Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Pyridine-Amido Aluminum Catalyst Precursors for 1,3-Butadiene Transition-Metal-Free Stereospecific Polymerization

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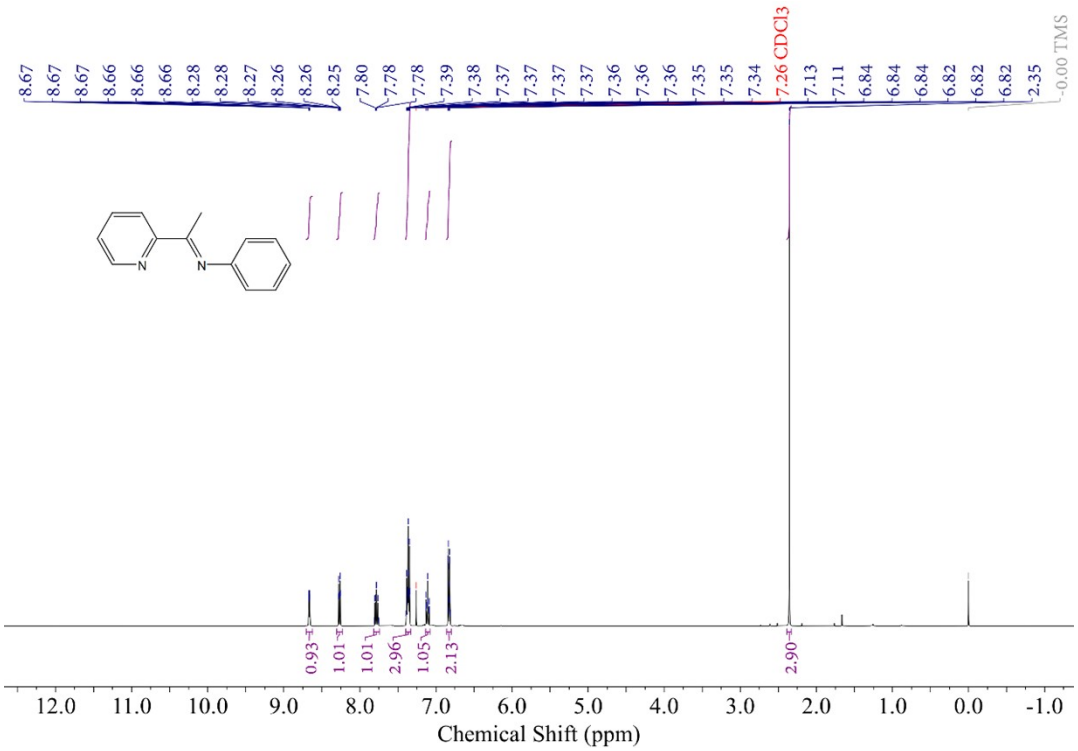

Figure S1 ^{1}H NMR spectrum of pro-ligand pyridine-2-C(Me)=N(Ph) (**1**).

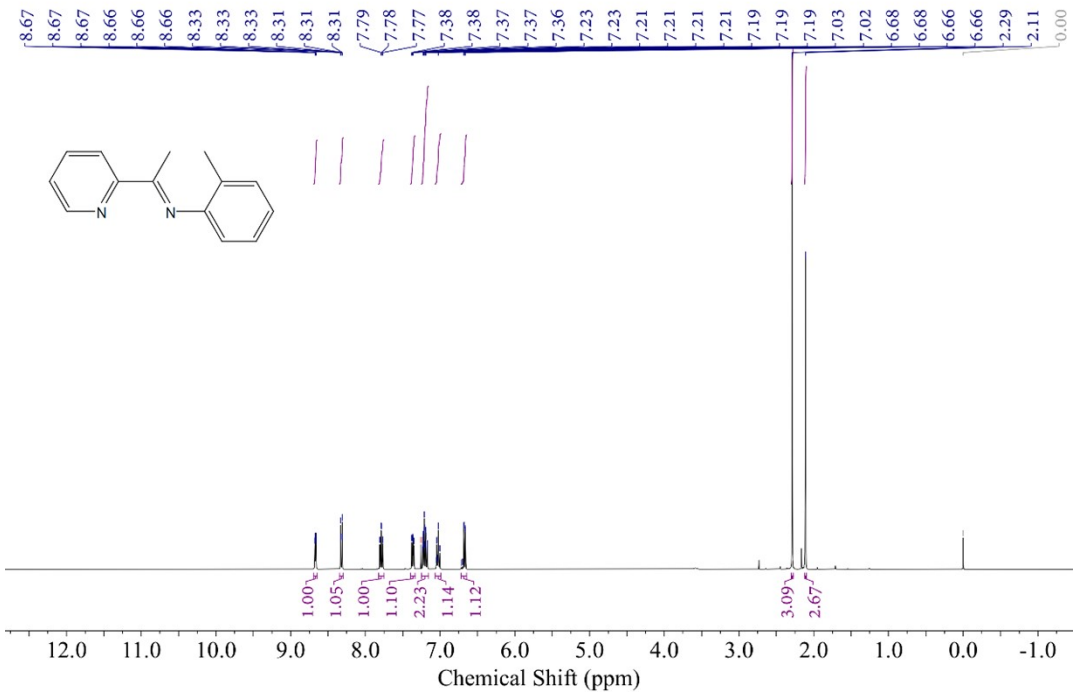

Figure S2 ^{1}H NMR spectrum of pro-ligand pyridine-2-C(Me)=N(2-(Me)C_6H_4) (**2**).

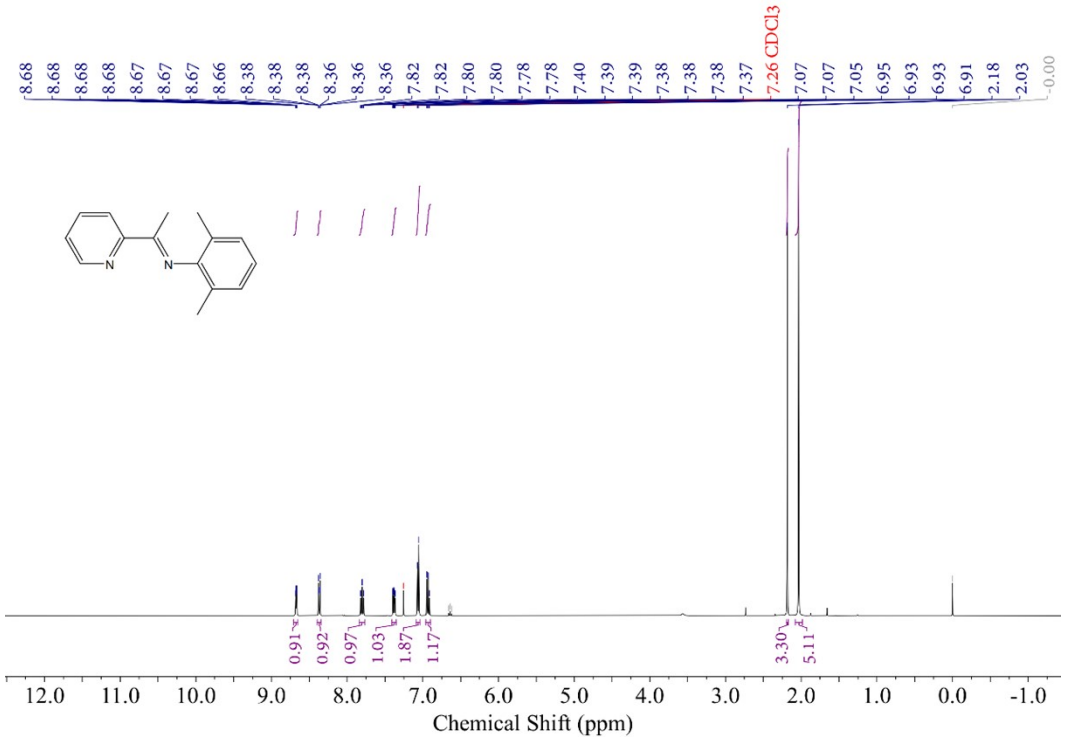

Figure S3 ^{1}H NMR spectrum of pro-ligand pyridine-2-C(Me)=N(2,6-$(Me)_2C_6H_3$) (**3**).

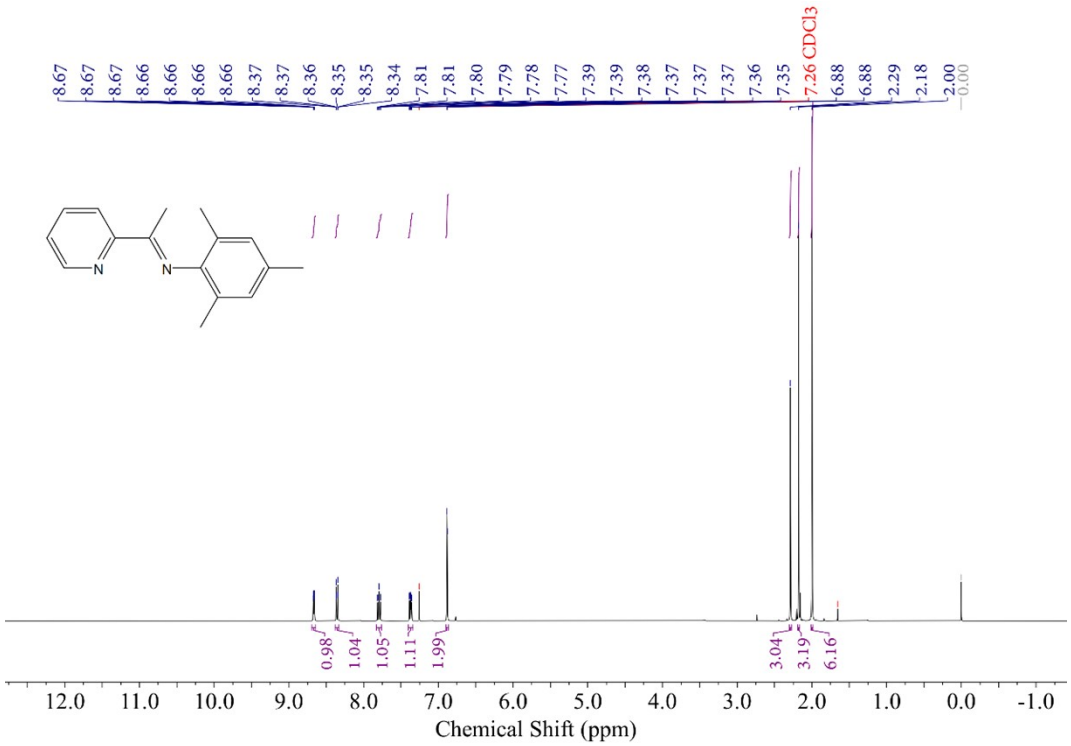

Figure S4 ^{1}H NMR spectrum of pro-ligand pyridine-2-C(Me)=N(2,4,6-$(Me)_3C_6H_2$) (**4**).

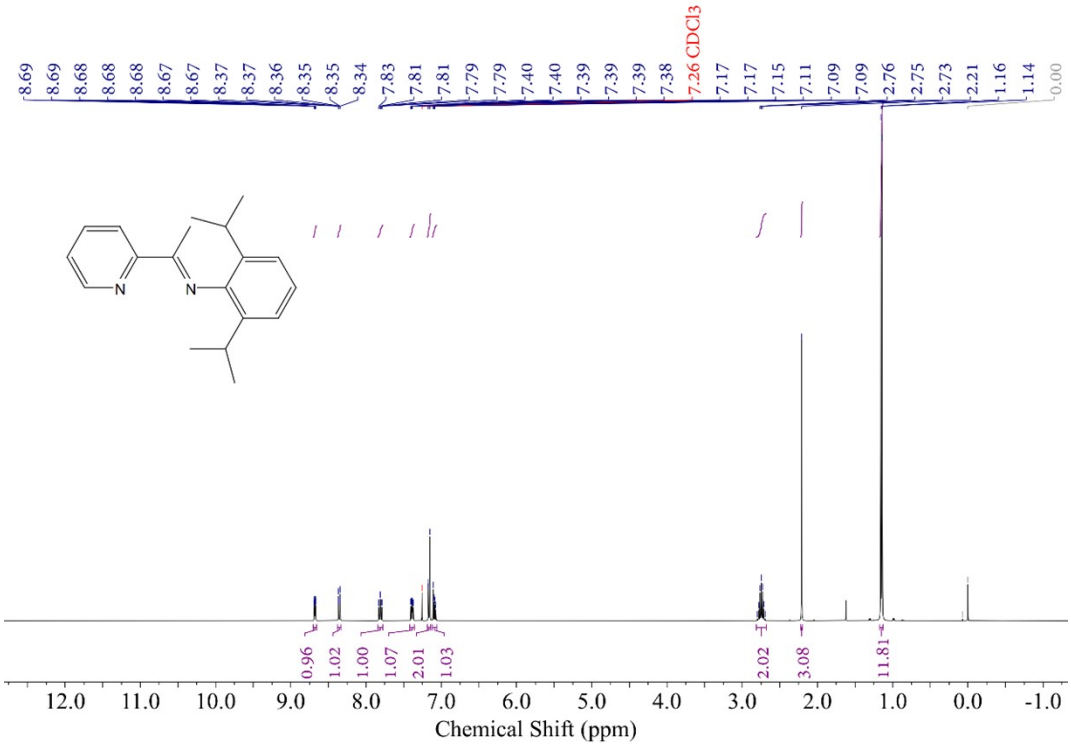

Figure S5 ^{1}H NMR spectrum of pro-ligand pyridine-2-C(Me)=N(2,6-(^{i}Pr)$_2$C$_6$H$_3$) (**5**).

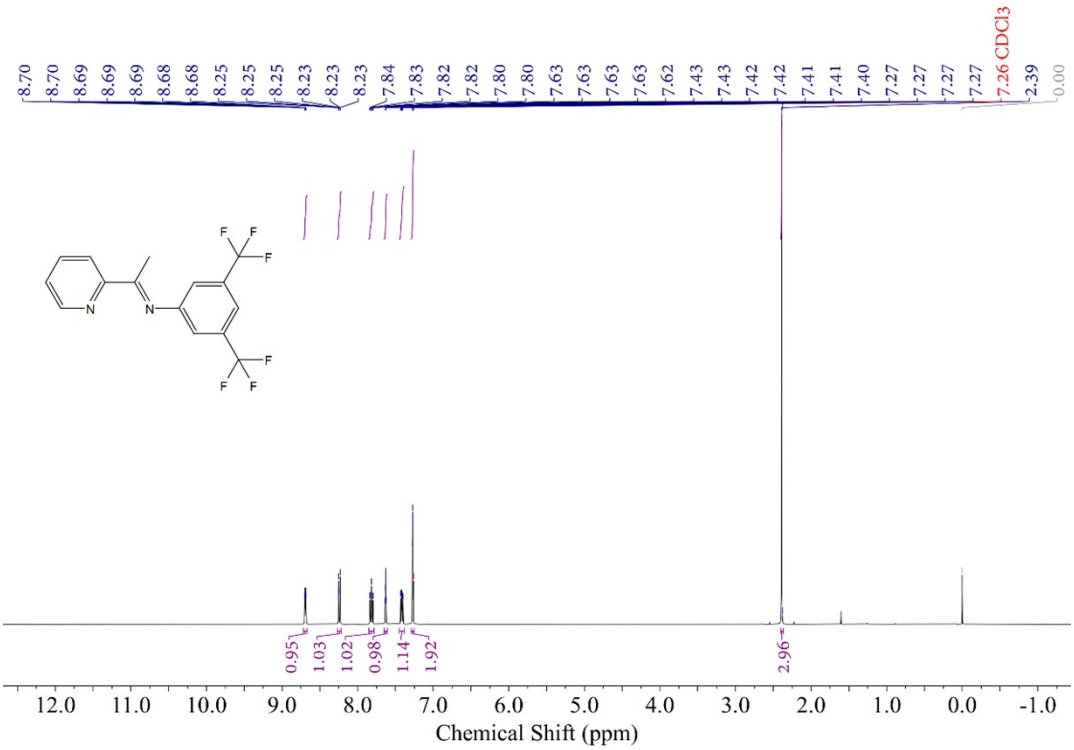

Figure S6 ^{1}H NMR spectrum of pro-ligand pyridine-2-C(Me)=N(3,5-(CF$_3$)$_2$C$_6$H$_3$) (**6**).

