Supporting information

Superbase/cellulose: An environmentally benign catalyst for chemical fixation of carbon dioxide into cyclic carbonates

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i) Catalyst recycle experiments

Next, a series of catalytic cycles were run to investigate the constancy of the catalyst for the cycloaddition reaction of PO (30 mL each time). In each cycle, the catalyst was recovered via distillation under vacuun, and then used for the next cycle. The results (Fig. S1) showed that the catalyst could be reusable for at least up to four times with high activity, while the selectivity of the product remains the same. The decrease in conversion is associated with the inevitable loss of catalyst during the catalyst recovery operation. As a rough calculation, a near 90% recover yield of catalyst was obtained after the 4th -reuse.

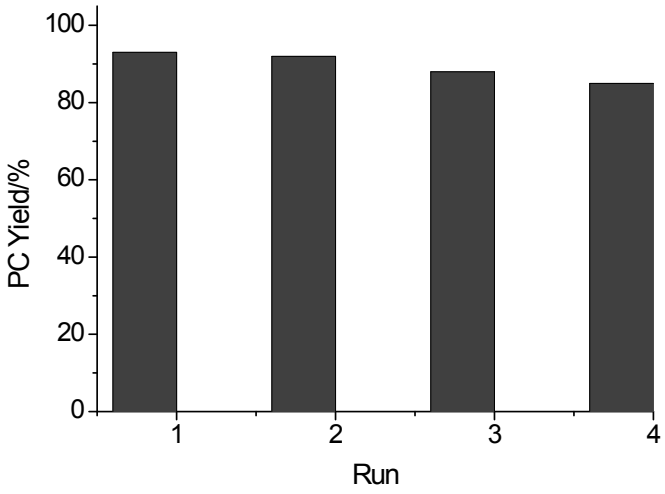


Fig. S1. Catalyst recycling for cycloaddition reaction.

Reaction condition: PO (30 mL, 25 ℃), DBU 6.75 g, cellulose 0.45 g, 120 ℃, 2.0 MPa, 2 h.

ii) Characterization of catalyst before and after use

XRD

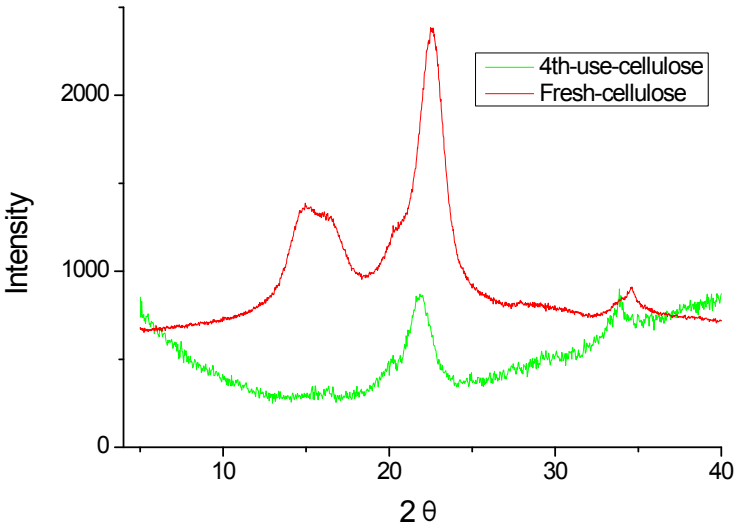


Fig. S2. XRD of fresh and recycled cellulose

TGA

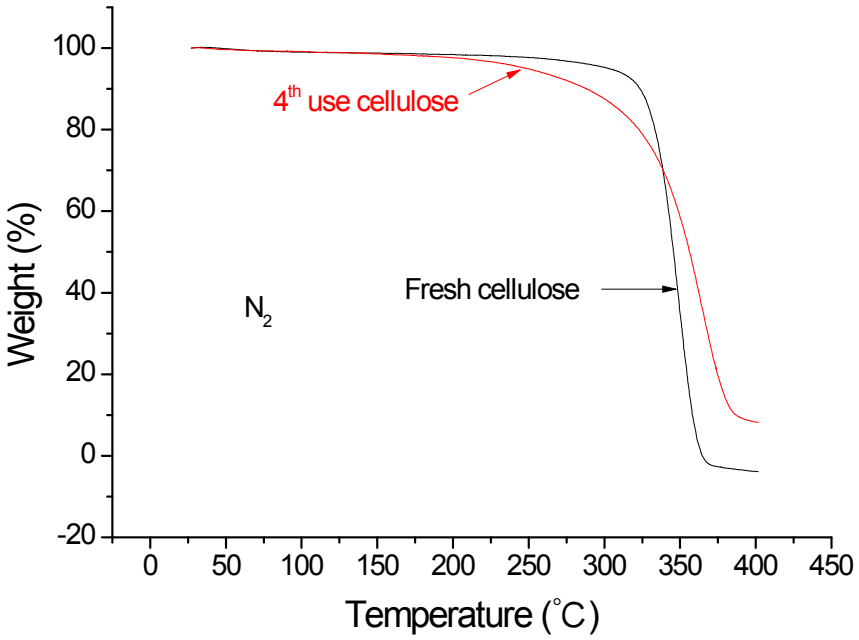


Fig. S3 TGA curves of fresh and recycled cellulose in the atmosphere of N_2.

SEM

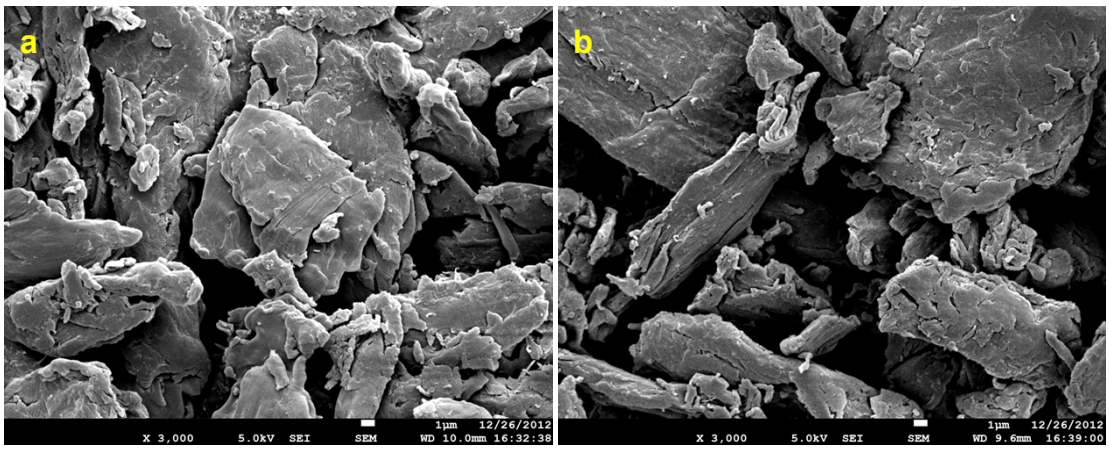


Fig. S4. SEM spectra of fresh cellulose (a) and 4th -reuse cellulose (b)

LC

Qualitative analysis procedure: After the reaction, un-reacted propylene oxide and the remaining CO_2 were evaporated from the obtained liquid samples. Remaining portion was then treated with dilute H_2SO_4 to reach a pH value of 2, and analyzed by liquid chromatography with a Waters e2695 separations module under the following conditions: column, bio-rad 87H, temperature, 65 ℃; flow-rate, 0.4 mL/min; eluent, dilute H_2SO_4 (pH=2); detector, Waters refractive index detector (RID), temperature, 50 ℃. Figure S5 showed the liquid chromatography detection result of product after 12 hours reaction at 120 ℃, 2 MPa.

