Supporting Information

Efficient synthesis of cyclic carbonates from atmospheric CO_2 using a positive charge delocalized ionic liquid catalyst

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Table of Contents

1. General Information

All commercially available materials were used as provided without further purification unless otherwise noted. Highly purified carbon dioxide and diluted CO_2 (mixture of 15% CO_2 and 85% N_2 in volume.) were supplied by Jinggong Gas Co., Ltd. Epichlorohydrin, 1-Bromo-2,3-epoxypropane, Allyl Glycidyl Ether, Glycidyl Phenyl Ether, tert-Butyl Glycidyl Ether, cyclohexene oxide, DMAP, 4-Aminopyridine, 4-(Methylamino)pyridine, DABCO were purchased from TCI (Shanghai) Development Co., Ltd. Styrene oxide, TMG, DBU, 4-Hydroxypyridine were purchased from Aladdin Reagent Co. Reactions were monitored by TLC on silica gel plates (GF254). The NMR spectras were recorded on a BRUKER-AV400 spectrometer in $CDCl_3$, DMSO-d_6, D_2O. Tetramethylsilane (TMS; δ = 0.00 ppm) served as internal standards for ^1H NMR. IR spectra were measured using a Nicolet 6700 FT-IR spectrometer and are reported in terms of frequency of absorption (cm^{-1}).

2. Experimental Section

2.1 Synthesis of catalysts

All of the catalysts were synthesized by using one-step method. In a typical reaction, [DMAPH]Br (**1a**) was prepared according to procedures reported earlier.[1] NH_4Br (489.8 mg, 5.0 mmol), DMAP (610.8 mg, 5.0 mmol) was poured into the round-bottom flask equipped with magnetic stirring bar. 3.0 mL of methanol was added to the reactor. And the reaction was kept stirring at ambient temperature for 3 h. Methanol was removed via rotary evaporation. Then the residue was dried under vacuum at 60 °C for 12 hours, giving the product as a white solid.

[4-OH-PyH] **(1d)** was prepared according to procedures reported earlier.[2] An equimolar amount of HBr was added dropwise to 4-hydroxypyridine, and the mixture was stirred for 4–5 h to ensure that the reaction was completed. Then, water was removed under reduced pressure. Then it was dried under vacuum of 60 °C for 12 hours and [4-OH-PyH]Br (**1d**) was obtained.

2.2 Procedure of the cycloaddition reaction of CO_2 with styrene oxide

In a typical experiment, an oven-dried two-necked round bottom flask equipped with a magnetic stirrer. SO (1225mg, 10 mmol), 1a (20.3 mg, 1 mol %) were added to the flask. A needle, connected to the CO_2 source, was dipped into the solution so that a total gas flow of 2.49×10^{-5} L/s was bubbled through the solution. And the reaction was placed in an oil-bath under desired temperature and reflux for 4 h. In the case of the catalytic runs employing industrial flue gas, the gas source was represented by the lecture bottle containing diluted CO_2. This was connected to the reaction flask in the same way as the pure gases. Following reaction, a sample of the reaction mixture was withdrawn to determine conversion by ^1H NMR.

3. Experimental Characterization Data

3.1 Characterization of the catalysts

[DMAPH]Br (1a): ^{1}H NMR (400 MHz, DMSO): δ=8.15–8.29 (m, 2H), 6.89 –7.06 (m, 2H), 3.17 (s, 6H). ^{13}C NMR (101MHz, DMSO): δ= 156.83, 139.27, 106.94, 39.50.

[4-NHCH$_3$-PyH] (1b): According to the synthetic procedure of [DMAPH]Br. ^{1}H NMR (400 MHz, D_2O): δ=7.92 (d, 2H), 6.73 (d, 2H), 2.88 (s, 3H).^{13}C NMR (101 MHz, D_2O): δ=158.85, 138.80, 28.65. ^{13}C NMR (101MHz, DMSO): δ= 153.63, 136.29, 103.94, 37.45

[4-NH$_2$-PyH] (1c): According to the synthetic procedure of [DMAPH]Br. ^{1}H NMR (400 MHz, D_2O) δ 7.94 (d, J = 9.3 Hz, 1H), 6.77 (d, J = 7.4 Hz, 1H), 4.80 (s, 2H).^{13}C NMR (101 MHz, D_2O) δ 159.45 (s), 140.36 (s), 108.44 (s).

[4-OH-PyH] (1d): ^{1}H NMR (400 MHz, D_2O) δ =7.83–7.94 (m, 2H), 6.54–6.64 (m, 2H).^{13}C NMR (101 MHz, D_2O): δ= 179.85 (s), 139.46 (s), 116.46 (s).

[DBUH]Cl (2a): According to the synthetic procedure of [DMAPH]Br. ^{1}H NMR (400 MHz, DMSO) δ 10.30 (s, 1H), 3.58 – 3.51 (m, 2H), 3.47 (t, *J* = 5.8 Hz, 2H), 3.44 – 3.23 (m, 2H), 3.22 (t, *J* = 5.7 Hz, 2H), 2.78 – 2.71 (m, 2H), 1.94 – 1.85 (m, 2H), 1.68 – 1.55 (m, 6H).^{13}C NMR (101 MHz, DMSO) δ 165.33 (s), 53.26 (s), 47.84 (s), 39.50 (s), 37.37 (s), 31.20 (s), 28.27 (s), 25.96 (s), 23.39 (s), 18.88 (s).

[DBUH]Br (2b): According to the synthetic procedure of [DMAPH]Br. ^{1}H NMR (400 MHz, DMSO) δ 9.60 (s, 1H), 3.56 (d, *J* = 9.0 Hz, 2H), 3.48 (s, 2H), 3.24 (s, 2H), 2.69 (d, *J* = 10.2 Hz, 2H), 1.91 (s, 2H), 1.61 (s, 6H).^{13}C NMR (101 MHz, DMSO) δ 165.34 (s), 53.34 (s), 47.86 (s), 39.50 (s), 37.39 (s), 31.52 (s), 28.19 (s), 25.89 (s), 23.29 (s), 18.83 (s).

[HMIM]Br (3): was prepared according to procedures reported earlier.[2] ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.17 (s, 1H), 7.71 (d, *J* = 22.2 Hz, 2H), 3.88 (s, 3H).^{13}C NMR (101

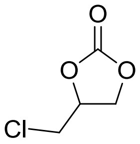
MHz, DMSO-d_6): δ 135.75 (s), 123.18 (s), 119.62 (s), 39.51 (s), 35.49 (s).

[HTMG]Br (4): According to the synthetic procedure of [DMAPH]Br. ^{1}H NMR (400 MHz, D_2O): δ 2.93 (s, 12H).^{13}C NMR (101MHz, D_2O): δ 161.30 (s), 38.85 (s).

[DABCOH]Br (5): According to the synthetic procedure of [DMAPH]Br. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.04 (s, 12H).^{13}C NMR (101 MHz, DMSO-d_6): δ 43.93 (s), 39.49 (s).

3.2 Characterization of the products

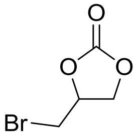
4-chloromethyl-1, 3-dioxolan-2-one (7a):



^{1}H NMR (400 MHz, $CDCl_3$) δ 4.99 (dd, J = 8.4, 3.6 Hz, 1H), 4.60 (t, J = 8.6 Hz, 1H), 4.42 (dd, J = 8.9, 5.7 Hz, 1H), 3.81 (dd, J = 12.2, 5.3 Hz, 1H), 3.74 (dd, J = 12.2, 3.7 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.64 (s), 74.64 (s), 67.17 (s), 44.33 (s).

IR (neat): ν =1794, 1396, 1170, 1078, 769,

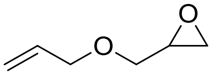
4- bromomethyl-1, 3-dioxolan-2-one (**7b**):



^{1}H NMR (400 MHz, $CDCl_3$) δ 4.95 (dt, *J* = 13.5, 5.3 Hz, 1H), 4.63 – 4.55 (m, 1H), 4.35 (dd, *J* = 8.9, 5.9 Hz, 1H), 3.58 (d, *J* = 5.2 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 154.46 (s), 74.28 (s), 68.42 (s), 31.90 (s).

IR (neat): ν =1794, 1478, 1394, 1160, 1065, 768, 715

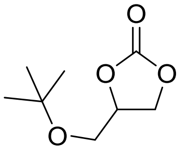
4-(allyloxy)-1, 3-dioxolan-2-one (7c):



^{1}H NMR (400 MHz, CDCl$_3$) δ 5.91 – 5.76 (m, 1H), 5.21 (dd, *J* = 28.4, 13.8 Hz, 2H), 4.86 – 4.75 (m, 1H), 4.48 (t, *J* = 8.4 Hz, 1H), 4.36 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.02 (dd, *J* = 5.5, 1.5 Hz, 2H), 3.67 (dd, *J* = 11.1, 3.6 Hz, 1H), 3.58 (dd, *J* = 11.1, 3.7 Hz, 1H).^{13}C NMR (101 MHz, CDCl$_3$) δ 155.27 (s), 133.94 (s), 117.94 (s), 75.38 (s), 72.74 (s), 69.08 (s), 66.49 (s).

IR (neat): ν =2858, 1817, 1783, 1479, 1394, 1176, 1048, 932, 774, 715

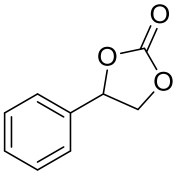
4-(tert-butoxy)-1, 3-dioxolan-2-one (7d):



^{1}H NMR (400 MHz, CDCl$_3$) δ 4.74 (dt, *J* = 8.2, 3.8 Hz, 1H), 4.43 (t, *J* = 8.3 Hz, 1H), 4.36 – 4.29 (m, 1H), 3.57 (dd, *J* = 10.5, 4.1 Hz, 1H), 3.46 (dd, *J* = 10.5, 3.5 Hz, 1H), 1.13 (s, 9H).^{13}C NMR (101 MHz, CDCl$_3$) δ 155.41 (s), 75.44 (s), 73.88 (s), 66.59 (s), 61.44 (s), 27.33 (s).

IR (neat): ν =2975, 1786, 1365, 1164, 1102, 1504, 1012, 883, 770, 712

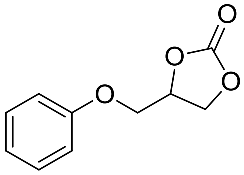
4-phenyl-1, 3-dioxolan-2-one (7e):



^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 (dd, *J* = 31.0, 8.4 Hz, 5H), 5.68 (t, *J* = 8.0 Hz, 1H), 4.80 (t, *J* = 8.4 Hz, 1H), 4.38 – 4.30 (m, 1H).^{13}C NMR (101 MHz, CDCl$_3$) δ 155.24 (s), 136.09 (s), 130.04 (s), 129.54 (s), 126.19 (s), 78.31 (s), 71.63 (s).

