Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Allyl complexes of scandium: synthesis and structure of neutral, cationic and anionic derivatives

Sabine Standfuss, Elise Abinet, Thomas P. Spaniol and Jun Okuda*

List of Contents

Synthesis and characterization

General conditions All experiments were performed under an inert atmosphere of argon using standard Schlenk-line or glovebox techniques. Allylpotassium, bis(allyl)calcium and the Brønsted acid $[NEt_3H][BPh_4]$ were prepared according to published procedures. All other chemicals were commercially available and used after appropriate purification. Toluene, THF, THF-d_8, 1,4-dioxane and *n*-pentane were dried over sodium benzophenone ketyl. All solvents were distilled prior to use. 1,3-butadiene was condensed onto molecular sieves and condensed into toluene to prepare a 1,3-butadiene stock solution in toluene. NMR spectra (Fig. S1a-S9b) were recorded using a Bruker DRX 400 spectrometer (^{1}H 400.1, ^{13}C 100.6). All chemical shifts are given in ppm. Chemical shifts for ^{1}H and $^{13}C\{^1H\}$ NMR spectra were referenced internally using residual solvent resonances and are reported relative to $SiMe_4$.

$[Sc(C_3H_5)_3(THF)_n]$ (1) In a 50 mL Schlenk flask, $ScCl_3$ (350 mg; 2.313 mmol) in THF (15 mL) was stirred overnight. After cooling to 0 °C, allylpotassium (550 mg; 6.860 mmol; 3 equiv.) in THF (7 mL) was added dropwise within 5 min. The yellow colored suspension was stirred for 30 min at 0 °C and then for 30 min at ambient temperature. The solids were separated by centrifugation (20 min, 3.5 x 10^3 rpm) and the dark yellow solution was reduced in vacuum, filtered and kept at −40 °C for three days. During this time yellow crystals precipitated which were dried in vacuum to afford $[Sc(C_3H_5)_3(THF)_{0.75}]$ (**1**) in 60 % yield (306 mg; 1.377 mmol).^{1}H NMR (400 MHz; THF-d_8; 25 °C): δ = 1.77 (m, 3H, β-THF); 2.97 (d,$^3J_{HH}$ = 12.1 Hz, 12H, CH_2CHCH_2); 3.62 (m, 3H, α-THF); 6.18 (quint, $^3J_{HH}$ = 12.1 Hz, 3H, CH_2CHCH_2). $^{13}C\{^1H\}$ NMR (100 MHz; THF-d_8; 25 °C): δ = 26.5 (β-THF); 68.4 (α-THF); 73.0 (CH_2CHCH_2); 145.1 (CH_2CHCH_2). Single crystals of $[Sc(C_3H_5)_3(THF)_2]$ (**1a**) were obtained from the dark yellow solution of **1** in THF at −40 °C suitable for single crystal X-ray diffraction and elemental analysis. Anal. Calcd for $C_{17}H_{31}O_2Sc$ (M = 312.38 g·mol^{-1}): C: 65.36 %; H: 10.00 %. Found: 65.30 %; H: 11.00 %.

$[Sc(C_3H_5)_3]$ (1b) In a 25 mL Schlenk flask, $ScCl_3$ (87 mg; 0.575 mmol) in THF (8 mL) was stirred overnight. The suspension was cooled down to 0 °C and a solution of $Ca(C_3H_5)_2$ (106 mg; 0.867 mmol; 1.5 equiv.) in THF (2 mL) was added within 5 min. The yellow colored suspension was stirred for 30 min at 0 °C and then for 30 min at ambient temperature. The suspension was filtered and the residue was washed with THF (2 mL). The volume of the dark yellow filtrate was reduced to 5 mL in vacuum, kept at −40 °C and yellow crystals slowly precipitated from the solution within five days. The volatiles were then removed in vacuum to afford **1b** as yellow powder in 70 % yield (68 mg; 0.404 mmol). ^{1}H NMR (400 MHz; THF-d_8; 25 °C): δ = 2.94 (d, $^3J_{HH}$ = 12.1 Hz, 12H, CH_2CHCH_2); 6.18 (quint, $^3J_{HH}$ = 12.1 Hz, 3H, CH_2CHCH_2).

$[Sc(C_3H_5)_3(THF)_n]$ (1) using $[Sc(C_3H_5)_2(THF)_{1.5}][BPh_4]$ (2a) and $K[Sc(C_3H_5)_4]$ (3a)
In a J. Young NMR tube $[Sc(C_3H_5)_2(THF)_{1.5}][BPh_4]$ (**2a**) (25 mg; 0.045 mmol; 1 equiv.) was dissolved in THF-d_8 (0.5 mL) and $K[Sc(C_3H_5)_4]$ (**3a**) (12 mg; 0.045 mmol; 1 equiv.) in THF-d_8 (0.2 mL) was added. The sample was analyzed by ^{1}H NMR spectroscopy and contained only tris(allyl)scandium **1** as only allyl compound. Quantitative yield according to ^{1}H NMR spectroscopy was obtained. ^{1}H NMR (400 MHz; THF-d_8; 25 °C): δ = 1.77 (m, 4H, β-THF); 2.95 (d, $^3J_{HH}$ = 12.05 Hz, 12H, CH_2CHCH_2); 3.62 (m, 4H, α-THF); 6.17 (quint, $^3J_{HH}$ = 12.05 Hz, 3H, CH_2CHCH_2).

$[Sc(C_3H_5)_2(THF)_3][BPh_4]$ (2a) $[Sc(C_3H_5)_3(THF)]$ (**1**) (102 mg; 0.425 mmol) was dissolved in THF (3.5 mL) and a solution of $[NEt_3H][BPh_4]$ (160 mg; 0.422 mmol; 1 equiv.) in THF (3.5 mL) was added within 2 min. A yellow colored precipitate was observed immediately. The solids were separated by centrifugation (20 min, 3.5 x 10^3 rpm) and the residue was washed with *n*-pentane (3 x 5 mL). The volatiles were removed in vacuum to afford $[Sc(C_3H_5)_2(THF)_{1.5}][BPh_4]$ (**2a**) as an intensively yellow colored powder in 80 % yield (187 mg; 0.336 mmol). ^{1}H NMR (400 MHz; THF-d_8; 25 °C): δ = 1.78 (m, 6H, β-THF); 3.10 (d, $^3J_{HH}$ = 12.6 Hz, 8H, CH_2CHCH_2); 3.62 (m, 6H, α-THF); 5.99 (quint, $^3J_{HH}$ = 12.6 Hz, 2H, CH_2CHCH_2); 6.71 (m, 4H, Ph-4); 6.86 (m, 8H, Ph-3); 7.27 (m, 8H, Ph-2). $^{13}C\{^1H\}$ NMR (100 MHz; THF-d_8; 25 °C): δ = 26.5 (β-THF); 68.4 (α-THF); 76.4 (CH_2CHCH_2); 122.0 (Ph-4); 125.9 (Ph-3); 137.4 (Ph-2); 146.3 (CH_2CHCH_2); 165.6 (q, $^1J_{BC}$ = 49.4 Hz, Ph-1). From a THF solution of **2a**, single crystals of $[Sc(C_3H_5)_2(THF)_3][BPh_4]$ (**2a**) suitable for single crystal X-ray diffraction were formed at −40 °C after one week. ^{1}H NMR (400 MHz; THF-d_8; 25 °C): δ = 1.77 (m, 12H, β-THF); 3.10 (d, $^3J_{HH}$ = 12.6 Hz, 8H, CH_2CHCH_2); 3.62 (m, 12H, α-THF); 5.99 (quint, $^3J_{HH}$ = 12.6 Hz, 2H, CH_2CHCH_2); 6.71 (m, 8H, Ph-4); 6.86 (m, 8H, Ph-3); 7.27 (m, 4H, Ph-2). Anal. Calcd for $C_{42}H_{54}BO_3Sc$ (M = 662.64 g·mol^{-1}): C: 76.13 %; H: 8.21 %. Found: C: 74.99 %; H: 7.43 %.

$[Sc(C_3H_5)_2(THF)_4][BPh_4]$ (2a') using $K[Sc(C_3H_5)_4]$ (3a)
$K[Sc(C_3H_5)_4]$ (**3a**) (15 mg; 0.060 mmol) was dissolved in THF (1 mL) and a solution of $[NEt_3H][BPh_4]$ (50 mg; 0.119 mmol; 2 equiv.) in THF (1 mL) was added at ambient temperature. Immediately a yellow colored precipitate was observed. After five minutes the suspension was filtered and the residue washed with *n*-pentane (2 mL) and dried in vacuum. An intensive yellow colored powder of $[Sc(C_3H_5)_2(THF)_4][BPh_4]$ (**2a'**) was obtained in 38 % yield (14 mg; 0.024 mmol). ^{1}H NMR (400 MHz; THF-d_8; 25 °C): δ = 1.77 (m, 16H, β-THF); 3.09 (d, $^3J_{HH}$ = 12.55 Hz, 8H, CH_2CHCH_2); 3.62 (m, 16H, α-THF); 5.99 (quint, $^3J_{HH}$ = 12.55 Hz, 2H, CH_2CHCH_2); 6.73 (m, 8H, Ph-4); 6.87 (m, 8H, Ph-3); 7.30 (m, 4H, Ph-2).

$[Sc(C_3H_5)_2(THF)_{2.25}][B(C_6H_3Cl_2)_4]$ (2b) To a solution of $[Sc(C_3H_5)_3(THF)_{1.5}]$ (69 mg; 0.250 mmol) in THF (2 mL) a solution of $[NMe_3H][B(C_6H_3Cl_2)_4]$ (**4**) (164 mg; 0.250 mmol) in THF (1.5 mL) was added at ambient temperature within 3 minutes. After 30 min the orange colored solution was evaporated for dryness and the volatiles were removed in vacuum to afford **2b** as an intensively yellow colored powder in 73 % yield (160 mg; 0.181 mmol). ^{1}H NMR (400 MHz; THF-d_8; 25 °C): δ = 1.77 (m, 9H, β-THF); 3.14 (d, $^3J_{HH}$ = 12.6 Hz, 8H, CH_2CHCH_2); 3.62 (m, 9H, α-THF); 6.03 (quint, $^3J_{HH}$ = 12.6 Hz, 2H, CH_2CHCH_2); 6.97 (m, 4H, Ph-4); 7.03 (m, 8H, Ph-2). ^{13}C{^{1}H} NMR (100 MHz; THF-d_8; 25 °C): δ = 26.5 (β-THF); 68.4 (α-THF); 76.3 (CH_2CHCH_2); 124.0 (Ph-4); 133.9 (Ph-3); 134.3 (Ph-2); 146.4 (CH_2CHCH_2); 166.0 (q, $^1J_{BC}$ = 49.4 Hz, Ph-1). Anal. Calcd for $C_{39}H_{40}BCl_8O_{2.25}Sc$ (M = 884.12 g·mol^{-1}): C: 52.98 %; H: 4.56 %. Found: C: 54.77 %; H: 4.96 %.

$[Sc(C_3H_5)_2(THF)_{2.25}][B(C_6F_5)_4]$ (2c)
$[Sc(C_3H_5)_3(THF)_{1.25}]$ (**1**) (200 mg; 0.774 mmol; 1.2 equiv.) was dissolved in THF (3.5 mL) and a solution of $[NPhMe_2H][B(C_6F_5)_4]$ (521 mg; 0.650 mmol) in THF (3 mL) was added. After 10 min at ambient temperature, the yellow solution was evaporated for dryness and washed with *n*-pentane (3 x 12 mL). The volatiles were removed in vacuum to give **2c** as an intensively yellow colored powder in 68 % yield (629 mg; 0.440 mmol). ^{1}H NMR (400 MHz; THF-d_8; 25 °C): δ = 1.78 (m, 9H, β-THF); 3.15 (d, $^3J_{HH}$ = 12.6 Hz, 8H, CH_2CHCH_2); 3.62 (m, 9H, α-THF); 6.04 (quint, $^3J_{HH}$ = 12.6 Hz, 2H, CH_2CHCH_2). ^{13}C{^{1}H} NMR (100 MHz; THF-d_8; 25 °C): δ = 26.5 (β-THF); 68.4 (α-THF); 76.2 (CH_2CHCH_2); 125.3 (m, Ph-1); 137.3 (d, $^1J_{CF}$ = 243.6 Hz, Ph-3); 139.3 (d, $^1J_{CF}$ = 244.5 Hz, Ph-4); 146.4 (CH_2CHCH_2); 149.2 (d, $^1J_{CF}$ = 244.5 Hz, Ph-2). Anal. calcd. for $C_{39}H_{28}BF_{20}O_{2.25}Sc$ (M = 968.37 g·mol^{-1}): C: 48.37 %; H: 2.91 %. Found: C: 47.80 %; H: 3.13 %.

