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CS_2/CO_2 Utilization Using Mukaiyama Reagent as a (Thio)carbonylating Promoter: A Proof-of-Concept Study

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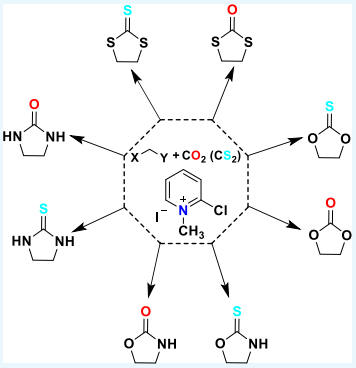
ABSTRACT: We report on the reaction of ethylene-terminated heteroatoms (C_2X; X = N, O, and S) with CS_2/CO_2 using Mukaiyama reagent (2-chloro-1-methylpyridinium iodide, CMPI) as a promoter for the preparation of imidazolidin-2-one, oxazolidin-2-one, 1,3-dioxolan-2-one, 1,3-dithiolan-2-one, and their thione counterparts at ambient temperature and pressure. Spectroscopic measurements, *viz.*, $^1H/^{13}C$ nuclear magnetic resonance (NMR) and *ex situ* attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy methods verified the reaction of CS_2/CO_2 with the ethylene-based substrates and subsequently the formation of cyclic products. The experimental data indicated the formation of the *enol*-form of imidazolidin-2-one and oxazolidin-2-one, while the *keto*-form was obtained for their thione correspondents. Furthermore, density functional theory calculations revealed the stability of the *keto*- over the *enol*-form for all reactions and pointed out the solvent effect in stabilizing the latter.



1. INTRODUCTION

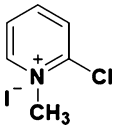
The utilization of CO_2 as a raw material for the production of intermediates/fine chemicals/value-added products is considered an attractive research theme that could be addressed in terms of market demands, economic feasibility, efficiency of using resources, and sustainability implications.[1−5] One of the common routes for CO_2 fixation is the cycloaddition (or copolymerization) of CO_2 with epoxide,[6] episulfide, or aziridine.[7,8] Moreover, it could be used for the synthesis of profitable products such as (a)cyclic urea/carbamate, isocyanate, carbonate, and their thione counterparts (in the case of CS_2) when reacted with simple amines or bifunctionalized scaffolds including diamines, amino alcohols, diols, and others.[9−22]

According to literature reports, olidine compounds were obtained by reacting phosgene[23] or urea with diamines[24] or amino alcohols.[25] Also, they were prepared upon catalyzing the reaction by Zn−Zr oxide,[26] triphenyl stibine oxide,[13,14] thiol/Fe_4S_4 cluster[12] or under catalyst-free conditions.[15] Moreover, ethylene urea or 2-pyrrolidone was used as the promoter for olidine synthesis.[27,28] (Thio)olidine compounds were synthesized using different sulfur-containing reagents (such as CS_2, thiophosgene, and isothiocyanate)[29] or elemental sulfur (S_8) with formaldehyde aminals,[30] silver carbene complex,[31] or chloroform.[32] In addition, olanes, e.g., cyclic carbonates, were prepared by the reaction of diols with CO_2 using a wide range of inorganic[33−36] and organic catalysts[37,38] or promoters.[18,19] For more details on the synthesis of olidine/olane compounds and their thiol analogues, see Table S1, Supporting Information.

The problems associated with the common (thio)-carbonylating agents such as phosgenes[39] and isocyanates[40] as well as conventional processes make it necessary to search for benign alternatives and safer methods to avoid potential catastrophes such as in Bhopal, India, 1984[41] and to eliminate toxic/hazardous byproducts.[42] Thus, green approaches are directed toward microwave-assisted,[43] solvent-free methods[44] by employing green carbonylating agents.[45−47] Interestingly, Dondoni group reacted CS_2 with monofunctionalized amine in the presence of triethylamine (Et_3N) and 2-chloro-1-methylpyridinium iodide, [Mukaiyama reagent (CMPI), Scheme 1] to prepare isothiocyanate.[48]

In this context, *N*-alkyl-2-halopyridinium salts have been used as promoters for the synthesis of different compounds[49,50] such as esters,[51−53] ketenes,[54,55] lactones,[56,57] lactams,[58−60]

Scheme 1. Chemical Structure of CMPI



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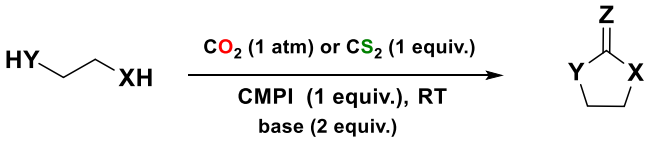
peptides,[61] amides,[62] carbodiimides,[63] thiocyanates,[64] pyrazole derivatives,[65] and different polymeric materials.[66]

The success story of CMPI lies in the fact that it acts as an oxygen sink, converting the bad leaving group into a good one upon a simple nucleophilic addition−elimination reaction. This might be a plausible gateway for synthetic chemists to use it as a (thio)carbonylation promoter. To our knowledge, there is no precedented route for the preparation of tailor-made, benign, non-phosgene intermediates, *viz.*, isocyanates from carbamates using CMPI, thus eliminating the toxicity associated with well-known hazardous materials.

As an augmentation to our research efforts on CO_2 capture using biorenewables,[67−72] biomaterials,[73,74] and small organic molecules/oligomers,[75,76] as well as CO_2 utilization catalyzed by poly(ionic liquid)s,[77] organocatalysts,[78] and metal oxide/inorganic complexes,[79−81] we provide a platform for the synthesis of olidines and olanes, including imidazolidin-2-one, oxazolidin-2-one, 1,3-dioxolan-2-one, 1,3-dithiolan-2-one, and their sulfur counterparts upon reacting CO_2 (CS_2) with ethylenediamine (*en*), monoethanolamine (MEA), ethylene glycol (EG), and ethane-1,2-dithiol (EDT), respectively, in the presence of CMPI as shown in Scheme 2.

