Supporting Information

Reactivity of Bridged and Nonbridged Zirconocenes Towards Biorenewable Itaconic Esters and Anhydride

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Part A: Experimental Details

Materials, Reagents, and Methods.

All synthesis and manipulations with air- and moisture-sensitive chemicals and reagents were performed using standard Schlenk techniques on a dual-manifold Schlenk line or in an inert gas (Ar or N_2)-filled glovebox. NMR-scale reactions were conducted in Teflon-valve-sealed J. Young-type NMR tubes. NMR (^{1}H, ^{13}C, and ^{19}F) spectra were recorded on a Varian Inova 400 MHz or 500 MHz spectrometer. Benzene-d_6 and toluene-d_8 were dried over sodium/potassium alloy and vacuum-distilled or filtered, whereas CD_2Cl_2, C_6D_5Br and $CDCl_3$ were dried over CaH_2 and vacuum-distilled. Chemical shifts were referenced to residual undeuterated solvent resonances and are reported as parts per million relative to $SiMe_4$. HPLC-grade organic solvents were first saturated with nitrogen during filling of the 20 L solvent reservoirs and then dried by passage through activated alumina (for Et_2O, THF, and CH_2Cl_2) followed by passage through Q-5 supported copper catalyst (for toluene and hexanes) stainless steel columns.

Lithium dimethylamide, trimethylsilyl trifluoromethanesulfonate (TMSOTf), methyl magnesium chloride (3.0 M solution in THF), and 2,6-di-*tert*-butyl-4-methylphenol (BHT-H) were purchased from Alfa Aesar Chemical Co., while triflic acid was purchased from Oakwook Chemical. Dimethyl itaconate (DMIA) and itaconic anhydride (IA) were purchased from Alfa Aesar Chemical Co., and they were purified by stirring a CH_2Cl_2 solution with activated CaH_2

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overnight, followed by filtration and sublimation of the resulting solid after evaporation (60 °C/200 mTorr and 45 °C/250 mTorr for DMIA and IA, respectively). Diisopropyl itaconate (D^iPrIA) was prepared following a literature procedure.[1] Methyl methacrylate (MMA) was purchased from Alfa Aesar Chemical Co., while dimethyl acrylamide (DMAA) was purchased from TCI America. D^iPrIA, MMA, and DMAA were dried over activated CaH_2 overnight, followed by vacuum distillation, degasification by three freeze-pump-thaw cycles, and finally they were stored in brown bottles at −30 °C inside a glovebox freezer. MMA was further purified by titration with tri(*n*-octyl)aluminum to a yellow end point followed by distillation under reduced pressure.[2] Tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, and (η^5-pentamethylcyclopentadienyl)(η^5-*n*-propylcyclopentadienyl)zirconium dichloride [Cp*(^{n}PrCp)$ZrCl_2$], were obtained as research gifts from Boulder Scientific Co.; $B(C_6F_5)_3$ was further purified by sublimation and Cp*(^{n}PrCp)$ZrCl_2$ was used without further purification. The $(C_6F_5)_3B\cdot THF$ adduct was prepared by addition of THF to a toluene solution of the borane at ambient temperature, followed by removal of the volatiles and drying under vacuum. Literature procedures were employed for the preparation of the following materials or compounds: *rac*-(EBI)ZrMe[OC(O^{i}Pr)=CMe_2] [**1**, EBI = ethylene-bis(η^5-indenyl)],[3-5] *rac*-(EBI)Zr^+(THF)[OC(O^{i}Pr)=CMe_2][$MeB(C_6F_5)_3$]$^-$ (**1**$^+$),[3-5] Li[OC(O^{i}Pr)=CMe_2],[6,7] and $[H(OEt_2)_2]^+[B(C_6F_5)_4]^-$.[8]

***In Situ* Generation of *rac*-(EBI)Zr[OC(OMe)=C(CH_2COOMe)CH_2C(Me_2)C(O^{i}Pr)=O]$^+$ [$MeB(C_6F_5)_3$]$^-$ (2a).** In an argon-filled glovebox, complex **1**$^+$ was cleanly generated *in situ* by mixing **1** (24.7 mg, 0.050 mmol) and $(C_6F_5)_3B\cdot THF$ (29.8 mg, 0.051 mmol) at room temperature in 0.4 mL of CD_2Cl_2 inside a 1.5 dram vial. The resulting dark red solution was chilled to −30 °C inside the glovebox freezer. Then, a stoichiometric amount of DMIA (7.9 mg, 0.050 mmol) was added via syringe at −30 °C from a stock solution in CD_2Cl_2. The subsequent red solution was quickly transferred to a Teflon-valve-sealed J. Young-type NMR tube, and immediately placed on a dry ice/acetone batch until it was analyzed by ^{1}H and ^{13}C NMR at −18 °C.

^{1}H NMR (CD_2Cl_2, −18 °C) of **2a**: δ 8.04 (d, J = 8.5 Hz, 1H, Ar H), 7.96 (d, J = 8.5 Hz, 1H, Ar H), 7.45 (d, J = 8.5 Hz, 1H, Ar H), 7.38–7.21 (m, 5H, Ar H), 6.28 (m, 3H, Cp H), 5.95 (d, J = 3.5 Hz, 1H, Cp H), 4.27 (sept, J = 6.3 Hz, 1H, –OC*H*Me$_2$), 4.31–3.93 (m, 4H, –CH$_2$C*H*$_2$– bridge), 3.66 (bs, 4H, α-THF, free), 3.64 (s, 3H, –OMe), 3.09 (s, 3H, –OMe), 2.89 (d, J = 16.5 Hz, 1H, C*H*$_2$C(O)OMe), 2.81 (d, J = 17.0 Hz, 1H, C*H*$_2$C(O)OMe), 2.29 (d, J = 16.0 Hz, 1H, –C*H*$_2$–), 1.80 (m, 4H, β-THF, free), 1.72 (d, J = 16.0 Hz, 1H, –C*H*$_2$–), 1.38 (d, J = 6.5 Hz, 3H, OCH*Me*$_2$), 1.23 (d, J = 6.5 Hz, 3H, OCH*Me*$_2$), 1.19 (s, 3H, C*Me*$_2$), 1.09 (s, 3H, C*Me*$_2$), 0.47 (s, br, 3H, B*Me*). ^{13}C NMR (CD_2Cl_2, −18 °C): δ 192.45 [*C*(O^{i}Pr)=O], 173.25 [*C*(OMe)=O], 158.62 [O*C*(OMe)=], 148.21 (d, $^1J_{C\text{-}F}$ = 235.5 Hz, Ar*C*–F), 137.45 (d, $^1J_{C\text{-}F}$ = 243.2 Hz, Ar*C*–F), 136.35 (d, $^1J_{C\text{-}F}$ = 246.6 Hz, Ar*C*–F), 133.85, 132.77, 131.77, 129.10, 128.29, 128.11, 127.35, 126.99, 126.64, 126.04, 125.36, 124.45, 123.91, 123.60, 123.39, 118.31, 116.81, 107.79, and 106.47(indenyl carbons), 79.16 (=*C*CH$_2$), 77.28 (O*C*HMe$_2$), 67.94 (α-THF, free), 53.40 (–O*Me*, overlapped with *C*D$_2$Cl$_2$), 51.89 (–O*Me*), 43.98 (*C*Me$_2$), 38.68 (–*C*H$_2$–), 36.00 [*C*H$_2$C(O)OMe], 30.64, 30.45 (–*C*H$_2$CH$_2$– bridge), 28.56 (C*Me*$_2$), 25.71 (β-THF, free), 23.44 (C*Me*$_2$), 21.94 (OCH*Me*$_2$), 20.70 (OCH*Me*$_2$), 10.05 (B-*C*H$_3$). ^{19}F NMR (CD_2Cl_2, 25 °C): δ −133.17 (d, $^3J_{F\text{-}F}$ = 19.2 Hz, 6F, o–Ar*F*), −165.35 (t, $^3J_{F\text{-}F}$ = 20.3 Hz, 3F, p–Ar*F*), −167.92 (m, 6F, m–Ar*F*).

***In Situ* Generation of *rac*-(EBI)Zr[OC(O^{i}Pr)=C(CH$_2$COO^{i}Pr)CH$_2$C(Me$_2$)C(O^{i}Pr)=O]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ (2b).** In an argon-filled glovebox, complex **1**$^+$ was cleanly generated *in situ* by mixing **1** (26.4 mg, 0.054 mmol) and (C$_6$F$_5$)$_3$B·THF (31.7 mg, 0.054 mmol) at room temperature in 0.4 mL of CD_2Cl_2 inside a 1.5 dram vial. The resulting dark red solution was chilled to −30 °C inside the glovebox freezer. Then, a stoichiometric amount of D^{i}PrIA (7.9 mg, 0.050 mmol) was added via syringe at −30 °C from a stock solution in CD_2Cl_2. The subsequent red solution was quickly transferred to a Teflon-valve-sealed J. Young-type NMR tube, and immediately placed on a dry ice/acetone batch until it was analyzed by ^{1}H and ^{13}C NMR at −18 °C.

^{1}H NMR (CD_2Cl_2, −18 °C) of **2b**: δ 8.06 (d, J = 8.5 Hz, 1H, Ar H), 7.92 (d, J = 9.0 Hz, 1H, Ar H), 7.44–7.21 (m, 6H, Ar H), 6.40 (s, br, 1H, Cp H), 6.26 (s, br, 1H, Cp H), 6.23 (s, br, 1H, Cp

H), 5.97 (s, br, 1H, Cp H), 4.93 (sept, J = 6.4 Hz, 1H, –OC*H*Me$_2$), 4.19 (bs, 1H, –OC*H*Me$_2$), 4.14–3.94 (m, 4H, –CH$_2$C*H*$_2$– bridge), 3.66 (bs, 4H, α-THF, free), 3.61 (bs, 1H, –OC*H*Me$_2$), 2.89 (d, J = 17.0 Hz, 1H, C*H*$_2$C(O)O^{i}Pr), 2.79 (d, J = 17.0 Hz, 1H, C*H*$_2$C(O)O^{i}Pr), 2.23 (d, J = 16.0 Hz, 1H, –C*H*$_2$–), 1.80 (m, 4H, β-THF, free), 1.71 (d, J = 16.0 Hz, 1H, –C*H*$_2$–), 1.37 (d, J = 6.0 Hz, 3H, OCH*Me*$_2$), 1.23–1.19 (m, 15H, OCH*Me*$_2$), 1.13 (s, br, 3H, C*Me*$_2$), 0.98 (s, 3H, C*Me*$_2$), 0.48 (s, br, 3H, B*Me*). ^{13}C NMR (CD$_2$Cl$_2$, −18 °C): δ 192.37 [*C*(O^{i}Pr)=O], 172.30 [*C*(O^{i}Pr)=O], 156.53 [O*C*(O^{i}Pr)=], 148.21 (d, $^1J_{C\text{-}F}$ = 235.8 Hz, Ar*C*–F), 137.52 (d, $^1J_{C\text{-}F}$ = 253.4 Hz, Ar*C*–F), 136.37 (d, $^1J_{C\text{-}F}$ = 249.2 Hz, Ar*C*–F), 132.60, 131.86, 129.11, 128.42, 128.01, 127.27, 126.95, 126.08, 125.84, 124.19, 123.85, 123.43, 122.64, 121.28, 118.47, 116.43, 107.06, and 106.15 (indenyl carbons), 83.50 (=*C*CH$_2$), 76.81 (O*C*HMe$_2$), 68.69 (O*C*HMe$_2$), 67.94 (O*C*HMe$_2$ overlapped with α-THF, free), 43.13 (*C*Me$_2$), 38.43 (–*C*H$_2$–), 36.92 [*C*H$_2$C(O)O^{i}Pr], 30.68, 30.51 (–*C*H$_2$CH$_2$– bridge), 28.99 (C*Me*$_2$), 25.71 (β-THF, free), 23.75 (C*Me*$_2$), 22.05, 21.90, 21.79, 21.73, 21.63, and 20.71 (OCH*Me*$_2$), 9.99 (B-*C*H$_3$). ^{19}F NMR (CD$_2$Cl$_2$, 25 °C): δ −133.13 (d, $^3J_{F\text{-}F}$ = 18.1 Hz, 6F, o–Ar*F*), −165.27 (t, $^3J_{F\text{-}F}$ = 20.3 Hz, 3F, p–Ar*F*), −167.84 (m, 6F, m–Ar*F*).

Isolation of *rac*-(EBI)Zr[OC(OMe)=C(CH$_2$CMe$_2$COO^{i}Pr)CH$_2$C(OMe)=O]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ (4a). In an argon-filled glovebox, a 30 mL glass reaction jar was charged with 56.6 mg of complex **1** (0.115 mmol) and dissolved in 3 mL of CH$_2$Cl$_2$. Complex **1**$^+$ was cleanly generated *in situ* by adding an equimolar amount of (C$_6$F$_5$)$_3$B·THF (67.2 mg, 0.115 mmol) in 1 mL of CH$_2$Cl$_2$ at room temperature. After stirring for 5 min, the reaction mixture was cooled to −30 °C inside the glovebox freezer, and then 18.2 mg of DMIA (0.115 mmol) were added via syringe from a prechilled stock solution in CH$_2$Cl$_2$. The reaction mixture was stirred for a total of 24 h at room temperature, after which time the color of the solution slowly changed from the initial red to orange. The solvent was evaporated *in vacuo*, the red residue was thoroughly washed with hexanes (3 × 5 mL), the supernatant decanted, and the volatiles were removed under vacuum. The residue was taken in 0.4 mL of CH$_2$Cl$_2$, cooled down to −30 °C inside the glovebox freezer and then hexanes (3 mL) were allowed to slowly diffuse to form a bright red oil after 3 days. The supernatant was

decanted, and the oil product was thoroughly dried under vacuum to obtain **4a** as a red foamy powder in quantitative yield. Anal. Calcd for $C_{53}H_{42}BF_{15}O_6Zr$: C, 54.79; H, 3.64. Found: C, 54.51; H, 3.81.

^{1}H NMR (CD_2Cl_2, 25 °C) of **4a**: δ 7.95 (d, J = 8.8 Hz, 1H, Ar H), 7.87 (d, J = 8.8 Hz, 1H, Ar H), 7.46 (d, J = 8.0 Hz, 1H, Ar H), 7.42–7.10 (m, 5H, Ar H), 6.42 (d, J = 3.6 Hz, 1H, Cp H), 6.34 (d, J = 3.6 Hz, 1H, Cp H), 6.31 (d, J = 3.2 Hz, 1H, Cp H), 6.07 (d, J = 3.2 Hz, 1H, Cp H), 4.89 (sept, J = 6.3 Hz, 1H, –OC*H*Me$_2$), 4.06 (m, 4H, –CH$_2$C*H*$_2$– bridge), 3.73 (s, 3H, –OMe), 3.15 (s, 3H, –OMe), 2.73 (d, J = 14.8 Hz, 1H, C*H*$_2$C(O)OMe), 2.67 (d, J = 14.8 Hz, 1H, C*H*$_2$C(O)OMe), 2.34 (d, J = 14.4 Hz, 1H, –C*H*$_2$–), 2.03 (d, J = 14.4 Hz, 1H, –C*H*$_2$–), 1.27 (d, J = 4.8 Hz, 3H, OCH*Me*$_2$), 1.22 (d, J = 6.0 Hz, 3H, OCH*Me*$_2$), 1.12 (s, 3H, C*Me*$_2$), 1.06 (s, 3H, C*Me*$_2$), 0.51 (s, br, 3H, B*Me*). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 189.08 [*C*(OMe)=O], 177.38 [*C*(O^{i}Pr)=O], 157.94 [O*C*(OMe)=], 148.70 (d, $^1J_{C\text{-}F}$ = 234.4 Hz, Ar*C*–F), 137.89 (d, $^1J_{C\text{-}F}$ = 245.3 Hz, Ar*C*–F), 136.88 (d, $^1J_{C\text{-}F}$ = 219.1 Hz, Ar*C*–F), 132.52, 130.83, 128.65, 128.51, 128.03, 127.64, 127.19, 125.77, 125.73, 125.06, 124.95, 124.56, 122.07, 121.61, 117.71, 117.53, 108.26, and 107.60 (indenyl carbons), 79.16 (=*C*CH$_2$), 68.02 (O*C*HMe$_2$), 58.45 (–O*Me*), 53.30 (–O*Me*, overlapped with *C*D$_2$Cl$_2$), 43.43 (*C*Me$_2$), 42.08 (–*C*H$_2$–), 37.77 [*C*H$_2$C(OMe)=O], 30.48, 29.91 (–*C*H$_2$CH$_2$– bridge), 25.83 (C*Me*$_2$), 25.07 (C*Me*$_2$), 21.81 (OCH*Me*$_2$), 21.76 (OCH*Me*$_2$), 10.35 (B-*C*H$_3$). ^{19}F NMR (CD_2Cl_2, 25 °C): δ −133.11 (d, $^3J_{F\text{-}F}$ = 18.1 Hz, 6F, o–Ar*F*), −165.24 (t, $^3J_{F\text{-}F}$ = 20.3 Hz, 3F, p–Ar*F*), −167.82 (m, 6F, m–Ar*F*).

Isolation of *rac*-(EBI)Zr[OC(O^{i}Pr)=C(CH$_2$CMe$_2$COO^{i}Pr)CH$_2$C(O^{i}Pr)=O]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ (4b). In an argon-filled glovebox, a 30 mL glass reaction jar was charged with 54.9 mg of complex **1** (0.112 mmol) and dissolved in 3 mL of CH_2Cl_2. Complex **1**$^+$ was cleanly generated *in situ* by adding an equimolar amount of $(C_6F_5)_3B\cdot THF$ (65.2 mg, 0.112 mmol) in 1 mL of CH_2Cl_2 at room temperature. After stirring for 5 min, the reaction mixture was cooled to −30 °C inside the glovebox freezer, and then 24.1 mg of D^{i}PrIA (0.112 mmol) were added via syringe from a prechilled stock solution in CH_2Cl_2. The reaction mixture was stirred for a total of 24 h at room

temperature. The solvent was evaporated *in vacuo*, the red residue was thoroughly washed with hexanes (3 × 5 mL), the supernatant decanted, and the volatiles were removed under vacuum. The residue was taken in 0.4 mL of CH_2Cl_2, cooled down to −30 °C inside the glovebox freezer and then hexanes (3 mL) were allowed to slowly diffuse to form a bright red oil after 3 days. The supernatant was decanted, and the oil product was thoroughly dried under vacuum to obtain **4b** as an orange foamy powder in quantitative yield. Anal. Calcd for $C_{57}H_{50}BF_{15}O_6Zr$: C, 56.21; H, 4.14. Found: C, 56.64; H, 4.25.

^{1}H NMR (CD_2Cl_2, 25 °C) of **4b**: δ 8.01 (d, J = 8.8 Hz, 1H, Ar H), 7.87 (d, J = 8.8 Hz, 1H, Ar H), 7.47 (d, J = 8.4 Hz, 1H, Ar H), 7.34–7.23 (m, 5H, Ar H), 6.40 (d, J = 3.6 Hz, 1H, Cp H), 6.35 (d, J = 3.6 Hz, 1H, Cp H), 6.28 (d, J = 3.6 Hz, 1H, Cp H), 6.01 (d, J = 3.6 Hz, 1H, Cp H), 4.93 (sept, J = 6.2 Hz, 1H, –OC*H*Me$_2$), 4.75 (sept, J = 6.3 Hz, 1H, –OC*H*Me$_2$), 4.08–3.98 (m, 4H, –CH$_2$C*H*$_2$– bridge), 3.76 (sept, J = 6.2 Hz, 1H, –OC*H*Me$_2$), 2.70 (d, J = 14.8 Hz, 1H, C*H*$_2$C(O)O^{i}Pr), 2.65 (d, J = 14.8 Hz, 1H, C*H*$_2$C(O)O^{i}Pr), 2.46 (d, J = 14.4 Hz, 1H, –C*H*$_2$–), 1.95 (d, J = 14.4 Hz, 1H, –C*H*$_2$–), 1.43 (d, J = 6.4 Hz, 3H, OCH*Me*$_2$), 1.23 (m, 12H, OCH*Me*$_2$), 1.14 (s, 3H, C*Me*$_2$), 1.09 (s, 3H, C*Me*$_2$), 0.97 (d, J = 6.0 Hz, 3H, OCH*Me*$_2$), 0.51 (s, br, 3H, B*Me*). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 188.12 [*C*(O^{i}Pr)=O], 177.32 [*C*(O^{i}Pr)=O], 156.65 [O*C*(OMe)=], 148.83 (d, $^1J_{C\text{-}F}$ = 235.9 Hz, Ar*C*–F), 137.87 (d, $^1J_{C\text{-}F}$ = 242.8 Hz, Ar*C*–F), 136.77 (d, $^1J_{C\text{-}F}$ = 248.3 Hz, Ar*C*–F), 132.67, 131.18, 128.69, 128.40, 127.95, 127.38, 126.82, 125.58, 125.38, 124.84, 124.75, 124.53, 122.17, 121.68, 117.75, 117.56, 107.27, and 106.67 (indenyl carbons), 81.71 (=*C*CH$_2$), 79.10 (O*C*HMe$_2$), 69.11 (O*C*HMe$_2$), 67.98 (O*C*HMe$_2$), 43.51 (*C*Me$_2$), 42.27 (–*C*H$_2$–), 38.36 [*C*H$_2$C(O^{i}Pr)=O], 30.62, 30.15 (–*C*H$_2$CH$_2$– bridge), 25.89 (C*Me*$_2$), 25.57 (C*Me*$_2$), 22.36, 21.99, 21.88, 21.83, 21.69, and 21.25 (OCH*Me*$_2$), 10.04 (B-*C*H$_3$). ^{19}F NMR (CD_2Cl_2, 25 °C): δ −133.12 (d, $^3J_{F\text{-}F}$ = 18.1 Hz, 6F, o–Ar*F*), −165.27 (t, $^3J_{F\text{-}F}$ = 20.3 Hz, 3F, p–Ar*F*), −167.83 (m, 6F, m–Ar*F*).

Isolation of *rac*-(EBI)ZrMe{OC[OC(O)CH$_2$]=C(CH$_2$CMe$_2$COO^{i}Pr)} (5). In an argon-filled glovebox, a 30 mL glass reaction jar was charged with 116.3 mg of complex **1** (0.236 mmol) and dissolved in 3 mL of CH_2Cl_2. An equimolar amount of itaconic anhydride (26.5 mg, 0.236

mmol) was dissolved in 1 mL of CH_2Cl_2 and quickly added at room temperature *via* pipette. The resulting bright yellow solution was stirred for 30 minutes at ambient temperature, and then the volatiles were removed under vacuum. The yellow residue was washed with 2 mL of hexanes and subsequently dried under vacuum to obtain complex **5** as a bright yellow powder. Yield: 130 mg (91%). Anal. Calcd for $C_{33}H_{36}O_5Zr$: C, 65.64; H, 6.01. Found: C, 65.37; H, 5.81.

^{1}H NMR (CD_2Cl_2, 25 °C) of **5**: δ 7.74 (d, J = 8.8 Hz, 1H, Ar H), 7.47 (d, J = 8.4 Hz, 1H, Ar H), 7.33 (pst, J = 8.8 Hz, 2H, Ar H), 7.24 (pst, J = 7.6 Hz, 1H, Ar H), 7.11 (psq, J = 7.5 Hz, 2H, Ar H), 6.99 (pst, J = 7.6 Hz, 1H, Ar H), 6.58 (d, J = 3.2 Hz, 1H, Cp H), 6.45 (d, J = 3.2 Hz, 1H, Cp H), 5.97 (d, J = 3.2 Hz, 1H, Cp H), 5.95 (d, J = 3.6 Hz, 1H, Cp H), 4.89 (sept, J = 6.3 Hz, 1H, OC*H*Me$_2$), 3.76–3.56 (m, 4H, –C*H*$_2$CH$_2$– bridge), 2.95 (s, 2H, C*H*$_2$C(O)O), 1.90 (s, 2H, –C*H*$_2$–), 1.19 (d, J = 6.4 Hz, 6H, OCH*Me*$_2$), 0.99 (s, 3H, C*Me*$_2$), 0.97 (s, 3H, C*Me*$_2$), −0.85 (s, 3H, Zr–C*H*$_3$). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 177.58 [*C*(O^{i}Pr)=O], 174.66 [CH$_2$*C*(O)=O], 156.01 [O*C*(OC)=], 127.18, 126.76, 125.92, 125.63, 125.24, 125.10, 124.80, 123.61, 123.23, 122.88, 122.45, 121.00, 119.77, 116.58, 113.82, 112.64, 106.75, and 104.35 (indenyl carbons), 76.83 (=*C*CH$_2$), 67.81 (O*C*HMe$_2$), 42.86 (*C*Me$_2$), 38.14 [*C*H$_2$C(O)=O], 35.37 (–*C*H$_2$–), 33.02 (Zr–*C*H$_3$), 28.78, 27.87 (–*C*H$_2$CH$_2$– bridge), 25.48, 25.07 (C*Me*$_2$), 21.91 (OCH*Me*$_2$).

***In Situ* Generation of *rac*-(EBI)ZrMe{OC[OC(O)CH$_2$]=C[CH$_2$CMe$_2$C(O^{i}Pr)=O]}$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ (6).** In an argon-filled glovebox, a 1.5 dram vial was charged with complex **1** (28.5 mg, 0.058 mmol) and 0.15 mL of CD_2Cl_2. Complex **5** was generated *in situ* by adding to **1** an equimolar amount of itaconic anhydride (6.50 mg, 0.058 mmol) from a stock solution in CD_2Cl_2 at room temperature; the subsequent yellow solution was cooled to −30 °C inside the glovebox freezer. In a separate 1.5 dram vial, a B(C$_6$F$_5$)$_3$ (29.9 mg, 0.058 mmol) solution in 0.25 mL CD_2Cl_2 was prepared and cooled to −30 °C inside the glovebox freezer. The pre-chilled B(C$_6$F$_5$)$_3$ solution was quickly added via pipette to the chilled solution of **5**, thoroughly mixed, and quickly transferred to a Teflon-valve-sealed J. Young-type NMR tube which was immediately placed on a dry ice/acetone batch until it was analyzed by ^{1}H and ^{19}F NMR at room temperature.

^{1}H NMR (CD_2Cl_2, 25 °C) of **6**: δ 8.01 (d, J = 8.0 Hz, 2H, Ar H), 7.42–7.31 (m, 6H, Ar H), 6.41 (d, J = 3.2 Hz, 2H, Cp H), 6.17 (s, br, 2H, Cp H), 4.94, 4.36 (s, br, 1H, OC*H*Me$_2$), 4.12 (s, 4H, –C*H*$_2$CH$_2$– bridge), 3.36 (s, br, 2H, C*H*$_2$C(O)O), 2.00 (s, br, 2H, –C*H*$_2$–), 1.37 (d, J = 6.0 Hz, 3H, OCH*Me*$_2$), 1.33 (d, J = 6.4 Hz, 3H, OCH*Me*$_2$), 1.30 (s, 3H, C*Me*$_2$), 1.25 (s, 3H, C*Me*$_2$), 0.49 (s, br, 3H, B*Me*). ^{19}F NMR (CD_2Cl_2, 25 °C): δ −133.03 (d, $^3J_{F\text{-}F}$ = 27.1 Hz, 6F, o–Ar*F*), −165.09 (t, $^3J_{F\text{-}F}$ = 20.3 Hz, 3F, p–Ar*F*), −167.71 (m, 6F, m–Ar*F*).

***In Situ* Generation of *rac*-(EBI)Zr{OC(NMe$_2$)=CCH$_2$C(CH$_2$CMe$_2$COO^{i}Pr)C [OC(O)]=O}$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (7).** In an argon-filled glovebox, a 1.5 dram vial was charged with complex **1** (27.7 mg, 0.056 mmol) and 0.1 mL of CD_2Cl_2. Complex **5** was generated *in situ* by adding to **1** an equimolar amount of itaconic anhydride (6.31 mg, 0.056 mmol) from a stock solution in CD_2Cl_2 at room temperature. In a separate 1.5 dram vial, $(C_6F_5)_3B\cdot$DMAA adduct was preformed by mixing $B(C_6F_5)_3$ (28.8 mg, 0.056 mmol) in 0.1 mL CD_2Cl_2 with an equimolar amount of DMAA (5.6 mg, 0.056 mmol) from a stock solution in CD_2Cl_2 at room temperature. Upon cooling at −30 °C inside the glovebox freezer, the $(C_6F_5)_3B\cdot$DMAA adduct solution in CD_2Cl_2 was added to the precooled solution of **5**. The resulting orange solution (total volume ~0.6 mL CD_2Cl_2) was quickly transferred to a Teflon-valve-sealed J. Young-type NMR tube, and immediately placed on a dry ice/acetone batch until it was analyzed by ^{1}H, ^{19}F, and ^{13}C NMR at room temperature.

^{1}H NMR (CD_2Cl_2, 25 °C) of **7**: δ 7.89 (d, J = 8.8 Hz, 1H, Ar H), 7.88 (d, J = 9.2 Hz, 1H, Ar H), 7.46 (d, J = 8.4 Hz, 1H, Ar H), 7.33–7.13 (m, 5H, Ar H), 6.57 (d, J = 3.6 Hz, 1H, Cp H), 6.55 (d, J = 3.6 Hz, 1H, Cp H), 6.14 (d, J = 3.2 Hz, 1H, Cp H), 6.02 (d, J = 3.2 Hz, 1H, Cp H), 4.94 (sept, J = 6.3 Hz, 1H, OC*H*Me$_2$), 4.07–3.95 (m, 6H, –C*H*$_2$CH$_2$– bridge, C*H*$_2$C(O)O), 3.26 (s, 3H, N*Me*$_2$), 2.79 (s, 3H, N*Me*$_2$), 2.52 (d, J = 4.0 Hz, 1H, C=C*H*), 2.29 (dd, J_1 = 26.0 Hz, J_2 = 10.8 Hz, 2H, C*H*$_2$CH=C), 2.22 (d, J = 14.8 Hz, 1H, –C*H*$_2$–), 2.08 (d, J = 14.8 Hz, 1H, –C*H*$_2$–), 1.96 (dd, J_1 = 15.2 Hz, J_2 = 5.6 Hz, 2H, C*H*$_2$CH=C), 1.24 (d, J = 6.4 Hz, 3H, OCH*Me*$_2$), 1.23 (d, J = 6.4 Hz, 3H, OCH*Me*$_2$), 1.18 (s, 3H, C*Me*$_2$), 1.15 (s, 3H, C*Me*$_2$), 0.51 (s, br, 3H, B*Me*). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 206.45 [*C*(O)=O], 177.75 [*C*(O^{i}Pr)=O], 176.95 [O*C*(NMe$_2$)=], 175.24 [CH$_2$*C*(O)=O], 148.70

(d, $^1J_{C\text{-}F}$ = 238.6 Hz, Ar*C*–F), 137.90 (d, $^1J_{C\text{-}F}$ = 244.3 Hz, Ar*C*–F), 136.81 (d, $^1J_{C\text{-}F}$ = 250.3 Hz, Ar*C*–F), 132.89, 130.69, 129.86, 128.17, 127.63, 127.46, 127.26, 126.18, 125.52, 125.41, 124.15, 124.14, 121.82, 121.14, 117.10, 116.33, 108.36, and 106.99 (indenyl carbons), 68.52 (O*C*HMe$_2$), 49.12 (C=*C*H), 47.94 (quaternary C), 47.87 (*C*H$_2$CH=C), 46.97 (*C*Me$_2$), 42.09 (–*C*H$_2$–), 40.58, 39.38 (N*Me*$_2$), 35.06 [*C*H$_2$C(O)=O], 30.63, 29.65 (–*C*H$_2$CH$_2$– bridge), 27.81, 27.06 (C*Me*$_2$), 21.82, 21.79 (OCH*Me*$_2$), 10.34 (B-*C*H$_3$). ^{19}F NMR (CD$_2$Cl$_2$, 25 °C): δ −133.12 (d, $^3J_{F\text{-}F}$ = 18.1 Hz, 6F, o–Ar*F*), −165.13 (t, $^3J_{F\text{-}F}$ = 20.3 Hz, 3F, p–Ar*F*), −167.77 (m, 6F, m–Ar*F*).

