ACS Catalysis

Letter

Cite This: ACS Catal. 2019, 9, 6006–6011

pubs.acs.org/acscatalysis

Carbon Dioxide-Catalyzed Stereoselective Cyanation Reaction

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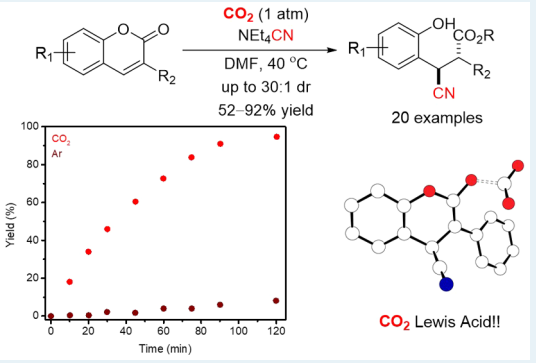
Supporting Information

ABSTRACT: We report a Michael-type cyanation reaction of coumarins by using CO_2 as a catalyst. The delivery of the nucleophilic cyanide was realized by catalytic amounts of CO_2, which forms cyanoformate and bicarbonate in the presence of water. Under ambient conditions, CO_2-catalyzed reactions afforded high chemo- and diastereoselectivity of β-nitrile carbonyls, whereas only low reactivities were observed under argon or N_2. Computational and experimental data suggest the catalytic role of CO_2, which functions as a Lewis acid, and a protecting group to mask the reactivity of the product, suppressing byproducts and polymerization. The utility of this convenient method was demonstrated by preparing biologically relevant heterocyclic compounds with ease.



KEYWORDS: *carbon dioxide, cyanation, cyanoformate, DFT calculation, coumarins*

The cyanoformate ion ($NC-CO_2^-$) is involved in the biological synthesis of ethylene at an Fe-containing enzyme (Figure 1a).[1,2] The formation of the cyanoformate ion from 1-aminocyclopropane-1-carboxylic acid is thought to protect the catalytically active Fe(III) center, which may be poisoned by cyanide ligation.[3−5] Although it is thermodynamically unstable, cyanoformate formed by combining cyanide and CO_2 may present a new opportunity in synthesis as a convenient source of highly nucleophilic cyanides avoiding the direct use of toxic hydrogen cyanide. Various surrogates of

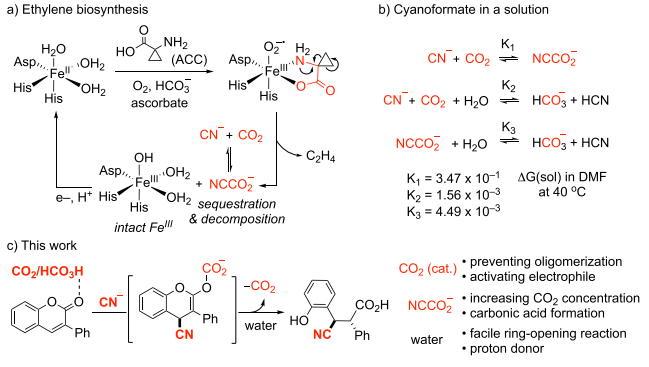
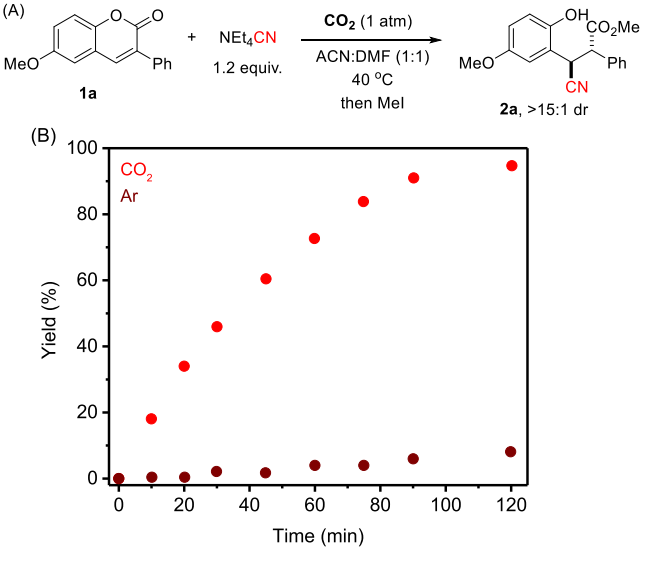


