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Intramolecular C–H bond activation induced by a scandium terminal imido complex

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Experiment Section

General Methods. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques or an MBraun glovebox. All solvents were purified from an MBraun SPS system. Samples of scandium complexes for NMR spectroscopic measurements were prepared in the glovebox by use of NMR tubes sealed by paraffin film. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AV600 (FT, 600 MHz for ^{1}H; 150 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by ^{1}H–^{1}H COSY and ^{1}H–^{13}C HMQC experiments when necessary. Elemental analysis was performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry (CIAC). 2,6-diisopropylaniline was dried over CaH_2 under stirring for 24 h and distilled under reduced pressure before use. 4-dimethylaminopyridine (DMAP) was purchased from Aldrich and sublimed before use.

X-ray Crystallographic Studies. Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed at –88.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package.[1] The raw frame data were processed using SAINT and SADABS to yield the reflection data file.[2] The structures were solved by using the SHELXTL program.[3] Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters.

Synthesis of the Complex (η^5:κ-C_5H_4–PPh_2=N–$C_6H_3{}^{i}Pr_2$)Sc(CH_2SiMe_3)(HN$C_6H_3{}^{i}Pr_2$) (2). Under a nitrogen atmosphere, to a mixture solution of hexane and toluene (10 mL) of **1** (0.321 g, 0.5 mmol), 1 equiv. of 2,6-diisopropylaniline (0.089 g, 0.5 mmol) was added slowly at room temperature. The mixture was stirred for 4 h to afford a yellow solution. Evaporation of the solvent left **2** as pale yellow crystalline solids (0.213 g, 58%). Recrystallization from hexane and toluene at –30 °C gave single crystals suitable for X-ray analysis. ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 0.11 (s, 2H, CH_2SiMe$_3$), 0.31 (s, 9H, CH$_2$SiMe_3), 0.55 (br s, 3H, Ar-CH(CH_3)$_2$), 0.90 (br s, 3H, Ar-CH(CH_3)$_2$), 1.10 (d, $^{3}J_{H–H}$ = 6.0 Hz, 6H, Ar-CH(CH_3)$_2$), 1.41 (d, $^{3}J_{H–H}$ = 6.0 Hz, 12H, Ar-CH(CH_3)$_2$), 1.46 (br s, 3H, Ar-CH(CH_3)$_2$), 2.89 (m, 1H, Ar-CH(CH$_3$)$_2$), 3.02–3.09 (sept, 2H, Ar-CH(CH$_3$)$_2$), 3.94 (m, 1H, Ar-CH(CH$_3$)$_2$), 5.51 (s, 1H,

Ar-N*H*), 6.78–7.07 (m, 16H, C_5H_4 and Ph-*H* and Ar-*H*), 7.31–7.34 (m, 2H, Ph-*H*), 7.71–7.74 ppm (m, 2H, Ph-*H*). ^{13}C NMR (150 MHz, C_6D_6, 128.06 ppm, 25 °C): δ 3.97 (s, 3C, CH_2SiMe_3), 22.89 (br s, 1C, Ar-CH(CH_3)$_2$), 23.30 (br s, 2C, Ar-CH(CH_3)$_2$), 24.68 (br s, 2C, Ar-CH(CH_3)$_2$), 25.46 (br s, 1C, Ar-CH(CH_3)$_2$), 25.58 (br s, 1C, Ar-CH(CH_3)$_2$), 28.24 (br s, 1C, Ar-CH(CH_3)$_2$), 29.91 (s, 1C, Ar-*C*H(CH$_3$)$_2$), 30.07 (s, 2C, Ar-*C*H(CH$_3$)$_2$), 30.84 (s, 1C, Ar-*C*H(CH$_3$)$_2$), 36.44 (br s, 1C, CH_2SiMe_3), 94.34 (d, J_{P-C} = 144.0 Hz, 1C, *ipso*-C_5H_4), 113.33 (d, $^3J_{P-C}$ = 9.0 Hz, 1C, C_5H_4), 116.54 (d, $^3J_{P-C}$ = 13.5 Hz, 1C, C_5H_4), 117.39 (s, 2C, Ar-*C*), 120.85 (d, $^3J_{P-C}$ = 15.0 Hz, 1C, C_5H_4), 121.05 (d, $^3J_{P-C}$ = 13.5 Hz, 1C, C_5H_4), 123.04 (s, 4C, Ar-*C*), 128.56 (s, 4C, Ph-*C*), 129.14 (d, $^2J_{P-C}$ = 10.5 Hz, 2C, Ph-*C*), 132.80 (s, 4C, Ph-*C*), 134.20 (d, $^2J_{P-C}$ = 10.5 Hz, 2C, Ar-*C*), 134.31 (s, 2C, Ph-*C*), 140.45 (d, $^2J_{P-C}$ = 9.0 Hz, 1C, *ipso*-Ar-*C*), 145.40 (s, 1C, Ar-*C*), 145.72 (s, 1C, Ar-*C*), 150.36 ppm (s, 1C, NHAr-*C*). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 10.78 ppm (s). Anal. Calcd for $C_{45}H_{60}N_2PScSi$ (%): C, 73.74; H, 8.25; N, 3.82. Found: C, 74.03; H, 8.15; N, 3.68.