$K[Sc(C_3H_5)_4]$ (3a) $ScCl_3$ (225 mg; 1.487 mmol) in THF (4 mL) stirred overnight in a 20 mL-Schlenk tube. After cooling to 0 °C, allylpotassium (477 mg; 5.950 mmol; 4 equiv.) in THF (7 mL) was added dropwise within 5 min. The slightly orange colored mixture was stirred for 20 min at 0 °C, for 30 min at ambient temperature and then solids were separated by centrifugation (20 min, 3.5 x 10^3 rpm). The orange colored solution was dried in vacuum and the remaining high-viscosity oil was washed with *n*-pentane (3 x 10 mL) to give a powder. The volatiles were removed in vacuum to afford **3a** as an orange colored powder in 58 % yield (214 mg; 0.862 mmol). ^{1}H NMR (400 MHz; THF-d_8; 25 °C): δ = 2.69 (d, $^3J_{HH}$ = 11.8 Hz, 16H, CH_2CHCH_2); 6.08 (quint, $^3J_{HH}$ = 11.8 Hz, 4H, CH_2CHCH_2). ^{13}C{^{1}H} NMR (100 MHz; THF-d_8; 25 °C): δ = 70.5 (CH_2CHCH_2); 145.0 (CH_2CHCH_2). Anal. calcd for $C_{12}H_{20}KSc$ (M = 248.34 g·mol^{-1}): C: 58.04 %; H: 8.12 %. Found: C: 56.79 %; H: 8.19 %.

$K[Sc(C_3H_5)_4]$ (3a) starting from $[Sc(C_3H_5)_3(THF)_{1.5}]$ (1)
$[Sc(C_3H_5)_3(THF)_{1.5}]$ (**1**) (69 mg; 0.250 mmol) was dissolved in THF (0.5 mL) and allylpotassium (20 mg; 0.249 mmol; 1 equiv.) in THF (0.5 mL) was added. After stirring for 10 min at ambient temperature the filtered solution was reduced in vacuum and the remaining oil was washed with *n*-pentane (3 x 10 mL). Drying in vacuum gave a tan colored powder in 50 % yield (31 mg; 0.125 mmol). ^{1}H NMR (400 MHz; THF-d_8; 25 °C): δ = 2.72 (d, $^3J_{HH}$ = 11.80 Hz, 16H, CH_2CHCH_2); 6.09 (quint, $^3J_{HH}$ = 11.80 Hz, 4H, CH_2CHCH_2).

$[Ca(THF)_{5.5}][Sc(C_3H_5)_4]_2$ (3b) In a 50 mL Schlenk flask, $ScCl_3$ (120 mg; 0.793 mmol; 2 equiv.) in THF (4 mL) was stirred overnight. The suspension was cooled down to 0 °C and a solution of $Ca(C_3H_5)_2$ (92 mg; 1.571 mmol; 4 equiv.) in THF (3.5 mL) was added within 4 min. The yellow colored suspension was stirred for 30 min at 0 °C, for 60 min at ambient temperature and then filtered. The volatiles were removed in vacuum to afford **3b** as a beige powder in 47 % yield (159 mg; 0.186 mmol). ^{1}H NMR (400 MHz; THF-d_8; 25 °C): δ =1.77 (m, 22H, β-THF); 2.75 (d, $^3J_{HH}$ = 11.8 Hz, 32H, CH_2CHCH_2); 3.62 (m, 22H, α-THF); 6.08 (quint, $^3J_{HH}$ = 11.8 Hz, 8H, CH_2CHCH_2). ^{13}C{^{1}H} NMR (100 MHz; THF-d_8; 25 °C): δ = 26.5 (β-THF); 68.4 (α-THF); 71.6 (CH_2CHCH_2); 145.1 (CH_2CHCH_2).

$[Mg(THF)_6][Sc(C_3H_5)_4]_2$ (3c) A THF suspension (50 mL) of $ScCl_3$ (502 mg, 3.32 mmol) was treated with a 2 mol·L^{-1} THF solution of $[Mg(C_3H_5)Cl]$ (5 mL, 3 equiv.) and 1,4-dioxane (20 mL) was added. After centrifugation and filtration, toluene was added and the resulting mixture was stored at −40 °C overnight. Crystalline material of was collected, washed with *n*-pentane and dried under vacuum. $[Mg(THF)_2][Sc(C_3H_5)_4]_2$ (**3c'**) was obtained as brown solid in 36 % yield (410 mg, 0.605 mmol). ^{1}H NMR of **3c'** (400 MHz; THF-d_8, 25 °C): δ = 1.77 (s, 13H, β-THF); 2.82 (br. d, $^3J_{HH}$ = 12.05 Hz, 32H, CH_2CHCH_2); 3.61 (s, 13H, α-THF); 6.18 (quint, $^3J_{HH}$ = 12.05 Hz, 8H, CH_2CHCH_2). $^{13}C\{^1H\}$ NMR (100 MHz; THF-d_8; 25 °C): δ = 26.4 (β-THF); 68.4 (α-THF); 69.6 (CH_2CHCH_2); 145.9 (CH_2CHCH_2). From a THF/*n*-pentane solution of **3c'**, single crystals of $[Mg(THF)_6][Sc(C_3H_5)_4]_2$ (**3c**) suitable for single crystal X-ray diffraction were formed at −40 °C.

$[NMe_3H][B(C_6H_3Cl_2)_4]$ (4) $[NMe_3H]Cl$ (0.427 g; 4.939 mmol) and $Na[B(C_6H_3Cl_2)_4]$ (3.054 g; 4.943 mmol; 1 equiv.) were suspended in distilled water (20 mL). Acetone was added until the solids were fully dissolved (ca. 130 mL). The solvent was removed and the beige colored product was precipitated with a mixture of dichloromethane/ *n*-pentane. After repeating this procedure for three times, the remaining colorless precipitate was suspended in distilled water (ca. 40 mL) and dissolved by adding acetone (ca. 120 mL). After crystallization at ambient temperature and filtration, the volatiles were removed in vacuum to afford **4** as colorless crystals in 70 % yield (2.264 g; 3.457 mmol). ^{1}H NMR (400 MHz; THF-d_8; 25 °C): δ = 2.90 (s, 9H, CH_3); 6.98 (m, 4H, Ph-4); 7.03 (m, 8H, Ph-2). $^{13}C\{^1H\}$ NMR (100 MHz; THF-d_8; 25 °C): δ = 45.7 (CH_3); 124.0 (Ph-4); 134.0 (Ph-3); 134.2 (Ph-2); 166.0 (q, $^1J_{BC}$ = 49.4 Hz, Ph-1). Anal. Calcd for $C_{27}H_{22}BCl_8N$ (M = 54.91 g·mol^{-1}): C: 49.52 %; H: 3.39 %. Found: C: 50.63 %; H: 3.98 %.

Polymerization of styrene – general conditions In a 25 mL Schlenk flask, styrene (752 mg; 7.220 mmol; 1000 equiv.) and aluminum triisopropylate (1M in hexane; 36 μL; 36 μmol; 5 equiv.) in toluene (4.2 mL) were stirred at 50 °C. **2c** (7 mg; 7.228 μmol; 1 equiv.) in toluene (5 mL) was added as fast as possible.* After stirring for exactly one hour at 50 °C** isopropyl alcohol (0.8 mL) was added. The reaction mixture was transferred into acidified methyl alcohol (150 mL) and the precipitated polystyrene was filtered and washed with methyl alcohol. Volatiles were removed in vacuum to afford polystyrene (analyzed by NMR and GPC). Furthermore test reactions without using the scavenger aluminum triisopropylate (Table 1: T1) or by using only scavenger without **2c** (Table 1: T2) led to no conversion.
*Polymerization was also tested by using an activator: $[NPhMe_2H][B(C_6F_5)_4]$ (5 mg; 6.240 μmol; 0.9 equiv.) added simultaneously with **2c** (5 mL toluene in total). This did not lead to noticeable changes (see Table 1; run 5 and 6).
** Conversion at ambient temperature was to low (see Table 1, run: 1–4).

Table S1 Polymerization of styrene

Run[a]	Activator[b]	Yield[c]	Tacticity[d]	M_n[e]	PDI	Catalyst efficiency[f]
1*	-	0.3	aPS	2158	1.08	0.13
2*	1 equiv.	0.3	aPS	1906	1.20	0.15
3**	-	2.7	aPS	2403	1.32	1.15
4**	1 equiv.	1.3	aPS	1924	1.36	0.72
T1**	-	-	-	-	-	-
T2**	-	-	-	-	-	-
5a#	-	6.2	aPS	1366	1.46	4.76
5b#	-	9.5	aPS	2052	1.38	4.83
5c#	-	8.2	aPS	1740	1.45	4.93
6a#	1 equiv.	11.4	aPS	1417	1.49	8.37
6b#	1 equiv.	9.7	aPS	1936	1.40	5.20

[a] General conditions: mass of complex = 7 mg; $[Al(CH_2CHMe_2)_3]$/[**2c**] = 5; [monomer]/[**2c**] = 1000; V_{total} = 10 mL; reaction time = 15 min (*) or 1 h(**); temperature = 25 °C or 50 °C (#; always 1h). [b] $[NPhMe_2H][B(C_6F_5)_4]$; [c] isolated polymer in [%]; [d] analyzed by ^{1}H NMR; [e] in g·mol^{-1}; [f] M_n(theory)/ M_n(GPC); [g] M_n(GPC)/ M (styrene)

Polymerization of 1,3-butadiene – general conditions In a 50 mL Schlenk flask, 1,3-butadiene in toluene (2.678 M; 5.4 mL; 14.461 mmol; 1000 equiv.) and aluminum triisopropylate (1M in hexane; 72 μL; 72 μmol; 5 equiv.) in toluene (9.5 mL) were stirred at 25 °C. **2c** (14 mg; 14.45 μmol; 1 equiv.) in toluene (5 mL) was added as fast as possible.* After stirring for exactly 15 min at 25 °C isopropyl alcohol (0.8 mL) was added. The reaction mixture was transferred into acidified methyl alcohol (250 mL) containing antioxidant (2,6-di-*tert*-butylphenol; 100 mg) and the precipitated polymer was

filtered and washed with methyl alcohol. Volatiles were removed in vacuum to afford a mixture of 1,4-*cis*-polybutadiene, 1,4-*trans*-polybutadiene and 1,2-polybutadiene (analyzed by NMR and GPC**). Furthermore test reactions without **2c** led to no conversion.

*Polymerization was also tested by using an activator: $[NPhMe_2H][B(C_6F_5)_4]$ (11 mg; 13.729 μmol; 0.95 equiv.) added simultaneously with **2c** (5 mL toluene in total). This led to higher yields and did not influence the microstructure of the polymers (see Table 2, run 1 and 2).

**Bimodal distribution was observed by GPC: a low molecular weight fraction (high UV activity) and a high molecular weight fraction (no UV activity). Table 3 shows only the low molecular weight fraction with high UV activity.

Table S2 Polymerization of 1,3-butadiene (bimodal distribution; refraction index)

Run[a]	Activator[b]	Yield[c]	Microstructure[d]	M_n[e,f]	M_p[e,f]	PDI[f]
1a	-	7.3	57.5 / 28.4 / 14.1	5942	4310	46
1b	-	7.2	56.0 / 27.9 / 16.1	8352	60444	24
2a	1 equiv.	21.7	57.6 / 24.9 / 17.4	5966	4094	49
2b	1 equiv.	28.8	61.7 / 25.8 / 12.5	9715	727700	61
Test	-	-	-	-	-	-

[a]General conditions: m(**2c**) = 14 mg; $[Al(CH_2CHMe_2)_3]$/[**2c**] = 5; [monomer]/[**2c**] = 1000; V_{total} = 20 mL; reaction time = 15 min; temperature = 25 °C; [b]$[NPhMe_2H][B(C_6F_5)_4]$; [c]isolated polymer in [%]; [d]1,4-*cis*/1,4-*trans*/1,2 (analyzed by NMR); [e]in g·mol^{-1}; [f] these values are caused by bimodal distribution (RI) which are due to oxidatively induced cross-linking.

