]^+$ 350.9418, found 350.9406.

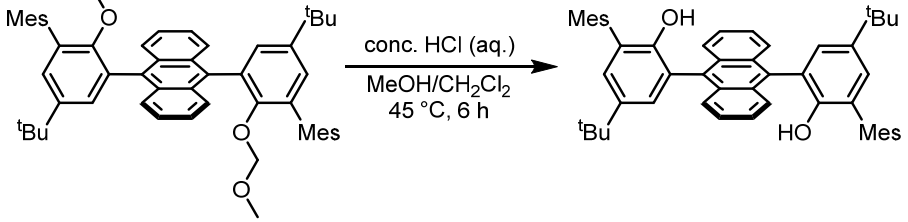


3-bromo-5-(*tert*-butyl)-2-(methoxymethoxy)-2',4',6'-trimethyl-1,1'-biphenyl. A Schlenk flask fitted with a screw-in Teflon stopper was charged with a solution of 2-bromomesitylene (24.1 mL, 157 mmol) in THF (500 mL) and cooled to –78 °C. A pentane solution of *tert*-butyllithium (174 mL, 1.9 M, 331 mmol) was added dropwise *via* cannula. The reaction was allowed to warm to room temperature and stirred for 1 h forming an orange solution. The reaction was then brought into a N_2-purged glovebox and $ZnCl_2$ (15.1 g, 110 mmol) was added slowly to the reaction resulting in the loss of the orange coloration. The mixture was allowed to stir at room temperature for 30 min. 1,3-dibromo-5-(*tert*-butyl)-2-(methoxymethoxy)benzene (50.0 g, 142 mmol) and $Pd(PPh_3)_4$ (1.82 g, 1.57 mmol) was added, the flask

sealed and warmed to 70 °C for 36 h. After cooling to room temperature, water (50 mL) was added to quench the reaction, and the mixture concentrated *in vacuo* to about 100 mL. The resulting suspension was taken up in CH_2Cl_2 (200 mL) and filtered through a silica gel plug, eluting further with CH_2Cl_2. The filtrate was then washed with water (2 × 200 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford the crude product as a pale yellow oil. The crude mixture can be purified *via* Kugelrohr distillation, providing the desired product as a viscous colorless oil that crystallizes on standing (41.2 g, 74.1%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, Ar*H*), 7.06 (d, $^4J_{H,H}$ = 2.2 Hz, 1H, Ar*H*) 6.94 (s, 2H, Ar*H*) 4.70 (s, 2H, CH_2), 2.99 (s, 3H, OCH_3), 2.32 (s, 3H, ArCH_3), 2.05 (s, 6H, ArCH_3) 1.30 (s, 9H, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 149.23 (aryl-*C*), 148.72 (aryl-*C*), 137.18 (aryl-*C*), 136.83 (aryl-*C*), 135.43 (aryl-*C*; coincidental overlap), 129.34 (aryl-*C*), 128.31 (aryl-*C*), 128.14 (aryl-*C*), 117.64 (aryl-*C*), 98.67 (*C*H$_2$), 56.88 (O*C*H$_3$), 34.64 (*C*(CH$_3$)$_3$), 31.44 (C(*C*H$_3$)$_3$), 21.18 (Ar*C*H$_3$), 20.72 (Ar*C*H$_3$); HRMS (FAB+) m/z Calcd. for $C_{21}H_{27}BrO_2$ [(M + H) – H_2]$^+$ 391.1096, found 391.1099.

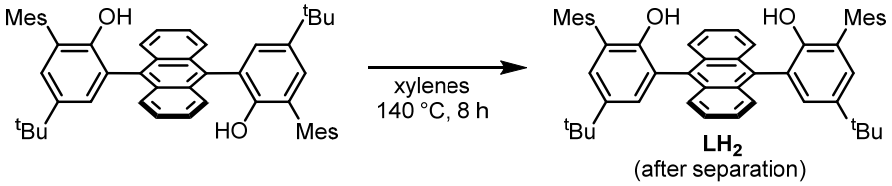


***Anti*-9,10-bis(5-(*tert*-butyl)-2-(methoxymethoxy)-2',4',6'-trimethyl-[1,1'-biphenyl]-3-yl)anthracene.** A Schlenk flask fitted with a screw-in Teflon stopper was charged with a solution of 3-bromo-5-(*tert*-butyl)-2-(methoxymethoxy)-2',4',6'-trimethyl-1,1'-biphenyl (20.0 g, 50.1 mmol) in THF (200 mL) and cooled to –78 °C. A pentane solution of *tert*-butyllithium (56.5 mL, 1.9 M, 107 mmol) was added dropwise *via* cannula. The reaction was allowed to warm to room temperature and stirred for 1 h forming a dark orange solution. The reaction was then brought into a N_2-purged and $ZnCl_2$ (4.89 g, 35.9 mmol) was added slowly to the reaction resulting in the formation of a cloudy pale yellow mixture. The reaction was allowed to stir at room temperature for 30 min after which 9,10-dibromoanthracene (7.73 g, 23.0 mmol) and $Pd(PPh_3)_4$ (591 mg, 0.51 mmol) was added. The flask was sealed and warmed to 70 °C for 48 h. After cooling to room temperature, water (20 mL) was added to quench the reaction, and the mixture concentrated *in vacuo* to about 50 mL. The resulting suspension was taken up in CH_2Cl_2 (200 mL) and filtered through a silica gel plug, eluting further with CH_2Cl_2. The filtrate was then washed with water (2 × 200 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford the crude product as a sticky yellow solid which was triturated in MeOH (250 mL) with aid of sonication, filtered and dried *in vacuo* to provide the product as a pale yellow powder (16.2 g, 88.2%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (app dd, $J_{H,H}$ = 6.8, 3.3 Hz, 4H, anth–*H*), 7.38 (app dd, $J_{H,H}$ = 6.8, 3.3 Hz, 4H, anth–*H*), 7.33 (d, $^4J_{H,H}$ = 2.5 Hz, 2H, Ar*H*), 7.27 (d, $^4J_{H,H}$ = 2.5 Hz, 2H, Ar*H*), 6.97 (s, 4H, Ar*H*), 4.06 (s, 4H, CH_2), 2.33 (s, 6H, ArCH_3), 2.27 (s, 12H, ArCH_3), 2.10 (s, 6H, OCH_3), 1.35 (s, 18H, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 151.09 (aryl-*C*), 147.11 (aryl-*C*), 136.94 (aryl-*C*), 136.78 (aryl-*C*), 136.27 (aryl-*C*), 134.72 (aryl-*C*), 134.29 (aryl-*C*), 132.29 (aryl-*C*), 130.34 (aryl-*C*), 129.11 (aryl-*C*), 128.64 (aryl-*C*), 128.15 (aryl-*C*), 127.18 (aryl-*C*), 125.25 (aryl-*C*), 97.98 (*C*H$_2$), 55.42 (O*C*H$_3$), 34.70 (*C*(CH$_3$)$_3$), 31.72 (C(*C*H$_3$)$_3$), 21.21 (Ar*C*H$_3$), 21.04 (Ar*C*H$_3$); HRMS (FAB+) m/z Calcd. for $C_{56}H_{62}O_4$ [M]$^+$ 798.4648, found 798.4674.

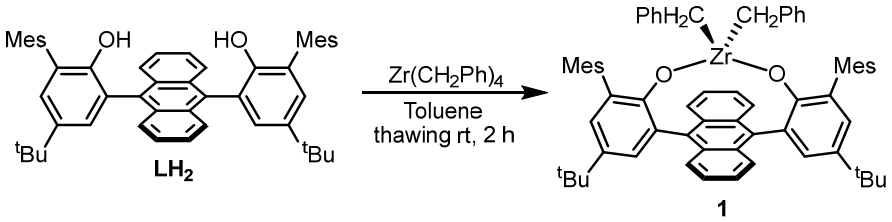


***Anti*-3,3''-(anthracene-9,10-diyl)bis(5-(*tert*-butyl)-2',4',6'-trimethyl-[1,1'-biphenyl]-2-ol).** A Schlenk flask fitted with a screw-in Teflon stopper was charged with *anti*-9,10-bis(5-(*tert*-butyl)-2-(methoxymethoxy)-2',4',6'-trimethyl-[1,1'-biphenyl]-3-yl)anthracene (15.0 g, 18.8 mmol), MeOH (100 mL) and CH_2Cl_2 (200 mL). Concentrated aqueous HCl (20 mL) was added, the flask sealed and heated to 45 °C, monitoring the progress of the reaction *via* ^{1}H NMR spectroscopy. After complete deprotection, about 6 h, the reaction was cooled and concentrated *in vacuo*. The

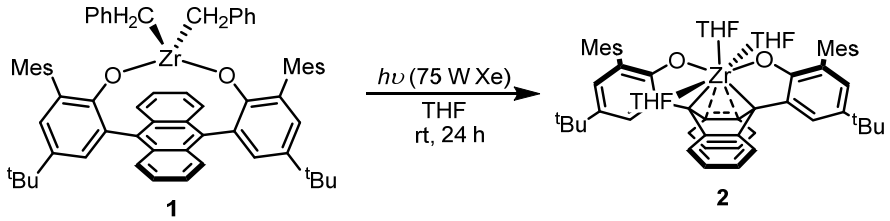
suspension was taken up in CH_2Cl_2 (250 mL) and washed with H_2O (2 × 200 mL) and then saturated aqueous $NaHCO_3$ (100 mL). The organic fraction was dried over $MgSO_4$, filtered and concentrated under reduced pressure to provide the product as a pale yellow solid (13.2 g, 98.9%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (app dd, $J_{H,H}$ = 6.8, 3.3 Hz, 4H, anth–*H*), 7.41 (app dd, $J_{H,H}$ = 6.8, 3.0 Hz, 4H, anth–*H*), 7.34 (d, $^4J_{H,H}$ = 2.5 Hz, 2H, Ar*H*), 7.27 (d, $^4J_{H,H}$ = 2.5 Hz, 2H, Ar*H*), 7.03 (s, 4H, Ar*H*), 4.47 (s, 2H, O*H*), 2.35 (s, 6H, ArCH_3), 2.22 (s, 12H, ArCH_3), 1.35 (s, 18H, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 148.56 (aryl-*C*), 143.58 (aryl-*C*), 137.67 (aryl-*C*), 137.50 (aryl-*C*), 133.68 (aryl-*C*), 133.28 (aryl-*C*), 130.73 (aryl-*C*), 128.76 (aryl-*C*), 128.68 (aryl-*C*), 127.64 (aryl-*C*), 126.94 (aryl-*C*), 126.54 (aryl-*C*), 125.72 (aryl-*C*), 124.03 (aryl-*C*), 34.55 (*C*(CH$_3$)$_3$), 31.86 (C(*C*H$_3$)$_3$), 21.28 (Ar*C*H$_3$), 20.67 (Ar*C*H$_3$); HRMS (FAB+) m/z Calcd. for $C_{52}H_{54}O_2$ $[M]^+$ 710.4124, found 710.4142.



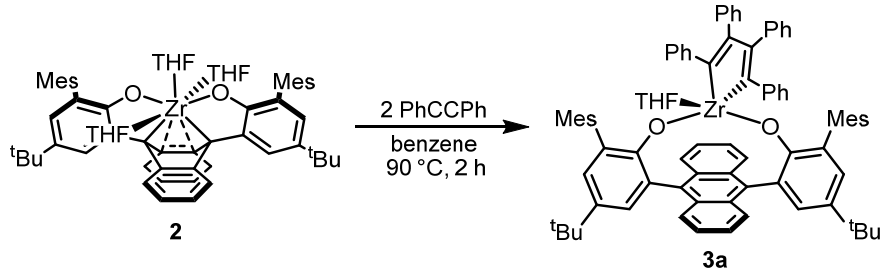
***Syn*-3,3''-(anthracene-9,10-diyl)bis(5-(*tert*-butyl)-2',4',6'-trimethyl-[1,1'-biphenyl]-2-ol) (LH_2).** A suspension of the *anti* atropisomer (13.0 g) in degassed xylenes (80 mL) was heated to reflux under N_2 for 6 h after which the yellow solution was cooled to room temperature and the volatiles removed *in vacuo*. The isomeric mixture was separated by silica gel column chromatography, eluting first with 1:4 CH_2Cl_2:hexanes to separate the anti-isomer, and then 1:3:16 EtOAc:CH_2Cl_2:hexanes to obtain the desired syn-isomer **LH_2** as a white to pale yellow solid after drying *in vacuo* (6.08 g 46.8%). The anti-isomer obtained (6.31 g, 48.5%) can be further isomerized and separated again by silica gel column chromatography to provide more desired syn-isomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (app dd, $J_{H,H}$ = 6.8, 3.2 Hz, 4H, anth–*H*), 7.43 (dd, $J_{H,H}$ = 6.8, 3.2 Hz, 4H, anth–*H*), 7.31 (d, $^4J_{H,H}$ = 2.5 Hz, 2H, Ar*H*), 7.28 (d, $^4J_{H,H}$ = 2.5 Hz, 2H, Ar*H*), 7.01 (s, 4H, Ar*H*), 4.50 (s, 2H, O*H*), 2.34 (s, 6H, ArCH_3), 2.21 (s, 12H, ArCH_3), 1.35 (s, 18H, C(CH_3)$_3$); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 148.59 (aryl-*C*), 143.50 (aryl-*C*), 137.62 (aryl-*C*), 137.42 (aryl-*C*), 133.77 (aryl-*C*), 133.35 (aryl-*C*), 130.75 (aryl-*C*), 128.65 (aryl-*C*), 128.62 (aryl-*C*), 127.74 (aryl-*C*), 126.93 (aryl-*C*), 126.60 (aryl-*C*), 125.79 (aryl-*C*), 123.92 (aryl-*C*), 34.53 (*C*(CH$_3$)$_3$), 31.85 (C(*C*H$_3$)$_3$), 21.27 (Ar*C*H$_3$), 20.69 (Ar*C*H$_3$); HRMS (FAB+) m/z Calcd. for $C_{52}H_{54}O_2$ $[M]^+$ 710.4124, found 710.4089.



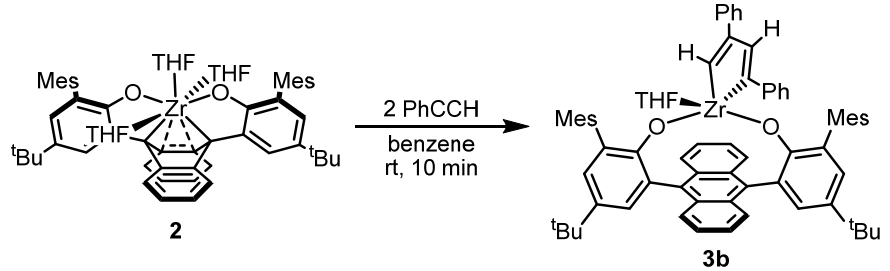
Synthesis of 1. All manipulations for this reaction until the workup was carried out in the glovebox in the absence of light to the extent possible. To a thawing solution of tetrabenzylzirconium (320.5 mg, 0.703 mmol) in toluene (20 mL), was added a thawing solution of **LH_2** (500 mg, 0.703 mmol) in toluene (10 mL) with stirring. The reaction was allowed to warm up to room temperature and stirred an additional 2 h, forming a yellow solution. The solution was filtered through a pad of diatomaceous earth and volatiles were removed *in vacuo* to afford **2** as a yellow solid (681 mg 98.6%). X-Ray quality single crystals were grown by slow diffusion of pentane into a saturated toluene solution at –35 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.06 (app dd, $J_{H,H}$ = 6.7, 3.2 Hz, 4H, anth–*H*), 7.95 (d, $^4J_{H,H}$ = 2.6 Hz, 2H, Ar*H*), 7.20 (d, $^4J_{H,H}$ = 2.5 Hz, 2H, Ar*H*), 7.12 (app dd, J = 6.7, 3.2 Hz, 4H, anth–*H*), 6.80 (s, 4H, Mes*H*), 6.78 – 6.66 (m, 6H, Ar*H*), 5.86 (d, J = 7.2 Hz, 4H, Ar*H*), 2.21 (s, 6H, ArCH_3), 2.09 (s, 12H, ArCH_3), 1.38 (s, 18H, C(CH_3)$_3$), 0.87 (s, 4H, PhCH_2); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 157.10 (aryl-*C*), 143.83 (aryl-*C*), 139.69 (aryl-*C*), 137.13 (aryl-*C*), 136.68 (aryl-*C*), 136.35 (aryl-*C*), 134.58 (aryl-*C*), 131.62 (aryl-*C*), 131.47 (aryl-*C*), 130.75 (aryl-*C*), 130.44 (aryl-*C*), 128.44 (aryl-*C*), 127.82 (aryl-C), 127.75 (aryl-*C*), 126.75 (aryl-*C*), 126.37 (aryl-*C*), 124.69 (aryl-*C*), 123.85 (aryl-*C*), 59.46 (Ph*C*H$_2$), 34.55 (*C*(CH$_3$)$_3$), 31.93 (C(*C*H$_3$)$_3$), 21.36 (Ar*C*H$_3$), 21.19 (Ar*C*H$_3$); Anal. Calcd. $C_{66}H_{66}O_2Zr$ (%): C, 80.69; H, 6.77. Found: C, 80.84; H, 6.62.



