Efficient One-Step Synthesis of 2-Arylfurans by Ceric Ammonium Nitrate (CAN)-Mediated Cycloaddition of 1,3-Dicarbonyl Compounds to Alkynes

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An efficient method for construction of 2-arylfurans has been developed by ceric(IV) ammonium nitrate-mediated oxidative cycloaddition of cyclic and acyclic 1,3-dicarbonyl compounds to several alkynes. Reactions of 1,3-cyclohexanedione, 1,3-cyclopentanedione, and 2,4-pentanedione with several alkynes furnish 2-arylfurans in 26-75% yields. Extension of this technology to more complex 4-hydroxy-2-quinolone and 3-hydroxy-1H-phenalen-1-one with phenylacetylene also affords furoquinolinone and furophenalenone derivative in moderate yields. Reaction of 4-hydroxycoumarins with phenylacetylene give linear and angular furocoumarin derivatives as a mixture of regioisomer in good yields. The mechanistic pathway for the formation of 2-arylfurans has been also described.

Introduction

Furans are one of the most important heteroaromatic compounds with widespread occurrence in nature.[1] They are frequently found in many natural products arising from plants and marine organisms.[2] Possessing a variety of biological activities, they are used as commercially pharmaceutical agents, flavor, fragrance compounds, insecticides and anti-leukemic agents.[3] Although numerous synthetic methods for the preparation of furans have been reported, single-step annulation approaches still remain rare.[4]

Oxidative cycloaddition reactions mediated by metal salts (Mn(III), Ce(IV), Co(II), Ag(I), V(V)) have become an important method for the synthesis of heterocycles.[5] Among these, CAN or Mn(III)-mediated cycloaddition of ketones and 1,3-dicarbonyl compounds to alkenes,[6] vinyl acetates,[7] cinnamic esters,[8] and enol ethers[9] have been studied extensively. However, the reaction of 1,3-dicarbonyl compounds with alkynes has not been investigated. We describe here one-step synthesis of a variety of substituted 2-arylfurans by CAN-mediated cycloaddition of 1,3-dicarbonyl compounds to alkynes.

Results and Discussion

Reaction of 1,3-cyclohexanedione (**1**) with phenylacetylene (**2a**) was attempted utilizing several oxidant reagents. Both $Mn(OAc)_3 \cdot 2H_2O$ and Ag_2CO_3/Celite gave the furan **3** in very low yields (4% and 13%), whereas CAN(IV) provided product in good yield (60%) as shown in Table 1. We found that CAN(IV) was the much superior reagent for this cycloaddition. The synthesized furan **3** was clearly assigned from spectroscopic data. The ^{13}C NMR spectrum of **3** showed the expected 14 carbons and the methine proton in furan ring exhibited absorption at δ 6.87 as a singlet.

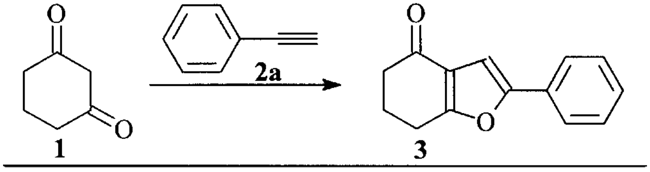
The reactions are typically carried out at 0 °C for 3 h starting from acyclic and cyclic 1,3-carbonyl compounds with several alkynes (3-fold excess) in the presence of CAN and excess of $NaHCO_3$ in acetonitrile. 2.2 equivalents of CAN(IV) are used to bring the reaction completion. The course of the reaction can be readily monitored by TLC.

First, reactions of dimedone **4** with several alkynes such as phenylacetylene (**2a**), 4-ethynyltoluene (**2b**), and 1-phenyl-1-propyne (**2c**) were examined (entries 1-3, Table 2). When **4** was treated with terminal alkyne **2a** in the presence of CAN(IV), trisubstituted furan **9** was obtained in good yield (74%). Similarly, with para-substituted phenyl acetylene (**2b**), trisubstituted furan **10** was also produced in good yield (74%). However, reaction of **4** with internal alkyne **2c** gave low yield of tetrasubstituted furan **11** in 26% yield. The other similar results are summarized in Table 2.

