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Ascorbic Acid Promoted Oxidative Arylation of Vinyl Arenes to 2-Aryl Acetophenones without Irradiation at Room Temperature under Aerobic Conditions

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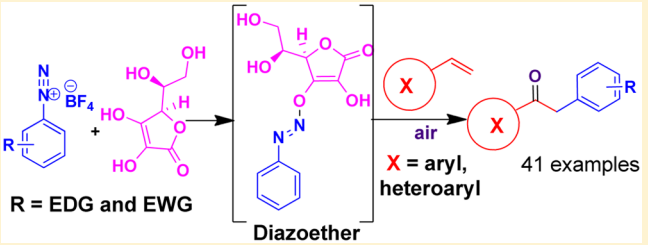
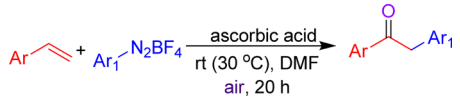
Supporting Information

ABSTRACT: A convenient and general protocol for oxidative arylation of vinyl arenes by aryl radicals generated in situ from arene diazonium fluoroborates promoted by ascorbic acid in air at room temperature has been developed in the absence of any additive and visible light irradiation. A series of diversely substituted 2-aryl acetophenones have been obtained in good yields by this procedure.



The ease of generation of aryl radicals from arene diazonium salts under visible light photocatalysis in the presence of eosin Y or $[Ru(bpy)_3]Cl_2$[1] has offered a powerful tool for arylation of various substrates leading to the synthesis of a wide variety of useful organic molecules.[2] As an arene diazonium ion functions as one electron oxidizing agent, interaction of a suitable reductant can also form an instant radical from the ion.[3,4] L-*threo* ascorbic acid (vitamin C) is reported to act as an appropriate reducing agent to generate an aryl radical from arene diazonium salt in the absence of a metal and visible light photocatalysis.[5] Recently Carrillo and co-workers reported the use of this protocol for the synthesis of 2-aryl heterocycles involving aryl radicals from arene diazonium salts.[6] We report here a metal free oxidative arylation of vinyl arenes by aryl radical generated in situ from aryl diazonium fluoroborate promoted by ascorbic acid at room temperature without any irradiation leading to the synthesis of 2-aryl acetophenones (Scheme 1). In the recent past Cai and his group reported similar oxidative arylation of vinyl arenes under visible light photocatalyzed conditions.[7] However, this procedure lacks generality being not applicable to electron-donating substituted and unsubstituted arene diazonium salts. Thus, it has limited scope being effective only to electron-withdrawing substrates.

Scheme 1. Ascorbic Acid Promoted Oxidative Arylation of Vinyl Arenes



2-Aryl acetophenones are versatile synthons, used as a common precursor for the synthesis of a large variety of organic molecules such as heterocycles (quinoxaline,[8] furan,[9] imidazole[10]), terminal alkenes,[11] α-hydroxy ketones,[12] 1,2-diketones,[13] ketones,[14] and aryl-substituted 2-aryl acetophenones[15] (Figure 1). They are also found as structural motifs in different biologically active molecules and pharmaceuticals such as oxcarbazepine (anticonvulsant activity) and ketotifen (H_1-antihistamine activity).[7] Thus, convenient synthesis of 2-aryl acetophenones is of much importance in organic synthesis.

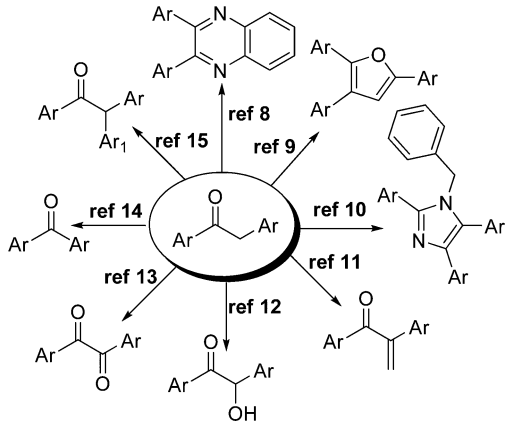


Figure 1. Use of 2-aryl acetophenones as important precursor.

