Electronic Supplementary Information

Selective Metalation of Phenol-Type Proligands for Preparative Organometallic Chemistry

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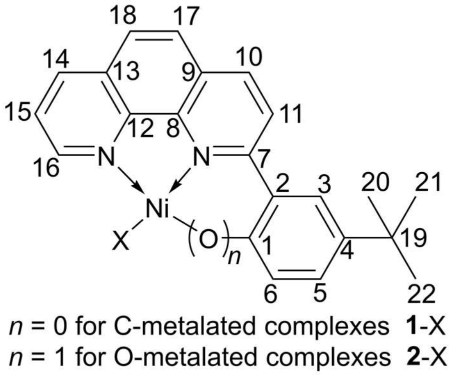
1 General Information

Manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of dry argon using standard Schlenk or glovebox techniques. SICAPENT (Merck Millipore), *n*Bu_4NCl, *n*BuLi (2.5 M in hexanes) and ethanethiol (Sigma Aldrich) and 4-*tert*-butylphenol (Acros Organics) were used as received. KBr (FT-IR grade; Sigma Aldrich) was dried under dynamic vacuum at 150 °C and stored in a glovebox. Sodium hydride (60% dispersion in mineral oil; Acros Organics) was washed with hexanes, dried under dynamic vacuum and stored in a glovebox. 1,10-Phenanthroline (anhydrous, 99+%; ChemPur) was treated at 80 °C under dynamic vacuum (~4 mbar) and stored in a glovebox. $Ni(cod)_2$ (abcr; cod = 1,5-cyclooctadiene) was dissolved in portions of toluene that contained additional cod (purified by percolation through activated neutral alumina), the solutions were filtered, and $Ni(cod)_2$ finally crystallized at -30 °C to afford dark yellow plate-shape crystals that were stored in a glove box at -35 °C. $NaN(SiMe_3)_2$ was prepared according to a literature procedure[1] from $HN(SiMe_3)_2$ (Alfa Aesar) and $NaNH_2$ (Sigma Aldrich) in hexanes. Pyridine was dried over and distilled from 3 Å MS and stored under argon. Trifluoromethanesulfonic acid anhydride (abcr) and pivaloyl chloride (Merck) were distilled and stored under argon and in a desiccator, respectively. 1,2-Difluorobenzene (abcr) was percolated through a column of activated neutral alumina under argon. Dichloromethane stabilized with ethanol (CHEMSOLUTE, Th. Geyer) was first distilled from P_2O_5, then from K_2CO_3 under argon. Tetrahydrofuran (THF), diethyl ether, toluene and pentane were predried over activated 3 Å molecular sieves (MS) and distilled from sodium benzophenone ketyl under argon. N,N-Dimethylformamide (DMF) was purified by percolation through a column of activated neutral alumina under argon directly into reaction vessels. THF-d_8 and C_6D_6 were dried over and distilled from NaK alloy, $CDCl_3$ was dried over and vacuum transferred from 3 Å MS. All solvents were stored over activated 3 Å MS or neutral/basic alumina (1,2-$C_6H_4F_2$, CH_2Cl_2) under argon. Molecular sieves and neutral/basic alumina were activated by heating under dynamic vacuum (10^{-3} mbar) at $T \leq 200$ °C for 24-48 h.

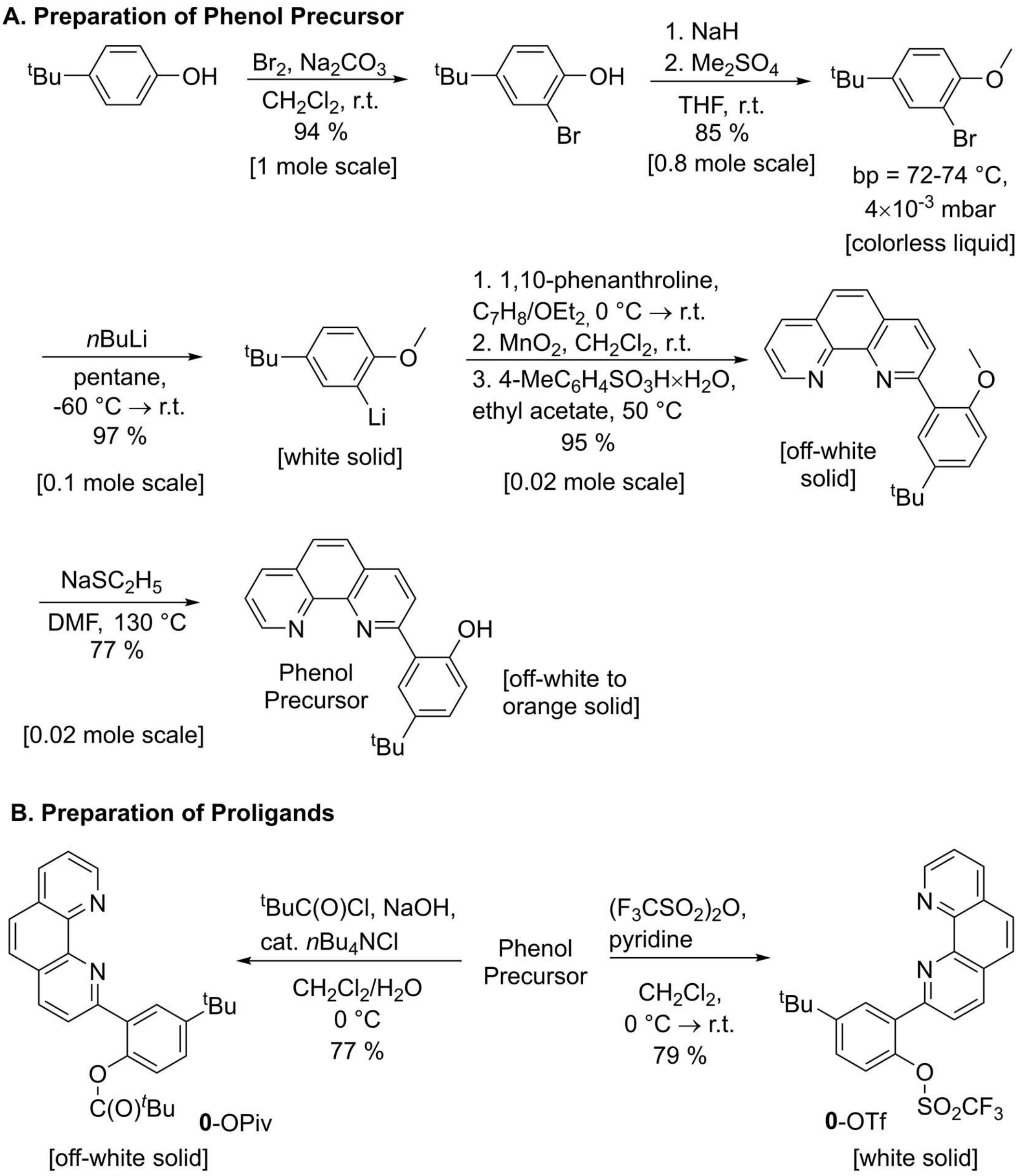
NMR data were acquired on Bruker Avance III HDX 600 (equipped with the BBO probe head CyroProbe Prodigy), AVII+500, AVII+400, and AVIII HD300 spectrometers. ^1H and $^{13}C\{^1H\}$-NMR chemical shifts are referenced to the residual proton and naturally abundant carbon resonances of the solvents: 7.16/128.06 (C_6D_6), 7.26/77.0 ($CDCl_3$). Scalar coupling constants J are given in Hz. In general, chemical shifts and integrals of co-crystallized solvents are excluded from reported NMR data for clarity. Electronic spectra were recorded in THF solutions at 26 °C on a PerkinElmer Lambda 1050 UV/vis/NIR photospectrometer in 3 mL quartz cuvettes sealed with Teflon stoppers. Electronic absorption data were processed using Spectragryph, Software for optical spectroscopy, Version 1.2.9 (Dr. Friedrich Menges, Oberstdorf, Germany). IR spectra from KBr pellets were recorded at r.t. on a Bruker Vertex 70 spectrometer, Bruker Opus 8.1 was used for data acquisition and processing, and Spectragryph for data analysis. X-Ray diffraction data were collected on a Bruker Smart APEXII diffractometer with graphite-monochromated MoKα radiation. The programs used were Bruker's APEX2 v2011.8-0, including SADABS for absorption correction and SAINT for structure solution, the WinGX suite of programs version 2013.3,[2] SHELXS and SHELXL for structure solution and refinement,[3] PLATON,[4] and ORTEP.[5] Crystals were, unless otherwise noted, coated in a perfluorinated polyether oil and mounted on a 100 μm MiTeGen MicroMounts™ loop that was placed on the goniometer head under a stream of dry nitrogen at 100 K. Microanalysis was done on a Vario Micro Cube system (Elementar Analysesysteme GmbH, Langenselbold, Germany). CCDC 1979878-1979882 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk). Deviating from IUPAC nomenclature, numeration is as shown in Scheme S1.



