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Synthesis, Structure, and Catalytic Activity of Dinuclear Aluminium Bis(amidinate) and Bis(guanidinate) Complexes

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1. General

All inorganic preparations were performed under an inert atmosphere of dinitrogen by means of standard Schlenk-line techniques, while the samples for analytics were handled in a glovebox (GS-Systemtechnik and MBraun). Traces of oxygen and moisture were removed from the inert gas by passing it over a BASF R 3-11 ($CuO/MgSiO_3$) catalyst, through concentrated sulfuric acid, over coarsely granulated silica gel, and finally through P_4O_{10}. Dichloromethane, diethyl ether, and *n*-pentane were freshly collected from a solvent purification system by M. Braun (MB SPS- 800). D_6-Benzene and toluene were used as p.a. grade and were distilled from Na/benzophenone prior to use. $CDCl_3$ was dried by distillation from calcium hydride.

Pyrrolidine, lead(II)oxide, pivaloylchloride, PCl_5, ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, 1,3(aminomethyl)benzylamine, 2,6-diisopropylaniline, trimethylaluminium (2 M toluene), iodine and ethylaluminium dichloride (1.8 M toluene) were purchased from Sigma- Aldrich. The bis(amidines) (**1a**, **1b**, **1c**)[1] as well as the bis(guanidines) (**2a**, **2b**, **2c**, **2d**)[1,2] were prepared according to published procedures.

Characterization. The NMR spectra were recorded with a Bruker Avance 400 spectrometer (T = 300 K) with δ referenced to external tetramethylsilane (^1H, ^{13}C, and ^{27}Al). ^1H and ^{13}C NMR spectra were calibrated by using the solvent residual peak ($CHCl_3$: δ(^1H) = 7.26) or (C_6D_6: δ(^1H) = 7.16) and the solvent peak ($CDCl_3$: δ(^{13}C) = 77.16) or (C_6D_6: δ(^{13}C) = 128.06), respectively. ^{27}Al NMR spectra were calibrated relative to external $Al(NO_3)_3{\cdot}9H_2O$. Notably, the broad resonance at about 60 ppm is a background signal associated with the probe. IR spectra were recorded with a Bruker ALPHA spectrometer equipped with a diamond ATR unit. Elemental analysis was performed with a Vario MICRO cube (Elementar Analysensysteme GmbH); the presence of residual solvent molecules was verified by ^1H NMR spectroscopy.

Size exclusion chromatography (SEC) was performed using a Shimadzu SEC system equipped with a LC-10AD vp pump, a RID-10A detector and a PSS SDV guard/linear M column. THF was used as eluent and a flow rate of 1 mL/min at 30 °C was applied. The instrument was calibrated using PLA or PS standards. Data was processed using WinGPC version 8.32.

2. Protio-ligand synthesis

Synthesis of N,N'-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanamide): A solution of pivaloylchloride (14.5 g, 120 mmol) in dichloromethane (30 mL) was added dropwise to a solution of 1,3(aminomethyl)benzylamine (8.16 g, 60.0 mmol) and trimethylamine (12.1 g, 120 mmol) in dichloromethane (400 mL). After stirring for three days at room temperature and 5 h under reflux, water (200 mL) was added to the white suspension giving a colorless biphasic solution. The organic phase was separated and washed with water (200 mL) and brine (200 mL). The product was dried over Na_2SO_4 and the solvent was removed yielding *N,N'*-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanamide) (17.5 g, 57.0 mmol, 96%) in analytically pure form as a white crystalline solid.

^{1}H-NMR (400 MHz, $CDCl_3$): *δ (ppm)* = 1.19 (s, 18 H, C(C*H*$_3$)$_3$), 4.35 (d, 65.7 Hz, 4 H, (C$_6$*H*$_4$)(C*H*$_2$)$_2$), 6.13 (s, 2 H, N*H*), 7.09 (d, *J* = 7.5 Hz, 2 H, CHC$_2$(C*H*)$_2$CH), 7.12(s, 1 H, C*H*C$_2$(CH)$_2$CH) 7.24 (t, *J* = 7.5 Hz, 1 H, CHC$_2$(CH)$_2$C*H*); ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 27.7 (C(*C*H$_3$)$_3$), 38.7 (*C*(CH$_3$)$_3$), 43.4 (N*C*H$_2$C$_6$H$_4$), 126.5 (*m*-*C*$_6$H$_4$), 126.7 (*o*-*C*$_6$H$_4$), 129.1 (*o*-*C*$_6$H$_4$), 139.3 (*i*-*C*$_6$H$_4$), 178.5 ((CH$_3$)$_3$*C**C*(O)NH).

Synthesis of (1Z,1'Z)-*N',N''*-(1,3-phenylenebis(methylene))bis(2,2- dimethylpro-panimidoyl chloride): Phosphorus pentachloride (23.9 g, 114 mmol) was added portionwise to a stirred solution of *N,N'*-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanamide) (17.5 g, 57.3 mmol) in toluene (300 mL). The reaction mixture was stirred at 100 °C for two days giving a yellow solution. The solvent was removed *en vacuo* yielding (1Z,1'Z)-*N',N''*-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanimidoyl chloride) (14.4 g, 42.0 mmol, 74 %) in analytically pure form as a dark brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): *δ (ppm)* = 1.35 (s, 18 H, C(C*H*$_3$)$_3$), 4.73 (d, *J* = 4.8 Hz, 4 H, (C*H*$_2$)$_2$C$_6$H$_4$), 7.19-7.41 (m, 4H, C$_6$*H*$_4$); ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ (ppm)* = 28.5 (C(*C*H$_3$)$_3$), 43.9 (*C*(CH$_3$)$_3$), 56.7 (N*C*H$_2$C$_6$H$_4$), 126.0 (*m*-*C*$_6$H$_4$), 127.5 (*o*-*C*$_6$H$_4$), 128.5 (*o*-*C*$_6$H$_4$), 138.8 (*i*-*C*$_6$H$_4$), 153.7 ((CH$_3$)$_3$*C**C*(Cl)N).

Synthesis of (1Z,1'Z)-*N',N''*-(1,3-phenylenebis(methylene))bis(N-(2,6-diisopropyl-phenyl)- 2,2-dimethylpropanimidamide) (**1d**): A solution of 2,6-diisopropylaniline (14.9 g, 84.2 mmol) in toluene (40 mL) was added to a stirred solution of (1Z,1'Z)-*N',N''*-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanimidoyl chloride) (14.4 g, 42.1 mmol) in toluene (160 mL). The reaction mixture was refluxed for three days giving a pale brown suspension. The suspension was cooled down to room temperature and the solvent was removed *en vacuo* giving a pale brown waxy solid. The raw product was suspended in ethylacetate (1000 mL) and stirred with a saturated sodium carbonate solution (1200 mL) over 1h giving a clear brown organic phase. The organic phase was separated and dried over sodium sulfate. The solvent was removed giving at first a brown oil that turned into a brown waxy solid after 16 h. The product was recrystallized from MeCN yielding **1d** (12.3 g, 19.7 mmol, 47 %) in analytically pure form as a white crystalline solid.

^{1}H NMR (400 MHz, $CDCl_3$): *δ(ppm)* = 1.19 (d, *J* = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.20 (d, *J* = 6.9 Hz, 12 H, CH(C*H*$_3$)$_2$), 1.34 (s, 18 H, C(C*H*$_3$)$_3$), 3.03 (sept, *J* = 6.9 Hz, 4 H C*H*CH$_3$)$_2$), 3.73 (d, *J* = 5.1 Hz, 4 H, (C*H*$_2$)$_2$C$_6$H$_4$), 6.69-7.21 (m, 10H, C$_6$*H*$_4$ + C$_6$*H*$_3$); ^{13}C{H} NMR (101 MHz, $CDCl_3$): *δ(ppm)* = 22.5 (CH(*C*H$_3$)$_2$), 23.2 (CH(*C*H$_3$)$_2$), 28.5 (C(*C*H$_3$)$_3$), 29.3 (*C*H(CH$_3$)$_2$), 38.8 (*C*(CH$_3$)$_3$), 47.8 (*C*H$_2$(C$_6$H$_4$)*C*H$_2$), 121.1 (*m*-*C*$_6$H$_3$), 122.0 (*p*-*C*$_6$H$_3$), 126.7 (*m*-*C*$_6$H$_4$), 126.9 (*o*-*C*$_6$H$_4$), 129.1 (*o*-*C*$_6$H$_4$), 137.3 (*o*-C$_6$H$_3$), 139.6 (*i*-*C*$_6$H$_4$), 146.2 (*i*-C$_6$H$_3$), 156.4 (N*C*(C(CH$_3$)$_3$)N); IR (ATR): $\tilde{\nu}$ [cm^{-1}] 3442 (w), 2958 (m), 2866 (w), 1653 (s), 1429 (m), 777 (m), 754 (m), 694 (m); HR MS (ESI-TOF): $[M + H]^+$ for *m/z* $C_{42}H_{62}N_4$ 623.5052, found 623.5032.

3. Crystallographic data

The intensity data were collected on a GV-50 diffractometer with TitanS2 detector from Rigaku Oxford Diffraction (formerly Agilent Technologies) applying a Mo Kα radiation (λ = 0.71073 Å fot compound **5d**), an Cu Kβ radiation (λ =1.39222 Å for compound **6b**), and an Cu Kα radiation (λ = 1.54184 Å for all other compounds). Data were corrected for Lorentz and polarization effects; an analytical absorption corrections were applied to the data.[3] The structures were solved by direct methods (SHELXT)[4] and refined by full-matrix least squares techniques against Fo^2 (SHELXL-2018)[5]. All hydrogen atoms were included at calculated positions with fixed thermal parameters. The crystal of **5d** and **6b** contains large voids, filled with disordered solvent molecules. The size of the voids are 324 and 973 $Å^3$/unit cell, respectively. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE routine of the program PLATON[6] resulting in 78 and 170 electrons/unit cell, respectively. Additional, the crystal of **5d** was a non-merohedral twin. The twin law was determined by PLATON[6] to (-1.000 0.003 0.000) (0.000 1.000 0.000) (0.000 0.986 -1.000). The contribution of the main component were refined to 0.5015(7). All non-hydrogen atoms were refined anisotropically.[5] Crystallographic data as well as structure solution and refinement details are summarized in Table S1. OLEX2[7] was used for structure representations.

Supporting Information available: Crystallographic data (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC-2020619 for **3a**, CCDC-2020620 for **3c**, CCDC-2020621 for **4a**, CCDC-2020622 for **4b**, CCDC-2020623 for **4c**, CCDC-2020624 for **5a**, CCDC-2020625 for **5b**, CCDC-2020626 for **5c**, CCDC-2020627 for **5d**, CCDC-2020628 for **6b**, and CCDC-2020629 for **7d**. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [E- mail: deposit@ccdc.cam.ac.uk].

Table S1. Crystal data and refinement details for the X-ray structure determinations.

Compound	**3a**	**3c**	**4a**
formula	$C_{40}H_{68}Al_2N_4$	$C_{42}H_{72}Al_2N_4$	$C_{40}H_{66}Al_2N_6$
fw ($g \cdot mol^{-1}$)	658.94	686.99	684.94
T/°C	-150(2)	-150(2)	-150(2)
crystal system	monoclinic	monoclinic	monoclinic
space group	P 2_1/n	P 2_1/n	P 2_1/n
a/ Å	9.1318(2)	9.79107(15)	9.8164(2)
b/ Å	13.1042(3)	15.9345(2)	14.8423(2)
c/ Å	17.6741(3)	13.7124(3)	14.3275(3)
α/°	90	90	90
β/°	103.849(2)	93.7704(16)	96.659(2)
γ/°	90	90	90
V/Å^3	2053.49(8)	2134.72(6)	2073.40(7)
Z	2	2	2
ρ ($g \cdot cm^{-3}$)	1.066	1.069	1.097
μ (cm^{-1})	8.54	8.39	8.79
measured data	11805	22674	13771
Θ_{max} [°]	73.583	73.748	74.129
data with I > 2σ(I)	3693	3863	3569
unique data (R_{int})	3998/0.0188	4231/0.0353	4086/0.0299
wR_2 (all data, on F^2)[a)]	0.0936	0.0962	0.0961
R_1 ($I > 2\sigma(I)$) [a)]	0.0337	0.0349	0.0355
S [b)]	1.036	1.046	1.046
Res. dens./$e \cdot Å^{-3}$	0.278/-0.217	0.281/-0.224	0.291/-0.237
absorpt method	gaussian	gaussian	gaussian
absorpt corr $T_{min}/_{max}$	0.918/0.952	0.868/0.947	0.901/0.942
CCDC No.	2020619	2020620	2020621

Continued Table S1. Crystal data and refinement details for the X-ray structure determinations.

Compound	**4b**	**4c**	**5a**	**5b**
formula	$C_{41}H_{68}Al_2N_6$	$C_{42}H_{70}Al_2N_6$	$C_{36}H_{56}Al_2I_4N4$	$C_{37}H_{58}Al_2I_4N_4$
fw ($g \cdot mol^{-1}$)	698.97	713.00	1106.40	1120.43
T/°C	-150(2)	-150(2)	-150(2)	-150(2)
crystal system	orthorhombic	monoclinic	triclinic	triclinic
space group	P c c n	P 2_1/n	P $\bar{1}$	P $\bar{1}$
a/ Å	29.8017(5)	10.1444(2)	9.5939(3)	10.2273(2)
b/ Å	18.1453(4)	15.2810(4)	10.3764(3)	13.8795(3)
c/ Å	15.8102(3)	14.1282(4)	12.9532(4)	17.1873(4)
α/°	90	90	75.031(3)	66.377(2)
β/°	90	91.173(2)	75.198(3)	86.7647(19)
γ/°	90	90	64.216(3)	87.4261(19)
V/Å^3	8549.5(3)	2189.65(9)	1106.42(7)	2231.06(10)
Z	8	2	1	2
ρ ($g \cdot cm^{-3}$)	1.086	1.081	1.661	1.668
μ (cm^{-1})	8.62	8.49	227.04	225.27
measured data	29700	14847	14271	25102
Θ_{max} [°]	74.662	73.552	74.011	74.341
data with I > 2σ(I)	7109	3925	4103	7720
unique data (R_{int})	8496/0.0279	4310/0.0232	4341/0.0420	8791/0.0469
wR_2 (all data, on F^2)[a)]	0.1167	0.0969	0.0805	0.0900
R_1 ($I > 2\sigma(I)$) [a)]	0.0415	0.0356	0.0290	0.0341
S [b)]	1.037	1.035	1.053	1.037
Res. dens./$e \cdot Å^{-3}$	0.271/-0.236	0.263/-0.200	0.931/-1.062	0.692/-0.911
absorpt method	gaussian	gaussian	gaussian	gaussian
absorpt corr $T_{min}/_{max}$	0.848/0.918	0.879/0.951	0.097/0.235	0.115/0.465
CCDC No.	2020622	2020623	2020624	2020625

Continued Table S1. Crystal data and refinement details for the X-ray structure determinations.

Compound	**5c**	**5d**	**6b**	**7d**
formula	$C_{38}H_{60}Al_2I_4N_4$	$C_{42}H_{60}Al_2I_4N_4$ [*]	$C_{37}H_{56}Al_2I_4N_6$ [*]	$C_{42}H_{60}Al_2Cl_4N_4$
fw ($g \cdot mol^{-1}$)	1134.46	1182.50 [*]	1146.43 [*]	816.70
°C	-150(2)	-150(2)	-150(2)	-150(2)
crystal system	monoclinic	Triclinic	orthorhombic	monoclinic
space group	P 2_1/n	P ī	P b c n	P 2_1/c
a/ Å	10.1421(2)	9.4936(3)	17.8187(3)	17.8904(2)
b/ Å	16.2451(3)	16.5995(4)	17.3288(2)	15.60507(14)
c/ Å	13.8772(3)	18.3183(5)	16.6003(3)	16.45733(19)
α/°	90	63.478(3)	90	90
ß/°	95.334(2)	85.190(3)	90	101.7305(12)
γ/°	90	89.826(3)	90	90
V/Å^3	2276.50(8)	2571.96(14)	5125.78(14)	4498.60(9)
Z	2	2	4	4
ρ ($g \cdot cm^{-3}$)	1.655	1.527 [*]	1.486 [*]	1.206
μ (cm^{-1})	220.85	24.87 [*]	145.93 [*]	30.15
measured data	13133	10326	47117	33016
Θ $_{max}$ [°]	73.316	25.146	74.377	73.413
data with I > 2σ(I)	4090	9320	6703	7842
unique data (R_{int})	4508/0.0339	10326/0.0224	7026/0.0533	8841/0.0233
wR_2 (all data, on F^2)[a]	0.0606	0.0854	0.0678	0.0801
R_1 ($I > 2\sigma(I)$) [a]	0.0251	0.0296	0.0256	0.0296
S [b]	1.024	1.030	1.052	1.038
Res. dens./e·Å^{-3}	0.563/-0.619	1.245/-0.632	1.128/-0.930	0.309/-0.381
absorpt method	gaussian	multi-scan	gaussian	gaussian
absorpt corr $T_{min}/_{max}$	0.165/0.399	0.93943/1.00000	0.059/0.344	0.525/0.768
CCDC No.	2020626	2020627	2020628	2020629

[*] derived parameters do not contain the contribution of the disordered solvent.

[a] Definition of the *R* indices: $R_1 = (\Sigma \,||F_o| - |F_c||)/\Sigma |F_o|$;

$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2) + (aP)^2+bP$; $P = [2F_c^2 + Max(F_O^2]/3$;

[b] $S = \{\Sigma[w(F_o^2-F_c^2)^2]/(N_o-N_p)\}^{1/2}$.

4. Cyclic voltammograms

All cyclic voltammetry measurements were performed in THF at 295 K using a three electrode setup, with a platinum disc electrode (working electrode, 3 mm diameter), a non-aqueous Ag/Ag+ electrode (pseudo-reference electrode) and a Pt-wire (auxiliary electrode), in combination with either a Potentiostat EmStat3+ by the company PalmSens, Compact Electrochemical Interfaces or *CHI 600E* Potentiostat by the company CH Instruments, Inc.. Bu_4NPF_6 (0.1 mol/L) was used as supporting electrolyte and all cyclic voltammograms are referenced against the Fc/Fc+ redox couple.

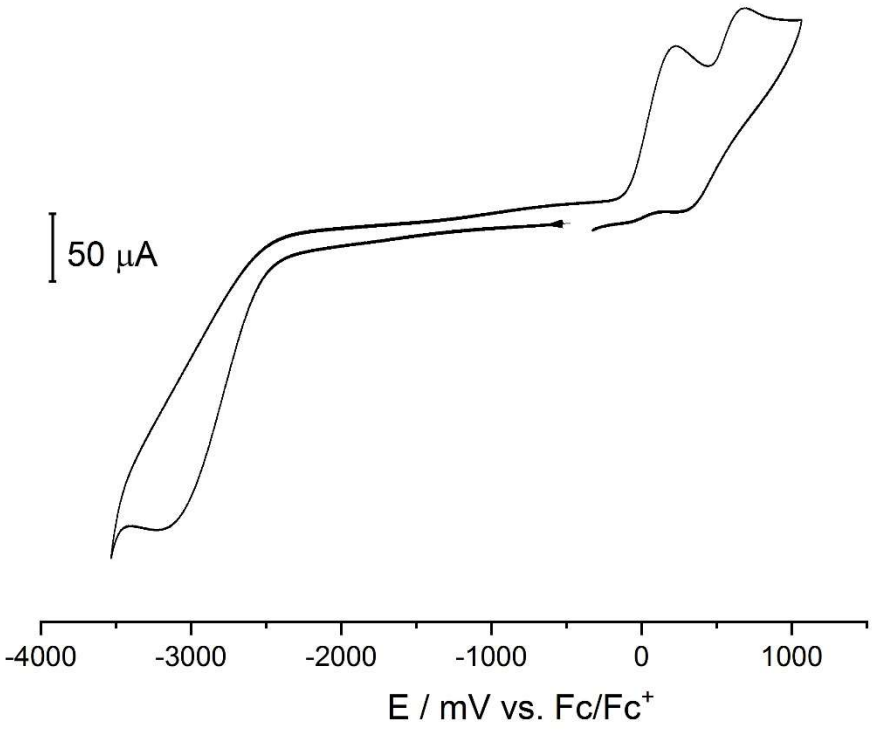

*Figure S1 Cyclic voltammogram of **5a** vs. Fc/Fc+.*

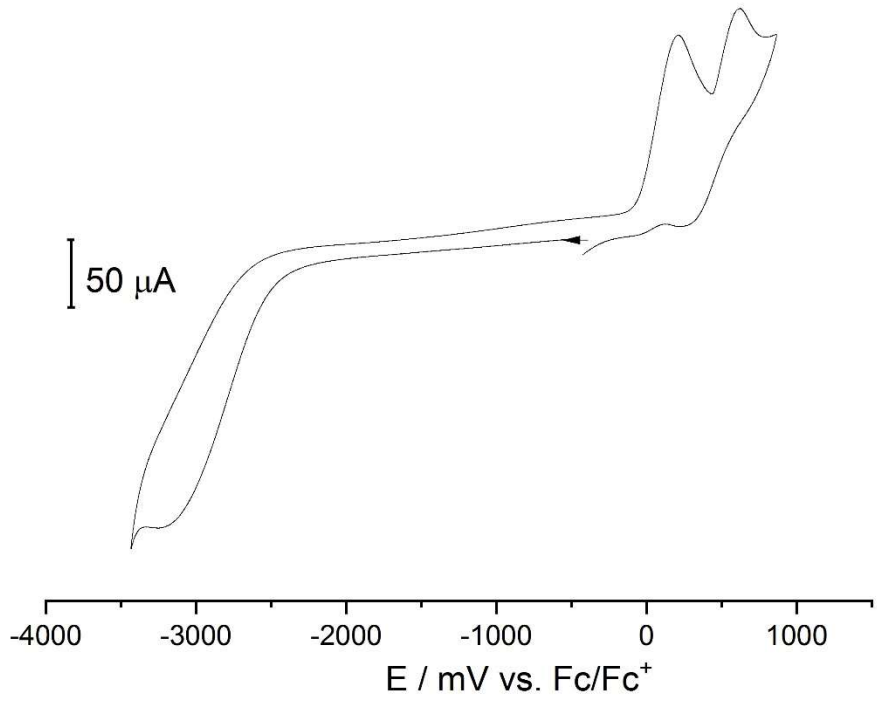

*Figure S2 Cyclic voltammogram of **5b** vs. Fc/Fc+.*

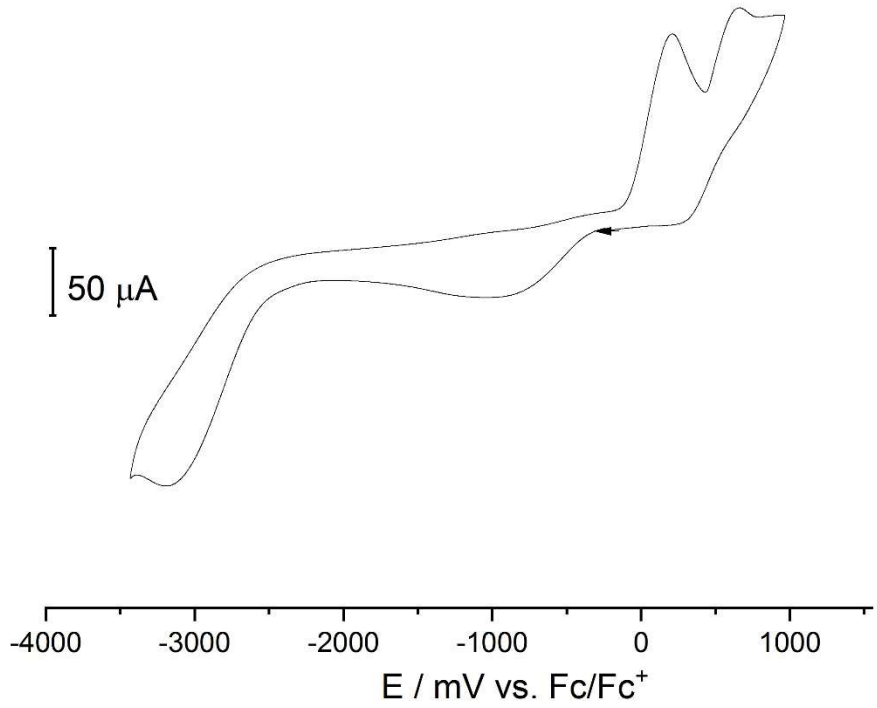

*Figure S3 Cyclic voltammogram of **5c** vs. Fc/Fc+.*

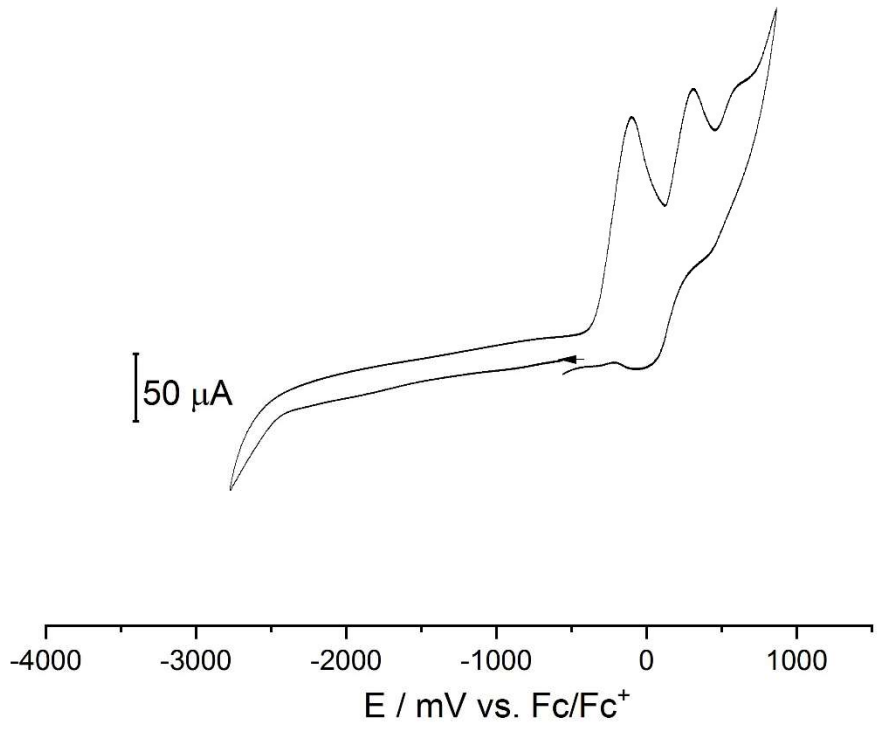

*Figure S4 Cyclic voltammogram of **5d** vs. Fc/Fc+.*

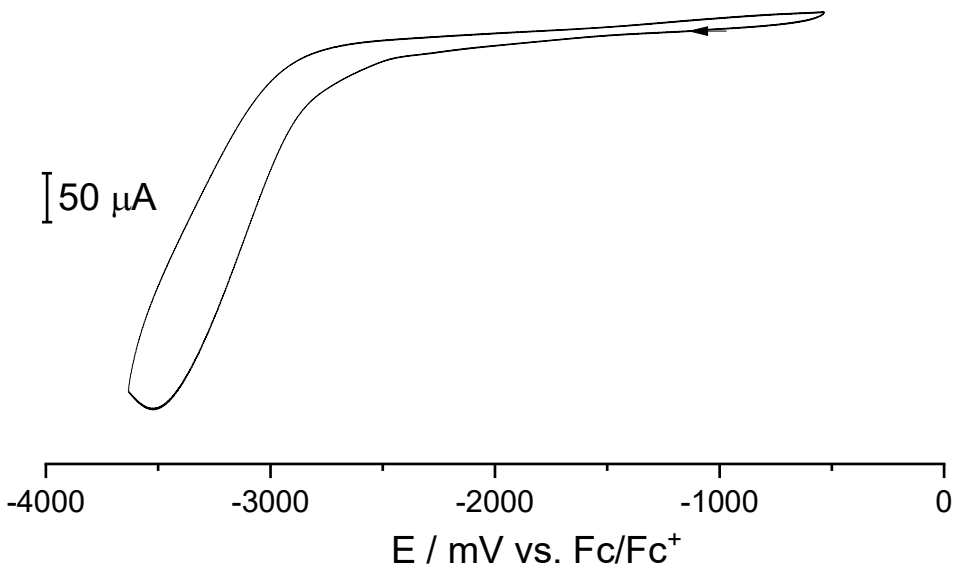

*Figure S5 Negative run of the cyclic voltammogram of **5d** vs. Fc/Fc+.*

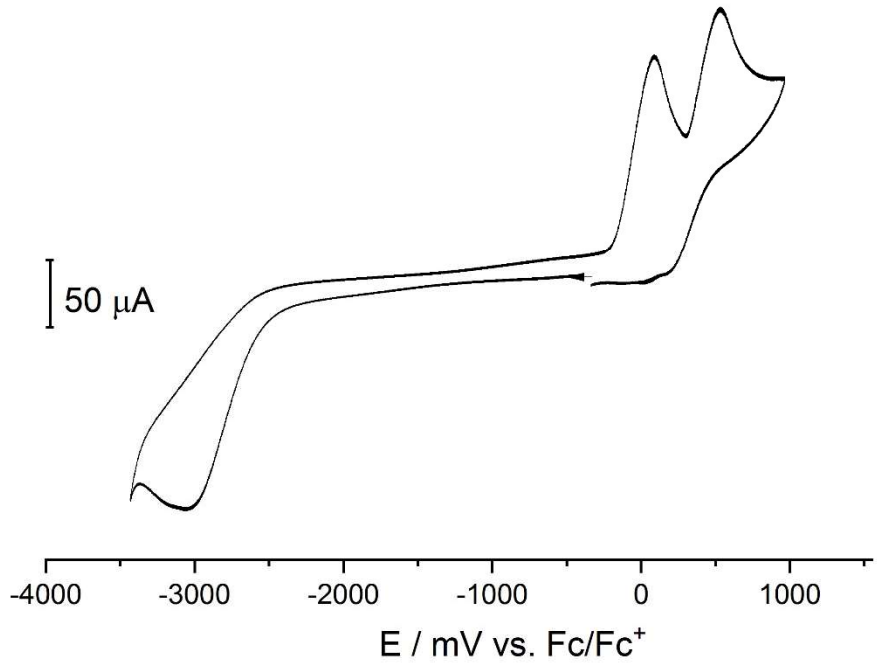

*Figure S6 Cyclic voltammogram of **6b** vs. Fc/Fc+.*

Table S2 Reduction potentials of the dinuclear aluminum complexes.

Compound number	Reduction potential [V]
5a	-3.23 V
5b	-3.25 V
5c	-3.20 V
5d	-
6b	-3.07 V

5. NMR and IR spectra

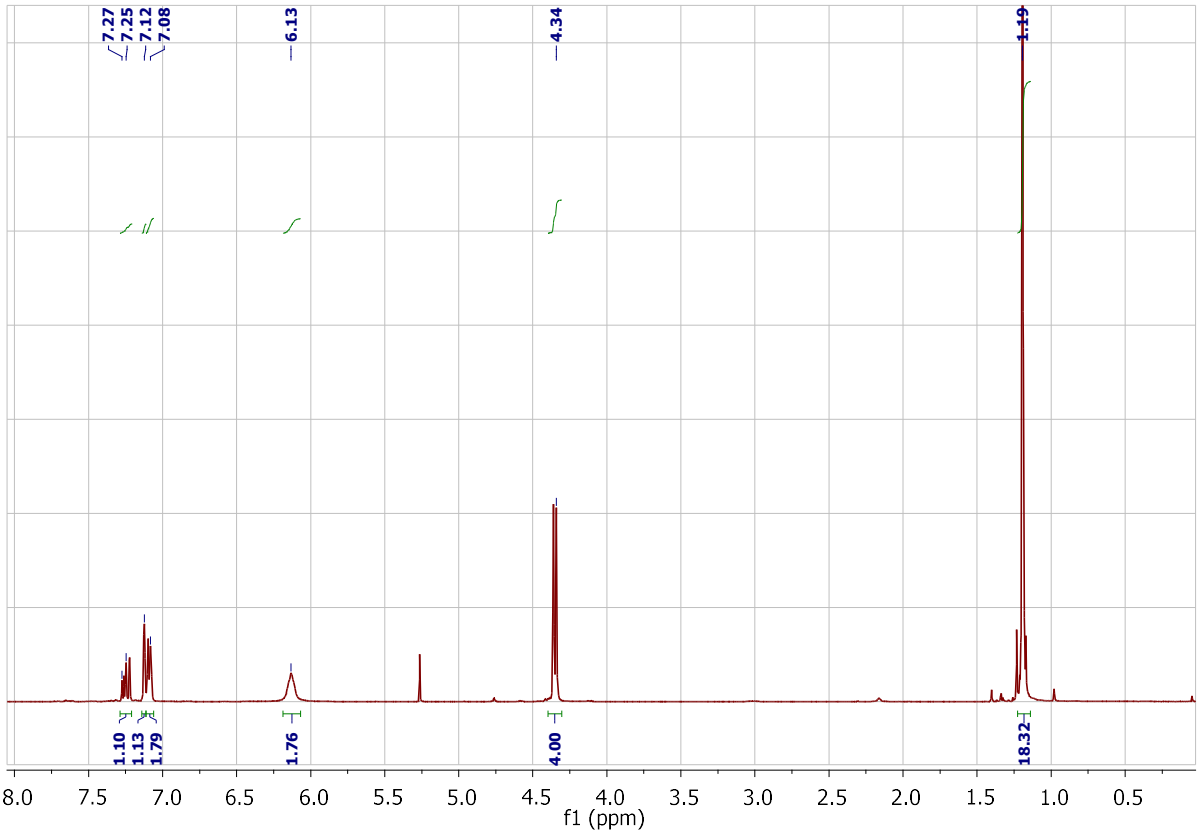

Figure S7 ^{1}H NMR spectrum (400 MHz) of N,N'-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanamide) in $CDCl_3$ at 300 K

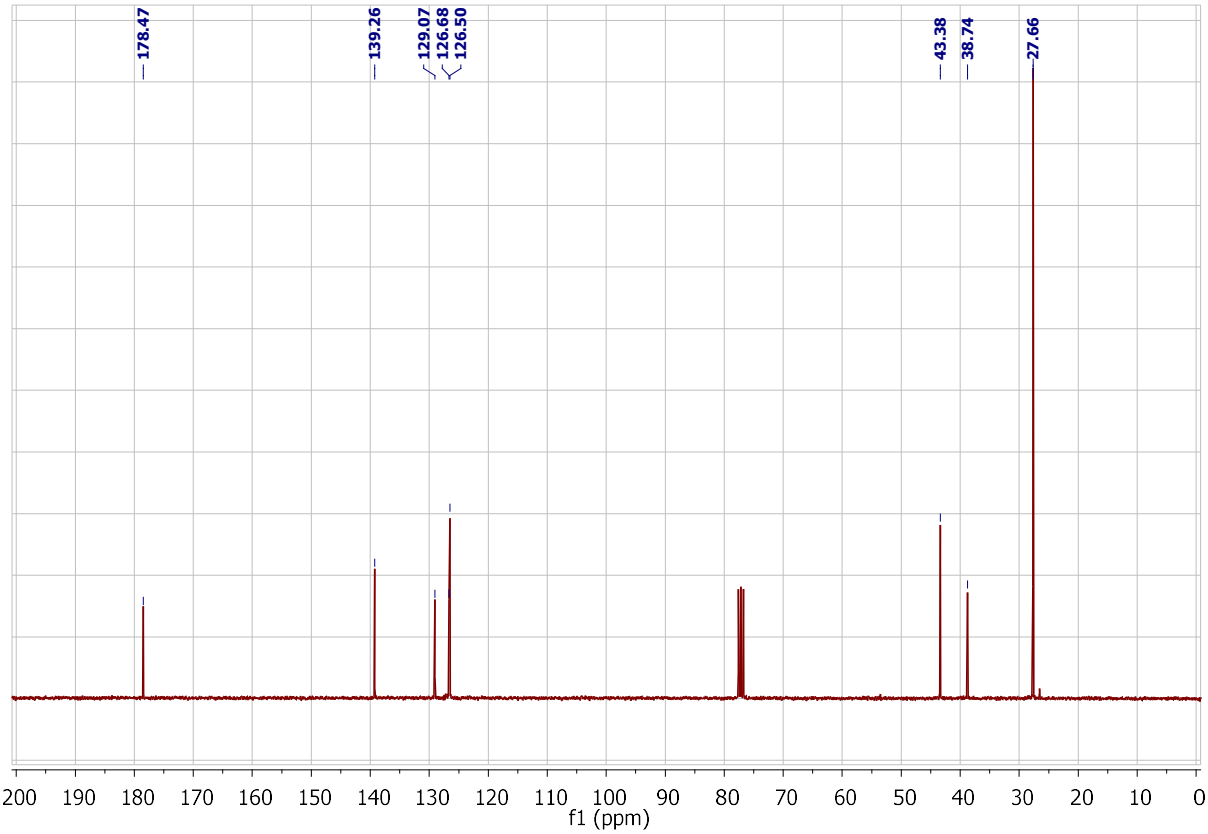

Figure S8 ^{13}C NMR spectrum (101 MHz) of N,N'-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanamide) in $CDCl_3$ at 300 K.

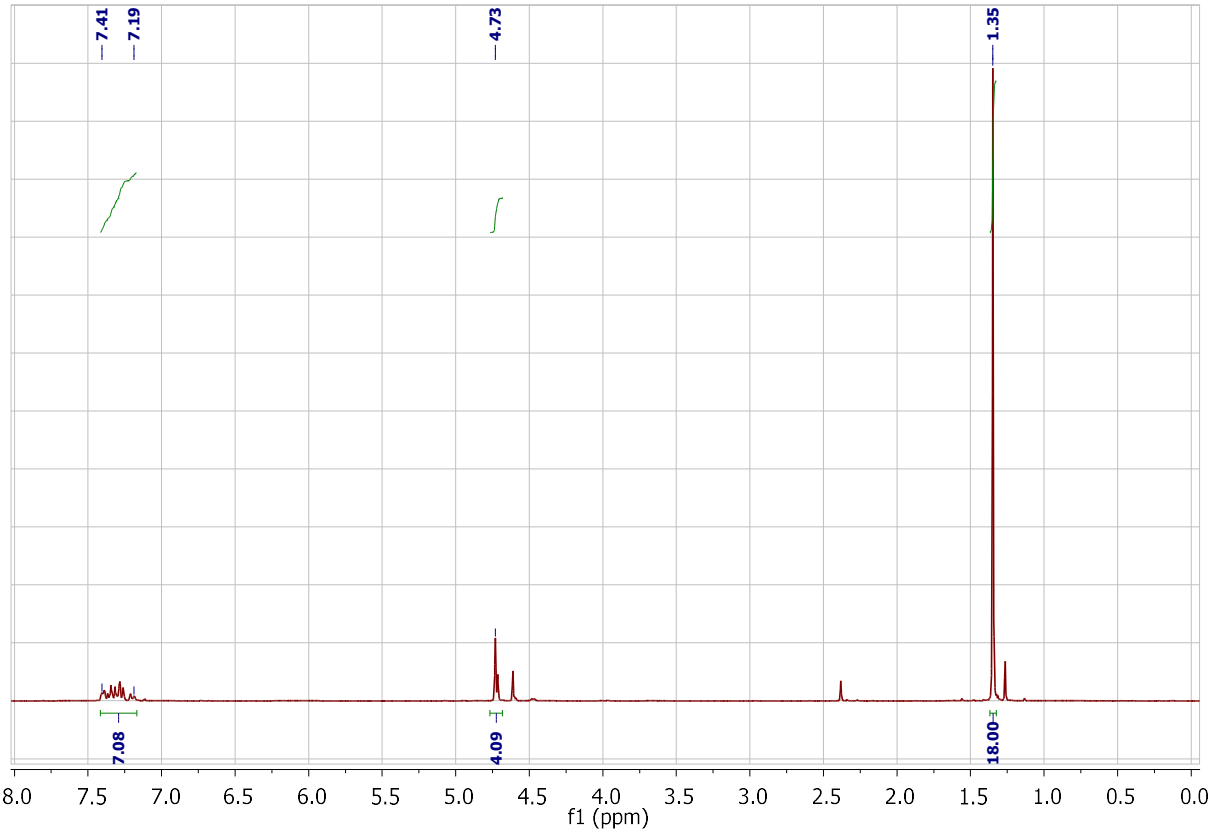

Figure S9 ^{1}H NMR spectrum (400 MHz) of (1Z,1'Z)-N',N''-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanimidoyl chloride) in $CDCl_3$ at 300 K.

