SUPPORTING INFORMATION

Facile C–H, C–F, C–Cl, and C–C Activation by Oxatitanacyclobutene Complexes

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A. General Information

General Experimental Procedures: All reactions were carried out in flame- or oven-dried (at 140 °C, for at least 4 hours) glassware under an atmosphere of nitrogen unless otherwise indicated. Air or moisture sensitive materials were synthesized and stored in a nitrogen filled glove box. Column chromatography was performed with silica gel from Grace Davison Discovery Sciences (35-75 μm), packed as a slurry and run under positive pressure. Analytical thin-layer chromatography (TLC) was performed on pre-coated glass silica gel plates with F-254 indicator purchased from EMD Chemicals Inc. Visualization was done by short wave (254 nm) ultraviolet light. Distillations were performed using a 3 cm short-path column either under reduced pressure or under positive pressure of nitrogen.

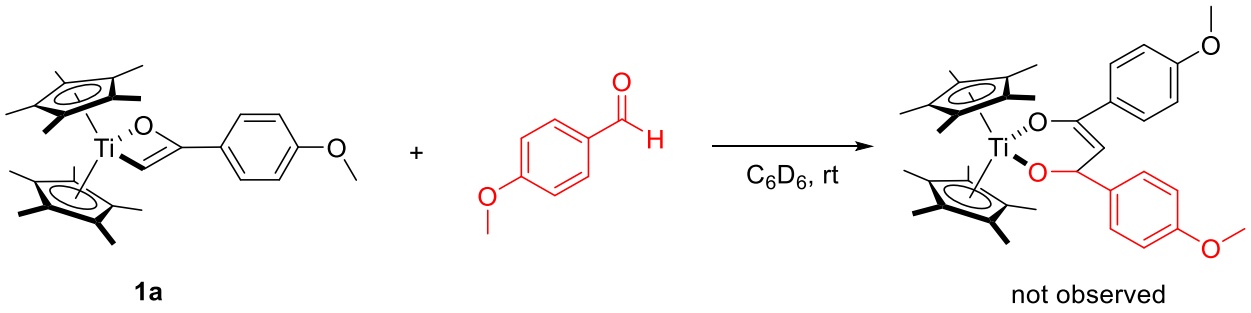
Instrumentation: ^{1}H, ^{2}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian Unity 500 MHz or a VXR-500 MHz (77 MHz for ^{2}H, 125 MHz for ^{13}C, 470 MHz for ^{19}F) spectrometer. Spectra were collected in C_6D_6 and referenced using residual protic solvent (^{1}H NMR: 7.15, ^{13}C NMR: 128.06 ppm for C_6D_6). ^{19}F NMR were referenced internally using C_6F_6 (^{19}F NMR: -163.04 ppm). Chemical shifts were reported in parts per million (ppm) and multiplicities are reported as follows: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants (*J*) are reported in Hertz and integrations are provided. High Resolution Mass Spectrometry was performed at the School of Chemical Sciences Mass Spectrometry Laboratory located at the University of Illinois at Urbana-Champaign. X-Ray crystallography was done at the George L. Clark X-Ray Facility and 3M Materials Laboratory at the University of Illinois at Urbana-Champaign. Microanalysis was performed at the School of Chemical Sciences Microanalysis Laboratory located at the University of Illinois at Urbana-Champaign. Bulk purity of samples are represented in section K by ^{1}H, ^{2}H, ^{19}F and ^{13}C NMR.

Materials: Solvents used for extraction, column chromatography and recrystallizations of air stable materials were reagent grade and used as received. Solvents for reactions, extractions and recrystallizations of air and water sensitive materials were dried on a Pure Process Technology Glass S3 Contour Solvent Purification system equipped with activated stainless steel columns following manufacture's recommendations for solvent preparation and dispensing. Solvents were then further dried by storing over 4 Å molecular sieves which had been activated by heating to 200 °C under dynamic vacuum for at least 24 hours. Phenylacetylene, hexafluorobenzene, 4-methoxybenzaldehyde, 2,2,2,-trifluoroacetophenone were distilled under reduced pressure, transferred to a nitrogen filled glove box and stored over activated molecular sieves for at least 24 hours prior to use. C_6D_6 was degassed by freeze-pump-thaw cycles and stored in a nitrogen filled glove box and dried over activated molecular sieves for at least 24 hours prior to use. 4-

methoxyphenylacetylene, 2-bromoiodobenzene, benzophenone imine (Oakwook Chemical), cyclobutyl phenyl ketone (Alfa Aesar), bromobenzene-d5, 4,4'-bismethoxybenzophenone, 4-methoxyphenyl cyclopropyl ketone (Aldrich Chemical) were used as received. Cp*H was obtained from Boulder Scientific and distilled prior to use. The following compounds were synthesized by known literature procedures: titanocene oxo[1], deuterated phenylacetylene PhCCD[2] and pentadeutero phenylacetylene C_6D_5CCH[3], 2-deuterobromobenzene[4], trichloroacetophenone[5], 3,5-bis(trifluoromethyl)phenyl acetylene[6].

B. Experimental Procedure for Scheme 1

To a 4 mL scintillation vial was added complex **1a** (0.015 mmol, 1.0 equiv), C_6D_6 (0.2 mL) and a magnetic stir bar. A solution of 4-methoxybenzaldehyde (0.022 mmol, 1.5 equiv) in C_6D_6 (0.3 mL) was added to the reaction vial. Reaction was stirred at room temperature for 45 minutes and a color change from green to yellow brown was observed.



1a not observed

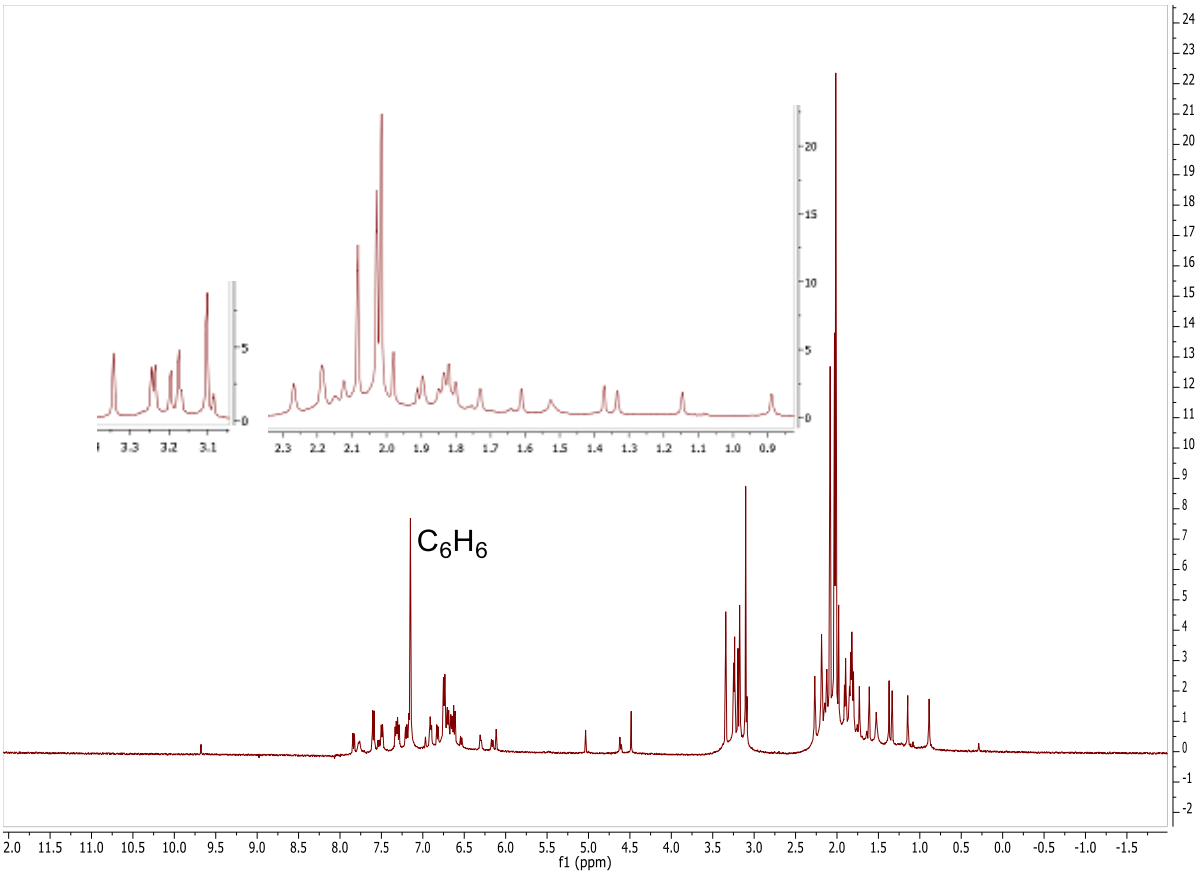
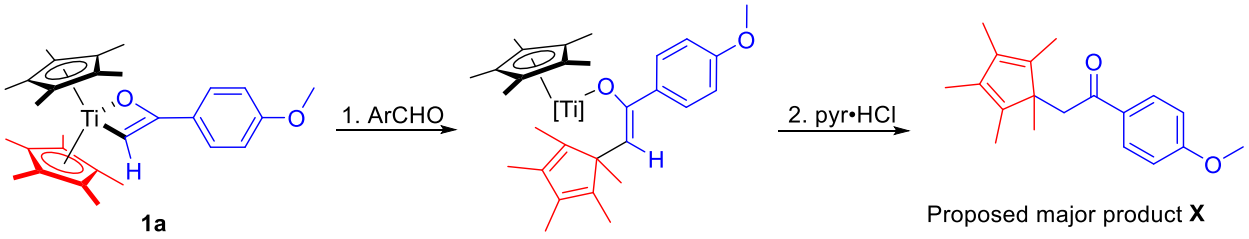


Figure S1: ^{1}H NMR spectrum of reaction between **1a** and *para*-methoxybenzaldehyde.

The insertion product was not observed, as determined by comparison with the proton NMR of authentic sample prepared from titanocene–oxo and α,β-unsaturated ketone; the diagnostic signals for the dioxatitanacyclohexene at 5.50, 1.94 and 1.83 ppm, were not observed. Rather an array of singlets between 2.5-0.5 ppm suggests that one of the Cp* is desymmetrized, this is consistent with reductive elimination of the Cp* and Ti–C bond **1a**. Further, the singlets arround 4.5 ppm suggest that there are several species in solution with vinyl C–H bonds.

This crude reaction mixture was treated with pyridine hydrochloride and the resulting mixture was analyzed by GC-MS. The major product had a molecule weight (m/z = 284) and fragmentation pattern (main fragments of m/z = 149, 134, 119 and 107) consistent with a reductive elimination product **X**:



Minor products with masses of 136 (2.78 min, pentamethylcyclopentadiene; 4.01 min, *para*-methoxybenzaldehyde), 150 (4.62 min, 4'-methoxyacetophenone), and 254 (5.9 min, unidentified) were also observed.

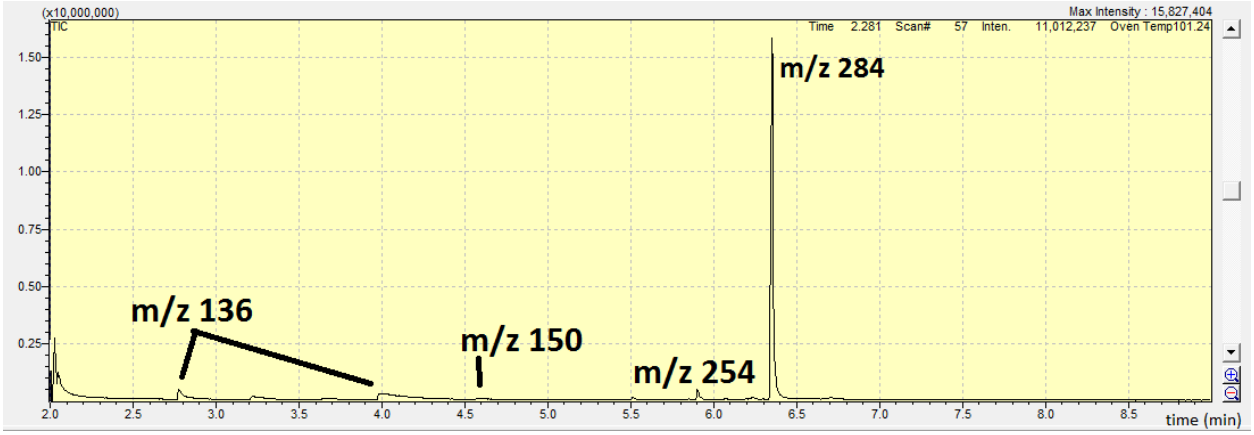


Figure S2: GC-MS trace of reaction mixture after treatment with py • HCl

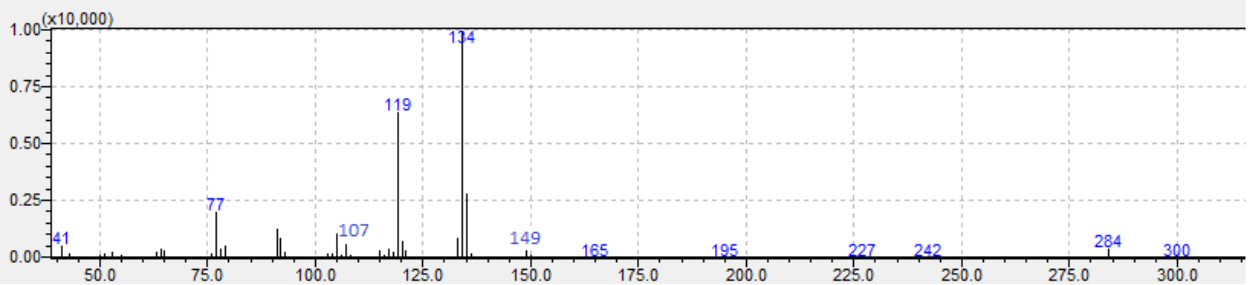
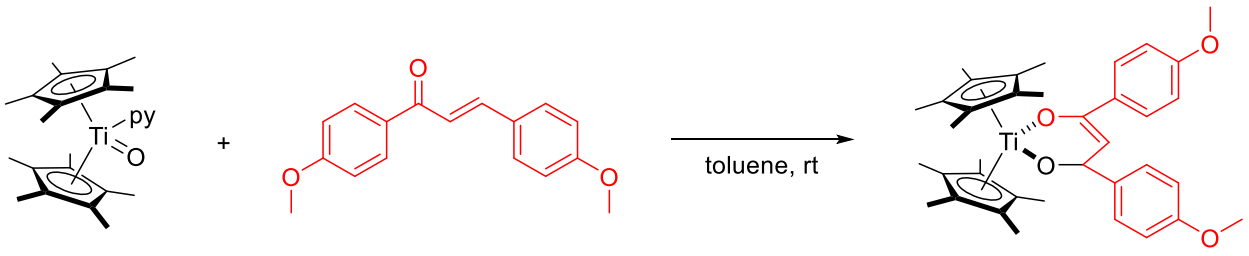


Figure S3: Fragmentation pattern of major protonation product.

Preparation of dioxatitanacyclohexene:



To a 20 mL scintillation vial was added titanocene oxo (0.253 mmol, 1.1 equiv), enone (0.23 mmol, 1.0 equiv), toluene (2.5 mL) and a magnetic stir bar. Reaction was stirred at room temperature for 3 hours before all volatiles were removed under vacuum. The brownish red residue was taken up in hexane, thoroughly stirred and kept at -30 °C for 30 min. Product was collected by filtration and washed with cold hexane. Reddish brown solid, 85% yield.

Data for dioxatitanacyclohexene complex:

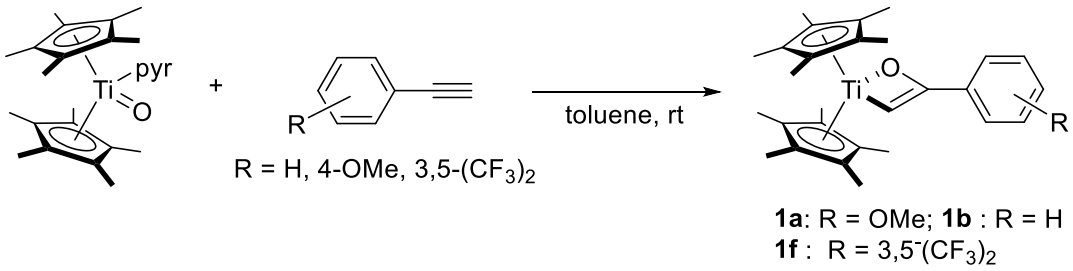
^{1}H NMR (500 MHz, Benzene-d_6) δ 7.86 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H), 7.69 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 7.01 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 6.93 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H), 6.66 (s, broad, 1H), 5.50 (d, $^{3}J_{HH}$ = 1.8 Hz, 1H), 3.41 (s, 3H), 3.38 (s, 3H), 1.94 (s, 15H), 1.83 (s, 15H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 160.28 , 159.38 , 158.87 , 141.34 , 135.68 , 128.50 , 126.87 , 125.09 , 124.39 , 113.75 , 113.61 , 98.12 , 83.23 , 54.86 , 54.84 , 12.44 , 11.99 .

HRMS (ESI/TOF) calculated for $C_{37}H_{46}O_4Ti$: 603.2954 $[MH]^+$ Found: 603.2952.

C. Experimental Procedure for Scheme 2

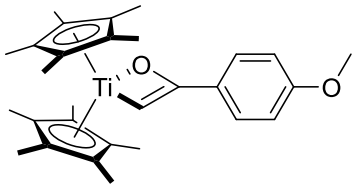
1. Synthesis of Oxatitanacyclobutenes 1



To a 20 mL scintillation vial was added bis(pentamethylcyclopentadienyl)titanium oxo (0.80 mmol, 1.0 equiv), toluene (5.0 mL) and a magnetic stir bar. Alkyne (0.96 mmol, 1.2 equiv) was added dropwise with stirring. Immediate color change from orange to green was observed. Reaction mixture was stirred at room temperature for 2 hours before all volatiles were removed under vacuum. The dark green residue was taken

up in hexane, filtered to remove any solid. The filtrated was concentrated and cooled to -30 °C overnight, affording dark green crystals. Product was collected by filtration, washed with cold hexane and dried under vacuum overnight.

*Characterization for **1a**: dark green solid, 92% yield*

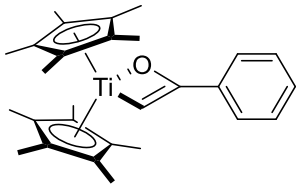


^{1}H NMR (500 MHz, Benzene-d_6) δ 7.94 (d, $^{3}J_{HH}$ = 9.0Hz, 2H), 7.60 (s, 1H), 6.93 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H), 3.34 (s, 3H), 1.75 (s, 30H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 166.19, 159.32, 126.40, 121.37, 113.98, 54.82, 11.65 , two signals are underneath solvent peaks.

HRMS (ESI/TOF) calculated for $C_{29}H_{38}O_2Ti$: 467.2430 $[MH]^+$ Found: 467.2433

*Characterization for **1b**: dark green solid, 95% yield*



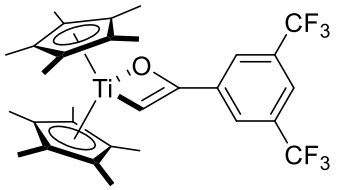
^{1}H NMR (500 MHz, Benzene-d_6) δ 8.01 (dd, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 1.5 Hz, 2H), 7.67 (s, 1H), 7.30 (dd, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HH}$ = 7.6 Hz, 2H), 7.12 (tt, $^{3}J_{HH}$ = 7.3 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H), 1.71 (s, 30H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 167.24, 135.68, 128.30, 126.53, 125.23, 121.45, 11.63. One signal is underneath solvent peaks.

NMR data in accordance with that previously reported.[7]

HRMS (ESI) calculated for $C_{28}H_{36}OTi$: 437.2324 $[MH]^+$ found: 437.2323.

*Characterization for **1f**: dark green solid, 88% yield*

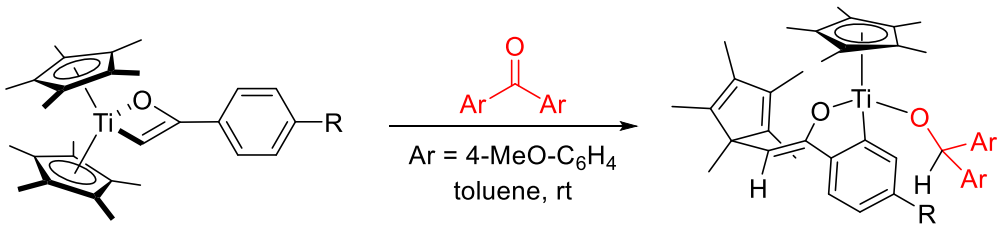


^{1}H NMR (500 MHz, Benzene-d_6) δ 8.44 (s, 2H), 7.69 (s, 1H), 7.58 (s, 1H), 1.57 (s, 30H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 168.64, 138.48, 131.72 (q, $^{2}J_{CF}$ = 32.6 Hz), 126.97, 124.57 (q, $^{1}J_{CF}$ = 273.4 Hz), 124.33 (q, $^{3}J_{CF}$ = 3.9 Hz), 122.17, 119.36 (hept, $^{3}J_{CF}$ = 3.9 Hz), 11.47.^{19}F NMR (470 MHz, Benzene-d_6) δ -62.92 (s).

HRMS (ESI) calculated for $C_{30}H_{34}F_6OTi$: 573.2071 $[MH]^+$ found: 573.2072.

2. Synthesis of Complexes 2

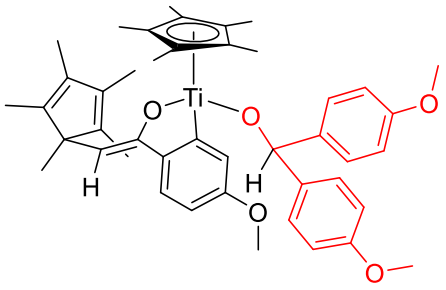


1a: R = OMe
1b: R = H

2a: R = OMe
2b: R = H

To a 20 mL scintillation vial was added oxatitanacyclobutene **1** (0.22 mmol, 1.0 equiv), 4,4'-bismethoxybenzophenone (0.21 mmol 0.95 equiv), toluene (3.0 mL) and a magnetic stir bar. Reaction was stirred at room temperature overnight. Solvent was removed under vacuum, the resulting red residue was taken up in hexane and filtered to remove any solid. The filtrate was evaporated to dryness and recrystallized from pentane.

*Characterization for **2a**, light brown solid, 74% yield*



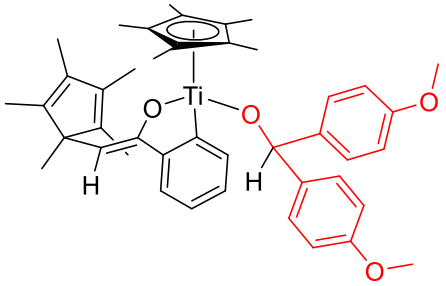
^{1}H NMR (500 MHz, Benzene-d_6) δ 7.40 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.26 (d, $^{3}J_{HH}$ = 8.0 Hz, 1H), 7.25 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H), 6.85 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H), 6.74 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H), 6.58 (d, $^{4}J_{HH}$ = 2.0 Hz, 1H), 6.56 (s, 1H), 6.55 (dd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 2.1 Hz, 1H), 4.62 (s, 1H), 3.37 (s, 3H), 3.29 (s, 3H), 3.25 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H), 1.86 (s, 6H), 1.84 (s, 15H), 1.46 (s, 3H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 196.79, 159.28, 158.14, 157.15, 150.72, 144.35, 143.28, 138.46, 138.38, 132.21, 131.71, 128.24, 127.70, 125.19, 123.94, 116.77, 114.04, 113.85, 113.05, 98.07, 87.62, 57.77, 54.76, 54.72, 54.65, 22.47, 11.53, 11.51, 11.41, 11.16, 10.98

Calcd for $C_{44}H_{52}O_5Ti$: C, 74.56; H, 7.39. Found: C, 73.89 ; H, 7.43.

HRMS (ESI) calculated for $C_{44}H_{52}O_5Ti$: 709.3372 $[MH]^+$ found: 709.3359.

*Characterization for **2b**, light orange brown solid, 51% yield*



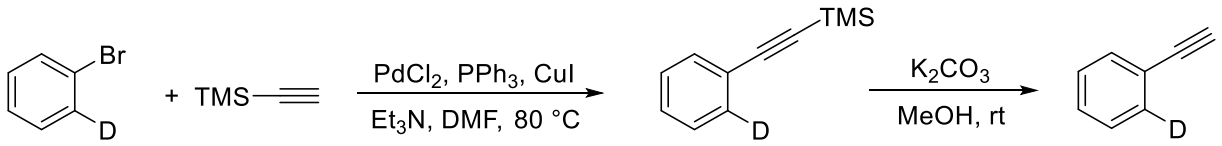
^{1}H NMR (500 MHz, Benzene-d_6) δ 7.37 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 7.27 (dd, $^3J_{HH}$ = 6.5 Hz, $^4J_{HH}$ = 2.0 Hz, 1H), 7.23 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 6.92 (m, 3H), 6.84 (d, $^3J_{HH}$ = 9.0 Hz, 2H), 6.73 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 6.56 (s, 1H), 4.71 (s, 1H), 3.29 (s, 3H), 3.25 (s, 3H), 1.99 (s, 3H), 1.98 (s, 3H), 1.85 (s, 6H), 1.82 (s, 15H), 1.44 (s, 3H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 196.31, 159.29, 159.28, 158.45, 158.03, 144.22, 143.09, 138.48, 138.37, 132.44, 132.39, 131.85, 128.11, 127.72, 126.59, 125.31, 125.19, 123.15, 114.04, 113.87, 99.75, 87.61, 57.74, 54.76, 54.74, 22.36, 11.53, 11.49, 11.40, 11.12, 10.94.

HRMS (ESI) calculated for $C_{43}H_{50}O_4Ti$: 679.3267 $[MH]^+$ Found: 679.3271.

D. Experimental Procedure for Scheme 4

1. Synthesis of *ortho*-deuterated phenylacetylene

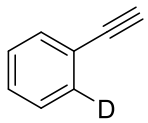


In a glovebox, a 250 mL pressure vessel containing a magnetic stir bar was charged with *ortho*-deuterated bromobenzene (15.87 mmol, 1.0 equiv) and DMF (25 mL), followed by $PdCl_2$ (1.59 mmol, 0.1 equiv), PPh_3 (1.59 mmol, 0.1 equiv) and CuI (1.59 mmol, 0.1 equiv). To this mixture was added trimethylsilylacetylene (20.63 mmol, 1.3 equiv) and triethylamine (25 mL). The vessel was capped, and heated in a fume hood at 70 °C overnight.

The content was then allowed to cool to room temperature and diluted with 60 mL diethylether. This mixture was then filtered through celite, and washed with diethylether to bring to total volume to 120 mL. The filtrate was washed with water (4 x 60 mL) and brine (2 x 50 mL), dried over magnesium sulfate. Solvents were removed by rotary evaporation. The product was purified by column chromatography (hexane) as light yellow oil.

Purified product from the previous step was dissolved in MeOH (60 mL), then K_2CO_3 (0.800 g) was added. The reaction mixture was stirred at room temperature overnight, poured into DCM (100 mL) and washed with brine (2 x 60 mL). Organic layer was dried over $MgSO_4$, filtered and concentrated by rotary evaporation. Alkyne product was purified by distillation as colorless liquid, 60% yield over 2 steps.

Data for 2-deuterophenylacetylene

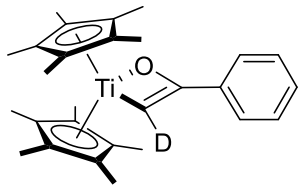


^{1}H NMR (500 MHz, Benzene-d_6) δ 7.38 (m, 1H), 6.90 (m, 3H), 2.71 (s, 1H).
^{2}H NMR (77 MHz, Benzene-d_6) δ 7.38 (s, 1H).
^{13}C NMR (126 MHz, Benzene-d_6) δ 132.36, 132.08 (t, $^1J_{CD}$ = 24.9 Hz), 128.82, 128.54, 128.42, 122.67, 83.88, 77.90

2. Synthesis of deuterated oxatitanacyclobutenes

Deuterated oxatitanacyclobutenes were synthesized following procedure described in part B for **1a, 1b** and **1f.**

*Data for **1c**, dark green solid, 94% yield*

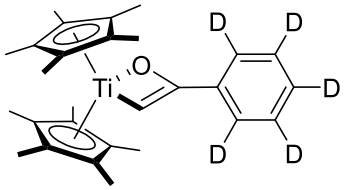


1c

^{1}H NMR (500 MHz, Benzene-d_6) δ 8.00 (dd $^3J_{HH}$ = 8.3 Hz, $^4J_{HH}$ = 1.3 Hz, 2H), 7.30 (t, $^3J_{HH}$ = 7.7 Hz, 2H), 7.12 (tt, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.3 Hz, 1H), 1.71 (s, 30H).
^{2}H NMR (77 MHz, Benzene-d_6) δ 7.70 (s, 1H).
^{13}C NMR (126 MHz, Benzene-d_6) δ 166.82 (t, $^1J_{CD}$ = 25.7 Hz), 135.65, 128.29, 126.51, 125.22, 121.44, 11.63. One signal is underneath solvent peaks.

HRMS (ESI) calculated for $C_{28}H_{35}DOTi$: 438.2387 $[MH]^+$ found: 438.2397.

*Data for **1d**, green solid, 85% yield*



1d

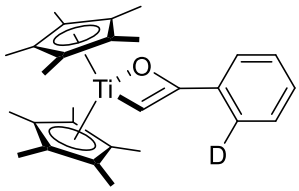
^{1}H NMR (500 MHz, Benzene-d_6) δ 7.67 (s, 1H), 1.71 (s, 30H).

^{2}H NMR (77 MHz, Benzene-d_6) δ 8.00 (s, 1H), 7.29 (s, 1H). One peak overlaps with solvent peak

^{13}C NMR (126 MHz, Benzene-d_6) δ 167.23, 135.51, 125.98 (t, $^1J_{CD}$ = 23.9 Hz), 124.80 (t, $^1J_{CD}$ = 24.3 Hz), 121.44, 11.64, two signals are underneath solvent peaks.

HRMS (ESI) calculated for $C_{28}H_{31}D_5OTi$: 442.2638 $[MH]^+$ found: 442.2632.

*Data for **1e**, green solid, 83% yield*



1e

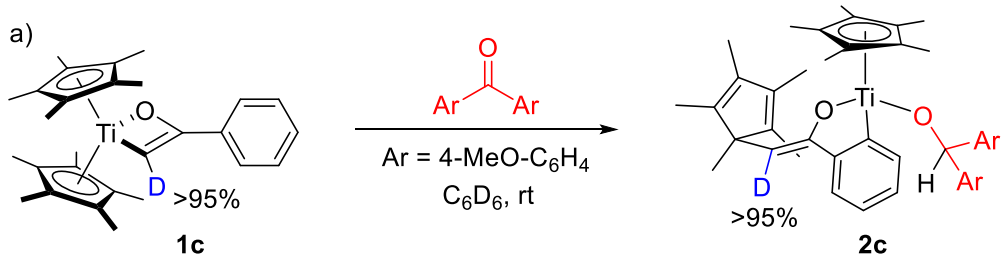
^{1}H NMR (500 MHz, Benzene-d_6) δ 8.00 (dd, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.3 Hz, 1H), 7.66 (s, 1H), 7.30 (m, 2H), 7.12 (td, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.3 Hz, 1H), 1.71 (s, 30H).

^{2}H NMR (77 MHz, Benzene-d_6) δ 8.00 (s, 1H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 167.24, 135.59, 126.51, 125.21, 121.44, 11.63 , two signals including the deuterated carbon are underneath solvent peaks.

HRMS (ESI) calculated for $C_{28}H_{35}DOTi$: 438.2387 $[MH]^+$ found: 438.2388.