Synthesis of the Complex (η^5-C_5H_4–PPh_2=N–$C_6H_3{}^iPr_2$)Sc=N$C_6H_3{}^iPr_2$(DMAP)$_2$ (3). Under a nitrogen atmosphere, to a solution of toluene (10 mL) of **2** (0.367 g, 0.5 mmol), 2 equiv. of 4-dimethylaminopyridine (DMAP) (0.122 g, 1.0 mmol) was added at room temperature. The yellow solution immediately became red. The mixture was stirred for 30 min, and then evaporation of the solvent left **3** as red crystalline solids (0.276 g, 62%), which must be stored at low temperature. Recrystallization from toluene at –30 °C gave red crystals. ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 1.12 (d, $^3J_{H-H}$ = 6.6 Hz, 12H, Ar-CH(C*H*$_3$)$_2$), 1.39 (d, $^3J_{H-H}$ = 7.2 Hz, 12H, Ar-CH(C*H*$_3$)$_2$), 2.01 (s, 12H, NMe_2), 3.91–3.95 (sept, 2H, Ar-C*H*(CH$_3$)$_2$), 4.25–4.30 (sept, 2H, Ar-C*H*(CH$_3$)$_2$), 5.84 (d, $^3J_{H-H}$ = 5.4 Hz, 4H, DMAP), 6.68 (br s, 2H, C_5H_4), 6.89–6.92 (m, 4H, Ph-*H* and C_5H_4), 7.01–7.07 (m, 4H, Ph-*H*), 7.25 (d, $^3J_{HH}$ = 7.2 Hz, 2H, Ar-*H*), 7.31–7.33 (m, 2H, Ar-*H*), 7.36 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, Ar-*H*), 7.78–7.81 (m, 4H, Ph-*H*), 8.70 ppm (s, 4H, DMAP). ^{1}H NMR (400 MHz, THF-d_8, 1.72 and 3.58 ppm, 25 °C): δ 0.69 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, Ar-CH(C*H*$_3$)$_2$), 0.85 (d, $^3J_{H-H}$ = 6.8 Hz, 12H, Ar-CH(C*H*$_3$)$_2$), 2.96 (s, 12H, NMe_2), 3.38–3.46 (sept, 2H, Ar-C*H*(CH$_3$)$_2$), 3.76–3.85 (sept, 2H, Ar-C*H*(CH$_3$)$_2$), 6.40 (s, 2H, C_5H_4), 6.47 (d, $^3J_{H-H}$ = 5.6 Hz, 4H, DMAP), 6.58 (d, $^3J_{H-H}$ = 7.8 Hz, 2H, C_5H_4), 6.79–6.83 (m, 4H, Ar-*H*), 6.92–6.96 (m, 4H, Ar-*H*), 7.13–7.20 (m, 4H, Ar-*H*), 7.44–7.48 (m, 4H, Ar-*H*), 8.44 ppm (s, 4H, DMAP). ^{13}C NMR (100 MHz, THF-d_8, 25.31 and 67.21 ppm, 25 °C): δ 23.96 (s, Ar-CH(*C*H$_3$)$_2$), 24.34 (s, Ar-CH(*C*H$_3$)$_2$), 27.63 (s, Ar-*C*H(CH$_3$)$_2$), 28.52 (s, Ar-*C*H(CH$_3$)$_2$), 38.75 (s, N(CH$_3$)$_2$), 106.72 (s, DMAP), 110.06 (s, C_5H_4), 112.91 (d, $^2J_{P-C}$ = 13.6 Hz, C_5H_4), 118.85 (s, C_5H_4), 119.20 (d, $^2J_{P-C}$ = 13.6 Hz, Ar-*C*), 121.22 (s, Ar-*C*), 122.70 (s, Ar-*C*), 128.26 (d, $^2J_{P-C}$ = 10.9 Hz, Ar-*C*), 130.54 (s, Ar-*C*), 132.89 (d, $^3J_{P-C}$ = 8.90 Hz, Ar-*C*), 135.63 (s, Ar-*C*), 135.79 (s, Ar-*C*), 136.52 (s, Ar-*C*), 139.62 (s, Ar-*C*), 143.44 (d, J_{P-C} = 6.3 Hz, Ar-*C*), 151.23 (s, DMAP), 155.40 (s, *ipso*-DMAP), 156.31 ppm (s, =NAr-*C*). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ –7.25 ppm (s). Anal. Calcd for $C_{55}H_{68}N_6PSc$ (%): C, 74.30; H, 7.71; N, 9.45. Found: C, 74.03; H, 7.56; N, 9.64.

