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Synthesis, characterization and catalytic studies of aluminium complexes containing sulfonamido–oxazolinate or –pyrazolinate ligands

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ABSTRACT

A series of sulfonamido–oxazolinate ligand precursors, **HNSO$_2$Ph^{H}Oxa**, **HNSO$_2$Ph^{Me}Oxa**, **HNSO$_2$Ph-^{TriMe}Oxa**, or sulfonamido–pyrazolinate ligand precursors, **HNSO$_2$Ph^{H}Pz^H**, **HNSO$_2$Ph^{Me}Pz^H**, **HNSO$_2$Ph-^{TriMe}Pz^H**, **HNSO$_2$Ph^{F}Pz^H**, **HNSO$_2$Ph^{H}Pz^{Me}**, **HNSO$_2$Ph^{Me}Pz^{Me}**, **HNSO$_2$Ph^{TriMe}Pz^{Me}**, have been prepared. Treatment of ligand precursors, HNSO$_2$Ph^{A}Oxa or HNSO$_2$Ph^{A}Pz^B, with 1.1 equiv. of AlMe$_3$ in THF affords aluminium sulfonamido–oxazolinate dimethyl complexes, (NSO$_2$Ph^{A}Oxa)AlMe$_2$ [A = H (**1**); A = Me (**2**); A = TriMe, (**3**)], or aluminium sulfonamido–pyrazolinate dimethyl complexes, (NSO$_2$Ph^{A}Pz^B)AlMe$_2$ [A = H, B = H (**4**); A = Me, B = H (**5**); A = TriMe, B = H (**6**); A = F, B = H (**7**); A = H, B = Me (**8**); A = Me, B = Me (**9**); A = TriMe, B = Me (**10**)]. The aluminium bis(sulfonamido–pyrazolinate) methyl complex **5′** was isolated from recrystallization of **5** as minor product. The molecular structures of compounds **2**, **5′** and **8** were determined by single-crystal X-ray diffraction techniques. Their catalytic activities towards the ring opening polymerization of ε-caprolactone in the presence of benzyl alcohol are also under investigation.

1. Introduction

Aliphatic polyesters, prepared from various lactones and/or lactides, having the thermoplastic, biocompatible and biodegradable properties make them to be the leading candidates in biomedical and pharmaceutical industries [1–5]. The major synthesized method employed in industry to prepare these polyesters has been the ring opening polymerization (ROP) using well-defined metal complexes with auxiliary ligands. There is a number of excellent initiators/catalysts have been examined for the ROP during the past decade [6–14]. The main challenge in elaborating catalytic systems effective for ROP is the development of novel efficient metal catalysts to produce the polymers bearing the properties of precisely molecular weight, narrow polydispersity index (PDI), efficient rate and high enantio- or regio-selectivity under mild conditions. Among these studies, the metal complexes supported by sulfonate [15,16] or sulfonamido [18–23] anionic multidentate ligands have been a focus of interest, mainly due to their good catalytic activities for ROP of cyclic esters. The magnesium complexes bearing sulfonate phenolate ligands have been prepared and displayed efficient catalytic activities for ROP of ε-caprolactone, L-lactide or trimethyl carbonate by the Lin's and Ko's groups [15,16]. However, the reactivity of magnesium bis-adduct complexes derived from bis-phenolate ligands show only moderate activity in the ROP of L-lactide in the presence of additional alcohols [17]. The Lin's group also reported the aluminium complexes containing sulfonamido/Schiff base ligand are efficient initiators for ROP of L-lactide in well-controlled fashion [19]. The Mountford's group reported that the metal complexes such as titanium [20], zirconium [20], aluminium [21] or indium [22], bearing tetradentate bis(sulfonamide)amino ligands also showed the well-controlled ROP of *rac*-lactide. Recently, some Group 1 metal complexes bearing cyclohexyl-backboned bis-sulfonamido ligand displayed the modest stereo-selectivity and well-controlled fashion for ROP of *rac*-lactide under lower temperature condition were reported by Lin's group [23].

In our previous reports, some zinc [24,25], aluminium [25] or magnesium [26] anilido–oxazolinate complexes, or aluminium anilido–pyrazolinate complexes [28] have shown their catalytic activities toward the ROP of ε-caprolactone or L-lactide. In view of the potential application of metal sulfonate or sulfonamido complexes in ROP, we are interested in exploring the catalytic behaviour of the metal complexes bearing related sulfonamido ligands derived from our previous works. On the other respect, the steric or

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electronic sulfonamides in general are attractive synthetic targets due to their relatively easy and simple preparation from the corresponding sulfonyl chlorides and related amines or anilines under mild conditions. Although aluminium complexes containing anionic multidentate ligands, such as β-diketiminates [29], anilido-iminates [30,31], amidinates [32,33] or phosphino-iminates [34,35], have been reported their catalytic activities for ROP of cyclic esters recently. However only few examples of aluminium complexes containing sulfonamido groups have been applied in ROP as initiators/catalysts [18,19,21]. Herein we report the synthesis and structures of aluminium complexes containing sulfonamido–oxazolinate or –pyrazolinate ligands. Their catalytic activities toward the ring opening polymerization of ε-caprolactone in the presence of benzyl alcohol are also examined.

2. Results and discussion

2.1. Preparations of sulfonamide ligand precursors

A series of sulfonamido–oxazolinate or –pyrazolinate ligand precursors [$HNSO_2Ph^ROxa$, Ph^R = phenyl (R = H), tolyl (R = Me) or mesityl (R = TriMe), $HNSO_2Ph^RPz^H$, Ph^R = phenyl (R = H), tolyl (R = Me), mesityl (R = TriMe) or 4-fluorophenyl (R = F) and $HNSO_2Ph^RPz^{Me}$, Ph^R = phenyl (R = H), tolyl (R = Me) or mesityl (R = TriMe)] were prepared by the reactions of 2-(4,4-dimethyl-4,5-dihydrooxazo-2-yl)-phenylamine, 1-(2-aminophenyl)pyrazole or 1-(3,5-dimethyl-2-aminophenyl)pyrazole with 1.1 molar equivalent of the corresponding substituted benzenesulfonyl chlorides and triethylamine in dichloromethane at room temperature, as shown in (Scheme 1). These ligand precursors were easily purified by column chromatography and afforded the satisfied yields. The N–H signals on ^1H NMR spectra for these ligand precursors were observed at the range of 12.29–12.56 ppm for oxazolinate sulfonamides and 8.68–10.10 ppm for pyrazolinate–sulfonamides. Since the NH of sulfonamides have been still reacted with excess sulfonyl chlorides in the presence of base to form bis-sulfonamides, the bis-pyrazole-sulfonamide by-product $N(SO_2Ph^R)_2Pz^H$ [Ph^R = phenyl (R = H), tolyl (R = Me) or 4-fluorophenyl (R = F)] could also be observed and collected with 7–17% isolated yields upon preparing the target compounds of $HNSO_2Ph^RPz^H$ [Ph^R = phenyl (R = H), tolyl (R = Me) or 4-fluorophenyl (R = F)], as shown in (Scheme S1). All of these sulfonamido ligand precursors and some bis-sulfonamides

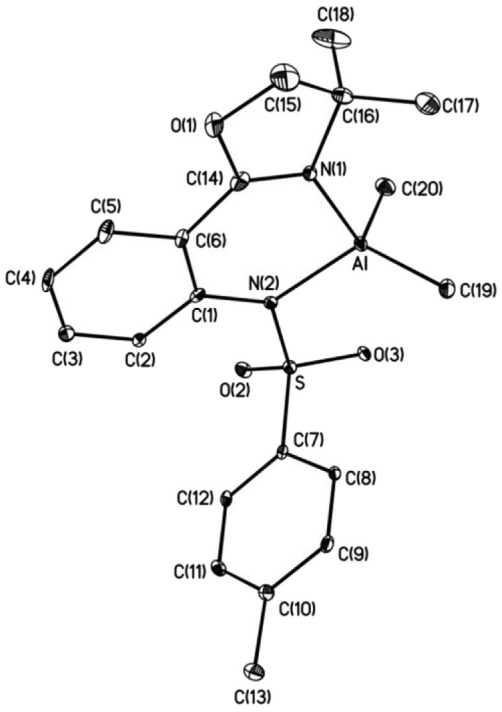
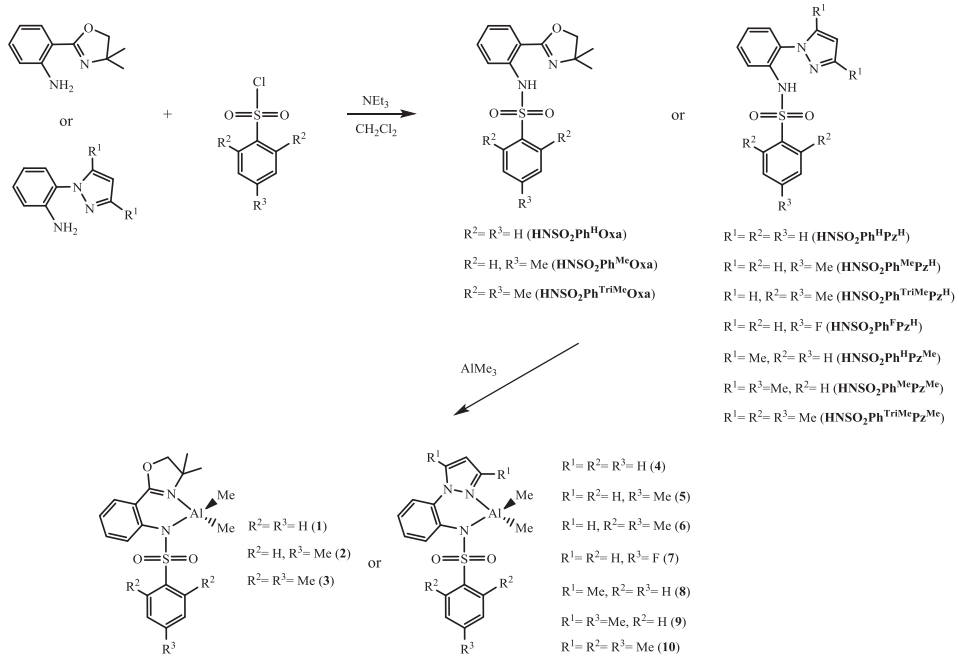


Fig. 1. Molecular structure of one of the crystallographically independent molecules of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al–N(1), 1.961(3); Al–N(2), 1.948(3); Al–C(19), 1.961(4); Al–C(20), 1.955(4); S–O(2), 1.435(3); S–O(3), 1.439(3); S–N(2), 1.635(3); S–C(7), 1.763(4); N(1)–C(14), 1.292(5); N(2)–C(1), 1.416(5); C(1)–C(6), 1.411(5); C(6)–C(14), 1.452(5); N(1)–Al–N(2), 90.69(13); C(19)–Al–C(20), 116.63(19); N(2)–Al–C(19), 117.22(15); N(2)–Al–C(20), 115.55(17); N(1)–Al–C(19), 105.29(16); N(1)–Al–C(20), 106.59(16); O(2)–S–O(3), 117.86(16); N(2)–S–C(7), 107.40(16).



