Supporting Information

Biomass-based ionic liquids efficiently catalyzed the cycloaddition reaction of epoxides with CO_2 by hydrogen-bonding and anion cooperative effect

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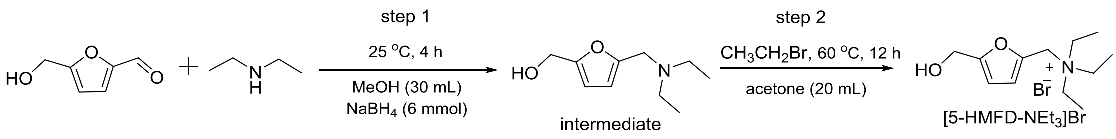
Keywords: *Biomass-based ionic liquids; Carbon dioxide; Cycloaddition; Hydrogen bonding; Single-component*

Contents

1. Procedures for synthesizing biomass-based ionic liquids

1.1. [5-HMFD-NEt$_3$]Br

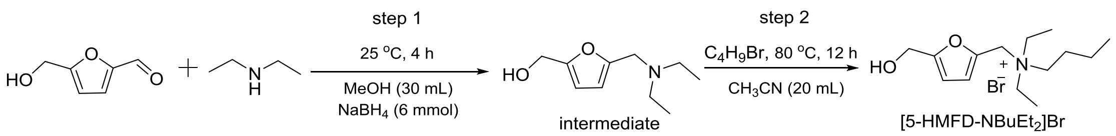
The first step is the same as shown in step 1 of Scheme 2 in the main text. Next, 5 mmol tertiary amine dissolved in 20 mL acetone was added 5.5 mmol ethyl iodide (CH_3CH_2Br), and the mixture was stirred at 60 ^oC for 12 h. After the reaction, acetone was used to wash the crude product many times to get [5-HMFD-NEt$_3$]Br as white solid in a 90% yield.



Scheme S1 Preparation of [5-HMFD-NEt$_3$]Br.

1.2. [5-HMFD-NBuEt$_2$]Br

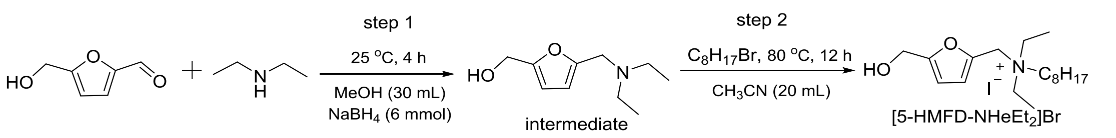
The first step is the same as shown in step 1 of Scheme 2 in the main text. Next, 5 mmol tertiary amine dissolved in 20 mL CH_3CN was added 5.5 mmol bromobutane (C_4H_9Br), and the mixture was stirred at 80 ^oC for 12 h. After the reaction, ethyl ether was used to wash the crude product many times to get [5-HMFD-NBuEt$_2$]Br as yellow oil in a 76% yield.



Scheme S2 Preparation of [5-HMFD-NBuEt$_2$]Br.

1.3. [5-HMFD-NHeEt$_2$]Br

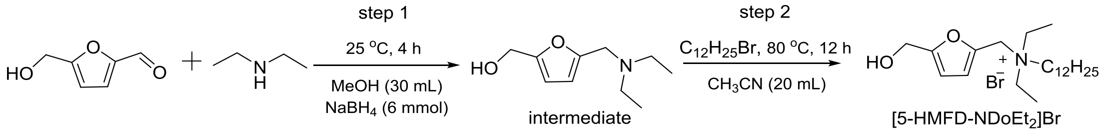
The first step is the same as shown in step 1 of Scheme 2 in the main text. Next, 5 mmol tertiary amine dissolved in 20 mL CH_3CN was added 5.5 mmol 1-bromooctane ($C_8H_{17}Br$), and the mixture was stirred at 80 ^oC for 12 h. After the reaction, ethyl ether was used to wash the crude product many times to get [5-HMFD-NHeEt$_2$]Br as yellow oil in a 70% yield.



Scheme S3 Preparation of [5-HMFD-NHeEt$_2$]Br.

1.4. [5-HMFD-NDoEt$_2$]Br

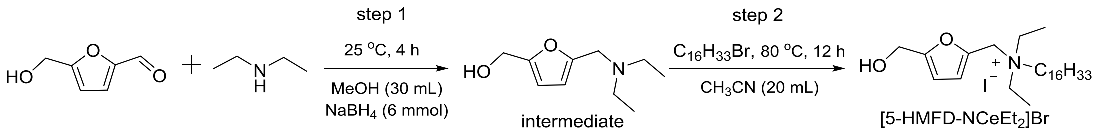
The first step is the same as shown in step 1 of Scheme 2 in the main text. Next, 5 mmol tertiary amine dissolved in 20 mL CH_3CN was added 5.5 mmol 1-bromododecane ($C_{12}H_{25}Br$), and the mixture was stirred at 80 °C for 12 h. After the reaction, EtOAc was used to wash the crude product many times to get [5-HMFD-NDoEt$_2$]Br as white solid in a 67% yield.



Scheme S4 Preparation of [5-HMFD-NDoEt$_2$]Br.

1.5. [5-HMFD-NCeEt$_2$]Br

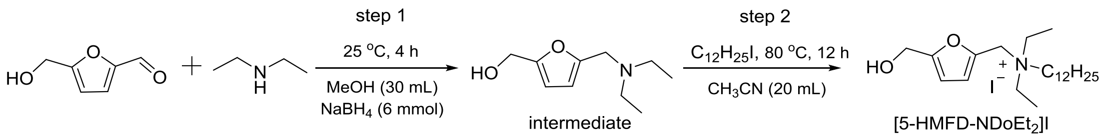
The first step is the same as shown in step 1 of Scheme 2 in the main text. Next, 5 mmol tertiary amine dissolved in 20 mL CH_3CN was added 5.5 mmol 1-bromohexadecane ($C_{16}H_{33}Br$), and the mixture was stirred at 80 °C for 12 h. After the reaction, EtOAc was used to wash the crude product many times to get [5-HMFD-NCeEt$_2$]Br as white solid in a 61% yield.



Scheme S5 Preparation of [5-HMFD-NCeEt$_2$]Br.

1.6. [5-HMFD-NDoEt$_2$]I

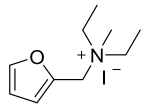
The first step is the same as shown in step 1 of Scheme 2 in the main text. Next, 5 mmol tertiary amine dissolved in 20 mL CH_3CN was added 5.5 mmol 1-iodododecane ($C_{12}H_{25}I$), and the mixture was stirred at 80 °C for 12 h. After the reaction, EtOAc was used to wash the crude product many times to get [5-HMFD-NDoEt$_2$]I as white solid in a 71% yield.



Scheme S6 Preparation of [5-HMFD-NDoEt$_2$]I.

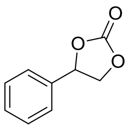
2. NMR data of [2-FD-$NMeEt_2$]I and the products

2.1. [2-FD-$NMeEt_2$]I



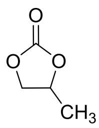
^{1}H NMR (400 MHz, D_2O) δ 7.65 (dd, *J* = 2.0, 0.8 Hz, 1H), 6.80 (d, *J* = 3.4 Hz, 1H), 6.55 (dd, *J* = 3.4, 1.9 Hz, 1H), 4.50 (s, 2H), 3.30 (tt, *J* = 7.2, 3.7 Hz, 4H), 2.94 (s, 3H), 1.36 (t, *J* = 7.3 Hz, 6H).^{13}C NMR (101 MHz, D_2O) δ 145.7, 142.0, 116.5, 111.2, 56.4, 56.1, 46.6, 7.2.

2.2. 4-phenyl-1,3-dioxolan-2-one (**2a**)



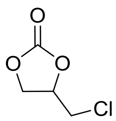
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 3H), 7.35 (dd, *J* = 7.4, 2.3 Hz, 2H), 5.67 (t, *J* = 8.0 Hz, 1H), 4.79 (t, *J* = 8.4 Hz, 1H), 4.32 (t, *J* = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 135.9, 129.8, 129.3, 126.0, 78.1, 71.3.

2.3. 4-methyl-1,3-dioxolan-2-one (**2b**)



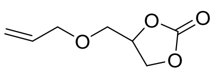
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (d, *J* = 6.6 Hz, 1H), 4.59 (t, *J* = 8.1 Hz, 1H), 4.06 (dd, *J* = 8.5, 7.2 Hz, 1H), 1.50 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.2, 73.8, 70.7, 19.3.

2.4. 4-methyl-1,3-dioxolan-2-one (**2c**)



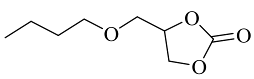
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.03 (dtd, *J* = 8.6, 5.3, 3.6 Hz, 1H), 4.62 (t, *J* = 8.6 Hz, 1H), 4.43 (dd, *J* = 8.9, 5.7 Hz, 1H), 3.84 (dd, *J* = 12.3, 4.9 Hz, 1H), 3.75 (dd, *J* = 12.3, 3.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.5, 74.5, 67.0, 44.1.

2.5. 4-((allyloxy)methyl)-1,3-dioxolan-2-one(**2d**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (td, *J* = 10.9, 5.2 Hz, 1H), 5.26 (dd, *J* = 25.8, 13.8 Hz, 2H), 4.85 (dtd, *J* = 9.2, 4.9, 4.4, 2.4 Hz, 1H), 4.52 (td, *J* = 8.4, 1.4 Hz, 1H), 4.42 (dd, *J* = 8.3, 6.2 Hz, 1H), 4.06 (d, *J* = 5.6 Hz, 2H), 3.76 – 3.67 (m, 1H), 3.62 (dd, *J* = 11.1, 3.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 133.7, 118.0, 117.9, 75.1, 72.6, 68.8, 66.3.

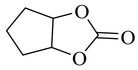
2.6. 4-((allyloxy)methyl)-1,3-dioxolan-2-one(**2e**)



^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 – 4.77 (m, 1H), 4.51 (td, *J* = 8.4, 1.3 Hz, 1H), 4.41 (ddd, *J* = 8.1, 6.2, 1.3 Hz, 1H), 3.71 – 3.65 (m, 1H), 3.64 – 3.58 (m, 1H), 3.51 (t, *J* = 6.5 Hz, 2H), 1.61 – 1.51 (m, 2H), 1.36 (h, *J*

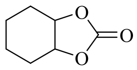
= 7.3 Hz, 2H), 0.92 (dd, *J* = 8.0, 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 75.1, 71.9, 69.6, 66.3, 31.5, 19.2, 13.9.

