Materials

All reactions were carried out under a nitrogen atmosphere using standard Schlenk and drybox techniques. Chemicals were purchased from Sigma-Aldrich, Strem Chemicals Inc., Oakwood Products, and Alfa-Aesar. They were used as received unless otherwise noted. Dry acetonitrile was obtained via distillation over CaH_2. Dichloromethane, pentane, toluene and tetrahydrofuran were dried and purified in a nitrogen atmosphere while using a Grubbs-type, two-column purification system (Innovative Technologies) and stored over activated 3 Å molecular sieves.[1] Deuterated NMR solvents ($CDCl_3$ and CD_2Cl_2) were purchased from Cambridge Isotope Laboratories and used as internal standards for all measurements [($CDCl_3$, ^1H 7.26) and (CD_2Cl_2, ^1H at 5.32 and ^{13}C at 53.84)]. 1,1-Bis(2-pyridyl)ethane, 2,6-bis[(2-pyridyl)ethyl]pyridine (Py_5Me_2),[2] and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (BAr_4')[3] were synthesized according to published procedures.

Syntheses

[CrOH(Py_5Me_2)][Cl]$_2$ [1^a]: Py_5Me_2 (0.499 g) was dissolved in 40.0 mL of dry acetonitrile, which was obtained using the freeze-pump-thaw method (3 cycles). $CrCl_2$ (0.138 g) was then added to the flask. The solution turned dark green immediately and was stirred at room temperature for 72 hours. The solvent was removed under reduced pressure to yield a dark green solid. Crude yield for [CrCl(Py_5Me_2)][Cl] is 0.486 g (76.3%). Excess deionized water was then added to this solid (20.0 mL) and let stir for 48 hours. This yielded a dark pink solution before the water was removed in vacuo. Crude yield of [CrOH(Py_5Me_2)][Cl]$_2$ is 0.578 g (90.1% based on [CrCl(Py_5Me_2)][Cl], overall yield of 68.7% for two steps). This was used without further purification for the synthesis of **1^b**.

[CrOH(Py_5Me_2)][B(C_8F_6)$_4$]$_2$ [1^b]: BAr_4' (0.743 g) was dissolved in 20.0 mL of diethyl ether. Crude **1^a** (0.254 g) was separately dissolved in 15.0 mL of deionized water. These two solutions were then combined in a round bottom flask and stirred rigorously for 30 seconds, then slowly stirred for an additional hour. The purple organic product was extracted (3x30 mL) with diethyl ether and removed through rotary evaporation. The obtained purple powder was concentrated in diethyl ether and layered with pentane to yield 0.341 g (44.5%) of dark purple crystals. Absorption spectrum: (DCM): λ_{max} (nm), ε ($M^{-1}cm^{-1}$); 549, 698; 394, 624. ATR/FTIR: $\tilde{\nu}_{OH}$: 3647 cm^{-1}, $\tilde{\nu}_{OD}$: 2690 cm^{-1}. Anal. Calcd for $C_{93}H_{50}B_2CrF_{48}N_5O$: C, 49.89; H, 2.25; N, 3.13. Found: C, 49.53; H, 2.57; N, 2.96. HR ESIMS (M^+) m/z calcd for $C_{29}H_{26}CrN_5O$ 256.075, found 256.077. Magnetic susceptibility (CD_2Cl_2): μ_{eff} = 3.42 μ_{BM}.

[CrCl(Py_5Me_2)][B(C_8F_6)$_4$]$_2$ [2^b]: 1^b (0.400g) was quantitatively dissolved in 15.0 mL of dry THF. To this mixture, excess chlorotrimethylsilane (TMS-Cl) (24.0 mL) was added drop-wise. This was kept stirring for 24 hours which yielded a fine, pink powder after repeated washing with hexanes. Yield 0.299 g (73.2%). Absorption spectrum: (DCM): λ_{max} (nm), ε ($M^{-1}cm^{-1}$); 517, 101; 327, 832. Anal. Calcd for $C_{93}H_{49}B_2ClCrF_{48}N_5$: C, 49.48; H, 2.19; N, 3.10. Found: C, 47.73; H, 1.10; N, 2.89. HR ESIMS (M+) m/z Calcd for $C_{29}H_{25}ClCrN_5$ 265.060, found 265.060. Magnetic susceptibility (CD_2Cl_2): μ_{eff} = 3.44 μ_{BM}.

(N,N-bis(2-hydroxy-3,5-dimethylbenzyl)-2-aminoethanol): 2,4-dimethylphenol (25.3 g), 37% formaldehyde solution (6.22 g), ethanolamine (6.33 g), and *n*-pentanol (10.0 mL) were added to a previously dried 100 mL round bottom flask. This was then set to reflux at 105°C for 72 hours, which yielded a biphasic yellow oil. This was washed with a saturated solution of NaCl and extracted in toluene (2x75 mL). This was rotary evaporated to yield a yellow oil with a white precipitate. The obtained solids were recrystallized from hot toluene to yield a white product. Yield 1.97 g (5.8%). ^{1}H NMR spectrum (400 MHz, $CDCl_3$): δ 6.86 (s, 2H, arom), 6.70 (s, 2H, arom), 3.87 (t, J=5.2Hz, 2H, $HOCH_2CH_2N$), 3.75 (s, 4H, NCH_2Ar), 2.71 (t, J=4.8Hz, 2H, $HOCH_2CH_2N$), 2.20 (s, 12H, $ArCH_3$).

Asymmetric Methyl $[O_3N]Ti(O^iPr)$ [3]: N,N-bis(2-hydroxy-3,5-dimethylbenzyl)-2-aminoethanol (1.45 g) was dissolved in dry toluene (15.0 mL) in a drybox. To this solution, titanium isopropoxide (1.25 g) was added drop-wise at room temperature to yield an orange/yellow solution, which was stirred for an additional 48 hrs. Solvent was removed under reduced pressure and washed with petroleum ether, yielding 0.962 g (54.1%) of a fine, yellow powder. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 6.90 (s, 2H, arom), 6.74 (s, 2H, arom), 4.86 (bs, 1H, $CH(CH_3)_2$), 4.30 (bs, 2H, OCH_2CH_2N), 3.90 (bs, 2H, NCH_2Ar), 3.61 (bs, 2H, OCH2CH_2N), 3.06 (bs, 2H, NCH_2Ar), 2.23 (s, 12H, CH_3Ar), 1.17 (m, 6H, $CH(CH_3)_2$). ^{13}C NMR (400 MHz, CD_2Cl_2): d 159.13, 131.21, 128.65, 127.90, 125.02, 123.84 (aryl), 78.96 (CHO), 70.91 (CH_2O), 59.92 (OCH_2N), 57.50 (CH_2N), 25.77 ($(CH_3)_2CHO$), 20.70 (aryl-CH_3), 16.70 (aryl-CH_3). Absorption spectrum: (DCM): λ_{max} (nm), ε ($M^{-1}cm^{-1}$); 332, 2810; 261, 15121. Anal. Calcd for $C_{23}H_{31}NO_4Ti$: C, 63.74; H, 7.21; N, 3.23. Found: C, 64.10; H, 7.97; N, 2.95.

