Tetrahedron 69 (2013) 9294–9302

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Efficient one-pot synthesis of biologically interesting diverse furo[2,3-*b*]pyran-6-ones by rhodium(II)-catalyzed cascade reactions of diazo compound with ethynyl compounds

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ARTICLE INFO

Article history:
Received 16 May 2013
Received in revised form 14 August 2013
Accepted 16 August 2013
Available online 27 August 2013

Keywords:
Cascade reaction
Diazo compound
Ethynyl compounds
Furo[2,3-*b*]pyran-6-ones
Rhodium(II) catalyst

ABSTRACT

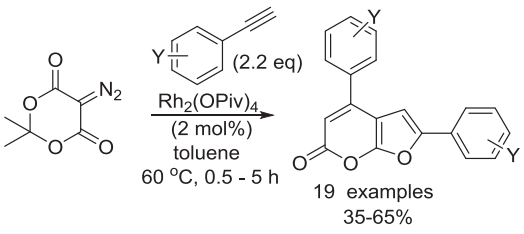
Rhodium(II)-catalyzed reactions of diazo compound and a variety of ethynyl compounds were carried out. These reactions provide a rapid route for preparing a variety of furo[2,3-*b*]pyran-6-one derivatives in one-pot via cascade reactions of metal carbenoid reaction/ketene formation/[2+2]cycloaddition/ring expansion.

1. Introduction

Furopyranone derivatives are important heterocycles that occur widely in nature.[1] These derivatives exhibit a variety of biological activities, such as, antibacterial,[2] antitumor,[3] and antiproliferative effects.[4] Because of their importance, a number of methods have been devised to synthesize furopyranone derivatives.[5] Among these, methods for synthesizing two furo[2,3-*c*]pyran-4-one compounds using multi-component reactions have been reported.[4a,6] Recently, another method of synthesizing furo[2,3-*b*]pyran-6-one derivatives using Co(III)-porphyrin catalyzed reactions of diazo compounds was developed.[7] Thus, there is still demand for a more convenient, efficient synthetic method that can efficiently provide a variety of furo[2,3-*b*]pyran-6-one derivatives.

We have been interested in the rhodium-catalyzed reactions of cyclic diazodicarbonyl compounds with several substrates. We developed a novel methodology for the synthesis of dihydrofurans, dihydrooxepins, oxindoles, oxazoles, cyclopropanes, and versatile β-substituted α-haloenones starting from cyclic diazodicarbonyl compounds.[8]

During our continuing studies on the development of a new methodology based on cyclic diazo compounds, we investigated the rhodium-catalyzed reactions of cyclic diazo compound derived from Meldrum's acid with phenylacetylene or arylacetylenes. We describe herein a general and facile method for an efficient one-pot synthesis of a variety of furo[2,3-*b*]pyran-6-one derivatives (Scheme 1).



Scheme 1.

2. Results and discussion

First, we investigated reactions between diazo compound **1** and ethynylbenzene in the presence of several metal catalysts (Table 1). When we tried reactions of **1** with 2.2 equiv of ethynylbenzene in the presence of 10 mol % of $In(OAc)_3$, $Cu(OAc)_2$, $Pd(OAc)_2$, $Co(PPh_3)_3Cl$, $Ru(PPh_3)_3Cl_2$, or $Au(PPh_3)_3Cl$ in toluene at 70 °C for 12 h, no products were produced (entries 1–6). We then examined

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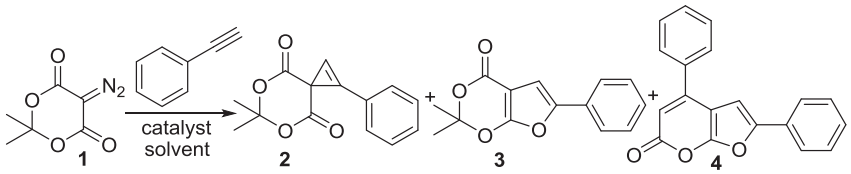
http://dx.doi.org/10.1016/j.tet.2013.08.054

Table 1
Effect of metal catalysts in the reaction of **1** with ethynylbenzene



Entry	Catalyst	Ethynylbenzene (equiv)	Solvent	Condition	Yield (%)		
					2	**3**	**4**
1	$In(OAc)_3$ (10 mol %)	2.2	Toluene	70 °C, 12 h	0	0	0
2	$Cu(OAc)_2$ (10 mol %)	2.2	Toluene	70 °C, 12 h	0	0	0
3	$Pd(OAc)_2$ (10 mol %)	2.2	Toluene	70 °C, 12 h	0	0	0
4	$Co(PPh_3)_3Cl$ (10 mol %)	2.2	Toluene	70 °C, 12 h	0	0	0
5	$Ru(PPh_3)_3Cl_2$ (10 mol %)	2.2	Toluene	70 °C, 12 h	0	0	0
6	$Au(PPh_3)_3Cl$ (10 mol %)	2.2	Toluene	70 °C, 12 h	0	0	0
7	$Rh_2(OCOCF_3)_4$ (2 mol %)	2.2	Toluene	60 °C, 12 h	0	0	10
8	$Rh_2(OAc)_4$ (2 mol %)	2.2	Toluene	60 °C, 6 h	0	0	20
9	$Rh_2(OPiv)_4$ (2 mol %)	2.2	Toluene	60 °C, 0.5 h	0	0	60
10	$Rh_2(OPiv)_4$ (2 mol %)	2.2	Toluene	80 °C, 0.5 h	0	0	35
11	$Rh_2(OPiv)_4$ (5 mol %)	2.2	Toluene	60 °C, 0.5 h	0	0	39
12	$Rh_2(OPiv)_4$ (2 mol %)	2.2	Benzene	60 °C, 0.5 h	0	0	41
13	$Rh_2(OPiv)_4$ (2 mol %)	2.2	PhF	60 °C, 0.5 h	0	0	56
14	$Rh_2(OPiv)_4$ (2 mol %)	1.0	Toluene	60 °C, 0.5 h	0	0	32

