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Efficient One-Pot Synthesis of Multi-Substituted Dihydrofurans by Ruthenium(II)-Catalyzed [3+2] Cycloaddition of Cyclic or Acyclic Diazodicarbonyl Compounds with Olefins

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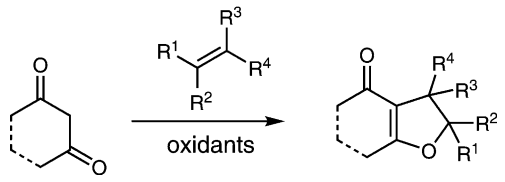
Abstract: Ruthenium(II)-phosphine complexes-catalyzed [3+2] cycloadditions were conducted to synthesize a variety of dihydrofurans by reactions of cyclic or acyclic diazodicarbonyl compounds with olefins. This method represents a direct and efficient one-pot synthesis for multi-substituted dihydrofurans under mild reaction conditions with an excellent regioselectivity. Furthermore, to reduce reaction times and increase yields of dihydrofurans, microwave-assisted tris(triphenylphosphine)ruthenium(II) chloride/1-butyl-3-methylimidazolium tetrafluoroborate $\{Ru(PPh_3)_3Cl_2/[Bmim]BF_4\}$-catalyzed reactions were also developed. The synthesized dihydrofurans can be readily converted into biologically interesting tetrahydroindoles.

Keywords: cycloaddition; diazo compounds; ionic liquids; microwave chemistry; ruthenium

Introduction

Dihydrofurans are one of the most commonly observed classes of structural units found in natural and synthetic products with biological activities.[1] Molecules containing the dihydrofuran moiety are widely used as pharmaceuticals, flavors, insecticides, and fish antifeedants.[2] Their important biological activities and usefulness as synthetic intermediates for natural products have attracted tremendous attention over the last two decades.[3]

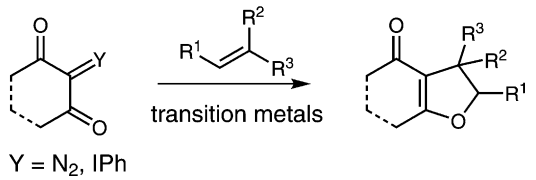
Numerous methods have already been developed for the synthesis of dihydrofurans.[4] In general, these methods are based on radical pathways *via* the oxidative cycloaddition of 1,3-dicarbonyl compounds to the appropriate olefins (Scheme 1). The oxidants used include cerium(IV) ammonium nitrate (CAN),[5] manganese(III) acetate $[Mn(OAc)_3]$,[6] and silver carbonate on Celite ($AgCO_3$/Celite).[7] However, the use of strong oxidants sometimes adversely affects olefin polymerization.[8] To achieve complete reactions, two equivalents of oxidants are needed, which makes product separation problematic.



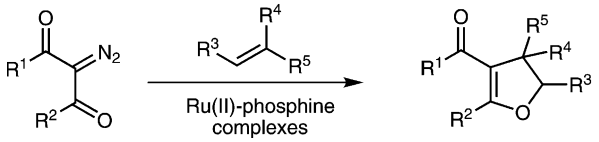
Scheme 1. Oxidant-mediated cycloaddition for the synthesis of dihydrofurans starting from 1,3-dicarbonyl compounds.

Transition metal-catalyzed reactions between diazodicarbonyls or iodonium ylides and olefins have also been reported (Scheme 2). Among these, Cu(I), Cu(II) and Rh(II) species are usually used as catalysts.[9] However, use of Cu(I) and Cu(II) metals results in complex mixtures due to the requirement for high temperatures.[10] On the other hand, silver(I) and rhodium(II) metals are better catalysts for metal carbenoid transformations,[11] although it has the drawback of insertion products[12] and α-chloro compounds[13] formed by reactions of solvents such as ethylene chloride, benzene, toluene, and 1,4-dioxane. Furthermore, reaction rates are not controllable, and explosions can occur due to the rapid emission of large amounts of N_2. Reactions of iodonium ylides provided α-iodo-β-phenoxyenones through an intramolecular thermal rearrangement.[14]

To overcome these issues, we have developed a facile methodology for synthesizing dihydrofurans by utilizing the $AgBF_4/[Bmim]BF_4$-catalyzed reactions of diazodicarbonyls.[15] However, this reaction is suitable for specific styrenes and vinyl acetates, whereas other olefins such as vinyl ethers, acrylates, 2,3-dihy-



Scheme 2. Transition metals-catalyzed cycloaddition for the synthesis of dihydrofurans starting from diazodicarbonyl compounds and iodonium ylides.



Scheme 3. Ru(II)-phosphine complexes-catalyzed [3+2] cycloaddition of diazodicarbonyls with olefins.

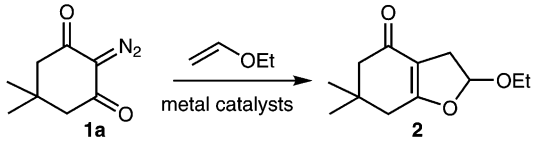
drofurans, 3,4-dihydropyrans, and 1,3-butadienes, tend to produce polymerized unidentified adducts.[15]

Although numerous methods have been reported for the synthesis of dihydrofurans, there is still a need for simpler, less toxic, more effective, and milder catalysts that are suitable for a wide range of olefins. A precedent for the formation of dihydrofurans from diazo compounds by chiral Ru(II) complex-catalyzed reactions has been previously reported by Müller and Chappellet.[16] Recently, Zhang et al. described Co(II)-porphyrin complex-catalyzed reactions of diazodicarbonyl compounds in the context of efficient metal catalyst development for the synthesis of multi-substituted furans starting from diazodicarbonyl compounds.[17] Our interest in developing a mild and efficient synthetic methodology that provided a variety of multi-substituted dihydrofurans caused us to search for more convenient and safer catalysts. Ru(II)-phosphine complexes appeared to be promising for the synthesis of multi-substituted dihydrofurans because of their availability, sustainability, lack of toxicity, and environmentally friendly properties.[18] Here, we report on the facile and efficient synthesis of multi-substituted dihydrofurans *via* the Ru(II)-phosphine complexes-catalyzed [3+2] cycloaddition of diazodicarbonyls to olefins (Scheme 3). In addition, the microwave-assisted $Ru(PPh_3)_3Cl_2$/[Bmim]BF_4-catalyzed reactions were also investigated with a view toward shortening reaction times and increasing yields.

Results and Discussion

Several transition metal catalysts were initially investigated for the synthesis of multi-substituted dihydrofurans starting from 2-diazo-5,5,-dimethylcyclohexane-1,3-dione (**1a**) and ethyl vinyl ether in different solvents. The results are summarized in Table 1. When 2 mol% of RuO_2, $Pd(PPh_3)_4$, $Pd(PPh_3)_2Cl_2$, $Pd(OAc)_2$, and $Co(PPh_3)_3Cl$ were used as catalysts in toluene at 70 °C for 24 h, no products were isolated

Table 1. Reaction of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (**1a**) with ethyl vinyl ether using various metal catalysts.



1a **2**

Entry	Catalyst	Solvent	Temperature	Time [h]	Yield [%]
1	RuO_2	toluene	70 °C	24	0
2	$Pd(PPh_3)_4$	toluene	70 °C	24	0
3	$Pd(PPh_3)_2Cl_2$	toluene	70 °C	24	0
4	$Pd(OAc)_2$	toluene	70 °C	24	0
5	$Co(PPh_3)_3Cl$	toluene	70 °C	24	0
6	$Ru(PPh_3)_2(\eta^5\text{-}C_5H_5)Cl$	toluene	70 °C	12	85
7	$[Ru(p\text{-cymene})Cl_2]_2$	toluene	70 °C	12	91
8	$Ru(PPh_3)_4Cl_2$	toluene	70 °C	12	92
9	$Ru(PPh_3)_3Cl_2$	toluene	70 °C	10	95
10	$Ru(PPh_3)_3Cl_2$	CH_2Cl_2	r.t.	120	15
11	$Ru(PPh_3)_3Cl_2$	toluene	r.t.	120	85
12	$Ru(PPh_3)_3Cl_2$	*n*-hexane	65 °C	10	20
13	$Ru(PPh_3)_3Cl_2$	benzene	70 °C	12	85
14	$Ru(PPh_3)_3Cl_2$	fluorobenzene	70 °C	10	72
15	$Ru(PPh_3)_3Cl_2$	THF	65 °C	10	30
16	$Ru(PPh_3)_3Cl_2$	dichloroethane	70 °C	10	65
17	$Ru(PPh_3)_3Cl_2$	acetonitrile	70 °C	12	40

