Supporting Information for:

Readily available Ti-based *in situ* catalytic system for oxo/imido heterometathesis

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General

Unless otherwise stated all manipulations were carried out under argon atmosphere using standard Schlenk techniques or MBraun UniLab glovebox. All glassware was dried in an oven at 130 °C for at least 2 h prior to use. Solvents were distilled from Na/benzophenone (THF, Et_2O, C_6H_6, C_6D_6, toluene, heptane) or CaH_2 (CH_2Cl_2, $CDCl_3$), degassed by 3 freeze-pump-thaw cycles and stored over activated 3 Å MS.

N-sulfinylanilines were prepared according to standard procedures[1-3] using Merck $SOCl_2$ ("for synthesis" grade) and freshly distilled or recrystallized anilines. $TolNH_2$ used in stoichiometric reactions and as additive in catalysis was additionally sublimed in vacuum. Benzophenone was dried with 3 Å MS as toluene solution with subsequent crystallization at low temperature. Adamantanone, xanthone, coumarin and 3,4-benzocoumarin were sublimed in vacuum. Fluorenone was used without additional purification. Acetylcymantrene was prepared by standard method. DMF was distilled from P_2O_5.

Silica (Degussa Aerosil, 200 $m^2\,g^{-1}$) was compacted with distilled water, calcined at 500 °C under air overnight, and then treated at 700 °C under high vacuum (*ca.* 10^{-5} mbar) for no less than 10 h (support referred to as $SiO_{2\text{-}700}$). The reported value of 0.26 mmol ≡SiOH per g was used in calculations.[4]

^1H, ^{13}C, ^{19}F NMR spectra were recorded using Bruker Avance 400, 300 and 600 spectrometers. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. ^1H chemical shifts were referenced relative to the residual solvent peak: 7.26 ($CDCl_3$), 7.16 (C_6D_6). ^{13}C chemical shifts were referenced relative to the solvent peak: 77.16 ($CDCl_3$), 128.06 (C_6D_6). ^{19}F spectra were referenced externally to $CFCl_3$. Quantitative ^1H NMR measurements were performed using ferrocene as internal standard (recycle delay (d1) in these experiments was set to 60 sec). Solution ^{15}N NMR spectra were recorded on Bruker Avance III 400 WB spectrometer and referenced *vs.* liquid NH_3 using CH_3NO_2 (10% in $CDCl_3$) as external standard (δ = 379.0 ppm *vs.* NH_3).

Solid-state NMR spectra were recorded on a Bruker Avance III 400 WB spectrometer equipped with 4.0 mm DVT MAS BB/HF probe (15 kHz) and 2.5 mm DVT MAS BB/HF probe (35 kHz) (^1H – 400.1 MHz, ^{13}C – 100.6 MHz, ^{15}N – 40.6 MHz, ^{81}Br – 100.25 MHz). The materials were loaded in ZrO_2 rotors inside a glovebox and tightly closed. Samples were spun at 9–14 kHz (4.0 mm probe) and 32–34 kHz (2.5 mm probe) at the magic angle (MAS). ^1H MAS spectra were recorded using single-pulse sequence with 30–45° pulse at 14 kHz (4.0 mm probe) and 34 kHz (2.5 mm probe) with a recycle delay of 5–8 sec. ^{13}C CP/MAS spectra were recorded with a recycle delay of 2–2.5 sec and CP contact time of 3–4 msec at 12 kHz. ^{15}N CP/MAS spectra were recorded with a recycle delay of 3–3.5 sec and contact times of 7–8 msec at 12–13 kHz. 2D ^{15}N–^1H CP FSLG HETCOR spectra were recorded at 12–13 kHz MAS (2.5 mm probe) in a rotor-synchronized mode using 400–500 µsec CP contact time with RF field 98 kHz for FSLG. High-speed proton-detected 2D ^1H–^{15}N D-HMQC spectra were recorded at 32.5–34 kHz MAS (2.5 mm probe) in a rotor-synchronized mode using 650 µsec $SR4_2^1$ recoupling with RF field 97.5–102 kHz (3 ν(r)). The ^{13}C, ^{15}N, and 2D HETCOR spectra were recorded under high-power proton decoupling conditions using "spinal64", D-HMQC spectra do not require decoupling due to high MAS speed. ^1H and ^{13}C chemical shifts were referenced relatively to external solid adamantane (δ_{13C} = 38.5 ppm for downfield resonance); ^{15}N chemical shifts were calculated to this scale and were verified using ^{15}N labelled glycine sample (δ_{15N} = 33.0 ppm). Magic angle was calibrated precisely to the spinning side bands in ^{81}Br spectra of the KBr sample.

IR spectra of silica and grafted materials were recorded using Shimadzu IRPrestige-21 instrument operated under ambient conditions with resolution 2 cm^{-1}. The samples were pressed into pellets inside a glovebox and transferred to the spectrometer in a home-made air-tight cell.

GC/FID was performed using Chromatec Crystal 5000.2 gas chromatograph equipped with a Restek RTX-35 column. For quantitative analysis all the relevant compounds were calibrated *vs.* C_6Me_6 that was used as internal standard in all experiments.

Elemental analyses were performed in Microanalysis laboratory of INEOS RAS. Metal content was determined by X-Ray fluorescence analysis using Spectroscan MAKC-GVM WDXRF spectrometer (Spectron Ltd.) with external standard method and 100- to 200-fold dilution of microsamples (5–10 mg) with emulsion polystyrene.[5]

Preparation of the materials

Representative procedure for grafting of $Ti(NEt_2)_4$ (1). A yellow solution of $Ti(NEt_2)_4$ (25 mg, 74.3 μmol) in benzene was added to a suspension of $SiO_{2\text{-}700}$ (290 mg) in benzene at RT. The suspension was slowly stirred overnight. The solid was separated by decantation and washed several times with benzene. The resulting solid was dried in high vacuum (*ca.* 10^{-5} mbar) for 1–2 h to afford **1** as yellow powder.

Washings and volatiles were collected and analyzed with ^{1}H NMR using ferrocene as internal standard or GC using C_6Me_6 as internal standard. The amount of $HNEt_2$ determined for 3 independent preparations: 0.89, 0.73, 1.20 equiv/Ti.

Elemental analysis data for several independently prepared samples:

#	Ti, wt%	N, wt%	C, wt%	Ti, mmol/g	T/N/C
1	0.90	0.99	3.44	0.19	0.8/3.0/12.0
2	0.94	0.98	3.24	0.20	0.9/3.1/12.0
3	1.20	n/a	n/a	0.25	n/a
4	1.05	n/a	n/a	0.22	n/a

Treatment of 1 with anilines. Stoichiometric reactions between **1** and anilines were carried out in a dual-compartment apparatus equipped with high-vacuum Teflon valves shown in **Fig. S1**. Material **1** and aniline were placed as solids in a compartment A and quickly closed. Compartment B was charged with C_6Me_6 (internal standard) and C_6H_6. The setup was taken out from the glovebox and connected to high-vacuum line. Both compartments were frozen with liquid nitrogen and evacuated. Compartment A was then closed and heated at 100°C for 30 min. The color of the solid changed from yellow to dark red. The valve of compartment A was then opened and volatiles were transferred to frozen compartment B in dynamic vacuum while maintaining A at 100°C (30 min). The heating was removed and the material was cooled to RT. Both compartments were closed and the setup disconnected from vacuum line. The solution of volatiles was analyzed with GC, and the solid material was introduced in the glovebox.

Fig. S1

Treatment of 1 with $TolNH_2$ (1a):

1) **1** (147 mg, 32.3 μmol Ti), $TolNH_2$ (18 mg, 168 μmol, 5.2 equiv/Ti). $HNEt_2$ evolved: 80 μmol (2.5 equiv/Ti), $TolNH_2$ reacted: 91 μmol (2.8 equiv/Ti). Elemental analysis (wt%): Ti 1.20% (0.25 mmol Ti g^{-1}), N 1.22%, C 5.93%; corresponding to Ti/N/C = 1/3.5/19.7.

2) **1** (157 mg, 34.5 μmol Ti), $TolNH_2$ (24 mg, 224 μmol, 6.5 equiv/Ti). $HNEt_2$ evolved: 101 μmol (2.9 equiv/Ti), $TolNH_2$ reacted: 102 μmol (3.0 equiv/Ti).

Treatment of 1 with ^{15}N labeled anisidine (1b):

1 (127 mg, 31.8 μmol Ti), *p*-$MeOC_6H_4{}^{15}NH_2$ (21 mg, 169 μmol, 6.1 equiv/Ti). $HNEt_2$: 95 μmol (3.0 equiv/Ti), anisidine reacted: 94 μmol (3.0 equiv/Ti). Elemental analysis (wt%): Ti 1.30% (0.27 mmol Ti g^{-1}), N 1.17%, C 5.98%; corresponding to Ti/N/C = 1/3.1/18.3.

IR spectroscopy

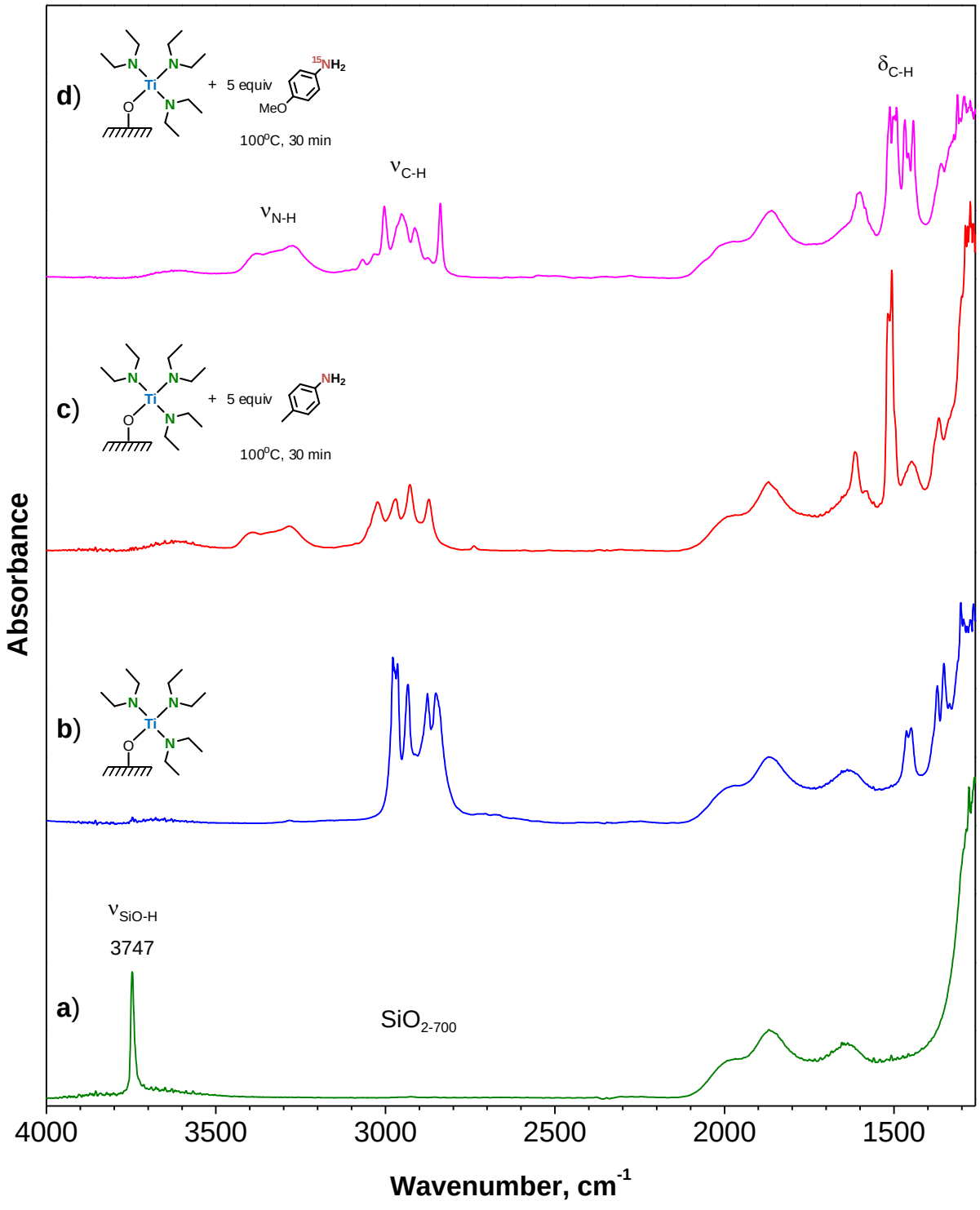


Fig. S2. IR spectra: (a) $SiO_{2\text{-}700}$, (b) **1**, (c) **1a**, (d) **1b**.

Solid-state NMR spectroscopy

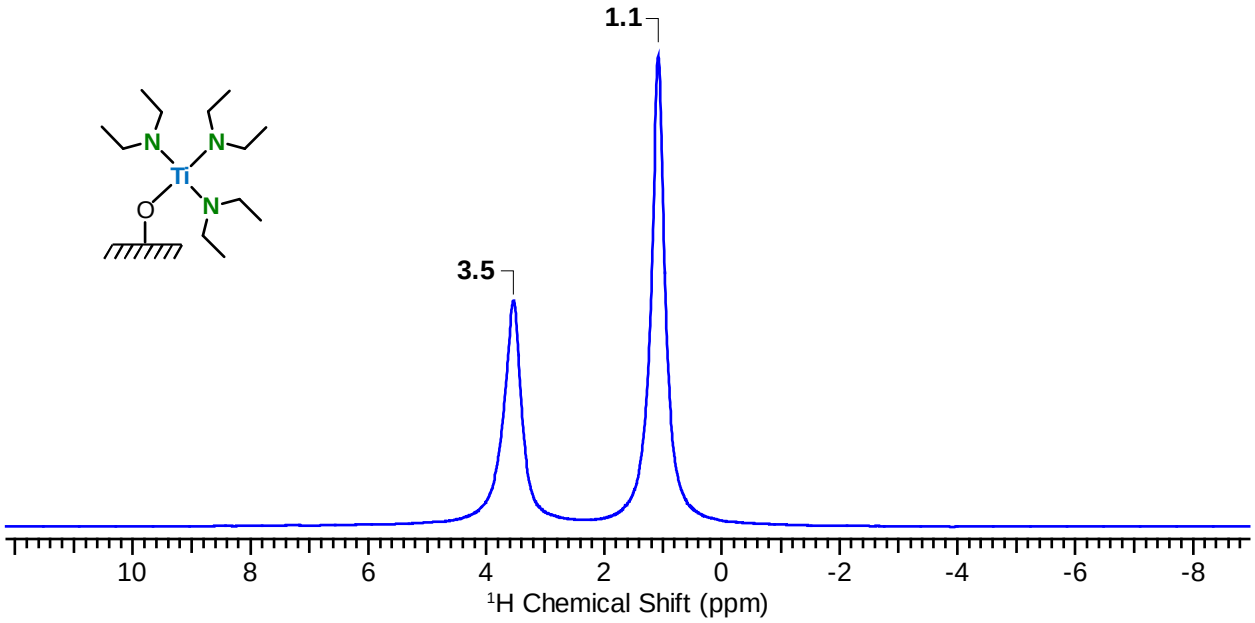


Fig. S3. ^{1}H MAS SSNMR spectrum of (≡SiO)Ti(NEt_2)$_3$ (**1**) (400 MHz; 4 mm; 14 kHz MAS; d1 5 s; ns 32; 20°C).