Scheme S1 General system of numeration used in this work.

1.1 Preparation of Proligands

The preparation of proligands is shown in Scheme S2. 2-Bromo-4-*tert*-butylanisol was prepared in two steps starting from 4-*tert*-butylphenol, adopting reported protocols.[6] ^{1}H NMR (300 MHz, CDCl$_3$, 25°C): δ=7.58 (d, J=2 Hz, 1H), 7.30 (dd, J=2, 9 Hz, 1H), 6.86 (d, J=9 Hz, 1H), 3.90 (s, 3H, -OCH_3), 1.32 ppm (s, 9H, C(CH_3)$_3$); ^{13}C NMR (75 MHz, CDCl$_3$, 25°C): δ=153.5, 145.0, 130.4, 125.2, 111.5, 111.2, 56.2 (-OCH$_3$), 34.1 (C(CH$_3$)$_3$), 31.4 ppm (C(CH$_3$)$_3$).



Scheme S2 Overview of Proligand Preparation.

(5-(*tert*-butyl)-2-methoxyphenyl)lithium. A solution of 23.1 g (18.5 mL, 95 mmol) of 2-Bromo-4-*tert*-butylanisol in pentane (100 mL) was cooled to -60 °C and 38 mL of *n*BuLi (2.5 M, 95 mmol) were added slowly by cannula. The product separates as a white solid while warming the reaction mixture to 0 °C within 3 h. The supernatant solution was removed by a cannula; the white residue was washed twice with pentane and finally dried under dynamic vacuum, yielding 15.67 g (92 mmol, 97 %) of a white powder. The compound was stored at r.t. in a glovebox and used without further purification.

2-(5-(*tert*-butyl)-2-methoxyphenyl)-1,10-phenanthroline. The following protocol has been adopted from literature procedures.[7] A yellow solution of 2.833 g (16.6 mmol) of (5-(*tert*-butyl)-2-methoxyphenyl)lithium in diethyl ether at 0 °C was transferred slowly by cannula into a pale red solution of 3 g (16.6 mmol) of 1,10-phenanthroline in toluene at 0 °C within 40 min, affording an initially dark green to black reaction mixture that turned red eventually. After stirring for 30 min at r.t., the reaction was quenched by addition of 90 mL of saturated NH_4Cl solution. The aqueous phase was extracted with CH_2Cl_2 and the organic phase washed with water, dried over Na_2SO_4, filtered and evaporated to dryness to afford a viscous orange liquid. The residue was dissolved in CH_2Cl_2 (125 mL), 7.94 g (91.3 mmol) of MnO_2 were added and the mixture was stirred overnight at r.t. The resulting mixture was filtered through a plug of silica gel 60 and the filtrate evaporated to dryness, affording a viscous yellow residue. To a yellow solution of the residue in ethyl acetate (125 mL) was added a catalytic amount of 4-toluenesulfonic acid hydrate, and the solution stirred at 50 °C for 18 h. In order to drive water elimination to completion, the formation of any precipitate must be avoided by adding further solvent; the reaction progress was monitored by ^1H NMR spectroscopy. The solution was washed with water, dried over Na_2SO_4, evaporated to dryness, and the solid residue was suspended in hexanes (100 mL), collected by filtration, and dried at 60 °C overnight under static vacuum ($\leq 10^{-2}$ mbar) over SICAPENT. Yield: 5.42 g (15.8 mmol, 95 %) of an off-white solid that was stored in a desiccator over SICAPENT. The compound was used without further purification but may be recrystallized from acetone, affording the hydrate whose NMR characteristics are reported in the following. ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ=9.18 (dd, J=2, 4 Hz, 1H), 8.21 (d, J=8 Hz, 2H), 8.21 (d, J=8 Hz, 2H), 8.05 (d, J=8 Hz, 1H), 7.96 (d, J=3 Hz, 1H, H-3), 7.80 (d, J=9 Hz, 1H), 7.75 (d, J=9 Hz, 1H), 7.59 (dd, J=4, 8 Hz, 1H), 7.43 (dd, J=3, 9 Hz, 1H, H-5), 6.97 (d, J=9 Hz, 1H, H-6), 3.82 (s, 3H, -OCH_3), 1.40 ppm (s, 9H, H20-22); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 25°C): δ=157.8, 155.1, 150.2, 146.5, 146.2, 143.7, 135.8, 135.1, 129.7, 128.9, 128.7, 127.3, 127.1, 126.4, 126.0, 125.5, 122.7, 111.2, 55.9 (-OCH_3), 34.3 (C19), 31.6 ppm (C20-C22).