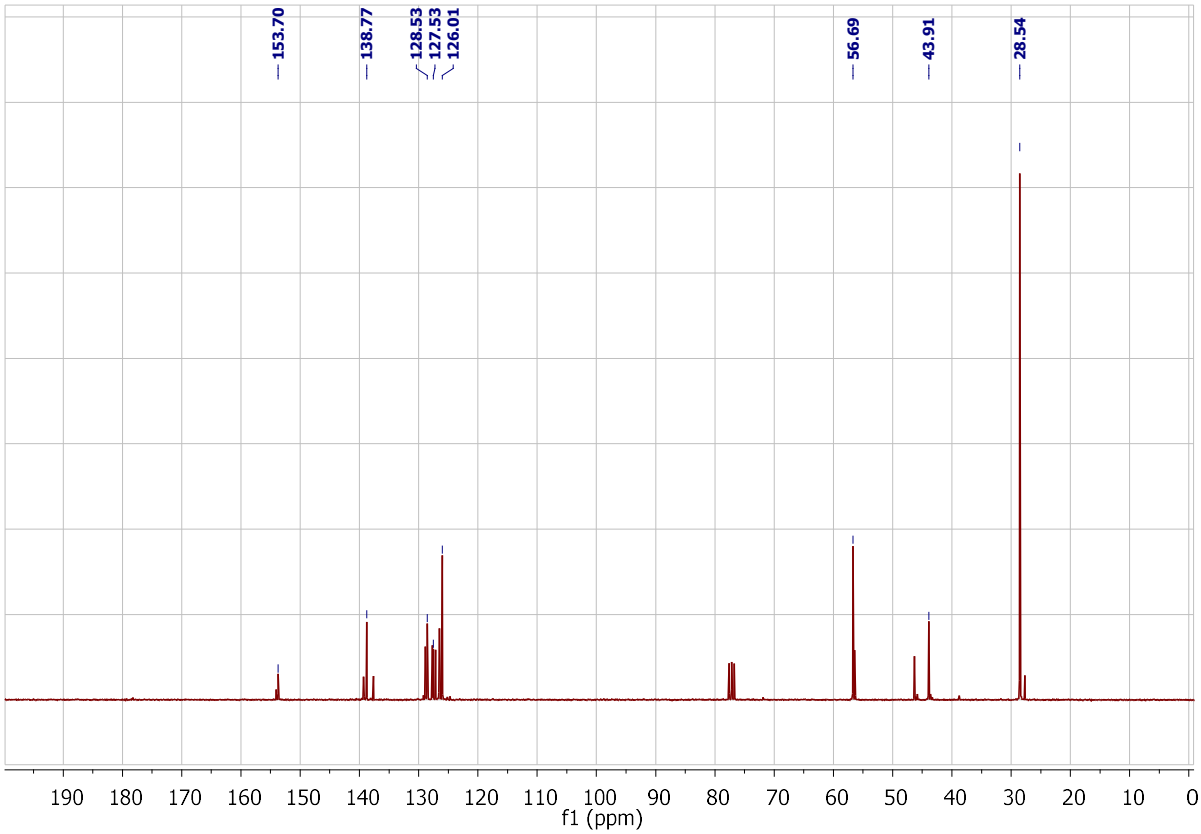

Figure S10 ^{13}C NMR spectrum (101 MHz) of (1Z,1'Z)-N',N''-(1,3-phenylenebis(methylene))bis(2,2-dimethylpropanimidoyl chloride) in $CDCl_3$ at 300 K.