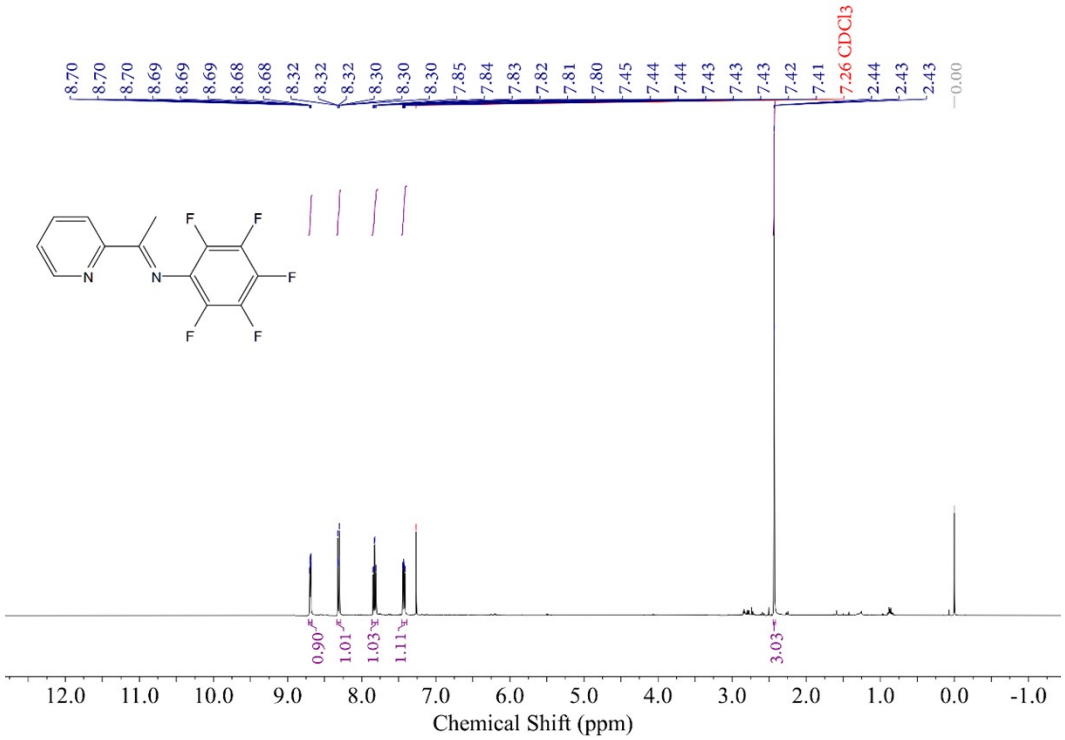

Figure S7 ^{1}H NMR spectrum of pro-ligand pyridine-2-C(Me)=N(C_6F_5) (**7**).

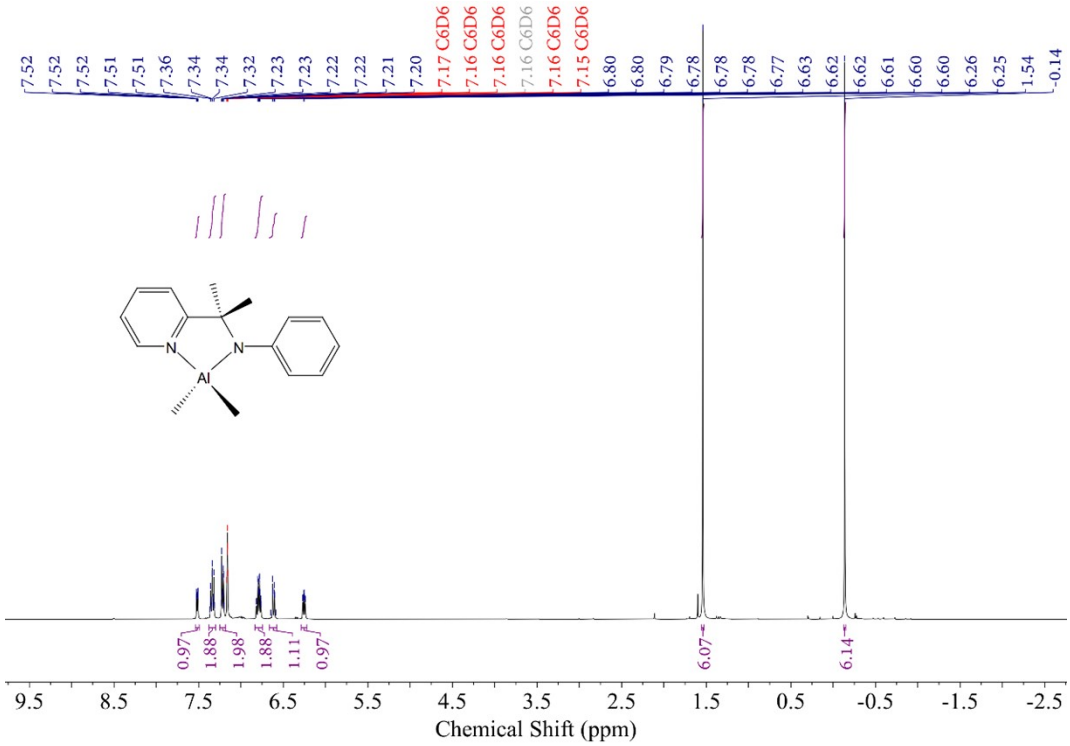

Figure S8 ^{1}H NMR spectrum of aluminum complex [pyridine-2-CMe_2N(Ph)-κ^2N,N']$AlMe_2$ (**1a**).

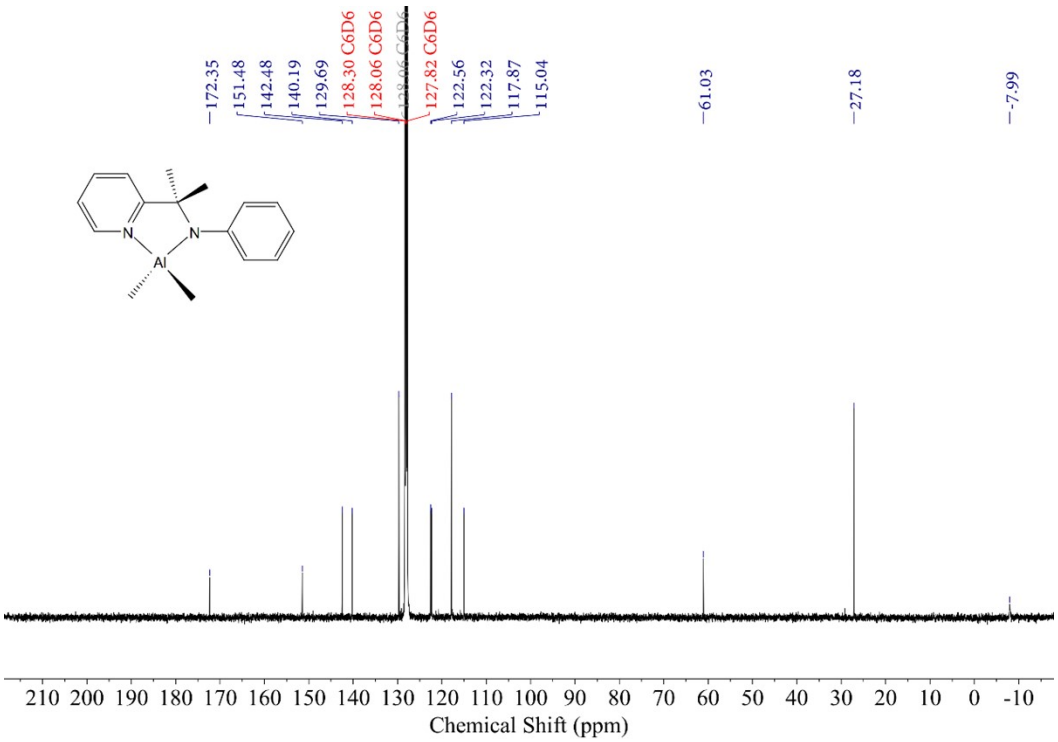

Figure S9 ^{13}C NMR spectrum of aluminum complex [pyridine-2-CMe$_2$N(Ph)-κ^{2}N,N']AlMe$_2$ (**1a**).

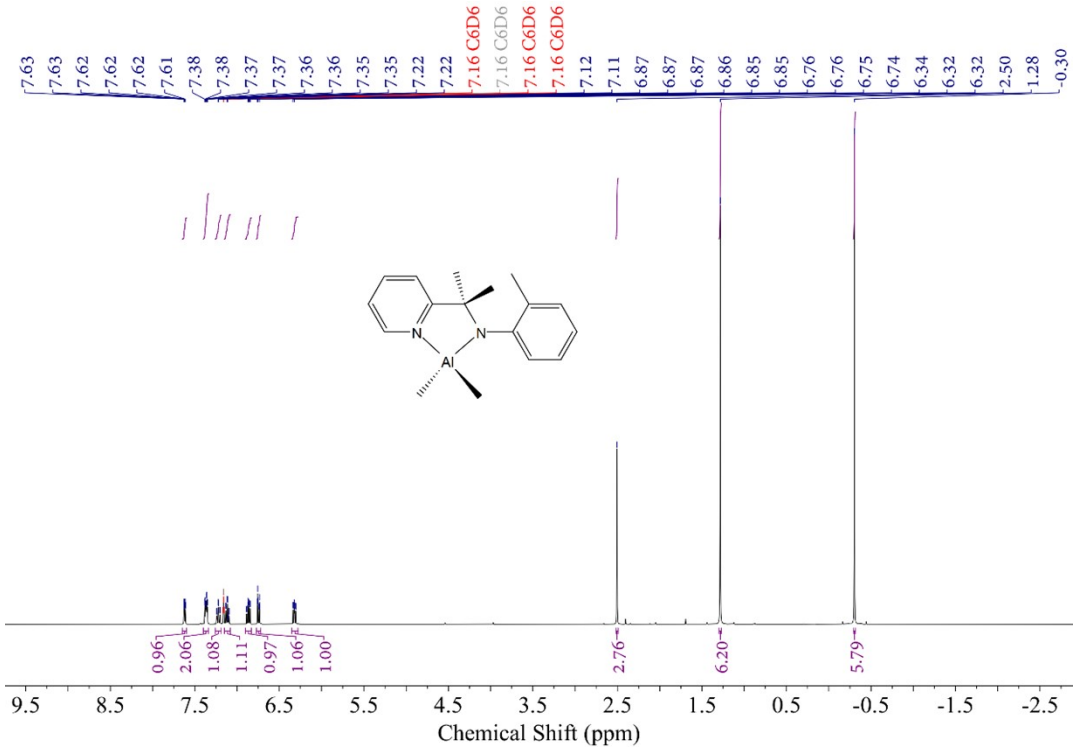

Figure S10 ^{1}H NMR spectrum of aluminum complex [pyridine-2-CMe$_2$N(2-(Me)C$_6$H$_4$)-κ^{2}N,N']AlMe$_2$ (**2a**).

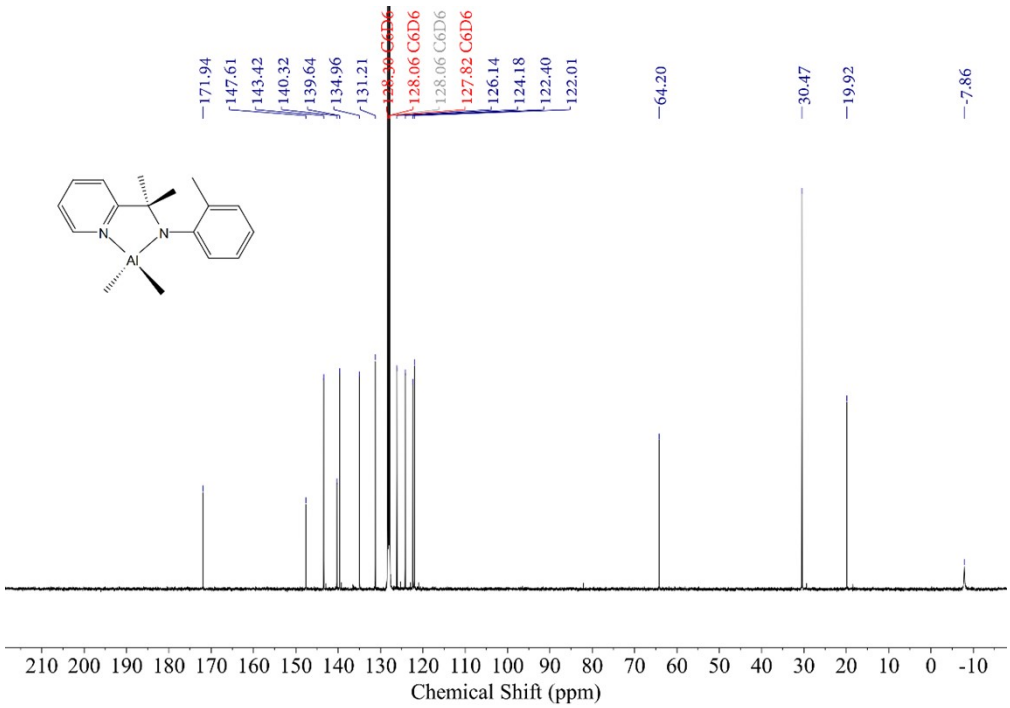

Figure S11 ^{13}C NMR spectrum of aluminum complex [pyridine-2-CMe_2N(2-$(Me)C_6H_4$)-κ^2N,N']$AlMe_2$ (**2a**).

