Electronic Supplementary Material (ESI) for Green Chemistry.

Electronic Supplementary Information For:

Efficient conversion of CO_2 into cyclic carbonates at room temperature catalyzed by Al-salen and imidazolium hydrogen carbonate ionic liquid

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1. Experimental method

1.1 Materials and characterization methods

Analytical-grade salicylaldehyde, ethylenediamine, (1R,2R)-diaminocyclohexene, O-phenylenediamine, 2,3-naphthalenediamine, potassium bicarbonate, 1,3-bis(2,4,6-trimethylphenyl)imidazolium Chloride and potassium bis(trimethylsilyl)amide were purchased from Aladdin Reagent Corporation. 1-ethyl-3-methylimidazolium bromide ([C_1C_2Im][Br]), 1-buty-3-methylimidazolium bromide ([C_1C_4Im][Br]), 1-hexyl-3-methylimidazolium bromide ([C_1C_6Im][Br]), 1-ethyl-2,3-dimethylimidazolium bromide ([C_1C_2ImCH_3][Br]) were purchased from Adamas-beta company. All solvents were dried by distilled. CO_2 (99.99%) was used as received without further purification. The NMR spectra were recorded by using Bruker AC-400 MHz spectrometers. High-resolution mass spectra were acquired with 6540 Q-TOF LC/MS. The reaction solution was analyzed by using a GC2014C gas chromatograph fitted with a RTX-5 column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID).

1.2 General procedure for the synthesis of salen ligands

The anhydrous ethanol solution (20 mL) of corresponding diamine (10 mmol) was added dropwise into the solution of salicylaldehyde (20 mmol) in anhydrous ethanol at room temperature. The resulting mixture was heated to reflux overnight. The resulting residue was filtered and washed with cold ethanol (20 ml × 3), then dried under vacuum to afford the desired products.

1.3 General procedure for the synthesis of SH_n-Al(Cl) compounds

Under nitrogen protection and constant stirring at room temperature, to a 50 mL Schlenk flask containing the corresponding salen ligand SH_n (3 mmol), anhydrous dichloromethane (20 mL) was added via a hypodermic syringe to dissolve the ligand, then 3.5 mL of Et_2AlCl (1.0 M solution in toluene, 3.5 mmol) was added slowly. The resulting mixture was refluxed for another 4 h. The solvent was removed under vacuum, and the residue was washed with anhydrous ether (10 ml × 3) and dried under vacuum to obtain the products.

1.4 General procedure for the synthesis of SH_n-$Al(CH_3)$ compounds

Under nitrogen protection and constant stirring at room temperature, to a 50 mL Schlenk flask containing the corresponding salen ligand SH_n (3 mmol), anhydrous dichloromethane (20 mL) was added via a hypodermic syringe to dissolve the ligand, then 3.5 mL of $AlMe_3$ (1.0 M solution in hexane, 3.5 mmol) was added slowly. The resulting mixture was refluxed for another 4 h. The solvent was removed under vacuum, and the residue was washed with anhydrous hexane (10 ml × 3) and dried under vacuum to obtain the products.

1.5 Synthesis of imidazolium hydrogen carbonate ionic liquids

Imidazolium hydrogen carbonate ionic liquids were synthesized using the same procedure reported in our pervious papers.[13a]

1.6 Synthesis of IMes-CO_2

An 50 mL Schlenk flask was charged with 1,3-bis(2,4,6-trimethylphenyl) imidazolium Chloride (3 mmol) and potassium bis(trimethylsilyl)amide (3.1 mmol). The reactor was purged by vaccum/dry nitrogen cycles for three times. Then, dry THF (20 mL) was added and the mixture was stirred at -30℃ for 2 hours. It was then allowed to stand for 2 hours. After that, dry CO_2 was bubbled into the obtained solution. After 4 hours, the solvent was evaporated under vaccum and the residue was washed with dry THF (5×10 mL). After dry under vaccum, IMes-CO_2 was obtained as white powder.

1.7 Catalytic reactions

The cycloaddition reaction were conducted in a 25 mL stainless autoclave (YZPR-25, YAN ZHENG INSTRUMENT). The catalyst (0.05 mmol), cocatalyst (0.05 mmol) and substrates (20 mmol) were charged into the stainless autoclave equipped with magnetic stirring and heating devices. The reactor was purged with CO_2 for three times and then charged with CO_2. Next, the stainless autoclave was heated to desirable temperature and stirred for 10 h (or 24h). After the reaction is completed, the remaining CO_2 is slowly discharged from the reactor. The pressure of CO_2 was controlled by a pressure reducing valve connected to the steel cylinder. The reaction solution was analyzed by using GC. The cyclic carbonates were purified by flash chromatography for NMR characterization.

The reactions that need to be performed at atmospheric pressure use Schlenk flask and CO_2 ballon rather than stainless autoclave.

1.8 Procedure for the recycle of catalytic system

After the catalytic reaction was completed and the remaining CO_2 was discharged from the reactor, the final mixture was added diethyl ether (30 mL). Styrene oxide and styrene carbonate are soluble in diethyl ether, while the catalyst and cocatalyst are insoluble in diethyl ether. The mixture of catalyst and cocatalyst were separated by centrifugation. The mixture of catalyst and cocatalyst were washed by diethyl ether (3×5ml). The recovered catalyst and cocatalyst was dried 10 h under vacuum and reused for the next running of catalytic reaction.

2.1 The chemical shift of Al-Me in SH_4-$Al(CH_3)$ in the ^1H NMR spectrum

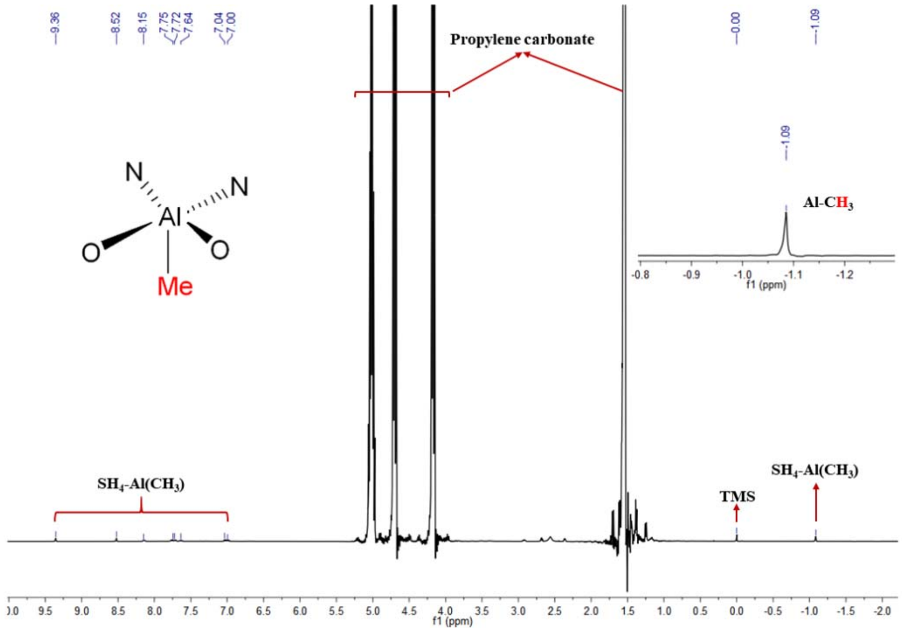

Fig. S1. ^1H NMR spectra of a mixture of SH_4-$Al(CH_3)$ and propylene carbonate in dual NMR cell. The $CDCl_3$ was placed in the inner cell, whereas samples were placed in the outer cell.

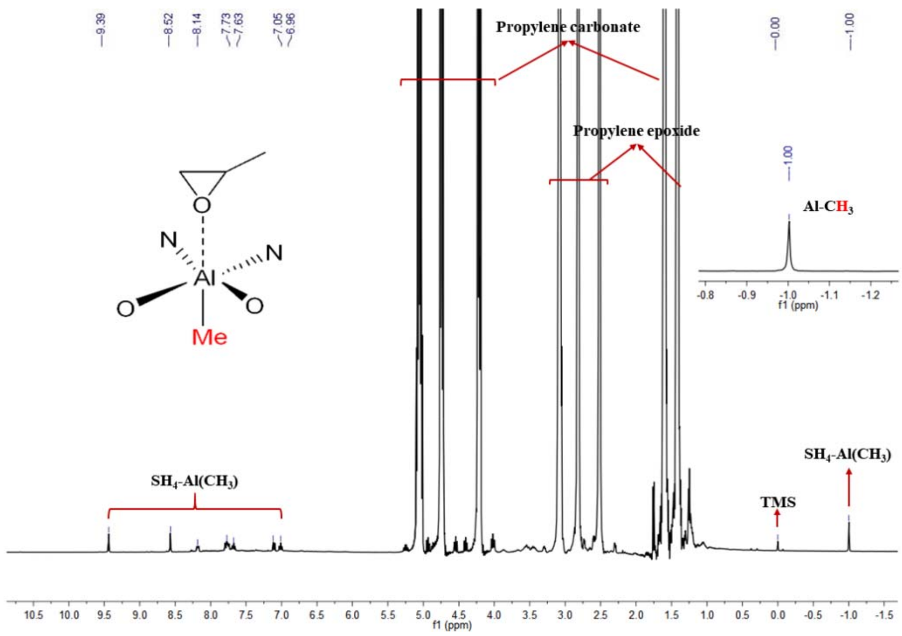

Fig. S2. [1]H NMR spectra of a mixture of SH_4-Al(CH_3), propylene carbonate and propylene epoxide in dual NMR cell. The $CDCl_3$ was placed in the inner cell, whereas samples were placed in the outer cell.

2.2 The separation efficiency of SH_4-Al(Cl) and [C_1C_6Im][HCO_3] in recovery operation

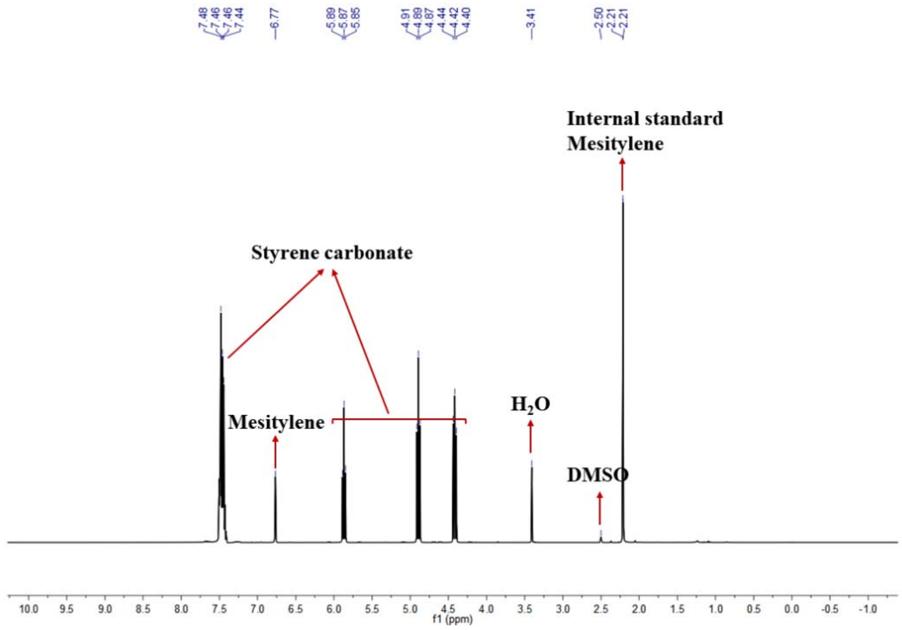

Fig. S3. [1]H NMR spectra of styrene carbonate extracted by diethyl ether. No observable signal of SH_4-Al(Cl) and [C_1C_6Im][HCO_3] were detected in styrene carbonate (diethyl ether extraction phase).

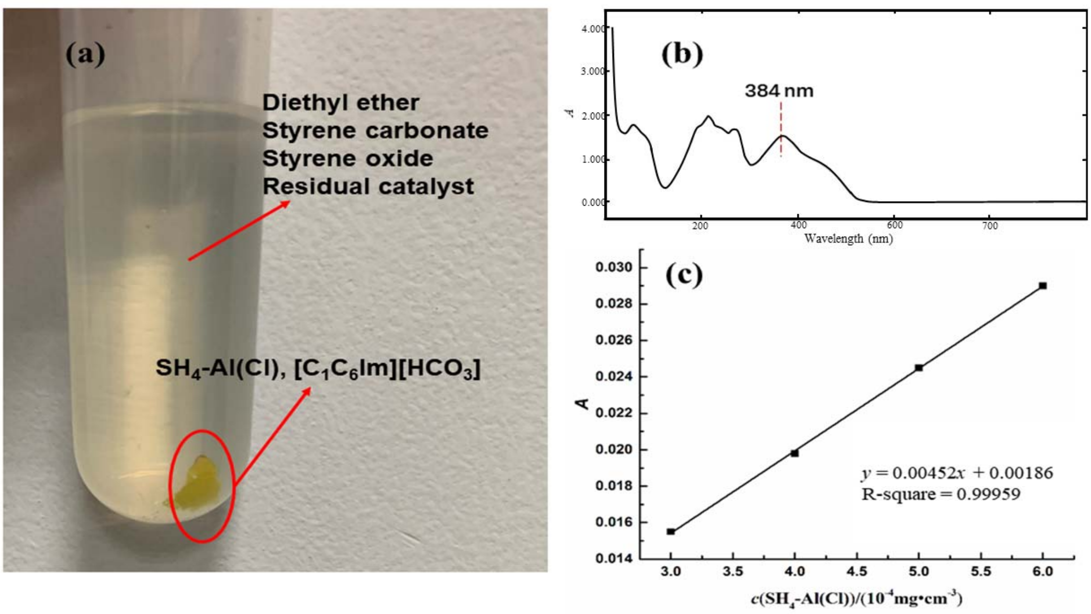

Fig. S4. (a) The photo of catalyst recovery operation; (b) UV absorption spectra of SH_4-Al(Cl) in methanol; (c) The standard curve obtained by measuring the absorbance of SH_4-Al(Cl) with different concentrations at 384 nm. The residual catalyst in the extraction phase was determined to be 0.318 mg by UV and the recovery rate of SH_4-Al(Cl) was 98.5%.

2.3 ^{13}C labeling experiments

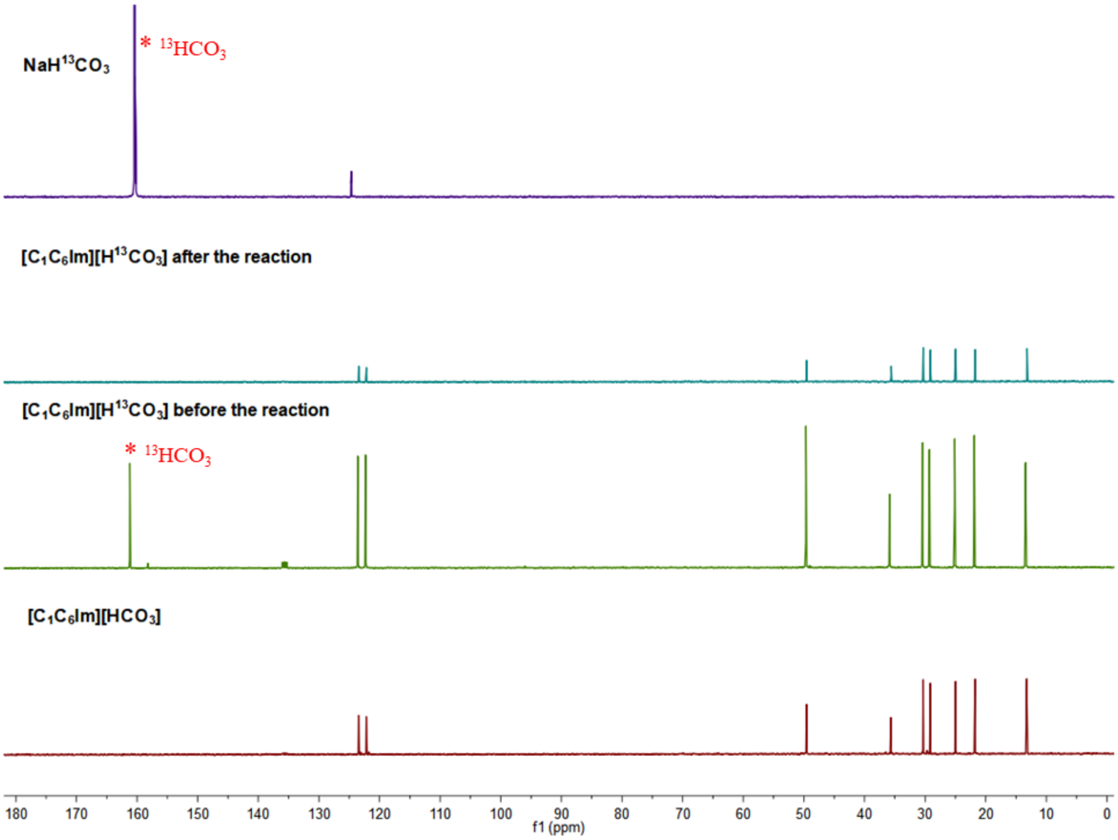

Fig. S5. ^{13}C NMR of ^{13}C-labeled $[C_1C_6Im][H^{13}CO_3]$ in D_2O. Reaction conditions: SH_4-Al(Cl) 0.25mol%, $[C_1C_6Im][HCO_3]$ 5mol%, styrene oxide 10mmol, 25°C, CO_2 pressure 1.0MPa, 20h.

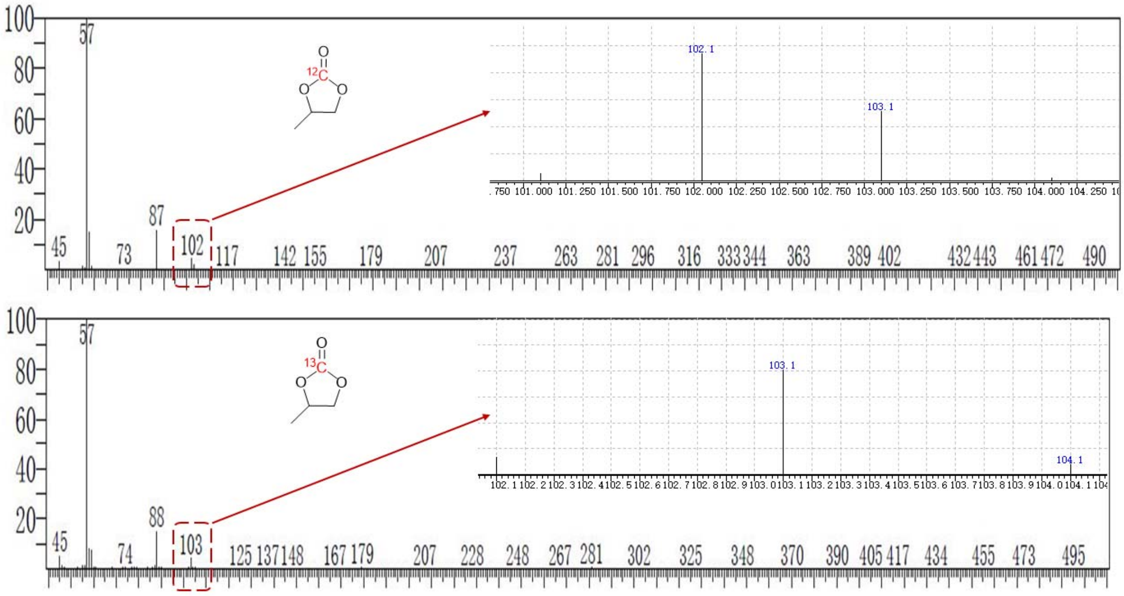

Fig. S6. MS spectrum of propylene carbonate synthesized by the reaction between [IMes][$H^{13}CO_3$] and propylene epoxide. Reaction conditions: SH_4-Al(Cl) 0.05mmol, [IMes][$H^{13}CO_3$] 0.3mmol, propylene epoxide 8.6mmol, 25°C, 36h.

2.4 Synthesis of propylene carbonate with [IMes][HCO_3] as carbon source without CO_2.

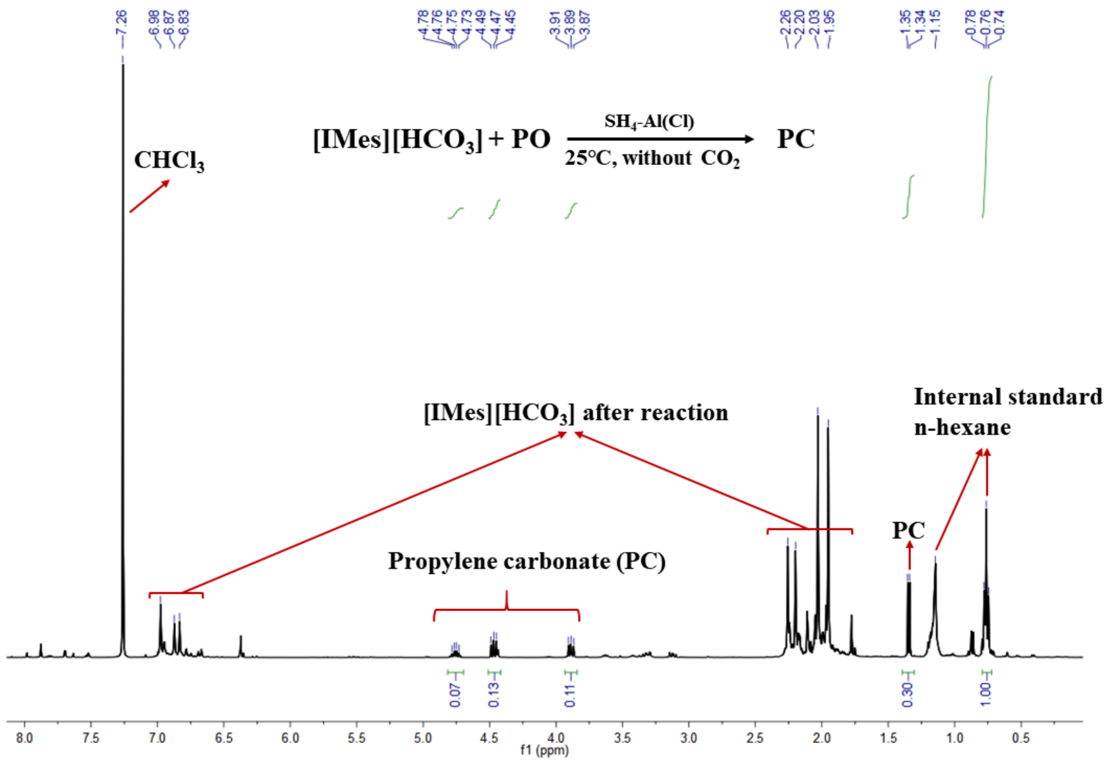

Fig. S7. [1]H NMR spectra of reaction mixture in $CDCl_3$. Reaction conditions: SH_4-Al(Cl) 0.05mmol, [IMes][HCO_3] 0.8mmol, propylene epoxide 8.6mmol, 25°C, 36h. After reaction, propylene epoxide was removed by vacuum distillation, the mixture was dissolved in $CDCl_3$, then 0.57mmol (0.072g) n-hexane was added as the internal standard. By calculating the area of methyl peak of PC and n-hexane, the yield of PC is 0.342mmol (42.8% based on [IMes][HCO_3]).

