Electronic Supplementary Material (ESI) for Dalton Transactions

Metallomacrocycles as Ligands: Synthesis and Characterisation of Aluminuim-Bridged Bisglyoximato Complexes of Palladium and Iron

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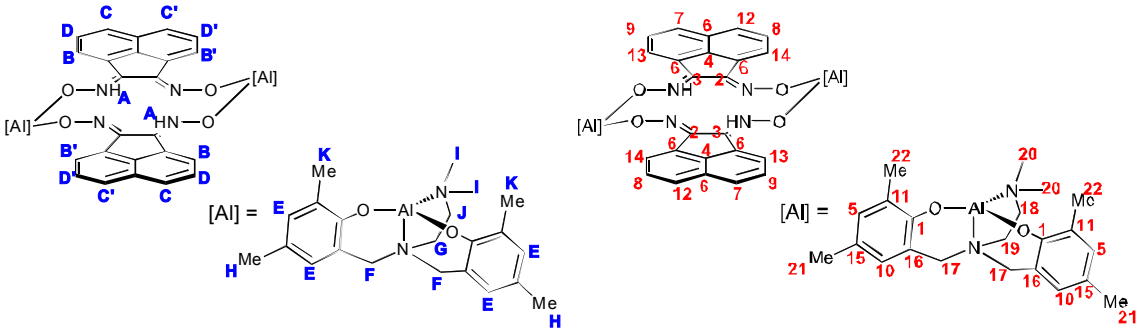
Supporting Information

I. Experimental Details

II. NMR Spectra

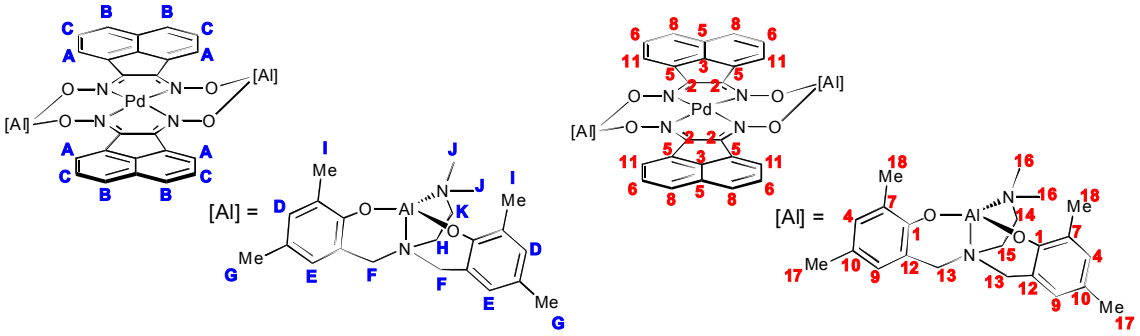
I. Experimental Section

General Considerations. Unless otherwise specified, all compounds were manipulated using a glove box under a nitrogen atmosphere. Solvents for all reactions were dried by Grubbs' method.[1] Benzene-d_6 was purchased from Cambridge Isotope Laboratories and vacuum distilled from sodium benzophenone ketyl. Chloroform-*d* and dichloromethane-d_2 were also purchased from Cambridge Isotope Laboratories and vacuum distilled from calcium hydride. Alumina and Celite were activated by heating under vacuum at 200 ˚C for 12 h. Acenaphthenequinonedioxime, tetradentate salan ligands (**1** and **6**^{tBu}), methyl aluminum complexes (**2**, **2**^{tBu}**,** and **7**^{tBu}), and metal glyoxime precursors (**4a-Fe** and **4b-Pd**) were all synthesized according to literature procedures.[2-4] All other materials were used as received. All ^{1}H, ^{13}C, and 2D NMR spectra were recorded on Varian Mercury 300 MHz, Varian 400 MHz, or Varian INOVA-500 or 600 MHz spectrometers at room temperature, unless denoted otherwise. Chemical shifts are reported with respect to internal solvent: 7.16 ppm and 128.06 (t) ppm (C_6D_6), 7.26 ppm and 77.16 ppm ($CDCl_3$), and 5.32 ppm and 53.84 ppm (CD_2Cl_2) for ^{1}H and ^{13}C NMR data, respectively. The chemical shifts in the ^{27}Al NMR data were referenced to a 1.1 M solution of $Al(NO_3)_3$ in D_2O. Elemental analysis was performed by Midwest Microlab, LLC (Indianapolis, IN).



Synthesis of 3b

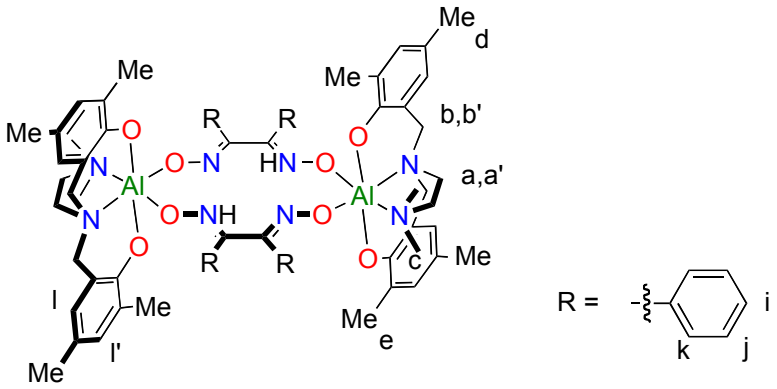
Al(salan) (0.17 g, 0.43 mmol, 1 equiv), acenaphthenequinonedioxime (0.09 g, 0.43 mmol, 1 equiv), and THF (10 mL) were added to 20 mL vial with a stirbar at -35 °C in the glovebox and the mixture was stirred for 12 h. Volatiles were removed under vacuum to yield a yellow orange residue (0.19 g, 74 % yield). **3b** was used as isolated without any further purification. X-ray quality crystals were grown from a vapor diffusion of pentane into toluene. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 14.33 (2H, s, A), 8.60 (2H, d, *J*=7.1, B), 8.35 (2H, d, *J*=7.0, B'), 7.94 (2H, d, *J*=8.2, C), 7.77 (2H, d, *J*=8.3, C'), 7.68 (2H, dd, *J*=8.3, 7.0, D), 7.56 (2H, dd, *J*=8.4, 7.0, D'), 6.74 (4H, d, *J*=2.4, E), 6.72 (4H, d, *J*=2.5, E), 4.97 (4H, d, *J*=12.7, F), 3.29 (4H, d, *J*=12.8, F), 2.76 (4H, t, *J*=6.0, G), 2.28 (2s, 24H, H, I), 2.12 (4H, t, *J*=6.0, J), 1.82 (s, 12H, K). ^{13}C NMR (101 MHz, C_6D_6): δ 158.59 (1), 144.92 (2), 144.71 (3), 137.09 (4), 132.67 (5), 130.65 (6), 129.98 (7), 129.18 (8), 128.33 (9), 127.92 (6), 127.56 (10), 126.74 (11), 126.18 (12), 125.66 (13), 123.86 (14), 123.06 (15), 121.25 (16), 64.56 (17), 58.11 (18), 50.24 (19), 48.18 (20), 20.64 (21), 16.06 (22) ppm. Anal. Calcd for $C_{68}H_{72}Al_2N_8O_8$: C, 68.90; H, 6.29; N, 9.45. Found: C, 69.01; H, 6.12; N, 9.18.



Synthesis of 5b-Pd

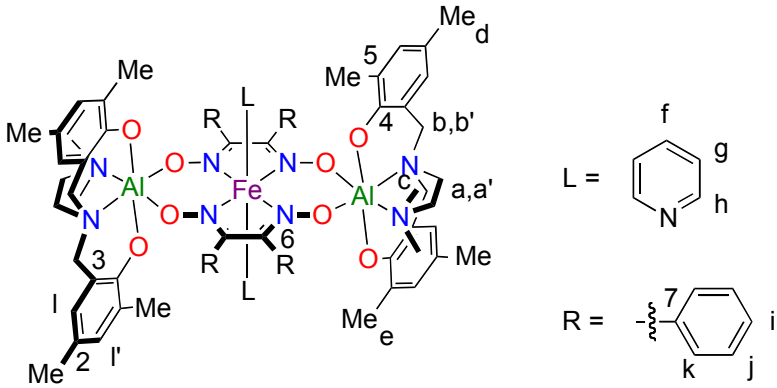
Route A: **5b-Pd** was also synthesized by the addition of **3b** (0.050 g, 0.042 mmol) to $Pd(OAc)_2$ (0.021 g, 0.095 mmol, 2.25 equiv) in THF (5 mL) in a 20 mL vial in the glovebox at room temperature. The mixture was stirred over 13 h during which time the mixture turned dark orange brown with precipitate. Volatiles were removed under vacuum and the desired product was isolated by washing over Celite with hexanes and collecting the filtrate from toluene. Volatiles were again removed *in vacuo*, and 0.033 g of pale orange solid was collected (61 % yield).

Route B: $Pd(OAc)_2$ (0.10 g, 0.45 mmol) and acenaphthenequinonedioxime (0.19 g, 0.89 mmol, 2 equiv) were added to a Schlenk tube with methanol (10 mL) and the mixture was stirred for 3 h resulting in a color change of the heterogeneous mixture to orange. Volatiles were removed under vacuum, dry THF (10 mL) was added via cannula and then removed *in vacuo* twice. **2** (0.35 g, 0.89 mmol, 2 equiv) and dry THF (10 mL) were added by syringe and the reaction was stirred for 12 h. Volatiles were removed under vacuum and the resulting yellow orange solid was brought into the glovebox. Stirred solid in THF (10 mL) for 1 h and collected yellow orange precipitate (0.36 g, 63 % yield) which includes 2 sets of peaks by ^{1}H NMR spectroscopy in a 10:1 ratio. X-ray quality crystals were grown from a vapor diffusion of hexanes into THF. ^{1}H NMR (600 MHz, C_6D_6): *major species:* δ 8.37 (2H, d, *J*=7.0, A), 8.16 (2H, d, *J*=7.0, A), 7.37 (2H, d, *J*=8.2, B), 7.32 (2H, d, *J*=8.4, B), 7.25 (2H, dd, *J*=7.2, *J*=8.0, C), 7.09 (2H, dd, *J*=7.0, *J*=8.3, C), 6.96 (4H, d, *J*=1.6, D), 6.74 (4H, d, *J*=1.9, E), 5.10 (2H, d, *J*=12.6, F), 3.01 (2H, d, *J*=12.7, F), 2.39 (12H, s, G), 2.36 (4H, t, *J*=5.8, H), 2.26 (12H, s, I), 2.17 (12H, s, J), 1.71 (4H, t, *J*=6.0, K) ppm; *minor species:* δ 8.66 (2H, d, *J*=6.7, A), 7.81 (2H, d, *J*=7.0, A), 7.44 (2H, d, *J*=8.2, B), 7.32 (2H, d, B), 7.22 (2H, dd, C), 7.04 (2H, dd, C), 6.95 (4H, d, *J*=1.6, D), 6.55 (4H, d, E), 4.93 (2H, d, *J*=13.0, F), 2.98 (2H, d, *J*=12.7, F), 2.63 (12H, s, G), 2.26 (6H, s, J), 2.23 (4H, t, H), 2.19 (12H, s, I), 2.11 (6H, s, J), 1.78 (4H, t, *J*=6.1, K) ppm. ^{13}C NMR (from 2D spectra, C_6D_6): δ 158.7 (1), 153.1 (2), 140.8 (3), 132.6 (4), 131.2 (5), 128.3 (6), 127.9 (6), 127.4 (7), 127.2 (8), 127.0 (9), 126.9 (8), 126.5 (5), 122.5 (10), 122.5 (11), 122.4 (11), 121.0 (12), 64.6 (13), 64.5 (13), 57.8 (14), 50.0 (15), 47.9 (16), 20.8 (17), 16.7 (18) ppm. Anal. Calcd for $C_{68}H_{72}Al_2N_8O_8Pd$: C, 63.33; H, 5.63; N, 8.69. Found: C, 63.20; H, 5.48; N, 8.39.



Synthesis of 3a

The macrocycle was synthesized following the synthesis procedure for **3b**. A stirring solution of **2** (0.158 g, 0.387 mmol) in THF was treated with a slurry of diphenylglyoxime (0.096 g, 0.398 mmol) in THF. The solution was stirred for 3 hours over which the solution became yellow. The solvent was removed *in vacuo* to yield a pale yellow solid. The macrocycle **3a** was used as isolated without any further purification. Yield 0.211 g, 88 %. ^{1}H NMR (300 MHz, C_6D_6) δ 14.41 (2H, s, N*H*), 7.86 (8H, m, k) 6.98 (4H, t, *J* = 7.6 Hz, i), 6.83 (8H, m, j), 6.76 (4H, s, l,l'), 6.69 (4H, s, l,l'), 4.89 (4H, d, *J* = 12.9 Hz, b,b'), 2.79 (4H, d, *J* = 13.1 Hz, b,b'), 2.38 (12H, s, e), 2.32 (4H, m, a,a'), 2.18 (12H, s, c), 2.15 (12H, s, d), 1.75 (4H, m, a,a') ppm. Anal. Calcd for $C_{72}H_{82}Al_2N_8O_8$: C, 69.66; H, 6.66; N, 9.03; Found: C, 69.07; H, 6.69; N, 8.69 %.

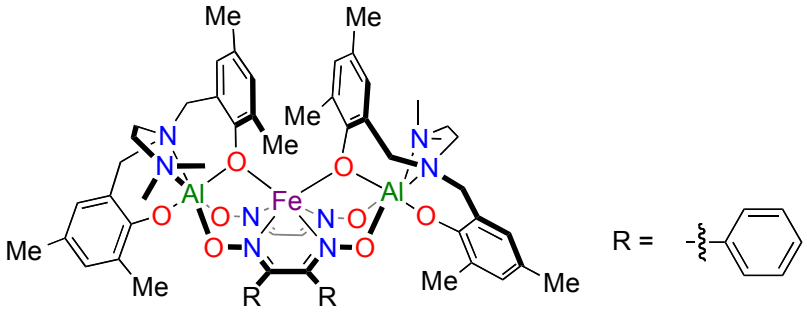


Synthesis of 5a-Fe

Route A: In a 20 ml vial (0.043 g, 0.062 mmol) of **4a-Fe** was stirred in about 2 ml of THF. To this was added (0.050 g, 0.126 mmol) of **2** as a solution in a small amount of THF. The reaction was stirred at ambient temperature for 3 days. Over the reaction time the solid **4a-Fe** became soluble. The volitiles were removed under vacuum and the resulting purple solid was washed with Et_2O and benzene. The benzene was removed from the benzene fraction via vacuum and the resulting solid was dissolved in minimal amounts of THF. Small amounts of hexanes were added to the saturated solution resulting in precipitation of a purple solid. The solid was collected via filtration over a fine frit. Yield 0.033 g, 36 %.

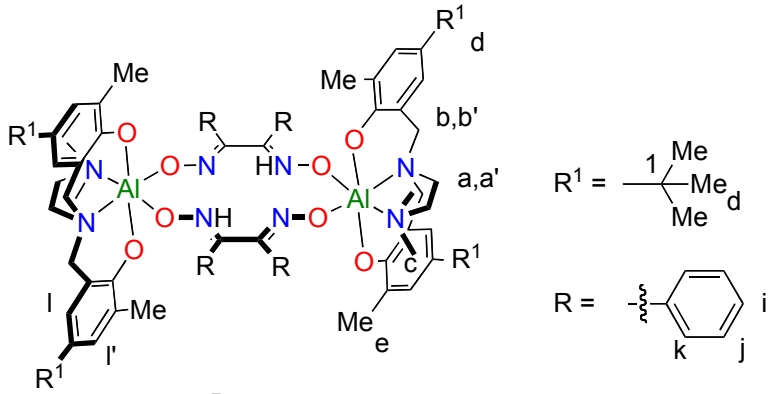
Route B: Sodium hexamethyldisilazide (0.030 g, 0.163 mmol) was added to a solution of **3a** (0.100 g, 0.081 mmol) in THF. The solution was stirred for 2 hours and the solvent was removed via vacuum. The resulting white residue was washed with pentane to remove the bis(trimethylsilyl)amine. The bis(trimethylsilyl)amine free solid was taken up in THF and mixed with a solution of $FeCl_2$ (0.010 g, 0.079 mmol) in THF. The solution immediately turned a dark

purple and was stirred for an hour. After an hour excess pyridine was added to the solution upon which the color changed from dark purple to a reddish purple. The solvent was removed *in vacuo* yielding the a purple red solid which was washed with ether. Yield 0.060 g, 52 %, about 90 % pure. To date, an analytically pure sample has yet to be obtained due to contamination of what is believed to be another isomer of the desired complex. ^{1}H NMR (500 MHz, C_6D_6) δ 9.30 (4H, d, *J*=5.6 Hz, h), 7.33 (4H, m, *J*=5.8 Hz, i), 6.98 (16H, m, j,l), 6.95 (4H, s, l'), 6.79 (2H, t, *J*=8.2 Hz, f), 6.63 (4H, m, g), 6.61 (4H, s, l), 4.61 (4H, d, *J*=13.0 Hz, b'), 2.61 (4H, d, *J*=12.9 Hz, b), 2.36 (6H, s, d), 2.15 (4H, m, a'), 1.97 (6H, s, e), 1.80 (6H, s, c), 1.64 (4H, m, a) ppm. ^{13}C{^{1}H} (126 MHz, C_6D_6) δ 159.08 (4), 158.35 (6), 156.67 (h), 135.70 (7), 134.57 (f), 131.41 (l'), 130.49 (i), 130.43 (k), 127.63 (j), 127.25 (l), 126.01 (5), 122.59 (g), 122.15 (3), 121.80 (2), 64.97 (b,b'), 58.18 (a,a'), 50.11 (a,a'), 47.68 (c), 20.89 (d), 16.74 (e) ppm. MS ESI (m/z): calcd, 1453.46 (M+); found 1452.7 (M+) (dipyridine) and 1390.2 (M+) (monopyridine with an oxygen)



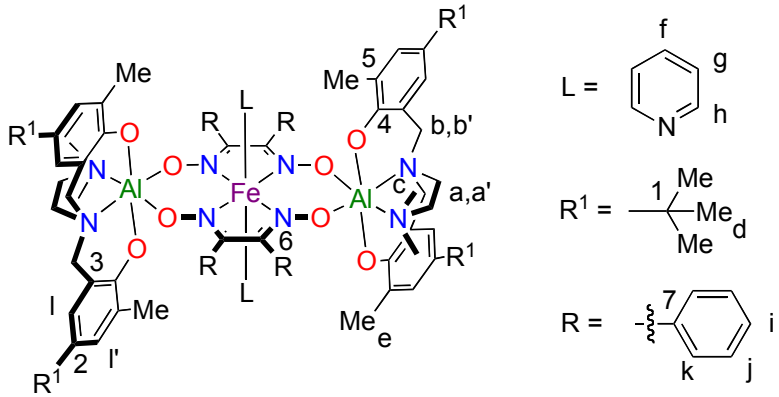
Synthesis of 5a-Fe-O bridge

A solution of **2** (0.248 g, 0.200 mmol) in THF was treated with a solution of Sodium hexamethyldisilazide (0.073 g, 0.400 mmol) also in THF. The solution was stirred for 3 hours over which the solution lost some of its color. After 3 hours the solvent was removed *in vacuo* resulting in a pale yellow white solid. The solid was washed with pentane resulting in a white THF soluble solid (0.116 g, 0.090 mmol, **3a-Na$_2$**). To a THF solution of this disodium salt was added a slurry of $FeCl_2$ in THF (0.0115 g, 0.091 mmol). Upon addition the solution immediately became a dark black with an orange hue. The solution was stirred for 4 hours and the THF was removed *in vacuo*. The resulting dark brown solid was washed with diethyl ether resulting in an orange solid which was extracted using DCM. The DCM was removed *in vacuo* resulting in a dark orange solid paramagnetic material. Alternatively, 4 can be synthesized by removing the pyridines from **5a-Fe**, by dissolving **5a-Fe** in a high boiling solvent and removing the solvent *in vacuo*. Crystals were grown from a concentrated solution of **5a-Fe** in THF layered with hexanes. Yield 0.066 g, 57 %. ^{1}H NMR (300 MHz, CD_2Cl_2) δ 18.46, 15.23, 12.84, 11.02, 10.67, 9.82, 8.97, 7.13, 6.68, 5.26, 4.96, 4.27 ppm.



Synthesis of 3a^{tBu}

The macrocycle was synthesized following the synthesis procedure for **3a**. A stirring solution of **2**^{tBu} (0.100 g, 0.021 mmol) in THF was treated with a slurry of diphenylglyoxime (0.050 g, 0.021 mmol) in THF. The solution was stirred for 3 hours over which the solution became yellow. The solvent was removed *in vacuo* to yield a pale yellow solid. The Al(salan)$_2$(diphenylglyoxime)$_2$ macrocycle was used as isolated without any further purification. ^{1}H NMR (300 MHz, C_6D_6) δ 14.10 (2H, s, N*H*), 7.85 (4H, d, *J* = 6.7 Hz, l,l') 7.61 (4H, t, *J* = 7.6 Hz, l,l'), 6.92 (8H, m, k), 6.82 (8H, m, j), 6.65 (4H, m, i), 4.82 (4H, d, *J* = 12.7 Hz, b,b'), 2.81 (4H, d, *J* = 12.9 Hz, b,b'), 2.32 (12H, s, e), 2.23 (4H, m, a,a'), 2.02 (12H, s, c), 1.78 (4H, m, a,a'), 1.48 (36H, s, d) ppm.



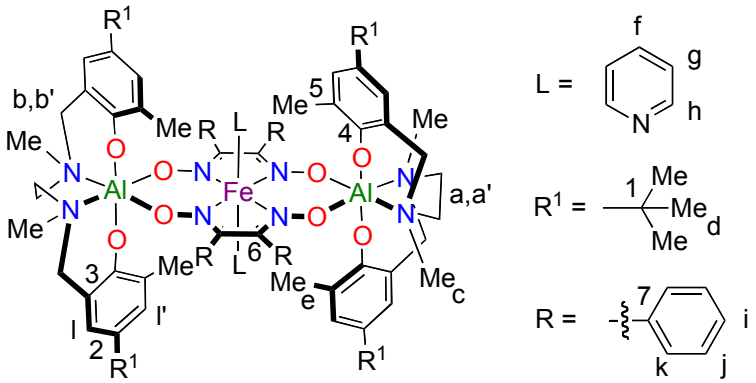
Synthesis of 5a^{tBu}-Fe

5a^{tBu}-Fe was synthesized and purified according to the synthesis procedures of **5a-Fe**.

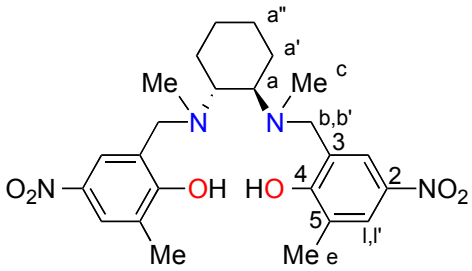
Route A: In a 20 ml vial 0.072 g (0.010 mmol) of **4a-Fe** was stirred in about 2 ml of THF. To this was added 0.110 g (0.023 mmol) of the **2**^{tBu} complex as a solution in a small amount of THF. The reaction was stirred at ambient temperature for 16 days. Over the reaction time the solid **4a-Fe** glyoxime became soluble. The volitiles were removed under vacuum and the resulting purple red solid was washed with hexanes, pentane, diethyl ether, and toluene. The toluene fraction was concentrated via vacuum and a small amount of hexanes was added to the saturated solution resulting in precipitation of a purple solid. The solid was collected via filtration over a fine frit. Yield 0.071 g, 44 %.

Route B: Sodium hexamethyldisilazide 0.036 g (0.200 mmol) was added to a solution of **3a^{tBu}** (0.141 g, 0.100 mmol) in THF. The solution was stirred for 2 hours and the solvent was removed via vacuum. The resulting white residue was washed with pentane to remove the bis(trimethylsilyl)amine. The bis(trimethylsilyl)amine free solid (0.126 g, 0.090 mmol) was taken up in THF and mixed with a solution of Fe(II)Cl$_2$ (0.011 g, 0.090 mmol) in THF. The

solution immediately turned a dark purple and was stirred for an hour. After an hour excess pyridine was added to the solution upon which the color changed from dark purple to a reddish purple. The solvent was removed in vacuo yielding a purple red solid which was washed with pentane and hexanes and extracted with diethyl ether. Yield 0.098 g, 67 %
^{1}H NMR (300 MHz, C_6D_6): δ 9.26 (4H, d, *J*=5.5 Hz, h), 7.41 (4H, d, *J*=8.4 Hz, g), 7.21 (8H, s, k), 6.97 (8H, s, j), 6.89 (8H, s, l), 6.83 (4H, t, *J*=6.7 Hz, i), 6.58 (2H, t, *J*=6.7 Hz, f), 4.65 (4H, d, *J*=12.9 Hz, b,b'), 2.71 (4H, d, *J*=13.3 Hz, b,b'), 2.15 (4H, m, a,a'), 2.08 (6H, s, e), 1.81 (6H, s, c), 1.63 (4H, m, a,a'), 1.44 (36H, s, d) ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 159.02 (4), 158.88 (6), 156.46 (h), 135.80 (7), 134.24 (2), 130.62 (f), 130.37 (k), 127.66 (j), 127.53 (i), 127.44 (l,l'), 125.67 (5), 123.18 (l,l'), 122.52 (g), 121.53 (3), 65.65 (b,b'), 58.10 (a,a'), 50.33 (a,a'), 47.64 (c), 33.90 (1), 32.33 (d), 17.12 (e) ppm. Anal. Calcd for $C_{94}H_{114}Al_2FeN_{10}O_8$: C, 69.62; H, 7.09; N, 8.64; Found C, 69.36; H, 7.33; N, 8.63

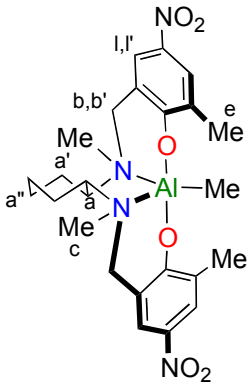


Synthesis of 8^{tBu}
In a round bottom flask **4a-Fe** (0.692 g, 0.98 mmol) was stirred in 10 ml of toluene at ambient temperature. To this purple slurry was added a solution of the **7^{tBu}** (0.999 g, 2.08 mmol) in toluene. The solution was stirred for 14 hours. After 14 hours toluene was removed in vacuo yielding a purple solid. The solid was washed with hexanes, Et_2O, and toluene. The toluene washed was pumped down to a solid yielding clean 6. Yield: 0.688 g, 43 % ^{1}H NMR (500 MHz, C_6D_6) δ 9.21 (4H, d, *J* = 4.9 Hz, h), 7.31 (8H, d, *J* = 7.3 Hz, k), 7.21 (4H, d, *J* = 2.4 Hz, l'), 7.01 (8H, t, *J* = 7.5 Hz, j), 6.94 (4H, m, i), 6.75 (2H, t, *J* = 7.6 Hz, f), 6.74 (4H, d, *J* = 2.5 Hz, l), 6.30 (4H, t, *J* = 7.0 Hz, g), 4.49 (4H, d, *J* = 12.8 Hz, b,b'), 2.69 (4H, d, *J* = 9.0 Hz, a,a'), 2.57 (4H, d, *J* = 13.1 Hz, b,b'), 2.14 (12H, s, e), 1.90 (12H, s, c), 1.38 (36H ,s, d), 0.89 (4H , d, *J* = 9.1 Hz, a,a') ppm. ^{13}C{^{1}H} NMR (126 MHz, C_6D_6) δ 158.90 (4), 157.44 (6), 156.83 (h), 135.99 (2), 135.87 (7), 134.16 (f), 130.58 (k), 127.75 (j), 127.43 (i), 126.90 (l'), 126.68 (5), 123.14 (l), 122.65 (g), 120.89 (3), 63.73 (b,b'), 49.97 (a,a'), 46.85 (c), 33.88 (1), 32.30 (d), 17.62 (e) ppm. Anal. Calcd for $C_{94}H_{114}Al_2FeN_{10}O_8$: C, 69.62; H, 7.09; N, 8.64; Found, C, 69.49; H, 6.96; N, 8.44;



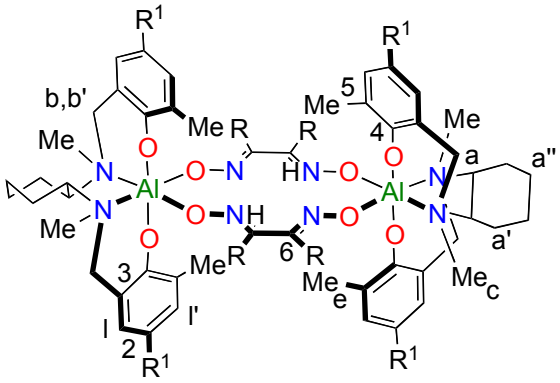
Synthesis of 9^{NO2}

This ligand variant was synthesized using a modified literature procedure.[5] A solution of N,N'-dimethylcyclohexane-1,2-diamine (0.233 g, 1.63 mmol) and diisopropylethylamine (0.424 g, 3.28 mmol) in THF (7.5 ml) at 0°C (ice bath) was treated with a cold solution (ice bath) of 2-(chloromethyl)-6-methyl-4-nitrophenol (0.661 g, 3.28 mmol) in THF (5 ml). The solution was stirred for 16 hours during which a yellow precipitate formed. The resulting slurry was filtered using a medium glass frit and washed with 3x 20 ml of cold MeOH. The resulting off white solid was dried under vacuum. Yield 0.298 g, 38 % ^{1}H NMR (300 MHz, $CDCl_3$), δ 11.99 (2H, br s, O*H*) 8.01 (2H, d, J = 2.8 Hz, l,l'), 7.84 (2H, d, J = 2.4 Hz, l,l'), 3.91 (4H, d, J = 13.2 Hz, b,b'), 3.59 (2H, br s, b,b'), 2.83 (2H, m, a), 2.29 (6H, s, e), 2.14 (6H, s, c), 2.11 (2H, m, a"), 1.91 (2H, s, a'), 1.27 (4H, br m, a',a") ppm. ^{13}C{^{1}H} NMR (from 2D spectra, 126 MHz, $(CD_3)_2SO$) δ 166.98 (4), 135.74 (2), 126.12 (5), 125.81 (l'), 127.34 (l), 122.58 (3), 62.56 (b,b'), 25.54 (c), 22.78 (a), 16.68 (a), 16.53 (e) ppm from . ESI-MS Calc. (M) 472.2322 Found. 473.2 (MH+)

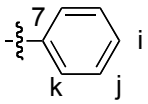


Synthesis of 10^{NO2}

The synthesis of **10^{NO2}** was synthesized using trimethylaluminum following a published procedure for similar aluminium alkyl complexes.[6,7] A freshly thawed slurry of **9^{NO2}** (0.024 g, 0.052 mmol) in toluene (5 ml) was treated with a thawed solution of trimethylaluminum (0.004g, 5.2 µl, 0.053 mmol). Upon mixing the solid particulates dissolved and the solution became a dark orange color which faded after a few minutes resulting in a light yellow solution. The solution was allowed to stir for 18 hours. During this time the solution became a slurry. The solvent was removed *in vacuo* resulting in a light yellow powder which was used without further purification. Yield 0.026 g, 99 % ^{1}H NMR (300 MHz, CD_2Cl_2), δ 8.04 (2H, m, l,l'), 7.85 (2H, m, l,l'), 4.00 (2H, *J* = 13.4 Hz, b,b'), 3.50 (2H, *J* = 13.0 Hz, b,b'), 2.95 (2H, m, a), 2.32 (3H, s, e), 2.28 (6H, m, e',c'), 2.18 (2H, m, a"), 2.10 (3H, s, c), 1.97 (2H, m, a'), 1.51(2H, m, a"), 1.25(2H, m, a'), -0.69 (3H, s, AlCH_3) ppm.