2.7. tetrahydro-4H-cyclopenta[d][1,3]dioxol-2-one(**2f**)



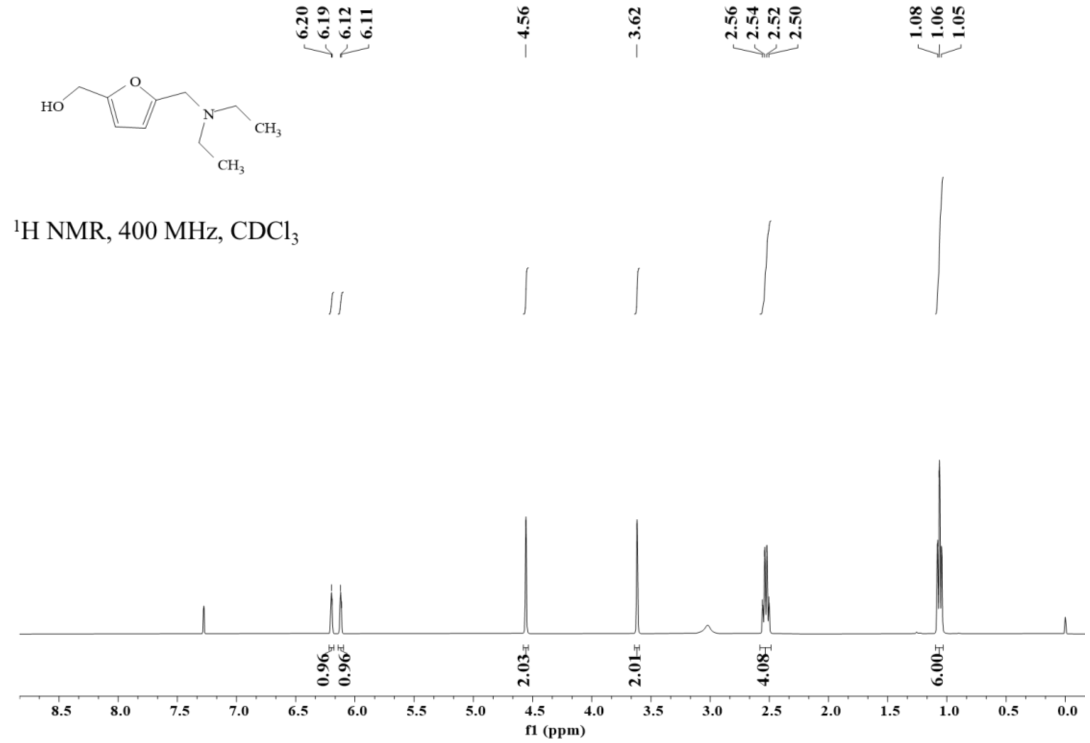
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (d, *J* = 3.9 Hz, 1H), 2.24 – 1.23 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.6, 155.5, 81.9, 75.8, 33.2, 21.6, 19.2.

2.8. hexahydrobenzo[d][1,3]dioxol-2-one(**2g)**



^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (q, *J* = 5.8, 5.0 Hz, 2H), 1.91 (dq, *J* = 9.4, 4.9 Hz, 4H), 1.62 (dd, *J* = 10.9, 5.6 Hz, 2H), 1.45 (dt, *J* = 11.5, 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.5, 75.9, 26.8, 19.2.

3. NMR spectra of biomass-based ionic liquids and the products



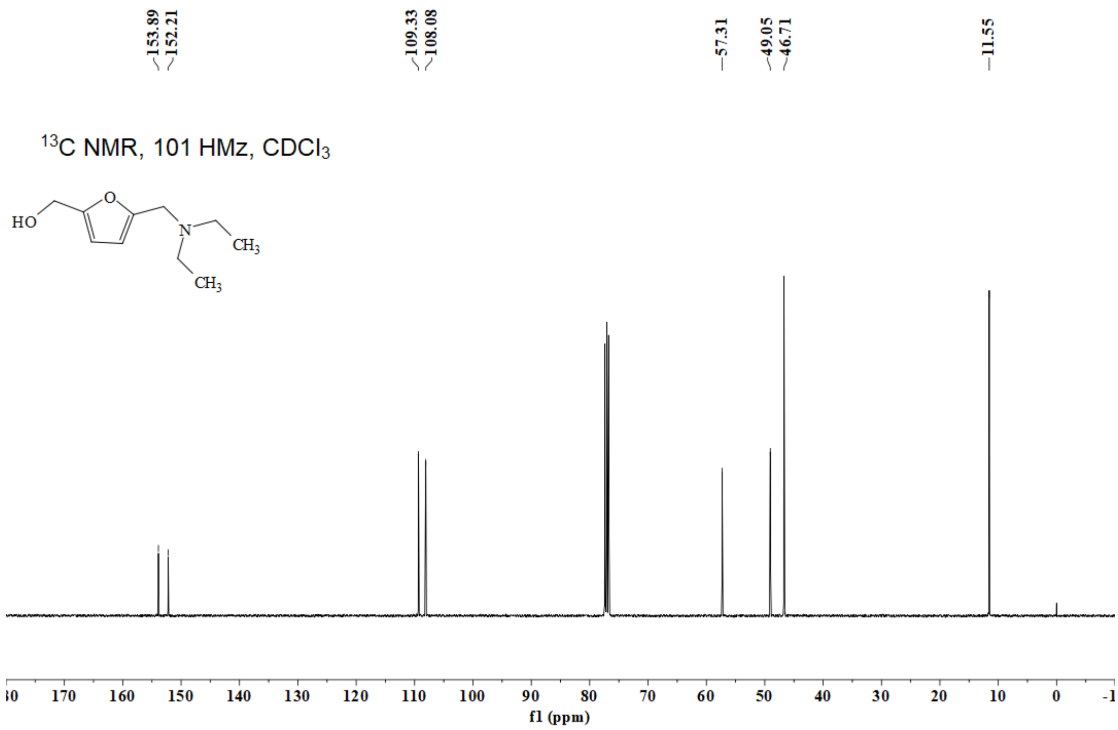


Fig. S1 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 5-((diethylamino)methyl)furan-2-yl)methanol (5-HMFD-NEt_2).

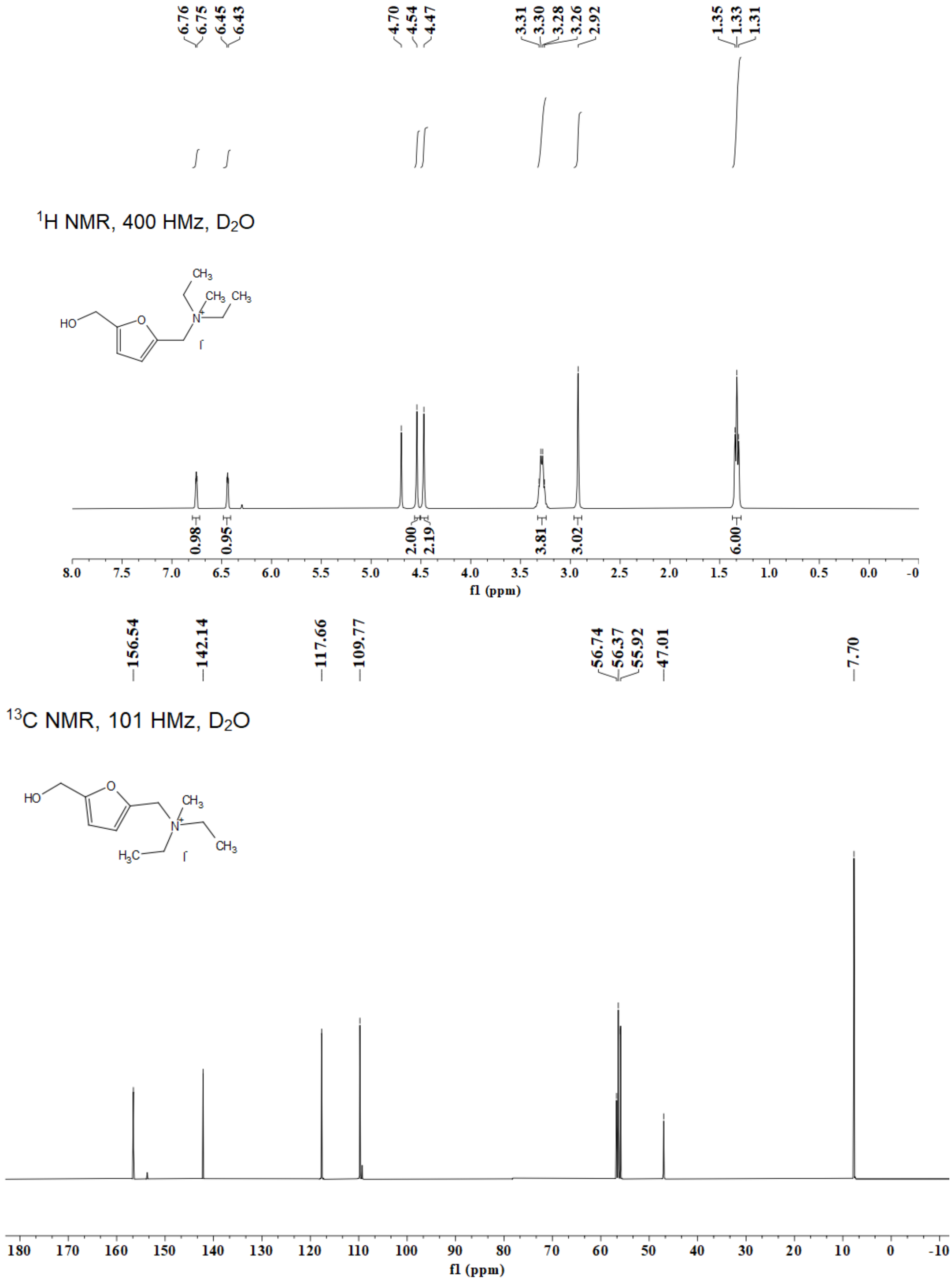
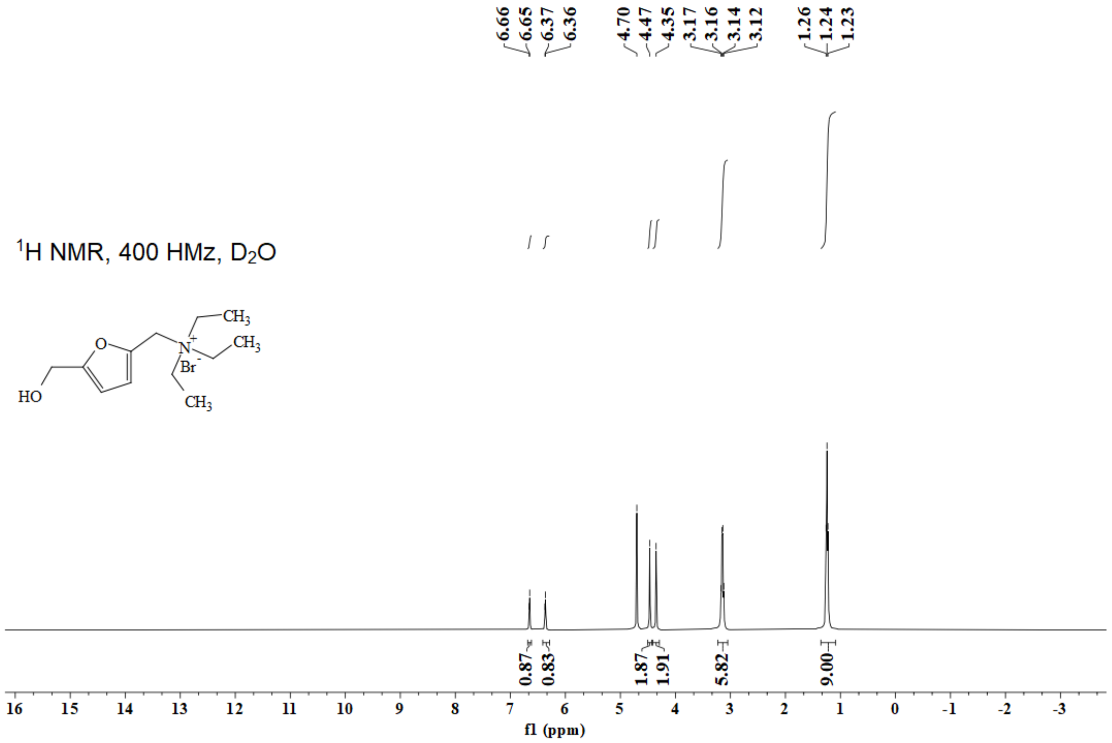


