Electronic Supplementary Information

One-pot Synthesis of Bio-based Polycarbonates from Dimethyl Carbonate and Isosorbide under Metal-free Condition

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PIC: ^{1}H NMR (600 MHz, $CDCl_3$): 3.86–4.07 (m, 4H, H1, H6, isosorbide), 4.51–4.55 (m, 1H, H4, isosorbide), 4.88 (t, 1H, H3, isosorbide), 5.06–5.11 (m, 2H, H2, H5, isosorbide). ^{13}C NMR (600 MHz, $CDCl_3$): 70.5 (C6, isosorbide), 73.0 (C1, isosorbide), 77.0 (C2, isosorbide), 80.8 (C5, isosorbide), 81.4 (C4, isosorbide), 85.6 (C3, isosorbide), 153.8, 153.5, 153.1 (C=O).

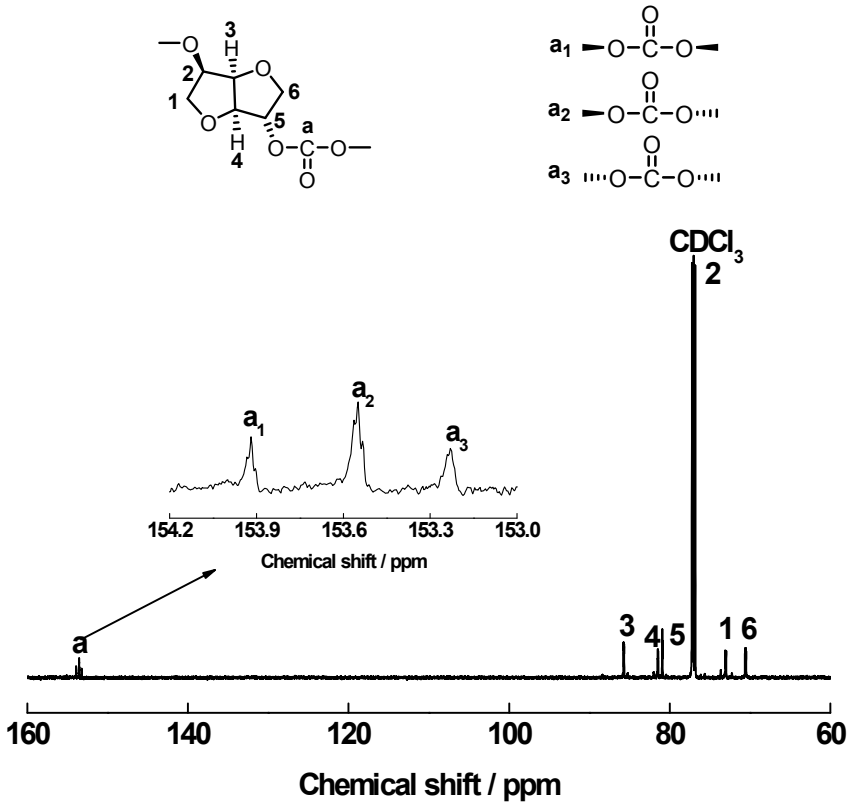

Fig. S1. Typical ^{13}C NMR spectrum of PIC catalyzed by TBD.

PDGIC: ^{1}H NMR (600 MHz, $CDCl_3$): 3.71 (d, 4H, -CH_2-C<u>H</u>$_2$-O-C<u>H</u>$_2$-CH_2-), 3.90–4.07 (m, 4H, H1, H6, isosorbide), 4.28-4.34 (m, 4H, -C<u>H</u>$_2$-CH_2-O-CH_2-C<u>H</u>$_2$-), 4.51–4.56 (m, 1H, H4, isosorbide), 4.88 (t, 1H, H3, isosorbide), 5.06–5.11 (m, 2H, H2, H5, isosorbide). ^{13}C NMR (600 MHz, $CDCl_3$): 67.1, 66.7 (-CH_2-<u>C</u>H$_2$-O-<u>C</u>H$_2$-CH_2-), 68.6 (-<u>C</u>H$_2$-CH_2-O-CH_2-<u>C</u>H$_2$-), 70.3 (C6, isosorbide), 73.0, 72.7 (C1, isosorbide), 76.9, 76.4 (C2, isosorbide), 80.9, 80.6 (C5, isosorbide), 81.2 (C4, isosorbide), 85.6, 85.4 (C3, isosorbide), 155.5-153.0 (<u>C</u>=O).