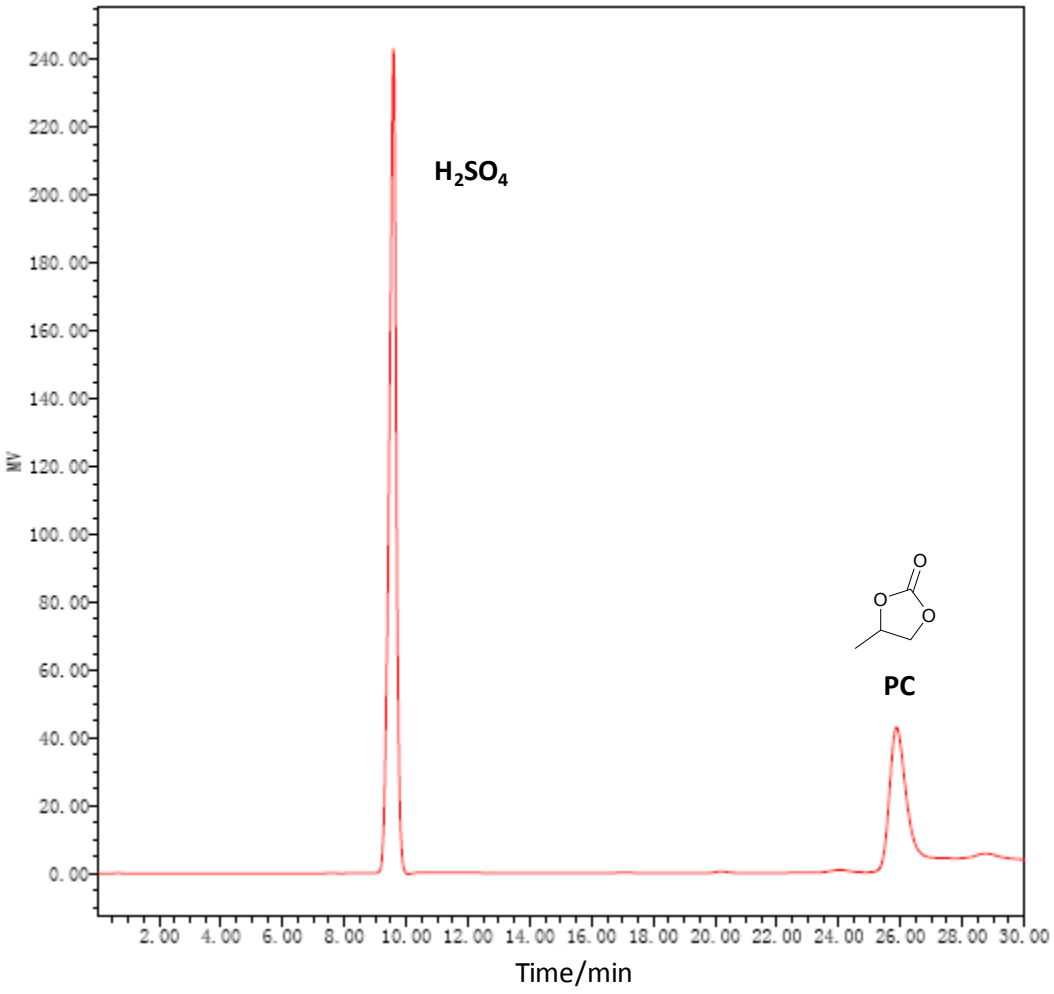


Fig. S5 Liquid chromatography detection result of liquid product after 12 hours reaction.

NMR

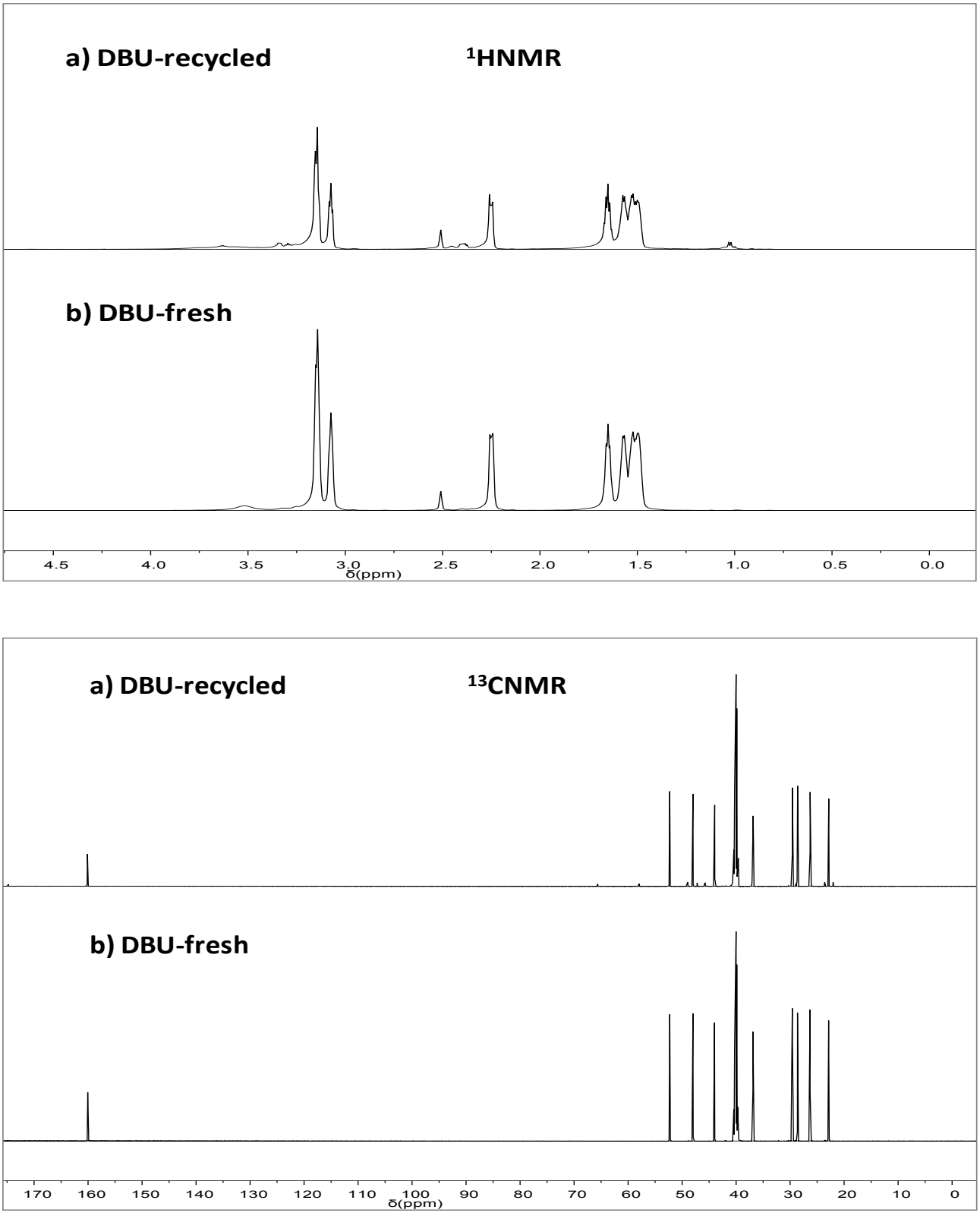


Fig. S6 NMR spectrum of recycled (after 4th -reuse) (a) and fresh (b) DBU.