4-(*tert*-butyl)-2-(1,10-phenanthrolin-2-yl)phenol. A suspension of 1.397 g (58.2 mmol) of NaH in DMF (300 mL) was cooled in an ice bath and 3.3 mL (44 mmol) of C_2H_5SH were added dropwise by syringe. Once H_2 formation had ceased, the solution was warmed to r.t. and 4.98 g (14.6 mmol) of 2-(5-(*tert*-butyl)-2-methoxyphenyl)-1,10-phenanthroline were added as solid. The resulting suspension was stirred at 130 °C for 2.5 h to afford a clear, bright yellow solution; reaction progress was monitored by ^1H NMR spectroscopy. The reaction was quenched by addition of saturated NH_4Cl solution (50 mL) and volatiles were removed under dynamic vacuum (~4 mbar) into a round bottom Schlenk flask immersed in liquid N_2. The viscous residue was taken up in CH_2Cl_2 and water, the organic phase was separated, washed with water and finally treated with 6 M HCl to precipitate the product as the hydrochloride salt. The separating orange solid was collected by filtration, washed with CH_2Cl_2, and finally dissolved in CH_2Cl_2 by addition of a diluted NaOH solution. The organic phase was washed with a saturated NaCl solution, dried over Na_2SO_4, filtered, evaporated to dryness, and the residual solid washed with hexanes, collected by filtration, and finally dried under static vacuum (< 10^{-2} mbar) over SICAPENT overnight at r.t. Yield: 3.68 g (11.2 mmol, 77 %) of an off-white to orange solid. The product was used without further purification but can be recrystallized from ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C): δ=9.16 (dd, *J*=2, 4 Hz, 1H), 8.27 (d, *J*=9 Hz, 1H), 8.19 (d, *J*=9 Hz, 2H), 8.18 (dd, *J*=2, 8 Hz, 2H), 7.96 (d, *J*=2 Hz, 1H, H-3), 7.71 (m, 2H), 7.59 (dd, *J*=4, 8 Hz, 1H), 7.45 (dd, *J*=2, 9 Hz, 1H, H-5), 7.14 (d, *J*=9 Hz, 1H, H-6), 1.41 ppm (s, 9H, H20-22); the phenol proton was not detected, likely owing to zwitterion formation through proton transfer to the phenanthroline moiety. $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$, 25°C): δ=159.4, 157.5, 150.6, 144.7, 142.7, 140.6, 137.1, 135.7, 129.5, 128.8, 126.2, 126.1, 125.6, 123.2, 122.5, 118.7, 118.2, 117.8, 34.2 (C19), 31.6 ppm (C20-C22).

Proligand 0-OPiv. 0.5 g (1.5 mmol) of 4-(*tert*-butyl)-2-(1,10-phenanthrolin-2-yl)phenol were mixed with 2 mL of a 2.5 M NaOH solution (5 mmol) and cooled in an ice bath. An ice cold solution of 0.18 mL (1.5 mmol) of pivaloyl chloride and 42 mg (0.15 mmol) nBu$_4$NCl in 2 mL of CH_2Cl_2 was added and the reaction mixture stirred vigorously for 20 min. The reaction mixture was diluted with water and the aqueous phase extracted with diethyl ether (3x 10 mL). The combined organic phase was washed with saturated NaCl solution, dried over Na_2SO_4, filtered, evaporated to dryness, and the solid residue washed with ice cold ethyl acetate and finally dried at 60 °C under vacuum (< 10^{-2} mbar) over SICAPENT overnight. Yield: 0.48 g (1.16 mmol, 77 %) of proligand **0**-OPiv as an off-white powder that was stored in a glovebox and used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$, 25°C): δ=9.19 (dd, *J*=2, 4 Hz, 1H), 8.25 (d, *J* =8 Hz, 1H), 8.24 (dd, *J* =2, 8 Hz, 1H), 7.80 (m, 2H), 7.77 (d, *J*=8 Hz, 1H), 7.77 (d, *J*=2 Hz, 1H, H-3), 7.61 (dd, *J*=4, 8 Hz, 1H), 7.46 (dd, *J*=3, 9 Hz, 1H, H-5), 7.09 (d, *J* = 8 Hz, 1H, H-6), 1.37 (s, 9H, C(C*H*$_3$)$_3$), 1.06 ppm (s, 9H, C(C*H*$_3$)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, 25°C): δ=176.9, 157.1, 150.3, 148.6, 146.5, 146.3, 146, 135.8, 135.7, 133.6, 128.8, 128.2, 127.3, 126.8, 126.4, 126.3, 124.3, 122.8, 122.1, 38.9 (*C*(CH$_3$)$_3$), 34.6 (*C*(CH$_3$)$_3$), 31.4 (C(*C*H$_3$)$_3$), 26.9 ppm (C(*C*H$_3$)$_3$). IR (ATR): $\tilde{\upsilon}$=1751 (s) cm^{-1} (C=O); elemental analysis calcd for $C_{27}H_{28}N_2O_2$: C 78.61, H 6.84, N 6.79 found: C 77.78, H 6.76, N 6.64.

Proligand 0-OTf. 1.75 g (5.33 mmol) of 4-(*tert*-butyl)-2-(1,10-phenanthrolin-2-yl)phenol and 0.86 mL (10.7 mmol) of pyridine were dissolved in 60 mL of CH_2Cl_2 and 1.1 mL (6.4 mmol) of trifluoromethanesulfonic acid anhydride added dropwise by syringe. The initially yellow solution gradually turned orange while stirring at r.t. overnight. The organic phase was washed with diluted Na_2CO_3 solution and water, dried over Na_2SO_4, filtered and evaporated to dryness, affording a pale yellow solid that was extracted with methanol, collected by filtration, and finally dried under vacuum over SICAPENT at 100 °C. Yield: 2.15 g (4.67 mmol, 79 %) of proligand **0**-OTf as a white powder that was stored in a glovebox and used without further purification. ^1H NMR (400 MHz, $CDCl_3$, 25°C): δ=9.21 (dd, J=2, 4 Hz, 1H), 8.34 (d, J=8 Hz, 1H), 8.25 (dd, J=2, 8 Hz, 1H), 7.97 (d, J=3 Hz, 1H), 7.91 (d, J=8 Hz, 1H), 7.83 (m, 2H), 7.63 (dd, J = 4, 8 Hz, 1H), 7.53 (dd, J = 3, 9 Hz, 1H), 7.36 (d, J = 9 Hz, 1H), 1.40 ppm (s, 9H, H-20-22); ^{13}C NMR (101 MHz, $CDCl_3$, 25°C): δ=154.7, 151.8, 150.5, 146.4, 146.3, 145.1, 136.3, 135.9, 134, 129.7, 129, 127.7, 127.6, 127.1, 126.2, 124.2, 123.1, 121.5, 118.3 (q, J_{CF}= 312 Hz, -$SO_2\mathit{C}F_3$), 34.9 (C19), 31.3 ppm (C20-22); ^{19}F NMR (376 MHz, $CDCl_3$, 25°C): δ=-73.9 ppm; IR (ATR): $\tilde{\upsilon}$=1405 (s), 1217 (s), 1132 (s), 856 (vs) cm^{-1}; elemental analysis calcd for $C_{23}H_{19}F_3N_2O_3S$: C 59.99, H 4.16, N 6.08, S 6.96 found: C 59.77, H 4.47, N 6.02, S 8.31; deviations of H and S values have been found for different samples and result from co-desorption of H_2O and SO_2 from device columns.

1.2 Preparation of Coordination Compounds

1-Tf and 2-(μ-Tf). 180 mg (0.65 mmol) of Ni(cod)$_2$ in THF (7 g) were combined with 301 mg (0.65 mmol) of **0**-OTf dissolved in THF (7 g), affording a dark green homogeneous solution within minutes. The solution color changed gradually to dark red within 1.5 h at r.t. and fine orange needles separated noticeably. The solvent was reduced to half volume after 4 h at r.t. and the reaction mixture stored at -30 °C overnight. An orange crystalline material was separated from a dark yellow-green supernatant solution by cannula filtration, washed with diethyl ether and dried under dynamic vacuum. Yield: 65 mg (0.13 mmol, 20 %) of **1**-Tf as a voluminous, bright orange crystalline solid. Storing the combined filtrates at 4 °C overnight afforded 115 mg (0,20 mmol) of **2**-(μ-Tf) as light green needles contaminated by individual orange crystals of **1**-Tf. Slow vapor diffusion of pentane (25 mL) into the concentrated filtrate (5 mL) afforded a pure batch of light green **2**-(μ-Tf): 146 mg (0.25 mmol). Total yield: 261 mg (0.45 mmol, 69 %) of **2**-(μ-Tf).