Table 2. Synthesis of a variety of multi-substituted dihydrofurans **3**–**28** by reactions of cyclic diazodicarbonyls with olefins in the presence of 2 mol % of $Ru(PPh_3)_3Cl_2$ in toluene.[a]

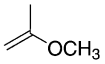
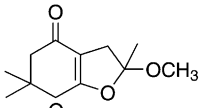
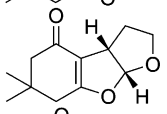
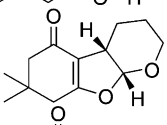
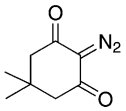
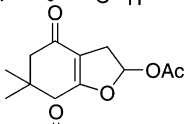
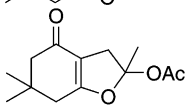
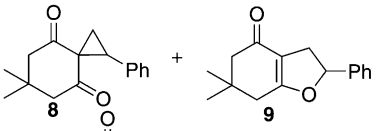
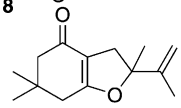
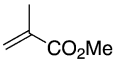
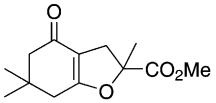
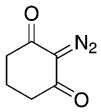
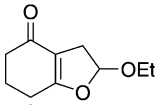
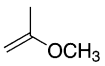
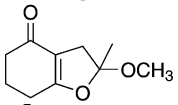
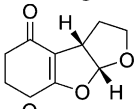
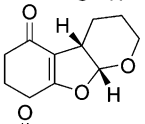
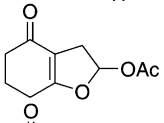
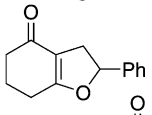
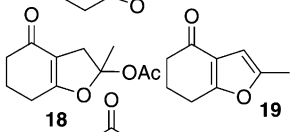
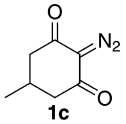
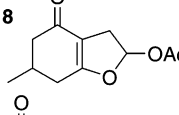
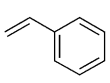
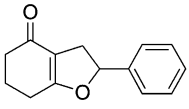
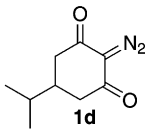
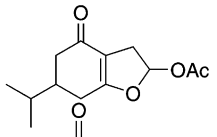
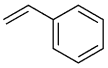
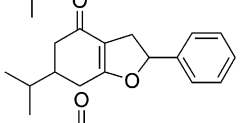
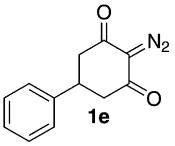
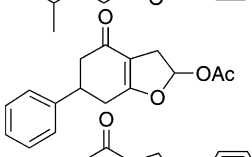
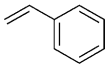
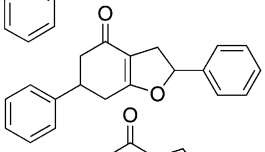
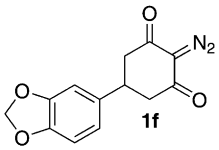
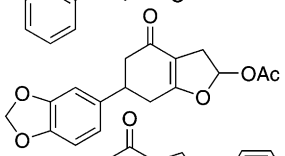
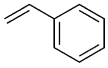
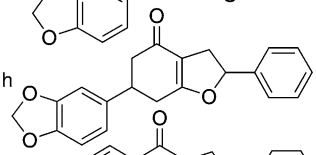
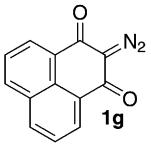
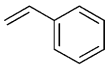
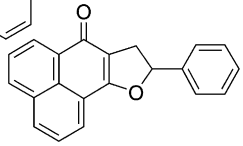
Entry	Diazodicarbonyl	Olefin	Conditions	Products	Yield [%][b]
1			70 °C, 15 h	 **3**	98
2			70 °C, 10 h	 **4**	97
3			70 °C, 10 h	 **5**	82
4	 **1a**		70 °C, 10 h	 **6**	75
5			70 °C, 15 h	 **7**	80
6			70 °C, 10 h	 **8** + **9**	18 + 75
7			70 °C, 20 h	 **10**	87
8			70 °C, 20 h	 **11**	73
9	 **1b**		70 °C, 24 h	 **12**	95
10			70 °C, 24 h	 **13**	91
11			70 °C, 12 h	 **14**	97
12			70 °C, 12 h	 **15**	80
13			70 °C, 24 h	 **16**	76
14			70 °C, 10 h	 **17**	75
15			70 °C, 24 h	 **18** **19**	76 + 12
16	 **1c**		70 °C, 15 h	 **20**	78
17			70 °C, 10 h	 **21**	72

Table 2. (Continued)

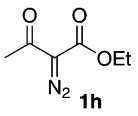
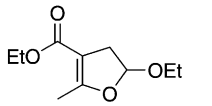
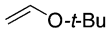
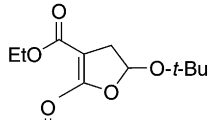
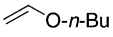
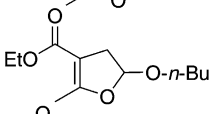
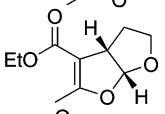
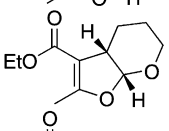
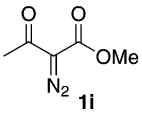
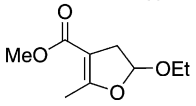
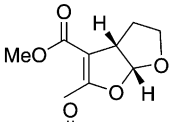
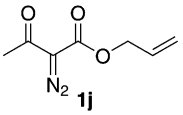
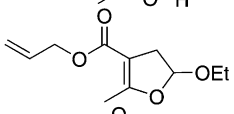
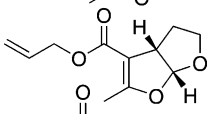
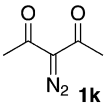
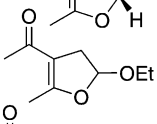
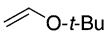
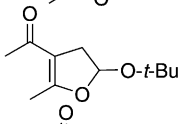
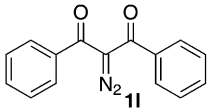
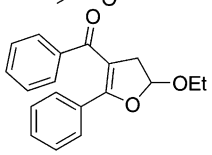
Entry	Diazodicarbonyl	Olefin	Conditions	Products		Yield [%][b]
18	 **1d**		70 °C, 15 h		**22**	77
19			70 °C, 12 h		**23**	71
20	 **1e**		70 °C, 15 h		**24**	79
21			70 °C, 11 h		**25**	70
22	 **1f**		70 °C, 15 h		**26**	70
23			70 °C, 10 h		**27**	68
24	 **1g**		70 °C, 10 h		**28**	74

[a] *Reaction scale:* cyclic diazodicarbonyls (1.0 mmol) and olefins (5.0 mmol).
[b] Isolated yields.

(entries 1–5). However, use of 2 mol% of $Ru(PPh_3)_2(\eta^5\text{-}C_5H_5)Cl$, $[Ru(p\text{-cymene})Cl_2]_2$, and $Ru(PPh_3)_4Cl_2$ in toluene at 70 °C for 12 h gave the desired cycloadduct **2** in 85%, 91%, and 92% yields, respectively (entries 6–8). Using $Ru(PPh_3)_3Cl_2$ as a catalyst, we attempted many reactions by changing solvents and temperatures (entries 9–17). The best yield (95%) was obtained in toluene at 70 °C for 10 h. Furthermore, these reactions did not produce insertion products or α-chlorination due to reaction of solvents.