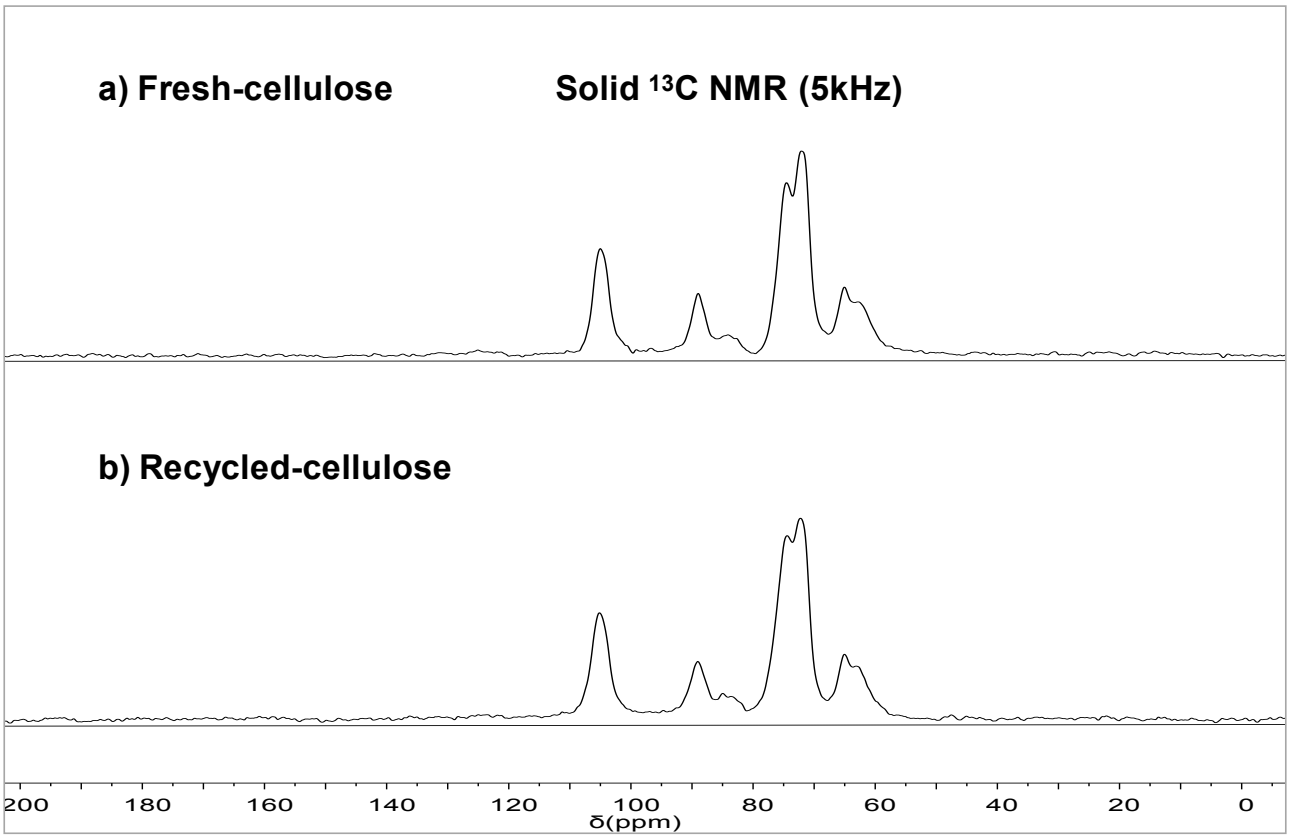
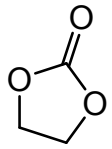


Fig. S7 NMR spectrum of cellulose before (a) and after (b) it had been used four times.

iii) Experimental characterization data for compounds 2a-2h

Spectral characteristics of the products (cyclic carbonates **2a–2h**) in Table 5 were provided as follows:

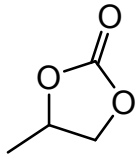
1, 3-dioxolan-2-one (**2a**):



^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 4.53 (t, J=10 Hz, 4H);

^{13}C NMR (100.4 MHz, $CDCl_3$), δ (ppm): 64.55, 156.36 (C=O).

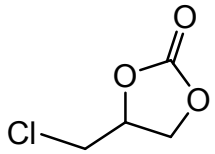
4-methyl-1, 3-dioxolan-2-one (**2b**):



^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm):1.49 (d, J=6.0 Hz, 3H), 4.05 (t, J=8.8 Hz, 1H), 4.60 (t, J=8.0 Hz, 1H), 4.86-4.94 (m, 1H);

^{13}C NMR (100.4 MHz, $CDCl_3$), δ (ppm): 19.15, 70.53, 73.48, 154.95 (C=O).

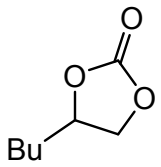
4-chloromethyl-1, 3-dioxolan-2-one (**2c**):



^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 3.72-3.85 (m, 2H), 4.43 (t, J=7.2 Hz, 1H), 4.62 (t, J=8.6 Hz, 1H), 4.99-5.05 (m, 1H);

^{13}C NMR (100.4 MHz, $CDCl_3$), δ (ppm): 43.84, 66.83, 75.49, 154.28 (C=O).

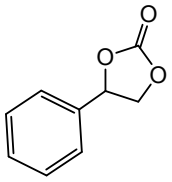
4-butyl-1, 3-dioxolan-2-one (**2d**):



^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 0.84 (t, J= 7.1 Hz, 3H); 1.29-1.41 (m, 2H); 1.62-1.76 (m, 2H); 3.93-4.02 (m, 2H); 4.47 (d, J=8.3Hz, 2H); 4.61-4.68 (m, 1H).

^{13}C NMR (75.5 MHz, $CDCl_3$), δ (ppm): 13.38, 21.85, 26.05, 33.09, 69.12, 76.89, 154.86 (C=O).

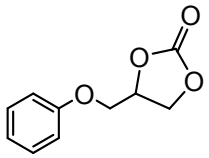
4-phenyl-1, 3-dioxolan-2-one (**2e**):



^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 4.34 (t, J=8.4 Hz, 1H), 4.80 (t, J=8.4 Hz, 1H), 5.68 (t, 1H, J=8.0 Hz), 7.35-7.44 (m, 5H);

^{13}C NMR (100.4 MHz, $CDCl_3$), δ (ppm): 71.13, 77.94, 125.83, 129.20, 129.71, 135.77, 154.78 (C=O).

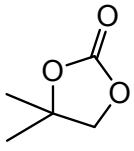
4-phenyloxymethyl-1, 3-dioxolan-2-one (**2f**):



^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 4.15 (dd, J=4.4 Hz, J=10.8 Hz, 1H), 4.24 (dd, J =3.6 Hz, J=10.8 Hz, 1H), 4.55 (dd, J=8.4 Hz, J= 6 Hz, 1H), 4.62 (t, J=8.4 Hz, 1H), 5.03 (m, 1H), 6.91 (d, J=8.0 Hz, 2H), 7.02 (t, J=7.4 Hz, 2H), 7.31 (t, J=8.0 Hz, 2H).

^{13}C NMR (100.4 MHz, $CDCl_3$), δ (ppm): 66.17, 68.84, 74.11, 114.57, 121.92, 129.62, 154.65 (C=O), 157.71 (C-O).

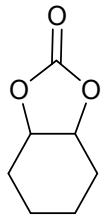
4,4-dimethyl-1,3-dioxolan-2-one (**2g**):



^{1}H NMR (600 MHz, DMSO), δ (ppm): 1.45 (s, 6H), 4.24 (s, 2H);

^{13}C NMR (150.9 MHz, DMSO), δ (ppm): 25.82, 40.27, 75.22, 82.32, 154.55 (C=O).

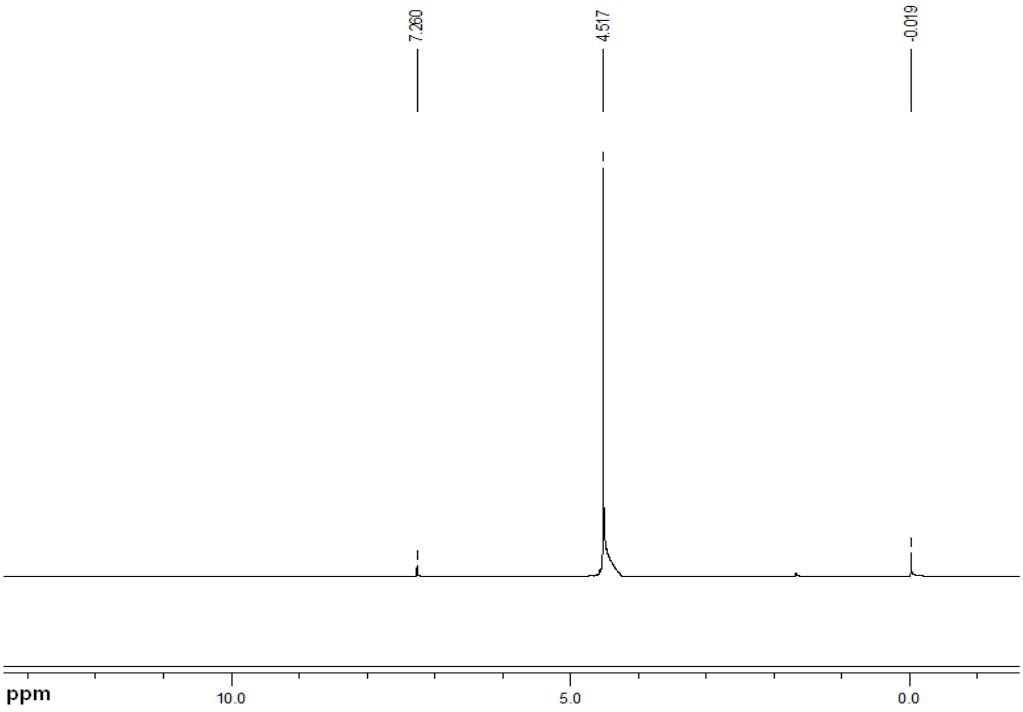
4, 5-tetramethylene-1, 3-dioxolan-2-one (2h):