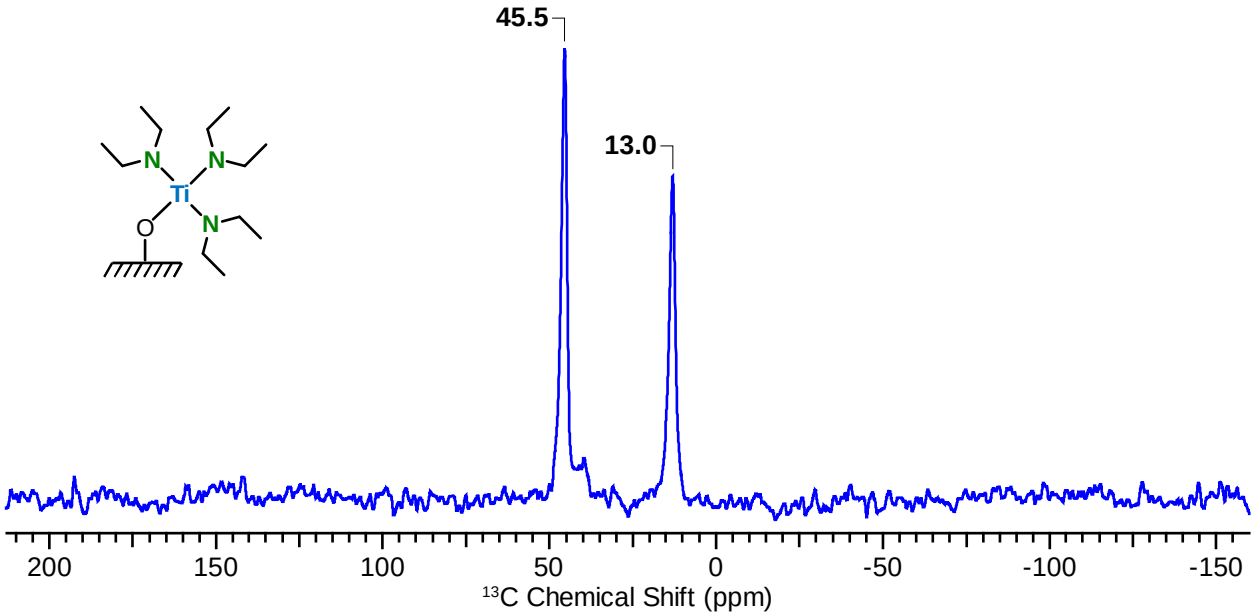


Fig. S4. ^{13}C CP/MAS SSNMR spectrum of (≡SiO)Ti(NEt_2)$_3$ (**1**) (100 MHz; 4 mm; 12 kHz MAS; CP contact time 4 ms; d1 2 s; ns 2,000; 20°C).

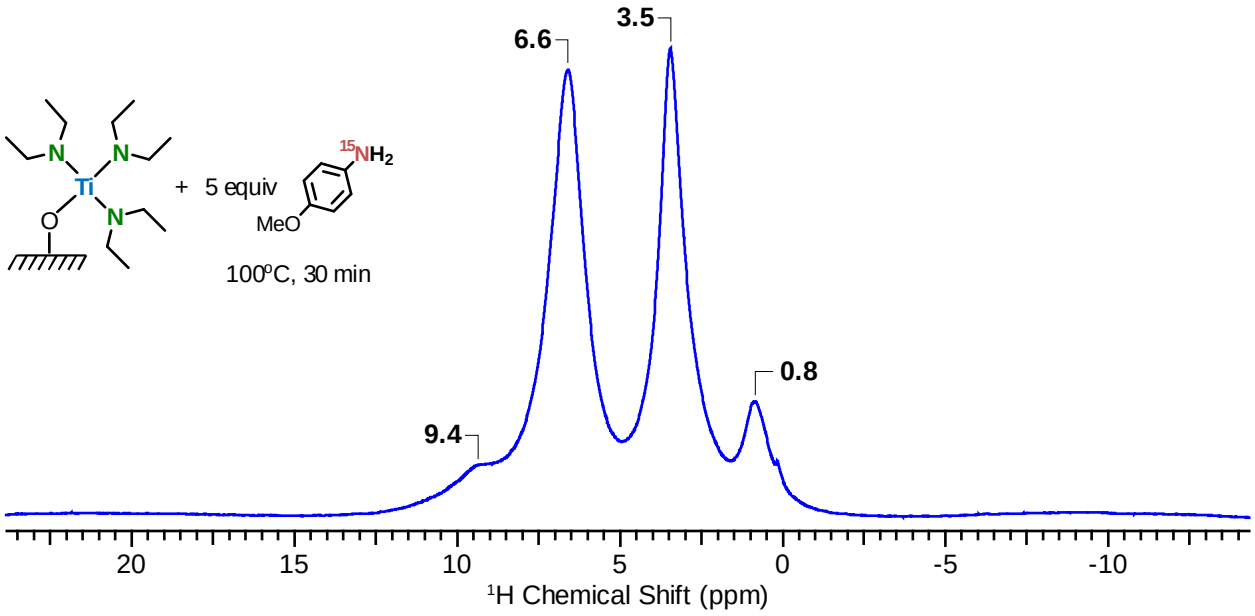


Fig. S5. ^{1}H MAS SSNMR spectrum of the material **1b** (400 MHz; 4 mm; 14 kHz MAS; d1 5 s; ns 32; 20°C).

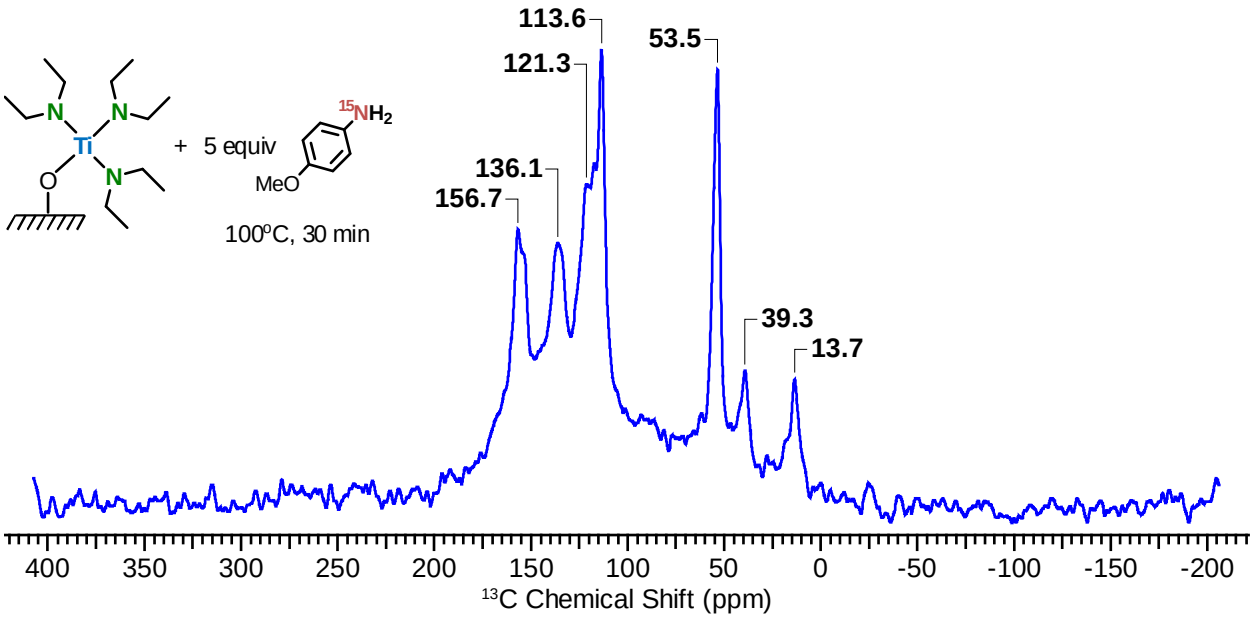


Fig. S6. ^{13}C CP/MAS SSNMR spectrum of the material **1b** (100 MHz; 4 mm; 12 kHz MAS; CP contact time 4 ms; d1 2 s; ns 40,000; 20°C).

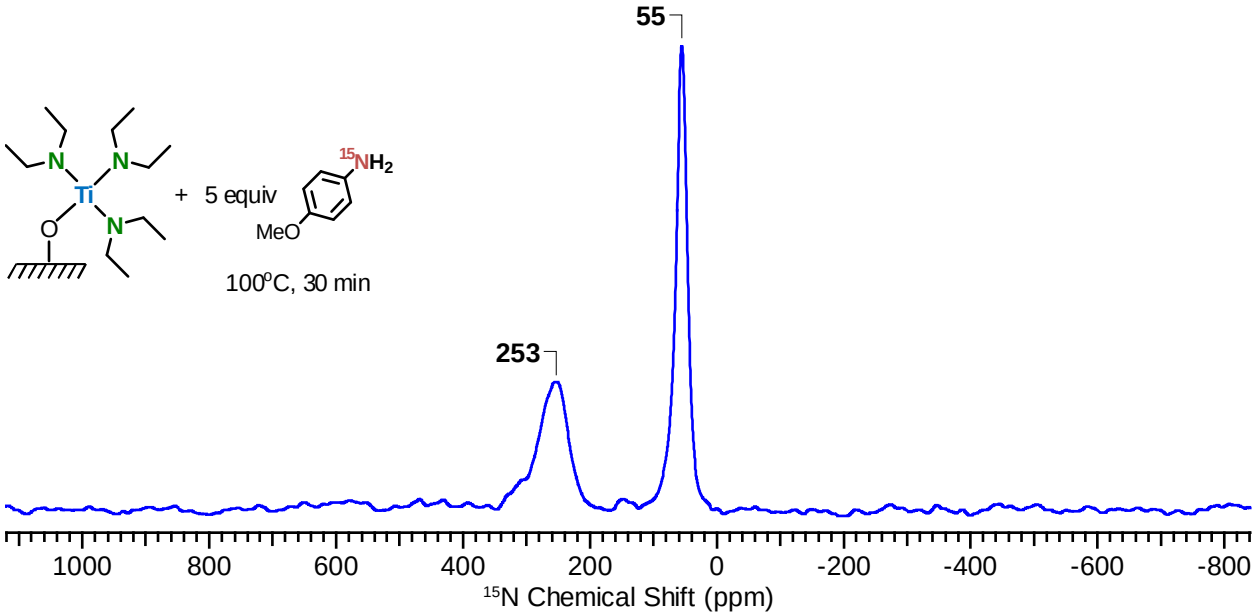


Fig. S7. ^{15}N CP/MAS SSNMR spectrum of the material **1b** (41 MHz; 4 mm; 13 kHz MAS; CP contact time 8 ms; d1 3 s; ns 46,000; 20°C).

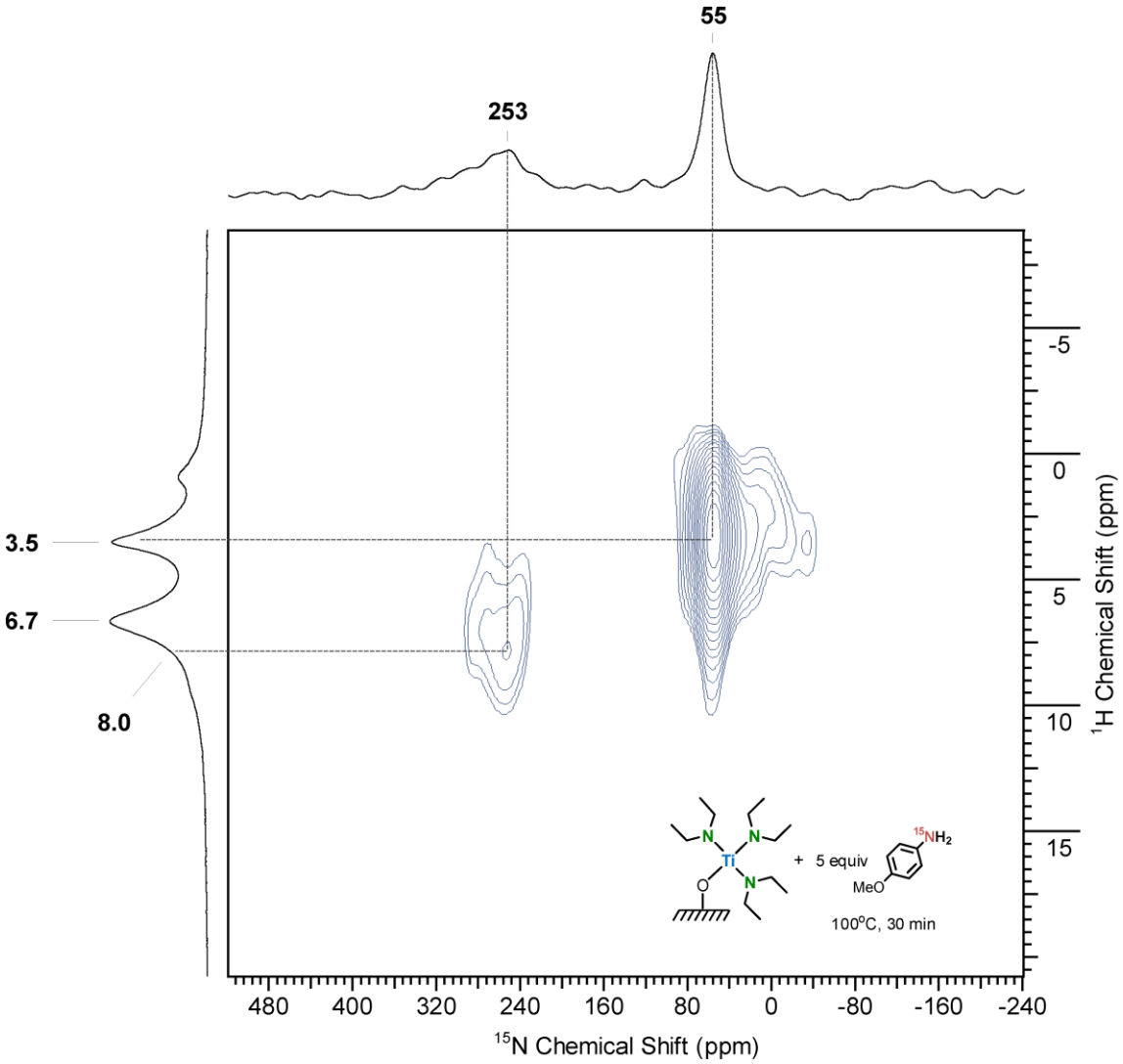


Fig. S8. ^{15}N–^{1}H HETCOR SSNMR spectrum of the material **1b** (41 MHz, 400 MHz; 2.5 mm; 12 kHz MAS; CP contact time 500 µs; d1 2.5 s; 1280 scans × 18 TD(F1) points; 20°C).