To optimize the reaction conditions a series of experiments were performed with variation of reaction parameters, such as solvent, reducing agent, and time for a representative reaction of 2-vinylnaphthalene (**1i**) and 4-nitrophenyl diazonium fluoroborate (**2c**). The results are summarized in Table 1. The use of THF, CH_3CN, DMSO, 1,4-dioxane, toluene, and NMP as solvent furnished relatively low yield (Table 1, entries 1−6) whereas DMF was found to be more effective compared

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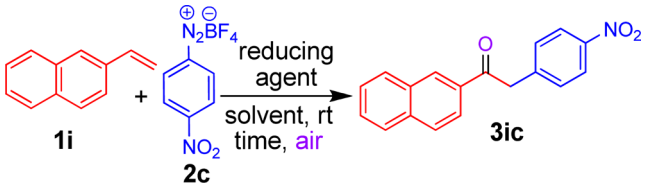
Table 1. Optimization of Reaction Conditions[a]



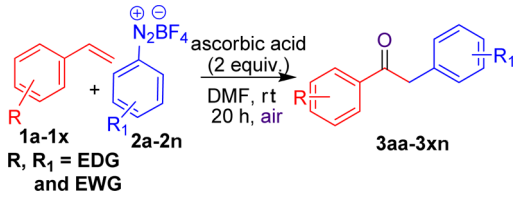
entry	diazonium fluoroborate (equiv)	reducing agent (equiv)	solvent	time (h)	yield (%)[b]
1	1	ascorbic acid (1)	THF	20	29
2	1	ascorbic acid (1)	CH_3CN	20	trace
3	1	ascorbic acid (1)	DMSO	20	23
4	1	ascorbic acid (1)	1,4-dioxane	20	
5	1	ascorbic acid (1)	toluene	20	5
6	1	ascorbic acid (1)	NMP	20	11
7	1	ascorbic acid (1)	DMF	20	53
8	1.5	ascorbic acid (1.5)	DMF	20	69
9	2	ascorbic acid (2)	DMF	20	85
10	3	ascorbic acid (3)	DMF	20	85
11	2	ascorbic acid (2)	DMF	24	85
12	2	ascorbic acid (2)	DMF	19	79
13	2	KI (2)	DMF	20	33
14	2	Ph-$NHNH_2$ (2)	DMF	20	21
15	2	vitamin E (2)	DMF	20	12
16	2	ascorbic acid (3)	DMF	20	85
17[c]	2	ascorbic acid (1)	DMF	20	
18	2		DMF	20	trace
19[d]	2	ascorbic acid (2)	DMF	20	73

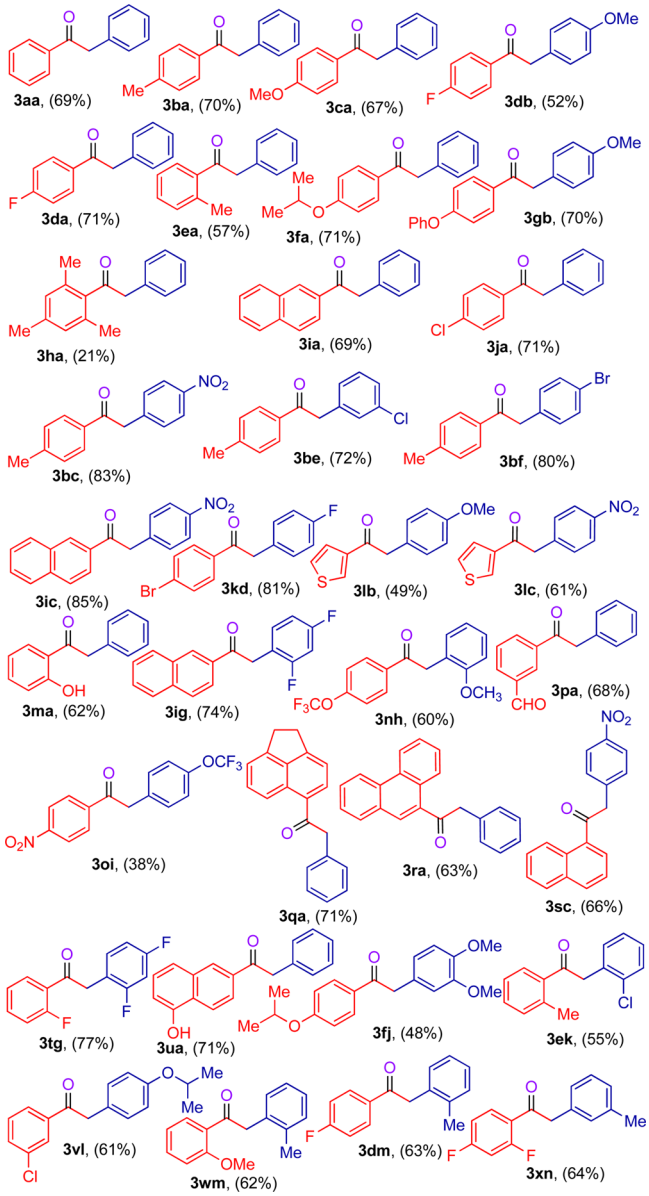
[a]Reaction conditions. [b]Isolated yields. [c]In the presence of TEMPO. [d]Under pure O_2.