Isolation of [Cp*(^{n}PrCp)Zr(HNMe$_2$)=NMe$_2$]$^+$[B(C$_6$F$_5$)$_4$]$^-$ (9$^+$). In an argon-filled glovebox, a 200 mL glass reaction jar was charged with 1.02 g of Cp*(^{n}PrCp)ZrCl$_2$ (2.52 mmol) and dissolved in 50 mL of dry THF. The solution was cooled to −30 °C inside the glovebox freezer, and then a solution of LiNMe$_2$ (490 mg, 9.60 mmol) in 15 mL of THF at −30 °C was added via pipette under vigorous stirring. The solution was allowed to warm to ambient temperature and stirred for another 3 h. Then, the solvent was thoroughly removed under vacuum, and the obtained crude material was extracted with 100 mL of hexanes and filtered through a pad of celite to form an orange oil. The oil was redissolved in 5 mL of hexanes, filtered through a plastic frit (0.45 μm pore size nylon filter); after removing the solvent of the filtrate, the product was left to crystallize in 1 mL of hexanes overnight at −30 °C in the glovebox freezer, after which time bright orange crystals were formed. The mother liquor was decanted and the crystals were dried under vacuum to yield spectroscopically pure product Cp*(^{n}PrCp)Zr(NMe$_2$)$_2$ (**9**) as an intense yellow solid. Yield: 400 mg (38%). ^{1}H NMR (C$_6$D$_6$, 25 °C) of **9**: δ 5.99 (pst, J = 2.8 Hz, 2H, η^5-C$_5$*H*$_4$^{n}Pr), 5.68 (pst, J = 2.6 Hz, 2H, η^5-C$_5$*H*$_4$^{n}Pr), 2.90 (s, 12 H, –N(C*H*$_3$)$_2$), 2.48 (t, J = 7.4 Hz, 2H, –C*H*$_2$CH$_2$CH$_3$), 1.89 (s, 15H, η^5-C$_5$*Me*$_5$), 1.61 (sextet, J = 7.4 Hz, 2H, –CH$_2$C*H*$_2$CH$_3$), 0.93 (t, J = 7.4 Hz, 3H, –CH$_2$CH$_2$C*H*$_3$). ^{13}C NMR (C$_6$D$_6$, 25 °C): δ 129.36 (η^5-*C*$_5$H$_4$^{n}Pr), 118.71 (η^5-*C*$_5$Me$_5$), 111.24, 108.16 (η^5-*C*$_5$H$_4$^{n}Pr), 48.64 (–N(*C*H$_3$)$_2$), 31.69 (–*C*H$_2$CH$_2$CH$_3$), 25.12 (–CH$_2$*C*H$_2$CH$_3$), 14.37 (–CH$_2$CH$_2$*C*H$_3$), 12.17 (η^5-C$_5$*Me*$_5$).

In an argon-filled glovebox, **9** (45.2 mg, 0.107 mmol) was charged in a 1.5 dram vial and dissolved in 0.3 mL of CH$_2$Cl$_2$, while [H(OEt$_2$)$_2$][B(C$_6$F$_5$)$_4$] (88.8, 0.107 mmol) was dissolved in 0.3

mL of CH_2Cl_2 in a different 1.5 dram vial. The two solutions were mixed via glass pipette upon cooling to −30 °C giving a bright yellow solution. The solution was immediately placed back inside the glovebox freezer, and a bright yellow precipitate formed after 2 days. The supernatant was removed, and the residue obtained in quantitative yield was redissolved in 0.4 mL of CH_2Cl_2. Single crystals suitable for X-Ray diffraction were grown from this CH_2Cl_2 solution at −30 °C. Anal. Calcd for $C_{46}H_{39}BF_{20}N_2Zr$: C, 50.14; H, 3.57; N, 2.54. Found: C, 49.74; H, 3.71; N, 2.34.

^{1}H NMR (CD_2Cl_2, 25 °C) of **9**$^+$: δ 6.40 (dd, J_1 = 5.4 Hz, J_2 = 2.6 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 6.08 (dd, J_1 = 5.2 Hz, J_2 = 2.4 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 6.88 (m, 2H, η^5-$C_5H_4{}^n$Pr), 3.04 (s, 6H, –N(CH_3)$_2$), 2.54–2.40 (m, , 9H, *H*N(CH_3)$_2$, –CH_2CH$_2$CH$_3$), 2.01 (s, 15H, η^5-C_5Me_5), 1.61 (sextet, J = 7.5 Hz, 2H, –CH$_2$$CH_2CH_3$), 0.90 (t, J = 7.4 Hz, 3H, –CH$_2$CH$_2$$CH_3$). ^{13}C NMR ($CD_2Cl_2$, 25 °C): δ 148.55 (d, $^1J_{C\text{-}F}$ = 239.2 Hz, Ar*C*–F), 138.65 (d, $^1J_{C\text{-}F}$ = 242.6 Hz, Ar*C*–F), 136.67 (d, $^1J_{C\text{-}F}$ = 246.2 Hz, Ar*C*–F), 133.44 (η^5-$C_5H_4{}^n$Pr), 123.55 (η^5-C_5Me_5), 117.48, 114.88, 113.98, 111.98 (η^5-$C_5H_4{}^n$Pr), 66.08 (free O(CH_2CH$_3$)$_2$), 51.19 (–N(CH_3)$_2$, 43.52, 42.84 (HN(CH_3)$_2$), 31.11 (–CH_2CH$_2$CH$_3$), 25.34 (–CH$_2$$CH_2CH_3$), 15.51 (free O(CH$_2$$CH_3$)$_2$), 13.70 (–CH$_2CH_2$$CH_3$), 12.63 ($\eta^5$-$C_5Me_5$). ^{19}F NMR ($CD_2Cl_2$, 25 °C): δ −133.09 (m, 6F, o–Ar*F*), −163.71 (t, $^3J_{F\text{-}F}$ = 20.3 Hz, 3F, p–Ar*F*), −167.57 (m, 6F, m–Ar*F*).

Isolation of [Cp*(^{n}PrCp)Zr(THF)Me]$^+$[MeB(C_6F_5)$_3$]$^-$ (10$^+$). In an argon-filled glovebox, a 200 mL glass reaction jar was charged with 5.00 g of Cp*(^{n}PrCp)$ZrCl_2$ (12.4 mmol), dissolved in 150 mL of dry Et_2O, and the solution was cooled to −30 °C inside the glovebox freezer. Subsequently, 8.5 mL of MeMgCl solution (3.0 M in THF, 25.5 mmol) were added under vigorous stirring and the mixture turned immediately into a milky slurry. The reaction mixture was allowed to warm to ambient temperature and stirred for an additional hour. An aliquot of the reaction mixture revealed quantitative and clean conversion to the title product. The reaction mixture was filtered through a medium porosity frit with a small pad of celite, and then the celite was washed with 3 × 50 mL of Et_2O. The volatiles were removed under vacuum, the resulting light tan residue was extracted with 150 mL of hexanes, and then filtered through a fine porosity frit with a small

pad of celite. The volatiles of the final filtrate were evaporated, and the remaining residue was redissolved in 10 mL of hexanes. The concentrated solution was cooled at −30 °C, and crystals formed after 2 h. The solvent was decanted, and the crystals were dried under vacuum for 5 h, affording an off-white powder as the spectroscopically pure product Cp*(^{n}PrCp)$ZrMe_2$ (**10**). Yield: 3.87 g (86%). ^{1}H NMR (C_6D_6, 25 °C) of **10**: δ 5.71 (pst, J = 2.6 Hz, 2H, η^5-$C_5H_4^n$Pr), 5.35 (pst, J = 2.6 Hz, 2H, η^5-$C_5H_4^n$Pr), 2.46 (t, J = 7.6 Hz, 2H, –$CH_2CH_2CH_3$), 1.73 (s, 15H, η^5-C_5Me_5), 1.60 (sextet, J = 7.4 Hz, 2H, –$CH_2CH_2CH_3$), 0.93 (t, J = 7.2 Hz, 3H, –$CH_2CH_2CH_3$), −0.34 (s, 6H, Zr–CH_3). ^{13}C NMR (C_6D_6, 25 °C): δ 129.20 (η^5-$C_5H_4^n$Pr), 117.13 (η^5-C_5Me_5), 111.94, 108.88 (η^5-$C_5H_4^n$Pr), 32.70 (Zr–CH_3), 32.54 (–$CH_2CH_2CH_3$), 25.34 (–$CH_2CH_2CH_3$), 14.21 (–$CH_2CH_2CH_3$), 11.68 (η^5-C_5Me_5).

In an argon-filled glovebox, **10** (44.0 mg, 0.121 mmol) was charged in a 1.5 dram vial and dissolved in 0.8 mL of CH_2Cl_2, while $(C_6F_5)_3B\cdot THF$ (70.7 mg, 0.121 mmol) was dissolved in 0.8 mL of CH_2Cl_2 in a different 1.5 dram vial. The two solutions were mixed via glass pipette upon cooling to −30 °C giving a bright yellow solution instantaneously. The solvent was evaporated and the residue was washed with hexanes (4 × 5 mL). The final product **10**$^+$ was thoroughly dried under vacuum to form a yellow oil in quantitative yield. Anal. Calcd for $C_{42}H_{40}BF_{15}OZr$: C, 53.23; H, 4.25. Found: C, 53.06; H, 4.25.

^{1}H NMR (CD_2Cl_2, 25 °C) of **10**$^+$: δ 6.25 (dd, J_1 = 5.4 Hz, J_2 = 2.6 Hz, 1H, η^5-$C_5H_4^n$Pr), 6.03 (dd, J_1 = 5.8 Hz, J_2 = 3.0 Hz, 1H, η^5-$C_5H_4^n$Pr), 5.90 (dd, J_1 = 5.8 Hz, J_2 = 3.0 Hz, 1H, η^5-$C_5H_4^n$Pr), 5.79 (dd, J_1 = 5.2 Hz, J_2 = 2.8 Hz, 1H, η^5-$C_5H_4^n$Pr), 3.66 (m, 4H, α–CH_2, THF), 2.45 (m, 1H, –$CH_2CH_2CH_3$), 2.33 (m, 1H, –$CH_2CH_2CH_3$), 2.07 (m, 4H, β–CH_2, THF), 1.98 (s, 15H, η^5-C_5Me_5), 1.59 (m, 2H, –$CH_2CH_2CH_3$), 0.92 (t, J = 7.4 Hz, 3H, –$CH_2CH_2CH_3$), 0.48 (s, br, 6H, Zr–CH_3, B–CH_3). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 148.65 (d, $^1J_{C\text{-}F}$ = 240.1 Hz, ArC–F), 137.88 (d, $^1J_{C\text{-}F}$ = 240.9 Hz, ArC–F), 136.69 (η^5-$C_5H_4^n$Pr), 136.75 (d, $^1J_{C\text{-}F}$ = 244.2 Hz, ArC–F), 124.60 (η^5-C_5Me_5), 116.67, 116.59, 114.11, 112.30 (η^5-$C_5H_4^n$Pr), 75.63 (α–CH_2, THF), 47.75 (Zr–CH_3), 32.09 (–$CH_2CH_2CH_3$), 25.67 (β–CH_2, THF), 25.19 (–$CH_2CH_2CH_3$), 13.78 (–$CH_2CH_2CH_3$), 12.01 (η^5-C_5Me_5), 10.57 (B–

CH_3). ^{19}F NMR (CD_2Cl_2, 25 °C): δ −133.20 (d, $^3J_{F\text{-}F}$ = 18.1 Hz, 6F, o–Ar*F*), −165.21 (t, $^3J_{F\text{-}F}$ = 20.3 Hz, 3F, p–Ar*F*), −167.85 (m, 6F, m–Ar*F*).

Synthesis of Cp*(^{n}PrCp)Zr(OTf)$_2$ (11). A similar procedure described for the preparation of *rac*-(EBI)Zr(OTf)$_2$ [3] was modified for the synthesis of Cp*(^{n}PrCp)Zr(OTf)$_2$. In an argon-filled glovebox, a 200 mL glass reaction jar was charged with 1.30 g of Cp*(^{n}PrCp)ZrMe$_2$ (3.57 mmol) and 100 mL of toluene. The clear solution was cooled to −30 °C inside the glovebox freezer, and then 0.66 mL of triflic acid (7.46 mmol) were slowly added. The reaction turned yellow immediately and a precipitate formed. The reaction was allowed to warm up to ambient temperature and stirred overnight, after which time the solution darkened and the precipitate dissolved. The solution mixture was filtered through a pad of celite and slow evaporation of the solvent produced golden color cylindrical crystals. Crystals of **11** were collected, washed with 3 × 5 mL of cold toluene followed by 3 × 10 mL of hexanes, and finally dried under vacuum for 4 h to obtain **11** as spectroscopically pure golden crystalline solid. Yield: 2.13 g (94%). Anal. Calcd for $C_{20}H_{26}F_6O_6S_2Zr$: C, 38.02; H, 4.15. Found: C, 38.31; H, 4.15.

^{1}H NMR (C_6D_6, 25 °C) of **11**: δ 6.36 (pst, J = 2.6 Hz, 2H, η^5-$C_5H_4{}^n$Pr), 6.07 (pst, J = 2.6 Hz, 2H, η^5-$C_5H_4{}^n$Pr), 2.41 (t, J = 7.6 Hz, 2H, –$CH_2CH_2CH_3$), 1.67 (s, 15H, η^5-C_5Me_5), 1.34 (sextet, J = 7.4 Hz, 2H, –$CH_2CH_2CH_3$), 0.75 (t, J = 7.2 Hz, 3H, –$CH_2CH_2CH_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 139.04 (η^5-$C_5H_4{}^n$Pr), 128.52 (η^5-C_5Me_5), 119.88 (q, $^1J_{C\text{-}F}$ = 318.2 Hz, CF_3SO_3–), 119.13, 117.74 (η^5-$C_5H_4{}^n$Pr), 30.82 (–$CH_2CH_2CH_3$), 24.58 (–$CH_2CH_2CH_3$), 13.54 (–$CH_2CH_2CH_3$), 11.50 (η^5-C_5Me_5). ^{19}F NMR (C_6D_6, 25 °C): δ −76.62 (CF_3SO_3–).

Isolation of Cp*(^{n}PrCp)Zr(THF)[OC(O^{i}Pr)=CMe$_2$]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (13$^+$). This synthesis involves three steps. In the first step, a 200 mL glass reaction jar was charged with 2.12 g of **10** (5.83 mmol), dissolved in 100 mL of toluene, and the clear solution was cooled to −30 °C inside the glovebox freezer. Separately, 1.32 g of TMSOTf (5.94 mmol) were charged in a 20 mL vial, dissolved in 10 mL of toluene and cooled to −30 °C inside the glovebox freezer. The cooled solution of TMSOTf was added to the vigorously stirring solution of **10** with a glass pipette, the

mixture was allowed to reach room temperature and then stirred overnight. An aliquot of the reaction mixture revealed 80% conversion to Cp*(^{n}PrCp)Zr(OTf)Me (**12**). Thus, the reaction mixture was cooled again to −30 °C, added 0.25 extra equivalents of TMSOTf and stirred for other 24 h. The clear reaction mixture was concentrated to 2 mL of toluene and layered with 3 mL of hexanes. Pale green crystals formed after cooling at −30 °C overnight, and the mother liquor was decanted and the crystals were rinsed with 3 × 1 mL of hexanes and dried under vacuum to afford 1.23 g of **12**. Concentrating the mother liquor and cooling it overnight produced a second crop of crystals (550 mg), in a total yield of 87%. ^{1}H NMR (C_6D_6, 25 °C) of **12**: δ 6.20 (dd, J_1 = 5.2 Hz, J_2 = 2.4 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 5.78 (dd, J_1 = 5.6 Hz, J_2 = 3.2 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 5.54 (dd, J_1 = 5.6 Hz, J_2 = 3.2 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 5.37 (dd, J_1 = 5.2 Hz, J_2 = 2.4 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 2.46 (m, 1H, –CH_2CH$_2$CH$_3$), 2.22 (m, 1H, –CH_2CH$_2$CH$_3$), 1.61 (s, 15H, η^5-C_5Me_5), 1.43 (m, 2H, –CH$_2$CH_2CH$_3$), 0.83 (t, J = 7.2 Hz, 3H, –CH$_2$CH$_2$CH_3), 0.33 (s, 3H, Zr–CH_3). ^{13}C NMR (C_6D_6, 25 °C): δ 133.92 (η^5-C_5H$_4{}^n$Pr), 121.69 (η^5-C_5Me$_5$), 120.11 (q, $^1J_{C\text{-}F}$ = 318.3 Hz, CF$_3$SO$_3$–), 115.47, 113.13, 112.89, 112.54 (η^5-C_5H$_4{}^n$Pr), 40.29 (Zr–CH$_3$), 31.71 (–CH$_2$CH$_2$CH$_3$), 25.03 (–CH$_2$$CH_2CH_3$), 13.90 (–CH$_2CH_2$$CH_3$), 11.33 ($\eta^5$-$C_5Me_5$). ^{19}F NMR ($C_6D_6$, 25 °C): δ −77.15 (CF_3SO$_3$–).

In the second step, a 200 mL glass reaction jar was charged with 1.23 g of **12** (2.47 mmol) and dissolved in 100 mL of dry toluene. The solution was cooled to −30 °C inside the glovebox freezer, and then 0.36 g of freshly prepared Li(OC(O^{i}Pr)=CMe$_2$) (2.64 mmol) were added under vigorous stirring while the solution turned bright yellow. The reaction was left to reach ambient temperature and then stirred for a total of 3 h, after which time an aliquot of the reaction mixture revealed full conversion to Cp*(^{n}PrCp)ZrMe[OC(O^{i}Pr)=CMe$_2$] (**13**). The volatiles were removed *in vacuo* and the remaining orange oily residue was extracted in 100 mL of hexanes and then filtered through a fine porosity frit with a small pad of celite. The solvent was evaporated and the extraction and filtration was repeated. Product **13** was obtained as a thick orange oil after thorough drying under vacuum. Yield: 810 mg (68%). ^{1}H NMR (C_6D_6, 25 °C) of **13**: δ 5.98 (dd, J_1 = 5.4 Hz, J_2 = 2.2 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 5.78 (dd, J_1 = 5.4 Hz, J_2 = 3.0 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 5.63 (dd, J_1 = 5.2 Hz, J_2 =

2.4 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 5.28 (dd, J_1 = 5.4 Hz, J_2 = 3.0 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 4.07 (sept, J = 6.1 Hz, 1H, OC*H*Me$_2$), 2.57 (m, 1H, –C*H*$_2$CH$_2$CH$_3$), 2.41 (m, 1H, –C*H*$_2$CH$_2$CH$_3$), 1.88 (s, 3H, =C*Me*$_2$), 1.79 (s, 15H, η^5-C_5*Me*$_5$), 1.66 (s, 3H, =C*Me*$_2$), 1.55 (m, 2H, –CH$_2$C*H*$_2$CH$_3$), 1.20 (d, J = 6.4 Hz, 3H, OCH*Me*$_2$), 1.18 (d, J = 6.4 Hz, 3H, OCH*Me*$_2$), 0.90 (t, J = 7.4 Hz, 3H, –CH$_2$CH$_2$C*H*$_3$), 0.15 (s, 3H, Zr–C*H*$_3$). ^{13}C NMR (C_6D_6, 25 °C): δ 154.00 [O*C*(O^{i}Pr)=], 130.36 (η^5-*C*$_5$H$_4{}^n$Pr), 118.35 (η^5-*C*$_5$Me$_5$), 114.21, 113.76, 109.57, 107.71 (η^5-*C*$_5$H$_4{}^n$Pr), 82.53 (=*C*Me$_2$), 67.40 (O*C*HMe$_2$), 31.69 (–*C*H$_2$CH$_2$CH$_3$), 27.48 (Zr–*C*H$_3$), 24.86 (–CH$_2$*C*H$_2$CH$_3$), 22.23, 22.06 (OCH*Me*$_2$), 18.24, 17.60 (=C*Me*$_2$), 14.22 (–CH$_2$CH$_2$*C*H$_3$), 11.47 (η^5-C_5*Me*$_5$).

In the third step, a similar procedure described for the preparation of *rac*-(EBI)Zr$^+$(THF)[OC(O^{i}Pr)=CMe$_2$][MeB(C_6F_5)$_3$]$^-$ [5] was modified for the synthesis of **13**$^+$. In an argon-filled glovebox, a 30 mL glass reaction jar was charged with 43.2 mg of Cp*(^{n}PrCp)ZrMe[OC(O^{i}Pr)=CMe$_2$] (0.090 mmol) and 3 mL of CH_2Cl_2; the light yellow solution was cooled to −30 °C inside the glovebox freezer. Separately, a 1.5 dram vial was charged with 52.6 mg (0.090 mmol) of (C_6F_5)$_3$B·THF, dissolved in 1 mL of CH_2Cl_2, and cooled to −30 °C inside the glovebox freezer. Both solutions were mixed via glass pipette, and the resulting mixture changed instantaneously to orange. The solution was stirred for 10 minutes, after which the volatiles were removed under vacuum to afford a viscous orange oil. The crude material was thoroughly washed with hexanes (3 × 5 mL) and subsequently dried under vacuum to form a sticky orange oil in quantitative yield. Anal. Calcd for $C_{48}H_{50}BF_{15}O_3Zr$: C, 54.29; H, 4.75. Found: C, 54.14; H, 4.66.

^{1}H NMR (CD_2Cl_2, 25 °C) of **13**$^+$: δ 6.28 (dd, J_1 = 5.2 Hz, J_2 = 2.8 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 6.21 (dd, J_1 = 5.0 Hz, J_2 = 2.6 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 6.18 (dd, J_1 = 5.4 Hz, J_2 = 3.0 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 6.04 (dd, J_1 = 5.0 Hz, J_2 = 2.2 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 4.16 (m, 2H, α–C*H*$_2$, THF), 4.02 (m, 3H, OC*H*Me$_2$, overlapping with α–C*H*$_2$, THF), 2.52 (m, 1H, –C*H*$_2$CH$_2$CH$_3$), 2.28 (m, 1H, –C*H*$_2$CH$_2$CH$_3$), 2.17 (m, 4H, β–C*H*$_2$, THF), 2.05 (s, 15H, η^5-C_5*Me*$_5$), 1.64 (s, 3H, =C*Me*$_2$), 1.53 (s, 3H, =C*Me*$_2$), 1.51 (m, 2H, –CH$_2$C*H*$_2$CH$_3$), 1.22 (d, J = 6.0 Hz, 3H, OCH*Me*$_2$), 1.20 (d, J = 5.2 Hz, 3H, OCH*Me*$_2$), 0.85 (t, J = 7.4 Hz, 3H, –CH$_2$CH$_2$C*H*$_3$), 0.49 (s, br, 3H, B–C*H*$_3$). ^{13}C NMR (CD_2Cl_2,

25 °C): δ 154.87 [O*C*(O^{i}Pr)=], 148.69 (d, $^1J_{C\text{-}F}$ = 235.3 Hz, Ar*C*–F), 137.88 (d, $^1J_{C\text{-}F}$ = 243.6 Hz, Ar*C*–F), 136.97 (η^5-$C_5H_4{}^n$Pr), 136.78 (d, $^1J_{C\text{-}F}$ = 246.8 Hz, Ar*C*–F), 126.79 (η^5-C_5Me$_5$), 120.09, 119.15, 114.48, 113.24 (η^5-$C_5H_4{}^n$Pr), 89.89 (=*C*Me$_2$), 77.77 (α–*C*H$_2$, THF), 72.60 (O*C*HMe$_2$), 30.76 (–*C*H$_2$CH$_2$CH$_3$), 25.98 (β–*C*H$_2$, THF), 24.60 (–CH$_2$*C*H$_2$CH$_3$), 22.26, 21.95 (OCH*Me*$_2$), 19.08, 17.73 (=C*Me*$_2$), 13.71 (–CH$_2$CH$_2$*C*H$_3$), 12.12 (η^5-C$_5$*Me*$_5$), 10.42 (B–*C*H$_3$). ^{19}F NMR (CD$_2$Cl$_2$, 25 °C): δ −133.12 ($^3J_{F\text{-}F}$ = 18.4 Hz, 6F, o–Ar*F*), −165.27 (t, $^3J_{F\text{-}F}$ = 21.6 Hz, 3F, p–Ar*F*), −167.86 (m, 6F, m–Ar*F*).

***In Situ* Generation of Cp*(^{n}PrCp)ZrMe[O=C(OMe)C(=CH$_2$)CH$_2$COOMe]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ (14a).** In an argon-filled glovebox, complex **10**$^+$ was cleanly generated *in situ* by mixing at room temperature complex **10** (25.2 mg, 0.069 mmol) and (C$_6$F$_5$)$_3$B·THF (41.3 mg, 0.071 mmol) in a total of 0.5 mL of CD$_2$Cl$_2$ inside a 1.5 dram vial. The bright yellow solution was chilled to −30 °C inside the glovebox freezer. Then, a stoichiometric amount of DMIA (11.0 mg, 0.069 mmol) was added via syringe at −30 °C from a stock solution in CD$_2$Cl$_2$. The subsequent red solution was quickly transferred to a Teflon-valve-sealed J. Young-type NMR tube, and immediately placed on a dry ice/acetone batch until it was analyzed by ^{1}H and ^{13}C NMR at −18 °C.

^{1}H NMR (CD$_2$Cl$_2$, −18 °C) of **14a**: δ 6.30 (s, 1H, C=C*H*$_2$), 6.20 (d, *J* = 2.0 Hz, 1H, η^5-C$_5$*H*$_4{}^n$Pr), 6.00 (d, *J* = 2.5 Hz, 1H, η^5-C$_5$*H*$_4{}^n$Pr), 5.95 (s, 1H, C=C*H*$_2$), 5.91 (d, *J* = 2.5 Hz, 1H, η^5-C$_5$*H*$_4{}^n$Pr), 5.82 (d, *J* = 2.0 Hz, 1H, η^5-C$_5$*H*$_4{}^n$Pr), 3.78 (s, 3H, –OMe), 3.72 (s, 3H, –OMe), 3.66 (m, 4H, α–C*H*$_2$, THF, free), 3.33 (d, *J* = 16.5 Hz, 1H, –C*H*$_2$–), 3.28 (d, *J* = 17.5 Hz, 1H, –C*H*$_2$–), 2.38 (m, 1H, –C*H*$_2$CH$_2$CH$_3$), 2.28 (m, 1H, –C*H*$_2$CH$_2$CH$_3$), 1.93 (s, 15H, η^5-C$_5$*Me*$_5$), 1.80 (m, 4H, β–C*H*$_2$, THF, free), 1.54 (m, 2H, –CH$_2$C*H*$_2$CH$_3$), 0.89 (t, *J* = 7.3 Hz, 3H, –CH$_2$CH$_2$C*H*$_3$), 0.43 (s, br, 3H, B–C*H*$_3$), 0.27 (s, 3H, Zr–C*H*$_3$). ^{13}C NMR (CD$_2$Cl$_2$, −18 °C): δ 183.10 [CH$_2$*C*(OMe)=O], 169.64 [*C*(OMe)=O], 148.21 (d, $^1J_{C\text{-}F}$ = 236.2 Hz, Ar*C*–F), 137.48 (d, $^1J_{C\text{-}F}$ = 243.0 Hz, Ar*C*–F), 136.33 (d, $^1J_{C\text{-}F}$ = 245.8 Hz, Ar*C*–F), 134.84 (η^5-*C*$_5$H$_4{}^n$Pr), 132.66 (C=*C*H$_2$), 131.08 (*C*=CH$_2$), 122.79 (η^5-*C*$_5$Me$_5$), 116.19, 115.21, 113.63, 111.66 (η^5-*C*$_5$H$_4{}^n$Pr), 67.99 (α–*C*H$_2$, THF, free), 56.69 (–OMe), 54.24 (–OMe, overlapped with CD$_2$Cl$_2$), 40.73 (Zr–*C*H$_3$), 39.22 (–*C*H$_2$–), 31.63 (–*C*H$_2$CH$_2$CH$_3$),

25.70 (β–CH_2, THF, free), 25.25 (–$CH_2CH_2CH_3$), 13.66 (–$CH_2CH_2CH_3$), 11.69 (η^5-C_5Me_5), 9.90 (B–CH_3). ^{19}F NMR (CD_2Cl_2, 25 °C): δ −133.18 (d, $^3J_{F\text{-}F}$ = 17.7 Hz, 6F, o–Ar*F*), −165.30 (t, $^3J_{F\text{-}F}$ = 20.3 Hz, 3F, p–Ar*F*), −167.91 (m, 6F, m–Ar*F*).

***In Situ* Generation of Cp*(^{n}PrCp)ZrMe[O=C(O^{i}Pr)C(=CH$_2$)CH$_2$COO^{i}Pr]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ (14b).** In an argon-filled glovebox, complex **10**$^+$ was cleanly generated *in situ* by mixing at room temperature complex **10** (29.5 mg, 0.081 mmol) and $(C_6F_5)_3B\cdot THF$ (48.3 mg, 0.083 mmol) in a total of 0.5 mL of CD_2Cl_2 inside a 1.5 dram vial. The bright yellow solution was chilled to −30 °C inside the glovebox freezer. Then, a stoichiometric amount of D^{i}PrIA (17.4 mg, 0.081 mmol) was added via syringe at −30 °C from a stock solution in CD_2Cl_2. The subsequent red solution was quickly transferred to a Teflon-valve-sealed J. Young-type NMR tube, and immediately placed on a dry ice/acetone batch until it was analyzed by ^{1}H and ^{13}C NMR at −18 °C.

^{1}H NMR (CD_2Cl_2, −18 °C) of **14b**: δ 6.26 (s, 1H, C=CH_2), 6.23 (d, J = 2.5 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 6.04 (d, J = 2.5 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 5.90 (s, 1H, C=CH_2), 5.88 (dd, J_1 = 5.5 Hz, J_2 = 3.0 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 5.79 (dd, J_1 = 4.8 Hz, J_2 = 2.3 Hz, 1H, η^5-$C_5H_4{}^n$Pr), 4.96 (sept, J = 6.3 Hz, 1H, OC*H*Me$_2$), 4.79 (sept, J = 6.3 Hz, 1H, OC*H*Me$_2$), 3.66 (m, 4H, α–CH_2, THF, free), 3.31 (d, J = 17.0 Hz, 1H, –CH_2–), 3.22 (d, J = 17.0 Hz, 1H, –CH_2–), 2.41 (m, 1H, –CH_2CH$_2$CH$_3$), 2.28 (m, 1H, –CH_2CH$_2$CH$_3$), 1.92 (s, 15H, η^5-C_5Me_5), 1.80 (m, 4H, β–CH_2, THF, free), 1.54 (m, 2H, –CH$_2$CH_2CH$_3$), 1.28 (d, J = 6.0 Hz, 3H, OCH*Me*$_2$), 1.27 (d, J = 6.5 Hz, 3H, OCH*Me*$_2$), 1.24 (d, J = 6.5 Hz, 3H, OCH*Me*$_2$), 1.22 (d, J = 6.0 Hz, 3H, OCH*Me*$_2$), 0.89 (t, J = 7.5 Hz, 3H, –CH$_2$CH$_2$CH_3), 0.44 (s, br, 3H, B–CH_3), 0.24 (s, 3H, Zr–CH_3). ^{13}C NMR (CD_2Cl_2, −18 °C): δ 181.95 [CH$_2$*C*(O^{i}Pr)=O], 168.42 [*C*(O^{i}Pr)=O], 148.20 (d, $^1J_{C\text{-}F}$ = 235.4 Hz, Ar*C*–F), 137.48 (d, $^1J_{C\text{-}F}$ = 243.5 Hz, Ar*C*–F), 136.39 (d, $^1J_{C\text{-}F}$ = 245.0 Hz, Ar*C*–F), 134.87 (η^5-*C*$_5$H$_4{}^n$Pr), 132.05 (C=*C*H$_2$), 131.62 (*C*=CH$_2$), 122.63 (η^5-*C*$_5$Me$_5$), 116.16, 115.06, 113.40, 111.34 (η^5-*C*$_5$H$_4{}^n$Pr), 76.04 (O*C*HMe$_2$), 71.91 (O*C*HMe$_2$), 67.98 (α–*C*H$_2$, THF, free), 40.08 (–*C*H$_2$–), 39.65 (Zr–*C*H$_3$), 31.69 (–*C*H$_2$CH$_2$CH$_3$), 25.72 (β–*C*H$_2$, THF, free), 25.30 (–CH$_2$*C*H$_2$CH$_3$), 21.52, 21.47, 21.24, 21.15 (OCH*Me*$_2$), 13.71 (–CH$_2$CH$_2$*C*H$_3$), 11.69 (η^5-C$_5$*Me*$_5$), 9.60 (B–*C*H$_3$). ^{19}F NMR (CD_2Cl_2, 25 °C): δ

−133.15 (d, $^3J_{F\text{-}F}$ = 18.4 Hz, 6F, o–Ar*F*), −165.35 (t, $^3J_{F\text{-}F}$ = 20.3 Hz, 3F, p–Ar*F*), −167.93 (m, 6F, m–Ar*F*).

Isolation of Cp*(^{n}PrCp)Zr[OC(Ome)=C(CH$_2$COOMe)CH$_2$C(Me$_2$)C(O^{i}Pr)=O]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ (15a). Inside an argon-filled glovebox, a 30 mL glass reaction jar was charged with 42.4 mg of complex **13** (0.089 mmol) and dissolved in 3 mL of CH_2Cl_2. Complex **13**$^+$ was cleanly generated *in situ* by adding 52.0 mg of $(C_6F_5)_3B\cdot THF$ (0.089 mmol) in 1 mL of CH_2Cl_2 at room temperature, accompanied by a rapid color change from light yellow to orange. After stirring for 5 min, the reaction mixture was cooled to −30 °C inside the glovebox freezer, and then 14.1 mg of DMIA (0.089 mmol) were added via syringe from a prechilled stock solution in CH_2Cl_2. The reaction mixture was stirred for a total of 15 min, during which time the color of the solution slowly turned bright yellow as it reached room temperature. The volatiles were removed under vacuum, and the oily yellow residue was thoroughly washed with hexanes (3 × 5 mL). Each washing cycle consisted in vigorous stirring for 5 minutes and then removal of the supernatant liquid with a glass pipette. A bright yellow foamy solid was obtained after drying the oily residue under vacuum for several h in quantitative yield. Anal. Calcd for $C_{51}H_{52}BF_{15}O_6Zr$: C, 53.36; H, 4.57. Found: C, 53.71; H, 4.40.

