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Regioselective Synthesis of Highly Functionalized Furans Through the Ru^{II}-Catalyzed [3+2] Cycloaddition of Diazodicarbonyl Compounds

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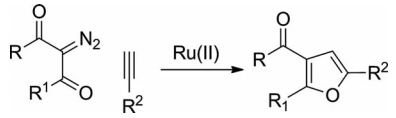
Keywords: Synthetic methods / Cycloaddition / Oxygen heterocycles / Ruthenium / Diazo compounds / Alkynes

A novel method for the Ru^{II}-catalyzed regioselective synthesis of highly functionalized furans from readily available cyclic and acyclic diazodicarbonyl compounds and terminal alkynes is described. The devised protocol offers a straightforward means to the construction of a variety of diverse furan derivatives through powerful cascade processes, including the formation of ruthenium carbenoid, cyclopropenation, ring-opening metathesis, and cyclization.

Introduction

Highly functionalized furans are among the most important molecules found in biologically active natural products, pharmaceuticals, and agrochemicals.[1] They have been widely used as important scaffolds and as building blocks for the construction of complex organic compounds and materials.[2] Because of their importance, numerous methods for the synthesis of substituted furans have been developed based on intra-[3] and intermolecular cyclization reactions.[4] Representative approaches include transition-metal-catalyzed reactions, which have become powerful tools for the preparation of a variety of furan derivatives:[5–9] Pd,[5] Au,[6] Ag,[7] Cu,[8] and Ru[9] are widely used as metal catalysts. The most direct and practical routes for the synthesis of highly functionalized furans involve transition-metal-catalyzed [3+2] cycloaddition reactions between diazo compounds and acetylenes.[10] In particular, Rh^{II}-,[10a–10f] Cu^{I}-,[10g] and Co^{II}[10h]-catalyzed reactions between diazodicarbonyl compounds and terminal alkynes have been successfully conducted. Although a number of transition-metal-catalyzed reactions between diazodicarbonyl compounds and alkynes have been reported for the synthesis of substituted furans, there still remains a need for novel and improved synthetic routes for the preparation of highly functionalized diverse furans with high chemo- and regioselectivities under mild conditions. We have reported on the decomposition of cyclic diazodicarbonyl compounds with various substrates as a powerful means for synthesizing heterocycles and novel organic compounds.[11] Recently we reported on Ru^{II}-catalyzed reactions between diazodicarbonyl compounds and olefins to afford multisubstituted dihydrofurans.[12] As part of our ongoing studies on the transition-metal-catalyzed transformations of diazodicarbonyl compounds to provide novel molecules, we became interested in the Ru^{II}-catalyzed cycloaddition of diazodicarbonyl compounds to terminal alkynes. To the best of our knowledge, the Ru^{II}-complex-catalyzed [3+2] cycloaddition of diazodicarbonyl compounds to alkynes has not been described previously.

Thus, we provide herein examples of mild Ru^{II}-complex-catalyzed cascade reactions between cyclic or acyclic diazodicarbonyl compounds and various terminal alkynes for the synthesis of diverse polyfunctionalized furan derivatives in good to excellent yields and with high regioselectivity (Scheme 1).



Scheme 1. Ru^{II}-catalyzed cycloaddition for the synthesis of furans starting from diazodicarbonyl compounds.

Results and Discussion

First, the use of several promising transition-metal catalysts were investigated for the synthesis of 6,7-dihydrobenzofuran starting from commercially available 2-diazo-5,5-dimethylcyclohexanedione (diazodimedone, **1a**) and phenylacetylene (**2a**) in toluene at 70 °C. The results are presented in Table 1. Various palladium catalysts were examined for their ability to activate cyclic diazodicarbonyl compound **1a**. In the presence of 10 mol-% $[Pd(PPh_3)_4]$ or $Pd(OAc)_2$, complex mixtures were formed and the desired product was not isolated (entries 1 and 2). Using 5 mol-% $[Co(PPh_3)_3Cl]$, $[Au\{P(tBu)_2(o\text{-biphenyl})\}Cl]$, or $[Au\{P(p\text{-}F_3CC_6H_4)_3\}Cl]$ as catalysts, the products were not formed

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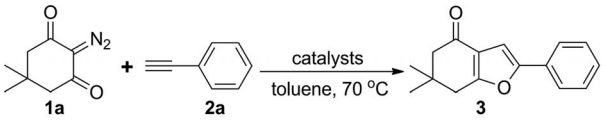
even after 24 h (entries 3–5). Cu^{I} and Cu^{II} catalysts were next tested. With 20 mol-% CuI, [Cu(PPh_3)Cl], or Cu($OAc)_2$, the desired products were not observed (entries 6–8). However, the use of 20 mol-% [Cu($acac)_2$] as catalyst resulted in the formation of the desired compound **3** in 32% yield (entry 9). Although the $InCl_3$-catalyzed transformation of diazo compounds has been reported, it was unsuitable for this reaction (entry 10).[13] Importantly, when 5 mol-% [Ru($PPh_3)_3$(^{5}-C_5H_5)Cl], [Ru($PPh_3)_4Cl_2$], [Ru(*p*-cymene)$Cl_2]_2$, or [Ru($PPh_3)_3Cl_2$] were used, the cyclic adduct **3** was produced in good yields (60–88%, entries 11–14) and no other regioisomer was isolated. The best yield (88%) was obtained with 5 mol-% [Ru($PPh_3)_3Cl_2$]. Furthermore, when the loading of [Ru($PPh_3)_3Cl_2$] was reduced to 2 mol-%, the yield was not reduced (entry 15). In the case of 10 mol-% RuO_2, no product was observed (entry 16).

Table 1. Optimization of catalysts for the synthesis of **3**.[a]



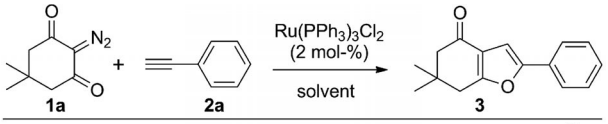
Entry	Catalysts	[loading]	Time (h)	Yield (%)[b]
1	Pd($PPh_3)_4$	10 mol-%	24	–[c]
2	Pd($OAc)_2$	10 mol-%	24	–[c]
3	Co($PPh_3)_3$Cl	5 mol-%	24	n.r.
4	Au[P(*t*-Bu)$_2$(*o*-biphenyl)]Cl	5 mol-%	24	n.r.
5	Au[P(*p*-$F_3CC_6H_4)_3$Cl	5 mol-%	24	n.r.
6	CuI	20 mol-%	24	n.r.
7	Cu(PPh_3)Cl	20 mol-%	24	n.r.
8	Cu($OAc)_2$	20 mol-%	24	n.r.
9	Cu($acac)_2$	20 mol-%	24	32
10	$InCl_3$	20 mol-%	24	n.r.
11	Ru($PPh_3)_2$(η^5-C_5H_5)Cl	5 mol-%	8	85
12	Ru($PPh_3)_4Cl_2$	5 mol-%	8	78
13	[Ru(*p*-cymene)$Cl_2]_2$	5 mol-%	12	60
14	Ru($PPh_3)_3Cl_2$	5 mol-%	6	88
15	Ru($PPh_3)_3Cl_2$	2 mol-%	6	88
16	RuO_2	10 mol-%	24	n.r.

[a] Reaction conditions: **1a** (1.0 mmol) and **2a** (3.0 mmol) in the presence of catalysts in toluene (2.0 mL) under nitrogen. [b] Isolated yields. [c] A complex reaction mixture was produced.

Further reactions were investigated in the presence of 2 mol-% [Ru($PPh_3)_3Cl_2$] in several solvents (Table 2). Interestingly, the reaction was favored by less polar solvents, such as *n*-hexane, benzene, dichloromethane, chlorobenzene, xylenes, or mesitylene. Reactions in polar aprotic solvents, such as DMSO or DMF, either gave no product or complex mixtures. Of the solvents screened, none produced a higher yield than toluene (88%). Polar protic solvents, such as methanol and water, were not tested because the formation of insertion products under these conditions is well known.[14]

After optimizing the reaction conditions, additional reactions were attempted between a variety of cyclic diazodicarbonyl compounds and acetylenes in the presence of 2 mol-% [Ru($PPh_3)_3Cl_2$] in toluene at 70 °C. The results are summarized in Table 3. The cyclic and acyclic diazodicarbonyl compounds **1b**–**1k** were readily prepared by the transfer of the diazo moiety from tosyl or mesyl azide and

Table 2. Optimization of the reaction solvent for the synthesis of **3**.



Entry	Solvent	Temp.	Time (h)	Yield (%)[b]
1	*n*-hexane	65 °C	24	74
2	benzene	70 °C	12	55
3	fluorobenzene	70 °C	10	60
4	chlorobenzene	70 °C	10	70
5	toluene	70 °C	8	88
6	*o*-xylene	70 °C	10	72
7	*m*-xylene	70 °C	10	65
8	*p*-xylene	70 °C	10	75
9	mesitylene	70 °C	12	68
10	CH_2Cl_2	r.t.	48	78
11	$CHCl_3$	r.t.	48	40
12	CCl_4	70 °C	12	70
13	EDC	70 °C	12	50
14	THF	60 °C	12	10
15	1,4-dioxane	70 °C	12	65
16	DMSO	70 °C	15	n.r.[c]
17	DMF	70 °C	8	–[d]
18	neat	70 °C	24	72

[a] Reaction conditions: **1a** (1.0 mmol) and **2a** (3.0 mmol) in the presence of [Ru($PPh_3)_3Cl_2$] (2 mol-%) in solvent (2.0 mL) under nitrogen. [b] Isolated yields. [c] No reaction. [d] Complex reaction mixture formed.

the corresponding cyclic 1,3-dicarbonyl compounds, as described previously.[15] The reactions between **1a** and 4-ethynyltoluene (**2b**), 3-ethynyltoluene (**2c**), 1-ethynyl-4-pentylbenzene (**2d**), or 1-ethynyl-4-methoxy-2-methylbenzene (**2e**), which possess an electron-donating group on the benzene ring, in the presence of 2 mol-% [Ru($PPh_3)_3Cl_2$] in toluene at 70 °C for 8–12 h gave the cycloadducts **4**–**7** in yields of 74–94% (entries 1–4). Treatment of **1a** with 1-ethynyl-3-fluorobenzene (**2f**) bearing an electron-withdrawing group on the benzene ring in the presence of 2 mol-% [Ru($PPh_3)_3Cl_2$] in toluene at 70 °C for 12 h provided the product **8** in 66% yield (entry 5). The reactions between **1a** and other acetylenes, such as 1-ethynylnaphthalene (**2g**), 6-methoxy-2-naphthylacetylene (**2h**), or 9-ethynylphenanthrene (**2i**), afforded the products **9**–**11** in yields of 84, 66, and 58%, respectively (entries 6–8). Using the aromatic heterocyclic compounds 3-ethynylthiophene (**2j**) and 2-ethynylpyridine (**2k**), compounds **12** and **13** bearing heterocyclic rings on the furanyl ring were produced in yields of 79 and 67%, respectively (entries 9 and 10). In the case of 5-ethynyl-1-methyl-1*H*-imidazole (**2l**), the reaction did not give any product, possibly due to the deactivation of [Ru($PPh_3)_3Cl_2$] by the formation of a Ru^{II}–imidazole complex (entry 11). Additional reactions between 2-diazocyclohexane-1,3-dione (**1b**), 2-diazo-5-methylcyclohexane-1,3-dione (**1c**), or 2-diazo-5-isopropylcyclohexane-1,3-dione (**1d**) and various terminal acetylenes were also attempted, and compounds **15**–**27** were produced in yields of 63–88% with excellent regioselectivity (entries 12–24). The reactions between 5-aryl-substituted cyclic 2-diazo-1,3-diketones (**1e** and **1f**) and various terminal acetylenes were also successful and gave the corresponding products **28**–**33** in yields of 54–75% (entries 25–

30). When 5-furyl-substituted **1g** was used, compounds **34**–**36** bearing a furyl ring on the cyclohexenone ring were produced in yields of 70–72% (entries 31–33). The reaction between diazodicarbonyl **1h**, which contains a five-membered ring, and phenylacetylene provided the desired compound **37** in a yield of 77% (entry 34). Thus, these reactions provide a rapid route to the synthesis of a variety of arylfurans with excellent regioselectivity.

Table 3. Synthesis of 2-arylfurans starting from various cyclic diazodicarbonyl compounds and alkynes.[a]

Entry	Diazodicarbonyls	Alkynes	Condition	Products	Yield (%)[b]
1		2b	70 °C, 8 h	4	85
2		2c	70 °C, 12 h	5	94
3		2d	70 °C, 12 h	6	74
4		2e	70 °C, 8 h	7	87
5	1a	2f	70 °C, 12 h	8	66
6		2g	70 °C, 8 h	9	84
7		2h	70 °C, 10 h	10	66
8		2i	70 °C, 8 h	11	58
9		2j	70 °C, 13 h	12	79
10		2k	70 °C, 15 h	13	67
11		2l	70 °C, 24 h	14	0
12	1b	2a	70 °C, 12 h	15	85
13		2f	70 °C, 15 h	16	69
14		2g	70 °C, 10 h	17	82
15		2a	70 °C, 8 h	18	84
16		2d	70 °C, 10 h	19	68
17	1c	2e	70 °C, 12 h	20	66
18		2f	70 °C, 12 h	21	68
19		2h	70 °C, 10 h	22	80
20		2a	70 °C, 8 h	23	78
21	1d	2b	70 °C, 8 h	24	88
22		2e	70 °C, 12 h	25	69
23		2f	70 °C, 10 h	26	81
24		2g	70 °C, 10 h	27	80
25		2b	70 °C, 12 h	28	78
26	1e	2d	70 °C, 11 h	29	72
27		2e	70 °C, 15 h	30	63
28		2f	70 °C, 14 h	31	71
29	1f	2i	70 °C, 15 h	32	54
30		2h	70 °C, 12 h	33	75
31	1g	2a	70 °C, 10 h	34	72
32		2e	70 °C, 12 h	35	71
33		2g	70 °C, 12 h	36	70
34	1h	2a	70 °C, 10 h	37	77

[a] Reaction conditions: cyclic diazodicarbonyl compound (1.0 mmol) and alkyne (3.0 mmol) in toluene (2.0 mL) in the presence of $[Ru(PPh_3)_3Cl_2]$ (2 mol-%) under nitrogen. [b] Isolated yields.