Analysis data for **1**-Tf: ^1H NMR (600 MHz, THF-d_8, 25 °C): δ=8.75 (s, 1H, H-16), 8.50 (d, J=8 Hz, 1H, H-14), 8.38 (d, J=8 Hz, 1H, H-10), 7.85 (m, 4H, H-11/-15/-17/-18), 7.49 (br s, 1H, H-3), 7.19 (br d, J=5 Hz, 1H, H-5 or H-6), 6.96 (br d, J=6 Hz, 1H, H-6 or H-5), 1.36 ppm (s, 9H, H-20-22); ^{13}C NMR (151 MHz, THF-d_8, 25 °C): δ=164.9 (C7), 151.4 (C16), 149.4 (C4), 147.9, 146.7 (C8), 145.8 (C12), 145.2, 138.7 (C14), 138.0 (C10), 137.3 (C5 or C6), 129.9, 128.1 (C6 or C5), 126.97, 126.92, 126.18 (C18), 121.1 (C3), 119.1, 35.1 (C19), 31.7 ppm (C20-22); two ^{13}C resonances have not been detected, including κ-O-CF$_3$SO$_2^-$; ^{19}F NMR (565 MHz, THF-d_8, 25 °C): δ=-86.8 ppm (br s, κ-O-CF_3SO$_2^-$); elemental analysis calcd for $C_{23}H_{19}F_3N_2NiO_2S$: C 54.90, H 3.81, N 5.57, S 6.37 found: C 54.72, H 3.87, N 6.02, S 6.34; IR (KBr): $\upsilon^{\sim}$=1158 and 1147 (vs, κ-O-CF_3SO$_2^-$), 960 cm^{-1} (vs); UV/Vis (THF): λ_{max} (ε)=305 (15900), 343 (shoulder, 12000), 358 (18000), 406 (5000), 476 (2300), 518 nm (shoulder, 900 mol^{-1}dm^{3}cm^{-1}); unit cell parameters: a=6.9629(8) Å, b=27.163(3) Å, c=11.1046(13) Å, α=90°, β=96.720(7)°, γ=90°, V=2085.8(4) Å^3, Z=4, P 21/n, CCDC deposition number 1979878.

Analysis data for **2**-(μ-Tf): elemental analysis calcd for $C_{54}H_{54}F_6N_4Ni_2O_9S_2$: C 54.12, H 4.54, N 4.67, S 5.35 found: C 54.28, H 4.47, N 4.94, S 5.50; IR (KBr): $\upsilon^{\sim}$=1299, 1278 and 1262 (vs, $CF_3SO_3^-$), 1158 and 1147 (vs, μ-O,O'-$CF_3SO_2^-$) cm^{-1}; unit cell parameters: a=12.8801(10) Å, b=14.0913(11) Å, c=17.4958(13) Å, α=81.586(2)°, β=77.019(3)°, γ=84.657(3)°, V=3055.0(4) Å^3, Z=2, P-1, CCDC deposition number 1979880.

1-N(SiMe$_3$)$_2$. 50 mg (99 µmol) of **1**-Tf and 19 mg (98 µmol) of NaN(SiMe$_3$)$_2$ were weighted out into a 25 mL Schlenk flask and dissolved in diethyl ether (10 mL) to afford a dark red solution. After stirring for additional 50 min, the solvent was removed and the dark red residue extracted with hexanes (5x 20 mL). The combined filtrates were concentrated under vacuum until dark red microcrystals formed and stored at -30 °C overnight. A crystalline solid was collected by filtration and dried under dynamic vacuum. Yield: 29 mg (55 µmol, 56 %) of **1**-N(SiMe$_3$)$_2$ as a dark red microcrystalline material. ^{1}H NMR (500 MHz, C_6D_6, 26°C): δ=8.94 (dd, J=1, 5 Hz, 1H, H-16), 8.07 (d, J=8 Hz, 1H, H-6), 7.44-7.41 (m, 2H, H-3/-5), 7.21 (m, 2H, H-10/-14), 6.96 (d, J=8 Hz, 1H, H-11), 6.89 (d, J=9 Hz, 1H, H-18), 6.80 (dd, J = 5, 8 Hz, 1H, H-15), 6.80 (d, J=9 Hz, 1H, H-17), 1.35 (s, 9H, H-20-22), 0.79 ppm (s, 18H, -N(Si(CH_3)$_2$)$_2$); ^{13}C NMR (126 MHz, C_6D_6, 26°C): δ=163.5 (C7), 149.2 (C16), 147.5 (C4), 147.3 (C1 or C2), 147.2 (C2 or C1), 145.9 (C8), 145.8 (C12), 142.4 (C6), 135.7 (C14), 133.8 (C10), 127.6 (C5), 125.7 (C18), 125.5 (C9), 124.9 (C15), 123.9 (C17), 119.5 (C3), 117.6 (C11), 34.4 (C19), 31.6 (C20-22), 7.3 ppm (s+d, J_{CSi}=53 Hz, -N(Si(CH$_3$)$_2$)$_2$); elemental analysis calcd for $C_{28}H_{37}N_3NiSi_2$: C 63.40, H 7.03, N 7.92 found: C 63.33, H 7.00, N 8.13; UV/Vis (THF): λ_{max} (ε)=313 (17300), 353 (10200), 372 (11100), 452 (5800), 536 (3200), 597 nm (900 mol^{-1}dm^{3}cm^{-1}); unit cell parameters: a=23.5957(7) Å, b=13.6797(4) Å, c=26.9113(8) Å, α=90°, β=101.4330(10)°, γ=90°, V=8514.1(4) Å^3, Z=8, P21/c, CCDC deposition number 1979882.

