# Ceric Ammonium Nitrate(CAN)-Mediated Oxidative Cycloaddition of 1,3-Dicarbonyls to Vinyl Sulfides. Application to the Synthesis of Evodone and Avicequinone-B

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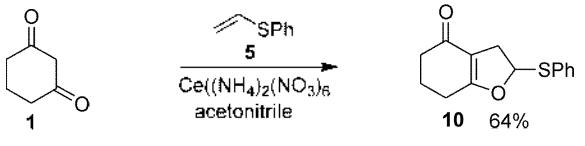
**Key Words :** Ceric ammonium nitrate, 1,3-Dicarbonyls, Vinyl sulfides, Evodone, Avicequinone-B

Oxidative addition reactions mediated by metal salts ($Mn^{III}$, $Ce^{IV}$, $Co^{II}$, and $V^{V}$) have received considerable attention in organic synthesis for the construction of carbon-carbon bonds.[1] Among these, manganese (III) acetate and ceric (IV) ammonium nitrate (CAN) have been used most efficiently. CAN-mediated oxidative cycloaddition of 1,3-dicarbonyl compounds to alkenes,[2] vinyl acetates,[3] enol silyl ethers,[4] and enol ethers[5] has been studied extensively. Although these reactions have aroused great interest in reactions for the synthesis of heterocyclic frameworks, there is little information available on the CAN-mediated oxidative cycloaddition to vinyl sulfides. We have been interested in Ag(I)/Celite-mediated cycloaddition of 1,3-dicarbonyl compounds to several substrates.[6] Recently, we have also reviewed the CAN-mediated oxidative cycloaddition of 1,3-dicarbonyl compounds with conjugated compounds.[7] Following our studies based on the CAN-mediated oxidative cycloaddition, we examined the reactions of 1,3-dicarbonyl compounds with a variety of vinyl sulfides. We report here our results on the CAN-mediated cycloaddition of cyclic 1,3-dicarbonyl compounds to vinyl sulfides. As an application of this methodology, we also describe the total synthesis of natural evodone and avicequinone-B.

## Results and Discussion

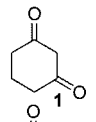
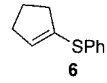
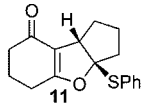
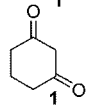
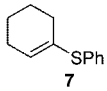
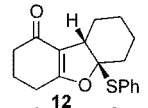
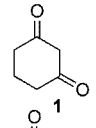
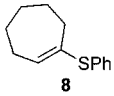
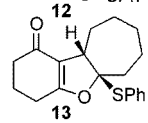
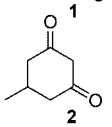
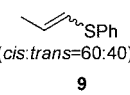
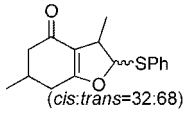
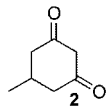
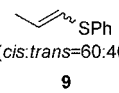
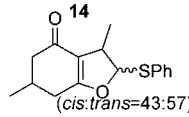
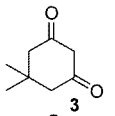
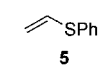
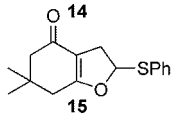
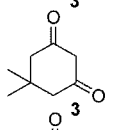
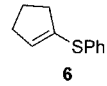
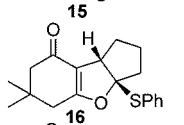
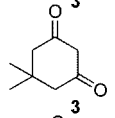
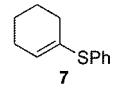
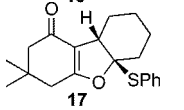
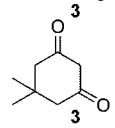
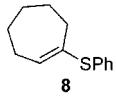
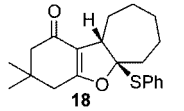
This strategy begins with the reaction of 1,3-dicarbonyls **1-4** and vinyl sulfides **5-9** in the presence of 2.2 equiv of CAN and an excess amount of $NaHCO_3$ in acetonitrile or THF. Reaction of 1,3-cyclohexanedione (**1**) with phenyl vinyl sulfide (**5**) at 0 °C in acetonitrile afforded dihydrofuran **10** in 64% yield (Scheme 1). The formation of **10** is supported by the observation of a carbonyl peak of enone in the IR spectrum at 1640 $cm^{-1}$ and the expected chemical shifts associated with methine proton at $\delta$ 6.09 of the dihydrofuran ring.

