Supporting Information

Self-Assembled Bimetallic Aluminum-Salen Catalyst for the Cyclic Carbonates Synthesis

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1. Materials and instrumentation

Experiments involving moisture and/or air sensitive components were performed in flame-dried glassware under a positive pressure of argon (99.999% was purchased from Sinil gas (Co.)) and/or carbon dioxide (99.99% was purchased from Sinil gas (Co.), filtered over drying column that packed with activated carbon and 4 Å molecular sieve). Oxiranes (epoxides) were distilled by calcium hydride and stored over 4 Å molecular sieve. Other reagents were commercially purchased by sigma Aldrich (Co.) (Saint Louis, MO, USA), Acros Organics (Co.) (Somerset, N.J., USA) Alfa

Aeser (Co.) (Haverhill, MA, USA) and were used as received without further purification for the reaction. Tetrahydrofuran (THF), dichloromethan (DCM) and *N*-dimethylformamide (DMF) were dried by J.C. Meyer solvent purification system.

Proton nuclear magnetic resonance (^{1}H NMR) was performed on a JEOL 400 Mhz NMR spectrometers. Chemical shift ^{1}H NMR spectra are reported as in units of ppm (part per million) downfield or up-field from $CDCl_3$ (7.26, singlet), DMSO-d6 (2.50, multiplet). High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 MStation mass spectrometer. All FTIR samples were mixed with mineral oil as powder on KBr windows. IR spectra were obtained using an ATR-IR spectrometer (AlPHA ll) with a universal sampling module (A230/D, QuickSnap) as an accessory. The solution IR was obtained by using Speca (Co.) "Omni-Cell traditional liquid transmission cell" with "Omni-Cell PTFE spacers rectangular 0.10 mm" with KBr windows.

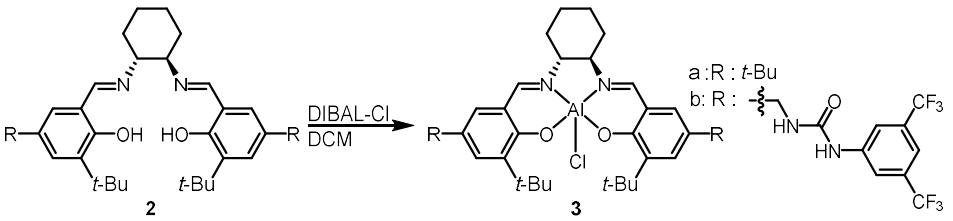
TLC was used on Merk (Co.) pre-coated 60 Å (F254) silica gel glass plates and the TLC spots were visualized under 254 nm, 365 nm UV light and iodine staining. All flash column chromatography was performed through Merk 230–400 Mesh 60 Å silica gel.

2. Catalyst preparation

Ligand 2a, 2b was prepared according to the literature[1].

Jacobson salen ligand aluminum chloride complex (**3a**) was prepared by following procedure. 437 mg (0.80 mmol, 1.00 equiv.) of Jacobson ligand (**2a**) and 0.84 mL of di(*iso*-butyl)aluminum chloride (DIBAL-Cl, *w*/*w* 25% in hexane, 0.80 mmol, 1 equiv.) placed in 50 mL Schlenk flask. 15 mL of dichloromethane (DCM) was added to flask. Stir for 20 hours in room temperature. After stir, the reaction mixture was dried under low pressure. And washed with 15 mL of dried hexane 3 times. 484 mg (99% yield) of yellow solid was prepared.

(R,R)-Bis(bis(3,5-trifluoromethylphenyl)ureido)-(salen)aluminum complex (**3b**) was prepared by following procedure. 91.6 mg (0.09 mmol, 1.00 equiv.) of (R,R)-Bis(bis(3,5-trifluoromethylphenyl)ureido)-(salen) (**2b**) and 0.10 mL of di(*iso*-butyl)aluminum chloride (DIBAL-Cl, *w*/*w* 25% in hexane, 0.09 mmol, 1.00 equiv.) placed in 10 mL Schlenk flask. 2 mL of dichloromethane (DCM) was added to flask. Stir for 20 hours in room temperature. After stir, the reaction mixture was dried under low pressure. And the crude solid was washed with 3 mL of dried hexane, 3 times. 110 mg (99% yield) of white-yellow solid was prepared.



1. Park, J.; Lang, K.; Abboud, K. A.; Hong, S.; *Chem. Eur. J.* **2011**, *17*, 2236–2245.

3. Cyclic carbonates synthesis

1 bar of CO_2 and 45 °C reaction condition

5000 equiv. of dried oxirane (47.0 mmol) was placed in a Teflon capped Schlenk flask, 1 equiv. (0.009 mmol) of catalyst and 1 equiv. (0.009 mmol) of ammonium halide were added to the flask. The mixture was degassed by lyophilization 3 times. The degassed mixture was heated up to room temperature. Dried CO_2 was packed in the flask and Teflon cap was closed. The mixture in flask was stirred for 3 hours at 45 °C. After stirred, the reaction mixture was cooled down to room temperature and filtered over silica-gel (5 cm) with DCM. The filtrate was concentrated under reduced pressure. Clear or off yellow oil was prepared.

10 bar of CO_2 and 90 °C reaction condition

5000 equiv. of dried oxirane (47.0 mmol) was placed in in a 10 mL stainless steel bomb reactor, 1 equiv. (0.009 mmol) of catalyst and 1 equiv. (0.009 mmol) of ammonium halide were added to the reactor. The reactor was purged to 5 bar of dried CO_2, 3 times. 10 bar of dried CO_2 was packed in the reactor through sealed gas connector. The reactor was stirred for 3 hours at 90 °C. After stirred the reaction mixture was cooled down to ambient temperature (ice bath, 30 min.) and filtered over silica-gel (5 cm) with DCM. The filtrate was concentrated under reduced pressure. Clear or off yellow oil was prepared.

4. X-ray experiment

Data were collected at 173 K on a Siemens SMART PLATFORM equipped with A CCD area detector and a graphite monochromator utilizing MoK_α radiation (λ = 0.71073 Å). Cell parameters were refined using up to 8192 reflections. A full sphere of data (1850 frames) was collected using the ω-scan method (0.3° frame width). The first 50 frames were re-measured at the end of data collection to monitor instrument and crystal stability (maximum correction on I was < 1 %). Absorption corrections by integration were applied based on measured indexed crystal faces.

The structure was solved by the Direct Methods in *SHELXTL6*, and refined using full-matrix least squares. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were calculated in ideal positions and were riding on their respective carbon atoms. The asymmetric unit consists of the Ni complex and a dimethylfromamide solvent molecule. All four CF3 groups have the fluorine atoms disordered. Each group was refined in two parts with their site occupation factors fixed at 0.5 after having refined to near this value. The C atoms, with their protons, are also disordered. They are atoms C1, C4 and C6. They were also refined in two parts each and given 0.5 values for each

disordered part. A total of 686 parameters were refined in the final cycle of refinement using 9198 reflections with I > 2σ(I) to yield R_1 and wR_2 of 5.51% and 11.03%, respectively. Refinement was done using F^2.

SHELXTL6 (2000). Bruker-AXS, Madison, Wisconsin, USA.

5. Crystal structure of bis-urea salen Ni complex (4)

CCDC : 2080102, 2080103

Table S1. Crystal data and structure refinement for park4.

