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Structural Study on a Naturally Occurring Terphenyl Quinone

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Two terphenyl quinones were synthesized for a structural study on a naturally occurring biologically active terphenyl quinone. 3-Methoxy-5,6-diphenylcyclohexa-3,5-dien-1,2-dione, a possible structure proposed by our analysis of the NMR spectra, was synthesized by Suzuki-Miyaura coupling and subsequent oxidation of the resulting substituted phenol, although not being identical to the natural product. Recently isolated 3-methoxy-2,5-diphenylcyclohexa-2,5-dien-1,4-dione was synthesized from a commercially available 2,5-diphenyl-1,4-benzoquinone in three steps in a good overall yield, and its NMR spectra were identical to those of the natural product.

Key words: terphenyl quinone; structural study; synthesis

Terphenyl is a common structural motif included in various naturally occurring products, largely isolated from microorganisms and mushrooms.[1] The diverse structure and wide variety of biological activities have attracted great attention these natural products.[2,3] In 2006, Singh and co-workers at the Merck company isolated a new *p*-terphenyl *o*-quinone as an amorphous yellow powder from a *Phoma* sp. as an inhibitor of parasite cyclic GMP-dependent protein kinase.[4] Its structure was characterized as that of compound **1** based on an NMR analysis (Fig. 1). The substitution pattern was elucidated by observing NOEs between methoxy protons and quinone proton H-5 and between H-5 and aromatic protons H-2″/H-6″ in the NOE differential spectrum. In the same year, we reported a synthesis of proposed compound **1**, although its NMR spectra were not identical to the reported data.[5] We next proposed that *o*-terphenyl *o*-quinone **2** would be another possible structure which could also explain the NOE data (from methoxy protons to the quinone proton) reported by Singh and co-workers. In order to compare their NMR spectra, we embarked on the synthesis of **2**, although an *o*-terphenyl compound has not been isolated from natural sources.[2,3]

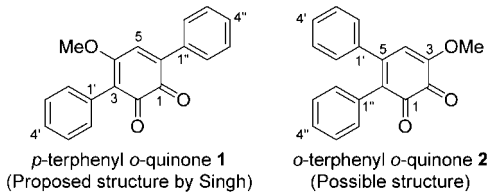
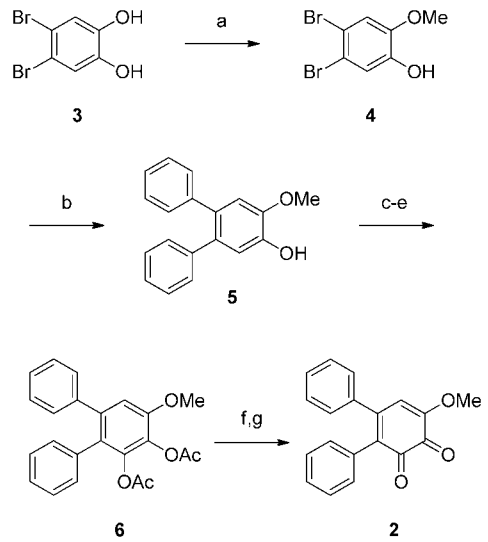


Fig. 1. Structures of *p*-Terphenyl *o*-Quinone **1** and *o*-Terphenyl *o*-Quinone **2**.



Scheme 1. Synthesis of *o*-Terphenyl *o*-Quinone **2**.
Reagents and conditions: (a) K_2CO_3, MeI, DMF, rt, 42%; (b) $PhB(OH)_2$, $Pd(PPh_3)_4$, Na_2CO_3, toluene-H_2O, 100 °C, 80%; (c) *m*CBPO, CH_2Cl_2, rt; (d) $LiAlH_4$, THF, rt; (e) Ac_2O, pyridine, rt, 9% (3 steps from **5**); (f) $LiAlH_4$, THF, rt; (g) Ag_2CO_3/Celite, benzene, rt, 97% (2 steps from **6**).

