Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Metal-Organic Insertion Light Initiated Radical (MILRad) Polymerization: Photo-initiated Radical Polymerization of Vinyl Polar Monomers with Various Palladium Diimine Catalysts

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General Information

Materials

Calcium hydride powder ($CaH_2 \geq 90\%$), diethyl ether anhydrous (≥ 99.7%), and acetonitrile ACS reagent (≥99.5%) 2,3-butanedione (97%), 2,6-dimethylaniline ((≥99%), and 2-tert-butylaniline (98%) were all purchased from Sigma-Aldrich and used as received. Acenaphthenequinone, and 2,6-Diisopropylaniline (90%) were purchased from Oakwood Chemical and used as received. Trifluoromethanesulfonic acid (98%), xylenes, ACS (≥98.5%), 2,4,6-Trimethylstyrene (95%), and p-Toluidine (≥99%) were purchased from Alfa Aesar and used as received. Formic acid (98-100%) was purchased from Millipore Sigma, and used as received. Methanol (99%), Methylene chloride (DCM, 99.9%), and pentane (99.5%) were purchased from Fischer Scientific. Sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]-borate ($NaBAr'_4$, 97%) and 3,5-bistrifluoromethylbenzonitrile (97%) was purchased from Matrix Scientific and used as received. Chloromethyl(1,5-cyclooctadiene) palladium(II) (99%) was purchased from Stream Chemicals, Inc and used as received. All monomers and solvents were degassed by three freeze-pump-thaw cycles under nitrogen gas. 2-Hydroxyethyl acrylate (HEA) (Sigma-Aldrich, 96%) was purified before use by first dissolving the monomer in water (25% by volume), then adding hydroquinone (0.2%) to inhibit thermal polymerization. The solution was extracted with hexane (25 times) to remove diacrylate, and the aqueous solution was then salted (250 g/L NaCl). HEA was then separated from the aqueous phase by multiple ether extraction (6 times) to remove acrylic acid. Hydroquinone (0.2%) was added to the ether solution. $MgSO_4$ (20% wt/v) was used to remove traces of water before evaporation of the ether phase. The purified monomer was subsequently distilled under pressure and degassed immediately prior to use. *n*-Butyl acrylate (99%), *t*-butyl acrylate (99%), glycidyl methacrylate (99%), styrene (99%) and dimethyl acrylamide (99%) were purchased from Sigma Aldrich, dried over CaH_2, distilled under vacuum, and degassed immediately before use. Methyl acrylate, methyl methacrylate, vinyl acetate, and isobutyl vinyl ether (Sigma Aldrich,

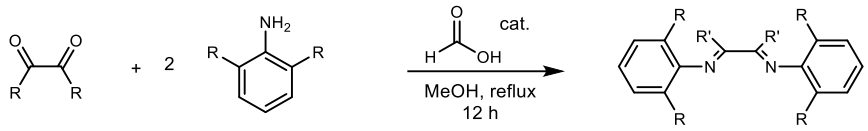
99%) was distilled over CaH_2, and degassed immediately prior to use. *N,N'*-isopropyl acrylamide (Sigma 99%) was used as received.

Instrumentation

Nuclear Magnetic Resonance (NMR) spectra were acquired at room temperature on a JEOL ECA 400 (400 MHz), ECA-500 (500 MHz), or ECA-600 (600 MHz) NMR spectrometer. Chemical shifts are measured relative to residual solvent peaks as an internal standard set to δ 5.32 and δ 54.00 (CD_2Cl_2), and δ 7.26 and δ 77.23 ($CDCl_3$) for ^{1}H and ^{13}C respectively. Gel permeation chromatography (GPC) was performed using a Tosoh high performance GPC system HLC-8320 equipped with an auto injector, a dual differential refractive index detector and TSKgel G series columns connected in series (7.8×300 mm TSKgel G5000Hxl, TSKgel G4000Hxl, TSKgel G3000Hxl). GPC analysis was carried out in HPLC grade tetrahydrofuran with a flow rate of 1.0 mL/min at 40 °C. Molecular weights (M_n and M_w) and molecular weight distributions (*Đ*) were calculated from poly(methyl methacrylate) (PMMA) standards with molecular weights of 800 to 2.2×10^6 g mol^{-1} provided by Polymer Standard Service (PSS). UV-Vis spectra were recorded using Agilent Carey 60 UV−vis spectrophotometer. Samples were housed in 1 cm quartz cuvettes with septum-sealed screw cap. Geometries for catalyst 1A, 1B, 2A, 2C, 2D and 3C were optimized at the M06-2X/6-31+G(d,p) level in implicit dichloromethane solvation, employing the polarized continuum model (PCM). [1,2] Vibrational frequency analyses verified the nature of the stationary points (see details in the ESI). Vertical excitation energies were computed using time-dependent density functional theory (TD-DFT) at the same level of theory. Molecular orbitals were plotted using VMD [3]. All calculations were performed employing Gaussian 09 [4].

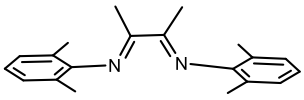
Experimental Methods

General synthesis for 2,3-substituted dimine ligands



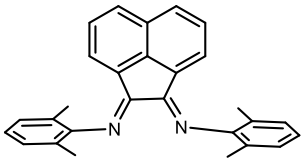
To a solution of the substituted aniline (2.10 equiv) in methanol or ethanol was added the selected di-ketone (1.00 equiv). Formic acid was then added as a catalyst. After heating to reflux for 12-24 hours, the reaction mixture was cooled to room temperature, concentrated under reduced pressure and cooled to -20 ℃ overnight. The resulting solid residue was recrystallized from cold ethanol, washed with cold methanol, and then dried *in vacuo* to afford the desired title compound as a yellow or red solid.

N,N'-Bis(2,6-dimethylaniline)-butane-2,3-diimine



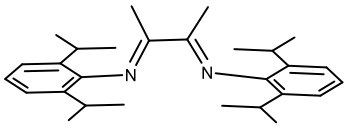
The general procedure for ligand synthesis was used with 2,3-butanedione (3.50g, 40.66 mmol), 2,6-dimethylaniline (6.75 ml, 54.9 mmol), 1.25 ml of formic acid and 150 ml of methanol in a 250 ml round bottom flask. Yield 85% (10.2 g). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.10 (m, 4H), 7.02 (m, 2H), 2.33 (s, 6H), 2.05 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 147.9, 127.5, 124.1, 122.8, 17.3, 15.4. This compound is known.[1]

***N,N'*-Bis(2,6-dimethylphenyl)acenaphthylene-1,2-diimine**



General procedure for ligands have been used with acenaphthenequinone (5.0 g, 27.4 mmol), 2,6-dimethylaniline (6.75 ml, 54.9 mmol), 1.25 ml of formic acid and 150 ml of methanol in a 250 ml round bottom flask. During reflux, the solution turned from yellow to red. The reaction was cooled to room temperature and excess solvent removed under reduced pressure and the residue subjected to vacuum for 6 hours. After washing with cold (-78^{o}C) hexane, the product extracted with room temperature hexane (3 × 100 ml), reduced to minimum volume and cooled to (-35^{o}C). Formation of orange/red crystals observed, and the product vacuum filtered, giving a 50% yield (5.3 g, 15.8 mmol). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.92 (d, *J* = 8.7 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.07-7.19 (m, 6H), 6.69 (d, *J* = 7.3 Hz, 2H), 2.11 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.81, 148.9, 141.4, 132.4, 129.9, 129.4, 128.7, 128.4, 125.1, 124.0, 122.9, 17.9. This compound is known.[2]

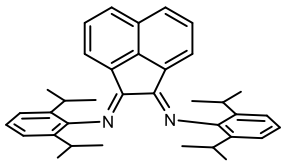
***N,N'*-Bis(2,6-diisopropylphenyl)butane-2,3-diimine**



The general procedure for ligand synthesis was used with 2,3-butanedione (3.50 g, 40.66 mmol), 2,6-diisopropylaniline (15.1 g, 85.4 mmol), 1.25 ml of formic acid and 150 ml of methanol in a 250 ml round bottom flask. Yield 82% (13.5 g). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.18 (m, 4H), 7.10 (m, 2H), 2.73 (sp, *J*

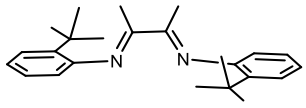
= 6.6 Hz, 4H), 2.07 (s, 6H), 1.22 (d, *J* = 5.9 Hz, 6H), 1.20 (d, *J* = 5.9 Hz, 6H), 1.18 (d, *J* = 5.9 Hz, 6H), 1.16 (d, *J* = 5.9, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.6, 146.8, 135.6, 124.2, 123.5, 28.9, 23.3, 22.9. This compound is known.[3]

***N,N*'-Bis(2,6-diisopropylphenyl)butane-2,3-diimine**



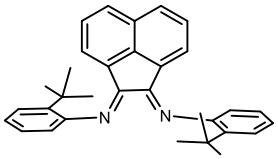
The general procedure for ligand synthesis was used with acenaphthenequinone (5.0 g, 27.4 mmol), 2,6-diisopropylaniline (10.5 g, 59.2 mmol), 1.25 ml formic acid and 150 ml of methanol in a 250 ml round bottom flask. Yield 90% (12.5g). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.22-7.30 (m, 6H), 6.66 (d, *J* = 6.9 Hz, 2H), 3.00-2.93 (m, 4H), 1.21 (d, *J* = 6.4 Hz, 12H), 0.99 (d, *J* = 6.9 Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 161.9, 147.6, 141.0, 135.6, 135.6, 131.3, 129.7, 129.0, 128.0, 124.4, 123.6, 123.5, 28.8, 23.6, 23.3. This compound is known.[4]

***N,N*'-Bis(2-(tert-butyl)phenyl)butane-2,3-diimine**



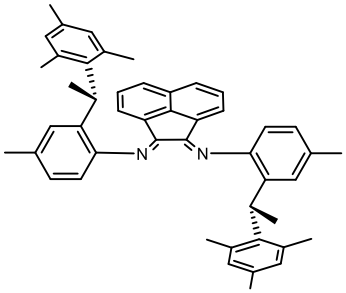
The general procedure for ligand synthesis was used with 2,3-butanedione (3.50g, 40.66 mmol), 2-*tert*-butylaniline (13 g, 87.1mmol), 1.25 ml of formic acid and 150 ml of methanol in a 250 ml round bottom flask. Yield 80% (11.3 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 7.3 Hz, 2H), 7.18 (d, *J* = 6.9 Hz, 2H), 7.08 (d, *J* = 7.3 Hz, 2H), 6.50 (d, *J* = 6.9 Hz, 2H), 2.18 (s, 6H), 1.33 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 168.7, 146.8, 135.6, 124.2, 123.5, 28.9, 23.3, 22.9. This compound is known.[4]

***N,N*'-Bis(2-(tert-butyl)phenyl)acenaphthylene-1,2-diimine**



The general procedure for ligand synthesis was used with acenaphthenequinone (5.0 g, 27.4 mmol), 2-*tert*-butylaniline (8.5 g, 57.0 mmol), 1.25 ml formic acid and 150 ml of methanol in a 250 ml round bottom flask. Yield 89 % (10.8 g). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.90 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.37 (dd, *J* = 7.6, 7.6 Hz, 2H), 7.22-7.27 (m, 4H), 6.93 (d, *J* = 6.9 Hz, 2H), 6.85 (d, *J* = 6.9 Hz, 2H), 1.37 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 159.9, 150.6, 141.8, 139.3, 131.2, 129.1, 128.8, 127.7, 126.83, 126.75, 124.6, 123.9, 119.0, 35.5, 29.8. This compound is known.[4]

***N,N*'-Bis(*rac*-4-methyl-2-(*sec*-(2,4,6-trimethylphenethyl)phenyl)acenaphthylene-1,2-diimine**

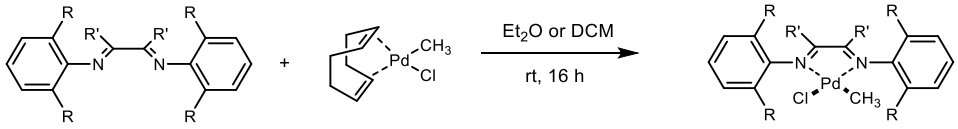


*Synthesis of rac-4-methyl-2-sec-(2,4,6-trimethylphenethyl))aniline***.** The procedure was adopted from literature.[5] *p*-Toluidine (3.08 g, 28.7 mmol) and 2,4,6-trimethylstyrene (3.09 mL, 19.1 mmol) in xylenes (5 mL) were combined in a 25 ml round bottom flask. Then the flask is closed with septum and sealed by a wire. CF_3SO_3H (0.34 mL, 3.8 mmol) was added to the solution and the solution was heated at 160 °C for overnight. The solution concentrated under vacuum, and column chromatography (90:10 hexanes: EtOAc) was used to purify the residue. 3.45 g (13.5 mmol) of a colorless solid was collected by chromatography (77% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16 (s, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.78 (s, 2H), 6.46 (d, *J*

= 7.8 Hz, 1H), 4.34 (q, *J* = 7.3 Hz, 1H), 3.14 (s, 2H), 2.29 (s, 3H), 2.21 (s, 3H), 2.14 (s, 6H), 1.60 (d, *J* = 7.3 Hz, 3H).

The procedure for diimine synthesis was adopted from literature[2]. In a round bottom flask acenaphthenequinone (1.2 g, 6.8 mmol), rac-4-methyl-2-(sec-(2,4,6- trimethylphenethyl))aniline (3.45 g, 13.6 mmol), glacial acetic acid (15.5 mL), and toluene (8 mL) were combined and sealed with septum. The solution was heated to 100°C for 3 h and the color changed to orange/red. After observation of solid particles in the solution, the solution is filtered by vacuum filtration and washed with hexanes (40 ml) and methanol (40 ml). After drying under vacuum the reaction gave 3.5 g of a yellow solid product. Yield (80 %). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.45 (s, 2H), 7.16 (d, *J* = 6.9 Hz, 2H), 7.08 (t, *J* = 7.7 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.66 (d, *J* = 6.9 Hz, 2H), 5.95 (br s, 2H), 5.34 (br s, 2H), 4.57 (q, *J* = 7.4 Hz, 2H), 2.50 (s, 6H), 2.40 (br s, 6H), 1.68 (br s, 6H), 1.55 (d, *J* = 7.4 Hz, 9H), 0.94 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 160.4, 148.2, 140.4, 138.4, 136.9, 134.1, 133.3, 132.1, 129.9, 129.6, 129.1, 128.8, 127.3, 127.2, 126.2, 122.7, 117.7, 36.1, 22.0, 21.3, 20.8 (br), 19.2, 16.3. This compound is known.[5]

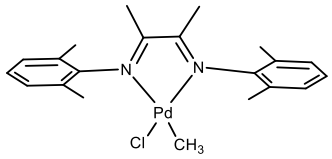
General method for the synthesis of 2,3-substituted dimine Pd(Me)(Cl) complexes



Briefly, diethyl ether or dichloromethane (10 ml) was added to a flame-dried 25 ml round bottom flask containing chloro(1,5-cyclooctadiene)methylpalladium(II) (1 equiv) and a slight excess of 2,3-diimine ligand (1.05 equiv). In diethyl ether, the formation of a yellow-orange, orange or red precipitate was observed within a few minutes upon mixing. In dichloromethane, a color change to deep red was observed over the course of the reaction. For reactions carried out in diethyl ether, the reaction mixture was stirred overnight and the diethyl ether and free cyclooctadiene were then removed via filtration. The solid product

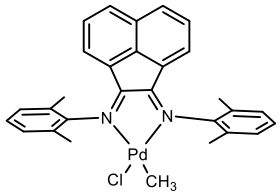
was washed twice with 10-20 mL of cold diethyl ether, then dried overnight *in vacuo*. For reactions in dichloromethane, the product was isolated by direct precipitation of the reaction mixture into pentanes, followed by filtration and washing. The product was then dried *en vacuo*. The resulting products were then characterized by NMR spectroscopy.