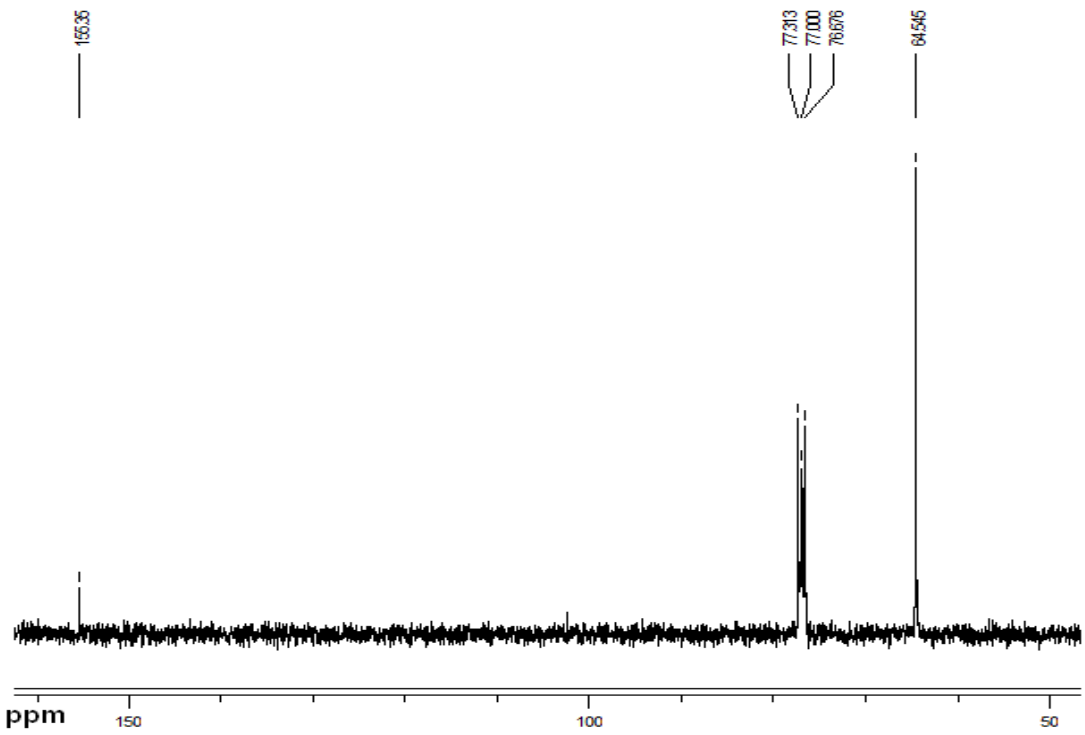
^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 1.40-1.51 (m, 2H); 1.54-1.73 (m, 2H); 1.89-1.92 (m, 4H); 4.68-4.71 (m, 2H); ^{13}C NMR (150.9 MHz, $CDCl_3$), δ (ppm): 19.11, 26.78, 75.75, 155.36 (C=O).