Scheme 1. Preparation of ligand precursors and complexes **1**–**10**.

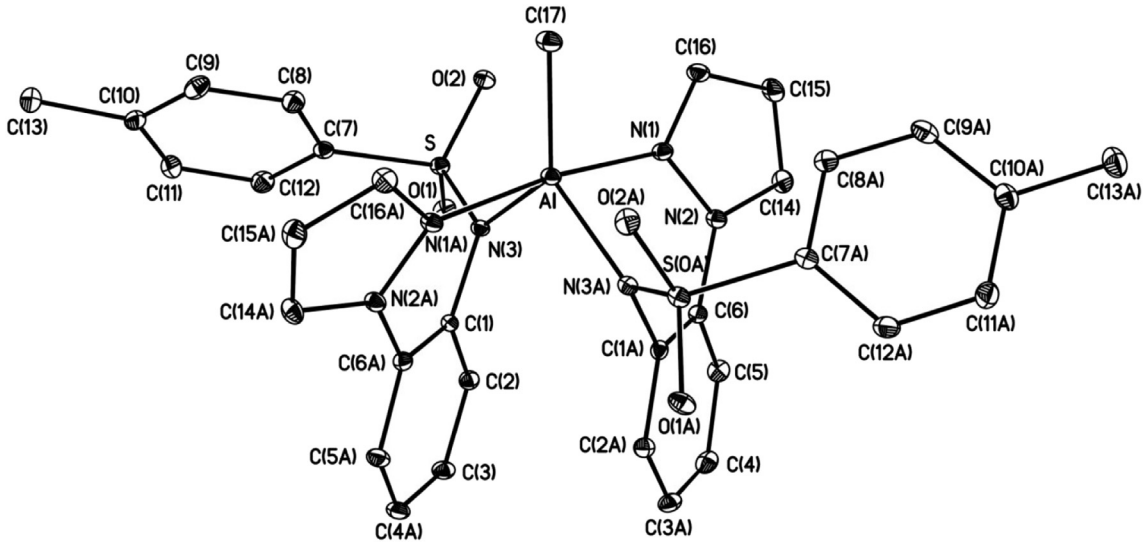


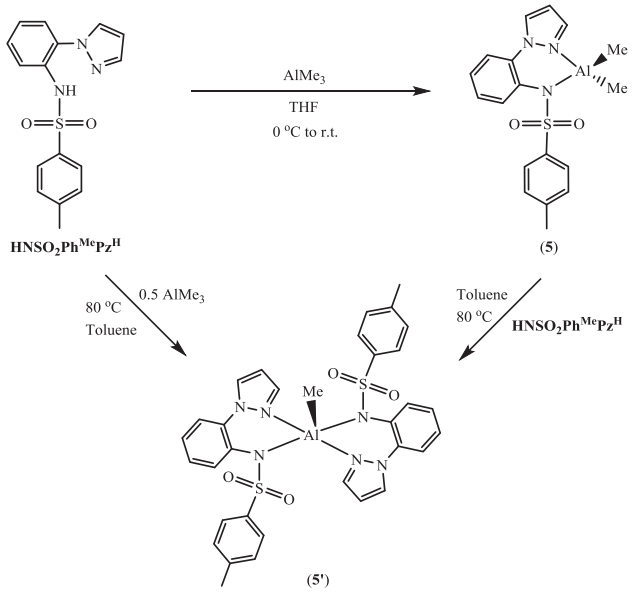
Fig. 2. Molecular structure of complex **5′**. Hydrogen atoms on carbon atoms omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al–C(17), 1.963(4); Al–N(1), 2.0859(19); Al–N(3), 1.922(2); Al–N(1A), 2.0859(19); Al–N(3A), 1.922(2); S–O(1), 1.4434(17); S–O(2), 1.4472(17); S–N(3), 1.6090(19); S–C(7), 1.770(2); N(1)–Al–N(1A), 172.28(12); N(1)–Al–N(3), 91.03(8); N(1)–Al–N(3A), 84.15(8); N(3)–Al–N(3A), 102.78(12); C(17)–Al–N(1), 93.86(6); C(17)–Al–N(3), 128.61(6); O(2)–S–O(3), 117.71(10); N(3)–S–C(7), 105.99(10).

were characterized by NMR spectroscopy as well as elemental analysis. The suitable crystals for the structural refinement of pyrazole bis-sulfonamide $N(SO_2Ph^F)_2Pz^H$ were isolated from concentrated dichloromethane solution, and the molecular structure was depicted in Fig. S1.

Treatment of ten oxazolinate- or pyrazolinate-based sulfonamido ligand precursors with 1.1 molar equivalent of $AlMe_3$ by alkane elimination in THF at room temperature for 1 h affords the desired aluminium dimethyl complexes **1**–**10** in moderate yields respectively. The disappearance of the N–H signal of sulfonamide and the appearance of the resonance for protons of methyl groups in the high-field region are consistent with the structures proposed in (Scheme 1). Due to the symmetric environment around the metal centre, one singlet corresponding to two methyl groups on the metal centre was observed in each case for these aluminium complexes. The ^{27}Al chemical shifts for di-alkyl complexes **1**–**10** appearing around the range of 103.8–142.0 ppm are within the expected region for a four-coordinate aluminium species in solution (*ca.* 60–180 ppm) [36], especially for our previous work {102.1–146.8 ppm for anilido–oxazolinate aluminium complexes [37] and 145.2–145.5 ppm for anilido–pyrazolinate aluminium complexes [28]}. Complexes **1**–**10** were all characterized by NMR spectroscopy as well as elemental analyses. However, attempts to synthesize related aluminium complexes containing alkoxide group (*i.e.* benzoxide or isopropoxide) have been proved unsuccessful.

Suitable crystals for structure determination of **2** were obtained from dichloromethane/hexane solution. The molecular structure is depicted in Fig. 1. The structure of **2** demonstrates a mononuclear form and the aluminium centre adopts a distorted tetrahedral geometry with the metal centre coordinated by two methyl groups and two nitrogen donor atoms of the oxazolinate and sulfonamido groups. The difference between $Al–N_{oxazoline}$ [Al–N(1) = 1.961(3) Å] and $Al–N_{sulfonamide}$ [Al–N(2) = 1.948(3) Å] bond distances might result from the π-donation ability of the anionic amido nitrogen [25,28,30,38,39]. The bond distance of $Al–N_{oxazoline}$ and the angle of $N_{oxazoline}–Al–N_{sulfonamide}$ and $C_{methyl}–Al–C_{methyl}$ [N(1)–Al–N(2) = 90.69(13)° and C(19)–Al–C(20) = 116.63(19)°] are comparable with those found in aluminium anilido–oxazolinate [25] [1.917(5)–1.963(1) Å for $Al–N_{oxazoline}$, 92.65(8)–93.66(8)° for $N_{oxazole}–Al–N_{anilido}$] or anilido–imino [30,38] [92.65(8)–95.51(18)° for $N_{imine}–Al–N_{anilido}$ and 111.6(2)–116.70(1)° for $C_{methyl}–Al–C_{methyl}$] complexes. The bond distance of $Al–N_{sulfonamide}$ is comparable with those found in aluminium complexes containing sulfonamido ligands [1.858(2)–1.952(2) Å for $Al–N_{sulfonamide}$] [18,19,21].

Trace crystals were collected upon recrystallizing **5** from the concentrated toluene solution at room temperature in few days. The molecular structure of **5′** is depicted in Fig. 2. The structure demonstrates a mononuclear five-coordinated aluminium complex, where the metal centre is coordinated by one methyl group and two pyrazolyl–sulfonamido groups. Based on the τ-value [$\tau = (\beta - \alpha)/60$] [40], the central aluminium adopts a distorted



Scheme 2. Preparation complex **5′**.

trigonal bipyramidal geometry ($\tau = 0.73$) with distorted axes of $N_{pyrazole}$–Al–$N_{pyrazole}$ [N(1)–Al–N(1A) = 172.28(12) Å]. The nitrogen atoms [N(3) and N(3A)] and carbon atom [C(17)] reside equatorially, forming angles subtended by aluminium [N(3)–Al–N(3A) = 102.78(12)°, N(3)–Al–C(17) = 128.61(6)° and N(3A)–Al–C(17) = 128.61(6)°]. The bond length of Al–$N_{pyrazole}$ [Al–N(1) = 2.0859(19) Å] is longer than the five-coordinated aluminium anilido–pyrazolinate [28] [2.012(3) Å for Al–$N_{pyrazole}$] complex. Comparing with complex **2** and the related aluminium anilido–oxazolinate complexes [25], the pyrazolinate group donates less electrons to aluminium centre than the oxazolinate group. The bond lengths of Al–$N_{sulfonamide}$ [Al–N(3) = 1.922(2) Å] and Al–C_{methyl} [Al–C(17) = 1.963(4) Å] and the angle of $N_{pyrazole}$–Al–$N_{sulfonamide}$ [N(3)–Al–N(3A) = 91.03(8)°] are comparable with those found in five-coordinated aluminium anilido-pyrazolinate [28] [1.964(3)–1.983(3) Å for Al–C_{methyl} and 88.23(11)° for $N_{pyrazole}$–Al–$N_{anilido}$] or sulfonamido [18,19,21] [1.895(2)–1.952(2) Å for Al–$N_{sulfonamide}$ and 1.949(2)–1.986(2) Å for Al–C_{alkyl}] complexes. Alternative routes can be achieved by treatment of **5** with 1 molar equivalent of $HNSO_2Ph^{Me}Pz^{H}$ in refluxing toluene or reaction of $HNSO_2Ph^{Me}Pz^{H}$ with 0.5 molar equivalent of $AlMe_3$ in refluxing toluene to afford the aluminium bis-pyrazolyl–sulfonamide complex **5′**. The synthetic routes are shown in (Scheme 2). Compared with complexes **1**–**10**, there are more remarkable differences by spectroscopic studies for **5′**, *i.e.* the more down-field aluminium-methyl signal on ^{1}H NMR spectrum (0.28 ppm) and the more up-filed signal on ^{27}Al NMR spectrum (56.7 ppm). The ^{27}Al chemical shift of **5′** is within the expected region for five-coordinate aluminium species in solution (*ca.* 20–60 ppm) [36]. Compound **5′** was characterized by elemental analyses as well.