the catalytic activities of several rhodium complexes in toluene. Treatment with electron-poor rhodium trifluoroacetate (2 mol %) as a catalyst in toluene at 60 °C for 12 h produced cycloadduct **4** in only 10% yield (entry 7), whereas treatment with rhodium acetate (2 mol %) at 60 °C for 6 h afforded **4** in 20% yield (entry 8). Using electron-rich rhodium pivalate (2 mol %) in toluene at 60 °C for 0.5 h, compound **4**, intractable material, catalyst, acetone, and remaining ethynylbenzene were shown by the crude ^{1}H NMR spectrum. After column chromatography, compound **4** was obtained in 60% yield. In this reaction, other possible products of **2** and **3** were not isolated. Elevating temperature to 80 °C and the use of 5 mol % of rhodium pivalate did not provide **4** in increased yield (entries 10 and 11). Other solvents such as benzene and fluorobenzene were less effective (entries 12 and 13). On the other hand, treatment of **1** with 1 equiv of ethynylbenzene in the presence of 2 mol % of rhodium pivalate in toluene at 60 °C for 0.5 h gave compound **4** in 32% yield. The structure of **4** was identified by analyzing spectral data and by comparing it with reported data.[7] The ^{1}H NMR spectrum of **4** showed two vinyl protons at δ=6.87 and 6.21 ppm as two singlets associated with a pyranone and a furan ring. The structure of **4** was further confirmed by its IR spectrum, which exhibited the expected carbonyl absorption at υ=1724 cm^{-1} due to an ester group.

To produce a variety of furo[2,3-*b*]pyran-6-one derivatives with different substituents on the benzene ring, additional reactions between diazo compounds and several ethynyl compounds were conducted in the presence of 2 mol % rhodium pivalate in toluene at 60 °C for 0.5–5 h. Results are summarized in Table 2. To investigate the influence of substituents on reactivity, a variety of ethynyl compounds bearing electron-donating and -withdrawing groups on the benzene ring were used. Reactions of several ethynyl compounds possessing an electron-donating group on the benzene ring were first attempted. Reaction of **1** with 3-ethynyltoluene, 4-ethynyltoluene, 1-ethynyl-2,4,5-trimethylbenzene, 1-ethynyl-4-*n*-propylbenzene, 1-*tert*-butyl-4-ethynylbenzene, 1-ethynyl-4-*n*-pentylbenzene, or 1-ethynyl-4-methoxy-2-methylbenzene in the presence of 2 mol % of $Rh_2(OPiv)_4$ in toluene at 60 °C for 0.5 h gave compounds **5a**–**5h** in 46–65% yield (entries 1–8, Table 2). Treatment with 1-fluoro-3-ethynylbenzene, 1-chloro-3-ethynylbenzene, 1-bromo-4-ethynylbenzene or 4-ethynyl-α,α,α-trifluorotoluene bearing an electron-withdrawing group on the benzene ring in toluene at 60 °C for 1–5 h afforded adducts **5i**–**5l** in 43, 40, 41, and 50% yields (entries 9–12), respectively. To confirm the structures of **5a**–**5l**, the structure of **5c** was determined by X-ray crystallographic analysis (Fig. 1).[9]

Further reactions were then attempted to produce furo[2,3-*b*]pyran-6-one derivatives bearing polyconjugated units. When **1** was treated with 1-ethynyl-4-phenoxybenzene in the presence of 2 mol % of $Rh_2(OPiv)_4$ in toluene at 60 °C for 0.5 h, **5m** was obtained in 45% yield (entry 13). Treatment with 1-ethynylnaphthalene at 60 °C for 1 h provided cycloadduct **5n** in 54% yield (entry 14), whereas that with 2-ethynyl-6-methoxynaphthalene at 60 °C for 1 h afforded compound **5o** in 35% yield (entry15). Interestingly, with 9-ethynylphenanthrene, cycloadduct **5p** was produced in 40% yield (entry 16). Reactions between diazo compound **1** and other ethynyl compounds without the phenylacetylene moiety were also successful. Treatment with 3-ethynylthiophene and 1-ethynylcyclohexene afforded cycloadducts **5q**–**5r** in 58 and 49% yields, respectively (entries 17 and 18). These reactions provide rapid synthetic routes to a variety of furo[2,3-*b*]pyran-6-one derivatives bearing polyconjugated units and other substituents on furopyranone rings. Based on similarities with compounds reported in the literature, the synthesized compounds **5m**–**5p** are expected to exhibit fluorescence properties.[10]

To further explore the scope and limitation of ethynyl compounds, reactions of non-conjugated terminal alkynes and disubstituted alkynes were next examined. As non-conjugated terminal alkynes, treatment of **1** with 1-hexyne in the presence of 2 mol % of rhodium pivalate in toluene at 60 °C for 0.5 h provided unexpected cyclopropene **6** in 56% yield, without any isolation of two possible dihydrofuran and furopyranone (Scheme 2). With 3-phenyl-1-propyne at 60 °C for 0.5 h, **7** was also produced in 62% yield. The structural assignments of **6** and **7** were identified by spectroscopic analysis. The ^{1}H NMR of **6** shows one vinylic proton on the cyclopropene ring at δ=6.16 ppm as a singlet and the *gem*-dimethyl peaks at δ=1.78 and 1.77 ppm as two singlets. The ^{1}H NMR of **7** exhibits one vinylic proton at δ=6.24 ppm as a singlet and one methylene proton at δ=3.80 ppm as a singlet. Further confirmation

Table 2
Rhodium(II)-catalyzed reactions of **1** with ethynyl compounds to give a variety of furo[2,3-*b*]pyran-6-one derivatives