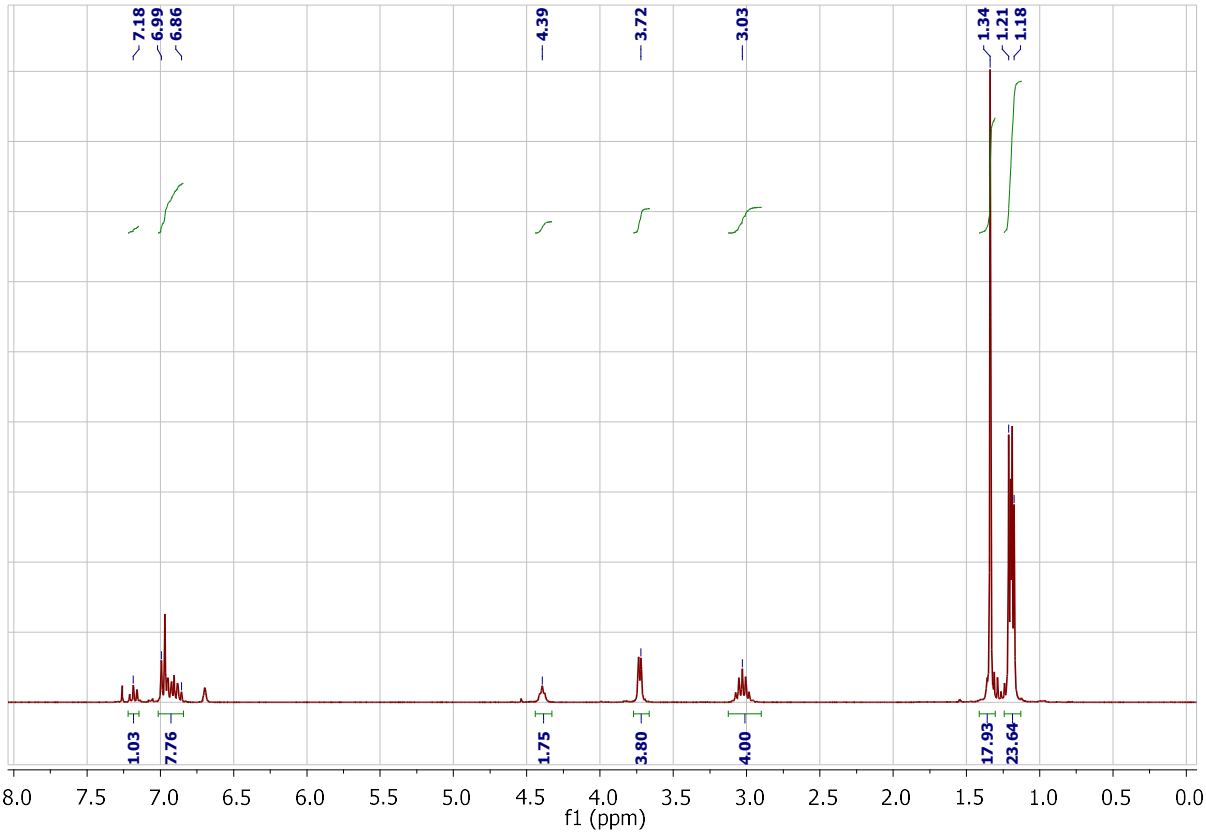

*Figure S11 ^{1}H NMR spectrum (400 MHz) of **1d** in $CDCl_3$ at 300 K.*

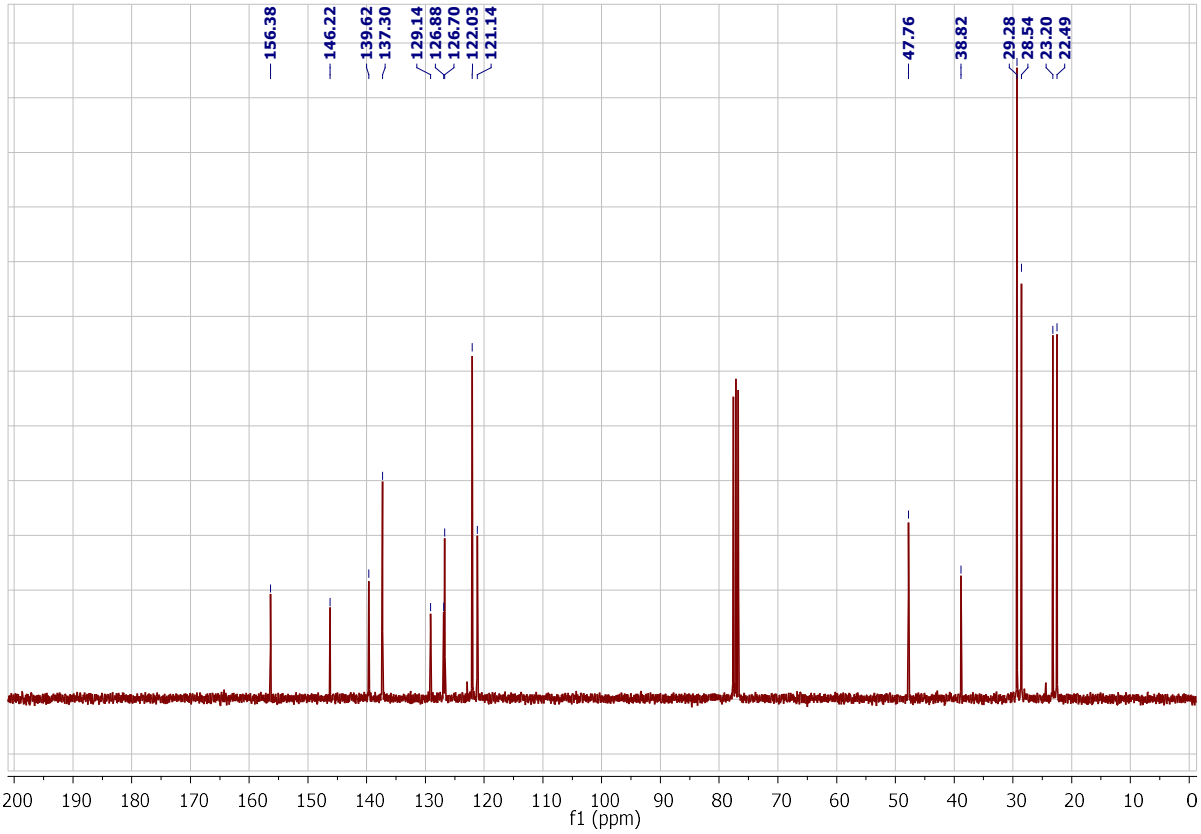

*Figure S12 ^{13}C NMR spectrum (101 MHz) of **1d** in $CDCl_3$ at 300 K.*

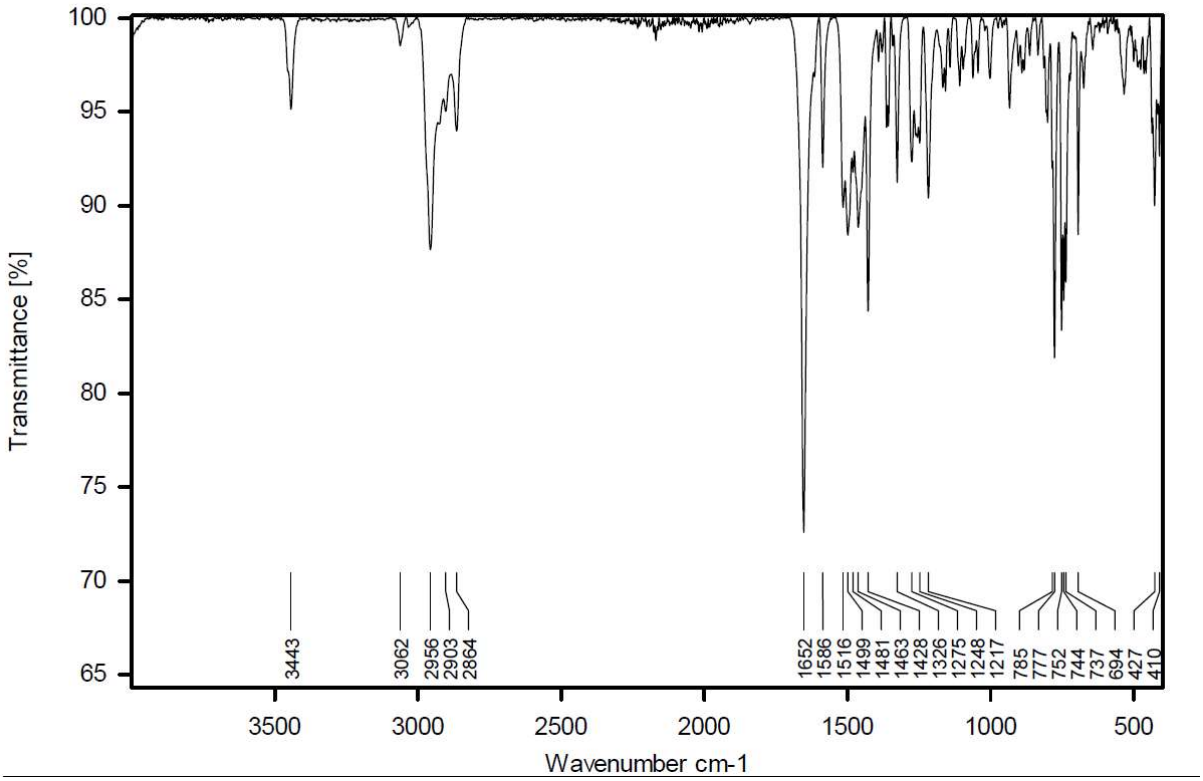

*Figure S13 ATR-IR spectrum of **1d**.*

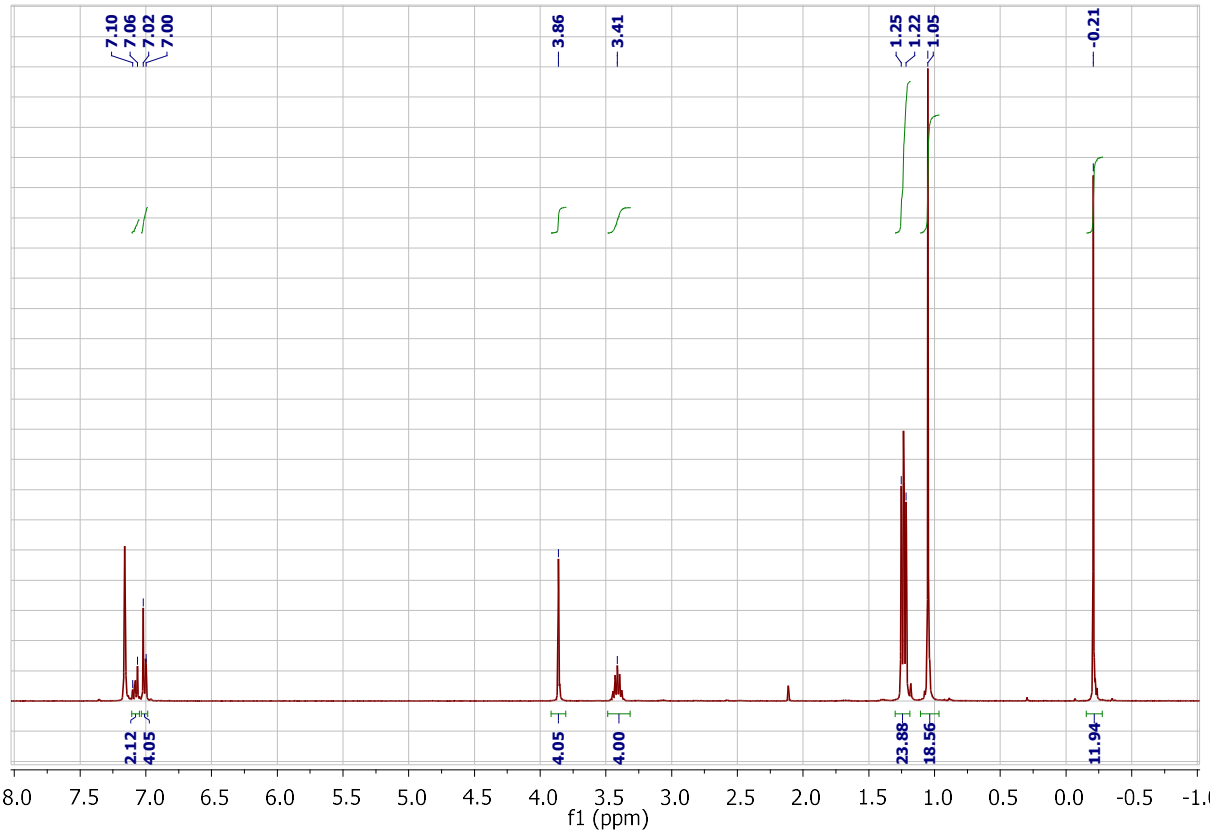

*Figure S14 ^{1}H NMR spectrum (400 MHz) of **3a** in C_6D_6 at 300 K.*

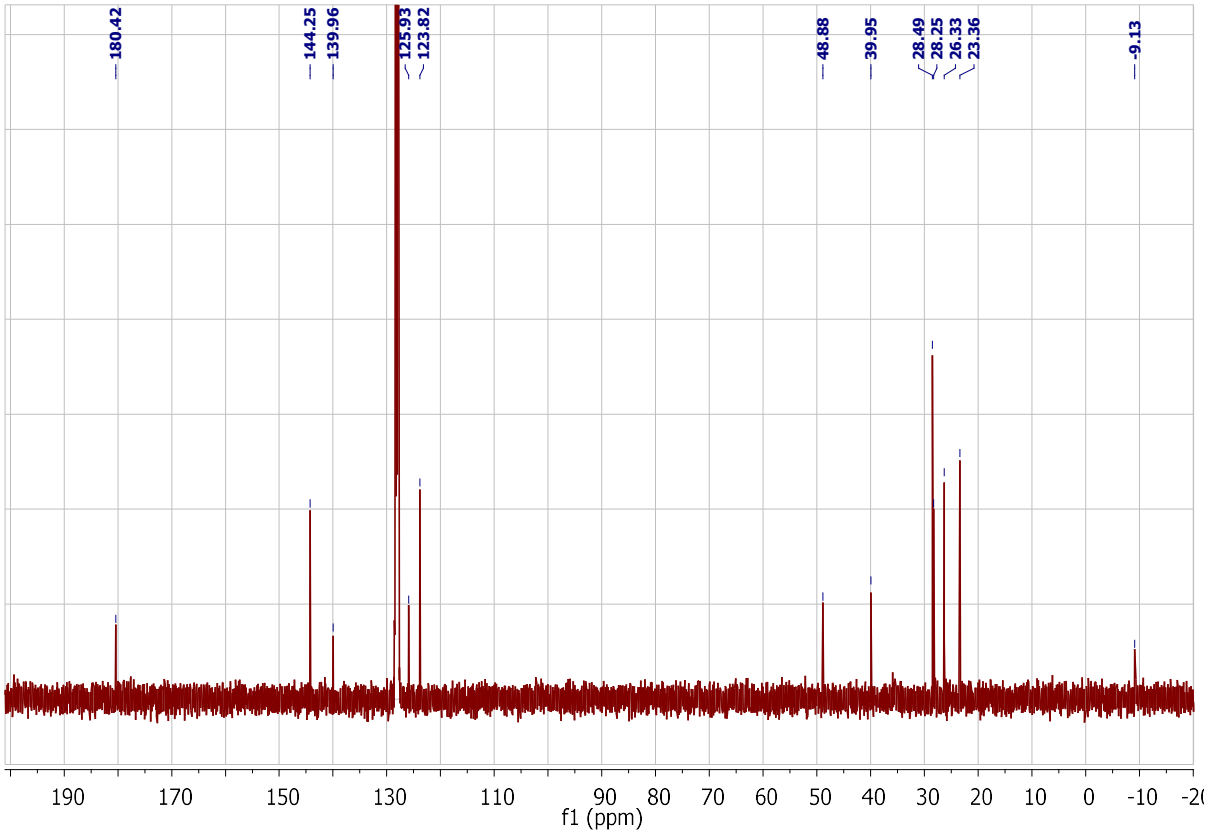

*Figure S15 ^{13}C NMR spectrum (101 MHz) of **3a** in C_6D_6 at 300 K.*

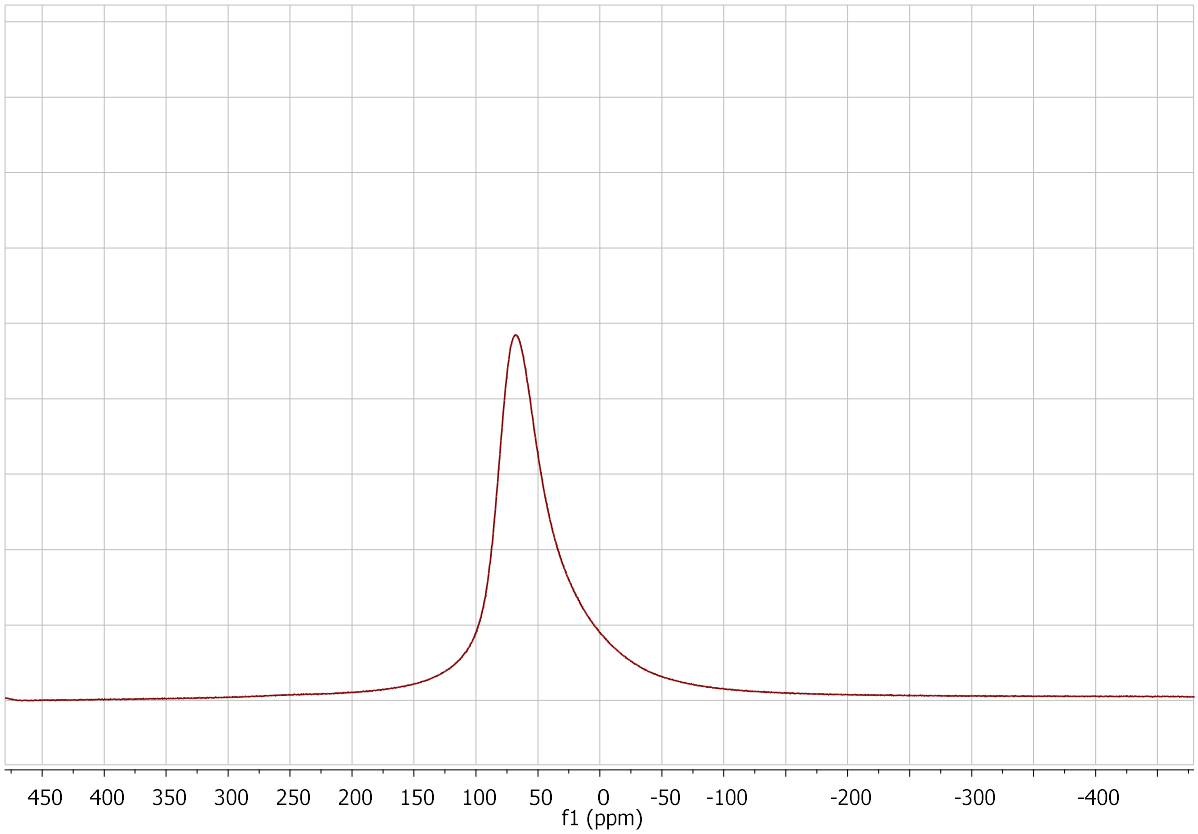

*Figure S16 ^{27}Al NMR spectrum (104 MHz) of **3a** in C_6D_6 at 300 K.*

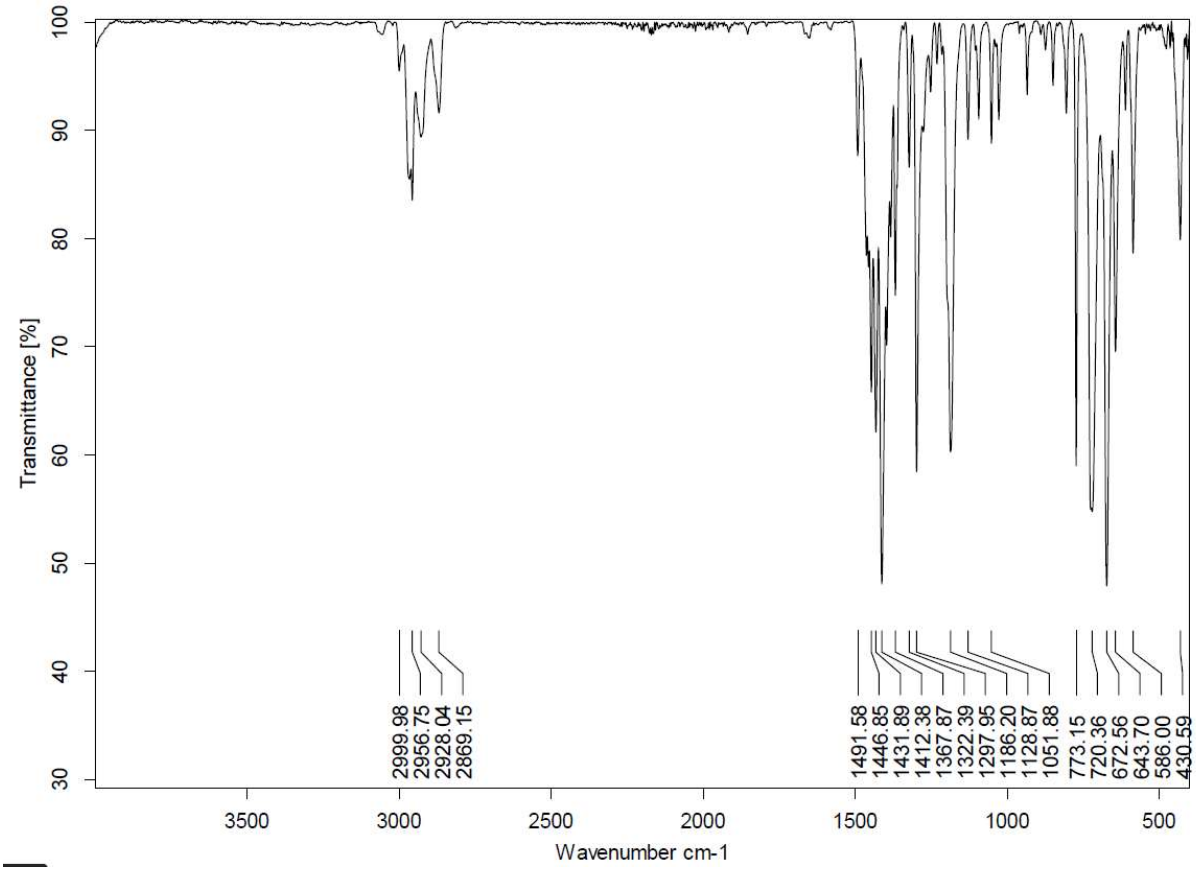

*Figure S17 ATR-IR spectrum of **3a**.*

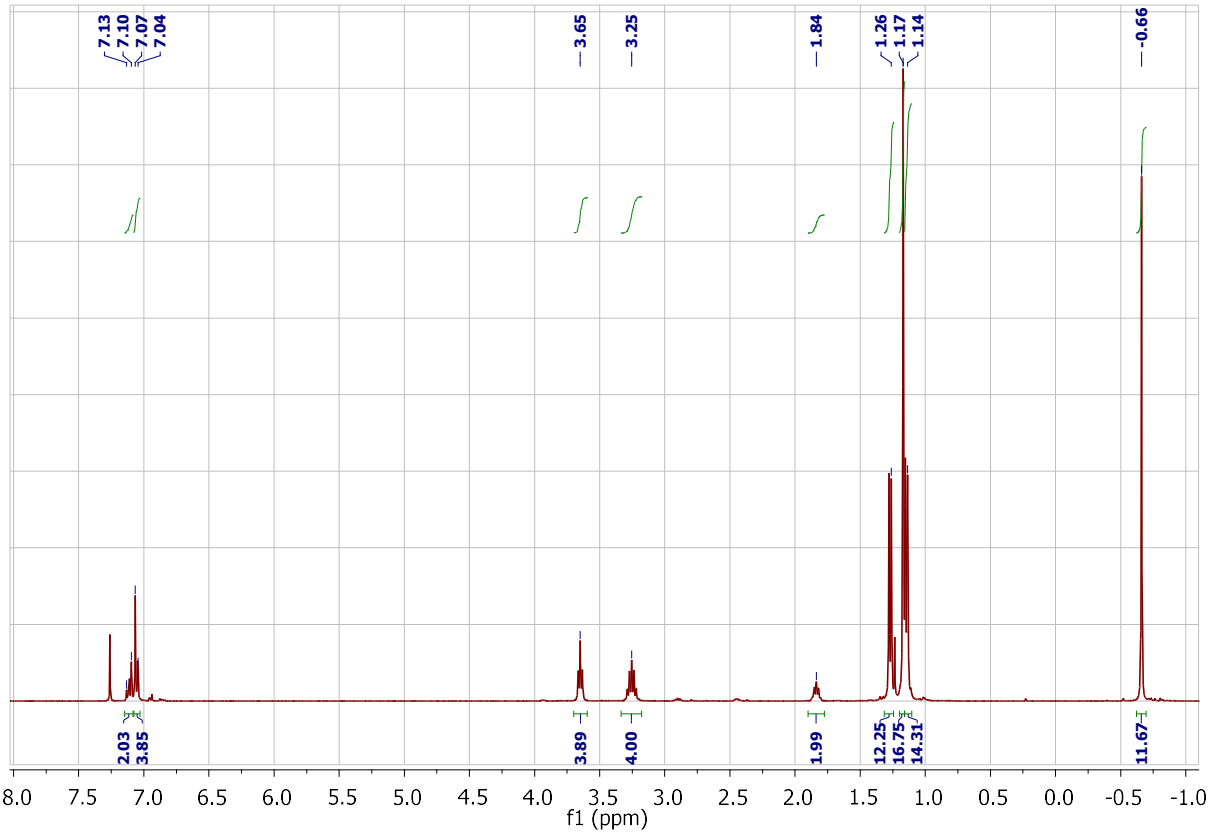

*Figure S18 [1]H NMR spectrum (400 MHz) of **3b** in $CDCl_3$ at 300 K.*

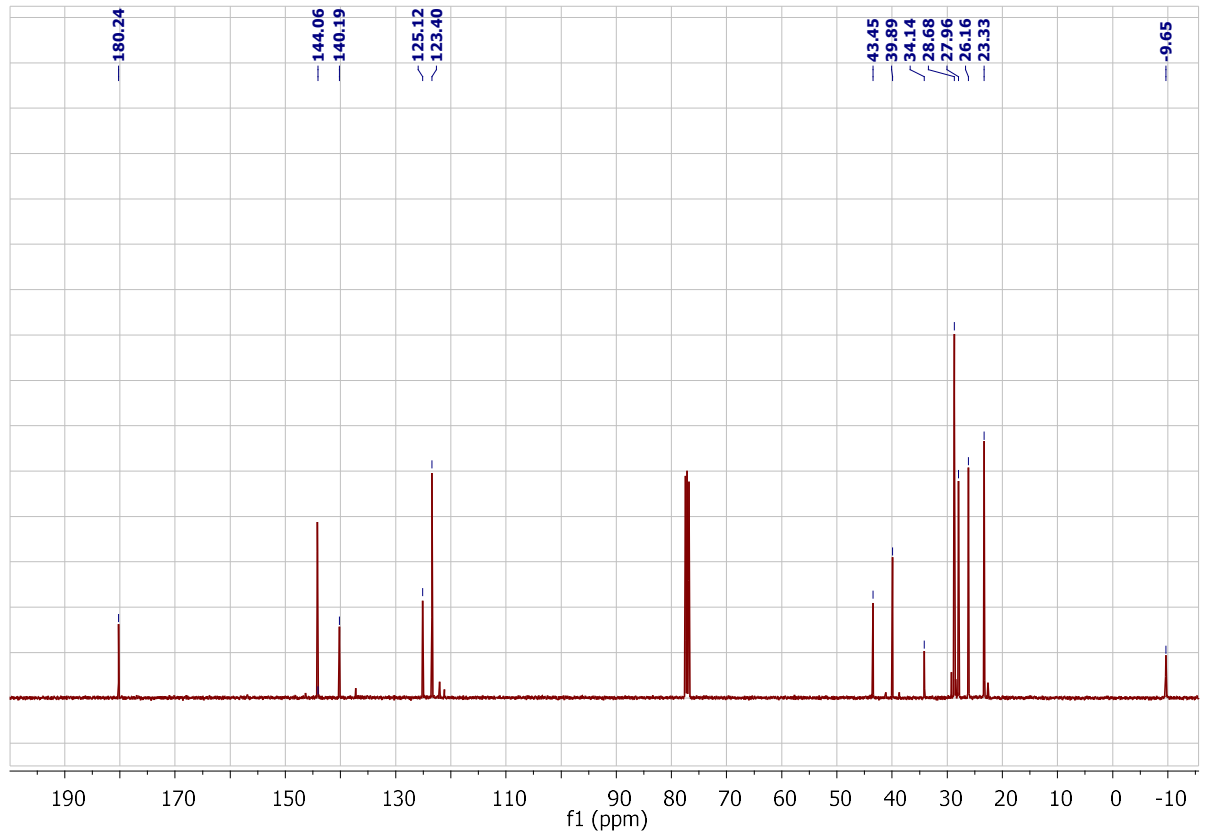

*Figure S19 [13]C NMR spectrum (101 MHz) of **3b** in $CDCl_3$ at 300 K.*

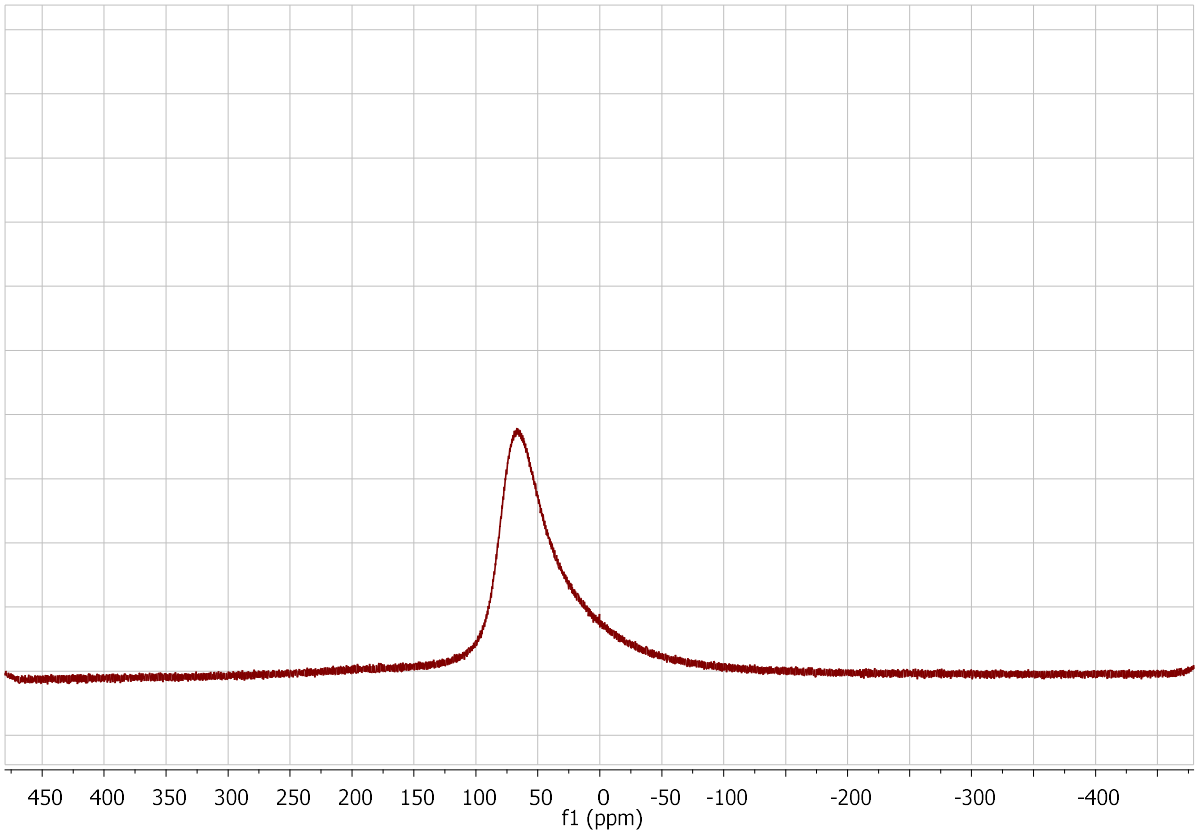

*Figure S20 ^{27}Al NMR spectrum (104 MHz) of **3b** in $CDCl_3$ at 300 K..*

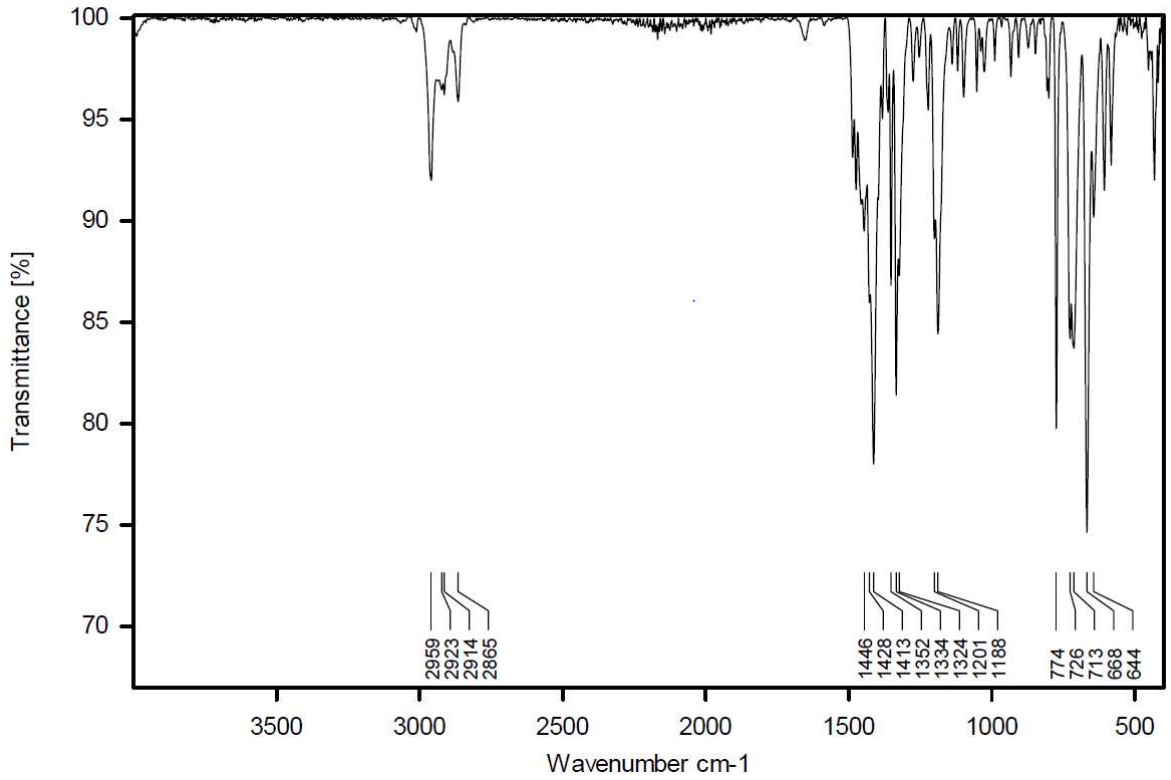

*Figure S21 ATR-IR spectrum of **3b**.*

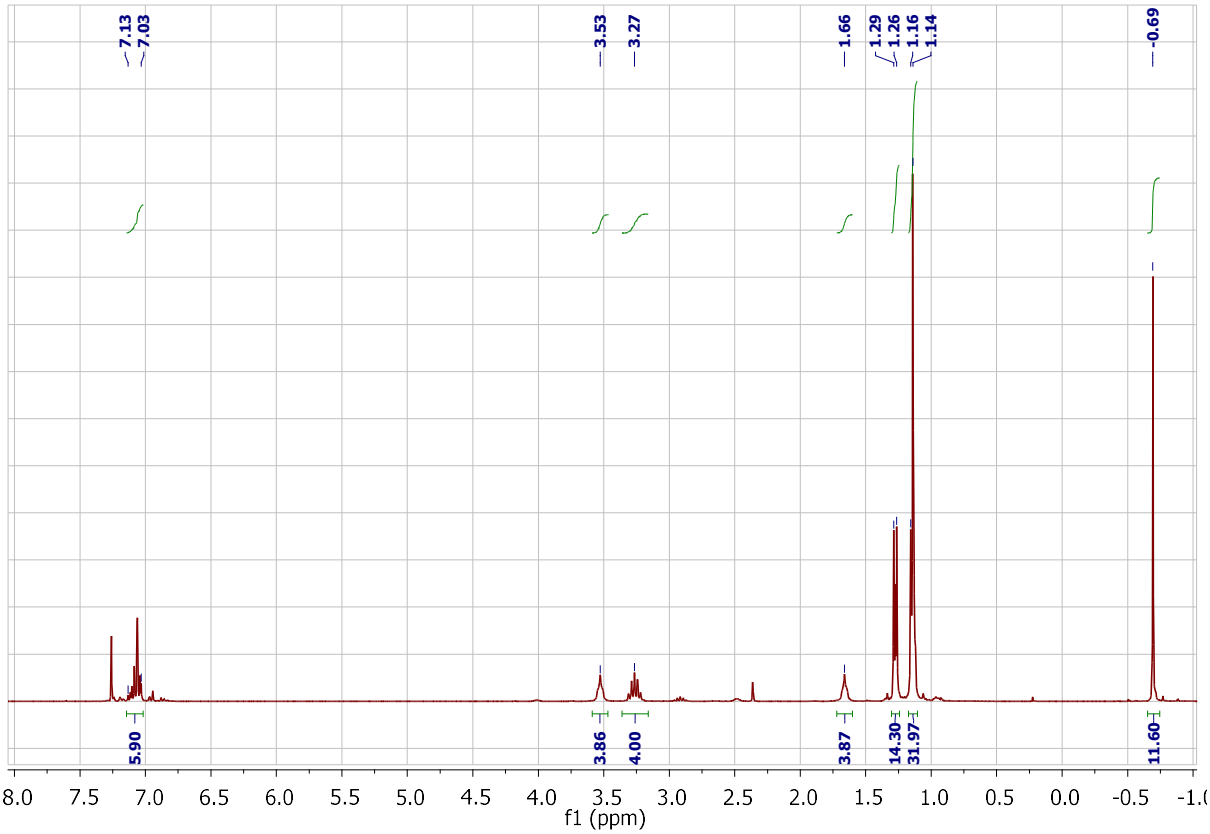

*Figure S22 ^{1}H NMR spectrum (400 MHz) of **3c** in $CDCl_3$ at 300 K.*

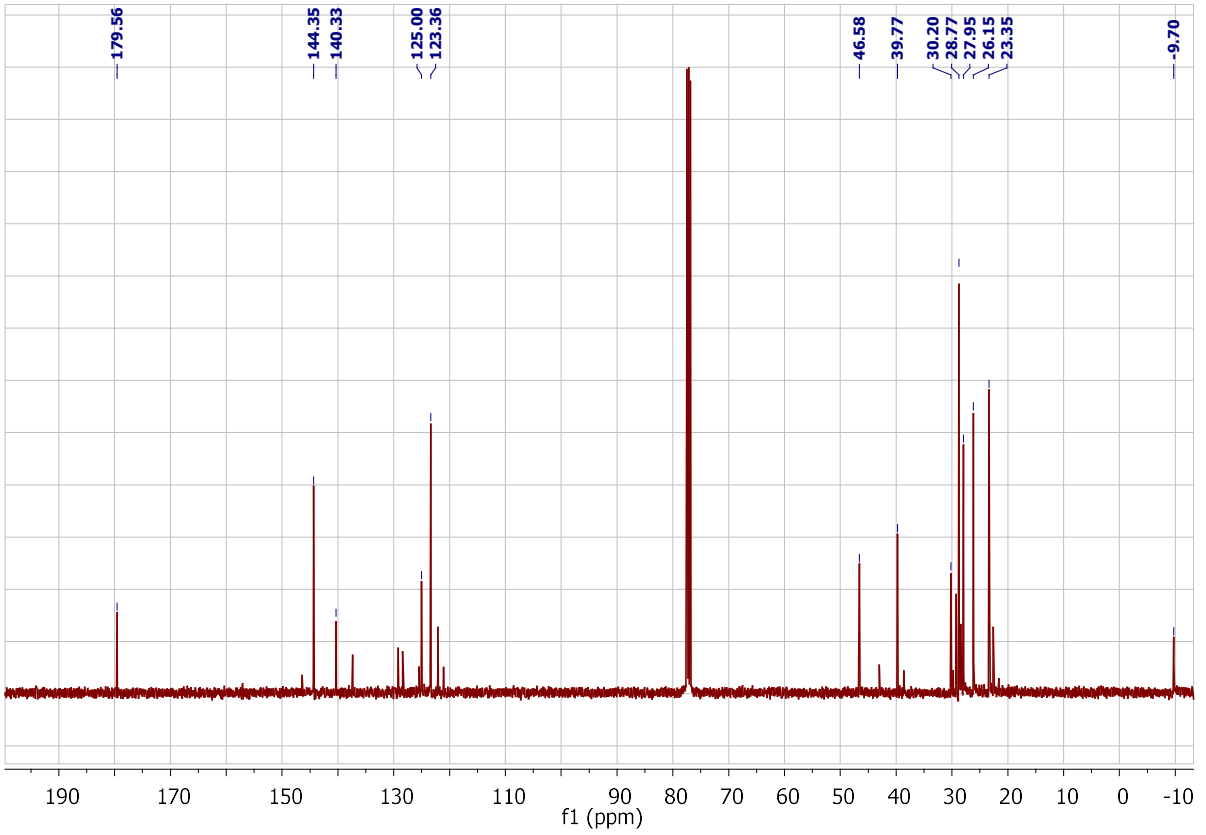

*Figure S23 ^{13}C NMR spectrum (101 MHz) of **3c** in $CDCl_3$ at 300 K.*

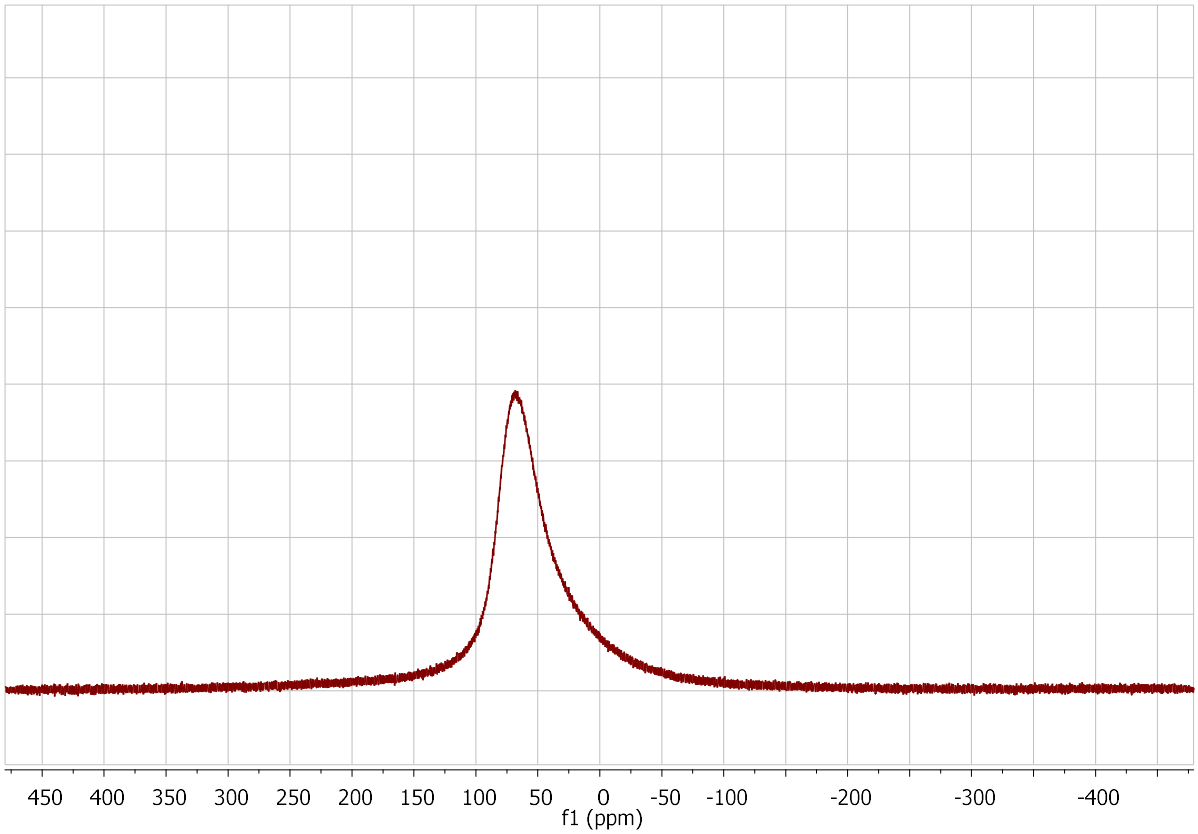

*Figure S24 ^{27}Al NMR spectrum (104 MHz) of **3c** in $CDCl_3$ at 300 K.*

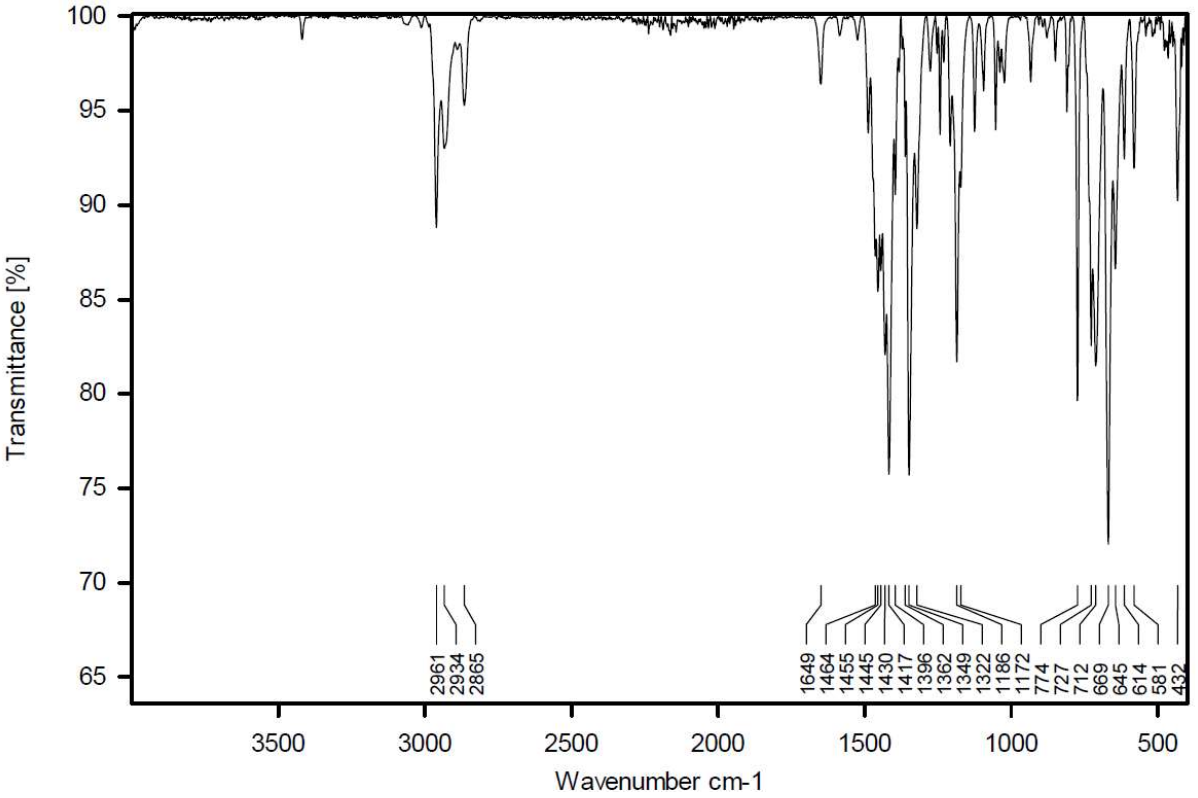

*Figure S25 ATR-IR spectrum of **3c**.*

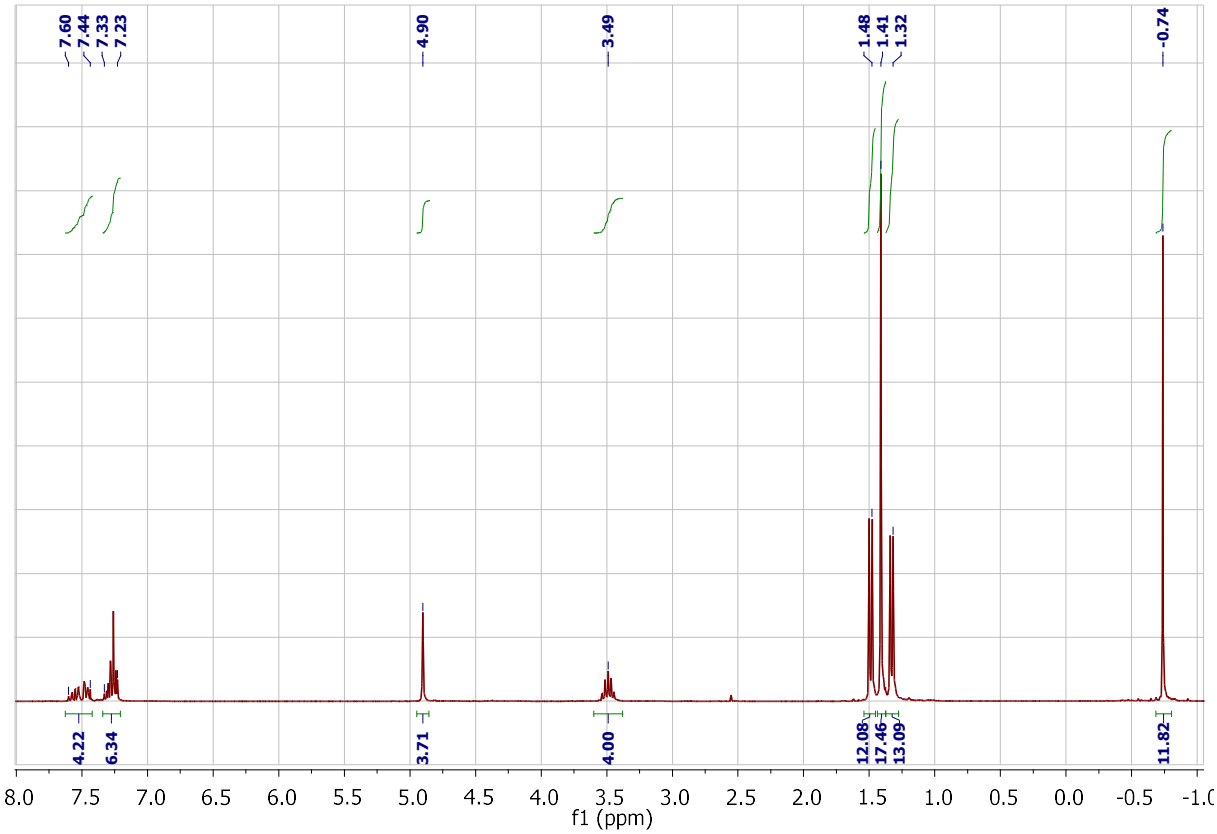

*Figure S26 [1]H NMR spectrum (400 MHz) of **3d** in C_6D_6 at 300 K.*

