

SUPPORTING INFORMATION FOR

A *N*-Aryloxy- β -diketiminate ligand and its 4*d*, 4*f*
and 5*f*-metals complexes

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Experimental details

General considerations

Unless otherwise noted, all reactions and manipulations were performed at 20 °C in a recirculating mBraun LabMaster DP inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware was dried overnight at 120 °C before use. All NMR spectra were obtained using a Bruker DPX 200 MHz spectrometer. Chemical shifts for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to solvent impurities. Elemental analyses were performed at Analytische Laboratorien at Lindlar (Germany) and Medac Ltd at Chobham (United Kingdom). Unless otherwise noted, reagents were purchased from commercial suppliers and dried over 4 Å molecular sieves prior to use. Celite (Aldrich) and 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. Tetrahydrofuran (THF), tetrahydrofuran- d_8 (THF- d_8), pentane, diethyl ether and benzene- d_6 were dried over a sodium(0)/benzophenone mixture and distilled before use. Triethylamine, dichloromethane

and dichloromethane- d_2 were dried over CaH_2 and distilled before use. $\text{ThCl}_4(1,4\text{-dimethoxyethane})_2$ ¹ and **3**² were prepared according to literature procedures.

Caution! Natural thorium (primary isotope ^{232}Th) is a weak α -emitter (4.012 MeV) with a half-life of 1.41×10^{10} years; manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere drybox in a radiation laboratory equipped with α - and β -counting equipment.

Synthesis of 2-amino-4,6-di-tert-butylphenol (1)

The procedure previously reported in the literature³ was modified as follows: In a fumehood, a 2.0 L beaker was charged with a magnetic stir bar, 3,5-di-tert-butylcyclohexa-3,5-diene-1,2-dione (16.6 g, 150 mmol) and methanol (425 mL). Addition of excess aqueous ammonium hydroxide (143 mL, 28-30 % NH₃) resulted in color change from red to dark yellow. After 15 min at room temperature, sodium borohydride (6.7 g, 177 mmol) was added and the mixture was stirred for 10 min at RT. The solution was then diluted with water (1.0 L) and precipitation of a green solid was observed. The solid was recovered by filtration and dissolved in diethyl ether. The organic fraction was collected and the aqueous layers washed with diethyl ether (2x20 mL). The volatiles were then removed under reduced pressure from the combined organic fractions to afford a green solid of **1**. The green powder was washed with pentane (100 mL), the resulting yellow solid was filtered off and dried under reduced pressure, affording **1** as a pale-yellow powder (13.6 g, 82 %).

¹H NMR (C₆D₆, 298 K): δ 1.32 (s, 9H, C(CH₃)₃); 1.57 (s, 9H, C(CH₃)₃); 2.20 (broad, 2H, NH); 6.06 (broad, 1H, OH); 6.52 (d, *J* = 2.0 Hz, 1H, Ar-H); 7.15 ppm (d, *J* = 2.0 Hz, 1H, Ar-H).

Synthesis of (Z)-4-((3,5-di-tert-butyl-2-hydroxyphenyl)amino)pent-3-en-2-one (2)

A 100 mL round bottom flask was charged with a stir bar, acetylacetone (3.7 mL, 36 mmol), **1** (4.0 g, 18 mmol) and THF (20 mL). The resulting solution was sheltered from light and stirred for 24 h at room temperature. Solvent and excess of acetylacetone were removed at 50 °C under reduced pressure to give a light yellow solid. Pentane (50 mL) was added and the suspension was immersed in an ultrasound bath (80 W, 40 kHz) for 10 min, yielding a white solid and a yellow solution. The solid was filtered off at -40 °C and washed with cold (-40 °C) pentane (10 mL) to afford **2** as a white powder (4.4 g, 80%). Colorless translucent crystals

were obtained by slow diffusion of pentane into a THF solution.

Anal. Calcd for $C_{19}H_{29}NO_2$: C, 75.21; H, 9.63; N, 4.62; Found : C 74.87; H, 9.72; N, 4.78; 1H NMR (C_6D_6 , 298 K): δ 1.18 (s, 9H, $C(CH_3)_3$); 1.52 (s, 3H, α - CH_3); 1.58 (s, 9H, $C(CH_3)_3$); 2.01 (s, 3H, α - CH_3); 4.95 (s, 1H, β -CH); 6.79 (d, J = 2.0 Hz, 1H, Ar-H); 7.41 (d, J = 2.0 Hz, 1H, Ar-H); 8.19 (s, 1H, OH); 11.9 ppm (s, 1H, NH); ^{13}C NMR (CD_2Cl_2 , 298 K) : δ 19.7 (s, α - CH_3); 28.7 (s, α - CH_3); 29.7 (s, $C(CH_3)_3$); 31.7 (s, $C(CH_3)_3$); 34.5 (s, $C(CH_3)_3$); 35.5 (s, $C(CH_3)_3$); 97.3 (s, β -CH); 123.2 (s, Ar); 123.4 (s, Ar); 125.6 (s, Ar); 137.2 (s, Ar); 142.0 (s, Ar); 149.6 (s, Ar); 164.2 (s, C-NH); 196.2 ppm (s, C=O).

Synthesis of 4

A 100 mL flask was charged with a stir bar, **3** (5.62 g, 21.7 mmol), triethyloxoniumtetrafluoroborate (4.12 g, 21.7 mmol), and methylene chloride (13 mL). The reaction mixture was stirred at RT for 15 min, generating *in situ* the *O*-alkylated cationic intermediate as a brown-orange solution, and evaporated off. **1** (5.05 g, 22.8 mmol) and THF (13mL) was then added and the resulting yellow suspension vigorously stirred for 30 min at RT, leading to a complete dissolution of the aminophenol. After an overnight drying under reduced pressure, pentane (150 mL) was added to the yellow-brown foam and immersed in an ultrasound bath (80 W, 40 kHz) for 90 min, yielding a well-defined white suspension. The white solid was recovered by filtration and washed with cold (-40 °C) diethyl ether (3x30 mL) to afford **4** as a white air-sensitive powder (9.16 g, 85 %). Colorless translucent crystals were obtained by slow diffusion of pentane into a THF solution.

Anal. Calcd for $C_{31}H_{47}BF_4N_2O$: C, 67.63; H, 8.61; N, 5.09; Found : C 66.67; H, 8.68; N, 4.82. The %C was found repeatedly low across a series of three independent samples (including isolated crystals), even in the presence of a burning agent. 1H NMR (THF- d_8 , 298 K) : δ 1.01 (d, J = 6.0 Hz, 6H, $CH(CH_3)_2$); 1.07 (d, J = 6.0 Hz, 6H, $CH(CH_3)_2$); 1.12 (s, 9H, $C(CH_3)_3$); 1.26 (s, 9H, $C(CH_3)_3$); 2.71 (s, 3H, α - CH_3); 2.77 (s, 3H, α - CH_3); 2.84 (m, 2H,

$CH(CH_3)_2$); 4.83 (s, 1H, β -CH); 6.66 (d, $J= 2.0$ Hz, 1H, Ar-H); 7.01-7.14 (m, 4H, Ar-H); 7.61 (s, 1H, OH); 9.36 (s, 1H, NH); 9.49 ppm (s, 1H, NH); ^{13}C NMR (THF- d_8 , 298 K): δ 22.6 (s, α -CH₃); 23.5 (s, α -CH₃); 23.9 (s, $CH(CH_3)_2$); 24.2 (s, $CH(CH_3)_2$); 29.0 (s, $CH(CH_3)_2$); 29.9 (s, $C(CH_3)_3$); 31.6 (s, $C(CH_3)_3$); 34.6 (s, $C(CH_3)_3$); 35.7 (s, $C(CH_3)_3$); 91.7 (s, β -CH); 121.8 (s, Ar); 123.9 (s, Ar); 124.6 (s, Ar); 124.7 (s, Ar); 130.1 (s, Ar); 132.0 (s, Ar); 138.6 (s, Ar); 142.4 (s, Ar); 146.1 (s, Ar); 149.0 (s, C-OH); 173.0 (s, C-NH); 173.4 ppm (s, C-NH).