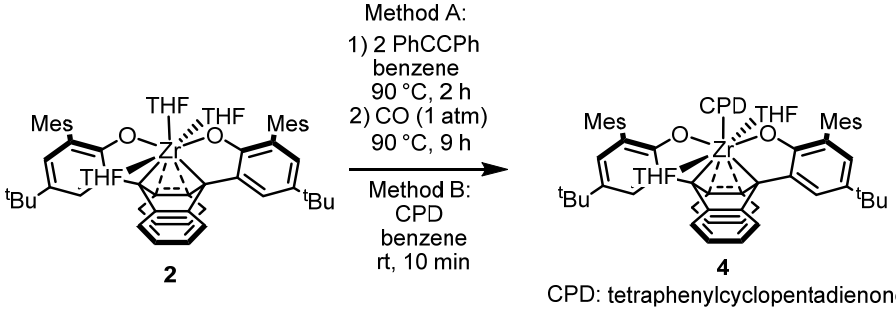
Synthesis of 2. A solution of **1** (1.00 g, 1.02 mmol) in THF (80 mL) was irradiated with light from a Xe arc lamp (75 W) with stirring. After 24 h, the volatiles were removed in vacuo, and the residue triturated with hexanes twice. Pentane (10 mL) was added and cooled to –35 °C overnight to allow precipitation. The suspension was filtered and the residue washed with cold pentane (5 mL), and then room temperature pentane (2 × 3 mL). The residue was extracted with diethyl ether and dried in vacuo to provide **2** as a deep red solid (587 mg 56.9%). X-ray quality single crystals were grown by cooling a saturated pentane to –35 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 7.88 (d, $^{4}J_{H,H}$ = 2.5 Hz, 2H, Ar*H*), 7.34 (app dd, $J_{H,H}$ = 5.7, 3.3 Hz, 4H, anth–*H*), 7.15 (d, $^{4}J_{H,H}$ = 2.5 Hz, 2H, Ar*H*), 6.90 (app dd, $J_{H,H}$ = 5.7, 3.2 Hz, 4H, anth–*H*), 6.82 (s, 4H, Mes*H*), 3.61 – 3.54 (m, 8H, THF-OCH_2), 3.18 – 3.11 (m, 4H, THF), 2.20 (s, 6H, ArCH_3), 2.16 (s, 12H, ArCH_3), 1.42 (s, 18H, C(CH_3)$_3$), 1.08 (m, 12H, THF-CH_2); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 161.54 (aryl-*C*), 140.71 (aryl-*C*), 140.40 (aryl-*C*), 139.39 (aryl-*C*), 136.78 (aryl-*C*), 135.71 (aryl-*C*), 135.11 (aryl-*C*), 127.50 (aryl-*C*), 126.42 (aryl-*C*), 128.30 (aryl-*C*), 124.22 (2C, aryl-*C*), 123.12 (aryl-*C*), 94.78 (Zr-*C*), 73.82 (THF-O*C*H$_2$), 69.55 (THF-O*C*H$_2$), 34.44 (*C*(CH$_3$)$_3$), 32.38 (C(*C*H$_3$)$_3$), 25.39 (THF-*C*H$_2$), 24.80 (THF-*C*H$_2$), 21.45 (Ar*C*H$_3$), 21.16 (Ar*C*H$_3$). Anal. Calcd. $C_{64}H_{73}O_5Zr$ (%): C, 75.85; H, 7.26. Found: C, 75.48; H, 6.97.



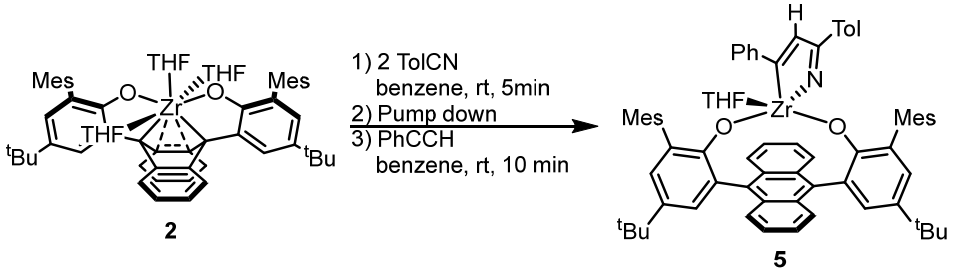
Synthesis of 3a. A solution of **2** (100 mg, 0.0986 mmol) and diphenylacetylene (35.2 mg, 0.197 mmol) in benzene (5 mL) was heated to 90 °C with stirring for 3 h. After cooling to room temperature, the volatiles were removed *in vacuo*. The residue was washed with cold pentane, extracted with benzene and filtered through diatomaceous earth. Concentration under vacuum provided **3a** as a yellow solid (89.6 mg 74.0%). X-ray quality single crystals were grown by slow diffusion of pentane into a saturated toluene solution at –35 °C. ^{1}H NMR (400 MHz, C_6D_6): δ 8.01 (app dd, $J_{H,H}$ = 6.7, 3.3 Hz, 2H, anth–*H*), 7.94 (d, $^{4}J_{H,H}$ = 2.5 Hz, 2H, Ar*H*), 7.92 (app dd, $J_{H,H}$ = 6.8, 3.2 Hz, 2H, anth–*H*), 7.45 (d, $^{4}J_{H,H}$ = 2.6 Hz, 2H, Ar*H*), 7.29 (s, 2H, Mes*H*), 7.02 (s, 2H, Mes*H*), 6.88 – 6.49 (m, 22H, Ar*H*), 5.46 (d, $^{3}J_{H,H}$ = 7.5 Hz, 2H, Ar*H*), 3.00 (s, 6H, ArCH_3), 2.71 (s, br, 4H, THF-OCH_2), 2.35 (s, 6H, ArCH_3), 2.08 (s, 6H, ArCH_3), 1.43 (s, 18H, C(CH_3)$_3$), 0.37 (s, br, 4H, THF-CH_2). ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 197.61 (Zr*C*), 193.83 (Zr*C*), 159.82 (ZrC(Ph)*C*), 157.29 (aryl-*C*), 154.70 (ZrC(Ph)*C*), 149.30 (aryl-*C*), 148.74 (aryl-*C*), 143.06 (aryl-*C*), 142.23 (aryl-*C*), 142.10 (aryl-*C*), 138.96 (aryl-*C*), 136.98 (aryl-*C*), 136.36 (aryl-*C*), 135.83 (aryl-*C*), 133.42 (aryl-*C*), 131.35 (aryl-*C*), 131.19 (aryl-*C*), 130.38 (aryl-*C*), 130.32 (aryl-*C*), 130.04 (aryl-*C*), 129.56 (aryl-*C*), 128.90 (aryl-*C*), 128.75 (aryl-*C*), 128.22 (aryl-*C*), 128.01 (aryl-*C*), 127.42 (aryl-*C*), 127.33 (aryl-*C*), 127.06 (aryl-*C*), 126.53 (aryl-*C*), 126.26 (aryl-*C*), 126.13 (aryl-*C*), 125.91 (aryl-*C*), 125.27 (aryl-*C*), 124.78 (aryl-*C*), 124.62 (aryl-*C*), 124.53 (aryl-*C*), 124.41 (aryl-*C*), 122.69 (aryl-*C*), 122.40 (aryl-*C*), 70.68 (THF-O*C*H$_2$), 34.61 (*C*(CH$_3$)$_3$), 32.00 (C(*C*H$_3$)$_3$), 23.72 (THF-OCH$_2$*C*H$_2$), 22.66 (Ar*C*H$_3$), 21.40 (Ar*C*H$_3$), 21.28 (Ar*C*H$_3$); Anal. Calcd. $C_{84}H_{79}O_3Zr$ (%): C, 82.17; H, 6.49. Found: C, 81.98; H, 6.72.



Synthesis of 3b. Phenylacetylene (22 μL, 0.20 mmol) was added to a stirred solution of **2** (100 mg, 0.099 mmol) in benzene (5 mL) at room temperature resulting in red-brown to a yellow-brown color change. After 10 min, the volatiles were removed *in vacuo* and the residue extracted with pentane and filtered over diatomaceous earth. Drying under reduced pressure provided **3b** as an orange powder (77.6 mg, 73.3%). X-ray quality single crystals were grown by slow diffusion of pentane into a saturated benzene solution at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ 8.28 (app dd, $J_{H,H}$ = 6.8, 3.3 Hz, 2H, anth–*H*), 7.96 (d, $^{4}J_{H,H}$ = 2.5 Hz, 2H, Ar*H*), 7.41 (d, J = 7.7 Hz, 2H, Ar*H*), 7.36 (d, $^{4}J_{H,H}$ = 2.6 Hz, 2H, Ar*H*), 7.28 – 7.19 (m, 5H, Ar*H*), 7.09 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.04 (d, $^{4}J_{H,H}$ = 4.3 Hz, 1H, ZrC*H*), 6.96 (t, *J* = 7.4 Hz, 2H), 6.91 (s, 2H, Mes*H*), 6.90 (s, 2H, Mes*H*), 6.88 – 6.81 (m, 3H), 6.22 (d, $^{4}J_{H,H}$ = 4.5 Hz, 1H, ZrC(Ph)C*H*), 5.87 (d, $^{3}J_{H,H}$ = 7.3 Hz, 2H, Ar*H*), 2.52 (app t, br, $^{3}J_{H,H}$ = 5.7 Hz, 4H, THF-OCH_2), 2.39 (s, 6H, ArCH_3), 2.24 (s, 6H, ArCH_3), 2.10 (s, 6H, ArCH_3), 1.44 (s, 18H, C(CH_3)$_3$), 0.51 (app t, br, $^{3}J_{H,H}$ = 5.7 Hz, 4H, THF-CH_2); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 199.14 (Zr*C*), 188.17 (Zr*C*), 156.93 (aryl-*C*), 155.93 (Zr*C*(Ph)), 150.75 (aryl-*C*), 146.99 (Zr*C*H), 143.97 (aryl-*C*), 142.80 (aryl-*C*), 139.24 (aryl-*C*), 136.58 (aryl-*C*), 136.45 (aryl-*C*), 135.32 (aryl-*C*), 135.04 (aryl-*C*), 131.91 (aryl-*C*), 131.26 (aryl-*C*), 131.18 (aryl-*C*), 130.08 (aryl-*C*), 129.04 (aryl-*C*), 128.59 (aryl-*C*), 128.06 (aryl-*C*), 127.56 (aryl-*C*), 127.51 (aryl-*C*), 127.49 (aryl-*C*), 126.93 (aryl-*C*), 126.63 (aryl-*C*), 126.46 (aryl-*C*), 125.96 (aryl-*C*), 125.70 (aryl-*C*), 125.45 (aryl-*C*), 124.47 (aryl-*C*), 123.24 (aryl-*C*), 70.52 (THF-O*C*H$_2$), 34.61 (*C*(CH$_3$)$_3$), 32.06 (C(*C*H$_3$)$_3$), 24.43 (THF-OCH$_2$*C*H$_2$), 21.31 (Ar*C*H$_3$), 21.28 (Ar*C*H$_3$), 21.07 (Ar*C*H$_3$); Anal. Calcd. $C_{72}H_{71}O_3Zr$ (%): C, 80.40; H, 6.65. Found: C, 80.67; H, 6.74.



Synthesis of 4. Method A: A J. Young NMR tube charged with a solution of **2** (20.0 mg, 0.197 mmol) and diphenylacetylene (7.0 mg, 0.039 mmol) in C_6D_6 (0.6 mL) was heated to 90 °C. After 2 h, the atmosphere in the tube was degassed and replaced with CO (1 atm) and the tube was heated for an additional 9 h after which ^{1}H NMR spectroscopy showed that the major product matched that of **4** synthesized via method B. **Method B:** To a solution of **2** (100 mg, 0.099 mmol) in benzene (5 mL) was added tetraphenylcyclopentadienone (37.9 mg, 0.099 mmol) at room temperature resulting in a red to yellow-brown color change. After 10 min, the volatiles were removed *in vacuo* and the solid residue washed with pentane and dried under reduced pressure to provide **4** as a dark brown powder (92.6 mg, 68.0%). ^{1}H NMR (400 MHz, C_6D_6): δ 7.93 – 7.89 (m, 6H, overlapping anth–*H* and Ar*H*), 7.56 (dd, $J_{H,H}$ = 8.2, 1.3 Hz, 4H, Ar*H*), 7.33 (d, $^{4}J_{H,H}$ = 2.6 Hz, 2H, Ar*H*), 7.20 (dd, $J_{H,H}$ = 8.0, 1.3 Hz, 4H, Ar*H*), 7.08 (s, 4H, Ar*H*), 7.04 (t, $^{3}J_{H,H}$ = 7.6 Hz, 4H, Ar*H*), 6.92 – 6.83 (m, 6H, Ar*H*), 6.83 (dd, $J_{H,H}$ = 6.7, 3.3 Hz, 4H, Ar*H*), 6.65 (t, $^{3}J_{H,H}$ = 7.3 Hz, 2H, Ar*H*), 2.83 (t, $^{3}J_{H,H}$ = 6.6 Hz, 8H, THF-OCH_2), 2.36 (s, 6H, ArCH_3), 2.22 (s, 12H, ArCH_3), 1.36 (s, 18H, C(CH_3)$_3$), 0.61 (d, $^{3}J_{H,H}$ = 6.1 Hz, 8H, THF-CH_2); ^{13}C{^{1}H} NMR (101 MHz, C_6D_6): δ 156.95 (C=O), 144.31 (aryl-*C*), 143.70 (aryl-*C*), 142.48 (aryl-*C*), 137.87 (aryl-*C*), 136.14 (aryl-*C*), 134.57 (aryl-*C*), 133.49 (aryl-*C*), 132.87 (aryl-*C*), 131.88 (aryl-*C*), 131.35 (aryl-*C*), 131.28 (aryl-*C*), 130.22 (aryl-*C*), 129.99 (aryl-*C*), 129.05 (aryl-*C*), 128.59 (aryl-*C*), 127.19 (aryl-*C*), 126.66 (aryl-*C*), 125.69 (aryl-*C*), 125.23 (aryl-*C*), 124.92 (aryl-*C*), 122.89 (aryl-*C*), 120.83 (aryl-*C*), 118.86 (Ph*C*), 110.21 (Ph*C*), 73.46 (THF-O*C*H$_2$), 34.56 (*C*(CH$_3$)$_3$), 31.81 (C(*C*H$_3$)$_3$), 22.90 (THF-OCH$_2$*C*H$_2$), 21.59 (Ar*C*H$_3$), 21.46 (Ar*C*H$_3$); Anal. Calcd. $C_{89}H_{86}O_5Zr$ (%): C, 80.56; H, 6.53. Found: C, 80.32; H, 6.28.