Cr-μO-Ti [4^b]: Complex **[3]** (0.023g) was dissolved in 9.00 mL of dry THF. The previously synthesized [$\mathbf{1}^b$] (0.125 g) was dissolved separately in 9.00 mL of dry THF. The $[O_3N]Ti(O^iPr)$ solution was added drop-wise to the $[CrOH(Py_5Me_2)][B(C_8F_6)_4]_2$ solution over 5 minutes at room temperature. This immediately yielded a burnt orange solution. This was kept stirring for 48 hours. The THF was removed under reduced pressure to yield a waxy, burnt orange solid. This was washed with pentane (2x15 mL) to yield a fine, burnt orange powder. Large, burnt orange crystals were obtained through vapor diffusion of pentane into a dichloromethane solution. Yield 0.110 g (74.6%). Absorption spectrum: (DCM): λ_{max} (nm), ε ($M^{-1}cm^{-1}$); 525, 61; 261, 54093. Anal. Calcd for $C_{113}H_{73}B_2CrF_{48}N_6O_4Ti$: C, 51.96; H, 2.82; N, 3.22. Found: C, 52.30; H, 2.23; N, 3.14. HR ESIMS (M^+) m/z calcd for $C_{49}H_{49}CrN_6O_4Ti$ 442.635, found 442.635. Magnetic susceptibility (CD_2Cl_2): $\mu_{eff} = 3.10\ \mu_{BM}$.

Measurements

^{1}H, ^{13}C NMR, and magnetic susceptibility measurements were taken at ambient temperatures on a 400 MHz Varian Unity Inova spectrometer. ATR/FT-IR measurements were obtained on a Bruker Vertex 80v FT-IR spectrometer using a Platinum ATR accessory. Electronic absorbance spectra were recorded on a Shimadzu UV-3600 UV-Visible spectrophotometer. Elemental analyses were obtained on a Perkin Elmer 2400 Series II CHNS/O instrument. Single crystal X-Ray measurements were performed on a Bruker-Nonius Kappa Axis X8 Apex2 diffractometer using an Oxford Cryosystems 700 Series Low Temperature accessory.

Determining the Energy of the Metal-to-Metal Charge Transfer Transition

The absorbance sum of $\mathbf{1}^b$ and **3** was plotted versus complex $\mathbf{4}^b$ (Figure 1A). The resulting mathematical difference of the two curves is depicted by the black curve in Figure 1B. Using Origin Pro 8, a baseline was generated at an absorbance of zero. Two individual Gaussian curves were independently fit to the absorption maxima of each transition present in the generated mathematical difference curve. The line width of the higher energy curve centered at 4.321 eV is .3106, with a height of 7178 $M^{-1}cm^{-1}$. Whereas the line width of the lower energy curve centered at 3.984 eV is .4324, with a height of 4945 $M^{-1}cm^{-1}$. The coefficient of determination for the multiple peak fits, R^2, was found to be 0.994. The calculated reduced χ^2 of the curve fits was found to be 35546.

References

[S1] A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
[S2] A. J. Canty, N. J. Minchin, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.*, 1986, **10**, 2205.
[S3] M. Brookhart, B. Grant, A. F. Volpe, *Organometallics*, 1992, **11**, 3920.

Crystallographic Details

Table S1 Crystal data and structure refinement for **1**[b].

Empirical formula	$C_{93}H_{50}B_2CrF_{48}N_5O$
Formula weight	2239.00
Temperature	110 K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	C 2/*c*
Unit Cell Dimensions	a = 19.817(5) Å
	b = 16.704(4) Å
	c = 28.732(7) Å
Volume	9510(4) $Å^3$
Z	4
Density (calculated)	1.564 g/cm^3
Absorption coefficient	0.265 cm^{-1}
F(000)	4468
Crystal Size	0.35 x 0.29 x 0.22 mm
Theta range for data collection	4.88 to 65.06°
Reflections collected	205349
Independent reflections	21029 [R(int) = .0413]
Completeness to Theta = 70.2°	99.8%
Refinement Method	Full matrix least-squares using F^2
Final R indices [I>2Σ(I)]	R1 = .0628, wR2 = .1706
R indices (all data)	R1 = .0846, wR2 = .1822
Largest diff. peak and hole	0.934 and 0.937 e.$Å^{-3}$

All crystal structure determinations were performed with a Bruker-Nonius X8 Kappa Apex2 diffractometer using MoKα radiation at a temperature of 110K. Suitable crystals of were selected under the microscope and mounted on MiTeGen mount using a minimum amount of Paratone N oil. Data were corrected for absorption and polarization effects using multi-scan methods (SADABS). The SQUEZZE procedure was implemented in PLATON in order to subtract out the solvent's contribution to the diffraction pattern. Structures were solved using direct methods. H atoms were placed at calculated positions and their isotropic displacement parameters refined as "riding" on the non-H atom to which they are bonded. Graphic representations of the resulting structure were produced using OLEX 2.