Synthesis of 5

A 100 mL flask was charged with a stir bar, **4** (2.31 g, 4.19 mmol) and diethyl ether (40 mL). Triethylamine (0.64 mL, 4.61 mmol) was slowly added to the white suspension using a syringe, leading to the immediate formation of a yellow suspension. The mixture was stirred for 2 h at RT. The white solid of triethylammoniumtetrafluoroborate was then filtered off through a Celite® padded coarse frit and the yellow solution was introduced into a 100 ml two-neck round bottom flask. The volatiles were removed under reduced pressure and the yellow oily residue was dried under reduced pressure at 50 °C overnight. THF (20 mL) was condensed in and *n*BuLi (5.24 mL, 8.38 mmol) was slowly added at -78°C under an argon flow, using a syringe. The resulting deep yellow solution was allowed to warm up to room temperature, leading to the formation of an orange solution with a yellow precipitate. After concentration of the solution to 10 mL, the solid was filtered off and washed with cold pentane (2x10 mL, -40°C). **5** was finally isolated as a pale-yellow air-sensitive powder (2.46 g, 95 %). Yellow crystals of [$\{Li_2(THF)_2L\}_2\} \cdot 0.5n$ -pentane were obtained by slow diffusion of pentane into a THF solution.

Anal. Calcd for $C_{39}H_{60}Li_2N_2O_3 \cdot 0.5C_6H_6$: C, 76.68; H, 9.65; N, 4.26; Found : C, 76.68; H, 9.62; N, 4.70; 1H NMR (C_6D_6 , 298 K): δ 1.18 (d, $J= 8.0$ Hz, 6H, $CH(CH_3)_2$); 1.26 (d, $J= 8.0$ Hz, 6H, $CH(CH_3)_2$); 1.34 (s, 9H, $C(CH_3)_3$); 1.73 (s, 9H, $C(CH_3)_3$); 1.96 (s, 3H, α -CH₃); 2.19 (s, 3H, α -CH₃); 3.50 (m, 2H, $CH(CH_3)_2$); 5.14 (s, 1H, β -CH); 6.85 (d, $J=2.0$ Hz, 1H, Ar-H);

7.10-7.30 ppm (m, 4H, Ar-H); ^{13}C NMR (C_6D_6 , 298 K): δ 23.7 (s, $\alpha\text{-CH}_3$); 23.9 (s, $\text{CH}(\text{CH}_3)_2$); 24.2 (s, $\text{CH}(\text{CH}_3)_2$); 24.6 (s, $\alpha\text{-CH}_3$); 25.5 (s, THF); 28.2 (s, $\text{CH}(\text{CH}_3)_2$); 31.1 (s, $\text{C}(\text{CH}_3)_3$); 32.3 (s, $\text{C}(\text{CH}_3)_3$); 34.2 (s, $\text{C}(\text{CH}_3)_3$); 35.3 (s, $\text{C}(\text{CH}_3)_3$); 68.1 (s, THF); 98.0 (s, $\beta\text{-CH}$); 118.1 (s, Ar); 120.2 (s, Ar); 123.5 (s, Ar); 128.4 (s, Ar); 135.8 (s, Ar); 136.2 (s, Ar); 140.6 (s, Ar); 145.6 (s, Ar); 149.2 (s, Ar); 154.2 (s, C-O); 161.3 (s, C=N); 170.2 (s, C=N).

Synthesis of 6

A 25 mL flask was charged with a stir bar, ZrCl_4 (102 mg, 0.438 mmol), **5** (271 mg, 0.438 mmol) and toluene (15 mL). The red-orange suspension was heated to 100 °C for 3 days, and then cooled to room temperature. The white precipitate of LiCl was removed by filtration over a fine porosity fritted filter and the volatiles removed under reduced pressure to yield **6** as a deep orange powder (235 mg, 86%). Red crystals of $\mathbf{6}\cdot\text{C}_6\text{H}_6$ were deposited from a benzene solution at RT.

Anal. Calcd for $\text{C}_{62}\text{H}_{88}\text{Cl}_4\text{N}_4\text{O}_2\text{Zr}_2$: C, 59.78; H, 7.12; N, 4.50; Found C, 59.60; H 7.11; N 4.50. ^1H NMR (C_6D_6 , 298 K): δ 1.16 (d, $J=6.0$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$); 1.32 (s, 9H, $\text{C}(\text{CH}_3)_3$); 1.37 (d, $J=6.0$ Hz, 6H, $\text{CH}(\text{CH}_3)_2$); 1.59 (s, 9H, $\text{C}(\text{CH}_3)_3$); 1.72 (s, 3H, $\alpha\text{-CH}_3$); 2.15 (s, 3H, $\alpha\text{-CH}_3$); 3.39 (m, 2H, $\text{CH}(\text{CH}_3)_2$); 5.66 (s, 1H, $\beta\text{-CH}$); 6.83 (s, 1H, Ar-H); 7.07 (m, 1H, Ar-H); 7.14 (m, 2H, Ar-H); 7.26 ppm (d, $J=2.0$ Hz, 1H, Ar-H); ^{13}C NMR (C_6D_6 , 298 K): δ 23.7 (s, $\alpha\text{-CH}_3$); 24.6 (s, $\alpha\text{-CH}_3$); 25.0 (s, $\text{CH}(\text{CH}_3)_2$); 25.3 (s, $\text{CH}(\text{CH}_3)_2$); 29.3 (s, $\text{CH}(\text{CH}_3)_2$); 30.1 (s, $\text{C}(\text{CH}_3)_3$); 31.9 (s, $\text{C}(\text{CH}_3)_3$); 34.6 (s, $\text{C}(\text{CH}_3)_3$); 35.0 (s, $\text{C}(\text{CH}_3)_3$); 109.8 (s, $\beta\text{-CH}$); 115.9 (s, Ar); 118.9 (s, Ar); 124.4 (s, Ar); 127.2 (s, Ar); 134.1 (s, Ar); 141.5 (s, Ar); 143.0 (s, Ar); 143.2 (s, Ar); 146.6 (s, Ar); 154.2 (s, C-O); 161.3 (s, C=N); 170.2 ppm (s, C=N).

