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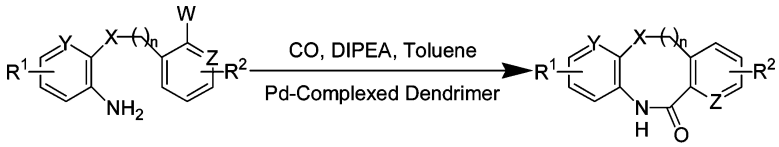

n = 0, 1; W = I, Br; X = O, S, NCH_3; Y, Z = CH, N

R^1, R^2 = H, F, Cl, CH_3, CH_3O, CF_3, CN, CH_3CO, CO_2CH_3, piperidinyl, morpholinyl

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Intramolecular Carbonylation Reactions with Recyclable Palladium-Complexed Dendrimers on Silica: Synthesis of Oxygen, Nitrogen, or Sulfur-Containing Medium Ring Fused Heterocycles

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Abstract: Palladium-complexed dendrimers supported on silica were evaluated as catalysts for intramolecular carbonylation reactions. The results showed that dendritic catalysts display high activity, affording oxygen, nitrogen, or sulfur-containing seven- or eight-membered ring fused heterocycles in excellent yields. Moreover, these catalysts have competitive advantages in that they can be easily recovered by simple filtration in air and reused for up to eight cycles with only a slight loss of activity.

Introduction

Medium-sized heterocycles are receiving a great deal of attention as their structural units are widely found in numerous natural products.[1] In particular, seven- and eight-membered ring heterocycles constitute a number of biologically interesting molecules.[2] The abundance of oxygen, nitrogen, or sulfur-containing medium rings in pharmaceuticals and agrochemicals continues to ensure that they are important synthetic targets for organic chemists. For example, dibenzoxazepinone derivatives represent an exciting field of research in medicinal chemistry due to their biological activity, including non-nucleoside inhibitors of HIV-1 RT and central nervous system agents.[3] Although these heterocycles can be prepared by conventional methods in multistep syntheses, the reactions often require severe conditions, and low yields of products are obtained in some cases. Therefore, it is important to develop a general and effective route to medium ring fused heterocycles.

The transition-metal-catalyzed carbonylation reaction is a powerful tool in organic chemistry. Reactions of this type provide a convenient and direct access to a large variety of heterocycles.[4] However, the difficulties associated with the separation of products from the reaction mixture and the recovery of the expensive, and sometimes toxic, catalysts are major drawbacks in these transformations. For the above reasons, many excellent homogeneous catalysts are not used on an industrial scale despite their benefits. Among the various approaches to address these problems, immobilization of a metal complex on a solid support offers the possibility for the recovery and reuse of catalysts,[5] but heterogeneous catalysts obtained in this way are usually accompanied by a significant decrease in activity.

Innovative methods for the development of environmentally friendly and economically viable catalytic systems are becoming more and more important in view of green chemistry. The advent of dendrimers provides a unique opportunity to combine

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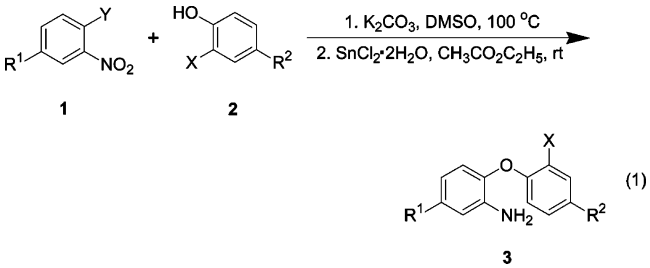
the advantages of both homogeneous and heterogeneous catalysts.[6,7] In fact, from the beginning, catalysis has been recognized as one of the most valuable applications of dendrimers. The key property of dendritic catalysts is their recovery and reuse by microfiltration[8] or precipitation[9] under specific conditions. Soluble dendritic catalysts have been successfully applied to a variety of organic reactions.[8−10] However, relatively few examples involve insoluble dendritic catalysts.[11] For instance, Dahan and Portnoy[11a] described the intramolecular Pauson−Khand reaction catalyzed by heterogeneous metallodendrimers. Sellner and Seebach[11b] investigated the use of polymer-supported chiral dendrimers for the enantioselective addition of diethylzinc to benzaldehyde. Recently, we reported that heterogeneous dendrimer−rhodium complexes are highly efficient catalysts for the hydroformylation of olefins at room temperature. The systems can be easily recovered by simple filtration in air and reused without loss of activity and selectivity.[12] These results stimulated us to explore intramolecular carbonylation reactions with recyclable palladium-complexed dendrimers on silica to form oxygen, nitrogen, or sulfur-containing medium ring fused heterocycles. We now demonstrate that heterogeneous dendrimer−palladium complexes are very effective catalysts for the synthesis of seven- and eight-membered ring fused heterocycles in excellent yields.

Results and Discussion

Synthesis of Dendritic Catalysts and Substrates. Palladium-complexed dendrimers on silica were synthesized by the modification of our previously reported method.[12c,d] Michael-type addition and amidation reactions were used to construct dendrimers supported on silica, followed by the phosphonation of dendrimers with diphenylphosphinomethanol. The resulting phosphonated dendrimers were then reacted with dichlorobis(benzonitrile)palladium(II) to give the dendrimer complexes **G0**−Pd−**G3**−Pd (Figure 1), which were characterized by solid-state ^{31}P NMR (complexed $\delta = 11$ ppm, uncomplexed $\delta = -27$ ppm). The ICP results showed the palladium contents of **G0**−Pd−**G3**−Pd are 0.57, 0.80, 0.52, and 0.29 mmol/g, respectively.

The requisite substrates are readily prepared by coupling and subsequent reduction reactions. For example, treatment of substituted 1-fluoro(chloro)-2-nitrobenzene **1** with 2-iodo(bromo)phenol **2** in the presence of potassium carbonate gave the corresponding nitro haloarenes, which were converted to 2-(2-halophenoxy)anilines **3** using tin(II) chloride dihydrate as the reducing reagent. The yields were 72−85% for the two steps (eq 1).[13] Other intramolecular carbonylation reaction precursors were also synthesized in a similar manner (see Supporting Information).



Optimization of Intramolecular Carbonylation Reaction Conditions. We selected 2-(2-iodophenoxy)aniline (**3**, $R^1 = R^2 = H$, X = I) as the model substrate and **G1**−Pd as the catalyst for the intramolecular carbonylation reaction in order to determine the optimized conditions. The influence of reaction temperature, solvent, and base was investigated, and the results are summarized in Table 1. The reaction temperature is

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(13) See Supporting Information for the preparation details.

