

Electronic Supplementary Information

**Synthesis of a polyaminocarboxylate-based aluminum complex
and its structural studies using $^1\text{H}\{^{13}\text{C}\}$ -HMBC NMR and a Karplus-type function**

Karel D. Klika,[†] Rana Alsalam,[‡] Mohammad Eftekhari[§] and Ata Makarem^{*‡}

[†]German Cancer Research Center (DKFZ), Molecular Structure Analysis, INF 280, D-69120 Heidelberg, Germany

[‡]University of Hamburg, Institute of Pharmacy, Bundesstraße 45, D-20146 Hamburg, Germany

[§] University of Neyshabur, Faculty of Sciences, Department of Chemistry, Neyshabur, Iran.

**corresponding author and project leader*

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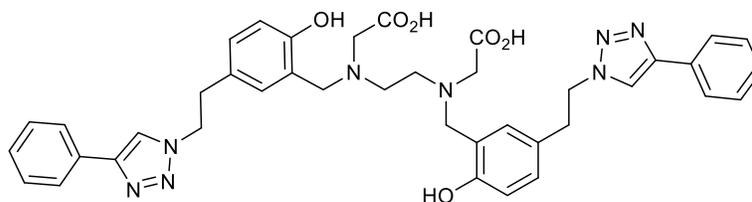
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General methodology

Chemicals and reagents were purchased from Fisher, Merck Scientific, TCI, VWR Chemicals and Sigma-Aldrich. NMR spectra were measured at 25 °C using a Bruker Avance III NMR instrument at a field strength of 9.4 T operating at 400 MHz for ^1H nuclei and 100 MHz for ^{13}C nuclei. Chemical shifts (δ) are reported in ppm relative to TMS ($\delta_{\text{H}} = 0$ ppm and $\delta_{\text{C}} = 0$ ppm) and spectra were referenced internally using the solvent peaks^{S1} as secondary references (^1H : $\delta_{\text{MeOD}} = 3.31$ ppm and $\delta_{\text{DMSO}} = 2.50$ ppm; ^{13}C : $\delta_{\text{MeOD}} = 49.00$ ppm, $\delta_{\text{DMSO}} = 39.52$ ppm). Coupling constants (J) are reported in Hz. The following abbreviations are used: s – singlet, d – doublet, ho – higher order, t – triplet, m – multiplet and br – broad. Signal assignments were made using 2D COSY, HMBC and HSQC spectra. The program TopSpin 3.6.1 was used for the processing and analysis of NMR spectra. High resolution mass spectra were recorded using a Bruker ApexQe hybrid 9.4 T FT-ICR instrument.

Density functional theory (DFT) calculations were run using Gaussian 09 software; default parameters for the self-consistent field (SCF) and geometry convergence criteria were employed throughout. Geometry optimization and frequency calculations were performed using a b3lyp functional and a 6-31g(d,p) basis set. The structures were optimized without symmetry constraints using a polarizable continuum model (PCM) to simulate the solution phase. Calculations were run using the SCRF keyword and selecting DMSO as the solvent.

Synthesis of 2,2'-[ethane-1,2-diylbis({2-hydroxy-5-[2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl]benzyl} azanediy)]diacetic acid (*HBED-NN chelator*)

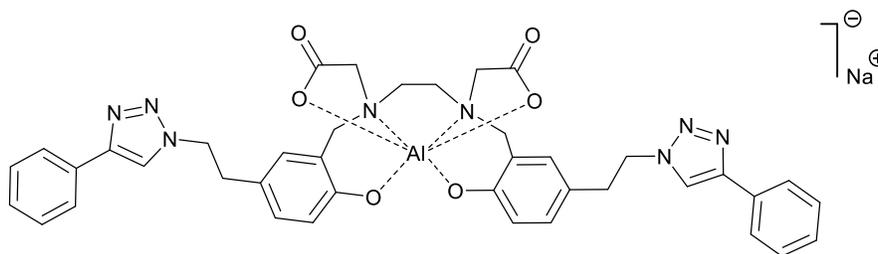


HBED-NN Chelator ($\text{C}_{40}\text{H}_{42}\text{N}_8\text{O}_6$, MW: 730.83 g mol⁻¹)

The HBED-NN chelator was prepared according to our previously reported procedure (colorless solid; 0.40 g, 0.54 mmol, 58%).^{S2}

^1H NMR (400 MHz, MeOD, 25 °C): δ = 8.13 (s, 2H, CHN), 7.74 (d, 4H, $^3J_{\text{H,H}}$ = 7.8 Hz, Ph-substituent, *ortho*-H), 7.40 (t, 4H, $^3J_{\text{H,H}}$ = 7.8 Hz, Ph-substituent, *meta*-H), 7.32 (t, 2H, $^3J_{\text{H,H}}$ = 7.8 Hz, Ph-substituent, *para*-H), 7.03 (dd, 2H, $^3J_{\text{H,H}}$ = 8.3 Hz, $^4J_{\text{H,H}}$ = 1.44 Hz, CHCHCO), 6.97 (s, br, 2H, CCHC), 6.78 (d, 2H, $^3J_{\text{H,H}}$ = 8.3 Hz, CHCHCO), 4.63 (t, 4H, $^3J_{\text{H,H}}$ = 6.7 Hz CCH₂CH₂N), 3.99 (s, 4H, ^{Bn}CH₂), 3.57 (s, 4H, CH₂CO₂), 3.15 (t, 4H, $^3J_{\text{H,H}}$ = 6.7 Hz, CCH₂CH₂N), 3.05 (s, 4H, N-C₂H₄-N) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, MeOD, 25 °C): δ = 171.8 (CO₂), 158.6 (COH), 148.6 (NCCH), 133.8 (CCHC), 132.3 (CHCHCO), 131.6 (Ph-substituent, *ipso*-C), 130.0 (Ph-substituent, *meta*-C), 129.4 (Ph-substituent, *para*-C), 126.6 (Ph-substituent, *ortho*-C), 122.4 (CHN), 120.2 (CCH₂CH₂N and ^{Bn}CH₂C), 116.9 (CHCHCO), 54.2 (^{Bn}C), 54.0 (CH₂CO₂), 52.9 (CCH₂CH₂N), 50.9 (N-C₂H₄-N), 36.5 (CCH₂CH₂N) ppm.