Synthesis of 5. *p*-Tolunitrile (23.2 mg, 0.198 mmol) was added to a solution of **2** (100 mg, 0.099 mmol) in benzene (5 mL) at room temperature resulting in the immediate formation of a deep purple solution. After 5 min, the volatiles were removed in vacuo. The resulting solid was taken up in benzene (5 mL) and phenylacetylene (10.8 µL, 0.099 mmol) was added forming a red-orange solution. After stirring an additional 10 min, the reaction was concentrated under vacuum and the residue washed with cold pentane and dried to provide **5** as a red brown solid (76.8 mg, 71.4%). X-ray quality single crystals were grown by slow diffusion of pentane into a saturated benzene solution at room temperature. ^{1}H NMR (400 MHz, C_6D_6): δ 8.34 (app dd, $J_{H,H}$ = 6.8, 3.2 Hz, 2H, anth–*H*), 8.05 (app dd, $J_{H,H}$ = 6.7, 3.3 Hz, 2H), 7.99 (d, $^{4}J_{H,H}$ = 2.5 Hz, 2H, Ar*H*), 7.67 (d, $^{2}J_{H,H}$ = 8.1 Hz, 2H, Tol–*H*), 7.47 (app dd, $J_{H,H}$ = 6.8, 3.3 Hz, 2H), 7.35 (d, J = 2.5 Hz, 2H, Ar*H*), 7.28 (s, 1H, alkenyl–*H*), 7.04 (d, $^{2}J_{H,H}$ = 8.0 Hz, 2H, Tol–*H*), 6.97 (t, $^{2}J_{H,H}$ = 7.6 Hz, 2H, Ar*H*), 6.91 (s, 2H, Mes*H*), 6.87 (m, 3H, anth–*H* and Ar*H*), 6.83 (s, 2H, Mes*H*), 5.84 (dd, J_{HH} = 8.1, 1.4 Hz, 2H, Ar*H*), 2.63 – 2.55 (m, 4H, THF-CH_2), 2.24 (s, 6H, ArCH_3), 2.23 (s, 6H, ArCH_3), 2.16 (s, 3H, ArCH_3), 2.11 (s, 6H, ArCH_3), 1.44 (s, 18H, C(CH_3)$_3$), 0.57 – 0.47 (m, 4H, THF-CH_2); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 210.36, 177.99, 156.96, 150.94, 147.50, 142.07, 140.20, 139.05, 136.75, 136.28, 135.59, 135.46, 135.06, 131.76, 130.85, 129.83, 129.62, 129.59, 128.97, 128.87, 128.43, 128.30, 127.95, 127.61, 127.54, 126.98, 126.77, 125.32, 124.78, 124.53, 70.92 (THF-O*C*H$_2$), 34.59 (*C*(CH$_3$)$_3$), 32.11 (C(*C*H$_3$)$_3$), 24.52 (THF-OCH$_2$*C*H$_2$), 21.48 (Ar*C*H$_3$), 21.28 (Ar*C*H$_3$), 21.25 (Ar*C*H$_3$), 20.81 (Ar*C*H$_3$); Anal. Calcd. $C_{72}H_{72}NO_3Zr$ (%): C, 79.30; H, 6.65; N, 1.28. Found: C, 79.63; H, 6.41; N, 1.66.

General Setup for Catalytic Pyrimidine Synthesis. In the glovebox, stock solutions of nitrile, alkyne, 1-adamantane (internal standard), and **2** in the appropriate solvent were measured with syringes and added in that order to a vial equipped with a Teflon-coated stir bar, additional solvent was added to ensure total volume of the reaction was 3 mL. The vial was capped with a PTFE-lined septum cap, taken out of the box, and placed into a preheated heating block at the appropriate temperature. After the reaction time, the reaction was cooled to room temperature and quenched by exposure to air with stirring. A small volume was taken, filtered through a pad of silica gel, and eluted with CH_2Cl_2 for GC-MS analysis. Parallel runs were also set up in the absence of 1-adamantane to obtain isolated yields.

2,4,6-Triphenylpyrimidine (6a).[6] Synthesized using the general setup using phenylacetylene (10.8 µL, 0.0987 mmol), benzonitrile (61.0 µL, 0.592 mmol) and **2** (5.0 mg, 4.9 µmol) in toluene (3 mL), and purified via silica gel column chromatography (5% EtOAc/hexanes). White solid. First run 28.8 mg (95%). Second run 28.5 mg (94%).

4,5-dibutyl-2,6-diphenylpyrimidine (6b).[6] Synthesized using the general setup using 5-decyne (17.8 µL, 0.0987 mmol), benzonitrile (61.0 µL, 0.592 mmol) and **2** (5.0 mg, 4.9 µmol) in toluene (3 mL), and purified via silica gel column chromatography (5% CH_2Cl_2/hexanes). White solid. First run 32.8 mg (96%) Second Run 32.6 mg (96%).

2,6-diphenyl-4-(trimethylsilyl)pyrimidine (6c). Synthesized using the general setup using trimethylsilylacetylene (14.1 µL, 0.0987 mmol), benzonitrile (61.0 µL, 0.592 mmol) and **2** (5.0 mg, 4.9 µmol) in toluene (3 mL), and purified via silica gel column chromatography (5% CH_2Cl_2, 1% triethylamine in hexanes). White solid. First run 29.2 mg (97%) Second Run 28.9 mg (96%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (dd, J = 8.1, 1.6 Hz, 1H), 8.67 (dd, J = 8.0, 1.8 Hz, 2H), 8.24 (dd, J = 7.8, 1.8 Hz, 2H), 7.78 (s, 1H), 7.66 – 7.46 (m, 5H), 0.43 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 178.35, 171.78, 163.32, 161.71, 138.68, 137.89, 136.39, 132.63, 130.67, 130.46, 129.10, 128.98, 128.77, 128.51, 128.49, 127.36, 119.46, -2.02; HRMS (FAB+) m/z Calcd. for $C_{19}H_{21}SiN_2$ $[M+H]^+$ 305.1474, found 305.1465.

6-phenyl-2,4-di(*p*-tolyl)pyrimidine (6d).[7] Synthesized using the general setup using phenylacetylene (10.8 µL, 0.0987 mmol), *p*-tolunitrile (69.4 mg, 0.592 mmol) and **2** (5.0 mg, 4.9 µmol) in toluene (3 mL), and purified via silica gel column chromatography (5% EtOAc/hexanes). White solid. First run 31.9 mg (96%) Second Run 31.7 mg (95%).

2,4-di(4-fluorophenyl)-6-phenylpyrimidine (6e). Synthesized using the general setup using phenylacetylene (10.8 µL, 0.0987 mmol), 4-fluorobenzonitrile (71.7 mg, 0.592 mmol) and **2** (5.0 mg, 4.9 µmol) in toluene (3 mL), and purified via silica gel column chromatography (5% EtOAc/hexanes). White solid. First run 33.0 mg (97%) Second Run 32.9 mg (97%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 – 8.67 (m, 2H), 8.31 – 8.23 (m, 4H), 7.94 (s, 1H), 7.59 – 7.54 (m, 3H), 7.28 – 7.18 (m, 4H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.00, 164.95 (d, $^{1}J_{CF}$ = 235.7 Hz), 164.86 (d, $^{1}J_{CF}$ = 229.9 Hz), 163.63 163.50, 137.42, 134.30 (d, $^{4}J_{CF}$ = 3.0 Hz), 133.65 (d, $^{4}J_{CF}$ = 3.1 Hz), 131.07, 130.68 (d, $^{3}J_{CF}$ = 8.7 Hz), 129.41 (d, $^{3}J_{CF}$ = 8.7 Hz), 129.09, 127.38, 116.11 (d, $^{2}J_{CF}$ = 21.8 Hz), 115.52 (d, $^{2}J_{CF}$ = 21.6 Hz), 109.90; ^{19}F NMR (376 MHz, $CDCl_3$): δ 109.80 (m), 110.55 (m); HRMS (FAB+) m/z Calcd. for $C_{22}H_{15}F_2N_2$ $[M+H]^+$ 345.1203, found 345.1206.

6-phenyl-2,4-bis[4-(trifluromethyl)phenyl]pyrimidine (6f). Synthesized using the general setup using phenylacetylene (10.8 µL, 0.0987 mmol), 4-(trifluoromethyl)benzonitrile (101.3 mg, 0.592 mmol) and **2** (5.0 mg, 4.9 µmol) in toluene (3 mL), and purified via silica gel column chromatography (3% EtOAc/hexanes). White solid. First run 37.4 mg (85%) Second Run 38.1 mg (87%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 8.36 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 8.29 – 8.24 (m, 2H), 8.04 (s, 1H), 7.82 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 7.78 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 7.60 – 7.56 (m, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.56, 163.60, 163.53, 141.17 (q, $^{4}J_{CF}$ = 1.1 Hz), 140.65 (q, $^{4}J_{CF}$ = 1.2 Hz)136.92, 136.92, 132.79 (q, $^{2}J_{CF}$ = 32.6 Hz), 132.55 (q, $^{2}J_{CF}$ = 32.3 Hz), 131.46, 129.22, 128.88, 127.76, 127.44, 126.07 (q, $^{3}J_{CF}$ = 3.7 Hz), 125.57 (q, $^{3}J_{CF}$ = 3.7 Hz), 122.97, 122.72, 111.31; ^{19}F NMR (376 MHz, $CDCl_3$): δ 62.66 (s), 62.77 (s).

Catalytic controls

Photoreduction of $ZrBn_4$ in the presence of anthracene. A quartz Schlenk tube was charged with a Teflon-coated stir bar, $ZrBn_4$ (50.0 mg, 0.110 mmol), anthracene (19.6 mg, 0.110 mmol) and tetrahydrofuran (1 mL). The flask was sealed and irradiated with light from a Xe arc lamp (75 W) with stirring at room temperature for 12 h forming a deep red brown suspension. The volatiles were removed *in vacuo*. 5 mg of the crude solid was then tested under the general catalytic conditions in place of **2**.

Photoreduction of $ZrBn_2Cl_2$ in the presence of anthracene. A thawing THF solution (0.5 mL) of $ZrBn_4$ (25.0 mg, 0.055 mmol) was added to a thawing THF suspension (0.5 mL) of $ZrCl_4$ (12.8 mg, 0.055 mmol) with stirring. After warming the mixture to room temperature the suspension was transferred to a quartz Schlenk tube was and anthracene (19.6 mg, 0.110 mmol) added. The flask was sealed and irradiated with light from a Xe arc lamp (75 W) with stirring at room temperature for 12 h forming a deep red brown solution. The volatiles were removed *in vacuo*. 5 mg of the crude solid was then tested under the general catalytic conditions in place of **2**.

Reduction of $ZrCl_4$ by $Mg(THF)_3(C_{14}H_{10})$. $Mg(THF)_3(C_{14}H_{10})$ (35.7 mg, 0.0859 mmol) was added to a thawing suspension of $ZrCl_4$ (20.0 mg, 0.0859 mmol) and was allowed to warm to room temperature turning from orange to yellow then brown green. After 10 min at room temperature, the volatiles were removed under reduced pressure and the residue extracted with benzene. Concentration of the filtrate provided an off-white solid. 5 mg of the crude solid was then tested under the general catalytic conditions in place of **2**.

In-situ reduction of $ZrCl_4$ by $Mg(THF)_3(C_{14}H_{10})$. Following the general setup for catalysis, using $ZrCl_4$ in place of **2**, $Mg(THF)_3(C_{14}H_{10})$ (2.3 mg) was added as a last step before sealing and heating the mixture.

In-situ reduction of $ZrCl_4$ by KC_8 in the presence of anthracene. Following the general setup for catalysis, using $ZrCl_4$ in place of **2**, anthracene (0.9 mg) and then KC_8 (0.7 mg) was added as a last step before sealing and heating the mixture.

Stoichiometric reactions from preformed (aza)zirconacyclopentadienes 3b and 5. To a solution **3b** or **5** (20.0 mg) in C_6D_6 (0.5 mL) in a J. Young tube was added either phenylacetylene or benzonitrile (5 equiv.). The tube was sealed and heated in an oil bath at 90 °C for 1 h.

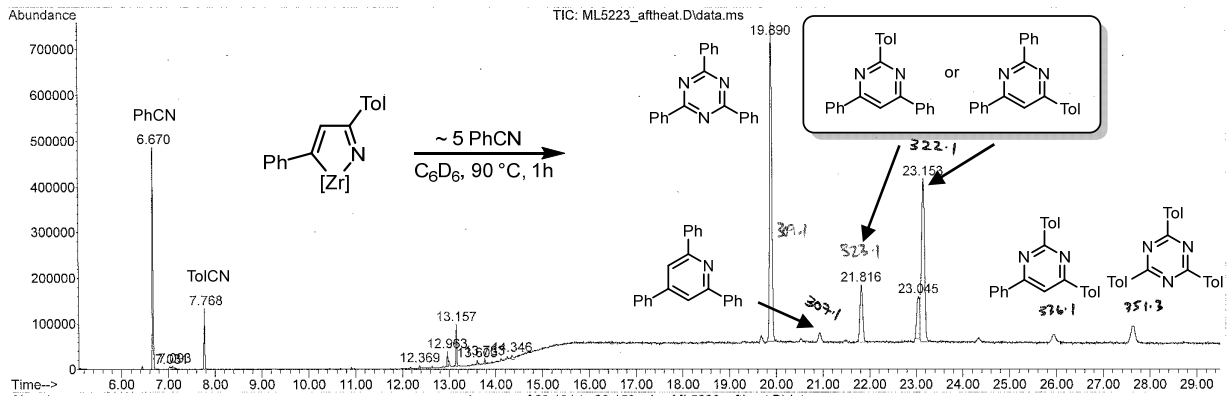


Figure S1. GC-MS chromatograph from reaction of 5 with benzonitrile (5 equiv.) after 1 h heating at 90 °C

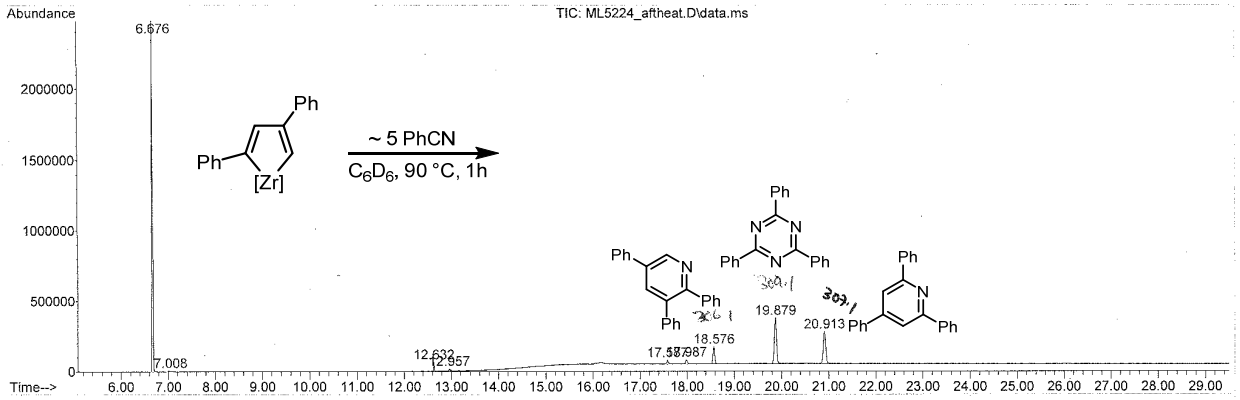


Figure S2. GC-MS chromatograph from reaction of 3b with benzonitrile (5 equiv.) after 1 h heating at 90 °C