Results and Discussion

The synthesis of *o*-terphenyl *o*-quinone **2** is summarized in Scheme 1. Known dibromocatechol **3**[6] was monomethylated to obtain **4** which was subjected to the conventional Suzuki-Miyaura cross-coupling conditions with phenylboronic acid, leading to *o*-terphenyl compound **5** in an 80% yield. The key oxidation at the *ortho*-position of phenol **5** was next examined. Such typical oxidation agents of phenol as Fremy's salt ($K_2[NO(SO_3)_2]$)[7] and molecular oxygen under basic conditions were ineffective, this being attributable to steric hindrance around the phenyl group. In addition, the oxidation of **5** using IBX (2-iodoxybenzoic acid),[8] chromic acid, CAN (ceric ammonium nitrate) and benzeneselenic acid anhydride[9] resulted in the formation of the undesired 4,5-diphenyl-1,2-benzoquinone as a major product. Although the oxidation of **5** using *m*CBPO (*m*-chlorobenzoyl peroxide)[10] provided a complex mixture of products, corresponding diacetate **6** was isolated in a 9% yield from the three steps after two-step transformation ($LiAlH_4$ and then Ac_2O in pyridine)

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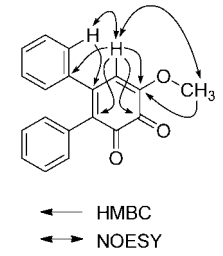


Fig. 2. NMR Spectral Data for *o*-Terphenyl *o*-Quinone **2**.

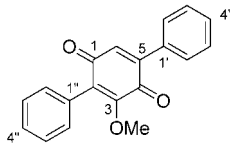
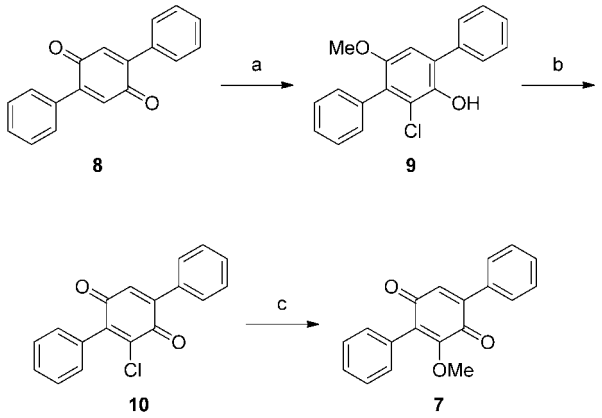


Fig. 3. Structure of *p*-Terphenyl *p*-Quinone **7**.



Scheme 2. Synthesis of *p*-Terphenyl *p*-Quinone **7**.
Reagents and conditions: (a) AcCl, MeOH, rt to 45 °C, 71%; (b) CAN, MeCN, rt, 99%; (c) NaOMe, MeOH, rt, 83%.

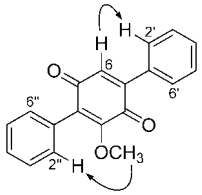


Fig. 4. Observed NOE for Synthesized *p*-Terphenyl *p*-Quinone **7**.

according to the procedure reported by Tada and co-workers.[11] The acetyl groups in **6** were finally removed with $LiAlH_4$, and subsequent oxidation by a freshly prepared Fetizon reagent (Ag_2CO_3 on Celite)[12] gave desired *o*-quinone **2** in a 97% yield from the two steps.

o-Terphenyl *o*-quinone **2** was obtained as an amorphous purple solid, the structure being confirmed by analyses of the NMR spectra, IR spectrum, and high-resolution mass spectrum. Selected 2D NMR spectral data are shown in Fig. 2. It was found that the NMR spectra of **2** were not identical to those of the reported data.[4]

Oberlies and co-workers have recently isolated a *p*-terphenyl compound as an inhibitor of phosphodiesterase 4B from an ascomycete fungus of the order *Chaetothyriales* (MSX 47445).[13] Its structure was assigned to be that of **7** by NMR and X-ray crystallographic analyses.* Since its NMR data were consistent with those of the compound reported by Singh and co-workers, the authors concluded both natural compounds to be the same (Fig. 3). A chemical synthesis of *p*-quinone **7** had not previously been reported, so we therefore synthesized **7** and ascertained the reason for Singh's and our misassignment of the structure.

