Supporting Information

Asymmetric Cycloaddition of CO_2 and Epoxide using Recyclable Bi-functional Polymeric Co(III) Salen Complexes under Mild Condition

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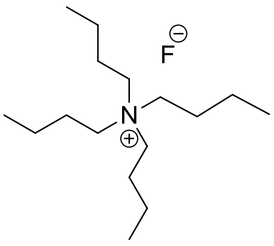
General Procedure for HKR of epichlorohydrin using catalyst 1a:

A solution of freshly prepared bifunctional Co(III) polymeric salen complex **1a** (0.01 mmol) in epichlorohydrin (100 mmol) was taken in an reaction vial and water (55 mmol) was added drop wise to it over a period of 30 min keeping under ice followed by stir at room temperature. After completion of the reaction the catalyst was precipitated out from the reaction mixture by addition of methanol and the unreacted epichlorohydrin was distilled out under reduced pressure. The catalyst which was precipitated out earlier was washed several times with methanol, dried overnight in a desiccator and used as such for next cycle. The catalyst was regenerated using acetic acid after 4 cycles.

Counter-ion source used for the synthesis of bifunctional polymeric Co(III) salen complex:

Catalyst	Counter-ion source
1a	Acetic Acid (CH_3COOH) (**a**)
1b	2,6-dimethyl pyridinium tosylate (**b**)
1c	Para nitrobenzoic acid ($NO_2C_6H_4COOH$) (**c**)
1d	Trifluoroacetic acid (CF_3COOH) (**d**)
1e	Trichloroacetic acid (CCl_3COOH) (**e**)
1f	Ferrocenium tetrafluoroborate (**f**)
1g	Ferrocenium hexafluorophosphate (**g**)

Additive tested for asymmetric cycloadditon of CO_2 to propylene oxide using catalyst 1e:



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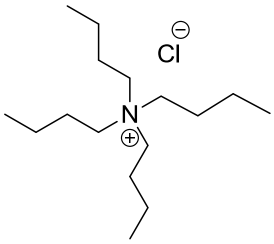

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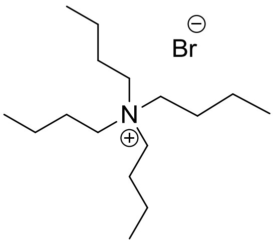

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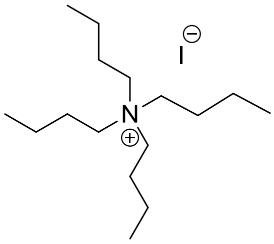

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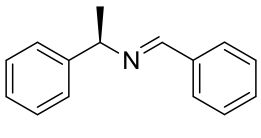
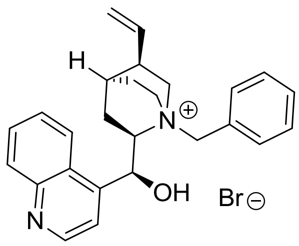


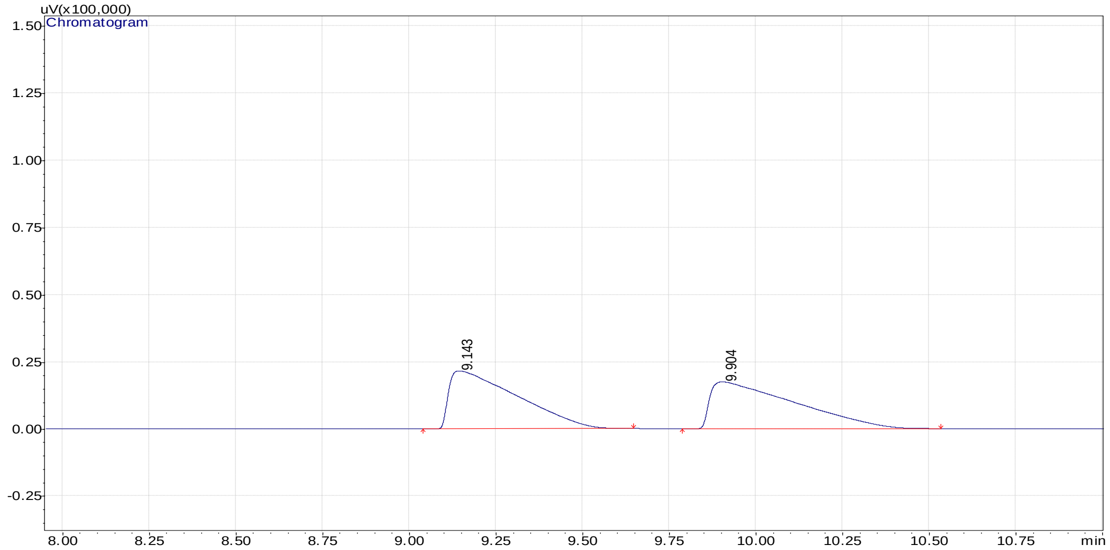
Chiral imine

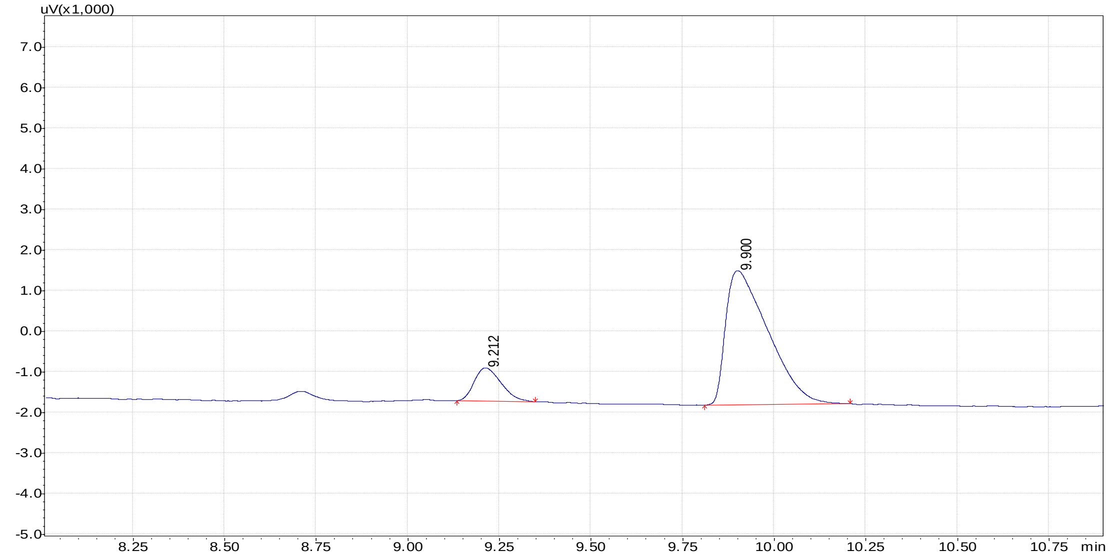


Cinchonine bromide salt

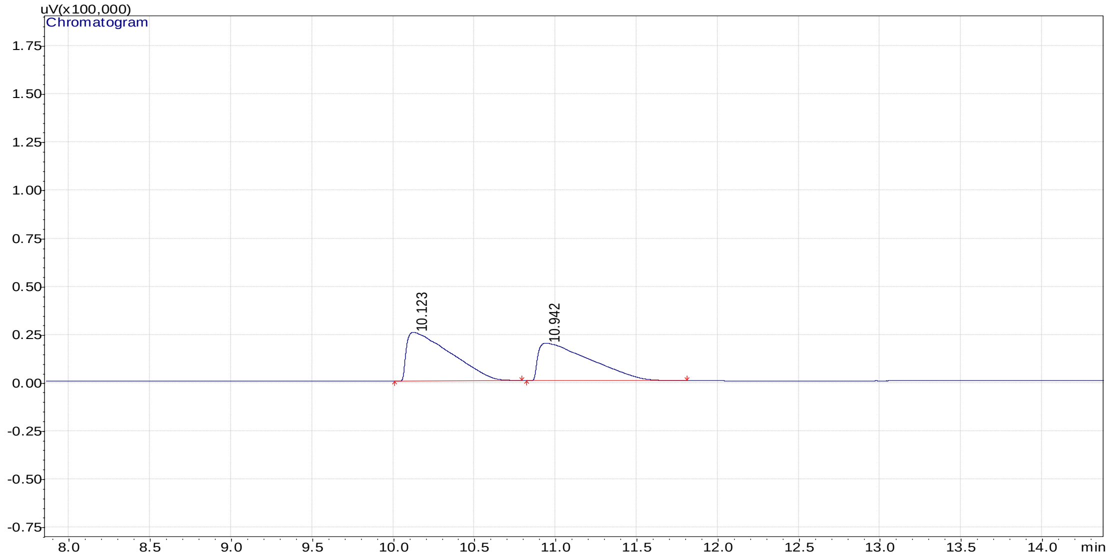
Characterization data of cyclic carbonate products:

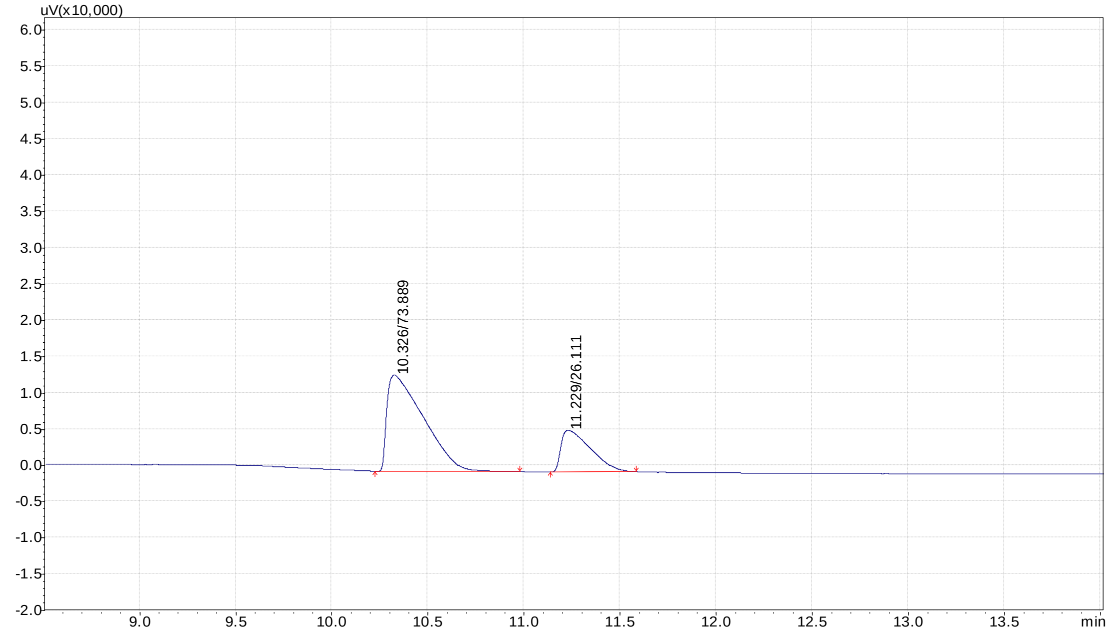
(S)-4-methyl-1,3-dioxolan-2-one: The product was isolated as colourless liquid after distillation. ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): δ: 4.98-4.81 (m, 1H), 4.63-4.55 (t, 1H, *J*=8Hz), 4.09-4.01(t, 1H, *J*=8Hz), 1.51-1.48 (d, 3H, *J*=6Hz); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS) δ: 155.2, 73.7, 70.7, 19.2; GC-MS: 102; GC analysis: Astec CHIRALDEX BTA column, 160 ^{o}C isothermal, t_R(minor) = 9.21 min, t_R(major) = 9.90 min. Area percentage ratio: 13.0:87.0.