Identification code	park4	
Empirical formula	C51 H55 F12 N7 Ni O5	
Formula weight	1132.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.3525(13) Å	α = 91.018(3)°.
	b = 13.0965(17) Å	β = 97.294(2)°.
	c = 20.515(3) Å	γ = 94.674(3)°.
Volume	2483.2(6) $Å^3$	
Z	2	
Density (calculated)	1.515 Mg/m^3	
Absorption coefficient	0.492 mm^{-1}	
F(000)	1172	
Crystal size	0.31 × 0.12 × 0.05 mm^3	
Theta range for data collection	1.56 to 27.50°.	
Index ranges	$-12 \le h \le 12$, $-14 \le k \le 17$, $-26 \le l \le 24$	
Reflections collected	27913	

Independent reflections	11151 [R(int) = 0.0294]
Completeness to theta = 27.50°	97.9 %
Absorption correction	None
Max. and min. transmission	0.9768 and 0.8632
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	11151 / 0 / 686
Goodness-of-fit on F^2	1.158
Final R indices [I>2sigma(I)]	R1 = 0.0551, wR2 = 0.1103 [9198]
R indices (all data)	R1 = 0.0695, wR2 = 0.1151
Largest diff. peak and hole	0.585 and -0.615 e.$Å^{-3}$

$R1 = \Sigma(||F_O| - |F_C||) / \Sigma|F_O|$ $wR2 = [\Sigma[w(F_O^2 - F_C^2)^2] / \Sigma[w(F_O^2)^2]]^{1/2}$

$S = [\Sigma[w(F_O^2 - F_C^2)^2] / (n-p)]^{1/2}$ $w = 1/[\sigma^2(F_O^2)+(m*p)^2+n*p]$, $p = [\max(F_O^2,0)+ 2* F_C^2]/3$, m & n are constants.

Table S2. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3) for park4. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ni1	2500(1)	-777(1)	-137(1)	12(1)
F1	12614(5)	4737(4)	3837(2)	24(1)
F2	12138(4)	4227(3)	4785(2)	18(1)
F3	11569(5)	5736(4)	4381(2)	18(1)
F1'	12473(5)	4941(4)	3704(2)	26(1)
F2'	12376(5)	4196(4)	4624(2)	26(1)
F3'	11496(5)	5639(4)	4542(2)	20(1)
F4	5311(5)	4424(3)	3058(2)	18(1)
F5	6520(5)	5782(3)	3497(2)	20(1)
F6	5742(5)	4707(4)	4183(3)	22(1)
F4'	5161(5)	4296(3)	3204(2)	18(1)
F5'	6573(5)	5744(4)	3305(2)	24(1)
F6'	5816(6)	4927(4)	4109(3)	27(2)
F7	62(6)	1141(5)	-5316(3)	25(2)
F8	747(5)	1271(4)	-4273(2)	20(1)
F9	50(6)	2573(4)	-4849(3)	24(1)
F7'	-130(6)	1238(5)	-5415(3)	25(2)
F8'	716(5)	1054(4)	-4396(2)	23(1)
F9'	231(6)	2570(4)	-4704(3)	23(1)
F10	-6715(6)	1967(4)	-5050(3)	27(2)
F11	-5334(7)	2648(5)	-5679(3)	23(2)
F12	-5169(5)	3281(3)	-4779(2)	20(1)

F10'	-6737(5)	1798(4)	-5169(3)	21(1)
F11'	-5156(7)	2578(5)	-5746(3)	25(2)
F12'	-5502(5)	3122(4)	-4690(2)	25(1)
O1	3395(2)	-1684(2)	432(1)	18(1)
O2	1919(2)	-1909(2)	-690(1)	17(1)
O3	6598(2)	1055(2)	3208(1)	18(1)
O4	-1802(2)	-1189(2)	-3436(1)	17(1)
O5	617(3)	8947(2)	2416(1)	31(1)
N1	3242(3)	379(2)	360(1)	21(1)
N2	1422(3)	94(2)	-651(1)	21(1)
N3	8210(3)	62(2)	2831(1)	17(1)
N4	8917(3)	1729(2)	3148(1)	16(1)
N5	-3669(3)	-1632(2)	-2861(1)	15(1)
N6	-3889(3)	-365(2)	-3613(1)	17(1)
N7	1690(3)	7604(2)	2895(1)	24(1)
C1	2908(7)	1360(4)	39(3)	14(1)
C6	1366(6)	1111(4)	-279(3)	15(1)
C1'	2332(7)	1277(5)	195(3)	16(1)
C6'	1976(6)	1195(4)	-546(3)	12(1)
C2	3037(3)	2306(2)	460(2)	22(1)
C3	2179(4)	3163(3)	175(2)	27(1)
C4	845(7)	2925(5)	-219(3)	21(1)
C4'	1529(6)	3044(5)	-563(3)	18(1)
C5	870(3)	1975(2)	-734(2)	23(1)
C7	4215(4)	408(2)	867(2)	23(1)
C8	4757(3)	-462(2)	1200(1)	17(1)
C9	4239(3)	-1479(2)	987(1)	14(1)

C10	4684(3)	-2303(2)	1402(1)	15(1)
C11	5664(3)	-2059(2)	1958(1)	15(1)
C12	6236(3)	-1052(2)	2148(1)	16(1)
C13	5758(3)	-264(2)	1770(1)	16(1)
C14	4039(3)	-3413(2)	1241(1)	16(1)
C15	2376(3)	-3460(2)	1210(2)	19(1)
C16	4437(3)	-3802(2)	586(2)	24(1)
C17	4590(3)	-4160(2)	1768(2)	22(1)
C18	421(3)	-164(2)	-1129(2)	20(1)
C19	47(3)	-1181(2)	-1392(1)	14(1)
C20	870(3)	-2003(2)	-1179(1)	14(1)
C21	520(3)	-2978(2)	-1523(1)	13(1)
C22	-727(3)	-3092(2)	-1968(1)	15(1)
C23	-1623(3)	-2296(2)	-2132(1)	14(1)
C24	-1204(3)	-1342(2)	-1861(1)	14(1)
C25	1494(3)	-3855(2)	-1384(2)	17(1)
C26	3068(3)	-3478(3)	-1472(2)	26(1)
C27	1430(4)	-4226(2)	-682(2)	25(1)
C28	1038(3)	-4778(2)	-1863(2)	20(1)
C29	7251(3)	-879(2)	2787(1)	18(1)
C30	7835(3)	951(2)	3071(1)	14(1)
C31	8848(3)	2716(2)	3404(1)	14(1)
C32	10149(3)	3232(2)	3691(1)	15(1)
C33	10184(3)	4230(2)	3927(1)	16(1)
C34	8941(3)	4748(2)	3899(1)	17(1)
C35	7651(3)	4224(2)	3612(1)	16(1)
C36	7579(3)	3222(2)	3370(1)	15(1)

C37	11626(3)	4745(2)	4221(2)	21(1)
C38	6304(3)	4787(2)	3575(2)	22(1)
C39	-3019(3)	-2535(2)	-2592(1)	16(1)
C40	-3030(3)	-1076(2)	-3312(1)	14(1)
C41	-3491(3)	356(2)	-4066(1)	15(1)
C42	-2062(3)	578(2)	-4196(1)	16(1)
C43	-1764(3)	1333(2)	-4633(2)	18(1)
C44	-2835(3)	1890(2)	-4953(1)	19(1)
C45	-4240(3)	1668(2)	-4819(1)	18(1)
C46	-4581(3)	911(2)	-4384(1)	17(1)
C47	-226(3)	1560(2)	-4775(2)	21(1)
C48	-5389(3)	2336(2)	-5096(2)	22(1)
C49	1689(4)	8510(3)	2613(2)	24(1)
C50	324(4)	7038(3)	2988(2)	36(1)
C51	3004(4)	7180(3)	3178(2)	34(1)

Table S3. Bond lengths [Å] and angles [°] for park4.