To explore the generality and scope of this [3+2] cycloaddition, reactions of several cyclic diazodicarbonyl compounds (**1a**–**1g**) with a variety of olefins were attempted under optimized reaction conditions. The results are summarized in Table 2. Reactions of **1a** with 2-methoxypropene, 2,3-dihydrofuran, or 3,4-dihydropyran in the presence of 2 mol% of $Ru(PPh_3)_3Cl_2$ in toluene at 70 °C for 10–15 h provided the cycloadducts **3–5** in 98, 97, and 82% yields, respectively (entries 1–3). Compound **4** was easily separated by column chromatography and identified by spectroscopic analyses. The ^{1}H NMR spectrum of **4** showed two methine protons on two dihydrofuran rings at $\delta =$ 6.23 (1 H, d, $J = 5.70$ Hz) and 3.62–3.54 (1 H, m) ppm. The *cis*-stereochemistry of **4** was confirmed by vicinal coupling constants between two dihydrofuran rings and by comparison with those of reported *cis*-compounds.[13c,19] Similarly, the *cis*-stereochemistry of **5** was also confirmed by the coupling constant ($J_{cis} =$ 7.8 Hz) between vicinal protons on both dihydrofuran and dihydropyran rings.[10a,13f,19] Treatment of **1a** with vinyl acetate or isopropenyl acetate gave products **6** and **7** in 75 and 80% yields, respectively (entries 4 and 5). Interestingly, with styrene, the compound **8** with a cyclopropane ring and the desired compound **9** were produced in 18 and 75% yields, respectively (entry 6). With 2,3-dimethyl-1,3-butadiene, product **10** was obtained in 87% yield (entry 7). Furthermore, the reaction was also successful using methyl methacrylate as an electron-deficient olefin. Treatment of **1a** with methyl methacrylate in the presence of 2 mol% of $Ru(PPh_3)_3Cl_2$ in toluene at 70 °C for 20 h provided cycloadduct **11** in 73% yield (entry 8). Similarly, the reaction between 2-diazocyclohexane-1,3-dione (**1b**) and ethyl vinyl ether, 2-methoxypropene, 2,3-dihydrofuran, 3,4-dihydropyran, vinyl acetate, or styrene afforded products **12–17** in 75–97% yield (entries 9–14). The *cis*-stereochemistry of **14** and **15** was also confirmed by the ^{1}H NMR coupling constants (**14**, $J_{cis} =$ 5.9 Hz; **15**, $J_{cis} = 7.8$ Hz) between vicinal protons on

Table 3. Synthesis of a variety of multi-substituted dihydrofurans **29**–**40** by reactions of acyclic diazodicarbonyls with olefins in the presence of 2 mol% of $Ru(PPh_3)_3Cl_2$ in toluene.[a]

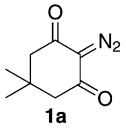
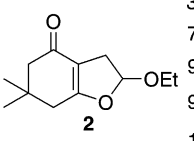
Entry	Diazodicarbonyl	Olefin	Conditions	Products		Yield [%][b]
1	 **1h**		70 °C, 4 h		**29**	90
2			70 °C, 6 h		**30**	81
3			70 °C, 6 h		**31**	87
4			70 °C, 12 h		**32**	88
5			70 °C, 15 h		**33**	71
6	 **1i**		70 °C, 4 h		**34**	90
7			70 °C, 12 h		**35**	85
8	 **1j**		70 °C, 4 h		**36**	88
9			70 °C, 12 h		**37**	76
10	 **1k**		70 °C, 6 h		**38**	85
11			70 °C, 6 h		**39**	82
12	 **1l**		70 °C, 10 h		**40**	85

[a] *Reaction scale:* acyclic diazodicarbonyls (1.0 mmol) and olefins (5.0 mmol).
[b] Isolated yields.

both dihydrofuran and dihydropyran rings.[19] When isopropenyl acetate was used, both the desired product **18** and the eliminated product **19** were produced in 76 and 12% yields, respectively (entry 15).

Next, reactions of other diazodicarbonyl compounds **1c**–**1f** with methyl, isopropyl, phenyl, or aryl substituents on the cyclohexane ring were examined. Treatment of 2-diazo-5-methylcyclohexane-1,3-dione (**1c**) or 2-diazo-5-isopropylcyclohexane-1,3-dione (**1d**) with vinyl acetate or styrene, respectively, provided the desired products **20** (78%), **21** (72%), **22** (77%), and **23** (71%) as a 1:1 mixture of diastereomers (entries 16–19). Similarly, reactions between 2-diazo-5-phenylcyclohexane-1,3-dione (**1e**) or 5-(benzo[*d*]-[1,3]dioxo-5-yl)-2-diazohexane-1,3-dione (**1f**) and vinyl acetate or styrene, respectively, provided cycloadducts **24**–**27** in 68–79% yield as a 1:1 mixture of diastereomers (entries 20–23). Treatment of 2-diazophenalene-1,3-dione (**1g**) with styrene afforded cycloadduct **28** in 74% yield (entry 24). These reactions provided a rapid approach for synthesizing a wide variety of multi-substituted dihydrofurans from cyclic

Table 4. Microwave irradiation synthesis of multi-substituted dihydrofuran **2** starting from cyclic diazodicarbonyl compound **1a** in the presence of 2 mol% of $Ru(PPh_3)_3Cl_2$.[a]

Entry	Diazodicarbonyl	Olefin	Additive	Time [min]	Conditions	Product	Yield [%][b]
1	 **1a**		-	60	neat, MW 600 W, 70 °C	 **2**	35
2			-	60	toluene, MW 600 W, 70 °C		30
3			$[Bmim]BF_4$	10	toluene, MW 300 W, 70 °C		75
4			$[Bmim]BF_4$	20	toluene, MW 300 W, 70 °C		98
5			$[Bmim]BF_4$	40	toluene, MW 300 W, 70 °C		92
6			$[Bmim]PF_6$	20	toluene, MW 300 W, 70 °C		15
7			[Bmim]Cl	20	toluene, MW 300 W, 70 °C		10
8			$[OMIM]PF_6$	20	toluene, MW 300 W, 70 °C		65
9			EMI-TFSI	20	toluene, MW 300 W, 70 °C		12

[a] Reactions were carried out with cyclic diazodicarbonyl compound (**1a**) (1.0 mmol) and ethyl vinyl ether (5.0 mmol) in toluene (5.0 mL) in the presence of 2 mol% of $Ru(PPh_3)_3Cl_2$ and 0.1 mL of additive under a nitrogen atmosphere.

[b] Isolated yields.

diazodicarbonyl compounds using $Ru(PPh_3)_3Cl_2$ catalyst.

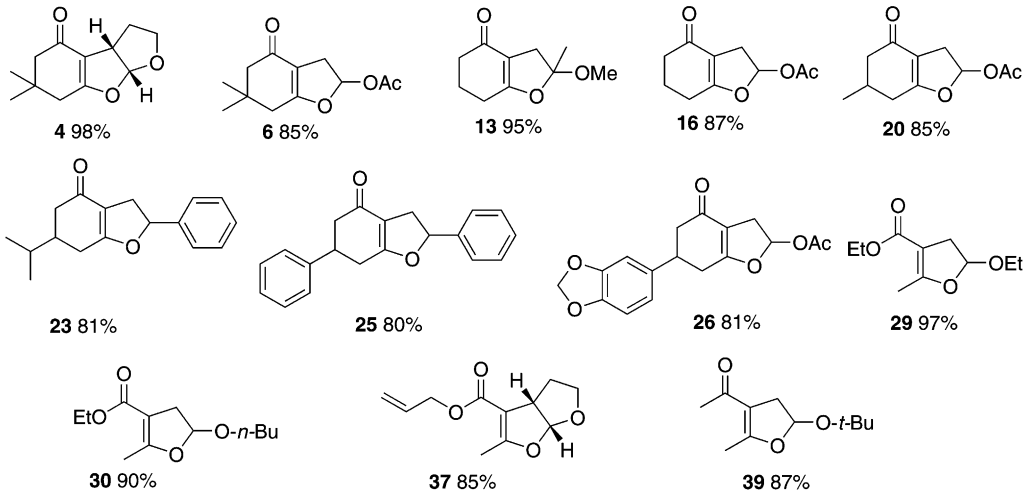
To investigate the usefulness of this methodology, other reactions of acyclic diazodicarbonyl compounds were attempted under the optimized reaction conditions. Results are summarized in Table 3. First, reactions between acyclic diazodicarbonyl compounds bearing a β-keto ester moiety and several olefins were examined. Reactions between ethyl-2-diazo-3-oxobutanoate (**1h**) and ethyl vinyl ether, *tert*-butyl vinyl ether, *n*-butyl vinyl ether, 2,3-dihydrofuran, or 3,4-dihydropyran in the presence of 2 mol% of $Ru(PPh_3)_3Cl_2$ in toluene at 70 °C for 4–15 h gave cycloadducts **29**–**33** in 71–90% yield (entries 1–5). Similarly, treatment of methyl-2-diazo-3-oxobutanoate (**1i**) or allyl 2-diazo-3-oxobutanoate (**1j**) with ethyl vinyl ether or 2,3-dihydrofuran provided products **34**–**37** in 76–90% yield (entries 6–9). Treatment of 3-diazopentane-2,4-dione (**1k**) or 2-diazo-1,3-diphenylpropane-1,3-dione (**1l**) bearing the 1,3-diketo moiety with vinyl acetate or 2,3-dihydrofuran afforded cycloadducts **38**–**40** in 82–85% yield (entries 10–12). The *cis*-stereochemisty of **32**, **33**, **35** and **37** was also assigned by ^1H NMR analysis of vicinal coupling constants.[19] These reactions provide a rapid approach to the synthesis of a variety of dihydrofurans starting from acyclic diazodicarbonyl compounds.