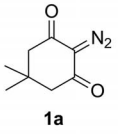
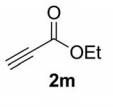
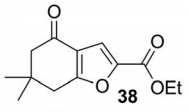
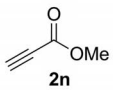
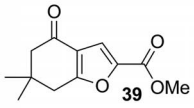
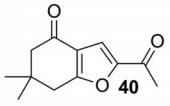
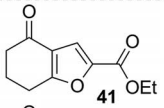
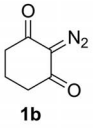
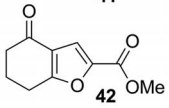
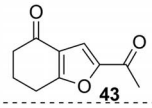
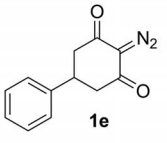
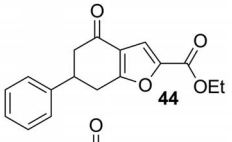
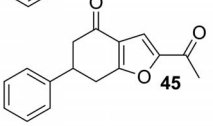
To extend the utility of these cycloadditions, additional reactions between cyclic diazodicarbonyl compounds and electron-deficient alkynes, namely ethyl propiolate (**2m**), methyl propiolate (**2n**), or 3-butyn-2-one (**2o**), were next investigated under the optimized reaction conditions. The results are summarized in Table 4. The reactions between **1a** and **2m**, **2n**, or **2o** in the presence of 2 mol-% [$Ru(PPh_3)_3Cl_2$] in toluene at 70 °C for 4–6 h afforded 2-carbonyl-substituted furans **38**, **39**, and **40** in yields of 55, 54, and 48%, respectively (entries 1–3). Similarly, treatment of **1b** or **1e** with the conjugated alkynes **2m**–**2o** gave cycloadducts **41**–**45** in yields of 42–52% (entries 4–8). Interestingly, in these cases, potential regioisomers produced by Rh^{II}-catalyzed reactions were not formed.[16]

To investigate the usefulness of this methodology, the reactions between acyclic diazodicarbonyl compounds **1i**–**1k** and phenylacetylene (**2a**) were attempted under the optimized reaction conditions (Table 5). The reaction between **1i** and **2a** in the presence of 2 mol-% [$Ru(PPh_3)_3Cl_2$] in toluene at 70 °C for 12 h gave both cyclopropene **46** and furan **47** in yields of 10 and 31%, respectively. The two compounds were readily separated by column chromatography and assigned on the basis of their spectroscopic data. In the ^1H NMR spectrum of **46**, the cyclopropene ring exhibits a proton signal at δ = 6.92 ppm, whereas the proton on the furanyl ring of **47** produced a peak at δ = 6.76 ppm. Similarly, the reaction between **1j** and **2a** provided cyclopropene **48** (10%) and furan **49** (29%), whereas that between **1k** and **2a** afforded compounds **50** (7%) and **51** (25%).

Our results show that the reactions of acyclic diazodicarbonyl compounds **1i**–**1k** with phenylacetylene gave furans in somewhat low yields when compared with those of cyclic diazodicarbonyl compounds. This is probably due to the low thermal stability of the acyclic diazodicarbonyl compounds.[17,18]

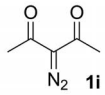
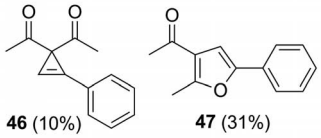
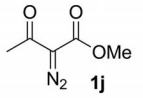
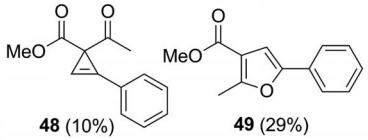
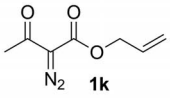
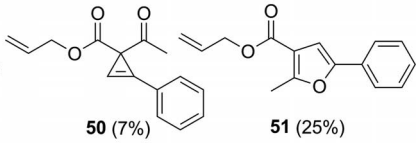
The chemo- and regioselectivity of the [$Ru(PPh_3)_3Cl_2$]-catalyzed reactions of cyclic diazodicarbonyl compounds were next examined (Scheme 2). First, the chemoselectivity of the reaction of **1a** with terminal acetylene and styrene was probed by conducting an intermolecular competition reaction [Scheme 2, Equation (1)]. The reaction of **1a** with phenylacetylene (**2a**) and styrene (**2p**) showed a 12:1 prefer-

Table 4. Synthesis of substituted furans starting from various cyclic diazodicarbonyl compounds and conjugated alkynes in the presence of [$Ru(PPh_3)_3Cl_2$].[a]

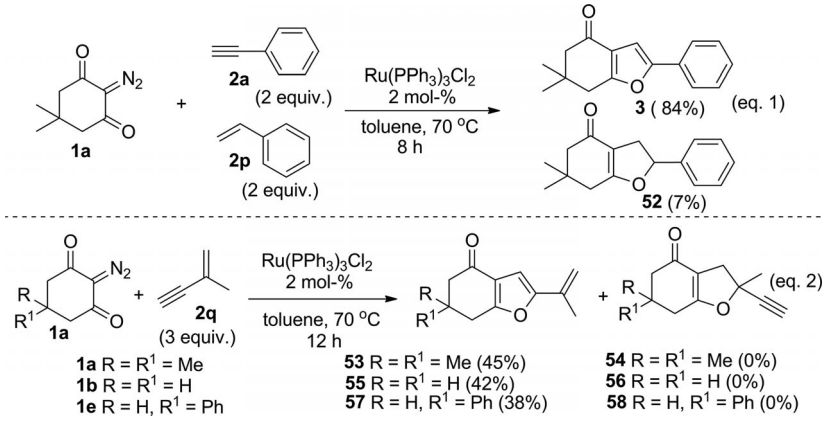
Entry	Diazodicarbonyls	Alkynes	Condition	Products	Yield (%)[b]
1	 **1a**	 **2m**	70 °C, 6 h	 **38**	55
2		 **2n**	70 °C, 4 h	 **39**	54
3		 **2o**	70 °C, 5 h	 **40**	48
4		**2m**	70 °C, 8 h	 **41**	52
5	 **1b**	**2n**	70 °C, 6 h	 **42**	50
6		**2o**	70 °C, 8 h	 **43**	45
7	 **1e**	**2m**	70 °C, 8 h	 **44**	48
8		**2o**	70 °C, 6 h	 **45**	42

[a] Reaction conditions: cyclic diazodicarbonyl compound (1.0 mmol) and alkyne (3.0 mmol) in toluene (2.0 mL) in the presence of [$Ru(PPh_3)_3Cl_2$] (2 mol-%) under nitrogen. [b] Isolated yields.

Table 5. Synthesis of substituted cyclopropenes and furans starting from acyclic diazodicarbonyl compounds and alkynes in the presence of $[Ru(PPh_3)_3Cl_2]$.[a]

Entry	Diazodicarbonyls	Alkynes	Condition	Products (yield)[b]
1	 **1i**	**2a**	70 °C, 12 h	 **46** (10%) **47** (31%)
2	 **1j**	**2a**	70 °C, 12 h	 **48** (10%) **49** (29%)
3	 **1k**	**2a**	70 °C, 12 h	 **50** (7%) **51** (25%)

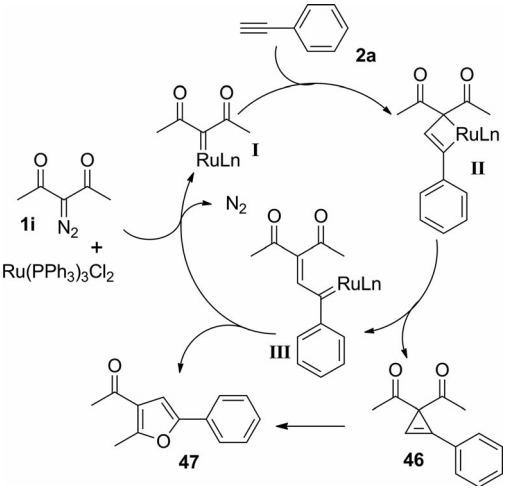
[a] Reaction conditions: acyclic diazodicarbonyl compound (1.0 mmol) and alkyne (3.0 mmol) in toluene (2.0 mL) in the presence of $[Ru(PPh_3)_3Cl_2]$ (2 mol-%) under nitrogen. [b] Isolated yields.



Scheme 2. Chemoselectivity and regioselectivity of $[Ru(PPh_3)_3Cl_2]$-catalyzed reactions.

ence for the formation of furan **3** in 84% yield, which is in accord with the higher nucleophilicity of the active alkyne. The reactions of various diazodicarbonyl compounds with 2-methyl-1-buten-3-yne (**2q**) also showed high regioselectivity [Scheme 2, Equation (2)]. For example, the reaction between **1a** and **2q** provided **53** (45%) as the sole product. Similarly, the reactions between **1b** or **1e** and **2q** gave compounds **55** and **57** as the sole products in yields of 42 and 38%, respectively.

We suggest a mechanism for the formation of cyclopropene **46** and furan **47** based on a comparison with reported Rh^{II}-[19] and Ru^{II}-catalyzed[20] reactions (Scheme 3). Diazodicarbonyl compound **1a** first reacts with 2 mol-% $[Ru(PPh_3)_3Cl_2]$ to give ruthenium carbenoid **I** with the loss of nitrogen. The coordination of **I** to phenylacetylene (**2a**) then leads to the formation of metallacyclobutene **II**[21] through the formation of a ruthenium π complex.[22] Subsequent ring-opening of intermediate **II** leads to the cyclopropene **46** or ruthenium carbenoid **III**.[17a,23] A carbonyl oxygen atom in **III** attacks the metal carbenoid carbon to produce furan **47** and regenerate the catalyst. In the presence of the Ru^{II} catalyst, cyclopropene **46** probably undergoes ring-opening cycloisomerization to afford the corresponding furan **47** as a major component. When toluene solutions of cyclopropenes **46**, **48**, and **50** were heated at 70 °C for 12 h in the presence of 2 mol-% $[Ru(PPh_3)_3Cl_2]$, the corresponding furans **47**, **49**, and **51** were obtained in yields of 76, 81, and 78%, respectively. Importantly, in the cases of cyclic diazodicarbonyl compounds, cyclopropene products were not isolated. Presumably, cyclopropene products directly undergo ring-opening cycloisomerization to give the corresponding furans through the relatively facile attack of the fixed carbonyl oxygen atoms on the cyclic rings compared with acyclic substrates.



Scheme 3. Mechanistic pathway for the Ru^{II}-catalyzed cascade synthesis of compounds **46** and **47**.

Conclusions

We have developed a novel and efficient method for synthesizing functionalized furans by the reaction of cyclic or acyclic diazodicarbonyl compounds with terminal alkynes in the presence of Ru^{II} complexes. Our results provide a new strategy for the construction of polysubstituted furan derivatives with high chemoselectivity and regioselectivity. Further investigations of Ru^{II}-complex-catalyzed transformations and functionalizations of diazodicarbonyl compounds are underway in our laboratory.

Experimental Section

General Experimental Methods: All alkynes and catalysts were obtained commercially from Sigma–Aldrich and used without further purification. The starting acyclic and cyclic diazodiarbonyls **1a**–**1k** were prepared by transfer of the diazo moiety of tosyl or mesyl azide to the corresponding acyclic and acyclic 1,3-dicarbonyl compounds, as described previously.[15] Solvents were purified according to standard methods. All experiments were carried out under nitrogen and glassware was oven-dried prior to use.

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

General Procedure for the Synthesis of Furans: Tris(triphenylphosphine)ruthenium(II) dichloride ($[Ru(PPh_3)_3Cl_2]$; 0.02 mol, 2 mol-%) was added to a solution of a cyclic diazodicarbonyl compound (1.0 mmol, 1 equiv.) and terminal alkyne (3.0 mmol, 3 equiv.) in toluene (2.0 mL) at room temperature. The reaction mixture was stirred at 70 °C for the indicated time and then cooled to room temperature. Water (15 mL) was added and the solution was extracted with ethyl acetate (EA; 3 × 15 mL). Evaporation of the solvent and purification by column chromatography on silica gel using hexane/ethyl acetate (6:1) as eluent gave the product.

6,6-Dimethyl-2-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (3):[24a–24g] Yield 88%; white solid; TLC (1:4 EA/hexane): R_f = 0.45; m.p. 100–101 °C. IR (KBr): $\tilde{\nu}$ = 2930 3059, 2957, 2874, 1676, 1455, 1219, 1124, 762, 692 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, J = 7.2 Hz, 2 H, Ar), 7.30 (uneven t, J = 7.5, 7.2 Hz, 2 H, Ar), 7.20 (uneven t, J = 7.2, 6.6 Hz, 1 H, Ar), 6.80 (s, 1 H, furan), 2.73 (s, 2 H, CH_2), 2.31 (s, 2 H, CH_2), 1.08 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.78, 165.75, 154.48, 129.77, 128.72, 127.97, 123.83, 121.63, 100.69, 51.94, 37.39, 35.20, 28.57 ppm. HRMS (EI^+): calcd. for $C_{16}H_{16}O_2$ 240.1150; found 240.1152.

6,6-Dimethyl-2-(*p*-tolyl)-6,7-dihydrobenzofuran-4(5*H*)-one (4):[24b,24f] Yield 85%; white solid; TLC (1:4 EA/hexane): R_f = 0.40; m.p. 123–124 °C. IR (KBr): $\tilde{\nu}$ = 3045, 2956, 1675, 1445, 1220, 1123, 1025, 811, 737 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.43 (d, J = 7.8 Hz, 2 H, Ar), 7.08 (d, J = 8.1 Hz, 2 H, Ar), 6.72 (s, 1 H, furan), 2.68 (s, 2 H, CH_2), 2.28 (s, 2 H, CH_2), 2.25 (s, 3 H, Ar-CH_3), 1.05 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.79, 165.41, 154.58, 137.81, 129.32, 126.95, 123.68, 121.46, 99.80, 51.81, 37.22, 35.10, 28.48, 21.17 ppm. HRMS (EI^+): calcd. for $C_{17}H_{18}O_2$ 254.1307; found 254.1305.