IR (neat): ν =2925, 1790, 1487, 1458, 1357, 1326, 1166, 1066, 906, 757, 697, 557,492

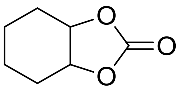
4-phenyloxymethyl-1, 3-dioxolan-2-one (7f):



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 6.86 (m, 5H), 5.02 (s, 1H), 4.60 (t, *J* = 8.4 Hz, 1H), 4.55 – 4.45 (m, 1H), 4.23 (d, *J* = 14.4 Hz, 1H), 4.12 (d, *J* = 14.0 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.04 (s), 155.07 (s), 129.96 (s), 122.21 (s), 115.06 (s), 74.50 (s), 67.13 (s), 66.49 (s).

IR (neat): ν =2926, 1801, 1774, 1601, 1586, 1482, 1454, 1396, 1245, 1161, 1089, 768, 693, 509

4, 5- cyclohexyl-1, 3-dioxolan-2-one (7g):



^{1}H NMR (400 MHz, $CDCl_3$) δ 4.67 (t, *J* = 3.7 Hz, 2H), 1.88 (dd, *J* = 11.2, 5.6 Hz, 4H), 1.65 – 1.55 (m, 2H), 1.46 – 1.36 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 155.67 (s), 76.05 (s), 27.06 (s), 19.45 (s).

IR (neat): ν =2867, 1789, 1352, 1207, 1167, 1139, 1034, 996, 781, 731, 587

4. References

[1] Yang, Z.; He, L.; Miao, C.; Chanfreau, S. Lewis basic ionic liquids-catalyzed conversion of carbon dioxide to cyclic carbonates. Adv. Synth. Catal. 2010, 352, 2233.

[2] Xiao, L.; Su, D.; Yue, C.; Wu, W. Protic ionic liquids: A highly efficient catalyst for synthesis of cyclic carbonate from carbon dioxide and epoxides. J. CO2 Util. 2014, 6, 1.

5. Copies of ^{1}H NMR and ^{13}C NMR Spectrum

DMAPH]Br (1a)

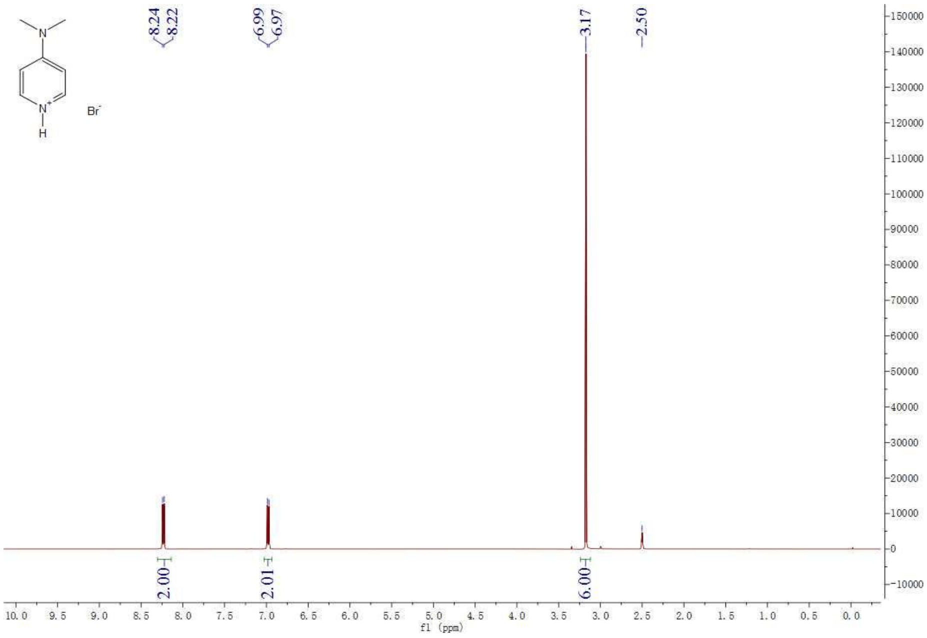


Figure S1. The ^{1}H NMR spectrum of [DMAPH]Br (**1a)**

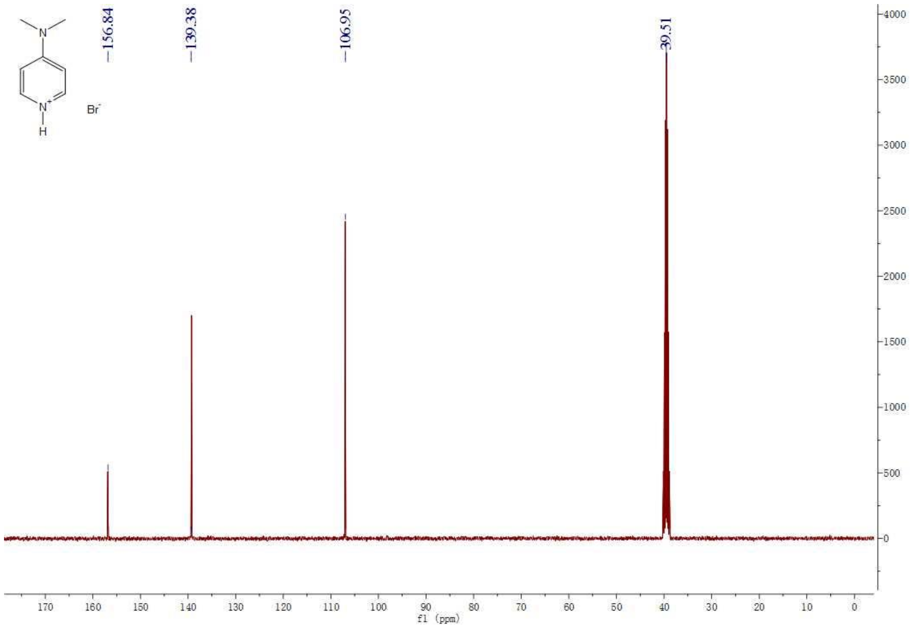


Figure S2. The ^{13}C NMR spectrum of [DMAPH]Br (**1a)**

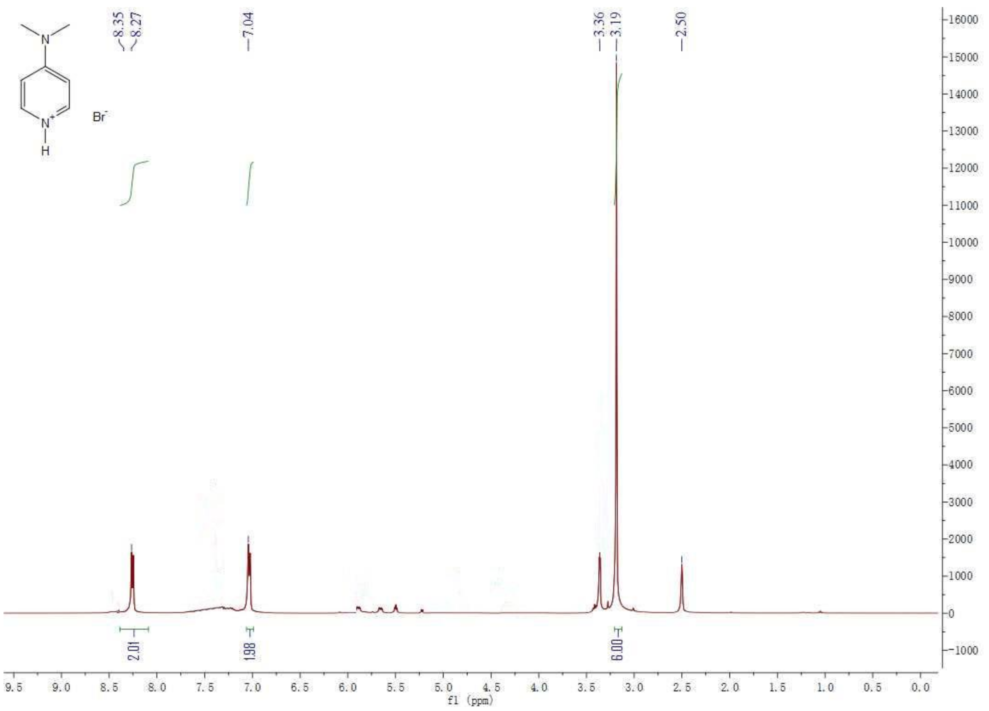


Figure S3. The ^{1}H NMR spectrum of recovered [DMAPH]Br (**1a**)

[4-NHCH$_3$-PyH]Br (1b)