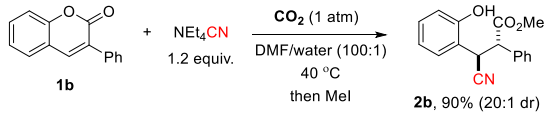
Figure 1. (a) Effects of cyanoformate in preserving the Fe(III) active center in the ethylene biosynthesis.[5] (b) CCSD(T)-calculated equilibria and potential advantage of CO_2 dissolution in cyanide and water-containing solutions. (c) Conjugate cyanation of coumarins.

Scheme 1. (A) Hydrocyanation and Ring-Opening Reaction of Coumarin 1a under CO_2 and (B) a Comparison of Reactivities of 1a under CO_2 (Red) and Argon (Brown) as a Function of Time



Received: March 15, 2019
Revised: May 1, 2019
Published: May 1, 2019

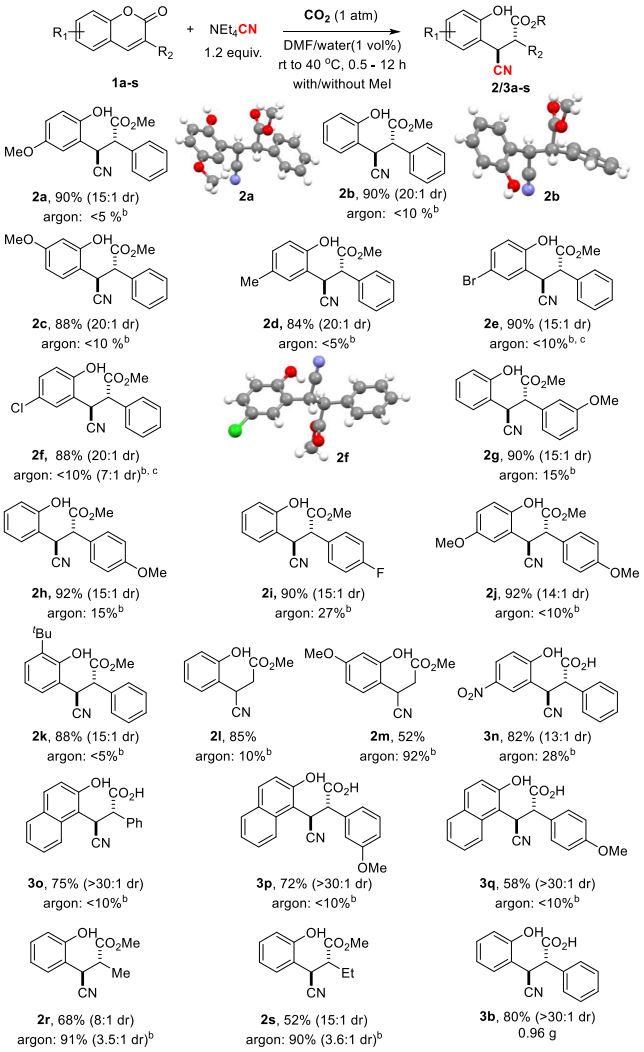
Table 1. Optimization of the Reaction Conditions[a]



entry	deviation from standard reaction condition	yield (%)[b]
1	none	99[c] (90)[d]
2	without additional water	90
3	argon or N_2 instead of CO_2	<10
4	Presaturation with CO_2	82
5	20−40 mol % of CO_2	67−81%
6	MeCN as a solvent	99[e]
7	at 25 °C	85
8	KCN instead of NEt_4CN	n.d.[f]
9	3 equiv NaCN + NBu_4Cl (10 mol %)	n.d.
10	3 equiv NaCN + 1.2 equiv NBu_4Cl	72%[g]
11	Lewis,[h] Brønsted[h] acids instead of CO_2	n.d.