Fig. S2 ^{1}H (top) and ^{13}C (bottom) NMR spectra of *N*-ethyl-*N*-((5-(hydroxymethyl)furan-2-yl)methyl)-*N*- methylethanaminium iodidee ([5-HMFD-$NMeEt_2$]I).



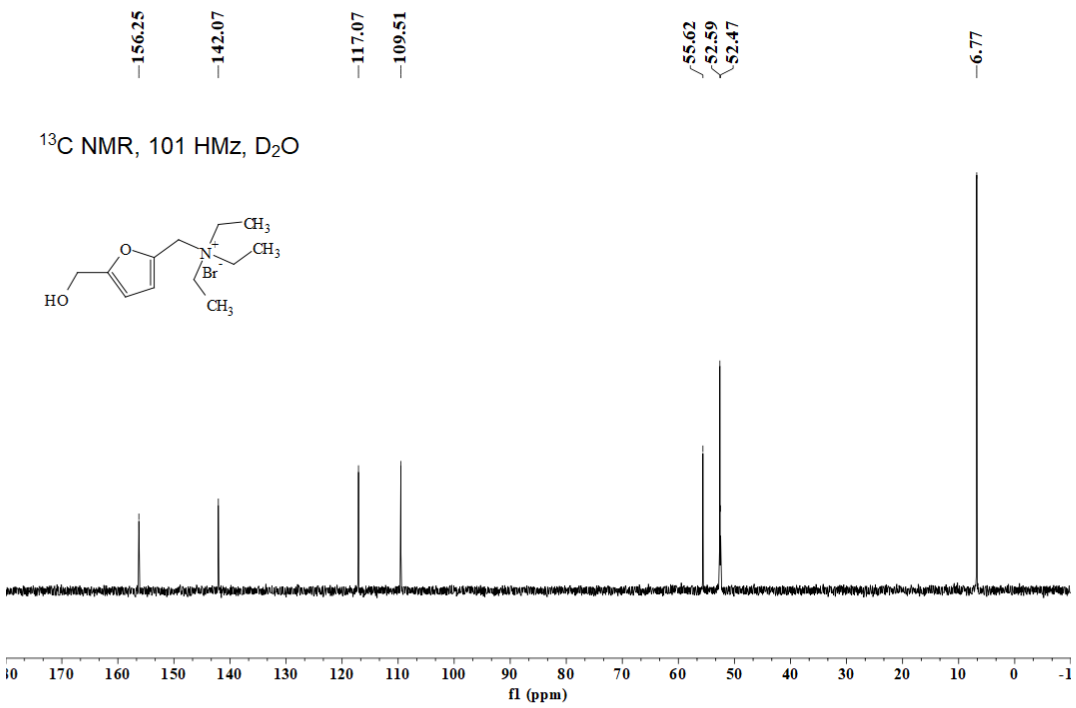


Fig. S3 ^{1}H (top) and ^{13}C (bottom) NMR spectra of *N*,*N*-diethyl-*N*-((5-(hydroxymethyl)furan-2-yl)methyl)ethanaminium bromide ([5-HMFD-NEt_3]Br).

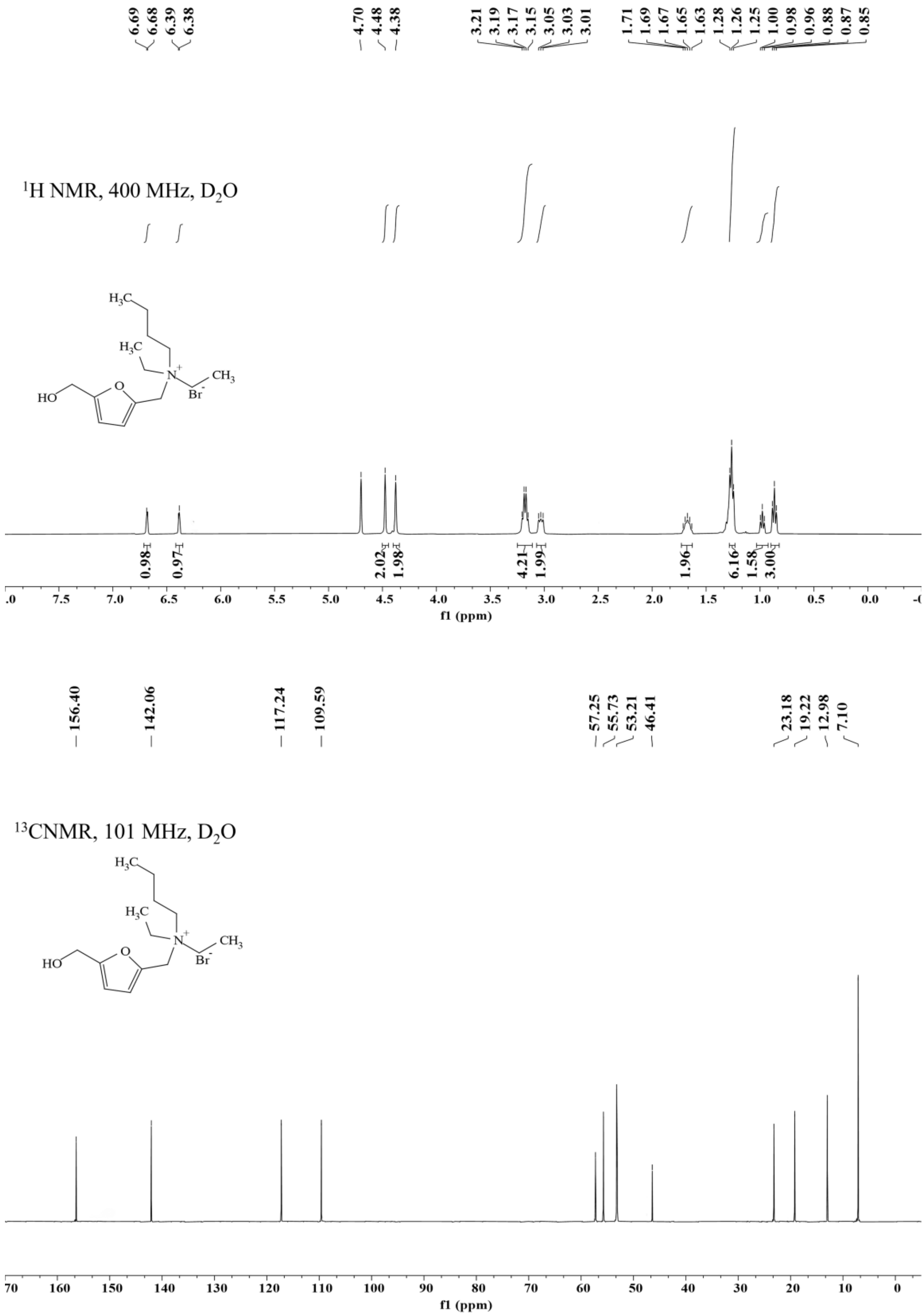


Fig. S4 ^{1}H (top) and ^{13}C (bottom) NMR spectra of *N*,*N*-diethyl-*N*-((5-(hydroxymethyl)furan-2-yl)methyl)butan-1-aminium bromide ([5-HMFD-NBuEt$_2$]Br).

