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Hydrosilane-Assisted Synthesis of Urea Derivatives from CO₂ and Amines

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Cite This: https://dx.doi.org/10.1021/acs.joc.0c02032 **Read Online** ACCESS III Metrics & More [DI Article Recommendations **SUPPORTING Information** ABSTRACT: A methodology employing CO2, amines, and FeCl₃ TBD phenylsilane was discussed to access aryl- or alkyl-substituted CO₂ + R−NH₂ PhSiH₃ urea derivatives. This procedure was characterized by adopting (1 atm) hydrosilane to promote the formation of ureas directly, without the

that FeCl₃ was a favorable additive for the generation of ureas, and this 1,5,7-triazabicyclo[4.4.0]dec-5-ene-catalyzed reaction might proceed through nucleophilic addition, silicon migration, and the subsequent formal substitution of silylcarbamate.

rea and its derivatives are important industrial raw materials and chemical intermediates. A range of pharmaceuticals, plant growth regulators, herbicides, guanidinate ligands, and asymmetric catalysts can be synthesized from ureas.¹ Despite the importance of ureas and its scale of annual production, their industrial synthesis mainly depends on the reaction of amines with toxic phosgene or its equivalents.⁴ Alternatively, the traditional synthesis of ureas also involves the reaction of amines with isocyanates³ or CO.⁴ Inevitably, these traditional synthesis methods can cause environmental and toxicological problems to some extent. In recent years, many transition metals (e.g., Pd,⁵ Mn,⁶ W,⁷ Au,⁸ Ni,⁹ Ru,¹⁰ Co¹¹) catalyzed reactions have been gradually exploited for urea synthesis. Nevertheless, in order to develop an environmentally friendly synthesis method of ureas, the use of readily available raw materials is still a research direction that deserves more attention.

need to prepare silylamines in advance. Control reactions suggested

As a building block in the synthesis of urea derivatives, carbon dioxide (CO_2) refers to a nontoxic, renewable, and abundant one-carbon (C1) source, so the utilization of CO_2 gained much attention during the past decades.¹² The direct synthesis of urea derivatives using CO2 and amines is usually performed at high temperature (130–170 °C) or high pressure (14-140 atm) environments.¹³ In order to improve the synthesis of ureas, a series of effective reactions have been developed, with CO₂ as the raw material (such as ionic liquid,¹⁴ Au,¹⁵ Cs,¹⁶ and Ce catalysis¹⁷).

Recently, silanes and amines or silvlamines have been used as starting materials to realize the conversion of CO₂ to ureas, which has attracted the attention of chemists. In 2016, Choi's group applied $Zn(OAc)_2$ /phen as catalyst for the synthesis of carbamates from amines, CO2, and silicate esters (Scheme 1a).¹⁸ Later, they further developed a superbase-derived protic ionic liquid catalyzed reaction to synthesize carbamate from amines, CO_2 , and silicate esters.¹⁹ In these two studies, N,N'disubstituted urea was captured as a minor product. Different from the reaction of silvlamines and supercritical CO_2 (140

Scheme 1. Application of Silane in CO₂ Conversion

a) By Choi's group (ref. 18, 19) $\begin{array}{c} \text{or} \\ \hline [DBUH][OAc] (ref. 19) \\ \hline \text{phen} MeCN 150 \ \text{°C} \end{array} \xrightarrow{R} \begin{array}{c} \text{R} \\ \text{N} \\ \text{H} \end{array} \xrightarrow{R'} \begin{array}{c} \text{R} \\ \text{O} \\ \text{R'} \\ \text{H} \\ \text{H} \end{array} \xrightarrow{R'} \begin{array}{c} \text{R} \\ \text{N} \\ \text{H} \\ \text{H} \\ \text{H} \end{array} \xrightarrow{R'} \begin{array}{c} \text{R} \\ \text{N} \\ \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{array} \xrightarrow{R'} \begin{array}{c} \text{R} \\ \text{N} \\ \text{H} \\ \text{H$ R-NH₂ CO₂ Si(OR') phen, MeCN, 150 °C (50 atm.) b) By Stephan's group (ref. 20, 21) In(N(SiMe₃)₂)Cl₂·(THF)_n (2 or 5 mol%) Pyridine (2 or 5 mol%) CO₂ R-NHSiMe₃ 110 °C (3 atm.) silvlamines c) By Beller's group (ref. 22) BuPAd₂ (4 mol%) CH₃ [RuCl₂(dmso)₄] (2 mol%) CO₂ + R-NH₂ + PhSiH₄ PhMe, 100 °C сн₃ (138 atm.) Ad = adamantv d) Our previous work (ref. 23a) TBD + ZnCl₂ ŅHR³ CO_2 + R^1 - NH_2 + $PhSiH_3$ + Ē MeCN e) This work: FeCl₃ (10 mol%) TBD (10 mol%) CO₂ + R-NH₂ + PhSiH₃ THF, 110 °C (1 atm.)

