

## Supporting Information

### A new route of CO<sub>2</sub> catalytic activation: syntheses of N-substituted carbamates from dialkyl carbonates and polyureas

Jianpeng Shang <sup>a,b</sup>, Shimin Liu <sup>a,b</sup>, Xiangyuan Ma <sup>a</sup>, Liujin Lu <sup>a</sup>, Youquan Deng <sup>a,\*</sup>

<sup>a</sup> Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, China, 730000. Fax: +86-931-4968116; Tel: +86-931-4968116;  
E-mail: ydeng@licp.acs.cn

<sup>b</sup> Graduate School of the Chinese Academy of Sciences, Beijing, China, 100039.

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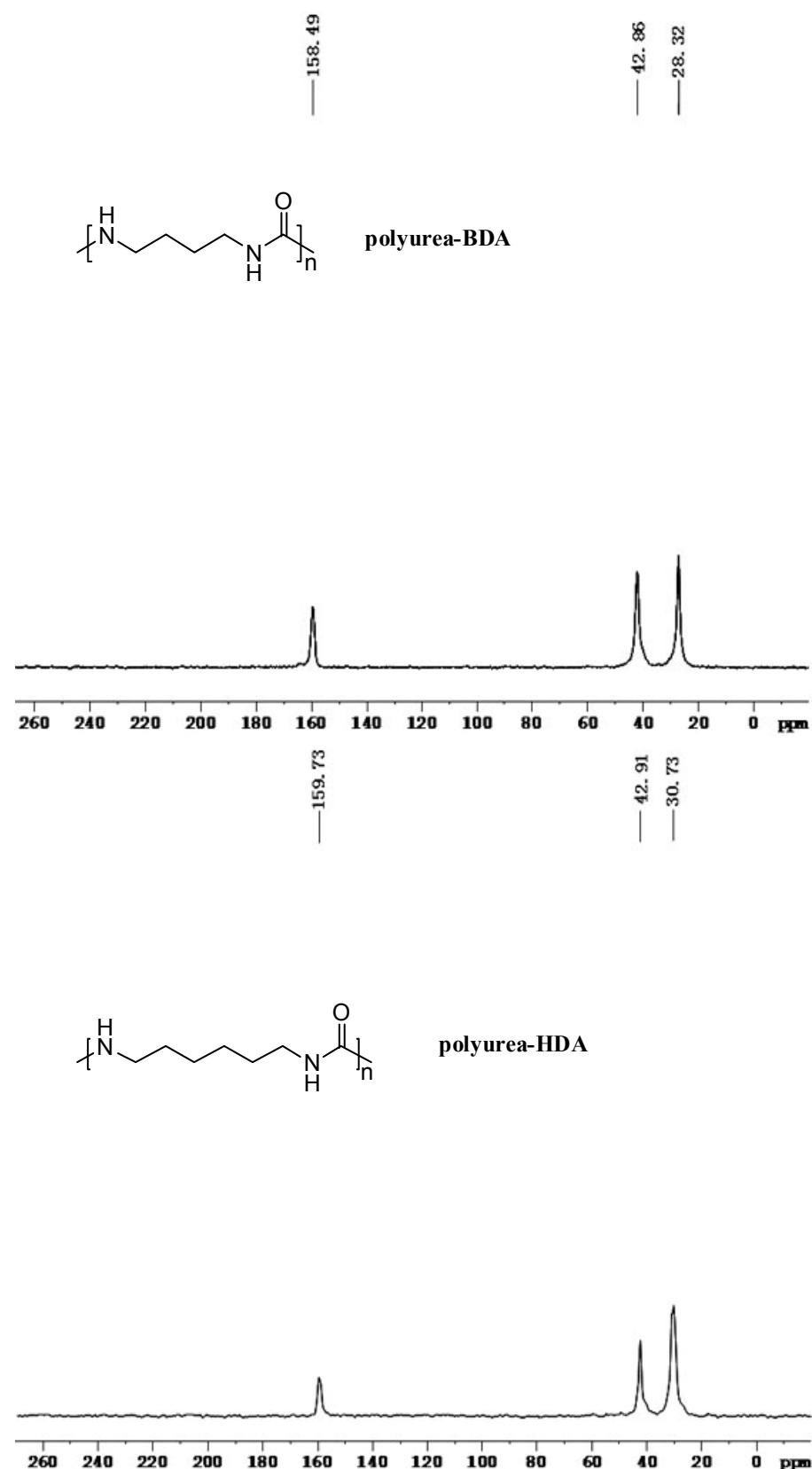
**Fig. S2** FT-IR spectra of the products of the solid products obtained from diamines and CO<sub>2</sub>

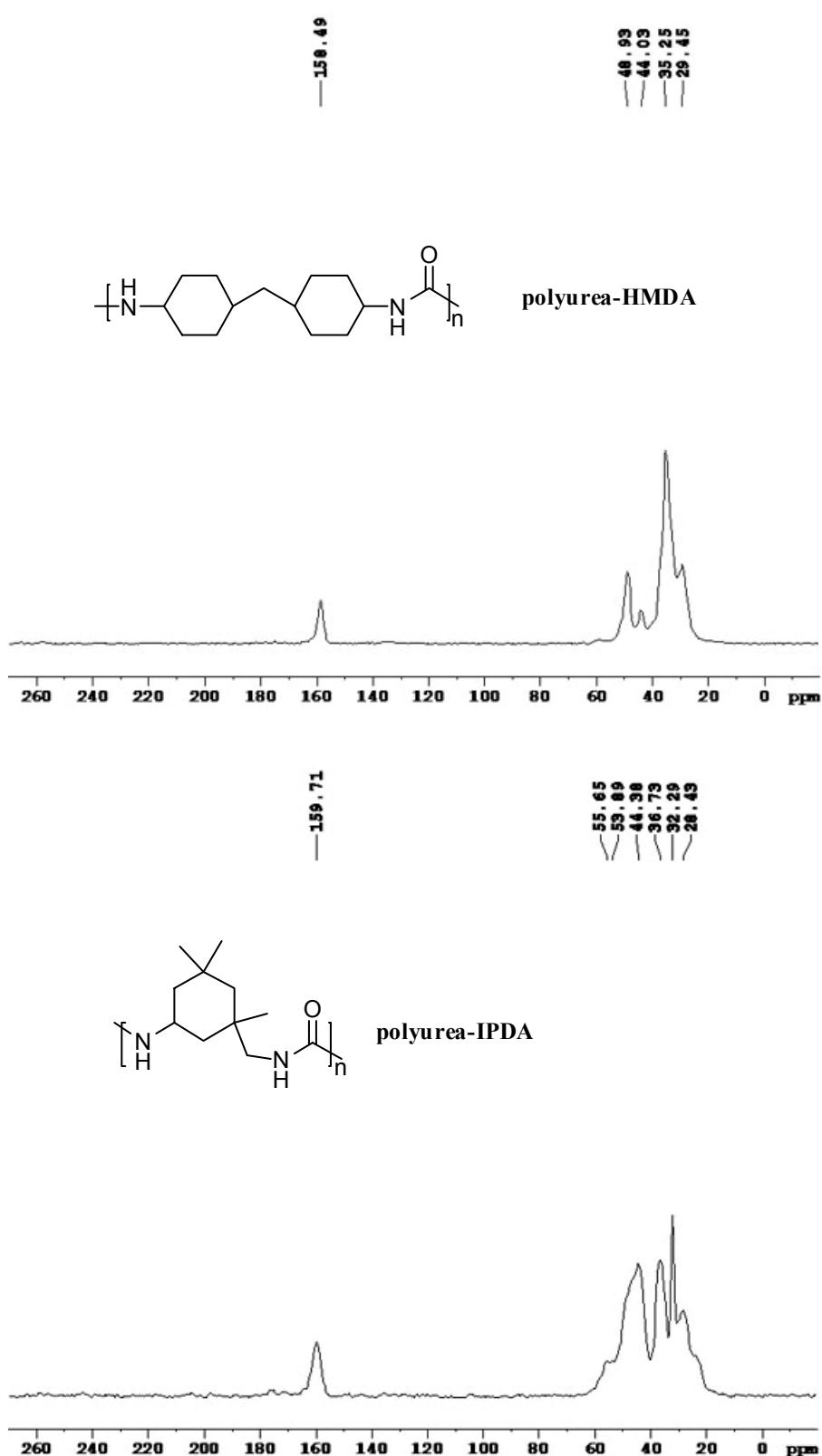
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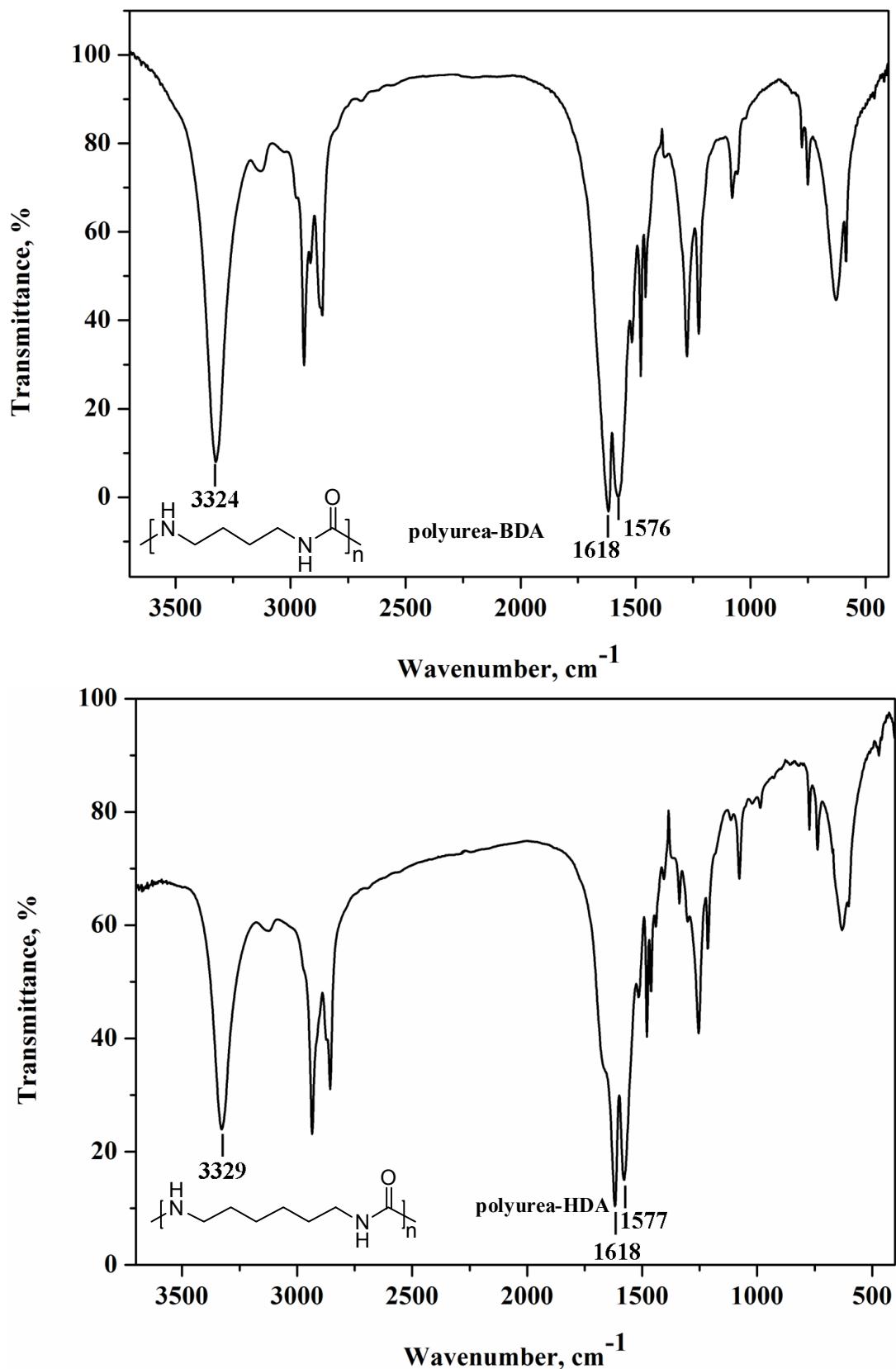
**Fig. S5** <sup>1</sup>H, <sup>13</sup>C NMR and MS results of the disubstituted ureas and N-substituted carbamates

