SUPPORTING INFORMATION

FOR

Multicomponent mechanochemical synthesis of cyclopentadienyl titanium *tert*-butoxy halides, $Cp_xTiX_y(O^tBu)_{4-(x+y)}$ (x, y = 1, 2; X = Cl, Br)

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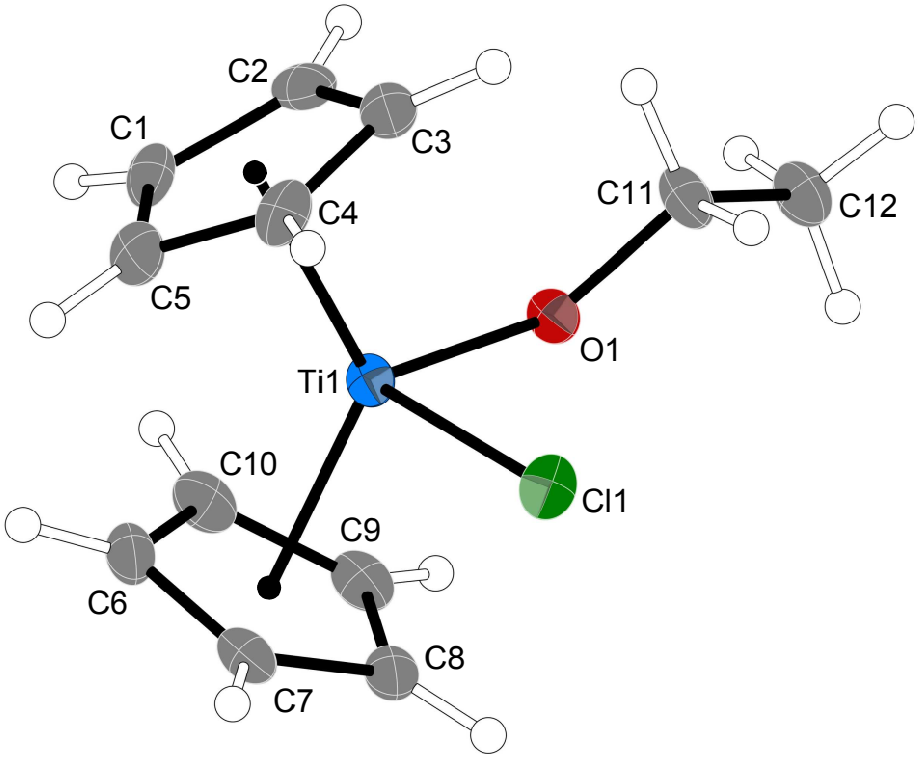
Figure S1. Diagram of $Cp_2TiCl(OEt)$



Thermal ellipsoid plot of $Cp_2TiCl(OEt)$, redetermined at 100 K (50% level); hydrogens have arbitrary radii. Selected bond distances (Å) and angles (deg): Ti1–O1, 1.858(3); Ti1–Cl1 = 2.4044(12); O1–C11, 1.419(5); Ti–Cp′(ring centroid), 2.085 (ave); O1–Ti1–Cl1, 93.15(10); Ti1–O1–C11, 133.3(2); Cp′–Ti–Cp′, 130.3.