atm) to furnish ureas,^{13d} Stephan and co-workers demonstrated a novel In-catalyzed reaction of pre-prepared silylamines with CO_2 (3 atm) to furnish ureas (Scheme 1b)²⁰ in 2017. Subsequently, an elegant synthesis method of urea

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derivatives from CO_2 (2–5 atm) and pre-prepared silylamines only with pyridine as the solvent was further developed by Stephan's group.²¹ Notably, Beller²² reported the methylation of amines combined with CO_2 (138 atm) and PhSiH₃ (Scheme 1c), and excess silane was indispensable for their methylation conversion. Combined with the above researches, we envisage that perhaps it is possible to introduce an appropriate amount of suitable silane to directly promote the reaction of CO_2 and amine for the formation of urea derivatives.

During the course of our ongoing program on the development of a methodology for the construction of heterocyclic molecules,²³ we developed a tandem methylenation–cyclization reaction, involving enaminone, primary aromatic amines, and two molecules of CO₂, to access tetrahydropyrimidines (Scheme 1d).^{23a} In this process, we discovered a new method for the formation of urea in the presence of amine, CO₂ (1 atm), and an appropriate amount of hydrosilane (Scheme 1e).

First, it was discovered that 1,3-diphenylurea was formed in 93% yield at 110 °C upon treatment of the model substrates (1a and CO₂) with 10 mol % of FeCl₃ and 1,5,7triazabicyclo[4.4.0]dec-5-ene (TBD) in THF (Table 1, entry 1, $PhSiH_3$ 1.5 equiv). When the amount of phenylsilane was reduced, the yield decreased as well (entries 2-4). Using 1.2 equiv of phenylsilane could still obtain 2a with excellent yield; therefore, we decided to use 1.2 equiv of phenylsilane for follow-up investigations. At 90 °C, only a small amount of 2a was obtained (entry 5, 24%). This result suggests that the reaction might proceed by the thermal access. Using other solvents (e.g., 1,4-dioxane, acetonitrile, and DMF) instead of THF could not give better results (entries 6-8), although acetonitrile and 1,4-dioxane also looked suitable for this reaction. Other common silanes, such as Ph₂SiH₂, Ph₃SiH, Et₂SiH, and polymethylhydrosiloxane (PMHS), could not effectively promote the formation of 2a. This may be related to the reduction ability of hydrosilane.²⁴ The influence of the catalyst on the reaction is also huge. When TBD was changed to glycine betaine (GB), 1,4-diazabicyclo[2.2.2]octane (DABCO), or pyridine, almost no target product was observed. For this transformation, 4-dimethylaminopyridine (DMAP) or 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was efficient, leading to 2a in 39% or 73% yield, respectively. Next, other acid catalysts were investigated (entries 19-23). However, only AgNO₃ could display a good catalytic effect (entry 23, 86%), while the yield was not as good as that catalyzed by FeCl₃ (entry 2). So, the optimal reaction conditions for the preparation of 2a included 10 mol % of TBD and FeCl₂ as the catalysts and 1.2 equiv of phenylsilane as the additive at 110 °C in THF. In addition, it is worth noting that, when the amount of FeCl₃ and TBD dropped from 0.1 to 0.05 equiv, 2a could also be obtained in 90% yield (entry 24: it will take longer).