(Ar-N=C(Me)-C(Me)=N-Ar)Pd(Me)(Cl) (Ar = 2,6-dimethylphenyl)



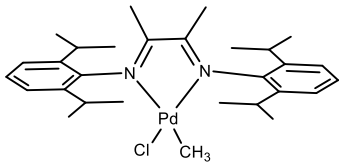
Using the above general procedure bis(2,6-dimethylaniline)-butane-2,3-diimine (315 mg 1.08 mmol, 1.06 equiv), and chloro(1,5 cyclooctadiene)methylpalladium(II) (270 mg, 1.02 mmol, 1 equiv) were combined with 10 ml of degassed DCM in a 25 ml flamed dried round bottom flask. The reaction mixture was stirred overnight. The reaction mixture was then directly added in a dropwise manner to the 150 ml of pentane to precipitate the product. The product was then collected by vacuum filtration and dried overnight in vacuo resulting 400 mg of the desired product. Yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.08-7.20 (m, 6H), 2.22 (s, 13H), 2.00 (s, 3H), 1.96 (s, 3H), 0.25 (s, 3H). ^{13}C NMR (150 MHz, CD_2Cl_2, ppm) δ 175.1, 170.4, 142.4, 142.8, 139.2, 138.7, 128.8, 127.0, 124.9, 123.6, 29.5, 28.9, 24.8, 29.7, 23.8, 23.8, 21.2, 20.2, 5.6 ppm. This compound is known.[6]

(Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(Cl) (Ar = 2,4-dimethylphenyl; An = acenaphthene)



Using the above general procedure bis(2,6-dimethylphenyl)acenaphthylene-1,2-diimine (415 mg 1.07 mmol, 1.05 equiv), and chloro(1,5 cyclooctadiene)methylpalladium(II) (270 mg, 1.02 mmol, 1 equiv) were combined with 10 ml of degassed DCM in a 25 ml flamed dried round bottom flask. The reaction mixture was stirred overnight. The reaction mixture was then directly added in a dropwise manner to the 150 ml of pentane to precipitate the product. The product was then collected by vacuum filtration and dried overnight in vacuo resulting 470 mg of the desired product. Yield 85%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.06 (dd, *J* = 16.3, 8.3 Hz, 2H), 7.44 (dd, *J* = 19.4, 7.8 Hz, 2H), 7.29-7.23 (m, 6H), 6.73 (d, *J* = 7.1 Hz, 1H), 6.54 (d, *J* = 7.4 Hz, 1H), 2.29 (d, *J* = 6.6 Hz, 12H), 0.57 (s, 3H). This compound is known.[7]

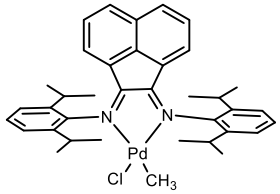
(Ar-N=C(Me)-C(Me)=N-Ar)Pd(Me)(Cl) (Ar = 2,6-diisopropylphenyl)



Using the above general procedure bis(2,6-diisopropylaniline)-butane-2,3-diimine (435 mg 1.08 mmol, 1.05 equiv), and chloro(1,5 cyclooctadiene)methylpalladium(II) (270 mg, 1.02 mmol, 1 equiv) were combined with 10 ml of diethyl ether in a 25 ml flamed dried round bottom flask. The product was then collected by vacuum filtration and dried overnight in vacuo resulting 520 mg of the desired product. Yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.36 – 7.26 (m, 6H), 3.08 (sep, *J* = 6.60 Hz, 2H), 3.02 (sep, *J* = 6.93 Hz, 2H), 2.06 (s, 3H), 2.05 (s, 3H), 1.42 (d, *J* = 7.31 Hz, 6H), 1.37 (d, *J* = 7.31 Hz, 6H), 1.20 (d, *J* =

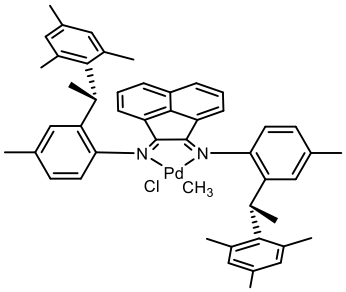
6.99 Hz, 6H), 1.19 (d, *J* = 6.99 Hz, 6H), 0.39 (s, 3H). ^{13}C NMR (150 MHz, CD_2Cl_2, ppm) δ 175.8, 170.4, 142.4, 142.2, 139.1, 138.5, 128.1, 127.3, 124.4, 123.7, 29.4, 28.9, 24.1, 29.9, 23.6, 23.4, 21.6, 20.2, 5.6. This compound is known.[8]

(Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(Cl) (Ar =2,4-diisopropylphenyl; An = acenaphthene)



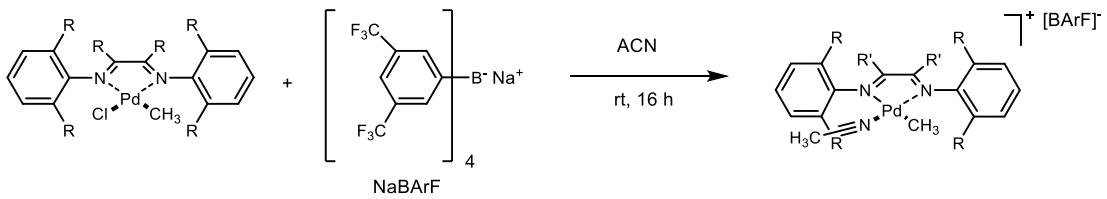
Using the above general procedure bis(2,6-diisopropylphenyl)acenaphthylene-1,2-diimine (535 mg 1.07 mmol, 1.05 equiv), and chloro(1,5 cyclooctadiene)methylpalladium(II) (270 mg, 1.02 mmol, 1 equiv) were combined with 15 ml of degassed DCM in a 25 ml flamed dried round bottom flask. The reaction mixture was stirred overnight. The reaction mixture was then directly added in a dropwise manner to the 150 ml of pentane to precipitate the product. The product was then collected by vacuum filtration and dried overnight in vacuo resulting 600 mg of the desired product. Yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.14-8.20 (m, 2H), 7.42-7.59 (m, 12H), 6.95 (d, J = 7.3 Hz, 1H), 6.54 (d, J = 7.3 Hz, 1H), 3.17-3.30 (m, 4H), 1.96 (d, J = 20.6 Hz, 3H), 1.64 (s, 5H), 1.37-1.55 (m, 11H), 0.96-1.13 (m, 11H), 0.83 (s, 3H) ^{13}C NMR (150 MHz, CD_2Cl_2, ppm) δ 175.08, 170.44, 142.44, 142.28, 139.12, 138.57, 128.18, 127.30, 124.49, 123.76, 29.45, 28.99, 24.08, 29.97, 23.68, 23.48, 21.62, 20.20. This compound is known.[8]

(Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(Cl) (Ar = *rac*-4-methyl-2-(sec-(2,4,6-trimethylphenethyl)phenyl; An = acenaphthene)



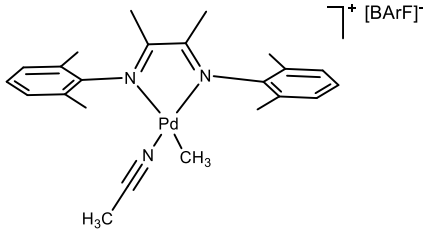
Using the above general procedure bis(rac-4-methyl-2-(sec-(2,4,6-trimethylphenethyl)phenyl)acenaphthylene-1,2-diimine. (700 mg, 1.07 mmol, 1.05 equiv), and chloro(1,5 cyclooctadiene)methylpalladium(II) (270 mg, 1.02 mmol, 1 equiv) were combined with 20 ml of degassed DCM in a 25 ml flamed dried round bottom flask. The reaction mixture was stirred overnight. The reaction mixture was then directly added in a dropwise manner to the 150 ml of pentane to precipitate the product. The product was then collected by vacuum filtration and dried overnight in vacuo resulting 660 mg of the desired product. Yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.82 (dd, *J* = 14.2, 8.2 Hz, 2H), 7.59 (s, 1H), 7.54 (s, 1H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.22-7.25 (m, 1H), 7.20 (t, *J* = 7.1 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.82 (d, *J* = 6.9 Hz, 1H), 6.56 (d, *J* = 7.3 Hz, 1H), 6.12 (s, 1H), 6.06 (s, 1H), 5.22 (s, 1H), 5.17 (s, 1H), 5.01 (q, *J* = 7.3 Hz, 1H), 4.70 (q, *J* = 7.3 Hz, 1H), 3.21 (s, 3H), 3.14 (s, 3H), 2.54 (s, 6H), 1.54-1.60 (multiple br s, 12H), 0.91 (s, 3H), 0.86 (s, 3H), 0.54 (s, 3H).

General procedure for the synthesis of cationic Pd(II) *α*-diimine complexes with acetonitrile ligand



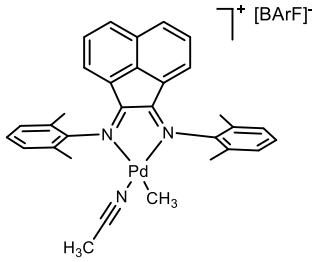
A previously published procedure was modified and used.[9] At room temperature, dichloromethane and acetonitrile was added to a flamed-dried flask containing sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr'_4$) and (Ar-N=C(Me)-C(Me)=N-Ar)Pd(Me)(Cl). As the reaction progressed, precipitation of sodium chloride (NaCl) was observed. After stirring overnight, NaCl was removed from the reaction mixture via filtration, and the solvent was evaporated. The solid was dissolved in a small amount of dichloromethane and filtered again with a 0.45 µm PTFE syringe filter. The filtrate was added dropwise to pentane to precipitate the desired product. The resulting solid was filtered, washed with pentane, and dried *in vacuo* to give the desired product as a solid compound. All cationic α-diimine Pd(II) complexes contained the $[B(3,5\text{-}C_6H_3(CF_3)_2)_4]^-$ counterion. Spectral data was similar for each complex. ^{1}H NMR (400 MHz, CD_2Cl_2) 7.73 (s, 8H), 7.57 (s, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2) ppm 162.3 (q, J_{CB} = 49.8 Hz, 4C), 135.4 (8C), 129.3 (q, J_{CF} = 30.3 Hz, 8C), 125.2 (q, J_{CF} = 272.7 Hz, 8C), 117.9 (4C). The NMR data for the BAr'_4 counterion matched those previously reported.[9]

(Ar-N=C(Me)-C(Me)=N-Ar)Pd(Me)(CH_3CN)]$^+$[B(3,5-$C_6H_3(CF_3)_2)_4]^-$ (Ar =2,6-dimethylphenyl)



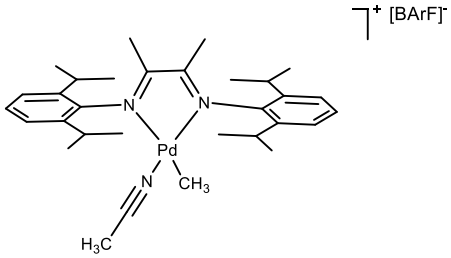
Catalyst 1A. Using the general procedure (Ar-N=C(Me)-C(Me)=N-Ar)Pd(Me)(Cl) (Ar =2,6-dimethylphenyl) (150 mg, 0.334 mmol, 1 equiv), NaBAr'F (310 mg, 0.350 mmol, 1.05 equiv), acetonitrile (5 ml) and dichloromethane (5 ml) were combined. The product was isolated as a yellow solid (350 mg, 80% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.14-7.22 (m, 6H), 2.23 (s, 6H), 2.17 (s, 6H), 2.16 (s, 3H), 2.14 (s, 3H), 1.78 (s, 3H), 0.38 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) ppm 180.3, 172.4, 162.3, 143.1, 135.4, 129.4, 129.2, 128.6, 128.4, 127.9, 127.6, 125.2, 20.4, 19.4, 18.2, 18.0, 5.2, 2.5 ppm.

(Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(CH_3CN)]$^+$[B(3,5-$C_6H_3(CF_3)_2)_4$]$^-$ (Ar =2,4-dimethylphenyl; An = acenaphthene)



Catalyst 1C. Using the general procedure (Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(Cl) (Ar =2,6-dimethylphenyl) (190 mg, 0.348 mmol, 1 equiv), NaBAr'F (325 mg, 0.367 mmol, 1.05 equiv), acetonitrile (5 ml) and dichloromethane (5 ml) were combined. The product was isolated as an orange-yellow solid (400 mg, 81% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.23 (s, 2H), 7.60 (s, 4H), 7.19-7.25 (m, 6H), 2.28 (s, 6H), 2.20 (s, 6H), 2.19 (s, 3H), 0.57 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) ppm 180.9, 173.2, 143.5, 143.0, 133.7, 129.6, 129.5, 128.8, 128.4, 128.2, 128.0, 119.6, 111.4, 22.9, 20.5, 19.5, 18.2, 18.1, 14.4, 6.87 ppm.

