Supporting Information for

Aluminum Alkyl Complexes Supported by Bidentate *N*,*N* Ligands: Synthesis, Structure, and Catalytic Activity for Guanylation of Amines

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Table S1. Summary of crystal and refinement data for Complexes 1-4

	1	**2**	**3**	**4**
formula	$C_{32}H_{54}Al_2N_4$	$C_{24}H_{34}Al_2N_4$	$C_{15}H_{21}AlN_2$	$C_{17}H_{17}AlN_2$
fw	548.75	432.51	256.32	276.31
T (K)	293(2)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073
crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
space group	C2/c	C2/c	P2(1)2(1)2(1)	P2(1)/c
a (Å)	14.861(2)	14.3230(13)	6.9650(11)	12.3588(18)
b (Å)	9.020(2)	12.9714(13)	8.7743(14)	7.2202(11)
c (Å)	25.302(5	13.7702(13)	25.862(4)	34.687(5)
α (deg)	90	90	90	90
β (deg)	93.384(4)	102.2310(10)	90	91.231(2)
γ (deg)	90	90	90	90
v ($Å^3$)	3385.7(2)	2500.3(4)	1580.5(4)	3094.5(8)
Z	4	4	4	8
D_{calcd} (mg/m^3)	1.077	1.149	1.077	1.186
μ mm^{-1}	0.111	0.133	0.115	0.123
F(000)	1200	928	552	1168
θ range (deg)	1.61 - 25.00	2.14 - 27.36	1.57 -27.38	1.65 -27.61
reflections collected/ unique	11594/2986	10457 / 2823	13573 / 3588	25505/ 7102
R (int)	0.0774	0.0323	0.0389	0.0594
goodness-of-fit on F^2	1.022	1.054	1.041	1.018
R_1, wR_2 [$I>2\sigma(I)$]	0.0678, 0.1460	0.0403, 0.1096	0.0419, 0.0972	0.0687,0.1563
R_1, wR_2 (all data)	0.1359, 0.1809	0.0491, 0.1170	0.0687, 0.1080	0.1414, 0.1882
Largest diff. peak and hole, e. $Å^{-3}$	0.372 and -0.219	0.208 and -0.236	0.175 and -0.128	0.324 and -0.225

Table S2. Summary of crystal and refinement data for complexes 5-7

	5	**6**	**7**
formula	$C_{19}H_{21}AlN_2$	$C_{21}H_{25}AlN_2$	$C_{38}H_{48}AlN_5$
fw	304.36	332.41	601.79
T (K)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
crystal system	Orthorhombic	Orthorhombic	Triclinic
space group	P2(1)2(1)2(1)	P2(1)2(1)2(1)	P-1
a (Å)	9.5117(8)	11.8395(9)	9.1613(13)
b (Å)	12.1110(10)	12.5102(10)	12.7665(18)
c (Å)	15.6113(13)	13.0265(11)	15.639(2)
α (deg)	90	90	96.060(2)
β (deg)	90	90	93.002(2)
γ (deg)	90	90	101.365(2)
v ($Å^3$)	1798.4(3)	1929.4(3)	1778.2(4)
Z	4	4	2
D_{calcd} (mg/m^3)	1.124	1.144	1.124
μ mm^{-1}	0.111	0.109	0.089
F(000)	648	712	648
ϴ range (deg)	2.13 - 27.6	2.26 - 27.47	1.64 - 27.65
reflections collected/ unique	15699 / 4202	16682 / 4418	15561 / 8080
R (int)	0.0313	0.0373	0.0333
goodness-of-fit on F^2	1.009	1.021	0.993
R_1, wR_2 [$I>2\sigma(I)$]	0.0431, 0.1132	0.0392, 0.0868	0.0584, 0.1374
R_1, wR_2 (all data)	0.0565, 0.1245	0.0663, 0.0984	0.1295, 0.1679
Largest diff. peak and hole, e. $Å^{-3}$	0.144 and -0.210	0.114 and -0.115	0.230 and -0.191