Suitable crystals for structure determination of **8** were obtained from tetrahydrofuran/hexane solution. The molecular structure is depicted in Fig. 3. Complex **8** is similar to **2** but with the dimethyl-pyrazolinate group instead of the oxazolinate group. The bond distance of Al–$N_{pyrazole}$ [Al–N(3) = 1.972(2) Å] is slightly longer than those found in aluminium anilido–oxazolinate [25] [1.9590(17) Å for Al–$N_{pyrazole}$] or anilido–imino [30,38] [1.917(5)–1.963(1) Å for Al–N_{imine}] complexes. The bond length of Al–$N_{sulfonamide}$ [Al–N(3) = 1.915(2) Å] and the angle of $N_{pyrazole}$–Al–$N_{sulfonamide}$ [N(1)–Al–N(3) = 91.03(9)°] are close to those discussed above for **2**.

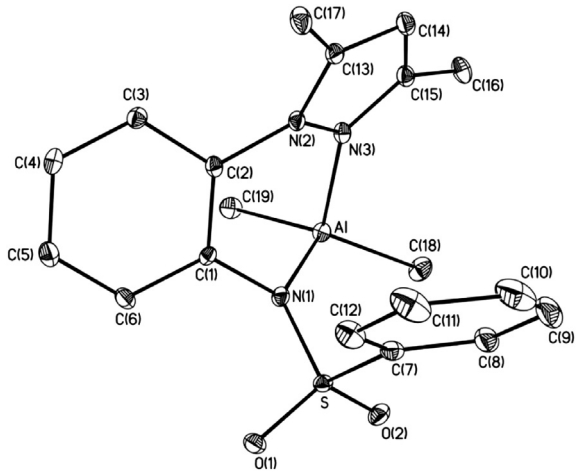


Fig. 3. Molecular structure of complex **8**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and bond angles (°): Al–N(1), 1.915(2); Al–N(3), 1.972(2); Al–C(18), 1.952(3); Al–C(19), 1.957(3); S–O(1), 1.4416(18); S–O(2), 1.4365(19); S–N(1), 1.607(2); S–C(7), 1.777(3); N(2)–N(3), 1.370(3); N(1)–C(1), 1.429(3); N(2)–C(2), 1.428(3); C(1)–C(2), 1.397(3); N(1)–Al–N(3), 91.03(9); C(18)–Al–C(19), 120.92(13); N(1)–Al–C(18), 115.93(11); N(1)–Al–C(19), 106.92(11); N(3)–Al–C(18), 110.70(11); N(3)–Al–C(19), 107.01(10); O(1)–S–O(2), 118.07(11); N(1)–S–C(7), 106.82(11).

The geometry of chelating six-membered ring of aluminium oxazolyl–sulfonamido complex **2** is almost co-planar with evidence of the dihedral angle (2.8°) between planes defined by N(1)–Al–N(2)/N(1)–C(14)–C(6)–C(1)–N(2). However, the distorted (half-chair form) six-membered ring of aluminium pyrazolyl-based sulfonamido complexes **5′** and **8** exhibit larger dihedral angles of N(1)–Al–N(2)/N(1)–C(14)–C(6)–C(1)–N(2) (39.5°) and N(1)–Al–N(2)/N(1)–C(14)–C(6)–C(1)–N(2) (41.7°), respectively. This phenomenon explains more aromatic character for the chelating ring of aluminium oxazolyl–sulfonamido complex than that of aluminium pyrazolyl–sulfonamido complex.

Although some aluminium complexes bearing sulfonamido group have been reported with the bonding between aluminium metal centre and oxygen atom of sulfonamido [Al–$O_{sulfonamide}$ = 1.854(2)–2.193(2) Å] [18,19,21]. The Al–$O_{sulfonamide}$ bond distances for complexes demonstrated here [2.536 Å and 3.992 Å for **2**; 3.069 Å and 4.255 Å for **5′**; 3.249 Å and 4.306 Å for **8**] indicating there are no coordinated covalent bonds between aluminium metal centre and oxygen atom of sulfonamido group. However, the existence of Al···$O_{sulfonamide}$ bond interaction could not be excluded due to the van der Walls radius between aluminium and oxygen [Al···O = 3.5 Å].

2.2. Catalytic studies of ring-opening polymerization

Since some aluminium sulfonamido complexes [18,19,21] and aluminium anilido–oxazolinate [25], anilidopyrazolate [28], β-diketiminates [29], anilido–iminates [30,31], amidinates [32,33] or phosphino–iminates [34,35] complexes have shown their catalytic activities in ROP, structure-related aluminium sulfonamido complexes **1**–**10** are expected to work as catalysts toward the ROP. The similar conditions used in our previous work [24–28] were introduced to examine the catalytic activities in the ROP of ε-caprolactone. Representative results are collected in Table 1. Under the same condition, the aluminium complexes containing pyrazolinate group (entries 4–7) exhibited better activities than those with dimethyl-pyrazolinate group (entries 8–10) or oxazolinate group (entries 1–3) in the presence of benzyl alcohol with the order of $Pz^{H} > Pz^{Me} >$ Oxa at 25 °C with a period of 30 min in toluene. This trend was observed under elevated temperature condition (entries 11–13) or in the absence of benzyl alcohol (entries 14–16). Upon comparing catalytic activity with complex **4** (entry 4), complex **7** containing electron-withdrawing substituent on phenyl group of sulfonamido species results in the inhibition of catalytic activity. The optimized conditions were reconfirmed using complex **4** as catalyst in dichloromethane or THF with poor conversions (entries 17–18). This might result from the competition between solvent and monomer or initiator. The analysis of end group were demonstrated by the ^{1}H NMR spectra of the polymers produced with or without the addition of benzyl alcohol (entries 12 and 15), as shown in Figs. 4 and 5. Peaks in Fig. 4 are assignable to the corresponding protons in the proposed structure, indicating the metal benzyl oxide complex might form first, followed by the monomer of the ring cleavage of acyl–oxygen bond to form a metal alkoxide intermediate, which further reacts with excess monomers to yield polyester [24–28]. However, no end group in Fig. 5 was found on the polymer produced without the addition of benzyl alcohol as initial agent. These are further supported by matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopic analysis in Figs. 6 and 7. The repeating mass is assigned to {H[ε-caprolactone]$_n$OBn} + Na^+ from entry 12 in Fig. 6, and the repeating mass is assigned to [ε-caprolactone]$_n$ + Na^+ from entry 15 in Fig. 7, which are consistent with the analysis of Figs. 4

Table 1
Polymerization of ε-caprolactone using compounds **1**–**12** as catalysts in toluene if not otherwise stated.[a]

Entry	Catalyst	[ε-CL]:[Al]:[BnOH]	T (°C)	t (min)	M_n (obsd)[b,k]	M_n (calcd)[c,k]	Conv. (%)[d]	Yield (%)[e]	M_w/M_n[b,k,l]
1	**1**	100:1:2	25	30	–	–	23	–	–
2	**2**	100:1:2	25	30	–	–	23	–	–
3	**3**	100:1:2	25	30	–	–	18	–	–
4	**4**	100:1:2	25	30	7800	5400	93	84	1.20
5	**5**	100:1:2	25	30	8000	4300	91	81	1.20
6	**6**	100:1:2	25	30	9200	5400	93	91	1.20
7	**7**	100:1:2	25	30	6700	4400	76	60	1.17
8	**8**	100:1:2	25	30	–	–	48	–	–
9	**9**	100:1:2	25	30	–	–	54	–	–
10	**10**	100:1:2	25	30	–	–	59	–	–
11	**1**	100:1:2	50	30	12,200	5500	95	90	1.30
12	**4**	100:1:2	50	10	6300	5700	98	77	1.13
13	**8**	100:1:2	50	25	5300	5300	91	70	1.11
14	**1**	100:1:0	50	150	–	–	17	–	–
15	**4**	100:1:0	50	150	21,000	11,100[f]	97	97	1.39
16	**8**	100:1:0	50	150	31,000	8000[f]	70	68	1.39
17[g]	**4**	100:1:2	25	30	–	–	11	–	–
18[h]	**4**	100:1:2	50	30	–	–	11	–	–
19	**4**	200:1:2	25	105	14,700	10,700	93	92	1.15
20	**4**	300:1:2	25	210	22,800	16,900	98	96	1.19
21	**4**	400:1:2	25	450	28,900	20.600	90	88	1.20
22	**4**	200:1:4	25	135	5200	5100	90	72	1.13
23	**4**	50:1:1	25	240	7800	5100	90	84	1.58
24	**5**	100:1:2	50	10	7600	5500	95	86	1.08
25	**5′**	50:1:1	50	10	6100	4700	81	46	1.34
26[i]	**11**	100:1:2	50	120	13,000	5500	95	94	1.06
27[j]	**12**	100:1:2	25	60	9100	5200	91	89	1.12
28[j]	**12**	100:1:2	50	12	8900	5400	92	86	1.11

[a] In 15 mL.
[b] Obtained from GPC analysis times 0.56.
[c] Calculated from [M(ε-CL) × [ε-CL]/[Al] × conversion/([BnOH]$_{eq}$)] + M(BnOH).
[d] Obtained from ^{1}H NMR analysis.
[e] Isolated yield.
[f] Calculated from (M(ε-CL) × [ε-CL]/[Al] × conversion).
[g] In CH_2Cl_2.
[h] In THF.
[i] Ref. [25].
[j] Ref. [28].
[k] M_w (weight average molecular weight).
[l] M_w (weight average molecular weight).

and 5 [41,42]. The mechanism for the formation of cyclic PCL might be initiated by ligand and end up with trans-esterification, which is similar to those reported in the literature [43,44]. The linear relationship between M_n and the monomer-to-initiator ([ε-CL]/[Al]) exhibited by complex **4** implies the "living" character of the polymerization process at 25 °C (entries 4, 19–21; PDIs = 1.15–1.20), and representative results are demonstrated in Fig. 8. The "immortal" character was examined using one, two and four equivalents benzyl alcohol as the chain transfer agent (entries 4, 22–23). The five-coordinated aluminium bis-sulfonamido complex **5′** also demonstrated catalytic activity, but with poor activity

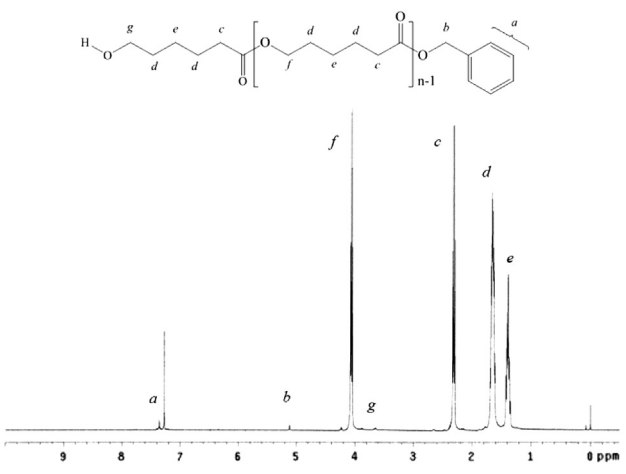


Fig. 4. ^{1}H NMR spectrum of poly(ε-caprolactone) initiated by **4** in toluene at 25 °C in the presence of BnOH (Table 1, entry 12).