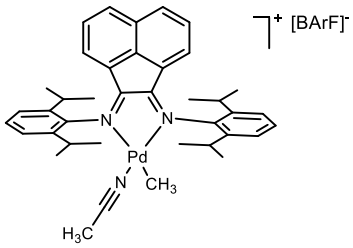
(Ar-N=C(Me)-C(Me)=N-Ar)Pd(Me)(CH_3CN)]$^+$[B(3,5-$C_6H_3(CF_3)_2)_4$]$^-$ (Ar =2,6-diisopropylphenyl)



Catalyst 2A. Using the general procedure (Ar-N=C(Me)-C(Me)=N-Ar)Pd(Me)(Cl) (Ar =2,6-diisopropylphenyl) (150 mg, 0.267 mmol, 1 equiv), NaBAr'$_4$ (250 mg, 0.282 mmol, 1.05 equiv), and acetonitrile (10 ml) were combined. The product was isolated as a yellow solid (350 mg, 91% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.41 – 7.32 (m, 6H), 2.89 (sep, *J* = 6.93 Hz, 2H), 2.85 (sep, *J* = 6.93 Hz, 2H),

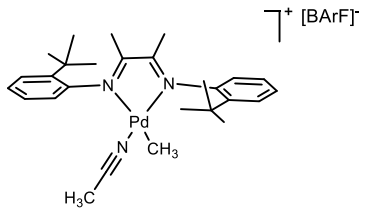
2.22 (s, 6H), 1.79 (s, 3H), 1.37 (d, *J* = 6.94 Hz, 6H), 1.32 (d, *J* = 6.94 Hz, 6H), 1.24 (d, *J* = 6.94 Hz, 6H), 1.20 (d, *J* = 6.94 Hz, 6H), 0.50 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 180.2, 172.5, 140.8, 140.7, 138.7, 138.0, 135.4, 129.5, 128.8, 127.9, 125.1, 124.8, 29.7, 29.4, 24.0, 23.9, 23.6, 23.2, 22.0, 20.4, 6.6, 3.2. This compound is known.[9-10]

(Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(CH_3CN)]$^+$[B(3,5-$C_6H_3(CF_3)_2)_4$]$^-$ (Ar =2,4-diisopropylphenyl; An = acenaphthene)



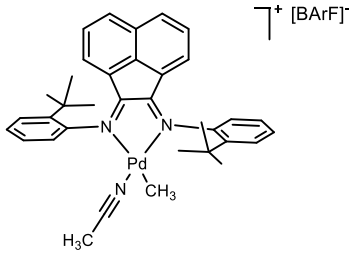
Catalyst 2C. Using the general procedure (Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(Cl) (Ar =2,6-diisopropylphenyl) (280 mg, 0.426 mmol, 1 equiv), NaBAr'F (400 mg, 0.451 mmol, 1.05 equiv), acetonitrile (6 ml) and dichloromethane (6 ml) were combined. The product was isolated as an orange-yellow solid (550 mg, 85% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.15 (dd, *J* = 8.5, 8.5 Hz, 2H), 7.42-7.58 (m, 8H), 6.95 (d, *J* = 7.1 Hz, 1H), 6.54 (d, *J* = 7.3 Hz, 1H), 3.18-3.32 (m, 4H), 1.92 (s, 3H), 1.43 (d, *J* = 6.9 Hz, 6H), 1.38 (d, *J* = 6.9 Hz, 6H), 1.07 (d, *J* = 6.9 Hz, 6H), 0.97 (d, *J* = 6.9 Hz, 6H), 0.84 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 176.8, 169.8, 146.4, 141.2, 140.5, 139.7, 138.6, 133.7, 133.0, 132.0, 129.7, 129.8, 126.8, 126.2, 125.8, 125.6, 121.9, 29.8, 29.6, 24.2, 23.9, 23.7, 23.3, 8.0, 2.8. This compound is known.[10]

(Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(CH_3CN)]$^+$[B(3,5-$C_6H_3(CF_3)_2)_4$]$^-$ (Ar =2-*tert*-butylphenyl)



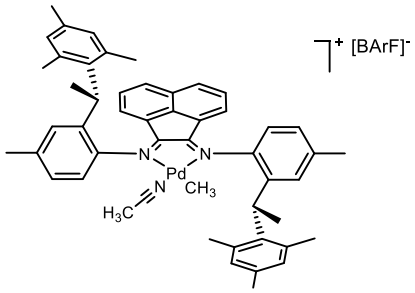
Catalyst 3A. To a flamed-dried round bottom flask equipped with a stirbar and argon balloon, was added chloro(1,5-cyclooctadiene)methylpalladium(II) (180mg, 0.679 mmol, 1.0 equiv) and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (602 mg, 0.679 mmol, 1.0 equiv). After cooling the flask in an acetonitrile/dry-ice bath (-40 °C), 25 mL of dichloromethane and 25 mL of acetonitrile were added slowly. The reaction was allowed to warm up to -20 °C, at which time stirring was stopped and the precipitate was allowed to settle. The reaction was then cannula filtered into another round bottom flask cooled in an ice-bath, and containing a suspension of *N*,*N*'-bis(2-(tert-butyl)phenyl)butane-2,3-diimine (237 mg, 0.680, 1.0 equiv) in 20 mL of acetonitrile. The reaction was stirred at room temperature overnight, and the solvents were removed under vacuum to give a yellow oil. The oil was diluted with 8 mL of dichloromethane and filtered into a stirring solution of pentanes. After allowing the product to settle, the solution was decanted and the precipitate washed with pentanes followed by removal of residual solvents in vacuo. The product was isolated as a yellow powder (750 mg, 80% yield). Two isomers were observed in the NMR in a ratio of 8.6:1. ^{1}H NMR (400 MHz, CD_2Cl_2): δ (major isomer) 7.54-7.62 (m, 2H), 7.26-7.42 (m, 4H), 6.65-6.75 (m, 2H), 2.24 (s, 3H), 2.21 (s, 3H), 1.76 (s, 3H), 1.48 (s, 9H), 1.46 (s, 9H), 0.59 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 180.3, 172.8, 145.3, 144.5, 140.7, 140.2, 130.0, 128.8, 128.2, 128.1, 123.1, 121.4, 121.1, 36.7, 36.2, 32.1, 31.4, 23.0, 21.3, 7.0, 2.4 ppm. This compound is known.[11]

(Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(CH_3CN)]$^+$[B(3,5-$C_6H_3(CF_3)_2)_4$]$^-$ (Ar =2 tertbutylphenyl; An = acenaphthene)



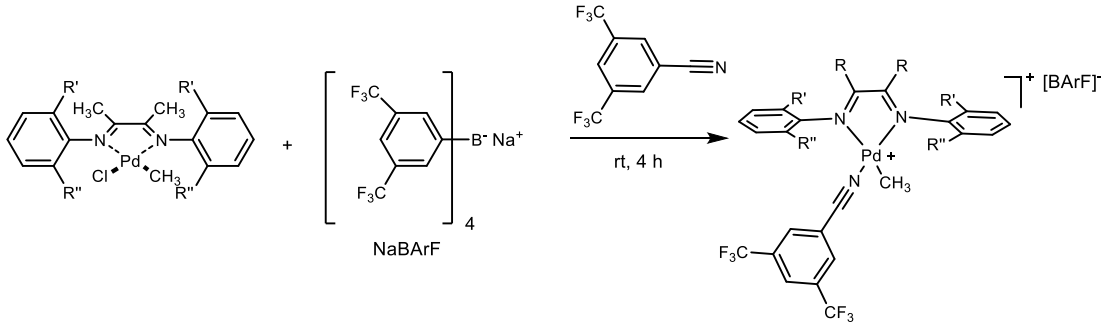
Catalyst 3C. Using a procedure similar to that describe above for the preparation of complex (Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(CH_3CN)]$^+$[B(3,5-$C_6H_3(CF_3)_2)_4$]$^-$ (Ar =2-*tert*-butylphenyl), (COD)PdMeCl (180 mg, 0.679 mmol, 1 equiv), NaBAr'$_4$ (602 mg, 0.679 mmol, 1 equiv), and *N*,*N*'-Bis(2-(tert-butyl)phenyl) acenaphthylene-1,2-diimine (302 mg, 0.679 mmol, 1 equiv) were combined. The product was isolated as an orange solid (790 mg, 79% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.12 (dd, *J* = 8.4, 8.4 Hz, 2H), 7.43-7.53 (m, 6H), 7.03-7.14 (m, 2H), 6.82 (d, *J* = 7.3 Hz, 1H), 6.42 (d, *J* = 7.3 Hz, 1H), 1.90 (s, 3H), 1.50 (s, 9H), 1.48 (s, 9H), 0.91 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 176.1, 169.1, 145.2, 143.9, 140.9, 140.7, 132.9, 132.2, 129.7, 128.2, 127.9, 127.0, 126.4, 126.0, 125.2, 122.9, 36.4, 35.9, 31.9, 31.9, 31.0, 7.5, 2.3 ppm.

(Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(CH_3CN)]$^+$[B(3,5-$C_6H_3(CF_3)_2)_4$]$^-$ (4-methyl-2-(sec-(2,4,6-trimethylphenethyl)phenyl; An = acenaphthene)



Catalyst 4C. Using the general procedure (Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(Cl) (4-methyl-2-(sec-(2,4,6-trimethylphenethyl)phenyl; An = acenaphthene) (450 mg, 0.556 mmol, 1 equiv), $NaBAr'_4$ (500 mg, 0.564 mmol, 1.0 equiv), acetonitrile (6 ml) and dichloromethane (9 ml) were combined. The product was isolated as an yellow solid (740 mg, 71% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.89-7.94 (m, 2H), 7.61 (d, *J* = 8.2 Hz, 2H), 7.29-7.38 (m, 4H), 7.06 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.3 Hz, 1H), 6.13 (s, 2H), 5.29 (s, 2H), 4.69-4.74 (m, 1H), 4.51 (q, *J* = 6.9 Hz, 1H), 3.09 (d, *J* = 11.4 Hz, 6H), 2.52 (d, *J* = 6.9 Hz, 6H), 1.91 (s, 3H), 1.53-1.68 (m, 12H), 0.97 (s, 3H), 0.93 (s, 3H), 0.69 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 176.2, 168.7, 145.4, 141.7, 141.3, 138.2, 137.9, 137.5, 137.4, 136.1, 135.9, 135.8, 135.4, 135.1, 134.6, 131.7, 131.0, 130.8, 130.5, 130.1, 129.6, 128.5, 128.1, 127.6, 127.6, 125.1, 125.1, 124.5, 124.2, 121.2, 120.5, 119.7, 36.9, 36.7, 22.7, 21.3, 21.1, 20.7, 19.1, 19.0, 16.2, 5.4, 2.3 ppm.

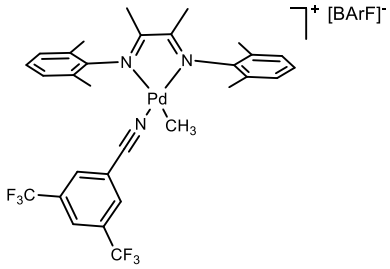
General Synthesis of cationic Pd(II) α-diimine complexes with benzonitrile ligand



A previously published procedure was modified and used.[9] At room temperature, dichloromethane and bis(trifluoromethyl)benzonitrile was added to a flamed-dried flask containing sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (NaBAr'F) and (Ar-N=C(Me)-C(Me)=N-Ar)Pd(Me)(Cl). As the reaction progressed, precipitation of sodium chloride (NaCl) was observed. After stirring for 4 h, NaCl was removed from the reaction mixture via filtration, and the solvent was evaporated. The solid was dissolved in a small

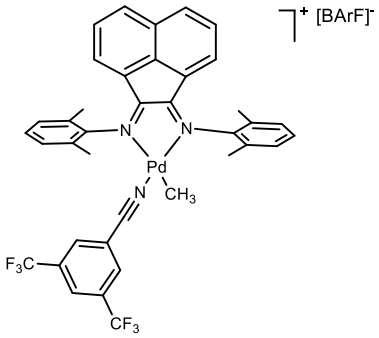
amount of dichloromethane and filtered again with a 0.45 µm PTFE syringe filter. The filtrate was added dropwise to pentane to precipitate the desired product. The resulting solid was filtered, washed with pentane, and dried *in vacuo* to give the desired product as a solid compound. All cationic α-diimine Pd(II) complexes contained the $[B(3,5\text{-}C_6H_3(CF_3)_2)_4]^-$ counterion. Spectral data was similar for each complex. ^{1}H NMR (400 MHz, CD_2Cl_2) 7.73 (s, 8H), 7.57 (s, 4H); ^{13}C NMR (100 MHz, CD_2Cl_2) ppm 162.3 (q, J_{CB} = 49.8 Hz, 4C), 135.4 (8C), 129.3 (q, J_{CF} = 30.3 Hz, 8C), 125.2 (q, J_{CF} = 272.7 Hz, 8C), 117.9 (4C). The NMR data for the BAr'$_4$ counterion matched those previously reported.[9]

(Ar-N=C(Me)-C(Me)=N-Ar)Pd(Me)(NCAr')]$^+$[B(3,5-C$_6$H$_3$(CF$_3$)$_2$)$_4$]$^-$ (Ar =2,6-dimethylphenyl; Ar' = 3,5-C$_6$H$_3$(CF$_3$)$_2$, An = acenaphthene)



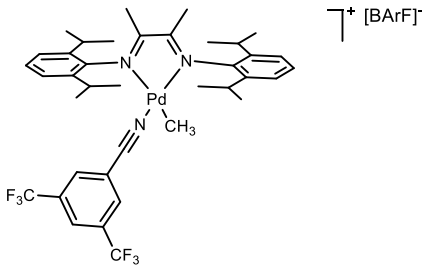
Catalyst 1B. Using the general procedure (Ar-N=C(Me)-C(Me)=N-Ar)Pd(Me)(Cl) (Ar =2,6-dimethylphenyl) (150 mg, 0.334 mmol, 1 equiv), NaBAr'F (310 mg, 0.350 mmol, 1.05 equiv), bis(trifluoromethyl)benzonitrile (200 mg, 0.836 mmol, 2.5 equiv) and dichloromethane (15 ml) were combined. The product was isolated as a yellow solid (400 mg, 79% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.14-7.22 (m, 6H), 2.23 (s, 6H), 2.17 (s, 6H), 2.16 (s, 3H), 2.14 (s, 3H), 0.38 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) ppm 180.3, 172.4, 162.3, 143.1, 135.4, 129.4, 129.2, 128.6, 128.4, 127.9, 127.6, 125.2, 20.4, 19.4, 18.2, 18.0, 5.2, 2.5 ppm.

(Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(NCAr')]$^{+}$[B(3,5-$C_6H_3(CF_3)_2)_4$]$^{-}$ (Ar =2,6-dimethylphenyl; Ar' = 3,5-$C_6H_3(CF_3)_2$, An = acenaphthene)



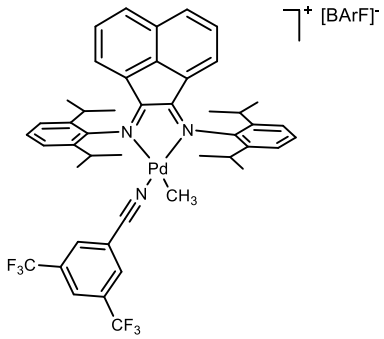
Catalyst 1D. Using the general procedure (Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(Cl) (Ar =2,6-dimethylphenyl) (190 mg, 0.348 mmol, 1 equiv), NaBAr'F (325 mg, 0.367 mmol, 1.05 equiv), bis(trifluoromethyl)benzonitrile (225 mg, 0.941 mmol, 2.5 equiv) and dichloromethane (15 ml) were combined. The product was isolated as an orange-yellow solid (400 mg, 81% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.23 (s, 2H), 7.60 (s, 4H), 7.19-7.25 (m, 6H), 2.28 (s, 6H), 2.20 (s, 6H), 2.19 (s, 3H), 0.57 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) ppm 180.9, 173.2, 143.5, 143.0, 133.7, 129.6, 129.5, 128.8, 128.4, 128.2, 128.0, 119.6, 111.4, 22.9, 20.5, 19.5, 18.2, 18.1, 14.4, 6.87 ppm. This compound is known.[7]

(Ar-N=C(Me)-C(Me)=N-Ar)Pd(Me)(NCAr')]$^{+}$[B(3,5-$C_6H_3(CF_3)_2)_4$]$^{-}$ (Ar =2,6-diisopropylphenyl; Ar' = 3,5-$C_6H_3(CF_3)_2$,)



Catalyst 2B. Using the general procedure (Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(Cl) (Ar =2,6-diisopropylphenyl) (280 mg, 0.426 mmol, 1 equiv), NaBAr'F (400 mg, 0.451 mmol, 1.05 equiv), bis(trifluoromethyl)benzonitrile (225 mg, 0.941 mmol, 2.5 equiv) and dichloromethane (6 ml) were combined. The product was isolated as an orange-yellow solid (550 mg, 85% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.15 (dd, *J* = 8.5, 8.5 Hz, 2H), 7.42-7.58 (m, 8H), 6.95 (d, *J* = 7.1 Hz, 1H), 6.54 (d, *J* = 7.3 Hz, 1H), 3.18-3.32 (m, 4H), 1.92 (s, 3H), 1.43 (d, *J* = 6.9 Hz, 6H), 1.38 (d, *J* = 6.9 Hz, 6H), 1.07 (d, *J* = 6.9 Hz, 6H), 0.97 (d, *J* = 6.9 Hz, 6H), 0.84 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 176.8, 169.8, 146.4, 141.2, 140.5, 139.7, 138.6, 133.7, 133.0, 132.0, 129.7, 129.8, 126.8, 126.2, 125.8, 125.6, 121.9, 29.8, 29.6, 24.2, 23.9, 23.7, 23.3, 8.0, 2.8 ppm. This compound is known.[9]

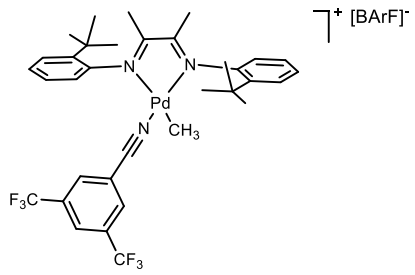
(Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(NCAr')]$^{+}$[B(3,5-$C_6H_3(CF_3)_2)_4$]$^{-}$ (Ar =2,4-diisopropylphenyl; Ar' = 3,5-$C_6H_3(CF_3)_2$; An = acenaphthene)



Catalyst 2D. Using the general procedure (Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(Cl) (Ar =2,6-diisopropylphenyl) (280 mg, 0.426 mmol, 1 equiv), NaBAr'F (400 mg, 0.451 mmol, 1.05 equiv), bis(trifluoromethyl)benzonitrile (280 mg, 1.17 mmol) and dichloromethane (15 ml) were combined. The product was isolated as a yellow solid (500 mg, 68% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.26 (s, 1H), 8.18 (t, J = 7.4 Hz, 2H), 7.49-7.61 (m, 12H), 6.98 (d, J = 7.3 Hz, 1H), 6.59 (d, J = 7.3 Hz, 1H), 3.36 (td, J = 13.4, 6.6 Hz, 1H), 3.23 (td, J = 13.5, 6.6 Hz, 1H), 1.41 (d, J = 6.6 Hz, 12H), 1.09 (d, J = 6.6 Hz, 6H), 1.01

(s, 3H), 0.99 (d, J = 6.9 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 177.0, 170.1, 146.3, 140.8, 139.2, 138.5, 133.9, 133.5, 133.02, 132.8, 131.5, 129.3, 126.5, 125.4, 125.1, 124.8, 124.7, 120.5, 120.3, 110.9, 29.3, 29.2, 23.7, 23.5, 23.16, 22.8, 8.8 ppm. This compound is known.[7]

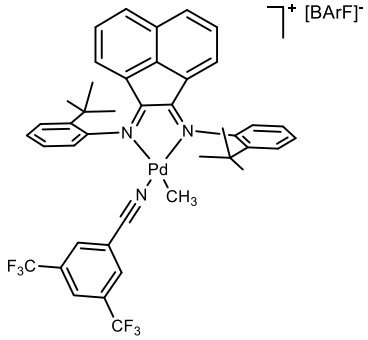
(Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(NCAr')]$^+$[B(3,5-$C_6H_3(CF_3)_2)_4$]$^-$ (Ar =2 tertbutylphenyl: Ar' = 3,5-$C_6H_3(CF_3)_2$)



Catalyst 3B. To a flamed-dried round bottom flask equipped with a stirbar and argon balloon, was added chloro(1,5-cyclooctadiene)methylpalladium(II) (180mg, 0.679 mmol, 1.0 equiv), sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (602 mg, 0.679 mmol, 1.0 equiv) and bis(trifluoromethyl)benzonitrile (170 mg, 0.711 mmol). After cooling the flask in an acetonitrile/dry-ice bath (-40 °C), 25 mL of dichloromethane was added slowly. The reaction was allowed to warm up to -20 °C, at which time stirring was stopped and the precipitate was allowed to settle. The reaction was then cannula filtered into another round bottom flask cooled in an ice-bath, and containing a suspension of *N*,*N*'-bis(2-(tert-butyl)phenyl)butane-2,3-diimine (237 mg, 0.680, 1.0 equiv) in 20 mL of diethyl ether. The reaction was stirred at room temperature overnight, and the solvents were removed under vacuum to give a yellow oil. The oil was diluted with 8 mL of dichloromethane and filtered into a stirring solution of pentanes. After allowing the product to settle, the solution was decanted, and the precipitate washed with pentanes followed by removal of residual solvents in vacuo. The product was isolated as a dark yellow powder (791 mg, 74% yield). Two isomers were observed in the NMR in a ratio of 6:1. ^{1}H NMR (400 MHz, CD_2Cl_2): δ (major

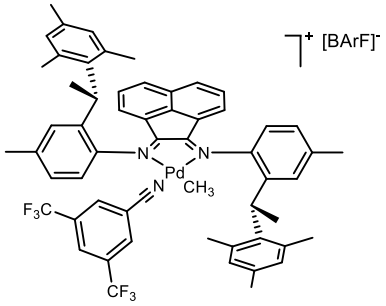
isomer) 8.20 (s, 1H), 7.59 (d, J = 11.2 Hz, 2H), 7.32-7.44 (m, 4H), 7.00 (d, J = 7.8 Hz, 1H), 6.80 (d, J = 6.9 Hz, 1H), 2.65 (s, 3H), 2.29 (s, 3H), 1.42-1.53 (m, 12H), 1.40 (m, 9H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 180.3, 172.8, 145.3, 144.5, 140.7, 140.2, 130.0, 128.8, 128.2, 128.1, 123.1, 121.4, 121.1, 36.7, 36.2, 32.1, 31.4, 23.0, 21.3, 7.0, 2.4 ppm.

(Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(NCAr')]$^+$[B(3,5-$C_6H_3(CF_3)_2)_4$]$^-$ (Ar =2 tertbutylphenyl; Ar' = 3,5-$C_6H_3(CF_3)_2$; An = acenaphthene)



Catalyst 3D. Using a procedure similar to that describe above for the preparation of complex (Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(CH_3CN)]$^+$[B(3,5-$C_6H_3(CF_3)_2)_4$]$^-$ (Ar =2-*tert*-butylphenyl), (COD)PdMeCl (180 mg, 0.679 mmol, 1 equiv), NaBAr'$_4$ (602 mg, 0.679 mmol, 1 equiv), bis(trifluoromethyl)benzonitrile (237 mg, 0.991 mmol, 1.5 equiv) and *N*,*N*'-Bis(2-(tert-butyl)phenyl) acenaphthylene-1,2-diimine (302 mg, 0.679 mmol, 1 equiv) were combined. The product was isolated as an orange-yellow solid (750 mg, 66% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.22 (s, 1H), 8.1 (m, 2H), 7.77-7.69 (m, 2H), 7.52-7.44 (m, 4H), 7.21 (d, J = 7.8 Hz, 1H), 7.17 (s, 1H), 7.04 (d, J = 7.8 Hz, 2H), 6.81 (d, J = 7.3 Hz, 1H), 6.66 (d, J = 11.9 Hz, 1H), 6.43 (d, J = 7.3 Hz, 1H), 1.53 (s, 9H), 1.40 (s, 9H) 1.33 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 176.1, 169.1, 145.2, 143.9, 140.9, 140.7, 132.9, 132.2, 129.7, 128.2, 127.9, 127.0, 126.4, 126.0, 125.2, 122.9, 36.4, 35.9, 31.9, 31.9, 31.0, 7.5, 2.3 ppm.

(Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(NCAr')]$^{+}$[B(3,5-$C_6H_3(CF_3)_2)_4]^-$ (4-methyl-2-(sec-(2,4,6-trimethylphenethyl)phenyl; Ar' = 3,5-$C_6H_3(CF_3)_2$; An = acenaphthene)



Catalyst 4D. Using the general procedure (Ar-N=C(An)-C(An)=N-Ar)Pd(Me)(Cl) (4-methyl-2-(sec-(2,4,6-trimethylphenethyl)phenyl; An = acenaphthene) (450 mg, 0.556 mmol, 1 equiv), $NaBAr'_4$ (500 mg, 0.564 mmol, 1.0 equiv), bis(trifluoromethyl)benzonitrile (160 mg, 0.669 mmol, 1.2 equiv) and dichloromethane (16 ml) were combined. The product was isolated as a yellow solid (650 mg, 62% yield). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.27 (s, 1H), 7.94 (t, *J* = 8.8 Hz, 2H), 7.74 (s, 2H), 7.65 (s, 1H), 7.60 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.9 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 7.1 Hz, 1H), 6.68-6.58 (1H), 6.15 (d, *J* = 7.3 Hz, 2H), 5.28 (s, 2H), 4.78 (q, *J* = 7.1 Hz, 1H), 4.54 (q, *J* = 7.0 Hz, 1H), 3.13 (s, 3H), 3.11 (s, 3H), 2.55 (s, 3H), 2.47 (s, 3H), 1.60-1.64 (m, 12H), 1.53 (s, 3H), 0.95 (s, 3H), 0.88 (d, *J* = 8.0 Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 176.6, 169.3, 145.7, 142.0, 141.2, 138.2, 137.9, 137.9, 137.5, 135.8, 135.5, 135.3, 134.3, 133.7, 133.5, 133.0, 132.0, 131.3, 130.9, 130.7, 130.6, 130.1, 129.8, 127.7, 125.3, 124.9, 124.3, 121.2, 120.5, 118.9, 111.2, 53.9, 53.7, 53.4, 53.1, 52.9, 36.8, 36.6, 22.8, 22.3, 21.2, 20.7, 19.1, 19.0, 16.3, 16.2, 13.8, 7.0 ppm.

Photopolymerization reaction setup

Reactions were carried out in flamed dried 4-dram vials equipped with magnetic stir bars and sealed with rubber septum stoppers. The reaction mixtures were irradiated with Sunnet RGB blue led light (λ_{max} = 460, 3600 lumens, 40W) purchased from Amazon. All reactions were hung from a glass crystallization dish from the same height and distance from the light source using aluminum wire. A stream of dry air and a temperature probe was used to keep the temperature of the reactor at 25 ℃. Reactions were covered in aluminum foil to prevent pre-exposure of light prior to reactions.

Figure S1. Polymerization setup.

General procedure for the photocontrolled polymerization using α-diimine Pd(II) catalyst. In a typical reaction, a quantitative amount of catalyst was measured out in a glove box to give molar ratios (included in the tables below) with respect to freshly distilled monomer. Once the catalyst was weighed out, it was transferred to a flame dried 4-dram vial which had been purged with nitrogen gas. The vials with the catalysts were then transferred to a glove bag under nitrogen air to conduct the polymerization. Freshly distilled DCM (6 mL) was used to fully dissolve the catalyst, then monomer was added to the reaction mixture and resealed with a rubber septum. All reaction vials were initially wrapped with aluminum foil to prevent pre-exposure to light. The reactions were then removed from the glove bag, and then wrapped with

aluminum wire and hung from a glass crystallization dish (Figure S6). Reactions conducted in the light had the aluminum covering removed and were then irradiated under blue LED light (λ_{max} = ~460 nm) for a period of 16 or 24 hours at room temperature. Reactions conducted in the dark had the aluminum covering kept on and were reacted for 16 or 24 hours at room temperature. After reactions were complete, GPC samples were prepared from aliquots of the reaction mixture to measure number-average molecular weight ($M_{n,\ GPC}$) and polydispersities (M_w/M_n). ^{1}H-NMR samples were prepared to measure monomer conversion.

Polymerization of methyl acrylate

Using the general procedure reported above, the homopolymerization of methyl acrylate in the light and in the dark was explored. Table S1 and S2 show the reaction conditions and results for MA polymerization with different catalyst. A typical ^{1}H NMR for poly(methyl acrylate) includes the following peaks: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.63 (br s, 3H), 2.27 (br s, 1H), 1.91 (br s, 1H), 1.65 (br s, 1H), 1.46 (br s, 1H).

Table S1. Methyl Acrylate (MA) polymerization in **light**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	25	6	1162:1	25	24	100	89	180	2.02	59	686
2	1b	2	29	6	1162:1	25	24	100	112	203	1.81	64	744
3	1c	2	27	6	1162:1	25	24	100	92	177	1.92	47	546
4	1d	2	31	6	1162:1	25	24	100	92	162	1.63	63	732
5	2a	2	27	6	1162:1	25	24	100	149	260	1.74	78	906
6	2b	2	31	6	1162:1	25	24	100	133	256	1.91	69	802
7	2c	2	29	6	1162:1	25	24	100	77	137	1.78	66	767
8	2d	2	33	6	1162:1	25	24	100	62	107	1.72	63	732
9	3a	2	26	6	1162:1	25	24	100	120	207	1.73	72	837
10	3b	2	30	6	1162:1	25	24	100	113	203	1.80	77	895
11	3c	2	28	6	1162:1	25	24	100	88	156	1.77	65	755
12	3d	2	32	6	1162:1	25	24	100	93	171	1.84	71	825
13	4c	2	32	6	1162:1	25	24	100	117	199	1.70	66	767
14	4d	2	35	6	1162:1	25	24	100	122	217	1.78	62	720

Table S2. Methyl Acrylate (MA) polymerization in **dark**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	25	6	1162:1	25	24	100	---	---	---	0	0
2	1b	2	29	6	1162:1	25	24	100	---	---	---	0	0
3	1c	2	27	6	1162:1	25	24	100	---	---	---	0	0
4	1d	2	31	6	1162:1	25	24	100	---	---	---	0	0
5	2a	2	27	6	1162:1	25	24	100	---	---	---	0	0
6	2b	2	31	6	1162:1	25	24	100	---	---	---	0	0
7	2c	2	29	6	1162:1	25	24	100	---	---	---	0	0
8	2d	2	33	6	1162:1	25	24	100	---	---	---	0	0
9	3a	2	26	6	1162:1	25	24	100	---	---	---	0	0
10	3b	2	30	6	1162:1	25	24	100	---	---	---	0	0
11	3c	2	28	6	1162:1	25	24	100	---	---	---	0	0
12	3d	2	32	6	1162:1	25	24	100	---	---	---	0	0
13	4c	2	32	6	1162:1	25	24	100	---	---	---	0	0
14	4d	2	35	6	1162:1	25	24	100	---	---	---	0	0

[a]Experimental conditions: solvent, dichloromethane (DCM); light source, blue LED light (λ_{max} = 460 nm). [b]Theoretical molecular weight was calculated based on 100% conversion of monomer from the following equation: $M_{n,th} = [M]_0/[Pd] \times MW^M$, where $[M]_0$, [Pd], and MW^M correspond to initial monomer concentration, initial Pd catalyst concentration, and molar mass of the monomer respectively. [c]Molecular weight and polydispersity index (M_w/M_n) were determined by GPC analysis with samples run in THF at 40°C calibrated to poly (methyl methacrylate) standards. [d]Monomer conversion was determined by using ^{1}H NMR spectroscopy.