^{1}H NMR (CD_2Cl_2, 25 °C) of **15a**: δ 6.56 (s, br, 1H, η^5-C$_5$*H*$_4$^{n}Pr), 6.35 (s, br, 1H, η^5-C$_5$*H*$_4$^{n}Pr), 6.00 (s, br, 1H, η^5-C$_5$*H*$_4$^{n}Pr), 5.94 (s, br, 1H, η^5-C$_5$*H*$_4$^{n}Pr), 4.96 (sept, *J* = 6.4 Hz, 1H, OC*H*Me$_2$), 3.66 (s, 3H, OC*H*$_3$), 3.43 (s, 3H, OC*H*$_3$), 3.10 (d, *J* = 16.8 Hz, 1H, C*H*$_2$C(O)OMe), 2.93 (d, *J* = 16.8 Hz, 1H, C*H*$_2$C(O)OMe), 2.64 (d, *J* = 16.0 Hz, 1H, –C*H*$_2$–), 2.37 (m, 1H, –C*H*$_2$CH$_2$CH$_3$), 2.06 (s, 15H, η^5-C$_5$*Me*$_5$), 2.01 (m, 1H, –C*H*$_2$CH$_2$CH$_3$), 1.84 (d, *J* = 15.6 Hz, 1H, –C*H*$_2$–), 1.51 (m, 2H, –CH$_2$C*H*$_2$CH$_3$), 1.49 (d, *J* = 6.4 Hz, 3H, OCH*Me*$_2$), 1.42 (d, *J* = 6.4 Hz, 3H, OCH*Me*$_2$), 1.40 (s, 6H, C*Me*$_2$), 0.85 (t, *J* = 7.4 Hz, 3H, –CH$_2$CH$_2$C*H*$_3$), 0.48 (s, br, 3H, B–C*H*$_3$). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 193.78 [*C*(O^{i}Pr)=O], 173.50 [*C*(OMe)=O], 160.38 [O*C*(OMe)=], 148.71 (d, $^1J_{C\text{-}F}$ = 239.9 Hz, Ar*C*–F), 137.89 (d, $^1J_{C\text{-}F}$ = 243.1 Hz, Ar*C*–F), 136.78 (d, $^1J_{C\text{-}F}$ = 246.0 Hz, Ar*C*–F), 134.75 (η^5-*C*$_5$H$_4$^{n}Pr), 126.58 (η^5-*C*$_5$Me$_5$), 120.77, 118.85, 118.21, 111.49 (η^5-*C*$_5$H$_4$^{n}Pr), 83.12 (=*C*CH$_2$), 76.47

(O*C*HMe$_2$), 54.96 (–O*Me*), 51.95 (–O*Me*), 45.00 (*C*Me$_2$), 38.51 (–*C*H$_2$–), 36.75 [*C*H$_2$C(O)OMe], 31.45 (C*Me*$_2$), 31.38 (–*C*H$_2$CH$_2$CH$_3$), 25.21 (–CH$_2$*C*H$_2$CH$_3$), 24.51 (C*Me*$_2$), 21.96, 21.78 (OCH*Me*$_2$), 13.71 (–CH$_2$CH$_2$*C*H$_3$), 12.00 (η^5-C$_5$*Me*$_5$), 10.46 (B–*C*H$_3$). ^{19}F NMR (CD$_2$Cl$_2$, 25 °C): δ −133.08 (d, $^3J_{F\text{-}F}$ = 19.20 Hz, 6F, o–Ar*F*), −165.30 (t, $^3J_{F\text{-}F}$ = 20.3 Hz, 3F, p–Ar*F*), −167.88 (m, 6F, m–Ar*F*).

Isolation of Cp*(^{n}PrCp)Zr[OC(O^{i}Pr)=C(CH$_2$COO^{i}Pr)CH$_2$C(Me$_2$)C(O^{i}Pr)=O]$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ (15b). Inside an argon-filled glovebox, a 30 mL glass reaction jar was charged with 46.8 mg of complex **13** (0.098 mmol) and dissolved in 3 mL of CH$_2$Cl$_2$. Complex **13**$^+$ was cleanly generated *in situ* by adding 57.2 mg of (C$_6$F$_5$)$_3$B·THF (0.098 mmol) in 1 mL of CH$_2$Cl$_2$ at room temperature, accompanied by a rapid color change from light yellow to orange. After stirring for 5 min, the reaction mixture was cooled to −30 °C inside the glovebox freezer, and then 21.0 mg of D^{i}PrIA (0.098 mmol) were added via syringe from a prechilled stock solution in CH$_2$Cl$_2$. The reaction mixture was stirred for a total of 15 minutes, during which time the color of the solution slowly turned bright yellow as it reached room temperature. The volatiles were removed under vacuum, and the oily yellow residue was thoroughly washed with hexanes (3 × 5 mL). Each washing cycle consisted in vigorous stirring for 5 minutes and then removal of the supernatant liquid with a glass pipette. A bright yellow foamy solid was obtained after drying the oily residue under vacuum for several h in quantitative yield. The elemental analyses gave unsatisfying results, presumably due to its limited thermal stability at ambient temperature.

^{1}H NMR (CD$_2$Cl$_2$, 25 °C) of **15b**: δ 6.60 (s, br, 1H, η^5-C$_5$*H*$_4$^{n}Pr), 6.37 (s, br, 1H, η^5-C$_5$*H*$_4$^{n}Pr), 6.00 (s, br, 1H, η^5-C$_5$*H*$_4$^{n}Pr), 5.94 (s, br, 1H, η^5-C$_5$*H*$_4$^{n}Pr), 4.98 (m, 2H, two OC*H*Me$_2$ overlapped), 4.08 (sept, *J* = 6.3 Hz, 1H, OC*H*Me$_2$), 3.14 (d, *J* = 16.4 Hz, 1H, C*H*$_2$C(O)O^{i}Pr), 2.95 (d, *J* = 16.8 Hz, 1H, C*H*$_2$C(O)O^{i}Pr), 2.64 (d, *J* = 15.6 Hz, 1H, –C*H*$_2$–), 2.40 (m, 1H, –C*H*$_2$CH$_2$CH$_3$), 2.04 (s, 16H, η^5-C$_5$*Me*$_5$ overlapped with C*H*$_2$CH$_2$CH$_3$), 1.90 (d, *J* = 15.6 Hz, 1H, –C*H*$_2$–), 1.51 (m, 2H, –CH$_2$C*H*$_2$CH$_3$), 1.49 (d, *J* = 6.0 Hz, 3H, OCH*Me*$_2$), 1.45 (s, 3H, C*Me*$_2$), 1.42 (d, *J* = 6.4 Hz, 3H, OCH*Me*$_2$), 1.40 (s, 3H, C*Me*$_2$), 1.29 (d, *J* = 6.0 Hz, 3H, OCH*Me*$_2$), 1.23 (m, 6H, OCH*Me*$_2$), 1.16 (d,

J = 6.0 Hz, 3H, OCHMe_2), 0.86 (t, J = 7.2 Hz, 3H, –$CH_2CH_2CH_3$), 0.50 (s, br, 3H, B–CH_3). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 193.71 [C(O^{i}Pr)=O], 172.51 [C(O^{i}Pr)=O], 158.51 [OC(O^{i}Pr)=], 148.69 (d, $^1J_{C\text{-}F}$ = 235.8 Hz, ArC–F), 137.88 (d, $^1J_{C\text{-}F}$ = 243.4 Hz, ArC–F), 136.77 (d, $^1J_{C\text{-}F}$ = 244.7 Hz, ArC–F), 134.33 (η^5-$C_5H_4{}^n$Pr), 126.37 (η^5-C_5Me_5), 120.86, 118.37, 118.16, 111.57 (η^5-$C_5H_4{}^n$Pr), 85.01 (=CCH$_2$), 76.34 (OCHMe$_2$), 69.75 (OCHMe$_2$), 68.08 (OCHMe$_2$), 44.98 (CMe$_2$), 37.79 (–CH$_2$–), 37.07 [CH$_2$C(O)O^{i}Pr], 32.02 (CMe_2), 31.34 (–CH$_2$CH$_2$CH$_3$), 25.37 (–CH$_2$$CH_2CH_3$), 24.62 (C$Me_2$), 22.68, 22.04, 21.99, 21.93, 21.77, and 21.47 (OCHMe_2), 13.69 (–CH$_2$CH$_2$$CH_3$), 11.97 ($\eta^5$-C$_5Me_5$), 10.44 (B–$CH_3$). ^{19}F NMR ($CD_2Cl_2$, 25 °C): δ −133.06 (d, $^3J_{F\text{-}F}$ = 19.20 Hz, 6F, o–ArF), −165.27 (t, $^3J_{F\text{-}F}$ = 20.5 Hz, 3F, p–ArF), −167.84 (m, 6F, m–ArF).

***In Situ* Generation of Cp*(^{n}PrCp)ZrMe{OC[OC(O)CH$_2$]=C(CH$_2$CMe$_2$COO^{i}Pr)} (17).** Inside an argon-filled glovebox, complex **17** was cleanly and instantaneously generated by mixing 31.6 mg of complex **13** (0.066 mmol) and 7.4 mg of IA (0.066 mmol) in 0.5 mL of CD_2Cl_2 at ambient temperature.

^{1}H NMR (CD_2Cl_2, 25 °C) of **17**: δ 5.90 (dd, J_1 = 5.4 Hz, J_2 = 2.6 Hz, 1H, η^5-C$_5H_4{}^n$Pr), 5.73 (pst, J = 2.8 Hz, 2H, η^5-C$_5H_4{}^n$Pr), 5.70 (dd, J_1 = 5.4 Hz, J_2 = 2.6 Hz, 1H, η^5-C$_5H_4{}^n$Pr), 4.92 (sept, J = 6.3 Hz, 1H, OCHMe$_2$), 3.04 (s, 2H, CH_2C(O)–O), 2.33 (m, 2H, –CH_2CH$_2$CH$_3$), 2.11 (s, 2H, –CH_2–), 1.91 (s, 15H, η^5-C$_5Me_5$), 1.51 (sextet, J = 7.4 Hz, 2H, –CH$_2$CH_2CH$_3$), 1.21 (d, J = 6.4 Hz, 6H, OCHMe_2), 1.07 (s, 3H, CMe_2), 1.05 (s, 3H, CMe_2), 0.89 (t, J = 7.4 Hz, 3H, –CH$_2$CH$_2$CH_3), −0.06 (s, 3H, Zr–CH_3). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 177.67 [CH$_2$$C$(O)–O], 174.94 [$C$(O^{i}Pr)=O], 158.51 [O$C$(OC)=], 132.18 ($\eta^5$-$C_5H_4{}^n$Pr), 119.85 ($\eta^5$-$C_5Me_5$), 113.85, 112.84, 110.78, 110.43 (η^5-$C_5H_4{}^n$Pr), 76.08 (=CCH$_2$), 67.82 (OCHMe$_2$), 42.84 (CMe$_2$), 38.22 (–CH$_2$–), 35.42 [CH$_2$C(O)–O], 31.61 (–CH$_2$CH$_2$CH$_3$), 30.32 (Zr–CH$_3$), 25.59, 25.15 (CMe_2), 24.86 (–CH$_2$$CH_2CH_3$), 21.91 (OCH$Me_2$), 14.09 (–CH$_2CH_2$$CH_3$), 11.57 ($\eta^5$-C$_5Me_5$).

General Polymerization Procedures.

Polymerizations were carried out in 20 mL glass reactors inside a glovebox for ambient temperature (~25 °C) runs. In control polymerizations of MMA and DMAA with cationic complexes **9**$^+$, **10**$^+$, and **13**$^+$, a predetermined amount of pre-catalyst (**9**, **10** or **13**) and activator — $[H(OEt_2)_2]^+B(C_6F_5)_4]^-$ for **9**, or $(C_6F_5)_3B{\cdot}THF$ for **10** and **13** — were premixed at room temperature in a 1:1 molar ratio to cleanly generate the corresponding cationic catalyst, and followed by rapid addition of the monomer (100 or 150 equivalents) to start the polymerization. For example, solutions of $(C_6F_5)_3B{\cdot}THF$ (20.5 mg, 0.035 mmol) and precatalyst **13** (16.7 mg, 0.035 mmol) were premixed in 3.0 mL of CH_2Cl_2 and stirred for 2 min to cleanly generate the active species **13**$^+$. Subsequently, the monomer DMAA (0.54 mL, $[DMAA]_0/[\mathbf{13}^+]$ = 150) was quickly added via syringe to the vigorously stirring solution, and the reaction was allowed to proceed with continuous stirring at ambient temperature.

Alternatively, polymerizations that required the pre-formation of itaconate-based complexes **2a**(**b**), **14a**(**b**), and **15a**(**b**) started with the pre-activation of the neutral zirconocenes **1**, **10**, and **13** with $(C_6F_5)_3B{\cdot}THF$ as described above. The solutions of **1**$^+$, **10**$^+$, and **13**$^+$ were stirred for 2 min at room temperature, and then cooled to −30 °C inside the glovebox freezer. The itaconate adducts and complexes were generated *in-situ* by adding one equivalent of the dialkyl itaconate from a prechilled stock solution, and then stirred for 2 min. To prevent any decomposition or complex evolution, the monomer was quickly added (100 or 150 equivalents) via syringe to start the polymerization. Polymerizations carried out by **4a**(**b**) were started similarly, but solutions of **1**$^+$ with stoichiometric amounts of dialkyl itaconates were stirred at room temperature for 48 h before the addition of the monomer, ensuring full conversion of **2a**(**b**) into the thermodynamic products **4a**(**b**). For instance, in a typical polymerization $(C_6F_5)_3B{\cdot}THF$ (18.8 mg, 0.032 mmol) and precatalyst **1** (15.7 mg, 0.032 mmol) were premixed in 3.0 mL of CH_2Cl_2, stirred for 2 min to cleanly generate the active species **1**$^+$, and then cooled to −30 °C inside the glovebox freezer. Complex **2a** was *in-situ* generated by addition of an equimolar amount of DMIA (5.05 mg, 0.032 mmol) from a precooled stock solution in CH_2Cl_2. After stirring the mixture for 2 min, the polymerization was

quickly started by adding DMAA (0.5 mL, $[DMAA]_0/[\mathbf{2a}]$ = 150) via syringe to the vigorously stirring solution, and the reaction was allowed to proceed with continuous stirring at ambient temperature.

For those polymerization runs with preformation of complex **5**, precatalyst **1** (14.1 mg, 0.029 mmol) was dissolved in 3 mL of CH_2Cl_2 and then, an equimolar amount of itaconic anhydride (3.21 mg, 0.029 mmol) was added from a stock solution in CH_2Cl_2 at ambient temperature. The bright yellow solution was cooled down to −30 °C, and the polymerization was immediately started by adding a solution of DMAA (or MMA) and $B(C_6F_5)_3$ (14.7 mg, 0.029 mmol), in [**5**]/[act]/[M] ratios of 1:1:150, via a glass pipette. The reaction was allowed to proceed with continuous stirring at ambient temperature for 24 h.

In all the cases, after the measured time interval, a 0.1 mL aliquot was taken from the reaction mixture via syringe and quickly quenched into a 1.5 mL vial containing 0.6 mL of undried "wet" $CDCl_3$ stabilized by 250 ppm of BHT-H; the quenched aliquots were later analyzed by ^{1}H NMR to obtain monomer conversion data. The remaining bulk polymerization reaction was quenched after the removal of the last aliquot by addition of 5 mL of 5% HCl-acidified methanol and precipitated into 100 mL of MeOH (for MMA runs) or Et_2O (for DMAA runs). The quenched mixture was stirred for 3 h, and the polymer obtained was filtered, washed with MeOH (or Et_2O), and dried in a vacuum oven at 50 °C overnight to a constant weight.

Polymer Characterizations.

Polymer number-average molecular weights (M_n) and molecular weight distributions or dispersities ($Đ = M_w/M_n$) were measured by gel permeation chromatography (GPC) analyses carried out at 40 ºC and a flow rate of 1.0 mL/min, with DMF as the eluent on a Waters University 1500 GPC instrument equipped with one PLgel 5 μm guard and three PLgel 5 μm mixed-C columns (Polymer Laboratories; linear range of MW = 200–2,000,000). The instrument was calibrated with

10 PMMA standards, and chromatograms were processed with Waters Empower software (version 2002).

The tacticity of the polymers was analyzed by ^{1}H and ^{13}C NMR based on that of PMMA.[3,5,9,10] The isolated low molecular weight samples were analyzed by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). The experiment was performed on a Microflex-LRF mass spectrometer (Bruker Daltonics, Billerica, MA) in positive ion, reflector mode using a 25 kV accelerating voltage. A thin layer of a 1% NaI solution was first deposited on the target plate, followed by 0.6 µl of both sample and matrix (dithranol, 10 mg/mL in MeOH). The mixture was then spotted on top of the NaI layer and allowed to air dry. External calibration was done using a peptide calibration mixture (4 to 6 peptides) on a spot adjacent to the sample. The raw data was processed in the FlexAnalysis software (version 3.4.7, Bruker Daltonics).

Table S1. Results of acrylates control polymerization by metallocene catalysts.[a]

run no.	Catalyst	Monomer	Time (h)	conv.[b] (%)	M_n[c] (kg/mol)	$Đ$[c]	I^*[d] (%)	[*mm*][e] (%)	[*mr*][e] (%)	[*rr*][e] (%)
1	**10**$^+$	MMA	24	100	13.8	1.21	109	2.6	22.8	74.6
2	**10**$^+$	DMAA	3	100	464 (70%)	1.23		n.d.	n.d.	n.d.
					43.7 (30%)	1.25				
3	**13**$^+$	MMA	24	100	17.5	1.20	86	3.3	23.5	73.2
4	**13**$^+$	DMAA	1	100	21.0	1.16	71	n.d.	n.d.	n.d.
5	**14a**	MMA	24	85	10.0	1.62	87	4.3	24.2	71.5
6	**14a**	DMAA	24	100	365(47%)	1.28		n.d.	n.d.	n.d.
					40.7(53%)	1.24				
7	**14b**	MMA	24	91	10.4	1.71	90	3.7	23.3	73.0
8	**14b**	DMAA	24	100	274(86%)	1.26		n.d.	n.d.	n.d.
					23.1(14%)	1.19				

[a]Conditions: solvent (DCM) = 3 mL; ambient temperature (~23 °C); $[M]_0/[catalyst]_0$ = 150, except for runs 5 to 8, where $[M]_0/[catalyst]_0$ = 100; n.d. = not determined. [b]Monomer (M) conversion measured by ^{1}H NMR. [c]Number-average molecular weight (M_n) and dispersity ($Đ$) determined by gel-permeation chromatography (GPC) relative to PMMA standards. [d]Initiator efficiency (I^*) = M_n(calcd)/M_n(exptl), where M_n(calcd) = MW(M) × $[M]_0/[catalyst]_0$ × conversion% + MW of chain-end groups. [e]Tacticity measured by ^{1}H NMR in $CDCl_3$.

X-Ray crystallography.

The molecular structure of $[Cp^*(^nPrCp)Zr(HNMe_2)=NMe_2]^+[B(C_6F_5)_4]^-$ (**9**$^+$) was determined by single crystal X-ray crystallography (Table S2). Single crystals were coated with Paratone-N oil and mounted under a cold stream of dinitrogen gas. Single crystal X-ray diffraction data were acquired on a Bruker Kappa APEX II CCD diffractometer with Mo Kα radiation (λ = 0.71073 Å) and a graphite monochromator. Initial lattice parameters were obtained from a least-squares analysis of more than 100 reflections; these parameters were later refined against all data. None of the crystals showed significant decay during data collection. Data were integrated and corrected for Lorentz and polarization effects using Bruker APEX3 software, and semi-empirical absorption corrections were applied using SCALE.[11] Space group assignments were based on systematic absences, E statistics, and successful refinement of the structures. Structures were solved using Direct Methods and were refined with the aid of successive Fourier difference maps against all data using the SHELXTL 6.14 software package.[12] Thermal parameters for all non-hydrogen atoms were refined anisotropically. All hydrogen atoms were assigned to ideal positions and refined using a riding model with an isotropic thermal parameter 1.2 times that of the attached carbon atom (1.5 times for methyl hydrogens). Crystallographic data for the structure of **9**$^+$ (CCDC 1548705) have been deposited with the Cambridge Crystallographic Data Center as supplementary publications. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

Part B: Crystal Structure Report for $[Cp^*(^nPrCp)Zr(HNMe_2)=NMe_2]^+[B(C_6F_5)_4]^-$ (9^+)

A clear light yellow rod-like specimen of $C_{184}H_{156}B_4F_{80}N_8Zr_4$, approximate dimensions 0.160 mm x 0.236 mm x 0.385 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. A total of 2022 frames were collected. The total exposure time was 14.04 h. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 9019 reflections to a maximum θ angle of 26.37° (0.80 Å resolution), of which 9019 were independent (average redundancy 1.000, completeness = 100.0%, R_{int} = 0.00%, R_{sig} = 6.87%) and 6336 (70.25%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.8112(9) Å, b = 20.5825(13) Å, c = 15.5423(10) Å, β = 92.875(3)°, volume = 4412.6(5) $Å^3$, are based upon the refinement of the XYZ-centroids of 9700 reflections above 20 σ(I) with 4.749° < 2θ < 62.06°. Data were corrected for absorption effects using the Multi-Scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.846. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8700 and 0.9430.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group $P2_1/n$, with Z = 1 for the formula unit, $C_{184}H_{156}B_4F_{80}N_8Zr_4$. The final anisotropic full-matrix least-squares refinement on F^2 with 645 variables converged at R1 = 5.58%, for the observed data and wR2 = 15.39% for all data. The goodness-of-fit was 1.081. The largest peak in the final difference electron density synthesis was 1.122 $e^-/Å^3$ and the largest hole was -0.582 $e^-/Å^3$ with an RMS deviation of 0.125 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.659 g/cm^3 and F(000), 2216 e^-. Twin fraction for domain one and two were 66.19% and 33.81%, respectively.

Table S2. Sample and crystal data for **9**$^+$.

Identification code	ec116	
Chemical formula	$C_{184}H_{156}B_4F_{80}N_8Zr_4$	
Formula weight	4407.28 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.160 x 0.236 x 0.385 mm	
Crystal habit	clear light yellow rod	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 13.8112(9) Å	α = 90°
	b = 20.5825(13) Å	β = 92.875(3)°
	c = 15.5423(10) Å	γ = 90°
Volume	4412.6(5) Å^3	
Z	1	
Density (calculated)	1.659 g/cm^3	
Absorption coefficient	0.372 mm^{-1}	
F(000)	2216	

Table S3. Data collection and structure refinement for **9**$^+$.

Theta range for data collection	1.64 to 26.37°	
Reflections collected	9019	
Independent reflections	9019 [R(int) = 0.0000]	
Coverage of independent reflections	100.0%	
Absorption correction		
Max. and min. transmission	0.9430 and 0.8700	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	9019 / 0 / 645	
Goodness-of-fit on F^2	1.081	
Δ/σ_{max}	0.001	
Final R indices	6336 data; I>2σ(I)	R1 = 0.0558, wR2 = 0.1288
	all data	R1 = 0.0985, wR2 = 0.1539
Weighting scheme	$w = 1/[\sigma^2(F_o^2)+(0.0698P)^2+8.5769P]$ where $P = (F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	1.122 and -0.582 eÅ^{-3}	
R.M.S. deviation from mean	0.125 eÅ^{-3}	

Part C: Additional Figures

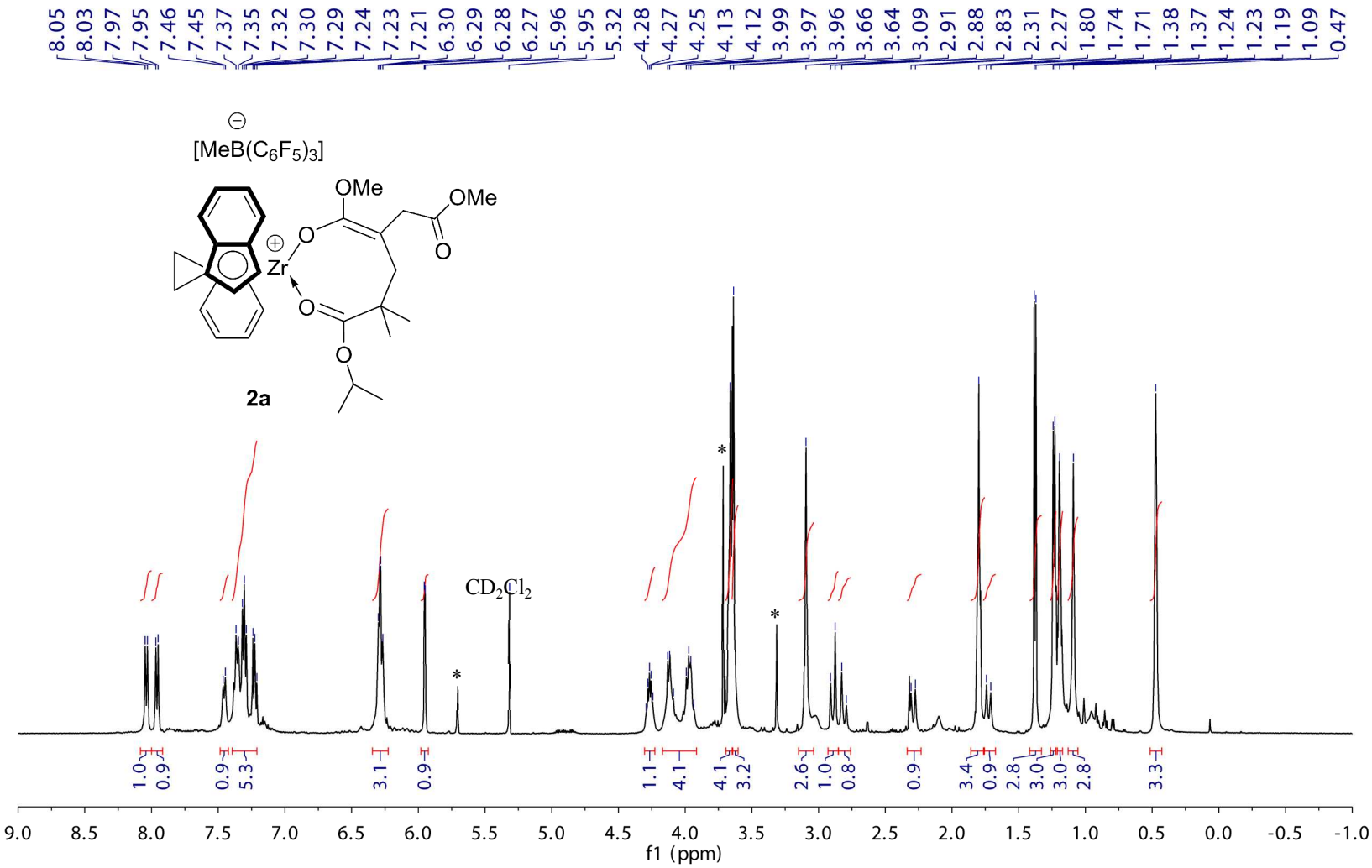

Figure S1. ^{1}H NMR spectrum (CD_2Cl_2, −18 °C, 500 MHz) of *rac*-(EBI)Zr[OC(OMe)=C(CH_2COOMe)CH_2C(Me_2)C(O^{i}Pr)=O]$^+$[MeB(C_6F_5)$_3$]$^-$ (**2a**). (* = excess dimethyl itaconate for comparison)

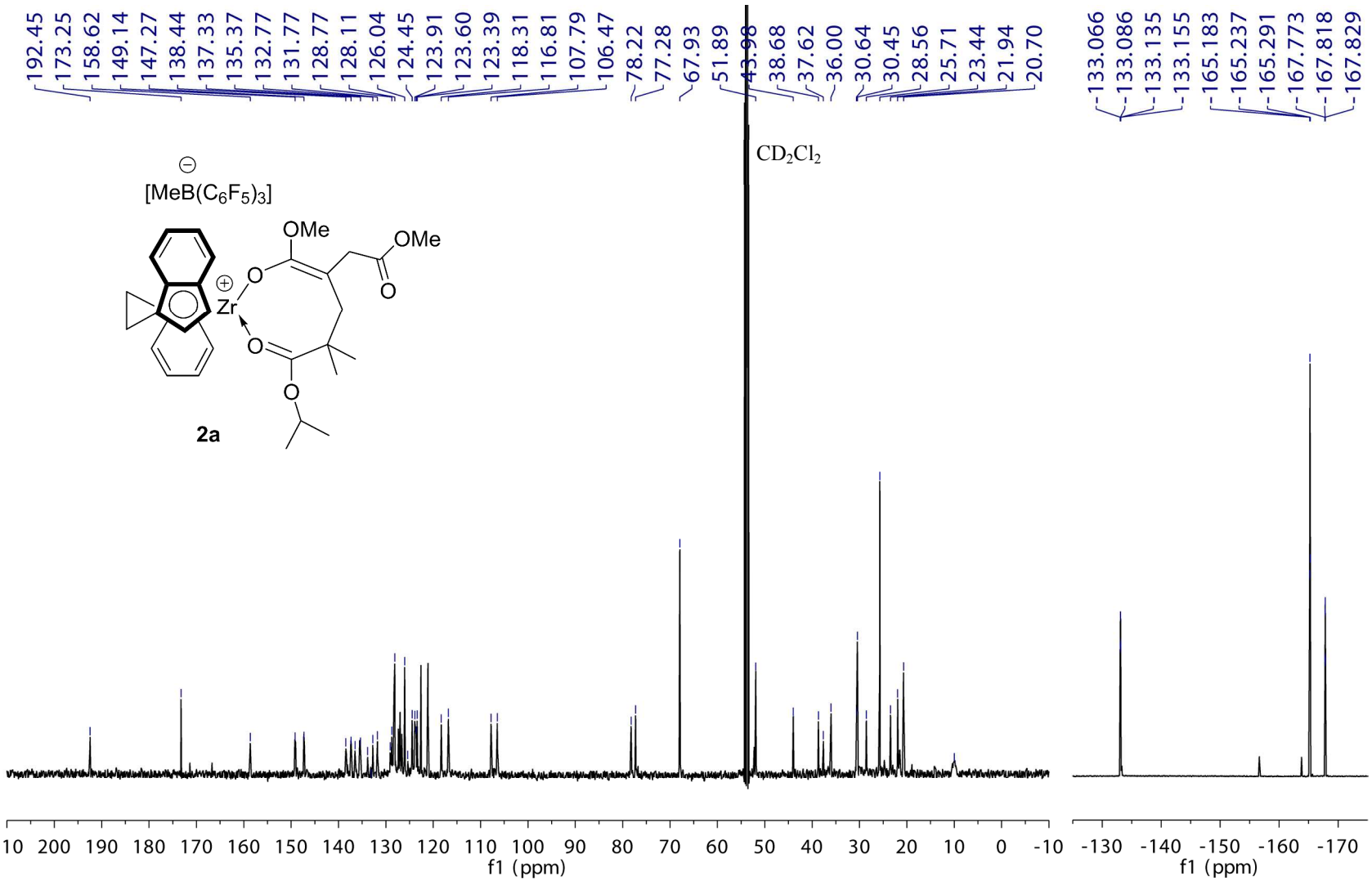

Figure S2. ^{13}C (left) and ^{19}F (right) NMR spectra (CD_2Cl_2, −18 °C, 500 MHz) of *rac*-(EBI)Zr[OC(OMe)=C(CH_2COOMe)CH_2C(Me_2)C(O^{i}Pr)=O]$^+$ [MeB(C_6F_5)$_3$]$^-$ (**2a**). Minor peaks due to excess (C_6F_5)$_3$B·THF used in the NMR scale reaction were also present in ^{19}F NMR.

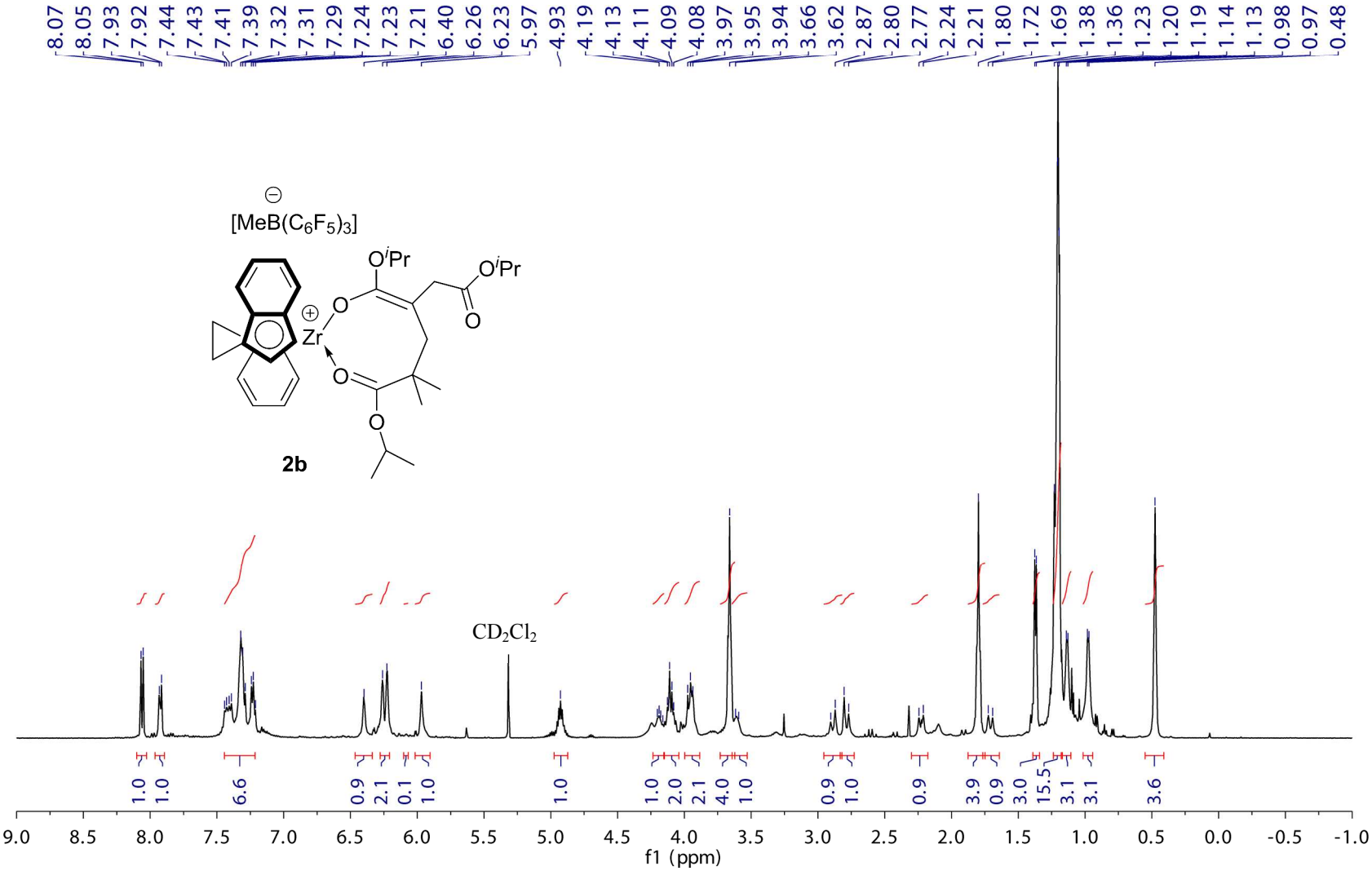

Figure S3. ^{1}H NMR spectrum (CD_2Cl_2, −18 °C, 500 MHz) of *rac*-(EBI)Zr[OC(O^{i}Pr)=C(CH_2COO^{i}Pr)CH_2C(Me_2)C(O^{i}Pr)=O]$^+$[MeB(C_6F_5)$_3$]$^-$ (**2b**).