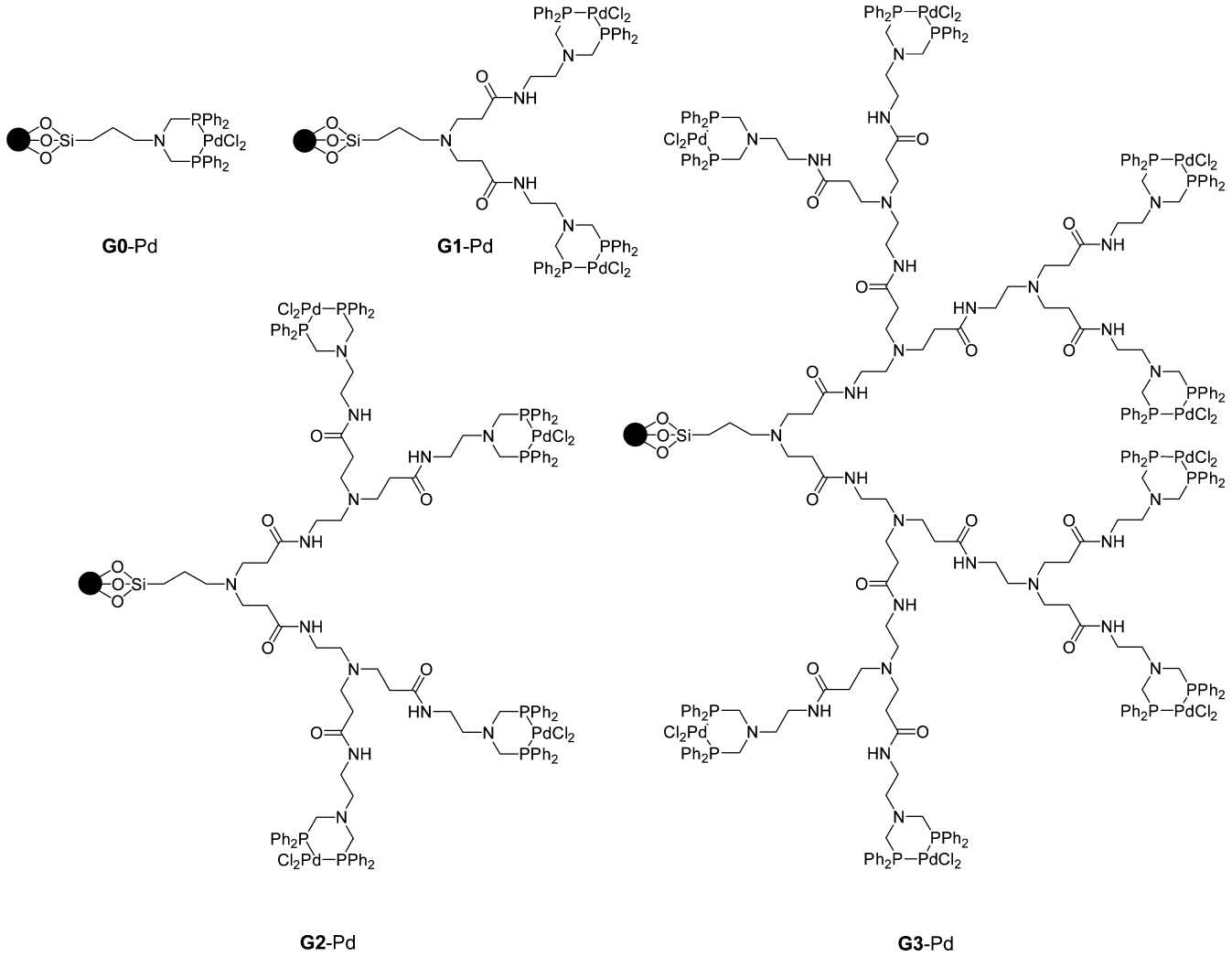


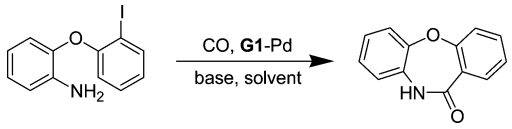
Figure 1. Structures of palladium-complexed dendrimers on silica **G0**−Pd−**G3**−Pd.

important for this transformation. Attempts to carry out the reaction of 2-(2-iodophenoxy)aniline in anhydrous toluene under 100 psi of carbon monoxide in the presence of **G1**−Pd and diisopropylethylamine at room temperature for 48 h did not afford the desired product, and the starting material was recovered unchanged (Table 1, entry 1). Increasing the temperature to 45 °C after 36 h resulted in 36% conversion of the iodinated arylamine to dibenzoxazepinone (Table 1, entry 2). When the carbonylation reaction proceeded at 60 and 70 °C for 22 h, 75 and 90% conversions were obtained, respectively (Table 1, entries 3 and 4). Complete conversion of the iodinated arylamine to dibenzoxazepinone was observed by raising the reaction temperature to 80 °C after 22 h (Table 1, entry 5).

We further explored the effect of solvent and base. Toluene proved to be the best solvent for this transformation (Table 1, entry 5). The reaction also worked well in benzene, dimethylformamide, tetrahydrofuran, acetonitrile, and 1,2-dimethoxyethane, affording >92% conversions (Table 1, entries 6−10), but only 61% conversion of the iodinated arylamine to dibenzoxazepinone occurred when the carbonylation reaction was run in dichloromethane (Table 1, entry 11). The use of an organic base, such as diisopropylethylamine (DIPEA) and 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), gave the desired product in full conversions (Table 1, entries 5 and 12), while there was 92% conversion when triethylamine was employed as the base (Table 1, entry 13). Potassium carbonate was also an effective base for the carbonylation reaction (Table 1, entry 14), but using another inorganic base, such as sodium carbonate, for this transformation resulted in only 73% conversion of the iodinated arylamine to dibenzoxazepinone (Table 1, entry 15). Intramolecular carbonylation did not take place in the absence of base (Table 1, entry 16).

