Reaction of (3-Furylmethyl)cobaloxime with Dienophiles. Variable Mode of the Reaction by the Type of Dienophiles

Masaru Tada,* Nobuyuki Mutoh, and Tamaki Shimizu

The Department of Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjukuku, Tokyo 169, Japan

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(3-Furylmethyl)cobaloxime reacts with dienophiles in three reaction modes: (a) a 1,4-addition with *N*-phenylmaleimide and maleic anhydride, (b) a 1,4-cycloaddition and concomitant 1,3-migration of the cobaloxime moiety with dimethyl acetylenedicarboxylate, and (c) a formal aromatic substitution on the furan ring with active carbonyl compounds such as 2-oxomalonate, hexafluoroacetone, and 2-oxoaldehydes. The adducts from 2-aryl-2-oxoacetaldehyde easily loose the cobaloxime moiety on heating and give 2-(2-aryl-2-oxoacetyl)-3-methylfuran.

A transition metal bound to a diene system may affect the reactivity of the diene. We[1] and Welker *et al.*[2] have shown the enhanced reactivity of butadien-2-ylcobaloxime in the Diels–Alder addition with a variety of dienophiles. This effect by the cobaloxime substituent is more prominent than those by stannyl, selenyl,[3] and silyl[4] substituents. An allylic metal–carbon bond can also interact with a π-system by $\sigma-\pi$ interaction[5] and raise the HOMO level of the π-system. With this background, the reactions of (3-furyl)methylbis(dimethylglyoximato)pyridinecobalt(III) (**1**) with dienophiles were examined in this study.

Cobaloxime **1** was prepared by the reaction of cobaloxime anion[6] with (3-furyl)methyl bromide which was obtained by our method utilizing the cobaloxime-mediated cyclization of 2,2-di(2-propynoxy)ethyl bromide followed by treatment with NBS and acid (Scheme 1).[7]

Cobaloxime **1** reacts efficiently with *N*-phenylmaleimide (**2**) and maleic anhydride (**3**) at room temperature in dichloromethane to give adducts **5** and **6**, respectively (Scheme 2). Products **5** and **6** were unstable and deteriorated during chromatography. The structure of **5** was characterized by an olefinic proton (H-5) at δ 5.96 (d, J = 1.3 Hz) and one of the two methine protons (H-3) at δ 4.92 (d, J = 1.3 Hz) which couple with each other.

The structure of **5** was confirmed by the following independent synthesis using the Diels–Alder addition between 3-(bromomethyl)furan and **2** followed by cobaloximation of the adduct[6] by cobaloxime anion. Exo-condensation of the imide and anhydride rings in **5** and **6** is shown by the lack of vicinal coupling between the protons next to the carbonyls (H-1 and H-2) and the protons at the bridgehead carbons (H-3 and H-4).[8]

The reaction of **1** with dimethyl acetylenedicarboxylate (**4**) gave product **7** quantitatively (Scheme 2). The structure of **7** was characterized by the two exo-methylene protons at δ 5.32 and 5.41 as singlets. Two methine protons at the bridgehead also appear as singlets at δ 4.99 and 5.18. Exo-orientation of the cobaloxime moiety is revealed by the lack of vicinal coupling between the methine proton at the bridgehead (δ 4.99, H-1) and the proton α to the cobalt (δ 1.92, H-3).[8] The reaction to give

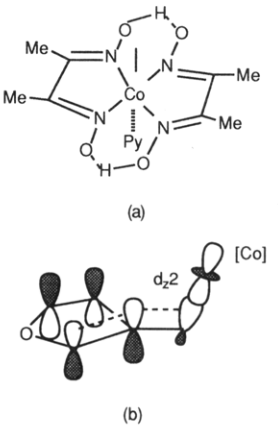
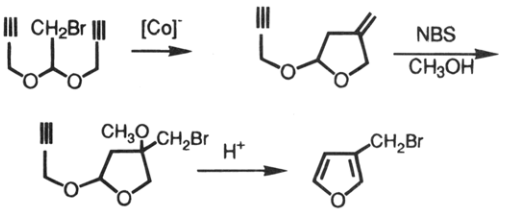
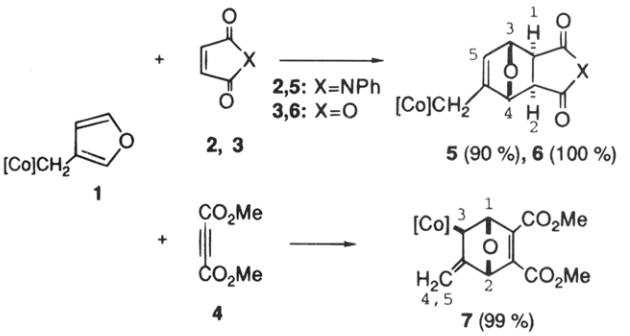


Figure 1. (a) Cobaloxime [Co] and (b) $\sigma-\pi$ conjugation.

