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Research Article

Pd(II)-NHC-Catalyzed Synthesis of Value-added Five-Membered Cyclic Carbonates from Vicinal Diols using Diphenyl Carbonate as Sustainable Carbonylation Agent

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ABSTRACT

Herein, using diphenyl carbonate as a green carbonyl source in a carbonylation reaction with Pd(II)-NHC catalysis, we demonstrate a useful, secure, and highly effective protocol for the synthesis of highly valuable cyclic carbonates from their respective diols. The different diols with electron-rich/electron-poor groups were effectively converted into their corresponding value-added cyclic carbonates products under Pd(II)-NHC catalysis using intermolecular carbonylation reactions under mild reaction conditions. In addition, this new system enables the synthesis of sterically challenging cyclic carbonates that are otherwise inaccessible, such as tetrasubstituted pinacol carbonates.

Key words: Carbonylation, Diphenyl carbonate, Palladium, Pd(II)–*bis*-N-heterocyclic carbene complexes, Pd-PEPPSI complexes, Value-added cyclic carbonates.

1. INTRODUCTION

To produce pharmaceuticals, herbicides, insecticides, dyes, polymers, and many other organic compounds, over 8 million tonnes of phosgene, a flexible and highly reactive C1 building block, are produced each year [1-3]. Phosgene is typically prepared and consumed at its site of production in the production of isocyanates, polycarbonates, polyurethanes, etc. due to its high toxicity and the risk of accidents. Phosgene can only be delivered in small amounts to other locations [4]. In addition, stringent safety precautions are required to avoid exposure to phosgene gas [5]. As a result, significant effort has been put into creating phosgene substitutes that enable safe and simple handling in industrial processes as well as in research labs [6]. For instance, liquid diphosgene [7,8] and solid triphosgene [9] are both frequently used in laboratories despite the fact that they are still toxic substances. Alkyl chloroformates [10] and 1,1'-carbonyldiimidazole [11,12] have emerged as the preferred reagents for carbonylation reactions as safer phosgene substitutes. Due to their high reactivities, these reagents must be handled and stored in dry, inert environments because they are still made from phosgene. It has also been extensively studied how carbon monoxide can be used directly in carbonylation reactions [13,14]. However, using this extremely toxic gas requires pricey high-pressure equipment and particular safety systems, which restricts its use. Another group of carbonylation reagents is organic carbonates [15-17]. Green chemistry advocates strongly favor the use of organic carbonates in carbonylation processes because they are less toxic and can be obtained from sources other than phosgene. As an example of a carbonylation reagent, dimethyl carbonate (DMC) is a stable liquid that is much simpler to work with than gaseous phosgene [18,19]. DMC has been used to develop a variety of carbonylation reactions, but it is much less reactive than phosgene. As a result, some of these reactions had difficult reaction conditions or had low efficiencies [20-22]. Diphenyl carbonate (DPC, 1) has received a lot of attention as an alternative reagent to DMC to get around these restrictions brought on by its poor reactivity. As a widely accessible, reasonably priced bench stable solid-1, it can be safely used in laboratories without the need for additional safety measures [23,24]. Bisphenol-A polycarbonate (commercialized by Asahi-Kasei), aliphatic polycarbonates [25], polyureas [26], and carbamates are examples of the high reactivity and synthetic utility of DPC [27]. However, all the aforementioned catalysts efficiently converted diols into cyclic carbonates, but relatively harsh conditions, expensive and risky phosphine ligands were required for carbonylation reactions. Numerous beneficial characteristics of the palladium catalyst, including the relatively high thermal stability of the Pd-MIC bonds, have been suggested as the cause of the simultaneous appearance of 1,2,3-triazolium-derived mesoionic carbenes (tz-MICs) ligands in the various cross-coupling reactions. Because these electron-rich carbenes firmly attach to the catalyst, it can be used repeatedly without experiencing a significant loss in stability. The tz-MICs palladium complexes, on the other hand, have been crucial

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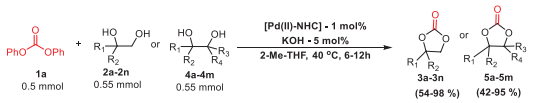
as catalysts in homogeneous catalysis [28-38], their applications in catalytic carbonylation reactions of diols into cyclic carbonates have surprisingly remained unexplored to date, and thus we were interested in pursuing the same using Pd-NHC metal complexes as a catalyst.

1.1. Experimental Section

Unless otherwise specified, all commercially available compounds were used in their entirety. Commercially available reagent-grade 2-Me-THF, Methanol, and THF were used. $CDCl_3$ solvent was used to record ^1H and $^{13}C\{^1H\}$ NMR on Bruker 400 and 500 MHz spectrometers. Chemical shifts (δ) are expressed in ppm relative to Toronto Mindfulness Scale (TMS), and coupling constants (J) are expressed in Hz. The solvent signals and chemical shifts used as references were converted to the TMS scale ($CDCl_3$, δC 77.0 ppm, δH 7.26 ppm). Analytical thin layer chromatography (TLC) using commercial aluminum sheets pre-coated with silica gel was used to monitor all of the catalytic reactions. Silica gel (Merck, 200–400 mesh) was used for column chromatography. The abbreviations for signal multiplicity in ^1H NMR spectra are singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublet (dd), doublet of triplet (dt), triplet of triplet (tt), multiplet (m) etc.

Considering above fact an efficient and eco-compatible synthesis of 1,3-dioxalanones (5 membered cyclic carbonates) using diphenyl carbonate as sustainable carbonylating agent is reported in this chapter (Scheme 1.1).



Scheme 1.1: Synthesis of 1,3-dioxolan-2ones via Vicinal Diols using Diphenyl Carbonate as Sustainable Carbonylation Agent

1.2. Preparation of Palladium bis-NHC Complexes (A-C)

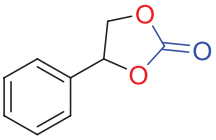
A mixture of silver-NHC complexes (1.0 mmol, 1.0 equiv) and (COD) $PdCl_2$ (0.50 mmol, 0.50 equiv) in CH_3CN (ca. 50 mL) was stirred at room temperature, until the formation of an off white AgCl precipitate was observed. The reaction mixture was filtered and the solvent was removed under vacuum to give the products **(A-C)** as light yellow solid [49].