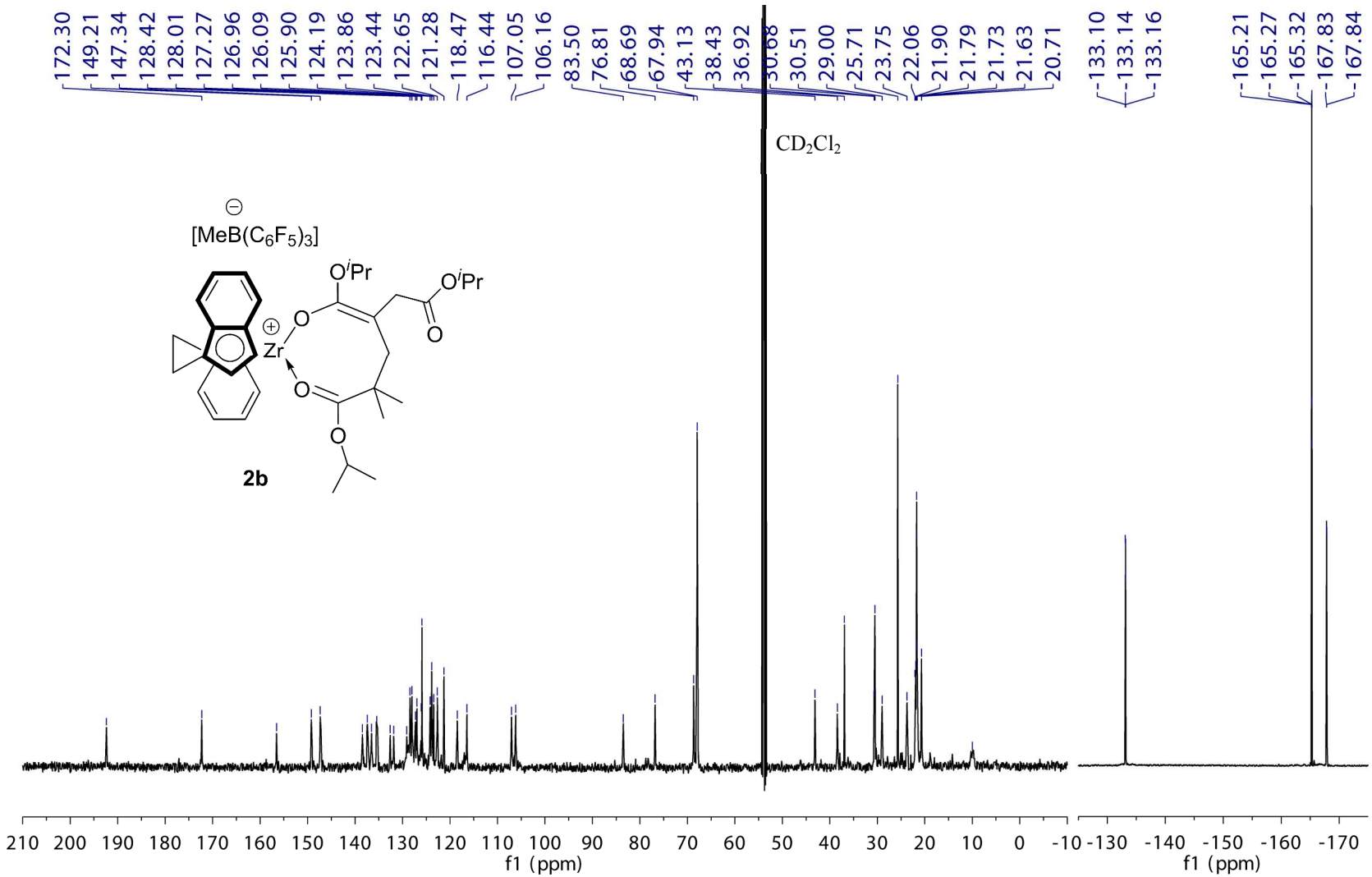

Figure S4. ^{13}C (left) and ^{19}F (right) NMR spectra (CD_2Cl_2, −18 °C, 500 MHz) of *rac*-(EBI)Zr[OC(O^{i}Pr)=C(CH_2COO^{i}Pr)CH_2C(Me_2)C(O^{i}Pr)=O]$^+$ [MeB(C_6F_5)$_3$]$^-$ (**2b**).

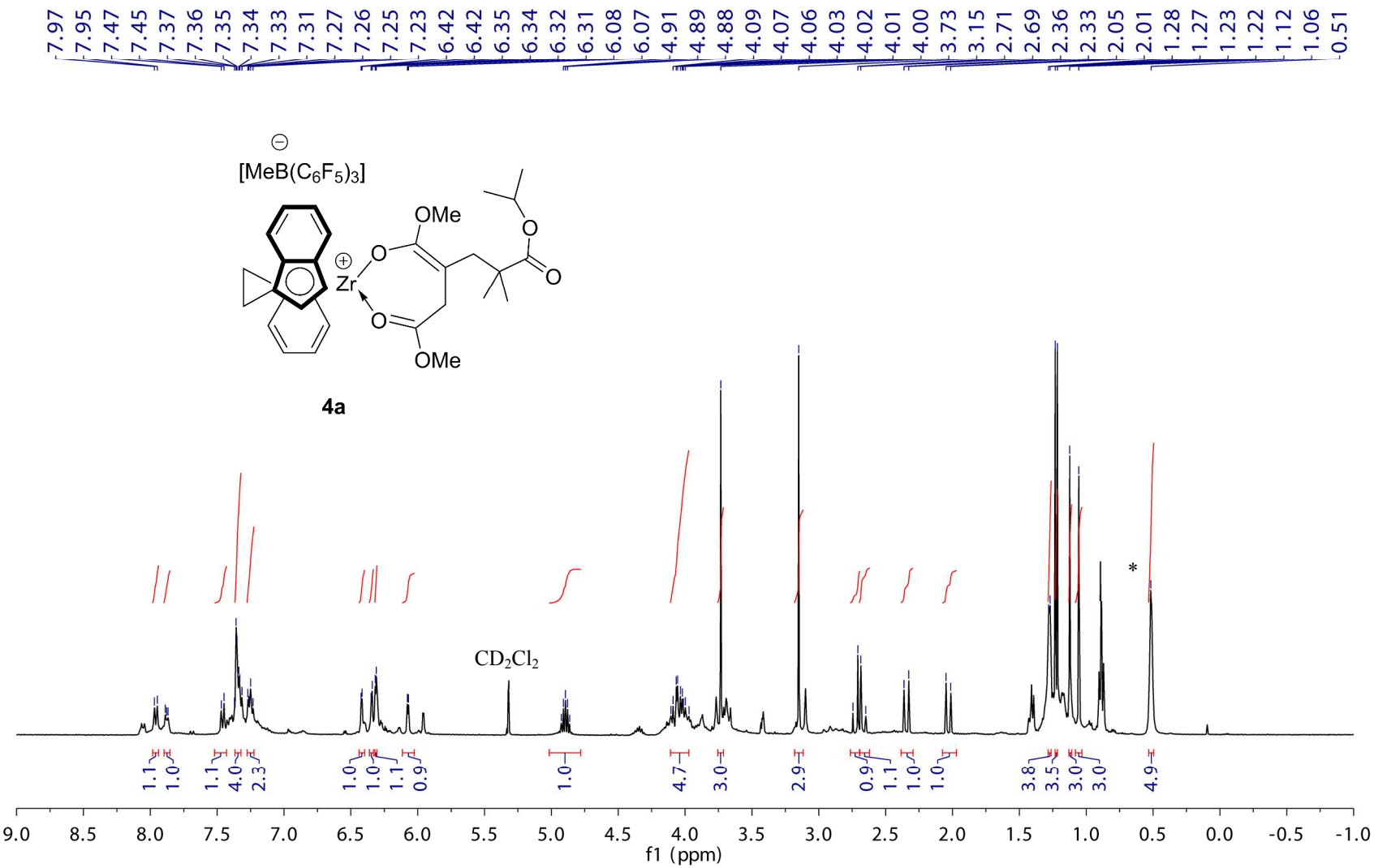

Figure S5. ^{1}H NMR spectrum (CD_2Cl_2, 25 °C, 400 MHz) of *rac*-(EBI)Zr[OC(OMe)=C($CH_2CMe_2COO^iPr$)CH_2C(OMe)=O]$^+$[MeB(C_6F_5)$_3$]$^-$ (**4a**). (* = hexanes)

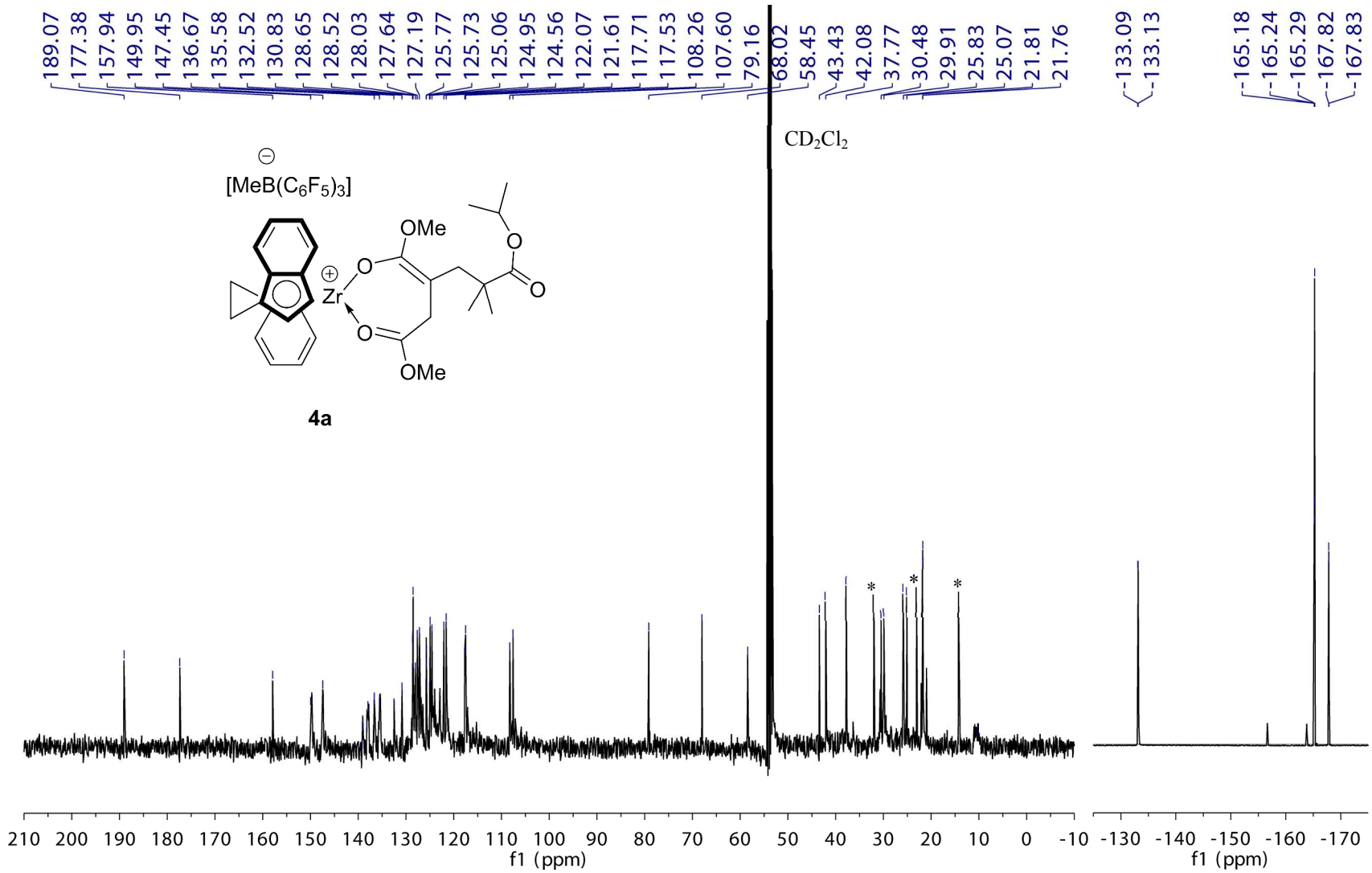

Figure S6. ^{13}C (left) and ^{19}F (right) NMR spectra (CD_2Cl_2, 25 °C, 400 MHz) of *rac*-(EBI)Zr[OC(OMe)=C($CH_2CMe_2COO^iPr$)CH_2C(OMe)=O]$^+$ [MeB(C_6F_5)$_3$]$^-$ (**4a**). * = hexanes; minor peaks due to excess (C_6F_5)$_3$B·THF used in the NMR scale reaction were also present in ^{19}F NMR.

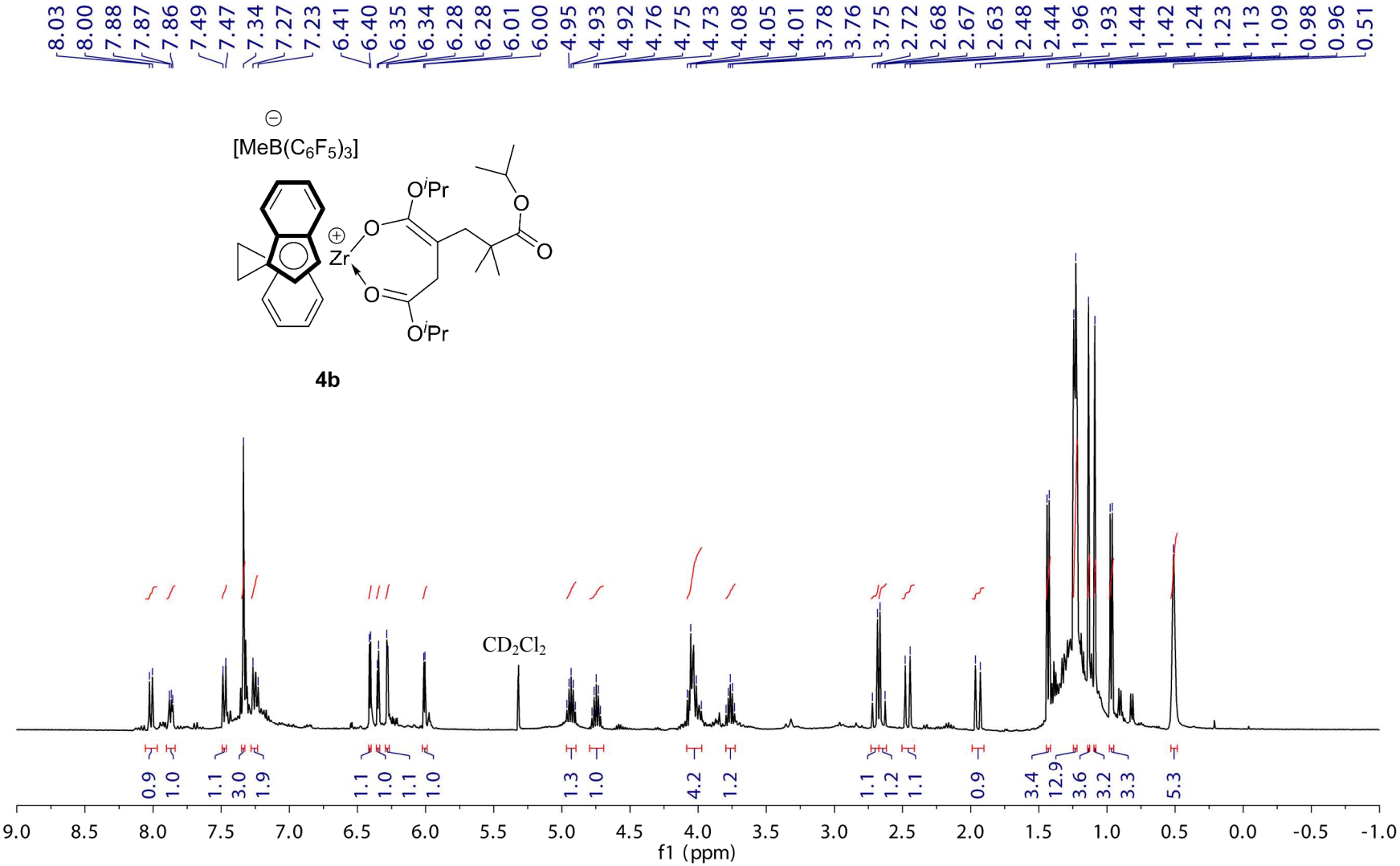

Figure S7. ^{1}H NMR spectrum (CD_2Cl_2, 25 °C, 400 MHz) of *rac*-(EBI)Zr[OC(O^{i}Pr)=C($CH_2CMe_2COO^iPr$)CH_2C(O^{i}Pr)=O]$^+$[MeB(C_6F_5)$_3$]$^-$ (**4b**).

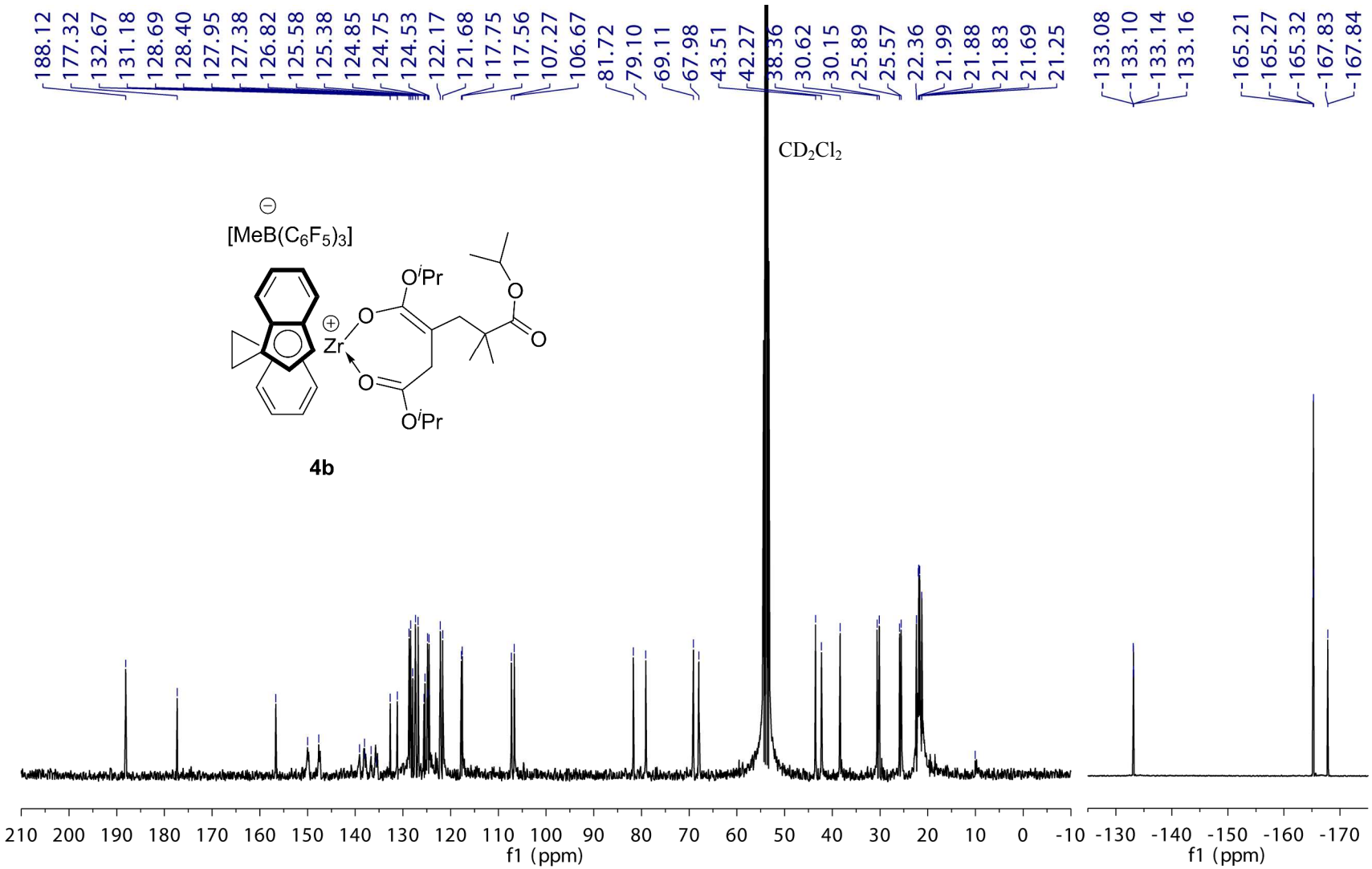

Figure S8. ^{13}C (left) and ^{19}F (right) NMR spectra (CD_2Cl_2, 25 °C, 400 MHz) of *rac*-(EBI)Zr[OC(O^{i}Pr)=C($CH_2CMe_2COO^iPr$)CH_2C(O^{i}Pr)=O]$^+$ $[MeB(C_6F_5)_3]^-$ (**4b**).

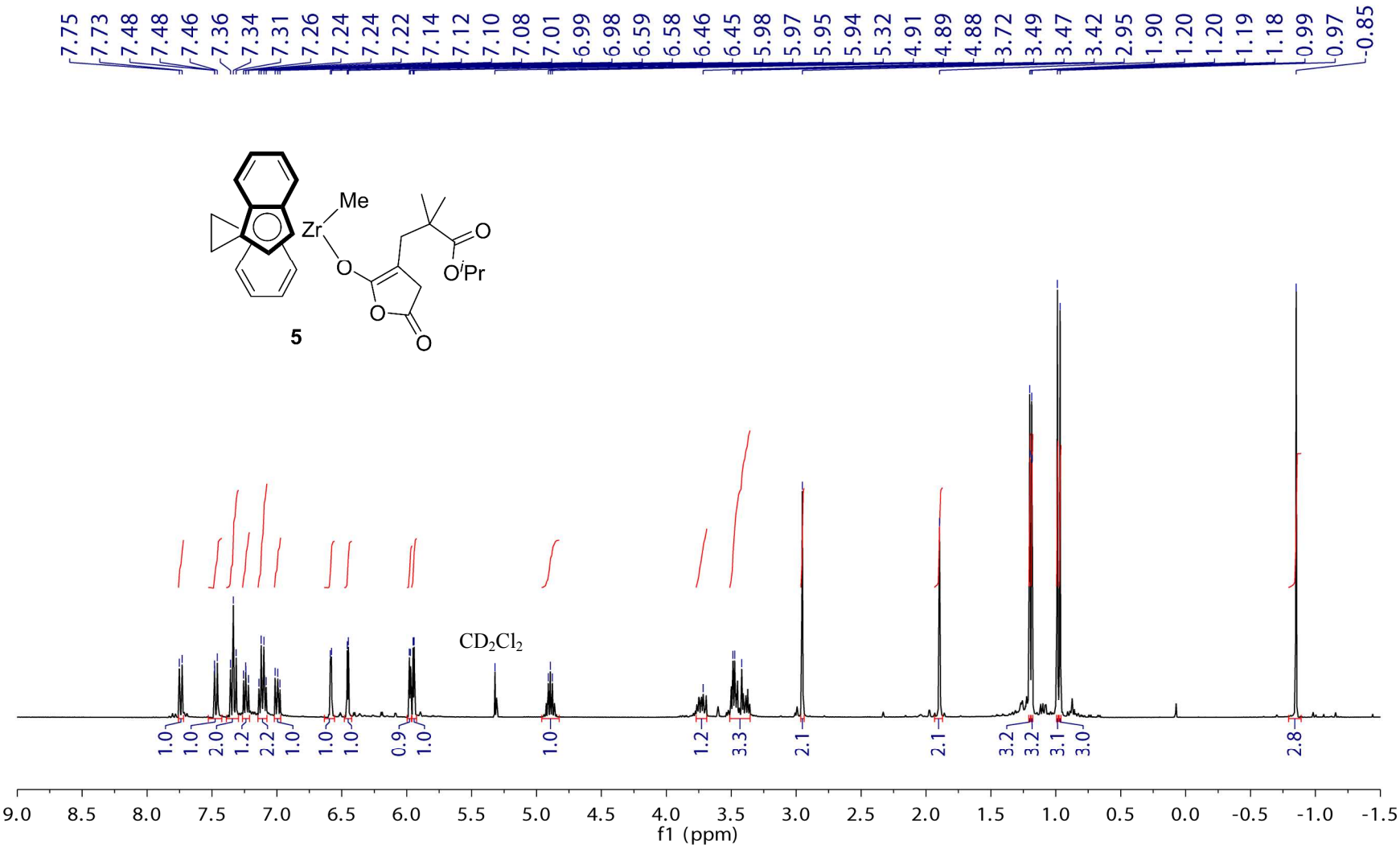

Figure S9. ^{1}H NMR spectrum (CD_2Cl_2, 25 °C, 400 MHz) of *rac*-(EBI)ZrMe{OC[OC(O)CH_2]=C($CH_2CMe_2COO^iPr$)} (**5**).

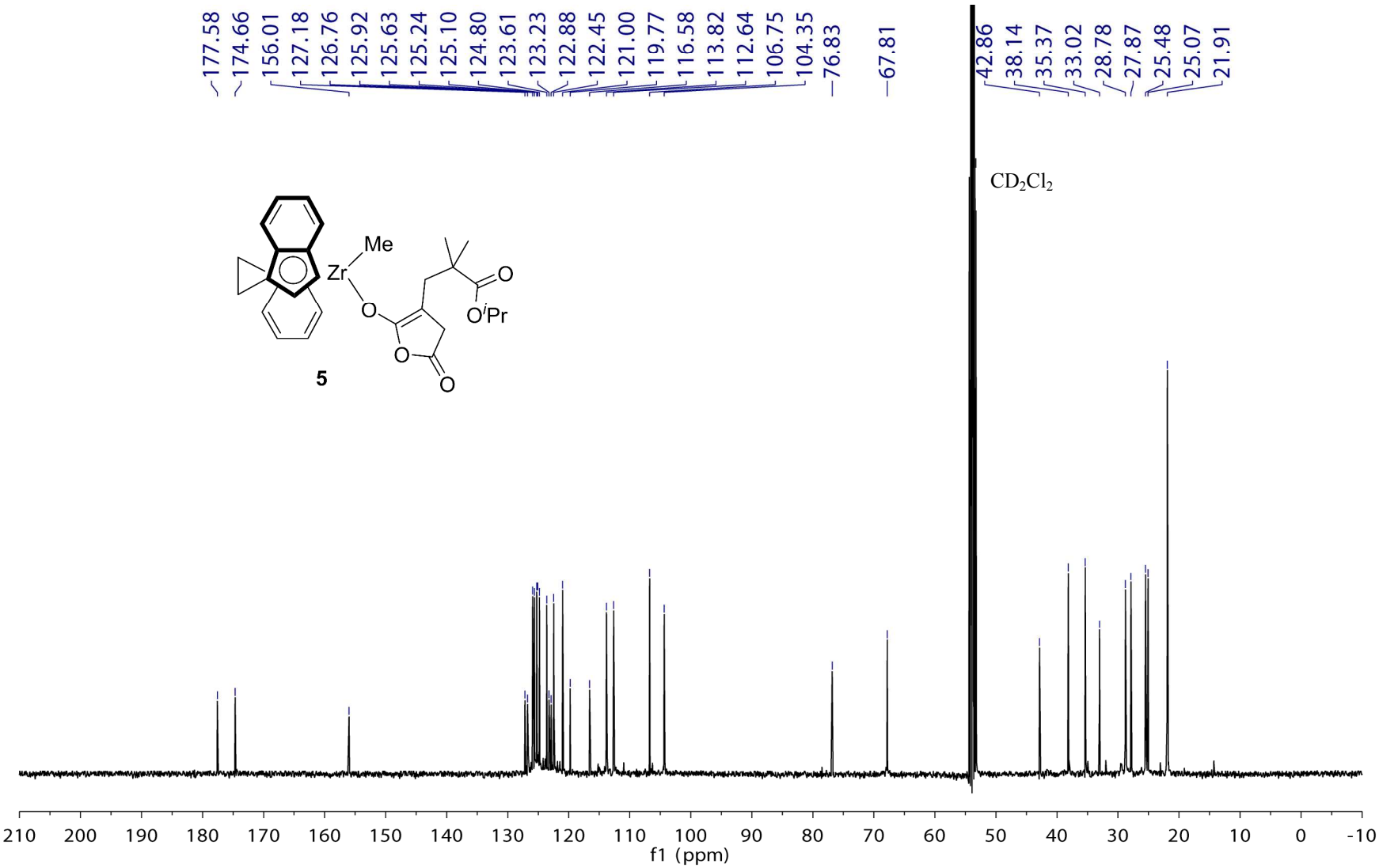

Figure S10. ^{13}C NMR spectrum (CD_2Cl_2, 25 °C, 400 MHz) of *rac*-(EBI)ZrMe{OC[OC(O)CH_2]=C($CH_2CMe_2COO^iPr$)} (**5**).

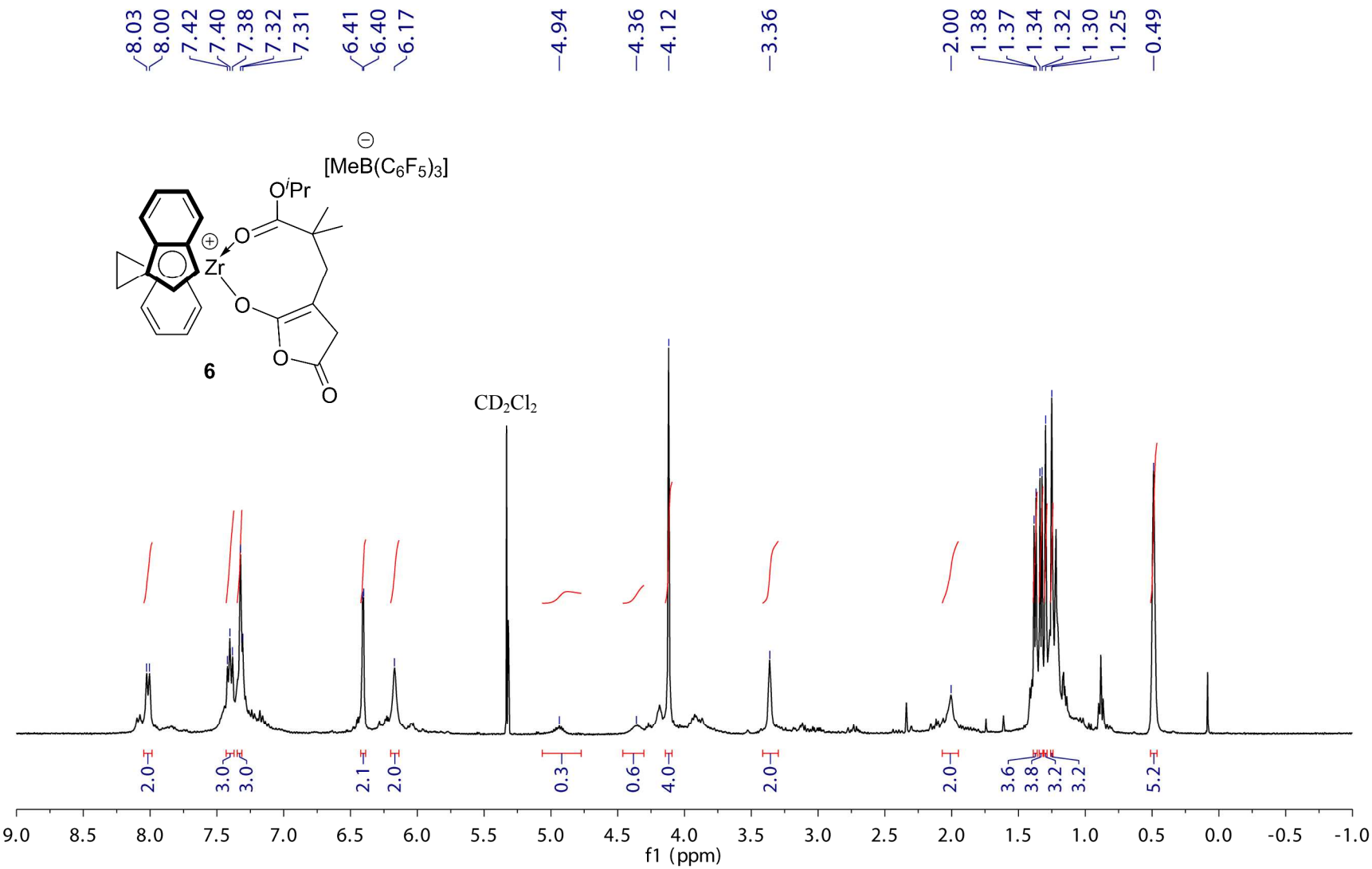

Figure S11. ^{1}H NMR spectrum (CD_2Cl_2, 25 °C, 400 MHz) of *rac*-(EBI)ZrMe{OC[OC(O)CH_2]=C[$CH_2CMe_2C(O^iPr)$=O]}$^+$[$MeB(C_6F_5)_3$]$^-$ (**6**).