Recyclability of Different Dendritic Catalysts. To evaluate the recyclability of different dendritic catalysts **G0**−Pd−**G3**−Pd, we selected 2-(2-iodophenoxy)aniline (**3**, $R^1 = R^2 = H$, X = I) as the substrate for the intramolecular carbonylation reaction. In a typical reaction, 1 mmol of **3** in 5 mL of toluene in the presence of 1.5 mmol of diisopropylethylamine with 15 mg of catalyst was treated with 100 psi of carbon monoxide at 80 °C for 22 h, and the results are listed in Table 2. The catalyst **G0**−Pd was found to be highly efficient for the intramolecular carbonylation reaction. The first two cycles gave quantitative conversion to the dibenzoxazepinone (Table 2, entries 1 and 2); 98−94% conversions were obtained from the third cycle to the fifth cycle (Table 2, entries 3−5), but by prolonging the reaction time to 36 h, the sixth cycle again afforded the desired product in full conversion (Table 2, entry 6). As seen from Table 2, **G1**−Pd showed the best recyclability. The dendritic catalyst

Table 1. Intramolecular Carbonylation of 2-(2-Iodophenoxy)aniline (**3**, $R^1 = R^2 = H$, X = I) with **G1**−Pd under Different Reaction Conditions[a]



Entry	Solvent	Base	Temp (°C)	Time (h)	Conversion[b] (%)
1	toluene	DIPEA	25	48	NR[c]
2	toluene	DIPEA	45	36	36
3	toluene	DIPEA	60	22	75
4	toluene	DIPEA	70	22	90
5	toluene	DIPEA	80	22	100
6	benzene	DIPEA	80	22	98
7	DMF	DIPEA	80	22	98
8	THF	DIPEA	80	22	96
9	CH_3CN	DIPEA	80	22	95
10	DME	DIPEA	80	22	92
11	CH_2Cl_2	DIPEA	80	22	61
12	toluene	DBU	80	22	100
13	toluene	Et_3N	80	22	92
14	toluene	K_2CO_3	80	22	100
15	toluene	Na_2CO_3	80	22	73
16	toluene	no	80	22	NR[c]

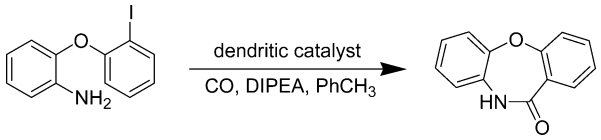
[a] With 1 mmol of 2-(2-iodophenoxy)aniline, 100 psi of CO, 15 mg of **G1**−Pd, 1.5 mmol of base and 5 mL of solvent. [b] Determined by GC. [c] No reaction.

can be recovered and reused up to eight cycles with only a slight loss of activity (Table 1, entries 7−14). Compared to **G0**−Pd and **G1**−Pd, the catalyst **G2**−Pd displayed somewhat lower activity (Table 2, entries 15−19). For example, the use of **G2**−Pd as the catalyst resulted in 98−90% conversions from the second cycle to the fifth cycle, whereas conversions ranged from 100 to 94% with **G0**−Pd (Table 2, entries 2−5 and 16−19).

The recyclability was considerably less successful when **G3**−Pd was used as the catalyst (Table 2, entries 20−24). The low activity of **G3**−Pd was attributed to steric crowding at the higher generation. It was expected that extending the chain length would relieve steric crowding and allow for increased catalyst loading. The dendritic catalyst **G3**(C6)−Pd was prepared by the use of 1,6-diaminohexane instead of the ethylenediamine linker, with 0.57 mmol/g palladium loading (see Supporting Information). Indeed, **G3**(C6)−Pd exhibited high activity with good recyclability comparable to the results obtained employing **G0**−Pd as the catalyst (Table 2, entries 1−5 and 25−29). Note that it is very easy to recover and reuse **G0**−Pd−**G3**−Pd by simple filtration in air.

Scope of the Intramolecular Carbonylation Reaction. (a) Synthesis of Seven-Membered Ring Fused Heterocycles. The intramolecular carbonylation of substituted 2-(2-iodophenoxy)-anilines **3** was effected to form seven-membered ring fused heterocycles under the optimized conditions, and the results are presented in Table 3. In all cases, the catalyst **G1**−Pd displayed high activity, and the carbonylation reaction proceeded very well, regardless of the nature of the substituents on the aromatic rings. Thus, iodinated arylamines **3** bearing either strongly electron-withdrawing or electron-donating substituents were efficiently converted to the corresponding dibenzoxazepinones **4** in excellent yields. Importantly, a wide variety of functional groups can be tolerated in this process, including chloro, methoxy, trifluoromethyl, cyano, acetyl, and methoxycarbonyl groups. Somewhat surprisingly, the presence of acetyl and

Table 2. Intramolecular Carbonylation of 2-(2-Iodophenoxy)aniline (**3**, $R^1 = R^2 = H$, X = I) with Different Palladium-Complexed Dendrimers[a]



Entry	Catalyst	Cycle	Conversion[b] (%)
1	**G0**−Pd	1	100
2	**G0**−Pd	2	100
3	**G0**−Pd	3	98
4	**G0**−Pd	4	97
5	**G0**−Pd	5	94
6[c]	**G0**−Pd	6	100
7	**G1**−Pd	1	100
8	**G1**−Pd	2	100
9	**G1**−Pd	3	98
10	**G1**−Pd	4	98
11	**G1**−Pd	5	97
12	**G1**−Pd	6	96
13	**G1**−Pd	7	95
14	**G1**−Pd	8	95
15	**G2**−Pd	1	100
16	**G2**−Pd	2	98
17	**G2**−Pd	3	95
18	**G2**−Pd	4	93
19	**G2**−Pd	5	90
20	**G3**−Pd	1	100
21	**G3**−Pd	2	83
22	**G3**−Pd	3	72
23	**G3**−Pd	4	65
24	**G3**−Pd	5	41
25	**G3**(C6)−Pd	1	100
26	**G3**(C6)−Pd	2	100
27	**G3**(C6)−Pd	3	97
28	**G3**(C6)−Pd	4	97
29	**G3**(C6)−Pd	5	95