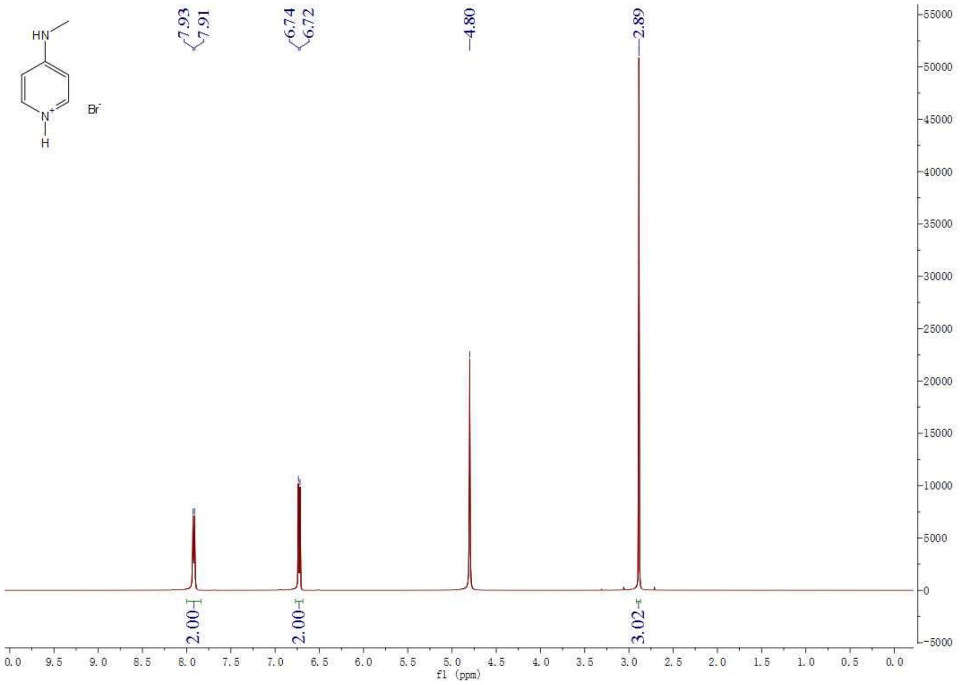


Figure S4. The ^{1}H NMR spectrum of [4-NHCH$_3$-PyH]Br (**1b)**

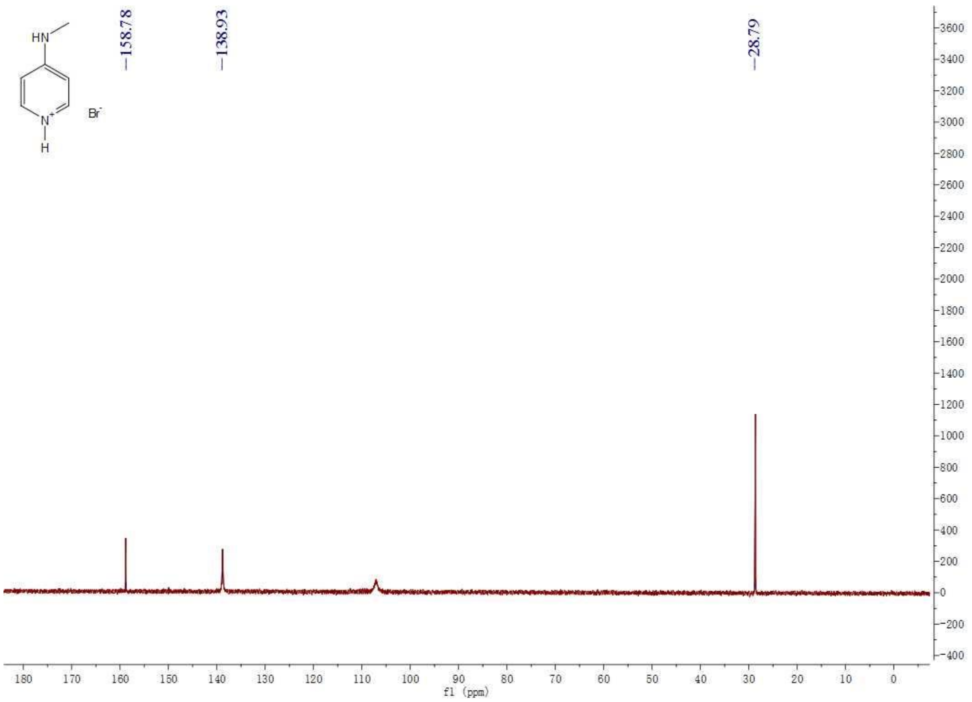


Figure S5. The ^{13}C NMR spectrum of [4-NHCH$_3$-PyH]Br (**1b)**

[4-NH$_2$-PyH]Br (1c)

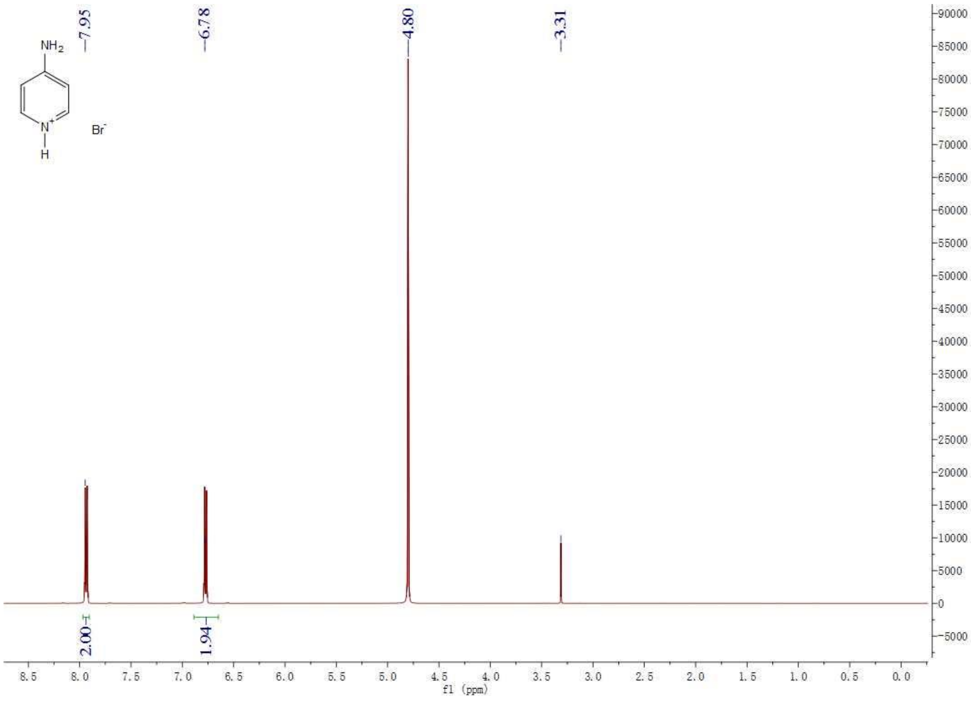


Figure S6. The ^{1}H NMR spectrum of [4-NH$_2$-PyH]Br (**1c)**

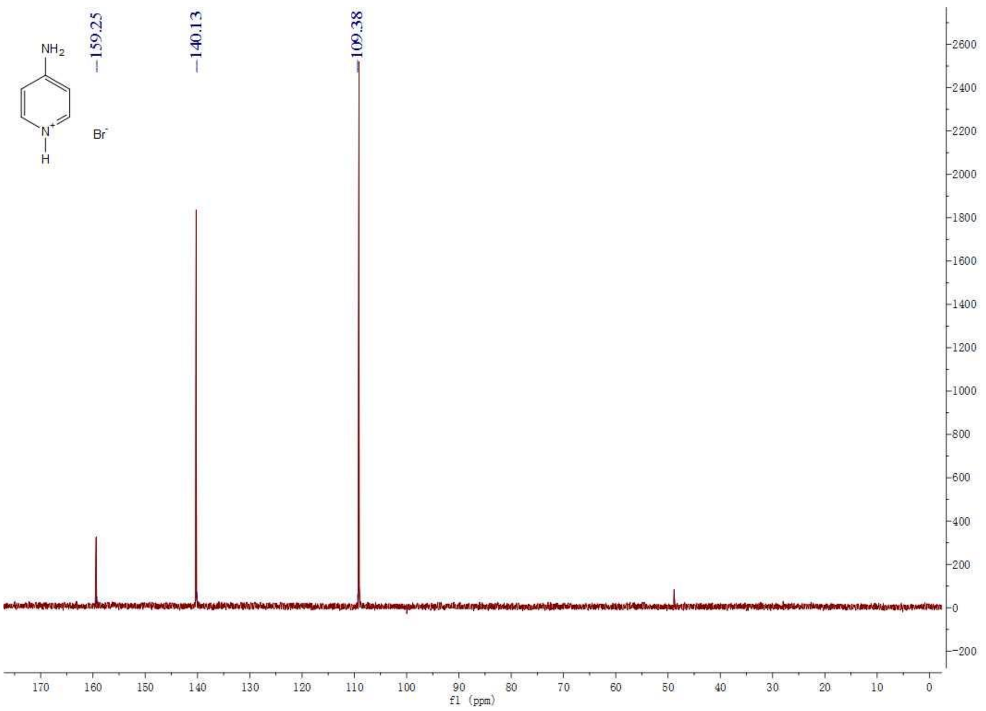


Figure S7. The ^{13}C NMR spectrum of [4-NH$_2$-PyH]Br (**1c)**

[4-OH-PyH]Br (1d)

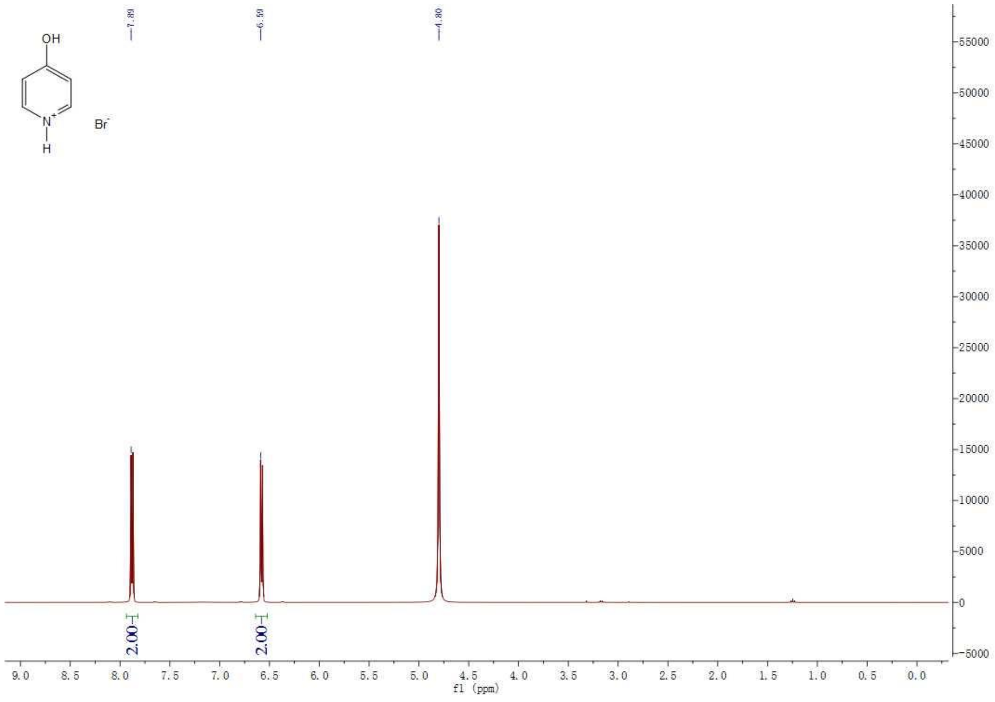


Figure S8. The ^{13}C NMR spectrum of [4-OH-PyH]Br (**1d)**

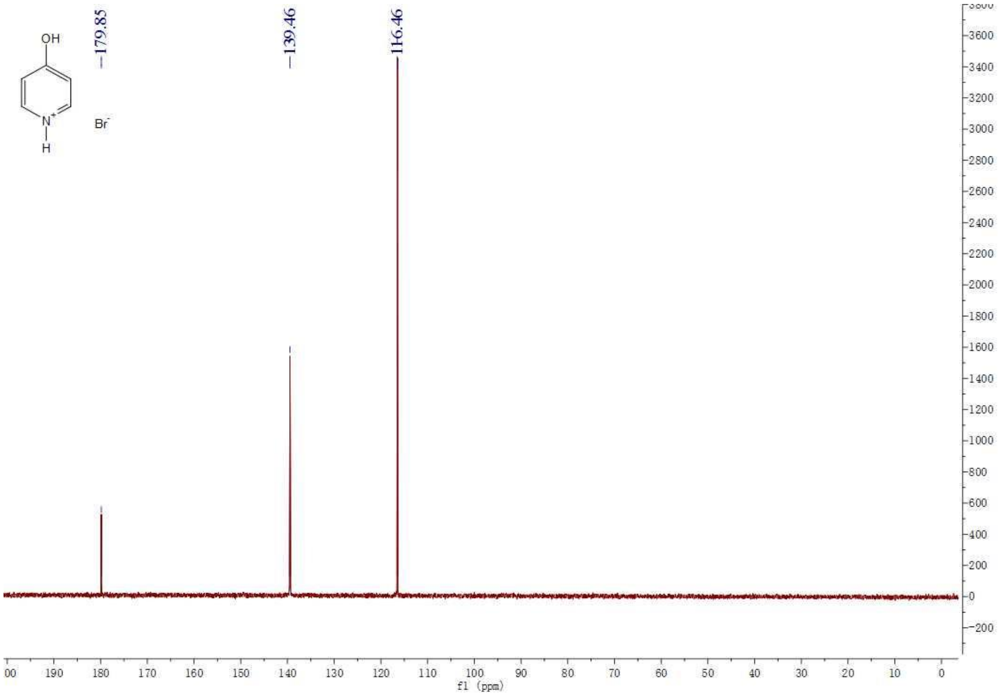


Figure S9. The ^{13}C NMR spectrum of [4-OH-PyH]Br (**1d)**

[DBUH]Cl (2a)