To minimize reaction time and increase yields of dihydrofurans, microwave-assisted reactions between **1a** and ethyl vinyl ether in the presence of 2 mol% of $Ru(PPh_3)_3Cl_2$ were attempted. Results are presented in Table 4. Microwave-assisted reactions have become a powerful tool in organic chemistry because reaction rates and yields can be markedly increased.[20] When **1a** and ethyl vinyl ether in the presence of 2 mol% of $Ru(PPh_3)_3Cl_2$ was irradiated under solvent-free conditions at 70 °C for 1 h at 600 W, the desired product **2** was isolated in 35% yield (entry 1). In toluene under the same conditions, **2** was also obtained in only 30% yield (entry 2). Ionic liquids were then added to these low-absorbing reaction mixtures to increase microwave absorbance.[21] Irradiation in the presence of 0.1 mL 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim]BF_4$) as an additive and 2 mol% of $Ru(PPh_3)_3Cl_2$ as a catalyst in toluene for 20 min at 300 W provided the desired product **2** in high yield (98%).

Under the optimized reaction conditions, further irradiation of cyclic and acyclic diazodicarbonyl compounds to afford the desired dihydrofurans was attempted. Results are presented in Table 5. As was expected, reactions of cyclic or acyclic diazodicarbonyls with 2,3-dihydrofuran, vinyl acetate, 2-methoxypropene, styrene, or *tert*-butyl vinyl ether provided the desired products at remarkably higher yields (80–98%) at reaction times of only 20 min.

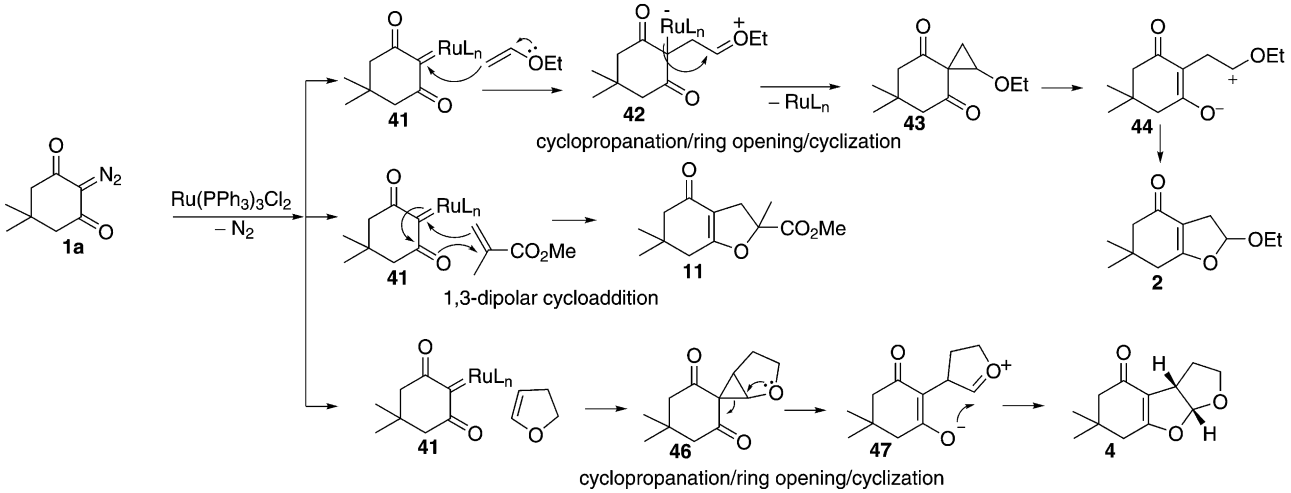
A plausible mechanism for the formation of dihydrofurans **2**, **4**, and **11** based on comparisons with reported Rh(II)-catalyzed[11c,22] and Ru(II)-catalyzed[18a–d] reactions is shown in Scheme 4. In the case of electron-rich olefins, diazo compound **1a** first gives the carbenoid (or carbene) **41** through the loss of a nitrogen by $Ru(PPh_3)_3Cl_2$ catalyst. The carbenoid **41** then reacts with the double bond of electron-rich ethyl vinyl ether to give intermediate **42**, which undergoes cyclization to give cyclopropane **43**. As evidence for this mechanism, molecules containing cyclopropane rings were also found to be produced during the metal-catalyzed reactions of diazo compounds.[23] Bond cleavage of **43** in the presence of $Ru(PPh_3)_3Cl_2$ catalyst gives a zwitterion **44**, which cyclizes to give the final dihydrofuran **2**. With the electron-deficient olefin bond of acrylates, the formation of dihydrofuran **11** seems to proceed *via* 1,3-dipolar cycloaddition

Table 5. Microwave irradiation synthesis of a variety of multi-substituted dihydrofurans in the presence of 2 mol% of $Ru(PPh_3)_3Cl_2$ and $[Bmim]BF_4$ at 70 °C for 20 min.[a,b]



[a] Reactions were carried out with acyclic and cyclic diazodicarbonyl compounds (1.0 mmol) and olefins (5.0 mmol) in toluene (5.0 mL) in the presence of 2 mol% of $Ru(PPh_3)_3Cl_2$ and 0.1 mL of $[Bmim]BF_4$ under a nitrogen atmosphere.

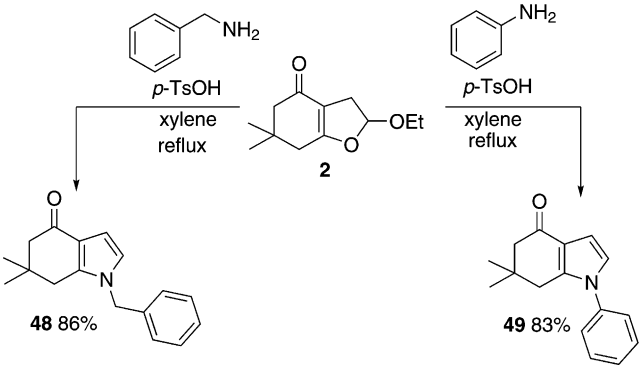
[b] Isolated yields.



Scheme 4. Proposed mechanism for the formation of **2**, **4** and **11**.

of metal carbenoid **41** to the double bond of the α,β-unsaturated ester. Evidence of this mechanism was also reported by other groups.[24] The mechanistic pathway for compound **4** is likely to proceed through a cyclopropanation reaction followed by a ring cleavage and cyclization.[25] The *cis*-stereochemistry of compound **4** is determined by a thermodynamically stable *cis*-ring junction.[26]

As an application of this methodology, the conversion of the synthesized dihydrofuran **2** to biologically interesting tetrahydroindoles was undertaken (Scheme 5). Treatment of **2** with benzylamine or aniline in the presence of *p*-TsOH in refluxing xylene for



Scheme 5. Synthesis of tetrahydroindole derivatives **48** and **49** from the synthesized dihydrofuran **2**.

18 h afforded the corresponding tetrahydroindoles **48** and **49** in 86% and 83% yield, respectively.[27] The structural assignments of **48** and **49** were readily made by ^{1}H NMR spectra due to the presence of two vicinal proton peaks associated with the newly produced pyrrole rings.

Conclusions

In summary, we have described a one-pot method for the synthesis of multi-substituted dihydrofurans by $Ru(PPh_3)_3Cl_2$ catalyzed [3+2] cycloaddition of cyclic or acyclic diazodicarbonyl compounds with a variety of olefins. Furthermore, microwave-assisted $Ru(PPh_3)_3Cl_2$/[Bmim]BF_4-catalyzed reactions afforded a rapid access to multi-substituted dihydrofurans in high yields. The conversion of synthesized dihydrofurans into tetrahydroindoles was also performed by reaction with amines. Further investigations of Ru(II)-catalyzed transformations and functionalizations of diazodicarbonyls are underway in our laboratory.

Experimental Section

General Experimental Methods

All olefins and catalysts were commercially available from Sigma–Aldrich and used without further purification. The starting acyclic/cyclic diazodiarbonyls **1a**–**1l** were prepared by the diazo transfer reaction of the corresponding acyclic/acyclic 1,3-dicarbonyls with tosyl azide or mesyl azide according to the known procedure.[28] Solvents for experiments were purified by standard methods. All experiments were carried out in a nitrogen atmosphere. Glassware was oven-dried prior to use.