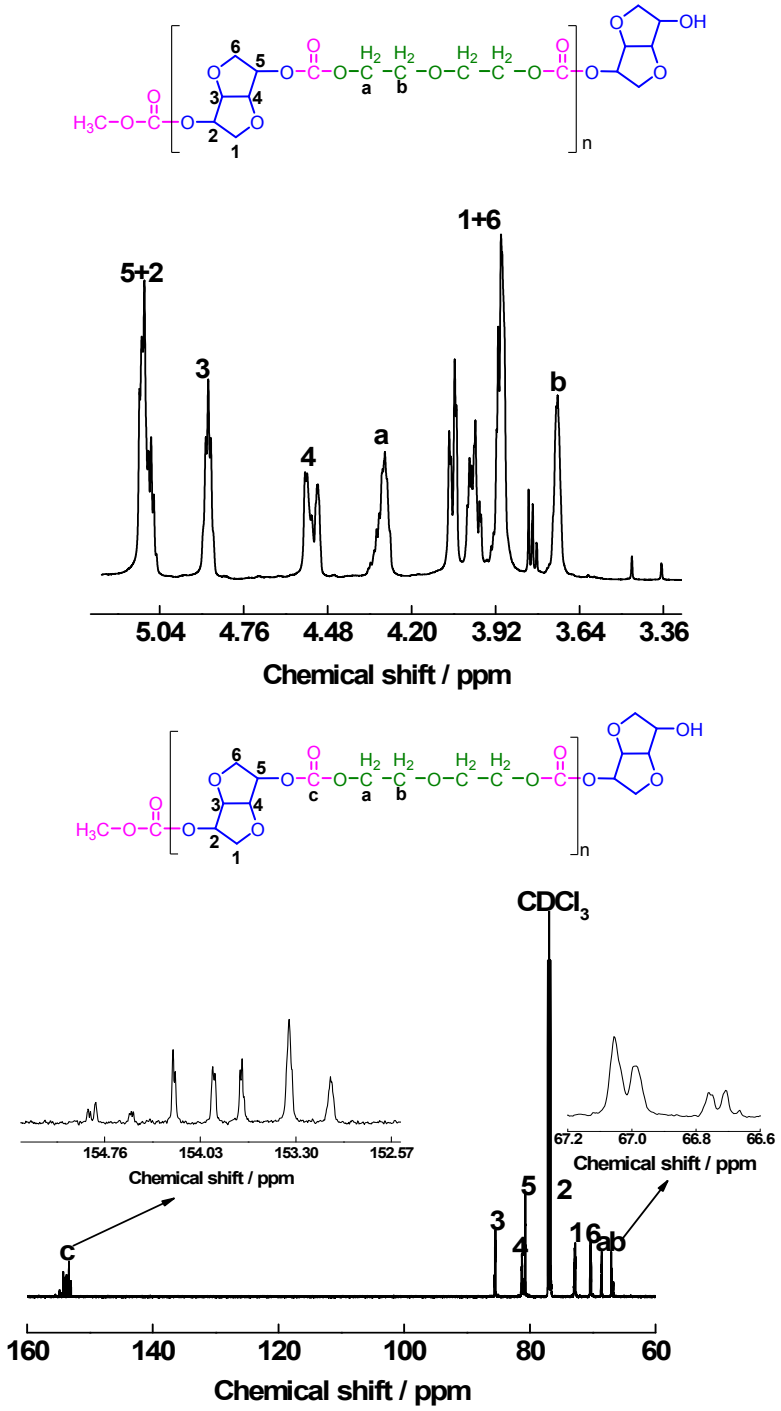

Fig. S2. ^{1}H NMR and ^{13}C NMR spectra of PDGIC.