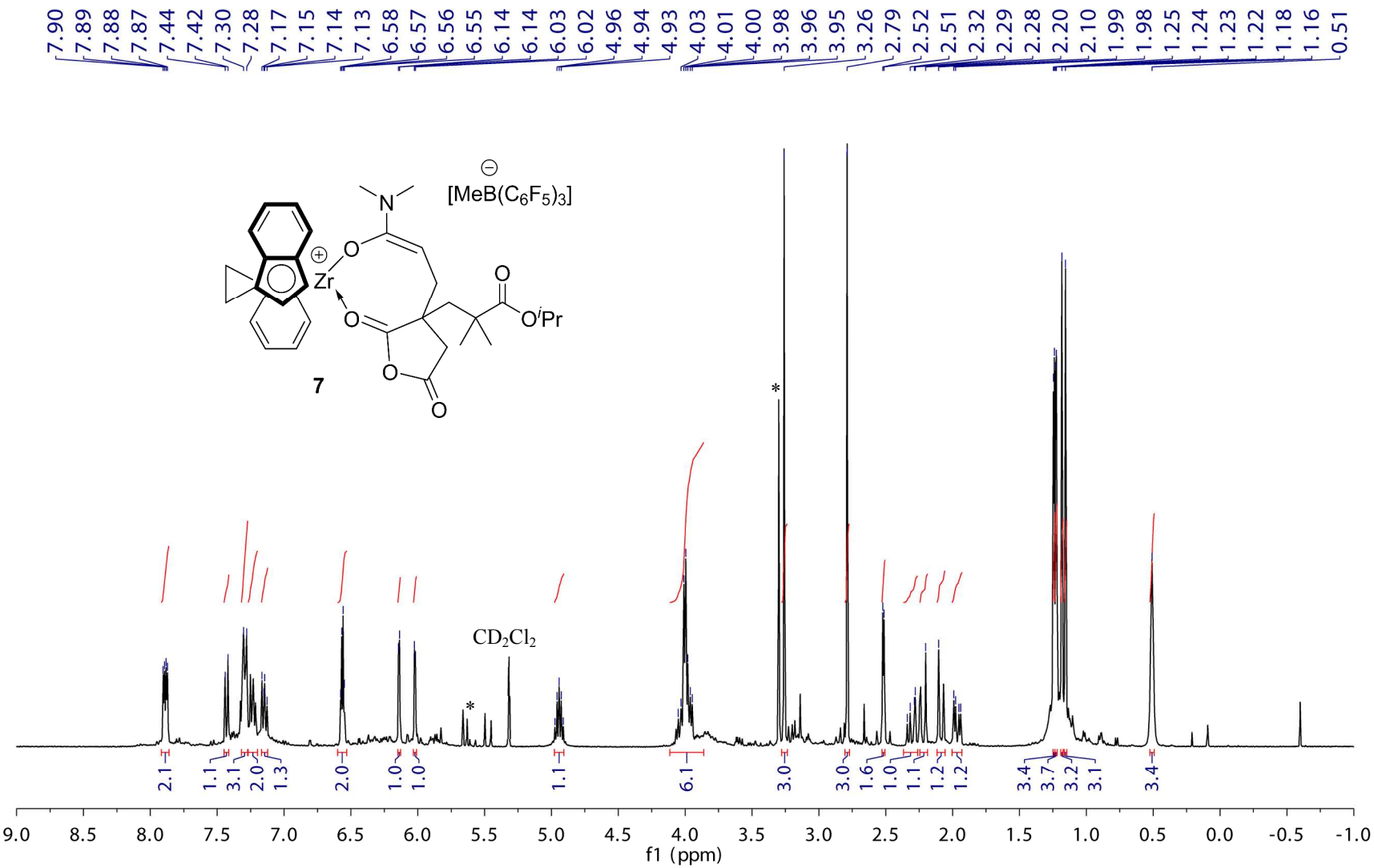

Figure S12. ^{1}H NMR spectrum (CD_2Cl_2, 25 °C, 400 MHz) of *rac*-(EBI)Zr{OC(NMe_2)=CCH_2C($CH_2CMe_2COO^iPr$)C[OC(O)]=O]}$^+$[MeB(C_6F_5)$_3$]$^-$ (**7**). (* = excess (C_6F_5)$_3$B·DMAA)

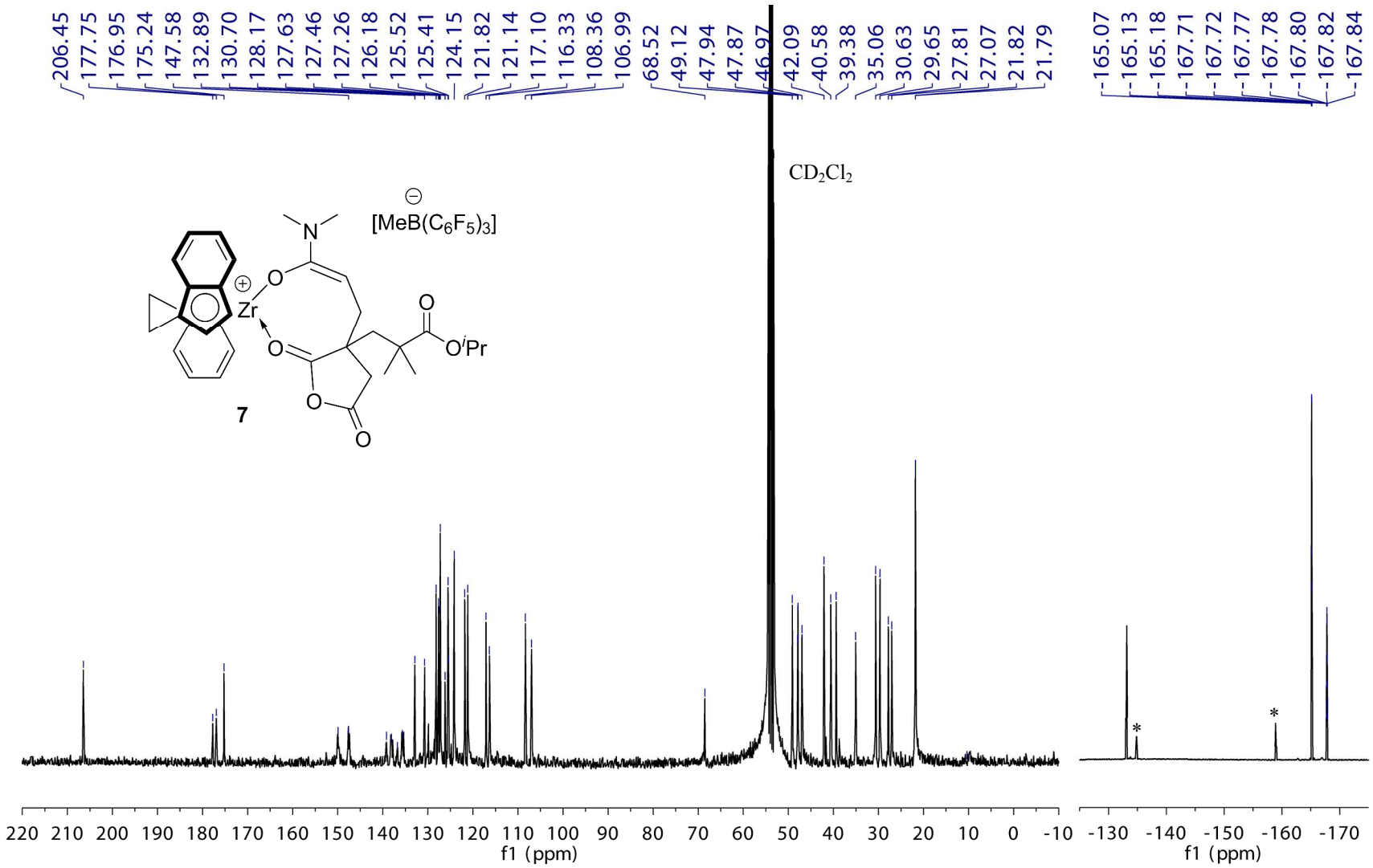

Figure S13. ^{13}C (left) and ^{19}F (right) NMR spectra (CD_2Cl_2, 25 °C, 400 MHz) of *rac*-(EBI)Zr{OC(NMe$_2$)=CCH$_2$C(CH$_2$CMe$_2$COO^{i}Pr)C[OC(O)]=O}$^+$ [MeB(C$_6$F$_5$)$_3$]$^-$ (**7**). (* = excess (C$_6$F$_5$)$_3$B·DMAA)

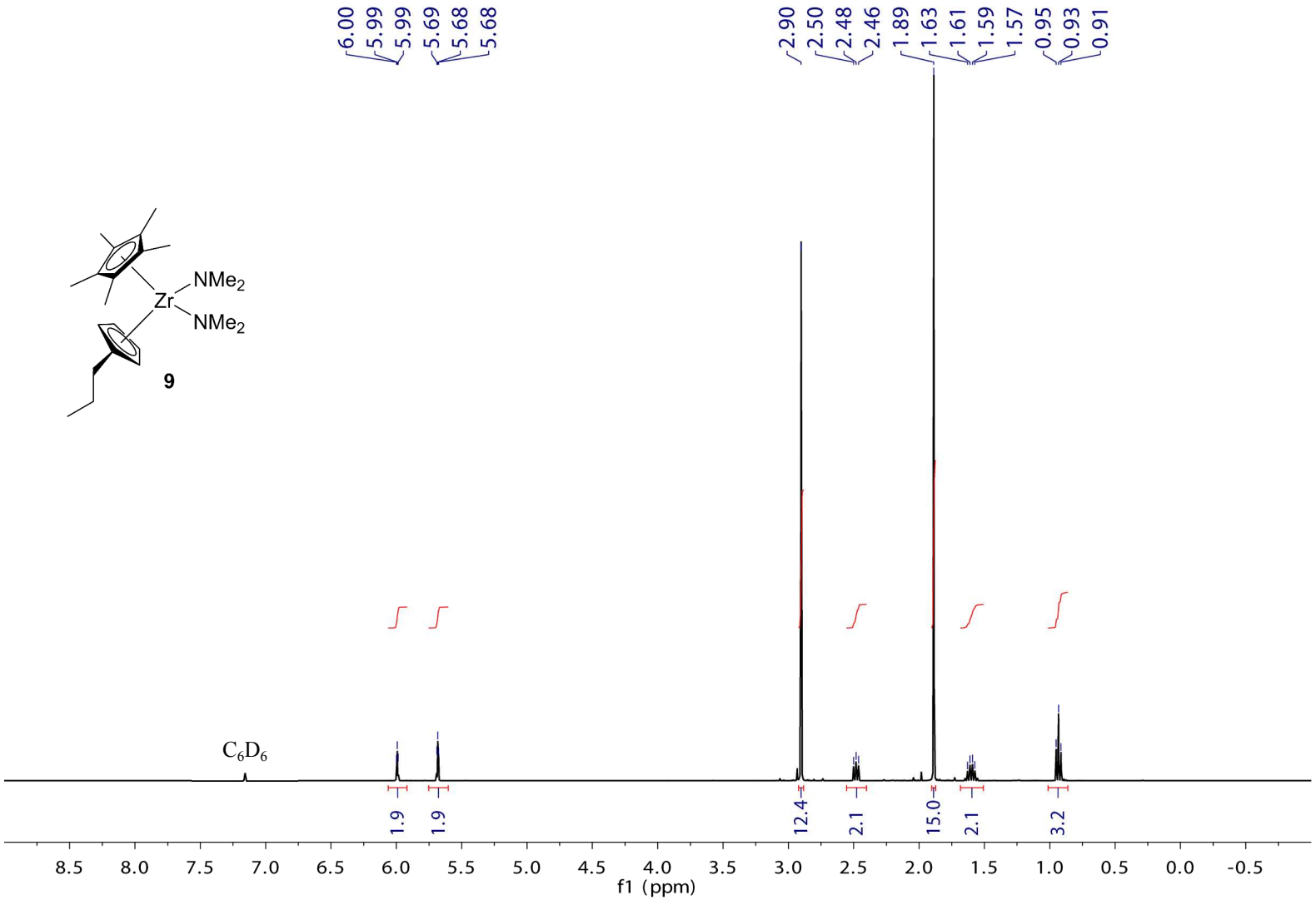

Figure S14. ^{1}H NMR spectrum (C_6D_6, 400 MHz, 25 °C) of Cp*(^{n}PrCp)Zr(NMe$_2$)$_2$ (**9**).

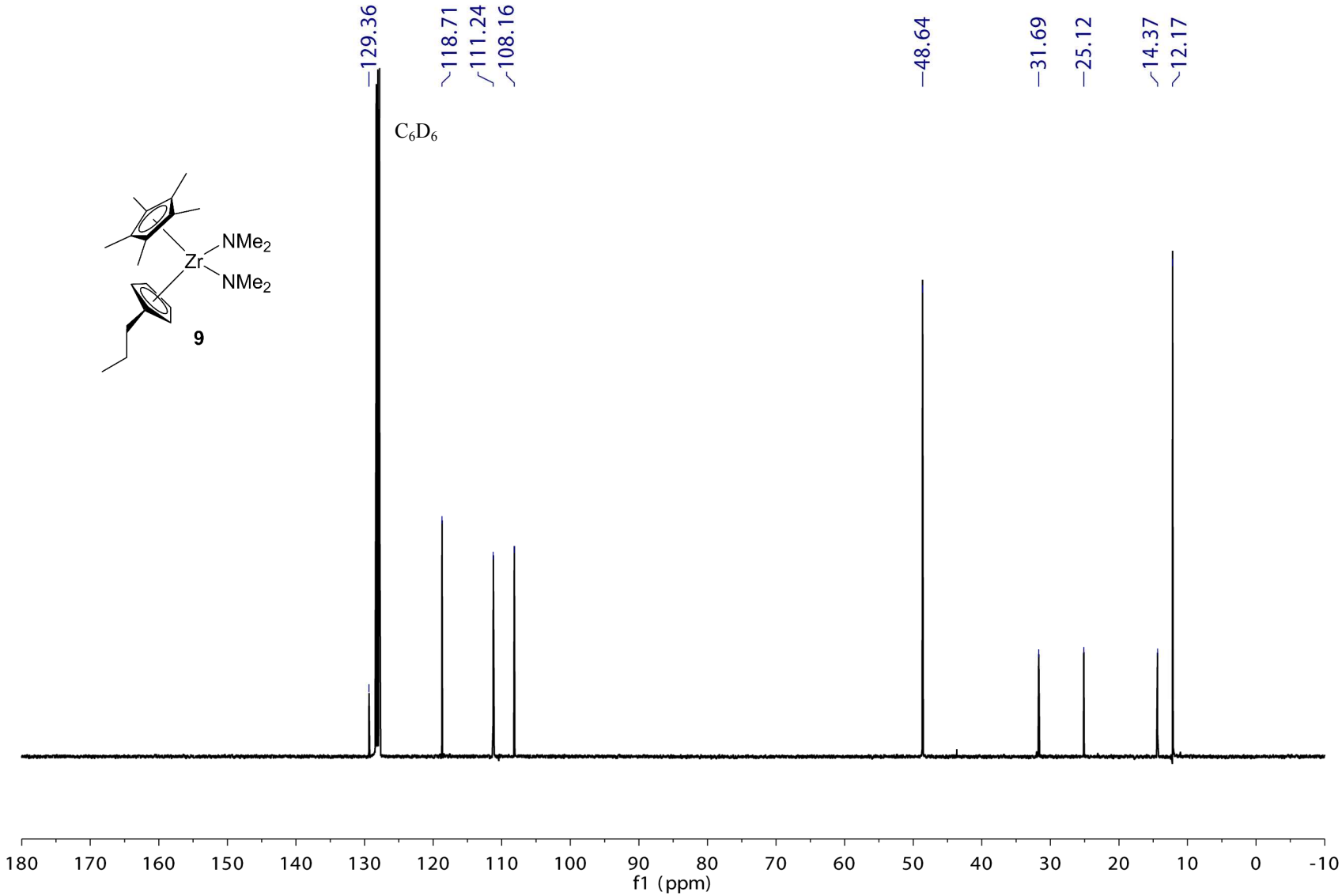

Figure S15. ^{13}C NMR spectrum (C_6D_6, 400 MHz, 25 °C) of Cp*(^{n}PrCp)Zr(NMe_2)$_2$ (**9**).

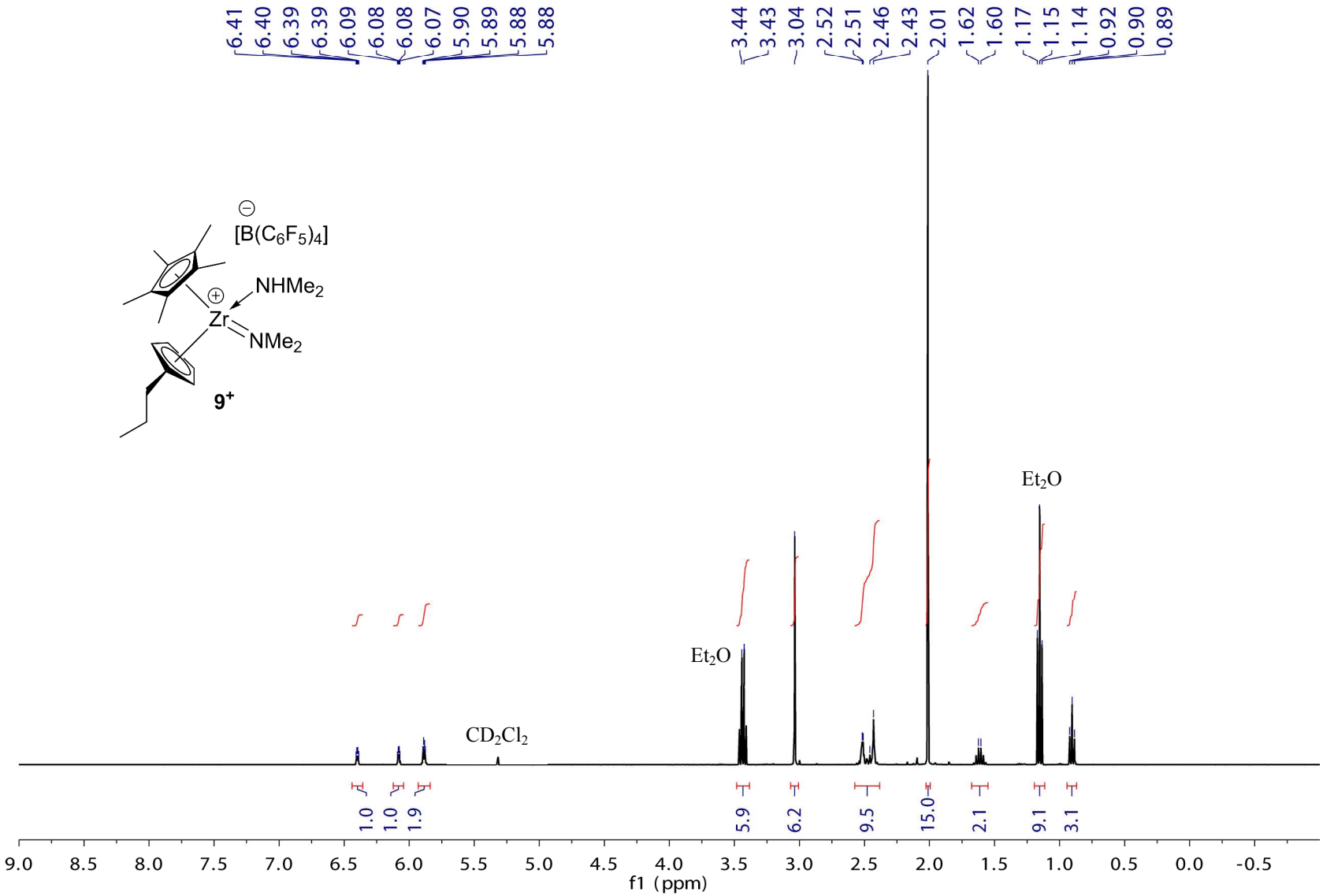

Figure S16. ^{1}H NMR spectrum (CD_2Cl_2, 25 °C, 400 MHz) of $[Cp^*(^nPrCp)Zr(HNMe_2)=NMe_2]^+ [B(C_6F_5)_4]^-$ (**9**$^+$).

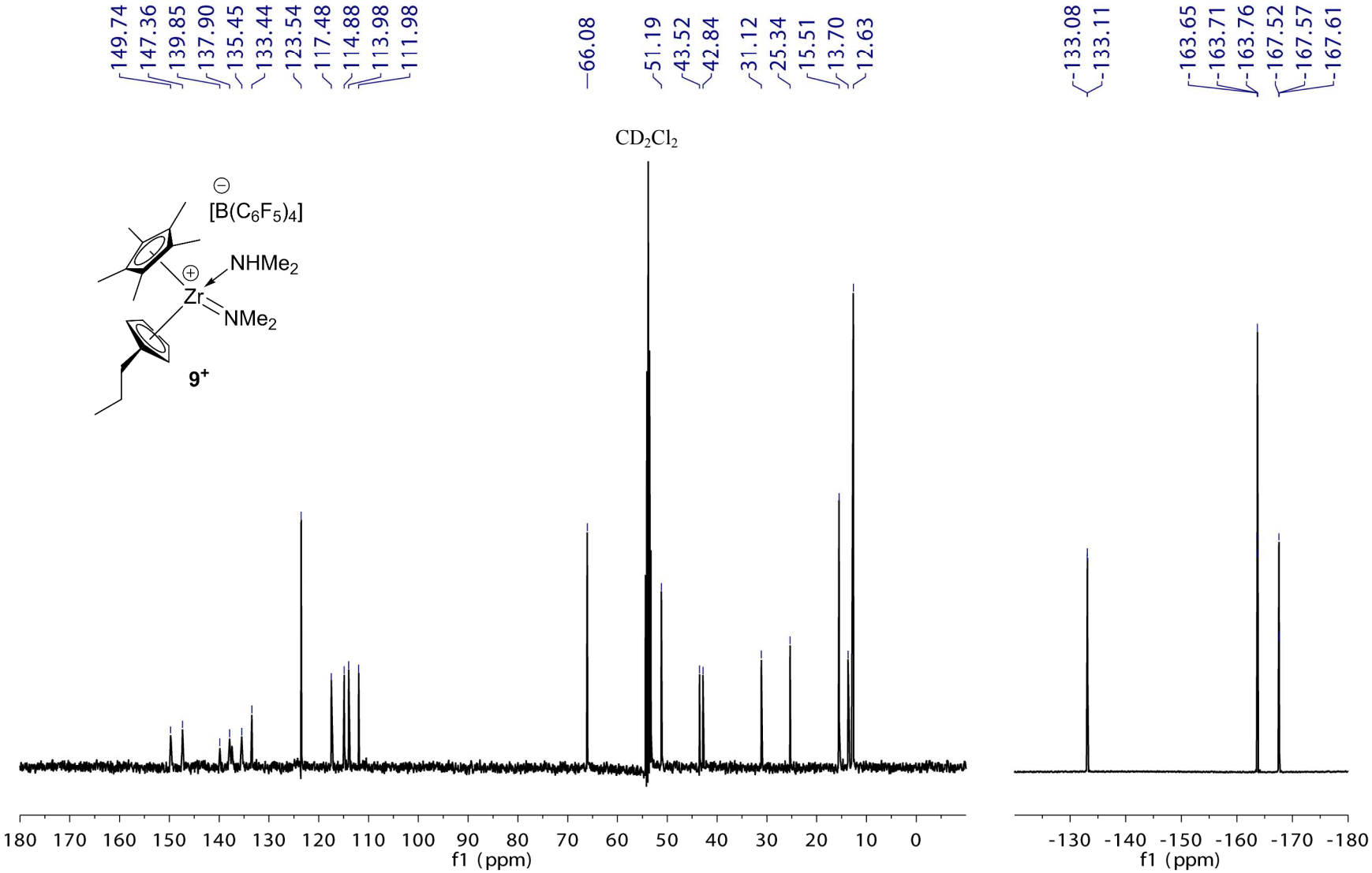

Figure S17. ^{13}C (left) and ^{19}F (right) NMR spectra (CD_2Cl_2, 25 °C, 400 MHz) of $[Cp^*(^nPrCp)Zr(HNMe_2)=NMe_2]^+[B(C_6F_5)_4]^-$ (**9**$^+$).

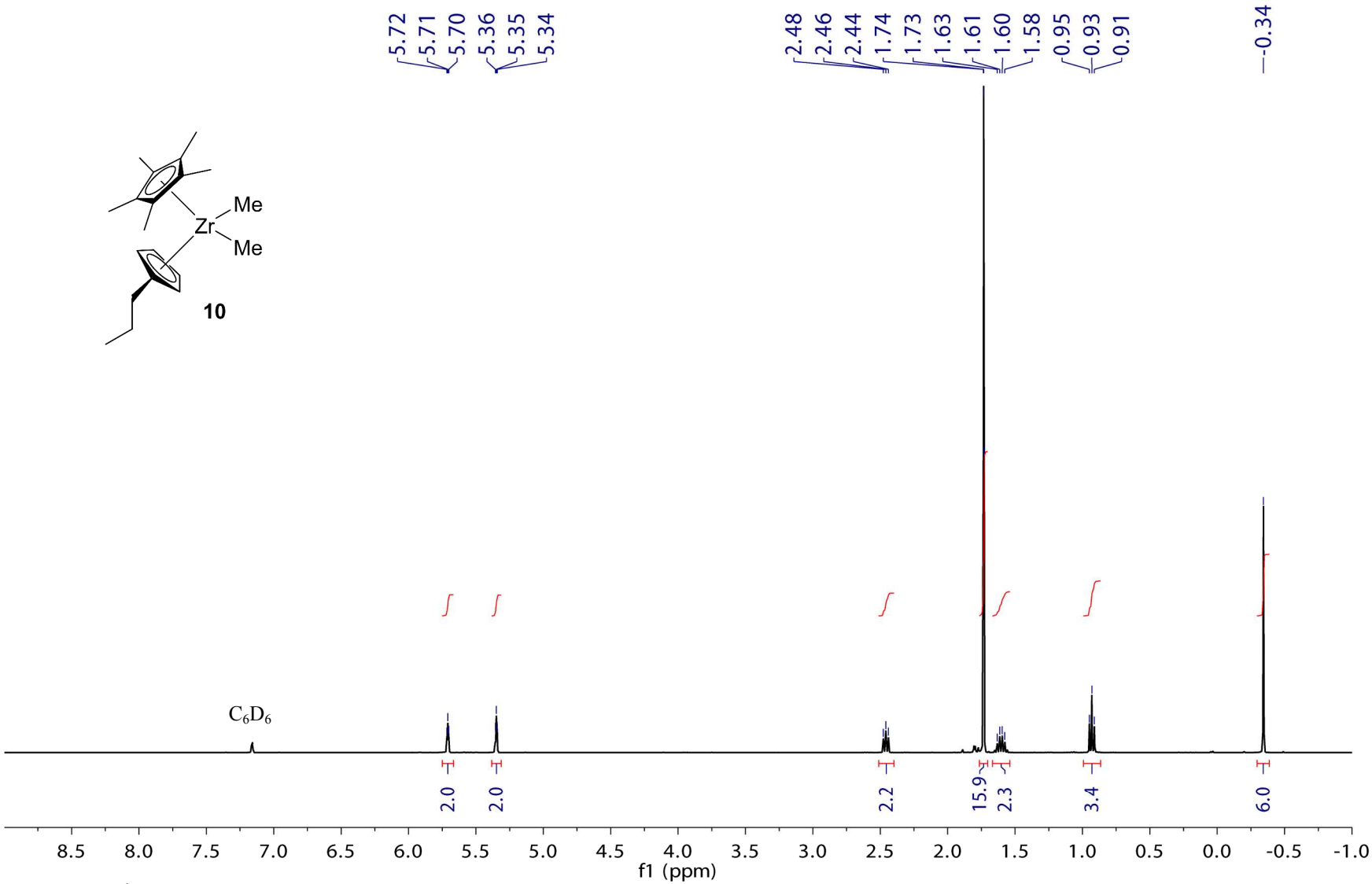

Figure S18. ^{1}H NMR spectrum (C_6D_6, 25 °C, 400 MHz) of Cp*(^{n}PrCp)$ZrMe_2$ (**10**).

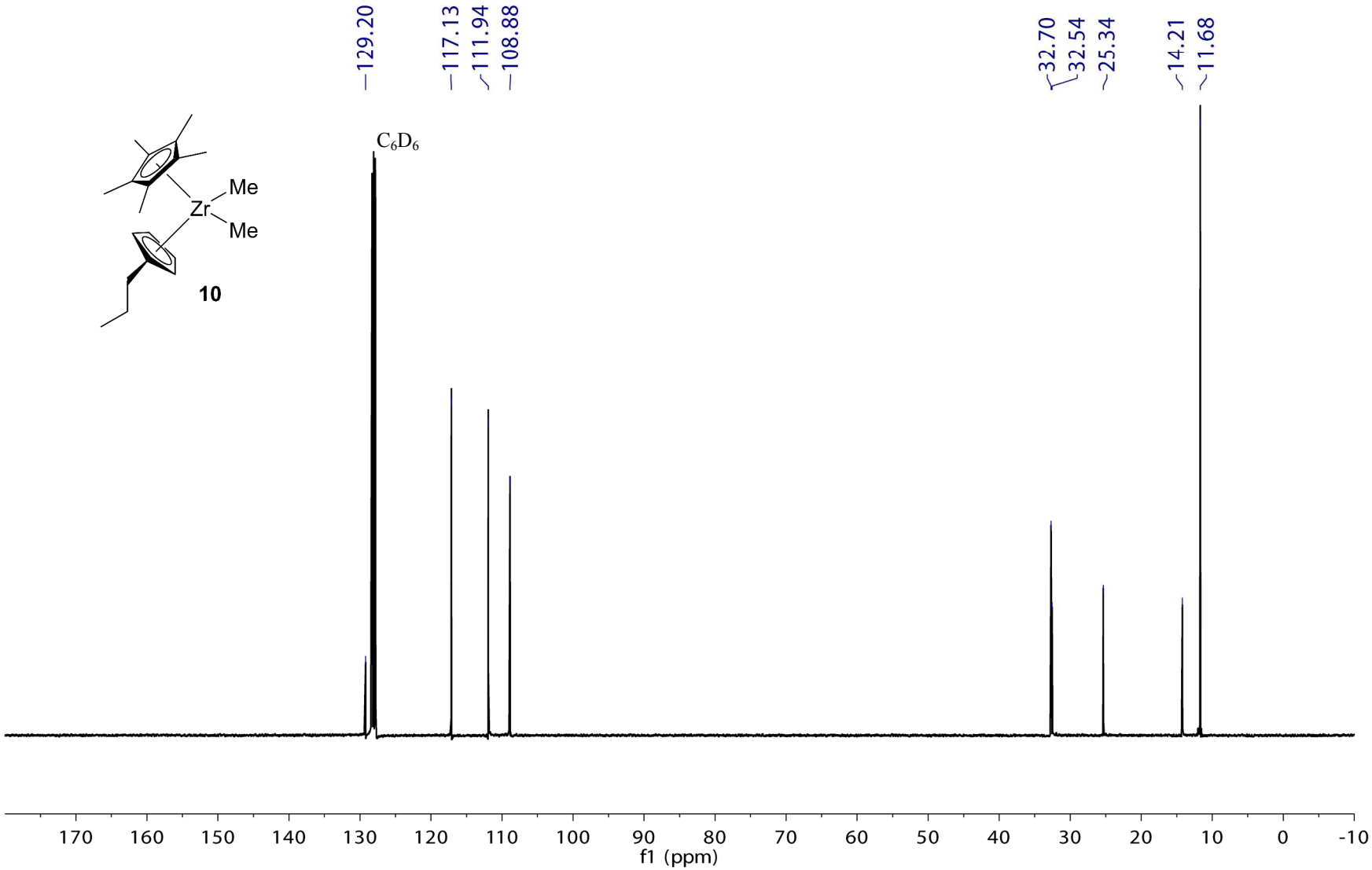

Figure S19. ^{13}C NMR spectrum (C_6D_6, 25 °C, 400 MHz) of Cp*(^{n}PrCp)$ZrMe_2$ (**10**).

