Remote Substituents Controlling Catalytic Polymerization by very Active and Robust Neutral Nickel(II) Complexes

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Supporting Information

General considerations

All manipulations of nickel complexes were carried out under an argon atmosphere (99.999% pure argon supplied by Messer). Toluene was distilled from sodium, ether and tetrahydofuran were distilled from sodium / benzophenone. Demineralised water was distilled under argon and degassed three times after distillation. Pyridine and pentane were distilled from KOH. [(tmeda)Ni(CH_3)$_2$][1] was supplied by MCAT (Konstanz, Germany). Ethylene of 3.5 grade was supplied by Praxair. NMR spectra were recorded on a Bruker ARX 300 spectrometer. 2D NMR spectra were recorded on a Bruker Avance 500 MHz spectrometer. ^{1}H and ^{13}C NMR spectra of polyethylenes were obtained in 1,1,2,2-tetrachloroethane-d_2 at 122 °C. The branching structure was assigned according to [2]. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC 7 or on a Pyris 1 DSC at a heating rate of 10 K min^{-1}. DSC data reported are second heats. Polymer crystallinities were calculated based on a melt enthalpy of 293 J g^{-1} for 100% crystalline polyethylene. GPC analyses were carried out by Basell GmbH, Ludwigshafen on a Waters150C or GPC2000 instrument equipped with Shodex columns at 135 °C in 1,2,4-trichlorobenzene. Data is referenced to linear polyethylene standards.

Ligand synthesis

General procedure for the preparation of 2,6-diaryl anilines. To a toluene solution (30 mL) of 0.75 g (3.0 mmol) 2,6-dibromoaniline was added an ethanol (6 mL) solution of 9.0 mmol arylboronic acid. To the mixture was added an aqueous 2M solution of Na_2CO_3 (2.2 mL, 24 mmol). The biphasic mixture was flushed with argon and 0.42 g (0.36 mmol) of $Pd(PPh_3)_4$ was added. The reaction mixture was stirred overnight at 90 °C. The organic layer was separated from the aqueous phase. The aqueous phase was extracted three times with diethyl ether. The combined organic fractions were dried over Na_2SO_4. The solvents were evaporated and the raw compound was purified by column chromatography (silica / toluene).

General procedure for the preparation of salicylaldimine ligands (1a-e). To a methanol (5 mL) solution of 3,5-diiodo-2-hydroxy benzaldehyde (166 mg, 0.61 mmol) was added a catalytic amount of formic acid and 2,6-diaryl aniline (0.55 mmol). The reaction mixture was stirred for 6 hours at room temperature. The yellow solid that precipitated was filtered, washed with cold methanol and dried to afford the salicylaldimine ligand. Ligand **1a** was additionally purified by column chromatography (toluene / silica).

1a: R = R' = CF_3. Yield: 65 %. ^{1}H NMR (300 MHz, C_6D_6): 13.0 (O*H*, s, 1H), 7.71 (ClC*H*Cl, d, $^4J_{HH}$ = 2.0 Hz, 1H), 7.55 and 7.49 (CCF_3C*H*C and CF_3C*H*CF_3, br s, 6H), 6.94 (CHC*H*CH, dd, $^3J_{HH}$ = 8.1 Hz, 1H), 6.84 (C*H*CHC*H*, d, $^3J_{HH}$ = 8.1 Hz, 2H), 6.57 (ClC*H*C, d, $^4J_{HH}$ = 2.0 Hz, 1H), 6.51 (C*H*N, s, 1H). ^{13}C NMR (75.4 MHz, C_6D_6): 168.42 (*C*N, s), 160.11 (*C*OH, s), 150.73, 145.06, 140.68, 140.35 (*Ph*, s), 132.07 (*C*CF_3, quartet, $^2J_{CF}$ = 33.4 Hz), 131.71, 131.03, 130.11, 126.90 (*Ph*, s), 123.5 (*Ph*, quartet, $^1J_{CF}$ = 273 Hz), 121.29, 119.12 (*Ph*, s), 87.33 (C(OH)*C*I, s), 80.52 (CH*C*ICH, s). Anal. Calcd. for ($C_{29}H_{13}F_{12}I_2NO$): C, 39.89; H, 1.50; N, 1.60. Found: C, 40.19; H, 1.62; N, 1.49.