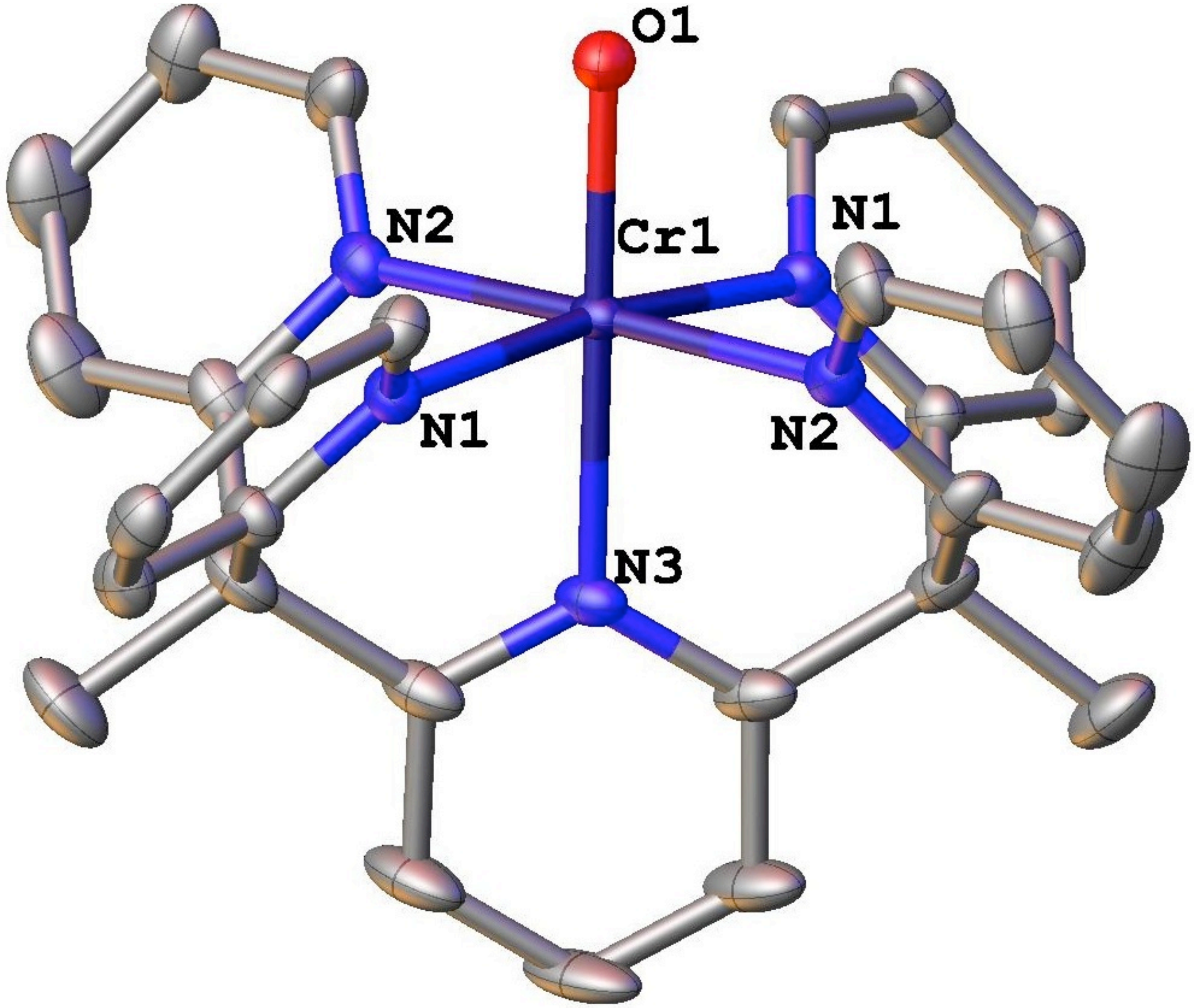

Figure S1 Symmetry Generated Crystal Structure of **1**^{b}

Table S2 Crystal data and structure refinement for **2**[b].

Empirical formula	$C_{101}H_{65}B_2ClCrF_{48}N_5O_2$
Formula weight	2401.65
Temperature	110 K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	C 2/*c*
Unit Cell Dimensions	a = 20.011(6) Å b = 16.672(6) Å c = 28.937(11) Å
Volume	9654(6) Å^3
Z	4
Density (calculated)	1.652g/cm^3
Absorption coefficient	0.295 cm^{-1}
F(000)	4820
Crystal Size	0.14 x 0.06 x 0.05 mm
Theta range for data collection	4.88 to 48.42°
Reflections collected	65421
Independent reflections	8272 [R(int) = .0977]
Completeness to Theta = 70.2°	98.0%
Refinement Method	Full matrix least-squares using F^2
Final R indices [I>2Σ (I)]	R1 = .0629, wR2 = .1551
R indices (all data)	R1 = .1195, wR2 = .1834
Largest diff. peak and hole	-0.549 and 0.594 e.A^{-3}

All crystal structure determinations were performed with a Bruker-Nonius X8 Kappa Apex2 diffractometer using MoKα radiation at a temperature of 110K. Suitable crystals of were selected under the microscope and mounted on MiTeGen mount using a minimum amount of Paratone N oil. Data were corrected for absorption and polarization effects using multi-scan methods (SADABS). Structures were solved using direct methods. H atoms were placed at calculated positions and their isotropic displacement parameters refined as “riding” on the non-H atom to which they are bonded. Graphic representations of the resulting structure were produced using OLEX 2.

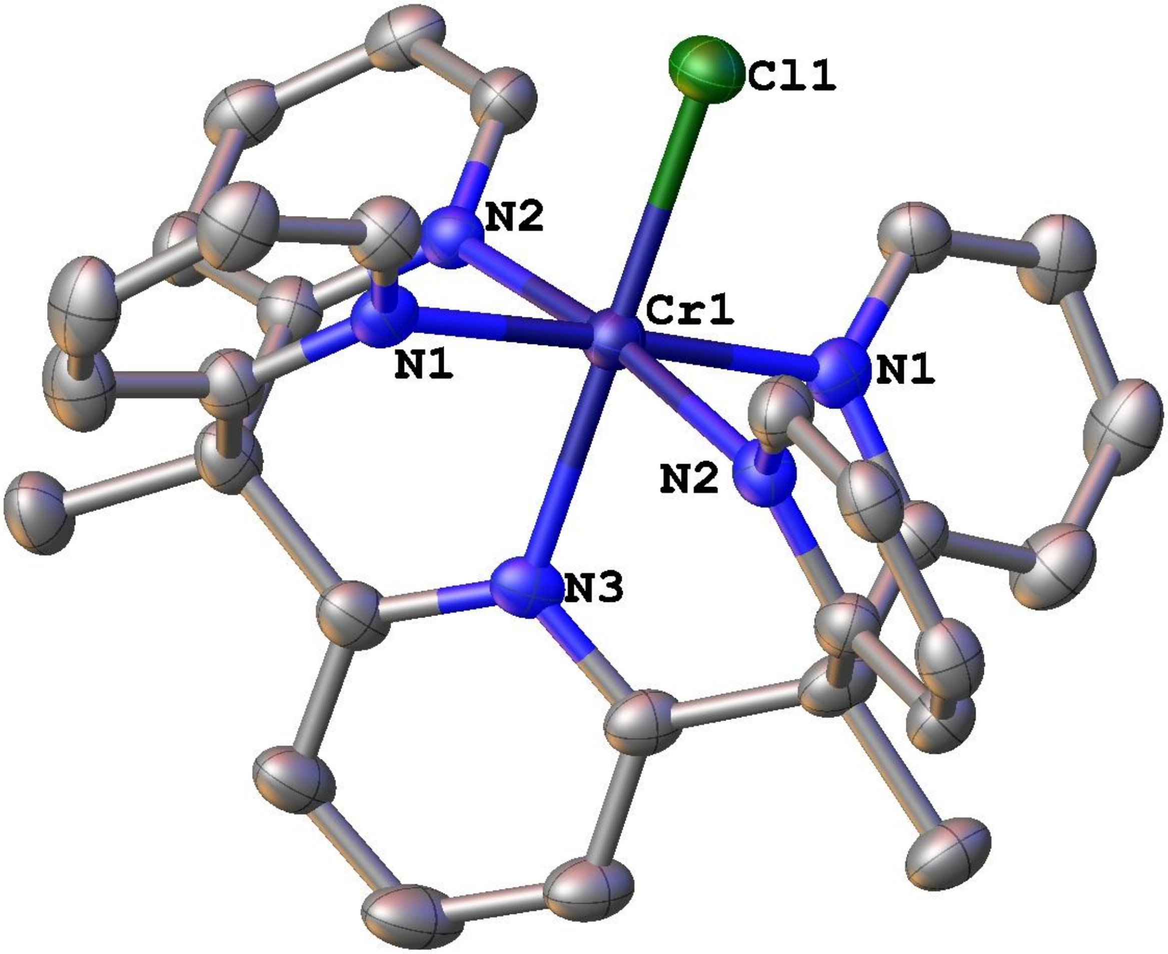

Figure S2 Symmetry Generated Crystal Structure of **2**[b]

Table S3 Crystal data and structure refinement for **4**[b].