NMR Spectra

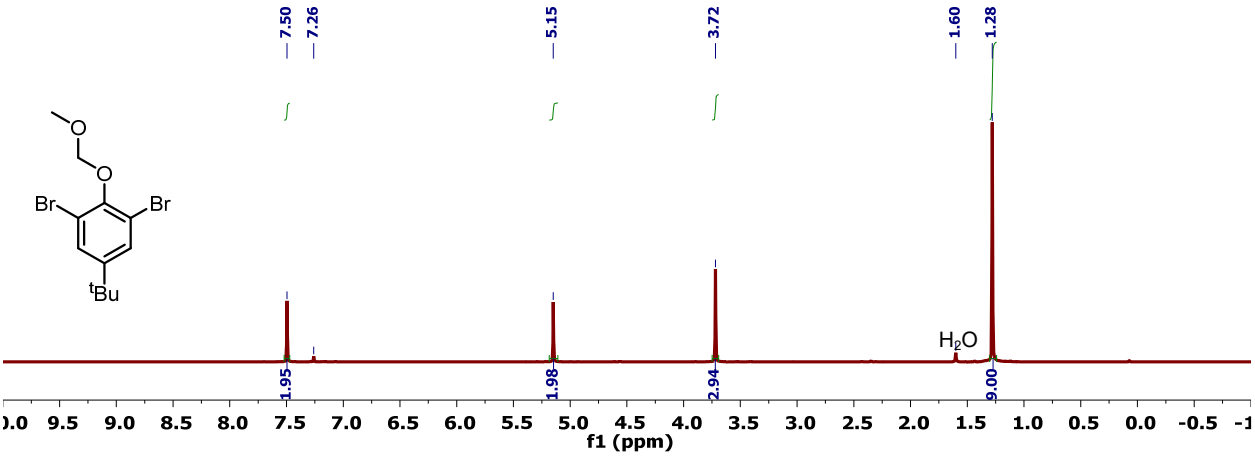


Figure S3. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 1,3-dibromo-5-(tert-butyl)-2-(methoxymethoxy)benzene

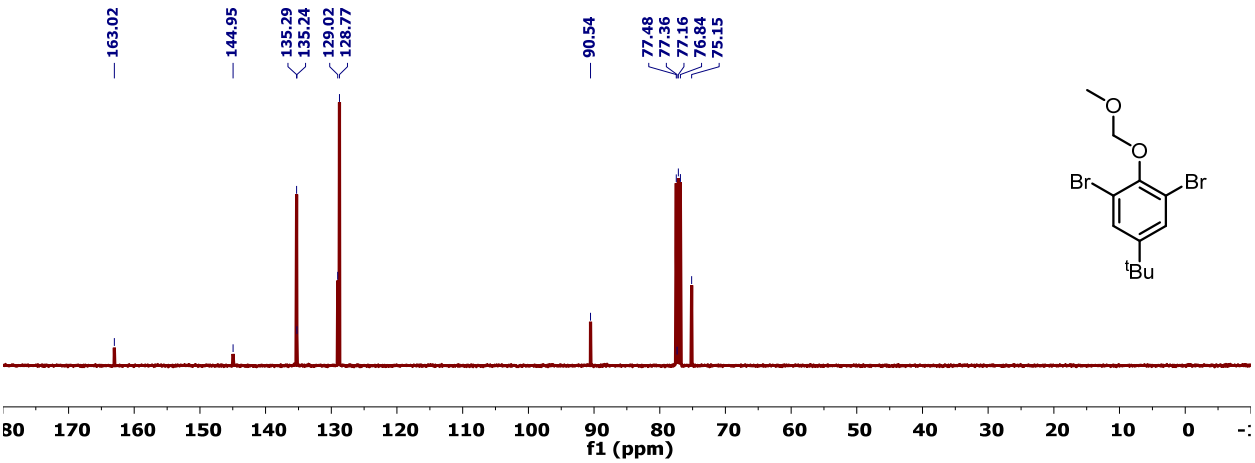


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of 1,3-dibromo-5-(tert-butyl)-2-(methoxymethoxy)benzene

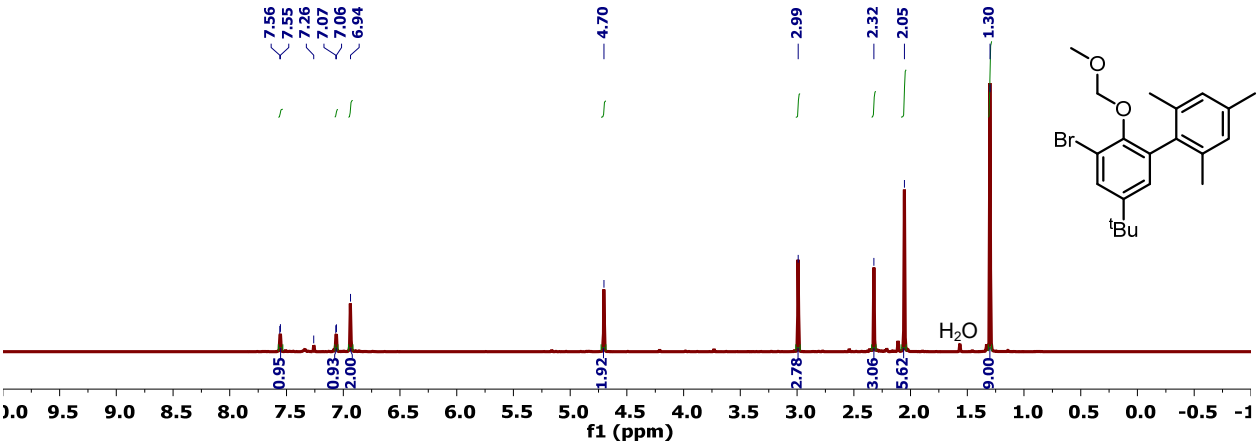


Figure S5. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3-bromo-5-(*tert*-butyl)-2-(methoxymethoxy)-2',4',6'-trimethyl-1,1'-biphenyl

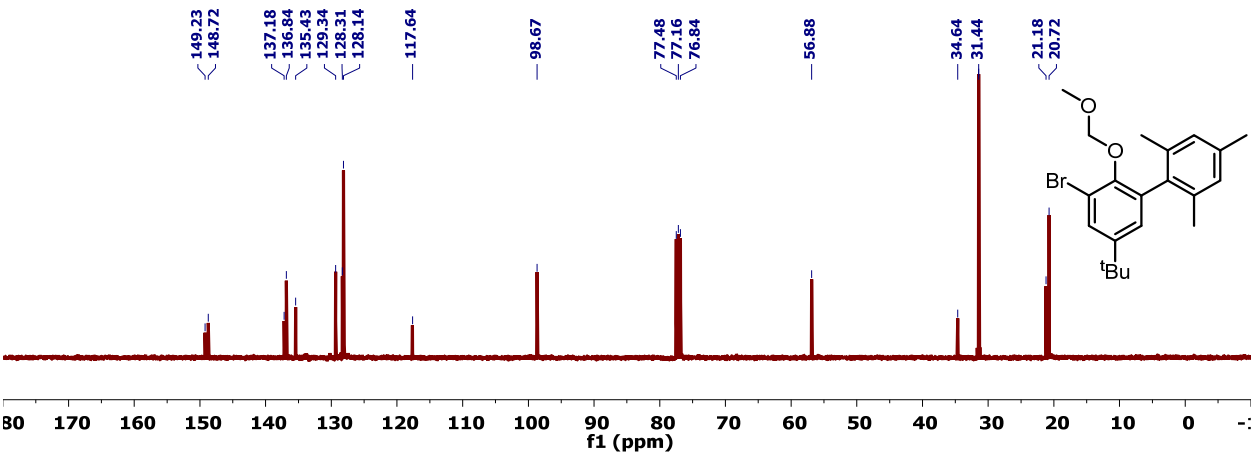


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (101MHz, $CDCl_3$) of 3-bromo-5-(*tert*-butyl)-2-(methoxymethoxy)-2',4',6'-trimethyl-1,1'-biphenyl

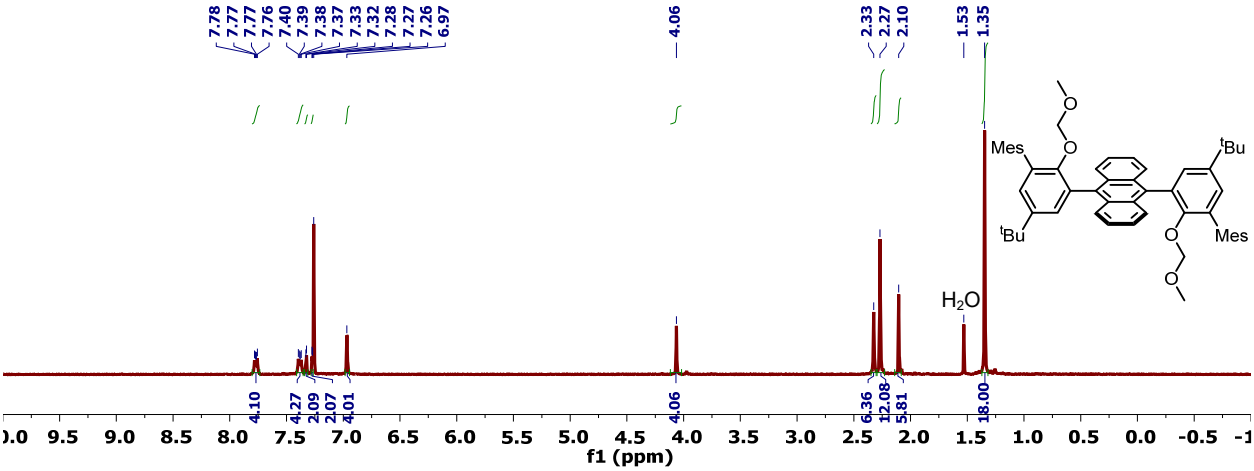


Figure S7. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *anti*-9,10-bis(5-(*tert*-butyl)-2-(methoxymethoxy)-2',4',6'-trimethyl-[1,1'-biphenyl]-3-yl)anthracene

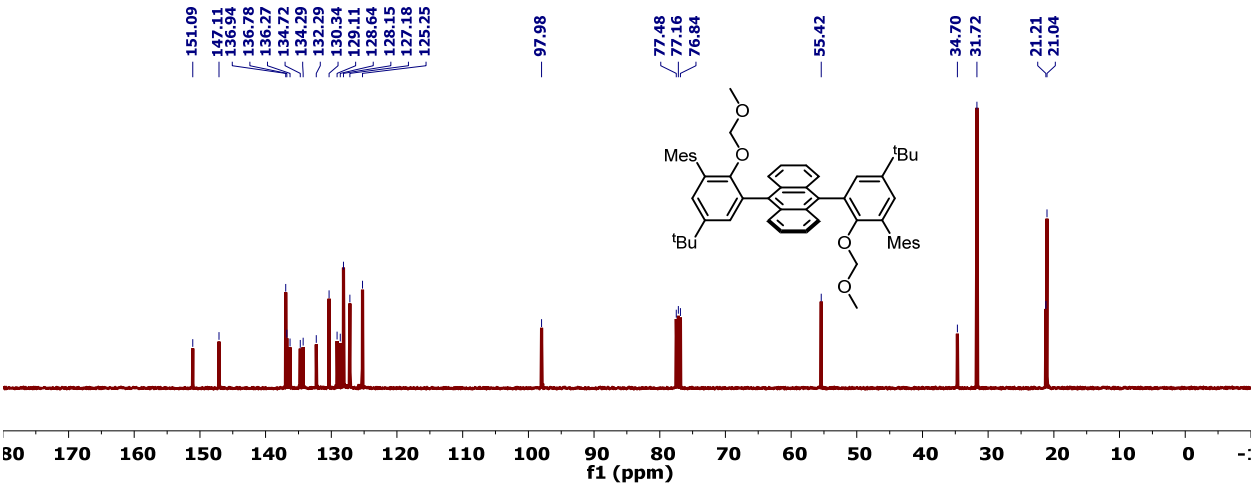


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (101MHz, $CDCl_3$) of *anti*-9,10-bis(5-(*tert*-butyl)-2-(methoxymethoxy)-2',4',6'-trimethyl-[1,1'-biphenyl]-3-yl)anthracene

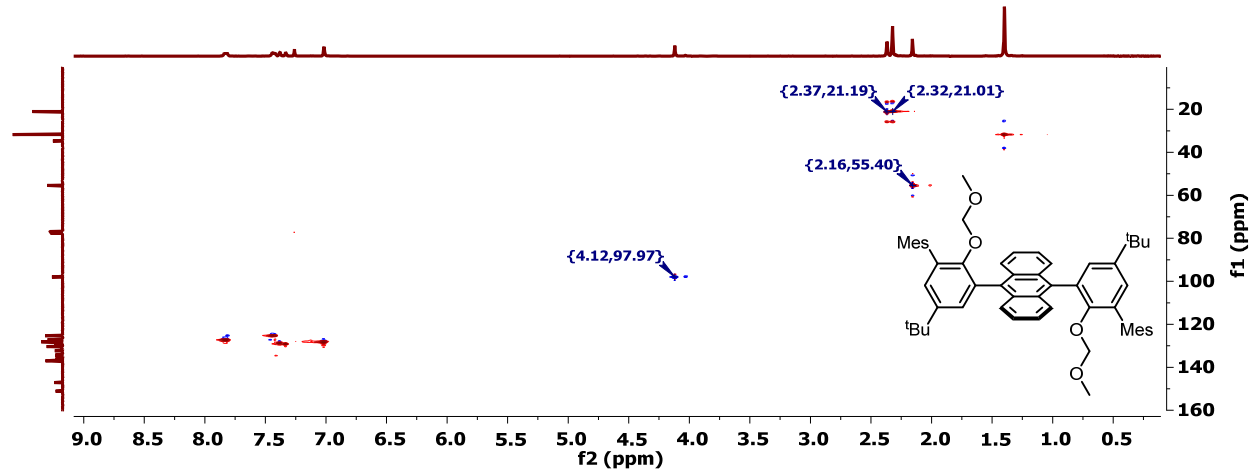


Figure S9. HSQC NMR spectrum of *anti*-9,10-bis(5-(*tert*-butyl)-2-(methoxymethoxy)-2',4',6'-trimethyl-[1,1'-biphenyl]-3-yl)anthracene

