

Co(acac)₃/BMMImCl as a base-free catalyst system for clean syntheses of *N,N'*-disubstituted ureas from amines and CO₂

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A base-free catalyst system Co(acac)₃/BMMImCl was developed for the carbonylation of amines with CO₂. 45%–81% isolated yields for *N,N'*-dialkylureas and 6%–23% isolated yields for *N,N'*-diaryureas were obtained. The catalyst system was recovered and reused without significant loss in activity. In this catalyst system, the base catalyst and chemical dehydrant were efficiently avoided. Different reaction conditions were also discussed and a postulated mechanism was proposed.

ionic liquids, base-free, *N,N'*-disubstituted ureas, amines, CO₂

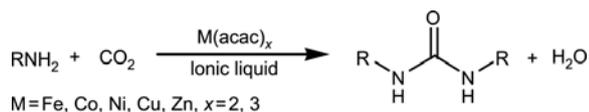
1 Introduction

N,N'-disubstituted ureas are significant chemical intermediates and industrial raw materials. They are widely used in the syntheses of herbicides, pesticides, pharmaceuticals and plant growth regulators [1–3]. Recently, *N,N'*-disubstituted ureas were considered to be one of the significant intermediates for the non-phosgene synthesis of polyurethane. In general, *N,N'*-disubstituted ureas were synthesized by the reaction of the corresponding amine with phosgene [4], isocyanate [5, 6], urea [7], or a mixture of CO and oxygen via oxidative carbonylation [8–10]. In the past decades, the utilization and fixation of CO₂ attracted wide attention because of its abundant, nontoxic, renewable and economic characteristics [11–14]. Using CO₂ as the carbonyl source for the production of *N,N'*-disubstituted ureas has also been extensively studied [15–19]. This is an ideal route from both an environmental and economic standpoint. However, only low to moderate activity was obtained for most catalyst

systems in this process. The incorporation of large amounts of chemical dehydrants (i.e., P₂S₅, HPO(OPh)₂, MeNSO₃, etc.) and strong bases (i.e., NEt₃, DBU, etc.) is worse [20–23]. Thus, the development of effective catalysts for the syntheses of *N,N'*-disubstituted ureas with CO₂ as the carbonyl source is highly desirable.

In our previous report, a catalyst system CsOH/BMImCl has been developed for the synthesis of *N,N'*-disubstituted ureas from amines and CO₂ with excellent yields [24]. In this catalyst system, BMImCl acts as a physical dehydrant instead of a chemical dehydrant and can be reused. However, a strong base CsOH was used, which has some drawbacks such as corrosion, deactivation, and maybe the destructive action to BMImCl under high temperature [25]. Herein, we developed a new efficient catalyst system, i.e., M(acac)_x/BMMImCl (M=Co, Ni, Fe, Cu, Zn), for the carbonylation of amines and CO₂ (Scheme 1), in which the strong base and the chemical dehydrants were completely avoided. Due to the significance of diphenylmethane diisocyanate (MDI) in industry, the carbonylation of aniline with CO₂ to *N,N'*-diphenylurea (DPU), which is the precursor for the non-phosgene synthesis of MDI, was chosen as a model

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Scheme 1 Syntheses of *N,N'*-disubstituted ureas from amines and CO₂.

reaction in this work.

2 Experimental

2.1 Reagents and instruments

Cobaltic acetylacetonate [Co(acac)₃] and tri(ethylenediamine) cobalt chloride [Co(en)₃Cl₃] were purchased from Acros Organics. Bis(cyclopentadienyl) cobalt [Co(C₅H₅)₂], tris(ethylenediamine) cobalt chloride [Co(dien)₃Cl₃], cobalt hexafluoro-2,4-pentanedionate [Co(C₅HF₆O₂)₂], and cobaltic 2,2,6,6-tetramethyl-3,5-heptanedionate [Co(C₁₁H₂₀O₂)₂] were purchased from Alfar Aesar. All the other chemicals were of AR grade and used as received. Qualitative and quantitative analyses were carried out with GC-MS (HP 6890/5973) and GC-FID (Agilent 6820, 1,4-dioxane was used as an internal standard). ¹H NMR spectra were recorded on a Bruker AMX 400 MHz spectrometer. The chemical shifts are reported relative to TMS. An IRIS Advantage ER/S inductively coupled plasma emission spectrometer (ICP-AES, TJA, USA) (RF power supply: 1.05 kW, Ar carrier gas flow rate 0.6 L min⁻¹, Ar auxiliary gas flow 1.0 L min⁻¹, Ar coolant gas flow rate 14.0 L min⁻¹, viewing height 15 mm, wavelength of element Co 228.616 nm) was used for cobalt ion determination after the catalyst system was reused for the third time. IR spectra were performed on a Thermo Nicolet 5700 FT-IR spectrophotometer in the region 400–4000 cm⁻¹. The samples were analyzed as films on the potassium bromide plates.