6,6-Dimethyl-2-(*m*-tolyl)-6,7-dihydrobenzofuran-4(5*H*)-one (5): Yield 94%; white solid; TLC (1:6 EA/hexane): R_f = 0.42; m.p. 81–82 °C. IR (KBr): $\tilde{\nu}$ = 3042, 2950, 2889, 1678, 1445, 1220, 1123, 1033, 787, 692 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.33 (m, 2 H, Ar), 7.16 (t, J = 7.5 Hz, 1 H, Ar), 6.99 (d, J = 7.2 Hz, 1 H, Ar), 6.75 (s, 1 H, furan), 2.68 (s, 2 H, CH_2), 2.27 (br. s, 5 H, CH_2, Ar-CH_3), 1.05 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.69, 165.56, 154.46, 138.22, 129.52, 128.69, 128.53, 124.28, 121.44, 120.89, 100.42, 51.77, 37.18, 35.06, 28.43, 21.31 ppm. HRMS (EI^+): calcd. for $C_{17}H_{18}O_2$ 254.1307; found 254.1308.

6,6-Dimethyl-2-(4-pentylphenyl)-6,7-dihydrobenzofuran-4(5*H*)-one (6): Yield 74%; brown solid; TLC (1:4 EA/hexane): R_f = 0.43; m.p. 96–97 °C. IR (KBr): $\tilde{\nu}$ = 3039, 2937, 1678, 1446, 1219, 1124, 1018, 813, 736 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.46 (d, J = 7.8 Hz, 2 H, thiophene), 7.10 (d, J = 7.8 Hz, 2 H, Ar), 6.73 (s, 1 H, furan), 2.69 (s, 2 H, CH_2), 2.51 (dd, J = 7.8, 7.2 Hz, 2 H, Ar-$CH_2CH_2CH_2CH_2CH_3$), 2.29 (s, 2 H, CH_2), 1.52 (dd, J = 6.9, 6.6 Hz, 2 H, Ar-$CH_2CH_2CH_2CH_2CH_3$), 1.22 (br. s, 4 H, Ar-$CH_2CH_2CH_2CH_2CH_3$), 1.06 (s, 6 H, 2 CH_3), 0.79 (t, J = 6.0 Hz, 3 H, Ar-$CH_2CH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.82, 165.45, 154.66, 142.94, 128.70, 127.17, 123.73, 121.49, 99.83, 51.83, 37.27, 35.57, 35.14, 31.31, 30.91, 28.49, 22.41, 13.94 ppm. HRMS (EI^+): calcd. for $C_{21}H_{26}O_2$ 310.1933; found 310.1936.

2-(4-Methoxy-2-methylphenyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one (7): Yield 87%; yellow solid; TLC (1:6 EA/hexane): R_f = 0.29; m.p. 114–115 °C. IR (KBr): $\tilde{\nu}$ = 3144, 2952, 1673, 1606, 1490, 1449, 1292, 1246, 1221, 1130, 1049, 1009, 810, 733, 643 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.1 Hz, 1 H, Ar), 6.76–6.74 (m, 2 H, Ar), 6.61 (s, 1 H, furan), 3.77 (s, 3 H, Ar-OCH_3), 2.75 (s, 2 H, CH_2), 2.40 (s, 3 H, Ar-CH_3), 2.35 (s, 2 H, CH_2), 1.12 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.00, 164.93, 159.06, 153.80, 136.47, 128.26, 121.90, 121.30, 116.32, 111.32, 102.80, 55.05, 51.81, 37.17, 35.11, 28.50, 21.94 ppm. HRMS (EI^+): calcd. for $C_{18}H_{20}O_3$ 284.1412; found 284.1411.

2-(3-Fluorophenyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one (8): Yield 66%; white solid; TLC (1:6 EA/hexane): R_f = 0.43; m.p.

93–94 °C. IR (KBr): ṽ = 3103, 2959, 2874, 1677, 1616, 1564, 1448, 1274, 1223, 1182, 1126, 941, 858, 785, 686, 624, 523, 483 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (uneven t, J = 7.8, 5.4 Hz, 1 H, Ar), 7.32 (s, 1 H, Ar), 7.30–7.27 (m, 1 H, Ar), 6.94 (t, J = 8.1 Hz, 1 H, Ar), 6.87 (s, 1 H, furan), 2.78 (s, 2 H, CH_2), 2.37 (s, 2 H, CH_2), 1.14 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.71, 166.07, 162.97 (d, $^1J_{C,F}$ = 243.9 Hz), 153.15 (d, J_{CF} = 2.8 Hz), 131.74 (d, $^3J_{C,F}$ = 8.3 Hz), 130.38 (d, $^3J_{C,F}$ = 8.3 Hz), 121.62, 119.45 (d, $^4J_{C,F}$ = 2.8 Hz), 114.73 (d, $^2J_{C,F}$ = 20.9 Hz), 110.70 (d, $^2J_{C,F}$ = 23.6 Hz), 101.76, 51.87, 37.30, 35.20, 28.53 ppm. HRMS (EI$^+$): calcd. for $C_{16}H_{15}FO_2$ 258.1056; found 258.1056.

6,6-Dimethyl-2-(1-naphthyl)-6,7-dihydrobenzofuran-4(5*H*)-one (9):[24b] Yield 84%; red liquid; TLC (1:6 EA/hexane): R_f = 0.37. IR (neat): ṽ = 3054, 2955, 2887, 1673, 1444, 1220, 1122, 1043, 967, 788, 733 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (d, J = 8.4 Hz, 1 H, Ar), 7.88 (d, J = 8.4 Hz, 1 H, Ar), 7.86 (d, J = 8.4 Hz, 1 H, Ar), 7.74 (d, J = 7.2 Hz, 1 H, Ar), 7.52–7.48 (m, 3 H, Ar), 6.98 (s, 1 H, furan), 2.87 (s, 2 H, CH_2), 2.45 (s, 2 H, CH_2), 1.20 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.12, 166.11, 153.73, 133.82, 130.06, 129.19, 128.62, 127.33, 126.84, 126.35, 126.10, 125.20, 125.02, 121.49, 105.21, 52.02, 37.48, 35.32, 28.68 ppm. HRMS (EI$^+$): calcd. for $C_{20}H_{18}O_2$ 290.1307; found 290.1305.

2-(6-Methoxy-2-naphthyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one (10): Yield 66%; brown solid; TLC (1:6 EA/hexane): R_f = 0.23; m.p. 174–175 °C. IR (KBr): ṽ = 3056, 2952, 1672, 1620, 1453, 1393, 1262, 1213, 1032, 750 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.80 (s, 1 H, Ar), 7.73–7.61 (m, 3 H, Ar), 7.13 (d, J = 7.8 Hz, 1 H, Ar), 7.07 (s, 1 H, Ar), 6.89 (s, 1 H, furan), 3.87 (s, 3 H, Ar-OCH_3), 2.76 (s, 2 H, CH_2), 2.36 (s, 2 H, CH_2), 1.14 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.79, 165.67, 157.89, 154.63, 134.00, 129.57, 128.58, 127.24, 124.93, 122.45, 122.26, 121.59, 119.33, 105.69, 100.31, 55.17, 51.82, 37.25, 35.13, 28.51 ppm. HRMS (EI$^+$): calcd. for $C_{21}H_{20}O_3$ 320.1412; found 320.1408.

6,6-Dimethyl-2-(9-phenanthryl)-6,7-dihydrobenzofuran-4(5*H*)-one (11): Yield 58%; brown liquid; TLC (1:6 EA/hexane): R_f = 0.37. IR (neat): ṽ = 3058, 2952, 2883, 1674, 1606, 1441, 1221, 1124, 1036, 955, 900, 826, 740, 628 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (d, J = 7.8 Hz, 1 H, Ar), 8.62 (d, J = 8.1 Hz, 1 H, Ar), 8.36 (d, J = 7.8 Hz, 1 H, Ar), 7.98 (s, 1 H, Ar), 7.87 (d, J = 7.5 Hz, 1 H, Ar), 7.66–7.55 (m, 4 H, Ar), 7.03 (s, 1 H, furan), 2.82 (s, 2 H, CH_2), 2.43 (s, 2 H, CH_2), 1.18 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.92, 166.00, 153.51, 130.86, 130.54, 130.17, 128.89, 128.86, 127.59, 127.30, 126.89, 126.88, 126.72, 125.92, 125.66, 122.98, 122.40, 121.32, 105.47, 51.87, 37.28, 35.15, 28.54 ppm. HRMS (EI$^+$): calcd. for $C_{24}H_{20}O_2$ 340.1463; found 340.1459.

6,6-Dimethyl-2-(3-thienyl)-6,7-dihydrobenzofuran-4(5*H*)-one (12): Yield 79%; brown solid; TLC (1:6 EA/hexane): R_f = 0.37; m.p. 102–103 °C. IR (KBr): ṽ = 3108, 2953, 2883, 1672, 1447, 1220, 1121, 1038, 852, 786 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40 (s, 1 H, thiophene), 7.26 (d, J = 4.8 Hz, 1 H, thiophene), 7.20 (d, J = 4.8 Hz, 1 H, thiophene), 6.61 (s, 1 H, furan), 2.70 (s, 2 H, CH_2), 2.30 (s, 2 H, CH_2), 1.07 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.83, 165.28, 151.33, 131.31, 126.53, 124.39, 121.25, 119.74, 100.28, 51.84, 37.25, 35.17, 28.50 ppm. HRMS (EI$^+$): calcd. for $C_{14}H_{14}O_2S$ 246.0715; found 246.0719.

6,6-Dimethyl-2-(2-pyridyl)-6,7-dihydrobenzofuran-4(5*H*)-one (13): Yield 67%; brown solid; TLC (1:6 EA/hexane): R_f = 0.23; m.p. 128–129 °C. IR (KBr): ṽ = 3063, 2954, 2885, 1675, 1609, 1444, 1218, 1130, 782, 625 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.54 (d, J = 3.9 Hz, 1 H, pyridine), 7.63 (dd, J = 7.8, 7.5 Hz, 1 H, pyridine), 7.56 (d, J = 8.1 Hz, 1 H, pyridine), 7.15–7.10 (m, 2 H, pyridine-H, furan-H), 2.78 (s, 2 H, CH_2), 2.34 (s, 2 H, CH_2), 1.09 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.56, 166.75, 153.53, 149.60, 148.20, 136.61, 122.37, 121.60, 118.83, 104.29, 51.85, 37.32, 35.11, 28.43 ppm. HRMS (EI$^+$): calcd. for $C_{15}H_{15}NO_2$ 241.1103; found 241.1107.

2-Phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (15):[24a,24c,24h] Yield 85%; white solid; TLC (1:6 EA/hexane): R_f = 0.25; m.p. 133–134 °C. IR (KBr): ṽ = 3098, 3057, 2946, 1669, 1445, 1355, 1136, 851, 756, 698 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, J = 7.5 Hz, 2 H, Ar), 7.31 (uneven t, J = 7.5, 6.9 Hz, 2 H, Ar), 7.21 (uneven t, J = 7.8, 6.9 Hz, 1 H, Ar), 6.80 (s, 1 H, furan), 2.85 (t, J = 6.0 Hz, 2 H, $CH_2CH_2CH_2$), 2.44 (dd, J = 6.6, 6.0 Hz, 2 H, $CH_2CH_2CH_2$), 2.16–2.08 (m, 2 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.50, 166.63, 154.07, 129.65, 128.69, 127.98, 123.82, 122.79, 100.73, 37.51, 23.33, 22.45 ppm. HRMS (EI$^+$): calcd. for $C_{14}H_{12}O_2$ 212.0837; found 212.0835.

2-(3-Fluorophenyl)-6,7-dihydrobenzofuran-4(5*H*)-one (16): Yield 69%; brown solid; TLC (1:6 EA/hexane): R_f = 0.24; m.p. 89–90 °C. IR (KBr): ṽ = 3075, 2948, 2891, 1675, 1607, 1443, 1261, 1229, 1167, 1005, 861, 788, 725, 691, 599, 521, 462 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37 (dd, J = 7.5, 5.7 Hz, 1 H, Ar), 7.32–7.29 (m, 2 H, Ar), 6.95 (dd, J = 8.4, 7.8 Hz, 1 H, Ar), 6.87 (s, 1 H, furan), 2.92 (t, J = 6.0 Hz, 2 H, $CH_2CH_2CH_2$), 2.50 (dd, J = 6.3, 6.0 Hz, 2 H, $CH_2CH_2CH_2$), 2.22–2.16 (m, 2 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.35, 166.93, 162.98 (d, $^1J_{C,F}$ = 244.0 Hz), 152.84, 131.69 (d, $^3J_{CF}$ = 8.8 Hz), 130.38 (d, $^3J_{CF}$ = 8.3 Hz), 122.84, 119.51 (d, $^4J_{CF}$ = 2.7 Hz), 114.78 (d, $^2J_{CF}$ = 21.5 Hz), 110.75 (d, $^2J_{CF}$ = 23.6 Hz), 101.86, 37.51, 23.33, 22.41 ppm. HRMS (EI$^+$): calcd. for $C_{14}H_{11}FO_2$ 230.0743; found 230.0741.

2-(1-Naphthyl)-6,7-dihydrobenzofuran-4(5*H*)-one (17): Yield 82%; brown liquid; TLC (1:6 EA/hexane): R_f = 0.20. IR (neat): ṽ = 3052, 2946, 2893, 1673, 1592, 1436, 1223, 1125, 1005, 977, 788, 732 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (d, J = 7.2 Hz, 1 H, Ar), 7.87 (d, J = 7.8 Hz, 1 H, Ar), 7.84 (d, J = 8.4 Hz, 1 H, Ar), 7.72 (d, J = 7.2 Hz, 1 H, Ar), 7.56–7.46 (m, 3 H, Ar), 6.99 (s, 1 H, furan), 2.97 (dd, J = 6.3, 6.0 Hz, 2 H, $CH_2CH_2CH_2$), 2.55 (dd, J = 6.6, 6.3 Hz, 2 H, $CH_2CH_2CH_2$), 2.26–2.18 (m, 2 H, $CH_2CH_2CH_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.60, 166.89, 153.31, 133.73, 130.01, 129.15, 128.54, 127.22, 126.78, 126.32, 126.04, 125.13, 124.94, 122.64, 105.25, 37.55, 23.39, 22.49 ppm. HRMS (EI$^+$): calcd. for $C_{18}H_{14}O_2$ 262.0994; found 262.0996.