Reaction of 1,3-cyclopentanedione (**7**) with **2a** gave the fused furan **17** in 28% yield (entry 9, Table 2). There is no direct precedent for CAN-mediated oxidative addition of 1,3-cyclopentanedione to other substrates by other groups, so it is noteworthy that reaction of 1,3-cyclopentanedione to acetylene gave the expected fused furan **17**. Furthermore, reaction of acyclic 2,4-pentanedione (**8**) with **2a** also gave the trisubstituted furan **18** in 38% yield (entry 10, Table 2).

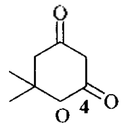
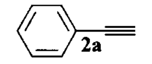
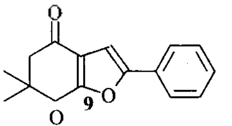
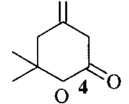
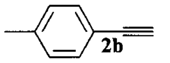
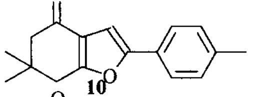
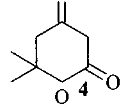
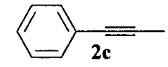
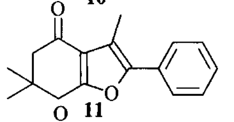
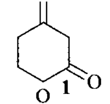
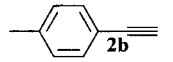
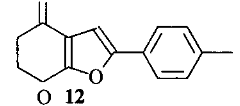
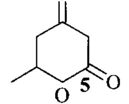
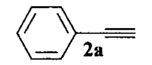
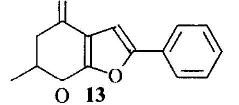
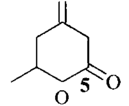
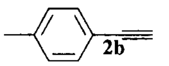
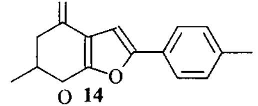
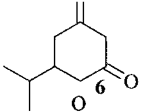
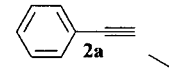
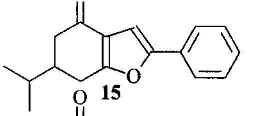
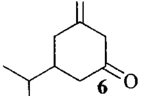
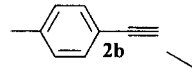
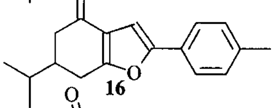
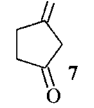
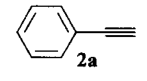
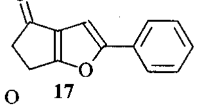
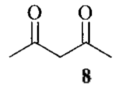
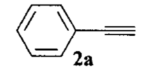
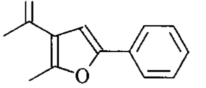
In order to extend the utility of this methodology, reactions of more complex compounds **19**-**22** with **2a** were investigated (Table 3). Reaction of 4-hydroxycoumarin **19** with **2a** at 0 °C for 3 h in acetonitrile gave furocoumarin **23** (46%) and furochromone **24** (16%) as a mixture of regioisomer (entry 1, Table 3). The mixture was easily separated by column chromatography and the two isomers were assigned from their spectroscopic data. The proton NMR spectra showed absorption at δ 7.18 as a singlet for

Table 1. Effect of oxidants in the reaction of 1,3-cyclohexanedione (**1**) and phenylacetylene (**2a**)



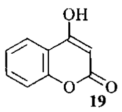
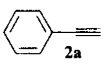
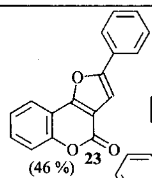
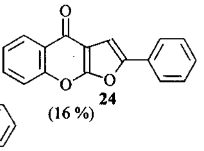
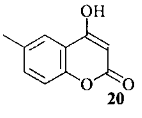
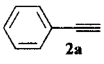
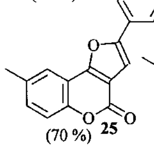
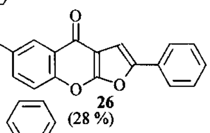
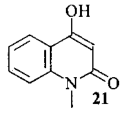
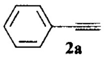
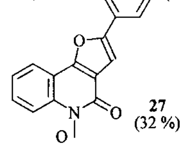
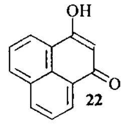
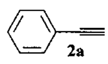
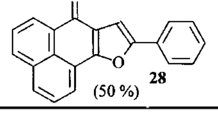
Oxidant	Solvent	Temp	Time (h)	Yield (%)
$Mn(OAc)_3 \cdot 2H_2O$	AcOH	80 °C	5	4
Ag_2CO_3/Celite	acetonitrile	reflux	5	13
$Ce(NH_4)_2(NO_3)_6$	acetonitrile	0 °C	3	60