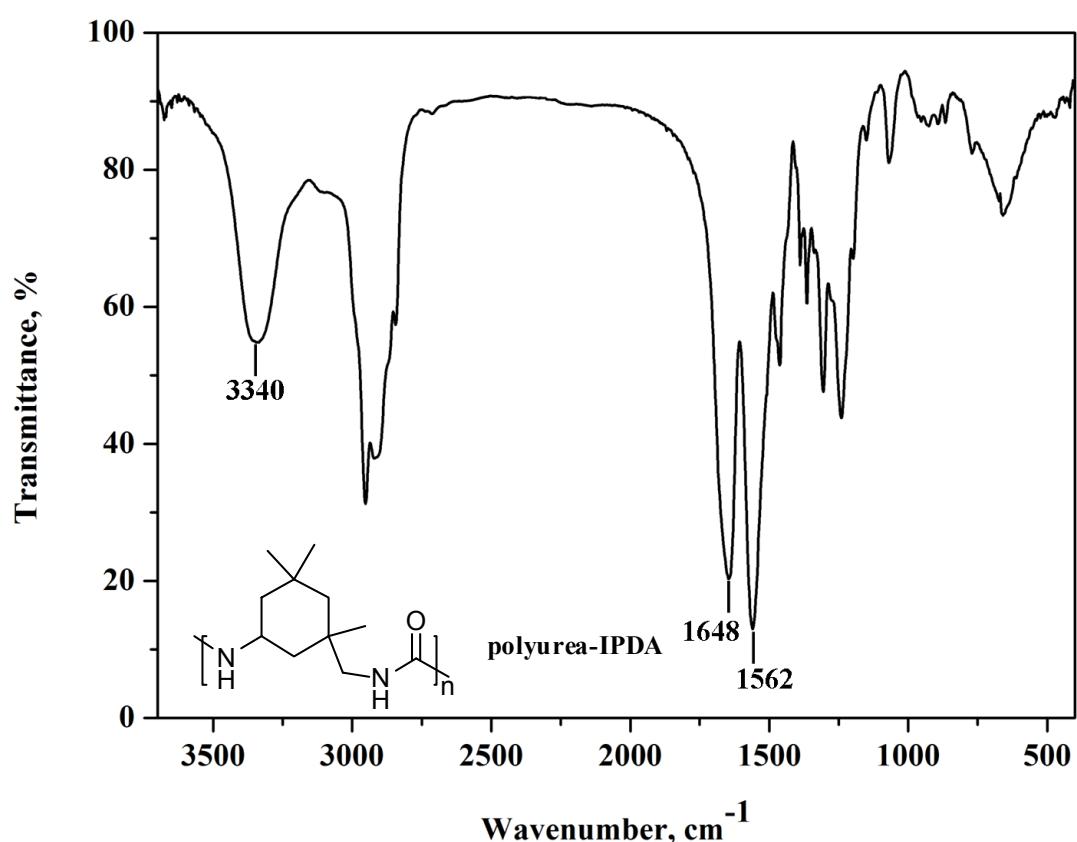
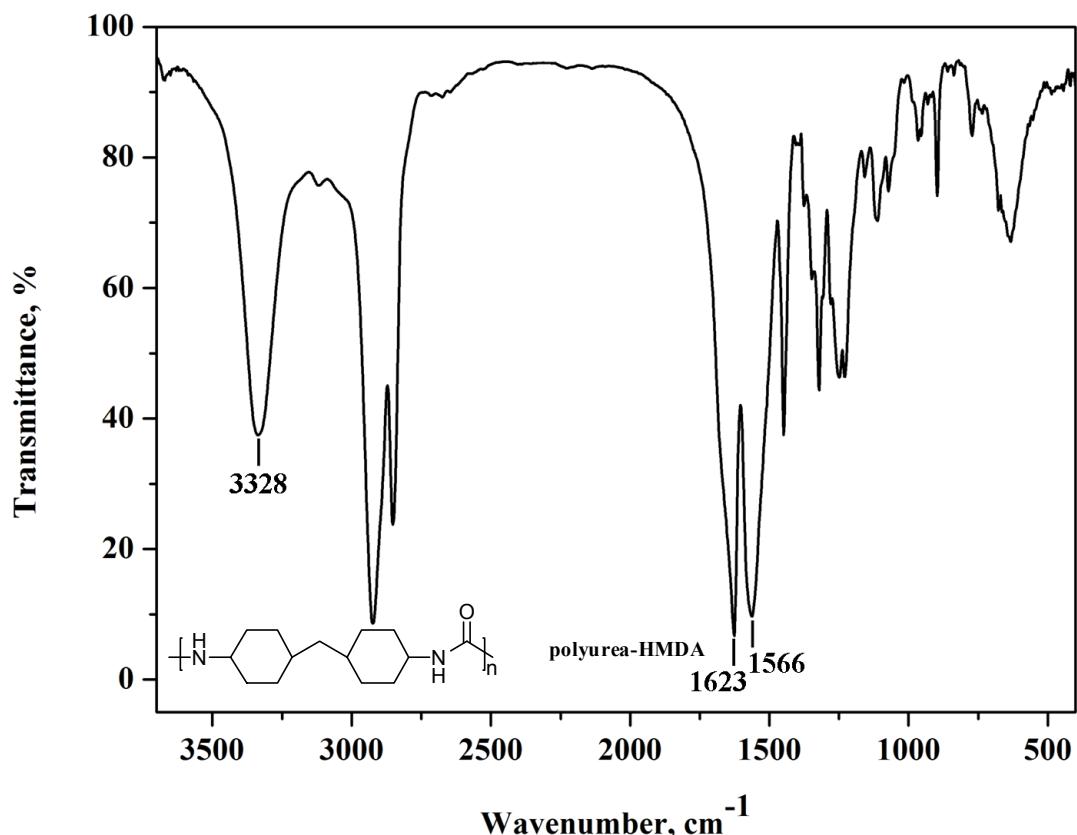
**Fig. S1 CP/MAS  $^{13}\text{C}$  NMR spectra of the solid products obtained from diamines and  $\text{CO}_2$**