PTGIC: ^{1}H NMR (600 MHz, $CDCl_3$): 3.64 (s, 4H, -CH_2-CH_2-O-C<u>H</u>$_2$-C<u>H</u>$_2$-O-C

H_2-CH_2-), 3.71 (d, 4H, -CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-), 3.89–4.07 (m, 4H, H1, H6, isosorbide), 4.27-4.33 (m, 4H, -CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-), 4.5 1–4.56 (m, 1H, H4, isosorbide), 4.88 (t, 1H, H3, isosorbide), 5.06–5.11 (m, 2H,H 2, H5, isosorbide). ^{13}C NMR (600 MHz, $CDCl_3$): 67.1, 66.8 (-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-), 68.6 (-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-), 70.3 (C6, isosorbi de), 73.0, 72.7 (C1, isosorbide), 76.9, 76.4 (C2, isosorbide), 80.9, 80.6 (C5 iso sorbide), 81.2 (C4, isosorbide), 85.6, 85.4 (C3, isosorbide), 155.5-153.0 (C=O).

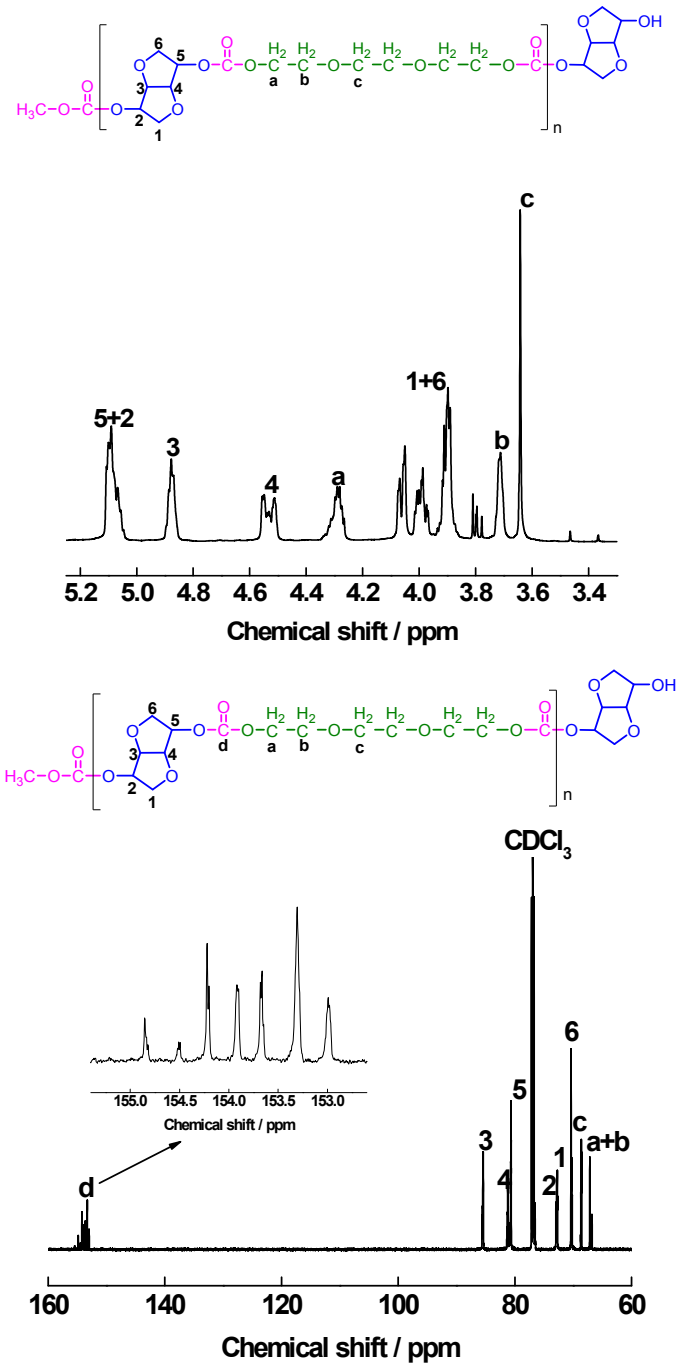

Fig. S3. ^{1}H NMR and ^{13}C NMR spectra of PTGIC.

PCMIC: ^{1}H NMR (600 MHz, CDCl3): 1.00–1.92 (m, 10H, C-ring, cyclohexane

group), 3.89–4.12 (m, 8H, -C$\underline{H}_2$-ring, H1, H6, isosorbide), 4.52–4.56 (m, 1H, H4, isosorbide), 4.88 (t, 1H, H3, isosorbide), 5.06–5.11 (m, 2H, H2, H5, isosorbide). ^{13}C NMR (600 MHz, $CDCl_3$): 28.3, 24.8 (C2, C3, C5, C6, C-ring, cyclohexane group), 36.8, 34.2 (C1, C4, C-ring, cyclohexane group), 70.3 (C6, isosorbide), 70.9 (-$\underline{C}H_2$-C-ring), 73.0, 72.7 (C1, isosorbide), 76.9, 76.4 (C2, isosorbide), 80.9, 80.6 (C5, isosorbide), 81.2 (C4, isosorbide), 85.6, 85.4 (C3, isosorbide), 155.7-153.0 ($\underline{C}$=O).