Table 2. Reaction of 1,3-dicarbonyl compounds with alkynes

Entry	Dicarbonyl	Alkyne	Furan	Yield (%)
1	 **4**	 **2a**	 **9**	74
2	 **4**	 **2b**	 **10**	74
3	 **4**	 **2c**	 **11**	26
4	 **1**	 **2b**	 **12**	69
5	 **5**	 **2a**	 **13**	75
6	 **5**	 **2b**	 **14**	70
7	 **6**	 **2a**	 **15**	65
8	 **6**	 **2b**	 **16**	54
9	 **7**	 **2a**	 **17**	28
10	 **8**	 **2a**	 **18**	38

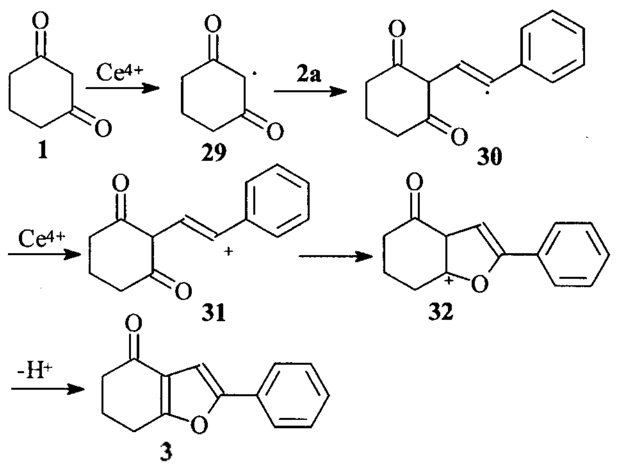
the furan methine proton of **23** and at δ 7.15 of **24**. The clear assignments come from IR carbonyl absorptions at 1736 cm^{-1} for ester group in furocoumarin **23** and at 1667 cm^{-1} for enone in furochromone **24**. Similarly, with 4-hydroxy-6-methylcoumarin (**20**), two regioisomers, **25** and **26**, were also obtained in 70 and 28% yields, respectively (entry 2, Table 3). These furocoumarin and furochromone derivatives have been reported to have various biological activities such as anticoagulant, insecticidal, anthelmintic, hypnotic, antifungal, and phytoalexin.[10] On the other hand, reaction of 4-hydroxy-2-quinolone (**21**) with **2a** gave furoquinolinone **27** as a single compound without any trace of regioisomer in 32% yield (entry 3, Table 3). The product has been clearly shown to be angular and not a linear furoquinolinone from its ^{1}H NMR and IR spectra by comparison with reported literature data.[11] Synthesis of these furoquinolone derivatives has been achieved by Claisen migration of allyloxyquinolin-2-one,[12] condensation of diethyl (2-propynyl)malonate with aromatic amines,[13] 3-halo-4-hydroxy-1-methylquinolin-2(1H)-one with copper(I) isopropenyl acetylide,[14] and Pd(0)-catalyzed coupling of *o*-bromonitrobenzene with 3-formyl-2-tributylstannylfuran.[15] However, in the above mentioned methods, both linear and angular furoquinolones were formed with low yields and many reaction steps.