Synthesis of 7

A 25 mL flask was charged with a stir bar, YbCl_3 (56.4 mg, 0.202 mmol), **5** (158 mg, 0.192 mmol) and pyridine (5.0 mL). The red-orange mixture was stirred for 15 min at room

temperature. After concentration to 1.0 mL, toluene (20 mL) was condensed in. The solution was filtered and evaporated to dryness to afford **7** as a deep orange powder (150 mg, 86%). Red monocrystals were obtained by slow diffusion of *n*-pentane into a pyridine solution of **7**. $^1\text{H NMR}$ (C_6D_6 , 298 K): δ -43.3 (s, 3H); -35.6 (s, 9H); -29.1 (s, 1H); -26.7 (s, 1H); -20.3 (s, 3H); -15.1 (s, 1H); -11.3 (s, 6H); -10.2 (s, 2H); -8.6 (s, 1H); -6.5 (s, 9H); -3.4 (s, 2H); 18.8 ppm (s, 6H), signals for coordinated pyridine molecules were not observed.

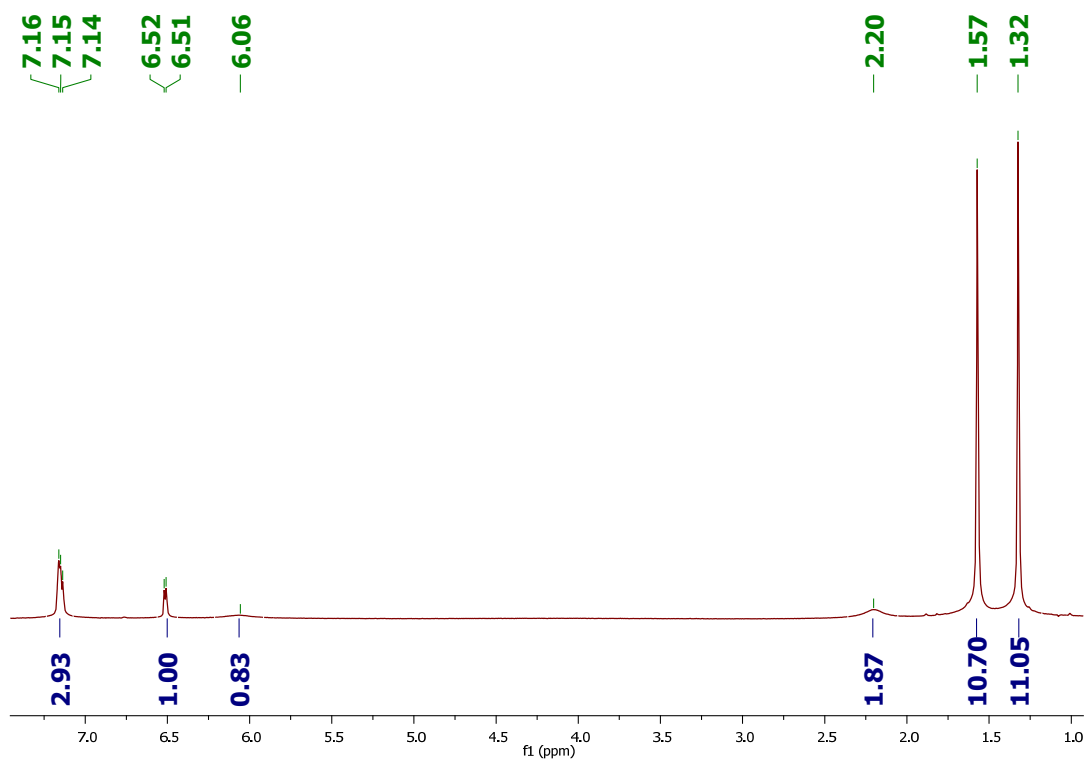
Synthesis of 8

A 25 mL flask was charged with a stir bar, $\text{ThCl}_4(\text{DME})_2$ (197 mg, 0.355 mmol), **5** (209 mg, 0.338 mmol) and toluene (15 mL). The yellow-orange mixture was heated to 100 °C for 3 days, and then cooled to room temperature. The solution was filtered and dried under reduced pressure at 50 °C, to provide **8** as a brown-yellow powder (259 mg, 88 %). Yellow monocrystals were deposited from a benzene solution of **8**.

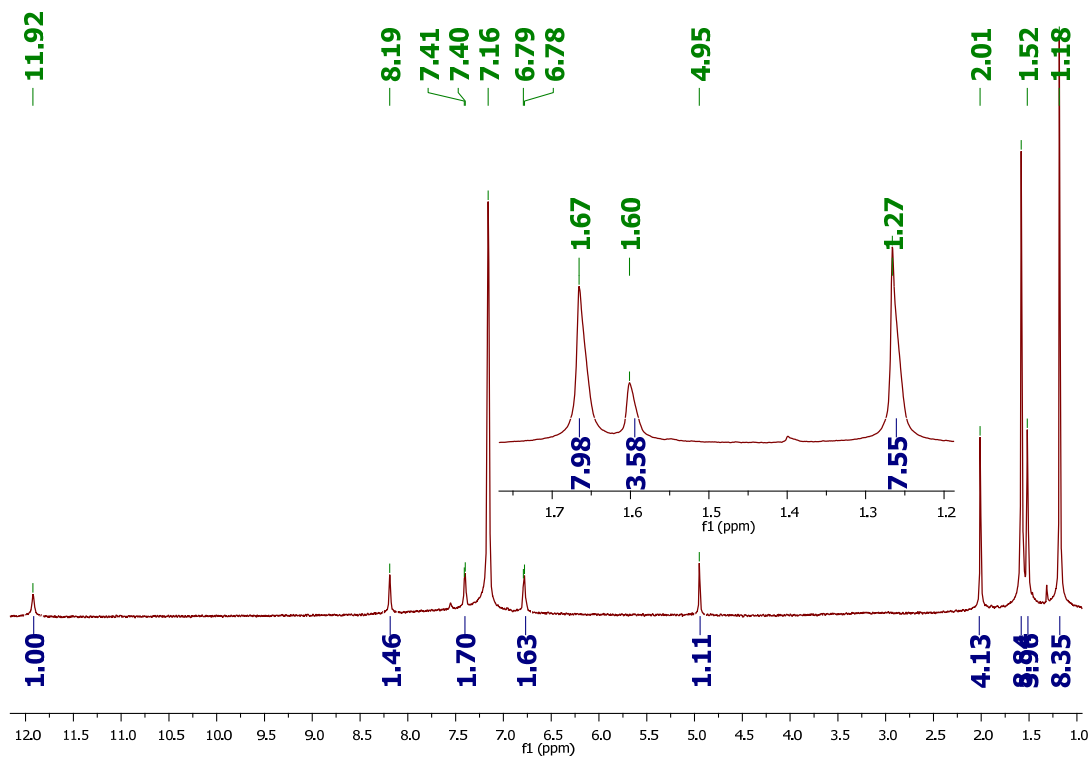
Anal. Calcd for $\text{C}_{70}\text{H}_{108}\text{Cl}_5\text{LiN}_4\text{O}_6\text{Th}_2\cdot\text{C}_6\text{H}_6$: C,49.93; H,6.29; N,3.06; Found C, 49.90; H, 6.30; N, 3.49; $^1\text{H NMR}$ (C_6D_6 , 298 K) : δ 0.90-1.32 (m, 12H, $\text{CH}(\text{CH}_3)_2$); 1.44 (s, 9H, $\text{C}(\text{CH}_3)_3$); 1.62 (s, 9H, $\text{C}(\text{CH}_3)_3$); 1.71 (s, 3H, $\alpha\text{-CH}_3$); 2.22 (s, 3H, $\alpha\text{-CH}_3$); 2.65 (s, 2H, DME); 2.70-2.90 (m, 2H, $\text{CH}(\text{CH}_3)_2$); 3.20 (s, 3H, DME); 3.40-3.70 (broad signal, 2H, DME); 5.26 (s, 1H, $\beta\text{-CH}$); 6.81 (s, 1H, Ar-H); 7.00-7.35 ppm (m, 4H, Ar-H). $^{13}\text{C NMR}$ ($\text{THF-}d_8$, 298 K) : δ 23.3 (s, $\alpha\text{-CH}_3$); 26.3 (s, $\alpha\text{-CH}_3$); 26.1 (s, $\text{CH}(\text{CH}_3)_2$); 28.2 (s, $\text{CH}(\text{CH}_3)_2$); 28.2 (s, $\text{CH}(\text{CH}_3)_2$); 30.0 (s, $\text{C}(\text{CH}_3)_3$); 32.2 (s, $\text{C}(\text{CH}_3)_3$); 34.5 (s, $\text{C}(\text{CH}_3)_3$); 34.9 (s, $\text{C}(\text{CH}_3)_3$); 58.7 (s, DME); 72.4 (s, DME); 91.8 (s, $\beta\text{-CH}$); 113.8 (s, Ar); 116.3 (s, Ar); 122.6(s, Ar); 123.7 (s, Ar); 125.0 (s, Ar); 134.2 (s, Ar); 137.4 (s, Ar); 141.8 (s, Ar); 147.5 (s, Ar); 152.1 (s, C-O); 161.2 (s, C=N); 164.9 ppm (s, C=N).