Merck, pre-coated silica gel plates (Art. 5554) with a fluorescent indicator were used for analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Bruker Avance DPX 300 MHz or a Varian VNS 300 MHz spectrometer in $CDCl_3$ as the solvent. Chemical shifts are reported in parts per million (ppm) and referenced to solvent residual resonances relative to TMS. IR spectra were recorded on a Bio-Rad Excalibur Series FTS 3000 spectrophotometer. All melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. High-resolution mass spectra (HR-MS) were recorded on a JMS-700 apparatus at Korea Basic Science Institute (Daegu Branch, South Korea).

General Procedure for the Synthesis of Multi-Substituted Dihydrofurans

Conventional method: To a solution of cyclic diazodicarbonyl compounds (1.0 mmol) and the corresponding olefins (5.0 mmol) in toluene (2.0 mL), tris(triphenylphosphine)ruthenium(II) dichloride [$Ru(PPh_3)_3Cl_2$] (2 mol%) was added at room temperature. The reaction mixture was stirred at 70 °C for the required time and then cooled to room temperature. Water (15 mL) was added and the solution was extracted with ethyl acetate (15 mL × 3). Evaporation of the solvent and purification by column chromatography on silica gel using hexane-ethyl acetate (4:1) gave the products.

Microwave irradiation experiments: $Ru(PPh_3)_3Cl_2$ (2 mol%) with [Bmim]BF_4 (0.1 mL), cyclic diazodicarbonyl compounds (1.0 mmol) and the corresponding olefins (5.0 mmol) were loaded into the microwave instrument vessel followed by dry toluene (5.0 mL). The vessel was sealed and irradiated with stirring at a ceiling temperature of 80 °C at 80–300 W maximum power level for 10–40 min. Upon completion of the reaction time the vessel was cooled with a stream of air. Water (15 mL) was added and the solution was extracted with ethyl acetate (15 mL × 3). Evaporation of the solvent and purification by column chromatography on silica gel using hexane-ethyl acetate (4:1) gave the products.

2-Ethoxy-6,6-dimethyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (2):[29] Yellow oil; IR (neat): ν = 2960, 2724, 1726, 1636, 1405, 1255, 1195, 1111, 1047, 880, 756 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.66–5.62 (m, 1H), 3.82–3.71 (m, 1H), 3.56–3.46 (m, 1H), 2.82 (ddd, J = 13.5, 7.2, 1.8 Hz, 1H), 2.54 (d, J = 15.9 Hz, 1H), 2.28–2.04 (m, 4H), 1.12 (t, J = 7.2 Hz, 3H), 1.00 (s, 3H), 0.96 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.3, 174.4, 110.6, 108.6, 64.8, 50.6, 37.5, 33.8, 32.4, 28.9, 28.1, 14.8.

2-Methoxy-2,6,6-trimethyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (3):[30] Yellow oil; IR (neat): ν = 2960, 1720, 1641, 1569, 1385, 1248, 1156, 1064, 934, 838, 742 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.16 (s, 3H), 2.77 (d, J = 15.9 Hz, 1H), 2.56 (d, J = 15.9 Hz, 1H), 2.21 (s, 2H), 2.11 (s, 2H), 1.50 (s, 3H), 1.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.3, 174.1, 115.1, 110.9, 50.5, 50.0, 37.3, 34.9, 33.8, 28.6, 28.4, 25.1.

6,6-Dimethyl-3,3a,5,6,7,8a-hexahydrofuro[2,3-*b*]benzofuran-4(2*H*)-one (4):[19a–d,31] Yellow oil; IR (neat): ν = 2955, 2873, 1723, 1637, 1405, 1253, 1076, 946, 886, 817, 661 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.23 (d, J = 5.7 Hz, 1H), 4.07 (dd, J = 7.5, 7.2 Hz, 1H), 3.69 (uneven t, J = 7.2, 6.3 Hz, 1H), 3.62–3.54 (m, 1H), 2.31 (s, 2H), 2.19 (d, J = 4.2 Hz, 2H), 2.08–2.01 (m, 2H), 1.01 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.5, 176.3, 113.0, 112.1, 67.8, 51.0, 43.6, 37.5, 33.9, 30.3, 28.8, 28.2.

7,7-Dimethyl-4,4a,6,7,8,9a-hexahydro-2*H*-pyrano[2,3-*b*]-benzofuran-5(3*H*)-one (5):[19a–d,31] Yellow oil; IR (neat): ν = 2957, 1725, 1638, 1402, 1225, 1139, 1080, 918, 844 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.84 (d, J = 7.8 Hz, 1H), 3.74–3.57 (m, 2H), 3.05–2.99 (m, 1H), 2.24 (s, 2H), 2.11 (d, J = 4.5 Hz, 2H), 1.84–1.68 (m, 2H), 1.62–1.53 (m, 1H), 1.48–1.38 (m, 1H), 1.01 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.5, 175.1, 114.2, 106.6, 60.0, 50.8, 37.3, 35.0, 33.6, 28.9, 27.9, 19.7, 19.0.

6,6-Dimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (6):[15,32] Yellow oil; IR (neat): ν = 2960, 2879, 1760, 1649, 1407, 1212, 1165, 1052, 946, 849, 780, 734 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.68 (dd, J = 7.5, 2.4 Hz, 1H), 3.02 (dd, J = 16.2, 7.5 Hz, 1H), 2.74 (dd, J = 16.2, 2.4 Hz, 1H), 2.30 (d, J = 8.1 Hz, 2H), 2.20 (d, J = 5.4 Hz, 2H), 2.06 (s, 3H), 1.08 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.5, 174.2, 169.4, 110.8, 98.8, 50.8, 37.2, 34.2, 31.7, 28.9, 28.2, 20.9.

2,6,6-Trimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (7):[30a,32b] Yellow oil; IR (neat): $\nu = 2961$, 1767, 1671, 1424, 1362, 1193, 1059, 865, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.23$ (s, 2H), 2.46 (s, 2H), 2.28 (s, 2H), 2.13 (s, 3H), 2.07 (s, 3H), 1.05 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 204.6$, 198.0, 167.3, 165.0, 121.7, 50.4, 42.4, 37.6, 32.8, 29.3, 28.0, 20.7.

6,6-Dimethyl-1-phenylspiro[2.5]octane-4,8-dione (8):[33] Yellow solid; mp 122–123 °C; IR (KBr): $\nu = 2955$, 2872, 1676, 1384, 1337, 1274, 1219, 1079, 781, 641 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.25$–7.13 (m, 5H), 3.19 (t, $J = 9.0$ Hz, 1H), 2.60–2.44 (m, 3H), 2.31–2.12 (m, 3H), 1.06 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 205.8$, 201.7, 133.1, 129.5, 128.8, 128.0, 127.9, 54.0, 53.2, 48.6, 48.5, 30.5, 29.3, 27.8, 22.1.

6,6-Dimethyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (9):[15,29a,32,34] Yellow oil; IR (neat): $\nu = 3064$, 2959, 1640, 1403, 1220, 1165, 1045, 961, 758, 701, 628 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.35$–7.23 (m, 5H), 5.70 (dd, $J = 10.2$, 7.5 Hz, 1H), 3.27–3.18 (m, 1H), 2.83–2.77 (m, 1H), 2.31 (s, 2H), 2.06 (s, 2H), 1.08 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 194.8$, 176.1, 140.6, 128.8, 128.5, 125.8, 111.4, 86.5, 50.9, 37.7, 34.1, 33.8, 28.8, 28.5.

6,6-Dimethyl-2-(prop-1-en-2-yl)-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (10):[10b,11c,35] Yellow oil; IR (neat): $\nu = 2957$, 2873, 1637, 1402, 1244, 1165, 1144, 1026, 907, 758, 639 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.90$, (s, 1H), 4.76 (s, 1H), 2.76 (d, $J = 14.7$ Hz, 1H), 2.55 (d, $J = 14.4$ Hz, 1H), 2.23 (s, 2H), 2.15 (s, 2H), 1.69 (s, 3H), 1.43 (s, 3H), 1.04 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 194.8$, 175.0, 146.4, 110.9, 110.0, 93.5, 50.7, 37.8, 37.2, 34.0, 28.7, 28.3, 26.0, 18.2. HR-MS: $m/z = 220.1464$ [M^+], calcd. for $C_{14}H_{20}O_2$: 220.1463.

Methyl 2,6,6-trimethyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-carboxylate (11):[15,32a,36] Yellow oil; IR (neat): $\nu = 2956$, 1741, 1644, 1450, 1402, 1237, 1172, 1030, 918, 813, 629 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.75$ (s, 3H), 3.14 (d, $J = 14.7$ Hz, 1H), 2.72 (d, $J = 14.7$ Hz, 1H), 2.31 (d, $J = 10.1$ Hz, 2H), 2.20 (s, 2H), 1.62 (s, 3H), 1.07 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 194.6$, 175.0, 172.3, 110.8, 89.3, 52.9, 50.9, 37.6, 37.1, 34.2, 28.7, 28.5, 24.6.