[a]Standard reaction condition: substrate (**1b**, 0.2 mmol) and NEt_4CN (0.24 mmol, 1.2 equiv) were dissolved in DMF/water (1 mL/0.01 mL) under CO_2 at 40 °C, and the yield was recorded after 1 h. MeI (0.6 mmol, 3 equiv) was added to isolate the methyl ester (**2b**) after workup. [b]^{1}H NMR yield using 1,3,5-trimethoxybenzene as an internal standard. [c]dr = 20:1. [d]Isolated yield (%). [e]dr = 6:1. [f]Not detected. [g]After 3 h. [h]Lewis acid and Brønsted acids (2 equiv): $Ti(O^iPr)_4$, $BF_3{\cdot}OEt_2$, $Cu(OAc)_2{\cdot}H_2O$, $FeCl_3{\cdot}6H_2O$, *m*-$ClC_6H_4CO_2H$, NH_4Cl, and *p*-nitrophenol were added instead of CO_2. MeCN was used as a solvent.

Scheme 2. Substrate Scope of the CO_2-Catalyzed Cyanation of Coumarins[a,b,c]



[a]Reaction conditions: **1** (0.4 mmol), NEt_4CN (0.48 mmol), DMF (2 or 4 mL), water (20 μL) and MeI (1.2 mmol). Products were isolated by crystalization or silica gel column chromatography. The control experiments under argon were conducted under identical conditions to the corresponding CO_2experiments. [b]For control experiments under argon, conversion of starting materials was recorded by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]See Supporting Information section 11 for more details.

HCN are known, but they are based on forming HCN *in situ*.[6] Recently, "shuttle" catalysis was introduced to deliver cyanide from less toxic alkyl nitriles.[7−9] Nonetheless, cyanides are indispensable as reagents for many reactions. Inspired by the ethylene biosynthesis, we envisaged that the cyanoformate may be useful in organic synthesis. Combining cyanide and CO_2 in solution affords cyanoformate,[5] as our experiments and calculations confirmed (Figure 1b), where the activities of the cyanoformate and bicarbonate remain uncovered.

To investigate this hypothesis (a synthetic application of cyanoformate in chemical reaction), we chose coumarin derivatives. There are currently no convenient procedures for accessing nitrile derivatives of coumarins, which represent densely functionalized synthons for organic synthesis. Owing to the divergent reactivity of alkyl nitriles to amines, carboxylic acids, aldehydes/ketones, and amides, cyanation is ubiquitous in natural products syntheses, pharmaceuticals, and polymers.[10−12] Hydrocyanation of unsaturated carbonyls is particularly interesting and results in β-cyano adducts, which can be further elaborated to γ-aminobutyric acids and 1,2-dicarboxylic acids.[13] However, 1,4-conjugate addition of hydrogen cyanide has been elusive due to competing 1,2-addition reactions.[14,15] Nagata and co-workers demonstrated that Lewis acids increased selectivity toward 1,4-addition, but an aluminum-based reagent was necessary starting from gaseous HCN.[16,17]

Herein, we report an operationally simple 1,4-cyanation reaction of activated substrates, namely coumarins, to afford β-cyano carboxylates using CO_2 and cyanide (Figure 1c). The presented reactions were highly chemo- and stereoselective even in the presence of water. A larger scale synthesis of α-aryl-β-cyano esters demonstrates the utility of the protocol for preparing heterocyclic compounds. In-depth computational analysis supports the proposed catalytic role of CO_2, bicarbonate, and carbonic acid as Lewis and Brønsted acids to selectively activate electrophiles.

Recently, CO_2-mediated organic reactions were reported[18−20] expanding its role beyond the well-known function as a cheap C1 source.[21−28] Fundamentally, adding CO_2 to cyanide and using it as a nucleophilic reagent is counterintuitive, as the nucleophilicity of cyanide is reduced upon forming cyanoformate.[5] Nevertheless, we were surprised to obtain high isolated yield (90%) of **2a** starting from coumarin **1a** with high diastereoselectivity (20:1 dr) under CO_2 atmosphere, whereas negligible reactivity was observed under N_2 or argon atmosphere (Scheme 1).