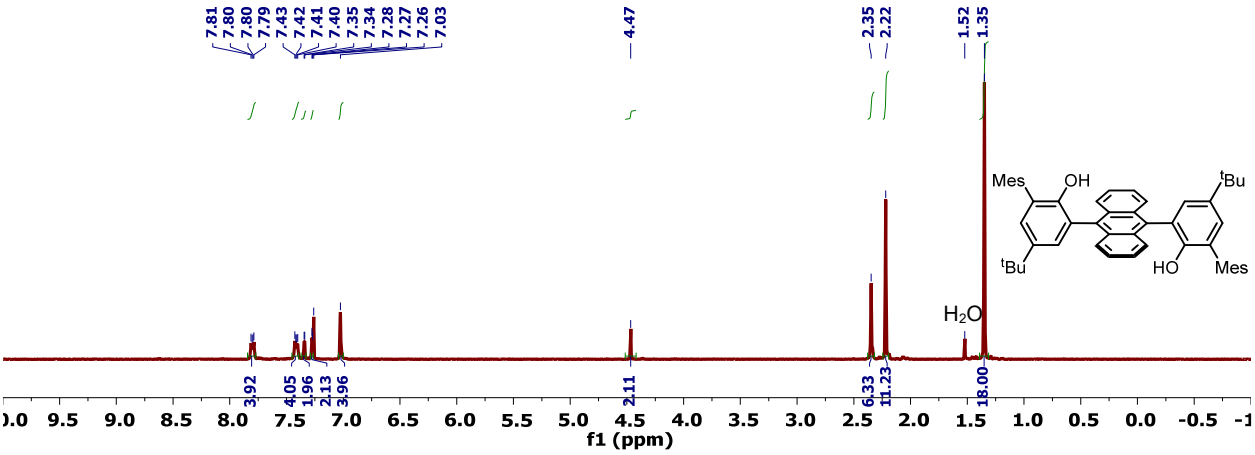


Figure S10. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *anti*-3,3''-(anthracene-9,10-diyl)bis(5-(*tert*-butyl)-2',4',6'-trimethyl-[1,1'-biphenyl]-2-ol)

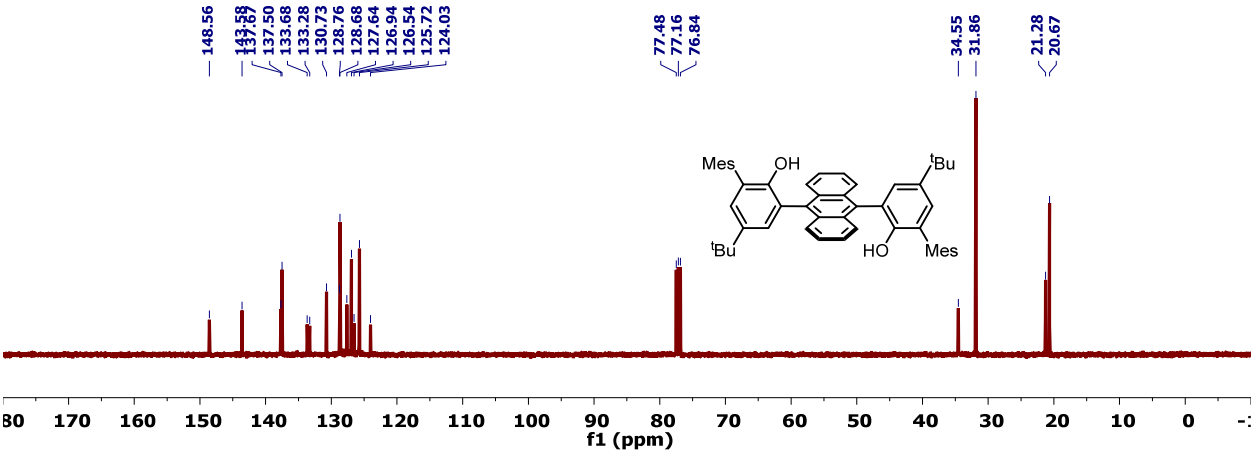


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum (101MHz, $CDCl_3$) of *anti*-3,3''-(anthracene-9,10-diyl)bis(5-(*tert*-butyl)-2',4',6'-trimethyl-[1,1'-biphenyl]-2-ol)

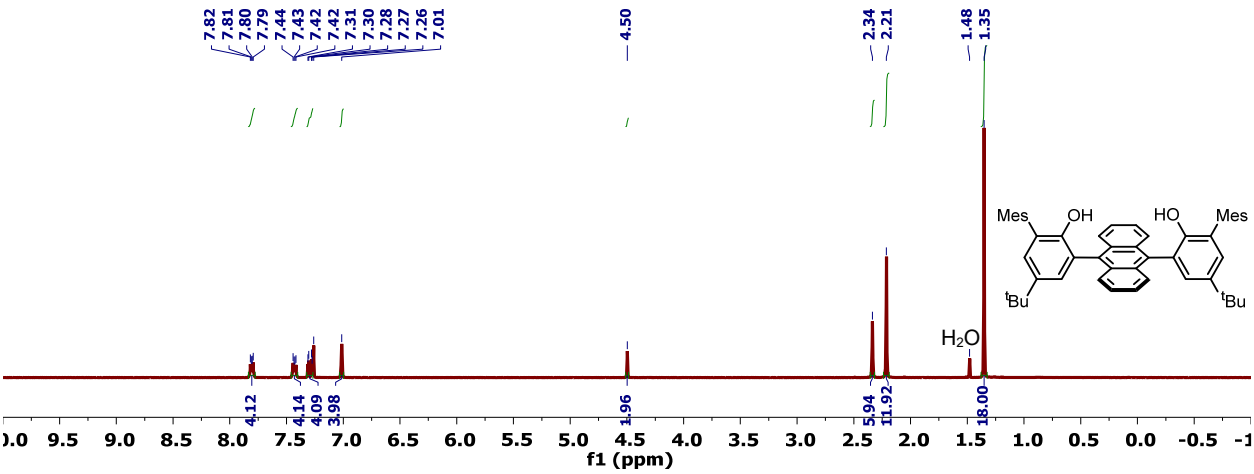


Figure S12. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *syn*-3,3''-(anthracene-9,10-diyl)bis(5-(*tert*-butyl)-2',4',6'-trimethyl-[1,1'-biphenyl]-2-ol) (LH_2)

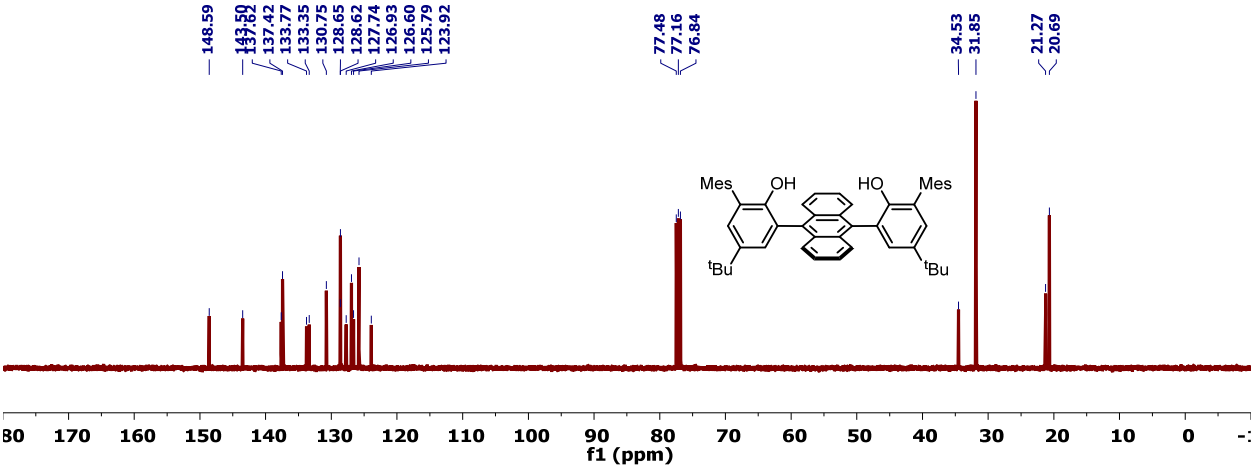


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum (101MHz, $CDCl_3$) of *syn*-3,3''-(anthracene-9,10-diyl)bis(5-(*tert*-butyl)-2',4',6'-trimethyl-[1,1'-biphenyl]-2-ol) (LH_2)