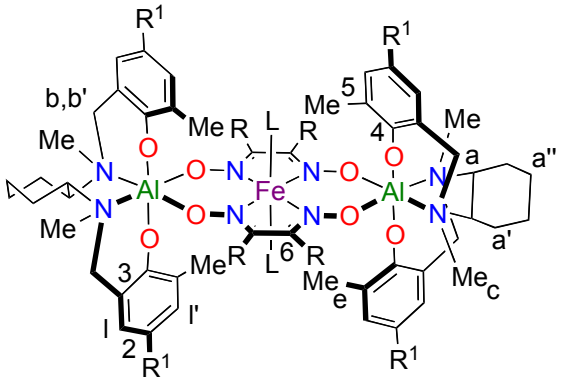


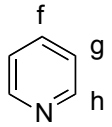
$R^1 = NO_2$

R = 

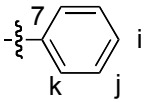
Synthesis of 11^{NO2}

The macrocycle was synthesized following the synthesis procedure for **3a**. A stirring solution of **10^{NO2}** (0.100 g, 0.019 mmol) in THF was treated with a slurry of diphenylglyoxime (0.046 g, 0.019 mmol) in THF. The solution was stirred for 3 hours over which the solution became yellow. The solvent was removed *in vacuo* to yield a pale yellow solid. **11^{NO2}** was used as isolated without any further purification. Yield 0.139 g, 97 %. ^{1}H NMR (300 MHz, C_6D_6) δ 13.98 (2H, s, N*H*), 7.77 (4H, d, *J* = 2.9 Hz, l,l'), 7.59 (12H, m, i and j), 7.29 (12H, m, k and l,l'), 4.41 (4H, d, *J* = 13.5 Hz, b,b'), 3.25 (4H, d, *J* = 13.6 Hz, b,b'), 2.44 (4H, m, a), 2.06 (12H, s, e), 1.92 (12H, s, c), 1.72 (4H, m, a'), 1.59 (4H, m, a"), 1.03 (4H, m, a'), 0.80 (4H, m, a") ppm. ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 165.86 (4), 149.36 (6), 136.44 (2), 130.11 (k), 128.28 (j), 127.97 (5), 127.40 (7), 126.39 (l'), 123.49 (l), 120.79 (3), 58.45 (b,b'), 56.39 (a), 39.97 (c), 24.01 (a"), 21.89 (a'), 16.18 (e) ppm. Anal. Calcd for $C_{76}H_{82}Al_2FeN_{12}O_{16}$: C, 61.95; H, 5.61; N, 11.41; Found: C, 61.91; H, 5.74; N, 11.29 %.



L = 

$R^1 = NO_2$

R = 

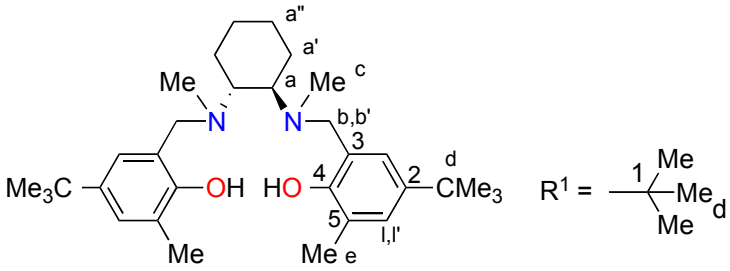
Synthesis of 12^{NO2}

Route A: To a slurry of **10^{NO2}** (0.150 g, 0.302 mmol) in toluene (5 ml) was added **4a-Fe** (0.101 g, 0.146 mmol) with THF (3 ml). The slurry was stirred for a total of 3 days, during which the solution took on a purple orange hue. From this colored solution a solid precipitated on the walls of the vial. After the allotted time the solvent was removed *in vacuo*. The solid was washed three times with hexanes to remove the excess toluene. The solid was fractioned with hexanes, diethylether, toluene, and THF. The desired product was found in the THF fraction. Yield 0.129 g, 52 %

Route B: Sodium hexamethyldisilazide (0.030 g, 0.163 mmol) was added to a solution of **11^{NO2}** (0.236 g, 0.160 mmol) in THF. The solution was stirred for 12 hours and the solvent was removed via vacuum. The resulting residue was washed with pentane to remove the

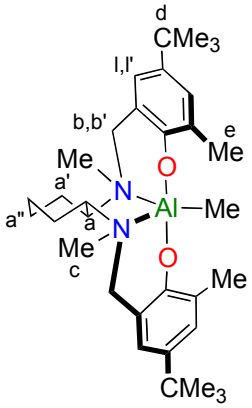
bis(trimethylsilyl)amine. The bis(trimethylsilyl)amine free solid (0.217 g, 0.143 mmol) was taken up in THF and mixed with a solution of $Fe(II)Cl_2$ (0.019 g, 0.146 mmol) in THF. The solution immediately turned a dark purple. The dark purple solution was stirred for 3 hours after which excess pyridine was added. Upon addition of pyridine the solution color changed from dark purple to a reddish purple. The solvent was removed *in vacuo* yielding a purple solid which was washed with benzene and extracted with THF. Yield 0.174 g, 72 %

^1H NMR (500 MHz, CD_2Cl_2), δ 8.61 (4H, s, h), δ 7.83 (4H, l',), δ 7.63 (d, 4H), δ 7.28 (m, 20H), δ 7.02 (dd, 4H), δ 6.37 (m, 2H), δ 4.15 (d, 4H), δ 2.89 (d, 4H), δ 1.80 (s, 12H), δ 1.75 (s, 12H) $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2) δ 166.85 (4), 159.75 (6), 155.16 (h), 135.81 (2), 134.82 (k), 129.75 (j), 128.35 (5) 128.25 (7) 127.76 (f), 126.35 (l'), 123.88 (l), 123.05 (g), 121.54 (3), 58.48 (b,b') , 56.27 (a), 40.97 (c), 24.40 (a"), 22.06 (a'), 16.69 (e) ppm. Anal. Calcd for $C_{86}H_{90}Al_2FeN_{14}O_{16}$: C, 61.28; H, 5.38; N, 11.63; Found: C, 61.13; H, 5.46; N, 11.43 %



Synthesis of 9^{tBu}

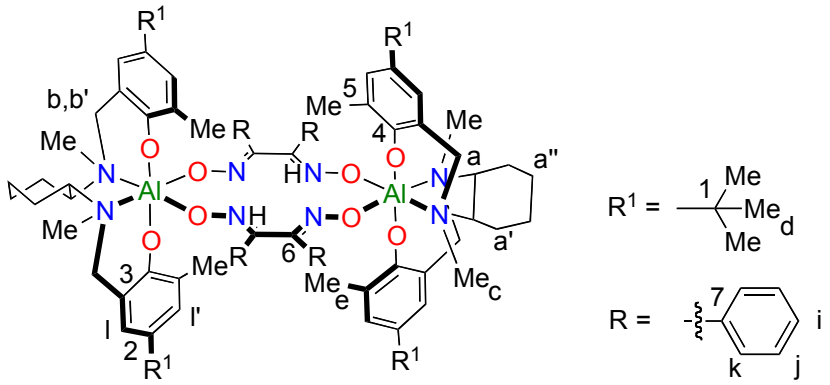
This compound was synthesized via a mannich condensation of the (R,R)-1,2-diammoniumcyclohexane mono-(+)-tartrate salt and 2-methyl-4-tert-butylphenol using a previously published procedure.[7,8] The amines were methylated following the same procedure resulting in the compound $\mathbf{9^{tBu}}$. ^1H NMR (300 MHz, $CDCl_3$), δ 10.01 (2H, br s, O*H*), 7.05 (2H, d, J = 2.1 Hz, l,l'), 6.82 (2H, d, J = 2.4 Hz, l,l'), 3.77 (2H, d, J = 13.2 Hz, b,b'), 3.66 (2H, d, J = 13.3 Hz, b,b'), 2.70 (2H, m, a), 2.20 (6H, s, e), 2.17 (6H, s, c), 2.01 (2H, m, a"), 1.81 (2H, d, a'), 1.27 (18H, s, d), 1.17 (4H, m, a',a") ppm. $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) δ 154.06 (4), 140.74 (2), 127.17 (l'), 124.73 (5), 123.32 (l), 121.26 (3), 61.65 (b,b'), 33.66 (1), 31.60 (d), 25.05 (c), 21.99 (a,a',a"), 16.23 (e) ppm. ESI-MS Calc. (M) 494.3872 Found. 495.3 (MH+)



Synthesis of 10^{tBu}

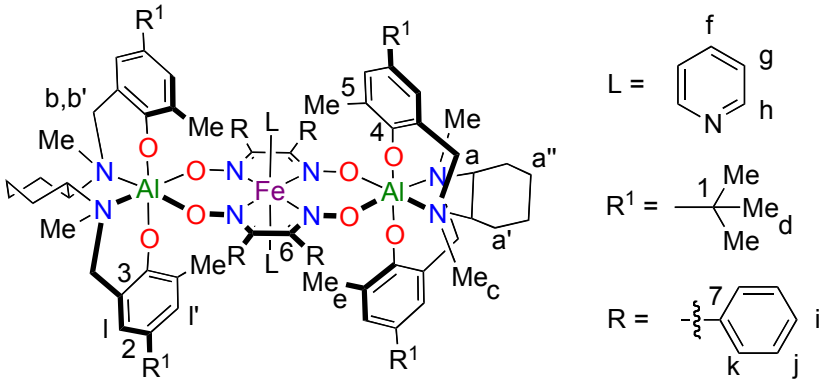
Compound $\mathbf{10^{tBu}}$ was synthesized using trimethylaluminum following a published procedure for similar aluminium alkyl complexes.[6,7] A slurry of $\mathbf{9^{tBu}}$ (0.956 g, 1.93 mmol) in toluene was

frozen in a coldwell. Upon freezing the solution was allowed to thaw upon which a freshly thawed solution of trimethylaluminum (0.139 g, 1.93 mmol) in toluene (3 ml) was added slowly. This mixture was allowed to warm to room temperature and left stirring for 12 hours. After 12 hours the solvent was removed in vacuo, yielding an off white solid which was used without further purification. Yield: 0.900 g, 87 % 1H NMR (300 MHz, C6D6) δ 7.32, 7.29, 6.90, 6.82, and 6.78 (l,l'), 3.61, 3.54, 3.32, 3.27, 2.79, 2.75, and 2.70 (b,b'), 2.63 and 2.43 (e), 2.29 and 1.99 (a), 1.88, 1.68, and 1.66 (c), 1.41, 1.39, and 1.39 (d), 1.21, 0.60, and 0.48 (a',a''), -0.40 (AlCH3) ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 156.06 (4), 155.89 (4), 138.33 (2), 137.68 (2), 127.43 (l'), 127.29 (l'), 126.93 (l'), 126.68 (5), 126.55 (5), 126.01 (5), 123.04 (l), 122.84 (l), 120.03 (3), 118.54 (3), 63.81 (b,b'), 60.73 (b,b'), 60.26 (b,b'), 59.48 (b,b'), 42.67, 36.77, 33.57 (1), 31.51 (d), 24.79 (a''), 24.54 (a''), 23.13(a'), 22.89 (a'), 22.72 (a'), 16.21 (e), 16.08 (e), 15.72 ($AlCH_3$) ppm multiple diastereomers in solution.^{27}Al NMR (104.7 MHz, 25 °C, CD_2Cl_2) δ 74.21 ppm, $\omega_{1/2}$ 6500 Hz.



Synthesis of 11^{tBu}

The macrocycle was synthesized following the synthesis procedure for **3a**. A stirring solution of **10^{tBu}** (0.105 g, 0.197 mmol) in THF was treated with a slurry of diphenylglyoxime (0.047 g, 0.196 mmol) in THF. The solution was stirred for 3 hours over which the solution became yellow. The solvent was removed in vacuo to yield a pale yellow solid. **11^{tBu}** was used as isolated without any further purification. It can also be purified through precipitation from pentane. Yield 0.145 g, 98 %. ^{1}H NMR (300 MHz, C_6D_6) δ 14.20 (2H, s, N*H*), 7.67 (8H, d, *J* = 7.1 Hz, k), 7.29 (4H, s, l,l'), 6.91 (12H, m, j,i), 6.78 (4H, m, l,l'), 4.54 (4H, d, *J* = 13.0 Hz, b,b'), 2.88 (4H, d, *J* = 13.1 Hz, b,b'), 2.57 (4H, m, a), 2.34 (12H, s, e), 2.06 (12H, s, c), 1.45 (36H, s, d), 1.25 (8H, m, a', a''), 0.38 (8H, m, a',a'') ppm. $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2) δ 156.69 (4), 148.27 (6), 136.31 (7), 131.56 (2), 130.12 (k), 128.76 (j), 127.53 (i), 126.99 (l'), 125.54 (5), 123.17 (l), 120.29 (3), 59.40 (b,b'), 55.56 (a), 39.89 (c), 33.49 (1), 31.67 (d), 24.31 (a''), 21.83 (a'), 16.05 (e). ^{27}Al NMR (104.7 MHz, 25 °C, CD_2Cl_2) δ 14.40 ppm, $\omega_{1/2}$ 4150 Hz. Anal. Calcd for $C_{92}H_{118}Al_2FeN_8O_8$: C, 72.80; H, 7.84; N, 7.38; Found: C, 72.68; H, 7.60; N, 7.12 %



Synthesis of 12^{tBu}

Route A: In a 100 mL round bottom, a solution of **10^{tBu}** (2.167 g, 4.05 mmol) was treated with a slurry of $Fe(DPG)_2(Py)_2$ (1.334 g, 1.93 mmol) in benzene at room temperature. The solution was stirred allowing for the produced methane to escape. After 24 hours the solvent was removed in vacuo. The crude solid was taken up in hexanes and filtered. The recovered solid was washed with diethyl ether and extracted with toluene. Purified **12^{tBu}** was precipitated from toluene by adding hexanes to the toluene mixture and cooling the mixture to -35˚C overnight. Another crop of purified solid can be obtained from the hexane fraction via cooling to -35˚C overnight. Yield 2.197 g, 66 %

Route B: Sodium hexamethyldisilazide (0.013 g, 0.069 mol) was added to a solution of **11^{tBu}** (0.503 g, 0.033 mol) in THF. The solution was stirred for 2 hours and the solvent was removed via vacuum. The resulting residue was triterated with THF to remove the bis(trimethylsilyl)amine. The bis(trimethylsilyl)amine free solid was taken up in THF and mixed with a slurry of $Fe(II)Cl_2$ (0.005 g, 0.039 mmol) in THF. The solution immediately turned a dark purple. The dark purple solution was stirred for one hour after which excess pyridine was added. Upon addition of pyridine the solution color changed from dark purple to a reddish purple. The solvent was removed in vacuo yielding a purple solid. The solid was washed with hexanes and a small amount of diethylether before it was extracted with toluene. The solvent was removed *in vacuo* yielding the same product as Route A. Yield 0.414 g, 72 %

^{1}H NMR (500 MHz, C_6D_6) δ 9.35 (4H, d, J = 5.5 Hz, h), 7.33 (8H, d, J = 7.4 Hz, k), 7.20 (4H, s, l'), 7.06 (8H, t, J = 7.4 Hz, j), 7.00 (4H, m, J = 7.1 Hz, i), 6.77 (2H, t, J = 7.6 Hz, f), 6.74 (4H, s, l), 6.34 (4H, t, J = 6.7 Hz, g), 4.54 (4H, d, J = 13.2 Hz, b'), 2.80 (4H, d, J = 13.4 Hz, b), 2.52 (4H, s, a), 2.17 (12H, s, e), 1.93 (12H, s, c), 1.35 (36H, s, d), 1.22 (4H, m, a'), 1.02 (4H, s, a''), 0.46 (4H, m, a'), 0.28 (4H, m, a'') ppm; ^{13}C{^{1}H} NMR (125.70 MHz, C_6D_6) δ 158.77 (6), 157.80 (4), 157.01 (h), 136.14 (7), 135.90 (2), 134.17 (f), 130.62 (k), 127.78 (j), 127.41 (i), 127.08 (l'), 126.17 (5), 122.82 (l), 122.56 (g), 121.27 (3), 59.90 (b,b'), 55.45 (a), 40.90 (c), 33.86 (1), 32.29 (d), 24.26 (a"), 21.78 (a'), 17.51 (e) ppm; ^{27}Al NMR (104.7 MHz, 25 °C, C_6D_6) δ 14.19 ppm, $\omega_{1/2}$ 9000 Hz. Anal. Calcd for $C_{102}H_{126}Al_2FeN_{10}O_8$: C, 70.82; H, 7.34; 8.10; Found C, 69.90; H, 7.24; N, 7.44 %

II. Nuclear Magnetic Resonance Spectra

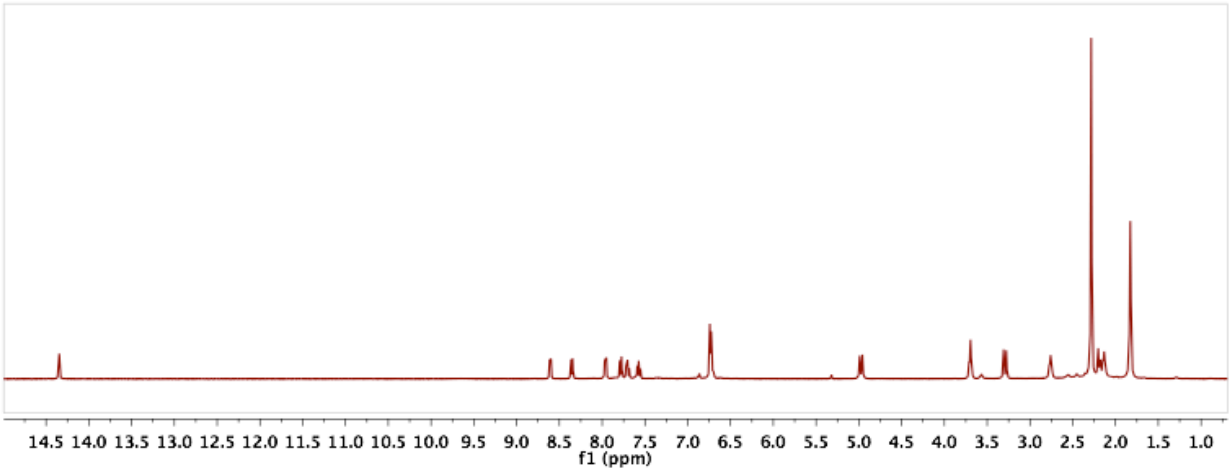


Figure S1. ^{1}H NMR spectrum of **3b** in CD_2Cl_2.

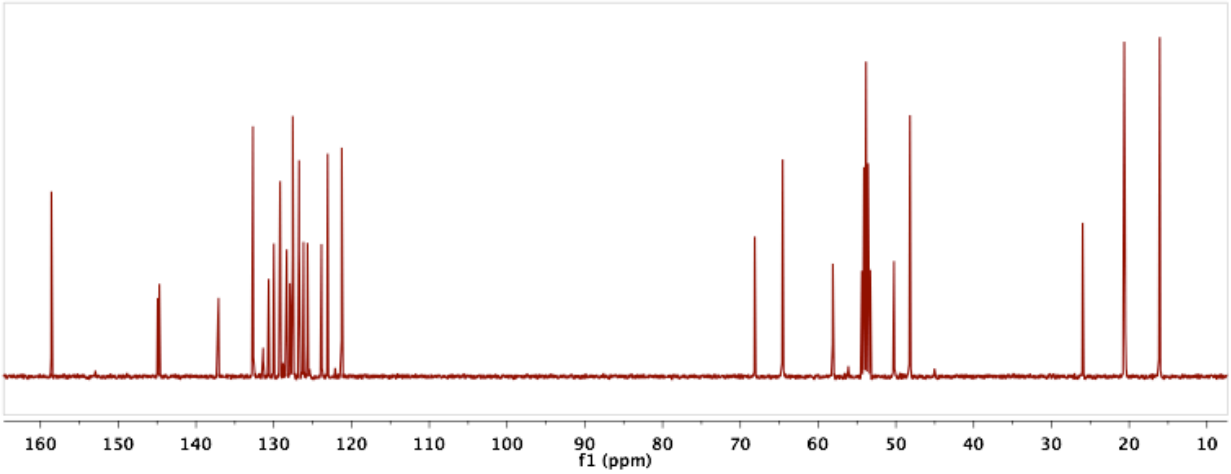


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of **3b** in CD_2Cl_2.

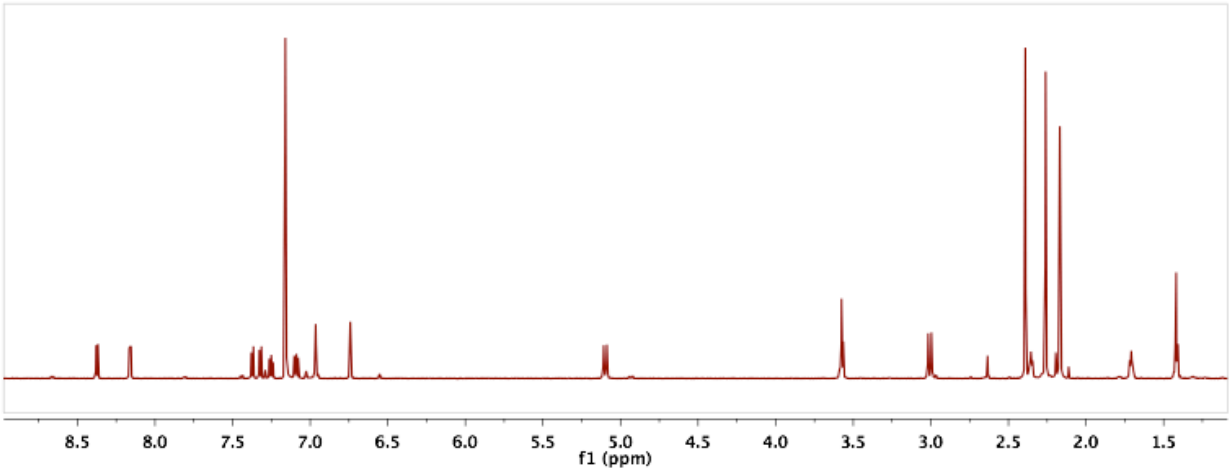


Figure S3. ^{1}H NMR spectrum of **5b-Pd** in C_6D_6.

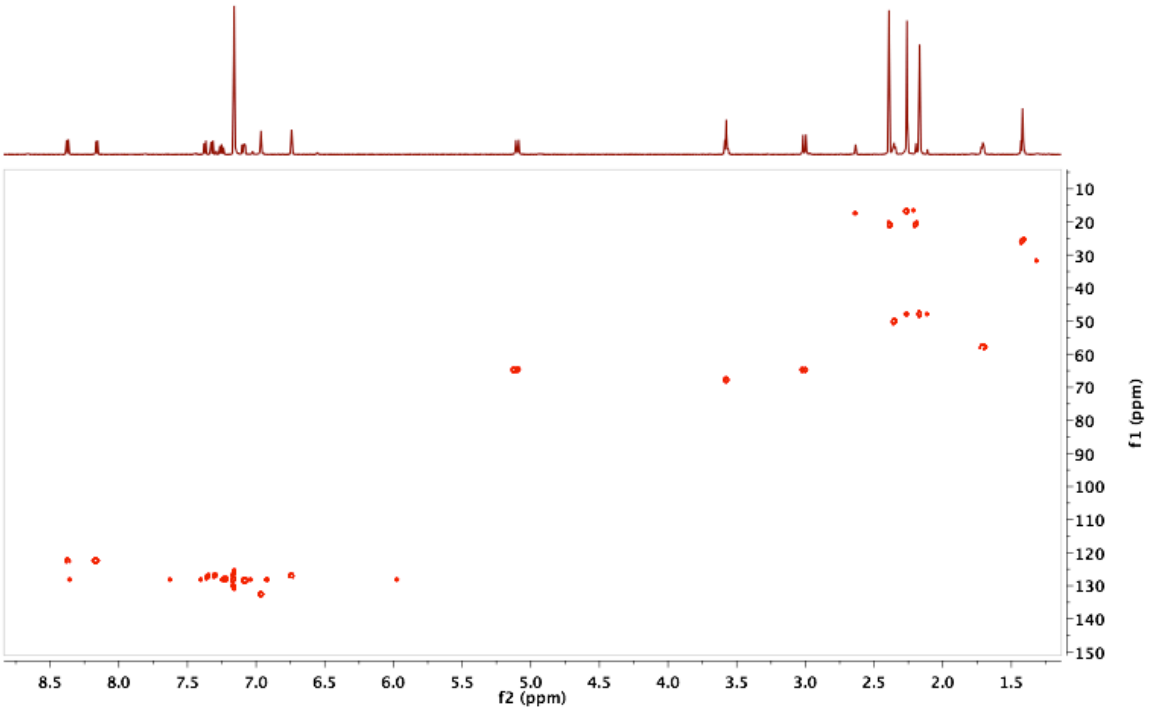


Figure S4. ^{1}H-^{13}C HSQCAD NMR spectrum of **5b-Pd** in C_6D_6.