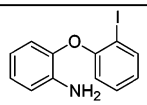
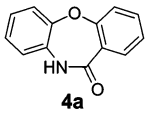
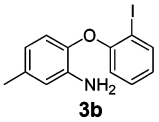
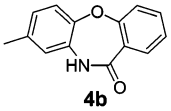
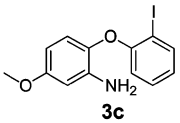
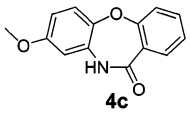
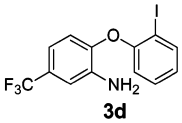
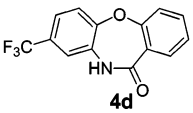
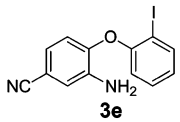
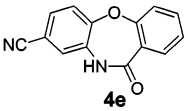
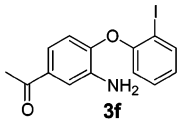
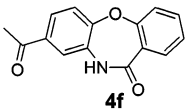
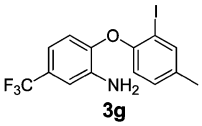
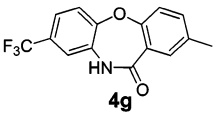
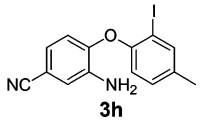
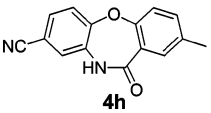
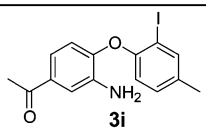
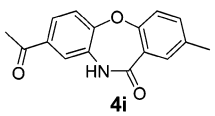
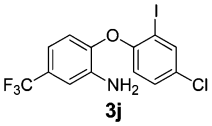
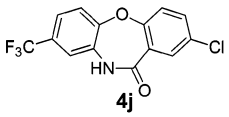
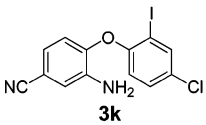
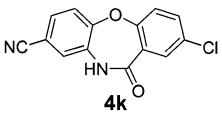
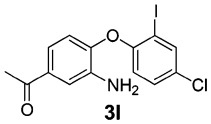
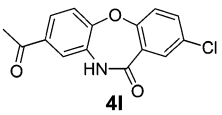
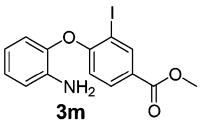
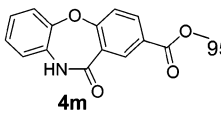
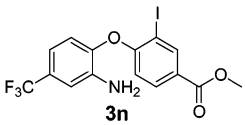
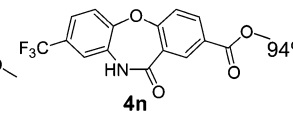
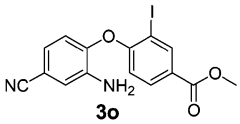
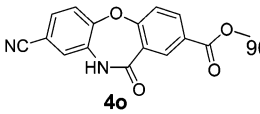
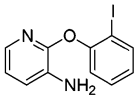
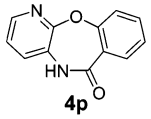
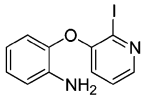
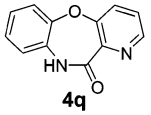
[a] With 1 mmol of 2-(2-iodophenoxy)aniline, 100 psi of CO, 15 mg of the dendritic catalyst, 1.5 mmol of DIPEA, 5 mL of toluene, 80 °C and 22 h. [b] Determined by GC. [c] Run for 36 h.

methoxycarbonyl groups on the aromatic rings did not have any impact on the intramolecular carbonylation reaction (Table 3, entries 6, 9, and 12−14). However, slightly lower yields were observed when a cyano group was on the aromatic rings (Table 3, entries 5, 8, 11, and 15). Furthermore, with **3p** and **3q** as pyridine-based substrates, pyridinyl-fused heterocycles **4p** and **4q** were obtained in 98 and 96% yields, respectively (Table 3, entries 16 and 17). It is important to note that the catalyst **G1**−Pd can be recovered and reused at least five cycles for all of these reactions (see Supporting Information).

Encouraged by the excellent results above, we attempted to utilize the relatively less reactive brominated arylamines as substrates for the intramolecular carbonylation reaction. When 2-(2-bromophenoxy)aniline[14] was subjected to reaction under the optimized conditions used for iodinated arylamines, 65% conversion occurred to the desired product. Performing the carbonylation reaction at 100 °C for 22 h gave 88% conversion. We were pleased to observe complete conversion of the brominated arylamine to dibenzoxazepinone **4a** by increasing the reaction temperature to 120 °C after 22 h. In the field of medicinal chemistry, introduction of a fluorine atom into molecules is one of the most efficient methods for the modifica-

(14) For the preparation of 2-(2-bromophenoxy)aniline, see: Wilshire, J. F. K. *Aust. J. Chem.* **1988**, *41*, 995−1001.

Table 3. Synthesis of Seven-Membered Ring Fused Heterocycles by **G1**−Pd-Catalyzed Intramolecular Carbonylation of Substituted 2-(2-Iodophenoxy)anilines[a]

Entry	Substrate	Product	Yield[b]
1	 **3a**	 **4a**	99%
2	 **3b**	 **4b**	97%
3	 **3c**	 **4c**	97%
4	 **3d**	 **4d**	98%
5	 **3e**	 **4e**	91%
6	 **3f**	 **4f**	94%
7	 **3g**	 **4g**	96%
8	 **3h**	 **4h**	91%
9	 **3i**	 **4i**	94%
10	 **3j**	 **4j**	97%
11	 **3k**	 **4k**	90%
12	 **3l**	 **4l**	95%
13	 **3m**	 **4m**	95%
14	 **3n**	 **4n**	94%
15	 **3o**	 **4o**	90%
16	 **3p**	 **4p**	98%
17	 **3q**	 **4q**	96%

[a] With 1 mmol of **3**, 100 psi of CO, 15 mg of **G1**−Pd, 1.5 mmol of DIPEA, 5 mL of toluene, 80 °C and 22 h. [b] Isolated yield.

tion of the lead compounds in view of biological activity.[15] For example, fluorinated aryl rings are often used as drug candidates in which a fluorine is substituted for a hydrogen to help block oxidation of the aromatic ring, alter metabolism pathways, and increase lipophilicity, which affects drug distribution.[16] In this context, seven fluorine-containing substrates **3r**−**3x** were prepared for **G1**−Pd catalyzed the intramolecular carbonylation reaction, and the results are illustrated in Table 4. As expected, all of these transformations took place smoothly and gave the desired products **4r**−**4x** in >90% isolated yields.

(b) Synthesis of Eight-Membered Ring Fused Heterocycles. The intramolecular carbonylation reaction was extended to the synthesis of eight-membered ring fused heterocycles. As can be seen from Table 5, the dendritic catalyst **G1**−Pd was found to be very efficient for carbonylation in all cases. Under the optimized conditions, the reactions of iodinated arylamines **5**[13] with either electron-withdrawing or electron-donating groups on the aromatic rings afforded the corresponding dibenzoxazocinones **6** in excellent yields. The wide functional group compatibility is a significant advantage for these transformations, as the intramolecular carbonylation reaction can encompass fluoro, chloro, methoxy, acetyl, and methoxycarbonyl groups. One can apply the reaction to a sterically hindered *ortho*-substituted arylamine **5c**, giving the desired product **6c** in slightly reduced yield (Table 5, entry 3). Heterocycles having piperidinyl or morpholinyl groups are the basic structures of many pharmacologically important compounds. Iodinated arylamines

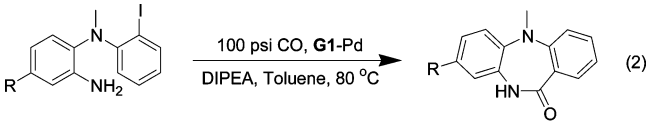
(15) (a) O'Hagen, D.; Rzepa, H. S. *Chem. Commun.* **1997**, 645−652. (b) Filler, R.; Kobayashi, Y.; Yagupolskii, L. M. *Biomedical Aspects of Fluorine Chemistry*; Elsevier: Amsterdam, 1993. (c) Mann, J. *Chem. Soc. Rev.* **1987**, *16*, 381−436. (d) Welch, J. T. *Tetrahedron* **1987**, *43*, 3123−3197.