II. Copies of ^{1}H NMR, ^{13}C NMR Spectra of complexes 1-7

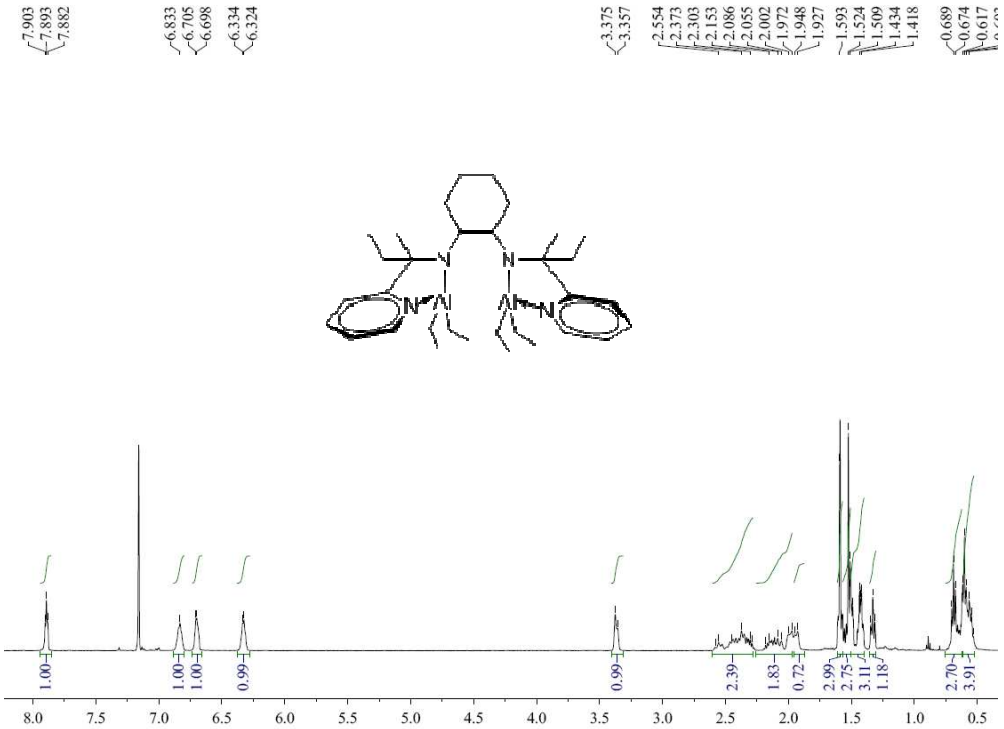

Figure S1. ^{1}H NMR spectrum (500 MHz, C_6D_6, 298 K) of complex **1**

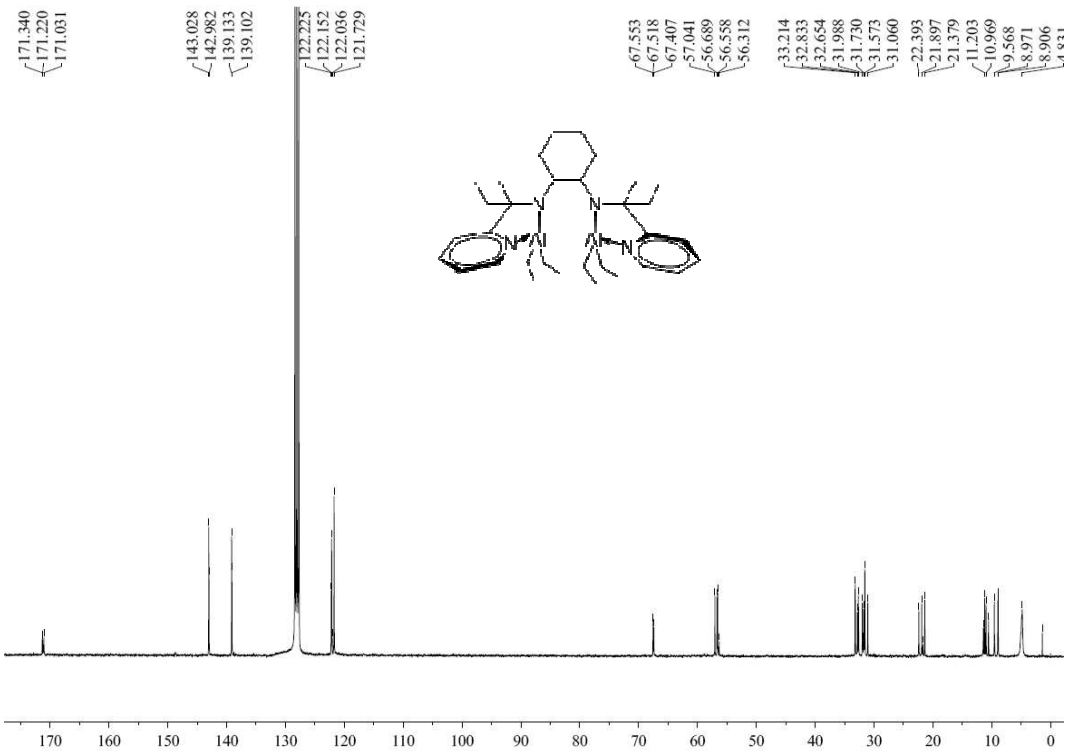

Figure S2. ^{13}C NMR spectrum (75 MHz, C_6D_6, 298 K) of complex **1**

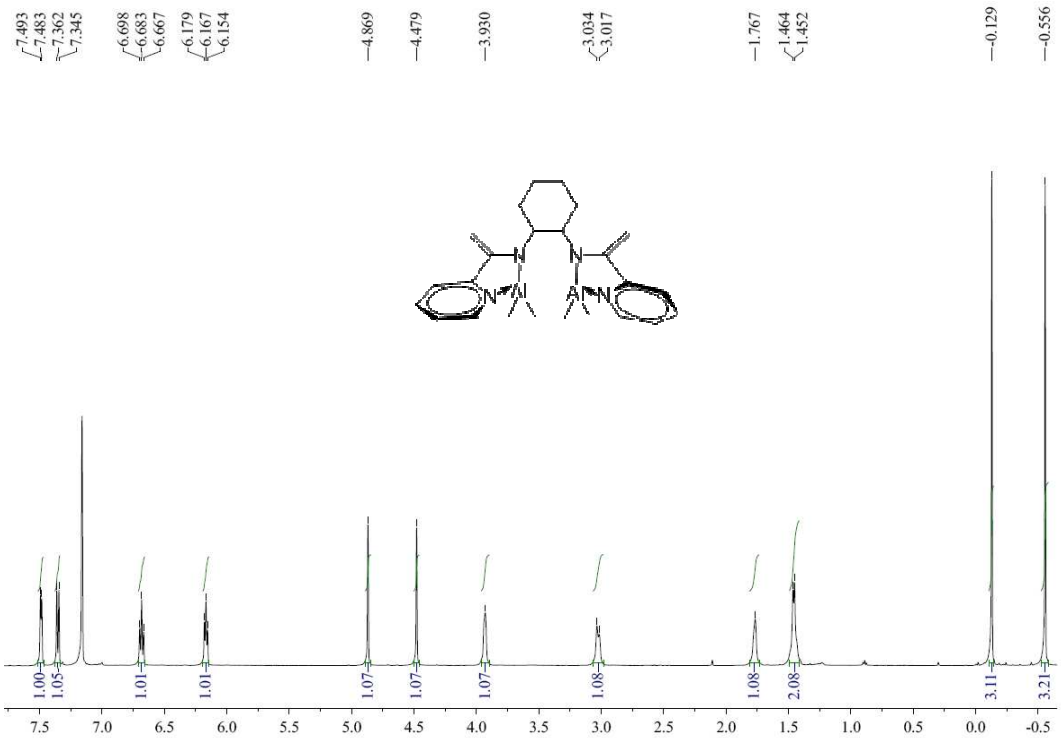