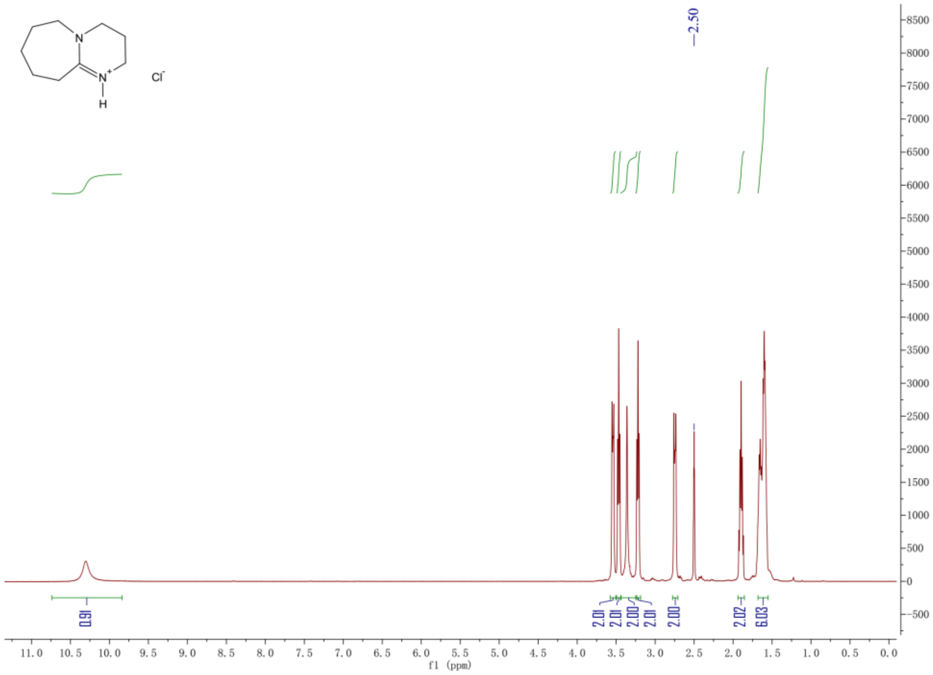


Figure S10. The ^{1}H NMR spectrum of [DBUH]Cl (**2a)**

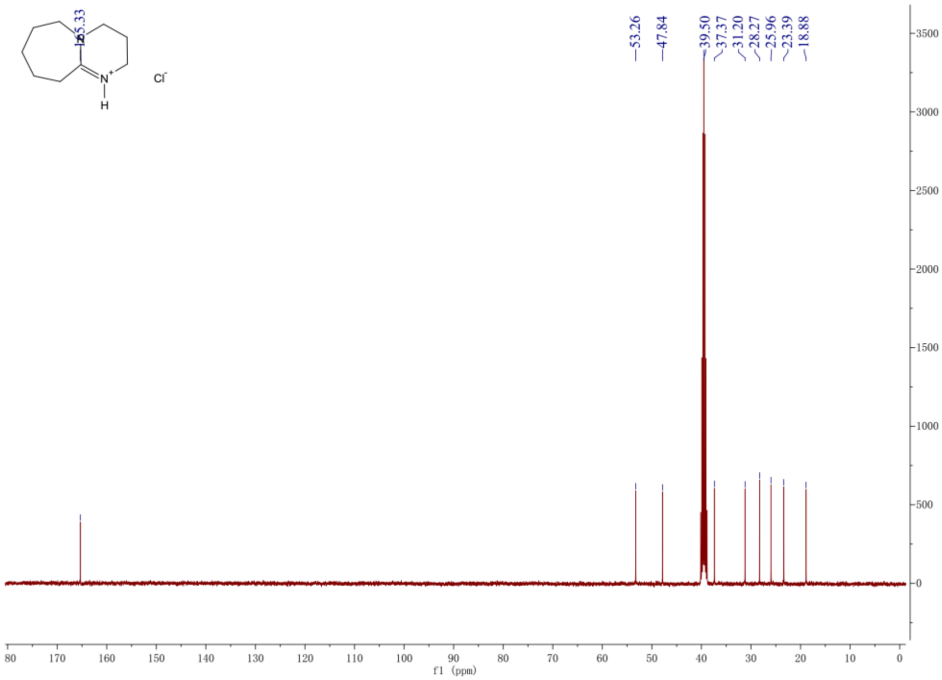


Figure S11. The ^{13}C NMR spectrum of [DBUH]Cl (**2a**)

[DBUH]Br (2b)

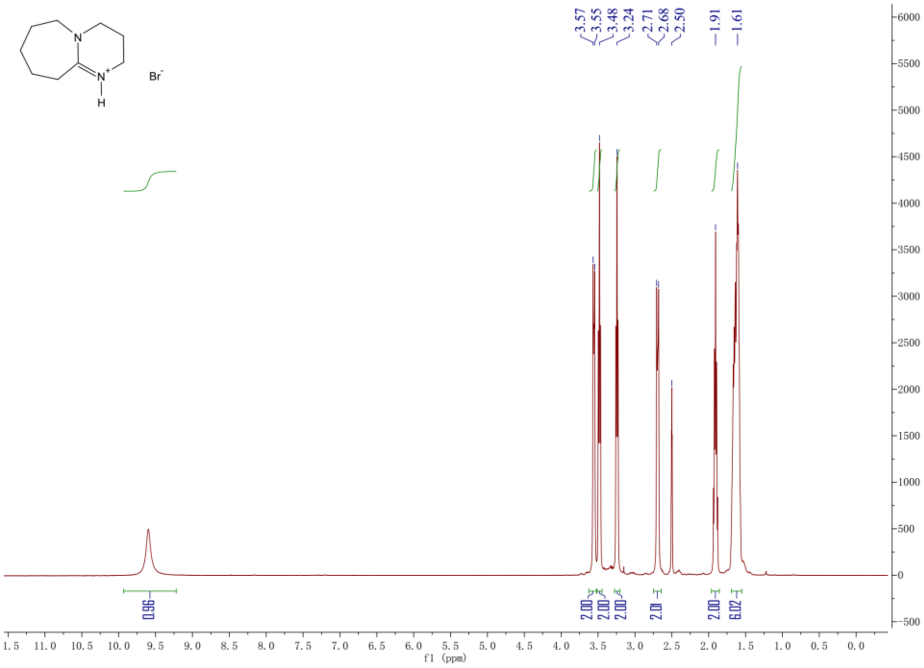


Figure S12. The ^{1}H NMR spectrum of [DBUH]Br (**2b**)

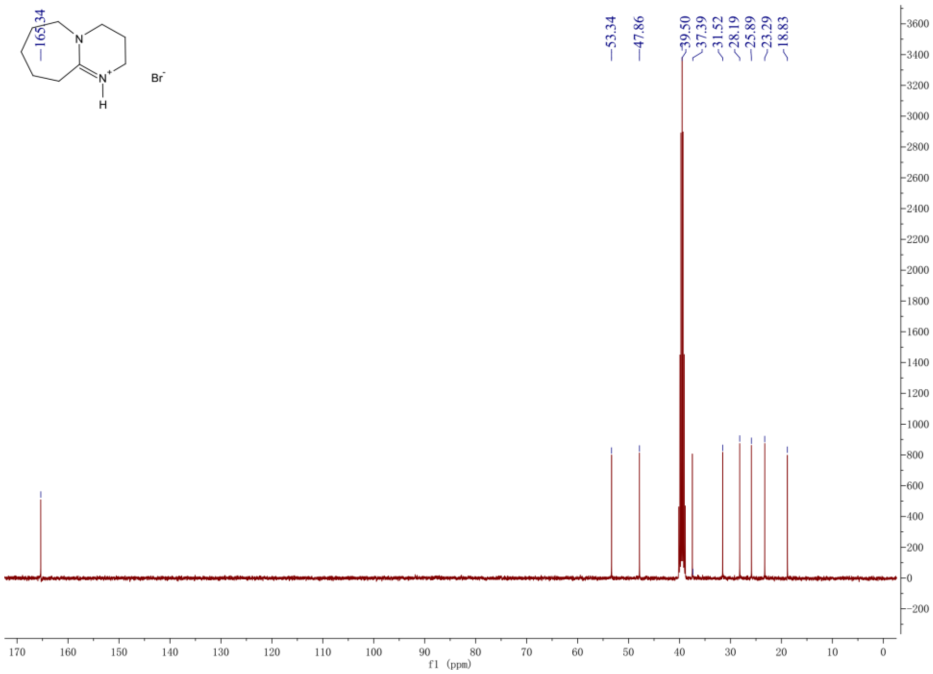


Figure S13. The ^{13}C NMR spectrum of [DBUH]Br (**2b**)

[HMIM]Br (3)