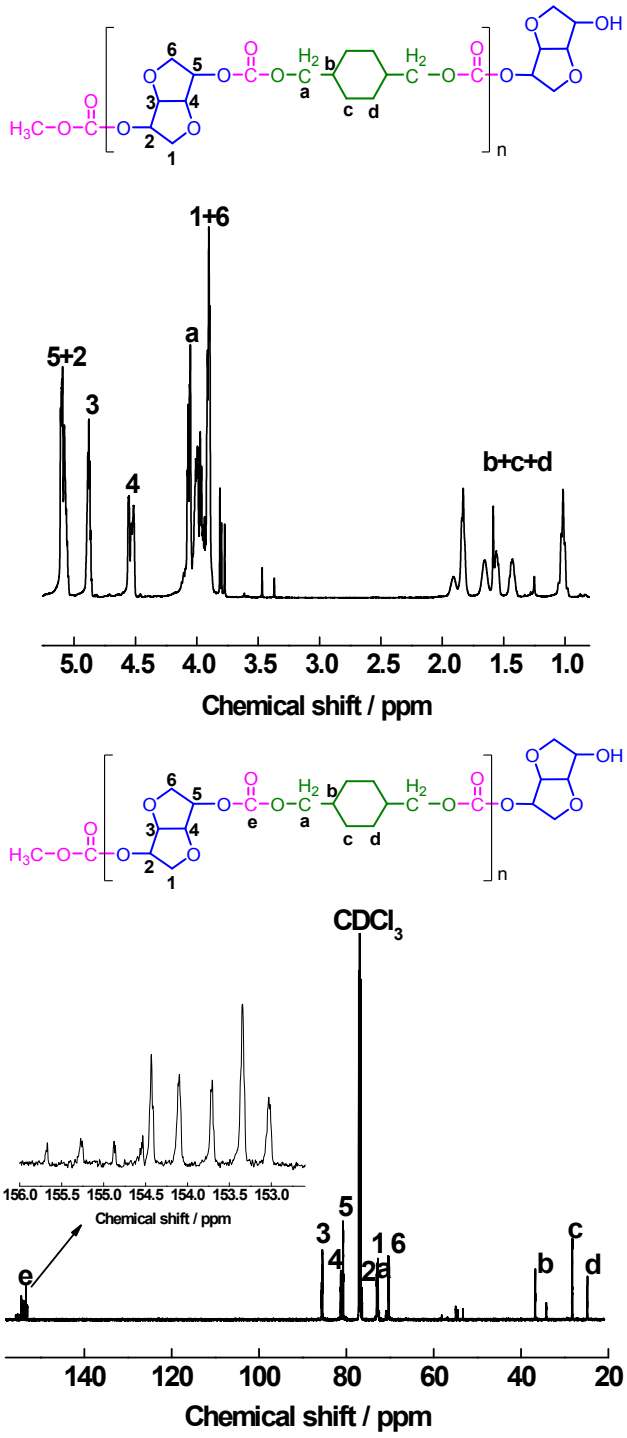

Fig. S4. ^{1}H NMR and ^{13}C NMR spectra of PCMIC.

PTMIC: ^{1}H NMR (600 MHz, $CDCl_3$): 1.25–2.53 (m, 14H, C-ring), 3.89–4.08 (m, 8H, -C$\underline{H}_2$-ring, H1, H6, isosorbide), 4.51–4.56 (m, 1H, H4, isosorbide), 4.88 (t, 1H, H3,

isosorbide), 5.06–5.11 (m, 2H, H2, H5, isosorbide). ^{13}C NMR (600 MHz, $CDCl_3$): 54.9-24.3 (C-ring), 70.3 (C6, isosorbide), 71.5 (-$\underline{C}H_2$-C-ring), 73.0, 72.7 (C1, isosorbide), 76.9, 76.4 (C2, isosorbide), 80.9, 80.6 (C5, isosorbide), 81.2 (C4, isosorbide), 85.6, 85.4 (C3, isosorbide), 155.3-153.0 ($\underline{C}$=O).