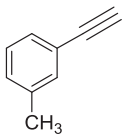
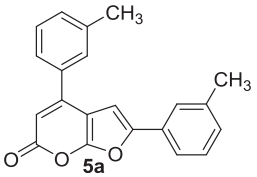
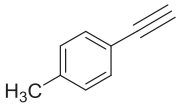
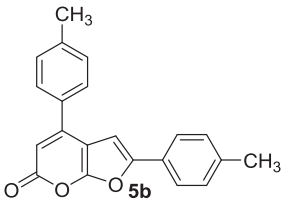
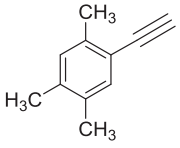
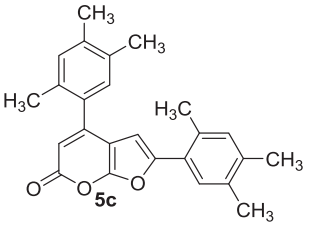
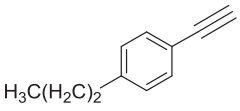
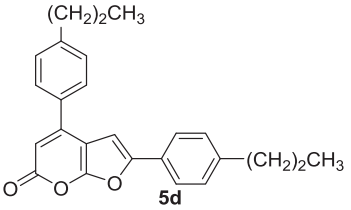
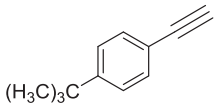
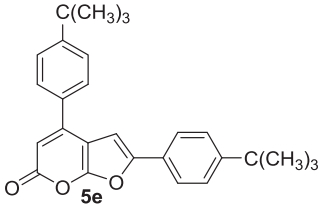
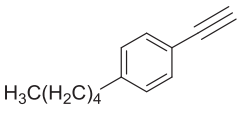
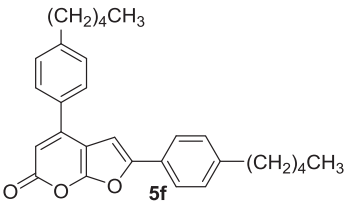
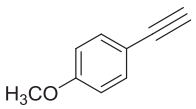
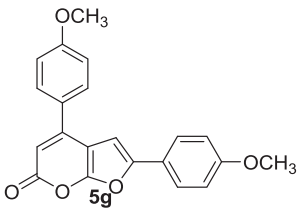
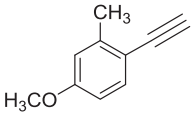
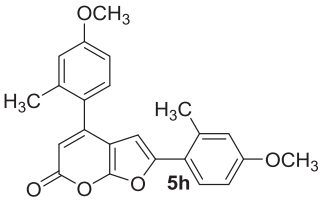
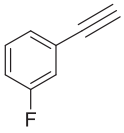
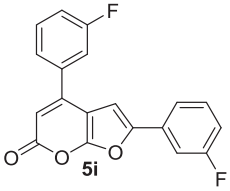
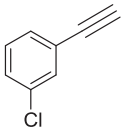
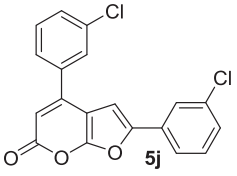
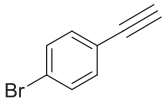
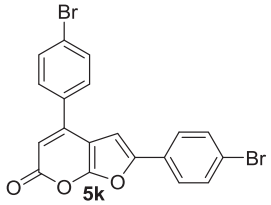
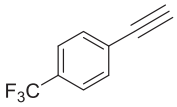
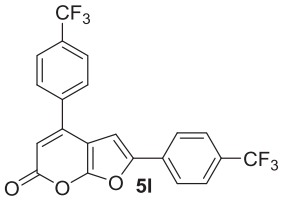
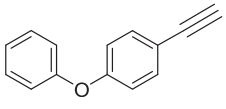
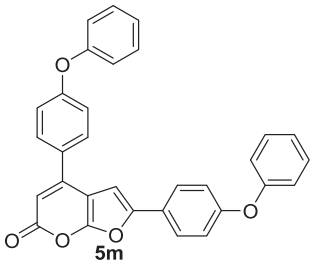
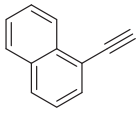
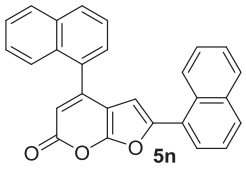
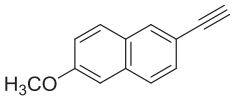
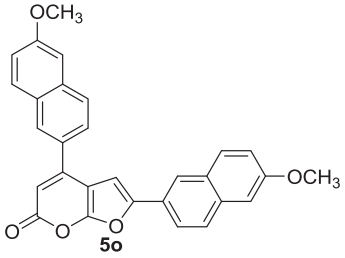
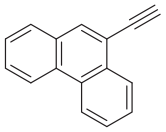
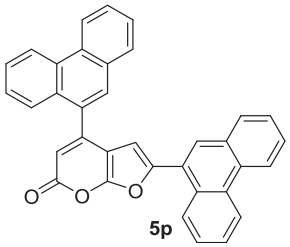
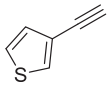
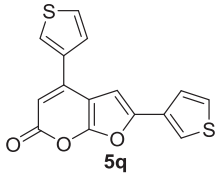
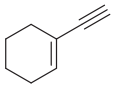
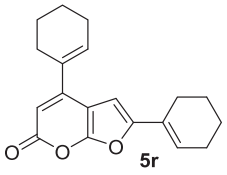
Entry	Arylacetylene	Temperature (°C)	Time (h)	Product	Yield[a] (%)
1		60	0.5	 **5a**	54
2		60	0.5	 **5b**	55
3		60	0.5	 **5c**	47
4		60	0.5	 **5d**	62
5		60	0.5	 **5e**	46
6		60	0.5	 **5f**	65
7		60	0.5	 **5g**	57

Table 2 (*continued*)