^{1}H NMR and ^{13}C NMR copies of product 2a-2h

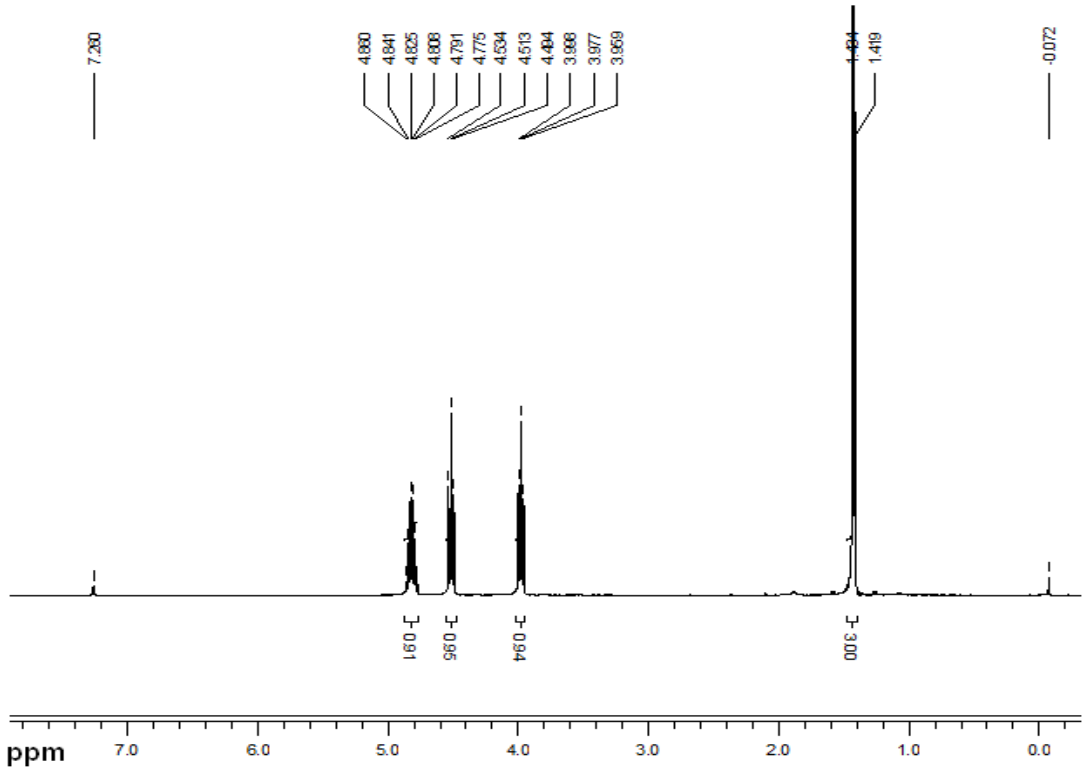
2a ^{1}H NMR



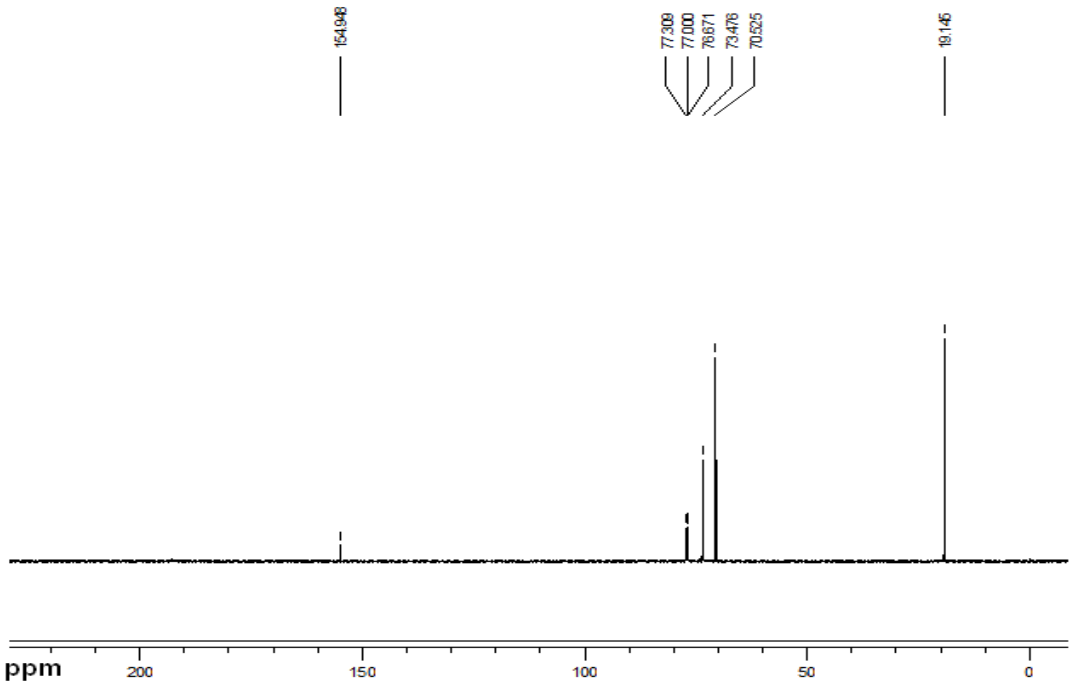
2a ^{13}C NMR



2b ^{1}H NMR



2b ^{13}C NMR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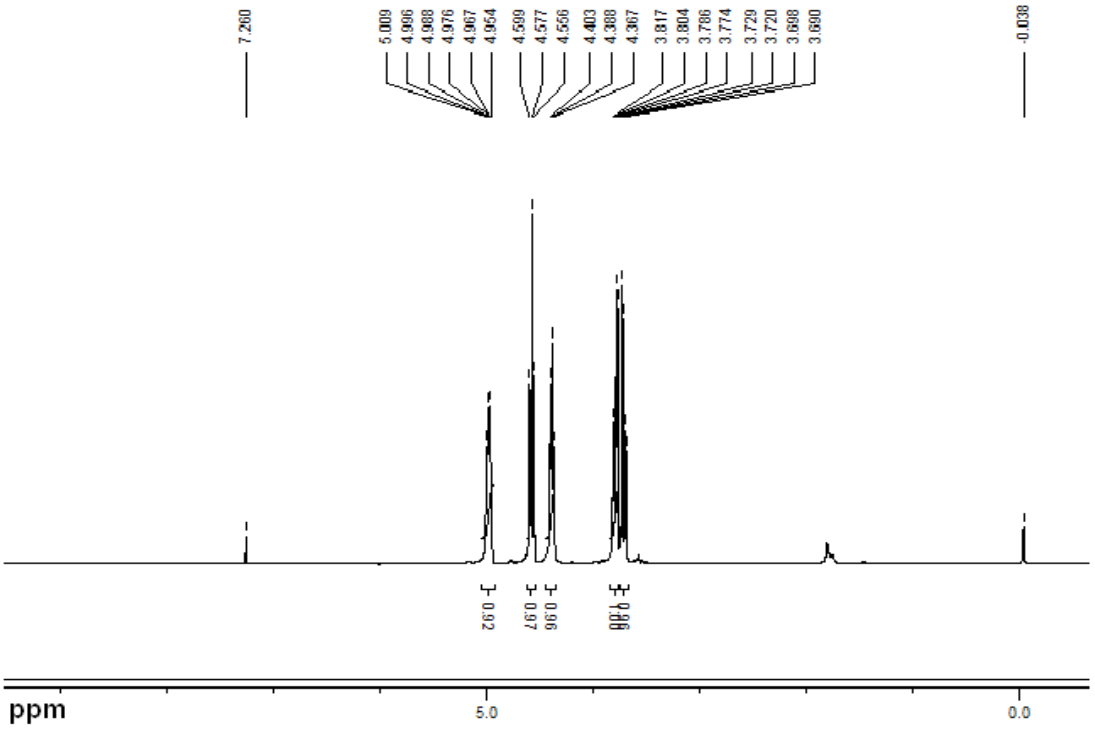
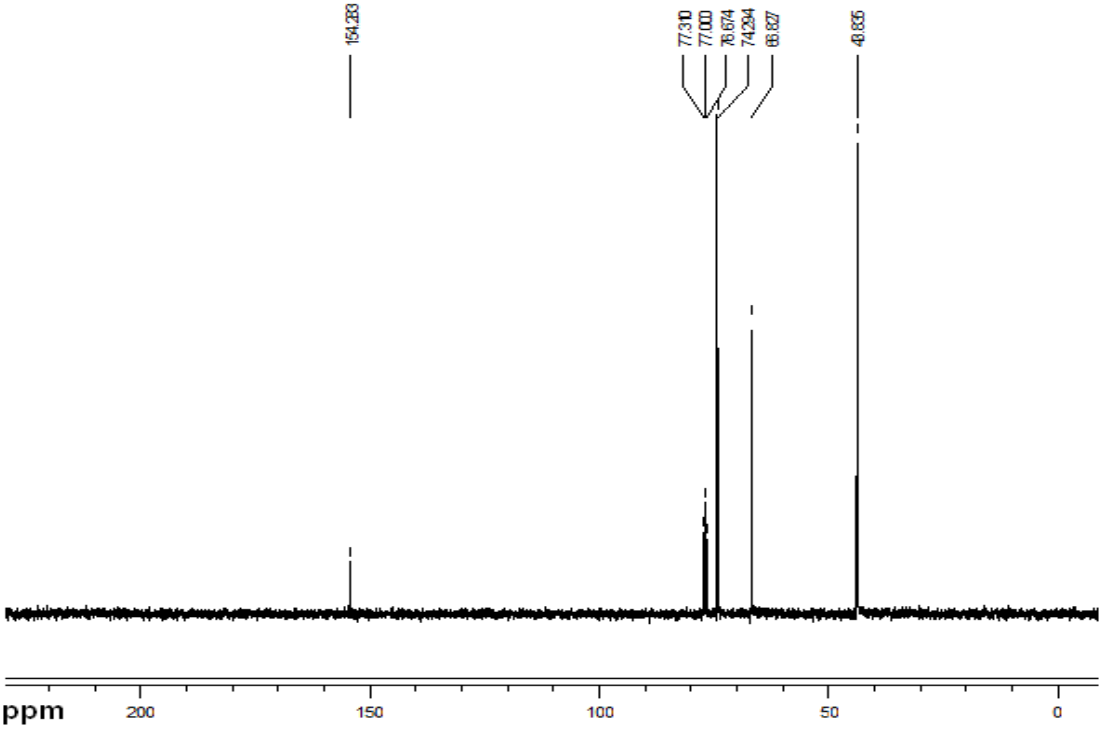
77.309
77.000
76.671
73.476
70.525
19.145
ppm
200
150
100
50
0

