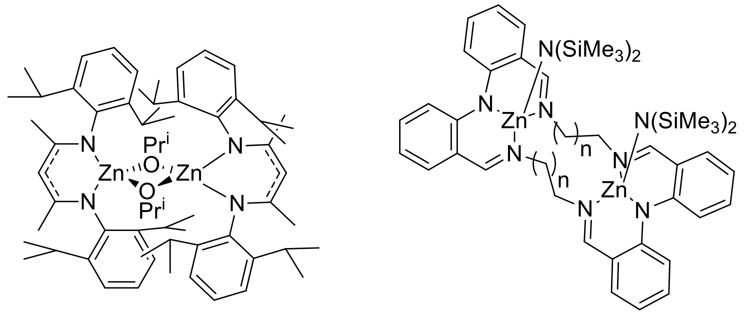
Electronic supplementary materials *Mendeleev Commun.*, 2020, **30**, 596–598

New dialkylenetriamine zinc complexes as highly efficient ROP catalysts

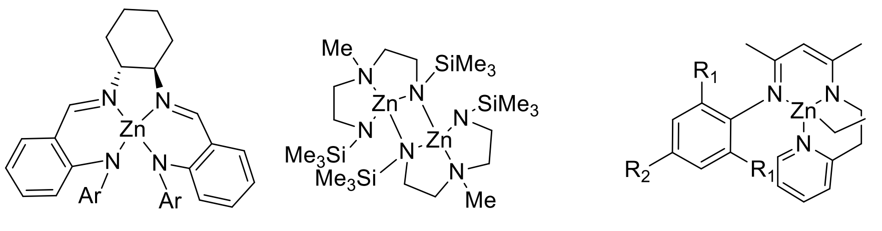
Ekaterina A. Kuchuk, Badma N. Mankaev, Valeriia A. Serova, Kirill V. Zaitsev, Andrei V. Churakov, Yury F. Oprunenko, Galina S. Zaitseva and Sergey S. Karlov

Table of contents



Coates G.W. et al, 1999

Williams C.K. et al, 2016



Yao W. et al, 2017

1, Bertrand G. et al, 2002

Chen H. and Hsu S.C.N. et al, 2016

Chart S1. Some zinc complexes containing nitrogen ligands, efficient in the ROP process

Experimental

General remarks. All manipulations were performed under a dry, oxygen-free argon atmosphere using standard Schlenk techniques. Solvents were dried by standard methods and distilled prior to use. Starting materials $MeN(CH_2CH_2NHC_6F_5)_2$,[S1] $BnN(CH_2CH_2NHC_6F_5)_2$ [**1a**],[S2] $Zn[N(SiMe_3)_2]_2$[S3] were synthesized according to the literature procedures. MeI (Aldrich), BnCl, C_6F_6, ε-caprolactone were distilled prior to use. Trimethylenecarbonate was obtained according to the literature procedure.[S4] $ZnCl_2$ was dried at high temperature in vacuo. ^1H (400.13 MHz), ^{13}C (100.61 MHz), ^{19}F (376.5 MHz), NMR spectra were recorded with a Bruker Avance 400 spectrometer at room temperature (if otherwise stated). Signals of pentafluorophenyl groups in ^{13}C spectra were not observed due to higher-order C–F coupling. ^1H and ^{13}C chemical shifts are reported in ppm relative to $CHCl_3$ (7.24 and 77.00 ppm for ^1H and ^{13}C respectively) or DMSO-d^6 (2.5 ppm for ^1H and 39.52 for ^{13}C); in ^{19}F NMR experiments $CFCl_3$ was used as an external standard. Elemental analyses were carried out by the Microanalytical Laboratory of INEOS RAS. Analysis of polymerization characteristics was performed in the laboratory of polymerization processes at MSU using GPC in DMF with 0.1 wt.% LiBr at 50°C on a ‘PolymerLabs’ GPC-120 chromatograph with two columns PLgel 5 μm MIXED B (M = (5×102)-(1×107)), equipped with differential refractometer. For calibration PMMA with narrow distribution were used. High-resolution mass spectra (HRMS) were registered on a Bruker Daltonics micrOTOF-Q II hybrid quadrupole time-of-flight mass spectrometer using electrospray ionization (ESI); measurements were done in positive ion mode. The voltage on the capillary was 4500 V; range of scanned masses, m/z 50-3000; external calibration (Electrospray Calibrant Solution; Fluka, Germany); nebulizer pressure: 0.4 bar; flow rate: 3 μl min^{-1}; nitrogen as dry gas (6 l/min); interface temperature: 180°C. The samples were injected into the mass spectrometer chamber using a syringe injection from acetonitrile solution (LC-MS grade; Panreac, Spain).

[S1] F. V. Cochran, P. J. Bonitatebus and R. R. Schrock, *Organometallics*, 2000, **19**, 2414.
[S2] E. K. Lermontova, M. Huan, A. V Churakov, J. A. K. Howard, M. V Zabalov, S. S. Karlov and G. S. Zaitseva, *Dalton Trans.*, 2009, 4695.
[S3] M. Bochmann, G. Bwembya and K.J. Webb, *Inorg. Synth.*, 1997, **31**, 19.
[S4] T. Ariga, T. Takata and T. Endo, *J. Polym. Sci., Part A: Polym. Chem.*, 1993, **31(2)**, 581.

Syntheses

Synthesis of pro-ligand

1,8-Bis(perfluorophenyl)-1,4,8-triazaoctane, $F_5C_6NH(CH_2)_2NH(CH_2)_3NHC_6F_5$. To a mixture of K_2CO_3 (22.00 g, 0.16 mol), MeCN (60 ml), triamine $H_2N(CH_2)_2NH(CH_2)_3NH_2$ (8.79 g, 0.075 mol) and C_6F_6 (46.51 g, 0.25 mol) were added. The mixture was refluxed for 20 hours. After the suspension was cooled, water (50 ml) was added. The organic layer was separated, the aqueous one was extracted twice with $CHCl_3$ (3×20 ml). The combined organic phases were dried with Na_2SO_4. The compound was purified by column chromatography (SiO_2, eluent – PE 70–100/ $CHCl_3$ (1:1); the fraction with R_f 0.56) was collected, yellow oil (27.73 g, 82%).

^{1}H NMR (δ, ppm, $CDCl_3$): 1.14 (br s, 1H, N*H*), 1.71–1.78 (m, 2H, $CH_2CH_2CH_2$), 2.76 (t, 2H, *J*=6.3 Hz, C*H*$_2$), 2.81–2.85 (m, 2H, C*H*$_2$), 3.32–3.46 (m, 4H, C*H*$_2$NHC$_6$F$_5$), 4.14, 4.35 (br s, 2H, N*H*C$_6$F$_5$). ^{13}C NMR (δ, ppm, $CDCl_3$): 30.21 (CH$_2$*C*H$_2$CH$_2$), 45.42, 45.68 (2t, 2*C*H$_2$NHC$_6$F$_5$, J_{C-F}=4.0 Hz), 47.58; 49.20 (2HN*C*H$_2$). ^{19}F NMR (δ, ppm, $CDCl_3$): -172.80–(-172.64) (m, 1F), -172.27–(-172.16) (m, 1F), -165.00–(-164.78) (m, 4F), -160.34–(-160.20) (m, 2F), -160.05–(-159.90) (m, 2F).

Synthesis of ligands

4-Methyl-1,8-bis(perfluorophenyl)-1,4,8-triazaoctane, $MeN[(CH_2)_2NHC_6F_5](CH_2)_3NHC_6F_5$ (1c). To a solution of triamine $F_5C_6NH(CH_2)_2NH(CH_2)_3NHC_6F_5$ (10.66 g, 0.024 mol) in MeCN (120 ml), K_2CO_3 (17.50 g, 0.130 mol) and CH_3I (1.86 ml, 0.030 mol) were added. The mixture was stirred at room temperature for 2 days. Water (100 ml) and ethyl acetate (50 ml) were added. The organic layer was separated, the aqueous one was extracted with ethyl acetate (3×50 ml). The combined organic phases were dried (Na_2SO_4) and concentrated to leave a yellow oil. Purification by column chromatography (SiO_2, eluent PE 70-100/EtOAc (1:2) to collect fraction with R_f =0.58) afforded compound **1c** (7.48 g, 68%) as light-yellow oil.