Empirical formula	$C_{115}H_{77}B_2Cl_4CrF_{48}N_6O_4Ti$
Formula weight	2782.14
Temperature	110(2) K
Wavelength	0.71073 Å
Crystal System	Monoclinic
Space Group	$P2_1/n$
Unit Cell Dimensions	a = 13.4112(3) Å
	b = 18.3529(5) Å
	c = 46.9774(11) Å
Volume	11562.4(5) $Å^3$
Z	4
Density (calculated)	1.598 g/cm^3
Absorption coefficient	0.389 cm^{-1}
F(000)	5588
Crystal Size	0.10 x 0.16 x 0.40 mm
Theta range for data collection	1.19 to 26.56°
Reflections collected	139961
Independent reflections	23703 [R(int) = .0414]
Completeness to Theta = 70.2°	98.3%
Refinement Method	Full matrix least-squares using F^2
Final R indices [I>2Σ(I)]	R1 = .0691, wR2 = .1800
R indices (all data)	R1 = .0858, wR2 = .1920
Largest diff. peak and hole	1.692 and -1.725$eÅ^{-3}$

All crystal structure determinations were performed with a Bruker-Nonius X8 Kappa Apex2 diffractometer using MoKα radiation at a temperature of 110K. Suitable crystals of were selected under the microscope and mounted on MiTeGen mount using a minimum amount of Paratone N oil. Data were corrected for absorption and polarization effects using multi-scan methods (SADABS). Structures were solved using direct methods. H atoms were placed at calculated positions and their isotropic displacement parameters refined as "riding" on the non-H atom to which they are bonded. Graphic representations of the resulting structure were produced using OLEX 2.

