

# Conversion of alkynes to cyclic imides and anhydrides using reactive iron carbonyls prepared from $\text{Fe}(\text{CO})_5$ and $\text{Fe}_3(\text{CO})_{12}$

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## Abstract

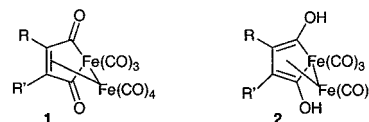
Alkyne–iron carbonyl complexes, prepared using  $\text{Fe}(\text{CO})_5$ – $\text{NaBH}_4$ – $\text{CH}_3\text{COOH}$ –amine–alkyne and  $\text{Fe}_3(\text{CO})_{12}$ –amine–alkyne reagent systems, react with excess of amine at 25 °C to give cyclic imides in moderate to good yields. Further, unsaturated iron carbonyl species, prepared using the  $\text{Fe}(\text{CO})_5$ –pyridine-*N*-oxide system, react with alkynes to give the corresponding anhydrides. © 2002 Published by Elsevier Science B.V.

**Keywords:** Alkynes; Iron carbonyl complexes; Double carbonylation; Cyclic imides

## 1. Introduction

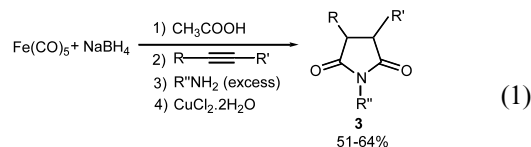
Transition metal mediated carbonylation reactions are of immense interest in synthetic chemistry [1]. Among these, the double carbonylation reactions are of special importance as they could lead to molecules with unusual structures that would otherwise require multi-step synthetic operations [2]. Among various metal carbonyls, iron carbonyls proved to be very much useful in the stoichiometric and catalytic mono- and double carbonylation reactions [3]. In recent years, it has been reported from this laboratory that alkynes react with iron carbonyl species, generated using  $\text{FeCl}_3$ ,  $\text{NaBH}_4$ –CO;  $\text{Fe}(\text{CO})_5$ ,  $\text{NaBH}_4$ – $\text{CH}_3\text{COOH}$  and  $\text{Fe}_3(\text{CO})_{12}$ –amine reagent systems to give a variety of products such as cyclobutenediones and benzoquinones [4–6]. These transformations, involving unsaturated iron carbonyl species and alkynes, were rationalised considering the intermediacy of maleoyl complexes of the type **1** or hydroxy ferrole complexes of the type **2** [2,5,7]. We report here the results of a detailed investigation on the reaction alkynes with iron carbonyl complexes, prepared using  $\text{Fe}(\text{CO})_5$ ,  $\text{NaBH}_4$ – $\text{CH}_3\text{COOH}$  and  $\text{Fe}_3(\text{CO})_{12}$ –amine reagent systems and excess of primary amine to obtain cyclic imides. Also, we report that unsaturated iron carbonyl species, generated in situ

using  $\text{Fe}(\text{CO})_5$ –pyridine-*N*-oxide, react with alkynes to give the corresponding anhydrides.



## 2. Results and discussion

Recently, others and we reported that amines facilitate the Pauson–Khand reaction of alkyne– $\text{Co}_2(\text{CO})_8$  complexes through creating vacant coordination site on cobalt [8,9]. In continuation of these efforts, we became interested in examining the effect of different amines on the reaction of iron carbonyl complexes **1** or **2**, formed in the reaction of alkynes with the  $\text{Fe}(\text{CO})_5$ – $\text{NaBH}_4$ – $\text{CH}_3\text{COOH}$  reagent system. We have observed that addition of excess of primary amines (25 mmol) to the iron carbonyl complexes, prepared at 25 °C in THF, gives the corresponding cyclic imides in moderate to good yields (51–64%) after  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  oxidation (Eq. (1)).