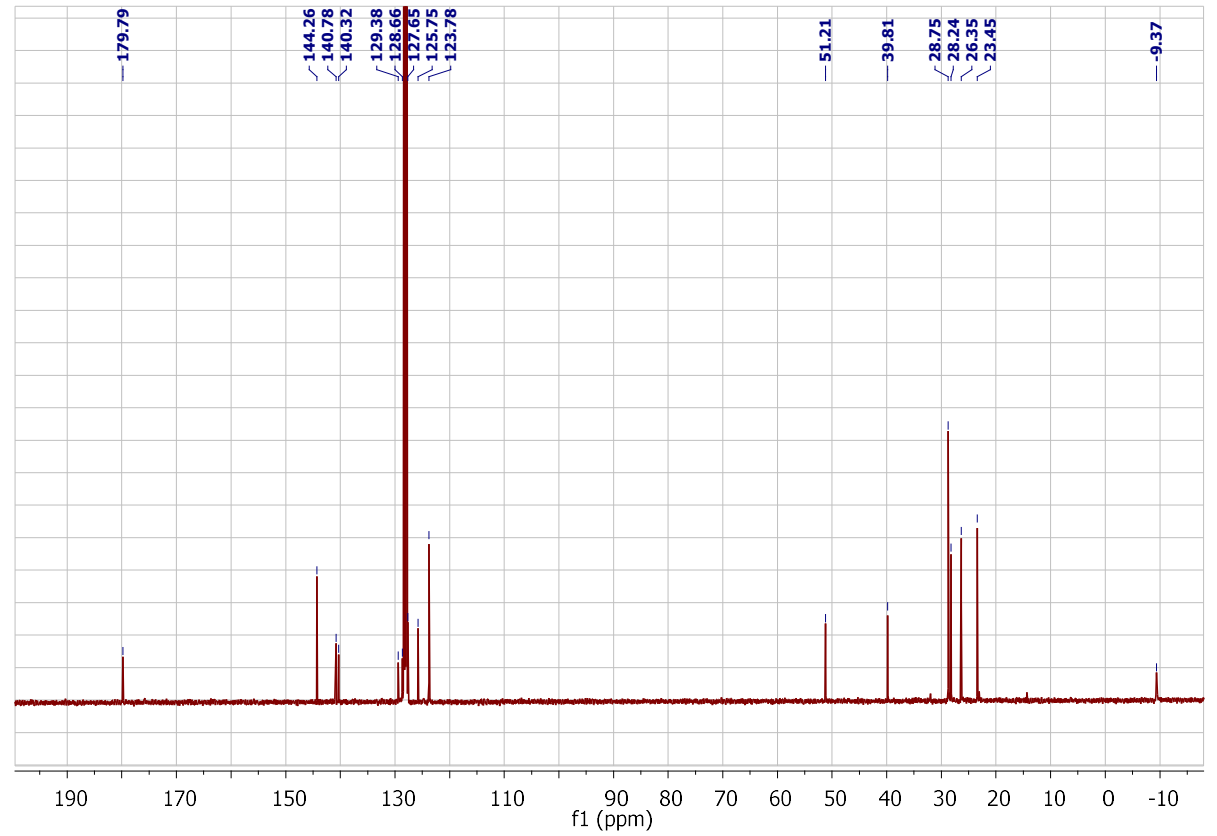

*Figure S27 [13]C NMR spectrum (101 MHz) of **3d** in C_6D_6 at 300 K.*

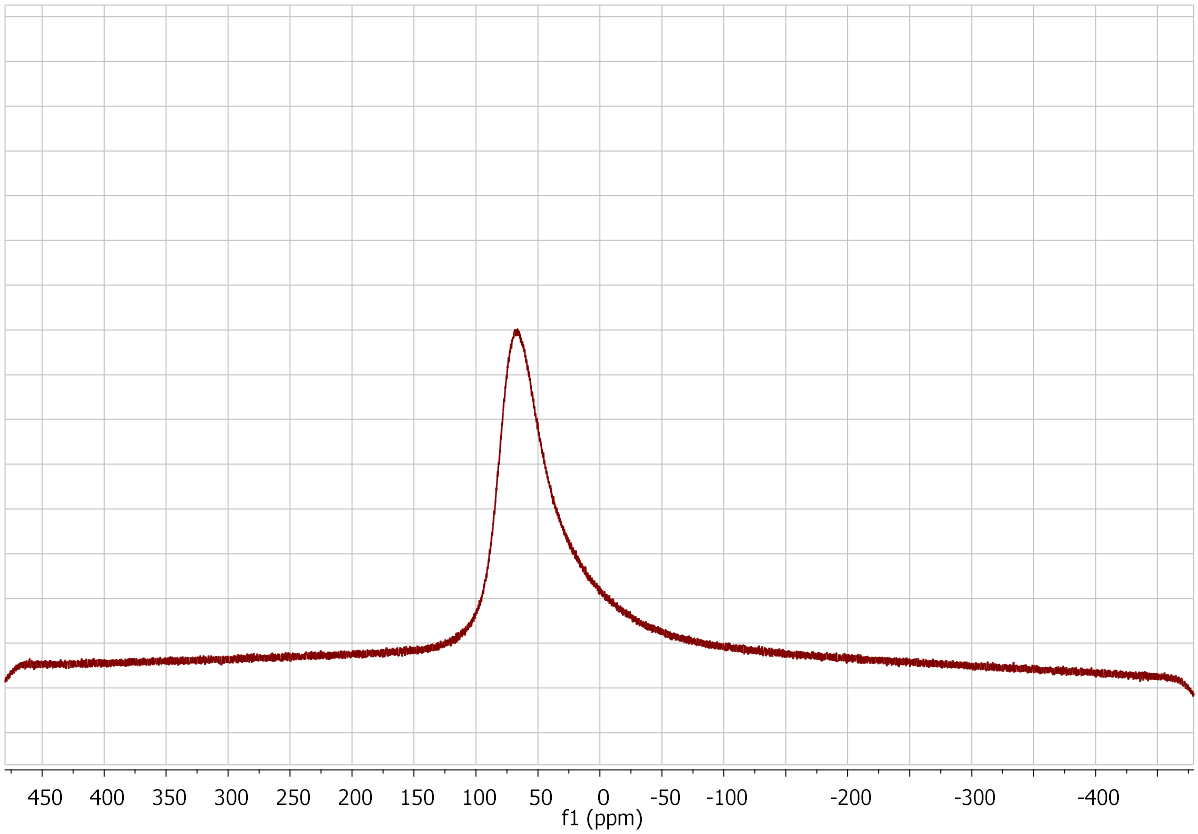

*Figure S28 ^{27}Al NMR spectrum (104 MHz) of **3d** in C_6D_6 at 300 K.*

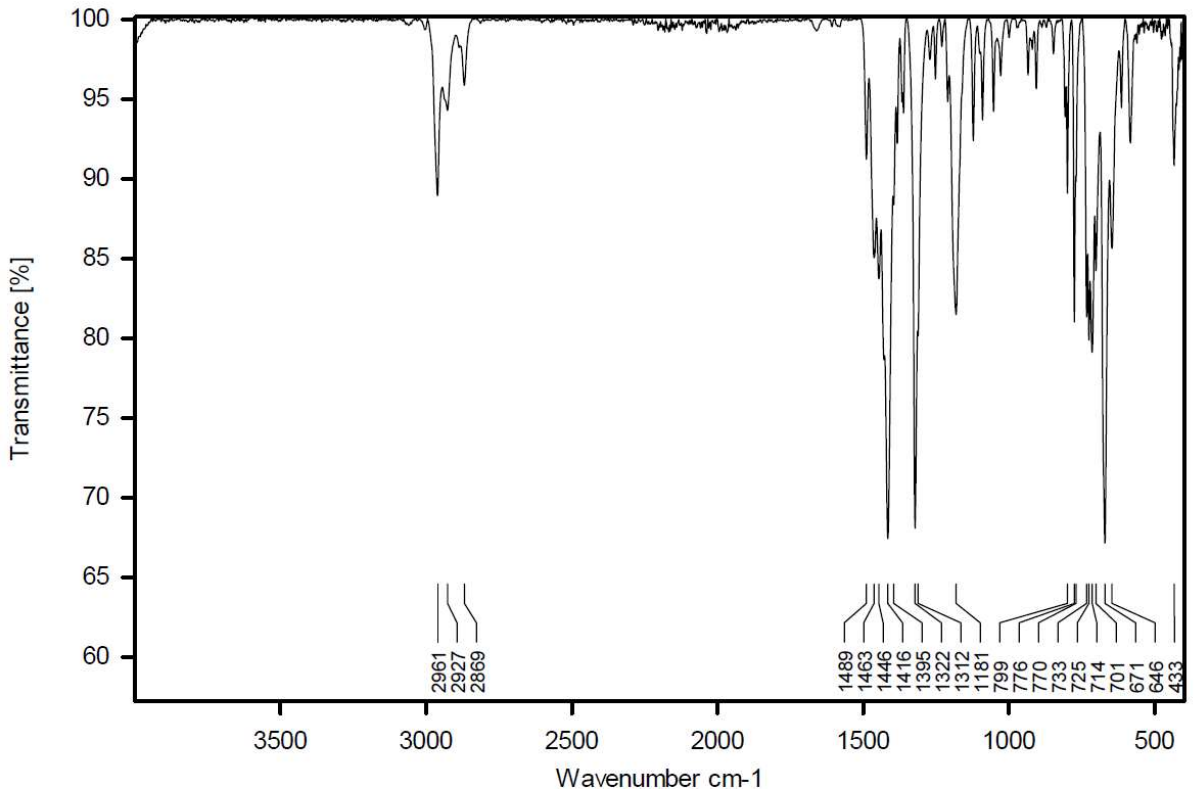

*Figure S29 ATR-IR spectrum of **3d**.*

*Figure S30 ^{1}H NMR spectrum (400 MHz) of **4a** in $CDCl_3$ at 300 K.*

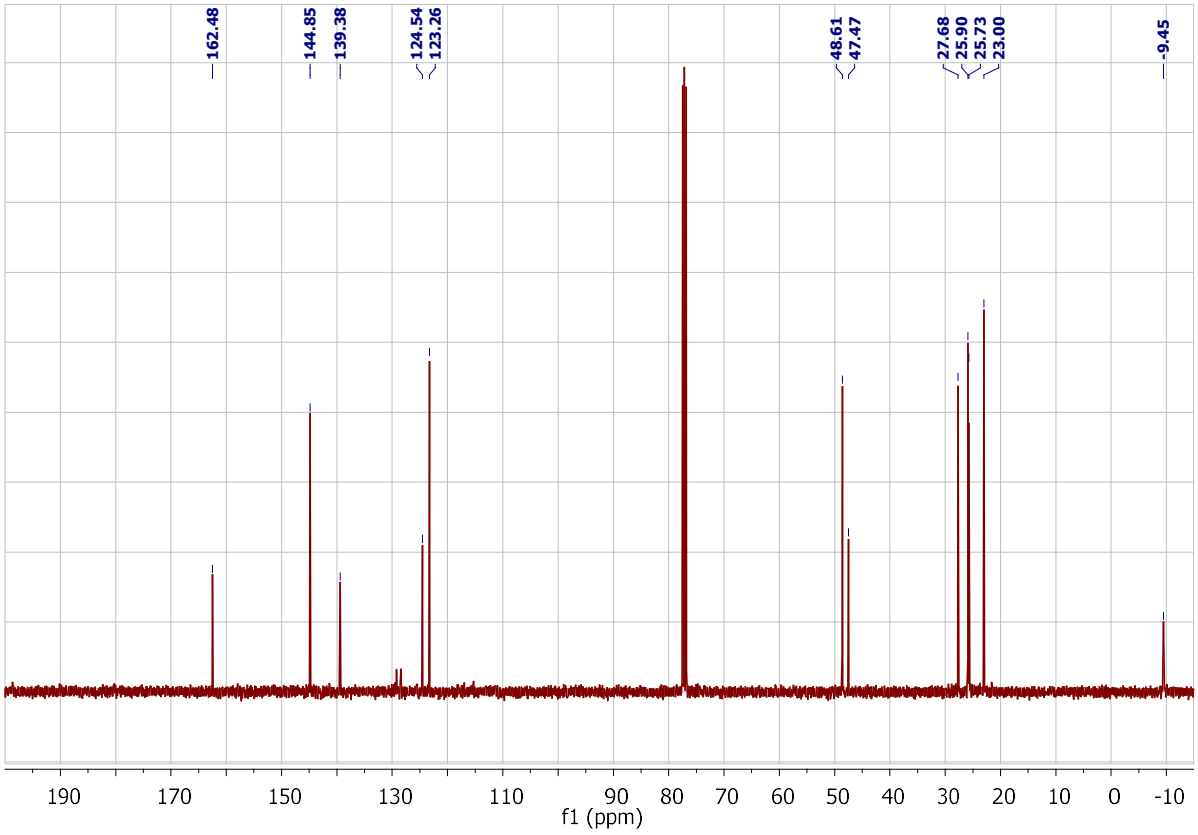

*Figure S31 ^{13}C NMR spectrum (101 MHz) of **4a** in $CDCl_3$ at 300 K.*

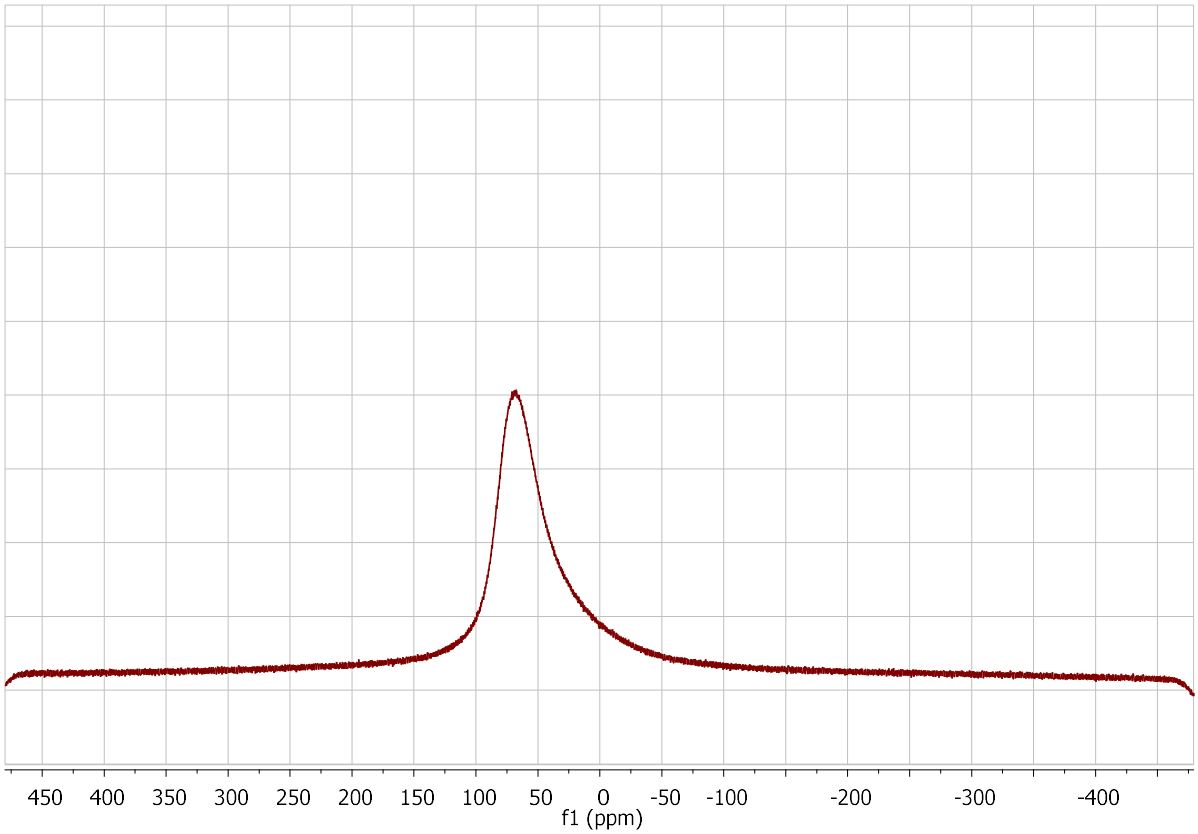

*Figure S32 ^{27}Al NMR spectrum (104 MHz) of **4a** in C_6D_6 at 300 K.*

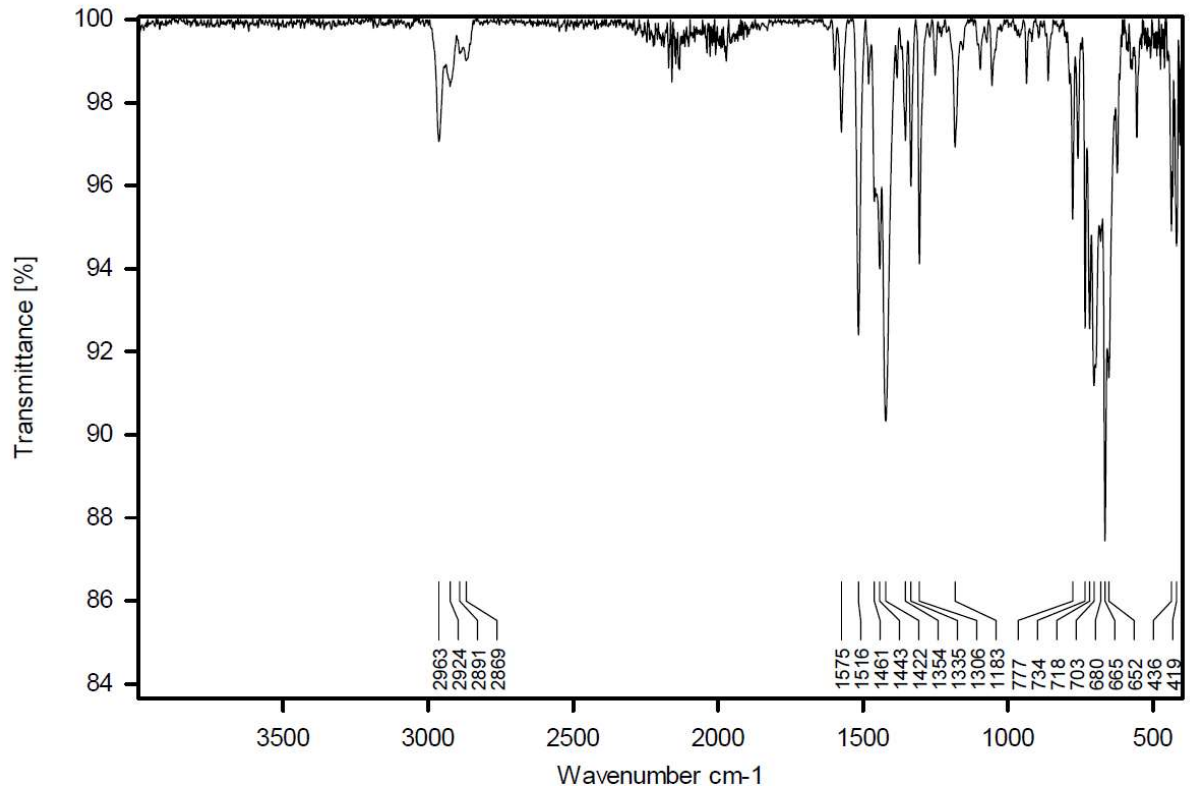

*Figure S33 ATR-IR spectrum of **4a**.*

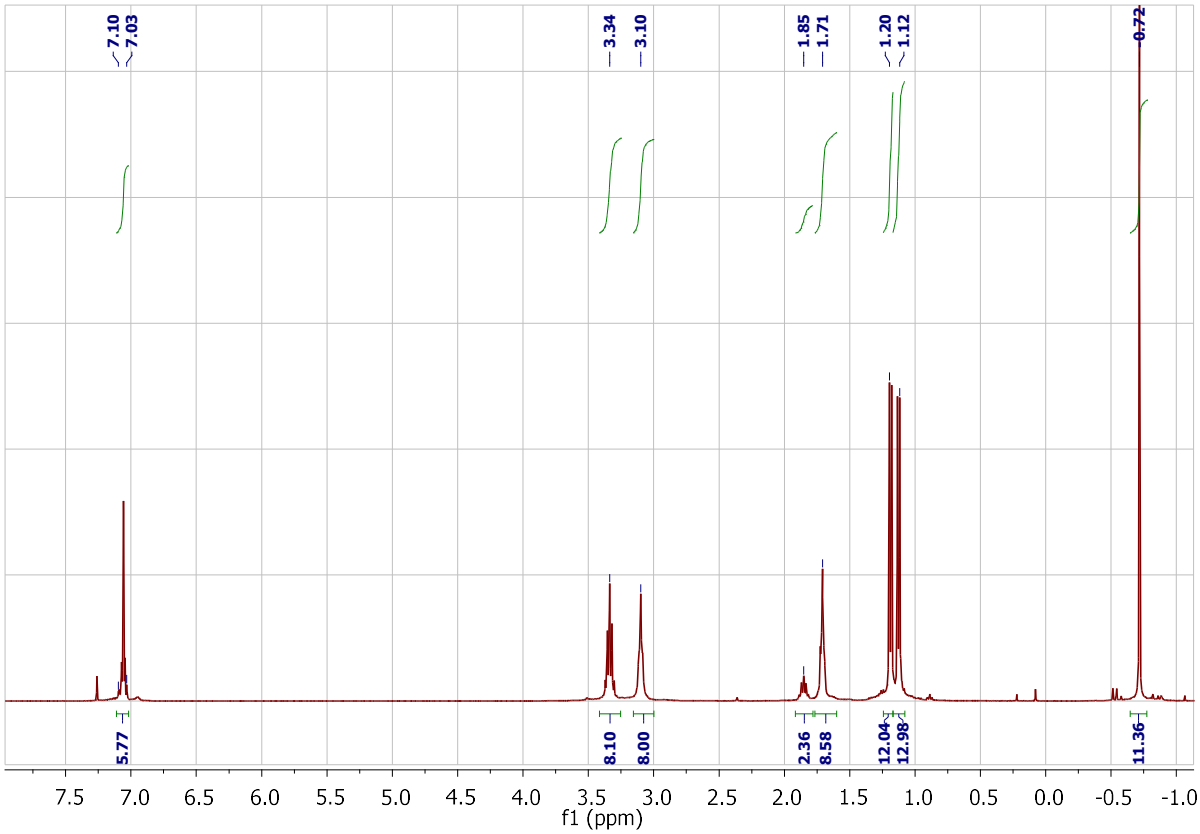

*Figure S34 ^{1}H NMR spectrum (400 MHz) of **4b** in $CDCl_3$ at 300 K.*

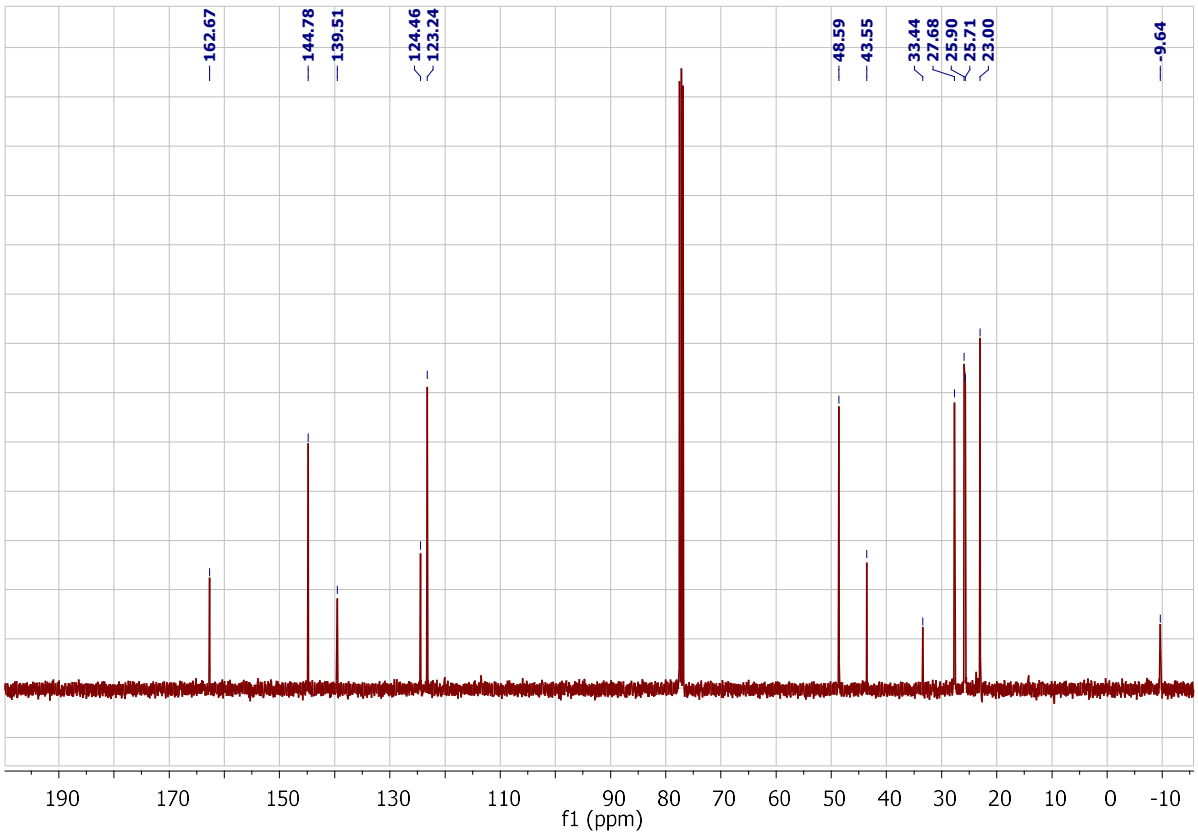

*Figure S35 ^{13}C NMR spectrum (101 MHz) of **4b** in $CDCl_3$ at 300 K.*

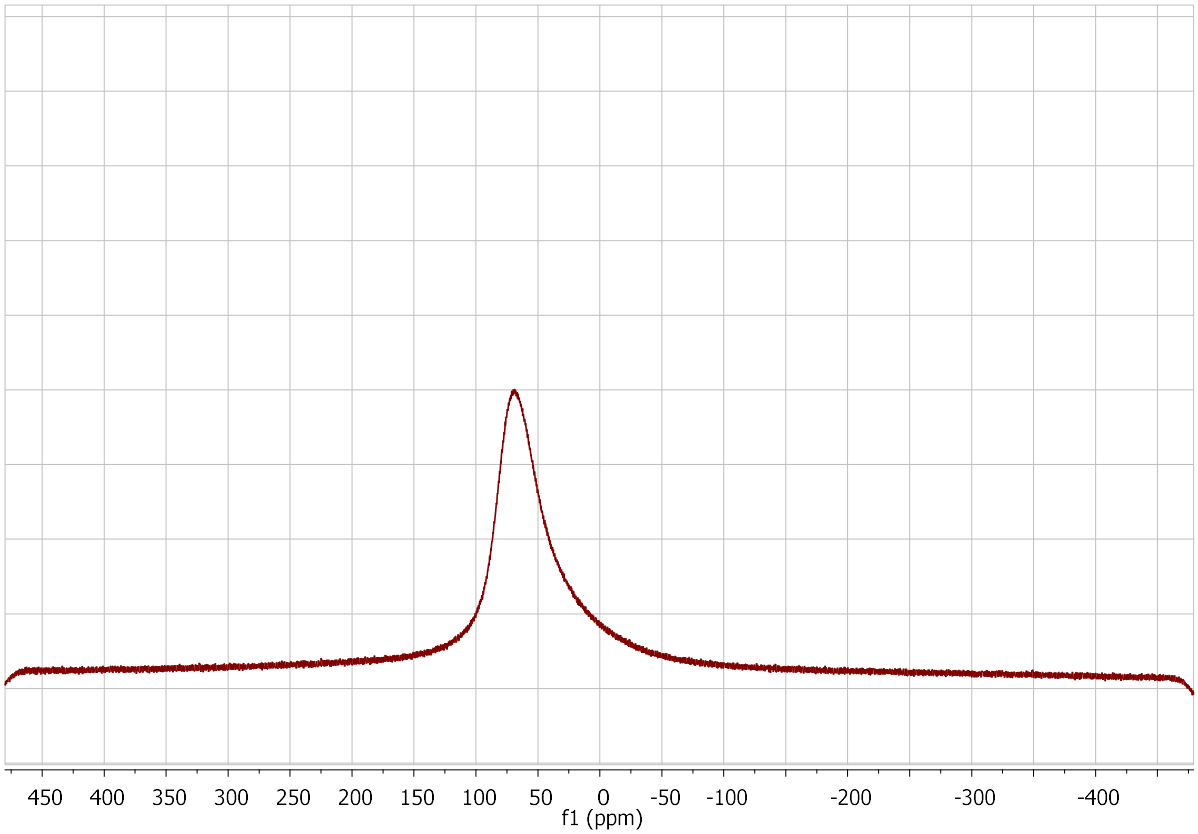

*Figure S36 ^{27}Al NMR spectrum (104 MHz) of **4b** in C_6D_6 at 300 K.*

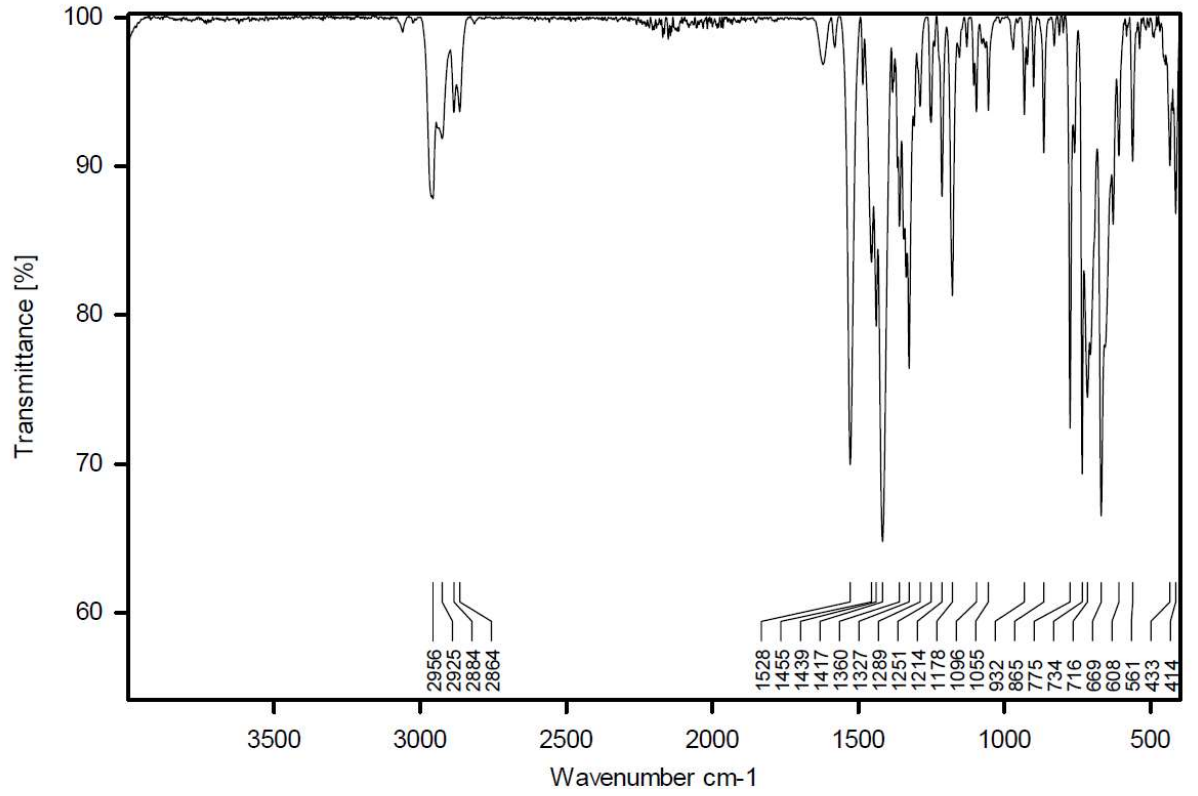

*Figure S37 ATR-IR spectrum of **4b**.*

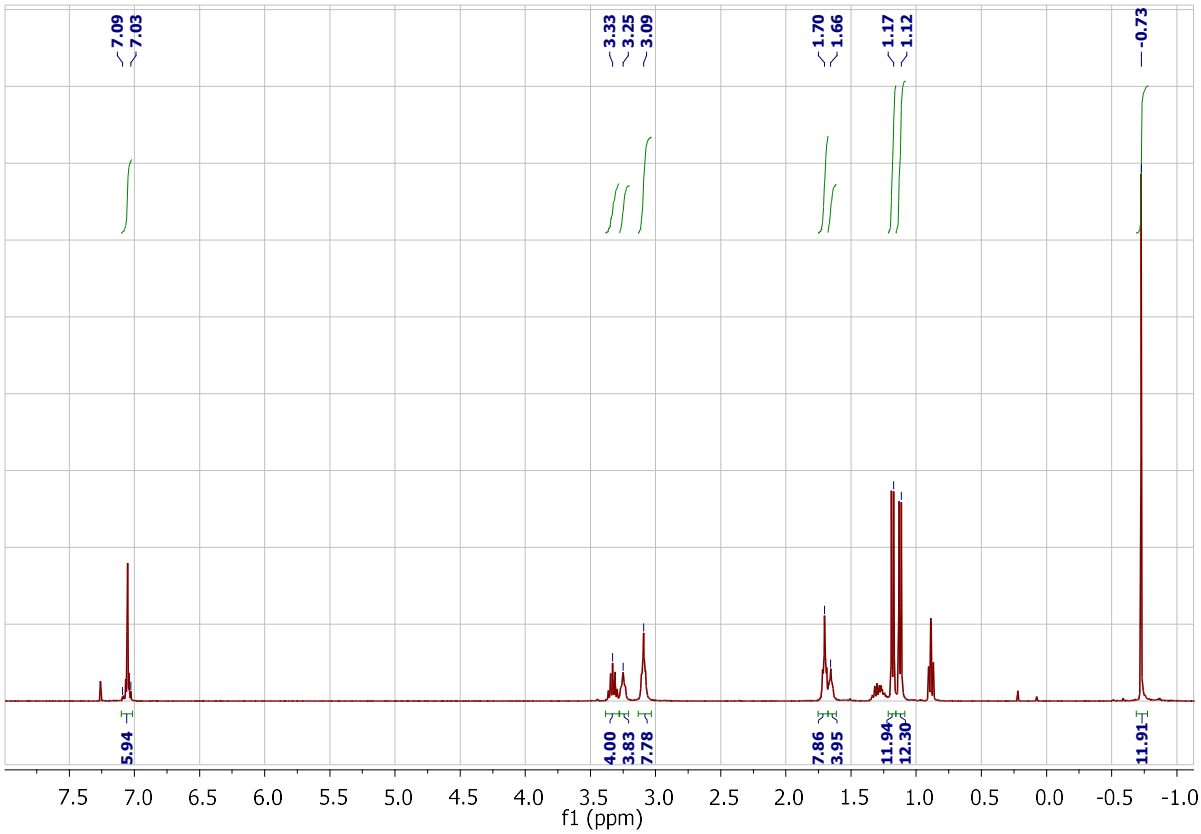

*Figure S38 ^{1}H NMR spectrum (400 MHz) of **4c** in $CDCl_3$ at 300 K.*

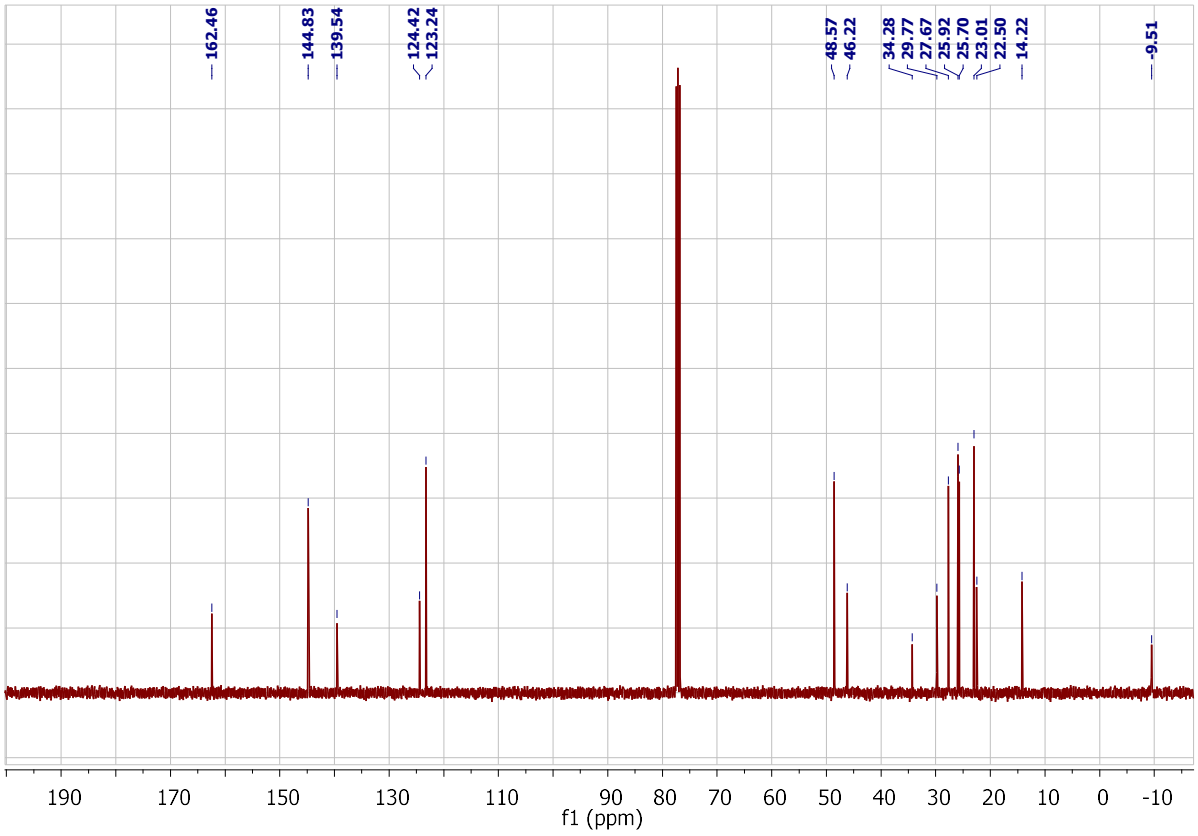

*Figure S39 ^{13}C NMR spectrum (101 MHz) of **4c** in $CDCl_3$ at 300 K.*

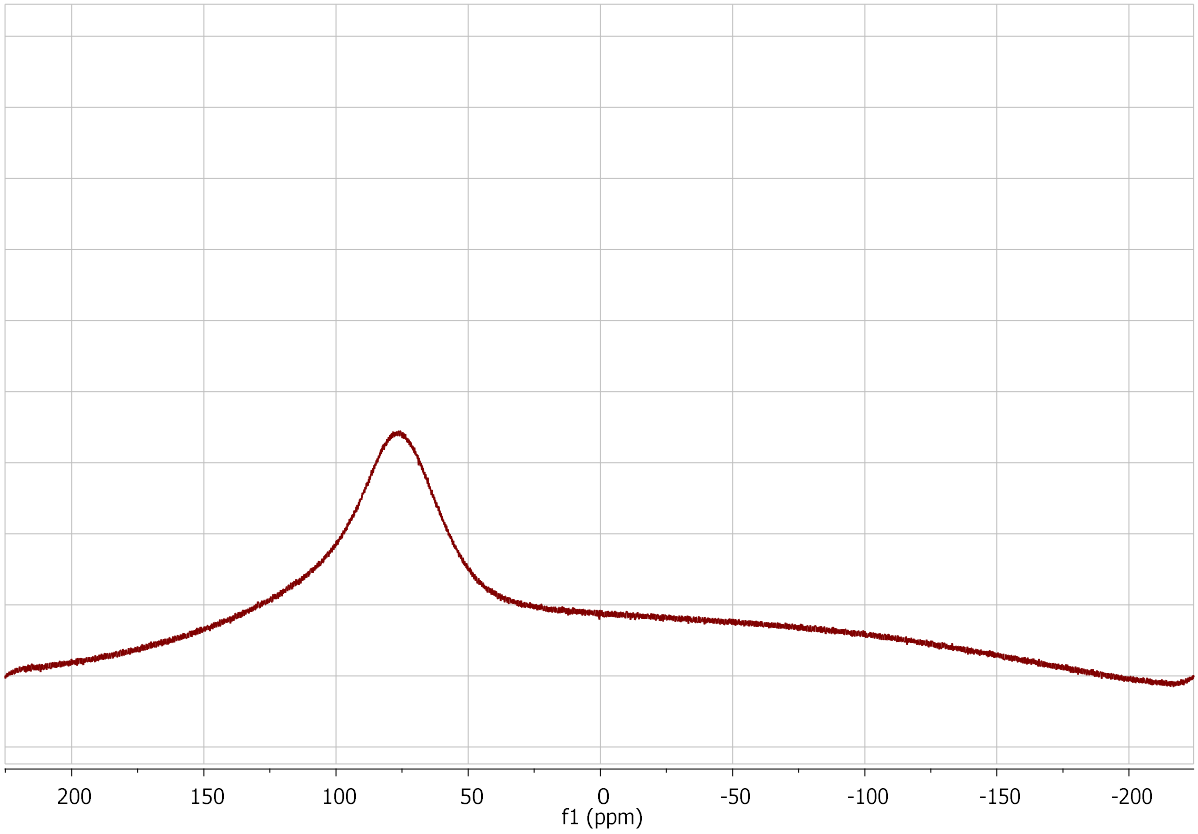

*Figure S40 ^{27}Al NMR spectrum (104 MHz) of **4c** in C_6D_6 at 300 K.*

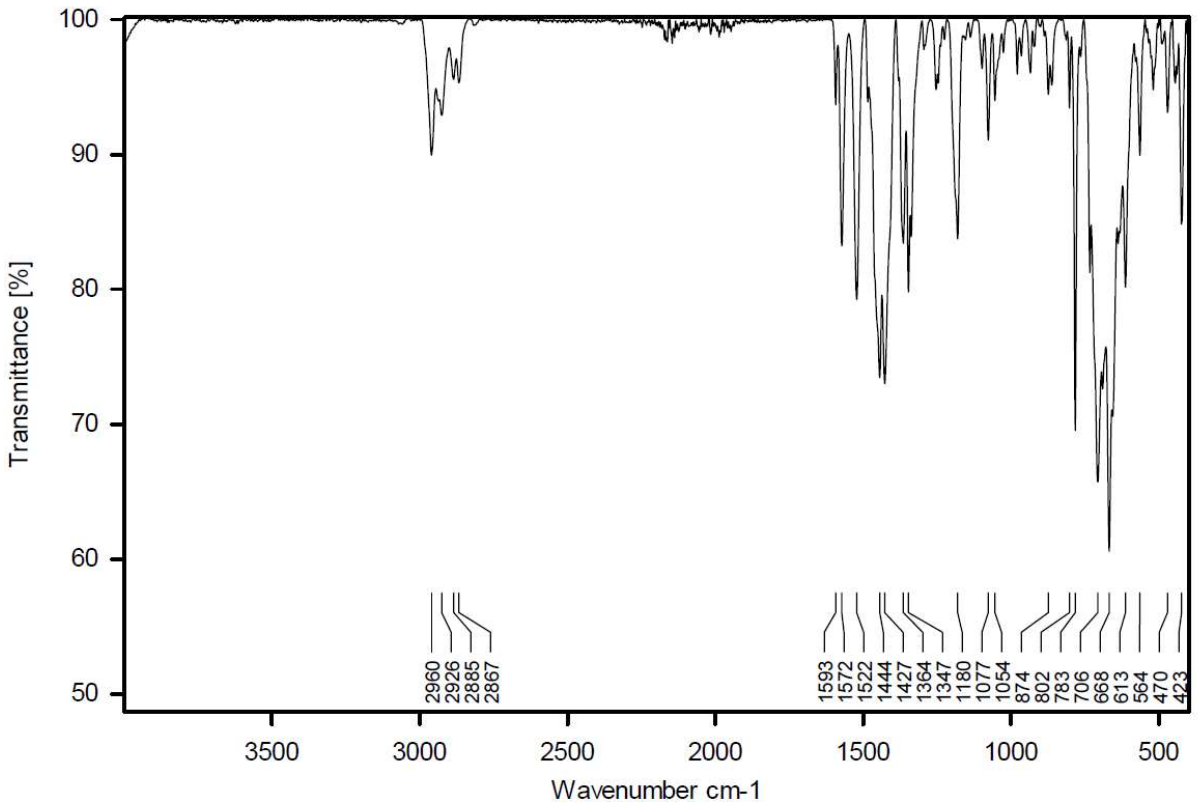

*Figure S41 ATR-IR spectrum of **4c.***

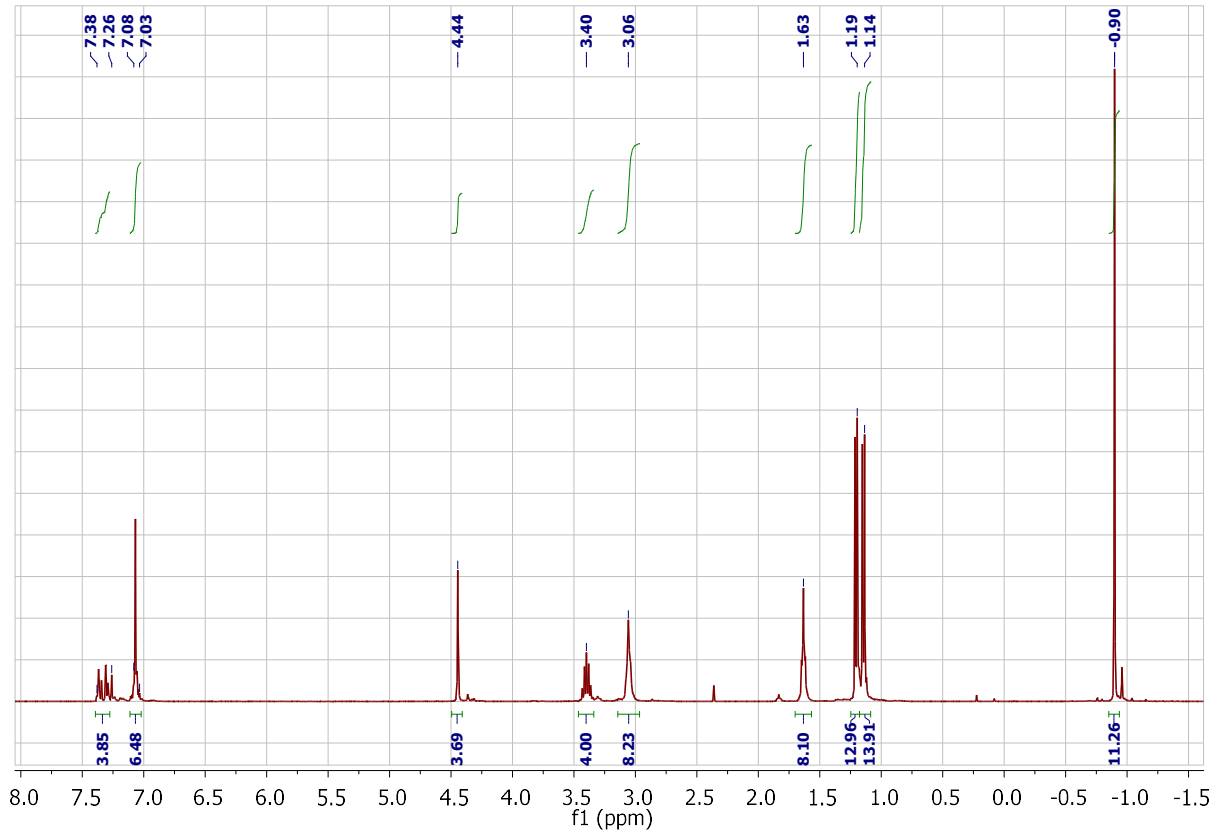

*Figure S42 ^{1}H NMR spectrum (400 MHz) of **4d** in $CDCl_3$ at 300 K.*

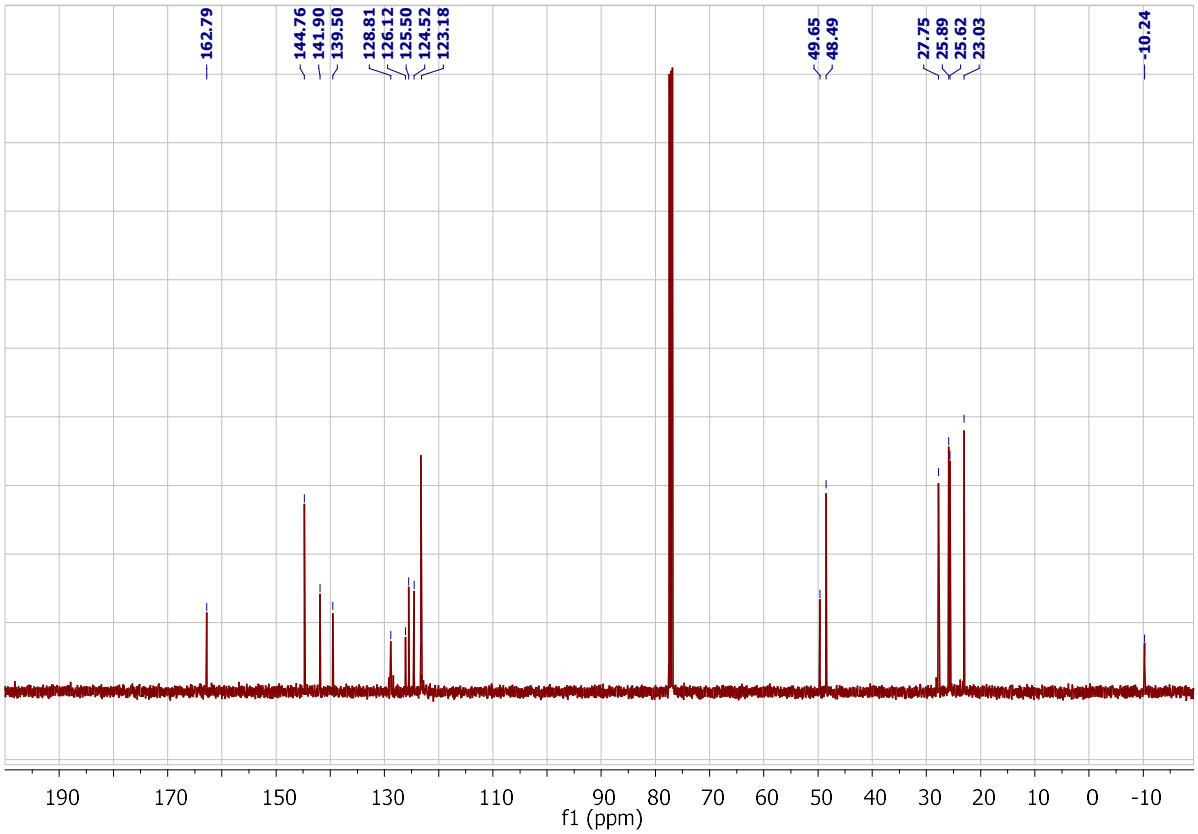