Figure S3. ^{1}H NMR spectrum (500 MHz, C_6D_6, 298 K) of complex **2**

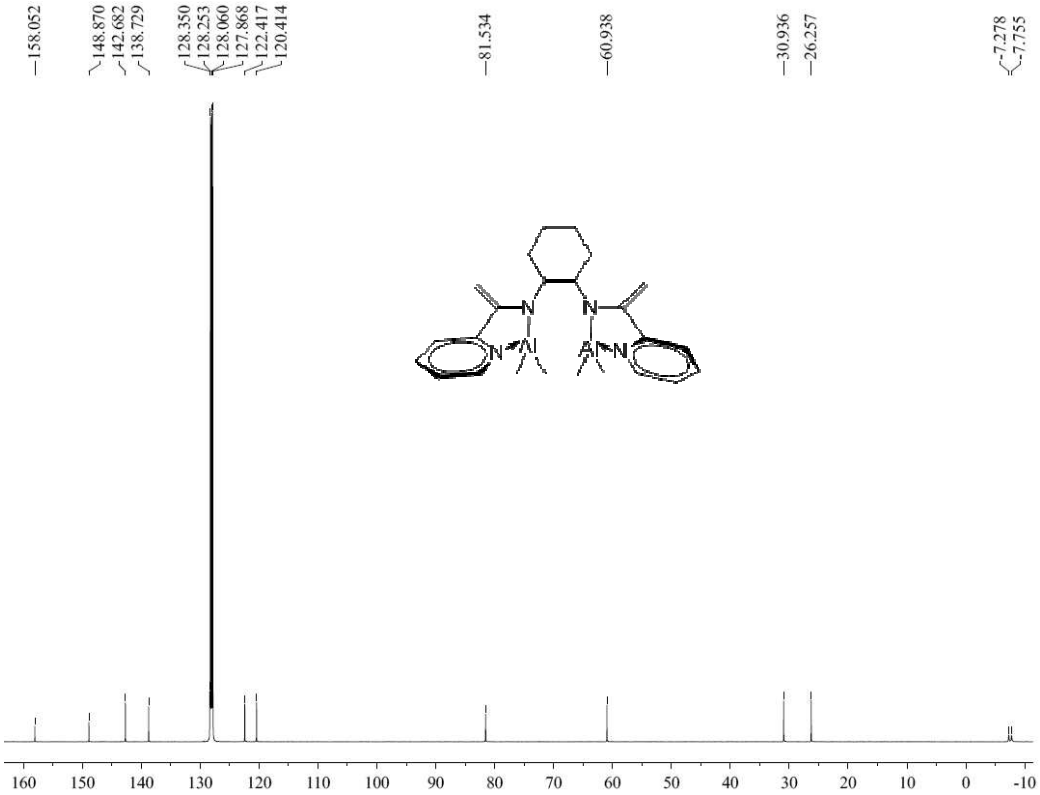

Figure S4. ^{13}C NMR spectrum (125 MHz, C_6D_6, 298 K) of complex **2**

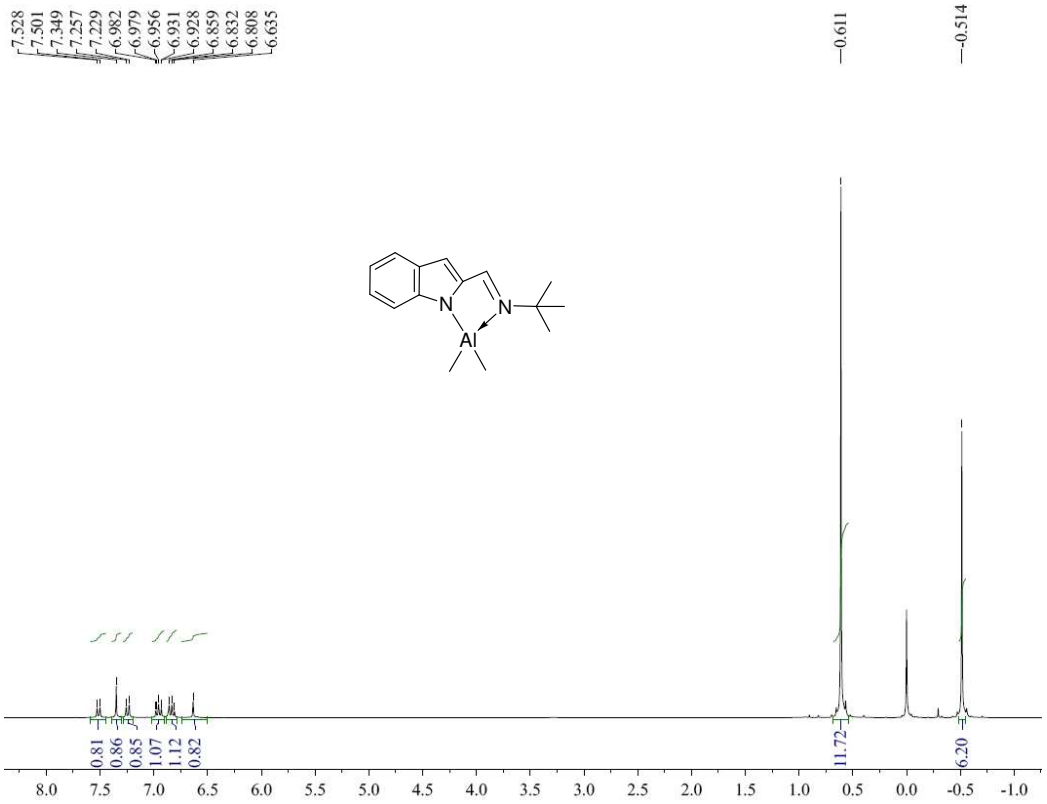

Figure S5. ^{1}H NMR spectrum (500 MHz, C_6D_6, 298 K) of complex **3**