3. Characterization results

The ^{1}H and ^{13}C NMR spectra of SH_1

^{1}H-NMR (400 MHz, DMSO-d_6): δ 13.39 (2H, OH), 8.59 (2H, Ar-CH=N-), 7.43-7.41 (2H, Ar-H), 7.34-7.30 (2H, Ar-H), 6.91-6.87 (4H, Ar-H), 3.92 (4H, =NCH_2-)

^{13}C-NMR (100 MHz, DMSO-d_6): δ 167.38 (Ar-CH=N-), 161.04, 132.82, 132.13, 119.06, 119.02, 116.94 (Ar), 59.24 (=NCH_2-)

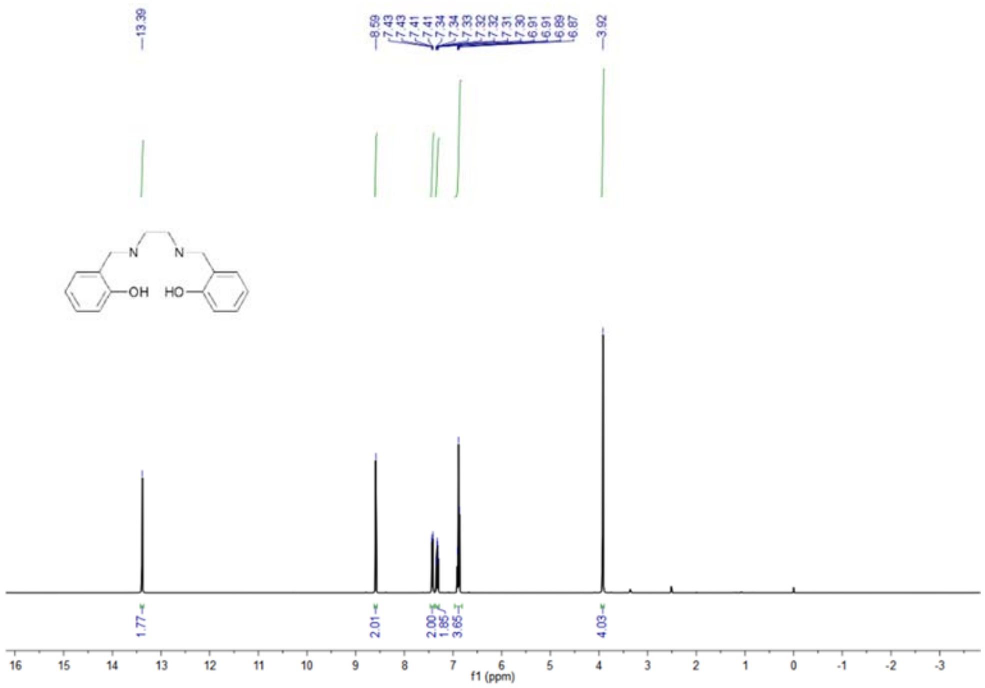

Fig. S8. ^{1}H NMR spectra of $\mathbf{SH_1}$ in DMSO

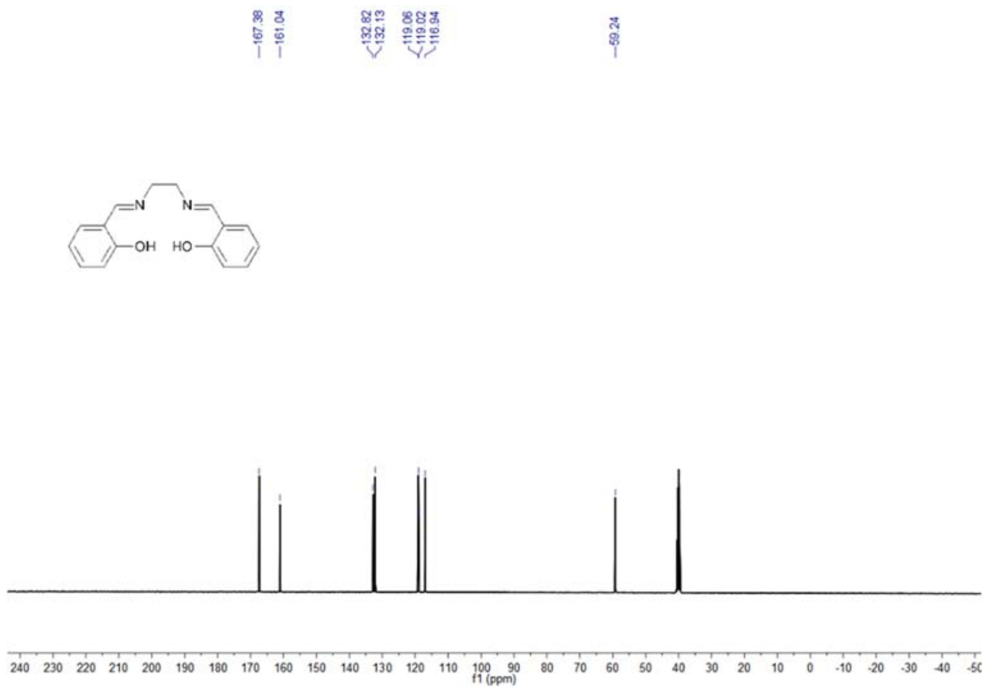

Fig. S9. ^{13}C NMR spectra of **SH_1** in DMSO

The ^{1}H and ^{13}C NMR spectra of SH_2

^{1}H-NMR (400 MHz, DMSO-d_6): δ 13.32 (2H, OH), 8.49 (2H, Ar-CH=N-), 7.35-7.25 (4H, Ar-H), 6.85-6.81 (4H, Ar-H), 3.44-3.37 (2H, =NCH-), 1.90-1.43 (8H, -CH_2-)

^{13}C-NMR (100 MHz, DMSO-d_6): δ 165.56 (Ar-CH=N-), 160.84, 132.70, 132.07, 119.02, 118.98, 116.81 (Ar), 71.8 (=NCH-), 33.0, 24.19 (-CH_2-)

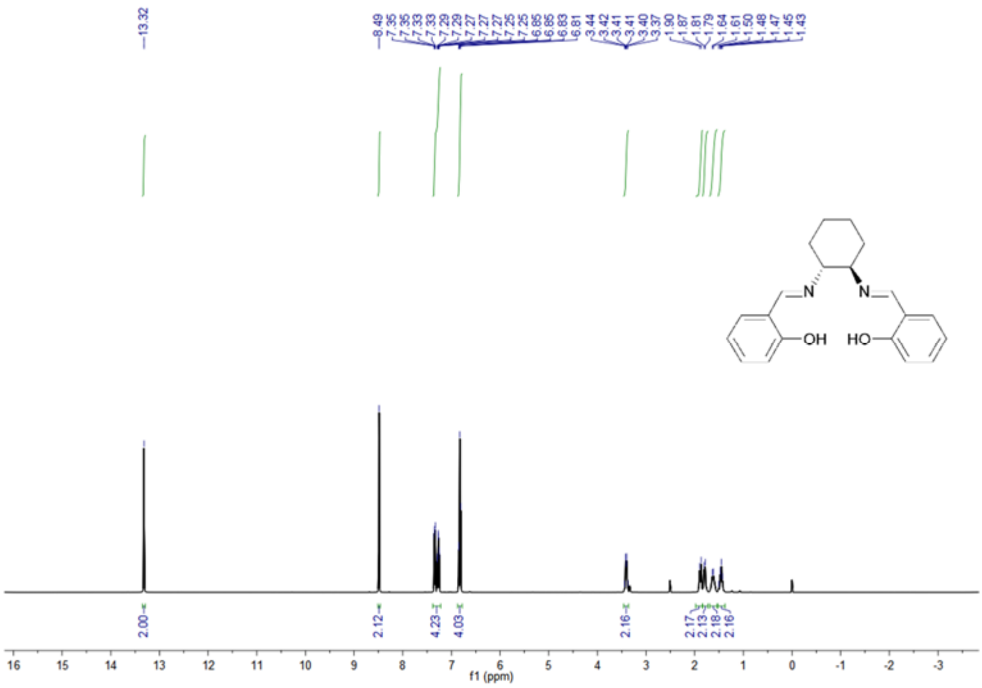

Fig. S10. ^{1}H NMR spectra of **SH_2** in DMSO

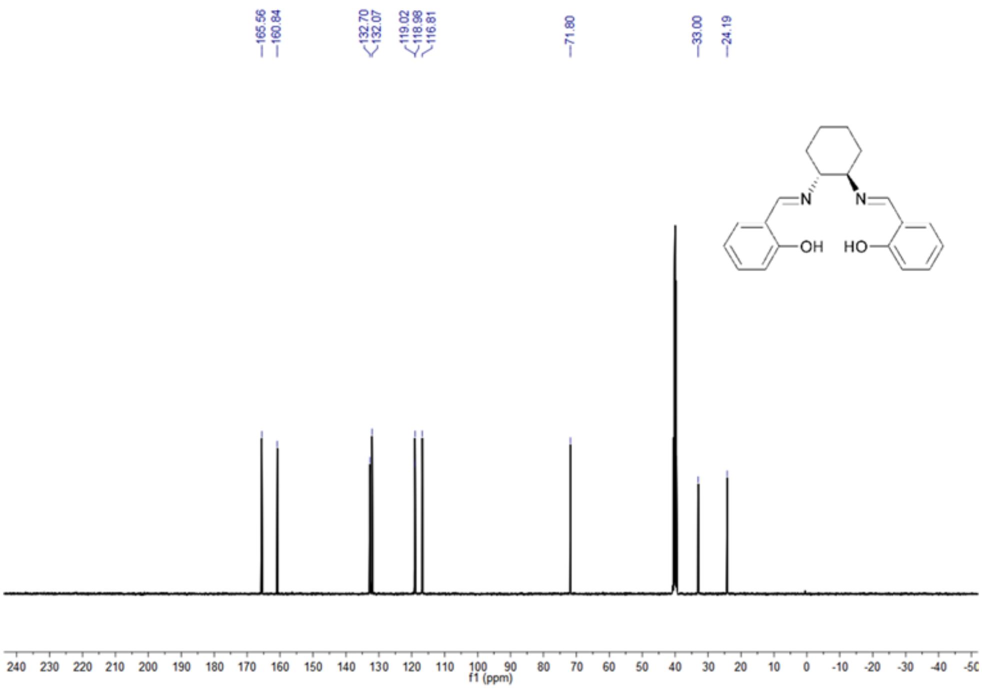

Fig. S11. ^{13}C NMR spectra of **SH_2** in DMSO

The ^{1}H and ^{13}C NMR spectra of SH_3

^{1}H-NMR (400 MHz, DMSO-d$_6$): δ 12.96 (2H, OH), 8.94 (2H, Ar-CH=N-), 7.69-7.67 (2H, Ar-H), 7.48-7.40 (6H, Ar-H), 7.00-6.97 (4H, Ar-H)

^{13}C-NMR (100 MHz, DMSO-d$_6$): δ 164.50 (Ar-CH=N-), 160.87, 142.74, 133.90, 132.93, 128.26, 120.22, 119.97, 119.54, 117.15 (Ar)

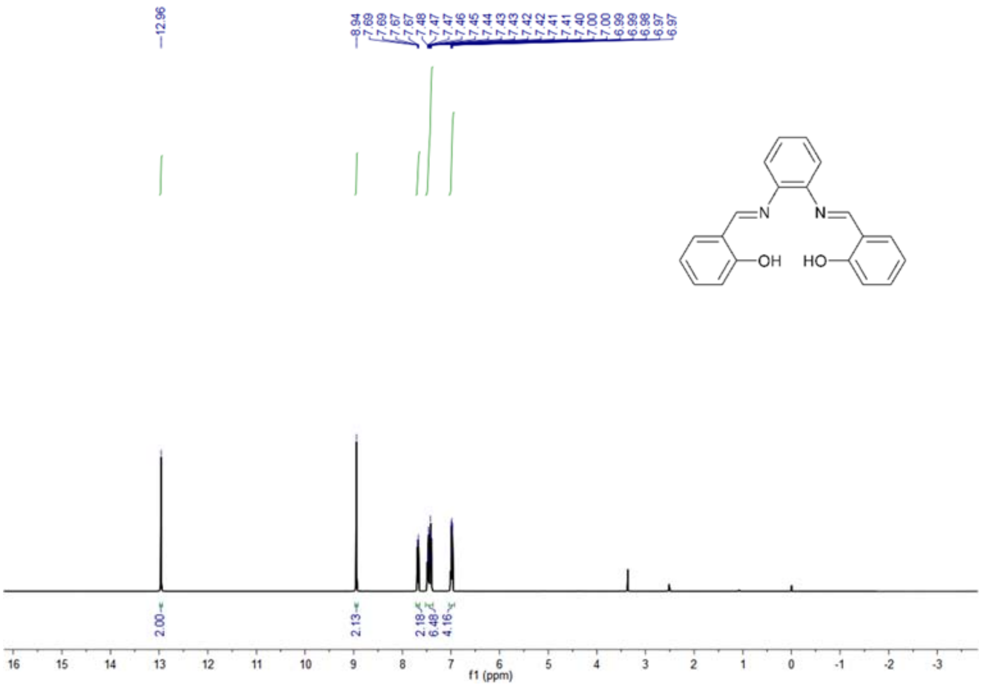

Fig. S12. ^{1}H NMR spectra of **SH_3** in DMSO

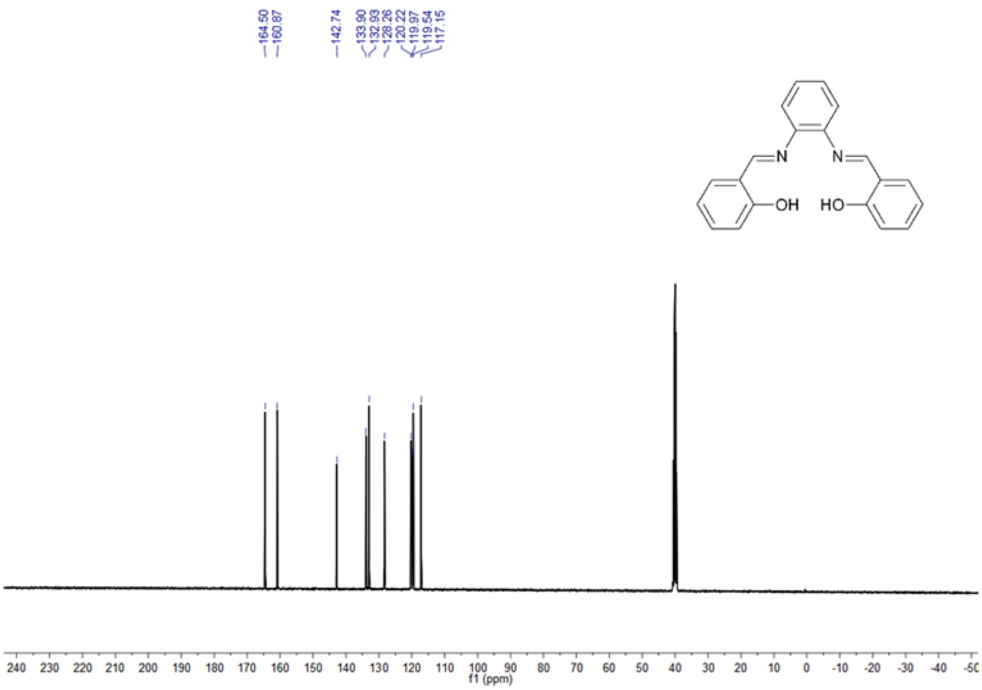

Fig. S13. ^{13}C NMR spectra of **SH_3** in DMSO

The ^{1}H and ^{13}C NMR spectra of SH_4

^{1}H-NMR (400 MHz, DMSO-d_6): δ 12.91 (2H, OH), 9.06 (2H, Ar-CH=N-), 7.99-7.96 (2H, Ar-H), 7.92 (2H, Ar-H), 7.75-7.72 (2H, Ar-H),7.54-7.52 (2H, Ar-H), 7.47-7.42 (2H, Ar-H), 7.03-6.99 (4H, Ar-H)

^{13}C-NMR (100 MHz, DMSO-d_6): δ 164.63 (Ar-CH=N-), 160.93, 142.87, 134.02, 132.89, 132.85, 128.20, 126.77, 120.05, 119.64, 117.20, 117.14(Ar)

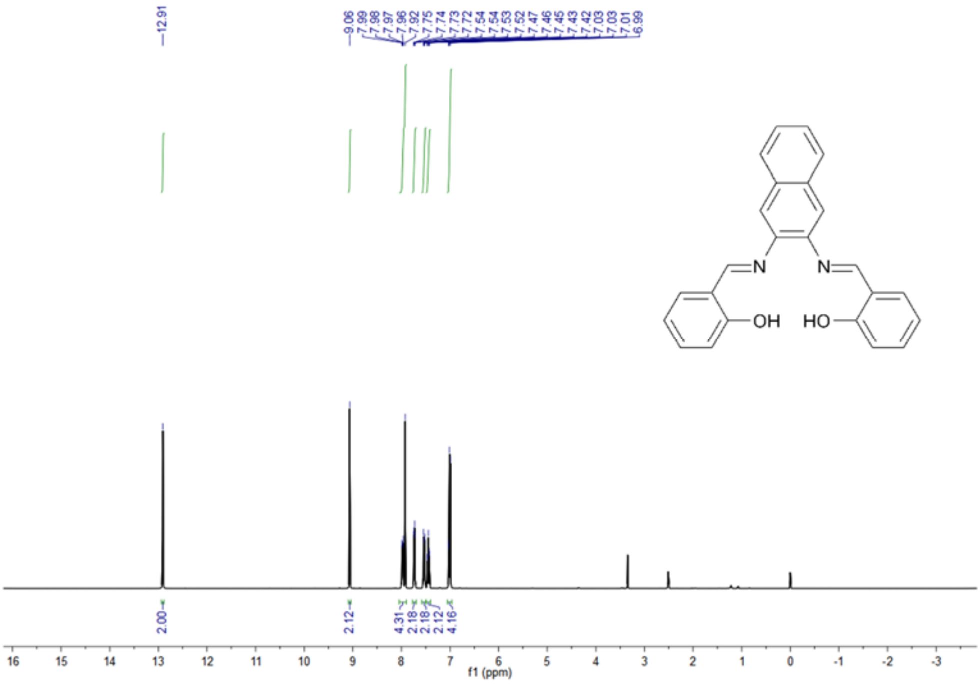

Fig. S14. ^{1}H NMR spectra of **SH_4** in DMSO

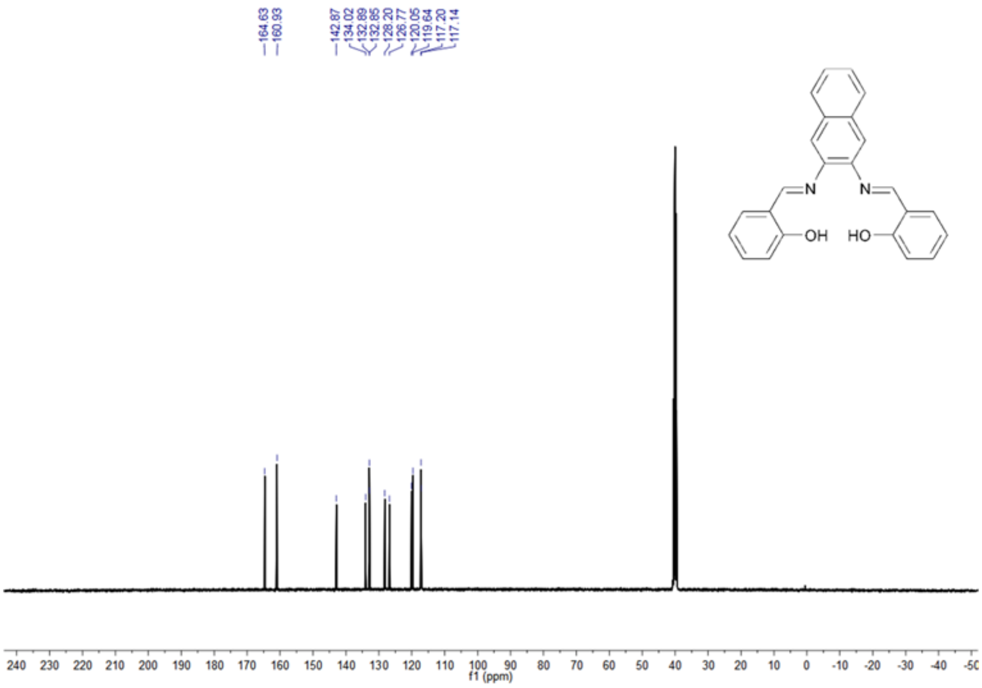

Fig. S15. ^{13}C NMR spectra of **SH_4** in DMSO

The ^{1}H and ^{13}C NMR spectra of SH_1-Al(Cl)

^{1}H-NMR (400 MHz, DMSO-d$_6$): δ 8.53 (2H, Ar-CH=N-), 7.41-7.36 (4H, Ar-H), 6.87-6.85 (2H, Ar-H), 6.75-6.71 (2H, Ar-H), 3.86 (4H, =NCH$_2$-)

^{13}C-NMR (100 MHz, DMSO-d$_6$): δ 167.57 (Ar-CH=N-), 164.95, 135.51, 134.60, 121.64, 120.04, 116.40 (Ar), 53.53 (=NCH$_2$-)