to others (Table 1, entry 7). The use of 1.5 equiv of 4-nitrophenyl diazonium fluoroborate with respect to 1 equiv of 2-vinylnaphthalene improved the yield (Table 1, entry 8). However, the best yield of product was obtained using 2 equiv of diazonium fluoroborate and 2 equiv of ascorbic acid for 1 equiv of styrene in DMF for 20 h at room temperature (Table 1, entry 9). The increase of the amount of 4-nitrophenyl diazonium fluoroborate and ascorbic acid beyond 2 equiv did not alter the outcome of the reaction (Table 1, entries 10 and 16). Other reducing agents, such as Ph-$NHNH_2$ and vitamin E, were not so effective (Table 1, entries 14 and 15) although KI provided relatively improved yield (Table 1, entry 13). The reaction did not proceed at all in the presence of TEMPO (Table 1, entry 17). In the absence of any reducing agent, only a trace amount of product was isolated (Table 1, entry 18).

Thus, in a typical reaction procedure a mixture of vinyl arene (1 equiv), aryl diazonium fluoroborate (2 equiv), and ascorbic acid (2 equiv) was stirred for 20 h under air at room temperature (TLC). Standard workup followed by column chromatography provided the product. A series of vinyl arenes and heteroarenes were subjected to reaction by this procedure to produce a library of 2-aryl/heteroaryl acetophenones involving a variety of diazonium salts. The results are summarized in Table 2. The diazonium fluoroborates with electron-withdrawing groups ($-NO_2$, $-F$, $-Cl$, $-OCF_3$) in the aromatic ring underwent efficient reaction with vinyl arenes to form the corresponding 2-aryl acetophenones (Table 2, **3bc**, **3be**, **3ic**, **3kd**, **3ld**, **3lc**, **3ig**, **3oi**, **3tg**, and **3ek**). Interestingly the

Table 2. Oxidative Arylation of Vinyl Arenes[a]





[a]Reaction conditions: vinyl arenes (1 equiv), aryl diazonium fluoroborate (2 equiv), ascorbic acid (2 equiv), air, room temperature, DMF, 20 h.

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aryl diazonium fluoroborates with electron-donating groups (−OMe, −Me, −$OCHMe_2$) in the aromatic ring at *-o*, *-m*, or *-p* positions reacted readily with vinyl arenes under this condition to produce the corresponding products (Table 2, **3db**, **3gb**, **3 lb**, **3nh**, **3fj**, **3vl**, **3wm**, **3dm**, and **3xn**). Reactions with unsubstituted aryl diazonium fluoroborate were also successful (Table 2, **3aa**, **3ba**, **3ca**, **3da**, **3ea**, **3fa**, **3ia**, **3ja**, **3ma**, **3pa**, **3ra**, and **3ua**). It is worthwhile to mention that recently Cai and co-workers reported virtually no reaction (trace of product) with challenging diazonium fluoroborates having electron-donating moieties (−OMe, −Me) in the aromatic ring and with unsubstituted aryl diazonium fluoroborate under visible light photoredox catalysis.[7] Obviously this demonstrates the superior efficacy of the present procedure over the other.[16] The vinyl heteroarene bearing thiophene unit (**1l**) and vinyl polynuclear hydrocarbons (**1q**, **1r**) were also found to be reactive under the reaction conditions. The halogen moieties (F, Cl, Br) in the aromatic ring are compatible. The halogen substituted acetophenones are of potential for further functionalization. The sterically hindered vinyl arenes bearing −Me group at two *ortho* positions provided relatively low yield of products (**3ea**, **3ha**). In general, when moderate or low yield of products were obtained, a substantial amount of vinyl arenes remained unreacted other than a small percentage of unidentifiable side products. Easily oxidizable −CHO functionality in the aromatic ring also remained unaffected under the reaction conditions (**3pa**). Reactions in the absence (dark) or in the presence of light did not show any marked difference in the formation of product (Table 3). The yields remained comparable in both the conditions.