Copolymerization of methyl acrylate and 2-hydroxyethyl acrylate

Using the above general procedure, the copolymerization of methyl acrylate with 2-hydroxyethyl acrylate (HEA) in the light and in the dark, was explored. Table S3 and S4 show the reaction conditions and results for MA-HEA polymerization with different Pd(II) catalyst. A typical ^{1}H NMR for poly(MA-co-HEA) includes the following peaks: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.63 (br s, 3H), 2.27 (br s, 1H), 1.91 (br s, 1H), 1.65 (br s, 1H), 1.46 (br s, 1H).

Table S3. Methyl Acrylate (MA) and 2-hydroxyethyl acrylate copolymerization in **light**

Entry	Catalyst	Monomer (mL) HEA	Monomer (mL) MA	Pd Cat. (mg)	DCM (mL)	[M]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,th}$[b] kg/mol	$M_{n,GPC}$[c] kg/mol	$M_{w,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α^d (%) HEA	α^d (%) MA	*DP*
1	1a	0.5	1.6	25	6	1175:1	25	16	100	34	64	1.90	35	7	136
2	1b	0.5	1.6	29	6	1175:1	25	16	100	125	267	2.13	43	12	214
3	1c	0.5	1.6	27	6	1175:1	25	16	100	146	262	1.80	36	1	85
4	1d	0.5	1.6	31	6	1175:1	25	16	100	30	74	2.46	14	7	99
5	2a	0.5	1.6	27	6	1175:1	25	16	100	118	236	2.00	94	78	959
6	2b	0.5	1.6	31	6	1175:1	25	16	100	340	671	1.97	92	73	902
7	2c	0.5	1.6	29	6	1175:1	25	16	100	150	316	2.11	81	61	764
8	2d	0.5	1.6	33	6	1175:1	25	16	100	203	402	1.98	65	37	500
9	3a	0.5	1.6	26	6	1175:1	25	16	100	239	485	2.03	80	59	742
10	3b	0.5	1.6	30	6	1175:1	25	16	100	190	355	1.87	74	56	700
11	3c	0.5	1.6	28	6	1175:1	25	16	100	168	295	1.75	70	43	569
12	3d	0.5	1.6	32	6	1175:1	25	16	100	370	653	1.76	37	9	171
13	4c	0.5	1.6	32	6	1175:1	25	16	100	290	640	2.20	94	66	841
14	4d	0.5	1.6	35	6	1175:1	25	16	100	323	719	2.22	84	61	770

Table S4. Methyl Acrylate (MA) and 2-hydroxyethyl acrylate copolymerization in **dark**

Entry	Catalyst	Monomer (mL) HEA	Monomer (mL) MA	Pd Cat. (mg)	DCM (mL)	[M]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,th}$[b] kg/mol	$M_{n,GPC}$[c] kg/mol	$M_{w,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α^d (%) HEA	α^d (%) MA	*DP*
1	1a	0.5	1.6	25	6	1175:1	25	16	100	---	---	---	0	0	0
2	1b	0.5	1.6	29	6	1175:1	25	16	100	---	---	---	0	0	0
3	1c	0.5	1.6	27	6	1175:1	25	16	100	---	---	---	0	0	0
4	1d	0.5	1.6	31	6	1175:1	25	16	100	---	---	---	0	0	0
5	2a	0.5	1.6	27	6	1175:1	25	16	100	---	---	---	0	0	0
6	2b	0.5	1.6	31	6	1175:1	25	16	100	---	---	---	0	0	0
7	2c	0.5	1.6	29	6	1175:1	25	16	100	---	---	---	0	0	0
8	2d	0.5	1.6	33	6	1175:1	25	16	100	---	---	---	0	0	0
9	3a	0.5	1.6	26	6	1175:1	25	16	100	---	---	---	0	0	0
10	3b	0.5	1.6	30	6	1175:1	25	16	100	---	---	---	0	0	0
11	3c	0.5	1.6	28	6	1175:1	25	16	100	---	---	---	0	0	0
12	3d	0.5	1.6	32	6	1175:1	25	16	100	---	---	---	0	0	0
13	4c	0.5	1.6	32	6	1175:1	25	16	100	---	---	---	0	0	0
14	4d	0.5	1.6	35	6	1175:1	25	16	100	---	---	---	0	0	0

[a]Experimental conditions: solvent, dichloromethane (DCM); light source, blue LED light (λ_{max} = 460 nm). [b]Theoretical molecular weight was calculated based on 100% conversion of monomer from the following equation: $M_{n,th} = [M]_0/[Pd] \times MW^M$, where $[M]_0$, [Pd], and MW^M correspond to initial monomer concentration, initial Pd catalyst concentration, and molar mass of the monomer respectively. [c]Molecular weight and polydispersity index (M_w/M_n) were determined by GPC analysis with samples run in THF at 40°C calibrated to poly (methyl methacrylate) standards. [d]Monomer conversion was determined by using ^{1}H NMR spectroscopy.

Polymerization of *tert*-Butyl Acrylate

Using the above general procedure, the homopolymerization of *tert*-butyl acrylate (tBA) in the light and in the dark was explored. Table S5 and S6 show the reaction conditions and results for *t*BA polymerization with different catalyst. A typical ^{1}H NMR for poly(*t*BA) includes the following peaks: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.30-2.10 (br s, 1H), 1.60-1.20 (br m, 11H).

Table S5. *tert*-Butyl Acrylate (*t*BA) polymerization in **light**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	23	6	780:1	25	16	100	44	182	4.16	26	203
2	1b	2	27	6	780:1	25	16	100	89	518	5.83	14	109
3	1c	2	25	6	780:1	25	16	100	90	270	2.98	30	234
4	1d	2	28	6	780:1	25	16	100	158	372	2.36	20	156
5	2a	2	25	6	780:1	25	16	100	332	746	2.25	86	671
6	2b	2	29	6	780:1	25	16	100	1224	2179	1.78	63	492
7	2c	2	27	6	780:1	25	16	100	138	297	2.16	49	382
8	2d	2	30	6	780:1	25	16	100	295	566	1.92	29	226
9	3a	2	24	6	780:1	25	16	100	206	437	2.12	73	570
10	3b	2	28	6	780:1	25	16	100	636	1333	2.10	60	468
11	3c	2	26	6	780:1	25	16	100	151	314	2.08	69	538
12	3d	2	29	6	780:1	25	16	100	169	395	2.34	24	187
13	4c	2	30	6	780:1	25	16	100	132	439	3.33	78	609
14	4d	2	33	6	780:1	25	16	100	465	889	1.91	75	585

Table S6. *tert*-Butyl Acrylate (*t*BA) polymerization in **dark**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	23	6	780:1	25	16	100	---	---	---	0	0
2	1b	2	27	6	780:1	25	16	100	---	---	---	0	0
3	1c	2	25	6	780:1	25	16	100	---	---	---	0	0
4	1d	2	28	6	780:1	25	16	100	---	---	---	0	0
5	2a	2	25	6	780:1	25	16	100	---	---	---	0	0
6	2b	2	29	6	780:1	25	16	100	---	---	---	0	0
7	2c	2	27	6	780:1	25	16	100	---	---	---	0	0
8	2d	2	30	6	780:1	25	16	100	---	---	---	0	0
9	3a	2	24	6	780:1	25	16	100	---	---	---	0	0
10	3b	2	28	6	780:1	25	16	100	---	---	---	0	0
11	3c	2	26	6	780:1	25	16	100	---	---	---	0	0
12	3d	2	29	6	780:1	25	16	100	---	---	---	0	0
13	4c	2	30	6	780:1	25	16	100	---	---	---	0	0
14	4d	2	33	6	780:1	25	16	100	---	---	---	0	0

[a]Experimental conditions: solvent, dichloromethane (DCM); light source, blue LED light (λ_{max} = 460 nm). [b]Theoretical molecular weight was calculated based on 100% conversion of monomer from the following equation: $M_{n,th} = [M]_0/[Pd] \times MW^M$, where $[M]_0$, [Pd], and MW^M correspond to initial monomer concentration, initial Pd catalyst concentration, and molar mass of the monomer respectively. [c]Molecular weight and polydispersity index (M_w/M_n) were determined by GPC analysis with samples run in THF at 40°C calibrated to poly (methyl methacrylate) standards. [d]Monomer conversion was determined by using ^{1}H NMR spectroscopy.

Polymerization of *n*-Butyl Acrylate

Using the above general procedure, the homopolymerization of *n*-butyl acrylate (tBA) in the light and in the dark was explored. Table S7 and S8 show the reaction conditions and results for *n*BA polymerization with different catalyst. A typical ^{1}H NMR for poly(*n*BA) includes the following peaks: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.10-3.90 (m, 1H), 2.30-2.20 (br s, 1H), 2.00-1.80 (br s, 1H), 1.70-1.50 (m, 3H), 1.45-1.30 (m, 3H), 1.00-0.85 (q, 3H).

Table S7. *n*-Butyl acrylate (nBA) polymerization in **light**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	24	6	780:1	25	16	100	222	387	1.74	37	288
2	1b	2	27	6	780:1	25	16	100	197	360	1.82	21	163
3	1c	2	25	6	780:1	25	16	100	261	464	1.77	43	335
4	1d	2	29	6	780:1	25	16	100	368	611	1.66	18	140
5	2a	2	26	6	780:1	25	16	100	359	608	1.69	47	366
6	2b	2	29	6	780:1	25	16	100	279	525	1.88	61	468
7	2c	2	27	6	780:1	25	16	100	251	443	1.76	43	335
8	2d	2	31	6	780:1	25	16	100	468	753	1.61	24	187
9	3a	2	25	6	780:1	25	16	100	120	198	1.65	63	491
10	3b	2	28	6	780:1	25	16	100	355	571	1.61	49	382
11	3c	2	26	6	780:1	25	16	100	273	464	1.70	56	436
12	3d	2	30	6	780:1	25	16	100	365	570	1.56	9	70
13	4c	2	30	6	780:1	25	16	100	211	422	1.99	64	499
14	4d	2	33	6	780:1	25	16	100	404	602	1.49	56	437

Table S8. *n*-Butyl acrylate (nBA) Polymerization in **dark**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	24	6	780:1	25	16	100	---	---	---	0	0
2	1b	2	27	6	780:1	25	16	100	---	---	---	0	0
3	1c	2	25	6	780:1	25	16	100	---	---	---	0	0
4	1d	2	29	6	780:1	25	16	100	---	---	---	0	0
5	2a	2	26	6	780:1	25	16	100	---	---	---	0	0
6	2b	2	29	6	780:1	25	16	100	---	---	---	0	0
7	2c	2	27	6	780:1	25	16	100	---	---	---	0	0
8	2d	2	31	6	780:1	25	16	100	---	---	---	0	0
9	3a	2	25	6	780:1	25	16	100	---	---	---	0	0
10	3b	2	28	6	780:1	25	16	100	---	---	---	0	0
11	3c	2	26	6	780:1	25	16	100	---	---	---	0	0
12	3d	2	30	6	780:1	25	16	100	---	---	---	0	0
13	4c	2	30	6	780:1	25	16	100	---	---	---	0	0
14	4d	2	33	6	780:1	25	16	100	---	---	---	0	0

[a]Experimental conditions: solvent, dichloromethane (DCM); light source, blue LED light (λ_{max} = 460 nm). [b]Theoretical molecular weight was calculated based on 100% conversion of monomer from the following equation: $M_{n,th} = [M]_0/[Pd] \times MW^M$, where $[M]_0$, [Pd], and MW^M correspond to initial monomer concentration, initial Pd catalyst concentration, and molar mass of the monomer respectively. [c]Molecular weight and polydispersity index (M_w/M_n) were determined by GPC analysis with samples run in THF at 40°C calibrated to poly (methyl methacrylate) standards. [d]Monomer conversion was determined by using ^{1}H NMR spectroscopy.

Polymerization of methyl methacrylate

Using the above general procedure, the homopolymerization of methyl methacrylate (MMA) in the light and in the dark was explored. Table S9 and S10 show the reaction conditions and results for MMA polymerization with different catalyst. A typical ^{1}H NMR for poly(MMA) includes the following peaks: ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.63 (br s, 3H), 2.27 (br s, 1H), 1.91 (br s, 1H), 1.65 (br s, 1H), 1.46 (br s, 1H).

Table S9. Methyl methacrylate (MMA) polymerization in **light**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	25	6	999:1	25	24	100	47	87	1.87	19	190
2	1b	2	29	6	999:1	25	24	100	99	191	1.93	19	190
3	1c	2	27	6	999:1	25	24	100	82	144	1.76	25	250
4	1d	2	30	6	999:1	25	24	100	75	131	1.75	19	190
5	2a	2	27	6	999:1	25	24	100	87	151	1.74	27	270
6	2b	2	30	6	999:1	25	24	100	96	177	1.84	23	230
7	2c	2	29	6	999:1	25	24	100	35	67	1.90	32	320
8	2d	2	32	6	999:1	25	24	100	44	78	1.77	20	200
9	3a	2	26	6	999:1	25	24	100	73	125	1.71	19	190
10	3b	2	29	6	999:1	25	24	100	89	160	1.80	22	220
11	3c	2	28	6	999:1	25	24	100	68	134	1.97	19	190
12	3d	2	31	6	999:1	25	24	100	74	142	1.92	21	210
13	4c	2	31	6	999:1	25	24	100	35	63	1.80	26	260
14	4d	2	34	6	999:1	25	24	100	70	127	1.81	24	240

Table S10. Methyl methacrylate (MMA) polymerization in **dark**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	25	6	999:1	25	24	100	---	---	---	0	0
2	1b	2	29	6	999:1	25	24	100	---	---	---	0	0
3	1c	2	27	6	999:1	25	24	100	---	---	---	0	0
4	1d	2	30	6	999:1	25	24	100	---	---	---	0	0
5	2a	2	27	6	999:1	25	24	100	---	---	---	0	0
6	2b	2	30	6	999:1	25	24	100	---	---	---	0	0
7	2c	2	29	6	999:1	25	24	100	---	---	---	0	0
8	2d	2	32	6	999:1	25	24	100	---	---	---	0	0
9	3a	2	26	6	999:1	25	24	100	---	---	---	0	0
10	3b	2	29	6	999:1	25	24	100	---	---	---	0	0
11	3c	2	28	6	999:1	25	24	100	---	---	---	0	0
12	3d	2	31	6	999:1	25	24	100	---	---	---	0	0
13	4c	2	31	6	999:1	25	24	100	---	---	---	0	0
14	4d	2	34	6	999:1	25	24	100	---	---	---	0	0

[a]Experimental conditions: solvent, dichloromethane (DCM); light source, blue LED light (λ_{max} = 460 nm). [b]Theoretical molecular weight was calculated based on 100% conversion of monomer from the following equation: $M_{n,th} = [M]_0/[Pd] \times MW^M$, where $[M]_0$, [Pd], and MW^M correspond to initial monomer concentration, initial Pd catalyst concentration, and molar mass of the monomer respectively. [c]Molecular weight and polydispersity index (M_w/M_n) were determined by GPC analysis with samples run in THF at 40°C calibrated to poly (methyl methacrylate) standards. [d]Monomer conversion was determined by using ^{1}H NMR spectroscopy.