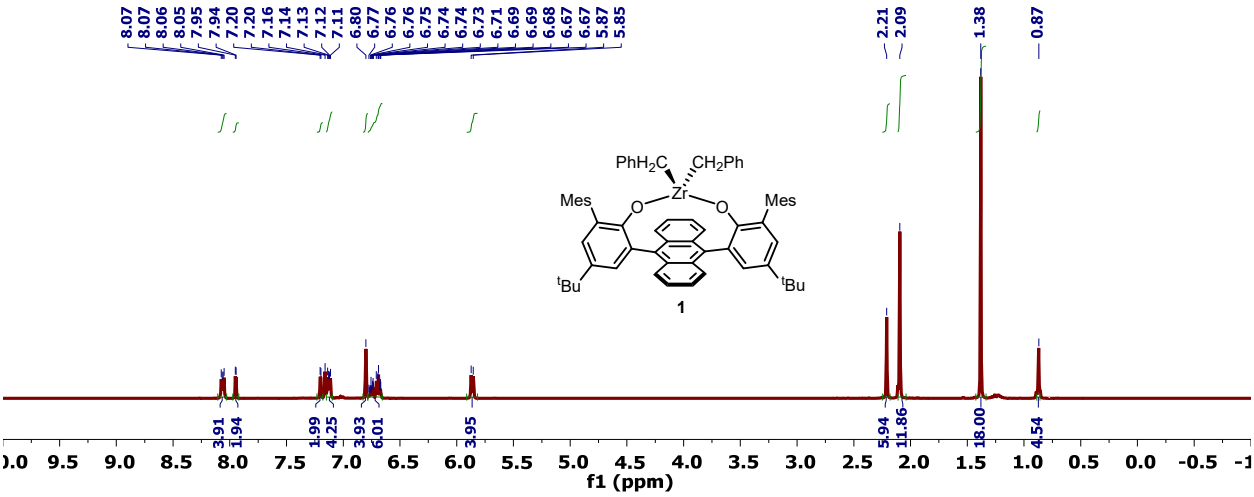


Figure S14. ^{1}H NMR spectrum (400 MHz, C_6D_6) of 1

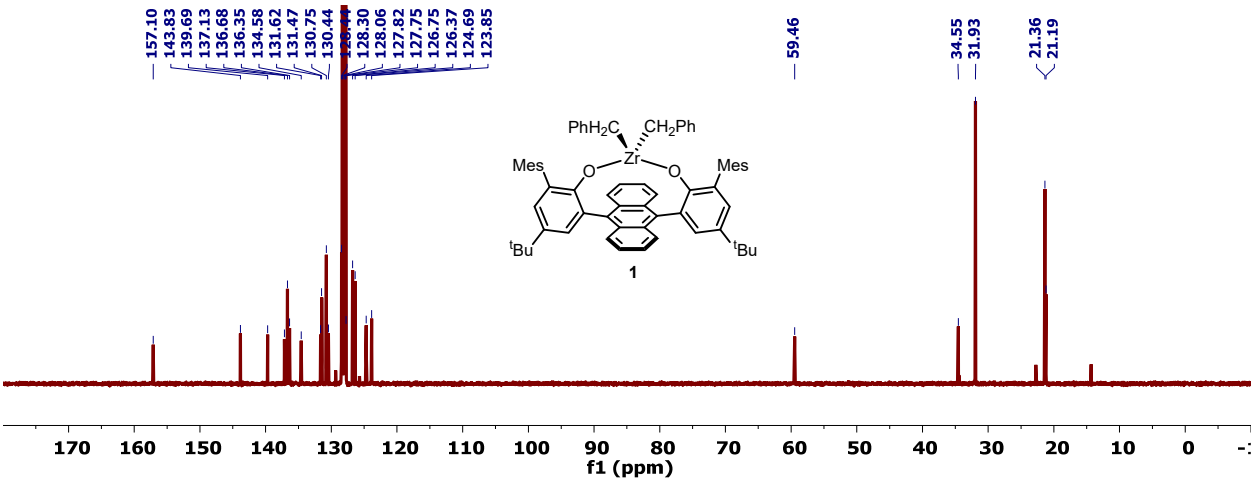


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum (101MHz, C_6D_6) of 1

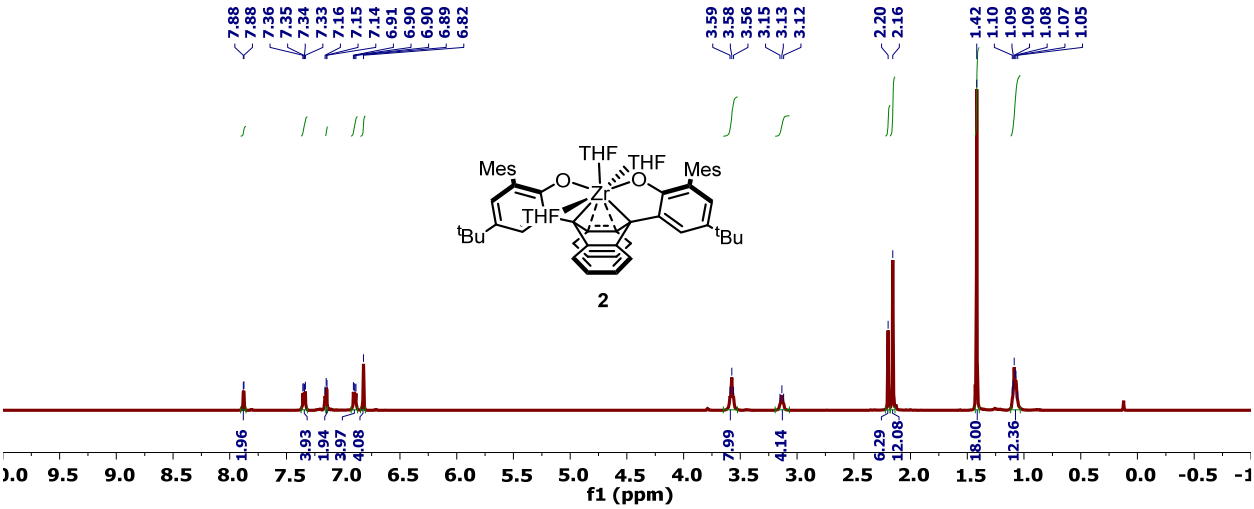


Figure S16. ^{1}H NMR spectrum (400 MHz, C_6D_6) of 2

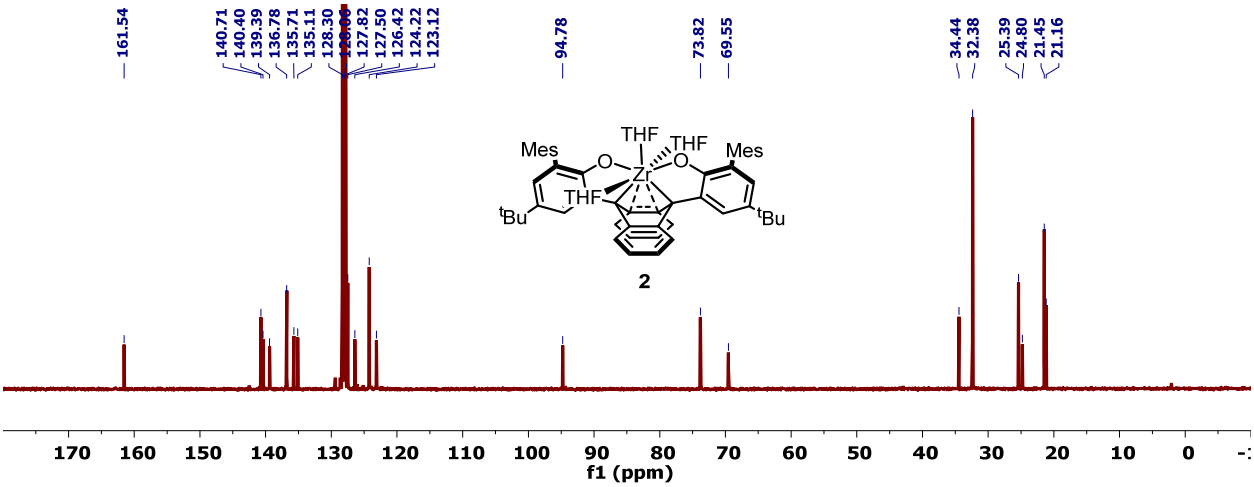


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum (101MHz, C_6D_6) of 2

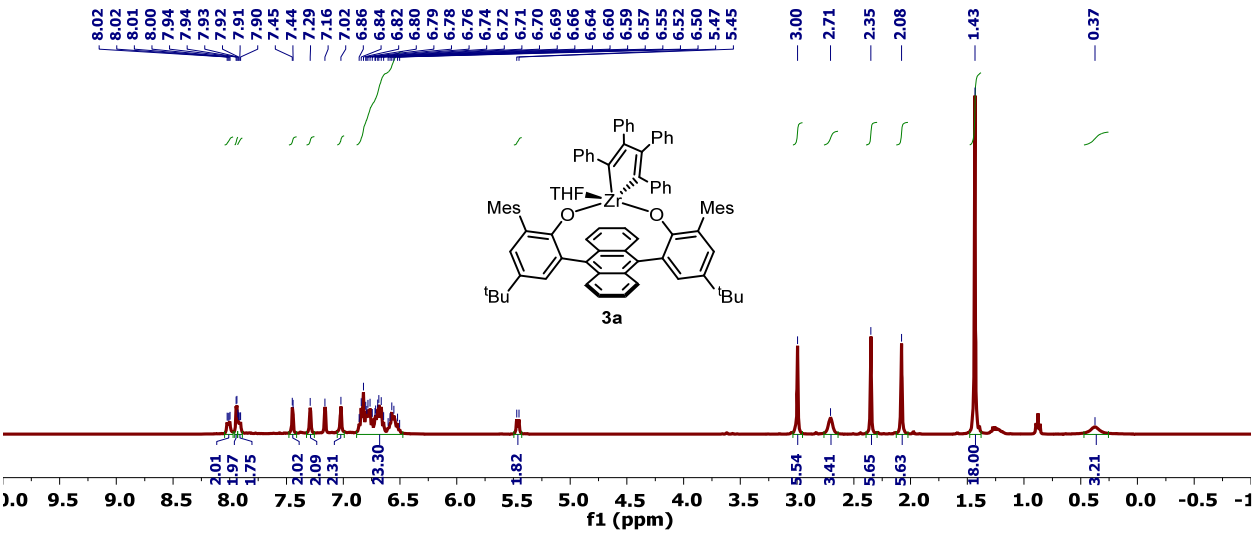


Figure S18. ^{1}H NMR spectrum (400 MHz, C_6D_6) of 3a

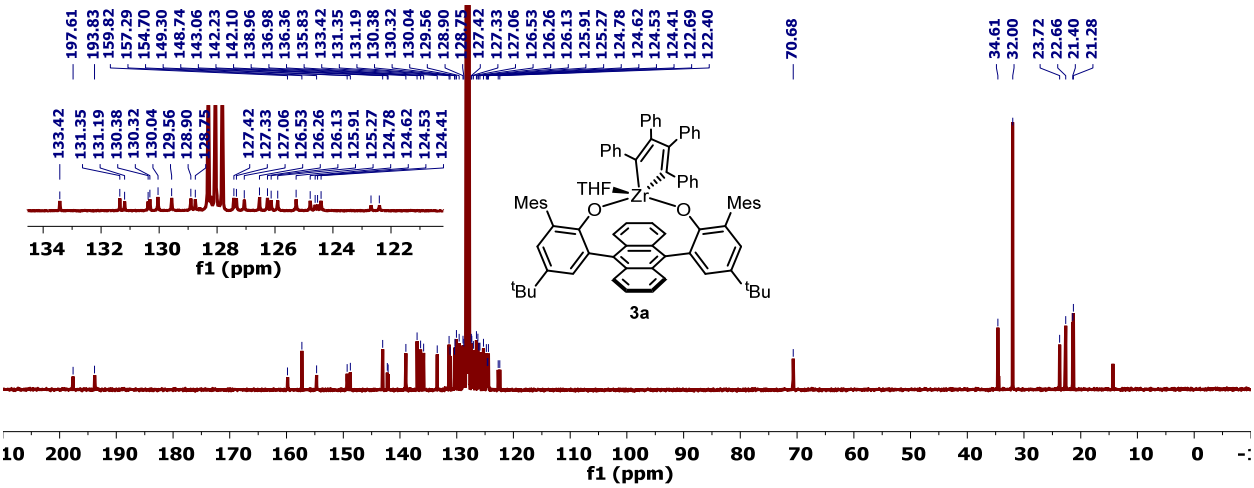


Figure S19. ^{13}C{^{1}H} NMR spectrum (101MHz, C_6D_6) of 3a

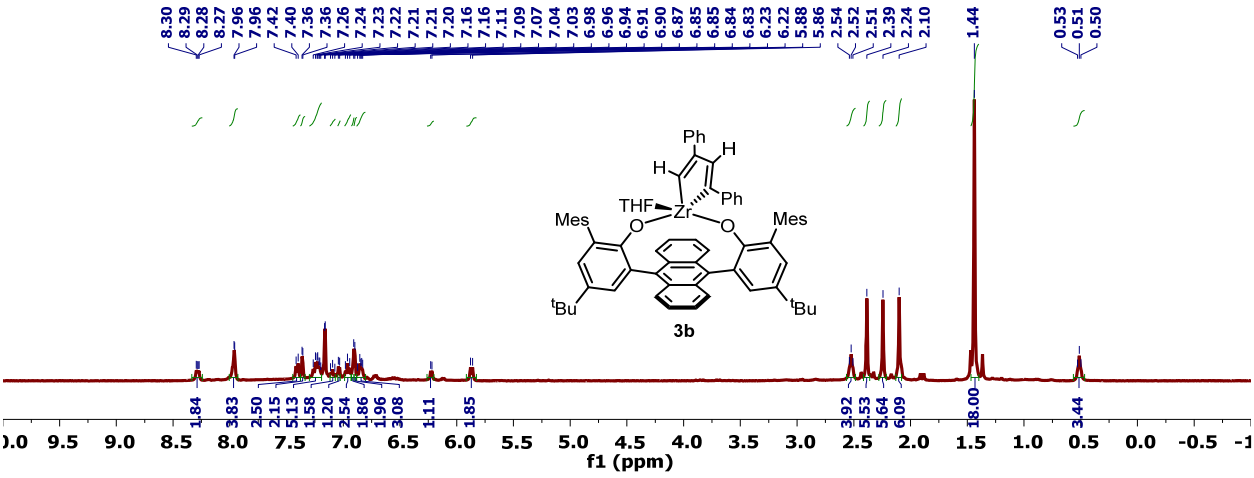


Figure S20. ^{1}H NMR spectrum (400 MHz, C_6D_6) of 3b

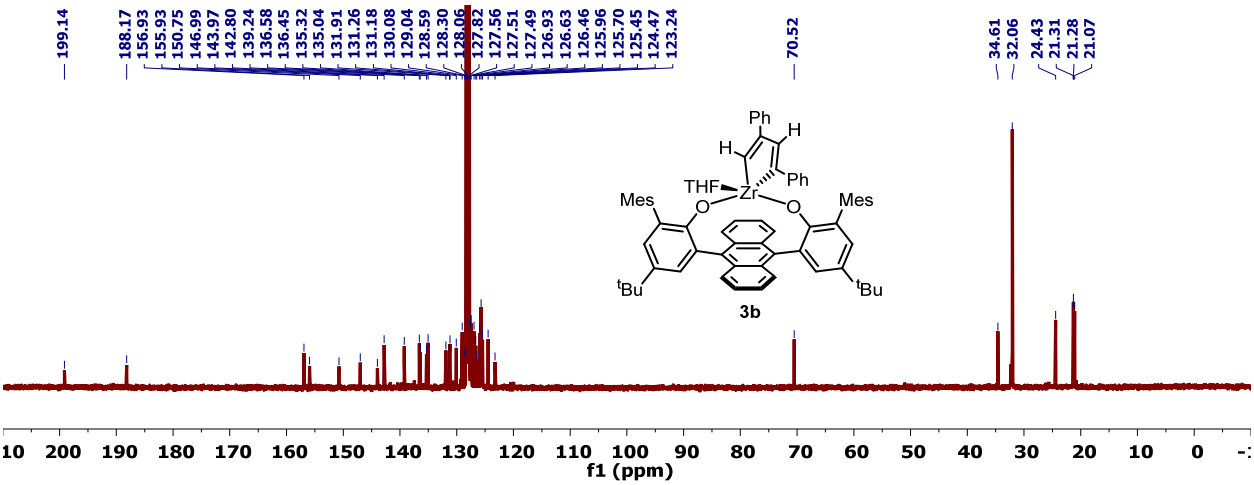


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum (101MHz, C_6D_6) of 3b

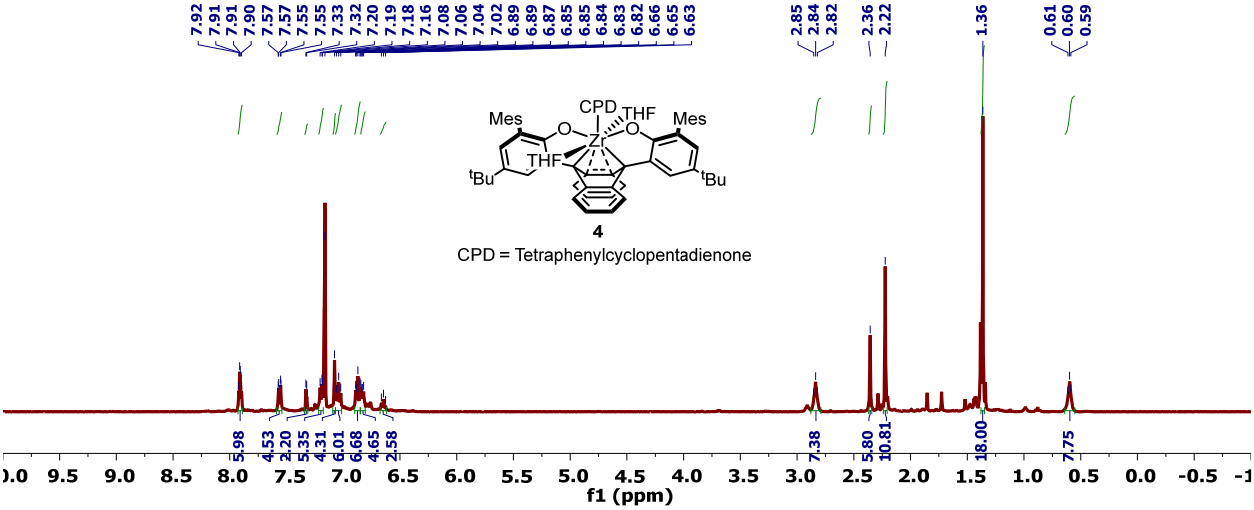


Figure S22. ^{1}H NMR spectrum (400 MHz, C_6D_6) of 4

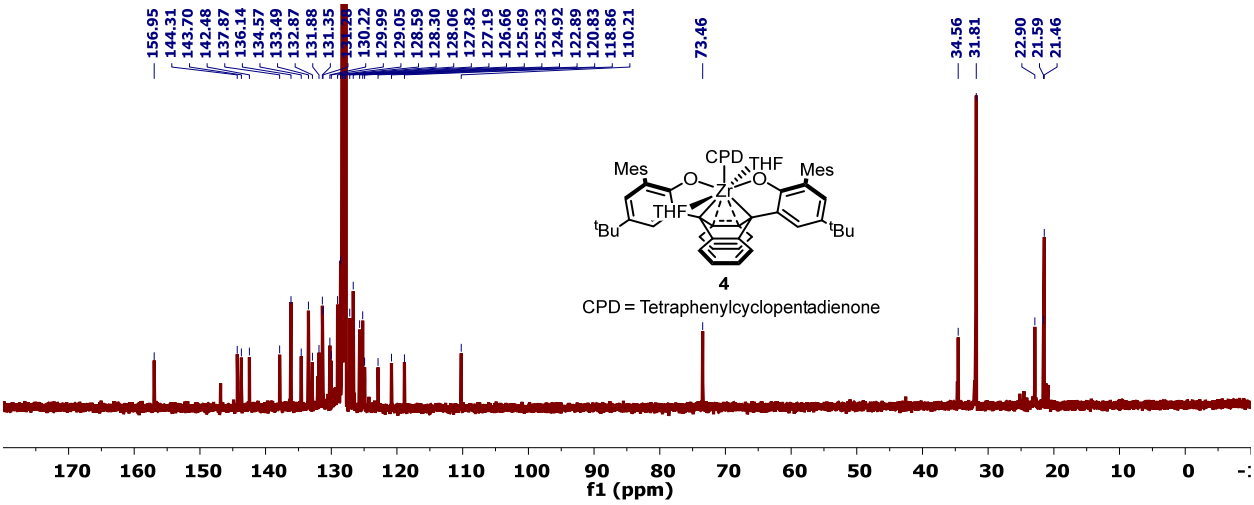


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum (101MHz, C_6D_6) of 4

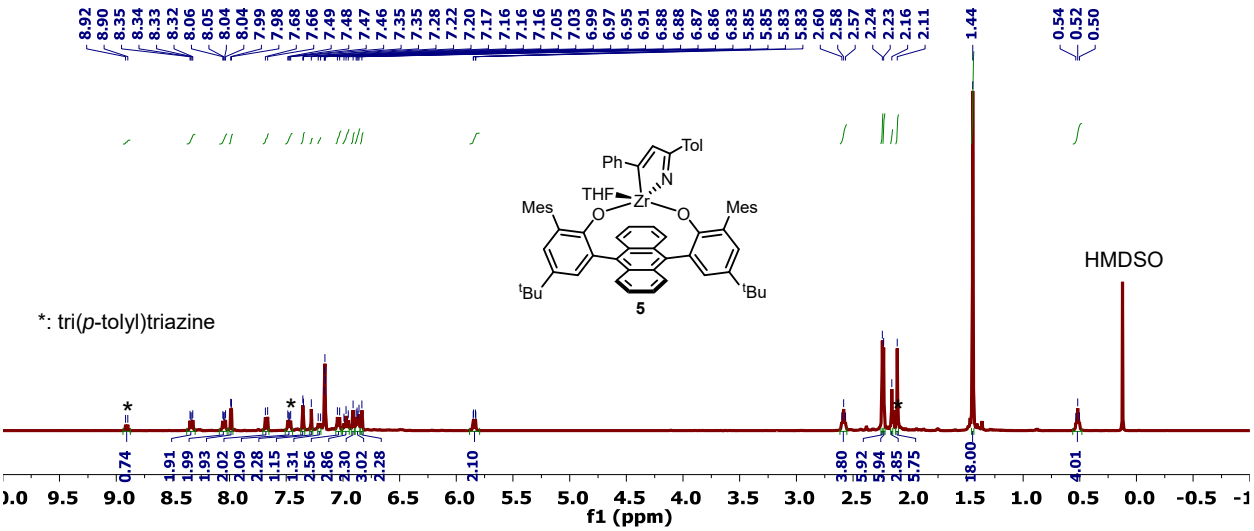


Figure S24. ^{1}H NMR spectrum (400 MHz, C_6D_6) of 5

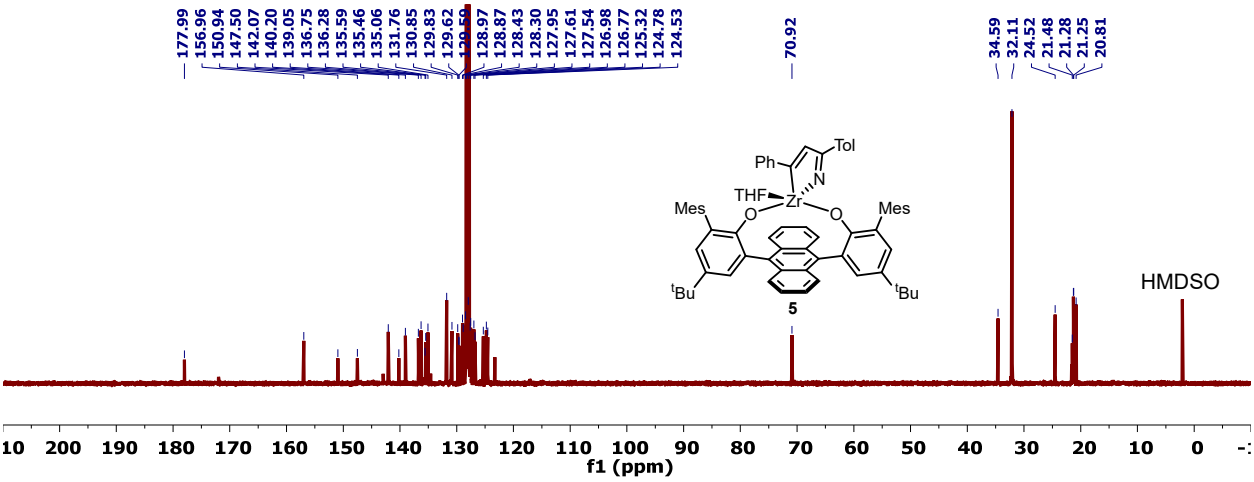


Figure S25. ^{13}C{^{1}H} NMR spectrum (101MHz, C_6D_6) of 5.