Table 1 summarizes the optimization of reaction conditions based on the methyl ester of the ring-opened product (**2b**) in the presence of an internal standard. The structure of **2b** was unambiguously confirmed by X-ray single crystal analysis

DOI: 10.1021/acscatal.9b01087
ACS Catal. 2019, 9, 6006−6011

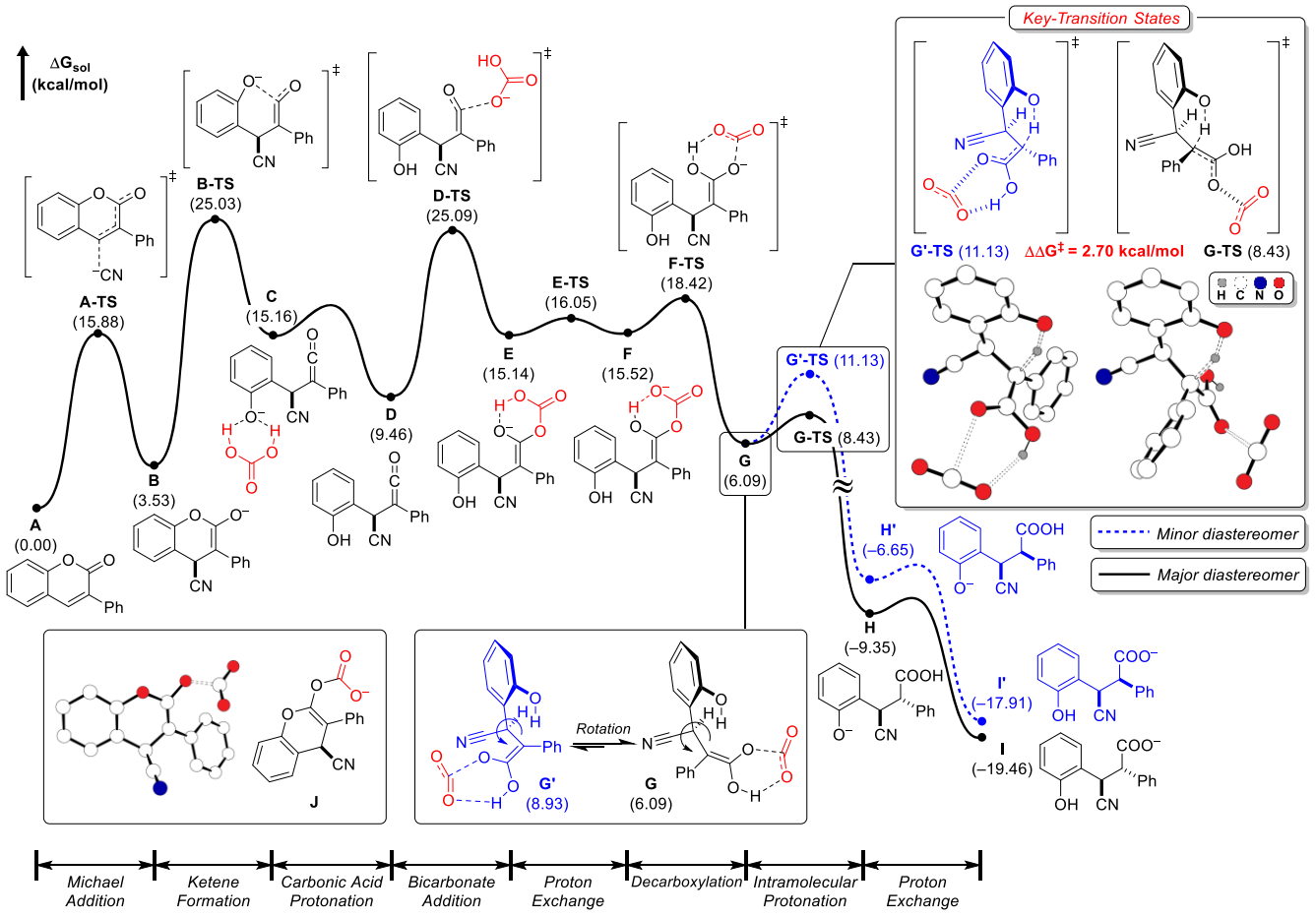


Figure 2. DFT calculated free energy profiles for the CO_2-catalyzed cyanation of coumarin. The black trace represents the pathway to the major diastereomer. The blue trace represents the pathway to the minor diastereomer. All of the H atoms are removed for clarity at the ORTEP view.