Figure S2: ^{1}H NMR of $Cp_2TiBr(O^tBu)$

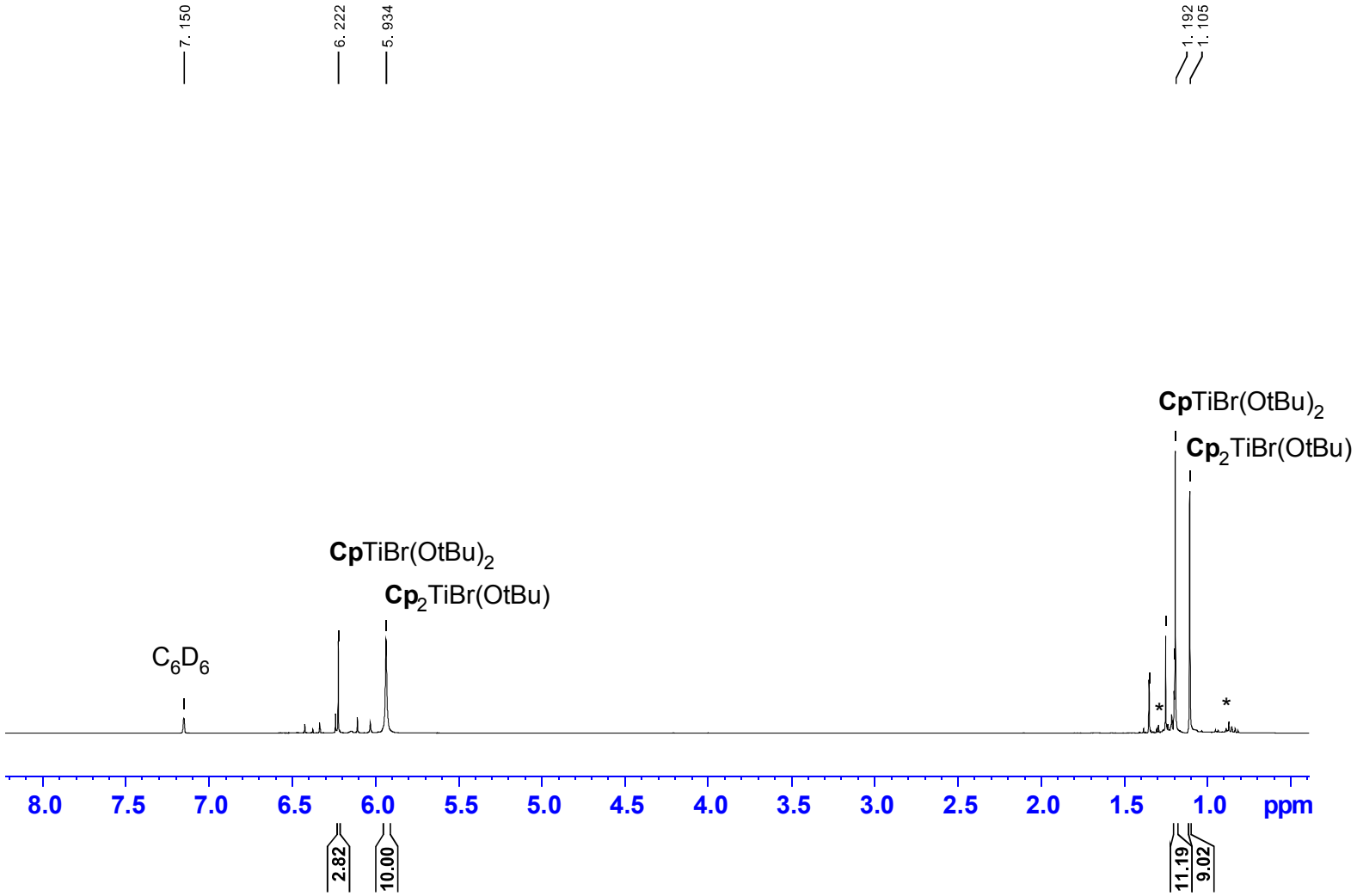


Figure S3: ^{1}H NMR of $CpTiBr(O^{t}Bu)_2$

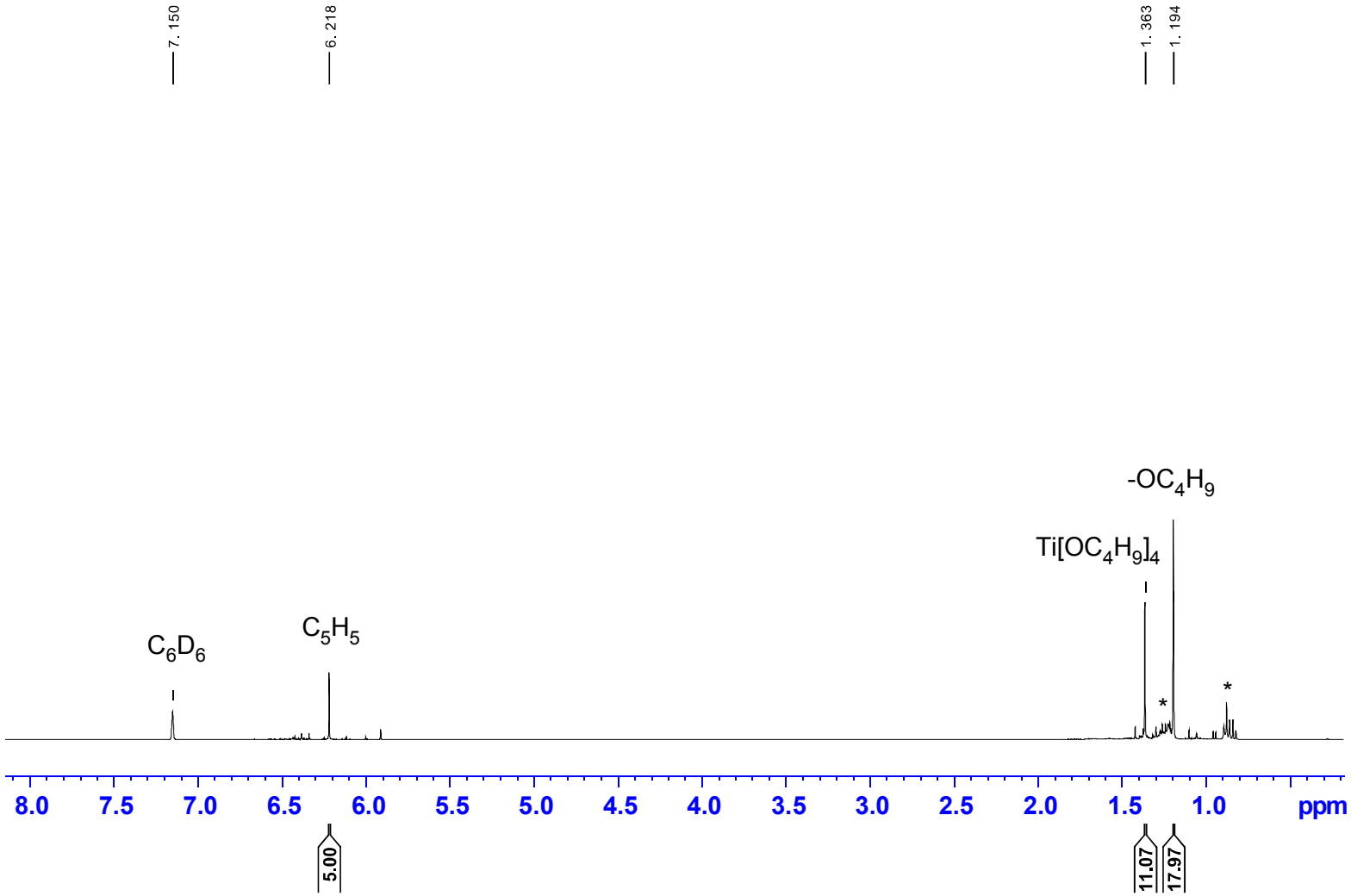


Table S1. Crystal Data and Summary of X–ray Data Collection

Compound	$Cp_2TiCl(OMe)$ (**1**)	$Cp_2TiCl(O^iPr)$ (**2**)	$Cp_2TiCl(O^tBu)$ (**3**)	$Cp_2TiBr(O^tBu)$ (**4**)	$CpTiBr_2(O^tBu)$ (**5**)
Empirical formula	$C_{11}H_{13}ClOTi$	$C_{13}H_{17}ClOTi$	$C_{14}H_{19}ClOTi$	$C_{14}H_{19}BrOTi$	$C_9H_{14}Br_2OTi$
Formula weight	244.58	272.61	286.64	331.08	345.92
Color of compound	orange	yellow	orange	yellow	yellow
Temperature/K	100	223	100	100	100
Crystal system	orthorhombic	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	*Pbca*	*Pnma*	*Pbca*	$P2_1/c$	$P2_1/c$
a/Å	12.4890(3)	13.0890(8)	15.01162(13)	15.0669(4)	12.9173(2)
b/Å	11.4556(2)	10.6775(6)	11.84446(11)	12.2725(3)	16.12491(19)