2.2 Preparation of ionic liquids

Ionic liquids BMImCl (1-butyl-3-methylimidazolium chloride), BMMImCl (1-butyl-2,3-dimethylimidazolium chloride), BMMImBr (1-butyl-2,3-dimethylimidazolium bromide), BMImBF₄ (1-butyl-3-methylimidazolium tetrafluoroborate), MMImBF₄ (1-butyl-2,3-dimethylimidazolium tetrafluoroborate), BMImNTf₂ (3-butyl-1-methylimidazolium) and BMMImNTf₂ (2-dimethylimidazolium bis(trifluoromethylsulfonyl) imide) were synthesized according to previous reports [26–28].

2.3 Typical procedure for the syntheses of *N,N'*-disubstituted ureas

Co(acac)₃ (0.2 mmol), BMMImCl (20 mmol) and amine (20 mmol) were added into a 90 mL stainless steel autoclave equipped with a magnetic stirrer. It was refreshed with CO₂ for three times, 5 MPa CO₂ was charged and reacted at

160 °C for 10–12 h. After that, the reactor was cooled to room temperature and the CO₂ was released slowly. Then, 10 mL acetonitrile or acetone and 20 mmol (1.76 g) of 1,4-dioxane (internal standard) were added into the reaction mixture and analyzed by GC-MS and GC-FID. Subsequently, 20 mL of distilled water was added and the product was precipitated gradually. After filtrated and washed by acetonitrile/water or acetone/water (1:2, 10 mL × 3), the final product was obtained.

2.4 Recycling of Co(acac)₃/BMMImCl

Acetonitrile/acetone, 1,4-dioxane and water were removed from the filtrate obtained above by rotary evaporation at 70–100 °C. Then the Co(acac)₃/BMMImCl mixture was washed by diethyl ether (15 mL × 4). After vacuum drying at 100 °C for 3 h, fresh aniline was added for the next run.

3 Results and discussion

3.1 Catalyst screening

Table 1 shows that only 10% aniline conversion with 60% DPU selectivity was obtained in the presence of BMMImCl (entry 1). Then various catalysts including Co(acac)₃, Ni(acac)₂, Fe(acac)₃, Cu(acac)₂ and Zn(acac)₂ were employed and 15%–25% aniline conversions with 87%–93% DPU selectivities were obtained (entries 2–7). Among all the metal complexes, Co(acac)₃ exhibited relatively higher catalytic activity, i.e., 25% conversion and 88% selectivity.

Table 1 Catalyst screening for the synthesis of DPU in BMMImCl*

Entry	Cat.	Con. (%) ^{a)}	Sel. (%) ^{b)}	Yield (%) ^{c)}
1	none	10	60	6
2	Fe(acac) ₃	19	89	17
3	Co(acac) ₂	15	93	14
4	Ni(acac) ₂	23	87	20
5	Cu(acac) ₂	17	88	15
6	Zn(acac) ₂	17	88	15
7	Co(acac) ₃	25	88	22
8	CoCl ₂	3	–	–
9	Co(AcO) ₂	20	90	18
10	Co(NO ₃) ₂ ·3H ₂ O	6	67	4
11	Co(en) ₃ Cl ₃	17	82	14
12	Co(CF ₃ COO) ₂	7	57	4
13	Co(C ₅ H ₅) ₂	18	83	15
14	Co(dien) ₃ Cl ₃	5	60	3
15	Co(C ₅ HF ₆ O ₂) ₂	17	71	12
16	Co(C ₁₁ H ₂₀ O ₂) ₂	15	87	13

*Reaction conditions: aniline 20 mmol, CO₂ 5 MPa, catalyst 0.2 mmol, BMMImCl 20 mmol, 160 °C, 12 h. a) The conversion of aniline determined by GC-FID with 1,4-dioxane as the internal standard; b) isolated yield of DPU/conversion of aniline; c) isolated yield to DPU.