1b: R = NO_2, R' = H. ^{1}H NMR (300 MHz, C_6D_6): 13.2 (O*H*, s, 1H), 8.28 ($C_6H_4NO_2$, m, 2H), 8.17 ($C_6H_4NO_2$, m, 2H), 7.99 (CIC*H*CI, d, $^4J_{HH}$ = 2.0 Hz, 1H), 7.83 (C*N*, s, 1H), 7.67 ($C_6H_4NO_2$, m, 2H), 7.55 (C*H*CHC*H*, d $^3J_{HH}$ = 8.1 Hz, 2H), 7.51 ($C_6H_4NO_2$, s, 2H), 7.51 (CHC*H*CH, t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.15 (CIC*H*C, d, $^4J_{HH}$ = 2.0 Hz, 1H). ^{13}C NMR (75.4 MHz, C_6D_6): 168.05 (*C*N, s), 160.08 (*C*OH, s), 150.33, 148.74, 144.61, 140.40, 140.11, 135.10, 132.79, 131.05, 129.27, 126.96, 124.47, 122.42, 119.67 (*Ph*, s), 87.55 (C(OH)*C*I, s), 80.65 (CH*C*ICH, s). Anal. Calcd. for ($C_{25}H_{15}I_2N_3O_5$): C, 43.44; H, 2.19; N, 6.08. Found: C, 43.95; H, 2.32; N, 6.06.

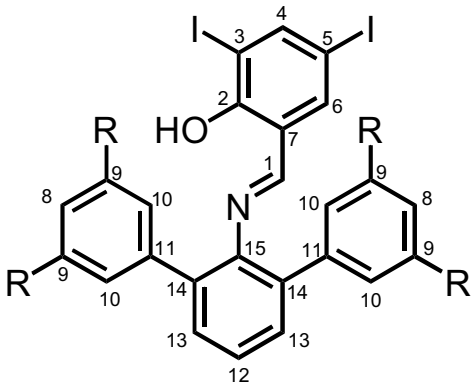
1c: R = R' = H. Yield: 80%. ^{1}H NMR (300 MHz, C_6D_6): 13.8 (O*H*, br s, 1H), 7.71 (CIC*H*CI, d, $^4J_{HH}$ = 2.0 Hz, 1H), 7.23 (C*H*CHC*H*, d, $^3J_{HH}$ = 7.0, 4H), 7.23 (CHC*H*CH, d, $^3J_{HH}$ = 7.0, 2H), 7.19 (C*H*N, s, 1H), 6.93 (CHC*H*CH, t, $^3J_{HH}$ = 7.0, 2H), 7.04 (CHC*H*CH, t, $^3J_{HH}$ = 7.0, 1H), 7.03 (CHC*H*CH, t, $^3J_{HH}$ = 7.0, 4H), 6.61 (CIC*H*C, d, $^4J_{HH}$ = 2.0 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): 166.99 (*C*N, s), 160.32 (*C*OH, s), 149.38, 144.72, 140.17, 139.47, 135.42, 130.51, 129.87, 128.72, 127.46, 126.55, 120.37 (*Ph*, s), 87.52 (C(OH)*C*I, s), 80.10 (CH*C*ICH, s). Anal. Calcd. for ($C_{25}H_{17}I_2NO$): C, 49.94; H, 2.85; N, 2.33. Found: C 49.79; H, 2.78; N, 2.33.