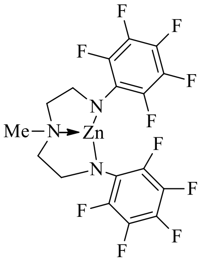
^{1}H NMR (δ, ppm, $CDCl_3$): 1.70–1.79 (m, 2H, $CH_2CH_2CH_2$), 2.24 (s, 3H, NC*H*$_3$), 2.49 (t, 2H, *J*=6.4 Hz, C*H*$_2$N), 2.57 (t, 2H, *J*=5.7 Hz, C*H*$_2$N), 3.35–3.45 (m, 4H, C*H*$_2$N), 4.20, 4.25 (2 br s, 2H, N*H*C$_6$F$_5$). ^{13}C NMR (δ, ppm, $CDCl_3$): 27.64 (CH$_2$*C*H$_2$CH$_2$), 41.47 (N*C*H$_3$), 43.24, 45.12 (2t, 2*C*H$_2$NHC$_6$F$_5$, J_{C-F}=4.0 Hz), 55.55, 57.06 (2CH$_3$N*C*H$_2$). ^{19}F NMR (δ, ppm, $CDCl_3$): -172.75–(-172.45) (m, 2F), -165.00–(-164.80) (m, 4F), -160.45–(-160.30) (m, 4F). HRMS of $C_{18}H_{15}F_{10}N_3$ (m/z): calculated $[M+H]^+$ 464.1179, found 464.1178.

4-Benzyl-1,8-bis(perfluorophenyl)-1,4,8-triazaoctane, $BnN[(CH_2)_3NHC_6F_5](CH_2)_2NHC_6F_5$ (1d). To a solution of triamine $F_5C_6NH(CH_2)_2NH(CH_2)_3NHC_6F_5$ (10.66 g, 0.024 mol) in MeCN (120 ml), K_2CO_3 (17.50 g, 0.130 mol) and $PhCH_2Cl$ (3.45 ml, 0.030 mol) were added. The mixture was refluxed for 30 h. The volatiles were removed in vacuum. To the solid residue, water (100 ml) and ethyl acetate (50 ml) were added. The layers were separated, the aqueous one was extracted with ethyl acetate (3×50 ml). The combined extracts were dried with Na_2SO_4. After the removal of the solvent, brown oily substannce was obtained. The product was purified by column chromatography (SiO_2, eluent – hexane/CH_2Cl_2 (9:1), fraction with R_f =0.56 was collected). Compound **1d** was obtained as light-yellow oil (9.08 g, 71%).

^{1}H NMR (δ, ppm, $\mathrm{CDCl_3}$): 1.69–1.79 (m, 2H, $\mathrm{CH_2C}H_2\mathrm{CH_2}$), 2.58 (t, 2H, J=6.4 Hz, $\mathrm{C}H_2\mathrm{N}$), 2.70 (t, 2H, J=5.3 Hz, $\mathrm{C}H_2\mathrm{N}$), 3.32–3.38 (m, 4H, $\mathrm{C}H_2\mathrm{N}$), 3.58 (s, 2H, $\mathrm{PhC}H_2\mathrm{N}$), 3.61, 4.28 (2 br s, 2H, $\mathrm{N}H\mathrm{C_6F_5}$), 7.22–7.36 (m, 5H, *Ph*, partially overlapped with residual protons of $\mathrm{CDCl_3}$). ^{13}C NMR (δ, ppm, $\mathrm{CDCl_3}$): 27.95 ($\mathrm{CH_2}C\mathrm{H_2CH_2}$); 43.09, 44.25, (2t, $2C\mathrm{H_2NHC_6F_5}$, $J_{\text{C-F}}$=3.7 Hz); 50.97, 53.32, 58.68 ($2C\mathrm{H_2NCH_2Ph}$ and $\mathrm{N}C\mathrm{H_2Ph}$), 127.38, 128.50, 128.82, 138.65 (Ph). ^{19}F NMR (δ, ppm, $\mathrm{CDCl_3}$): -172.64–(-172.45) (m, 1F), -172.24–(-172.06) (m, 1F), -164.78–(-164.42) (m, 4F), -160.31–(-160.13) (m, 2F), -160.04–(-159.85) (m, 2F). HRMS of $\mathrm{C_{24}H_{19}F_{10}N_3}$ (m/z): calculated $[\mathrm{M+H}]^+$ 540.1492, found 540.1491.

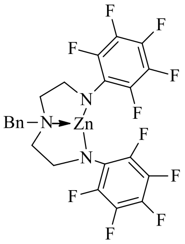
Synthesis of zinc complexes

Zinc 4-methyl-1,7-bis(perfluorophenyl)-1,4,7-triazaheptane-1,7-diide (2a)



To a solution of $\mathrm{Zn[N(SiMe_3)_2]_2}$ in a round-bottom Schlenk flask (0.57 g, 1.50 mmol) in toluene (5 ml), ligand **1a** (0.66 g, 1.50 mmol) in 10 ml of toluene (10 ml) was added at room temperature. Formation of white precipitate was observed. The mixture was stirred at room temperature for 8 h. The precipitate was filtered, washed with hexane (3×2 ml) and dried *in vacuo* to afford complex **2a** (0.69 g, 90% from theory) as a white powder. The reaction mixture can be additionally heated for the reaction to complete faster.

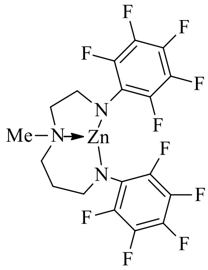
NMR ^{1}H (δ, ppm, DMSO-d$_6$): 2.43 (s, 3H, $\mathrm{NC}H_3$), 2.51–2.60 (m, 2H, $\mathrm{C}H_2$), 2.75–2.88 (m, 2H, $\mathrm{C}H_2$), 3.61 (br s, 4H, $\mathrm{C}H_2$). NMR ^{13}C (δ, ppm, DMSO-d$_6$): 41.74 ($\mathrm{N}C\mathrm{H_3}$), 44.59 (br), 55.25 ($\mathrm{N}C\mathrm{H_2}$). NMR ^{19}F (δ, ppm, DMSO-d$_6$): -187.12–(-186.75) (m, 2F), -168.39–(-168.11) (m, 4F), -165.55–(-165.33) (m, 4F). Elemental analysis: Calcd. ($\mathrm{C_{17}H_{11}N_3F_{10}Zn}$): C, 39.83; H, 2.16; N, 8.20. Found: C, 38.92; H, 2.81; N, 7.98 %.



Zinc 4-benzylmethyl-1,7-bis(perfluorophenyl)-1,4,7-triazaheptane-1,7-diide (2b), solvate with toluene. To a solution of $\mathrm{Zn[N(SiMe_3)_2]_2}$ in a round-bottom Schlenk flask (0.67 g, 1.80 mmol) in 5 ml of toluene ligand **1b** (0.94 g, 1.80 mmol) in 10 ml of toluene was added at room temperature. Formation of white precipitate was observed. Reaction mixture was stirred for 12 h at 100°C. Then precipitate was filtered, washed with hexane (3×2 ml) and dried in vacuo to afford **2b** (0.96 g, 84% from theory $\mathrm{2C_{23}H_{15}N_3F_{10}Zn{*}C_7H_8}$) as a white powder.