Synthesis of the Complex [η^5-C_5H_4–P(η^1-C_6H_4)Ph=N–$C_6H_3{}^iPr_2$]ScNHC$_6$H$_3{}^i$Pr$_2$(DMAP)$_2$ (4). Under a nitrogen atmosphere, a red toluene solution of **3** (0.178 g, 0.2 mmol) was stirred at room temperature for 24 h. The red solution slowly became colorless. Recrystallization from toluene and hexane at room temperature gave colorless crystalline solids (0.096 g, 54%), which are suitable for X-ray analysis. ^{1}H NMR (600 MHz, C_6D_6, 7.16 ppm, 25 °C): δ 1.27 (d, $^3J_{H-H}$ = 6.0 Hz, 6H, Ar-CH(CH_3)$_2$), 1.29 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, Ar-CH(CH_3)$_2$), 1.33 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, Ar-CH(CH_3)$_2$), 1.38 (d, $^3J_{H-H}$ = 6.0 Hz, 6H, Ar-CH(CH_3)$_2$), 1.97 (s, 12H, NMe$_2$), 3.29–3.33 (sept, 2H, Ar-CH(CH$_3$)$_2$), 4.16–4.20 (sept, 2H, Ar-CH(CH$_3$)$_2$), 5.65 (s, 4H, DMAP), 5.88 (s, 1H, Ar-NH), 6.02 (s, 1H, ScC$_6H_4$P), 6.41 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, C$_5H_4$), 6.84 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, ScC$_6H_4$P), 7.01 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, C$_5H_4$), 7.12 (d, $^3J_{H-H}$ = 7.2 Hz, 3H, Ar-H), 7.18 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, Ar-H), 7.33 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, Ar-H), 7.36 (d, $^3J_{H-H}$ = 3.0 Hz, 2H, Ar-H), 7.94–7.97 (m, 2H, Ar-H), 8.05 (d, $^3J_{H-H}$ = 5.4 Hz, 1H, ScC$_6H_4$P), 8.19 (d, $^3J_{H-H}$ = 4.8 Hz, 4H, DMAP), 8.46 ppm (t, $^3J_{H-H}$ = 7.2 Hz, 1H, ScC$_6H_4$P). ^{1}H NMR (600 MHz, THF-d_8, 1.72 and 3.58 ppm, 25 °C): δ 0.86 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, Ar-CH(CH_3)$_2$), 0.89 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, Ar-CH(CH_3)$_2$), 1.01 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, Ar-CH(CH_3)$_2$), 1.12 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, Ar-CH(CH_3)$_2$), 2.91 (s, 