Oxidative Addition of 1,3-Dicarbonyl Compounds to Terminal Acetylenes Mediated by Cerium(IV) Ammonium Nitrate

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Abstract: Cerium(IV) ammonium nitrate mediated oxidative addition of 1,3-dicarbonyl compounds to terminal acetylenes to yield multisubstituted furan derivatives is reported here. The simplicity of the reaction and the ease of execution are particularly noteworthy.

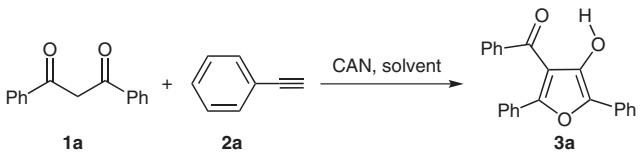
Key words: cerium(IV) ammonium nitrate, oxidative addition, terminal acetylenes, multisubstituted furans, 1,3-dicarbonyl compounds

Multisubstituted furans are important intermediates in organic synthesis.[1] In addition furans are also structural elements in many natural products and pharmaceutically important compounds.[2] There are numerous methods for the synthesis of furans owing to their tremendous importance,[3] but there are few syntheses based on the single-electron oxidative addition mechanism.[4] In our pursuit of developing mild synthetic protocols for heterocyclic and carbocyclic constructions using oxidants like cerium(IV) ammonium nitrate (CAN), we came across a mild method for furan synthesis which is reported in this paper. It is well known that CAN is a very versatile reagent for the single-electron oxidation of a variety of organic compounds.[5] Over the years, CAN has been used in a variety of C–C and C–heteroatom bond formations both stoichiometrically and catalytically.[6] The facile formation of dihydrofurans by the oxidative addition of 1,3-dicarbonyl compounds to alkenes is one of the most exploited reactions mediated by this reagent.[7] The trapping of the electrophilic radical generated by CAN from 1,3-diones has been successfully performed using various electron-rich substrates like vinyl sulfides,[8] glycals,[9] and methylenecyclopropanes[10] to cite a few. To the best of our knowledge, apart from some isolated reports,[11,12] there has not been a systematic investigation of the CAN-mediated addition of malonate radicals to terminal acetylenes. On the basis of mechanistic considerations, we surmised that the use of acetylenes instead of alkenes would probably result in the formation of furans in place of dihydrofurans. As expected, detailed experiments performed in our laboratory in this direction have shown the facile formation of multisubstituted furan derivatives in moderate to good yields.

As an initial experiment, 1,3-diphenylpropane-1,3-dione (**1a**) was treated with phenylacetylene (**2a**) in 1:1 molar ratio in acetonitrile as solvent using 2.3 mmol of CAN at room temperature in an atmosphere of nitrogen. On completion of the reaction as indicated by TLC, the reaction mixture was worked up and subjected to column chromatography on silica gel (100–200 mesh) to yield a product which was characterized by spectral analysis to be the tetrasubstituted furan derivative **3a** in 56% yield (Table 1 entry 3). Optimization of the reaction conditions (Table 1) led to the formation of the same product in 90% overall yield (entry 5).

The IR spectrum of **3a** revealed OH stretching at 3459 cm^{-1} while the benzoyl carbonyl stretching was observed at 1663 cm^{-1}. The OH proton was observed at δ = 7.28 ppm in the ^1H NMR. The benzoyl carbon was observed at δ = 193.57 ppm while the furan carbons resonated at δ = 192.59, 188.41, 171.54, and 153.00 ppm in the ^{13}C NMR spectrum. The mass spectral data also matched with the assigned structure.

Table 1 CAN-Mediated Reaction of 1,3-Diphenylpropane-1,3-dione (**1a**) with Phenylacetylene (**2a**)



1a **2a** **3a**

Entry	CAN (mmol)	Solvent	Temp (°C)	Time (h)	Atm	Yield (%)
1	1.1	MeOH	r.t.	12	N_2	30
2	2.3	MeOH	0–r.t.	12	N_2	37
3	2.3	MeCN	0–r.t.	12	N_2	56
4	2.3	MeCN	0–r.t.	12	N_2	40
5	2.3	MeCN	–5–r.t.	3	air	90