Table 3. Reaction of more complex compounds with phenylacetylene

Entry	Dicarbonyl compound	Phenylacetylene	Furan (yield)	
1	 **19**	 **2a**	 **23** (46 %)	 **24** (16 %)
2	 **20**	 **2a**	 **25** (70 %)	 **26** (28 %)
3	 **21**	 **2a**	 **27** (32 %)	
4	 **22**	 **2a**	 **28** (50 %)	

Next, reaction of 3-hydroxy-1H-phenalen-1-one (**22**) with **2a** at 0 °C for 3 h gave interesting furophenalenone derivative **28** in 50% yield, which was reported to have various biological activities such as antibiotic, antimicrobial, antifungal, and phytoalexin[16] (entry 4, Table 3).

Although the exact mechanism of the reaction is still not clear, it is best described as shown in Scheme 1. The 1,3-dicarbonyl compound **1** is first oxidized by CAN(IV) to generate the α-oxoalkyl radical **29**, which then attacks the alkyne to give the radical **30**. The adduct **30** now undergoes fast oxidation by CAN(IV) to a vinylic carbocation **31**. Cyclization of the cation **31** furnishes intermediate **32**, which finally undergoes elimination to give the furan **3**. In most cases, only single adducts were obtained, but 4-hydroxy-



Scheme 1

coumarins, **19** and **20** gave a mixture of linear and angular adducts (entries 1 and 2, Table 3). The formation of linear and angular adduct may involve the trapping of the intermediate vinylic cation by both carbonyl and ester carbonyl group.

In conclusion, the CAN-mediated cycloaddition of 1,3-dicarbonyl compounds to alkynes offers a facile and new strategy for the synthesis of substituted furans. More reactions and applications will be investigated, now in progress in our laboratory.

Experimental

All experiments were carried out under a nitrogen atmosphere. Merck precoated silica gel plates (Art. 5554) with fluorescent indicator were used for analytical TLC. Flash column chromatography was performed using silica gel 9385 (Merck). Melting points were determined in cover glass on a Fisher-Johns apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Bruker Model ARX (300 MHz) spectrometer. ^{13}C NMR spectra were acquired using a Bruker Model ARX (75 MHz) spectrometer. IR spectra were recorded on a Jasco FTIR 5300 spectrophotometer. High resolution mass spectra were obtained VG-MICROMASS Autospec spectrometer.

2-Phenyl-4,5,6,7-tetrahydrobenzo[b]furan-4-one (3). A solution of 1,3-cyclohexanedione (**1**) (112 mg, 1.0 mmol) and phenylacetylene (**2a**) (306 mg, 3.0 mmol) in acetonitrile (5 mL) was added dropwise to a stirred mixture of CAN (1.206 g, 2.2 mmol) and NaHCO$_3$ (420 mg, 5.0 mmol) in acetonitrile (10 mL) at 0 °C. The reaction mixture was stirred for 3 h, diluted with acetonitrile and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by column chromatograpy on silica gel to give furan **3** (140 mg, 60%) as a solid: mp 135 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.65-7.25 (5H, m), 6.87 (1H, s), 2.94 (2H, t, *J*=6.2 Hz), 2.51 (2H, dd, *J*=6.0, 5.5 Hz), 2.20 (2H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 194.39, 166.60, 154.20, 129.78, 128.75, 128.74, 128.03, 123.93, 123.94, 122.90, 100.84, 37.59, 23.41, 22.53; IR (KBr) 3099, 2943, 1668, 1610, 1591, 1560, 1485, 1460, 1437, 1238, 1221, 1186, 10922, 875, 765, 696 cm^{-1}.

6,6-Dimethyl-2-phenyl-4,5,6,7-tetrahydrobenzo[b]furan-4-one (9). Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**4**) (140 mg, 1.0 mmol) with phenylacetylene (**2a**) (306 mg, 3.0 mmol) afforded **9** (177 mg, 74%) as a solid: mp 103 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.67-7.27 (5H, m), 6.89 (1H, s), 2.83 (2H, s), 2.41 (2H, s), 1.18 (6H, s); IR (KBr) 3101, 2957, 1672, 1610, 1458, 1437, 1224, 1130, 1049, 1014, 760, 690 cm^{-1}.