The catalytic activities of other cobalt salts, i.e., $\text{Co}(\text{C}_5\text{H}_5)_2$, $\text{Co}(\text{dien})_3\text{Cl}_3$, $\text{Co}(\text{C}_5\text{HF}_6\text{O}_2)_2$, $\text{Co}(\text{C}_{11}\text{H}_{20}\text{O}_2)_2$, CoCl_2 , $\text{Co}(\text{AcO})_2$, and $\text{Co}(\text{NO}_3)_2$, were also investigated. However, only 3%–20% aniline conversions were obtained (entries 8–16), which were apparently lower than that using $\text{Co}(\text{acac})_3$. In these reactions, a detectable amount of phenyl isocyanate (PI) was also formed.

3.2 Solvent screening

The effect of several solvents was investigated and the results were shown in Table 2. No DPU (<1% yield) formed if solely $\text{Co}(\text{acac})_3$ was used without addition of the solvent, although 7% conversion for aniline was observed (entry 1). By applying THF, toluene, or DMF as solvents, similar results were obtained and *N*-phenyl formamide and phenyl isocyanate as the main products were observed through GC-MS (entries 2–4). Furthermore, several ionic liquids based on imidazolium cations were used in this reaction (entries 5–11). When ionic liquids based on BF_4^- and NTf_2^- anions were employed, the yield to DPU was <2% and *N*-methylaniline and phenyl isocyanate were the major by-products. To our delight, ionic liquids with Cl^- and Br^- anions could apparently improve the catalytic efficiency. The aniline conversion was 15%–24% and the selectivity to DPU reached 60%–92%. Among them, the reaction performed in BMMImCl gave the best result, i.e., 24% aniline conversion with 92% DPU selectivity. The strong hydrogen bond between ionic liquid BMMImCl and H_2O was the possible reason for its high activity [29–31], which could promote dehydration of the reaction intermediate to yield DPU.

3.3 The effect of reaction temperature

The influence of reaction temperature on the synthesis of

Table 2 Solvents screening for the synthesis of DPU*

Entry	Solvents	Con. (%) ^{a)}	Sel. (%) ^{b)}	Yield (%) ^{c)}
1	none	7	–	<1
2	THF	3	–	<1
3	Toluene	4	–	<1
4	DMF	8	–	<1
5	BMImBF ₄	22	–	<1
6	BMImNTf ₂	7	–	<1
7	BMMImNTf ₂	8	–	<1
8	BMMImBF ₄	17	12	2
9	BMImCl	15	60	9
10	BMMImCl	24	92	22
11	BMMImBr	16	75	12

*Reaction conditions: aniline 20 mmol, CO_2 5 MPa, $\text{Co}(\text{acac})_3$ 0.2 mmol, solvent 20 mmol, 160 °C, 10 h. a) The conversion of aniline determined by GC-FID with 1,4-dioxane as the internal standard; b) isolated yield of DPU/conversion of aniline; c) isolated yield to DPU.

DPU is shown in Figure 1. The conversion of aniline (X_{An}) increased from 15% to 27% when the reaction temperature was raised from 150 °C to 190 °C. The DPU selectivity (S_{DPU}) increased initially and reached the maximum of 92% at 160–170 °C. If the reaction temperature was further increased, the DPU selectivity decreased and *N*-methylaniline or *N,N*-dimethylaniline formed due to the decomposition of BMMImCl. The highest DPU yield (22%, Y_{DPU}) was obtained at 160 °C. Therefore, 160 °C is appropriate for this reaction.