1d: R = R' = CH_3. Yield: 80 %. ^{1}H NMR (300 MHz, C_6D_6): 14.0 (O*H*, s, 1H), 7.71 (CIC*H*CI, d, $^4J_{HH}$ = 2.0 Hz, 1H), 7.35 (C*H*CHC*H*, d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.31 (C*H*N, s, 1H), 7.15 (CHC*H*CH, t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.06 (CC*H*CMe, s, 4H), 6.66 (CMeC*H*CMe, s, 2H), 6.60 (CIC*H*C, d, $^4J_{HH}$ = 2.0 Hz, 1H), 2.11 (CH_3, s, 12H). ^{13}C NMR (75.4 MHz, C_6D_6): 166.23 (*C*N, s), 160.32 (*C*OH, s), 149.11, 144.67, 140.11, 139.48, 138.10, 135.75, 130.25, 129.14, 127.91, 126.48, 120.41 (*Ph*, s), 87.33 (C(OH)*C*I, s), 78.90 (CH*C*ICH, s), 21.26 (*C*H_3, s). Anal. Calcd. for ($C_{29}H_{25}I_2NO$): C, 52.99; H, 3.83; N, 2.13. Found: C, 53.28; H, 3.81; N, 2.28.

1e: R =R' = OCH_3. Yield: 85 %. ^{1}H NMR (300 MHz, C_6D_6): 14.2 (O*H*, s, 1H), 7.69 (CIC*H*CI, d, $^4J_{HH}$ = 2.0 Hz, 1H), 7.42 (C*H*CHC*H*, d, $^3J_{HH}$ = 8.1 Hz, 2H), 7.38 (C*H*N, s, 1H), 7.06 (CHC*H*CH, t, $^3J_{HH}$ = 8.1 Hz, 1H), 6.68 (CC*H*CO, d, $^4J_{HH}$ = 2.4 Hz, 4H), 6.65 (CIC*H*C, d,

$^4J_{HH}$ = 2.0 Hz, 1H), 6.39 (COC*H*CO, t, $^4J_{HH}$ = 2.4 Hz, 2H), 3.32 (OCH_3, s, 12H). ^{13}C NMR (75.4 MHz, C_6D_6): 166.26 (*C*N, s), 161.39 (*C*OH, s), 160.29 (*C*OCH$_3$), 149.39, 144.61, 141.40, 140.26, 135.35, 130.36, 126.56, 120.43, 108.22, 100.13 (*Ph*, s), 87.33 (C(OH)*C*I, s), 80.34 (CH*C*ICH, s), 54.94 (O*C*H$_3$, s). Anal. Calcd. for ($C_{29}H_{25}I_2NO_5$): C, 48.29; H, 3.49; N, 1.94. Found: C, 49.20; H, 3.94; N, 1.83.

Table S1. Assignment of ^{13}C NMR signals in **1a-e**.



Carbon number	OCH_3, OCH_3	CH_3, CH_3	H, H	H, NO_2	CF_3, CF_3
1	166.26	166.23	166.99	168.05	168.42
2	160.29	160.32	160.32	160.08	160.11
3	87.33	87.33	87.52	87.55	87.33
4	149.39	149.11	149.38	148.74	150.73
5	80.34	78.90	80.10	80.65	80.52
6	140.26	140.11	140.17	140.11	140.35
7	120.43	120.41	120.37	119.67	119.12
8	100.12	129.14	127.46	[a]	121.29
9	161.40	138.10	128.72	[a]	132.07
10	108.22	127.91	129.87	[a]	130.11
11	135.35	135.75	135.42	135.10	131.71
12	126.56	126.48	126.55	126.96	126.90
13	130.36	130.25	130.51	131.05	131.03
14	141.40	139.48	139.47	140.40	140.68
15	144.61	144.67	144.72	144.61	145.06

[a] not listed (monosubstitution results in additional peaks for carbons 8 to 10).