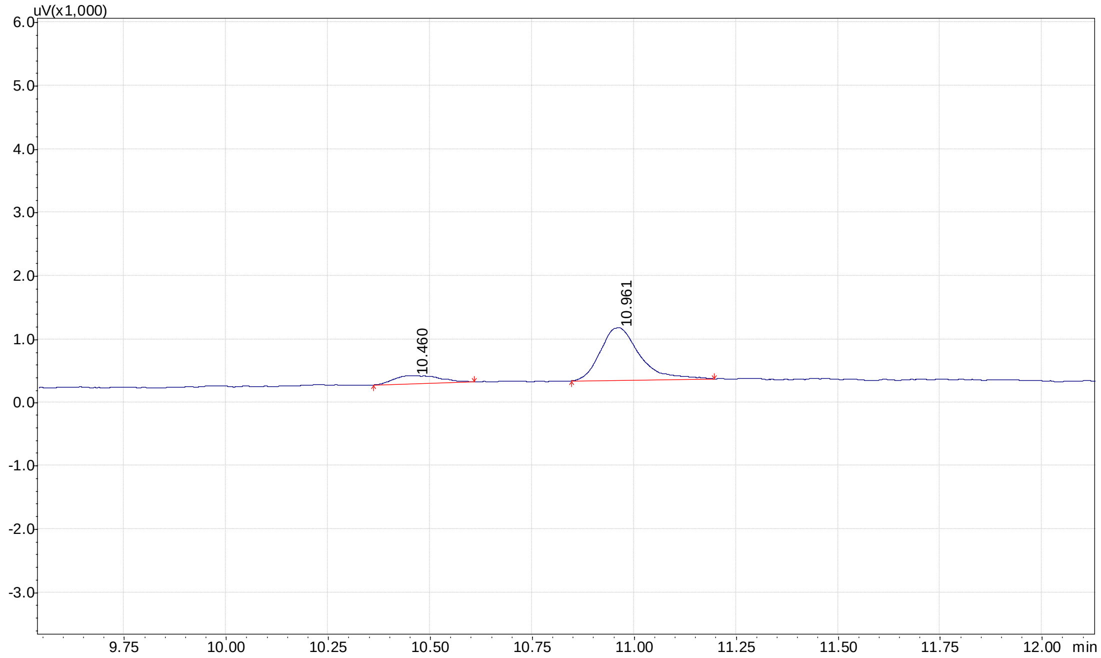


(R)-4-ethyl-1,3-dioxolan-2-one: The product was isolated as colourless liquid after distillation (Catalyst **1e** with opposite configuration was used). ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): δ: 4.76-4.63 (m, 1H), 4.59-4.51 (t, 1H, *J*=8Hz), 4.14-4.06 (t, 1H, *J*=8Hz), 1.84-1.75 (m, 2H,), 1.07-1.00 (t, 3H, *J*=6Hz); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS) δ: 155.2, 78.0, 69.0, 26.9, 8.4; GC-MS: 116; GC analysis: Astec CHIRALDEX BTA column, 160 ^{o}C isothermal, t_R(major) = 10.33 min, t_R(minor) = 11.23 min). Area percentage ratio: 73.9:26.1.

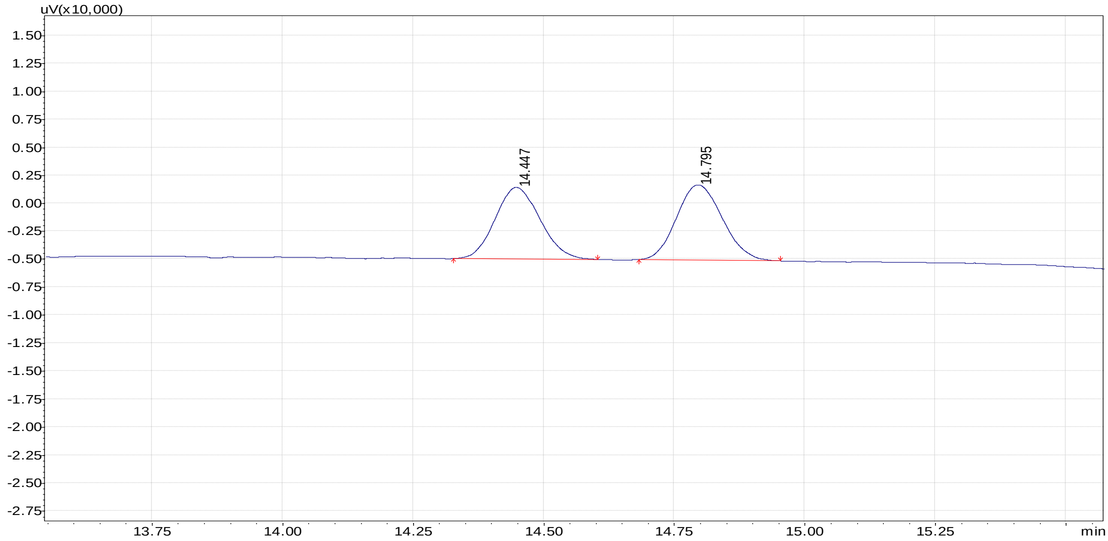


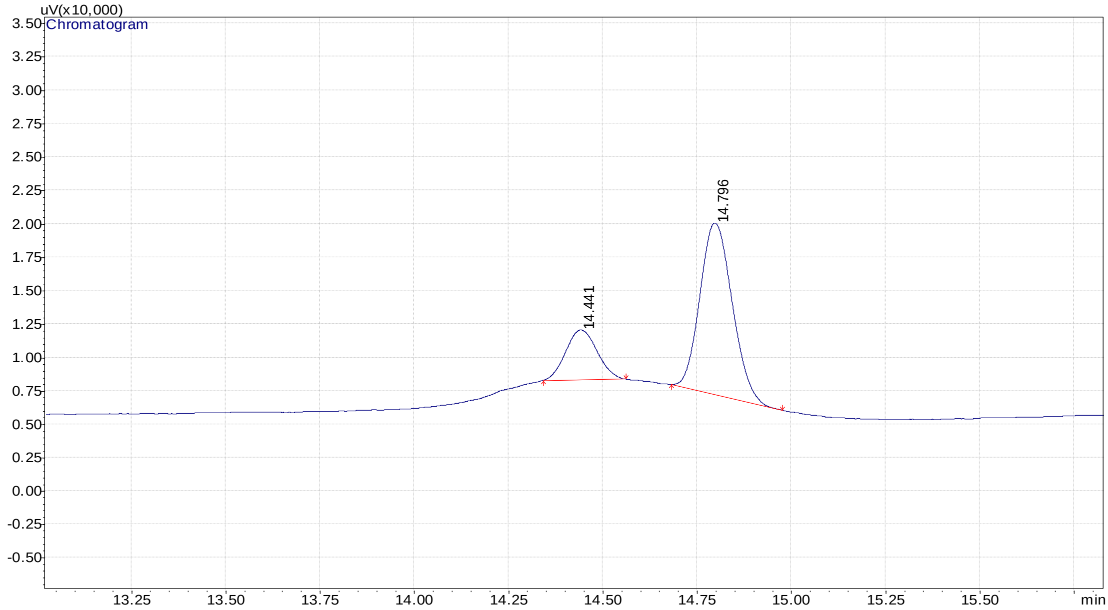


(S)-4-butyl-1,3-dioxolan-2-one: The product was isolated as colourless liquid after distillation. ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): δ: 4.76-4.66 (m, 1H), 4.59-4.51 (t, 1H, *J*=8Hz), 4.12-4.04(t, 1H, *J*=8Hz), 1.83-1.68 (m, 2H), 1.42-1.37 (m, 4H), 0.96-0.89 (t, 3H, *J*=6Hz); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS) δ: 155.2, 77.1, 69.4, 33.5, 26.4, 22.2, 13.8; GC-MS: 144; GC analysis: Astec CHIRALDEX BTA column, 160 ^{o}C isothermal, t_R(minor) = 10.46 min, t_R(major) = 10.96 min. Area percentage ratio: 85.5:14.5.