NMR ^{1}H (δ, ppm, DMSO-d$_6$): 2.52–2.60, 2.70–2.83, 3.52–3.64, 3.67–3.79 (4 m, 8H, $4\mathrm{C}H_2$), 3.95 (s, 2H, $\mathrm{NC}H_2\mathrm{Ph}$), 7.35–7.45 (m, 5H, *Ar*). NMR ^{13}C (δ, ppm, DMSO-d$_6$): 44.33, 50.38, 54.87 ($\mathrm{N}C\mathrm{H_2}$, $\mathrm{NC}H_2\mathrm{Ph}$), 128.08, 128.18, 131.35, 132.37 (*Ar*). NMR ^{19}F (δ, ppm, DMSO-d$_6$): -186.87–(-186.62) (m, 2F), -168.30–(-167.98) (m, 4F), -165.44–(-164.97) (m, 4F). Elemental analysis: Calcd. ($\mathrm{C_{23}H_{15}N_3F_{10}Zn}$): C, 46.92; H, 2.57; N, 7.14; ($\mathrm{2C_{23}H_{15}N_3F_{10}Zn{*}C_7H_8}$: C, 50.14; H, 3.02; N, 6.62) Found: C, 48.91; H, 3.20; N, 6.76 %.

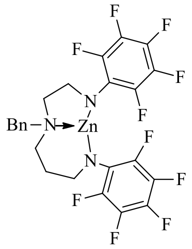
Zinc 4-methyl-1,8-bis(perfluorophenyl)-1,4,8-triazaoctane-1,8-diide (2c)



To a solution of $Zn[N(SiMe_3)_2]_2$ (0.63 g, 1.63 mmol) in toluene (12 ml) in a round-bottom Schlenk flask, ligand **1c** (0.76 g, 1.64 mmol) in toluene (6 ml) was added at room temperature. The mixture was stirred at 90°C for 15 h. The volatiles were removed under reduced pressure, the residue was washed with hexane (3×2 ml) and dried in vacuo to afford complex **2c** (0.58 g, 67%) as a slightly beige powder.

NMR ^{1}H (δ,ppm, DMSO-d$_6$): 1.73–1.84 (m, 2H, CH_2), 2.37 (s, 3H, NCH_3), 2.51–2.59 (m, 1H), 2.62–2.71 (m, 1H), 2.77–2.85 (m, 1H), 2.86–2.94 (m, 1H), 3.41–3.50 (m, 1H), 3.52–3.71 (m, 3H) (CH_2). NMR ^{13}C (δ, ppm, DMSO-d$_6$): 28.21 ($CH_2CH_2CH_2$), 42.69 (CH_3N), 45.21, 52.53 (2m, 2$CH_2NC_6F_5$), 58.37, 59.05 (2CH_2N). NMR ^{19}F (δ, ppm, DMSO-d$_6$): -186.60–(-186.26) (m, 1F), -184.80–(-184.55) (m, 1F), -168.65–(-168.24) (m, 4F) (two signals overlapped), -164.63–(-164.34) (m, 2F), -161.54–(-161.24) (m, 2F).

Zinc 4-benzyl-1,8-bis(perfluorophenyl)-1,4,8-triazaoctane-1,8-diide (2d)



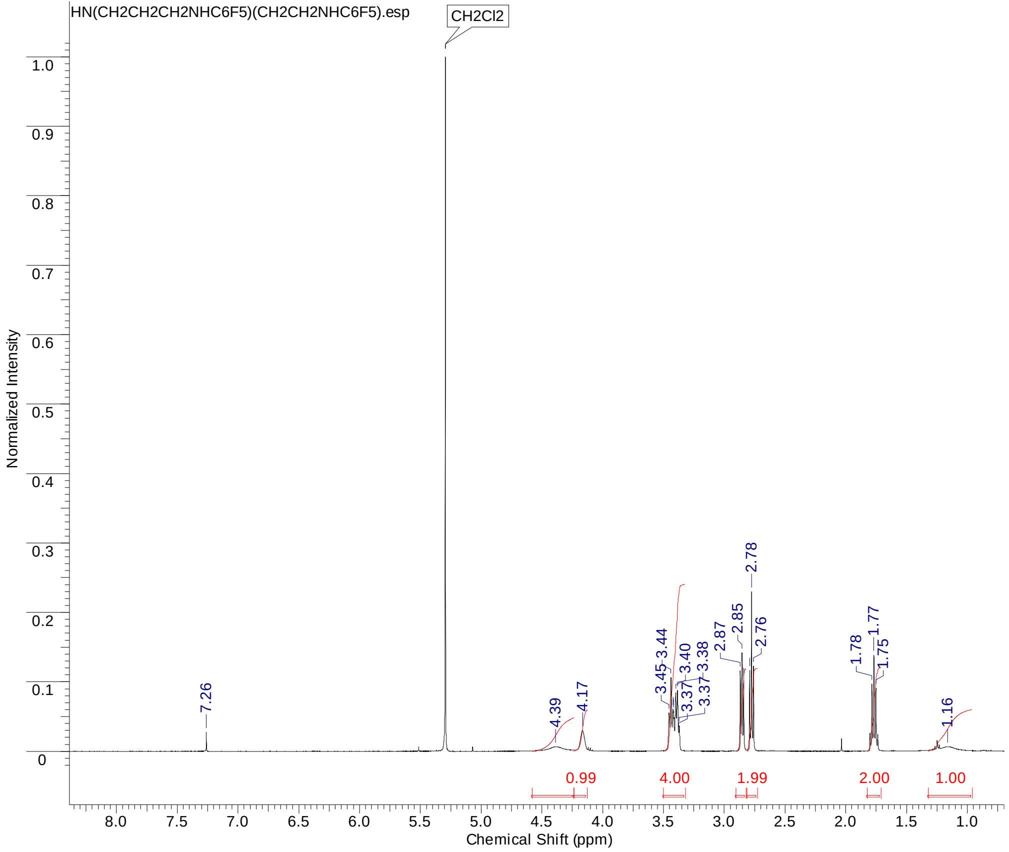
To a solution of $Zn[N(SiMe_3)_2]_2$ (0.49 g, 1.28 mmol) in toluene (5 ml) in a round-bottom Schlenk flask, ligand **1d** (0.69 g, 1.28 mmol) in toluene (13 ml) was added at room temperature. The mixture was stirred at 95°C for 12 h. After cooling to room temperature, formation of light brown needle crystals was observed. The precipitate was filtered and washed with hexane (3×5 ml) and dried *in vacuo* to afford **2d** (0.48 g, 58% from theory $2C_{24}H_{17}N_3F_{10}Zn{*}C_7H_8$) as a white powder. Single crystals were obtained by cooling of hot toluene solution.

NMR ^{1}H (δ, ppm, DMSO-d$_6$): 1.59–1.73 (m, 2H, CH_2), 1.80–1.94 (m, 2H, CH_2) 2.54–2.66 (m, 2H, CH_2), 2.76–2.88 (m, 2H, CH_2), 3.34–3.46 (m, 1H, CH_2), 3.57–3.70 (m, 2H, CH_2), 3.70–3.79 (m, 1H, CH_2), 3.82 (d, 1H, J=13.7 Hz, PhCH_2), 4.05 (d, 1H, J=13.7 Hz, PhCH_2), 7.33–7.43 (m, 5H, *Ph*). NMR ^{13}C (δ, ppm, DMSO-d$_6$): 27.99, 44.95, 52.41, 54.62, 55.98, 57.92 (CH_2), 128.04, 128.07, 131.56, 132.18 (*Ph*). NMR ^{19}F (δ, ppm, DMSO-d$_6$): -186.47–(-186.19) (m, 1F), -184.88–(-184.61) (m, 1F), -168.50–(-168.18) (m, 4F), -164.62–(-164.31) (m, 2F), -161.68–(-161.37) (m, 2F). Elemental analysis: Calcd. ($C_{24}H_{17}N_3F_{10}Zn$): C, 47.82; H, 2.84; N, 6.97. ($2C_{24}H_{17}N_3F_{10}Zn{*}C_7H_8$: C, 50.90; H, 3.26; N, 6.48) Found: C, 49.83; H, 3.50; N, 6.53 %.