Complex synthesis

To an ether (10 mL) solution of [(tmeda)Ni(CH_3)$_2$] (100 mg, 0.49 mmol) was added 0.49 mmol of a salicylaldimine ligand (**1**) at -30 °C. Then 0.5 mL of pyridine was added to the reaction mixture. The temperature was raised to 0 °C and the orange / red mixture was stirred for 2 h. The solvent was removed *in vacuo* and the residue was washed with cold pentane. A red to orange solid was obtained in isolated yields of more than 90 %.

2a: R = R' = CF_3. ^{1}H NMR (300 MHz, C_6D_6): 8.7-6.4 (aryl, br m 17H), -0.61 (NiCH_3, s, 3H). ^{13}C NMR (75.4 MHz, C_6D_6): 167.5 (*C*N, s), 163.9 (*C*O, s), 151.4 (pyridine), 150.2, 141.8, 141.4 (*Ph*, s), 136.3 (pyridine), 133.3 (*Ph*, s), 131.9 (*C*CF_3, q, $^2J_{CF}$ = 33.3 Hz), 130.8, 130.7, 128.1, 126.8 (*Ph*, s), 123.9 (*C*CF_3, q, $^1J_{CF}$ = 272 Hz), 123.4 (pyridine), 121.4, 119.5 (*Ph*, s), 97.0 (C(O)*C*I, s), 72.9 (CH*C*ICH, s), -7.5 (Ni*C*H_3, s). Anal. Calcd. for ($C_{35}H_{20}F_{12}I_2N_2NiO$): C, 41.01; H, 1.97; N, 2.73. Found: C, 41.10; H, 2.06; N, 2.51.

2b: R = NO_2, R' = H. ^{1}H NMR (300 MHz, CD_2Cl_2): 8.6-7.0 (pyridine, br, 5H), 8.78 (*Ph*, br t, 2H), 8.27 (*Ph*, m, 2H), 7.99 (*Ph*, m, 2H), 7.84 (CIC*H*CI, d, $^4J_{HH}$ = 2.0 Hz, 1H), 7.71 (*Ph*, m, 2H), 7.50 (C*H*N, s, 1H), 7.45 (*Ph*, m, 3H), 7.03 (CIC*H*C, d, $^4J_{HH}$ = 2.0 Hz, 1H), -0.92 (NiCH_3, s, 3H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): 167.2 (*C*N, s), 163.5 (*C*O, s), 149.7, 149.3, 148.5, 141.7, 140.9, 136.3, 133.7, 131.0, 129.6, 127.0, 125.2, 122.5, 120.1 (*Ph*, s), 96.5 (C(O)*C*I, s), 72.0 (CH*C*ICH, s), -7.6 (Ni*C*H_3, s). Anal. Calcd. for ($C_{31}H_{22}I_2N_4NiO_5$): C, 44.17; H, 2.63; N, 6.65. Found: C, 43.64; H, 2.70; N, 6.66.

2c: R = R' = H. ^{1}H NMR (300 MHz, C_6D_6): 8.27 (pyridine, br s, 2H), 8.03 (CIC*H*CI, d, $^4J_{HH}$ = 2.0 Hz, 1H), 7.76 (C*H*CHC*H*, d, $^3J_{HH}$ = 7.0, 4H), 7.4-7.1 (C*H*N, s, 1H and *Ph*, m, 9H), 6.91 (CIC*H*C, d, $^4J_{HH}$ = 2.0 Hz, 1H), 6.69 (pyridine, br s, 1H), 6.38 (pyridine, br s, 2H), -0.51 (NiCH_3, s, 3H). ^{13}C NMR (75.4 MHz, C_6D_6): 168.0 (*C*N, s), 163.7 (*C*O, s), 151.8 (pyridine), 149.9, 149.2, 141.9, 140.2, 136.2 (*Ph*, s), 135.8 (pyridine), 130.6, 130.5, 128.7,127.5, 126.5 (*Ph*, s), 122.8 (pyridine), 121.1 (*Ph*, s), 97.5 (C(O)*C*I, s), 72.0 (CH*C*ICH, s), -7.5 ($NiCH_3$, s).