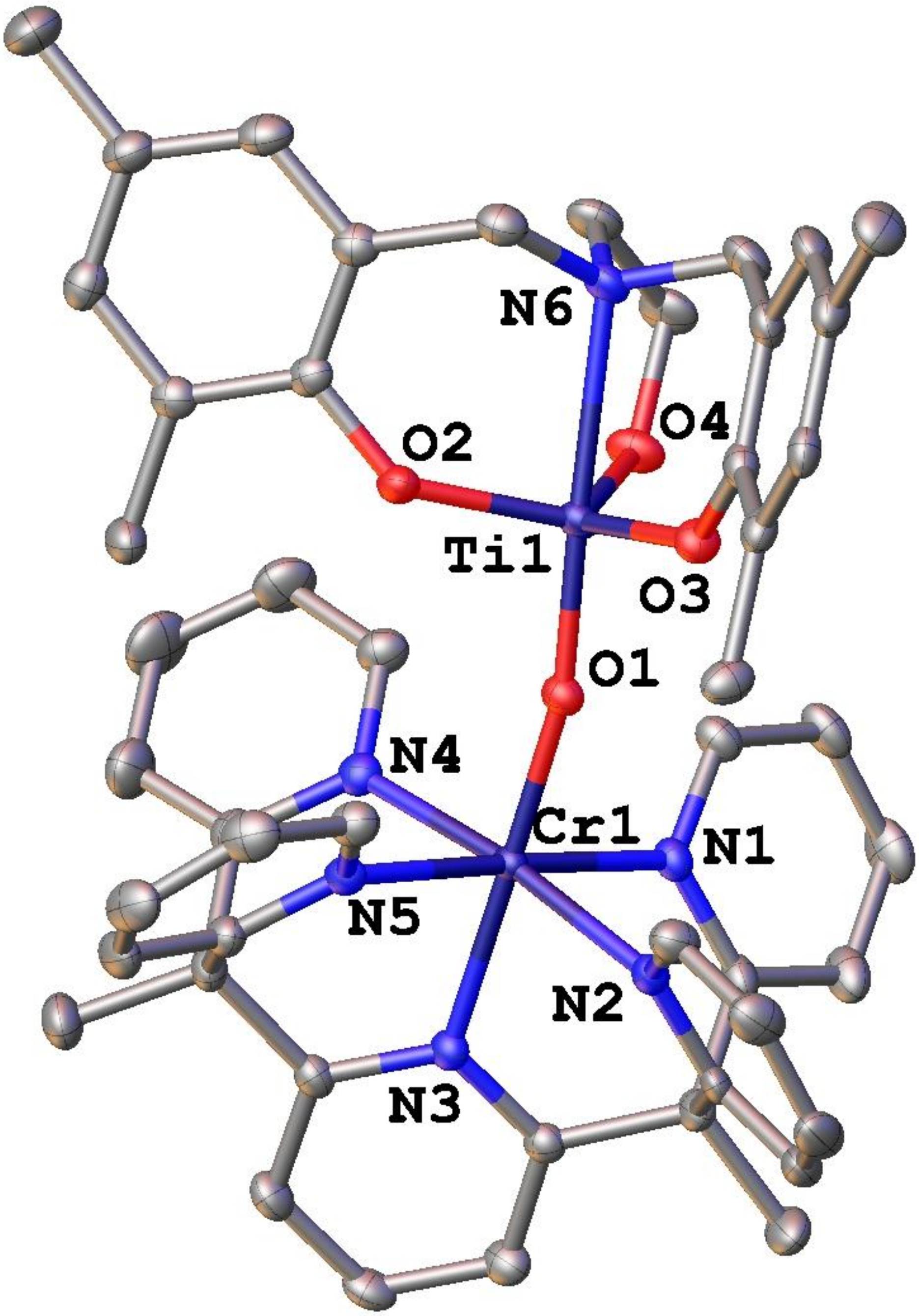

Figure S3 Crystal Structure of **4**^{b}

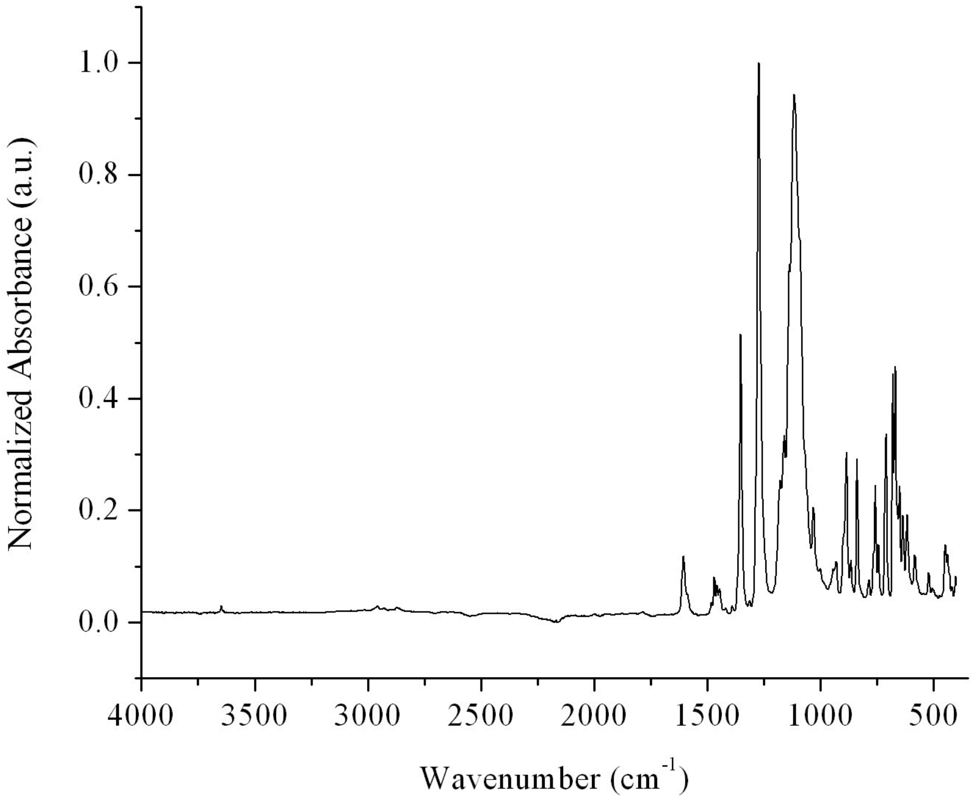

Figure S4 Solid State ATR-FT-IR Spectrum of **1**^{b}

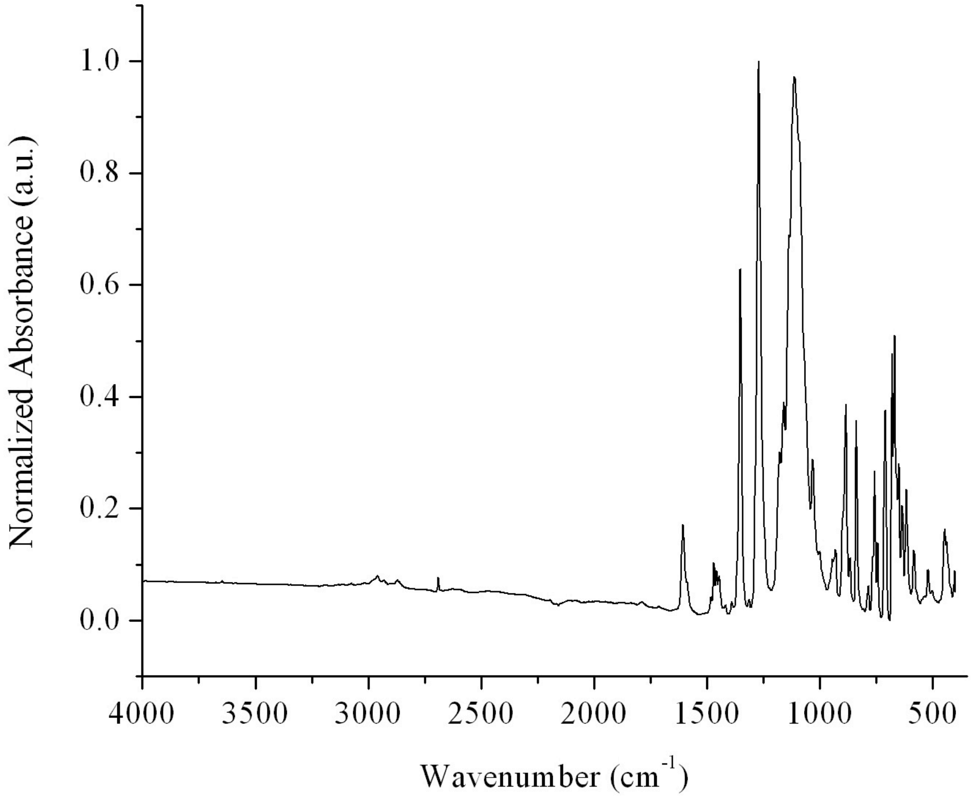

Figure S5 Solid State ATR-FT-IR Spectrum of Deuterated **1**^{b}

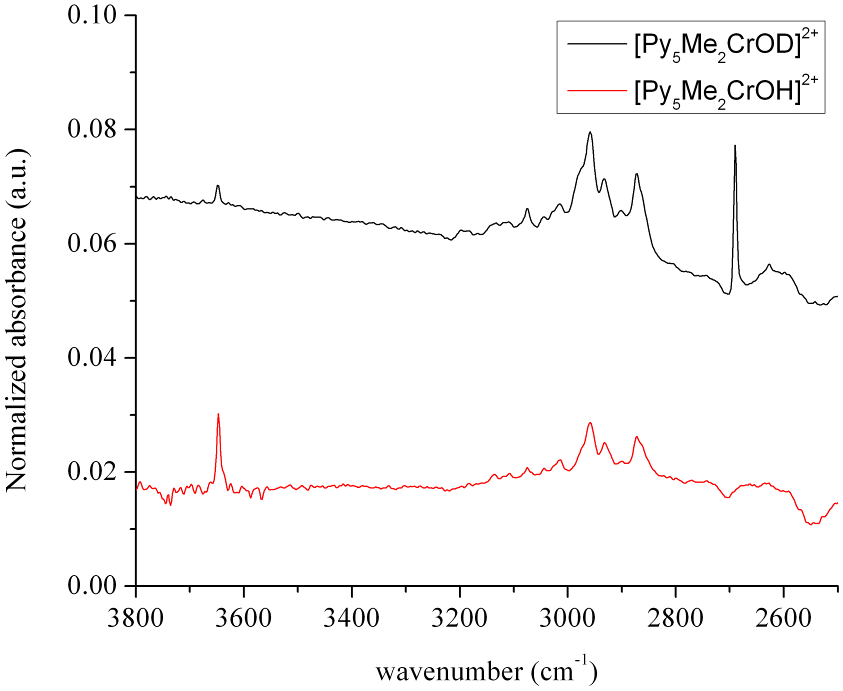

Figure S6 Solid State ATR-FT-IR Spectrum of Protonated and Deuterated **1**^{b}