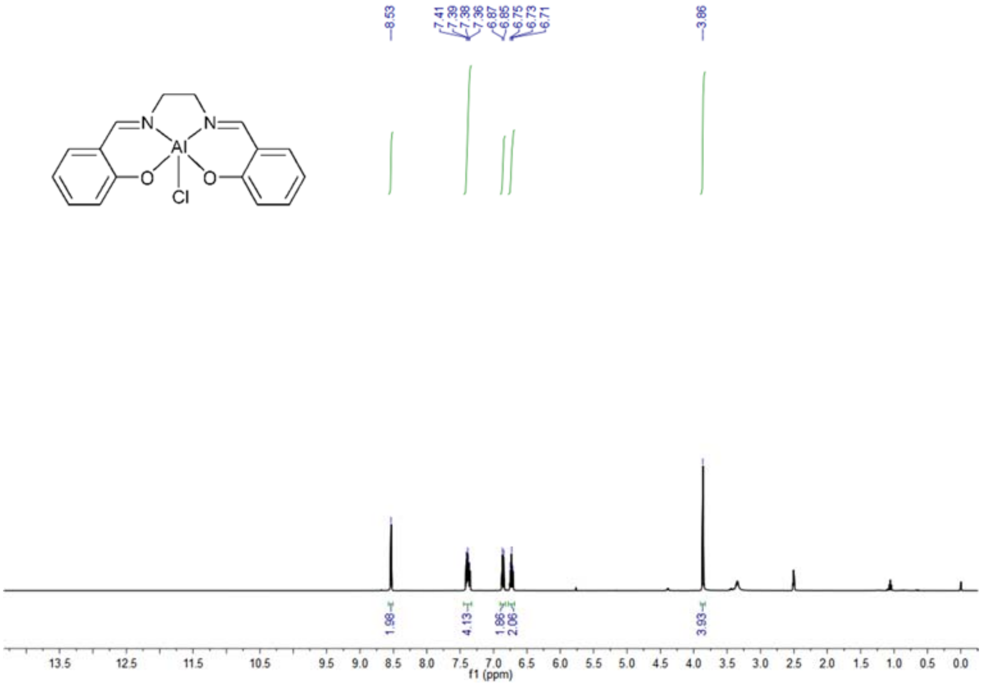

Fig. S16. ^{1}H NMR spectra of **SH_1-Al(Cl)** in DMSO

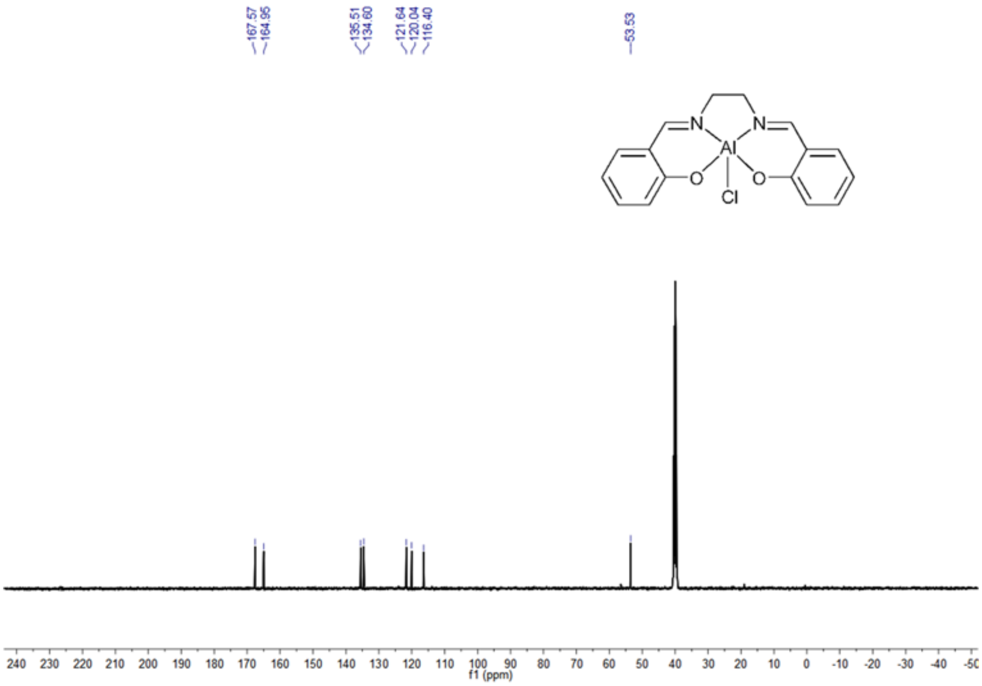

Fig. S17. ^{13}C NMR spectra of **SH_1-Al(Cl)** in DMSO

The ^{1}H and ^{13}C NMR spectra of SH_2-Al(Cl)

^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.37 (2H, Ar-CH=N-), 7.53-7.51 (2H, Ar-H), 7.40-7.35 (2H, Ar-H), 6.87-6.85 (2H, Ar-H), 6.75-6.71 (2H, Ar-H), 3.37-3.36 (2H, =NCH-), 2.57-2.54 (2H, -CH_2-), 1.95-1.93 (2H, -CH_2-), 1.40-1.37 (2H, -CH_2-)

^{13}C-NMR (100 MHz, DMSO-d_6): δ 164.80 (Ar-CH=N-), 163.74, 135.50, 135.25, 121.53, 120.12, 116.32 (Ar), 63.64 (=NCH-), 27.38, 23.87 (-CH_2-)

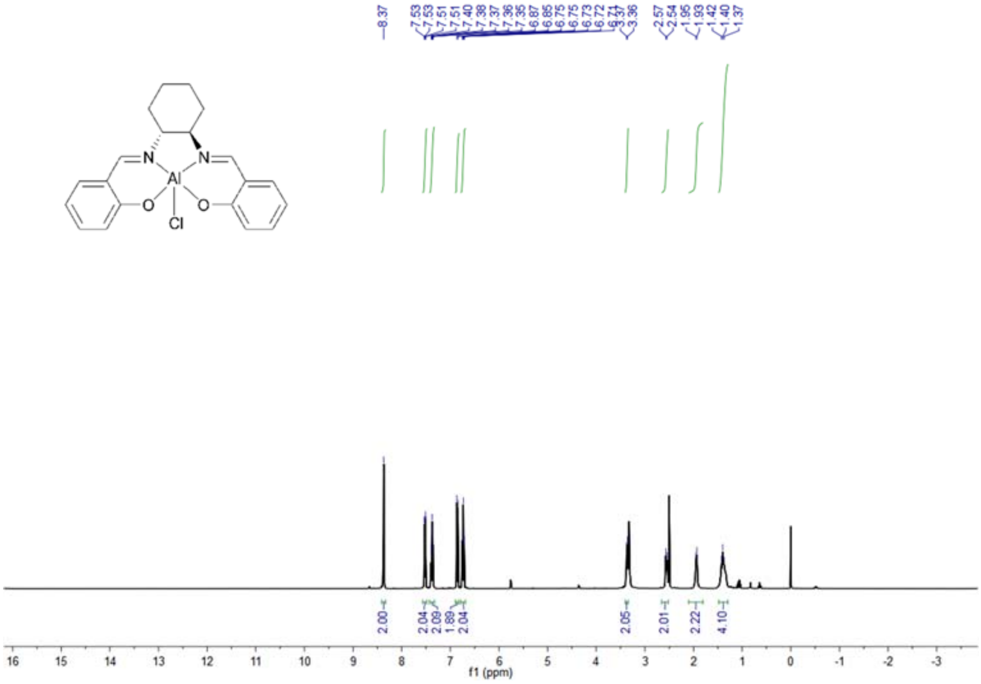

Fig. S18. ^{1}H NMR spectra of **SH_2-Al(Cl)** in DMSO

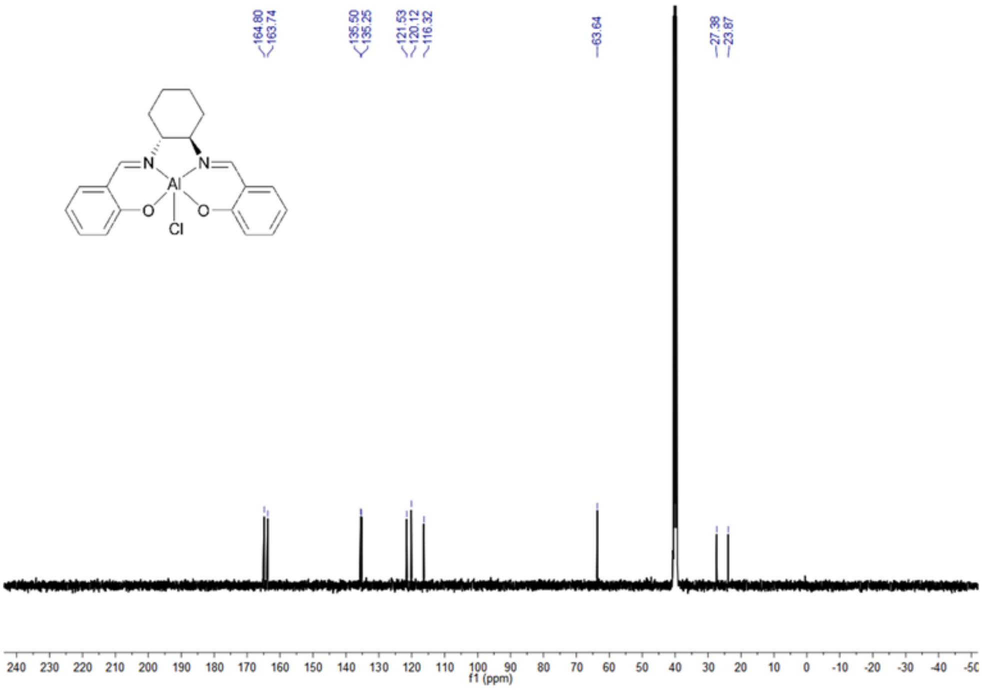

Fig. S19. ^{13}C NMR spectra of **SH_2-Al(Cl)** in DMSO

The ^1H and ^{13}C NMR spectra of SH_3-Al(Cl)

^1H-NMR (400 MHz, DMSO-d_6): δ 9.35 (2H, Ar-CH=N-), 8.19-8.16 (2H, Ar-H), 7.73-7.71 (2H, Ar-H), 7.54-7.50 (4H, Ar-H), 6.98-6.96 (2H, Ar-H), 6.87-6.83 (2H, Ar-H)

^{13}C-NMR (100 MHz, DMSO-d_6): δ 165.94 (Ar-CH=N-), 162.04, 137.94, 137.34, 136.32, 129.25, 121.91, 120.08, 117.57, 117.14 (Ar)

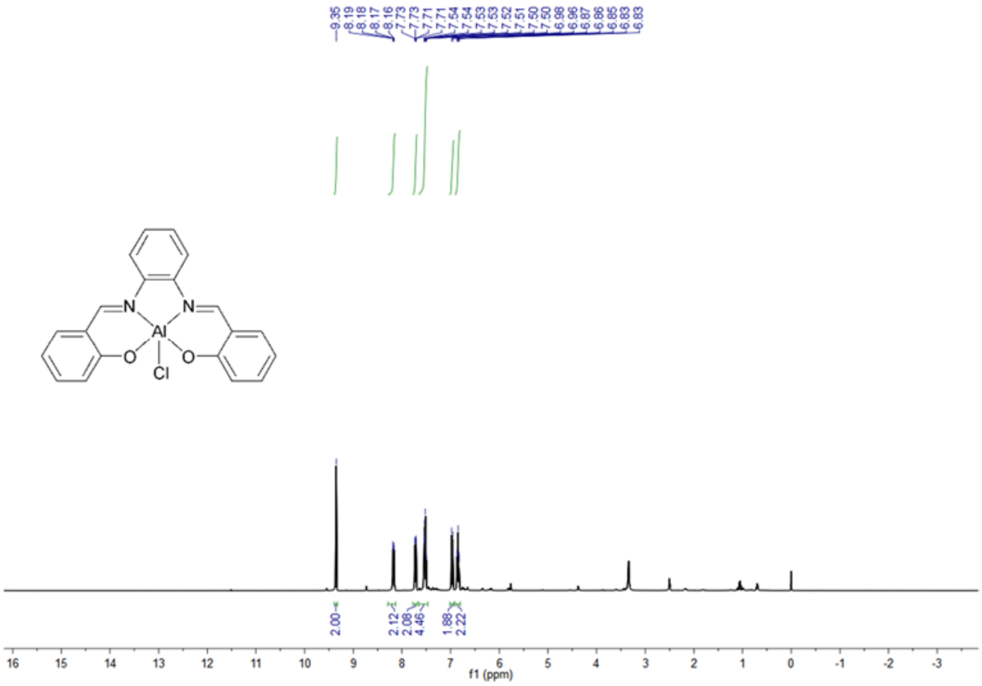

Fig. S20. ^1H NMR spectra of **SH_3-Al(Cl)** in DMSO

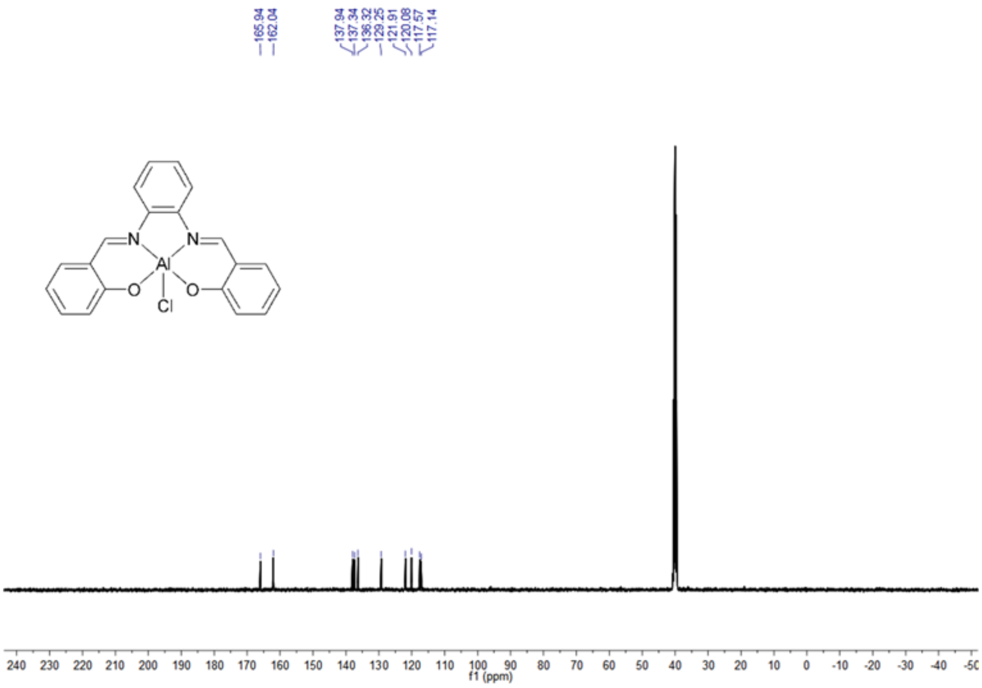

Fig. S21. [13]C NMR spectra of **SH_3-Al(Cl)** in DMSO

The [1]H and [13]C NMR spectra of SH_4-Al(Cl)

[1]H-NMR (400 MHz, DMSO-d_6): δ 9.54 (2H, Ar-CH=N-), 8.72 (2H, Ar-H), 8.01-7.99 (2H, Ar-H), 7.77-7.75 (2H, Ar-H),7.63-7.60 (2H, Ar-H), 7.56-7.52 (2H, Ar-H), 7.00-6.98 (2H, Ar-H), 6.90-6.86 (2H, Ar-H)

[13]C-NMR (100 MHz, DMSO-d_6): δ 166.26 (Ar-CH=N-), 162.89, 137.53, 136.81, 136.34, 132.84, 128.56, 127.80, 122.00, 120.28, 117.28, 115.53(Ar)

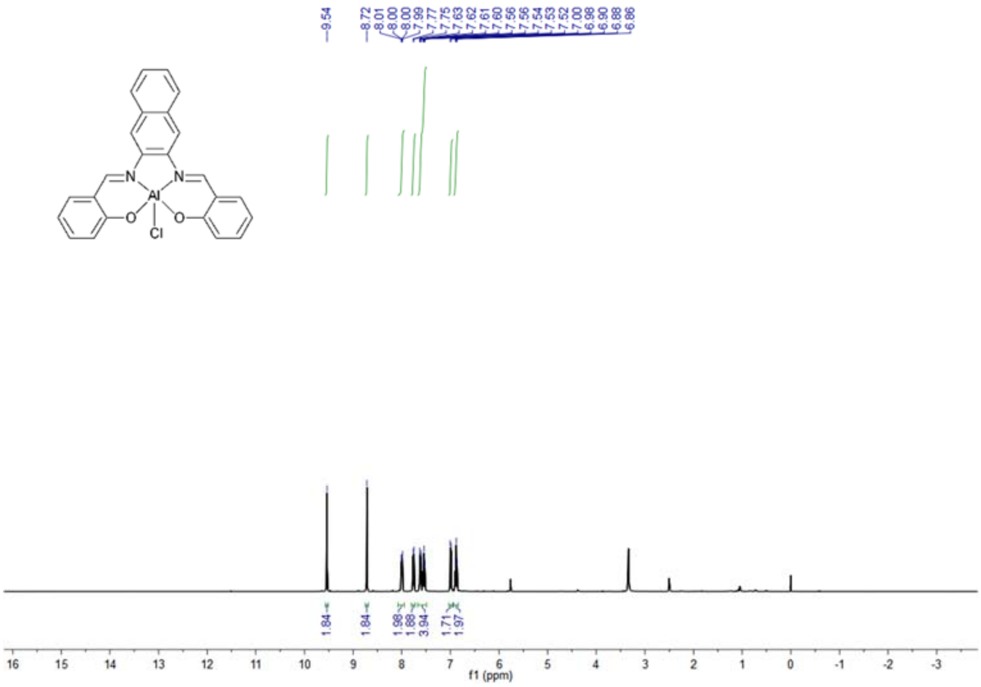

Fig. S22. [1]H NMR spectra of **SH_4-Al(Cl)** in DMSO

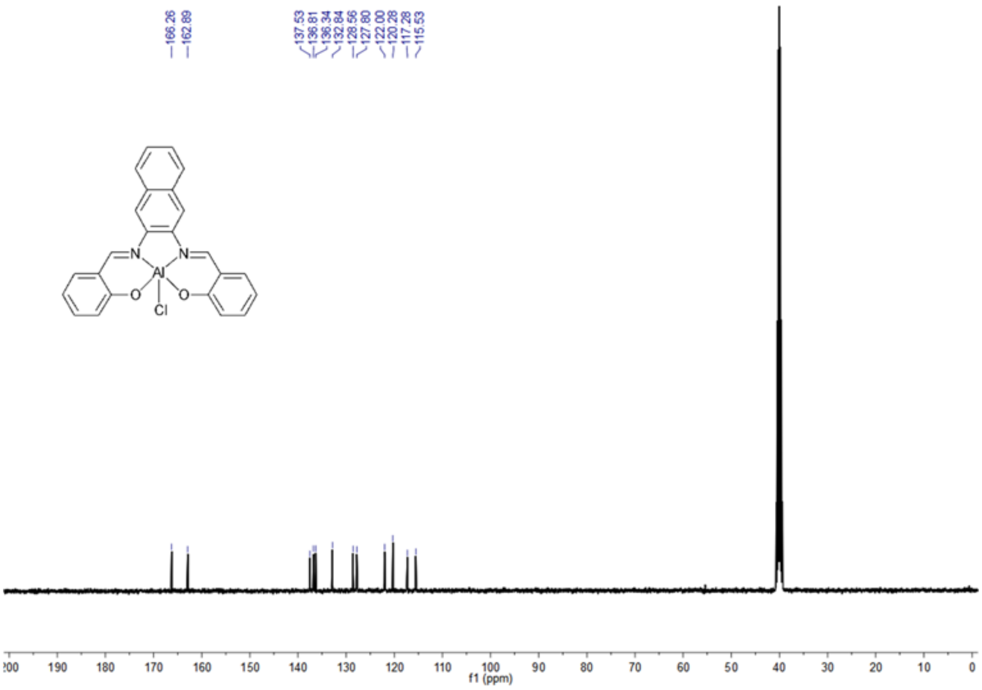

Fig. S23. [13]C NMR spectra of **SH_4-Al(Cl)** in DMSO

The ^{1}H and ^{13}C NMR spectra of SH_3-Al(CH_3)

^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.26 (2H, Ar-CH=N-), 8.07-8.05 (2H, Ar-H), 7.64-7.61 (2H, Ar-H), 7.54-7.46 (4H, Ar-H), 6.92-6.90 (2H, Ar-H), 6.84-6.80 (2H, Ar-H), -1.31(3H, Al-Me)

^{13}C-NMR (100 MHz, DMSO-d_6): δ 166.27 (Ar-CH=N-), 163.77, 138.74, 137.12, 135.44, 129.24, 121.87, 119.68, 117.71, 117.03 (Ar)