Table S3 Polymerization of 1,3-butadiene (low molecular weight fraction of bimodal distribution; UV)

Run[a]	Activator[b]	Yield[c]	Low Mw fraction [%]	M_n[e,g]	M_p[e,g]	PDI[g]	Catalyst efficiency[g,h]
1a	-	7.3	46	2301	2940	1,60	0,79
1b	-	7.2	36	2574	2991	1,51	0,54
2a	1 equiv.	21.7	42	1878	2572	1,66	2,63
2b	1 equiv.	28.8	22	1834	2475	1,63	1,87
Test	-	-	-	-	-	-	-

[a]General conditions: m(**2c**) = 14 mg; $[Al(CH_2CHMe_2)_3]$/[**2c**] = 5; [monomer]/[**2c**] = 1000; V_{total} = 20 mL; reaction time = 15 min; temperature = 25 °C; [b]$[NPhMe_2H][B(C_6F_5)_4]$; [c]isolated polymer in [%]; in g·mol^{-1}; [g]low molecular weight fraction (UV); [h]M_n(theory)*Integral/ M_n(GPC)

Crystal Structure Determinations Single-crystal X-ray diffraction measurements were performed on a Bruker AXS diffractometer equipped with an Incoatec microsource and an APEX area detector using MoK_α radiation. **Table S4** shows experimental parameters and refinement results. The data reductions were performed with the Bruker SAINT software[1a] and absorption corrections were carried out using the program Mulabs as implemented in the program system Platon.[1b] The structures were solved by direct methods using the program SIR-92.[1c] All refinements were carried out by the full-matrix least squares method using SHELXL-97 as implemented in the WinGX program system.[1d,e] The graphical representations in Figures 1–3 were performed with the program DIAMOND.[1f] Compound **1a** contains two crystallographically independent molecules in the unit cell; the carbon atoms C25 and C29 (middle position within one allyl ligand) are disordered; the disorder could be modeled well using split positions. A similar disorder was also found for compound **2a** where the central carbon atom of one allyl fragment C5 was refined with split positions. Compound **3c** shows crystallographic inversion symmetry for the anionic fragment with the magnesium atom on the centre of inversion; this structure contains an additional molecule of thf that is disordered. CCDC-832188 (**1a**), CCDC-832189 (**2a**) and CCDC-832190 (**3c**) contain the supplementary crystallographic data for this paper which can be obtained free of charge from The Crystallographic Data Centre via www.ccdc.cam.ac.uk/dada_request/cif.

Table S4 Crystallographic data for complexes [Sc(η^1-C_3H_5)(η^3-C_3H_5)$_2$(THF)$_2$] (**1a**) (CCDC No 832188), [Sc(η^3-C_3H_5)$_2$(THF)$_3$][B(C_6H_5)$_4$] (**2a**) (CCDC No 832189) and [Mg(THF)$_6$][Sc(η^1-C_3H_5)$_2$(η^3-C_3H_5)$_2$]$_2$ (**3c**) (CCDC No 832190)

Compound	**1a**	**2a**	**3c**
Empirical formula	$C_{17}H_{31}O_2Sc$	$C_{18}H_{34}O_3Sc•C_{24}H_{20}B$	$C_{24}H_{48}MgO_6•2(C_{12}H_{20}Sc)•2(C_4H_8O)$
M [g·mol^{-1}]	312.38	662.62	1019.62
Crystal size [mm^3]	0.46 × 0.34 × 0.22	0.38 × 0.36 × 0.27	0.21 × 0.20 × 0.11
Crystal color and habit	yellow block	yellow block	yellow block
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$C2/c$	$P2_1/n$
a [Å]	14.341(6)	31.6886(18)	13.0491(12)
b [Å]	21.027(9)	9.9269(6)	11.3146(10)
c [Å]	11.963(5)	23.1586(13)	20.4870(18)
α [°]	90.00	90.00	90.00
β [°]	104.738(7)	93.9940(10)	97.444(4)
γ [°]	90.00	90.00	90.00
V [Å^3]	3489(3)	7267.3(7)	2999.3(5)
Z	8	8	2
Density [g·cm^{-3}]	1.189	1.211	1.129
T [K]	100(2)	100(2)	130(2)
μ(MoK$_\alpha$) [mm^{-1}]	0.422	0.240	0.284
F(000)	1360	2848	1116
θ range [°]	1.47–26.71	2.11–30.49	2.39–26.49
hkl indices	−18–17, ±26, ±15	−44–45, ±14, −32–33	−14–16, ±14,−24–25
Number of refl. collected	41084	53345	43819
Number of refl. observed (I> 2σ(I))	4296	7566	1929
Number of ind. refl. (R_{int})	7333 (0.1140)	10704 (0.0840)	6000 (0.2219)
Data/rest./par.	7333 / 0 / 360	10704 / 0 / 434	6000 / 21 / 294
R_1, wR_2 (I> 2 σ(I))	0.0753, 0.1986	0.0475, 0.1055	0.0670, 0.1349
R_1, wR_2 (all data)	0.1171, 0.2238	0.0684, 0.1134	0.2375, 0.1759
Goodness-of-fit on F^2	0.974	0.947	0.841
Largest diff. in peak and hole [e·Å^{-3}]	1.565 and −0.599	0.509 and −0.517	0.850 and −0.464

[1] a) Bruker, *SAINT-Plus*, Bruker AXS Inc., Madison, Wisconsin, USA, 1999; b) Bruker, *SADABS*, Bruker AXS Inc., Madison, Wisconsion, USA, 2004; c) A. L. Spek, *Acta Crystallogr. D*, 2008, **65**, 148; d) A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.*, 1993, **27**, 343; e) G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112; f) L. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837; g) K. Brandenburg, *Diamond*, Crystal Impact GbR, Bonn, Germany, 2004.

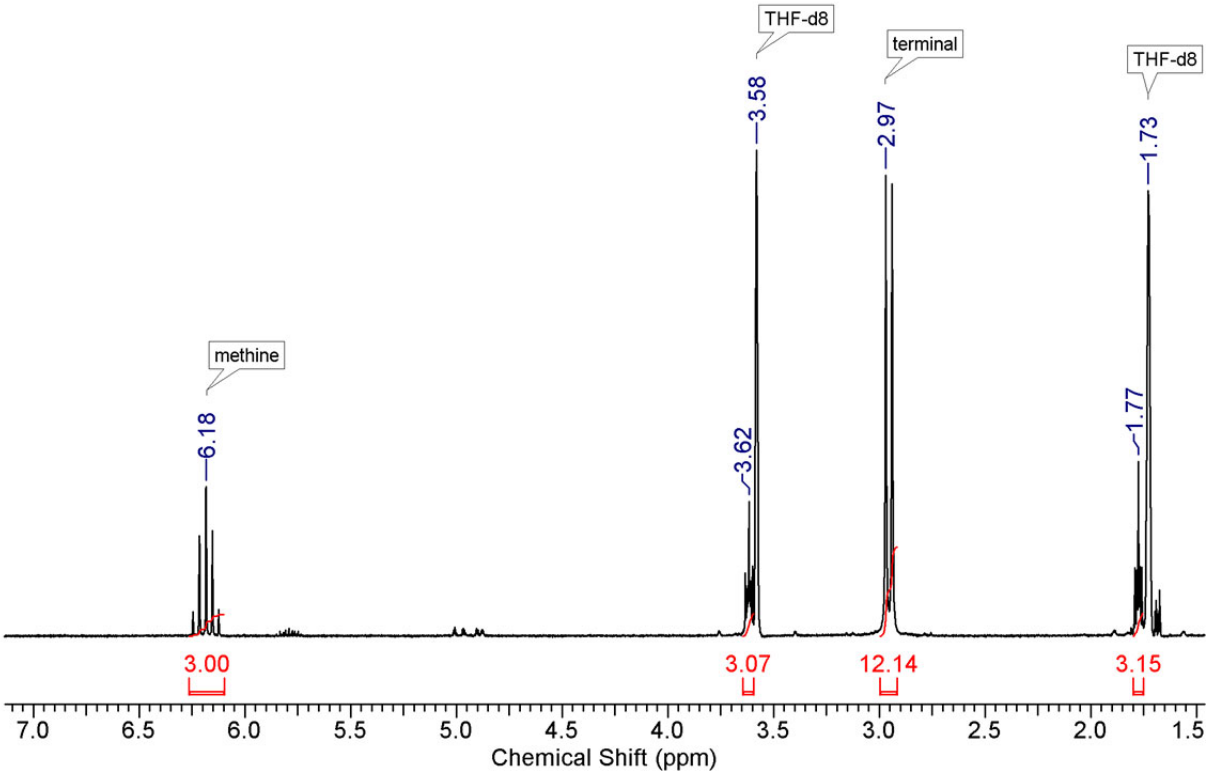

Fig. S1a. ^{1}H NMR spectrum of $[Sc(C_3H_5)_3(THF)_{0.75}]$ (1) in THF-d_8 at +25 °C.

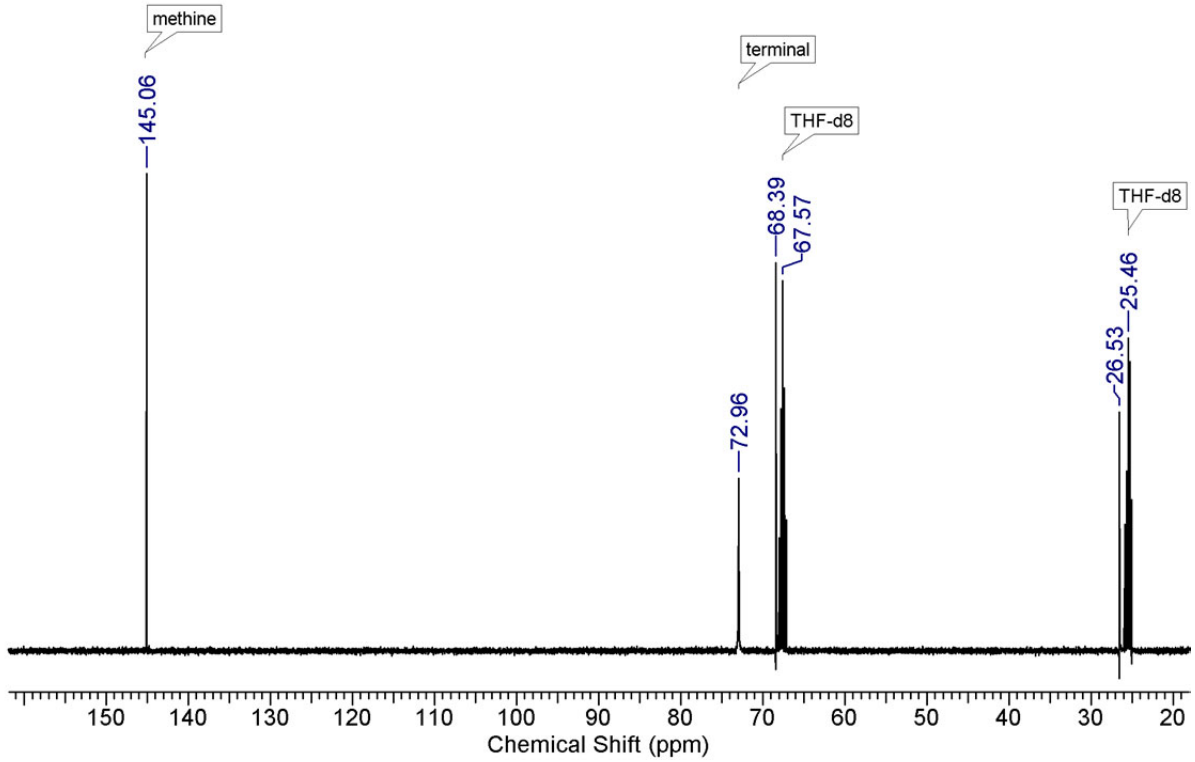

Fig. S1b. $^{13}C\{^{1}H\}$ NMR spectrum of $[Sc(C_3H_5)_3(THF)_{0.75}]$ (**1**) in THF-d_8 at +25 °C.