Synthesis of sodium aluminum(III){2,2'-[ethane-1,2-diylbis{2-oxido-5-[2-(4-phenyl-1H-1,2,3-triazol-1-yl)ethyl]benzyl}azanediyl)]diacetate} ([Al-HBED-NN]⁻Na⁺)



[Al-HBED-NN]⁻Na⁺ (C₄₀H₃₈AlN₈NaO₆, MW: 776.77 g mol⁻¹)

Stock solution **Al1**: In a 1 mL flask, 550 μL of an aqueous solution of NaOAc (1 M) were mixed with 100 μL of an aqueous AlCl₃ solution (1 M). The resulting pH was \sim 4.

To a solution of the HBED-NN chelator (20 mg, 27 μmol) in 2 mL of DMF at room temperature were added 275 μL of fresh **Al1** (1.6 eq Al³⁺ and 8.8 eq NaOAc). The reaction mixture was stirred at 90 °C for 5 min following which it was cooled to room temperature, diluted with water and then centrifuged. The solid residue was washed with water followed by a dilute NaHCO₃ solution (or alternatively, with THF) and then dried *in vacuo* to give the desired product as a colorless solid (17 mg, 22 μmol , 80%). ^1H NMR (400 MHz, DMSO, 25 °C): δ = 8.44 (s, 2H, CHN), 7.81 (ho m, 4H, Ph-substituent, *ortho*-H), 7.44 (ho m, 4H, Ph-substituent, *meta*-H), 7.32 (ho m, 2H, Ph-substituent, *para*-H), 6.85 (dd, 2H, $^3J_{\text{H,H}}$ = 8.3 Hz, $^4J_{\text{H,H}}$ = 2.2 Hz, CHCHCO), 6.66 (d, 2H, $^4J_{\text{H,H}}$ = 2.0 Hz, CCHC), 6.43 (d, 2H, $^3J_{\text{H,H}}$ = 8.2 Hz, CHCHCO), 4.53 (ho m, 4H, CCH₂CH₂N),

4.04 (d, 2H, $^2J_{H,H} = -13.2$ Hz, $^{Bn}CH_2[H_b]$), 3.43 (d, 2H, $^2J_{H,H} = -13.2$ Hz, $^{Bn}CH_2[H_a]$), 3.25 (d, 2H, $^2J_{H,H} = -17.2$ Hz, $CH_2[H_b]CO_2$), 3.00 (t, 4H, $^3J_{H,H} = 7.5$ Hz, CCH_2CH_2N), 2.91 (d, 2H, $^2J_{H,H} = -17.2$ Hz, $CH_2[H_a]CO_2$), 2.79 (ho m, 4H, N-C₂H₄-N) ppm. $^{13}C\{^1H\}$ NMR (100 MHz, d₆-DMSO, 25 °C): $\delta = 171.6$ (CO₂), 160.9 (^{Ph}O C), 146.0 (NCCH), 130.9 (Ph-substituent, *ipso*-C), 129.7 (CCHC), 129.0 (CHCHCO), 128.9 (Ph-substituent, *meta*-C), 127.7 (Ph-substituent, *para*-C), 125.1 (Ph-substituent, *ortho*-C), 122.4 (CCH₂CH₂N), 121.4 (CHN), 120.8 ($^{Bn}CH_2C$), 119.6 (CHCHCO), 60.85 (^{Bn}C), 56.9 (CCH₂CO₂), 55.9 (N-C₂H₄-N), 51.4 (CCH₂CH₂N), 35.2 (CCH₂CH₂N) ppm. HRMS (ESI⁻): m/z [M]⁻ Calcd for C₄₀H₃₈AlN₈O₆: 753.2735; Found: 753.2730 (100%).

Structural data of isomers I–III

Portions of the HMBC spectrum of $[\text{Al-HBED-NN}]^-\text{Na}^+$ showing regions for all observed and unobserved ^1H - ^{13}C three-bond correlations for the chelate cage are presented in Fig. S1. Structural details of the DFT-optimized $[\text{Al-HBED}]^-$ structures of isomers I–III including expected vs. observed correlations and dihedral and bond angles are presented in Tables S1–5.