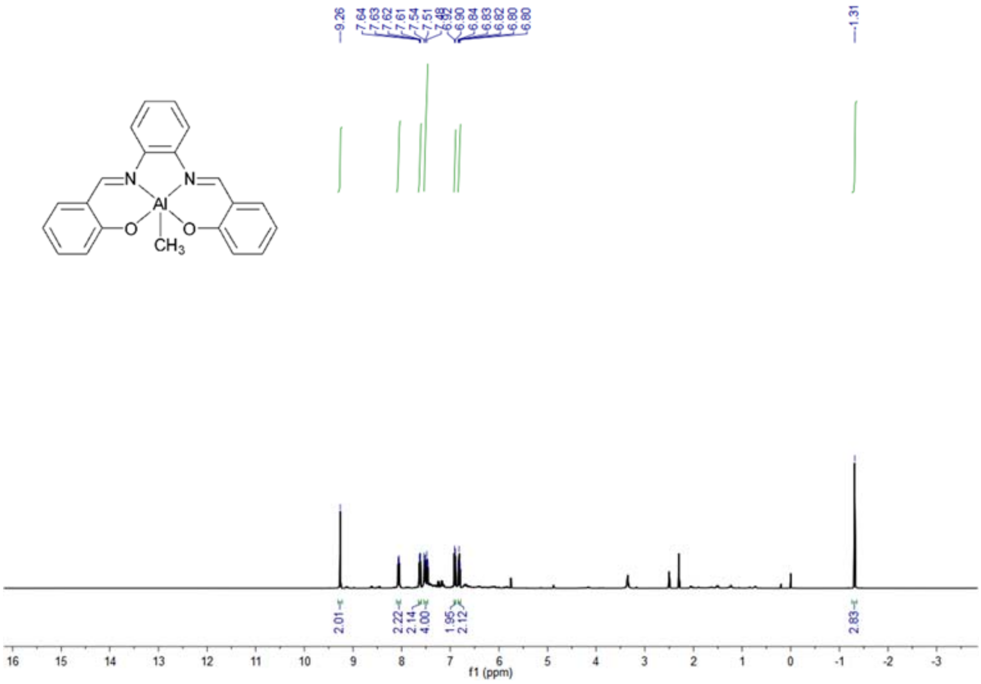

Fig. S24. ^{1}H NMR spectra of **SH_3-Al(CH_3)** in DMSO

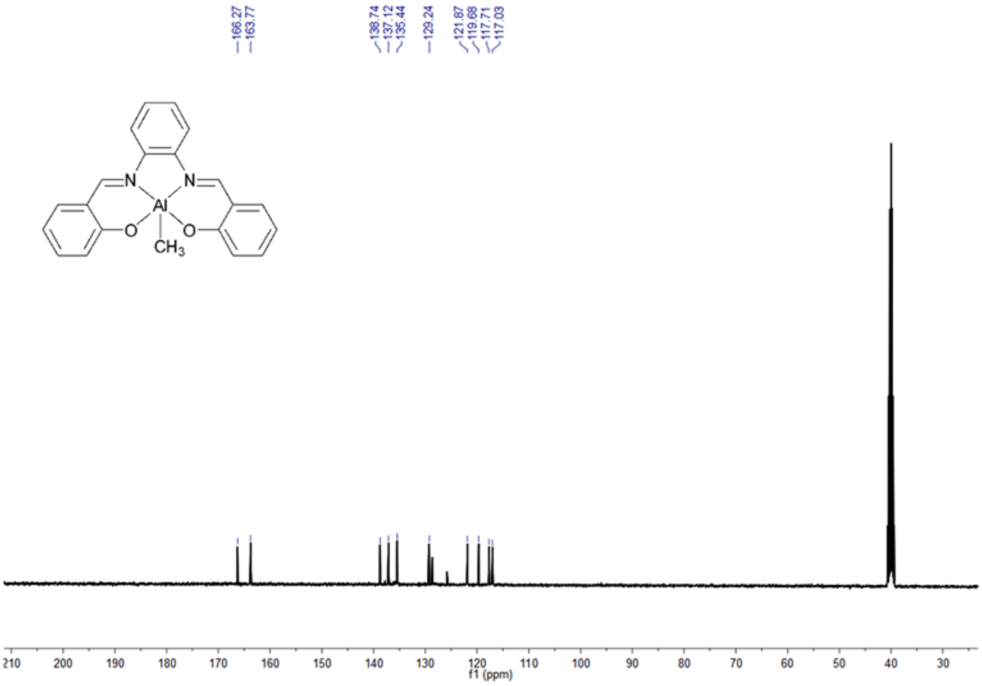

Fig. S25. ^{13}C NMR spectra of **SH_3-Al(CH_3)** in DMSO

The ^{1}H and ^{13}C NMR spectra of SH_4-Al(CH_3)

^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.41 (2H, Ar-CH=N-), 8.54 (2H, Ar-H), 7.99-7.98 (2H, Ar-H), 7.67-7.65 (2H, Ar-H),7.61-7.59 (2H, Ar-H), 7.54-7.48 (2H, Ar-H), 6.93-6.91 (2H, Ar-H), 6.86-6.82 (2H, Ar-H), -1.26 (3H, Al-CH_3)

^{13}C-NMR (100 MHz, DMSO-d_6): δ 166.56 (Ar-CH=N-), 164.72, 137.81, 137.31, 135.48, 133.01, 128.52, 127.59, 121.92, 119.82, 117.15, 115.59(Ar)

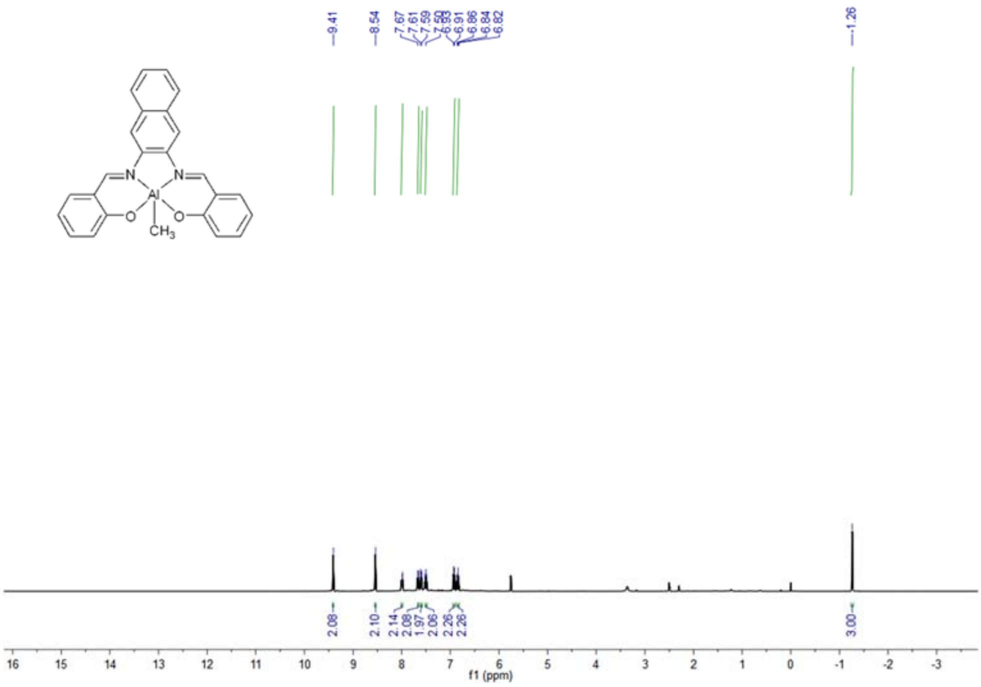

Fig. S26. ^{1}H NMR spectra of **SH_4-Al(CH_3)** in DMSO

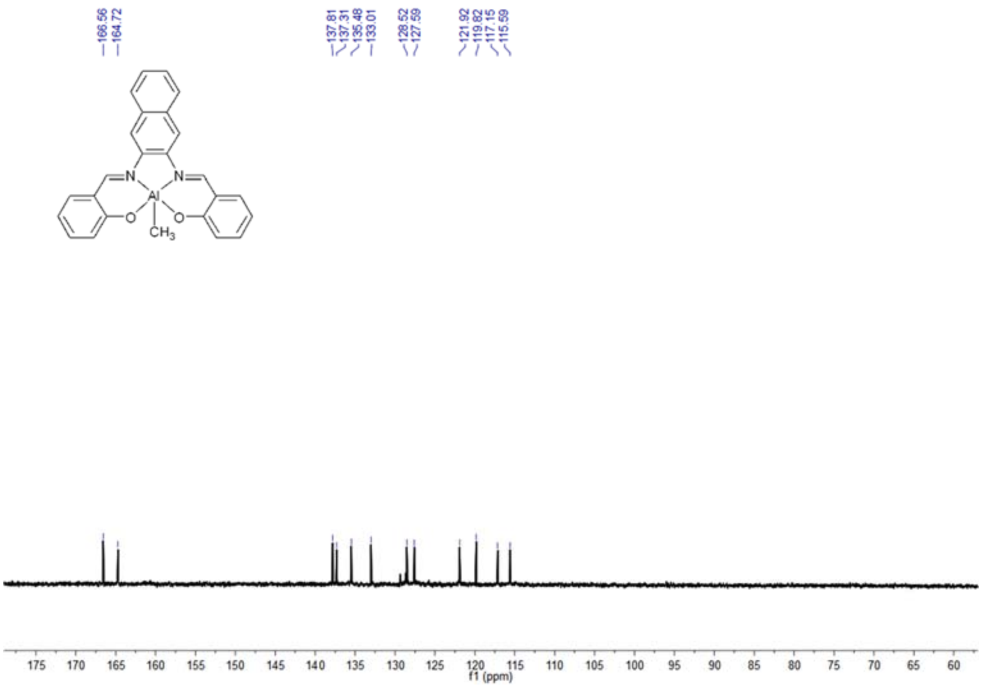

Fig. S27. ^{13}C NMR spectra of **SH_4-Al(CH_3)** in DMSO

The ^{1}H and ^{13}C NMR spectra of [IMes][Cl]

^{1}H-NMR, (400 MHz, CD_3OD): δ 8.06-8.05 (1H, N-CH-N), 6.58-6.57 (2H, CH-CH), 5.70 (4H, Ar-H), 0.90 (6H, Ar-CH_3), 0.70 (12H, Ar-CH_3)

^{13}C-NMR, (100 MHz, CD_3OD): δ 140.01 (N-CH-N), 137.05 (CH-CH), 132.83, 129.46, 128.04, 123.69 (Ar), 18.37, 14.63 (Ar-CH_3)

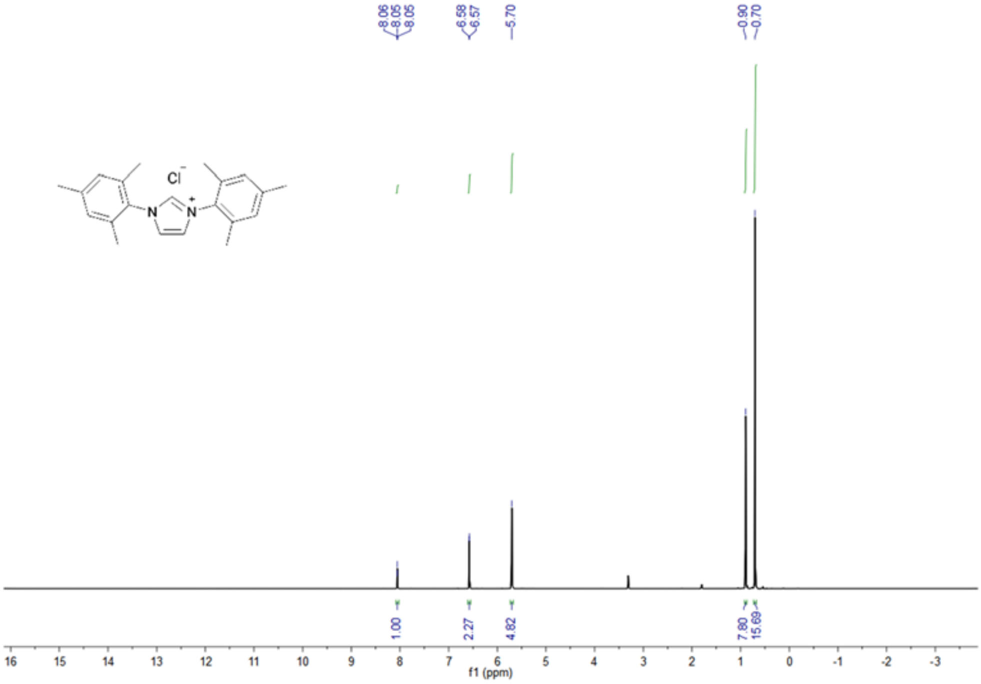

Fig. S28. ^{1}H NMR spectra of **[IMes][Cl]** in CD_3OD

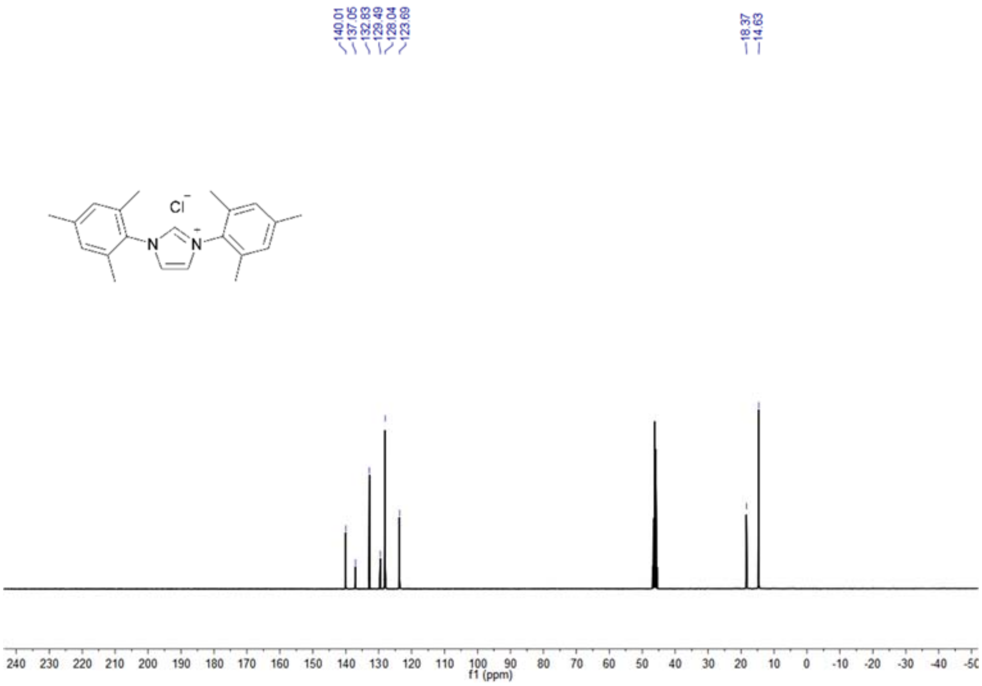

Fig. S29. ^{13}C NMR spectra of **[IMes][Cl]** in CD_3OD

The ^{1}H and ^{13}C NMR spectra of IMes-CO_2

^{1}H-NMR, (400 MHz, CD_3OD): δ 6.52 (2H, CH-CH), 5.66 (4H, Ar-H), 0.86 (6H, Ar-CH_3), 0.65 (12H, Ar-CH_3)

^{13}C-NMR, (100 MHz, CD_3OD): δ 158.46 (N-C-N), 140.00 (CH-CH), 132.76, 129.41, 127.97, 123.57 (Ar), 18.26, 14.51 (Ar-CH_3)

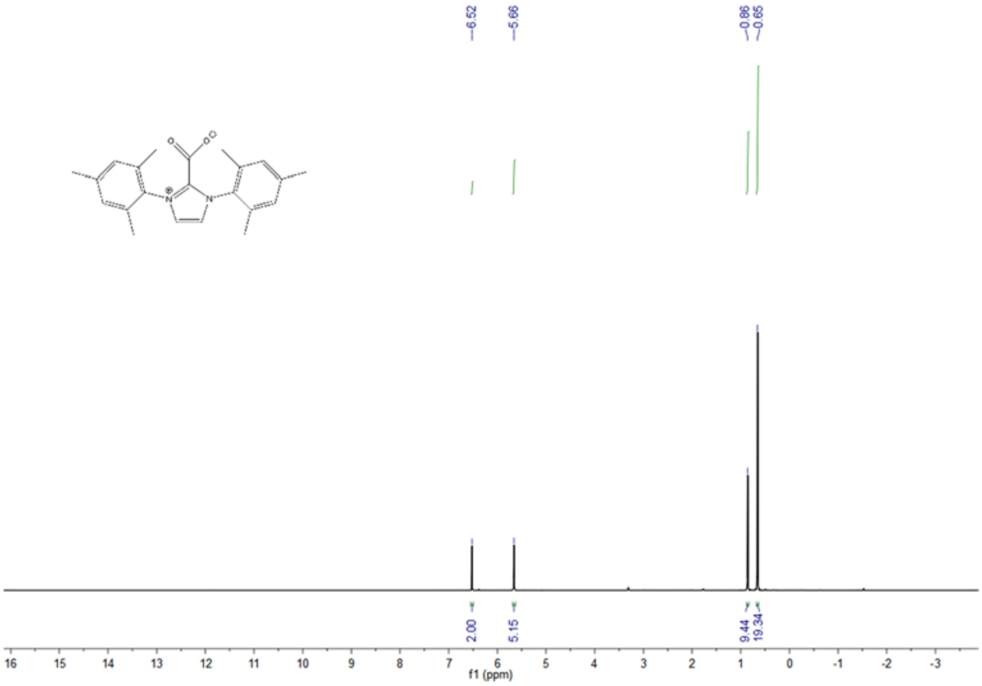

Fig. S30. ^{1}H NMR spectra of **IMes-CO_2** in CD_3OD

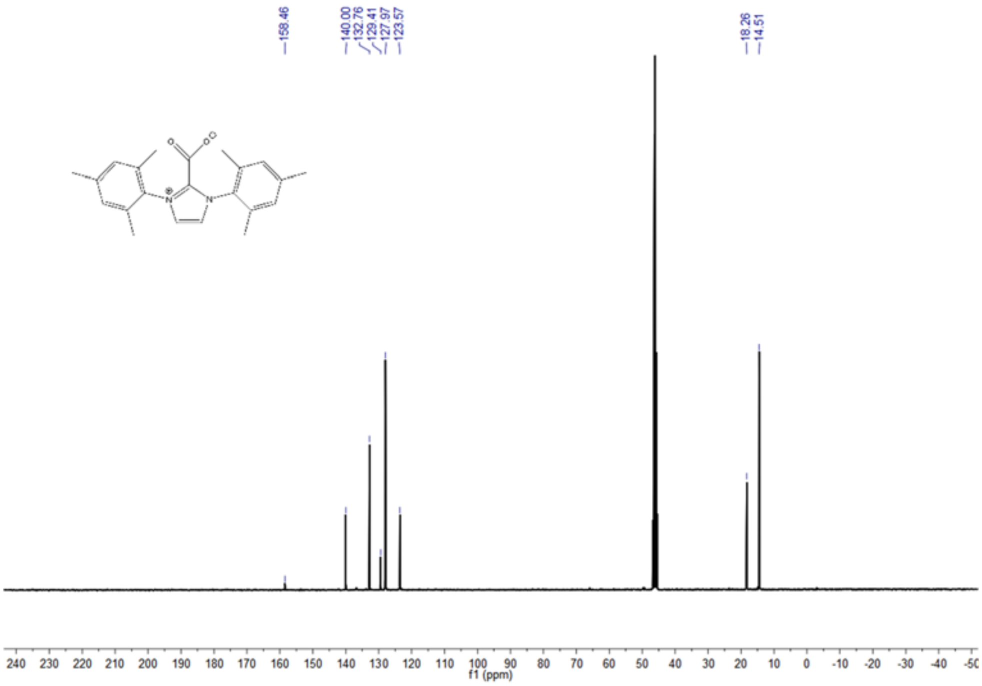

Fig. S31. ^{13}C NMR spectra of **IMes-CO_2** in CD_3OD

The ^{1}H and ^{13}C NMR spectra of $[C_1C_2ImCH_3][HCO_3]$

^{1}H-NMR, (400 MHz, DMSO-d_6): δ 1.36-1.33 (t, 3H, $-CH_3$), 2.66 (s, 3H, $C-CH_3$), 3.83 (s, 2H, $N-CH_3$), 4.25-4.19 (t, $N-CH_2-$), 7.79-7.78 (d, 1H, -CH=C-), 7.83 (d, 1H, -C=CH-)

^{13}C-NMR, (100 MHz, DMSO-d_6): δ 9.94 ($C-CH_3$)15.44 ($-CH_3$), 35.27 ($N-CH_3$), 43.26 ($N-CH_2-$), 120.81 (-CH=), 122.80 (=CH-), 144.53 (N-C-N)

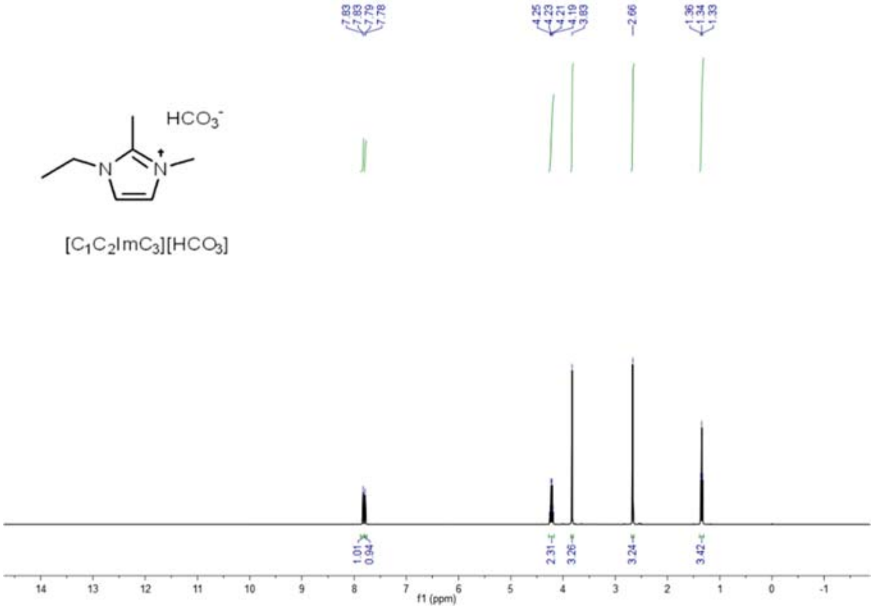

Fig. S32. ^{1}H NMR spectra of $[C_1C_2ImCH_3][HCO_3]$ in DMSO

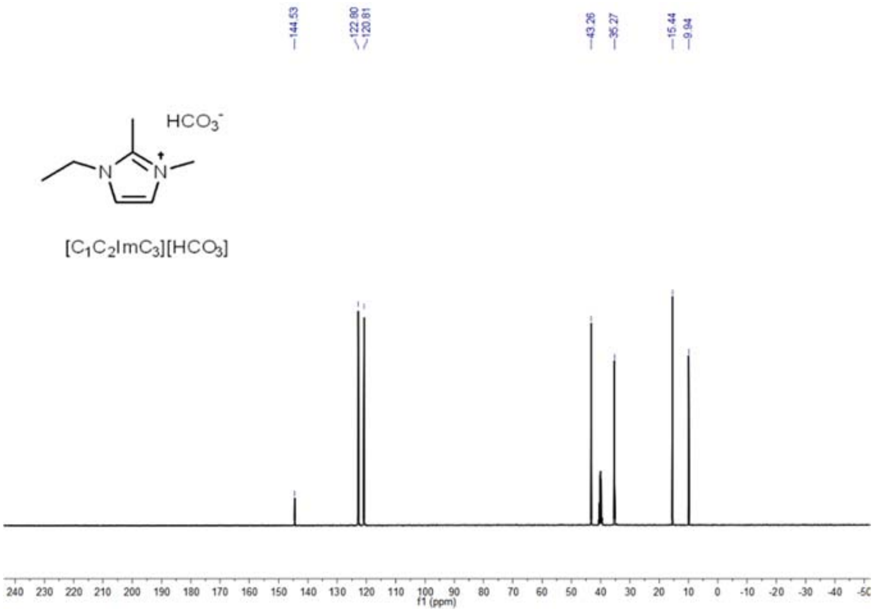

Fig. S33. ^{13}C NMR spectra of $[C_1C_2ImCH_3][HCO_3]$ in DMSO

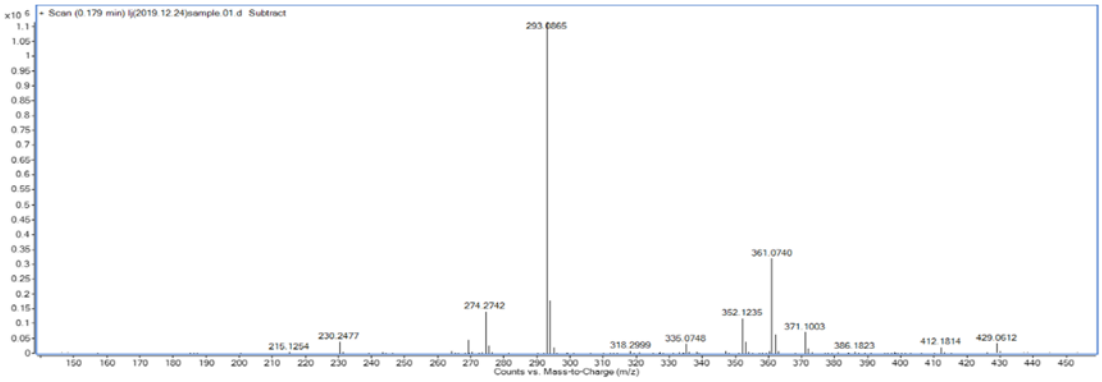

Fig. S34. MS spectrum of **SH_1-Al(Cl)** (*m/z* calcd for $[C_{16}H_{14}AlN_2O_2]^+$ 293.0865, found 293.0865)