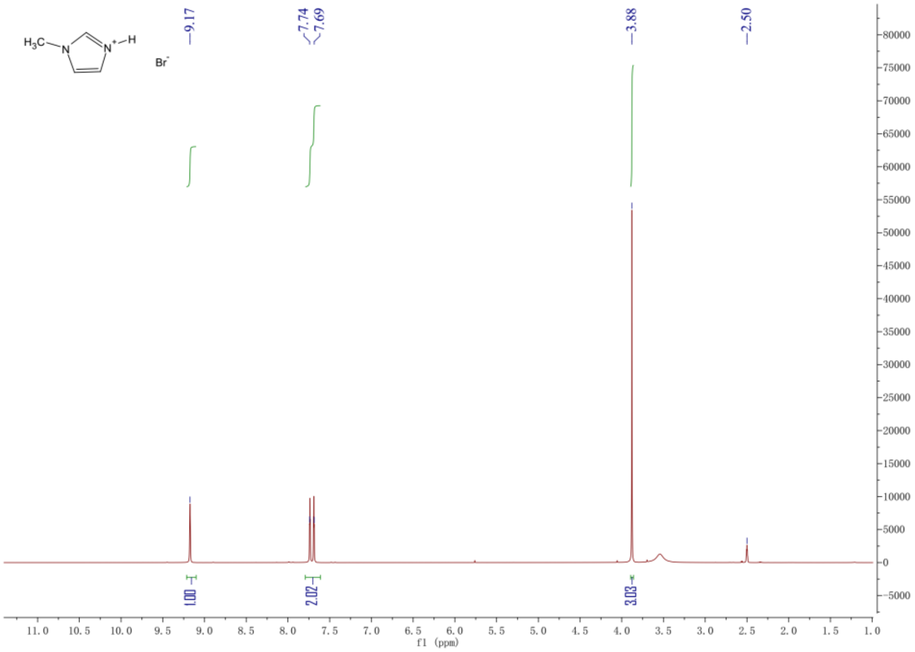


Figure S14. The ^{1}H NMR spectrum of [HMIM]Br (**3**)

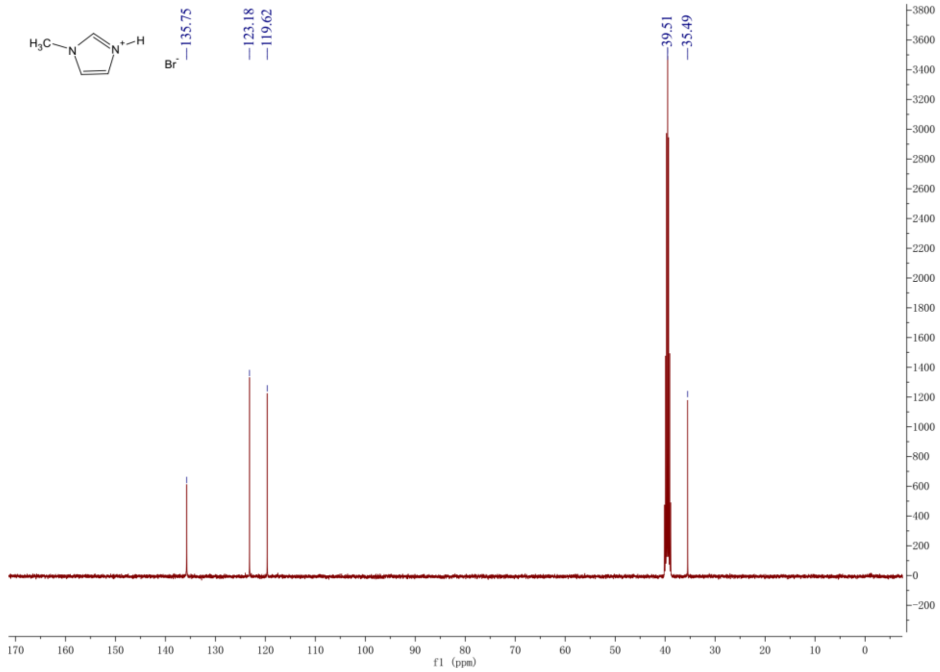


Figure S15. The ^{13}C NMR spectrum of [HMIM]Br (**3**)

[HTMG]Br (4)

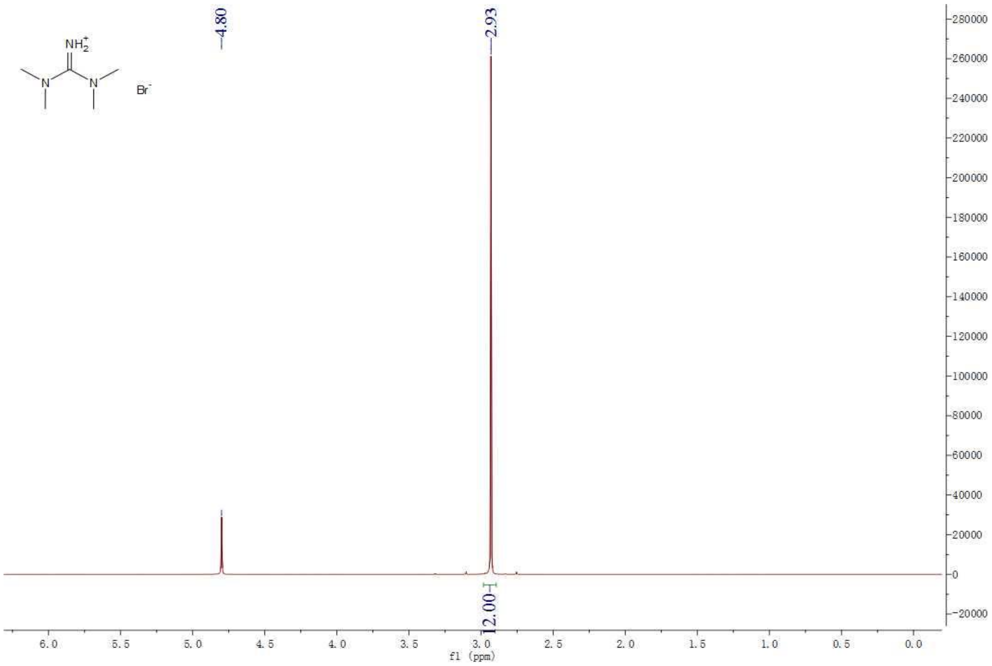


Figure S16. The ^{1}H NMR spectrum of [HTMG]Br (**4**)

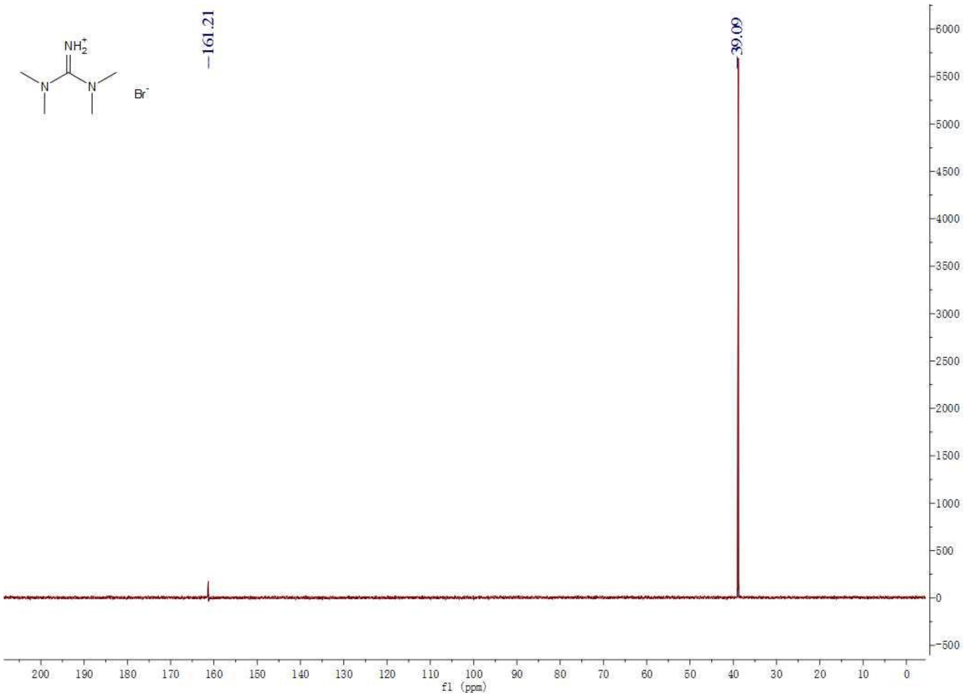


Figure S17. The ^{13}C NMR spectrum of [HTMG]Br (**4**)

[DABCOH]Br (5)

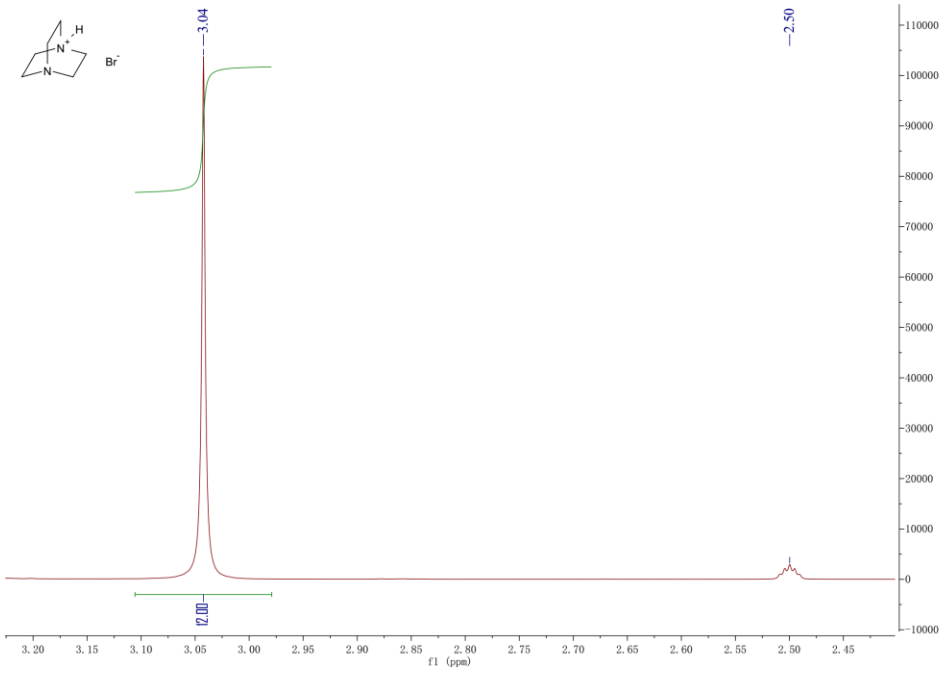


Figure S18. The ^{1}H NMR spectrum of [DABCOH]Br (**5**)