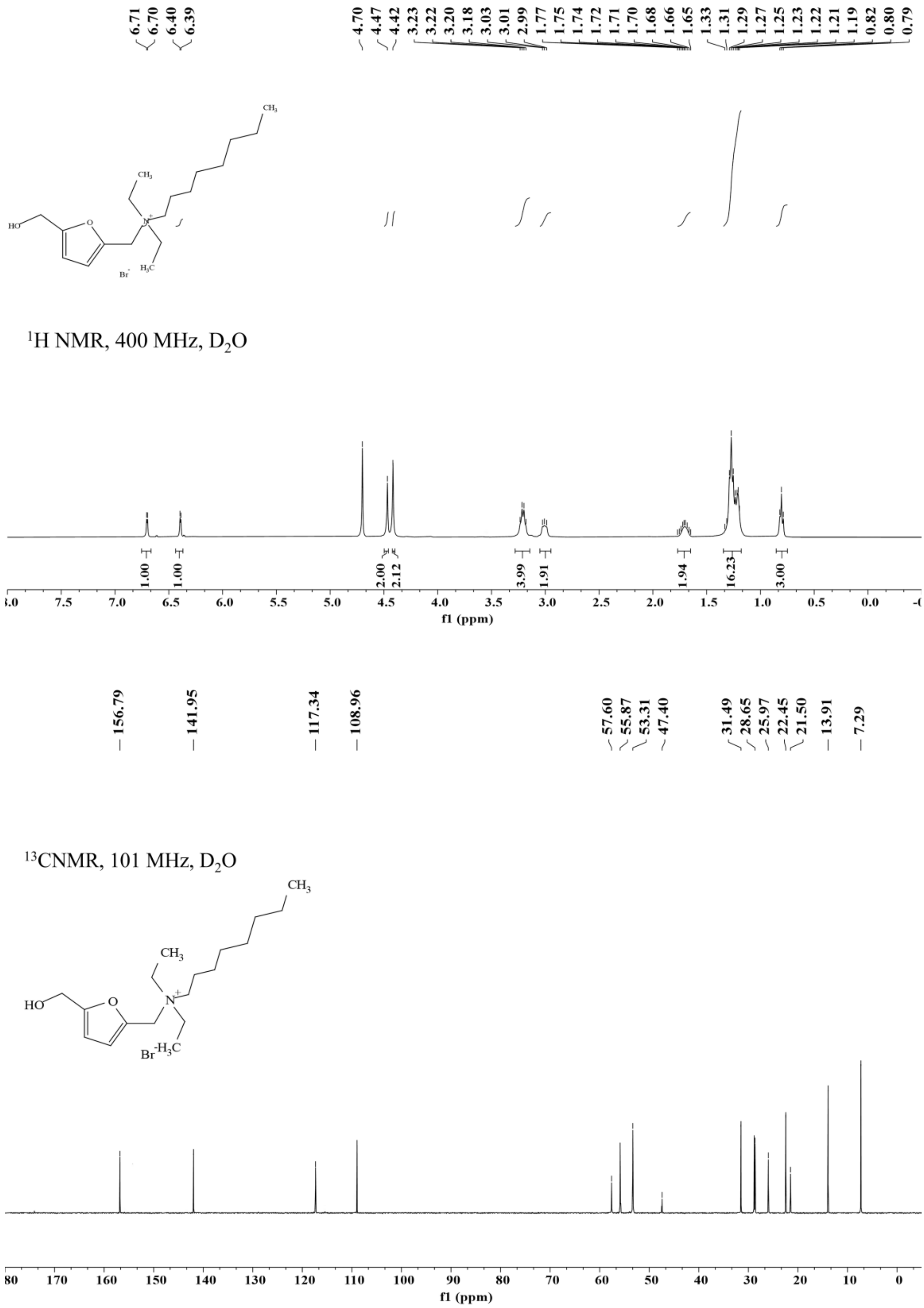
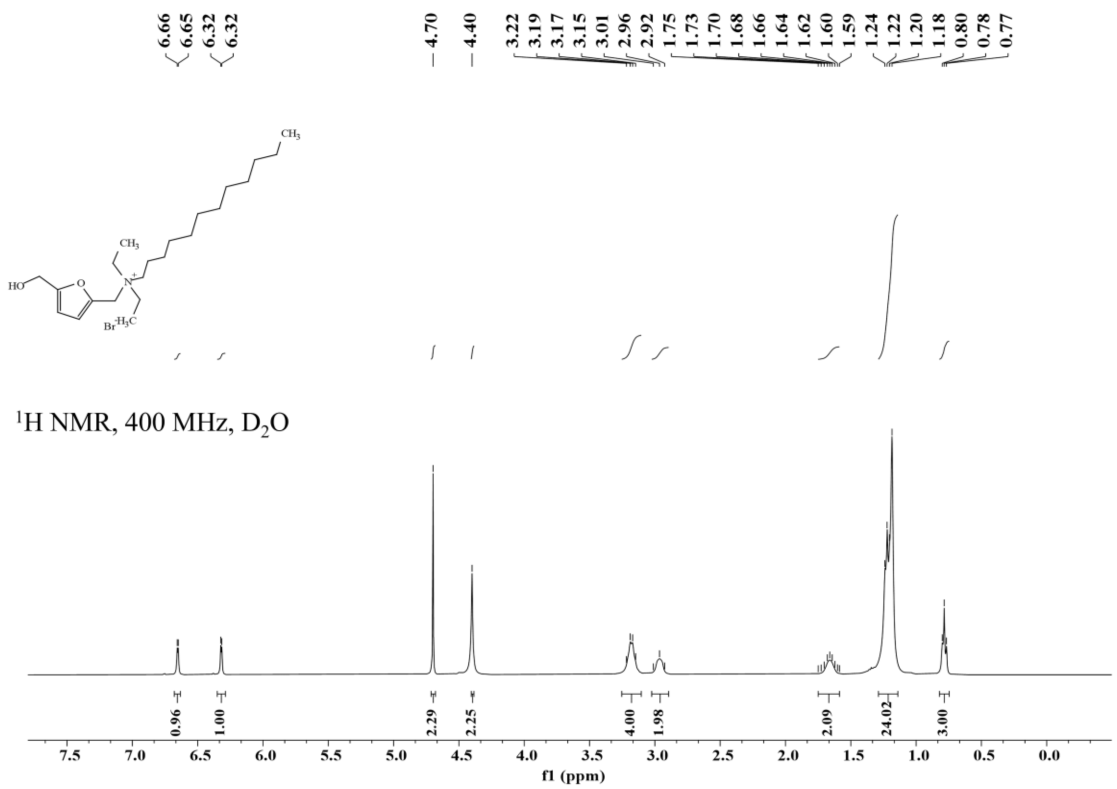


Fig. S5 [1]H (top) and [13]C (bottom) NMR spectra of *N*,*N*-diethyl-*N*-((5-(hydroxymethyl)furan-2-yl)methyl)octan-1-aminium bromide ([5-HMFD-NHeEt$_2$]Br).



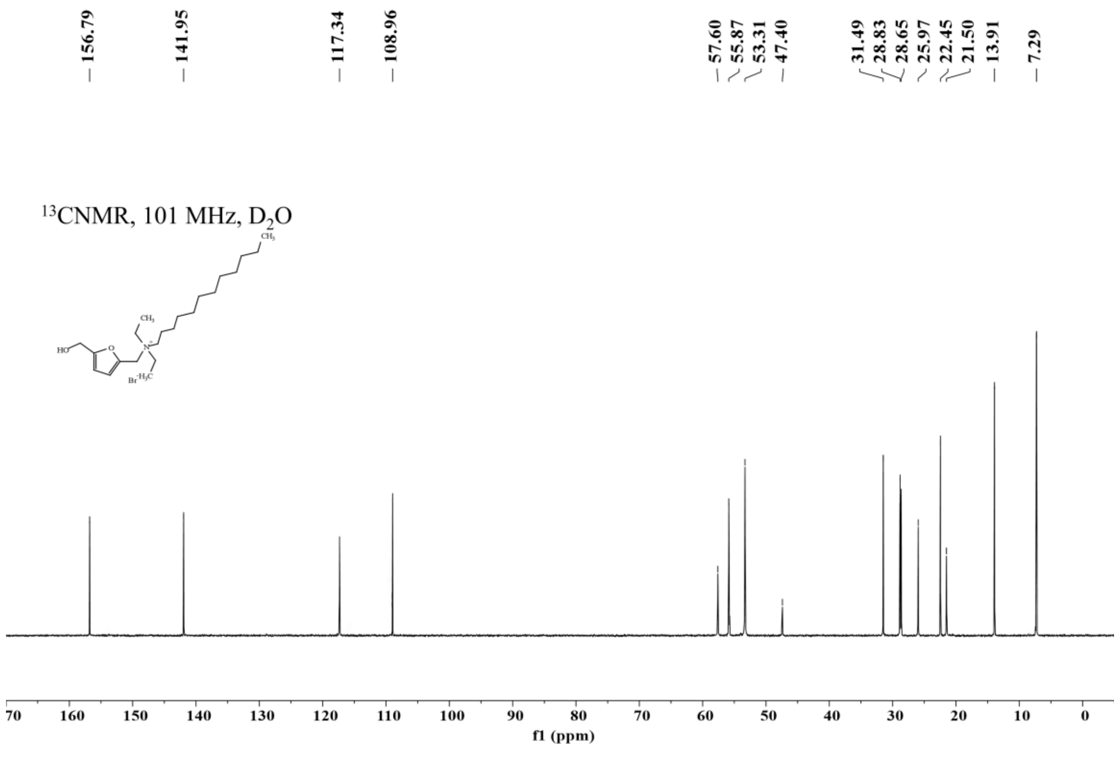
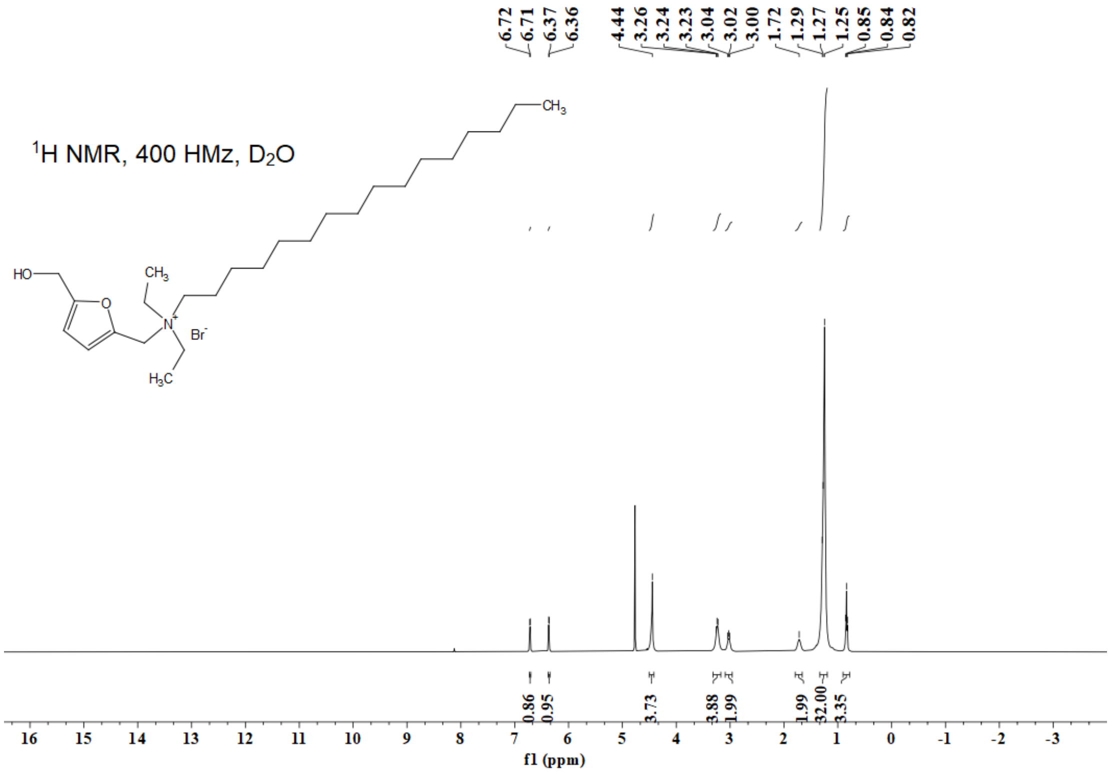


Fig. S6 ^{1}H (top) and ^{13}C (bottom) NMR spectra of *N*,*N*-diethyl-*N*-((5-(hydroxymethyl)furan-2-yl)methyl)dodecan-1-aminium bromide ([5-HMFD-NDoEt$_2$]Br).