3. NMR data for labeling study



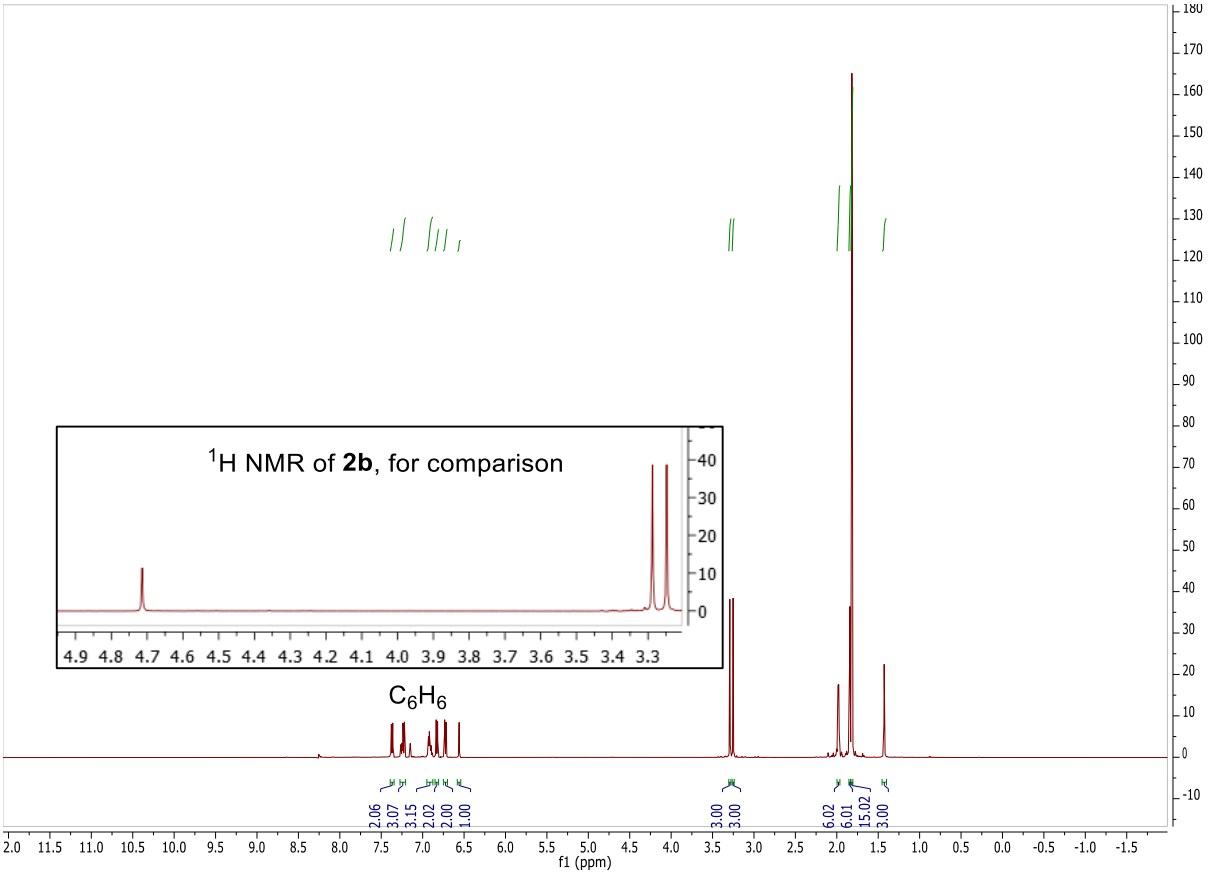


Figure S4: ^{1}H NMR spectrum of reaction between **1c** with bismethoxybenzophenone. The singlet at 4.71 ppm corresponding to the alkene proton is not observed.

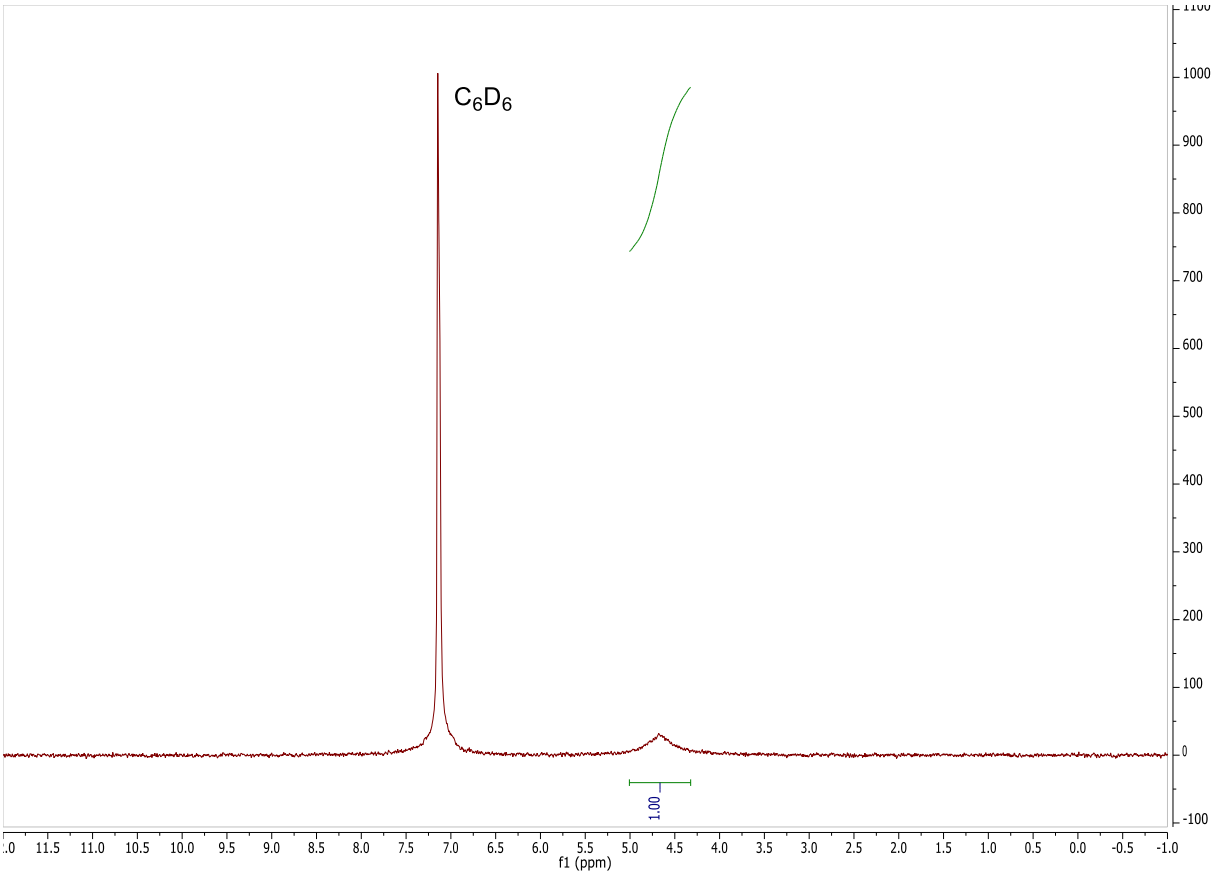


Figure S5: ^{2}H NMR spectrum of reaction between **1c** with bismethoxybenzophenone. The peak at 4.71 corresponding to the alkene deuterium is observed.

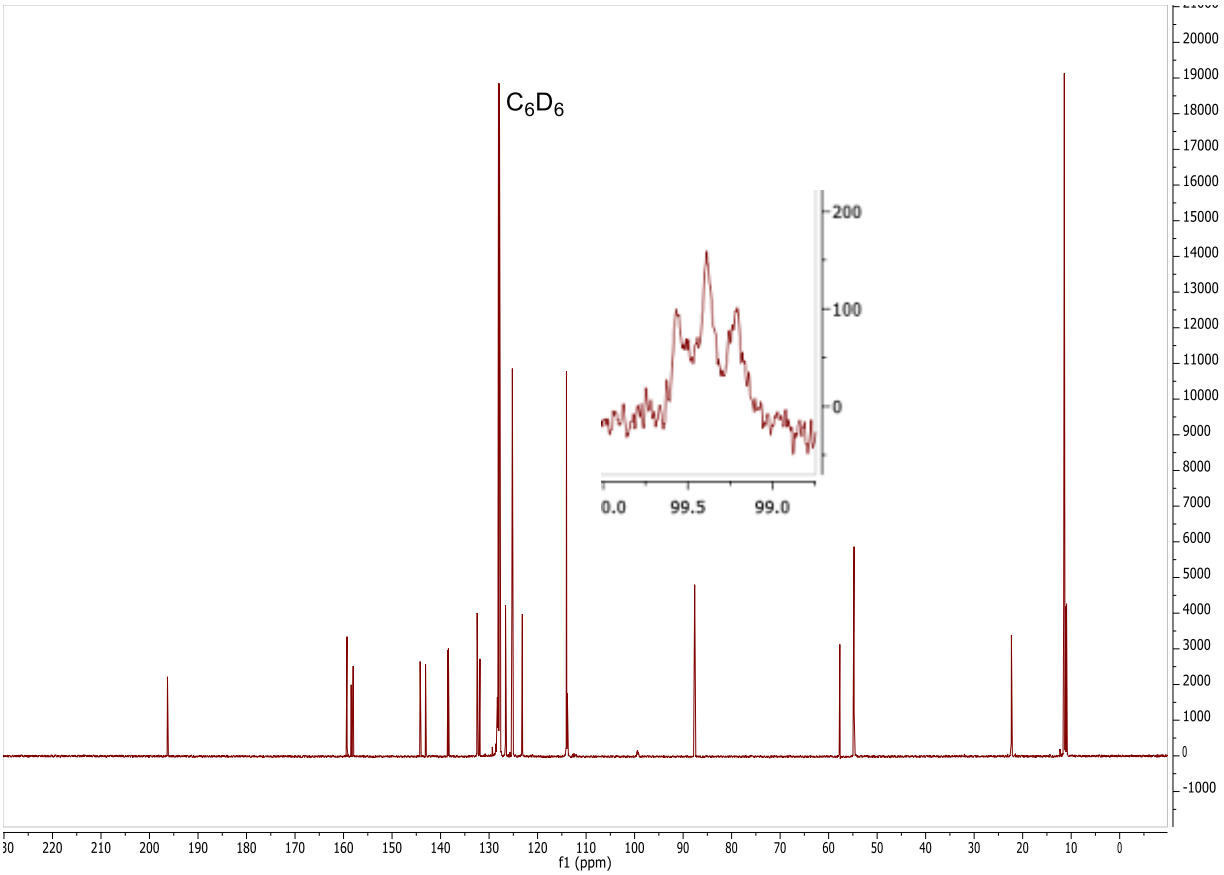
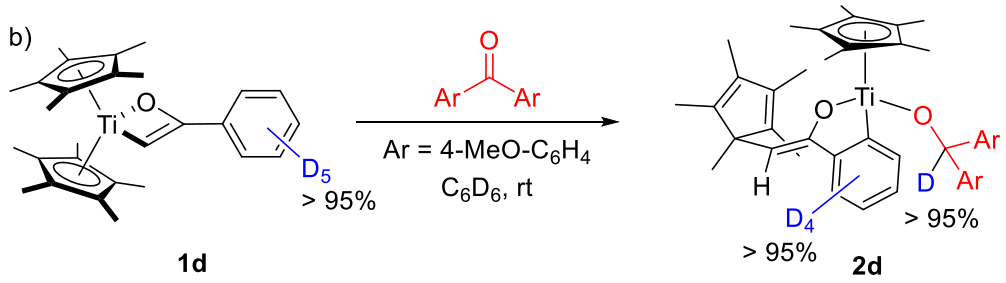


Figure S6: ^{13}C NMR spectrum of reaction between **1c** with bismethoxybenzophenone. The signal at 99.4 ppm correspond to the alkene carbon attached to deterium is much weaker in intensity but the splitting pattern can be observed.



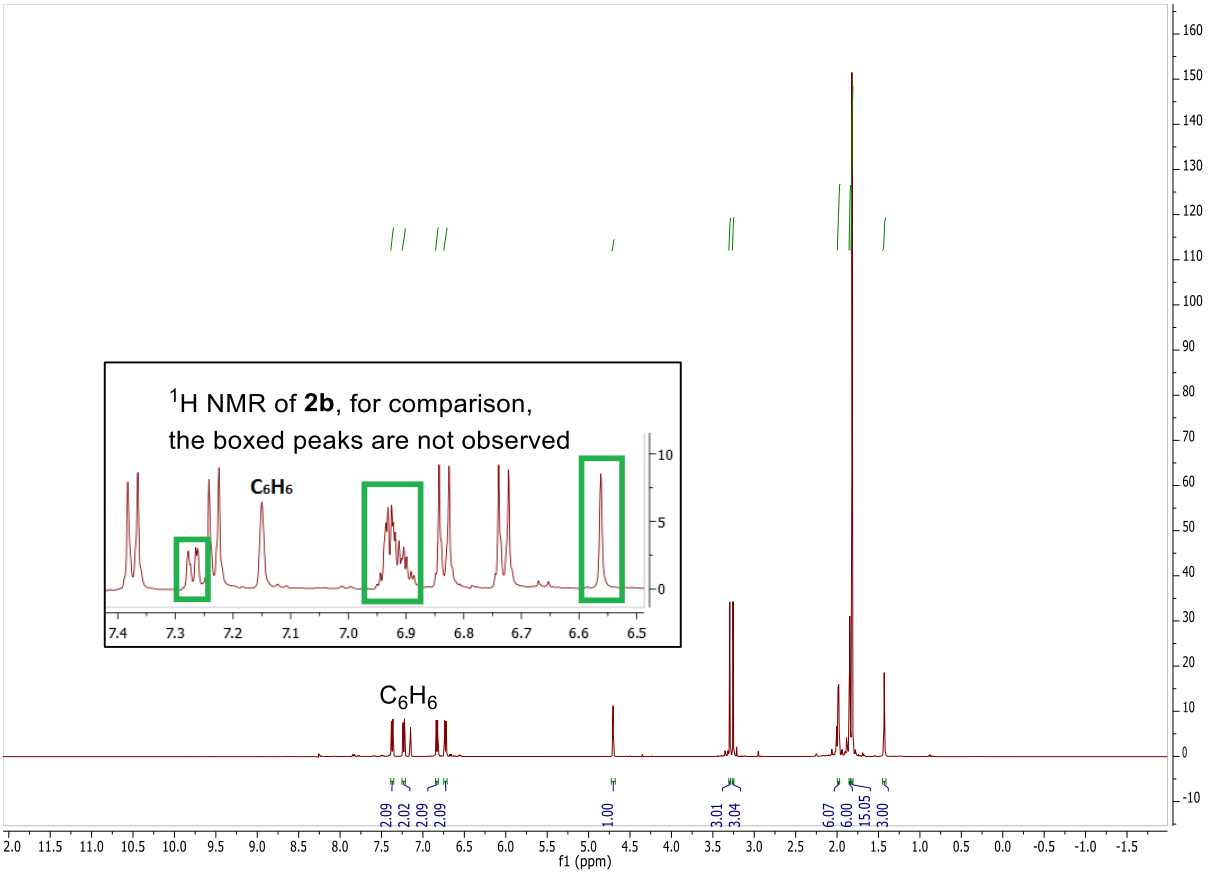


Figure S7: ^{1}H NMR spectrum of reaction between **1d** with bismethoxybenzophenone. The peak at 6.56 ppm corresponding to the alkoxide deuterium is not observed. In the aromatic region, only the 4 doublets corresponding to alkoxide's phenyl rings are observed.

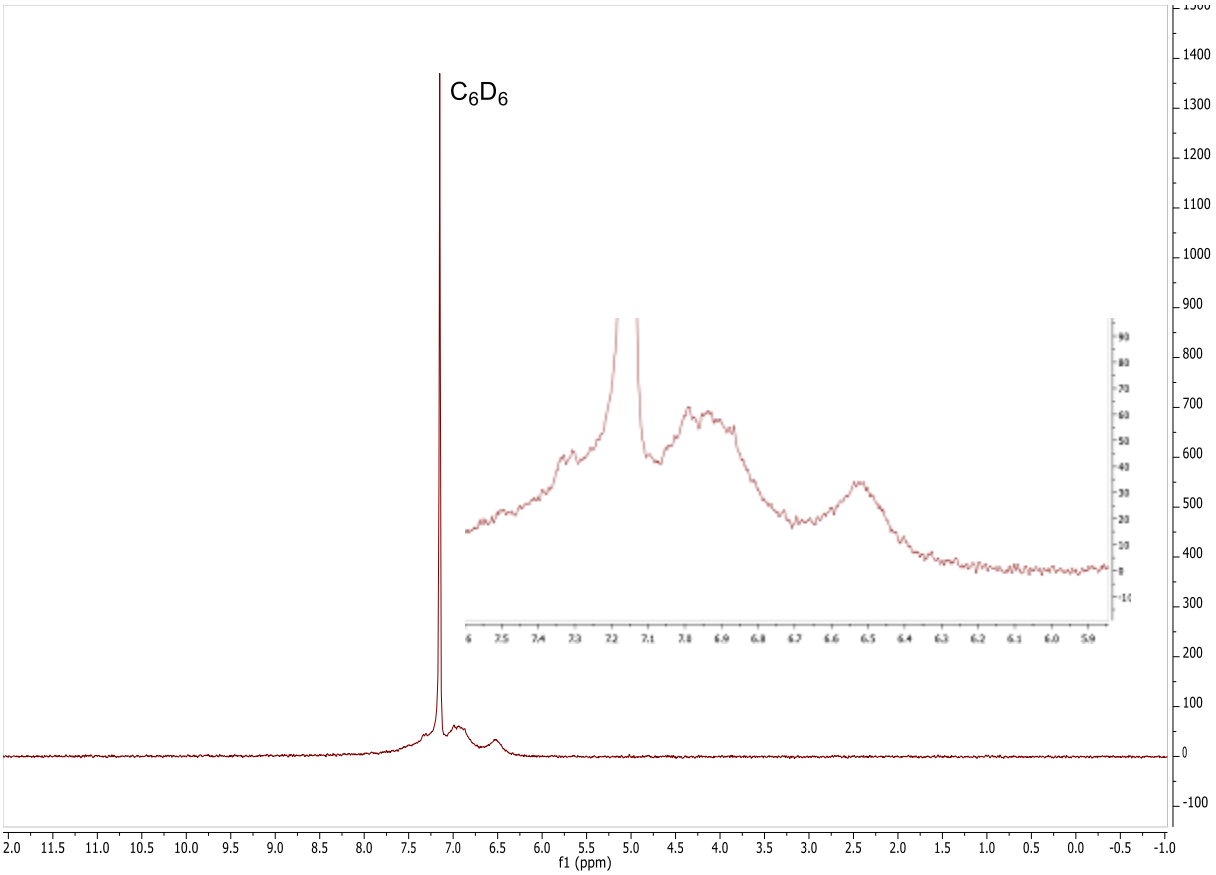


Figure S8: ^{2}H NMR spectrum of reaction between **1d** with bismethoxybenzophenone. The signals corresponding to the alkoxide deuterium and the phenyl ring of the metallacycle are observed. Attempts to record NMR spectra in other deuterated solvents were not successful as these solvents were not compatible with this reaction.

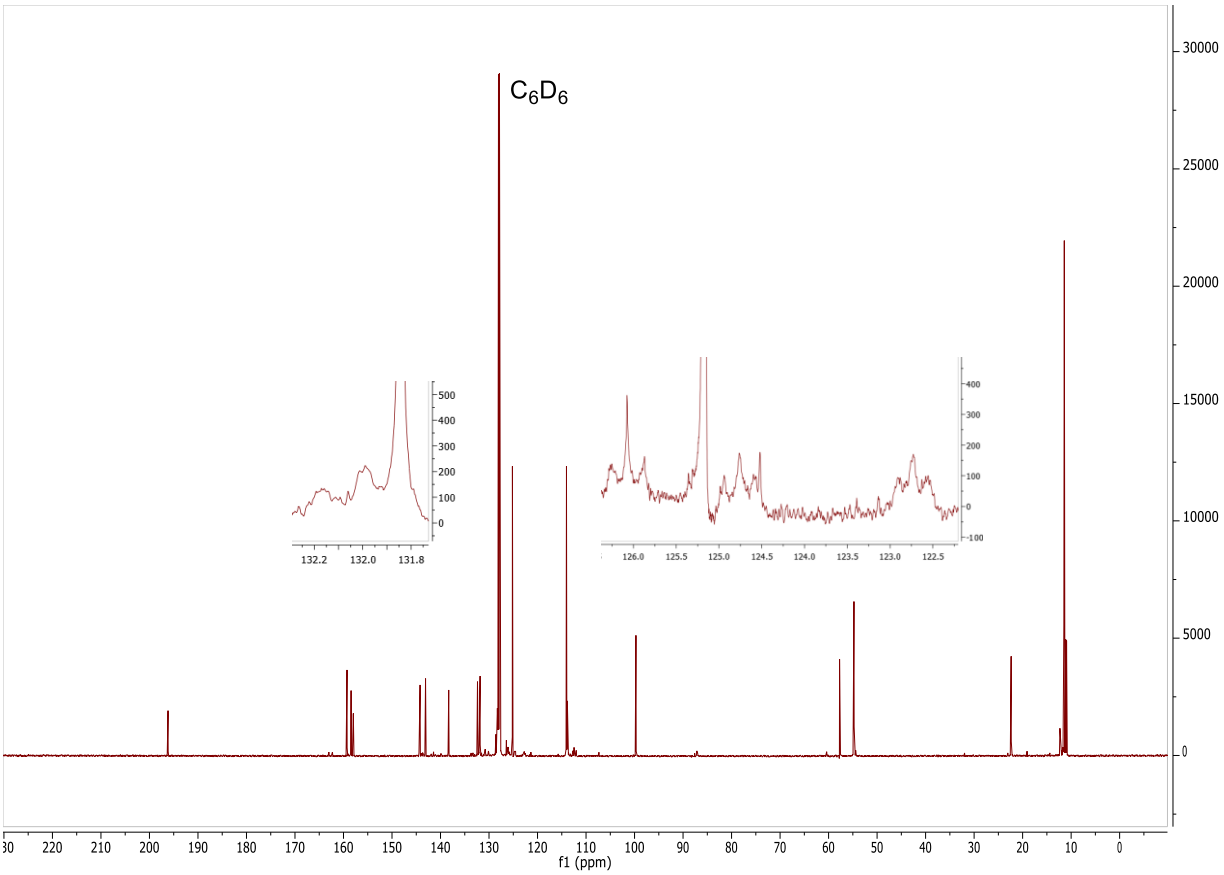


Figure S9: ^{13}C NMR spectrum of reaction between **1d** with bismethoxybenzophenone. The triplets corresponding to the carbons attached to deuterium can be observed.

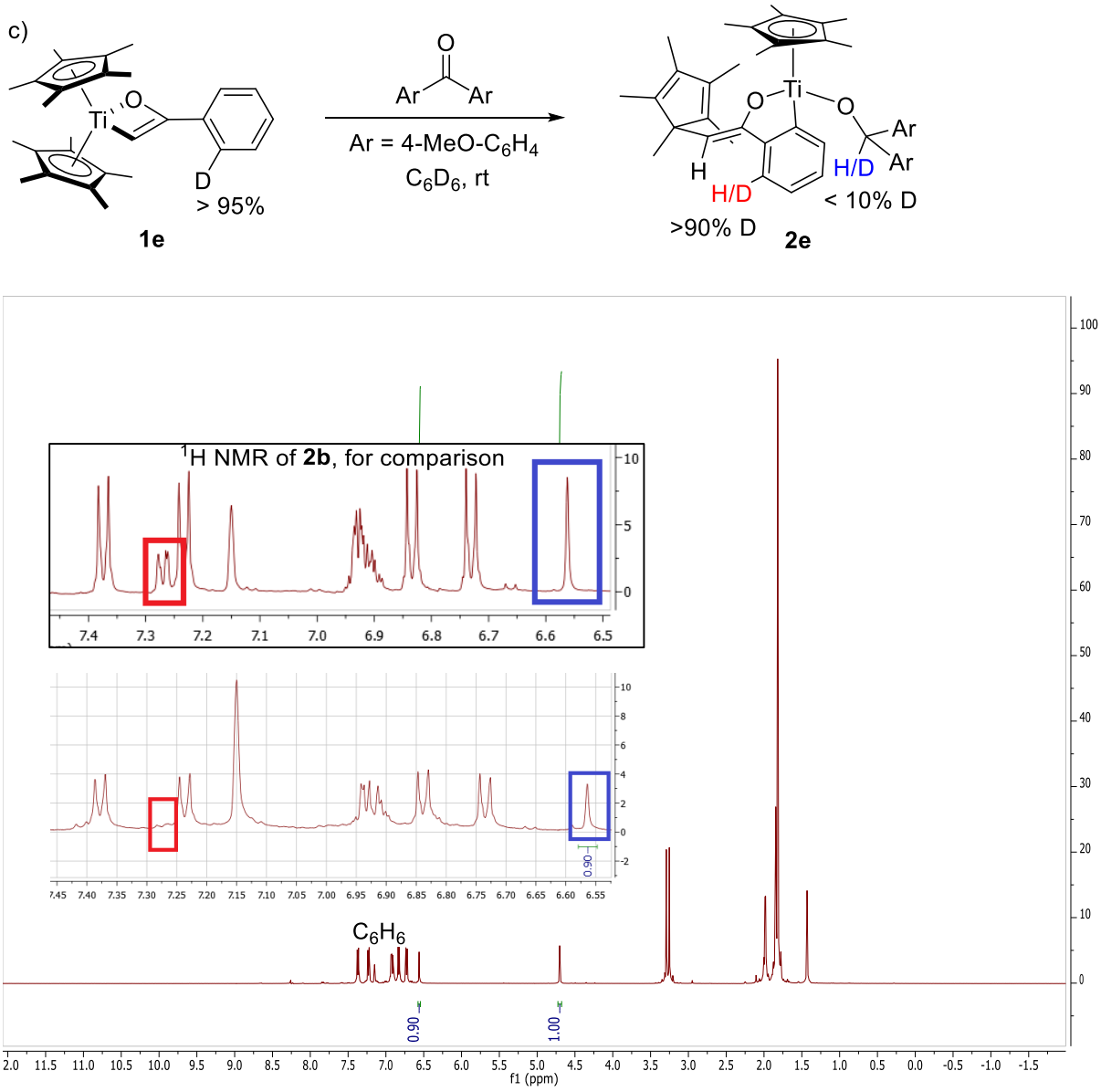


Figure S10: ^{1}H NMR spectrum of reaction between **1e** with bismethoxybenzophenone affording **2e**. The peak at 6.56 ppm corresponding to the alkoxide proton integrates to 0.90 versus the alkene peak at 4.71 ppm.

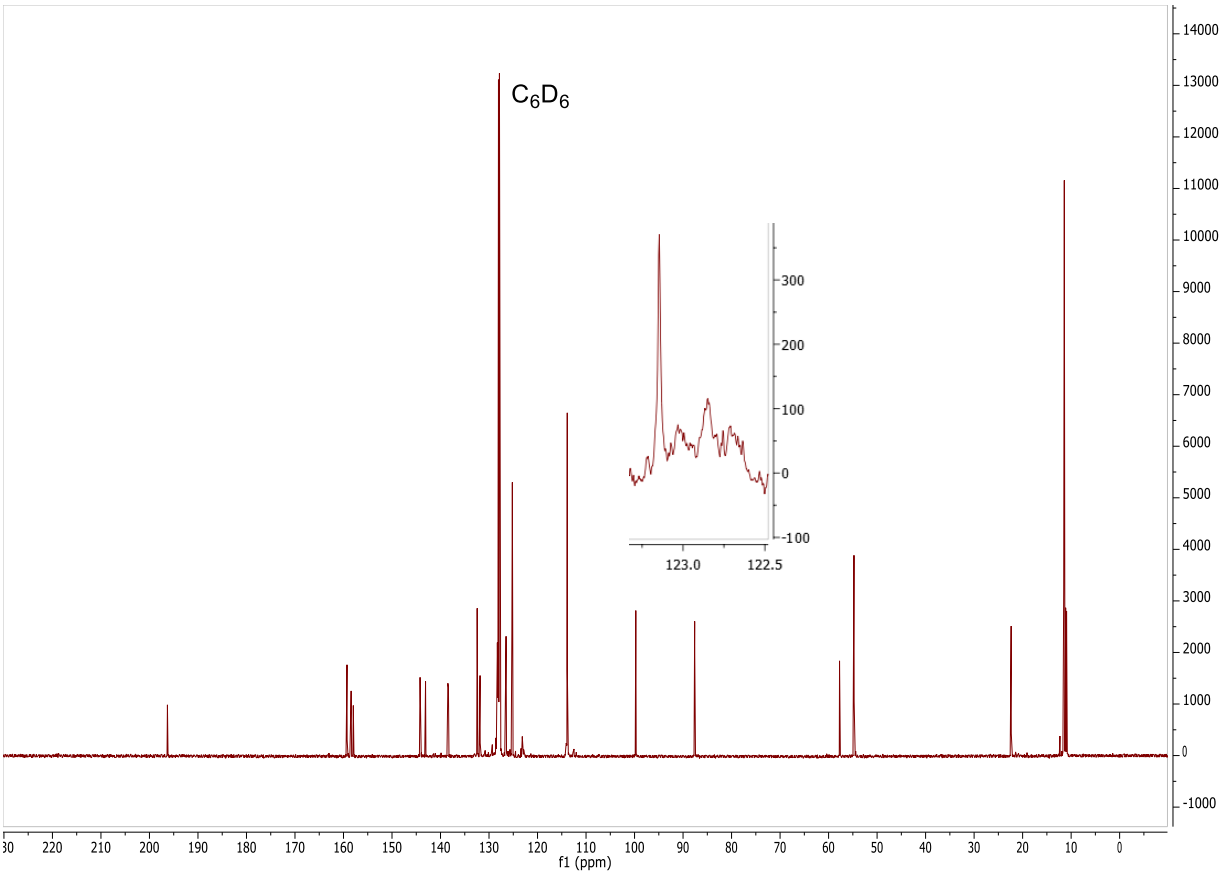
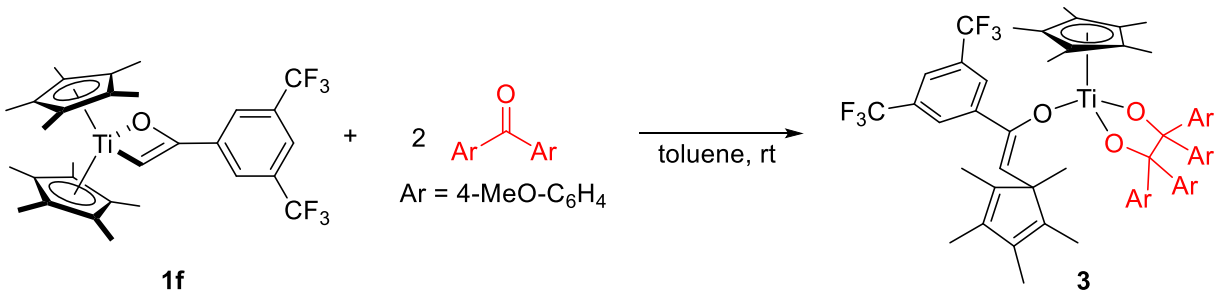


Figure S11: ^{13}C NMR spectrum of reaction between **1e** with bismethoxybenzophenone. Compared to Figure S7, only one triplet is shown. The deuterium incorporation at the alkoxide carbon is too low for the triplet pattern to be observed.

E. Experimental Procedure for Scheme 5



1f **3**

To a 20 mL scintillation vial was added **1f** (0.27 mmol, 1.0 equiv), 4,4'-bismethoxybenzophenone (0.49 mmol, 1.8 equiv), toluene (4.0 mL) and a magnetic stir bar. Reaction mixture was stirred at room temperature overnight before solvent was removed under vacuum. The resulting solid was stirred

thoroughly with hexane. Product was collected by filtration, washed with hexane and dried under vacuum overnight. **3** was isolated as a toluene solvated complex.