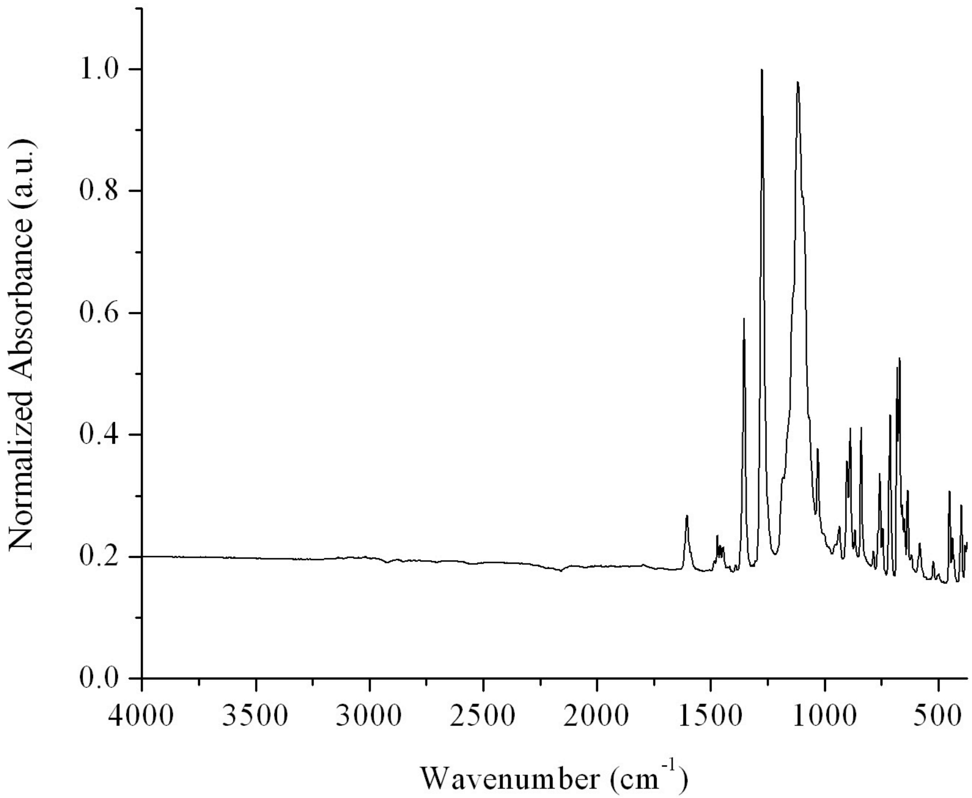

Figure S7 Solid State ATR-FT-IR Spectrum of **2**^{b}

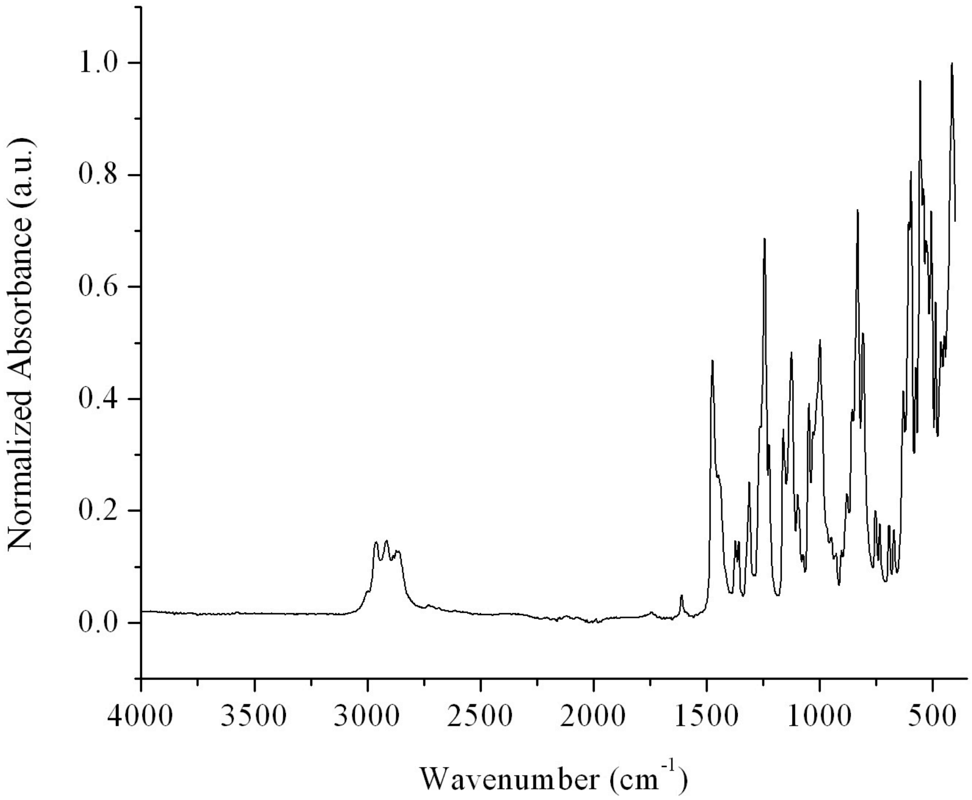

Figure S8 Solid State ATR-FT-IR Spectrum of **3**

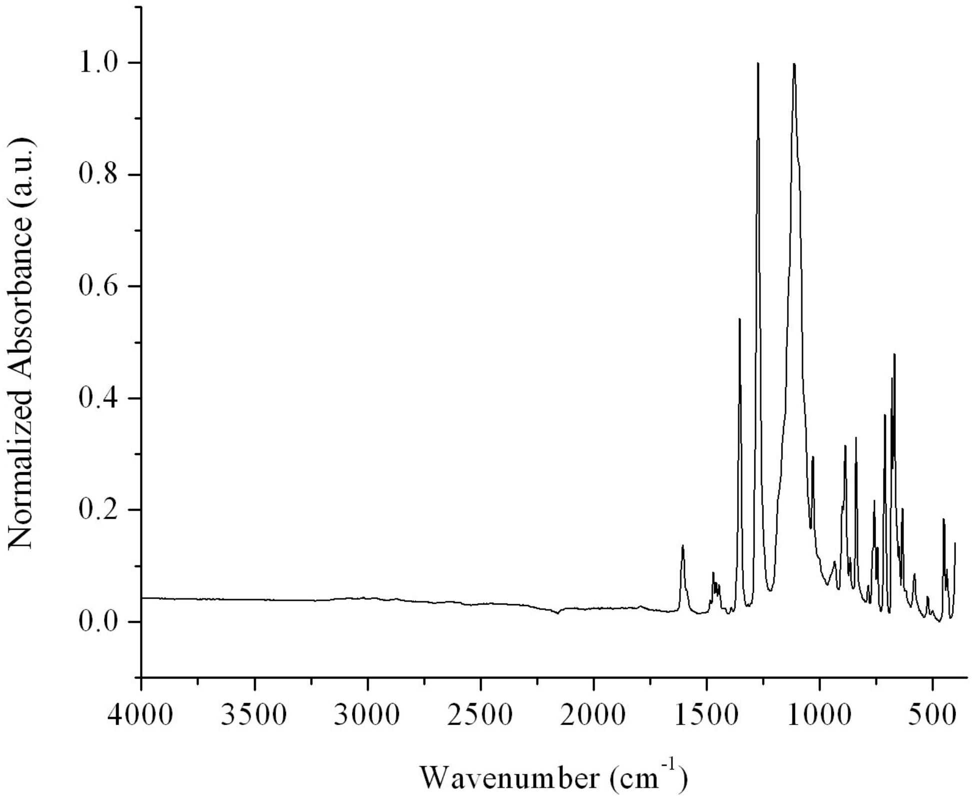

Figure S9 Solid State ATR-FT-IR Spectrum of **4**^{b}

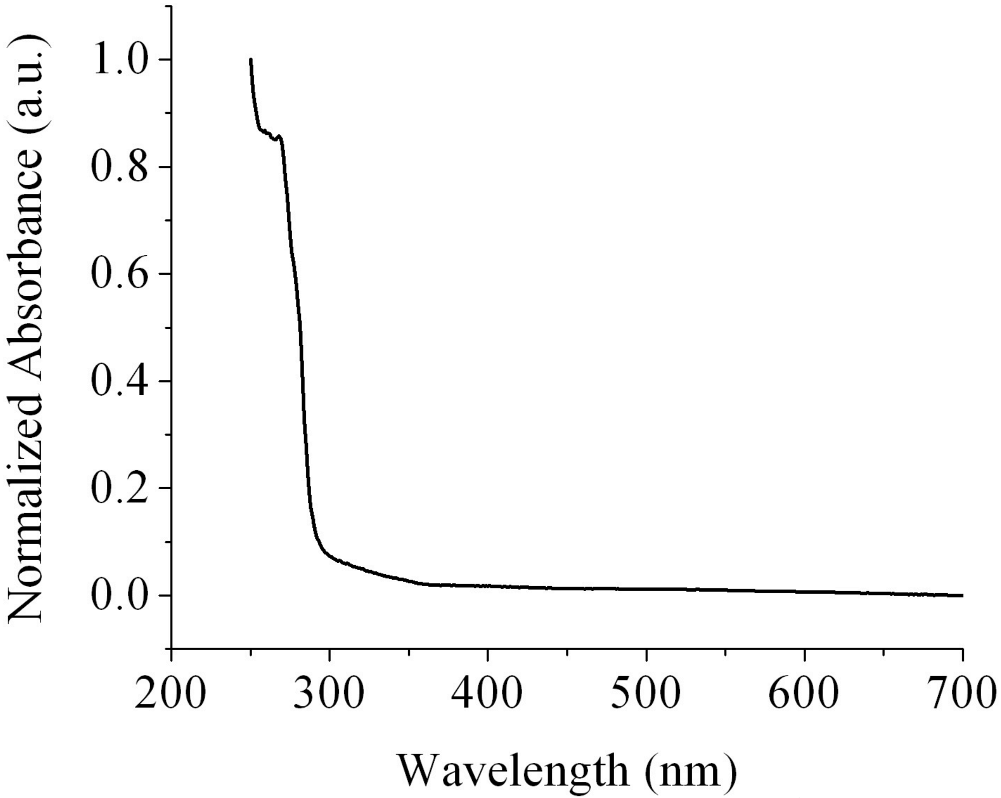

Figure S10 EAS of **1**^{b} in Dichloromethane (1.0E^{-4} M)