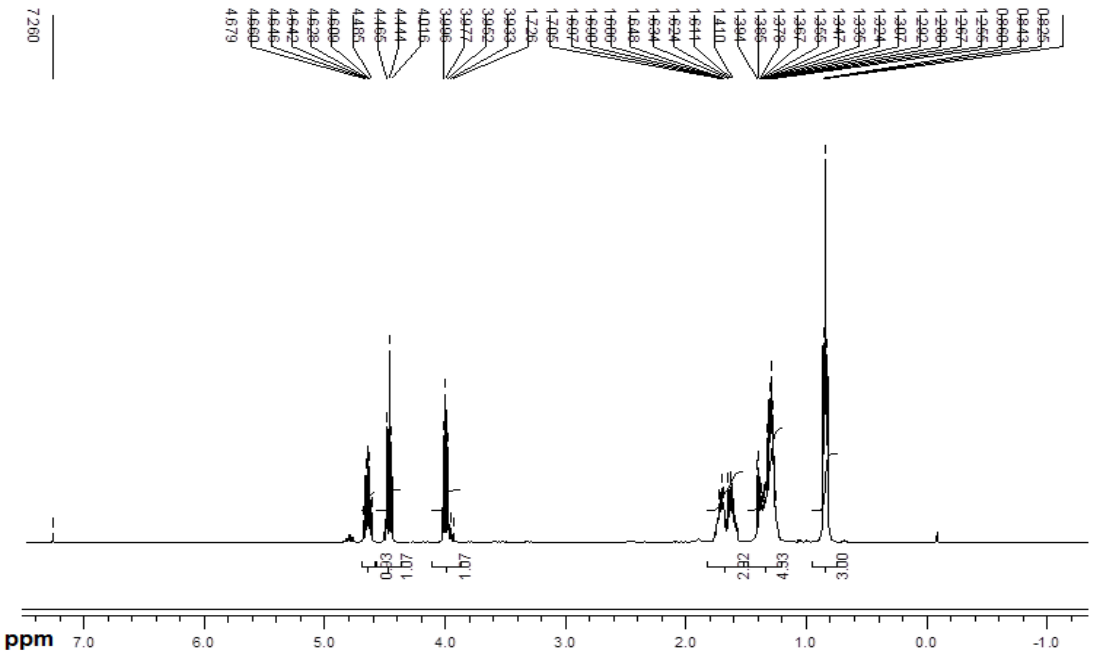
2c ^{1}H NMR



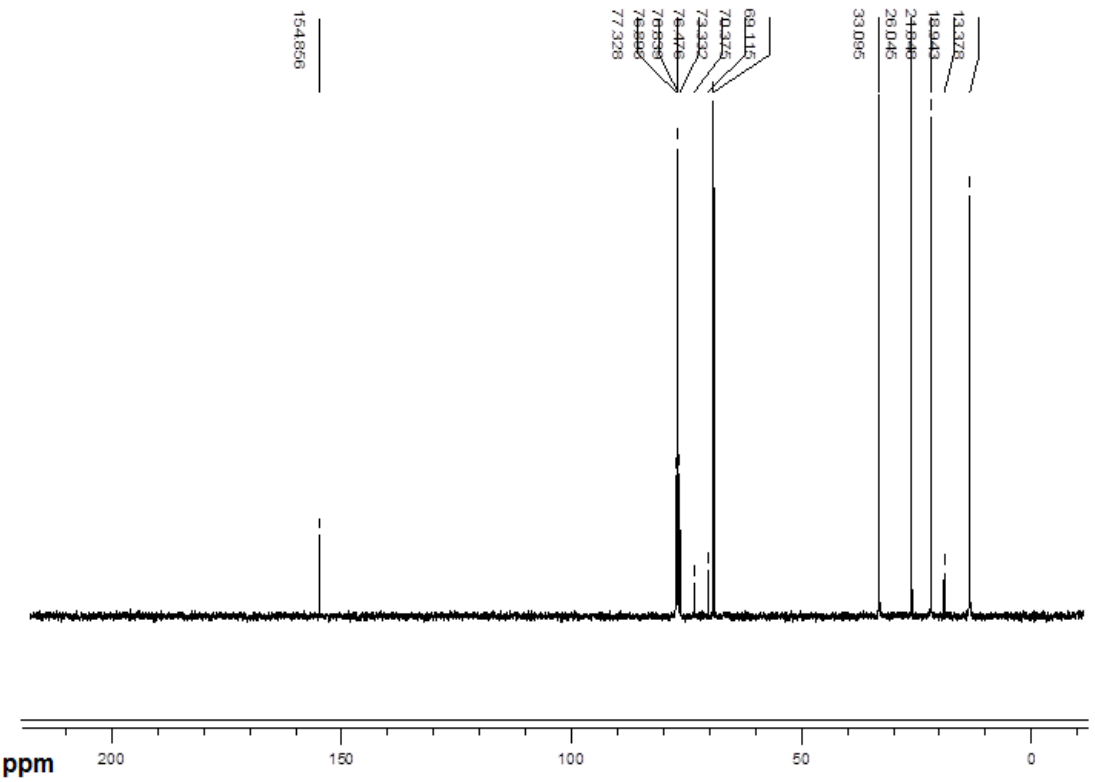
2c ^{13}C NMR



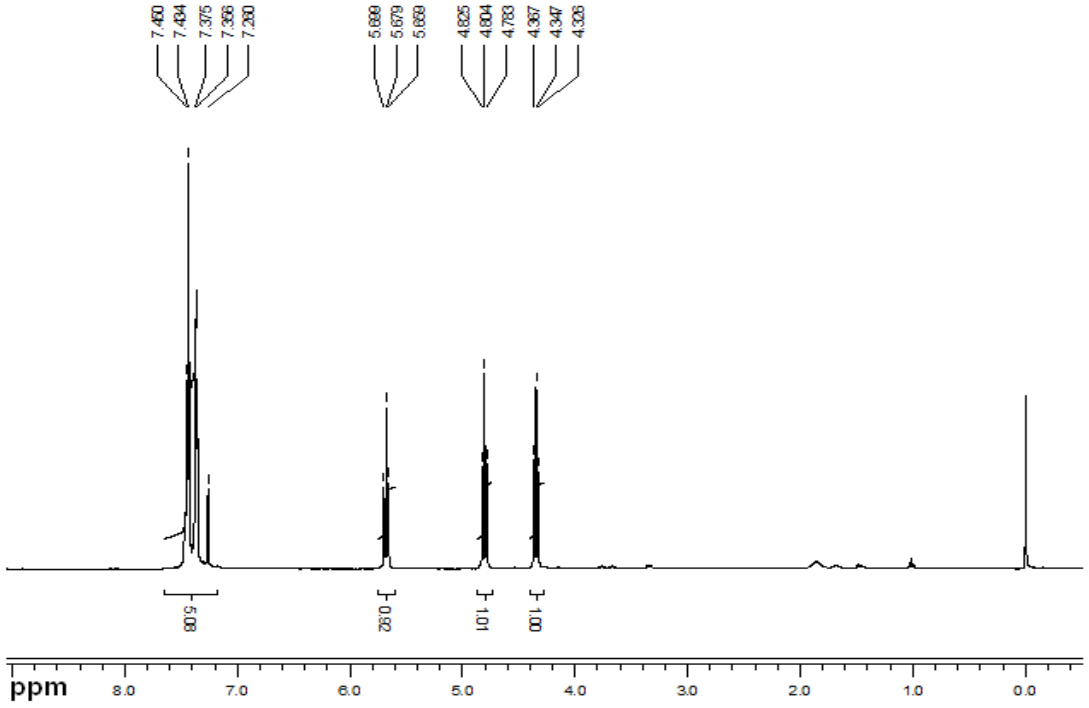
2d ^{1}H NMR



