

Combined Suzuki Coupling – Wittig Olefination Reaction in Aqueous Medium

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Bromoarene carbaldehydes and bromoheteroarene carbaldehydes underwent a one-pot Suzuki cross coupling and Wittig olefination in aqueous medium to give compounds with extended π -systems.

Key words: Suzuki Cross Coupling, Wittig Olefination, Aqueous Medium, One Pot Reaction

Introduction

One-pot, multicomponent reactions are of interest as they often lead to reduction of solvent and necessitate less time for work-up than the corresponding consecutive reaction sequence. Recently, we have shown examples of such multicomponent reactions in form of one-pot Wittig olefinations combined with metal catalysed cross-coupling reactions [1]. Thus far, these reactions have been carried out in organic solvents such as THF, dioxane or DME or in biphasic media [1]. In the following, a protocol for a combined Suzuki-Miyaura coupling – Wittig olefination procedure in purely aqueous medium is forwarded.

Stabilized and semi-stabilized Wittig reagents react only very slowly with water, even at elevated temperatures [2]. Therefore, it is possible to carry out Wittig olefinations with these phosphoranes in aqueous [3] or in biphasic medium [4]. In fact we and other authors have shown that water is an effective medium for the reaction of such phosphoranes, especially with carbaldehydes. This may be due to the high relative concentrations of carbonyl component and phosphorane in organic droplets formed by the two components within the aqueous medium. Nevertheless, due to the generally low reactivity of carbonylmethylidenephosphoranes such as **3a** and **3c**, these more stabilized phosphoranes undergo Wittig olefination only with very reactive ketones [5], even under these conditions.

Suzuki cross coupling reactions have been reported to occur in aqueous medium [6, 7], although the bulk

of such transformations has been carried out in various organic solvents [8], where usually the presence of at least a small amount of water [8] is needed, or in a biphasic medium. A number of different palladium catalysts have been forwarded for the Suzuki cross coupling reactions in water, where in certain cases also additives have been used as mass transfer promoters [9].

While both Wittig olefination and Suzuki cross coupling are known to proceed in water, the combination of Wittig olefination and Suzuki cross coupling reaction in an aqueous medium has not yet been studied. Here, the authors report on the scope and limitations of a one-pot protocol in water. A number of commercially available palladium compounds were screened as catalysts for this transformation.

Results

Initially, bromoarene (or heteroarene) carbaldehydes were reacted with a number of areneboronic acids and stabilized and semi-stabilized phosphoranes/phosphonium salts, utilizing bis(triphenylphosphanyl)palladium(II) dichloride [10] as catalyst precursor in an aqueous Na₂CO₃ solution. Additional triphenylphosphane (2 equiv. for every equiv. of catalyst) was added. As phosphoranes, stabilized acyl-substituted **3a** and **3c** were used as well as (alkoxycarbonyl)methylidene(triphenyl)phosphoranes **3b** and **3e**. Semi-stabilized benzyldiene(triphenyl)phosphorane was used in form of its phosphonium bromide. The reactions with *p*-bromobenzaldehyde (**2a**) and 5-

Table 1. Scope of the one pot Suzuki cross-coupling / Wittig olefination in aqueous medium.


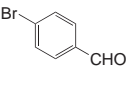

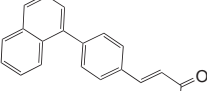
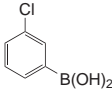
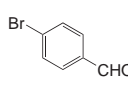

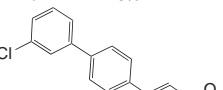

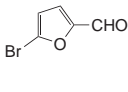

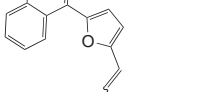
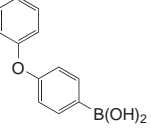
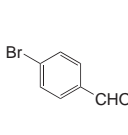
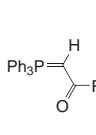
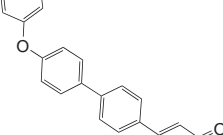
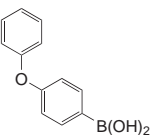
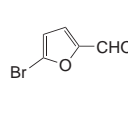
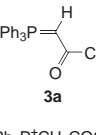
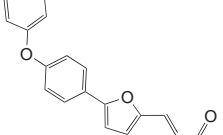
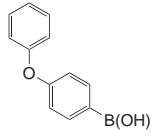
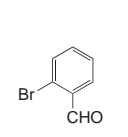
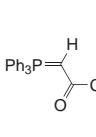
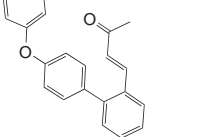
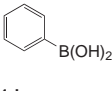
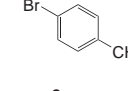