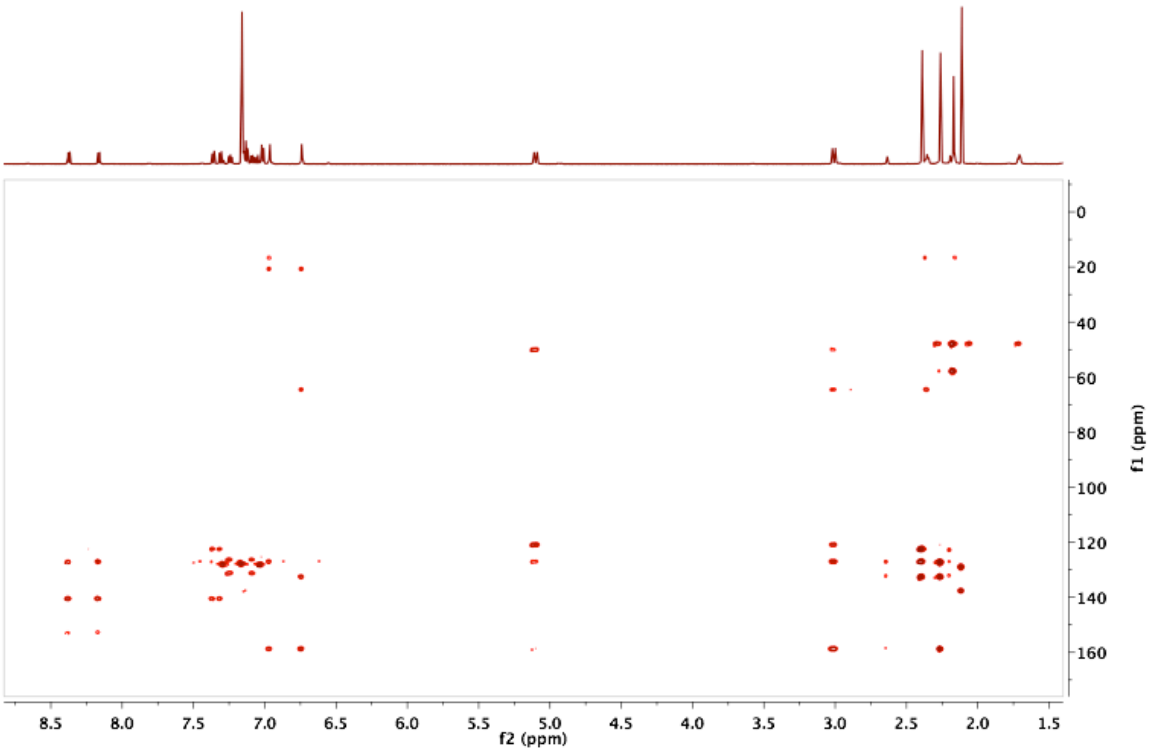


Figure S5. ^{1}H-^{13}C gHMBCAD NMR spectrum of **5b-Pd** in C_6D_6.

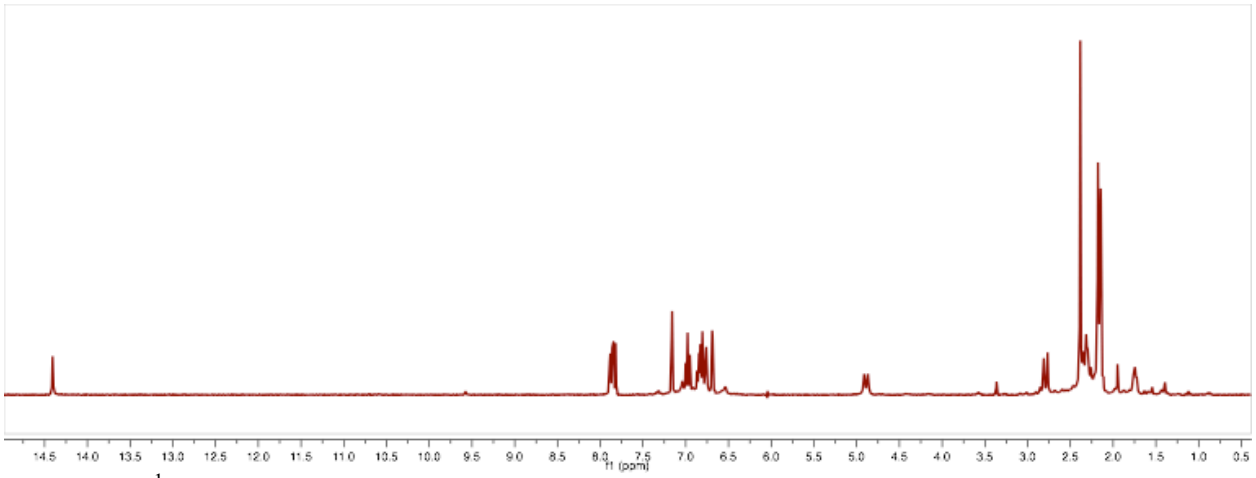


Figure S6. ^{1}H NMR spectrum of **3a** in C_6D_6.

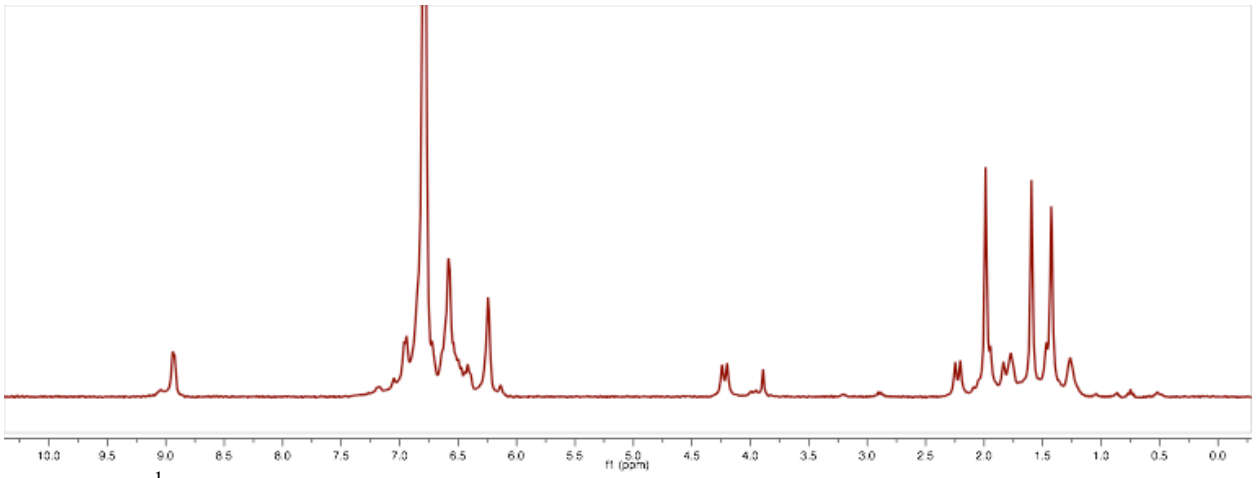


Figure S7. ^{1}H NMR spectrum of **5a-Fe** in C_6D_6.

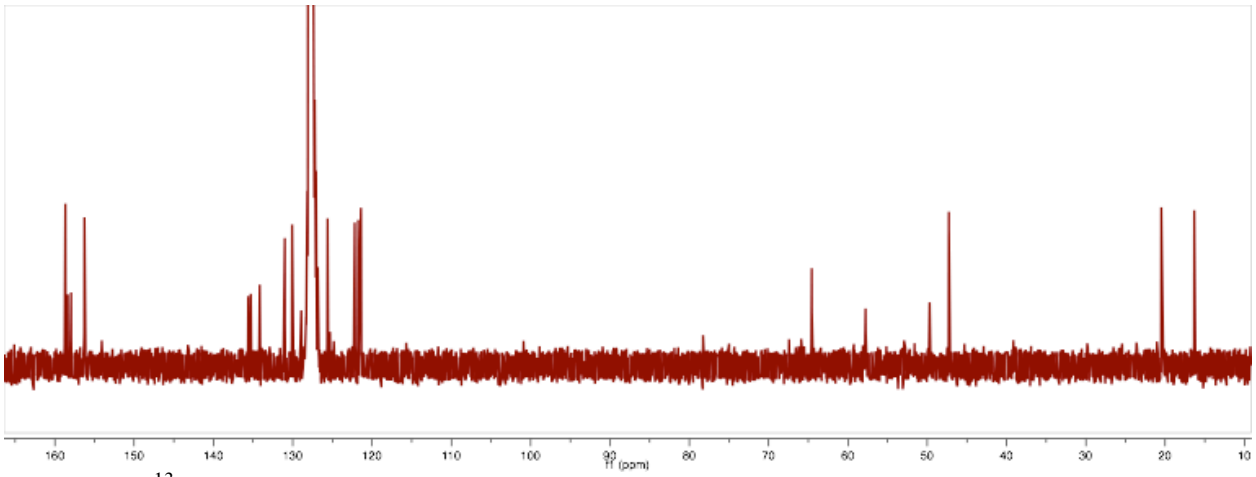


Figure S8. ^{13}C NMR spectrum of **5a-Fe** in C_6D_6.

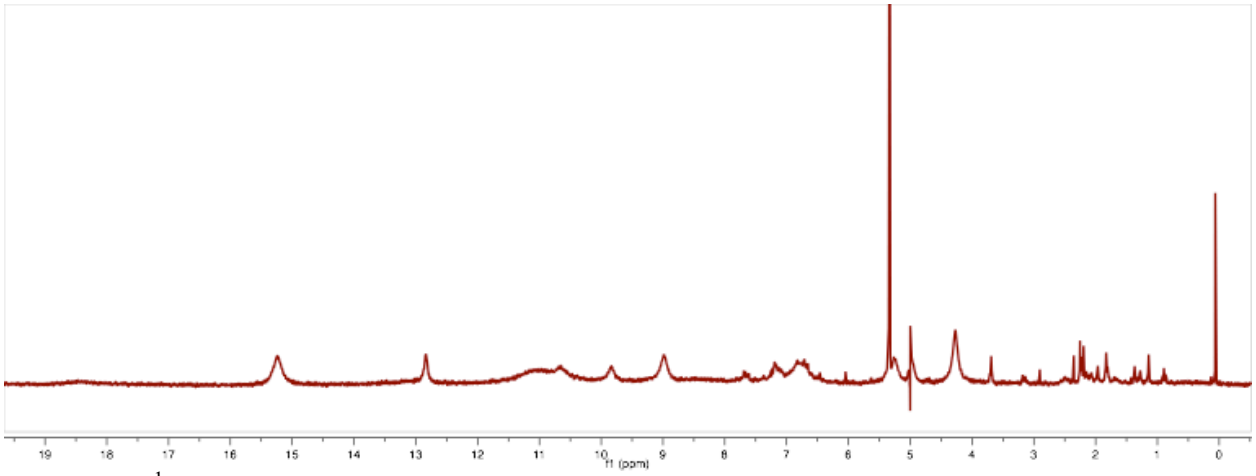


Figure S9. ^{1}H NMR spectrum of **5a-Fe-O bridge** in CD_2Cl_2.

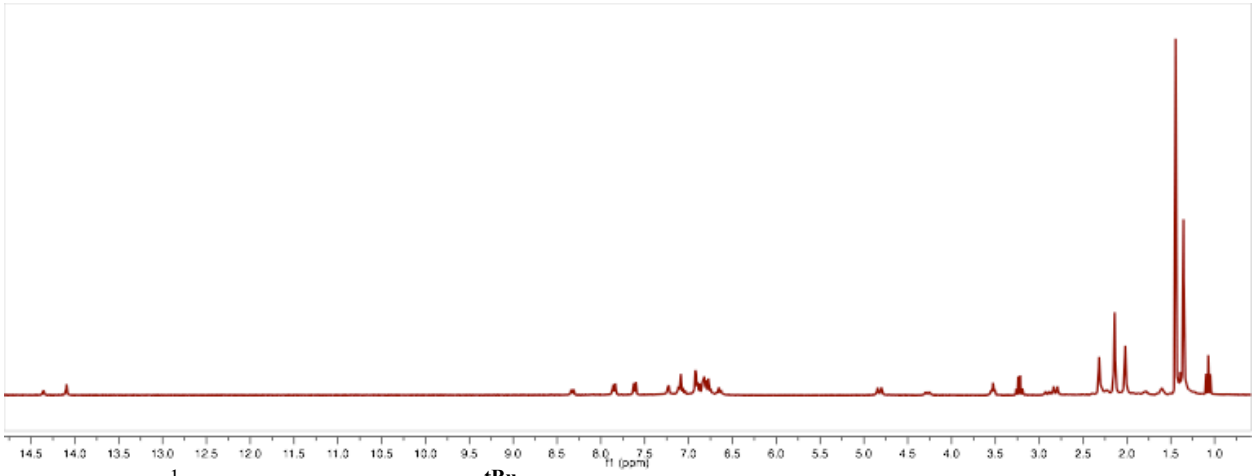


Figure S10. ^{1}H NMR spectrum of **3a^{tBu}** in C_6D_6.

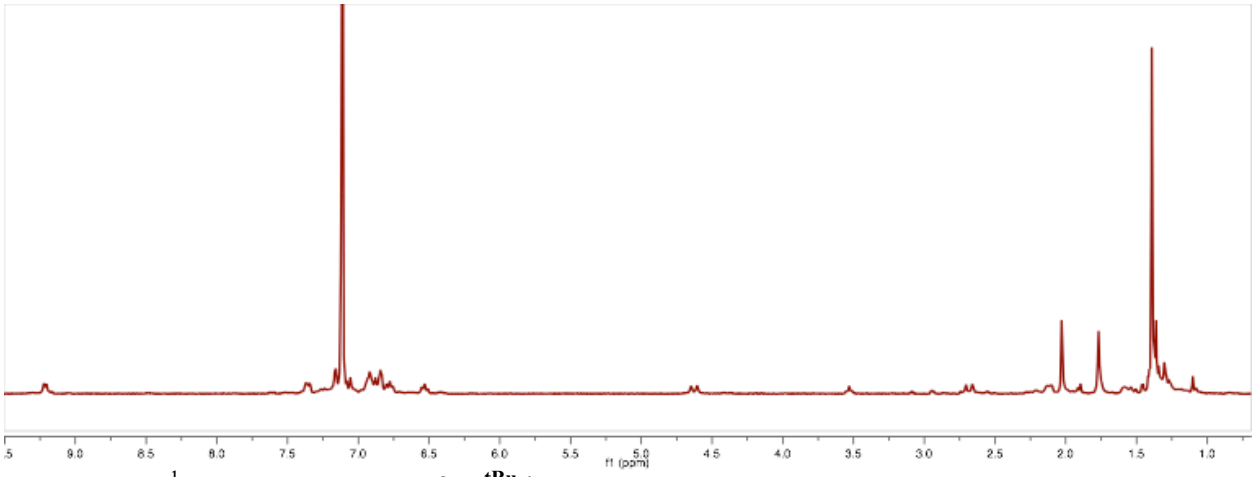


Figure S11. ^{1}H NMR spectrum of **5a^{tBu}** in C_6D_6.

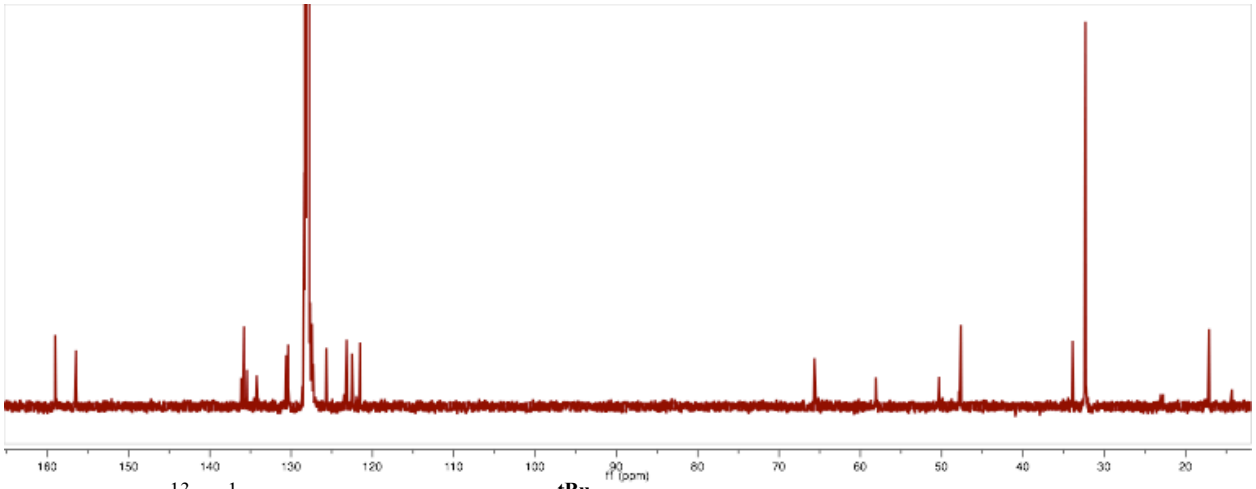


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **5a^{tBu}** in C_6D_6.

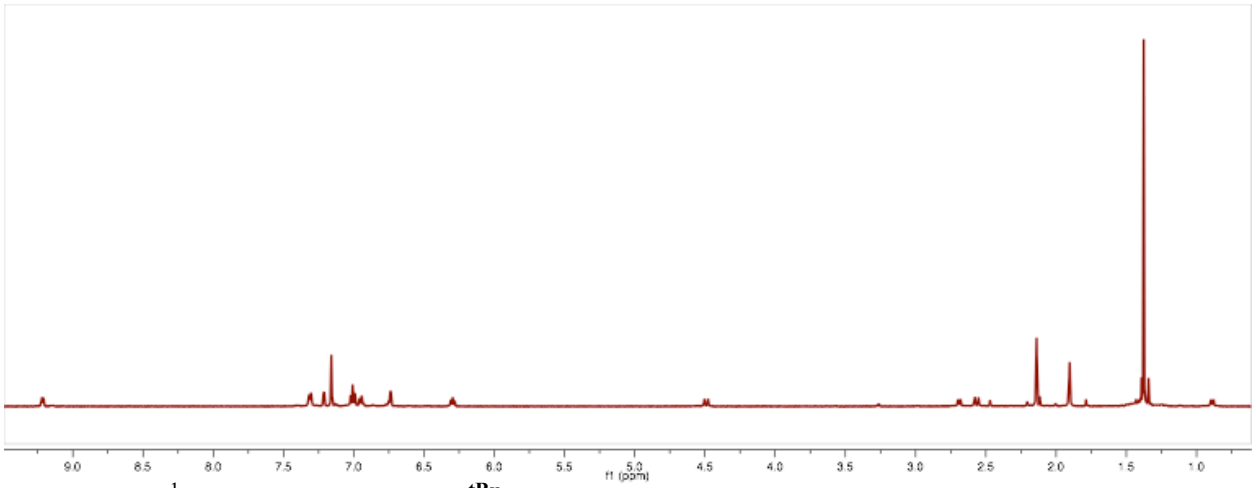


Figure S13. ^{1}H NMR spectrum of **8^{tBu}** in C_6D_6.

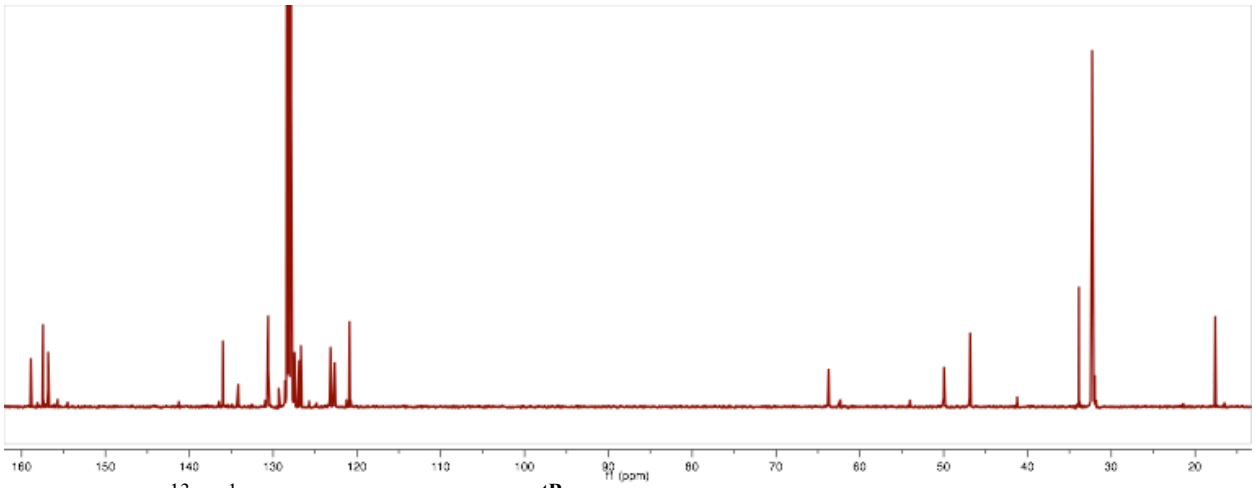


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **8^{tBu}** in C_6D_6.

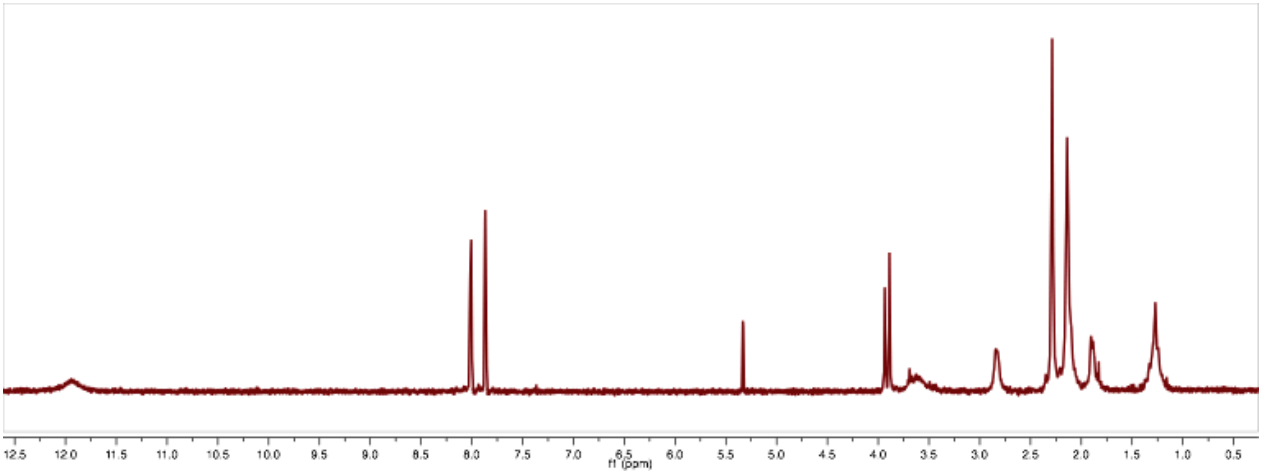


Figure S15. ^{1}H NMR spectrum of $\mathbf{9^{NO2}}$ in CD_2Cl_2

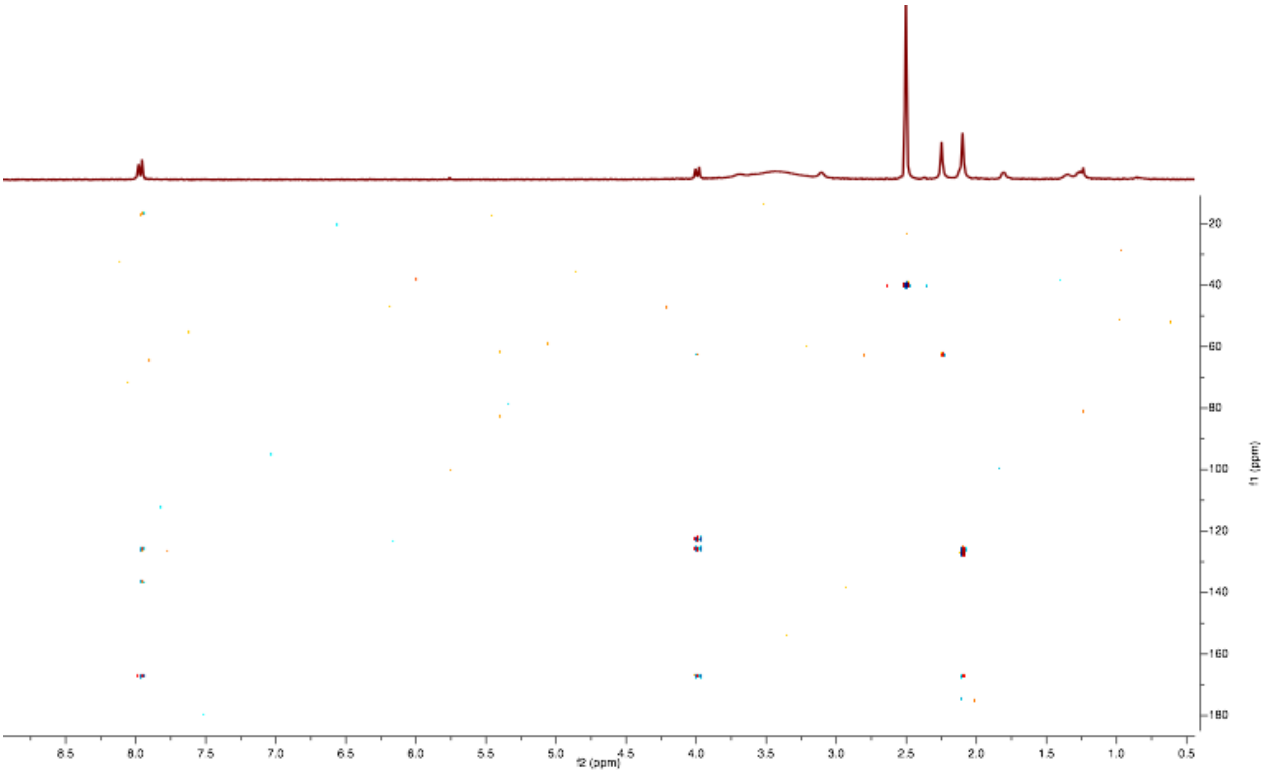


Figure S16. ^{1}H-^{13}C gHMBCAD NMR spectrum of $\mathbf{9^{NO2}}$ in $(CD_3)_2SO$.