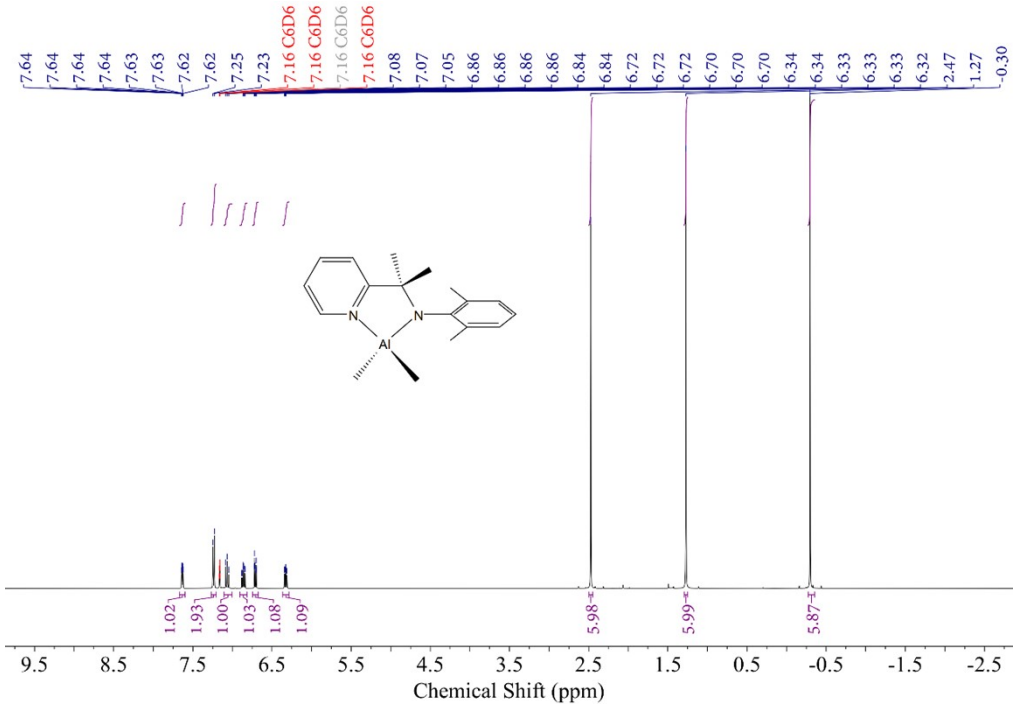

Figure S12 ^{1}H NMR spectrum of aluminum complex [pyridine-2-CMe_2N(2,6-$(Me)_2C_6H_3$)-κ^2N,N']$AlMe_2$ (**3a**).

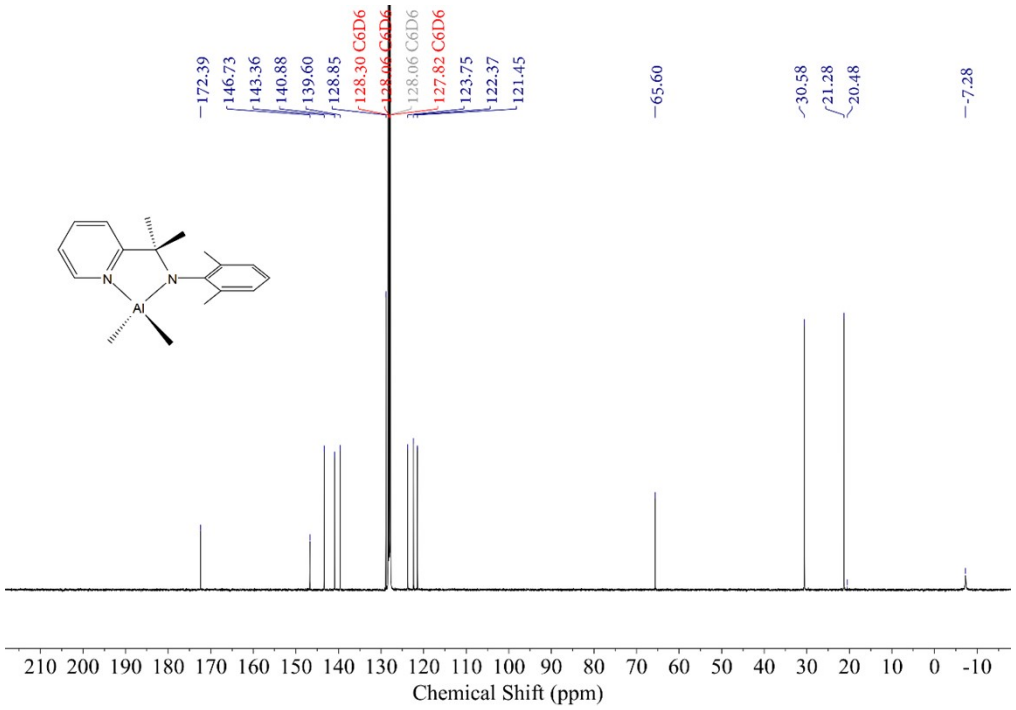

Figure S13 ^{13}C NMR spectrum of aluminum complex [pyridine-2-CMe_2N(2,6-$(Me)_2C_6H_3$)-κ^2N,N']$AlMe_2$ (**3a**).

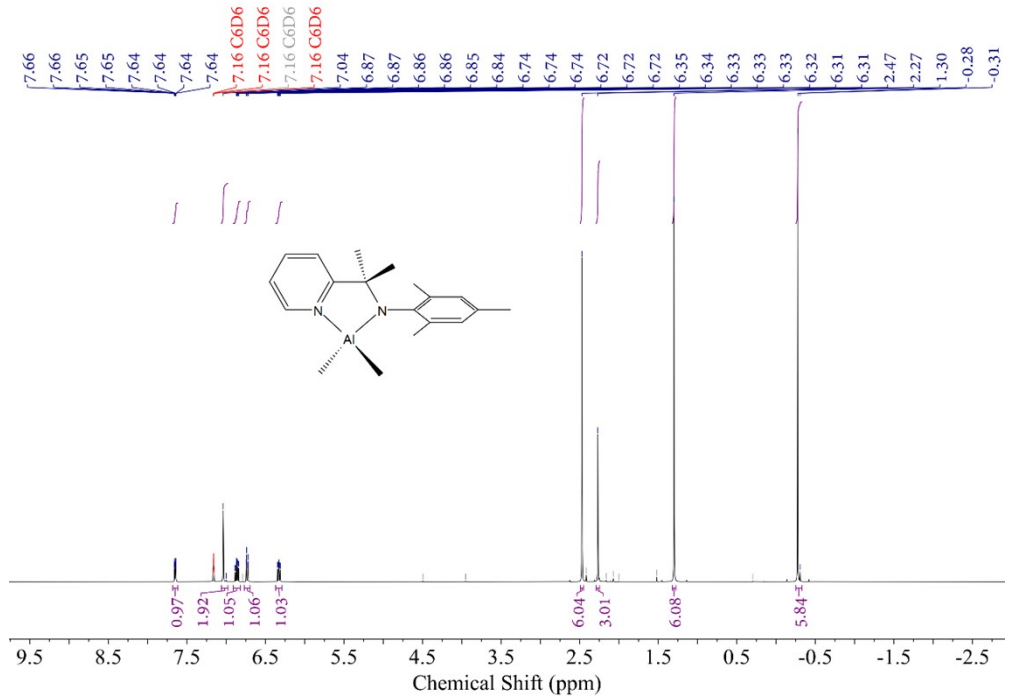

Figure S14 ^{1}H NMR spectrum of aluminum complex [pyridine-2-CMe_2N(2,4,6-$(Me)_3C_6H_2$)-κ^2N,N']$AlMe_2$ (**4a**).

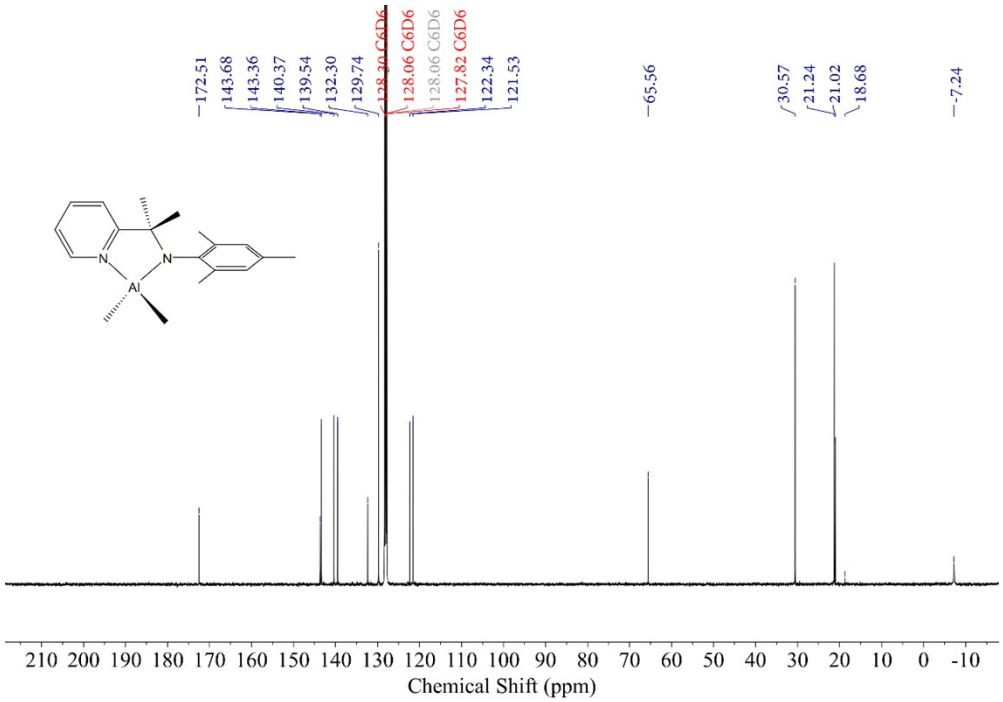

Figure S15 ^{13}C NMR spectrum of aluminum complex [pyridine-2-CMe_2N(2,4,6-$(Me)_3C_6H_2$)-κ^2N,N']$AlMe_2$ (**4a**).

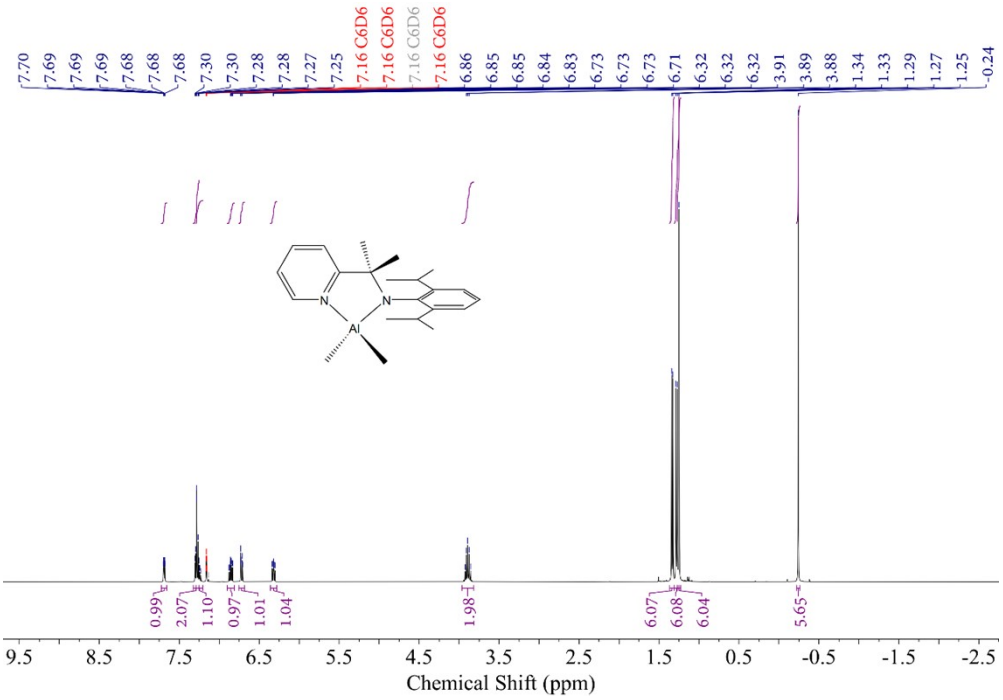

Figure S16 ^1H NMR spectrum of aluminum complex [pyridine-2-CMe_2N(2,6-$(^iPr)_2C_6H_3$)-κ^2N,N']$AlMe_2$ (**5a**).

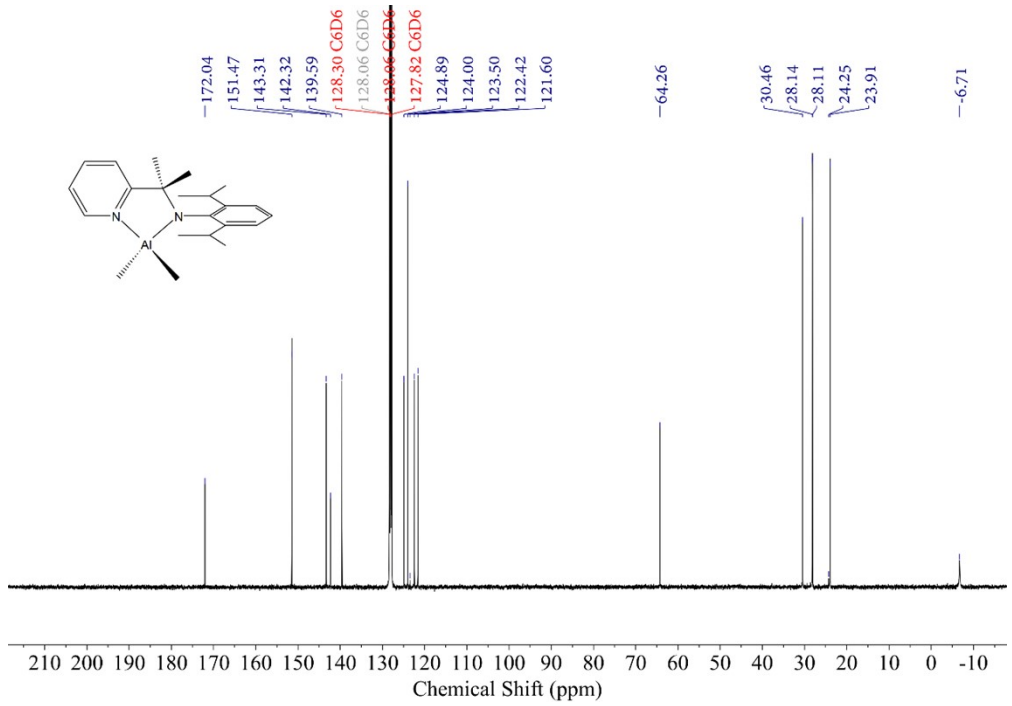

Figure S17 ^{13}C NMR spectrum of aluminum complex [pyridine-2-CMe_2N(2,6-(^{i}Pr)$_2$$C_6H_3$)-$\kappa^2$N,N']$AlMe_2$ (**5a**).