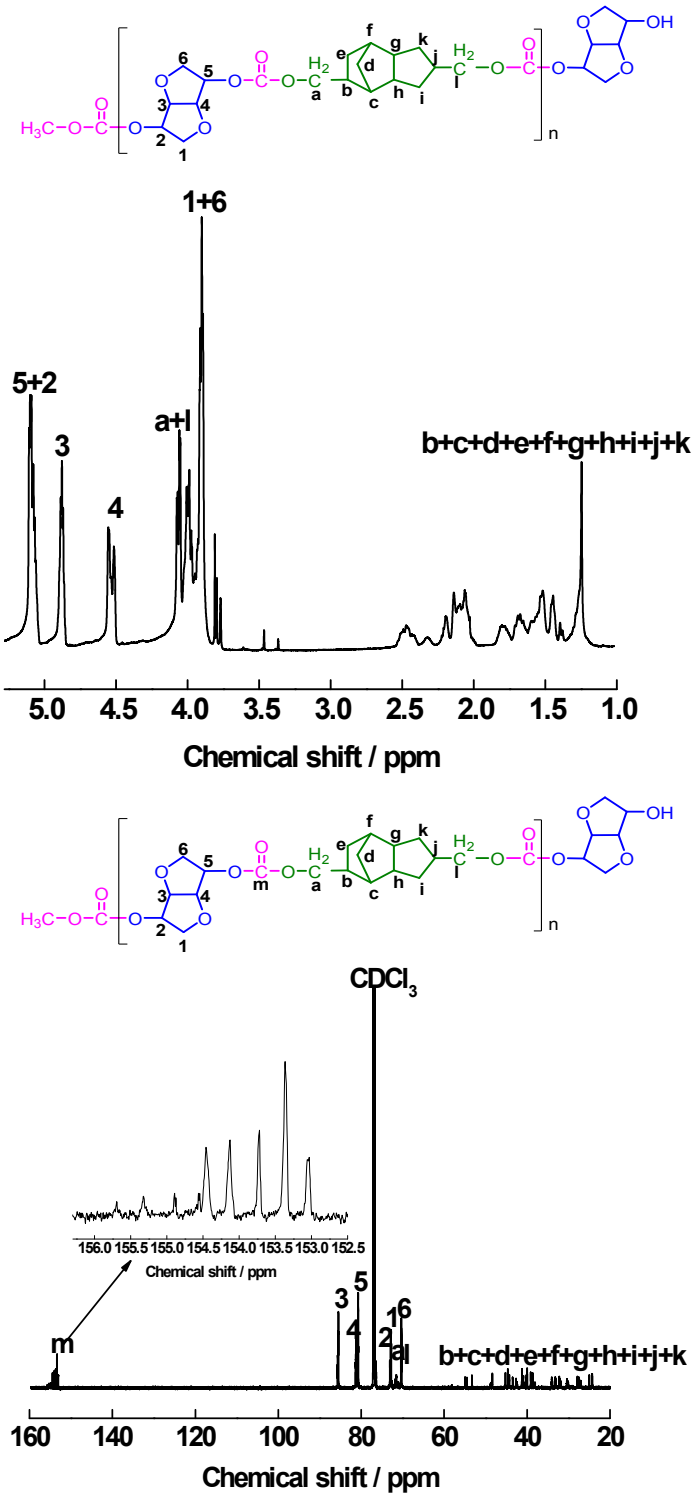

Fig. S5. ^{1}H NMR and ^{13}C NMR spectra of PTMIC.

PCDIC: ^{1}H NMR (600 MHz, $CDCl_3$): 1.25–2.22 (m, 10H, C-ring, cyclohexane group), 3.89–4.08 (m, 4H, H1, H6, isosorbide), 4.51–4.55 (m, 1H, H4, isosorbide), 4.88 (t, 1H,

H3, isosorbide), 5.07–5.11 (m, 2H, H2, H5, isosorbide). ^{13}C NMR (600 MHz, $CDCl_3$): 26.8 (C-ring, cyclohexane group), 70.3 (C6, isosorbide), 73.0, 72.7 (C1, isosorbide), 76.9, 76.4 (C2, isosorbide), 80.9, 80.6 (C5, isosorbide), 81.2 (C4, isosorbide), 85.6, 85.4 (C3, isosorbide), 155.0-153.0 (C=O).