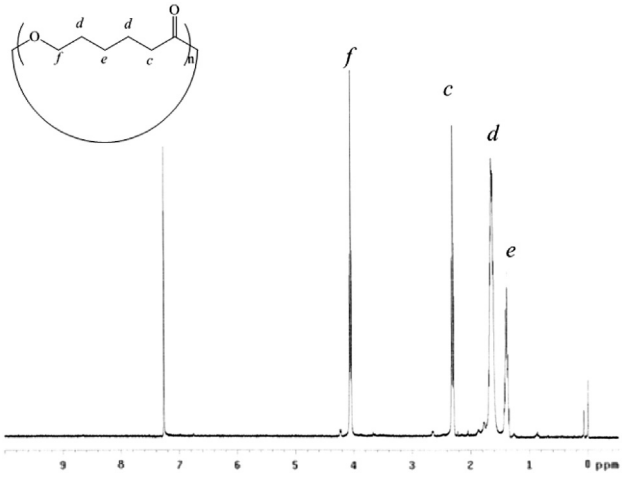


Fig. 5. ^{1}H NMR spectrum of poly(ε-caprolactone) initiated by **4** in toluene at 25 °C in the absence of BnOH (Table 1, entry 15).

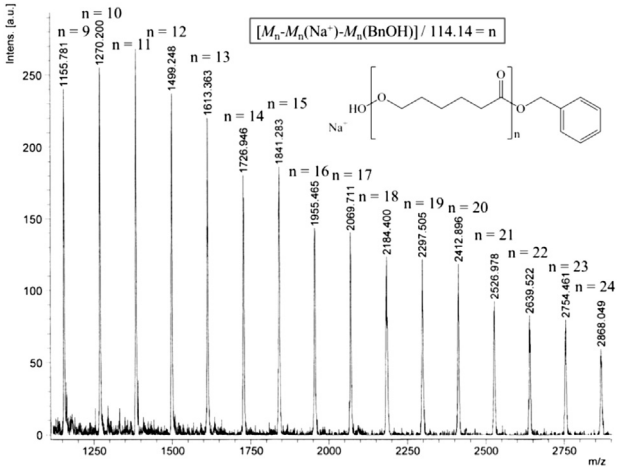


Fig. 6. MALDI-TOF mass spectrum of poly(ε-caprolactone) initiated by **4** in toluene at 25 °C in the presence of BnOH (Table 1, entry 12).

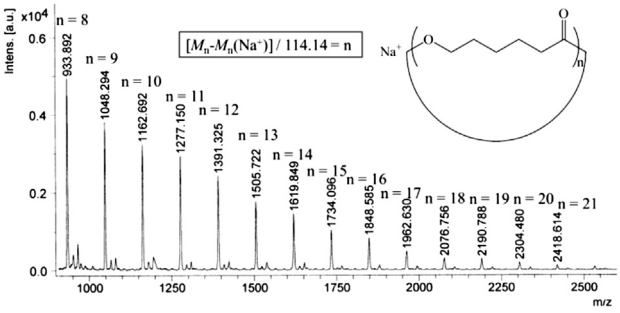


Fig. 7. MALDI-TOF mass spectrum of poly(ε-caprolactone) initiated by **4** in toluene at 25 °C in the absence of BnOH (Table 1, entry 15).

comparing with **5** at 50 °C within 10 min (entries 24–25). This might result from the bulkier environment around five-coordinated aluminium centre and the modification of Lewis acidity of metal centre caused by the ligands. Optimized conditions were introduced to examine the catalytic activities of structure-related aluminium anilido–oxazolinate complex (**11**) and anilido-pyrazolinate complexes (**12**) (entries 26–28), as shown in (Scheme 3). Based on the experimental results, introduction of sulfonamido group into these two systems can enhance the

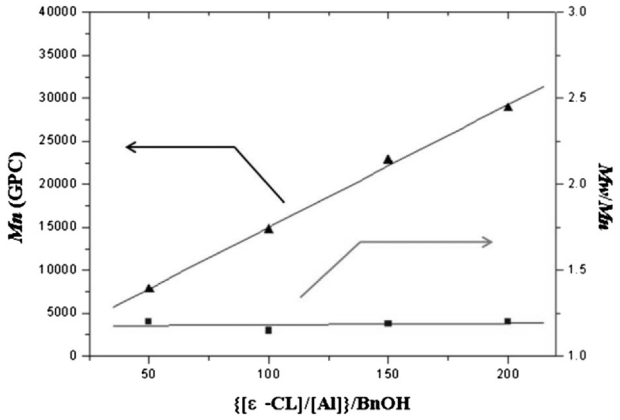


Fig. 8. Polymerization of ε-caprolactone initiated by **4** in toluene at 25 °C in the presence of BnOH (Table 1, entries 4, 19–21).

catalytic activities (entries 4, 11–12 and 26–28). Furthermore comparing with other structurally related aluminium complexes, the catalytic activity of complex **4** is more active than aluminium anilido–aldiminate [30] or aluminium anilido–iminate [31] complexes. Trials have been done by the reactions between aluminium dimethyl complexes **1**, **4** or **8** with two molar equivalent benzyl alcohols within 5 min at room temperature using benzene-d_6 as solvent to understand the details of active species of polymerization *in situ* with benzyl alcohol (Fig. S2). Although the syntheses of aluminium alkoxide complexes were failed, the similar phenomena were observed and consistent with our previous work [28]. Based on the ^{1}H NMR spectrometric studies, the active species could be formulated as a $[(BnO)_2AlMe]_n$ derivative. The activity of polymerization might be assessed by the determination of the mixed compounds from the protonation of the aluminium anilidopyrazolate complex and benzyl alcohol [32,45].

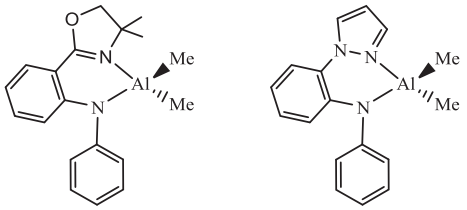
3. Conclusions

A series of oxazolinate- or pyrazolinate-based sulfonamido ligand precursors and related aluminium complexes **1**–**10** have been prepared and characterized. The molecular structures are reported as four-coordinated aluminium dimethyl complexes (for **2** and **8**) and five-coordinated aluminium monomethyl complex (for **5′**). All aluminium complexes were found to be active in catalyzing the polymerization of ε-caprolactone in the presence of benzyl alcohol with well-controlled M_n and narrow PDIs. Compounds with pyrazolinate group seem to be more active than those with dimethyl-pyrazolinate and oxazolinate group. Introduction of sulfonamido group indeed proved the enhancement of catalytic activity for ROP of ε-caprolactone comparing with our previously related works. Complex **4** exhibited efficient activities for controlled polymerization of ε-caprolactone with "living" and "immortal" characters under the optimized condition. The activity of ROP might be assessed by the determination of the mixed compounds from the protonation of the aluminium anilido–pyrazolate complex and benzyl alcohol resulting in the formation of the ligand precursor and the $[(BnO)_2AlMe]_n$ derivatives.

4. Experimental

4.1. General conditions

All manipulations were carried out under an atmosphere of dinitrogen using standard Schlenk-line or drybox techniques. Solvents were refluxed over the appropriate drying agent and distilled prior to use. Deuterated solvents were dried over molecular sieves. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded either on Varian Mercury-400 (400 MHz) or Varian Inova-600 (600 MHz) spectrometers in chloroform-*d* at ambient temperature unless stated otherwise and referenced internally to the residual solvent peak and reported as parts per million relative to tetramethylsilane. ^{27}Al {^{1}H} NMR spectra were referenced externally using Al(acac)$_3$ at



(**11**)[5b] (**12**)[6]

Scheme 3. Molecular structures of complexes **11** and **12**.

δ = 0 ppm. Elemental analyses were performed by an Elementar Vario ELIV instrument. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometric studies of poly(ε-caprolactone) were performed by using Bruker Autoflex III TOF/TOF spectrometer. The Gel Permeation Chromatography (GPC) measurements were performed in THF at 35 °C with a Waters 1515 isocratic High Performance Liquid Chromatography (HPLC) pump, a Waters 2414 refractive index detector, and Waters styragel column (HR4E). Molecular weights and molecular weight distributions were calculated using polystyrene as standard.

p-Toluenesulfonyl chloride (Acros), benzenesulfonyl chloride (Alfa Aesar), 2-mesitylenesulfonyl chloride (Alfa Aesar), 4-fluorobenzenesulfonyl chloride (Acros), 9-anthracenmethanol (Acros) and trimethylaluminium (1.0 M in heptane, Aldrich) were used as supplied. Trimethylamine (TMEDIA), benzyl alcohol (TEDIA) and ε-caprolactone (Acros) were dried over CaH_2 and distilled before use. 2-(4,4-dimethyl-4,5-dihydrooxazo-2-yl)-phenylamine [46], 1-(2-aminophenyl)pyrazole [47] and 1-(3,5-dimethyl-2-aminophenyl)pyrazole [48] were prepared by the modified literature's methods.