The doubling of the product yield on increasing the amount of CAN revealed that two moles of CAN were required for the reaction (entries 1 and 3). An appreciable increase in the product yield was also observed by passing air through the reaction mixture (entries 4 and 5). The rate of the reaction was also found to increase by passing air which proves the catalytic effect of air in promoting this

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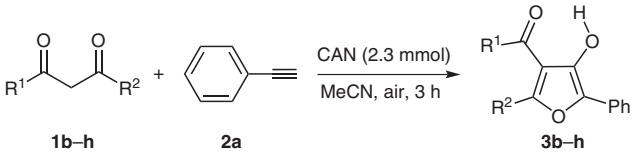
reaction. The increase in the reaction rate can be probably attributed to the re-oxidation of the Ce(III) species back to Ce(IV), thus maintaining the concentration of Ce(IV) in the reaction mixture.

Subsequently, the generality of the reaction was studied using several 1,3-dicarbonyl compounds and the results are summarized in Table 2.

Table 2 CAN-Mediated Reaction of 1,3-Dicarbonyl Compounds **1b–h** with Phenylacetylene (**2a**)



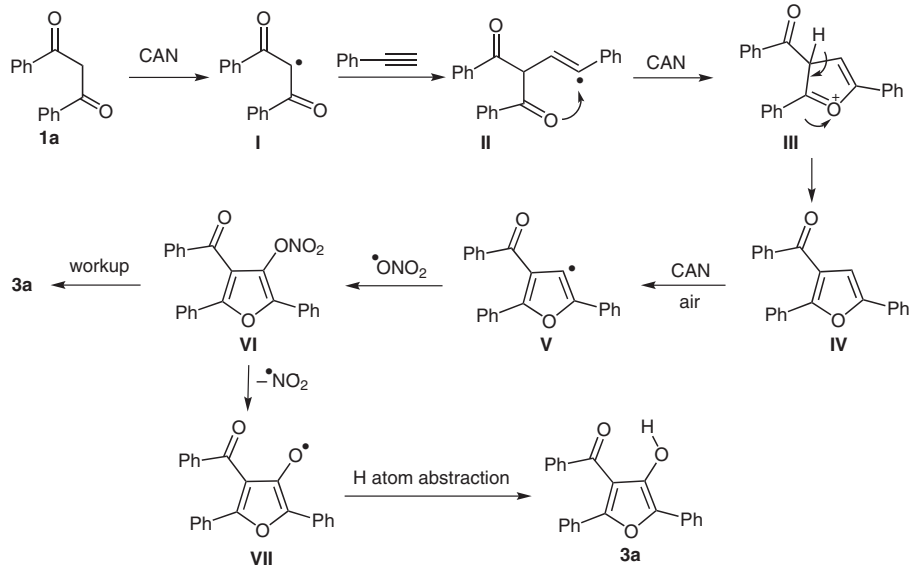
1b–h **2a** **3b–h**

Entry	1,3-Dione	R^1	R^2	Product	Yield (%)
1	**1b**	Ph	Me	**3b**	65
2	**1c**	Me	Me	**3c**	31
3	**1d**	OEt	OEt	**3d**	42
4	**1e**	O*i*-Pr	O*i*-Pr	**3e**	56
5	**1f**	Ph	OEt	**3f**	81
6	**1g**	Me	OEt	**3g**	77
7	**1h**	3-pyridyl	OMe	**3h**	30

Mechanistically, the reaction is presumed to occur via the initial formation of the electrophilic radical **I** from the dicarbonyl compound **1a** followed by its addition to the less hindered side of the terminal acetylene **2a** to generate the vinyl radical species **II** (Scheme 1). The latter is a highly reactive species, known in the literature[13] which probably undergoes cyclization followed by CAN oxidation to yield **III** which gets converted into the trisubstituted furan **IV**. Further oxidation by CAN to the radical **V** and trapping by the nitrato radical yields **VI**. The mass spectral analysis (FAB+) of the crude mixture of the reaction of **1a** shows a peak at *m*/*z* 386.57 (*m*/*z* calcd for **VI** $C_{23}H_{15}NO_5$ is 386.37). On the basis of a similar literature precedent[12] it can be presumed that hydrolysis of the nitrate **VI** during workup and/or the separation procedure yields the final hydroxylated product **3a**. The exact driving force for conversion of the trisubstituted furan into the tetrasubstituted furan is unknown, but the extra stability achieved due to the strong intramolecular H-bonding of the hydroxy group proton to the carbonyl oxygen giving rise to a six-membered H-bonded structure may be invoked to explain the formation of the product **3a**. Alternate pathways for the formation of the product **3a** are as follows. Nitrato radicals are proved oxygen atom synthons for the radical cyclization reactions of alkynes.[13] Homolytic fragmentation of the labile O–NO_2 bond of **VI** can yield **VII** which can abstract a hydrogen atom and form the product **3a**. Alternatively, trapping of the intermediate **V** by molecular oxygen and its rearrangement to the final product may also occur. The exact mechanism for the formation of **3a** may probably involve all these pathways.