3.4 The effect of reaction time

The results for the synthesis of DPU from CO_2 and aniline with different reaction time are shown in Figure 2. It suggests that 10 h is suitable for this reaction. The DPU yield was not improved further with the reaction time prolonged to 16 h and the selectivity decreased from 94% to 84%, in which more phenyl isocyanate formed through the thermal decomposition of DPU.

3.5 The effect of reaction pressure

The pressure of CO_2 also has great effect on the reaction and the results with varied CO_2 pressures are presented in

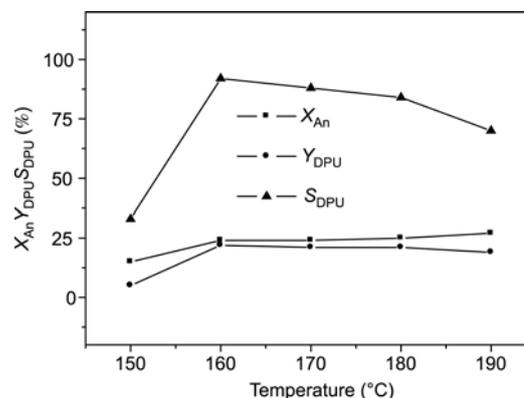


Figure 1 The effect of temperature on the synthesis of DPU.

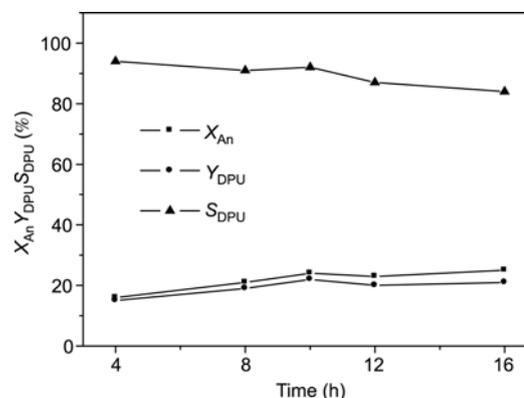


Figure 2 The effect of reaction time on the synthesis of DPU.

Table 3. When the CO₂ pressure was increased from 1 MPa to 5 MPa, both the conversion of aniline and the yield of DPU increased correspondingly. This indicates that higher CO₂ pressure was beneficial to the reaction. However, for safety consideration, an initial CO₂ pressure of 5 MPa was adopted in our studies, which could provide a pressure of 8–10 MPa during the reaction.

3.6 The substrate scope

After the optimization of reaction conditions, the universality of the catalyst for various aromatic and aliphatic amines was studied over Co(acac)₃/BMMImCl catalyst system and the results are shown in Table 4. When several aromatic amines were separately used in this reaction, 7%–28% conversion with 77%–90% urea selectivity was obtained, in

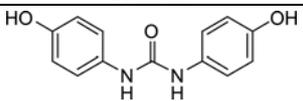
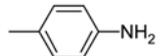
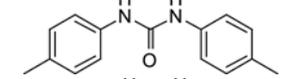
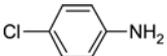
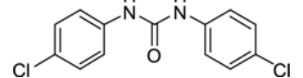
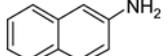
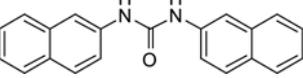
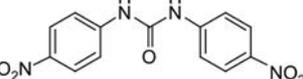
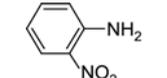
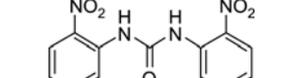
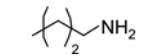
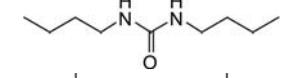
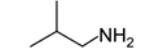
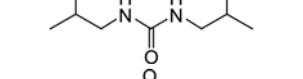
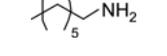
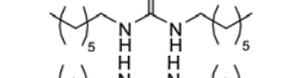
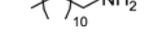
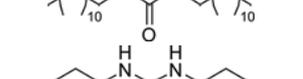
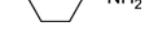
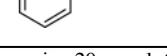
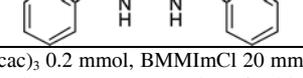
which the aromatic amines with an electron-donating group gave higher conversion than those with an electron-withdrawing group (entries 1–6). For example, the yields of *N,N'*-bis(4-hydroxyphenyl)urea and *N,N'*-bis(4-methylphenyl)urea were both 23%, while the yields of *N,N'*-dinaphthyl-