Polymerization of glycidyl methacrylate

Using the above general procedure, the homopolymerization of glycidyl methacrylate (GMA) in the light and in the dark was explored. Table S11 and S12 show the reaction conditions and results for GMA polymerization with different catalyst. A typical ^{1}H NMR for poly(GMA) includes the following peaks: ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.36-4.19 (br s, 1H), 3.86-3.67 (br s, 1H), 3.23 (s, 1H), 2.84 (s, 1H), 2.63 (s, 1H), 1.80-2.00 (m, 2H), 0.70-1.20 (m, 3H).

Table S11. Glycidyl Methacrylate Polymerization in **light**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	28	6	704:1	25	24	100	66	116	1.74	57	401
2	1b	2	32	6	704:1	25	24	100	184	311	1.68	34	239
3	1c	2	30	6	704:1	25	24	100	77	152	1.97	57	401
4	1d	2	34	6	704:1	25	24	100	159	294	1.85	30	211
5	2a	2	30	6	704:1	25	24	100	35	63	1.83[e]	81	570
6	2b	2	34	6	704:1	25	24	100	106	326	3.07[e]	16	113
7	2c	2	32	6	704:1	25	24	100	79(4)	143(5)	1.82(1.15)[f]	55	387
8	2d	2	36	6	704:1	25	24	100	142(3)	227(6)	1.60(1.73)[f]	61	429
9	3a	2	29	6	704:1	25	24	100	46	85	1.84	67	472
10	3b	2	33	6	704:1	25	24	100	95	172	1.81	43	303
11	3c	2	31	6	704:1	25	24	100	77	149	1.93	58	408
12	3d	2	35	6	704:1	25	24	100	94	179	1.91	15	106
13	4c	2	35	6	704:1	25	24	100	38	58	1.52	74	521
14	4d	2	40	6	704:1	25	24	100	128	226	1.77	42	296

Table S12. Glycidyl Methacrylate Polymerization in **dark**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	28	6	704:1	25	24	100	---	---	---	0	0
2	1b	2	32	6	704:1	25	24	100	---	---	---	0	0
3	1c	2	30	6	704:1	25	24	100	---	---	---	0	0
4	1d	2	34	6	704:1	25	24	100	---	---	---	0	0
5	2a	2	30	6	704:1	25	24	100	---	---	---	0	0
6	2b	2	34	6	704:1	25	24	100	---	---	---	0	0
7	2c	2	32	6	704:1	25	24	100	---	---	---	0	0
8	2d	2	36	6	704:1	25	24	100	---	---	---	0	0
9	3a	2	29	6	704:1	25	24	100	---	---	---	0	0
10	3b	2	33	6	704:1	25	24	100	---	---	---	0	0
11	3c	2	31	6	704:1	25	24	100	---	---	---	0	0
12	3d	2	35	6	704:1	25	24	100	---	---	---	0	0
13	4c	2	35	6	704:1	25	24	100	---	---	---	0	0
14	4d	2	40	6	704:1	25	24	100	---	---	---	0	0

[a]Experimental conditions: solvent, dichloromethane (DCM); light source, blue LED light (λ_{max} = 460 nm). [b]Theoretical molecular weight was calculated based on 100% conversion of monomer from the following equation: $M_{n,th} = [M]_0/[Pd] \times MW^M$, where $[M]_0$, [Pd], and MW^M correspond to initial monomer concentration, initial Pd catalyst concentration, and molar mass of the monomer respectively. [c]Molecular weight and polydispersity index (M_w/M_n) were determined by GPC analysis with samples run in THF at 40°C calibrated to poly (methyl methacrylate) standards. [d]Monomer conversion was determined by using ^{1}H NMR spectroscopy. [e]Appearance of a bimodal GPC trace. [f]Appearance of two separate GPC traces.

Polymerization of dimethyl acrylamide

Using the above general procedure, the homopolymerization of dimethyl acrylamide (DMAA) in the light and in the dark was explored. Table S13 and S14 show the reaction conditions and results for DMAA polymerization with different catalyst. A typical ^{1}H NMR for poly(DMAA) includes the following peaks: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.08 (s, 3H), 3.00 (s, 3H), 2.47 (bs, 1H), 1.70 (bs, 1H), 1.27 (bs, 1H).

Table S13. Dimethyl Acrylamide (DMAA) Polymerization in **light**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	25	6	1009:1	25	24	100	251	414	1.65	29	293
2	1b	2	29	6	1009:1	25	24	100	258	435	1.68	32	323
3	1c	2	27	6	1009:1	25	24	100	0	0	0	0	0
4	1d	2	31	6	1009:1	25	24	100	0	0	0	0	0
5	2a	2	28	6	1009:1	25	24	100	497	1,041	2.10	44	444
6	2b	2	31	6	1009:1	25	24	100	593	1,228	2.07	33	333
7	2c	2	29	6	1009:1	25	24	100	0	0	0	0	0
8	2d	2	33	6	1009:1	25	24	100	0	0	0	0	0
9	3a	2	27	6	1009:1	25	24	100	512	1,035	2.02	8	81
10	3b	2	30	6	1009:1	25	24	100	668	1,346	2.02	12	121
11	3c	2	28	6	1009:1	25	24	100	254	457	1.80	72	726
12	3d	2	32	6	1009:1	25	24	100	328	584	1.78	5	50
13	4c	2	32	6	1009:1	25	24	100	581	1154	1.99	73	737
14	4d	2	36	6	1009:1	25	24	100	557	1,241	2.23	56	565

Table S14. Dimethyl Acrylamide (DMAA) Polymerization in **dark**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	25	6	1009:1	25	24	100	0	0	0	0	0
2	1b	2	29	6	1009:1	25	24	100	0	0	0	0	0
3	1c	2	27	6	1009:1	25	24	100	0	0	0	0	0
4	1d	2	31	6	1009:1	25	24	100	0	0	0	0	0
5	2a	2	28	6	1009:1	25	24	100	0	0	0	0	0
6	2b	2	31	6	1009:1	25	24	100	0	0	0	0	0
7	2c	2	29	6	1009:1	25	24	100	0	0	0	0	0
8	2d	2	33	6	1009:1	25	24	100	0	0	0	0	0
9	3a	2	27	6	1009:1	25	24	100	0	0	0	0	0
10	3b	2	30	6	1009:1	25	24	100	0	0	0	0	0
11	3c	2	28	6	1009:1	25	24	100	0	0	0	0	0
12	3d	2	32	6	1009:1	25	24	100	0	0	0	0	0
13	4c	2	32	6	1009:1	25	24	100	0	0	0	0	0
14	4d	2	36	6	1009:1	25	24	100	0	0	0	0	0

[a]Experimental conditions: solvent, dichloromethane (DCM); light source, blue LED light (λ_{max} = 460 nm). [b]Theoretical molecular weight was calculated based on 100% conversion of monomer from the following equation: $M_{n,th} = [M]_0/[Pd] \times MW^M$, where $[M]_0$, [Pd], and MW^M correspond to initial monomer concentration, initial Pd catalyst concentration, and molar mass of the monomer respectively. [c]Molecular weight and polydispersity index (M_w/M_n) were determined by GPC analysis with samples run in THF at 40°C calibrated to poly (methyl methacrylate) standards. [d]Monomer conversion was determined by using ^{1}H NMR spectroscopy.

Polymerization of N-isopropyl acrylamide

Using the above general procedure, the homopolymerization of n-isopropyl acrylamide (NIPAm) in the light and in the dark was explored. Table S15 and S16 show the reaction conditions and results for NIPAm polymerization with different catalyst. A typical ^{1}H NMR for poly(NIPAm) includes the following peaks: ^{1}H NMR (400 MHz, CD_3OD, ppm): δ 7.63 (bs, 1H), 3.96 (bs, 1H), 2.08 (bs, 1H), 1.58 (bs, 2H), 1.15 (s, 6H).

Table S15. N-isopropylacrylamide (NIPAm) Polymerization in **light**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	26	6	880:1	25	24	100	---	---	---	0	0
2	1b	2	30	6	880:1	25	24	100	---	---	---	0	0
3	1c	2	28	6	880:1	25	24	100	---	---	---	0	0
4	1d	2	32	6	880:1	25	24	100	---	---	---	0	0
5	2a	2	28	6	880:1	25	24	100	140	302	2.16	12	106
6	2b	2	32	6	880:1	25	24	100	338	727	2.15	4	35
7	2c	2	31	6	880:1	25	24	100	---	---	---	0	0
8	2d	2	35	6	880:1	25	24	100	---	---	---	0	0
9	3a	2	27	6	880:1	25	24	100	317	727	2.29	19	167
10	3b	2	32	6	880:1	25	24	100	349	666	1.91	3	26
11	3c	2	29	6	880:1	25	24	100	187	385	2.06	19	167
12	3d	2	33	6	880:1	25	24	100	216	280	1.29	3	26e
13	4c	2	33	6	880:1	25	24	100	374	718	1.92	30	264
14	4d	2	37	6	880:1	25	24	100	371	746	2.01	34	299

Table S16. N-isopropylacrylamide (NIPAm) Polymerization in **dark**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	26	6	880:1	25	24	100	---	---	---	0	0
2	1b	2	30	6	880:1	25	24	100	---	---	---	0	0
3	1c	2	28	6	880:1	25	24	100	---	---	---	0	0
4	1d	2	32	6	880:1	25	24	100	---	---	---	0	0
5	2a	2	28	6	880:1	25	24	100	---	---	---	0	0
6	2b	2	32	6	880:1	25	24	100	---	---	---	0	0
7	2c	2	31	6	880:1	25	24	100	---	---	---	0	0
8	2d	2	35	6	880:1	25	24	100	---	---	---	0	0
9	3a	2	27	6	880:1	25	24	100	---	---	---	0	0
10	3b	2	32	6	880:1	25	24	100	---	---	---	0	0
11	3c	2	29	6	880:1	25	24	100	---	---	---	0	0
12	3d	2	33	6	880:1	25	24	100	---	---	---	0	0
13	4c	2	33	6	880:1	25	24	100	---	---	---	0	0
14	4d	2	37	6	880:1	25	24	100	---	---	---	0	0

[a]Experimental conditions: solvent, dichloromethane (DCM); light source, blue LED light (λ_{max} = 460 nm). [b]Theoretical molecular weight was calculated based on 100% conversion of monomer from the following equation: $M_{n,th} = [M]_0/[Pd] \times MW^M$, where $[M]_0$, [Pd], and MW^M correspond to initial monomer concentration, initial Pd catalyst concentration, and molar mass of the monomer respectively. [c]Molecular weight and polydispersity index (M_w/M_n) were determined by GPC analysis with samples run in THF at 40°C calibrated to poly(methyl methacrylate) standards. [d]Monomer conversion was determined by using ^{1}H NMR spectroscopy.

Polymerization of vinyl acetate

Using the above general procedure, the homopolymerization of vinyl acetate (VAc) in the light and in the dark was explored. Table S17 and S18 show the reaction conditions and results for VAc polymerization with different catalyst. No polymer was formed in any of the reactions.

Table S17. Vinyl Acetate (VAc) Polymerization in **light**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	25	6	1162:1	25	16	100	---	---	---	0	0
2	1b	2	28	6	1162:1	25	16	100	---	---	---	0	0
3	1c	2	26	6	1162:1	25	16	100	---	---	---	0	0
4	1d	2	30	6	1162:1	25	16	100	---	---	---	0	0
5	2a	2	27	6	1162:1	25	16	100	---	---	---	0	0
6	2b	2	30	6	1162:1	25	16	100	---	---	---	0	0
7	2c	2	29	6	1162:1	25	16	100	---	---	---	0	0
8	2d	2	32	6	1162:1	25	16	100	---	---	---	0	0
9	3a	2	26	6	1162:1	25	16	100	---	---	---	0	0
10	3b	2	29	6	1162:1	25	16	100	---	---	---	0	0
11	3c	2	27	6	1162:1	25	16	100	---	---	---	0	0
12	3d	2	31	6	1162:1	25	16	100	---	---	---	0	0
13	4c	2	31	6	1162:1	25	16	100	---	---	---	0	0
14	4d	2	35	6	1162:1	25	16	100	---	---	---	0	0

Table S18. Vinyl Acetate (VAc) Polymerization in **dark**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	25	6	1162:1	25	16	100	---	---	---	0	0
2	1b	2	28	6	1162:1	25	16	100	---	---	---	0	0
3	1c	2	26	6	1162:1	25	16	100	---	---	---	0	0
4	1d	2	30	6	1162:1	25	16	100	---	---	---	0	0
5	2a	2	27	6	1162:1	25	16	100	---	---	---	0	0
6	2b	2	30	6	1162:1	25	16	100	---	---	---	0	0
7	2c	2	29	6	1162:1	25	16	100	---	---	---	0	0
8	2d	2	32	6	1162:1	25	16	100	---	---	---	0	0
9	3a	2	26	6	1162:1	25	16	100	---	---	---	0	0
10	3b	2	29	6	1162:1	25	16	100	---	---	---	0	0
11	3c	2	27	6	1162:1	25	16	100	---	---	---	0	0
12	3d	2	31	6	1162:1	25	16	100	---	---	---	0	0
13	4c	2	31	6	1162:1	25	16	100	---	---	---	0	0
14	4d	2	35	6	1162:1	25	16	100	---	---	---	0	0

[a]Experimental conditions: solvent, dichloromethane (DCM); light source, blue LED light (λ_{max} = 460 nm). [b]Theoretical molecular weight was calculated based on 100% conversion of monomer from the following equation: $M_{n,th} = [M]_0/[Pd] \times MW^M$, where $[M]_0$, [Pd], and MW^M correspond to initial monomer concentration, initial Pd catalyst concentration, and molar mass of the monomer respectively. [c]Molecular weight and polydispersity index (M_w/M_n) were determined by GPC analysis with samples run in THF at 40°C calibrated to poly (methyl methacrylate) standards. [d]Monomer conversion was determined by using ^{1}H NMR spectroscopy.