1.2.1. General method for producing cyclic carbonates

In an oven-dried reaction tube equipped with a magnetic stir bar, Pd(II)–NHC **[cat-C],** (3.45 mg, 0.005 mmol, 1 mol%), and KOH (1.4 mg, 0.025 mmol, 5 mol %) were added to a solution of DPC **1** (0.10 g, 0.50 mmol, 1.0 equiv.) and a vicinal diol **2** (0.55 mmol, 1.1 equiv.) in 2-Me-THF (1.0 mL). The resulting mixture was stirred at the specified temperature in an oil bath. Acetic acid was added to the reaction mixture after the reaction had finished, as determined by TLC or 1H NMR spectroscopy. To obtain the desired cyclic carbonate **3a**, the obtained mixture was directly purified by flash column chromatography on silica gel (hexanes/ethyl acetate was gradually changed from 9:1 to 4:1).

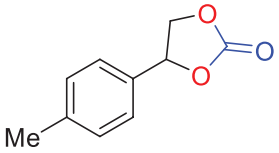
1.3. Characterization of all the Cyclic Carbonate Products

1.3.1. 4-Phenyl-1,3-dioxolan-2-one (3a):37



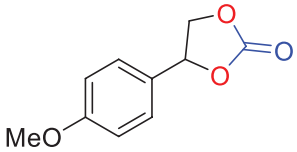
Following the general procedure, **3a** was obtained as a white solid (73.8 mg, 0.45 mmol, 90%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.39–7.40 (m, 3H), 7.29–7.30 (m, 2H), 5.65 (t, J = 8.0 Hz, 1H), 4.85 (t, J = 8.7 Hz, 1H), 4.63 (dd, J = 8.7, 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 138.5, 127.9, 126.2 (2C), 124.8 (2C), 77.5, 70.1.

1.3.2. 4-(p-Tolyl)-1,3-dioxolan-2-one (3b):60



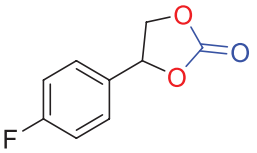
Following the general procedure at 30°C for 2 h, **3b** was obtained as a white solid (78 mg, 88%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 4H), 5.44 (t, J = 8.0 Hz, 1H), 4.72 (t, J = 8.4 Hz, 1H), 3.94 (t, J = 8.4 Hz, 1H), 2.34 (s, 3H); 13C NMR (100 MHz, $CDCl_3$) δ 153.8, 140.8, 131.6, 127.8 (2C), 123.9 (2C), 77.0, 70.1, 21.4.

1.3.3. 4-(4-methoxyphenyl)-1,3-dioxolan-2-one (3c):60



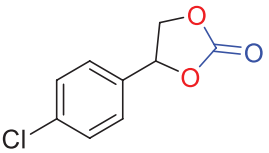
Following the general procedure, **3c** was obtained as a slightly yellow oil (22.3 mg, 0.115 mmol, 23%). ^1H NMR (400 MHz, $CDCl_3$) δ = 3.90 (s, 3H), 4.65 (t, J = 8.0 Hz, 1H), 5.34 (dd, J = 8.0, 8.5 Hz, 1H), 5.82 (t, J = 8.1 Hz, 1H), 6.79–7.20 (m, 2H), 7.25–7.43 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 57.4 (CH_3), 72.4 (CH_2), 76.0 (CH), 112.6 (2 x CH), 126.5 (2 x CH), 128.5 (CH), 153.9 (C), 159.8 (C) ppm.

1.3.4. 4-(4-Fluorophenyl)-1,3-dioxolan-2-one (3d):61



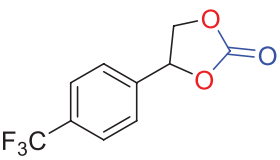
Following the general procedure at 30°C for 2 h, **3d** was obtained as a colorless oil (63 mg, 69%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.35–7.33 (m, 2H), 7.12–7.14 (m, 2H), 5.47 (t, J = 8.0 Hz, 1H), 4.87 (t, J = 8.4 Hz, 1H), 4.65 (t, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5 (d, J = 248.0 Hz), 152.8, 132.5 (d, J = 3.3 Hz), 125.9 (d, J = 8.6 Hz, 2C), 115.3 (d, J = 23.0 Hz, 2C), 76.4, 69.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ–110.0.

1.3.5. 4-(4-chlorophenyl)-1,3-dioxolan-2-one (3e):61



Following the general procedure, **3e** was obtained as a colorless oil (97.3 mg, 0.49 mmol, 98%). ^1H NMR (400 MHz, $CDCl_3$) δ = 4.20 (m, 1H), 4.91 (t, J = 8.4 Hz, 1H), 5.59 (t, J = 8.6 Hz, 1H), 7.29-7.36 (m, 2H), 7.39–7.46 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 72.2 (CH_2), 76.3 (CH), 126.4 (2 x CH), 128.7 (2 x CH), 133.4 (C), 134.9 (C), 153.5 (C) ppm.

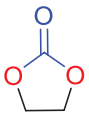
1.3.6. 4-(4-(trifluoromethyl)phenyl)-1,3-dioxolan-2-one (3f):61



Following the general procedure, **3f** was obtained as a colorless oil (99.8 mg, 0.425 mmol, 85%). ^1H NMR (400 MHz, $CDCl_3$) δ = 4.52 (dd,

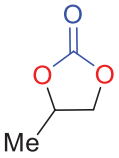
J = 7.6, 8.7 Hz, 1H), 4.76 (t, J = 8.4 Hz, 1H), 5.65 (t, J = 7.9 Hz, 1H), 7.49 (d, J = 8.1 Hz, 2H), 7.82 (d, J = 8.2 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 72.1 (CH2), 78.0 (CH), 124.7 (d, J = 272.6 Hz, C), 126.7 (2 x CH), 127.5 (q, J = 3.9 Hz, 2 x CH), 131.0 (q, J = 32.8 Hz, C), 142.0 (C), 153.5 (C) ppm; ^{19}F NMR (282 MHz, $CDCl_3$) δ = −61.4 (CF3) ppm;.