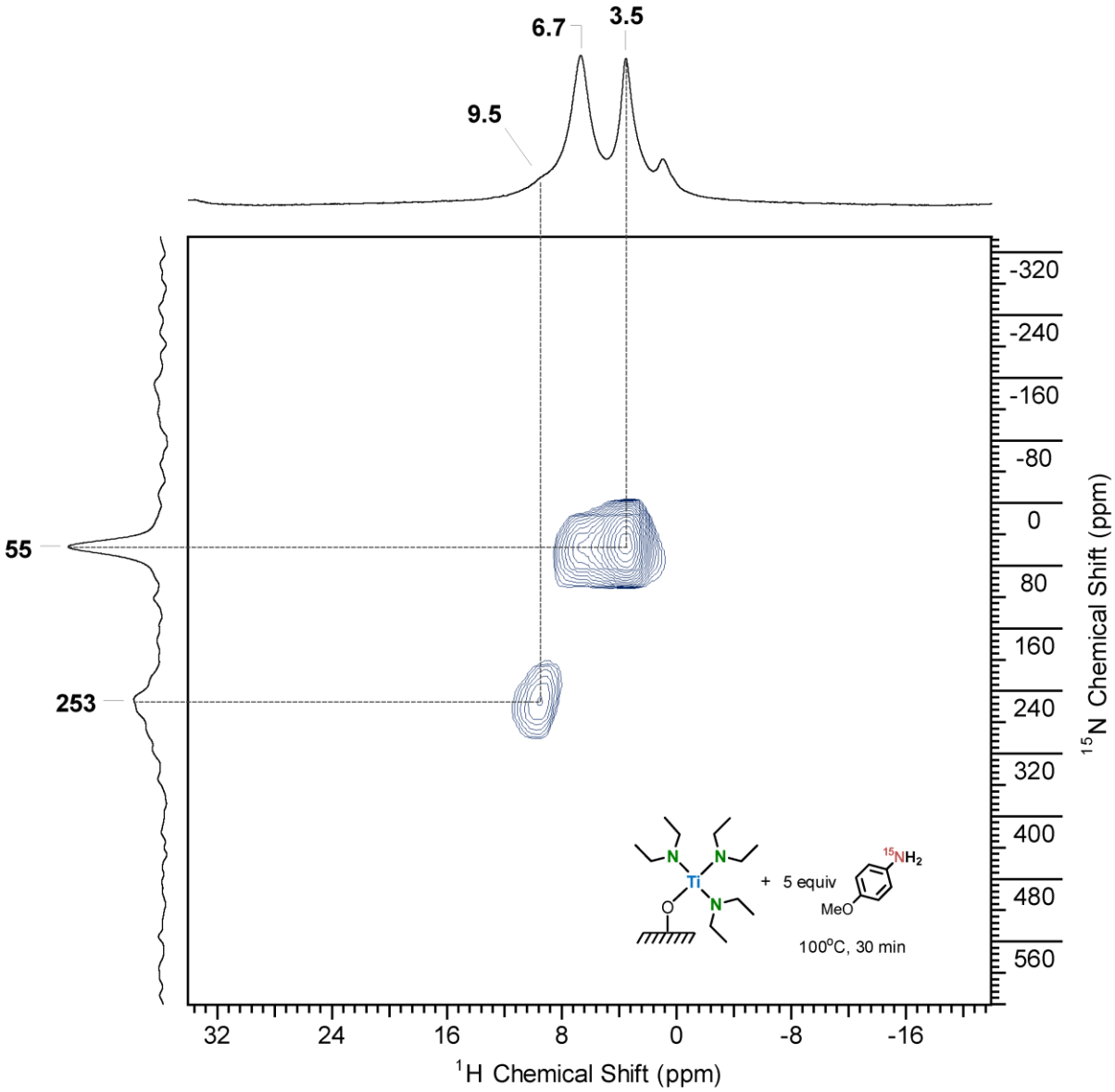


Fig. S9. ^{1}H–^{15}N D-HMQC SSNMR spectrum of the material **1b** (400 MHz, 41 MHz; 2.5 mm; 32.5 kHz MAS; 650 µs recoupling; d1 3 s; 384 scans × 36 TD(F1) points; 20°C).

^{15}N NMR reference compounds

Ti(=N*t*Bu)(Me$_2$Pyr)$_2$(py)$_2$

The compound was synthesized as previously reported.[6] ^{15}N chemical shifts were measured at natural abundance by ^{15}N INEPT and ^{1}H–^{15}N HMBC spectra. The measurements were performed at 10 °C to suppress the dynamics of pyrrolyl ligands.

^{15}N NMR (41 MHz, C_6D_6, 10 °C): δ 468.1 (=N*t*Bu), 278.7 (py), 257.4 (Me_2Pyr).

Ti(=NC$_6$H$_4$OMe)Cl$_2$(py)$_3$

Ti(=N*t*Bu)Cl$_2$(py)$_2$[7] (1.054 g, 3.02 mmol) was dissolved in CH_2Cl_2 (20 mL) and pyridine (550 µL, 6.8 mmol) was added at RT *via* syringe. The resulting red-orange solution was stirred for 15 min. A solution of *p*-anisidine (377 mg, 3.06 mmol) in CH_2Cl_2 (10 mL) was added at RT and the reaction mixture was stirred overnight. The solution turned from red-orange to yellow-green. The solvent was evaporated under vacuum, the yellow residue was extracted with CH_2Cl_2 and filtered to give a brown solution. The solvent was evaporated under vacuum and the brown residue was triturated in heptane to give the product as yellow powder. Yield: 1.070 g (74%). ^{1}H NMR corresponds to that previously reported.[8] The compound was used in the next step without further purification.

^{1}H NMR (300 MHz, CD_2Cl_2, 20°C): δ 9.07 (br d, ^{3}J = 5.0) and 8.70 (br s; 6H in total, eq and ax *o*-py), 7.85 (br t, ^{3}J = 7.5) and 7.71 (br t, ^{3}J = 7.2; 3H in total, eq and ax *p*-py), 7.39 (br t, ^{3}J = 6.5) and 7.26 (br s; 6H in total, eq and ax *m*-py), 6.82 (d, ^{3}J = 8.5, 2H, C_6H_4), 6.57 (d, 2H, C_6H_4), 3.68 (s, 3H, O*Me*). The ratio of the integrals of the corresponding signals of eq and ax pyridines differs from 2:1 likely due to dynamic behavior in solution.

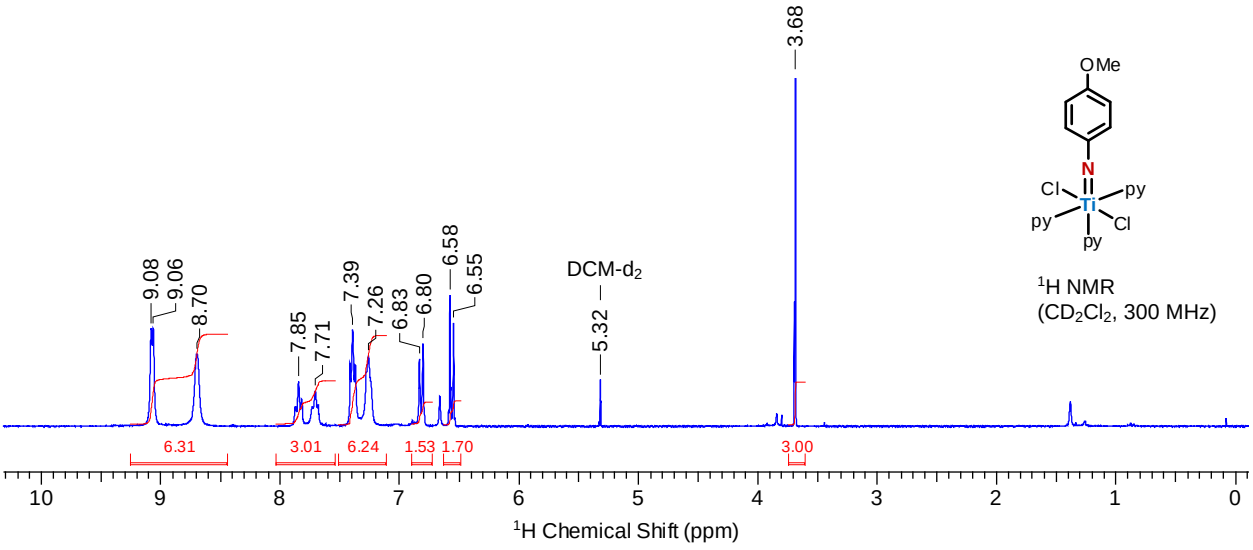


Fig. S10. ^{1}H NMR spectrum of Ti(=NC$_6$H$_4$OMe)Cl$_2$(py)$_3$.

Ti(=NC$_6$H$_4$OMe)(Me$_2$Pyr)$_2$(py)$_2$

To a green solution of Ti(=NC$_6$H$_4$OMe)Cl$_2$(py)$_3$ (243 mg, 0.51 mmol) in THF (20 mL) was added a solution of NaMe$_2$Pyr (146 mg, 1.25 mmol) in THF (10 mL) at −84 °C and the reaction mixture was stirred overnight at RT. The solution turned from green to red-orange. The solvent was evaporated under vacuum, and the orange residue was extracted with CH_2Cl_2 and filtered to give a dark red solution. After evaporation of the solvent the resulting solid was washed with heptane to afford the product as brown powder. Yield: 189 mg (72%).

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 8.12 (d, ^3J = 4.8, 4H, *o*-py), 7.89 (t, ^3J = 7.6, 2H, *p*-py), 7.42 (t, ^3J = 6.7, 4H, *m*-py), 6.59 (d, ^3J = 8.9, 2H, C$_6H_4$), 6.50 (d, ^3J = 8.9, 2H, C$_6H_4$), 5.77 (br s, 2H, CH_{Me2Pyr}), 5.61 (br s, 2H, CH_{Me2Pyr}), 3.66 (s, 3H, O*Me*), 2.37 (br s, 6H, *Me*$_2$Pyr), 1.59 (br s, 6H, *Me*$_2$Pyr).

^{13}C NMR (100 MHz, CD_2Cl_2, 25 °C): δ 157.2 (quat *C*N), 154.1 (quat *C*O), 151.6 (*o*-py), 139.6 (*p*-py), 137.2 (quat of Me$_2$Pyr), 131.9 (quat of Me$_2$Pyr), 125.2 (*m*-py), 123.2 (*C*H$_{Ar}$), 113.3 (*C*H$_{Ar}$), 107.0 (*C*H of Me$_2$Pyr), 55.7 (O*Me*), 18.7 (*Me*$_2$Pyr), 16.5 (*Me*$_2$Pyr).

^{1}H–^{15}N HMBC NMR (400 MHz, 41 MHz, CD_2Cl_2, 10 °C): δ 428.1 (=NAr), 276.5 (py), 262.8 (Me$_2$Pyr).

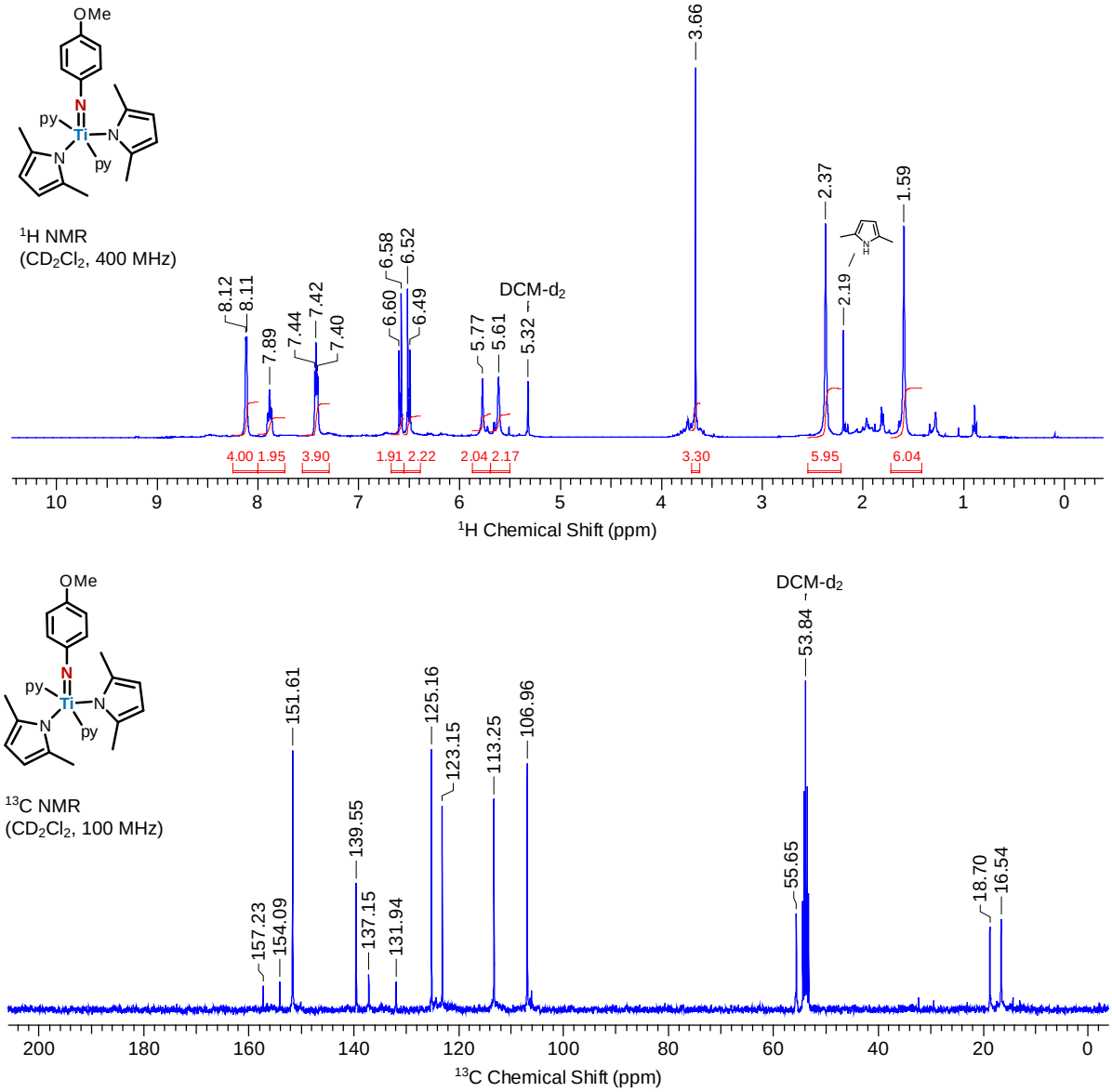


Fig. S11. ^{1}H and ^{13}C NMR spectra of Ti(=NC$_6$H$_4$OMe)(Me$_2$Pyr)$_2$(py)$_2$.