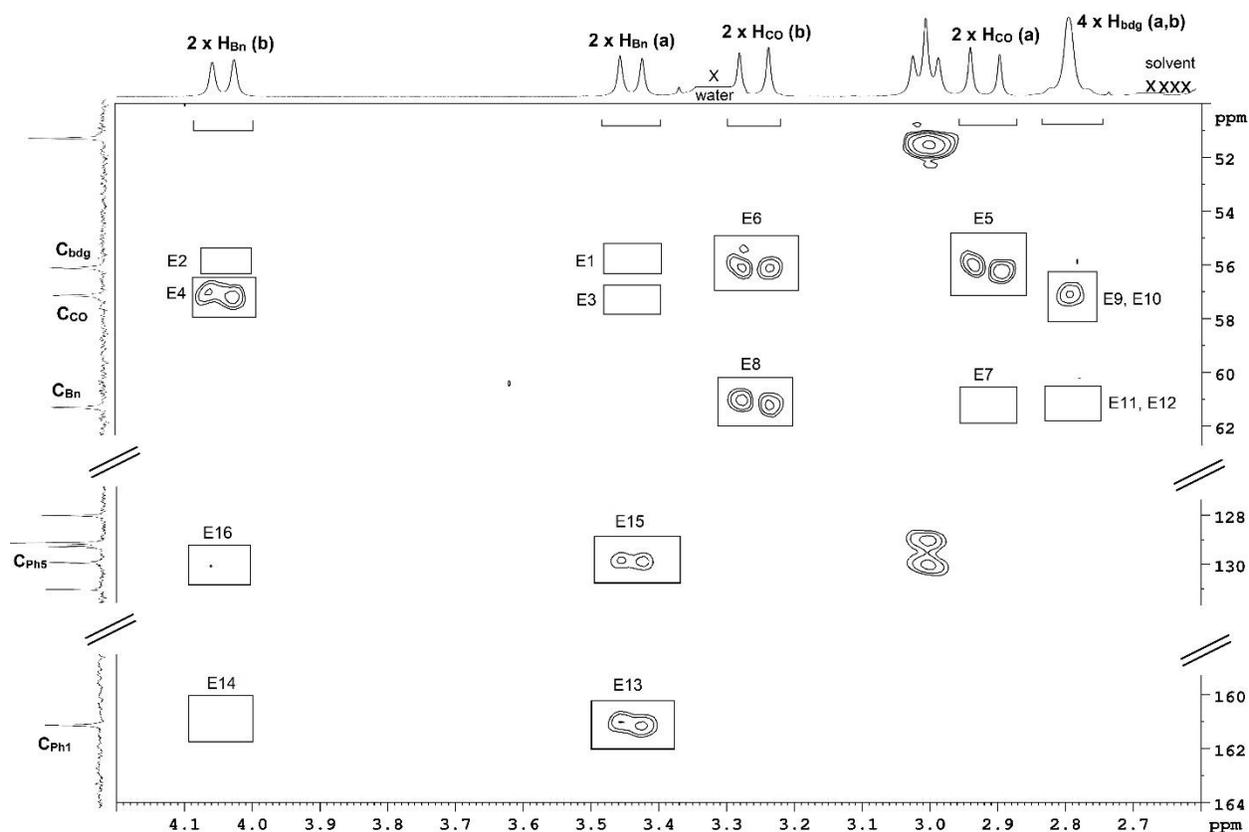
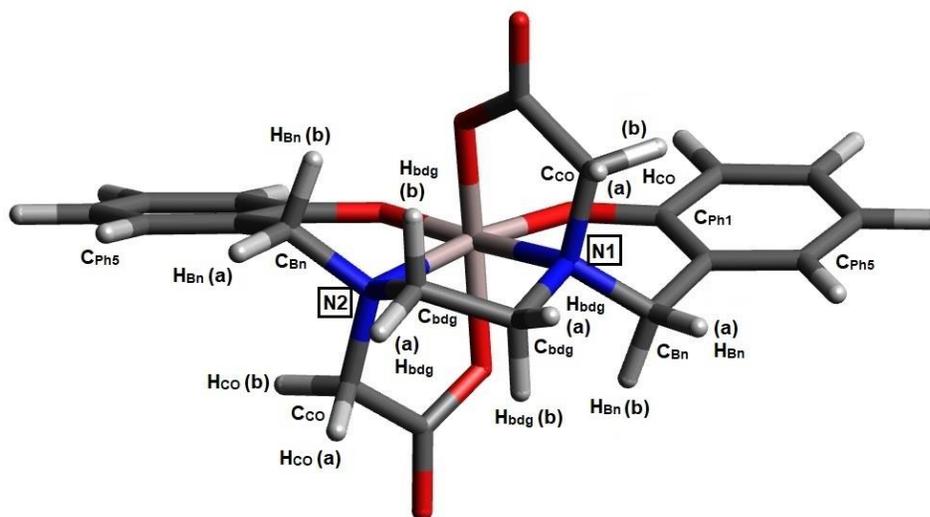
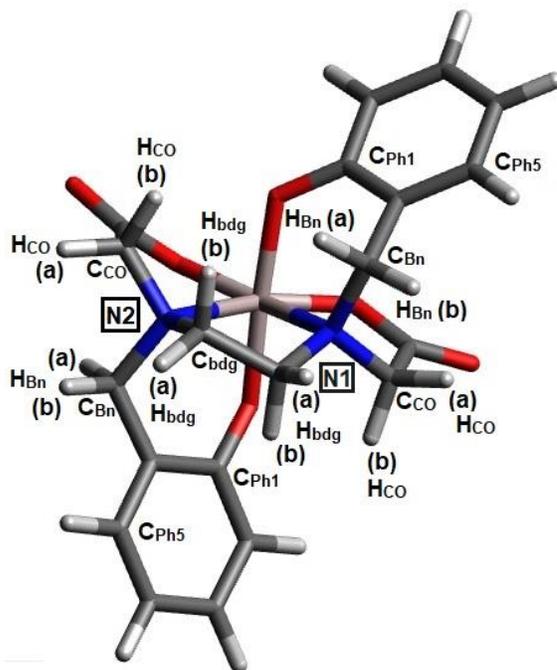


Fig. S1 Portions of the $^1\text{H}\{^{13}\text{C}\}$ -HMBC spectrum of $[\text{Al-HBED-NN}]^-\text{Na}^+$ showing regions for all observed and unobserved ^1H - ^{13}C three-bond correlations for the chelate cage.