Next, other oxidative cycloaddition reactions of several 1,3-dicarbonyl compounds with a variety of vinyl sulfides were investigated. Reactions that were carried out with cyclic vinyl sulfides were also successful. When 1,3-cyclohexanedione (**1**) was treated with vinyl sulfide **6**, cycloadduct **11** was obtained in 57% yield (entry 1). Treatment of **1** with the vinyl sulfide 7 afforded cycloadduct **12** in 81% yield. In large-sized ring systems, cycloaddition reaction was also successful. Treatment of **1** with vinyl sulfide **8** gave




**Scheme 1**

**Table 1.** Reaction of 1,3-dicarbonyl compounds with vinyl sulfides

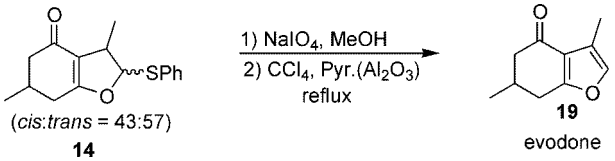
| Entry | 1,3-Dicarbonyl compound | Vinyl sulfide | Solvent | Product | Yield (%) |
|---|---|---|---|---|---|
| 1 |  **1** |  **6** | $CH_3CN$ |  **11** | 57 |
| 2 |  **1** |  **7** | $CH_3CN$ |  **12** | 81 |
| 3 |  **1** |  **8** | $CH_3CN$ |  **13** | 80 |
| 4 |  **2** |  (*cis:trans*=60:40) **9** | $CH_3CN$ |  (*cis:trans*=32:68) | 50 |
| 5 |  **2** |  (*cis:trans*=60:40) **9** | THF |  (*cis:trans*=43:57) | 68 |
| 6 |  **3** |  **5** | $CH_3CN$ |  **15** | 60 |
| 7 |  **3** |  **6** | $CH_3CN$ |  **16** | 58 |
| 8 |  **3** |  **7** | $CH_3CN$ |  **17** | 77 |
| 9 |  **3** |  **8** | $CH_3CN$ |  **18** | 71 |

cycloadduct **13** in 80% yield. The stereochemistry of **11-13** is assigned as *cis* by spectroscopic analysis and by the analogy with the earlier reported data.[8] On the other hand, reaction of **2** with phenyl 1-propenyl sulfide **9** with a 3 : 2 ratio of stereoisomers, demonstrates a moderate solvent dependence. When **2** was treated in acetonitrile (0 °C, 6 h), cycloadduct **14** was obtained in 50% yield as a 32 : 68 mixture of *cis*- and *trans*-isomers (entry 4). When THF was used, the yield was increased to 68%, but the stereoselectivity toward *trans*-isomer was decreased (entry 5). The stereochemical assignment of *cis*- and *trans*-isomers was made by observation of coupling constants between vicinal protons of the dihydrofuran ring. Similarly, reaction of dicarbonyl compound **3** with vinyl sulfides **5-8** gave the expected dihydrofurans **15-18** in 58-77% yields. The results are summarized in Table 1.