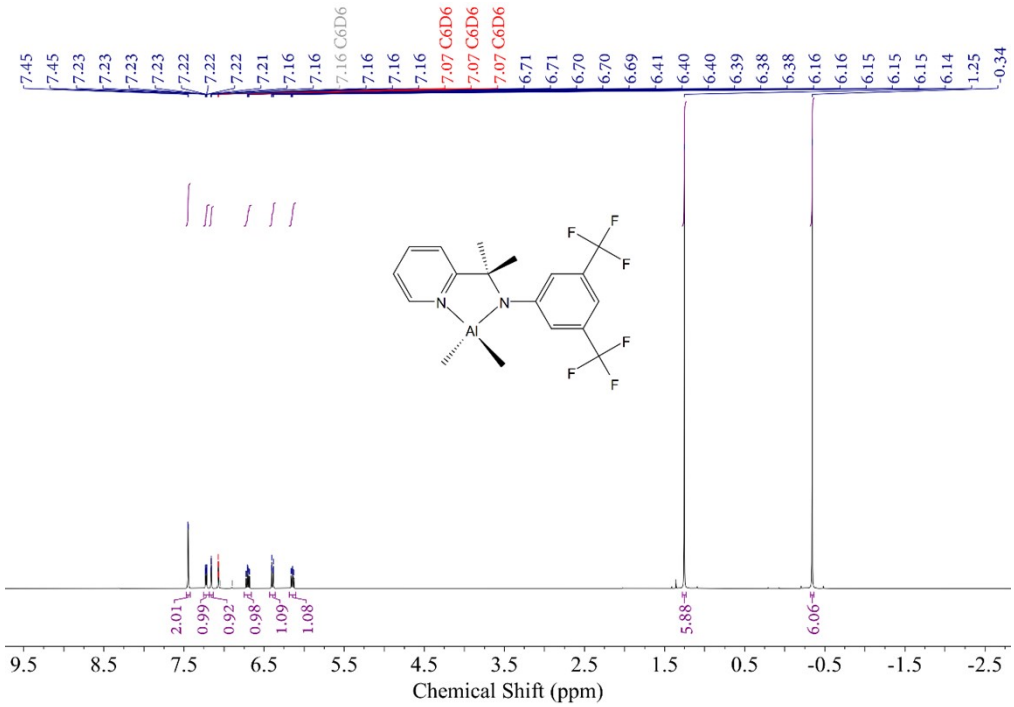

Figure S18 ^{1}H NMR spectrum of aluminum complex [pyridine-2-CMe_2N(3,5-$(CF_3)_2C_6H_3$)-κ^2N,N']$AlMe_2$ (**6a**).

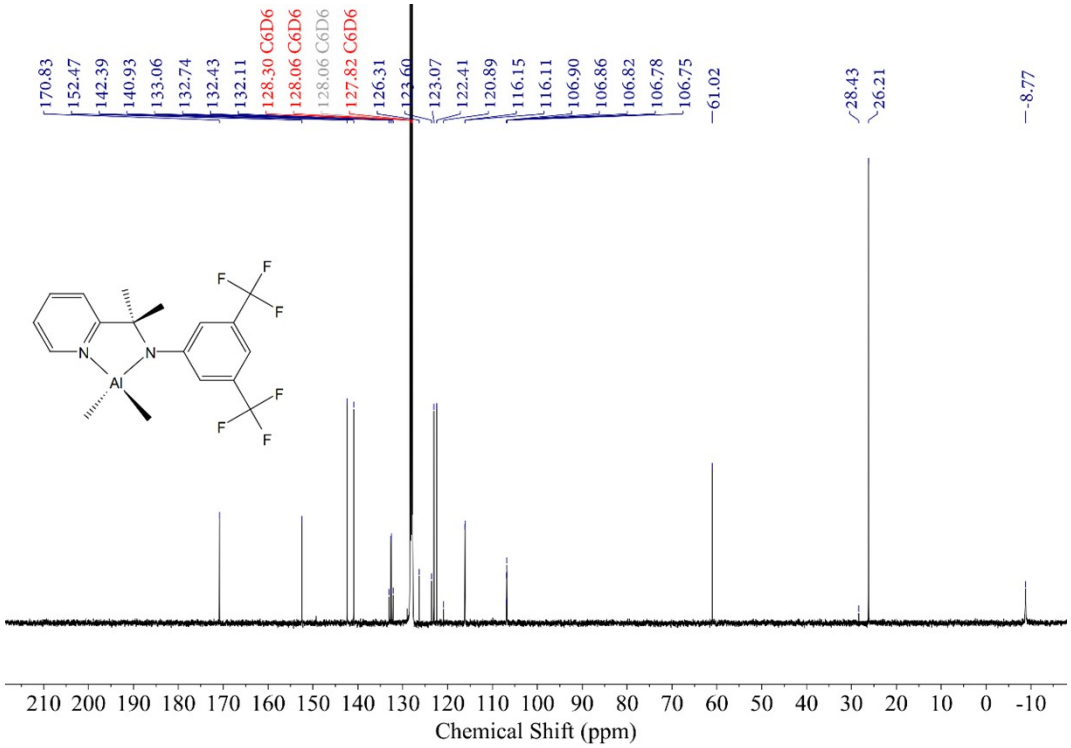

Figure S19 ^{13}C NMR spectrum of aluminum complex [pyridine-2-CMe_2N(3,5-$(CF_3)_2C_6H_3$)-κ^2N,N']$AlMe_2$ (**6a**).

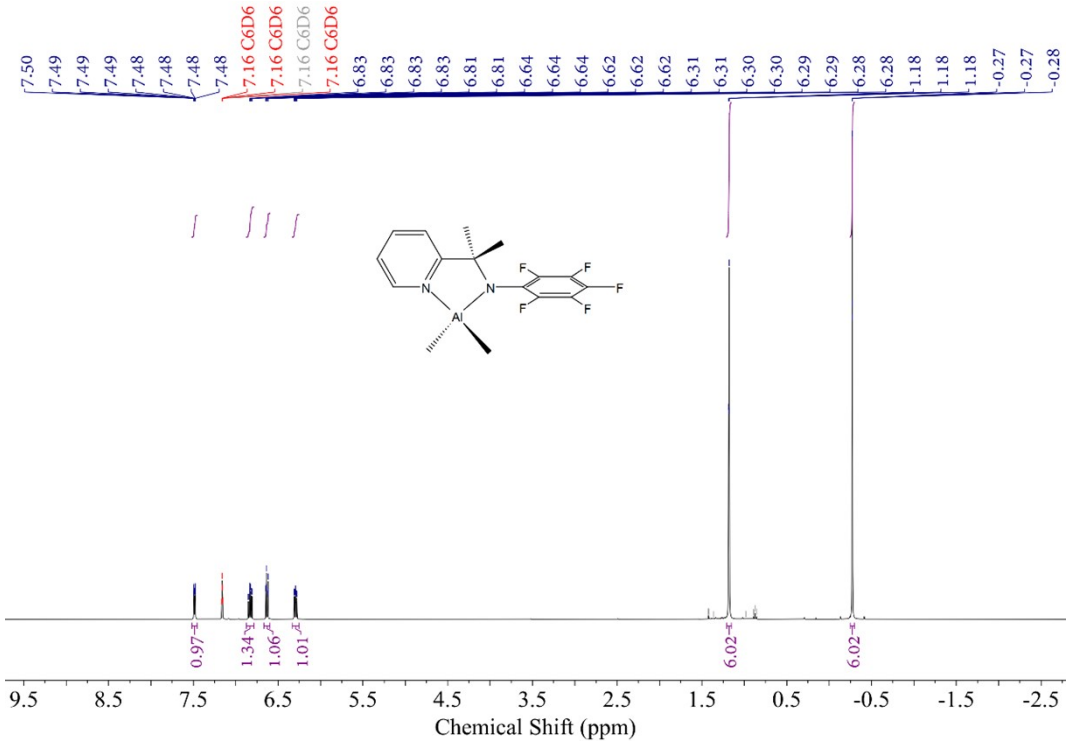

Figure S20 ^{1}H NMR spectrum of aluminum complex [pyridine-2-$CMe_2N(C_6F_5)$-κ^2N,N']$AlMe_2$ (**7a**).

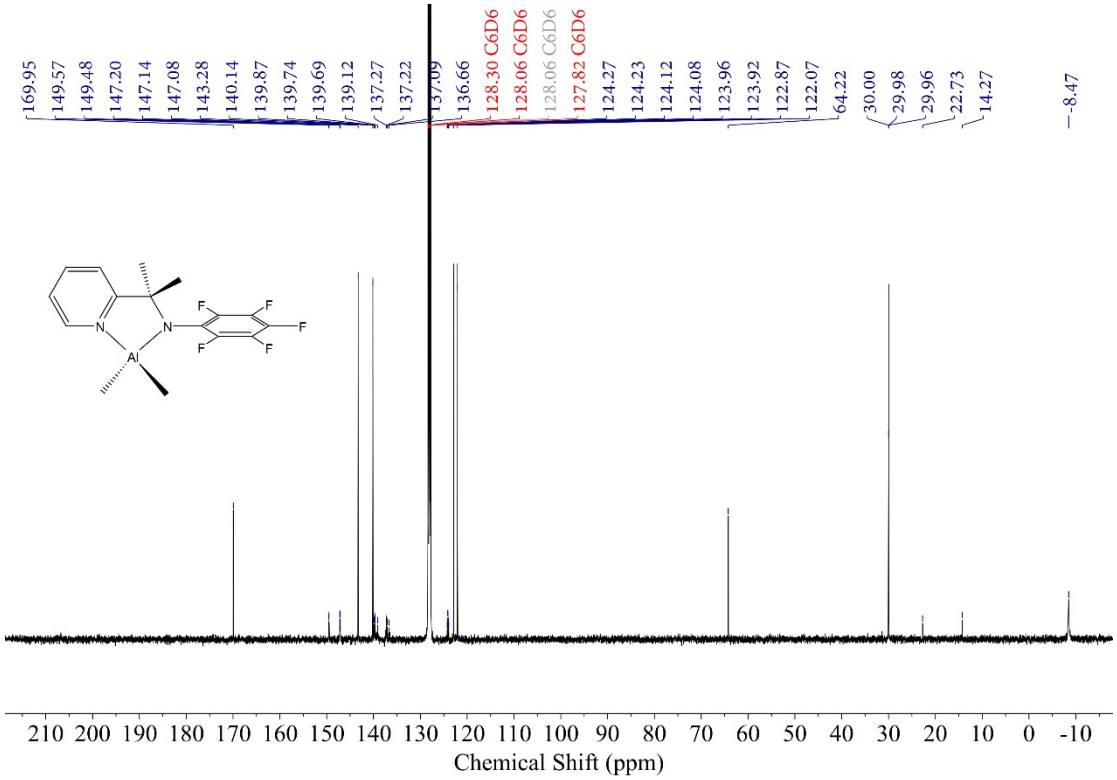

Figure S21 ^{13}C NMR spectrum of aluminum complex [pyridine-2-$CMe_2N(C_6F_5)$-κ^2N,N']$AlMe_2$ (**7a**).

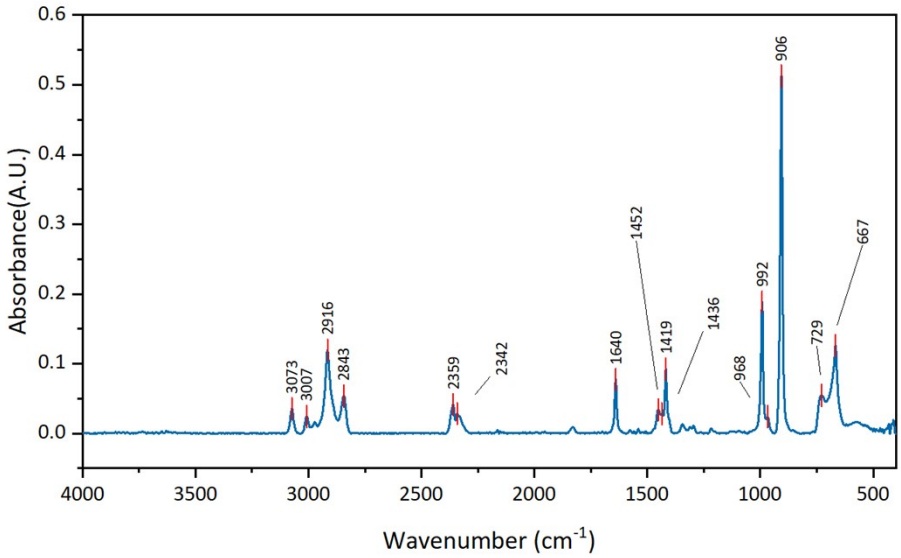

Figure S22. FTIR spectrum of polybutadiene (Table 1, entry 1).

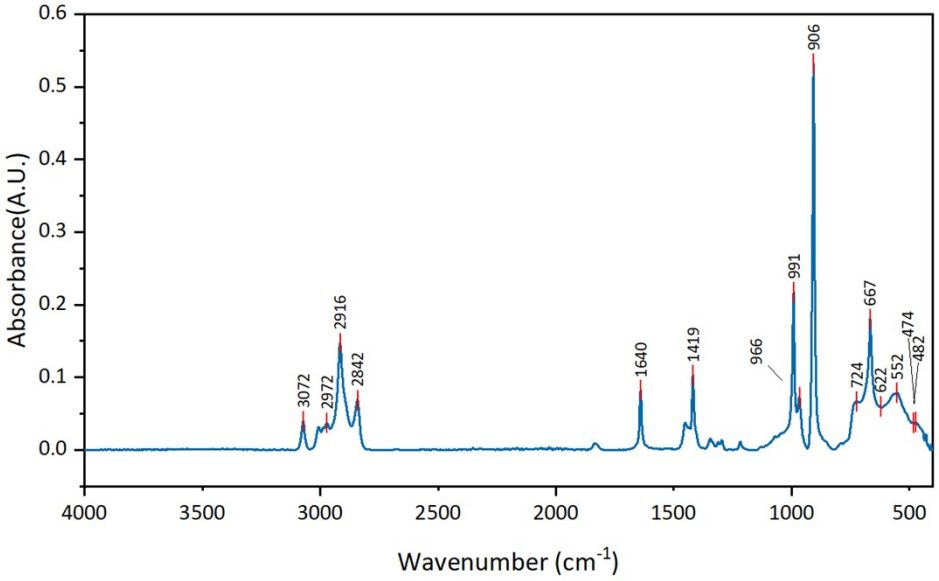

Figure S23. FTIR spectrum of polybutadiene (Table 1, entry 2).