Scheme 2. Proposed Synthesis of Functionalized Olidine/Olane Using CMPI as a (Thio)carbonylation Promoter



X = NH, Y = NH, Z = O (1) X = O, Y = O, Z = O (5)
X = NH, Y = NH, Z = S (2) X = O, Y = O, Z = S (6)
X = NH, Y = O, Z = O (3) X = S, Y = S, Z = O (7)
X = NH, Y = O, Z = S (4) X = S, Y = S, Z = S (8)

2. RESULTS AND DISCUSSION

2.1. Synthesis of Imidazolidin-2-one (1). Upon bubbling CO_2 in *en*/DCM solution for 60 min, a white precipitate was obtained. As shown in Figure 1, the ^{13}C NMR spectrum of the product measured in deuterium oxide (D_2O) indicated the formation of an ammonium carbamate adduct as inferred from the chemical shift at 164.5 ppm (blue trace).[82] The decomposition of the obtained adduct into ammonium bicarbonate was detected due to the emergence of a new peak at 160.4 ppm.[83] This was verified using labeled sodium bicarbonate ($NaH^{13}CO_3$) (Figure S1, Supporting Information). The formation of the carbamate adduct was further supported by *ex situ* ATR-FTIR measurements of the precipitate that indicated the appearance of a new peak at 1660 cm^{-1}, which was assigned for the carbonyl group of the CO_2 adduct,[82] as well as the disappearance of the asymmetric stretching frequency peak of the primary amine group upon carbamation (Figure S2, Supporting Information).

In order to attain compound **1**, the carbamate adduct was mixed with a solution of CMPI/DCM under N_2 atmosphere. Afterward, a yellow precipitate was obtained, which was dissolved in deuterated dimethyl sulfoxide (DMSO-d_6) and analyzed using ^{13}C NMR spectroscopy. For the sake of comparison, the spectra of the starting materials are shown in Figure 2. The chemical shifts associated with **C-3** to **C-7** of CMPI (green trace) showed an upfield shift upon the formation of the pyridinium carbamate salt; however, the **C-2** peak was downfield shifted from 146.9 to *ca.* 152.7 ppm (purple trace) due to the inductive effect of the activated carbamate.

Later on, Et_3N was added to the reaction mixture to drive the intramolecular attack of the terminal amine on the carbamate carbonyl by neutralizing the salt (*vide supra*) and subsequently deprotonating the proposed cyclic product **1** (black trace). The analysis of the reaction mixture verified the formation of (a) *N*-methyl-2-pyridinoate, as deduced from the chemical shift of the **C-2** peak from 152.7 to 143.0 ppm and (b) the *enol*-form of **1**, as **C3′** was upfield-shifted from 158.8 to 152.7 ppm. This was fortified by the new chemical shift of the protons located at carbons labeled **3**−**7** upon the formation of the pyridinium carbamate salt (Figure S3, Supporting Information). A representative reaction mechanism is proposed in Scheme 3.

The presumed reaction product **1** was separated from the reaction mixture, exploiting its ability to capture CO_2 in non-aqueous media.[76] Herein, the reaction crop was dissolved in DMSO, then sodium hydride (NaH) was added for activation purposes. The solution was bubbled with CO_2 until it became turbid. Upon adding concentrated hydrochloric acid to the filtrate dissolved in D_2O, ^{13}C NMR measurement confirmed the exclusive existence of **1** in the *keto*-form (Figure 3).

2.2. Synthesis of Imidazolidine-2-thione (2). Using the same reaction conditions, **2** was obtained using CS_2 instead of CO_2, where the formation of the ammonium ethylenethiocarbamate adduct was confirmed in DMSO-d_6 by the emergence of a new peak at 183.5 ppm (green trace, Figure 4).[84] This was supported by the ATR-FTIR measurements, which were consistent with the previously obtained spectrum of the carbamate adduct (Figure S4, Supporting Information).

However, the addition of CMPI to the thiocarbamate adduct produced the *enol* form of the thiopyridinium salt as deduced from the chemical shifts associated with **C3′** at 164.5 ppm (purple trace, Figure 4) and the thiol proton at 1.21 ppm (Figure S5, Supporting Information). In this respect, Nguyen and co-workers[85] reported on the stability of thiones and thiols in polar aprotic solvents and in the gas phase. The double bond between the carbon atom and the high electronegative heteroatom is energetically more stable than C═S. This makes our results show good agreement with the literature. In the cyclization step (upon adding Et_3N), *N*-methyl-2-pyridinethione acts as the leaving group to generate the *keto*- and *enol*-forms of **2** as indicated by peaks emerging at 183.4 [thione (−C═S)] and 152.7 [thiol (−C−SH)] ppm, respectively (black trace, Figure 4). Once again, the desired product was obtained upon activating the reaction crop by NaH, bubbling CO_2,[76] and then dissolving the obtained precipitate in D_2O. This was confirmed by ^{13}C NMR measurements of the solution together with the decarbonized species as shown in Figure 5 (green and black traces, respectively).

2.3. Synthesis of Oxazolidin-2-one (3). As shown in Scheme 4, the reaction of primary amines with CO_2 in non-aqueous media leads to the formation of an unstable zwitterionic intermediate that rapidly rearranges through intramolecular proton transfer to the produce carbamic acid (following a 1:1 mechanism). In the presence of an excessive amount of amine, the latter is rapidly deprotonated to form an ammonium carbamate adduct *via* a 2:1 mechanism. If DMSO is used as a reaction medium, carbamic acid is expected to be