Scheme 1



Scheme 2



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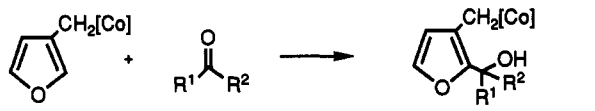
Scheme 3

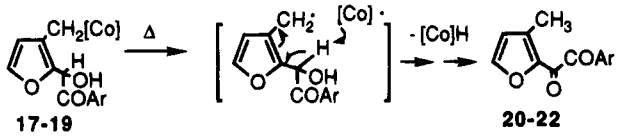


1 **8 - 13** **14** (96 %), **15** (91 %), **16** (97 %), **17** (70 %), **18** (74 %), **19** (69 %)

8, 14 (R^1=R^2=CO_2Et) **9, 15** (R^1 = R^2 = CF_3)
10, 16 (R^1=H, R^2=CO_2Me)

11, 17 (R^1=H, R^2=COPh) **12, 18** (R^1=H, R^2=COPhCl(*p*))
13, 19 (R^1=H, R^2=$COPhNO_2$(*p*))

Scheme 4



17-19 **20-22**

7 is a hitherto unknown type, which is a diene addition with subsequent 1,3-rearrangement of the cobaloxime moiety.

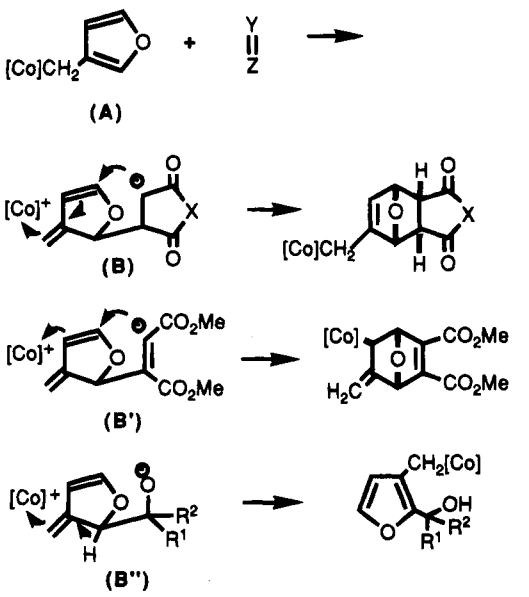
Diethyl 2-oxomalonate (**8**), hexafluoroacetone (**9**), and ethyl glyoxalate (**10**) react with cobaloxime **1** to give adducts **14**, **15**, and **16**, respectively, in excellent yields (Scheme 3). The structure of **14** is characterized by one set of doublets due to the furan protons at δ 5.71 and 7.05.

Similarly 2-oxoaldehydes **11**, **12**, and **13** gave adducts **17**, **18**, and **19** (Scheme 3). In the reactions with those 2-oxo aldehydes the degradation of the primary products gave the byproducts **20**, **21**, and **22** which explains the lower yields of the adducts **17**–**19**. These byproducts were formed also on heating of the ethanol solutions of **17**–**19**. The formation of products **20**–**22** can be accounted for by the homolytic cleavage of the allyl–cobalt bond and the elimination of the hydrogen atom which is activated by furan, hydroxy, and carbonyl groups (Scheme 4). This type of hydrogen abstraction by the cobaloxime radical is well known and takes place very easily even with nonactivated β-hydrogen in alkyl radicals.[9] The reactions of 2-oxo aldehydes **11**–**13** were rather slow (75 h) when the hydrate[9–11] or dimeric hemiacetal[12] forms were used.