We then extended our studies to cyclic 1,3-dicarbonyl compounds. It was observed that the reaction of dimedone (**5**) with phenylacetylene (**2a**) in the presence of CAN led to the formation of the trisubstituted furan **6a** in 56% yield (Table 3, entry 1). The structure of the product was unambiguously confirmed based on spectral analysis.

The stability of the fused furan **6a** is probably the reason why it is not further oxidized to form the tetrasubstituted furan as in the case of the reaction of acyclic diones even by passing air. However the reaction of other cyclic diones like cyclohexane-1,3-dione, cyclopentane-1,3-dione, indane-1,3-dione, and Meldrum's acid did not lead to any product formation. The reaction of these latter diones in methanol as the solvent led to intractable reaction mixtures, while in acetonitrile solvent, the reaction resulted in

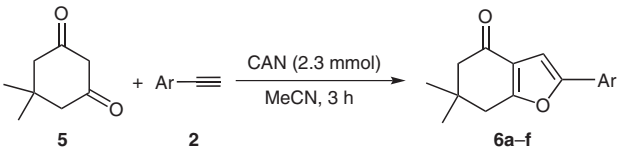


Scheme 1 Postulated mechanism for the reaction

the oxidation of phenylacetylene alone yielding a benzoic acid derivative.

Subsequently, various other terminal acetylenes **2b–g** were reacted with dimedone (**5**) in the presence of CAN; the fused furans **6b–g** were formed in moderate yields (Table 3). Terminal acetylenes with electron-withdrawing groups attached to the phenyl ring were found to be sluggish in their reactivity.

Table 3 CAN-Mediated Reaction of Dimedone (**5**) with Arylacetylenes **2a–g**



5 **2** **6a–f**

Entry	Acetylene	Ar	Product	Yield (%)
1	**2a**	Ph	**6a**	56
2	**2b**	1-naphthyl	**6b**	41
3	**2c**	2-naphthyl	**6c**	42
4	**2d**	4-PhC_6H_4	**6d**	44
5	**2e**	4-MeOC_6H_4	**6e**	37
6	**2f**	4-MeC_6H_4	**6f**	40
7	**2g**	4-ClC_6H_4	**6g**	21

In conclusion we have developed a new method for the preparation of tetrasubstituted and fused furans by the oxidative addition of terminal acetylenes to 1,3-dicarbonyl compounds in the presence of cerium(IV) ammonium nitrate. The prepared furans have potential antioxidant activity and this is being tested.

NMR spectra were recorded at 500 MHz (^{1}H) and 125 MHz (^{13}C) on a Bruker Avance DPX NMR spectrometer, except for the compounds **6a–g** which were recorded at 300 and 75 MHz, relative to TMS as the internal standard. IR spectra were recorded on a Shimadzu FT-IR spectrophotometer. Mass spectra were recorded under FAB or EIMS at 5000 resolution using a Jeol mass spectrometer. Melting points were recorded on a Büchi melting point apparatus and are uncorrected. Cerium(IV) ammonium nitrate (CAN) was purchased from Merck Specialities Pvt. Ltd. and was used as such without further purification. Commercial grade anhyd solvents were used. All reactions were monitored by TLC, visualization was effected with UV and/or by developing in I_2. Gravity column chromatography was performed using 100–200 mesh silica gel eluting with hexane–EtOAc. The phenylacetylene used for the study was purchased from Aldrich Chemical Co. All other terminal acetylenes were prepared by Sonogashira coupling method. All 1,3-dicarbonyl compounds were commercially available and were used as such without further purification. Dimedone purchased was purified by recrystallization (acetone).