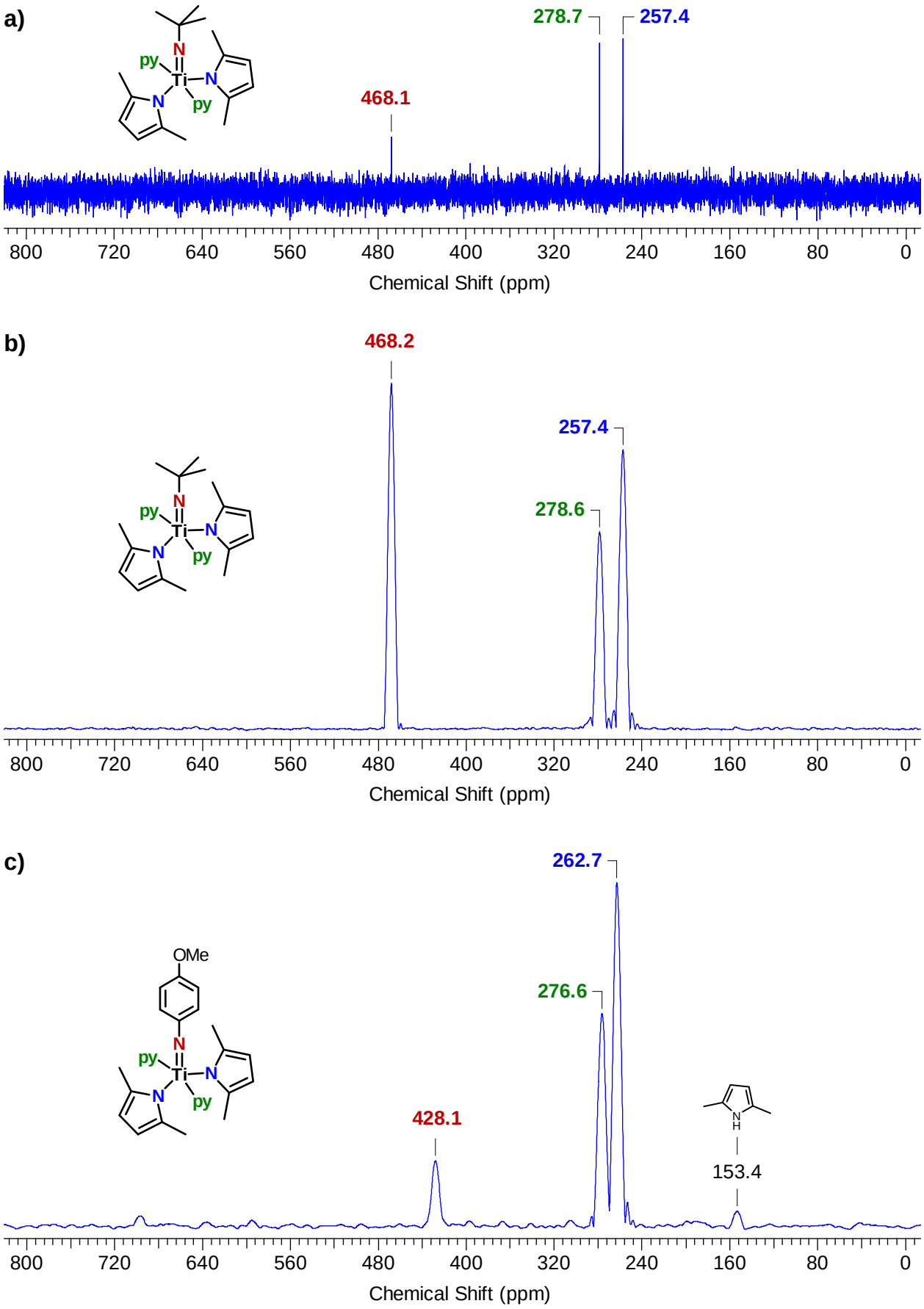


Fig. S12. ^{15}N INEPT spectrum of Ti(=N*t*Bu)(Me_2Pyr)$_2$(py)$_2$ at 10°C (a). ^{15}N spectra of Ti(=NR)(Me_2Pyr)$_2$(py)$_2$ reconstructed from ^{1}H–^{15}N HMBC: R = *t*Bu (b), C_6H_4OMe (c).

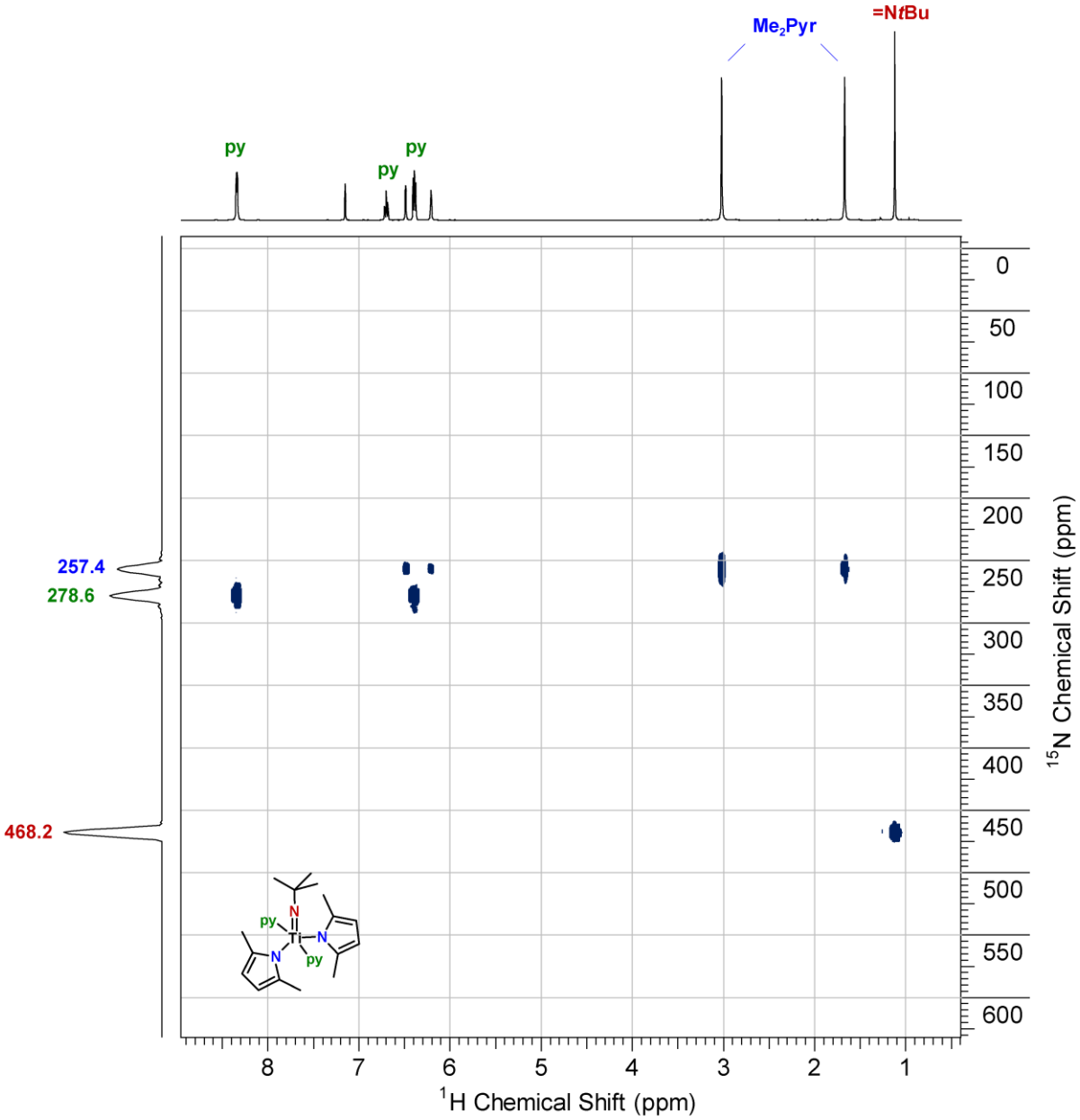


Fig. S13. $^{1}H–^{15}N$ HMBC spectrum of Ti(=N*t*Bu)(Me_2Pyr)$_2$(py)$_2$ at 10 °C.

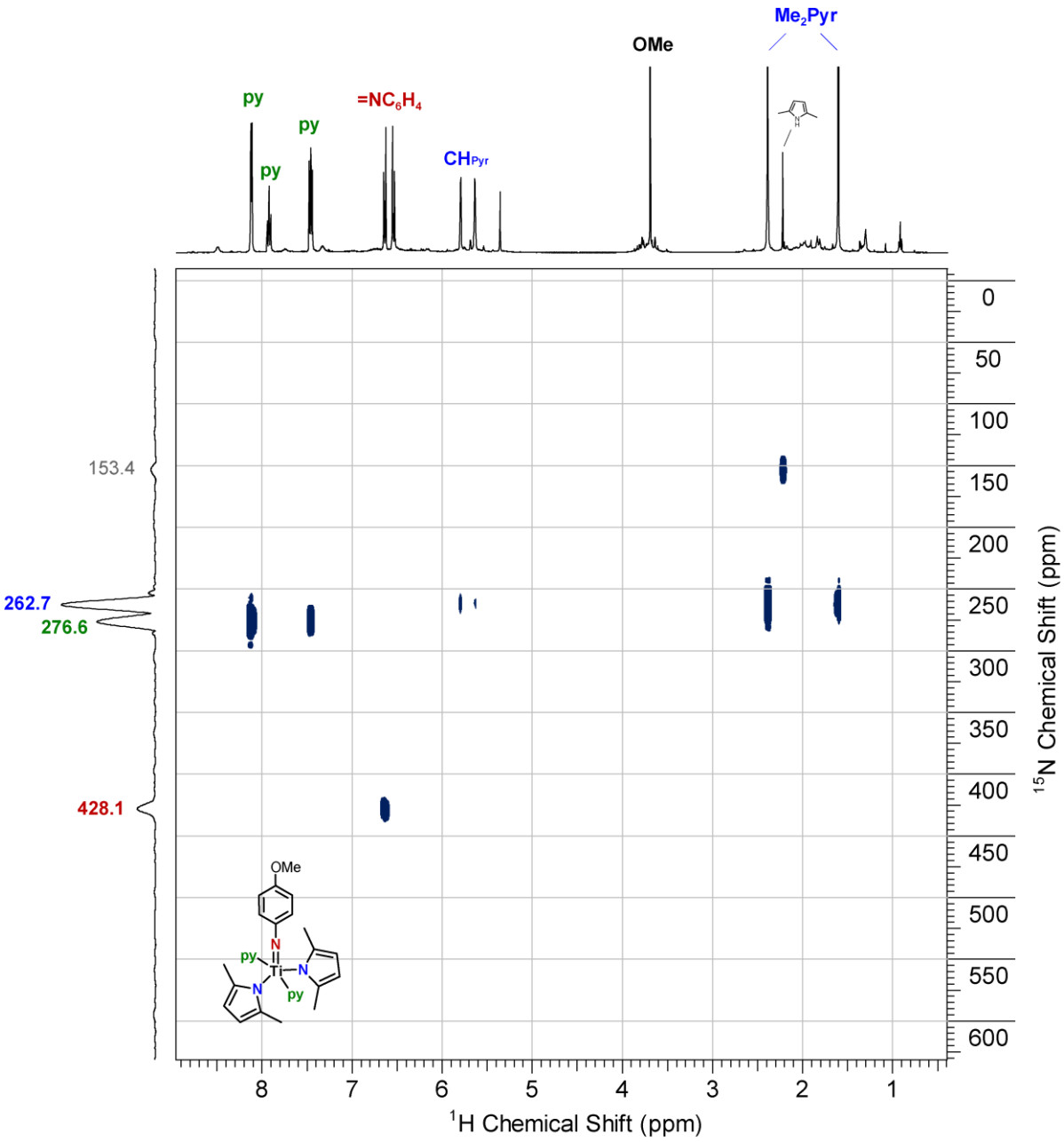


Fig. S14. $^{1}H–^{15}N$ HMBC spectrum of Ti(=NC_6H_4OMe)(Me_2Pyr)$_2$(py)$_2$ at 10 °C.

4-MeOC$_6$H$_4$^{15}NH$_2$

^{1}H NMR (600 MHz, $CDCl_3$, 20°C): δ 6.75 (d, ^3J = 8.5, 2H, C$_6$*H*$_4$), 6.65 (d, 2H, C$_6$*H*$_4$), 3.75 (s, 3H, O*Me*), 3.26 (br s, 2H, N*H*$_2$).

^{13}C NMR (151 MHz, $CDCl_3$, 20°C): δ 152.9 (quat *C*O), 140.0 (d, $^1J_{C–N}$ = 10.4, quat *C*N), 116.5 (*C*H$_{Ar}$), 114.9 (*C*H$_{Ar}$), 55.8 (O*Me*).

^{15}N NMR (61 MHz, $CDCl_3$, 20°C): δ 47.7.