12H, NMe$_2$), 3.01–3.05 (sept, 2H, Ar-CH(CH$_3$)$_2$), 3.55–3.61 (sept, 2H, Ar-CH(CH$_3$)$_2$), 5.44 (s, 1H, Ar-NH), 5.60 (s, 1H, C$_5H_4$), 6.21 (s, 1H, C$_5H_4$), 6.26 (s, 1H, C$_5H_4$), 6.29 (t, $^3J_{H-H}$ = 15.0 Hz, 1H, ScC$_6H_4$P), 6.33 (d, $^3J_{H-H}$ = 6.0 Hz, 4H, DMAP), 6.44 (s, 1H, C$_5H_4$), 6.55–6.59 (m, 1H, ScC$_6H_4$P), 6.75 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, Ar-H), 6.80 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, Ar-H), 7.08 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, Ar-H), 7.12 (d, $^3J_{H-H}$ = 7.2 Hz, 1H, Ar-H), 7.24 (t, $^3J_{H-H}$ = 6.6 Hz, 2H, Ar-H), 7.31 (t, $^3J_{H-H}$ = 7.2 Hz, 1H, Ar-H), 7.58–7.61 (m, 2H, Ar-H), 7.67 (d, $^3J_{H-H}$ = 6.6 Hz, 1H, ScC$_6H_4$P), 7.82 (t, $^3J_{H-H}$ = 6.0 Hz, 1H, ScC$_6H_4$P), 7.94 ppm (d, $^3J_{H-H}$ = 6.0 Hz, 4H, DMAP). ^{13}C NMR (150 MHz, THF-d_8, 25.31 and 67.21 ppm, 25 °C): δ 23.87 (s, Ar-CH(CH_3)$_2$), 23.95 (s, Ar-CH(CH_3)$_2$), 24.18 (s, Ar-CH(CH_3)$_2$), 24.33 (s, Ar-CH(CH_3)$_2$), 28.83 (s, Ar-CH(CH$_3$)$_2$), 31.00 (s, Ar-CH(CH$_3$)$_2$), 38.69 (s, N(CH$_3$)$_2$), 106.60 (s, DMAP), 111.04 (d, $^2J_{P-C}$ = 12.0 Hz, C_5H_4), 113.24 (d, $^2J_{P-C}$ = 12.0 Hz, C_5H_4), 114.50 (s, C_5H_4), 118.27 (s, Ar-C), 119.91 (d, $^2J_{P-C}$ = 10.5 Hz, Ar-C), 120.31 (d, $^3J_{P-C}$ = 9.0 Hz, Ar-C), 122.41 (s, Ar-C), 123.23 (s, Ar-C), 127.96 (d, $^2J_{P-C}$ = 10.5 Hz, Ar-C), 128.27 (d, $^2J_{P-C}$ = 10.5 Hz, Ar-C), 130.30 (s, Ar-C), 132.88 (d, $^3J_{P-C}$ = 9.0 Hz, Ar-C), 133.01 (s, Ar-C), 133.15 (d, J_{P-C} = 9.0 Hz, Ar-C), 135.79 (s, Ar-C), 135.97 (s, Ar-C), 143.07 (d, J_{P-C} = 6.0 Hz, Ar-C), 151.93 (s, 1C, NHAr-C), 151.51 (s, DMAP), 155.29 (s, *ipso*-DMAP), 192.12 ppm (d, $^2J_{P-C}$ = 43.5 Hz, ScC_6H_4P). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ –5.59 ppm (s). Anal. Calcd for $C_{55}H_{68}N_6PSc$ (%): C, 74.30; H, 7.71; N, 9.45. Found: C, 74.11; H, 7.64; N, 9.53.