Furans 3a–h and Benzofurans 6a–g; General Procedure

A soln of 1,3-dicarbonyl compound (1.0 mmol) and terminal acetylene (1.0 mmol) in anhyd MeCN (5 mL) was added to a two-necked round-bottom flask fitted with a pressure-equalizing funnel containing a soln of CAN (2.3 mmol) in anhyd MeCN (5 mL). Air was then bubbled through both the solns. The CAN soln was then added dropwise to the flask and the mixture was allowed to stir at –5 °C and the temperature was gradually allowed to rise to r.t. When the starting materials were fully consumed as indicated by TLC, the solvent was rotary evaporated and the crude residue was extracted with CH_2Cl_2. The organic layer was washed with brine soln (3 × 10 mL) and dried (anhyd Na_2SO_4). After removing the solvent, the residue was subjected to column chromatography (silica gel, 100–200 mesh, hexane–EtOAc) to yield the product.

(4-Hydroxy-2,5-diphenylfuran-3-yl)phenylmethanone (3a)

Yellow oil; yield: 306 mg (90%).

IR (neat): 3459, 3065, 1663, 1597, 1448, 1014 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.05–8.03 (m, 1 H), 7.99–7.97 (m, 1 H), 7.91–7.89 (m, 1 H), 7.84–7.79 (m, 2 H), 7.56–7.48 (m, 2 H), 7.46–7.41 (m, 4 H), 7.39–7.35 (m, 4 H), 7.28 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.57, 192.59, 188.41, 171.54, 153.00, 136.34, 135.89, 134.02, 133.97, 133.65, 133.62, 133.58, 130.66, 130.30, 130.22, 129.41, 129.16, 129.01, 128.85, 128.79, 128.68, 128.64, 128.42.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{16}O_3$: 340.1099; found: 340.1090.

(4-Hydroxy-2-methyl-5-phenylfuran-3-yl)phenylmethanone (3b)

Yellow oil; yield: 181 mg (65%).

IR (neat): 3369, 3061, 2928, 1692, 1599, 1450 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.92–7.89 (m, 3 H), 7.87–7.86 (m, 1 H), 7.59–7.55 (m, 2 H), 7.46–7.43 (m, 5 H), 2.36 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.56, 194.69, 188.63, 171.41, 150.70, 136.39, 135.87, 134.12, 133.80, 133.61, 130.62, 130.20, 130.03, 128.88, 128.84, 128.69, 128.54, 28.18.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{18}H_{14}O_3$: 278.0976; found: 278.0981.

1-(4-Hydroxy-2-methyl-5-phenylfuran-3-yl)ethanone (3c)

Yellow oil; yield: 67 mg (31%).

IR (neat): 3413, 3065, 2922, 1662, 1595, 1448 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.22–7.96 (m, 2 H), 7.68–7.63 (m, 1 H), 7.57–7.46 (m, 3 H), 2.45 (s, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 202.38, 195.50, 189.56, 152.07, 136.23, 134.26, 130.15, 129.57, 128.88, 128.70, 128.54, 30.66, 27.33.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{13}H_{12}O_3$: 216.0820; found: 216.0819.

Ethyl 2-Ethoxy-4-hydroxy-5-phenylfuran-3-carboxylate (3d)

Yellow oil; yield: 116 mg (42%).

IR (neat): 3453, 2967, 1734, 1675, 1597, 1449 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.96–7.84 (m, 1 H), 7.65–7.63 (m, 1 H), 7.53 (s, 1 H), 7.52–7.49 (m, 1 H), 7.34–7.27 (m, 2 H), 4.52–4.19 (m, 4 H), 1.69–1.35 (m, 6 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 195.23, 187.75, 166.01, 163.22, 161.67, 135.46, 134.76, 133.00, 127.88, 127.75, 127.56, 60.70, 55.78, 13.00, 12.78.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{15}H_{16}O_5$: 277.1031; found: 277.1025.

Isopropyl 4-Hydroxy-2-isopropoxy-5-phenylfuran-3-carboxylate (3e)
Yellow oil; yield: 170 mg (56%).