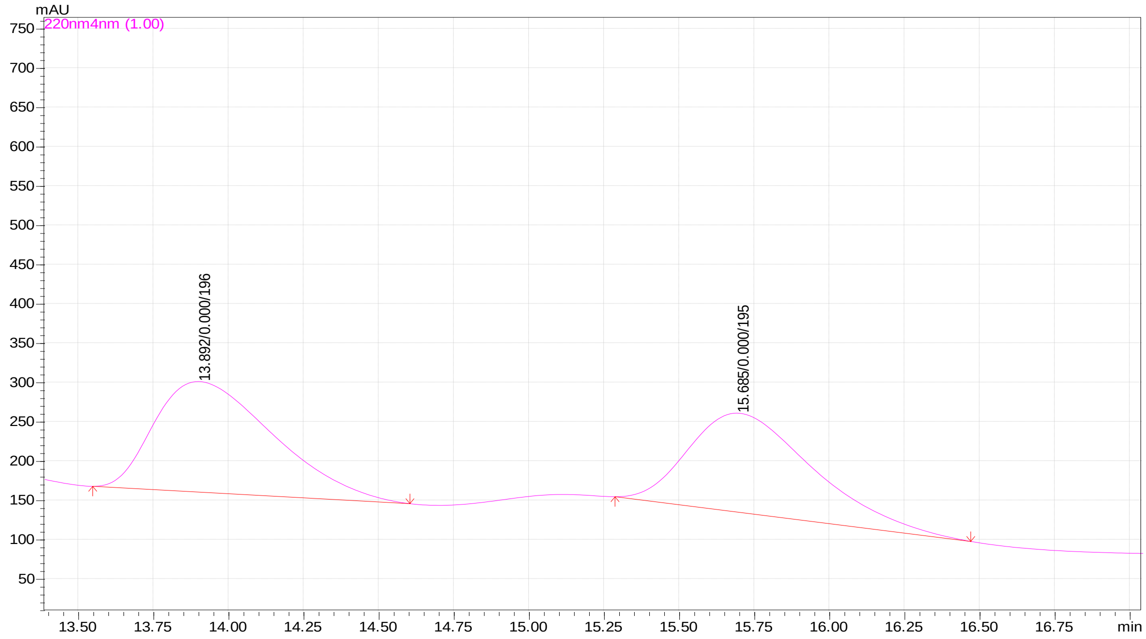


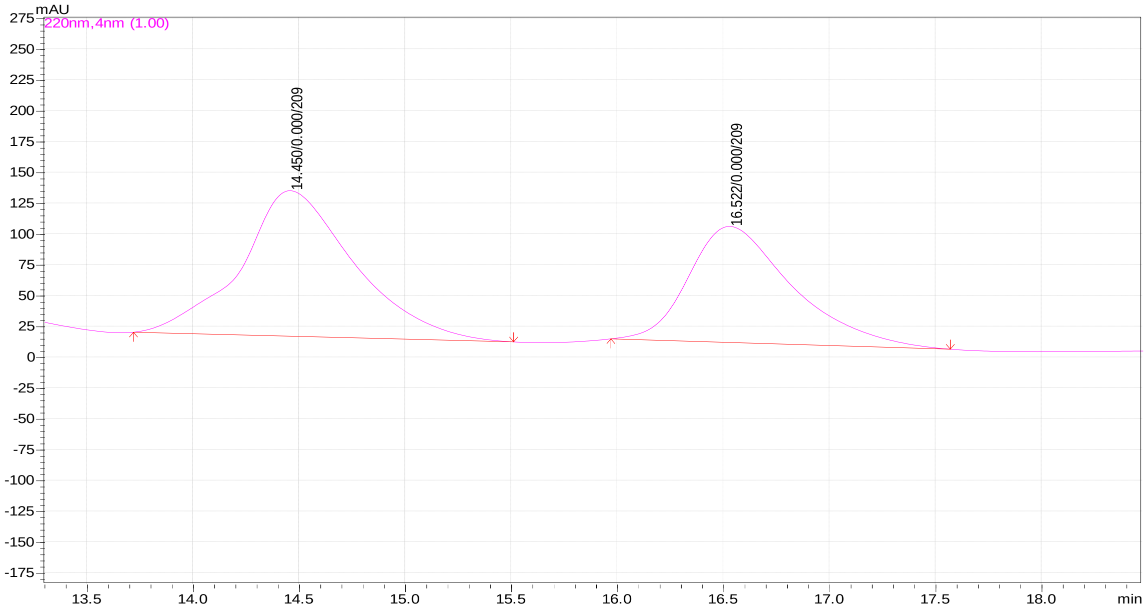
(S)-4-(chloromethyl)-1,3-dioxolan-2-one: The product was isolated as colourless liquid after distillation. ^{1}H NMR (200 MHz, CDCl$_3$, 25°C, TMS): δ: 5.10-4.99 (m, 1H), 4.66-4.58 (t, 1H, *J*=8Hz), 4.45-4.37(t, 1H, *J*=8Hz), 3.91-3.71 (qd, 2H, *J*=12Hz, 4Hz); ^{13}C NMR (50 MHz, CDCl$_3$, 25°C, TMS) δ: 154.6, 74.5, 67.0, 44.2; GC-MS: 144; GC analysis: Astec CHIRALDEX BTA column, 160 ^{o}C isothermal, t$_R$(minor) = 14.44 min, t$_R$(major) = 14.79 min. Area percentage ratio: 76.4:23.6.





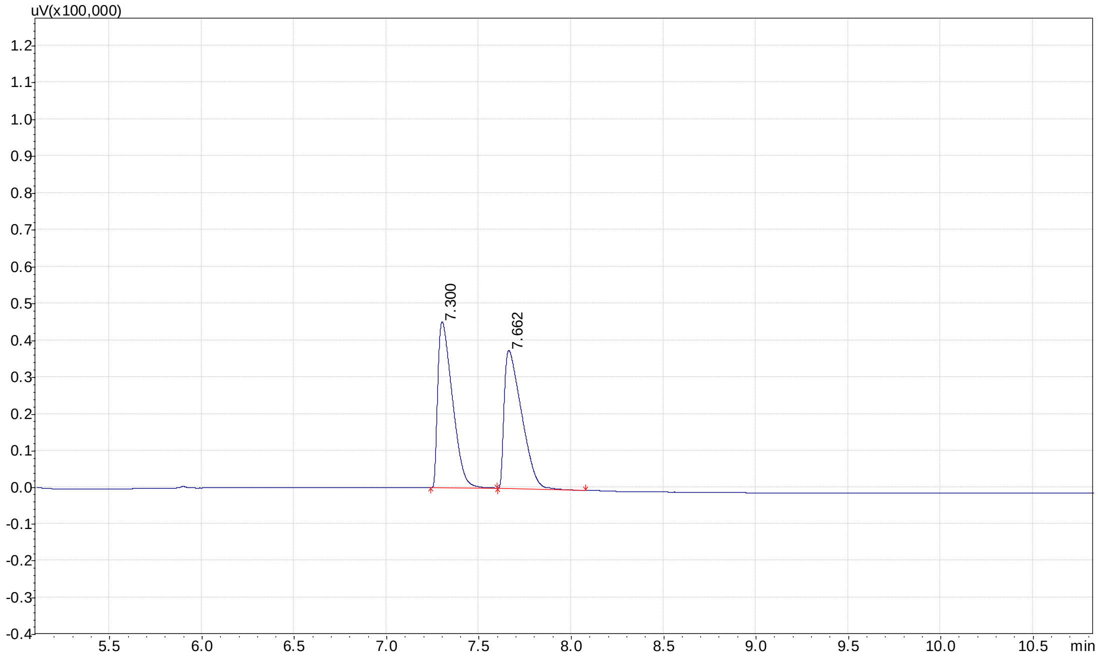
(S)-4-phenyl-1,3-dioxolan-2-one: The product was isolated as colourless liquid after purification by column chromatography. ^{1}H NMR (200 MHz, $CDCl_3$, 25°C, TMS): δ: 7.44-7.38 (m, 5H), 5.71-5.63 (t, 1H, *J*=8Hz), 4.84-4.76(t, 1H, *J*=8Hz), 4.37-4.29 (t, 1H, *J*=8Hz); ^{13}C NMR (50 MHz, $CDCl_3$, 25°C, TMS) δ: 154.9, 135.8, 129.7, 129.2, 125.9, 71.2; GC-MS: 164; HPLC analysis: Chiralcel OD coulmn, 1.0 ml/min, Hexane:IPA 90:10, t_R(minor) = 14.45 min, t_R(major) = 16.52 min. Area percentage ratio: 56.7:43.3. (220 nm)

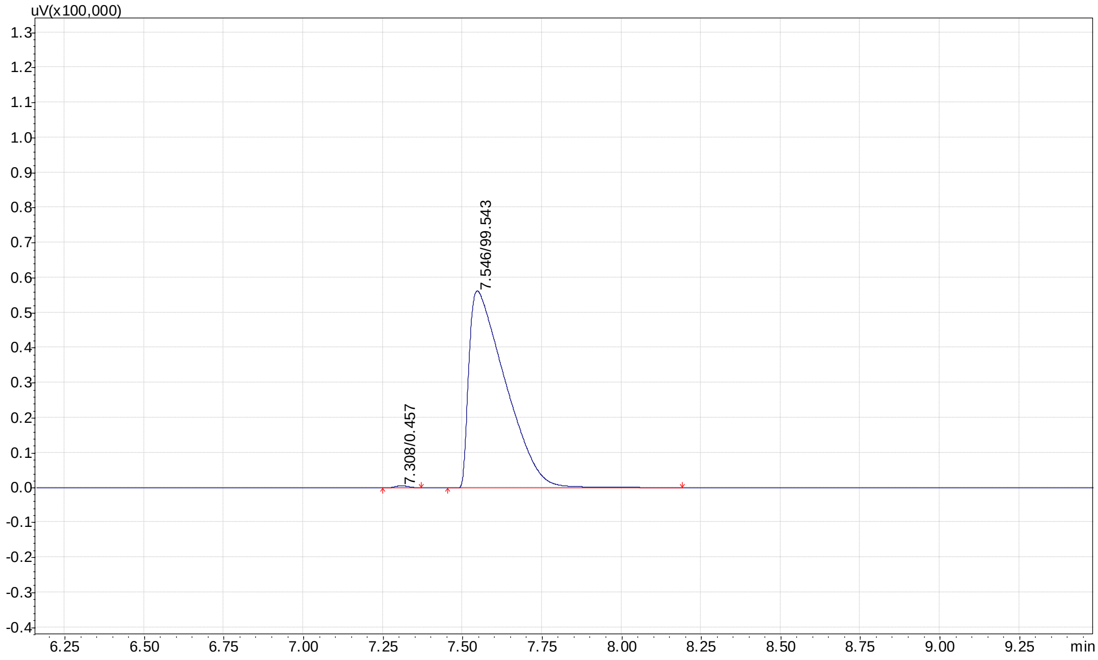




GC profile of (S)-epichlorohydrin obtained by HKR of racemic epichlorohydrin using catalyst 1a:

GC analysis: Astec CHIRALDEX BTA column, 70 ^{o}C isothermal, t_R(minor) = 7.31 min, t_R(major) = 7.54 min. Area percentage ratio: 99.54:0.45.