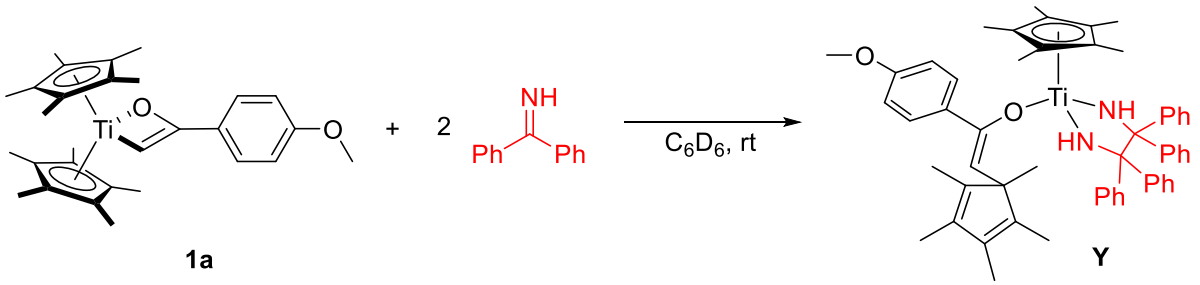
*Data for **3 • toluene**, light orange solid, 75% yield.*

^{1}H NMR (500 MHz, Benzene-d_6) δ 7.68 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H), 7.54 (s, 3H), 7.49 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H), 7.38 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H), 7.37 (d, $^{3}J_{HH}$ = 8.6 Hz, 2H), 6.85 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H), 6.70 (d, $^{3}J_{HH}$ = 8.3 Hz, 2H), 6.62 (d, $^{3}J_{HH}$ = 8.5 Hz, 2H), 6.46 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 4.49 (s, 1H), 3.34 (s, 3H), 3.23 (s, 3H), 3.21 (s, 3H), 2.95 (s, 3H), 2.17 (s, 3H), 1.97 (s, with a shoulder at 1.98, integrate together to 18H), 1.95 (s, 3H), 1.83 (s, 3H), 1.79 (s, 3H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 159.14, 158.88, 158.48, 158.44, 158.29, 144.32, 144.00, 142.86, 141.04, 140.49, 140.04, 139.46, 132.50, 132.46, 131.86, 131.27 (q, $^{2}J_{CF}$ = 33.0 Hz), 130.79, 130.26, 126.73, 125.74 (m), 123.96 (q, $^{1}J_{CF}$ = 273.7 Hz), 120.37 (m), 117.52, 115.22, 113.72, 112.75, 112.63, 112.28, 112.08, 109.84, 60.30, 54.71, 54.67, 54.62, 54.27, 19.08, 12.27, 11.86, 11.57, 11.51, 11.38.
^{19}F NMR (470 MHz, Benzene-d_6) δ -62.36.
Calcd for $C_{60}H_{62}F_6O_7Ti \bullet (1/2)C_7H_8$: C, 69.09; H, 5.98. Found: C, 69.05; H, 5.98.

F. Reaction of 1a with imine

Adding 1 equivalent of benzophenone imine to a solution of **1a** in C_6D_6 resulted in an immediate color change from green to reddish brown. ^{1}H NMR indicated 50% conversion of **1a** to a single reductive elimination product (see NMR spectra below), tentatively assigned to be **Y**. Full conversion was achieved with 2 equivalents of imine.



1a **Y**

Procedure: To a 4 mL scintillation vial containing **1a** (0.181 mmol, 1.0 equiv) and a magnetic stir bar was added a solution of benzophenone imine (0.372 mmol, 2.05 equiv.) in toluene (2.0 mL). An immediate color change to deep red was observed. Reaction was stirred overnight at room temperature before all

volatiles were removed under vacuum. The resulting red oil was taken up in pentane and the solvent was allowed to slowly evaporate over two weeks, resulting in formation of red needles of **Y**, 82% yield.

HRMS (ESI/TOF) calculated for $C_{55}H_{60}N_2O_2Ti$: 829.4219 $[MH]^+$ Found: 829.2429.

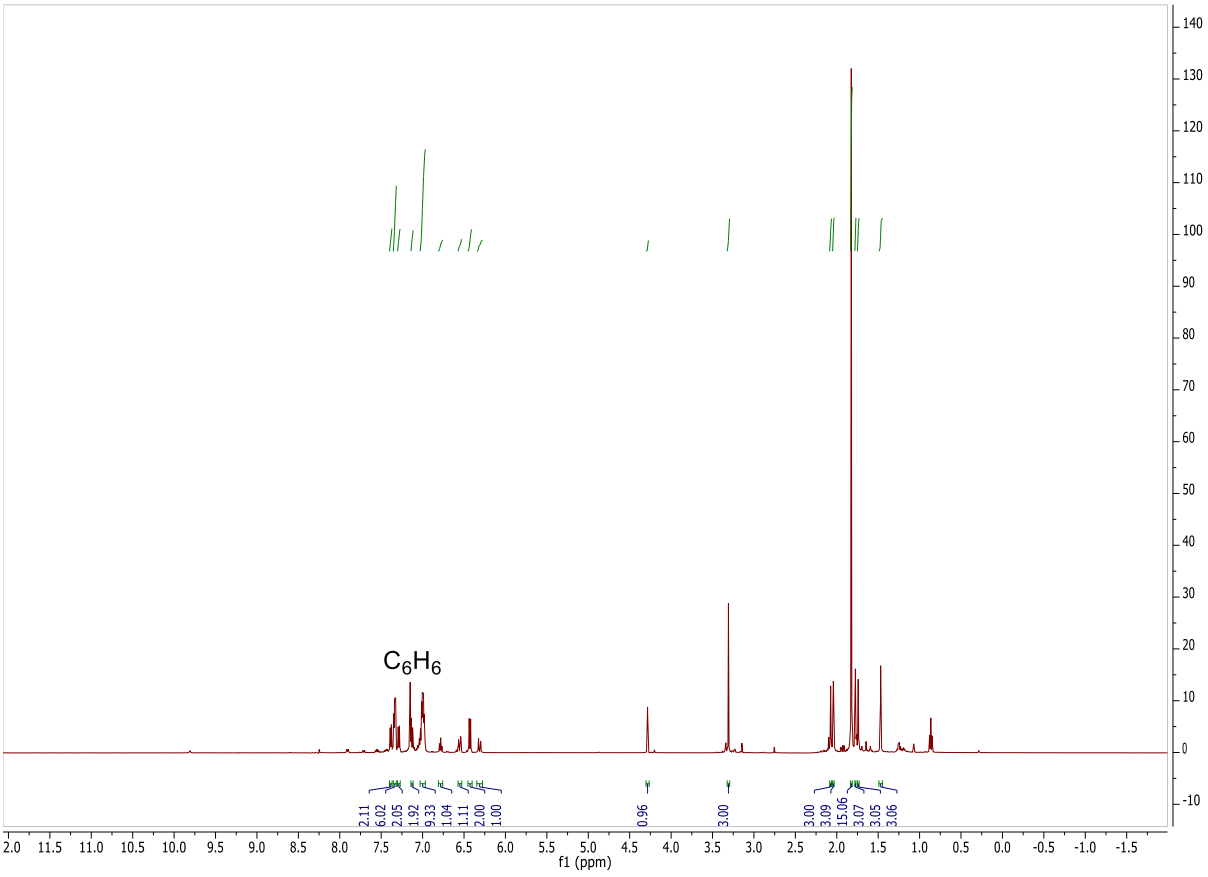


Figure S12: ^{1}H NMR spectrum of the product generated in reaction of **1a** and benzophenone imine. The characteristics of enol ligand resulted from reductive elimination of Cp* and Ti–C bond in **1a** can be observed in the Cp* region and the singlet at 4.28.

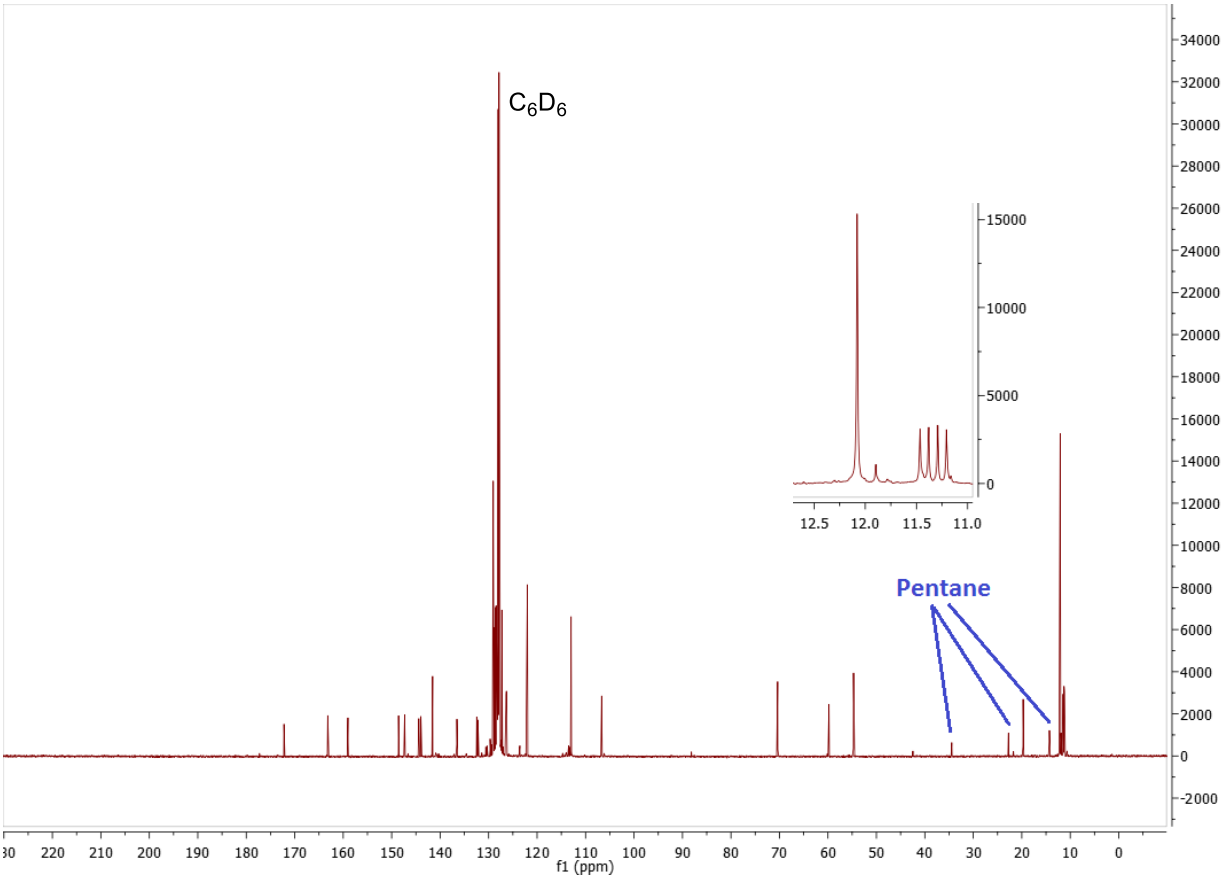
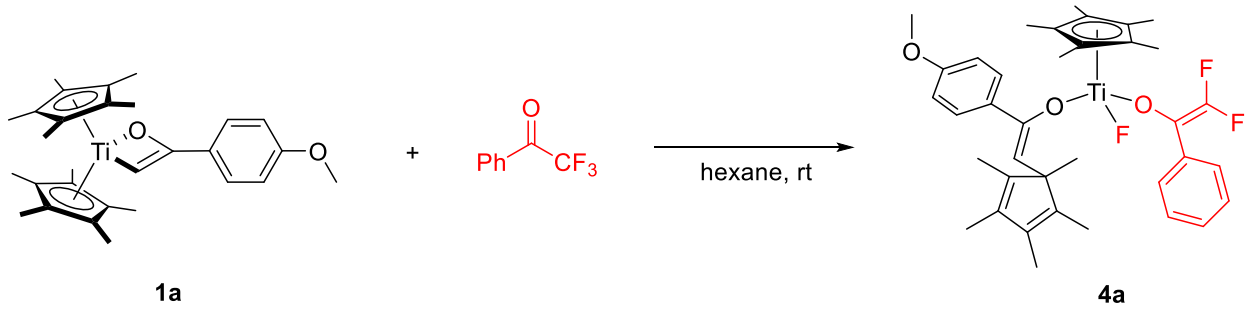


Figure S13: ^{13}C NMR spectrum of product **Y**.

G. Experimental Procedure for Scheme 7



1a **4a**

To a 20 mL scintillation vial was added **1a** (0.32 mmol, 1.0 equiv), hexane (4.0 mL) and a magnetic stir bar. Trifluoroacetophenone (0.35mmol, 1.09 equiv) was added dropwise with stirring; a color change from green to yellow was observed and yellow solid gradually crashed out of solution. Reaction mixture was stirred at room temperature for 3 hours then cooled to -30 °C for 2 hours. Product was collected by filtration, washed with cold hexane and dried under vacuum overnight.

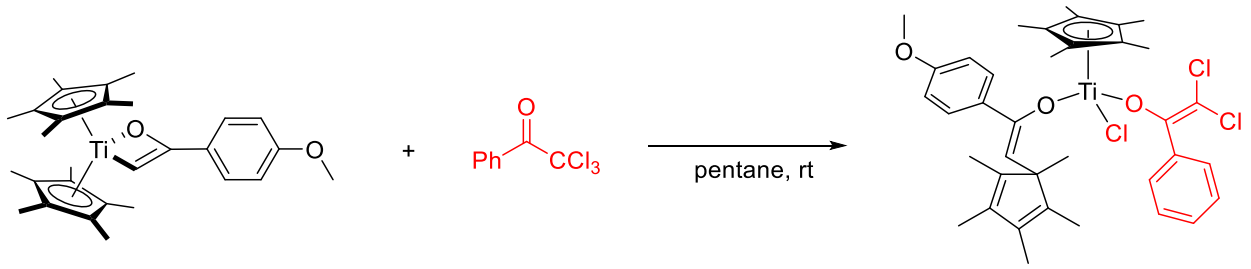
*Data for **4a**, yellow solid, 83% yield.*

^{1}H NMR (500 MHz, Benzene-d_6) δ 7.77 (dd, $^{3}J_{HH}$ = 8.5 Hz, $^{4}J_{HH}$ = 1.3 Hz, 2H), 7.53 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.20 (dd, $^{3}J_{HH}$ = 8.4 Hz, $^{3}J_{HH}$ = 7.5 Hz, 2H), 7.02 (tt, $^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{HH}$ = 1.3 Hz, 1H), 6.84 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 4.43 (s, 1H), 3.32 (s, 3H), 1.98 (s, 3H), 1.96 (s, 3H), 1.84 (s, 3H), 1.79 (s, 3H), 1.76 (s, 15H), 1.55 (s, 3H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 161.68, 159.81, 156.71, 154.42, 152.12, 143.40, 142.56, 134.87, 133.89 (dd, $^{3}J_{CF}$ = 7.7, 2.0 Hz), 133.43, 133.35, 128.62, 127.86, 126.70 (dd, $^{2}J_{CF}$ = 6.9, 3.5 Hz), 125.08 (dd, $^{1}J_{CF}$ = 34.6, 18.2 Hz), 113.85, 110.37, 58.82, 54.84, 20.91, 11.53, 11.48, 11.01, 10.97, 10.89.

^{19}F NMR (470 MHz, Benzene-d_6) δ -81.22, -99.73 (d, $^{2}J_{FF}$ = 65.8 Hz), -115.84 (d, $^{2}J_{FF}$ = 66.4 Hz).

Calcd for $C_{37}H_{43}F_3O_3Ti$: C, 69.37; H, 6.77. Found: C, 69.13; H, 6.57.



1a **4b**

To a 20 mL scintillation vial was added **1a** (0.21 mmol, 1.0 equiv), pentane (2.6 mL) and a magnetic stir bar. Trichlororoacetophenone (0.23mmol, 1.09 equiv) was added dropwise with stirring; a color change from green to dark brown was observed and solid gradually crashed out of solution. Reaction mixture was stirred at room temperature for 2 hours. Product was collected by filtration, washed with cold pentane and dried under vacuum overnight.

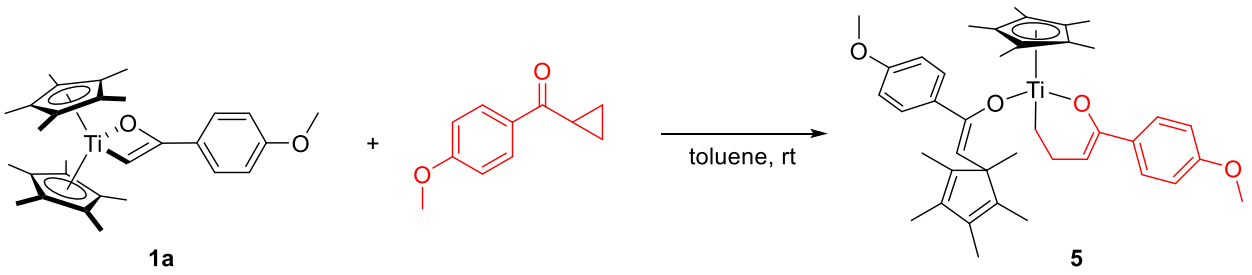
*Data for **4b**, reddish orange solid, 51% yield.*

^{1}H NMR (500 MHz, Benzene-d_6) δ 7.46 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H), 7.43 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 7.13 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H), 7.03 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H), 6.70 (d, $^{3}J_{HH}$ = 8.7 Hz, 2H), 4.37 (s, 1H), 3.29 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.80 (s, 15H), 1.79 (s, 3H), 1.75 (s, 3H), 1.59 (s, 3H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 163.18, 159.76, 158.80, 143.25, 142.77, 136.32, 134.76, 133.64, 130.13, 129.47, 129.01, 128.35, 128.23, 113.79, 112.13, 104.87, 59.27, 54.86, 20.38, 12.11, 11.61, 11.41, 11.19, 11.02.

Calcd for $C_{37}H_{43}Cl_3O_3Ti$: C, 64.41; H, 6.28. Found: C, 64.27; H, 6.17.

H. Experimental Procedure for Scheme 8



1a **5**

To a 20 mL scintillation vial was added **1a** (0.35 mmol, 1.0 equiv), 4-methoxyphenyl cyclopropyl ketone (0.33 mmol, 0.94 equiv), toluene (3.0 mL) and a magnetic stir bar. Reaction mixture was stirred at room temperature overnight before solvent was removed under vacuum. The resulting brown residue was dissolved in pentane and kept at -30 °C overnight. A layer of dense oil precipitated at the bottome of the vial. The solution part was pipetted to another vial and kept at -30 °C for 4 days. Brown solid precipitated and was collected by filtration, washed with cold pentane and dried under vacuum overnight.

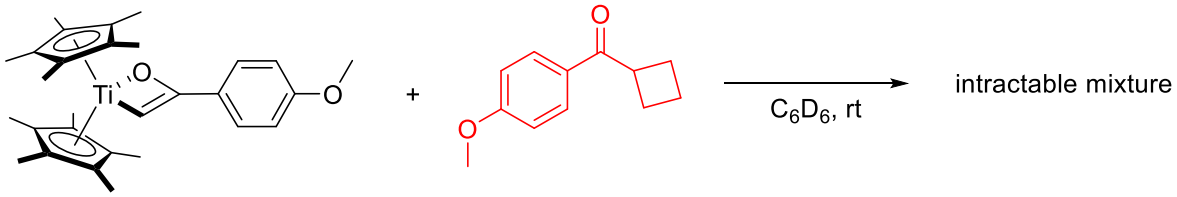
*Data for **5**, light yellow brown solid, 40% yield*

^{1}H NMR (500 MHz, Benzene-d_6) δ 7.70 (d, $^3J_{HH}$ = 8.6 Hz, 2H), 7.44 (d, $^3J_{HH}$ = 8.5 Hz, 2H), 6.84 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 6.74 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 5.60 (dd, $^3J_{HH}$ = 6.1, 3.1 Hz, 1H), 4.38 (s, 1H), 3.39 (m, 2H), 3.31 (s, 3H), 3.29 (s, 3H), there is one multiplet underneath the 2 singlets at 3.31 and 3.29ppm, integrates to 1H, 3.10 (m, 1H), 2.05 (s, 3H), 2.00 (s, 3H), 1.78 (s, 15H), 1.77 (s, 3H), 1.74 (s, 3H), 1.46 (s, 3H).

^{13}C NMR (126 MHz, Benzene-d_6) δ 160.92, 159.53, 159.45, 158.93, 143.51, 143.38, 135.69, 132.96, 132.86, 131.62, 127.61, 126.14, 123.03, 113.84, 113.63, 107.91, 103.03, 82.82, 58.95, 54.80, 54.77, 32.34, 21.00, 11.61, 11.48, 11.20, 11.11, 10.81.

Calcd for $C_{40}H_{50}O_4Ti$: C, 74.75; H, 7.84. Found: C, 74.47 ; H, 7.89.

Reaction of 1a and cyclobutyl phenyl ketone



1a

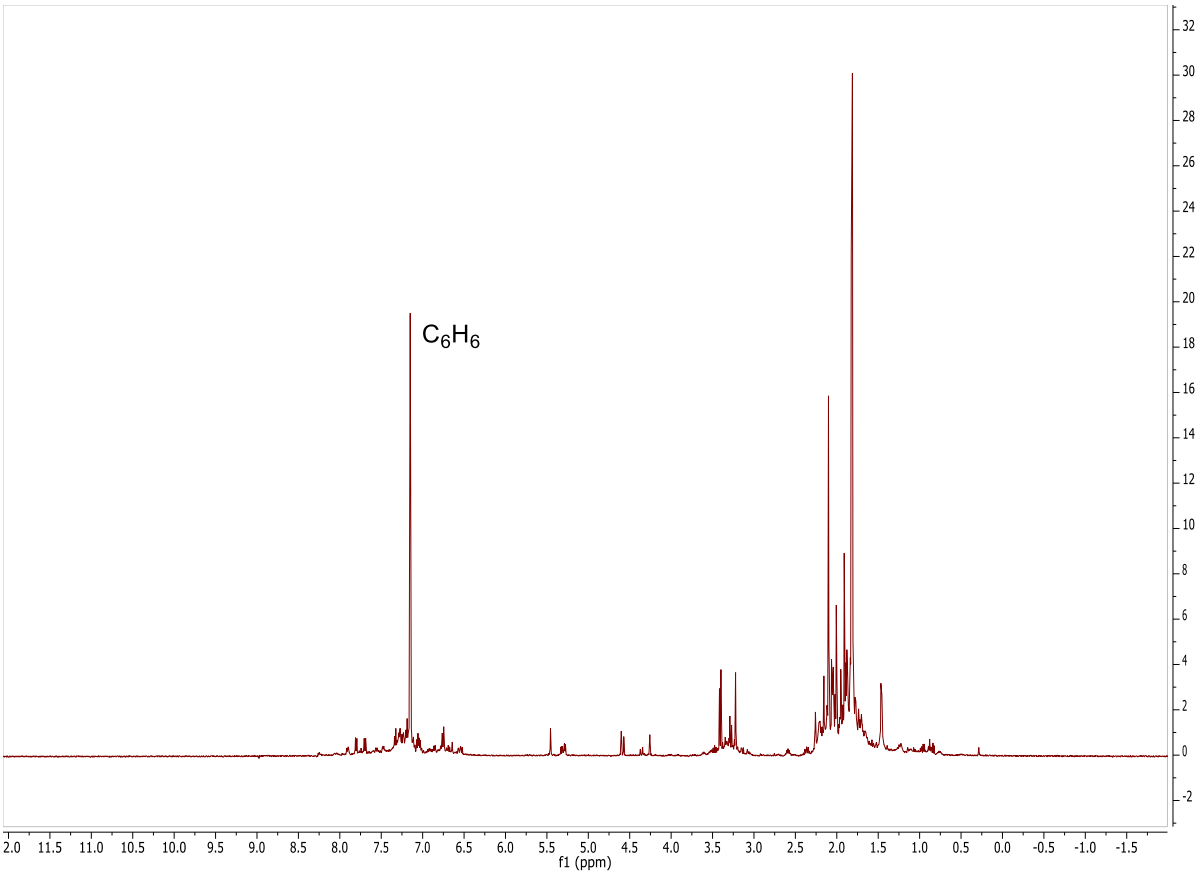


Figure S14: ^{1}H NMR spectrum of reaction between **1a** and cyclobutyl phenyl ketone.

I. Crystallographic Data

X-Ray Diffraction Techniques: Data for **2a** and **4a** were collected on a Bruker D8 Venture equipped with a four-circle kappa diffractometer and Photon 100 detector. An Iμs microfocus Mo (λ = 0.71073 Å) source supplied the multi-mirror monochromated incident beam. The sample was mounted on a 0.3mm loop with the minimal amount of Paratone-N oil. Data was collected as a series of φ and/ or ω scans. Data was collected 100K. Data was integrated and filtered for statistical outliers using SAINT (Bruker, 2014) then corrected for absorption by integration SADABS v2014/2 (Bruker, 2014). The structure was phased by direct methods using the shelx software package SHELX-2014-4 (Sheldrick, 2014).

Data for **3** was collected on a Bruker Kappa four-circle diffractometer equipped with an APEXII CCD detector. A fine-focus sealed tube Mo (λ = 0.71073 Å) source supplied the graphite monochromated incident beam. The sample was mounted on a 0.3mm loop with the minimal amount of Paratone-N oil. Data was collected as a series of φ and/ or ω scans. Data was collected 100K. Data was integrated and filtered for statistical outliers using SAINT (Bruker, 2014) then corrected for absorption by integration

SADABS v2014/2 (Bruker, 2014). The structure was phased by direct methods using the shelx software package SHELX-2014-7 (Sheldrick, 2014).

References:

Bruker (2014). SAINT, SHELXTL, XCIF, XPREP. Bruker AXS, Inc., Madison, Wisconsin, USA.

Bruker (2014). SADABS, TWINABS. Bruker AXS, Inc., Madison, Wisconsin, USA.

Sheldrick, G.M. (2014) SHELX-2014-3, SHELXS, SHELXL. Gottingen, Germany.

1. Crystallographic Data for 2a•THF

Recrystallization procedure: Single crystals suitable for X-ray crystallography was grown from a THF solution of **2a**. In a 4 mL scintillation vial, **2a** (50 mg) was dissolved in THF (1mL). This vial, without capping, was placed inside a 20 mL scintillation vial containing pentane, and the whole set up was kept at -30 °C for 4 days.

Table S1: Crystal data and structure refinement for **2a•THF**.

Empirical formula	C48 H60 O6 Ti	
Formula weight	780.86	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.5881(4) Å	α= 96.3761(15)°.
b = 12.7845(6) Å	β= 90.3364(15)°.	
c = 19.5964(8) Å	γ = 104.8609(16)°.	
Volume	2065.42(16) $Å^3$	
Z	2	
Density (calculated)	1.256 Mg/m^3	
Absorption coefficient	0.256 mm^{-1}	
F(000)	836	
Crystal size	0.353 x 0.184 x 0.176 mm^3	
Theta range for data collection	2.455 to 25.423°.	
Index ranges	-10<=h<=10, -15<=k<=15, -23<=l<=23	

Reflections collected	74631
Independent reflections	7605 [R(int) = 0.0274]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Integration
Max. and min. transmission	0.99930 and 0.99864
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7605 / 129 / 566
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0391, wR2 = 0.0992
R indices (all data)	R1 = 0.0423, wR2 = 0.1020
Extinction coefficient	0.0491(16)
Largest diff. peak and hole	0.399 and -0.330 e.Å^{-3}

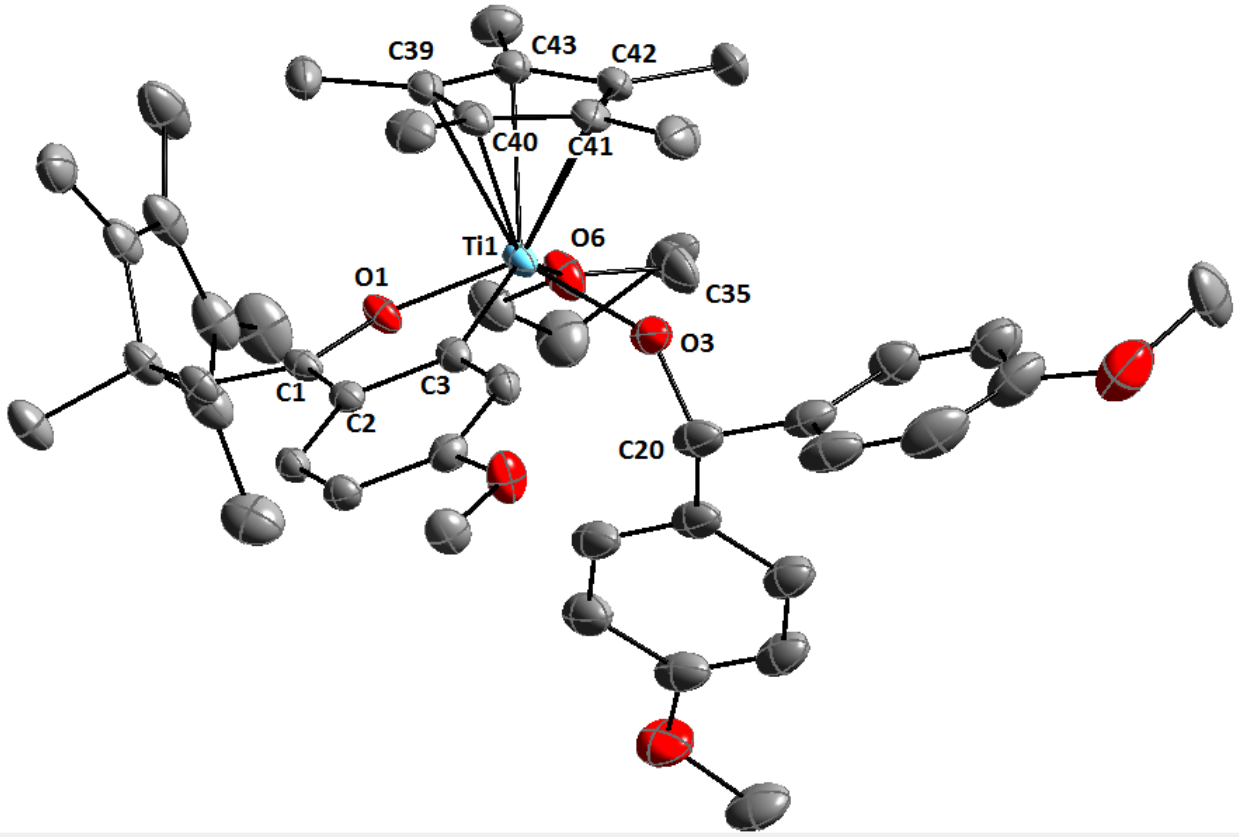


Figure S15. Crystal structure of **2a•THF** with selective atoms labelled. Hydrogen atoms were omitted for clarity. Ellipsoids are drawn at 50% probability level.

Table S2: Selected bond lengths and angles for **2a•THF**

Bond (Å)		Angle (°)	
Ti(1)-O(3)	1.8351(12)	O(3)-Ti(1)-O(1)	128.15(5)
Ti(1)-O(1)	1.9273(11)	O(3)-Ti(1)-C(3)	87.91(6)
Ti(1)-C(3)	2.1461(16)	O(1)-Ti(1)-C(3)	77.52(5)
Ti(1)-O(6)	2.2575(12)	O(3)-Ti(1)-O(6)	82.59(5)
Ti(1)-C(43)	2.3832(16)	O(1)-Ti(1)-O(6)	79.06(4)
Ti(1)-C(39)	2.3854(16)	C(3)-Ti(1)-O(6)	141.01(5)
Ti(1)-C(42)	2.3998(15)	C(1)-O(1)-Ti(1)	123.33(10)
Ti(1)-C(40)	2.4002(16)	C(20)-O(3)-Ti(1)	143.86(11)
Ti(1)-C(41)	2.4109(16)	C(35)-O(6)-Ti(1)	124.1(4)

2. Crystallographic data for 3

Crystals suitable for X-ray diffraction were grown by layering pentane on top of a toluene solution of **3**.