2-N(SiMe$_3$)$_2$. 67 mg (0.10 mmol) of **2**-(μ-Tf) and 19 mg (0.10 mmol) of NaN(SiMe$_3$)$_2$ were weighted out into a 25 mL Schlenk flask and dissolved in diethyl ether (10 mL) to afford a bright red solution. After stirring for additional 30 min, the solvent was removed and the dark red residue extracted with toluene. The combined filtrates were concentrated under vacuum until red crystals formed, and crystallization was completed by vapor diffusion of pentane overnight at r.t. Bright red crystalline flake shaped crystals were collected by filtration, washed with pentane and dried under dynamic vacuum. Yield: 32 mg (0.06 mmol, 60 %) of **2**-N(SiMe$_3$)$_2$. ^{1}H NMR (500 MHz, C$_6$D$_6$, 26°C): δ=9.44 (dd, J=1, 5 Hz, 1H, H-16), 7.85-7.81 (m, 2H, H-3/-11), 7.50 (d, J=9 Hz, 1H, H-6), 7.29-7.23 (m, 2H, H-5/-10), 7.21 (dd, J=1, 8 Hz, 1H, H-14), 6.89 (d, J=9 Hz, 1H, H-17), 6.79 (d, J=9 Hz, 1H, H-18), 6.68 (dd, J=5, 8 Hz, 1H, H-15), 1.36 (s, 9H, H-20-22), 0.94 ppm (s+d, J_{HSi}=7 Hz, 18H, -N(Si(CH_3)$_2$)$_2$); ^{13}C NMR (126 MHz, C$_6$D$_6$, 26°C): δ=164.6 (C1), 153.0 (C7), 152.3 (C16), 144.4 (C8), 144.3 (C12), 137.4 (C4), 136.5 (C14), 134.2 (C10), 131.3 (C5), 127.7 (C13), 126.3 (C17), 125.5 (C9), 125.2 (C6), 123.9 (C18), 123.0 (C15), 122.6 (C3), 121.7 (C11), 117.7 (C2), 34.5 (C19), 32.0 (C20-22), 6.9 ppm (s+d, J_{CSi}=53 Hz, -N(Si(CH$_3$)$_2$)$_2$); elemental analysis calcd for C$_{28}$H$_{37}$N$_3$NiOSi$_2$: C 61.54, H 6.82, N 7.69 found: C 61.83, H 6.64, N 7.95; UV/Vis (THF): $\lambda_{\max}$ (ε)=306 (27200), 363 (19800), 440 (5300), 475 (5300), 492 (shoulder, 5400), 538 nm (shoulder, 2900 mol^{-1}dm^{3}cm^{-1}); unit cell parameters: a=11.9534(7) Å, b=13.7247(7) Å, c=17.1253(10) Å, α=90°, β=93.5720(10)°, γ=90°, V=2804.1(3) Å^3, Z=4, P21/c, CCDC deposition number 1979879.

Solvent Influence on Metalation Selectivity of 0-OTf. The chemoselectivity of the reaction of Ni(cod)$_2$ and **0**-OTf toward **1**-Tf (κ^3-N,N',C-metalation) and **2**-(μ-Tf) (κ^3-N,N',O-metalation) was studied on a 54 μmol scale in diethyl ether and toluene, respectively. The solubility of **0**-OTf in either solvent is too low to achieve a 30 mM reactant concentration. *A) Toluene*. A light green solid separated from the initial suspension of white **0**-OTf in a yellow solution of Ni(cod)$_2$ in toluene (1.3 g) within 10 min, which converted gradually into a pale orange solid over the course of 3 h at r.t. After stirring the reaction mixture overnight, the solvent was removed under vacuum leaving an orange solid to which THF (0.6 g) was added. A dark red solution formed instantaneously after addition of 10 mg (54 μmol) of NaN(SiMe$_3$)$_2$ dissolved in THF (0.6 g) and was stirred for additional 30 min and finally dried under vacuum. The residual red solid was extracted with toluene and the solvent removed from the combined filtrate to afford a dark red solid. *B) Diethyl ether*. Addition of diethyl ether (5-10 mL) to a mixture of Ni(cod)$_2$ and **0**-OTf formed a yellow suspension at first that gradually turned into a green solution from which a light green solid separated noticeably within 30 minutes at r.t.

Stirring overnight resulted in the gradual conversion of the green into a pale orange solid. Volatiles were removed under vacuum, and 10 mg (54 µmol) of $NaN(SiMe_3)_2$ added to the pale orange residue followed by diethyl ether (10 mL), which resulted in a red solution instantaneously that was stirred for 30 min at r.t., filtered and dried under vacuum, leaving a dark red solid residue. For both reactions, the red residual solids dissolved completely in C_6D_6 (0.5 mL), and the selectivity of ligand metalation was determined by integration of ^{1}H NMR peaks at 8.94 (dd) and 0.79 (s) that are characteristic of **1**-$N(SiMe_3)_2$ relative to those at 9.44 (dd) and 0.94 (s) that are characteristic of **2**-$N(SiMe_3)_2$; ratios **1**-$N(SiMe_3)_2$:**2**-$N(SiMe_3)_2$ were 0.57:0.43 for toluene and 0.39:0.61 for diethyl ether.

1-OPiv. Solutions of 100 mg (0.24 mmol) of **0**-OPiv in 4 mL of THF and 70 mg (0.25 mmol) of $Ni(cod)_2$ in 8 mL of THF were combined at r.t. The initially clear yellow solution turned dark green within a few minutes and finally dark red over a period of 4 h at r.t. while fine red needles separated. Slow vapor diffusion of pentane (40 mL) into the reaction mixture cooled in an ice bath overnight afforded fine dark red needles that were separated from the supernatant solution by cannula filtration, washed with pentane and finally dried under dynamic vacuum. Yield: 67 mg (0.14 mmol, 59 %) of **1**-OPiv in form of thin, dark red needles. The chemoselectivity of the metalation of **0**-OPiv toward **1**-OPiv was determined by repeating the reaction on a 60 µmol scale. After stirring for 3 h at r.t. the solvent was removed under vacuum and 11 mg (60 µmol) of $NaN(SiMe_3)_2$ were added to the dark red solid residue in a glovebox. Addition of diethyl ether (10 mL) afforded a dark red solution that was stirred for 30 min at r.t., cannula-filtered, dried under dynamic vacuum, and the dark red residual solid was dissolved completely in C_6D_6 (0.5 mL). Comparison to ^{1}H NMR spectroscopic data of independently prepared **1**-$N(SiMe_3)_2$ and **2**-$N(SiMe_3)_2$ corroborated selective κ^3-*N*,*N'*,*C*-metalation of proligand **0**-OPiv. ^{1}H NMR (600 MHz, THF-d_8, 25 °C): δ=8.38 (d, *J*=8 Hz, 1H, H-10), 8.36 (dd, *J*=1, 8 Hz, 1H, H-14), 8.17 (dd, *J*=1, 5 Hz, 1H, H-16), 7.75 (d, *J*=9 Hz, 1H, H-17), 7.60 (dd, *J*=5, 8 Hz, 1H, H-15), 7.56 (d, *J*=9 Hz, 1H, H-18), 7.50 (d, *J*=9 Hz, 1H, H-11), 7.32 (d, *J*=2 Hz, 1H, H-3), 7.16 (dd, *J*=2, 8 Hz, 1H, H-5), 6.93 (d, *J*=8 Hz, 1H, H-6), 1.38 (s, 9H, H-20-22), 1.32 ppm (s, 9H, $-C(O)C(C\mathit{H}_3)_3$); ^{13}C NMR (151 MHz, THF-d_8, 25 °C): δ=184.0 (C23), 163.2 (C7), 149.4 (C16), 149.1 (C1), 148.1 (C4), 147.4 (C2), 145.7 (C12), 145.6 (C8), 138.0 (C14), 137.1 (C10), 136.8 (C6), 129.6 (C13), 127.4 (C5), 126.7 (C9), 126.2 (C15), 125.6 (C18), 120.2 (C3), 118.5 (C11), 39.9 ($-C(O)\mathit{C}(CH_3)_3$), 35.0 (C19), 31.9 (C20-22), 29.4 ppm ($-C(O)C(C\mathit{H}_3)_3$); elemental analysis calcd for $C_{27}H_{28}N_2NiO_2$: C 68.82, H 5.99, N 5.94 found: C 68.57, H 5.79, N 6.49; IR (KBr): $\tilde{\upsilon}$=1752 cm^{-1} (vs, C(O)); UV/Vis (THF): λ_{max} (ε)=310 (23500), 349 (13800), 366 (17600), 430 (7200), 510 (3600), 560 nm (shoulder, 1000

$mol^{-1}dm^3cm^{-1}$); unit cell parameters: a=14.4635(13) Å, b=6.9797(6) Å, c=25.786(2) Å, α=90°, β=100.159(5)°, γ=90°, V=2562.3(4) $Å^3$, Z=4, P2/c, CCDC deposition number 1979881.