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Table 1  
Reaction of primary amines on alkynes- iron carbonyl complexes

Entry	Alkyne	Amine	Product <sup>a</sup>	Yield <sup>b</sup> (%)	
				method A <sup>c</sup>	method B <sup>c</sup>
	$R-C\equiv C-H$	$CH_3(CH_2)_3NH_2$			
1.	$R = C_6H_{11}$	$CH_3(CH_2)_3NH_2$	<b>3a</b>	57	65
2.	$R = Ph$	$CH_3(CH_2)_3NH_2$	<b>3b</b>	55	45
3.	$R = C_6H_{13}$	$CH_3(CH_2)_3NH_2$	<b>3c</b>	62	61
4.	$Ph-C\equiv C-Ph$	$CH_3(CH_2)_3NH_2$		55	51 <sup>d</sup>
5.		$CH_3(CH_2)_3NH_2$		64	58 <sup>d</sup>
6.		$CH_3(CH_2)_3NH_2$		61	50 <sup>d</sup>
7.	$Ph-C\equiv C-Ph$	$CH_3(CH_2)_7NH_2$		53	46 <sup>d</sup>
8.	$C_5H_{11}-C\equiv C-H$	$PhCH_2NH_2$		51	55

<sup>a</sup> Products were identified from the spectral data IR, <sup>13</sup>C-NMR, <sup>1</sup>H-NMR, mass and elemental analysis and comparison with the data reported for similar derivatives [2b,14].

<sup>b</sup> Yields are of products isolated by column chromatography and based on the amount of the alkynes used.

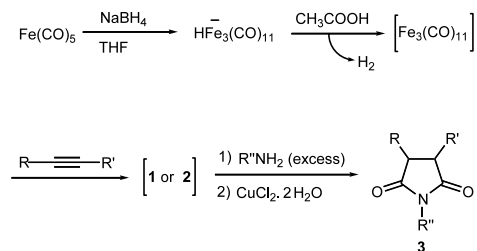
<sup>c</sup> Method A:  $Fe(CO)_5/NaBH_4/CH_3COOH$ /alkyne reagent system; Method B:  $(Fe_3CO)_{12}/RNH_2$ /alkyne reagent system.

<sup>d</sup> Stereochemistry assigned on the basis of <sup>1</sup>H-NMR data. These data are comparable with the data reported for similar derivatives [15].

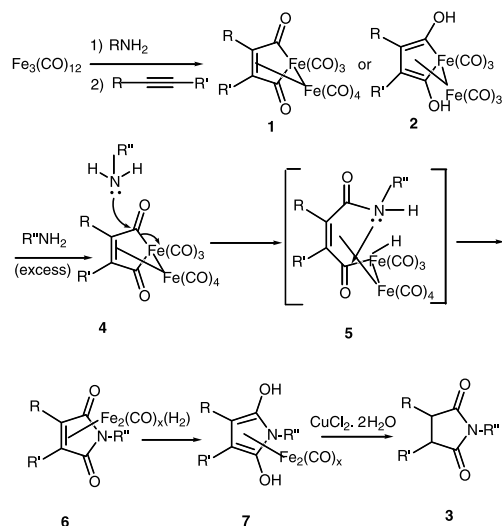
Several alkynes were converted to the corresponding cyclic imides using different primary amines [2b]. This reagent system can tolerate various functional groups as is evident from Table 1. It was thought that the  $HFe_3(CO)_{11}^-$  species, generated using  $Fe(CO)_5-NaBH_4-CH_3COOH$ , would give the coordinatively unsaturated ' $Fe_3(CO)_{11}$ ' species which, in turn, could react with alkynes to produce the intermediate alkyne-iron carbonyl complexes of the type 1 or 2 (Scheme 1).

Previously, we have reported that the reaction with  $Fe_3(CO)_{12}$  (6 mmol), *n*-butylamine (2.75 mmol) and alkyne gives the corresponding cyclobutenediones in 28–61% after  $CuCl_2 \cdot 2H_2O$  oxidation under these conditions [6]. However, addition of excess primary amine

(12.5 mmol) to the iron carbonyl complexes prepared in this way, leads to the corresponding cyclic imides in

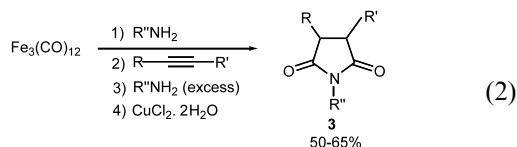


Scheme 1.



Scheme 2.

moderate to good yields (50–65%) after  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  oxidation (Eq. (2)) along with traces of cyclobutenediones (2–5%). Various alkynes were converted to the corresponding cyclic imides using different amines and the results are summarised in Table 1. Whereas the use primary amines gave cyclic amides, secondary and tertiary amines such as pyrrolidine, piperidine and triethylamine led to the formation of a mixture of the corresponding benzoquinones and cyclobutenediones as reported [6]. The formation of cyclic imides can be tentatively explained by the sequence of reactions and intermediates as shown in the (Scheme 2) [2,6,10a].