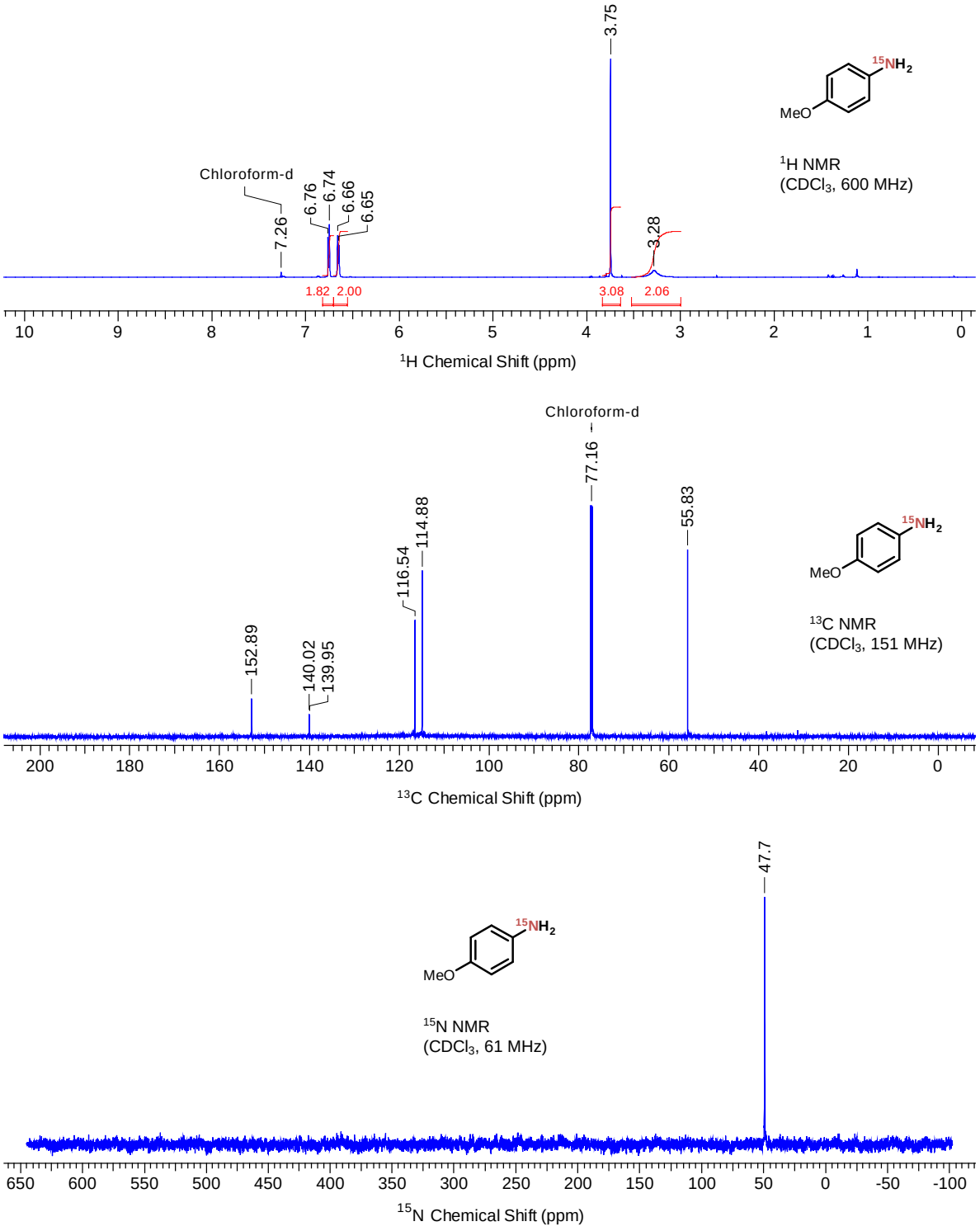
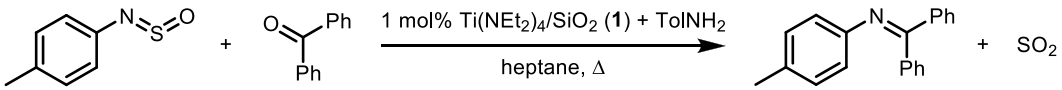


Fig. S15. NMR spectra of ^{15}N labeled *p*-anisidine.

Catalytic activity studies

Oxo/imido heterometathesis catalytic activity was assessed using a previously described[6, 9] test reaction between benzophenone and *N*-sulfinyl-*p*-toluidine in boiling heptane at 1 mol% catalyst loading. The catalyst (typically 15−25 mg) was placed in a double-neck Schlenk flask, equipped with a backflow condenser and a septum, and the appropriate volume of stock solution of Ph_2CO (0.15 M), TolNSO (0.15 M), C_6Me_6 (internal standard) and the desired amount of $TolNH_2$ in dry heptane was added. The flask was immediately immersed in a preheated oil bath and the reaction was stirred under reflux. Aliquots of the reaction mixture were taken over the course of the reaction and analyzed with GC/FID. The conversions of the reagents were determined from their consumption with respect to the internal standard; the conversion into imine product was calculated using calibration made with the isolated Ph_2C=NTol and usually matched well with the consumption of Ph_2CO. The TON and TOF were calculated with respect to the total amount of metal in the catalyst determined by elemental analysis.



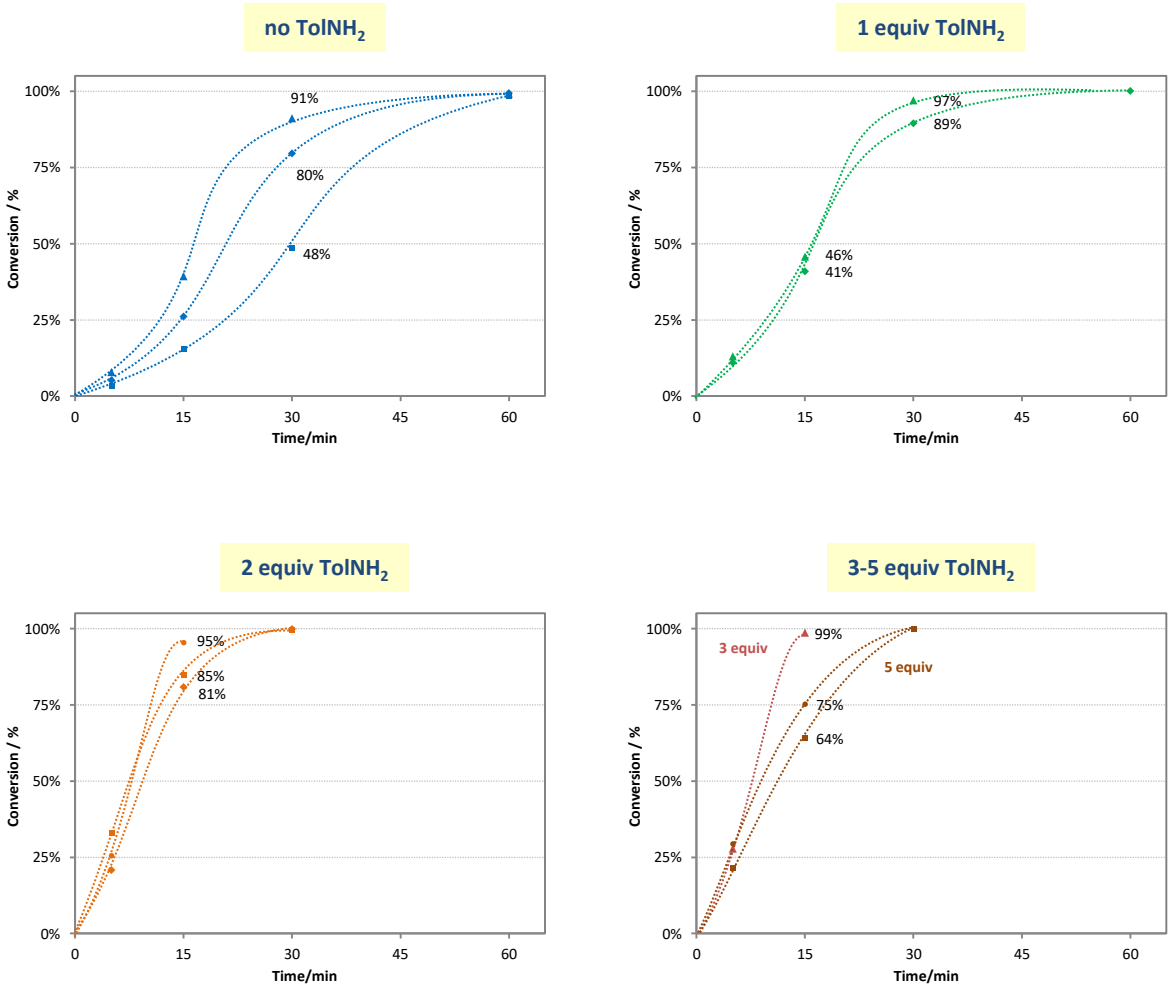
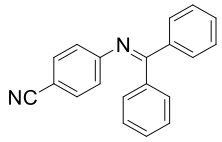


Fig S16. Reproducibility of the catalytic runs with different amount of $TolNH_2$ additive.

Preparation and characterization of organic compounds

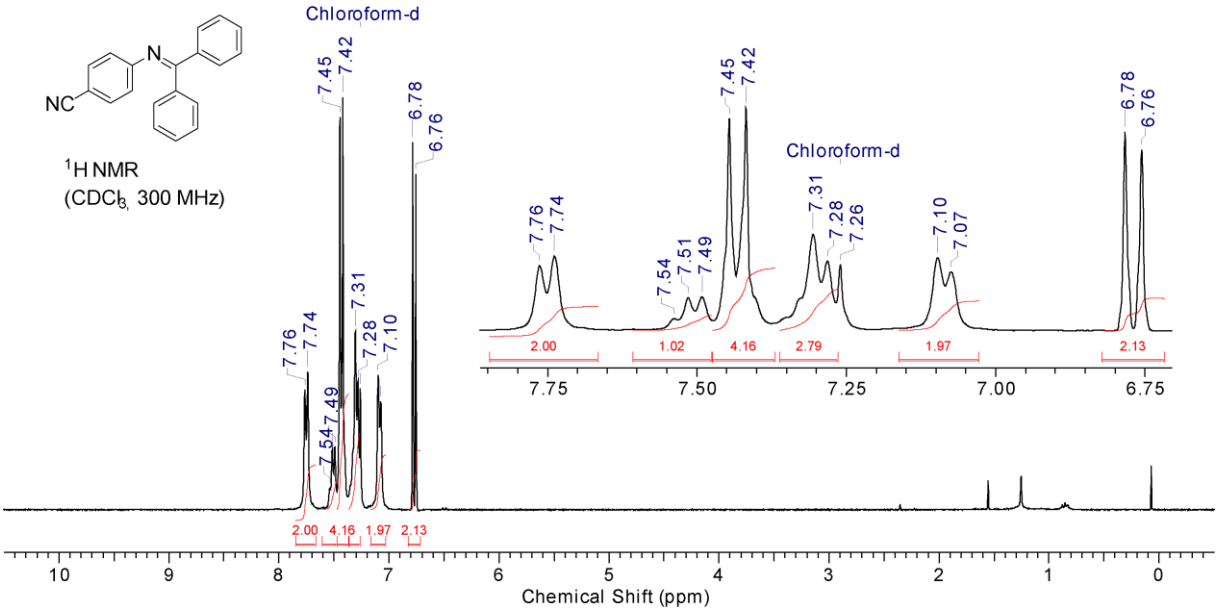
General procedure. A double-neck Schlenk flask equipped with a backflow condenser on one neck and a septum on the other was charged with **1** (1 mol% Ti) under argon. A solution of ketone, *N*-sulfinylamine, and 2 mol% $TolNH_2$ in dry heptane or toluene was prepared in a separate Schlenk flask and added to the catalyst *via* cannula. The mixture was stirred under reflux and the reaction progress was monitored with GC/FID by taking aliquots of the solution (at the exception of cymantrene derivative **3i** where the reaction was monitored by TLC). After the end of the reaction further manipulations were performed under air using standard reagent grade solvents (at the exception of sulfurdiimine **3l** that was handled under argon and using dry solvents). The catalyst was filtered off using a glass filter, the product was isolated by crystallization from an appropriate solvent and dried in vacuum.

4-((diphenylmethylene)amino)benzonitrile (3a)[10]

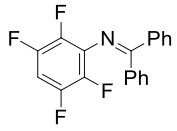


Loading: **1** (18 mg, 4.0 µmol Ti, 1 mol%), TolNH$_2$ (70 µL of 0.114 M solution in heptane, 8.0 µmol, 2 mol%), benzophenone (72 mg, 0.40 mmol), *N*-sulfinyl-4-aminobenzonitrile (69 mg, 0.42 mmol), toluene (5 mL). Reaction time 1.5 h. Reaction mixture was filtered and the catalyst was washed with toluene thrice. The product was isolated in several crops as yellow powder by recrystallization from boiling toluene. Yield 98 mg (87%); mp 126–127 °C (lit.[10] 125–126 °C).

^{1}H NMR (300 MHz, $CDCl_3$, 23°C): δ 7.75 (d, ^3J = 7.5, 2H), 7.51 (t, ^3J = 7.0, 1H), 7.45–7.41 (m, 4H), 7.31–7.28 (m, 3H), 7.09 (d, ^3J = 6.7, 2H), 6.77 (d, ^3J = 8.5, 2H).