2 Additional Crystallographic Information

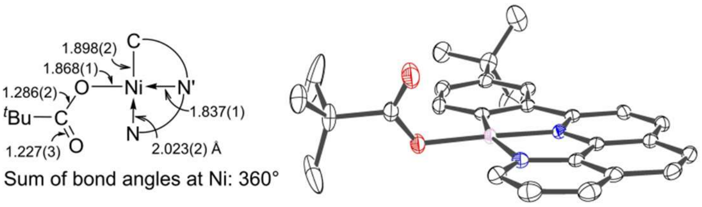


Fig. S1 ORTEP representation and selected metrics of the molecular structure of **1**-OPiv; thermal displacement ellipsoids at 50 % probability, H-atoms and co-crystallized 1,2-$C_6H_4F_2$ omitted for clarity, color code: C black, N blue, O red, Ni plum.

3 Additional Spectroscopic Data

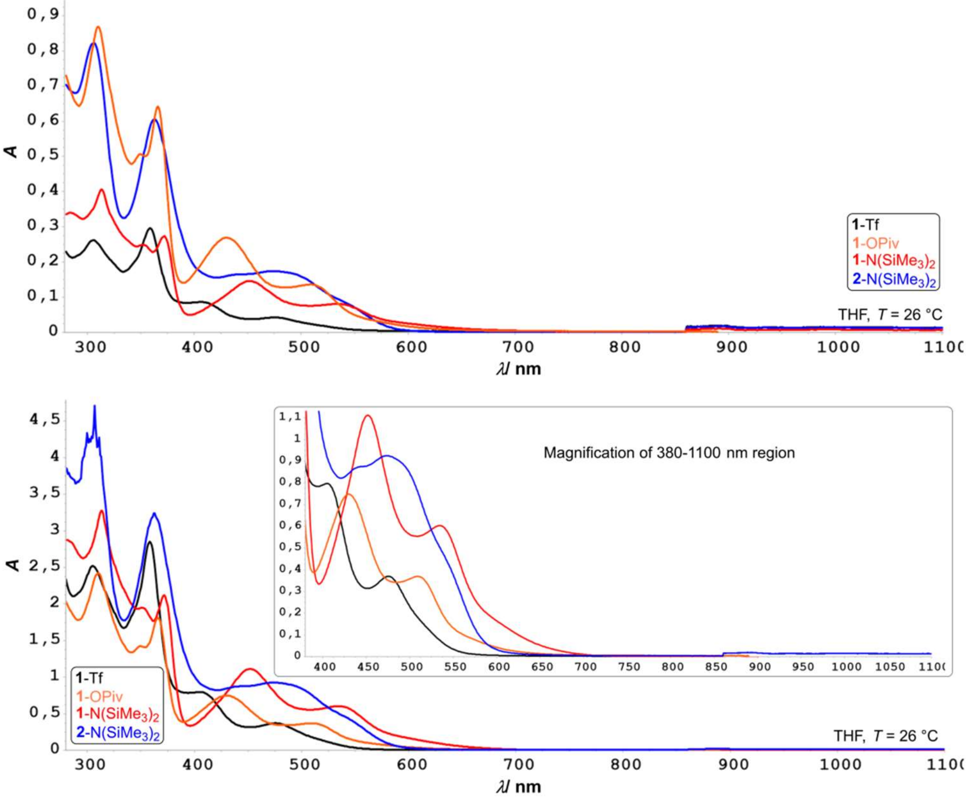


Fig. S2 UV-vis absorption spectra: top spectrum (absorbance A vs λ) is identical to that shown in Fig. 3 of the main text (plotted as molar extinction coefficient ε vs λ), bottom spectra of ~10-fold higher concentrated samples; changes in A at $\lambda \geq 860$ nm result from detector change.

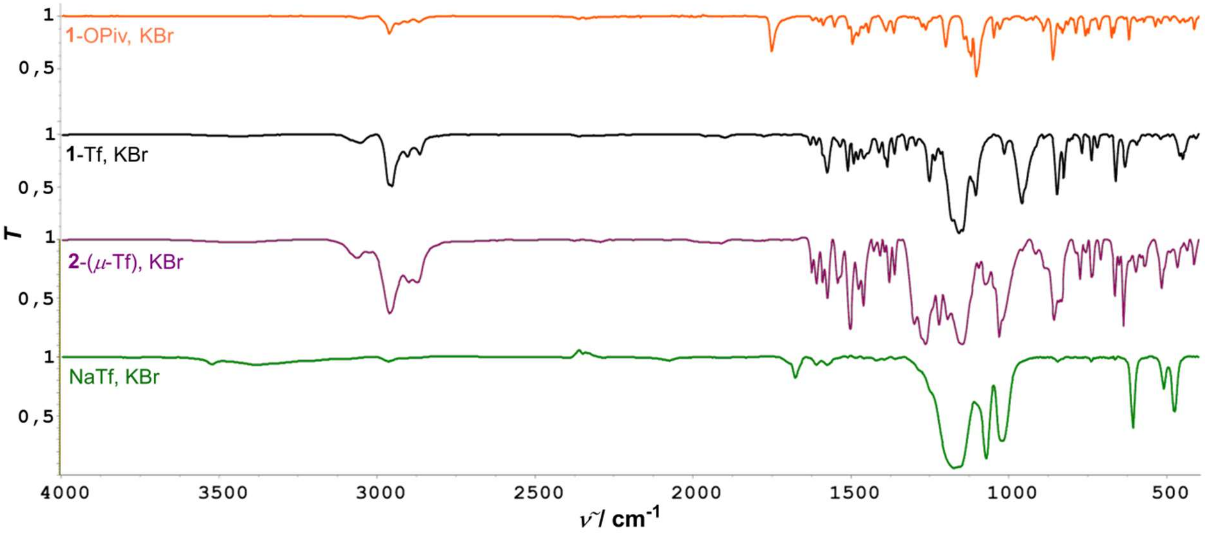


Fig. S3 IR spectra (KBr); Piv = C(O)^{t}Bu, Tf = CF_3SO_2.

4 Details on (TD-)DFT Computations

4.1 General Computational Information.

Electronic structure calculations on the complexes have been performed through density-functional theory (DFT) methods using the ORCA program package.[8] For all optimizations triple-ξ-valence TZVP[9] basis sets were used with the generalized gradient approximated functional BP86.[10] Molecular orbitals and electronic properties were extracted from single-point calculations in the optimized positions with the global hybrid functional TPSSh.[11] Grimme's third generation D3 correction of dispersion was used;[12] medium effects were approximated in a dielectric continuum approach (COSMO), parameterized for THF.[13] Structures of the complexes have been identified as stationary points through the absence of imaginary modes in harmonic frequency calculations; modes at −5.3 cm^{-1} (**2**-$N(SiMe_3)_2$) and −12.2 cm^{-1} (**1**-Tf), both due to -CH_3 rotations are typical artefacts of DFT-based numerical frequency scans. Computed structures frontier orbital landscapes are shown in Fig. **S4**-Fig. **S7**. For each complex the 40 lowest optical electronic transitions were assessed with ORCA implemented TD-DFT methods within Tamm-Dancoff approximation. Details on relevant transitions are given in Table S1-Table S4.