*Figure S43 ^{13}C NMR spectrum (101 MHz) of **4d** in $CDCl_3$ at 300 K.*

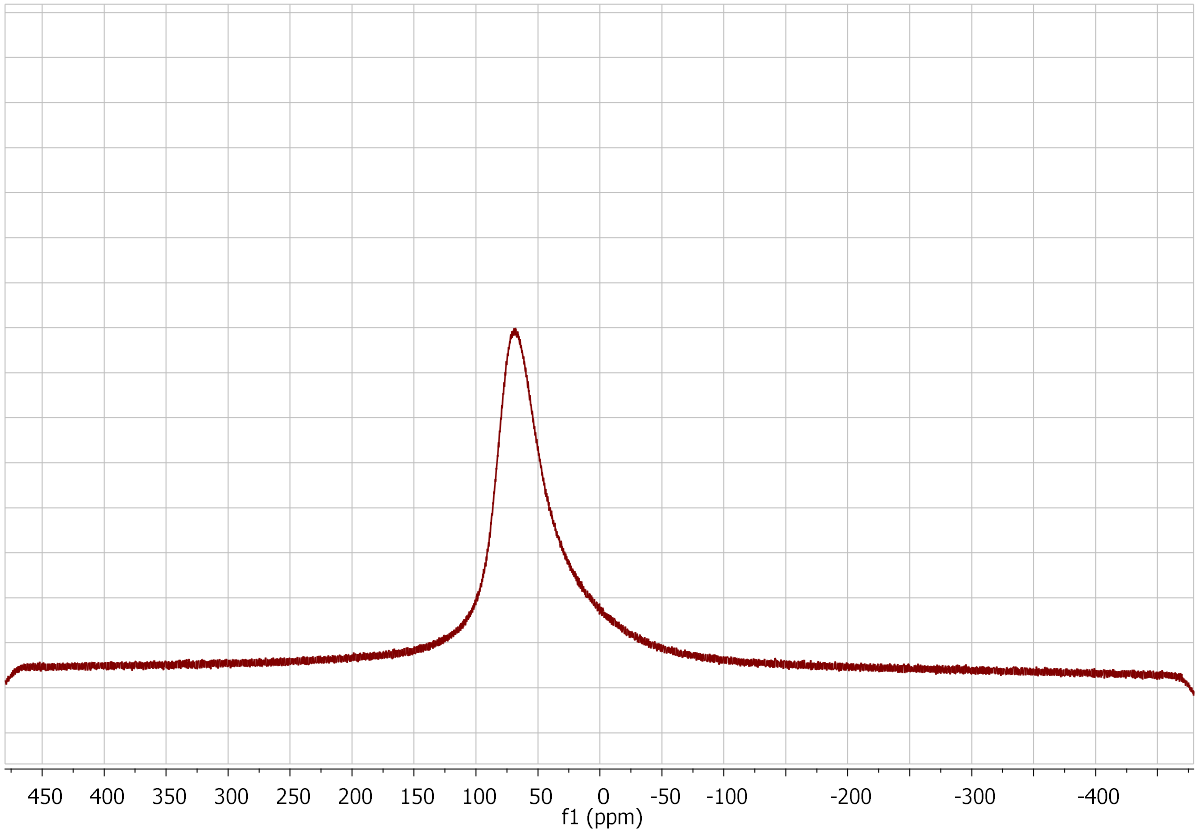

*Figure S44 ^{27}Al NMR spectrum (104 MHz) of **4d** in C_6D_6 at 300 K.*

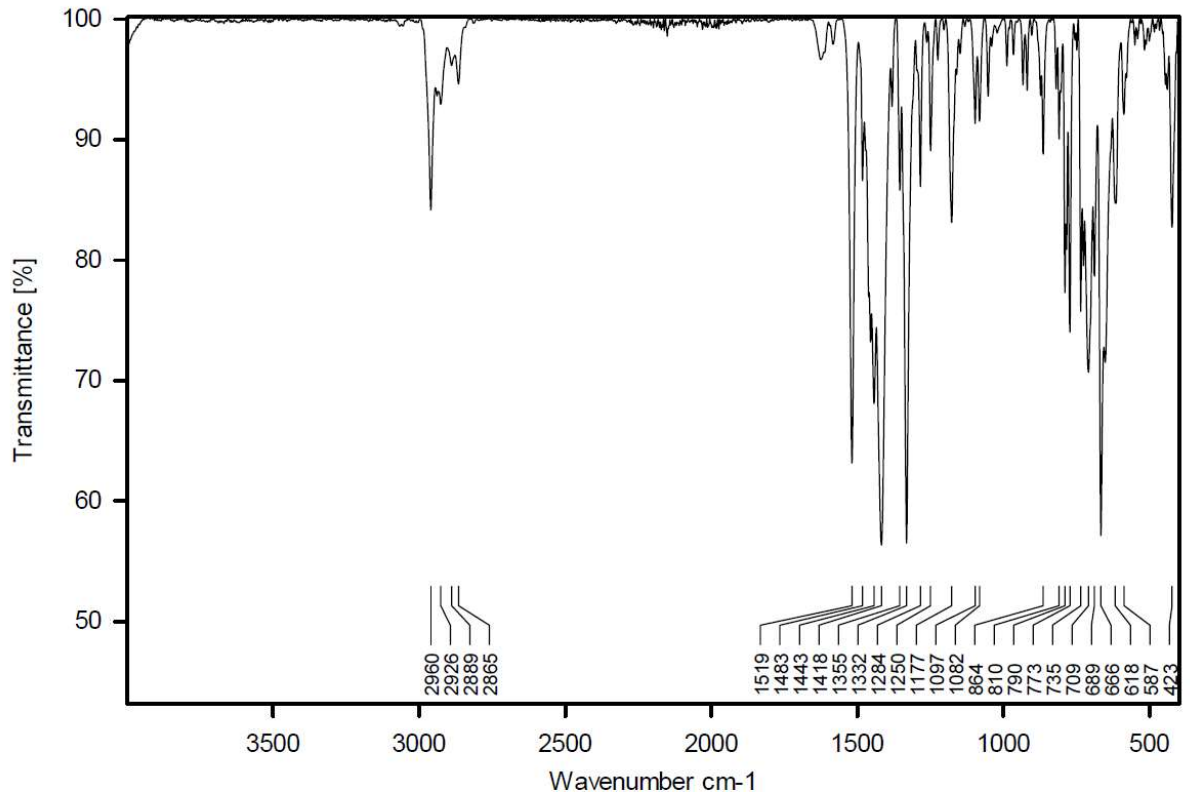

*Figure S45 ATR-IR spectrum of **4d**.*

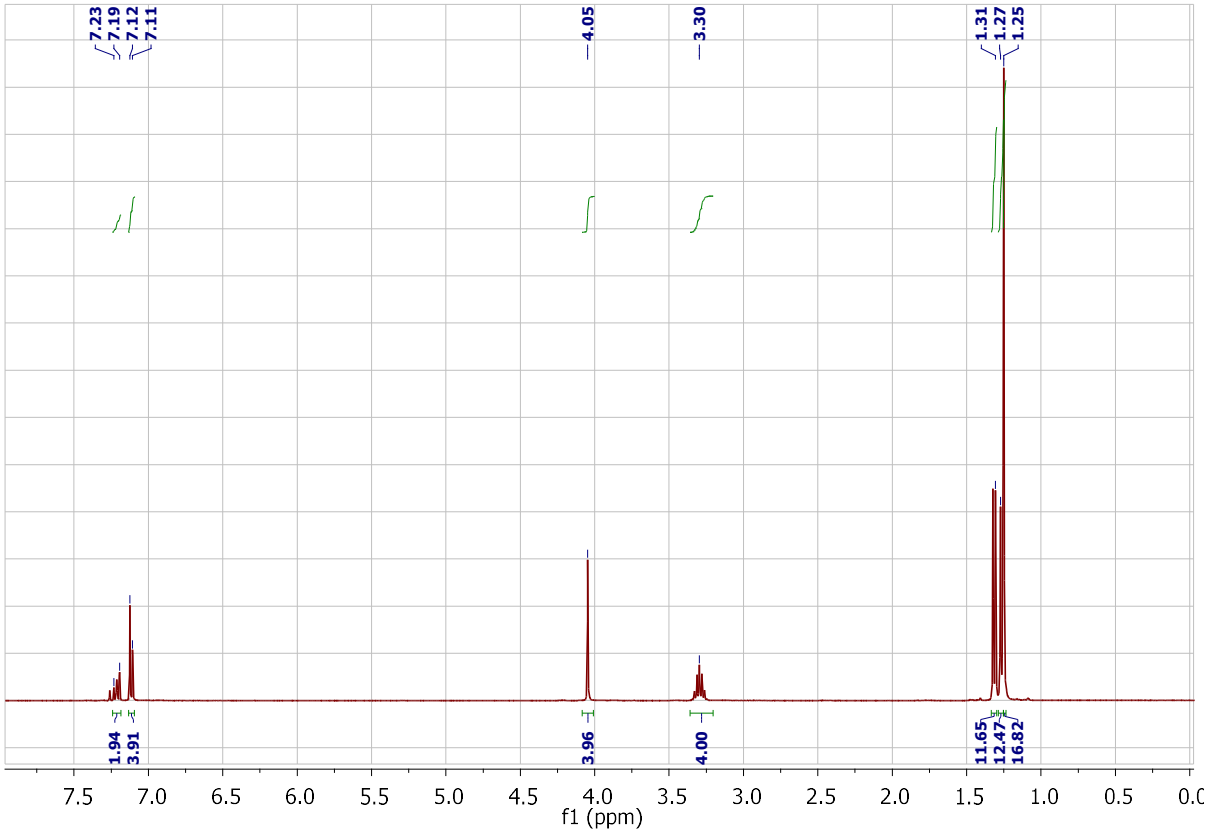

*Figure S46 ^{1}H NMR spectrum (400 MHz) of **5a** in $CDCl_3$ at 300 K.*

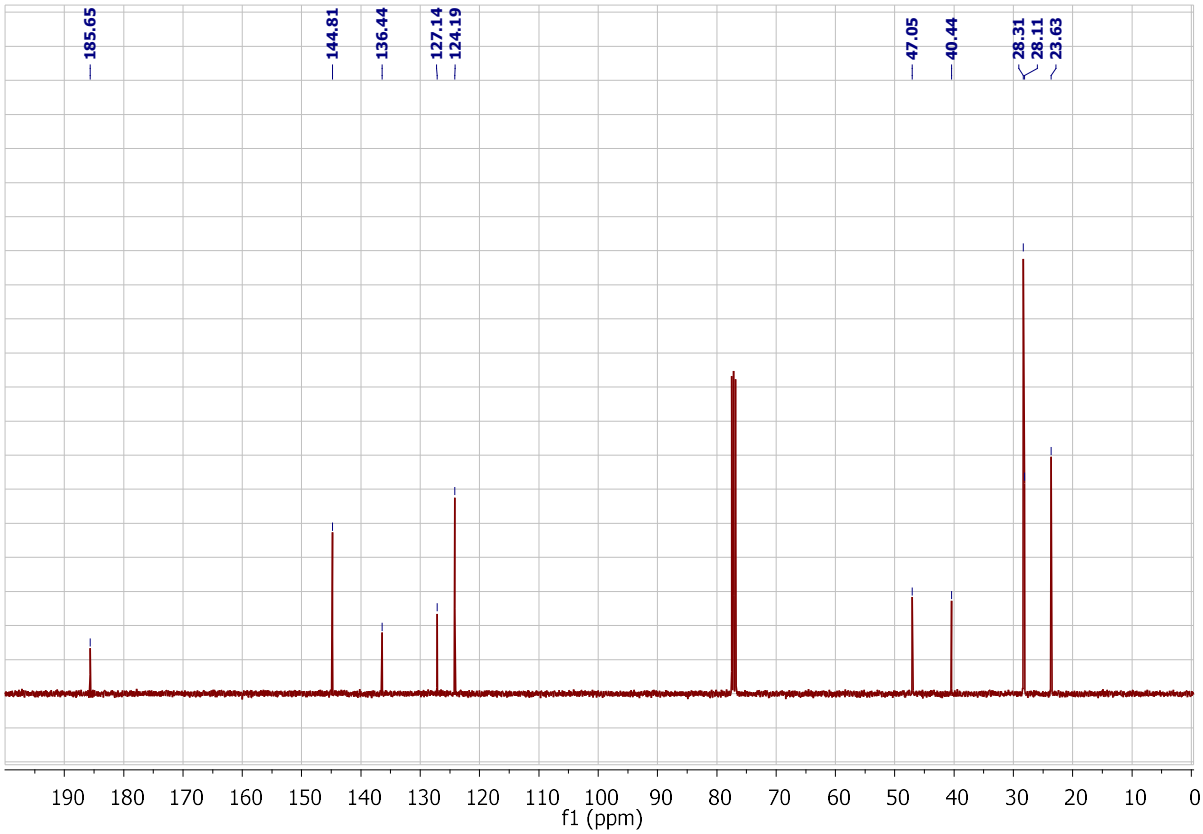

*Figure S47 ^{13}C NMR spectrum (101 MHz) of **5a** in $CDCl_3$ at 300 K.*

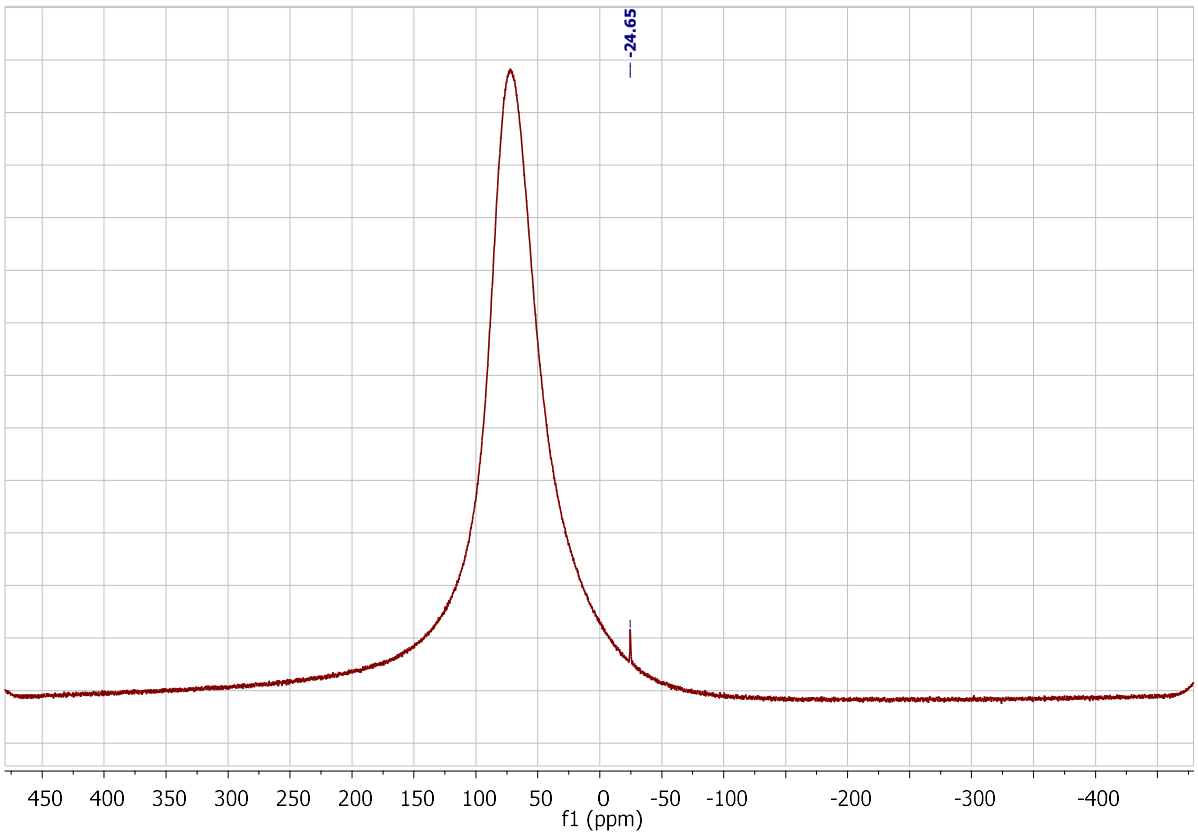

*Figure S48 ^{27}Al NMR spectrum (104 MHz) of **5a** in $CDCl_3$ at 300 K.*

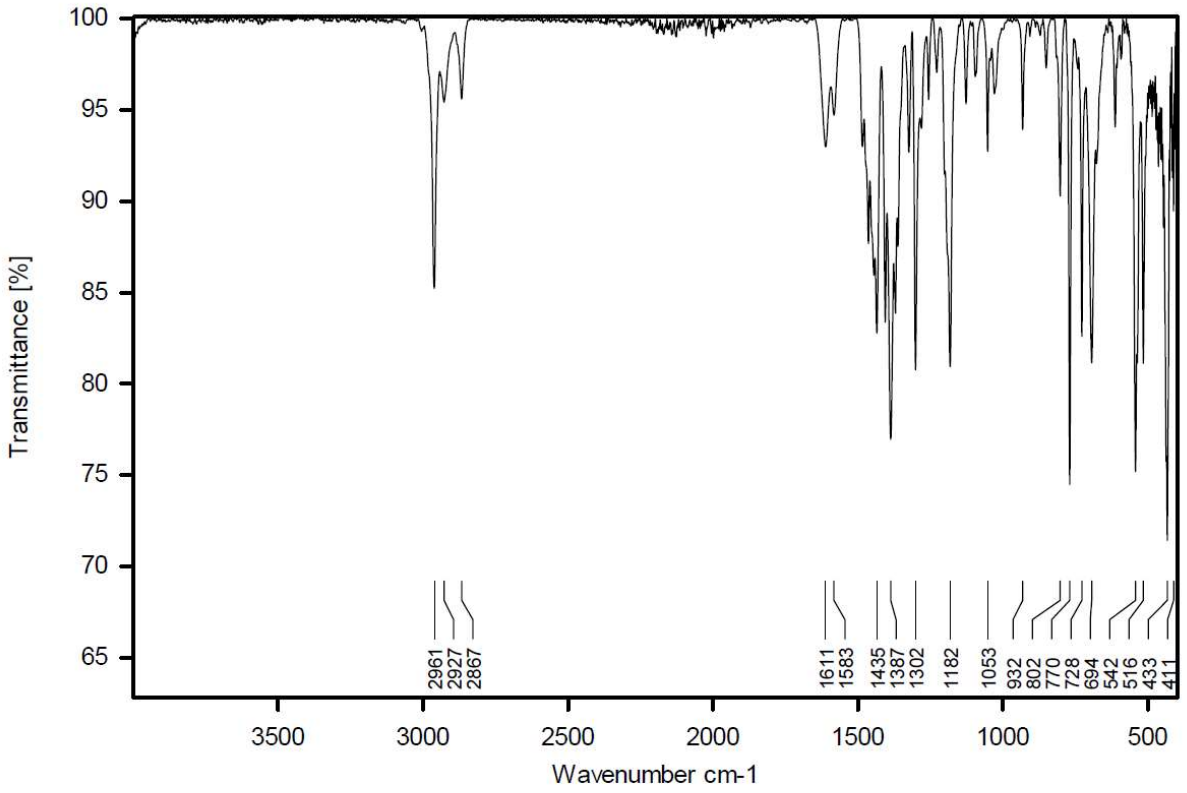

*Figure S49 ATR-IR spectrum of **5a**.*

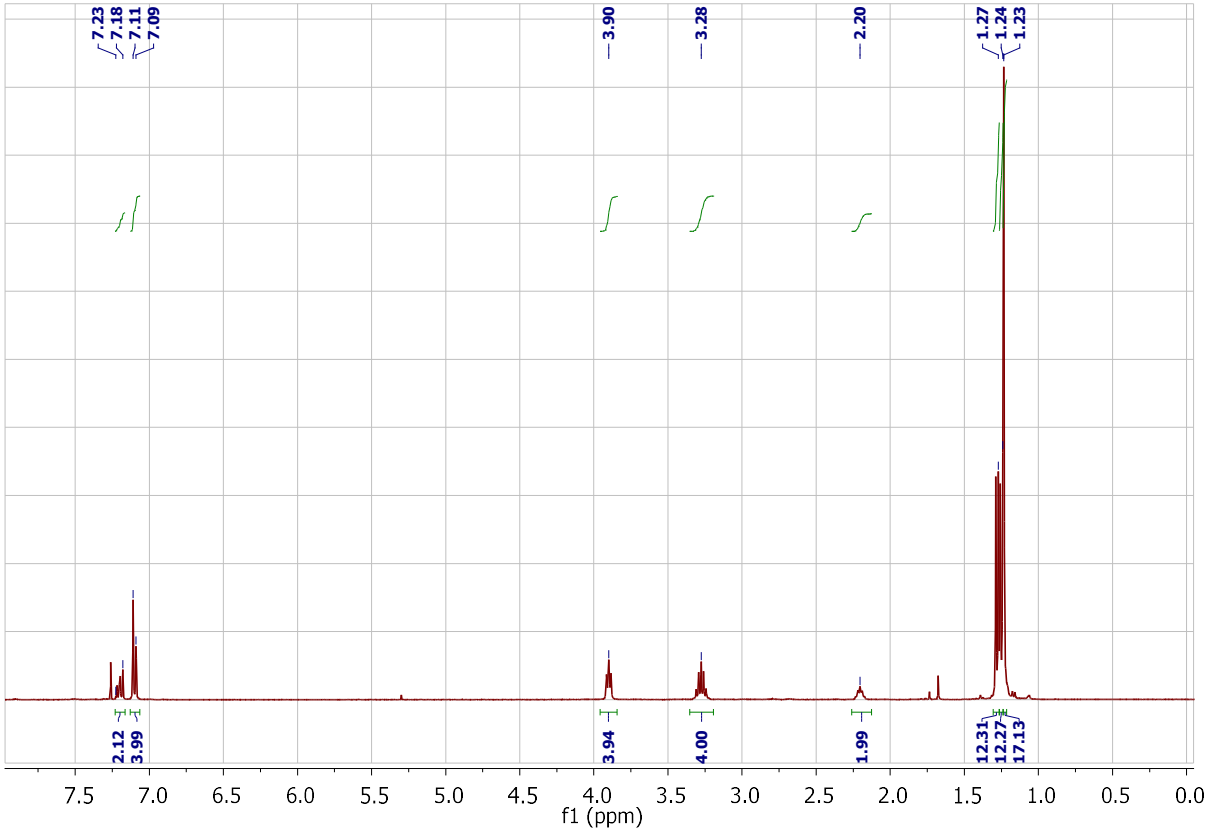

*Figure S50 ^{1}H NMR spectrum (400 MHz) of **5b** in $CDCl_3$ at 300 K.*

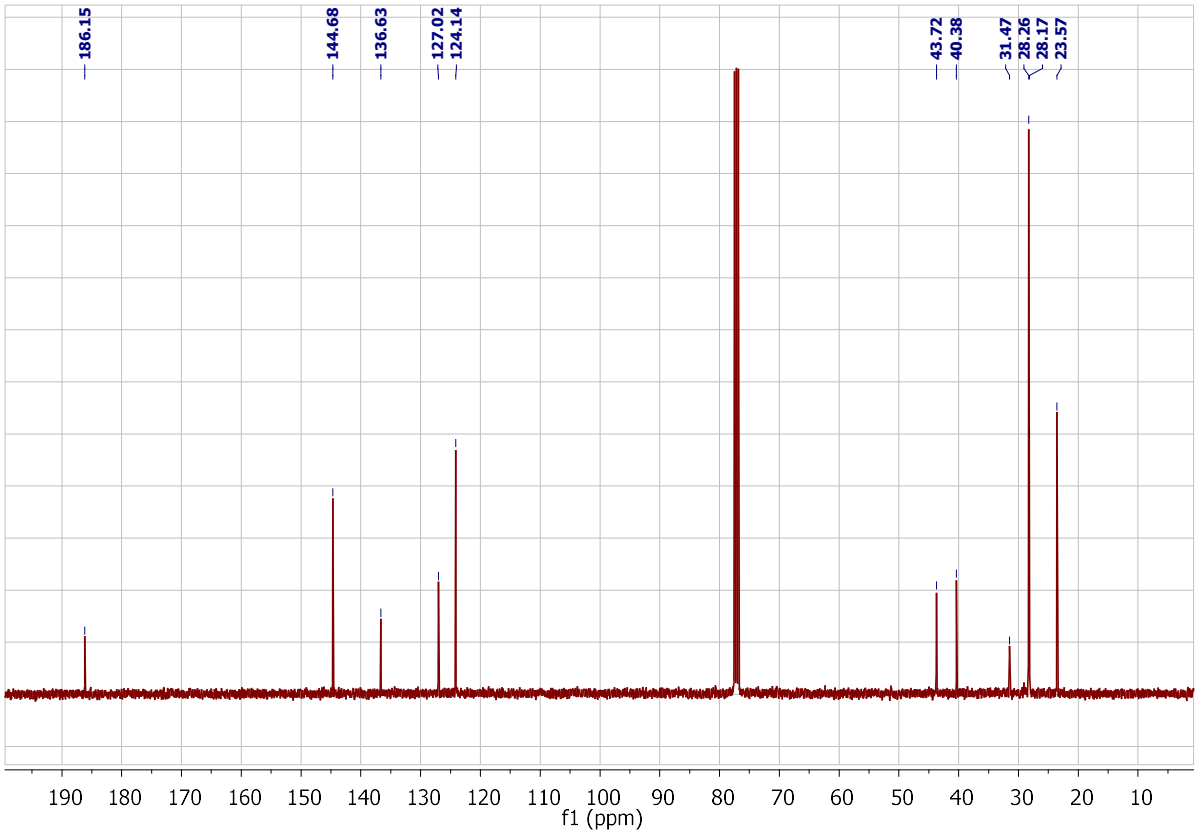

*Figure S51 ^{13}C NMR spectrum (101 MHz) of **5b** in $CDCl_3$ at 300 K.*

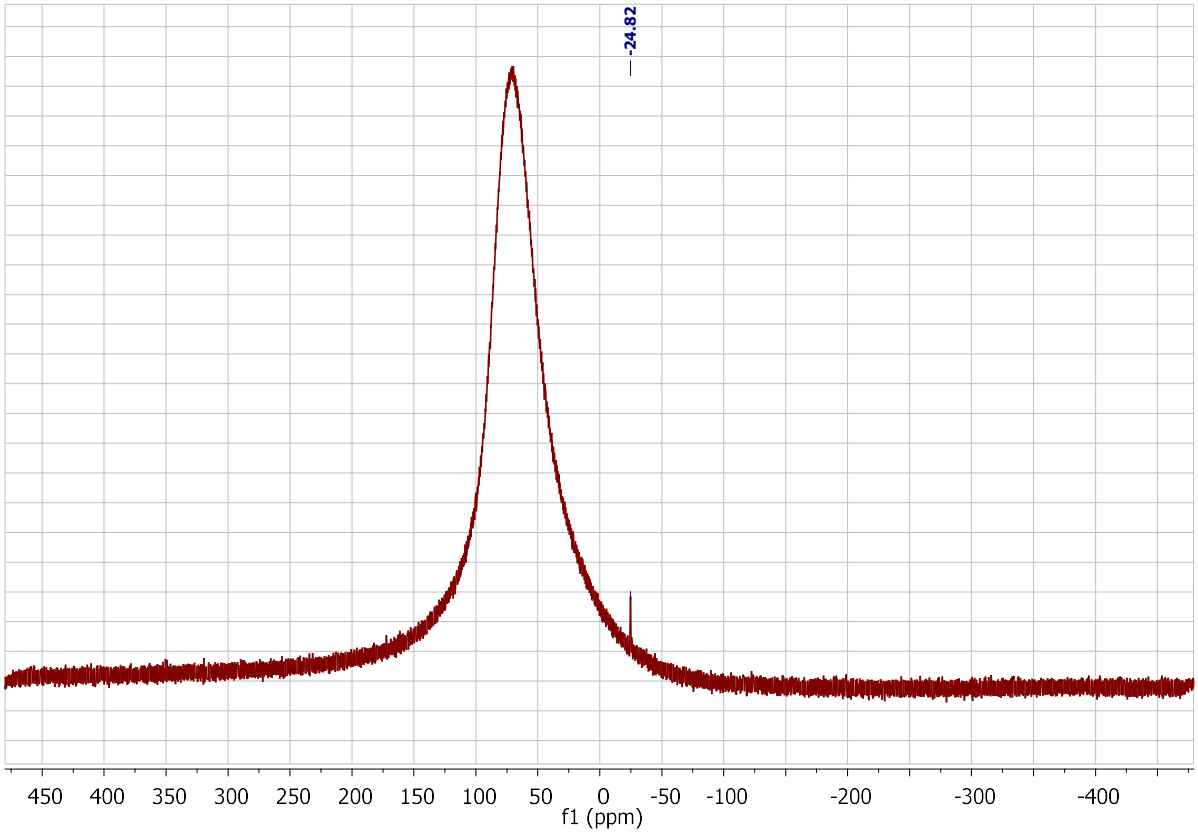

*Figure S52 ^{27}Al NMR spectrum (104 MHz) of **5b** in $CDCl_3$ at 300 K.*

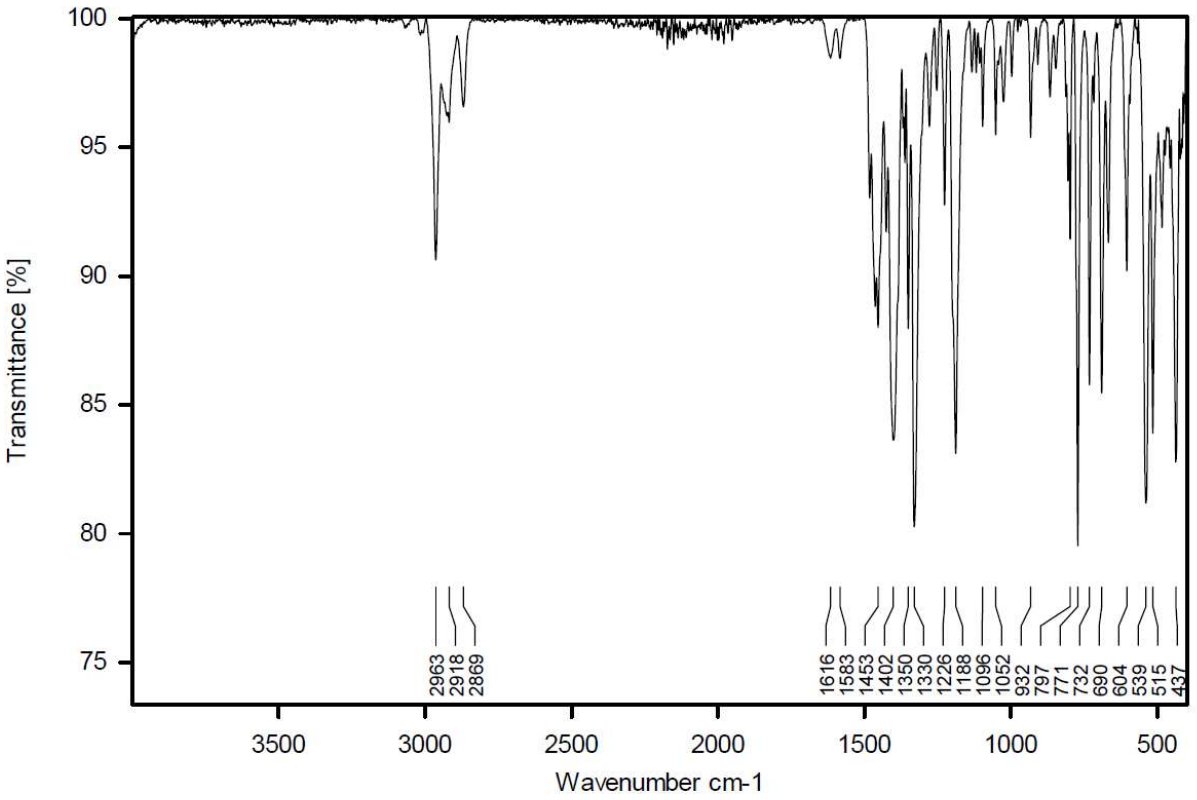

*Figure S53 ATR-IR spectrum of **5b.***

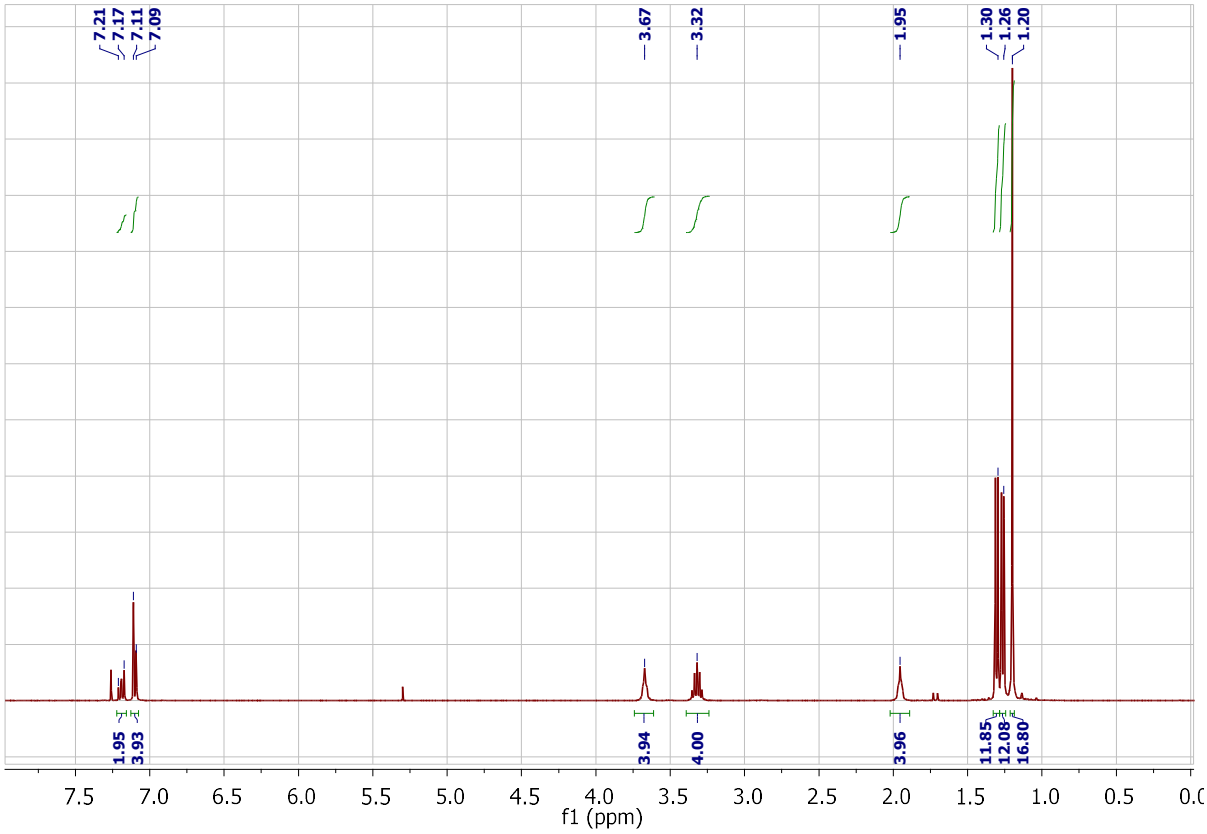

*Figure S54 ^{1}H NMR spectrum (400 MHz) of **5c** in $CDCl_3$ at 300 K.*

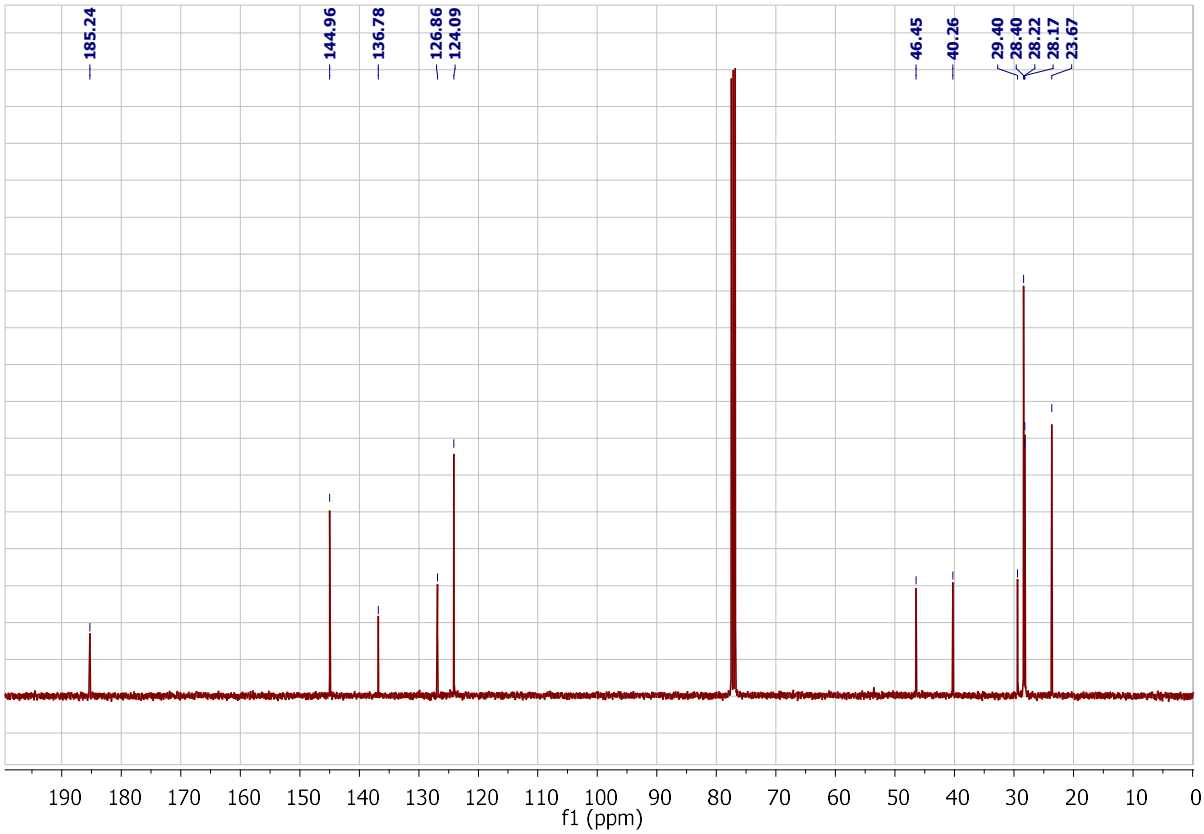

*Figure S55 ^{13}C NMR spectrum (101 MHz) of **5c** in $CDCl_3$ at 300 K.*

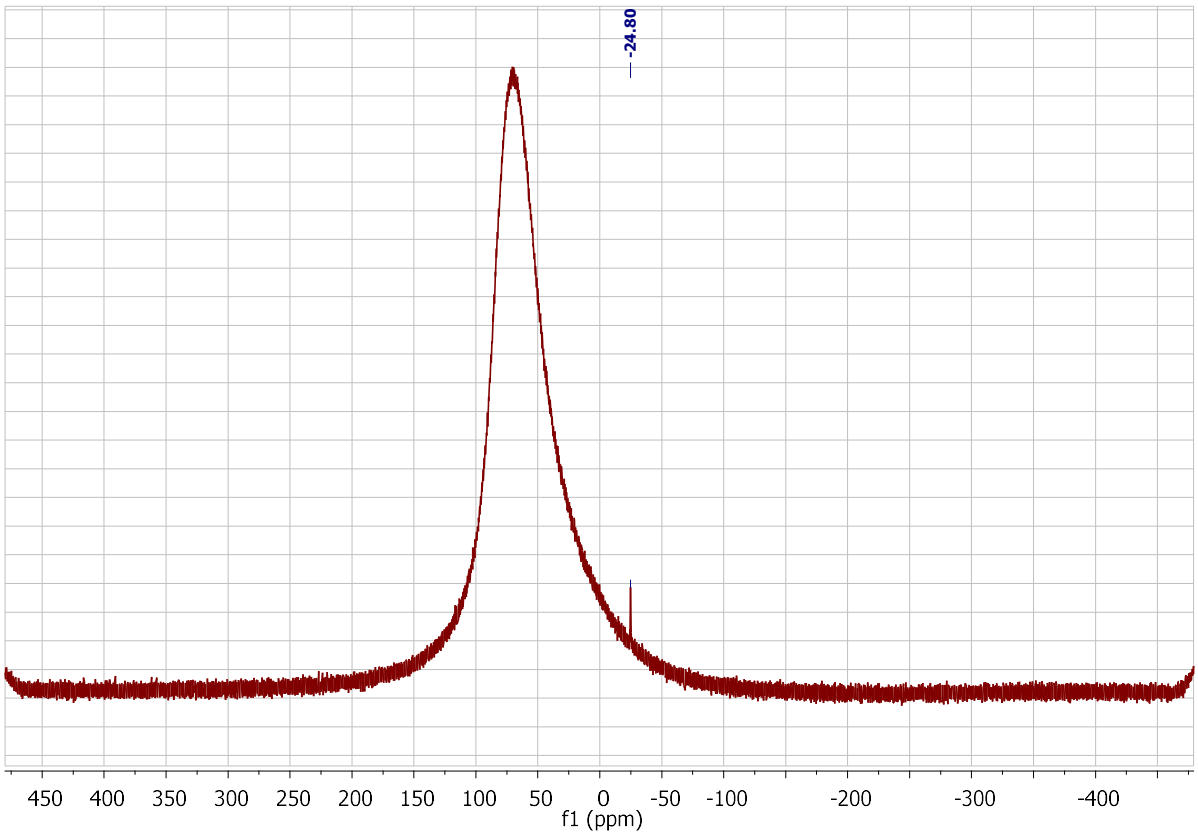

*Figure S56 ^{27}Al NMR spectrum (104 MHz) of **5c** in $CDCl_3$ at 300 K.*

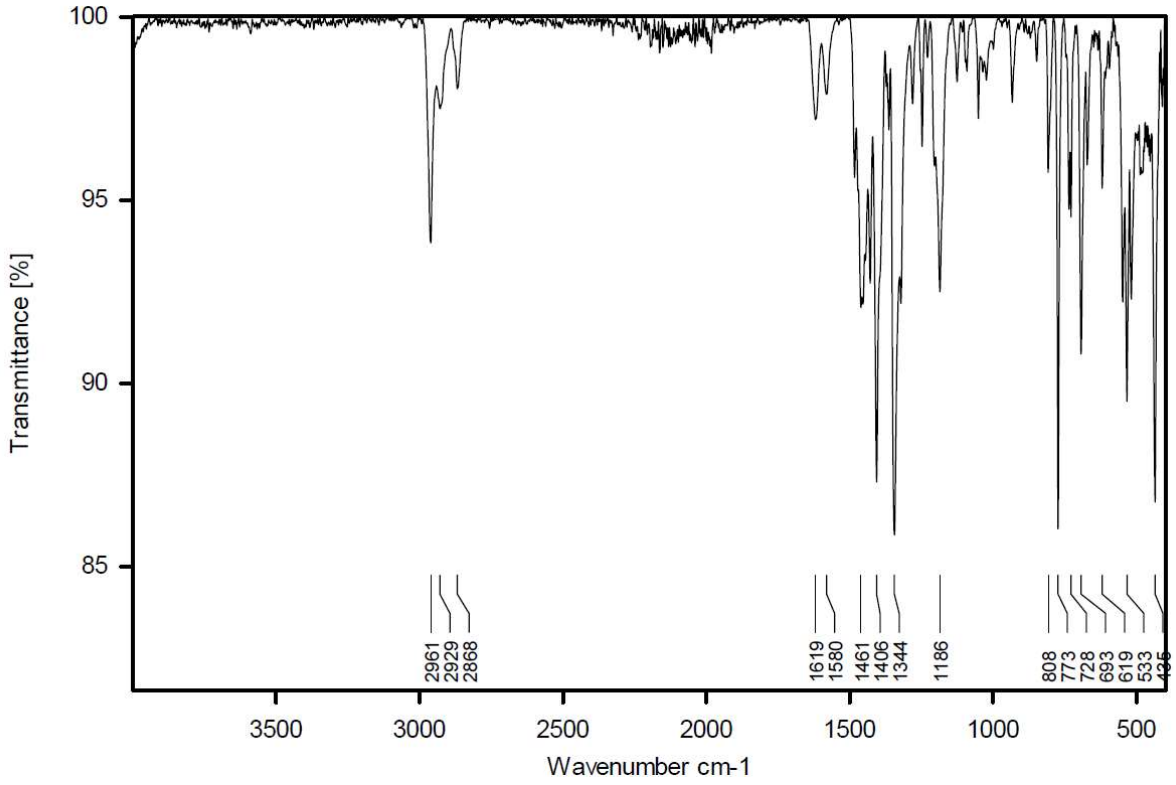

*Figure S57 ATR-IR spectrum of **5c.***

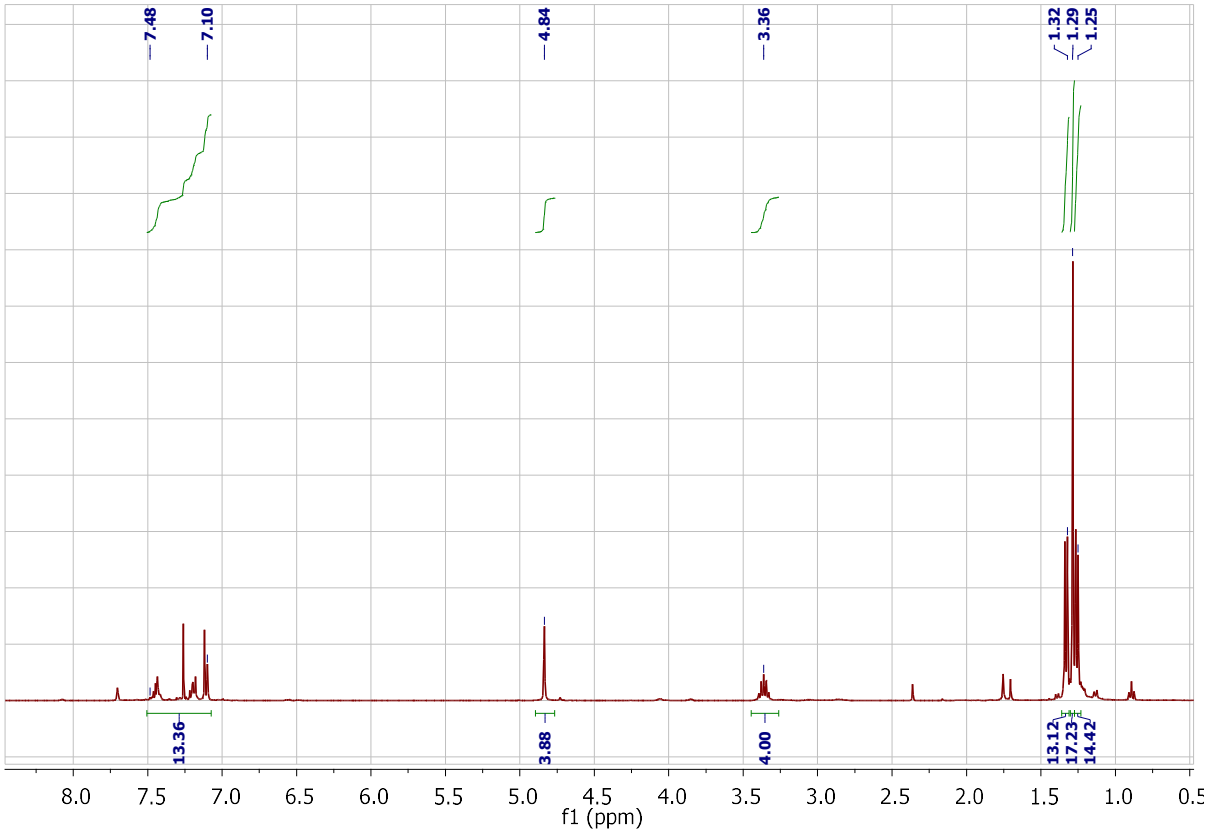

*Figure S58 ^{1}H NMR spectrum (400 MHz) of **5d** in $CDCl_3$ at 300 K.*

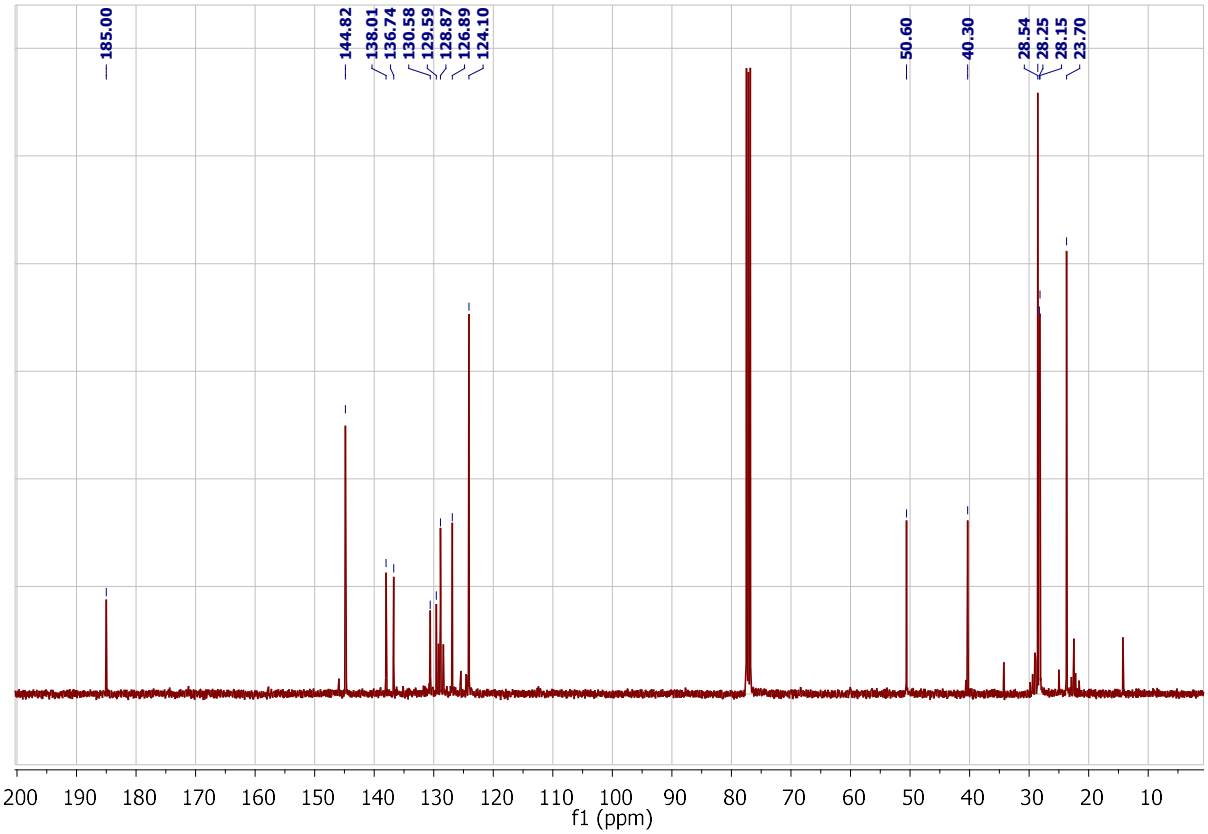