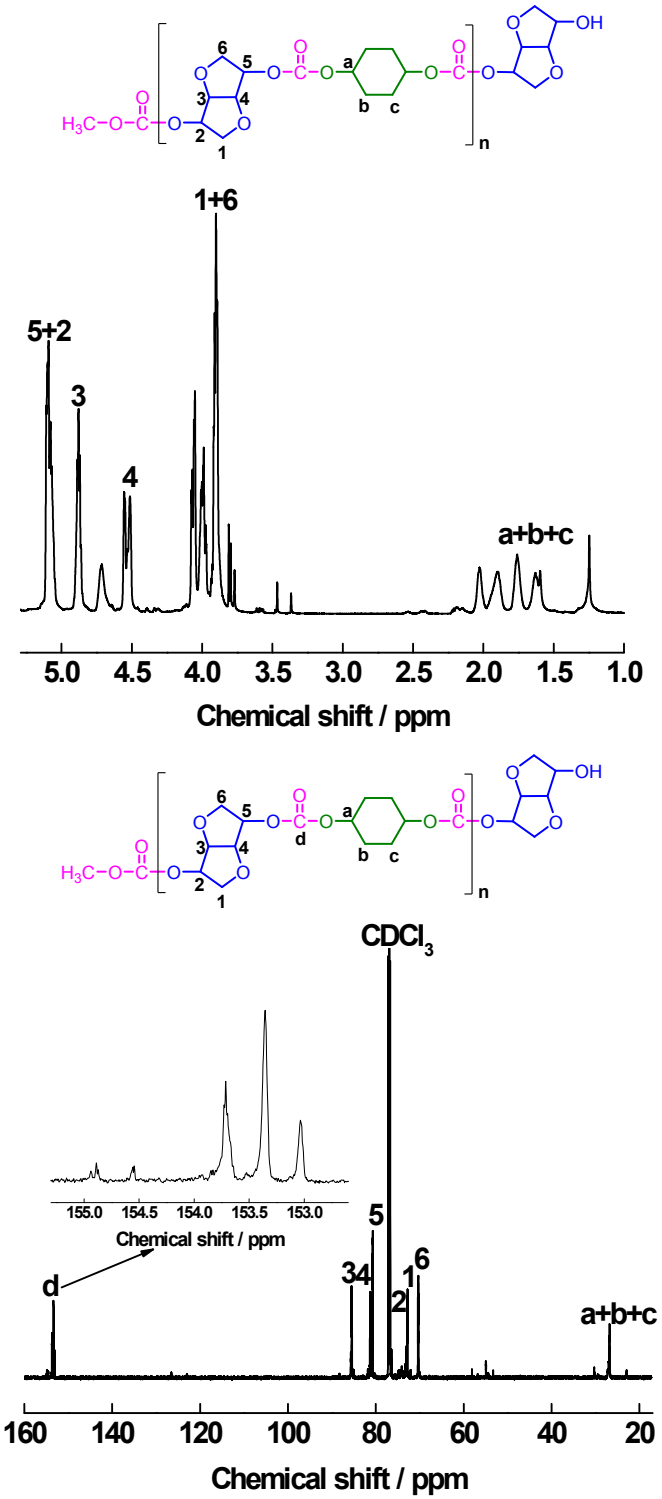

Fig. S6. ^{1}H NMR and ^{13}C NMR spectra of PCDIC.

PHDIC: ^{1}H NMR (600 MHz, $CDCl_3$): 1.40 (d, 4H, -CH_2-CH_2-C$\underline{H}_2$-C$\underline{H}_2$-CH_2-CH_2-), 1.67 (d, 4H, -CH_2-C$\underline{H}_2$-CH_2-CH_2-C$\underline{H}_2$-CH_2-), 3.89–4.08 (m, 4H, H1, H6, isosorbide), 4.10-4.18 (m, 4H, -C$\underline{H}_2$-CH_2-CH_2-CH_2-CH_2-C$\underline{H}_2$-), 4.52–4.55 (m, 1H,H