Entry	Arylacetylene	Temperature (°C)	Time (h)	Product	Yield[a] (%)
8		60	0.5	 **5h**	52
9		60	1	 **5i**	43
10		60	1	 **5j**	40
11		60	2	 **5k**	41
12		60	5	 **5l**	50
13		60	0.5	 **5m**	45
14		60	1	 **5n**	54

(*continued on next page*)

Table 2 (*continued*)

Entry	Arylacetylene	Temperature (°C)	Time (h)	Product	Yield[a] (%)
15		60	1	 **5o**	35
16		60	1	 **5p**	40
17		60	0.5	 **5q**	58
18		60	0.5	 **5r**	49

[a] Isolated yield.

for the structural assignment of **6** and **7** was obtained from spectral data of their ^{13}C NMR by comparison with those of reported compound **8** (Fig. 2).[11] The ^{13}C NMR of **6** clearly shows two vinylic carbons at δ=108.6 and 87.6 ppm and a quaternary carbon at δ=30.1 ppm on the cyclopropene ring, whereas **7** exhibits two vinylic carbons at δ=107.2 and 89.9 ppm and a quaternary carbon at δ=30.5 ppm.

However, efforts to prepare the desired products from disubstituted alkynes were unsuccessful. Reaction of **1** with diphenylacetylene or 1-phenyl-1-propyne gave intractable decomposed mixtures without any isolation of pure products.

The Co(III)-complex catalyzed formation of compound **4** from diazo compound **1** was recently reported to occur via double and iterative radical cyclization processes.[7] However, the Rh(II)-catalyzed formation of **4** may be explained as shown in Scheme 3. We propose that the diazo compound **1** first gives a carbenoid **9** by displacement of nitrogen by $Rh_2(OPiv)_4$. The carbenoid **9** is then trapped by the triple bond of ethynylbenzene to give intermediate **10**, which may give intermediate **3** via cyclopropenation intermediate **2** followed by a ring cleavage and a cyclization.[12] As an evidence of this mechanism, the cyclopropenes **6** and **7** were isolated from reactions of diazo compound **1** and non-conjugated terminal alkynes. The formation of cyclopropenes followed by direct ring opening and cyclization to give corresponding furans from diazodicarbonyl compounds has been also reported.[13] Conversion of intermediate **3** to final product **4** is explained by ketene formation followed by [2+2]cycloaddition and subsequent ring expansion.[14] Ketene formation from the 2,2-dimethyl-4*H*-1,3-dioxin-4-one moiety in **3** and [2+2]cycloaddition via the trapping of olefins or alkynes have already described.[15] Importantly, in the present study, the expected cycloadduct **4a** formed by [4+2]cycloaddition was not isolated.

3. Conclusion

In conclusion, the rhodium(II)-catalyzed reactions of the cyclic diazo compound **1** with a variety of ethynyl compounds are investigated. These reactions provide a rapid approach for synthesizing a variety of biologically interesting furo[2,3-*b*]pyran-6-one derivatives in one-pot cascade reactions of metal carbenoid

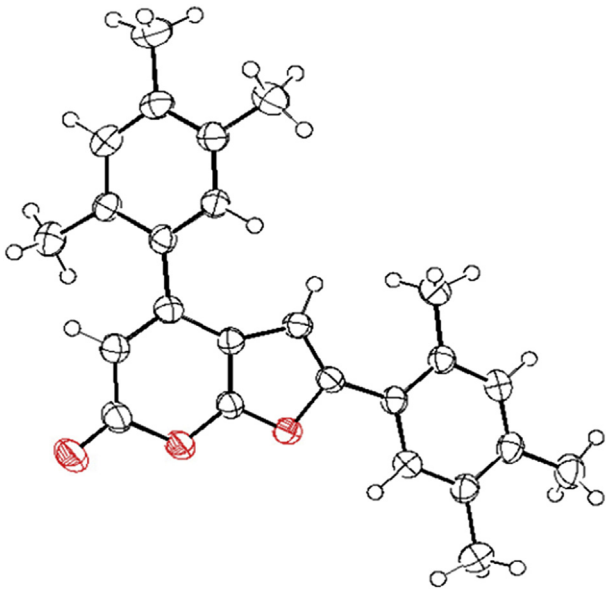


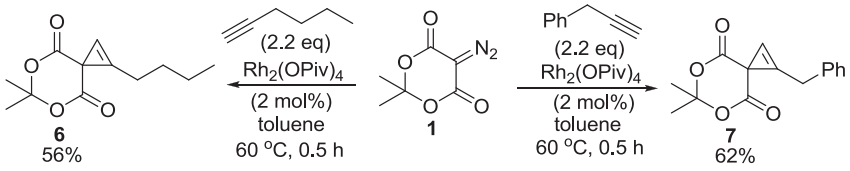
Fig. 1. X-ray structure of compound **5c**.

reaction/ketene formation/[2+2]cycloaddition/subsequent ring expansion. This methodology has the advantages of mild reaction conditions, efficient catalytic ability, and simple experimentation requirements.

4. Experimental

4.1. General

All experiments were carried out under nitrogen atmosphere. 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). Melting points were determined with micro-cover glasses on a Fisher-Johns apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian-VNS (300 MHz) spectrometer in $CDCl_3$ using 7.24 ppm as the solvent chemical shift. ^{13}C NMR spectra were recorded on a Varian-VNS (75 MHz) spectrometer in $CDCl_3$ using 77.0 ppm as the solvent chemical shift. IR spectra were recorded on a JASCO FTIR 5300 spectrophotometer. High-resolution mass spectra were obtained with a JEOL JMS-700 spectrometer at the Korea Basic Science Institute.



Scheme 2.