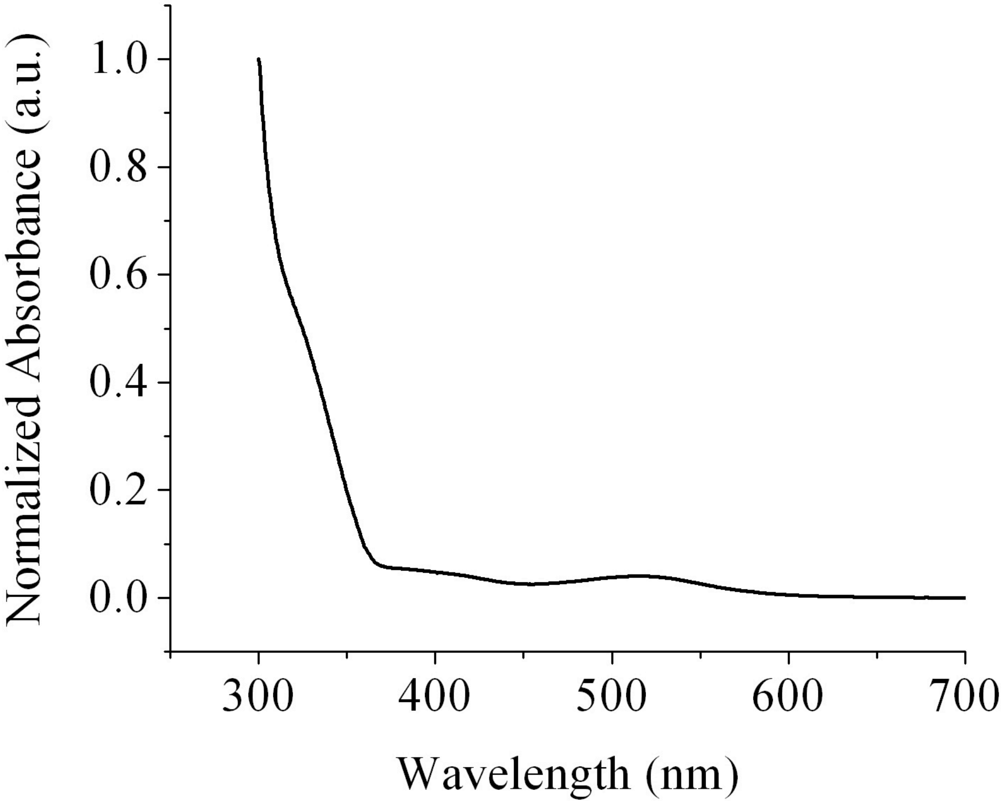

Figure S11 EAS of **2**^{b} in Tetrahydrofuran (1.0E^{-3} M)

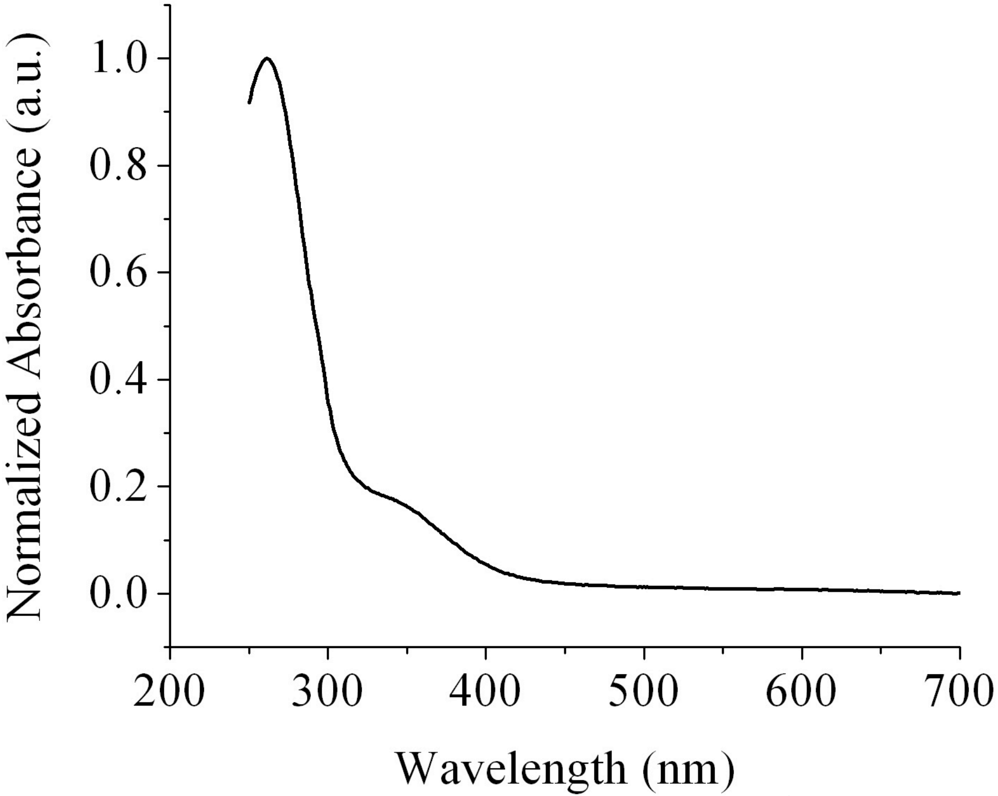

Figure S12 EAS of **3** in Dichloromethane (1.0E^{-4} M)