1.3.7. 1,3-Dioxolan-2-one (3 g):63



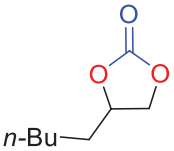
Following the general procedure at 30 °C for 2 h, **3e** was obtained as a colorless oil (40 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.57 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 154.5, 63.6 (2C).

1.3.8. 4-Methyl-1,3-dioxolan-2-one (3h):50



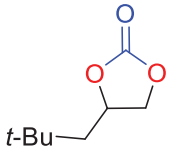
Following the general procedure at 30°C for 2 h, **3f** was obtained as a colorless oil (46 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.79–4.85 (m, 1H), 4.58 (dd, J = 8.4, 8.0 Hz, 1H), 3.85 (dd, J = 8.4, 8.0 Hz, 1H), 1.37 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 71.4, 69.5, 18.0.

1.3.9. 4-pentyl-1,3-dioxolan-2-one (3i):64



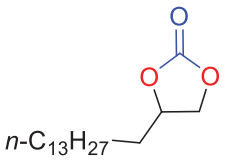
Following the general procedure, **3g** was obtained as a colorless oil (66.3 mg, 0.46 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.95 (t, J = 7.0 Hz, 1H), 1.17–1.43 (m, 4H), 1.67–1.82 (m, 1H), 1.72–1.89 (m, 1H), 4.12 (dd, J = 7.2, 8.4 Hz, 1H), 4.36 (t, J = 8.1 Hz, 1H), 4.59 (dq, J = 5.4, 7.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.8 (CH_3), 21.4 (CH_2), 25.6 (CH_2), 32.7 (CH_2), 69.4 (CH_2), 75.8 (CH), 154.2 (C) ppm.

1.3.10. 4-(tert-Butyl)-1,3-dioxolan-2-one (3j):64



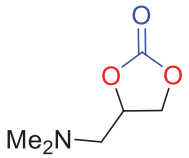
Following the general procedure, **3g** was obtained as a colorless oil (66.3 mg, 0.46 mmol, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 0.93 (t, J = 7.0 Hz, 1H), 1.16–1.43 (m, 4H), 1.47–1.62 (m, 1H), 1.64–1.78 (m, 1H), 4.26 (dd, J = 7.2, 8.4 Hz, 1H), 4.66 (t, J = 8.1 Hz, 1H), 4.72 (dq, J = 5.4, 7.5 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 13.8 (CH_3), 21.4 (CH_2), 25.6 (CH_2), 34.7 (CH_2), 68.5 (CH_2), 75.8 (CH), 154.2 (C) ppm.

1.3.11. 4-Tetradecyl-1,3-dioxolan-2-one (3k):XX(Kim paper)



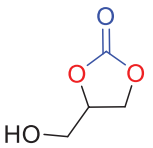
Following the general procedure at 30°C for 2 h, **3g** was obtained as a white solid (0.12 g, 84%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83–4.76 (m, 1H), 4.61 (t, J = 8.1 Hz, 1H), 4.15 (dd, J = 8.3, 7.3 Hz, 1H), 1.74–1.85 (m, 1H), 1.71–1.73 (m, 1H), 1.52–1.57 (m, 24H), 0.85 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 76.0, 70.3, 31.8, 30.9, 29.63, 29.62, 29.60, 29.57, 29.56, 29.40 (2C), 29.2, 28.1, 24.5, 21.6, 13.1.

1.3.12. 4-((dimethylamino)methyl)-1,3-dioxolan-2-one (3l):50



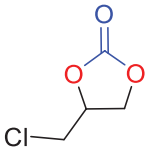
Following the general procedure, **3i** was obtained as a yellow oil (10.9 mg, 0.075 mmol, 15%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.41 (s, 6H), 2.81 (t, J = 6.2 Hz, 2H), 4.42 (dd, J = 7.0, 8.5 Hz, 1H), 4.61 (t, J = 8.3 Hz, 1H), 4.88 (ddt, J = 5.9, 7.2, 8.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 44.5 (2 x CH_3), 59.4 (CH_2), 67.2 (CH_2), 72.2 (CH), 152.0 (C) ppm.

1.3.13. 4-(hydroxymethyl)-1,3-dioxolan-2-one (3m):50



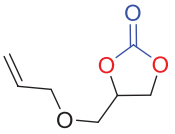
Following the general procedure, **5a** was obtained as a colorless oil (56.1 mg, 0.475 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.70 (t, J = 6.2 Hz, 1H), 3.85 (ddd, J = 3.5, 6.7, 12.9 Hz, 1H), 3.97 (ddd, J = 3.0, 5.3, 12.9 Hz, 1H), 4.34–4.56 (m, 2H), 4.75 (ddt, J = 3.2, 6.6, 8.3 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ = 62.8 (CH2), 64.9 (CH2), 75.7 (CH), 153.5 (C) ppm.

1.3.14. 4-(Chloromethyl)-1,3-dioxolan-2-one (3n):50



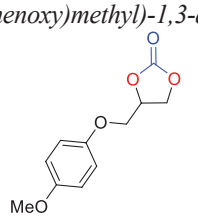
Following the general procedure at 30°C for 4 h, **3i** was obtained as a white solid (53 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.87 (dtd, J = 9.0, 5.6, 4.0 Hz, 1H), 4.56–4.66 (m, 1H), 4.65 (dd, J = 9.0, 5.6 Hz, 1H), 3.65 (ddd, J = 16.0, 12.0, 4.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 72.3, 65.9, 44.7.