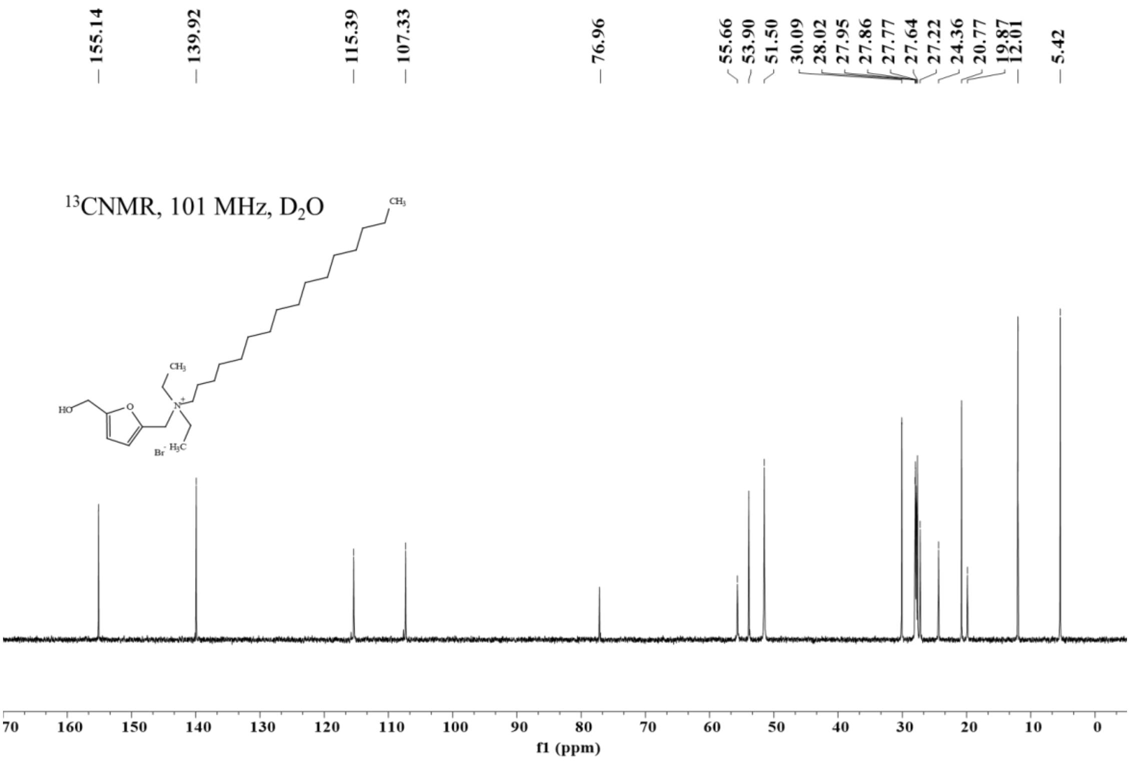
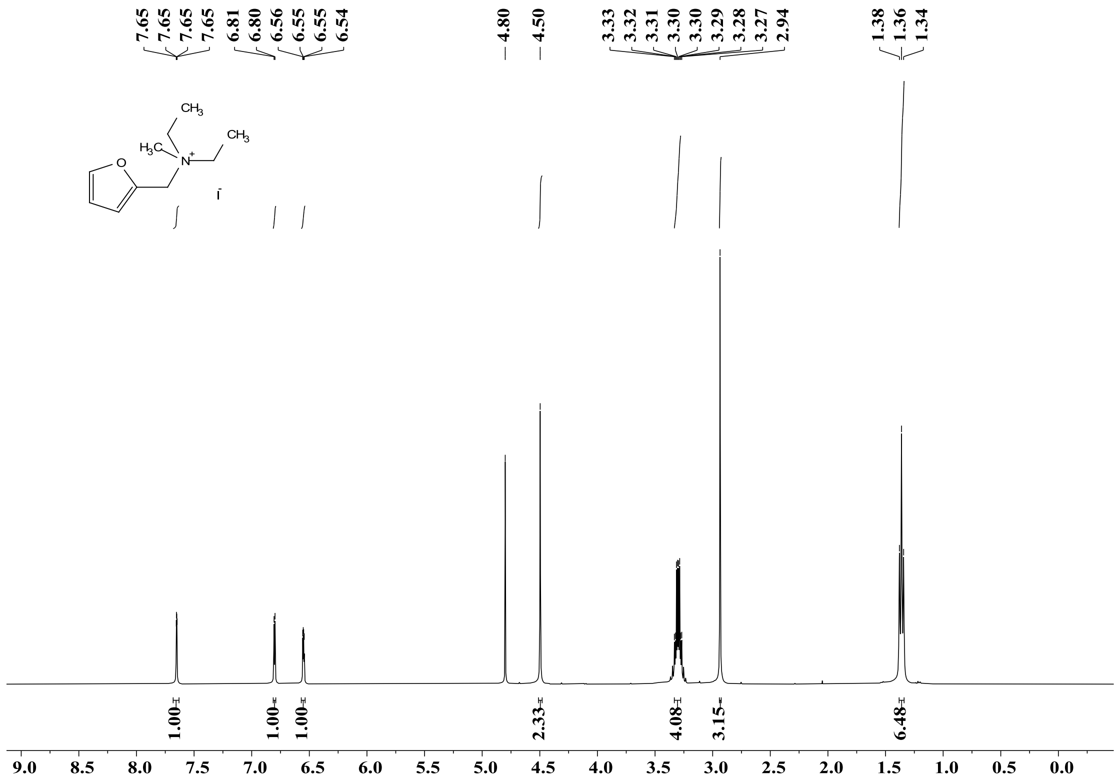


Fig. S7 [1]H (top) and [13]C (bottom) NMR spectra of *N*,*N*-diethyl-*N*-((5-(hydroxymethyl)furan-2-yl)methyl)hexadecan-1-aminium bromide ([5-HMFD-NCeEt$_2$]Br).



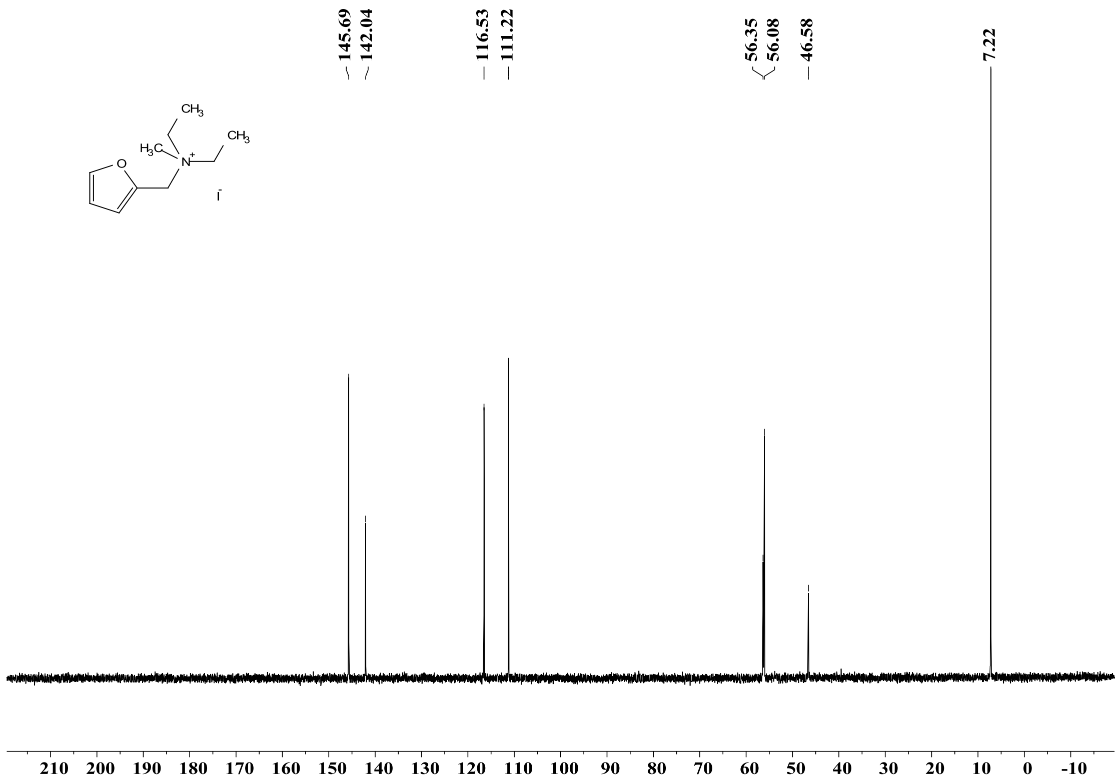
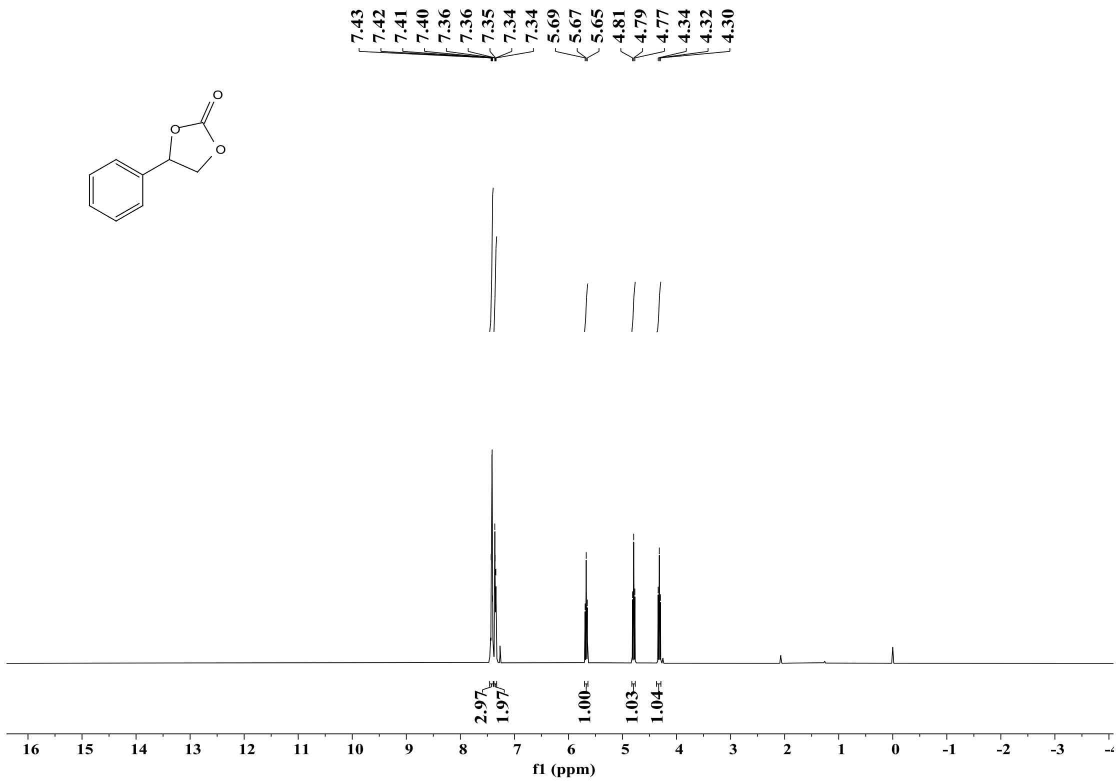


Fig. S8 ^{1}H (top) and ^{13}C (bottom) NMR spectra of *N*-ethyl-*N*-(furan-2-ylmethyl)-*N*-methylethanaminium iodide ([2-FD-NMeEt_2]I).