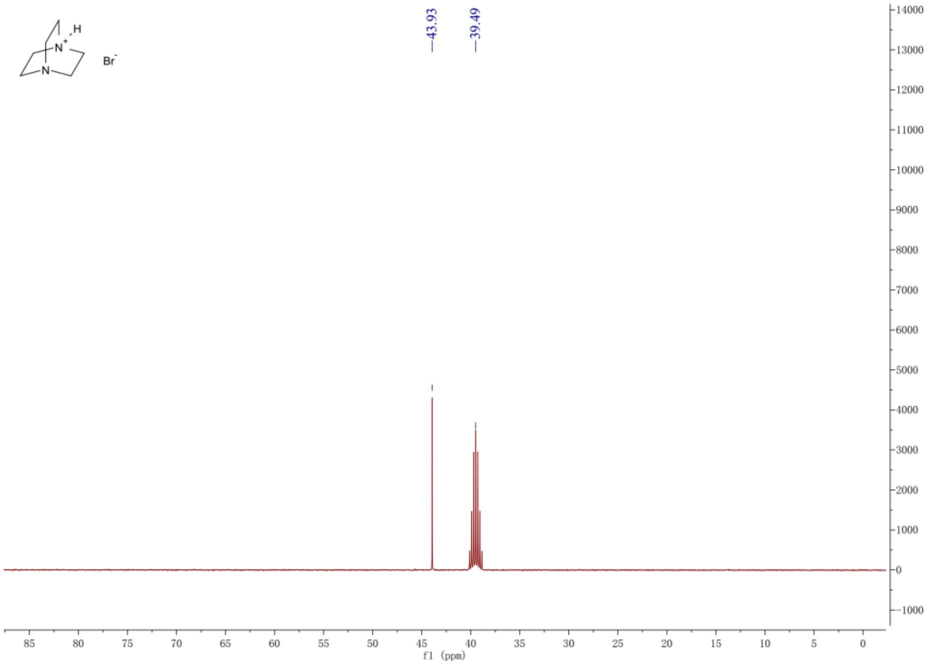


Figure S19. The ^{13}C NMR spectrum of [DABCOH]Br (**5**)

4-chloromethyl-1, 3-dioxolan-2-one (7a)

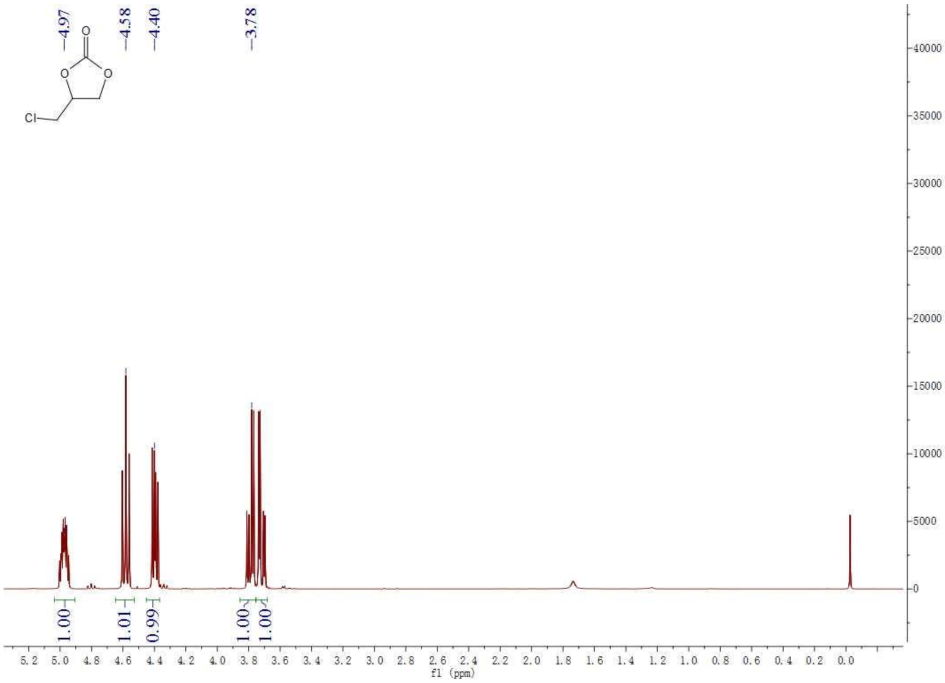


Figure S20. The ^{1}H NMR spectrum of **7a**

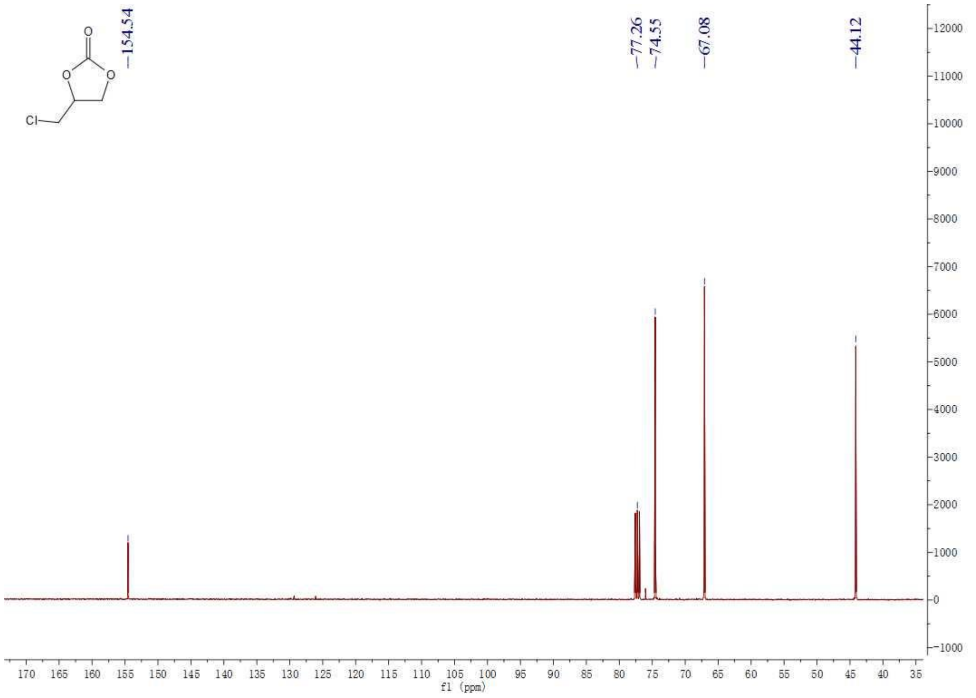


Figure S21. The ^{13}C NMR spectrum of **7a**

4- bromomethyl-1, 3-dioxolan-2-one (7b)

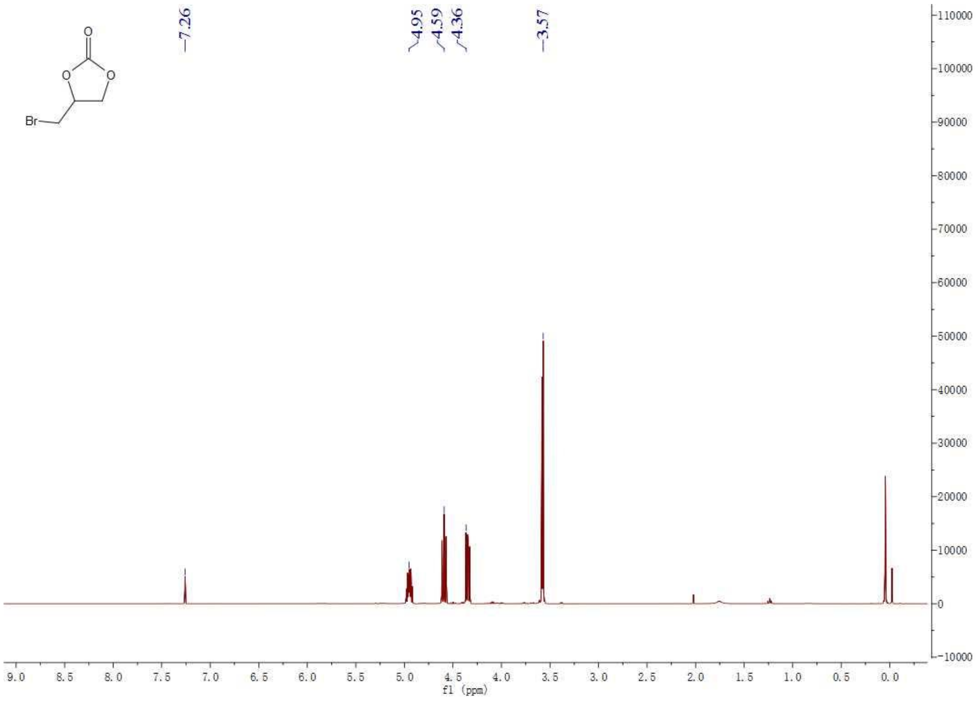


Figure S22. The ^{1}H NMR spectrum of **7b**

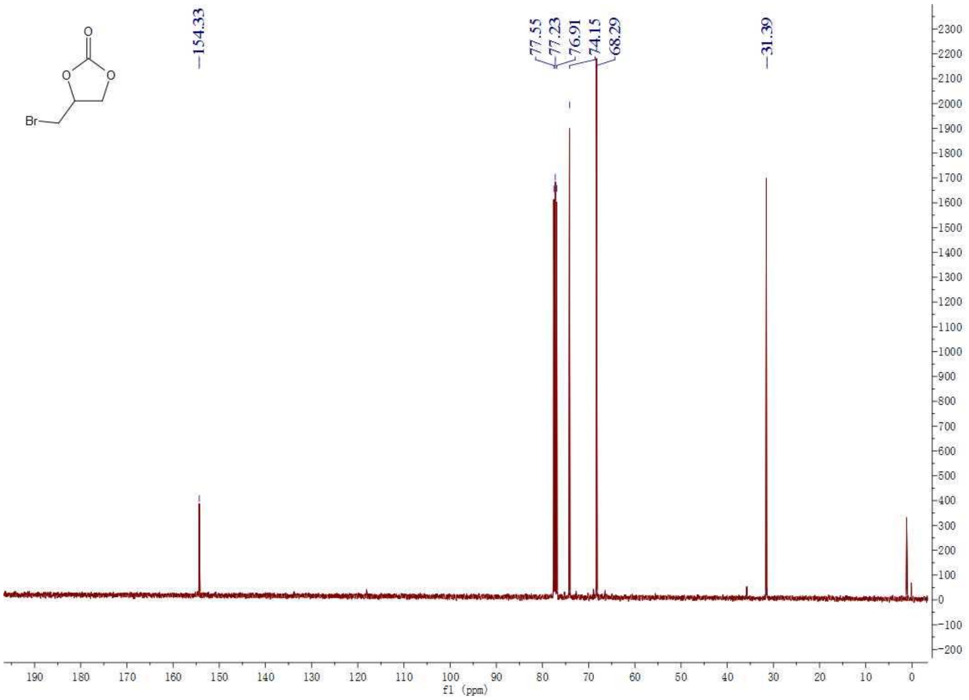


Figure S23. The ^{13}C NMR spectrum of **7b**

4-(Allyloxy)-1, 3-dioxolan-2-one (7c)