2-Ethoxy-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (12):[29a,37] Yellow oil; IR (neat): $\nu = 2949$, 1722, 1632, 1406, 1245, 1180, 1112, 903, 742 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.64$–5.60 (m, 1H), 3.82–3.72 (m, 1H), 3.56–3.46 (m, 1H), 2.81 (dd, $J = 15.9$, 7.2 Hz, 1H), 2.53 (dd, $J = 15.6$, 1.5 Hz, 1H), 2.37–2.30 (m, 2H), 2.21 (uneven t, $J = 6.6$, 6.3 Hz, 2H), 2.01–1.87 (m, 2H), 1.12 (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 195.1$, 175.7, 112.0, 108.3, 64.8, 36.1, 32.5, 23.6, 21.3, 14.7.

2-Methoxy-2-methyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (13):[30] Yellow oil; IR (neat): $\nu = 2949$, 1713, 1640, 1384, 1268, 1185, 1104, 1044, 835, 742, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.19$ (s, 3H), 2.78 (d, $J = 15.6$ Hz, 1H), 2.59 (d, $J = 15.6$ Hz, 1H), 2.37 (s, 2H), 2.27 (dd, $J = 5.47$, 5.4 Hz, 2H), 2.00–1.94 (m, 2H), 1.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 195.3$, 175.5, 114.9, 112.5, 50.1, 36.1, 35.5, 24.7, 23.5, 21.4.

3,3a,5,6,7,8a-Hexahydrofuro[2,3-*b*]benzofuran-4(2*H*)-one (14):[29a,34] Yellow oil; IR (neat): $\nu = 2949$, 1713, 1640, 1384, 1268, 1185, 1104, 1044, 835, 742 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.22$ (d, $J = 5.9$ Hz, 1H), 4.18–4.04 (m, 1H), 3.72–3.60 (m, 2H), 2.51–2.42 (m, 2H), 2.35–2.30 (m, 2H), 2.09–1.99 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 194.8$, 177.2, 113.3, 112.5, 67.5, 43.5, 36.3, 30.0, 23.4, 21.3.

4,4a,6,7,8,9a-Hexahydro-2*H*-pyrano[2,3-*b*]benzofuran-5(3*H*)-one (15):[19a–c,37c] Yellow oil; IR (neat): $\nu = 2949$, 1728, 1634, 1403, 1234, 1145, 1079, 918, 829, 770 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.87$ (d, $J = 7.8$ Hz, 1H), 3.79–3.64 (m, 2H), 3.08–3.00 (m, 1H), 2.50–2.37 (m, 2H), 2.29 (dd, $J = 7.2$, 5.4 Hz, 2H), 1.99 (dd, $J = 6.6$, 6.0 Hz, 2H), 1.92–1.44 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 195.4$, 176.4, 116.1, 106.6, 60.5, 36.5, 35.0, 23.6, 21.5, 20.3, 19.1.

4-Oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (16):[15,29a,32b] Yellow oil; IR (neat): $\nu = 2951$, 1760, 1649, 1407, 1216, 1165, 1053, 938, 872, 775 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.67$ (d, $J = 7.5$ Hz, 1H), 3.01 (dd, $J = 16.2$, 6.6 Hz, 1H), 2.75 (d, $J = 16.2$ Hz, 1H), 2.52–2.46 (m, 2H), 2.35–2.31 (m, 2H), 2.07 (s, 3H), 2.04–1.98 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 195.2$, 175.3, 169.4, 112.2, 98.5, 36.4, 31.9, 23.4, 21.5, 20.9.

2-Phenyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (17):[15,29a,34b,37c] Yellow oil; IR (neat): $\nu = 3032$, 2948, 1634, 1495, 1454, 1402, 1289, 1231, 1182, 1061, 1022, 997, 907, 760, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.32$–7.21 (m, 5H), 5.66 (dd, $J = 10.5$, 8.1 Hz, 1H), 3.23–3.14 (m, 1H), 2.81–2.73 (m, 1H), 2.45–2.39 (m, 2H), 2.32–2.28 (m, 2H), 2.02–1.94 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 195.6$, 177.5, 140.4, 128.6, 128.3, 125.7, 112.8, 86.2, 36.2, 33.7, 23.7, 21.5; HR-MS: $m/z = 214.1001$ [M^+], calcd. for $C_{14}H_{14}O_2$: 214.0994.

2-Methyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (18):[32b] Yellow oil; IR (neat): $\nu = 2955$, 1767, 1672, 1427, 1361, 1199, 1067, 910, 846, 711 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.20$ (s, 2H), 2.56 (dd, $J = 6.0$, 5.7 Hz, 2H), 2.39 (dd, $J = 6.9$, 5.7 Hz, 2H), 2.12 (s, 3H), 2.04 (s, 3H), 2.00–1.96 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 204.6$, 197.9, 167.1, 166.8, 122.7, 37.7, 36.4, 29.2, 28.5, 20.7, 20.6.

2-Methyl-6,7-dihydrobenzofuran-4(5*H*)-one (19):[38] Yellow oil; IR (neat): $\nu = 2950$, 1676, 1584, 1433, 1358, 1238, 1123, 1055, 1011, 938, 893, 811.8, 7.9, 641 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.14$ (s, 1H), 2.74 (dd, $J = 6.3$, 6.0 Hz, 2H), 2.37 (dd, $J = 6.6$, 6.0 Hz, 2H), 2.20 (s, 3H), 2.10–2.04 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 194.5$, 165.9, 152.4, 121.8, 101.7, 37.4, 23.1, 22.5, 13.2.

6-Methyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (20):[15,32b] 1:1 mixture of diastereomers; yellow oil; IR (neat): $\nu = 2928$, 1736, 1633, 1404, 1205, 1142, 1049, 736 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.70$–6.66 (m, 1H), 3.04–2.97 (m, 1H), 2.77–2.70 (m, 1H), 2.52–2.48 (m, 2H), 2.43–2.34 (m, 2H), 2.07 (s, 3H), 2.06–2.03 (m, 1H), 1.09–1.06 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 194.9$, 175.0, 169.4, 111.9, 98.7, 45.0, 31.9, 31.5, 31.3, 29.8, 20.9; HR-MS: $m/z = 210.0894$ [M^+], calcd. for $C_{11}H_{14}O_4$: 210.0892.

6-Methyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (21):[15,19d,29a] 1:1 mixture of diastereomers; yellow oil; IR (neat): $\nu = 3034$, 2957, 1634, 1495, 1454, 1402, 1248, 1211, 1138, 1053, 1028, 924, 901, 760, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.33$–7.18 (m, 5H), 5.71–5.64 (m, 1H), 3.24–3.13 (m, 1H), 2.82–2.72 (m, 1H), 2.52–2.45 (m, 1H), 2.41–2.23 (m, 2H), 2.17–2.04 (m, 2H), 1.05 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 195.5$, 177.4,

140.4, 130.2, 128.5, 125.8, 112.4, 86.7, 44.7, 33.7, 31.8, 29.8, 20.9.

6-Isopropyl-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (22): 1:1 mixture of diastereomers; yellow oil; IR (neat): $\nu = 2961, 1761, 1651, 1404, 1226, 1202, 1049, 939\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.72–6.67$ (m, 1H), 3.07–2.96 (m, 1H), 2.79–2.71 (m, 1H), 2.52–2.39 (m, 2H), 2.46–2.13 (m, 2H), 2.09 (s, 3H), 2.00–1.96 (m, 1H), 1.67–1.58 (m, 1H), 0.91 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 195.2, 175.6, 169.3, 112.0, 98.7, 41.0, 40.6, 31.8, 31.7, 26.9, 20.8, 19.7, 19.5$; HR-MS: $m/z = 238.1209$ [M^+], calcd. for $C_{13}H_{18}O_4$: 238.1205.

6-Isopropyl-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (23): 1:1 mixture of diastereomers; yellow oil; IR (neat): 2959, 1640, 1452, 1402, 1248, 1209, 1049, 758, 700 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.37–7.28$ (m, 5H), 5.79–5.71 (m, 1H), 3.28–3.21 (m, 1H), 2.90–2.83 (m, 1H), 2.55–2.46 (m, 2H), 2.34–2.08 (m, 2H), 2.03–2.00 (m, 1H), 1.68–1.60 (m, 1H), 0.94 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 195.6, 177.9, 140.4, 128.8, 128.5, 125.9, 112.5, 86.9, 41.3, 40.6, 33.8, 32.0, 29.7, 27.6, 19.6$; HR-MS: $m/z = 256.1466$ [M^+], calcd. for $C_{17}H_{20}O_2$: 256.1463.