NMR Spectra

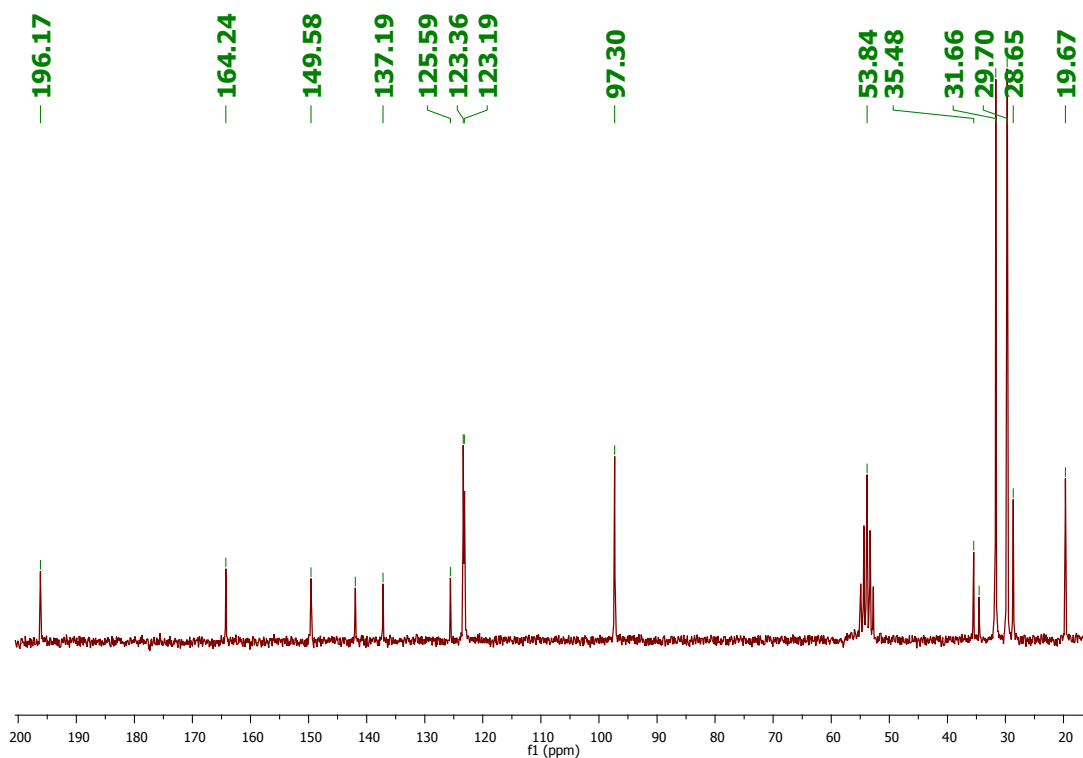
^1H NMR spectrum of **1** in C_6D_6 (298 K)



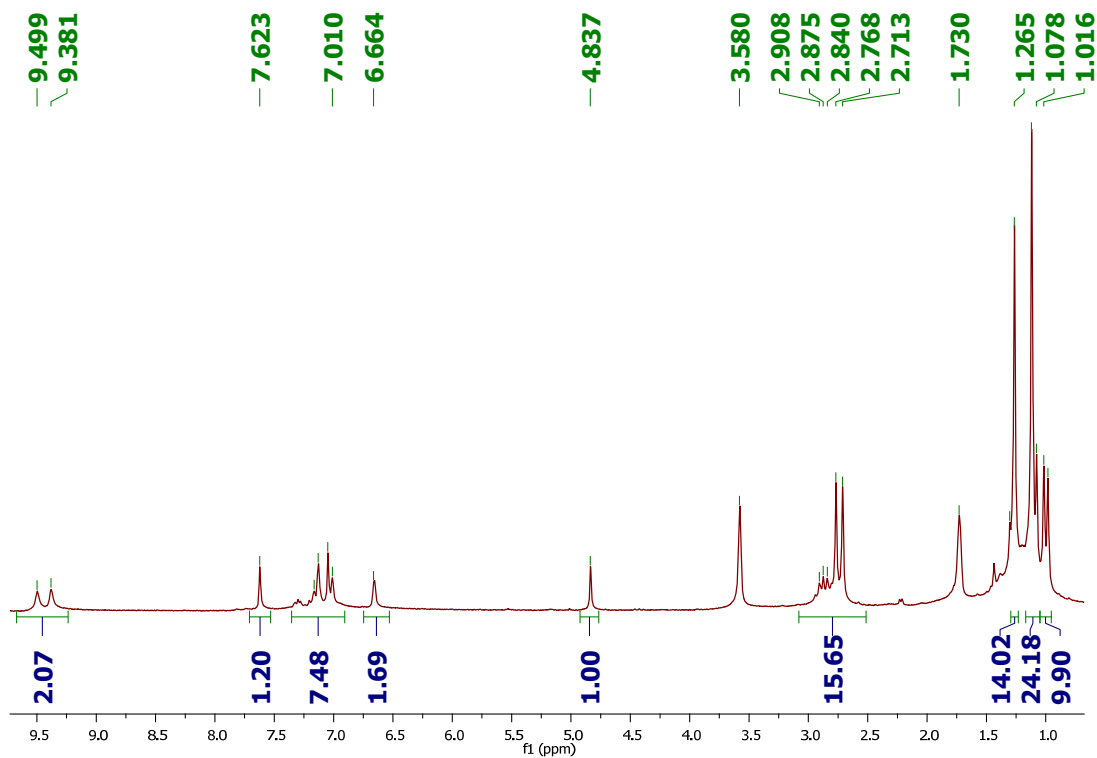
^1H NMR spectrum of **2** in C_6D_6 (298 K)