4.2. $HNSO_2Ph^HOxa$

To a flask containing 2-(4,4-dimethy-4,5-dihydro-oxazo-2-yl)-phenylamine (0.950 g, 5.0 mmol) in 15 mL dichloromethane, a solution of benzenesulfonyl chloride (0.970 g, 5.5 mmol) in 15 mL dichloromethane was added at room temperature. To this reaction mixture, NEt_3 (0.765 mL, 5.5 mmol) was added via syringe at 0 °C. After one hour of stirring, all the volatiles were pumped off. The residue was dissolved in ethyl acetate and washed with deionized water. Collect organic layer to afford crude product. Crude product was washed with methanol (5 mL × 3) to yield white solid (1.29 g, 78%). Anal. Calc. for $C_{17}H_{18}N_2O_3S$: C, 61.80; H, 5.49; N, 8.48. Found: C, 61.88; H, 5.56; N, 8.35. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.33 (br, 1H, −N*H*), 7.83 (m, 2H, C_6H_5), 7.70–7.75 (overlap, 2H, C_6H_5), 7.47 (m, 1H, C_6H_5), 7.34–7.40 (overlap, 3H, C_6H_5), 7.02 (m, 1H, C_6H_5), 4.01 (s, 2H, Oxa-CH_2), 1.39 (s, 6H, Oxa-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 161.5, 139.8, 138.9, 114.3, 67.8 (C_{ipso}–C_6H_5), 132.6, 132.2, 129.1, 128.7, 127.0, 122.7, 118.8 (*C*H–C_6H_5), 77.9 (s, Oxa-CH_2), 28.3 (s, Oxa-CH_3).

4.3. $HNSO_2Ph^{Me}Oxa$

To a flask containing 2-(4,4-dimethy-4,5-dihydro-oxazo-2-yl)-phenylamine (0.95 g, 5.0 mmol) and toluenesulfonyl chloride (1.05 g, 5.5 mmol), 30 mL dichloromethane were added at room temperature. To this reaction mixture, NEt_3 (0.765 mL, 5.5 mmol) was added via syringe at 0 °C. After two hour of stirring, all the volatiles were pumped off. The residue was dissolved in ethyl acetate and washed with deionized water. Collect organic layer to afford crude product. Crude product was washed with methanol (5 mL × 3) to afford white solid (1.24 g, 72.0%). Anal. Calc. for $C_{18}H_{20}N_2O_3S$: C, 62.77; H, 5.85; N, 8.13. Found: C, 62.53; H, 5.81; N, 8.13. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.29 (br, 1H, −N*H*), 7.70–7.74 (overlap, 4H, C_6H_5), 7.35 (m, 1H, C_6H_5), 7.17 (m, 2H, C_6H_5), 7.01 (m, 1H, C_6H_5), 4.02 (s, 2H, Oxa-CH_2), 2.34 (s, 3H, −CH_3), 1.40 (s, 6H, Oxa-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 161.5, 143.2, 138.8, 136.6, 113.9, 67.6 (C_{ipso}–C_6H_5), 131.9, 129.1, 129.0, 126.7, 122.4, 118.2 (*C*H–C_6H_5), 77.6 (s, Oxa-CH_2), 28.1 (s, Oxa-CH_3), 21.1 (s, −CH_3).

4.4. $HNSO_2Ph^{TriMe}Oxa$

The procedure for the preparation of **$HNSO_2Ph^{TriMe}Oxa$** was similar to that used for **$HNSO_2Ph^{Me}Oxa$** but with 2-mesitylenesulfonyl chloride (1.20 g, 5.5 mmol). A white solid was obtained (1.04 g, 56.0%). Anal. Calc. for $C_{20}H_{24}N_2O_3S$: C, 64.49; H, 6.49; N, 7.52. Found: C, 64.48; H, 6.71; N, 7.25. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.56 (br, 1H, −N*H*), 7.75 (m, 1H, C_6H_5), 7.25–7.33 (overlap, 2H, C_6H_5), 6.90–6.96 (overlap, 3H, C_6H_5), 4.07 (s, 2H, Oxa-CH_2), 2.71 (s, 6H, *o*-CH_3–Ph), 2.24 (s, 3H, *p*-CH_3–Ph), 1.41 (s, 6H, Oxa-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 161.7, 142.3, 139.3, 139.2, 133.8, 112.3, 67.9 (C_{ipso}–C_6H_5), 132.2, 131.9, 129.3, 121.2, 115.6 (*C*H–C_6H_5), 77.9 (Oxa-CH_2), 28.3 (Oxa-CH_3), 22.8 (*o*-CH_3–Ph), 20.8 (*p*-CH_3–Ph).

4.5. $HNSO_2Ph^HPz^H$

To a flask containing 1-(2-aminophenyl)pyrazole (0.796 g, 5.0 mmol) in 15 mL dichloromethane, a solution of benzenesulfonyl chloride (0.970 g, 5.5 mmol) in 15 mL dichloromethane was added at room temperature. To this mixture solution, NEt_3 (0.765 mL, 5.5 mmol) was added via syringe at 0 °C. After one hour of stirring, all the volatiles were pumped off and the residue was extracted with toluene 5 mL × 3. Crude product was purified by column chromatography (hexane/ethyl acetate 3:1). The second band was collected to afford white solid (0.958 g, 64.0%). The third band was collected to afford di-substituted side product, **$Pz^HN(SO_2Ph^H)_2$**, as white solid (0.375 g, 17.0%). Data for **$HNSO_2Ph^HPz^H$**: Anal. Calc. for $C_{15}H_{13}N_3O_2S$: C, 60.18; H, 4.38; N, 14.04. Found: C, 59.74; H, 4.26; N, 13.64. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.09 (br, 1H, −N*H*), 7.77 (dd, J = 8.0 & 1.4 Hz, 1H, C_6H_5), 7.72 (d, J = 2.0 Hz, 1H, C_6H_5), 7.38 (m, 3H, C_6H_5), 7.27–7.33 (overlap, 2H, C_6H_5), 7.12–7.23 (overlap, 4H, C_6H_5), 6.33 (m, 1H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 138.7, 131.4, 129.8 (C_{ipso}–C_6H_5), 141.0, 132.3, 129.3, 128.6, 127.8, 126.4, 126.1, 125.8, 121.7, 107.3 (*C*H–C_6H_5). Data for **$Pz^HN(SO_2Ph^H)_2$**: Anal. Calc. for $C_{21}H_{17}N_3O_4S_2$: C, 57.39; H, 3.90; N, 9.56. Found: C, 57.20; H, 3.69; N, 9.15. NMR (400 MHz, $CDCl_3$): δ (ppm) 8.17 (m, 1H, C_6H_5), 7.84–7.87 (overlap, 4H, C_6H_5), 7.62–7.69 (overlap, 3H, C_6H_5), 7.58 (td, J = 7.8 & 1.2 Hz, 1H, C_6H_5), 7.47–7.51 (overlap, 5H, C_6H_5), 7.32 (m, 1H, C_6H_5), 6.95 (dd, J = 8.0 & 1.4 Hz, 1H, C_6H_5), 6.10 (t, J = 2.0 Hz, 1H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 140.7, 138.7, 127.7 (C_{ipso}–C_6H_5), 141.2, 134.0, 132.6, 131.5, 131.4, 129.1, 128.7, 128.0, 127.8, 107.4 (*C*H–C_6H_5) [49,50].

4.6. $HNSO_2Ph^{Me}Pz^H$

To a flask containing 1-(2-aminophenyl)pyrazole (0.796 g, 5.0 mmol) and toluenesulfonyl chloride (1.05 g, 5.5 mmol), 30 mL dichloromethane were added at room temperature. To this reaction mixture, NEt_3 (0.765 mL, 5.5 mmol) was added via syringe at 0 °C. After one hour of stirring, all the volatiles were pumped off. The residue was extracted with toluene (5 mL × 3). Crude product was purified by column chromatography (hexane/ethyl acetate 3:1). The second band was collected to afford pale-white solid (1.05 g, 67.0%). The third band was collected to afford di-substituted side product, **$Pz^HN(SO_2Ph^{Me})_2$**, as white solid (0.165 g, 7.0%). Data for **$HNSO_2Ph^{Me}Pz^H$**: Anal. Calc. for $C_{16}H_{15}N_3O_2S$: C, 61.32; H, 4.82; N, 13.41. Found: C, 61.60; H, 5.08; N, 13.50. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.04 (br, 1H, −N*H*), 7.73–7.77 (overlap, 2H, C_6H_5), 7.26–7.34 (overlap, 4H, C_6H_5), 7.14–7.20 (overlap, 2H, C_6H_5), 7.01 (d, J = 8.4 Hz, 2H, C_6H_5), 6.36 (m, 1H, C_6H_5), 2.30 (s, 3H, −CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.1, 135.7, 131.0, 129.8 (C_{ipso}–C_6H_5), 140.8, 129.2, 129.1, 127.6, 126.3, 125.8, 125.2, 121.6, 107.1 (*C*H–C_6H_5), 21.2 (−CH_3). Data for **$Pz^HN(SO_2Ph^{Me})_2$**: Anal. Calc. for $C_{23}H_{21}N_3O_4S_2$: C, 59.08; H, 4.53; N, 8.99. Found: C, 59.05; H, 4.73; N, 8.40. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.20 (m, 1H, C_6H_5), 7.71 (d, J = 8.4 Hz, 4H, C_6H_5), 7.67 (dd, J = 8.0 & 1.6 Hz, 1H, C_6H_5), 7.52–7.58 (overlap, 2H, C_6H_5), 7.31 (m, 2H, C_6H_5), 7.26 (dd, J = 8.0 & 0.4 Hz, 4H, C_6H_5), 6.96 (d, J = 8.4 Hz, 1H, C_6H_5), 6.13 (m, 1H, C_6H_5), 2.46 (s, 6H, −CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 145.1, 140.7, 135.9, 131.3

(C_{ipso}–C_6H_5), 141.0, 132.6, 131.5, 129.3, 129.2, 127.9, 127.7, 107.3 (*C*H–C_6H_5), 21.6 (–*C*H$_3$) [51].