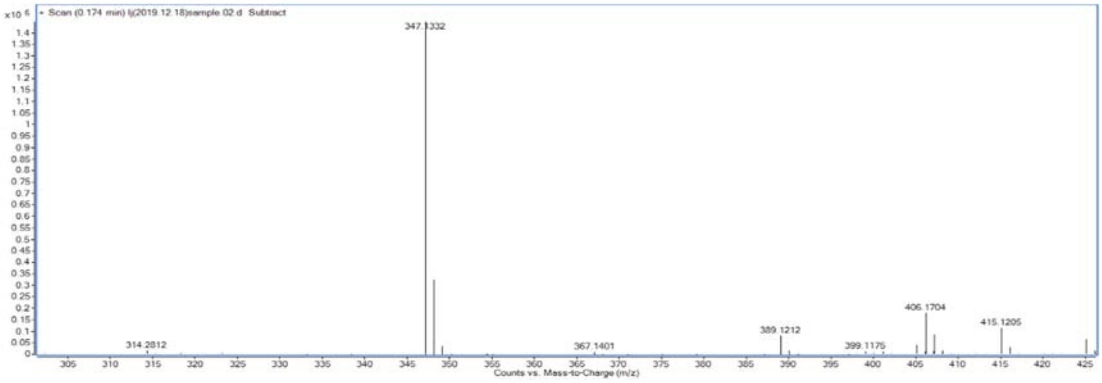

Fig. S35. MS spectrum of **SH_2-Al(Cl)** (*m/z* calcd for $[C_{20}H_{20}AlN_2O_2]^+$ 347.1335, found 347.1332)

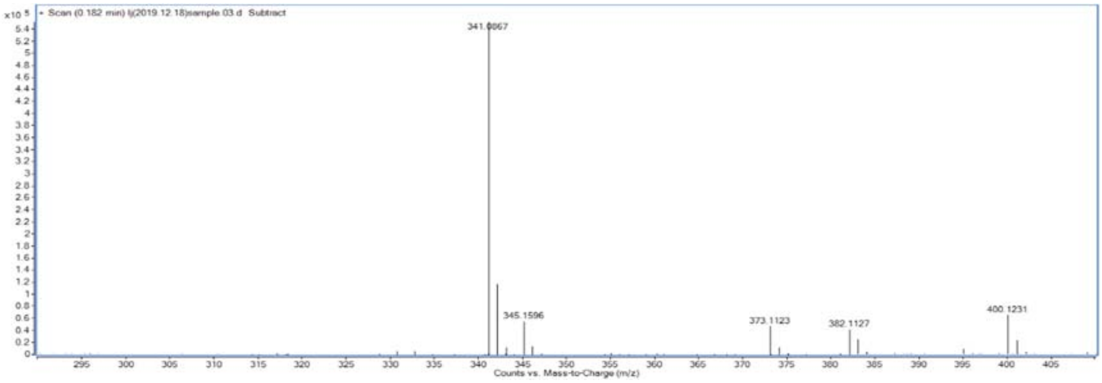

Fig. S36. MS spectrum of **SH_3-Al(Cl)** (*m/z* calcd for $[C_{20}H_{14}AlN_2O_2]^+$ 341.0865, found 341.0867)

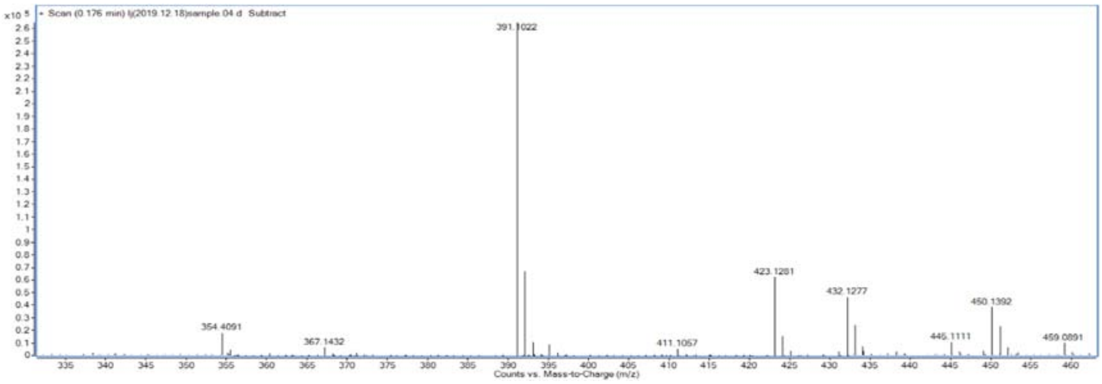

Fig. S37. MS spectrum of **SH_4-Al(Cl)** (*m/z* calcd for $[C_{24}H_{16}AlN_2O_2]^+$ 391.1022, found 391.1022)

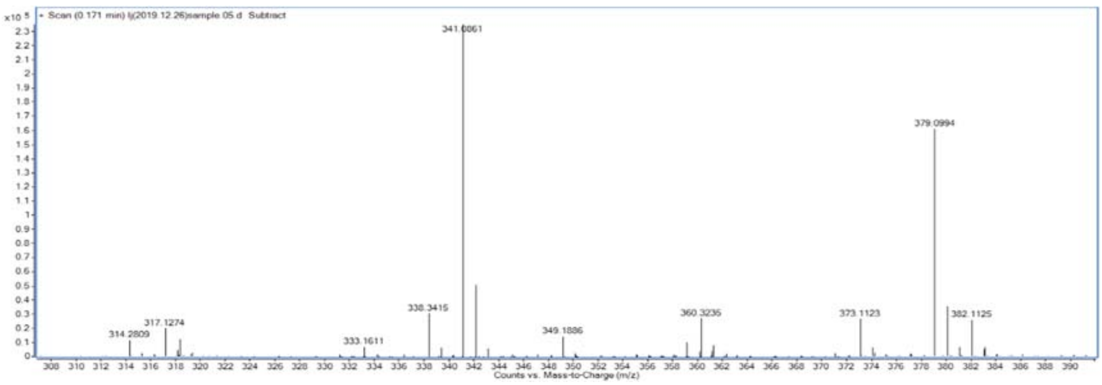

Fig. S38. MS spectrum of **SH_3-Al(CH_3)** (*m/z* calcd for $[C_{20}H_{14}AlN_2O_2]^+$ 341.0865, found 341.0861, m/z calcd for $[C_{21}H_{17}AlN_2O_2 + Na]^+$ 379.1003, found 379.0994)

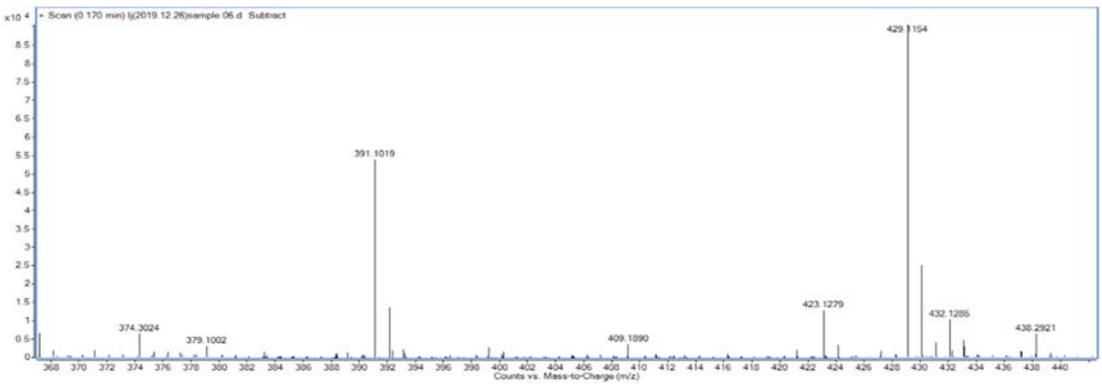

Fig. S39. MS spectrum of **SH_4-Al(CH_3)** (*m/z* calcd for $[C_{24}H_{16}AlN_2O_2]^+$ 391.1022, found 391.1019, m/z calcd for $[C_{25}H_{19}AlN_2O_2 + Na]^+$ 429.1160, found 429.1154)

The [1]H and [13]C NMR spectra of 4-Methyl-1,3-dioxolan-2-one

^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.94-4.86 (1H, O-CH-), 4.61-4.57 (1H, O-CH_2), 4.07-4.03 (1H, O-CH_2), 1.48-1.46 (3H, -CH_3)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.13, 73.75, 70.65, 18.92

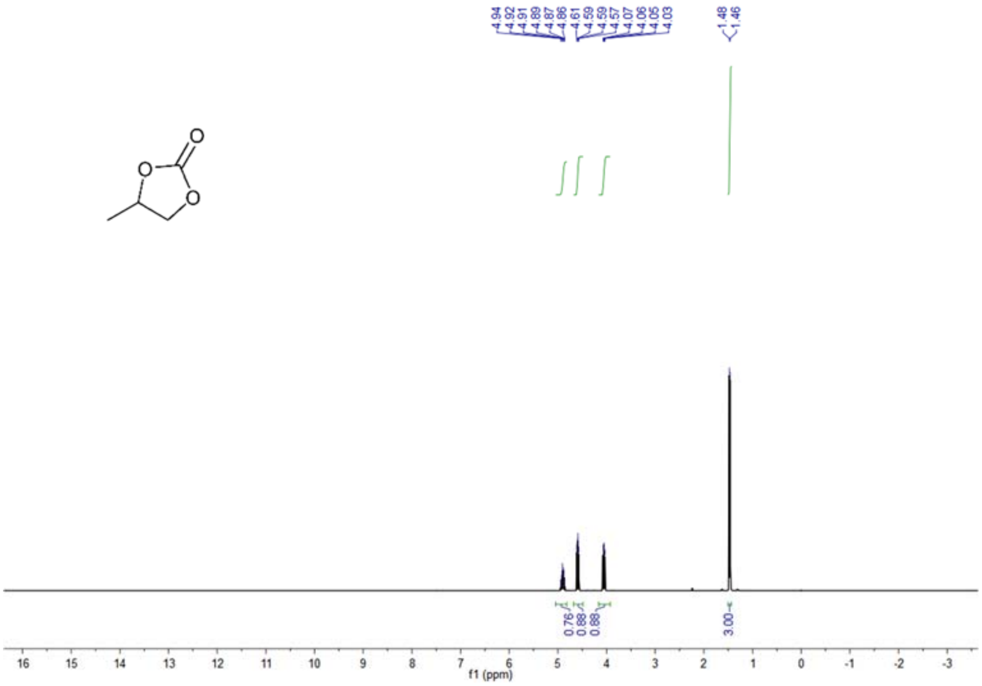

Fig. S40. ^{1}H NMR spectra of **4-Methyl-1,3-dioxolan-2-one** in $CDCl_3$

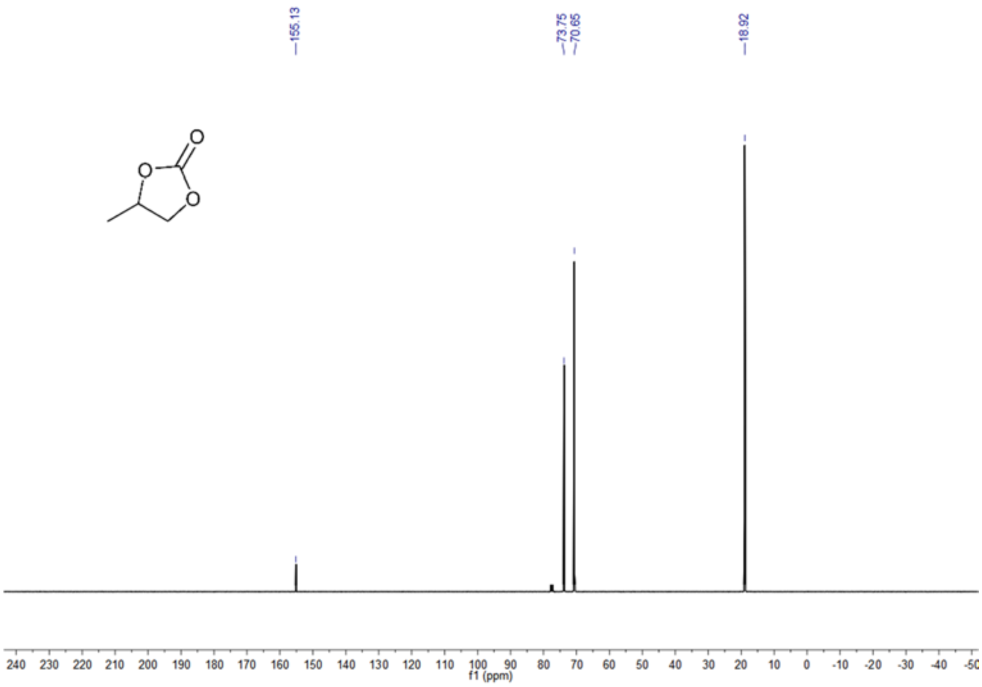

Fig. S41. ^{13}C NMR spectra of **4-Methyl-1,3-dioxolan-2-one** in $CDCl_3$

The ¹H and ¹³C NMR spectra of 4-(Chloromethyl)-1,3-dioxolan-2-one

¹H-NMR (400 MHz, $CDCl_3$): δ 5.1-5.06 (1H, O-CH-), 4.65-4.61 (1H, O-CH_2), 4.43-4.39 (1H, O-CH_2), 3.90-3.87 (1H, Cl-CH_2), 3.78-3.76 (1H, Cl-CH_2)

¹³C-NMR (100 MHz, $CDCl_3$): δ 154.70, 74.68, 66.99, 44.48

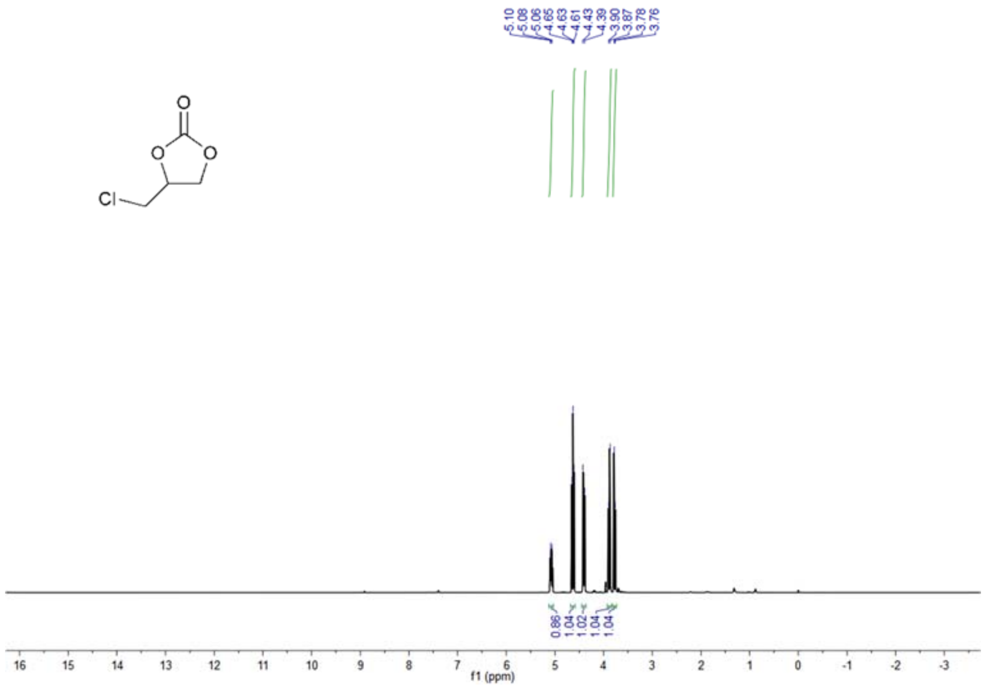

Fig. S42. ¹H NMR spectra of **4-(Chloromethyl)-1,3-dioxolan-2-one** in $CDCl_3$

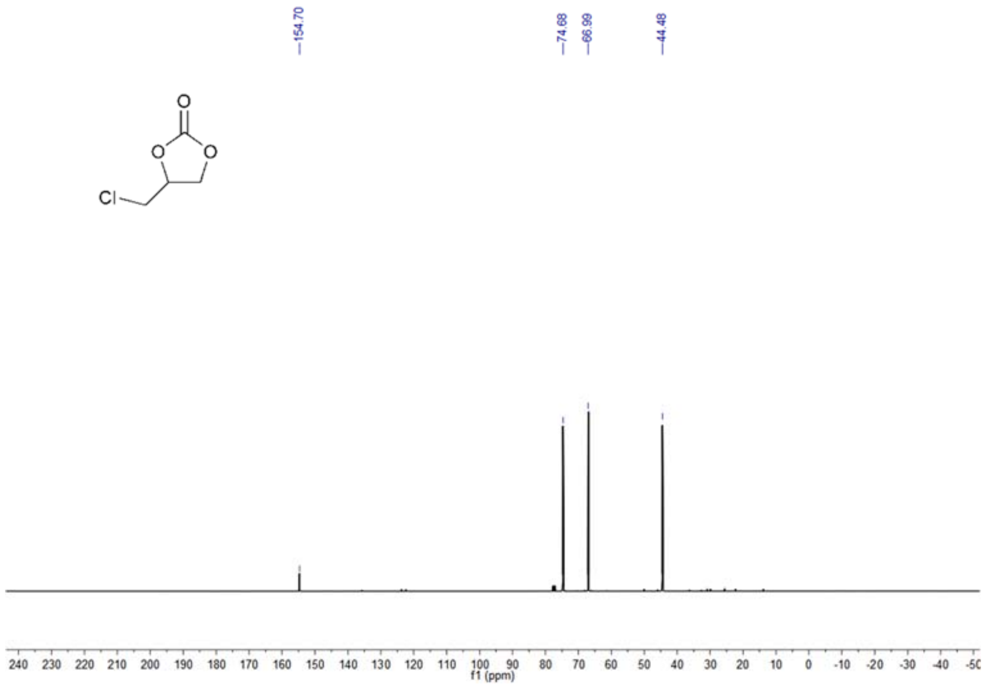

Fig. S43. ¹³C NMR spectra of **4-(Chloromethyl)-1,3-dioxolan-2-one** in $CDCl_3$

The ^{1}H and ^{13}C NMR spectra of 4,4-Dimethyl-1,3-dioxolan-2-one

^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.19 (2H, O-CH_2), 1.51 (6H, -CH_3)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.54, 81.87, 75.17, 25.57

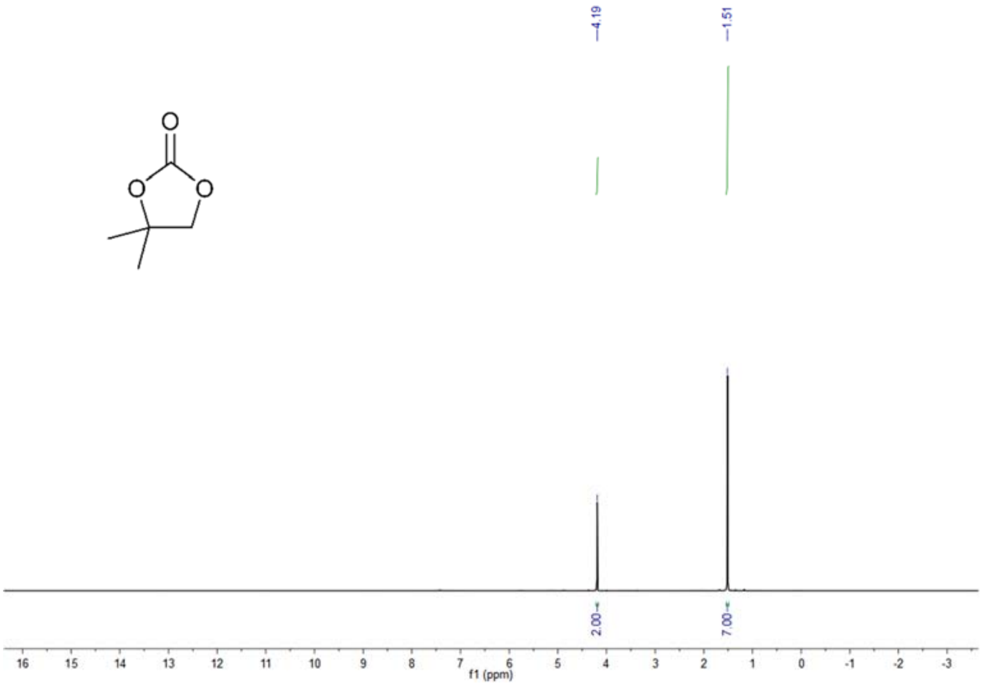

Fig. S44. ^{1}H NMR spectra of **4,4-Dimethyl-1,3-dioxolan-2-one** in $CDCl_3$

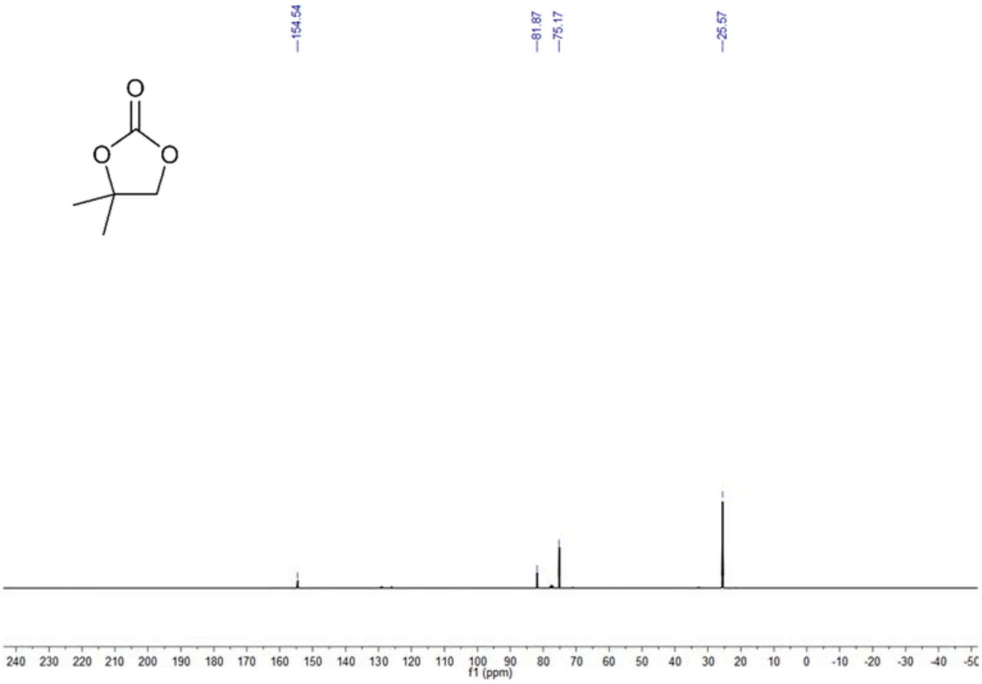

Fig. S45. ^{13}C NMR spectra of **4,4-Dimethyl-1,3-dioxolan-2-one** in $CDCl_3$

The ^{1}H and ^{13}C NMR spectra of 4-(Chloromethyl)-4-methyl-1,3-dioxolan-2-one

^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.53-4.50 (1H, O-CH_2), 4.24-4.22 (1H, O-CH_2), 3.79-3.68 (2H, Cl-CH_2), 1.62 (3H, -CH_3)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.08, 81.96, 72.03, 48.76, 22.85