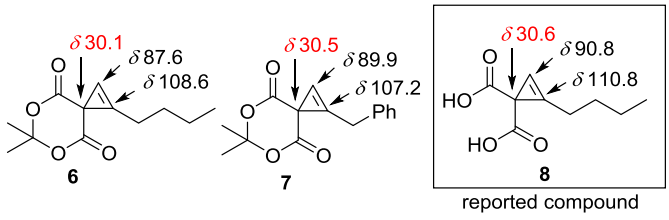
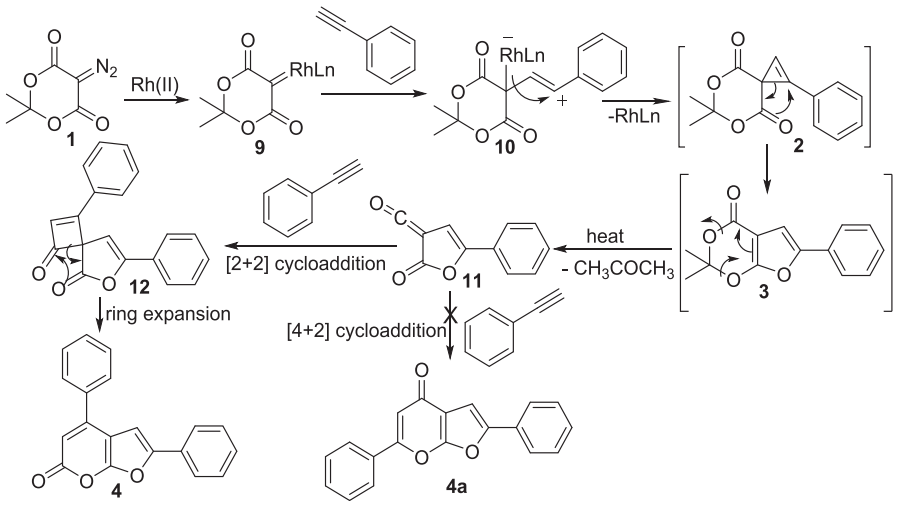


Fig. 2. Comparison of ^{13}C NMR chemical shifts of synthesized compounds **6** and **7** with reported compound **8**.

4.2. General procedure for the synthesis of 6*H*-furo[3,2-*b*] pyran-6-ones (4 and 5a–5r)

To a solution of diazo compound **1** (0.5 mmol) and alkynes (1.1 mmol) in toluene (2 mL) was added rhodium(II) pivalate (0.01 mmol). The reaction mixture was stirred at 60 °C for 0.5–5 h. The solvent was evaporated in rotary evaporator under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel to give the product.



Scheme 3.

*4.2.1. 2,4-Diphenyl-6H-furo[2,3-b]pyran-6-one (**4**).* Reaction of **1** (85 mg, 0.5 mmol) and phenylacetylene (112 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **4** (86 mg, 60%) as a solid: mp 88–90 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.62 (4H, m), 7.55–7.52 (3H, m), 7.39 (2H, t, J=7.5 Hz), 7.30 (1H, d, J=7.5 Hz), 6.87 (1H, s), 6.21 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 159.1, 154.0, 148.7, 135.3, 131.0, 129.4, 129.1, 128.5, 127.7, 123.7, 105.0, 101.0, 99.9; IR (KBr) 1724, 1607, 1526, 1379, 1295, 1195, 826, 761, 687 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{12}O_3$: 288.0786. Found: 288.0790.

*4.2.2. 2,4-Di-m-tolyl-6H-furo[2,3-b]pyran-6-one (**5a**).* Reaction of **1** (85 mg, 0.5 mmol) and 3-ethynyltoluene (127 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5a** (85 mg, 54%) as a solid: mp 98–100 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46–7.41 (5H, m), 7.36–7.33 (1H, m), 7.30–7.25 (1H, m), 7.12 (1H, d, J=7.2 Hz), 6.84 (1H, s), 6.19 (1H, s), 2.45 (3H, s), 2.38 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 158.9, 154.0, 148.7, 139.1, 138.6, 135.2, 131.5, 129.2, 129.1, 128.8, 128.8, 128.1, 124.7, 124.2, 120.8, 104.6, 100.7, 99.76, 21.5, 21.4; IR (KBr) 2933, 1729, 1609, 1528, 1294, 1182, 786 cm^{-1}; HRMS m/z (M^+) calcd for $C_{21}H_{16}O_3$: 316.1099. Found: 316.1099.

*4.2.3. 2,4-Di-p-tolyl-6H-furo[2,3-b]pyran-6-one (**5b**).* Reaction of **1** (85 mg, 0.5 mmol) and 4-ethynyltoluene (127 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5b** (87 mg, 55%) as a solid: mp 70–72 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.51 (4H, m), 7.33 (2H, d, J=7.8 Hz), 7.11 (2H, d, J=7.8 Hz), 6.81 (1H, s), 6.18 (1H, s), 2.43 (3H, s), 2.35 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 158.5, 154.0, 149.0, 141.5, 138.6, 132.6, 130.1, 129.8, 127.7, 126.4, 123.8, 104.3, 100.4, 100.0, 21.6, 21.5; IR (KBr) 2938, 1755, 1615, 1427, 1199, 1018, 817, 520 cm^{-1}; HRMS m/z (M^+) calcd for $C_{21}H_{16}O_3$: 316.1099. Found: 316.1099.

*4.2.4. 2,4-Bis(2,4,5-trimethylphenyl)-6H-furo[2,3-b]pyran-6-one (**5c**).* Reaction of **1** (85 mg, 0.5 mmol) and 1-ethynyl-2,4,5-trimethylbenzene (158 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5c** (87 mg, 47%) as a solid: mp 168–170 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (1H, s), 7.12 (1H, s), 7.09 (1H, s), 7.00 (1H, s), 6.36 (1H, s), 6.02 (1H, s), 2.38 (3H, s), 2.31–2.29 (9H, m), 2.26 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 158.0, 155.3, 148.6, 138.2, 137.0, 134.4, 134.2, 132.6, 132.5, 132.3, 132.2, 132.0, 129.2, 128.0, 125.5, 106.5, 103.9, 100.9, 21.0, 19.4, 19.4, 19.3, 19.1; IR (KBr) 2930, 1727, 1611, 1516, 1452, 1376, 1174, 1020, 851, 745 cm^{-1}; HRMS m/z (M^+) calcd for $C_{25}H_{24}O_3$: 372.1725. Found: 372.1723.