Table S3. Crystal data and structure refinement for **3**.

Empirical formula	C66.26 H71.47 F6 O7 Ti	
Formula weight	1141.78	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.695(2) Å	α = 90.607(8)°.
b = 14.142(2) Å	β = 98.046(9)°.	
c = 17.854(3) Å	γ = 97.865(9)°.	
Volume	2895.1(8) $Å^3$	
Z	2	
Density (calculated)	1.310 Mg/m^3	
Absorption coefficient	0.221 mm^{-1}	
F(000)	1202	
Crystal size	0.398 x 0.175 x 0.154 mm^3	
Theta range for data collection	1.776 to 28.381°.	
Index ranges	-15<=h<=15, -18<=k<=18, -23<=l<=23	

Reflections collected	79102
Independent reflections	14405 [R(int) = 0.0610]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Integration
Max. and min. transmission	1.0000 and 0.9178
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14405 / 527 / 849
Goodness-of-fit on F^2	1.028
Final R indices [I>2sigma(I)]	R1 = 0.0481, wR2 = 0.1209
R indices (all data)	R1 = 0.0619, wR2 = 0.1309
Extinction coefficient	n/a
Largest diff. peak and hole	0.778 and -0.534 e.Å^{-3}

Figure S16: Crystal structure of **3** with selective atoms labelled. Hydrogen atoms were omitted for clarity. Ellipsoids are drawn at 50% probability level.

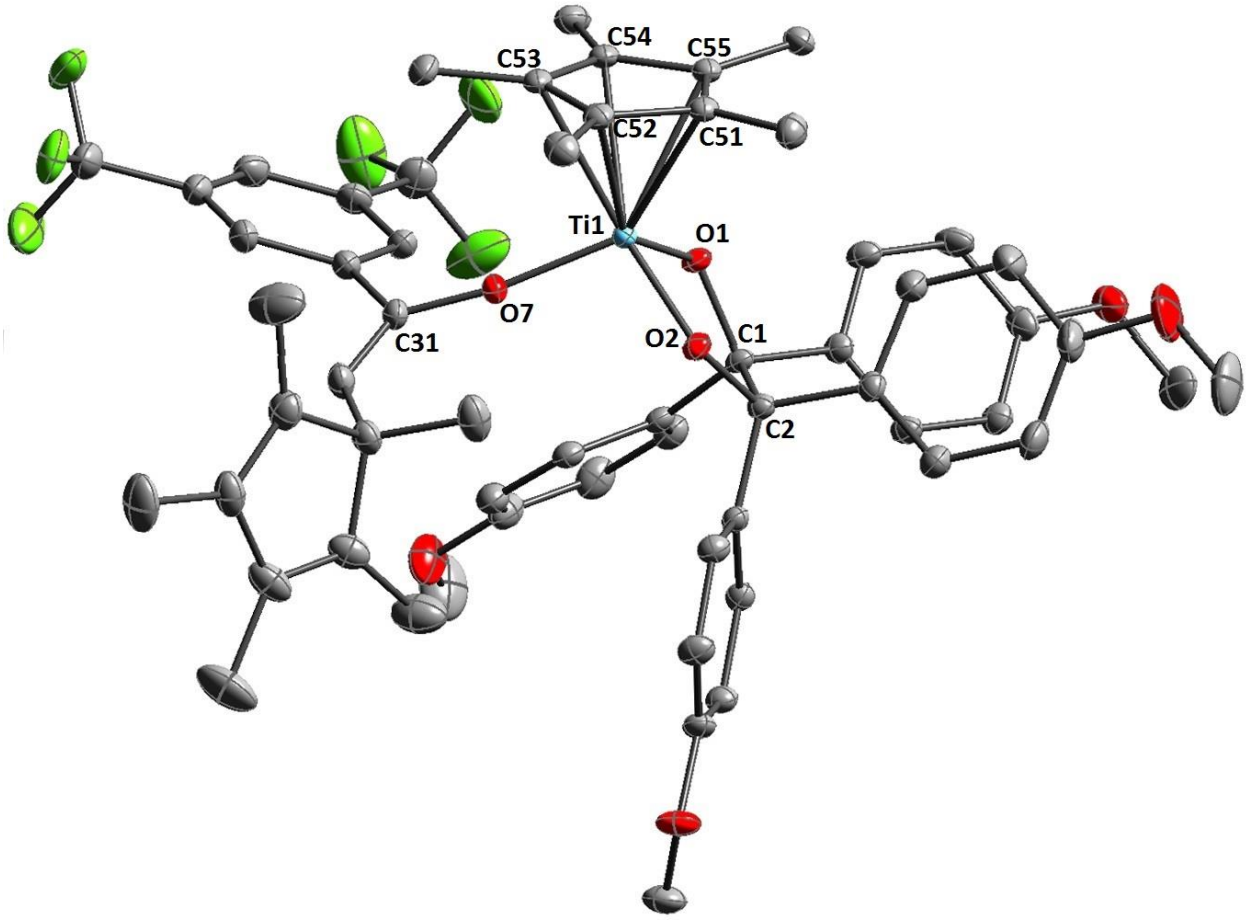


Table S4. Selected bond lengths and angles for **3 • toluene**

Bond (Å)		Angle (°)	
Ti(1)-O(2)	1.8288(12)	O(2)-Ti(1)-O(7)	101.92(5)
Ti(1)-O(7)	1.8405(12)	O(2)-Ti(1)-O(1)	82.60(5)
Ti(1)-O(1)	1.8517(12)	O(7)-Ti(1)-O(1)	110.51(5)
Ti(1)-C(52)	2.3691(16)	O(2)-Ti(1)-C(52)	110.93(6)
Ti(1)-C(51)	2.3816(16)	O(7)-Ti(1)-C(52)	99.62(6)
Ti(1)-C(54)	2.3970(16)	O(1)-Ti(1)-C(52)	143.79(6)
Ti(1)-C(55)	2.4119(16)	C(31)-O(7)-Ti(1)	171.44(11)
Ti(1)-C(53)	2.4165(16)		

3. Crystallographic Data for 4a:

Single crystals suitable for X-ray crystallography were grown by diffusing pentane into a toluene solution of **4a** at -30 °C.

Table S5. Crystal data and structure refinement for **4a**

Empirical formula	C44 H51 F3 O3 Ti	
Formula weight	732.74	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.5108(4) Å	α = 93.8914(19)°.
	b = 11.2738(5) Å	β = 92.505(2)°.
	c = 21.4377(11) Å	γ = 92.180(2)°.
Volume	1807.80(16) $Å^3$	
Z	2	
Density (calculated)	1.346 Mg/m^3	
Absorption coefficient	0.293 mm^{-1}	
F(000)	776	
Crystal size	0.417 x 0.242 x 0.084 mm^3	
Theta range for data collection	2.537 to 26.431°.	

Index ranges	-9<=h<=9, -14<=k<=14, -26<=l<=26
Reflections collected	63080
Independent reflections	7386 [R(int) = 0.0474]
Completeness to theta = 25.242°	99.9 %
Absorption correction	Integration
Max. and min. transmission	0.99965 and 0.99839
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7386 / 0 / 408
Goodness-of-fit on F^2	1.104
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1239
R indices (all data)	R1 = 0.0579, wR2 = 0.1283
Extinction coefficient	n/a
Largest diff. peak and hole	0.550 and -0.556 e

Figure S17: Crystal structure of **4a** with selective atoms labelled. Hydrogen atoms were omitted for clarity. Ellipsoids are drawn at 50% probability level.

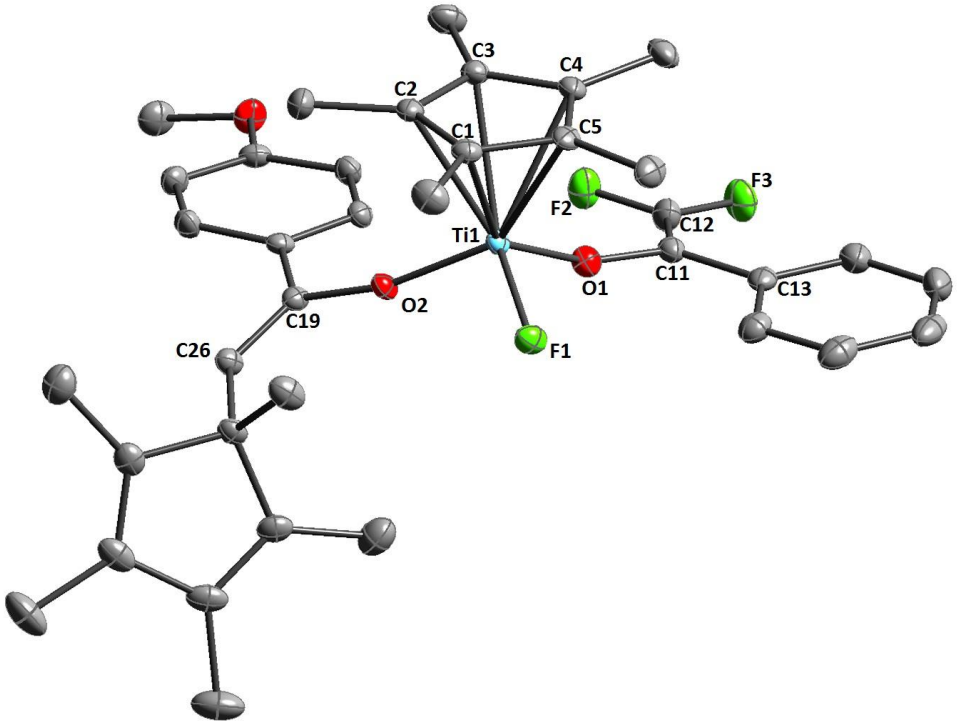


Table S6: Selected bond lengths and angles for **4a**

Bond (Å)		Angle (°)	
Ti(1)-O(2)	1.8101(14)	O(2)-Ti(1)-F(1)	101.94(6)
Ti(1)-F(1)	1.8299(12)	O(2)-Ti(1)-O(1)	103.85(7)
Ti(1)-O(1)	1.8455(16)	F(1)-Ti(1)-O(1)	101.34(7)
Ti(1)-C(3)	2.351(2)	C(11)-O(1)-Ti(1)	156.06(14)
Ti(1)-C(1)	2.355(2)	C(19)-O(2)-Ti(1)	167.36(14)
Ti(1)-C(2)	2.361(2)	C(12)-C(11)-O(1)	117.05(19)
Ti(1)-C(5)	2.362(2)	O(1)-C(11)-C(13)	117.86(19)
Ti(1)-C(4)	2.379(2)	C(26)-C(19)-O(2)	123.11(18)
O(1)-C(11)	1.352(3)	O(2)-C(19)-C(20)	114.45(17)

J. References

(1) Smith, M. R.; Matsunaga, P. T.; Andersen, R. A. *J. Am. Chem. Soc.* **1993**, *113*, 7049–7050.

(2) Ball, L. T.; Lloyd-Jones, G. C.; Russell, C. A. *Chem. Eur. J.* **2012**, *18*, 2931–2937.

(3) Lennox, A. J. J.; Lloyd-Jones, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 7431–7441.

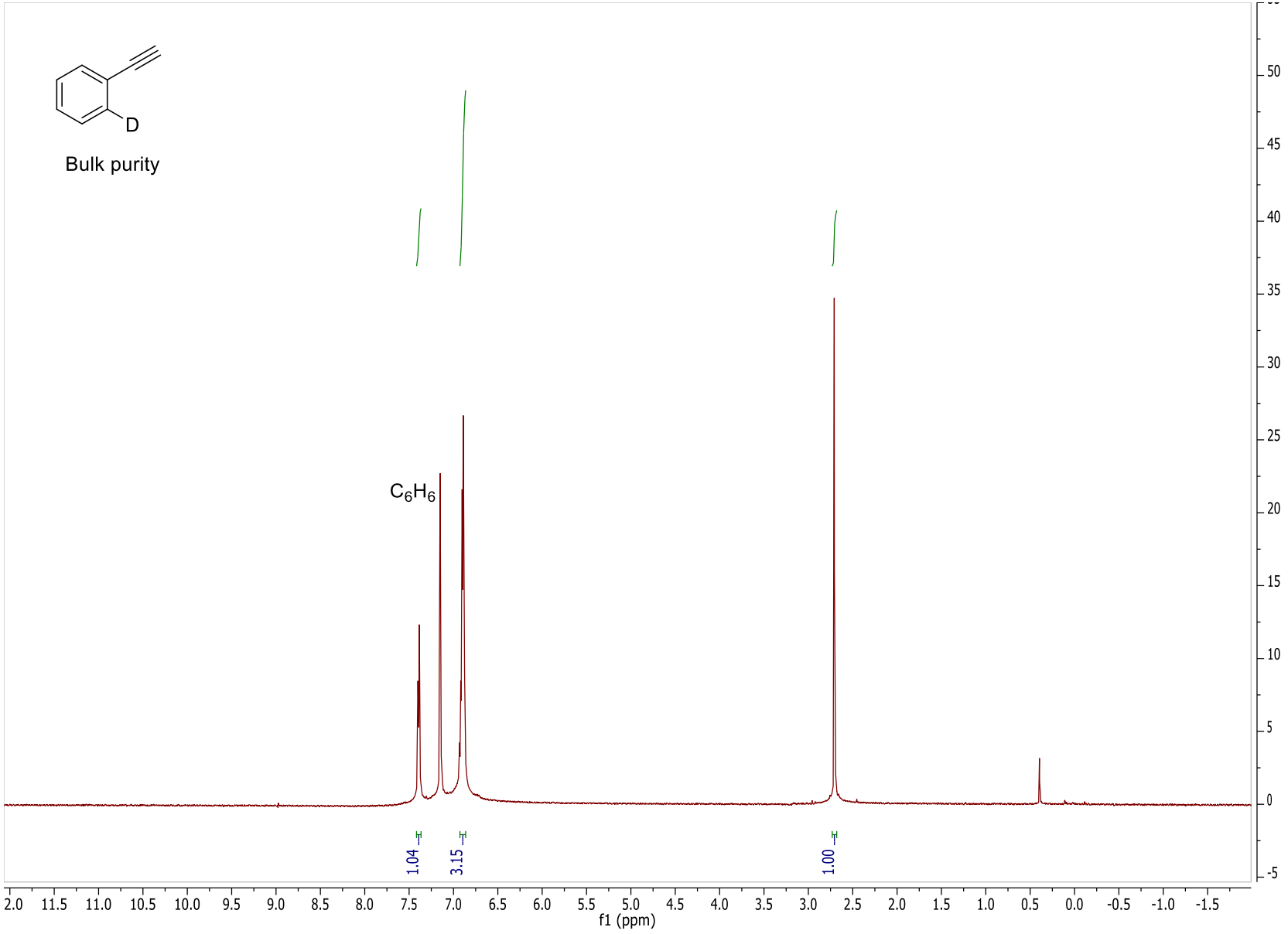
(4) Luo, C. Z.; Gandeepan, P.; Jayakumar, J.; Parthasarathy, K.; Chang, Y. W.; Cheng, C. H. *Chem. Eur. J.* **2013**, *19*, 14181–14186.

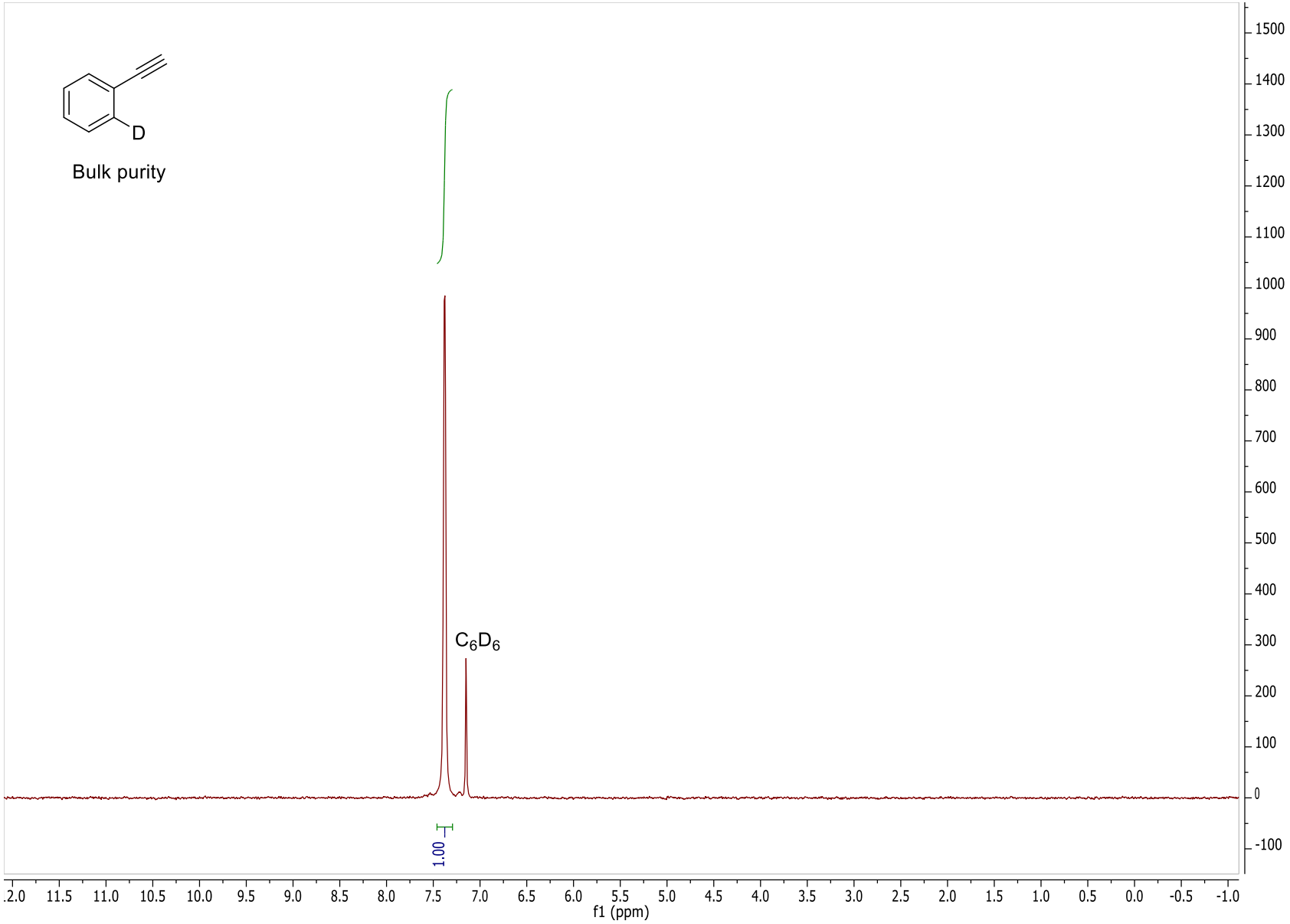
(5) Imanishi, T.; Fujiwara, Y.; Sawama, Y.; Monguchi, Y.; Sajiki, H. *Adv. Synth. Catal.* **2012**, *354* , 771–776.

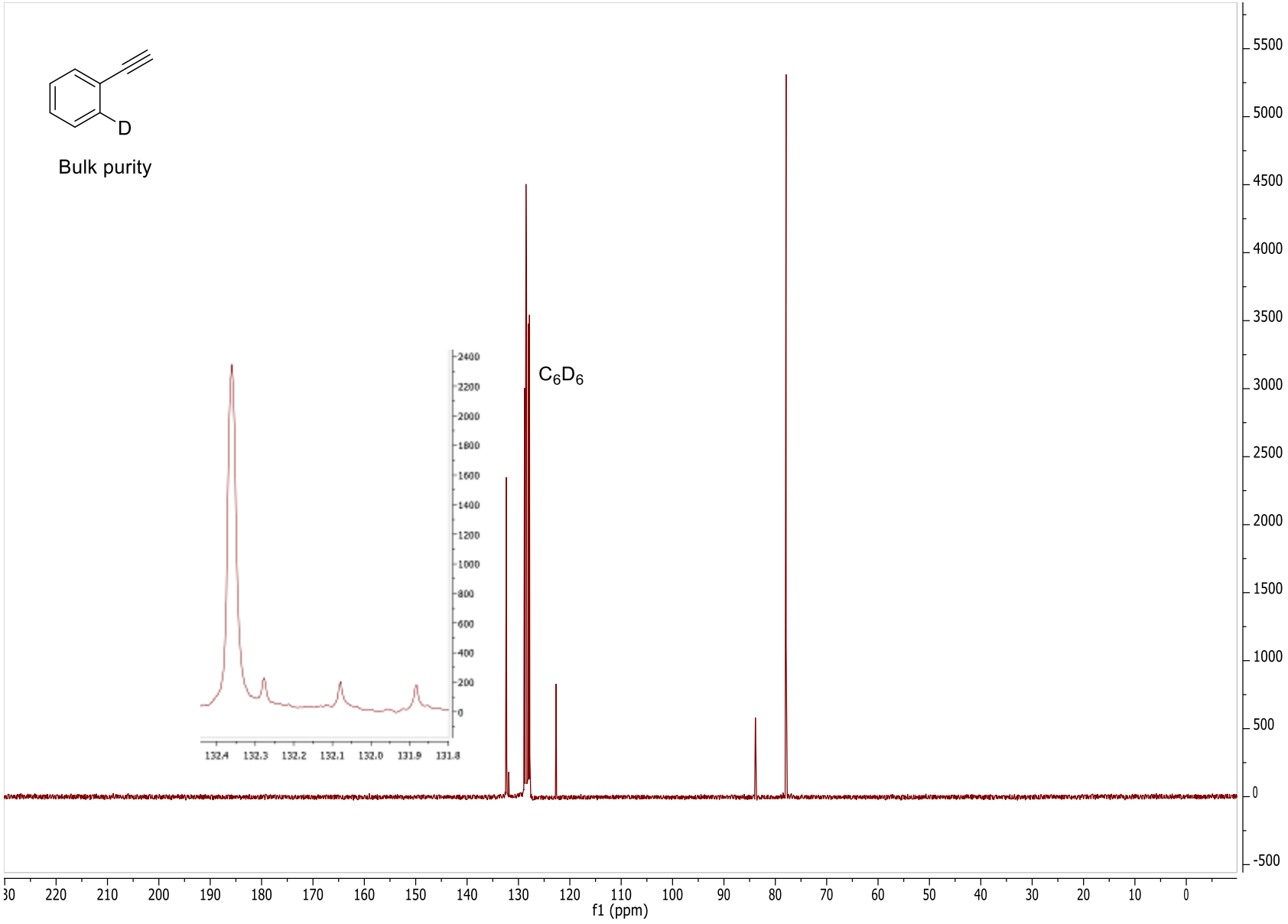
(6) Mujkic, M.; Lentz, D. *Dalt. Trans.* **2012**, *41*, 839.

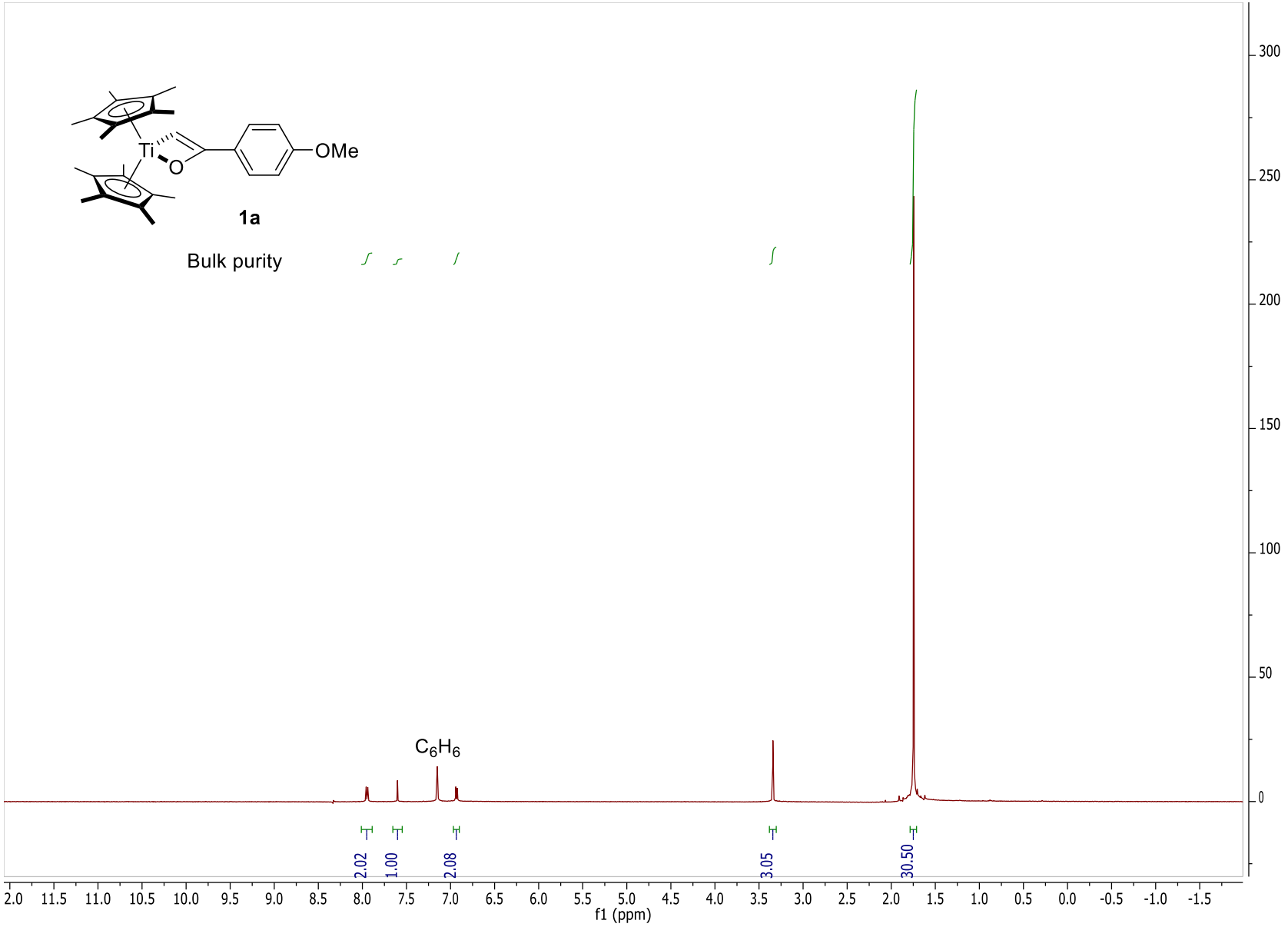
(7) Polse, J. L.; Andemen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1995**, *117*, 5393–5394.

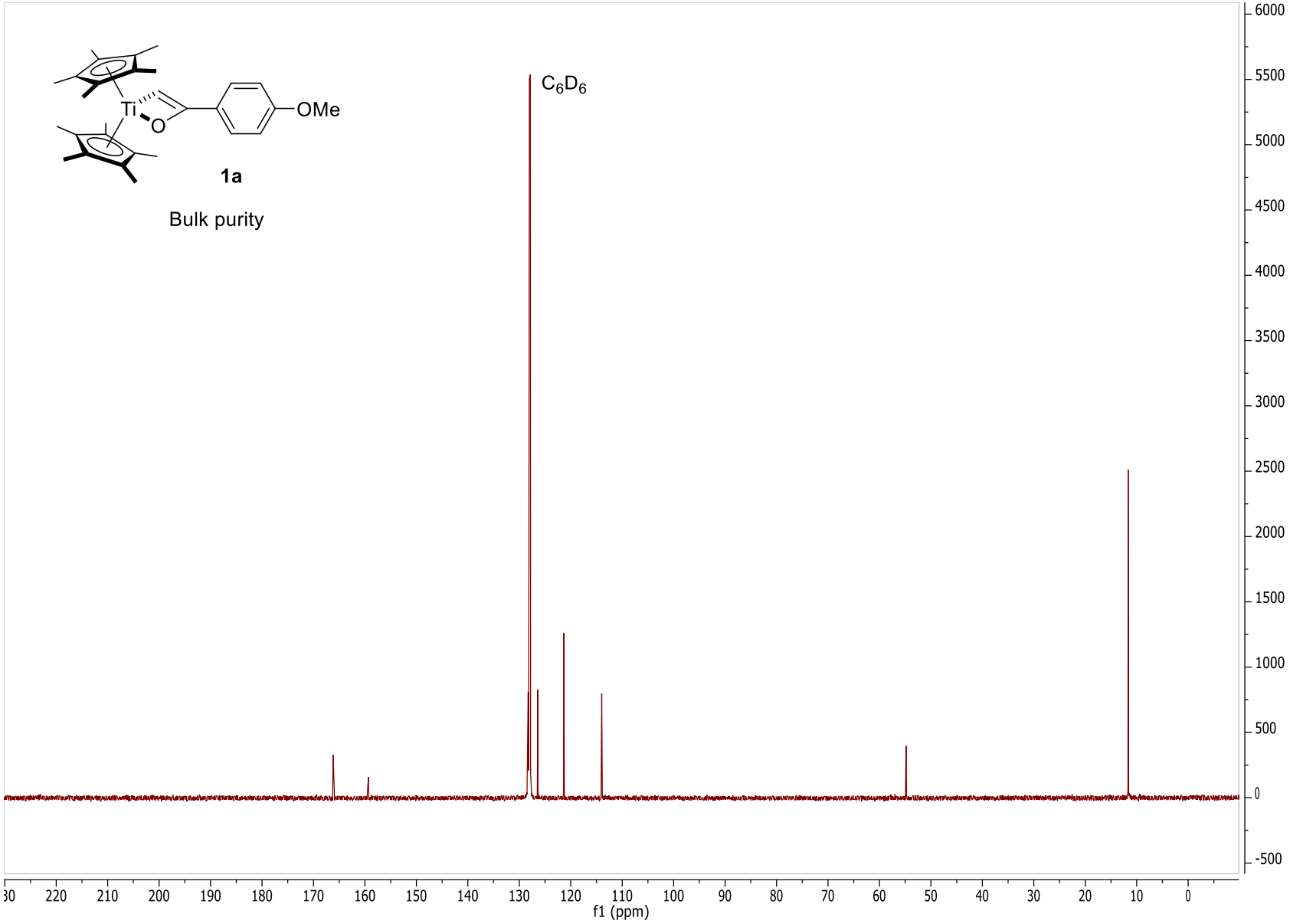
K. NMR Spectra

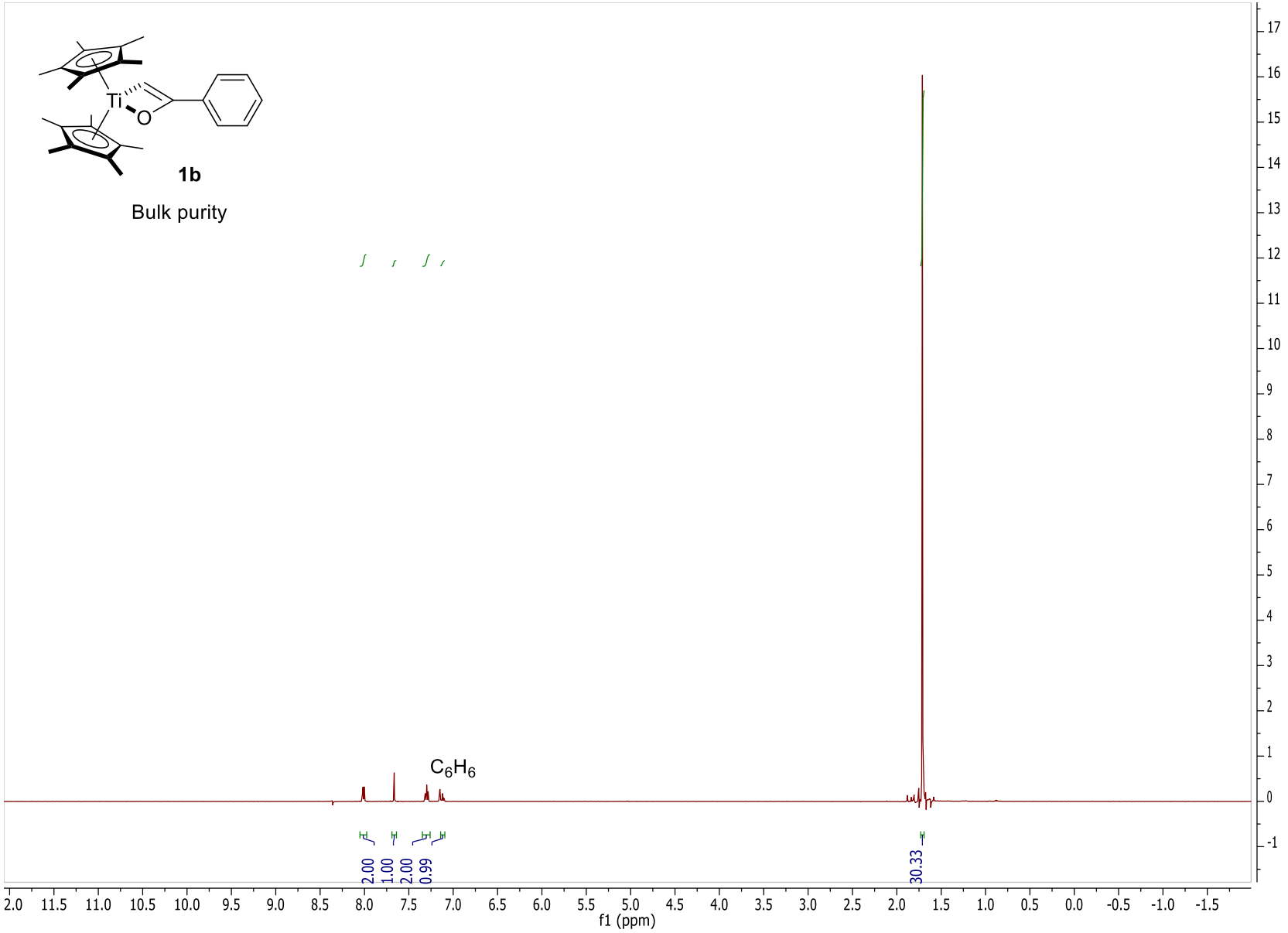

D
Bulk purity
C6H6
1.04
3.15
1.00
f1 (ppm)