6-Methyl-2-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (18):[24a,24i] Yield 84%; white solid; TLC (1:6 EA/hexane): R_f = 0.37; m.p. 97–98 °C. IR (KBr): ṽ = 3055, 2952, 2892, 1674, 1610, 1441, 1218, 1133, 1052, 1012, 914, 752, 695 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, J = 8.1 Hz, 2 H, Ar), 7.36 (t, J = 7.2 Hz, 2 H, Ar), 7.26 (uneven t, J = 6.9, 6.6 Hz, 1 H, Ar), 6.85 (s, 1 H, furan), 3.02–2.95 (m, 1 H, $CH_2CH_{2a}CH_{2b}$), 2.61–2.43 (m, 3 H, $CH_{2a}CHCH_{2b}$), 2.28–2.19 (m, 1 H, $CH_{2b}CHCH_2$), 1.16 (d, J = 6.3 Hz, 3 H, $CHCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.93, 166.24, 165.24, 129.68, 128.66, 127.93, 123.79, 122.40, 100.68, 45.95, 31.36, 30.62, 20.95 ppm. HRMS (EI$^+$): calcd. for $C_{15}H_{14}O_2$ 226.0994; found 226.0995.

6-Methyl-2-(4-pentylphenyl)-6,7-dihydrobenzofuran-4(5*H*)-one (19): Yield 68%; brown solid; TLC (1:6 EA/hexane): R_f = 0.53; m.p. 86–87 °C. IR (KBr): ṽ = 3037, 2936, 2871, 1677, 1446, 1218, 1131, 1046, 1012, 823, 736 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52 (d, J = 7.8 Hz, 2 H, Ar), 7.16 (d, J = 7.8 Hz, 2 H, Ar), 6.78 (s, 1

H, furan), 3.00–2.93 (m, 1 H, CH_2CHCH_{2a}), 2.60–2.39 (m, 5 H, $CH_{2a}CHCH_{2b}$, Ar-$CH_2CH_2CH_2CH_2CH_3$), 2.26–2.17 (m, 1 H, $CH_{2b}CHCH_2$), 1.59 (t, J = 6.9 Hz, 2 H, Ar-$CH_2CH_2CH_2CH_2CH_3$), 1.30 (br. s, 4 H, Ar-$CH_2CH_2CH_2CH_2CH_3$), 1.14 (d, J = 6.3 Hz, 3 H, $CHCH_3$), 0.87 (dd, J = 6.6, 6.0 Hz, 3 H, Ar-$CH_2CH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.93, 165.94, 154.52, 142.95, 128.67, 127.18, 123.78, 122.36, 99.90, 45.93, 35.55, 31.34, 31.31, 30.97, 30.63, 22.39, 20.93, 13.89 ppm. HRMS (EI$^+$): calcd. for $C_{20}H_{24}O_2$ 296.1776; found 296.1779.

2-(4-Methoxy-2-methylphenyl)-6-methyl-6,7-dihydrobenzofuran-4(5*H*)-one (20): Yield 66%; brown solid; TLC (1:6 EA/hexane): R_f = 0.33; m.p. 75–76 °C. IR (KBr): $\tilde{\nu}$ = 3049, 2948, 1671, 1604, 1447, 1246, 1223, 1136, 1048, 1009, 847, 813, 733, 639 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, J = 8.7 Hz, 1 H, Ar), 6.75–6.73 (m, 2 H, Ar), 6.59 (s, 1 H, furan), 3.76 (s, 3 H, Ar-OCH_3), 2.99–2.92 (m, 1 H, CH_2CHCH_{2a}), 2.58–2.46 (m, 3 H, $CH_{2a}CHCH_{2b}$), 2.39 (s, 3 H, Ar-CH_3), 2.26–2.17 (m, 1 H, $CH_{2b}CHCH_2$), 1.14 (d, J = 6.3 Hz, 3 H, $CHCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.07, 165.43, 159.12, 153.68, 136.55, 128.34, 122.16, 121.90, 116.32, 111.30, 102.86, 55.02, 45.90, 31.26, 30.64, 21.81, 20.93 ppm. HRMS (EI$^+$): calcd. for $C_{17}H_{18}O_3$ 270.1256; found 270.1252.

2-(3-Fluorophenyl)-6-methyl-6,7-dihydrobenzofuran-4(5*H*)-one (21): Yield 68%; brown solid; TLC (1:6 EA/hexane): R_f = 0.33; m.p. 117–118 °C. IR (KBr): $\tilde{\nu}$ = 3105, 2954, 2893, 1675, 1605, 1444, 1269, 1218, 1145, 1055, 862, 787, 686, 615, 518, 485 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (dd, J = 7.5, 4.2 Hz, 1 H, Ar), 7.19–7.15 (m, 2 H, Ar), 6.81 (dd, J = 7.8, 7.5 Hz, 1 H, Ar), 6.73 (s, 1 H, furan), 2.91–2.84 (m, 1 H, CH_2CHCH_{2a}), 2.50–2.32 (m, 3 H, $CH_{2a}CHCH_{2b}$), 2.16–2.07 (m, 1 H, $CH_{2b}CHCH_2$), 1.05 (d, J = 6.3 Hz, 3 H, $CHCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.80, 166.54, 162.88 (d, $^1J_{CF}$ = 244.4 Hz), 152.87 (d, $^4J_{CF}$ = 2.8 Hz), 131.64 (d, $^3J_{CF}$ = 8.3 Hz), 130.30 (d, $^3J_{CF}$ = 8.8 Hz), 122.38, 119.40 (d, $^4J_{CF}$ = 2.7 Hz), 114.66 (d, $^2J_{CF}$ = 21.4 Hz), 110.61 (d, $^2J_{CF}$ = 23.6 Hz), 101.72, 45.87, 31.27, 30.57, 20.91 ppm. HRMS (EI$^+$): calcd. for $C_{15}H_{13}FO_2$ 244.0900; found 244.0897.

2-(6-Methoxy-2-naphthyl)-6-methyl-6,7-dihydrobenzofuran-4(5*H*)-one (22): Yield 80%; brown solid; TLC (1:6 EA/hexane): R_f = 0.23; m.p. 197–198 °C. IR (KBr): $\tilde{\nu}$ = 3076, 2949, 1673, 1617, 1448, 1390, 1218, 1126, 1025, 881, 811 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.01 (s, 1 H, Ar), 7.74–7.63 (m, 3 H, Ar), 7.13 (d, J = 9.0 Hz, 1 H, Ar), 7.09 (s, 1 H, Ar), 6.89 (s, 1 H, furan), 3.90 (s, 3 H, Ar-OCH_3), 3.06–2.99 (m, 1 H, CH_2CHCH_{2a}), 2.64–2.45 (m, 3 H, $CH_{2a}CHCH_{2b}$), 2.30–2.21 (m, 1 H, $CH_{2b}CHCH_2$), 1.18 (d, J = 6.0 Hz, 3 H, $CHCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.15, 166.30, 157.97, 154.58, 134.09, 129.66, 128.66, 127.32, 125.00, 122.56, 122.40, 119.41, 105.77, 100.44, 55.28, 46.04, 31.47, 30.73, 21.08 ppm. HRMS (EI$^+$): calcd. for $C_{20}H_{18}O_3$ 306.1256; found 306.1258.

6-Isopropyl-2-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (23):[24i] Yield 78%; yellow liquid; TLC (1:6 EA/hexane): R_f = 0.42. IR (neat): $\tilde{\nu}$ = 3056, 2956, 2886, 1673, 1611, 1447, 1219, 1135, 1047, 1008, 828, 754, 693 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, J = 7.5 Hz, 2 H, Ar), 7.37 (dd, J = 7.8, 7.2 Hz, 2 H, Ar), 7.27 (dd, J = 7.2, 6.8 Hz, 1 H, Ar), 6.85 (s, 1 H, furan), 3.00–2.98 (m, 1 H, CH_2CHCH_{2a}), 2.66–2.54 (m, 2 H, $CH_{2a}CHCH_{2b}$), 2.27 (dd, J = 15.9, 12.9 Hz, 1 H, $CH_{2b}CHCH_2$), 2.12–2.09 (m, 1 H, CH_2CHCH_2), 1.73–1.66 (m, 1 H, $CHCH_3$), 0.97 (d, J = 6.6 Hz, 6 H, 2 $CHCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.34, 166.86, 154.18, 129.57, 128.59, 127.85, 123.67, 122.34, 100.49, 41.83, 41.66, 31.79, 26.79, 19.70, 19.39 ppm. HRMS (EI$^+$): calcd. for $C_{17}H_{18}O_2$ 254.1307; found 254.1304.

6-Isopropyl-2-(*p*-tolyl)-6,7-dihydrobenzofuran-4(5*H*)-one (24):[24i] Yield 88%; white solid; TLC (1:6 EA/hexane): R_f = 0.42; m.p. 92–93 °C. IR (KBr): $\tilde{\nu}$ = 2956, 2888, 1673, 1609, 1447, 1266, 1216, 1132, 1009, 813, 734, 644, 504 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, J = 7.8 Hz, 2 H, Ar), 7.15 (d, J = 7.8 Hz, 2 H, Ar), 6.76 (s, 1 H, furan), 2.96–2.89 (m, 1 H, CH_2CHCH_{2a}), 2.63–2.51 (m, 2 H, $CH_{2a}CHCH_{2b}$), 2.33 (s, 3 H, Ar-CH_3), 2.28–2.19 (m, 1 H, $CH_{2b}CHCH_2$), 2.11–2.06 (m, 1 H, CH_2CHCH_2), 1.73–1.62 (m, 1 H, $CHCH_3$), 0.96 (d, J = 6.9 Hz, 6 H, 2 $CHCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.07, 166.41, 154.40, 137.72, 129.23, 126.91, 123.63, 122.30, 99.70, 41.82, 41.64, 31.77, 26.76, 21.05, 19.64, 19.36 ppm. HRMS (EI$^+$): calcd. for $C_{18}H_{20}O_2$ 268.1463; found 268.1462.

6-Isopropyl-2-(4-methoxy-2-methylphenyl)-6,7-dihydrobenzofuran-4(5*H*)-one (25): Yield 69%; brown liquid; TLC (1:6 EA/hexane): R_f = 0.27. IR (neat): $\tilde{\nu}$ = 2955, 1673, 1605, 1489, 1451, 1294, 1245, 1224, 1138, 1049, 1006, 845, 811, 730, 643 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, J = 8.1 Hz, 1 H, Ar), 6.77–6.75 (m, 2 H, Ar), 6.60 (s, 1 H, furan), 3.78 (s, 3 H, Ar-OCH_3), 2.99–2.92 (m, 1 H, CH_2CHCH_{2a}), 2.67–2.54 (m, 2 H, $CH_{2a}CHCH_{2b}$), 2.41 (s, 3 H, Ar-CH_3), 2.32–2.22 (m, 1 H, $CH_{2b}CHCH_2$), 2.16–2.12 (m, 1 H, CH_2CHCH_2), 1.73–1.64 (m, 1 H, $CHCH_3$), 0.97 (d, J = 6.6 Hz, 6 H, 2 $CHCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.61, 166.14, 159.12, 153.78, 136.59, 128.36, 122.26, 121.95, 116.36, 111.33, 102.83, 55.10, 42.01, 41.77, 31.91, 26.85, 21.93, 19.79, 19.50 ppm. HRMS (EI$^+$): calcd. for $C_{19}H_{22}O_3$ 298.1569; found 298.1565.

2-(3-Fluorophenyl)-6-isopropyl-6,7-dihydrobenzofuran-4(5*H*)-one (26): Yield 81%; brown solid; TLC (1:6 EA/hexane): R_f = 0.38; m.p. 66–67 °C. IR (KBr): $\tilde{\nu}$ = 3074, 2959, 2887, 1677, 1607, 1449, 1271, 1218, 1173, 1147, 1044, 941, 862, 787, 689, 522, 475 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.16 (m, 3 H, Ar), 6.83 (t, J = 8.1 Hz, 1 H, Ar), 6.73 (s, 1 H, furan), 2.89–2.82 (m, 1 H, CH_2CHCH_{2a}), 2.56–2.43 (m, 2 H, $CH_{2a}CHCH_{2b}$), 2.20–2.11 (m, 1 H, $CH_{2b}CHCH_2$), 2.03–1.99 (m, 1 H, CH_2CHCH_2), 1.65–1.54 (m, 1 H, $CHCH_3$), 0.86 (d, J = 8.1 Hz, 6 H, 2 $CHCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.21, 167.18, 162.92 (d, J_{CF} = 243.9 Hz), 152.98 (d, J_{CF} = 3.3 Hz), 131.68 (d, J_{CF} = 8.9 Hz), 130.34 (d, J_{CF} = 8.8 Hz), 122.47, 119.42 (d, J_{CF} = 2.7 Hz), 114.70 (d, J_{CF} = 20.9 Hz), 110.65 (d, J_{CF} = 23.6 Hz), 101.68, 41.90, 41.76, 31.87, 26.87, 19.75, 19.45 ppm. HRMS (EI$^+$): calcd. for $C_{17}H_{17}FO_2$ 272.1213; found 272.1210.

6-Isopropyl-2-(1-naphthyl)-6,7-dihydrobenzofuran-4(5*H*)-one (27): Yield 80%; brown liquid; TLC (1:6 EA/hexane): R_f = 0.43. IR (neat): $\tilde{\nu}$ = 3053, 2956, 2887, 1673, 1597, 1445, 1220, 1128, 1036, 970, 913, 789, 736 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.33 (d, J = 7.5 Hz, 1 H, Ar), 7.85 (d, J = 9.0 Hz, 1 H, Ar), 7.82 (d, J = 8.7 Hz, 1 H, Ar), 7.71 (d, J = 7.2 Hz, 1 H, Ar), 7.55–7.45 (m, 3 H, Ar), 6.97 (s, 1 H, furan), 3.00–2.93 (m, 1 H, CH_2CHCH_{2a}), 2.66–2.57 (m, 2 H, $CH_{2a}CHCH_{2b}$), 2.28 (dd, J = 15.9, 12.9 Hz, 1 H, $CH_{2b}CHCH_2$), 2.14–2.09 (m, 1 H, CH_2CHCH_2), 1.72–1.62 (m, 1 H, $CHCH_3$), 0.95 (d, J = 6.6 Hz, 6 H, 2 $CHCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.39, 167.09, 153.45, 133.65, 129.87, 129.02, 128.47, 127.14, 126.69, 126.16, 125.95, 125.05, 124.85, 122.21, 105.02, 41.85, 41.71, 31.80, 26.84, 19.68, 19.39 ppm. HRMS (EI$^+$): calcd. for $C_{21}H_{20}O_2$ 304.1463; found 304.1461.