Table S1 Dihedral angles of the chelate cage and expected vs. observed correlations for isomer II

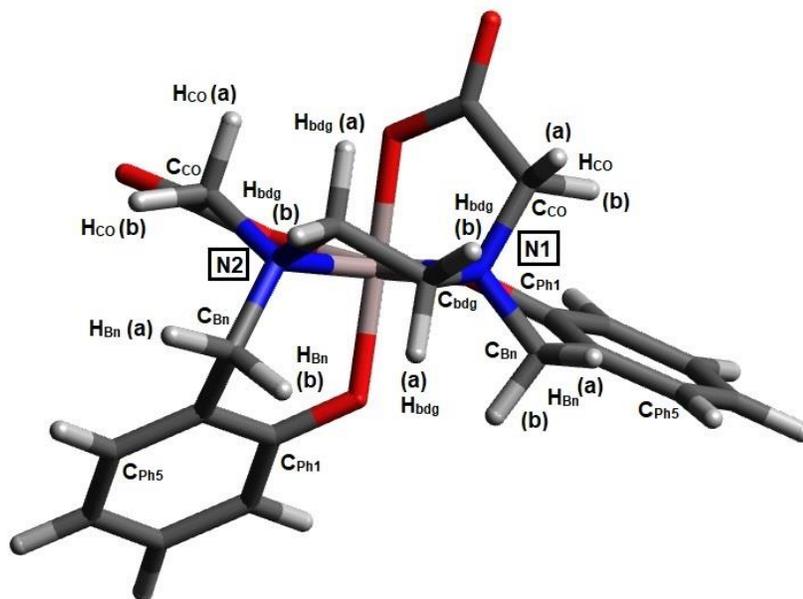
Entry	Nuclei ^a	Dihedral angle (°)		Correlation	
		N1 ^b	N2 ^b	Expected	Observed
E1	H _{Bn} (a), C _{bdg}	59.56	59.57	No	No
E2	H _{Bn} (b), C _{bdg}	56.29	56.28	No	No
E3	H _{Bn} (a), C _{Co}	65.01	65.00	No	No
E4	H _{Bn} (b), C _{Co}	179.15	179.15	Yes	Yes
E5	H _{Co} (a), C _{bdg}	27.86	27.86	Yes	Yes
E6	H _{Co} (b), C _{bdg}	146.15	146.15	Yes	Yes
E7	H _{Co} (a), C _{Bn}	96.09	96.08	No	No
E8	H _{Co} (b), C _{Bn}	22.21	22.21	Yes	Yes
E9	H _{bdg} (a), C _{Co}	46.19	46.18	No	Yes ^c
E10	H _{bdg} (b), C _{Co}	163.20	163.19	Yes	Yes
E11	H _{bdg} (a), C _{Bn}	78.69	78.69	No	No
E12	H _{bdg} (b), C _{Bn}	38.32	38.32	No	No
E13	H _{Bn} (a), C _{Ph1}	167.12	167.11	Yes	Yes
E14	H _{Bn} (b), C _{Ph1}	74.40	74.41	No	No
E15	H _{Bn} (a), C _{Ph5}	15.75	15.77	Yes	Yes
E16	H _{Bn} (b), C _{Ph5}	102.73	102.72	No	No

Table S2 Dihedral angles of the chelate cage and expected vs. observed correlations for isomer I



Entry	Nuclei ^a	Dihedral angle (°)		Correlation	
		N1 ^b	N2 ^b	Expected	Observed
E1	H _{Bn} (a), C _{bdg}	39.57	173.62	Yes	No
E2	H _{Bn} (b), C _{bdg}	75.14	58.96	No	No
E3	H _{Bn} (a), C _{CO}	167.59	45.25	Yes	No
E4	H _{Bn} (b), C _{CO}	52.87	69.40	No	Yes
E5	H _{CO} (a), C _{bdg}	89.37	81.18	No	Yes
E6	H _{CO} (b), C _{bdg}	30.28	40.04	No	Yes
E7	H _{CO} (a), C _{Bn}	34.06	44.30	No	No
E8	H _{CO} (b), C _{Bn}	153.71	165.51	Yes	Yes
E9	H _{bdg} (a), C _{CO}	84.70	93.90	No	Yes ^c
E10	H _{bdg} (b), C _{CO}	33.69	23.33	Yes	Yes
E11	H _{bdg} (a), C _{Bn}	39.81	29.01	No	No
E12	H _{bdg} (b), C _{Bn}	158.20	146.25	Yes	No
E13	H _{Bn} (a), C _{Ph1}	64.38	67.99	No	Yes
E14	H _{Bn} (b), C _{Ph1}	178.59	174.53	Yes	No
E15	H _{Bn} (a), C _{Ph5}	109.47	107.29	No	Yes
E16	H _{Bn} (b), C _{Ph5}	7.56	10.19	Yes	No

Table S3 Dihedral angles of the chelate cage and expected vs. observed correlations for isomer **III** using averaged values for predicting correlations



Entry	Nuclei ^a	Dihedral angle (°), N1 ^b	Expected correlation	Dihedral angle (°), N2 ^b	Expected correlation	Correlation	
						Combined	Observed
E1	H _{Bn} (a), C _{bdg}	59.00	No	76.85	No	No	No
E2	H _{Bn} (b), C _{bdg}	56.92	No	38.14	No	No	No
E3	H _{Bn} (a), C _{Co}	65.75	No	51.10	No	No	No
E4	H _{Bn} (b), C _{Co}	178.32	Yes	166.08	Yes	Yes	Yes
E5	H _{Co} (a), C _{bdg}	34.38	No	28.27	Yes	Yes	Yes
E6	H _{Co} (b), C _{bdg}	152.81	Yes	91.57	No	No	Yes ^c
E7	H _{Co} (a), C _{Bn}	90.37	No	152.64	Yes	No	No
E8	H _{Co} (b), C _{Bn}	28.05	Yes	32.81	No	Yes	Yes
E9	H _{bdg} (a), C _{Co}	157.84	Yes	33.83	No	Yes	Yes
E10	H _{bdg} (b), C _{Co}	41.20	No	84.32	No	No	Yes ^c
E11	H _{bdg} (a), C _{Bn}	32.43	No	158.86	Yes	Yes	No
E12	H _{bdg} (b), C _{Bn}	84.21	No	40.71	No	No	No
E13	H _{Bn} (a), C _{Ph1}	158.82	Yes	178.88	Yes	Yes	Yes
E14	H _{Bn} (b), C _{Ph1}	82.76	No	64.20	No	No	No
E15	H _{Bn} (a), C _{Ph5}	24.06	Yes	7.04	Yes	Yes	Yes
E16	H _{Bn} (b), C _{Ph5}	94.37	No	109.87	No	No	No