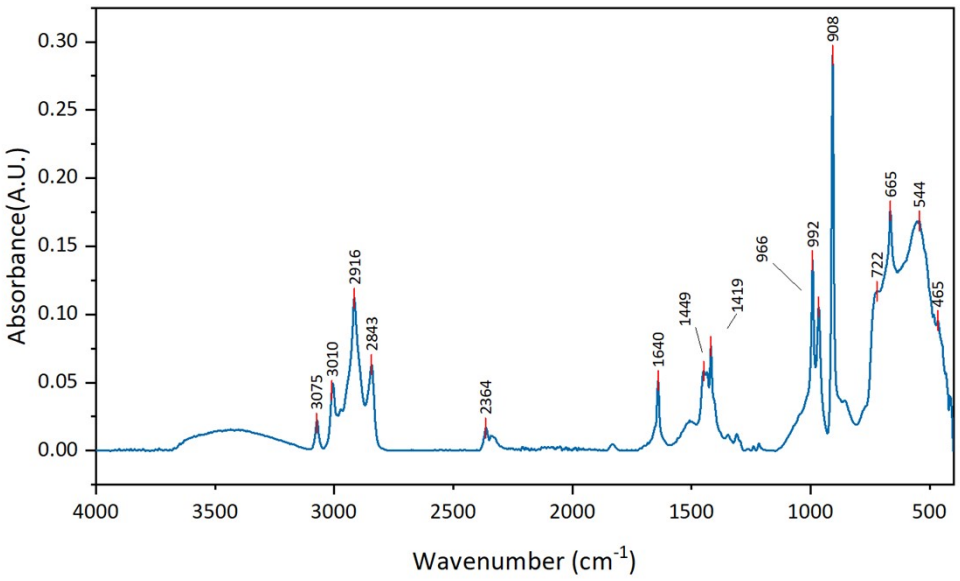

Figure S24. FTIR spectrum of polybutadiene (Table 1, entry 3).

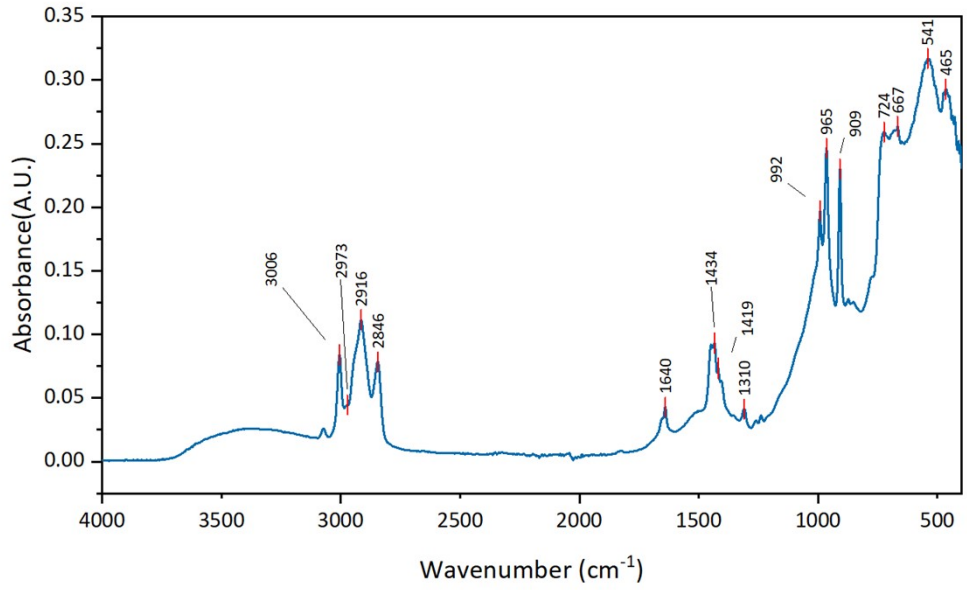

Figure S25. FTIR spectrum of polybutadiene (Table 1, entry 4).

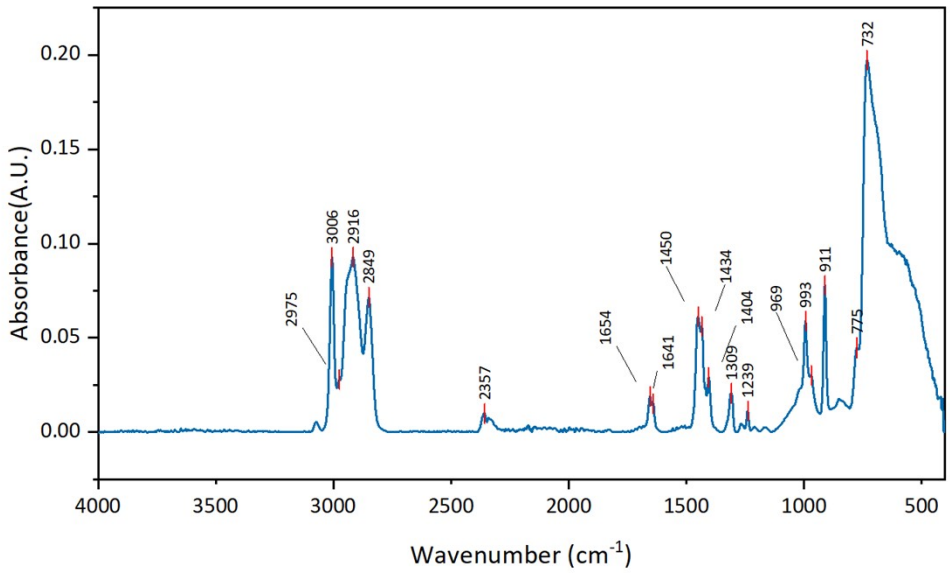

Figure S26. FTIR spectrum of polybutadiene (Table 1, entry 5).

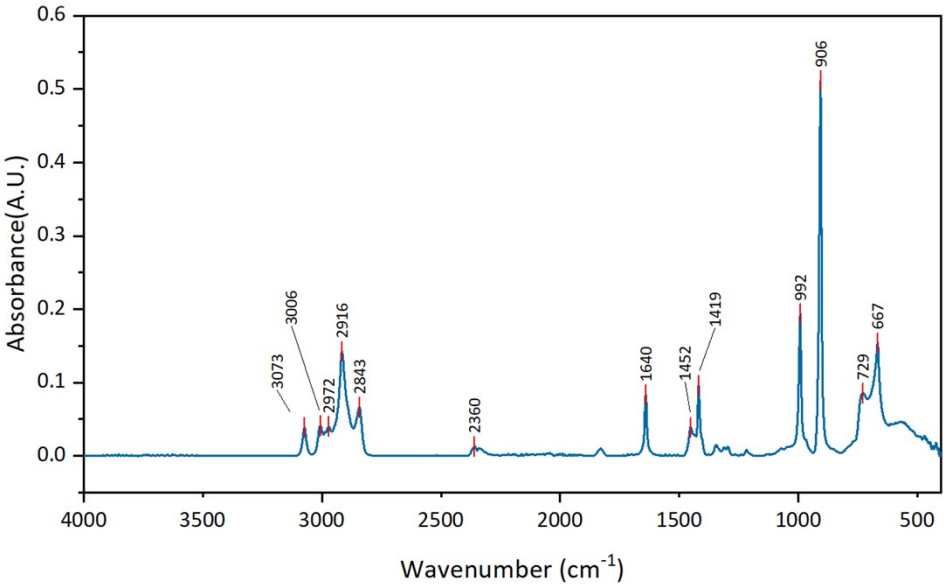

Figure S27. FTIR spectrum of polybutadiene (Table 1, entry 6).

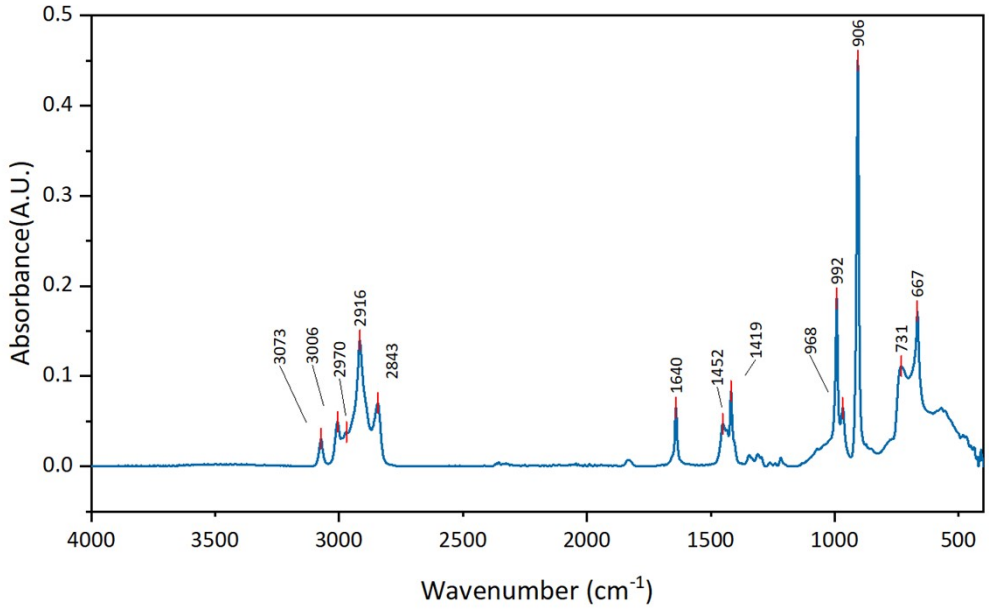

Figure S28. FTIR spectrum of polybutadiene (Table 1, entry 7).

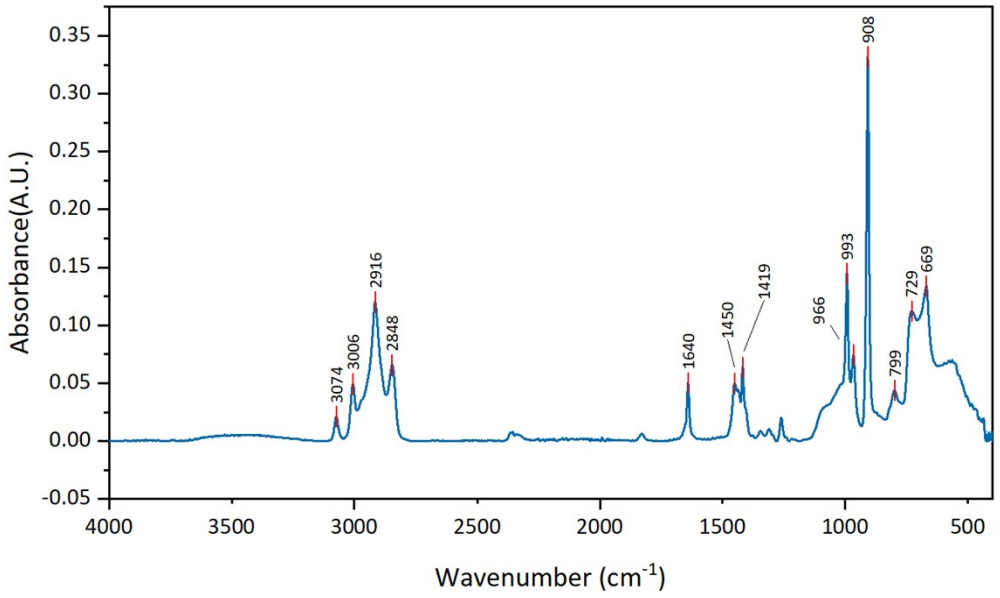

Figure S29. FTIR spectrum of polybutadiene (Table 1, entry 8).

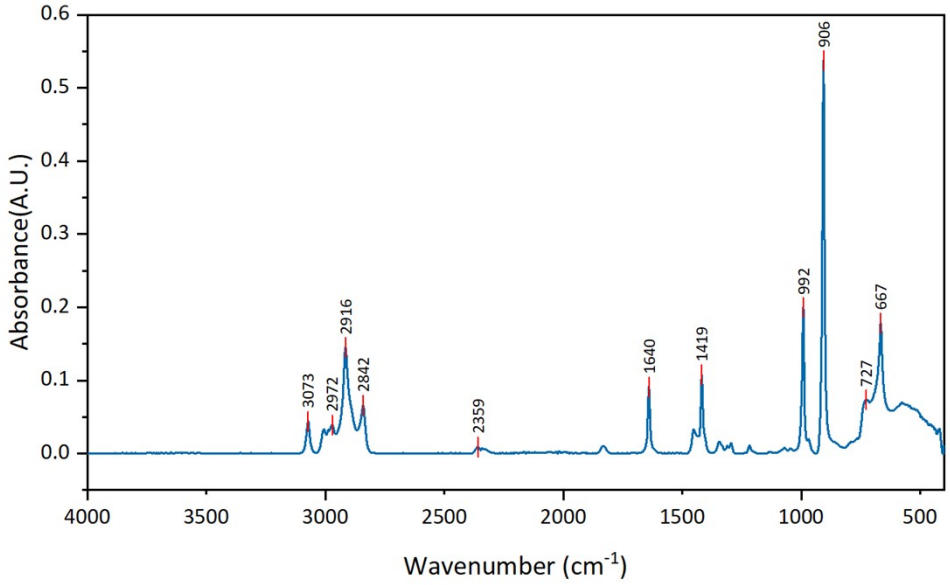

Figure S30. FTIR spectrum of polybutadiene (Table 2, entry 1).

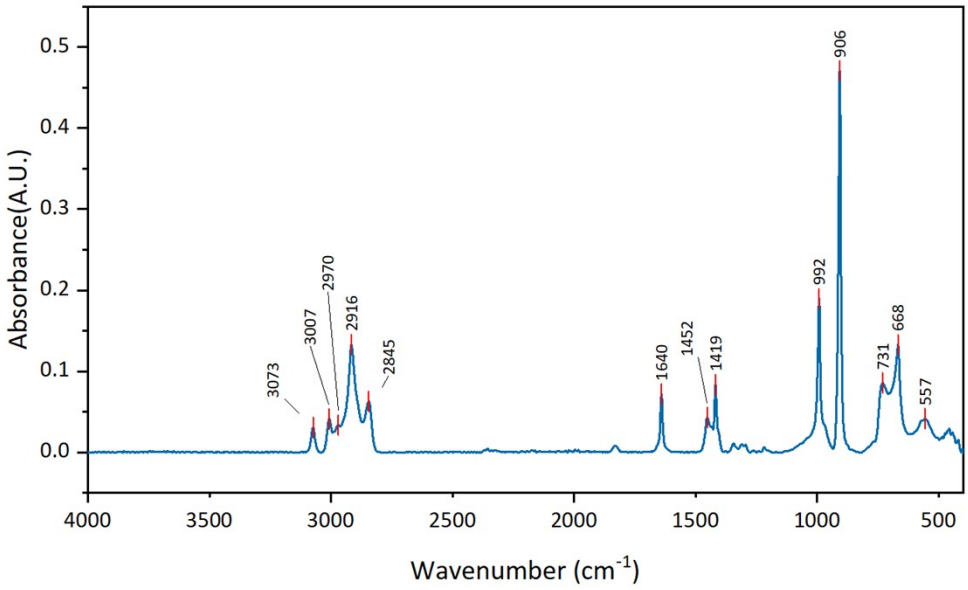

Figure S31. FTIR spectrum of polybutadiene (Table 2, entry 2).