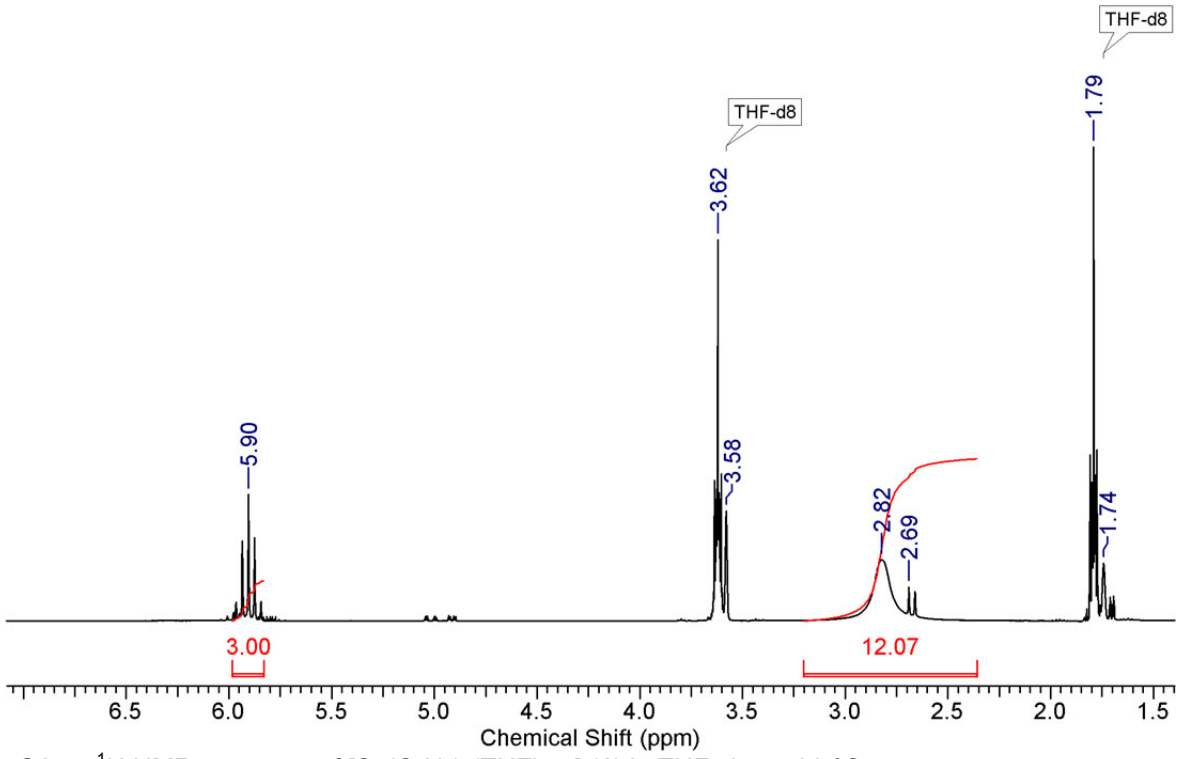

Fig. S1c. ^{1}H NMR spectrum of $[Sc(C_3H_5)_3(THF)_{0.75}]$ (**1**) in THF-d_8 at −80 °C.

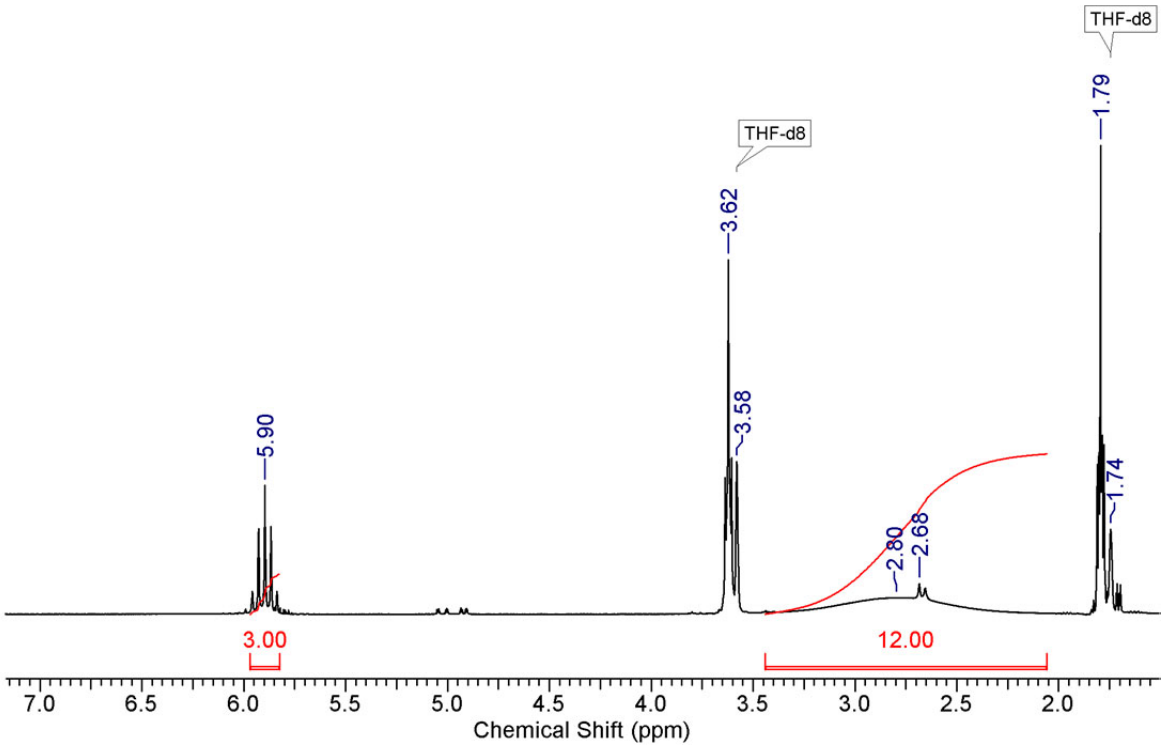

Fig. S1d. ^{1}H NMR spectrum of $[Sc(C_3H_5)_3(THF)_{0.75}]$ (**1**) in THF-d_8 at −95 °C.

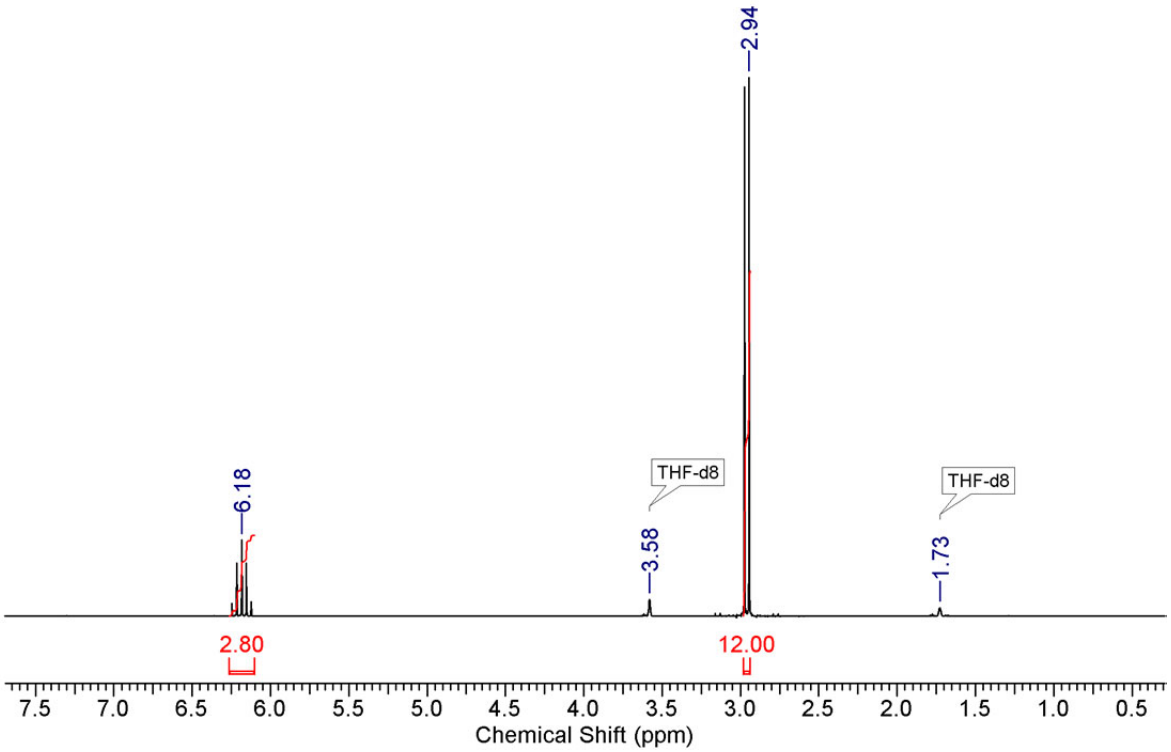

Fig. S2. ^{1}H NMR spectrum of $[Sc(C_3H_5)_3]$ (**1b**) in THF-d_8 at +25 °C.

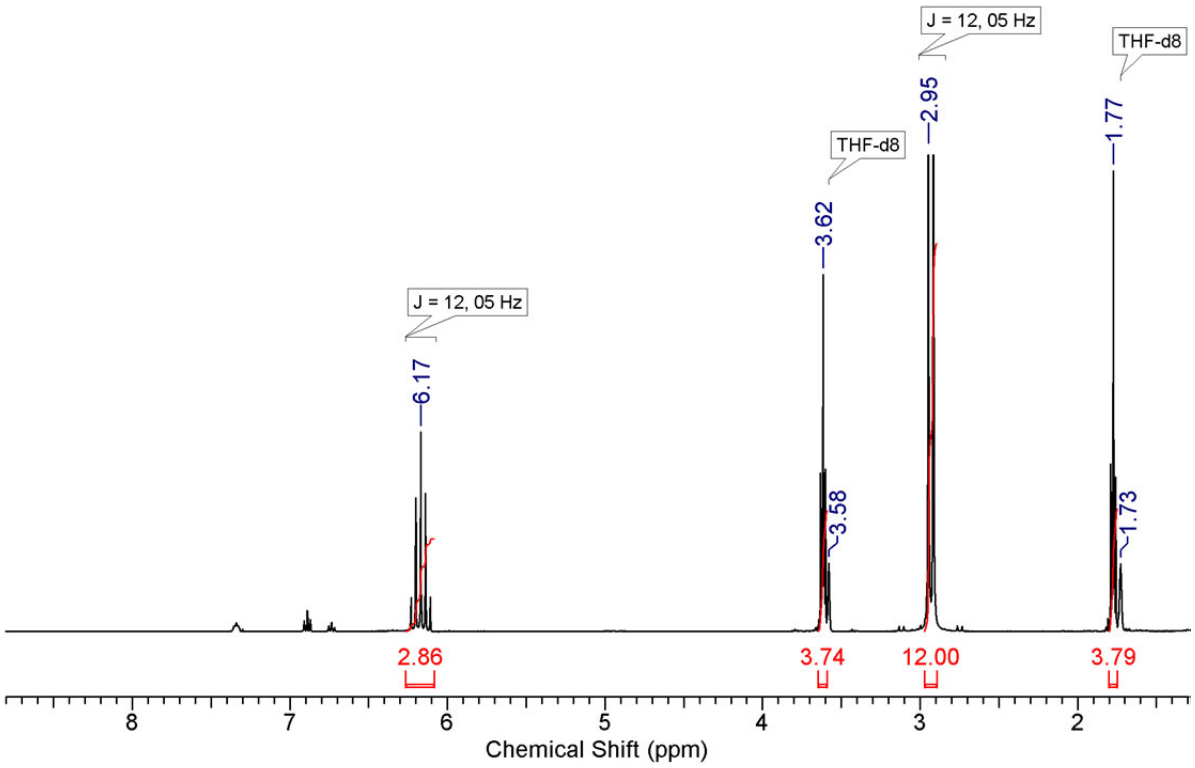

Fig. S3. ^{1}H NMR spectrum of $[Sc(C_3H_5)_3(THF)]$ (**1**) using $[Sc(C_3H_5)_2(THF)_{1.5}][BPh_4]$ (**2a**) and $K[Sc(C_3H_5)_4]$ (**3a**) in THF-d_8 at +25 °C.