Products **16**–**19** contain asymmetric centers, and the NMR signals due to the two methylene protons next to cobalt and the four methyl groups on cobaloxime ligand are therefore nonequivalent.[13] The former signals appear as an AB-quartet at δ *ca.* 2.6 and 2.7 and the latter signals appear as two singlets at δ 2.0–2.1.

The reaction of the carbonyl dienophiles **8**–**13** can be regarded as a formal concerted ene-reaction followed by aromatization, but the reaction with acetylenedicarboxylate (**4**) can hardly be a concerted process.

Scheme 5



The reactivities of *N*-phenylmaleimide (**2**) and maleic anhydride (**3**) with cobaloxime **1** (3 h at room temperature) are somewhat higher than the reactivity with 3-methylfuran (6 h in refluxing ether). However, the 1,4-addition did not take place with conventional dienophiles such as benzoquinone, dimethyl maleate, and methyl acrylate, nor with carbonyl dienophiles such as 1,1,1-trifluoroacetophenone and ethyl 2-(4-nitrophenyl)-2-oxoacetate. These features suggest that the present reactions proceed by a different mechanism from a concerted Diels–Alder addition or ene-reaction and can be explained by the mechanism summarized in Scheme 5.

Probable electrophilic attack of the dienophile at the electron rich C_2-position of the furan ring causes the heterolytic fission of the carbon–cobalt bond to give the ion pair (B's in Scheme 5). The reaction with *N*-phenylmaleimide (**2**) and maleic anhydride (**3**) proceed in a formal Diels–Alder mode, and recombination of the cobaloxime cation at the exo-methylene regenerates a primary alkylcobaloxime (**B**). In the reaction with dimethyl acetylenedicarboxylate (**4**), the similar attacking mode as above generates a more strained 7-oxabicyclo-[2.2.1]heptadiene system other than a 7-oxabicyclo[2.2.1]-heptene system, and the cobaloxime cation attacks alternatively the endocyclic double bond to retain the *exo*-methylene (**B'**). Nucleophilicity of an oxygen anion is weak, and the ion pair from the carbonyl dienophiles aromatizes by the attack of cobaloxime cation at the *exo*-methylene with concomitant proton elimination (**B''**). Unfortunately, effect of the solvent on the reaction rate could not be tested due to the poor solubility in nonpolar solvents. Due to these limitations, we cannot eliminate the possibility of a diradical mechanism in place of the ion pair mechanism. The variation found in the reactions of cobaloxime **1** with dienophiles is noteworthy in any case.

Allylstannanes,[14] allylsilanes,[15] and allyliron complexes[16,17] react with dienophiles to give [2 + 3]-adducts. In these reactions the 1,2-rearrangement of the metal

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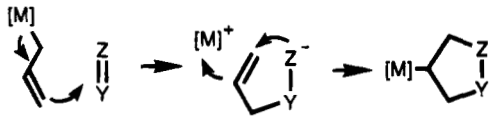
Scheme 6



function occurs together with the cycloaddition (Scheme 6). The reaction of (3-furylmethyl)cobaloxime (**1**), however, involves the 1,3-rearrangement of the metal function or its return to the original site with concomitant cycloaddition.

The reaction reported here opens a new synthetic strategy for the syntheses of oxabicyclo[2.2.1] structure and 2,3-disubstituted furan derivatives.

Experimental Section

General. A flask containing solvent, cobaloxime **1**, and one of the dienophiles was dipped in an ultrasonic bath, and the mixture was deaerated by bubbling argon into the mixture. NMR spectra were measured with $CDCl_3$ as a solvent and tetramethylsilane as an internal standard at 90, 270z, and 400 MHz for ^{1}H-NMR and at 68 MHz for ^{13}C-NMR. Chemical shifts (δ value) are expressed in ppm and the J value are recorded in hertz.

Dienophiles **2**–**4**, **8**, and **9** were commercially available and used without purification. Carbonyl dienophiles **10**,[18] **11**,[12] and **13**[19] were synthesized by the reported methods.