4-Oxo-6-phenyl-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (24):[29] 1:1 mixture of diastereomers; yellow oil; IR (neat): $\nu = 3030, 2932, 1761, 1647, 1495, 1404, 1364, 1258, 1227, 1202, 1165, 1049, 939, 856, 764, 702, 621\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.20$ (d, $J = 7.2$ Hz, 2H), 7.15–7.12 (m, 3H), 6.65 (dd, $J = 7.5$, 2.4 Hz, 1H), 3.41–3.24 (m, 1H), 3.03–2.92 (m, 1H), 2.75–2.68 (m, 1H), 2.61–2.56 (m, 2H), 2.52–2.48 (m, 2H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 193.2, 174.2, 168.8, 141.9, 128.3, 126.6, 126.2, 111.9, 98.4, 43.2, 39.6, 31.4, 30.4, 20.4$.

2,6-Diphenyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (25): 1:1 mixture of diastereomers; yellow oil; IR (neat): $\nu = 2944, 1632, 1402, 1248, 1207, 1046, 932, 764, 702\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.32–7.26$ (m, 5H), 7.23–7.19 (m, 5H), 5.78–5.71 (m, 1H), 3.49–3.38 (m, 1H), 3.33–3.21 (m, 1H), 2.92–2.82 (m, 1H), 2.72–2.65 (m, 2H), 2.62–2.59 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 194.0, 176.5, 142.6, 140.5, 128.9, 128.6, 127.2, 126.8, 126.0, 125.8, 112.9, 87.0, 43.9, 40.5, 33.9, 31.5$; HR-MS: $m/z = 290.1308$ [M^+], calcd. for $C_{20}H_{18}O_2$: 290.1307.

6-(Benzo[*d*][1,3]dioxol-5-yl)-4-oxo-2,3,4,5,6,7-hexahydrobenzofuran-2-yl acetate (26): 1:1 mixture of diastereomers; yellow oil; IR (neat): $\nu = 2922, 1759, 1645, 1491, 1443, 1404, 1246, 1200, 1040, 980, 853, 810, 775, 733\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.75–6.64$(m, 4H), 5.92(s, 2H), 3.43–3.26(m, 1H), 3.11–3.01(m, 1H), 2.83–2.73(m, 1H), 2.67–2.63-(m, 2H), 2.57–2.53(m, 2H), 2.09(s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 193.6, 174.4, 169.3, 147.9, 146.5, 136.1, 119.7, 112.1, 108.4, 107.0, 101.0, 98.8, 44.3, 40.2, 31.9, 31.4, 20.9$; HR-MS: $m/z = 316.0947$ [M^+], calcd. for $C_{17}H_{16}O_6$: 316.0947.

6-(Benzo[*d*][1,3]dioxol-5-yl)-2-phenyl-2,3,6,7-tetrahydrobenzofuran-4(5*H*)-one (27): 1:1 mixture of diastereomers; yellow oil; IR (neat): $\nu = 3027, 2926, 1736, 1603, 1491, 1450, 1246, 1041, 739, 700\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.38–7.27$ (m, 5H), 6.75–6.60 (m, 3H), 5.90 (s, 2H), 5.80–5.73 (m, 1H), 3.40–3.23 (m, 2H), 2.92–2.83 (m, 1H), 2.69–2.63 (m, 2H), 2.58–2.54 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 193.7, 176.3, 147.7, 146.4, 140.4, 136.4, 128.7, 128.4, 125.7, 119.7, 112.7, 108.3, 107.0, 100.9, 86.6, 44.3, 40.0, 33.7, 31.7$; HR-MS: $m/z = 334.1201$ [M^+], calcd. for $C_{21}H_{18}O_4$: 334.1205.

9-Phenyl-8,9-dihydro-7*H*-phenaleno[1,2-*b*]furan-7-one (28): Yellow oil; IR (neat): $\nu = 2926, 1734, 1636, 1580, 1435, 1379, 1325, 1219, 1020, 878, 845, 777, 700\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 8.59$ (d, $J = 7.5$ Hz, 1H), 8.17 (d, $J = 8.1$ Hz, 1H), 8.11–8.03 (m, 2H), 7.74–7.67 (m, 1H), 7.61–7.55 (m, 1H), 7.44–7.36 (m, 5H), 6.04–5.98 (m, 1H), 3.72–3.63 (m, 1H), 3.27–3.19 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 181.6, 166.7, 140.8, 135.3, 135.1, 134.1, 133.3, 133.0, 130.0, 128.8, 128.5, 127.4, 126.8, 126.7, 126.4, 125.9, 114.8, 86.8, 35.3$; HR-MS: $m/z = 298.0996$ [M^+], calcd. for $C_{21}H_{14}O_2$: 298.0994.

Ethyl 5-ethoxy-2-methyl-4,5-dihydrofuran-3-carboxylate (29):[30b,39] Yellow oil; IR (neat): $\nu = 2978, 2932, 1700, 1654, 1445, 1379, 1338, 1264, 1234, 1188, 1083, 949, 842, 759\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.44$ (dd, $J = 7.2$, 3.0 Hz, 1H), 4.08 (q, $J = 6.9$ Hz, 2H), 3.83–3.72 (m, 1H), 3.55–3.45 (m, 1H), 2.93 (ddd, $J = 15.9$, 7.5, 1.8 Hz, 1H), 2.63 (dd, $J = 15.9$, 1.8 Hz, 1H), 2.14 (s, 3H), 1.21–1.13 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 165.8, 165.6, 104.8, 101.4, 64.1, 59.3, 36.3, 14.9, 14.3, 13.9$.

Ethyl 5-(*tert*-butoxy)-2-methyl-4,5-dihydrofuran-3-carboxylate (30):[30b,40] Yellow oil; IR (neat): $\nu = 2976, 1698, 1651, 1447, 1377, 1336, 1262, 1232, 1165, 1084, 1019, 946, 897, 843, 765\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.71$ (dd, $J = 7.8$, 3.6 Hz, 1H), 4.08 (q, $J = 7.2$ Hz, 2H), 2.93 (ddd, $J = 15.6$, 7.5, 1.8 Hz, 1H), 2.59 (dd, $J = 15.6$, 1.8 Hz, 1H), 2.13 (s, 3H), 1.21–1.16 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 165.9, 165.7, 100.9, 100.0, 75.4, 59.1, 37.2, 28.5, 14.3, 14.1$.

Ethyl 5-butoxy-2-methyl-4,5-dihydrofuran-3-carboxylate (31):[40] Yellow oil; IR (neat): $\nu = 2965, 2872, 1701, 1654, 1457, 1380, 1339, 1263, 1232, 1181, 1083, 1020, 952, 913, 834, 761\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.46$ (dd, $J = 7.5$, 3.0 Hz, 1H), 4.11 (q, $J = 7.2$ Hz, 2H), 3.79–3.71 (m, 1H), 3.49–3.42 (m, 1H), 2.95 (ddd, $J = 15.9$, 7.5, 2.1 Hz, 1H), 2.70–2.63 (m, 1H), 2.17 (s, 3H), 1.55–1.48 (m, 2H), 1.36–1.28 (m, 2H), 1.22 (t, $J = 7.2$ Hz, 3H), 0.87 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 165.8, 165.6, 105.1, 101.4, 68.4, 59.3, 36.3, 31.4, 19.0, 14.3, 13.9, 13.6$; HR-MS: $m/z = 228.1358$ [M^+], calcd. for $C_{12}H_{20}O_4$: 228.1362.

Ethyl 2-methyl-3a,4,5,6a-tetrahydrofuro[2,3-*b*]furan-3-carboxylate (32):[19b–c] Yellow oil; IR (neat): $\nu = 2982, 2887, 1701, 1646, 1448, 1376, 1325, 1235, 1147, 1086, 1021, 965, 919, 858, 828, 773\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 6.02$ (d, $J = 6.3$ Hz, 1H), 4.14 (q, $J = 7.2$ Hz, 2H), 4.01–3.95 (m, 1H), 3.68–3.58 (m, 2H), 2.16 (s, 3H), 2.04–1.99 (m, 2H), 1.23 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 168.5, 165.4, 109.5, 103.4, 66.9, 59.5, 46.9, 31.5, 14.3, 14.0$.