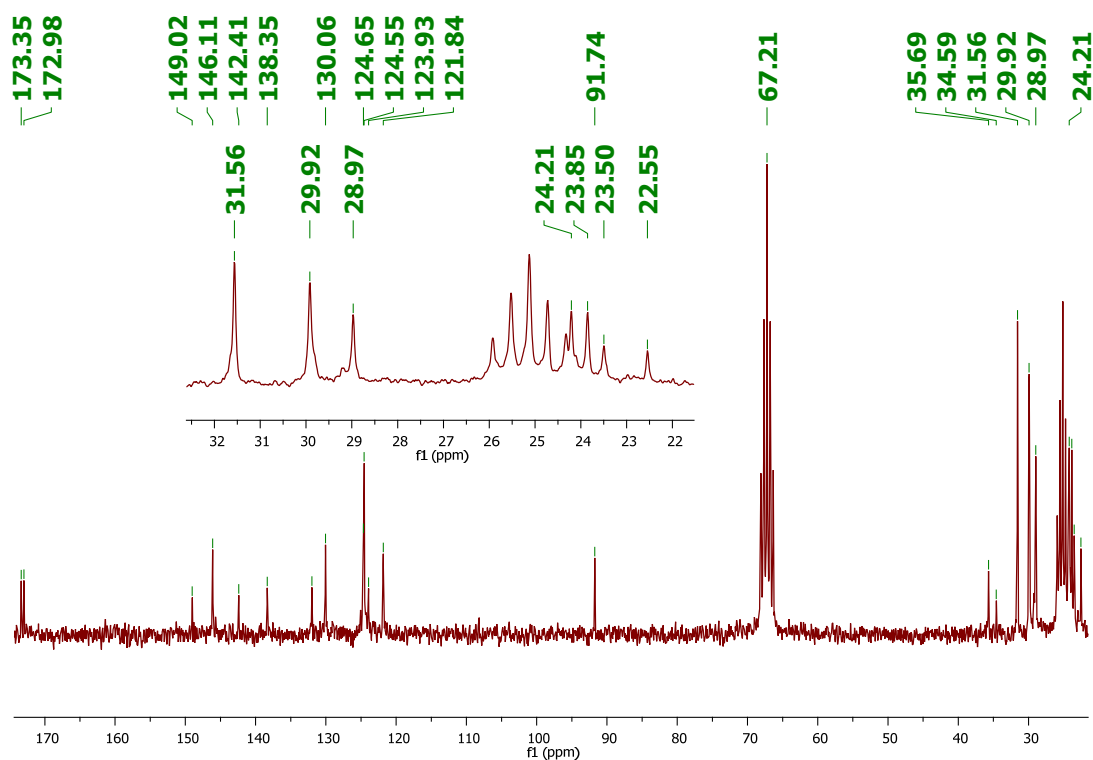
^{13}C NMR spectrum of **2** in CD_2Cl_2 (298 K)



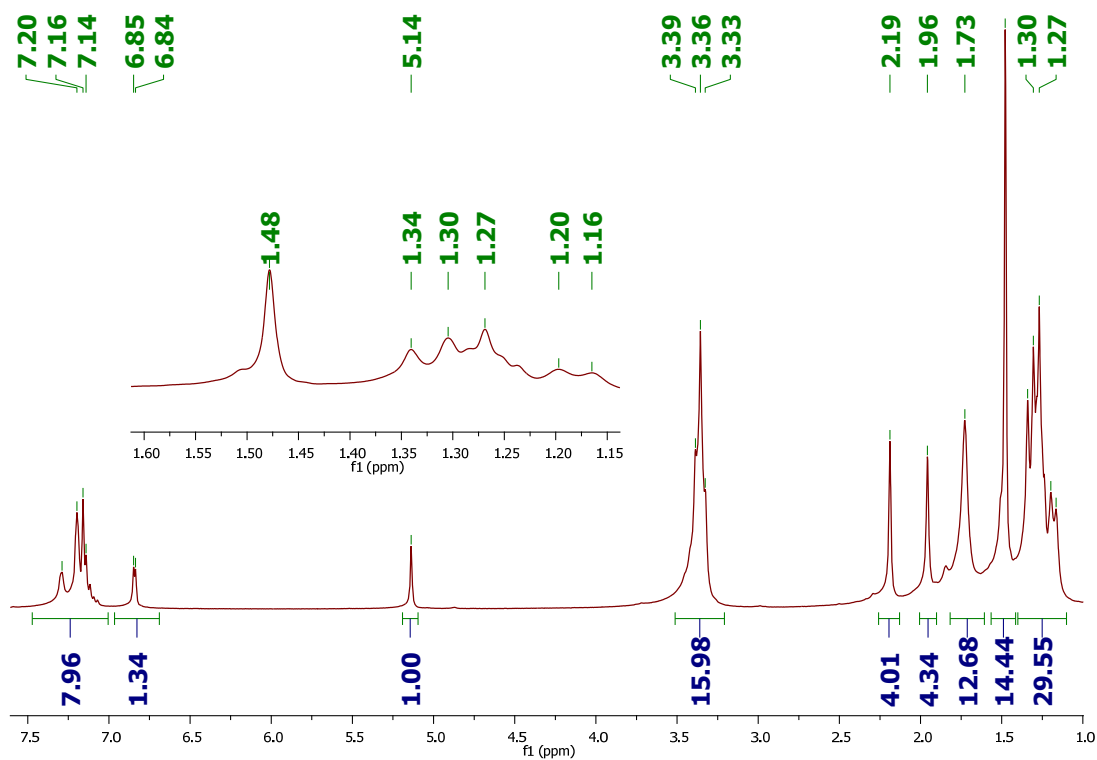
^1H NMR spectrum of **4** THF- d_8 (298 K)



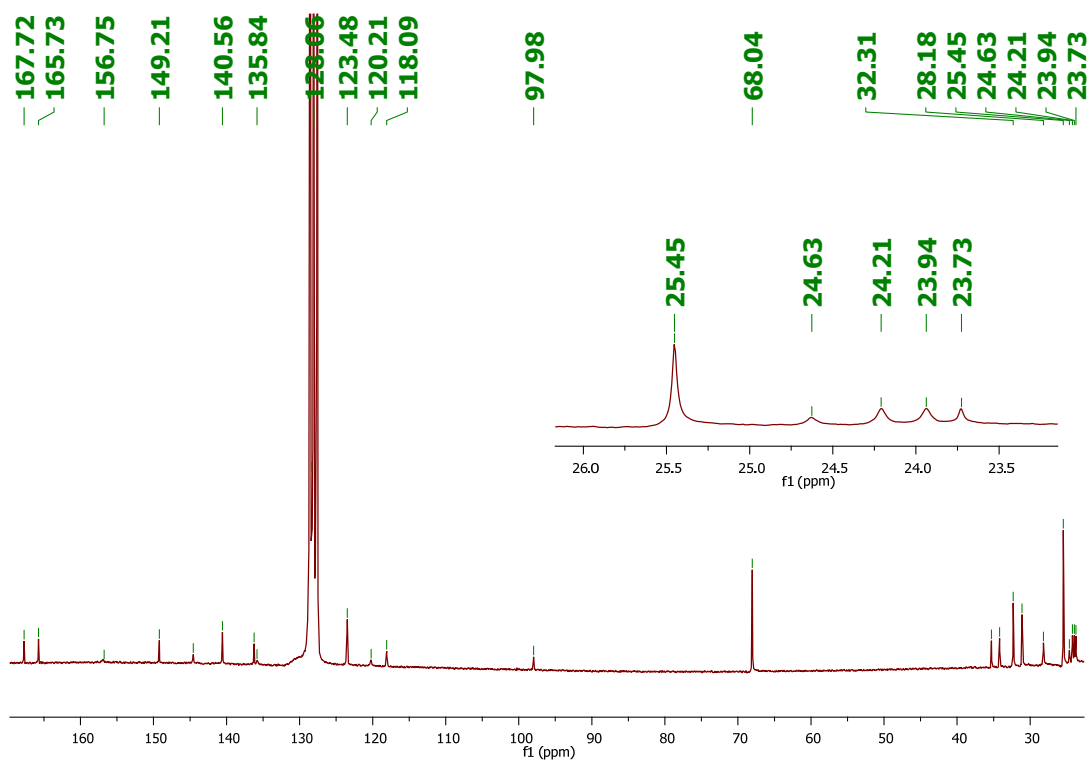
^{13}C NMR spectrum of **4** in $\text{THF-}d_8$ (298 K)