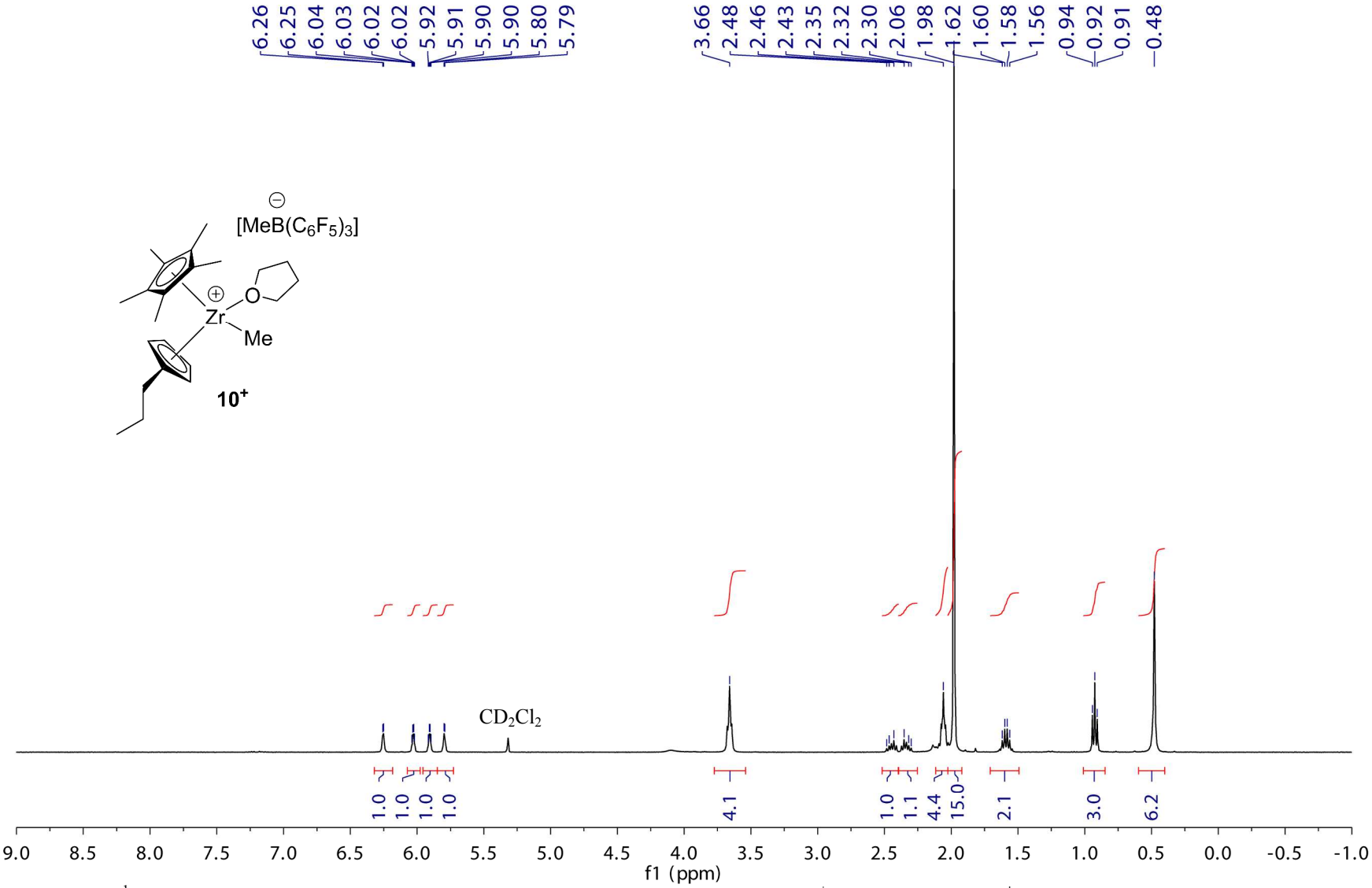

Figure S20. ^{1}H NMR spectrum (CD_2Cl_2, 25 °C, 400 MHz) of $[Cp^*(^{n}PrCp)Zr(THF)Me]^{+}[MeB(C_6F_5)_3]^{-}$ (**10**$^{+}$).

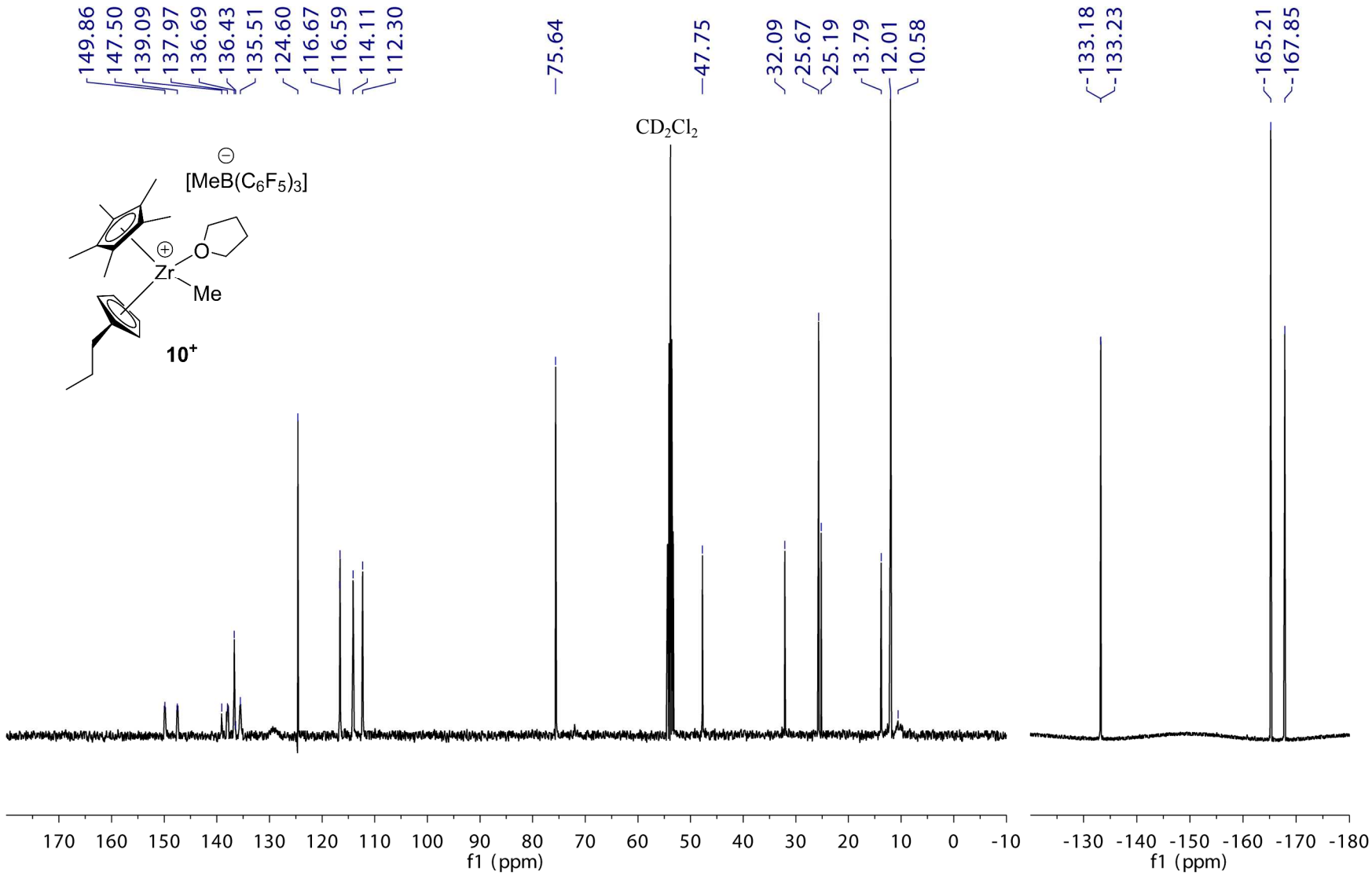

Figure S21. ^{13}C (left) and ^{19}F (right) NMR spectra (CD_2Cl_2, 25 °C, 400 MHz) of $[Cp^*(^nPrCp)Zr(THF)Me]^+[MeB(C_6F_5)_3]^-$ (**10**$^+$).

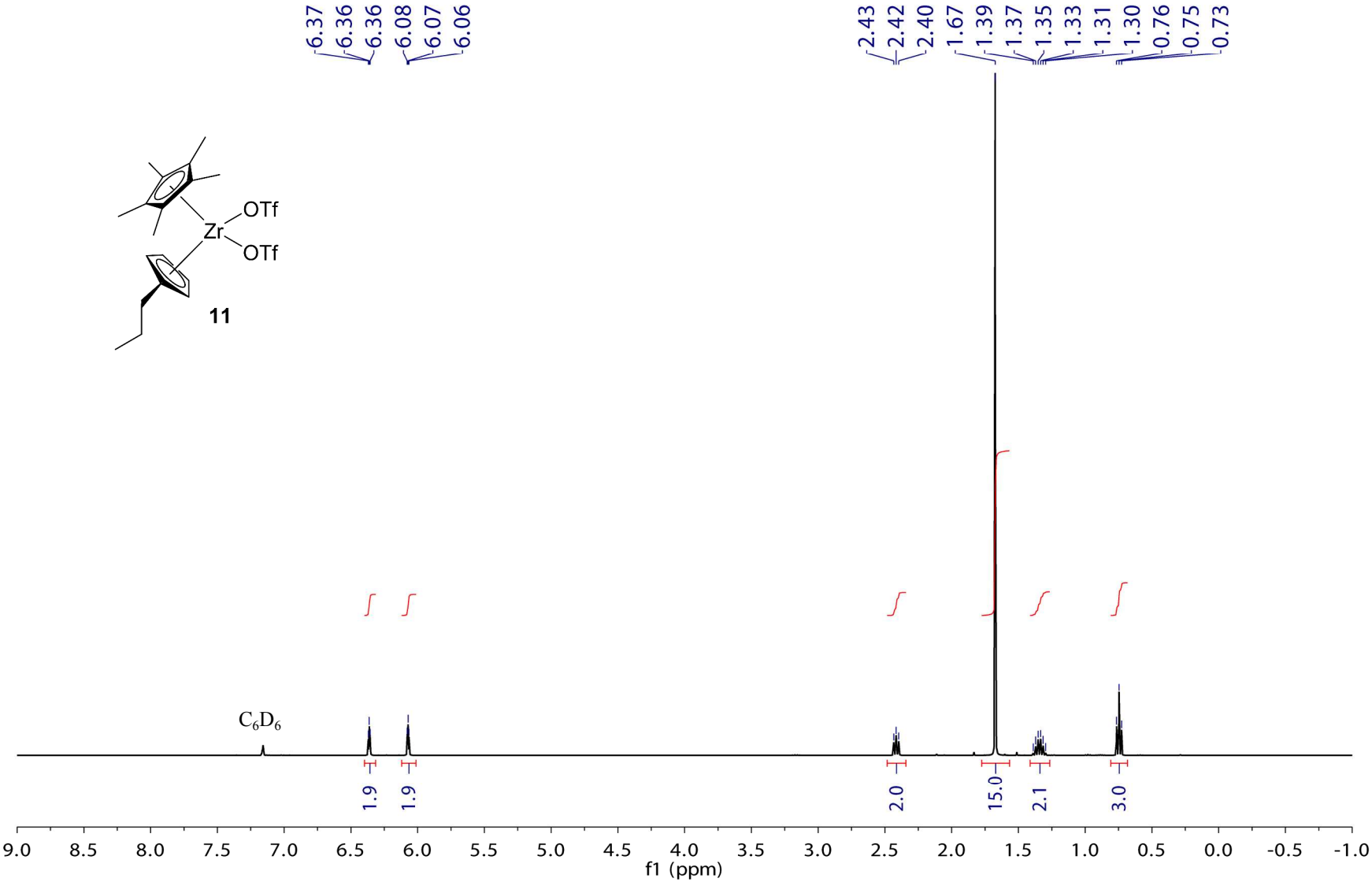

Figure S22. ^{1}H NMR spectrum (C_6D_6, 25 °C, 400 MHz) of Cp*(^{n}PrCp)Zr(OTf)$_2$ (**11**).

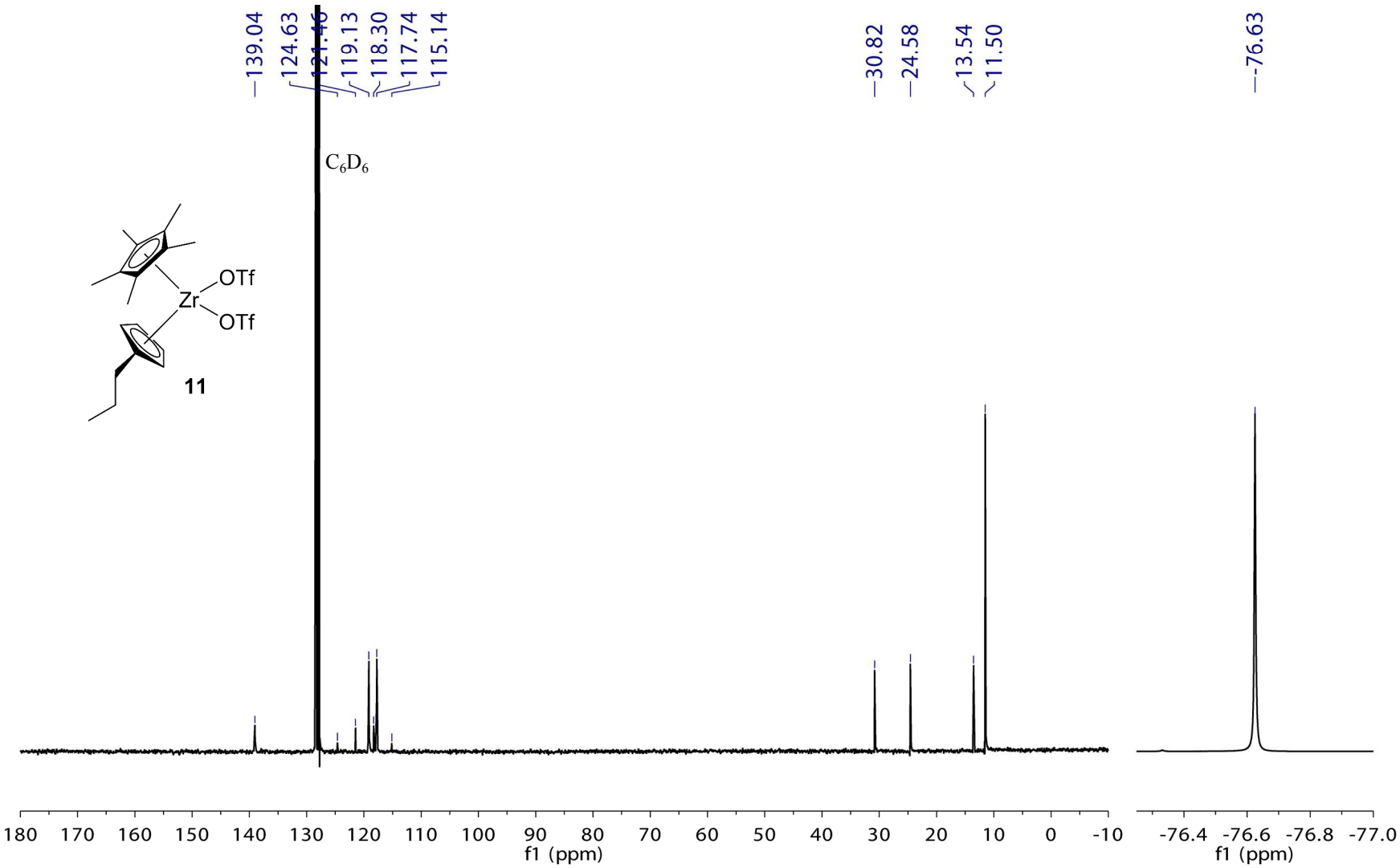

Figure S23. ^{13}C (left) and ^{19}F (right) NMR spectra (C_6D_6, 25 °C, 400 MHz) of Cp*(^{n}PrCp)Zr(OTf)$_2$ (**11**).

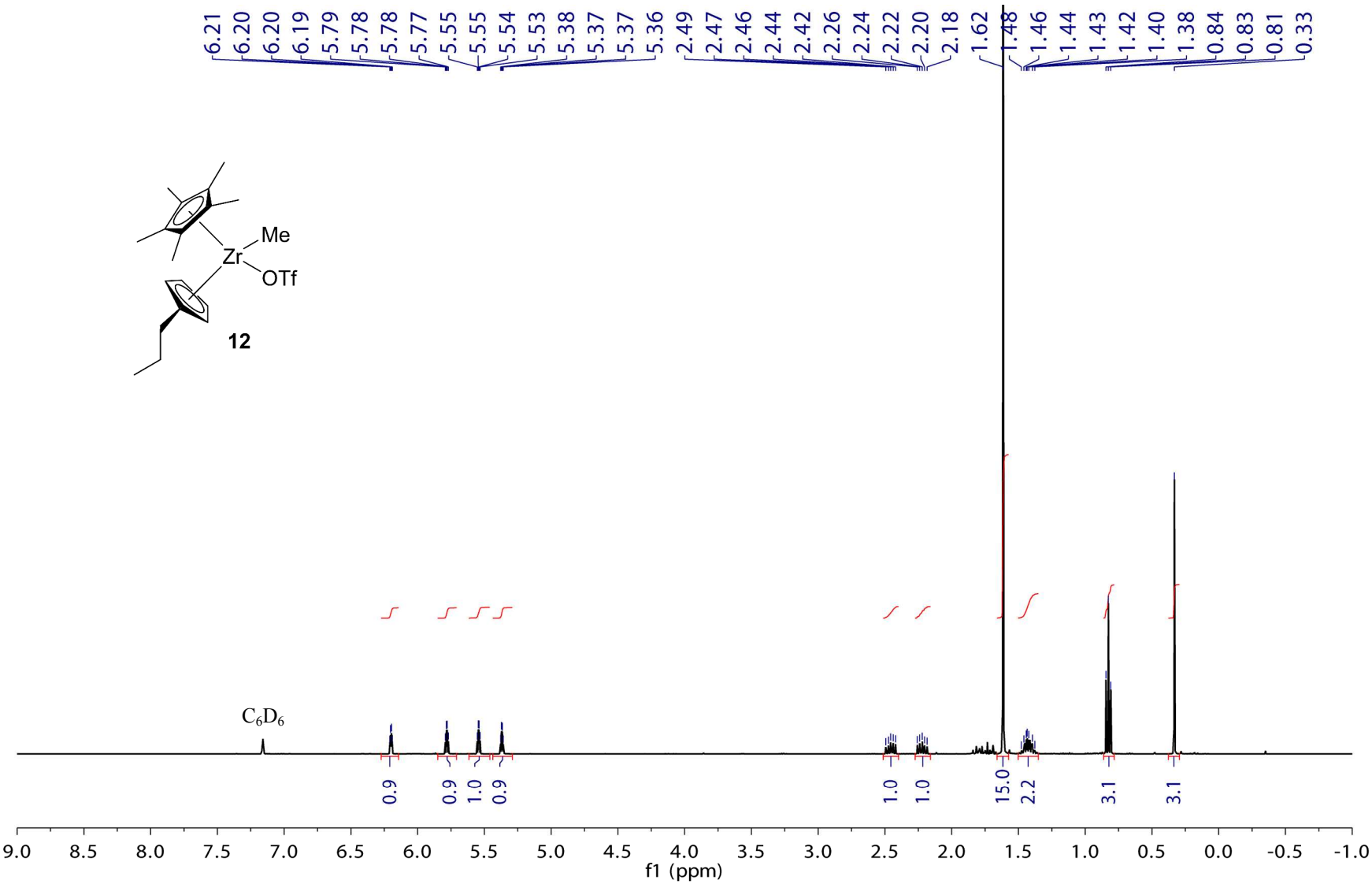

Figure S24. ^{1}H NMR spectrum (C_6D_6, 25 °C, 400 MHz) of Cp*(^{n}PrCp)Zr(OTf)Me (**12**).

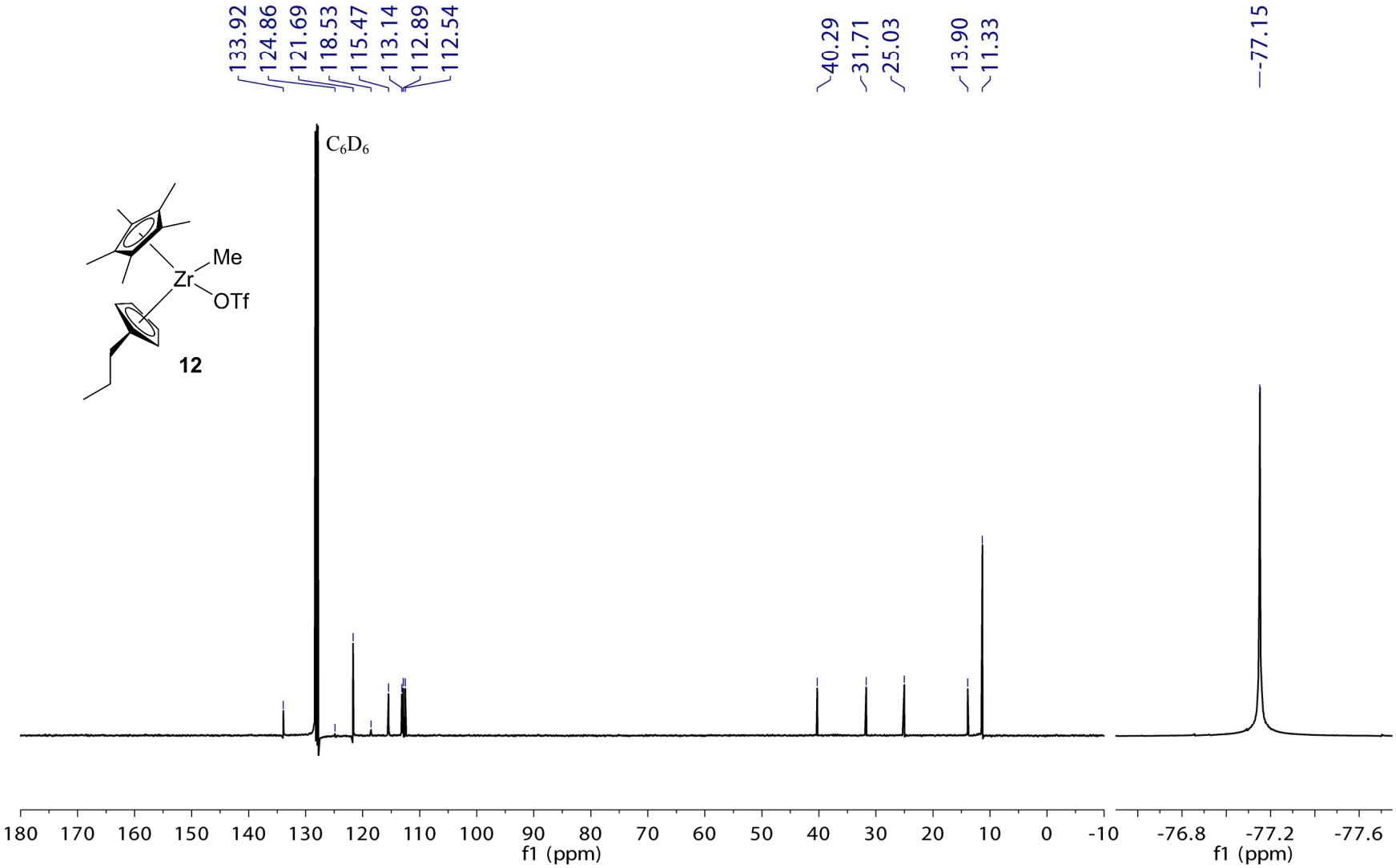

Figure S25. ^{13}C (left) and ^{19}F (right) NMR spectra (C_6D_6, 25 °C, 400 MHz) of Cp*(^{n}PrCp)Zr(OTf)Me (**12**).

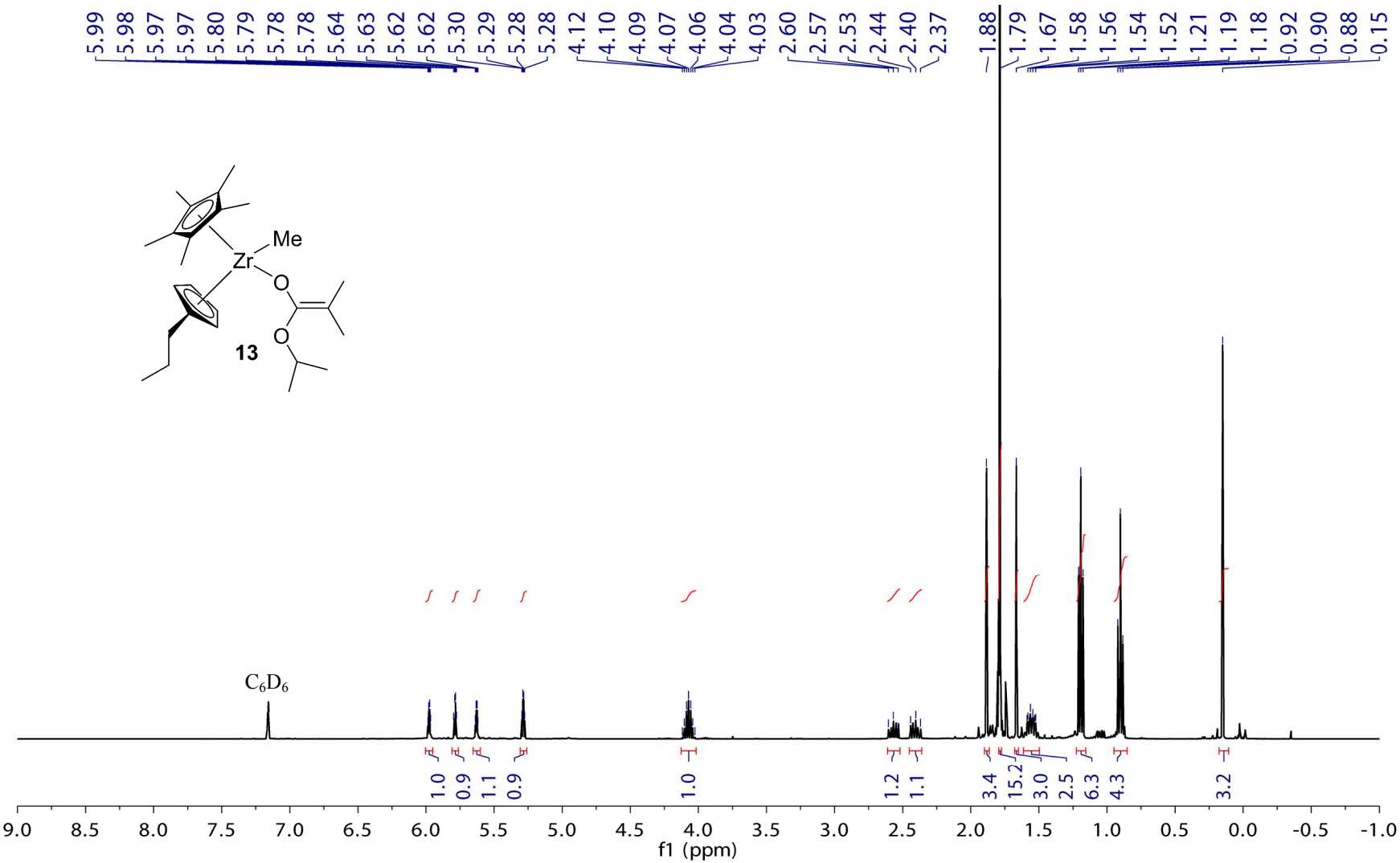

Figure S26. ^{1}H NMR spectrum (C_6D_6, 25 °C, 400 MHz) of Cp*(^{n}PrCp)ZrMe[OC(O^{i}Pr)=CMe$_2$] (**13**).

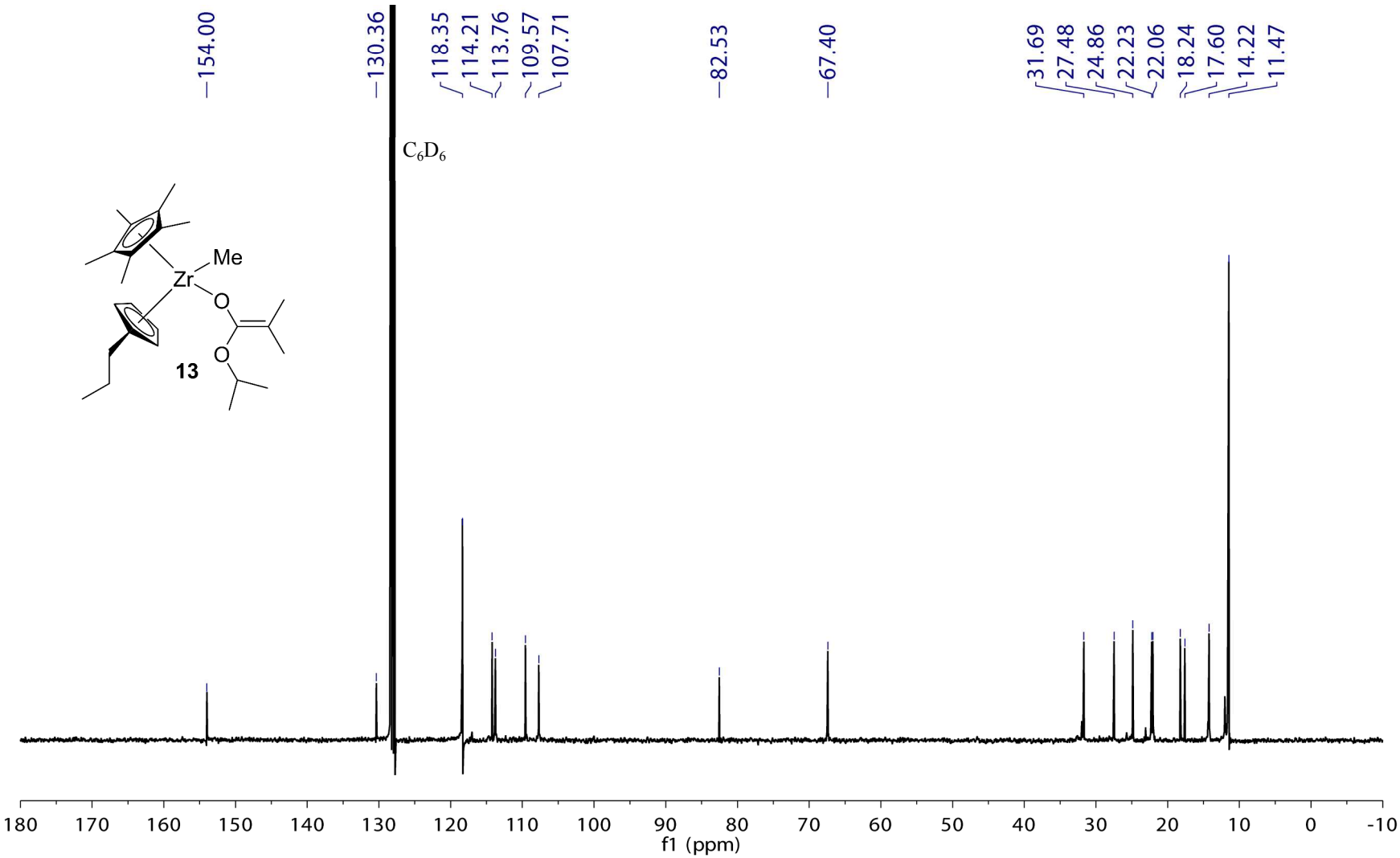

Figure S27. ^{13}C NMR spectrum (C_6D_6, 25 °C, 400 MHz) of Cp*(^{n}PrCp)ZrMe[OC(O^{i}Pr)=CMe$_2$] (**13**).