1.3.15. 4-((Allyloxy)methyl)-1,3-dioxolan-2-one (5a):37



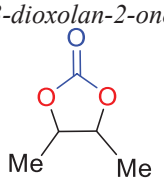
Following the general procedure at 30°C for 2 h, **3j** was obtained as a colorless oil (74 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81−5.92 (m, 1H), 5.38−5.42 (m, 2H), 4.74−4.82 (m, 1H), 4.58 (t, J = 8.4 Hz, 1H), 4.47 (dd, J = 8.4, 6.0 Hz, 1H), 4.14−4.21 (m, 2H), 3.79−3.81 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 132.6, 116.7, 74.0, 71.4, 67.7, 65.1.

1.3.16. 4-((4-methoxyphenoxy)methyl)-1,3-dioxolan-2-one (5b):37



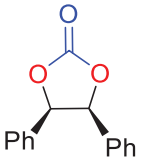
Following the general procedure at 30°C for 2 h, **3j** was obtained as a colorless oil (74 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86–5.91 (m, 1H), 5.38–5.42 (m, 2H), 4.79–4.88 (m, 1H), 4.58 (t, J = 8.4 Hz, 1H), 4.47 (dd, J = 8.4, 6.0 Hz, 1H), 4.02–4.03 (m, 2H), 3.67–3.78 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 131.6, 116.7, 74.0, 71.4, 67.7, 65.1.

1.3.17. 4,5-Dimethyl-1,3-dioxolan-2-one (5c):37



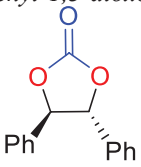
Following the general procedure at 30°C for 12 h, **5a** was isolated as a mixture of two inseparable diastereomers (48 mg, 83%, 88:12 dr). *Majordiastereoisomer*: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85–4.89 (m, 2H), 1.45 (d, J = 6.3 Hz, 6H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 153.6, 76.0 (2C), 13.3 (2C). *Minor diastereoisomer*: ^{1}H NMR (400MHz, $CDCl_3$) δ 4.46–4.54 (m, 2 H), 1.34 (d, J = 6.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ152.5, 78.8 9 (2C), 17.3 (2C).

1.3.18. (4S,5R)-4,5-diphenyl-1,3-dioxolan-2-one (5d):65



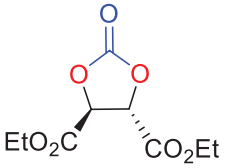
The general procedure was applied at 40°C for 12 h. The reaction was quenched with a portion of acetic acid and diluted with ethyl acetate. The mixture was washed with 35% NaOH (10 mL × 2). The organic layer was washed with water (10 mL × 2) and brine (10 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvents were removed under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel to afford **5b** as a white solid. (106 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.35 (m, 6H), 6.95–6.97 (m, 4H), 5.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 131.6 (2C), 127.8 (2C), 126.2 (4C), 126.1 (4C), 82.5 (2C).

1.3.19. (4R,5R)-4,5-diphenyl-1,3-dioxolan-2-one (5e):37



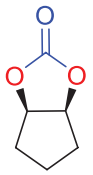
The general procedure was applied at 30 °C for 12 h. The reaction was quenched with a portion of acetic acid and diluted with ethyl acetate. The mixture was washed with 35% NaOH (10 mL × 2). The organic layer was washed with water (10 mL × 2) and brine (10 mL) and dried over anhydrous $MgSO_4$. After filtration, the solvents were removed under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel to afford **5c** as a white solid. (107 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.47 (m, 6H), 7.37−7.52 (m, 4H), 5.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 133.7 (2C), 130.7 (2C), 129.2 (4C), 127.0 (4C), 84.3 (2C).

1.3.20. Diethyl (4S,5S)-2-oxo-1,3-dioxolane-4,5-dicarboxylate (5f):37



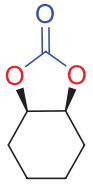
Following the general procedure at 100°C for 12 h, **5d** was obtained as a colorless oil (60 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (s, 2H), 4.24 (q, J = 7.2 Hz, 4H), 1.39 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0 (2C), 1521.1, 73.8 (2C), 62.3 (2C), 12.9 (2C).

1.3.21. (3aR,6aS)-Tetrahydro-4H-cyclopenta[d][1,3]dioxol-2-one (5g):37



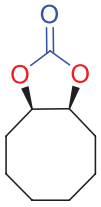
Following the general procedure at 30°C for 12 h, **5e** was obtained as a white solid (64 mg, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14–5.20 (m, 2H), 2.13–2.30 (m, 2H), 1.87–1.91 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 80.9 (2C), 32.0 (2C), 22.4.

1.3.22. (3aR,7aS)-Hexahydrobenzo[d][1,3]dioxol-2-one (5h):37



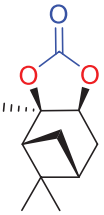
Following the general procedure at 30°C for 12 h, **5f** was obtained as a white solid (62 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.59–4.44 (m, 2H), 1.87–1.96 (m, 4H), 1.63–1.71 (m, 2H), 1.42–1.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.3, 74.7 (2C), 25.6 (2C), 18.0 (2C).

1.3.23. (3aR,9aS)-Octahydrocycloocta[d][1,3]dioxol-2-one (5i):66



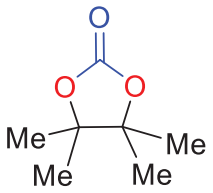
Following the general procedure at 60°C for 12 h, **5g** was obtained as a white solid (82 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.61–4.75 (m, 2H), 2.18–2.42 (m, 4H), 1.72–1.84 (m, 2H), 1.29–1.31 (m, 4H), 1.22–1.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 81.0 (2C), 26.0 (2C), 24.9 (2C), 23.1 (2C).

1.3.24. (3aR,4R,6R,7aS)-3a,5,5-Trimethylhexahydro-4,6-methanobenzo[d][1,3]dioxol-2-one (5j):37



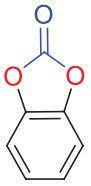
Following the general procedure at 30°C for 12 h, **5h** was obtained as a white solid (89 mg 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.58 (dd, J = 8.4, 1.8 Hz, 1H), 2.31–2.33 (m, 2H), 2.20 (t, J = 5.4 Hz, 1H), 1.99–2.09 (m, 2H), 1.55 (s, 3H), 1.33 (s, 3H), 1.28 (d, J = 11.6 Hz, 1H), 0.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 87.0, 77.2, 50.1, 38.63, 38.62, 33.2, 26.8, 26.7, 25.9, 23.8.