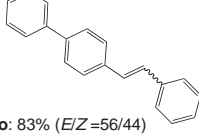
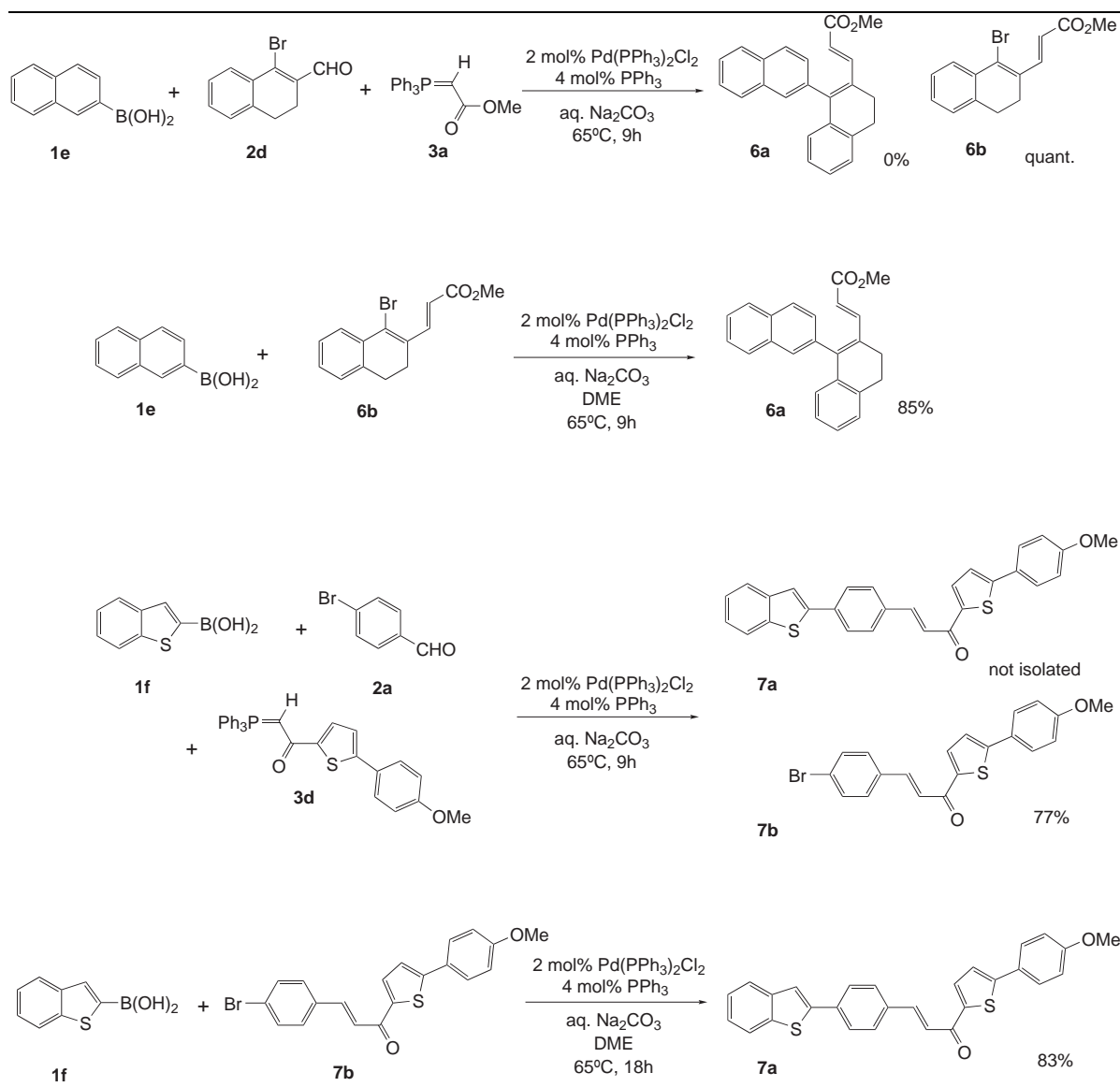
$\text{Ar}^1\text{-B(OH)}_2$ 1	+ Br- $\text{Ar}^2\text{-CHO}$ 2	+ $\text{Ph}_3\text{P=CHR}^2$ 3	$\xrightarrow[\text{65}^\circ\text{C, 9h}]{\text{aq. Na}_2\text{CO}_3}$ 2 mol% Pd(PPh ₃) ₂ Cl ₂ 4 mol% PPh ₃	$\text{Ar}^1\text{-Ar}^2\text{HC=CHR}^1$ 4
 1a	 2a	 3a: R = CH ₃ 3b: R = OCH ₃ 3c: R = Ph		 4a: R = CH ₃ : 93% 4b: R = OCH ₃ : 99% 4c: R = Ph: 78%
 1b	 2a	 3a / 3c		 4d: for R = CH ₃ : 85% 4e: for R = Ph: 64%
 1a	 2b	 3a - 3c		 4f: for R = CH ₃ : 87% (only <i>E</i> -isomer) 4g: for R = OCH ₃ : 87% (<i>E</i> -); 11% (<i>Z</i> -) 4h: for R = Ph: 39% (only <i>E</i> -isomer)
 1c	 2a	 3a - 3c		 4i: for R = CH ₃ : 69% 4j: for R = Ph: 49% 4k: for R = OCH ₃ : 78%
 1c	 2b	 3a 5a: $\text{Ph}_3\text{P}^+\text{CH}_2\text{COCH}_3\text{Cl}^-$		 4m with phosphorane: 88% 4m with phosphonium salt: quant.
 1c	 2c	 3a		 4n: 49%
 1d	 2a	 5b: $\text{Ph}_3\text{P}^+\text{CH}_2\text{Ph Br}^-$		 4o: 83% (<i>E/Z</i> = 56/44)

Table 2. Limitation of the one pot Suzuki cross-coupling / Wittig olefination in aqueous medium.

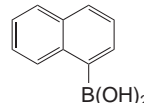
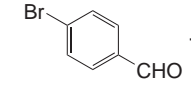
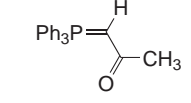
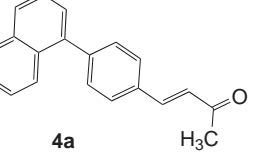
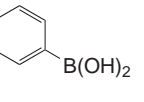
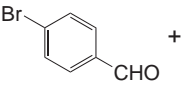
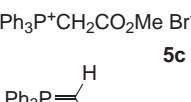
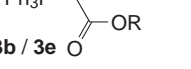
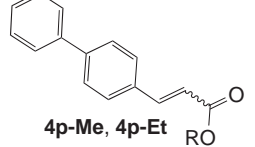
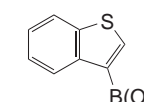
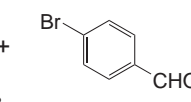
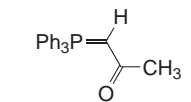
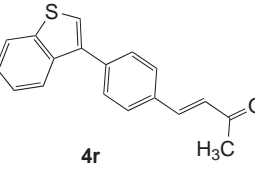
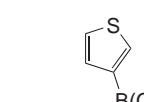
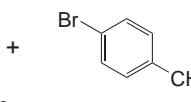
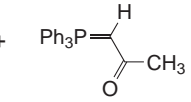
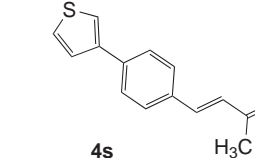


bromothien-2-yl carbaldehyde (**2b**) gave the desired products, where alkoxy carbonyl substituted **3b** and acetyl substituted **3a** gave similarly good yields and the yields with phenacyl substituted **3c** were slightly lower (Table 1). In all cases, the keto-carbonyl substituted phosphoranes **3a** and **3c** gave only *E*-alkenes, while alkoxy carbonyl substituted **3b** and **3d** usually gave *E/Z*-isomeric mixtures in varying proportions. When bromofuran carbaldehyde (**2b**) was used as a building block, more *Z*-isomer (**Z-4g**, 11%) was formed

than with *p*-substituted benzaldehydes, probably due to the directing effect of the furan oxygen. The semi-stabilized benzylidene(triphenyl)phosphorane, gained from **5b**, shows little stereoselectivity (**E-4o:Z-4o** = 56:44) as would be expected under the conditions used. However, **E**- and **Z-4o** can be separated by simple column chromatography on silica gel (hexane).

o-Formylarylhalides are known to give poorer yields in reactions such as these. In the case of 2-bromobenzaldehyde (**2c**), the desired product **4n**

Table 3. Screening of different Pd-catalysts for the one pot Suzuki cross-coupling / Wittig olefination procedure in aqueous medium.