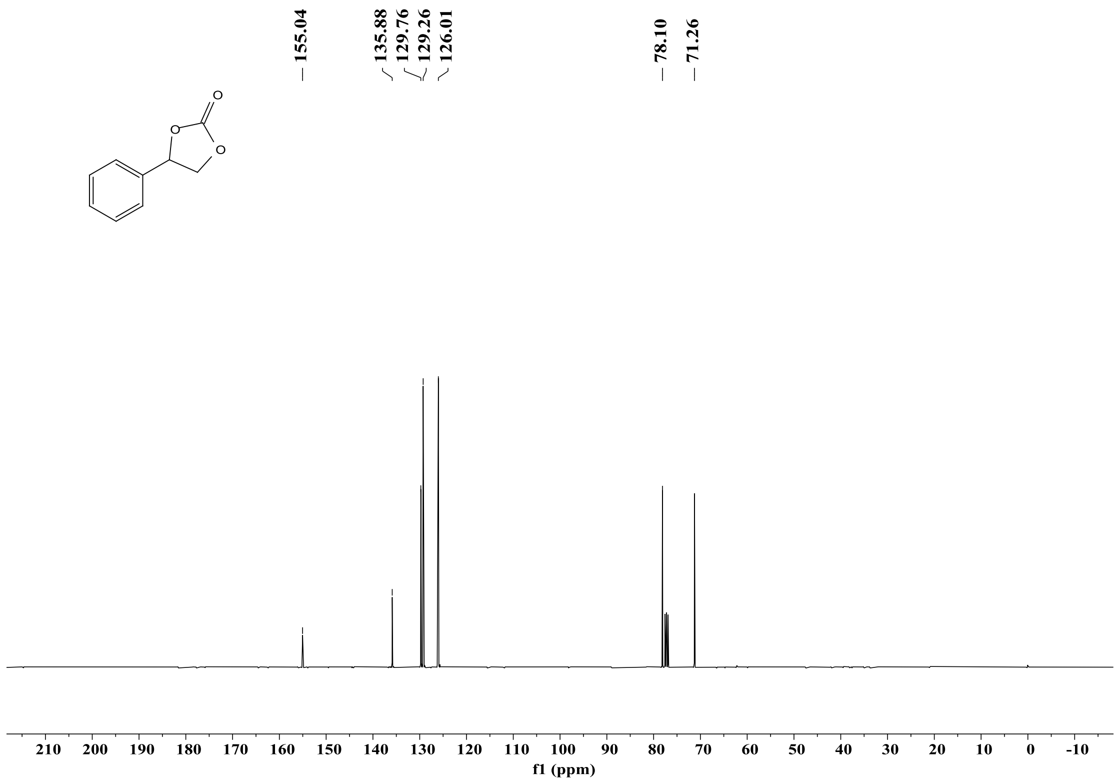


Fig. S9 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 4-phenyl-1,3-dioxolan-2-one (**2a**).

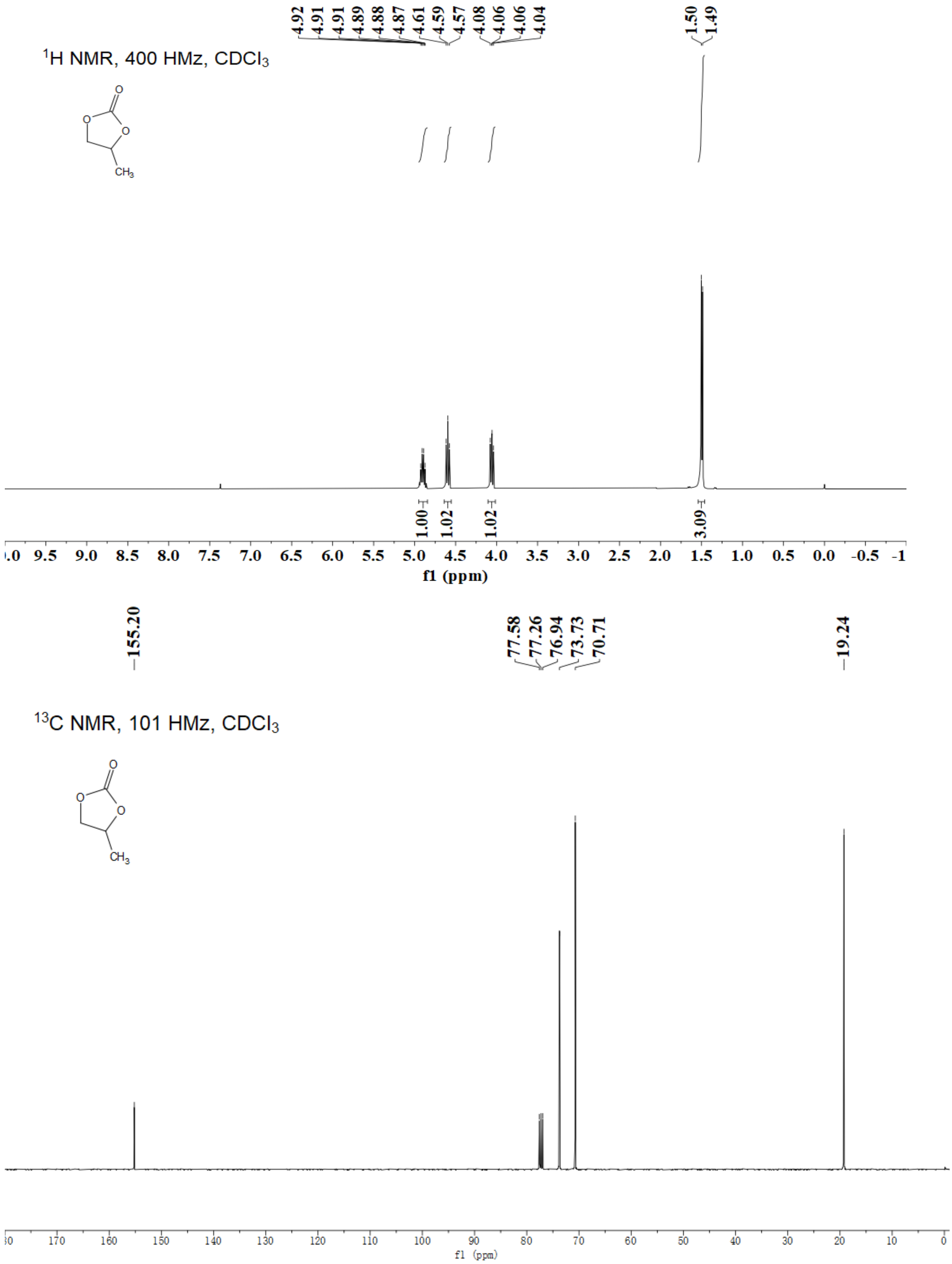
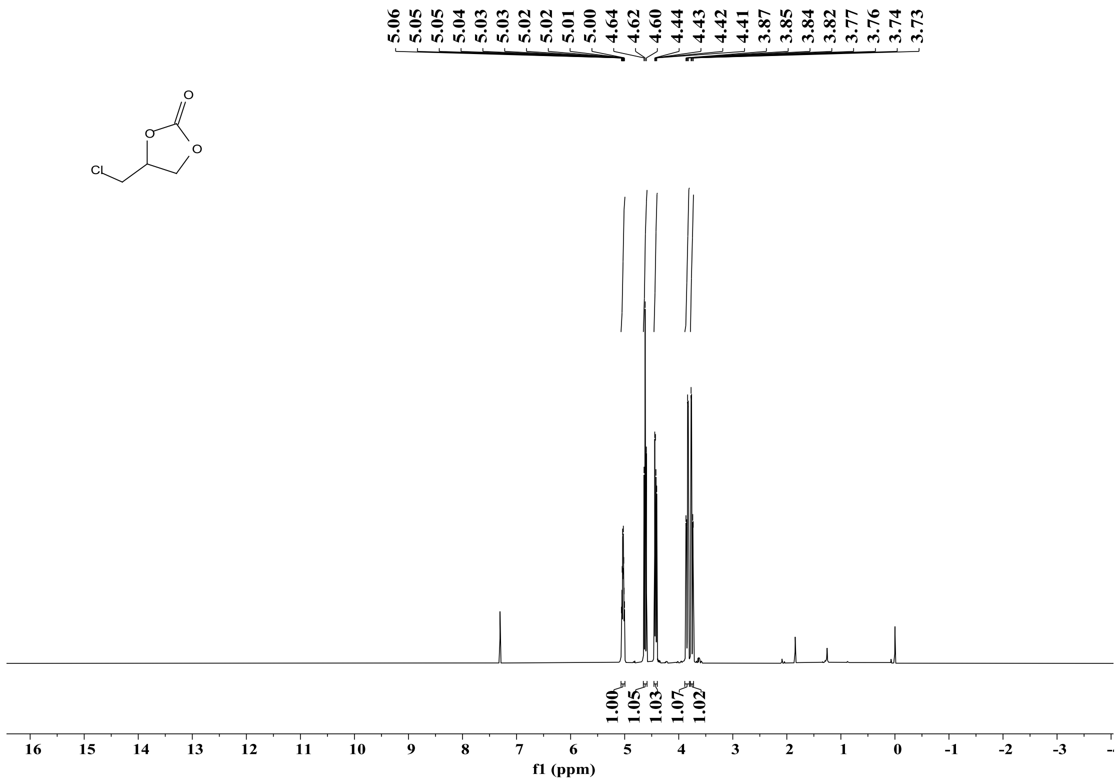


Fig. S10 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 4-methyl-1,3-dioxolan-2-one (**2b**).