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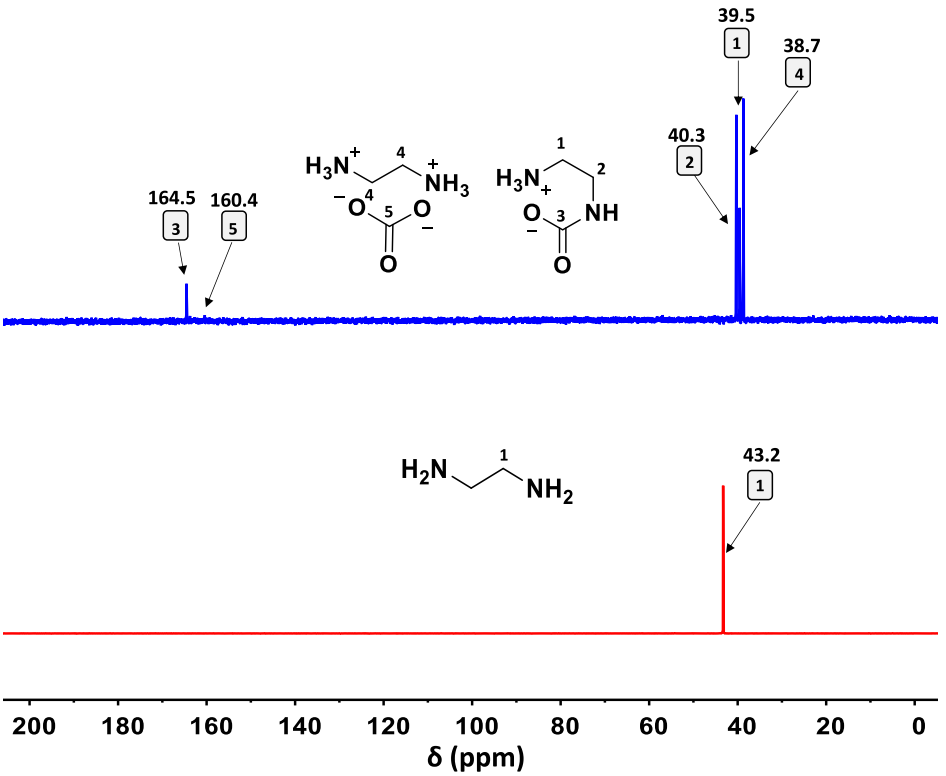

Figure 1. ^{13}C NMR spectra of *en* dissolved in D_2O before (red trace) and after bubbling (blue trace) with CO_2.

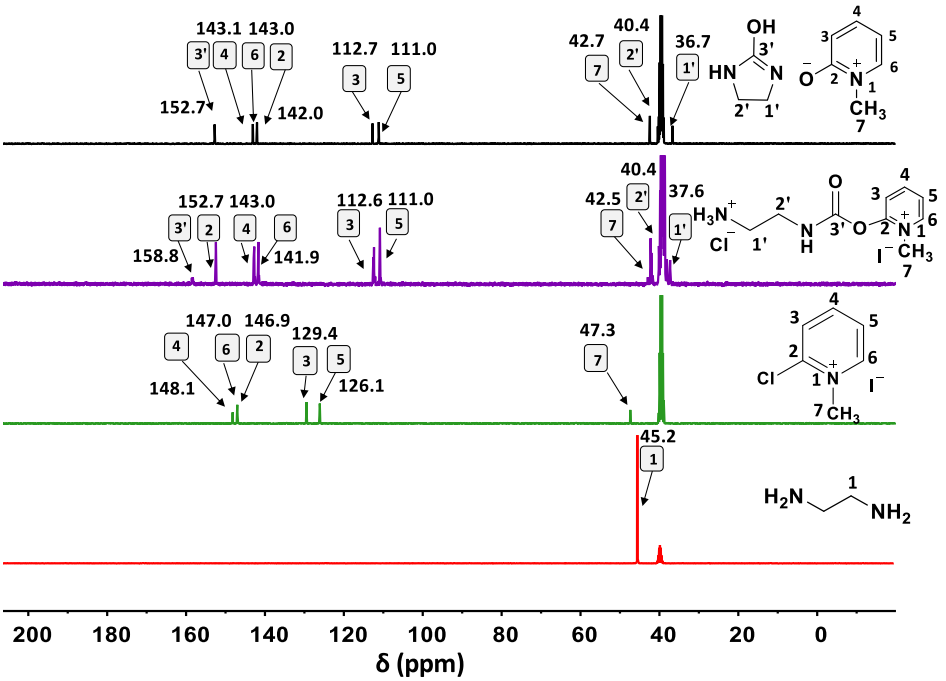

Figure 2. ^{13}C NMR spectra measured in DMSO-d_6 of *en* (red trace), CMPI (green trace), pyridinium carbamate salt (purple trace), and the reaction mixture (black trace).

the more favored product due to hydrogen-bonding interactions.[86] In our case, bubbling MEA/DMSO-d_6 solution with CO_2 resulted in a new peak at 158.5 ppm, which indicated the formation of carbamic acid, with a small amount of ammonium carbamate adduct (green trace, Figure S6, Supporting Information). This was fortified by the emergence of a new peak at 1700 cm^{-1} in the IR spectrum of the product (Figure S7, Supporting Information).

In order to prepare **3**, Et_3N and CMPI were added to the MEA-CO_2 adduct solution in DCM under N_2 atmosphere, where a white precipitate was collected after 1 h, which contained a mixture of oxazolidin-2-one (*enol* form) and *N*-methyl-2-pyridinoate as inferred from the chemical shift

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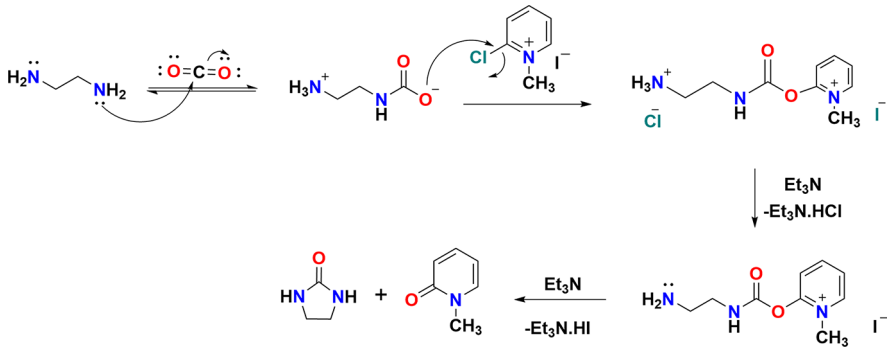
Scheme 3. Postulated Reaction Mechanism for *en* to Yield Ethylene Urea[a]



[a]The reaction is mediated *via* CMPI, which acts as the oxygen-sink promoter.