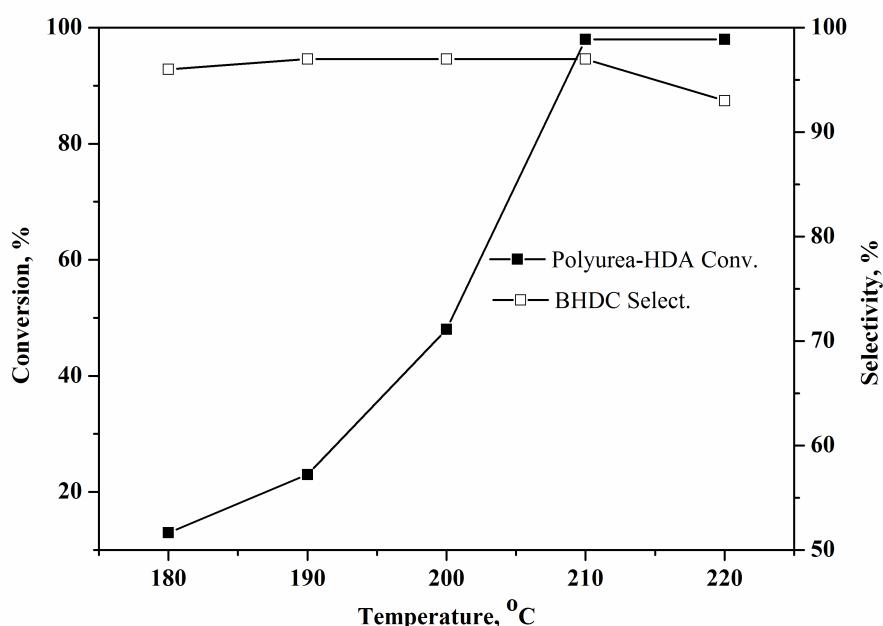


**Fig. S2 FT-IR spectra of the products of the solid products obtained from diamines and CO<sub>2</sub>**

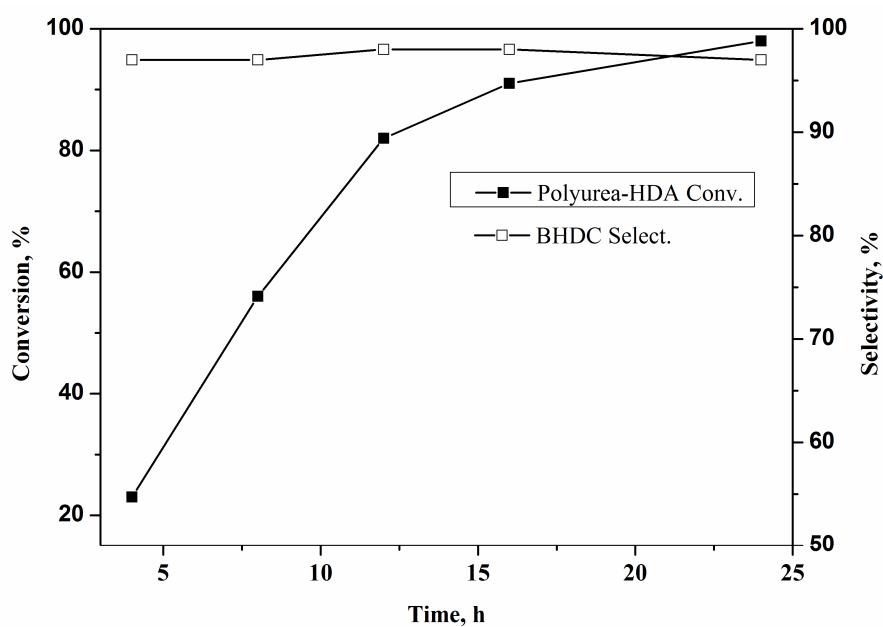




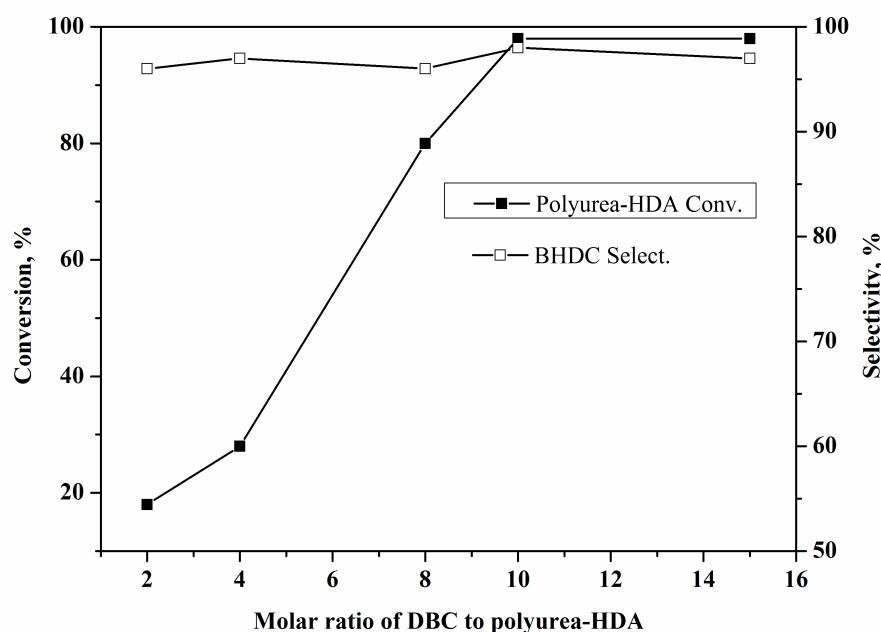
**Fig. S3 Effects of the reaction conditions on the reaction of polyurea-HDA and DBC**



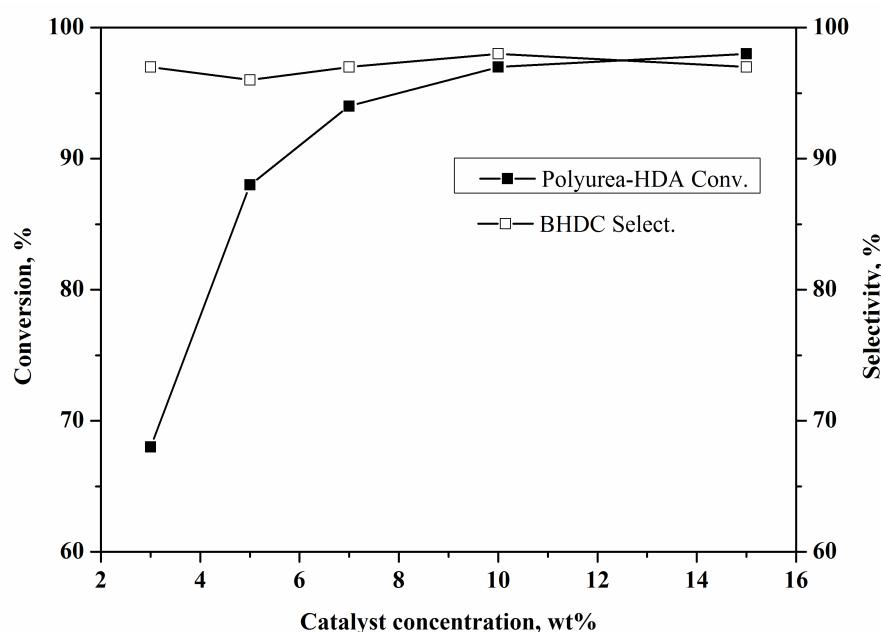
The effects of reaction temperature on the reaction were investigated in the range of 180–220 °C. The conversion of polyurea-HDA rapidly increased to 98% with increasing reaction temperature up to 210 °C, indicating that such reaction was relatively sensitive to the temperature and the higher temperature favors the conversion of polyurea-HDA to BHDC. When it further increased up to 220 °C, the conversion of polyurea-HDA has little changes, but the selectivity of BHDC decreased from 98% at 210 °C to 93% at 220 °C because the thermal decomposition of BHDC could take place easily at higher temperature. The occurrence of the thermal decomposition of BHDC was determined by FT-IR analysis with a peak at 2260 cm<sup>-1</sup>, which could be attributed to the isocyanate group (NCO).