Table S4 Dihedral angles of the chelate cage and expected vs. observed correlations for isomer **III** based on predicting a correlation if one dihedral angle is favorable

Entry	Nuclei ^a	Dihedral angle (°), N1 ^b	Expected correlation	Dihedral angle (°), N2 ^b	Expected correlation	Correlation	
						Combined	Observed
E1	H _{Bn} (a), C _{bdg}	59.00	No	76.85	No	No	No
E2	H _{Bn} (b), C _{bdg}	56.92	No	38.14	No	No	No
E3	H _{Bn} (a), C _{CO}	65.75	No	51.10	No	No	No
E4	H _{Bn} (b), C _{CO}	178.32	Yes	166.08	Yes	Yes	Yes
E5	H _{CO} (a), C _{bdg}	34.38	No	28.27	Yes	Yes	Yes
E6	H _{CO} (b), C _{bdg}	152.81	Yes	91.57	No	Yes	Yes
E7	H _{CO} (a), C _{Bn}	90.37	No	152.64	Yes	Yes	No
E8	H _{CO} (b), C _{Bn}	28.05	Yes	32.81	No	Yes	Yes
E9	H _{bdg} (a), C _{CO}	157.84	Yes	33.83	No	Yes	Yes
E10	H _{bdg} (b), C _{CO}	41.20	No	84.32	No	No	Yes ^c
E11	H _{bdg} (a), C _{Bn}	32.43	No	158.86	Yes	Yes	No
E12	H _{bdg} (b), C _{Bn}	84.21	No	40.71	No	No	No
E13	H _{Bn} (a), C _{Ph1}	158.82	Yes	178.88	Yes	Yes	Yes
E14	H _{Bn} (b), C _{Ph1}	82.76	No	64.20	No	No	No
E15	H _{Bn} (a), C _{Ph5}	24.06	Yes	7.04	Yes	Yes	Yes
E16	H _{Bn} (b), C _{Ph5}	94.37	No	109.87	No	No	No

Table S5 Selected bond angles (°) and bond lengths (Å) for isomers **I–III**

Angle ^{b,d}	I ^e	II	III ^e	[Ti-HBED] ^f
C _{C=O} –O–Al, N1	116.1	122.0	119.8	124.7
C _{C=O} –O–Al, N2	113.9	121.9	118.5	123.0
C _{Ph} –O–Al, N1	123.0	133.5	129.3	140.1
C _{Ph} –O–Al, N2	134.8	133.5	122.0	140.3
C _{CO} –N–Al, N1	100.4	106.8	106.3	108.0
C _{CO} –N–Al, N2	99.2	106.8	101.7	106.6
C _{Bn} –N–Al, N1	116.0	110.3	108.6	112.2
C _{Bn} –N–Al, N2	113.8	110.3	115.0	113.1

C _{bdg} -N-Al, N1	106.0	106.0	107.6	106.8
C _{bdg} -N-Al, N2	108.5	106.0	105.1	107.7
O _{CO} -Al-O _{CO}	113.3	165.6	87.0	156.7
O _{CO,N1} -Al-O _{Ph,N1}	91.3	97.1	92.6	100.1
O _{CO,N1} -Al-O _{Ph,N2}	84.7	92.6	173.0	93.0
O _{CO,N1} -Al-N _{N1}	83.5	81.1	80.7	77.4
O _{CO,N1} -Al-N _{N2}	164.7	88.2	86.1	84.7
O _{CO,N2} -Al-O _{Ph,N1}	85.3	92.6	102.8	93.2
O _{CO,N2} -Al-O _{Ph,N2}	95.6	97.1	96.3	100.5
O _{CO,N2} -Al-N _{N1}	161.7	88.2	162.4	84.6
O _{CO,N2} -Al-N _{N2}	80.8	81.1	82.8	77.6
O _{Ph} -Al-O _{Ph}	176.0	95.9	92.8	109.7
O _{Ph,N1} -Al-N _{N1}	87.2	90.6	90.4	86.0
O _{Ph,N1} -Al-N _{N2}	95.3	171.5	174.3	163.8
O _{Ph,N2} -Al-N _{N1}	93.0	171.5	94.7	163.1
O _{Ph,N2} -Al-N _{N2}	88.6	90.6	88.1	85.3
N-Al-N	83.3	83.5	83.9	80.0
O _{CO,N1} -Al	1.885	1.908	1.940	1.954
O _{CO,N2} -Al	1.895	1.908	1.876	1.956
O _{Ph,N1} -Al	1.895	1.830	1.834	1.812
O _{Ph,N2} -Al	1.881	1.830	1.865	1.812
N _{N1} -Al	2.154	2.168	2.119	2.246
N _{N2} -Al	2.134	2.168	2.173	2.234

^a "C_{CO}" refers to the methylene carbon adjacent to the carbonyl carbon.

^b N1 and N2 refer to the half of the ligand in which the measurement was made.