Ni1-N2	1.842(2)
Ni1-N1	1.846(3)
Ni1-O2	1.853(2)
Ni1-O1	1.855(2)
F1-C37	1.289(5)
F2-C37	1.403(5)
F3-C37	1.340(5)
F1'-C37	1.417(6)
F2'-C37	1.284(5)
F3'-C37	1.355(6)
F4-C38	1.368(5)
F5-C38	1.318(5)
F6-C38	1.417(6)
F4'-C38	1.341(5)
F5'-C38	1.397(6)
F6'-C38	1.256(6)
F7-C47	1.297(7)
F8-C47	1.365(5)
F9-C47	1.346(6)
F7'-C47	1.389(7)
F8'-C47	1.327(6)
F9'-C47	1.355(6)
F10-C48	1.309(6)
F11-C48	1.276(7)
F12-C48	1.375(5)

F10'-C48	1.382(6)
F11'-C48	1.415(7)
F12'-C48	1.332(6)
O1-C9	1.310(3)
O2-C20	1.307(3)
O3-C30	1.242(3)
O4-C40	1.227(3)
O5-C49	1.223(4)
N1-C7	1.290(4)
N1-C1	1.493(6)
N1-C1'	1.525(6)
N2-C18	1.287(4)
N2-C6'	1.495(6)
N2-C6	1.531(6)
N3-C30	1.346(4)
N3-C29	1.458(4)
N3-H3	0.79(4)
N4-C30	1.369(4)
N4-C31	1.395(4)
N4-H4	0.82(3)
N5-C40	1.355(4)
N5-C39	1.458(4)
N5-H5	0.89(3)
N6-C40	1.383(4)
N6-C41	1.399(4)
N6-H6	0.86(4)
N7-C49	1.330(4)

N7-C51	1.448(4)
N7-C50	1.460(5)
C1-C2	1.486(6)
C1-C6	1.513(8)
C1-H1A	1.0000
C6-C5	1.543(6)
C6-H6A	1.0000
C1'-C2	1.512(7)
C1'-C6'	1.514(8)
C1'-H1'A	1.0000
C6'-C5	1.532(6)
C6'-H6'A	1.0000
C2-C3	1.515(4)
C2-H2A	0.9900
C2-H2B	0.9900
C2-H2C	0.9900
C2-H2D	0.9900
C3-C4	1.407(7)
C3-C4'	1.559(7)
C3-H3A	0.9900
C3-H3B	0.9900
C3-H3C	0.9900
C3-H3D	0.9900
C4-C5	1.622(7)
C4-H4A	0.9900
C4-H4B	0.9900
C4'-C5	1.499(7)

C4'-H4'A	0.9900
C4'-H4'B	0.9900
C5-H5A	0.9900
C5-H5B	0.9900
C5-H5C	0.9900
C5-H5D	0.9900
C7-C8	1.433(4)
C7-H7A	0.9500
C8-C13	1.410(4)
C8-C9	1.421(4)
C9-C10	1.442(4)
C10-C11	1.384(4)
C10-C14	1.542(4)
C11-C12	1.412(4)
C11-H11A	0.9500
C12-C13	1.371(4)
C12-C29	1.519(4)
C13-H13A	0.9500
C14-C16	1.530(4)
C14-C17	1.540(4)
C14-C15	1.545(4)
C15-H15A	0.9800
C15-H15B	0.9800
C15-H15C	0.9800
C16-H16A	0.9800
C16-H16B	0.9800
C16-H16C	0.9800

C17-H17A	0.9800
C17-H17B	0.9800
C17-H17C	0.9800
C18-C19	1.428(4)
C18-H18A	0.9500
C19-C24	1.416(4)
C19-C20	1.417(4)
C20-C21	1.441(4)
C21-C22	1.383(4)
C21-C25	1.532(4)
C22-C23	1.409(4)
C22-H22A	0.9500
C23-C24	1.365(4)
C23-C39	1.518(4)
C24-H24A	0.9500
C25-C27	1.535(4)
C25-C28	1.541(4)
C25-C26	1.548(4)
C26-H26A	0.9800
C26-H26B	0.9800
C26-H26C	0.9800
C27-H27A	0.9800
C27-H27B	0.9800
C27-H27C	0.9800
C28-H28A	0.9800
C28-H28B	0.9800
C28-H28C	0.9800

C29-H29A	0.9900
C29-H29B	0.9900
C31-C32	1.397(4)
C31-C36	1.401(4)
C32-C33	1.383(4)
C32-H32A	0.9500
C33-C34	1.388(4)
C33-C37	1.506(4)
C34-C35	1.394(4)
C34-H34A	0.9500
C35-C36	1.387(4)
C35-C38	1.505(4)
C36-H36A	0.9500
C39-H39A	0.9900
C39-H39B	0.9900
C41-C46	1.401(4)
C41-C42	1.404(4)
C42-C43	1.382(4)
C42-H42A	0.9500
C43-C44	1.392(4)
C43-C47	1.510(4)
C44-C45	1.385(4)
C44-H44A	0.9500
C45-C46	1.390(4)
C45-C48	1.503(4)
C46-H46A	0.9500
C49-H49A	0.9500

C50-H50A	0.9800
C50-H50B	0.9800
C50-H50C	0.9800
C51-H51A	0.9800
C51-H51B	0.9800
C51-H51C	0.9800

N2-Ni1-N1	85.93(11)
N2-Ni1-O2	94.02(10)
N1-Ni1-O2	173.75(11)
N2-Ni1-O1	173.20(11)
N1-Ni1-O1	94.74(10)
O2-Ni1-O1	86.05(9)
C9-O1-Ni1	128.39(19)
C20-O2-Ni1	128.00(18)
C7-N1-C1	118.6(3)
C7-N1-C1'	121.8(3)
C1-N1-C1'	25.4(3)
C7-N1-Ni1	125.9(2)
C1-N1-Ni1	113.9(3)
C1'-N1-Ni1	111.0(3)
C18-N2-C6'	119.4(3)
C18-N2-C6	118.4(3)
C6'-N2-C6	32.3(3)
C18-N2-Ni1	126.7(2)
C6'-N2-Ni1	113.2(2)
C6-N2-Ni1	110.3(2)

C30-N3-C29	122.3(3)
C30-N3-H3	122(3)
C29-N3-H3	115(3)
C30-N4-C31	127.2(2)
C30-N4-H4	115(2)
C31-N4-H4	116(2)
C40-N5-C39	119.8(2)
C40-N5-H5	116(2)
C39-N5-H5	121(2)
C40-N6-C41	126.4(2)
C40-N6-H6	119(2)
C41-N6-H6	114(2)
C49-N7-C51	122.7(3)
C49-N7-C50	120.0(3)
C51-N7-C50	117.0(3)
C2-C1-N1	118.1(4)
C2-C1-C6	111.0(4)
N1-C1-C6	102.0(4)
C2-C1-H1A	108.5
N1-C1-H1A	108.5
C6-C1-H1A	108.5
C1-C6-N2	103.7(4)
C1-C6-C5	110.8(4)
N2-C6-C5	112.9(4)
C1-C6-H6A	109.8
N2-C6-H6A	109.8
C5-C6-H6A	109.8