The effects of the reaction time on the synthesis of BHDC were performed over MgO-ZnO catalyst. At the initial 12 h, the conversion of polyurea-HDA rapidly increased with increasing the reaction time, but with further prolonging the reaction time to 24 h, the conversion of polyurea-HDA increased slowly, which might be due to a decrease in the amount of polyurea-HDA and an increase in the amount of BHDC with increasing the reaction time. The selectivity of BHDC decreased slowly with increasing reaction time, and a small amount of thermal decomposition byproduct was detected.

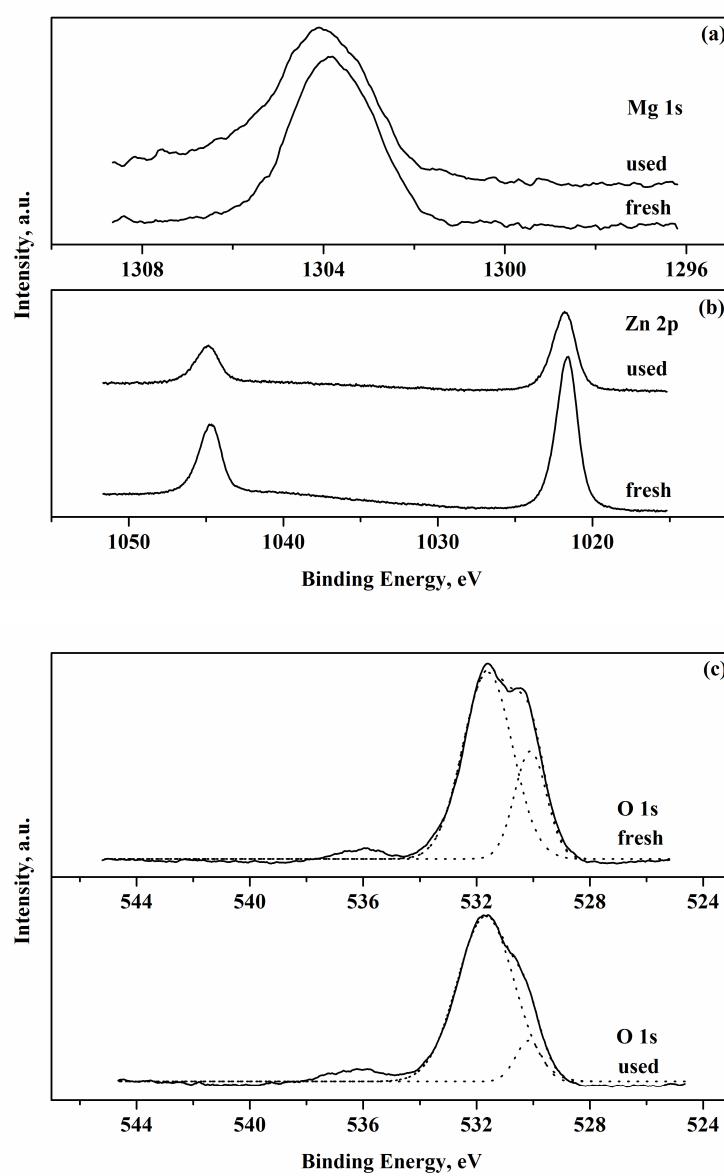


The effects of the molar ratios of DBC and polyurea-HDA were further studied. The molar ratio of the DBC and polyurea-HDA varied from 2 to 15. The conversion of the polyurea-HDA increased obviously up to the molar ratio of 10 and kept unchanged when the molar ratio of DBC and polyurea-HDA reached to 15, but the selectivity of the BHDC remained almost constant. This could be ascribed to the fact that the increase of DBC amount not only promote the reaction shifting to the right side, but also increase the amount of the polyurea-HDA dissolved in the DBC.

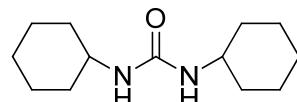


The effects of the catalyst concentration on the reaction were also examined. The conversion of the polyurea-HDA increased with increasing the amount of the catalyst and reached to a maximum of 98% conversion at the catalyst concentration of 10 wt% (based on the mass of charged polyurea-HDA). With further increasing the catalyst concentration, the conversion of the polyurea-HDA showed little changes. However, the selectivity of BHDC was almost not changed.

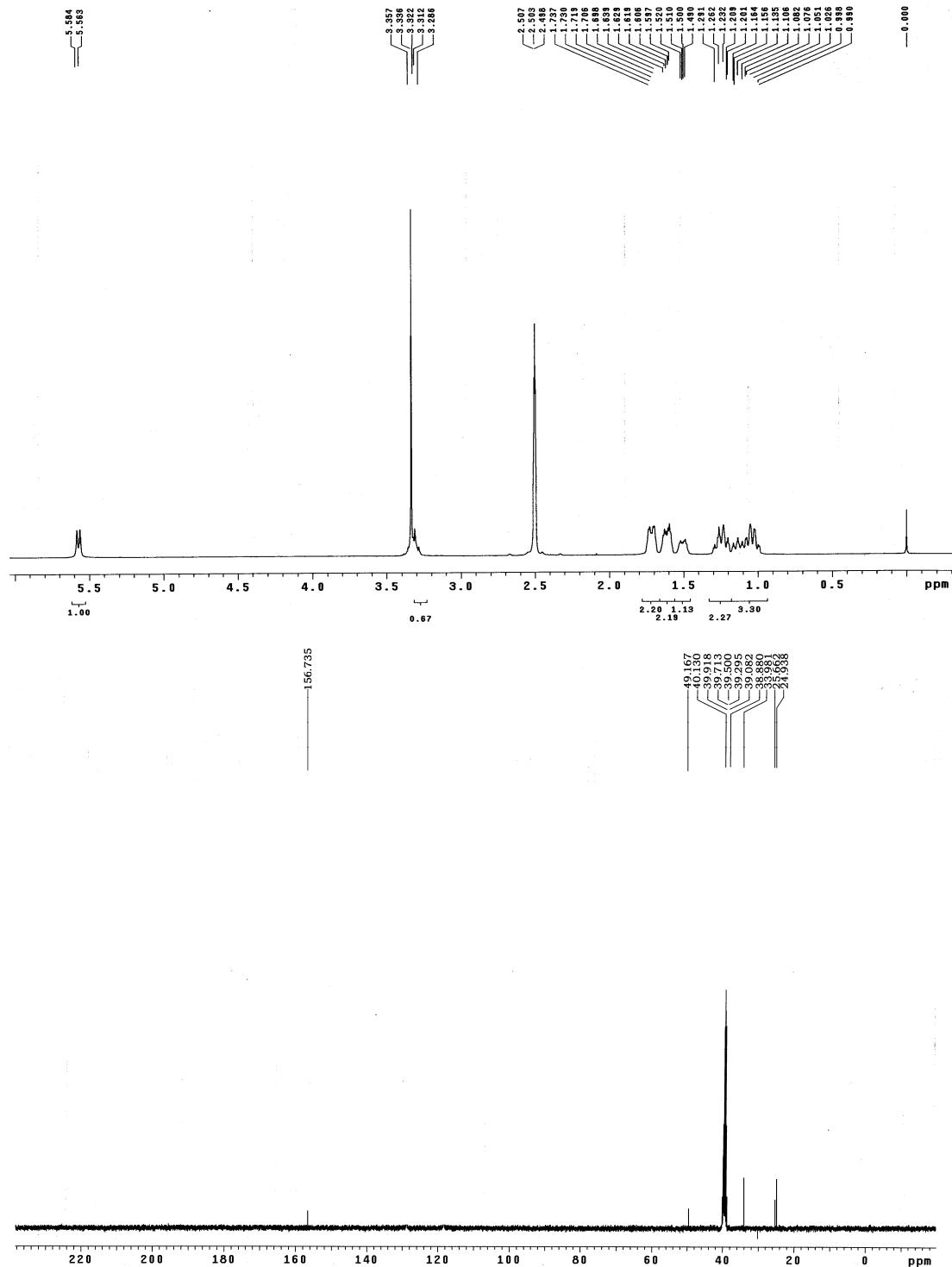
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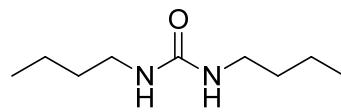