6,6-Dimethyl-2-(4-methylphenyl)-4,5,6,7-tetrahydrobenzo[b]furan-4-one (10). Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**4**) (140 mg, 1.0 mmol) with 4-ethynyltoluene (**2b**) (348 mg, 3.0 mmol) afforded **10** (188 mg, 74%) as a solid: mp 125-126 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.54 (2H, d, *J*=8.2 Hz), 7.20 (2H, d, *J*=8.1 Hz), 6.82 (1H, s), 2.82 (2H, s), 2.40 (2H, s), 2.37 (3H, s), 1.17 (6H, s); IR (KBr) 3109, 2961, 1668, 1595, 1560, 1502, 1444, 1410, 1369, 1219, 1120, 1045, 1010, 904, 814, 642 cm^{-1}.

3,6,6-Trimethyl-2-(4-methylphenyl)-4,5,6,7-tetrahydrobenzo[b]furan-4-one (11). Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**4**) (140 mg, 1.0 mmol) with 1-phenyl-1-propyne (**2c**) (348 mg, 3.0 mmol) afforded **11** (66 mg, 26%) as a solid: mp 86-88 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.67-7.30 (5H, m), 2.78 (2H, s), 2.48 (3H, s), 2.39 (2H, s), 1.17 (6H, s); IR (KBr) 3080, 2961, 1660, 1568, 1491, 1413, 1383, 1325, 1060, 1010, 769, 702 cm^{-1}.

2-(4-Methylphenyl)-4,5,6,7-tetrahydrobenzo[b]furan-4-one (12). Reaction of 1,3-cyclohexanedione (**1**) (112 mg, 1.0 mmol) with 4-ethynyltoluene (**2b**) (348 mg, 3.0 mmol) afforded **12** (156 mg, 69%) as a solid: mp 120-121 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.55 (2H, d, *J*=8.1 Hz), 7.21 (2H, d, *J*=8.0 Hz), 6.83 (1H, s), 2.95 (2H, t, *J*=6.2 Hz), 2.53 (2H, dd, *J*=6.8, 6.1 Hz), 2.37 (3H, s), 2.22 (2H, m); ^{13}C NMR (75 MHz, CDCl$_3$) δ 194.89, 166.78, 154.87, 138.44, 129.88, 129.87, 127.52, 124.35, 124.34, 123.31, 100.50, 38.03, 23.84, 22.99, 21.68; IR (KBr) 3026, 2953, 1674, 1597, 1500, 1440, 1410, 1359, 1236, 1207, 1184, 1132, 997, 925, 893, 808, 727 cm^{-1}.

6-Methyl-2-phenyl-4,5,6,7-tetrahydrobenzo[b]furan-4-one (13). Reaction of 5-methyl-1,3-cyclohexanedione (**5**) (126 mg, 1.0 mmol) with phenylacetylene (**2a**) (306 mg, 3.0 mmol) afforded **13** (171 mg, 75%) as a solid: mp 103-104 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.65-7.31 (5H, m), 6.88 (1H, s), 3.05 (1H, dd, *J*=16.4, 4.4 Hz), 2.67-2.24 (3H, m), 2.28 (1H, dd, *J*=16.5, 10.4 Hz), 1.20 (3H, d, *J*=6.4 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 194.50, 166.73, 154.81, 130.25, 129.19, 129.18, 128.46, 124.35, 124.34, 122.96, 101.23, 46.51, 31.94, 31.18, 21.49; IR (KBr) 3099, 2961, 1672, 1610, 1458, 1439, 1410, 1226, 1136, 1053, 1010, 914, 858, 758, 690 cm^{-1}; HRMS m/z (M$^+$) for C$_{15}$H$_{14}$O$_2$, calcd 226.0994. found 226.0961.