Anal. Calcd. for $C_{31}H_{24}I_2N_2NiO$: C, 49.44; H, 3.21; N, 3.72. Found: C, 49.07; H, 3.09; N, 3.73.

2d: R = R' = CH_3. ^{1}H NMR (300 MHz, CD_2Cl_2): 8.29 (pyridine, br s, 2H), 7.8-6.9 (pyridine, br s, 2H and C*H*N, s, 1H and *Ph*, m, 11H), 6.70 (pyridine, br s, 1H), 2.29 (CH_3, s, 12H), -1.12 (NiCH_3, s, 3H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): 166.0 (*C*N, s), 162.1 (*C*O, s), 150.8 (pyridine), 148.6, 147.7, 140.7, 138.8, 137.0, 135.1 (pyridine), 129.0, 127.9, 127.5, 127.1, 125.2, 122.4 (pyridine), 119.9, 95.6 (C(O)*C*I, s), 70.4 (CH*C*ICH, s), 20.5 (C*C*H_3, s), -9.2 (Ni*C*H_3, s). Anal. Calcd. for $C_{35}H_{32}I_2N_2NiO$: C, 51.95; H, 3.99; N, 3.46. Found: C, 51.03; H, 3.80; N, 3.20.

2e: R = R' = OCH_3. ^{1}H NMR (300 MHz, CD_2Cl_2): 8.43 (pyridine, br s, 2H), 7.86 (CIC*H*CI, d, $^4J_{HH}$ = 2.0 Hz, 1H), 7.62 (pyridine, br s, 1H), 7.50 (C*H*N, s, 1H), 7.42-7.28 (C*H*CHC*H* + CHC*H*CH, m, 3H), 7.14 (pyridine, br s, 2H), 7.04 (CIC*H*C, d, $^4J_{HH}$ = 2.0 Hz, 1H), 6.82 (CC*H*COCH$_3$, d, $^4J_{HH}$ = 2.4 Hz, 4H), 6.53 (C(OCH$_3$)C*H*C(OCH$_3$), t, $^4J_{HH}$ = 2.4 Hz, 2H), 3.79 (OCH_3, s, 12H), -0.98 (NiCH_3, s, 3H). ^{13}C NMR (75.4 MHz, CD_2Cl_2): 166.8 (*C*N, s), 163.2 (*C*O, s), 160.9 (*Ph*, s), 151.7 (pyridine), 149.4, 149.0, 141.7 (*Ph*, s), 136.7 (pyridine), 135.7, 130.1, 126.3 (*Ph*, s), 123.5 (pyridine), 120.9, 108.7, 101.6, 99.9 (*Ph*, s), 96.6 (C(O)*C*I, s), 71.7 (CH*C*ICH, s), 55.7 (O*C*H_3, s), -8.2 (Ni*C*H_3). Anal. Calcd. for ($C_{35}H_{32}I_2N_2NiO_5$): C, 48.15; H, 3.69; N, 3.21. Found: C, 47.80; H, 3.86; N, 3.35.

In variable temperature NMR spectroscopy with **2a** (^{19}F), **2c** (^{1}H) and **2d** (^{1}H) at temperatures down to –60 °C only one signal for the substituent R and R' was observed, demonstrating a fast rotation in solution of the 3,5-substituted aryl rings along the aryl-aryl bond to the N-aryl moiety, at these low temperatures.

Ethylene polymerization in non-aqueous media was carried out in a 300 mL stainless steel mechanically stirred (1000 rpm) autoclave equipped with a heating/cooling jacket supplied by a thermostat controlled by a thermocouple dipping into the polymerization mixture. The autoclave was charged with a toluene (100 mL) solution of complex **2** under argon.

In experiments with the *in situ* catalyst, the autoclave was charged with a solution of 40 μmol of ligand **1** in 95 mL of toluene. The solution was saturated with ethylene at ambient pressure, and a solution of 40 μmol of [(tmeda)Ni(CH_3)$_2$] in 5 mL toluene was added under stirring.