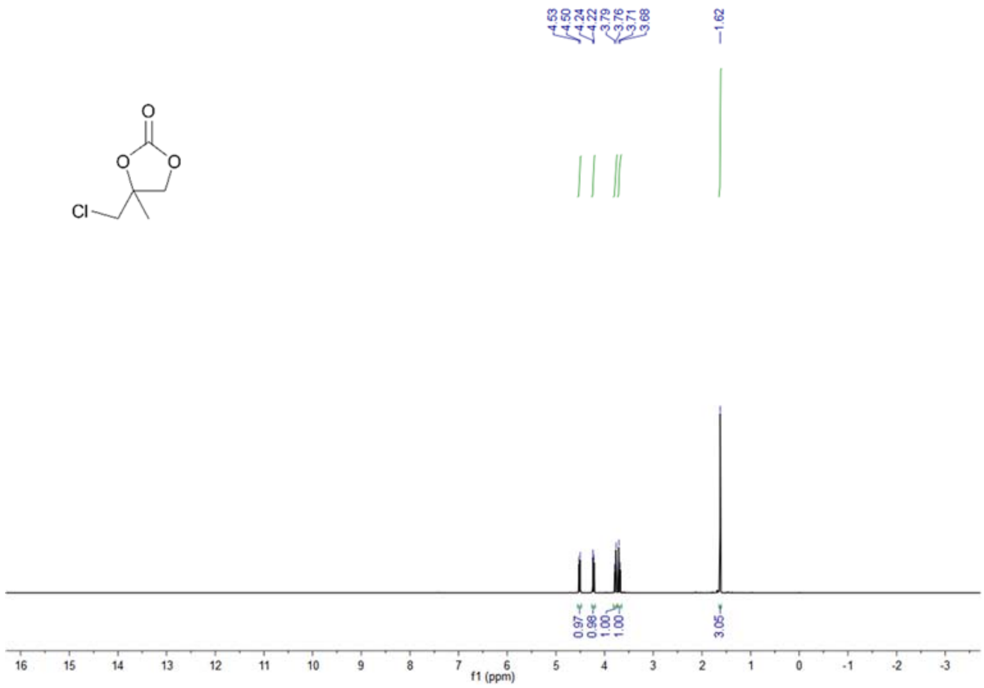

Fig. S46. ^{1}H NMR spectra of **4-(Chloromethyl)-4-methyl-1,3-dioxolan-2-one** in $CDCl_3$

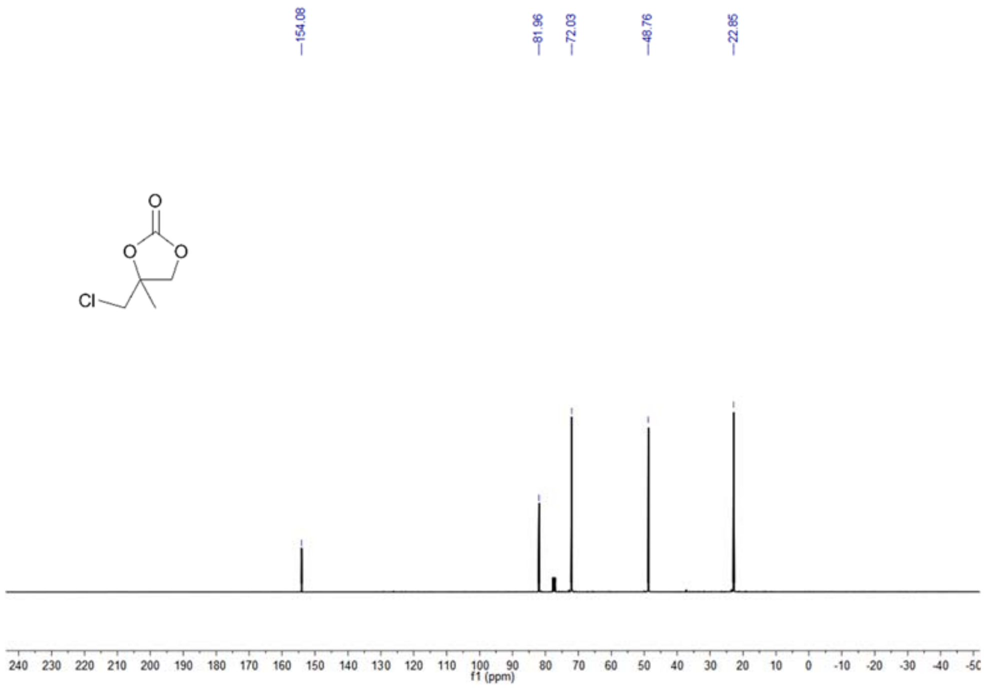

Fig. S47. ^{13}C NMR spectra of **4-(Chloromethyl)-4-methyl-1,3-dioxolan-2-one** in $CDCl_3$

The [1]H and [13]C NMR spectra of 4-Ethyl-1,3-dioxolan-2-one

[1]H-NMR (400 MHz, $CDCl_3$): δ 4.76-4.69 (1H, O-CH), 4.59-4.55 (1H, O-CH_2), 4.13-4.10 (1H, O-CH_2), 1.82-1.75 (2H, -CH_2-), 1.03-0.99 (3H, -CH_3)

[13]C-NMR (100 MHz, $CDCl_3$): δ 155.13, 78.07, 68.96, 26.48, 8.10

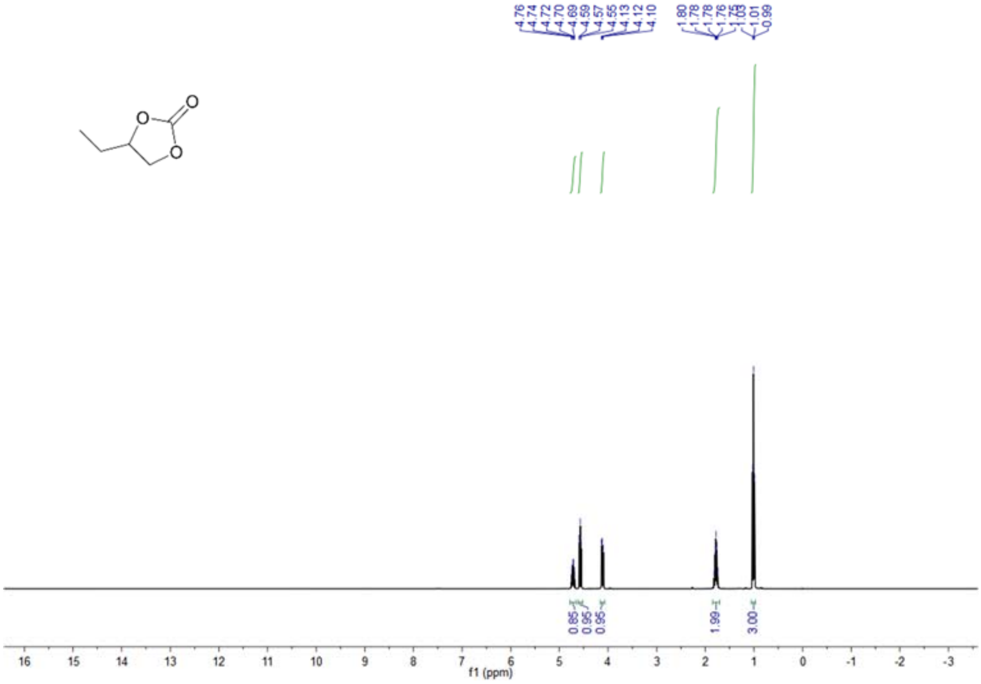

Fig. S48. [1]H NMR spectra of **4-Ethyl-1,3-dioxolan-2-one** in $CDCl_3$

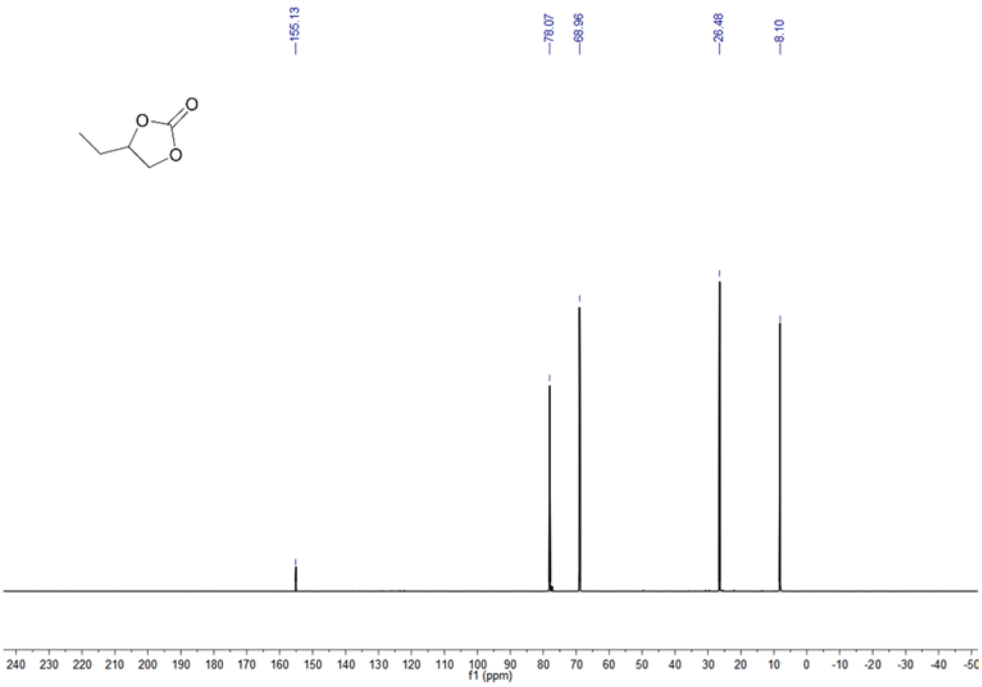

Fig. S49. [13]C NMR spectra of **4-Ethyl-1,3-dioxolan-2-one** in $CDCl_3$

The ^{1}H and ^{13}C NMR spectra of 4-Butyl-1,3-dioxolan-2-one

^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.78-4.71 (1H, O-CH), 4.59-4.55 (1H, O-CH_2), 4.11-4.07 (1H, O-CH_2), 1.79-1.70 (2H, -CH_2-), 1.41-1.37 (4H, -CH_2-), 0.94-0.91 (3H, -CH_3)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.09, 77.12, 69.35, 33.20, 26.26, 22.04, 13.54

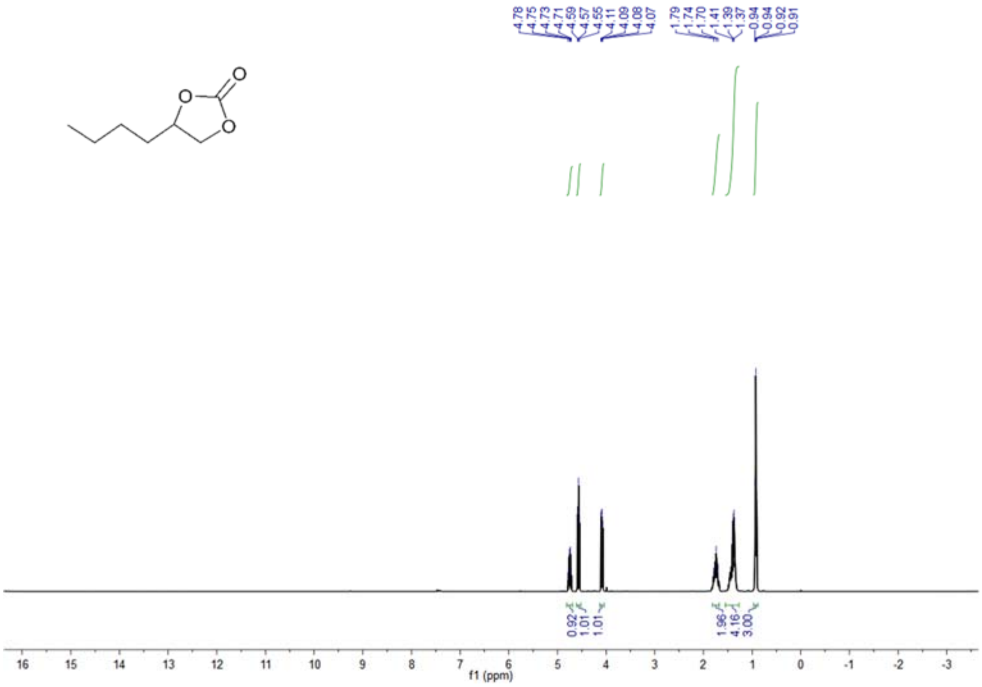

Fig. S50. ^{1}H NMR spectra of **4-Butyl-1,3-dioxolan-2-one** in $CDCl_3$

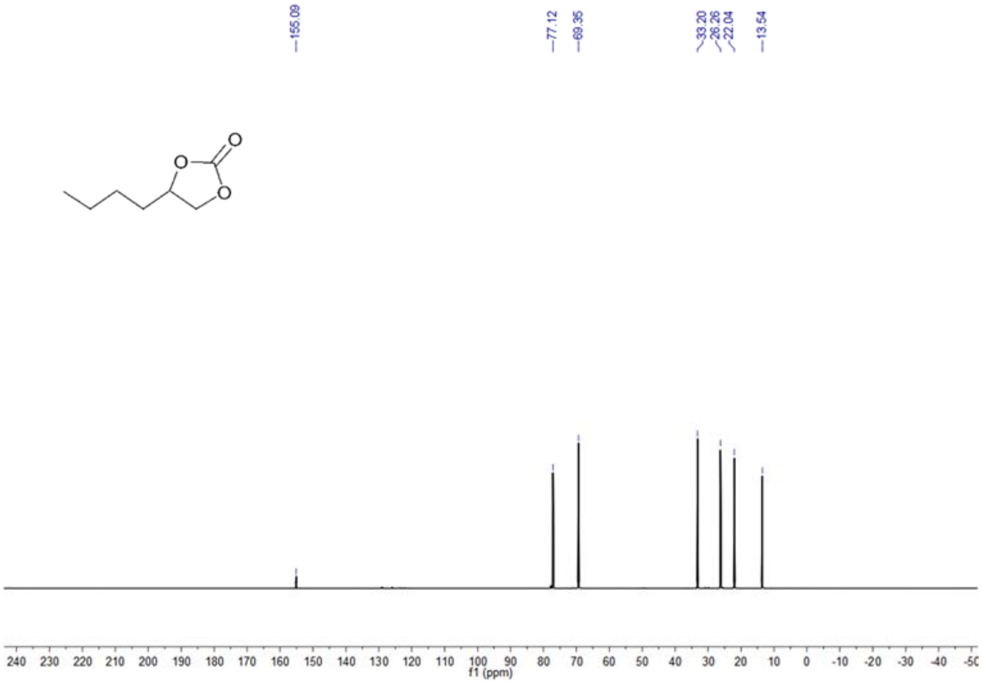

Fig. S51. ^{13}C NMR spectra of **4-Butyl-1,3-dioxolan-2-one** in $CDCl_3$

The ^{1}H and ^{13}C NMR spectra of 4-Hexyl-1,3-dioxolan-2-one

^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.73 (1H, O-CH), 4.55 (1H, O-CH_2), 4.09-4.07 (1H, O-CH_2), 1.78-1.71(2H, -CH_2-), 1.49-1.28 (8H, -CH_2-), 0.89 (3H, -CH_3)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.14, 77.15, 69.41, 33.67, 31.42, 28.68, 24.22, 22.34, 13.84

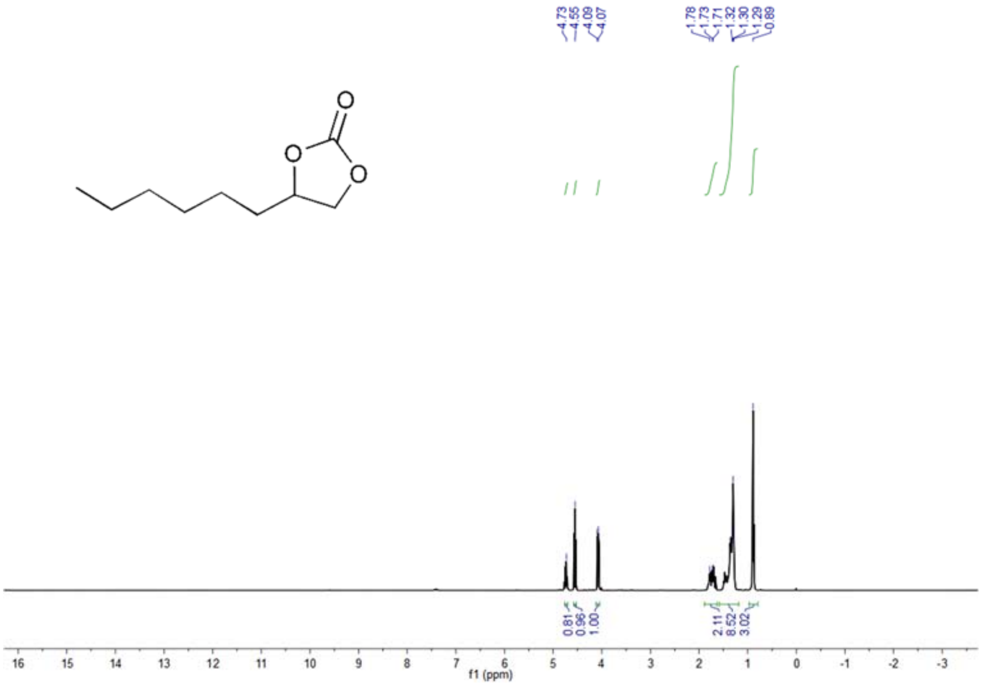

Fig. S52. ^{1}H NMR spectra of **4-Hexyl-1,3-dioxolan-2-one** in $CDCl_3$

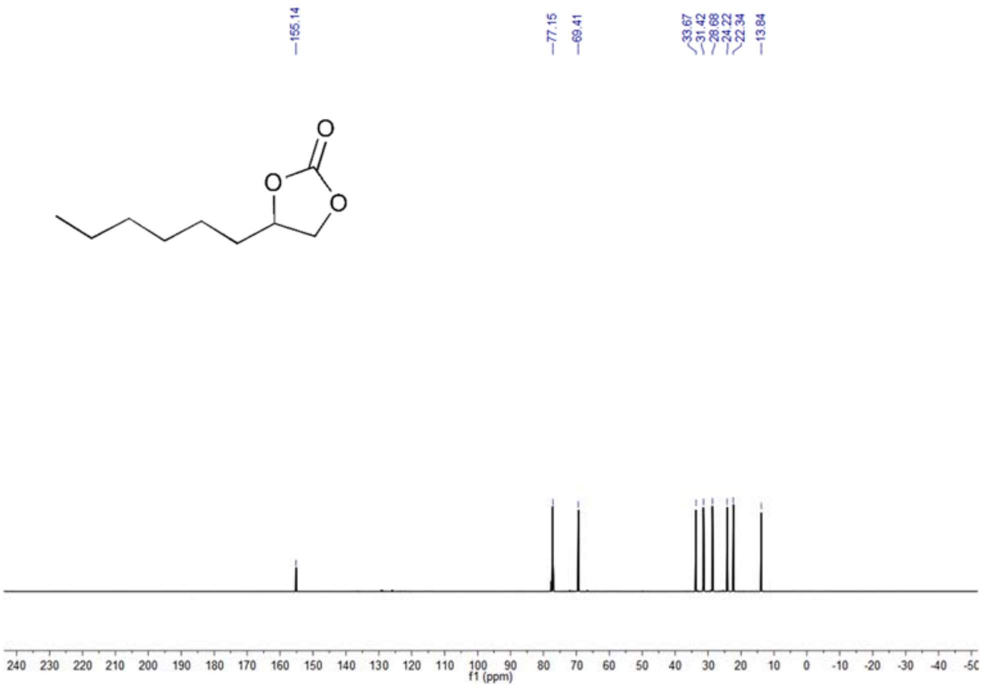

Fig. S53. ^{13}C NMR spectra of **4-Hexyl-1,3-dioxolan-2-one** in $CDCl_3$

The ^{1}H and ^{13}C NMR spectra of 4-Phenyl-1,3-dioxolan-2-one

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.41-7.33 (5H, Ar-H), 5.68-5.64 (1H, O-CH), 4.79-4.75 (1H, O-CH_2), 4.32-4.28 (1H, O-CH_2)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.02, 135.93, 129.70, 129.22, 126.01, 78.08, 71.23