(Scheme 2). The methylation of the *β*-cyano carboxylate intermediate was completely chemoselective without dimethylation.[28] A control experiment with $^{13}CO_2$ strongly suggested no incorporation of atmospheric CO_2 in the final product (Figures S2 and S3). Reaction with D_2O instead of H_2O gave identical results (99% NMR yield, >15:1 dr) with >75% H−D exchange at both acidic protons on stereogenic carbons (Figure S6).

Interestingly, small amounts of water (~1 vol %) improved the reaction rate, yield, and selectivity toward the *syn*-product (entries 1 and 2), which may be due to water promoting the decomposition of cyanocarboxylate and faster release of cyanide.[3] When the same reaction was carried out under N_2 or argon atmosphere, only a trace amount (<10%) of **2b** was found with the majority of substrate remaining unreacted (entry 3). As a control experiment, a saturated solution was prepared by purging a solution of tetraethylammonium cyanide with CO_2. The use of this solution afforded 82% yield of **2b** without additional gaseous CO_2, confirming that the cyanation is feasible with dissolved CO_2 (entry 4). Moreover, we tested reactions with reduced CO_2 amounts (20−40 mol % with respect to coumarin **1b**) and found up to 81% conversion of **1b** to the desired product, suggesting a potential turnover of CO_2 (up to 3 TON, entry 5). Acetonitrile was a compatible solvent; however, the diastereoselectivity was reduced to 6:1, while lower conversion was observed at room temperature (entries 6 and 7). Various insoluble cyanide sources were inferior to soluble ammonium cyanide (entry 8 and Table S1). Catalytic amounts of NBu_4Cl (10 mol %) were employed to evaluate a potential phase-transfer catalysis, but excess stoichiometric amounts of NBu_4Cl (1.2 equiv) were necessary to mediate the cyanation reaction (entries 9 and 10). Various Lewis and Brønsted acids, such as $BF_3{\cdot}OEt_2$, $Ti(O^iPr)_4$, $Sc(OTf)_3$, Fe(III), Cu(II), NH_4Cl, and HCl, with and without water showed negligible activity, implying a superior performance of CO_2 and water in promoting nucleophilic cyanide addition reactions. To the best of our knowledge, this new reaction protocol employing tetraethylammonium cyanide with CO_2 is the only method to selectively deliver cyanide for the conjugate addition reaction of coumarins.

With the optimized reaction conditions in our hands, we verified the generality of the cyanation reaction by varying the electronic properties of coumarins. The relative stereochemistry of products was unambiguously determined by X-ray single crystallography of products **2a**, **2b**, and **2f** (Scheme 2). High diastereoselectivity and isolated yield were obtained with corresponding *β*-cyano carboxylic esters/acids (**2a−2s**/**3n−q**) under CO_2 without sophisticated purification. The same reactions in the absence of CO_2 (under argon or N_2), in general, afforded inferior conversion and diastereoselectivity of the cyanation products. Practical reaction conditions allowed us to smoothly convert coumarin **1b** to carboxylic acid product **3b** (0.96 g) after a single crystallization step. Various substituents (R_2) on the 3-position were tolerated, including free carboxylic acid. For example, 3-carboxycoumarin, **1l**, was converted to the corresponding methyl ester (**2l**) after