Crystal data of **2:** $C_{45}H_{60}N_2PScSi$; M_r = 732.97; triclinic; space group P–1; a = 12.1570(15), b = 12.3456(15), c = 15.2613(19) Å; α = 84.741(2)°, β = 77.710(2)°, γ = 72.545(2)°; V = 2134.0(5) Å^3; Z = 2;

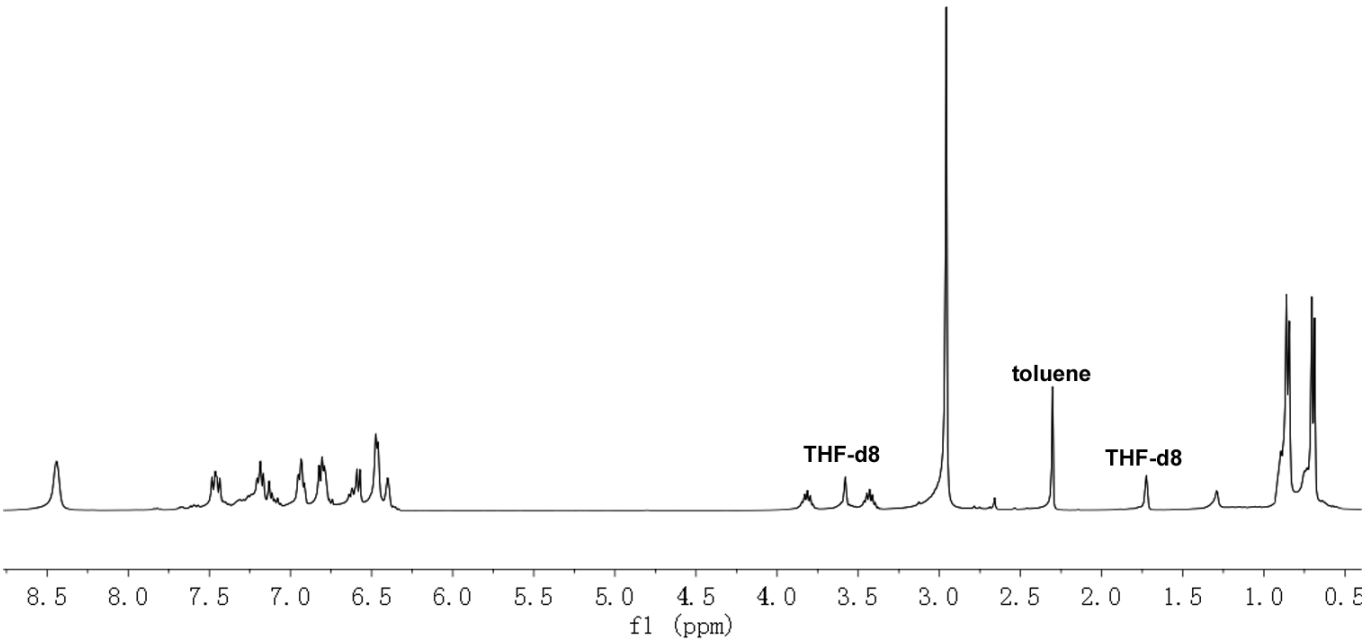
ρ_{calcd} = 1.141 g cm^{-3}; μ(Mo$_{Ka}$) = 2.69 cm^{-1}; F(000) = 788; 11811 reflections collected, 8235 unique with $I_o > 2\sigma(I_o)$; GOF = 1.090; Final $R1$ = 0.0623, $wR2$ = 0.1919 (all data).

Crystal data of **4:** $C_{55}H_{68}N_6PSc$; M_r = 889.08; triclinic; space group P–1; a = 9.9885(5), b = 17.1263(9), c = 17.6568(9) Å; α = 79.8850(10)°, β = 82.1400(10)°, γ = 79.1570(10)°; V = 2903.6(3) Å^3; Z = 2; ρ_{calcd} = 1.01 g cm^{-3}; μ(Mo$_{Ka}$) = 1.90 cm^{-1}; F(000) = 952; 16249 reflections collected, 11355 unique with $I_o > 2\sigma(I_o)$; GOF = 1.035; Final $R1$ = 0.0560, $wR2$ = 0.1598 (all data).