IR (neat): 3459, 2982, 1733, 1675, 1598, 1449 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.09–8.07 (m, 1 H), 7.98–7.96 (m, 1 H), 7.78 (s, 1 H), 7.61–7.57 (m, 2 H), 7.52–7.28 (m, 1 H), 5.29–5.11 (m, 2 H), 1.35–1.18 (m, 12 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 196.26, 188.80, 166.61, 163.82, 162.30, 137.23, 136.23, 134.44, 133.95, 128.94, 128.61, 70.12, 69.27, 21.65, 21.63, 21.48, 21.40.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{20}O_5$: 304.1311; found: 304.1315.

(2-Ethoxy-4-hydroxy-5-phenylfuran-3-yl)phenylmethanone (3f)
Yellow oil; yield: 250 mg (81%).

IR (neat): 3319, 2960, 1723, 1682, 1598, 1450 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.05–8.03 (m, 2 H), 7.88–7.87 (m, 1 H), 7.82–7.79 (m, 1 H), 7.54–7.49 (m, 2 H), 7.48 (s, 1 H), 7.40–7.36 (m, 4 H), 4.19 (q, *J* = 18 Hz, 2 H), 1.14 (t, *J* = 15 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 193.26, 188.29, 172.13, 163.72, 145.00, 136.37, 134.25, 133.81, 133.55, 130.35, 129.72, 129.56, 129.03, 128.95, 128.78, 128.68, 128.58, 62.48, 14.06.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{19}H_{16}O_4$: 308.1049; found: 308.1045.

1-(2-Ethoxy-4-hydroxy-5-phenylfuran-3-yl)ethanone (3g)
Yellow oil; yield: 189 mg (77%).

IR (neat): 3432, 2957, 1731, 1668, 1597, 1450 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.90–7.85 (m, 1 H), 7.54–7.52 (m, 1 H), 7.44–7.39 (m, 4 H), 4.21–4.11 (m, 2 H), 2.36 (s, 3 H), 1.28 (t, *J* = 15 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 199.10, 192.63, 188.05, 164.33, 144.78, 140.04, 134.99, 133.09, 131.31, 129.44, 127.75, 62.59, 29.00, 13.00.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{14}O_4$: 247.0926; found: 247.0936.

(4-Hydroxy-2-methoxy-5-phenylfuran-3-yl)pyridin-3-ylmethanone (3h)
Yellow oil; yield: 89 mg (30%).

IR (neat): 3060, 2956, 1719, 1450, 1266, 1176 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 10 Hz, 1 H), 8.12 (d, *J* = 5 Hz, 1 H), 7.71 (d, *J* = 10 Hz, 2 H), 7.46–7.40 (m, 5 H), 7.09 (s, 1 H), 3.38 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 170.01, 163.36, 153.59, 148.85, 136.00, 132.91, 130.58, 129.25, 129.00, 128.88, 128.53, 128.48, 128.26, 124.14, 117.25, 107.84, 51.86.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{13}NO_4$: 296.0878; found: 296.0884.

6,6-Dimethyl-2-phenyl-6,7-dihydrobenzofuran-4(5*H*)-one (6a)
White solid; mp 100–102 °C; yield: 134 mg (56%).

IR (KBr): 2962, 2867, 1667, 1431, 1222, 764 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.64 (d, *J* = 7.3 Hz, 2 H), 7.39 (uneven t, *J* = 7.8, 7.2 Hz, 2 H), 7.29 (d, *J* = 7.3 Hz, 1 H), 6.88 (s, 1 H), 2.83 (s, 2 H), 2.40 (s, 2 H), 1.19 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.44, 165.54, 154.59, 129.86, 128.77, 128.03, 123.93, 121.76, 100.84, 52.02, 37.53, 35.29, 28.72.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{16}O_2$: 240.1184; found: 240.1180.

6,6-Dimethyl-2-naphthalen-1-yl-6,7-dihydrobenzofuran-4(5*H*)-one (6b)
White solid; mp 171–173 °C; yield: 120 mg (41%).

IR (KBr): 3056, 2961, 2876, 1685, 1444 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.32 (d, *J* = 6.8 Hz, 1 H), 7.89–7.83 (m, 2 H), 7.72 (d, *J* = 7 Hz, 1 H), 7.57–7.47 (m, 3 H), 6.98 (s, 1 H), 2.88 (s, 2 H), 2.44 (s, 2 H), 1.22 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.07, 165.61, 154.02, 134.08, 130.41, 129.25, 128.67, 128.25, 127.85, 127.6, 127.61, 126.86, 126.65, 126.45, 126.11, 125.22, 125.17, 122.71, 121.77, 105.42, 52.21, 37.76, 37.72, 35.30, 28.81.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{20}H_{18}O_2$: 290.1340; found: 290.1342.