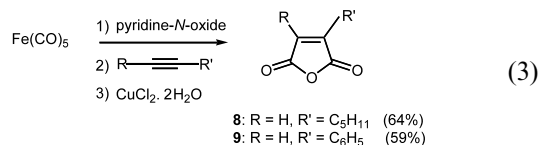
Presumably, the amine would react with  $\text{Fe}_3(\text{CO})_{12}$  to give the  $\text{Fe}_3(\text{CO})_{11}$  or ‘amine- $\text{Fe}(\text{CO})_4$ ’ and ‘ $\text{Fe}_2(\text{CO})_8$ ’ species, which on further reaction with alkynes, could give the intermediate complexes of type **1** or **2**. In the presence of excess amine, the intermediate of the type **5** would result that on subsequent transformations could lead to the species such as **6** and **7**. Finally, decomplexation using  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  would give the corresponding cyclic imides **3**.

It is well-known that the hydrido iron carbonyls reduce  $\alpha,\beta$  unsaturated carbonyl compounds [10,11]. Accordingly, it is reasonable to consider the intermediacy of such complexes under the present conditions.

However, the formation of other iron carbonyl species cannot be ruled out. We have attempted to isolate the intermediate iron carbonyl complexes that would be formed before  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  oxidation. Unfortunately, only a complex mixture of unidentified iron carbonyl

complexes could be isolated by column chromatography. However, these unidentified iron carbonyl complexes upon  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  oxidation gave the corresponding cyclic imides. We have also made attempts to prepare acyl and  $\text{Ph}_3\text{P}$  derivatives of the intermediate iron complexes but these efforts were not successful. It may be of interest to note that the complexes of the type **1** or **2** have proven applications in the preparation of highly functionalised aromatic compounds [12].

The  $\text{Fe}(\text{CO})_5$  is known to undergo decarbonylation with  $\text{R}_3\text{N}^+ \text{O}^-$  to give the unsaturated ‘ $\text{Fe}(\text{CO})_4$ ’ species [13]. Accordingly, it was of interest to examine the reaction alkynes with unsaturated iron carbonyl species prepared in this way. We have observed that the reaction of alkynes with  $\text{Fe}(\text{CO})_5$  in the presence of pyridine-*N*-oxide (1:1) at 70 °C gives the corresponding anhydride after  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  oxidation (Eq. (3)). Presumably, the pyridine-*N*-oxide further oxidises the intermediate alkyne-iron complexes to produce the corresponding anhydride. It was thought that the use of lesser amount of the amine-oxide would prevent the anhydride formation. Accordingly, in another run,  $\text{Fe}(\text{CO})_5$  and pyridine-*N*-oxide were used in 2:1 ratio. Surprisingly, a mixture of benzoquinones (60% yield) was obtained in this case.



### 3. Conclusion

In conclusion, simple, convenient procedures were developed for the preparation of cyclic imides from alkynes using the readily available iron carbonyl reagents. The methods described should be useful for further synthetic exploitations as the cyclic imide derivatives are an important class of compounds that are of interest to medicinal chemistry [16]. Also, the conversion of alkynes to the corresponding cyclic anhydrides using  $\text{Fe}(\text{CO})_5$  and pyridine-*N*-oxide would further illustrate the scope of applications of the reactive iron carbonyls prepared in this way.

### 4. Experimental

#### 4.1. General methods

$^1\text{H-NMR}$  (200 MHz) and  $^{13}\text{C-NMR}$  (50 MHz) spectra were taken in  $\text{CDCl}_3$  with  $\text{Me}_4\text{Si}$  as reference ( $\delta = 0$  ppm). The chemical shifts are reported in ppm on the  $\delta$

scale relative to  $\text{CDCl}_3$  (77.0 ppm), and coupling constants are reported in hertz. Chromatographic purification was conducted by column chromatography using 100–200 mesh silica gel obtained from Acme Synthetic Chemicals, India. The alkynes (except 1-heptyne) were prepared by following a reported procedure [17]. THF supplied by E-Merck, India, was distilled over sodium-benzophenone ketyl before use.  $\text{Fe}_3(\text{CO})_{12}$  reagent was prepared following a reported procedure [18]. Iron pentacarbonyl supplied by Fluka was used. All reactions and manipulations were conducted under a dry nitrogen atmosphere. All yields reported are isolated yields of materials judged homogeneous by TLC, IR and NMR spectroscopy.