Commercially available 2,5-diphenyl-1,4-benzoquinone **8** was transformed into chlorophenol **9** with HCl in MeOH in a 71% yield (Scheme 2).[15] Phenol **9** was oxidized by using CAN to provide chloroquinone **10**, this being subjected to sodium methoxide in MeOH to afford desired *p*-terphenyl *p*-quinone **7** in a good overall yield as an orange solid. The NMR spectra of **7** were good agreement with the reported data.[4,13] The NOE differential spectra showed NOEs from quinone proton H-6 to H-2′/H-6′ and from methoxy protons to H-2″/H-6″ (Fig. 4 and Supplemental Figs. 1 and 2; see the *Biosci. Biotechnol. Biochem.* Web site). These observations were also good agreement with those reported by Oberlies and co-workers.[13] It should be noted that no signal enhancement of quinone proton H-6 in the NOE differential spectrum was apparent by irradiating the methoxy protons which was observed by Singh and co-workers, and that the NOESY data showed no correlation between the methoxy protons and quinone proton H-6 (Supplemental Fig. 3).

Conclusions

Two terphenyl quinones, 3-methoxy-5,6-diphenylcyclohexa-3,5-dien-1,2-dione and 3-methoxy-2,5-diphenylcyclohexa-2,5-dien-1,4-dione, were synthesized for a structural study on a naturally occurring terphenyl quinone. The NMR spectra of the latter quinone were identical to those of the natural compound. This result indicates that the structural misassignment of **1** by Singh and co-workers was due to the observed signal enhancement in the NOE differential spectra which may be attributable to noise in the NMR measurements.

Experimental

General information. Infrared spectra (IR) were recorded on a Jasco FT/IR-4100 type A spectrophotometer and are reported in wave number (cm^{-1}). Ultraviolet spectra (UV) were recorded on a Jasco V-530 spectrophotometer and are reported in wave length (nm). Proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on a Varian Gemini-2000 (300 MHz), Bruker ARX-400 (400 MHz), Bruker AVANCE-400 (400 MHz), Bruker AMX-600 (600 MHz), or Jeol ECA-600 (600 MHz) instrument. NMR samples were dissolved in $CDCl_3$, and chemical shifts are reported in ppm relative to tetramethylsilane ($\delta = 0.00$). ^{1}H-NMR data are expressed as chemical shift, integration, multiplicity (s = singlet, m = multiplet), coupling constant(s), and assignment. Carbon nuclear magnetic resonance (^{13}C-NMR) spectra were recorded on a Varian Gemini-2000 (75 MHz), Bruker ARX-400 (100 MHz), or Bruker AVANCE-400 (100 MHz) instrument. NMR samples were dissolved in $CDCl_3$, and chemical shifts are reported in ppm relative to the solvent ($CDCl_3$ as $\delta = 77.0$). Melting point (mp) data were recorded on Yanaco MP-S3 melting point apparatus and are uncorrected. The low-resolution mass spectrum

* Oberlies and co-workers named compound **7** betulinan C in ref. 13, although this name had already been used for a different compound in ref. 14.

(LR-MS) was recorded on a Bruker Esquire 3000 ESI mass spectrometer and is expressed in m/z. High-resolution mass spectra (HR-MS) were recorded on an Applied Biosystems Mariner ESI-TOF spectrometer and are expressed in m/z.