 1a	 2a	 3a	$\xrightarrow[\text{cat.}]{\text{aq. Na}_2\text{CO}_3}$ Pd(PPh ₃) ₂ Cl ₂ /PPh ₃ : 93% PdCl ₂ : 50% Pd/C: 31% (10w% Batch B62685C)	 4a
 1d	 2a	 5c  3b / 3e	$\xrightarrow[\text{cat.}]{\text{aq. Na}_2\text{CO}_3}$ Pd(PPh ₃) ₂ Cl ₂ /PPh ₃ : R = Me, with phosphonium salt 5c : 90%; <i>E/Z</i> 97/3 R = Me, with phosphorane 3b : 92%, <i>E/Z</i> 9/1 with phosphorane 3b : 89%; <i>E/Z</i> 97/3 Pd(acac) ₂ : R = Me, with phosphorane 3b : 87%; <i>E/Z</i> 97/3 Pd(OAc) ₂ : R = Me, with phosphorane 3b : 56%; <i>E/Z</i> 97/3 Pd/C: R = Et, with phosphorane 3e : 63%; only <i>E</i> -isomer detected Pd(OH) ₂ :	 4p-Me, 4p-Et
 1g	 2a	 3a	$\xrightarrow[\text{cat.}]{\text{aq. Na}_2\text{CO}_3}$ Pd(PPh ₃) ₂ Cl ₂ /PPh ₃ : 67% PdCl ₂ : 19% Pd/C: 53% (10w% Batch B62685C)	 4r
 1h	 2a	 3a	$\xrightarrow[\text{cat.}]{\text{aq. Na}_2\text{CO}_3}$ Pd(PPh ₃) ₂ Cl ₂ /PPh ₃ : 90% PdCl ₂ : 34% Pd/C: 32% (10w% Batch B62685C)	 4s

formed only in 49% yield. Here, interestingly only **E-4n** was isolated, although it is known that **2c** gives appreciable amounts of *Z*-product (in CHCl_3 : quant. yield, *E* : *Z* = 9 : 1), when subjected solely to the Wittig reaction.

In two instances the one-pot transformation failed to proceed (Table 2). Thus, 1-bromo-2-formyl-3,4-dihydronaphthalene (**2d**) undergoes no Suzuki coupling under these conditions, and only the Wittig product **6b** can be isolated. In this case, some of the naphthaleneboronic acid **1e** is hydrolysed, but also binaphthyl is formed as the homo-coupling product. Compound **6b**, however, undergoes Suzuki coupling with naphthalene-2-boronic acid (**1e**) in a biphasic system of DME and aq. Na_2CO_3 . Also, the reaction of *p*-bromobenzaldehyde (**2a**) with benzothiophene-2-boronic acid **1f** and phosphorane **3d** [1a] did not give the desired product. Here, again only the Wittig product forms, which can be filtered off from the ether extract of the reaction mixture. In all the cases discussed, the Wittig olefination is the faster reaction. That the Suzuki reaction proceeds generally with benzothiophene-2-boronic acid (**1f**) can be seen in the fact, that when **2a** is used in a slight excess over phosphorane **3d**, the Suzuki coupling product of **2a** and **1f**, 2-(4-formylphenyl)benzothiophene, can be isolated. Wittig product **7b** is very sparingly soluble in aqueous medium and most organic solvents, and it has a high melting point, making it difficult for the Suzuki cross-coupling to proceed. Again, a biphasic Suzuki reaction of **7b** in DME / aq. Na_2CO_3 gives **7a**, albeit after a prolonged reaction time (18 h, 65 °C). Also, **7a** is sparingly soluble in many organic solvents and can be filtered off from the ether extract of the reaction mixture.

A number of different palladium catalysts (2 mol% Pd vs. the halide) were screened for this one-pot Wittig olefination – Suzuki cross coupling protocol in aqueous medium. Of these, the aforementioned $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and $\text{Pd}(\text{acac})_2$ gave the best results. Slightly lower yields were found for $\text{Pd}(\text{OAc})_2$. The exchange of phosphorane to phosphonium salt did not change yield or *E/Z* selectivity of the reaction appreciably, when $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{PPh}_3$ was used as catalyst (Table 3). A fair yield (**E-4p-Et**, 63%) was found with $\text{Pd}(\text{OH})_2$ (Pearlman's catalyst), a catalytic system not often used in metal catalysed cross-coupling reactions. PdCl_2 and Pd/C showed lower and more variable yields. It must be noted that the Pd/C used was from a commercial source [11], where the reactivity of dif-

ferent commercially available Pd/Cs may vary in their catalytic activity.

In conclusion, the authors have shown a novel one pot Wittig-olefination / Suzuki cross coupling protocol in aqueous medium. Phosphoranes suitable for the reaction must either be stabilized or semi-stabilized. Best results were found for haloarene carbaldehyde (halo-hetarene carbaldehyde) that are either liquid or have a low melting point. Melting point or hydrophobicity of the boronic acid and/or phosphorane do not play a large role for the outcome of the reaction. Important is a relative good solubility of the initial Wittig product in either organic or aqueous media, as due to the different kinetics of Wittig reaction and Suzuki cross coupling reaction for the most part the Wittig olefination proceeds the Suzuki cross-coupling. $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2/\text{PPh}_3$ and $\text{Pd}(\text{acac})_2$ as catalysts give good results, but the reaction also proceeds with a number of other Pd catalysts.