Preparation of Cobaloxime 1. 3-(Bromomethyl)furan was prepared by the method reported previously by us.[7] A mixture of $CoCl_2 \cdot 6H_2O$ (2.4 g, 10 mmol), dimethylglyoxime (2.2 g, 20 mmol), and sodium hydroxide (0.80 g, 20 mmol) in 35 mL of deaerated methanol was stirred for 15 min under ice-cooling, and to the mixture was added 0.81 mL of pyridine (10 mmol) and further stirred for 15 min. The mixture was then treated with the solution of sodium borohydride (190 mg, 5 mmol) and sodium hydroxide (400 mg, 10 mmol) in 5 mL of methanol. After stirring for 30 min under ice-cooling, the reaction mixture was treated with 3-(bromomethyl)furan (1.80 g, 11 mmol) and stirred for 4 h at the same temperature. The mixture was then filtered through Celite powder, concentrated, and subjected to chromatography on Florisil column (35 × 50 mm, chloroform) to remove polar components. The crude product thus obtained was recrystallized from ethanol to yield cobaloxime **1** as orange crystals (3.6 g, 80%): mp. 132–133 °C dec. ^{1}H-NMR (270 MHz) δ 2.03 (12H, s), 2.60 (2H, s), 6.07 (1H, s), 7.13 (1H, s), 7.23 (1H, s), 7.29 (2H, t, J = 6.8), 7.69 (1H, t, J = 6.8), 8.56 (2H, d, J = 6.8), 18.25–18.35 (2H, br s); ^{13}C-NMR (68 MHz) δ 11.97, 112.47, 125.16, 129.54, 137.39, 138.94, 141.31, 149.16, 150.24 (one peak is overlapped); IR(KBr) 3448, 1561, 1451, 1236, 1093, 1012 cm^{-1}. Anal. Calcd for $C_{18}H_{24}N_5O_5Co$: C, 48.11; H, 5.38; N, 15.59. Found: C, 48.21; H, 5.52; N, 15.60.

Reactions of Cobaloxime 1 with *N*-Phenylmaleimide (2), Maleic Anhydride (3), and Dimethyl Acetylenedicarboxylate (4). A flask containing **1** (90 mg, 0.2 mmol) was flushed with argon and one of the dienophiles (**2**, **3**, or **4**) (0.3 mmol) dissolved in 3 mL of alcohol-free dry dichloromethane was added. The reaction mixture was stirred for a certain period (**2**, 3 h; **3**, 5 h; **4**, 4 h) at room temperature. The reaction mixture was concentrated and the residue was subjected to Florisil column chromatography (26 × 60 mm) with chloroform as eluent. The products thus obtained were highly pure but remained amorphous in spite of efforts at crystallization. The structures proposed depend on the synthesis of adduct **5** by an unambiguous route.

5: orange powder; ^{1}H-NMR (270 MHz) δ 2.13 (6H, s), 2.19 (6H, s), 2.22 (2H, s), 2.90 (1H, d, J = 6.6), 2.98 (1H, d, J = 6.6), 4.92 (1H, d, J = 1.3), 4.94 (1H, s), 5.96 (1H, d, J = 1.3), 7.24–7.50 (7H, m), 7.71 (1H, t, J = 6.7), 8.52 (2H, d, J = 6.7), 18.20–18.40 (2H, br s); IR($CHCl_3$) 1775, 1713 cm^{-1}.

6: orange powder; ^{1}H-NMR (90 MHz) δ 2.12 (6H, s), 2.17 (6H, s), 2.21 (2H, s), 3.05 (1H, d, J = 6.8), 3.11 (1H, d, J = 6.8), 4.92 (1H, d, J = 1.3), 4.99 (1H, s), 5.96 (1H, d, J = 1.3), 7.20 (2H, t, J = 6.6), 7.71 (1H, t, J = 6.6), 8.52 (2H, d, J = 6.6), 18.10–18.25 (2H, br s); IR($CHCl_3$) 1736 cm^{-1}.

7: orange powder; ^{1}H-NMR (400 MHz) δ 1.92 (1H, s), 2.16 (6H, s), 2.17 (6H, s), 3.73 (3H, s), 3.75 (3H, s), 4.99 (1H, s), 5.18 (1H, s), 5.32 (1H, s), 5.41 (1H, s), 7.30 (2H, t, J = 6.6), 7.71 (1H, t, J = 6.6), 8.59 (2H, d, J = 6.6), 18.10–18.25 (2H, br s); IR ($CHCl_3$) 1736 cm^{-1}.