4.2 Results of (TD-)DFT Computations.

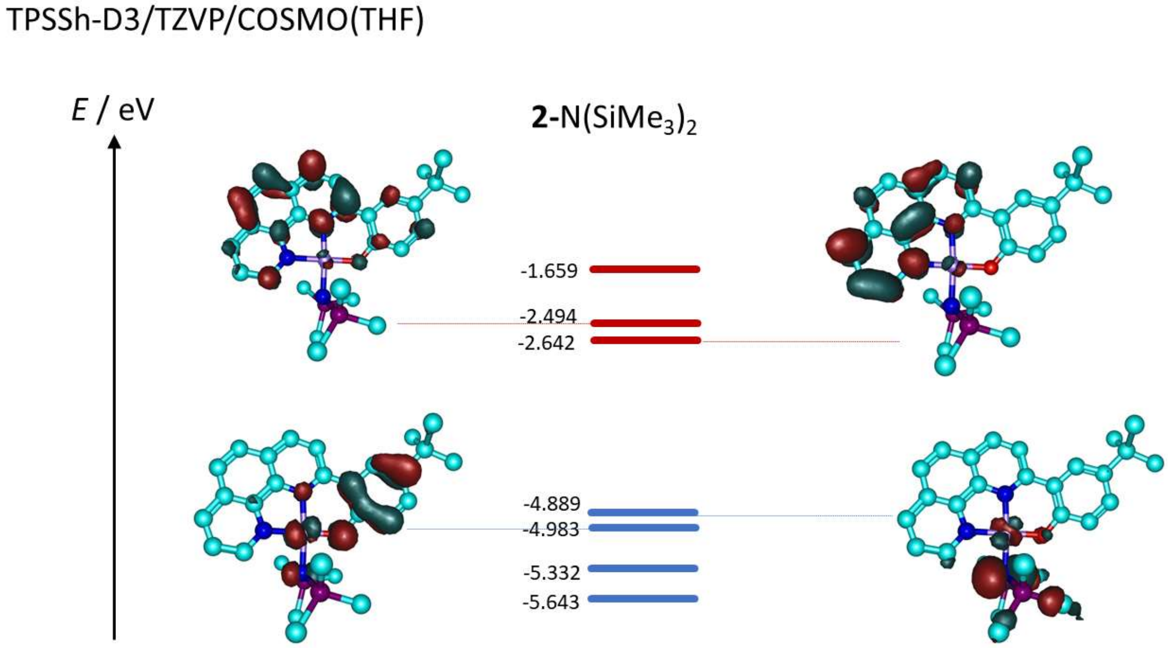


Fig. S4 Kohn-Sham frontier MOs of **2**-N$(SiMe_3)_2$; TPSSh-D3/TZVP/COSMO(THF) level of theory.

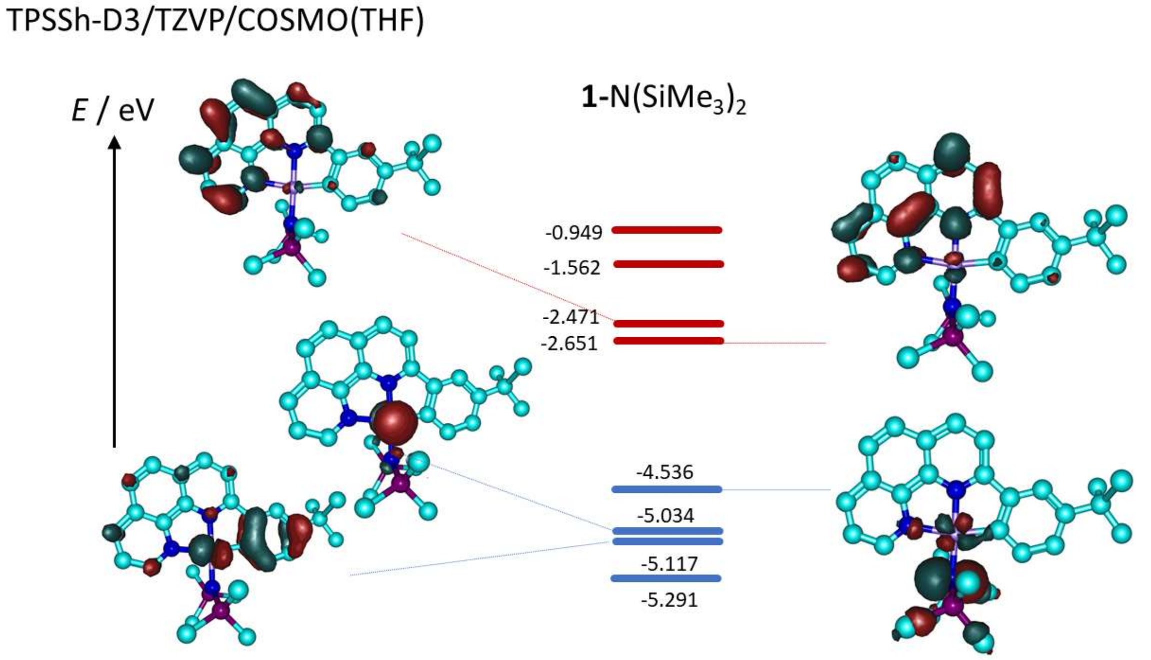


Fig. S5 Kohn-Sham frontier MOs of **1**-N$(SiMe_3)_2$; TPSSh-D3/TZVP/COSMO(THF) level of theory.