Table 3 Effect of initial CO₂ pressure on the synthesis of DPU*

Initial CO ₂ pres. (MPa)	Con. (%) ^{a)}	Sel. (%) ^{b)}	Yield (%) ^{c)}
1	15	27	4
3	17	65	11
5	24	92	22

*Reaction conditions: aniline 20 mmol, Co(acac)₃ 0.2 mmol, BMMImCl 20 mmol, 160 °C, 10 h. a) The conversion of aniline determined by GC-FID with 1,4-dioxane as the internal standard; b) isolated yield of DPU/conversion of aniline; c) isolated yield to DPU.

Table 4 Scope and limitations for the syntheses of *N,N'*-disubstituted ureas*

	Reactants	Products	Con. (%) ^{a)}	Sel. (%) ^{b)}	Yield (%) ^{c)}
1			28	82	23
2			27	85	23
3			21	90	19
4			13	77	10
5			8	88	7
6			7	86	6
7			85	91	77
8			73	92	67
9			72	92	66
10			53	85	45
11			86	94	81
12			76	89	68

* Reaction conditions: amine 20 mmol, CO₂ 5 MPa, Co(acac)₃ 0.2 mmol, BMMImCl 20 mmol, 160 °C, 10 h. a) The conversion of aniline determined by GC-FID with 1,4-dioxane as the internal standard; b) isolated yield to DPU/conversion of aniline; c) isolated yield to DPU. For the ¹H NMR spectral characterizations for most of the products see [36].

lurea, *N,N'*-bis(4-nitrophenyl)urea and *N,N'*-bis(2-nitrophenyl)urea were 10%, 7%, and 6%, respectively. If aliphatic amines such as *n*-butylamine, isobutylamine, 1-heptylamine, 1-dodecylamine, cyclohexylamine, and benzylamine were employed, much higher yields to the corresponding products, i.e., 45%–81%, were obtained (entries 7–12). The above results also show that the aliphatic amines have much higher reactivity than the aromatic amines, and the reactivity of aliphatic amines employed in this reaction decreased in the following order: *N,N'*-dicyclohexylurea > *N,N'*-di-*n*-butylurea > *N,N'*-dibenzylurea > *N,N'*-diisobutylurea > *N,N'*-di-*n*-heptylurea > *N,N'*-di-*n*-dodecylurea, in which the *N,N'*-dicyclohexylurea gave the best results (86% conversion with 94% selectivity).

3.7 Recycling of catalysts

The recycling of $\text{Co}(\text{acac})_3/\text{BMMImCl}$ was also tested and the data are listed in Table 5. It was found that $\text{Co}(\text{acac})_3/\text{BMMImCl}$ could be recovered and reused after water and unreacted aniline were removed, and 18% DPU yield was obtained when it was reused for the third time. These results show that the $\text{Co}(\text{acac})_3/\text{BMMImCl}$ catalyst system could be used at least four times with a slight decrease in DPU yield. After the catalyst system was recycled for 4 times, the loss of BMMImCl was about 11% confirmed by an electronic analytical balance and the $\text{Co}(\text{acac})_3$ loss was 17% determined by ICP-AES, which may be responsible for the decrease of DPU yield. In our opinion, partial loss of the active components might occur during the post-treatment process. As shown in Figure 3, FT-IR spectroscopy illustrates that solely BMMImCl was detected in $\text{Co}(\text{acac})_3/\text{BMMImCl}$ catalyst system due to the very low content of $\text{Co}(\text{acac})_3$. The catalyst system remained basically invariable after the reaction. This result confirmed the stability of the catalyst during the reaction. Photos for the catalyst recovery procedure are shown in Figure 4.