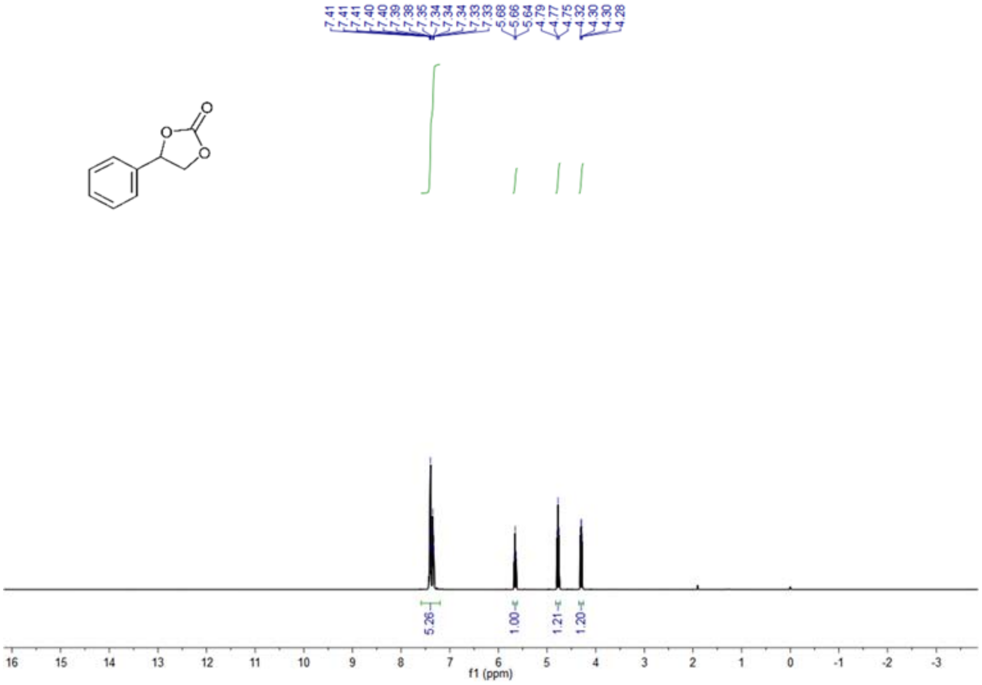

Fig. S54. ^{1}H NMR spectra of **4-Phenyl-1,3-dioxolan-2-one** in $CDCl_3$

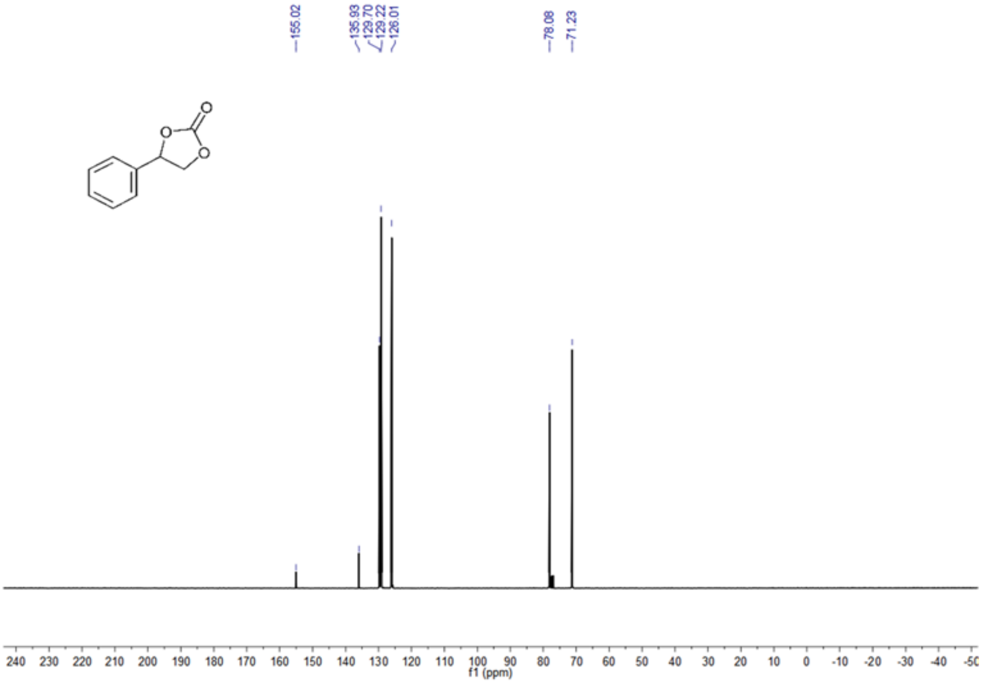

Fig. S55. ^{13}C NMR spectra of **4-Phenyl-1,3-dioxolan-2-one** in $CDCl_3$

The ^{1}H and ^{13}C NMR spectra of 4-(Phenoxymethyl)-1,3-dioxolan-2-one

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.95-7.91 (2H, Ar-H), 7.66-7.62 (1H, Ar-H), 7.55-7.52 (2H, Ar-H), 5.67-5.64 (1H, O-CH), 5.25-5.13 (2H, O-CH_2), 4.88-4.84 (1H, O-CH_2), 4.77-4.74 (1H, O-CH_2)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 156.77, 153.75, 128.67, 120.94, 113.61, 73.21, 65.89, 65.20

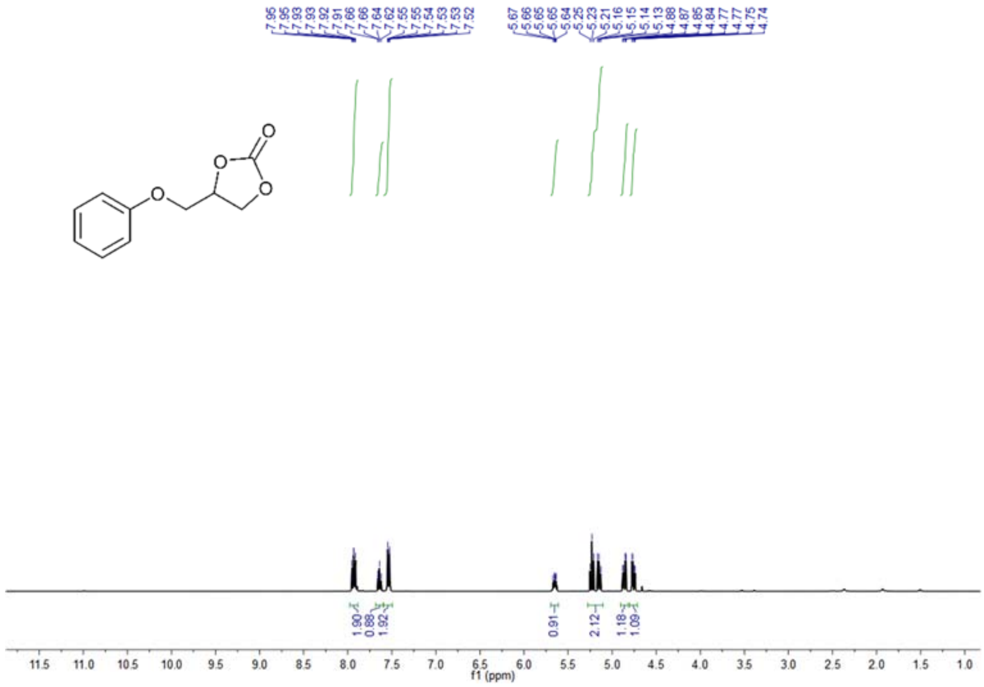

Fig. S56. ^{1}H NMR spectra of **4-(Phenoxymethyl)-1,3-dioxolan-2-one** in $CDCl_3$

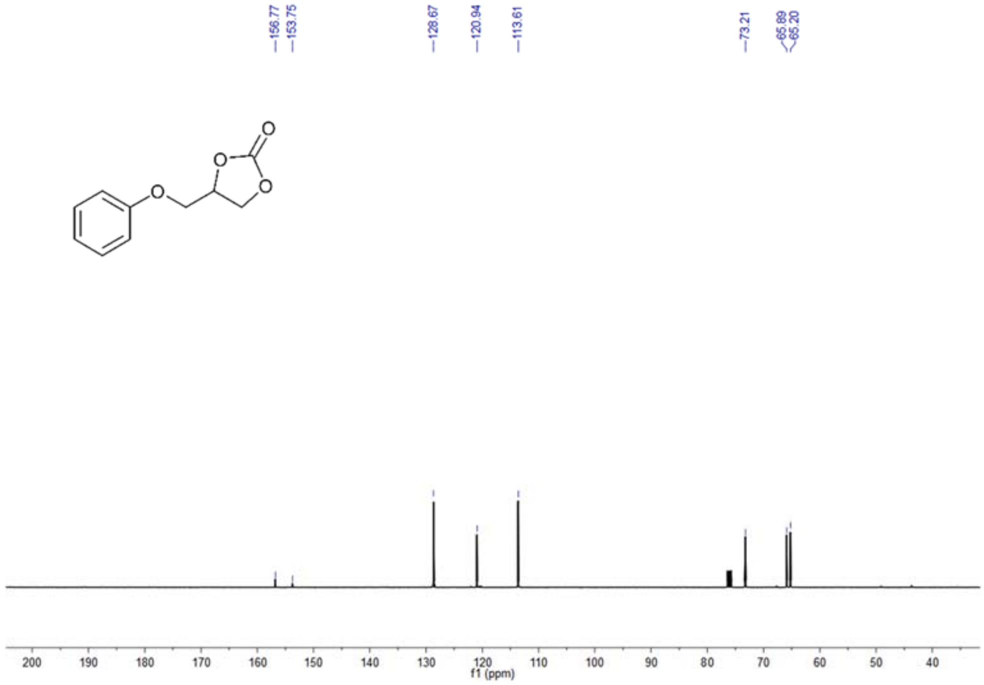

Fig. S57. ^{13}C NMR spectra of **4-(Phenoxymethyl)-1,3-dioxolan-2-one** in $CDCl_3$

The ^{1}H and ^{13}C NMR spectra of 4-((Allyloxy)methyl)-1,3-dioxolan-2-one

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.92-5.82 (1H, =CH-), 5.30-5.17 (2H, $=CH_2$), 4.91-4.86 (1H, O-CH), 4.55-4.50 (1H, O-CH_2), 4.38-4.34 (1H, O-CH_2), 4.05-4.03 (2H, O-CH_2), 3.73-3.69 (1H, O-CH_2), 3.62-3.58 (1H, O-CH_2)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.16, 133.93, 117.10, 75.39, 72.08, 68.93, 66.13

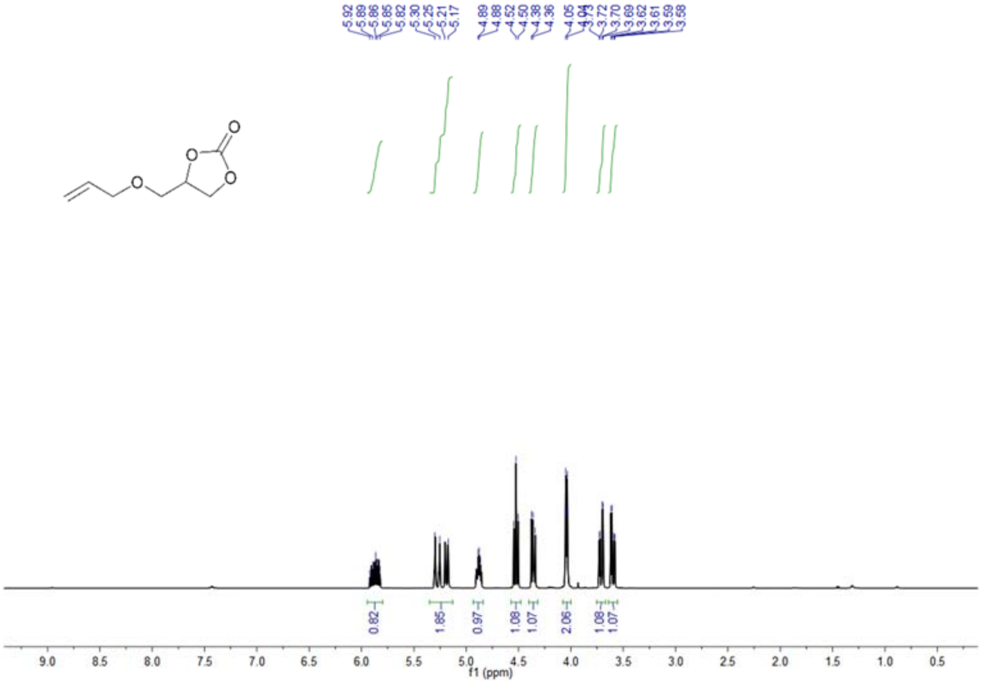

Fig. S58. ^{1}H NMR spectra of **4-((Allyloxy)methyl)-1,3-dioxolan-2-one** in $CDCl_3$

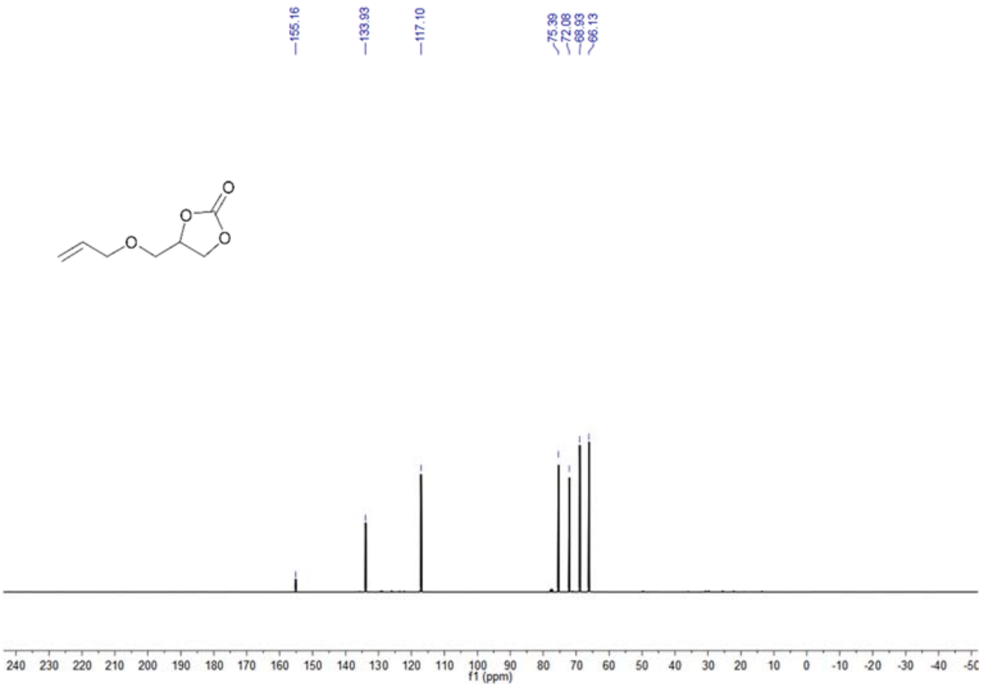

Fig. S59. ^{13}C NMR spectra of **4-((Allyloxy)methyl)-1,3-dioxolan-2-one** in $CDCl_3$

The ¹H and ¹³C NMR spectra of 4-((Tert-butoxy)methyl)-1,3-dioxolan-2-one

^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.85-4.79 (1H, O-CH), 4.52-4.48 (1H, O-CH_2), 4.39-4.36 (1H, O-CH_2), 3.66-3.63 (1H, O-CH_2), 3.54-3.50 (1H, O-CH_2), 1.20 (9H, -CH_3)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.30, 75.43, 73.60, 66.38, 61.22, 21.17

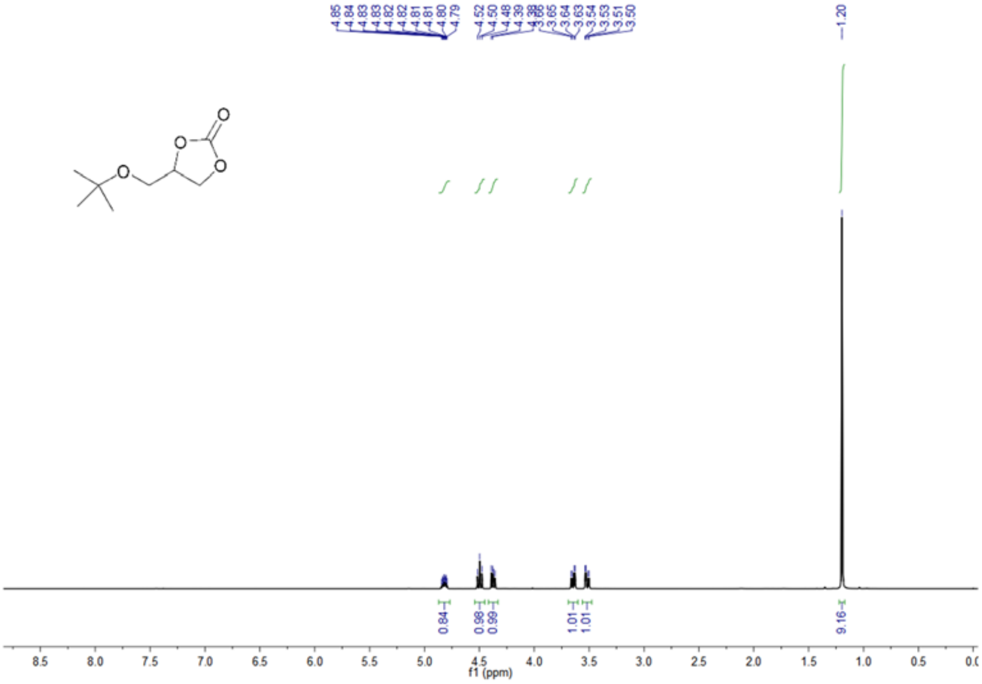

Fig. S60. ^{1}H NMR spectra of **4-((Tert-butoxy)methyl)-1,3-dioxolan-2-one** in $CDCl_3$

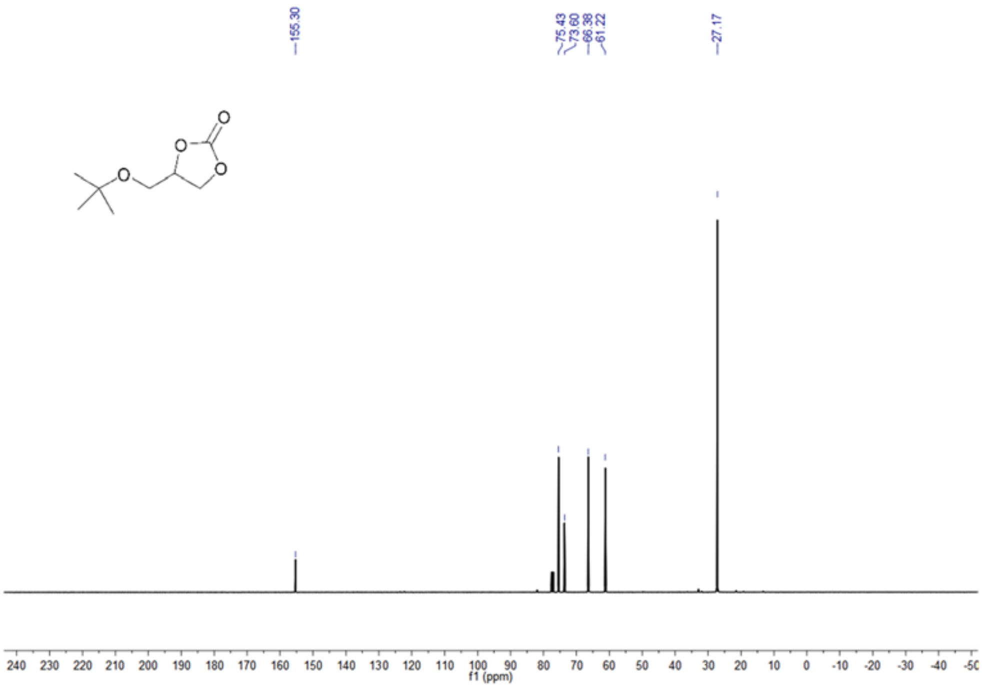

Fig. S61. ^{13}C NMR spectra of **4-((Tert-butoxy)methyl)-1,3-dioxolan-2-one** in $CDCl_3$

The ^{1}H and ^{13}C NMR spectra of 4-(benzyloxymethyl)-1,3-dioxolan-2-one

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.30-7.27 (5H, Ar-H), 4.75-4.74 (1H, O-CH), 4.52-4.51 (2H, Ar-CH_2), 4.41-4.36 (1H, O-CH_2), 4.30-4.26 (1H, O-CH_2), 3.67-3.64 (1H, O-CH_2), 3.54-3.52 (1H, O-CH_2)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.26, 137.42, 128.55, 127.98, 127.70, 75.37, 73.50, 69.04, 66.29

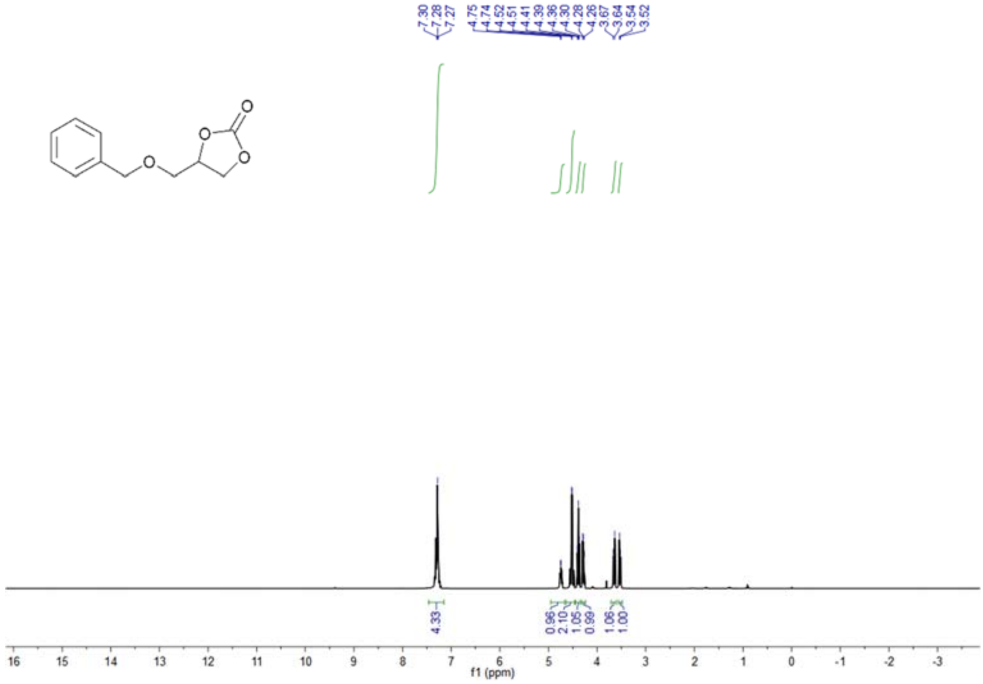

Fig. S62. ^{1}H NMR spectra of **4-(benzyloxymethyl)-1,3-dioxolan-2-one** in $CDCl_3$