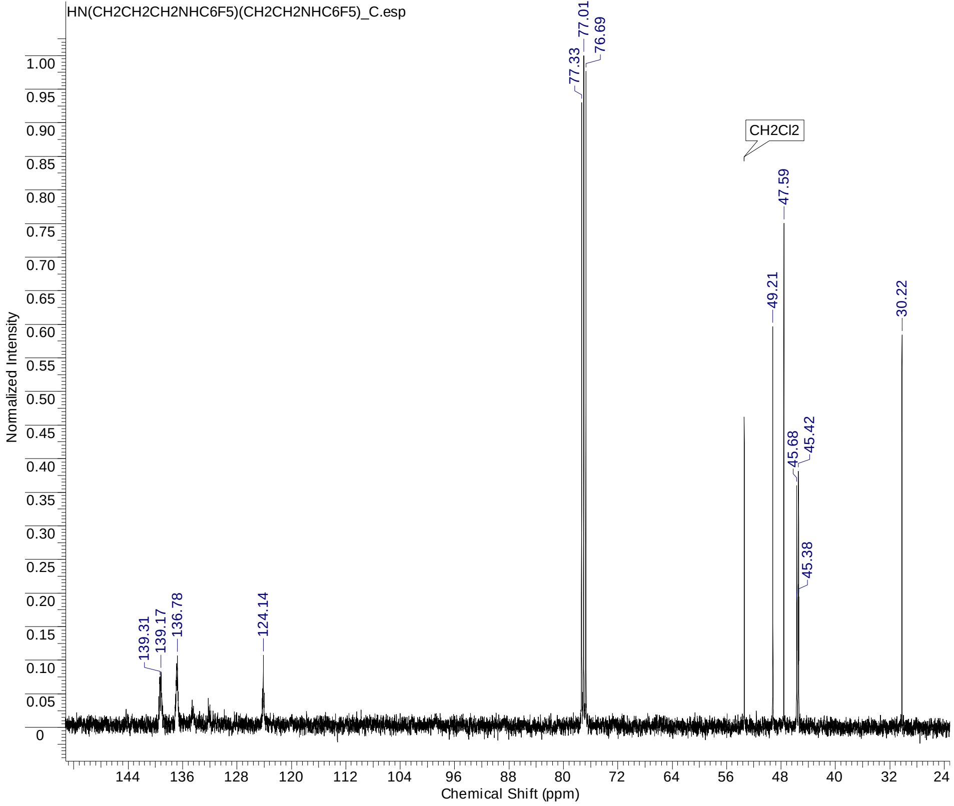
General Procedure for polymer synthesis. Under argon, a Schlenk flask was charged with catalyst **2b** (0.0724 g, 0.114 mmol), ε-caprolactone (1.4035 g, 12.29 mmol). The flask was transferred to an oil bath with temperature adjusted to 95°C. Conversion was analyzed by taking an aliquot after 30 min from the beginning of reaction and analyzed by ^{1}H NMR. After the completion of the reaction, the polymer was dissolved in a minimal amount of dichloromethane at heating and poured in a glass equipped with stirring bar with methanol (200 ml). Stirring was continued until the precipitate was formed. The precipitate was filtered off and dried *in vacuo*.

Spectra of the compounds

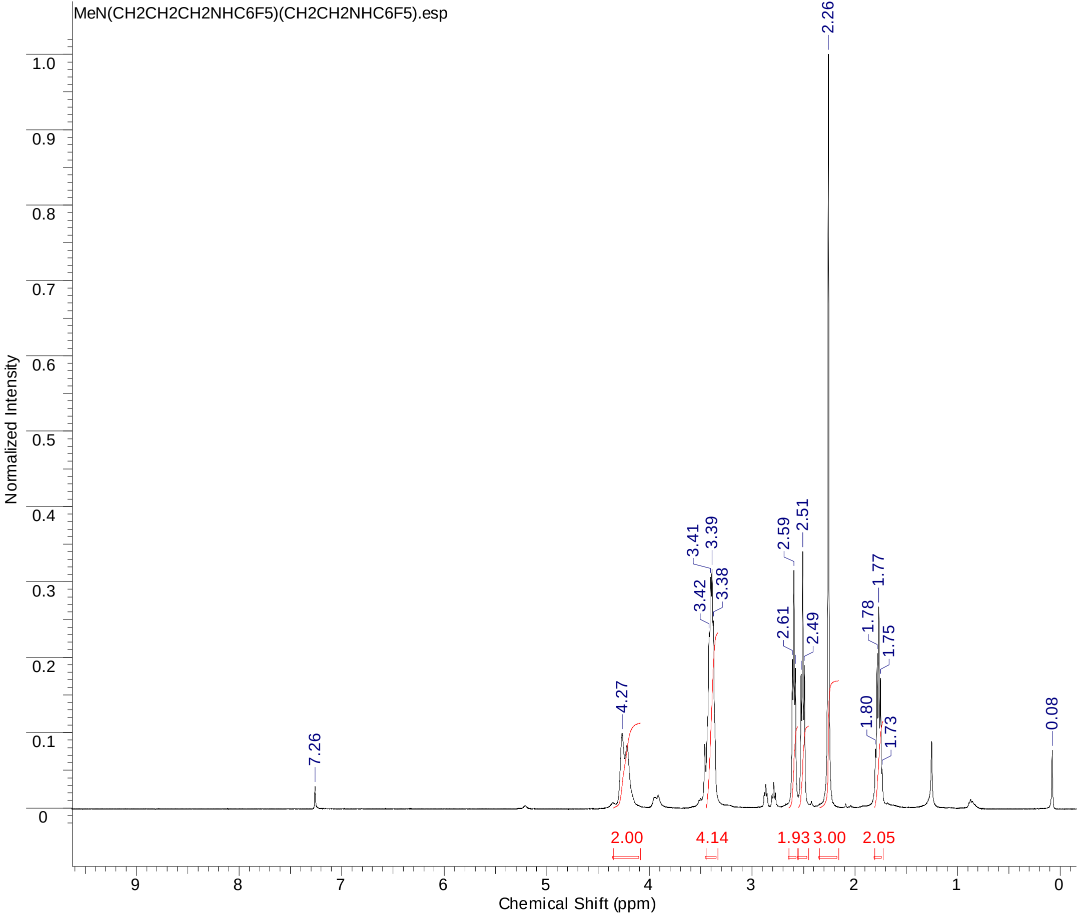
^{1}H spectrum for compound $HN(CH_2CH_2NHC_6F_5)(CH_2CH_2CH_2NHC_6F_5)$



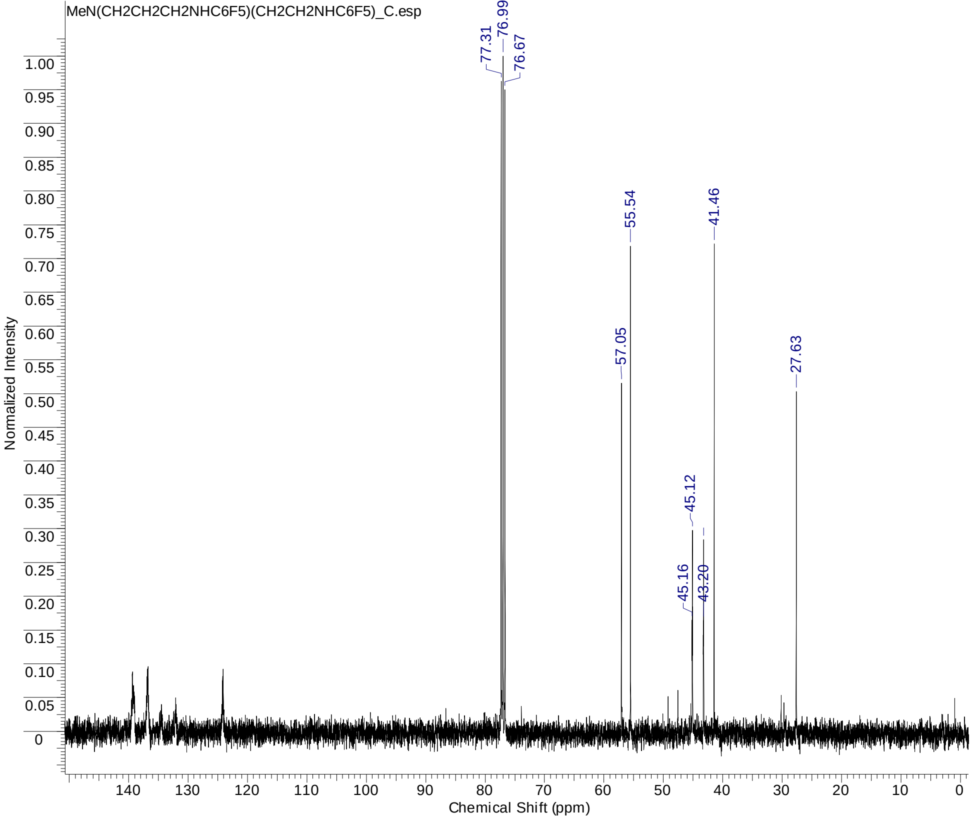
^{13}C spectrum for compound $HN(CH_2CH_2NHC_6F_5)(CH_2CH_2CH_2NHC_6F_5)$