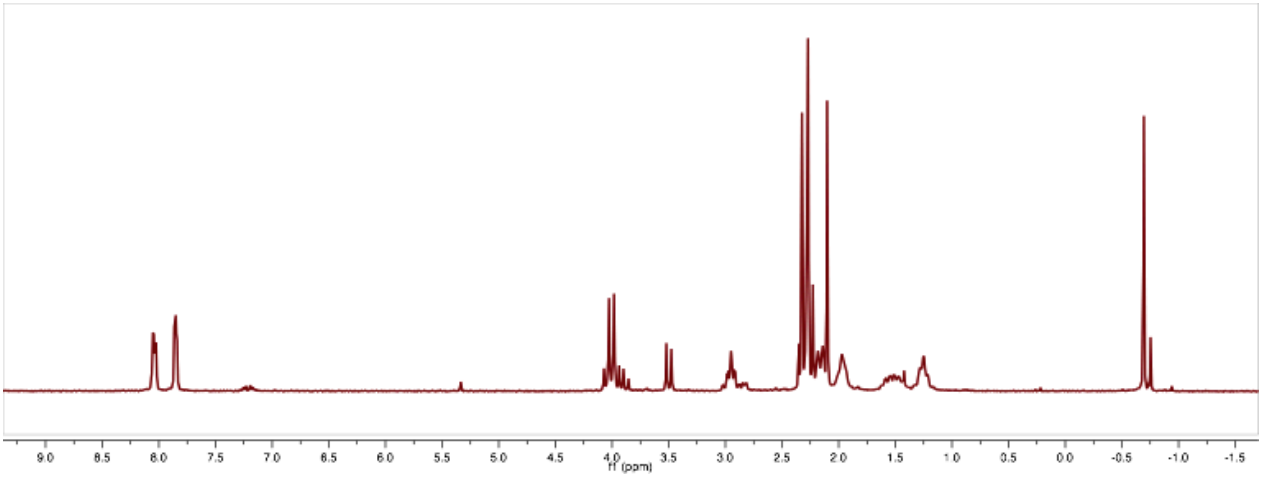


Figure S17. ^{1}H NMR spectrum of **10**^{NO2} in CD_2Cl_2

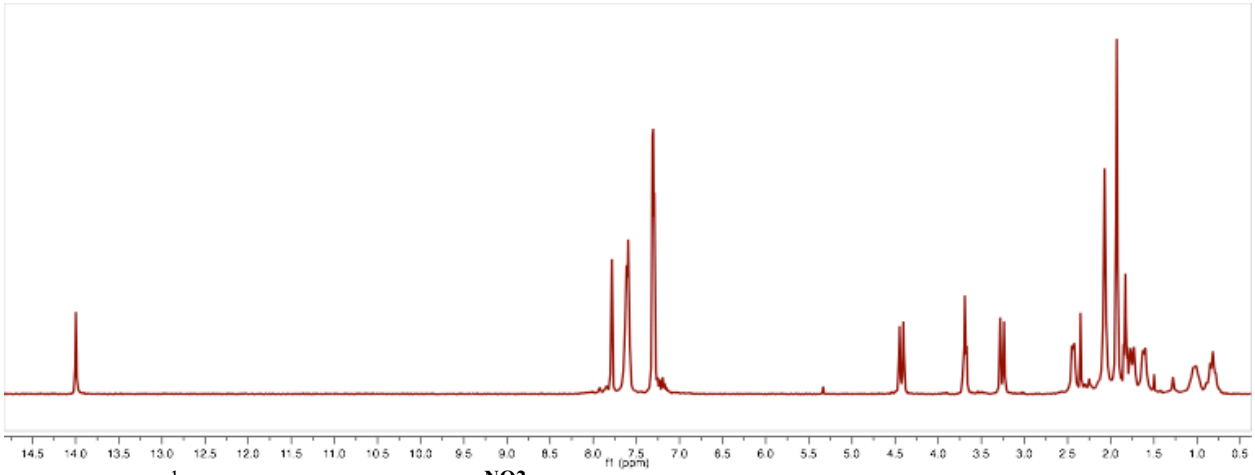


Figure S18. ^{1}H NMR spectrum of **11**^{NO2} in CD_2Cl_2.

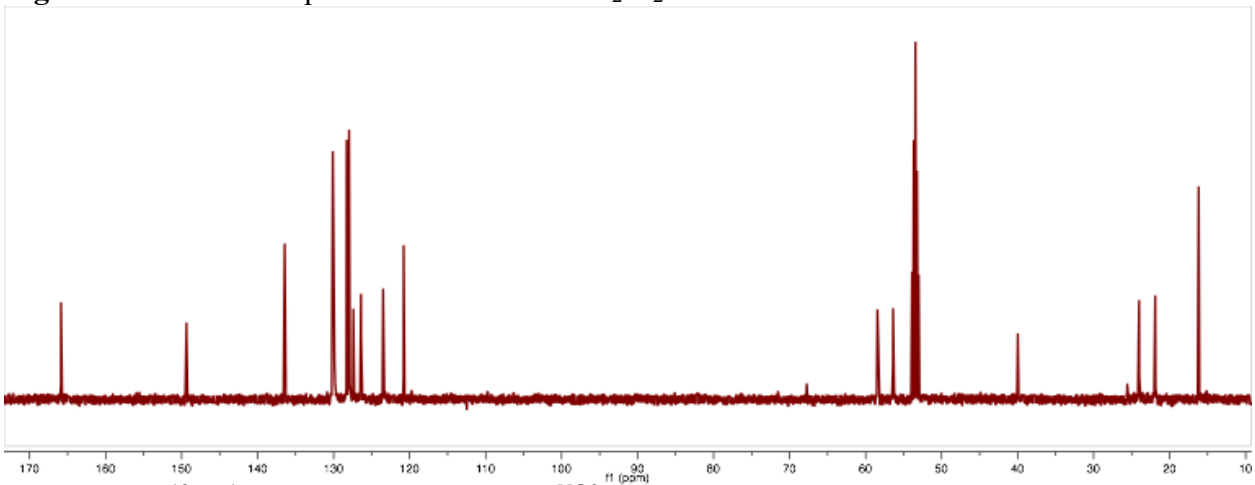


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of **11**^{NO2} in CD_2Cl_2.

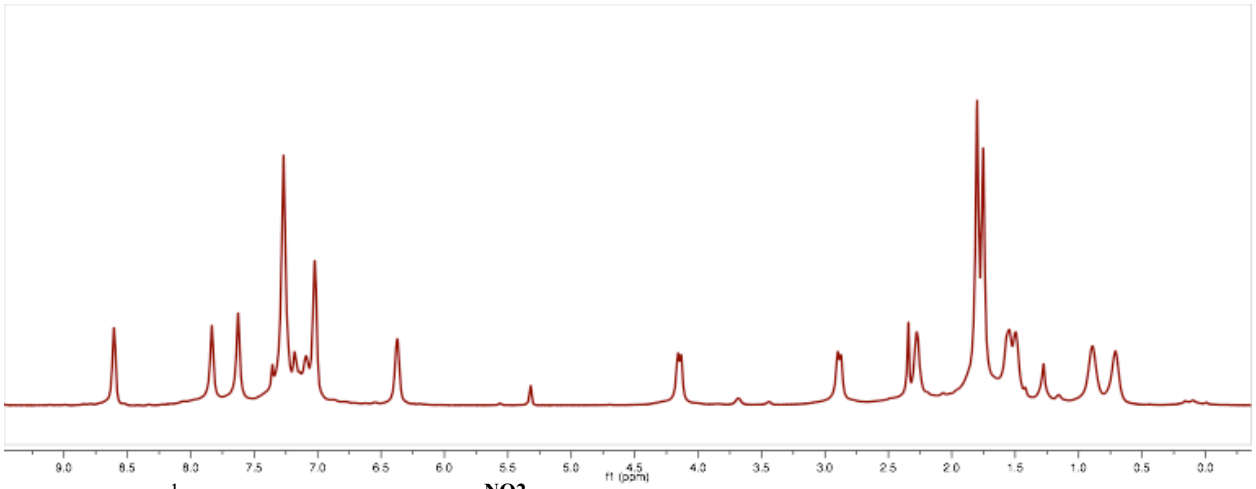


Figure S20. ^{1}H NMR spectrum of $\mathbf{12^{NO2}}$ in CD_2Cl_2.

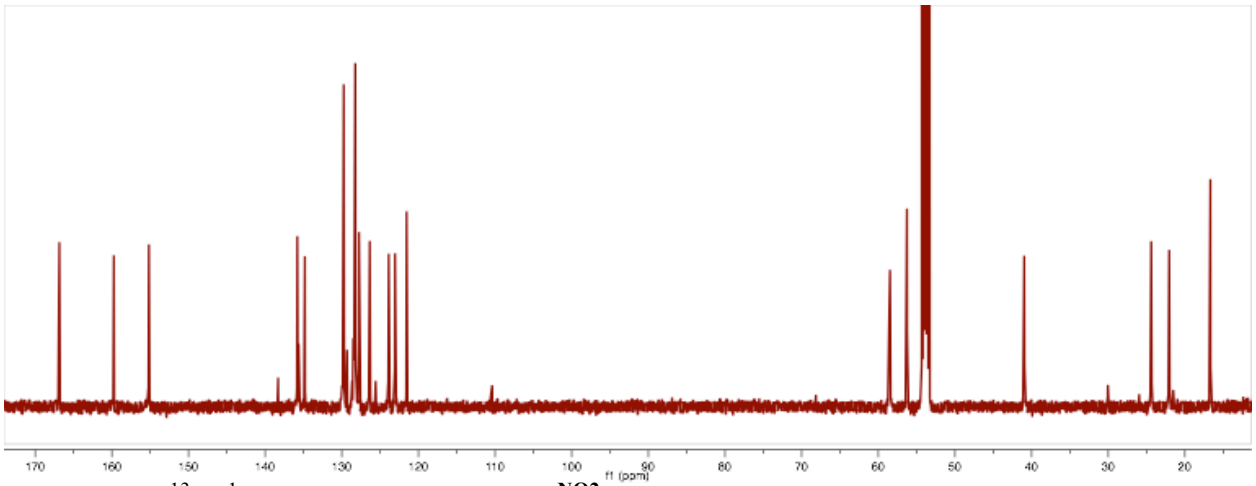


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of $\mathbf{12^{NO2}}$ in CD_2Cl_2.

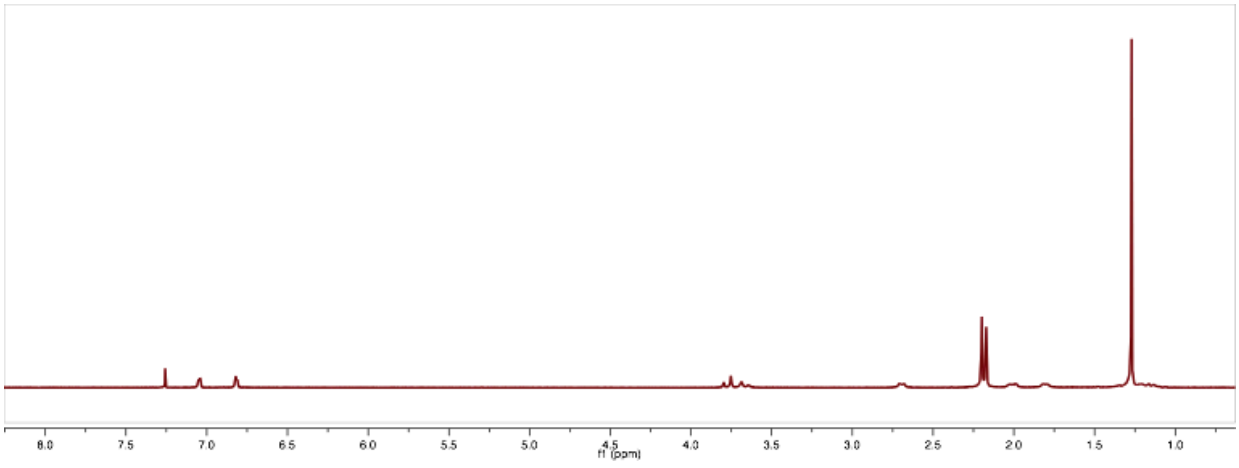


Figure S22. ^{1}H NMR spectrum of $\mathbf{9^{tBu}}$ in $CDCl_3$

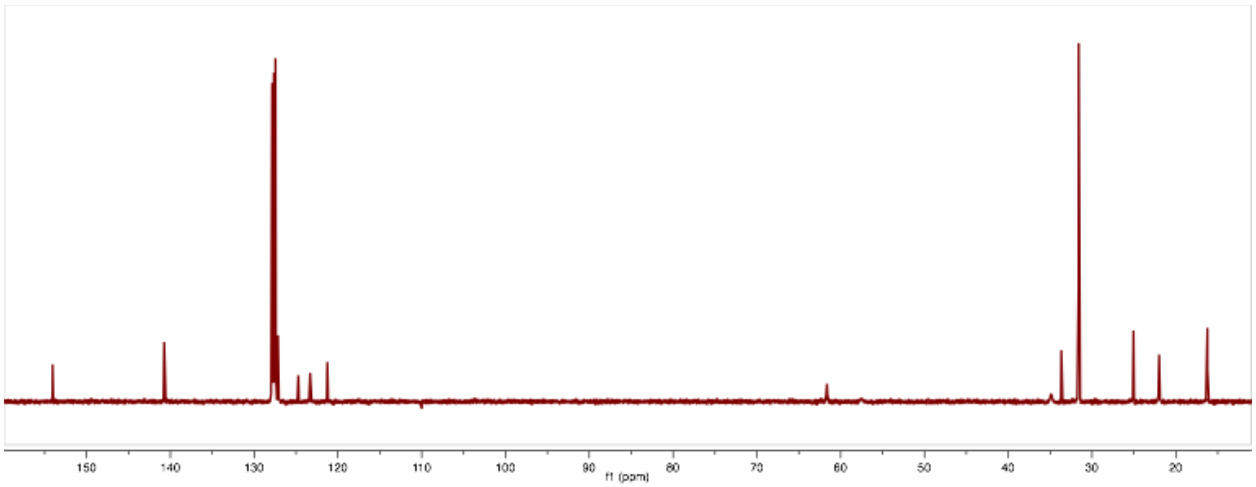


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of **9^{tBu}** in C_6D_6

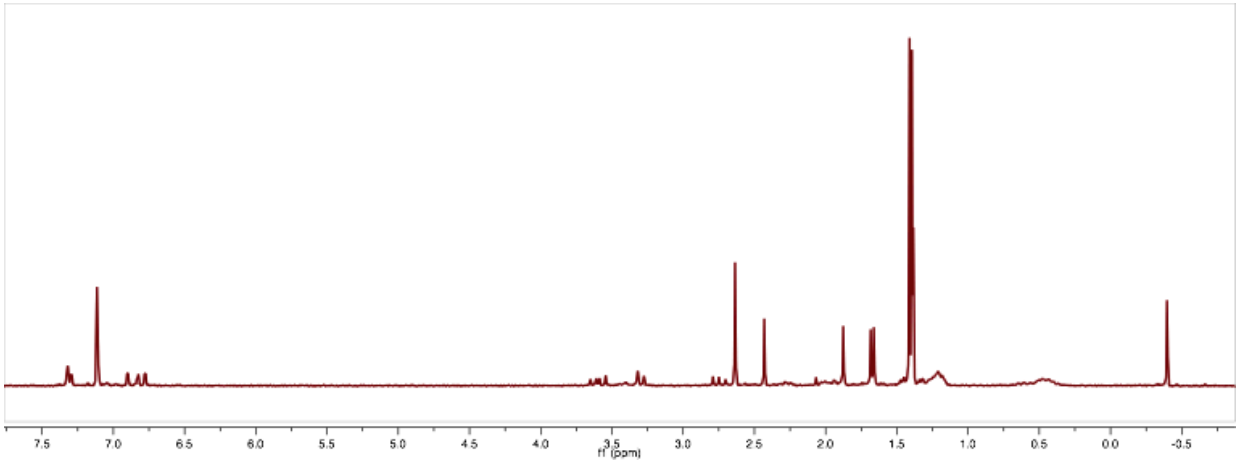


Figure S24. ^{1}H NMR spectrum of **10^{tBu}** in C_6D_6

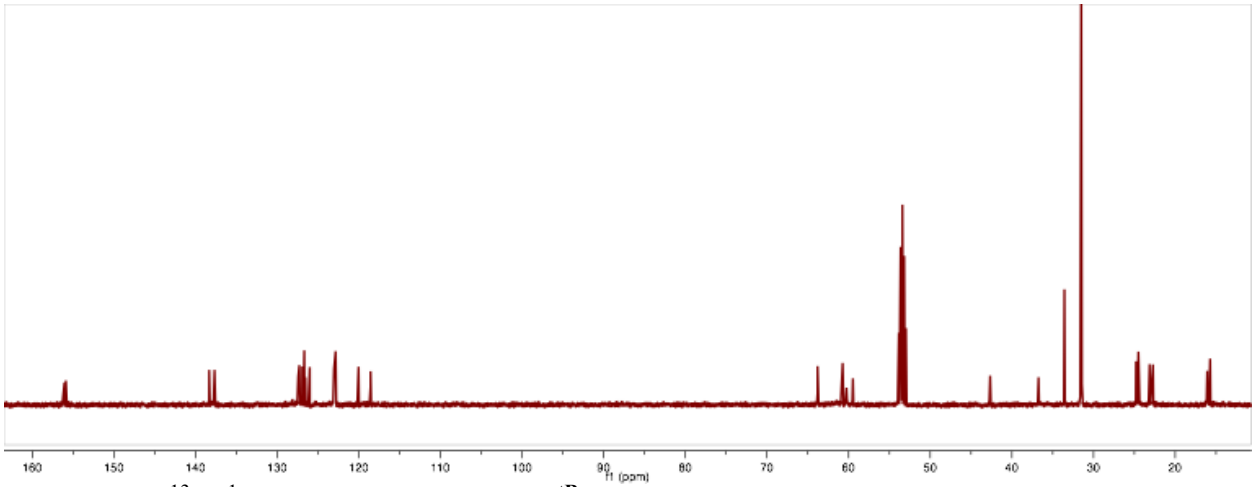


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of **10^{tBu}** in CD_2Cl_2

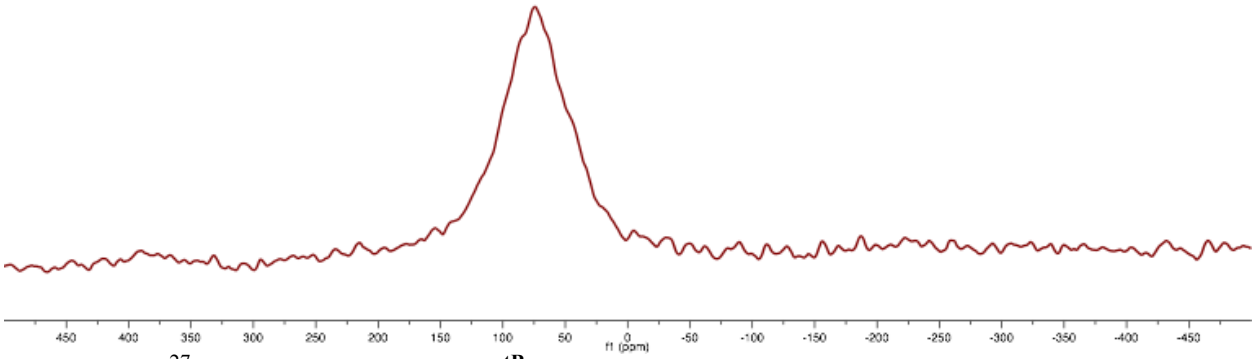


Figure S26. ^{27}Al NMR spectrum of **10^{tBu}** in CD_2Cl_2

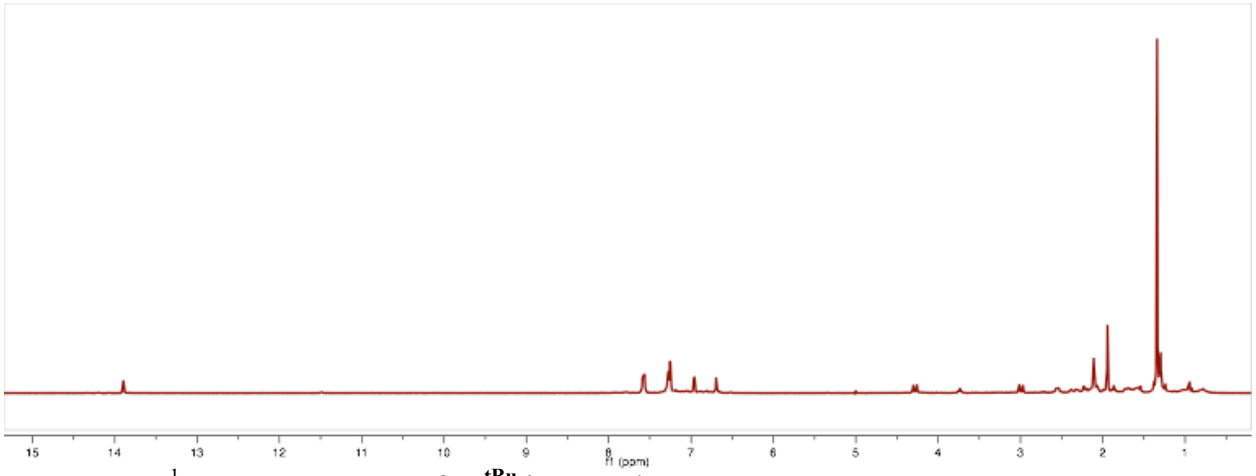


Figure S27. ^{1}H NMR spectrum of **11^{tBu}** in CD_2Cl_2.

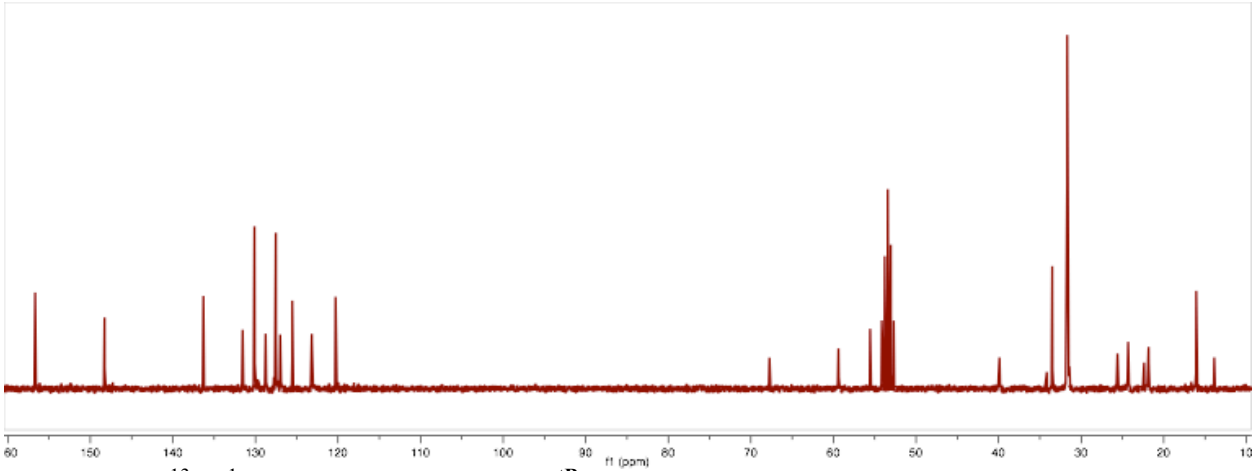


Figure S28. ^{13}C{^{1}H} NMR spectrum of **11^{tBu}** in CD_2Cl_2.

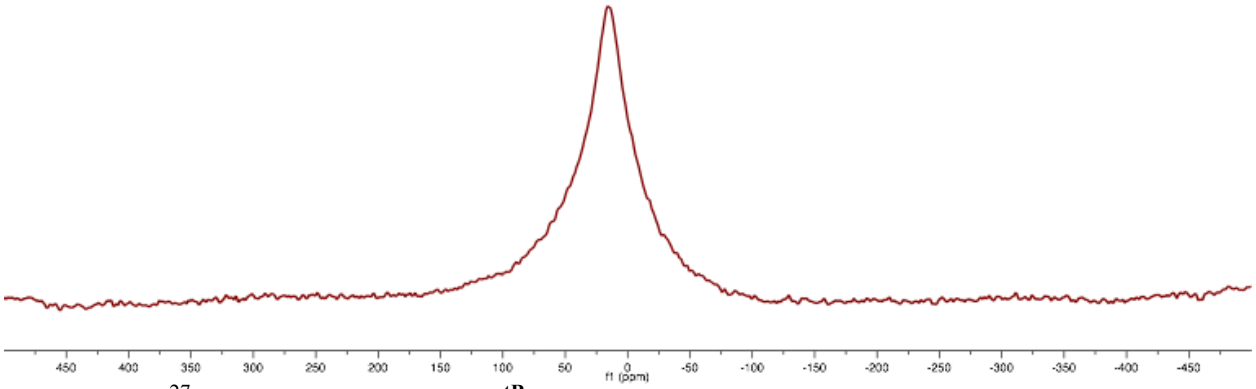


Figure S29. ^{27}Al NMR spectrum of **11^{tBu}** in CD_2Cl_2.

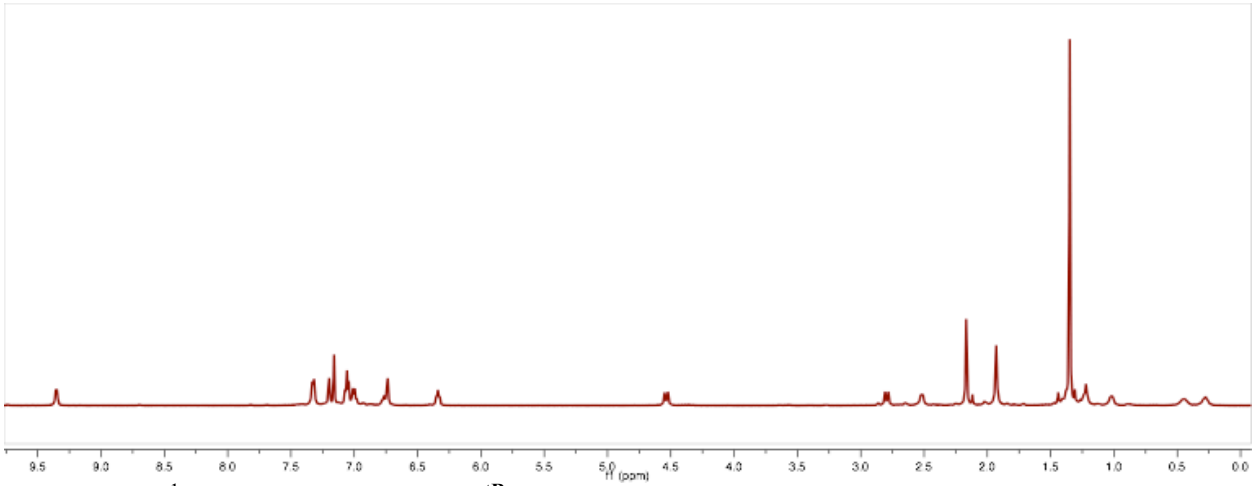


Figure S30. ^{1}H NMR spectrum of **12^{tBu}** in C_6D_6.

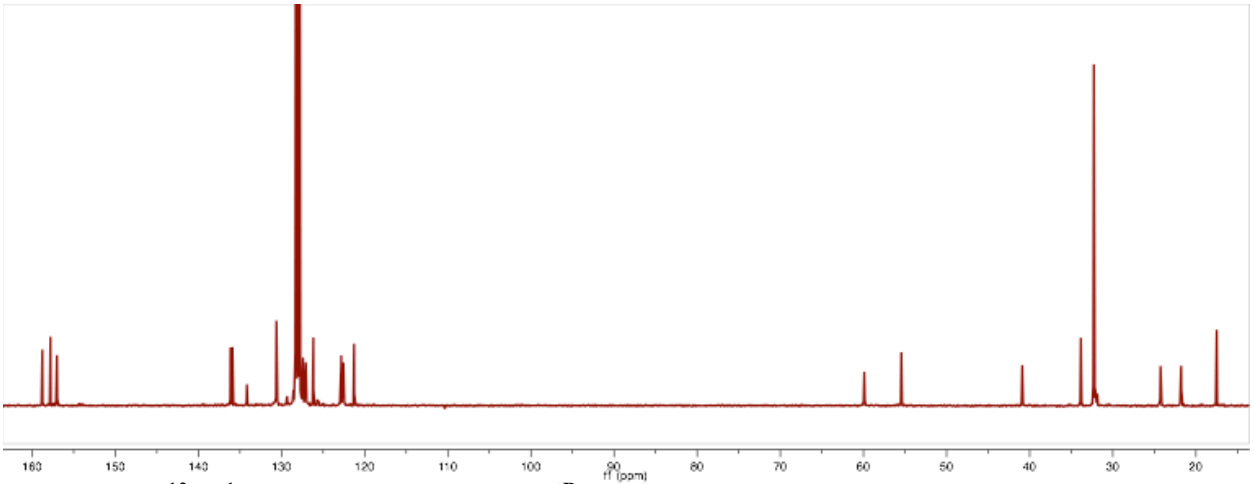


Figure S31. ^{13}C{^{1}H} NMR spectrum of **12^{tBu}** in C_6D_6.