6-Phenyl-2-(*p*-tolyl)-6,7-dihydrobenzofuran-4(5*H*)-one (28): Yield 78%; brown solid; TLC (1:6 EA/hexane): R_f = 0.43; m.p. 67–68 °C. IR (KBr): $\tilde{\nu}$ = 3032, 2941, 1738, 1674, 1498, 1445, 1216, 1133, 1028, 814, 755, 700, 507 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.48 (d, J = 7.8 Hz, 2 H, Ar), 7.28 (d, J = 6.3 Hz, 2 H, Ar), 7.24–7.12 (m, 5 H, Ar), 6.79 (s, 1 H, furan), 3.54–3.49 (m, 1 H, CH_2CHCH_2),

3.0–2.99 (m, 2 H, CH_2CHCH_2), 2.73–2.43 (m, 2 H, CH_2CHCH_2), 2.29 (s, 3 H, Ar-CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.11, 165.50, 154.91, 142.40, 138.15, 129.46, 128.84, 128.62, 127.21, 126.75, 126.67, 123.90, 99.99, 44.87, 41.20, 31.21, 21.28 ppm. HRMS (EI^+): calcd. for $C_{21}H_{18}O_2$ 302.1307; found 302.1308.

2-(4-Pentylphenyl)-6-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (29): Yield 72%; brown solid; TLC (1:6 EA/hexane): R_f = 0.46; m.p. 64–65 °C. IR (KBr): $\tilde{\nu}$ = 3033, 2931, 2863, 1739, 1677, 1605, 1495, 1447, 1215, 1130, 1008, 817, 756, 699, 513 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.50 (d, J = 8.1 Hz, 2 H, Ar), 7.29 (d, J = 6.3 Hz, 2 H, Ar), 7.24–7.13 (m, 5 H, Ar), 6.80 (s, 1 H, furan), 3.58–3.48 (m, 1 H, CH_2CHCH_2), 3.22–3.00 (m, 2 H, CH_2CHCH_2), 2.74–2.71 (m, 2 H, CH_2CHCH_2), 2.54 (dd, J = 7.8, 7.5 Hz, 2 H, Ar-$CH_2CH_2CH_2CH_2CH_3$), 1.59–1.49 (m, 2 H, Ar-$CH_2CH_2CH_2CH_2CH_3$), 1.25 (br. s, 4 H, Ar-$CH_2CH_2CH_2CH_2CH_3$), 0.82 (dd, J = 6.6, 5.1 Hz, 3 H, Ar-$CH_2CH_2CH_2CH_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.12, 165.52, 154.99, 143.27, 142.43, 128.86, 128.84, 127.22, 126.77, 126.69, 123.95, 122.72, 100.02, 44.90, 41.23, 35.69, 31.42, 31.23, 31.01, 22.51, 14.02 ppm. HRMS (EI^+): calcd. for $C_{25}H_{26}O_2$ 358.1933; found 358.1930.

2-(4-Methoxy-2-methylphenyl)-6-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (30): Yield 63%; brown solid; TLC (1:6 EA/hexane): R_f = 0.28; m.p. 84–85 °C. IR (KBr): $\tilde{\nu}$ = 3029, 2947, 2845, 1674, 1605, 1493, 1449, 1292, 1246, 1221, 1131, 1049, 1009, 812, 750, 701 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, J = 9.3 Hz, 1 H, Ar), 7.29 (d, J = 6.9 Hz, 2 H, Ar), 7.25–7.18 (m, 3 H, Ar), 6.74–6.72 (m, 2 H, Ar), 6.62 (s, 1 H), 3.75 (s, 3 H, Ar-OCH_3), 3.59–3.48 (m, 1 H, CH_2CHCH_2), 3.21–3.00 (m, 2 H, CH_2CHCH_2), 2.74–2.71 (m, 2 H, CH_2CHCH_2), 2.39 (s, 3 H, Ar-CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.27, 165.04, 159.31, 154.16, 142.45, 136.80, 128.85, 128.55, 127.21, 126.76, 122.55, 121.92, 116.46, 111.47, 103.06, 55.22, 44.89, 41.27, 31.18, 22.02 ppm. HRMS (EI^+): calcd. for $C_{22}H_{20}O_3$ 332.1412; found 332.1416.

6-(Benzo[*d*][1,3]dioxol-5-yl)-2-(3-fluorophenyl)-6,7-dihydrobenzofuran-4(5*H*)-one (31): Yield 71%; brown liquid; TLC (1:6 EA/hexane): R_f = 0.23. IR (neat): $\tilde{\nu}$ = 3062, 2896, 1736, 1676, 1606, 1491, 1444, 1240, 1139, 1036, 932, 862, 803, 732, 701, 600, 519, 446 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40 (dd, J = 7.8, 6.9 Hz, 1 H, Ar), 7.35–7.32 (m, 2 H, Ar), 6.98 (dd, J = 8.4, 7.8 Hz, 1 H, Ar), 6.92 (s, 1 H, Ar), 6.77–6.72 (m, 3 H, Ar-2H, furan-H), 5.95 (s, 2 H, OCH_2O), 3.56–3.46 (m, 1 H), 3.25–3.00 (m, 2 H), 2.74–2.71 (m, 2 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.66, 165.89, 162.96 (d, J_{CF} = 243.9 Hz), 153.31 (d, J_{CF} = 2.8 Hz), 147.88, 146.58, 136.14, 131.58 (d, J_{CF} = 8.8 Hz), 130.34 (d, J_{CF} = 8.8 Hz), 122.69, 119.77, 119.54 (d, J_{CF} = 3.3 Hz), 114.89 (d, J_{CF} = 21.5 Hz), 110.79 (d, J_{CF} = 23.6 Hz), 108.42, 107.03, 101.83, 101.07, 45.08, 40.89, 31.43 ppm. HRMS (EI^+): calcd. for $C_{21}H_{15}FO_4$ 350.0954; found 350.0958.

6-(Benzo[*d*][1,3]dioxol-5-yl)-2-(9-phenanthryl)-6,7-dihydrobenzofuran-4(5*H*)-one (32): Yield 54%; brown liquid; TLC (1:4 EA/hexane): R_f = 0.43. IR (neat): $\tilde{\nu}$ = 3058, 2956, 2895, 1737, 1674, 1495, 1443, 1242, 1127, 1038, 935, 813, 740 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.75 (d, J = 8.1 Hz, 1 H, Ar), 8.67 (d, J = 8.1 Hz, 1 H, Ar), 8.35 (d, J = 7.5 Hz, 1 H, Ar), 8.01 (s, 1 H, Ar), 7.91 (d, J = 7.2 Hz, 1 H, Ar), 7.72–7.58 (m, 4 H, Ar), 7.05 (s, 1 H, Ar), 6.81–6.66 (m, 3 H, Ar-2H, furan-H), 5.96 (s, 2 H, OCH_2O), 3.63–3.52 (m, 1 H, CH_2CHCH_2), 3.35–3.07 (m, 2 H, CH_2CHCH_2), 2.80–2.77 (m, 2 H, CH_2CHCH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.03, 166.01, 153.93, 147.95, 146.64, 136.33, 130.97, 130.69, 130.39, 129.05, 129.04, 127.96, 127.52, 127.07, 127.06, 126.89, 125.97, 125.79, 123.13, 122.56, 119.86, 119.55, 108.51, 107.14, 101.13, 100.97, 45.29, 41.15, 31.69 ppm. HRMS (EI^+): calcd. for $C_{29}H_{20}O_4$ 432.1362; found 432.1366.

6-(Benzo[*d*][1,3]dioxol-5-yl)-2-(6-methoxy-2-naphthyl)-6,7-dihydrobenzofuran-4(5*H*)-one (33): Yield 75%; brown solid; TLC (1:4 EA/hexane): R_f = 0.30; m.p. 211–212 °C. IR (KBr): $\tilde{\nu}$ = 3027, 2905, 1661, 1626, 1485, 1390, 1216, 1030, 923, 808, 599 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.05 (s, 1 H, Ar), 7.76–7.66 (m, 3 H, Ar), 7.15 (d, J = 9.0 Hz, 1 H, Ar), 7.11 (s, 1 H, Ar), 6.94 (s, 1 H, Ar), 6.80–6.72 (m, 3 H, Ar-2H, furan-H), 5.95 (s, 2 H, OCH_2O), 3.91 (s, 3 H, Ar-OCH_3), 3.57–3.46 (m, 1 H, CH_2CHCH_2), 3.26–3.19 (m, 1 H, CH_2CHCH_2), 3.10–3.01 (m, 1 H, CH_2CHCH_2), 2.75–2.71 (m, 2 H, CH_2CHCH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.90, 165.61, 158.13, 155.06, 147.97, 146.65, 136.42, 134.25, 129.73, 128.73, 127.41, 124.96, 122.88, 122.62, 119.87, 119.50, 108.51, 107.16, 105.90, 101.13, 100.53, 55.33, 45.25, 41.08, 31.62 ppm. HRMS (EI^+): calcd. for $C_{26}H_{20}O_5$ 412.1311; found 412.1308.

6-(2-Furyl)-2-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (34): Yield 72%; yellow liquid; TLC (1:6 EA/hexane): R_f = 0.40. IR (neat): $\tilde{\nu}$ = 3119, 3058, 2956, 2904, 1674, 1438, 1330, 1216, 1137, 1008, 920, 812, 743, 700, 605 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.70 (d, J = 7.5 Hz, 2 H, Ar), 7.47–7.41 (m, 3 H, Ar), 7.37–7.30 (m, 1 H, furan), 6.94 (s, 1 H, furan), 6.36 (br. s, 1 H, furan), 6.16 (d, J = 3.3 Hz, 1 H, furan), 3.79–3.70 (m, 1 H, CH_2CHCH_2), 3.43–3.53 (m, 1 H, CH_2CHCH_2), 3.26–3.17 (m, 1 H, CH_2CHCH_2), 2.97–2.77 (m, 2 H, CH_2CHCH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.37, 164.90, 155.41, 154.74, 141.70, 129.60, 128.77, 128.17, 123.96, 122.72, 110.18, 105.09, 100.77, 42.02, 34.36, 28.49 ppm. HRMS (EI^+): calcd. for $C_{18}H_{14}O_3$ 278.0943; found 278.0944.

6-(2-Furyl)-2-(4-methoxy-2-methylphenyl)-6,7-dihydrobenzofuran-4(5*H*)-one (35): Yield 71%; brown solid; TLC (1:6 EA/hexane): R_f = 0.37; m.p. 140–141 °C. IR (KBr): $\tilde{\nu}$ = 3122, 2938, 2853, 1671, 1604, 1495, 1448, 1294, 1244, 1207, 1137, 1051, 803, 741, 631 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.4 Hz, 1 H, Ar), 7.34 (br. s, 1 H, Ar), 6.79–6.77 (m, 2 H, Ar), 6.65 (s, 1 H, furan), 6.30 (br. s, 1 H, furan), 6.10 (d, J = 2.7 Hz, 1 H, furan), 3.81 (s, 3 H, Ar-OCH_3), 3.73–3.64 (m, 1 H, CH_2CHCH_2), 3.36–3.28 (m, 1 H, CH_2CHCH_2), 3.18–3.09 (m, 1 H, CH_2CHCH_2), 2.91–2.71 (m, 2 H, CH_2CHCH_2), 2.43 (s, 3 H, Ar-CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.59, 164.19, 159.39, 155.56, 154.29, 141.69, 136.84, 128.61, 122.56, 121.91, 116.50, 110.19, 105.03, 103.04, 55.23, 42.07, 34.46, 28.48, 21.97 ppm. HRMS (EI^+): calcd. for $C_{20}H_{18}O_4$ 322.1205; found 322.1206.

6-(2-Furyl)-2-(1-naphthyl)-6,7-dihydrobenzofuran-4(5*H*)-one (36): Yield 70%; brown liquid; TLC (1:6 EA/hexane): R_f = 0.36. IR (neat): $\tilde{\nu}$ = 3123, 3054, 2960, 2907, 1677, 1590, 1442, 1220, 1131, 1019, 790, 740 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.32 (d, J = 8.7 Hz, 1 H, Ar), 7.89 (d, J = 6.9 Hz, 1 H, Ar), 7.87 (d, J = 8.1 Hz, 1 H, Ar), 7.74 (d, J = 6.6 Hz, 1 H, Ar), 7.54–7.48 (m, 3 H, Ar), 7.37 (br. s, 1 H, furan), 7.00 (s, 1 H, furan), 6.32 (br. s, 1 H, furan), 6.14 (d, J = 3.0 Hz, 1 H, furan), 3.80–3.70 (m, 1 H, CH_2CHCH_2), 3.44–3.37 (m, 1 H, CH_2CHCH_2), 3.27–3.18 (m, 1 H, CH_2CHCH_2), 2.98–2.77 (m, 2 H, CH_2CHCH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.55, 165.23, 155.45, 154.03, 141.76, 133.85, 130.14, 129.37, 128.64, 127.17, 126.91, 126.51, 126.15, 125.19, 124.99, 122.61, 110.22, 105.31, 105.12, 42.13, 34.48, 28.62 ppm. HRMS (EI^+): calcd. for $C_{22}H_{16}O_3$ 328.1099; found 328.1096.

2-Phenyl-4*H*-indeno[1,2-*b*]furan-4-one (37):[10e] Yield 77%; red solid; TLC (1:6 EA/hexane): R_f = 0.60; m.p. 153–154 °C. IR (KBr): $\tilde{\nu}$ = 3111, 3059, 2926, 1712, 1610, 1466, 1413, 1269, 1177, 909, 871,

755, 719 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46 (d, J = 7.5 Hz, 2 H, Ar), 7.25–7.21 (m, 3 H, Ar), 7.15 (d, J = 7.2 Hz, 1 H, Ar), 7.10 (dd, J = 8.4, 7.2 Hz, 1 H, Ar), 6.97 (dd, J = 7.5, 7.2 Hz, 1 H, Ar), 6.91 (d, J = 6.9 Hz, 1 H, Ar), 6.47 (s, 1 H, furan) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 184.96, 174.07, 160.07, 138.10, 133.79, 132.82, 129.54, 128.83, 128.63, 128.08, 125.03, 123.55, 123.44, 116.82, 100.92 ppm. HRMS (EI$^+$): calcd. for $C_{17}H_{10}O_2$ 246.0681; found 246.0681.