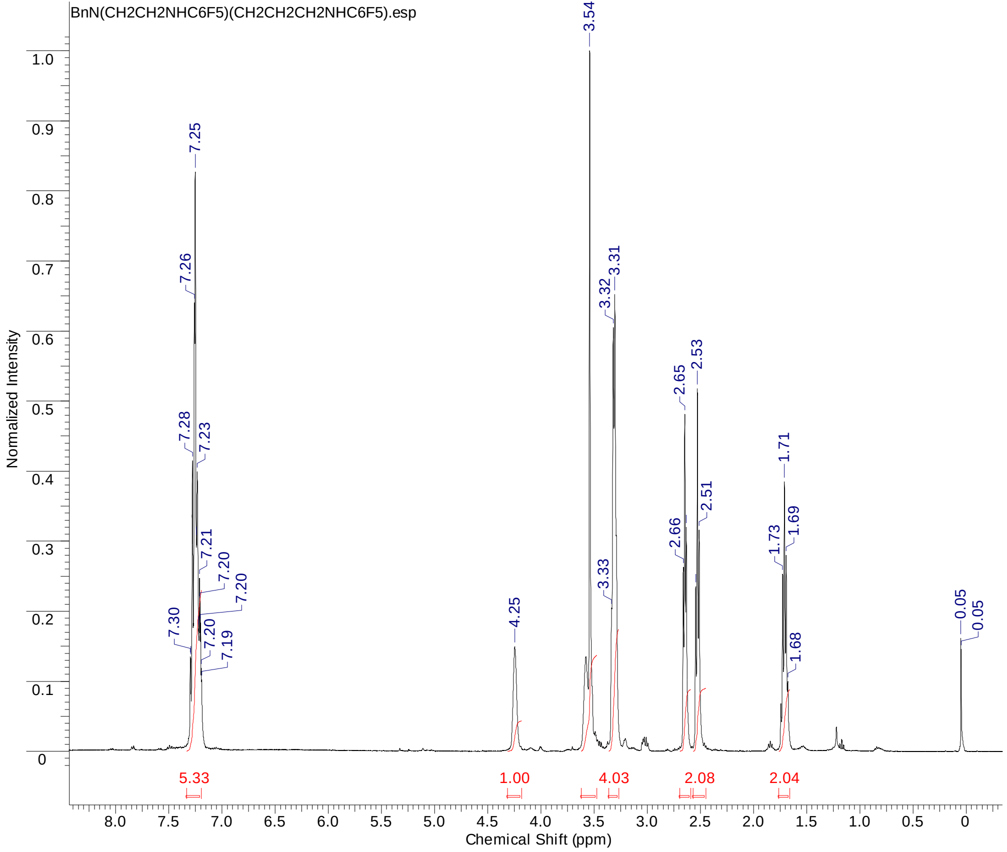
^{1}H spectrum of ligand 1c



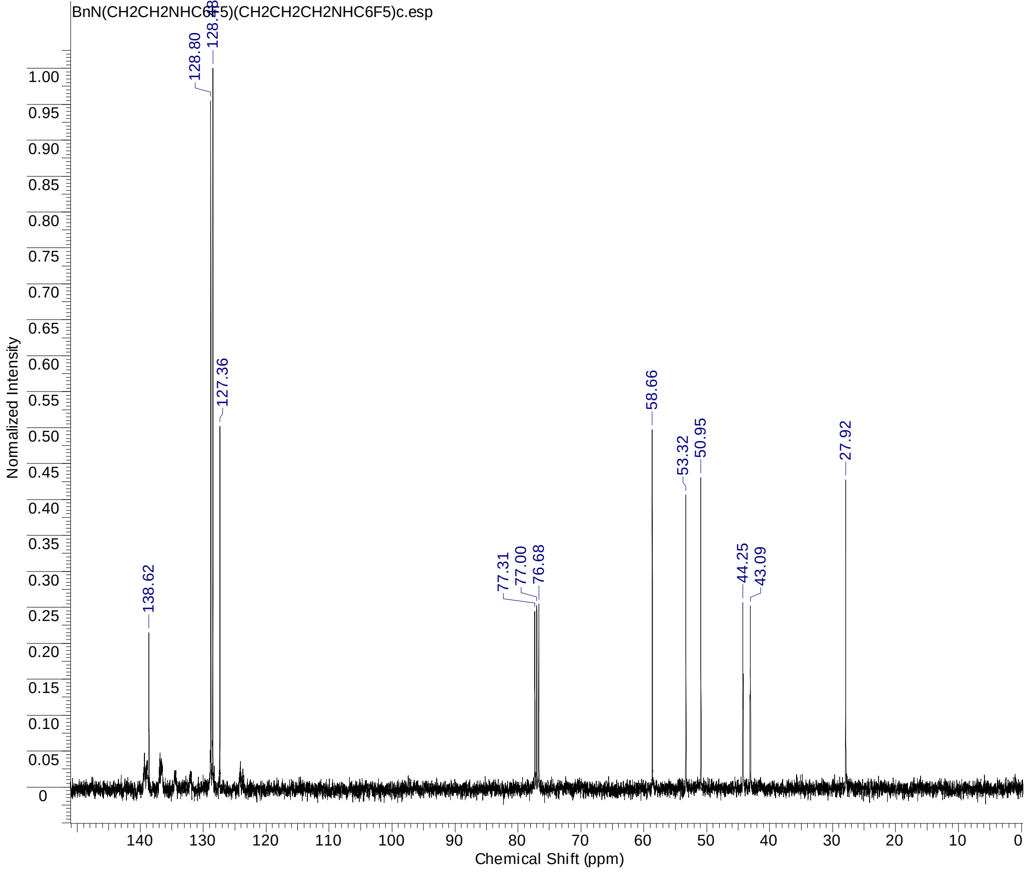
^{13}C spectrum of ligand 1c



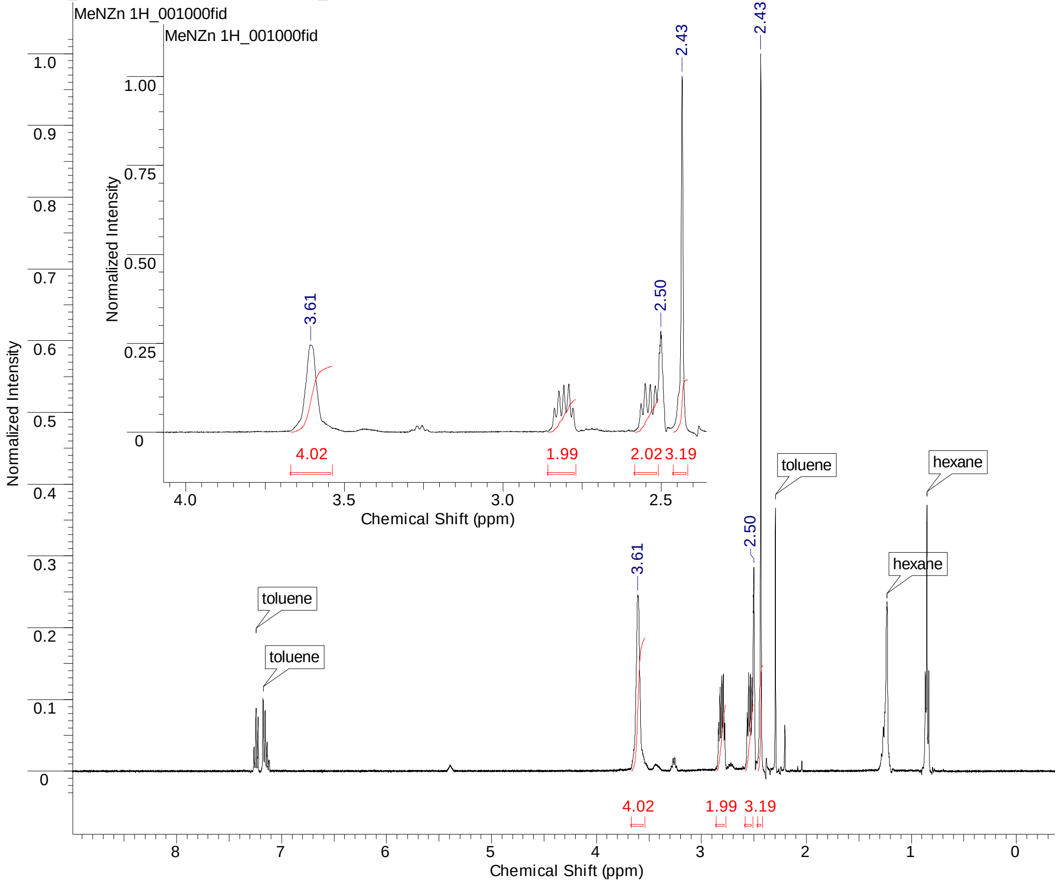
^{1}H spectrum of ligand 1d



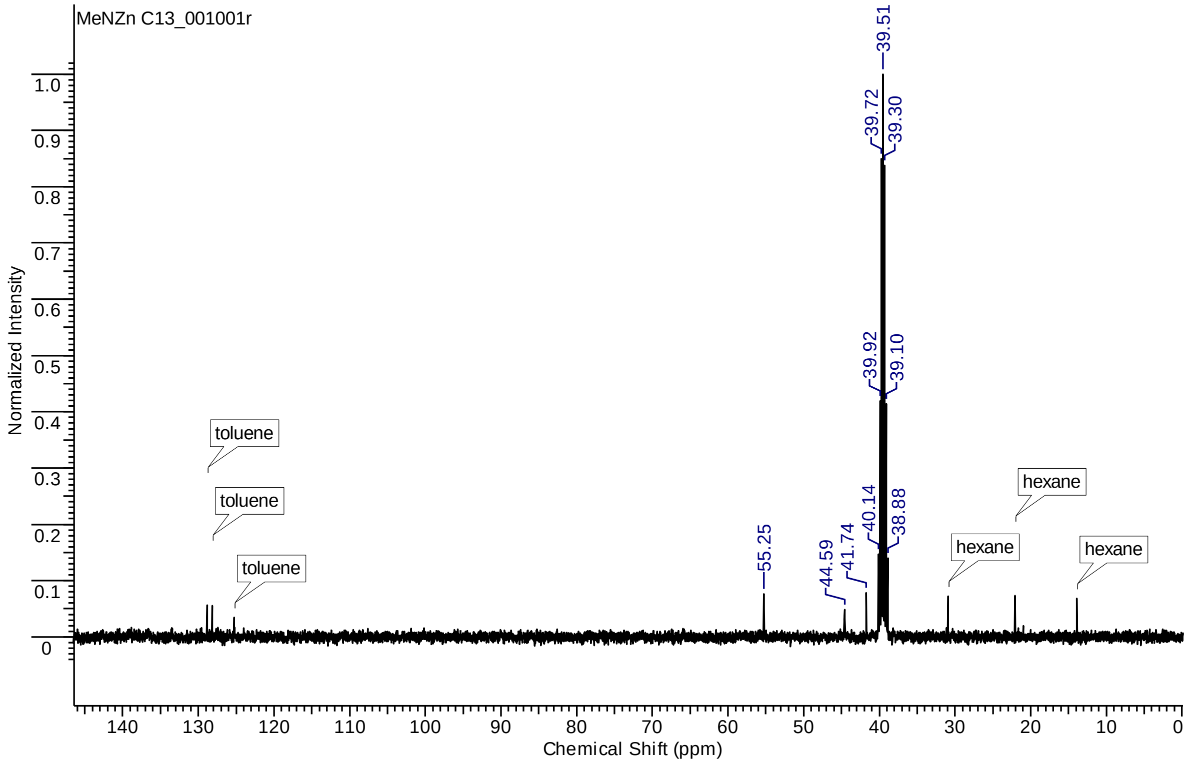
^{13}C spectrum of ligand 1d



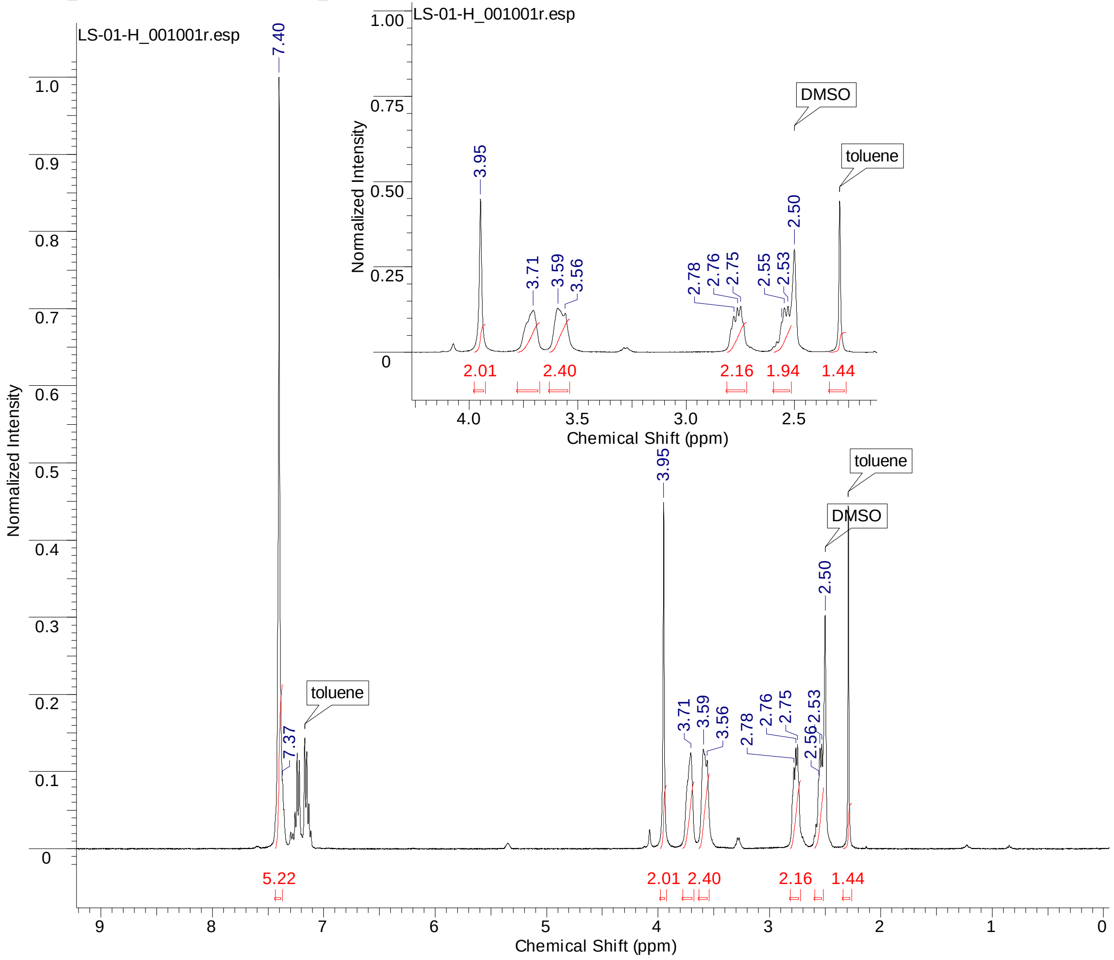