In order to verify the necessity of each component, several control experiments were carried out (entries 25-27). Without PhSiH₃, no **2a** was obtained (entry 25 vs entry 2), indicating that PhSiH₃ was crucial for the formation of urea derivatives. When the reaction was conducted in the absence of TBD, the corresponding urea **2a** could not be observed (entry 3). Combined with existing reports,²⁵ this result revealed that TBD's activation to CO₂ is indispensable. A suitable Lewis acid catalyst is also required. To perform the reaction without ferric

Table 1. Optimization of the Reaction Conditions^a

CO₂ + Ph−NH₂ (1 atm) 1a		+ PhSiH ₃	Cat. (10 mol%) Additive (10 mol%)		O Ph C Ph		
			THF	THF, 110 °C		N [/] N [/]	
Entry	Silane (y eq.)	Solvent	Cat.	Additive	Time (h)	Yield ^b (%)	
1	PhSiH ₃ (1.5)	THF	TBD	FeCl ₃	24	93	
2	PhSiH ₃ (1.2)	THF	TBD	FeCl ₃	24	92	
3	PhSiH ₃ (1.0)	THF	TBD	FeCl ₃	24	88	
4	PhSiH ₃ (0.5)	THF	TBD	FeCl ₃	24	32	
5	PhSiH ₃ (1.2)	THF	TBD	FeCl ₃	24	24 ^c	
6	PhSiH ₃ (1.2)	1,4-dioxane	TBD	FeCl ₃	27	88	
7	PhSiH ₃ (1.2)	MeCN	TBD	FeCl ₃	27	86	
8	PhSiH ₃ (1.2)	DMF	TBD	FeCl ₃	27	trace	
9	Ph ₂ SiH ₂ (1.2)	THF	TBD	FeCl ₃	24	ND	
10	Ph ₃ SiH (1.2)	THF	TBD	FeCl ₃	24	ND	
11	Et ₃ SiH (1.2)	THF	TBD	FeCl ₃	24	ND	
12	EtO ₃ SiH (1.2)	THF	TBD	FeCl ₃	24	56	
13	PMHS (1.2)	THF	TBD	FeCl ₃	24	ND	
14	PhSiH ₃ (1.2)	THF	GB	FeCl ₃	24	ND	
15	PhSiH ₃ (1.2)	THF	DMAP	FeCl ₃	24	39	
16	PhSiH ₃ (1.2)	THF	DABCO	FeCl ₃	24	trace	
17	PhSiH ₃ (1.2)	THF	DBU	FeCl ₃	19	73	
18	PhSiH ₃ (1.2)	THF	Pyridine	FeCl ₃	21	ND	
19	PhSiH ₃ (1.2)	THF	TBD	ZnCl ₂	24	13	
20	PhSiH ₃ (1.2)	THF	TBD	AICI ₃	24	trace	
21	PhSiH ₃ (1.2)	THF	TBD	HOTf	22	ND	
22	PhSiH ₃ (1.2)	THF	TBD	BF ₃ ·Et₂O	40	45	
23	PhSiH ₃ (1.2)	THF	TBD	AgNO ₃	45	86	
24	PhSiH ₃ (1.2)	THF	TBD (<mark>5 mol</mark>	%) FeCl ₃ (5 mol%)	48	90	
25	-	THF	TBD	FeCl ₃	24	0	
26	PhSiH ₃ (1.2)	THF	-	FeCl ₃	24	0	
27	PhSiH ₃ (1.2)	THF	TBD	-	24	38	
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^{*a*}Reaction conditions: CO_2 (1 atm), 1a (0.75 mmol), 3 mL of THF as solvent. ^{*b*}Isolated yield, ND = no detected. ^{*c*}The reaction was carried out at 90 °C.

chloride, 2a was only isolated in 38% yield. This shows that ferric chloride is a favorable additive for the formation of ureas.

With the standard reaction conditions in hand (Table 1, entry 2) and by employing a variety of amines, the substrate scope of the reaction was explored. As shown in Table 2, the ureas derived from primary amines were obtained in good yields regardless of the nature of the substituents. Aniline derivatives bearing electron-donating (e.g., 4-NMe₂, 4-OMe, 3,4-dimethoxy, and 3,4,5-trimethoxy) groups were suitable for the reaction, offering the corresponding ureas 2b-2e in good yields. Alkyl-substituted phenyl was also compatible (2f-2h, 80-86%), even bearing sterically hindered *tert*-butylphenyl group. The substrates with electron-withdrawing (e.g., R = *p*-FPh, *p*-ClPh, *p*-BrPh, *p*-CO₂Et, *p*-CF₃) groups were also tolerable to furnish corresponding aryl-substituted urea derivatives (2i-2m, 69-82%). It is noteworthy that, when R was an alkyl substituent (such as, benzyl, *N*-butyl, and

Table 2. Scope of the Reaction⁴



^{*a*}The reactions were carried out under the optimized reaction conditions. ^{*b*}Isolated yield. ^{*c*}1.5 equiv of $PhSiH_3$ was used. ^{*d*}No **2s** was obtained, but further N-formylation product was observed.