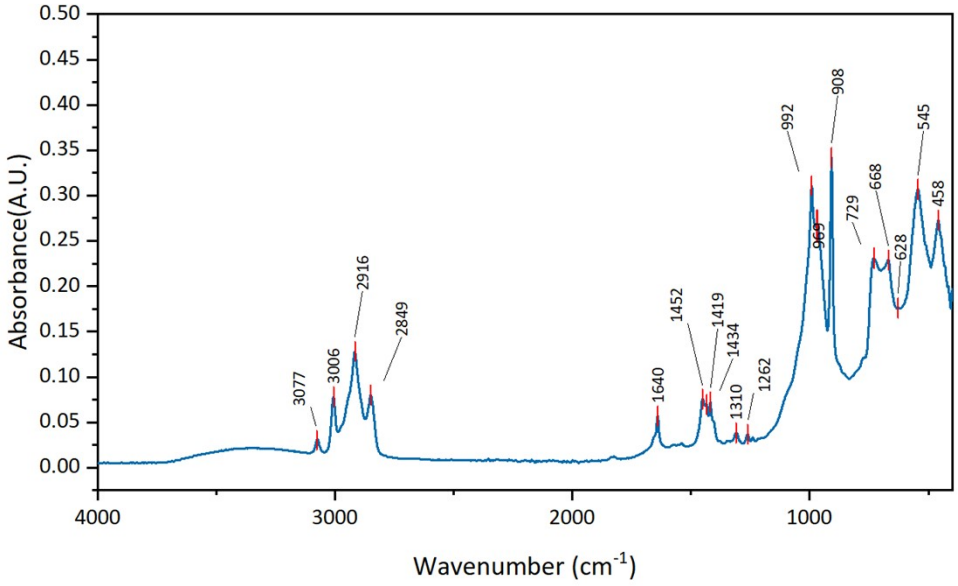

Figure S32. FTIR spectrum of polybutadiene (Table 2, entry 3).

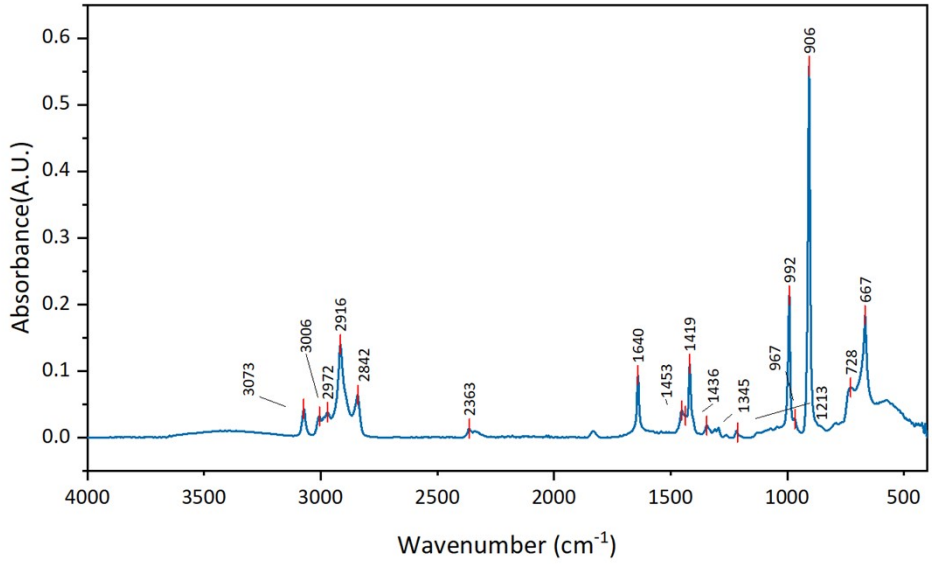

Figure S33. FTIR spectrum of polybutadiene (Table 2, entry 4).

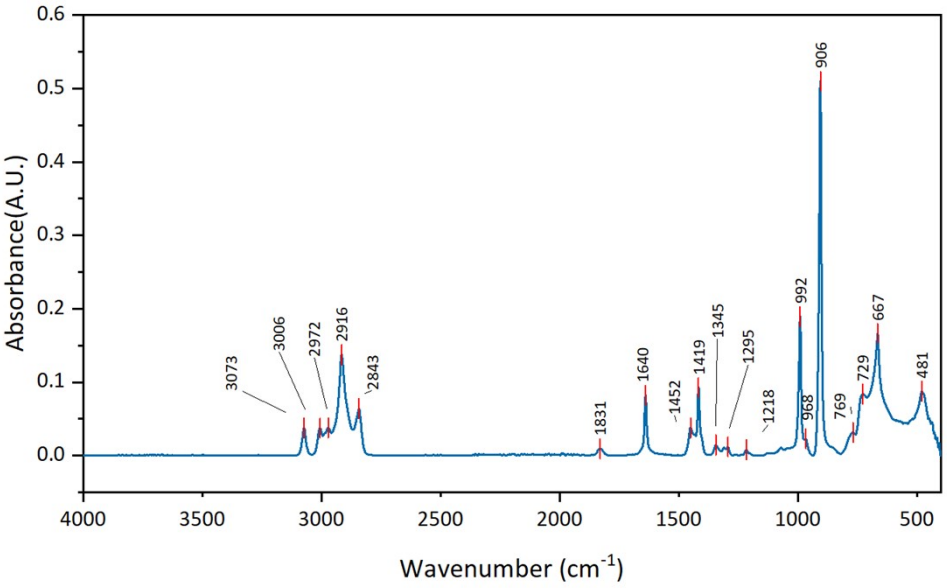

Figure S34. FTIR spectrum of polybutadiene (Table 2, entry 5).

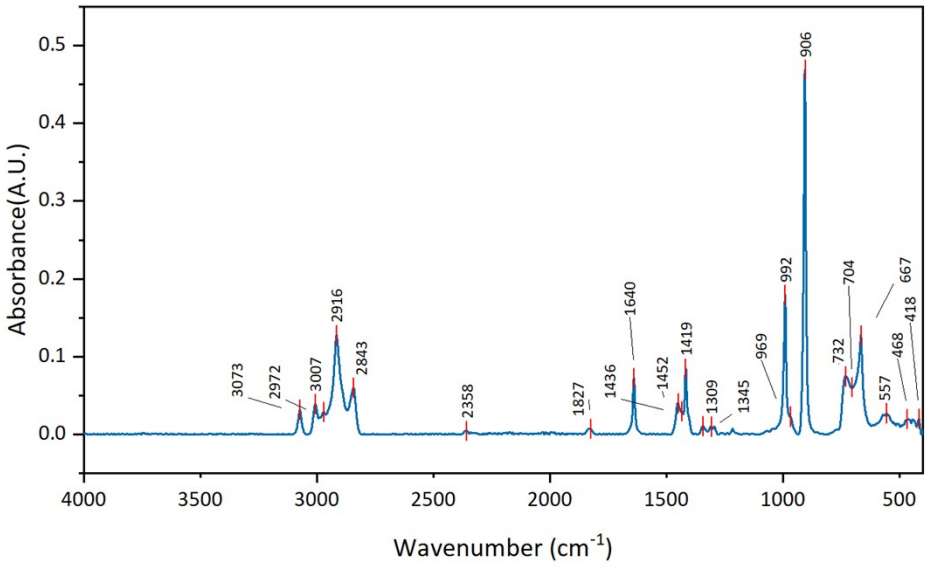

Figure S35. FTIR spectrum of polybutadiene (Table 2, entry 6).

Table S1. ICP-OES analysis data of the complex **7a**

elements	conc. (ppm)
Be	0.07
Na	74.26
Mg	50.05
K	91.05
Ca	58.70
Ti	2.37
V	0.09
Cr	2.22
Mn	0.06
Fe	22.72
Co	0.13
Ni	1.10
Cu	1.25
Zn	116.91
Ga	0.03
As	0.06
Se	1.31
Rb	0.02
Sr	1.08
Zr	0.03
Mo	0.30
Ag	0.22
Cd	0.05
Sn	0.13
Sb	0.11
Cs	0.00
Ba	2.89
Pb	0.21
Be	0.07

Table S2. Crystal data and structure refinement for Al complex **1a**.

entry	data
empirical formula	$C_{16}H_{21}AlN_2$
formula weight	268.33
CCDC number	2128578
temperature (K)	298.15
crystal system	monoclinic
space group	$P2_1/n$
a (Å)	8.3546(6)
b (Å)	10.7094(8)
c (Å)	17.5246(12)
α (°)	90
β (°)	97.6480(10)
γ (°)	90
volume (Å3)	1554.03(19)
Z	4
$\rho_{calcd.}$ (Mg m^{-3})	1.147
μ (mm^{-1})	0.120
F(000)	576.0
crystal size (mm)	0.21 × 0.2 × 0.19
2Θ range (°)	4.468 to 54.96
index ranges	$-10 \leq h \leq 10$, $-13 \leq k \leq 13$, $-22 \leq l \leq 22$
reflections collected	17321
independent reflections	3538 [R_{int} = 0.0398, R_{sigma} = 0.0403]
data/restraints/parameters	3538/0/176
goodness-of-fit on F^2	1.026
final R indexes [I>=2σ (I)]	R1 = 0.0461, wR2 = 0.1184
final R indexes [all data]	R1 = 0.0701, wR2 = 0.1302
largest diff. peak and hole (e^oA^{-3})	0.21/-0.23

Table S3. Crystal data and structure refinement for Al complex **3a**.

entry	data
empirical formula	$C_{18}H_{25}AlN_2$
formula weight	296.38
CCDC number	2175057
temperature (K)	298.15
crystal system	orthorhombic
space group	$P2_12_12_1$
a (Å)	8.8305(14)
b (Å)	12.0231(19)
c (Å)	16.870(3)
α (°)	90
β (°)	90
γ (°)	90
volume (Å3)	1791.1(5)
Z	4
$\rho_{calcd.}$ (Mg m^{-3})	1.099
μ (mm^{-1})	0.110
F(000)	640.0
crystal size (mm)	0.22 × 0.12 × 0.1
2Θ range (°)	4.16 to 55.06
index ranges	$-11 \leq h \leq 11$, $-15 \leq k \leq 15$, $-21 \leq l \leq 21$
reflections collected	20576
independent reflections	4005 [R_{int} = 0.1136, R_{sigma} = 0.1118]
data/restraints/parameters	4005/0/197
goodness-of-fit on F^2	1.002
final R indexes [I>=2σ (I)]	R1 = 0.0567, wR2 = 0.1001
final R indexes [all data]	R1 = 0.1579, wR2 = 0.1251
largest diff. peak and hole (e^oA^{-3})	0.14/-0.15
Flack parameter	0.4(2)

Table S4. Crystal data and structure refinement for Al complex **4a**.

entry	data
empirical formula	$C_{19}H_{27}AlN_2$
formula weight	310.40
CCDC number	2175058
temperature (K)	300.00
crystal system	orthorhombic
space group	$P2_12_12_1$
a (Å)	8.0744(4)
b (Å)	12.6305(8)
c (Å)	18.8429(11)
α (°)	90
β (°)	90
γ (°)	90
volume (Å3)	1921.67(19)
Z	4
$\rho_{calcd.}$ (Mg m^{-3})	1.073
μ (mm^{-1})	0.105
F(000)	672.0
crystal size (mm)	0.23 × 0.21 × 0.19
2Θ range (°)	5.394 to 57.652
index ranges	$-10 \le h \le 9$, $-16 \le k \le 16$, $-25 \le l \le 25$
reflections collected	64951
independent reflections	4863 [R_{int} = 0.0837, R_{sigma} = 0.0372]
data/restraints/parameters	4863/0/206
goodness-of-fit on F^2	1.030
final R indexes [I>=2σ (I)]	R1 = 0.0504, wR2 = 0.1168
final R indexes [all data]	R1 = 0.0853, wR2 = 0.1332
largest diff. peak and hole (e^oA^{-3})	0.18/-0.27
Flack parameter	0.00(5)

Table S5. Crystal data and structure refinement for Al complex **5a**.

entry	data
empirical formula	$C_{22}H_{33}AlN_2$
formula weight	352.48
CCDC number	2175059
temperature (K)	300.00
crystal system	monoclinic
space group	$P2_1/n$
a (Å)	8.6071(14)
b (Å)	16.636(3)
c (Å)	15.272(3)
α (°)	90
β (°)	91.136(6)
γ (°)	90
volume (Å3)	2186.3(6)
Z	4
$\rho_{calcd.}$ (Mg m^{-3})	1.071
μ (mm^{-1})	0.099
F(000)	768.0
crystal size (mm)	0.25 × 0.15 × 0.12
2Θ range (°)	5.33 to 49.996
index ranges	$-10 \leq h \leq 9$, $-19 \leq k \leq 19$, $-18 \leq l \leq 18$
reflections collected	28010
independent reflections	3801 [R_{int} = 0.1456, R_{sigma} = 0.0838]
data/restraints/parameters	3801/0/235
goodness-of-fit on F^2	1.055
final R indexes [I>=2σ (I)]	R1 = 0.0722, wR2 = 0.1730
final R indexes [all data]	R1 = 0.1409, wR2 = 0.2165
largest diff. peak and hole (e^oA^{-3})	0.20/-0.22

Table S6. Crystal data and structure refinement for Al complex **6a**.

entry	data
empirical formula	$C_{18}H_{19}AlF_6N_2$
formula weight	404.33
CCDC number	2175060
temperature (K)	298.15
crystal system	triclinic
space group	P1
a (Å)	8.5573(6)
b (Å)	8.8128(6)
c (Å)	13.3517(9)
α (°)	87.3090(10)
β (°)	77.9280(10)
γ (°)	89.4530(10)
volume (Å3)	983.55(12)
Z	2
$\rho_{calcd.}$ (Mg m^{-3})	1.365
μ (mm^{-1})	0.162
F(000)	416.0
crystal size (mm)	0.13 × 0.12 × 0.11
2Θ range (°)	3.122 to 57.45
index ranges	$-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-17 \leq l \leq 17$
reflections collected	11894
independent reflections	4690 [R_{int} = 0.0266, R_{sigma} = 0.0348]
data/restraints/parameters	4690/186/304
goodness-of-fit on F^2	1.034
final R indexes [I>=2σ (I)]	R1 = 0.0503, wR2 = 0.1280
final R indexes [all data]	R1 = 0.0801, wR2 = 0.1431
largest diff. peak and hole (e^oA^{-3})	0.20/-0.21

Table S7. Crystal data and structure refinement for Al complex **7a**.

entry	data
empirical formula	$C_{16}H_{16}AlF_5N_2$
formula weight	358.29
CCDC number	2175061
temperature (K)	298.15
crystal system	monoclinic
space group	$P2_1/n$
a (Å)	14.4175(13)
b (Å)	8.7391(8)
c (Å)	14.9864(13)
α (°)	90
β (°)	110.1920(10)
γ (°)	90
volume (Å3)	1772.2(3)
Z	4
$\rho_{calcd.}$ (Mg m^{-3})	1.343
μ (mm^{-1})	0.162
F(000)	736.0
crystal size (mm)	0.2 × 0.17 × 0.15
	MoKα (λ = 0.71073)
2Θ range (°)	3.38 to 55.01
index ranges	-18 ≤ h ≤ 18, -11 ≤ k ≤ 11, -19 ≤ l ≤ 19
reflections collected	20204
independent reflections	4069 [R_{int} = 0.0332, R_{sigma} = 0.0310]
data/restraints/parameters	4069/0/221
goodness-of-fit on F^2	1.038
final R indexes [I>=2σ (I)]	R1 = 0.0518, wR2 = 0.1396
final R indexes [all data]	R1 = 0.0835, wR2 = 0.1584
largest diff. peak and hole (e^oA^{-3})	0.23/-0.23

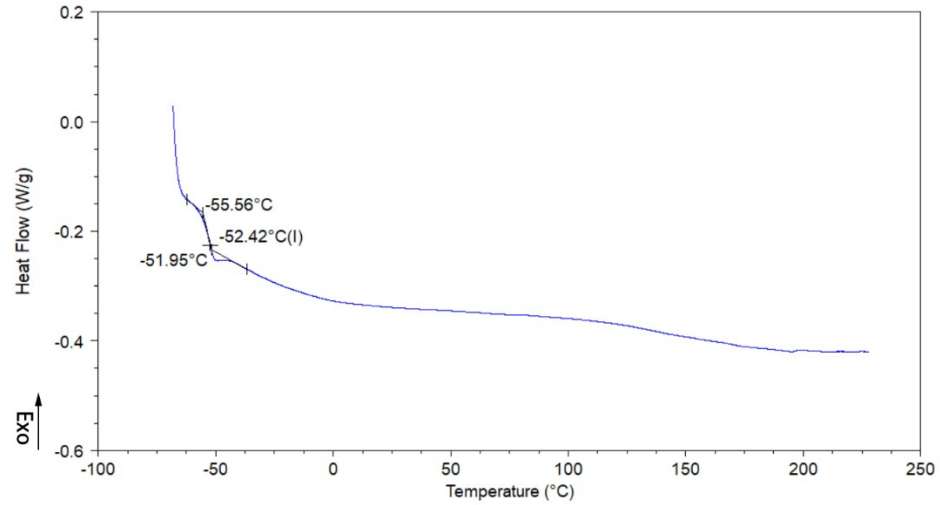

Figure S36. DSC curve of polybutadiene (Table 1, entry 1).