The autoclave was flushed with ethylene, and a constant ethylene pressure was then applied and the reaction mixture was brought rapidly to the desired temperature. After a specified reaction time the autoclave was rapidly cooled and depressurised. The polymerization mixture was poured into a threefold volume of methanol to precipitate any dissolved low molecular weight material. The polymer was isolated by filtration, washed three times with methanol and dried in vacuo.

Ethene polymerization in aqueous emulsion. In a Schlenk tube, a solution of catalyst precursor **2** in a mixture of toluene (2 mL) and hexadecane (0.3 mL) was added to an aqueous (98 mL water) solution of 0.75 g sodium dodecyl sulphate. The mixture was homogenized under an argon atmosphere by means of an ultrasonic homogenizer (Bandelin HD2200 with KE76 tip, operated at 120 W, two minutes). The resulting miniemulsion was cannula-transferred to the aformentioned 300 mL autoclave. The autoclave was flushed with ethylene, and a constant ethylene pressure of 40 bar was then applied and the reaction mixture was brought rapidly to the desired temperature. The emulsion was filtered through glass wool to seperate any coagulate and to determine its amount. For determination of yields and for further polymer analysis a specified portion of the latex was precipitated by pouring into excess methanol. The polymer was washed three times with methanol and dried in vacuo.

Ethylene polymerization with complex 2a and 2c probing for catalyst stability. A 600 mL stainless steel autoclave fully automated with respect to temperature and pressure control as well as monitoring of monomer uptake was charged with a toluene (300 mL) solution containing 30 μmol of **2**. The autoclave was pressurised with ethylene (11 bar) and the temperature of the reaction mixture was adjusted to 60 °C. The ethylene uptake was monitored by means of a mass flow meter. After a specified reaction time the autoclave was rapidly cooled and depressurised. The reaction mixture was poured into a threefold excess of methanol. The polymer was isolated by filtration and washed three times with methanol.

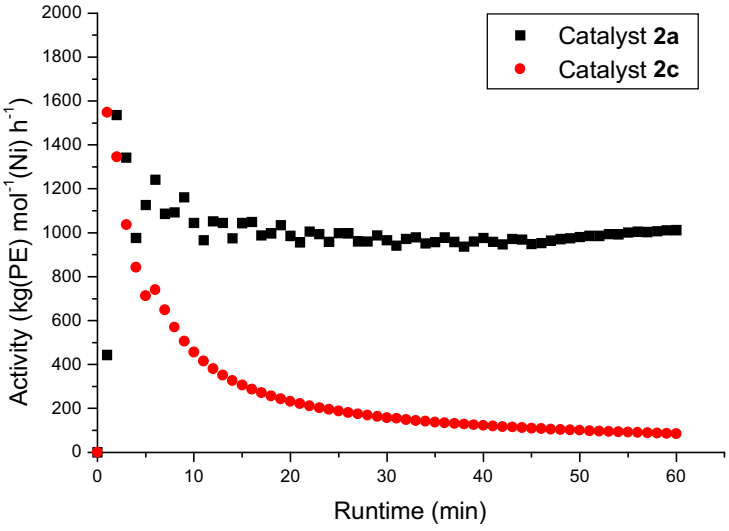


Figure S1. Catalyst stability over time with precursors **2a** and **2c** (60 °C and 10 bar ethylene pressure).