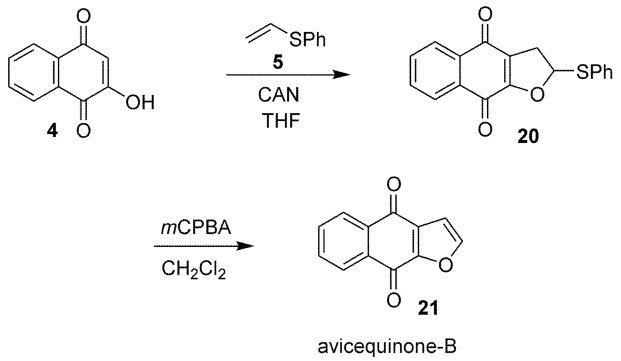
Next, we turned our attention to the synthesis of evodone, a furanomonoterpene isolated from *Evodia hortensis*.[9] Fischer reported that evodone exhibited strong germination inhibitory activities and stimulatory effects towards *Schizachyrium scoparium* seeds.[10] Our conversion to evodone was carried out by the *syn*-elimination of sulfide **14** (Scheme 2). The adduct **14** was first treated with sodium periodate in aqueous methanol at room temperature for 24 h to form the corresponding *cis*- and *trans*-sulfoxide, which upon refluxing for 3 h with pyridine and active alumina in carbon tetrachloride gave evodone **19** (63%, 2 steps). This similar epimerization of *cis*-sulfoxide had been reported by Yoshikoshi.[11] The spectroscopic properties of our synthetic material agreed well with those reported in the literature.[12]

Another application of this methodology to the total synthesis of avicequinone-B was next examined. Recently, avicequinone-B **21** was isolated from the stem bark of *Avicennia alba*.[13] It has been shown to have a great cancer chemopreventive activity against Epstein-Barr virus early antigen (EBV-EA) activation, without showing any cytotoxicity.[14] The synthesis of avicequinone-B was started from the commercially available 2-hydroxy-1,4-naphthoquinone (**4**) (Scheme 3). Reaction of **4** with phenyl vinyl sulfide (2-fold excess) in the presence of 2.2 equivalents of CAN at room temperature for 12 h in THF afforded dihydrofuronaphthoquinone **20** in 53% yield, without formation of any other possible regioisomers. Treatment of **20** with *m*CPBA in $CH_2Cl_2$ at room temperature for 24 h afforded avicequinone-B **21** in 85% yield. The spectroscopic properties of our synthetic material **21** agreed well with those reported in the literature.[13]

In conclusion, CAN-mediated oxidative cycloaddition of 1,3-dicarbonyls to vinyl sulfides is described. This method




**Scheme 2**




**Scheme 3**

provides a simple and efficient synthesis of substituted dihydrofurans, and has also been applied to the synthesis of evodone and furonaphthoquinone natural products.

## Experimental Section

All experiments were carried out under a nitrogen atmosphere. Merck precoated 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 microcover glasses on a Fisher-Johns apparatus and are uncorrected. Proton nuclear magnetic resonance ($^1$H NMR) spectra were recorded on a Bruker Model ARX (300 MHz) spectrometer. IR spectra were recorded on a JASCO FTIR 5300 spectrophotometer. Mass and high resolution mass spectra were obtained with a JEOL JMS-700 spectrometer at the Korea Basic Science Institute.

**General Procedure.** To a solution of 1,3-dicarbonyl compound (1.0 mmol) and vinyl sulfide (2.0 mmol) in acetonitrile (20 mL) or THF (20 mmol) was added CAN (1.206 g, 2.2 mmol) and $NaHCO_3$ (420 mg, 5.0 mmol) at 0 °C or room temperature. The reaction mixture was stirred at 0 °C for 6 h in acetonitrile or for 12 h at room temperature in THF. The mixture was diluted with water and extracted with ethyl acetate (3 × 50 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on silica gel to give product.

**2-Phenylsulfanyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (10)**[6b]. Reaction of 1,3-cyclohexanedione (**1**) (112 mg, 1 mmol) with phenyl vinyl sulfide (**5**) (272 mg, 2 mmol) in acetonitrile (20 mL) afforded **10** (158 mg, 64%) as a liquid: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.54-7.33 (5H, m), 6.09 (1H, dd, $J$ = 9.9, 5.9 Hz), 3.25 (1H, dd, $J$ = 15.5, 9.9 Hz), 2.83 (1H, dd, $J$ = 15.5, 5.9 Hz), 2.45 (2H, m), 2.32 (2H, m), 2.02 (2H, m); IR (neat) 2943, 1640, 1481, 1440, 1394, 1222, 1178, 1058, 1021, 900, 870, 839 cm$^{-1}$.