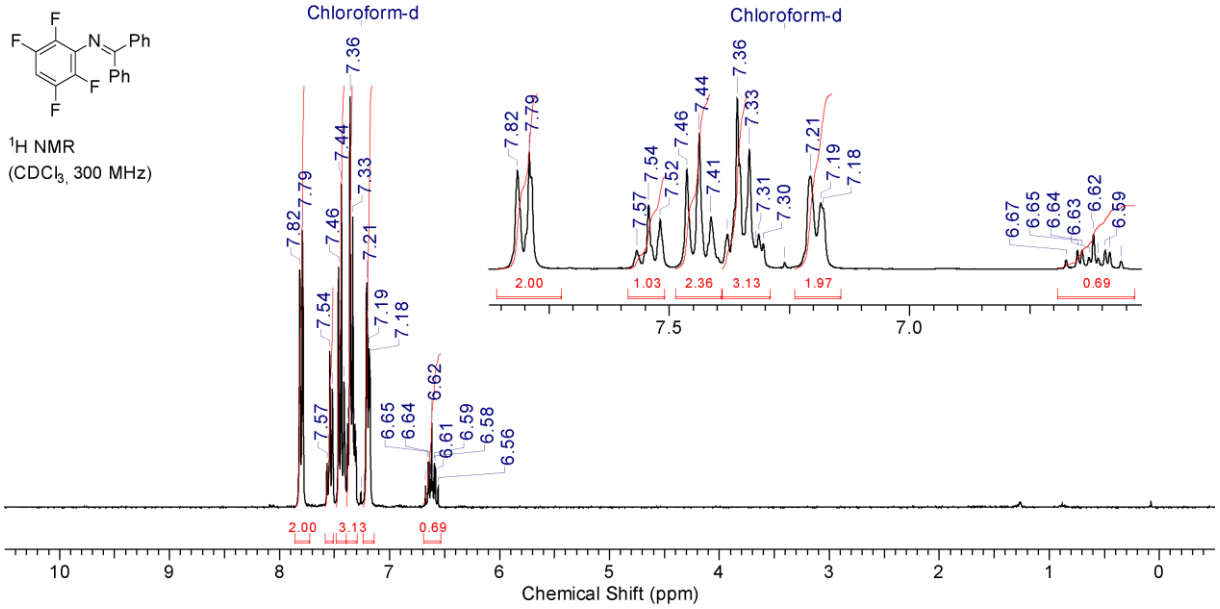
***N*-(diphenylmethylene)-2,3,5,6-tetrafluoroaniline (3b)**[6, 11]

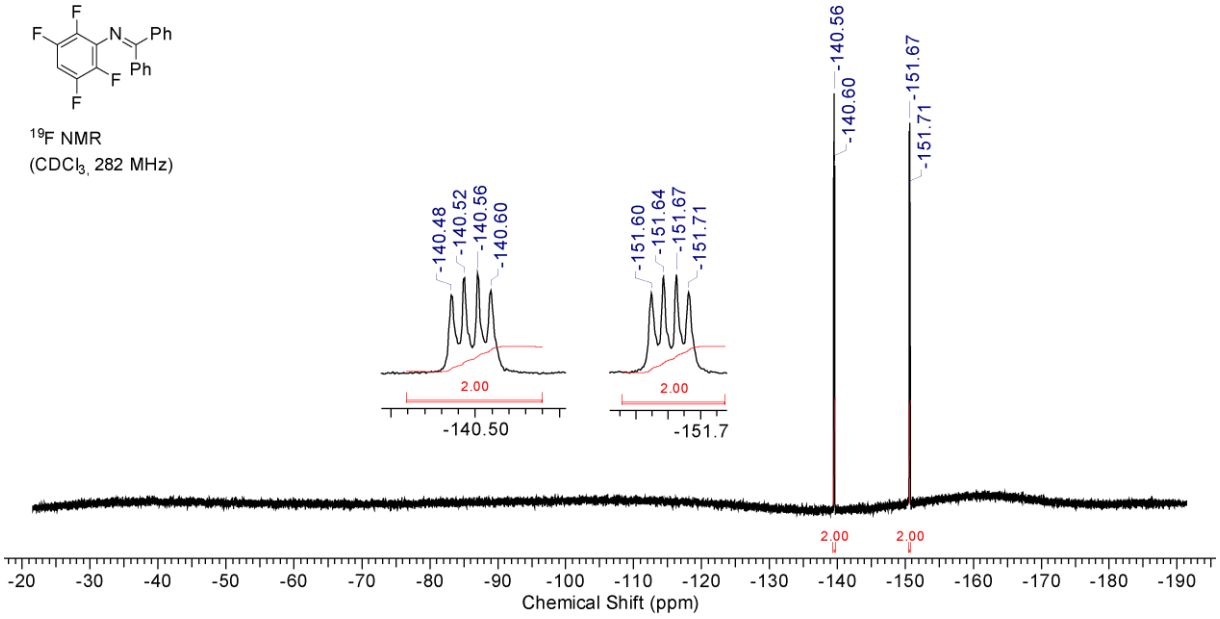


Loading: **1** (22 mg, 4.8 µmol Ti, 1 mol%), $TolNH_2$ (85 µL of 0.114 M solution in heptane, 9.6 µmol, 2 mol%), benzophenone (89 mg, 0.49 mmol), *N*-sulfinyl-2,3,5,6-tetrafluoroaniline (66 µL, 0.51 mmol), heptane (3.5 mL). Reaction time 2.5 h. After the reaction the catalyst was washed with CH_2Cl_2 twice. The product was isolated in several crops as off-white plates by recrystallization from boiling heptane. Yield 141 mg (88%); mp 105–106 °C (lit.[11] 102–104 °C).

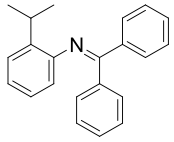
^{1}H NMR (300 MHz, $CDCl_3$, 22°C): δ 7.81 (d, ^3J = 7.3, 2H), 7.54 (t, ^3J = 7.3, 1H), 7.44 (t, ^3J = 7.5, 2H), 7.38–7.30 (m, 3H), 7.20 (d, ^3J = 6.7, 2H), 6.62 (tt, $^3J_{H-F}$ = 10.0, $^4J_{H-F}$ = 7.1, C_6HF_4, 1H).

^{19}F NMR (282 MHz, $CDCl_3$, 22°C): δ −140.54 (dd, $^3J_{F-F}$ = 22, $^5J_{F-F}$ = 11, 2F), −151.66 (dd, 2F).



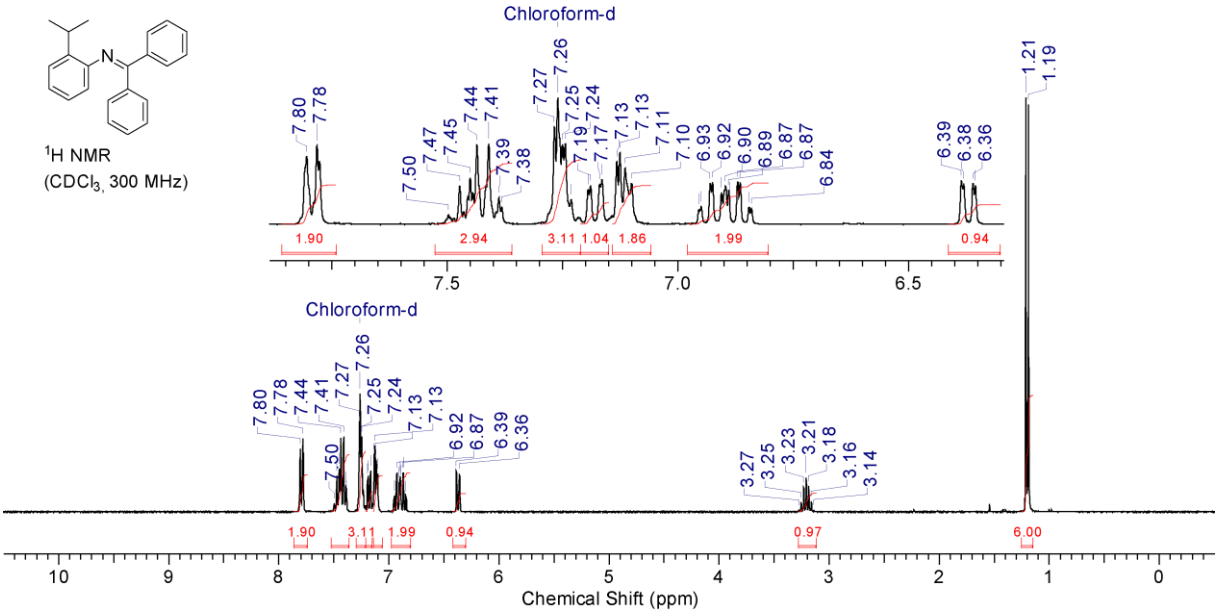


***N*-(diphenylmethylene)-2-isopropylaniline (3c)**[10]

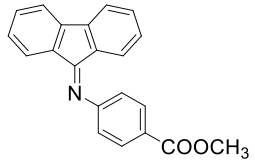


Loading: **1** (19 mg, 4.7 µmol Ti, 1 mol%), TolNH$_2$ (83 µL of 0.114 M solution in heptane, 9.5 µmol, 2 mol%), benzophenone (86 mg, 0.46 mmol), *N*-sulfinyl-2-isopropylaniline (82 µL, 0.48 mmol), heptane (3 mL). Reaction time 4 h. The product was isolated as yellow-orange crystals by crystallization from heptane. Yield 129 mg (91%); mp 83–84 °C (lit.[10] 84–87 °C).

^{1}H NMR (300 MHz, $CDCl_3$, 22°C): δ 7.79 (d, ^3J = 6.7, 2H), 7.50–7.38 (m, 3H), 7.27–7.23 (m, 3H), 7.18 (dd, ^3J = 7.5, ^4J = 1.5, 1H), 7.13–7.10 (m, 2H), 6.95–6.84 (m, 2H), 6.36 (dd, ^3J = 7.6, ^4J = 1.5, 1H), 3.21 (sept, ^3J = 6.9, 1H, C*H*$(CH_3)_2$), 1.20 (d, 6H, CH$(CH_3)_2$).

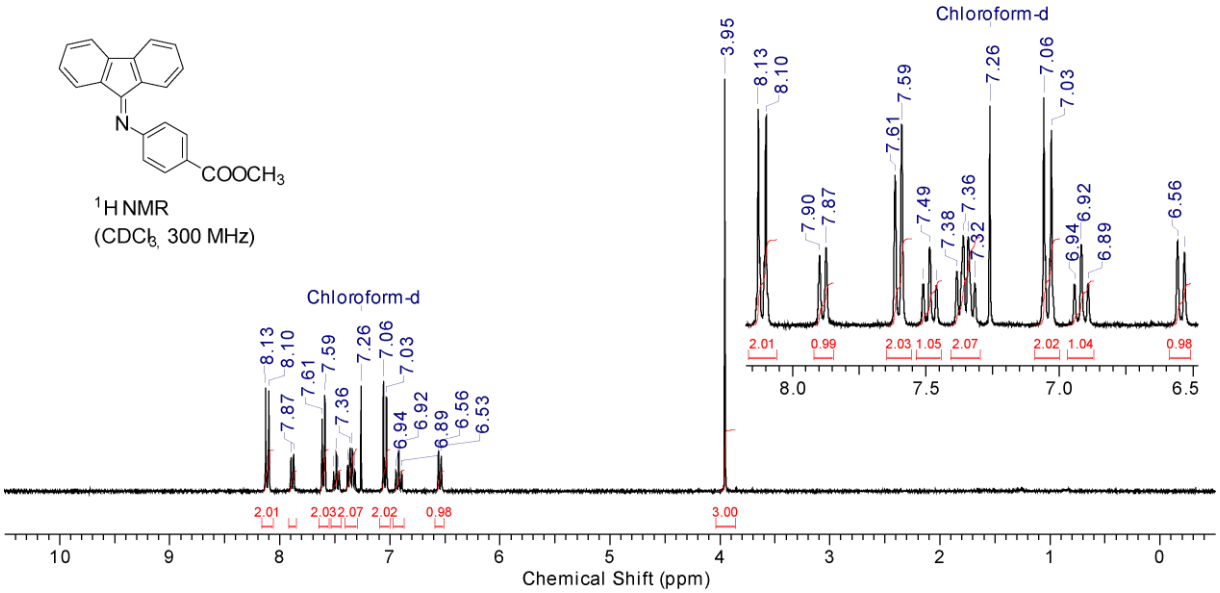


methyl 4-((9H-fluoren-9-ylidene)amino)benzoate (3d)[10]

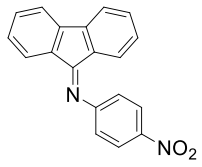


Loading: **1** (15 mg, 3.3 µmol Ti, 1 mol%), $TolNH_2$ (58 µL of 0.114 M solution in heptane, 6.6 µmol, 2 mol%), fluorenone (60 mg, 0.33 mmol), methyl *N*-sulfinyl-4-aminobenzoate (61 mg, 0.31 mmol), toluene (5 mL). Reaction time 2 h. Reaction mixture was filtered and the catalyst was washed with toluene thrice. The product was isolated as bright yellow needles by recrystallization from boiling toluene. Yield 97 mg (66%); mp 174–175 °C (lit.[10] 172–173 °C).

^{1}H NMR (300 MHz, $CDCl_3$, 23°C): δ 8.12 (d, ^3J = 8.8, 2H), 7.89 (d, ^3J = 7.3, 1H), 7.60 (d, ^3J = 7.4, 2H), 7.49 (t, ^3J = 7.4, 1H), 7.38–7.32 (m, 2H), 7.05 (d, ^3J = 8.4, 2H), 6.92 (t, ^3J = 7.7, 1H), 6.55 (d, ^3J = 7.7, 1H), 3.95 (s, 3H, COOCH_3).

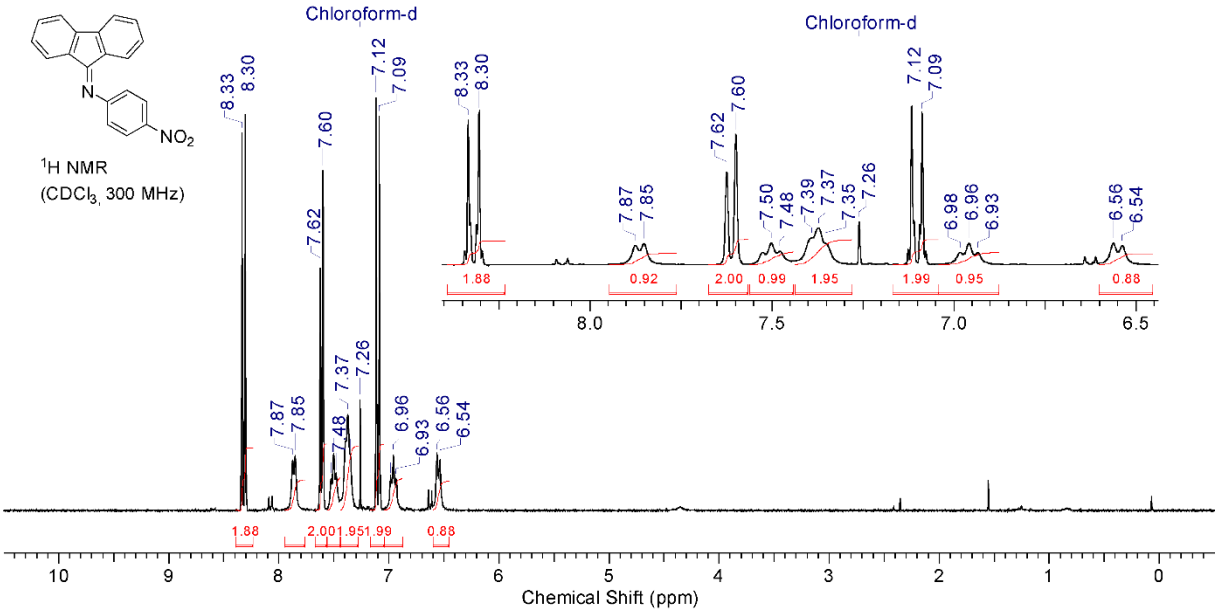


***N*-(4-nitrophenyl)fluorenimine (3e)**[10]

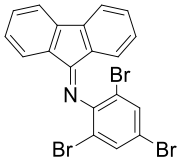


Loading: **1** (16 mg, 4 µmol Ti, 1 mol%), $TolNH_2$ (70 µL of 0.114 M solution in heptane, 8.0 µmol, 2 mol%), fluorenone (72 mg, 0.40 mmol), *N*-sulfinyl-4-nitroaniline (76 mg, 0.41 mmol), toluene (3 mL). Reaction time 1.5 h. The product was isolated as bright-yellow crystals by recrystallization from boiling toluene. Yield 104 mg (87%); mp 187–188 °C (lit.[10] 187–189 °C).