Polymerization of styrene

Using the above general procedure, the homopolymerization of styrene (St) in the light and in the dark was explored. Table S19 and S20 show the reaction conditions and results for St polymerization with different catalyst. A typical ^{1}H NMR for poly(St) includes the following peaks: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50-7.20 (m, 5H), 6.74 (dd, 1H), 5.76 (d, 1H), 5.25 (d, 1H)

Table S19. Styrene (St) Polymerization in **light**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	26	6	960:1	25	24	100	0	0	0	0	0
2	1b	2	29	6	960:1	25	24	100	47	93	1.99	11	106
3	1c	2	28	6	960:1	25	24	100	36	61	1.70	26	250
4	1d	2	31	6	960:1	25	24	100	32	57	1.76	40	384
5	2a	2	27	6	960:1	25	24	100	---	---	---	0	0
6	2b	2	31	6	960:1	25	24	100	---	---	---	0	0
7	2c	2	29	6	960:1	25	24	100	39	66	1.71	7	67
8	2d	2	31	6	960:1	25	24	100	38	75	1.98	24	230
9	3a	2	24	6	960:1	25	24	100	---	---	---	0	0
10	3b	2	32	6	960:1	25	24	100	---	---	---	0	0
11	3c	2	29	6	960:1	25	24	100	---	---	---	0	0
12	3d	2	33	6	960:1	25	24	100	---	---	---	0	0
13	4c	2	32	6	960:1	25	24	100	12	24	1.92	62	595
14	4d	2	33	6	960:1	25	24	100	35	67	1.91	15	144

Table S20. Styrene (St) Polymerization in **dark**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	*DP*
1	1a	2	26	6	960:1	25	24	100	---	---	---	0	0
2	1b	2	29	6	960:1	25	24	100	---	---	---	0	0
3	1c	2	28	6	960:1	25	24	100	25	46	1.80	83	797
4	1d	2	31	6	960:1	25	24	100	26	49	1.86	61	586
5	2a	2	27	6	960:1	25	24	100	---	---	---	0	0
6	2b	2	31	6	960:1	25	24	100	---	---	---	0	0
7	2c	2	29	6	960:1	25	24	100	---	---	---	0	0
8	2d	2	31	6	960:1	25	24	100	41	91	2.24	7	67
9	3a	2	24	6	960:1	25	24	100	---	---	---	0	0
10	3b	2	32	6	960:1	25	24	100	---	---	---	0	0
11	3c	2	29	6	960:1	25	24	100	---	---	---	0	0
12	3d	2	33	6	960:1	25	24	100	---	---	---	0	0
13	4c	2	32	6	960:1	25	24	100	12	23	1.92	67	643
14	4d	2	33	6	960:1	25	24	100	31	58	1.85	20	192

[a]Experimental conditions: solvent, dichloromethane (DCM); light source, blue LED light (λ_{max} = 460 nm). [b]Theoretical molecular weight was calculated based on 100% conversion of monomer from the following equation: $M_{n,th} = [M]_0/[Pd] \times MW^M$, where $[M]_0$, [Pd], and MW^M correspond to initial monomer concentration, initial Pd catalyst concentration, and molar mass of the monomer respectively. [c]Molecular weight and polydispersity index (M_w/M_n) were determined by GPC analysis with samples run in THF at 40°C calibrated to poly (methyl methacrylate) standards. [d]Monomer conversion was determined by using ^{1}H NMR spectroscopy.

Polymerization of isobutyl vinyl ether

Using the above general procedure, the homopolymerization of isobutyl vinyl ether (IBVE) in the light and in the dark was explored. Table S21 and S22 show the reaction conditions and results for VAc polymerization with different catalyst. A typical ^{1}H NMR for poly(VAc) includes the following peaks: ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.70-3.28 (bs, 1H), 3.28-2.90 (t, 2H), 1.93-1.67 (m, 2H), 1.67-1.27 (m, 1H), 0.87 (s, 6H).

Table S21. Isobutyl Vinyl Ether (IBVE) Polymerization in **light**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	DP
1	1a	2	26	6	999:1	25	16	100	15	32	2.14	99	989
2	1b	2	30	6	999:1	25	16	100	18	35	2.02	99	989
3	1c	2	28	6	999:1	25	16	100	12	23	1.92	99	989
4	1d	2	32	6	999:1	25	16	100	12	26	2.10	99	989
5	2a	2	28	6	999:1	25	16	100	11	25	2.27	99	989
6	2b	2	32	6	999:1	25	16	100	9	25	2.69	99	989
7	2c	2	31	6	999:1	25	16	100	12	27	2.35	99	989
8	2d	2	35	6	999:1	25	16	100	11	26	2.27	99	989
9	3a	2	27	6	999:1	25	16	100	12	31	2.65	99	989
10	3b	2	32	6	999:1	25	16	100	16	36	2.21	99	989
11	3c	2	29	6	999:1	25	16	100	13	33	2.55	99	989
12	3d	2	33	6	999:1	25	16	100	20	43	2.18	99	989
13	4c	2	33	6	999:1	25	16	100	9	14	1.64	99	989
14	4d	2	37	6	999:1	25	16	100	14	27	2.00	99	989

Table S22. Isobutyl Vinyl Ether (IBVE) Polymerization in **dark**

Entry	Catalyst	Monomer (mL)	Pd Cat. (mg)	DCM (mL)	[MA]:[Pd][a]	Temp (Celsius)	Time hours	$M_{n,\,th.}$[b] kg/mol	$M_{n,\,GPC}$[c] kg/mol	$M_{w,\,GPC}$[c] kg/mol	$Đ$ (M_w/M_n)	α[d] (%)	DP
1	1a	2	26	6	999:1	25	16	100	17	37	2.07	95	949
2	1b	2	30	6	999:1	25	16	100	14	33	2.32	98	979
3	1c	2	28	6	999:1	25	16	100	14	23	1.70	99	989
4	1d	2	32	6	999:1	25	16	100	14	25	1.87	99	989
5	2a	2	28	6	999:1	25	16	100	12	25	2.15	99	989
6	2b	2	32	6	999:1	25	16	100	11	27	2.34	99	989
7	2c	2	31	6	999:1	25	16	100	12	27	2.37	99	989
8	2d	2	35	6	999:1	25	16	100	12	26	2.13	99	989
9	3a	2	27	6	999:1	25	16	100	13	33	2.56	99	989
10	3b	2	32	6	999:1	25	16	100	14	32	2.21	99	989
11	3c	2	29	6	999:1	25	16	100	15	37	2.44	96	959
12	3d	2	33	6	999:1	25	16	100	19	37	1.93	90	899
13	4c	2	33	6	999:1	25	16	100	9	14	1.60	99	989
14	4d	2	37	6	999:1	25	16	100	14	27	1.97	99	989

[a]Experimental conditions: solvent, dichloromethane (DCM); light source, blue LED light (λ_{max} = 460 nm). [b]Theoretical molecular weight was calculated based on 100% conversion of monomer from the following equation: $M_{n,th} = [M]_0/[Pd] \times MW^M$, where $[M]_0$, [Pd], and MW^M correspond to initial monomer concentration, initial Pd catalyst concentration, and molar mass of the monomer respectively. [c]Molecular weight and polydispersity index (M_w/M_n) were determined by GPC analysis with samples run in THF at 40°C calibrated to poly (methyl methacrylate) standards. [d]Monomer conversion was determined by using ^{1}H NMR spectroscopy.

Optimized Coordinate

Level of theory: M062X
Basis Set: 6-31+G(d,p) for C H N F, Lanl2dz for Pd
Phase: Dichloromethane Solvent

1A

	X	Y	Z
N	1.70332	-0.78083	-0.72371
P	-0.02263	0.00017	0.21382
d			
C	1.81081	-0.61220	-1.99312
C	0.66952	0.09597	-2.69870
N	-0.27044	0.52366	-1.94616
C	-1.43812	1.18306	-2.42013
C	2.72314	-1.43660	0.03587
C	-2.50007	0.41779	-2.92226
C	-3.67961	1.08647	-3.26181
C	-3.79377	2.46571	-3.10195
C	-1.53271	2.56907	-2.22483
C	-2.72594	3.19854	-2.58542
C	-2.36859	-1.07556	-3.06728
H	-4.51494	0.51246	-3.65279
H	-4.71642	2.96867	-3.37321
C	-0.37336	3.33365	-1.64420
H	-2.81552	4.27305	-2.45224
C	3.71504	-0.65217	0.63672
C	4.65834	-1.30325	1.43514
C	4.60098	-2.68184	1.62930
C	2.62641	-2.82038	0.22540
C	3.59008	-3.43135	1.03121
C	3.73964	0.83864	0.42829
H	5.43965	-0.71755	1.91088
H	5.34048	-3.17179	2.25425
C	1.51231	-3.60207	-0.41840
H	3.53890	-4.50435	1.19186
C	0.46053	-0.63912	2.04615
N	-1.81556	0.88660	0.86342
H	-0.32077	-0.38176	2.76169
H	0.59155	-1.72378	1.98368
H	1.40800	-0.16102	2.31346
C	-2.82354	1.44365	0.87302
C	-4.09721	2.14908	0.86045
H	-3.98353	3.11183	1.36071
H	-4.39422	2.30664	-0.17922

H	-4.85057	1.55188	1.37573
C	0.71827	0.24438	-4.18799
C	2.98424	-1.05830	-2.80775
H	-0.11475	0.85291	-4.54076
H	1.65862	0.70978	-4.49524
H	0.66779	-0.73918	-4.66694
H	2.64942	-1.67920	-3.64337
H	3.48881	-0.18436	-3.23328
H	3.69723	-1.61914	-2.20513
H	-0.62880	4.38751	-1.52050
H	-0.08852	2.92708	-0.66608
H	0.51027	3.26849	-2.28789
H	-3.33318	-1.52351	-3.31167
H	-1.66524	-1.34060	-3.86435
H	-1.99842	-1.52942	-2.14120
H	4.53614	1.29662	1.01701
H	3.90453	1.09445	-0.62391
H	2.78450	1.29123	0.72316
H	1.53482	-4.64354	-0.09358
H	0.53503	-3.17683	-0.15883
H	1.59003	-3.58602	-1.51127

Point Group = C_1
NIm = 0
Total electronic and zero-point energies = -1184.37734 a.u.

1B

	X	Y	Z
N	1.83044	-0.49945	-0.12310
P	-0.02377	0.23542	0.57277
d			
C	1.86805	-0.95175	-1.32508
C	0.57439	-0.93408	-2.11879
N	-0.44508	-0.44534	-1.52227
C	-1.73142	-0.35277	-2.12726
C	2.99964	-0.46065	0.70121
C	-2.61482	-1.43489	-2.00825
C	-3.89698	-1.29084	-2.54527
C	-4.28561	-0.10458	-3.16504
C	-2.10384	0.86377	-2.71631
C	-3.39462	0.96395	-3.24328
C	-2.17795	-2.69785	-1.31448
H	-4.59668	-2.11844	-2.46569
H	-5.28741	-0.00833	-3.57360
C	-1.13048	2.01135	-2.76901
H	-3.70143	1.89619	-3.71035

C	3.80026	0.68746	0.66821
C	4.89453	0.73768	1.53479
C	5.16763	-0.31765	2.40274
C	3.23726	-1.53123	1.57155
C	4.34275	-1.44028	2.42082
C	3.47099	1.82043	-0.26683
H	5.53184	1.61721	1.52774
H	6.02058	-0.26185	3.07121
C	2.32317	-2.72719	1.57784
H	4.55049	-2.25871	3.10412
C	0.65375	0.73564	2.38407
N	-2.01337	0.86115	0.95002
H	-0.15019	1.16965	2.97914
H	1.03798	-0.17711	2.84892
H	1.46504	1.45468	2.23530
C	-3.10856	0.98135	0.60651
C	-4.45061	1.09880	0.11364
C	0.57743	-1.47286	-3.51645
C	3.10310	-1.47407	-1.98920
H	-0.39419	-1.32692	-3.98816
H	1.34502	-0.97509	-4.11551
H	0.81051	-2.54232	-3.50851
H	2.91729	-2.46613	-2.40922
H	3.37795	-0.81397	-2.81897
H	3.93749	-1.52854	-1.29148
H	-1.61395	2.90958	-3.15721
H	-0.73054	2.23168	-1.77172
H	-0.27485	1.78077	-3.41323
H	-3.01803	-3.38453	-1.19688
H	-1.39576	-3.21576	-1.88059
H	-1.76530	-2.47450	-0.32363
H	4.14040	2.66547	-0.09840
H	3.56664	1.51608	-1.31514
H	2.43790	2.15954	-0.12160
H	2.60107	-3.41987	2.37387
H	1.27988	-2.42351	1.72815
H	2.36637	-3.26854	0.62626
C	-4.84510	2.28199	-0.51723
C	-6.11890	2.34858	-1.06552
C	-6.98755	1.26179	-0.99889
C	-5.30545	-0.00315	0.19805
C	-6.57281	0.09530	-0.36281
H	-4.16400	3.12371	-0.58225
C	-6.54659	3.58773	-1.80662
H	-7.97986	1.32684	-1.43419

H	-4.97927	-0.91716	0.68342
C	-7.48204	-1.10499	-0.35055
F	-7.24597	-1.89992	0.70301
F	-8.77446	-0.75246	-0.31623
F	-7.30866	-1.85568	-1.45527
F	-7.86163	3.81396	-1.67886
F	-5.89952	4.67883	-1.37306
F	-6.29335	3.47765	-3.12458

Point Group = C_1
NIm = 0
Total electronic and zero-point energies = -2049.87861 a.u.

2A

	X	Y	Z
N	-0.31709	1.17325	1.59081
P	0.08316	-0.26118	0.03461
d			
C	-0.57150	2.37453	1.20606
C	-0.56656	2.66775	-0.28686
C	-0.87617	3.52302	2.11814
C	-0.86304	4.06848	-0.73885
N	-0.30561	1.68129	-1.05781
C	-0.25998	1.78142	-2.48510
C	-0.31200	0.85368	2.99592
C	0.97743	2.04519	-3.11389
C	1.00471	2.05537	-4.51390
C	-0.13143	1.80377	-5.27253
C	-1.42739	1.49919	-3.22916
C	-1.32888	1.52549	-4.62576
C	2.29716	2.34129	-2.40412
H	1.94672	2.26599	-5.01212
H	-0.08264	1.81774	-6.35646
C	-2.80440	1.18292	-2.64868
H	-2.22003	1.31986	-5.21187
C	-1.50828	0.40986	3.59938
C	-1.46352	0.09432	4.96279
C	-0.29354	0.19991	5.70275
C	0.89817	0.95658	3.71502
C	0.86970	0.62442	5.07492
C	-2.84909	0.17725	2.90062
H	-2.37526	-0.24416	5.44668
H	-0.28783	-0.04863	6.75889
C	2.26578	1.33924	3.14637
H	1.78994	0.70218	5.64685
H	-1.86158	3.93352	1.87730

H	-0.85866	3.22606	3.16523
H	-0.14699	4.32337	1.95917
H	-0.82623	4.13615	-1.82634
H	-1.85389	4.37999	-0.39672
H	-0.13896	4.76954	-0.31446
C	2.88733	0.20033	2.32848
C	2.36067	2.66974	2.38930
H	3.92039	0.45223	2.06797
H	2.88918	-0.73629	2.89383
H	2.34079	0.03151	1.39669
C	-3.43857	1.35206	2.11024
C	-2.84163	-1.10133	2.05355
H	-3.85389	-1.31410	1.69493
H	-2.19336	-0.99893	1.17908
H	-2.49104	-1.95862	2.63582
C	2.33181	3.70655	-1.70344
C	2.78106	1.24262	-1.45304
H	3.81536	1.44563	-1.15700
H	2.18242	1.21233	-0.53862
H	2.74359	0.25359	-1.91924
C	0.39191	-1.86327	1.18813
N	0.42397	-1.39340	-1.71687
H	-0.34457	-2.62044	0.90831
H	1.40496	-2.22287	0.99211
H	0.27482	-1.56859	2.23434
C	0.53057	-1.62516	-2.84034
C	0.65717	-1.88048	-4.26778
H	-0.07449	-2.63060	-4.57115
H	0.47052	-0.94398	-4.80070
H	1.66476	-2.23628	-4.48739
H	-3.41438	0.93079	-3.52290
C	-2.85173	-0.03655	-1.72326
C	-3.48768	2.38505	-1.98226
H	-3.89469	-0.30490	-1.52613
H	-2.35006	-0.90308	-2.16412
H	-2.38361	0.17485	-0.75804
H	-4.55408	2.17532	-1.85545
H	-3.08047	2.57665	-0.98599
H	-3.38468	3.29463	-2.58123
H	3.03300	2.39466	-3.21381
H	3.36799	3.97423	-1.47549
H	1.90212	4.49506	-2.32818
H	1.79266	3.68346	-0.75272
H	-3.55054	-0.00275	3.72262
H	-4.49174	1.14346	1.89860

H	-3.39063	2.28585	2.67737
H	-2.94582	1.49386	1.14421
H	3.41534	2.93986	2.27898
H	1.94522	2.60569	1.37963
H	1.86350	3.47953	2.93054
H	2.89820	1.46191	4.03244

Point Group = C_1
NIm = 0
Total electronic and zero-point energies = -1498.49388 a.u.