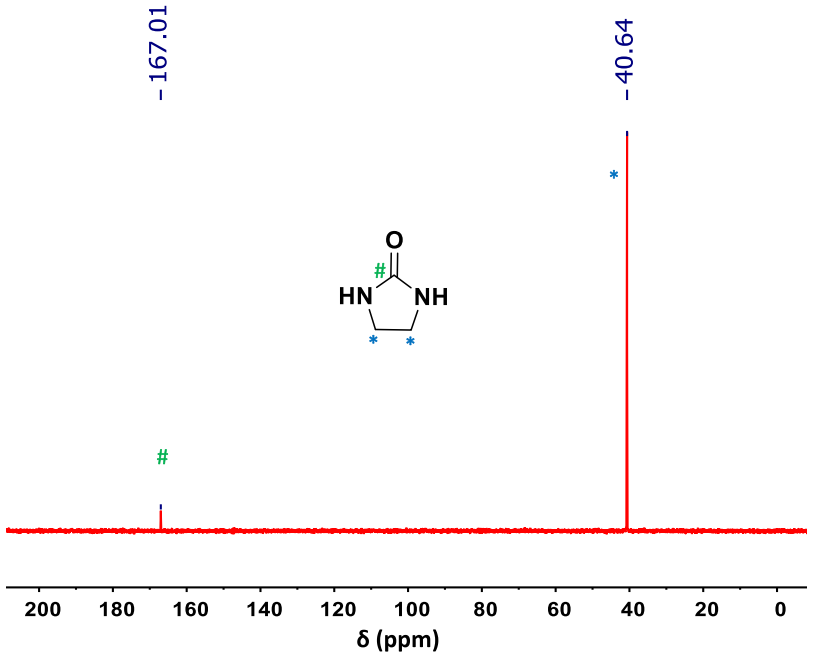


Figure 3. ^{13}C NMR spectrum measured in D_2O for **1**.

observed at 152.9 ppm together with an upfield shift of **C-3** to **C-7** of CMPI (black and purple traces, Figure S6, Supporting Information) as well as their protons (black trace, Figure S8, Supporting Information).

2.4. Synthesis of Oxazolidine-2-thione (4). In contrast to the MEA/CO_2 scenario, analyzing the viscous mixture MEA/CS_2 showed that thiocarbamate was the major product over the carbamic acid counterpart as demonstrated by the new peaks that emerged at 188.7 and 202.5 ppm, with the presence of a small amount of unreacted MEA (green trace, Figure S9, Supporting Information). This was confirmed by the newly emerged peaks at 2.88 and 3.58 ppm in the ^{1}H NMR spectrum (Figure S10, Supporting Information).

In order to obtain the thione target product, the carbamate adduct was reacted with CMPI in DCM. Analyzing the formed yellow precipitate indicated a mixture of **4** and *N*-methylpyridine-2-thione (black trace, Figure S9, Supporting Information), where the chemical shift of C═S in the product was observed at 188.6 ppm and that of pyridone was observed at 178.9 ppm. This finding was supported by an upfield shift of the protons located at carbons labeled **3**−**7** in the ^{1}H NMR spectrum (black trace, Figure S10, Supporting Information).

It is worth mentioning that these oxazolidine compounds do not absorb CO_2 successfully as the former diazolidine. This could be attributed to the resonance stabilization of the active enolate species and the less nucleophilic character of oxygen in comparison with nitrogen in cyclic urea. In the case of oxazolidine-2-thione, presumably, the presence of oxygen weakens the ability of the anion to react with the electrophilic carbon of CO_2. Unfortunately, several separation strategies such as metathesis with silver salts, extraction, thin layer (conventional and reversed phase) as well as column chromatography have been employed with no success in separating the oxazolidine compounds and the associated pyridinoate/pyridone.

2.5. Synthesis of 1,3-Dioxolan-2-one (5). In order to synthesize olanes, **5** was obtained by a two-step reaction, first, the activated EG with Et_3N was bubbled with CO_2 for 2 h to generate triethylammonium 2-hydroxyethyl carbonate, which was characterized by NMR and IR analyses. The ^{13}C NMR spectrum measured in DMSO-d_6 indicated the formation of the adduct, as inferred by the chemical shifts at 61.0, 66.4, and 158.0 ppm (green trace, Figure S11, Supporting Information). These results were supported using ^{1}H NMR analysis by the

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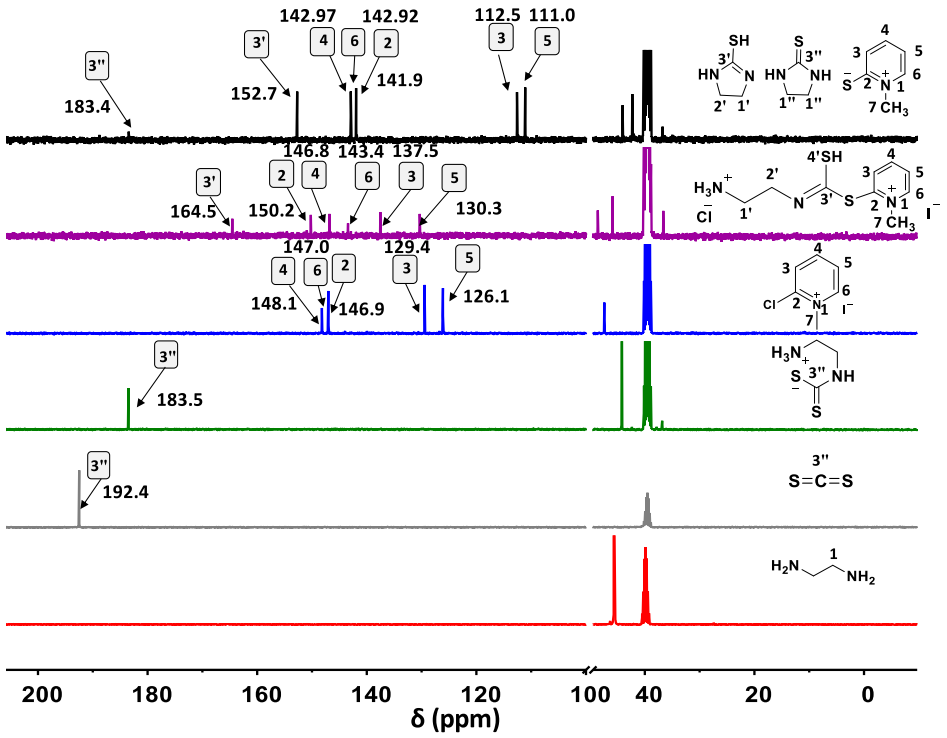