6,6-Dimethyl-2-naphthalen-2-yl-6,7-dihydrobenzofuran-4(5*H*)-one (6c)
White solid; mp 137–139 °C; yield: 122 mg (42%).

IR (KBr): 2962, 1681, 1452, 1357, 1216 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 8.15 (s, 1 H), 7.88–7.84 (m, 3 H), 7.72 (d, *J* = 8.5 Hz, 1 H), 7.51–7.49 (m, 2 H), 7.01 (s, 1 H), 2.87 (s, 2 H), 2.43 (s, 2 H), 1.20 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.62, 171.49, 165.91, 154.67, 133.39, 132.95, 128.62, 128.21, 127.81, 127.14, 126.65, 126.28, 122.55, 122.05, 121.88, 101.41, 52.03, 37.57, 35.32, 28.72.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{20}H_{18}O_2$: 290.1340; found: 290.1341.

2-Biphenyl-4-yl-6,6-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one (6d)
White solid; mp 170–172 °C; yield: 139 mg (44%).

IR (KBr): 2955, 1674, 1573, 1445, 1404, 1216 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.4 Hz, 2 H), 7.63–7.59 (m, 4 H), 7.44 (uneven t, *J* = 7.7, 7.1 Hz, 2 H), 7.35 (d, *J* = 7.2 Hz, 1 H), 6.91 (s, 1 H), 2.84 (s, 2 H), 2.41 (s, 2 H), 1.20 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.43, 165.64, 140.79, 140.41, 128.86, 127.54, 127.46, 126.95, 124.35, 121.88, 100.97, 52.05, 37.59, 35.32, 28.76.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{22}H_{20}O_2$: 316.1497; found: 316.1498.

2-(4-Methoxyphenyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one (6e)
White solid; mp 131–133 °C; yield: 100 mg (37%).

IR (KBr): 3117, 2962, 1681, 1593, 1499, 1452 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, *J* = 8.8 Hz, 2 H), 6.91 (d, *J* = 8.8 Hz, 2 H), 6.73 (s, 1 H), 3.83 (s, 3 H), 2.81 (s, 2 H), 2.39 (s, 2 H), 1.18 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.51, 165.04, 159.58, 125.44, 122.87, 121.77, 114.24, 99.18, 55.23, 52.04, 37.56, 35.32, 28.77.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{18}O_3$: 270.1289; found: 270.1291.

6,6-Dimethyl-2-*p*-tolyl-6,7-dihydrobenzofuran-4(5*H*)-one (6f)
White solid; mp 122–124 °C; yield: 102 mg (40%).

IR (KBr): 3110, 2962, 1681, 1499, 1445, 1222, 838 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53 (d, *J* = 8.1 Hz, 2 H), 7.18 (d, *J* = 8.0 Hz, 2 H), 6.81 (s, 1 H), 2.81 (s, 2 H), 2.39 (s, 2 H), 2.39 (s, 3 H), 1.18 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.48, 165.25, 154.84, 137.88, 129.47, 127.21, 123.93, 121.75, 100.09, 52.03, 37.55, 35.30, 28.75, 21.36.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{18}O_2$: 254.1340; found: 254.1344.

2-(4-Chlorophenyl)-6,6-dimethyl-6,7-dihydrobenzofuran-4(5*H*)-one (6g)

White solid; mp 161–163 °C; yield: 57 mg (21%).

IR (KBr): 3097, 2969, 2928, 1667, 1492, 1452 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.62 (d, *J* = 8.6 Hz, 2 H), 7.40 (d, *J* = 8.6 Hz, 2 H), 6.91 (s, 1 H), 2.86 (s, 2 H), 2.44 (s, 2 H), 1.23 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.25, 165.70, 153.47, 133.79, 129.00, 128.32, 125.10, 121.80, 101.32, 51.95, 37.46, 35.25, 28.68.

HRMS (EI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{15}ClO_2$: 274.0794; found: 274.0797.

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