*4.2.5. 2,4-Bis(4-propylphenyl)-6H-furo[2,3-b]pyran-6-one (**5d**).* Reaction of **1** (85 mg, 0.5 mmol) and 1-ethynyl-4-propylbenzene (158 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5d** (115 mg, 62%) as a solid: mp 160–162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57–7.52 (4H, m), 7.33 (2H, d, J=8.1 Hz), 7.19 (2H, d, J=8.1 Hz), 6.82 (1H, s), 6.17 (1H, s), 2.66 (2H, t, J=7.8 Hz), 2.58 (2H, t, J=7.8 Hz), 1.73–1.60 (4H, m), 1.00–0.91 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 158.8, 153.7, 148.7, 146.0, 143.1, 132.5, 129.3, 128.9, 127.5, 126.4, 123.5, 104.0, 100.1, 99.6, 37.8, 37.7, 24.3, 13.7, 13.7; IR (KBr) 2943, 1713, 1600, 1509, 1291, 1188, 1015, 809 cm^{-1}; HRMS m/z (M^+) calcd for $C_{25}H_{24}O_3$: 372.1725. Found: 372.1725.

*4.2.6. 2,4-Bis(4-tert-butylphenyl)-6H-furo[2,3-b]pyran-6-one (**5e**).* Reaction of **1** (85 mg, 0.5 mmol) and 4-*tert*-butylphenylacetylene (173 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5e** (92 mg, 46%) as a solid: mp 220–222 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61–7.55 (6H, m), 7.42 (2H, d, J=8.1 Hz), 6.86 (1H, s), 6.18 (1H, s), 1.39 (9H, s), 1.33 (9H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 158.8, 154.4, 153.6, 151.5, 148.6, 132.2, 127.3, 126.1, 125.7, 123.4, 104.0, 100.3, 99.6, 34.9, 34.6, 31.1; IR (KBr) 2955, 1724, 1602, 1514, 1375, 1273, 1013, 831, 550 cm^{-1}; HRMS m/z (M^+) calcd for $C_{27}H_{28}O_3$: 400.2038. Found: 400.2038.

*4.2.7. 2,4-Bis(4-pentylphenyl)-6H-furo[2,3-b]pyran-6-one (**5f**).* Reaction of **1** (85 mg, 0.5 mmol) and 1-ethynyl-4-pentylbenzene (189 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5f** (143 mg, 65%) as a solid: mp 118–120 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48–7.44 (4H, m), 7.25 (2H, d, J=7.8 Hz), 7.11 (2H, d, J=7.8 Hz), 6.74 (1H, s), 6.09 (1H, s), 2.60 (2H, t, J=7.5 Hz), 2.51 (2H, t, J=7.5 Hz), 1.58–1.50 (4H, m), 1.27–1.23 (8H, m), 0.83–0.78 (6H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 158.8, 153.7, 148.7, 146.3, 143.4, 132.5, 129.2, 128.8, 127.5, 126.3, 123.5, 104.0, 100.1, 99.6, 35.7, 35.6, 31.4, 31.4, 30.9, 30.8, 22.4, 13.9; IR (KBr) 2932, 1713, 1602, 1513, 1375, 1190, 1014, 821, 747 cm^{-1}; HRMS m/z (M^+) calcd for $C_{29}H_{32}O_3$: 428.2351. Found: 428.2349.

*4.2.8. 2,4-Bis(4-methoxyphenyl)-6H-furo[2,3-b]pyran-6-one (**5g**).* Reaction of **1** (85 mg, 0.5 mmol) and 4-ethynylanisole (145 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5g** (99 mg, 57%) as a solid: mp 203–205 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (2H, d, J=8.7 Hz), 7.57 (2H, d, J=8.7 Hz), 7.03 (2H, d, J=8.7 Hz), 6.92 (2H, d, J=8.7 Hz), 6.74 (1H, s), 6.14 (1H, s), 3.88 (3H, s), 3.82 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8, 159.7, 158.7, 153.3, 148.6, 129.2, 127.5, 125.1, 121.8, 114.6, 114.3, 103.2, 99.6, 99.2, 55.5, 55.3; IR (KBr) 2924, 1722, 1602, 1513, 1249, 1173, 1021, 821, 632 cm^{-1}; HRMS m/z (M^+) calcd for $C_{21}H_{16}O_5$: 348.0998. Found: 348.0998.

*4.2.9. 2,4-Bis(4-methoxy-2-methylphenyl)-6H-furo[2,3-b]pyran-6-one (**5h**).* Reaction of **1** (85 mg, 0.5 mmol) and 1-ethynyl-4-methoxy-2-methylbenzene (160 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5h** (98 mg, 52%) as a solid: mp 123–125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 (1H, d, J=8.1 Hz), 7.18 (1H, d, J=7.8 Hz), 6.79–6.69 (4H, m), 6.22 (1H, s), 5.93 (1H, s), 3.78 (3H, s), 3.74 (3H, s), 2.33 (3H, s), 2.27 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4, 159.6, 159.4, 157.9, 154.9, 148.3, 137.0, 136.7, 129.7, 128.6, 127.5, 116.6, 116.5, 111.5, 111.5, 106.4, 103.3, 101.1, 55.3, 55.2, 21.9, 21.5; IR (KBr) 2943, 1727, 1604, 1513, 1291, 1247, 1162, 1109, 1048, 855, 797 cm^{-1}; HRMS m/z (M^+) calcd for $C_{23}H_{20}O_5$: 376.1311. Found: 376.1309.