D
Bulk purity
C6D6
1.00
f1 (ppm)


D
Bulk purity
C_6D_6
f1 (ppm)


Ti
O
OMe
1a
Bulk purity
C6H6
2.02
1.00
2.08
3.05
30.50
f1 (ppm)


Ti
O
OMe
1a
Bulk purity
C6D6
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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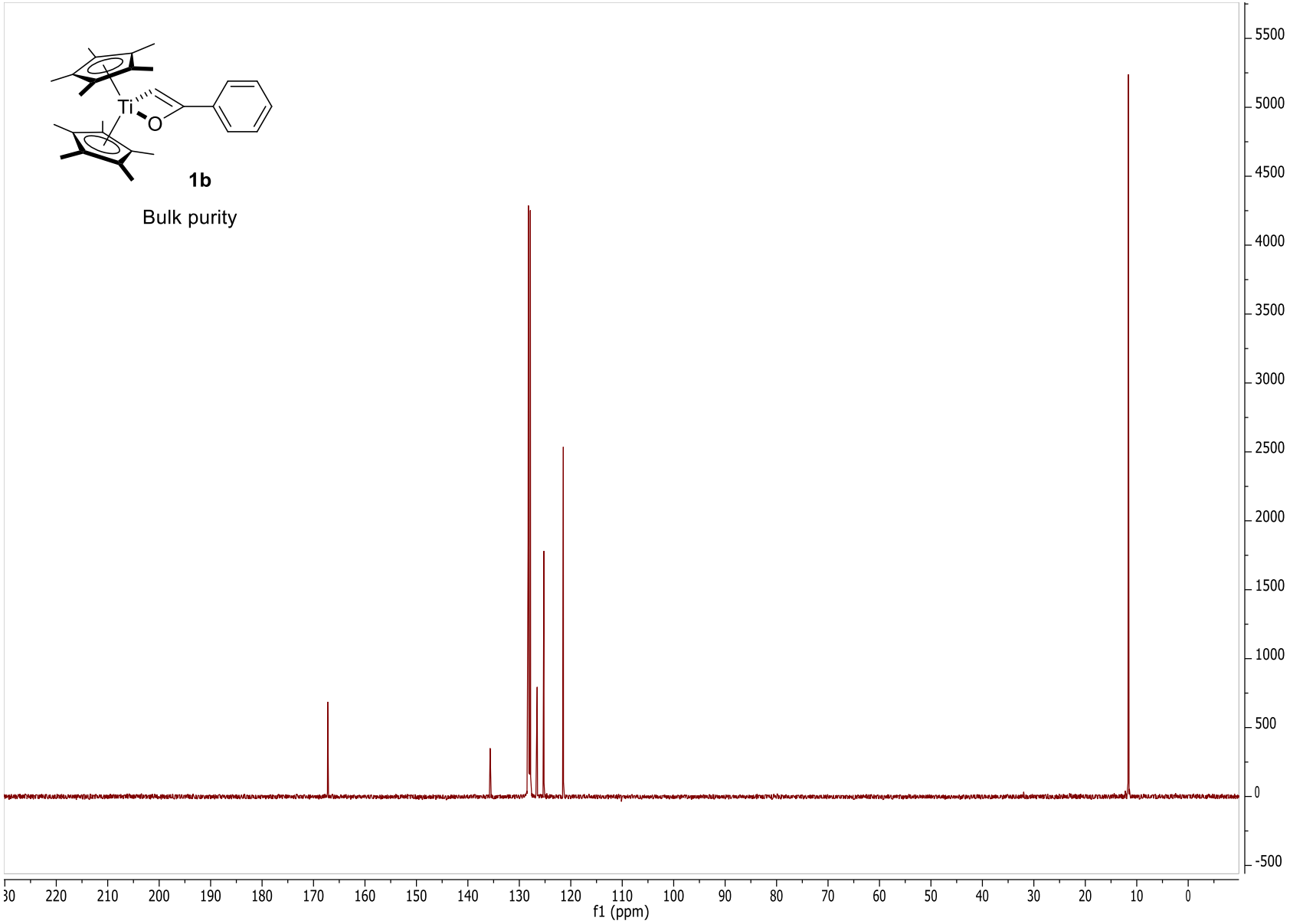
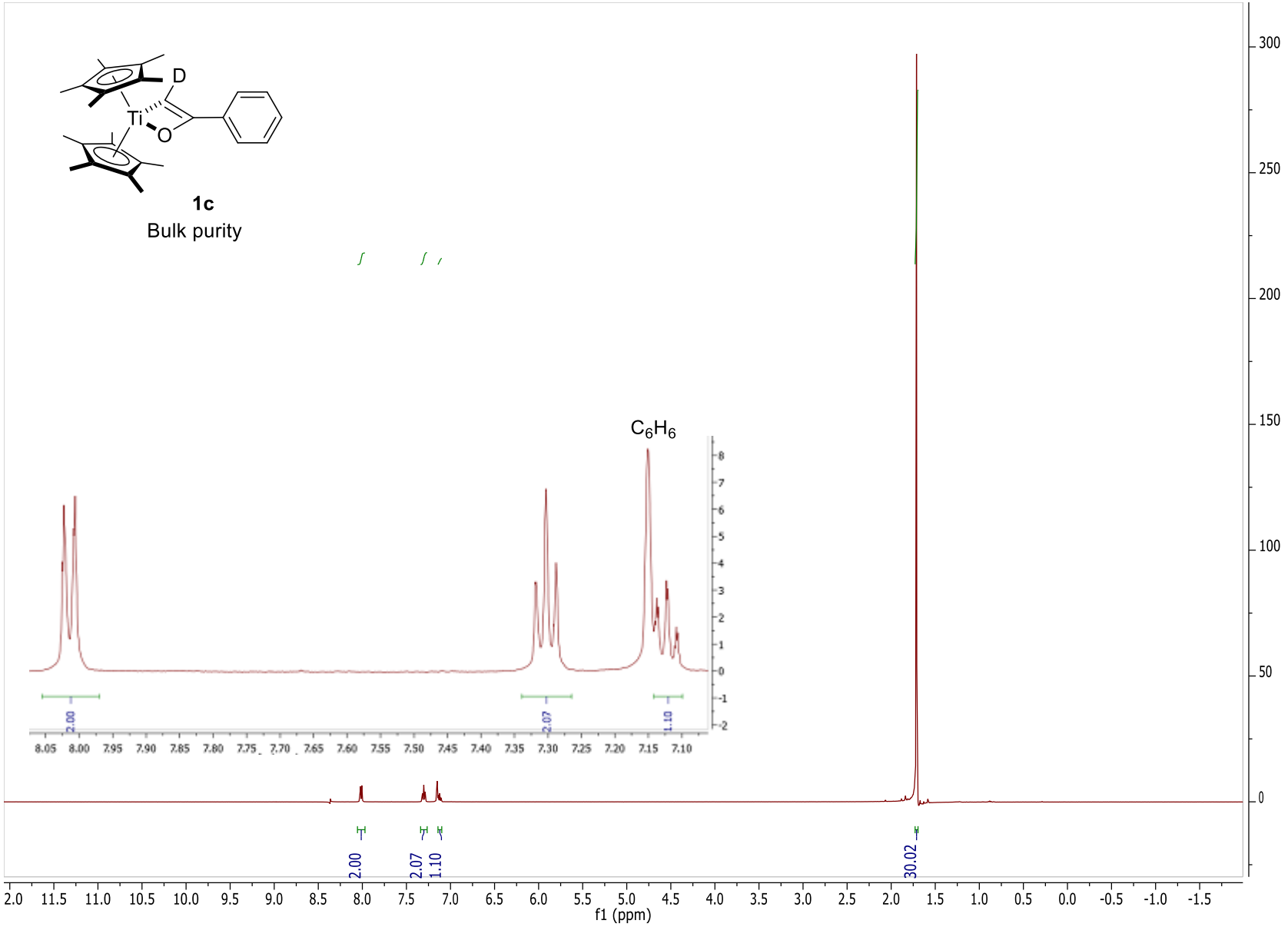
O
1b
Bulk purity
C6H6
2.00
1.00
2.00
0.99
30.33
f1 (ppm)


Ti
O
1b
Bulk purity
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
30
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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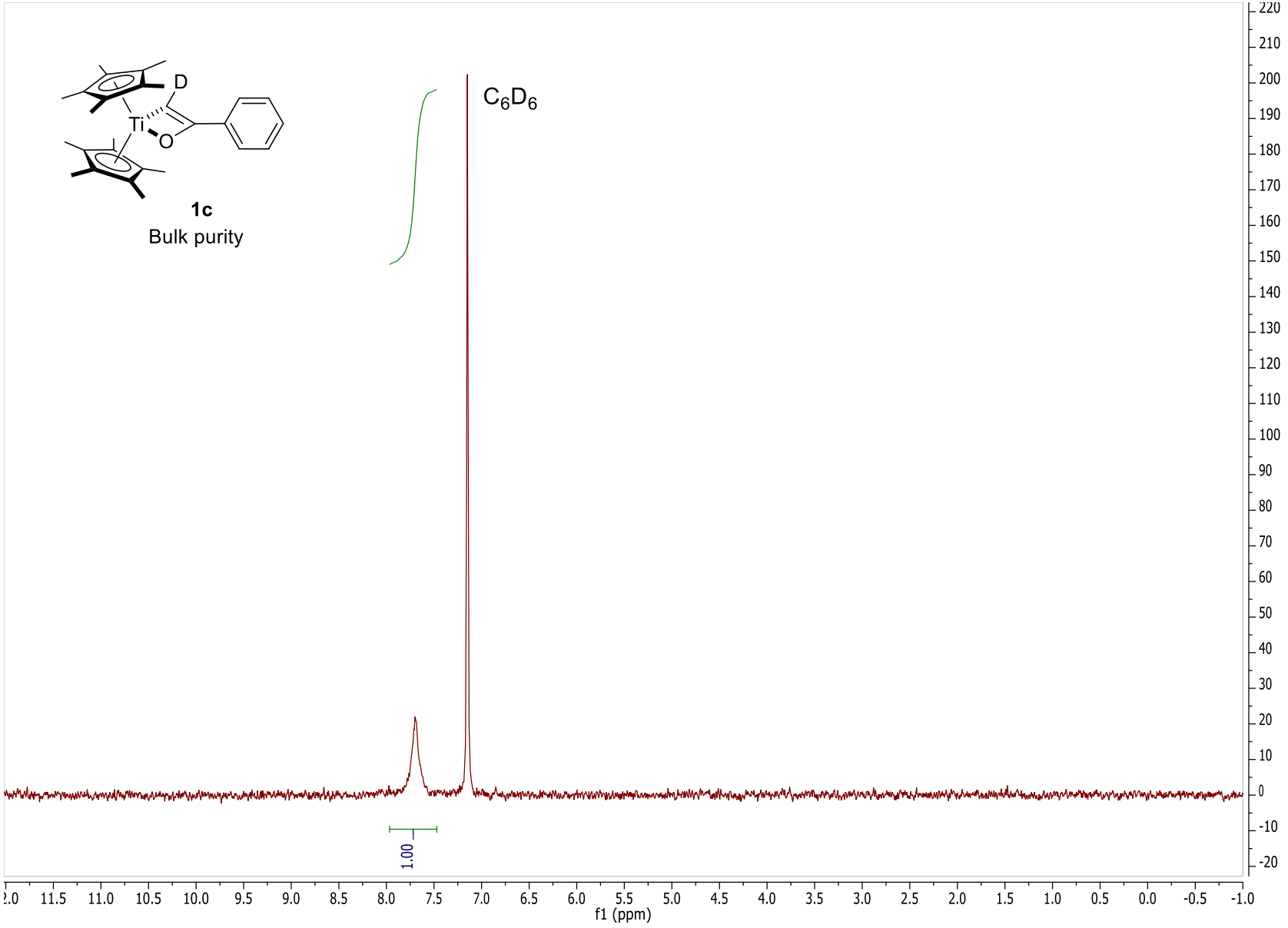
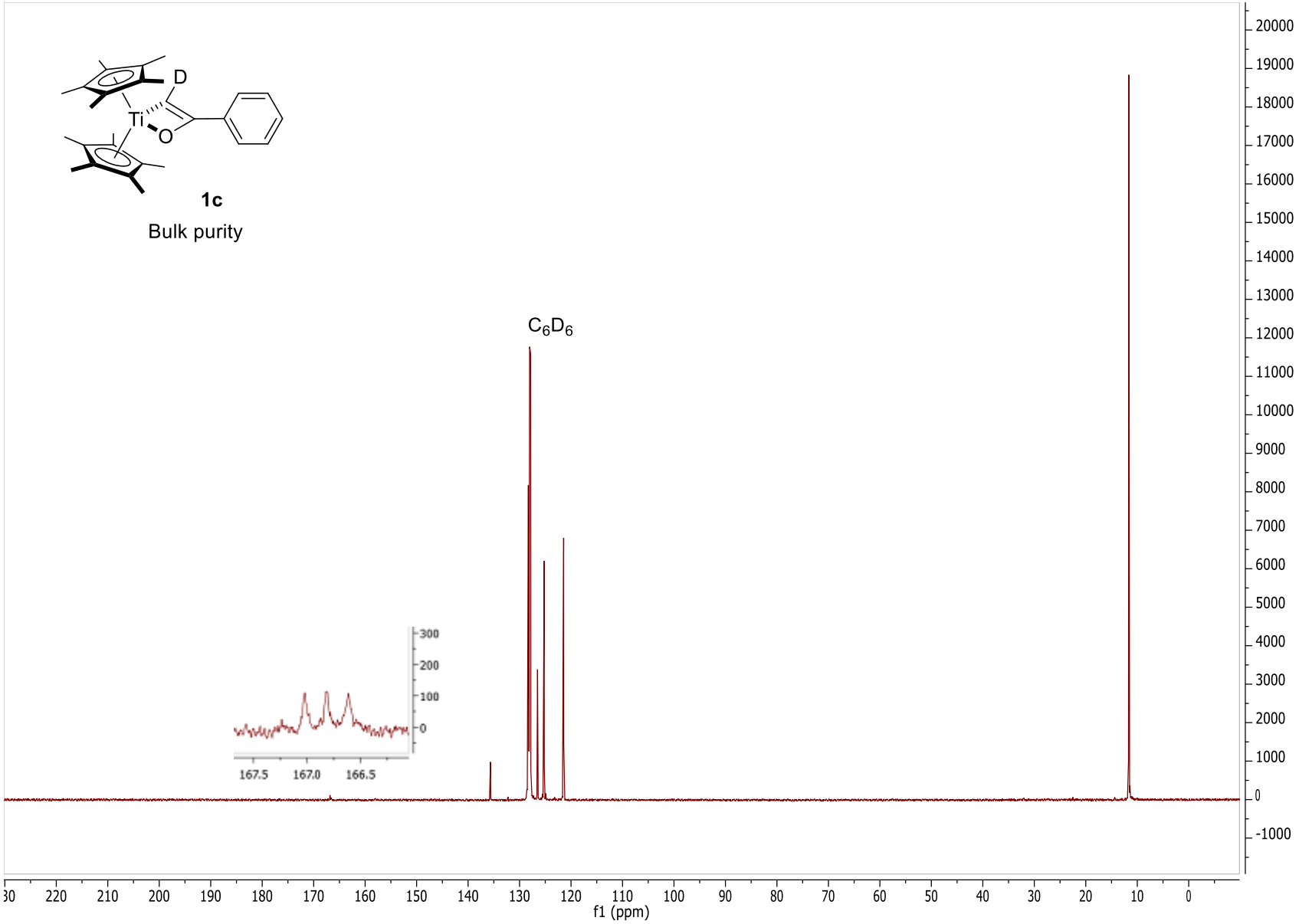
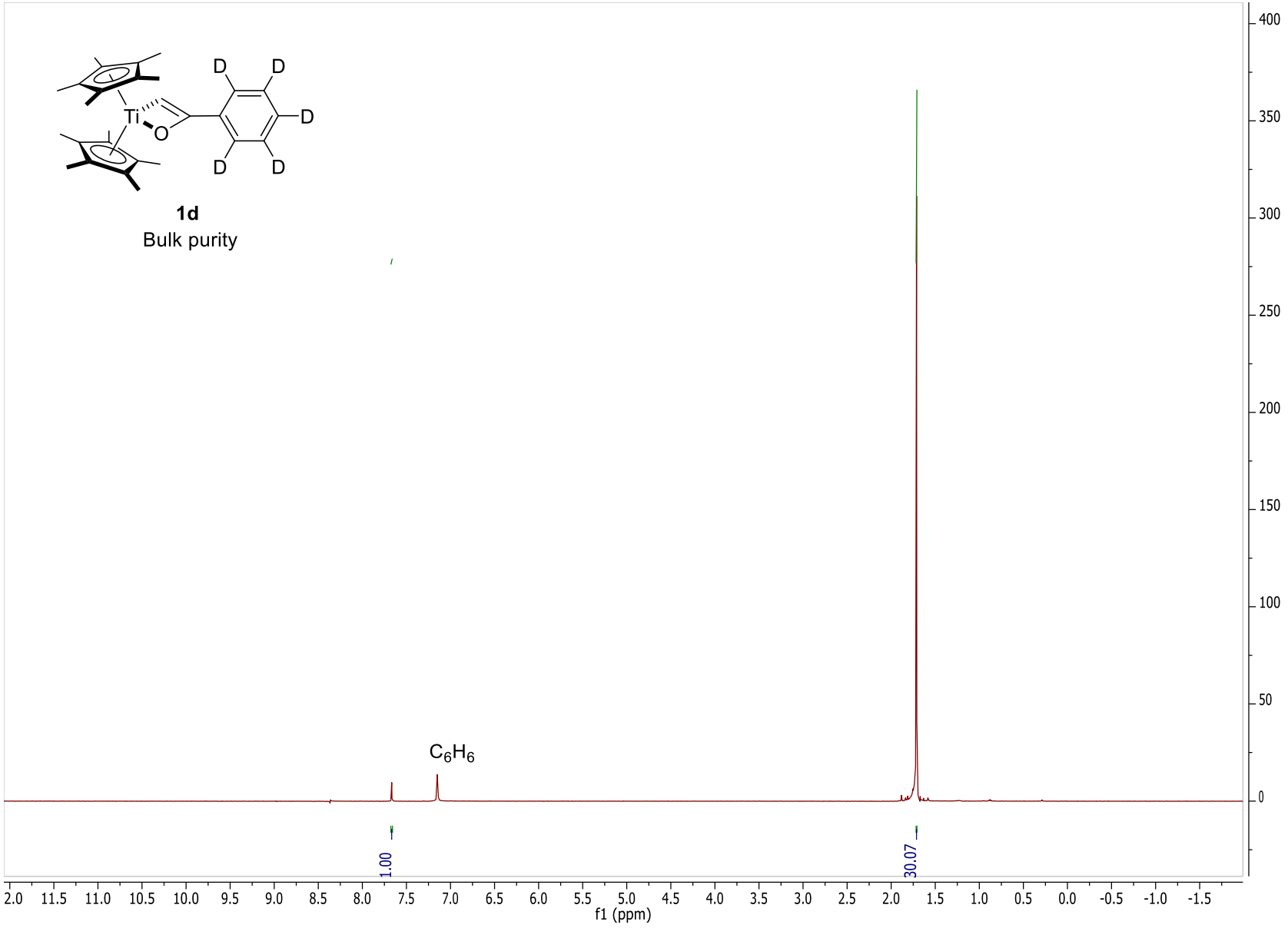
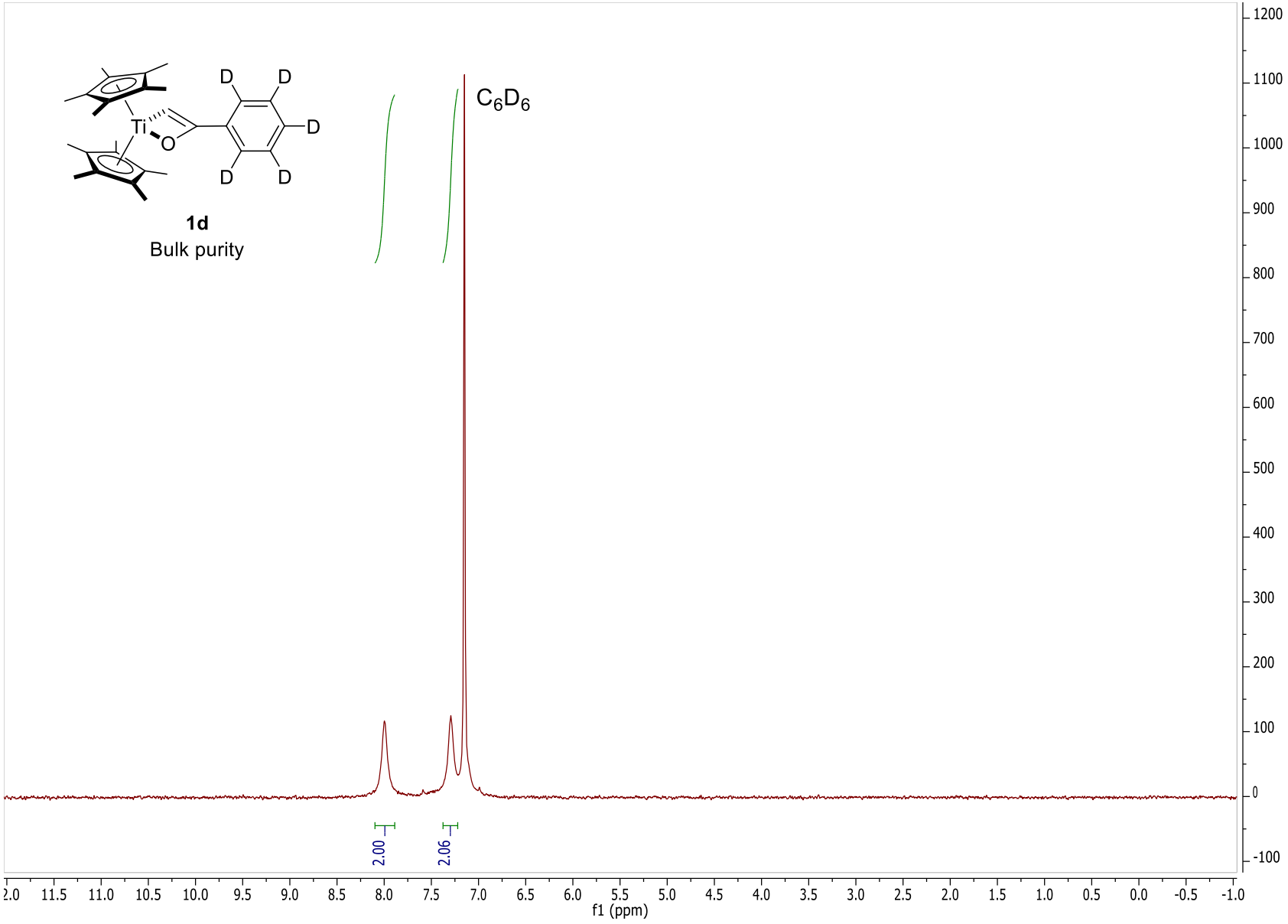
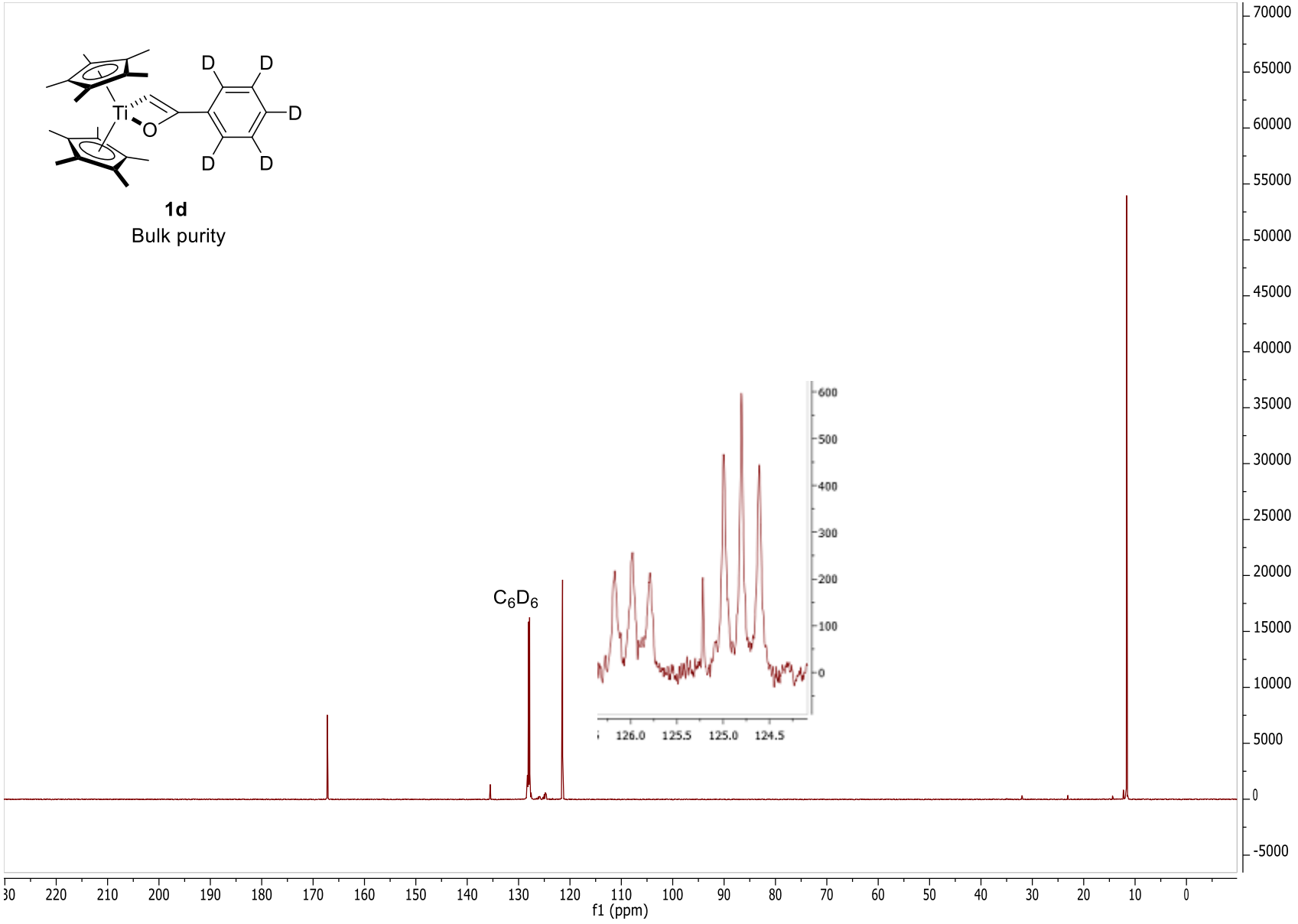
Ti
O
1c
Bulk purity
C6H6
2.00
2.07
1.10
30.02
f1 (ppm)

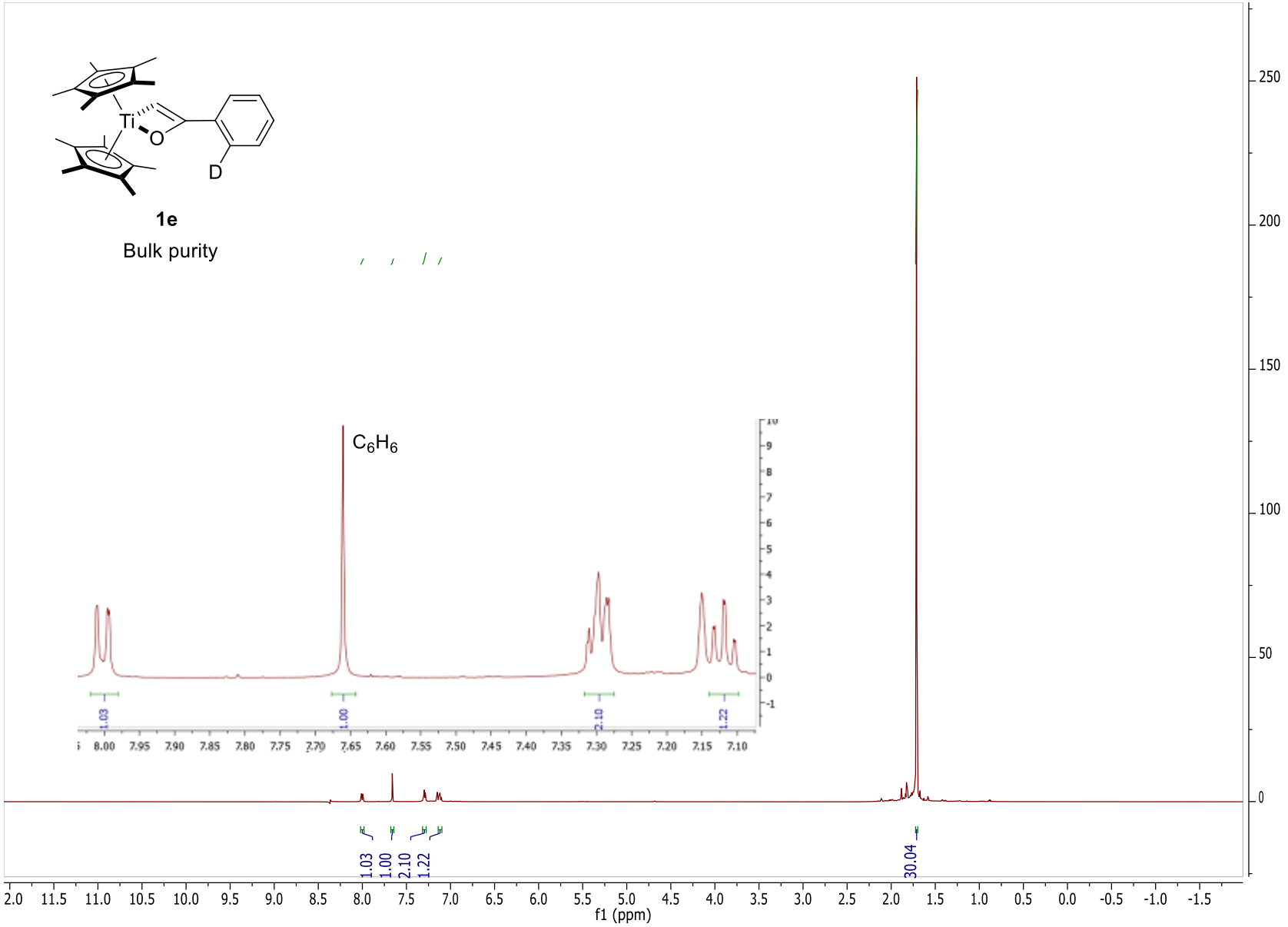

D
Ti
O
1c
Bulk purity
C6D6
1.00
f1 (ppm)