*Figure S59 ^{13}C NMR spectrum (101 MHz) of **5d** in $CDCl_3$ at 300 K.*

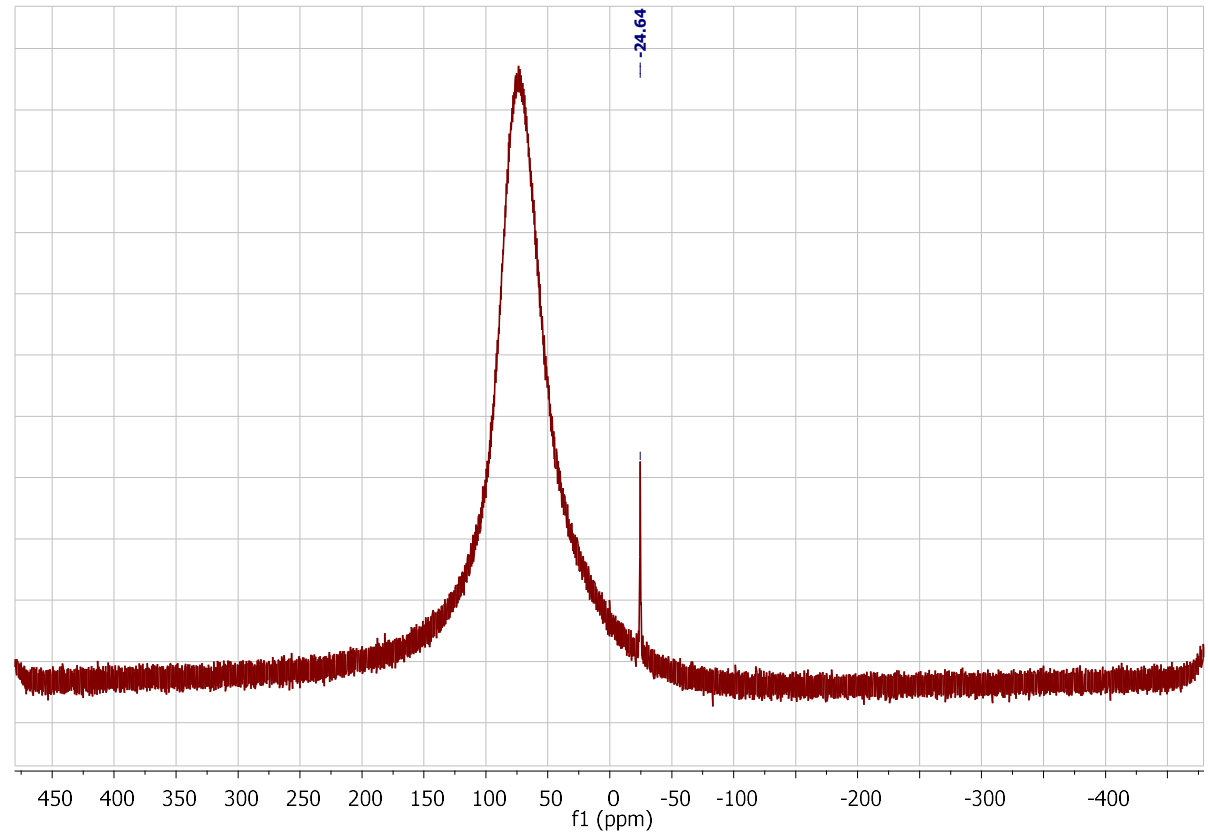

*Figure S60 ^{27}Al NMR spectrum (104 MHz) of **5d** in $CDCl_3$ at 300 K..*

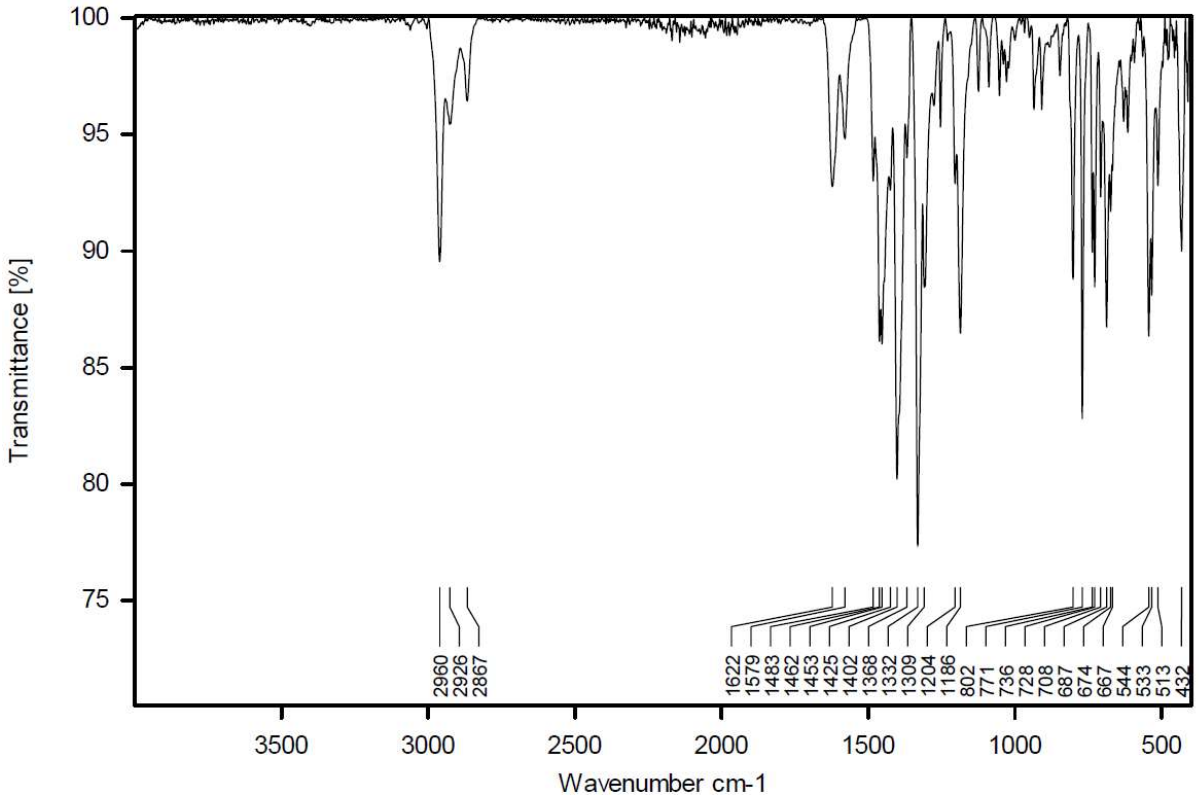

*Figure S61 ATR-IR spectrum of **5d**.*

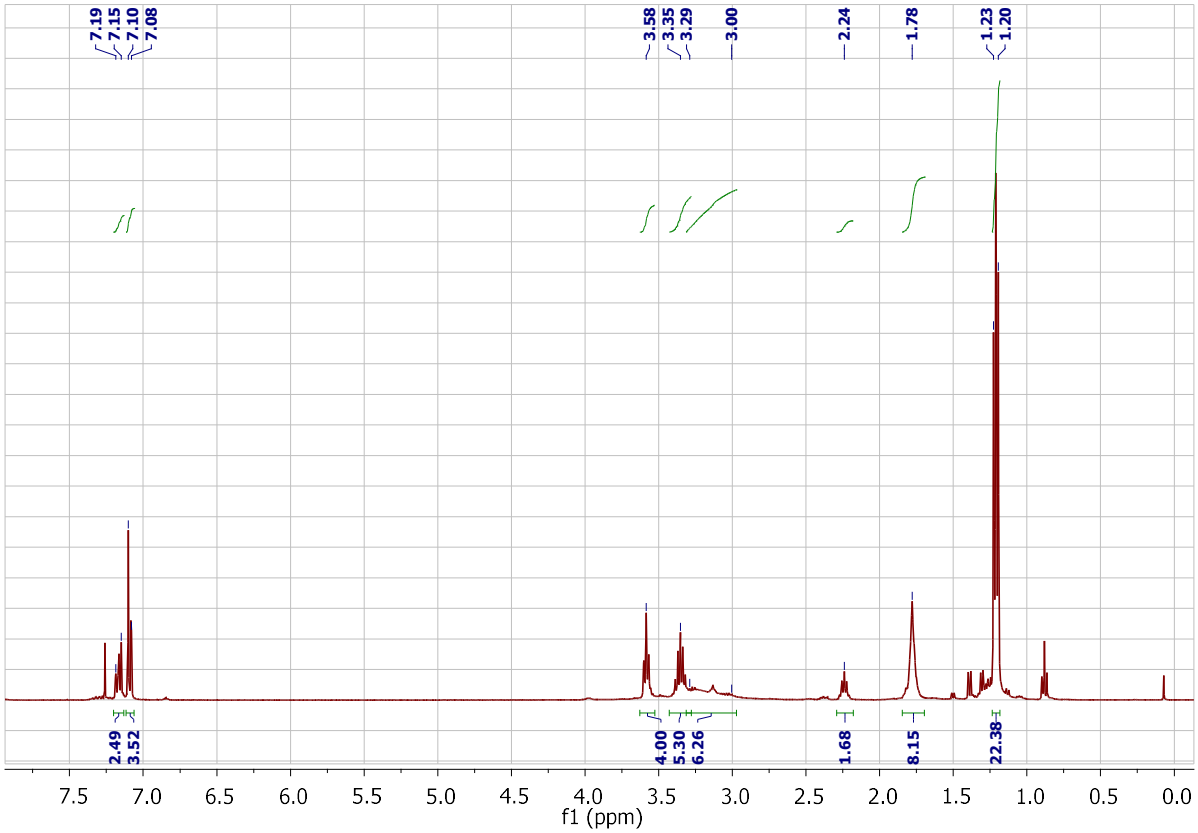

*Figure S62 ^{1}H NMR spectrum (400 MHz) of **6b** in $CDCl_3$ at 300 K.*

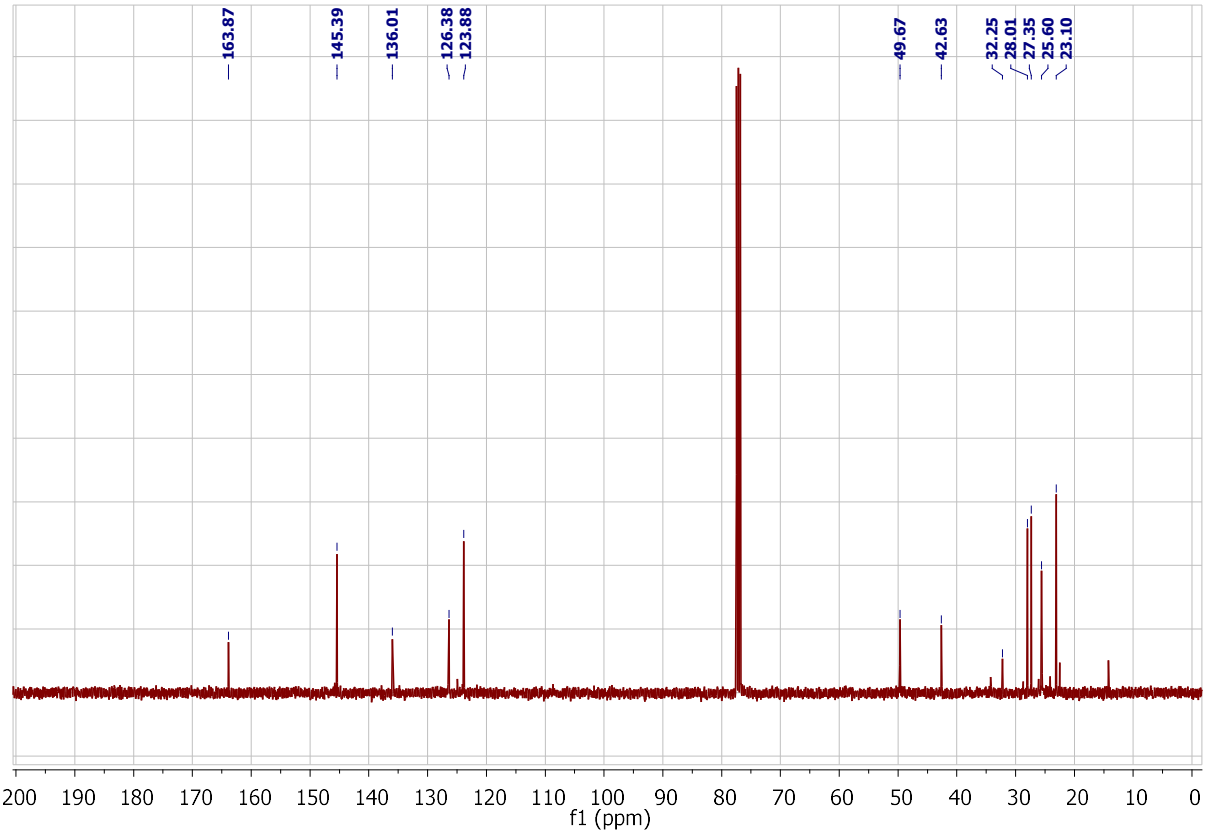

*Figure S63 ^{13}C NMR spectrum (101 MHz) of **6b** in $CDCl_3$ at 300 K.*

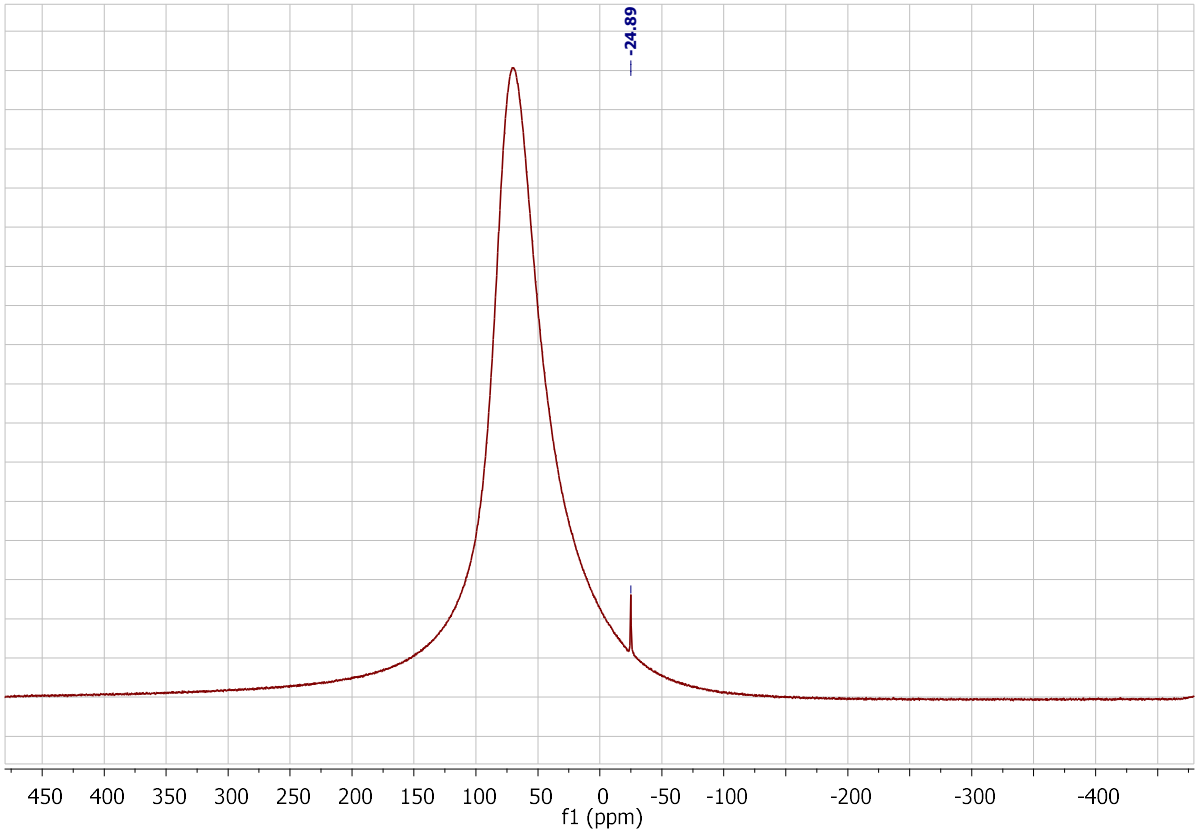

*Figure S64 ^{27}Al NMR spectrum (104 MHz) of **6b** in $CDCl_3$ at 300 K.*

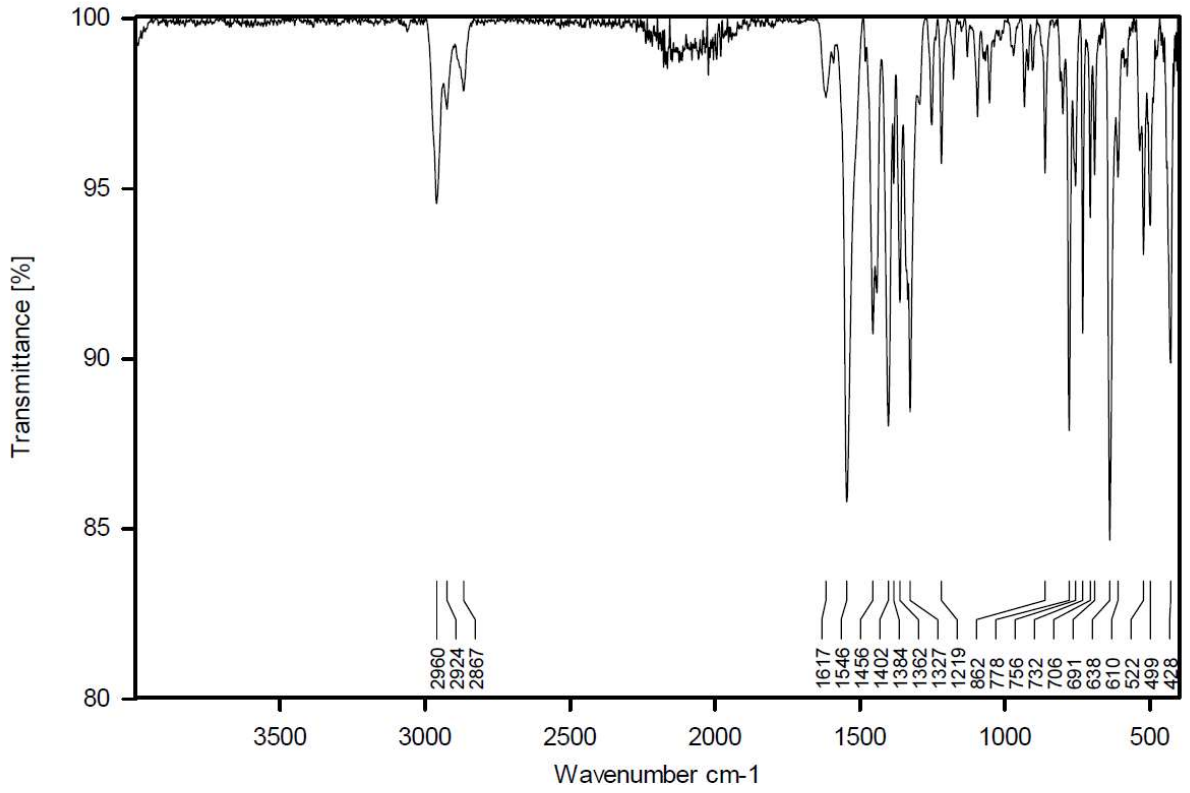

*Figure S65 ATR-IR spectrum of **6b**.*

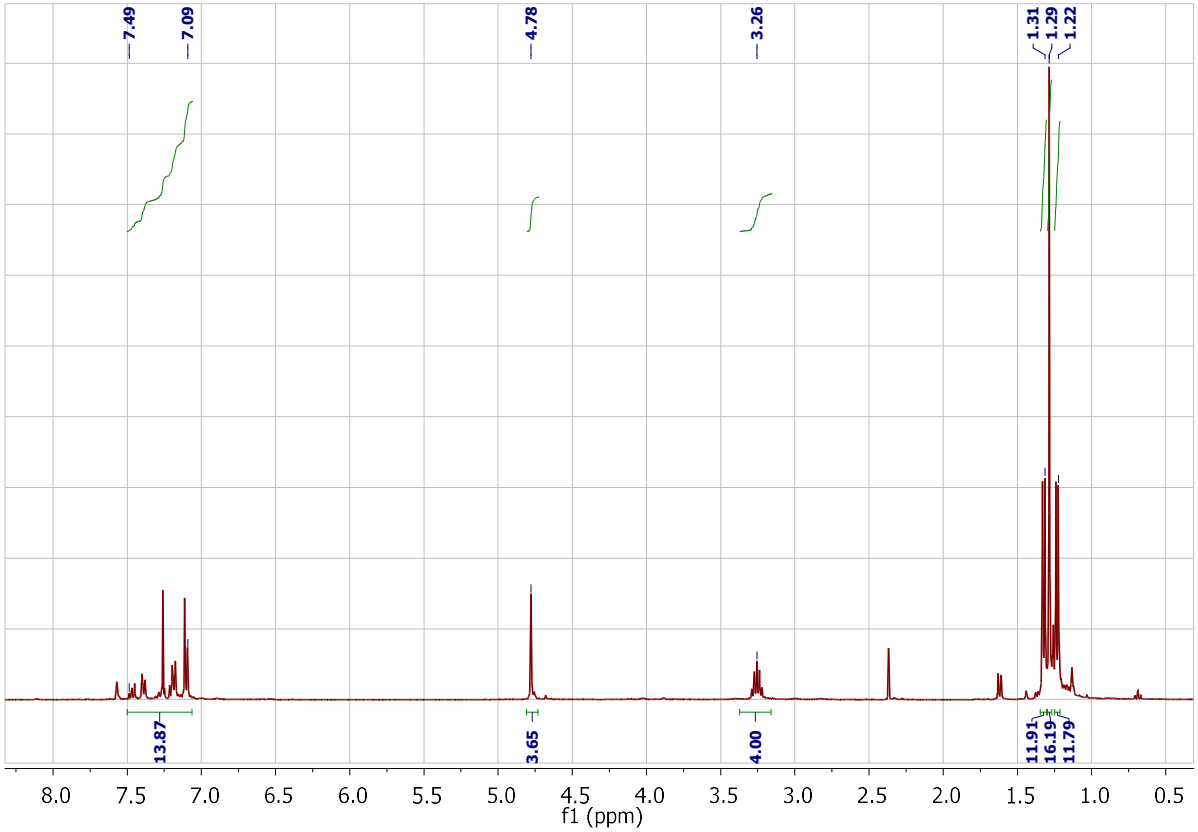

*Figure S66 ^{1}H NMR spectrum (400 MHz) of **7d** in $CDCl_3$ at 300 K.*

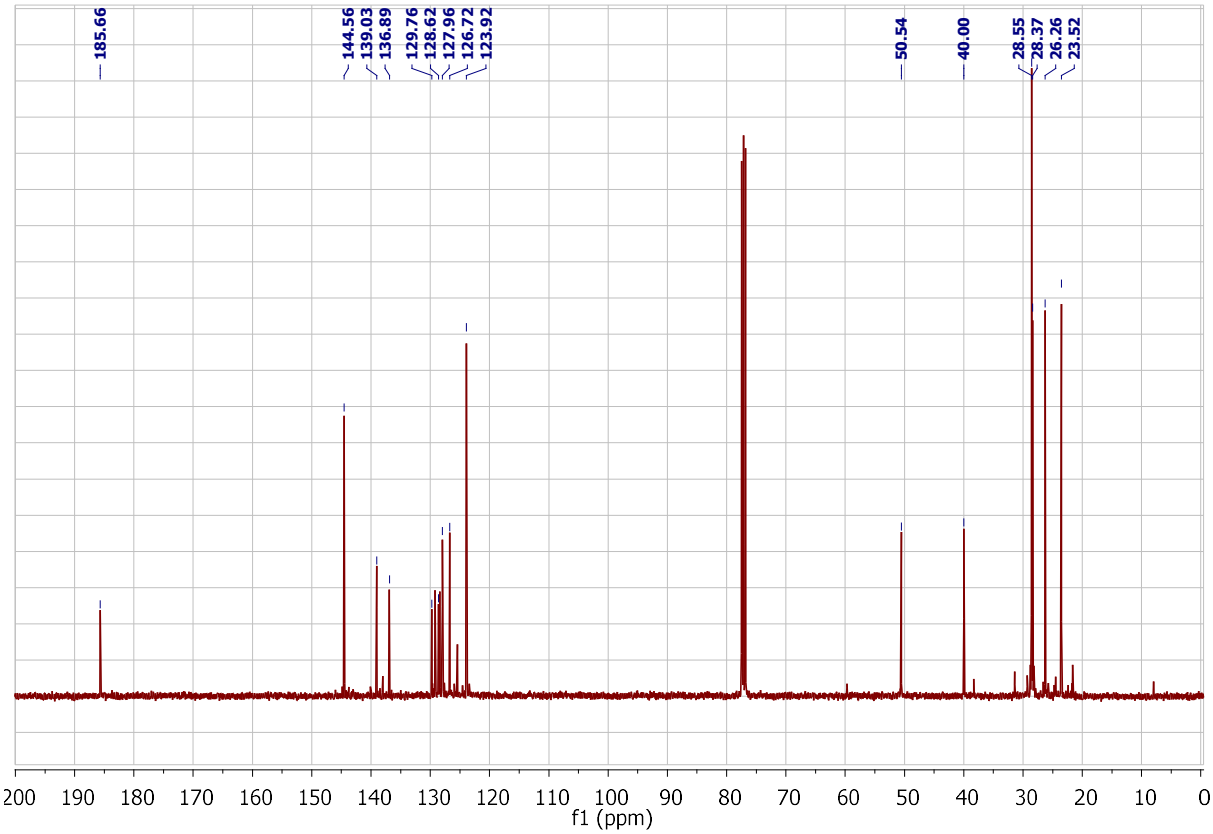

*Figure S67 ^{13}C NMR spectrum (101 MHz) of **7d** in $CDCl_3$ at 300 K.*

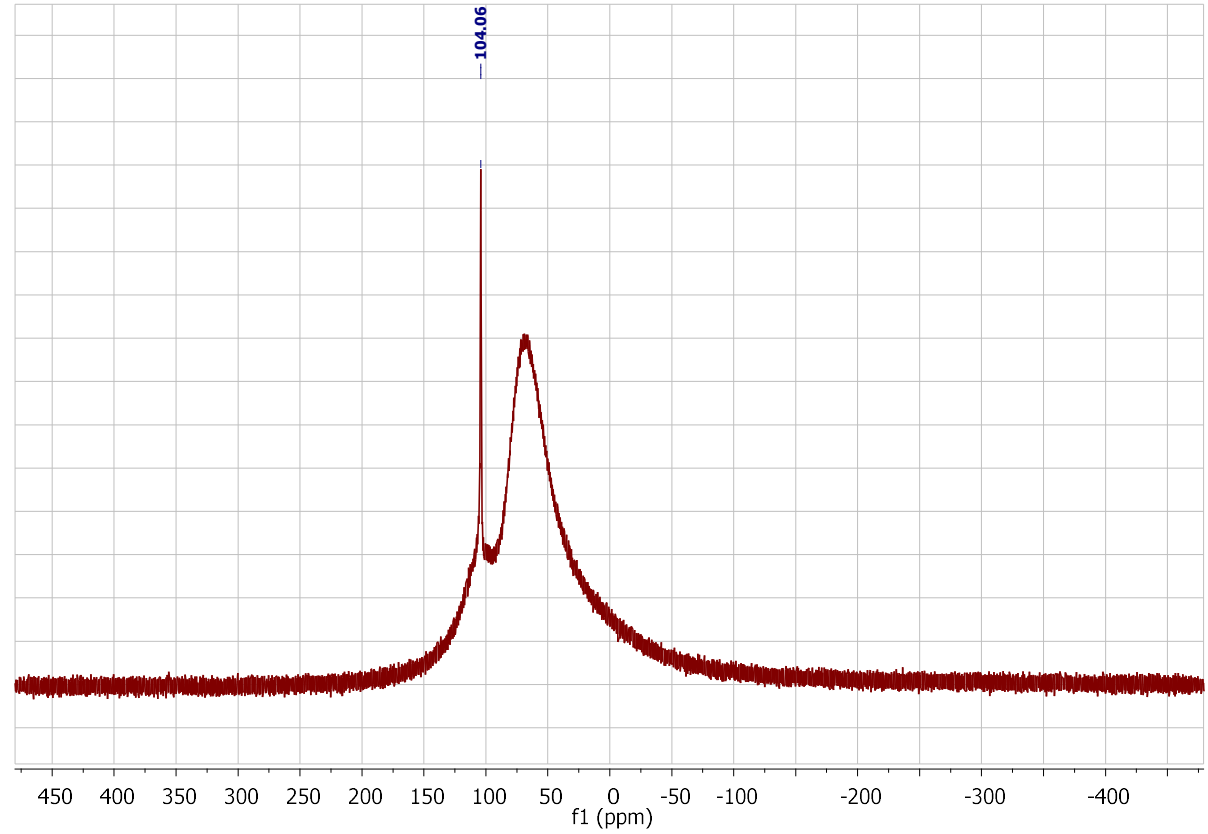

*Figure S68 ^{27}Al NMR spectrum (104 MHz) of **7d** in $CDCl_3$ at 300 K.*

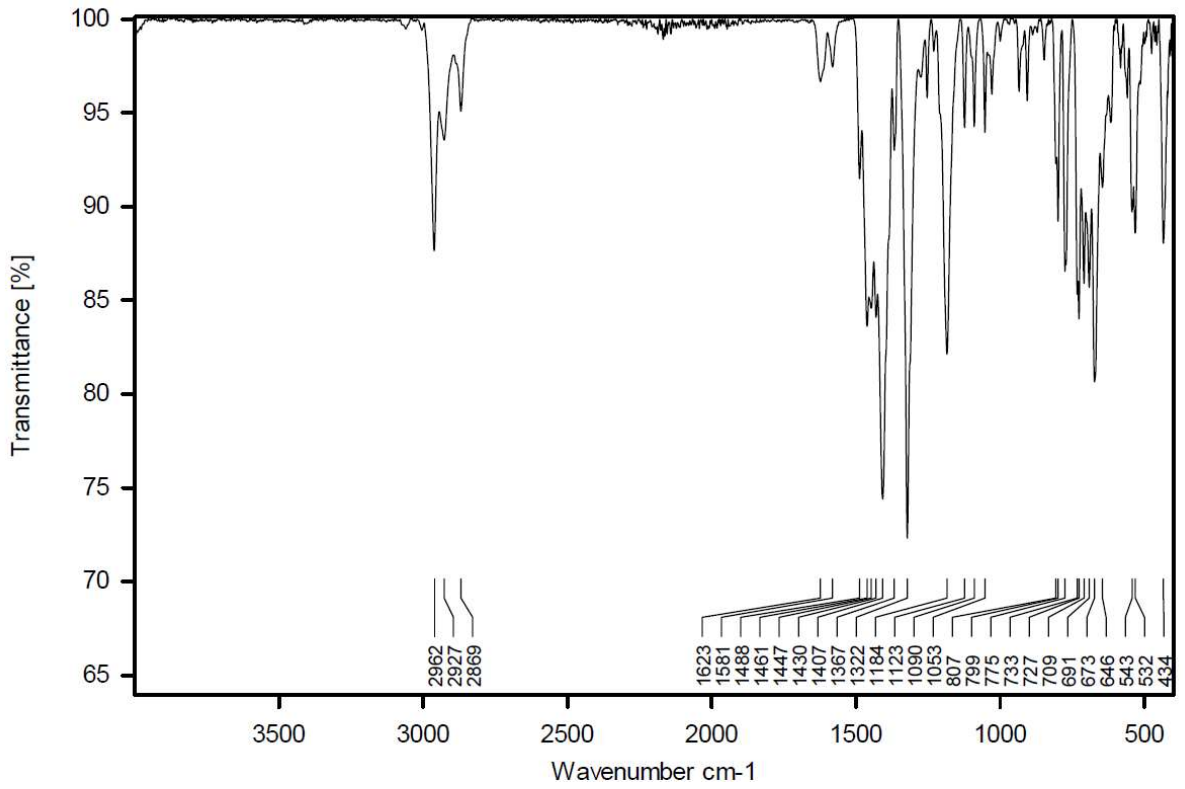

*Figure S69 ATR-IR spectrum of **7d**.*

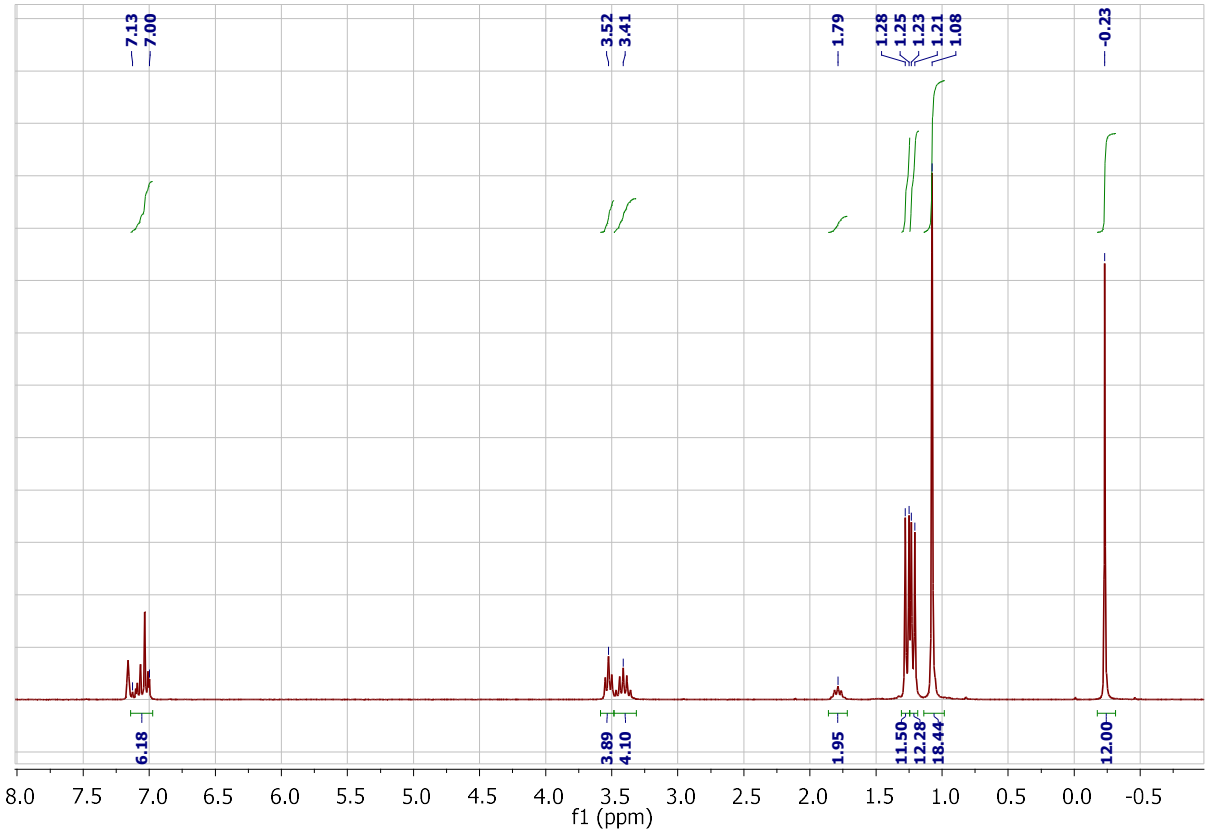

*Figure S70 ^{1}H NMR spectrum (250 MHz) of **3b** in C_6D_6 at 300 K before the addition of benzyl alcohol.*

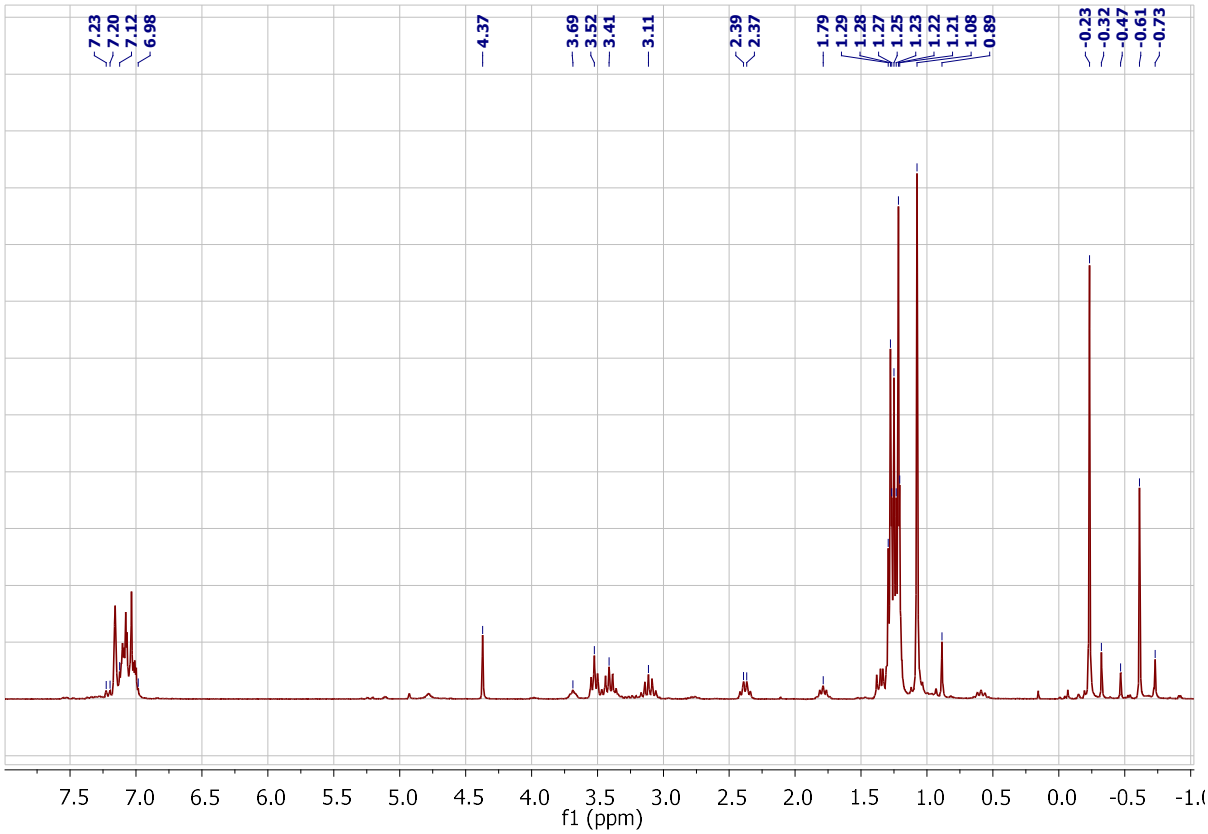

*Figure S71 ^{1}H NMR spectrum (250 MHz) of **3b** in C_6D_6 at 300 K after the addition of one equivalent of benzyl alcohol. The signals at -0.73 and 4.37 ppm account for $Me_2Al(OBn)$.*

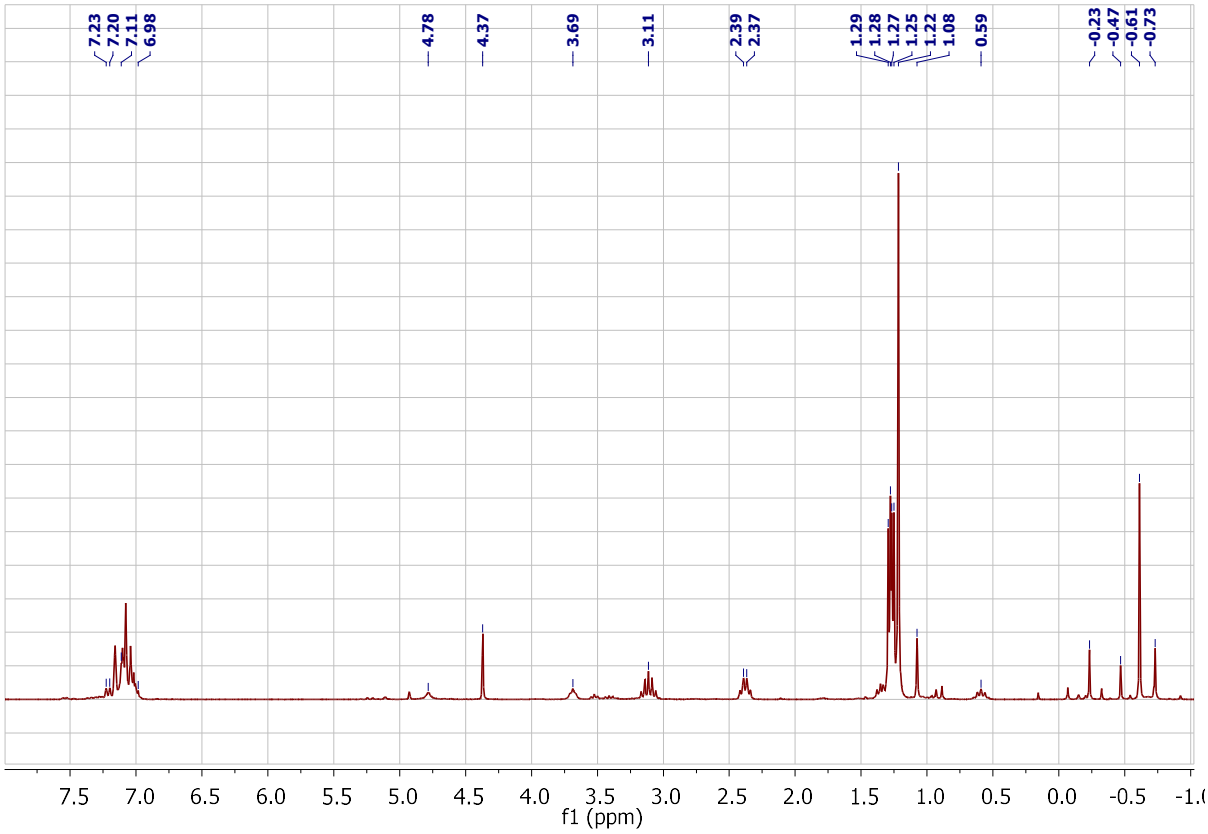

*Figure S72 ^{1}H NMR spectrum (250 MHz) of **3b** in C_6D_6 at 300 K before the addition of two equivalents of benzyl alcohol. The signals at -0.73 and 4.37 ppm account for $Me_2Al(OBn)$.*