cyclohexyl groups), the corresponding products were also obtained in good yields (2n-2p). The indole group could be introduced by adopting tryptamine (e.g., 5-methoxytrypt-amine) as starting material (2q, 73%), and the N-H part of the indole was compatible with the reaction. Treatment of

sterically hindered *o*-toluidine under the standard reaction conditions furnished 2r in 71% yield. An intramolecular cyclization reaction of 2-(aminomethyl)aniline 1s and CO₂ did not furnish 2s, but a further N-formylation product (from 2s) was observed, which is being investigated in our laboratory. When different amines are used simultaneously (e.g., 1c:1o = 1:1), 2c, 2o, and unsymmetric 1-butyl-3-(4-methoxyphenyl)urea were obtained as a mixture. It is worth noting that secondary amines (such as *N*-methylaniline and dibenzylamine) were not suitable to form ureas. The structure of the products was ascertained by nuclear magnetic resonance analysis and further confirmed by X-ray analysis of 2a.²⁶

Next, the reaction mechanism was explored and studied. Since the cross-dehydrocoupling of hydrosilanes with amines has been implemented,²⁷ we speculate that the corresponding silylamine may also be generated as the initial intermediate at high temperature in our reaction. Moreover, the pre-prepared silvlamines (e.g., RNH(SiMe₃)) reacted with CO₂ to prepare ureas and disilyl-ether (e.g., (Me₃Si)₂O), which has been proposed by Stephan²¹ (through a key silylcarbamate intermediate). Therefore, a seemingly feasible reaction path through the silvlamine and silvlcarbamate intermediates was presented to us. To further support this inference, ESI-MS analysis²⁸ was performed during the reaction process. After the reaction (1a with PhSiH₃ and CO₂, under the standard conditions) had progressed for 5 h, a sample was taken from the reaction mixture for ESI-MS analysis. Fortunately, the characteristic signals of the possible silylcarbamate PhNHCO2-SiH₂Ph and disilyl-ether (PhH₂Si)₂O were observed (see Figure S1), which suggests silylcarbamate may be a possible intermediate and implies the generation of disilyl-ether during the reaction process. It should be pointed out that, although we attempted to capture or isolate the possible, unstable silylamines,²⁹ no significant and clean products were observed. The remaining silicon-hydrogen bond may cause further transformation, which leads to the difficulty of separation of the corresponding intermediate.

On the basis of the above results and the well reported literatures, the possible reaction mechanism is depicted in Figure 1. Initially, cross-dehydrocoupling of hydrosilane with amines occurs to form silylamine I.²⁷ Subsequently, under the activation of hydrogen bond interaction, intermediate II is generated through the nucleophilic addition between CO₂ and $I.^{25}$ The N_{sp}^2 atom of TBD, as a Brønsted base, may grab the H atom of silvlamine I to facilitate this process. This similar catalytic process has also been suggested by Wang^{25a} and Cantat^{25b} in TBD-catalyzed reactions of amines with CO₂. Next, after a silicon migration,²¹ II is converted to intermediate III that further undergoes proton migration to afford silylcarbamates IV. Finally, a formal substitution process (IV to $2)^{20,21}$ between IV and additional silvlamine I proceeds to form ureas. In this procedure, ferric chloride, as a beneficial additive, may coordinate with the carbonyl group to enhance its electrophilicity,³⁰ which may promote the corresponding nucleophilic addition or substitution. Alternatively, the addition of amine 1 and CO2, followed by coupling with hydrosilane to form IV, might also be involved during the reaction.