C2-C1'-C6'	114.8(5)
C2-C1'-N1	114.5(4)
C6'-C1'-N1	103.8(4)
C2-C1'-H1'A	107.8
C6'-C1'-H1'A	107.8
N1-C1'-H1'A	107.8
N2-C6'-C1'	101.8(4)
N2-C6'-C5	115.7(4)
C1'-C6'-C5	106.4(4)
N2-C6'-H6'A	110.8
C1'-C6'-H6'A	110.8
C5-C6'-H6'A	110.8
C1-C2-C1'	25.6(3)
C1-C2-C3	115.0(3)
C1'-C2-C3	110.4(3)
C1-C2-H2A	108.5
C1'-C2-H2A	130.6
C3-C2-H2A	108.5
C1-C2-H2B	108.5
C1'-C2-H2B	87.5
C3-C2-H2B	108.5
H2A-C2-H2B	107.5
C1-C2-H2C	84.8
C1'-C2-H2C	109.6
C3-C2-H2C	109.6
H2A-C2-H2C	26.7
H2B-C2-H2C	128.6

C1-C2-H2D	125.7
C1'-C2-H2D	109.6
C3-C2-H2D	109.6
H2A-C2-H2D	84.0
H2B-C2-H2D	25.0
H2C-C2-H2D	108.1
C4-C3-C2	119.8(4)
C4-C3-C4'	39.7(3)
C2-C3-C4'	117.0(3)
C4-C3-H3A	107.4
C2-C3-H3A	107.4
C4'-C3-H3A	134.1
C4-C3-H3B	107.4
C2-C3-H3B	107.4
C4'-C3-H3B	71.2
H3A-C3-H3B	106.9
C4-C3-H3C	130.7
C2-C3-H3C	108.0
C4'-C3-H3C	108.0
H3A-C3-H3C	66.2
H3B-C3-H3C	42.6
C4-C3-H3D	70.0
C2-C3-H3D	108.0
C4'-C3-H3D	108.0
H3A-C3-H3D	43.6
H3B-C3-H3D	139.7
H3C-C3-H3D	107.3

C3-C4-C5	113.1(4)
C3-C4-H4A	108.9
C5-C4-H4A	108.9
C3-C4-H4B	108.9
C5-C4-H4B	108.9
H4A-C4-H4B	107.8
C5-C4'-C3	111.7(4)
C5-C4'-H4'A	109.3
C3-C4'-H4'A	109.3
C5-C4'-H4'B	109.3
C3-C4'-H4'B	109.3
H4'A-C4'-H4'B	108.0
C4'-C5-C6'	110.5(4)
C4'-C5-C6	117.7(4)
C6'-C5-C6	31.7(3)
C4'-C5-C4	37.8(3)
C6'-C5-C4	116.8(4)
C6-C5-C4	102.5(4)
C4'-C5-H5A	125.8
C6'-C5-H5A	123.4
C6-C5-H5A	111.3
C4-C5-H5A	111.3
C4'-C5-H5B	73.5
C6'-C5-H5B	79.5
C6-C5-H5B	111.3
C4-C5-H5B	111.3
H5A-C5-H5B	109.2

C4'-C5-H5C	109.6
C6'-C5-H5C	109.6
C6-C5-H5C	126.8
C4-C5-H5C	130.3
H5A-C5-H5C	49.1
H5B-C5-H5C	60.2
C4'-C5-H5D	109.6
C6'-C5-H5D	109.6
C6-C5-H5D	78.3
C4-C5-H5D	72.7
H5A-C5-H5D	59.1
H5B-C5-H5D	167.7
H5C-C5-H5D	108.1
N1-C7-C8	126.0(3)
N1-C7-H7A	117.0
C8-C7-H7A	117.0
C13-C8-C9	121.4(3)
C13-C8-C7	117.1(3)
C9-C8-C7	121.4(3)
O1-C9-C8	122.4(3)
O1-C9-C10	119.8(3)
C8-C9-C10	117.7(2)
C11-C10-C9	118.0(3)
C11-C10-C14	121.4(3)
C9-C10-C14	120.6(2)
C10-C11-C12	124.0(3)
C10-C11-H11A	118.0

C12-C11-H11A	118.0
C13-C12-C11	118.0(3)
C13-C12-C29	122.9(3)
C11-C12-C29	119.0(3)
C12-C13-C8	120.7(3)
C12-C13-H13A	119.6
C8-C13-H13A	119.6
C16-C14-C17	107.0(2)
C16-C14-C10	111.2(2)
C17-C14-C10	112.1(2)
C16-C14-C15	109.5(2)
C17-C14-C15	107.5(2)
C10-C14-C15	109.3(2)
C14-C15-H15A	109.5
C14-C15-H15B	109.5
H15A-C15-H15B	109.5
C14-C15-H15C	109.5
H15A-C15-H15C	109.5
H15B-C15-H15C	109.5
C14-C16-H16A	109.5
C14-C16-H16B	109.5
H16A-C16-H16B	109.5
C14-C16-H16C	109.5
H16A-C16-H16C	109.5
H16B-C16-H16C	109.5
C14-C17-H17A	109.5
C14-C17-H17B	109.5

H17A-C17-H17B	109.5
C14-C17-H17C	109.5
H17A-C17-H17C	109.5
H17B-C17-H17C	109.5
N2-C18-C19	125.2(3)
N2-C18-H18A	117.4
C19-C18-H18A	117.4
C24-C19-C20	121.3(3)
C24-C19-C18	117.3(3)
C20-C19-C18	121.4(3)
O2-C20-C19	122.8(3)
O2-C20-C21	119.5(2)
C19-C20-C21	117.7(2)
C22-C21-C20	117.7(3)
C22-C21-C25	121.9(3)
C20-C21-C25	120.4(2)
C21-C22-C23	123.9(3)
C21-C22-H22A	118.1
C23-C22-H22A	118.1
C24-C23-C22	118.3(3)
C24-C23-C39	122.8(3)
C22-C23-C39	118.9(3)
C23-C24-C19	120.4(3)
C23-C24-H24A	119.8
C19-C24-H24A	119.8
C21-C25-C27	110.2(2)
C21-C25-C28	112.0(2)

C27-C25-C28	108.0(2)
C21-C25-C26	109.3(2)
C27-C25-C26	110.0(3)
C28-C25-C26	107.3(2)
C25-C26-H26A	109.5
C25-C26-H26B	109.5
H26A-C26-H26B	109.5
C25-C26-H26C	109.5
H26A-C26-H26C	109.5
H26B-C26-H26C	109.5
C25-C27-H27A	109.5
C25-C27-H27B	109.5
H27A-C27-H27B	109.5
C25-C27-H27C	109.5
H27A-C27-H27C	109.5
H27B-C27-H27C	109.5
C25-C28-H28A	109.5
C25-C28-H28B	109.5
H28A-C28-H28B	109.5
C25-C28-H28C	109.5
H28A-C28-H28C	109.5
H28B-C28-H28C	109.5
N3-C29-C12	115.3(2)
N3-C29-H29A	108.4
C12-C29-H29A	108.4
N3-C29-H29B	108.4
C12-C29-H29B	108.4