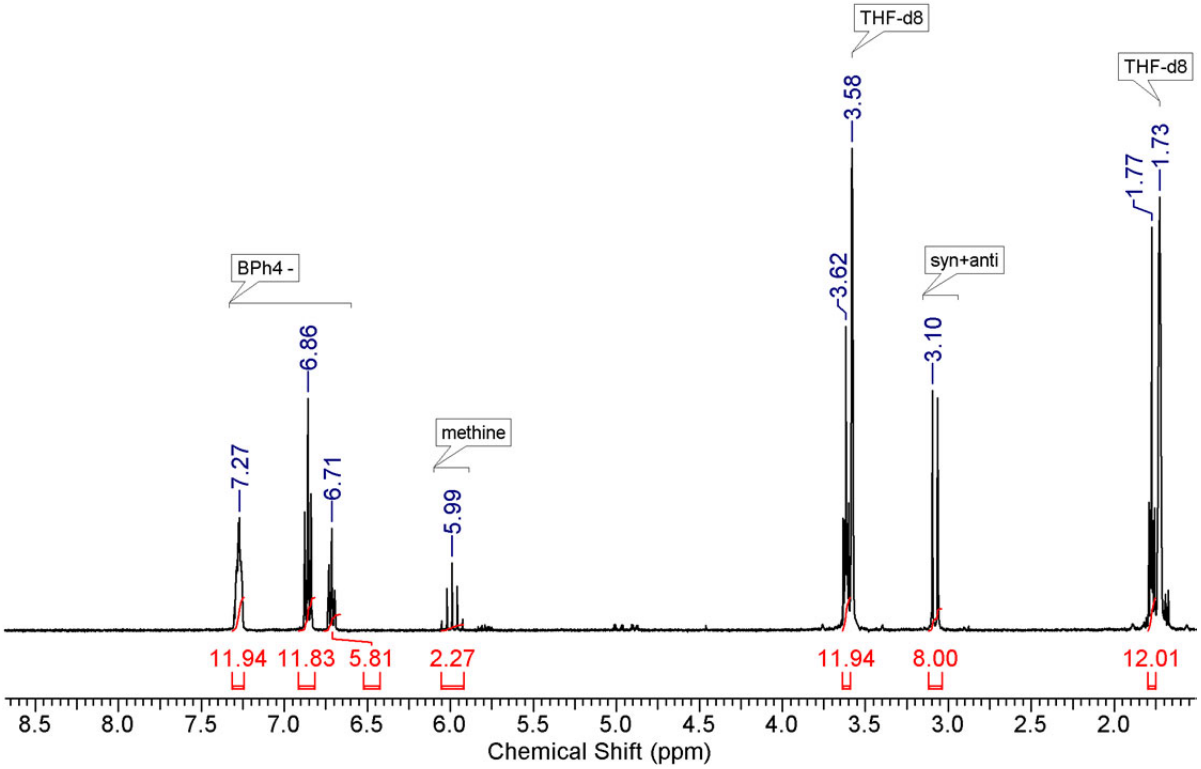

Fig. S4a. ^{1}H NMR spectrum of $[Sc(C_3H_5)_2(THF)_3][BPh_4]$ (**2a**) in THF-d_8 at +25 °C.

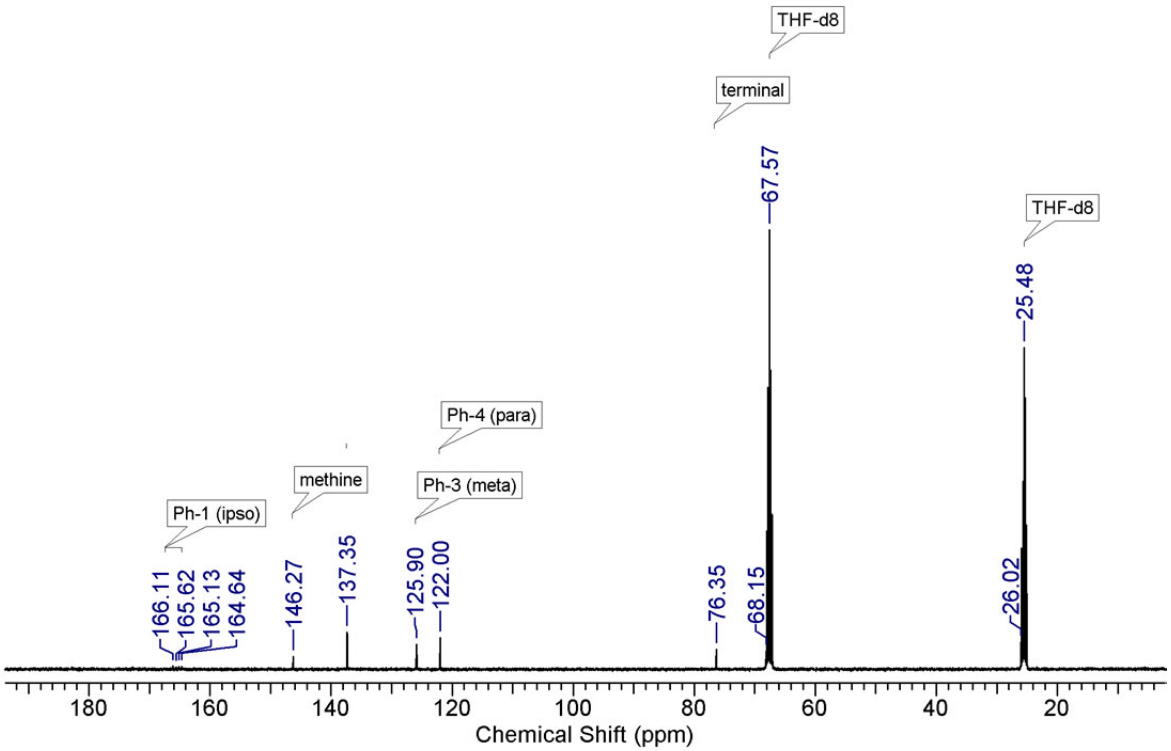

Fig. S4b. $^{13}C\{^{1}H\}$ NMR spectrum of $[Sc(C_3H_5)_2(THF)_3][BPh_4]$ (**2a**) in THF-d_8 at +25 °C.

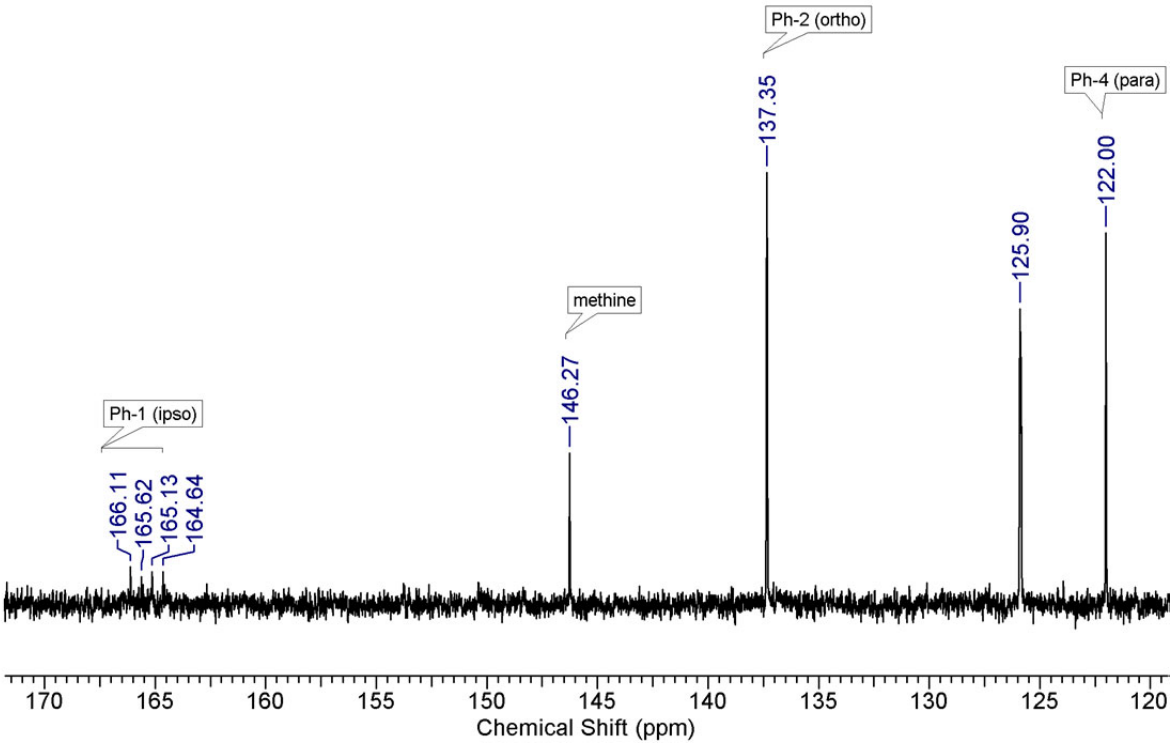

Fig. S4c. $^{13}C\{^{1}H\}$ NMR spectrum of $[Sc(C_3H_5)_2(THF)_3][BPh_4]$ (**2a**) in THF-d_8 at +25 °C, δ = 120–170 ppm.

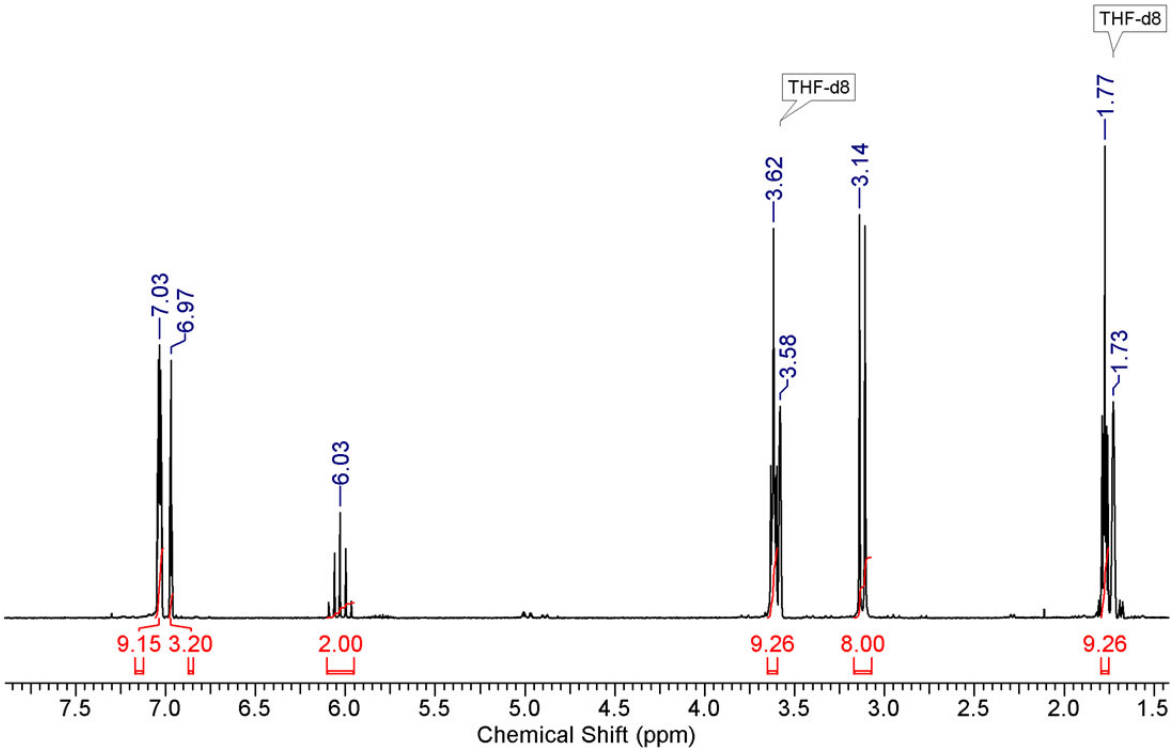

Fig. S5a. ^{1}H NMR spectrum of $[Sc(C_3H_5)_2(THF)_{2.25}][B(C_6H_3Cl_2)_4]$ (**2b**) in THF-d_8 at +25 °C.

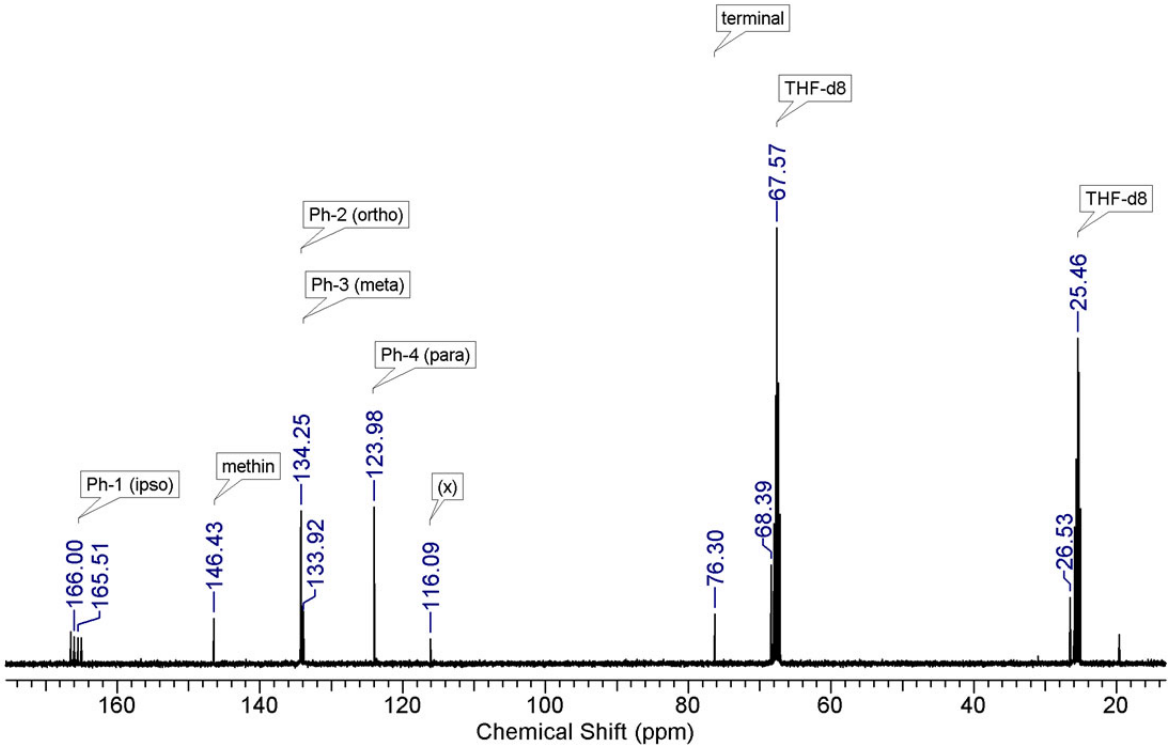

Fig. S5b. $^{13}C\{^{1}H\}$ NMR spectrum of $[Sc(C_3H_5)_2(THF)_{2.25}][B(C_6H_3Cl_2)_4]$ (**2b)** in THF-d_8 at +25 °C.