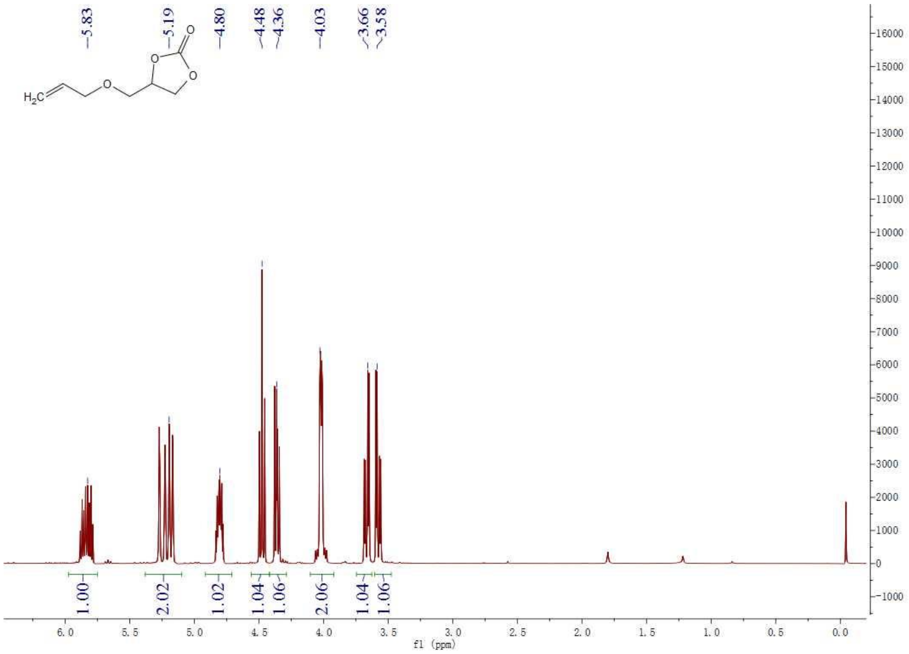


Figure S24. The ^{1}H NMR spectrum of **7c**

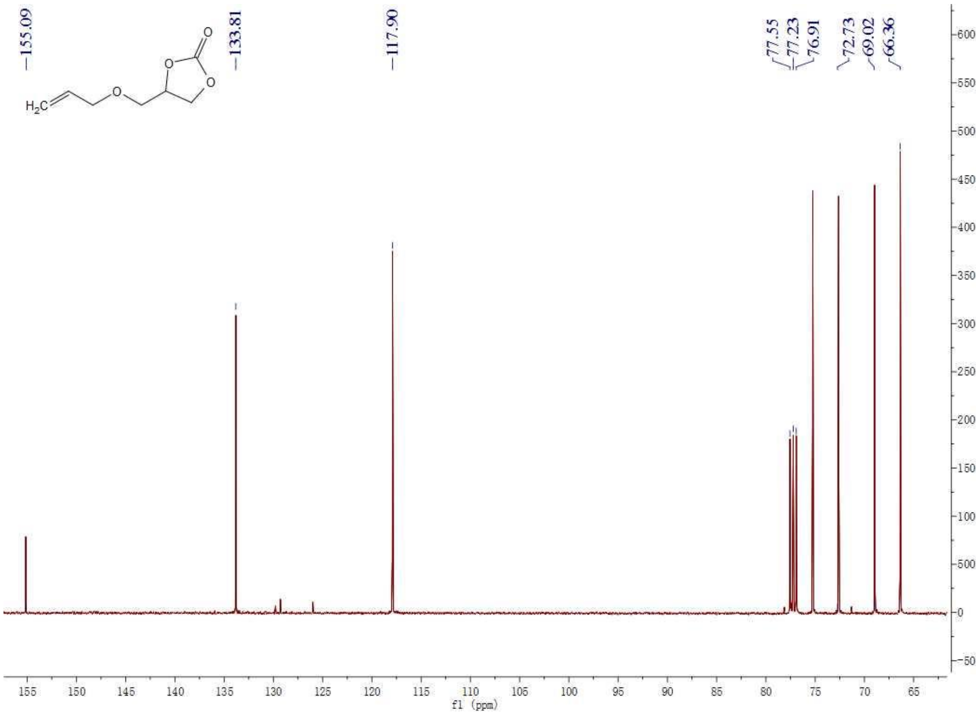


Figure S25. The ^{13}C NMR spectrum of **7c**

4-(*tert*-Butoxy)-1, 3-dioxolan-2-one (7d)

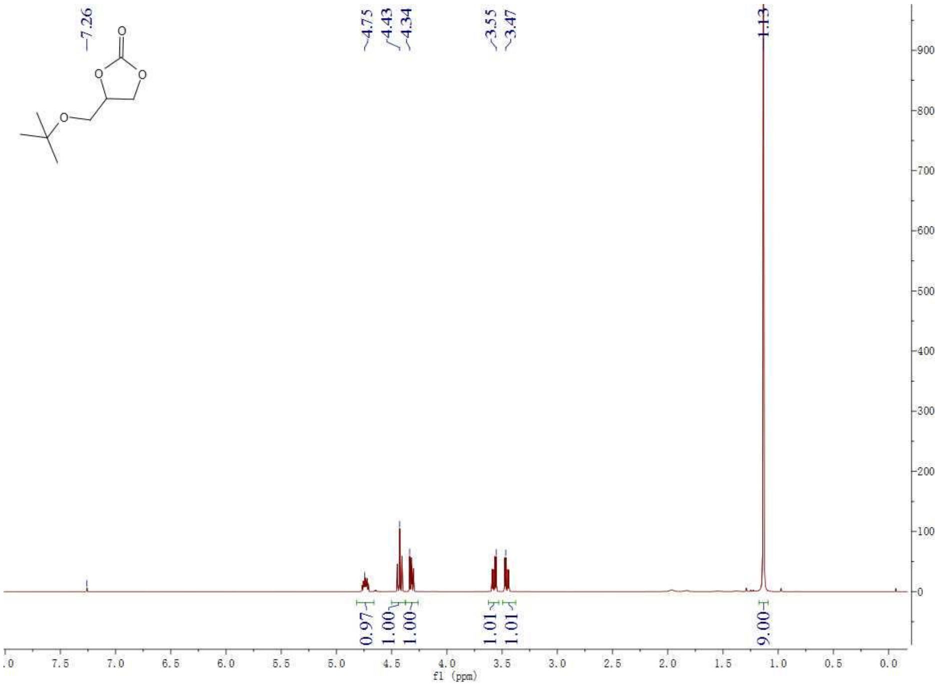


Figure S26. The ^{1}H NMR spectrum of **7d**

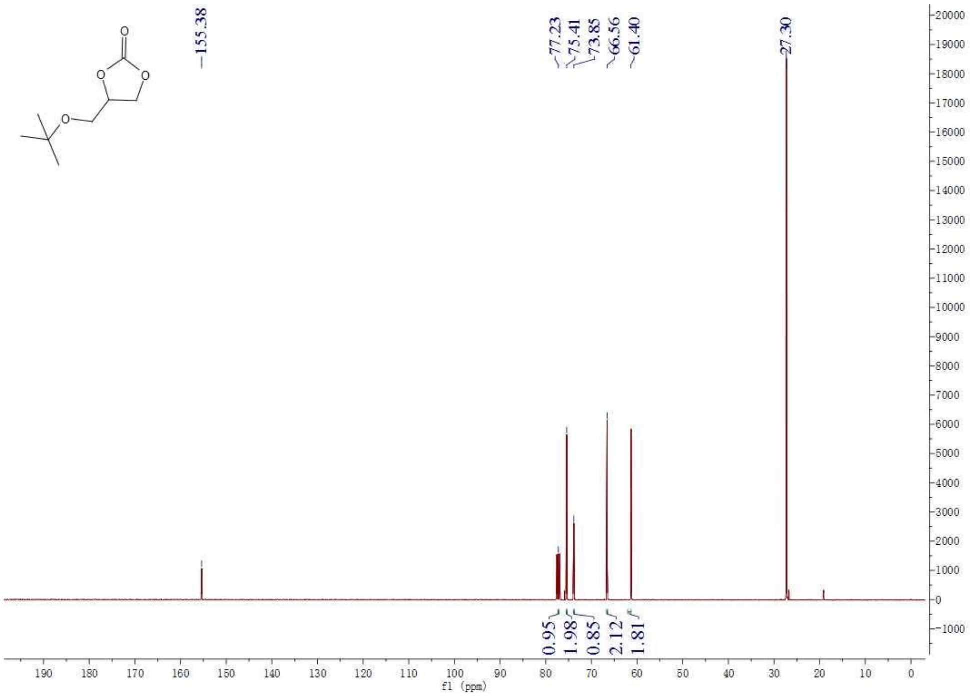


Figure S27. The ^{13}C NMR spectrum of **7d**

4-phenyl-1, 3-dioxolan-2-one (7e)