4, isosorbide), 4.88 (t, 1H, H3, isosorbide), 5.04–5.11 (m, 2H, H2, H5, isosorbide). ^{13}C NMR (600 MHz, $CDCl_3$): 25.0 (-$\underline{C}H_2$-CH_2-CH_2-CH_2-CH_2-$\underline{C}H_2$-), 28.2(-CH_2-$\underline{C}H_2$-CH_2-CH_2-$\underline{C}H_2$-CH_2-), 68.0, 67.5 (-CH_2-CH_2-$\underline{C}H_2$-$\underline{C}H_2$-CH_2-CH_2-), 70.3 (C6, isosorbide), 73.0, 72.7 (C1, isosorbide), 76.9, 76.4 (C2, isosorbide), 80.9,80.6 (C5, isosorbide), 81.2 (C4, isosorbide), 85.6, 85.4 (C3, isosorbide), 155.5-153.0 ($\underline{C}$=O).

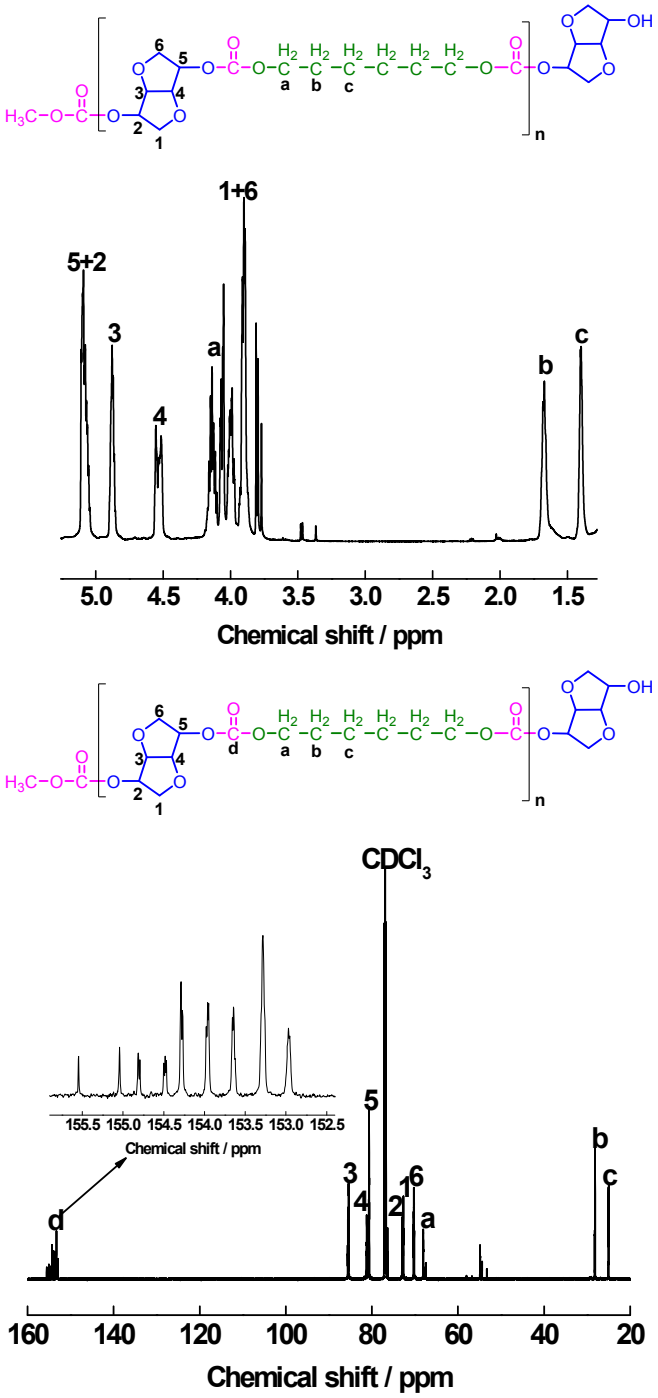

Fig. S7. ^{1}H NMR and ^{13}C NMR spectra of PHDIC.