H29A-C29-H29B	107.5
O3-C30-N3	122.4(3)
O3-C30-N4	122.8(3)
N3-C30-N4	114.9(2)
N4-C31-C32	116.9(2)
N4-C31-C36	124.3(3)
C32-C31-C36	118.8(3)
C33-C32-C31	120.5(3)
C33-C32-H32A	119.7
C31-C32-H32A	119.7
C32-C33-C34	121.7(3)
C32-C33-C37	117.7(3)
C34-C33-C37	120.6(3)
C33-C34-C35	117.2(3)
C33-C34-H34A	121.4
C35-C34-H34A	121.4
C36-C35-C34	122.5(3)
C36-C35-C38	120.2(3)
C34-C35-C38	117.3(3)
C35-C36-C31	119.3(3)
C35-C36-H36A	120.4
C31-C36-H36A	120.4
F2'-C37-F1	89.2(4)
F2'-C37-F3	118.3(4)
F1-C37-F3	105.0(4)
F2'-C37-F3'	107.0(4)
F1-C37-F3'	117.5(4)

F3-C37-F3'	15.8(3)
F2'-C37-F2	17.4(3)
F1-C37-F2	106.3(4)
F3-C37-F2	109.1(3)
F3'-C37-F2	95.4(3)
F2'-C37-F1'	105.3(4)
F1-C37-F1'	16.2(3)
F3-C37-F1'	94.8(4)
F3'-C37-F1'	109.2(4)
F2-C37-F1'	122.1(3)
F2'-C37-C33	114.5(3)
F1-C37-C33	114.0(3)
F3-C37-C33	113.1(3)
F3'-C37-C33	112.4(3)
F2-C37-C33	109.1(3)
F1'-C37-C33	108.1(3)
F6'-C38-F5	91.6(4)
F6'-C38-F4'	102.1(4)
F5-C38-F4'	116.7(4)
F6'-C38-F4	115.8(4)
F5-C38-F4	106.0(3)
F4'-C38-F4	16.2(3)
F6'-C38-F5'	107.9(4)
F5-C38-F5'	16.9(3)
F4'-C38-F5'	107.7(3)
F4-C38-F5'	94.5(3)
F6'-C38-F6	12.6(4)

F5-C38-F6	104.2(4)
F4'-C38-F6	96.8(4)
F4-C38-F6	112.1(4)
F5'-C38-F6	120.5(4)
F6'-C38-C35	116.1(3)
F5-C38-C35	114.4(3)
F4'-C38-C35	113.5(3)
F4-C38-C35	111.1(3)
F5'-C38-C35	109.0(3)
F6-C38-C35	108.9(3)
N5-C39-C23	114.2(2)
N5-C39-H39A	108.7
C23-C39-H39A	108.7
N5-C39-H39B	108.7
C23-C39-H39B	108.7
H39A-C39-H39B	107.6
O4-C40-N5	123.1(3)
O4-C40-N6	123.4(3)
N5-C40-N6	113.5(2)
N6-C41-C46	117.4(3)
N6-C41-C42	123.6(3)
C46-C41-C42	118.8(3)
C43-C42-C41	119.5(3)
C43-C42-H42A	120.2
C41-C42-H42A	120.2
C42-C43-C44	122.3(3)
C42-C43-C47	119.2(3)

C44-C43-C47	118.5(3)
C45-C44-C43	117.7(3)
C45-C44-H44A	121.2
C43-C44-H44A	121.2
C44-C45-C46	121.6(3)
C44-C45-C48	118.9(3)
C46-C45-C48	119.2(3)
C45-C46-C41	120.1(3)
C45-C46-H46A	120.0
C41-C46-H46A	120.0
F7-C47-F8'	93.8(4)
F7-C47-F9	104.7(4)
F8'-C47-F9	119.6(4)
F7-C47-F9'	113.4(4)
F8'-C47-F9'	107.3(4)
F9-C47-F9'	13.7(3)
F7-C47-F8	107.9(4)
F8'-C47-F8	15.9(3)
F9-C47-F8	107.6(4)
F9'-C47-F8	94.4(4)
F7-C47-F7'	11.9(4)
F8'-C47-F7'	105.7(4)
F9-C47-F7'	98.1(4)
F9'-C47-F7'	108.7(4)
F8-C47-F7'	119.6(4)
F7-C47-C43	114.7(4)
F8'-C47-C43	113.0(3)

F9-C47-C43	110.0(3)
F9'-C47-C43	112.9(3)
F8-C47-C43	111.6(3)
F7'-C47-C43	109.0(3)
F11-C48-F10	108.6(4)
F11-C48-F12'	110.2(4)
F10-C48-F12'	91.6(4)
F11-C48-F12	97.4(4)
F10-C48-F12	108.0(4)
F12'-C48-F12	17.9(3)
F11-C48-F10'	100.9(4)
F10-C48-F10'	13.5(4)
F12'-C48-F10'	104.9(4)
F12-C48-F10'	120.7(4)
F11-C48-F11'	8.9(5)
F10-C48-F11'	113.4(4)
F12'-C48-F11'	116.6(4)
F12-C48-F11'	102.3(4)
F10'-C48-F11'	104.2(4)
F11-C48-C45	117.2(4)
F10-C48-C45	114.6(4)
F12'-C48-C45	111.7(3)
F12-C48-C45	109.5(3)
F10'-C48-C45	110.7(3)
F11'-C48-C45	108.4(4)
O5-C49-N7	125.8(3)
O5-C49-H49A	117.1

N7-C49-H49A	117.1
N7-C50-H50A	109.5
N7-C50-H50B	109.5
H50A-C50-H50B	109.5
N7-C50-H50C	109.5
H50A-C50-H50C	109.5
H50B-C50-H50C	109.5
N7-C51-H51A	109.5
N7-C51-H51B	109.5
H51A-C51-H51B	109.5
N7-C51-H51C	109.5
H51A-C51-H51C	109.5
H51B-C51-H51C	109.5

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for park4.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ni1	14(1)	10(1)	12(1)	0(1)	0(1)	1(1)
O1	23(1)	11(1)	18(1)	0(1)	-5(1)	2(1)
O2	20(1)	13(1)	18(1)	-2(1)	-4(1)	2(1)
O3	10(1)	19(1)	26(1)	0(1)	3(1)	1(1)
O4	12(1)	20(1)	20(1)	4(1)	4(1)	4(1)
O5	40(1)	25(1)	28(1)	3(1)	4(1)	8(1)
N1	30(1)	10(1)	22(1)	0(1)	-4(1)	5(1)
N2	26(1)	10(1)	25(1)	1(1)	-7(1)	2(1)
N3	10(1)	17(1)	22(1)	-3(1)	0(1)	0(1)
N4	9(1)	17(1)	22(1)	-3(1)	4(1)	2(1)
N5	11(1)	19(1)	16(1)	4(1)	2(1)	3(1)
N6	11(1)	18(1)	22(1)	5(1)	5(1)	3(1)
N7	33(2)	20(1)	19(1)	0(1)	4(1)	4(1)
C2	20(2)	11(2)	34(2)	-4(1)	-3(1)	1(1)
C3	42(2)	14(2)	27(2)	2(1)	6(2)	8(1)
C5	21(2)	15(2)	31(2)	5(1)	-5(1)	2(1)
C7	34(2)	12(2)	20(2)	-4(1)	-7(1)	1(1)
C8	17(1)	14(2)	18(2)	2(1)	0(1)	0(1)
C9	12(1)	14(2)	16(1)	1(1)	2(1)	0(1)
C10	14(1)	12(1)	19(1)	1(1)	2(1)	2(1)
C11	15(1)	14(2)	17(1)	2(1)	1(1)	2(1)
C12	12(1)	19(2)	16(1)	-1(1)	1(1)	0(1)