Experimental Section

General: Boronic acids **1a–h** and aldehydes **2a–c** were purchased from Aldrich. Phosphoranes **3b**, **3e** [12], **3a**, **3c** [13], **3d** [1a], and the phosphonium salts **5a** [13], **5b** [14] and **5c** [12] were synthesized according to literature procedures. 1-Bromo-2-formyl-3,4-dihydronaphthalene (**2d**) was synthesized from α -tetralone (Aldrich) by Arnold-Vilsmeier reaction [15]. The palladium catalysts were obtained commercially: Pd/C (Kishida), PdCl_2 (Wako), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (Aldrich), $\text{Pd}(\text{OAc})_2$ (Kishida), $\text{Pd}(\text{OH})_2$ (Aldrich), $\text{Pd}(\text{acac})_2$ (Aldrich).

Melting points were measured on a Yanaco microscopic hotstage and are uncorrected. IR spectra were measured with JASCO IR-700 and Nippon Denshi JIR-AQ20M machines. ^1H and ^{13}C NMR spectra were recorded with a JEOL EX-270 (^1H at 270 MHz and ^{13}C at 67.8 MHz) and JEOL Lambda 400 spectrometer (^1H at 395 MHz and ^{13}C at 99.45 MHz). In some cases, the assignment of the carbon signals was aided by DEPT (distortionless enhancement by polarisation transfer) measurements, where (+) denotes either primary or tertiary carbons, (–) secondary carbons and (C_{quat}) quaternary carbons. The chemical shifts are relative to TMS (solvent CDCl_3 , unless otherwise noted). Mass spectra were measured with a JMS-01-SG-2 spectrometer [electron impact mode (EI), 70 eV or fast atom bombardment (FAB)]. Column chromatography was carried out on Wakogel 300. All reactions were run under an inert atmosphere.

General procedure

4-[5'-(4''-Phenoxyphenyl)furan-2'-yl]but-3-en-2-one (**4m**): A deaerated mixture of 5-bromofuran-2-yl carbalde-

hyde (**2b**) (350 mg, 2.0 mmol), acetylmethylidenetriphenylphosphorane (**3a**) (1.2 g, 3.7 mmol), 4-phenoxybenzene boronic acid (**1c**) (760 mg, 3.5 mmol), Pd(PPh₃)₂Cl₂ (28 mg, 4 · 10⁻² mmol), and triphenylphosphane (21 mg, 8 · 10⁻² mmol) in aq. Na₂CO₃ (1.4 M, 15 ml) was held at 65 °C for 9 h. Thereafter, the reaction mixture was cooled and extracted with chloroform (3 × 15 ml). The organic phase was dried over anhydrous MgSO₄ and concentrated *in vacuo*. The residue was subjected to column chromatography on silica gel (hexane/ether/CHCl₃ 3:1:1) to give **4m** (535 mg, 88%) as a yellow solid; m.p. 95 °C. – IR (KBr): ν = 1655, 1626, 1589, 1486, 1023, 965, 791, 754 cm⁻¹. – ¹H NMR (270 MHz, CDCl₃): δ = 2.35 (s, 3H, CH₃), 6.67 (d, 1H, ³J = 3.5 Hz), 6.68 (d, 1H, ³J = 15.6 Hz), 6.74 (d, 1H, ³J = 3.5 Hz), 7.02–7.08 (m, 4H), 7.14 (m, 1H), 7.25–7.40 (m, 3H), 7.69 (d, 2H, ³J = 8.6 Hz). – ¹³C NMR (67.8 MHz, CDCl₃): δ = 27.5, 118.8, 121.3, 126.1, 126.6, 126.8, 127.6, 128.9, 129.6, 132.2, 133.2, 137.9, 141.3, 141.9, 142.9, 198.3. – MS (EI, 70 eV): m/z (%) = 304 (100) [M⁺], 289 (79) [M⁺–CH₃]. – HRMS (EI): found: 304.1099; calcd. for C₂₀H₁₆O₃: 304.1099. – C₂₀H₁₆O₃ (304.3): calcd. C 78.93, H 5.30; found C 78.86, H 5.29.

Physical and spectroscopic characterisation for the other products obtained: *E*- and *Z*-4-phenylstilbenes, **E-4o** [16a] and **Z-4o** [16b], as well as methyl *E*-phenylcinnamate (**E-4p-Me**) [17] and ethyl *E*-phenylcinnamate (**E-4p-Et**) [1d] have been described previously.

4-[4-(Naphthalen-1-yl)phenyl]but-3-en-2-one (**4a**): Colorless solid, m.p. 85 °C. – IR (KBr): ν = 1658, 1618, 1255, 1177, 994, 803, 778 cm⁻¹. – ¹H NMR (270 MHz, CDCl₃): δ = 2.43 (s, 3H, CH₃), 6.81 (d, 1H, ³J = 16.2 Hz), 7.42–7.94 (m, 10H), 7.67 (d, 2H, ³J = 8.1 Hz). – ¹³C NMR (67.8 MHz, CDCl₃): δ = 27.6, 125.4, 125.7, 125.9, 126.3, 126.9, 127.2, 128.1, 128.2 (2C), 128.4, 130.7 (2C), 131.3, 133.4, 133.8, 139.2, 143.1, 143.2, 198.4. – MS (EI, 70 eV): m/z (%) = 272 (100) [M⁺], 257 (28), 228 (32), 202 (26). – HRMS (EI): found 272.1200; calcd. for C₂₀H₁₆O: 272.1201.

Methyl (*E*)-*p*-(Naphthalen-1-yl)cinnamate (**4b**): Colorless solid, m.p. 123 °C. – IR (KBr): ν = 3040, 2942, 1712, 1631, 1503, 1435, 1323, 1196, 1172, 1013, 996, 839, 802, 781 cm⁻¹. ¹H NMR (270 MHz, CDCl₃): δ = 3.84 (s, 3H, COOCH₃), 6.52 (d, 1H, ³J = 15.9 Hz), 7.35–7.86 (m, 7H), 7.53 (d, 2H, ³J = 8.4 Hz), 7.65 (d, 2H, ³J = 8.4 Hz), 7.79 (d, 1H, ³J = 15.9 Hz). – ¹³C NMR (67.8 MHz, CDCl₃): δ = 51.7, 117.9, 125.4, 125.7, 125.9, 126.2, 126.9, 128.0 (2C), 128.4, 130.6 (3C), 131.3, 133.4, 133.8, 139.3, 142.9, 144.5, 167.5. – MS (EI, 70 eV): m/z (%) = 288 (100) [M⁺]. – HRMS (EI): found 288.1148; calcd. for C₂₀H₁₆O₂: 288.1150. – C₂₀H₁₆O₂ (288.3): calcd. C 83.31, H 5.59; found C 83.13, H 5.59.