c/Å	14.6289(3	9.3276(6)	15.51368(15)	15.5128(4)	12.6854(2)
α/°	90	90	90	90	90
β/°	90	90	90	90.079(2)	111.141(2)
γ/°	90	90	90	90	90
Volume/Å^3	2092.94(7)	1303.61(14)	2758.40(4)	2868.44(12)	2464.42(7)
Z	8	4	8	8	8
ρ_{calc} g/cm^3	1.555	1.389	1.380	1.380	1.865
μ/mm^{-1}	1.056	3.365	6.878	3.365	13.187
F(000)	1008	1344	1200	1344	1344
Crystal size/mm^3	0.45 × 0.28 × 0.11	0.443 × 0.118 × 0.094	0.223 × 0.125 × 0.084	0.37 × 0.27 × 0.19	0.32 × 0.17 × 0.034
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2Θ range for data collect/°	6.456 to 65.458	3.113 to 29.770	11.094 to 145.054	3.762 to 28.415	7.338 to 144.476
Index ranges	-18 ≤ h ≤ 8, -16 ≤ k ≤ 16, -21 ≤ l ≤ 21	-16 ≤ h ≤ 18, -14 ≤ k ≤ 14, -12 ≤ l ≤ 12	-18 ≤ h ≤ 18, -14 ≤ k ≤ 14, -18 ≤ l ≤ 19	-20 ≤ h ≤ 20, -16 ≤ k ≤ 16, -19 ≤ l ≤ 21	-15 ≤ h ≤ 15, -19 ≤ k ≤ 19, -11 ≤ l ≤ 15