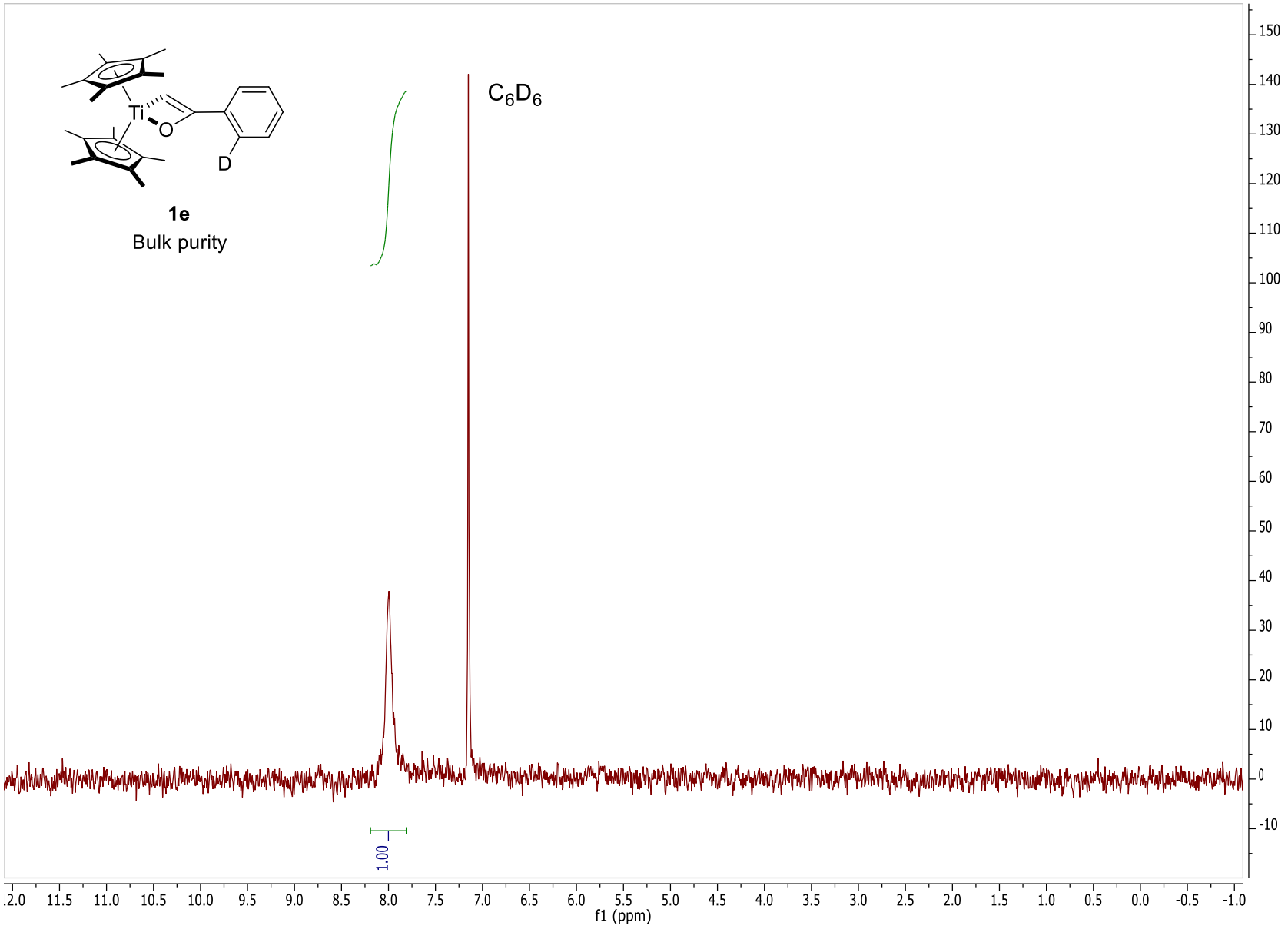

D
Ti
O
1c
Bulk purity
C6D6
167.5
167.0
166.5
f1 (ppm)


D
D
D
D
D
Ti
O
1d
Bulk purity
C6H6
1.00
30.07
f1 (ppm)


D
D
D
D
D
Ti
O
1d
Bulk purity
C6D6
2.00
2.06
f1 (ppm)


D
D
D
D
D
Ti
O
1d
Bulk purity
C6D6
f1 (ppm)


Ti
O
D
1e
Bulk purity
C6H6
1.03
1.00
2.10
1.22
30.04
f1 (ppm)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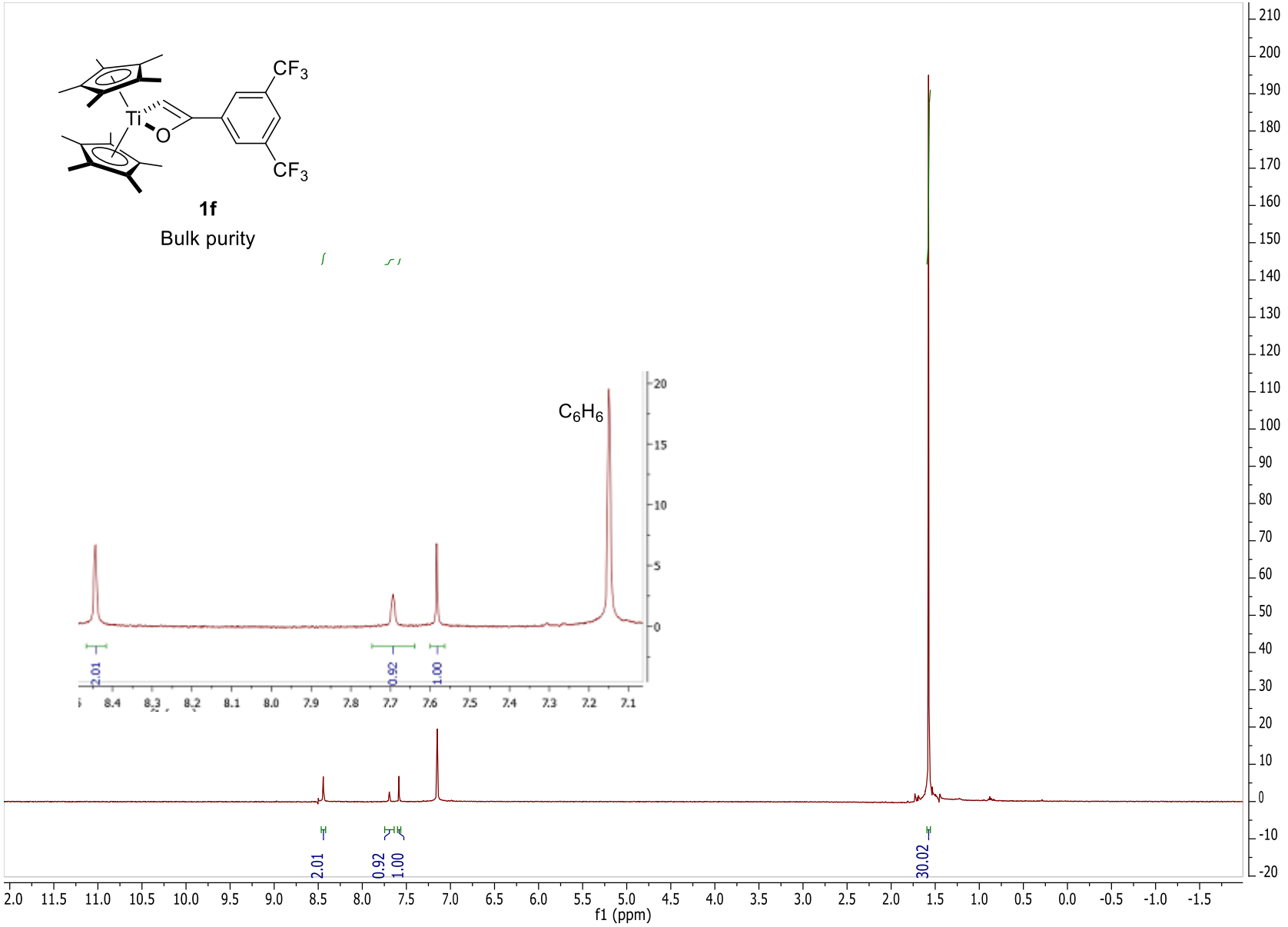
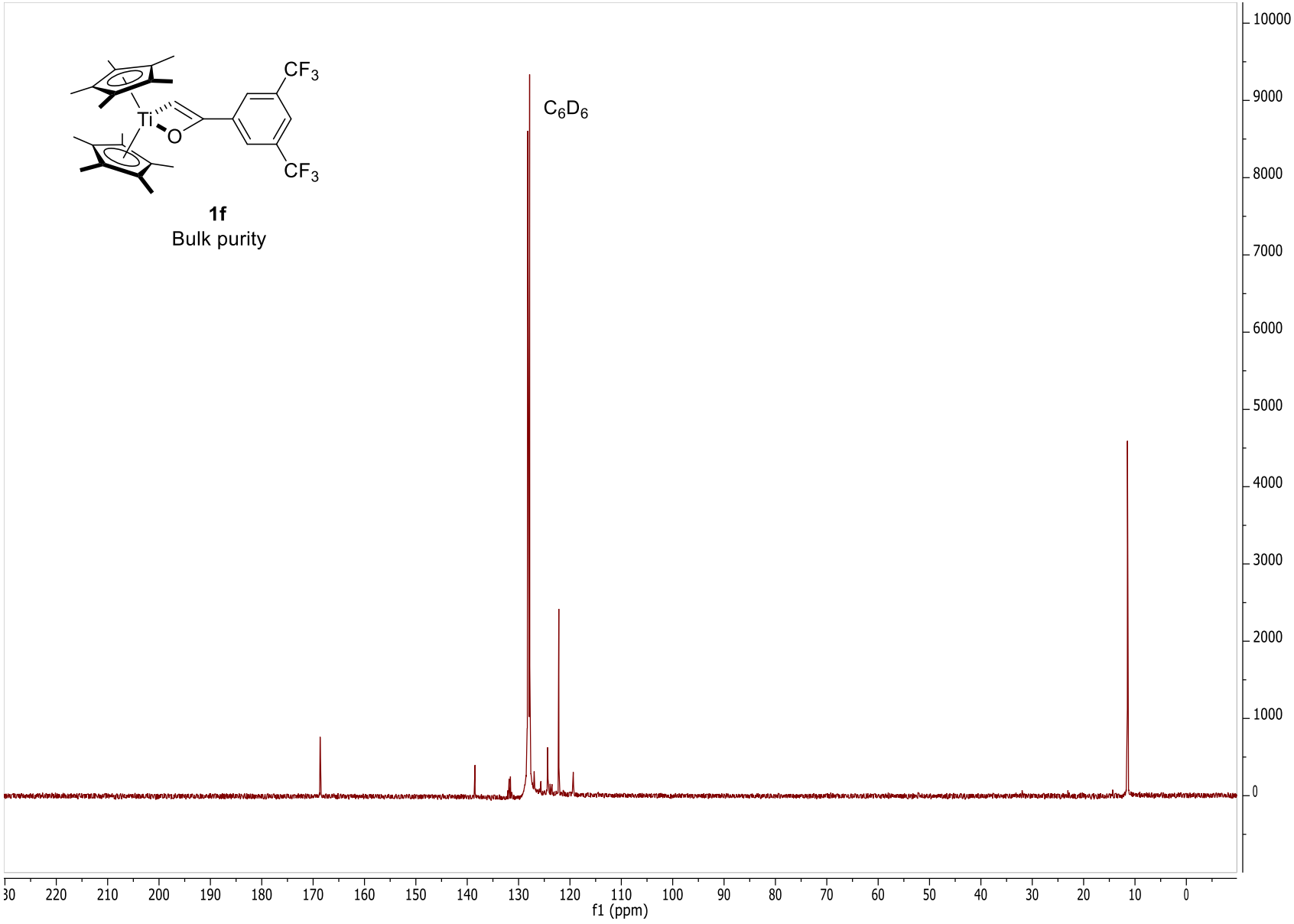
O
D
1e
Bulk purity
C6D6
1.00
f1 (ppm)


CF3
Ti
O
CF3
1f
Bulk purity
C6H6
2.01
0.92
1.00
30.02
f1 (ppm)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Ti
O
CF3
1f
Bulk purity
C6D6
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9000
8000
7000
6000
5000
4000
3000
2000
1000
0
220
210
200
190
180
170
160
150
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130
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110
100
90
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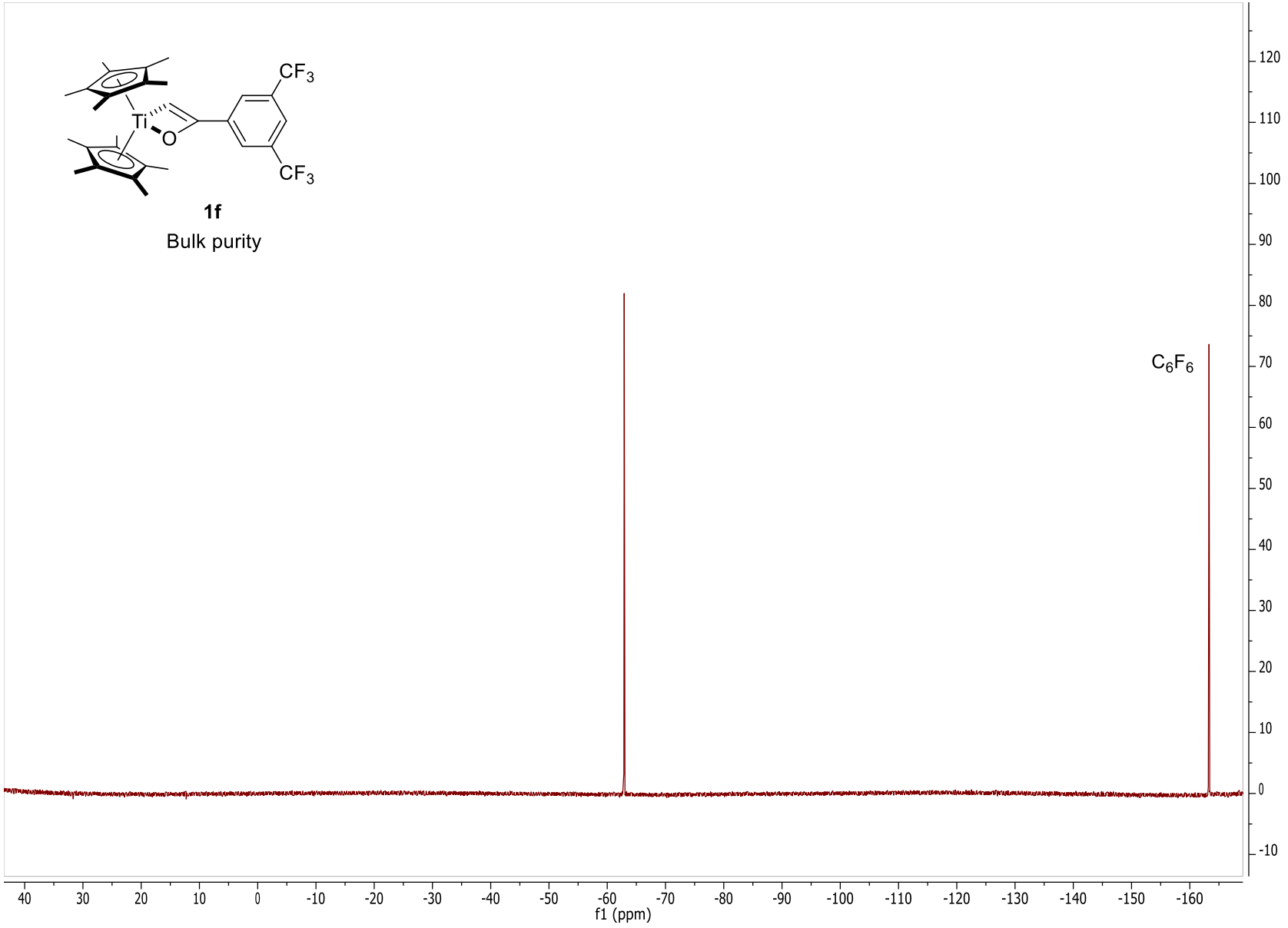
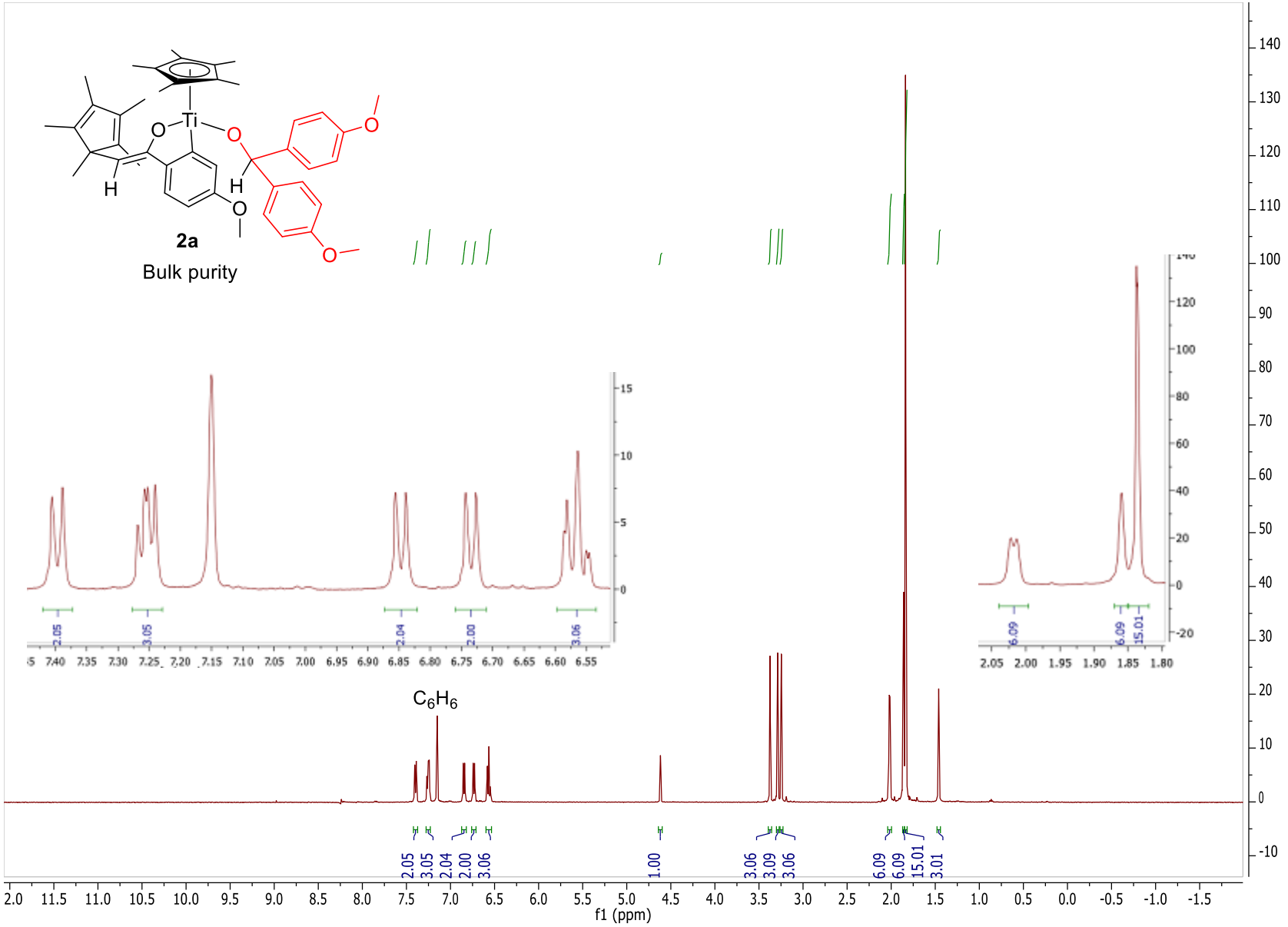
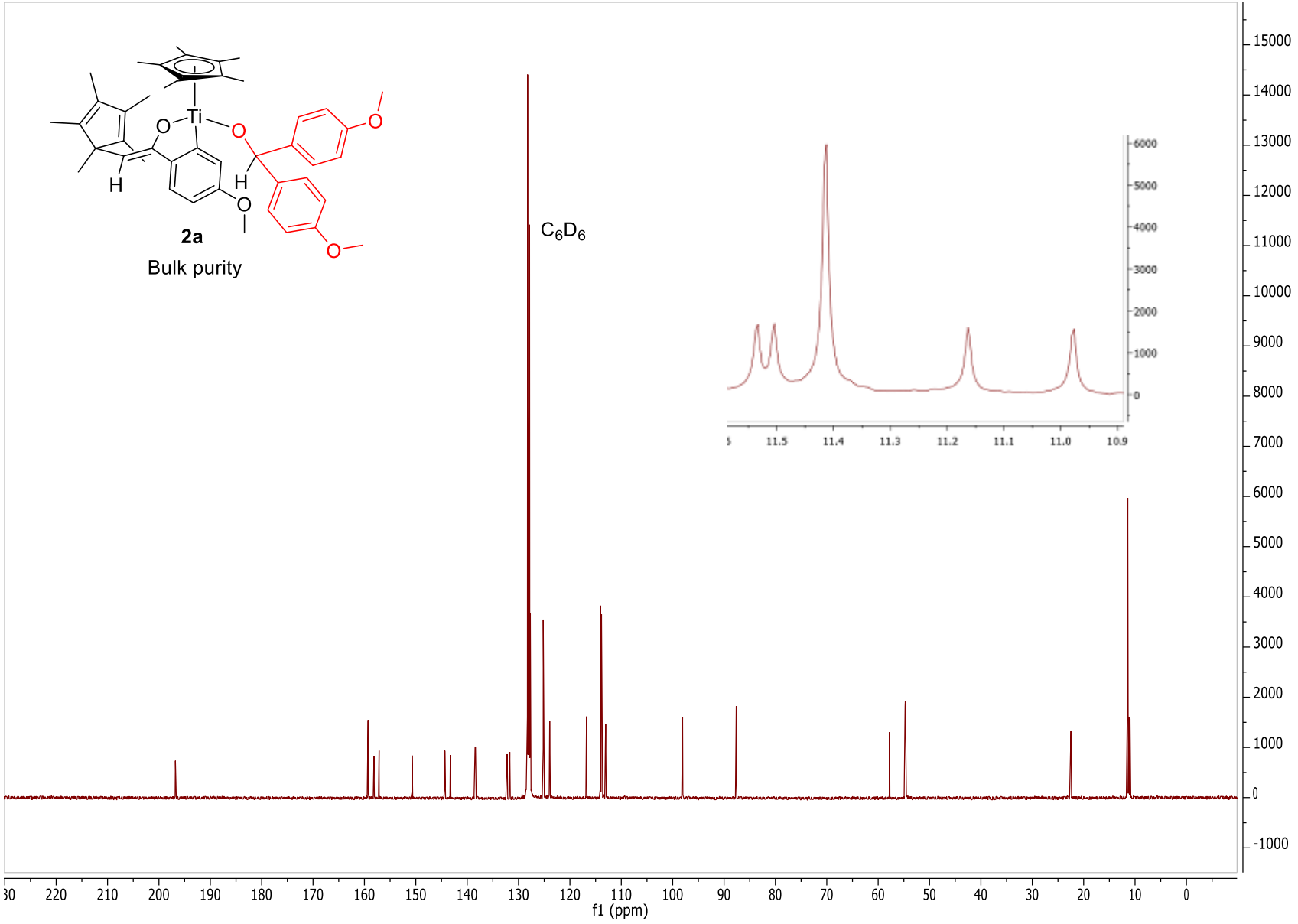
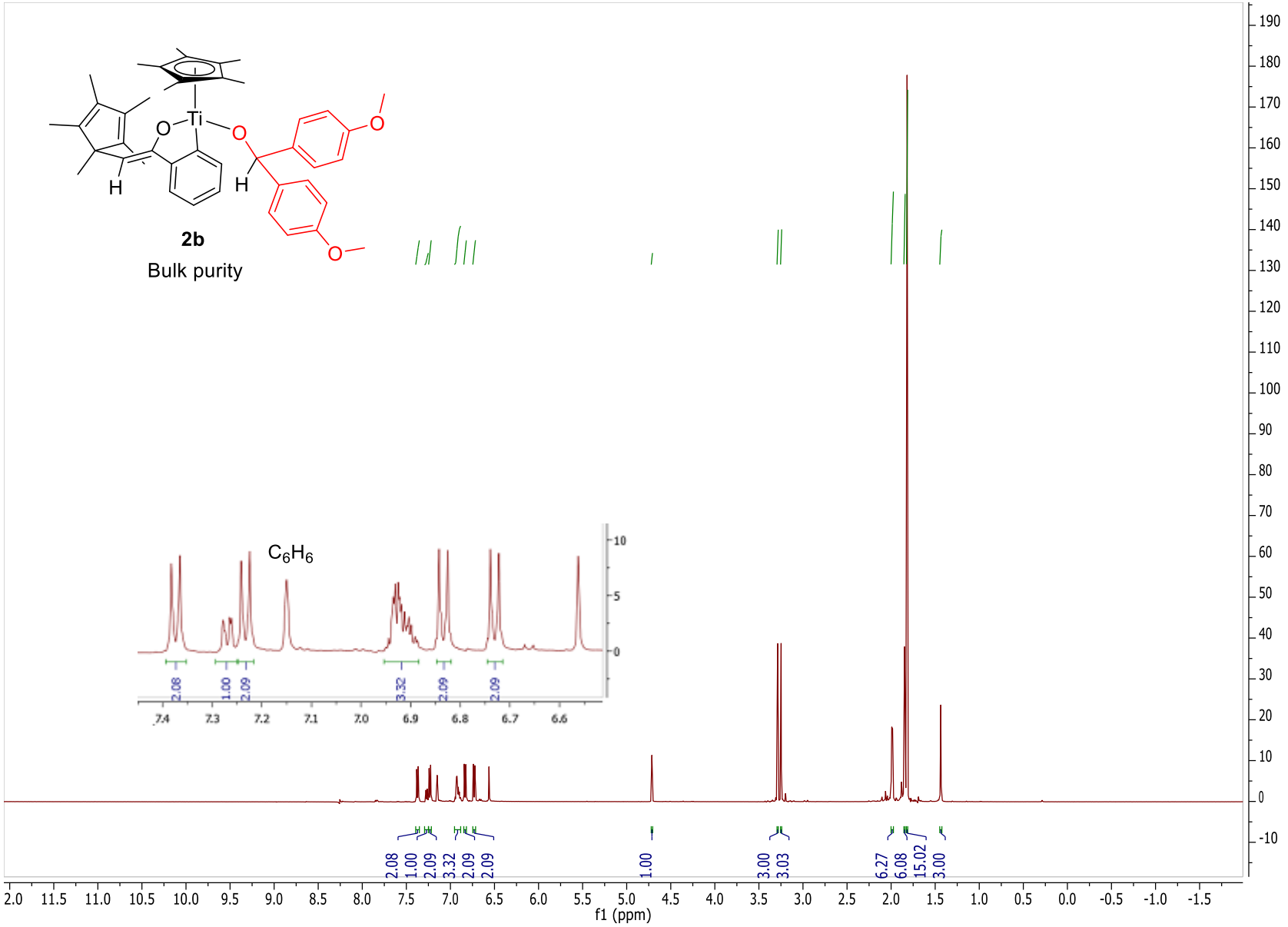
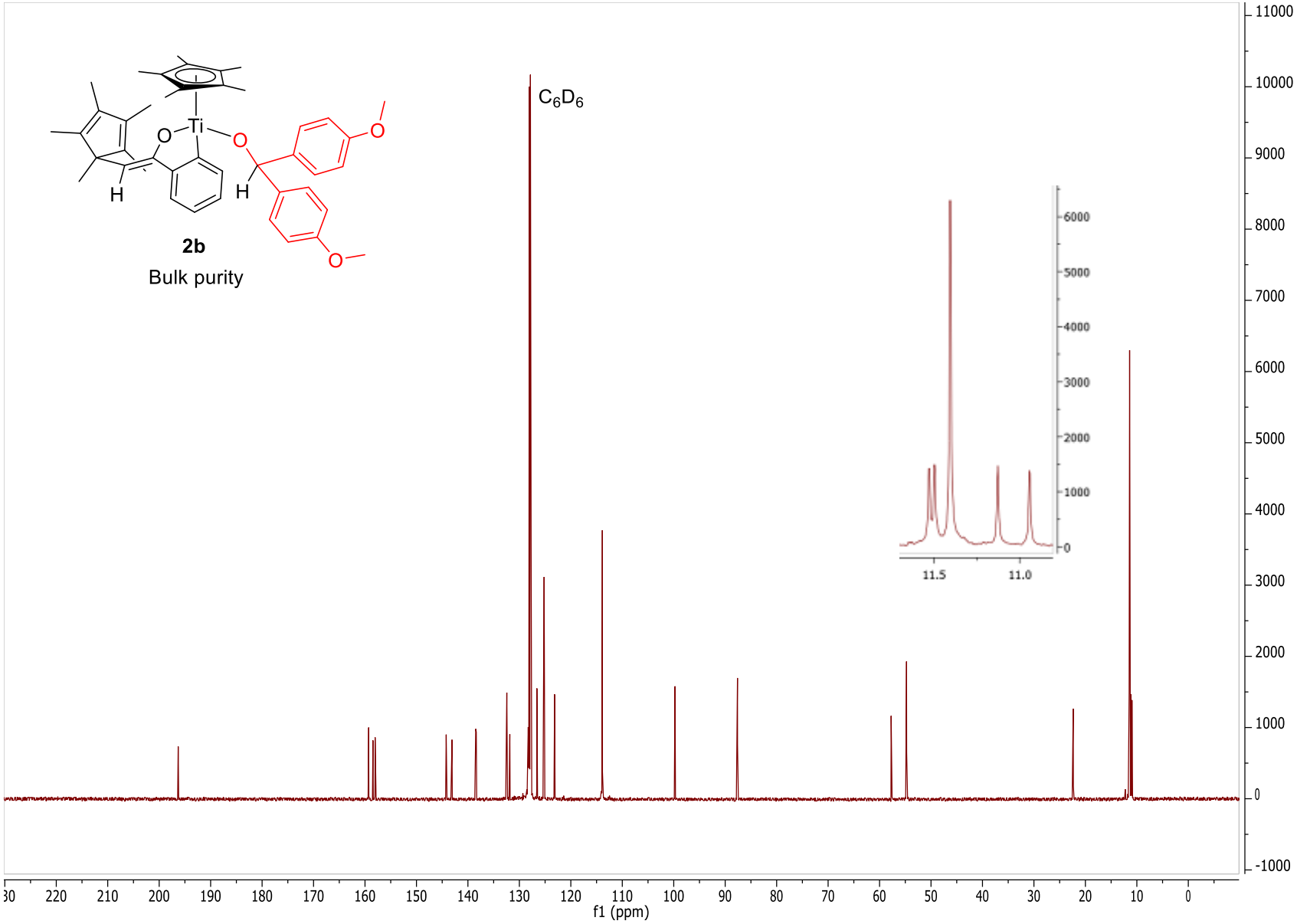
70
60
50
40
30
20
10
0
f1 (ppm)