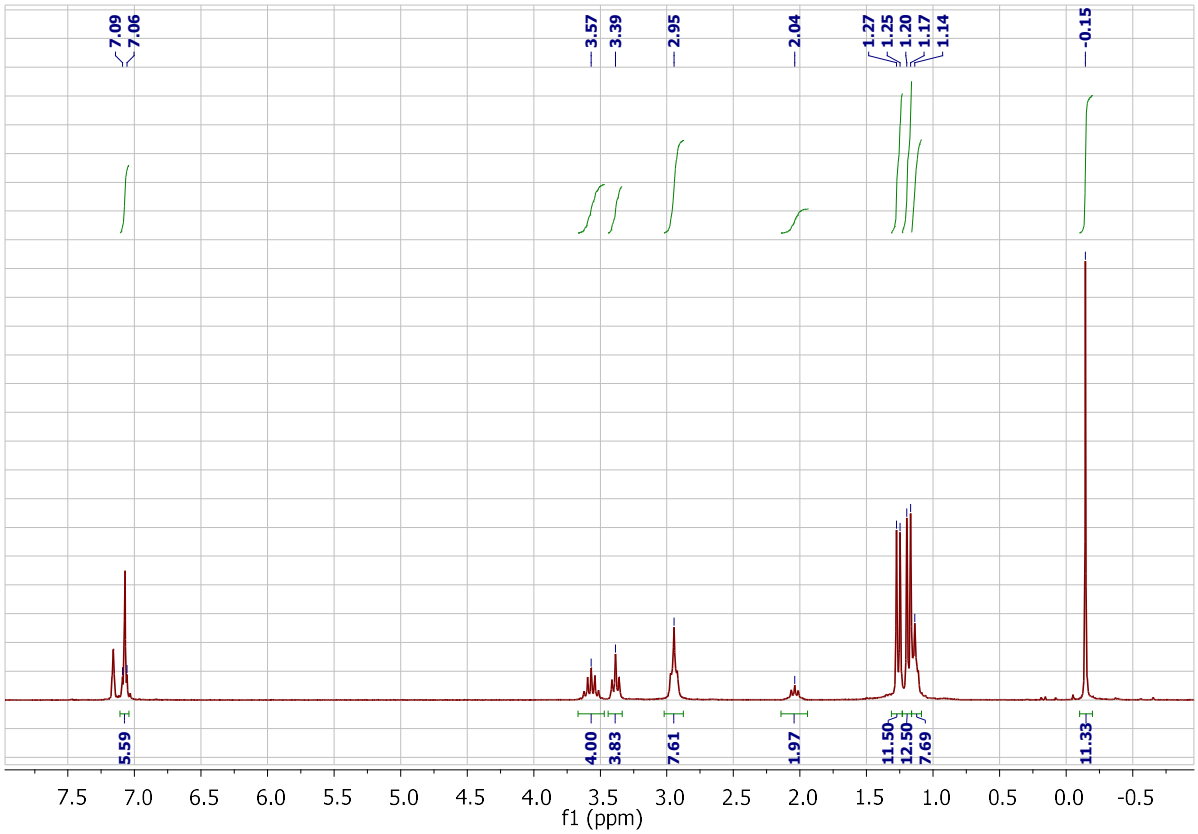

*Figure S73 ^{1}H NMR spectrum (250 MHz) of **4b** in C_6D_6 at 300 K before the addition of benzyl alcohol.*

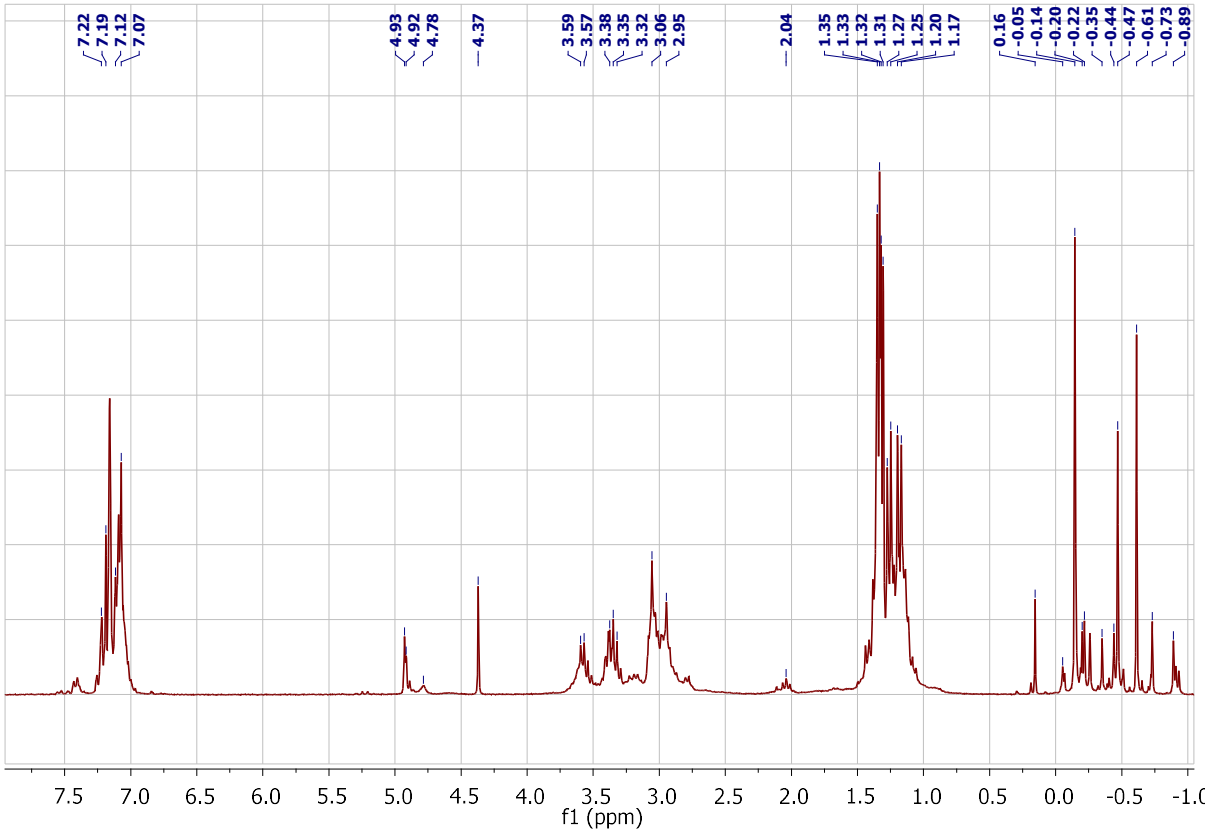

*Figure S74 ^{1}H NMR spectrum (250 MHz) of **4b** in C_6D_6 at 300 K after the addition of one equivalent of benzyl alcohol. The signals at -0.73 and 4.37 ppm account for $Me_2Al(OBn)$.*

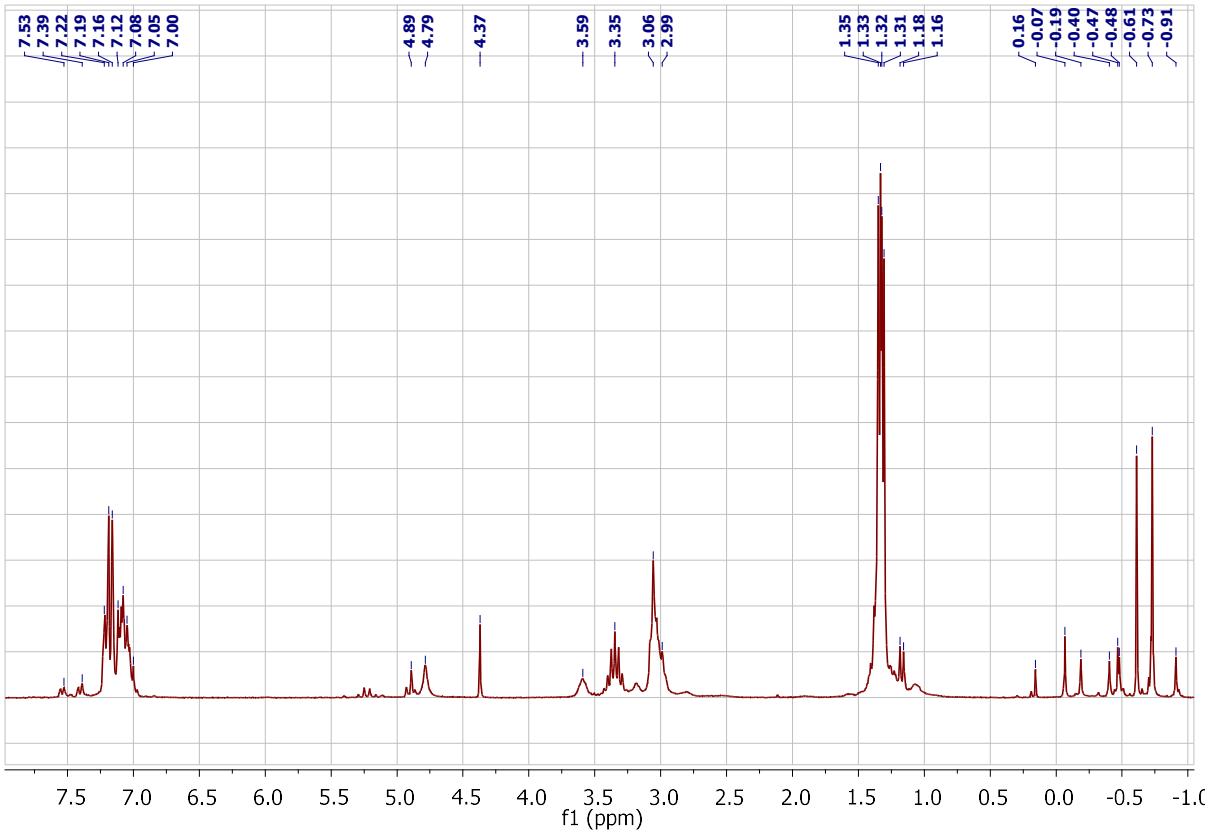

*Figure S75 ^{1}H NMR spectrum (250 MHz) of **4b** in C_6D_6 at 300 K before the addition of two equivalents of benzyl alcohol. The signals at -0.73 and 4.37 ppm account for $Me_2Al(OBn)$.*

6. Size exclusion chromatography

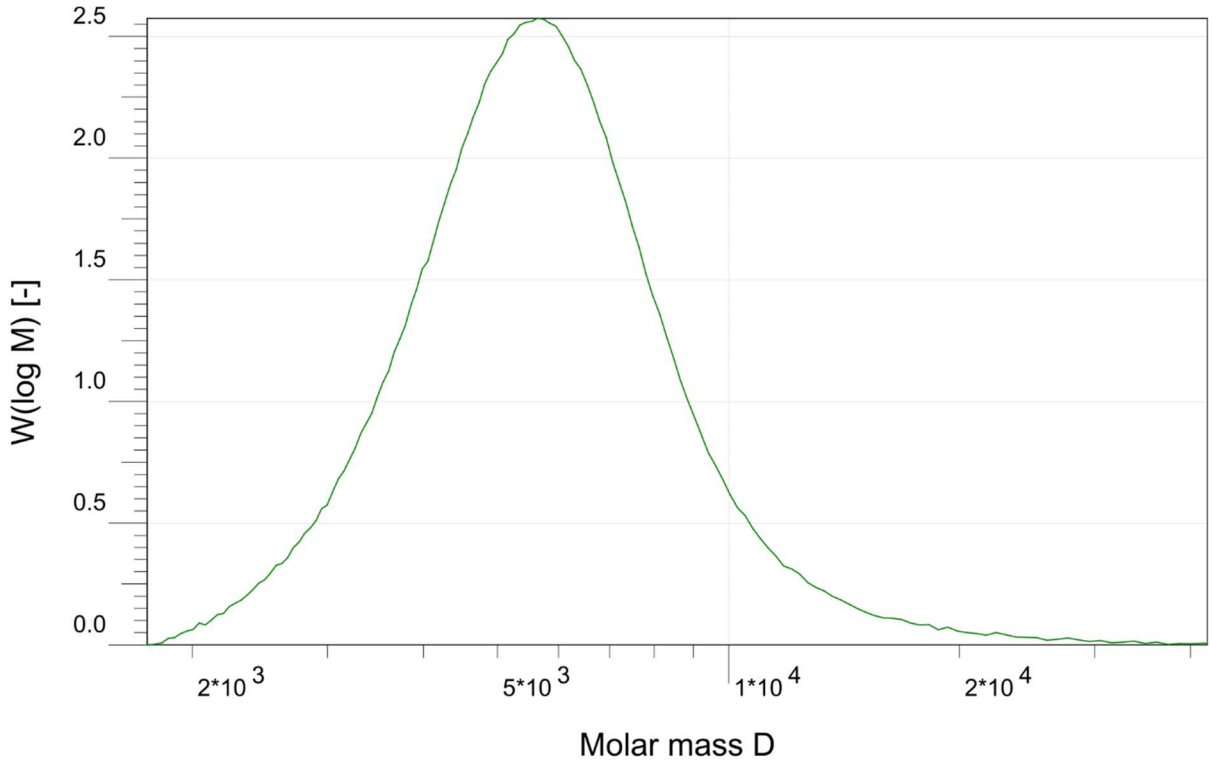

*Figure S76 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 80 °C, 25 h, catalyst **3a**.*

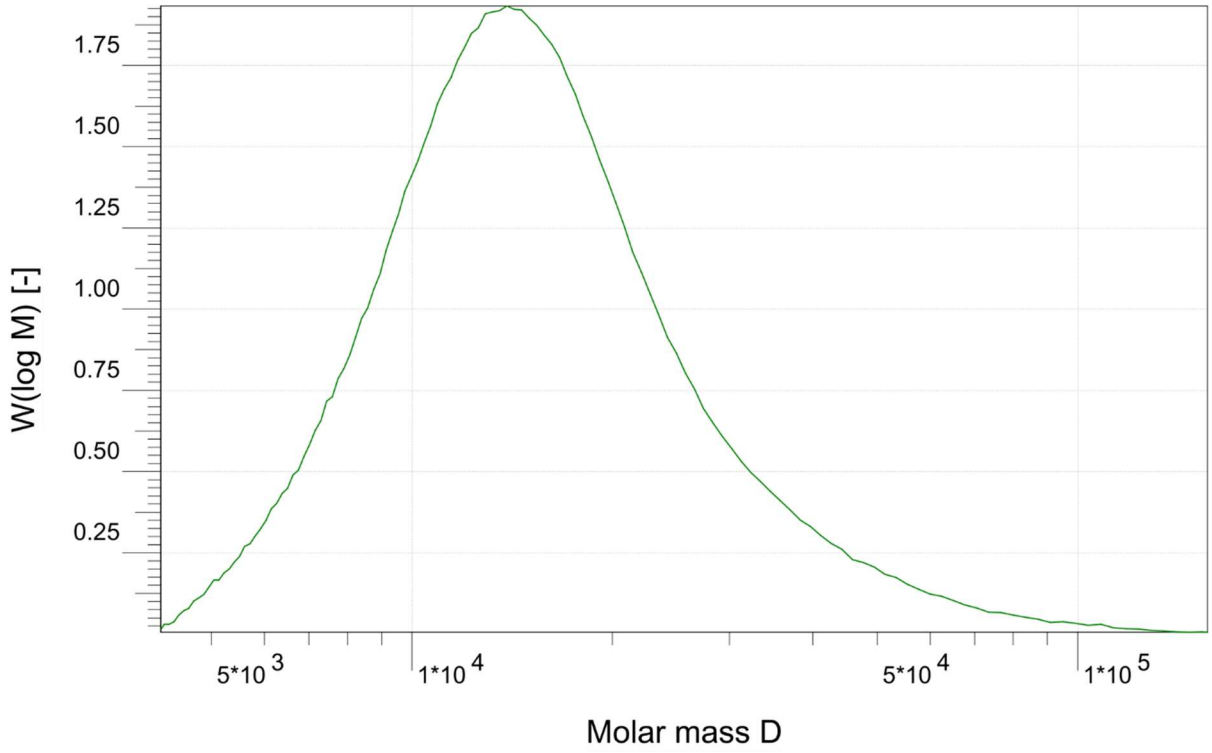

*Figure S77 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 90 °C, 25 h, catalyst **3a**.*

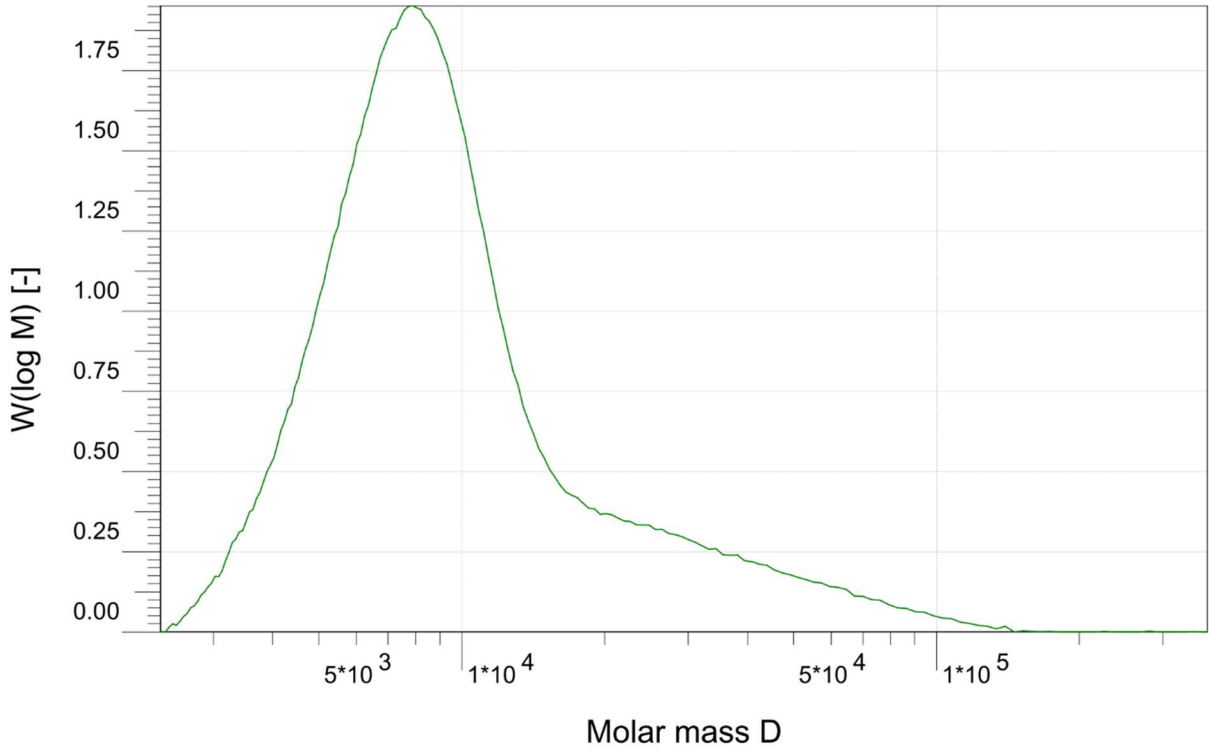

*Figure S78 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 80 °C, 25 h, catalyst **3b**.*

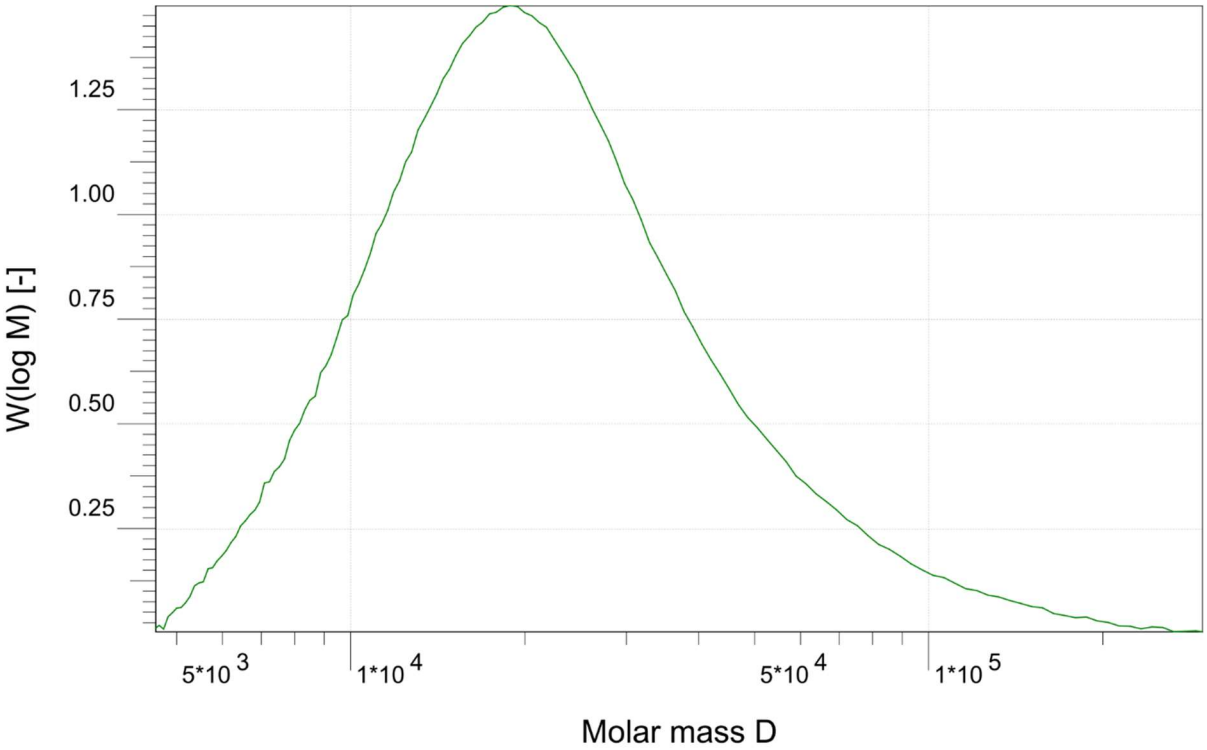

*Figure S79 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 90 °C, 25 h, catalyst **3b**.*

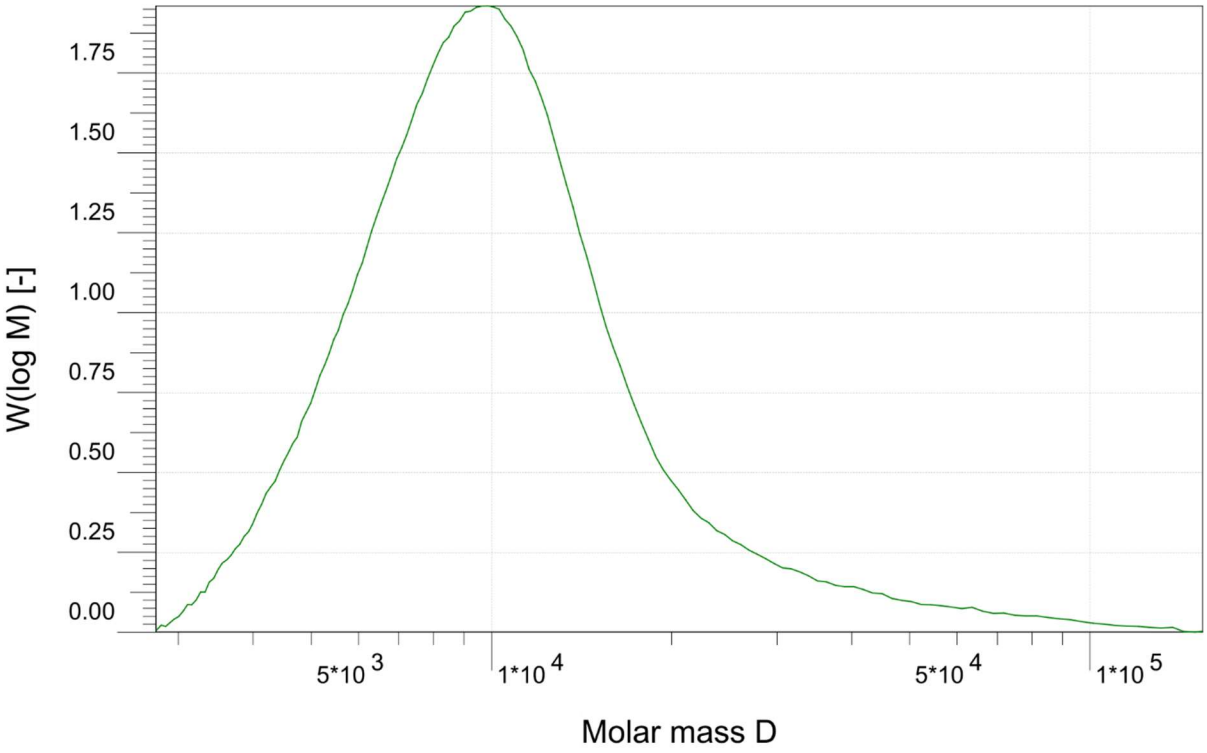

*Figure S80 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 80 °C, 25 h, catalyst **3c**.*

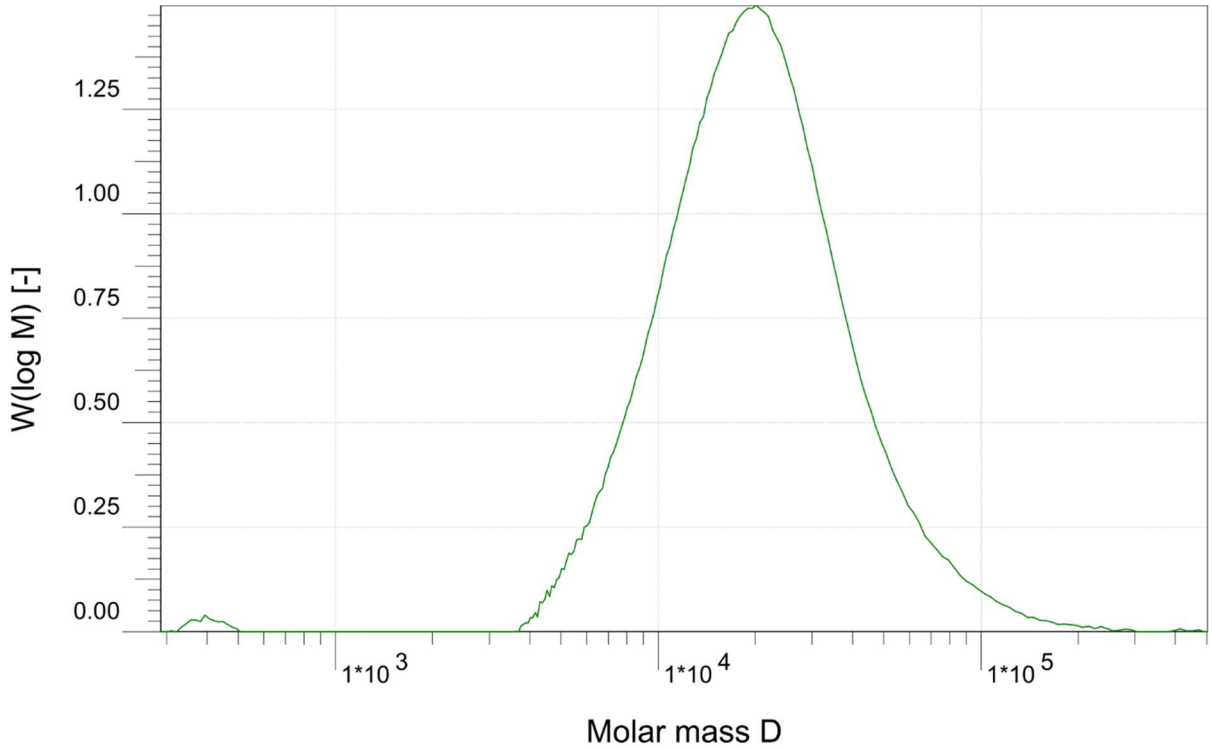

*Figure S81 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 90 °C, 25 h, catalyst **3c**.*

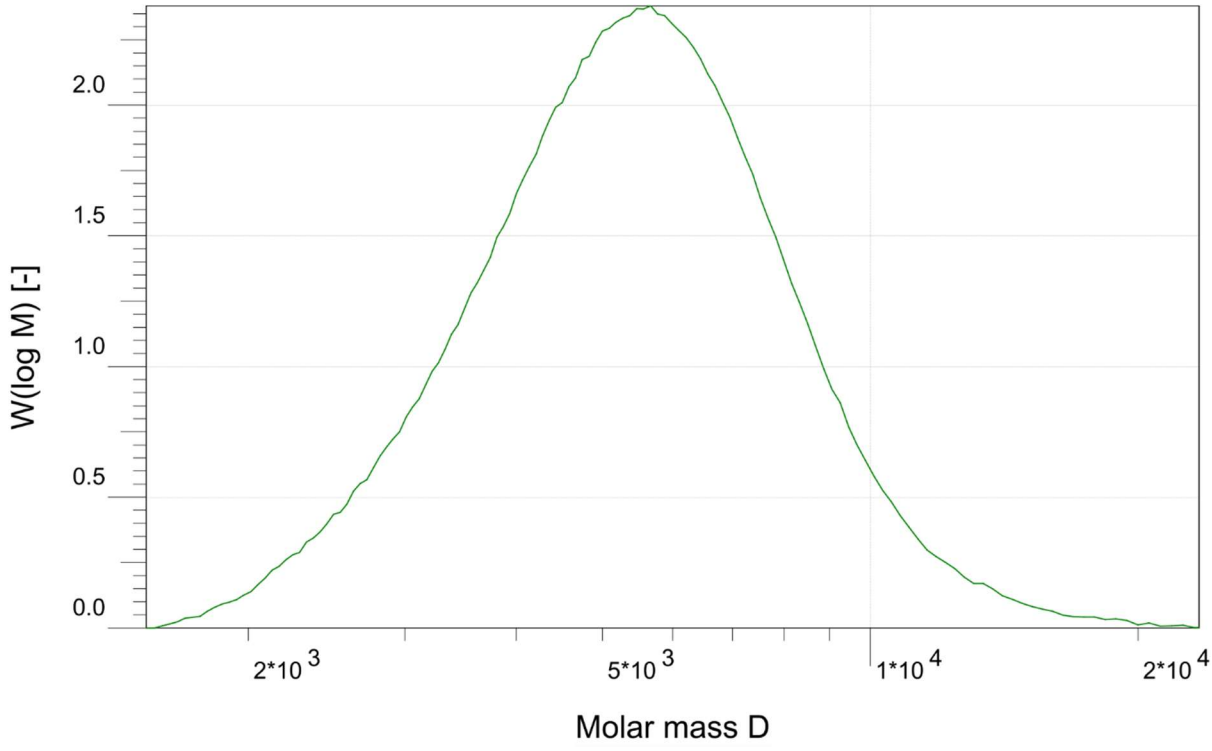

*Figure S82 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 80 °C, 25 h, catalyst **3d**.*

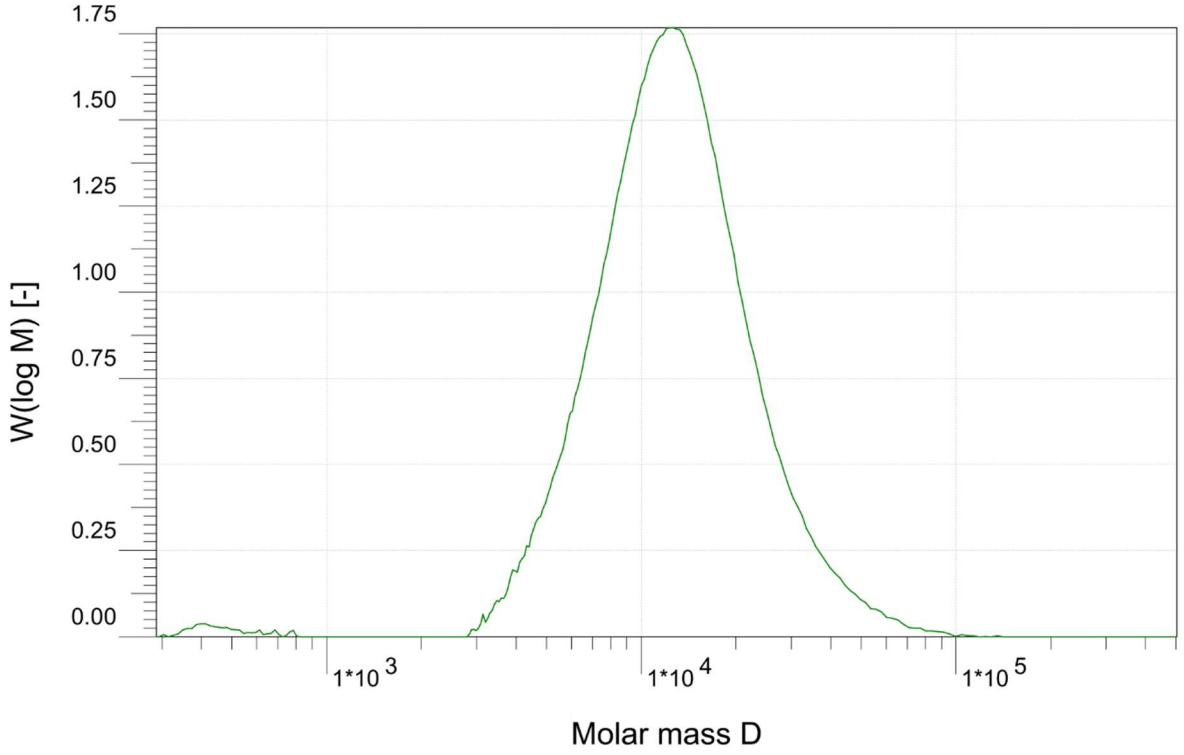

*Figure S83 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 90 °C, 25 h, catalyst **3d**.*

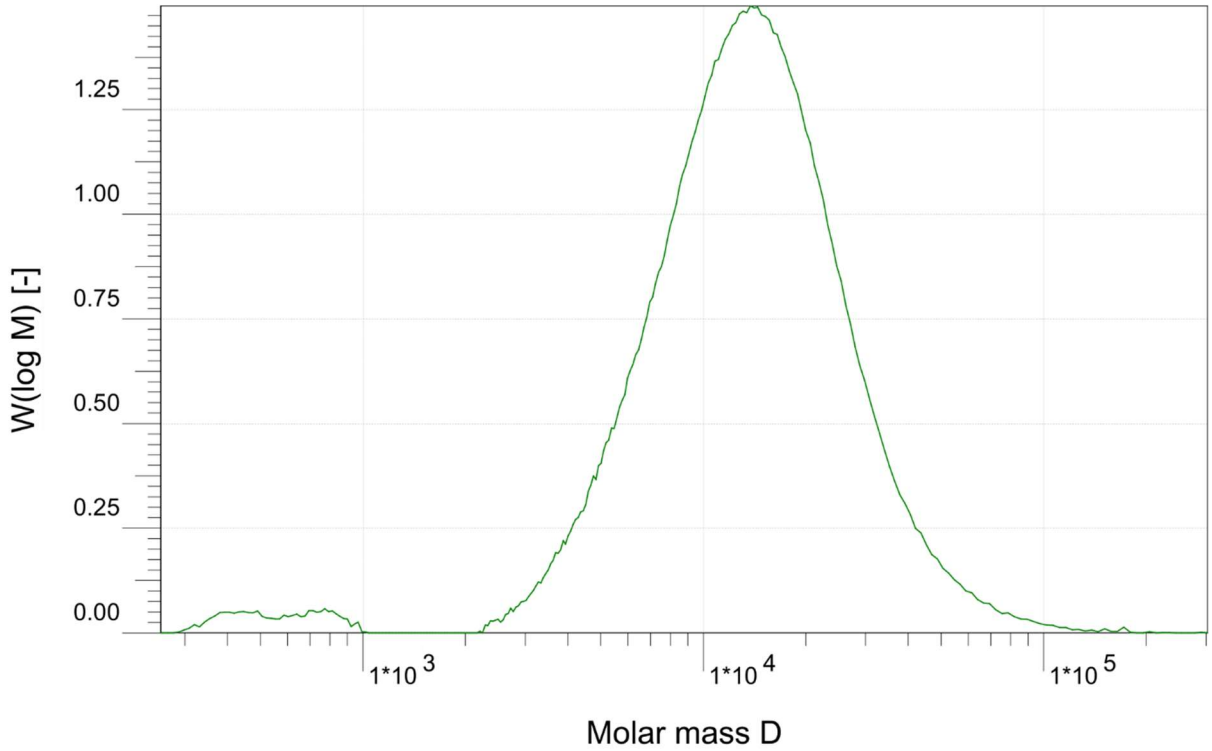

*Figure S84 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 80 °C, 25 h, catalyst **4a**.*

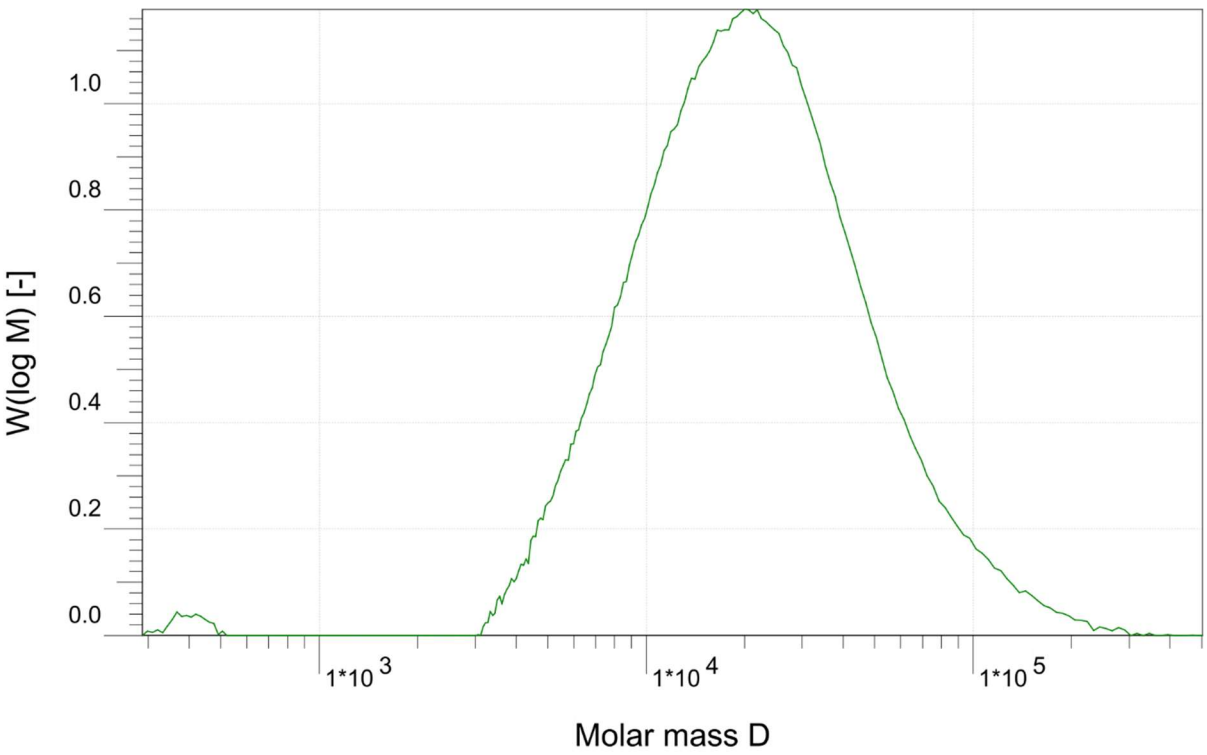

*Figure S85 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 90 °C, 25 h, catalyst **4a**.*