Ethyl 2-methyl-4,5,6,7a-tetrahydro-3a*H*-furo[2,3-*b*]pyran-3-carboxylate (33):[19c] Yellow oil; IR (neat): $\nu = 2949, 1698, 1639, 1448, 1381, 1258, 1223, 1142, 1093, 930, 857, 767\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.75$ (d, $J = 7.8$ Hz, 1H), 4.17 (q, $J = 7.2$ Hz, 2H), 3.97–3.94 (m, 1H), 3.78–3.74 (m, 2H), 2.22 (s, 3H), 1.98–1.83 (m, 2H), 1.68–1.59 (m, 2H), 1.26 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 167.4, 165.8, 106.9, 104.0, 60.8, 59.4, 37.9, 22.1, 19.8, 14.4, 14.3$.

Methyl 5-ethoxy-2-methyl-4,5-dihydrofuran-3-carboxylate (34):[41] Yellow oil; IR (neat): $\nu = 2976, 2945, 1703, 1651, 1440, 1378, 1340, 1265, 1234, 1189, 1089, 971, 929, 760\ cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 5.44$ (dd, $J = 7.2$, 2.1 Hz,

1H), 3.81–3.71 (m, 1H), 3.60 (s, 3H), 3.54–3.44 (m, 1H), 2.91 (dd, $J=15.9$, 7.5 Hz, 1H), 2.62 (d, $J=15.9$ Hz, 1H), 2.13 (s, 3H), 1.14 (dd, $J=7.2$, 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=166.1$, 165.9, 104.9, 101.1, 64.1, 50.6, 36.3, 14.9, 13.9.

Methyl 2-methyl-3a,4,5,6a-tetrahydrofuro[2,3-*b*]furan-3-carboxylate (35):[42] Yellow oil; IR (neat): $\nu=2985$, 2954, 2882, 1695, 1643, 1445, 1385, 1236, 1190, 1442, 1091, 1025, 952, 916, 828, 774, 687 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=6.03$ (d, $J=6.3$ Hz, 1H), 4.02–3.96 (m, 1H), 3.68–3.58 (m, 5H), 2.18 (s, 3H), 2.04–2.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=168.8$, 165.8, 109.6, 103.3, 66.9, 50.8, 46.9, 31.5, 14.0.

Allyl 5-ethoxy-2-methyl-4,5-dihydrofuran-3-carboxylate (36): Yellow oil; IR (neat): $\nu=2978$, 2932, 1702, 1651, 1446, 1384, 1337, 1263, 1191, 111, 1076, 935, 759 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=5.98$–5.85 (m, 1H), 5.51 (dd, $J=7.2$, 3.0 Hz, 1H), 5.28 (dd, $J=17.4$, 1.5 Hz, 1H), 5.18 (d, $J=10.5$ Hz, 1H), 4.59 (d, $J=5.4$ Hz, 2H), 3.88–3.78 (m, 1H), 3.61–3.51 (m, 1H), 3.00 (ddd, $J=15.9$, 7.2, 1.8 Hz, 1H), 2.72 (dd, $J=15.9$, 1.8 Hz, 1H), 2.21 (s, 3H), 1.21 (dd, $J=7.2$, 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=166.5$, 165.3, 132.8, 117.4, 105.1, 101.3, 64.2, 64.1, 36.4, 35.1, 14.2; HR-MS: $m/z=212.1045$ [M$^+$], calcd. for $C_{11}H_{16}O_4$: 212.1049.

Allyl 2-methyl-3a,4,5,6a-tetrahydrofuro[2,3-*b*]furan-3-carboxylate (37): Yellow oil; IR (neat): $\nu=3084$, 2976, 2931, 1703, 1651, 1444, 1382, 1333, 1262, 1190, 1110, 1076, 937, 759 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=6.06$ (d, $J=6.3$ Hz, 1H), 5.99–5.86 (m, 1H), 5.36–5.18 (m, 2H), 4.70 (d, $J=5.7$ Hz, 2H), 4.04–3.99 (m, 1H), 3.73–3.62 (m, 2H), 2.21 (s, 3H), 2.08–2.04 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=169.1$, 165.0, 132.7, 117.6, 109.7, 103.3, 67.0, 64.3, 47.0, 31.6, 14.2; HR-MS: $m/z=210.0895$ [M$^+$], calcd. for $C_{11}H_{14}O_4$: 210.0892.

1-(5-Ethoxy-2-methyl-4,5-dihydrofuran-3-yl)ethanone (38):[30b,39,43] Yellow oil; IR (neat): $\nu=2978$, 2931, 1720, 1671, 1613, 1429, 1382, 1234, 1195, 1110, 1047, 928, 772, 623 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=5.49$ (dd, $J=7.5$, 2.4 Hz, 1H), 3.87–3.77 (m, 1H), 3.60–3.50 (m, 1H), 3.03 (ddd, $J=15.6$, 7.5, 1.2 Hz, 1H), 2.72 (d, $J=15.6$ Hz, 1H), 2.21 (s, 3H), 2.15 (s, 3H), 1.19 (dd, $J=7.2$, 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=194.2$, 165.7, 111.4, 104.9, 64.4, 37.1, 29.4, 15.0, 14.9.

1-(5-(*tert*-Butoxy)-2-methyl-4,5-dihydrofuran-3-yl)ethanone (39):[39,40,43] Yellow oil; IR (neat): $\nu=2975$, 1718, 1670, 1611, 1427, 1385, 1233, 1170, 1103, 929, 848, 773, 623 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=5.73$ (dd, $J=7.8$, 3.6 Hz, 1H), 3.01 (ddd, $J=15.3$, 7.8, 0.9 Hz, 1H), 2.66 (d, $J=15.3$ Hz, 1H), 2.16 (s, 3H), 2.11 (s, 3H), 1.22 (brs, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=194.2$, 165.8, 111.0, 100.1, 75.7, 38.1, 31.1, 28.6, 15.1.

(5-Ethoxy-2-phenyl-4,5-dihydrofuran-3-yl)(phenyl)-methanone (40):[44] Yellow oil; IR (neat): $\nu=2975$, 2928, 1731, 1683, 1598, 1449, 1265, 1178, 1105, 1004, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.18$–6.96 (m, 10H), 5.50 (d, $J=5.7$ Hz, 1H), 4.07–3.97 (m, 1H), 3.75–3.65 (m, 1H), 2.92–2.75 (m, 2H), 1.21 (t, $J=6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=190.3$, 164.5, 133.8, 133.4, 131.2, 130.0, 129.5, 127.8, 127.6, 126.8, 117.9, 100.9, 65.1, 42.3, 14.9.

General Procedure for the Synthesis of Tetrahydroindoles 48 and 49

To a solution of furan **2** (1.0 mmol) and aniline (3.0 mmol) or benzylamine (3.0 mmol) in xylene (8.0 mL) was added *p*-toluenesulfonic acid (PTSA, 5 mol%) room temperature. The reaction mixture was refluxed for 18 h. After cooling to room temperature, the solution was brought to pH 1 by addition of 1M HCl (5 mL). The aqueous mixture was extracted with EtOAc (3×10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the drying agent and the solvent, the residue was purified by column chromatography on silica gel using hexane-ethyl acetate (1:1) to give **48** or **49**.

1-Benzyl-6,6-dimethyl-6,7-dihydro-1*H*-indol-4(5*H*)-one (48):[27e] Yellow oil; IR (neat): $\nu=2957$, 1651, 1504, 1469, 1359, 1258, 727 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.30$–7.15 (m, 5H), 6.90 (d, $J=7.5$, Hz, 1H), 6.51–6.47 (m, 1H), 4.92 (s, 2H), 2.39 (s, 2H), 2.20 (s, 2H), 0.95 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=193.5$, 142.4, 136.5, 128.7, 127.6, 126.1, 123.0, 119.8, 105.3, 51.6, 50.2, 35.4, 35.3, 28.4; HR-MS: $m/z=253.1466$ [M$^+$], calcd. for $C_{17}H_{19}NO$: 253.1467.

6,6-Dimethyl-1-phenyl-6,7-dihydro-1*H*-indol-4(5*H*)-one (49): Brown solid, mp 155–156 °C; IR (KBr): $\nu=2946$, 1652, 1503, 1461, 1272, 694 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.40$ (d, $J=7.5$ Hz, 2H), 7.31 (d, $J=7.5$ Hz, 1H), 7.22 (d, $J=7.5$ Hz, 2H), 6.72 (d, $J=3.0$ Hz, 1H), 6.60 (d, $J=3.0$ Hz, 1H), 2.55 (s, 2H), 2.30 (s, 2H), 1.00 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=194.0$, 142.2, 138.6, 129.4, 127.7, 124.9, 123.3, 120.6, 106.1, 51.8, 36.9, 35.7, 28.4; HR-MS: $m/z=239.1308$ [M$^+$], calcd. for $C_{16}H_{17}NO$: 239.1310.

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