1.3.25. 4,4,5,5-Tetramethyl-1,3-dioxolan-2-one (5k):37



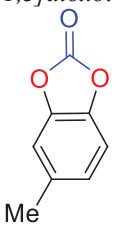
Following the general procedure at 100°C for 12 h, **5i** was obtained as a white solid (66 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.49 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.8, 84.9 (2C), 21.2 (2C).

1.3.26. Benzo[d][1,3]dioxol-2-one (5l):67



Following the general procedure with **1** (0.75 mmol) and **4j** (0.50 mmol) at 30°C for 12 h, **5j** was obtained as a white solid (44 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.52 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 141.2 (2C), 121.8 (2C), 113.4 (2C).

1.3.27. 5-Methylbenzo[d][1,3]dioxol-2-one (5m):67



Following the general procedure with **1** (0.75 mmol) and **4k** (0.50 mmol) at 30°C for 12 h, **5k** was obtained as a white solid (62 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 8.2 Hz, 1H), 7.15 (s, 1H), 7.12–7.99 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.5, 142.2, 141.1, 134.2, 124.1, 111.8, 109.8, 20.4.

1.4. Mercury Drop Experiment Performed at Varying Time Intervals

1.4.1. Mercury addition at the start of the reaction

A 10 mL vial was charged with a mixture of DPC (**1**, 0.10 g, 0.50 mmol, 1.0 equiv), a vicinal diol (0.55 mmol, 1.1 equiv) and KOH (5.6 mg, 0.1 mmol, 20 mol%) in molar ratio of 1:5 and mercury (0.121 g, 0.603 mmol) was added subsequently. The palladium complex-C (17.2 mg, 0.025 mmol, 5 mol%) was added to the mixture, followed by 2-Me-THF (ca. 2 mL) solvent, and closed reaction tube containing the reaction mixture was placed in a preheated oil bath and stirred at 40°C for 6 h. The reaction mixture was cooled to room temperature, and acetic acid/water (ca. 12 mL) was added. The resulting mixture was extracted with EtOAc (ca. 50 mL). The water layer was further extracted with EtOAc (ca. 3 × 20 mL). The crude mixture was purified by flash column chromatography using silica gel as stationary phase and hexane/ethyl acetate (95:5 v/v) as an eluent to afford the pure ketone product **3a** as colorless oil in 99% (81.0 mg) yield.

1.4.2. Mercury addition after 2 h of reaction time

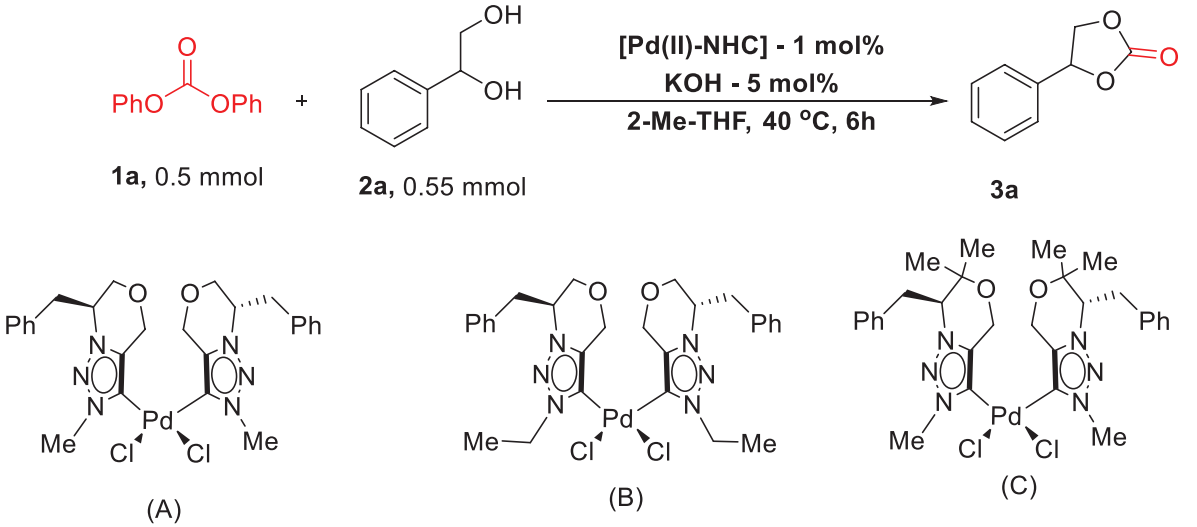
A 10 mL vial was charged with a mixture of 1-phenylethan-1-ol (61.1 mg, 0.5 mmol, 1 eq) and KOH (5.6 mg, 0.1 mmol, 20 mol%) in molar ratio of 5:1. The palladium complex-C (17.2 mg, 0.025 mmol, 5 mol%) was added to the mixture, followed by toluene (ca. 2 mL), and then the reaction mixture was heated at 100°C for 2 h. Mercury (0.126 g, 0.628 mmol) was added, and the reaction mixture was further heated at 100°C for 4 h. The reaction mixture was cooled to room temperature, and water (ca. 12 mL) was added. The resulting mixture was extracted with EtOAc (ca. 50 mL). The water layer was further extracted with EtOAc (ca. 3 × 20 mL). The crude mixture was purified by flash column chromatography using silica gel as stationary phase and hexane/ethyl acetate (95:5 v/v) as an eluent to afford the pure ketone product **2a** as colorless oil in 72% (44.7 mg) yield.