1-(4-(*E*)-[Benzoylphenyl]phenyl)naphthalene (**4c**): Pale yellow solid, m.p. 123 °C. – IR (KBr): ν = 1661, 1600, 1554, 1504, 1393, 1328, 1300, 1212, 1177, 1016, 1000, 799, 777,

688 cm⁻¹. ¹H NMR (270 MHz, CDCl₃): δ = 7.42–8.07 (m, 15H), 7.62 (d, 1H, ³J = 15.7 Hz), 7.77 (d, 2H, ³J = 8.6 Hz). – ¹³C NMR (67.8 MHz, CDCl₃): δ = 122.1, 125.4, 125.7, 125.9, 126.3, 126.9, 128.1, 128.4 (2C), 128.5 (2C), 128.6 (2C), 130.7 (2C), 131.3, 132.8, 133.8, 133.9, 138.3, 139.3, 143.2, 144.5, 190.5. – MS (EI, 70 eV): m/z (%) = 334 (100) [M⁺], 207 (31). – HRMS (EI): found 334.1362; calcd. for C₂₅H₁₈O: 334.1358.

(*E*)-4-(Acetylenyl)-3'-chlorobiphenyl (**4d**): Slowly solidifying oil. – IR (KBr): ν = 1663, 1360, 1262, 1102, 1010, 979, 867, 821, 787, 682, 590, 561 cm⁻¹. – ¹H NMR (270 MHz, CDCl₃): δ = 2.40 (s, 3H, CH₃), 6.76 (d, 1H, ³J = 16.5 Hz), 7.32–7.65 (m, 8H), 7.51 (s, 1H). – ¹³C NMR (67.8 MHz, CDCl₃): δ = 27.69, 125.18, 127.17, 127.34, 127.61, 127.89, 128.84, 130.16, 134.01, 134.87, 141.74, 141.91, 142.63, 198.25. – MS (EI, 70 eV): m/z (%) = 258 (33) [{³⁷Cl}M⁺], 256 (100) [{³⁵Cl}M⁺], 241 (89), 178 (62), 145 (40). – HRMS (EI): found: 256.0656; calcd. for C₁₆H₁₃O³⁵Cl: 256.0655.

(*E*)-4-(Benzoylenyl)-3'-chlorobiphenyl (**4e**): Slowly solidifying oil. – IR (KBr): ν = 1653, 1604, 1579, 1219, 975, 832, 791, 770, 692 cm⁻¹. – ¹H NMR (270 MHz, CDCl₃): δ = 7.33–7.65 (m, 10H), 7.74 (d, 2H, ³J = 8.4 Hz), 7.85 (d, 1H, ³J = 15.7 Hz), 8.06 (m, 2H). – ¹³C NMR (67.8 MHz, CDCl₃): δ = 122.31, 125.20, 127.19, 127.60, 127.87, 128.52, 128.66, 129.04, 130.15, 132.84, 134.47, 134.86, 138.20, 141.79, 141.98, 144.07, 190.44. – MS (EI, 70 eV): m/z (%) = 320 (35) [{³⁷Cl}M⁺], 318 (100) [{³⁵Cl}M⁺], 254 (11), 241 (15), 207 (53), 178 (54). – HRMS (EI): found 318.0812; calcd. for C₂₁H₁₅O³⁵Cl: 318.0811.

1-[5-(*E*)-(Acetylenyl)furan-2-yl]naphthalene (**4f**): Yellow oil. – IR (neat): ν = 3052, 2924, 1663, 1612, 1555, 1504, 1392, 1360, 1281, 1254, 1181, 1024, 968, 793 cm⁻¹. – ¹H NMR (270 MHz, CDCl₃): δ = 2.37 (s, 3H, CH₃), 6.74 (d, 1H, ³J = 15.7 Hz), 6.85 (m, 2H), 7.37 (d, 1H, ³J = 15.7 Hz), 7.50–7.59 (m, 3H), 7.79 (d, 1H, ³J = 7.3 Hz), 7.82–7.92 (m, 2H), 8.41 (d, 1H, ³J = 7.3 Hz). – ¹³C NMR (67.8 MHz, CDCl₃): δ = 27.9, 112.2, 117.8, 124.0, 125.2, 125.3, 126.2, 126.7, 127.1, 127.5, 128.7, 129.3, 129.6, 130.2, 131.0, 150.7, 156.2, 197.8. – MS (EI, 70 eV): m/z (%) = 262 (100) [M⁺], 247 (90), 219 (48), 191 (66), 189 (58). – HRMS (EI): found 262.0994; calcd. for C₁₈H₁₄O₂: 262.0994.

Methyl (*Z*)-3-[5'-(naphthalen-1'-yl)furan-2'-yl]acrylate (**Z-4g**): Yellow oil. – IR (neat): ν = 3052, 2992, 2946, 1714, 1633, 1504, 1436, 1415, 1391, 1253, 1172, 1026, 919, 796 cm⁻¹. – ¹H NMR (270 MHz, CDCl₃): δ = 3.79 (s, 3H, COOCH₃), 5.81 (d, 1H, ³J = 12.9 Hz), 6.87 (d, 1H, ³J = 3.3 Hz), 6.93 (d, 1H, ³J = 12.9 Hz), 7.49–7.56 (m, 3H), 7.78 (dd, 1H, ³J = 7.4 Hz, ³J = 1.3 Hz), 7.80–7.91 (m, 3H), 8.42 (m, 1H). – ¹³C NMR (67.8 MHz, CDCl₃): δ = 51.4, 112.4, 113.7, 119.2, 125.3, 125.4, 126.1, 126.6, 126.8, 127.8, 128.6, 129.2, 130.3, 130.5, 134.0, 150.7, 155.0, 166.6. – MS (EI, 70 eV): m/z (%) = 278 (100) [M⁺], 254 (60),