*4.2.10. 2,4-Bis(3-fluorophenyl)-6H-furo[2,3-b]pyran-6-one (**5i**).* Reaction of **1** (85 mg, 0.5 mmol) and 1-ethynyl-3-fluorobenzene (132 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5i** (69 mg, 43%) as a solid: mp 128–130 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39–7.37 (3H, m), 7.34–7.27 (3H, m), 7.20–7.18 (1H, m), 6.99–6.96 (1H, m), 6.84 (1H, s), 6.18 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 161.4, 159.0, 158.9, 152.3, 147.4, 137.0, 136.9, 131.1, 130.7, 123.3, 119.3, 117.9, 115.4, 114.7, 110.7, 105.6, 101.6, 99.4; IR (KBr) 2928, 1761, 1715, 1588, 1437, 1240, 1181, 1076, 926, 784, 692 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{10}F_2O_3$: 324.0598. Found: 324.0599.

*4.2.11. 2,4-Bis(3-chlorophenyl)-6H-furo[2,3-b]pyran-6-one (**5j**).* Reaction of **1** (85 mg, 0.5 mmol) and 3-chloro-1-ethynylbenzene (149 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5j** (71 mg, 40%) as a solid: mp 198–200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57–7.56 (2H, m), 7.49–7.45 (4H, m), 7.31–7.19 (2H, m), 6.82 (1H, s), 6.16 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 158.8, 152.2, 147.3, 136.7, 135.4, 135.1, 130.9, 130.6, 130.4, 130.2, 128.4, 127.5, 125.6, 123.6, 121.7, 105.7, 101.6, 99.4; IR (KBr) 3084, 1748, 1606, 1526, 1261, 1180, 1094, 785 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{10}Cl_2O_3$: 356.0007. Found: 356.0007.

*4.2.12. 2,4-Bis(4-bromophenyl)-6H-furo[2,3-b]pyran-6-one (**5k**).* Reaction of **1** (85 mg, 0.5 mmol) and 1-bromo-4-ethynylbenzene (199 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol)

afforded **5k** (91 mg, 41%) as a solid: mp 228–230 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (2H, d, J=8.4 Hz), 7.55–7.49 (6H, m), 6.84 (1H, s), 6.20 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.1, 158.9, 152.5, 147.7, 133.9, 132.6, 132.1, 129.0, 127.7, 125.5, 125.1, 105.2, 101.1, 99.4; IR (KBr) 2925, 1714, 1597, 1520, 1296, 1194, 1007, 816 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{10}Br_2O_3$: 443.8997. Found: 443.9001.

*4.2.13. 2,4-Bis(4-(trifluoromethyl)phenyl)-6H-furo[2,3-b]pyran-6-one (**5l**).* Reaction of **1** (85 mg, 0.5 mmol) and 4-ethynyl-α,α,α-trifluorotoluene (187 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5l** (106 mg, 50%) as a solid: mp 158–160 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (2H, d, J=8.1 Hz), 7.76–7.73 (4H, m), 7.65 (2H, d, J=8.1 Hz), 6.94 (1H, s), 6.26 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.6, 152.1, 147.3, 138.4, 131.9, 128.2, 127.9, 126.4, 126.3, 126.3, 126.1, 126.0, 125.1, 123.7, 106.4, 102.4, 99.5; IR (KBr) 3125, 1728, 1616, 1528, 1325, 1127, 837, 672 cm^{-1}; HRMS m/z (M^+) calcd for $C_{21}H_{10}F_6O_3$: 424.0534. Found: 424.0532.

*4.2.14. 2,4-Bis(4-phenoxyphenyl)-6H-furo[2,3-b]pyran-6-one (**5m**).* Reaction of **1** (85 mg, 0.5 mmol) and 1-ethynyl-4-phenoxybenzene (213 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5m** (106 mg, 45%) as a solid: mp 162–164 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.54 (4H, m), 7.42–7.33 (4H, m), 7.21–6.98 (10H, m), 6.79 (1H, s), 6.18 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2, 159.5, 157.7, 155.7, 148.3, 130.0, 129.8, 129.4, 129.3, 126.5, 125.3, 124.5, 123.9, 123.8, 119.9, 119.5, 119.3, 118.9, 118.4, 118.3, 103.9, 99.9, 99.6; IR (KBr) 1730, 1587, 1489, 1237, 1171, 1015, 840, 754, 689 cm^{-1}; HRMS m/z (M^+) calcd for $C_{31}H_{20}O_5$: 472.1311. Found: 472.1310.

*4.2.15. 2,4-Di(naphthalen-1-yl)-6H-furo[2,3-b]pyran-6-one (**5n**).* Reaction of **1** (85 mg, 0.5 mmol) and 1-ethynylnaphthalene (167 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5n** (105 mg, 54%) as a solid: mp 88–90 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23–8.21 (1H, m), 8.00–7.95 (3H, m), 7.84 (2H, d, J=7.8 Hz), 7.68 (1H, d, J=6.9 Hz), 7.58–7.47 (7H, m), 6.48 (1H, s), 6.32 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 158.5, 154.1, 147.8, 133.7, 133.7, 133.0, 130.5, 129.9, 129.8, 129.5, 128.6, 127.0, 126.6, 126.5, 126.4, 126.1, 125.3, 125.1, 125.0, 124.6, 107.7, 105.8, 101.4; IR (KBr) 3055, 1743, 1620, 1521, 1397, 1238, 1175, 961, 910, 781, 730 cm^{-1}; HRMS m/z (M^+) calcd for $C_{27}H_{16}O_3$: 388.1099. Found: 388.1099.