C13	17(1)	12(2)	20(2)	-3(1)	2(1)	-2(1)
C14	14(1)	13(2)	21(2)	-1(1)	0(1)	1(1)
C15	15(1)	16(2)	24(2)	0(1)	2(1)	-1(1)
C16	26(2)	18(2)	28(2)	-1(1)	7(1)	2(1)
C17	22(2)	14(2)	29(2)	4(1)	-1(1)	0(1)
C18	23(2)	15(2)	20(2)	3(1)	-4(1)	3(1)
C19	16(1)	12(1)	13(1)	1(1)	3(1)	0(1)
C20	15(1)	14(2)	14(1)	2(1)	3(1)	1(1)
C21	14(1)	12(1)	14(1)	2(1)	3(1)	1(1)
C22	17(1)	13(1)	15(1)	-1(1)	3(1)	-1(1)
C23	14(1)	18(2)	10(1)	2(1)	2(1)	-1(1)
C24	14(1)	16(2)	14(1)	3(1)	4(1)	2(1)
C25	18(1)	13(2)	20(2)	-1(1)	0(1)	1(1)
C26	16(1)	22(2)	40(2)	-8(2)	1(1)	2(1)
C27	39(2)	14(2)	20(2)	0(1)	-6(1)	4(1)
C28	20(1)	15(2)	24(2)	-4(1)	0(1)	3(1)
C29	16(1)	17(2)	18(2)	1(1)	-4(1)	0(1)
C30	13(1)	17(2)	12(1)	2(1)	-1(1)	1(1)
C31	14(1)	14(2)	13(1)	1(1)	1(1)	0(1)
C32	11(1)	18(2)	18(1)	1(1)	2(1)	2(1)
C33	13(1)	18(2)	16(1)	0(1)	1(1)	0(1)
C34	17(1)	16(2)	17(1)	0(1)	1(1)	2(1)
C35	16(1)	18(2)	15(1)	2(1)	2(1)	1(1)
C36	12(1)	18(2)	16(1)	0(1)	1(1)	0(1)
C37	16(1)	17(2)	29(2)	-4(1)	1(1)	1(1)
C38	18(1)	19(2)	28(2)	-3(1)	-2(1)	2(1)
C39	14(1)	16(2)	17(1)	1(1)	1(1)	0(1)

C40	12(1)	16(2)	13(1)	-1(1)	0(1)	0(1)
C41	15(1)	14(2)	16(1)	-2(1)	2(1)	1(1)
C42	15(1)	15(2)	17(1)	0(1)	2(1)	3(1)
C43	18(1)	17(2)	18(2)	-2(1)	3(1)	1(1)
C44	26(2)	16(2)	16(1)	1(1)	3(1)	4(1)
C45	23(2)	16(2)	15(1)	-4(1)	0(1)	4(1)
C46	16(1)	16(2)	18(1)	-1(1)	2(1)	1(1)
C47	24(2)	19(2)	23(2)	3(1)	10(1)	2(1)
C48	27(2)	21(2)	18(2)	0(1)	-2(1)	5(1)
C49	32(2)	21(2)	19(2)	-3(1)	6(1)	-1(1)
C50	42(2)	28(2)	39(2)	1(2)	9(2)	-3(2)
C51	45(2)	33(2)	26(2)	1(2)	2(2)	11(2)

Table S5. Hydrogen coordinates (× 10^4) and isotropic displacement parameters ($Å^2$ × 10^3) for park4.

	x	y	z	U(eq)
H3	9010(40)	-10(30)	2759(19)	35(11)
H4	9730(40)	1550(30)	3143(16)	17(9)
H5	-4600(40)	-1560(20)	-2851(16)	17(8)
H6	-4780(40)	-390(30)	-3556(17)	27(10)
H1A	3539	1477	-316	16
H6A	711	1013	68	18
H1'A	1408	1146	389	19
H6'A	2865	1347	-763	15
H2A	4071	2564	545	26
H2B	2716	2127	888	26
H2C	4035	2399	345	26
H2D	3092	2332	945	26
H3A	1998	3605	547	33
H3B	2807	3582	-89	33
H3C	2815	3808	233	33
H3D	1374	3238	438	33
H4A	577	3538	-467	25
H4B	91	2755	69	25
H4'A	780	3532	-658	22
H4'B	2301	3215	-841	22
H5A	-102	1788	-978	27
H5B	1562	2139	-1052	27

H5C	538	1912	-1212	27
H5D	19	1832	-498	27
H7A	4608	1066	1035	28
H11A	5971	-2603	2227	18
H13A	6106	422	1895	20
H15A	1992	-2988	879	28
H15B	2120	-3262	1640	28
H15C	1961	-4160	1090	28
H16A	4104	-3344	236	36
H16B	3973	-4495	485	36
H16C	5490	-3817	616	36
H17A	4362	-3933	2198	33
H17B	5640	-4175	1784	33
H17C	4120	-4849	1659	33
H18A	-112	366	-1323	24
H22A	-996	-3745	-2176	18
H24A	-1754	-783	-1987	17
H26A	3101	-3244	-1921	39
H26B	3690	-4042	-1392	39
H26C	3411	-2910	-1159	39
H27A	431	-4464	-631	38
H27B	1769	-3660	-367	38
H27C	2049	-4791	-600	38
H28A	44	-5040	-1819	30
H28B	1689	-5319	-1760	30
H28C	1091	-4563	-2315	30
H29A	6662	-872	3155	21

H29B	7851	-1467	2846	21
H32A	11015	2894	3723	18
H34A	8969	5430	4067	20
H36A	6680	2884	3183	18
H39A	-2823	-2978	-2961	19
H39B	-3724	-2927	-2352	19
H42A	-1306	212	-3985	19
H44A	-2611	2405	-5253	23
H46A	-5553	771	-4302	20
H49A	2603	8848	2559	29
H50A	-483	7396	2775	54
H50B	251	6991	3459	54
H50C	285	6347	2791	54
H51A	3844	7627	3087	51
H51B	3048	6496	2985	51
H51C	3009	7132	3655	51