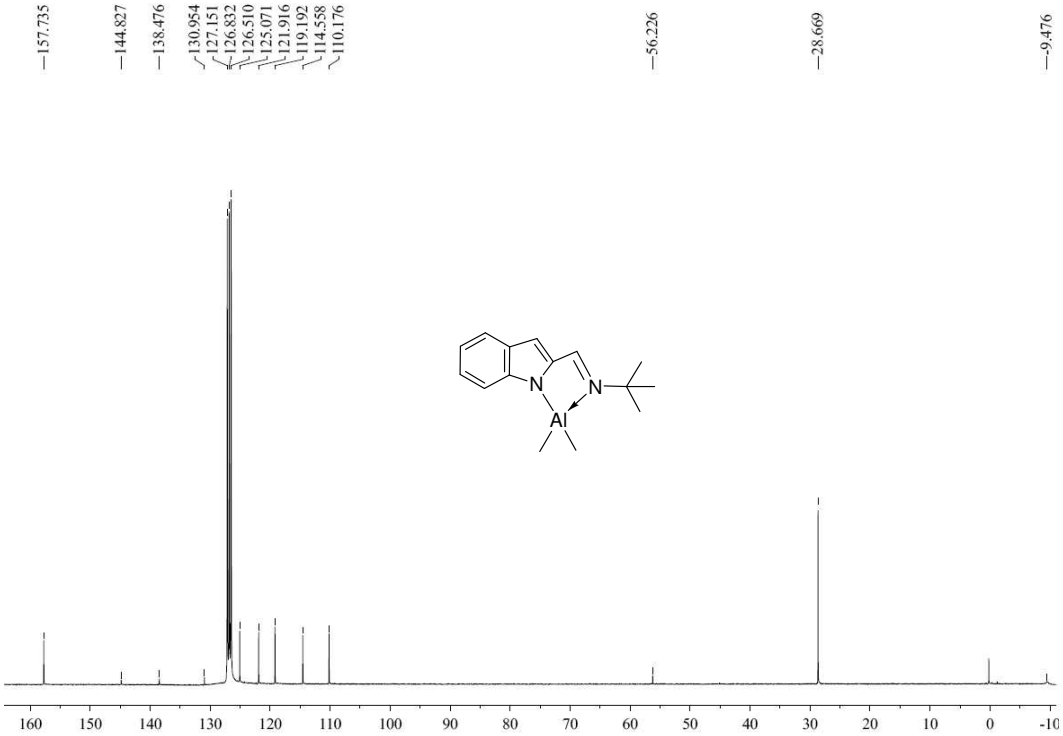

Figure S6. ^{13}C NMR spectrum (75 MHz, C_6D_6, 298 K) of complex **3**

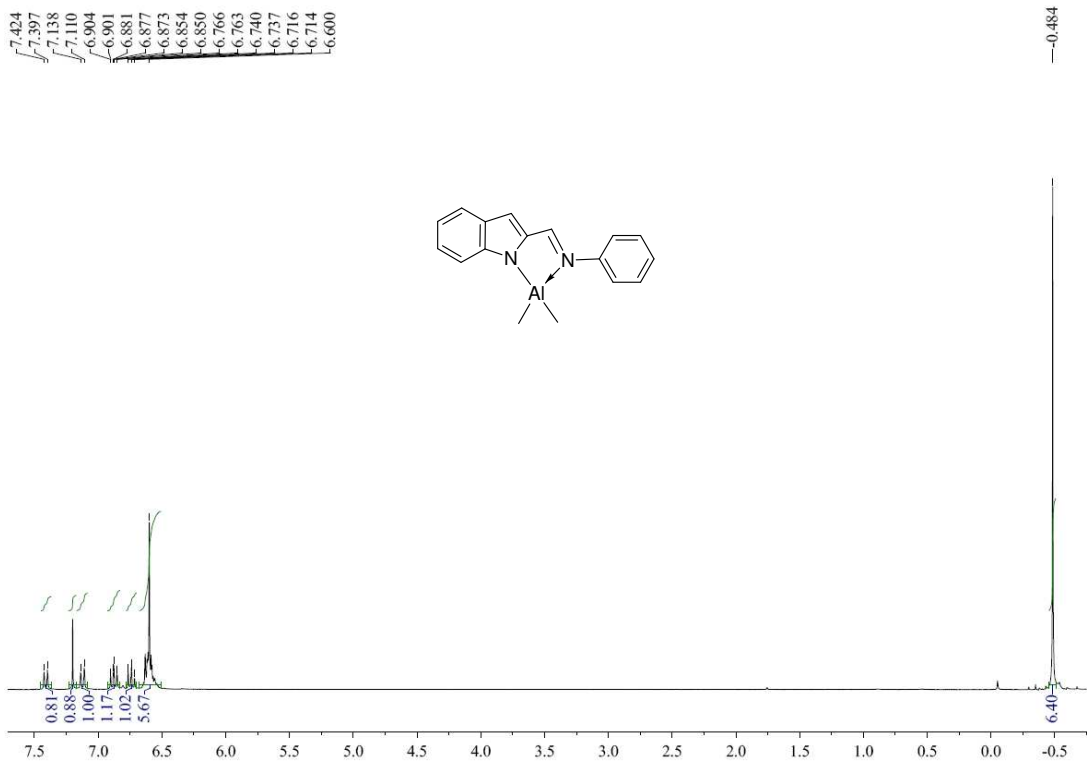

Figure S7. ^{1}H NMR spectrum (300 MHz, C_6D_6, 298 K) of complex **4**

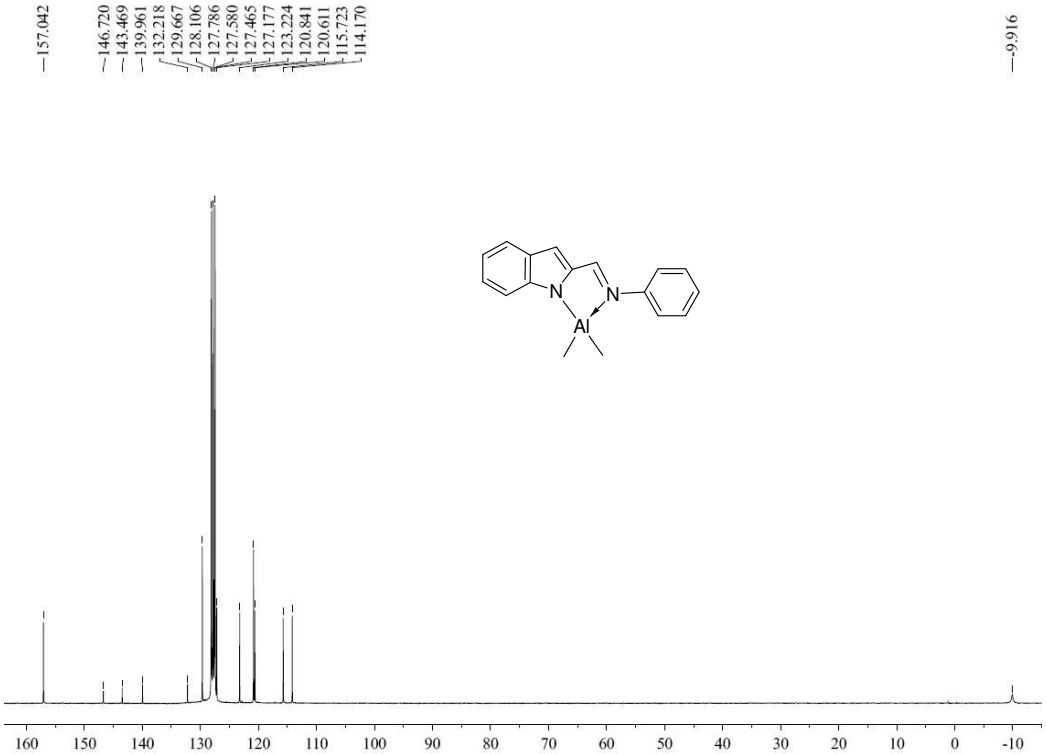

Figure S8. ^{13}C NMR spectrum (75 MHz, C_6D_6, 298 K) of complex **4**