2d ^{13}C NMR



2e ^{1}H NMR



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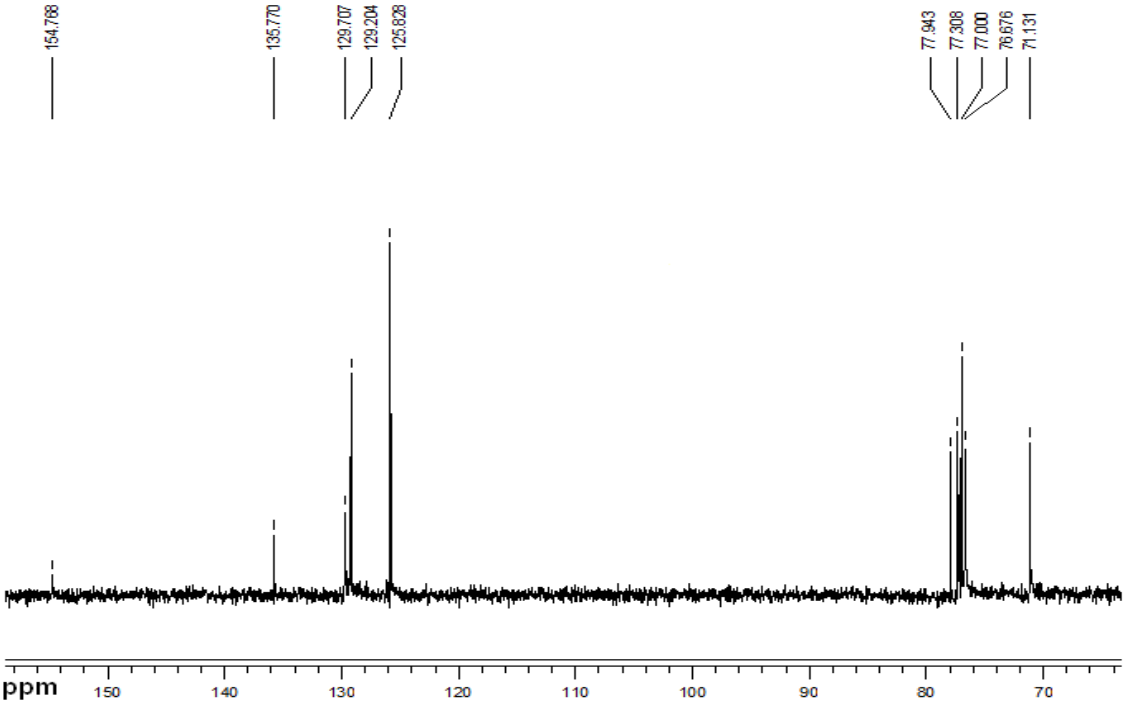
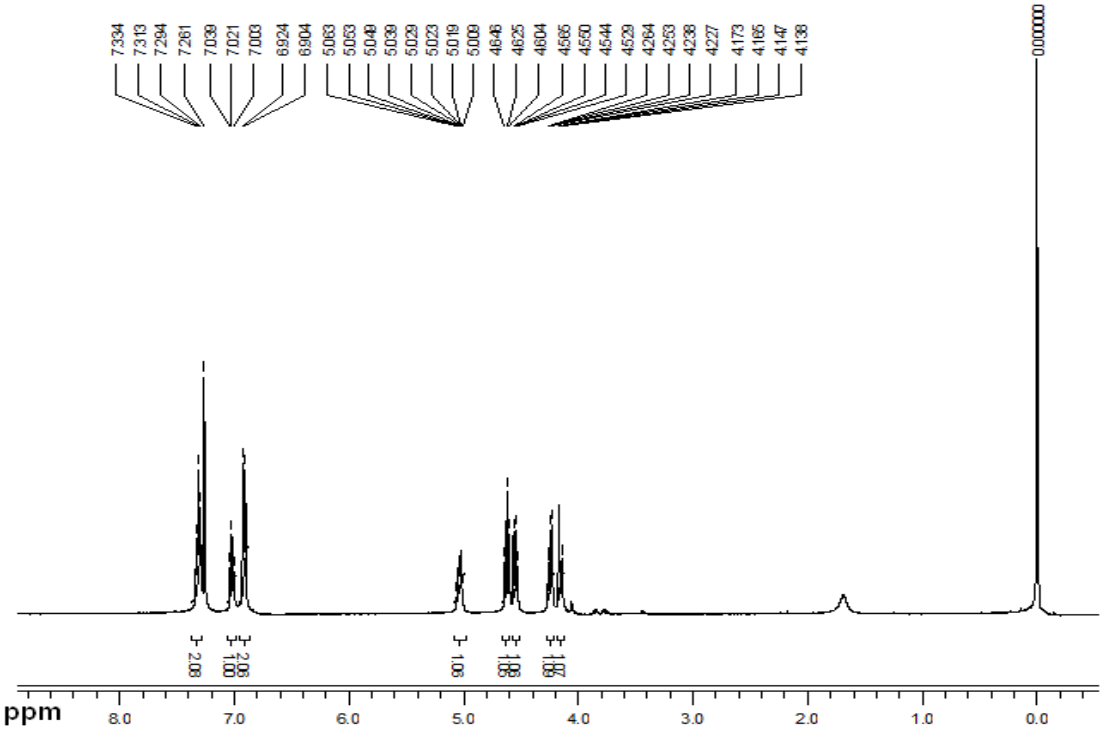