2C

	X	Y	Z
N	-3.39233	1.32803	0.00533
Pd	-5.11641	0.01007	0.00476
C	-2.27160	0.70233	0.00181
C	-2.24514	-0.82007	-0.00221
C	-0.86994	1.15407	0.00067
C	-0.83228	-1.22855	-0.00565
N	-3.35029	-1.45605	-0.00200
C	-3.41126	-2.88283	-0.00558
C	-3.35707	2.76517	0.00913
C	-3.48146	-3.56635	1.22868
C	-3.57582	-4.96280	1.18858
C	-3.61661	-5.66112	-0.01239
C	-3.48550	-3.55999	-1.24310
C	-3.57974	-4.95663	-1.20988
C	-3.42610	-2.92105	2.61242
H	-3.61975	-5.50683	2.12798
H	-3.69013	-6.74368	-0.01506
C	-3.43463	-2.90757	-2.62367
H	-3.62673	-5.49582	-2.15192
C	-3.32725	3.44688	-1.22596
C	-3.22091	4.84218	-1.18512
C	-3.15517	5.53677	0.01630
C	-3.32315	3.44019	1.24778
C	-3.21694	4.83569	1.21415
C	-3.43062	2.80827	-2.61159
H	-3.18693	5.38863	-2.12317
H	-3.06515	6.61808	0.01907
C	-3.42191	2.79406	2.63027
H	-3.17985	5.37706	2.15502
C	-4.81222	2.21073	2.90886
C	-2.32501	1.78290	2.99448
H	-4.88447	1.91637	3.96078
H	-5.59927	2.94062	2.69764

H	-5.00261	1.32056	2.30285
C	-2.33508	1.79892	-2.98485
C	-4.82193	2.22669	-2.88885
H	-4.89764	1.93806	-3.94211
H	-5.01053	1.33327	-2.28707
H	-5.60816	2.95555	-2.67112
C	-2.00871	-2.49281	3.01916
C	-4.42252	-1.78338	2.85700
H	-4.45860	-1.56038	3.92806
H	-4.12618	-0.86375	2.34547
H	-5.43199	-2.04751	2.52830
C	-6.51280	1.43026	0.01067
N	-6.54196	-1.55713	0.00279
H	-7.12004	1.29962	-0.88824
H	-7.11713	1.29498	0.91085
H	-6.01274	2.40275	0.01237
C	-6.86944	-2.66224	0.00035
C	-7.23352	-4.07156	-0.00230
H	-7.81862	-4.29733	-0.89489
H	-6.31177	-4.66169	-0.00474
H	-7.81641	-4.30127	0.89073
H	-3.72109	-3.71056	-3.31212
C	-4.43175	-1.76859	-2.85910
C	-2.01854	-2.47732	-3.03283
H	-4.47134	-1.54007	-3.92887
H	-5.44015	-2.03436	-2.52845
H	-4.13366	-0.85164	-2.34381
H	-2.00713	-2.22243	-4.09718
H	-1.68498	-1.59405	-2.48099
H	-1.29181	-3.27730	-2.86186
H	-3.71026	-3.72760	3.29765
H	-1.99383	-2.24346	4.08477
H	-1.28249	-3.29181	2.84164
H	-1.67704	-1.60664	2.47083
H	-3.30479	3.64913	-3.30247
H	-2.35569	1.63813	-4.06713
H	-1.33840	2.15775	-2.71329
H	-2.49376	0.82275	-2.51758
H	-2.34208	1.61623	4.07593
H	-2.48504	0.80925	2.52243
H	-1.32927	2.14338	2.72165
H	-3.29397	3.63119	3.32529
C	-0.24142	2.38280	0.00284
C	1.17753	2.41574	0.00056
C	1.94400	1.26658	-0.00373

C	-0.07967	-0.02725	-0.00375
C	1.32356	-0.01223	-0.00606
H	-0.79665	3.31483	0.00622
H	1.67046	3.38179	0.00228
C	1.97305	-1.27725	-0.01047
C	1.23606	-2.44574	-0.01231
C	-0.18338	-2.44344	-0.00993
H	3.02786	1.33557	-0.00536
H	3.05818	-1.31956	-0.01239
H	1.75316	-3.39913	-0.01568
H	-0.72828	-3.38260	-0.01149

Point Group = C_1

NIm = 0

Total electronic and zero-point energies = -1803.21199 a.u.

2D

	X	Y	Z
N	4.87202	1.27660	0.01762
P	6.56394	-0.00331	0.03562
d			
C	3.75024	0.65757	0.00523
C	3.72476	-0.86162	-0.00035
N	4.83076	-1.49643	0.01475
C	4.88175	-2.91879	-0.01296
C	4.90607	2.70492	0.01779
C	4.78829	-3.58079	-1.24746
C	4.88452	-4.97430	-1.24488
C	5.08056	-5.67853	-0.05701
C	5.11510	-3.59687	1.19156
C	5.20188	-4.99184	1.14854
C	4.59062	-2.80148	-2.52125
H	4.81247	-5.50878	-2.18864
H	5.15527	-6.76167	-0.07552
C	5.25864	-2.83031	2.47923
H	5.37467	-5.53775	2.07236
C	4.93994	3.37019	1.24958
C	4.99419	4.76585	1.22656
C	5.02249	5.45971	0.01826
C	4.95540	3.36993	-1.21374
C	5.00909	4.76555	-1.19022
C	4.90266	2.59280	2.53820
H	5.01668	5.30799	2.16750
H	5.06440	6.54403	0.01838
C	4.93523	2.59344	-2.50344
H	5.04314	5.30744	-2.13095

C	7.85619	1.51041	0.04837
N	8.00857	-1.56744	0.03471
H	8.87719	1.12809	0.05799
H	7.66307	2.10236	-0.85133
H	7.64529	2.10013	0.94551
C	8.20892	-2.70439	0.05296
C	8.38610	-4.12787	0.07305
C	2.31156	-1.26711	-0.01648
C	2.35524	1.11654	-0.00767
H	5.53494	-3.49838	3.29706
H	6.02568	-2.05169	2.38749
H	4.32375	-2.32762	2.74946
H	4.69732	-3.45351	-3.38989
H	3.59400	-2.34720	-2.56068
H	5.32123	-1.98870	-2.60122
H	5.05911	3.25466	3.39149
H	3.93823	2.08944	2.67036
H	5.67596	1.81559	2.55130
H	5.09652	3.25745	-3.35413
H	5.71302	1.82063	-2.51053
H	3.97498	2.08518	-2.64646
C	8.62631	-4.77399	1.28723
C	8.71962	-6.16122	1.29459
C	8.57083	-6.89603	0.12313
C	8.23416	-4.84433	-1.11872
C	8.32979	-6.22731	-1.07589
H	8.72831	-4.20287	2.20424
C	8.92142	-6.86884	2.60869
H	8.63972	-7.97948	0.14423
H	8.03134	-4.32635	-2.04930
C	8.12559	-7.04397	-2.32443
F	7.96373	-6.27611	-3.41002
F	9.16513	-7.86161	-2.55572
F	7.03428	-7.82395	-2.21918
F	9.43388	-8.09519	2.44505
F	9.74556	-6.18506	3.41697
F	7.75638	-7.01034	3.26886
C	1.56101	-0.06227	-0.01917
C	0.15958	-0.03827	-0.02808
C	-0.49619	-1.30090	-0.03467
C	1.65603	-2.47890	-0.01993
C	0.23544	-2.47233	-0.02957
H	-1.58144	-1.33932	-0.04338
H	2.19394	-3.42168	-0.01642
H	-0.28641	-3.42302	-0.03365

C	-0.45183	1.24604	-0.02736
C	0.32005	2.39166	-0.01749
C	1.73941	2.35074	-0.00676
H	-1.53512	1.32262	-0.03380
H	-0.16880	3.35971	-0.01691
H	2.30650	3.27586	0.00262

Point Group = C_1
NIm = 0
Total electronic and zero-point energies = -2354.59227 a.u.

3C

	X	Y	Z
N	-3.35416	1.32201	-0.16297
P	-5.08150	0.04066	0.00597
d			
C	-2.24379	0.69139	-0.04042
C	-2.23890	-0.82625	0.03997
C	-0.83855	1.12730	-0.01894
C	-0.83398	-1.25625	-0.02423
N	-3.34568	-1.43962	0.19893
C	-3.42534	-2.86422	0.17636
C	-3.34036	2.75791	-0.15931
C	-3.53464	-3.65703	1.34052
C	-3.66043	-5.03906	1.12294
C	-3.69772	-5.60961	-0.14848
C	-3.47948	-3.42530	-1.10480
C	-3.61179	-4.79820	-1.27561
C	-3.48452	-3.08997	2.77117
H	-3.73419	-5.70391	1.97396
H	-3.79852	-6.68517	-0.25013
H	-3.41737	-2.76172	-1.96260
H	-3.64656	-5.22102	-2.27405
C	-3.32716	3.54359	-1.33153
C	-3.29044	4.93227	-1.11991
C	-3.28538	5.51124	0.14731
C	-3.36108	3.32700	1.11742
C	-3.32933	4.70580	1.28064
C	-3.33327	2.97456	-2.76490
H	-3.26567	5.59686	-1.97346
H	-3.25604	6.59182	0.24079
H	-3.39546	2.66457	1.97778
H	-3.33802	5.13749	2.27570
C	-2.03980	2.19024	-3.05754
C	-4.54929	2.05937	-2.98601
H	-4.56114	1.72057	-4.02721

H	-4.52318	1.17154	-2.34995
H	-5.48300	2.59634	-2.78997
C	-2.10506	-2.46554	3.05437
C	-4.58249	-2.03398	2.98537
H	-4.54632	-1.68010	4.02098
H	-4.45888	-1.16605	2.33349
H	-5.57504	-2.46121	2.80723
C	-6.45326	1.47109	-0.16071
N	-6.53077	-1.49823	0.11024
H	-7.05455	1.25778	-1.04788
H	-7.06833	1.43077	0.74179
H	-5.94553	2.43415	-0.25136
C	-6.87796	-2.59620	0.15543
C	-7.27037	-3.99659	0.21965
H	-8.05341	-4.19533	-0.51319
H	-6.39080	-4.60862	-0.00115
H	-7.63394	-4.22602	1.22266
C	-3.70724	-4.19105	3.81950
H	-2.04588	-2.17977	4.10976
H	-1.30178	-3.18049	2.84791
H	-1.92611	-1.56627	2.46189
C	-3.42124	4.09817	-3.81043
H	-2.01213	1.92679	-4.12000
H	-1.15340	2.79205	-2.83182
H	-1.97800	1.25878	-2.49116
C	-0.19851	2.34910	-0.01749
C	1.22106	2.36547	-0.02935
C	1.97316	1.20696	-0.04596
C	-0.06405	-0.06429	-0.03286
C	1.33828	-0.06532	-0.04759
H	-0.74625	3.28560	-0.00824
H	1.72620	3.32521	-0.02559
C	1.97220	-1.33865	-0.05902
C	1.22078	-2.49752	-0.05060
C	-0.19917	-2.47887	-0.02900
H	3.05769	1.26361	-0.05471
H	3.05662	-1.39483	-0.07411
H	1.72615	-3.45708	-0.05895
H	-0.75362	-3.41186	-0.01652
H	-3.69796	-3.73489	4.81334
H	-4.67386	-4.68853	3.68956
H	-2.91650	-4.94727	3.79601
H	-3.46719	3.64591	-4.80495
H	-4.32014	4.70866	-3.67943
H	-2.54437	4.75257	-3.78607

Point Group = C_1
NIm = 0
Total electronic and zero-point energies = -1646.13556 a.u.

TD-DFT results

Level of theory: M06X

Basis set: 6-31+G(d,p) with C H N F elements, Lanl2dz with Pd.
Phase: Dichloromethane solvent
Computations searched for singlet excited-states with transitions between 360-380 nm. All transitions listed are for specific excited states. Transitions marked in red refer to HOMO to LUMO or HOMO-1 to LUMO transitions that are referenced and shown in the paper.

1A

Singlet-A 3.3896 eV 365.77 nm f=0.0083 <S**2>=0.000
97 ->105 -0.11836
103 ->104 0.65031

1B

Singlet-A 3.4155 eV 363.01 nm f=0.0033 <S**2>=0.000
141 ->155 -0.18976
145 ->155 0.10132
146 ->155 0.15011
147 ->152 0.10949
151 ->152 0.59643

2A

Singlet-A 3.3517 eV 369.91 nm f=0.0008 <S**2>=0.000
129 ->137 0.23546
135 ->136 0.61697

2C

Singlet-A 3.1953 eV 388.01 nm f=0.0002 <S**2>=0.000
157 ->160 -0.13682
157 ->161 -0.14254
158 ->160 0.63406

2D

Singlet-A 3.2113 eV 386.09 nm f=0.0068 <S**2>=0.000
173 -> 178 0.12251
174 -> 176 0.53404

175 -> 176 0.35476

3C

Excited State 3:
Singlet-A 3.2992 eV 375.80 nm f=0.0034 <S**2>=0.000
133 ->146 0.18798
134 ->146 -0.19197
135 ->146 -0.19867
136 ->146 0.12749
141 ->144 -0.11020
141 ->145 -0.10863
142 ->144 0.46544
143 ->144 0.23393

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