2. RESULTS AND DISCUSSION

2.1. Carbonylation reaction of various diols into value-added cyclic carbonates using DPC as a green carbonyl source (GCS) under Pd(II)–NHC Catalysis

In this study, we concentrated on the carbonylation reaction of different diols into their corresponding value-added carbonates using DPC as a GCS under Pd(II)-NHC catalysis, which led to the formation of cyclic carbonates as shown in Scheme 1.2. Continuing our efforts to develop sustainable chemistry under Pd(II)-NHC catalysis, we began our research by screening various Pd(II)-NHC complexes as catalysts in the carbonylation reaction of various diols into their corresponding value-added carbonates at 40°C for 6 h, using **2a** as the model substrate, **1a** DPC as a GCS, and 2-Me-THF (1 mL) as the solvent. The cyclic carbonate product **3a** is produced by the Pd(II)-NHC catalyst-**C** in 98% yield, indicating that the catalyst is very efficient [entries 1–3, Table 1]. KOH and TBD produced comparable isolated yields of the cyclic carbonate **3a** despite the fact that different bases were tested to find the best reaction conditions [entries 4–15, Table 1]. The best solvent, according to a quick solvent screening, seems to be 2-Me-THF [entries 16–28, Table 1]. No product was produced in the control experiments without a catalyst, proving that under ideal conditions, the direct formation of cyclic carbonate from diols and (DPC) as a GCS is essentially a catalytic process [entry 29, Table 1]. It is important to note that the carbonylation reactions can be easily carried out in the lab using standard procedures without the use of specialized tools such as a glovebox, Schlenk lines, a high-pressure reactor, or an inert atmosphere. It is also practical to carry out this Pd-NHC-catalyzed reaction without thoroughly drying the solvents.

We investigated substrate scope for carbonylation reactions, as shown in Scheme 2. After establishing the ideal circumstances, we looked into the variety of diol substrates. According to Scheme 2, under the ideal circumstances, a variety of terminal and internal vicinal 1,2-diols **2** and **4** easily reacted with **1** (DPC) to produce the corresponding cyclic carbonates **3** and **5**. First, we investigated the extent of terminal vicinal 1,2-diols. However, the terminal vicinal 1,2-diols containing electron-donating groups such as –Me (methyl), and -OMe (methoxy), at the para position of the aromatic ring of vicinal 1,2-diols were tolerated and yielded the corresponding value-added cyclic carbonates (**3b–c**), in good yields [54–64%, Scheme 2]. An electron-withdrawing groups such as –F (fluoro), -Cl (chloro), and -CF3 (trifluoromethane) at the C-4 position of the aromatic ring of vicinal 1,2-diols were highly reactive for carbonylation reaction and afforded cyclic carbonates (**3d–f**) in excellent yields [84–98%, Scheme]. When ethylene glycol (**2 g**), an un-substituted 1,2-diol also took part in the carbonylation reaction to produce ethylene carbonate (**3 g**), with a fantastic yield (82%). Furthermore, different terminal 1,2-diols with various alkyl substituents smoothly converted to the corresponding cyclic carbonates (**3i–k**) in very good to excellent yields [84–96%, Scheme 2], indicating that neither steric nor electronic variations of the alkyl substituents

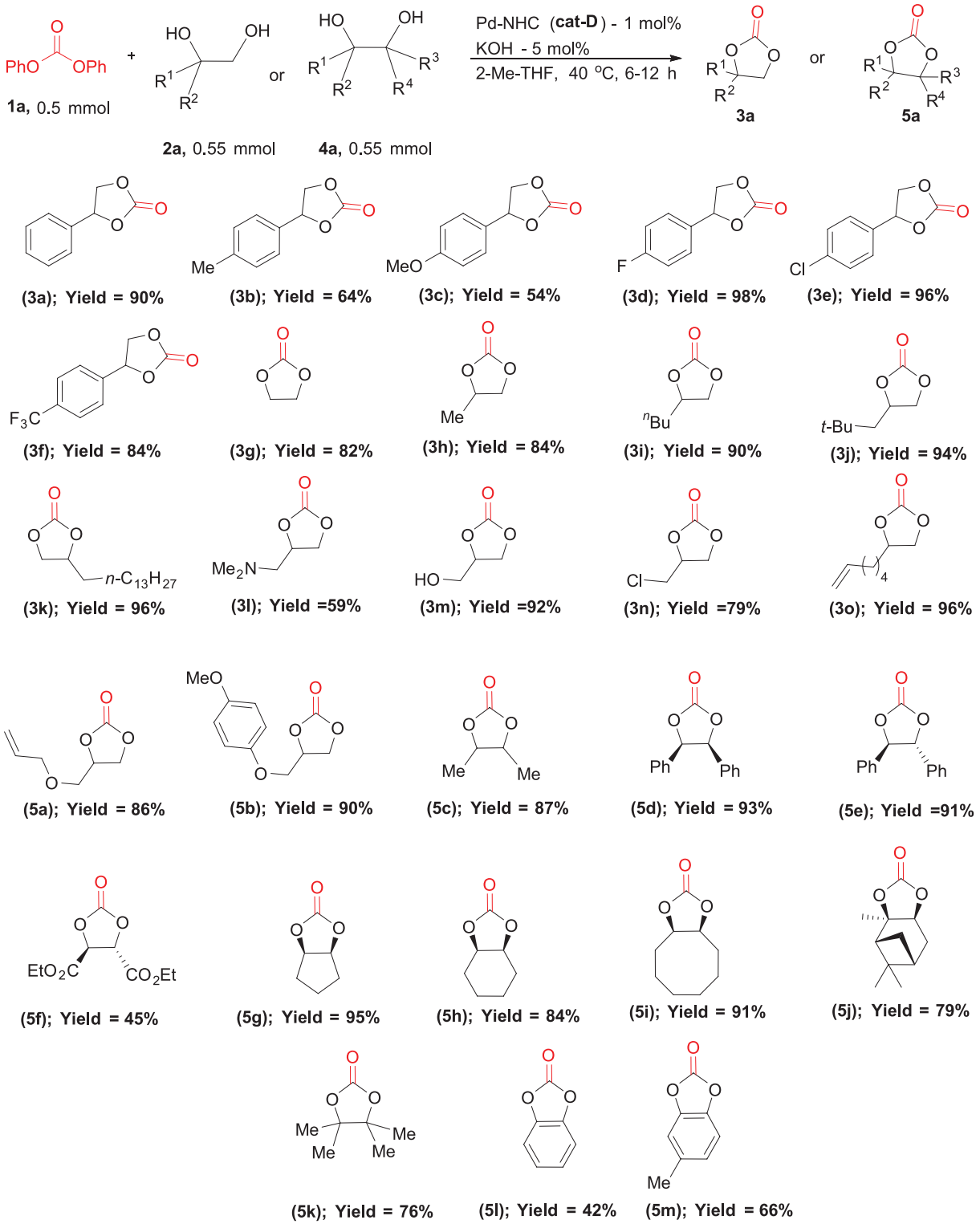


Scheme 1.2: Pd(II)–NHC catalyzed carbonylation reaction of various diols into value-added cyclic carbonates.