**8a-Phenylsulfanyl-1,2,3,3a,5,6,7,8a-octahydro-8-oxacyclopenta[*a*]inden-4-one (11).** Reaction of 1,3-cyclohexanedione (**1**) (112 mg, 1 mmol) with vinyl sulfide **6** (352 mg, 2 mmol) in acetonitrile (20 mL) afforded **11** (163 mg, 57%) as a solid:

mp 42-43 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.59-7.56 (2H, m), 7.35-7.26 (3H, m), 3.52 (1H, d, $J$ = 9.1 Hz), 2.41-1.48 (m, 12H); IR (neat) 3057, 2946, 2868, 1638, 1476, 1439, 1399, 1364, 1258, 1213, 1181, 1138, 1055, 1003, 909 cm$^{-1}$; HRMS m/z (M$^+$) calcd for $C_{17}H_{18}O_2S$: 286.1028. Found: 286.1025.

**5a-Phenylsulfanyl-3,4,5a,6,7,8,9,9a-octahydro-2*H*-dibenzofuran-1-one (12)**. Reaction of 1,3-cyclohexanedione (**1**) (112 mg, 1 mmol) with vinyl sulfide 7 (381 mg, 2 mmol) in acetonitrile (20 mL) afforded **12** (243 mg, 81%) as a solid: mp 96-97 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.58-7.53 (2H, m), 7.37-7.29 (3H, m), 3.16 (1H, dd, $J$ = 6.7, 5.9 Hz), 2.41-2.37 (2H, m), 2.27-2.18 (2H, m), 1.98-1.89 (4H, m), 1.60-1.41 (6H); IR (neat) 3057, 2946, 2866, 1638, 1474, 1454, 1439, 1399, 1248, 1181, 1136, 1061, 999 cm$^{-1}$; HRMS m/z (M$^+$) calcd for $C_{18}H_{20}O_2S$: 300.1185. Found: 300.1185.

**9a-Phenylsulfanyl-1,2,3,4b,5,6,7,8,9a-decahydro-10-oxabenzo[*a*]azulen-4-one (13)**. Reaction of 1,3-cyclohexanedione (**1**) (112 mg, 1 mmol) with vinyl sulfide **8** (409 mg, 2 mmol) in acetonitrile (20 mL) afforded **13** (252 mg, 80%) as a solid: mp 80-81 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.55-7.51 (2H, m), 7.42-7.29 (3H, m), 3.21 (1H, d, $J$ = 9.2 Hz), 2.43-2.38 (2H, m), 2.32-2.16 (2H, m), 2.04-1.89 (4H, m), 1.76-1.35 (8H, m); IR (neat) 3057, 2930, 2853, 1642, 1453, 1439, 1397, 1362, 1277, 1256, 1225, 1179, 1136, 1063, 995, 984 cm$^{-1}$; MS (EI) m/z 204 (M$^+$-PhSH) (100), 189 (30), 176 (63), 175 (46), 148 (43), 125 (20), 105 (17), 91 (20), 77 (14), 55 (18).

**3,6-Dimethyl-2-phenylsulfanyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (14)**[6b]. Method A: Reaction of 5-methyl-1,3-cyclohexanedione (**2**) (126 mg, 1 mmol) with phenyl 1-propenyl sulfide **9** (308 mg, 2 mmol) in acetonitrile (20 mL) afforded **14** (137 mg, 50%) as a 32 : 68 mixture of *cis*- and *trans*-isomer: *cis*-isomer; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.55-7.30 (5H, m), 6.10 (1H, d, $J$ = 9.0 Hz), 3.57 (1H, m), 2.53-2.11 (5H, m), 1.36 (3H, d, $J$ = 7.0 Hz), 1.11 (3H, d, $J$ = 7.1 Hz); IR (neat) 2953, 1642, 1439, 1395, 1204, 1138, 1023, 911, 881, 847 cm$^{-1}$. *trans*-isomer: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.53-7.30 (5H, m), 5.55 (1H, d, $J$ = 5.6 Hz), 3.21 (1H, m), 2.53-2.04 (5H, m), 1.31 (3H, d, $J$ = 6.8 Hz), 1.10 (3H, d, $J$ = 6.2 Hz); IR (neat) 2945, 1641, 1397, 1205, 1022, 890 cm$^{-1}$.