**Fig. S5**  $^1\text{H}$ ,  $^{13}\text{C}$  NMR and MS results of the disubstituted ureas and N-substituted carbamates

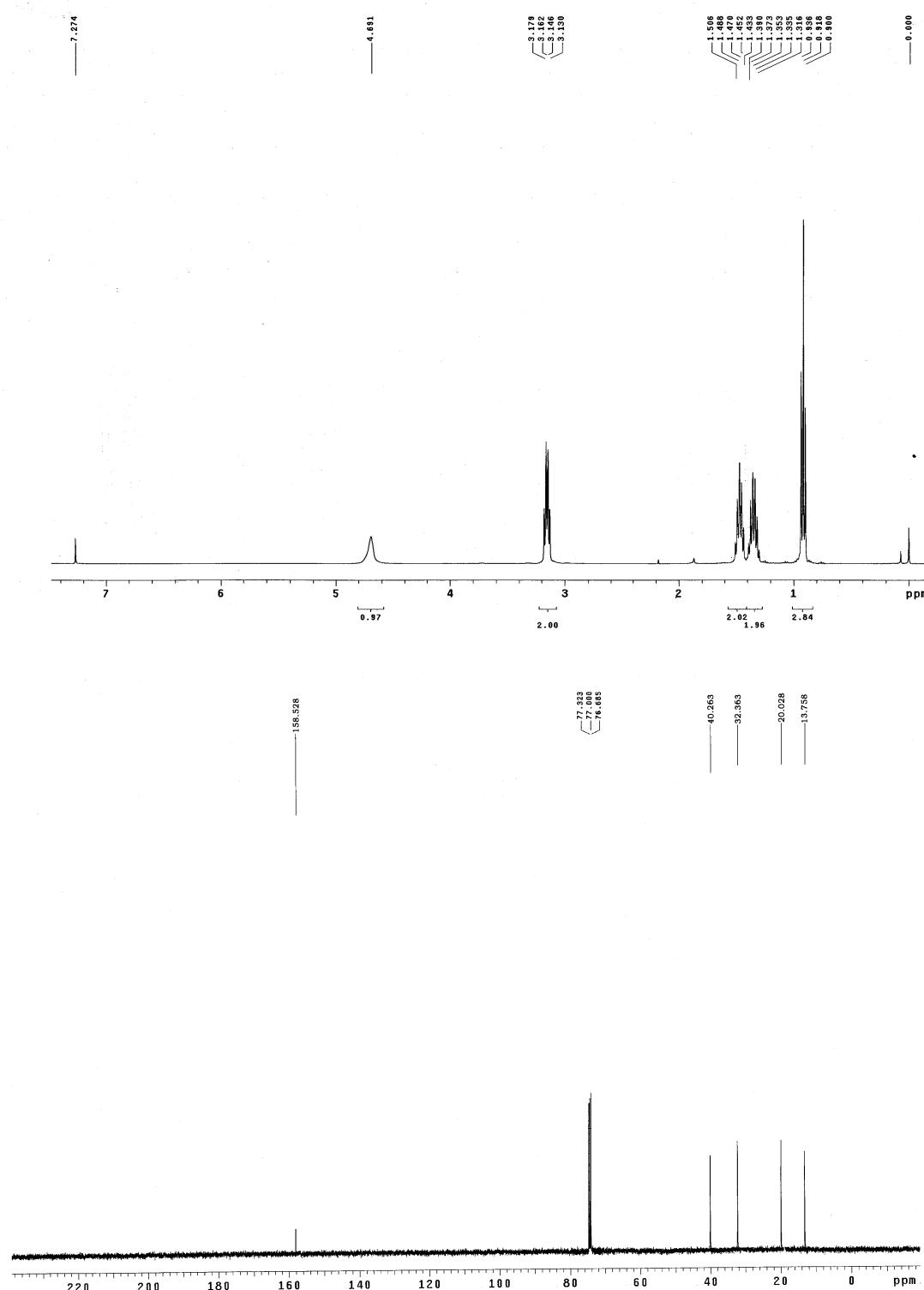


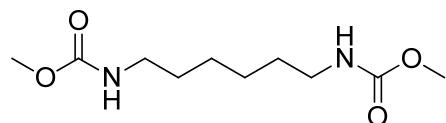
1,3-dicyclohexylurea:  $^1\text{H}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 400 MHz):  $\delta$  = 0.99-1.29 (m, 10H), 1.49-1.52 (m, 2H), 1.60-1.64 (m, 4H), 1.70-1.74 (m, 4H), 3.29-3.34 (m, 2H), 5.56-5.58 (d, 2H).  $^{13}\text{C}$  NMR ( $\text{CD}_3\text{SOCD}_3$ , 100 MHz)  $\delta$  = 25.0, 25.6, 34.0, 49.2, 156.7. MS, m/z: 41 (18%), 56 (100%), 61 (25%), 70 (15%), 99 (29%), 143 (21%), 224 (22%).



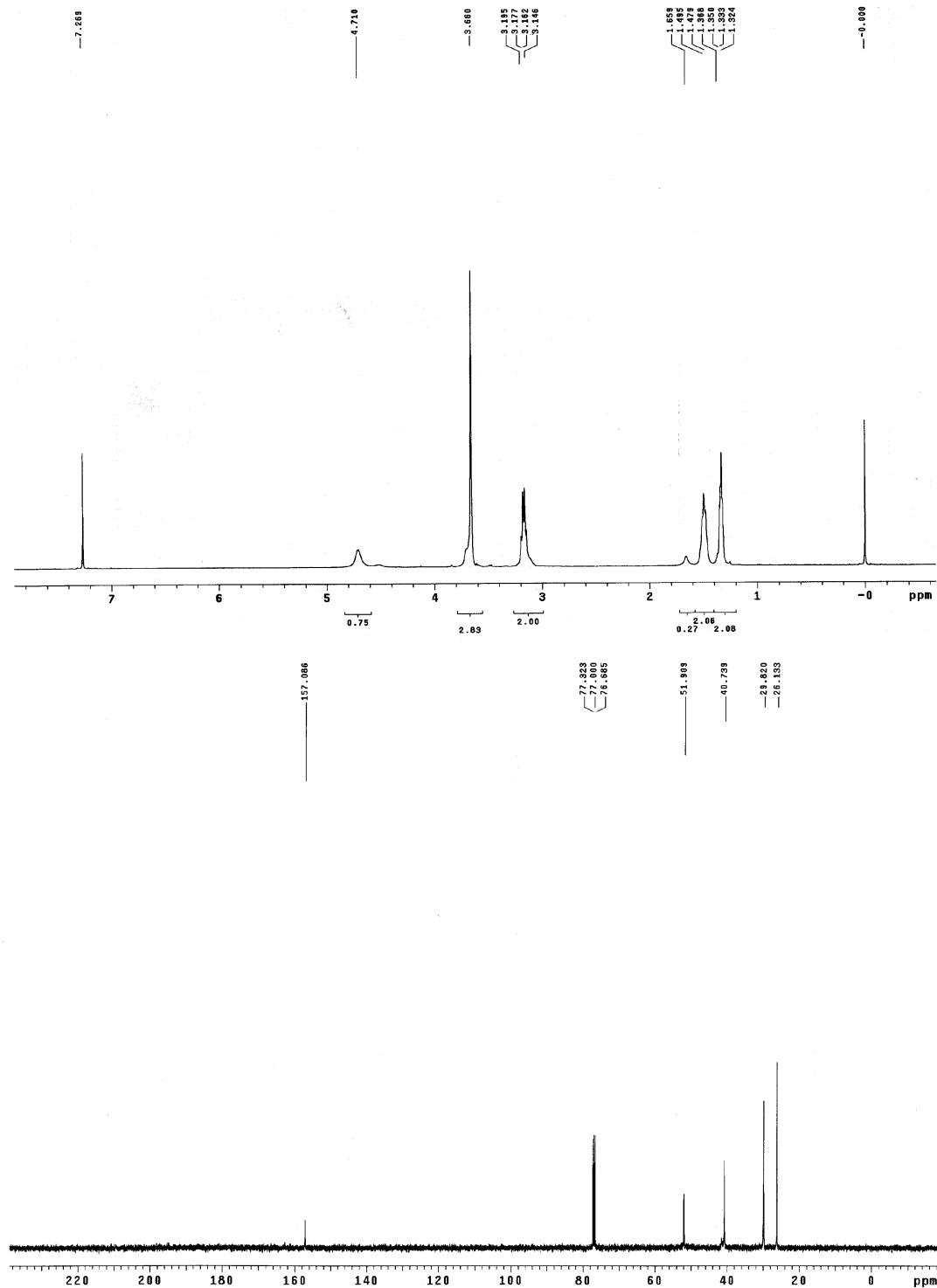


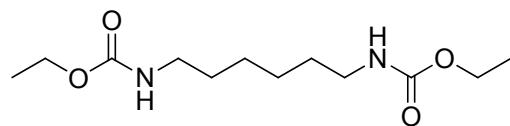
1,3-dibutylurea:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 0.90-0.94 (t, 6H), 1.32-1.39 (m, 4H), 1.43-1.51 (m, 4H), 3.13-3.18 (m, 4H), 4.69 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  = 13.8, 20.0, 32.4, 40.3, 158.5. MS, m/z: 57 (100%), 74 (53%), 87 (29%), 101 (45%), 115 (4%), 129 (22%), 143 (13%), 157 (11%), 172 (45%).