Ethyl 6,6-Dimethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran-2-carboxylate (38):[16] Yield 55%; yellow liquid; TLC (1:6 EA/hexane): R_f = 0.40. IR (neat): $\tilde{\nu}$ = 3131, 2962, 1725, 1690, 1593, 1545, 1451, 1372, 1285, 1220, 1152, 1027, 859, 762 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.33 (s, 1 H, furan), 4.32 (q, J = 7.2 Hz, 2 H, OCH_2CH$_3$), 2.78 (s, 2 H, CH_2), 2.36 (s, 2 H, CH_2), 1.33 (t, J = 7.2 Hz, 3 H, OCH$_2CH_3$), 1.10 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.11, 168.75, 158.36, 144.94, 121.22, 113.60, 61.32, 51.90, 37.40, 35.11, 28.40, 14.20 ppm. HRMS: calcd. for $C_{13}H_{16}O_4$ 236.1049; found 236.1046.

Methyl 6,6-Dimethyl-4-oxo-4,5,6,7-tetrahydrobenzofuran-2-carboxylate (39):[16] Yield 54%; yellow liquid; TLC (1:6 EA/hexane): R_f = 0.38. IR (neat): $\tilde{\nu}$ = 2958, 1730, 1687, 1593, 1545, 1447, 1288, 1219, 1150, 1032, 762 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (s, 1 H, furan), 3.89 (s, 3 H, OCH_3), 2.80 (s, 2 H, CH_2), 2.39 (s, 2 H, CH_2), 1.13 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.18, 168.91, 158.83, 144.68, 121.32, 113.89, 52.28, 51.96, 37.46, 35.18, 28.47 ppm. HRMS: calcd. for $C_{12}H_{14}O_4$ 222.0892; found 222.0893.

2-Acetyl-6,6-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one (40):[16] Yield 48%; white solid; TLC (1:6 EA/hexane): R_f = 0.35; m.p. 80–81 °C. IR (KBr): $\tilde{\nu}$ = 3110, 2956, 1673, 1581, 1525, 1451, 1281, 1222, 1134, 1085, 1038, 964 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (s, 1 H, furan), 2.78 (s, 2 H, CH_2), 2.42 (s, 3 H, $COCH_3$), 2.39 (s, 2 H, CH_2), 1.11 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.28, 186.22, 169.38, 152.20, 121.36, 113.75, 51.88, 37.40, 35.10, 28.41, 28.26, 26.80 ppm. HRMS (EI$^+$): calcd. for $C_{12}H_{14}O_3$ 206.0943; found 206.0941.

Ethyl 4-Oxo-4,5,6,7-tetrahydrobenzofuran-2-carboxylate (41):[16] Yield 52%; white solid; TLC (1:6 EA/hexane): R_f = 0.35; m.p. 54–55 °C. IR (KBr): $\tilde{\nu}$ = 3003, 2978, 2938, 1713, 1689, 1592, 1544, 1441, 1372, 1306, 1208, 1187, 1148, 1018, 1001, 892 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (s, 1 H, furan), 4.34 (q, J = 7.2 Hz, 2 H, OCH_2CH$_3$), 2.94 (dd, J = 6.3, 6.0 Hz, 2 H, CH$_2$CH$_2CH_2$), 2.51 (dd, J = 6.9, 6.0 Hz, 2 H, CH_2CH$_2$CH$_2$), 2.23–2.14 (m, 2 H, CH$_2CH_2$CH$_2$), 1.34 (t, J = 7.2 Hz, 3 H, OCH$_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.70, 169.56, 158.43, 144.63, 122.41, 113.77, 61.39, 37.61, 23.56, 22.17, 14.24 ppm. HRMS (EI$^+$): calcd. for $C_{11}H_{12}O_4$ 208.0736; found 208.0738.

Methyl 4-Oxo-4,5,6,7-tetrahydrobenzofuran-2-carboxylate (42):[16] Yield 50%; white solid; TLC (1:6 EA/hexane): R_f = 0.30; m.p. 67–68 °C. IR (KBr): $\tilde{\nu}$ = 3130, 2954, 1728, 1687, 1591, 1545, 1438, 1297, 1213, 1145, 1004, 763, 727 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (s, 1 H, furan), 3.87 (s, 3 H, OCH_3), 2.93 (t, J = 6.3 Hz, 2 H, CH$_2$CH$_2CH_2$), 2.51 (dd, J = 6.9, 6.0 Hz, 2 H, CH_2CH$_2$CH$_2$), 2.22–2.15 (m, 2 H, CH$_2CH_2$CH$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.68, 169.65, 158.78, 144.26, 122.40, 113.94, 52.24, 37.57, 23.51, 22.11 ppm. HRMS: calcd. for $C_{10}H_{10}O_4$ 194.0579; found 194.0577.

2-Acetyl-6,7-dihydrobenzofuran-4(5*H*)-one (43):[16] Yield 45%; yellow solid; TLC (1:6 EA/hexane): R_f = 0.28; m.p. 54–55 °C. IR (KBr): $\tilde{\nu}$ = 3123, 2956, 1647, 1583, 1531, 1450, 1359, 1300, 1215, 1141, 1081, 1006, 969, 732, 695, 625 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 (s, 1 H, furan), 2.91 (dd, J = 6.3, 6.0 Hz, 2 H, CH$_2$CH$_2CH_2$), 2.48 (dd, J = 6.9, 6.0 Hz, 2 H, CH_2CH$_2$CH$_2$), 2.39 (s, 3 H, $COCH_3$), 2.20–2.12 (m, 2 H, CH$_2CH_2$CH$_2$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.69, 186.21, 170.07, 151.73, 122.42, 113.72, 37.48, 25.85, 23.45, 21.98 ppm. HRMS: calcd. for $C_{10}H_{10}O_3$ 178.0630; found 178.0633.

Ethyl 4-Oxo-6-phenyl-4,5,6,7-tetrahydrobenzofuran-2-carboxylate (44):[16] Yield 48%; yellow solid; TLC (1:6 EA/hexane): R_f = 0.40; m.p. 72–73 °C. IR (KBr): $\tilde{\nu}$ = 3030, 2982, 1725, 1687, 1592, 1544, 1450, 1285, 1215, 1145, 1029, 857, 763, 700 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35 (s, 1 H, furan), 7.33–7.28 (m, 2 H, Ar), 7.25–7.20 (m, 3 H, Ar), 4.31 (q, J = 7.2 Hz, 2 H, OCH_2CH$_3$), 3.57–3.47 (m, 1 H, CH$_2CH$CH$_2$), 3.45–3.01 (m, 2 H, CH$_2$CHCH_2), 2.74 (d, J = 8.4 Hz, 2 H, CH_2CHCH$_2$), 1.31 (t, J = 7.2 Hz, 3 H, OCH$_2CH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.27, 168.62, 158.32, 145.05, 141.70, 128.93, 127.41, 126.66, 122.25, 113.65, 61.43, 44.91, 40.78, 31.24, 14.21 ppm. HRMS: calcd. for $C_{17}H_{16}O_4$ 284.1049; found 284.1050.

2-Acetyl-6-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (45):[16] Yield 42%; yellow solid; TLC (1:6 EA/hexane): R_f = 0.35; m.p. 134–135 °C. IR (KBr): $\tilde{\nu}$ = 3125, 3060, 2956, 2917, 1680, 1585, 1531, 1449, 1363, 1277, 1217, 1137, 1031, 965, 852, 762, 736, 701, 649 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (s, 1 H, furan), 7.32–7.27 (m, 2 H, Ar), 7.23–7.19 (m, 3 H, Ar), 3.57–3.46 (m, 1 H, CH$_2CH$CH$_2$), 3.24–3.10 (m, 2 H, CH$_2$CHCH_2), 2.73 (d, J = 8.4 Hz, 2 H, CH_2CHCH$_2$), 2.40 (s, 3 H, $COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.35, 186.25, 152.19, 147.25, 141.54, 128.90, 127.40, 126.60, 122.32, 113.65, 44.84, 40.65, 31.20, 25.92 ppm. HRMS: calcd. for $C_{16}H_{14}O_3$ 254.0943; found 254.0943.

1,1-Diacetyl-2-phenylcycloprop-2-ene (46): Yield 10%; yellow liquid; TLC (1:6 EA/hexane): R_f = 0.25. IR (neat): $\tilde{\nu}$ = 3140, 3062, 3003, 2925, 1765, 1689, 1610, 1489, 1418, 1358, 1262, 1210, 1025, 765, 699 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46–7.43 (m, 2 H, Ar), 7.35–7.30 (m, 3 H, Ar), 6.92 (s, 1 H, cyclopropene), 2.11 (s, 6 H, 2 $COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 207.18, 130.61, 129.95, 128.92, 123.63, 113.87, 96.95, 47.67, 28.31 ppm. HRMS (EI$^+$): calcd. for $C_{13}H_{12}O_2$ 200.0837; found 200.0839.

3-Acetyl-2-methyl-5-phenylfuran (47):[10f,24c,24j] Yield 31%; yellow liquid; TLC (1:6 EA/hexane): R_f = 0.55. IR (neat): $\tilde{\nu}$ = 3059, 3004, 2923, 2854, 1673, 1609, 1555, 1489, 1406, 1358, 1235, 1159, 1071, 1026, 950, 762, 693, 632 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, J = 7.5 Hz, 2 H, Ar), 7.34–7.29 (m, 2 H, Ar), 7.20 (dd, J = 7.0, 6.0 Hz, 1 H, Ar), 6.76 (s, 1 H, furan), 2.58 (s, 3 H, $COCH_3$), 2.37 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.15, 157.90, 151.61, 129.85, 128.72, 127.72, 123.62, 123.17, 105.03, 29.13, 14.50 ppm. HRMS (EI$^+$): calcd. for $C_{13}H_{12}O_2$ 200.0837; found 200.0838.

Methyl 1-Acetyl-2-phenylcycloprop-2-ene-1-carboxylate (48):[24k] Yield 10%; yellow liquid; TLC (1:6 EA/hexane): R_f = 0.22. IR (neat): $\tilde{\nu}$ = 3144, 3060, 3004, 2953, 2845, 1731, 1614, 1443, 1358, 1272, 1045, 979, 764, 702 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.40 (m, 2 H, Ar), 7.27–7.24 (m, 3 H, Ar), 6.82 (s, 1 H, furan), 3.52 (s, 3 H, CO_2CH_3), 2.05 (s, 3 H, $COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.58, 171.32, 130.30, 129.83, 128.63, 123.55, 112.65, 95.99, 51.67, 40.13, 27.44 ppm. HRMS: calcd. for $C_{13}H_{12}O_3$ 216.0786; found 216.0788.

Methyl 2-Methyl-5-phenylfuran-3-carboxylate (49):[24k] Yield 29%; yellow liquid; TLC (1:6 EA/hexane): R_f = 0.60. IR (neat): $\tilde{\nu}$ = 3135, 3065, 2951, 1854, 1719, 1611, 1444, 1237, 1098, 1046, 762, 661 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, J = 7.2 Hz, 2 H, Ar), 7.30 (t, J = 7.5 Hz, 2 H, Ar), 7.19 (dd, J = 7.5, 7.2 Hz, 1

H, Ar), 6.80 (s, 1 H, furan), 3.77 (s, 3 H, CO_2CH_3), 2.57 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.48, 158.75, 151.77, 130.02, 128.71, 127.64, 123.62, 115.10, 105.39, 51.37, 13.87 ppm. HRMS: calcd. for $C_{13}H_{12}O_3$ 216.0786; found 216.0788.

Allyl 1-Acetyl-2-phenylcycloprop-2-ene-1-carboxylate (50): Yield 7%; yellow liquid; TLC (1:6 EA/hexane): R_f = 0.23. IR (neat): $\tilde{\nu}$ = 3141, 3077, 2944, 1729, 1650, 1447, 1417, 1361, 1233, 1097, 1041, 991, 934, 765, 698 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.48 (m, 2 H, Ar), 7.36–7.33 (m, 3 H, Ar), 6.86 (s, 1 H, cyclopropene), 5.88–5.71 (m, 1 H, $OCH_2CH{=}CH_2$), 5.20–5.06 (m, 2 H, $OCH_2CH{=}CH_2$), 4.55–4.53 (m, 2 H, CH_2, $OCH_2CH{=}CH_2$), 2.15 (s, 3 H, $COCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 205.76, 170.77, 131.70, 130.52, 130.09, 128.82, 123.76, 117.86, 112.97, 95.99, 65.31, 40.51, 27.83 ppm. HRMS: calcd. for $C_{15}H_{14}O_3$ 242.0943; found 242.0944.

Allyl 2-Methyl-5-phenylfuran-3-carboxylate (51): Yield 25%; yellow liquid; TLC (1:6 EA/hexane): R_f = 0.58. IR (neat): $\tilde{\nu}$ = 3133, 3083, 2931, 1717, 1610, 1410, 1232, 1094, 1042, 928, 762, 691, 662 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, J = 7.5 Hz, 2 H, Ar), 7.31 (dd, J = 7.8, 7.2 Hz, 2 H, Ar), 7.19 (dd, J = 7.5, 7.2 Hz, 1 H, Ar), 6.82 (s, 1 H, furan), 6.02–5.89 (m, 1 H, $OCH_2CH{=}CH_2$), 5.32 (dd, J = 17.4, 1.5 Hz, 1 H, $OCH_2CH{=}CH_{2a}$), 5.21 (dd, J = 10.5, 1.2 Hz, 1 H, $OCH_2CH{=}CH_{2b}$), 4.69 (d, J = 5.7 Hz, 2 H, $OCH_2CH{=}CH_2$), 2.58 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.66, 158.90, 151.78, 132.37, 129.99, 128.70, 127.64, 123.63, 118.10, 115.08, 105.41, 64.86, 13.95 ppm. HRMS: calcd. for $C_{15}H_{14}O_3$ 242.0943; found 242.0942.

6,6-Dimethyl-2-phenyl-1,2,3,6-tetrahydrobenzofuran-4(5*H*)-one (52):[12] Yield 7%.

6,6-Dimethyl-2-(prop-1-en-2-yl)-6,7-dihydrobenzofuran-4(5*H*)-one (53):[16] Yield 45%; yellow liquid; TLC (1:6 EA/hexane): R_f = 0.45. IR (neat): $\tilde{\nu}$ = 3118, 2949, 2892, 1676, 1445, 1379, 1219, 1122, 1034, 894, 820, 647 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.48 (s, 1 H, furan), 5.49 (s, 1 H, $CH_{2a}{=}CCH_3$), 4.99 (s, 1 H, $CH_{2b}{=}CCH_3$), 2.73 (s, 2 H, CH_2), 2.34 (s, 2 H, CH_2), 1.97 (s, 3 H, $CH_2{=}CCH_3$), 1.12 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.94, 165.99, 155.46, 132.10, 121.25, 111.08, 102.10, 51.90, 37.37, 35.22, 25.59, 19.15 ppm. HRMS (EI^+): calcd. for $C_{13}H_{16}O_2$ 204.1150; found 204.1149.