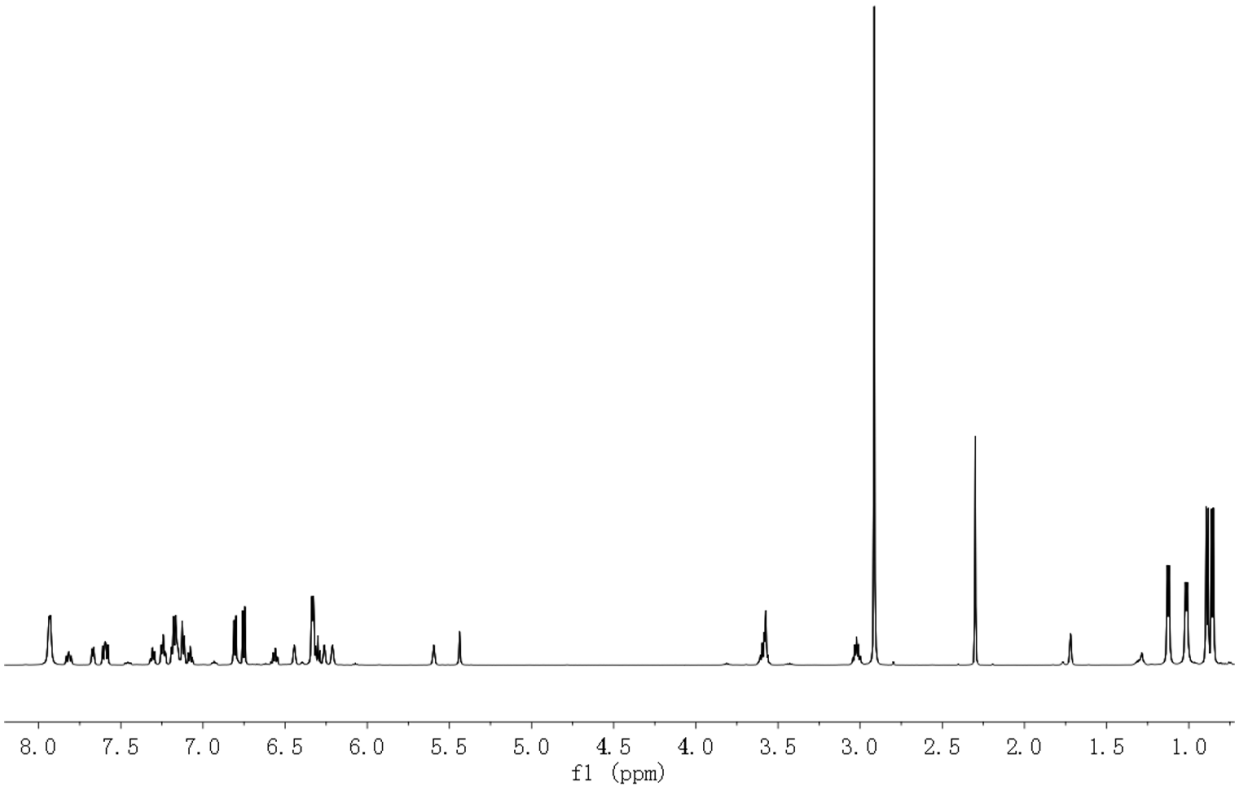
1 Bruker, *SMART Version 5.054*.

2 *SAINT* and *SADABS*, *Version 6.22*; Bruker AXS Inc., Madison, WI (USA), 2000.

3 G. M. Sheldrick, *SHELXTL NT*, *Version 6.12*; Bruker AXS Inc., Madison, WI (USA), 2000.



SFigure 2 ^{1}H NMR spectrum of **3** (THF-d_8, 25 °C).



SFigure 3 ^{1}H NMR spectrum of **4** (THF-d_8, 25 ^{o}C).