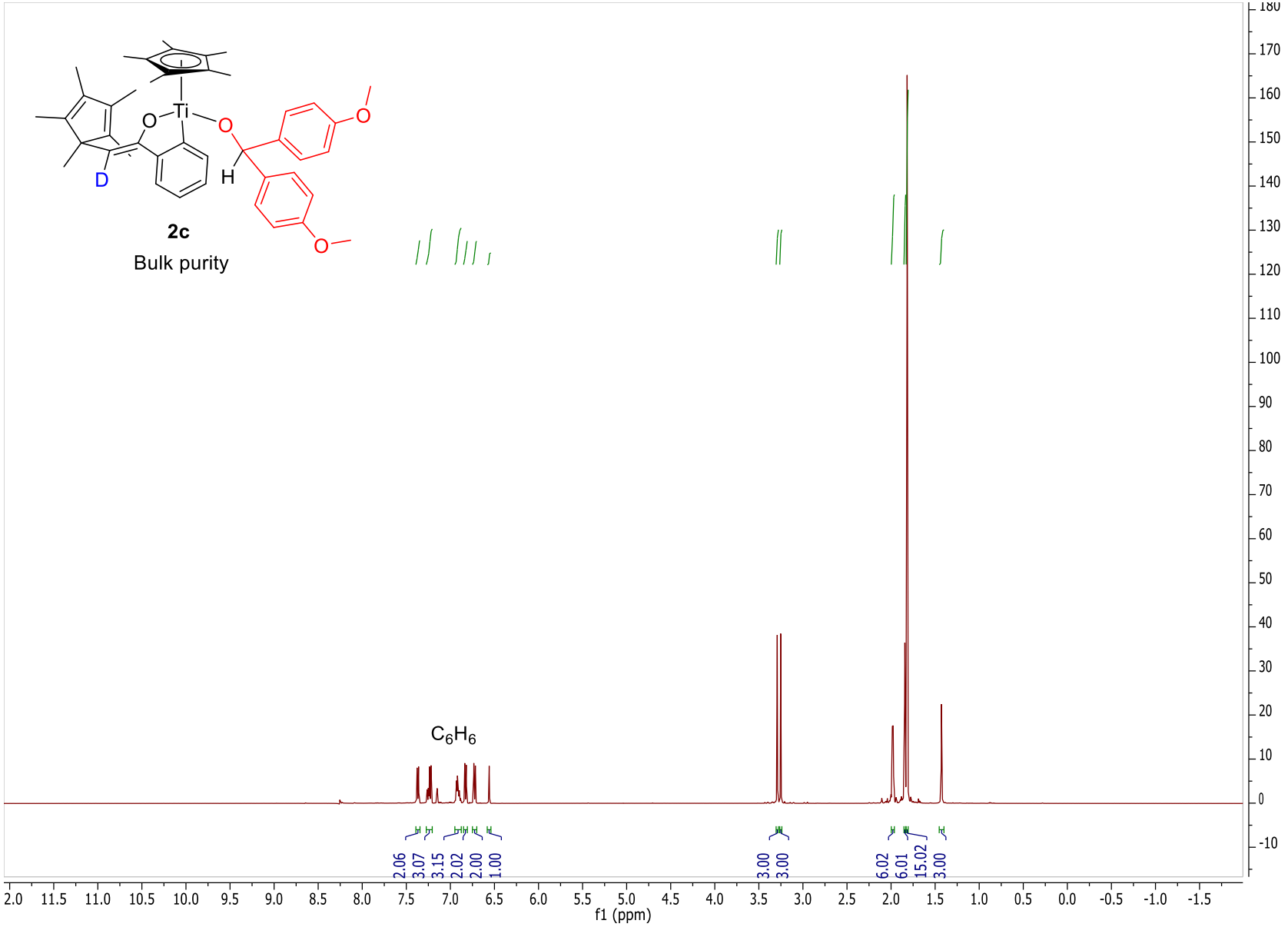

CF3
Ti
O
CF3
1f
Bulk purity
C6F6
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)


2a
Bulk purity
C6H6
f1 (ppm)


2a
Bulk purity
C6D6
f1 (ppm)


2b
Bulk purity
C6H6
f1 (ppm)


2b
Bulk purity
C6D6
f1 (ppm)


Ti
O
O
O
O
D
H
2c
Bulk purity
C6H6
2.06
3.07
3.15
2.02
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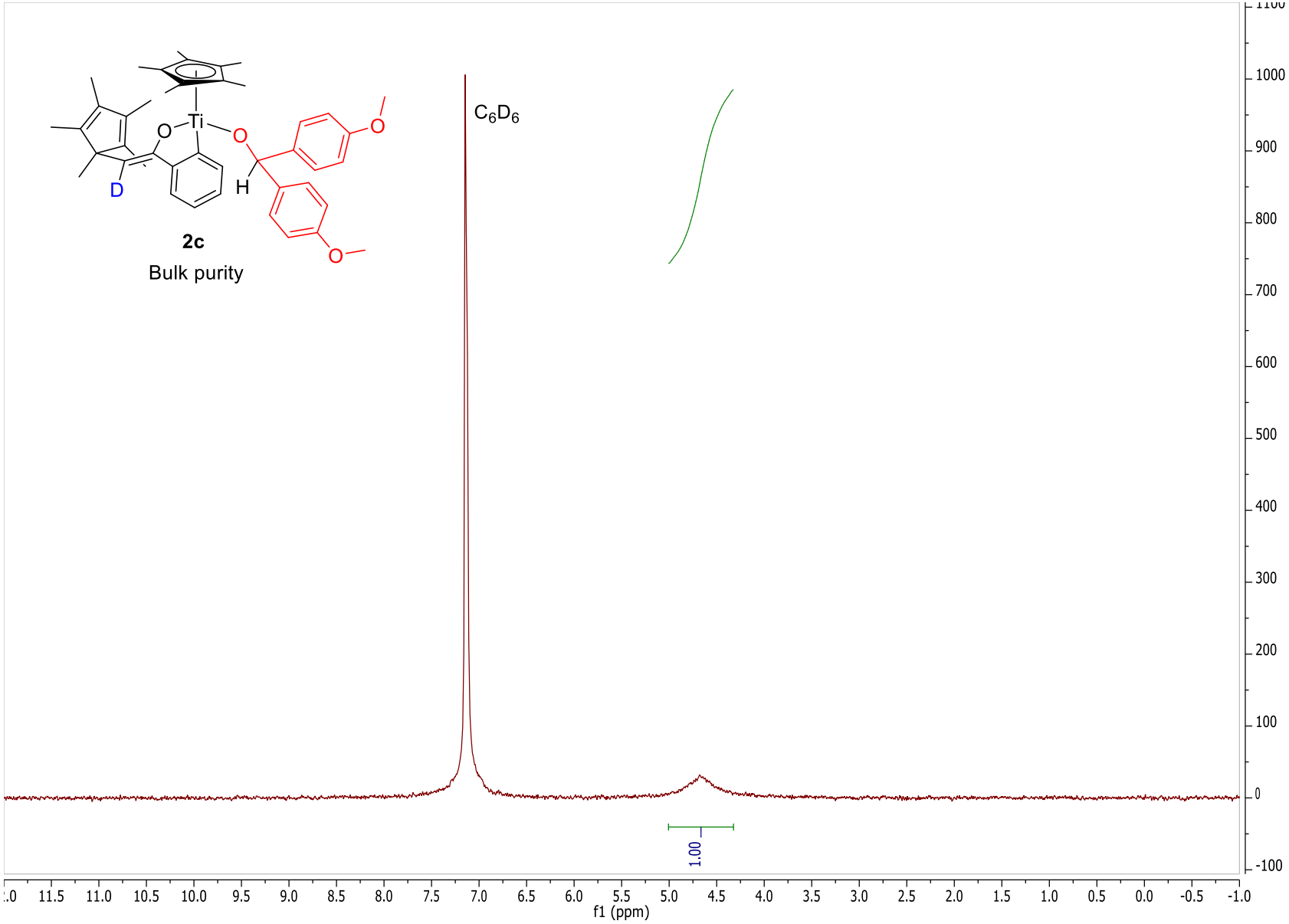
6.02
6.01
15.02
3.00
f1 (ppm)


Ti
O
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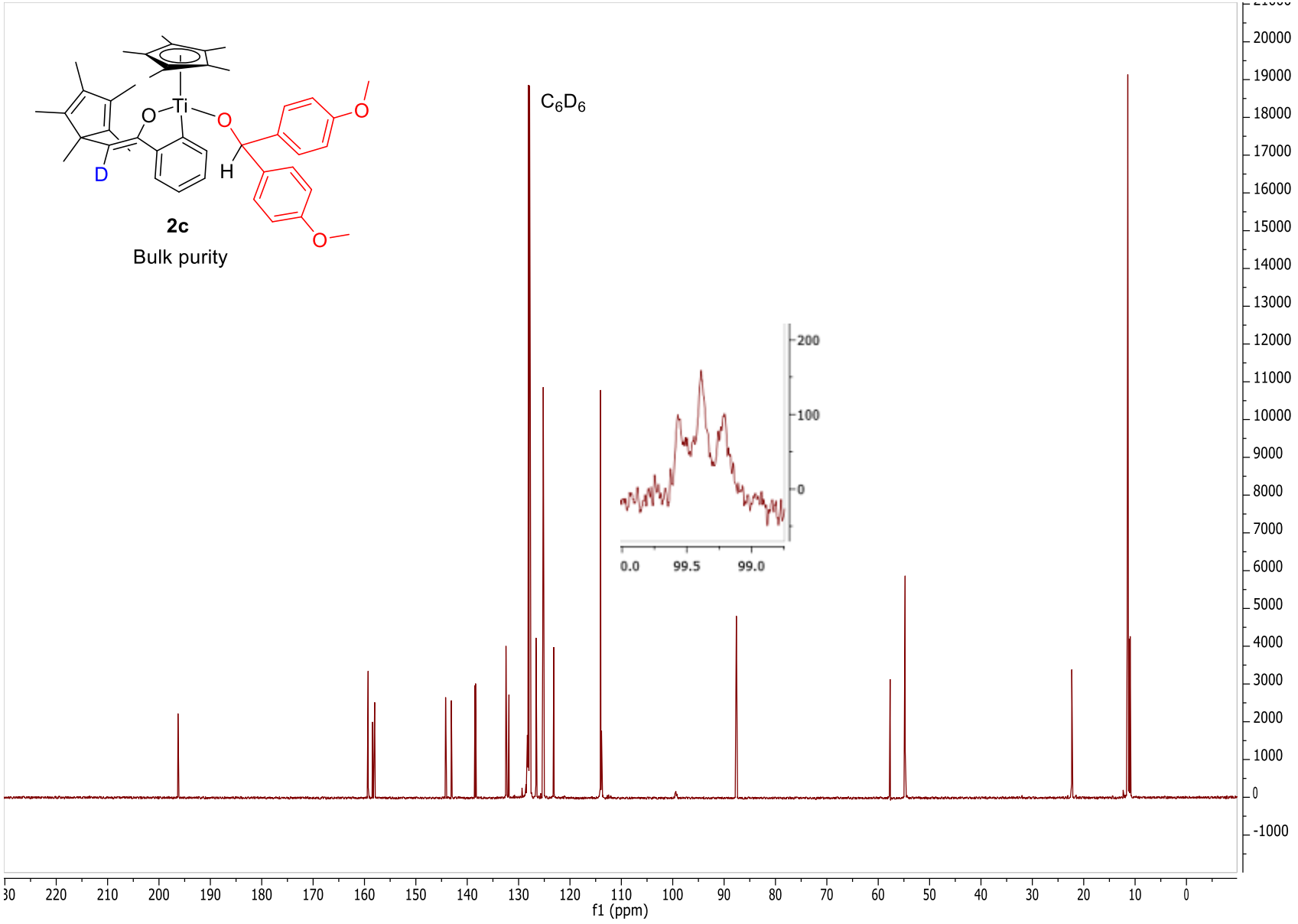
O
O
D
H
2c
Bulk purity
C6D6
1.00
f1 (ppm)


Ti
O
O
O
O
D
H
2c
Bulk purity
C6D6
200
100
0
0.0
99.5
99.0
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
220
210
200
190
180
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40
30
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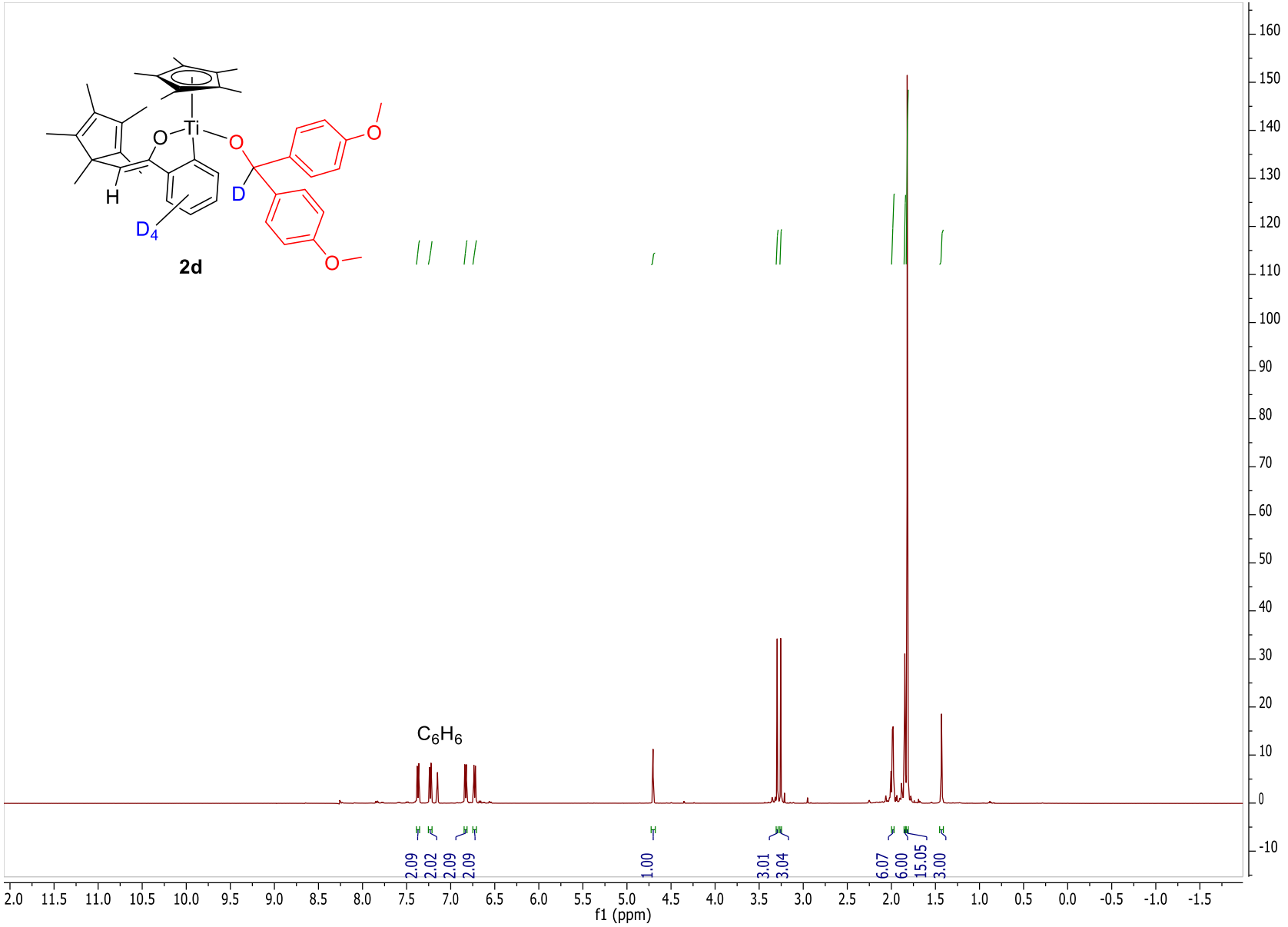
10
0
f1 (ppm)


Ti
O
O
O
O
H
D
D4
2d
C6H6
2.09
2.02
2.09
2.09
1.00
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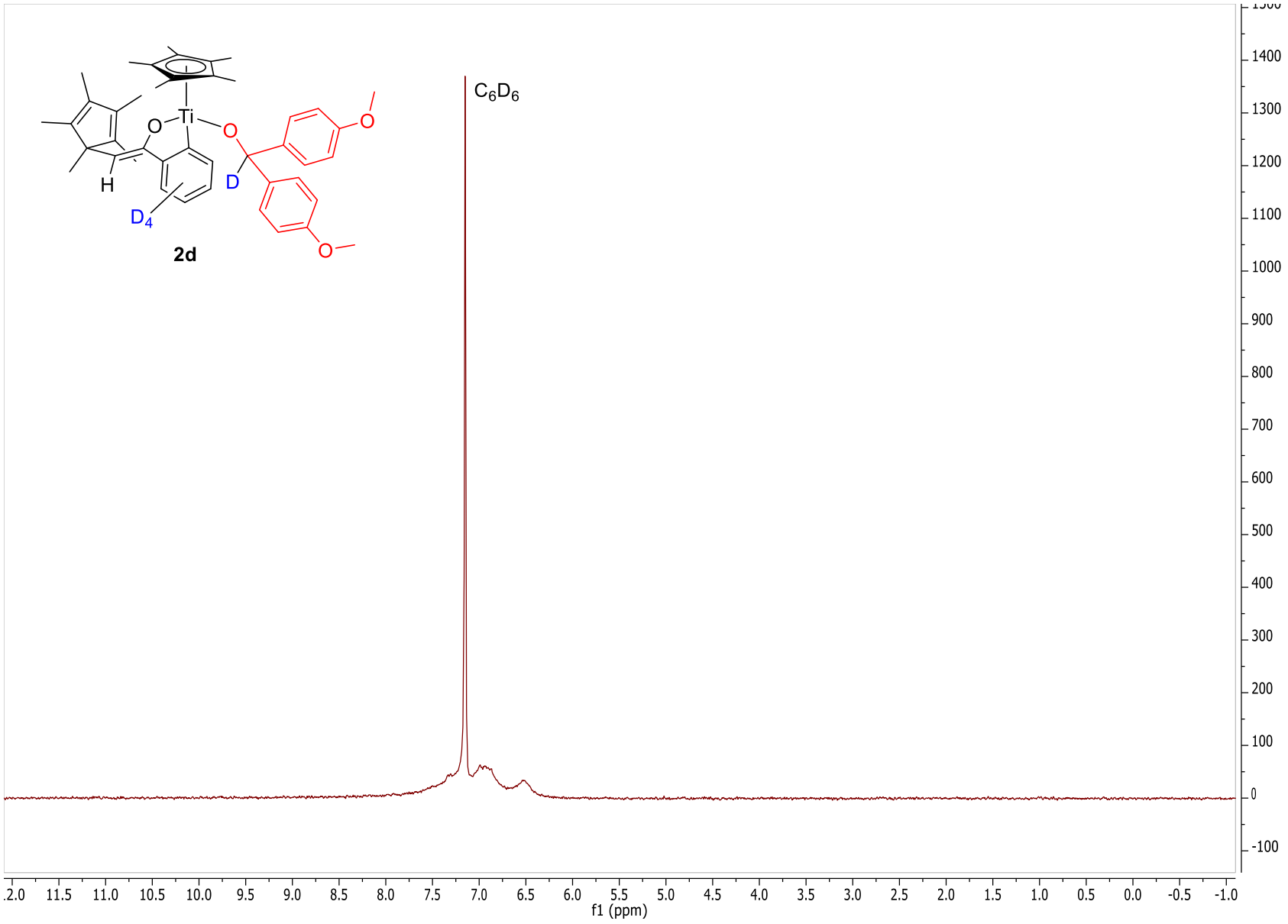
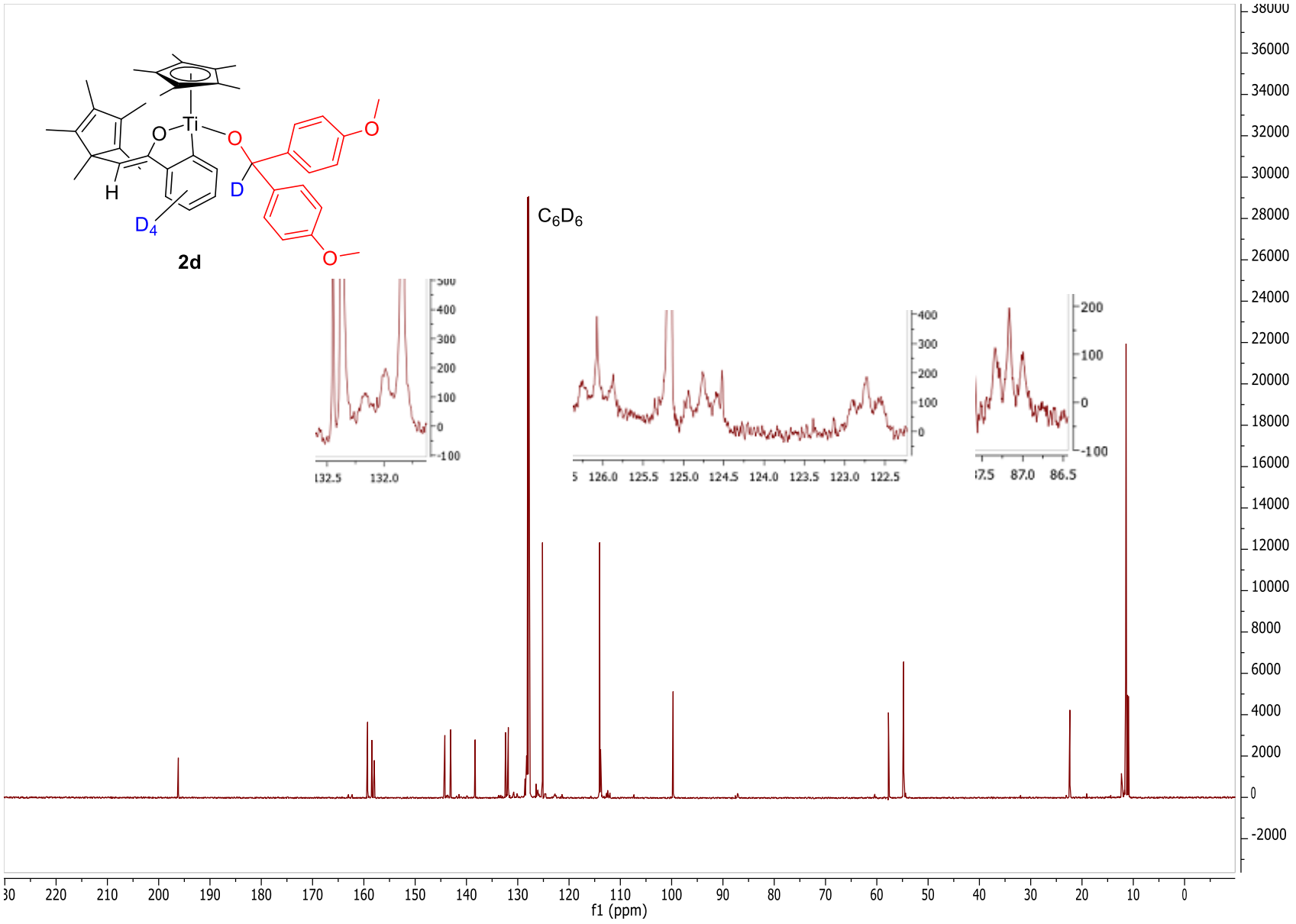
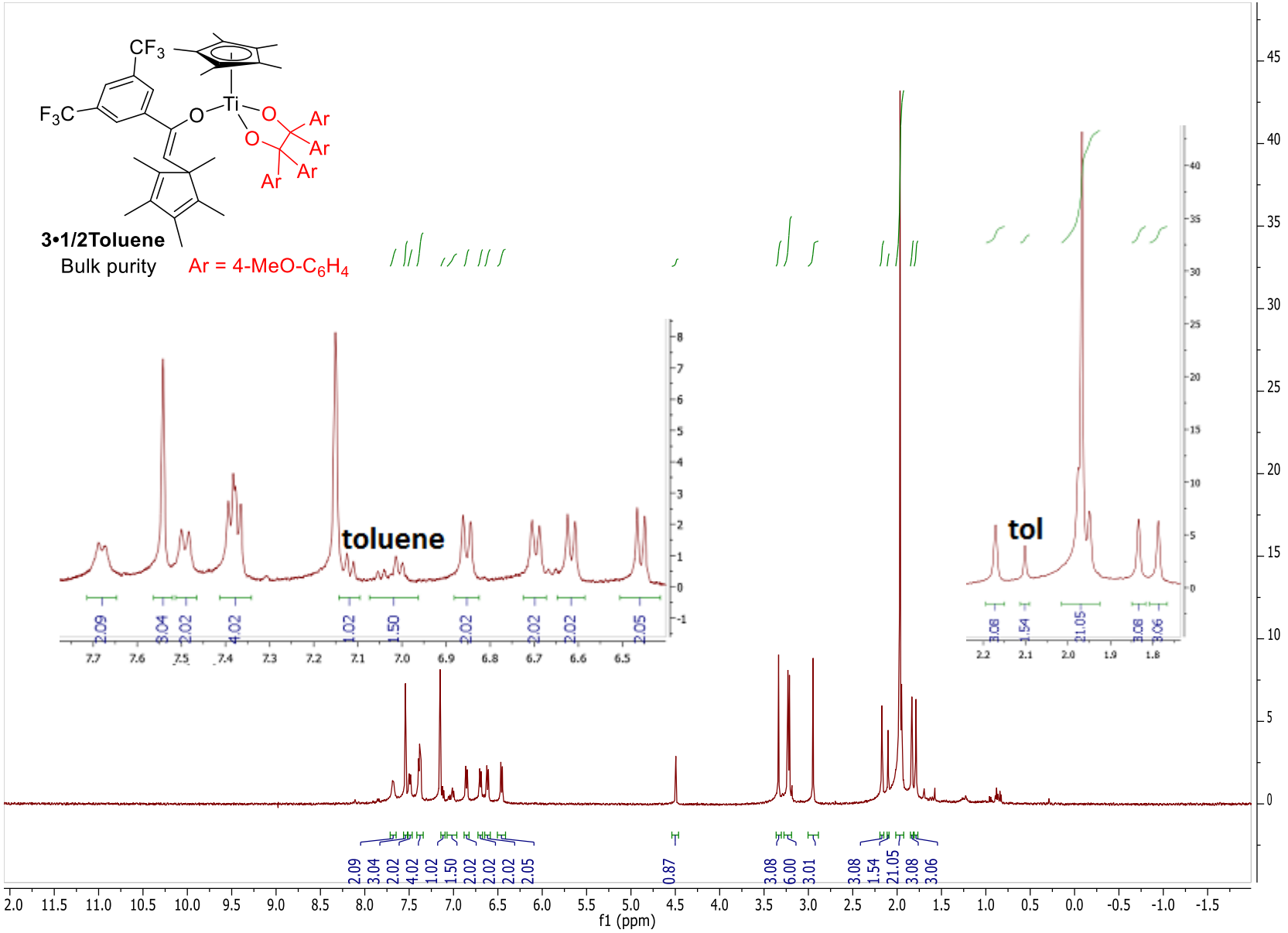
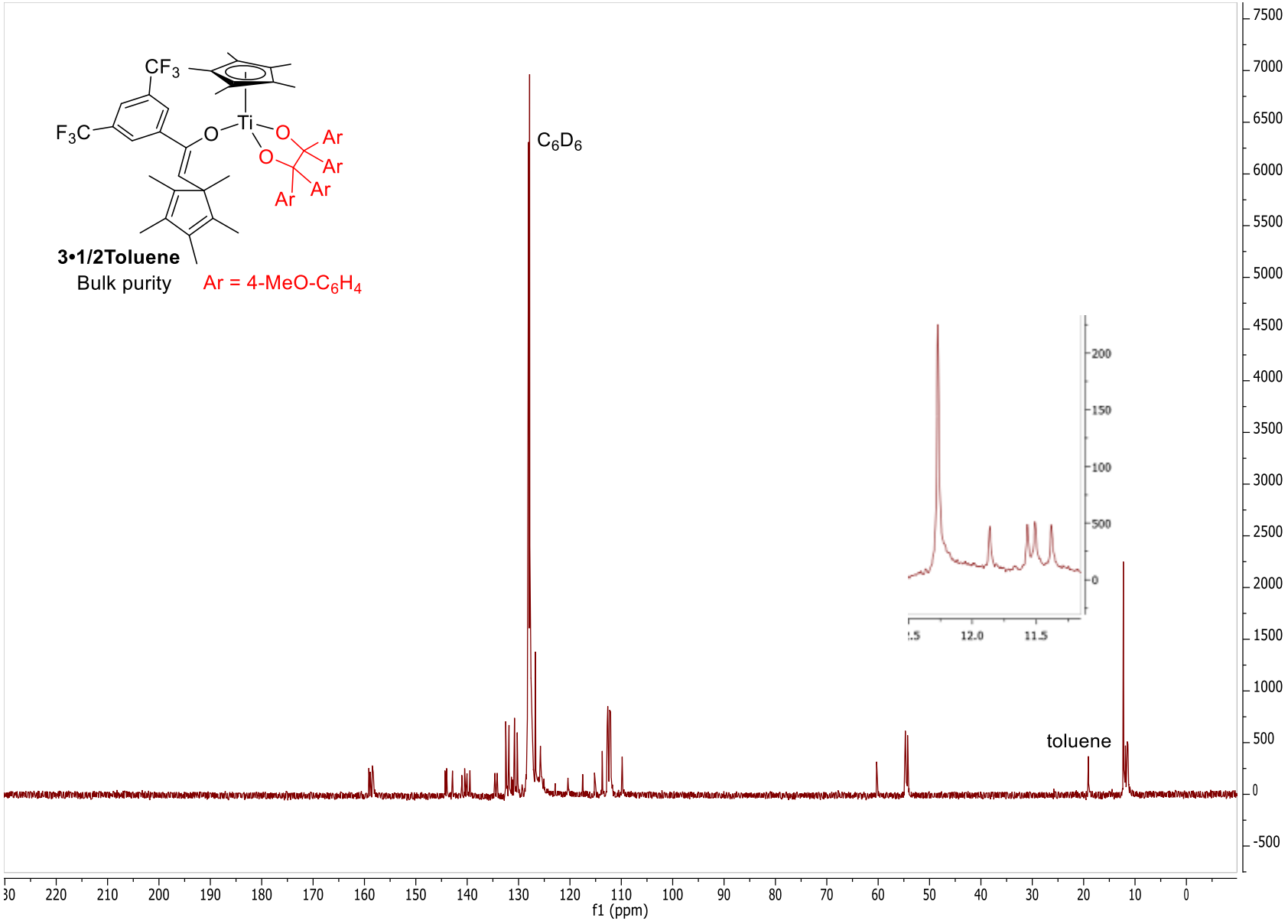
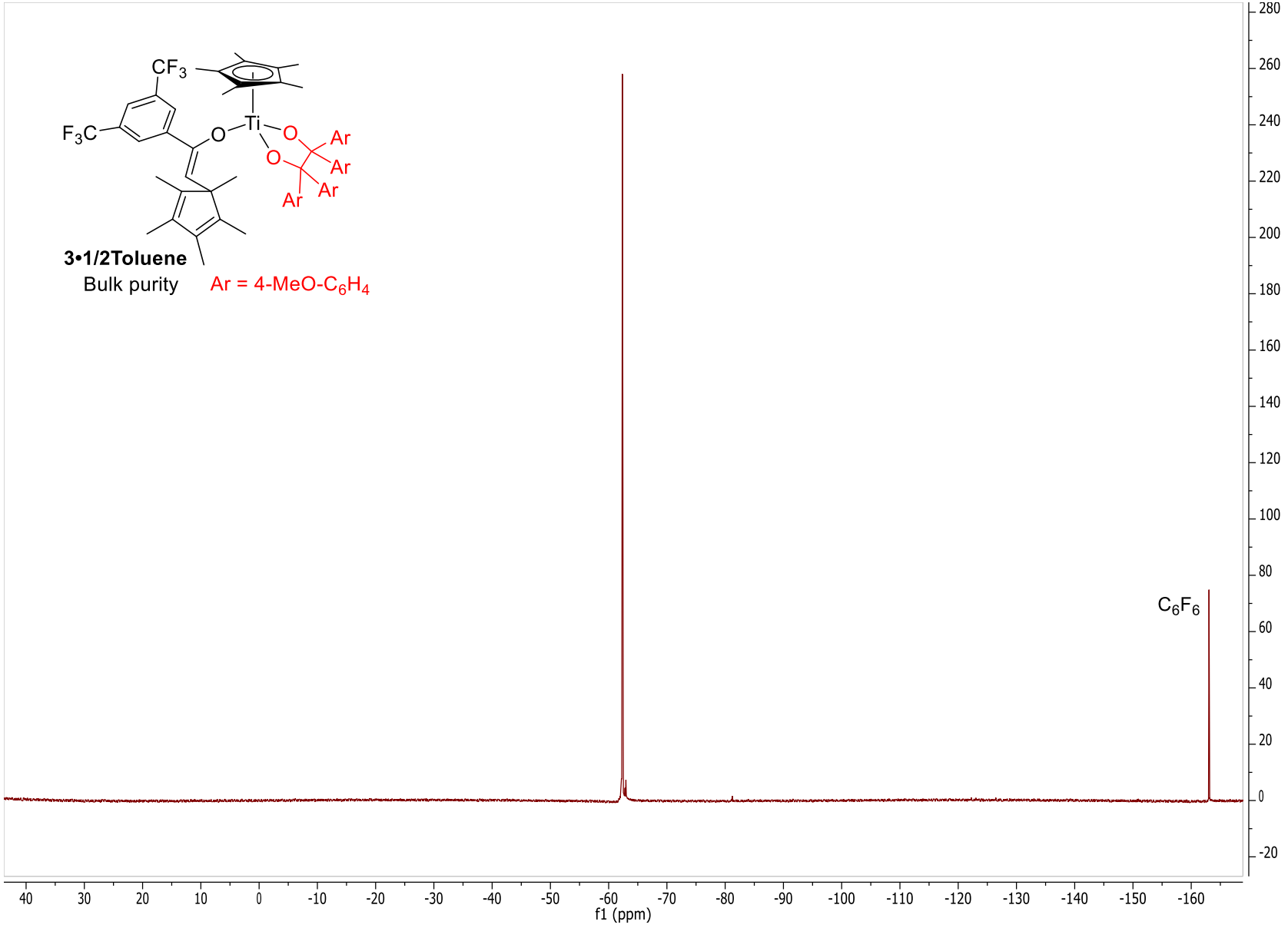
6.07
6.00
15.05
3.00
f1 (ppm)