#### 4.2. Representative procedure for the preparation of imides using $\text{Fe}_3(\text{CO})_{12}$ and amine

A mixture of  $\text{Fe}_3(\text{CO})_{12}$  (3.02 g, 6 mmol) and *n*-butylamine (0.201 g, 2.75 mmol) in THF (50 ml) was stirred for 30 min at 25 °C. 1-Heptyne (0.12 g, 1.25 mmol) was added and stirred for 4 h. *n*-Butylamine (9 g, 12.5 mmol) was added and the contents were further stirred for 12 h. The metal carbonyl complex was decomposed using  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (3.4 g, 20 mmol) in acetone (25 ml). Saturated aq. NaCl (20 ml) was added and the contents were extracted with ether (100 ml). The combined organic extract was washed with brine (15 ml), dried over anhydrous  $\text{MgSO}_4$  and concentrated. The residue was subjected to column chromatography (silica gel,  $\text{C}_6\text{H}_{12}$ -EtOAc). Ethyl acetate (1%) in  $\text{C}_6\text{H}_{12}$  eluted the cyclic imide derivative (0.182 g, 65%). This procedure was followed for the conversion of other alkynes to the corresponding cyclic imides.

##### 4.2.1. Compound 3a

Yield: 0.182 g (65%); IR (neat): 1772, 1703  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (200 MHz) ( $\text{CDCl}_3$ ):  $\delta$  0.6–1.87 (m, 18H), 1.92 (m, 1H), 2.1 (d,  $J = 13.6$  Hz, 1H), 2.6 (d,  $J = 13.2$  Hz, 1H), 3.3 (t,  $J = 7.3$  Hz, 2H);  $^{13}\text{C-NMR}$  (50 MHz) ( $\text{CDCl}_3$ ):  $\delta$  13.2 and 13.5 ( $-\text{CH}_3$ ), 19.7, 22.1, 26.1, 29.4, 31.0, 31.2, 34.0 ( $-\text{CH}_2$ ), 38.0 ( $-\text{CH}$ ), 39.5 ( $-\text{CH}_2$ ), 176.4 and 179.6 ( $-\text{CO}$ ); MS (EI):  $m/z$  225 ( $\text{M}^+$ ), 168 (B). Anal. Calc. for  $\text{C}_{13}\text{H}_{23}\text{O}_2\text{N}$ : C, 69.33; H, 10.22; N, 6.22. Found: C, 69.32; H, 10.27; N, 6.21%.

##### 4.2.2. Compound 3b

Yield: 0.128 g (45%); IR (neat): 1766, 1707  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (200 MHz) ( $\text{CDCl}_3$ ):  $\delta$  0.6–1.8 (m, 5H), 2.81 (d,  $J = 13.3$  Hz, 1H), 2.85 (d,  $J = 13.5$  Hz, 1H), 3.1 (q, 2H), 3.8 (t, 2H), 4.01 (t, 1H), 7–7.5 (m, 5H);  $^{13}\text{C-NMR}$  (50 MHz) ( $\text{CDCl}_3$ ):  $\delta$  10.1 ( $-\text{CH}_3$ ), 18.6, 21.5, 27.7 ( $-\text{CH}_2$ ), 36.2 ( $-\text{CH}$ ), 38.5 ( $-\text{CH}_2$ ), 128.0, 128.8, 132.4 ( $-\text{CH}$ ), 172.5 and 175.9 ( $-\text{CO}$ ).

##### 4.2.3. Compound 3c

Yield: 0.181 g (61%); IR (neat): 1786, 1703  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (200 MHz) ( $\text{CDCl}_3$ ):  $\delta$  0.8–1.9 (m, 20H), 2.09 (m, 1H), 2.3 (d,  $J = 13.3$  Hz, 1H), 2.7 (d,  $J = 13.2$  Hz, 1H), 3.4 (t,  $J = 7.2$  Hz, 2H);  $^{13}\text{C-NMR}$  (50 MHz) ( $\text{CDCl}_3$ ):  $\delta$  13.3 and 13.7 ( $-\text{CH}_3$ ), 19.8, 22.3, 26.4, 28.8, 29.5, 31.2, 31.3, 34.1 ( $-\text{CH}_2$ ), 38.2 ( $-\text{CH}$ ), 39.6 ( $-\text{CH}_2$ ), 176.4 and 179.7 ( $-\text{CO}$ ).