*4.2.16. 2,4-Bis(6-methoxynaphthalen-2-yl)-6H-furo[2,3-b]pyran-6-one (**5o**).* Reaction of **1** (85 mg, 0.5 mmol) and 2-ethynyl-6-methoxynaphthalene (200 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5o** (78 mg, 35%) as a solid: mp 188–190 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11–8.03 (2H, m), 7.90–7.85 (1H, m), 7.78–7.70 (4H, m), 7.60–7.58 (1H, m), 7.20–7.12 (4H, m), 7.01 (1H, s), 6.32 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 158.9, 158.0, 153.7, 148.7, 135.5, 134.1, 131.8, 130.0, 129.9, 129.5, 129.1, 128.3, 127.7, 127.4, 127.3, 124.7, 122.2, 121.8, 119.8, 119.4, 105.7, 105.5, 104.2, 100.4, 99.8, 96.4, 55.2, 55.1; IR (KBr) 2941, 1709, 1614, 1484, 1393, 1266, 1199, 1027, 851, 731 cm^{-1}; HRMS m/z (M^+) calcd for $C_{29}H_{20}O_5$: 448.1311. Found: 448.1313.

*4.2.17. 2,4-Di(phenanthren-9-yl)-6H-furo[2,3-b]pyran-6-one (**5p**).* Reaction of **1** (85 mg, 0.5 mmol) and 9-ethynylphenanthrene (222 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5p** (98 mg, 40%) as a solid: mp 156–158 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81–8.62 (4H, m), 8.23 (1H, d, J=7.5 Hz), 8.04–7.85 (5H, m), 7.78–7.53 (8H, m), 6.52 (1H, s), 6.42 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 158.4, 154.2, 147.8, 131.8, 130.7, 130.6, 130.5, 130.5, 130.2, 129.1, 129.0, 128.8, 128.5, 128.4, 128.0, 127.9, 127.5, 127.4, 127.2, 127.1, 126.9, 126.9, 126.8, 126.7, 125.9, 125.3, 124.8, 123.1, 122.9, 122.5, 122.3, 107.5, 106.0, 101.3; IR (KBr) 2923, 1714, 1646, 1533, 1411, 1266, 1166, 1032, 962, 826, 750 cm^{-1}; HRMS m/z (M^+) calcd for $C_{35}H_{20}O_3$: 488.1412. Found: 488.1411.

*4.2.18. 2,4-Di(thiophen-3-yl)-6H-furo[2,3-b]pyran-6-one (**5q**).* Reaction of **1** (85 mg, 0.5 mmol) and 3-ethynylthiophene (118 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5q** (87 mg, 58%) as a solid: mp 189–191 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (1H, s), 7.51–7.49 (2H, m), 7.42–7.36 (2H, m), 7.30–7.28 (1H, m), 6.76 (1H, s), 6.23 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.6, 158.7, 147.4, 145.7, 136.4, 130.3, 127.6, 127.1, 127.0, 126.2, 124.0, 120.3, 103.4, 100.4, 98.9; IR (KBr) 3122, 1710, 1522, 1409, 1279, 786 cm^{-1}; HRMS m/z (M^+) calcd for $C_{15}H_8O_3S_2$: 299.9915. Found: 299.9912.

*4.2.19. 2,4-Dicyclohexenyl-6H-furo[2,3-b]pyran-6-one (**5r**).* Reaction of **1** (85 mg, 0.5 mmol) and 1-ethynylcyclohexene (116 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **5r** (72 mg, 49%) as a solid: mp 142–144 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.50 (1H, s), 6.29 (2H, s), 5.89 (1H, s), 2.30–2.24 (4H, m), 2.22–2.17 (4H, m), 1.77–1.62 (8H, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.3, 158.2, 154.7, 149.5, 134.7, 133.7, 125.5, 124.3, 101.5, 99.8, 98.1, 26.4, 26.0, 25.1, 24.3, 22.3, 22.0, 21.9, 21.5; IR (KBr) 2930, 1719, 1511, 1278, 1128, 817, 557 cm^{-1}; HRMS m/z (M^+) calcd for $C_{19}H_{20}O_3$: 296.1412. Found: 296.1414.

*4.2.20. 1-Butyl-6,6-dimethyl-5,7-dioxaspiro[2.5]oct-1-ene-4,8-dione (**6**).* Reaction of **1** (85 mg, 0.5 mmol) and 1-hexyne (90 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **6** (63 mg, 56%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.16 (1H, s), 2.55–2.50 (2H, m), 1.78 (3H, s), 1.77 (3H, s), 1.64–1.54 (2H, m), 1.45–1.33 (2H, m), 0.88 (3H, t, J=7.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 108.6, 104.3, 87.6, 30.1, 28.3, 27.7, 27.7, 22.9, 22.0, 13.4; IR (neat) 3143, 2955, 2871, 1742, 1461, 1388, 1290, 1204, 1128, 1016, 922, 832, 740 cm^{-1}; HRMS m/z (M^+) calcd for $C_{12}H_{16}O_4$: 224.1049. Found: 224.1047.

*4.2.21. 1-Benzyl-6,6-dimethyl-5,7-dioxaspiro[2.5]oct-1-ene-4,8-dione (**7**).* Reaction of **1** (85 mg, 0.5 mmol) and 3-phenyl-1-propyne (128 mg, 1.1 mmol) under $Rh_2(OPiv)_4$ (6 mg, 0.01 mmol) afforded **7** (81 mg, 62%) as a liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21–7.14 (5H, m), 6.24 (1H, s), 3.80 (2H, s), 1.65 (3H, s), 1.44 (3H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 133.8, 128.8, 127.4, 107.2, 104.4, 89.9, 30.5, 29.4, 27.6, 27.3; IR (neat) 3146, 2999, 1739, 1628, 1386, 1289, 1202, 1127, 1018, 922, 837, 739 cm^{-1}; HRMS (FAB) m/z (M^+) calcd for $C_{15}H_{14}O_4$: 258.0892. Found: 258.0896.

Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2012R1A1A4A01009620).

Supplementary data

^{1}H NMR, ^{13}C NMR spectra and X-ray data of synthesized compounds. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.08.054.

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