CONCLUSION

In summary, we herein report on the reaction of CO_2 with amines and phenylsilane to furnish aryl- or alkyl-substituted urea derivatives. The characteristic of this synthetic method of ureas is to utilize silane directly, without the need to prepare silylamine in advance. Control experiments revealed that phenylsilane was indispensable and ferric chloride was a favorable additive for the formation of ureas. This TBDcatalyzed multicomponent reaction might proceed through nucleophilic addition of CO_2 with silylamine, silicon migration, and the subsequent formal substitution of silylcarbamate. Further investigations on the detailed reaction mechanism are in progress.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out in carbon dioxide except noted. Anhydrous 1,4-dioxane and tetrahydrofuran were distilled from sodium and benzophenone. Anhydrous acetonitrile and DMF were prepared by distillation from CaH₂. Compounds 1a-1s were purchased from Energy Chemical (Shanghai) Co. Ltd. Commercially, available reagents were used without further purification. Reactions were monitored by thin layer chromatography using UV light to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel (300-400 mesh). ¹H NMR spectra were recorded at 500 or 400 MHz; ¹³C NMR spectra were recorded at 125 or 100 MHz, and in CDCl₃ or (CD₃)₂SO (containing 0.03% TMS) solutions. ¹H NMR spectra were recorded with Me₄Si ($\delta = 0.00$) as the internal reference, and ¹³C NMR spectra were recorded with CDCl₃ (δ = 77.00) or DMSO- d_6 ($\delta = 39.52$) as the internal reference. High-resolution mass spectra were obtained using a Bruker Maxis Impact mass spectrometer with a TOF (for ESI) analyzer. Single crystal X-ray diffraction data were collected in Bruker SMARTAPEX diffractometers with molvbdenum cathodes.

Synthesis and Characterization of 2. To a well-dried 25 mL seal tube containing a magnetic stirring bar was added TBD (10.4 mg, 0.075 mmol). Then, the vessel was evacuated and refilled with CO₂ for five times. Under a stream of CO₂, to this vessel were added amine (0.75 mmol), THF (2.0 mL), PhSiH₃ (111 μ L, 0.9 mmol), and FeCl₃ (12 mg, 0.075 mmol). Then the vessel was sealed at atmospheric pressure of CO₂ (1 atm), and the resulting mixture was stirred in a 110 °C oil bath for the corresponding time (see Table 2). The reaction could be monitored by TLC analysis. The resulting mixture was concentrated under reduced pressure and subjected to column chromatography for purification directly.

1,3-Diphenylurea²⁰ (2a). White solid; 92% yield (73 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 5/1); mp: 229–230 °C; ¹H NMR (500 MHz, DMSO- d_6): δ 8.64 (s, 2H), 7.45 (d, J = 7.9 Hz, 4H), 7.29–7.26 (m, 4H), 6.98–6.95 (m, 2H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6): δ 152.5, 139.7, 128.8, 121.8, 118.2.

1,3-Bis(4-(dimethylamino)phenyl)urea²⁰ (**2b**). Yellow solid; 84% yield (94 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 1/1); mp: 236–238 °C; ¹H NMR (500 MHz, DMSO- d_6): δ 8.13 (s, 2H), 7.24 (d, J = 9.0 Hz, 4H), 6.68 (d, J = 8.9 Hz, 4H), 2.82 (s, 12H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6): δ 153.1, 146.2, 130.0, 119.9, 113.2, 40.8.

1,3-Bis(4-methoxyphenyl)urea²⁰ (2c). White solid; 81% yield (83 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 2/1); mp: 238–240 °C; ¹H NMR (500 MHz, DMSO-d₆): δ 8.36 (s, 2H), 7.34 (d, J = 9.0 Hz, 4H), 6.85 (d, J = 8.9 Hz, 4H), 3.71 (s, 6H); ¹³C{¹H} NMR (125 MHz, DMSO-d₆): δ 154.3, 152.9, 132.9, 119.9, 114.0, 55.2.

1,3-Bis(3,4-dimethoxyphenyl)urea³¹ (2d). Yellow solid; 88% yield (110 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 1/1); mp: 206–208 °C; ¹H NMR (500 MHz, DMSO- d_6): δ 8.40 (s, 2H), 7.19 (s, 2H), 6.86 (s, 4H), 3.74 (s, 6H), 3.71 (s, 6H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6): δ 152.8, 148.8, 143.9, 133.5, 112.5, 110.1, 103.9, 55.9, 55.4; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₇H₂₁N₂O₅ 333.1445; Found 333.1452.

1,3-Bis(3,4,5-trimethoxyphenyl)urea (**2e**). Yellow solid; 76% yield (112 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 1/1); mp: 164–165 °C; ¹H NMR (500 MHz, DMSO- d_6): δ 8.54 (s, 2H), 6.78 (s, 4H), 3.76 (s, 12H), 3.61 (s, 6H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6): δ 152.9, 152.5, 135.8, 132.5, 96.1, 60.1, 55.7; HRMS (ESI) *m/z*: [M + H]⁺ Calcd for $C_{19}H_{25}N_2O_7$ 393.1656; Found 393.1651.