##### 4.2.4. Compound 3d

Yield: 0.195 g (51%); IR (neat): 1778, 1705  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (200 MHz) ( $\text{CDCl}_3$ ):  $\delta$  1–1.8 (m, 7H), 3.6 (t,  $J = 7.3$  Hz, 2H), 4.1 (d,  $J = 10$  Hz, 2H), 7.15–7.6 (m, 10H);  $^{13}\text{C-NMR}$  (50 MHz) ( $\text{CDCl}_3$ ):  $\delta$  13.7 ( $-\text{CH}_3$ ), 20.2, 29.9, 39.1 ( $-\text{CH}_2$ ), 55.3 ( $-\text{CH}$ ), 128.2, 128.5, 129.1 ( $-\text{CH}$ ), 136.9 (phenyl C-1), 176.5 ( $-\text{CO}$ ); MS (EI):  $m/z$  307 ( $\text{M}^+$ ), 265 (B). Anal. Calc. for  $\text{C}_{20}\text{H}_{21}\text{O}_2\text{N}$ : C, 78.12; H, 6.84; N, 4.56. Found: C, 78.25; H, 6.90; N, 4.52%.

##### 4.2.5. Compound 3e

Yield: 0.25 g (58%); IR (neat): 1766, 1689  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (200 MHz) ( $\text{CDCl}_3$ ):  $\delta$  0.75–1.53 (m, 18H), 1.62 (s, 3H), 2.44 (q,  $J = 5.8$  Hz, 1H), 2.7 (d,  $J = 3.8$  Hz, 1H), 3.4 (t,  $J = 7.2$  Hz, 2H), 7.2–7.4 (m, 5H);  $^{13}\text{C-NMR}$  (50 MHz) ( $\text{CDCl}_3$ ):  $\delta$  13.4 and 13.7 ( $-\text{CH}_3$ ), 19.9, 22.1, 24.6 ( $-\text{CH}_2$ ), 25.1 ( $-\text{CH}_3$ ), 29.5, 31.2, 31.3 ( $-\text{CH}_2$ ), 38.3 ( $-\text{CH}$ ), 42.7 ( $-\text{CH}_2$ ), 57.0 ( $-\text{CH}$ ), 74.8 (quaternary), 125.6, 127.7, 128.2 ( $-\text{CH}$ ), 143.6 (phenyl C-1), 178.5 and 179.1 ( $-\text{CO}$ ); MS (EI):  $m/z$  347 ( $\text{M}^+$ ), 329 (B). Anal. Calc. for  $\text{C}_{21}\text{H}_{31}\text{O}_2\text{N}$ : C, 73.04; H, 8.98; N, 4.05. Found: C, 73.10; H, 9.15; N, 4.11%.

##### 4.2.6. Compound 3f

Yield: 0.193 g (50%); IR (neat): 3487, 1766, 1693  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (200 MHz) ( $\text{CDCl}_3$ ):  $\delta$  0.8–1.0 (m, 14H), 1.2–1.8 (m, 14H), 2.43 (q,  $J = 5.7$  Hz, 1H), 2.78 (d,  $J = 3.8$  Hz, 1H), 3.45 (t,  $J = 7.1$  Hz, 2H);  $^{13}\text{C-NMR}$  (50 MHz) ( $\text{CDCl}_3$ ):  $\delta$  7.2, 7.6, 13.3, 13.6 ( $-\text{CH}_3$ ), 19.8, 22.1, 25.1, 28.2, 28.8, 29.2, 29.4, 31.5 ( $-\text{CH}_2$ ), 38.2 ( $-\text{CH}$ ), 42.1 ( $-\text{CH}_2$ ), 51.6 ( $-\text{CH}$ ), 75.6 (quaternary), 178.9 and 179.5 ( $\text{CO}$ ); MS (EI):  $m/z$  293 ( $\text{M}^+ - \text{H}_2\text{O}$ ), 282 (B). Anal. Calc. for  $\text{C}_{18}\text{H}_{33}\text{O}_3\text{N}$ : C, 69.45; H, 10.61; N, 4.50. Found: C, 69.51; H, 10.60; N, 5.00%.