4.7. $HNSO_2Ph^{TriMe}Pz^H$

The procedure for the preparation of **$HNSO_2Ph^{TriMe}Pz^H$** was similar to that used for **$HNSO_2Ph^{Me}Pz^H$** but with 2-mesitylenesulfonyl chloride (1.20 g, 5.5 mmol) and 20 mL dichloromethane. The second band was collected to afford white solid (0.96 g, 56.0%). Anal. Calc. for $C_{18}H_{19}N_3O_2S$: C, 63.32; H, 5.61; N, 12.31. Found: C, 63.18; H, 5.49; N, 12.53. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.97 (br, 1H, –N*H*), 7.75 (d, J = 1.2 Hz, 1H, C_6H_5), 7.55 (dd, J = 8.0 & 1.2 Hz, 1H, C_6H_5), 7.51 (dd, J = 2.4 & 0.4 Hz, 1H, C_6H_5), 7.19–7.26 (overlap, 2H, C_6H_5), 7.13 (m, 1H, C_6H_5), 6.79 (br, 2H, C_6H_5), 6.40 (m, 1H, C_6H_5), 2.41 (s, 6H, *o*-C*H*$_3$–Ph), 2.22 (s, 3H, *p*-C*H*$_3$–Ph). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 142.1, 138.8, 133.4, 130.2, 130.1 (C_{ipso}–C_6H_5), 141.0, 132.6, 131.5, 129.3, 129.2, 127.9, 127.7, 107.3 (*C*H–C_6H_5), 21.6 (–*C*H$_3$).

4.8. $HNSO_2Ph^FPz^H$

The procedure for the preparation of **$HNSO_2Ph^FPz^H$** was similar to that used for **$HNSO_2Ph^{Me}Pz^H$** but with 4-fluorobenzene-sulfonyl chloride (2.92 g, 15 mmol). Crude product was purified by column chromatography (hexane/ethyl acetate 5:1). The second band was collected to afford orange-red oil. The oil was triturated with ethanol to afford orange solid (1.33 g, 28.0%). The third band was collected to afford di-substituted side product, **$Pz^HN(SO_2Ph^F)_2$**, as white solid (0.71 g, 10.0%). Data for **$HNSO_2Ph^FPz^H$**: Anal. Calc. for $C_{15}H_{12}FN_3O_2S$: C, 56.77; H, 3.81; N, 13.24. Found: C, 56.80; H, 3.88; N, 12.96. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.10 (br, 1H, –N*H*), 7.74–7.79 (overlap, 2H, C_6H_5), 7.32–7.40 (overlap, 4H, C_6H_5), 7.17–7.27 (overlap, 2H, C_6H_5), 6.89 (t, J = 8.4 Hz, 2H, C_6H_5), 6.37 (br, 1H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 166.0, 163.4, 134.6, 131.4 (C_{ipso}–C_6H_5), 141.0, 129.2, 129.1, 129.0, 127.9, 126.4, 126.1, 121.6, 115.9, 115.7, 107.3 (*C*H–C_6H_5). Data for **$Pz^HN(SO_2Ph^F)_2$**: Anal. Calc. for $C_{21}H_{15}F_2N_3O_4S_2$: C, 53.05; H, 3.18; N, 8.84. Found: C, 53.51; H, 3.34; N, 9.07. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12 (m, 1H, C_6H_5), 7.87–7.90 (overlap, 4H, C_6H_5), 7.57–7.66 (overlap, 2H, C_6H_5), 7.51 (d, J = 1.6 Hz, 1H, C_6H_5), 7.35 (m, 1H, C_6H_5), 7.14–7.18 (overlap, 4H, C_6H_5), 6.97 (dd, J = 8.0 & 1.6 Hz, 1H, C_6H_5), 6.16 (m, 1H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.2, 164.6, 140.6, 134.6, 127.7 (C_{ipso}–C_6H_5), 141.3, 132.5, 132.3, 132.2, 131.7, 131.4, 128.2, 128.0, 116.2, 116.0, 107.5 (*C*H–C_6H_5).

4.9. $Pz^HN(SO_2Ph^F)_2$

To a flask containing 1-(2-aminophenyl)pyrazole (0.159 g, 1.0 mmol) and 4-fluorobenzene-sulfonyl chloride (0.428 g, 1.0 mmol), 30 mL THF were added at room temperature. To this reaction mixture, NEt_3 (0.31 mL, 2.2 mmol) was added via syringe at 0 °C. The reaction mixture was warmed up to 50 °C. After one hour of stirring, all the volatiles were pumped off. The residue was extracted with toluene (5 mL × 3). Crude product was purified by column chromatography (hexane/ethyl acetate 3:1). The second band was collected to afford white solid (0.357 g, 75.0%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12 (m, 1H, C_6H_5), 7.87–7.90 (overlap, 4H, C_6H_5), 7.57–7.66 (overlap, 2H, C_6H_5), 7.51 (d, J = 1.6 Hz, 1H, C_6H_5), 7.35 (m, 1H, C_6H_5), 7.14–7.18 (overlap, 4H, C_6H_5), 6.97 (dd, J = 8.0 & 1.6 Hz, 1H, C_6H_5), 6.16 (m, 1H, C_6H_5). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.2, 164.6, 140.6, 134.6, 127.7 (C_{ipso}–C_6H_5), 141.3, 132.5, 132.3, 132.2, 131.7, 131.4, 128.2, 128.0, 116.2, 116.0, 107.5 (*C*H–C_6H_5).

4.10. $HNSO_2Ph^HPz^{Me}$

The procedure for the preparation of **$HNSO_2Ph^HPz^{Me}$** was similar to that used for **$HNSO_2Ph^HPz^H$** but with 2-(3,5-dimethylpyrazol-1-yl)phenylamine (0.94 g, 5.0 mmol) and benzenesulfonyl chloride (0.970 g, 5.5 mmol). Crude product was purified by column chromatography (hexane/ethyl acetate 2:1). The second band was collected to afford pink solid (0.98 g, 60.0%). Anal. Calc. for $C_{17}H_{17}N_3O_2S$: C, 62.36; H, 5.23; N, 12.83. Found: C, 62.34; H, 5.25; N, 12.92. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.99 (br, 1H, –N*H*), 7.79 (dd, J = 8.0 & 1.6 Hz, 1H, C_6H_5), 7.33–7.46 (overlap, 4H, C_6H_5), 7.25–7.30 (overlap, 2H, C_6H_5), 7.19 (td, J = 8.4 & 1.3 Hz, 1H, C_6H_5), 7.01 (dd, J = 8.0 & 1.2 Hz, 1H, C_6H_5), 5.86 (s, 1H, C_6H_5), 2.31 (s, 3H, –C*H*$_3$), 1.68 (s, 3H, –C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.2, 140.9, 139.1, 131.6, 131.1 (C_{ipso}–C_6H_5), 132.4, 128.6, 128.3, 126.4, 126.0, 125.6, 124.9, 106.9 (*C*H–C_6H_5), 13.4 (–*C*H$_3$), 11.8 (–*C*H$_3$).

4.11. $HNSO_2Ph^{Me}Pz^{Me}$

The procedure for the preparation of **$HNSO_2Ph^{Me}Pz^{Me}$** was similar to that used for **$HNSO_2Ph^{Me}Pz^H$** but with 2-(3,5-dimethylpyrazol-1-yl)phenylamine (0.94 g, 5.0 mmol) and toluenesulfonyl chloride (1.05 g, 5.5 mmol). Crude product was purified by column chromatography (hexane/ethyl acetate 5:1). The second band was collected to afford pink solid (1.02 g, 60.0%). Anal. Calc. for $C_{18}H_{19}N_3O_2S$: C, 63.32; H, 5.61; N, 12.31. Found: C, 63.45; H, 6.01; N, 12.30. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.92 (br, 1H, –N*H*), 7.34 (dd, J = 8.0 & 1.0 Hz, 1H, C_6H_5), 7.34 (m, 1H, C_6H_5), 7.27 (m, 2H, C_6H_5), 7.17 (m, 1H, C_6H_5), 7.07 (d, J = 8.0 Hz, 2H, C_6H_5), 6.99 (dd, J = 8.0 & 1.4 Hz, 1H, C_6H_5), 5.88 (s, 1H, C_6H_5), 2.33 (s, 3H, –C*H*$_3$), 2.31 (s, 3H, –C*H*$_3$), 1.70 (s, 3H, –C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.2, 143.2, 140.8, 136.2, 131.8, 131.0 (C_{ipso}–C_6H_5), 129.2, 128.4, 126.5, 125.7, 125.4, 125.0, 106.9 (*C*H–C_6H_5), 21.3 (–*C*H$_3$), 13.4 (–*C*H$_3$), 11.6 (–*C*H$_3$).

4.12. $HNSO_2Ph^{TriMe}Pz^{Me}$

The procedure for the preparation of **$HNSO_2Ph^{TriMe}Pz^{Me}$** was similar to that used for **$HNSO_2Ph^{TriMe}Pz^H$** but with 2-(3,5-dimethylpyrazol-1-yl)phenylamine (0.94 g, 5.0 mmol). Crude product was purified by column chromatography (hexane/ethyl acetate 5:1). The second band was collected to afford pale-yellow solid (0.83 g, 45.0%). Anal. Calc. for $C_{20}H_{23}N_3O_2S$: C, 65.01; H, 6.27; N, 11.37. Found: C, 65.16; H, 6.58; N, 11.57. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.68 (br, 1H, –N*H*), 7.73 (dd, J = 8.0 & 1.2 Hz, 1H, C_6H_5), 7.32 (m, 1H, C_6H_5), 7.16 (td, J = 7.8 & 1.3 Hz, 1H, C_6H_5), 7.03 (dd, J = 8.0 & 1.2 Hz, 1H, C_6H_5), 6.75 (br, 2H, C_6H_5), 5.89 (br, 1H, C_6H_5), 2.28 (s, 6H, *o*-C*H*$_3$–Ph), 2.27 (s, 3H, –C*H*$_3$), 2.22 (s, 3H, –C*H*$_3$), 1.73 (s, 3H, –C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 150.5, 142.0, 141.0, 139.0, 133.9, 132.0, 131.3 (C_{ipso}–C_6H_5), 131.6, 128.3, 125.7, 125.5, 125.3, 109.6 (*C*H–C_6H_5), 22.8 (–*C*H$_3$), 20.7 (–*C*H$_3$), 13.4 (–*C*H$_3$), 11.4 (–*C*H$_3$).