Reflections collected	17 721	8461	15 770	26 410	23 134
Independent reflections	3612 [R_{int} = 0.0271, R_{sigma} = 0.0215]	1808 [R_{int} = 0.0863, R_{sigma} = 0.0486]	2724 [R_{int} = 0.0254, R_{sigma} = 0.0150]	6965 [R_{int} = 0.0577, R_{sigma} = 0.0508]	4810 [R_{int} = 0.0450, R_{sigma} = 0.0264]
Data/restraints/parameters	3612/1/138	1808/156/133	2724/0/157	6965/25/355	4810/0/241
Goodness-of-fit on F^2	1.054	1.112	1.050	0.993	1.083
Final *R* indexes [$I > 2\sigma(I)$]	R1 = 0.0319, wR2 = 0.0659	R1 = 0.0601, wR2 = 0.1394	R1 = 0.0233, wR2 = 0.0593	R1 = 0.0485, wR2 = 0.1165	R1 = 0.0312, wR2 = 0.0812
Final *R* indexes [all data]	R1 = 0.0618, wR2 = 0.1285	R1 = 0.0713, wR2 = 0.1461	R1 = 0.0241, wR2 = 0.0599	R1 = 0.0618, wR2 = 0.1285	R1 = 0.0322, wR2 = 0.0824
Largest diff. peak/hole/e Å^{-3}	0.45/-0.44	0.39/-0.46	0.23/-0.30	1.18/-0.87	1.20/-0.73