Figure 4. Partial ^{13}C NMR spectra of *en* (red trace), CS_2 (gray trace), and *en* after reaction with CS_2 (green trace), CMPI (blue trace), thiopyridinium salt (purple trace), and the reaction mixture (black trace) measured in DMSO-d_6.

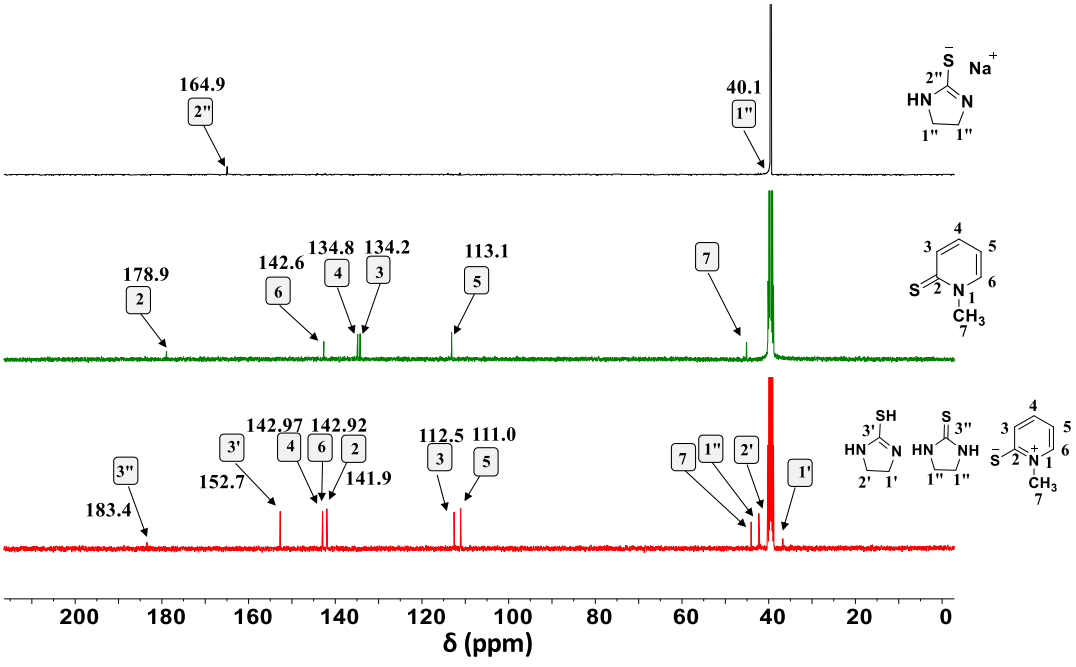

Figure 5. ^{13}C NMR spectra of the reaction mixture (red trace), *N*-methyl-2-pyridinethione (green trace), and sodium ethylene thiourea (black trace).

appearance of new peaks at 3.35 and 4.56 ppm together with ATR-FTIR measurement by the emergence of three new peaks at 1637, 1390, and 1288 cm^{-1} attributed to asymmetric and symmetric stretchings of (C═O), respectively[87] (Figures S12 and 13, Supporting Information).

Second, CMPI was added together with Et_3N to the carbonate adduct in 5 mL of acetonitrile (CH_3CN) as the solvent. A white precipitate was collected after 3 h, which was referred to as **5**, and it was deduced from the chemical shifts at 69.5 and 159.1 ppm, with *N*-methyl-2-pyridinoate shown as black traces in Figure S11, Supporting Information. The ^1H NMR spectrum indicated the appearance of a new peak at 5.04 ppm, which was assigned to **C-1′** of ethylene carbonate (EC) (black trace, Figure S12, Supporting Information).

2.6. Synthesis of 1,3-Dioxolane-2-thione (6). The synthesis of **6** started with the reaction of CS_2 with activated

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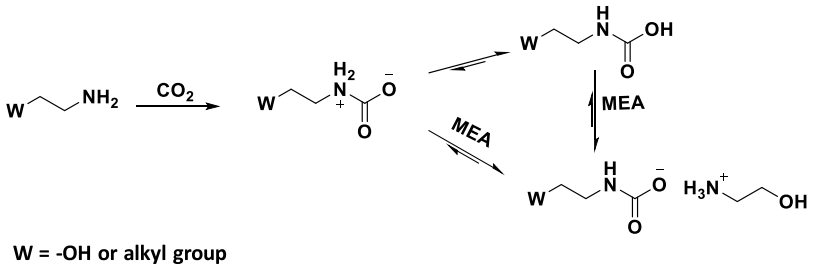
Scheme 4. General Reaction Scheme of Primary Amines with CO_2 in a Non-Aqueous Solvent