(16) (a) Rosenblum, S. B.; Huynh, T.; Afonso, A.; Davis, H. R., Jr.; Yumibe, N.; Clader, J. W.; Burnett, D. A. *J. Med. Chem.* **1998**, *41*, 973−980. (b) Park, B. K.; Kitteringham, N. R. *Drug Metab. Rev.* **1994**, *26*, 605−643. (c) Abel, S. M.; Back, D. J.; Maggs, J. L.; Park, B. K. *J. Steroid Biochem. Mol. Biol.* **1993**, *46*, 833−839.

5k and **5l** were subjected to the intramolecular carbonylation reaction, and the corresponding dibenzoxazocinones **6k** and **6l** were obtained in 94 and 96% yields, respectively (Table 5, entries 11 and 12). The use of **5p** as the substrate afforded the naphthyl tetracyclic heterocycle **6p** (Table 5, entry 16). In the case of **5q**, the intramolecular carbonylation reaction furnished the desired product **6q** in 99% isolated yield, in which oxygen is on the other side of eight-membered ring (Table 5, entry 17). The dendritic catalyst **G1**−Pd can be recovered and reused at least five times for all of these transformations (see Supporting Information).

The brominated arylamines **5r**−**5x** also proved to be viable substrates for the intramolecular carbonylation reaction. Treatment of substituted 2-(2-bromobenzyloxy)anilines **5r**−**5x** in anhydrous toluene with 100 psi of carbon monoxide in the presence of **G1**−Pd and diisopropylethylamine at 120 °C for 22 h afforded the corresponding eight-membered ring fused heterocycles **6r**−**6x** in high yields. The results are presented in Table 6.

(c) Synthesis of Nitrogen or Sulfur-Containing Medium Ring Fused Heterocycles. By changing the atom connecting the two aromatic rings from oxygen to nitrogen, one can isolate dibenzodiazepinones **8** in excellent yields. Specifically, substituted *N*-methyl-*N*-(2-iodophenyl)-1,2-benzenediamines **7**[13] (R = H, CF_3) were used as the substrates for the intramolecular carbonylation reaction in the presence of **G1**−Pd, affording 98 and 96% yields of the desired products **8a** and **8b**, respectively (eq 2).

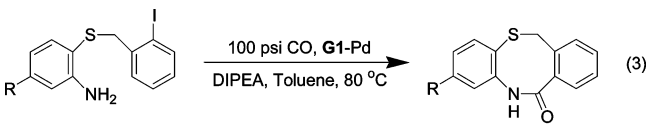


(2)

7a R = H
7b R = CF_3

8a R = H, 98%
8b R = CF_3, 96%

The carbonylation of sulfur-containing compounds is a challenge in palladium-based methods because of the strong affinity of sulfur for palladium, often resulting in low, if any, catalytic activity. We were gratified to observe that **G1**−Pd efficiently catalyzed the intramolecular carbonylation of substituted 2-(2-iodobenzylthio)anilines **9**[13] (R = H, Cl, CF_3) and gave rise to the corresponding dibenzothiazocinones **10** in 92−97% yields. Therefore, the sulfur atom did not have any influence on these transformations (eq 3).



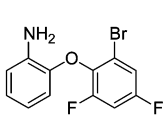
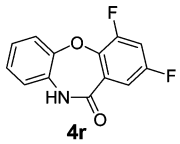
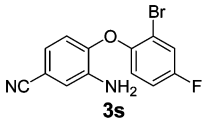
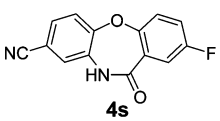
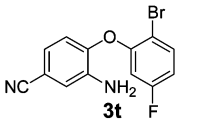
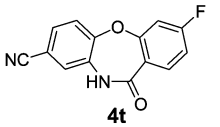
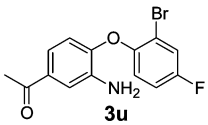
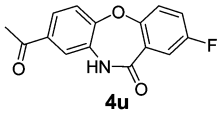
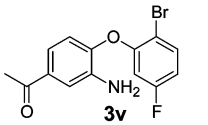
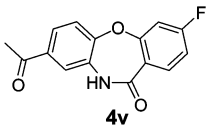
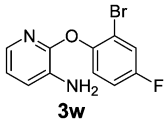
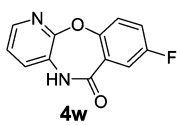
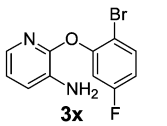
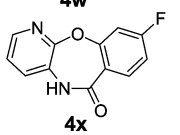
(3)

9a R = H
9b R = Cl
9c R = CF_3

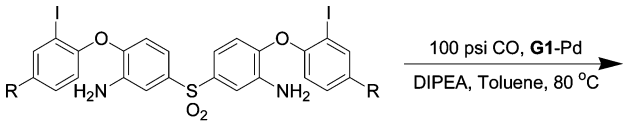
10a R = H, 97%
10b R = Cl, 92%
10c R = CF_3, 95%

(d) Intramolecular Double Insertion of Carbon Monoxide. The intramolecular double insertion of carbon monoxide was next carried out with **G1**−Pd as the catalyst. Typically, 0.5 mmol of substituted 3-amino-4-(2-iodophenoxy)phenyl sulfones **11**[13] (R = H, CH_3, Cl) and 1.5 mmol of diisopropylethylamine in 5 mL of anhydrous toluene with 15 mg of **G1**−Pd were subjected to 100 psi of carbon monoxide at 80 °C for 22 h, affording the desired products **12** in 90−93% yields (eq 4).

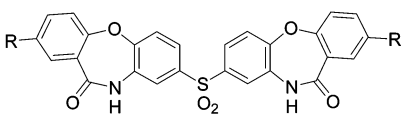
Table 4. Synthesis of Seven-Membered Ring Fused Heterocycles by **G1**−Pd-Catalyzed Intramolecular Carbonylation of Substituted 2-(2-Bromophenoxy)anilines[a]

Entry	Substrate	Product	Yield[b]
1	 **3r**	 **4r**	98%
2	 **3s**	 **4s**	90%
3	 **3t**	 **4t**	91%
4	 **3u**	 **4u**	94%
5	 **3v**	 **4v**	95%
6	 **3w**	 **4w**	97%
7	 **3x**	 **4x**	98%

[a] With 1 mmol of **3**, 100 psi of CO, 15 mg of **G1**−Pd, 1.5 mmol of DIPEA, 5 mL of toluene, 120 °C and 22 h. [b] Isolated yield.