DOI: 10.1021/acscatal.9b01087
ACS Catal. 2019, 9, 6006−6011

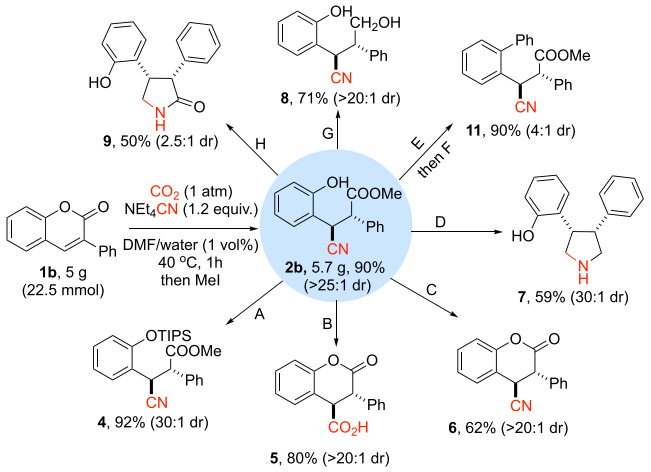


Figure 3. Functional group transformations of *β*-cyano carboxylate derivatives **2b**. Reaction conditions: (A) **2b** (0.2 mmol), TIPSCl (1.5 equiv), imidazole (3 equiv), DMF (1 mL), rt, 3 h; (B) **2b** (0.2 mmol), 10 M HCl (2 mL), 70 °C, 16 h; (C) **2b** (0.2 mmol), Amberlyst-15 (50 mg), toluene (3 mL), 100 °C, 16 h; (D) **2b** (1 mmol), $BH_3{\cdot}Me_2S$ (2 mmol), THF (10 mL), reflux, 10 h; (E) **2b** (1.78 mmol), pyridine (2 equiv, 3.56 mmol), triflic anhydride (1.2 equiv, 2.14 mmol), 0 °C to rt, 2 h, triflate protected phenol **10** was isolated in 93% yield (30:1 dr); (F) **10** (0.2 mmol) $PhB(OH)_2$ (1.1 equiv, 0.22 mmol), $Pd(PPh_3)_4$ (0.05 equiv, 0.01 mmol), NEt_3 (2 equiv, 0.4 mmol), toluene/ethanol (3:1, 3 mL), microwave, 120 °C, 30 min; (G) 2b (1 mmol), $LiBH_4$ (2 M in THF, 2 equiv, 2 mmol), THF (10 mL), 50 °C, 2 h; (H) (i) **2b** (1 mmol), Pd/C (5 mol %), HCl (0.05 mL), MeOH (5 mL), H_2 (1 atm), 48 h, (ii) NEt_3 (1.2 equiv), toluene, reflux, 12 h.

decarboxylation. Moreover, we observed increased diastereoselectivity for products **2f**, **2r**, and **2s** under CO_2 (>15:1 dr) compared to reactions under argon, where higher conversion was observed presumably due to stronger background reactions of alkyl substrates (see the Supporting Information for more details). It is worth noting here that cyanation reactions under argon generated unidentifiable byproducts including oligomers, which hampered the isolation of the product.

Although crystallization might improve the diastereoselectivity of the reaction, we ascribed the origin of high stereoselectivity (up to 30:1 dr) under the CO_2 enriched solution to the presence of water and CO_2. As mentioned earlier, a D_2O experiment confirmed that two acidic protons are exchangeable, indicating potential racemization.[29] A set of control experiments with independently prepared cyanated product (**6**) subjected to the reaction conditions showed a facile elimination reaction to the starting material, confirming low barriers for the cyanation reaction, as confirmed by DFT calculations, summarized in Figures 2 and S7. In our DFT calculations, various reactivities of the enolate **B** have been considered, and we obtained intermediate **J** where CO_2 is bound to the exocyclic oxygen atom of the enolate. This CO_2 is significantly bent at an angle of 139° and the distance between its central carbon and the enolate oxygen was 1.631 Å (Mayer bond order = 0.58), implying that the CO_2 acts as a Lewis acid. The resulting enolate **B** traverses the transition state **B-TS** at 25.0 kcal/mol. The ring opening reaction affords ketene intermediate **C**, which explains the observed reactivity with nucleophilic reagents, such as MeOH, ^{i}PrOH, and pyrrolidine, to give the corresponding esters and the amide (Table S6).

Several mechanistic scenarios involving the ketene were examined to shed light on the diastereoselective protonation, as detailed in the Supporting Information. As shown in Figure 2, the carbonate addition to the C═O bond is most plausible traversing **D-TS** at 25.1 kcal/mol to afford intermediate **E**, which quickly rearranges to form the proton exchange product **F**. On the basis of the experimental observations, the involvement of CO_2 and related equilibria is plausible at the diastereoselective protonation step. With carbon dioxide not fully dissociated, the decarboxylation step is estimated to be downhill in energy by 9.4 kcal/mol. Notably, two major rotational isomers (**G** and **G′**) were identified to undergo facile intramolecular protonation with the barrier of only 2.3 kcal/mol, in the presence of weakly bound CO_2. The energy difference between the rotamers were maintained for the corresponding transition states leading to a differentiation for the *si*- and *re*-face protonation. The observed transition states **G-TS** and **G′-TS** showed a remarkable energy difference (2.7 kcal/mol), consistent with the experimental diastereoselectivity. In the absence of CO_2 binding, as illustrated in Supporting Information, the gap between two proton transfer barriers was reduced significantly, which results in the reduced diastereoselectivity, confirmed by experiments.