Table 1: Reaction optimization for carbonylation reaction of various diols into value-added cyclic carbonates using diphenyl carbonates as a green carbonyl source under palladium (II)-NHC catalysis[a]

Entry[a]	Pd-catalysts (0.005 mmol, 1 mol %)	Base (0.025 mmol, 5 mol %)	Solvent (mL)	Isolated Yield (%)[b]
1	catalyst-A (1)	KOH (5)	2-Me-THF	82
2	catalyst-B (1)	KOH (5)	2-Me-THF	86
3	catalyst-C (1)	KOH (5)	2-Me-THF	90
4	catalyst-C (1)	TBD (5)	2-Me-THF	87
5	catalyst-C (1)	MTBD (5)	2-Me-THF	63
6	catalyst-C (1)	DBU (5)	2-Me-THF	53
7	catalyst-C (1)	DABCO (5)	2-Me-THF	10
8	catalyst-C (1)	DMAP (5)	2-Me-THF	7
9	catalyst-C (1)	TEA (5)	2-Me-THF	n.d.
10	catalyst-C (1)	K_2CO_3 (5)	2-Me-THF	14
11	catalyst-C (1)	Na_2CO_3 (5)	2-Me-THF	7
12	catalyst-C (1)	Cs_2CO_3 (5)	2-Me-THF	23
13	catalyst-C (1)	NaOH (5)	2-Me-THF	68
15	catalyst-C (1)	Pyridine (5)	2-Me-THF	n.d.
16	catalyst-C (1)	KOH (5)	THF	80
17	catalyst-C (1)	KOH (5)	1, 4-dioxane	80
18	catalyst-C (1)	KOH (5)	DMF	70
19	catalyst-C (1)	KOH (5)	CH_3CN	33
20	catalyst-C (1)	KOH (5)	CCl_4	n.d.
21	catalyst-C (1)	KOH (5)	o-xylene	n.d.
22	catalyst-C (1)	KOH (5)	Cl-benzene	25
23	catalyst-C (1)	KOH (5)	tBuOH	25
24	catalyst-C (1)	KOH (5)	iPrOH	52
25	catalyst-C (1)	KOH (5)	1, 2-DCE	22
26	catalyst-C (1)	KOH (5)	Toluene	15
27	catalyst-C (1)	KOH (5)	H_2O	n.d.
28	catalyst-C (1)	KOH (5)	$CHCl_3$	Trace
29	-	KOH (5)	2-Me-THF	n.d.[c]

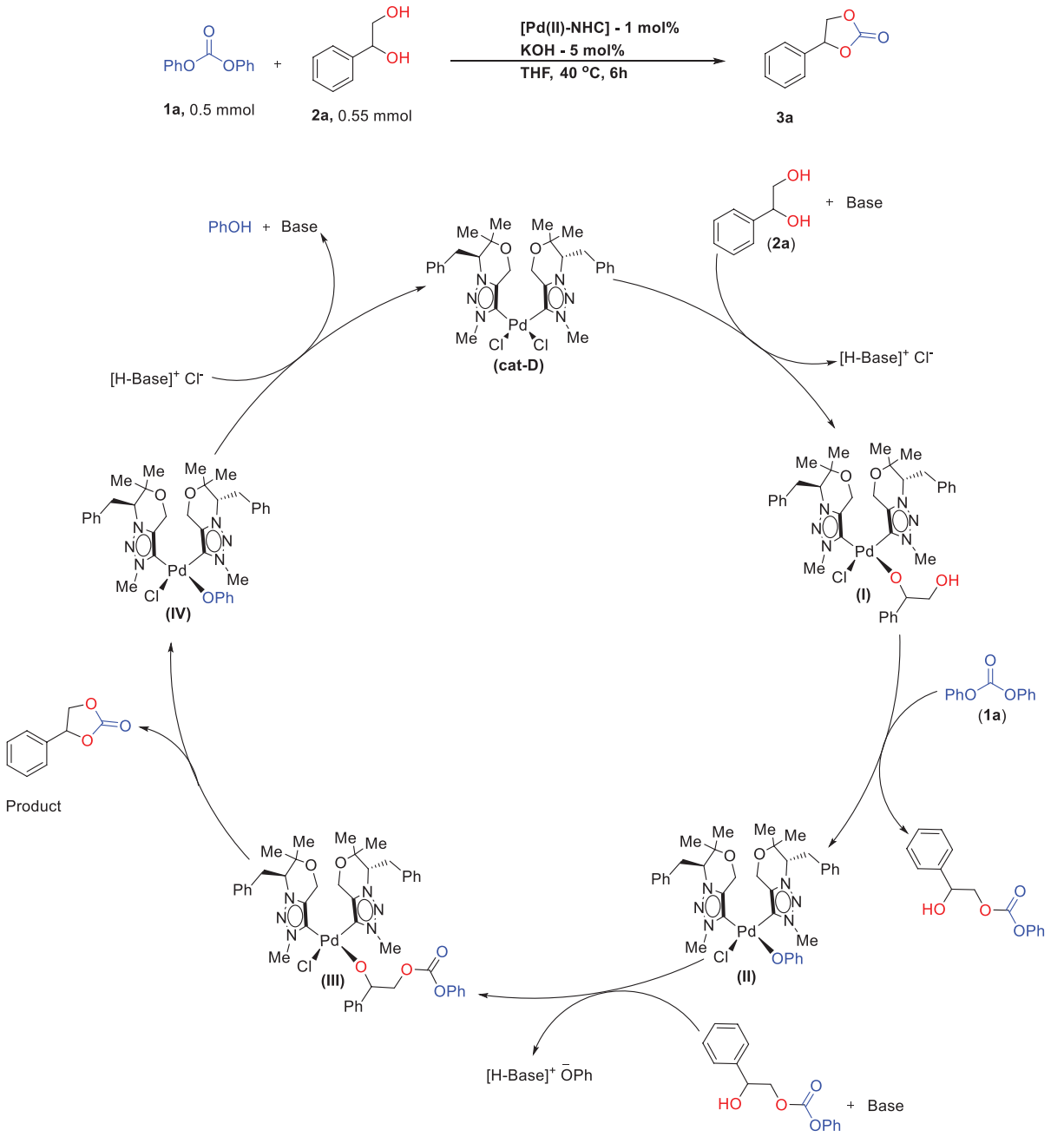
[a]All reactions were conducted at 40°C for 6 h using (Pd-NHC)/KOH/DPC/Diols in 0.005 mmol, 0.025 mmol, 0.5 mmol, and 0.55 mmol with 1-mL of 2-Me-THF as the solvent. [b]Isolated 3a yield. [c]A 2-h reaction was conducted without a catalyst. Me: Methyl, tBuOH: tert-Butyl, Pd: Palladium