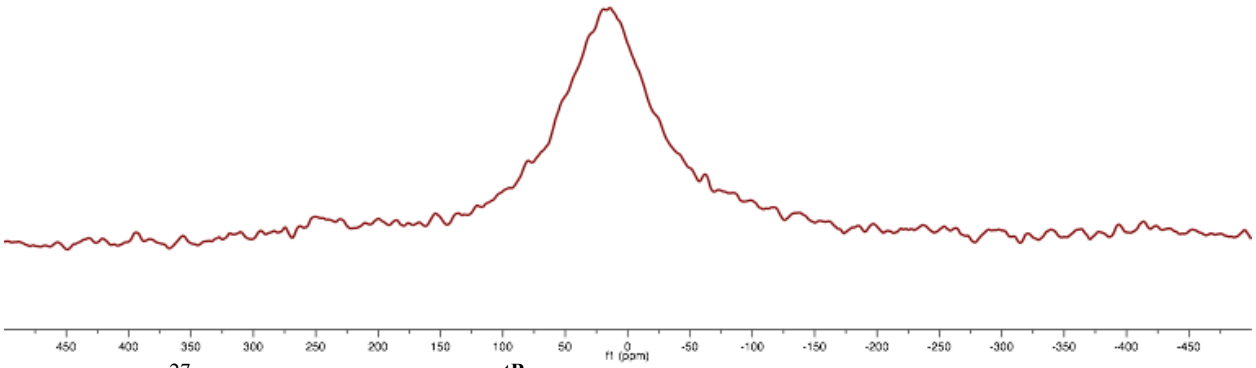


Figure S32. ^{27}Al NMR spectrum of **12^{tBu}** diphenylglyoxime macrocycle in C_6D_6.

III. Electrochemical Data

General Considerations. Electrochemical measurements were recorded in a glovebox under a N2 atmosphere using a Pine Instrument Company Bipotentiostat, at 1mM of the complex of interest, in DCM containing 0.1 M $nBu_4N(ClO_4)$ as the supporting electrolyte. For the electrochemistry a platinum working electrode, a platinum wire auxiliary electrode, and a 0.01M $Ag/AgNO_3$ nonaqueous reference electrode were used for all measurements.

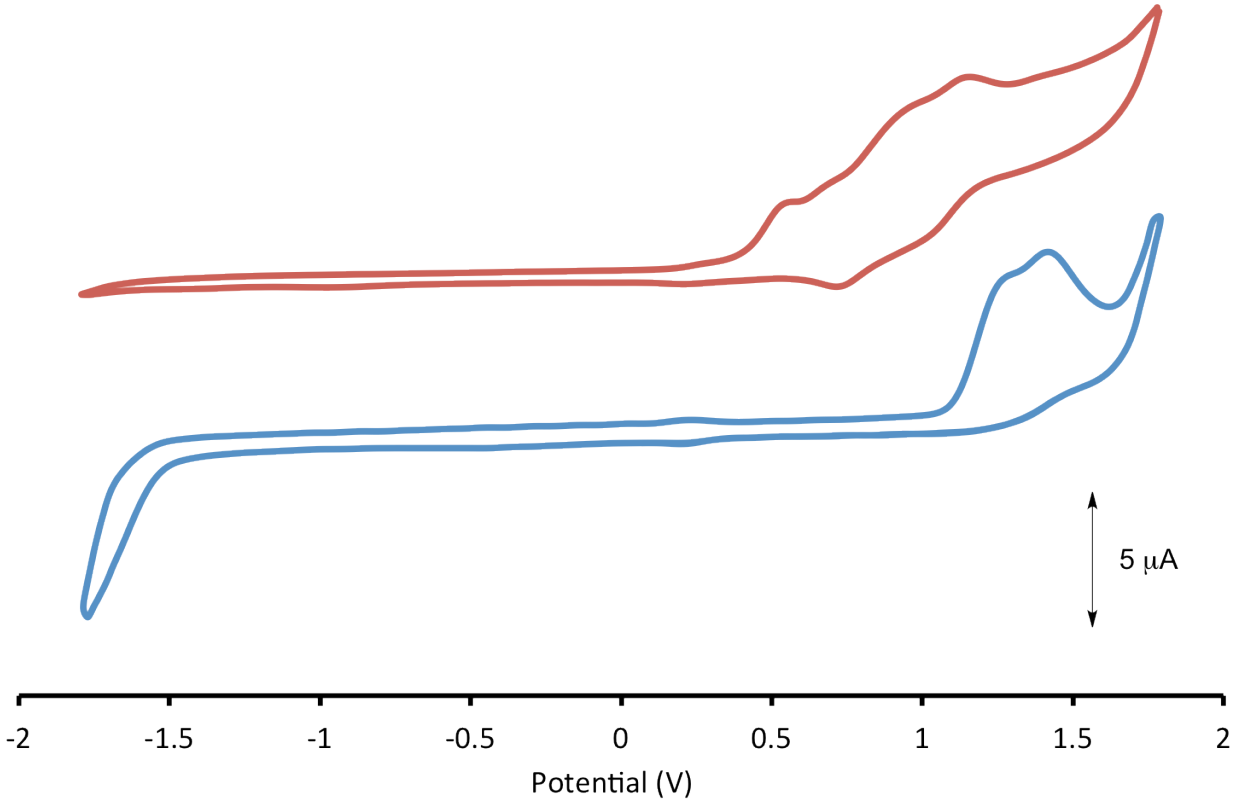


Figure S33. Cyclic voltammograms of 1 mM solutions of $\mathbf{11}^{NO2}$ (blue) and $\mathbf{11}^{tBu}$ (red) using a 100 mV/s scan rate, both referenced to Fc/Fc^+.

IV. Crystallographic Data

Table S1. Crystal and refinement data for **3b, 3b^{tBu}**, **5b-Pd-*anti***, and **5b-Pd-*syn***.

	3b	**3b^{tBu}**	**5b-Pd-*anti***	**2-cis**
CCDC Deposition #		861066	861065	862109
Empirical formula	$C_{68}H_{70}Al_2N_8O_8$	$C_{92}H_{120}N_8O_8Al_2 \bullet 4(C_4H_8O)$	$C_{68}H_{72}N_8O_8Al_2Pd \bullet 6(C_4H_8O)$	$C_{68}H_{72}N_8O_8Al_2Pd \bullet 0.5(C_6H_{14}) \bullet 1.45(C_4H_8O)$
Formula weight	1181.28	1808.34	1722.32	1437.33
Crystallization Solvent	pentane/toluene	THF/hexanes	THF/hexane	THF/hexane
Crystal Habit	Plate	Plate	Fragment	Block
Crystal size, mm^3	0.23 x 0.19 x 0.19	0.26 x 0.16 x 0.04	0.12 x 0.07 x 0.03	0.16 x 0.11 x 0.08
Crystal color	yellow	Pale Yellow	Yellow	Orange
θ range for lattice determination		2.42 to 27.61	2.29 to 22.92°	2.35 to 29.82°
a, Å	12.0569(6)	11.9403(6)	10.9146(3)	18.5492(17)
b, Å	18.5626(10)	12.7271(7)	16.3913(5)	19.7138(17)
c, Å	18.9548(11)	17.7934(9)	24.2331(7)	20.515(3)
a, °	78.418(3)	98.660(2)	90	90
b, °	76.313(3)	103.176(2)	101.8030(10)	102.794(3)
γ, °	76.094(3)	106.624(2)	90	90
Volume, Å^3	3954.1(4)	2454.4(2)	4243.7(2)	10039.7(4)
Z	2	1	2	4
Crystal system	Triclinic	Triclinc	Monoclinic	Monoclinic
Space group	$P\bar{1}$	P-1	P $2_1/c$	P $2_1/n$
Density (calculated)	0.992	1.223	1.348 Mg/m^3	1.305 Mg/m^3
F(000)	1248	978	1824	3020
θ range for data collection, °	1.72 to 30.00	1.21 to 27.71	1.51 to 25.38	1.34 to 30.52
Completeness to θ °	99.3%	93.3%	93.9%	99.4%
Index ranges	$-16 \le h \le 16$ $-26 \le k \le 26$ $-26 \le l \le 26$	$-15 \le h \le 15$ $-16 \le k \le 16$ $-12 \le l \le 23$	$-12 \le h \le 13$ $-19 \le k \le 19$ $-28 \le l \le 27$	$-18 \le h \le 26$ $-28 \le k \le 27$ $-29 \le l \le 28$
Data collection scan type			ω scans; 6 settings	ω scans; 10 settings
Reflections collected	143111	10751	35112	111672
Independent reflections	22895 [R_{int}= 0.0433]	10751[R_{int}= 0.0000]	7335 [R_{int}= 0.0608]	22234 [R_{int}= 0.0594]
Absorption coefficient, mm^{-1}	0.086	0.095	0.309	0.340
Absorption correction	Semi-empirical from equivalents	None	None	None
Max. and min. transmission	0.8626 and 0.8200	0.9962 and 0.9756	0.9908 and 0.9636	0.9733 and 0.9476

Hydrogen placement	Geometric positions	Geometric positions	Geometric positions	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)	SHELXL-97 (Sheldrick, 2008)	SHELXL-97 (Sheldrick, 2008)	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2	Full matrix least-squares on F^2	Full matrix least-squares on F^2	Full matrix least-squares on F^2
Data / restraints / parameters	22895/0/818	10751 / 0 / 601	7335 / 30 / 531	22234 / 66 / 875
Treatment of hydrogen atoms	Riding	Riding	Riding	Riding
Goodness-of-fit on F2	1.096	3.445	2.000	1.788
Final R indices [I>2s(I), 4802 reflections]	R1 = 0.0515 wR2 = 0.1498	R1 = 0.0643 *w*R2 = 0.0858	R1 = 0.0567 *w*R2 = 0.0814	R1 = 0.0504 *w*R2 = 0.0681
R indices (all data)	R1 = 0.0654 wR_2 = 0.1566	R1 = 0.0836 *w*R2 = 0.0863	R1 = 0.0970 *w*R2 = 0.0838	R1 = 0.0911 *w*R2 = 0.0698
Type of weighting scheme used	Sigma	Sigma	Sigma	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$	$w=1/\sigma^2(Fo^2)$	$w=1/\sigma^2(Fo^2)$	$w=1/\sigma^2(Fo^2)$
Max shift/error		0.001	0.001	0.003
Average shift/error	0	0	0	0
Largest diff. peak and hole, e.Å^{-3}	1.066 and -0.296	0.649 and -0.520	0.941 and -0.678	1.745 and -1.010
Type of diffractometer	Bruker KAPPA APEX II	Bruker KAPPA APEX II	Bruker KAPPA APEX II	Bruker KAPPA APEX II
Wavelength, Å MoKa	0.71073	0.71073	0.71073	0.71073
Data Collection Temperature	100(2) K	100(2) K	100(2) K	100(2) K
Structure solution program	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods	Direct methods	Direct methods	Direct methods
Secondary solution method	Difference Fourier map	Difference Fourier map	Difference Fourier map	Difference Fourier map

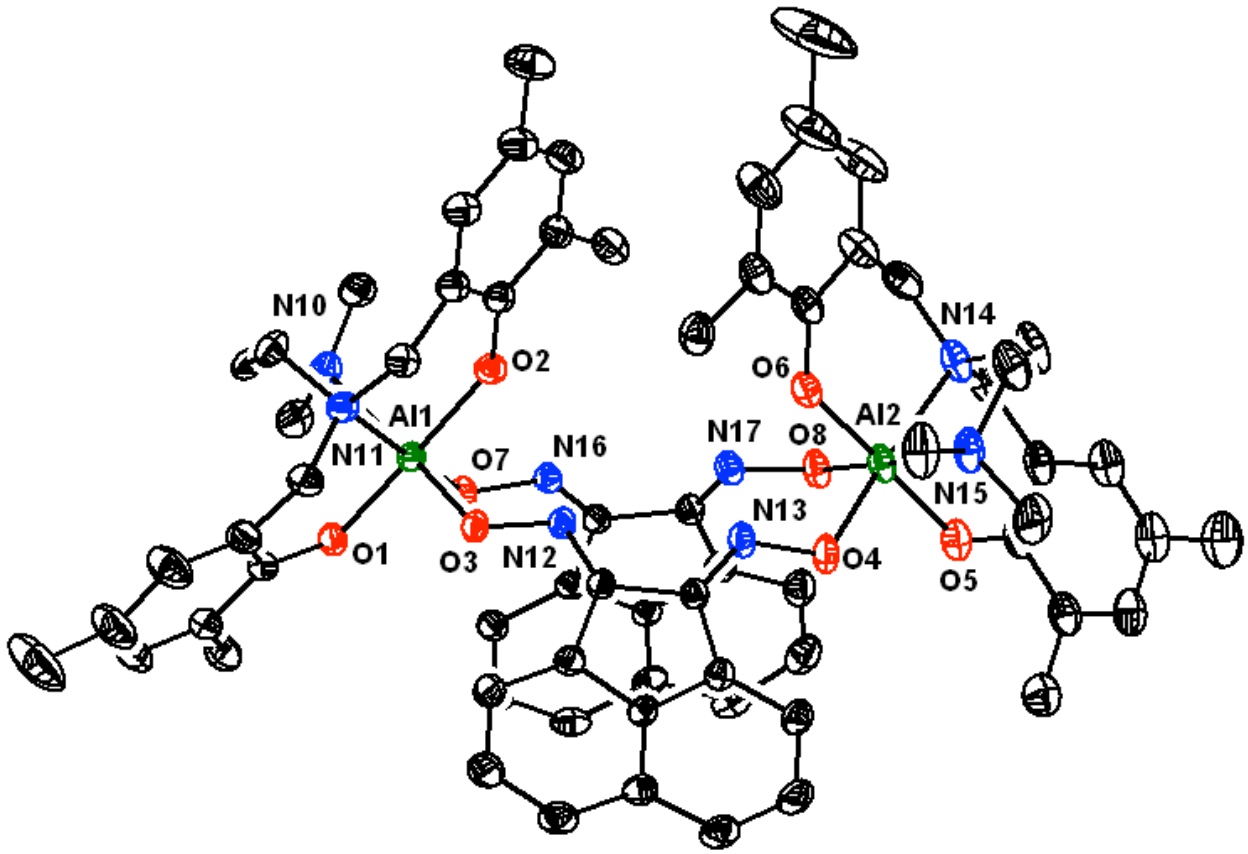


Figure S34. Structural drawing of **3b** with 50% thermal probability ellipsoids.

Special Refinement Details for 3b. A dichroic yellow plate of suitable size (0.23 x 0.19 x 0.19 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a glass fiber. Low temperature (100 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K$_\alpha$ = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[1] An absorption correction was applied using SADABS.[2] The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2. The structure was solved in the triclinic $P\bar{1}$ space group using XS[3] (incorporated in SHELXTL). No missed symmetry was reported by the ADDSYM program in PLATON.[4] All non-hydrogen atoms were refined by using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. Three disordered toluene solvent molecules (the crystallization solvent) were found within the asymmetric unit. These could not be satisfactorily modeled and were removed using the SQUEEZE protocol included in PLATON[4] (311 e/cell; Z = 2), the results of which are appended to the end of the CIF. The structure was refined (weighted least squares refinement on F^2) to convergence using the updated reflections file. The final least-squares refinement converged to R_1 = 0.0515 ($I > 2\sigma(I)$, 17531 data) and wR_2 = 0.1566 (F^2, 22895 data, 818 parameters). The final CIF is available as supporting material.

Table S2. Atomic coordinates **(x 10^4)** and equivalent isotropic displacement parameters **(Å^{2}x 10^3)** for **3b**. **U(eq)** is defined as one third of the trace of the orthogonalized **U^{ij}** tensor.

	x	y	z	U(eq)
Al(1)	1482(1)	10585(1)	1696(1)	19(1)
Al(2)	3139(1)	6918(1)	3853(1)	24(1)
C(4)	1752(1)	11275(1)	128(1)	29(1)
C(5)	3133(1)	11509(1)	783(1)	27(1)
C(6)	2377(1)	12208(1)	1051(1)	29(1)
C(7)	2677(2)	12903(1)	751(1)	45(1)
C(8)	2058(2)	13558(1)	1023(1)	53(1)
C(9)	1099(2)	13501(1)	1592(1)	42(1)
C(10)	755(1)	12826(1)	1899(1)	29(1)
C(11)	1413(1)	12162(1)	1637(1)	24(1)
C(12)	2439(3)	14298(1)	721(1)	85(1)
C(13)	-307(1)	12791(1)	2502(1)	35(1)
C(14)	3435(1)	10303(1)	427(1)	25(1)
C(15)	3039(1)	9627(1)	331(1)	24(1)
C(16)	3564(1)	9271(1)	-285(1)	28(1)
C(17)	3342(1)	8585(1)	-341(1)	31(1)
C(18)	2565(1)	8270(1)	230(1)	30(1)
C(19)	2007(1)	8608(1)	849(1)	26(1)
C(20)	2243(1)	9303(1)	898(1)	23(1)
C(21)	3936(1)	8194(1)	-997(1)	42(1)
C(22)	1214(1)	8237(1)	1476(1)	33(1)
C(23)	183(1)	9370(1)	3529(1)	19(1)
C(24)	488(1)	8588(1)	3902(1)	20(1)
C(25)	-610(1)	9820(1)	4062(1)	19(1)
C(26)	-797(1)	9313(1)	4724(1)	20(1)
C(27)	-198(1)	8565(1)	4655(1)	22(1)
C(28)	-301(1)	8021(1)	5264(1)	28(1)
C(29)	-999(1)	8239(1)	5933(1)	34(1)
C(30)	-1537(1)	8968(1)	6006(1)	31(1)
C(31)	-1443(1)	9543(1)	5386(1)	24(1)
C(32)	-1905(1)	10322(1)	5358(1)	26(1)
C(33)	-1746(1)	10814(1)	4713(1)	25(1)
C(34)	-1093(1)	10575(1)	4044(1)	22(1)
C(38)	3651(1)	5300(1)	3770(1)	39(1)
C(39)	2204(1)	6066(1)	3036(1)	32(1)
C(40)	3014(1)	6293(1)	2335(1)	35(1)
C(41)	3177(2)	5952(1)	1715(1)	57(1)
C(42)	3800(2)	6219(1)	1039(1)	66(1)
C(43)	4280(2)	6839(1)	996(1)	47(1)
C(44)	4155(1)	7193(1)	1599(1)	32(1)
C(45)	3524(1)	6910(1)	2278(1)	27(1)
C(46)	3995(4)	5843(2)	371(2)	127(2)
C(47)	4628(1)	7888(1)	1529(1)	35(1)
C(48)	1639(1)	5787(1)	4337(1)	31(1)
C(49)	1845(1)	5676(1)	5106(1)	30(1)
C(50)	1323(1)	5153(1)	5641(1)	36(1)
C(51)	1372(1)	5076(1)	6378(1)	37(1)
C(52)	1980(1)	5533(1)	6571(1)	35(1)
C(53)	2527(1)	6050(1)	6059(1)	31(1)
C(54)	2458(1)	6129(1)	5311(1)	28(1)
C(55)	761(2)	4536(1)	6959(1)	50(1)
C(56)	3172(1)	6539(1)	6276(1)	39(1)
C(57)	3856(1)	9593(1)	2895(1)	20(1)
C(58)	4151(1)	8884(1)	3395(1)	20(1)
C(59)	4906(1)	8990(1)	3845(1)	21(1)
C(60)	5079(1)	9735(1)	3606(1)	21(1)
C(61)	4467(1)	10126(1)	3045(1)	21(1)

C(62)	4520(1)	10867(1)	2788(1)	27(1)
C(63)	5217(1)	11197(1)	3086(1)	33(1)
C(64)	5822(1)	10813(1)	3622(1)	32(1)
C(65)	5755(1)	10055(1)	3913(1)	26(1)
C(66)	6282(1)	9586(1)	4481(1)	32(1)
C(67)	6117(1)	8862(1)	4716(1)	32(1)
C(68)	5418(1)	8547(1)	4403(1)	26(1)
C(1A)	-264(3)	10375(2)	813(2)	32(1)
C(2A)	-1040(3)	11348(2)	1553(2)	30(1)
C(3A)	470(2)	11519(2)	477(2)	25(1)
C(1B)	-643(3)	10341(2)	1185(2)	33(1)
C(2B)	-666(2)	11635(2)	1153(2)	31(1)
C(3B)	735(2)	10939(1)	254(1)	25(1)
C(35)	5789(1)	6574(1)	3197(1)	44(1)
C(36)	5335(1)	5959(1)	4414(1)	46(1)
C(37)	4798(1)	5540(1)	3428(1)	43(1)
N(10)	84(1)	10930(1)	1063(1)	26(1)
N(11)	2498(1)	10942(1)	684(1)	22(1)
N(12)	3075(1)	9664(1)	2504(1)	21(1)
N(13)	3707(1)	8309(1)	3433(1)	24(1)
N(14)	2647(1)	5950(1)	3733(1)	28(1)
N(15)	4891(1)	6192(1)	3726(1)	30(1)
N(16)	624(1)	9594(1)	2854(1)	20(1)
N(17)	1346(1)	8121(1)	3579(1)	23(1)
O(1)	1104(1)	11515(1)	1935(1)	23(1)
O(2)	1705(1)	9635(1)	1485(1)	22(1)
O(3)	2812(1)	10358(1)	2127(1)	23(1)
O(4)	3840(1)	7704(1)	3949(1)	28(1)
O(5)	2989(1)	6626(1)	4829(1)	29(1)
O(6)	3409(1)	7233(1)	2867(1)	25(1)
O(7)	400(1)	10315(1)	2550(1)	23(1)
O(8)	1582(1)	7443(1)	4000(1)	26(1)

Table S3. Selected Bond lengths **[Å]** and angles **[°]** for **3b.**

Al(1)-O(1)	1.7978(9)	O(7)-Al(1)-N(11)	172.65(4)
Al(1)-O(2)	1.8289(9)	O(3)-Al(1)-N(11)	89.56(4)
Al(1)-O(7)	1.8873(9)	O(1)-Al(1)-N(10)	87.79(4)
Al(1)-O(3)	1.8894(9)	O(2)-Al(1)-N(10)	88.40(4)
Al(1)-N(11)	2.0947(11)	O(7)-Al(1)-N(10)	90.13(4)
Al(1)-N(10)	2.1956(11)	O(3)-Al(1)-N(10)	171.98(4)
Al(2)-O(5)	1.7983(10)	N(11)-Al(1)-N(10)	82.59(4)
Al(2)-O(6)	1.8188(10)	O(5)-Al(2)-O(6)	175.05(4)
Al(2)-O(8)	1.8800(9)	O(5)-Al(2)-O(8)	89.56(4)
Al(2)-O(4)	1.9107(10)	O(6)-Al(2)-O(8)	93.86(4)
Al(2)-N(14)	2.0908(11)	O(5)-Al(2)-O(4)	88.29(4)
Al(2)-N(15)	2.2040(11)	O(6)-Al(2)-O(4)	87.71(4)
N(12)-O(3)	1.3470(12)	O(8)-Al(2)-O(4)	97.67(4)
N(13)-O(4)	1.3374(12)	O(5)-Al(2)-N(14)	91.23(5)
N(16)-O(7)	1.3366(12)	O(6)-Al(2)-N(14)	92.24(5)
N(17)-O(8)	1.3549(12)	O(8)-Al(2)-N(14)	91.67(4)
O(1)-Al(1)-O(2)	174.00(4)	O(4)-Al(2)-N(14)	170.64(4)
O(1)-Al(1)-O(7)	86.97(4)	O(5)-Al(2)-N(15)	87.91(4)
O(2)-Al(1)-O(7)	88.39(4)	O(6)-Al(2)-N(15)	89.02(4)
O(1)-Al(1)-O(3)	90.81(4)	O(8)-Al(2)-N(15)	173.93(4)
O(2)-Al(1)-O(3)	93.60(4)	O(4)-Al(2)-N(15)	87.77(4)
O(7)-Al(1)-O(3)	97.68(4)	N(14)-Al(2)-N(15)	82.87(4)
O(1)-Al(1)-N(11)	91.70(4)		
O(2)-Al(1)-N(11)	92.41(4)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1

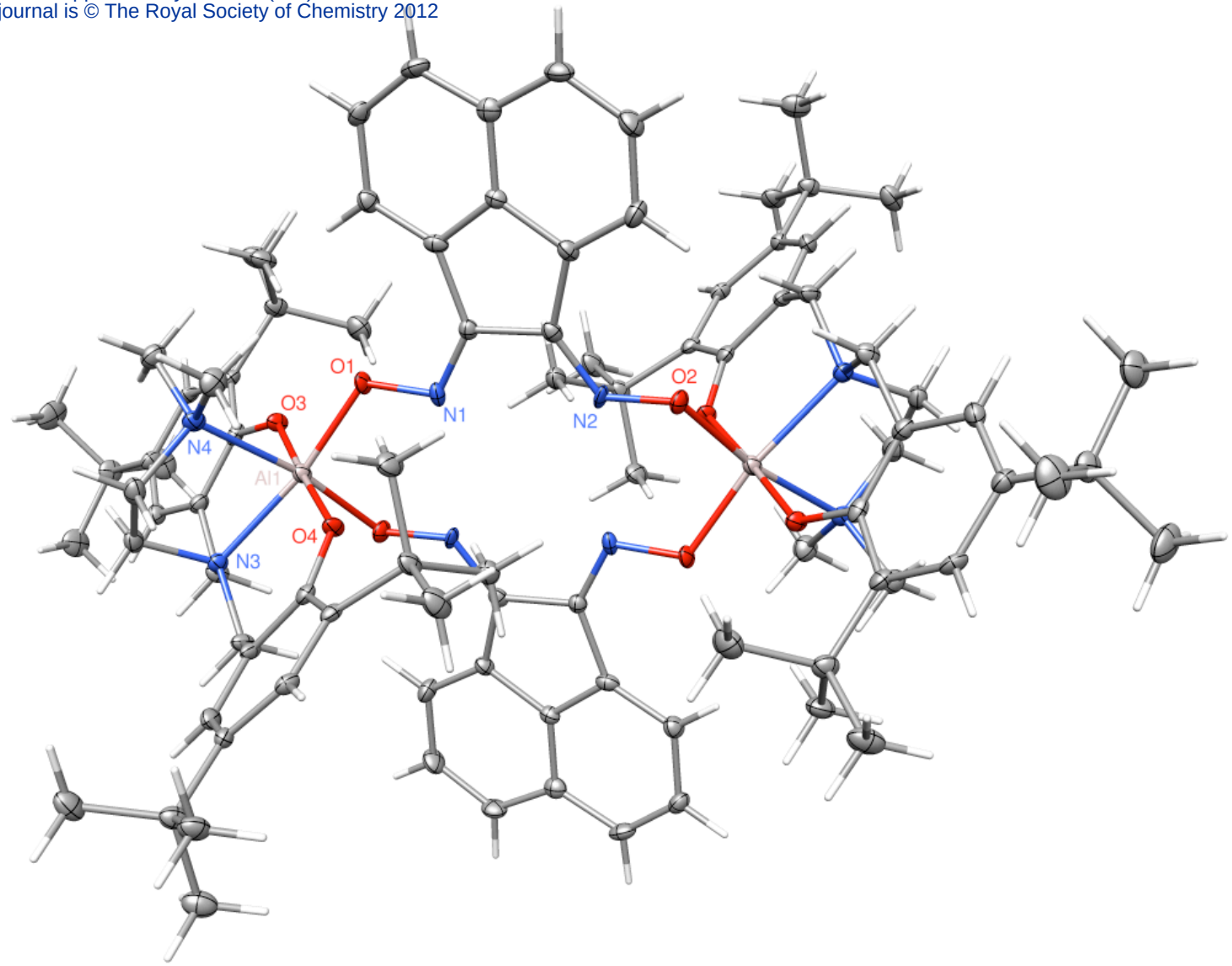


Figure S35. Structural drawing of **3b^{tBu}** with 50% thermal probability ellipsoids.