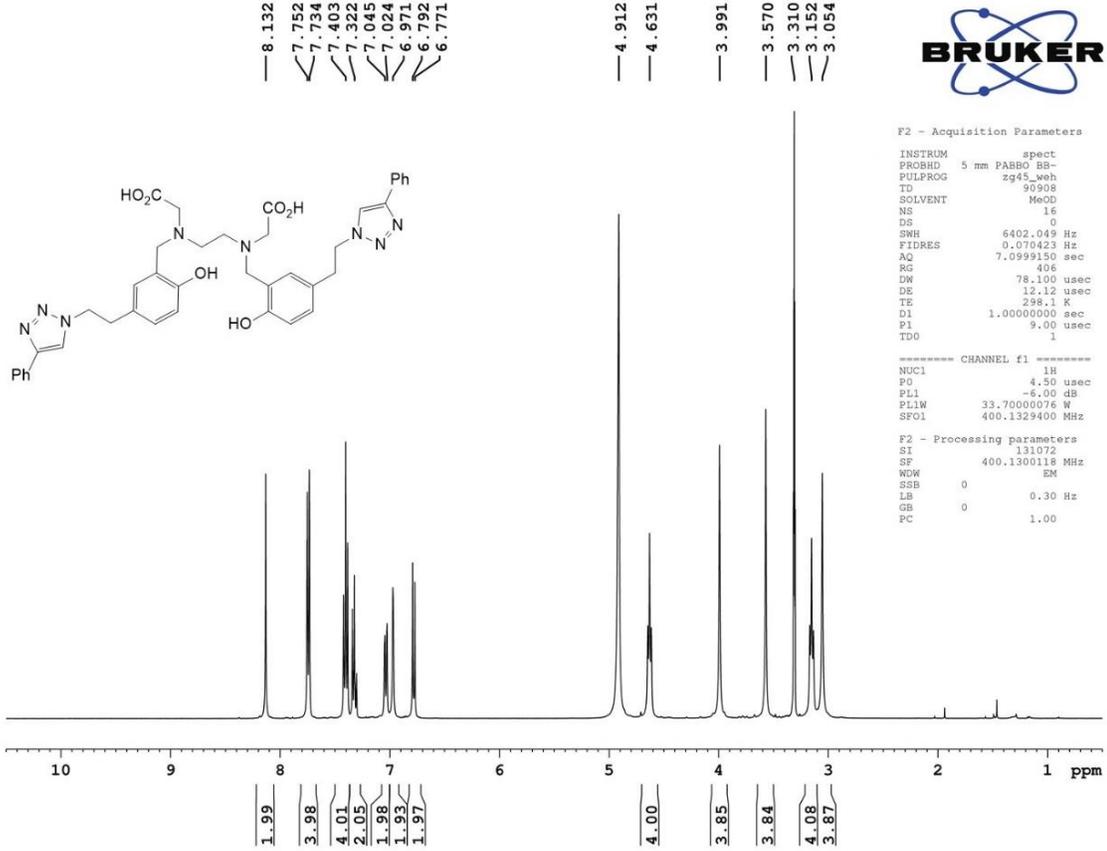
^c Due to overlap of the H_{bdg} (a) and (b) protons for which a correlation is expected for one of them.

^d "C_{C=O}" refers to the carbonyl carbon.

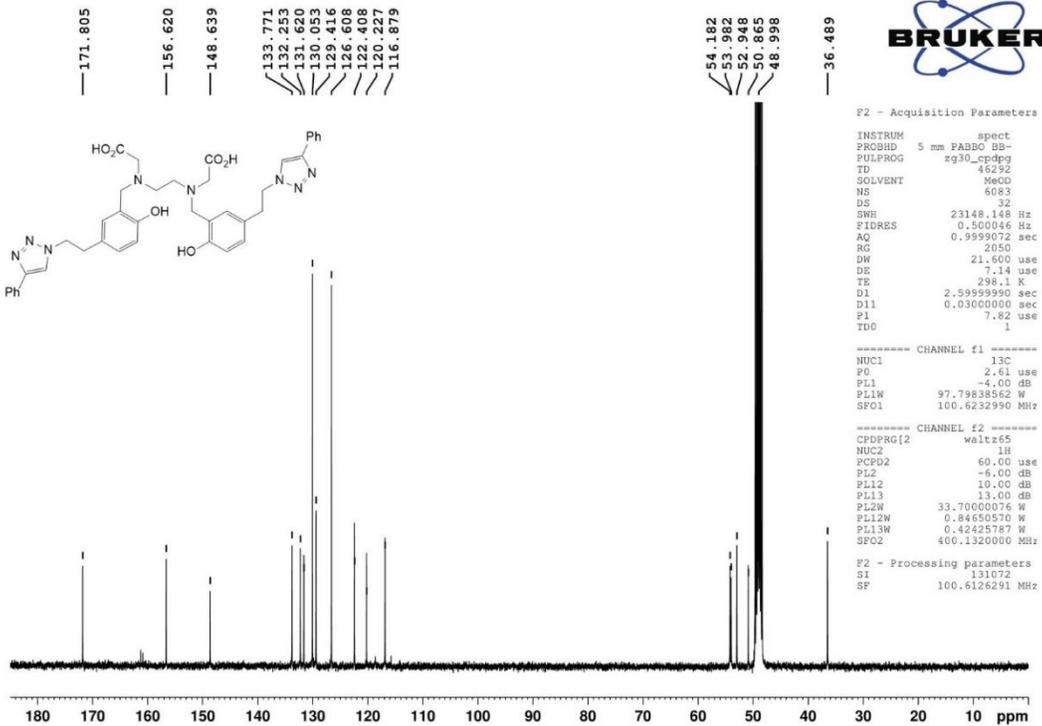
^e For isomers I and III and [Ti-HBED], yellow highlights indicate a large deviation on the side experiencing steric interaction between the phenyl and the acetyl groups; blue highlights indicate a large deviation on the other side. A large bond angle deviation is defined as > 4°.