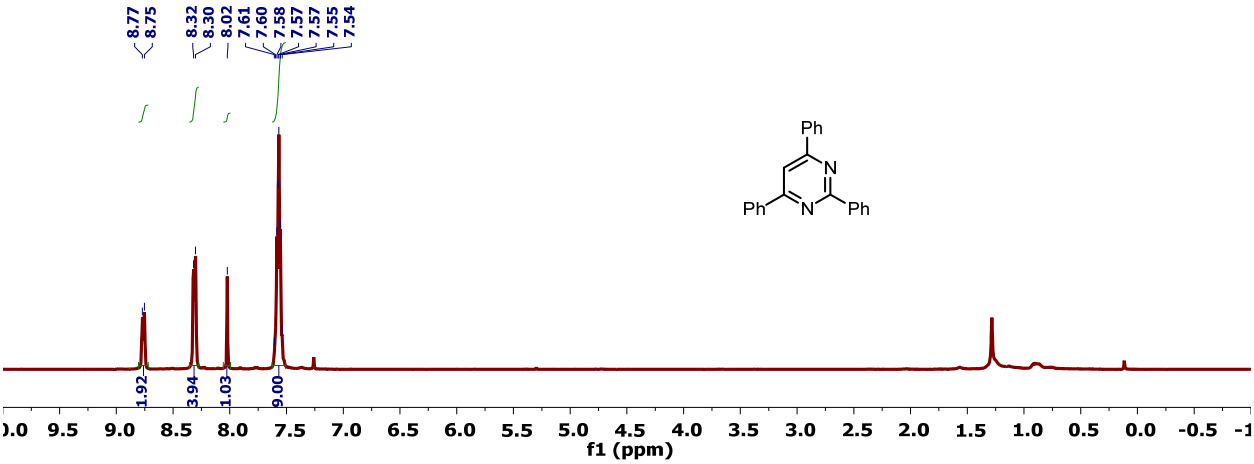


Figure S26. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6a

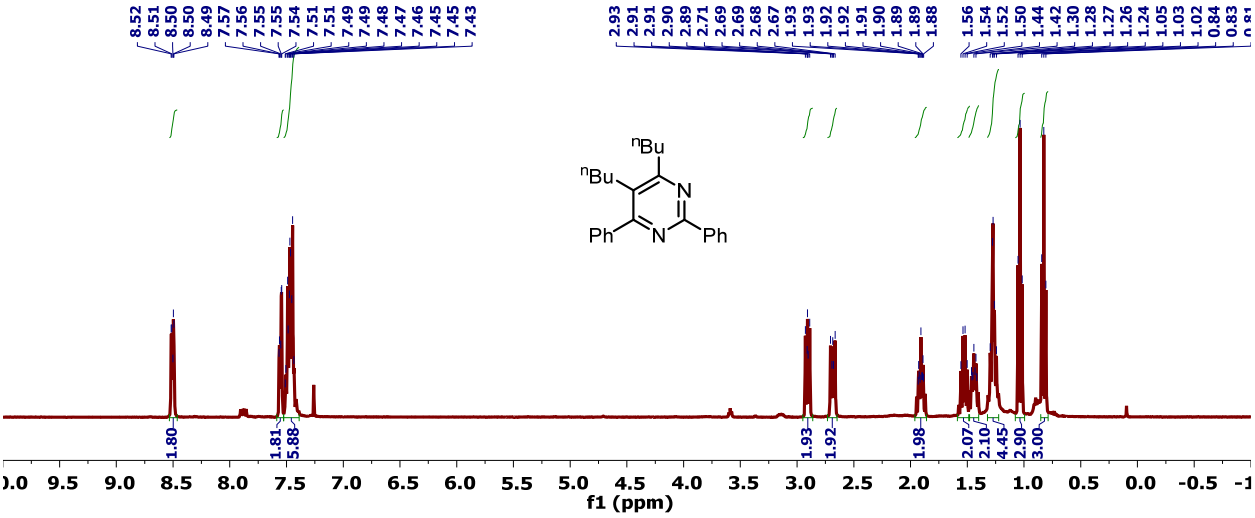


Figure S27. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6b

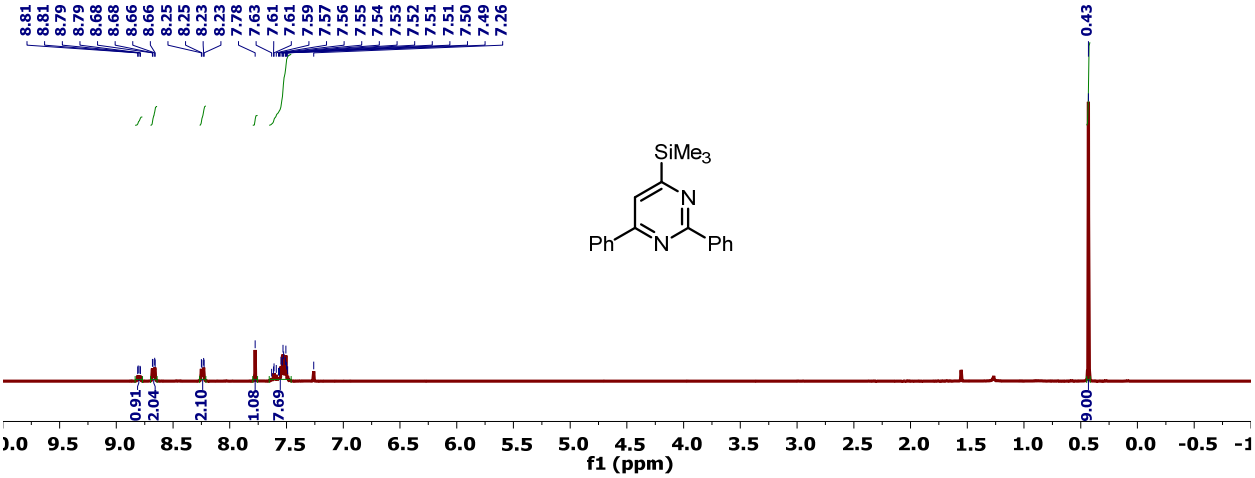


Figure S28. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6c

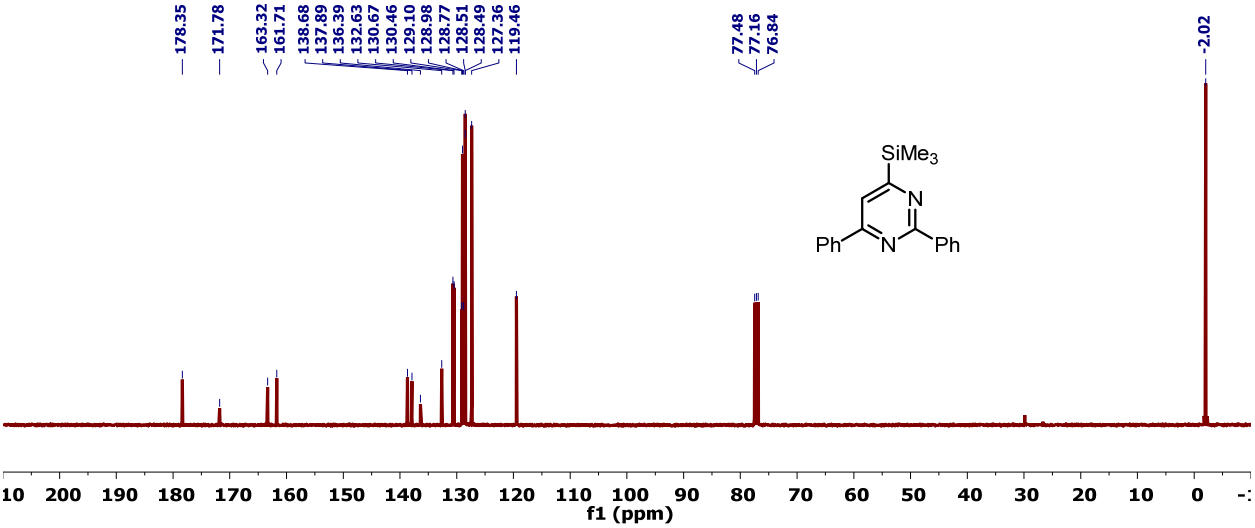


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of 6c

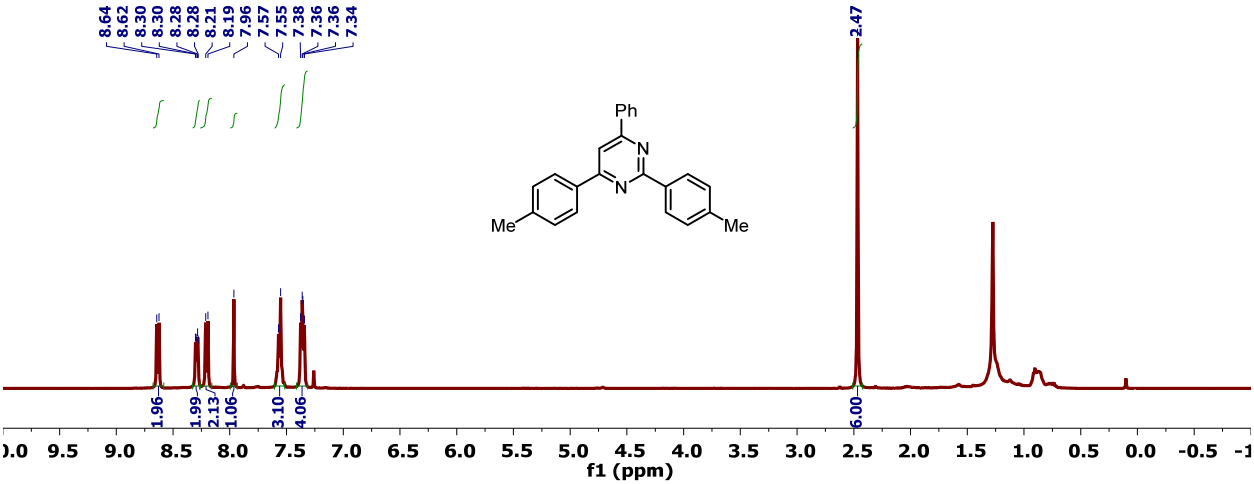


Figure S30. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6d

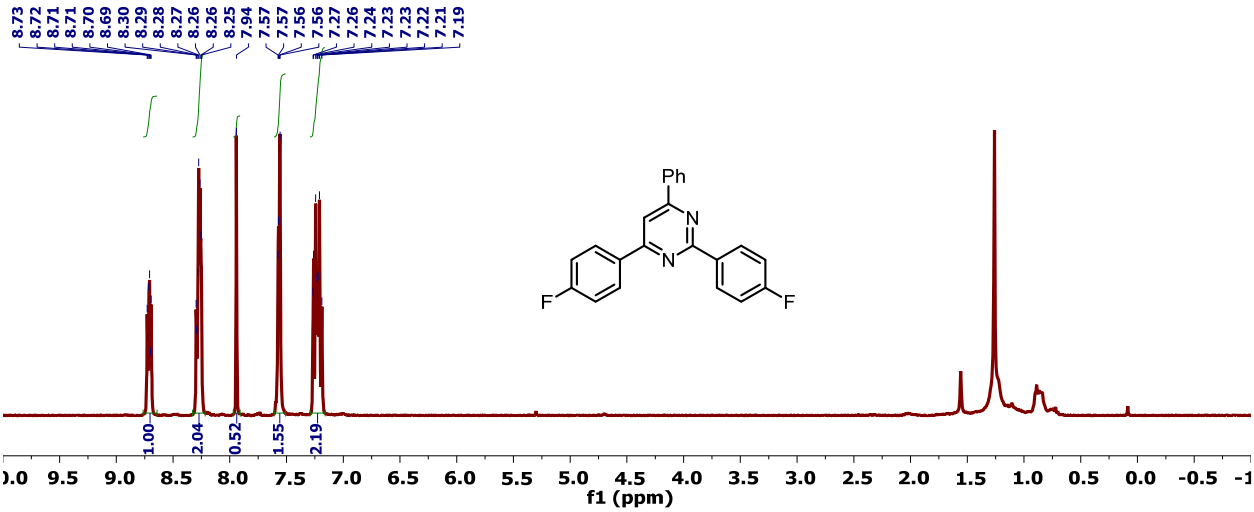


Figure S31. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6e

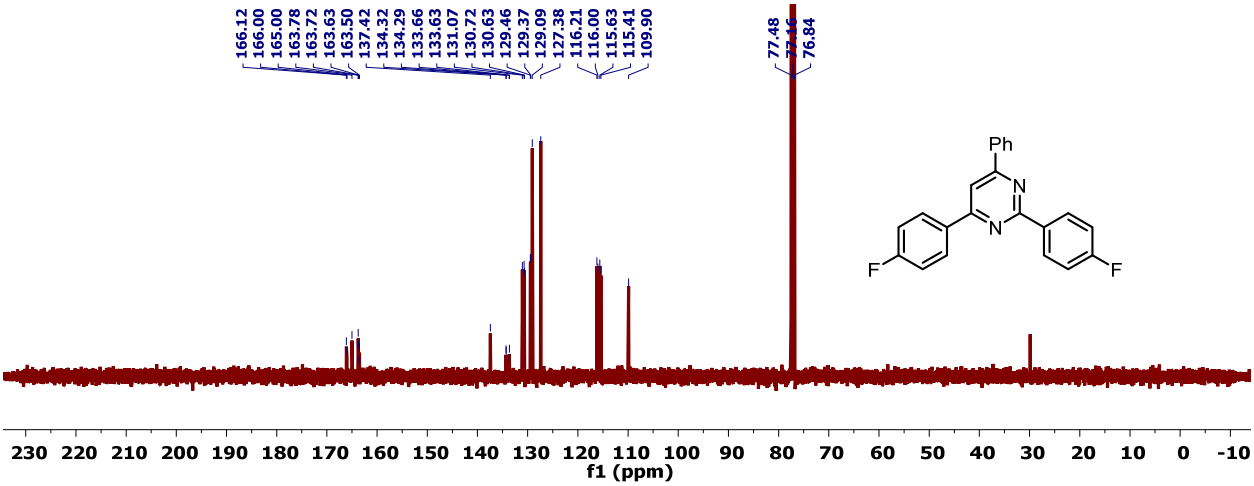


Figure S32. ^{13}C{^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of 6e

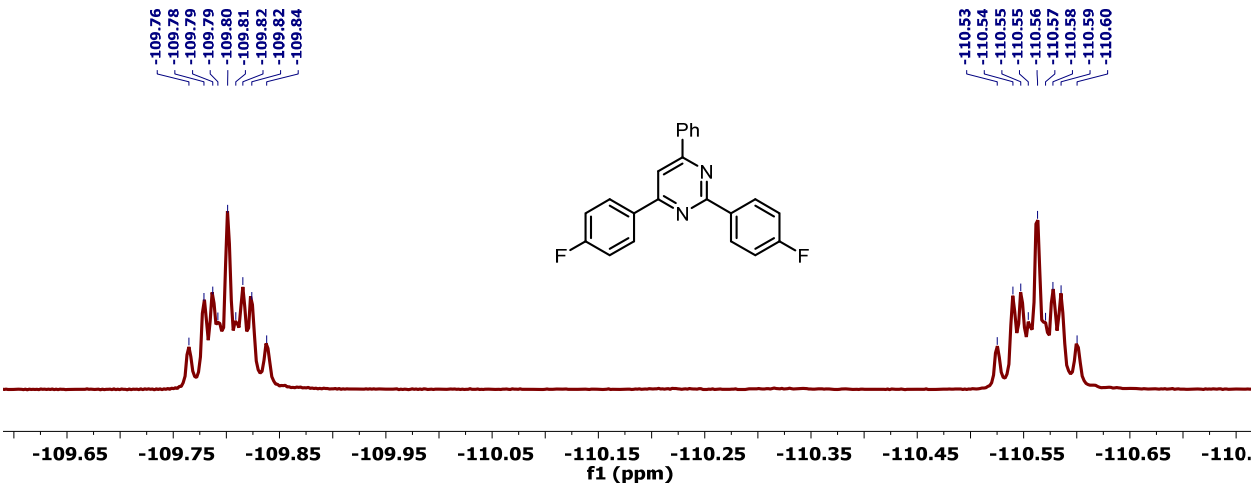


Figure S33. ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 6e

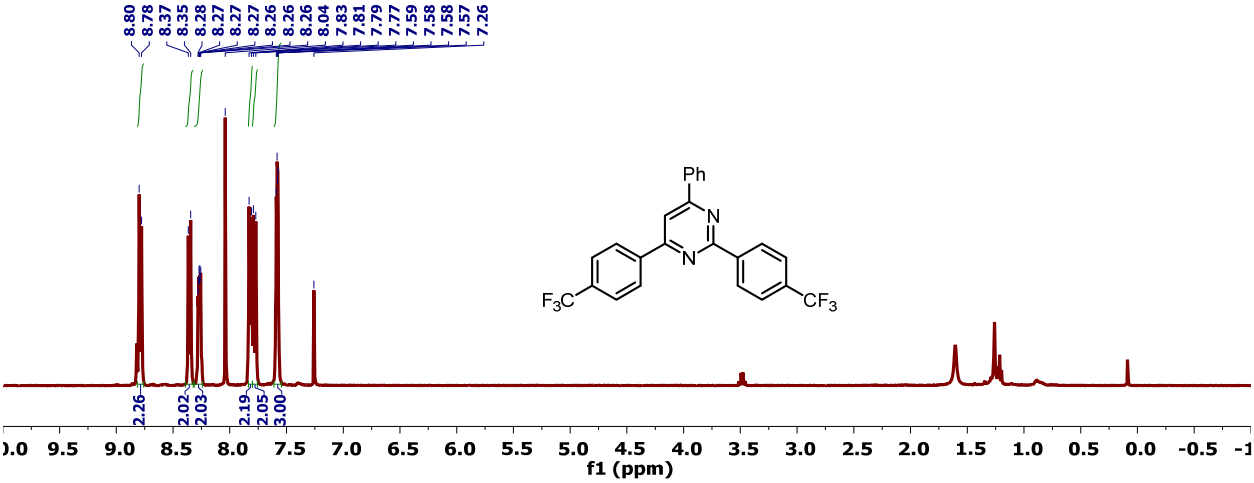


Figure S34. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 6f

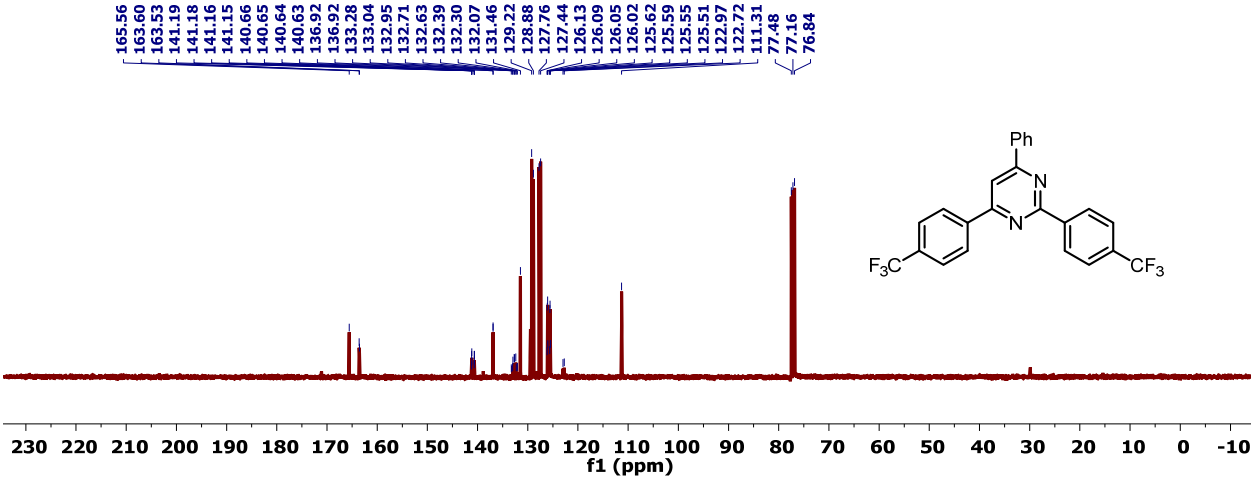


Figure S35. $^{13}C\{^{1}H\}$ NMR spectrum (101 MHz, $CDCl_3$) of 6f

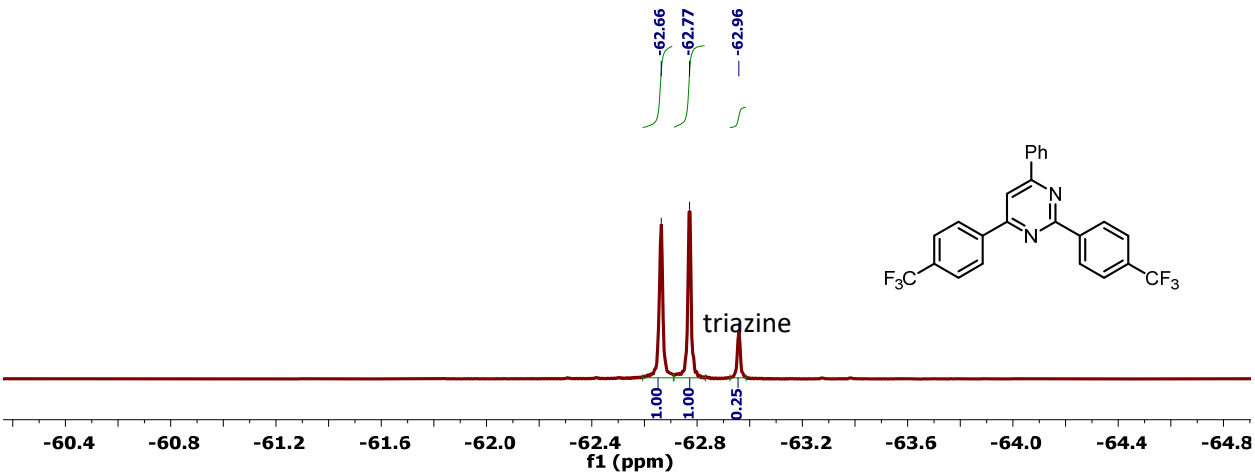
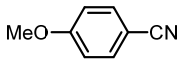
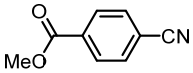
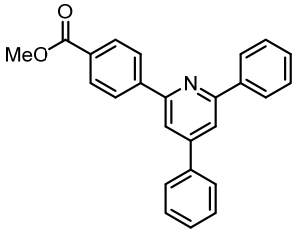
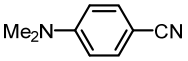
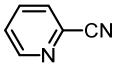
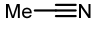
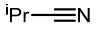
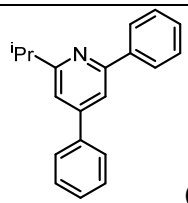
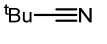
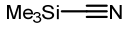
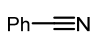
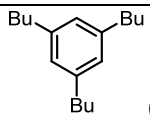
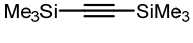
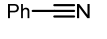
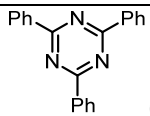


Figure S36. ^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 6f

Table S1. Additional substrates screened under optimized catalytic conditions.[a]

Entry	Alkyne	Nitrile	Products[b] (Yields[c])
1			nd
2			 (<5%)
3			nd
4			nd
5			nd
6			 (<5%)
7			nd
8			nd
9			 (<5%)
10			nd
11			nd
12			 (37%)

[a]optimized conditions: 6:1 nitrile:alkyne, 5 mol% **3a**, toluene (3 mL), 105 °C, 1h; [b]nd: not detected by GC-MS; [c]yields approximated from GC-MS based on PhCCH or PhCN consumption.

Crystallographic Information

CCDC deposition numbers 1853068, 1853069 and 1853070 contain the supplementary crystallographic data for this paper.[8] These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Refinement Details. In each case, crystals were mounted on a glass fiber or MiTeGen loop using Paratone oil, then placed on the diffractometer under a nitrogen stream. Low temperature (100 K) X-ray data were obtained on a Bruker D8 VENTURE Kappa Duo PHOTON 100 CMOS based diffractometer (Mo IμS HB micro-focus sealed X-ray tube, Kα = 0.71073 Å OR Cu IμS HB micro-focused X-ray tube, Kα = 1.54178). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEXII software.[9] Absorption corrections were applied using SADABS.[10] Space groups were determined on the basis of systematic absences and intensity statistics and the structures were solved in the Olex 2 software interface[11] by intrinsic phasing using XT (incorporated into SHELXTL)[12] and refined by full-matrix least squares on F2. All non-hydrogen atoms were refined using anisotropic displacement parameters, except in some cases with heavily distorted solvent. Hydrogen atoms were placed in the idealized positions and refined using a riding model. The structure was refined (weighed least squares refinement on F2) to convergence. Graphical representation of structures with 50% probability thermal ellipsoids were generated using Diamond 3 visualization software.[13] Structure of **5** was not submitted to CCDC due to poor quality.