11



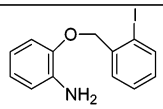
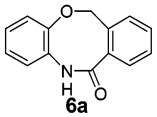
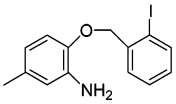
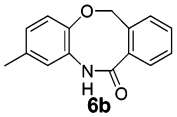
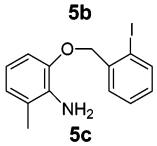
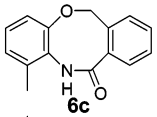
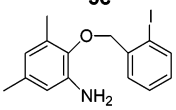
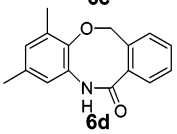
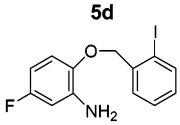
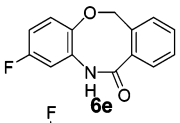
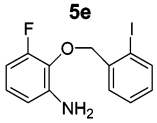
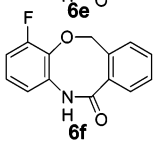
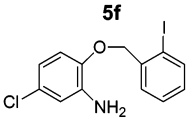
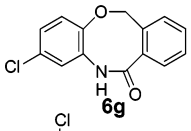
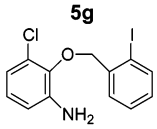
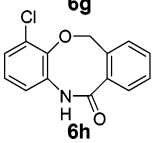
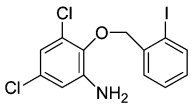
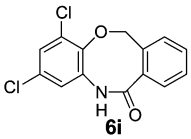
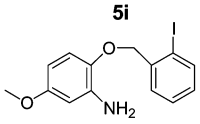
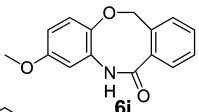
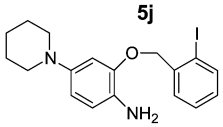
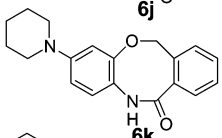
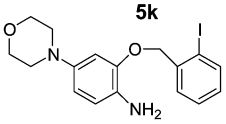
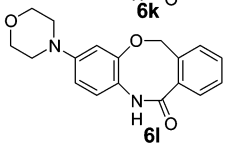
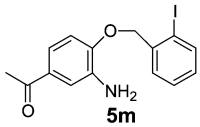
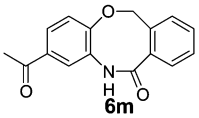
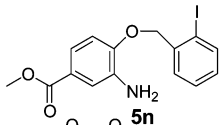
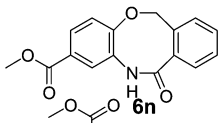
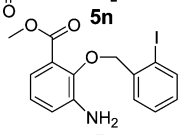
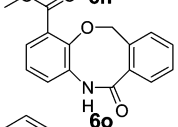
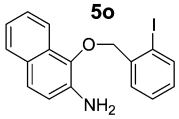
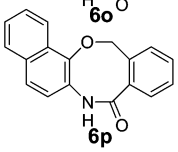
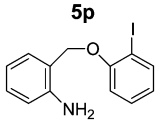
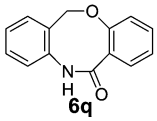
(4)

12a R = H, 92%
12b R = CH_3, 93%
12c R = Cl, 90%

Similarly, the iodinated arylamine **13**[13] was smoothly converted to the corresponding pentacyclic heterocycle **14** in 88% yield under the same conditions (eq 5). These examples further demonstrate the efficiency of the intramolecular carbonylation reaction for the construction of fused heterocycles in the presence of dendritic catalysts.

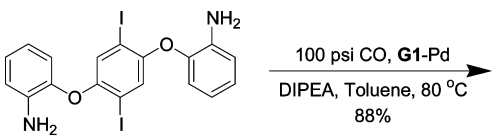
(e) Synthesis of a Six-Membered Ring Fused Heterocycle. After the synthesis of seven- and eight-membered ring fused

Table 5. Synthesis of Eight-Membered Ring Fused Heterocycles by **G1**−Pd-Catalyzed Intramolecular Carbonylation of Substituted 2-(2-Iodobenzyloxy)anilines[a]

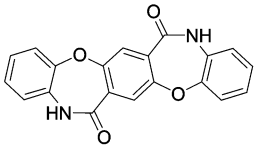
Entry	Substrate	Product	Yield[b]
1	 **5a**	 **6a**	98%
2	 **5b**	 **6b**	97%
3	 **5c**	 **6c**	91%
4	 **5d**	 **6d**	96%
5	 **5e**	 **6e**	98%
6	 **5f**	 **6f**	95%
7	 **5g**	 **6g**	97%
8	 **5h**	 **6h**	94%
9	 **5i**	 **6i**	96%
10	 **5j**	 **6j**	97%
11	 **5k**	 **6k**	94%
12	 **5l**	 **6l**	96%
13	 **5m**	 **6m**	94%
14	 **5n**	 **6n**	95%
15	 **5o**	 **6o**	93%
16	 **5p**	 **6p**	97%
17	 **5q**	 **6q**	99%

[a] With 1 mmol of **5**, 100 psi of CO, 15 mg of **G1**−Pd, 1.5 mmol of DIPEA, 5 mL of toluene, 80 °C and 22 h. [b] Isolated yield.

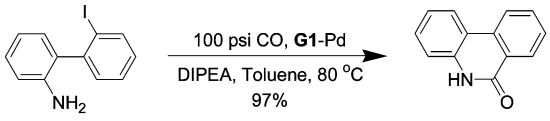
heterocycles, we were interested in exploring whether the intramolecular carbonylation reaction could be applied to the preparation of a six-membered ring. 2-(2-Iodophenyl)aniline (**15**),[17] on reaction with carbon monoxide in the presence of **G1**−Pd, gave 6(5*H*)-phenanthridinone (**16**) in 97% yield (eq 6).