^f Ref S3

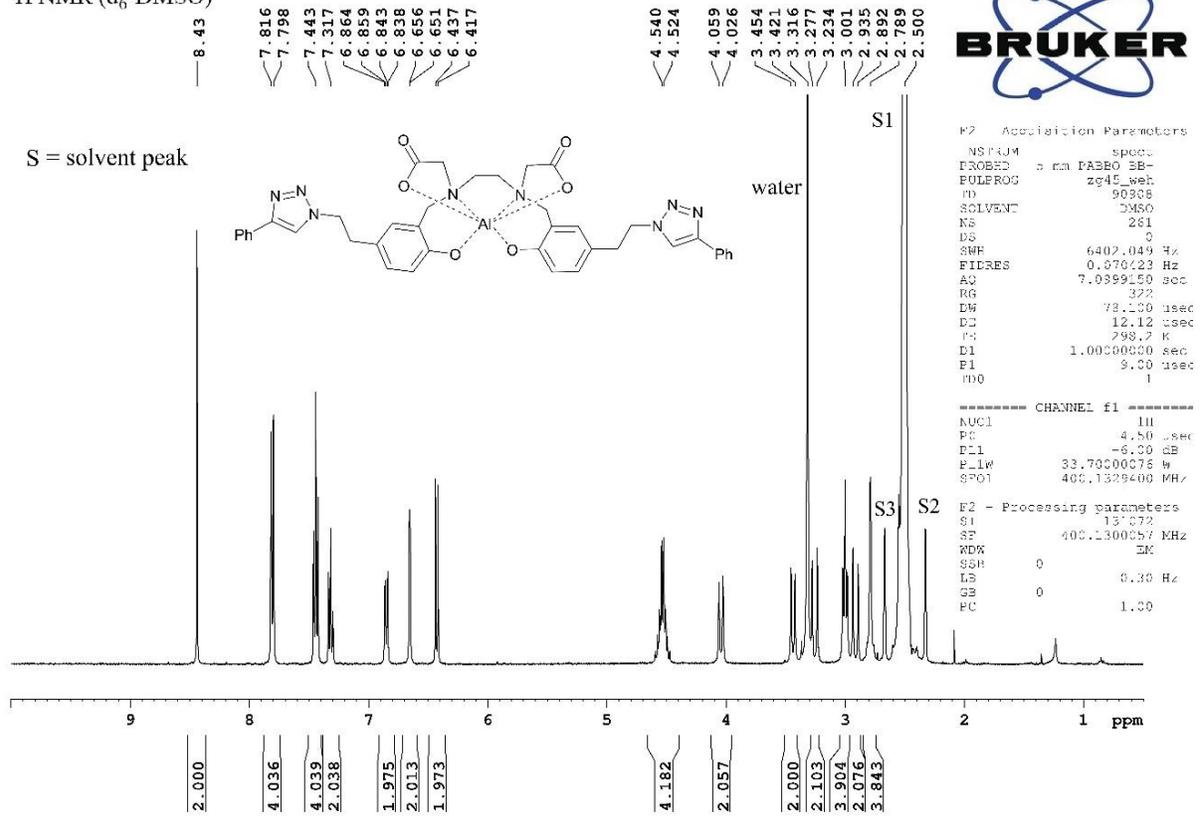
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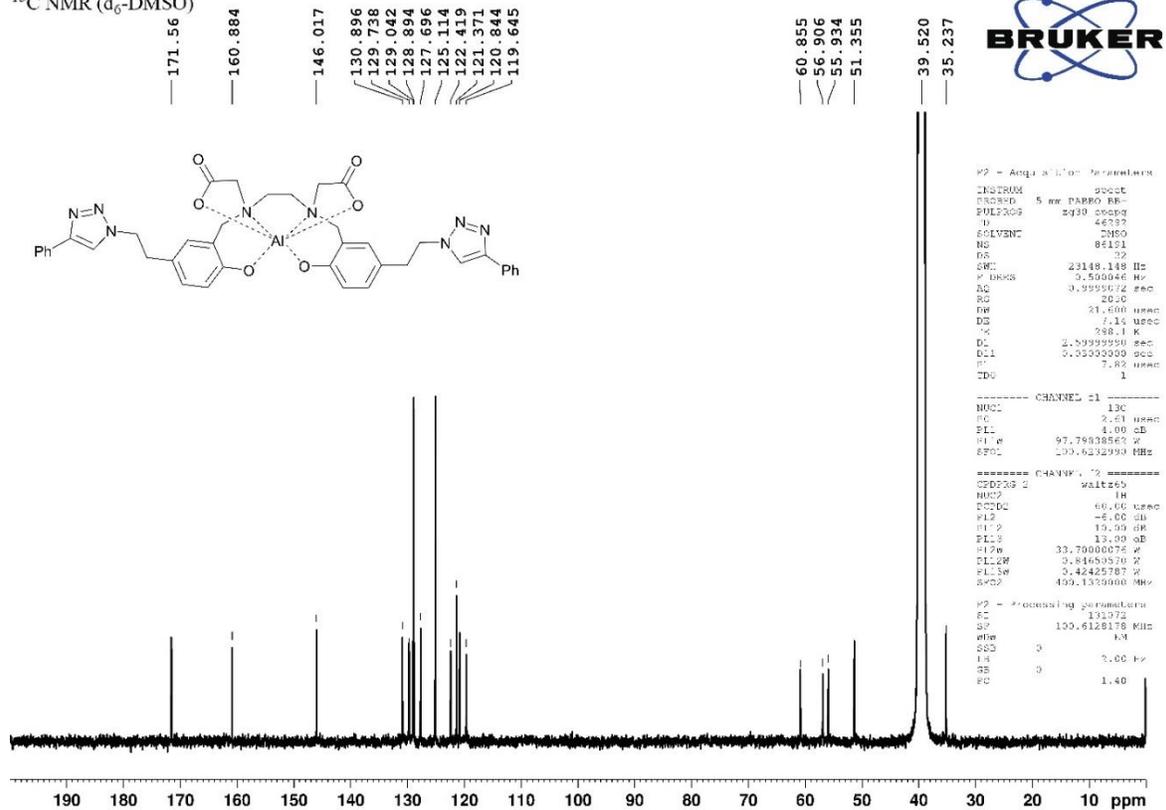
¹³C NMR (MeOD)