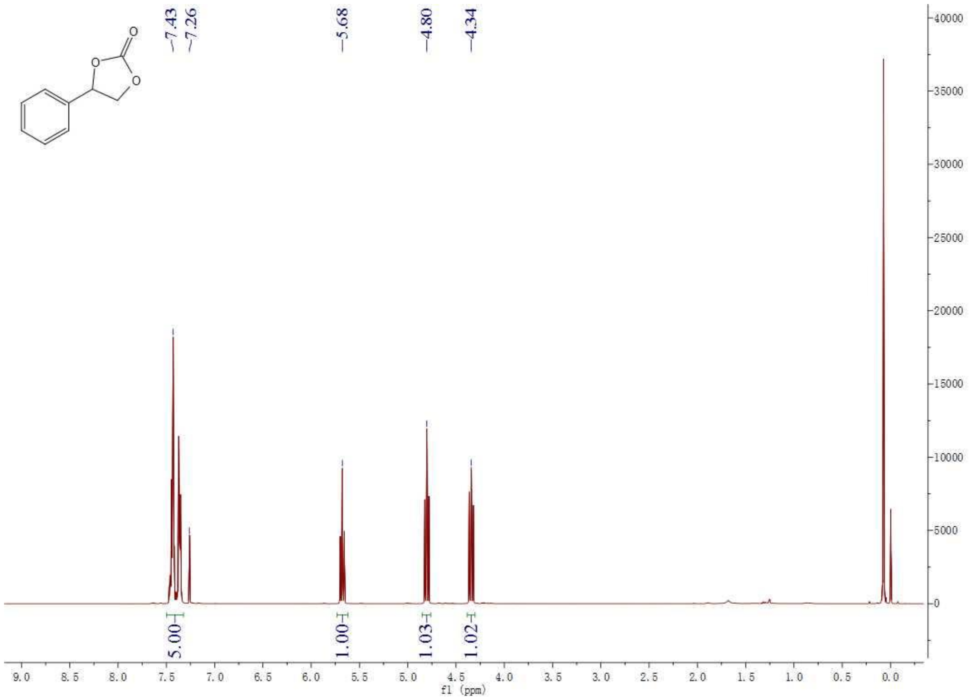


Figure S28. The ^{1}H NMR spectrum of **7e**

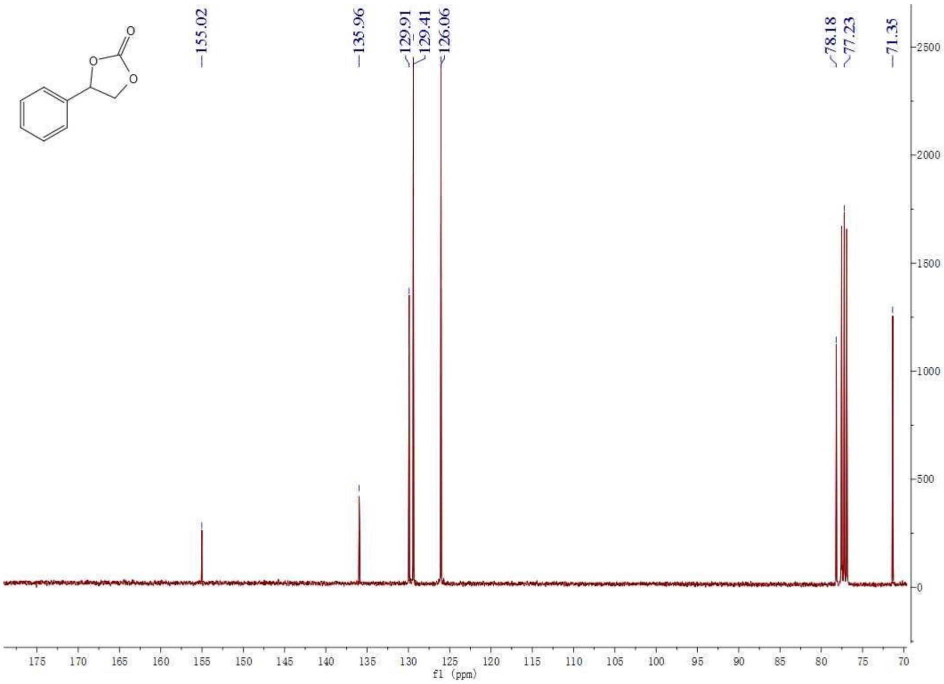


Figure S29. The ^{13}C NMR spectrum of **7e**

4-phenyloxymethyl-1, 3-dioxolan-2-one (7f)

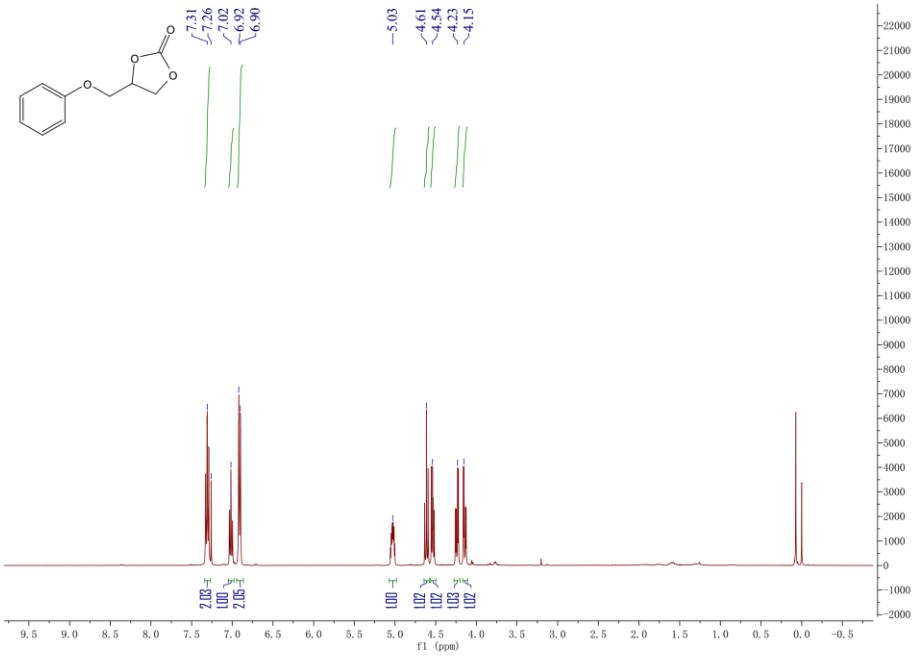


Figure S30. The ^{1}H NMR spectrum of **7f**

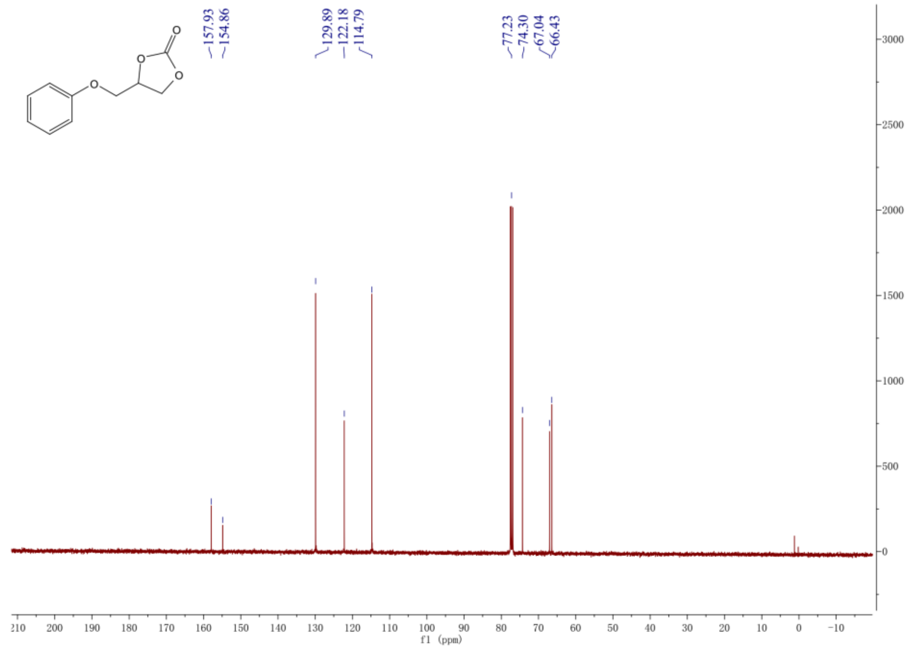


Figure S31. The ^{13}C NMR spectrum of **7f**

4, 5- cyclohexyl-1, 3-dioxolan-2-one (7g)

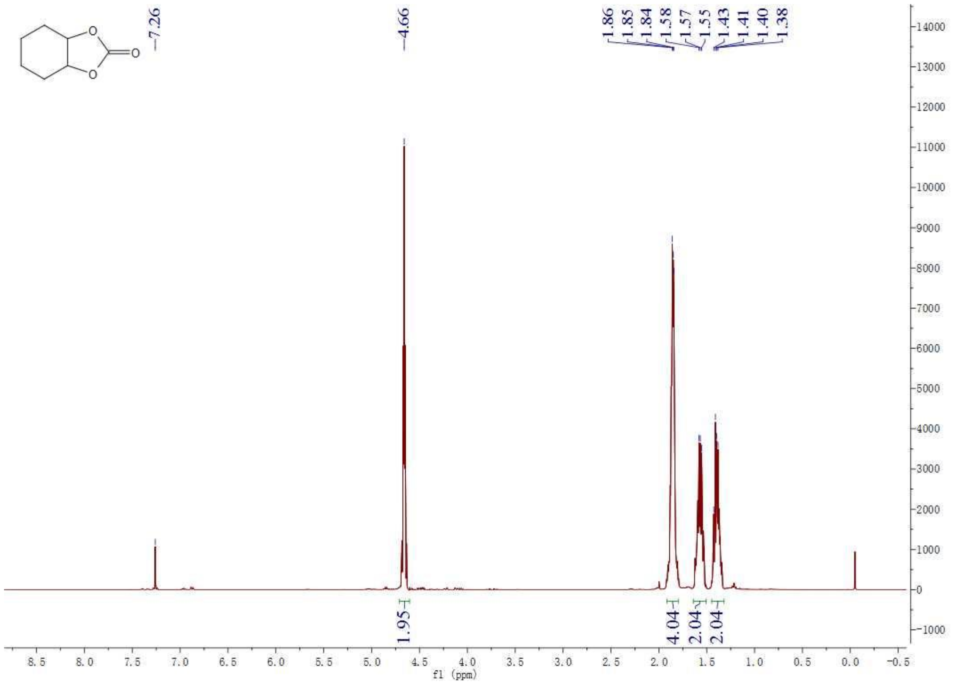


Figure S32. The ^{1}H NMR spectrum of **7g**

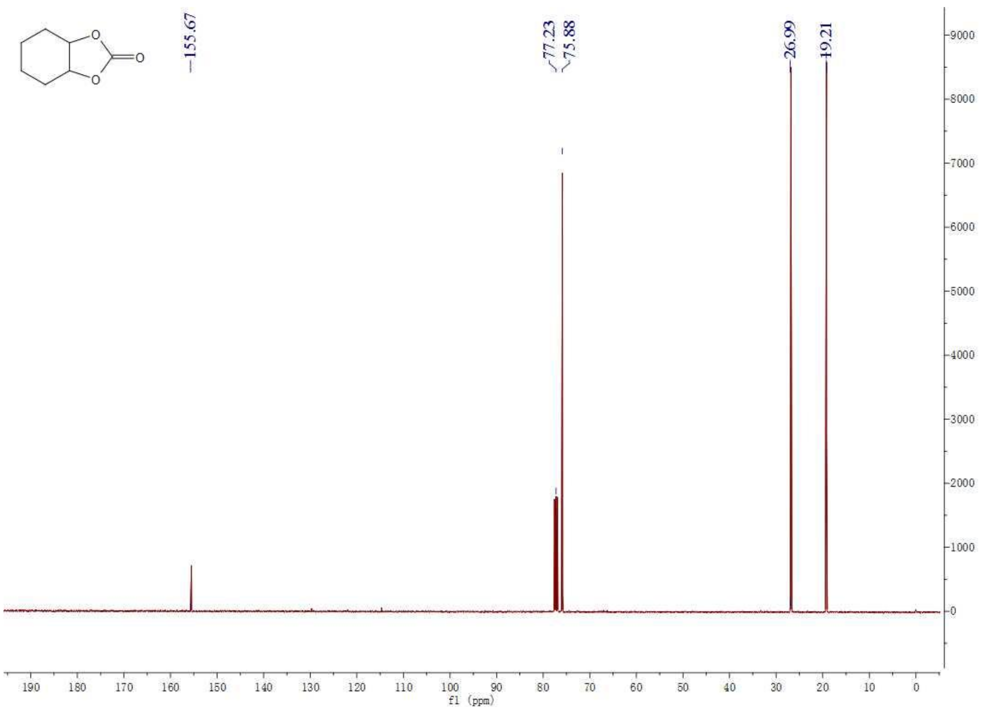


Figure S33. The ^{13}C NMR spectrum of **7g**