13



14 (5)



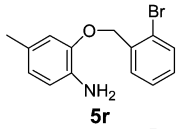
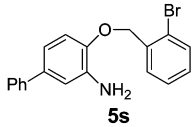
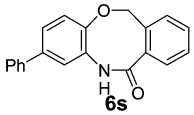
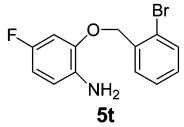
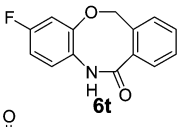
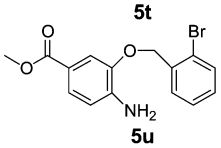
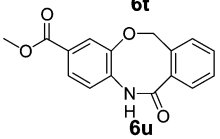
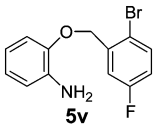
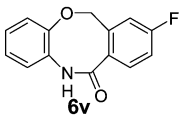
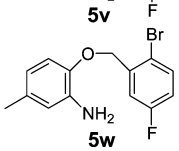
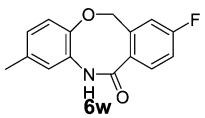
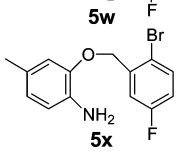
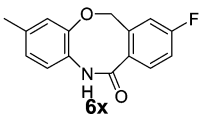
15 **16** (6)

Summary

In conclusion, we have developed a general and highly efficient method for the synthesis of oxygen, nitrogen, or sulfur-containing medium ring fused heterocycles by intramolecular

(17) For the preparation of 2-(2-iodophenyl)aniline (**15**), see: Cade, J. A.; Pilbeam, A. *J. Chem. Soc.* **1964**, 114−121.

Table 6. Synthesis of Eight-Membered Ring Fused Heterocycles by **G1**−Pd-Catalyzed Intramolecular Carbonylation of Substituted 2-(2-Bromobenzyloxy)anilines[a]

Entry	Substrate	Product	Yield[b]
1	 **5r**	 **6r**	98%
2	 **5s**	 **6s**	95%
3	 **5t**	 **6t**	96%
4	 **5u**	 **6u**	94%
5	 **5v**	 **6v**	98%
6	 **5w**	 **6w**	96%
7	 **5x**	 **6x**	97%

[a] With 1 mmol of **5**, 100 psi of CO, 15 mg of **G1**−Pd, 1.5 mmol of DIPEA, 5 mL of toluene, 120 °C and 22 h. [b] Isolated yield.

carbonylation reactions with recyclable palladium-complexed dendrimers on silica as catalysts. This process can tolerate a wide array of functional groups, including halide, ether, nitrile, ketone, and ester. The dendritic catalysts show high activity for these transformations, affording the desired heterocycles in excellent yields. Importantly, these catalysts are easily recovered by simple filtration in air and can be reused up to the eight cycles with only a slight loss of activity. This research should have broad applications in organic synthesis.

Experimental Section

Carbon monoxide, a powerful asphyxiant, should be used with care. To use and work with carbon monoxide safely, reactions must be carried out in a properly working fumehood with carbon monoxide detectors installed nearby.

General Procedure for the Intramolecular Carbonylation Reaction. A glass liner containing the substrate (1 mmol), dendritic catalyst (15 mg), diisopropylethylamine (1.5 mmol), and toluene (5 mL) was placed in a 45 mL autoclave equipped with a magnetic stirring bar. The autoclave was flushed three times with carbon monoxide and pressurized to 100 psi. The autoclave was then placed in an oil bath preset to the desired temperature on a stirring hot plate (80 °C for iodides and 120 °C for bromides). After 22 h, the autoclave was removed from the oil bath and cooled to room temperature prior to the release of excess carbon monoxide. The reaction mixture was filtered and washed with dichloromethane. The combined solvent was evaporated in vacuo, and the residue was purified by silica gel chromatography with a mixture of hexane and ethyl acetate as the eluant to afford the product. The recovered catalyst was reused for subsequent cycles.

2-Methyl-8-acetyldibenz[*b,f*][1,4]oxazepin-11(10*H*)-one (4i): mp 269−270 °C; IR (neat) 1685, 1660 cm^{-1}; ^1H NMR (500 MHz, CD_3SOCD_3) δ 10.60 (s, 1H), 7.74−7.71 (m, 2H), 7.56 (d, J = 2.0 Hz, 1H), 7.43−7.40 (m, 2H), 7.24 (d, J = 8.5 Hz, 1H), 2.52 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (500 MHz, CD_3SOCD_3) δ 197.29, 166.43, 156.92, 154.68, 135.97, 135.94, 135.36, 132.35, 132.23, 126.69, 125.73, 122.46, 122.13, 121.34, 27.54, 20.92; MS (EI) *m*/*z* 267 [M^+]; HRMS calcd for $C_{16}H_{13}NO_3$ 267.0895, found 267.0875.

8-Fluoropyrido[2,3-*b*][1,4]benzoxazepin-6(5*H*)-one (4w): mp 296−297 °C; IR (neat) 1658 cm^{-1}; ^1H NMR (500 MHz, CD_3SOCD_3) δ 10.78 (s, 1H), 8.04 (dd, J = 1.8, 5.0 Hz, 1H), 7.61 (dd, J = 1.5, 8.0 Hz, 1H), 7.53−7.47 (m, 2H), 7.41 (dd, J = 5.0, 8.5 Hz, 1H), 7.32 (dd, J = 4.7, 7.8 Hz, 1H); ^{13}C NMR (500 MHz, CD_3SOCD_3) δ 164.83, 159.65 (d, J = 241.2 Hz), 155.86, 153.74, 143.93, 131.81, 127.43 (d, J = 7.8 Hz), 126.68, 124.06 (d, J = 8.5 Hz), 123.65, 122.23 (d, J = 23.5 Hz), 117.80 (d, J = 25.3 Hz); MS (EI) *m*/*z* 230 [M^+]; HRMS calcd for $C_{12}H_7FN_2O_2$ 230.0492, found 230.0471.

3-(4-Morpholinyl)-6*H*-dibenz[*b,f*][1,4]oxazocin-11(12*H*)-one (6l): mp 242−243 °C; IR (neat) 1660 cm^{-1}; ^1H NMR (500 MHz, CD_3SOCD_3) δ 9.41 (s, 1H), 7.40−7.28 (m, 4H), 6.80 (d, J = 8.5 Hz, 1H), 6.49−6.44 (m, 2H), 5.33 (s, 2H), 3.64 (t, J = 4.6 Hz, 4H), 2.97 (t, J = 4.6 Hz, 4H); ^{13}C NMR (500 MHz, CD_3SOCD_3) δ 173.22, 152.78, 151.68, 137.86, 132.47, 130.92, 129.77, 129.66, 128.84, 128.26, 121.65, 110.36, 107.71, 73.13, 66.78, 48.69; MS (EI) *m*/*z* 310 [M^+]; HRMS calcd for $C_{18}H_{18}N_2O_3$ 310.1317, found 310.1301.