Full labelling schemes of the ORTEP plots of 2a and 2c

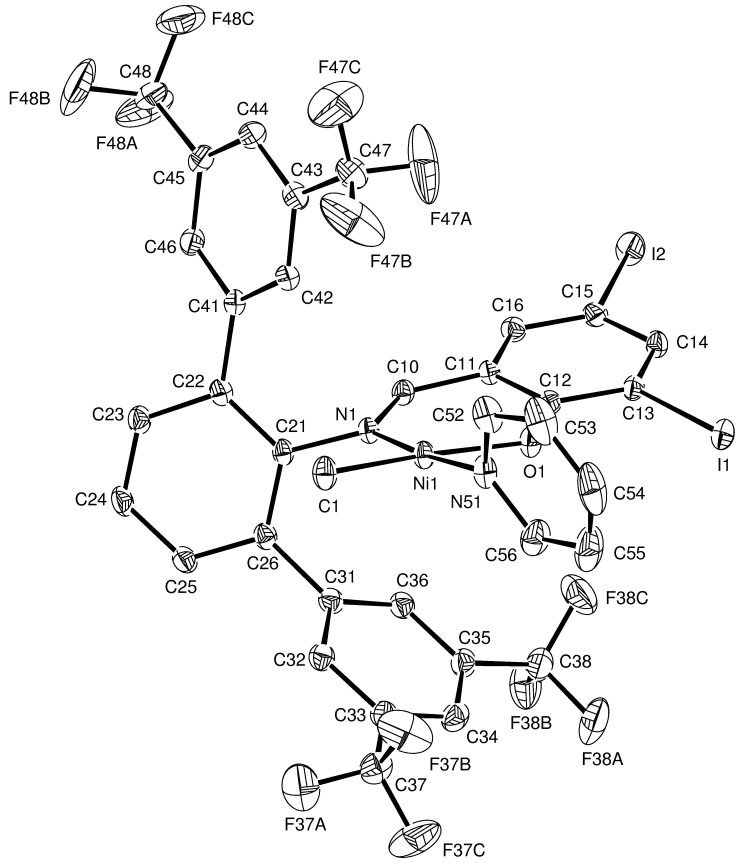


Figure S2. X-ray crystal structure of **2a**. The thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

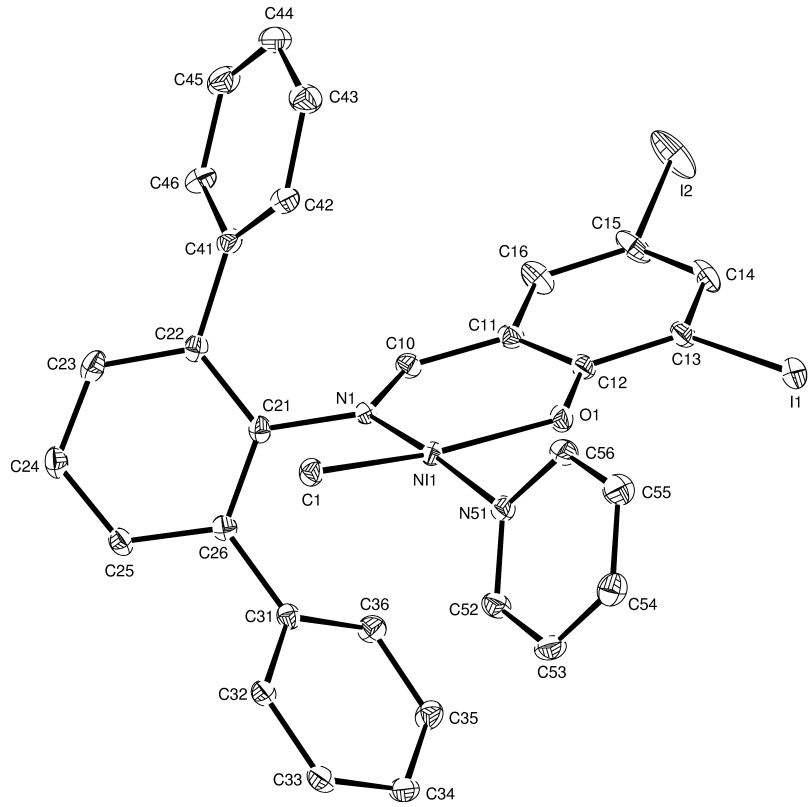


Figure S3. X-ray crystal structure of **2a**. The thermal ellipsoids are drawn at the 50 % probability level. Hydrogen atoms have been omitted for clarity.

References

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