*4,5-Dibromo-2-methoxyphenol (**4**).* To a solution of dibromocatechol **3**[6] (8.10 g, 30.2 mmol) in DMF (91 mL) were added K_2CO_3 (4.13 g, 30.2 mmol) and MeI (1.9 mL, 30.6 mmol) at room temperature under nitrogen. After being stirred at room temperature for 22 h, the reaction was quenched with H_2O. The aqueous layer was extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 12:1 to 6:1 to 1:1) to give **4** (3.57 g, 42%) as a white powder. Mp 91–92 °C (lit.[16] 92–93 °C); IR (KBr) ν_{max} (cm^{-1}): 3388, 1492, 1433, 1264, 1203, 1027, 865, 797; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.18 (1H, s, Ar), 7.06 (1H, s, Ar), 5.57 (1H, s, –OH), 3.88 (3H, s, –OMe); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 146.4, 145.6, 119.1, 115.5, 115.4, 113.8, 56.3; LR-MS (ESI, negative): calcd. for $C_7H_5Br_2O_2$ (M − H), 279; found, 279. The NMR data for **4** are identical to the reported data.[16]

*2-Methoxy-4,5-diphenylphenol (**5**).* To a solution of **4** (900 mg, 3.19 mmol) in toluene (9 mL) was added a solution of Na_2CO_3 (2.0 M in H_2O, 2.3 mL, 4.7 mmol) at room temperature. The resulting mixture under nitrogen was degassed three times by freezing the mixture under reduced pressure. To the resulting mixture were added $PhB(OH)_2$ (819 mg, 6.73 mmol) and $Pd(PPh_3)_4$ (370 mg, 0.306 mmol). After being stirred at 100 °C overnight, the reaction was quenched with H_2O. The aqueous layer was extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was separated by silica gel column chromatography (hexane/EtOAc = 4:1) to give **5** (704 mg, 80%) as a white solid. Mp 147–148 °C (lit.[17] 146–148 °C); IR (KBr) ν_{max} (cm^{-1}): 3290, 1487, 1156, 1031, 1014, 767, 701; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.24–7.08 (10H, m, Ph), 7.04 (1H, s, Ar), 6.92 (1H, s, Ar), 5.64 (1H, s, –OH), 3.96 (3H, s, –OMe); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 145.8, 144.8, 141.6, 141.1, 133.8, 132.6, 129.94, 129.91, 127.83, 127.76, 126.2, 116.6, 113.0, 56.1; HR-MS (ESI, positive): calcd. for $C_{19}H_{16}O_2Na$ (M + Na), 299.1043; found, 299.1028. The NMR data for **5** are identical to the reported data.[17]

4,5-Diphenyl-1,2-benzoquinone. To a stirred solution of benzeneseleninic anhydride (16.6 mg, 0.0461 mmol) in THF (1 mL) was added a solution of **5** (10.2 mg, 0.0369 mmol) in THF (2 mL) at room temperature under nitrogen. After being stirred at 50 °C for 18 h, the reaction was quenched with a saturated aqueous solution of $NaHCO_3$ at room temperature. The aqueous layer was extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The residue was separated by preparative thin-layer chromatography (hexane/EtOAc = 9:1) to give 4,5-diphenyl-1,2-benzoquinone (5.9 mg, 61%) as a brown oil. IR (KBr) ν_{max} (cm^{-1}): 1661, 1355, 1283, 862, 769, 700; UV (MeOH) λ_{max} (log ε): 206 (4.53), 225 (4.31), 277 (3.92), 349 (3.36) nm; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ (ppm): 7.38–7.29 (2H, m, Ph), 7.29–7.20 (4H, m, Ph), 7.08–7.00 (4H, m, Ph), 6.54 (2H, s, Ar); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ (ppm): 180.1, 153.9, 137.0, 129.6, 129.3, 128.4, 128.2; HR-MS (ESI, positive): calcd. for $C_{18}H_{12}O_2Na$ (M + Na), 283.0730; found, 283.0724.

*1,2-Diacetoxy-3-methoxy-5,6-diphenylbenzene (**6**).* To a solution of **5** (50 mg, 0.18 mmol) in CH_2Cl_2 (5 mL) was added *m*CBPO (134 mg, 0.431 mmol) at room temperature under nitrogen. After being stirred at room temperature for 18 h, the reaction was quenched with a saturated aqueous solution of $Na_2S_2O_3$. The aqueous layer was extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated.