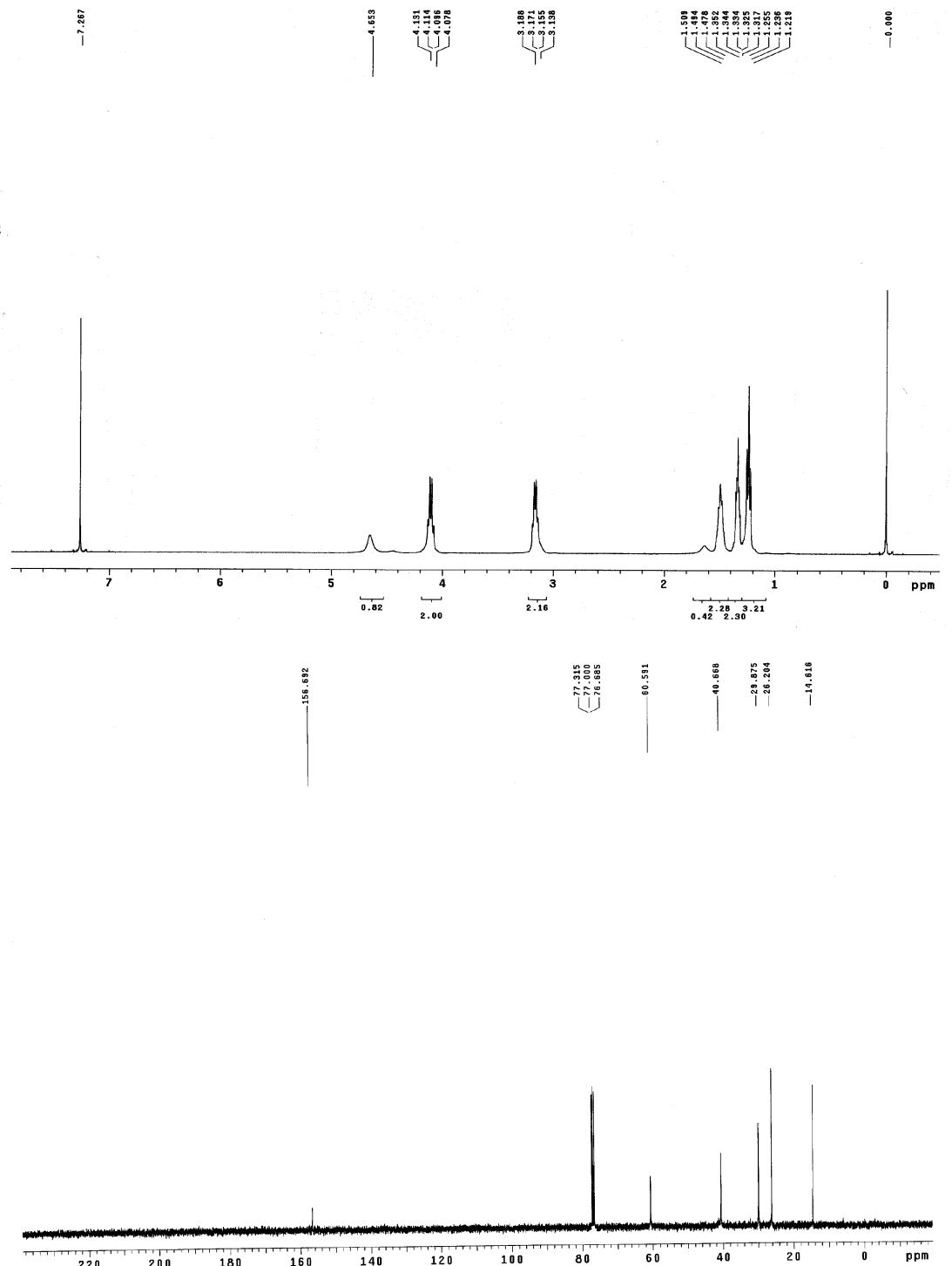
Dimethyl hexamethylenedicarbamate:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 1.32-1.37 (m, 4H), 1.48-1.50 (m, 4H), 3.15-3.20 (m, 4H), 3.66 (s, 6H), 4.71 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 26.1, 29.8, 40.7, 51.9, 157.0. MS, m/z: 30 (12%), 44 (40%), 59 (25%), 88 (100%), 130 (18%), 144(10%).

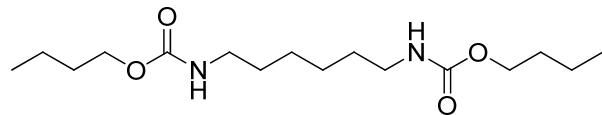




Diethyl hexamethylenedicarbamate:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,

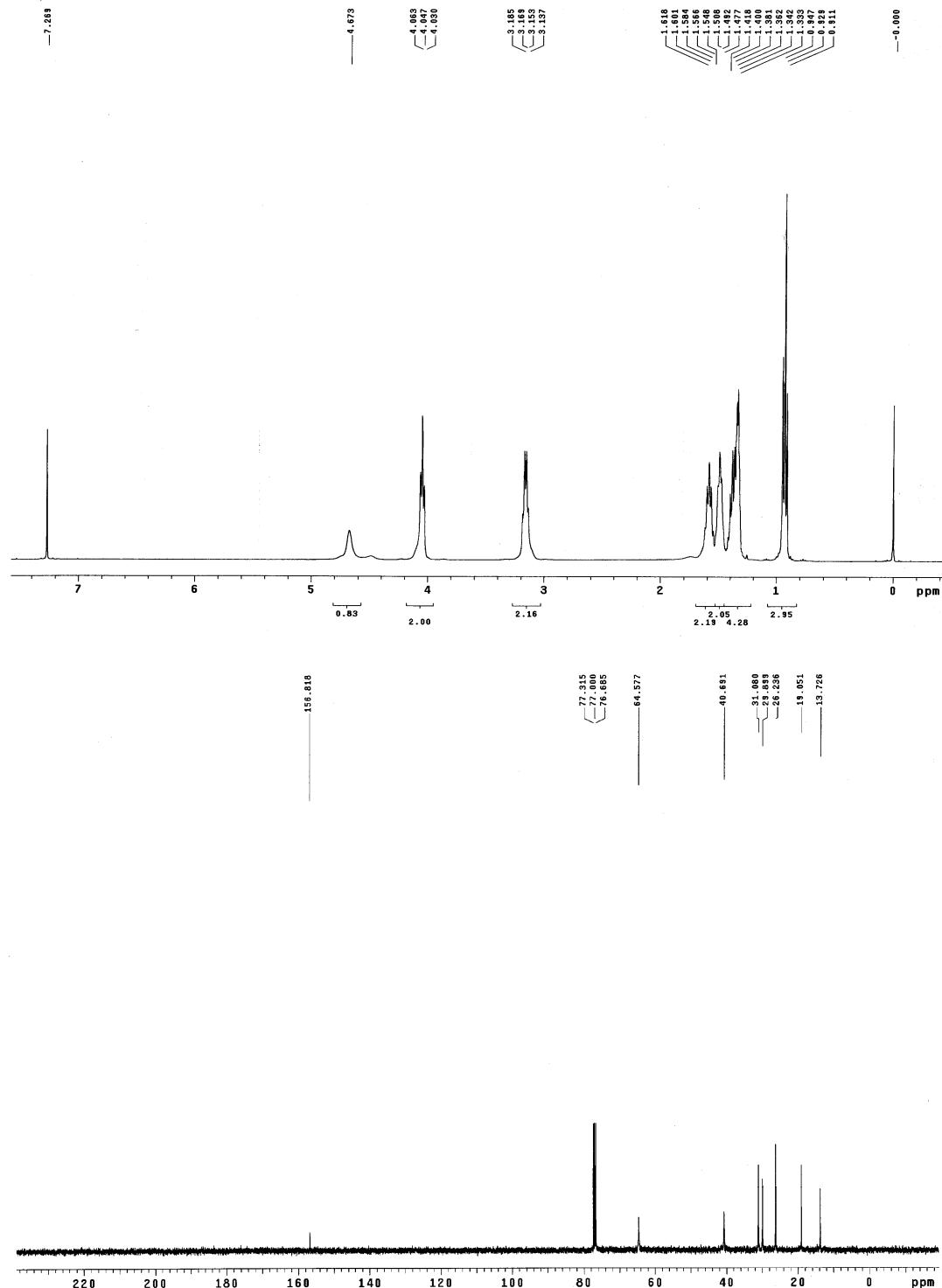
400 MHz):  $\delta$  = 1.22-1.26 (t, 6H), 1.32-1.35 (m, 4H), 1.48-1.51 (4H, m), 3.14-3.19 (m, 4H), 4.08-4.13 (m, 4H), 4.65 (s, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 14.6, 26.2, 29.9, 40.7, 60.6, 156.7. MS, m/z: 30 (42%), 41 (10%), 56 (14%), 74 (31%), 82 (10%), 98 (21%), 116 (10%), 130 (70%), 141 (15%), 158 (31%), 169 (18%), 215 (16%).