*1,3-Di-p-tolylurea*²⁰ (2f). Yellow solid; 83% yield (75 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 8/1); mp: 243–245 °C; ¹H NMR (500 MHz, DMSO- d_6): δ 8.49 (s, 2H), 7.32 (d, J = 8.4 Hz, 4H), 7.07

(d, J = 8.2 Hz, 4H), 2.24 (s, 6H); ¹³C{¹H} NMR (125 MHz, DMSOd₆): δ 152.6, 137.2, 130.5, 129.1, 118.2, 20.3.

1,3-Bis(4-ethylphenyl)urea (2g). White solid; 80% yield (81 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 8/1); mp: 218–220 °C; ¹H NMR (500 MHz, DMSO- d_6): δ 8.50 (s, 2H), 7.34 (d, J = 8.4 Hz, 4H), 7.10 (d, J = 8.3 Hz, 4H), 2.54 (q, J = 7.5 Hz, 4H), 1.15 (t, J = 7.6Hz, 6H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6): δ 152.6, 137.4, 137.0, 127.9, 118.3, 27.5, 15.8; HRMS (ESI) m/z: [M + H]⁺ Calcd for C₁₇H₂₁N₂O 269.1648; Found 269.1650.

1,3-Bis(4-(tert-butyl)phenyl)urea³¹ (2h). White solid; 86% yield (105 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 10/1); mp: 267–268 °C; ¹H NMR (500 MHz, DMSO- d_6): δ 8.51 (s, 2H), 7.36 (d, J = 8.6 Hz, 4H), 7.28 (d, J = 8.6 Hz, 4H), 1.26 (s, 18H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6): δ 152.6, 144.0, 137.1, 125.3, 118.0, 33.9, 31.3. 1,3-Bis(4-fluorophenyl)urea³¹ (2i). Yellow solid; 69% yield (64

1,3-Bis(4-fluorophenyl)urea³¹ (2i). Yellow solid; 69% yield (64 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 5/1); mp: 260–262 °C; ¹H NMR (500 MHz, DMSO- d_6): δ 8.78 (s, 2H), 7.48–7.45 (m, 4H), 7.14–7.10 (m, 4H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6): δ 157.3 (d, *J* = 236.6 Hz), 152.8, 136.1 (d, *J* = 2.3 Hz), 120.0 (d, *J* = 7.6 Hz), 115.3 (d, *J* = 22.1 Hz).

1,3-Bis(4-chlorophenyl)urea²⁰ (2j). Yellow solid; 82% yield (86 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 5/1); mp: 245–247 °C; ¹H NMR (500 MHz, DMSO- d_6): δ 8.85 (s, 2H), 7.48 (d, J = 8.9 Hz, 4H), 7.33 (d, J = 8.8 Hz, 4H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6): δ 152.3, 138.5, 128.6, 125.5, 119.8.

1,3-Bis(4-bromophenyl)urea²⁰ (2k). White solid; 78% yield (108 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 5/1); mp: 292–294 °C; ¹H NMR (500 MHz, DMSO- d_6): δ 8.86 (s, 2H), 7.46–7.42 (m, 8H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6): δ 152.3, 139.0, 131.5, 120.2, 113.4.

Diethyl 4,4'-(*Carbonylbis(azanediyl))dibenzoate*³² (21). White solid; 73% yield (98 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 3/1); mp: 211–213 °C; ¹H NMR (400 MHz, DMSO- d_6): δ 9.19 (s, 2H), 7.90 (d, J = 8.8 Hz, 4H), 7.60 (d, J = 8.8 Hz, 4H), 4.28 (q, J = 7.1 Hz, 4H), 1.30 (t, J = 7.1 Hz, 6H); ¹³C{¹H} NMR (100 MHz, DMSO- d_6): δ 165.9, 152.3, 144.4, 130.8, 123.6, 118.0, 60.8, 14.7.

DMSO- d_6): δ 165.9, 152.3, 144.4, 130.8, 123.6, 118.0, 60.8, 14.7. 1,3-Bis(4-(trifluoromethyl)phenyl)urea³³ (**2m**). White solid; 69% yield (90 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 5/1); mp: 228–230 °C; ¹H NMR (400 MHz, DMSO- d_6): δ 9.22 (s, 2H), 7.70– 7.64 (m, 8H); ¹³C{¹H} NMR (100 MHz, DMSO- d_6): δ 152.1, 143.1, 126.1, 124.5 (q, J = 269.5 Hz), 122.2 (q, J = 32.2 Hz), 118.1. 1,3-Dibenzylurea²¹ (**2n**). White solid; 72% yield (65 mg), $R_f = 0.2$

1,3-Dibenzylurea²¹ (**2n**). White solid; 72% yield (65 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 5/1); mp: 157–159 °C; ¹H NMR (500 MHz, DMSO- d_6): δ 7.31–7.22 (m, 10H), 6.43 (s, 2H), 4.24 (d, J = 3.4 Hz, 4H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6): δ 158.1, 140.9, 128.2, 127.0, 126.6, 43.0.