^{1}H spectrum of compound 2a



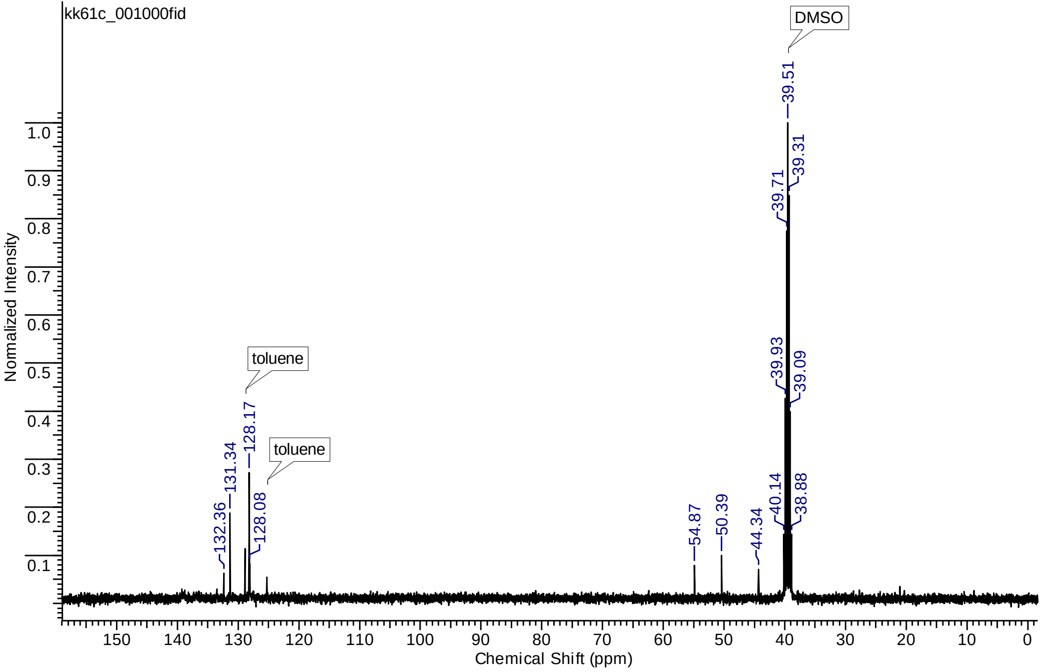
^{13}C spectrum of compound 2a



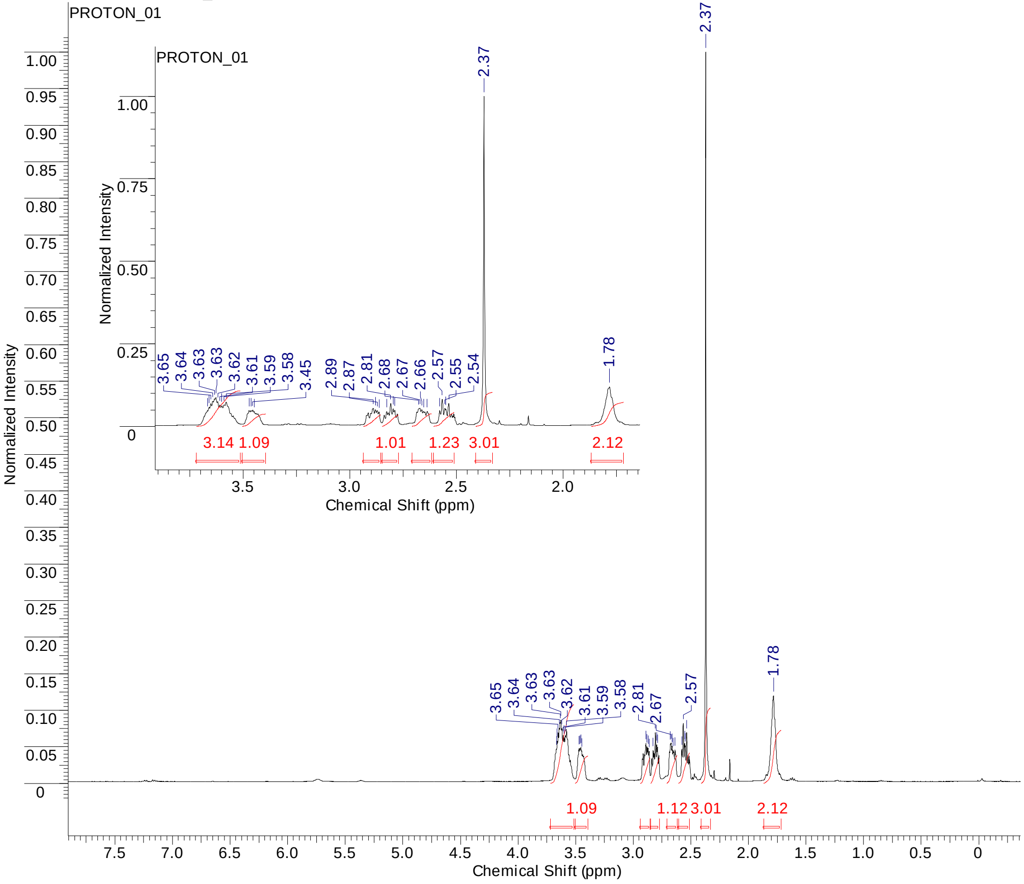
^{1}H spectrum of compound 2b



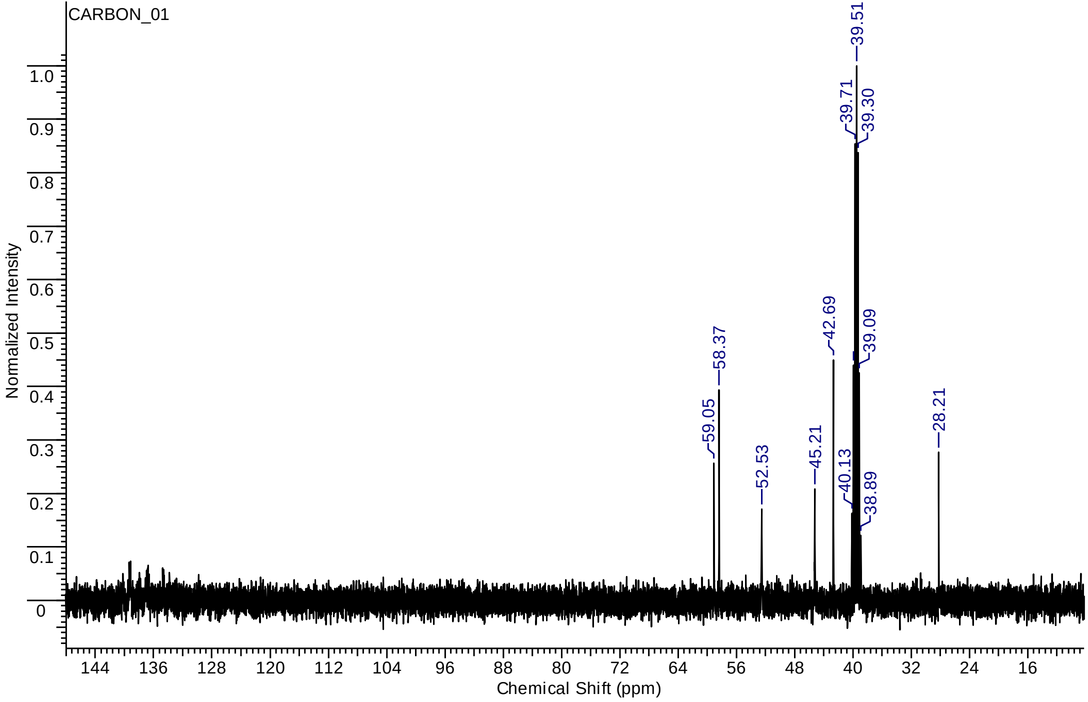
^{13}C spectrum of compound 2b



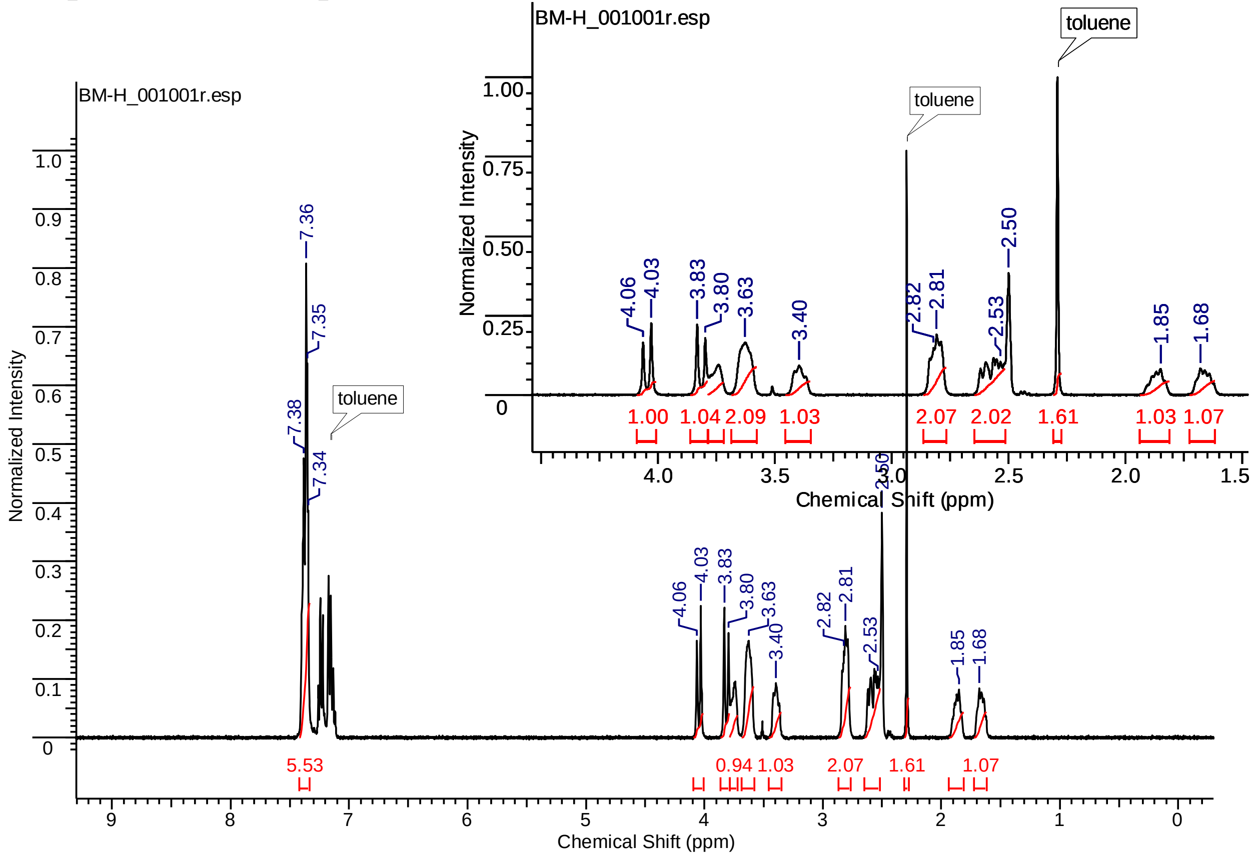
^{1}H spectrum of compound 2c



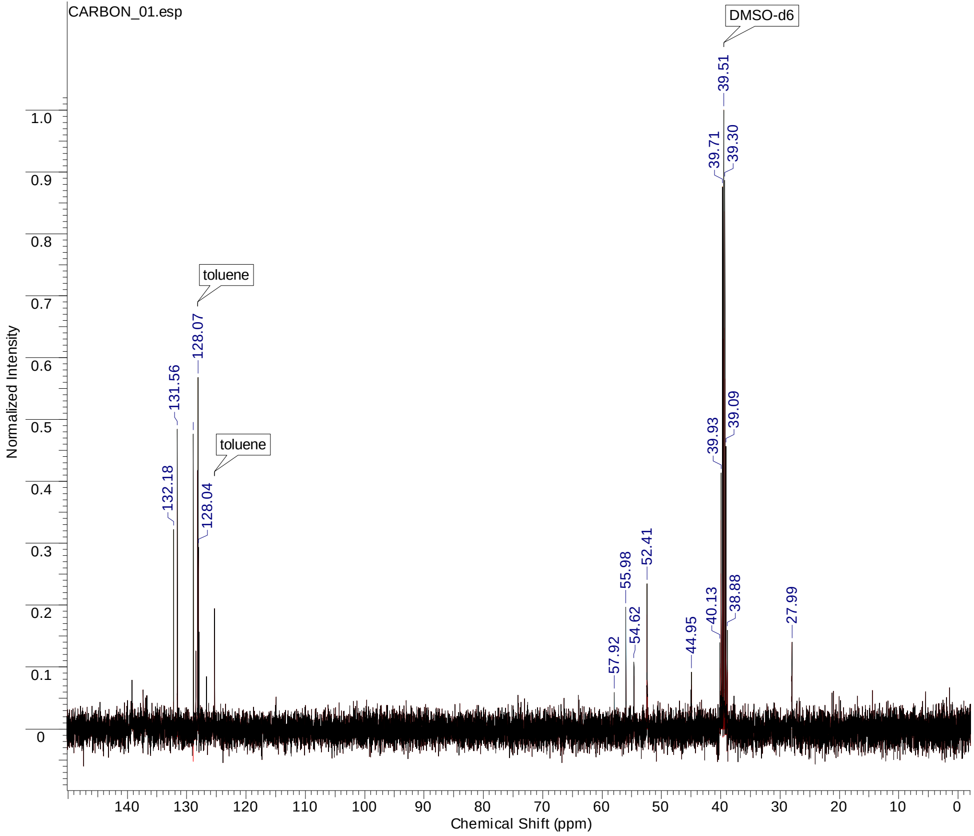
^{13}C spectrum of compound 2c



^{1}H spectrum of compound 2d



^{13}C spectrum of compound 2d



Selected bond lengths (Å) and angles (degrees) for 2d: Zn(1)-N(12) 1.940(2), Zn(1)-N(11) 2.073(2), Zn(1)-N(21) 2.093(2), Zn(1)-N(13) 2.167(2), Zn(2)-N(22) 1.937(2), Zn(2)-N(21) 2.065(2), Zn(2)-N(11) 2.085(2), Zn(2)-N(23) 2.187(2), N(12)-Zn(1)-N(11) 147.63(12), N(12)-Zn(1)-N(21) 115.31(10), N(11)-Zn(1)-N(21) 88.89(8), N(12)-Zn(1)-N(13) 87.26(9), N(11)-Zn(1)-N(13) 96.07(8), N(21)-Zn(1)-N(13) 125.26(8), N(22)-Zn(2)-N(21) 140.98(9), N(22)-Zn(2)-N(11) 118.63(9) N(21)-Zn(2)-N(11) 89.32(8), N(22)-Zn(2)-N(23) 85.52(9), N(21)-Zn(2)-N(23) 101.53(8), N(11)-Zn(2)-N(23) 123.90(8).