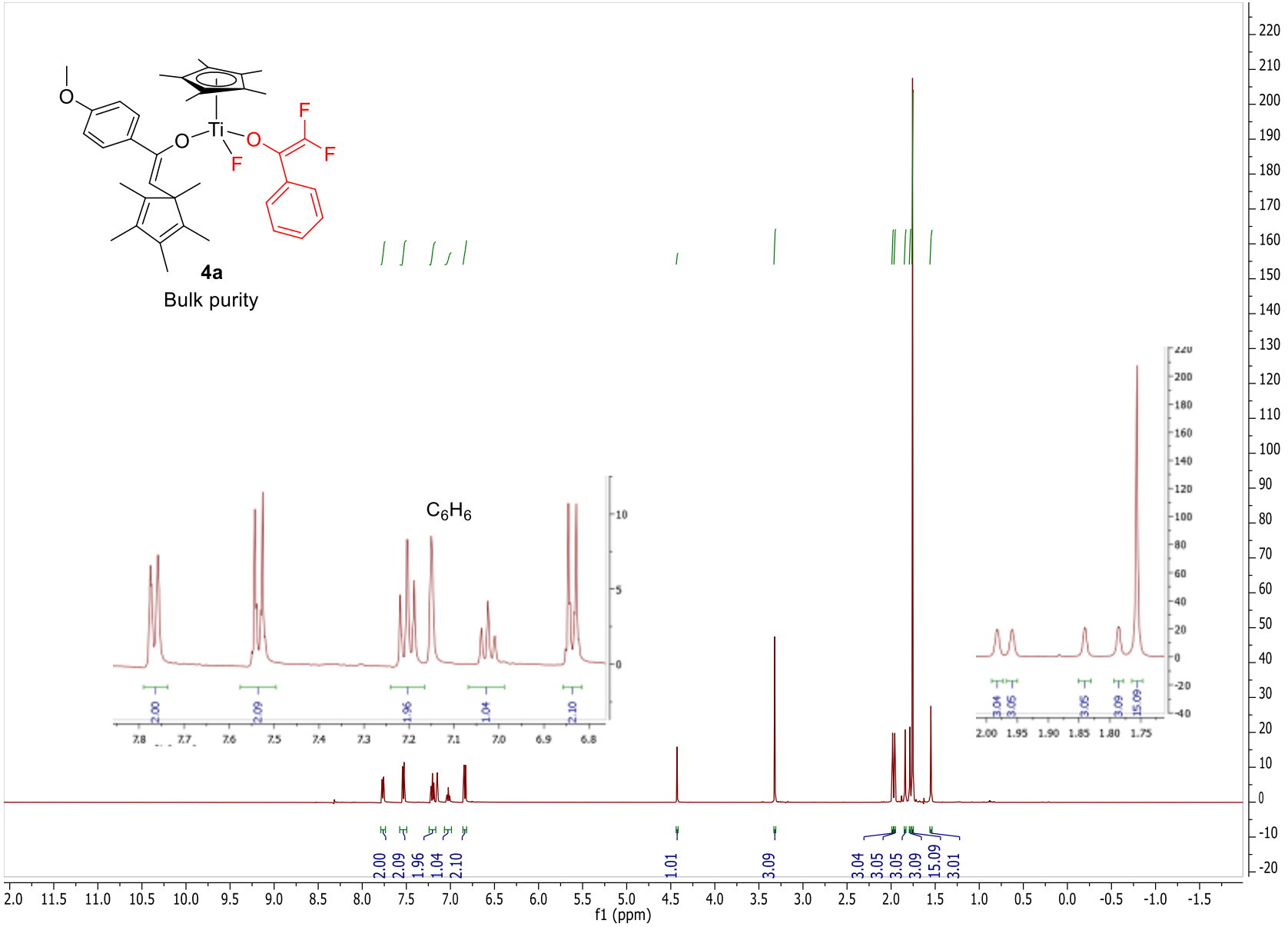

C6D6
O
Ti
O
O
H
D
D4
O
2d
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
.2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

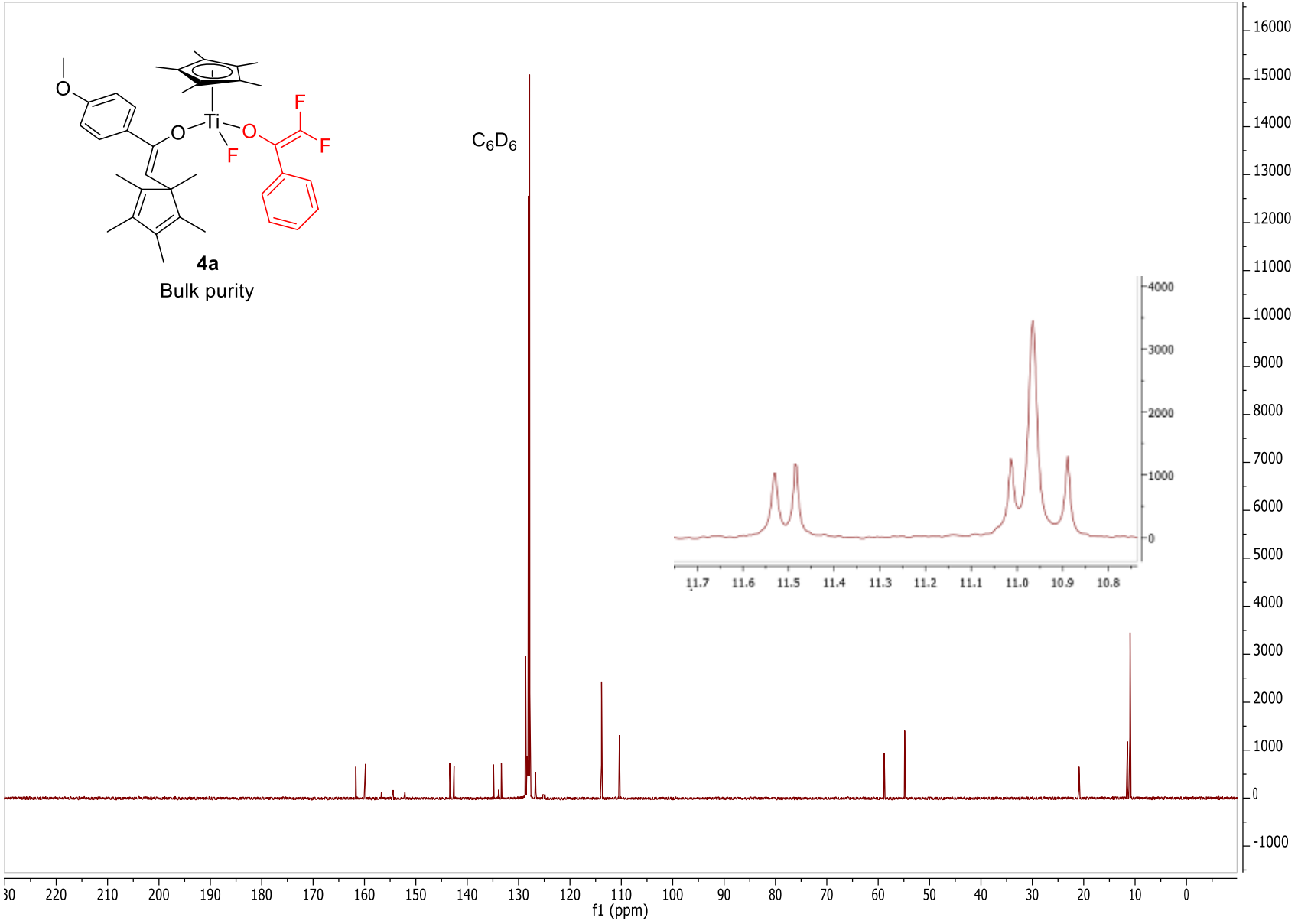

2d
C6D6
f1 (ppm)

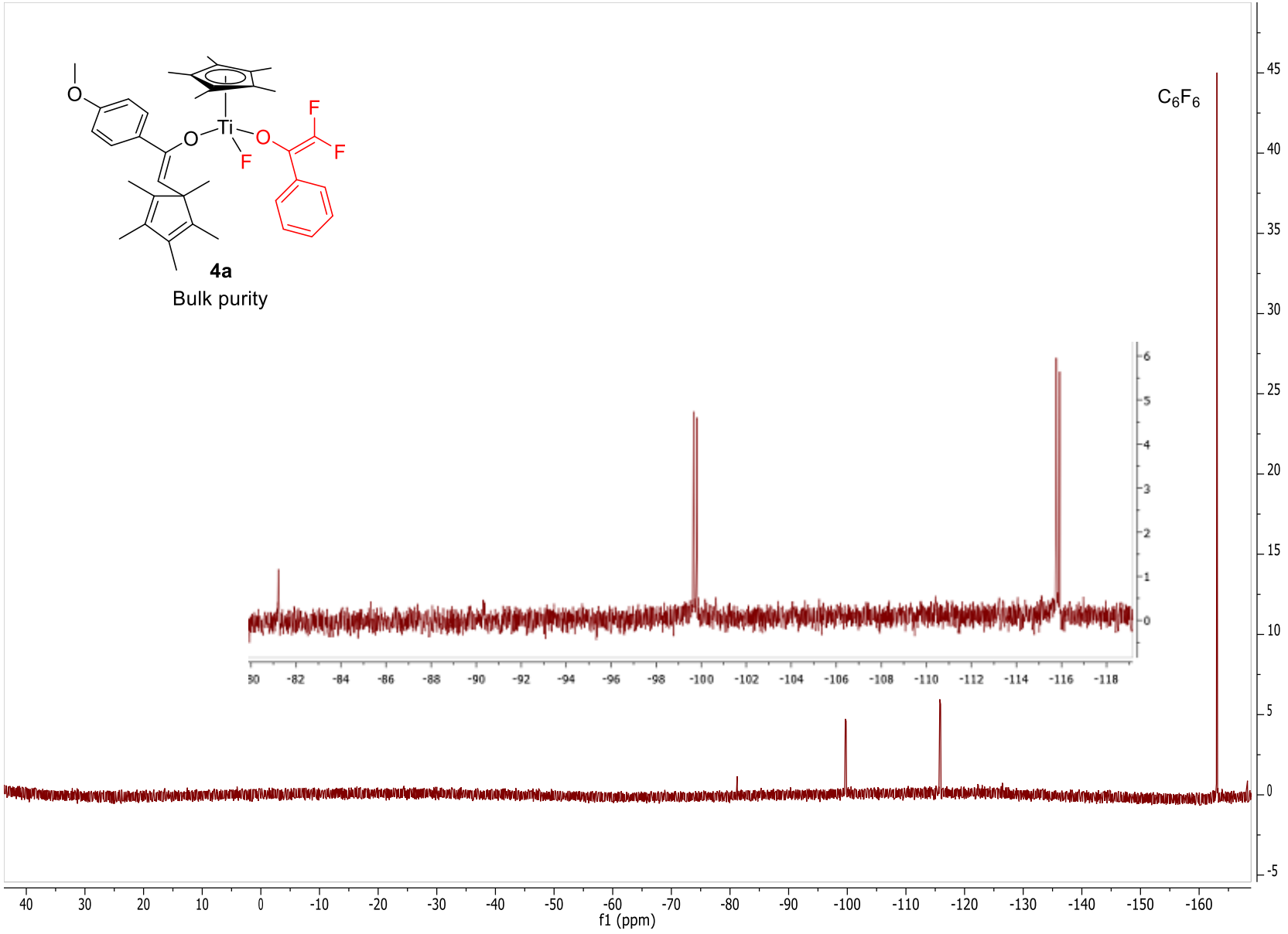

CF3
F3C
O
Ti
O
O
Ar
Ar
Ar
Ar
3•1/2Toluene
Bulk purity
Ar = 4-MeO-C6H4
toluene
tol
2.09
3.04
2.02
4.02
1.02
1.50
2.02
2.02
2.02
2.05
0.87
3.08
6.00
3.01
3.08
1.54
21.05
3.08
3.06
f1 (ppm)

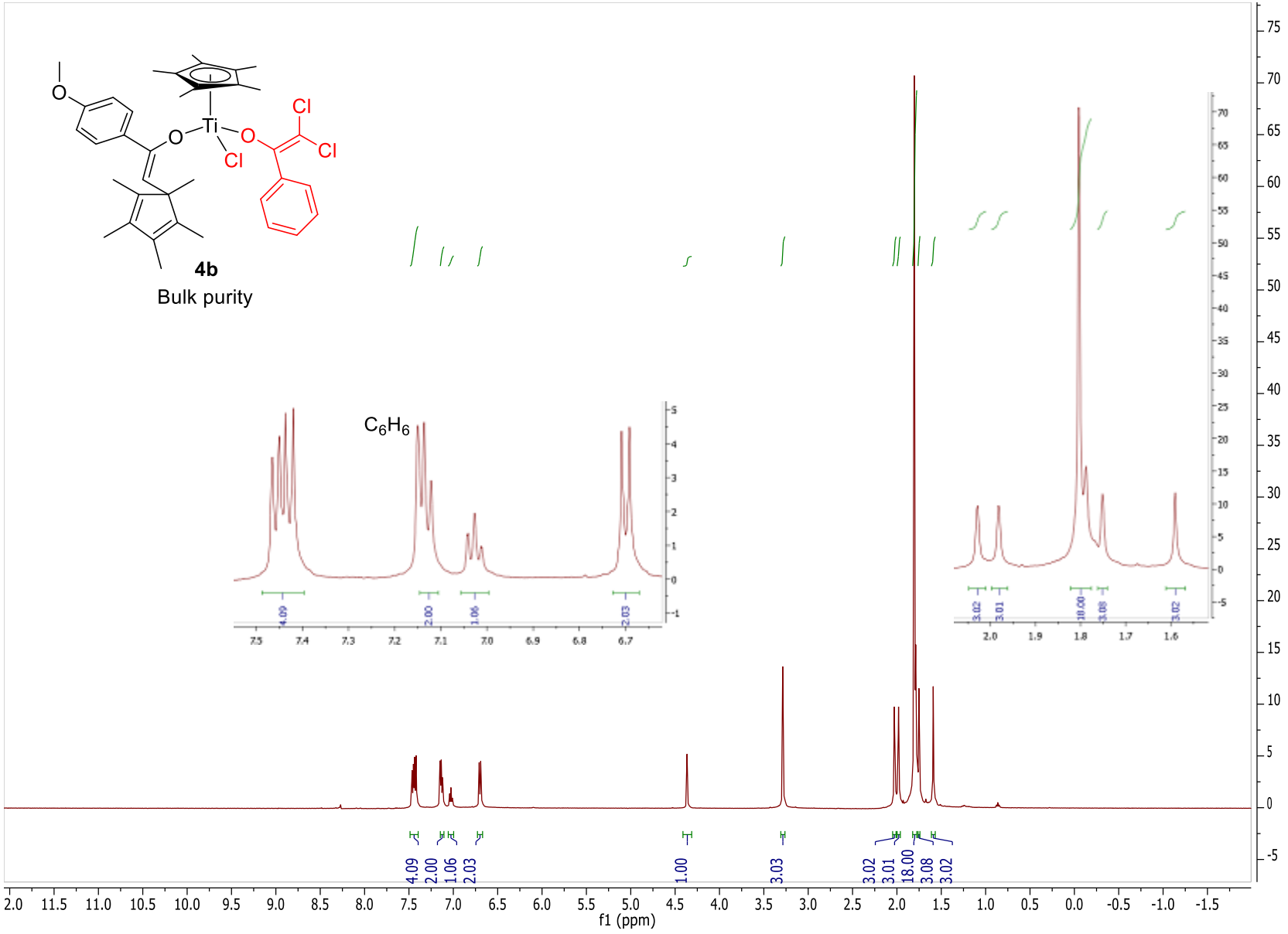

CF3
F3C
O
Ti
O
O
Ar
Ar
Ar
Ar
3•1/2Toluene
Bulk purity
Ar = 4-MeO-C6H4
C6D6
toluene
f1 (ppm)

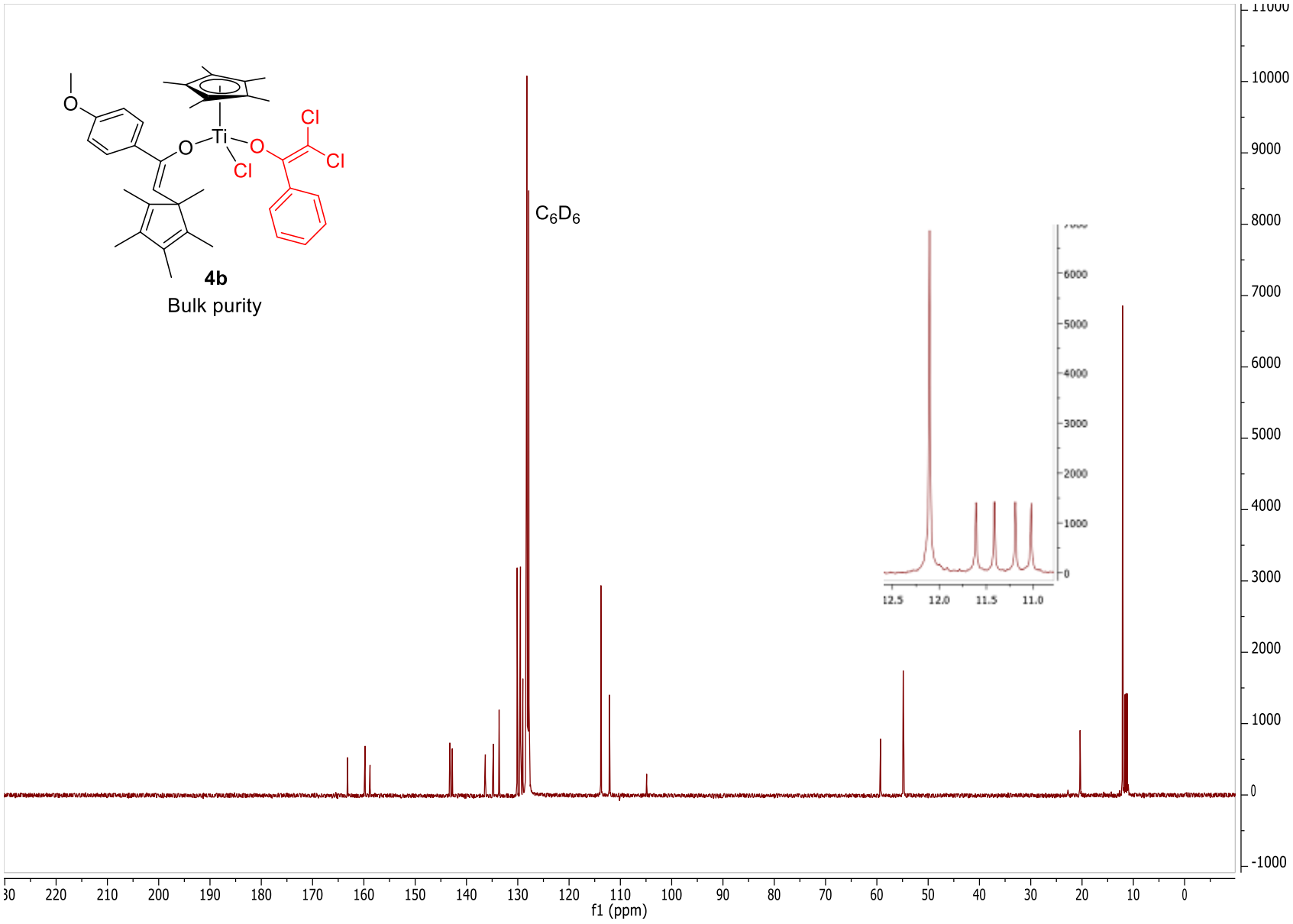

CF3
F3C
O
Ti
O
O
Ar
Ar
Ar
Ar
3•1/2Toluene
Bulk purity
Ar = 4-MeO-C6H4
C6F6
f1 (ppm)

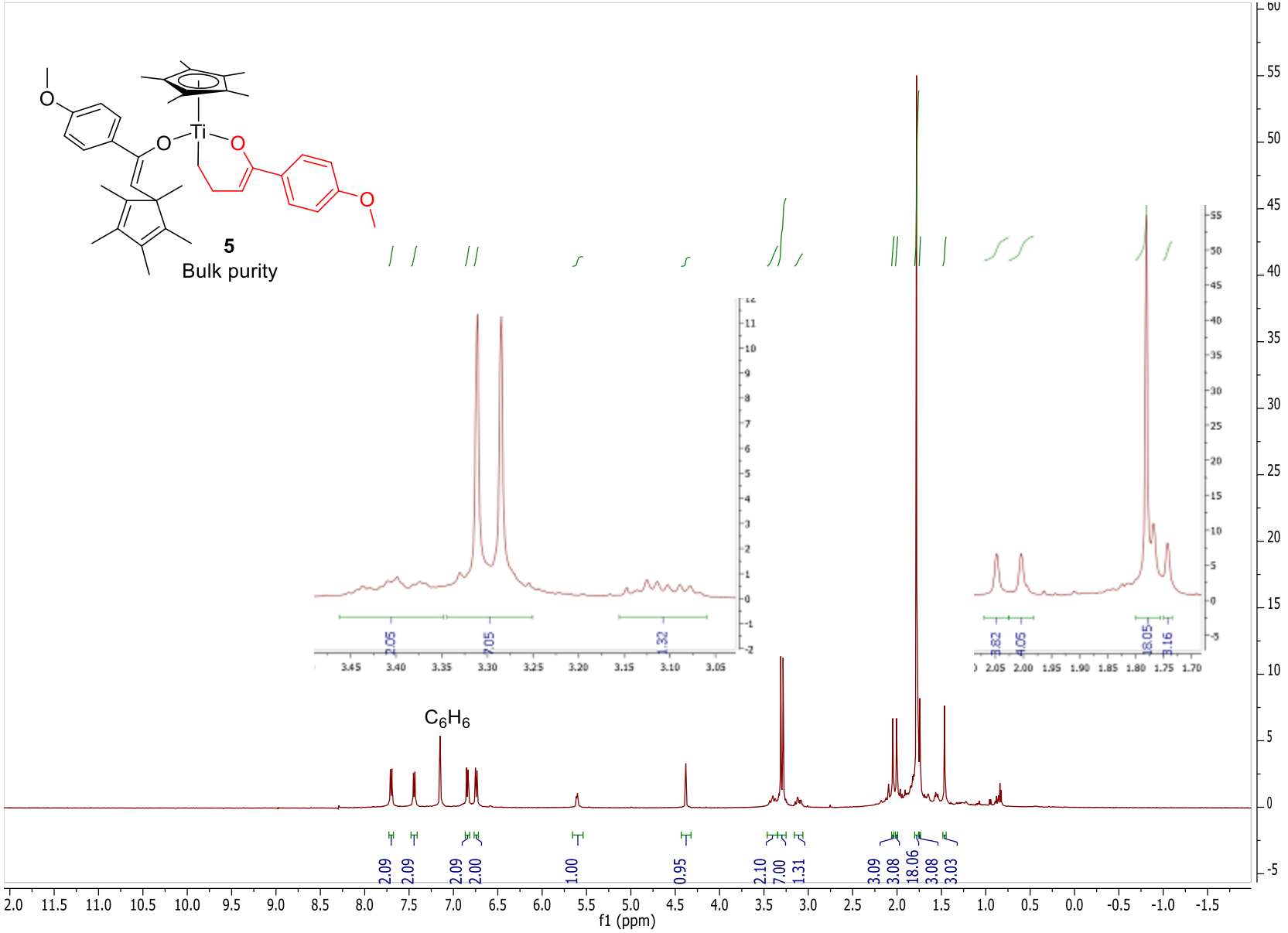

O
Ti
O
F
F
F
4a
Bulk purity
C6H6
f1 (ppm)

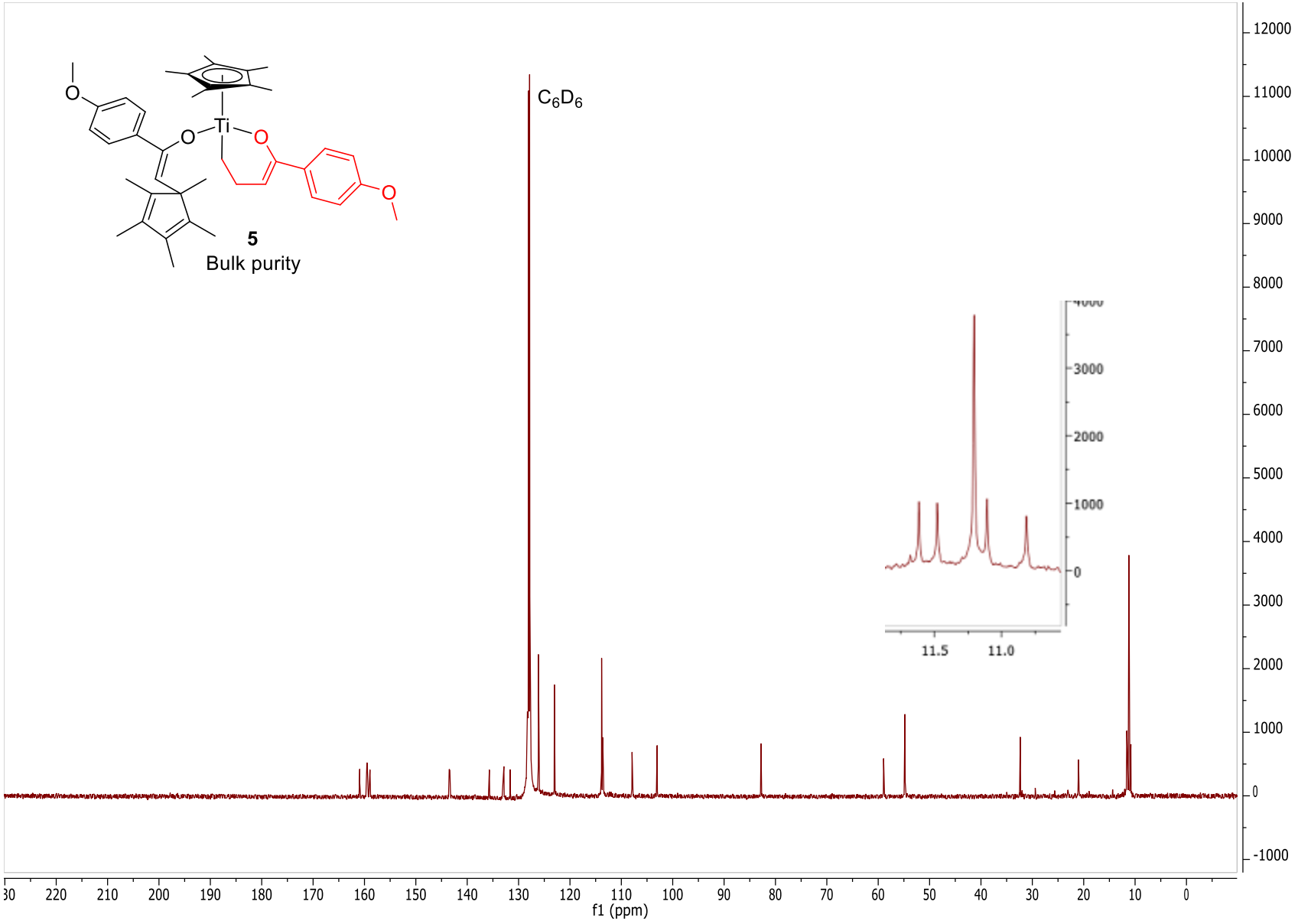

O
Ti
O
F
O
F
F
4a
Bulk purity
C6D6
f1 (ppm)


O
Ti
O
F
F
F
4a
Bulk purity
C_6F_6
f1 (ppm)


O
Ti
O
Cl
O
Cl
Cl
4b
Bulk purity
C6H6
4.09
2.00
1.06
2.03
1.00
3.03
3.02
3.01
18.00
3.08
3.02
f1 (ppm)


O
Ti
O
Cl
O
Cl
Cl
4b
Bulk purity
C_6D_6
f1 (ppm)


O
Ti
O
O
O
5
Bulk purity
C6H6
2.09
2.09
2.09
2.00
1.00
0.95
2.10
7.00
1.31
3.09
3.08
18.06
3.08
3.03
f1 (ppm)


O
Ti
O
O
O
5
Bulk purity
C6D6
11.5
11.0
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
3000
2000
1000
0
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)