##### 4.2.7. Compound 3g

Yield: 0.207 g (46%); IR (neat): 1776, 1707  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (200 MHz) ( $\text{CDCl}_3$ ):  $\delta$  0.9–1.8 (m, 15H), 3.7 (t,  $J = 7.4$  Hz, 2H), 4.1 (d,  $J = 10$  Hz, 2H), 7.1–7.4 (m, 10H);  $^{13}\text{C-NMR}$  (50 MHz) ( $\text{CDCl}_3$ ):  $\delta$  14.1 ( $-\text{CH}_3$ ), 22.6, 26.8, 27.7, 29.1, 31.7, 39.3 ( $-\text{CH}_2$ ), 55.3 ( $-\text{CH}$ ), 127.7, 129.1 ( $-\text{CH}$ ), 136.9 (phenyl C-1), 176.3 ( $\text{CO}$ ); MS (EI):  $m/z$  363 ( $\text{M}^+$ ), 265 (B). Anal. Calc. for  $\text{C}_{24}\text{H}_{29}\text{O}_2\text{N}$ : C, 79.34; H, 7.98; N, 3.86. Found: C, 79.52; H, 8.10; N, 3.88%.

#### 4.2.8. Compound **3h**

Yield: 0.177 g (55%); IR (neat): 1766, 1707  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (200 MHz) ( $\text{CDCl}_3$ ):  $\delta$  0.91–0.92 (m, 12H), 2.4 (d,  $J = 13.4$  Hz, 1H), 2.77 (d,  $J = 13.6$  Hz, 1H), 4.2 (s, 2H), 7.2–7.4 (m, 5H);  $^{13}\text{C-NMR}$  (50 MHz) ( $\text{CDCl}_3$ ):  $\delta$  10.1 ( $-\text{CH}_3$ ), 18.6, 21.5, 27.5, 27.7, 30.6 ( $-\text{CH}_2$ ), 36.2 ( $-\text{CH}$ ), 38.5 ( $-\text{CH}_2$ ), 128.0, 128.8 ( $-\text{CH}$ ), 132.4 (phenyl C-1), 172.5 and 175.9 (CO).

#### 4.3. Typical procedure for the preparation of maleic anhydride derivatives using $\text{Fe}(\text{CO})_5$ and pyridine *N*-oxide

$\text{Fe}(\text{CO})_5$  (1.3 ml, 10 mmol) and pyridine *N*-oxide (0.95 g, 10 mmol) in THF (80 ml) were stirred until the colour changed from light yellow to dark brown at 67 °C (ca. 1 h). 1-Heptyne (0.19 g, 2 mmol) was added and the refluxing was continued for further 12 h. The metal carbonyl complex was decomposed using  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (3.4 g, 20 mmol) in acetone (10 ml). Saturated aq. NaCl (25 ml) was added and the resulting solution was extracted with ether (100 ml), washed with brine (20 ml), dried over anhydrous  $\text{MgSO}_4$  and concentrated. The residue was subjected to column chromatography (silica gel,  $\text{C}_6\text{H}_{12}$ –EtOAc). Ethyl acetate (3%) in  $\text{C}_6\text{H}_{12}$  eluted the anhydride (0.214 g, 64%).

#### 4.3.1. Compound **8**

Yield: 0.214 g (64%); IR (neat): 3111, 1842, 1772  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (200 MHz) ( $\text{CDCl}_3$ ):  $\delta$  0.8–1.9 (m, 11H), 6.5 (s, 1H);  $^{13}\text{C-NMR}$  (50 MHz) ( $\text{CDCl}_3$ ):  $\delta$  13.7 ( $-\text{CH}_3$ ), 22.1, 25.8, 26.5, 31.1 ( $-\text{CH}_2$ ), 128.4 ( $-\text{CH}$ ), 153.8 (quaternary), 164.0 and 165.8 ( $-\text{CO}$ ).

#### 4.3.2. Compound **9**

Yield: 0.204 g (59%); IR (neat): 3117, 1839, 1765  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  (200 MHz) ( $\text{CDCl}_3$ ):  $\delta$  7–7.5 (m, 6H);  $^{13}\text{C-NMR}$  (50 MHz) ( $\text{CDCl}_3$ ):  $\delta$  127.4, 128.8, 129.2 ( $-\text{CH}$ ), 138.2 (phenyl C-1), 146.5 ( $-\text{CH}$ ), 146.6 (quaternary), 163.6 and 164.5 ( $-\text{CO}$ ).

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