Method B: Reaction of 5-methyl-1,3-cyclohexanedione (**2**) (126 mg, 1 mmol) with vinyl sulfide **9** (308 mg, 2 mmol) in THF (20 mL) afforded **14** (188 mg, 68%) as a 43 : 57 mixture of *cis*- and *trans*-isomer.

**6,6-Dimethyl-2-phenylsulfanyl-3,5,6,7-tetrahydro-2*H*-benzofuran-4-one (15)**[6b]. Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**3**) (140 mg, 1 mmol) with phenyl vinyl sulfide (**5**) (272 mg, 2 mmol) in acetonitrile (20 mL) afforded **15** (165 mg, 60%) as a liquid: $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.54-7.31 (5H, m), 6.11 (1H, dd, $J$ = 10.0, 6.1 Hz), 3.27 (1H, dd, $J$ = 15.5, 10.0 Hz), 2.82 (1H, dd, $J$ = 15.5, 6.1 Hz), 2.31 (2H, s), 2.20 (2H, m), 1.08 (3H, s), 1.07 (3H, s); IR (neat) 2953, 1644, 1400, 1304, 1273, 1213, 1167, 1043, 912, 877 cm$^{-1}$.

**6,6-Dimethyl-8a-phenylsulfanyl-1,2,3,3a,5,6,7,8a-octahydro-8-oxacyclopenta[*a*]inden-4-one (16)**. Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**3**) (140 mg, 1 mmol) with vinyl sulfide **6** (353 mg, 2 mmol) in acetonitrile (20 mL) afforded **16** (182 mg, 58%) as a solid: mp 73-74 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.58-7.56 (2H, m), 7.36-7.22 (3H, m), 3.56 (1H, d, $J$ = 8.3 Hz), 2.27-1.91 (6H, m), 1.82-1.75 (2H, m), 1.60-1.45 (2H, m), 1.02 (3H, s), 0.85 (3H, s); IR (neat) 3059, 2959, 2870, 1640, 1472, 1400, 1350, 1302, 1250, 1208, 1163, 1142, 1034, 912 cm$^{-1}$; HRMS m/z (M$^+$) calcd for $C_{19}H_{22}O_2S$: 314.1341. Found: 314.1337.

**3,3-Dimethyl-5a-phenylsulfanyl-3,4,5a,6,7,8,9,9a-octahydro-2*H*-dibenzofuran-1-one (17)**. Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**3**) (140 mg, 1 mmol) with vinyl sulfide 7 (381 mg, 2 mmol) in acetonitrile (20 mL) afforded **17** (253 mg, 77%) as a solid: mp 81-82 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.56-7.52 (2H, m), 7.38-7.22 (3H, m), 3.16 (1H, dd, $J$ = 6.1, 6.0 Hz), 2.27 (2H, m), 2.13 (2H, m), 1.98-1.86 (4H, m), 1.63-1.60 (2H, m), 1.47-1.42 (2H, m), 1.06 (6H, s); IR (neat) 3052, 2955, 2861, 1634, 1439, 1400, 1348, 1298, 1263, 1229, 1167, 1134, 1015, 947 cm$^{-1}$; HRMS m/z (M$^+$) calcd for $C_{20}H_{24}O_2S$: 328.1498. Found: 328.1499.