Authentic Synthesis of the Adduct 5. A mixture of 3-(bromomethyl)furan (966 mg, 6 mmol) and *N*-phenylmaleimide (866 mg, 5 mmol) in 20 mL of dichloromethane was refluxed for 8 h under an argon atmosphere. Chromatography of the residue after solvent removal on silica gel (26 × 50 mm) to remove polar materials and recrystallization from ethanol gave the adduct: mp 126–128 °C; ^{1}H-NMR (270 MHz) δ 3.12 (1H, d, J = 6.6), 3.30 (1H, d, J = 6.6), 4.17 (2H, s), 5.34 (1H, s), 5.38 (1H, d, J = 1.3), 6.47 (1H, d, J = 1.3), 7.25–7.29 (2H, m); EI-MS (70 eV) m/z = 335 (M$^+$, 2.5%). Anal. Calcd for $C_{15}H_{12}BrNO_3$: C, 53.91; H, 3.62; N, 4.19. Found: C, 54.00; H, 3.52; N, 4.20.

Cobaloximation of the adduct obtained above was carried out in the same manner as for the synthesis of cobaloxime **1** and the obtained product was shown to be identical with the adduct **5** by spectral comparison.

Reactions of Cobaloxime 1 with Diethyl 2-Oxomalonate (8), Hexafluoroacetone (9), Ethyl Glyoxalate (10), 2-Phenyl-2-oxoacetaldehyde (11), 2-(4-Chlorophenyl)-2-oxoacetaldehyde (12), and 2-(4-Nitrophenyl)-2-oxoacetaldehyde (13). A flask containing cobaloxime **1** (90 mg, 0.2 mmol) was flushed with argon and one of the carbonyl compounds **8**–**13** dissolved in 3 mL of alcohol-free dry dichloromethane was added. The reaction mixture was stirred for a certain period (**8**, 6 h; **9**, 8 h; **10**, 6 h; **11**–**13**, 10 h) at room temperature. A workup similar to that for the reaction with olefinic dienophiles and Florisil chromatography gave crystalline products which were purified by recrystallization from ethanol. In the cases of reactions with **11**, **12**, and **13**, secondary products **17**, **18**, and **19** were obtained in crystalline forms from chromatography and purified by recrystallization from ethanol.

14: mp 132–133 °C dec; ^{1}H-NMR (270 MHz) δ 1.23 (6H, t, J = 7.3), 1.99 (12H, s), 2.75 (2H, s), 4.23 (4H, q, J = 7.3), 5.71 (1H, d, J = 1.7), 7.05 (1H, d, J = 1.7), 7.28 (2H, t, J = 6.7), 7.67 (1H, t, J = 6.7), 8.43 (2H, J = 6.7), 13.60–14.30 (3H, br s); IR ($CHCl_3$) 1741, 1603 cm^{-1}. Anal. Calcd for $C_{25}H_{34}N_5O_{10}Co$: C, 48.16; H, 5.50; N, 11.23. Found: C, 47.99; H, 5.69; N, 11.22.

15: mp 150–153 °C dec; ^{1}H-NMR (90 MHz) δ 2.00–2.11 (12H, br s), 2.88 (2H, s), 5.85 (1H, d, J = 1.7), 7.19 (1H, d, J = 1.7), 7.32 (2H, t, J = 6.3), 7.73 (1H, t, J = 6.3), 8.47 (2H, d, J = 6.3), 13.65–13.90 (3H, br s); IR(KBr) 1606, 951 cm^{-1}. Anal. Calcd for $C_{21}H_{24}F_6N_5O_6Co$: C, 40.99; H, 3.93; N, 11.38. Found: C, 41.10; H, 3.99; N, 11.33.

16: mp 135–137 °C dec; ^{1}H-NMR (90 MHz) δ 1.24 (3H, t, J = 7.3), 2.00 (6H, s), 2.10 (6H, s), 2.61 and 2.75 (2H, d, J = 8.2), 4.23 (2H, q, J = 7.3), 5.14 (1H, s), 5.87 (1H, d, J = 1.7), 7.05 (1H, d, J = 1.7), 7.28 (2H, t, J = 6.7), 7.67 (1H, t, J = 6.7), 8.43 (2H, d, J = 6.7), 13.60–14.30 (3H, br s); IR($CHCl_3$) 1602, 1013 cm^{-1}. Anal. Calcd for $C_{22}H_{30}N_5O_8C0$: C, 47.92; H, 5.48; N, 12.70. Found: C, 47.95; H, 5.35; N, 12.79.