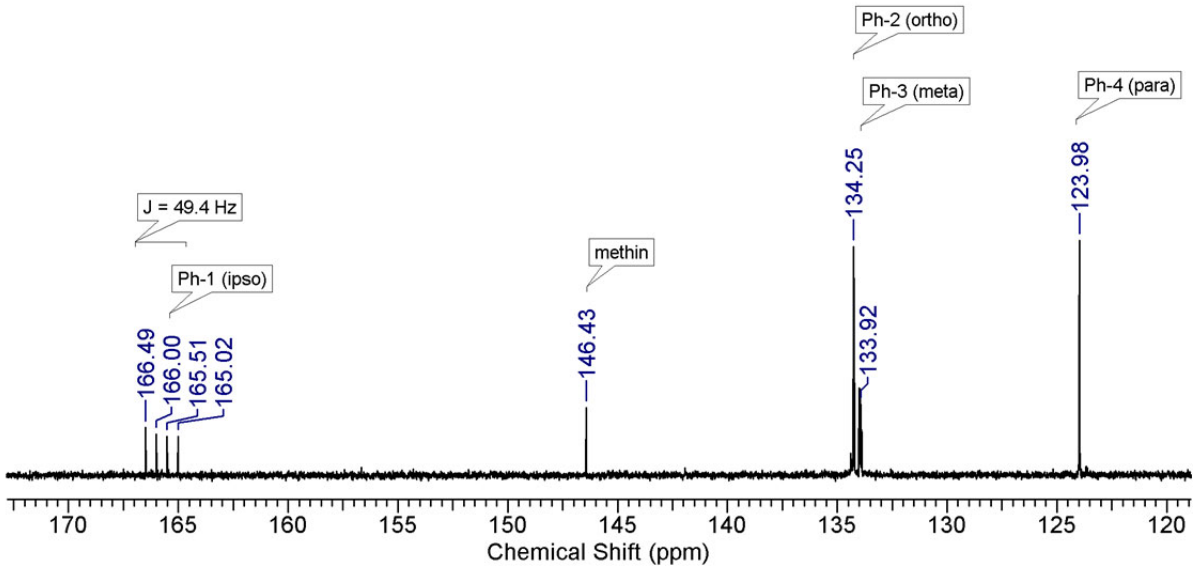

Fig. S5c. $^{13}C\{^{1}H\}$ NMR spectrum of $[Sc(C_3H_5)_2(THF)_{2.25}][B(C_6H_3Cl_2)_4]$ (**2b)** in THF-d_8 at +25 °C, δ= 120–170 ppm.

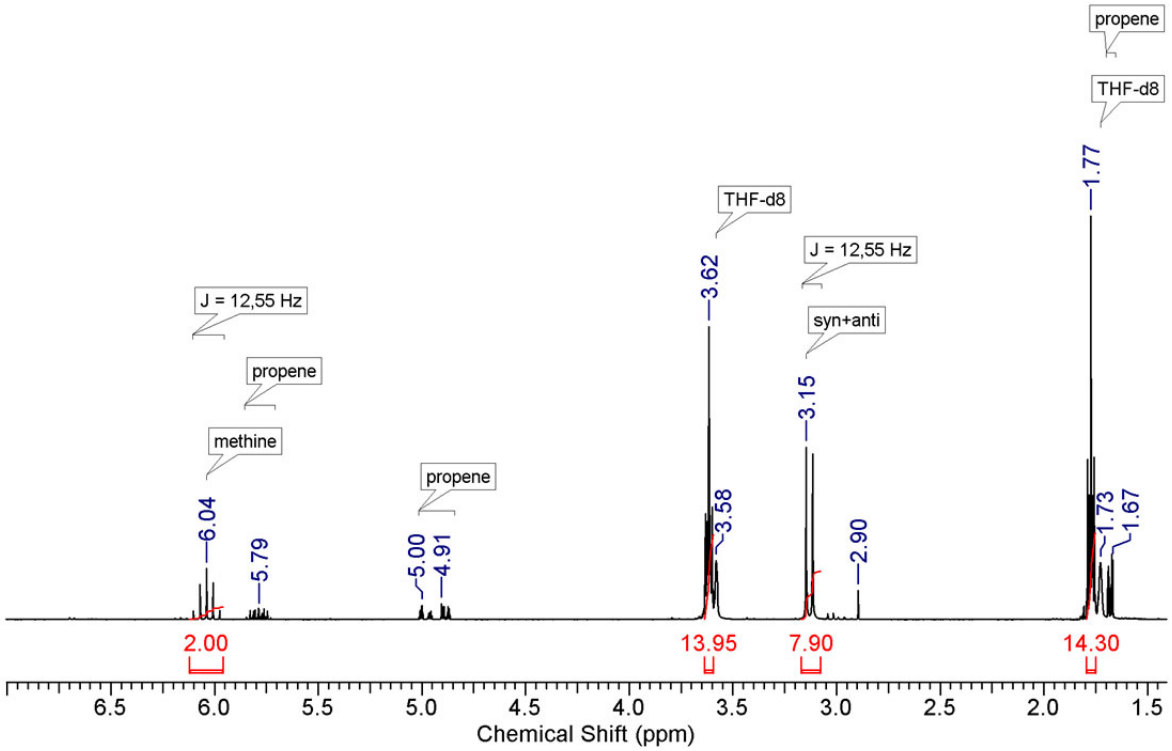

Fig. S6a. ^{1}H NMR spectrum of $[Sc(C_3H_5)_2(THF)_{2.25}][B(C_6F_5)_4]$ (**2c**) in THF-d_8 at +25 °C.

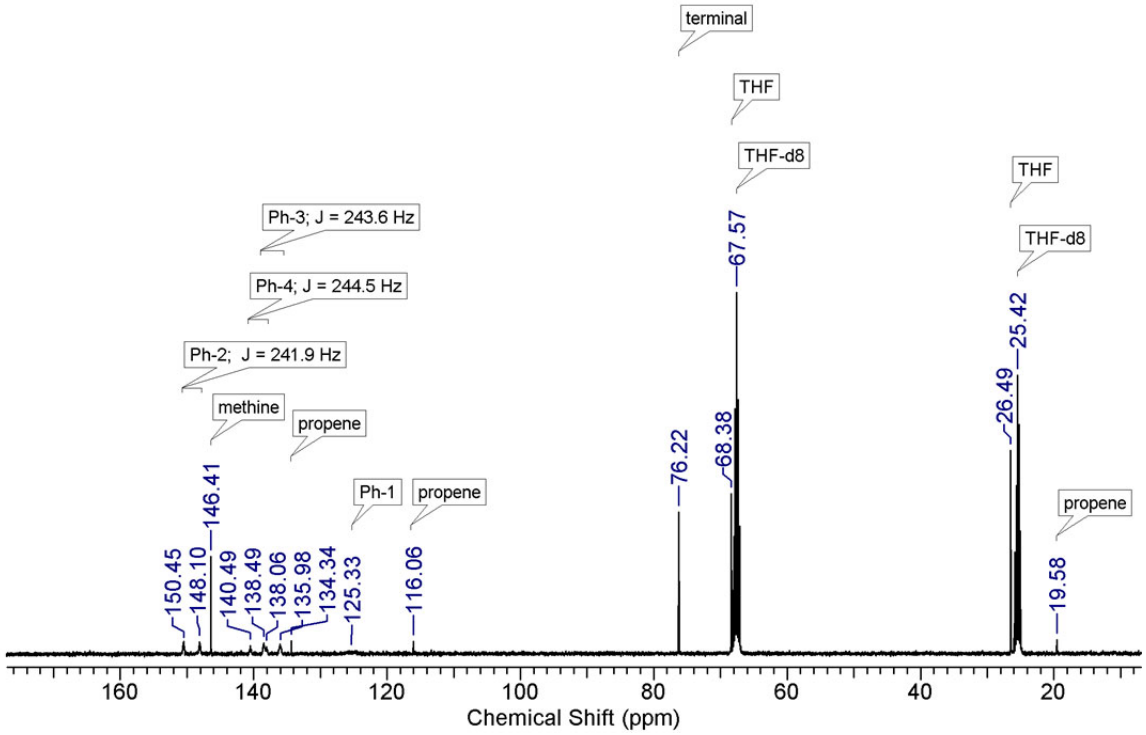

Fig. S6b. ^{13}C{^{1}H} NMR spectrum of $[Sc(C_3H_5)_2(THF)_{2.25}][B(C_6F_5)_4]$ (**2c**) in THF-d_8 at +25 °C.

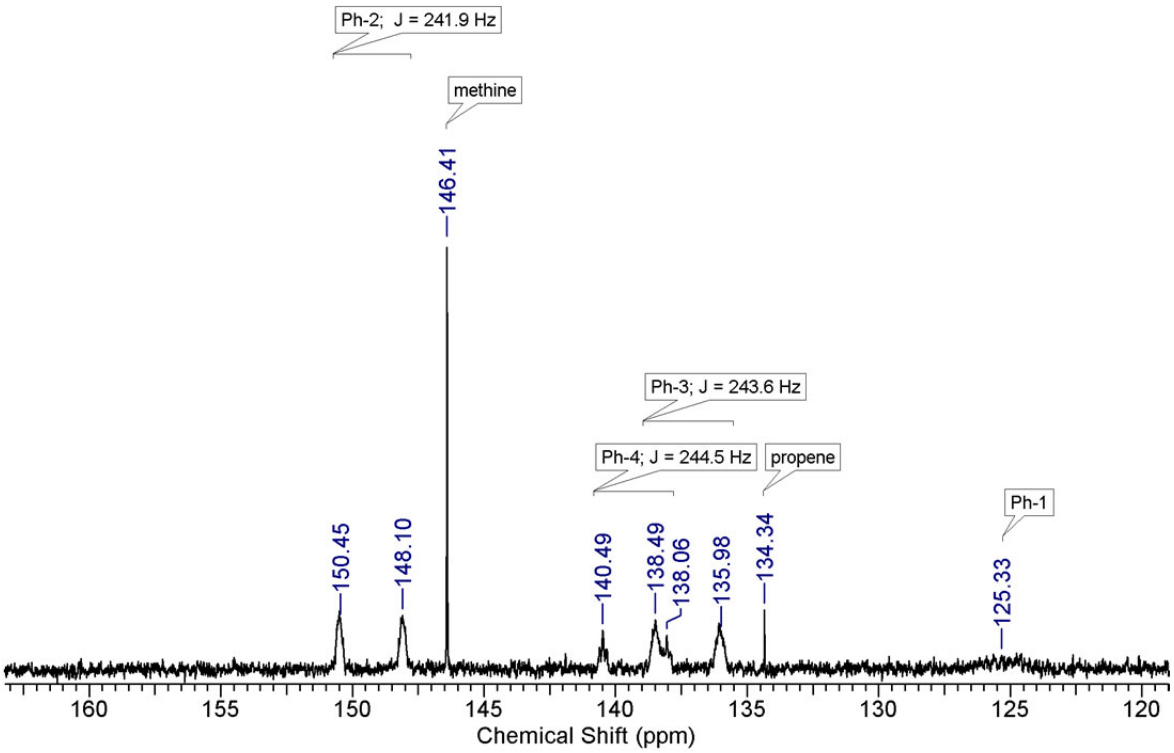

Fig. S6c. $^{13}C\{^{1}H\}$ NMR spectrum of $[Sc(C_3H_5)_2(THF)_{2.25}][B(C_6F_5)_4]$ (**2c**) in THF-d_8 at +25 °C, δ = 120–160 ppm.