Special Refinement Details for 3b^{tBu}. Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. The crystal is a merohedral twin, with both ROTAX[9] and TwinRotMax confirming an 17% twin component related to the major component by 180º rotation around ***c****. The structure was refined with a single batch scale factor and an HKLF5 format reflection file, generated by Platon[10].

Table S4. Atomic coordinates **(x 10^4)** and equivalent isotropic displacement parameters **($Å^2$x 10^3)** for **3b^{tBu}**. **U(eq)** is defined as one third of the trace of the orthogonalized **U^{ij}** tensor.

	x	y	z	U_{eq}
Al(1)	2519(1)	7426(1)	6494(1)	12(1)
O(1)	2511(1)	6788(1)	5477(1)	13(1)
O(2)	-1674(1)	3929(1)	3214(1)	14(1)
O(3)	3942(1)	7190(1)	6849(1)	13(1)
O(4)	1050(1)	7613(1)	6099(1)	13(1)
N(1)	1433(2)	6093(2)	4969(1)	12(1)
N(2)	-636(2)	4577(2)	3777(1)	13(1)
N(3)	2750(2)	8373(2)	7631(1)	12(1)
N(4)	3462(2)	9103(2)	6343(1)	14(1)
C(1)	1413(2)	5935(2)	4231(2)	11(1)
C(2)	289(2)	5216(2)	3602(1)	12(1)
C(3)	2325(2)	6391(2)	3824(2)	13(1)
C(4)	3547(2)	7012(2)	4066(2)	15(1)
C(5)	4141(2)	7249(2)	3478(2)	16(1)
C(6)	3552(2)	6893(2)	2683(2)	18(1)
C(7)	2288(2)	6249(2)	2408(2)	15(1)
C(8)	1540(2)	5789(2)	1614(2)	20(1)
C(9)	328(2)	5141(2)	1449(2)	21(1)
C(10)	-210(2)	4892(2)	2057(2)	18(1)
C(11)	480(2)	5320(2)	2832(2)	12(1)
C(12)	1720(2)	6016(2)	2999(2)	12(1)
C(13)	3505(2)	9570(2)	7735(2)	16(1)
C(14)	3290(2)	9923(2)	6952(2)	19(1)
C(15)	3359(2)	7900(2)	8256(2)	15(1)
C(16)	4596(2)	7831(2)	8246(2)	14(1)
C(17)	5482(2)	8052(2)	8970(2)	15(1)
C(18)	6549(2)	7802(2)	9013(2)	15(1)
C(19)	6693(2)	7322(2)	8298(2)	15(1)
C(20)	5852(2)	7086(2)	7555(2)	14(1)
C(21)	4773(2)	7378(2)	7533(2)	14(1)
C(22)	7520(2)	7993(2)	9798(2)	18(1)
C(23)	7666(2)	6866(2)	9915(2)	30(1)
C(24)	7197(2)	8518(2)	10503(2)	26(1)
C(25)	8754(2)	8777(2)	9780(2)	30(1)
C(26)	6017(2)	6462(2)	6805(2)	16(1)
C(27)	7277(2)	6305(2)	6962(2)	25(1)
C(28)	5905(2)	7078(2)	6127(2)	20(1)
C(29)	5025(2)	5291(2)	6520(2)	25(1)
C(30)	1529(2)	8296(2)	7753(1)	14(1)
C(31)	721(2)	8706(2)	7184(1)	12(1)
C(32)	178(2)	9454(2)	7460(2)	15(1)
C(33)	-688(2)	9754(2)	6952(2)	12(1)
C(34)	-1047(2)	9203(2)	6153(2)	13(1)
C(35)	-560(2)	8422(2)	5836(2)	12(1)
C(36)	420(2)	8229(2)	6360(2)	14(1)
C(37)	-1227(2)	10615(2)	7272(2)	15(1)
C(38)	-209(2)	11729(2)	7704(2)	22(1)
C(39)	-1903(2)	10177(2)	7858(2)	23(1)
C(40)	-2112(2)	10857(2)	6611(2)	20(1)
C(41)	-1122(2)	7736(2)	4971(2)	14(1)
C(42)	-221(2)	7980(2)	4479(1)	19(1)
C(43)	-1526(2)	6476(2)	4960(2)	17(1)
C(44)	-2253(2)	8006(2)	4550(2)	22(1)
C(45)	4778(2)	9333(2)	6438(2)	20(1)
C(46)	2942(2)	9287(2)	5551(2)	21(1)

O(1C)	5683(2)	6750(2)	1577(1)	38(1)
C(1C)	5235(3)	5566(2)	1279(2)	42(1)
C(2C)	6277(3)	5133(2)	1516(2)	45(1)
C(3C)	7174(2)	6025(2)	2211(2)	47(1)
C(4C)	6695(3)	6991(2)	2224(2)	42(1)
O(1D)	2045(2)	6808(2)	-121(1)	53(1)
C(1D)	1706(3)	7773(3)	80(2)	64(1)
C(2D)	2869(4)	8755(3)	378(2)	65(1)
C(3D)	3722(3)	8225(3)	775(2)	47(1)
C(4D)	3295(2)	7057(2)	248(2)	34(1)

Table S5. Bond lengths **[Å]** and angles **[°]** for **3b^{tBu}**.

Al(1)-O(3)	1.7988(16)	O(3)-Al(1)-O(1)	86.96(8)
Al(1)-O(4)	1.8318(16)	O(4)-Al(1)-O(1)	91.00(8)
Al(1)-O(1)	1.8646(17)	O(3)-Al(1)-O(2)#1	89.77(7)
Al(1)-O(2)#1	1.9423(17)	O(4)-Al(1)-O(2)#1	89.32(7)
Al(1)-N(3)	2.108(2)	O(1)-Al(1)-O(2)#1	99.38(7)
Al(1)-N(4)	2.198(2)	O(3)-Al(1)-N(3)	90.35(8)
O(1)-N(1)	1.354(2)	O(4)-Al(1)-N(3)	91.86(8)
O(2)-N(2)	1.349(2)	O(1)-Al(1)-N(3)	170.78(8)
O(2)-Al(1)#1	1.9423(17)	O(2)#1-Al(1)-N(3)	89.42(8)
O(3)-C(21)	1.323(3)	O(3)-Al(1)-N(4)	91.58(7)
O(4)-C(36)	1.334(3)	O(4)-Al(1)-N(4)	89.66(8)
N(1)-C(1)	1.292(3)	O(1)-Al(1)-N(4)	89.70(8)
N(2)-C(2)	1.303(3)	O(2)#1-Al(1)-N(4)	170.88(8)
N(3)-C(15)	1.487(3)	N(3)-Al(1)-N(4)	81.56(8)
N(3)-C(13)	1.489(3)	N(1)-O(1)-Al(1)	117.86(13)
N(3)-C(30)	1.501(3)	N(2)-O(2)-Al(1)#1	113.03(13)
N(4)-C(45)	1.478(3)		
N(4)-C(14)	1.481(3)	Symmetry transformations used to generate equivalent atoms:	
N(4)-C(46)	1.487(3)	#1 -x,-y+1,-z+1	
O(3)-Al(1)-O(4)	177.61(9)		

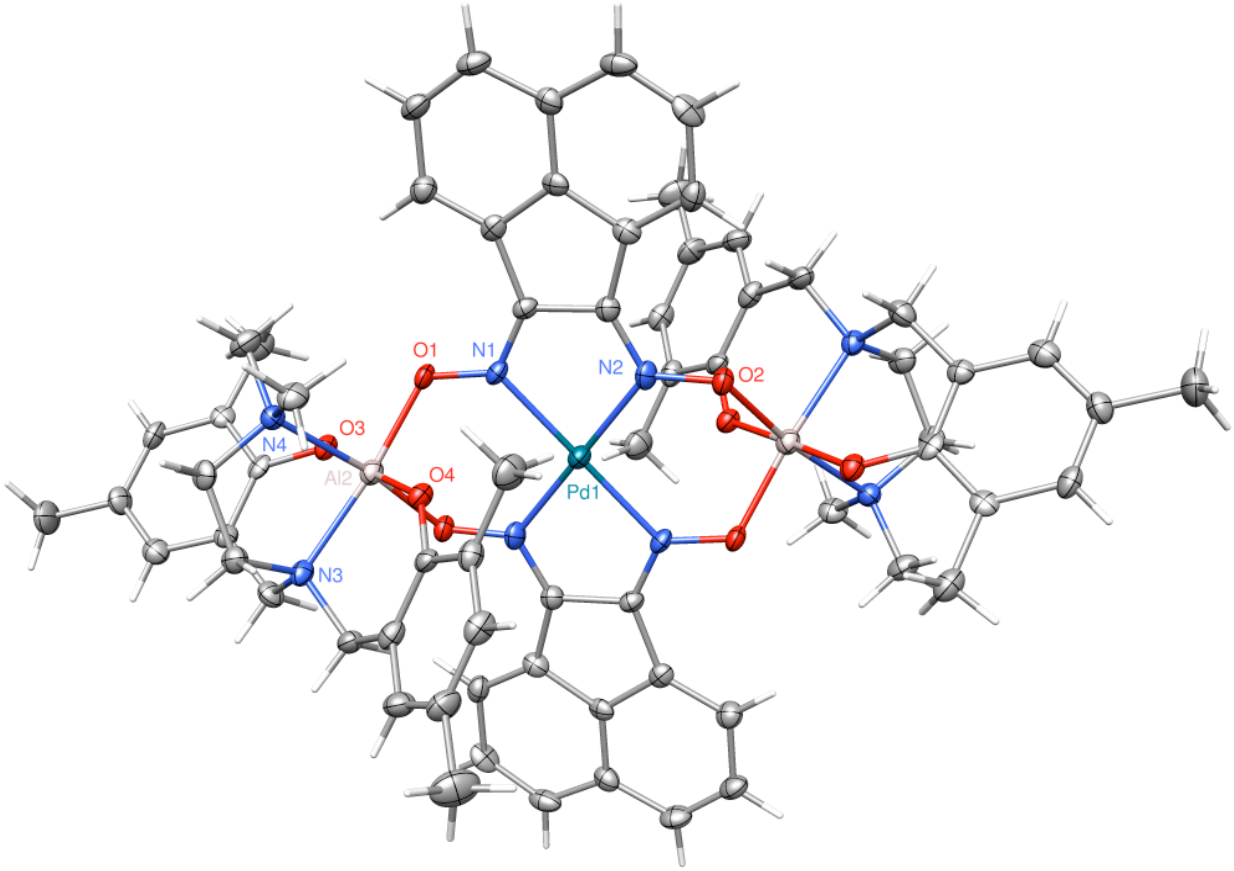


Figure S36. Structural drawing of **5b-Pd-*anti*** with 50% thermal probability ellipsoids.

Special Refinement Details for 5b-Pd-*anti*. Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. The crystal is small and relatively weakly diffracting at higher resolution resulting in the completeness in the highest shell of 94% while being 99.9% complete at 2q≤46º. The molecule sits on a center of symmetry therefore the asymmetric unit contains half of the atoms. The asymmetric unit contains three solvent sites occupied by THF, one of which is disordered over two orientations. The disordered molecules were restrained to have similar geometry to the THF in one of the fully occupied sites, using SAME command.

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **5b-Pd-*anti***. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Pd(1)	5000	0	5000	20(1)	1
Al(2)	6407(1)	132(1)	3789(1)	21(1)	1
O(1)	6703(2)	917(2)	4376(1)	20(1)	1
O(2)	5359(2)	1(2)	6261(1)	21(1)	1
O(3)	6044(2)	945(2)	3276(1)	21(1)	1
O(4)	6805(2)	-661(2)	4313(1)	21(1)	1
N(1)	6427(3)	723(2)	4868(1)	18(1)	1
N(2)	5729(3)	273(2)	5803(1)	20(1)	1

N(3)	6364(3)	-760(2)	3159(1)	20(1)	1
N(4)	8390(3)	202(2)	3736(1)	20(1)	1
C(1)	7054(4)	1020(2)	5338(2)	18(1)	1
C(2)	6707(4)	749(2)	5862(2)	19(1)	1
C(3)	8114(4)	1581(2)	5490(2)	19(1)	1
C(4)	8811(3)	2057(2)	5198(2)	25(1)	1
C(5)	9793(4)	2536(2)	5517(2)	26(1)	1
C(6)	10080(4)	2533(2)	6090(2)	27(1)	1
C(7)	9377(4)	2052(2)	6404(2)	22(1)	1
C(8)	9565(4)	1964(2)	6995(2)	28(1)	1
C(9)	8833(4)	1458(3)	7237(2)	25(1)	1
C(10)	7828(4)	1007(2)	6908(2)	23(1)	1
C(11)	7600(3)	1087(2)	6335(2)	21(1)	1
C(12)	8402(3)	1593(2)	6086(2)	19(1)	1
C(13)	7670(3)	-973(2)	3117(2)	24(1)	1
C(14)	8511(3)	-231(2)	3210(2)	24(1)	1
C(15)	8843(3)	1053(2)	3700(2)	27(1)	1
C(16)	9220(3)	-177(2)	4228(2)	26(1)	1
C(17)	5633(4)	-469(2)	2605(2)	24(1)	1
C(18)	6062(3)	313(2)	2388(2)	20(1)	1
C(19)	6277(3)	384(3)	1843(2)	26(1)	1
C(20)	6591(4)	1118(3)	1637(2)	25(1)	1
C(21)	6651(3)	1798(3)	1974(2)	24(1)	1
C(22)	6448(3)	1761(2)	2523(2)	19(1)	1
C(23)	6176(3)	996(2)	2738(2)	19(1)	1
C(24)	6796(4)	1206(3)	1036(2)	38(1)	1
C(25)	6484(3)	2505(2)	2891(2)	28(1)	1
C(26)	5726(4)	-1525(2)	3297(2)	24(1)	1
C(27)	6301(4)	-1932(2)	3841(2)	23(1)	1
C(28)	6309(4)	-2776(3)	3873(2)	27(1)	1
C(29)	6758(4)	-3188(3)	4366(2)	29(1)	1
C(30)	7248(3)	-2726(3)	4835(2)	25(1)	1
C(31)	7284(3)	-1883(3)	4828(2)	23(1)	1
C(32)	6795(4)	-1473(3)	4322(2)	20(1)	1
C(33)	6739(4)	-4110(3)	4396(2)	45(1)	1
C(34)	7835(4)	-1397(3)	5342(2)	34(1)	1
O(1C)	-313(5)	3335(4)	3928(3)	198(3)	1
C(1C)	607(5)	3490(3)	3606(2)	59(2)	1
C(2C)	1039(7)	4328(4)	3700(4)	154(4)	1
C(3C)	382(8)	4667(5)	4145(4)	225(7)	1
C(4C)	-662(8)	4150(5)	4096(4)	222(7)	1
O(1D)	1434(7)	683(5)	2089(3)	219(4)	1
C(1D)	2596(7)	916(4)	2176(3)	106(3)	1
C(2D)	2829(5)	1492(5)	2640(3)	93(2)	1
C(3D)	1822(7)	1367(4)	2959(3)	92(2)	1
C(4D)	851(5)	910(4)	2513(3)	85(2)	1
O(1E)	3794(7)	3020(4)	3788(3)	139(3)	0.614(5)
C(1E)	4665(5)	2444(3)	4073(2)	14(2)	0.614(5)
C(2E)	5603(6)	2865(4)	4489(3)	43(3)	0.614(5)
C(3E)	5347(7)	3768(5)	4385(3)	74(3)	0.614(5)
C(4E)	4070(5)	3768(3)	4125(2)	13(2)	0.614(5)
O(1F)	4651(7)	3366(5)	3674(3)	40(3)	0.386(5)
C(1F)	5718(9)	3814(5)	3938(4)	42(4)	0.386(5)
C(2F)	6316(10)	3399(8)	4454(4)	76(5)	0.386(5)
C(3F)	5631(19)	2593(10)	4451(7)	280(20)	0.386(5)
C(4F)	4466(15)	2768(11)	4101(7)	410(30)	0.386(5)

Table S7. Selected bond lengths [Å] and angles [°] for **5b-Pd-*anti***.

Pd(1)-N(2)	1.997(3)	Pd(1)-N(2)#1	1.997(3)

Pd(1)-N(1)#1	2.034(3)	N(2)-Pd(1)-N(2)#1	180.0
Pd(1)-N(1)	2.034(3)	N(2)-Pd(1)-N(1)#1	98.19(13)
		N(2)#1-Pd(1)-N(1)#1	81.81(13)
		N(2)-Pd(1)-N(1)	81.81(13)
		N(2)#1-Pd(1)-N(1)	98.19(13)
		N(1)#1-Pd(1)-N(1)	180.0

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1

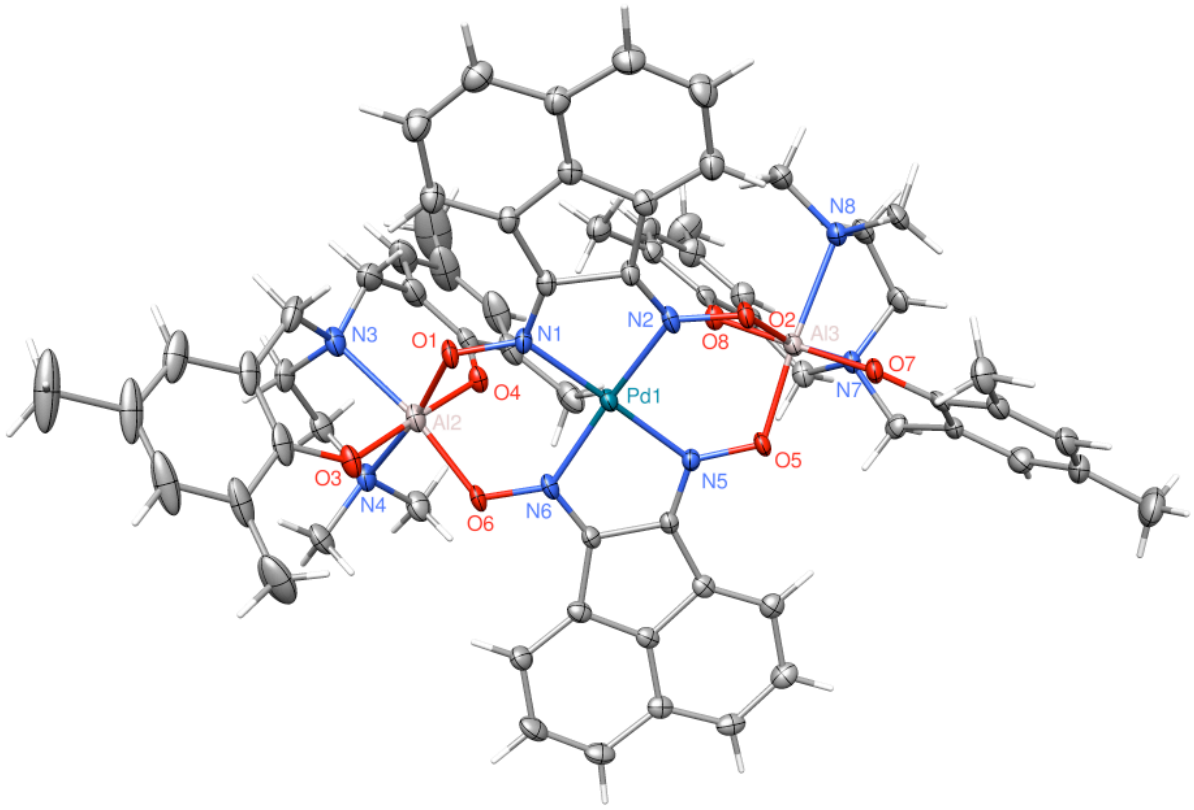


Figure S37. Structural drawing of **5b-Pd-*syn*** with 50% thermal probability ellipsoids.

Special Refinement Details for **5b-Pd-*syn***. Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. The crystal contains solvent of crystallization, hexane distributed across a center of symmetry and THF in a general position. This second site solvent region is disordered and was modeled with three THF molecules restrained to be similar. Each was assigned a separate free variable for occupancy and temperature factor. The final model has a total occupancy of one and one-half and is consistent with the initial calculated electron density map.

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5b-Pd-*syn***. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Pd(1)	2078(1)	4606(1)	2105(1)	17(1)	1
Al(2)	1225(1)	4706(1)	3519(1)	22(1)	1
Al(3)	3261(1)	5111(1)	1030(1)	18(1)	1
O(1)	1953(1)	4040(1)	3446(1)	21(1)	1
O(2)	3325(1)	4251(1)	1447(1)	20(1)	1
O(3)	617(1)	4037(1)	3665(1)	26(1)	1

O(4)	1812(1)	5393(1)	3355(1)	21(1)	1
O(5)	2207(1)	5178(1)	769(1)	19(1)	1
O(6)	690(1)	4725(1)	2631(1)	19(1)	1
O(7)	3269(1)	4682(1)	254(1)	20(1)	1
O(8)	3268(1)	5520(1)	1820(1)	19(1)	1
N(1)	2328(1)	4072(1)	2962(1)	18(1)	1
N(2)	3027(1)	4179(1)	1977(1)	19(1)	1
N(3)	1663(1)	4766(1)	4559(1)	26(1)	1
N(4)	439(1)	5457(1)	3752(1)	23(1)	1
N(5)	1804(1)	5109(1)	1232(1)	16(1)	1
N(6)	1050(1)	4895(1)	2160(1)	19(1)	1
N(7)	3354(1)	6054(1)	555(1)	18(1)	1
N(8)	4470(1)	5156(1)	1256(1)	21(1)	1
C(1)	2922(1)	3705(1)	3008(2)	18(1)	1
C(2)	3294(1)	3751(1)	2442(2)	18(1)	1
C(3)	3343(1)	3246(1)	3502(2)	18(1)	1
C(4)	3277(1)	2999(1)	4110(2)	25(1)	1
C(5)	3833(2)	2558(1)	4459(2)	31(1)	1
C(6)	4423(2)	2359(1)	4202(2)	29(1)	1
C(7)	4488(1)	2584(1)	3571(2)	23(1)	1
C(8)	5041(2)	2399(1)	3219(2)	30(1)	1
C(9)	5031(2)	2651(2)	2598(2)	31(1)	1
C(10)	4477(1)	3113(1)	2270(2)	27(1)	1
C(11)	3942(1)	3306(1)	2601(2)	20(1)	1
C(12)	3952(1)	3031(1)	3238(2)	19(1)	1
C(13)	1145(2)	5150(1)	4880(2)	28(1)	1
C(14)	753(2)	5710(2)	4434(2)	29(1)	1
C(15)	1776(2)	4073(2)	4862(2)	34(1)	1
C(16)	1091(2)	3647(2)	4782(2)	34(1)	1
C(17)	1004(2)	3226(2)	5306(2)	46(1)	1
C(18)	392(2)	2805(2)	5251(2)	57(1)	1
C(19)	-125(2)	2817(2)	4653(2)	60(1)	1
C(20)	-76(2)	3225(2)	4107(2)	42(1)	1
C(21)	560(2)	3649(2)	4179(2)	32(1)	1
C(22)	318(2)	2340(2)	5822(2)	88(2)	1
C(23)	-633(2)	3215(2)	3468(2)	58(1)	1
C(24)	2411(2)	5090(2)	4698(2)	34(1)	1
C(25)	2438(2)	5790(2)	4420(2)	32(1)	1
C(26)	2767(2)	6321(2)	4824(2)	47(1)	1
C(27)	2831(2)	6960(2)	4552(2)	58(1)	1
C(28)	2574(2)	7055(2)	3877(2)	48(1)	1
C(29)	2238(2)	6535(2)	3455(2)	32(1)	1
C(30)	2155(1)	5896(2)	3741(2)	25(1)	1
C(31)	3203(2)	7538(2)	4995(2)	102(2)	1
C(32)	1975(2)	6633(2)	2714(2)	37(1)	1
C(33)	315(1)	6044(1)	3287(2)	31(1)	1
C(34)	-304(1)	5149(1)	3724(2)	31(1)	1
C(35)	1121(1)	5320(1)	1102(1)	16(1)	1
C(36)	706(1)	5181(1)	1619(2)	17(1)	1
C(37)	-64(1)	5384(1)	1351(1)	20(1)	1
C(38)	-717(1)	5316(1)	1562(1)	23(1)	1
C(39)	-1371(1)	5520(1)	1122(2)	28(1)	1
C(40)	-1395(1)	5783(1)	496(2)	26(1)	1
C(41)	-725(1)	5860(1)	265(2)	20(1)	1
C(42)	-651(1)	6088(1)	-369(2)	23(1)	1
C(43)	29(1)	6080(1)	-534(2)	25(1)	1
C(44)	674(1)	5841(1)	-89(2)	22(1)	1
C(45)	625(1)	5631(1)	533(2)	18(1)	1
C(46)	-81(1)	5652(1)	709(2)	18(1)	1
C(47)	4141(1)	6158(1)	521(2)	24(1)	1
C(48)	4667(1)	5870(1)	1129(2)	24(1)	1
C(49)	2882(1)	6068(1)	-130(2)	23(1)	1

C(50)	3048(1)	5540(1)	-598(2)	21(1)	1
C(51)	2984(1)	5698(2)	-1271(2)	28(1)	1
C(52)	3079(2)	5215(2)	-1744(2)	30(1)	1
C(53)	3257(1)	4562(2)	-1510(2)	29(1)	1
C(54)	3336(1)	4378(1)	-840(2)	23(1)	1
C(55)	3218(1)	4868(1)	-374(2)	20(1)	1
C(56)	2981(2)	5400(2)	-2476(2)	48(1)	1
C(57)	3524(2)	3668(1)	-602(2)	32(1)	1
C(58)	3088(1)	6624(1)	925(2)	24(1)	1
C(59)	3451(1)	6698(1)	1648(2)	21(1)	1
C(60)	3703(1)	7327(2)	1919(2)	27(1)	1
C(61)	3971(2)	7411(2)	2598(2)	30(1)	1
C(62)	3986(1)	6848(2)	3010(2)	30(1)	1
C(63)	3746(1)	6211(2)	2761(2)	24(1)	1
C(64)	3486(1)	6135(2)	2071(2)	20(1)	1
C(65)	4243(2)	8087(2)	2889(2)	46(1)	1
C(66)	3733(1)	5611(1)	3218(2)	30(1)	1
C(67)	4789(1)	4679(1)	834(1)	26(1)	1
C(68)	4807(1)	4990(1)	1959(2)	27(1)	1
C(1C)	5549(2)	4362(2)	3764(2)	92(2)	1
C(2C)	5104(2)	4348(2)	4333(2)	85(2)	1
C(3C)	5254(2)	5000(2)	4748(2)	71(1)	1
O(1D)	1545(3)	3032(4)	6972(3)	134(2)	0.524(2)
C(1D)	1778(5)	3442(4)	7571(5)	134(2)	0.524(2)
C(2D)	2111(5)	2987(5)	8101(4)	134(2)	0.524(2)
C(3D)	2293(5)	2409(4)	7805(5)	134(2)	0.524(2)
C(4D)	2125(5)	2493(4)	7096(5)	134(2)	0.524(2)
O(1E)	3996(4)	2865(4)	6427(4)	52(2)	0.309(4)
C(1E)	4152(5)	3220(6)	7078(5)	52(2)	0.309(4)
C(2E)	3554(5)	3676(5)	7098(5)	52(2)	0.309(4)
C(3E)	3140(5)	3775(5)	6428(5)	52(2)	0.309(4)
C(4E)	3304(5)	3184(6)	6028(5)	52(2)	0.309(4)
O(1F)	3830(4)	3611(4)	6025(4)	206(3)	0.617(5)
C(1F)	3283(6)	3036(6)	5905(5)	206(3)	0.617(5)
C(2F)	3449(6)	2593(5)	6491(6)	206(3)	0.617(5)
C(3F)	3412(6)	3200(6)	6937(5)	206(3)	0.617(5)
C(4F)	4022(6)	3634(5)	6779(5)	206(3)	0.617(5)

Table S9. Selected bond lengths [Å] and angles [°] for **5b-Pd-*syn*.**

Pd(1)-N(5)	2.011(2)	N(5)-Pd(1)-N(1)	177.77(9)
Pd(1)-N(1)	2.014(2)	N(5)-Pd(1)-N(6)	81.68(9)
Pd(1)-N(6)	2.0160(19)	N(1)-Pd(1)-N(6)	97.86(9)
Pd(1)-N(2)	2.0198(19)	N(5)-Pd(1)-N(2)	98.33(9)
N(6)-Pd(1)-N(2)	170.67(9)	N(1)-Pd(1)-N(2)	81.77(9)