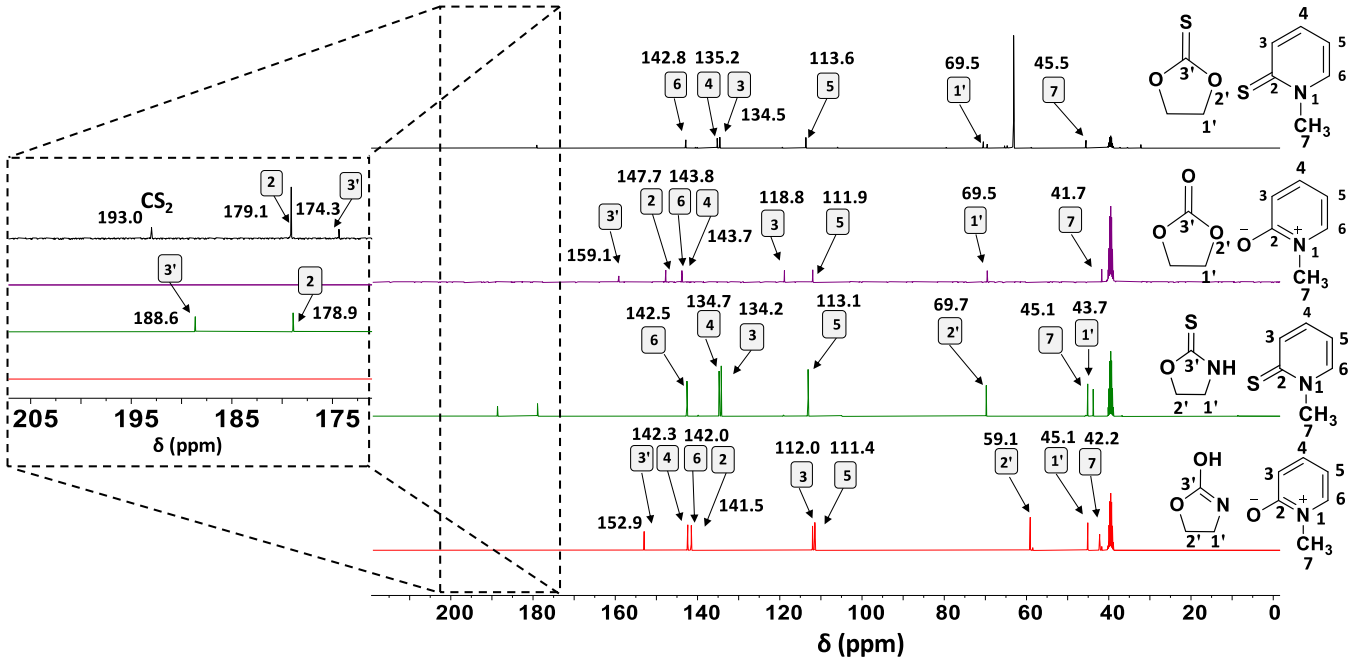


Figure 6. ^{13}C NMR spectra of the reaction crop of oxazolidin-2-one (red trace), oxazolidine-2-thione (green trace), 1,3-dioxolan-2-one (purple trace), and 1,3-dioxolane-2-thione (black trace).

EG in DMSO-d_6 to form a carbonodithioate adduct. The ^{13}C NMR spectrum indicated the formation of the adduct, as inferred from the chemical shifts at 61.0, 66.4, and 184.8 ppm which were assigned to **C-1**, **C-2**, and **C-3** (C═S) of the product, respectively (Figure 6). These data were supported by ^{1}H NMR, with two new emerging peaks at 3.61 (**C-1**) and 4.22 (**C-2**) ppm, respectively, (green trace, S15, Supporting Information). Then, CMPI was added with another mole of Et_3N to the carbonodithioate adduct dissolved in 5 mL of CH_3CN solution, which was evaporated in a later stage to give a clear yellow solution containing 1,3-dioxolane-2-thione and *N*-methylpyridin-2-thione. ^{13}C NMR indicated the formation of the former by the emergence of chemical shifts centered at 69.5 and 174.3 ppm, while the latter was as inferred from the peak at 179.1 ppm, which was assigned to **C-2** (C═S) (black traces, Figure S14, Supporting Information). In the ^{1}H NMR spectrum, formation of **6** was indicated by the appearance of a new peak at 3.63 ppm, assigned to **C-1′** (black trace, Figure S15, Supporting Information).

2.7. Synthesis of 1,3-Dithiolan-2-one/-thione (7 and 8). Starting with ethanedithiol, **7** was prepared, which contained trace amounts of the disulfide bridge compound (2,2′-disulfanediylbis(ethan-1-ol)) as a result of oxidation; the addition of Et_3N resulted in the reverse formation of the starting material as proven in the NMR spectrum (blue trace, Figures S16 and S17, Supporting Information).[88,89] The mechanism of the reduction process is proposed in Scheme S1, Supporting Information.

Afterward, dithiol was activated using NaH, followed by the formation of the sodium carbonothioate adduct upon bubbling the solution with CO_2. The spectrum of the latter white precipitate showed the emergence of two new peaks at 2.71 and 2.85 ppm for the product once dissolved in DMSO-d_6 (green trace, Figure S16, Supporting Information). This was further supported by ATR-FTIR measurement by the appearance of a new peak at 1637 cm^{-1} attributed to the asymmetric stretching of (C═O) (Figure S18, Supporting Information). Finally, the whitish adduct was further dissolved in CH_3CN to which solid CMPI was added and stirred for about an hour till the formation of a white precipitate. The crude product was collected by filtration, which was later referred to as a mixture of **7**, and it was inferred from the chemical shifts at 30.4 and 157.6 ppm together with *N*-methyl-2-pyridinolate shown in Figure S17 (black traces, Supporting Information). This was confirmed by ^{1}H NMR analysis by the appearance of a new peak at 3.91 ppm for **C-1′** of **7** (black traces, Figure S16, Supporting Information). In the case of CS_2, a yellowish precipitate was formed for adducts and the final product, as inferred from the chemical shift values shown in Figures S19 and S20 (Supporting Information). The

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Table 1. Calculated Thermodynamic Parameters[a] for the *keto*-(*k*)/*enol*-Forms (*e*) of the Final Products; Values are Given in kcal/mol.