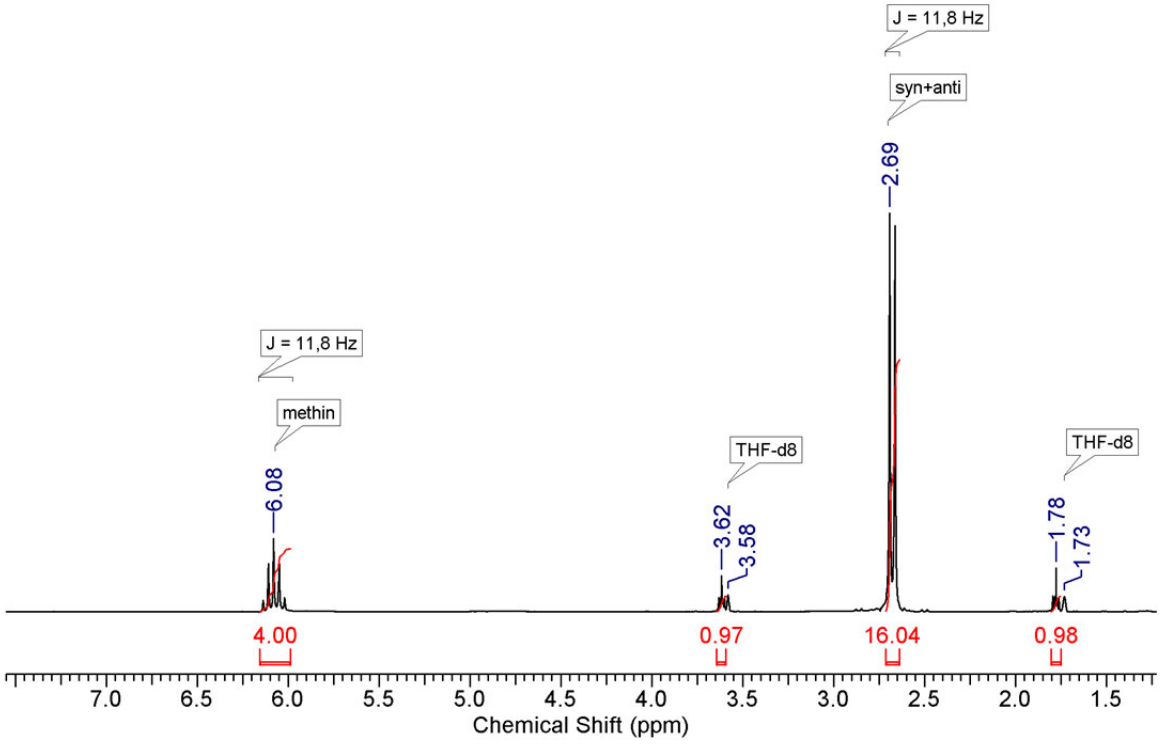

Fig. S7a. ^{1}H NMR spectrum of $K[Sc(C_3H_5)_4]$ (**3a**) in THF-d_8 at +25 °C.

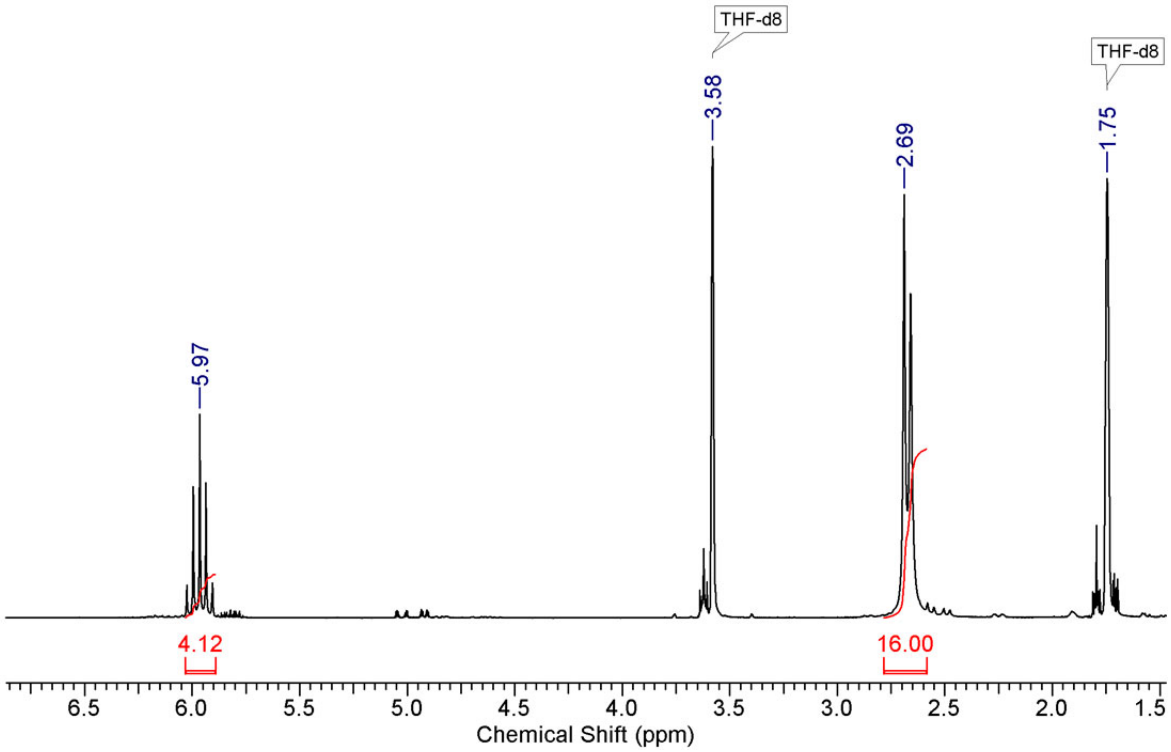

Fig. S7b. ^{1}H NMR spectrum of K[Sc(C_3H_5)$_4$] (**3a**) in THF-d_8 at −95 °C.

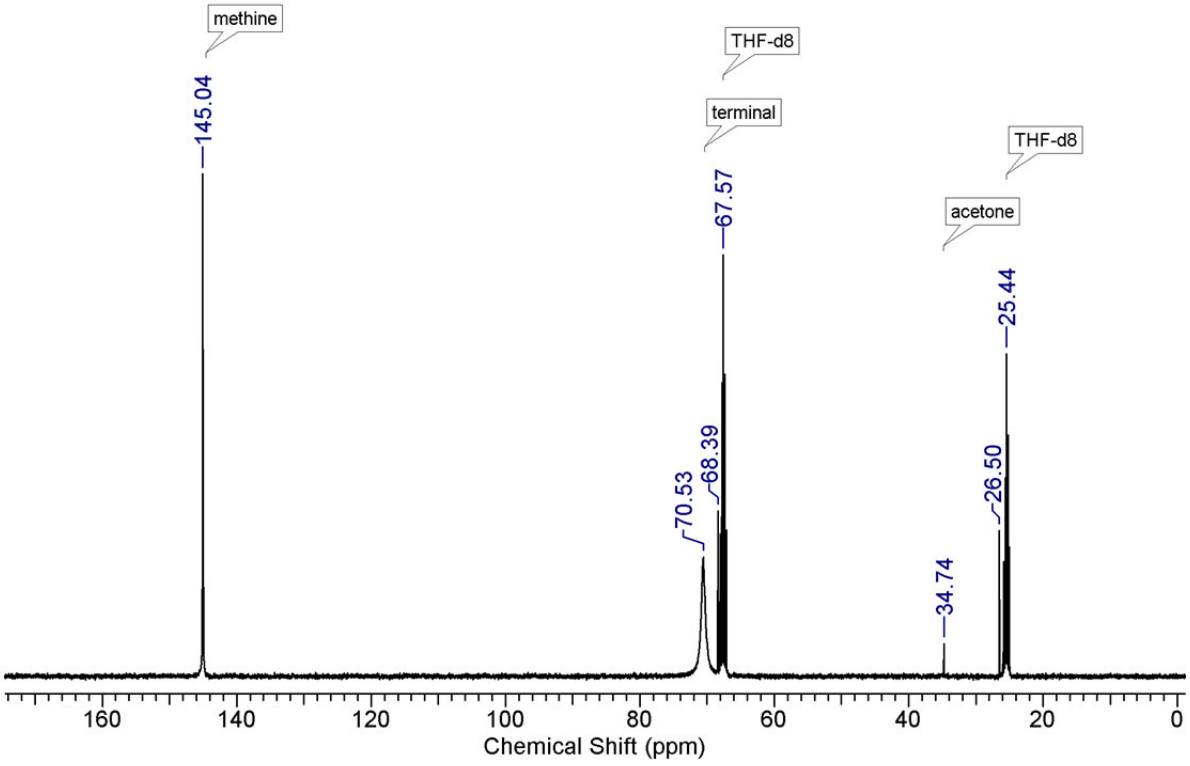

Fig. S7c. ^{13}C{^{1}H} NMR spectrum of K[Sc(C_3H_5)$_4$] (**3a**) in THF-d_8 at +25 °C.

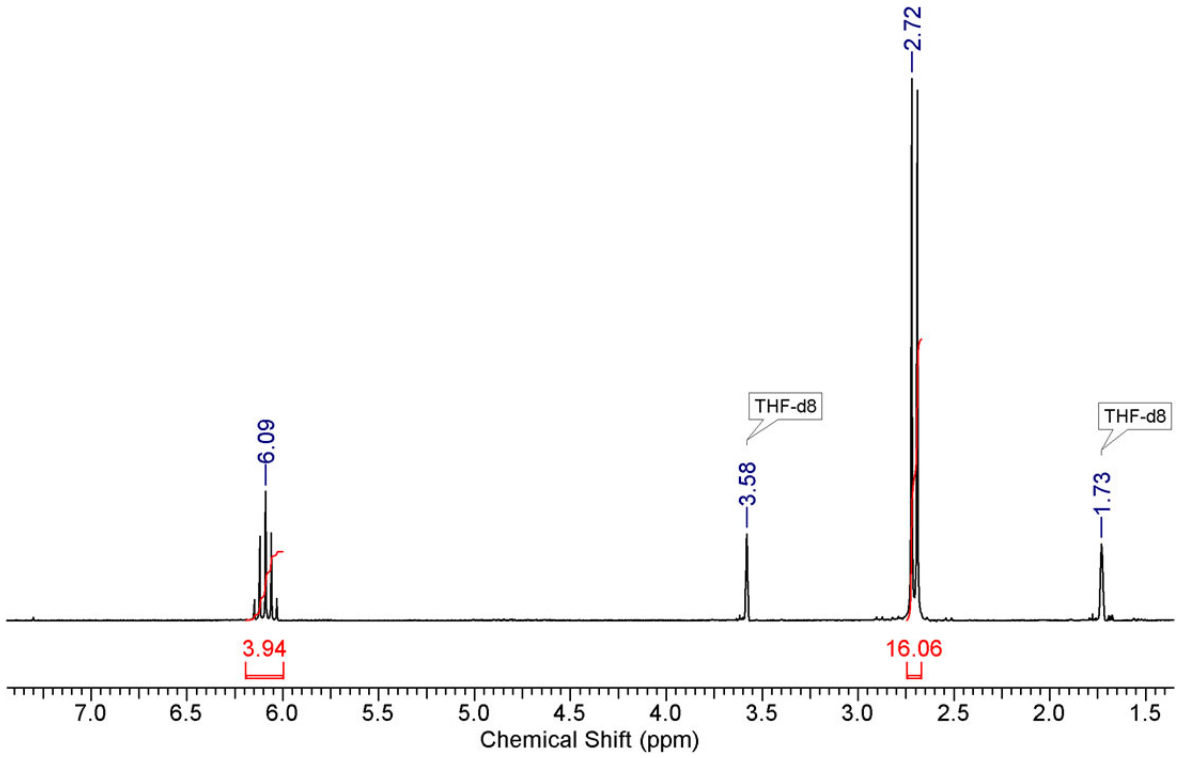

Fig. S7d. ^{1}H NMR spectrum of K[Sc(C_3H_5)$_4$] (**3a**) in THF-d_8 at +25 °C; [starting from [Sc(C_3H_5)$_3$(THF)$_{1.5}$] (**1**)].