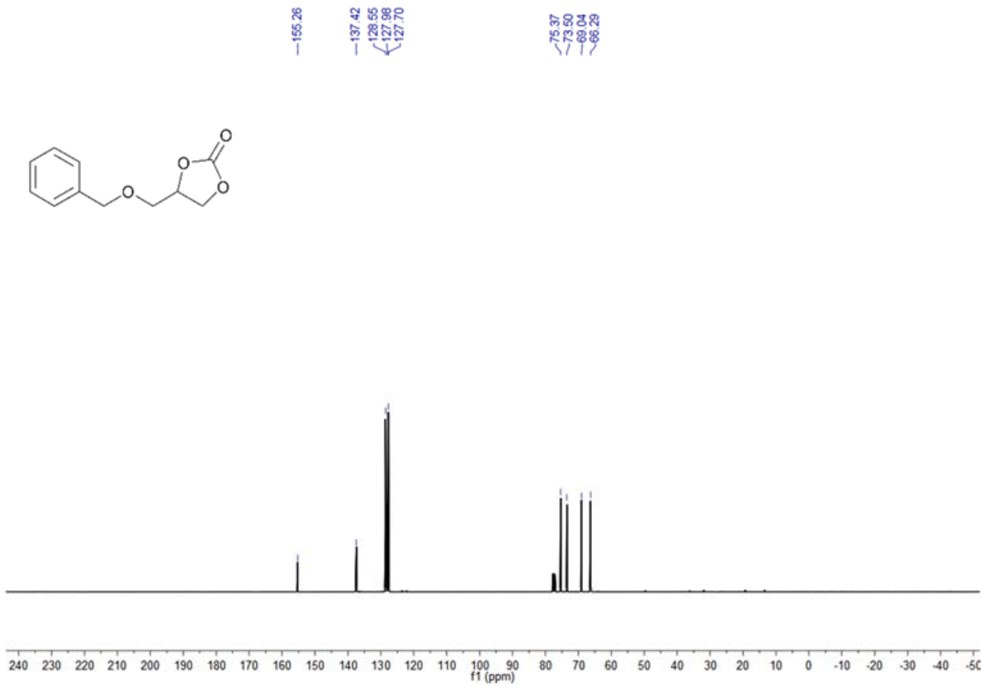

Fig. S63. ^{13}C NMR spectra of **4-(benzyloxymethyl)-1,3-dioxolan-2-one** in $CDCl_3$

The ^{1}H and ^{13}C NMR spectra of 4-(But-3-en-1-yl)-1,3-dioxolan-2-one

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.81-5.79 (1H, =CH-), 5.11-5.03 (2H, =CH_2), 4.77-4.74 (1H, O-CH), 4.58-4.53 (1H, O-CH_2), 4.12-4.08 (1H, O-CH_2), 2.22-2.19 (2H, -CH_2-), 1.93-1.79 (2H, -CH_2-)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.05, 136.25, 116.14, 76.47, 69.37, 32.91, 28.58

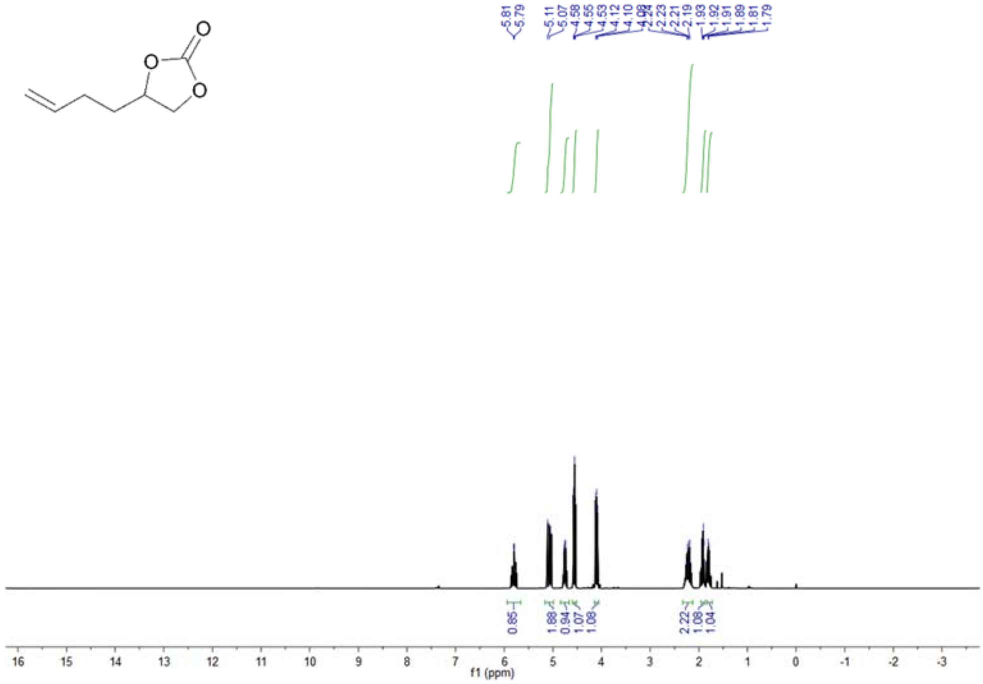

Fig. S64. ^{1}H NMR spectra of **4-(But-3-en-1-yl)-1,3-dioxolan-2-one** in $CDCl_3$

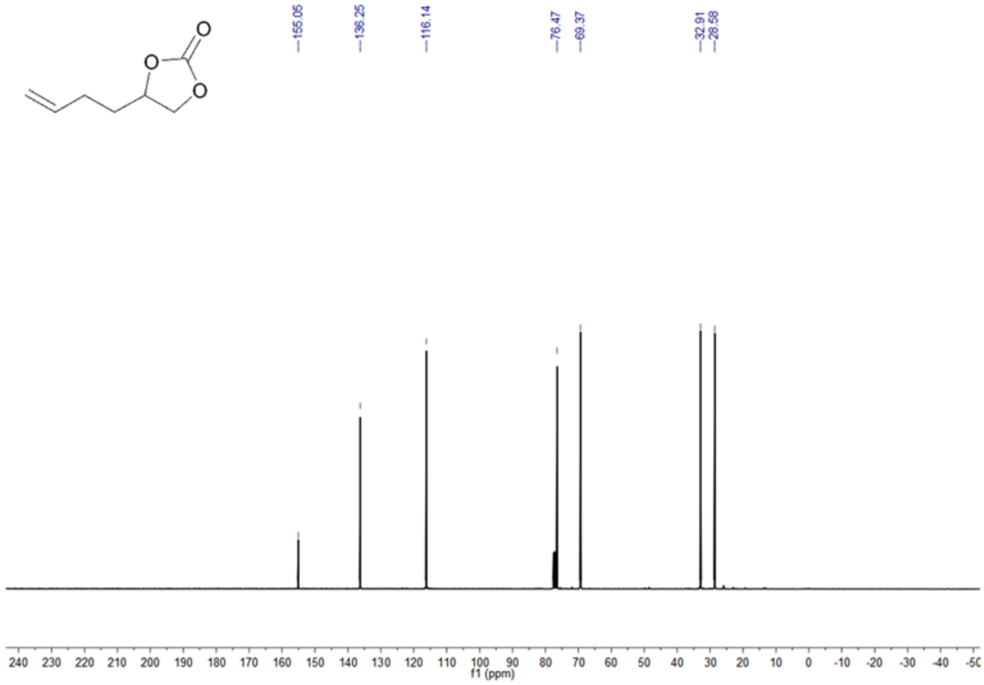

Fig. S65. ^{13}C NMR spectra of **4-(But-3-en-1-yl)-1,3-dioxolan-2-one** in $CDCl_3$

The ^{1}H and ^{13}C NMR spectra of Cyclohexene carbonate

^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.75-4.73 (2H, O-CH), 1.92-1.86 (4H, $-CH_2-$), 1.61-1.58 (4H, $-CH_2-$), 1.47-1.44 (4H, $-CH_2-$)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.37, 75.76, 26.56, 18.97

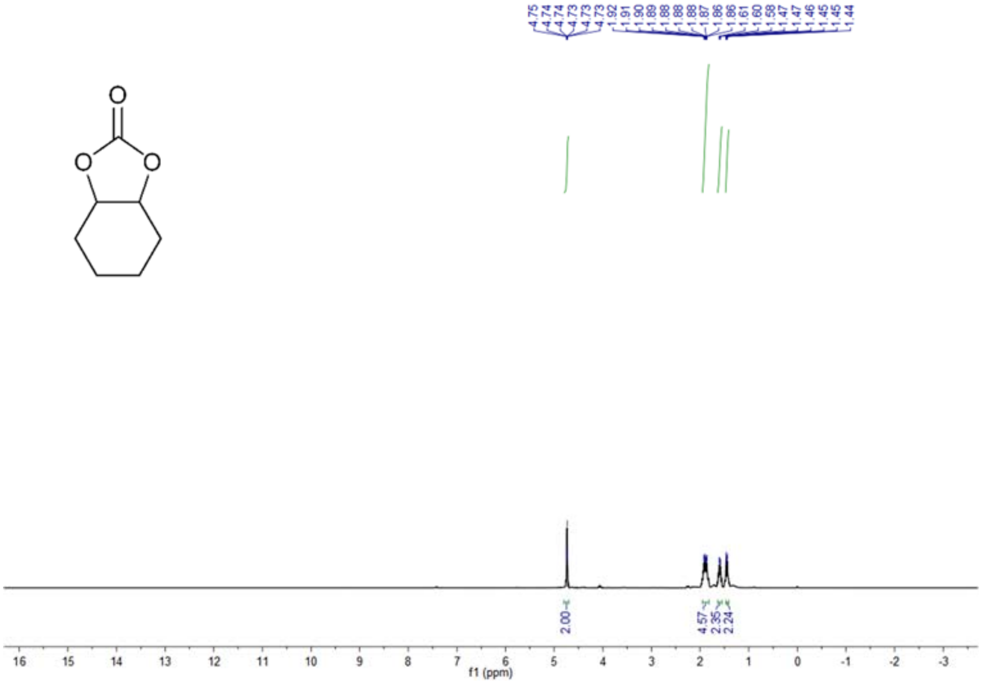

Fig. S66. ^{1}H NMR spectra of **Cyclohexene carbonate** in $CDCl_3$

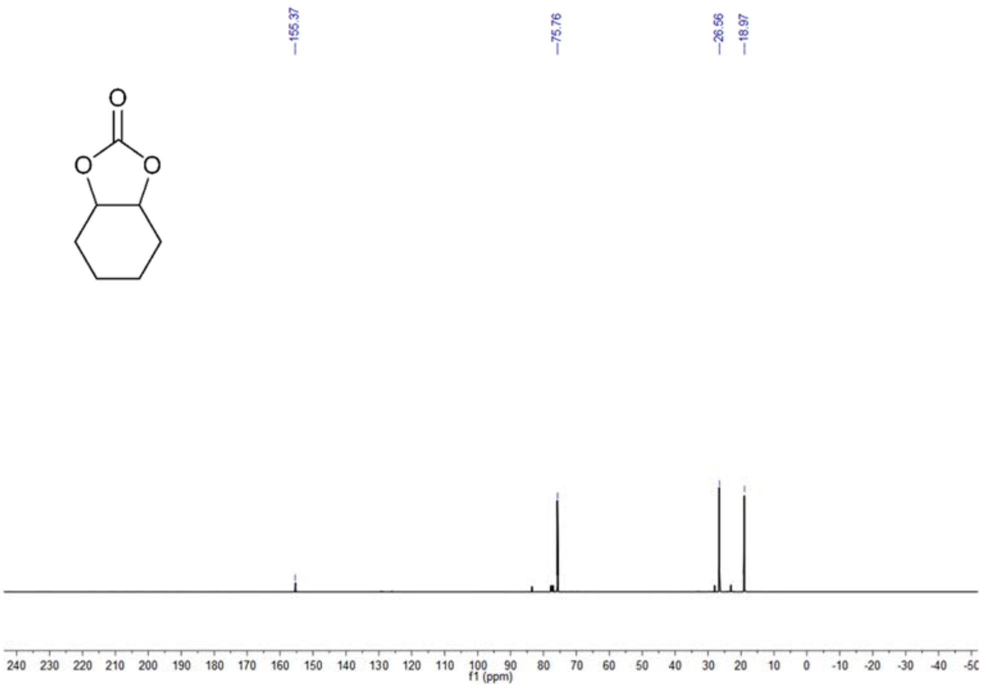

Fig. S67. ^{13}C NMR spectra of **Cyclohexene carbonate** in $CDCl_3$

The ^{1}H and ^{13}C NMR spectra of 1,2-Cyclopentylene carbonate

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.15-5.13 (2H, O-CH), 2.14-2.11 (2H, $-CH_2-$), 1.82-1.72 (4H, $-CH_2-$)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 155.53, 81.89, 33.03, 21.52

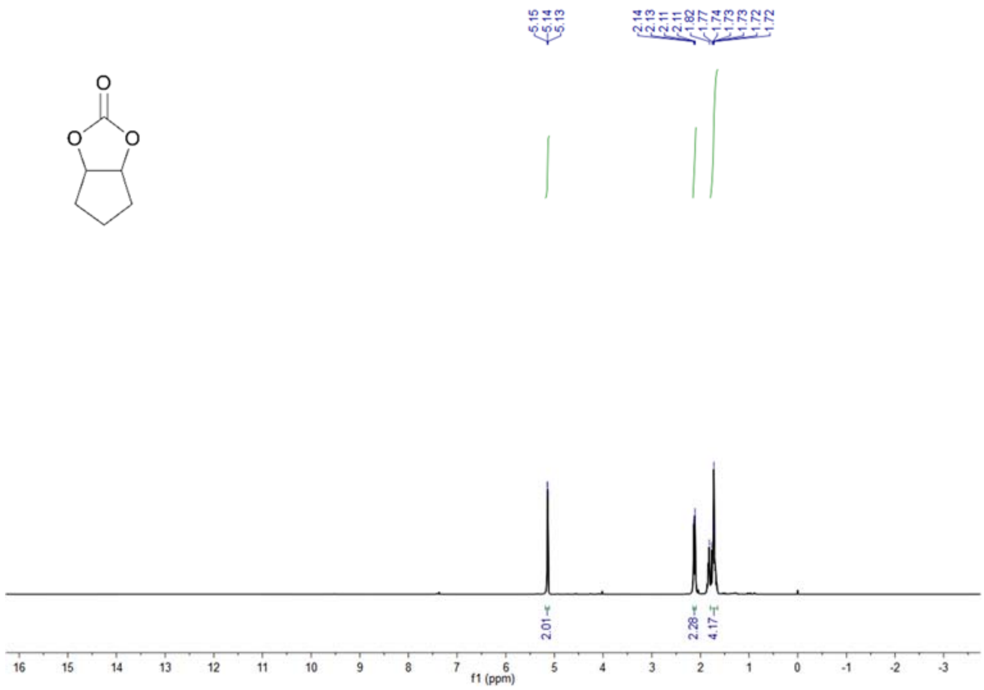

Fig. S68. ^{1}H NMR spectra of **1,2-Cyclopentylene carbonate** in $CDCl_3$

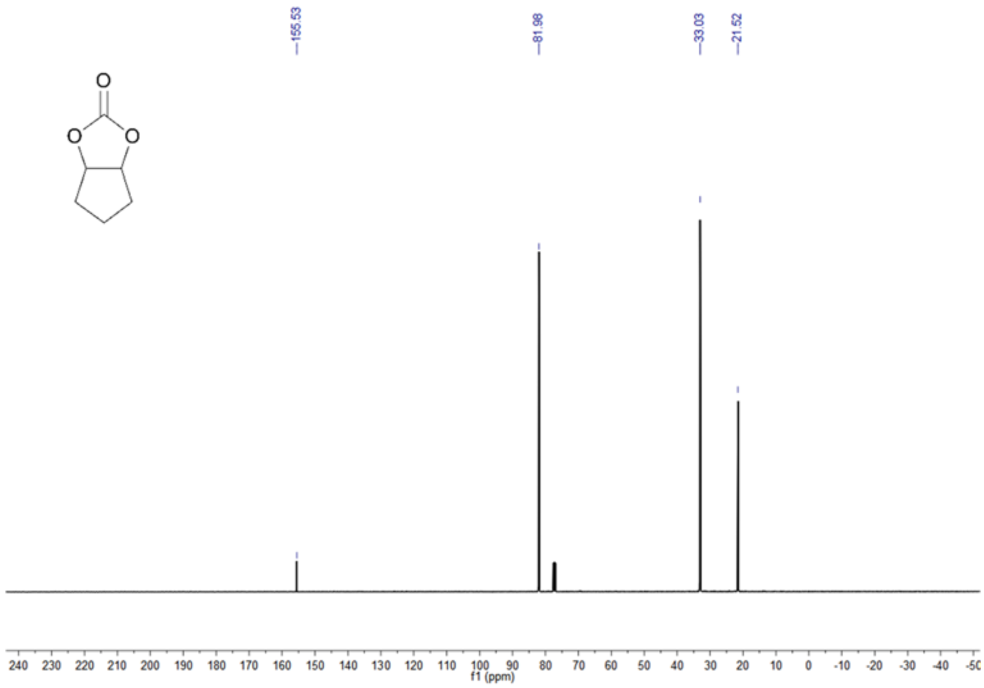

Fig. S69. ^{13}C NMR spectra of **1,2-Cyclopentylene carbonate** in $CDCl_3$

The ^{1}H and ^{13}C NMR spectra of Tetrahydrofuro[3,4-d]-1,3-dioxol-2-one

^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.26-5.25 (2H, O-CH), 4.23-4.22 (2H, $-CH_2-$), 3.60-3.56 (2H, $-CH_2-$)

^{13}C-NMR (100 MHz, $CDCl_3$): δ 154.62, 80.28, 72.95

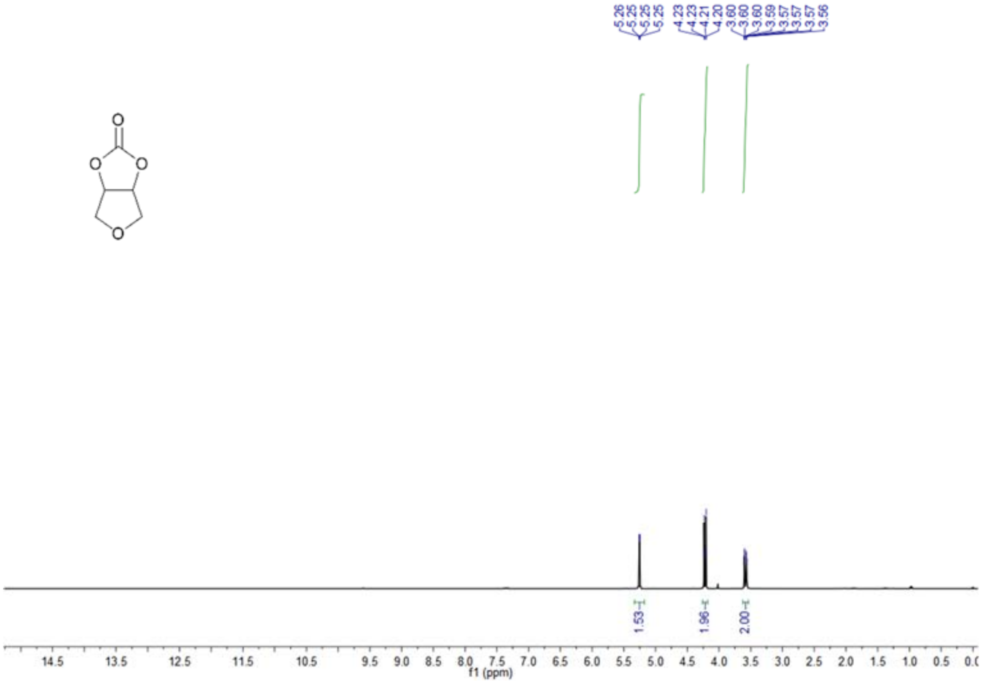

Fig. S70. ^{1}H NMR spectra of **Tetrahydrofuro[3,4-d]-1,3-dioxol-2-one** in $CDCl_3$

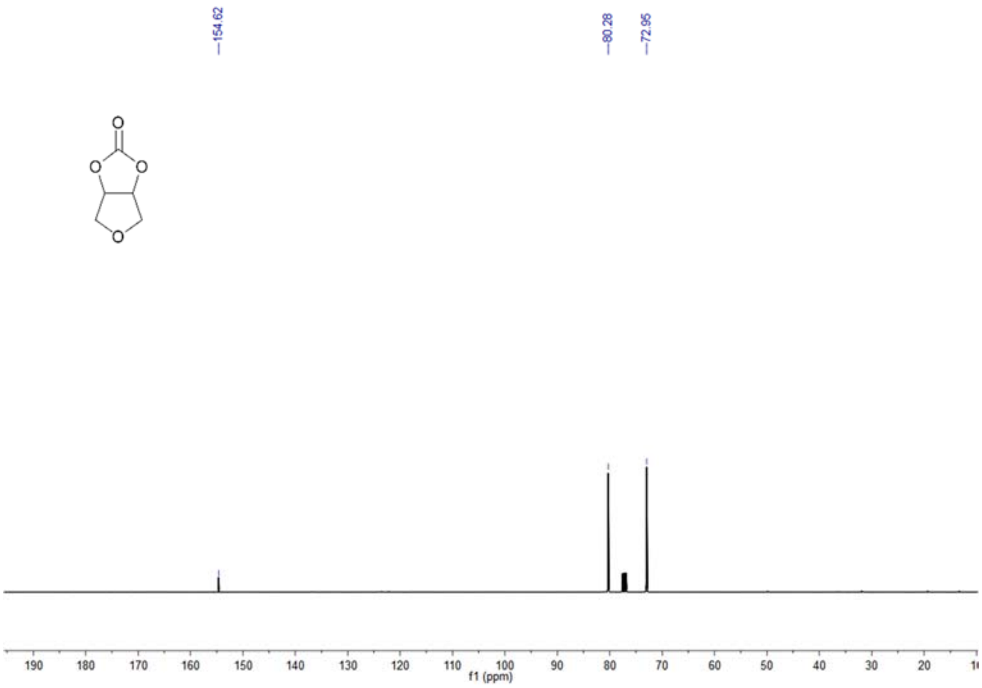

Fig. S71. ^{13}C NMR spectra of **Tetrahydrofuro[3,4-d]-1,3-dioxol-2-one** in $CDCl_3$