entry	substrate	ΔE_{rel}	ΔH_{rel}	$T\Delta S_{rel}$	ΔG_{rel} (*k*−*e*)
1	imidazolidin-2-one	−22.60 [−22.86][b]	−22.74 [−23.01][b]	−0.69 [−0.69][b]	−22.05 [−22.31][b]
2	imidazolidine-2-thione	−19.84 [−20.36][b]	−20.14 [−20.57][b]	−1.15 [−0.85][b]	−18.99 [−19.71][b]
3	oxazolidin-2-one	−20.53 [−21.50][b]	−20.70 [−21.71][b]	−0.50 [−0.55][b]	−20.20 [−21.15][b]
4	oxazolidine-2-thione	−14.99 [−16.11][b]	−15.35 [−16.45][b]	−0.86 [−0.78][b]	−14.49 [−15.66][b]
5	imidazolidin-2-one-DMSO	−16.18[c]	−15.99[c]	0.60[c]	−16.60[c]
6	imidazolidine-2-thione-DMSO	−19.08[c]	−18.65[c]	1.36[c]	−20.02[c]
7	oxazolidin-2-one-DMSO	−16.14[c]	−16.01[c]	0.70[c]	−16.71[c]
8	oxazolidine-2-thione-DMSO	−17.64[c]	−17.97[c]	−1.36[c]	−16.61[c]

[a]Calculated using the B3LYP/6-311++G(d,p) basis set, and the values are given relative to the *enol*-form in all reactions. [b]Values are calculated in DCM, and values in brackets are calculated in DMSO. [c]Values calculated in the presence of explicit DMSO molecules.

chemical shift of the starting materials and the obtained products (**1**−**8**) is summarized in the Supporting Information.

2.8. Density Functional Theory (DFT) Calculations. The quantum chemical calculations were used to understand the stability of the *keto*/*enol*-forms in the different investigated reactions using the B3LYP/6-311++G(d,p) level of theory[90] in Gaussian 09.[91] The applied method has been used previously to predict reliable geometries and vibrational frequencies of hydrogen-bonded systems.[92] In order to investigate the solvent effects, the calculations were also carried out in DCM and DMSO at the same level using the polarizable continuum model. Table 1 lists the thermodynamic parameters for the tautomerism (relative to the *enol*-form) of the olidine products. The calculated free energy values indicated higher stability for the *keto*-compared to the *enol*-forms in DCM as well as in DMSO, with a slight preference in the latter. The experimental data indicated the formation of the *enol*-form of the olidine, whereas the olidine-thione counterpart was found in the *keto*-form. This can be understood in terms of the greater bond energy of C═O than C═N in the case of urea (**1**) and urethane (**3**), while C═S has lower energy than C═N for both thiourea (**2**) and thiourethane (**4**).[93] The discrepancy between the experimental and theoretical data can be understood by applying explicit DMSO molecules to unveil the effect of solvent on tautomerization. In general, the free energy values were lower than those calculated using in the absence of explicit solvent (DMSO) molecules. For **1** and **2**, the energy values indicated higher stability of the *keto*-from of the latter (−20.02 kcal/mol) compared to the former (−16.60 kcal/mol). This might be explained by the stabilization of the *enol*-form (**1**) upon the formation of hydrogen bonding with DMSO, which highlights the role of solvent in assisting tautomerization.

The relative energy difference between *keto*/*enol* forms of the olidine-thione compounds was also calculated in the presence of *N*-methyl pyridonate/N-methyl-2-pyridinethione as the reaction mixture (Table 2). The values again revealed higher stability for the *keto*-over its *enol*-forms, with a lower energy difference in the case of **3** and **4** compared to **1** and **2**. The optimized structures are given in Tables S2 and S3.

3. CONCLUSIONS

We introduced a novel methodology for the synthesis of different heterocyclic compounds by reacting a set of ethylene-terminated heteroatoms (C_2X; X = N, O, and S) with CO_2 and CS_2 using Mukaiyama reagent as a promoter in a basic medium under ambient conditions. The resulting intermediates/products were verified using a combination of $^1H/^{13}C$ NMR and *ex situ* ATR-FTIR spectroscopy methods. Notably, the formation of the *enol*-products was favored in the case of urea and urethane, while the *keto*-forms were obtained for the corresponding sulfur heterocyclic compounds. DFT calculations highlighted the effect of DMSO on the *keto*−*enol* tautomerization.

Table 2. Calculated Thermodynamic Parameters[a] (in DCM) for the *keto*-/*enol*-Product Mixed with Pyridone; Values are Given in kcal/mol.

sample	ΔE_{rel}	ΔH_{rel}	$T\Delta S_{rel}$	ΔG_{rel}
imidazolidin-2-one	−19.66	−19.78	−0.65	−19.12
imidazolidine-2-thione	−19.19	−19.25	0.77	−20.03
oxazolidin-2-one	−16.01	−15.96	−0.01	−15.95
oxazolidine-2-thione	−15.76	−15.95	−0.66	−15.28

[a]Calculated using the B3LYP/6-311++G(d,p) basis set, and the values are given relative to the *enol*-form in all reaction systems.

4. EXPERIMENTAL SECTION

4.1. Materials. All chemicals were used without purification. Ethylenediamine (99%), ethylene glycol (99%), Mukaiyama reagent (CMPI, 97%), triethylamine (99.5%), and dichloromethane (99.9%) were purchased from Loba Chemie, TEDIA, Aldrich, Fisher, and AZ chem, respectively. Ethanolamine (98%) and DMSO-d_6 (99.5 atom % D) were acquired from Sigma-Aldrich, ethane-1,2-dithiol (98%) was obtained from Fluka, carbon disulfide (CS_2, 99%) was bought from Panreac Quimica, CO_2 and N_2 (industrial grade) were purchased from Advanced Technical Gases Co. (Amman, Jordan). Unless otherwise stated, all isolated reaction products (intermediates) during the synthesis of **1**−**8** were identified by $^1H/^{13}C$ NMR and *ex situ* ATR-FTIR spectroscopic measurements to verify the presumed structures.