8-Fluoro-3-methyl-6*H*-dibenz[*b,f*][1,4]oxazocin-11(12*H*)-one (6x): mp 220−221 °C; IR (neat) 1660 cm^{-1}; ^1H NMR (500 MHz, CD_3SOCD_3) δ 9.61 (s, 1H), 7.38 (dd, J = 5.5, 8.0 Hz, 1H), 7.17−7.14 (m, 2H), 6.84 (d, J = 8.0 Hz, 2H), 6.73 (dd, J = 1.5, 8.0 Hz, 1H), 5.33 (s, 2H), 2.15 (s, 3H); ^{13}C NMR (500 MHz, CD_3SOCD_3) δ 172.14, 163.02 (d, J = 245.6 Hz), 151.68, 138.44, 135.59 (d, J = 7.6 Hz), 133.62, 131.13 (d, J = 8.6 Hz), 128.25, 127.50, 124.90, 122.49, 116.48 (d, J = 21.2 Hz), 115.45 (d, J = 21.9 Hz), 73.07, 21.10; MS (EI) *m*/*z* 257 [M^+]; HRMS calcd for $C_{15}H_{12}FNO_2$ 257.0852, found 257.0828.

5,10-Dihydro-5-methyl-8-trifluoromethyl-11*H*-dibenzo[*b,e*][1,4]-diazepin-11-one (8b): mp 240−241 °C; IR (neat) 1662 cm^{-1}; ^1H NMR (500 MHz, CD_3SOCD_3) δ 10.40 (s, 1H), 7.64 (dd, J = 1.8, 7.8 Hz, 1H), 7.50 (dt, J = 1.5, 7.5 Hz, 1H), 7.43 (dd, J = 2.5, 8.5 Hz, 1H), 7.35−7.33 (m, 2H), 7.21 (d, J = 8.5 Hz, 1H), 7.10 (dt, J = 1.0, 8.0 Hz, 1H), 3.29 (s, 3H); ^{13}C NMR (500 MHz, CD_3SOCD_3) δ 168.87, 152.68, 148.42, 148.40, 134.02, 133.77, 127.30, 125.02 (q, J = 32.1 Hz), 124.84 (q, J = 269.9 Hz), 124.05, 122.30 (q, J = 3.7 Hz), 120.92, 118.95, 118.63 (q, J = 3.6 Hz), 38.51; MS (EI) *m*/*z* 292 [M^+]; HRMS calcd for $C_{15}H_{11}F_3N_2O$ 292.0823, found 292.0801.

2-Chloro-6*H*-dibenzo[*b,f*][1,4]thiazocin-11(12*H*)-one (10b): mp 294−295 °C; IR (neat) 1665 cm^{-1}; ^1H NMR (500 MHz, CD_3SOCD_3) δ 9.93 (s, 1H), 7.31−7.27 (m, 2H), 7.20−7.16 (m, 4H), 7.10 (dd, J = 2.5, 8.5 Hz, 1H), 4.39 (s, 1H), 4.10 (s, 1H); ^{13}C NMR (500 MHz, CD_3SOCD_3) δ 173.15, 140.81, 138.38, 134.36, 132.33, 132.11, 131.92, 130.94, 129.70, 129.30, 128.53, 128.26, 126.03, 35.53; MS (EI) *m*/*z* 275 [M^+]; HRMS calcd for $C_{14}H_{10}ClNOS$ 275.0172, found 275.0151.

10,11-Dihydro-2-methyl-11-oxodibenz[*b,f*][1,4]oxazepine-8-sulfone (12b): mp 192−194 °C; IR (neat) 1660 cm^{-1}; ^1H NMR (500 MHz, CD_3SOCD_3) δ 10.63 (s, 2H), 7.69 (d, J = 2.0 Hz, 2H), 7.64 (dd, J = 2.0, 8.5 Hz, 2H), 7.49 (d, J = 5.8 Hz, 4H), 7.35−7.33 (m, 2H), 7.18−7.16 (m, 2H), 2.24 (s, 6H); ^{13}C NMR (500 MHz, CD_3SOCD_3) δ 166.15, 156.53, 154.63, 138.79, 136.16, 136.04, 133.37, 132.22, 125.44, 125.27, 123.84, 121.48, 121.28, 20.91; MS (EI) *m*/*z* 512 [M^+]; HRMS calcd for $C_{28}H_{20}N_2O_6S$ 512.1042, found 512.1019.

8*H*,16*H*-5,13-Dioxa-8,16-diazadibenzo[*d,d′*]benzo[1,2-*a*;4,5-*a′*]dicycloheptene-7,15-dione (14): mp >300 °C; IR (neat) 1662 cm^{-1}; ^1H NMR (500 MHz, CD_3SOCD_3) δ 10.76 (s, 2H), 7.67 (s, 2H), 3.38 (dd,

J = 1.3, 7.8 Hz, 2H), 7.19−7.11 (m, 6H); ^{13}C NMR (500 MHz, CD_3SOCD_3) δ 164.56, 155.74, 150.55, 130.99, 130.01, 126.60, 125.94, 123.64, 122.18, 121.80; MS (EI) m/z 344 [M^+]; HRMS calcd for $C_{20}H_{12}N_2O_4$ 344.0797, found 344.0771.

6(5*H*)-Phenanthridinone (16):[18] mp 292−293 °C; IR (neat) 1660 cm^{-1}; ^{1}H NMR (500 MHz, CD_3SOCD_3) δ 11.68 (s, 1H), 8.49 (d, J = 8.5 Hz, 1H), 8.37 (d, J = 7.5 Hz, 1H), 8.31 (dd, J = 1.5, 8.0 Hz, 1H), 7.84 (dt, J = 1.7, 7.5 Hz, 1H), 7.64 (dt, J = 1.0, 7.5 Hz, 1H), 7.47 (dt, J = 1.5, 7.5 Hz, 1H), 7.35 (dd, J = 1.3, 8.2 Hz, 1H), 7.25 (dt, J = 1.5, 7.7 Hz, 1H); ^{13}C NMR (300 MHz, CD_3SOCD_3) δ 161.48, 137.22, 134.92, 133.48, 130.24, 128.60, 128.14, 126.34, 123.93, 123.29, 122.94, 118.22, 116.78; MS (EI) m/z 195 [M^+]; HRMS calcd for $C_{13}H_9NO$ 195.0684, found 195.0662.

(18) Lamba, J. J. S.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11723−11736.

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Supporting Information Available: Experimental details, characterization data, Tables 7−14 of recycling and reuse of the dendritic catalyst **G1**−Pd for intramolecular carbonylation reactions, and copies of ^{1}H NMR and ^{13}C NMR spectra for the final products. This material is available free of charge via the Internet at http://pubs.acs.org.

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