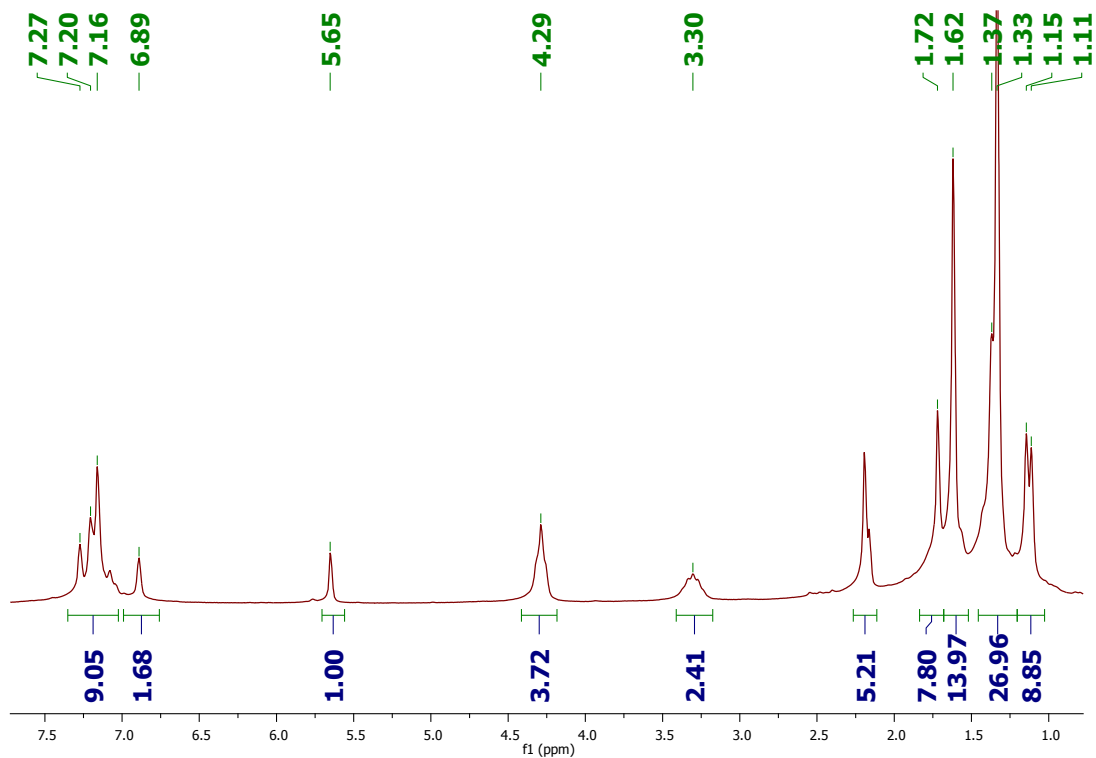
^1H NMR spectrum of **5** in C_6D_6 (298 K)



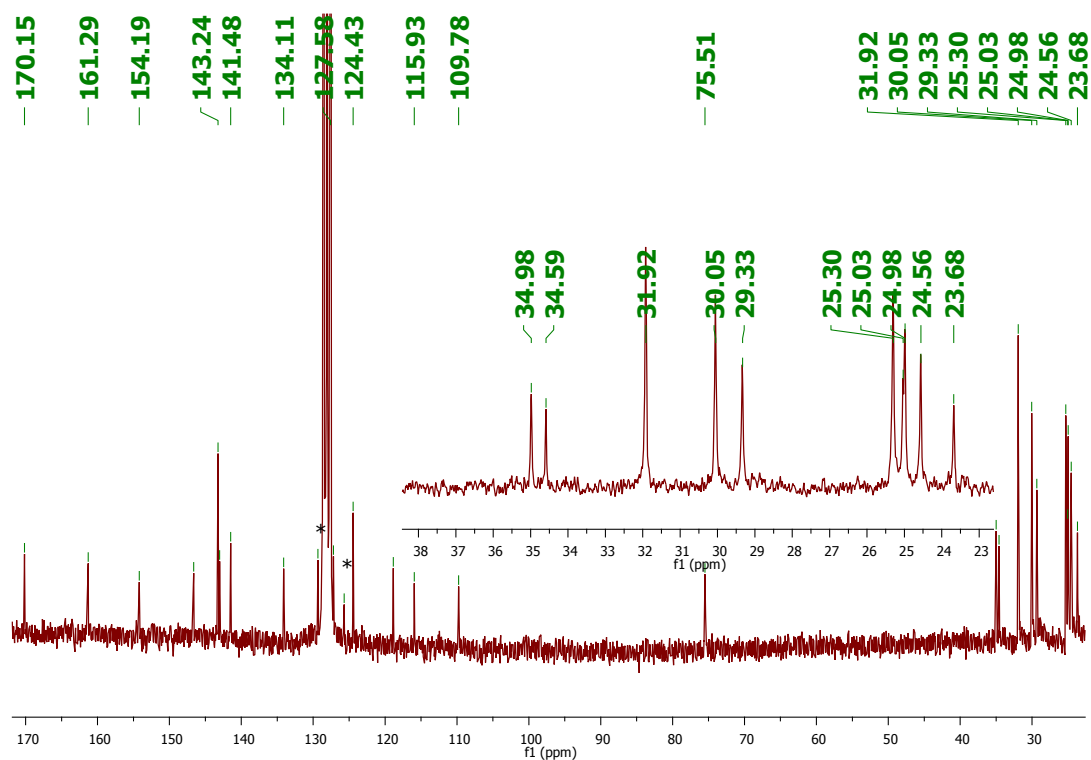
^{13}C NMR spectrum of **5** C_6D_6 (298 K)