2-(Prop-1-en-2-yl)-6,7-dihydrobenzofuran-4(5*H*)-one (55):[16] Yield 42%; yellow liquid; TLC (1:6 EA/hexane): R_f = 0.30. IR (neat): $\tilde{\nu}$ = 3118, 2948, 2887, 1675, 1447, 1365, 1215, 1182, 1132, 1004, 891, 820, 726, 695, 620 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 6.46 (s, 1 H, furan), 5.47 (s, 1 H, $CH_{2a}{=}CCH_3$), 4.98 (s, 1 H, $CH_{2b}{=}CCH_3$), 2.85 (t, J = 6.3 Hz, 2 H, $CH_2CH_2CH_2$), 2.45 (dd, J = 7.2, 6.0 Hz, 2 H, $CH_2CH_2CH_2$), 2.18–2.09 (m, 2 H, $CH_2CH_2CH_2$), 1.95 (s, 3 H, $CH_2{=}CCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 194.47, 166.80, 155.08, 131.98, 122.42, 111.13, 102.11, 37.47, 23.31, 22.45, 19.09 ppm. HRMS: calcd. for $C_{11}H_{12}O_2$ 176.0837; found 176.0839.

6-Phenyl-2-(prop-1-en-2-yl)-6,7-dihydrobenzofuran-4(5*H*)-one (57): Yield 38%; yellow liquid; TLC (1:6 EA/hexane): R_f = 0.40. IR (neat): $\tilde{\nu}$ = 3056, 3031, 2943, 1735, 1673, 1447, 1218, 1128, 1033, 946, 895, 811, 736, 701 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.28–7.26 (m, 2 H, Ar), 7.22–7.20 (m, 3 H, Ar), 6.47 (s, 1 H, furan), 5.46 (s, 1 H, $CH_{2a}{=}CCH_3$), 4.96 (s, 1 H, $CH_{2b}{=}CCH_3$), 3.48–3.43 (m, 1 H, CH_2CHCH_2), 3.11 (dd, J = 17.1, 5.1 Hz, 1 H, CH_2CHCH_{2a}), 2.98 (dd, J = 17.1, 10.8 Hz, 1 H, CH_2CHCH_{2b}), 2.68 (d, J = 8.4 Hz, 2 H, CH_2CHCH_2), 1.93 (s, 3 H, $CH_2{=}CCH_3$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 192.93, 165.86, 155.60, 142.34, 131.96, 128.81, 127.17, 126.69, 122.32, 111.40, 102.10, 44.78, 41.11, 31.13, 19.11 ppm. HRMS: calcd. for $C_{17}H_{16}O_2$ 252.1150; found 252.1154.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra for compounds **3**–**13**, **15**–**51**, **53**, **55**, and **57**.

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[1] a) M. P. Doyle, M. A. McKervey, T. Ye, *Modern Catalytic Methods for Organic Synthesis with Diazo Compounds*, Wiley, New York, **1998**; b) H. M. L. Davies, J. R. Manning, *Nature* **2008**, *451*, 417–424; c) M. Ge, E. J. Corey, *Tetrahedron Lett.* **2006**, *47*, 2319–2321; d) T. C. Maier, G. C. Fu, *J. Am. Chem. Soc.* **2006**, *128*, 4594–4595; e) B. Liu, S.-F. Zhu, W. Zhang, C. Chen, Q.-L. Zhou, *J. Am. Chem. Soc.* **2007**, *129*, 5834–5835; f) E. C. Lee, G. C. Fu, *J. Am. Chem. Soc.* **2007**, *129*, 12066–12067; g) C. Chen, S.-F. Zhu, B. Liu, L.-X. Wang, Q.-L. Zhou, *J. Am. Chem. Soc.* **2007**, *129*, 12616–12617; h) S.-F. Zhu, C. Chen, Y. Cai, Q.-L. Zhou, *Angew. Chem. Int. Ed.* **2008**, *47*, 932–934; *Angew. Chem.* **2008**, *120*, 946–948.

[2] a) F. M. Dean, in: *Advances in Heterocyclic Chemistry* (Ed.: A. R. Katritzky), Academic Press, New York, **1982**, vol. 30, p. 167–238; b) F. M. Dean, M. V. Sargent, in: *Comprehensive Heterocyclic Chemistry*, vol. 4, part 3 (Eds.: C. W. Bird, G. W. H. Cheeseman), Pergamon Press, New York, **1984**, p. 531–598; c) B. H. Lipshutz, *Chem. Rev.* **1986**, *86*, 795–819.

[3] a) T. Xu, G. Dong, *Angew. Chem. Int. Ed.* **2012**, *51*, 7567–7571; *Angew. Chem.* **2012**, *124*, 7685–7689; b) P. Prasanna, K. Balamurugan, S. Perumal, J. C. Menéndez, *Green Chem.* **2011**, *13*, 2123–2129; c) Y. Liu, H. K. Jacobs, A. S. Gopalan, *Tetrahedron Lett.* **2011**, *52*, 2935–2939; d) J. Hu, L. Liu, X. Wang, Y. Hu, S. Yang, Y. Liang, *Green Sustainable Chem.* **2011**, *1*, 165–169; e) H. Jiang, W. Yao, H. Cao, H. Huang, D. Cao, *J. Org. Chem.* **2010**, *75*, 5347–5350; f) S. Samanta, R. Jana, J. K. Ray, *Tetrahedron Lett.* **2009**, *50*, 6751–6754; g) P. Jakubec, D. M. Cockfield, D. J. Dixon, *J. Am. Chem. Soc.* **2009**, *131*, 16632–16633; h) J. A. Ragan, J. A. Murry, M. J. Castaldi, A. K. Conrad, B. P. Jones, B. Li, T. W. Makowski, R. McDermott, B. J. Sitter, T. D. White, G. R. Young, *Org. Process Res. Dev.* **2001**, *5*, 498–507; i) D. Schinzer, G. Panke, *J. Org. Chem.* **1996**, *61*, 4496–4497; j) R. L. Danheiser, E. J. Stoner, H. Koyama, D. S. Yamashita, C. A. Klade, *J. Am. Chem. Soc.* **1989**, *111*, 4407–4413.

[4] a) L. Xia, Y. R. Lee, *Org. Biomol. Chem.* **2013**, *11*, 6097–6107; b) K. Fuchibe, Y. Aoki, T. Akiyama, *Chem. Lett.* **2005**, *34*, 538–539; c) W.-L. Lin, B. P. Taduri, R.-S. Liu, *Synthesis* **2002**, 2457–2463; d) I. Nakamura, B. H. Oh, S. Saito, Y. Yamamoto, *Angew. Chem. Int. Ed.* **2001**, *40*, 1298–1300; *Angew. Chem.* **2001**, *113*, 1338–1340; e) C.-R. Liu, B.-H. Zhu, J.-C. Zheng, X.-L. Sun, Z. Xie, Y. Tang, *Chem. Commun.* **2011**, *47*, 1342–1344; f) S. R. Mothe, D. Susanti, P. W. H. Chan, *Tetrahedron Lett.* **2010**, *51*, 2136–2140; g) J.-C. Zheng, C.-Y. Zhu, X.-L. Sun, Y. Tang, L.-X. Dai, *J. Org. Chem.* **2008**, *73*, 6909–6912; h) G.-W. Wang, Y.-W. Dong, P. Wu, T.-T. Yuan, Y.-B. Shen, *J. Org. Chem.* **2008**, *73*, 7088–7095; i) G. Savitha, R. Sudhakar, P. T. Perumal, *Tetrahedron Lett.* **2008**, *49*, 7260–7263; j) X.-C. Huang, Y.-L. Liu, Y. Liang, S.-F. Pi, F. Wang, J.-H. Li, *Org. Lett.* **2008**, *10*, 1525–1528; k) G. Savitha, S. K. Niveditha, D. Muralidharan, P. T. Perumal, *Tetrahedron Lett.* **2007**, *48*, 2943–2947; l) V. Cadierno, J. Gimeno, N. Nebra, *Adv. Synth. Catal.* **2007**, *349*, 382–394; m) W. Chen, X. Huang, H. Zhou, L. Ren, *Synthesis* **2006**, 609–614; n) A.-I. Tsai, C.-H. Lin, C.-P. Chuang, *Heterocycles* **2005**, *65*, 2381–2394; o) W. Zhang, C. D. Huo, Z. G. Liu, Z. L. Liu, *Chin. Chem. Lett.* **2004**, *15*, 389–391; p) D. Nematollahi, D. Habibi, M. Rahmati, M. Rafiee, *J.*

Org. Chem. **2004**, *69*, 2637–2640; q) C. Li, D. Zhang, X. Zhang, S. Wu, X. Gao, *Org. Biomol. Chem.* **2004**, *2*, 3464–3469.

[5] a) B. Gabriele, R. Mancuso, V. Maltese, L. Veltri, G. Salerno, *J. Org. Chem.* **2012**, *77*, 8657–8668; b) C.-H. Cho, R. C. Larock, *ACS Comb. Sci.* **2011**, *13*, 272–279; c) J.-R. Wang, K. Manabe, *J. Org. Chem.* **2010**, *75*, 5340–5342; d) Z. Gu, X. Wang, W. Shu, S. Ma, *J. Am. Chem. Soc.* **2007**, *129*, 10948–10956; e) M. C. Willis, D. Taylor, A. T. Gillmore, *Org. Lett.* **2004**, *6*, 4755–4757; f) Y. Liao, M. Reitman, Y. Zhang, R. Fathi, Z. Yang, *Org. Lett.* **2002**, *4*, 2607–2609; g) Y. Hu, Z. Yang, *Org. Lett.* **2001**, *3*, 1387–1390; h) B. Gabriele, G. Salerno, F. De Pascali, M. Costa, G. P. Chiusoli, *J. Org. Chem.* **1999**, *64*, 7693–7699; i) Y. Fukuda, H. Shiragami, K. Utimoto, H. Nozaki, *J. Org. Chem.* **1991**, *56*, 5816–5819; j) S. Cacchi, G. Fabrizi, A. Goggiamani, *Curr. Org. Chem.* **2006**, *10*, 1423–1455; k) Y. Hu, Z. Yang, *Org. Lett.* **2001**, *3*, 1387–1390.

[6] a) J. Li, L. Liu, D. Ding, J. Sun, Y. Ji, J. Dong, *Org. Lett.* **2013**, *15*, 2884–2887; b) M. Hoffmann, S. Miaskiewicz, J.-M. Weibel, P. Pale, A. Blanc, *Beilstein J. Org. Chem.* **2013**, *9*, 1774–1780; c) A. Rodríguez, W. J. Moran, *Tetrahedron Lett.* **2011**, *52*, 2605–2607; d) A. S. K. Hashmi, W. Yang, F. Rominger, *Angew. Chem. Int. Ed.* **2011**, *50*, 5762–5765; *Angew. Chem.* **2011**, *123*, 5882–5885; e) A. S. K. Hashmi, T. Häffner, M. Rudolph, F. Rominger, *Eur. J. Org. Chem.* **2011**, 667–671; f) Y. Li, K. A. Wheeler, R. Dembinski, *Adv. Synth. Catal.* **2010**, *352*, 2761–2766; g) C. Praveen, P. Kiruthiga, P. T. Perumal, *Synlett* **2009**, 1990–1996; h) Y. Chen, Y. Lu, G. Li, Y. Liu, *Org. Lett.* **2009**, *11*, 3838–3841; i) A. Aponick, C.-Y. Li, J. Malinge, E. F. Marques, *Org. Lett.* **2009**, *11*, 4624–4627; j) C. H. Oh, S. J. Lee, J. H. Lee, Y. J. Na, *Chem. Commun.* **2008**, 5794–5796; k) C.-Y. Zhou, P. W. H. Chan, C.-M. Che, *Org. Lett.* **2006**, *8*, 325–328; l) J. Zhang, H.-G. Schmalz, *Angew. Chem. Int. Ed.* **2006**, *45*, 6704–6707; *Angew. Chem.* **2006**, *118*, 6856–6859; m) A. S. K. Hashmi, M. Wölfle, F. Ata, M. Hamzic, R. Salathé, W. Frey, *Adv. Synth. Catal.* **2006**, *348*, 2501–2508; n) A. W. Sromek, M. Rubina, V. Gevorgyan, *J. Am. Chem. Soc.* **2005**, *127*, 10500–10501; o) S. S. Sohn, J. W. Bode, *Org. Lett.* **2005**, *7*, 3873–3876; p) A. S. K. Hashmi, P. Sinha, *Adv. Synth. Catal.* **2004**, *346*, 432–438.

[7] a) W.-L. Chen, J. Li, Y.-H. Zhu, L.-T. Ye, W. Hu, W.-M. Mo, *ARKIVOC* **2011**, *ix*, 381–392; b) H. Cao, H. Jiang, H. Huang, *Synthesis* **2011**, 1019–1036; c) A. Blanc, K. Tenbrink, J.-M. Weibel, P. Pale, *J. Org. Chem.* **2009**, *74*, 4360–4363; d) S. Kim, P. H. Lee, *Adv. Synth. Catal.* **2008**, *350*, 547–551; e) S. J. Hayes, D. W. Knight, M. D. Menzies, M. O'Halloran, W.-F. Tan, *Tetrahedron Lett.* **2007**, *48*, 7709–7712; f) S. Arimitsu, G. B. Hammond, *J. Org. Chem.* **2007**, *72*, 8559–8561; g) J. A. Marshall, C. A. Sehon, *J. Org. Chem.* **1995**, *60*, 5966–5968; h) W. W. Crew, R. J. Madix, *J. Am. Chem. Soc.* **1993**, *115*, 729–736; i) J. A. Marshall, X. J. Wang, *J. Org. Chem.* **1991**, *56*, 960–969.