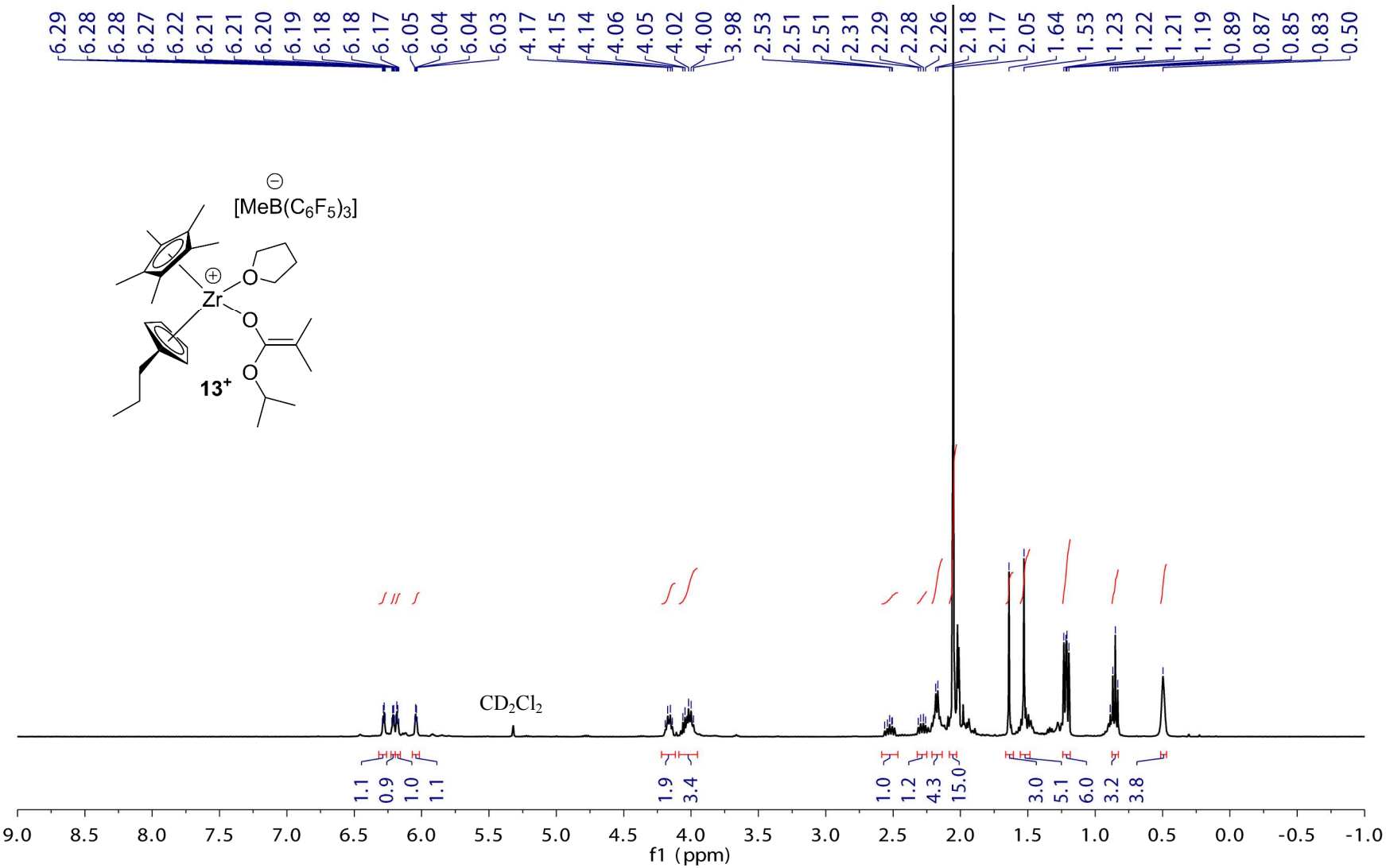

Figure S28. ^{1}H NMR spectrum (CD_2Cl_2, 25 °C, 400 MHz) of Cp*(^{n}PrCp)Zr(THF)[OC(O^{i}Pr)=CMe$_2$]$^+$ [MeB(C_6F_5)$_3$]$^-$ (**13**$^+$).

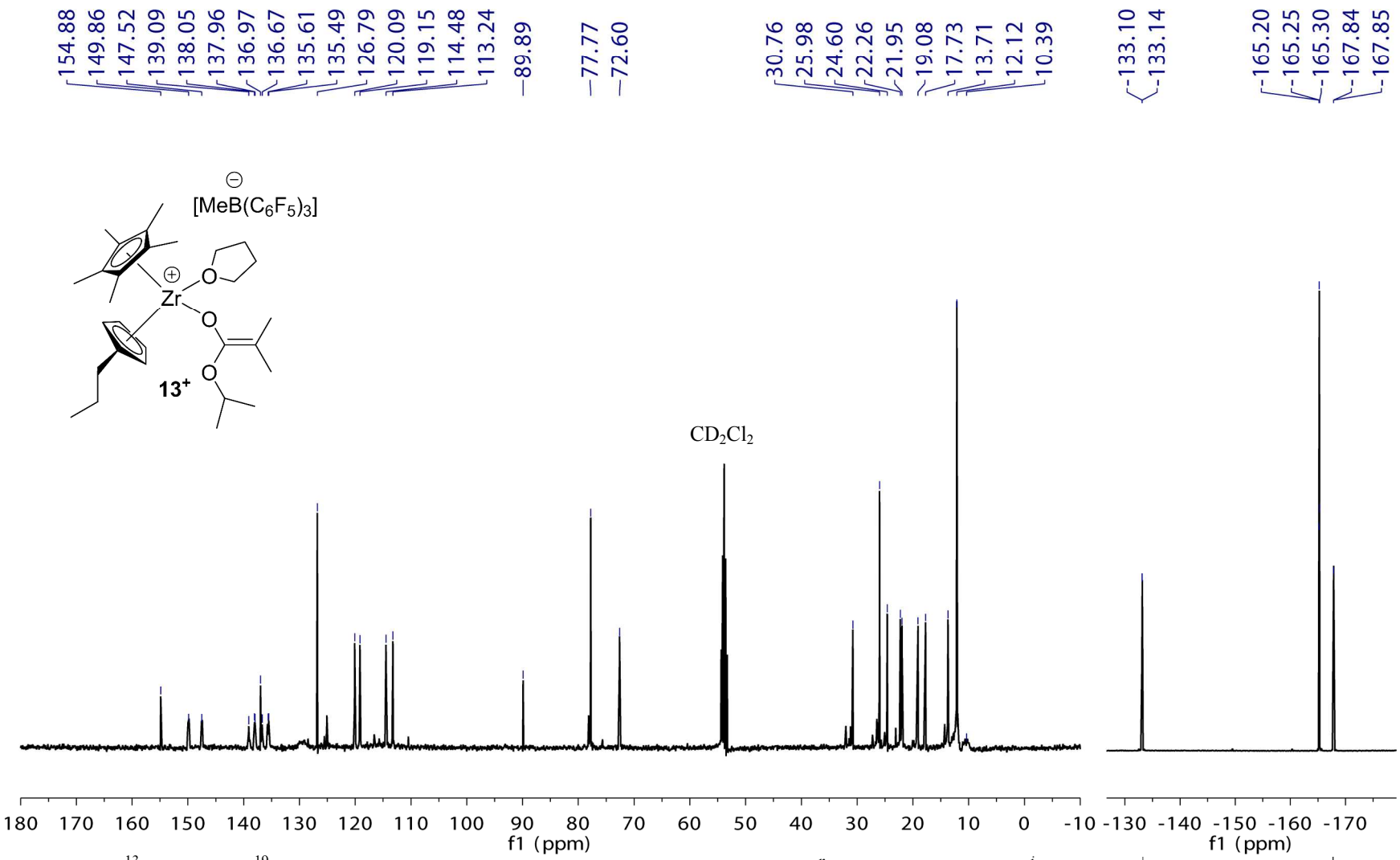

Figure S29. ^{13}C (left) and ^{19}F (right) NMR spectra (CD_2Cl_2, 25 °C, 400 MHz) of Cp*(^{n}PrCp)Zr(THF)[OC(O^{i}Pr)=CMe$_2$]$^+$[MeB(C$_6$F$_5$)$_3$]$^-$ (**13**$^+$).

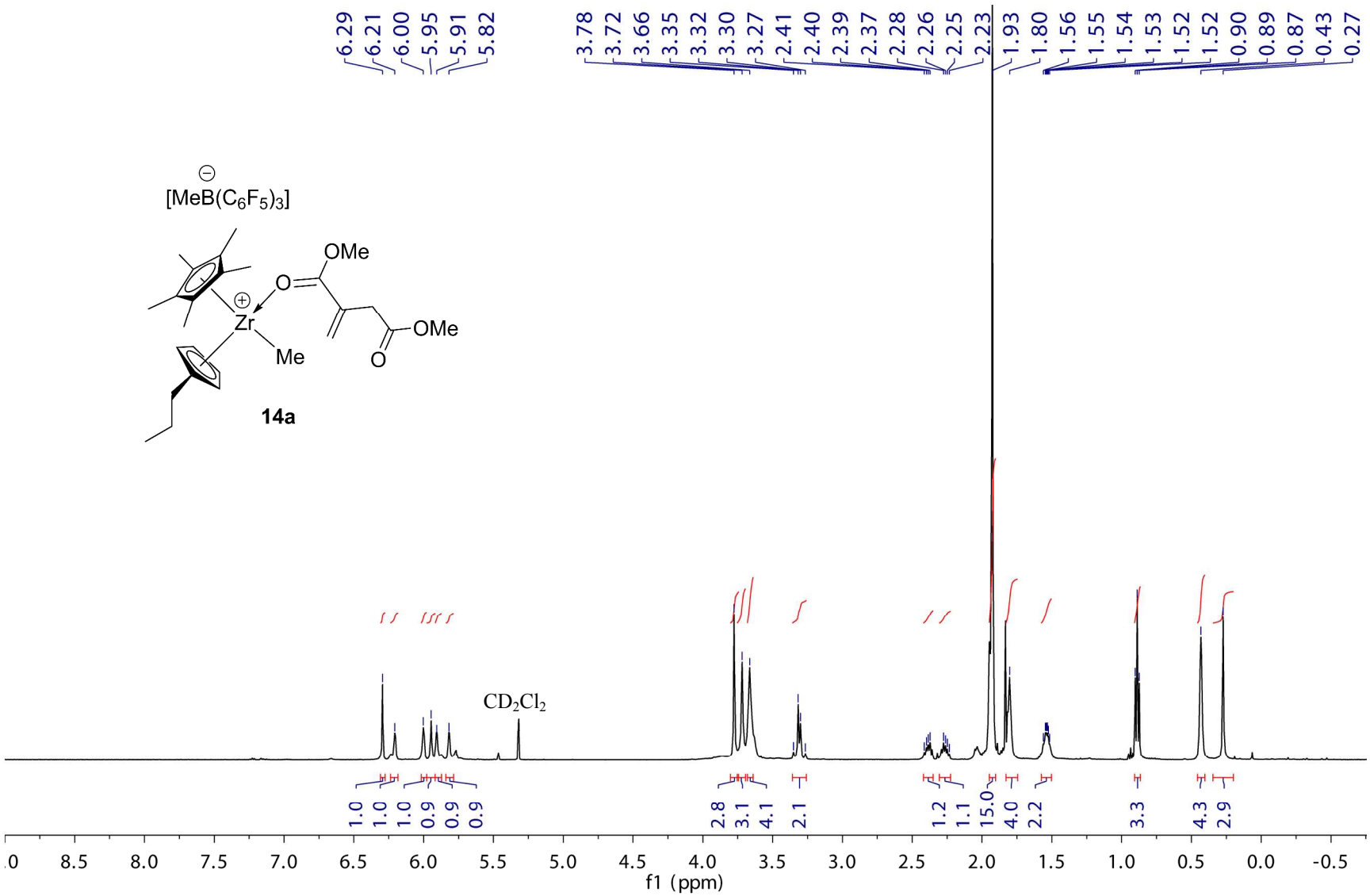

Figure S30. ^{1}H NMR spectrum (CD_2Cl_2, −18 °C, 500 MHz) of Cp*(^{n}PrCp)ZrMe[O=C(OMe)C(=CH_2)CH_2COOMe]$^+$ [MeB(C_6F_5)$_3$]$^-$ (**14a**).

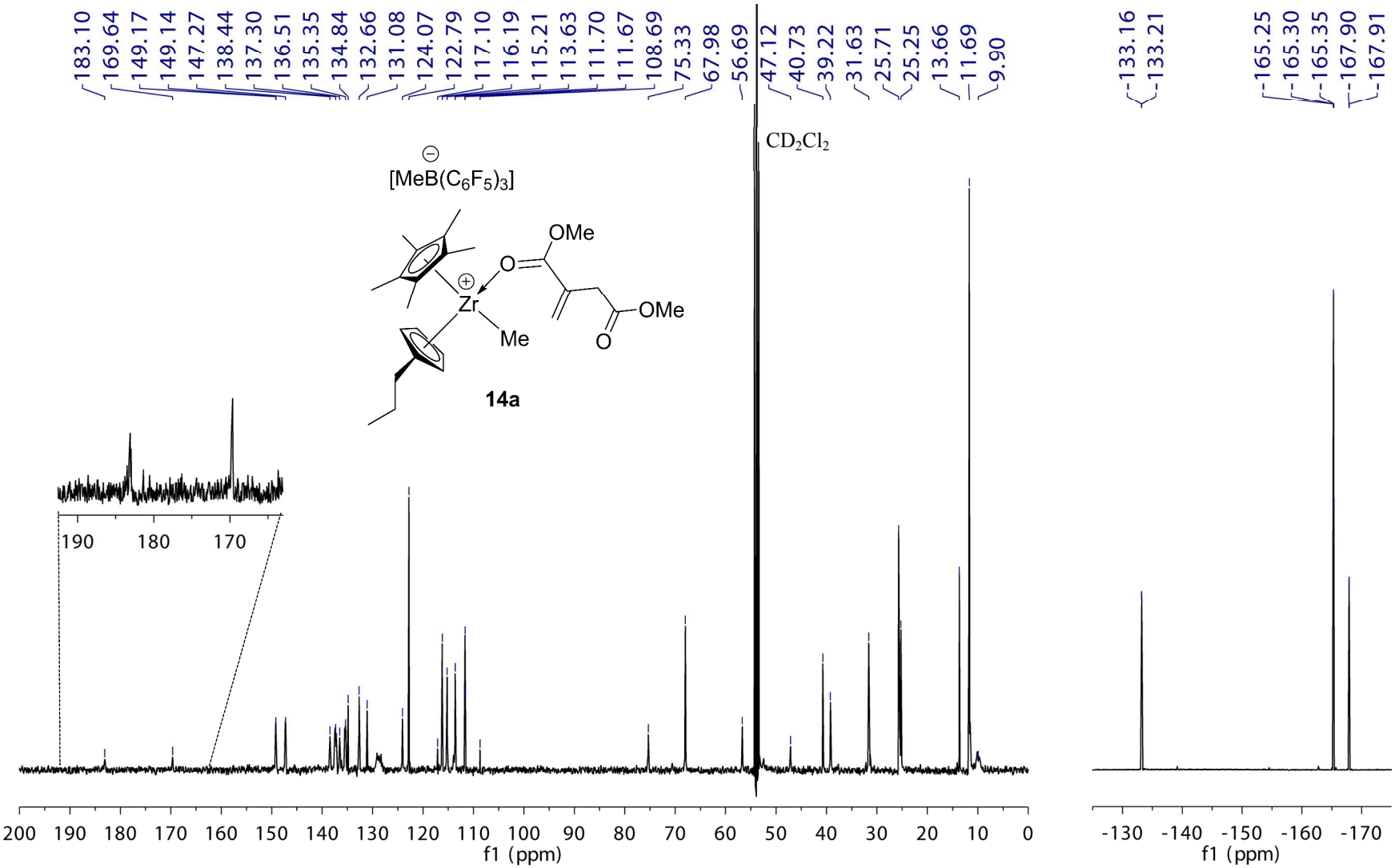

Figure S31. ^{13}C (left) and ^{19}F (right) NMR spectra (CD_2Cl_2, −18 °C, 500 MHz) of Cp*(^{n}PrCp)ZrMe[O=C(OMe)C(=CH_2)CH_2COOMe]$^+$ [MeB(C_6F_5)$_3$]$^-$ (**14a**).

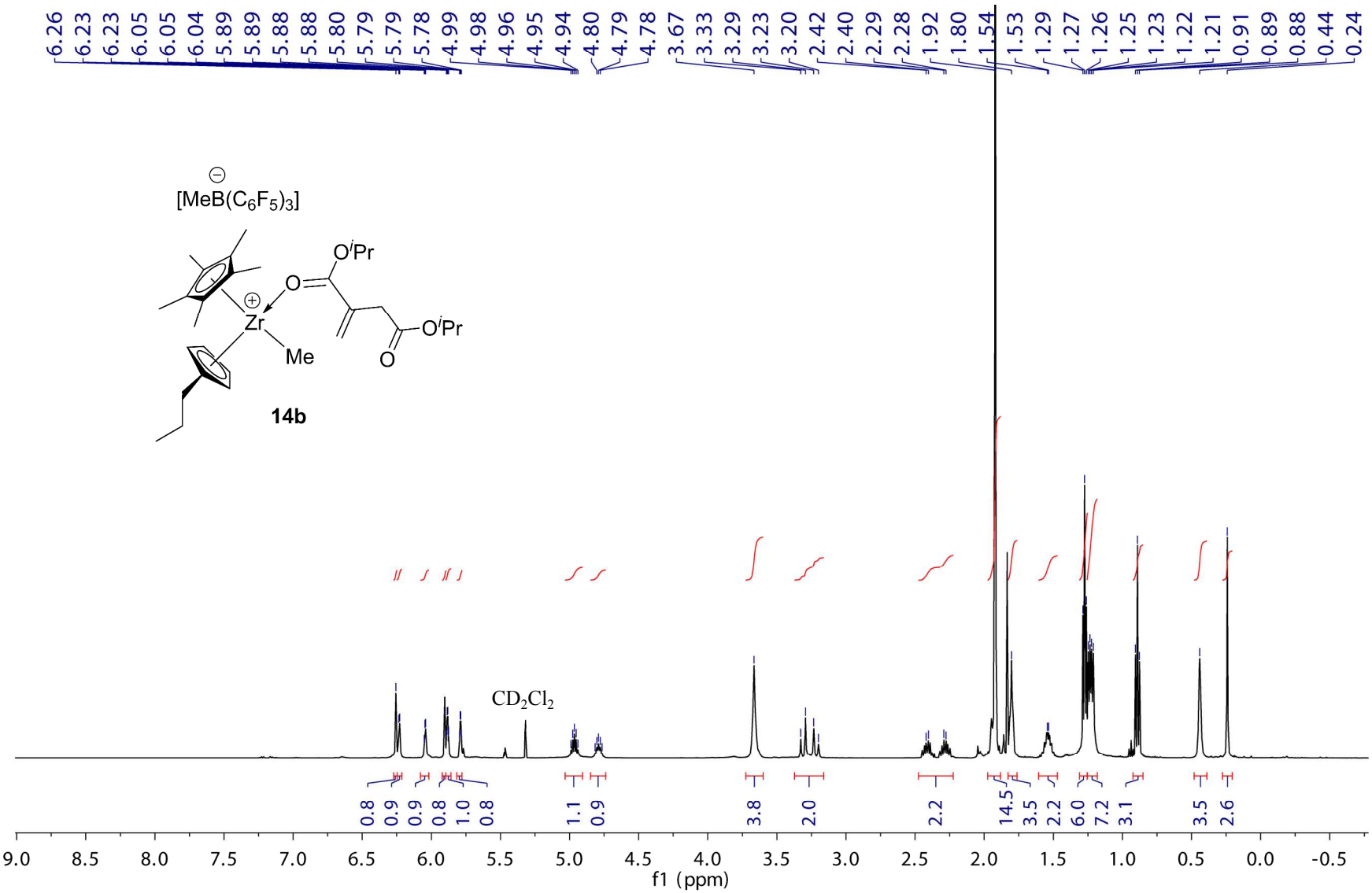

Figure S32. ^{1}H NMR spectrum (CD_2Cl_2, −18 °C, 500 MHz) of Cp*(^{n}PrCp)ZrMe[O=C(O^{i}Pr)C(=CH_2)CH_2COO^{i}Pr]$^+$ [MeB(C_6F_5)$_3$]$^-$ (**14b**).

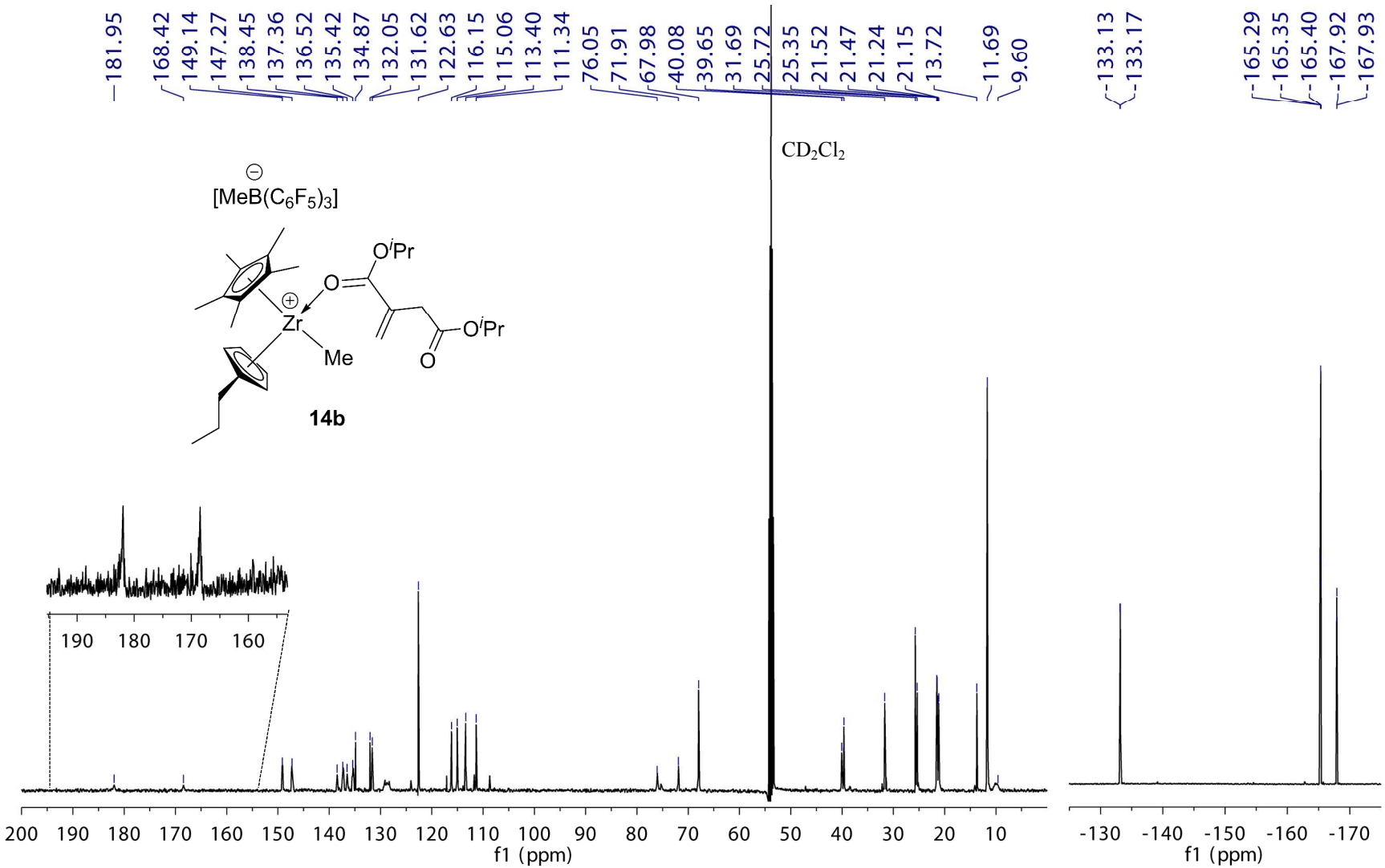

Figure S33. ^{13}C (left) and ^{19}F (right) NMR spectra (CD_2Cl_2, −18 °C, 500 MHz) of Cp*(^{n}PrCp)ZrMe[O=C(O^{i}Pr)C(=CH_2)CH_2COO^{i}Pr]$^{+}$ [MeB(C_6F_5)$_3$]$^{-}$ (**14b**).

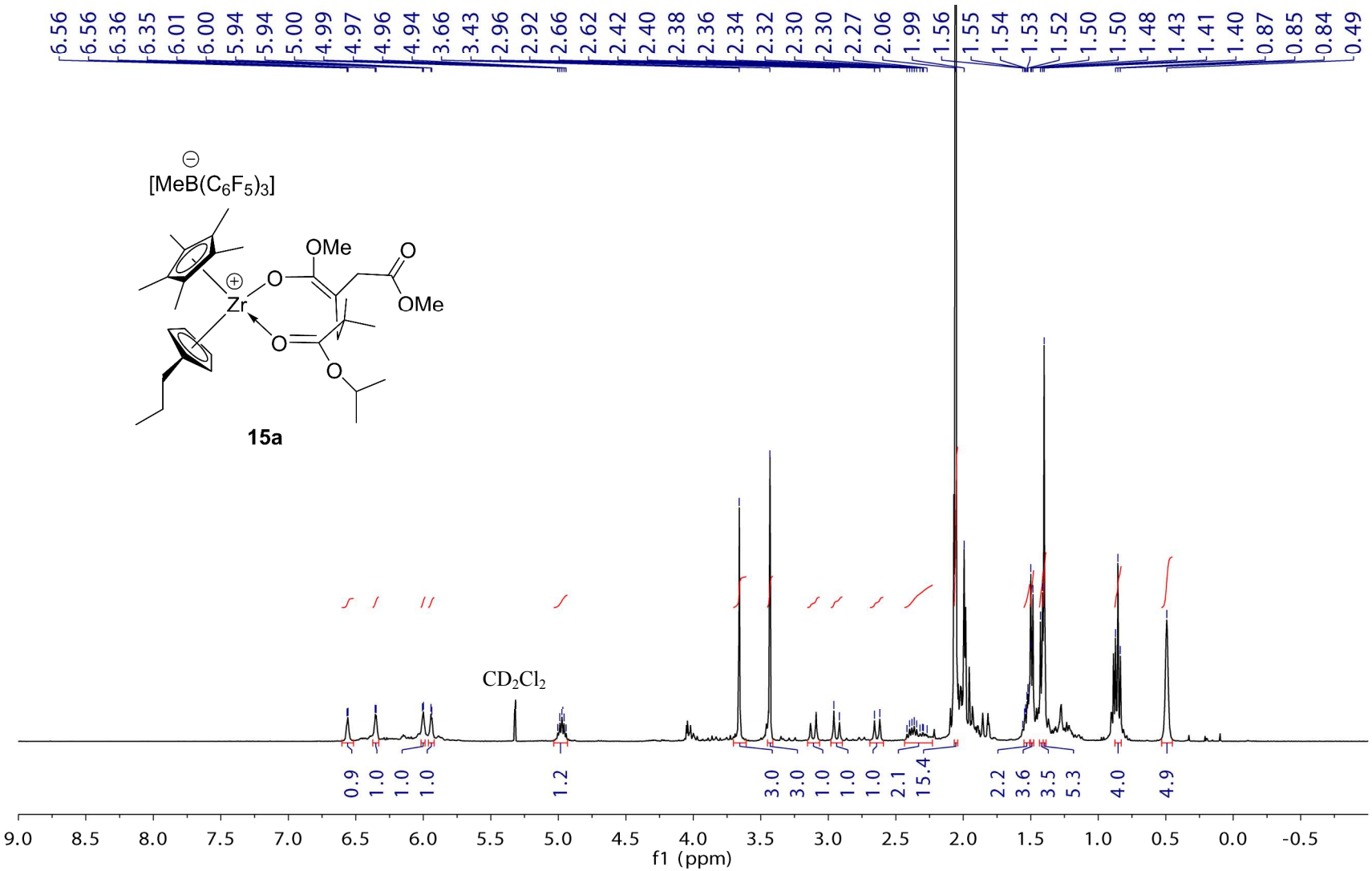

Figure S34. ^{1}H NMR spectrum (CD_2Cl_2, 25 °C, 400 MHz) of Cp*(^{n}PrCp)Zr[OC(OMe)=C(CH_2COOMe)CH_2C(Me_2)C(O^{i}Pr)=O]$^{+}$ [MeB(C_6F_5)$_3$]$^{-}$ (**15a**).

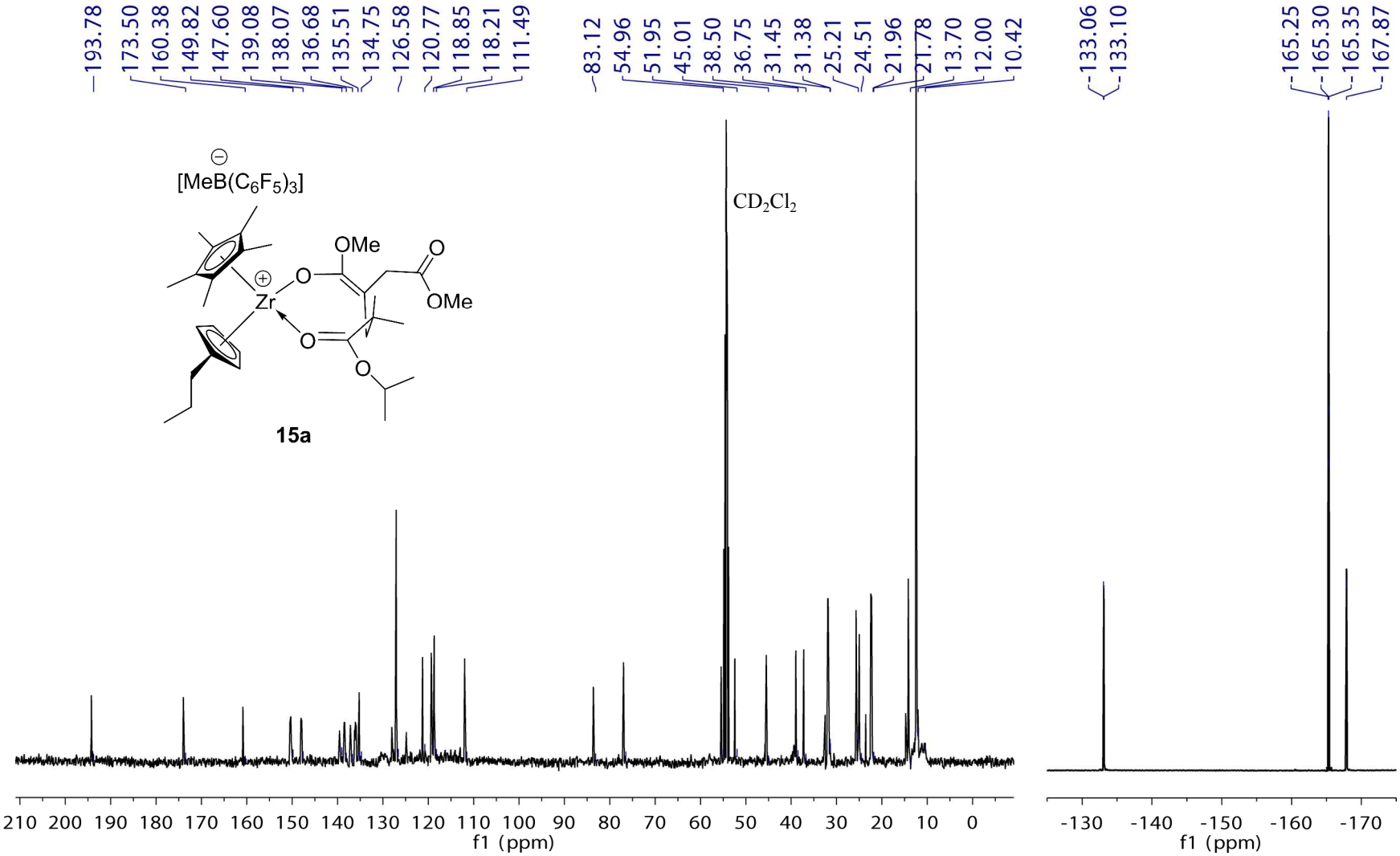

Figure S35. ^{13}C (left) and ^{19}F (right) NMR spectra (CD_2Cl_2, 25 °C, 400 MHz) of Cp*(^{n}PrCp)Zr[OC(OMe)=C(CH_2COOMe)CH_2C(Me_2)C(O^{i}Pr)=O]$^{+}$[MeB(C_6F_5)$_3$]$^{-}$ (**15a**).

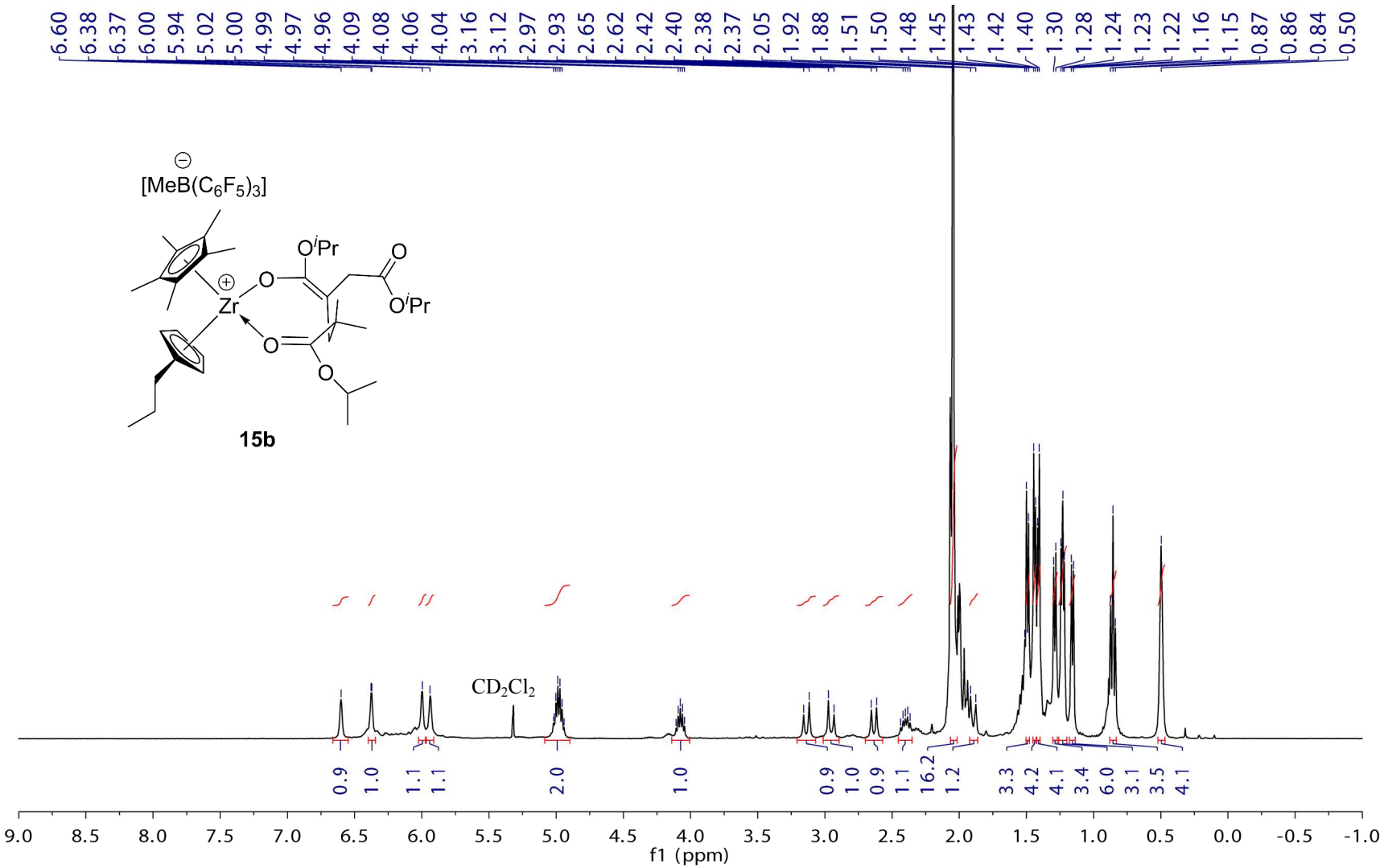

Figure S36. ^{1}H NMR spectrum (CD_2Cl_2, 25 °C, 400 MHz) of Cp*(^{n}PrCp)Zr[OC(O^{i}Pr)=C(CH_2COO^{i}Pr)CH_2C(Me_2)C(O^{i}Pr)=O]$^+$ [MeB(C_6F_5)$_3$]$^-$ (**15b**).