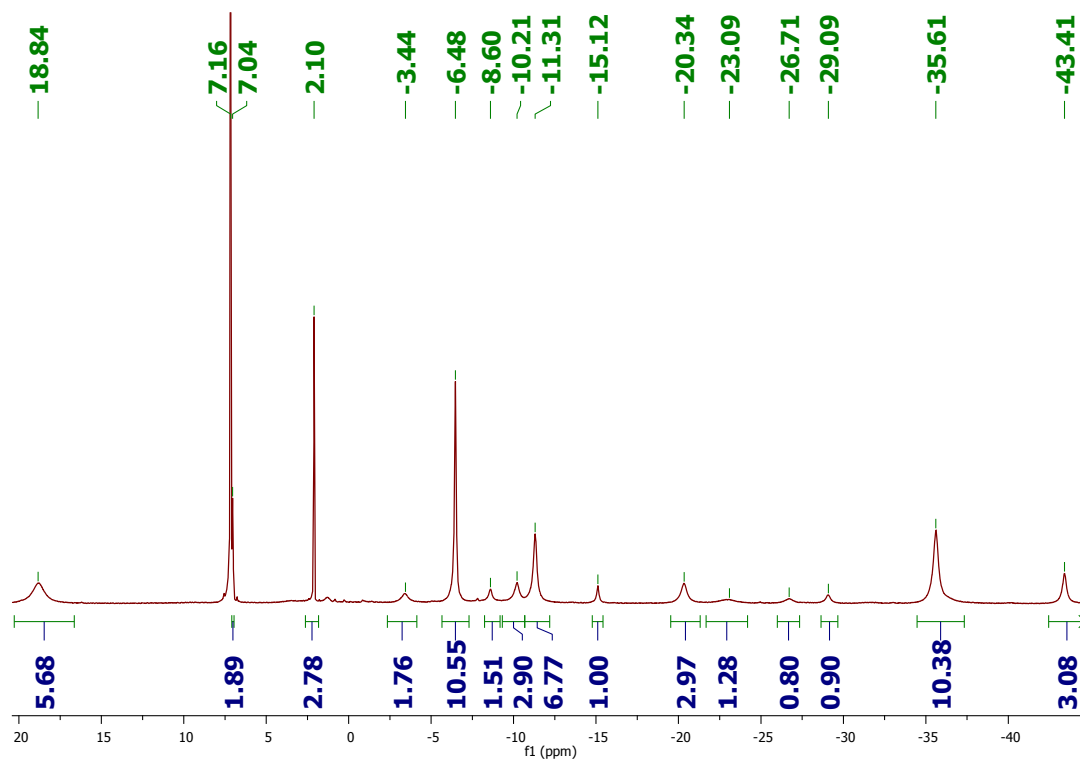
^1H NMR spectrum of **6** in C_6D_6 (298K)



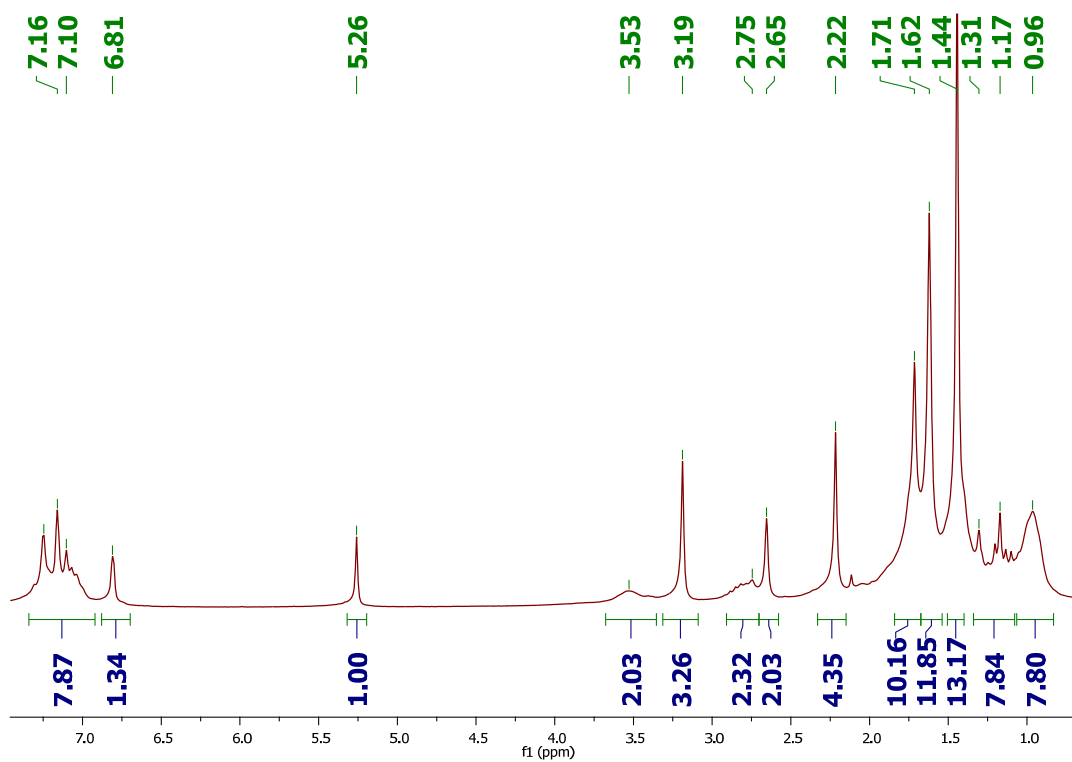
^{13}C NMR spectrum of **6** C_6D_6 (298 K)



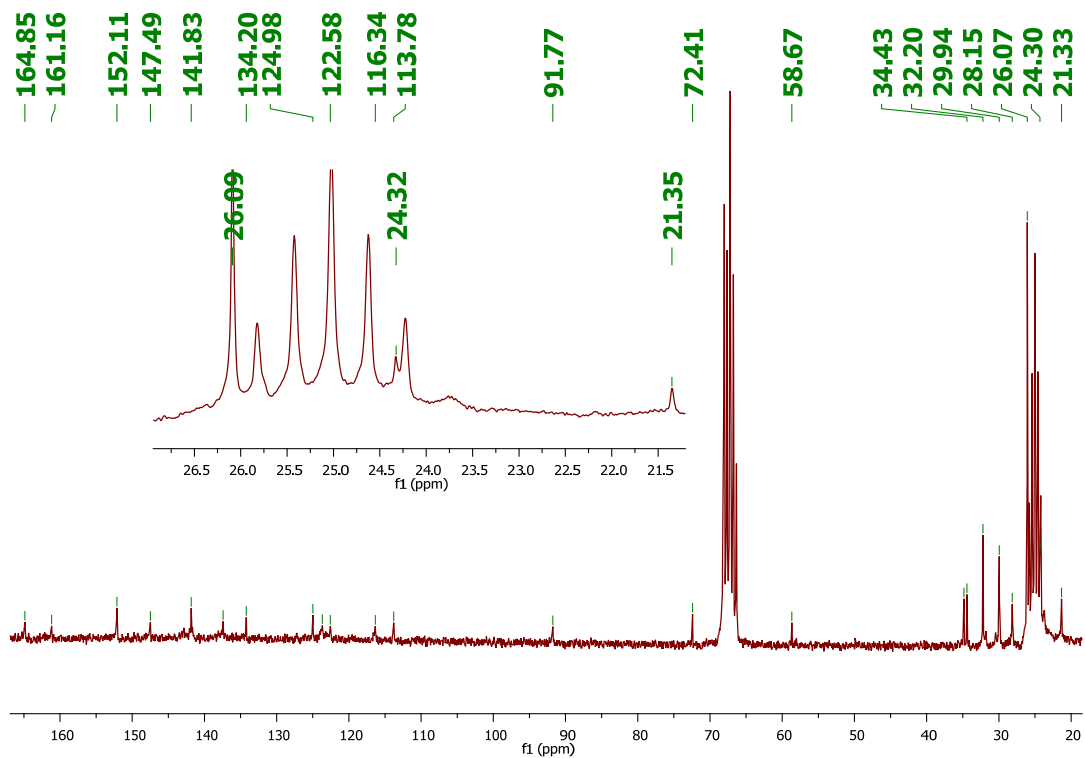
^1H NMR spectrum of **7** in C_6D_6 (298 K)