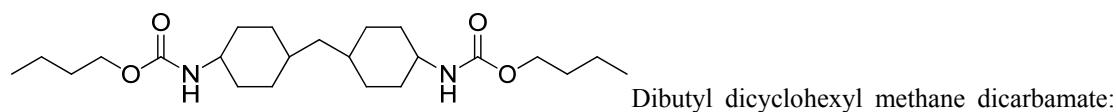




Dibutyl hexamethylenedicarbamate (BHDC):

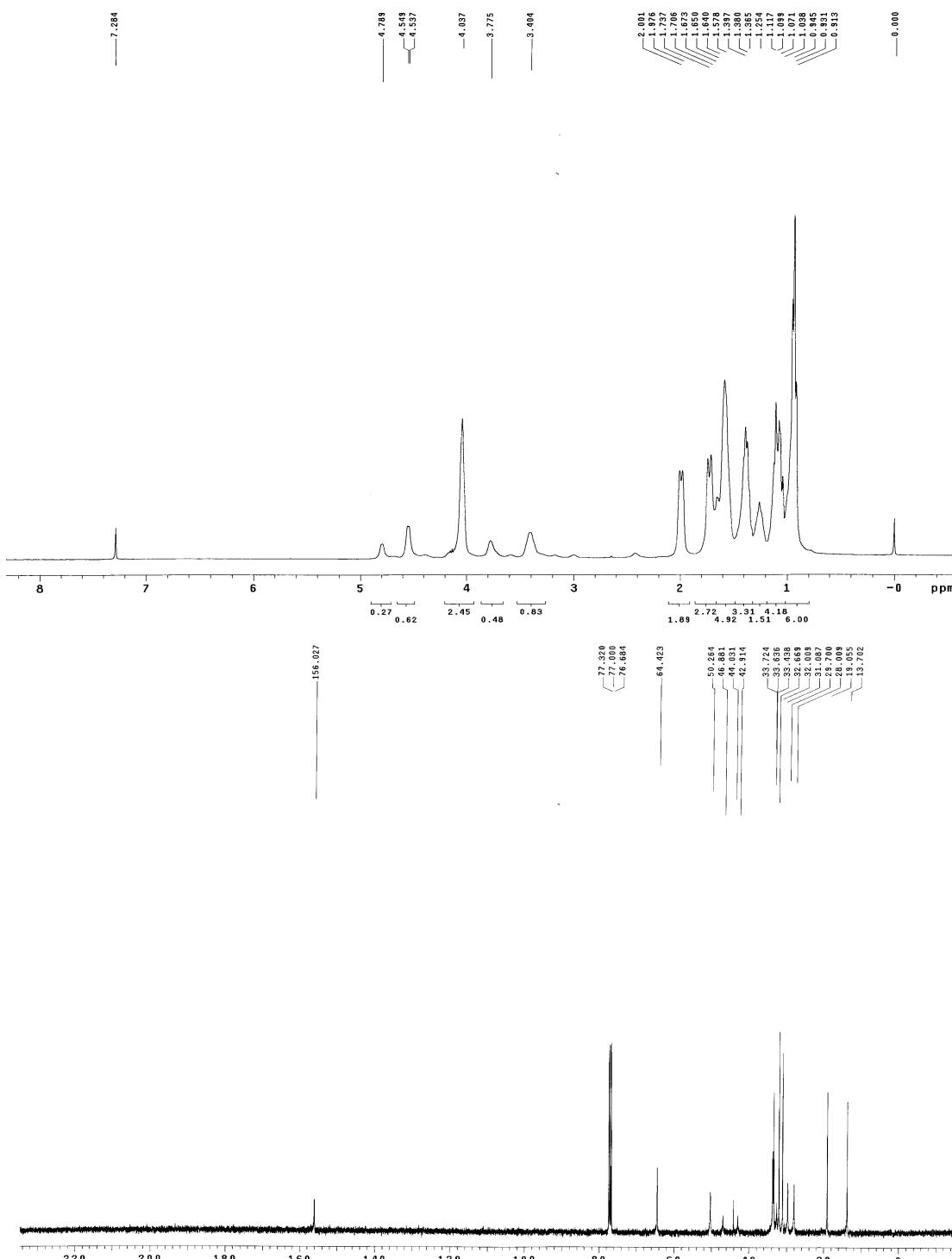
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 0.91-0.95 (t, 6H), 1.33-1.62 (m, 16H), 3.14-3.19 (m, 4H), 4.03-4.06 (t, 4H), 4.67 (s, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 13.7, 19.1, 26.2, 29.9, 31.1, 40.7, 64.6, 156.8. MS, m/z : 30 (23%), 41 (33%), 57 (32%), 74 (27%), 98 (25%), 143 (22%), 168 (12%), 186 (25%), 243 (11%).

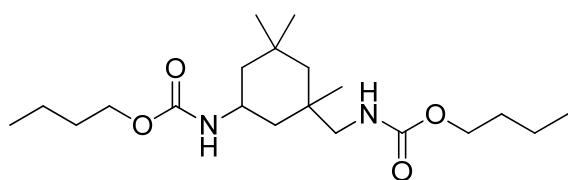




Dibutyl dicyclohexyl methane dicarbamate:

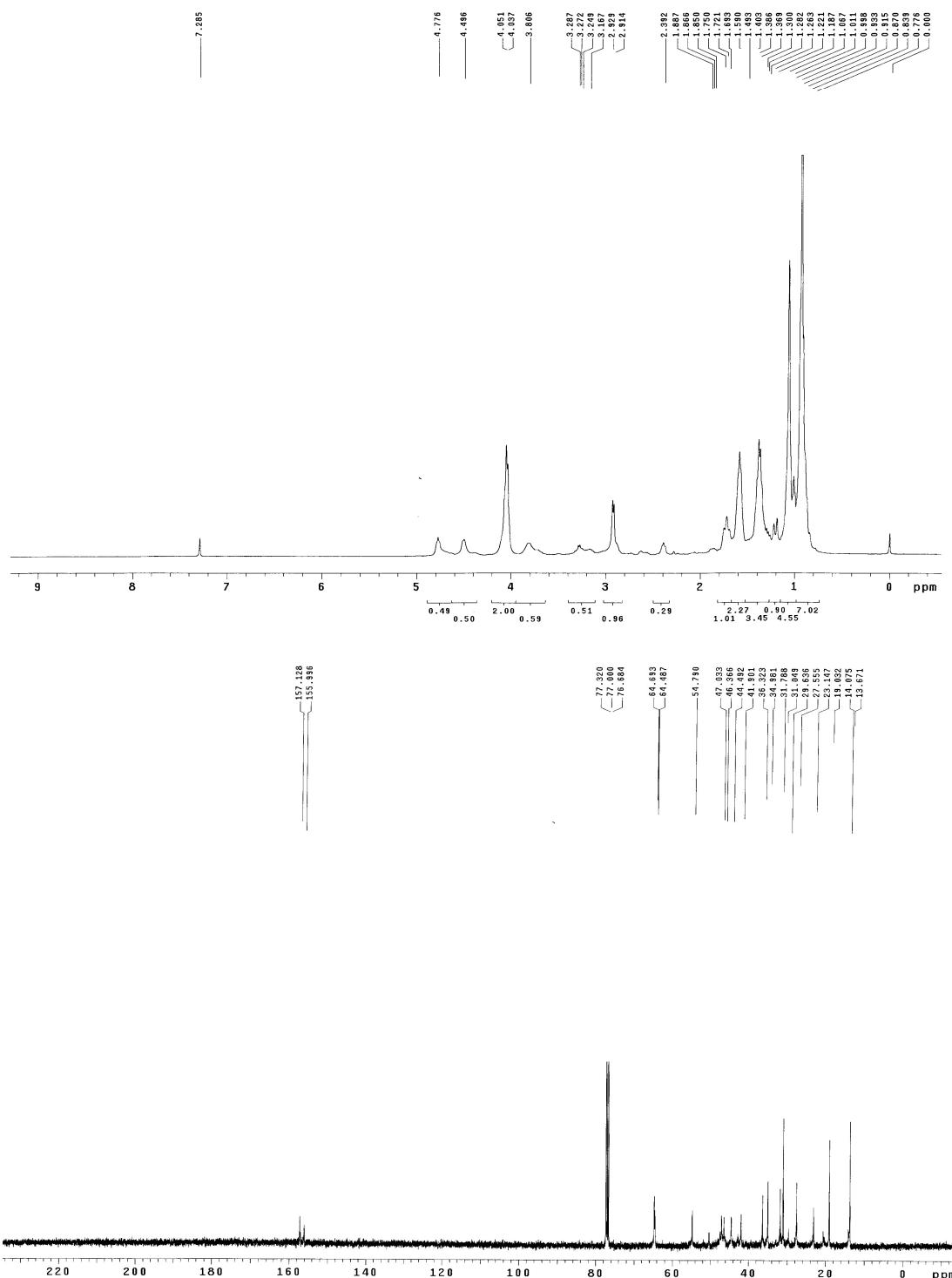
<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 0.91-0.95 (t, 6H), 1.04-2.00(m, 28H), 3.40-3.78 (s, 2H), 4.04 (s, 4H), 4.54-4.79 (s, 2H) <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ = 13.7, 19.1, 28.0, 29.7, 31.1, 32.0, 32.7, 33.4, 33.6, 33.7, 42.9, 44.0, 46.9, 50.3, 64.4, 156.0. MS, m/z : 29(20%), 41 (66%), 56 (100%), 67 (23%), 81 (97%), 95 (37%), 118 (29%), 138 (20%), 156 (70%), 176 (22%), 199 (28%), 212 (37%), 233 (14%), 309 (28%).

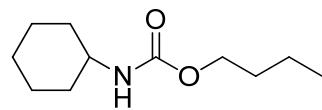




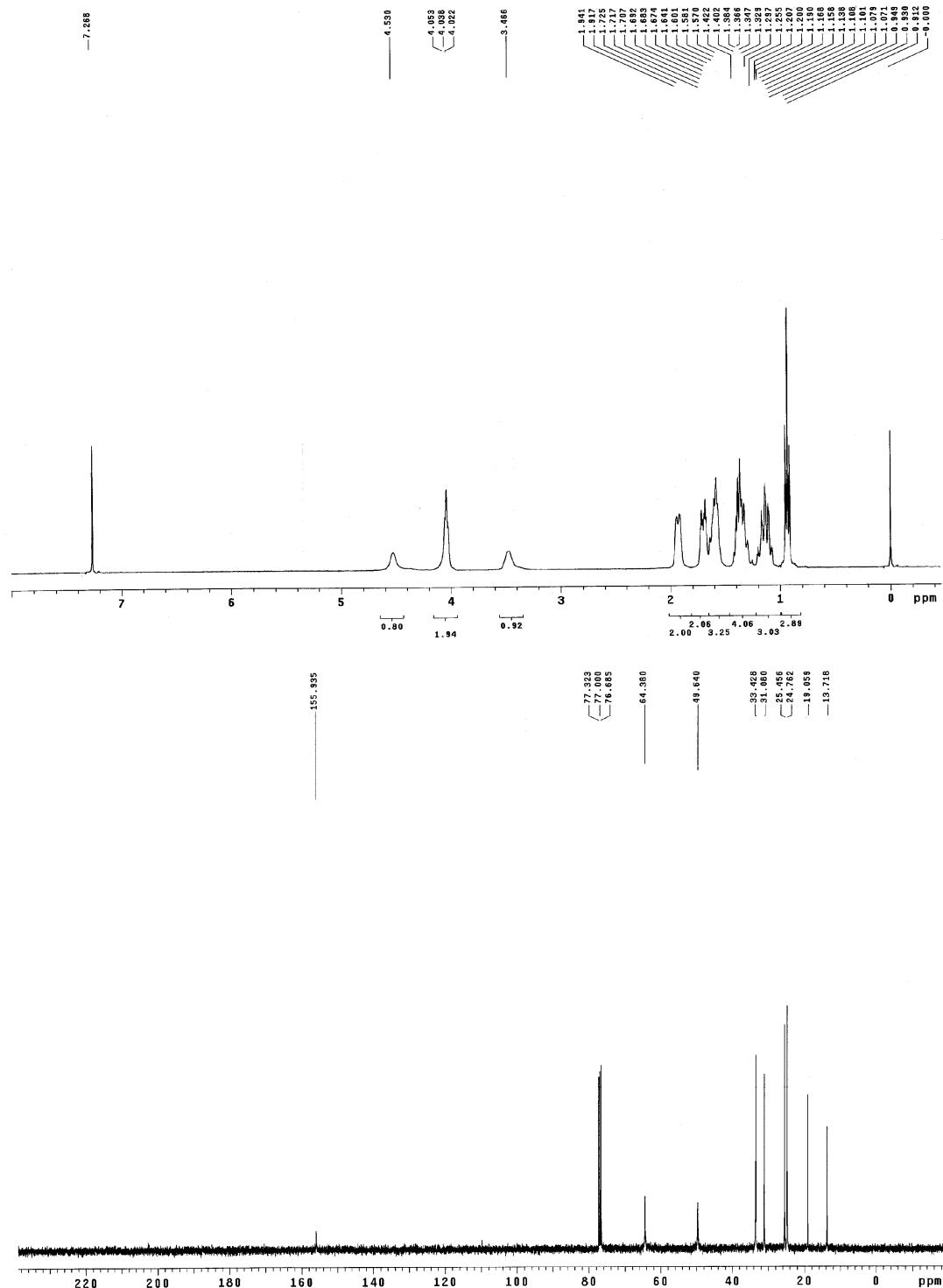
Dibutyl isophorone dicarbamate:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ,

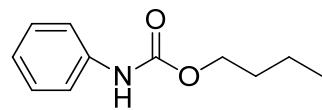
400 MHz):  $\delta$  = 0.78-1.08 (m, 15H), 1.19-1.89 (m, 14H), 2.91-2.93 (d, 2H), 3.81 (s, 1H), 4.04-4.05 (m, 4H), 4.50 (s, 1H), 4.78 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 13.8, 14.1, 19.0, 23.1, 27.6, 29.6, 31.0, 31.8, 35.0, 36.3, 41.9, 44.5, 46.4, 47.0, 54.8, 64.5, 64.7, 156.0, 157.1. MS, m/z : 41 (17%), 55 (13%), 62 (22%), 81 (13%), 110 (10%), 118 (34%), 123 (100%), 184 (18%), 241 (23%), 269 (15%).





Butyl cyclohexylcarbamate:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz):  $\delta$  = 0.91-0.95 (t, 3H), 1.07-1.21 (m, 2H), 1.26-1.42 (m, 4H), 1.57-1.64 (m, 4H), 1.73-1.67 (m, 2H), 1.92-1.94 (m, 2H), 3.47 (s, 1H), 4.02-4.05 (t, 2H), 4.53 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  = 13.7, 19.1, 24.8, 25.5, 31.1, 33.4, 50.0, 64.4, 156.0. MS, m/z : 29 (35%), 41 (62%), 56 (93%), 62 (35%), 83 (21%), 100 (26%), 118 (15%), 142 (51%), 156 (100%), 199 (12%).





Butyl N-phenylcarbamate:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz, ):  $\delta$  = 0.94-0.97 (t, 3H), 1.39-1.47 (m, 2H), 1.60-1.70 (m, 2H), 4.15-4.19 (t, 2H), 6.60 (s, 1H), 7.04-7.07 (t, 1H), 7.28-7.32 (t, 2H), 7.37-7.39 (d, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz, ):  $\delta$  = 13.7, 19.0, 30.9, 65.0, 118.6, 123.2, 129.0, 138.0, 153.8. MS, m/z : 29 (18%), 41 (28%), 57 (28%), 65 (25%), 77 (21%), 93 (96%), 106 (10%), 120 (15%), 137 (48%).