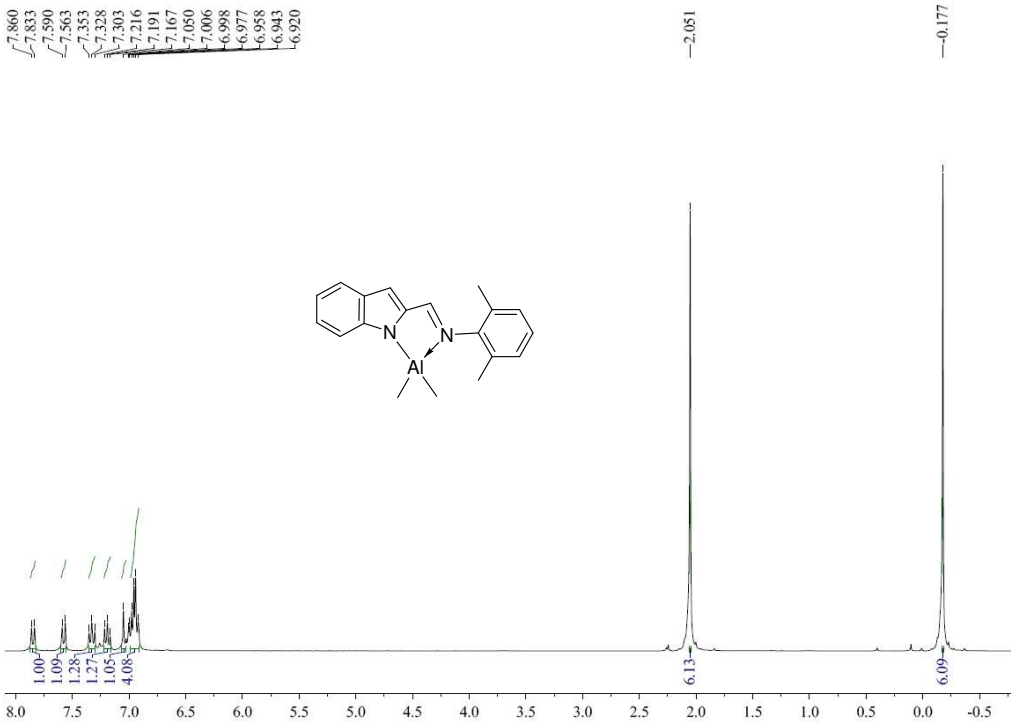

Figure S9. ^{1}H NMR spectrum (300 MHz, C_6D_6, 298 K) of complex **5**

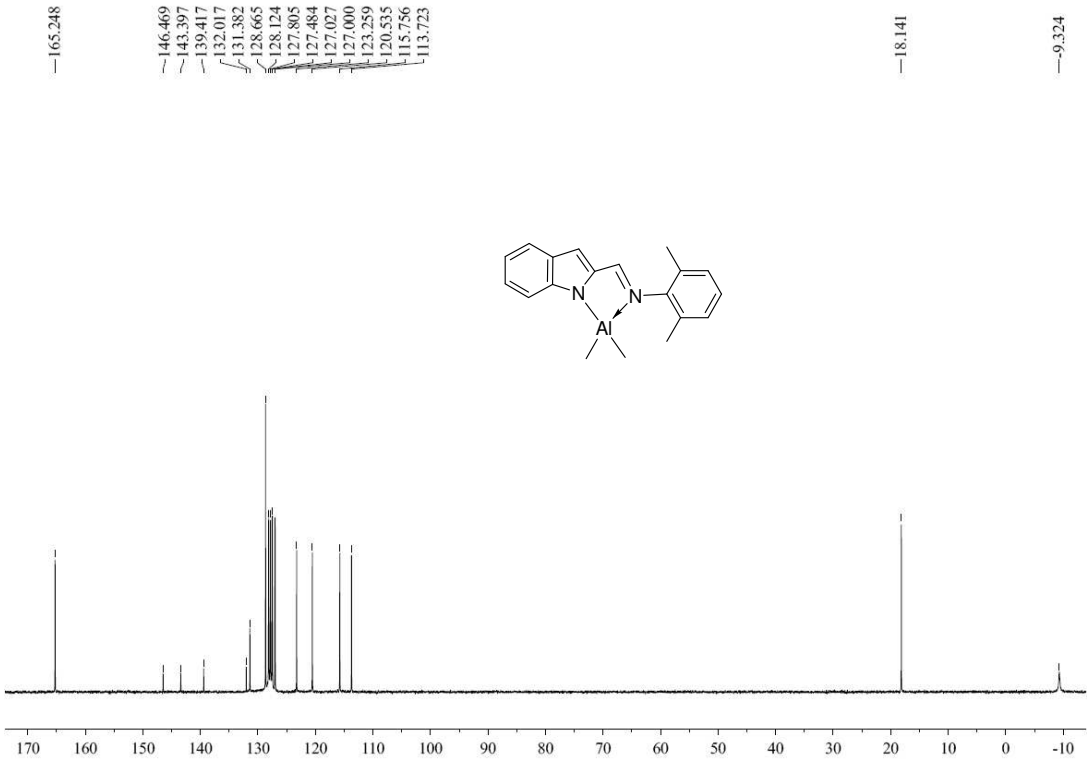

Figure S10. ^{13}C NMR spectrum (75 MHz, C_6D_6, 298 K) of complex **5**

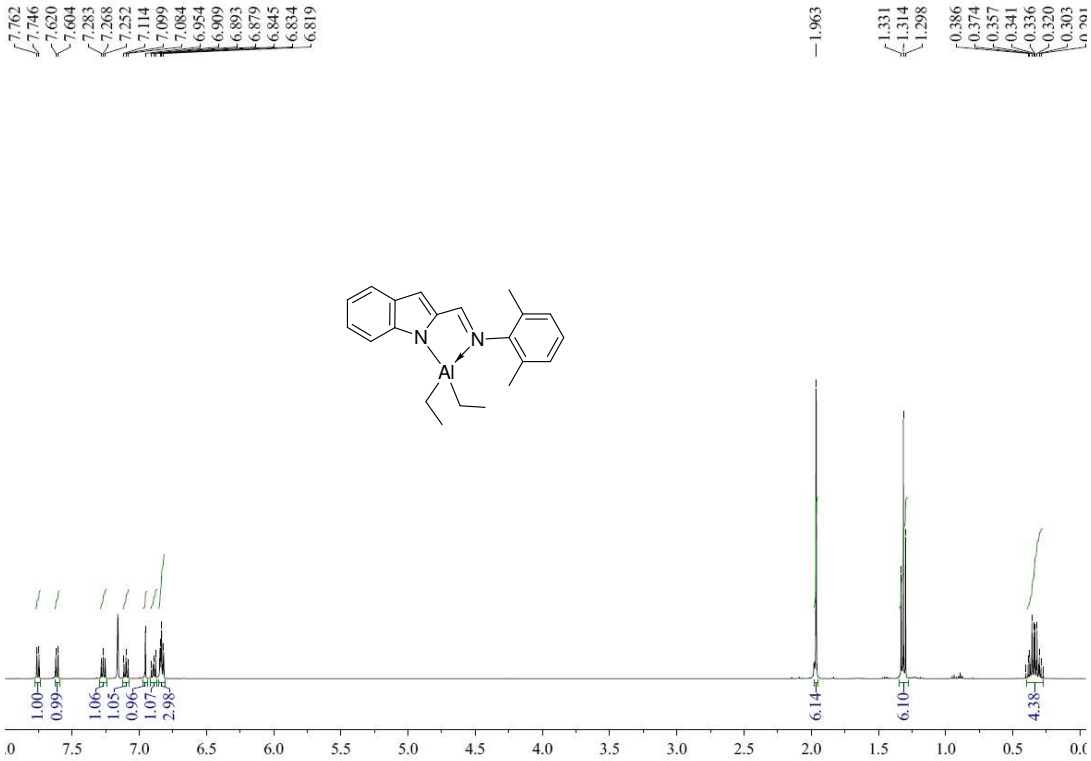