253 (58). – HRMS: found 278.0943; calcd. for $C_{18}H_{14}O_3$: 278.0943 and methyl (*E*)-3-[5'-(naphthalen-1'-yl)furan-2'-yl]-acrylate (**E-4g**): Yellow oil. – IR (neat): ν = 2946, 1700, 1645, 1359, 1174, 1020, 974, 925, 804 cm^{-1} . – 1H NMR (270 MHz, $CDCl_3$): δ = 3.81 (s, 3H, $COOCH_3$), 6.44 (d, 1H, 3J = 15.7 Hz), 6.80 (d, 1H, 3J = 3.5 Hz), 6.82 (d, 1H, 3J = 3.5 Hz), 7.49–7.58 (m, 4H), 7.79 (dd, 1H, 3J = 7.3 Hz, 3J = 1.4 Hz), 7.89 (m, 2H), 8.42 (m, 1H). – ^{13}C NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135): δ = 51.7 (+, OCH_3), 111.9 (+, CH), 115.1 (+, CH), 116.9 (+, CH), 125.2 (+, CH), 125.3 (+, CH), 126.1 (+, CH), 126.7 (+, CH), 127.0 (+, CH), 127.5 (C_{quat}), 128.7 (+, CH), 129.5 (+, CH), 130.2 (C_{quat}), 131.1 (+, CH), 134.0 (C_{quat}), 150.7 (C_{quat}), 155.9 (C_{quat}), 167.6 (C_{quat} , CO). – MS (EI, 70 eV): m/z (%) = 278 (100) [M^+], 247 (24). – HRMS (EI): found 278.0940; calcd. for $C_{18}H_{14}O_3$: 278.0943.

(*E*)-5-Benzoylthienyl-2-naphthalen-1'-ylfuran (**4h**): Dark yellow oil. – IR (neat): ν = 3056, 2922, 1659, 1603, 1556, 1334, 1298, 1258, 1219, 1178, 1015, 701, 657 cm^{-1} . – 1H NMR (270 MHz, $CDCl_3$): δ = 6.79 (d, 1H, 3J = 3.5 Hz), 6.85 (d, 1H, 3J = 3.5 Hz), 7.62 (d, 1H, 3J = 15.1 Hz), 7.77 (d, 1H, 3J = 7.0 Hz), 7.18–7.98 (m, 12H). – ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 111.3, 119.5, 120.0, 125.0, 125.5, 126.3, 127.6, 128.3, 128.5, 128.6, 129.2, 129.3, 129.5, 129.6, 130.3, 132.4, 134.0, 138.3, 151.5, 156.1, 189.9. – MS (EI, 70 eV): m/z (%) = 324 (18) [M^+]. – HRMS (EI): found 324.1152; calcd. for $C_{23}H_{16}O_2$: 324.1150.

(*E*)-4-Acetylthienyl-4'-phenoxy-biphenyl (**4i**): Pale yellow flaky solid, m. p. 166 °C. – IR (KBr) ν = 1663, 1592, 1492, 1361, 1274, 1258, 979, 812, 749, 690 cm^{-1} . – 1H NMR (270 MHz, $CDCl_3$): δ = 2.40 (s, 3H, CH_3), 6.75 (d, 1H, 3J = 16.2 Hz), 7.05–7.62 (m, 13H), 7.59 (d, 1H, 3J = 16.2 Hz). – ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 27.5, 119.0, 119.2, 123.6, 126.9, 127.3, 128.3, 128.8, 129.8, 133.1, 134.9, 142.6, 142.9, 157.5, 159.7, 198.3. – MS (EI, 70 eV): m/z (%) = 314 (100) [M^+], 299 (33) 178 (34). – HRMS (EI): found 314.1305; calcd. for $C_{22}H_{18}O_2$: 314.1307.

4-(*E*)-Benzoylthienyl-4'-phenoxy-biphenyl (**4j**): Pale yellow solid, m. p. 177 °C. – IR (KBr) ν = 3058, 1659 cm^{-1} ; 1H NMR (270 MHz, $CDCl_3$): δ = 7.05–8.03 (m, 15H), 7.62 (d, 2H, 3J = 8.4 Hz), 7.67 (d, 2H, 3J = 8.4 Hz), 7.85 (d, 1H, 3J = 15.7 Hz). – ^{13}C NMR (67.8 MHz, $CDCl_3$, DEPT 90, DEPT 135): δ = 119.0 (+, CH), 119.2 (+, CH), 121.8 (+, CH), 123.6 (+, CH), 127.3 (+, CH), 128.4 (+, CH), 128.5 (+, CH), 128.6 (+, CH), 129.0 (+, CH), 129.8 (+, CH), 132.7 (+, CH), 133.6 (C_{quat}), 135.0 (C_{quat}), 138.3 (C_{quat}), 142.6 (C_{quat}), 144.4 (+, CH), 156.9 (C_{quat}), 157.5 (C_{quat}), 190.5 (C_{quat} , CO). – MS (EI, 70 eV) m/z (%) = 376 (89) [M^+], 314 (100), 299 (41), 178 (63). – HRMS (EI): found 376.1461; calcd. for $C_{27}H_{20}O_2$: 376.1463. $C_{27}H_{20}O_2 \cdot 0.1H_2O$ (377.9): calcd. C 85.73, H 5.38; found C 85.63, H 5.28.

Methyl 4-(*E*)-(4'-phenoxyphenyl)cinnamate (**4k**): Colorless solid, m. p. 193 °C. – IR (KBr) ν = 2944, 1718, 1638,

1592, 1492, 1438, 1337, 1311, 1276, 1190, 1169, 984, 821, 760 cm^{-1} . – 1H NMR (270 MHz, $CDCl_3$): δ = 3.82 (s, 3H, $COCH_3$), 6.46 (d, 1H, 3J = 15.7 Hz), 7.05–7.58 (m, 13H), 7.72 (d, 1H, 3J = 15.7 Hz). – ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 52.6, 118.4, 119.9 (2C), 120.1 (2C), 124.4, 128.1 (2C), 129.2 (2C), 129.5 (2C), 130.7 (2C), 134.0, 135.9, 143.2, 145.2, 157.8, 158.3, 168.3. – MS (EI, 70 eV): m/z (%) = 330 (100) [M^+], 299 (13), 206 (10), 178 (15). – HRMS (EI): found 330.1254; calcd. for $C_{22}H_{18}O_3$: 330.1256. $C_{22}H_{18}O_3 \cdot 0.1H_2O$ (331.9): calcd. C 79.54, H 5.52; found C 79.58, H 5.51.