Special Refinement Details for 1. **1** crystallizes in a P-1 space group with one molecule in the asymmetric cell along with 1 cocrystallized molecule of pentane. Part of the pentane molecule was disordered over 2 positions (occupancies 71% and 29%). There is additional solvent disorder which could not be satisfactorily modelled and was masked in Olex2. The volume of the solvent accessible void space was found to be 233.7 $Å^3$ in which 32.5 e- were located.

Special Refinement Details for 2. **2** crystallizes in a P-1 space group with one molecule in the asymmetric cell along with 1.6 cocrystallized molecules of tetrahydrofuran and 0.4 cocrystallized molecules of pentane. The pentane solvent is positionally disordered with a tetrahydrofuran molecule (44% and 56% occupancies, respectively). Part of the other tetrahydrofuran molecule was disordered over 2 positions (occupancies 87% and 13%), with the smaller part refined isotropically.

Special Refinement Details for 3a. **3a** crystallizes in the P-1 space group with one molecule in the asymmetric cell along with 1 cocrystallized molecule of pentane and 0.5 cocrystallized molecule of toluene. Both *tert*-butyl groups of the ligand are positionally disordered (69% and 31%, and 92% and 8% occupancies), with the former having bonds retained to be equal. The minor 8% part was refined isotropically. 3 of the 4 phenyl groups bound to the zirconacyclopentadiene motif are disordered over 2 positions and model with the same free varible (occupancies 51% and 49%). Due to the disorder the solvent molecules were refined isotropically. The toluene solvent is disorder with a pentane solvent (both fixed at 50% occupancy) while another pentane molecule is positionally disordered at a symmetry element (occupancy 50%) restraining bonds to be equal.

Table S2. Crystal data and structure refinement for 1, 2, 3a and 5

	1	2	3a	5
CCDC Number[8]	1853068	1853069	1853070	-
Empirical formula	$C_{71}H_{78}O_2Zr$	$C_{72.44}H_{93.75}O_{6.57}Zr$	$C_{92.42}H_{96.5}O_3Zr$	$C_{77}H_{85}NO_3Zr$
Formula weight	1054.55	1160.69	1346.44	1163.67
Temperature/K	100.15	100	100.0	100.02
Crystal system	triclinic	triclinic	triclinic	monoclinic
Space group	P-1	P-1	P-1	$P2_1/c$
a/Å	11.101(4)	12.4092(6)	12.350(2)	13.2545(11)
b/Å	12.844(4)	12.7750(8)	12.845(2)	25.037(2)
c/Å	21.787(7)	20.5948(17)	27.404(4)	19.9334(16)
α/°	101.462(14)	93.281(3)	78.961(7)	90
β/°	99.260(9)	103.293(4)	80.374(5)	107.996(3)
γ/°	93.809(11)	99.373(3)	63.052(12)	90
Volume/Å^3	2989.4(17)	3119.7(4)	3787.6(11)	6291.2(9)
Z	2	2	2	4
ρ_{calc}g/cm^3	1.172	1.236	1.181	1.229
μ/mm^{-1}	0.227	0.229	0.195	1.803
Crystal size/mm^3	0.4 × 0.2 × 0.1	0.22 × 0.16 × 0.11	0.25 × 0.25 × 0.09	0.09 × 0.05 × 0.03
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54178)
2Θ range/°	4.698 to 61.314	4.398 to 73.656	4.58 to 69.918	5.848 to 105.636
GOF	1.057	1.038	1.147	1.065
R_1,[a] wR_2[b] [I>2 σ(I)]	0.0396, 0.0990	0.0423, 0.0902	0.0661, 0.1721	0.0979, 0.2382

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$. [b] $wR_2 = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$

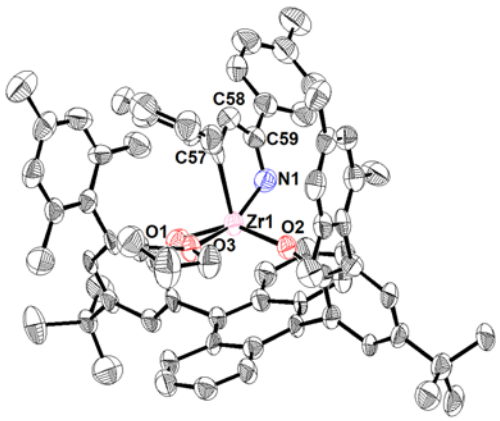


Figure S37. Solid-state structure of 5; thermal ellipsoids shown at 50% probability. Solvent molecules and hydrogen atoms omitted for clarity; relevant bond distances (Å): Zr1–O1 1.984(7), Zr1–O2 1.981(7), Zr1–C57 2.27(1), Zr1–N1 2.043(9), C57–C58 1.34(1), C58–C59 1.46(2), C59–N1 1.27(1)

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