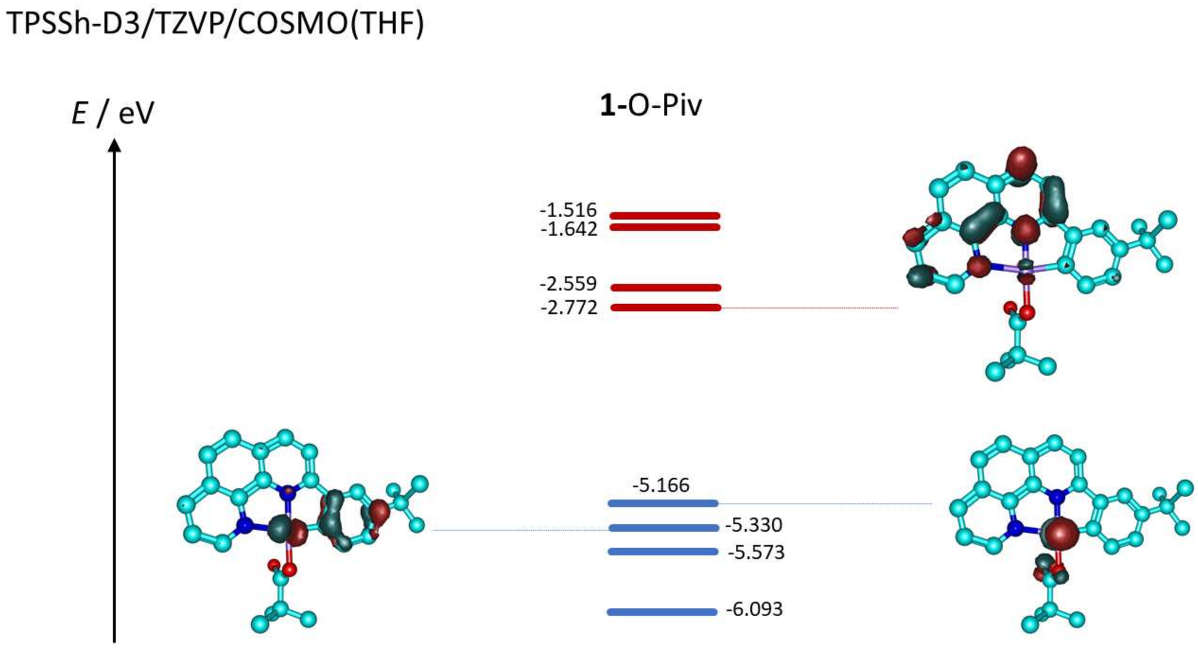


Fig. S6 Kohn-Sham frontier MOs of **1**-OPiv; TPSSh-D3/TZVP/COSMO(THF) level of theory.

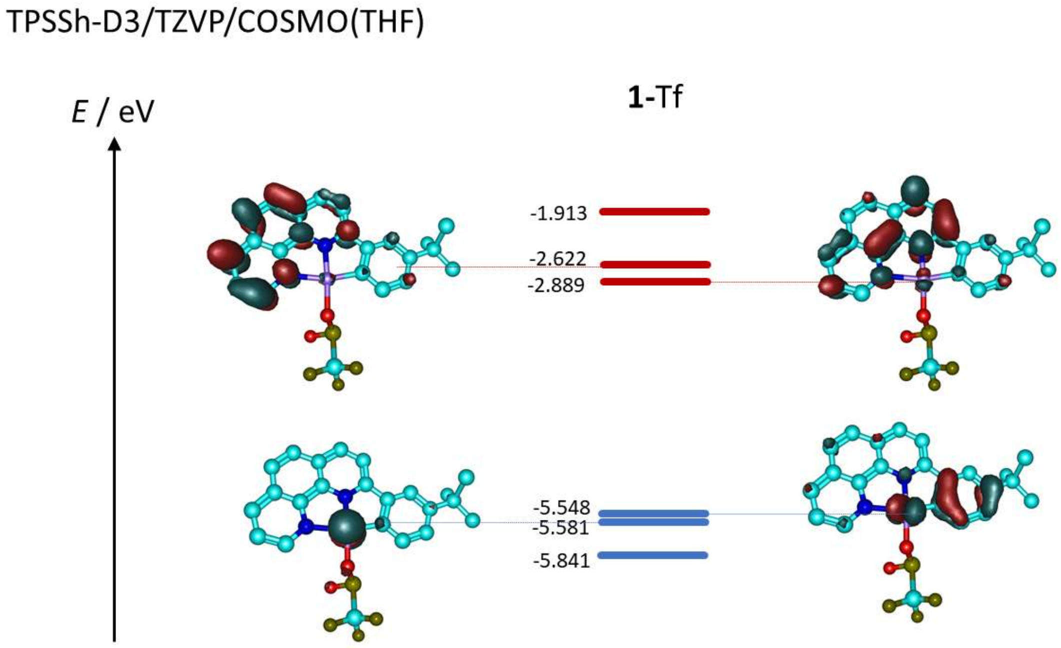


Fig. S7 Kohn-Sham frontier MOs of **1**-Tf; TPSSh-D3/TZVP/COSMO(THF) level of theory.

Table S1 Selected electronic transitions of **1**-OPiv; TPSSh-D3/TZVP/COSMO(THF) level of theory

transition	***ν*/ cm^{-1}**	***λ*/ nm**	***f*$_{osc}$**	**character**
5	12930.8	773.3	0.0011	H→L (98%)
8	15749.7	635.0	0.0008	H-1→L (94%)
13	17744.6	563.6	0.0088	H-2→L (40%)// H-1→L+1 (30%)
15	19011.5	526.0	0.0302	H-2→L+1 (70%)
18	21402.4	467.2	0.0453	H-1→L+1 (36%)// H→L+3 (35%)
21	23495.2	425.6	0.0216	mixed
22	23311.2	429.0	0.0030	H-3→L (50%)
26	22027.7	454.0	0.0092	H-4→L (76%)
35	25550.0	391.4	0.0172	H-1→L+2 (88%)
37	26170.3	382.1	0.0724	H-5→L (62%)

Table S2 Selected electronic transitions of **1**-Tf; TPSSh-D3/TZVP/COSMO(THF) level of theory

transition	***ν*/ cm^{-1}**	***λ*/ nm**	***f*$_{osc}$**	**character**
7	15259.7	655.3	0.0015	H-1→L (80%)
9	16804.9	595.1	0.0004	H→L (80%)
11	19192.1	521.0	0.0069	H-2→L (39%)// H-1→L+2 (30%)
16	22617.2	442.1	0.0023	H-2→L+2 (70%)
17	21162.4	472.5	0.0502	H→L+1 (45%)// H-2→L+1 (23%)
21	23480.0	425.9	0.0203	mixed
22	22181.6	450.8	0.0075	H-3→L (60%)
23	23442.4	426.6	0.0251	mixed
30	24382.9	410.1	0.0223	H-5→L (47%)// H-4→L (37%)
33	26730.8	374.1	0.0645	mixed

Table S3 Selected electronic transitions of **1**-N(SiMe$_3$)$_2$; TPSSh-D3/TZVP/COSMO(THF) level of theory

transition	**ν/ cm^{-1}**	**λ/ nm**	**f_{osc}**	**character**
2	10080.3	992.0	0.0004	H→L (97%)
7	13639.9	733.1	0.0017	H-1→L (98%)
10	15416.8	648.6	0.0018	H-2→L (89%)
17	17101.4	584.7	0.0111	H-3→L (46%)// H-2→L+1 (34%)
19	18398.9	543.5	0.0285	H-3→L+1 (73%)
20	20531.8	487.0	0.0107	H→L+2 (46%)// H→L+3 (44%)
22	20523.0	487.3	0.0070	H→L+2 (54%)// H→L+3 (40%)
23	21540.3	464.2	0.0827	mixed
31	25728.3	388.7	0.0172	mixed
36	26091.6	383.3	0.0429	H-4→L (64%)

Table S4 Selected electronic transitions of **2**-N(SiMe$_3$)$_2$; TPSSh-D3/TZVP/COSMO(THF) level of theory

transition	**ν/ cm^{-1}**	**λ/ nm**	**f_{osc}**	**character**
6	12840.2	778.8	0.0007	H→L (97%)
9	14262.0	701.2	0.0071	H-1→L (90%)
14	17331.4	577.0	0.0133	H-1→L+1 (65%)
16	18794.8	532.1	0.013	H→L+2 (65%)
21	19935.4	501.6	0.0116	H-3→L (56%)
23	21381.0	467.7	0.0059	mixed
25	23386.5	427.6	0.0022	H-3→L+2 (78%)
27	23658.6	422.7	0.0303	H-3→L+1 (44%)// H-2→L+2 (30%)
33	24717.8	404.6	0.0659	H-4→L+1 (62%)
38	25999.4	384.6	0.0830	mixed

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