Figure S11. ^{1}H NMR spectrum (500 MHz, C_6D_6, 298 K) of complex **6**

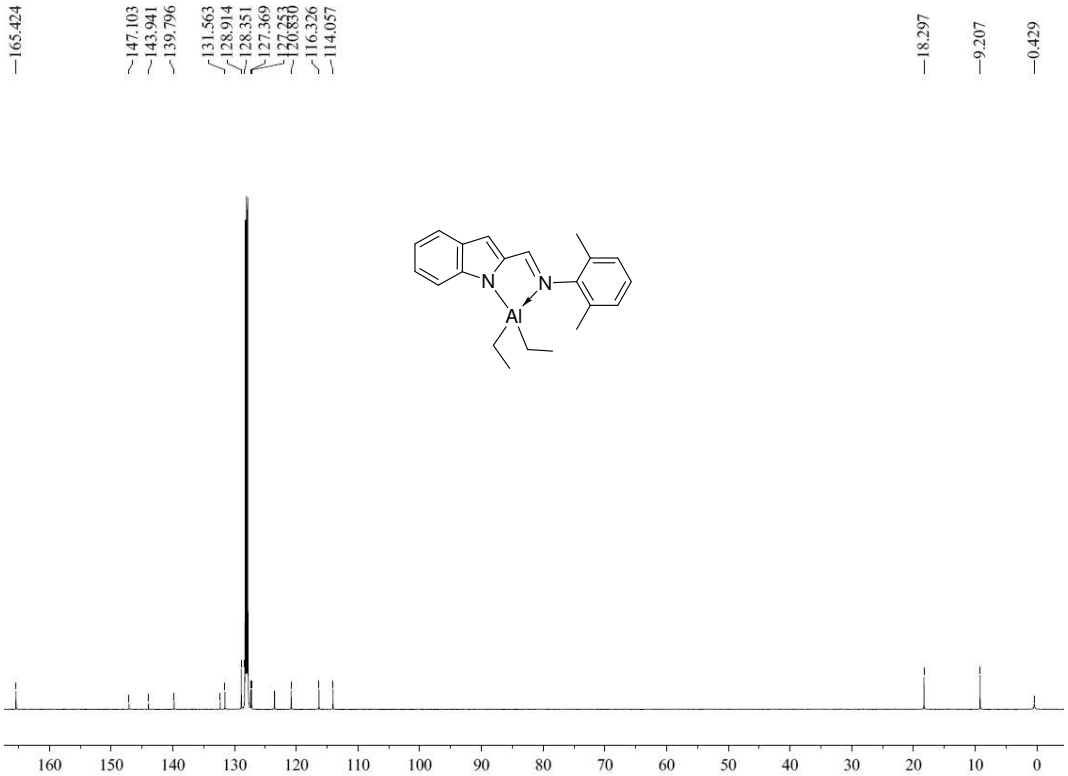

Figure S12. ^{13}C NMR spectrum (125 MHz, C_6D_6, 298 K) of complex **6**

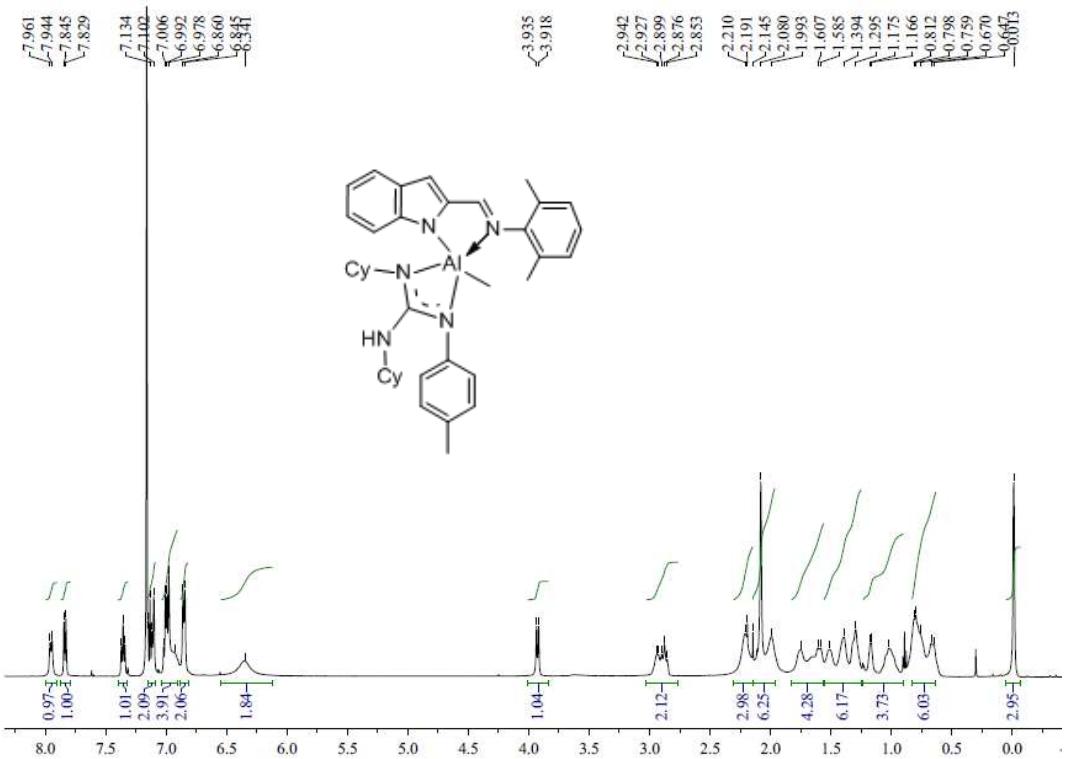

Figure S13. ^{1}H NMR spectrum (500 MHz, C_6D_6, 298 K) of complex **7**