The residue was dissolved in THF (5.5 mL) and to the resulting solution was added $LiAlH_4$ (23 mg, 0.61 mmol) at 0 °C under nitrogen. The resulting mixture was warmed to room temperature, and then stirred at room temperature for 3 h. The reaction was quenched with H_2O at 0 °C. The aqueous layer was extracted with EtOAc. The organic layer was successively washed with 1 M HCl, a saturated aqueous solution of $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, and concentrated.

The residue was dissolved in pyridine (1.5 mL) and to the resulting solution was added Ac_2O (0.75 mL) at room temperature. After being stirred at room temperature for 1.5 h, the reaction was quenched with 1 M HCl. The aqueous layer was extracted with EtOAc. The organic layer was successively washed with 1 M HCl, a saturated aqueous solution of $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was purified by silica gel column chromatography (hexane/EtOAc = 9:1) and preparative thin-layer chromatography (toluene:Et_2O = 3:1) to afford diacetate **6** (6.2 mg, 9% yield from the 3 steps) as an amorphous white solid. IR (KBr) ν_{max} (cm^{-1}): 1777, 1483, 1369, 1346, 1208, 1105, 1096, 736, 704; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.20–7.13 (6H, m, Ph), 7.10–7.07 (2H, m, Ph), 7.05–7.01 (2H, m, Ph), 6.94 (1H, s, Ar), 3.90 (3H, s, –OMe), 2.33 (3H, s, Ac), 1.96 (3H, s, Ac); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 168.2, 167.8, 150.8, 141.3, 140.3, 139.7, 135.1, 130.5, 129.5, 127.7, 127.6, 127.5, 126.7, 126.6, 126.3, 111.6, 56.1, 20.2, 19.9; HR-MS (ESI, positive): calcd. for $C_{23}H_{20}O_5Na$ (M + Na), 399.1203; found, 399.1214.

*3-Methoxy-5,6-diphenylcyclohexa-3,5-dien-1,2-dione (**2**).* To a solution of diacetate **6** (4.0 mg, 0.011 mmol) in THF (0.5 mL) was added $LiAlH_4$ (1.6 mg, 0.044 mmol) at 0 °C under nitrogen. After being stirred at room temperature for 1 h, the reaction was quenched with H_2O at 0 °C. The aqueous layer was extracted with EtOAc. The organic layer was successively washed with 1 M HCl, a saturated aqueous solution of $NaHCO_3$ and brine, dried over anhydrous $MgSO_4$, and concentrated to give a crude catechol.

To a solution of this crude catechol in benzene (1 mL) was added a freshly prepared Fetizon reagent[12] (34 mg, 0.060 mmol) at room temperature under nitrogen. After being stirred at room temperature for 1.5 h, the reaction mixture was filtered and concentrated to give **2** (3.0 mg, 97% for the 2 steps) as an amorphous purple solid. IR (KBr) ν_{max} (cm^{-1}): 1697, 1665, 1649, 1624, 1337, 1096, 1074, 719, 698; UV (MeOH) λ_{max} (log ε): 206 (4.76), 229 (4.48), 350 (3.66) nm; ^{1}H-NMR ($CDCl_3$, 600 MHz) δ (ppm): 7.29–7.24 (3H, m, H-3′ and H-4′), 7.20–7.18 (3H, m, H-3″ and H-4″), 7.16–7.14 (2H, m, H-2′), 6.97–6.96 (2H, m, H-2″), 6.22 (1H, s, H-4), 3.84 (3H, s, –OMe); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 178.6, 174.8, 151.8, 149.5, 138.9, 133.1, 131.7, 130.9, 129.1, 128.4, 128.3, 127.9, 127.6, 114.0, 56.0; HR-MS (ESI, positive): calcd. for $C_{19}H_{14}O_3Na$ (M + Na), 313.0835; found, 313.0824.