6-Methyl-2-(4-methylphenyl)-4,5,6,7-tetrahydrobenzo[b]furan-4-one (14). Reaction of 5-methyl-1,3-cyclohexanedione (**5**) (126 mg, 1.0 mmol) with 4-ethynyltoluene (**2b**) (348 mg, 3.0 mmol) afforded **14** (168 mg, 70%) as a solid: mp 138-139 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.54 (2H, d, *J*=8.1 Hz), 7.20 (2H, d, *J*=8.0 Hz), 6.82 (1H, s), 3.04 (1H, dd, *J*=16.4, 4.4 Hz), 2.66-2.54 (3H, m), 2.37 (3H, s), 2.28 (1H, dd, *J*=11.0, 10.4 Hz), 1.20 (3H, d, *J*=6.4 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 194.46, 166.45, 155.04, 138.42, 129.87, 129.86, 127.55, 124.31, 124.32, 122.92, 100.44, 46.51, 31.92, 31.19, 21.69, 21.49; IR (KBr) 3109, 2953, 1682, 1597, 1502, 1444, 1408, 1325, 1219, 1136, 1051, 1005, 914, 858, 823, 634 cm^{-1}.

6-Isopropyl-2-phenyl-4,5,6,7-tetrahydrobenzo[b]furan-4-one (15). Reaction of 5-isopropyl-1,3-cyclohexanedione hydrate (**6**) (154 mg, 1.0 mmol) with phenylacetylene (**2a**) (306 mg, 3.0 mmol) afforded **15** (164 mg, 65%) as a solid: mp 78 °C; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.68-7.27 (5H, m), 6.87 (1H, s), 3.02 (1H, dd, *J*=17.1, 4.8 Hz), 2.68 (1H, dd, *J*=17.1, 11.0 Hz), 2.61 (1H, dd, *J*=16.2, 3.0 Hz), 2.32 (1H, dd, *J*=16.1, 12,7 Hz), 2.15 (1H, m), 1.76 (1H, m), 0.98 (6H, d, *J*=6.9 Hz); ^{13}C NMR (75 MHz, CDCl$_3$) δ 194.70, 167.32, 154.83, 130.24, 129.18. 129.17, 128.44, 124.31, 124.30, 123.00, 101.12, 42.48, 42.32, 32.40, 27.43, 20.28, 19.99; IR (KBr) 3101, 2961, 1674, 1608, 1456, 1437, 1408, 1217, 1140, 1051, 1001, 852, 761, 694 cm^{-1}.

6-Isopropyl-2-(4-methylphenyl)-4,5,6,7-tetrahydrobenzo[b]furan-4-one (16). Reaction of 5-isopropyl-1,3-cyclohexanedione hydrate (**6**) (154 mg, 1.0 mmol) with 4-ethynytoluene (**2b**) (348 mg, 3.0 mmol) afforded **16** (144 mg, 54%) as a solid: mp 91 °C; ^{1}H NMR (300 MHz, CDCl$_3$)

δ 7.54 (2H, d, J=8.1 Hz), 7.20 (2H, d, J=8.0 Hz), 6.81 (1H, s), 3.01 (1H, dd, J=17.1, 4.9 Hz), 2.67 (1H, dd, J=17.1, 11.0 Hz), 2.60 (1H, dd, J=16.0, 3.0 Hz), 2.30 (1H, dd, J=15.9, 12.3 Hz), 2.16 (1H, m), 1.74 (1H, m), 1.00 (6H, d, J=6.9 Hz); IR (KBr) 2961, 1680, 1581, 1502, 1448, 1410, 1215, 1134, 1049, 999, 922, 808, 736, 609 cm^{-1}.

2-Phenyl-4,5,6-trihydrocyclopenta[b]furan-4-one (17). Reaction of 1,3-cyclopentanedione (**7**) (96 mg, 1.0 mmol) with phenylacetylene (**2a**) (306 mg, 3.0 mmol) afforded **17** (56 mg, 28%) as a solid: mp 152-153 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.29 (5H, m), 6.71 (1H, s), 3.07-2.98 (4H, m); IR (KBr) 3097, 2922, 1695, 1606, 1591, 1554, 1487, 1454, 1431, 1406, 1361, 1236, 1197, 999, 906, 825, 763, 704 cm^{-1}.

3-Acetyl-5-phenyl-2-methylfuran (18). Reaction of 2,4-pentanedione (**8**) (100 mg, 1.0 mmol) with phenylacetylene (**2a**) (306 mg, 3.0 mmol) afforded **18** (76 mg, 38%) as a solid: mp 48-50 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.27 (5H, m), 6.85 (1H, s), 2.66 (3H, s), 2.46 (3H, s); IR (KBr) 3105, 1672, 1610, 1579, 1556, 1404, 1236, 1157, 1068, 1024, 951, 844, 760, 690, 663 cm^{-1}.