[8] a) H. Yu, W. Zhong, T. He, W. Gu, B. Yin, *Tetrahedron Lett.* **2013**, *54*, 1256–1260; b) H. Cao, H. Zhan, J. Cen, J. Lin, Y. Lin, Q. Zhu, M. Fu, H. Jiang, *Org. Lett.* **2013**, *15*, 1080–1083; c) B. Yin, H. Yu, Z. Li, W. Zhong, W. Gu, *Synthesis* **2012**, *44*, 3735–3742; d) H. Cao, H.-F. Jiang, X.-S. Zhou, C.-R. Qi, Y.-G. Lin, J.-Y. Wu, Q.-M. Liang, *Green Chem.* **2012**, *14*, 2710–2714; e) T. Wang, J. Liu, Z. Lv, H. Zhong, H. Chen, C. Niu, K. Li, *Tetrahedron* **2011**, *67*, 3476–3482; f) S. Cacchi, G. Fabrizi, A. Goggiamani, *Org. Biomol. Chem.* **2011**, *9*, 641–652; g) W. Liu, H. Jiang, M. Zhang, C. Qi, *J. Org. Chem.* **2010**, *75*, 966–968; h) H. Cao, H. Jiang, W. Yao, X. Liu, *Org. Lett.* **2009**, *11*, 1931–1933; i) J. Barluenga, L. Riesgo, R. Vicente, L. A. López, M. Tomás, *J. Am. Chem. Soc.* **2008**, *130*, 13528–13529; j) M. Carril, R. SanMartin, I. Tellitu, E. Domínguez, *Org. Lett.* **2006**, *8*, 1467–1470; k) C.-Y. Chen, P. G. Dormer, *J. Org. Chem.* **2005**, *70*, 6964–6967; l) J. T. Kim, A. V. Kel′in, V. Gevorgyan, *Angew. Chem. Int. Ed.* **2003**, *42*, 98–101; *Angew. Chem.* **2003**, *115*, 102–105.

[9] a) S. J. Pridmore, P. A. Slatford, J. E. Taylor, M. K. Whittlesey, J. M. J. Williams, *Tetrahedron* **2009**, *65*, 8981–8986; b) T. J. Donohoe, L. P. Fishlock, A. R. Lacy, P. A. Procopiou, *Org. Lett.* **2007**, *9*, 953–956; c) Y. Nishibayashi, M. Yoshikawa, Y. Inada, M. D. Milton, M. Hidai, S. Uemura, *Angew. Chem. Int. Ed.* **2003**, *42*, 2681–2684; *Angew. Chem.* **2003**, *115*, 2785–2788; d) B. Çetinkaya, N. Gürbüz, T. Seçkin, I. Özdemir, *J. Mol. Catal. A* **2002**, *184*, 31–38; e) B. Çetinkaya, I. Özdemir, C. Bruneau, P. H. Dixneuf, *Eur. J. Inorg. Chem.* **2000**, 29–32; f) B. Çetinkaya, B. Alici, I. Özdemir, C. Bruneau, P. H. Dixneuf, *J. Organomet. Chem.* **1999**, *575*, 187–192; g) B. Seiller, C. Bruneau, P. H. Dixneuf, *J. Chem. Soc., Chem. Commun.* **1994**, 493–494.

[10] a) W. Pang, S. Zhu, Y. Xin, H. Jiang, S. Zhu, *Tetrahedron* **2010**, *66*, 1261–1266; b) P. Müller, Y. F. Allenbach, G. Bernardinelli, *Helv. Chim. Acta* **2003**, *86*, 3164–3178; c) S. Tollari, G. Palmisano, S. Cenini, G. Cravotto, G. B. Giovenzana, A. Penoni, *Synthesis* **2001**, 735–740; d) F. R. Kinder, A. Padwa, *Tetrahedron Lett.* **1990**, *31*, 6835–6838; e) M. J. Rosenfeld, B. K. R. Shankar, H. Shechter, *J. Org. Chem.* **1988**, *53*, 2699–2705; f) H. M. L. Davies, K. R. Romines, *Tetrahedron* **1988**, *44*, 3343–3348; g) A. K. Swenson, K. E. Higgins, M. G. Brewer, W. W. Brennessel, M. G. Coleman, *Org. Biomol. Chem.* **2012**, *10*, 7483–7486; h) X. Cui, X. Xu, L. Wojtas, M. M. Kim, X. P. Zhang, *J. Am. Chem. Soc.* **2012**, *134*, 19981–19984.

[11] a) M. K. B. Somai, Y. R. Lee, *Org. Lett.* **2013**, *15*, 4288–4291; b) M. K. B. Somai, Y. R. Lee, S. H. Kim, *Mol. Diversity* **2013**, *17*, 679–691; c) M. K. B. Somai, Y. R. Lee, S. H. Kim, *Tetrahedron* **2013**, *69*, 9294–9302; d) X. Wang, Y. R. Lee, *Bull. Korean Chem. Soc.* **2013**, *34*, 1735–1740; e) P. Neupane, X. Li, J. H. Jung, Y. R. Lee, S. H. Kim, *Tetrahedron* **2012**, *68*, 2496–2508; f) K. B. S. Magar, Y. R. Lee, *Bull. Korean Chem. Soc.* **2012**, *33*, 4150–4154; g) L. Xia, Y. R. Lee, S. H. Kim, W. S. Lyoo, *Bull. Korean Chem. Soc.* **2011**, *32*, 1554–1558; h) Y. R. Lee, J. C. Hwang, *Eur. J. Org. Chem.* **2005**, 1568–1577; i) Y. R. Lee, B. S. Cho, H. J. Kwon, *Tetrahedron* **2003**, *59*, 9333–9347; j) Y. R. Lee, J. Y. Suk, *Tetrahedron* **2002**, *58*, 2359–2367; k) Y. R. Lee, J. Y. Suk, *Chem. Commun.* **1998**, 2621–2622; l) Y. R. Lee, *Synth. Commun.* **1998**, *28*, 865–869; m) M. C. Pirrung, Y. R. Lee, *J. Chem. Soc., Chem. Commun.* **1995**, 673–674; n) M. C. Pirrung, Y. R. Lee, *J. Am. Chem. Soc.* **1995**, *117*, 4814–4821.

[12] L. Xia, Y. R. Lee, *Adv. Synth. Catal.* **2013**, *355*, 2361–2374.

[13] a) P. R. Krishna, Y. L. Prapurna, M. Alivelu, *Tetrahedron Lett.* **2011**, *52*, 3460–3462; b) P. R. Krishna, E. R. Sekhar, F. Mongin, *Tetrahedron Lett.* **2008**, *49*, 6768–6772; c) N. Jiang, C.-J. Li, *Chem. Commun.* **2004**, 394–395; d) S. Sengupta, S. Mondal, *Tetrahedron Lett.* **2000**, *41*, 6245–6248; e) S. Sengupta, S. Mondal, *Tetrahedron Lett.* **1999**, *40*, 8685–8688.

[14] a) D. Ghosh, J. Lo, D. Morton, D. Valette, J. Xi, J. Griswold, S. Hubbell, C. Egbuta, W. Jiang, J. An, H. M. L. Davies, *J. Med. Chem.* **2012**, *55*, 8464–8476; b) J. H. Hansen, H. M. L. Davies, *Chem. Sci.* **2011**, *2*, 457–461; c) X. Han, L. Jiang, M. Tang, W. Hu, *Org. Biomol. Chem.* **2011**, *9*, 3839–3843; d) S.-F. Zhu, Y. Cai, H.-X. Mao, J.-H. Xie, Q.-L. Zhou, *Nat. Chem.* **2010**, *2*, 546–551; e) H. Saito, R. Iwai, T. Uchiyama, M. Miyake, S. Miyairi, *Chem. Pharm. Bull.* **2010**, *58*, 872–874; f) Y. Yue, X. Guo, Z. Chen, L. Yang, W. Hu, *Tetrahedron Lett.* **2008**, *49*, 6862–6865; g) C. Y. Im, T. Okuyama, T. Sugimura, *Eur. J. Org. Chem.* **2008**, 285–294; h) S.-F. Zhu, C. Chen, Y. Cai, Q.-L. Zhou, *Angew. Chem. Int. Ed.* **2008**, *47*, 932–934; *Angew. Chem.* **2008**, *120*, 946–948; i) T. C. Maier, G. C. Fu, *J. Am. Chem. Soc.* **2006**, *128*, 4594–4595; j) R. Paulissen, H. Reimlinger, E. Hayez, A. J. Hubert, P. Teyssié, *Tetrahedron Lett.* **1973**, *14*, 2233–2236.

[15] a) M. Presset, D. Mailhol, Y. Coquerel, J. Rodriguez, *Synthesis* **2011**, 2549–2552; b) M. Kitamura, N. Tashiro, S. Miyagawa, T. Okauchi, *Synthesis* **2011**, 1037–1044; c) M. Kitamura, N. Tashiro, R. Sakata, T. Okauchi, *Synlett* **2010**, 2503–2505; d) M. Kitamura, N. Tashiro, T. Okauchi, *Synlett* **2009**, 2943–2944; e) D. B. Ramachary, V. V. Narayana, K. Ramakumar, *Tetrahedron Lett.* **2008**, *49*, 2704–2709; f) J. C. Lee, J. Y. Yuk, *Synth. Commun.* **1995**, *25*, 1511–1515; g) J. S. Baum, D. A. Shook,

H. M. L. Davies, H. D. Smith, *Synth. Commun.* **1987**, *17*, 1709–1716; h) D. F. Taber, R. E. Ruckle Jr., M. J. Hennessy, *J. Org. Chem.* **1986**, *51*, 4077–4078.
[16] Y. R. Lee, S. H. Yoon, *Synth. Commun.* **2006**, *36*, 1941–1951.
[17] a) J. Chen, S. Ma, *Chem. Asian J.* **2010**, *5*, 2415–2421; b) S. Ma, J. Zhang, *J. Am. Chem. Soc.* **2003**, *125*, 12386–12387; c) A. Padwa, J. M. Kassir, S. L. Xu, *J. Org. Chem.* **1991**, *56*, 6971–6972.
[18] a) V. A. Nikolaev, A. V. Ivanov, A. A. Shakhmin, J. Sieler, L. L. Rodina, *Tetrahedron Lett.* **2012**, *53*, 3095–3099; b) V. V. Popik, V. A. Nikolaev, *J. Chem. Soc. Perkin Trans. 2* **1993**, 1791–1793; c) H. M. L. Davies, K. R. Romines, *Tetrahedron* **1988**, *44*, 3343–3348.
[19] a) F. M. Wong, J. Wang, A. C. Hengge, W. Wu, *Org. Lett.* **2007**, *9*, 1663–1665; b) Y. R. Lee, J. C. Hwang, *Eur. J. Org. Chem.* **2005**, 1568–1577.
[20] a) V. K.-Y. Lo, Z. Guo, M. K.-W. Choi, W.-Y. Yu, J.-S. Huang, C.-M. Che, *J. Am. Chem. Soc.* **2012**, *134*, 7588–7591; b) N. D. Koduri, H. Scott, B. Hileman, J. D. Cox, M. Coffin, L. Glicksberg, S. R. Hussaini, *Org. Lett.* **2012**, *14*, 440–443; c) F. Cambeiro, S. López, J. A. Varela, C. Saá, *Angew. Chem. Int. Ed.* **2012**, *51*, 723–727; *Angew. Chem.* **2012**, *124*, 747–751; d) M. Austeri, D. Rix, W. Zeghida, J. Lacour, *Org. Lett.* **2011**, *13*, 1394–1397.
[21] J. M. O'Connor, H. Ji, M. Iranpour, A. L. Rheingold, *J. Am. Chem. Soc.* **1993**, *115*, 1586–1588.
[22] a) J. Le Paih, S. Dérien, I. Özdemir, P. H. Dixneuf, *J. Am. Chem. Soc.* **2000**, *122*, 7400–7401; b) F. Monnier, D. Castillo, S. Dérien, L. Toupet, P. H. Dixneuf, *Angew. Chem. Int. Ed.* **2003**, *42*, 5474–5477; *Angew. Chem.* **2003**, *115*, 5632–5635; c) S. Dérien, P. H. Dixneuf, *J. Organomet. Chem.* **2004**, *689*, 1382–1392; d) M. Eckert, F. Monnier, G. T. Shchetnikov, I. D. Titanyuk, S. N. Osipov, L. Toupet, S. Dérien, P. H. Dixneuf, *Org. Lett.* **2005**, *7*, 3741–3743; e) F. Monnier, C. Vovard-Le Bray, D. Castillo, V. Aubert, S. Dérien, P. H. Dixneuf, L. Toupet, A. Ienco, C. Mealli, *J. Am. Chem. Soc.* **2007**, *129*, 6037–6049; f) C. Vovard-Le Bray, S. Dérien, P. H. Dixneuf, M. Murakami, *Synlett* **2008**, 193–196; g) J. L. Paih, C. Vovard-Le Bray, S. Dérien, P. H. Dixneuf, *J. Am. Chem. Soc.* **2010**, *132*, 7391–7397; h) C. Vovard-Le Bray, S. Dérien, P. H. Dixneuf, *C. R. Chim.* **2010**, *13*, 292–303; i) T. Braun, G. Münch, B. Windmüller, O. Gevert, M. Laubender, H. Werner, *Chem. Eur. J.* **2003**, *9*, 2516–2530.
[23] a) S. T. Diver, *Coord. Chem. Rev.* **2007**, *251*, 671–701.
[24] a) M. Zheng, L. Huang, W. Wu, H. Jiang, *Org. Lett.* **2013**, *15*, 1838–1841; b) A. Sivan, A. Deepthi, V. Nandialath, *Synthesis* **2011**, 2466–2470; c) T. Aoyama, T. Nagaoka, T. Takido, M. Kodomari, *Synthesis* **2011**, 619–625; d) M. Shekarchi, F. Ellahiyan, T. Akbarzadeh, A. Shafiee, *J. Heterocycl. Chem.* **2003**, *40*, 427–433; e) Y. Li, A. Usman, I. A. Razak, H. K. Fun, S. Chantrapromma, Y. Zhang, J. H. Xu, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2002**, *58*, o992–o993; f) T. Ogawa, T. Murafuji, K. Iwata, H. Suzuki, *Chem. Lett.* **1989**, 325–328; g) J. Yoshida, S. Yano, T. Ozawa, N. Kawabata, *J. Org. Chem.* **1985**, *50*, 3467–3473; h) O. Alagoz, M. Yilmaz, A. Tarik Pekel, *Synth. Commun.* **2006**, *36*, 1005–1013; i) Y. R. Lee, M. W. Byun, B. S. Kim, *Bull. Korean Chem. Soc.* **1998**, *19*, 1080–1083; j) C. He, S. Guo, J. Ke, J. Hao, H. Xu, H. Chen, A. Lei, *J. Am. Chem. Soc.* **2012**, *134*, 5766–5769; k) J. F. Briones, H. M. L. Davies, *Tetrahedron* **2011**, *67*, 4313–4317.

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