NMR spectra:

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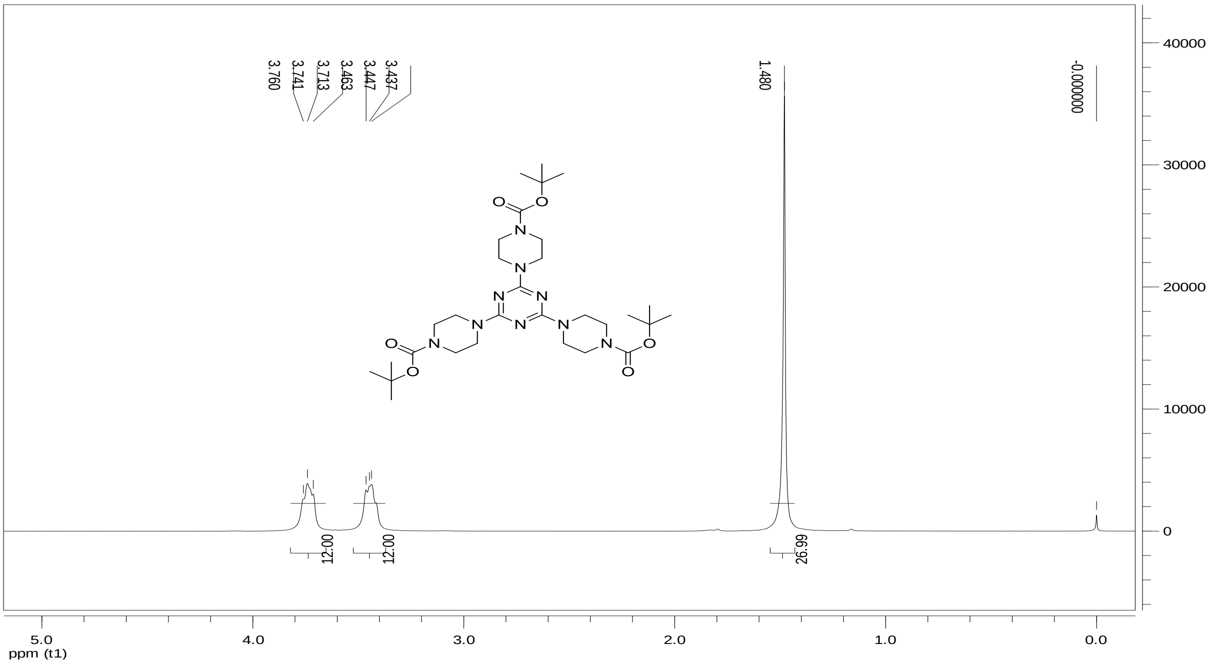
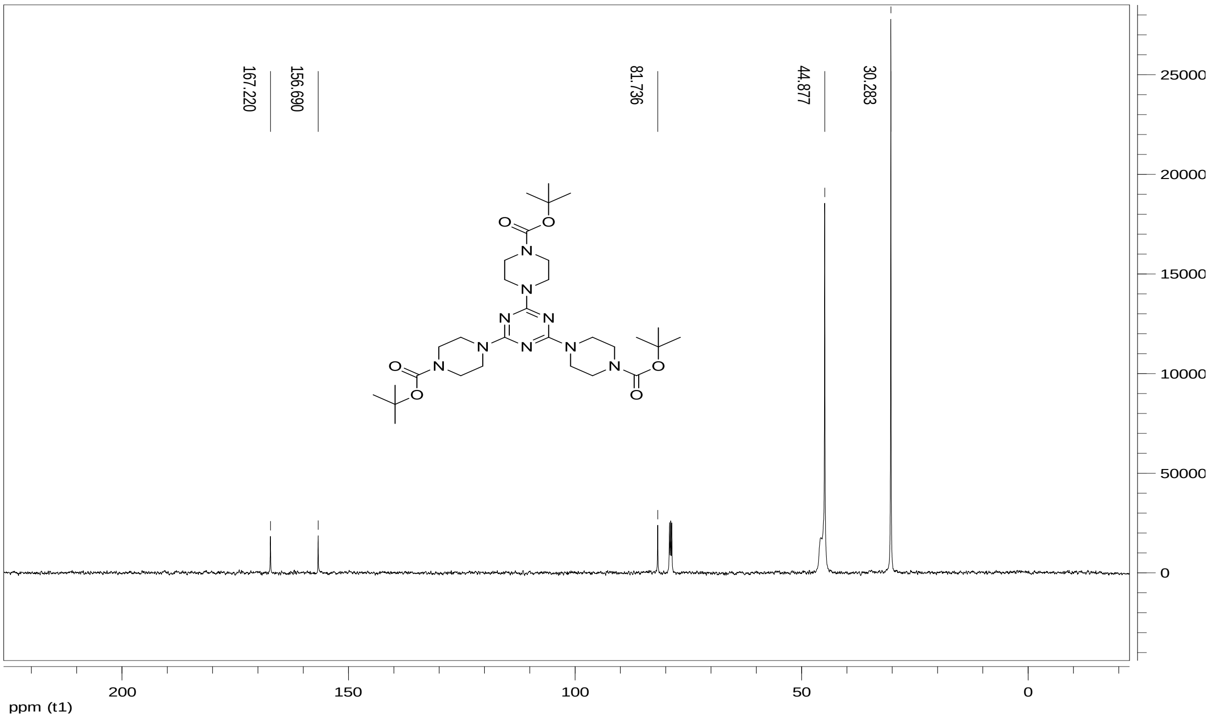
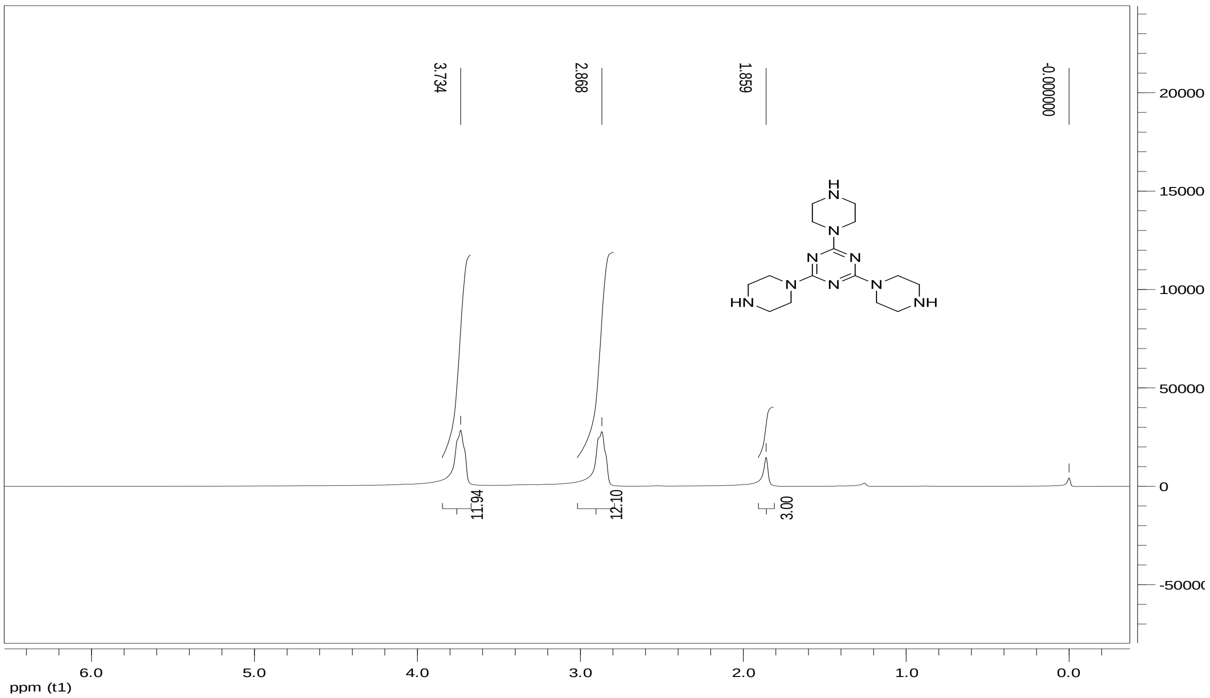