2f ^{1}H NMR



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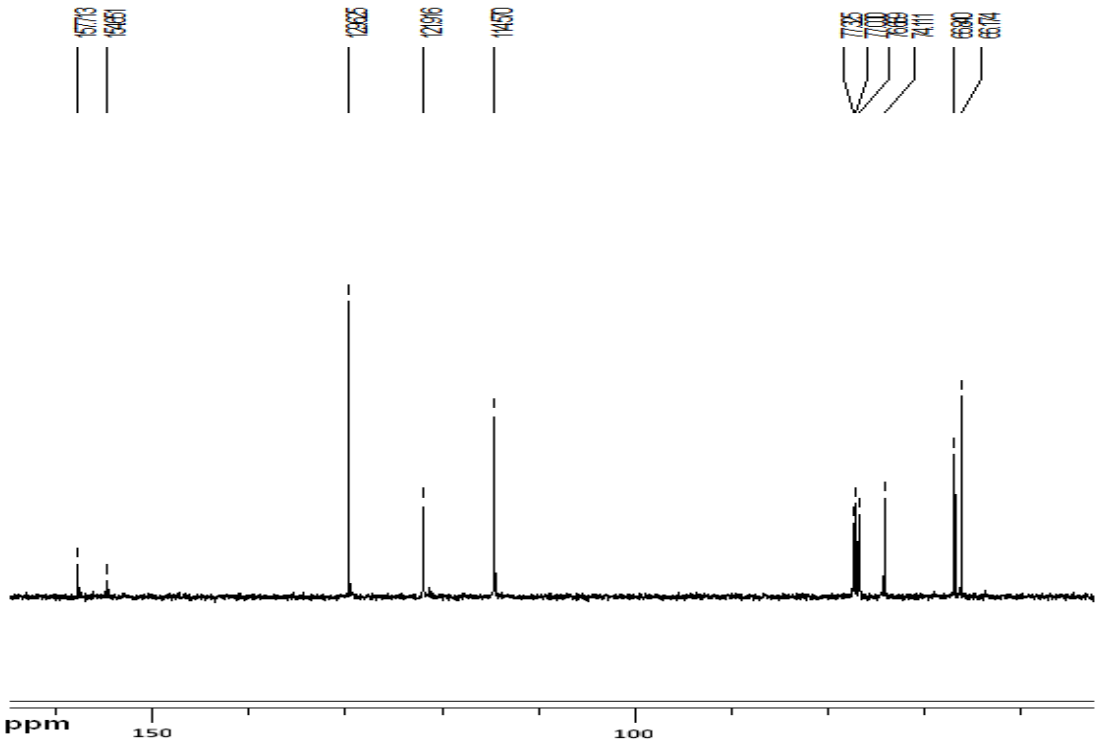
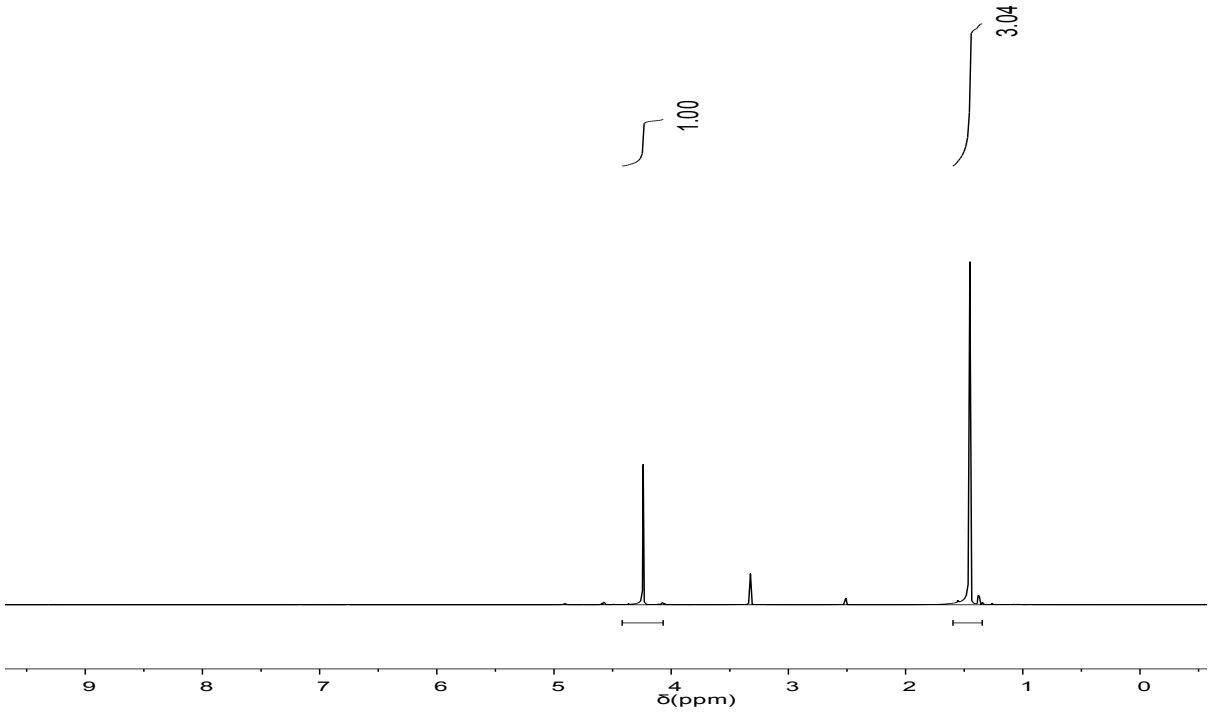
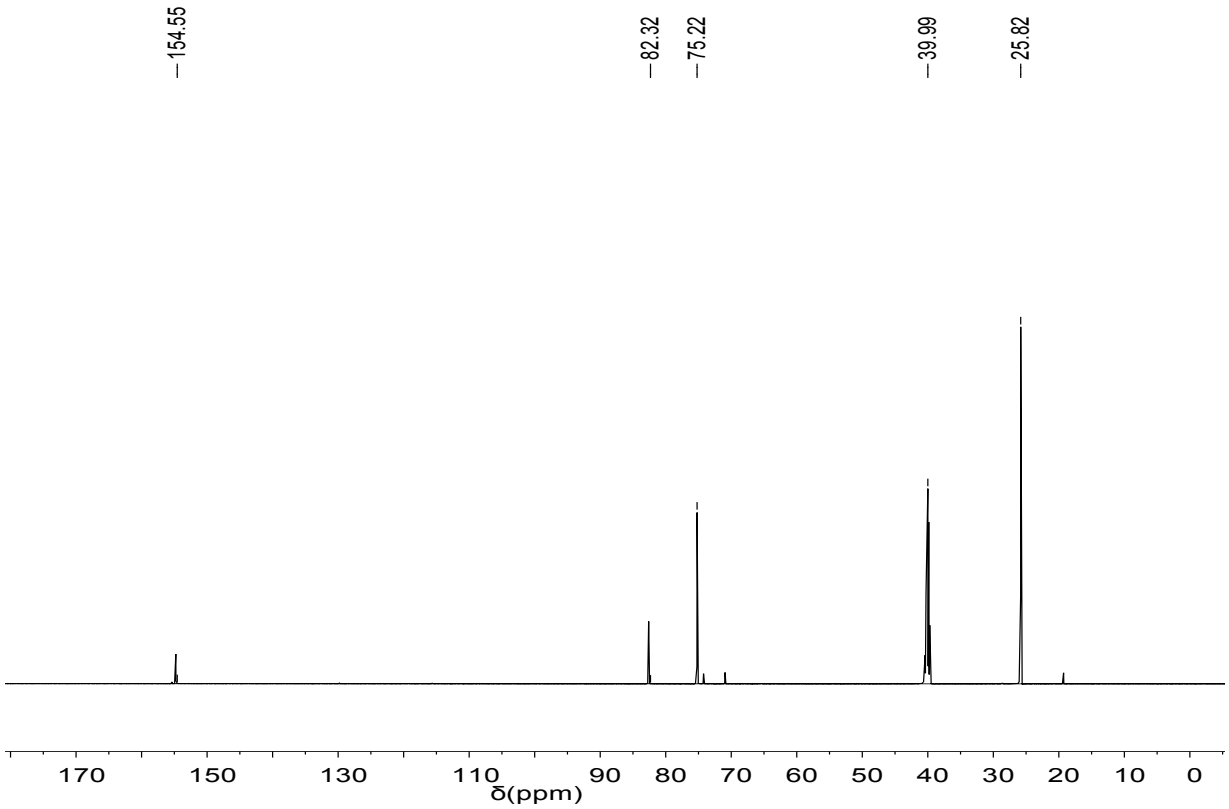


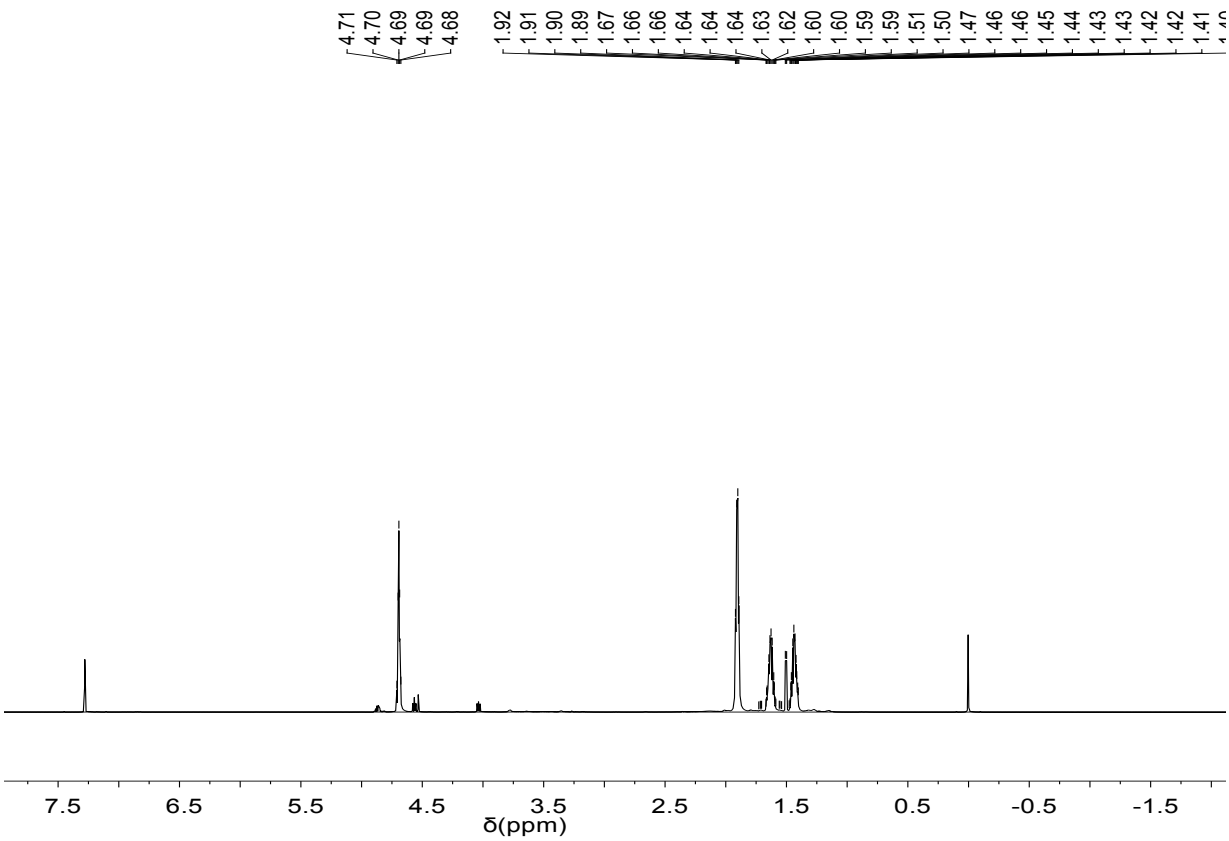
2g ^{1}H NMR



2g ^{13}C NMR



2h ^{1}H NMR



2h ^{13}C NMR