3.8 Possible mechanisms

Based on the aforementioned results, we proposed a mechanism for this reaction (Scheme 2). Amines could react with carbon dioxide to form carbamic acid (I) and ammonium

Table 5 Recycling of $\text{Co}(\text{acac})_3/\text{BMMImCl}$ catalyst system*

Recycle time	Con. (%) ^{a)}	Sel. (%) ^{b)}	Yield (%) ^{c)}
fresh	24	92	22
1	22	91	20
2	20	95	19
3	20	90	18

*Reaction conditions: aniline 20 mmol, CO_2 5 MPa, $\text{Co}(\text{acac})_3$ 0.2 mmol, BMMImCl 20 mmol, 160 °C, 10 h. a) The conversion of aniline determined by GC-FID with 1,4-dioxane as the internal standard; b) isolated yield of DPU/conversion of aniline; c) isolated yield to DPU.

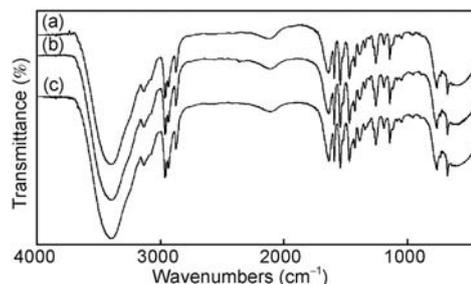


Figure 3 FT-IR spectra of catalyst samples. (a) BMMImCl ; (b) the unused $\text{Co}(\text{acac})_3/\text{BMMImCl}$; (c) the recovered $\text{Co}(\text{acac})_3/\text{BMMImCl}$.

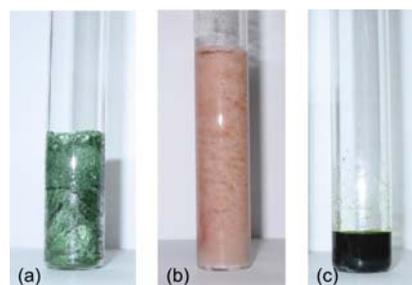
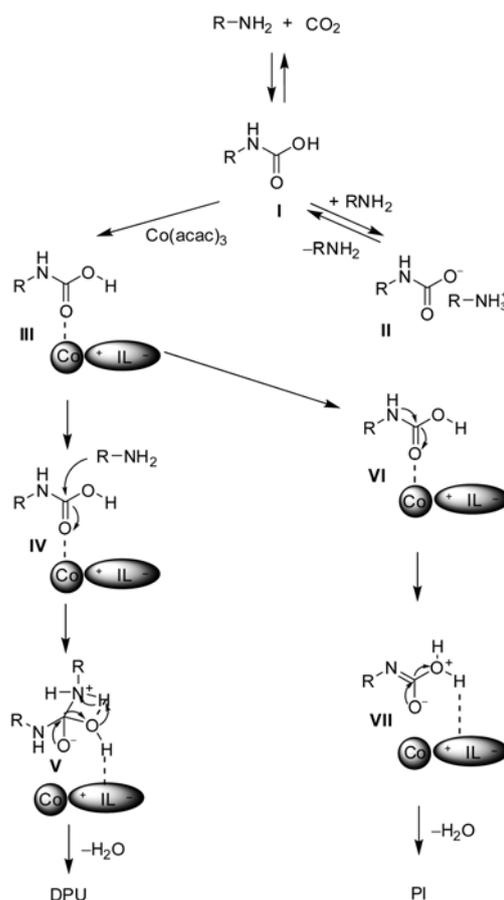


Figure 4 (a) The resulting mixture after the reaction of aniline with CO_2 ; (b) the precipitated DPU after acetonitrile/water was added into the resulting mixture; (c) the recovered $\text{Co}(\text{acac})_3/\text{BMMImCl}$ catalyst system.



Scheme 2 The proposed mechanism for the synthesis of DPU from aniline and CO_2 .

carbamate salts (II) [32]. Co(acac)₃ activated the carbonyl group of carbamic acid (III) [33–35]. It was followed by the nucleophilic attack of amine on the carbonyl carbon atom (IV) and then hydrophilic ionic liquid drew off water from transitional (V) by the hydrogen bond between the ionic liquid and water to obtain the product DPU. The proposed mechanism could also explain the formation of PI. After the activation of the carbonyl bond by Co(acac)₃ (VI), PI could be obtained via intramolecular dehydration (VII).