17: mp 105–108 °C dec; ^{1}H-NMR (270 MHz) δ 2.10 (12H, s), 2.58 and 2.75 (2H, d, J = 8.4), 5.83 (1H, s), 5.90 (1H, d, J = 2.0), 7.04 (1H, d, J = 2.0), 7.29–7.37 (4H, m), 7.46 (1H, t, J = 7.2), 7.73 (1H, t, J = 6.8), 7.82 (2H, d, J = 7.2), 8.55 (2H, d, J = 6.8), 13.90–14.00 (3H, br s); IR($CHCl_3$) 1700, 1602 cm^{-1}. Anal. Calcd for $C_{26}H_{30}N_5O_7Co$: C, 53.52; H, 5.18; N, 12.00. Found: C, 53.71; H, 5.31; N, 11.93.

18: mp 124–125 °C dec; ^{1}H-NMR (270 MHz) δ 2.09 (6H, s), 2.10 (6H, s), 2.58 and 2.70 (2H, d, J = 8.3), 5.77 (1H, s), 5.90

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(1H, d, J = 1.7), 7.04 (1H, d, J = 1.7), 7.31 (2H, d, J = 8.6), 7.32 (2H, t, J = 6.9), 7.73 (1H, t, J = 6.9), 7.79 (2H, d, J = 8.6), 8.54 (2H, d, J = 6.9), 13.95–14.10 (3H, br s); IR($CHCl_3$) 1709, 1604 cm^{-1}. Anal. Calcd for $C_{26}H_{29}N_5O_7ClCo$: C, 53.52; H, 5.18; N, 12.00. Found: C, 53.71; H, 5.31; N, 11.93.

19: mp 161–164 °C dec; ^{1}H-NMR (90 MHz) δ 2.13 (12H, s), 2.60 (1H, d, J = 8.4), 2.80 (1H, d, J = 8.4), 5.99 (1H, s), 6.16 (1H, d, J = 2.0), 7.21–7.37 (3H, m), 7.72 (1H, t, J = 6.7), 8.34 (4H, s), 8.52 (2H, d, J = 6.7), 13.80–14.45 (3H, br s). The pure **19** could not be obtained for elemental analysis due to the thermal instability and recrystallization from ethanol gave **22** as a degradation product of **19**.

20: mp 81–83 °C; ^{1}H-NMR (270 MHz) δ 2.44 (3H, s), 6.49 (1H, d, J = 1.8), 7.47–7.55 (3H, m) 7.66 (1H, t, J = 7.3), 7.99 (2H, d, J = 7.3); ^{13}C-NMR (68 MHz) δ 11.81, 116.25, 128.95, 129.92, 132.65, 134.74, 135.22, 146.47, 147.64, 183.40, 192.88; IR (KBr) 1675, 1652 cm^{-1}. Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 72.96; H, 4.72.

21: mp 114–115 °C; ^{1}H-NMR (270 MHz) δ 2.44 (3H, s), 6.50 (1H, d, J = 1.7), 7.49 (2H, d, J = 8.6), 7.53 (1H, d, J = 1.7), 7.93 (2H, d, J = 8.6); ^{13}C-NMR (68 MHz) δ 11.86, 116.39, 129.41, 131.07, 131.25, 135.65, 141.45, 146.38, 147.83, 182.73, 191.52; IR (KBr) 1678, 1644 cm^{-1}. Anal. Calcd for $C_{13}H_9O_3Cl$: C, 62.79: H, 3.65. Found: C, 62.66; H, 3.58.

22: mp 139–141 °C; ^{1}H-NMR (270 MHz) δ 2.49 (3H, s), 6.54 (1H, d, J = 1.7), 7.55 (1H, d, J = 1.7), 8.17 (2H, d, J = 8.2), 8.36 (2H, d, J = 8.2); ^{13}C-NMR (68 MHz) δ 11.93, 116.62, 124.10, 130.94, 136.48, 137.10, 146.20, 148.23, 151.14, 181.65, 190.62; IR (KBr) 1687, 1641 cm^{-1}. Anal. Calcd for $C_{13}H_9NO_5$: C, 60.24; H, 3.50; N, 5.40. Found: C, 60.41; H, 3.43; N, 5.37.

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