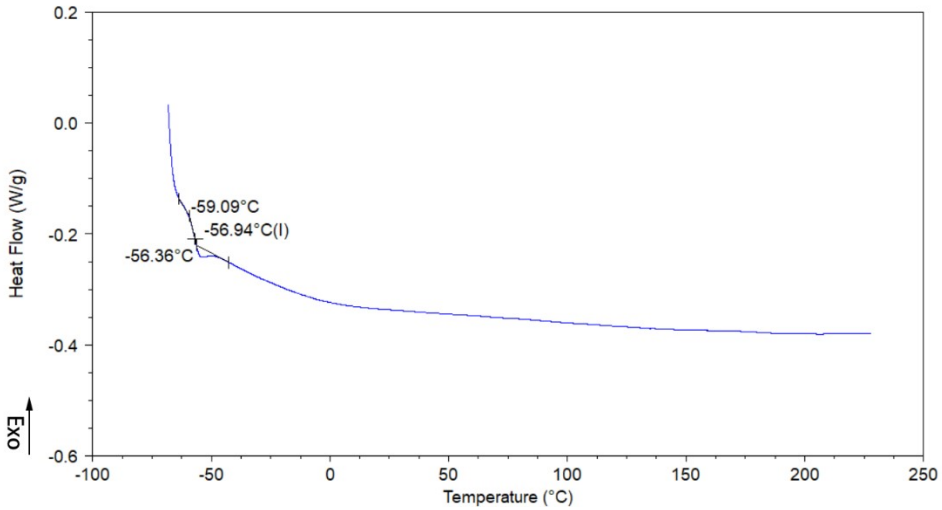

Figure S37. DSC curve of polybutadiene (Table 1, entry 2).

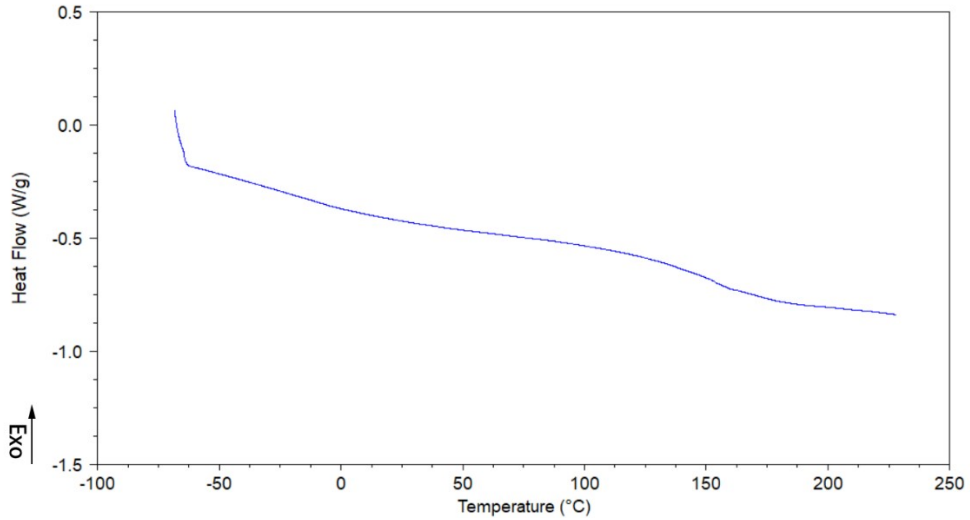

Figure S38. DSC curve of polybutadiene (Table 1, entry 3).

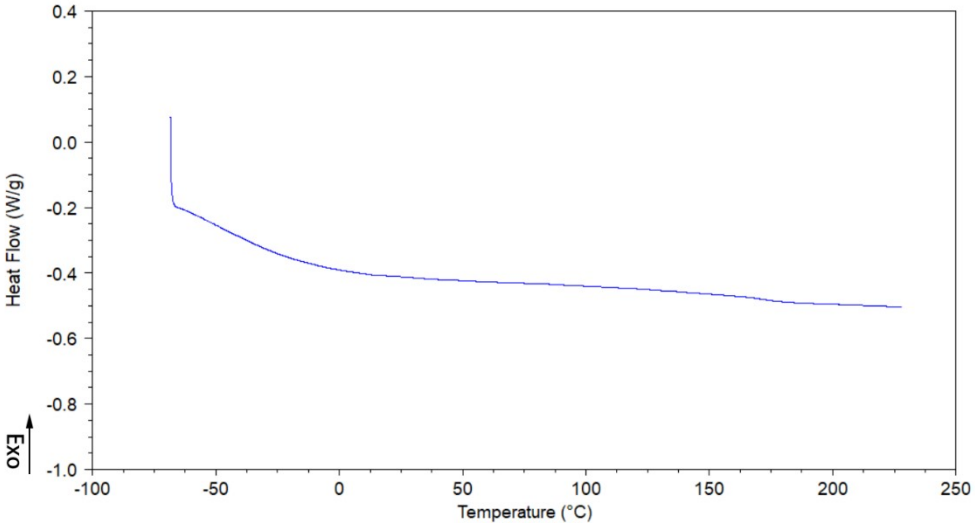

Figure S39. DSC curve of polybutadiene (Table 1, entry 5).

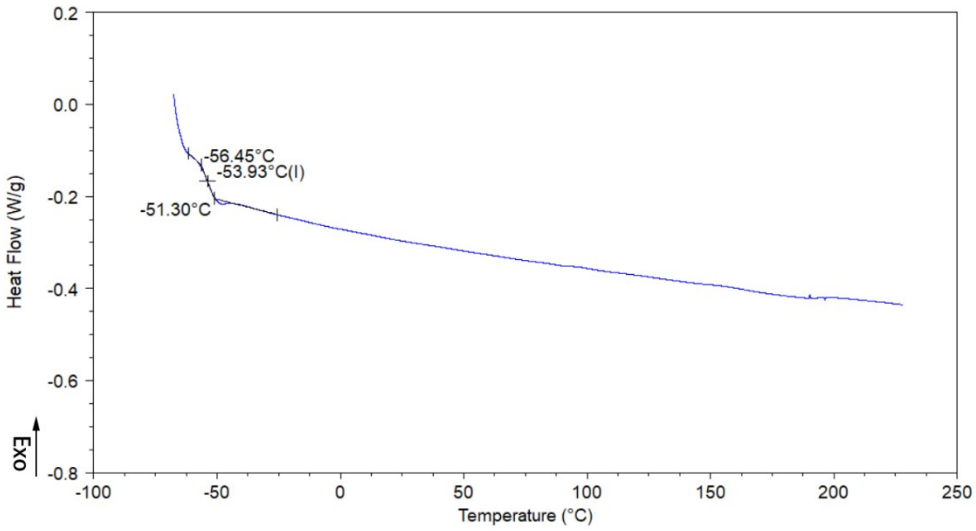

Figure S40. DSC curve of polybutadiene (Table 1, entry 6).

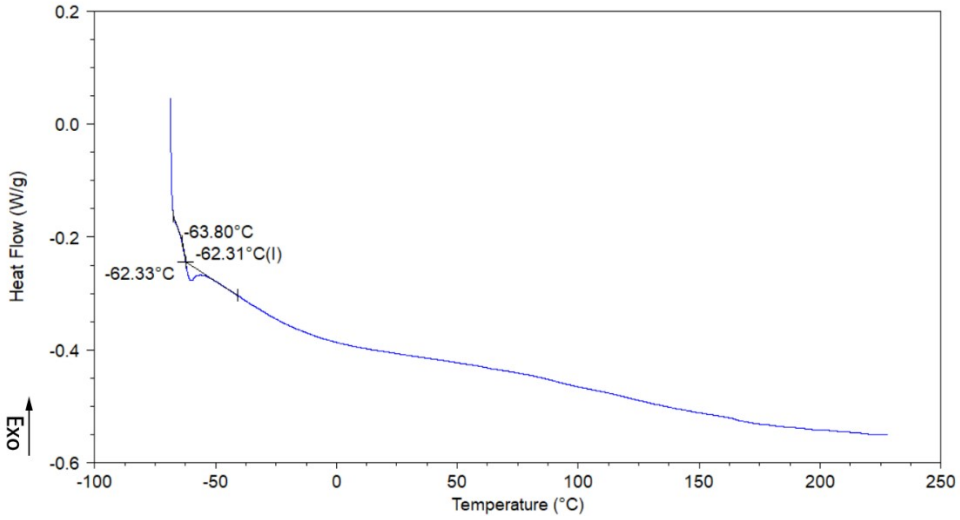

Figure S41. DSC curve of polybutadiene (Table 1, entry 7).

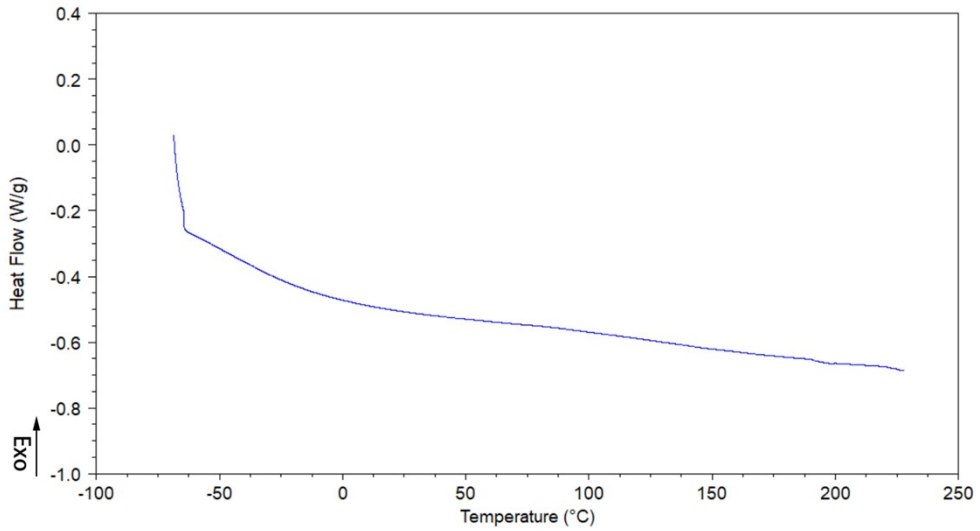

Figure S42. DSC curve of polybutadiene (Table 1, entry 8).

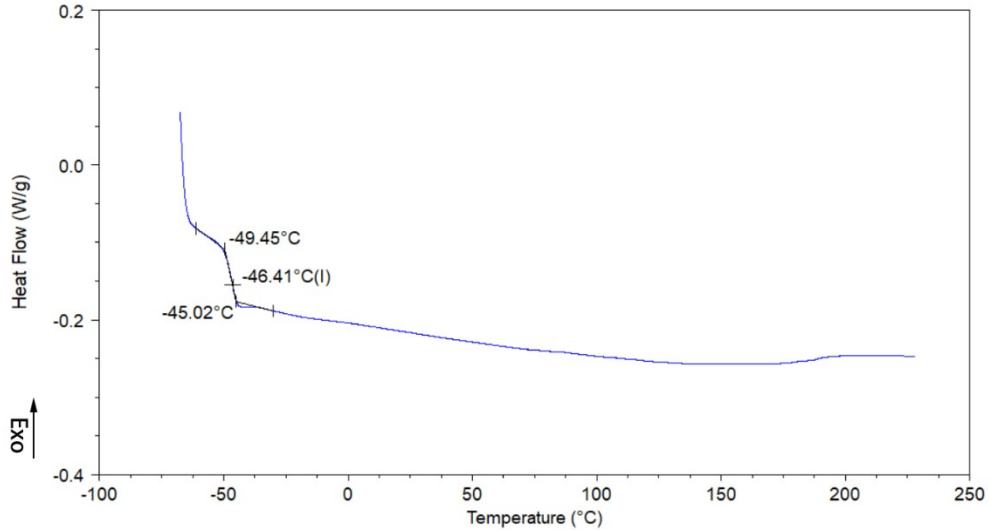

Figure S43. DSC curve of polybutadiene (Table 2, entry 1).

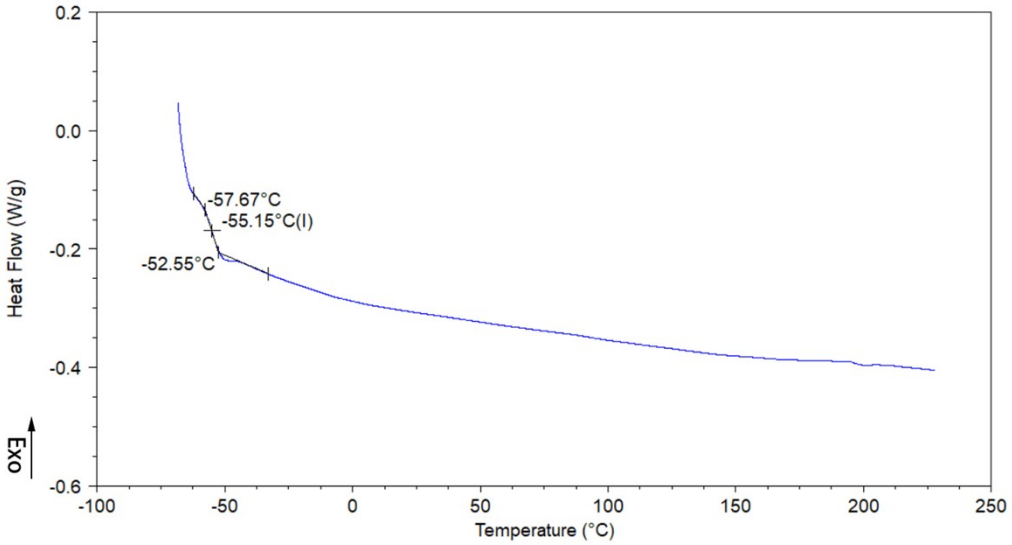

Figure S44. DSC curve of polybutadiene (Table 2, entry 2).