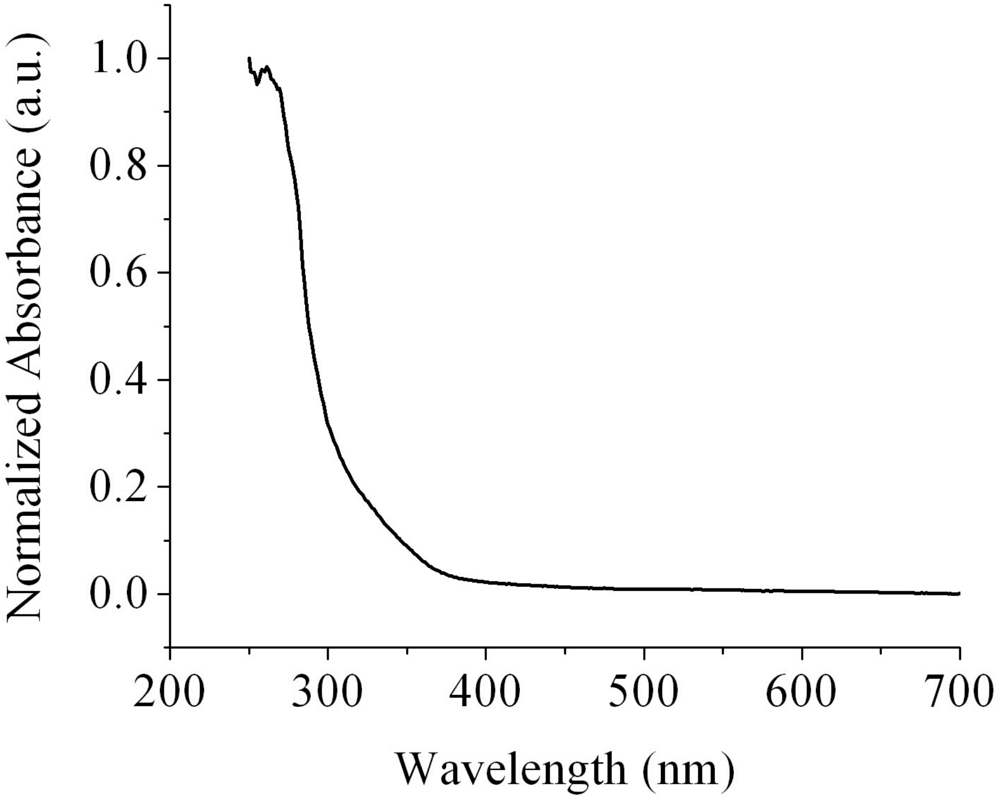

Figure S13 EAS of **4^{b}** in Dichloromethane (5.0E^{-5} M)

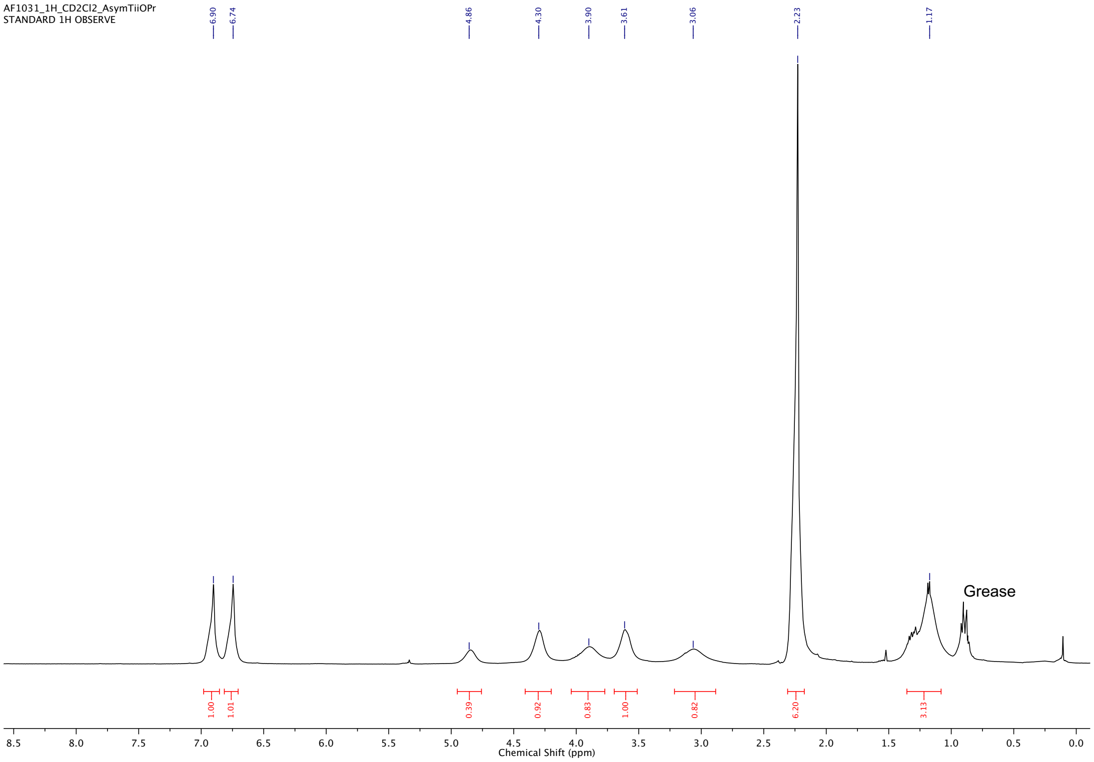

Figure S14 ^{1}H NMR of **3**

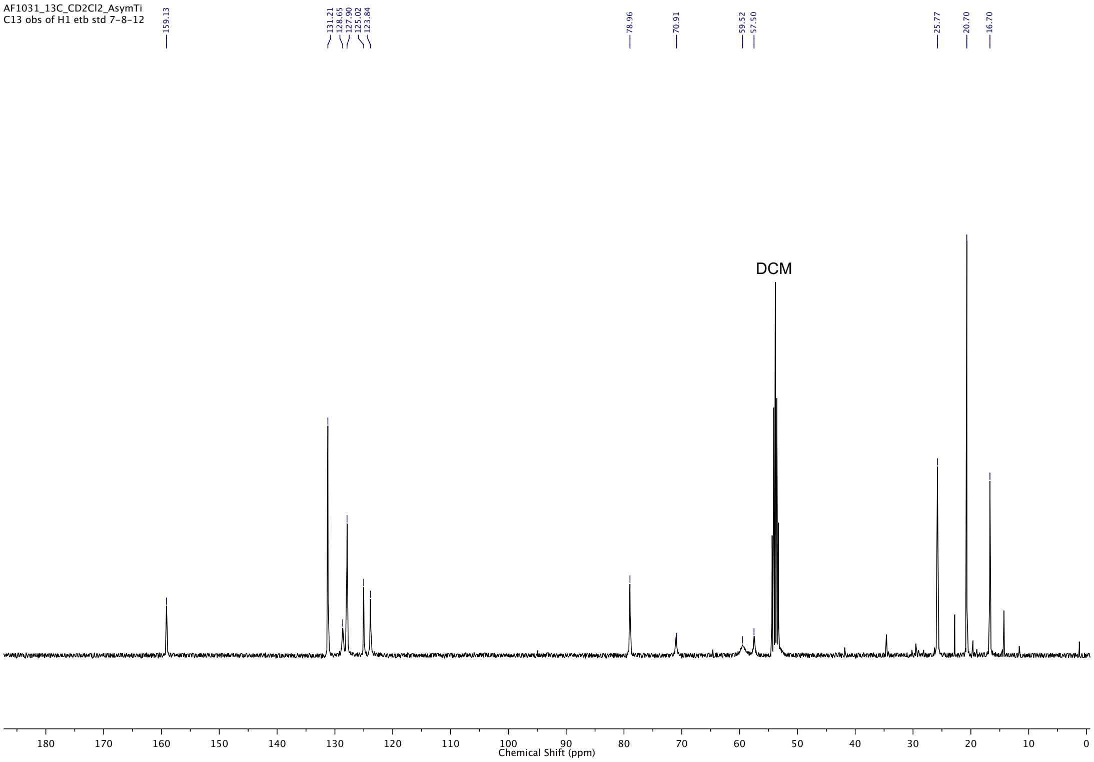

Figure S15 ^{13}C NMR of **3**