4-[5'-(4''-Phenoxyphenyl)furan-2'-yl]but-3-en-2-one (**4m**): Pale yellow solid, m. p. 95 °C. – IR (KBr) ν = 1655, 1626, 1589, 1486, 1023, 965, 791, 754 cm^{-1} . – 1H NMR (270 MHz, $CDCl_3$): δ = 2.35 (s, 3H, CH_3), 6.67 (d, 1H, 3J = 3.5 Hz), 6.68 (d, 1H, 3J = 15.6 Hz), 6.74 (d, 1H, 3J = 3.5 Hz), 7.02–7.08 (m, 4H), 7.14 (m, 1H), 7.25–7.40 (m, 3H), 7.69 (d, 2H, 3J = 8.6 Hz). – ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 27.5, 118.8, 121.3, 126.1, 126.6, 126.8, 127.6, 128.9, 129.6, 132.2, 133.2, 137.9, 141.3, 141.9, 142.9, 198.3. – MS (EI, 70 eV): m/z (%) = 304 (100) [M^+], 289 (79) [M^+ - CH_3]. – HRMS: found 304.1099; calcd. for $C_{20}H_{16}O_3$: 304.1099. – $C_{20}H_{16}O_3$ (304.1): calcd. C 78.93, H 5.30; found C 78.86, H 5.29.

2'-Acetylthienyl-4'-phenoxybiphenyl (**4n**): Colorless oil. – IR (neat): ν = 3058, 2954, 2924, 2856, 1671, 1589, 1508, 1489, 1358, 1243, 1169, 1021, 1004, 980, 869, 842, 759 cm^{-1} . – 1H NMR (270 MHz, $CDCl_3$): δ = 2.26 (s, 3H, CH_3), 6.65 (d, 1H, 3J = 15.9 Hz), 6.99–7.48 (m, 12H), 7.58 (d, 1H, 3J = 15.9 Hz), 7.69 (m, 1H). – ^{13}C NMR (δ , $CDCl_3$) 27.2, 118.2 (2C), 119.4 (2C), 123.7, 126.9, 127.7, 128.3, 129.0, 129.9 (2C), 130.1, 130.4, 132.2 (2C), 132.7, 134.6, 142.2, 156.7, 157.3, 198.5. – MS (EI, 70 eV): m/z (%) = 314 (30) [M^+], 271 (32), 178 (100). – HRMS: found 314.1308; calcd. for $C_{22}H_{18}O_2$: 314.1307; and 4-(2'-bromophenyl)-but-3-en-2-one as a colorless oil. – IR (neat): ν = 3060, 3000, 2918, 1670, 1609, 1465, 1438, 1359, 1283, 1257, 1203, 1177, 1026, 974, 563 cm^{-1} . – 1H NMR (270 MHz, $CDCl_3$) δ = 2.43 (s, 3H, CH_3), 6.62 (d, 1H, 3J = 16.2 Hz), 7.01–7.37 (m, 2H), 7.59–7.64 (m, 2H), 7.89 (d, 1H, 3J = 16.2 Hz). – ^{13}C NMR (67.8 MHz, $CDCl_3$) 28.1, 126.5, 128.7, 128.7, 130.8, 132.3, 134.4, 142.8, 199.2. – MS (FAB, 3-nitrobenzyl alcohol): m/z (%) = 227 (39) [$\{^{81}Br\}MH^+$], 225 (41) [$\{^{79}Br\}MH^+$]. – MS (EI, 70 eV): m/z (%) = 226 (5) [$\{^{81}Br\}M^+$], 224 (5) [$\{^{79}Br\}M^+$], 211 (11) [$\{^{81}Br\}M^+$ - CH_3], 209 (11) [$\{^{79}Br\}M^+$ - CH_3], 183 (8), 181 (9), 145 (100). – HRMS: found 223.9837; calcd. for $C_{10}H_9O^{79}Br$: 223.9837.

4-[4'-(Benzo[*b*]thien-3''-yl)phenyl]but-3-en-2-one (**4r**): Yellow crystals, m. p. 104 °C. – IR (KBr) ν = 1683, 1597, 1320, 1172, 989, 821, 796, 764, 736 cm^{-1} . – 1H NMR (600 MHz, $CDCl_3$): δ = 2.40 (s, 3H, CH_3), 6.77 (d, 1H, 3J = 16.2 Hz), 7.39 (m, 2H), 7.44 (s, 1H), 7.57 (d,

1H, $^3J = 16.2$ Hz), 7.62 (d, 2H, $^3J = 8.3$ Hz), 7.65 (d, 2H, $^3J = 8.3$ Hz), 7.91 (m, 2H). – ^{13}C NMR (67.8 MHz, CDCl_3): $\delta = 27.6, 122.7, 123.0, 124.2, 124.6, 124.7, 127.2, 128.7$ (2C), 129.2 (2C), 133.6, 137.2, 137.5, 138.2, 140.8, 142.9, 198.3. – MS (EI, 70 eV): m/z (%) = 278 (93) [M^+]. – HRMS (EI): found 278.0764; calcd. for $\text{C}_{18}\text{H}_{14}\text{OS}$: 278.0765. – $\text{C}_{18}\text{H}_{14}\text{OS}$ (278.4): calcd. C 77.66, H 5.12; found C 77.57, H 5.12.

(*E*)-4-[4'-(Thien-3"-yl)phenylbut-3-en-2-one (**4s**): Pale brown crystals. – IR (KBr): $\nu = 1658, 1360, 1263, 979, 782\text{ cm}^{-1}$. – ^1H NMR (270 MHz, CDCl_3): $\delta = 2.38$ (s, 3H, CH_3), 6.72 (d, 1H, $^3J = 16.4$ Hz), 7.40 (dd, 1H, $J = 1.7$ Hz, $J = 1.3$ Hz), 7.42 (dd, 1H, $J = 3.1$ Hz, $J = 1.3$ Hz), 7.51 (d, 1H, $^3J = 16.4$ Hz), 7.51 (dd, 1H, $^3J = 2.1$ Hz, $J = 1.7$ Hz), 7.56 (d, 2H, $^3J = 8.3$ Hz), 7.62 (d, 2H, $^3J = 8.3$ Hz). – ^{13}C NMR (67.8 MHz, CDCl_3): $\delta = 27.5, 121.3, 126.1, 126.6, 126.8$ (2C), 126.9 (2C), 128.9, 133.2, 137.9, 141.3, 142.9, 198.3. – MS (EI, 70 eV): m/z (%) = 228 (100) [M^+]. – HRMS (EI): found 228.0607; calcd. for $\text{C}_{14}\text{H}_{12}\text{OS}$: 228.0609. – $\text{C}_{14}\text{H}_{12}\text{OS} \cdot 0.1\text{H}_2\text{O}$ (230.1): calcd. C 73.07, H 5.34; found C 73.10, H 5.28.