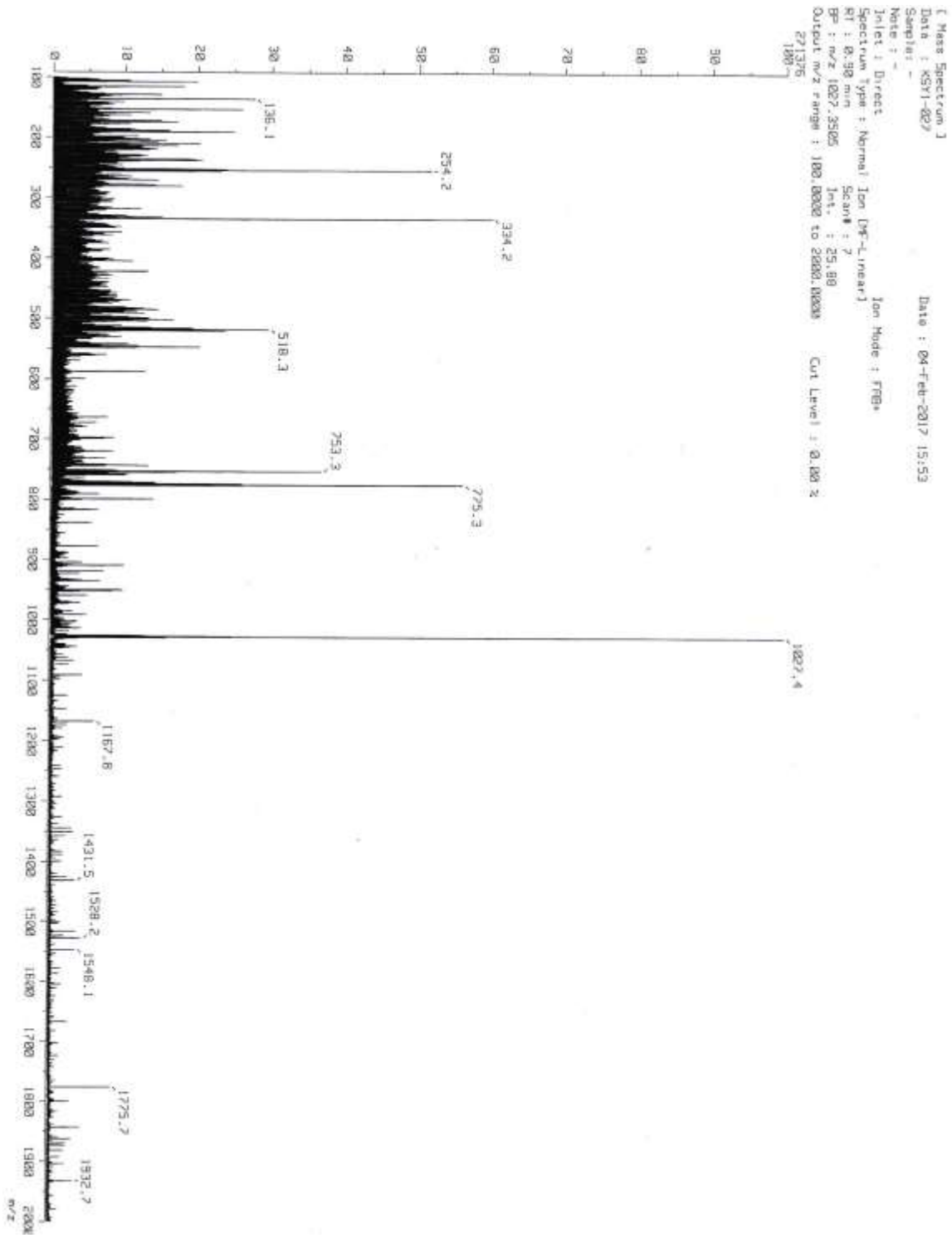
Table S6. Hydrogen bonds for park4 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N3-H3...O5#1	0.79(4)	2.28(4)	2.983(3)	149(4)
N4-H4...O4#2	0.82(3)	2.04(3)	2.837(3)	162(3)
N5-H5...O3#3	0.89(3)	2.08(3)	2.906(3)	154(3)
N6-H6...O3#3	0.86(4)	2.06(4)	2.849(3)	153(3)

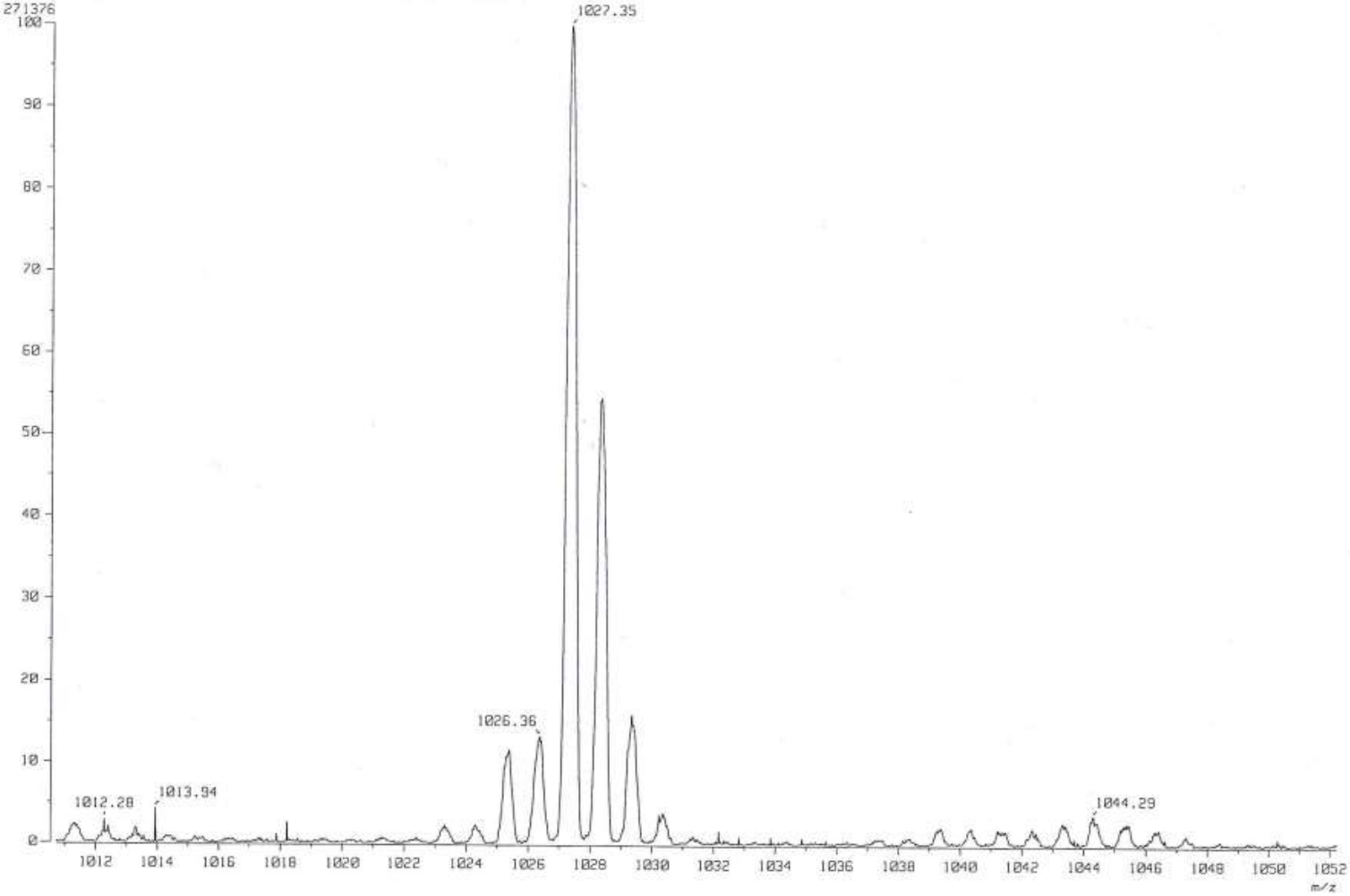
Symmetry transformations used to generate equivalent atoms:

#1 x+1,y-1,z #2 -x+1,-y,-z #3 -x,-y,-z

6. Mass spectrum of a bis-urea salen aluminum catalyst (3b)



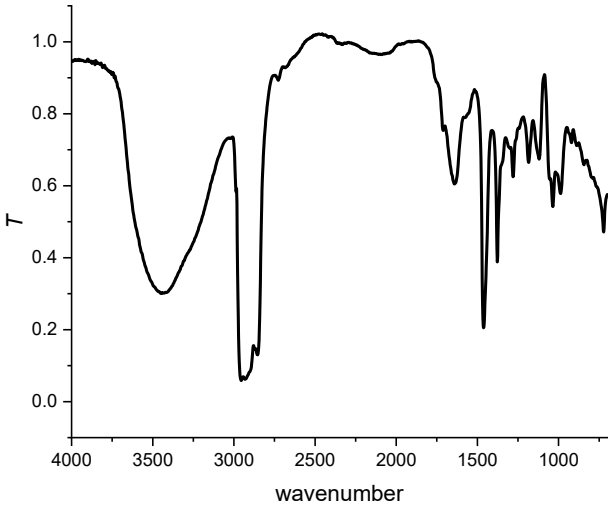
[Mass Spectrum]
Data : KSY1-027 Date : 04-Feb-2017 15:53
Sample: -
Note : -
Inlet : Direct Ion Mode : FAB+
Spectrum Type : Normal Ion (MF-Linear)
RT : 0.90 min Scan# : 7
BP : m/z 1027.3505 Int. : 25.88
Output m/z range : 1010.7349 to 1052.2083 Cut Level : 0.00 %



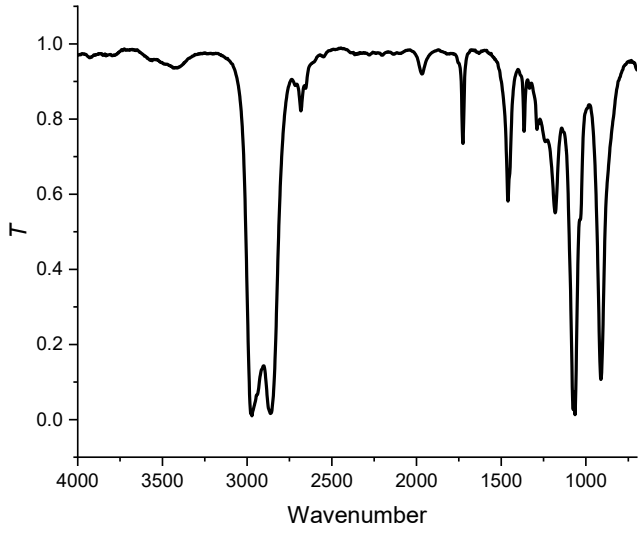
[Mass Spectrum] Page: 1
Data : KSY1-027 Date : 04-Feb-2017 15:53
Sample: -
Note : -
Inlet : Direct Ion Mode : FAB+
Spectrum Type : Normal Ion [MF-Linear]
RT : 0.90 min Scan# : 7
BP : m/z 1027.3505 Int. : 25.88
Output m/z range : 1011.0000 to 1052.0000 Cut Level : 1.00 %

m/z	Int.	Norm.
1011.3302	0.61	2.36
1012.2801	0.76	2.92
1012.4105	0.55	2.11
1013.3049	0.50	1.94
1013.3981	0.29	1.12
1013.9387	1.11	4.30
1017.8764	0.31	1.19
1018.2126	0.68	2.64
1023.3008	0.61	2.34
1024.2938	0.61	2.36
1024.5187	0.27	1.05
1025.3809	3.03	11.69
1026.3561	3.45	13.32
1027.3505	25.88	100.00
1028.3453	14.15	54.68
1029.3407	4.15	16.02
1030.3553	1.02	3.94
1031.3329	0.29	1.11
1032.1604	0.46	1.79
1032.8190	0.26	1.00
1033.8541	0.26	1.00
1039.3771	0.58	2.25
1040.3774	0.54	2.10
1041.2084	0.51	1.99
1042.3230	0.55	2.13
1042.4930	0.32	1.22
1043.3059	0.73	2.82
1044.2893	0.96	3.72
1045.3677	0.72	2.78
1046.4088	0.52	2.01
1047.3179	0.34	1.30

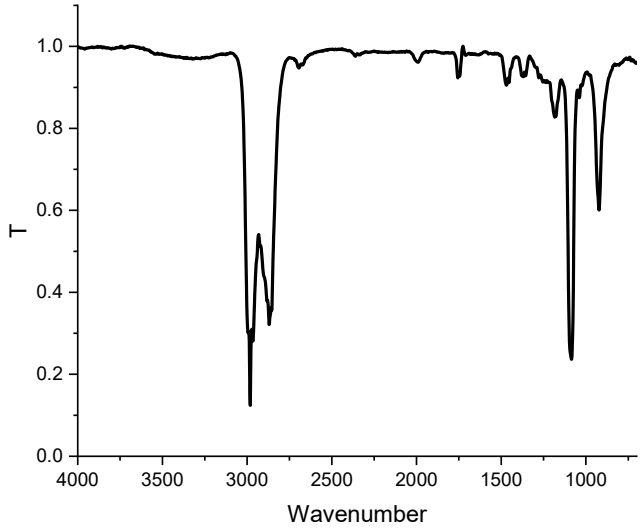
7. FTIR spectrum of bis-urea salen aluminum catalyst (3b)



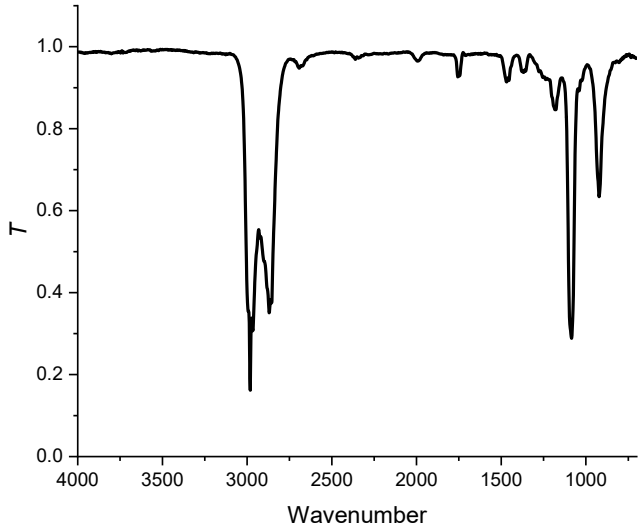
FTIR spectrum of bis-urea salen aluminum catalyst (**3b**) powder.



FTIR spectrum of bis-urea salen aluminum catalyst (**3b**) in THF solution (3 mM).



FTIR spectrum of bis-urea salen aluminum catalyst (**3b**) in THF solution (1.5 mM).



FTIR spectrum of bis-urea salen aluminum catalyst (**3b**) in THF solution (1 mM).