Table S10. Crystal and refinement data for **5a-Fe-O-bridge**, **8^{tBu}**, and **12^{NO2}**

	5a-Fe-O-bridge	**8^{tBu}**	**12^{NO2}**
CCDC Deposition #	861067		861069
Empirical formula	$C_{72}H_{80}N_8O_8Al_2Fe$	$C_{94}H_{114}Al_2FeN_{10}O_8$	$C_{86}H_{90}N_{14}O_{16}Al_2Fe \bullet C_4H_{10}O \bullet 3.5(C_4H_8O)$
Formula weight	1295.25	1621.76	2012.01
Crystallization Solvent	THF/hexane	THF/pentane	THF/diethyl ether
Crystal Habit	Block	Plate	Block
Crystal size, mm^3	0.13 x 0.08 x 0.04	0.23 x 0.19 x 0.19	0.27 x 0.19 x 0.09
Crystal color	Purple	Purple	Purple/red
θ range for lattice determination	2.40 to 19.40°		2.28 to 20.39°
a, Å	22.511(4)	14.7358(11)	23.9420(6)
b, Å	10.8586(19)	20.2952(15)	27.0271(6)
c, Å	28.663(5)	33.354(3)	15.5154(3)
a, °	90	77.202(2)	90
b, °	109.657(2)	88.031(2)	90
g, °	90	74.307(2)	90
Volume, $Å^3$	6598(2)	9361.2(12)	10039.7(4)
Z	4	4	4
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	C 2/*c*	P$\bar{1}$	P 2_12_12 (#18)
Density (calculated)	1.304 Mg/m^3	1.151 Mg/m^3	1.331 Mg/m^3
F(000)	2736	3456	4264
θ range for data collection, °	2.40 to 27.52	1.55 to 25.00	1.86 to 23.28
Completeness to θ = 26.43°	99.8%	96.4%	99.8%
Index ranges	$-29 \le h \le 27$ $0 \le k \le 14$ $0 \le l \le 37$	$-17 \le h \le 17$ $-24 \le k \le 24$ $-39 \le l \le 39$	$-26 \le h \le 26$ $-28 \le k \le 30$ $-17 \le l \le 17$
Data collection scan type	ω scans; 7 settings		ω scans; 7 settings
Reflections collected	7969	162520	110120
Independent reflections	7969 [R_{int}= 0.0695]	31783 [R_{int}= 0.0881]	14452 [R_{int}= 0.0903]
Absorption coefficient, mm^{-1}	0.318		0.246
Absorption correction	Semi-empirical from equivalents (TWINABS)	Semi-empirical from equivalents	None
Max. and min. transmission	0.7455 and 0.5816	0.7456 and 0.6949	0.9782 and 0.9367

Hydrogen placement	Geometric positions	Geometric positions	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 2008)	SHELXL-97 (Sheldrick, 2008)	SHELXL-97 (Sheldrick, 2008)
Refinement method	Full matrix least-squares on F^2	Full matrix least-squares on F^2	Full matrix least-squares on F^2
Data / restraints / parameters	7969 / 0 / 448	31783/ 12 / 2140	14452 / 36 / 1258
Treatment of hydrogen atoms	Riding	Riding	Riding
Goodness-of-fit on F2	1.423	1.009	1.681
Final R indices [I>2s(I), 4802 reflections]	R1 = 0.0537 *w*R2 = 0.0804	R1 = 0.0650 *w*R2 = 0.1428	R1 = 0.0570 *w*R2 = 0.0558
R indices (all data)	R1 = 0.0931 *w*R2 = 0.0866	R1 = 0.1279 *w*R2 = 0.1609	R1 = 0.0877 *w*R2 = 0.0577
Type of weighting scheme used	Sigma	Sigma	Sigma
Weighting scheme used	$w=1/s^2(Fo^2)$	$w=1/s^2(Fo^2)$	$w=1/s^2(Fo^2)$
Max shift/error	0.002		0.011
Average shift/error	0		0
Largest diff. peak and hole, e.Å^{-3}	0.634 and -0.475	1.799 and -1.030	0.831 and -0.527
Type of diffractometer	Bruker KAPPA APEX II	Bruker KAPPA APEX II	Bruker KAPPA APEX II
Wavelength, Å MoKa	0.71073	0.71073	0.71073
Data Collection Temperature	100(2) K	100(2) K	100(2) K
Structure solution program	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick, 2008)	SHELXS-97 (Sheldrick, 2008)
Primary solution method	Direct methods	Direct methods	Direct methods
Secondary solution method	Difference Fourier map	Difference Fourier map	Difference Fourier map

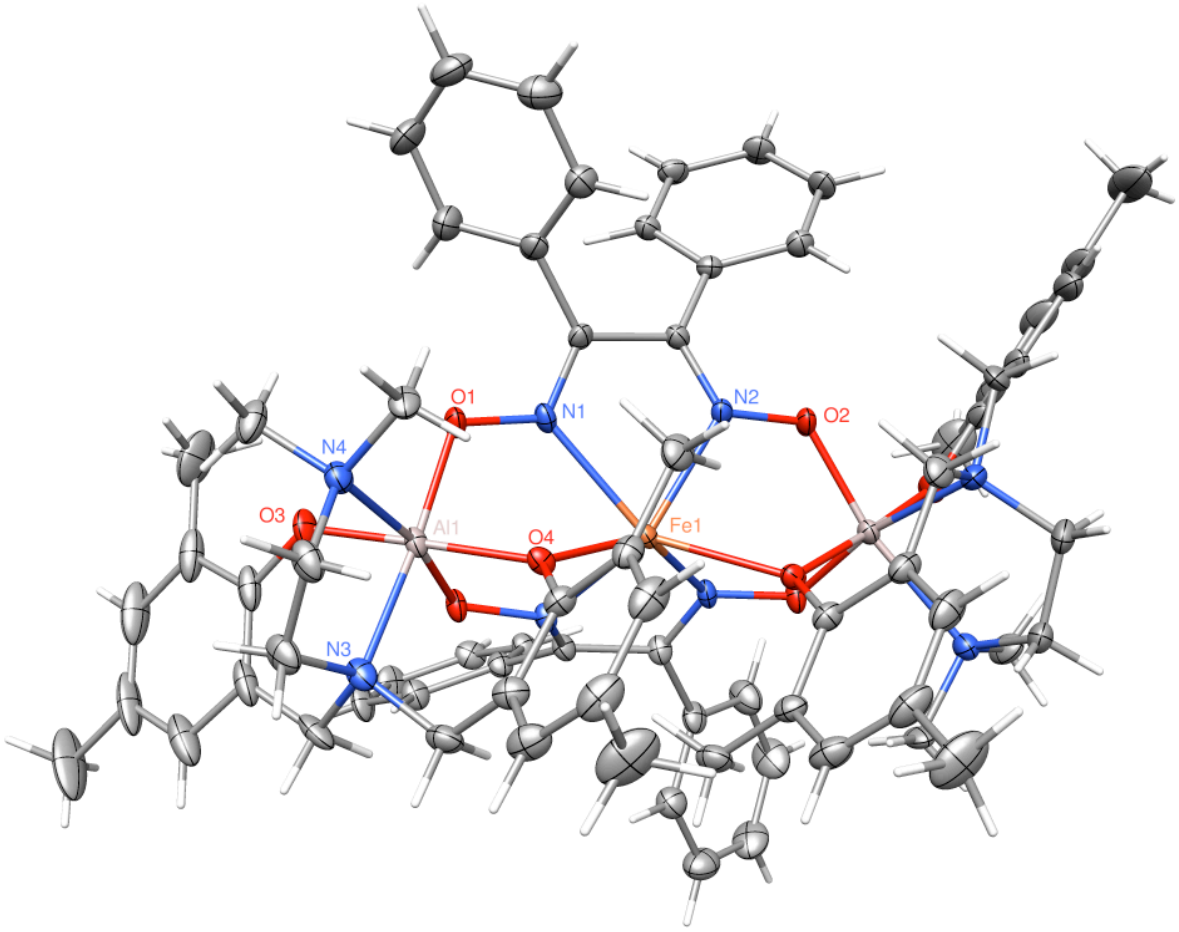


Figure S38. Structural drawing of **5a-Fe-O-bridge** with 50% thermal probability ellipsoids.

Special Refinement Details for 5a-Fe-O-bridge. Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. The crystal is a non-merohedral twin. The twin relationship was defined using CELL_NOW where 119 of 143 reflections fit domain one and the remaining 24 reflections fitting domain two. There were 61 overlapped reflections. Simultaneous integration of both domains led to an HKLF5 format reflection file. The final refined twin ratio is 70:30. Additionally, the molecule sits on a two-fold rotation axis and the ethane bridge between N3 and N4 is disordered resulting in alternate positions for C34-C36 (A and B). The ratio of the populations for the disordered atoms is 62:38.

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **5a-Fe-O-bridge**. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}	Occ
Fe(1)	0	2074(1)	2500	14(1)	1
Al(1)	1142(1)	2104(1)	3610(1)	16(1)	1
O(1)	451(1)	1228(1)	3632(1)	20(1)	1
O(2)	-1319(1)	1276(1)	1895(1)	18(1)	1
O(3)	1688(1)	1061(1)	4035(1)	24(1)	1
O(4)	568(1)	3173(1)	3135(1)	15(1)	1
N(1)	-7(1)	1074(2)	3183(1)	17(1)	1
N(2)	-930(1)	1348(2)	2368(1)	15(1)	1
N(3)	1900(1)	3343(2)	3686(1)	21(1)	1
N(4)	1123(1)	3079(2)	4273(1)	20(1)	1

C(1)	-548(1)	707(2)	3190(1)	17(1)	1
C(2)	-1040(1)	607(2)	2690(1)	16(1)	1
C(3)	-720(1)	522(2)	3646(1)	20(1)	1
C(4)	-379(1)	-245(2)	4029(1)	32(1)	1
C(5)	-571(1)	-413(3)	4434(1)	40(1)	1
C(6)	-1086(1)	207(3)	4473(1)	38(1)	1
C(7)	-1420(1)	983(2)	4097(1)	34(1)	1
C(8)	-1243(1)	1119(2)	3683(1)	25(1)	1
C(9)	-1533(1)	-355(2)	2578(1)	18(1)	1
C(10)	-1396(1)	-1459(2)	2843(1)	19(1)	1
C(11)	-1817(1)	-2428(2)	2733(1)	23(1)	1
C(12)	-2399(1)	-2312(2)	2360(1)	26(1)	1
C(13)	-2546(1)	-1216(2)	2099(1)	26(1)	1
C(14)	-2123(1)	-250(2)	2202(1)	21(1)	1
C(15)	2460(1)	2677(2)	3639(1)	28(1)	1
C(16)	2685(1)	1541(2)	3955(1)	30(1)	1
C(17)	3317(1)	1191(3)	4051(1)	43(1)	1
C(18)	3550(1)	80(3)	4286(1)	49(1)	1
C(19)	3144(2)	-666(3)	4428(1)	50(1)	1
C(20)	2521(1)	-345(2)	4347(1)	37(1)	1
C(21)	2283(1)	777(2)	4102(1)	27(1)	1
C(22)	4229(1)	-292(3)	4374(1)	72(1)	1
C(23)	2087(2)	-1165(3)	4506(1)	50(1)	1
C(24)	1730(1)	4289(2)	3276(1)	25(1)	1
C(25)	1159(1)	5038(2)	3231(1)	21(1)	1
C(26)	1180(1)	6321(2)	3252(1)	27(1)	1
C(27)	642(1)	7011(2)	3194(1)	30(1)	1
C(28)	78(1)	6379(2)	3122(1)	27(1)	1
C(29)	33(1)	5099(2)	3100(1)	19(1)	1
C(30)	584(1)	4425(2)	3152(1)	18(1)	1
C(31)	665(2)	8400(2)	3204(1)	44(1)	1
C(32)	-580(1)	4445(2)	3030(1)	24(1)	1
C(33)	2083(1)	3956(2)	4180(1)	28(1)	1
C(34A)	1532(2)	4187(4)	4340(1)	26(1)	0.619(5)
C(35A)	1329(3)	2271(5)	4707(2)	30(1)	0.619(5)
C(36A)	473(2)	3502(5)	4229(1)	23(1)	0.619(5)
C(34B)	1820(3)	3386(7)	4536(2)	26(2)	0.381(5)
C(35B)	965(4)	2172(9)	4620(3)	32(2)	0.381(5)
C(36B)	744(4)	4162(8)	4255(2)	28(2)	0.381(5)

Table S12. Selected bond lengths [Å] and angles [°] for **5a-Fe-O-bridge**.

Fe(1)-N(2)	2.1481(18)	Al(1)-N(3)	2.1263(19)
Fe(1)-N(2)#1	2.1481(18)	Al(1)-N(4)	2.1868(18)
Fe(1)-O(4)	2.1913(13)		
Fe(1)-O(4)#1	2.1914(13)		
Fe(1)-N(1)#1	2.2427(16)		
Fe(1)-N(1)	2.2427(16)		
Al(1)-O(3)	1.8086(16)		
Al(1)-O(1)	1.8415(16)		
Al(1)-O(2)#1	1.8590(15)		
Al(1)-O(4)	1.9206(15)		

N(2)-Fe(1)-N(2)#1	136.93(9)	O(3)-Al(1)-O(4)	177.45(7)
N(2)-Fe(1)-O(4)	127.39(5)	O(1)-Al(1)-O(4)	87.83(7)
N(2)#1-Fe(1)-O(4)	78.02(6)	O(2)#1-Al(1)-O(4)	90.53(6)
N(2)-Fe(1)-O(4)#1	78.03(6)	O(3)-Al(1)-N(3)	89.27(7)
N(2)#1-Fe(1)-O(4)#1	127.39(5)	O(1)-Al(1)-N(3)	168.93(7)
O(4)-Fe(1)-O(4)#1	114.02(7)	O(2)#1-Al(1)-N(3)	90.56(7)
N(2)-Fe(1)-N(1)#1	87.81(6)	O(4)-Al(1)-N(3)	90.90(7)
N(2)#1-Fe(1)-N(1)#1	71.50(6)	O(3)-Al(1)-N(4)	85.72(7)
O(4)-Fe(1)-N(1)#1	144.55(6)	O(1)-Al(1)-N(4)	87.57(7)
O(4)#1-Fe(1)-N(1)#1	73.31(6)	O(2)#1-Al(1)-N(4)	169.35(7)
N(2)-Fe(1)-N(1)	71.50(6)	O(4)-Al(1)-N(4)	96.82(7)
N(2)#1-Fe(1)-N(1)	87.81(6)	N(3)-Al(1)-N(4)	81.66(7)
O(4)-Fe(1)-N(1)	73.31(6)		
O(4)#1-Fe(1)-N(1)	144.55(6)	Symmetry transformations used to generate equivalent atoms:	
N(1)#1-Fe(1)-N(1)	122.06(9)	#1 -x,y,-z+1/2	
O(3)-Al(1)-O(1)	92.49(7)		
O(3)-Al(1)-O(2)#1	86.92(7)		
O(1)-Al(1)-O(2)#1	100.44(7)		

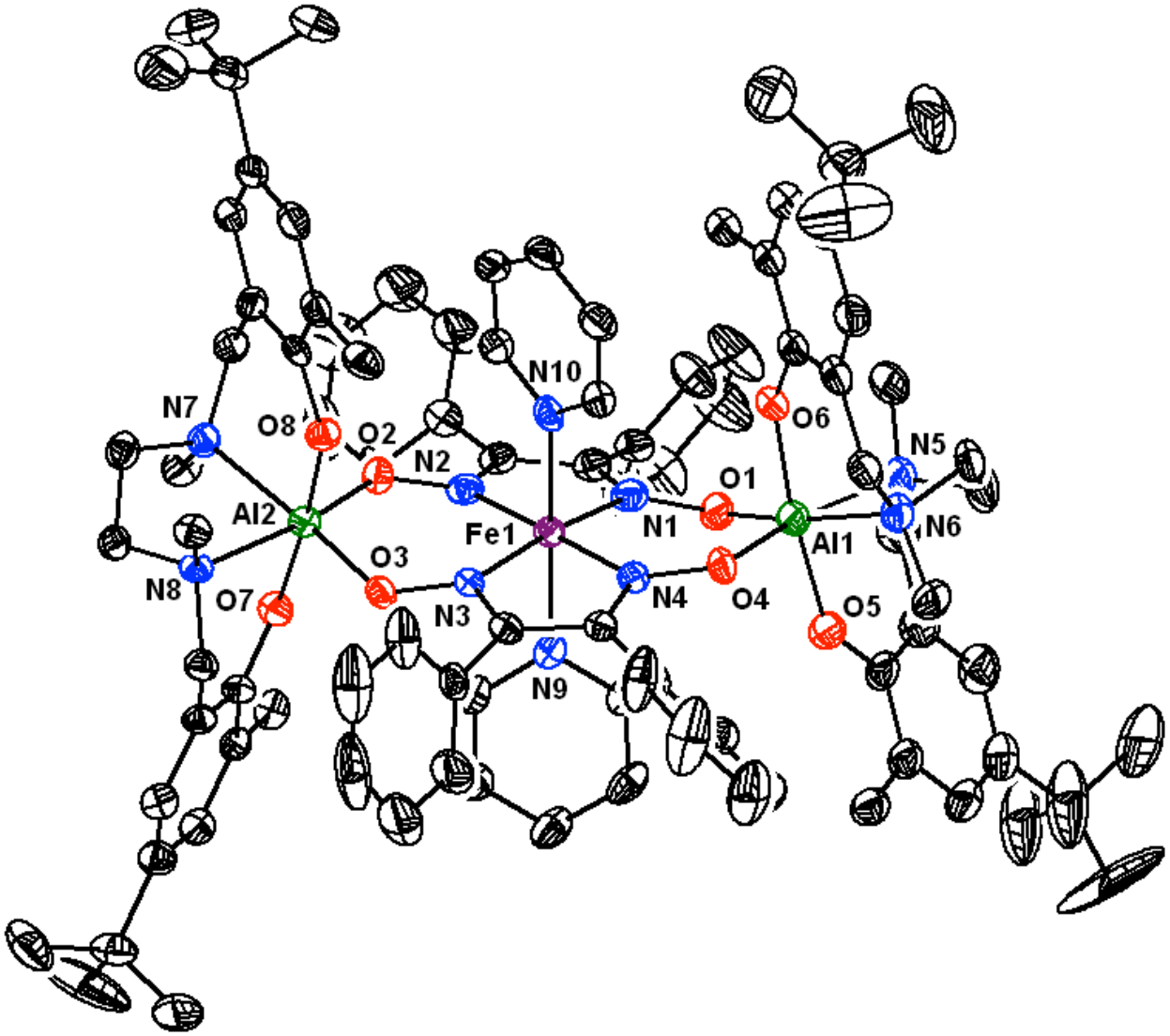


Figure S39. Structural drawing of $\mathbf{8^{tBu}}$ with 50% thermal probability ellipsoids.

Special Refinement Details for $\mathbf{8^{tBu}}$. A deep purple plate of suitable size (0.23 x 0.19 x 0.19 mm) was selected from a representative sample of crystals of the same habit using an optical microscope and mounted onto a glass fiber. Low temperature (100 K) X-ray data were obtained on a Bruker APEXII CCD based diffractometer (Mo sealed X-ray tube, K_α = 0.71073 Å). All diffractometer manipulations, including data collection, integration and scaling were carried out using the Bruker APEXII software.[1] An absorption correction was applied using SADABS.[2] The space group was determined on the basis of systematic absences and intensity statistics and the structure was solved by direct methods and refined by full-matrix least squares on F^2. The structure was solved in the triclinic *P* EMBED Equation.3 space group using XS[3] (incorporated in SHELXTL). No missed symmetry was reported by the ADDSYM program in PLATON.[4] All non-hydrogen atoms were refined by using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and refined using a riding model. Multiple disordered toluene solvent molecules (the crystallization solvent) were found within the asymmetric unit. These could not be satisfactorily modeled and were removed using the SQUEEZE protocol included in PLATON,[4] the results of which are appended to the end of the CIF. The structure was refined (weighted least squares refinement on F^2) to convergence using the updated reflections file. The final least-squares refinement converged to R_1 = 0.0650 ($I > 2\sigma(I)$, 31783 data) and wR_2 = 0. 1609 (F^2, 22895 data, 2140 parameters). Disorder within two phenyl moieties was addressed, however, despite use of restraints (12), the elongated thermal parameters are still evident as noted in the checkCIF. These result from unresolved disorder in the *tert*-butyl moieties and less than ideal crystal quality. The final CIF is available as supporting material.

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **8**^{tBu}. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(2A)	8942	6325	3921	54
Al(1A)	9687(1)	8503(1)	2921(1)	29(1)
Al(2A)	6152(1)	6892(1)	4117(1)	20(1)
Al(1B)	2031(1)	1945(1)	1276(1)	33(1)
Al(2B)	-1601(1)	4055(1)	2427(1)	23(1)
C(1A)	9620(2)	6693(2)	3712(1)	19(1)
C(3A)	11244(2)	6202(1)	3482(1)	26(1)
C(4A)	12211(1)	5938(1)	3556(1)	31(1)
C(5A)	12593(1)	5869(1)	3943(1)	31(1)
C(6A)	12008(2)	6065(1)	4257(1)	33(1)
C(7A)	11040(2)	6329(1)	4183(1)	27(1)
C(8A)	10658(1)	6398(1)	3796(1)	20(1)
C(9A)	9184(2)	5622(2)	4161(1)	19(1)
C(10A)	9701(2)	5073(2)	3998(1)	25(1)
C(11A)	9942(3)	4395(2)	4236(1)	29(1)
C(12A)	9660(3)	4269(2)	4638(1)	35(1)
C(13A)	9153(3)	4813(2)	4806(1)	33(1)
C(14A)	8918(3)	5486(2)	4569(1)	27(1)
C(15A)	6904(2)	8916(2)	2997(1)	23(1)
C(16A)	6663(3)	9541(3)	2640(1)	47(1)
C(17A)	6800(3)	10178(2)	2677(2)	67(2)
C(18A)	6651(4)	10741(3)	2334(3)	104(3)
C(19A)	6382(4)	10641(6)	1971(3)	132(5)
C(20A)	6238(4)	10017(5)	1925(2)	123(4)
C(21A)	6384(3)	9452(3)	2270(2)	82(2)
C(22A)	6201(2)	8650(2)	3250(1)	20(1)
C(23A)	5211(2)	9055(2)	3255(1)	22(1)
C(24A)	4997(3)	9728(2)	3327(1)	28(1)
C(25A)	4065(3)	10111(2)	3353(1)	37(1)
C(26A)	3352(3)	9820(2)	3314(1)	44(1)
C(27A)	3551(3)	9155(2)	3242(1)	48(1)
C(28A)	4476(3)	8773(2)	3212(1)	33(1)
C(29A)	11798(3)	7815(2)	2878(1)	32(1)
C(30A)	11321(3)	9091(2)	2750(1)	37(1)
C(31A)	10775(3)	9302(2)	2347(1)	43(1)
C(32A)	9321(3)	10065(2)	2538(2)	63(2)
C(33A)	11376(2)	8361(2)	3448(1)	28(1)
C(34A)	10881(3)	8977(2)	3623(1)	31(1)
C(35A)	9922(3)	9289(2)	3539(1)	32(1)
C(36A)	9464(3)	9854(2)	3723(1)	37(1)
C(37A)	9986(3)	10087(2)	3971(1)	44(1)
C(38A)	10951(3)	9786(2)	4053(1)	38(1)
C(39A)	11375(3)	9232(2)	3876(1)	33(1)
C(40A)	8423(3)	10178(2)	3637(2)	52(1)
C(41A)	11487(3)	10084(2)	4328(1)	44(1)
C(42A)	12514(3)	9656(2)	4408(1)	50(1)
C(43A)	11462(3)	10844(2)	4121(2)	56(1)
C(44A)	11004(4)	10068(3)	4746(2)	67(2)
C(45A)	9252(3)	9360(3)	2054(2)	75(2)
C(46A)	9674(3)	8733(3)	1877(1)	61(2)
C(47A)	10031(3)	8064(3)	2130(1)	53(1)
C(48A)	10442(4)	7480(4)	1955(2)	65(2)
C(49A)	10451(5)	7593(4)	1524(2)	100(3)
C(50A)	10089(5)	8253(5)	1266(2)	104(3)
C(51A)	9717(4)	8815(4)	1449(2)	96(2)
C(52A)	10880(3)	6770(3)	2238(2)	67(2)
C(53A)	10163(8)	8350(7)	798(2)	176(5)

C(54A)	9182(8)	8823(6)	603(2)	218(7)
C(55A)	10806(6)	8807(5)	636(2)	196(5)
C(56A)	10328(9)	7704(5)	652(2)	217(6)
C(57A)	6583(3)	5774(2)	4949(1)	29(1)
C(58A)	5023(2)	6038(2)	4653(1)	26(1)
C(59A)	4603(3)	6779(2)	4709(1)	28(1)
C(60A)	3983(2)	7392(2)	4026(1)	30(1)
C(61A)	4644(2)	7990(2)	4434(1)	26(1)
C(62A)	5288(3)	7972(2)	4776(1)	25(1)
C(63A)	6226(3)	7556(2)	4808(1)	24(1)
C(64A)	6810(3)	7559(2)	5136(1)	26(1)
C(65A)	6429(3)	7969(2)	5414(1)	32(1)
C(66A)	5496(3)	8388(2)	5391(1)	32(1)
C(67A)	4942(3)	8370(2)	5069(1)	29(1)
C(68A)	7816(3)	7126(2)	5170(1)	34(1)
C(69A)	5124(3)	8840(2)	5706(1)	41(1)
C(70A)	5564(3)	9447(2)	5629(1)	51(1)
C(71A)	5368(5)	8417(2)	6136(1)	96(2)
C(72A)	4055(4)	9166(3)	5656(2)	103(2)
C(73A)	6397(2)	5315(2)	4364(1)	24(1)
C(74A)	5802(2)	5329(2)	4003(1)	23(1)
C(75A)	5454(2)	5964(2)	3704(1)	20(1)
C(76A)	4892(2)	5957(2)	3377(1)	22(1)
C(77A)	4695(2)	5333(2)	3349(1)	25(1)
C(78A)	5002(3)	4715(2)	3643(1)	26(1)
C(79A)	5560(2)	4732(2)	3967(1)	25(1)
C(80A)	4470(3)	6626(2)	3069(1)	29(1)
C(81A)	4733(3)	4034(2)	3635(1)	30(1)
C(82A)	5622(3)	3445(2)	3622(1)	42(1)
C(83A)	4107(3)	4134(2)	3254(1)	44(1)
C(84A)	4177(3)	3835(2)	4018(1)	38(1)
C(85A)	8878(3)	8172(2)	4077(1)	28(1)
C(86A)	8969(3)	8499(2)	4388(1)	42(1)
C(87A)	8186(3)	8803(2)	4585(1)	48(1)
C(88A)	7324(3)	8792(2)	4458(1)	35(1)
C(89A)	7273(3)	8453(2)	4146(1)	26(1)
C(90A)	6959(2)	7033(2)	2963(1)	23(1)
C(91A)	6720(2)	6892(2)	2602(1)	24(1)
C(92A)	7293(3)	6955(2)	2265(1)	28(1)
C(93A)	8105(3)	7151(2)	2309(1)	30(1)
C(94A)	8303(3)	7287(2)	2677(1)	30(1)
C(1B)	-740(3)	2346(2)	1430(1)	29(1)
C(2B)	-1465(3)	2804(2)	1627(1)	25(1)
C(3B)	-899(3)	1949(2)	1132(1)	47(6)
C(4B)	-1266(4)	2268(2)	737(1)	43(4)
C(5B)	-1405(4)	1861(3)	472(1)	70(6)
C(6B)	-1178(4)	1135(3)	603(2)	117(10)
C(7B)	-811(4)	816(2)	998(2)	103(7)
C(8B)	-671(3)	1223(2)	1263(2)	89(7)
C(3C)	-1050(3)	1873(2)	1203(1)	28(3)
C(4C)	-878(3)	1977(3)	784(1)	41(2)
C(5C)	-1132(4)	1562(3)	552(1)	59(3)
C(6C)	-1557(4)	1042(3)	738(2)	71(3)
C(7C)	-1729(4)	938(2)	1156(2)	51(2)
C(8C)	-1475(4)	1353(2)	1389(1)	31(2)
C(9B)	-2481(3)	2927(2)	1549(1)	28(1)
C(10B)	-3142(12)	2732(8)	1882(5)	36(4)
C(11B)	-4090(16)	2878(10)	1798(7)	52(5)
C(12B)	-4410(3)	3188(3)	1417(2)	68(2)
C(13B)	-3834(11)	3387(9)	1079(5)	57(3)
C(14B)	-2856(13)	3212(10)	1159(5)	54(5)
C(10C)	-2920(11)	2493(9)	1744(5)	75(5)