The utility of this highly stereoselective processes was demonstrated in a larger scale reaction (22.5 mmol) of **1b**. Owing to the high crystallinity of the product, methyl ester **2b** and carboxylic acid **3b** were precipitated in high yield and selectivity (80−90%, >25:1 dr, Figure 3). The employed ammonium cation can be recycled in high purity as tetraethylammonium iodide after methylation (see section 12, Supporting Information), avoiding HCN generation.[30,31]

Obtained product **2a** was subjected to functional group transformations to demonstrate the application potential of cyanated coumarins (Figure 3).[32] The phenolic −OH group on **2a** was protected to triisopropylsilyl ether **4** in high yield and diastereoselectivity. The hydrolysis of nitrile groups (**2b** and **3b**) under acidic conditions resulted in the same cyclic 1,4-dicarbonyl **5** with good yield and diastereoselectivity (80%, 20:1 dr). Acid-catalyzed reaction afforded 4-cyanodihydrocoumarin derivative **6** (62% 20:1 dr) starting from methyl ester **2b**. A borane reduction of methyl ester **2b** smoothly afforded pyrrolidine derivative **7** (59%, 30:1 dr) upon reduction of the nitrile group to a primary amine and *in situ* cyclization. A selective reduction of methyl ester **2b** over the nitrile group was performed with $LiBH_4$ to furnish *γ*-cyano alcohol **8** (71% yield, >20:1 dr). Biologically important five-membered lactam derivative **9** was synthesized via the reduction of nitrile functional group with H_2 over Pd/C, followed by cyclization in toluene under reflux (50% yield in two steps, 2.5:1 dr). Further structural diversification in the *ortho*-position of the aromatic substituent was achieved via Suzuki coupling of corresponding triflate derivative **10** to produce biaryl derivative **11** in high isolated yield (90%) with slightly diminished dr (4:1) due to the basic reagents in the reaction.

In conclusion, a catalytic application of CO_2 and its equilibria with water and cyanide (to form cyanoformate) were demonstrated by a 1,4-conjugate cyanation reaction of coumarins. This new and practical synthetic methodology enabled us to access various heterocycles of biological relevance. The role of CO_2 was confirmed by mechanistic studies and computational analysis, pinpointing the critical involvement of CO_2 in the product determining step and while affecting the reaction rate.[33] The proposed mechanism showed

DOI: 10.1021/acscatal.9b01087
ACS Catal. 2019, 9, 6006−6011

a potential asymmetric catalysis where CO_2 is involved in a stereoselective step.[29] We are currently investigating various (chiral) ammonium and metal salts to expand the scope of CO_2-catalyzed organic transformations.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b01087.

Methods, procedures, and characterization data; tables of screening data, tested Lewis and Brønsted acids, effects of CO_2 on cyanation, and crystal data; NMR spectra; free energy profiles; XYZ coordinates; ORTEP structures; HPLC chromatogram (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The generous support from the Department of Chemistry, University of Copenhagen, the Novo Nordisk Fonden (NNF17OC0027598), and the Villum Fonden (00019062) is gratefully acknowledged. The authors thank Christian Tortzen for his support in NMR spectroscopy. We thank the National Research Foundation (2018R1A2B2005585) and the Institute for Basic Science in Korea (IBS-R010-A1) for financial support.

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(29) White, D. A. Cyanocarboxylation of Activated Olefins. *J. Chem. Soc., Perkin Trans. 1* **1976**, *1*, 1926−1930. Note: Methyl ester **2b** was treated under basic conditions, which showed erosion of diastereoselectivity (25:1 dr → 1:1 dr), suggesting the importance of

DOI: 10.1021/acscatal.9b01087
ACS Catal. 2019, 9, 6006−6011

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DOI: 10.1021/acscatal.9b01087
ACS Catal. 2019, 9, 6006−6011