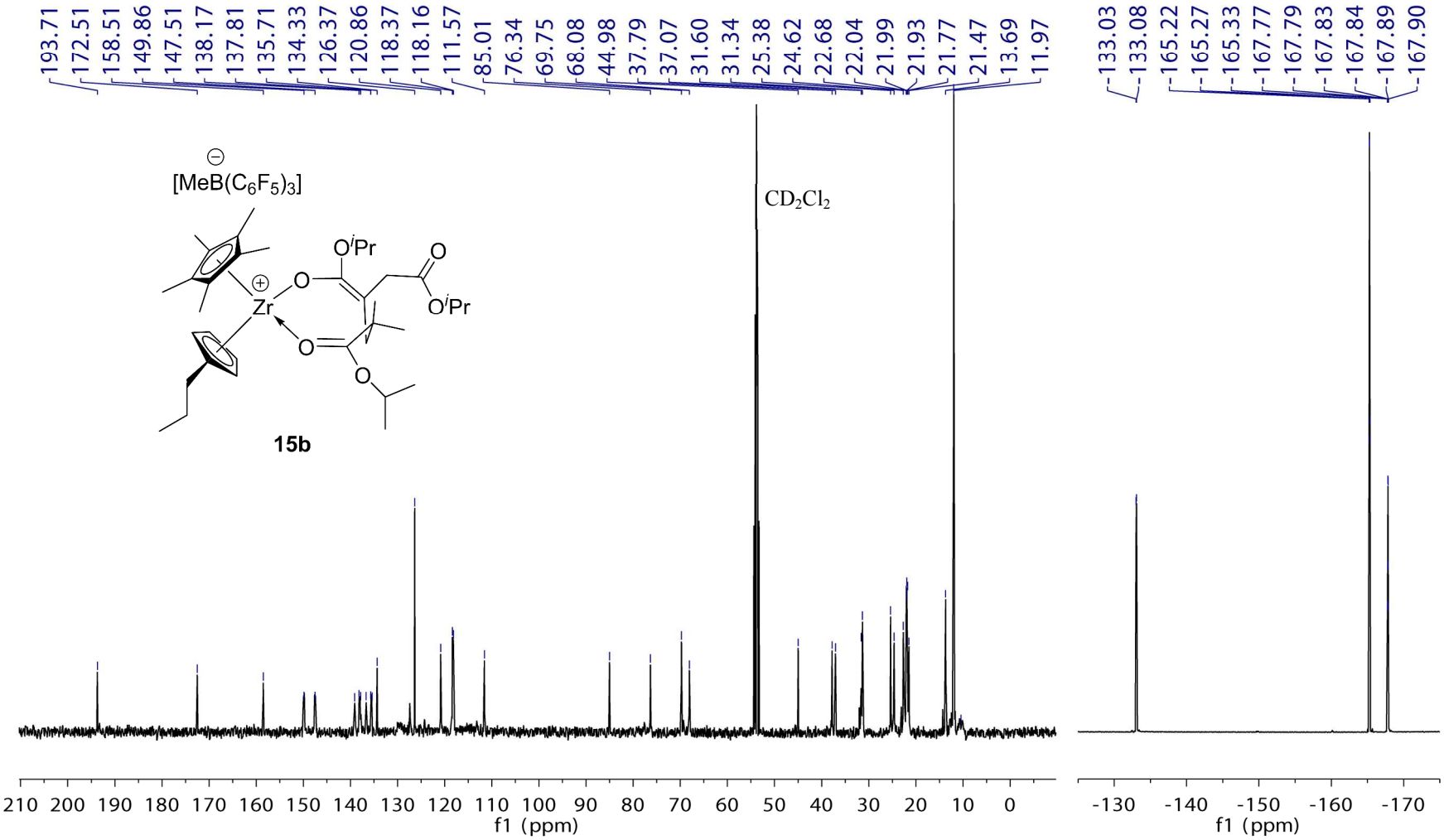

Figure S37. ^{13}C (left) and ^{19}F (right) NMR spectra (CD_2Cl_2, 25 °C, 400 MHz) of Cp*(^{n}PrCp)Zr[OC(O^{i}Pr)=C(CH_2COO^{i}Pr)CH_2C(Me_2)C(O^{i}Pr)=O]$^{+}$ [MeB(C_6F_5)$_3$]$^{-}$ (**15b**).

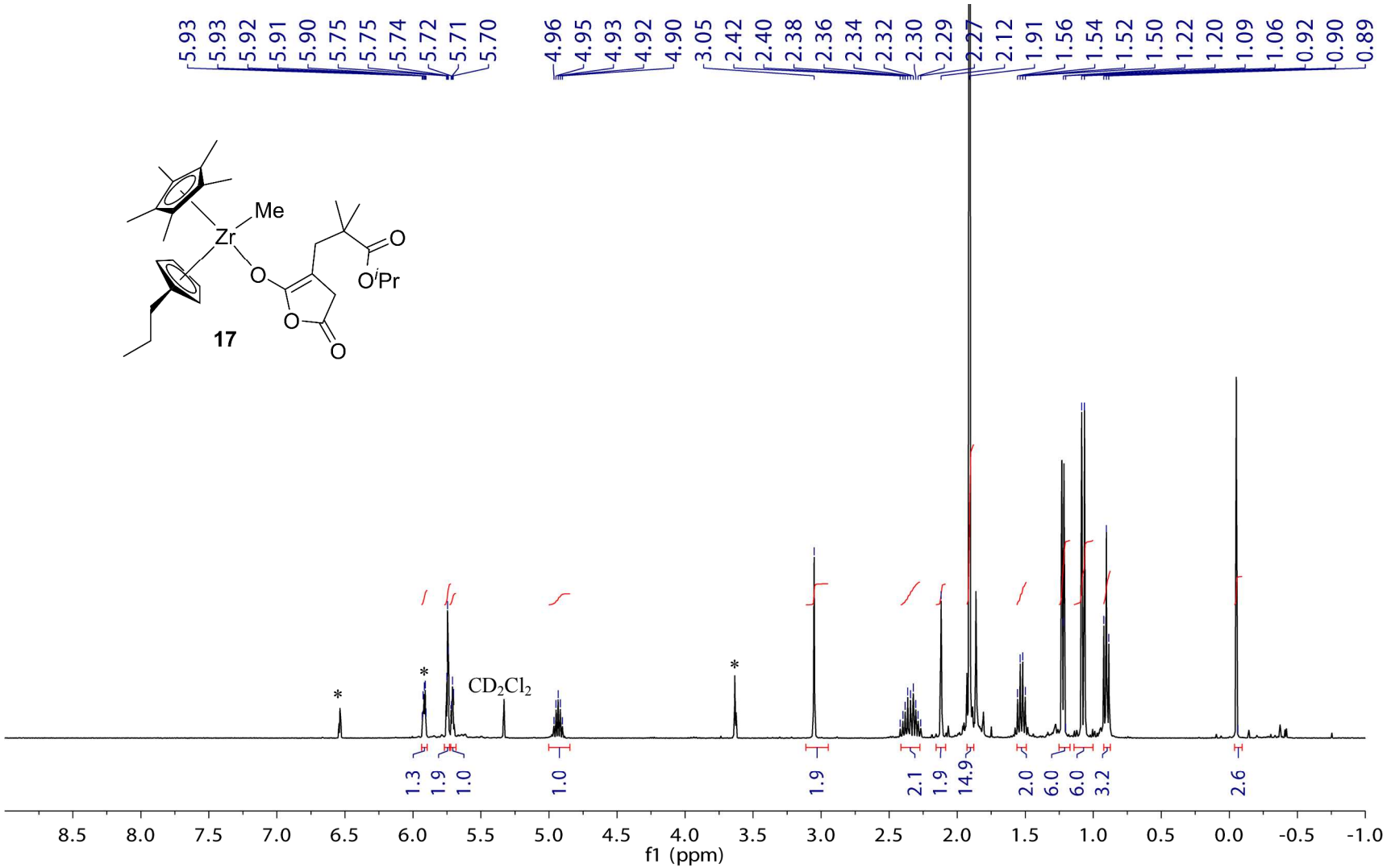

Figure S38. ^{1}H NMR spectrum (CD_2Cl_2, 25 °C, 400 MHz) of Cp*(^{n}PrCp)ZrMe{OC[OC(O)CH_2]=C($CH_2CMe_2COO^{i}Pr$)} (**17**). (* = excess itaconic anhydride for comparison).

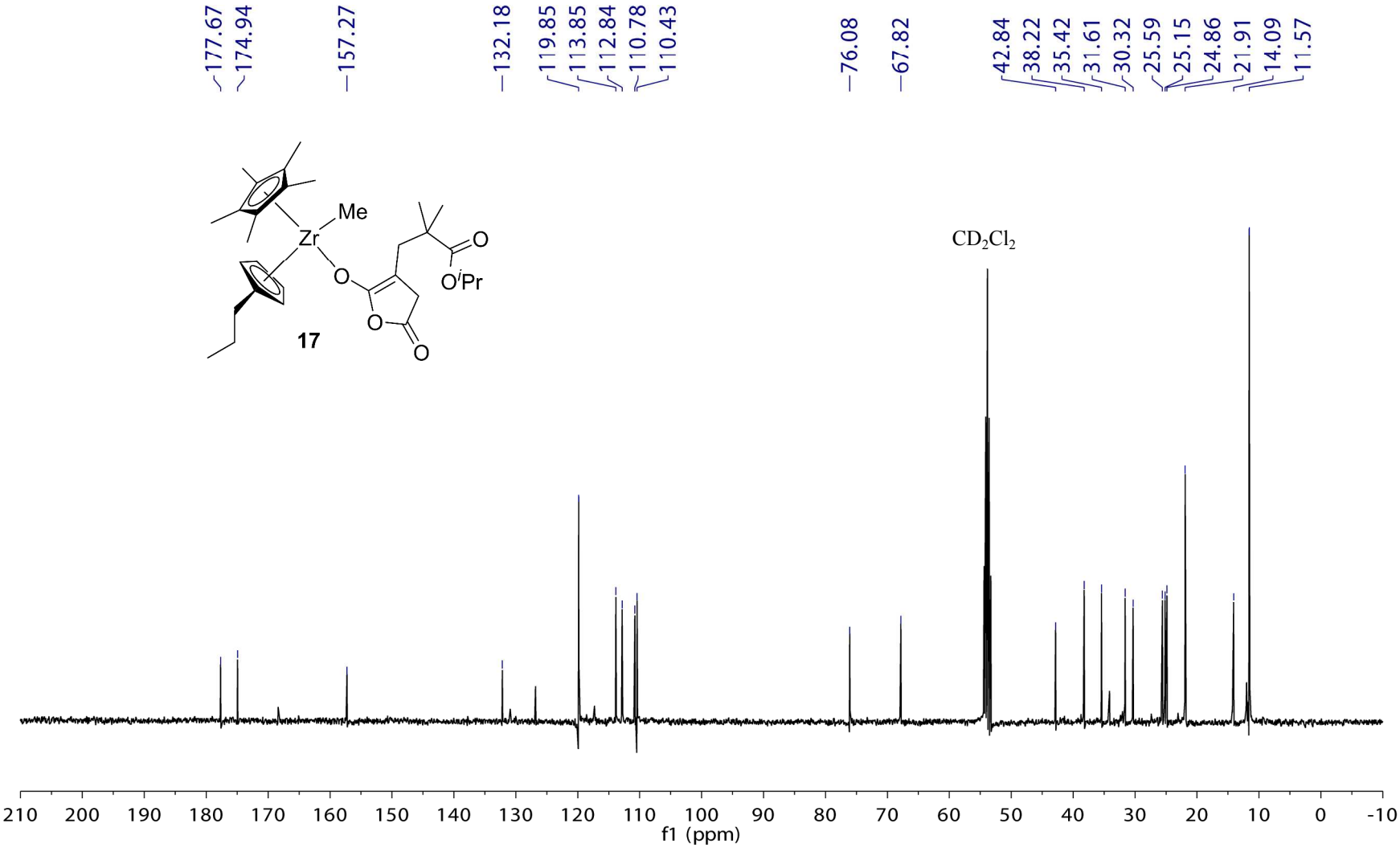

Figure S39. ^{13}C NMR spectrum (CD_2Cl_2, 25 °C, 400 MHz) of Cp*(^{n}PrCp)ZrMe{OC[OC(O)CH_2]=C($CH_2CMe_2COO^iPr$)} (**17**).

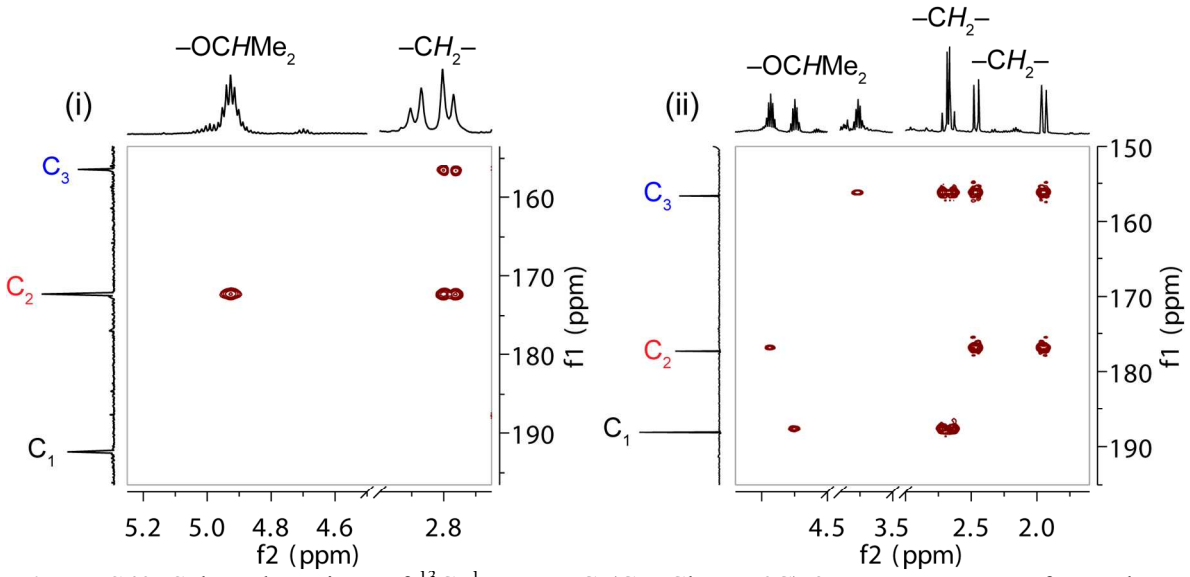

Figure S40. Selected portions of $^{13}C–^{1}H$ HMBC (CD_2Cl_2, −5 °C) 2D NMR spectra of complexes **2b** (i) and **4b** (ii) are shown for comparison.

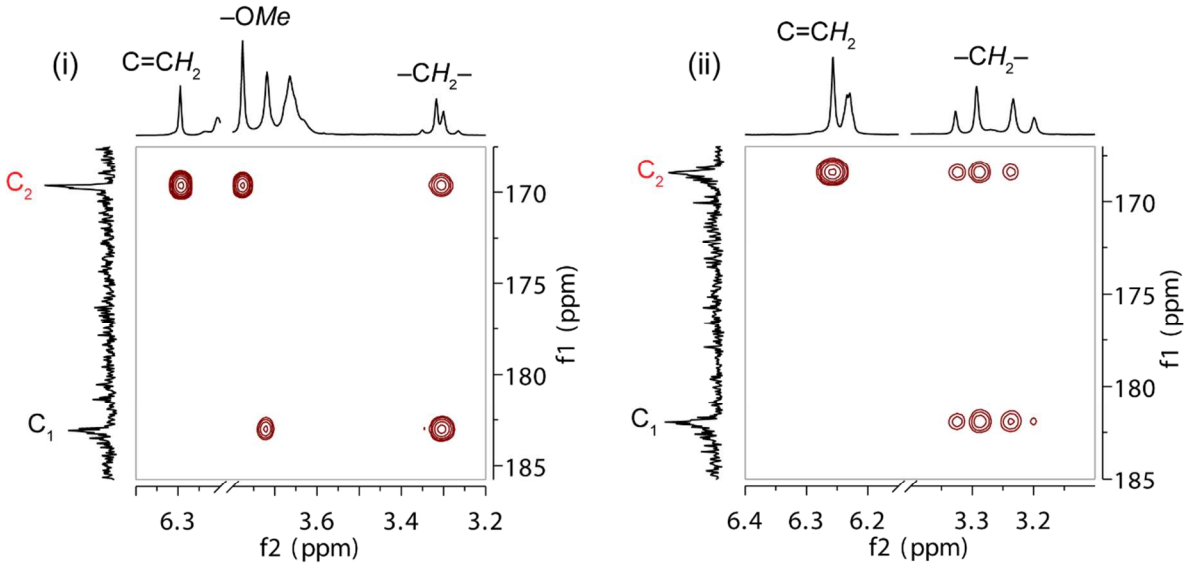

Figure S41. Selected portions of $^{13}C–^{1}H$ HMBC (CD_2Cl_2, −5 °C) 2D NMR spectra of complexes **14a** (i) and **14b** (ii) are shown for comparison.

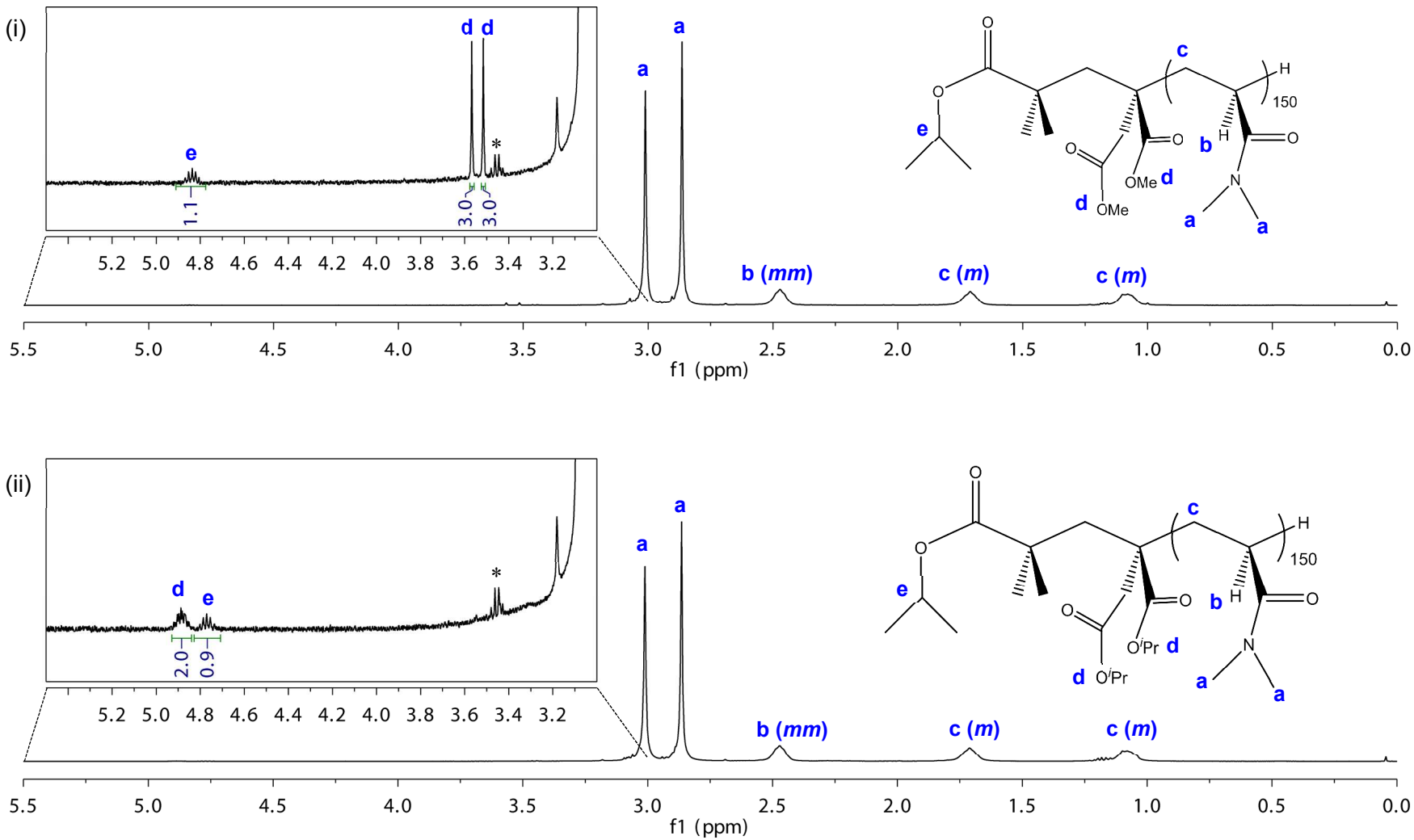

Figure S42. ^{1}H NMR spectra ($CDCl_3$, 25 °C) of highly *it*-PDMAA obtained by catalysts **2a** (i) and **2b** (ii), highlighting the characteristic signals of the polymer end-groups (* = residual Et_2O).

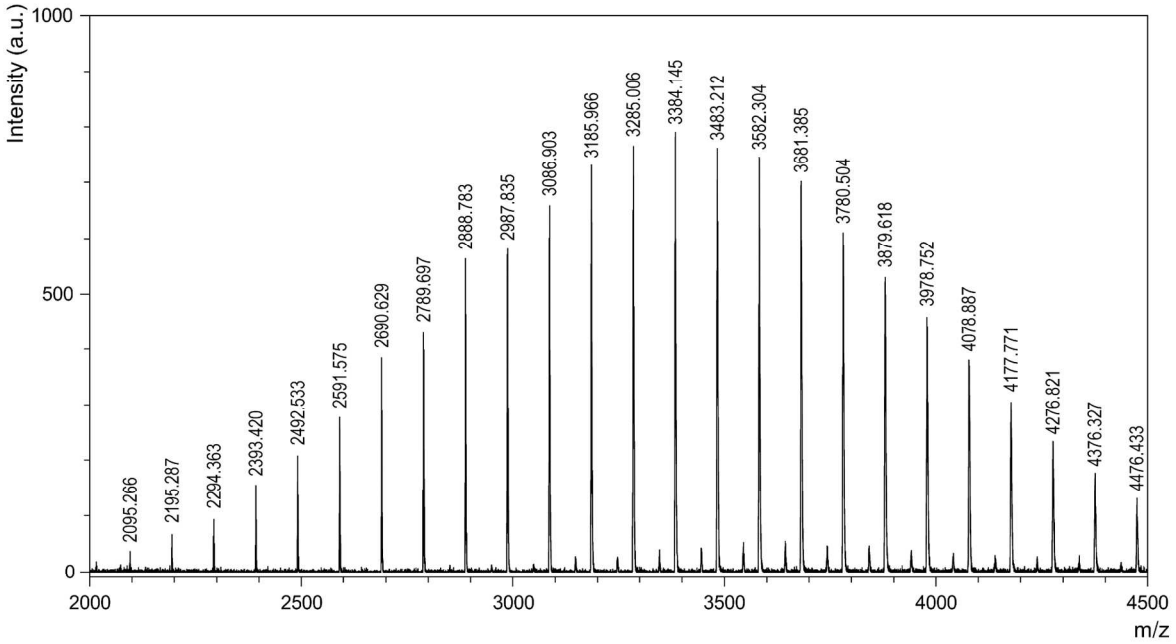

Figure S43. Portion of the MALDI-TOF mass spectrum of the low-molecular-weight PDMAA produced by **15a** at ambient temperature in CH_2Cl_2.

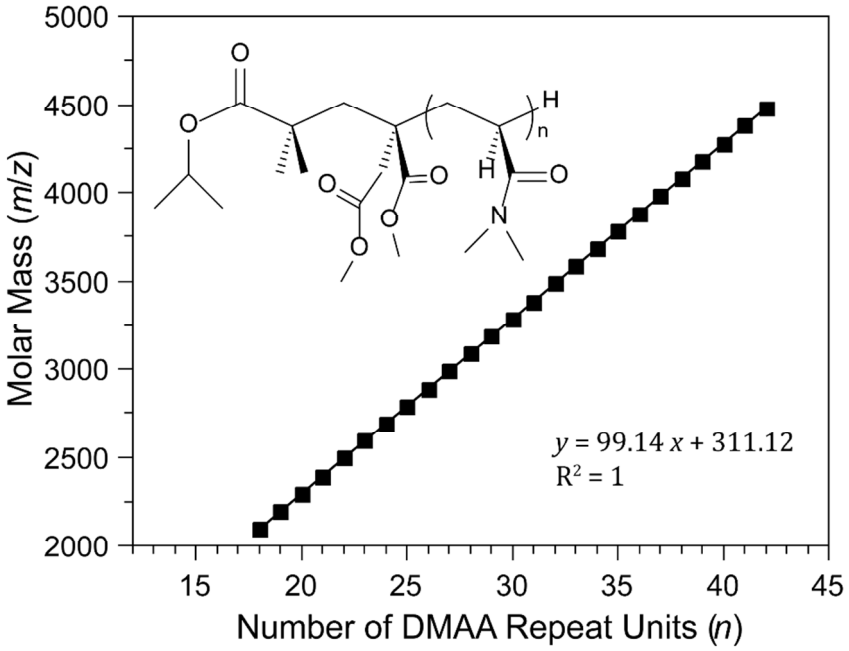

Figure S44. Plot of *m*/*z* values from the MALDI-TOF spectrum in Figure S43 vs the number of DMAA repeat units (*n*).

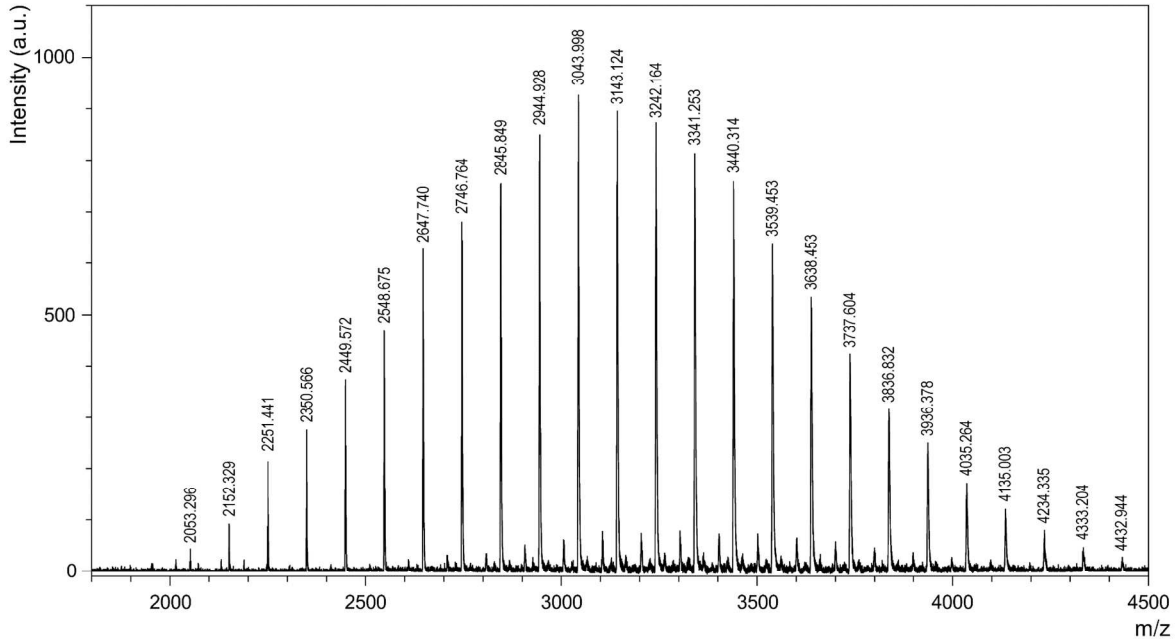

Figure S45. Portion of the MALDI-TOF mass spectrum of the low-molecular-weight PDMAA produced by **15b** at ambient temperature in CH_2Cl_2.

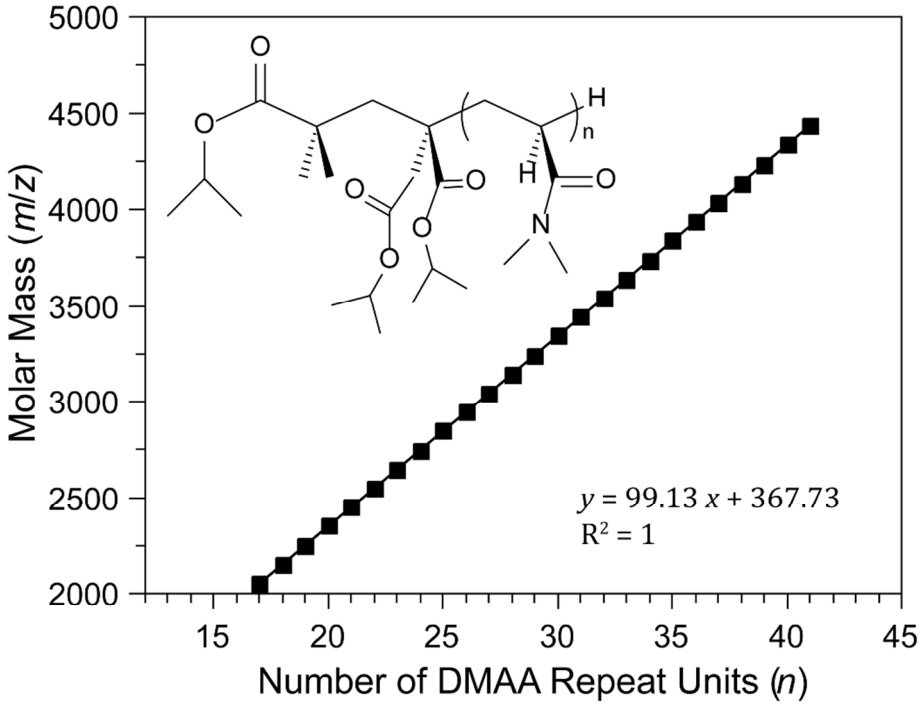

Figure S46. Plot of *m*/*z* values from the MALDI-TOF spectrum in Figure S45 vs the number of DMAA repeat units (*n*).

Part D: References

(1) Otsu, T.; Yamagishi, K.; Yoshioka, M. *Macromolecules* **1992**, *25*, 2713-2716.

(2) Allen, R. D.; Long, T. E.; McGrath, J. E. *Polym. Bull. (Berlin)* **1986**, *15*, 127-134.

(3) Bolig, A. D.; Chen, E. Y. X. *J. Am. Chem. Soc.* **2004**, *126*, 4897-4906.

(4) Mariott, W. R.; Rodriguez-Delgado, A.; Chen, E. Y. X. *Macromolecules* **2006**, *39*, 1318-1327.

(5) Rodriguez-Delgado, A.; Chen, E. Y. X. *Macromolecules* **2005**, *38*, 2587-2594.

(6) Ning, Y.; Caporaso, L.; Correa, A.; Gustafson, L. O.; Cavallo, L.; Chen, E. Y. X. *Macromolecules* **2008**, *41*, 6910-6919.

(7) Rodriguez-Delgado, A.; Chen, E. Y. X. *J. Am. Chem. Soc.* **2005**, *127*, 961-974.

(8) Jutzi, P.; Müller, C.; Stammler, A.; Stammler, H.-G. *Organometallics* **2000**, *19*, 1442-1444.

(9) Ning, Y.; Chen, E. Y. X. *J. Am. Chem. Soc.* **2008**, *130*, 2463-2465.

(10) Zhang, Y.; Ning, Y.; Caporaso, L.; Cavallo, L.; Chen, E. Y. X. *J. Am. Chem. Soc.* **2010**, *132*, 2695-2709.

(11) Sheldrick, G. M. *SADABS*

(12) Sheldrick, G, M. *SHELXTL*, v. 6.12; Bruker AXS: Madison, WI, 1999.