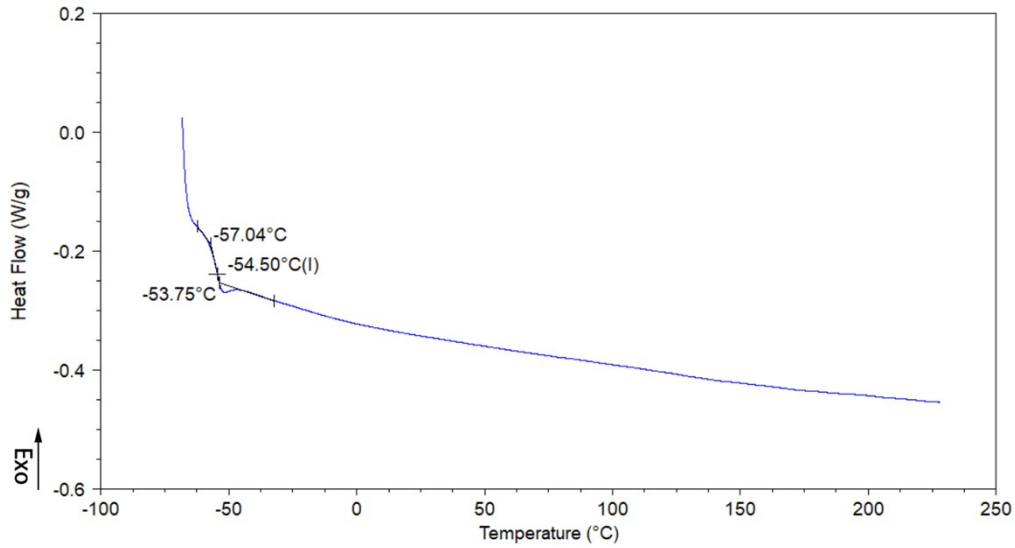

Figure S45. DSC curve of polybutadiene (Table 2, entry 4).

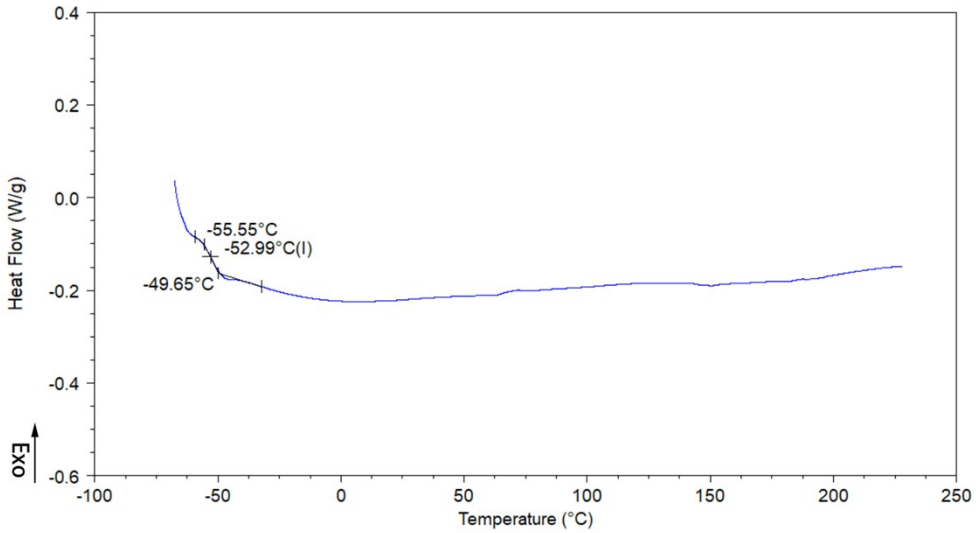

Figure S46. DSC curve of polybutadiene (Table 2, entry 5).

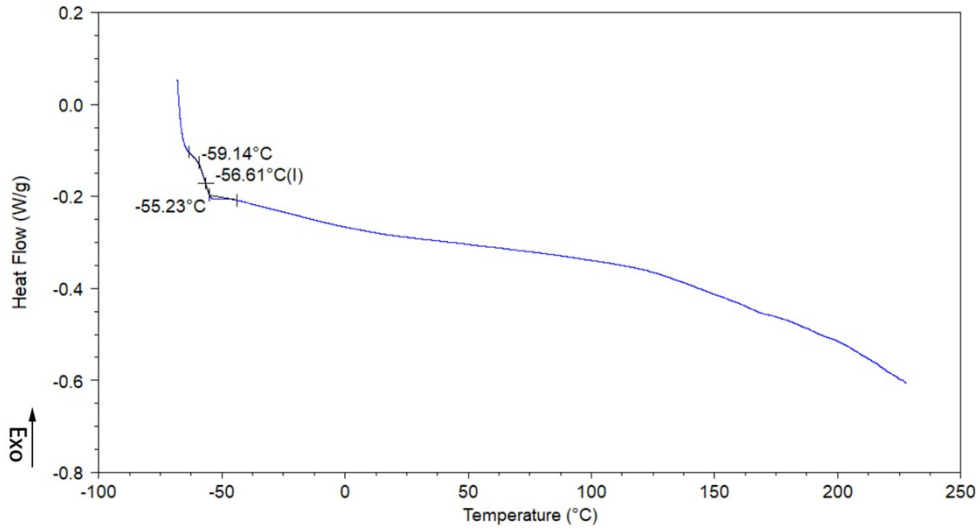

Figure S47. DSC curve of polybutadiene (Table 2, entry 6).

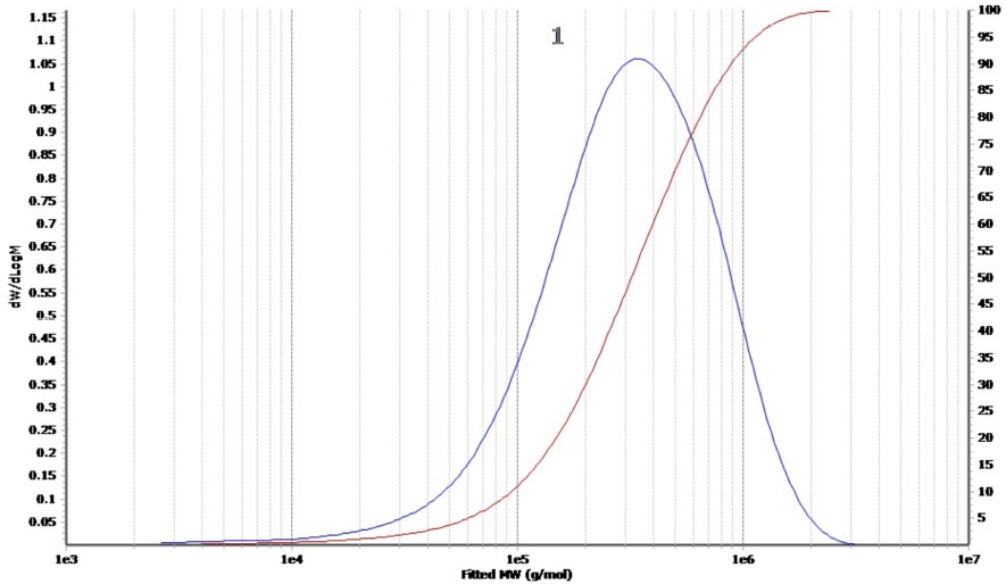

Figure S48. GPC curve of polybutadiene (Table 1, entry 1).

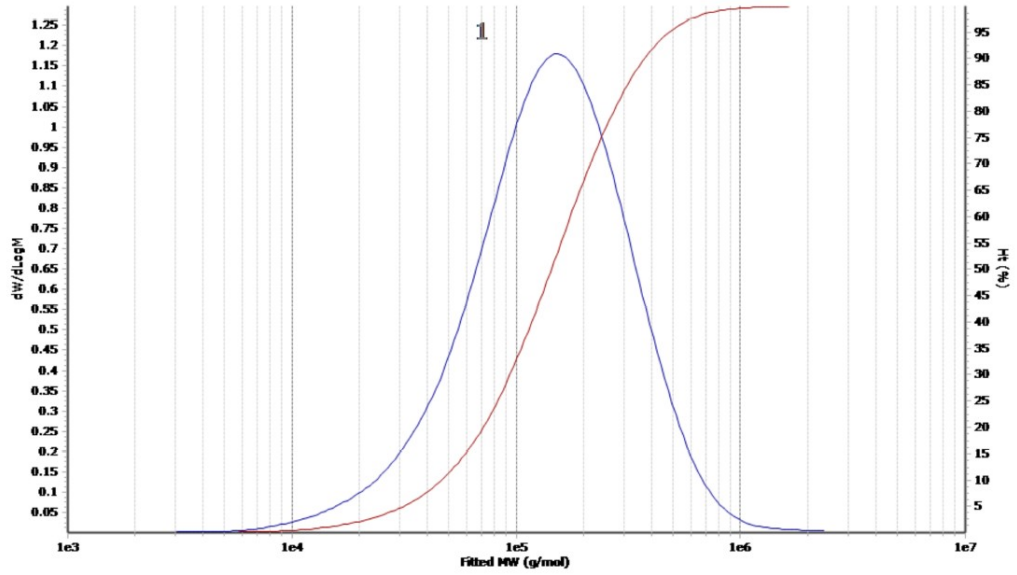

Figure S49. GPC curve of polybutadiene (Table 1, entry 2).

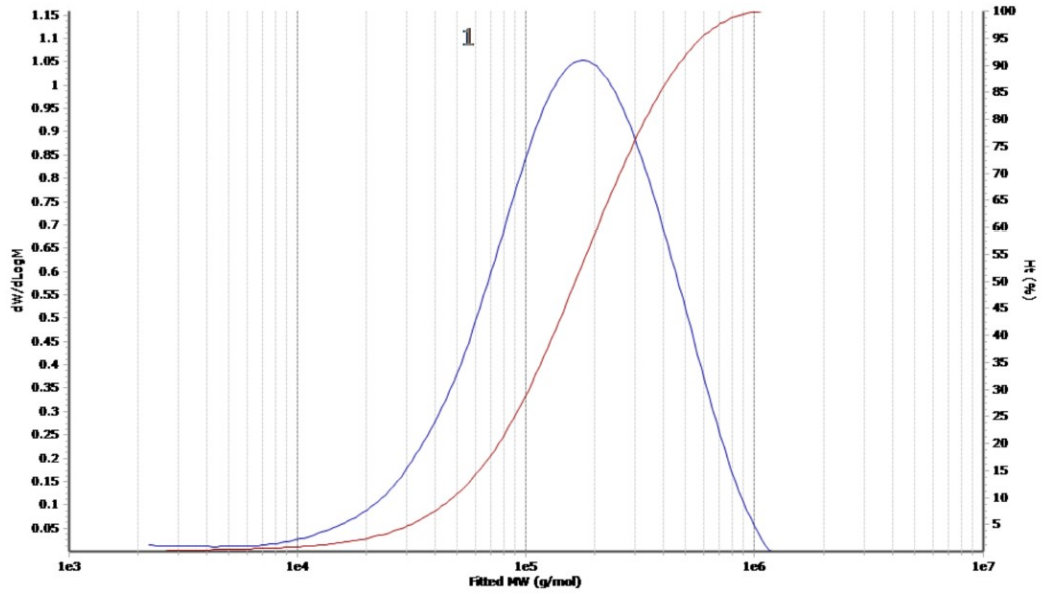

Figure S50. GPC curve of polybutadiene (Table 1, entry 3).

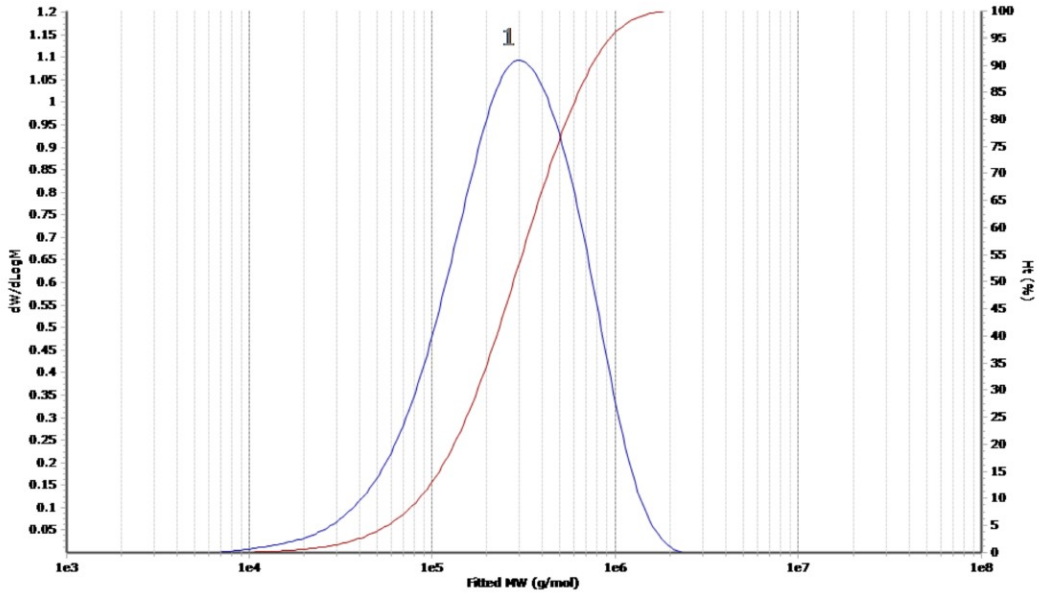

Figure S51. GPC curve of polybutadiene (Table 1, entry 5).

Table S8. Selected Average Interatomic Distances (Å) and Selected Average Angles (deg) for Al Complexes **1a, 3a, 4a, 5a, 6a, and 7a**.

	1a	**3a**	**4a**	**5a**	**6a**	**7a**
Al-N1	1.9560(15)	1.959(3)	1.991(3)	1.957(3)	1.9510(15)	1.970(2)
Al-N2	1.8634(14)	1.831(3)	1.848(2)	1.830(3)	1.8687(15)	1.8394(16)
Al-C_{Me1}	1.960(2)	1.963(4)	1.965(4)	1.972(4)	1.949(2)	1.959(3)
Al-C_{Me2}	1.961(2)	1.967(4)	1.974(4)	1.963(5)	1.949(2)	1.952(3)
N1−Al1−N2	84.98(6)	84.94(14)	84.48(11)	85.56(13)	84.95(6)	83.81(8)
C_{Me1}−Al1−C_{Me2}	117.11(10)	112.8(2)	112.8(2)	110.8(2)	116.85(11)	116.18(15)
Dihedral angles of two aromatic ring planes	1.235	91.803	79.854	89.143	166.121	89.304