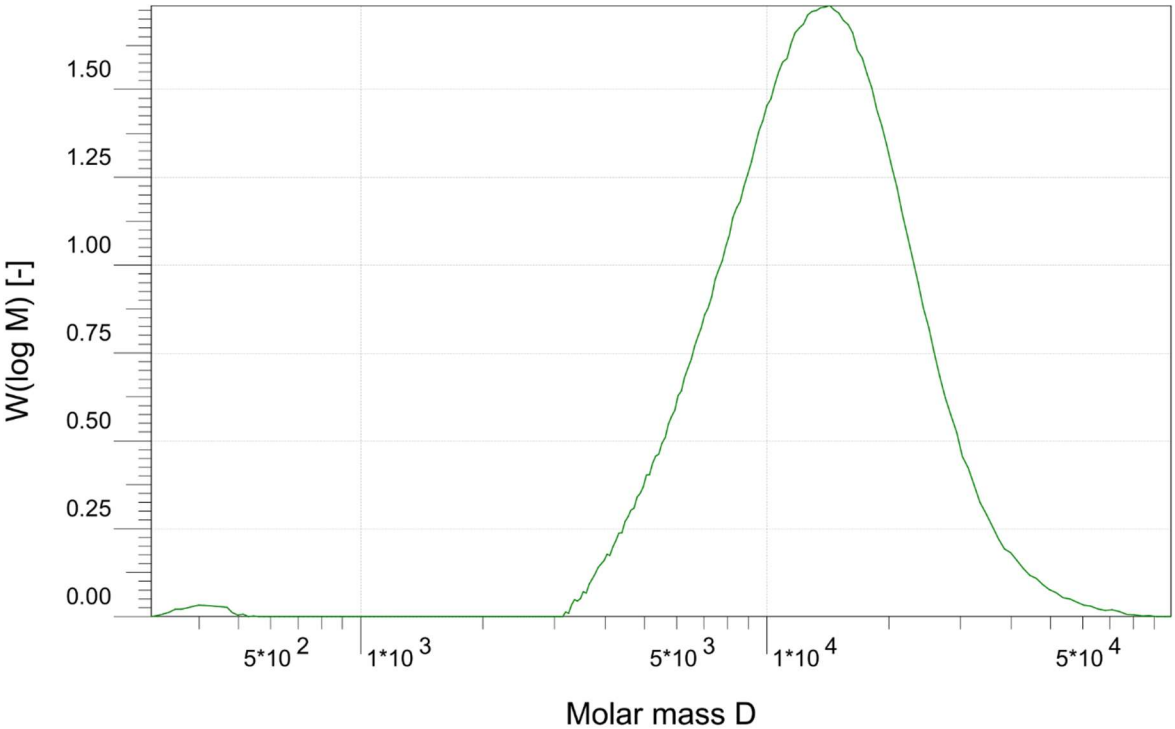

*Figure S86 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 80 °C, 25 h, catalyst **4b**.*

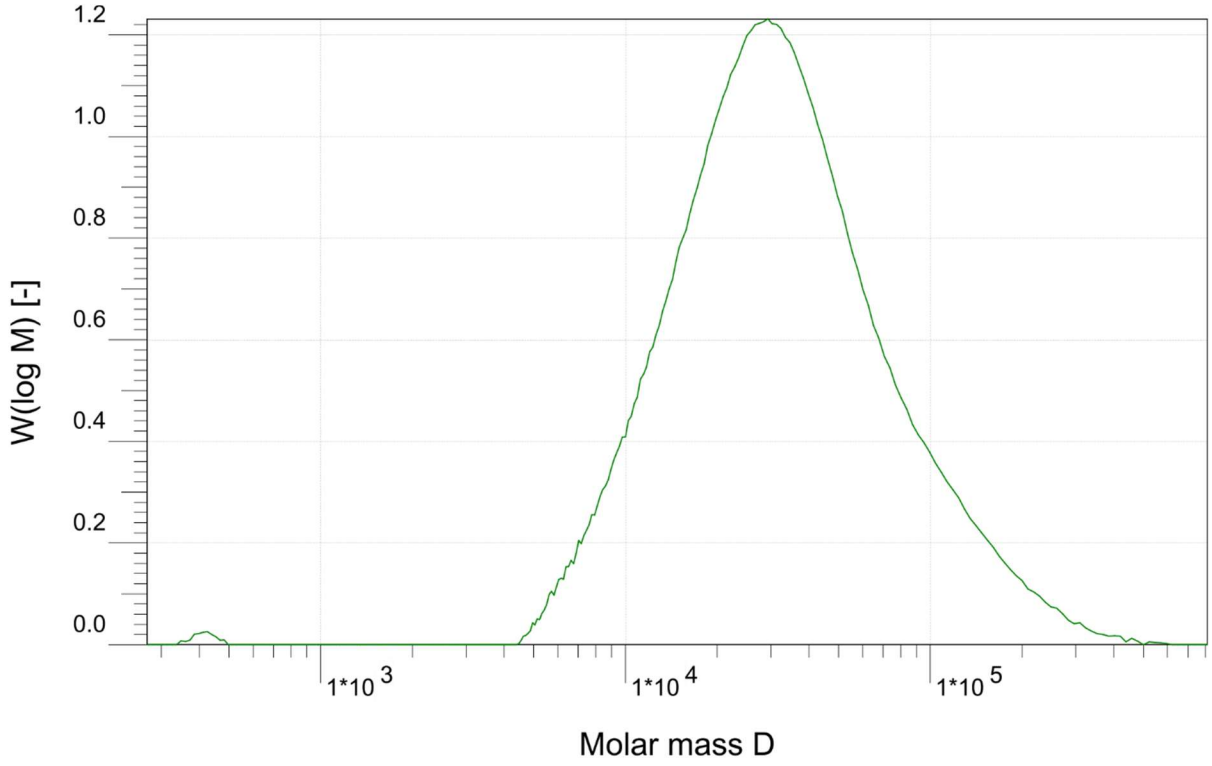

*Figure S87 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 90 °C, 25 h, catalyst **4b**.*

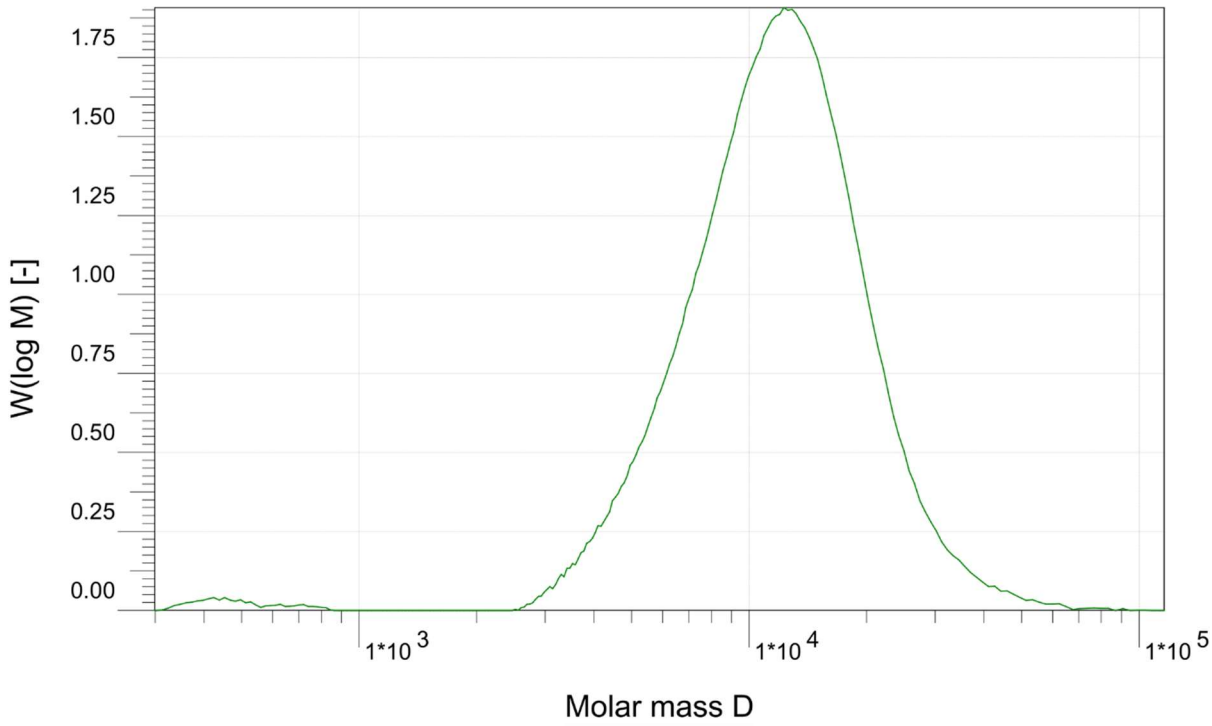

*Figure S88 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 80 °C, 25 h, catalyst **4c**.*

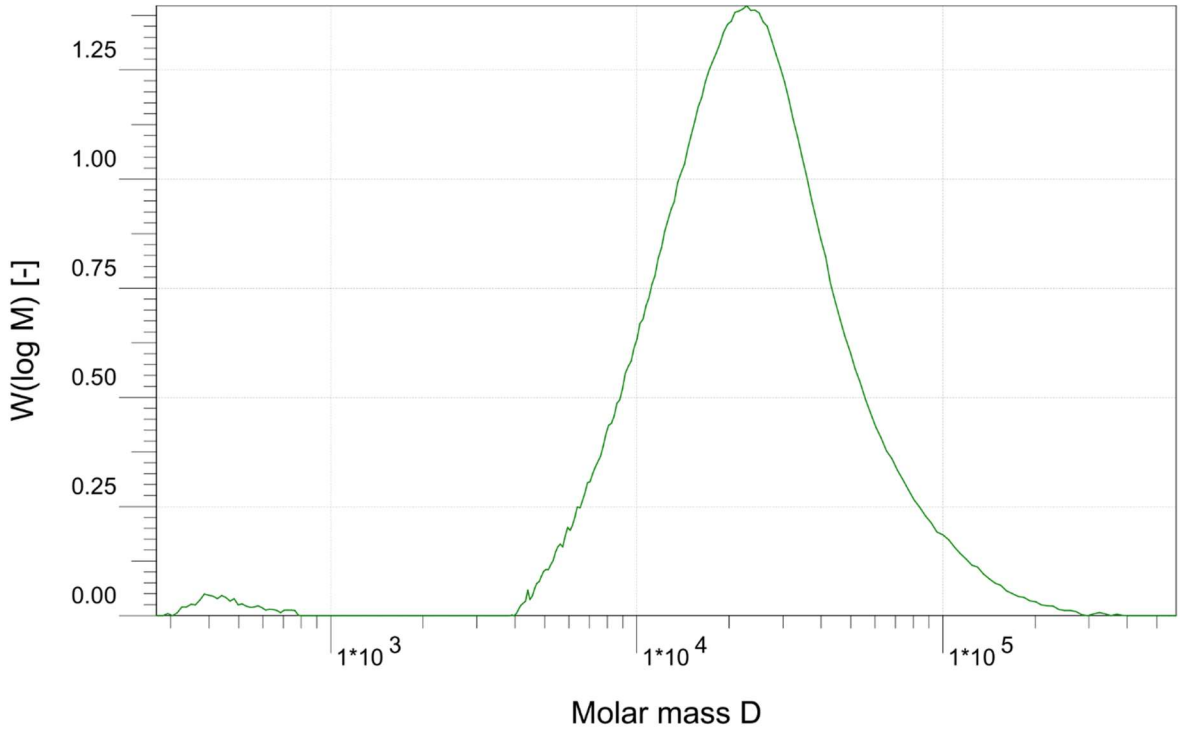

*Figure S89 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 90 °C, 25 h, catalyst **4c**.*

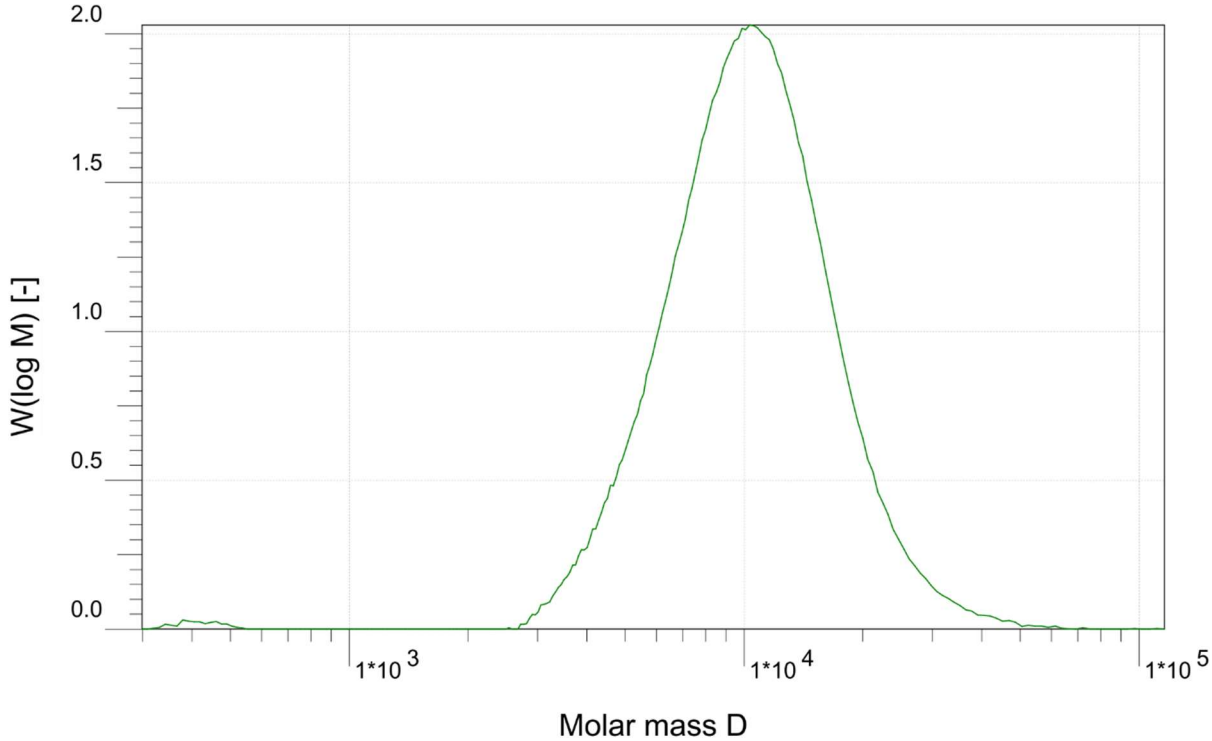

*Figure S90 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 80 °C, 25 h, catalyst **4d**.*

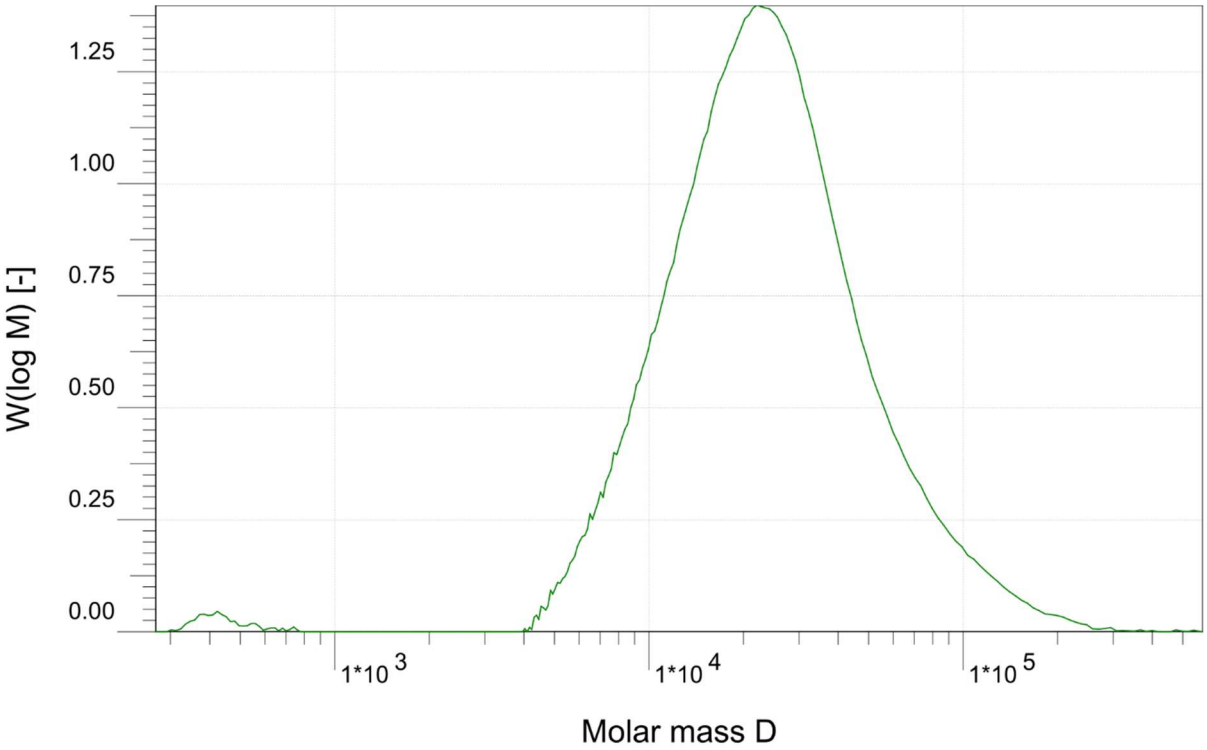

*Figure S91 SEC Elugram of PLA, conditions: Toluene 1.5 mL, catalyst / monomer = 1:200, [catalyst] = 1*10^{-2} M, [monomer] = 2 M, temp. = 90 °C, 25 h, catalyst **4d**.*

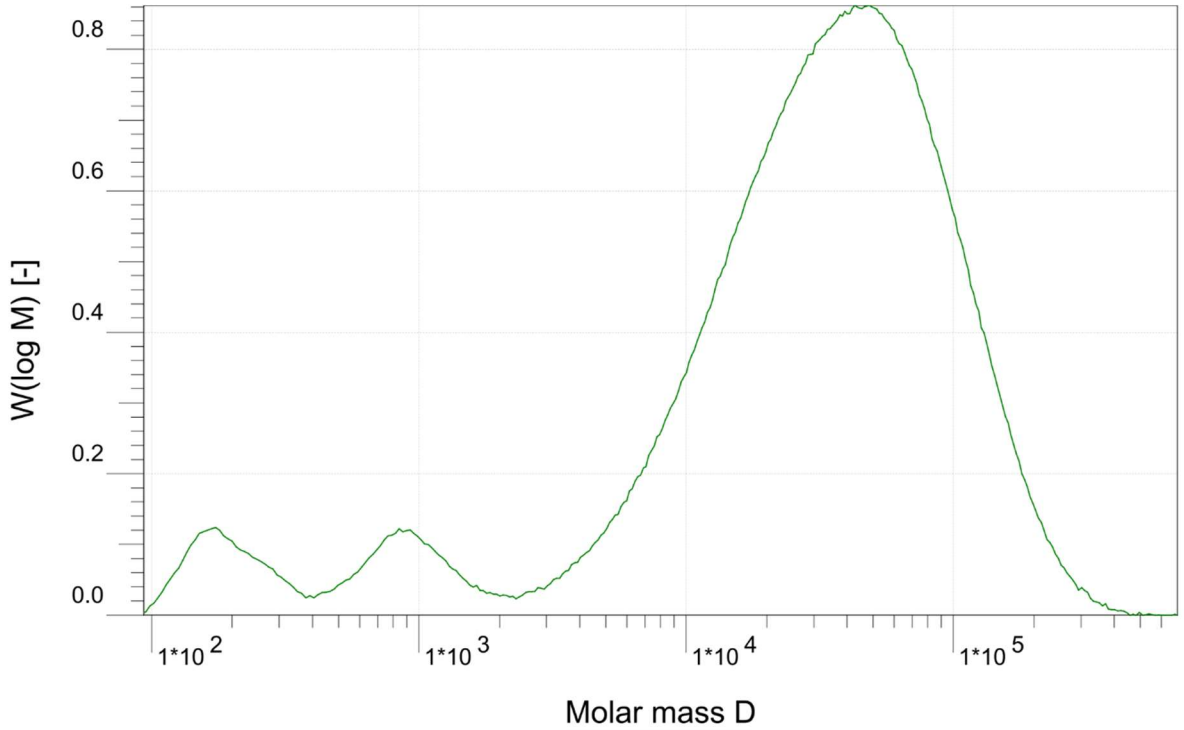

*Figure S92 SEC Elugram of PCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = 7*10^{-2} M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **3a**.*

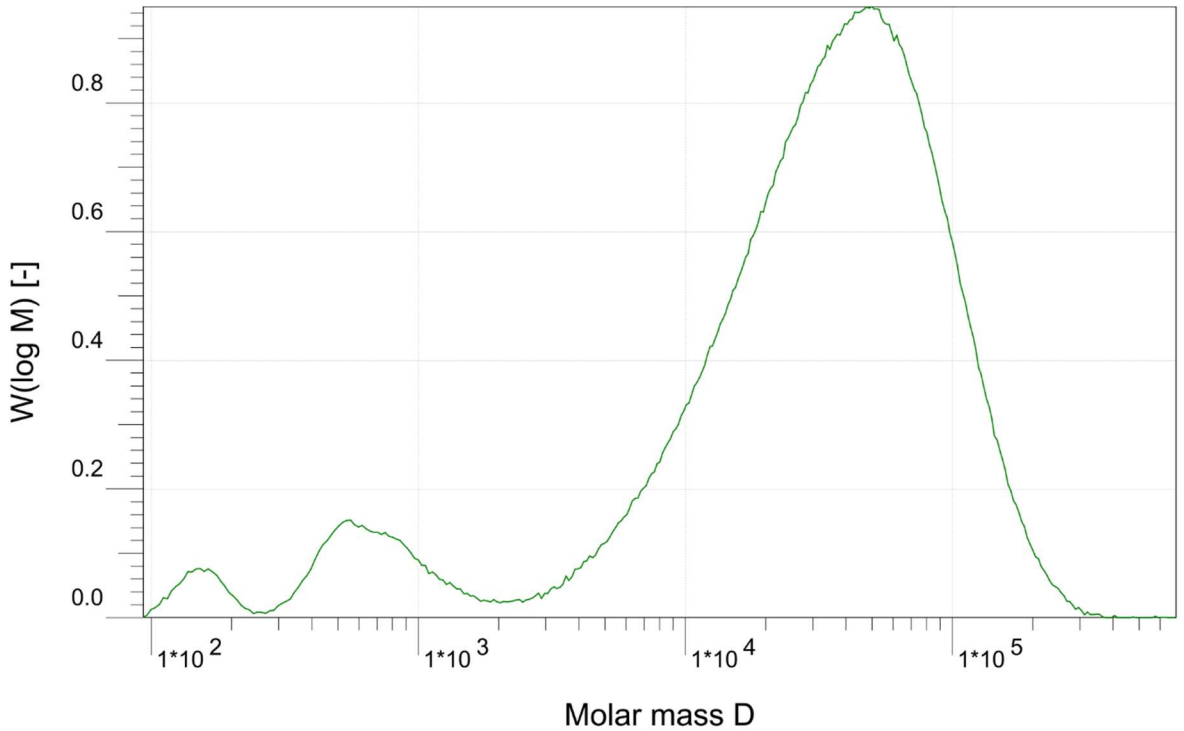

*Figure S93 SEC Elugram of PCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = 7*10^{-2} M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **3b**.*

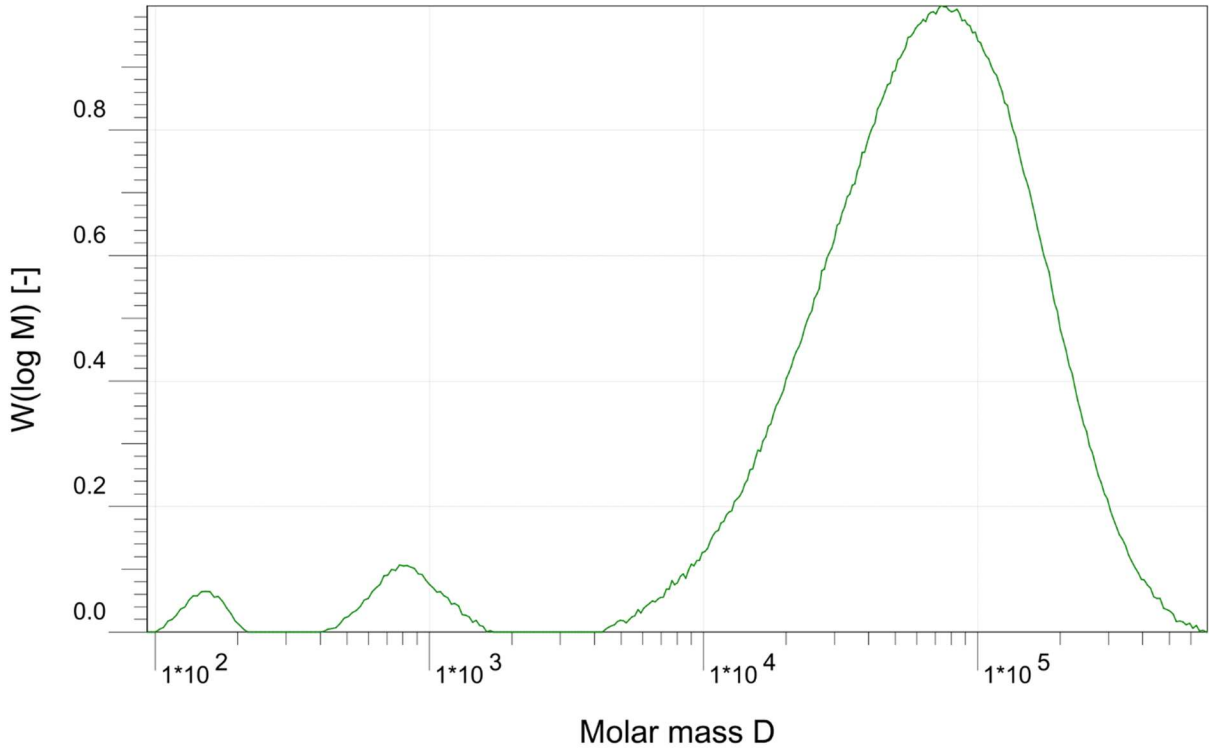

*Figure S94 SEC Elugram of PCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = 7*10^{-2} M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **3c**.*

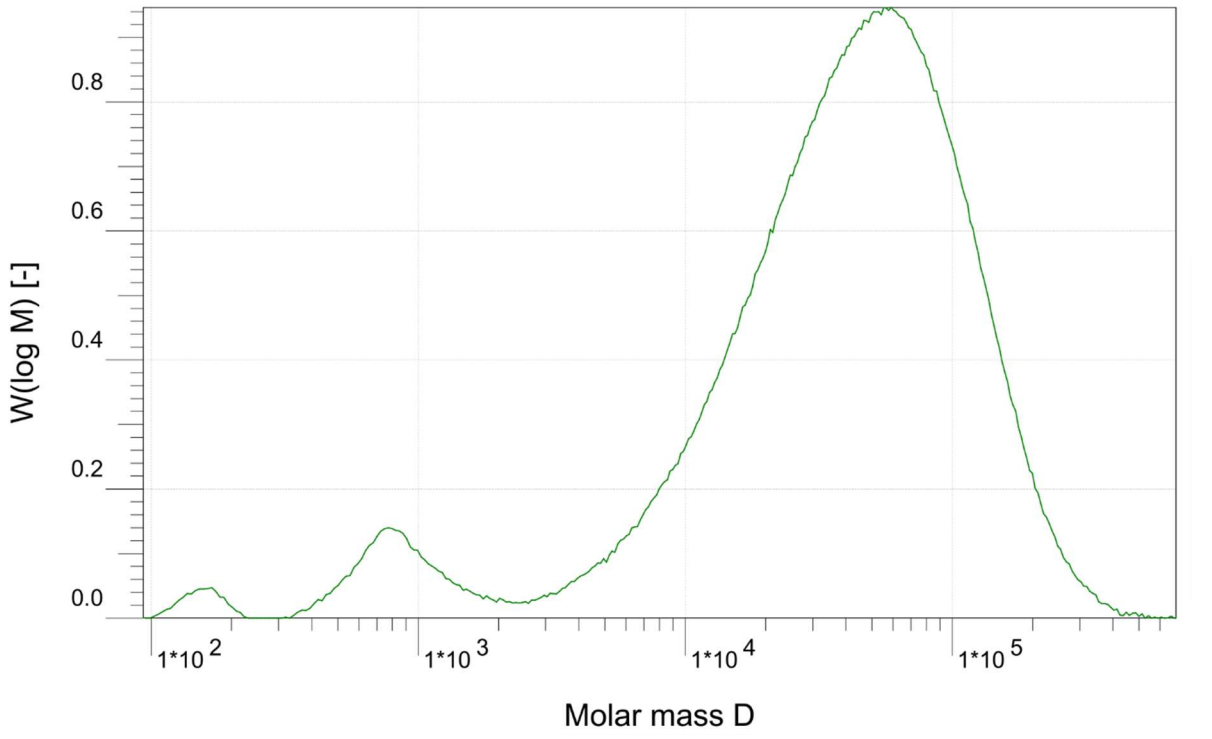

*Figure S95 SEC Elugram of PCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = 7*10^{-2} M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **3d**.*

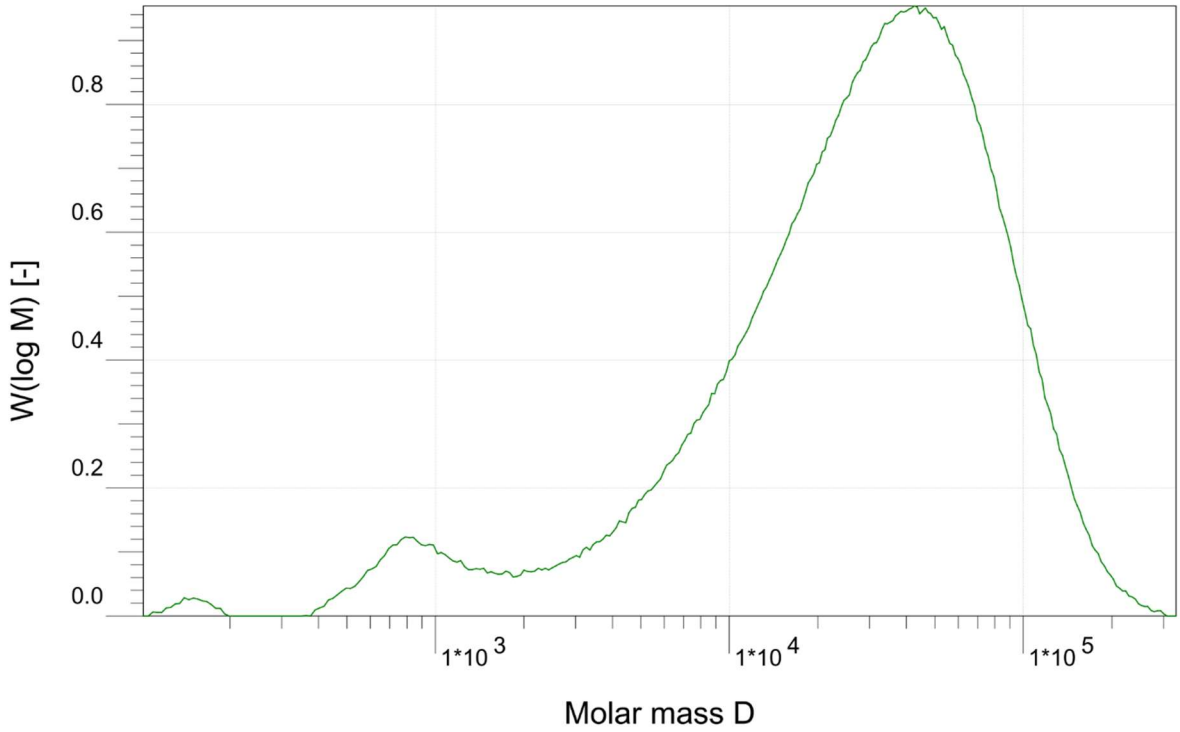

*Figure S96 SEC Elugram of PCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = 7*10^{-2} M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **4a**.*

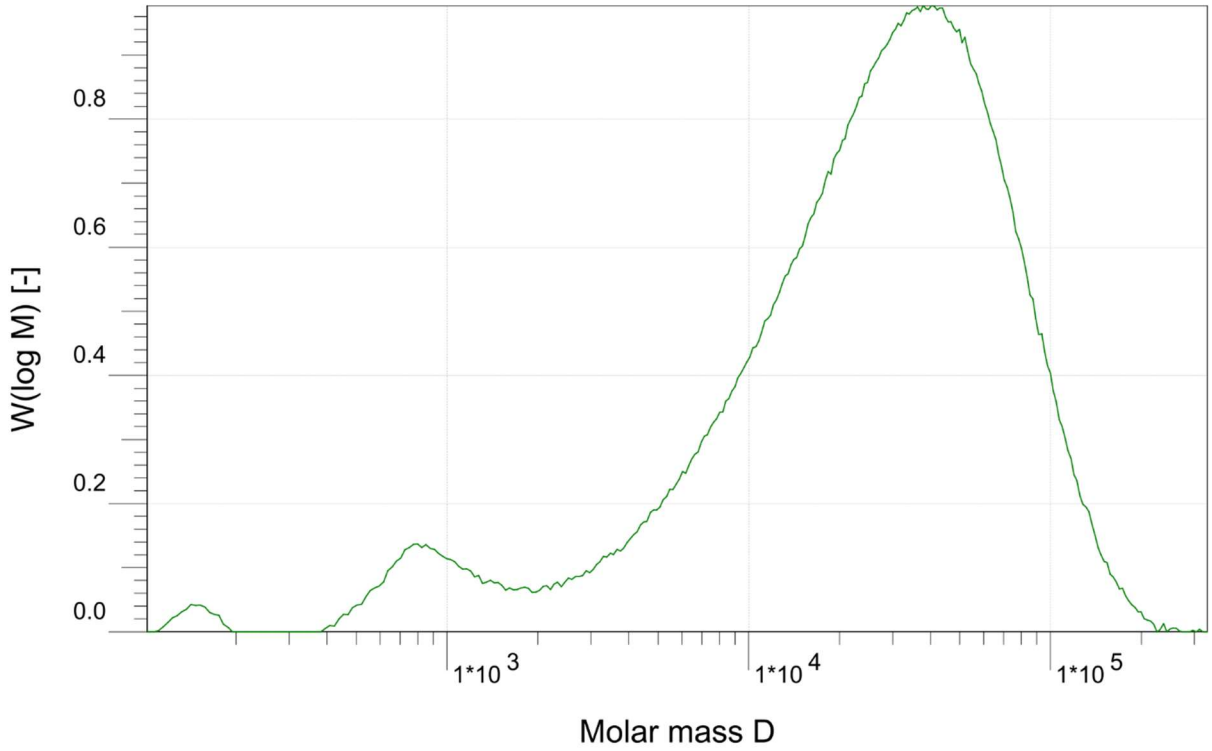

*Figure S97 SEC Elugram of PCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = 7*10^{-2} M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **4b**.*

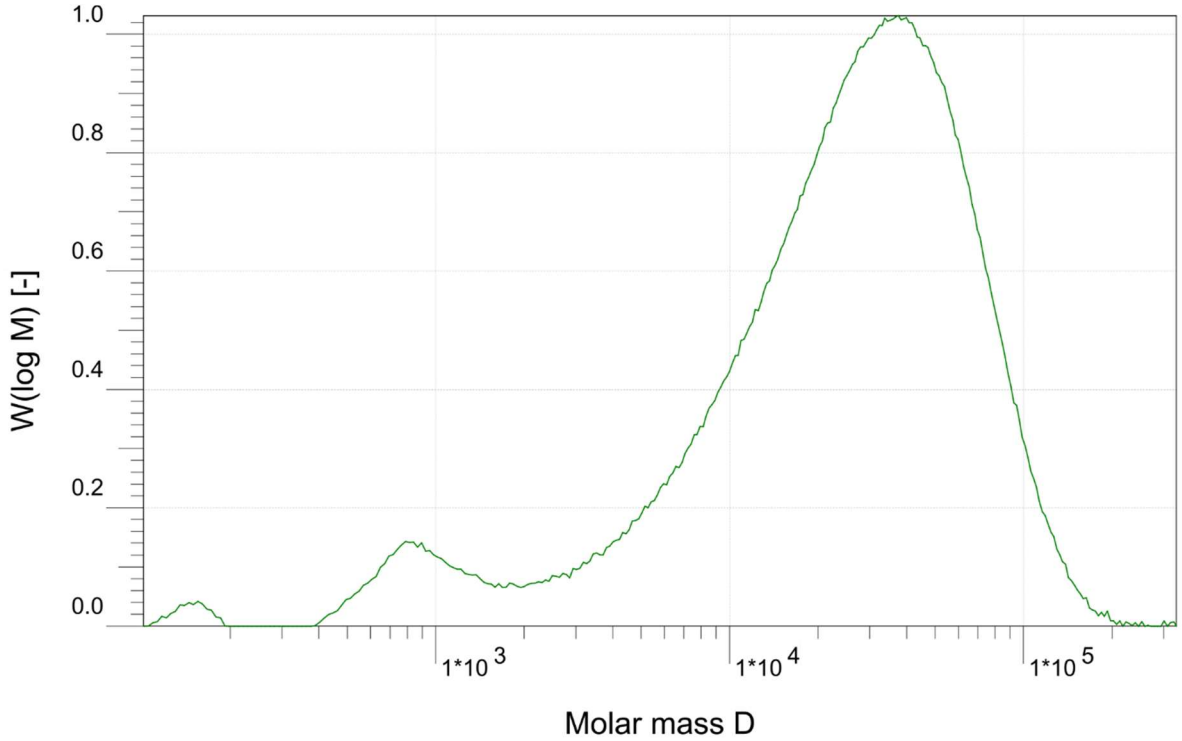

*Figure S98 SEC Elugram of PCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = 7*10^{-2} M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **4c**.*

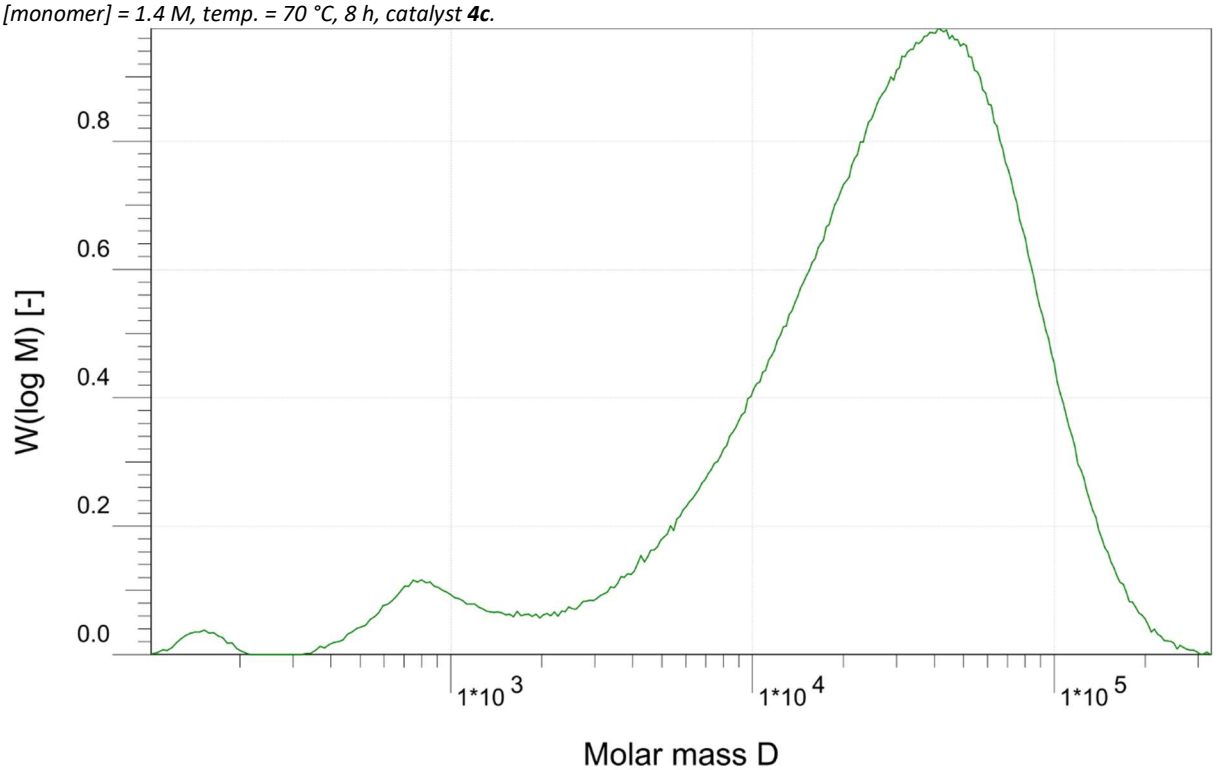

*Figure S99 SEC Elugram of PCL, conditions: Toluene 2.1 mL, catalyst / monomer = 1:200, [catalyst] = 7*10^{-2} M, [monomer] = 1.4 M, temp. = 70 °C, 8 h, catalyst **4d**.*

7. References

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