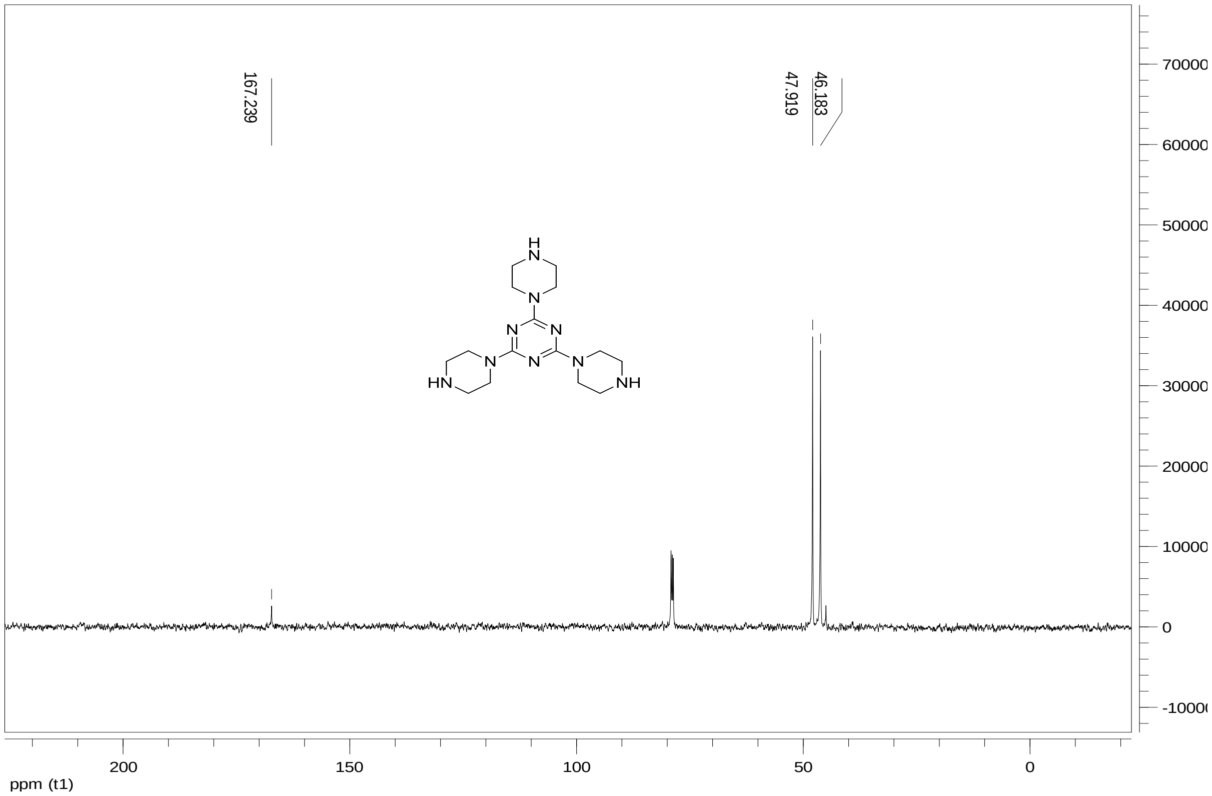
*^{13}C NMR of compound **A**:*



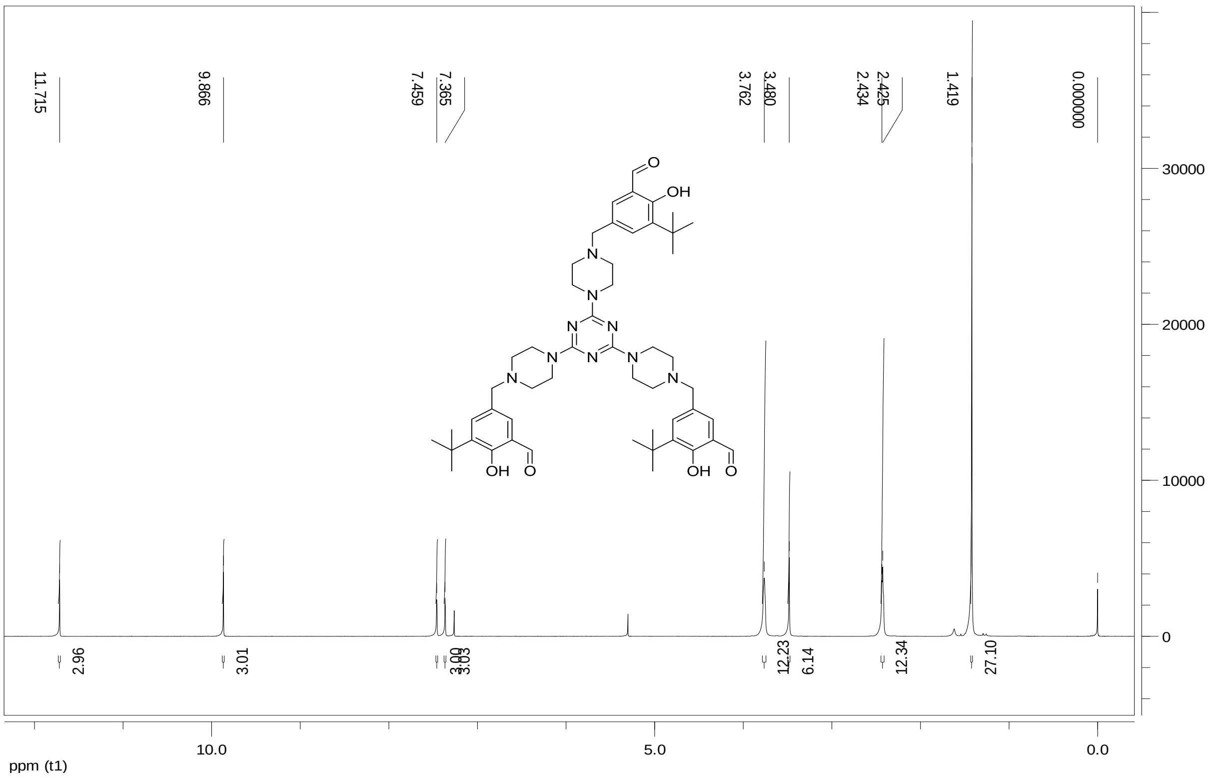
^{1}H NMR of compound **B**:



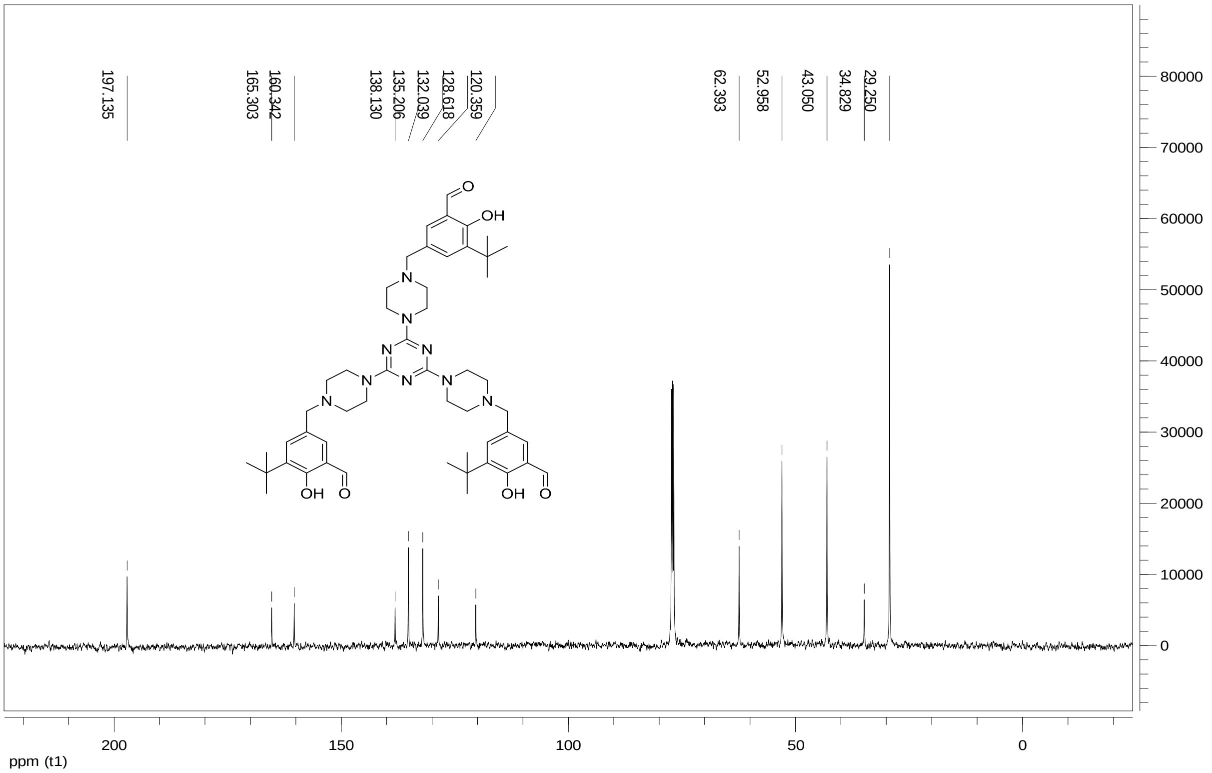
^{13}C NMR of compound **B**:



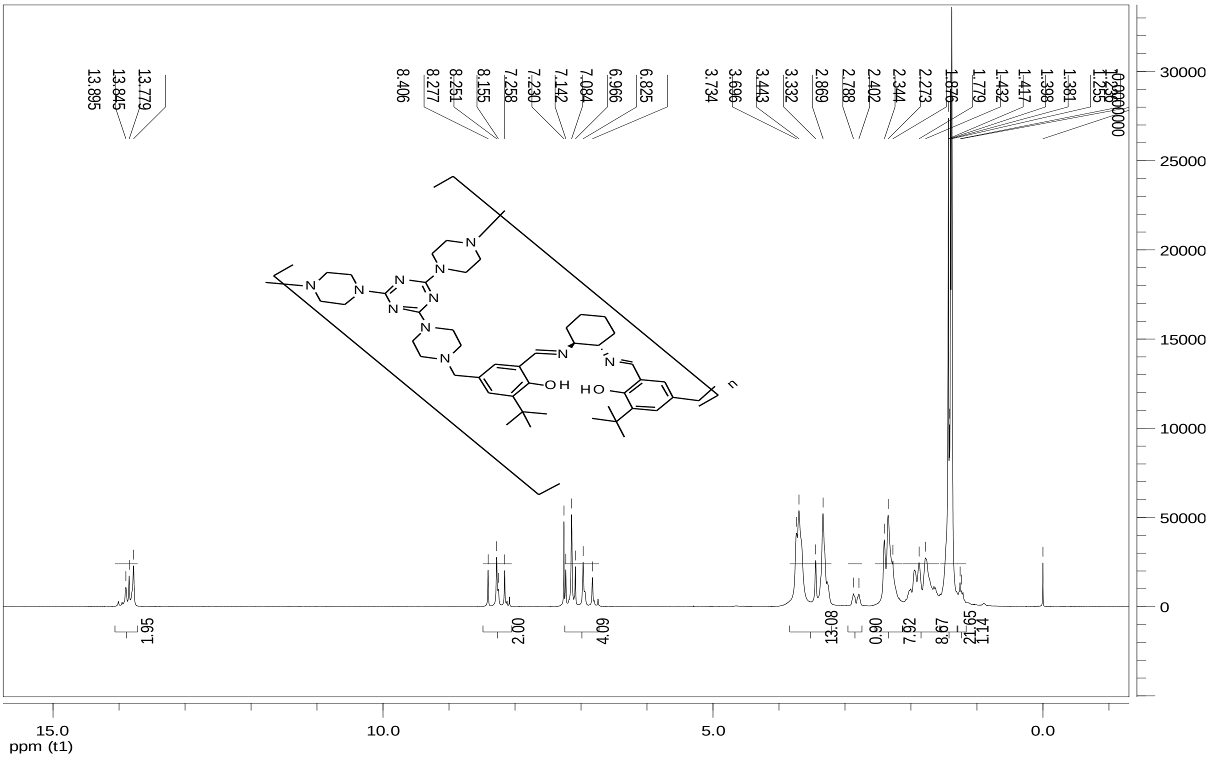
^{1}H NMR of compound ***C****:*



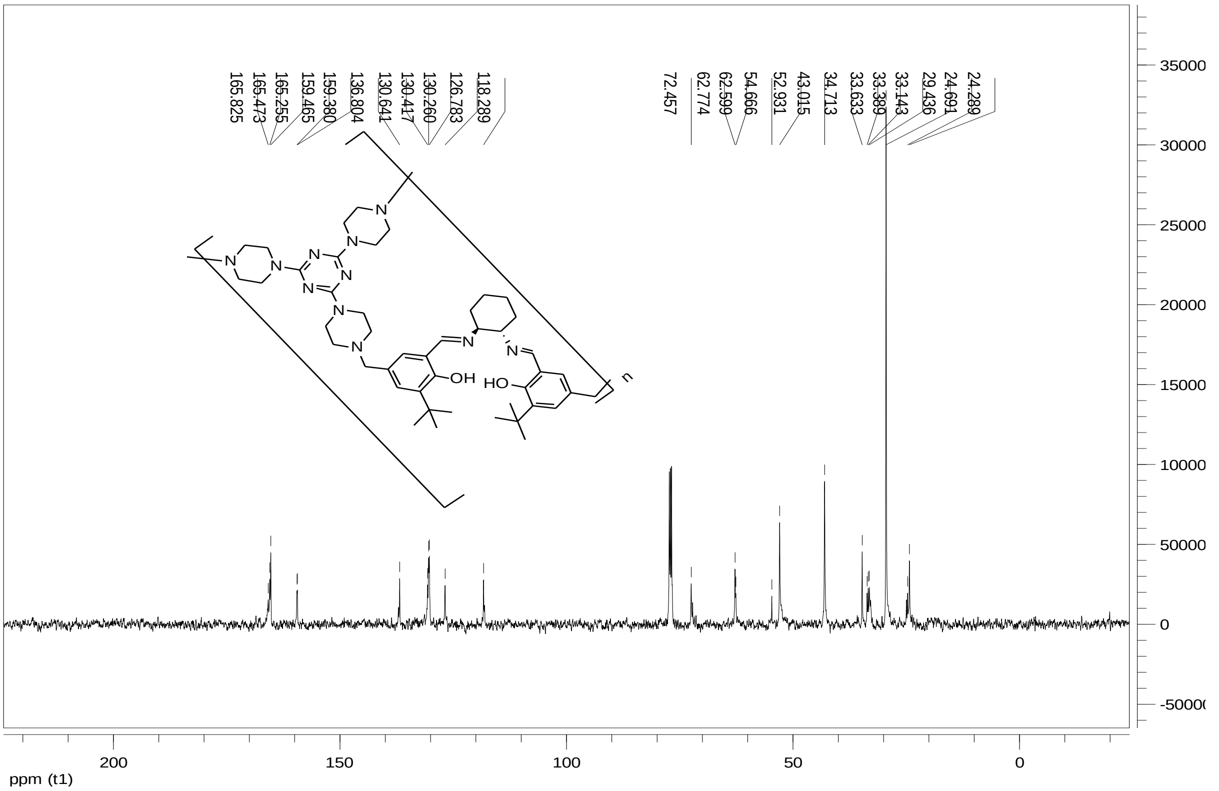
^{13}C NMR of compound ***C****:*



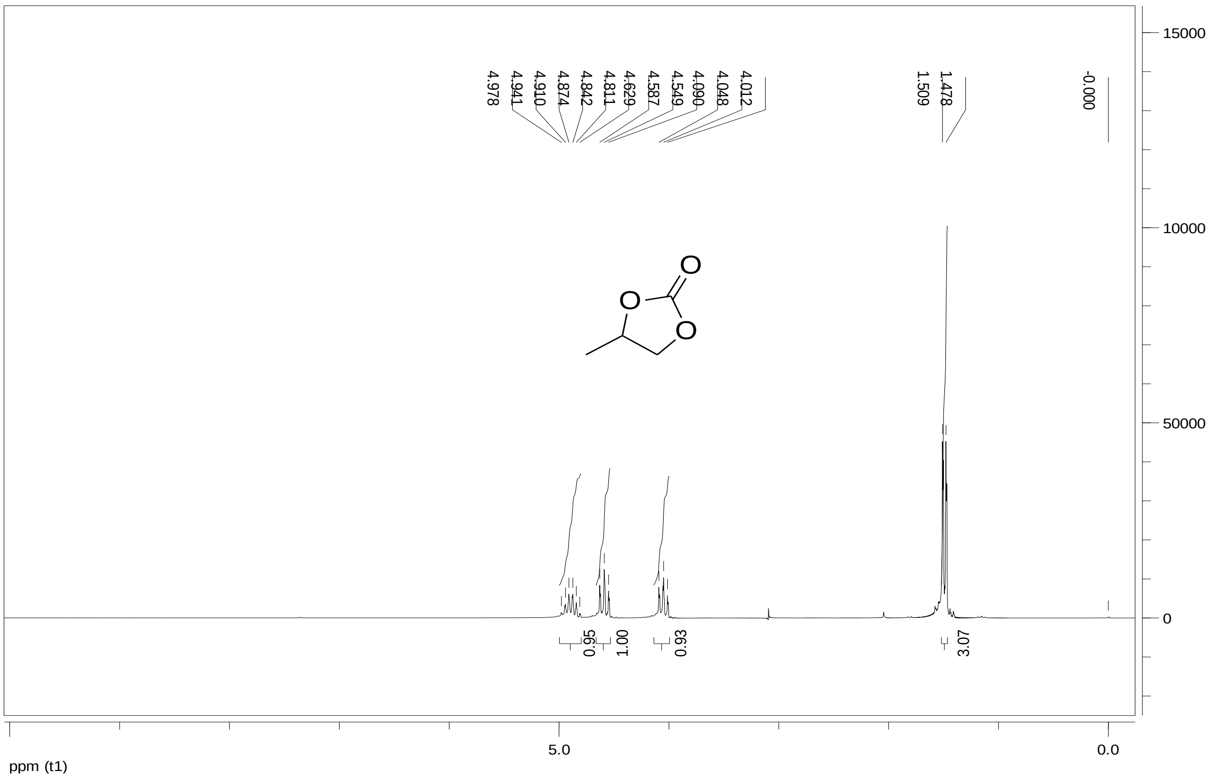
*^{1}H NMR of compound **1'**:*



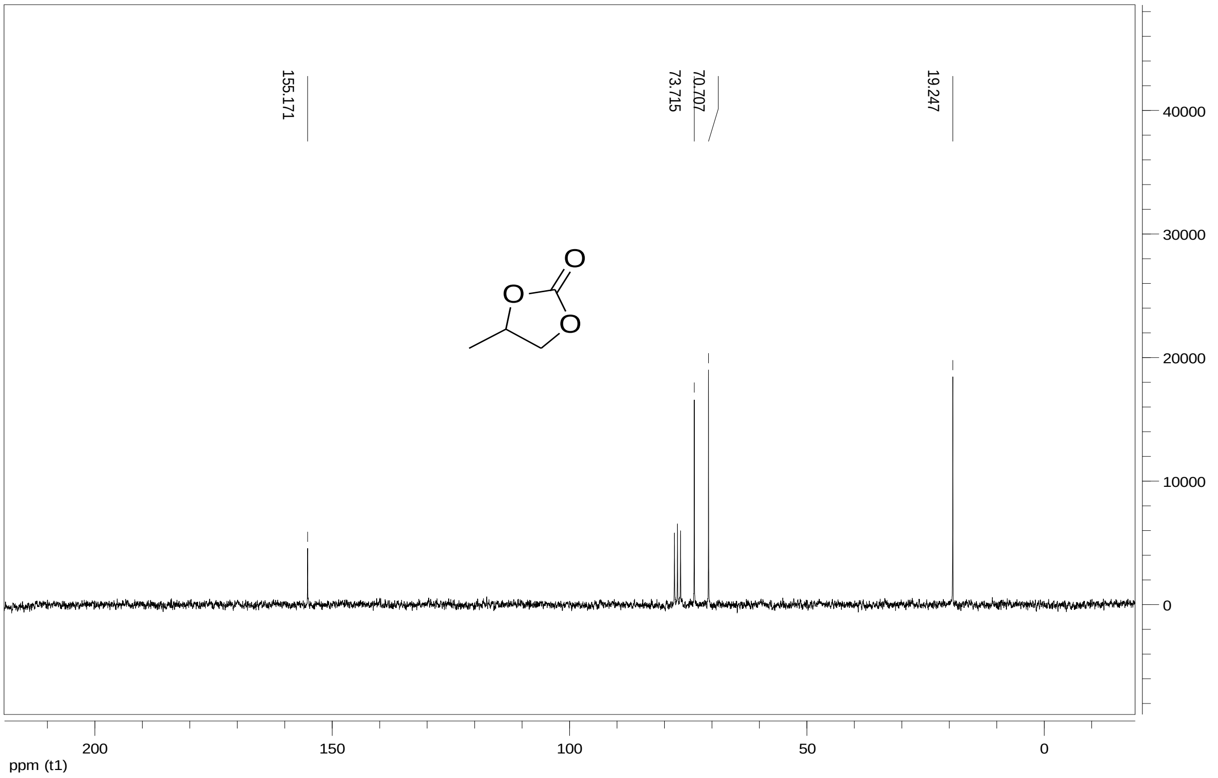
*^{13}C NMR of compound **1'**:*



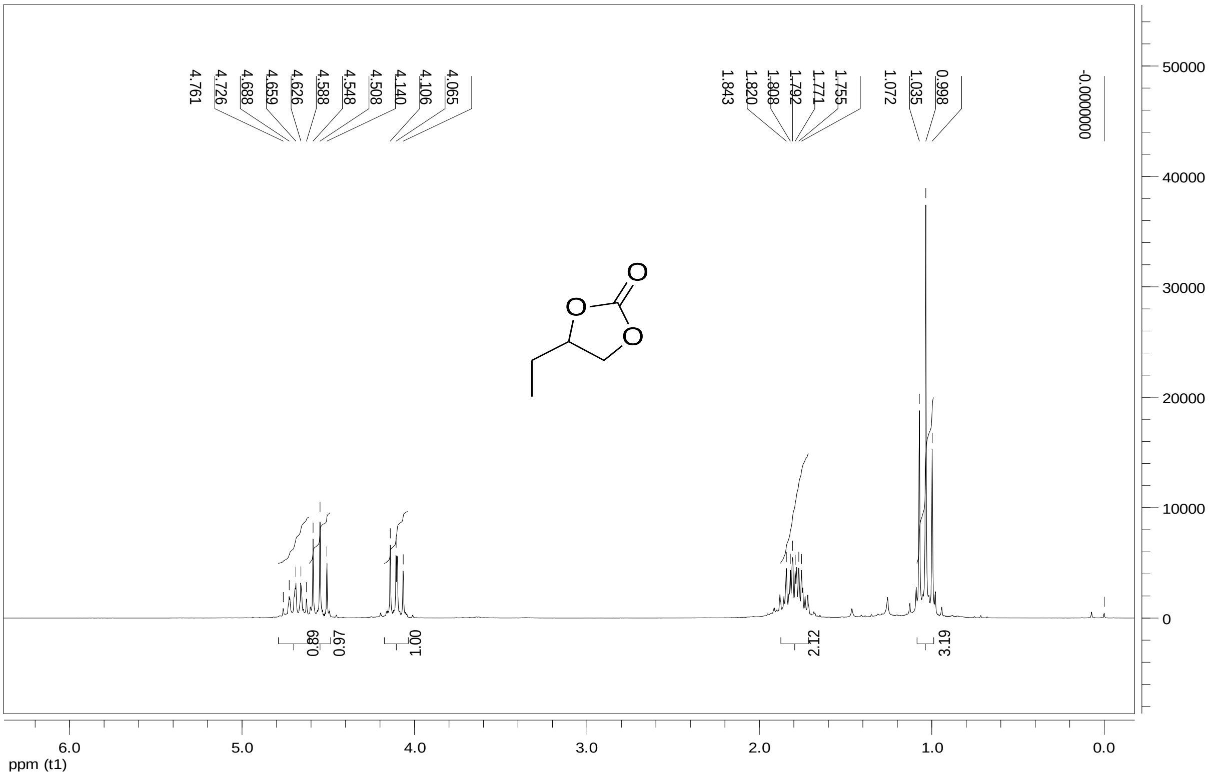
^{1}H NMR of chiral 4-methyl-1,3-dioxolan-2-one:



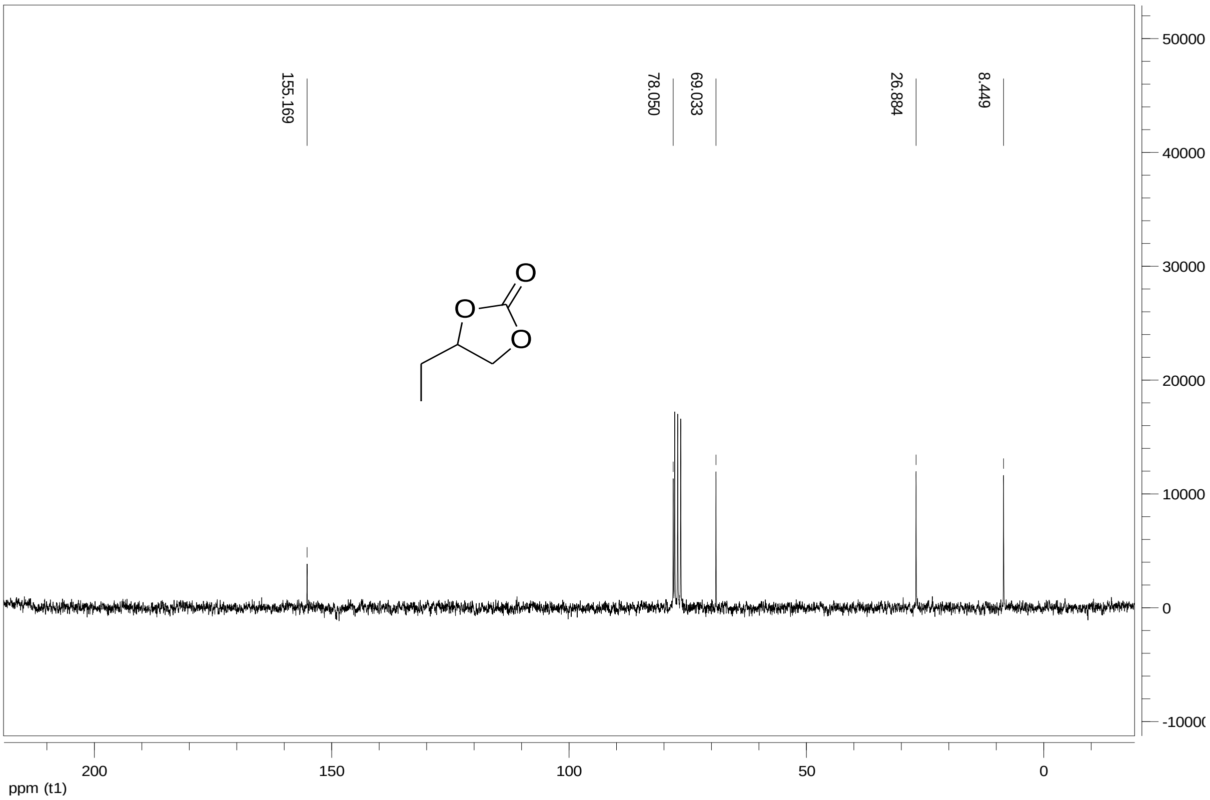
^{13}C NMR of chiral 4-methyl-1,3-dioxolan-2-one:



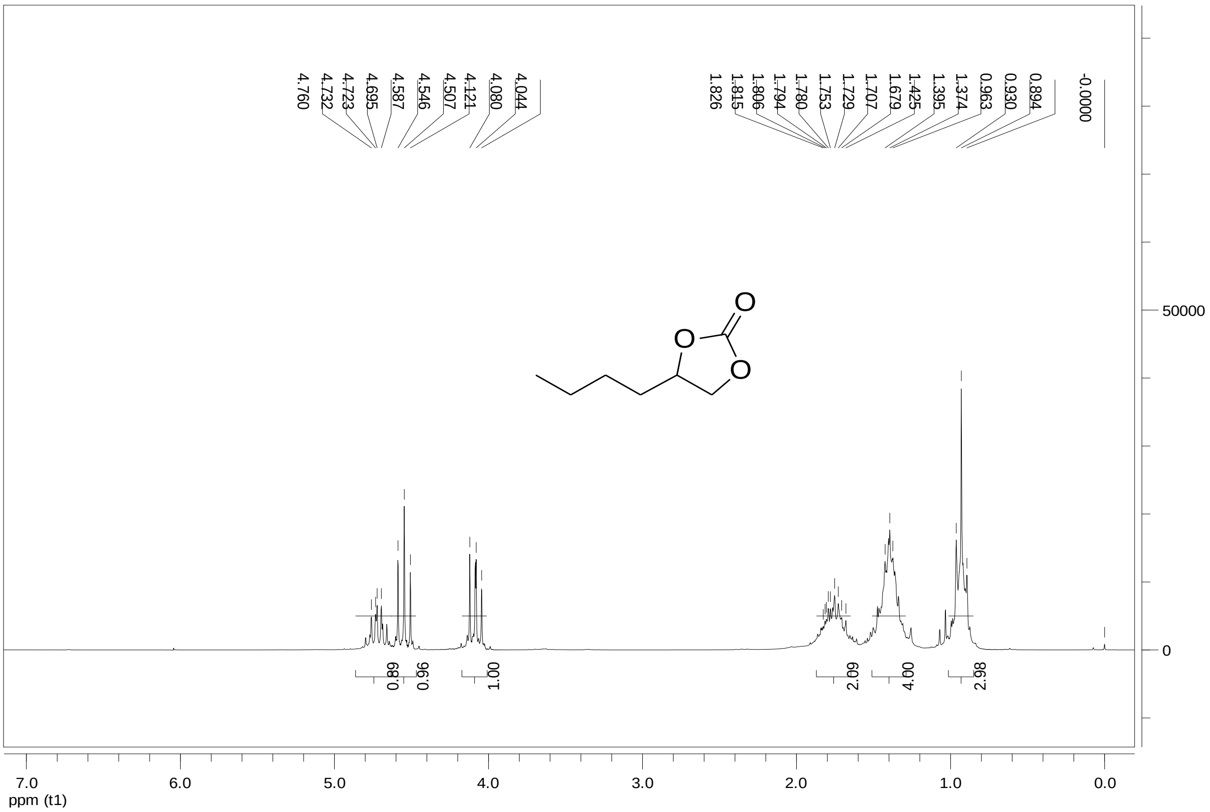
^{1}H NMR of chiral 4-ethyl-1,3-dioxolan-2-one:



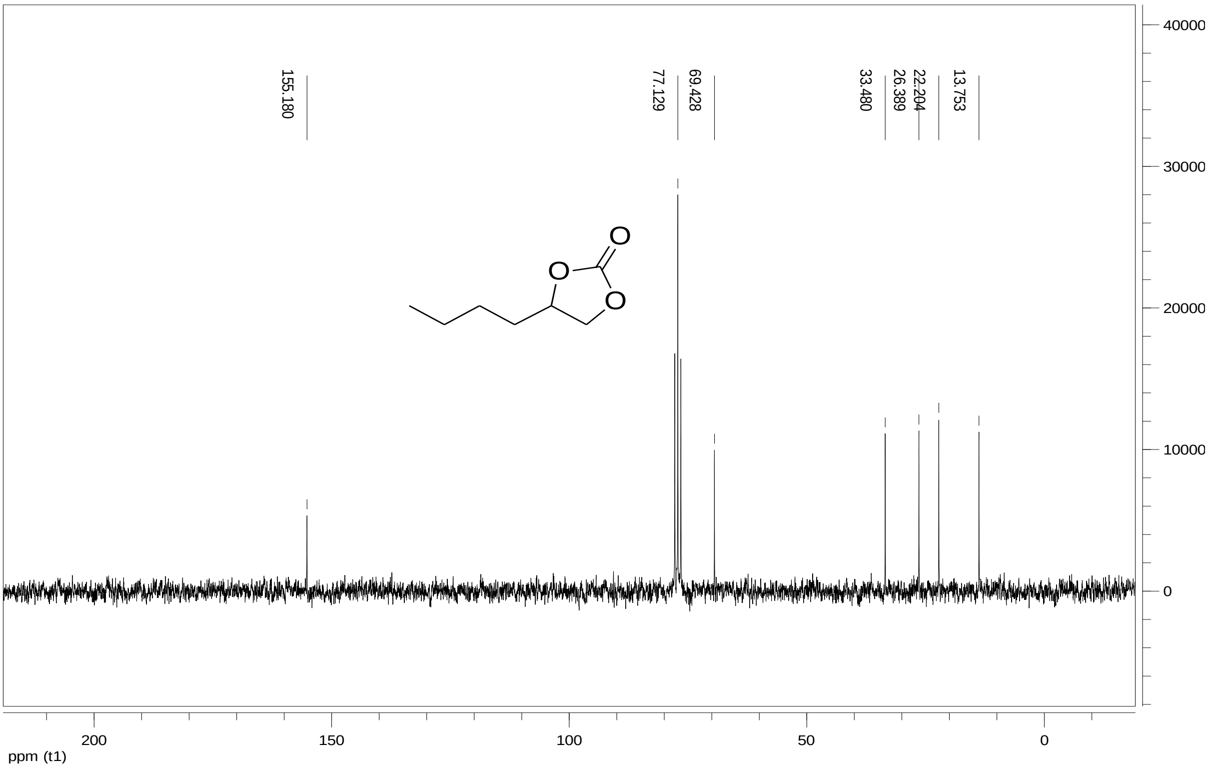
^{13}C NMR of chiral 4-ethyl-1,3-dioxolan-2-one:



^{1}*H NMR of chiral 4-butyl-1,3-dioxolan-2-one:*



^{13}*C NMR of chiral 4-butyl-1,3-dioxolan-2-one:*



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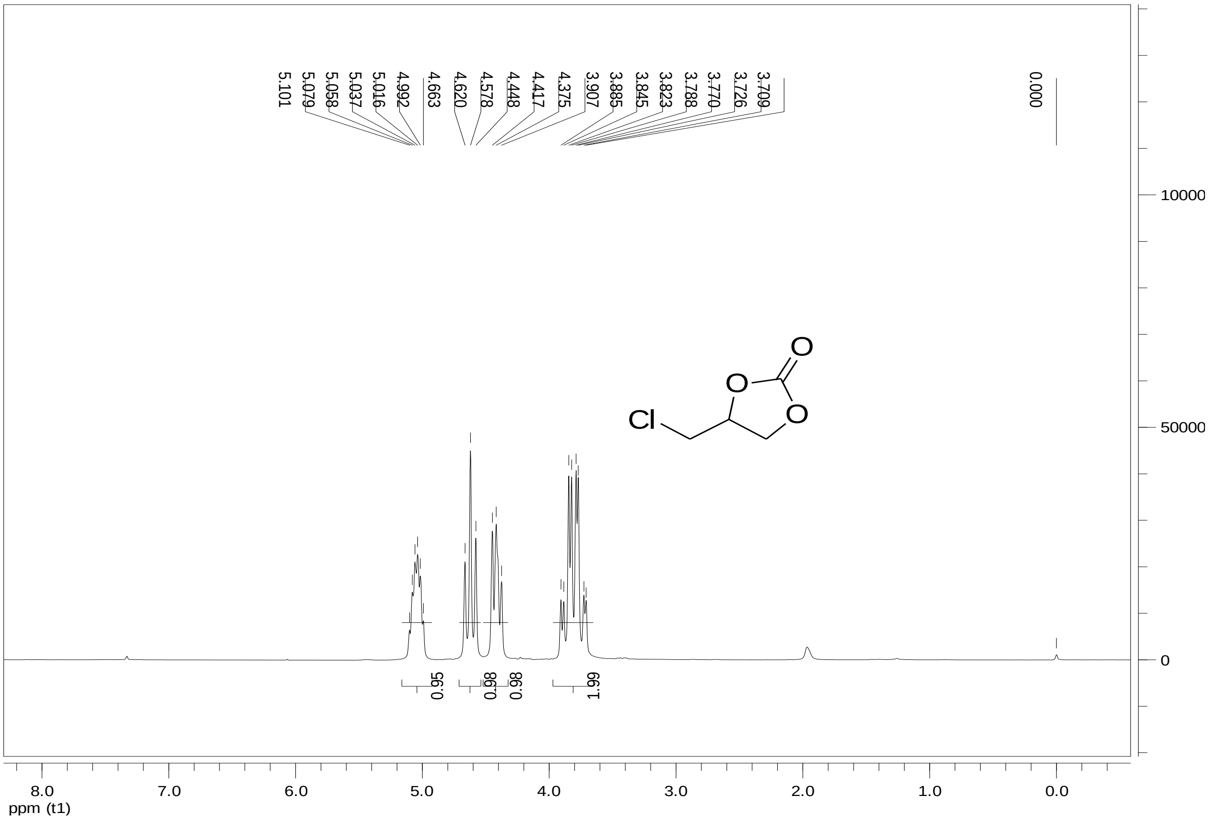
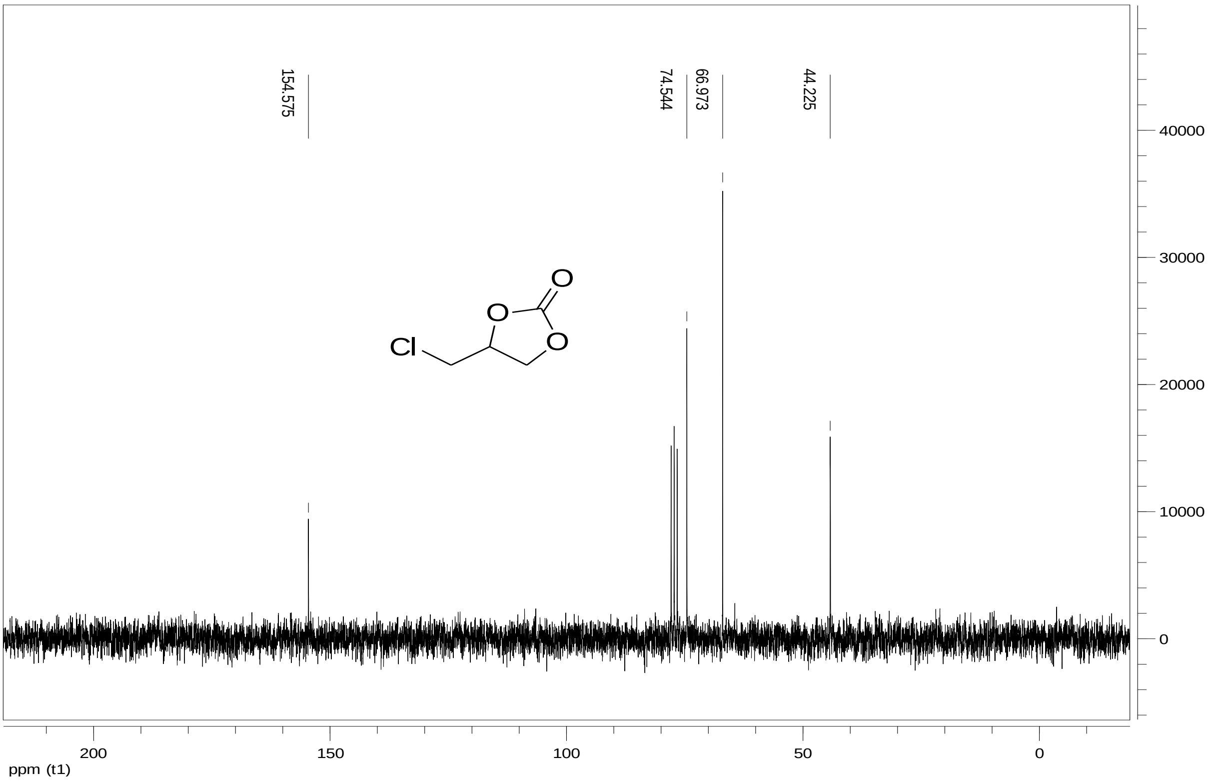


^{13}C NMR of chiral 4-(chloromethyl)-1,3-dioxolan-2-one:



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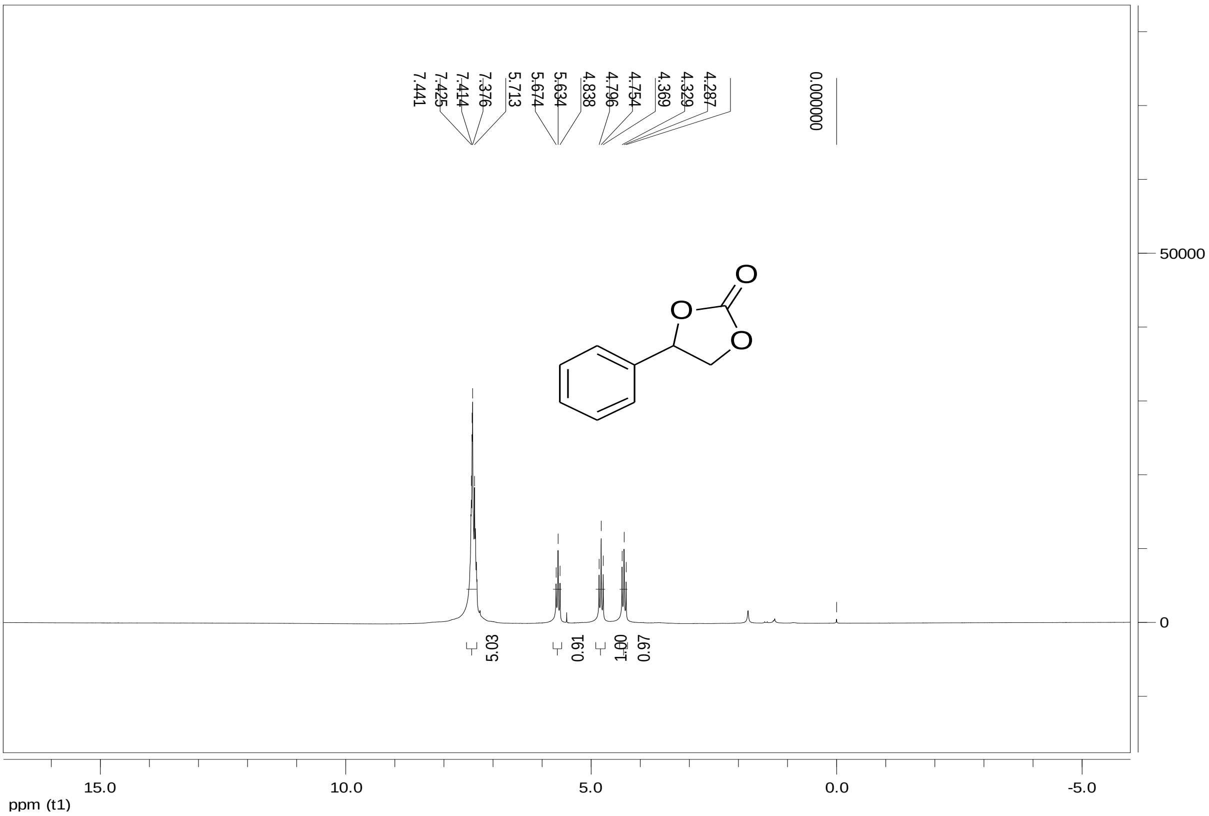

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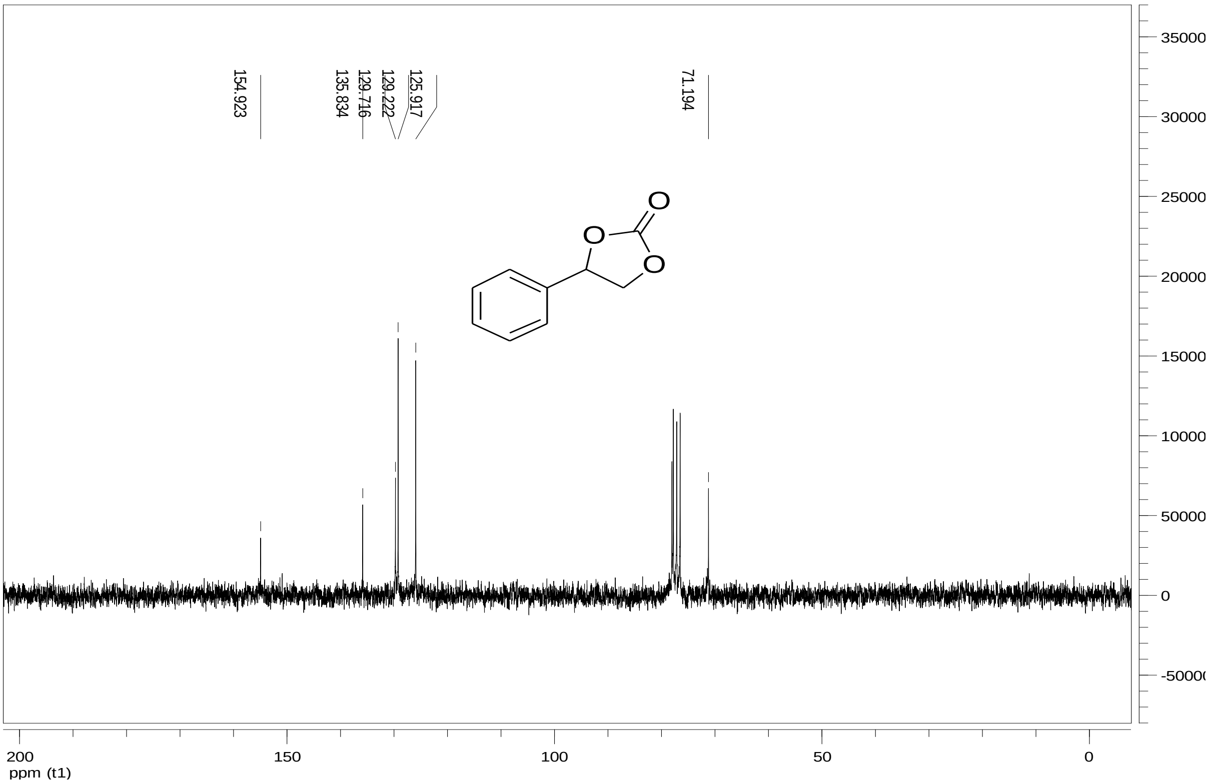

D2O exchange- ^{1}*H NMR of compound* ***1’:***