4.13. $(NSO_2Ph^HOxa)AlMe_2$ (**1**)

To a flask containing **$HNSO_2Ph^HOxa$** (0.33 g, 1.0 mmol) and 15 mL THF, 1.1 mL $AlMe_3$ (1.0 M in heptane, 1.1 mmol) was added at 0 °C. The reaction mixture was allowed to warm to room temperature and reacted for one hour. All the volatiles were removed under reduced pressure to afford pale-yellow solid. The crude product was washed with 5 mL hexane to afford white solid (0.228 g, 57%). Anal. Calc. for $C_{19}H_{23}N_2O_3SAl$: C, 59.05; H, 6.00; N, 7.25. Found: C, 59.38; H, 5.92; N, 6.70. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.00 (d, J = 7.8 Hz, 2H, C_6H_5), 7.88 (dd, J = 7.8 & 1.5 Hz, 1H, C_6H_5), 7.53 (t, J = 7.2 Hz, 1H, C_6H_5), 7.47 (t, J = 7.5 Hz, 2H, C_6H_5), 7.40

(d, J = 8.4 Hz, 1H, C_6H_5), 7.29 (m, 1H, C_6H_5), 6.88 (t, J = 7.5 Hz, 1H, C_6H_5), 4.25 (s, 2H, Oxa-CH_2), 1.59 (s, 6H, Oxa-CH_3), −0.47 (s, 6H, Al−CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.1, 145.1, 140.5, 110.9, 68.2 (C_{ipso}−C_6H_5), 135.2, 132.5, 131.0, 129.0, 127.8, 120.3, 118.8 (CH−C_6H_5), 79.2 (Oxa-CH_2), 27.0 (Oxa-CH_3), −5.1 (Al−CH_3). ^{27}Al NMR (156 MHz): δ 103.8 ($\Delta\nu_{1/2}$ = 6203.7).

4.14. ($NOxaSO_2Ph^{Me}$)$AlMe_2$ (**2**)

The procedure for the preparation of **2** was similar to that used for **1** but with $HNOxaSO_2Ph^{Me}$ (0.344 g, 1.0 mmol). A white solid was obtained (0.272 g, 68.0%). Anal. Calc. for $C_{20}H_{25}N_2O_3SAl$: C, 59.98; H, 6.29; N, 7.00. Found: C, 60.14; H, 6.33; N, 6.92. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.87−7.89 (overlap, 3H, C_6H_5), 7.39 (d, J = 9.0 Hz, 1H, C_6H_5), 7.26−7.30 (overlap, 3H, C_6H_5), 6.87 (t, J = 7.5 Hz, 1H, C_6H_5), 4.25 (s, 2H, Oxa-CH_2), 2.38 (s, 3H, CH_3), 1.57 (s, 6H, Oxa-CH_3), −0.47 (s, 6H, Al−CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 167.1, 145.0, 143.3, 137.3, 110.8, 68.1 (C_{ipso}−C_6H_5), 135.1, 130.9, 129.6, 127.8, 120.2, 118.5 (CH−C_6H_5), 79.1 (Oxa-CH_2), 26.9 (Oxa-CH_3), 21.5 (−CH_3), −5.1 (Al−CH_3). ^{27}Al NMR (156 MHz):δ 133.5 ($\Delta\nu_{1/2}$ = 7273.5).

4.15. ($NOxaSO_2Ph^{TriMe}$)$AlMe_2$ (**3**)

The procedure for the preparation of **3** was similar to that used for **1** but with $HNOxaSO_2Ph^{TriMe}$ (0.372 g, 1.0 mmol). A white solid was obtained (0.257 g, 60.0%). Anal. Calc. for $C_{22}H_{29}N_2O_3SAl$: C, 61.66; H, 6.82; N, 6.54. Found: C, 61.50; H, 7.05; N, 6.29. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89 (m, 1H, C_6H_5), 7.27 (m, 1H, C_6H_5), 7.15 (dd, J = 8.4 & 0.6 Hz, 1H, C_6H_5), 6.88−6.92 (overlap, 3H, C_6H_5), 4.28 (s, 2H, Oxa-CH_2), 2.64 (s, 6H, o-CH_3−Ph), 2.27 (s, 3H, p-CH_3−Ph), 1.59 (s, 6H, Oxa-CH_3), −0.52 (s, 6H, Al−CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.2, 145.8, 135.1, 132.0, 130.9, 110.7, 68.0 (C_{ipso}−C_6H_5), 141.8, 138.4, 135.9, 120.2, 118.7 (CH−C_6H_5), 79.4 (Oxa-CH_2), 26.9 (Oxa-CH_3), 22.9 (o-CH_3−Ph), 20.8 (p-CH_3−Ph), −5.3 (Al−CH_3). ^{27}Al NMR (156 MHz): δ 122.8 ($\Delta\nu_{1/2}$ = 10349.8).

4.16. ($NPz^HSO_2Ph^H$)$AlMe_2$ (**4**)

The procedure for the preparation of **4** was similar to that used for **1** but with $HNPz^HSO_2Ph^H$ (0.299 g, 1.0 mmol). A white solid was obtained (0.313 g, 88.0%). Anal. Calc. for $C_{17}H_{18}N_3O_2SAl$: C, 57.45; H, 5.11; N, 11.82. Found: C, 57.74; H, 5.33; N, 11.39. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.88 (d, J = 3.0 Hz, 1H, C_6H_5), 7.85 (d, J = 1.8 Hz, 1H, C_6H_5), 7.76 (d, J = 8.4 Hz, 1H, C_6H_5), 7.62 (d, J = 7.8 Hz, 2H, C_6H_5), 7.38 (t, J = 7.2 Hz, 1H, C_6H_5), 7.26−7.31 (overlap, 4H, C_6H_5), 7.11 (t, J = 7.5 Hz, 1H, C_6H_5), 6.58 (t, J = 1.6 Hz, 1H, C_6H_5), −0.61 (s, 6H, Al−CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 133.1, 129.0, 128.7 (C_{ipso}−C_6H_5), 140.7, 131.9, 130.9, 128.6, 126.4, 125.8, 124.1, 120.6, 108.3 (CH−C_6H_5), −8.8 (Al−CH_3). ^{27}Al NMR (156 MHz): δ 111.6 ($\Delta\nu_{1/2}$ = 8593.2).

4.17. ($NPz^HSO_2Ph^{Me}$)$AlMe_2$ (**5**)

The procedure for the preparation of **5** was similar to that used for **1** but with $HNPz^HSO_2Ph^{Me}$ (0.313 g, 1.0 mmol). A white solid was obtained (0.258 g, 70.0%). Anal. Calc. for $C_{18}H_{20}N_3O_2SAl$: C, 58.52; H, 5.46; N, 11.37. Found: C, 58.71; H, 5.46; N, 10.97. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.96 (d, J = 1.8 Hz, 1H, C_6H_5), 7.87 (d, J = 1.8 Hz, 1H, C_6H_5), 7.71 (d, J = 7.8 Hz, 1H, C_6H_5), 7.58 (d, J = 7.8 Hz, 2H, C_6H_5), 7.32 (d, J = 7.8 Hz, 1H, C_6H_5), 7.23 (t, J = 7.5 Hz, 1H, C_6H_5), 7.11 (d, J = 8.4 Hz, 2H, C_6H_5), 7.07 (t, J = 7.5 Hz, 1H, C_6H_5), 6.61 (br, 1H, C_6H_5), 2.31 (s, 3H, −CH_3), −0.61 (s, 6H, Al−CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 142.9, 137.5, 133.2, 128.0 (C_{ipso}−C_6H_5), 140.9, 130.7, 129.4, 128.9, 126.8, 124.5, 123.5, 120.5, 108.2 (CH−C_6H_5), 21.3 (−CH_3), −8.4 (Al−CH_3). ^{27}Al NMR (156 MHz): δ 106.6 ($\Delta\nu_{1/2}$ = 102.31).

4.18. ($NSO_2Ph^{Me}Pz^H$)$_2AlMe$ (**5′**)

There are two methods to prepare as following: (**I**) To a flask containing **$HSO_2Ph^{Me}Pz^H$** (0.627 g, 2.0 mmol) and 15 mL dry toluene, $AlMe_3$ (1.10 mL, 1.10 mmol) were added at 0 °C under nitrogen. The reaction mixture was allowed to warm to room temperature and reacted in oil bath at 80 °C. After 12 h of stirring, the white suspension was filtered and the filtrate was pumped to dryness to afford white solid (0.533 g, 80%). (**II**) To a flask containing **5** (0.369 g, 1.0 mmol) in toluene, a toluene solution of **$HNSO_2Ph^{Me}Pz^H$** (0.313 g, 1.0 mmol) was added. The reaction mixture was heated in oil bath at 80 °C. After 12 h of stirring, the white suspension was filtered and the filtrate was pumped to dryness to afford white solid (0.505 g, 76%). Anal. Calc. for $C_{33}H_{31}AlN_6O_4S_2$: C, 59.45; H, 4.69; N, 12.60. Found: C, 58.88; H, 4.54; N, 12.86. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.22 (d, J = 1.8 Hz, 2H, C_6H_5), 7.36 (d, J = 1.8 Hz, 2H, C_6H_5), 7.08 (dd, J = 8.4 & 1.5 Hz, 2H, C_6H_5), 6.97−7.00 (overlap, 6H, C_6H_5), 6.80 (d, J = 8.4 Hz, 4H, C_6H_5), 6.72 (m, 2H, C_6H_5), 6.66 (dd, J = 8.4 & 1.2 Hz, 2H, C_6H_5), 6.43 (t, J = 2.4 Hz, 2H, C_6H_5), 2.20 (s, 6H, −CH_3), 0.28 (s, 3H, Al−CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 141.1, 138.9, 133.2, 132.2 (C_{ipso}−C_6H_5), 141.3, 129.8, 129.1, 128.5, 127.9, 125.7, 124.9, 120.0, 106.8 (CH−C_6H_5), 21.2 (−CH_3), −5.2 (Al−CH_3). ^{27}Al NMR (156 MHz): δ 56.7 ($\Delta\nu_{1/2}$ = 5462.2).

4.19. ($NPz^HSO_2Ph^{TriMe}$)$AlMe_2$ (**6**)

The procedure for the preparation of **6** was similar to that used for **1** but with $HNPz^HSO_2Ph^{TriMe}$ (0.41 g, 1.0 mmol). A white solid was obtained (0.258 g, 65.0%). Anal. Calc. for $C_{20}H_{24}N_3O_2SAl$: C, 60.44; H, 6.09; N, 10.57. Found: C, 60.09; H, 6.30; N, 11.02. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 8.05 (d, J = 3.0 Hz, 1H, C_6H_5), 7.95 (d, J = 2.4 Hz, 1H, C_6H_5), 7.38 (dd, J = 8.4 & 1.2 Hz, 1H, C_6H_5), 7.33 (dd, J = 8.4 & 1.5 Hz, 1H, C_6H_5), 7.20 (td, J = 7.8 & 1.6 Hz, 1H, C_6H_5), 7.10 (m, 1H, C_6H_5), 6.85 (s, 2H, C_6H_5), 6.70 (t, J = 2.4 Hz, 1H, C_6H_5), 2.51 (s, 6H, o-CH_3−Ph), 2.25 (s, 3H, p-CH_3−Ph), −0.65 (s, 6H, Al−CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 141.5, 138.9, 135.7, 134.5, 129.1 (C_{ipso}−C_6H_5), 140.6, 131.7, 131.4, 129.0, 124.5, 123.8, 121.4, 108.4 (CH−C_6H_5), 22.7 (o-CH_3−Ph), 20.7 (p-CH_3−Ph), −8.8 (Al−CH_3). ^{27}Al NMR (156 MHz): δ 134.9 ($\Delta\nu_{1/2}$ = 7256.9).