4 Conclusions

In summary, a base-free Co(acac)₃/BMMImCl catalyst system was developed for the syntheses of *N,N'*-disubstituted ureas from amines and CO₂. Good yields to *N,N'*-dialkylureas and acceptable yields to *N,N'*-diarylureas were obtained when the reaction was carried out at 160 °C for 10 h. In comparison with the reported catalyst systems, the Co(acac)₃/BMMImCl not only exhibits good catalytic performance but also avoids the use of strong organic base or a large amount of chemical dehydrants as sacrificial agents, which is more consistent with the rules of green chemistry.

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- 36 ¹H NMR spectral characterizations for most of the products are as follows:
- N,N'-Di-n-butylurea.** ¹H NMR (CDCl₃, 400 MHz): δ=0.90–0.94 (t, J=7.2, 6H), 1.32–1.39 (m, 4H), 1.43–1.51 (m, 4H), 3.13–3.18 (t, J=6.6, 4H), 4.69 (s, 2H).
- N,N'-Diisobutylurea.** ¹H NMR (CDCl₃, 400 MHz): δ=0.90–0.92 (d, J=6.4, 12H), 1.71–1.74 (m, 2H), 2.97–3.00 (t, J=6.2, 4H), 5.00 (s, 2H).
- N,N'-Di-n-heptylurea.** ¹H NMR (CDCl₃, 400 MHz): δ=0.86–0.89 (t, J=6.8, 6H), 1.27–1.30 (m, 16H), 1.45–1.50 (m, 4H), 3.12–3.16 (t, J=7.0, 4H), 4.597 (s, 2H).
- N,N'-Di-n-dodecylurea.** ¹H NMR (CDCl₃, 400 MHz): δ=0.86–0.90 (t, J=7, 6H), 1.25–1.29 (m, 36H), 1.48–1.51 (m, 4H), 3.13–3.17 (t, J=7, 4H).
- N,N'-Dicyclohexylurea.** ¹H NMR (CD₃SOCD₃, 400 MHz): δ = 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, J=8.4, 2H).
- N,N'-Dibenzylurea.** ¹H NMR (CD₃SOCD₃, 400 MHz): δ=4.20–4.21 (d, J=6.4, 4H), 6.41–6.44 (t, J=6, 2H), 7.19–7.31 (m, 10H).
- N,N'-Diphenylurea.** ¹H NMR (CD₃SOCD₃, 400 MHz): δ=6.95–6.99 (t, J=7.4, 2H), 7.26–7.30 (t, J=7.8, 4H), 7.45–7.47 (d, J=7.6, 4H), 8.66 (s, 2H).
- N,N'-Bis(4-methylphenyl)urea.** ¹H NMR (CD₃SOCD₃, 400 MHz): δ = 2.21 (s, 6H), 7.03–7.05 (d, J=8.4, 4H), 7.29–7.31 (d, J=8.4, 4H), 8.47 (s, 2H).
- N,N'-Bis(4-chlorophenyl)urea.** ¹H NMR (CD₃SOCD₃, 400 MHz): δ = 7.32–7.34 (d, J=8.8, 4H), 7.48–7.50 (d, J=8.8, 4H), 8.86 (s, 2H).
- N,N'-Bis(4-hydroxyphenyl)urea.** ¹H NMR (CD₃SOCD₃, 400 MHz): δ=6.63–6.65 (d, J=8.8, 4H), 7.15–7.17 (d, J=8.8, 4H), 8.15 (s, 2H), 8.99 (s, 2H).
- N,N'-Di-1-naphthylurea.** ¹H NMR (CD₃SOCD₃, 400 MHz): δ = 7.49–7.53 (t, J=7.8, 2H), 7.56–7.59 (t, J=7.2, 2H), 7.63–7.67 (m, 4H), 7.95–7.97 (d, J=8, 2H), 8.09–8.10 (d, J=7.6, 2H), 8.25–8.27 (d, J=8.4, 2H), 9.192 (s, 2H).
- N,N'-Bis(4-nitrophenyl)urea.** ¹H NMR (CD₃SOCD₃, 400 MHz): δ=7.72–7.74 (d, J=8.4, 4H), 8.22–8.24 (d, J=9.6, 4H), 9.69 (s, 2H).