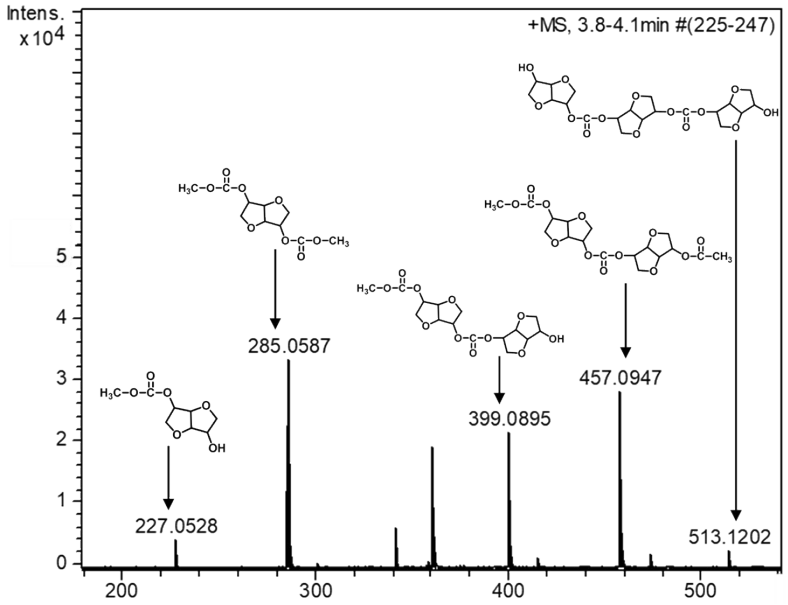

Fig. S8. ESI-MS spectrum of the key intermediates prepared at 98 °C.

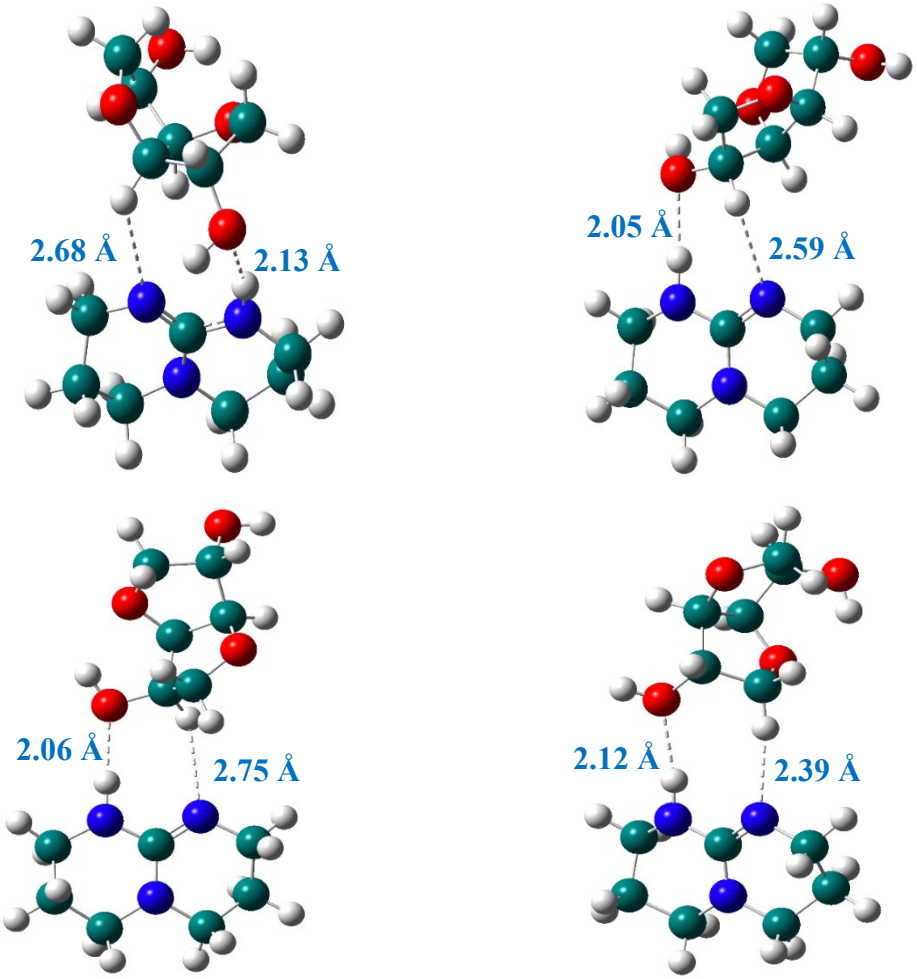

Fig. S9. Interaction of TBD and ISB