^1H NMR spectrum of **8** in C_6D_6 (298 K)



^{13}C NMR spectrum of **8** in $\text{THF-}d_8$ (298 K)



Crystallography

Data were collected on a Nonius Kappa-CCD area-detector diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$),⁴ and processed with HKL2000.⁵ Absorption effects in the metal ion complexes (except that of Li) were corrected with SCALEPACK.⁵ The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with SHELXTL.⁶ All non-hydrogen atoms were refined with anisotropic displacement parameters. Three fluorine atoms in [(2,6-ⁱPr₂-C₅H₃)N=CMe₂][BF₄] are disordered over two sites, which have been refined with occupancy parameters constrained to sum to unity and with restraints on displacement parameters and some bond lengths and angles. Restraints on displacement parameters and two bond lengths were also applied for the carbon atoms of one THF molecule in 4·2THF. The solvent pentane molecule in [5]₂·0.5*n*-pentane is located around an inversion centre and is very badly resolved; a complete molecule with an occupancy factor of 0.25 has been refined with restraints on bond lengths, angles and displacement parameters. In these two structures, the highest residual electron density peak is located near the badly resolved solvent molecule. In 7·0.5C₅H₅N, a void in the lattice indicates the presence of other, unresolved solvent molecules. The hydrogen atoms bound to oxygen and nitrogen atoms were found on Fourier-difference maps when present, and the carbon-bound hydrogen atoms were introduced at calculated positions in all compounds; all were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH₃). CCDC-878332-878338 contain the supplementary crystallographic data for compounds **2**, **4**·(THF)₂, [5]₂·0.5*n*-pentane, **6**·benzene, **7**·(pyridine)_{0.5}, **8**·(benzene)₂ and [(2,6-ⁱPr₂-C₅H₃)N=CMe₂][BF₄]. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for 2: $C_{19}H_{29}NO_2$, $M = 303.43$, orthorhombic, space group $Pca2_1$, $a = 20.6064(16)$, $b = 6.1496(3)$, $c = 28.352(2)$ Å, $V = 3592.8(4)$ Å³, $Z = 8$, $T = 150(2)$ K. Refinement of 413 parameters on 3495 independent reflections out of 133527 measured reflections ($R_{\text{int}} = 0.028$) led to $R1 = 0.056$, $wR2 = 0.129$, $\Delta\rho_{\text{min}} = -0.20$, $\Delta\rho_{\text{max}} = 0.20$ e Å⁻³.

Crystal data for 4·2THF: $C_{39}H_{63}BF_4N_2O_3$, $M = 694.72$, triclinic, space group $P\bar{1}$, $a = 10.7837(6)$, $b = 11.0362(4)$, $c = 19.8110(11)$ Å, $\alpha = 101.642(3)$, $\beta = 93.665(2)$, $\gamma = 117.839(3)^\circ$, $V = 2007.63(19)$ Å³, $Z = 2$, $T = 150(2)$ K. Refinement of 454 parameters on 7587 independent reflections out of 91910 measured reflections ($R_{\text{int}} = 0.040$) led to $R1 = 0.074$, $wR2 = 0.228$, $\Delta\rho_{\text{min}} = -0.56$, $\Delta\rho_{\text{max}} = 0.99$ e Å⁻³.

Crystal data for [5]₂·0.5*n*-pentane: $C_{80.5}H_{126}Li_4N_4O_6$, $M = 1273.61$, triclinic, space group $P\bar{1}$, $a = 11.1501(14)$, $b = 11.5801(10)$, $c = 16.331(2)$ Å, $\alpha = 74.761(7)$, $\beta = 80.257(6)$, $\gamma = 81.093(7)^\circ$, $V = 1991.6(4)$ Å³, $Z = 1$, $T = 150(2)$ K. Refinement of 469 parameters on 7523 independent reflections out of 54371 measured reflections ($R_{\text{int}} = 0.089$) led to $R1 = 0.077$, $wR2 = 0.234$, $\Delta\rho_{\text{min}} = -0.25$, $\Delta\rho_{\text{max}} = 0.77$ e Å⁻³.

Crystal data for 6·C₆H₆: $C_{68}H_{94}Cl_4N_4O_2Zr_2$, $M = 1323.71$, triclinic, space group $P\bar{1}$, $a = 9.3601(5)$, $b = 12.7048(9)$, $c = 16.1239(12)$ Å, $\alpha = 73.543(3)$, $\beta = 77.583(4)$, $\gamma = 79.236(4)^\circ$, $V = 1779.6(2)$ Å³, $Z = 1$, $T = 100(2)$ K. Refinement of 373 parameters on 6756 independent reflections out of 75556 measured reflections ($R_{\text{int}} = 0.070$) led to $R1 = 0.077$, $wR2 = 0.224$, $\Delta\rho_{\text{min}} = -1.14$, $\Delta\rho_{\text{max}} = 2.79$ e Å⁻³.

Crystal data for 7·0.5C₅H₅N: $C_{48.5}H_{61.5}ClN_{5.5}OYb$, $M = 946.02$, monoclinic, space group $C2/c$, $a = 41.3998(7)$, $b = 13.7026(3)$, $c = 18.7083(5)$ Å, $\beta = 111.5953(7)^\circ$, $V = 9868.0(4)$ Å³, $Z = 8$, $T = 150(2)$ K. Refinement of 577 parameters on 15063 independent reflections out of 150085 measured reflections ($R_{\text{int}} = 0.069$) led to $R1 = 0.048$, $wR2 = 0.136$, $\Delta\rho_{\text{min}} = -2.11$, $\Delta\rho_{\text{max}} = 0.90$ e Å⁻³.

Crystal data for 8·2C₆H₆: C₈₂H₁₂₀Cl₅LiN₄O₆Th₂, $M = 1906.09$, triclinic, space group $P\bar{1}$, $a = 13.0701(3)$, $b = 17.5574(6)$, $c = 20.6952(8)$ Å, $\alpha = 107.545(2)$, $\beta = 100.357(2)$, $\gamma = 97.811(3)^\circ$, $V = 4361.9(3)$ Å³, $Z = 2$, $T = 100(2)$ K. Refinement of 929 parameters on 26603 independent reflections out of 239700 measured reflections ($R_{\text{int}} = 0.048$) led to $R1 = 0.032$, $wR2 = 0.066$, $\Delta\rho_{\text{min}} = -1.32$, $\Delta\rho_{\text{max}} = 1.75$ e Å⁻³.

Crystal data for [(2,6-ⁱPr₂-C₅H₃)N=CMe₂][BF₄]: C₁₅H₂₄BF₄N, $M = 305.16$, monoclinic, space group $P2_1/n$, $a = 8.7358(7)$, $b = 8.3794(4)$, $c = 22.5730(18)$ Å, $\beta = 90.125(4)^\circ$, $V = 1652.4(2)$ Å³, $Z = 4$, $T = 150(2)$ K. Refinement of 223 parameters on 3124 independent reflections out of 48369 measured reflections ($R_{\text{int}} = 0.022$) led to $R1 = 0.065$, $wR2 = 0.190$, $\Delta\rho_{\text{min}} = -0.47$, $\Delta\rho_{\text{max}} = 0.52$ e Å⁻³.

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