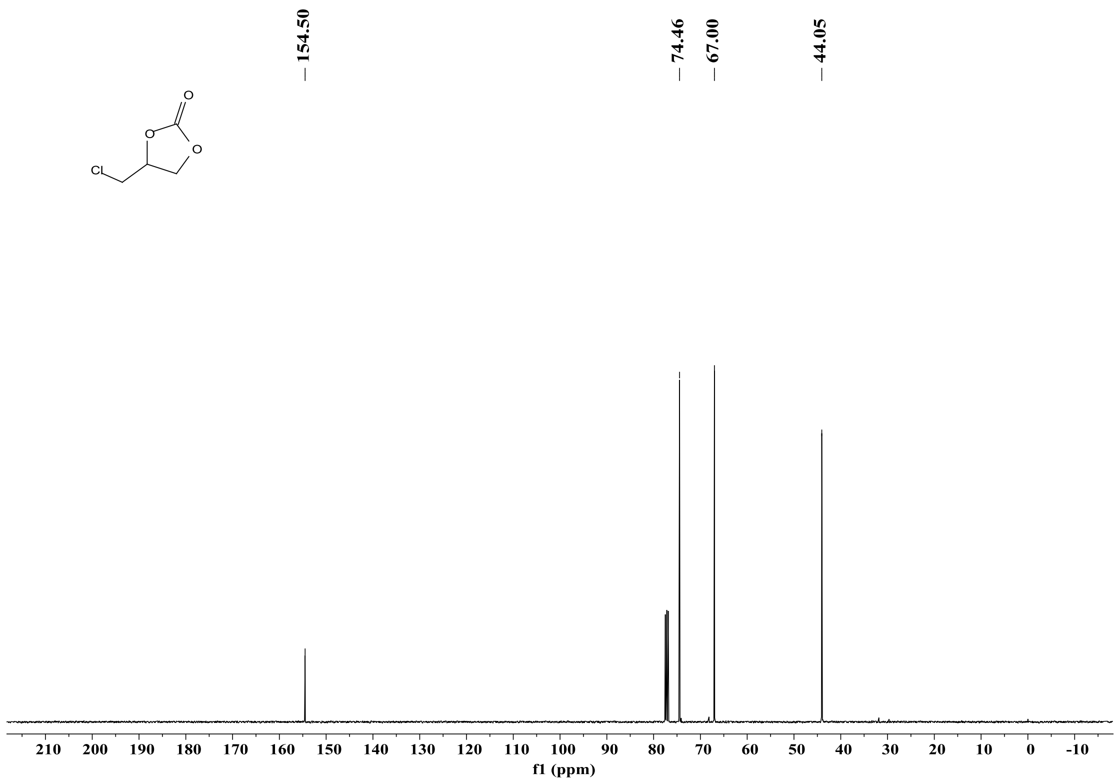


Fig. S11 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 4-(chloromethyl)-1,3-dioxolan-2-one (**2c**).

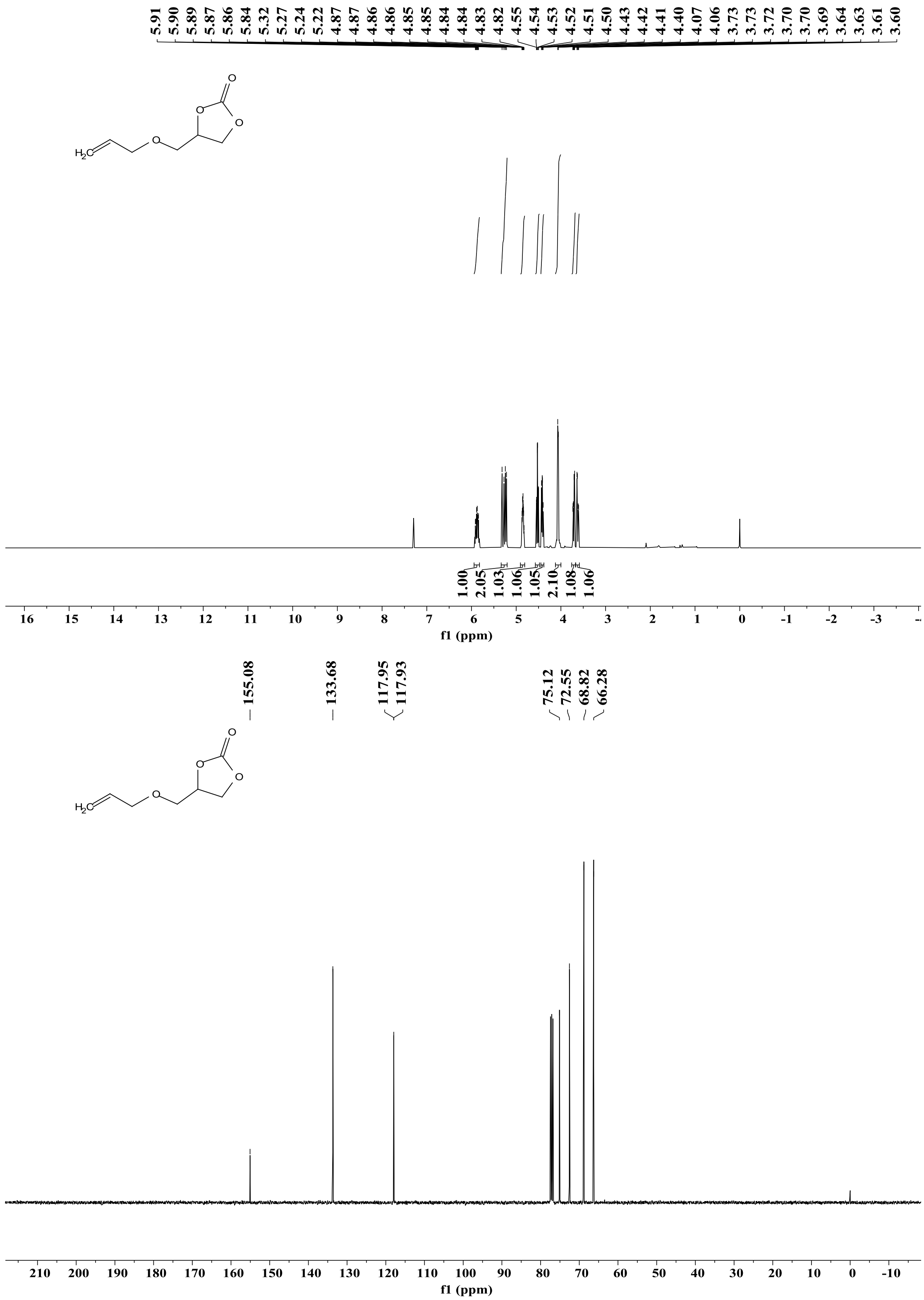


Fig. S12 ^{1}H (top) and ^{13}C (bottom) NMR spectra of 4-((allyloxy)methyl)-1,3-dioxolan-2-one (**2d**).

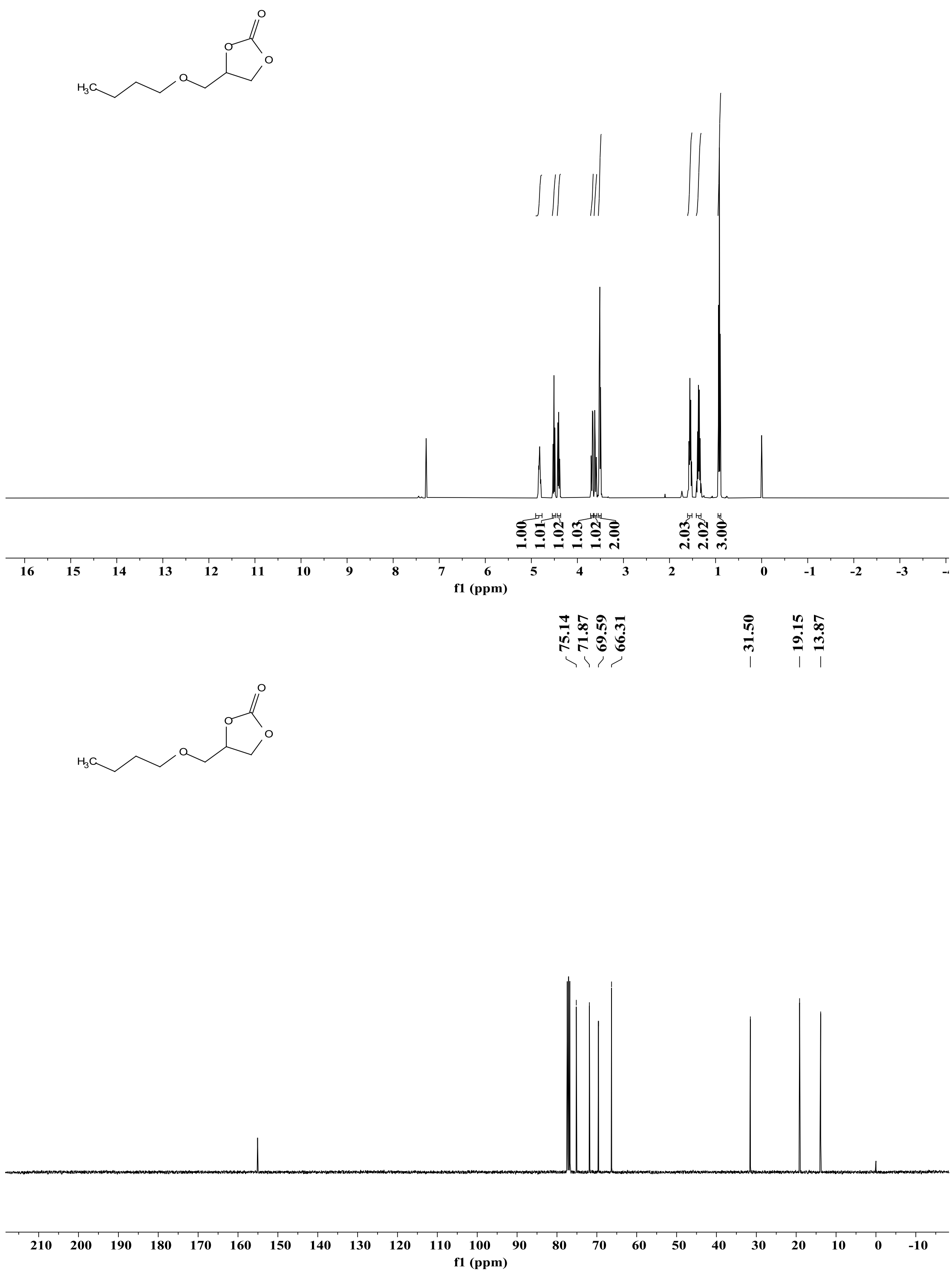


Fig. S13 ¹H (top) and ¹³C (bottom) NMR spectra of 4-(butoxymethyl)-1,3-dioxolan-2-one (**2e**).