Methyl [-1,2-dihydro-4-(naphthalen-2-yl)naphthalen-3-yl]acrylate (**6a**): Colorless solid, m. p. 128 °C. – IR (KBr): $\nu = 3052, 2932, 1717, 1612, 1431, 1306, 1169, 847, 821, 744\text{ cm}^{-1}$. – ^1H NMR (270 MHz, CDCl_3): $\delta = 2.68$ (dd, 2H, $^3J = 8.4$ Hz, $^3J = 7.0$ Hz), 2.96 (dd, 2H, $^3J = 8.4$ Hz, $^3J = 7.0$ Hz), 3.63 (s, 3H, COOCH_3), 6.06 (d, 1H, $^3J = 15.9$ Hz), 6.68 (d, 1H, $^3J = 8.1$ Hz), 7.03 (m, 1H), 7.17–7.54 (m, 5H), 7.45 (d, 1H, $^3J = 15.9$ Hz), 7.67 (s, 1H), 7.81–7.93 (m, 3H). – ^{13}C NMR (67.8 MHz, CDCl_3): $\delta = 24.3, 28.0, 51.4, 117.2, 126.3, 126.3, 126.5, 127.3, 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 129.6, 131.8, 132.8, 133.2, 135.2, 136.1, 136.9, 144.1, 144.5, 167.8$. – MS (EI, 70 eV): m/z (%) = 340 (57) [M^+], 281 (100), 265 (44), 252 (14). – HRMS (EI): found 340.1460; calcd. for $\text{C}_{24}\text{H}_{20}\text{O}_2$: 340.1463. – $\text{C}_{24}\text{H}_{20}\text{O}_2$ (220.3): calcd. C 84.68, H 5.92; found: C 84.67, H 5.95.

Methyl 3-(1'-bromo-3',4'-dihydronaphthalen-2'-yl)acrylate (**6b**): Colorless oil. – IR (neat): $\nu = 3062, 3018, 2948, 1717, 1614, 1307, 1277, 1233, 1171, 1038, 977, 946, 857,$

761 cm^{-1} . – ^1H NMR (270 MHz, CDCl_3): $\delta = 2.58$ (dd, 2H, $^3J = 8.4$ Hz, $^3J = 7.3$ Hz), 2.88 (dd, 2H, $^3J = 8.4$ Hz, $^3J = 7.3$ Hz), 3.81 (s, 3H, COOCH_3), 6.13 (d, 1H, $^3J = 15.9$ Hz), 7.15 (m, 1H), 7.24–7.28 (m, 2H), 7.78 (m, 1H), 8.11 (d, 1H, $^3J = 15.9$ Hz). – ^{13}C NMR (67.8 MHz, CDCl_3): $\delta = 25.9, 27.5, 52.8, 120.0, 127.0, 127.0, 128.7, 129.3, 129.5, 133.3, 133.9, 137.2, 144.3, 167.4$. – MS (EI, 70 eV): m/z (%) = 294 (11) [$\{^{81}\text{Br}\}\text{M}^+$], 292 (11) [$\{^{79}\text{Br}\}\text{M}^+$], 213 (100). – HRMS: found 292.0100; calcd. for $\text{C}_{14}\text{H}_{13}\text{O}_2^{79}\text{Br}$: 292.0099.

(*E*)-5-(4-Anisyl)-thien-2-yl-4-(benzothien-2-yl)phenylvinylketone (**7a**): Greenish powder, m. p. 178 °C (dec.). – IR (KBr): $\nu = 1649, 1540, 1522, 1434, 1255, 1176, 1030, 829, 798, 576\text{ cm}^{-1}$. – ^1H NMR (270 MHz, CDCl_3): $\delta = 3.86$ (s, 3H, OCH_3), 6.94 (d, 2H, $^3J = 8.9$ Hz), 6.98–7.84 (m, 14H), 7.43 (s, 1H). – ^{13}C NMR (67.8 MHz, CDCl_3): $\delta = 55.43, 114.58$ (2C), 120.40, 121.56, 122.02, 122.31, 123.02, 123.80, 124.73, 124.77, 126.82 (2C), 127.69 (2C), 129.07 (2C), 129.78, 132.21, 133.02, 133.12, 134.71, 136.29, 142.06, 142.63, 153.33, 160.55, 187.46.

(*E*)-5-(4-Anisyl)-thien-2-yl-4-bromophenylvinylketone (**7b**): Pale yellow solid, m. p. 229 °C. – IR (KBr): $\nu = 1653, 1598, 1450, 1250, 1110, 1068, 1030, 830, 795, 764\text{ cm}^{-1}$. – ^1H NMR (270 MHz, CDCl_3): $\delta = 3.86$ (s, 3H, OCH_3), 6.96 (d, 2H, $^3J = 8.6$ Hz), 7.28 (d, 1H, $^3J = 4.0$ Hz), 7.40 (d, 1H, $^3J = 15.7$ Hz), 7.51 (d, 2H, $^3J = 8.6$ Hz), 7.55 (d, 2H, $^3J = 8.6$ Hz), 7.63 (d, 2H, $^3J = 8.6$ Hz), 7.77 (d, 1H, $^3J = 15.7$ Hz), 7.80 (d, 1H, $^3J = 4.0$ Hz); ^{13}C NMR (67.8 MHz, CDCl_3): $\delta = 55.36, 114.59$ (2C), 122.05, 123.05, 124.71, 126.17, 127.71 (2C), 129.79 (2C), 132.22 (2C), 133.13, 133.83, 142.08, 143.16, 153.49, 160.59, 181.34. – MS (FAB, 3-nitrobenzyl alcohol): m/z (%) = 401 (2.5) [$\{^{81}\text{Br}\}\text{MH}^+$], 399 (2.4) [$\{^{79}\text{Br}\}\text{MH}^+$]. – HRMS (FAB): found 399.0058; calcd. for $\text{C}_{20}\text{H}_{16}\text{O}_2^{79}\text{BrS}$: 399.0054.

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