Scheme 2: Selected results for carbonylation reaction of various diols into value-added cyclic carbonates using diphenyl carbonates as a green carbonyl source under Pd(II)–NHC Catalysis.

affected the carbonylation reaction's efficiency. When the terminal vicinal 1,2-diols containing various electron donating/withdrawing substituents were also converted to the corresponding cyclic carbonates (**3l–o**) in good to excellent yields [59–96%, Scheme 2], next, we looked at internal vicinal diols with different hydroxyl group substitution patterns [Scheme 2].

In fact, it has been reported that numerous catalysts can use CO_2 as the C1 source to change epoxides into cyclic carbonates [39,40]. The number and size of the substituents surrounding the three-membered heterocyclic are severely constrained by these catalytic methods [41-46]. Contrarily, the size and number of substituents at either position of the diols had little impact on the carbonylation that resulted, making this a very practical and useful technique for the production of different cyclic carbonates. Following that, a variety of internal 1,2-diols (4a–4m), including cyclic ones, produced the corresponding cyclic carbonates (5a–5m) with isolated yields ranging



Scheme 3: Proposed reaction mechanism for the carbonylation reaction of various diols into value-added cyclic carbonates using diphenyl carbonates as a green carbonyl source catalyzed under Pd(II)–NHC catalyst-C.

from 42% to 95%, much to our surprise as shown in Scheme 2. Under standard reaction conditions, a variety of 1,2-disubstituted vicinal diols smoothly underwent the anticipated carbonylation reaction and producing the corresponding cyclic carbonates (5a–5m). However, the cyclic carbonate **5f** was produced by the ester-functionalized diol **4f** at a conversion rate of only 45%. It appears likely that the Pd-NHC catalyst, KOH base, and ester functional groups will interact together and produce a number of side products. At 40°C in 16 h, the cis-1,2-cyclooctanediol (**4i**) demonstrated good efficiency and produced bicyclic carbonate (**5i**) in a 91% yield. In addition, the enantioenriched trisubstituted diol (**4j**) produced an excellent yield of 79% from the Pd-NHC-catalyzed reaction that successfully gave access to tricyclic carbonate (**5j**). Furthermore, we were happy to discover that the sterically more crowded vicinal diol **4k** was also well tolerated and produced the corresponding tetrasubstituted cyclic carbonate **5k** in 76% yield, which cannot be produced by coupling CO_2 with 2,3-dimethyl-2,3-epoxybutane [47]. Fortunately, we also discovered that aromatic 1,2-diols can use the developed reaction conditions. Catechol carbonates **5l** and **5m**, were produced by the carbonylation of catechol (**4l**) and 4-methylcatechol (**4m**) [48].

A plausible reaction mechanism for the Pd-NHC complex (D) catalyzed the carbonylation reaction of various diols into value-added cyclic carbonates using DPC as a GCS is proposed in light of the experimental findings and previously reported findings [Scheme 3]. The carbonylation reaction's mechanism might be comparable to some previously reported examples involving related catalytic systems [56-58]. First off, in the presence of KOH, Pd–NHC catalyst-C reaction with a diol molecule produces an intermediate called an alkoxide (I). Second, the intermediate (I) react with DPC and produces a 2-hydroxy-2-phenylethyl phenyl carbonate and metal

phenoxide species (II). Third, the specie (II) react with the base and 2-hydroxy-2-phenylethyl phenyl carbonate and gives the metal alkoxy phenyl carbonate intermediate (III) by cyclization of carbonate ring to produces the cyclic carbonate as product and metal phenoxide specie (IV). In the last step, the catalytic cycle is then produced by the intermediate (IV) and H–Base, which evolves Phenol and backs the catalyst-C as shown in Scheme 3.

3. CONCLUSION

Finally, using Pd(II)–NHC as a catalyst, we developed efficient protocols for the carbonylation reaction of various diols into their corresponding highly valuable cyclic carbonates. The different diols with electron-rich/electron-poor groups were effectively converted into their corresponding value-added cyclic carbonate products under Pd(II)-NHC catalysis using intermolecular carbonylation reactions under mild reaction conditions. This protocol is a highly efficient, economical, and environmentally friendly alternative to all other methods which requires harsh reaction conditions/hazardous solvents and reagents. All these catalysis products (heterocyclic compounds) were characterized by NMR spectroscopy.

4. ACKNOWLEDGMENT

The authors also, gratefully acknowledge the Department of Chemistry, University of Allahabad, Prayagraj. AK gratefully acknowledges UGC, New Delhi for the award of a Senior Research Fellowship and Junior Research Fellowship, respectively.

5. COMPETING INTEREST

The authors declare no competing financial interest.

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