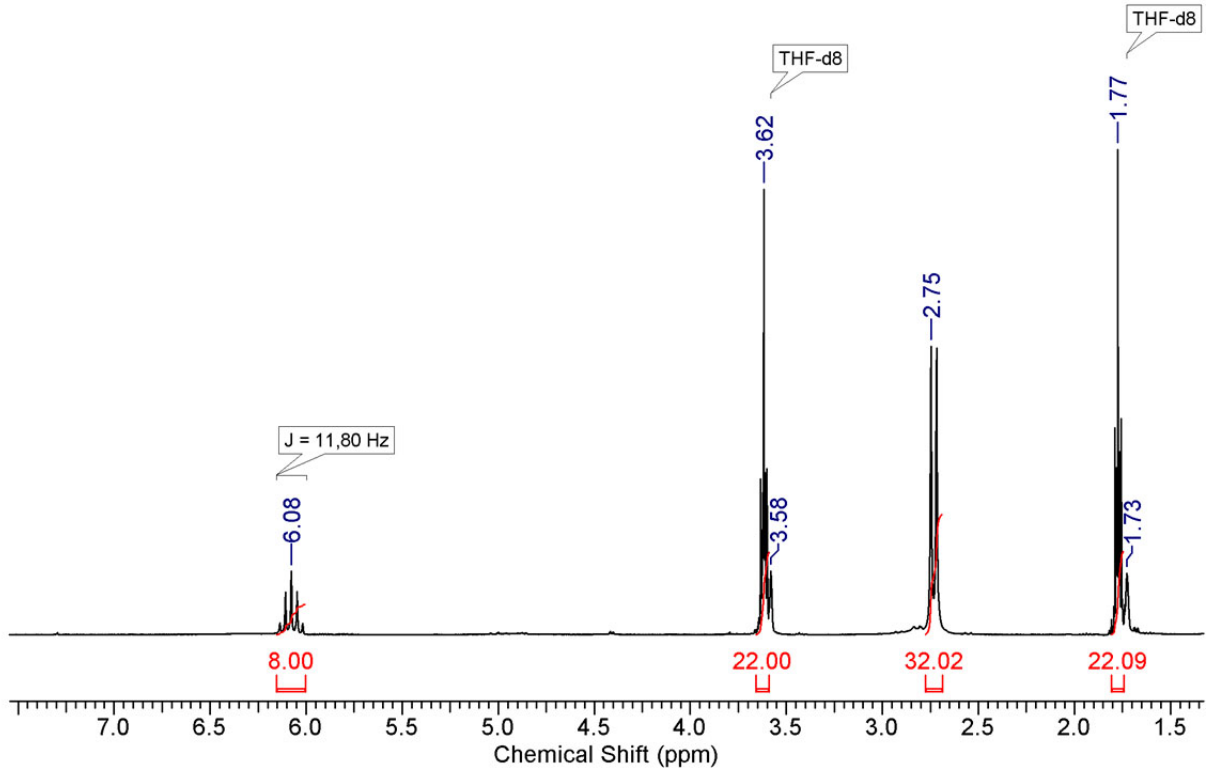

Fig. S8a. ^{1}H NMR spectrum of [Ca(THF)$_{5.5}$][Sc(C_3H_5)$_4$]$_2$ (**3b**) in THF-d_8 at +25 °C.

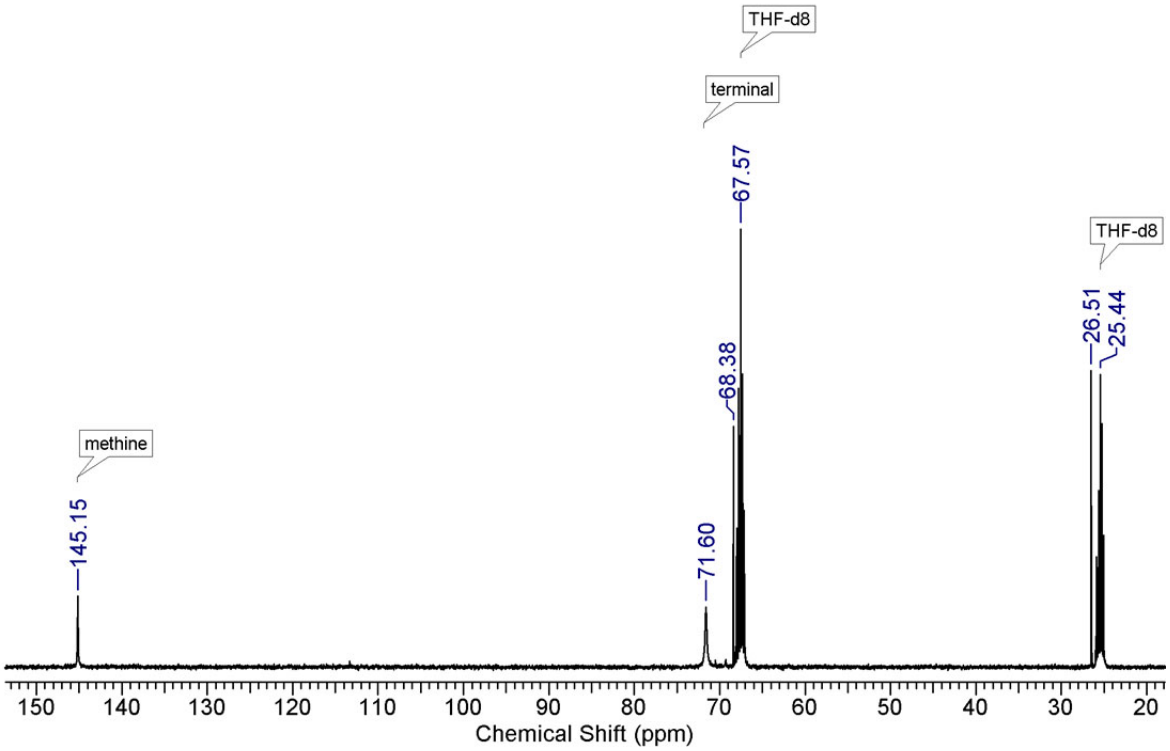

Fig. S8b. $^{13}C\{^{1}H\}$ NMR spectrum of $[Ca(THF)_{5.5}][Sc(C_3H_5)_4]_2$ (**3b**) in THF-d_8 at +25 °C.

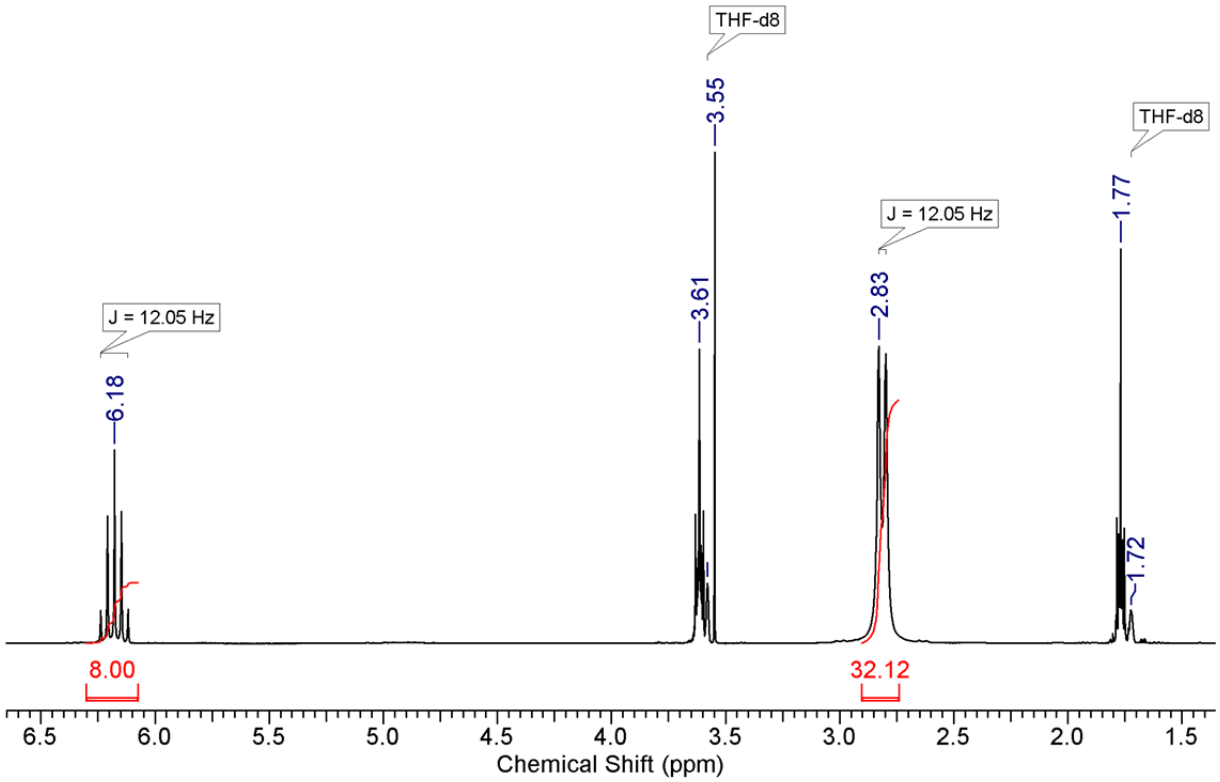

Fig. S9a. ^{1}H NMR spectrum of $[Mg(THF)_2][Sc(C_3H_5)_4]_2$ (**3c'**) in THF-d_8 at +25 °C.

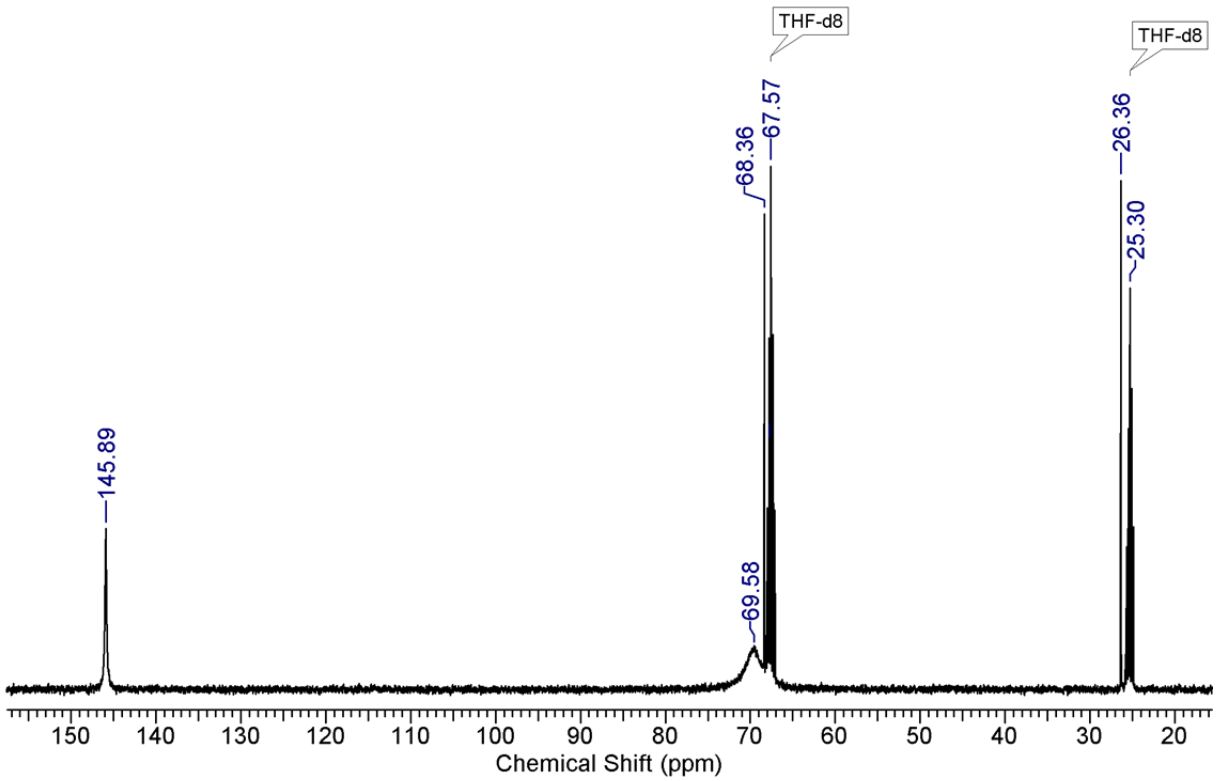

Fig. S9b. $^{13}C\{^{1}H\}$ NMR spectrum of $[Mg(THF)_2][Sc(C_3H_5)_4]_2$ (**3c'**) in THF-d_8 at +25 °C.