^{1}H NMR (300 MHz, $CDCl_3$, 22°C): δ 8.32 (d, ^3J = 8.8, 2H, C_6H_4), 7.86 (d, ^3J = 7.2, 1H), 7.61 (d, ^3J = 7.5, 2H), 7.50 (br t, ^3J = 7.1, 1H), 7.37 (br t, ^3J = 5.7, 1H), 7.10 (d, ^3J = 8.8, 2H, C_6H_4), 6.96 (br t, ^3J = 7.2, 1H), 6.55 (d, ^3J = 7.4, 1H).

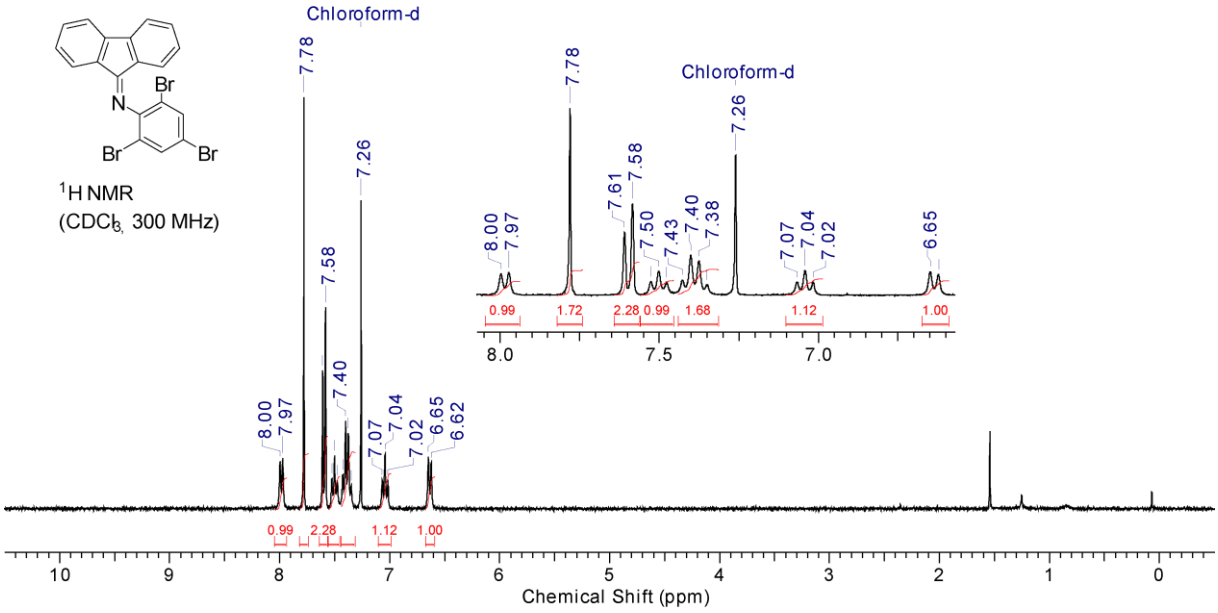


***N*-(2,4,6-tribromophenyl)fluorenimine (3f)[6, 11]**

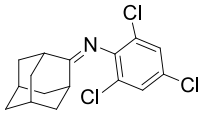


Loading: **1** (19 mg, 4.2 µmol Ti, 1 mol%), $TolNH_2$ (83 µL of 0.114 M solution in heptane, 9.5 µmol, 2 mol%), fluorenone (85 mg, 0.472 mmol), *N*-sulfinyl-2,4,6-tribromoaniline (183 mg, 0.487 mmol), toluene (5 mL). Reaction time 4 h. Reaction mixture was filtered and the catalyst was washed with toluene thrice and with CH_2Cl_2 once. The product was isolated in several crops as yellow powder by recrystallization from boiling toluene. Yield 201 mg (86%); mp 218–219 °C (lit.[11] 220–221 °C).

^{1}H NMR (300 MHz, $CDCl_3$, 23°C): δ 7.99 (d, ^3J = 7.3, 1H), 7.78 (s, 2H, $C_6H_2Br_3$), 7.59 (app d, ^3J = 7.4, 2H), 7.50 (t, ^3J = 7.3, 1H), 7.43–7.35 (m, 2H), 7.04 (t, ^3J = 7.5, 1H), 6.64 (t, ^3J = 7.6, 1H).

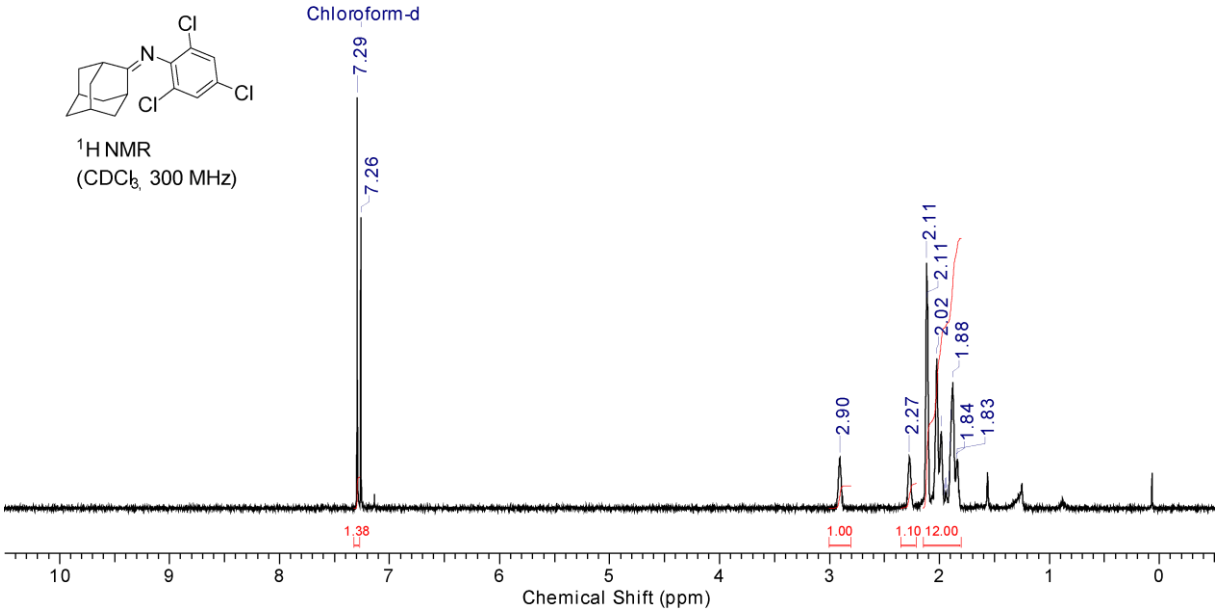


***N*-(2-adamantylidene)-2,4,6-trichlorophenylaniline (3g)**[6]

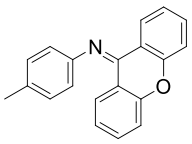


Loading: **1** (20 mg, 4.4 µmol Ti, 1 mol%), $TolNH_2$ (78 µL of 0.114 M solution in heptane, 8.9 µmol, 2 mol%), adamantanone (67 mg, 0.45 mmol), *N*-sulfinyl-2,4,6-trichloroaniline (110 mg, 0.45 mmol), heptane (5 mL). Reaction time 4 h. The product precipitates from the reaction mixture at room temperature. After the reaction it was extracted with CH_2Cl_2 and catalyst was washed with CH_2Cl_2 twice. The filtrate was concentrated in vacuum and the product crystallized at −20 °C in several crops as pale yellow crystals. Yield 121 mg (83%); mp 139–141 °C (lit.[6] 138–139 °C).

^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ 7.29 (s, 2H, $C_6H_2Cl_3$), 2.90 (s, 1H), 2.27 (s, 1H), 2.11–1.83 (m, 12H).

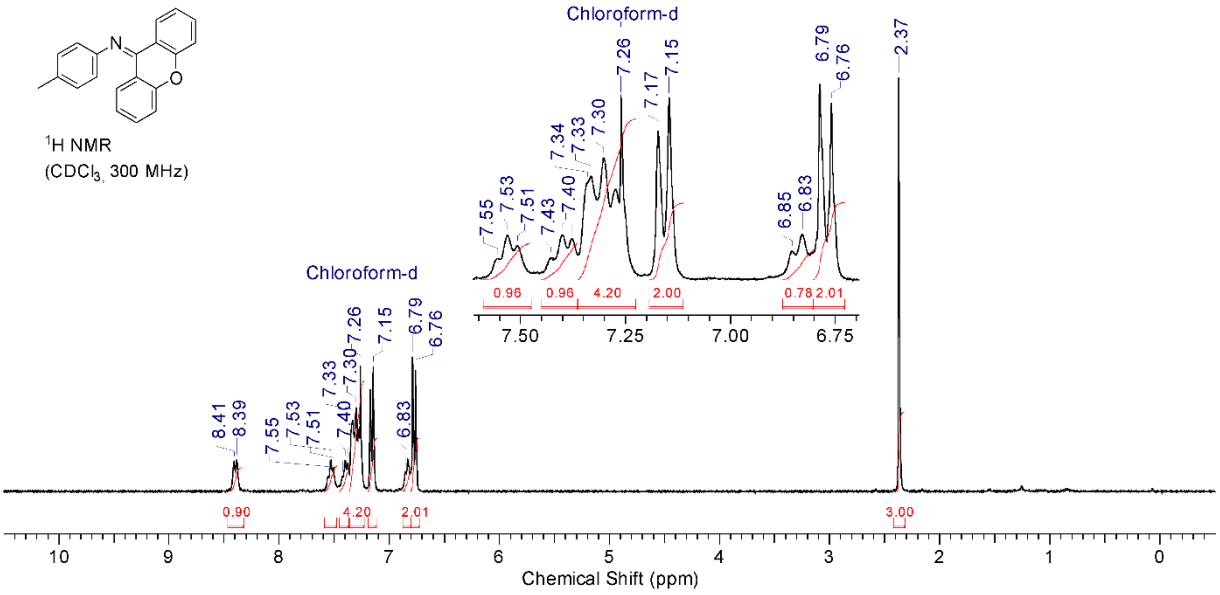


4-methyl-*N*-(*9H*-xanthene-9-ylidene)aniline (3h)[12]

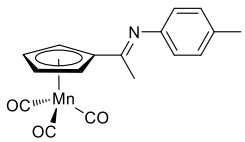


Loading: **1** (20 mg, 4.4 µmol Ti, 1 mol%), $TolNH_2$ (77 µL of 0.114 M solution in heptane, 8.8 µmol, 2 mol%), xanthone (86 mg, 0.44 mmol), *N*-sulfinyl-4-methylaniline (62 µL, 0.46 mmol), toluene (3 mL). Reaction time 3 h. The product was isolated in several crops as yellow-orange needles by recrystallization from hot toluene. Yield 112 mg (90%); mp 108–109 °C (lit.[12] 111–112.5 °C).

^{1}H NMR (300 MHz, $CDCl_3$, 23°C): δ 8.40 (d, ^3J = 7.6, 1H), 7.54 (t, ^3J = 7.0, 1H), 7.40 (t, ^3J = 7.5, 1H), 7.34–7.26 (m, 4H), 7.16 (d, ^3J = 8.2, 2H, *Tol*), 6.84 (t, ^3J = 7.3, 1H), 6.78 (d, 2H, *Tol*), 2.37 (s, 3H, $C_6H_4CH_3$).