2-Phenyl-4H-furo[3,2-c]benzopyran-4-one (23) and 2-phenyl-4H-furo[2,3-b]benzopyran-4-one (24). Reaction of 4-hydroxycoumarin (**19**) (150 mg, 0.92 mmol) with phenylacetylene (**2a**) (282 mg, 2.8 mmol) afforded **23** (112 mg, 46%) and **24** (38 mg, 16%) as a mixture of regioisomer. The mixture was separated by chromatography with 6 : 1 hexane:ethylacetate. **23**: mp 178 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98-7.37 (9H, m), 7.18 (1H, s); IR (KBr) 3108, 2919, 1736, 1632, 1487, 1451, 1424, 1364, 1318, 1281, 1233, 1186, 1103, 1076, 1057, 1030, 960, 914, 891, 852, 831 cm^{-1}; HRMS m/z (M^+) for $C_{17}H_{10}O_3$, calcd 262.0630. found 262.0631. **24**: mp 165-167 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.37-7.34 (9H, m), 7.15 (1H, s); IR (KBr) 3092, 2919, 2851, 1667, 1613, 1557, 1501, 1485, 1458, 1294, 1267, 1229, 1202, 1155, 1101, 1011, 937, 901, 870 cm^{-1}; HRMS m/z (M^+) for $C_{17}H_{10}O_3$, calcd 262.0630. found 262.0629.

8-Methyl-2-phenyl-4H-furo[3,2-c]benzopyran-4-one (25) and 6-methyl-2-phenyl-4H-furo[2,3-b]benzopyran-4-one (26). Reaction of 4-hydroxy-6-methylcoumarin (**20**) (100 mg, 0.57 mmol) with phenylacetylene (**2a**) (174 mg, 1.7 mmol) afforded **25** (110 mg, 70%) and **26** (45 mg, 28%) as a regioisomer. The mixture was separated by chromatography with 6 : 1 hexane:ethylacetate. **25**: mp 165-167 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83-7.32 (7H, m), 7.40 (1H, s), 7.16 (1H, s), 2.47 (3H, s); IR (KBr) 3113, 3050, 2922, 1738, 1637, 1572, 1508, 1487, 1427, 1358, 1233, 1182, 1115, 1057, 1005, 982, 916, 808 cm^{-1}. **26**: mp 192-193 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (1H, s), 7.71-7.33 (7H, m), 7.14 (1H, s), 2.48 (3H, s); IR (KBr) 3110, 2919, 1657, 1613, 1564, 1499, 1485, 1443, 1279, 1211, 1154, 1115, 1009, 907, 818 cm^{-1}.

5-Methyl-2-phenyl-4,5-dihydrofuro[3,2-c]quinolin-4-one (27). Reaction of 4-hydroxy-2-quinolone (**21**) (80 mg, 0.45 mmol) with phenylacetylene (**2a**) (138 mg, 1.4 mmol) afforded **27** (40 mg, 32%) as a solid: mp 164-165 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11-7.34 (9H, m), 7.28 (1H, s), 3.71 (3H, s); IR (KBr) 3096, 1651, 1601, 1585, 1471, 1433, 1354, 1279, 1246, 1107, 968, 916, 827 cm^{-1}.

9-Methyl-7H-phenaleno[1,2-b]furan-7-one (28). Reaction of 3-hydroxy-1H-phenalen-1-one (**22**) (100 mg, 0.5 mmol) with phenylacetylene (**2a**) (150 mg, 1.5 mmol) afforded **28** (73 mg, 50%) as a solid: mp 168 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74-7.36 (11H, m), 7.28 (1H, s); IR (KBr) 2918, 2851, 1649, 1588, 1508, 1487, 1468, 1439, 1379, 1258, 1202, 1020, 883, 841 cm^{-1}; HRMS m/z (M^+) for $C_{21}H_{12}O_2$, calcd 296.0838. found 296.0846.

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