1,3-Dibutylurea³⁴ (20). White solid; 75% yield (48 mg), $R_f = 0.3$ (petroleum ether/ethyl acetate/dichloromethane = 7/1/2); mp: 71– 72 °C; ¹H NMR (500 MHz, CDCl₃): δ 4.69 (s, br, 2H), 3.15 (t, J = 7.1 Hz, 4H), 1.50–1.44 (m, 4H), 1.38–1.31 (m, 4H), 0.92 (t, J = 7.4 Hz, 6H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 158.7, 40.2, 32.3, 20.0, 13.8.

1,3-Dicyclohexylurea³⁵ (**2p**). White solid; 68% yield (60 mg), $R_f = 0.3$ (petroleum ether/ethyl acetate/dichloromethane = 7/1/2); mp: 224–226 °C; ¹H NMR (400 MHz, DMSO- d_6): δ 5.57 (s, br, 2H), 3.52–3.25 (m, 2H), 1.72–1.51 (m, 10H), 1.25–1.06 (m, 10H); ¹³C{¹H} NMR (100 MHz, DMSO- d_6): δ 47.5, 33.3, 25.3, 24.4 (due to poor solubility, carbon atom in carbonyl group is not shown); HRMS (ESI) m/z: $[M + H]^+$ Calcd for C₁₃H₂₅N₂O 225.1961; Found 225.1964.

1,3-Bis(2-(5-methoxy-1*H*-indol-3-yl)ethyl)urea (**2q**). Colorless oil; 73% yield (111 mg), $R_f = 0.2$ (ethyl acetate); ¹H NMR (500 MHz, CDCl₃): δ 8.11 (s, 2H), 7.20 (d, J = 8.8 Hz, 2H), 7.05−6.93 (m, 2H), 6.84−6.83 (m, 4H), 4.37 (s, br, 2H), 3.82 (s, 6H), 3.39 (t, J = 6.3 Hz, 4H), 2.82 (t, J = 6.4 Hz, 4H); ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 153.9, 131.5, 127.7, 123.1, 112.6, 112.1, 112.0, 100.6, 55.9, 40.6, 25.7; HRMS (ESI) m/z: $[M + H]^+$ Calcd for C₂₃H₂₇N₄O₃ 407.2078; Found 407.2083.

1,3-Di-o-tolylurea³⁶ (2r). White solid; 71% yield (64 mg), $R_f = 0.2$ (petroleum ether/ethyl acetate = 5/1); mp 235–237 °C; ¹H NMR

(500 MHz, DMSO- d_6): δ 8.25 (s, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.19–7.13 (m, 4H), 6.97–6.94 (m, 2H), 2.27 (s, 6H); ¹³C{¹H} NMR (125 MHz, DMSO- d_6): δ 153.0, 137.5, 130.2, 127.7, 126.1, 122.7, 121.5, 18.1.

Gram-Scale Preparation (for 2a). To a well-dried 250 mL seal tube containing a magnetic stirring bar was added TBD (0.1044 g, 0.75 mmol). Then, the vessel was evacuated and refilled with CO₂ for five times. Under a stream of CO₂, to this vessel were added THF (20 mL), PhNH₂(0.68 mL, 7.5 mmol), PhSiH₃(1.1 mL, 9.0 mmol), and FeCl₃ (0.12 g, 0.75 mmol). Then the vessel was sealed at atmospheric pressure of CO₂ (1 atm), and the resulting mixture was stirred in a 110 °C oil bath for 36 h. The reaction could be monitored by TLC analysis. The resulting mixture was subjected to column chromatography for purification (petroleum ether/ethyl acetate = 5:1) to give pure 2a (0.65 g, 82%).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02032.

¹H and ¹³C NMR spectra for compounds **2** (PDF)

Crystallographic details for compound 2a (CIF)

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Notes

The authors declare no competing financial interest.

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