4.20. ($NPz^HSO_2Ph^F$)$AlMe_2$ (**7**)

The procedure for the preparation of **7** was similar to that used for **1** but with $HNPz^HSO_2Ph^F$ (0.317 g, 1.0 mmol). A white solid was obtained (0.224 g, 60.0%). Anal. Calc. for $C_{17}H_{17}FN_3O_2SAl$: C, 54.68; H, 4.59; N, 11.25. Found: C, 54.28; H, 4.90; N, 11.08. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.89 (m, 1H, C_6H_5), 7.79 (dd, J = 8.4 & 1.2 Hz, 2H, C_6H_5), 7.63−7.67 (overlap, 2H, C_6H_5), 7.29−7.35 (overlap, 2H, C_6H_5), 7.16 (m, 1H, C_6H_5), 6.97 (m, 2H, C_6H_5), 6.63 (t, J = 2.4 Hz, 1H, C_6H_5), −0.62 (s, 6H, Al−CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 165.7, 163.2 (C_{ipso}−C_6H_5), 137.1, 133.2 (J_{C-F} = 12.4 Hz), 140.8, 130.8, 129.28, 129.26, 129.2, 126.2, 124.3, 120.7, 115.9, 115.7, 108.3 (CH−C_6H_5), −8.9 (Al−CH_3). ^{27}Al NMR (156 MHz): δ 127.0 ($\Delta\nu_{1/2}$ = 10418.0).

4.21. ($NPz^{Me}SO_2Ph^H$)$AlMe_2$ (**8**)

The procedure for the preparation of **8** was similar to that used for **1** but with $HNPz^{Me}SO_2Ph^H$ (0.327 g, 1.0 mmol). A white solid was obtained (0.268 g, 70.0%). Anal. Calc. for $C_{19}H_{22}N_3O_2SAl$: C, 59.51; H, 5.78; N, 10.96. Found: C, 59.81; H, 6.16; N, 10.55. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.87 (dd, J = 7.8 & 1.2 Hz, 1H, C_6H_5), 7.43 (td, J = 8.1 & 1.4 Hz, 1H, C_6H_5), 7.39 (m, 2H, C_6H_5), 7.29 (t, J = 7.5 Hz, 1H, C_6H_5), 7.16−7.22 (overlap, 3H, C_6H_5), 6.96 (dd, J = 7.8 & 1.2 Hz, 1H, C_6H_5), 5.96 (s, 1H, C_6H_5), 2.38 (s, 3H, −CH_3), 1.96 (s, 3H, −CH_3), −0.72 (s, 6H,

Al–CH_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 151.0, 143.8, 142.5, 135.2, 130.9 (C_{ipso}–C_6H_5), 131.4, 130.7, 129.3, 128.0, 125.3, 125.2, 123.8, 108.8 (*C*H–C_6H_5), 13.0 (–*C*H_3), 12.7 (–*C*H_3), –9.8 (Al–*C*H_3). ^{27}Al NMR (156 MHz): δ 142.0 ($\Delta\nu_{1/2}$ = 9324.6).

4.22. ($NPz^{Me}SO_2Ph^{Me}$)$AlMe_2$ (**9**)

The procedure for the preparation of **9** was similar to that used for **1** but with $HNPz^{Me}SO_2Ph^{Me}$ (0.341 g, 1.0 mmol). A white solid was obtained (0.278 g, 70.0%). Anal. Calc. for $C_{20}H_{24}N_3O_2SAl$: C, 60.44; H, 6.09; N, 10.57. Found: C, 60.19; H, 5.83; N, 10.38. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.85 (dd, *J* = 7.8 & 1.5 Hz, 1H, C_6H_5), 7.41 (m, 1H, C_6H_5), 7.26–7.29 (overlap, 2H, C_6H_5), 7.19 (td, *J* = 7.8 & 1.0 Hz, 1H, C_6H_5), 6.94–6.98 (overlap, 3H, C_6H_5), 5.99 (br, 1H, C_6H_5), 2.39 (s, 3H, –*C*H_3), 2.29 (s, 3H, –*C*H_3), 1.98 (s, 3H, –*C*H_3), –0.72 (s, 6H, Al–*C*H_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 151.4, 143.7, 141.1, 140.2, 136.0, 131.0 (C_{ipso}–C_6H_5), 131.4, 129.7, 128.7, 125.8, 125.0, 123.8, 108.8 (*C*H–C_6H_5), 21.3 (–*C*H_3), 13.4 (–*C*H_3), 12.8 (–*C*H_3), –9.6 (Al–*C*H_3). ^{27}Al NMR (156 MHz): δ 117.4 ($\Delta\nu_{1/2}$ = 8559.8).

4.23. ($NPz^{Me}SO_2Ph^{TriMe}$)$AlMe_2$ (**10**)

The procedure for the preparation of **10** was similar to that used for **1** but with $HNPz^{Me}SO_2Ph^{TriMe}$ (0.369 g, 1.0 mmol). A white solid was obtained (0.258 g, 65.0%). Anal. Calc. for $C_{20}H_{24}N_3O_2SAl$: C, 62.10; H, 6.63; N, 9.87. Found: C, 62.42; H, 7.10; N, 9.86. ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 7.63 (d, *J* = 8.4 Hz, 1H, C_6H_5), 7.28 (t, *J* = 7.2 Hz, 1H, C_6H_5), 7.15 (t, *J* = 7.2 Hz, 1H, C_6H_5), 7.01 (d, *J* = 7.8 Hz, 1H, C_6H_5), 6.70 (br, 2H, C_6H_5), 6.17 (br, 1H, C_6H_5), 2.40 (s, 3H, –*C*H_3), 2.31 (s, 6H, *o*-*C*H_3–Ph), 2.18 (s, 3H, *p*-*C*H_3–Ph), 2.07 (s, 3H, –*C*H_3), –0.75 (s, 6H, Al–*C*H_3). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm) 151.6, 144.2, 140.4, 138.7, 136.2, 131.6 (C_{ipso}–C_6H_5), 131.1, 129.6, 129.3, 125.0, 124.4, 108.9 (*C*H–C_6H_5), 22.6 (*o*-*C*H_3–Ph), 20.6 (*p*-*C*H_3–Ph), 13.3 (–*C*H_3), 12.4 (–*C*H_3), –9.4 (Al–*C*H_3). ^{27}Al NMR (156 MHz): δ 109.6 ($\Delta\nu_{1/2}$ = 8913.9).

4.24. Polymerization procedure of ε-caprolactone

Typically, to a flask containing prescribed amount of monomers (ε-caprolactone) and catalyst precursors (0.125 mmol) were added 15 mL (containing 0.25 mmol benzyl alcohol) toluene. The reaction mixture was stirred at prescribed temperature for the prescribed time. After the reaction was quenched by the addition of 5 mL acetic acid solution (0.35 N), the resulting mixture was poured into 25 mL *n*-heptane to precipitate polymers. Crude products were recrystallized from THF–hexane and dried *in vacuo* up to a constant weight. Conversion was determined from ^{1}H NMR in $CDCl_3$ by comparison with remaining monomer.

Table 2
Summary of crystal data for compounds **2**, **5′** and **8**.

	2	**5′**	**8**
Formula	$C_{20}H_{25}AlN_2O_3S$	$C_{33}H_{31}AlN_6O_4S_2$	$C_{19}H_{22}AlN_3O_2S$
Fw	400.46	666.74	383.44
T, K	100(2)	100(2)	100(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2(1)/*n*	*C*2/*c*	*Cc*
a, Å	9.6494(7)	18.547(2)	14.8142(4)
b, Å	19.8856(14)	14.6025(12)	9.1392(4)
c, Å	10.5417(9)	12.6021(13)	16.1837(6)
α°	90	90	90
β°	97.995(7)	115.724(14)	116.253(6)
γ°	90	90	90
V, Å^3	2003.1(3)	3074.7(5)	1965.10(12)
z	4	4	4
ρ_{calc}, Mg/m^3	1.328	1.440	1.296
μ(Mo Kα), mm^{-1}	0.228	0.252	0.227
Reflections collected	9864	12,588	10,556
No. of parameters	244	217	235
R1[a]	0.0731	0.0503	0.0409
wR2[a]	0.1329	0.1135	0.1075
GoF[b]	1.000	1.002	0.991

[a] $R1 = [\Sigma|F_0| - |F_c|]/\Sigma|F_0|]$; $wR2 = [\Sigma w(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$, $w = 0.10$.
[b] $GoF = [\Sigma w(F_0^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

4.25. Crystal structure data

Crystals were grown from CH_2Cl_2/hexane solution for **2**, concentrated toluene solution **5′**, THF/hexane solution **8** and concentrated CH_2Cl_2 solution $\mathbf{N(SO_2Ph^F)_2Pz^H}$ and isolated by filtration. Suitable crystals were mounted on Mounted CryoLoop (HAMPTON RESEARCH, size: 0.5–0.7 mm) using perfluoropolyether vacuum oil (Aldrich, FOMBLIN®Y) and cooled rapidly in a stream of cold nitrogen gas using an Oxford Diffraction Limited GEMINT S. For crystals **6** and **7**, empirical absorption correction was based on spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm from CrysAlis RED, Oxford Diffraction Ltd. The space group determination was based on a check of the Laue symmetry and systematic absences and was confirmed using the structure solution. The structure was solved by direct methods using a SHELXTL package [52]. All non-H atoms were located from successive Fourier maps, and hydrogen atoms were refined using a riding model. Anisotropic thermal parameters were used for all non-H atoms, and fixed isotropic parameters were used for H atoms. Some details of the data collection and refinement are given in Table 2 (for **2**, **5′** and **8**) and Table S1 [for $\mathbf{HN(SO_2Ph^F)_2Pz^H}$].

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.12.022.

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