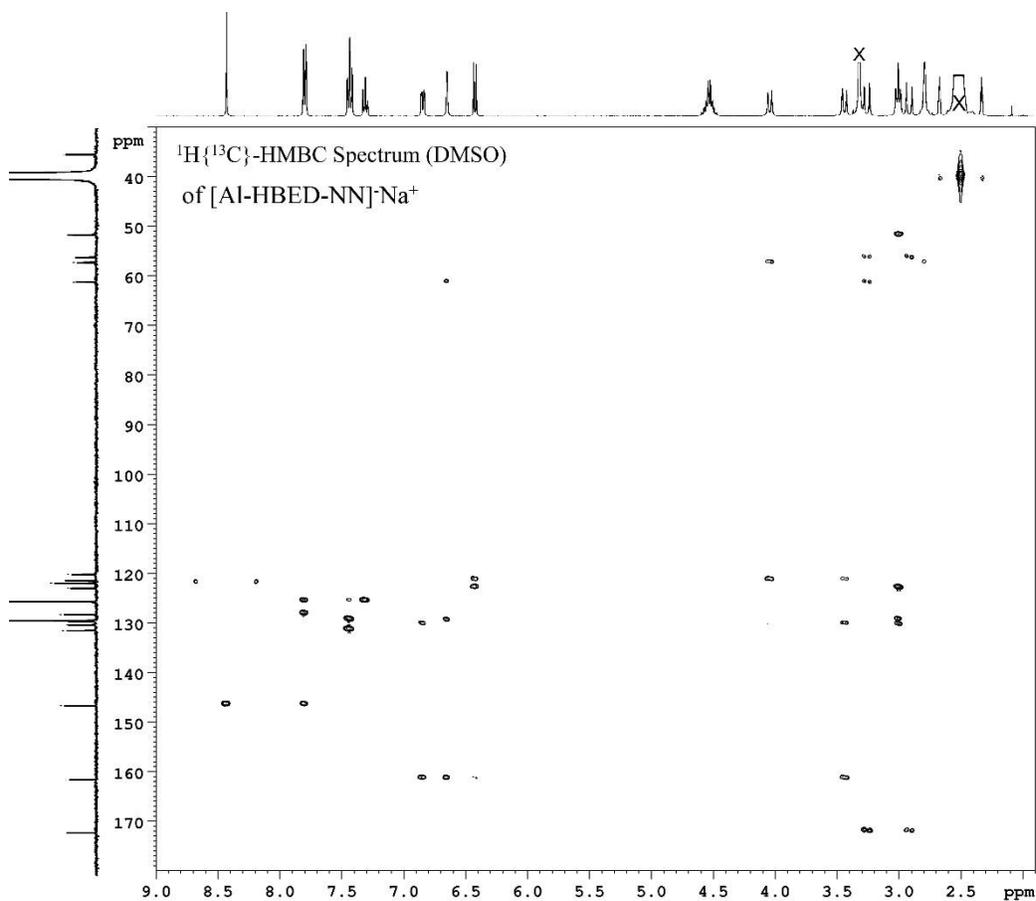


¹H NMR (d₆-DMSO)



¹³C NMR (d₆-DMSO)





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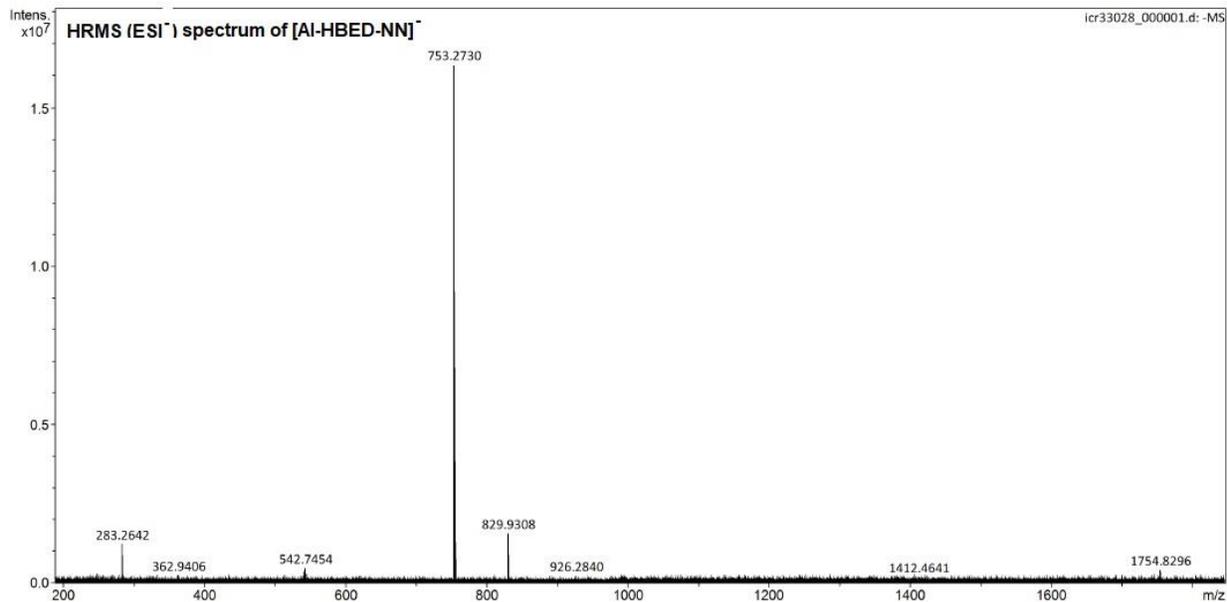
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F1 - Processing parameters
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SI 2048
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