**2,2-Dimethyl-9a-phenylsulfanyl-1,2,3,4b,5,6,7,8,9a-decahydro-10-oxabenzo[*a*]azulen-4-one (18)**. Reaction of 5,5-dimethyl-1,3-cyclohexanedione (**3**) (140 mg, 1 mmol) with vinyl sulfide **8** (409 mg, 2 mmol) in acetonitrile (20 mL) afforded **18** (242 mg, 71%) as a solid: 102-103 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.55-7.50 (2H, m), 7.37-7.21 (3H, m), 3.21 (1H, d, $J$ = 9.2 Hz), 2.29 (2H, m), 2.16 (2H, m), 1.98-1.90 (4H, m), 1.66-1.38 (6H, m), 1.10 (3H, s), 1.08 (3H, s); IR (neat) 2943, 1640, 1481, 1440, 1394, 1222, 1178, 1058, 1021, 900, 870, 839 cm$^{-1}$; MS m/z 232 (M$^+$-PhSH) (81), 204 (10), 176 (33), 167 (5), 153 (24), 148 (15), 110 (27), 97 (230, 81 (20), 58 (33).

**Evodone (19)**[9]. To a solution of **14** (137 mg, 0.5 mmol) in methanol (10 mL) was added a solution of $NaIO_4$ (214 mg, 1.0 mmol) in water (5 mL) at rom temperature. The reaction mixture was stirred for 24 h at room temperature. After evaporation of solvent, the residue was diluted with water and extracted with ethyl acetate (3 × 30 mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give residue. The residue was dissolved in $CCl_4$ (10 mL) containing active $Al_2O_3$ (500 mg) and pyridine (300 mg) and the mixture was stirred at reflux for 3 h. Removal of solvent gave an oil which was purified by flash column chromatography on silica gel to give **19** (52 mg, 63%) as a solid: mp 70 °C (lit. mp 70-71 °C); $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 7.06 (1H, s), 2.92-2.21 (5H, m), 2.18 (3H, s), 1.14 (3H, d, $J$ = 6.3 Hz); IR (KBr) 3000, 2966, 1662, 1603, 1560, 1456, 1440, 1430, 1410, 1390, 1324, 1242, 1139, 1080, 1045, 1001 cm$^{-1}$.

**2-Phenylsulfanyl-2,3-dihydronaphtho[2,3-b]furan-4,9-dione (20)**. Reaction of 2-hydroxy-1,4-naphtoquinone (**4**) (174 mg, 1 mmol) with phenyl vinyl sulfide (**5**) (272 mg, 2 mmol) in THF (20 mL) afforded **20** (163 mg, 53%) as a solid: mp. 151-152 °C; $^1$H NMR (300 MHz, $CDCl_3$) $\delta$ 8.15-8.02 (2H, m), 7.73-7.64 (2H, m), 7.59-7.57 (2H, m), 7.34-

7.31 (3H, m), 6.26 (1H, dd, $J$ = 10.0, 6.1 Hz), 3.63 (1H, dd, $J$ = 18.2, 10.0 Hz), 3.18 (1H, dd, $J$ = 18.2, 6.1 Hz); IR (KBr) 3059, 2955, 1678, 1645, 1593, 1485, 1391, 1289, 1173, 1092, 999, 897, 789 $cm^{-1}$; HRMS m/z ($M^+$) calcd for $C_{18}H_{12}O_3S$: 308.0508. Found: 308.0508.

**Avicequinone-B (21)**[13]. To a solution of **20** (154 mg, 0.5 mmol) in dichloromethane (5 mL) was added mCPBA (148 mg, 70%, 0.6 mmol) at room temperature and the reaction mixture was stirred under nitrogen for 24 h. Saturated aqueous $NaHCO_3$ solution was added, and the aqueous layer was extracted with dichloromethane ($3 \times 30$ mL). The combined organic extracts were washed with brine, dried ($MgSO_4$), and evaporated under reduced pressure to give the residue. The residue was purified by flash column chromatography on sillica gel (*n*-hexane/ethyl acetate = 5 : 1) to give **21** (84 mg, 85%) as a solid: mp 218-220 °C; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 8.25-8.19 (2H, m), 7.80-7.75 (2H, m), 7.78 (1H, d, $J$ = 1.6 Hz), 7.01 (1H, d, $J$ = 1.8 Hz); IR (KBr) 3111, 1684, 1585, 1555, 1475, 1365, 1207, 951, 777, 713 $cm^{-1}$.

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