*2-Chloro-4-methoxy-3,6-diphenylphenol (**9**).* MeOH (60 mL) and AcCl (1.3 mL, 18.3 mmol) were mixed at 0 °C for 30 min. To this solution was added 2,5-diphenyl-1,4-benzoquinone **8** (330 mg, 1.27 mmol) at 0 °C, and then the resulting mixture was stirred at room temperature for 12 h and at 45 °C for 20 h. After being cooled to room temperature, the volatile compounds were evaporated. The residue was separated by silica gel column chromatography (hexane/CH_2Cl_2 = 2:1) to give **9** (280.1 mg, 71%) as a white solid. Mp 192–193 °C; IR (KBr) ν_{max} (cm^{-1}): 1401, 1215, 1192, 1045, 837, 756, 696; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.63–7.60 (2H, m, Ph), 7.52–7.42 (8H, m, Ph), 6.89 (1H, s, Ar), 5.51 (1H, s, –OH), 3.70 (3H, s, –OMe); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 151.0, 142.7, 137.5, 135.2, 130.2, 129.5, 129.2, 128.5, 128.04, 127.96, 127.8, 127.7, 121.2, 112.5, 56.6; HR-MS (ESI, positive): calcd. for $C_{19}H_{15}O_2NaCl$ (M + Na), 333.0653; found, 333.0639.

*3-Chloro-2,5-diphenylcyclohexa-2,5-dien-1,4-dione (**10**).* To a solution of **9** (40.5 mg, 0.130 mmol) in MeCN (8 mL) was added CAN (139 mg, 0.254 mmol) at room temperature. After being stirred at room temperature for 10 min, the reaction was quenched with H_2O. The aqueous layer was extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated. The residue was separated by silica gel column chromatography (hexane/CH_2Cl_2 = 3:2 to 1:1) to give **10** (38.1 mg, 99%) as a yellow solid. Mp 174–178 °C; IR (KBr) ν_{max} (cm^{-1}): 1666, 1644, 1444, 1417, 756, 693; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.57–7.45 (8H, m, Ph), 7.37–7.33 (2H, m, Ph), 7.01 (1H, s, Ar); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 184.4, 179.4, 145.9, 143.4, 140.9, 132.7, 132.4, 130.9, 130.5, 129.7, 129.6, 129.3, 128.6, 128.1; HR-MS (ESI, positive): calcd. for $C_{18}H_{11}O_2NaCl$ (M + Na), 317.0340; found, 317.0326.

*3-Methoxy-2,5-diphenylcyclohexa-2,5-dien-1,4-dione (**7**).* To a solution of **10** (38.1 mg, 0.130 mmol) in MeOH (8 mL) was added a solution of NaOMe (a 0.87 M solution in MeOH, 1.5 mL, 0.13 mmol) at room temperature. After being stirred at room temperature for 20 min, to the reaction mixture was added sodium methoxide (a 0.87 M solution in MeOH, 0.1 mL, 1 μmol). After being stirred at room temperature for 10 min, the reaction was quenched with a saturated aqueous solution of NH_4Cl. The aqueous layer was extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated. The residue was separated by silica gel column chromatography (hexane/CH_2Cl_2 = 1:1 to 1:2) to give **7** (31.7 mg, 83%) as an orange solid, together with recovered **10** (2.7 mg, 7%). Mp 167–170 °C; IR (KBr) ν_{max} (cm^{-1}): 1660, 1640, 1266, 1092, 766, 707, 691; UV (MeOH/THF, 1:1) λ_{max} ($\log \varepsilon$): 211 (4.29), 236 (4.29), 331 (3.82) nm; ^{1}H-NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.55–7.51 (2H, m, Ph), 7.48–7.38 (6H, m, Ph), 7.37–7.32 (2H, m, Ph), 6.90 (1H, s, Ar), 3.82 (3H, s, –OMe); ^{13}C-NMR ($CDCl_3$, 100 MHz) δ (ppm): 187.1, 183.1, 155.2, 144.3, 132.8, 132.5, 130.5, 130.02, 130.00, 129.2, 128.7, 128.5, 127.9, 61.4; HR-MS (ESI, positive): calcd. for $C_{19}H_{14}O_3Na$ (M + Na), 313.0835; found, 313.0835.

Acknowledgments

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