C(11C)	-3885(13)	2603(11)	1689(6)	90(6)
C(12C)	-4410(3)	3188(3)	1417(2)	68(2)
C(13C)	-3957(10)	3649(9)	1228(4)	57(3)
C(14C)	-2980(10)	3507(7)	1271(4)	44(4)
C(15B)	1937(3)	2874(2)	2244(1)	23(1)
C(16B)	1208(3)	3265(2)	2473(1)	23(1)
C(17B)	2946(3)	2658(2)	2368(1)	27(1)
C(18B)	3410(3)	3117(2)	2454(2)	53(1)
C(19B)	4342(3)	2866(3)	2604(2)	76(2)
C(20B)	4796(3)	2168(3)	2670(2)	66(2)
C(21B)	4356(3)	1708(2)	2582(1)	46(1)
C(22B)	3443(3)	1954(2)	2431(1)	35(1)
C(23B)	1414(3)	3495(2)	2845(1)	31(1)
C(24B)	1267(3)	4212(3)	2825(2)	48(1)
C(25B)	1434(3)	4454(4)	3157(2)	75(2)
C(26B)	1757(4)	4001(5)	3507(2)	91(3)
C(27B)	1919(4)	3290(4)	3555(2)	88(2)
C(28B)	1728(3)	3033(3)	3206(1)	61(2)
C(29B)	1513(3)	1716(2)	443(1)	48(1)
C(30B)	3115(3)	1141(2)	696(1)	51(1)
C(31B)	3530(3)	1755(2)	672(1)	48(1)
C(32B)	4204(3)	1508(2)	1362(1)	45(1)
C(33B)	-3723(3)	4181(2)	2394(1)	33(1)
C(34B)	-3290(3)	5167(2)	2557(1)	29(1)
C(35B)	-2782(2)	4873(2)	2971(1)	26(1)
C(36B)	-1338(3)	5232(2)	2823(1)	28(1)
C(37B)	1790(3)	676(2)	987(1)	46(1)
C(38B)	2417(3)	173(2)	1329(1)	45(1)
C(39B)	2760(3)	418(2)	1637(1)	36(1)
C(40B)	3369(3)	-61(2)	1945(1)	34(1)
C(41B)	3603(3)	-776(2)	1944(1)	44(1)
C(42B)	3257(3)	-1030(2)	1641(1)	47(1)
C(43B)	2676(3)	-543(2)	1333(1)	48(1)
C(44B)	3780(3)	195(2)	2265(1)	37(1)
C(45B)	3554(5)	-1823(3)	1642(2)	109(2)
C(46B)	4434(7)	-2207(3)	1872(3)	205(6)
C(47B)	3704(5)	-1923(3)	1208(2)	107(2)
C(48B)	2723(4)	-2096(3)	1768(2)	109(2)
C(49B)	3541(3)	2690(2)	1021(1)	38(1)
C(50B)	2887(3)	3240(2)	701(1)	36(1)
C(51B)	1962(3)	3220(2)	645(1)	33(1)
C(52B)	1388(3)	3740(2)	337(1)	33(1)
C(53B)	1749(3)	4273(2)	110(1)	41(1)
C(54B)	2663(3)	4314(2)	173(1)	42(1)
C(55B)	3220(3)	3780(2)	465(1)	43(1)
C(56B)	395(3)	3720(2)	270(1)	40(1)
C(57B)	3029(3)	4917(2)	-77(1)	51(1)
C(58B)	2255(4)	5598(2)	-186(2)	71(2)
C(59B)	3453(4)	4714(3)	-469(2)	95(2)
C(60B)	3782(5)	5046(3)	162(2)	117(3)
C(61B)	-1264(3)	4161(2)	3297(1)	25(1)
C(62B)	-1609(2)	3521(2)	3469(1)	22(1)
C(63B)	-1915(2)	3161(2)	3213(1)	21(1)
C(64B)	-2214(2)	2561(2)	3394(1)	23(1)
C(65B)	-2156(2)	2328(2)	3818(1)	28(1)
C(66B)	-1849(3)	2681(2)	4081(1)	30(1)
C(67B)	-1583(2)	3281(2)	3893(1)	27(1)
C(68B)	-2613(3)	2201(2)	3125(1)	28(1)
C(69B)	-1795(3)	2427(2)	4551(1)	37(1)
C(70B)	-2102(4)	3044(2)	4761(1)	60(2)
C(71B)	-2453(5)	1968(3)	4700(2)	106(3)
C(72B)	-785(4)	2035(3)	4682(2)	116(3)

C(73B)	-3237(3)	4983(2)	1851(1)	31(1)
C(74B)	-2674(3)	5498(2)	1688(1)	25(1)
C(75B)	-1739(3)	5365(2)	1812(1)	24(1)
C(76B)	-1228(3)	5856(2)	1646(1)	28(1)
C(77B)	-1662(3)	6446(2)	1353(1)	32(1)
C(78B)	-2585(3)	6581(2)	1213(1)	33(1)
C(79B)	-3083(3)	6102(2)	1389(1)	30(1)
C(80B)	-221(3)	5713(2)	1787(1)	35(1)
C(81B)	-3025(3)	7250(2)	882(1)	43(1)
C(82B)	-3073(4)	7899(2)	1059(2)	74(2)
C(83B)	-3997(3)	7280(2)	736(2)	66(2)
C(84B)	-2389(4)	7266(3)	503(1)	68(2)
C(85B)	-201(2)	2059(2)	2681(1)	26(1)
C(86B)	-48(3)	1512(2)	3017(1)	34(1)
C(87B)	685(3)	916(2)	3017(1)	42(1)
C(88B)	1215(3)	898(2)	2671(1)	36(1)
C(89B)	1027(3)	1464(2)	2343(1)	28(1)
C(90B)	-633(3)	4267(2)	1296(1)	32(1)
C(91B)	-680(3)	4887(2)	1013(1)	36(1)
C(92B)	140(3)	5059(2)	884(1)	38(1)
C(93B)	983(3)	4600(2)	1046(1)	36(1)
C(94B)	974(3)	3986(2)	1327(1)	32(1)
Fe(1A)	7904(1)	7662(1)	3481(1)	19(1)
Fe(1B)	233(1)	2918(1)	1897(1)	23(1)
N(1A)	9256(2)	7315(2)	3477(1)	20(1)
N(2A)	8057(2)	6752(1)	3847(1)	19(1)
N(3A)	6553(2)	8026(1)	3488(1)	19(1)
N(4A)	7766(2)	8529(2)	3076(1)	22(1)
N(5A)	11157(2)	8430(1)	3004(1)	27(1)
N(6A)	9758(2)	9373(2)	2433(1)	47(1)
N(7A)	6036(2)	5932(1)	4556(1)	22(1)
N(8A)	4742(2)	7290(1)	4331(1)	23(1)
N(9A)	8033(2)	8143(1)	3948(1)	21(1)
N(10A)	7729(2)	7252(1)	3004(1)	23(1)
N(1B)	123(2)	2356(2)	1509(1)	29(1)
N(2B)	-1126(2)	3115(2)	1869(1)	26(1)
N(3B)	348(2)	3372(1)	2338(1)	20(1)
N(4B)	1592(2)	2699(1)	1935(1)	24(1)
N(5B)	2120(2)	1321(2)	815(1)	40(1)
N(6B)	3427(2)	1968(2)	1073(1)	39(1)
N(7B)	-3061(2)	4632(2)	2297(1)	25(1)
N(8B)	-1750(2)	4624(1)	2911(1)	22(1)
N(9B)	338(2)	2056(2)	2343(1)	24(1)
N(10B)	183(2)	3806(2)	1459(1)	26(1)
O(1A)	9892(2)	7669(1)	3318(1)	22(1)
O(2A)	7365(2)	6443(1)	3990(1)	21(1)
O(3A)	5938(2)	7760(1)	3745(1)	21(1)
O(4A)	8414(2)	8702(1)	2807(1)	33(1)
O(5A)	9426(2)	9073(1)	3290(1)	32(1)
O(6A)	10024(2)	7962(1)	2538(1)	37(1)
O(7A)	6595(2)	7164(1)	4538(1)	24(1)
O(8A)	5630(2)	6560(1)	3739(1)	22(1)
O(1B)	814(2)	1877(1)	1370(1)	33(1)
O(2B)	-1776(2)	3598(1)	2021(1)	26(1)
O(3B)	-341(2)	3655(1)	2575(1)	23(1)
O(4B)	2230(2)	2390(1)	1686(1)	28(1)
O(5B)	2542(2)	1104(1)	1635(1)	36(1)
O(6B)	1600(2)	2738(1)	878(1)	33(1)
O(7B)	-1984(2)	3383(1)	2804(1)	26(1)
O(8B)	-1285(2)	4780(1)	2080(1)	24(1)

Table S14. Bond lengths [Å] and angles [°] for **8^{tBu}**.

Al(1A)-O(5A)	1.833(3)	O(4A)-Al(1A)-N(5A)	171.35(12)
Al(1A)-O(6A)	1.837(3)	O(1A)-Al(1A)-N(5A)	86.83(11)
Al(1A)-O(4A)	1.844(3)	N(6A)-Al(1A)-N(5A)	82.65(13)
Al(1A)-O(1A)	1.862(2)	O(7A)-Al(2A)-O(8A)	173.18(11)
Al(1A)-N(6A)	2.144(3)	O(7A)-Al(2A)-O(2A)	91.43(11)
Al(1A)-N(5A)	2.155(3)	O(8A)-Al(2A)-O(2A)	91.87(11)
Al(2A)-O(7A)	1.817(3)	O(7A)-Al(2A)-O(3A)	96.10(11)
Al(2A)-O(8A)	1.832(3)	O(8A)-Al(2A)-O(3A)	89.08(11)
Al(2A)-O(2A)	1.856(2)	O(2A)-Al(2A)-O(3A)	101.56(10)
Al(2A)-O(3A)	1.872(2)	O(7A)-Al(2A)-N(8A)	87.45(11)
Al(2A)-N(8A)	2.173(3)	O(8A)-Al(2A)-N(8A)	88.48(11)
Al(2A)-N(7A)	2.206(3)	O(2A)-Al(2A)-N(8A)	172.25(11)
Fe(1A)-N(1A)	1.926(3)	O(3A)-Al(2A)-N(8A)	86.19(10)
Fe(1A)-N(3A)	1.928(3)	O(7A)-Al(2A)-N(7A)	88.71(11)
Fe(1A)-N(4A)	1.932(3)	O(8A)-Al(2A)-N(7A)	85.27(11)
Fe(1A)-N(2A)	1.936(3)	O(2A)-Al(2A)-N(7A)	91.02(10)
Fe(1A)-N(10A)	2.006(3)	O(3A)-Al(2A)-N(7A)	166.39(11)
Fe(1A)-N(9A)	2.051(3)	N(8A)-Al(2A)-N(7A)	81.29(11)
N(1A)-O(1A)	1.356(3)	N(1A)-Fe(1A)-N(3A)	178.93(12)
N(2A)-O(2A)	1.356(3)	N(1A)-Fe(1A)-N(4A)	98.15(12)
N(3A)-O(3A)	1.362(3)	N(3A)-Fe(1A)-N(4A)	81.25(12)
N(4A)-O(4A)	1.350(3)	N(1A)-Fe(1A)-N(2A)	80.85(12)
		N(3A)-Fe(1A)-N(2A)	99.83(12)
O(5A)-Al(1A)-O(6A)	175.54(13)	N(4A)-Fe(1A)-N(2A)	174.99(12)
O(5A)-Al(1A)-O(4A)	89.55(12)	N(1A)-Fe(1A)-N(10A)	92.39(11)
O(6A)-Al(1A)-O(4A)	93.76(13)	N(3A)-Fe(1A)-N(10A)	88.45(11)
O(5A)-Al(1A)-O(1A)	95.09(12)	N(4A)-Fe(1A)-N(10A)	85.40(12)
O(6A)-Al(1A)-O(1A)	87.18(12)	N(2A)-Fe(1A)-N(10A)	89.73(11)
O(4A)-Al(1A)-O(1A)	101.63(11)	N(1A)-Fe(1A)-N(9A)	89.76(11)
O(5A)-Al(1A)-N(6A)	90.97(14)	N(3A)-Fe(1A)-N(9A)	89.36(11)
O(6A)-Al(1A)-N(6A)	86.09(14)	N(4A)-Fe(1A)-N(9A)	91.38(11)
O(4A)-Al(1A)-N(6A)	89.14(12)	N(2A)-Fe(1A)-N(9A)	93.52(11)
O(1A)-Al(1A)-N(6A)	167.66(13)	N(10A)-Fe(1A)-N(9A)	176.36(11)
O(5A)-Al(1A)-N(5A)	87.88(12)	Symmetry transformations used to generate	
O(6A)-Al(1A)-N(5A)	88.41(12)	equivalent atoms: #1 -x,y,-z+1/2	

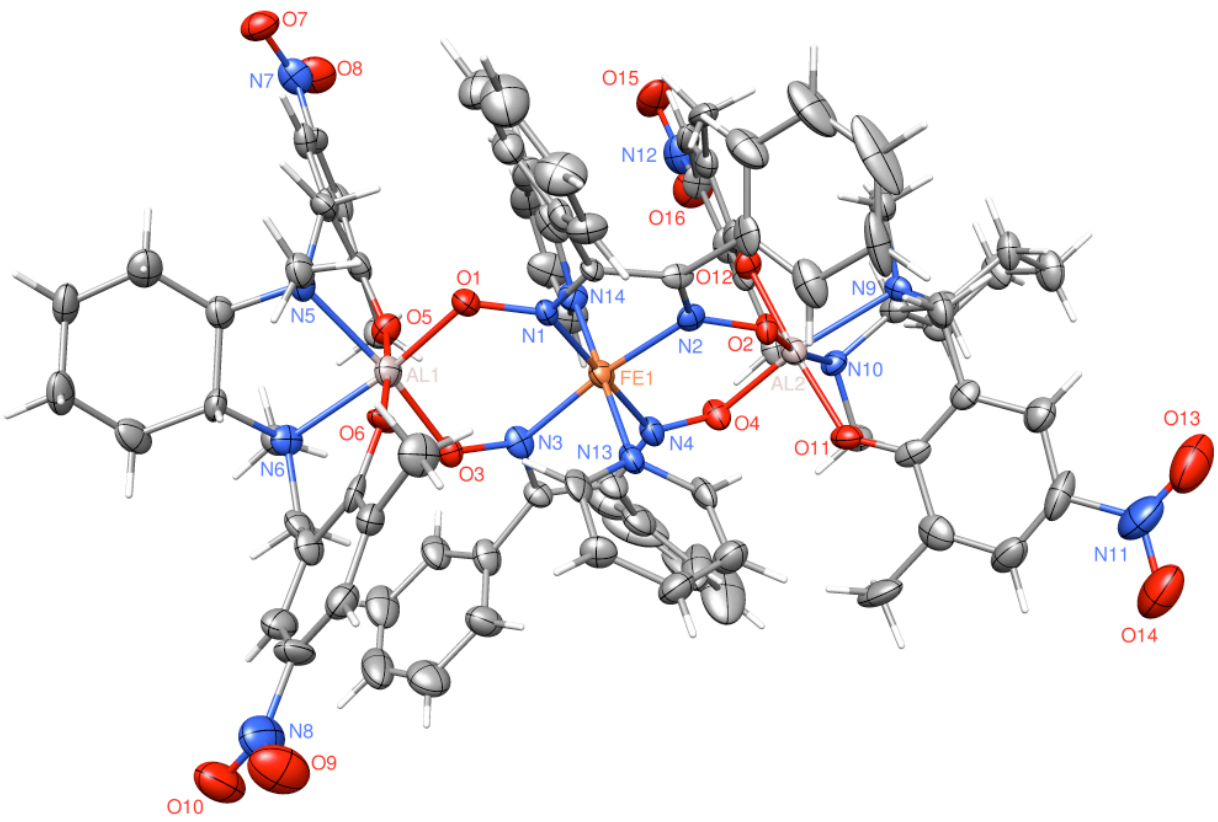


Figure S40. Structural drawing of $\mathbf{12^{NO2}}$ with 50% thermal probability ellipsoids.

Special Refinement Details for $\mathbf{12^{NO2}}$. Crystals were mounted on a glass fiber using Paratone oil then placed on the diffractometer under a nitrogen stream at 100K. The crystal contains numerous solvent sites, one containing diethyl ether, and four others which contain THF. One of the THF sites sits on the two-fold along the c-axis.

Table S15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for $\mathbf{12^{NO2}}$. U(eq) is defined as the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
Fe(1)	3157(1)	1488(1)	8227(1)	25(1)
Al(1)	2020(1)	1149(1)	9720(1)	27(1)
Al(2)	4264(1)	2039(1)	6912(1)	26(1)
O(1)	2782(1)	1182(1)	9950(2)	29(1)
O(2)	4335(1)	1542(1)	7714(2)	25(1)
O(3)	2014(1)	1152(1)	8537(2)	26(1)
O(4)	3501(1)	2021(1)	6673(2)	30(1)
O(5)	1892(1)	1820(1)	9731(2)	29(1)
O(6)	2092(1)	465(1)	9731(2)	26(1)
O(7)	1912(2)	3257(1)	12862(2)	46(1)
O(8)	1822(2)	3768(1)	11806(2)	54(1)
O(9)	1121(2)	-1560(1)	8561(3)	65(1)
O(10)	410(2)	-1096(1)	8292(3)	62(1)
O(11)	4358(1)	1590(1)	6026(2)	30(1)

O(12)	4219(1)	2495(1)	7789(2)	27(1)
O(13)	6534(2)	523(2)	4878(3)	82(2)
O(14)	5950(2)	225(2)	3970(3)	74(1)
O(15)	3743(2)	4664(1)	8849(3)	58(1)
O(16)	3578(2)	4717(1)	7485(3)	65(1)
N(1)	3200(2)	1220(1)	9371(2)	20(1)
N(2)	3960(2)	1443(1)	8344(2)	23(1)
N(3)	2367(2)	1418(1)	8029(3)	27(1)
N(4)	3105(2)	1766(1)	7089(2)	27(1)
N(5)	1908(2)	1151(1)	11065(2)	25(1)
N(6)	1142(2)	1024(1)	9686(3)	27(1)
N(7)	1861(2)	3341(2)	12097(3)	39(1)
N(8)	897(2)	-1150(2)	8569(3)	52(2)
N(9)	5154(1)	2127(1)	6912(2)	22(1)
N(10)	4302(2)	2640(1)	6025(2)	26(1)
N(11)	6054(2)	495(2)	4588(3)	60(2)
N(12)	3707(2)	4472(2)	8129(4)	51(1)
N(13)	3229(2)	811(1)	7706(2)	27(1)
N(14)	3072(2)	2173(1)	8727(3)	29(1)
C(1)	3696(2)	1090(2)	9634(3)	19(1)
C(2)	4130(2)	1196(2)	9024(3)	21(1)
C(3)	3820(2)	852(2)	10484(3)	26(1)
C(4)	4075(2)	393(2)	10512(3)	34(1)
C(5)	4217(2)	166(2)	11274(4)	51(2)
C(6)	4109(2)	421(2)	12048(4)	63(2)
C(7)	3863(2)	880(2)	12040(3)	49(2)
C(8)	3713(2)	1100(2)	11255(3)	36(2)
C(9)	4733(2)	1058(2)	9146(3)	30(1)
C(10)	5022(2)	1222(2)	9872(3)	49(2)
C(11)	5566(2)	1081(2)	9991(5)	65(2)
C(12)	5822(3)	773(3)	9431(5)	83(3)
C(13)	5546(2)	616(2)	8690(4)	52(2)
C(14)	4987(2)	757(2)	8560(3)	42(2)
C(15)	1286(2)	1160(2)	11252(3)	30(1)
C(16)	1122(2)	1029(2)	12163(3)	38(2)
C(17)	498(2)	1002(2)	12283(3)	38(2)
C(18)	254(2)	636(2)	11666(3)	41(2)
C(19)	364(2)	804(2)	10744(3)	40(2)
C(20)	990(2)	836(2)	10567(3)	29(1)
C(21)	2194(2)	1581(2)	11467(3)	27(1)
C(22)	1994(2)	2082(2)	11192(3)	24(1)
C(23)	1988(2)	2466(2)	11772(3)	29(1)
C(24)	1844(2)	2938(2)	11494(3)	26(1)
C(25)	1666(2)	3022(2)	10648(3)	38(2)
C(26)	1650(2)	2638(2)	10065(3)	29(1)
C(27)	1858(2)	2165(2)	10318(3)	25(1)
C(28)	1429(2)	2717(2)	9164(3)	43(2)
C(29)	2178(2)	705(2)	11458(3)	31(1)
C(30)	1008(2)	654(2)	9001(3)	34(2)
C(31)	1245(2)	161(2)	9102(3)	29(1)
C(32)	954(2)	-253(2)	8823(3)	37(2)
C(33)	1198(2)	-718(2)	8854(3)	37(2)
C(34)	1738(2)	-790(2)	9165(3)	34(1)
C(35)	2030(2)	-391(2)	9477(3)	30(1)

C(36)	1800(2)	93(2)	9440(3)	28(1)
C(37)	2602(2)	-449(2)	9881(3)	40(2)
C(38)	828(2)	1477(2)	9442(3)	36(1)
C(39)	2188(2)	1530(2)	7259(3)	25(1)
C(40)	2611(2)	1757(2)	6739(3)	34(1)
C(41)	1622(2)	1381(2)	6981(3)	36(2)
C(42)	1163(2)	1685(2)	7083(3)	41(2)
C(43)	623(2)	1507(2)	6936(4)	55(2)
C(44)	543(2)	1028(2)	6675(4)	65(2)
C(45)	994(2)	718(2)	6547(3)	57(2)
C(46)	1536(2)	894(2)	6706(3)	43(2)
C(47)	2497(2)	2024(2)	5920(4)	43(2)
C(48)	2715(2)	1864(2)	5152(4)	70(2)
C(49)	2649(3)	2139(3)	4394(4)	111(4)
C(50)	2367(3)	2581(3)	4436(5)	108(4)
C(51)	2135(3)	2757(2)	5200(5)	97(3)
C(52)	2207(2)	2467(2)	5937(4)	63(2)
C(53)	5308(2)	2452(2)	6178(3)	30(1)
C(54)	5899(2)	2659(2)	6233(3)	35(2)
C(55)	6029(2)	3003(2)	5456(3)	43(2)
C(56)	5607(2)	3404(2)	5435(3)	40(2)
C(57)	5020(2)	3200(2)	5332(3)	35(1)
C(58)	4875(2)	2862(2)	6079(3)	27(1)
C(59)	5435(2)	1630(2)	6849(3)	34(1)
C(60)	5317(2)	1343(2)	6048(3)	28(1)
C(61)	5738(2)	1083(2)	5657(3)	36(2)
C(62)	5611(3)	782(2)	4963(4)	49(2)
C(63)	5090(3)	749(2)	4611(3)	44(2)
C(64)	4668(2)	1036(2)	4967(3)	39(2)
C(65)	4767(2)	1335(2)	5702(3)	28(1)
C(66)	4068(2)	1028(2)	4604(3)	56(2)
C(67)	5352(2)	2326(2)	7763(3)	33(1)
C(68)	3873(2)	3015(2)	6256(3)	35(2)
C(69)	3927(2)	3260(2)	7117(3)	31(1)
C(70)	3806(2)	3748(2)	7232(4)	34(2)
C(71)	3849(2)	3959(2)	8027(4)	33(1)
C(72)	4048(2)	3708(2)	8735(3)	34(2)
C(73)	4196(2)	3213(2)	8661(3)	31(1)
C(74)	4119(2)	2967(2)	7849(3)	34(2)
C(75)	4459(2)	2928(2)	9379(3)	41(2)
C(76)	4162(2)	2479(2)	5136(3)	35(2)
C(77)	2962(2)	418(2)	8048(3)	31(1)
C(78)	3003(2)	-65(2)	7689(3)	30(1)
C(79)	3325(2)	-141(2)	6979(3)	37(2)
C(80)	3601(2)	258(2)	6628(3)	38(2)
C(81)	3535(2)	734(2)	7002(3)	30(1)
C(82)	3230(2)	2294(2)	9540(4)	39(2)
C(83)	3142(2)	2747(2)	9928(3)	43(2)
C(84)	2881(2)	3119(2)	9444(4)	50(2)
C(85)	2730(2)	3006(2)	8607(4)	51(2)
C(86)	2825(2)	2536(2)	8272(4)	41(2)
O(3B)	4563(4)	2212(3)	2922(5)	270(4)
C(1B)	5614(4)	1914(3)	3356(6)	216(5)
C(2B)	5177(4)	2044(4)	2499(6)	184(5)

C(4B)	4332(3)	2305(3)	1977(5)	136(3)
C(5B)	3714(3)	2346(3)	2418(5)	170(4)
O(1C)	1298(2)	8857(2)	5502(4)	114(2)
C(1C)	1861(3)	8919(3)	5247(5)	107(3)
C(2C)	2174(3)	9094(3)	6032(5)	107(3)
C(3C)	1787(3)	9028(5)	6716(5)	292(9)
C(4C)	1277(3)	8871(4)	6415(5)	160(4)
O(1D)	0	10000	5329(5)	168(5)
C(2D)	402(5)	9802(5)	4753(5)	219(6)
C(3D)	281(4)	9862(4)	3974(5)	161(5)
O(1E)	2181(3)	963(2)	3690(3)	108(2)
C(1E)	1769(3)	701(3)	4250(5)	130(3)
C(2E)	2001(4)	264(3)	4591(6)	128(4)
C(3E)	2586(4)	425(4)	4661(7)	226(7)
C(4E)	2690(3)	721(4)	3833(5)	190(6)
O(1F)	1661(4)	3623(4)	7264(6)	288(5)
C(1F)	2137(5)	3770(4)	6849(8)	236(6)
C(2F)	2356(5)	4277(5)	7060(9)	315(8)
C(3F)	2065(5)	4452(4)	7714(7)	258(7)
C(4F)	1595(4)	4064(4)	7845(6)	172(4)

Table S16. Selected bond lengths [Å] and angles [°] for **12**^{NO2}.

Fe(1)-N(1)	1.920(4)	N(1)-Fe(1)-N(4)	178.92(17)
Fe(1)-N(4)	1.923(4)	N(1)-Fe(1)-N(3)	99.41(17)
Fe(1)-N(3)	1.926(4)	N(4)-Fe(1)-N(3)	80.11(17)
Fe(1)-N(2)	1.935(4)	N(1)-Fe(1)-N(2)	80.56(17)
Fe(1)-N(13)	2.007(4)	N(4)-Fe(1)-N(2)	100.08(18)
Fe(1)-N(14)	2.018(4)	N(3)-Fe(1)-N(2)	170.04(16)
		N(1)-Fe(1)-N(13)	91.41(15)
		N(4)-Fe(1)-N(13)	89.52(15)
		N(3)-Fe(1)-N(13)	86.07(16)
		N(2)-Fe(1)-N(13)	83.97(15)
		N(1)-Fe(1)-N(14)	89.73(15)
		N(4)-Fe(1)-N(14)	89.33(16)
		N(3)-Fe(1)-N(14)	92.94(16)
		N(2)-Fe(1)-N(14)	97.02(16)
		N(13)-Fe(1)-N(14)	178.60(17)

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