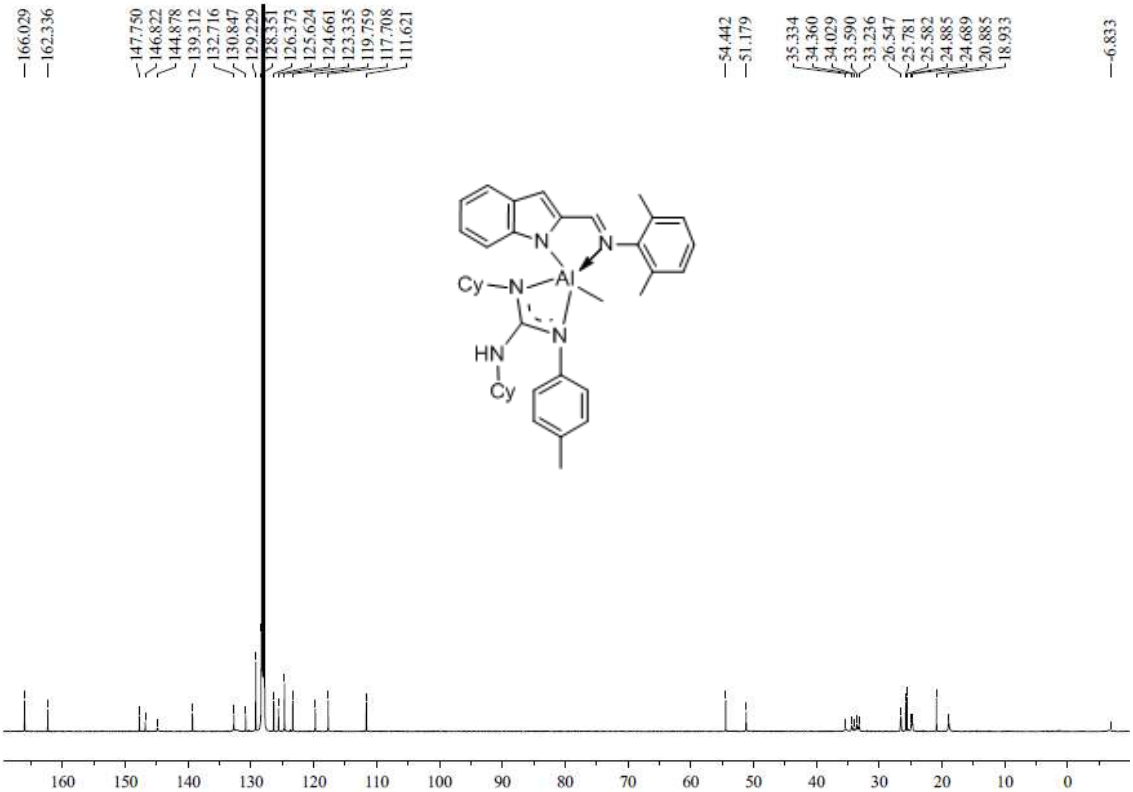

Figure S14. ^{13}C NMR spectrum (125 MHz, C_6D_6, 298 K) of complex **7**

III. ^{1}H NMR probing spectra of the guanylation of anilines with carbodiimides by complex 5

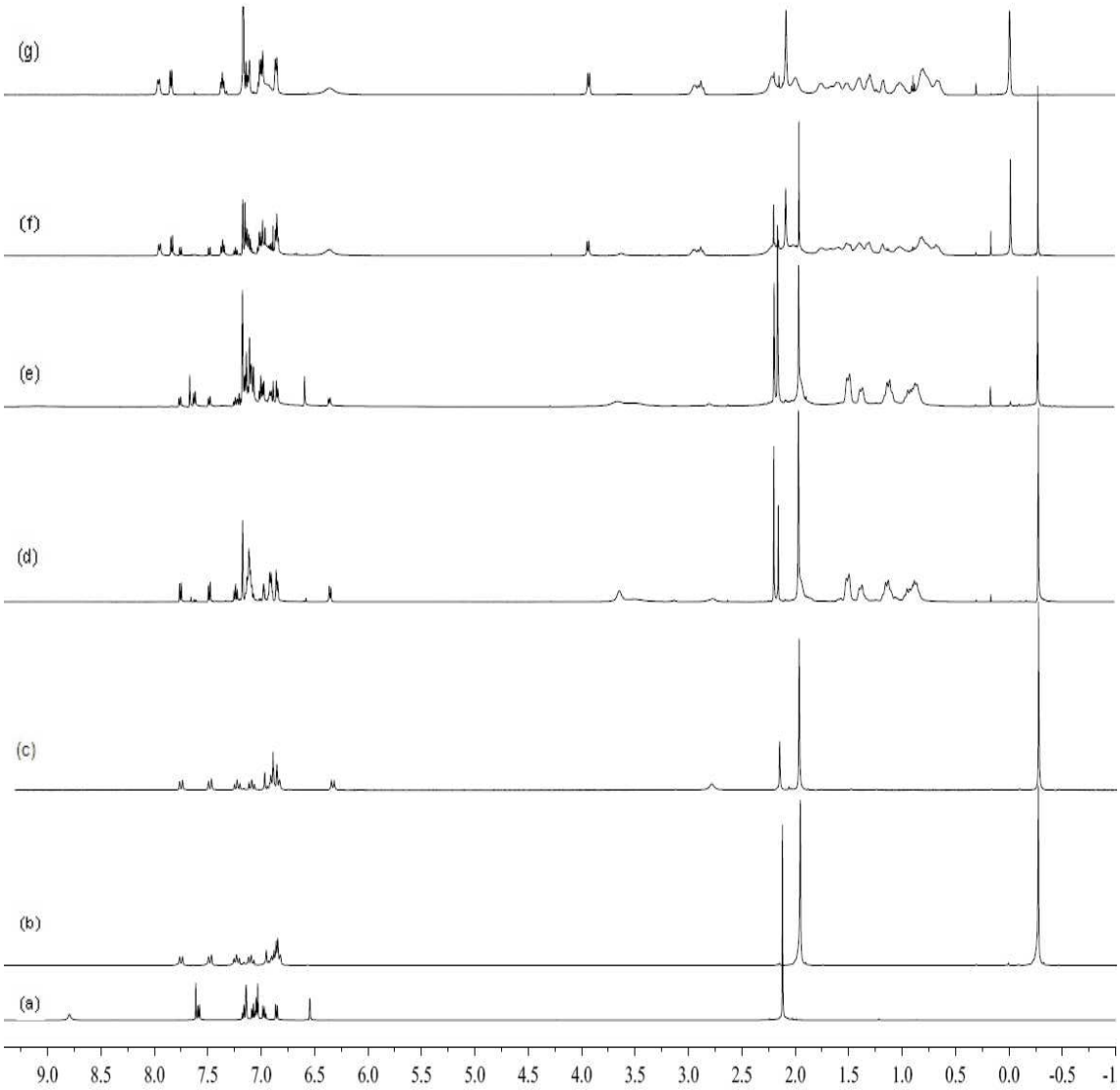

Figure S15. ^{1}H NMR probing spectra (500 MHz, C_6D_6) of the guanylation reaction by complex **5**

(a) **L^{4}H**, (b) Complex **5**, (c) Complex **5** + 4-Me$C_6H_4NH_2$ at 80 °C for 12h,

(d) Complex **5** + 4-Me$C_6H_4NH_2$ + CyN=C=NCy after 1h, (e) Complex **5** +

4-Me$C_6H_4NH_2$ + CyN=C=NCy after 16 h, (f) Complex **5** + 4-Me$C_6H_4NH_2$ +

CyN=C=NCy after 22 h, (g) Complex **7.**