4.2. Instruments. ^1H and ^{13}C nuclear NMR spectra were measured using AVANCE-III 400 MHz (^1H: 400.13 MHz, ^{13}C: 100.61 MHz) equipped with a FTNMR Nano Bay spectrometer (Bruker, Switzerland). *Ex situ* ATR-FTIR spectra were recorded using a Bruker Vertex 70-FT-IR spectrometer at RT coupled with a Vertex Pt-ATR-FTIR accessory. Elemental analysis (EA) was performed using a CHN elemental analyzer EA3000 instrument (Euro Vector, Italy).

4.3. Synthesis of Imidazolidin-2-one (1). *en* (2.25 mmol) was dissolved in 20 mL of DCM, and the solution was directly bubbled with CO_2 for 60 min using a needle. The adduct appeared as a white precipitate, which was collected by decanting the DCM, washed with diethylether (10 mL × 2), and dried at RT (yield 89%). To the suspension of the latter

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carbamate in DCM, CMPI (2.70 mmol) was added. The reaction was carried out under N_2 gas for 2 h at RT (yield 81%). Then, Et_3N (6.75 mmol) was dropwise added and left to stir for 2 h to yield the *enol*-pyridinoate adduct, which was dissolved in 3.0 mL DMSO, and activated with 2.25 mmol NaH. Then, the solution was bubbled with CO_2 for 1 h and the salt was collected after filtration. Finally, a drop of concentrated HCl was added and stirred for 1 h to form **1**. EA (%) calculated for $\mathbf{C_6H_{16}N_4O_4}$: N, 26.92; C, 34.61; H, 7.69. Found: N, 26.13; C, 34.08; H, 8.03. $\mathbf{C_9H_{13}N_3O_2}$: N, 21.52; C, 55.37; H, 6.71. Found: N, 21.47; C, 55.80; H, 6.54. $\mathbf{C_3H_6N_2O}$: N, 32.54; C, 41.85; H, 7.08. Found: N, 32.49; C, 42.28; H, 7.25.

4.4. Synthesis of Imidazolidine-2-thione (2). Following the same procedure of **1**, the thiocarbamate adduct was formed by adding an equal molar ratio of CS_2 to *en* (1.49 mmol) in 20 mL DCM, and the reaction was carried out under N_2 gas for 3 h (yield 98%). CMPI (1.78 mmol) was added to a suspension of the latter, where a yellow precipitate was obtained after 2 h (yield 77%). The addition of Et_3N (4.47 mmol) resulted in the formation of **2** a yellow precipitate, which was separated from the reaction mixture by activation with NaH, bubbling CO_2 and acidification with HCl.

4.5. Synthesis of Carbamic Acid and Oxazolidin-2-one (3). MEA (1.95 mmol) was bubbled with CO_2 gas without any solvent for 30 min. Upon adding a mixture of 5.85 mmol of Et_3N and 1.95 mmol of CMPI in 5.0 mL of DCM. Oxazolidin-2-one/pyridinoate was collected after stirring the reaction mixture for 1 h under N_2 atmosphere. Note: in order to confirm the entity of carbamic *versus* carbamate in the initial step spectroscopically, MEA (1.95 mmol) was dissolved in 1.0 mL DMSO-d_6 and bubbled with CO_2 for 30 min. EA (%) calculated for $\mathbf{C_9H_{12}N_2O_3}$: N, 14.28; C, 55.09; H, 6.16. Found: N, 14.24; C, 55.07; H, 6.12.

4.6. Synthesis of Thiocarbamic Acid and Oxazolidine-2-thione (4). The same procedure used for **3** was followed using CS_2 (1.95 mmol) as a thiocarbonylating agent to synthesize **4**, where oxazolidine-2-thione/pyridinethione was separated as a yellowish precipitate.

4.7. Synthesis of 1,3-Dioxolan-2-one (5). EG (1.6 mmol) was activated using Et_3N (2.4 mmol) to form the alkoxide, which was bubbled with CO_2 and kept stirring for 2 h until a gummy product was obtained, which was identified as the carbonate adduct. Et_3N (2.4 mmol) was added to the adduct to deprotonate the other terminus of EG resulting in a clear solution, to which CMPI (1.9 mmol) and 5.0 was added followed by addition of 5.0 mL CH_3CN were addd, and the reaction was left under N_2 gas for 3 h at RT with continues stirring. The adduct of **5** 1,3-Dioxolan-2-one/pyridinoate was collected upon evaporating acetonitrile as a white solid product. EA (%) calculated for $\mathbf{C_9H_{11}NO_4}$: N, 7.10; C, 54.82; H, 5.62. Found: N, 6.90; C, 54.80; H, 5.59.

4.8. Synthesis of 1,3-Dioxolane-2-thione (6). The same procedure used for **5** was followed using CS_2 (1.60 mmol) as a thiocarbonylating agent to synthesize **6.** 1,3-Dioxolane-2-thione/pyridinethione was separated as a yellowish precipitate.

4.9. Synthesis of 1,3-Dithiolan-2-one (7). Et_3N (2.4 mmol) was added to EDT (1.6 mmol) to reduce the disulfide bond involved in the starting material. Afterward, NaH (2.4 mmol) was added to deprotonate EDT. The solution was bubbled with CO_2 for 1 h using a needle to produce the sodium triethylammonium carbonothioate adduct. CMPI (1.9 mmol) was added, followed by a consecutive addition of 5.0 mL of CH_3CN. After 1 h, 1,3-dithiolan-2-one/pyridinoate was obtained.

4.10. Synthesis of 1,3-Dithiolane-2-thione (8). The same procedure used for synthesis of **7** was followed, after the reduction with Et_3N (2.4 mmol), deprotonation with NaH (2.4 mmol), and reacting with CS_2 (1.6 mmol) for 1 h, the carbonotrithioate adduct was produced. Then, CMPI (1.9 mmol) and CH_3CN (5.0 mL) were added to the reaction mixture. After stirring for 2 h, 1,3-dithiolane-2-thione/pyridinethione was produced.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c01774.

$^1H/^{13}C$ NMR and ATR-FTIR spectroscopic data and DFT-optimized structures (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

CMPI, Mukaiyama reagent; *en*, ethylenediamine; MEA, monoethanolamine; EG, ethylene glycol; EDT, ethane-1,2-dithiol

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