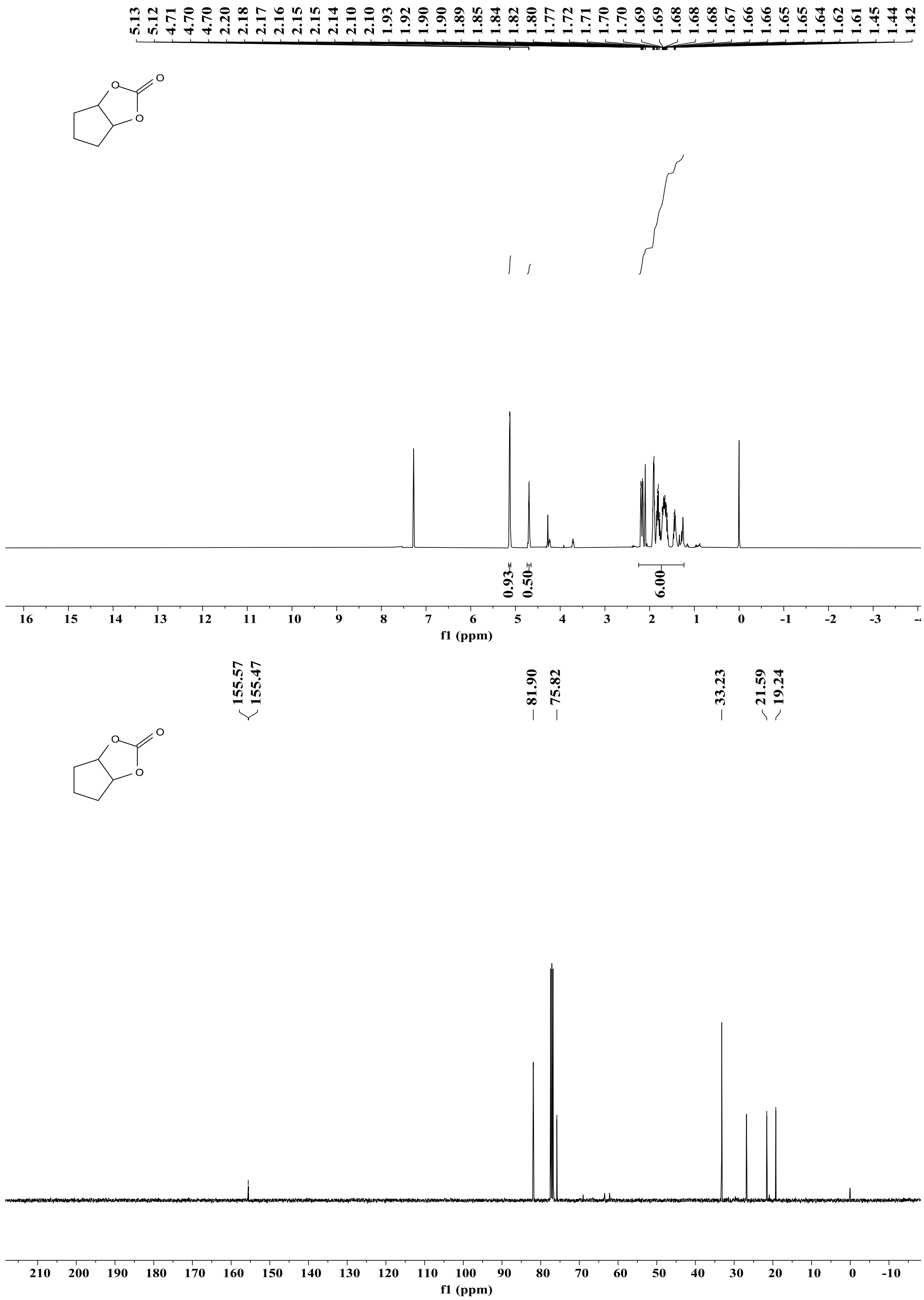


Fig. S14 ^{1}H (top) and ^{13}C (bottom) NMR spectra of tetrahydro-4H-cyclopenta[d][1,3]dioxol-2-one (**2f**).

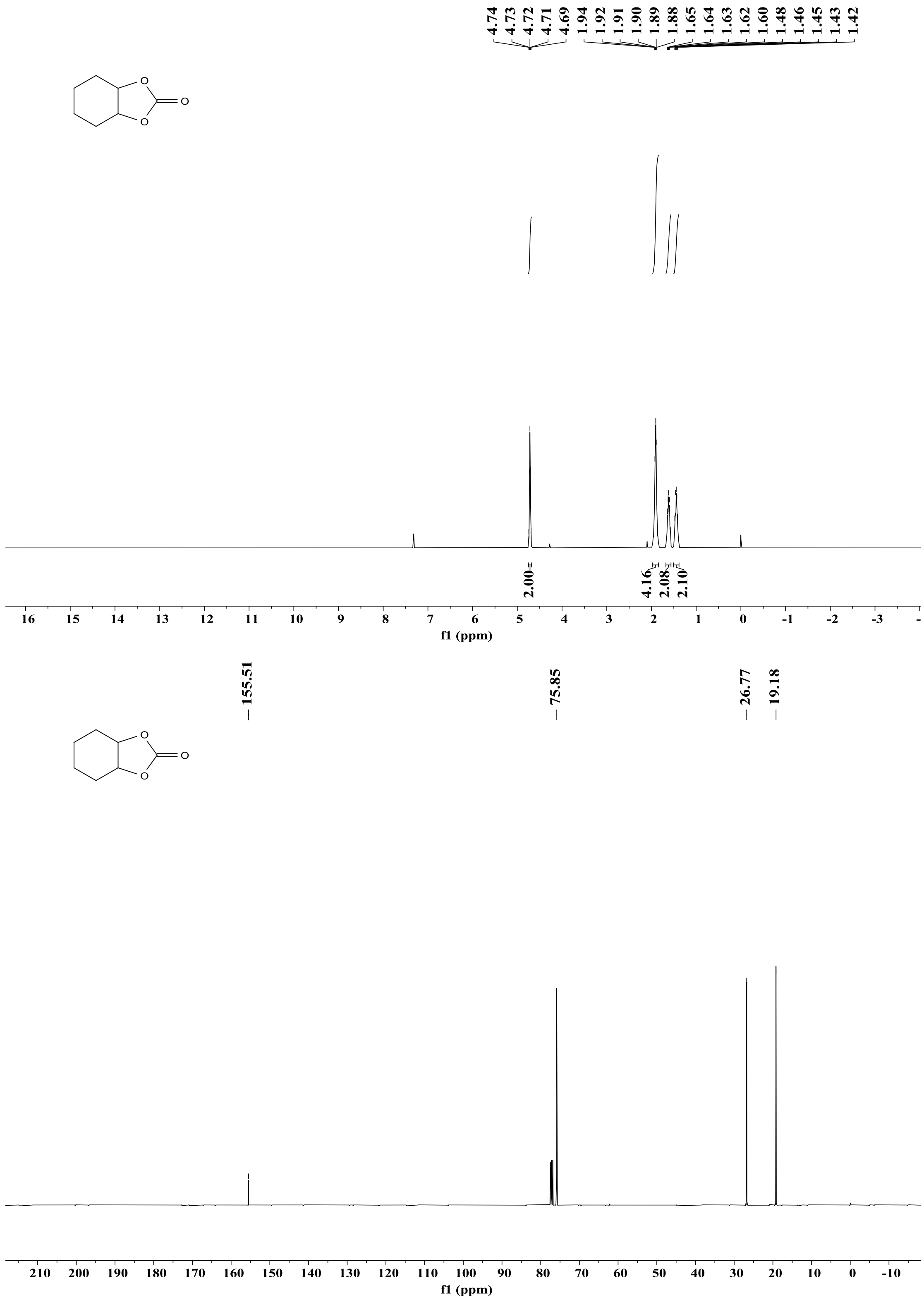


Fig. S15 ^{1}H (top) and ^{13}C (bottom) NMR spectra of hexahydrobenzo[d][1,3]dioxol-2-one (**2g**).

4. IR spectra to test the hydrogen bonding effect and confirm the configuration of 2f and 2g

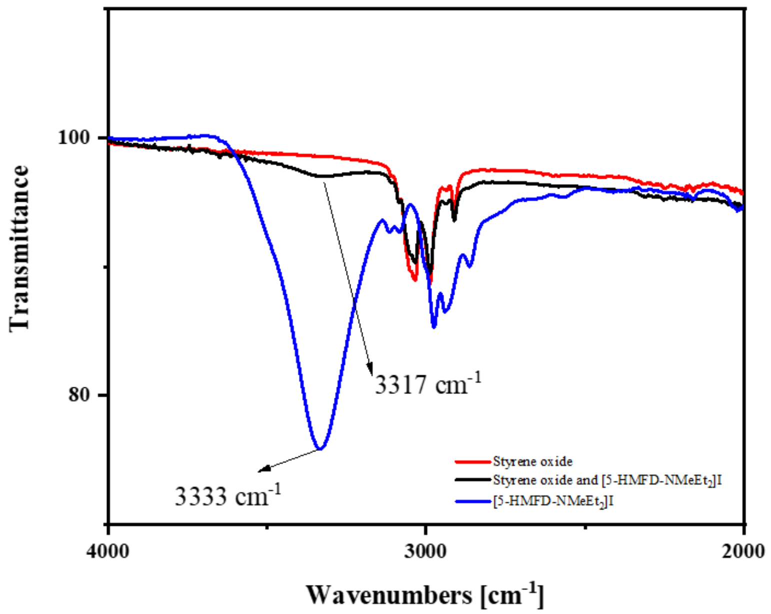


Fig. S16 IR spectra of [5-HMFD-NMeEt$_2$]I, styrene oxide, and the mixture of [5-HMFD-NMeEt$_2$]I and styrene oxide.

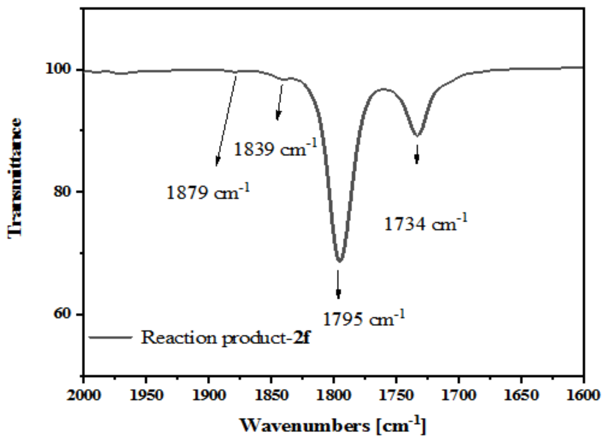


Fig. S17 IR spectrum of **2f**.

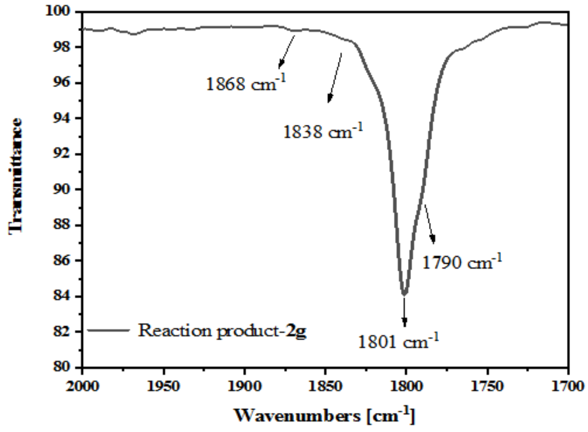


Fig. S18 IR spectrum of **2g**.