4-methyl-*N*-(1-cymantrenylethylidene)aniline (3i)

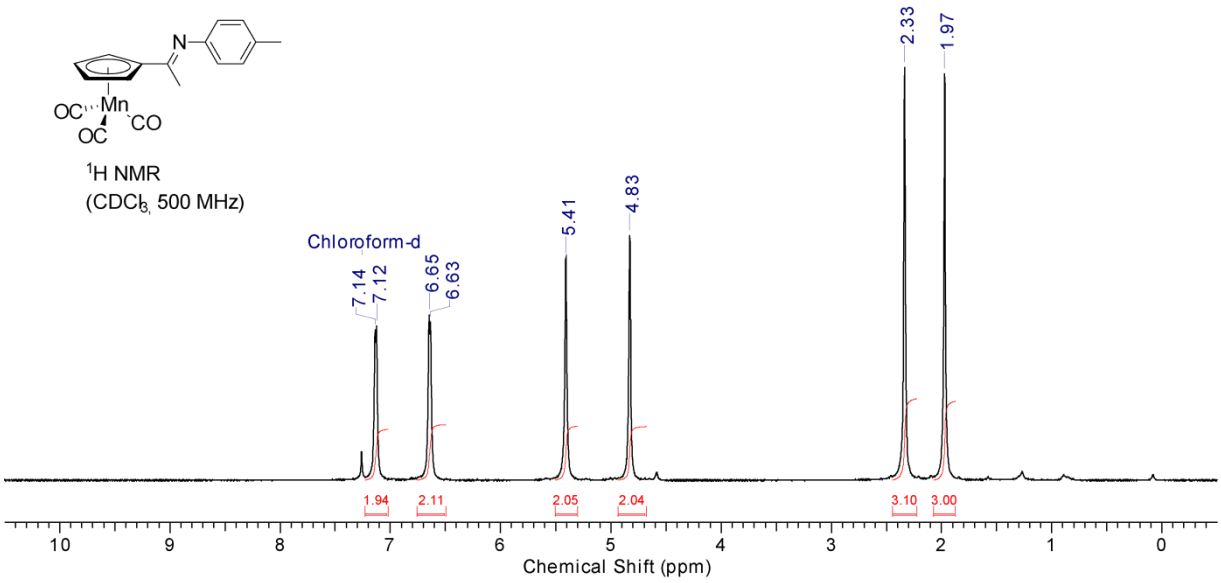


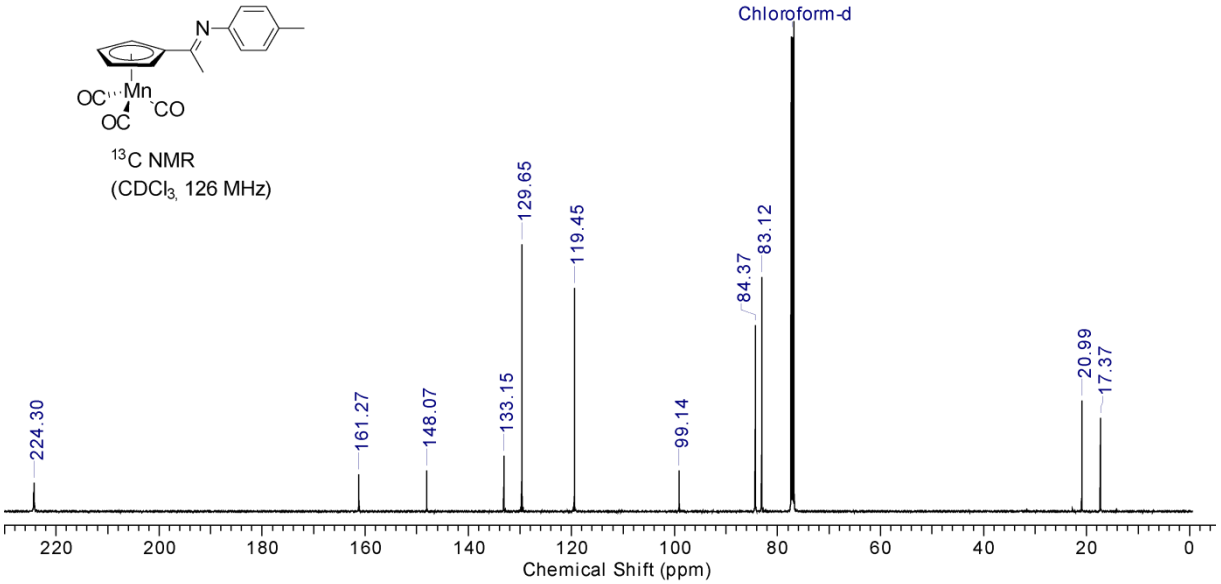
Loading: **1** (23 mg, 5.75 µmol Ti, 1 mol%), $TolNH_2$ (101 µL of 0.114 M solution in heptane, 11.5 µmol, 2 mol%), acetylcymantrene (141.5 mg, 0.575 mmol), *N*-sulfinyl-4-methylaniline (88 mg, 0.575 mmol), toluene (4 mL). Reaction time 1 h. Reaction mixture was filtered and the catalyst was washed with toluene thrice. The product was isolated in several crops as yellow powder by recrystallization from hexane at +5 °C. Yield 160 mg (82%); mp 76–78 °C. **IR** (toluene, cm^{-1}): ν 2024 (C≡O), 1940 (C≡O), 1636 (C=N).

^{1}H NMR (500 MHz, $CDCl_3$, 25°C): δ 7.13 (d, ^{3}J = 6.6, 2H, *Tol*), 6.64 (d, 2H, *Tol*), 5.41 (br s, 2H, *Cp*), 4.83 (br s, 2H, *Cp*), 2.33 (s, 3H, $C_6H_4CH_3$), 1.97 (s, 3H, $C(CH_3)$=N).

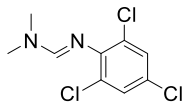
^{13}C NMR (126 MHz, $CDCl_3$, 25°C): δ 224.30 (quat *C*O), 161.27 (quat *C*=N), 148.07 (quat *C*N), 133.15 (quat), 129.65 (*C*H, C_6H_4), 119.45 (*C*H, C_6H_4), 99.14 (quat, Cp), 84.37 (*C*H, Cp), 83.12 (*C*H, Cp), 20.99 (CH_3), 17.37 ($C(CH_3)$=N).

Anal. Found (Calcd, $C_{17}H_{14}MnNO_3$, %): C, 60.85 (60.91); H, 4.28 (4.21); N, 4.21 (4.18).



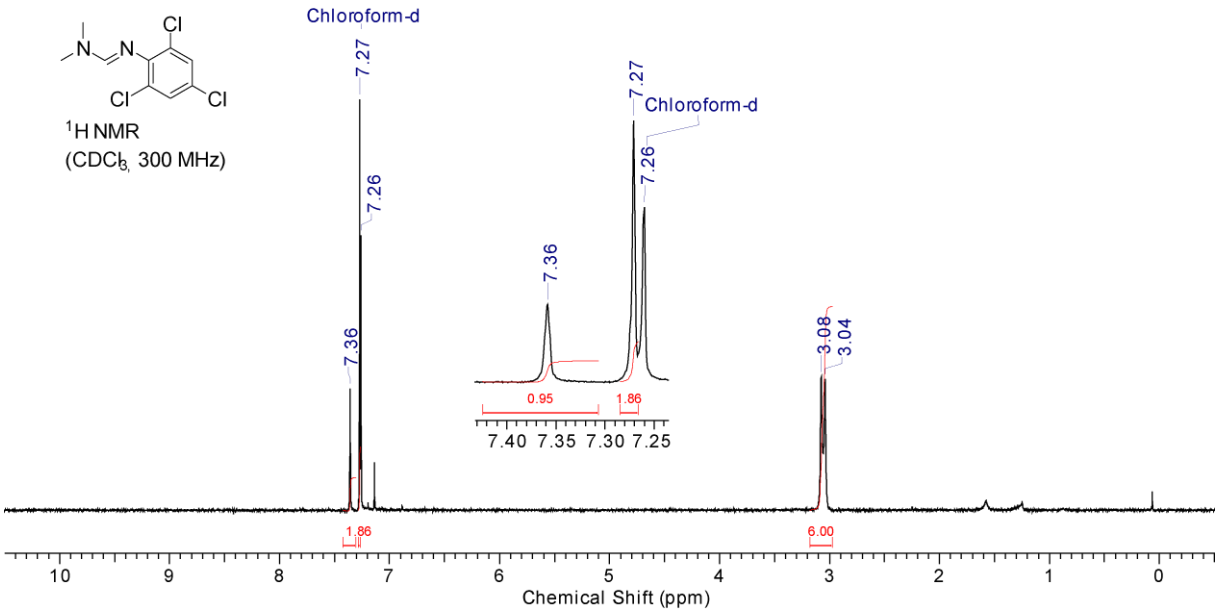


***N*,*N*-dimethyl-*N*′-(2,4,6-trichlorophenyl)formamidine (3j)**[13]

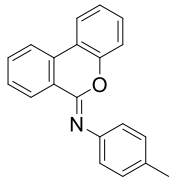


Loading: **1** (20 mg, 4.4 µmol Ti, 1 mol%), $TolNH_2$ (78 µL of 0.114 M solution in heptane, 8.9 µmol, 2 mol%), *N,N*-dimethylformamide (38 mg, 0.52 mmol), *N*-sulfinyl-2,4,6-trichloroaniline (111 mg, 0.46 mmol), heptane (5 mL). Reaction time 4 h. Reaction mixture was filtered and the catalyst was washed with heptane thrice. The product was isolated as yellow oily crystals by recrystallization from heptane at −20 °C. Yield 68%; mp 64–65 °C (lit.[13] 70–71 °C).

^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ 7.36 (s, 1H, C*H*=N), 7.27 (s, 2H, $C_6H_2Cl_3$), 7.10 (d, ^3J = 10.7, N(CH_3)$_2$).

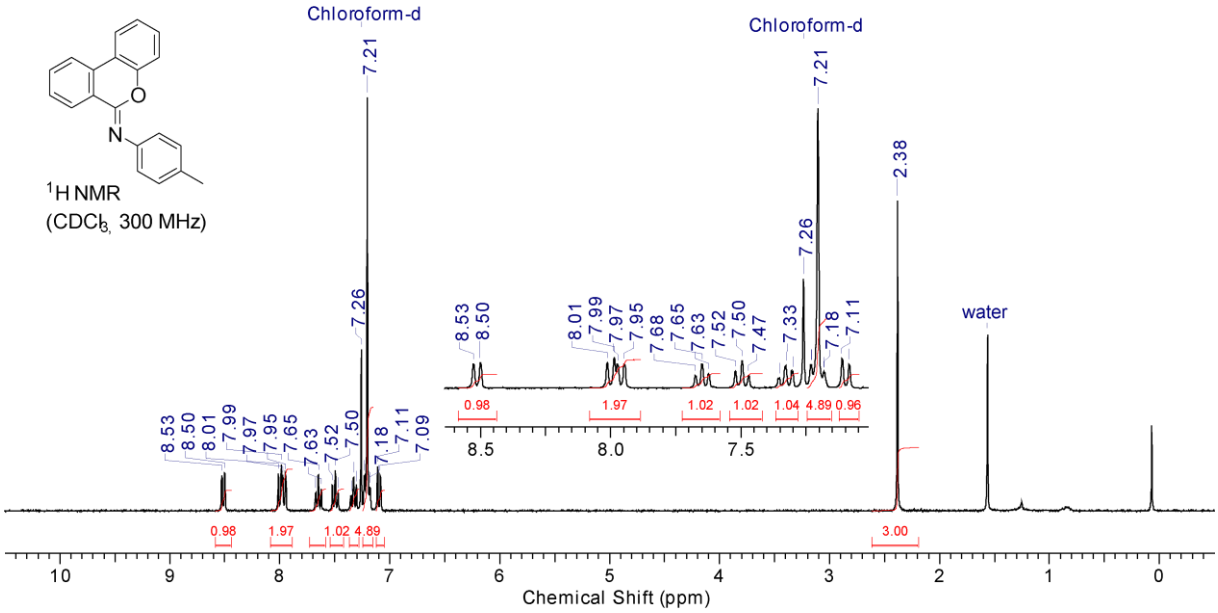


***N*-(4-methylphenyl)-6*H*-benzo[*c*]chromen-6-imine (3k)**[14]

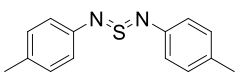


Loading: **1a** (24 mg, 6.0 µmol Ti, 1 mol%), 3,4-benzocoumarin (114 mg, 0.58 mmol), *N*-sulfinyl-4-methylaniline (85 mg, 0.55 mmol), toluene (5 mL). Reaction time 24 h. Reaction mixture was filtered and the catalyst was washed with toluene thrice. The product was isolated in several crops as off-white crystals by recrystallization from toluene/heptane. Yield 111 mg (68%); mp 98–100 °C (lit.[14] 104–105 °C).

^{1}H NMR (300 MHz, $CDCl_3$, 20°C): δ 8.52 (d, ^3J = 8.0, 1H), 8.01–7.94 (m, 2H), 7.65 (t, ^3J = 7.6, 1H), 7.50 (t, ^3J = 7.7, 1H), 7.33 (t, ^3J = 7.7, 1H), 7.23–7.18 (m, 5H), 7.10 (d, ^3J = 8.0, 1H), 2.38 (s, 3H, CH_3).

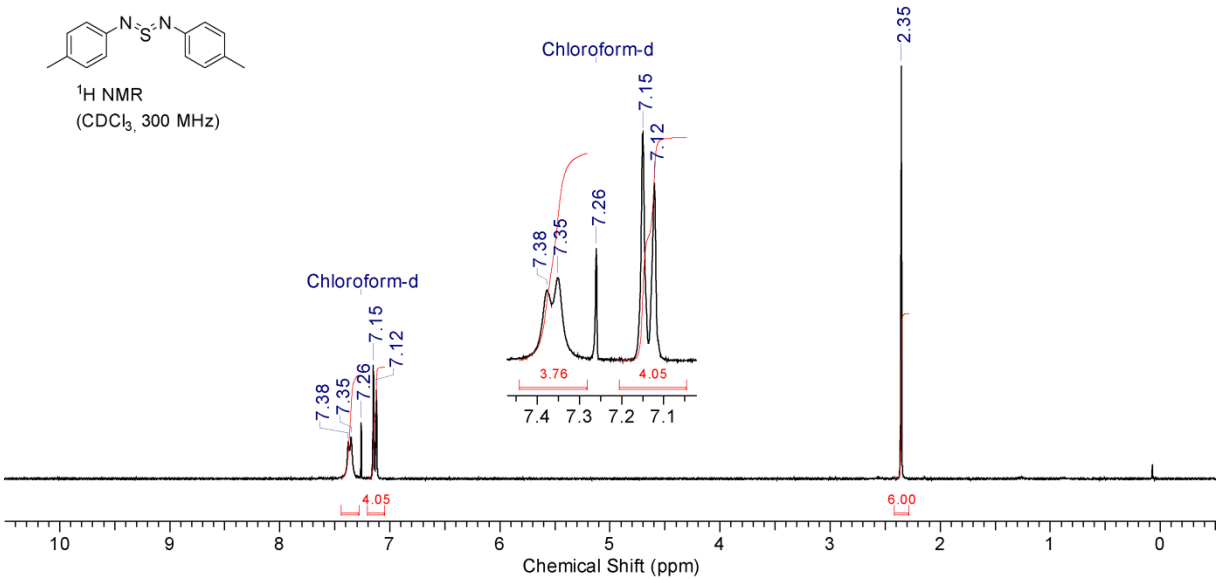


***bis*(4-methylphenyl)sulfurdiimine (3l)**[11]



Loading: **1** (17 mg, 3.7 µmol Ti, 1 mol%), $TolNH_2$ (66 µL of 0.114 M solution in heptane, 7.4 µmol, 2 mol%), *N*-sulfinyl-4-methylaniline (51 µL, 0.38 mmol), heptane (2.5 mL). Reaction time 18 h, conversion *ca.* 75%. The product was handled under argon atmosphere; isolated as red-orange crystals by crystallization from dry heptane. Yield 33 mg (72%); mp 44–46 °C (lit.[11] 40–42 °C).

^{1}H NMR (300 MHz, $CDCl_3$, 21°C): δ 7.37 (br d, 4H), 7.14 (d, ^3J = 8.1, 4H), 2.35 (s, 6H, CH_3).



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