Table 3. Outcome of Reactions in Absence and in the Presence of Light

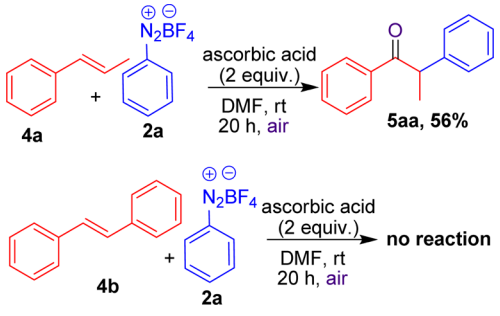
vinyl styrene (**1**)	aryl diazonium fluoroborate (**2**)	products (**3**)	yield in presence of light (%)	yield in absence of light
1a	**2a**	**3aa**	69	67
1c	**2a**	**3ca**	67	66
1b	**2f**	**3bf**	80	78

Although reaction of *β*-methylstyrene (**4a**) with phenyl diazonium fluoroborate (**2a**) was successful, stilbene failed to undergo any reaction (Scheme 2).

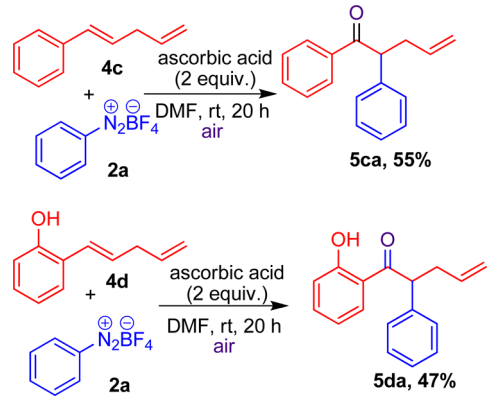
The reaction shows excellent regioselectivity with vinyl arenes bearing an allyl substituent at the *β*-position. The aryl radical interacts selectively at the styrenyl double bond leaving the allyl double bond intact (Scheme 3).

Similar regioselectivity was also observed in the vinyl arenes bearing propargyl moiety at the *β*-position (Scheme 4).

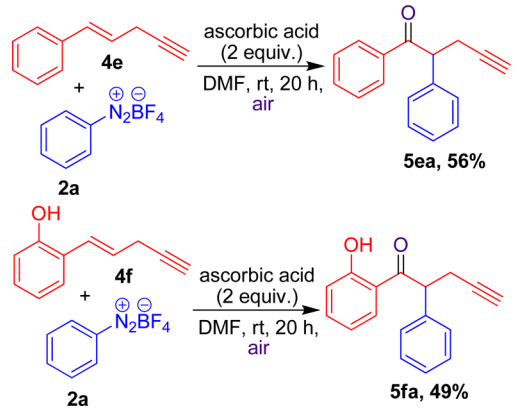
Scheme 2. Reaction with *β*-Substituted Styrene



Scheme 3. Regioselective Oxidative Arylation of *β*-Allyl Substituted Vinyl Arenes

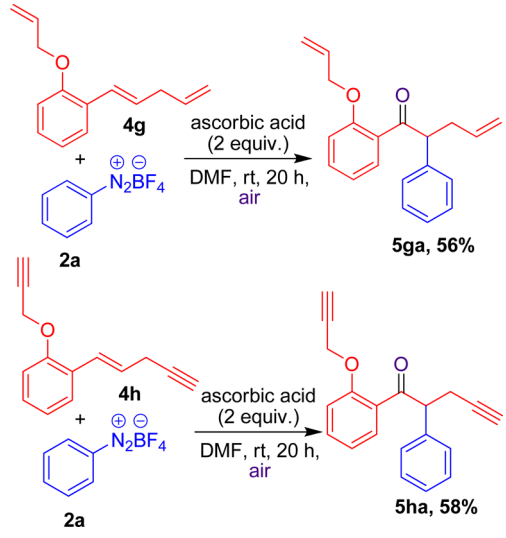


Scheme 4. Regioselective Oxidative Arylation of *β*-Propargyl Substituted Vinyl Arenes



To extend it further, when the compounds **4g and 4h** containing multiple double and triple bonds were subjected to reaction with phenyl diazonium fluoroborate, the products **5ga** and **5ha** were obtained via radical attack selectively at *β* styryl carbon keeping the double and triple bonds inert (Scheme 5).

Scheme 5. Regioselective Oxidative Arylation of Substrates Containing Multiple Double and Triple Bonds



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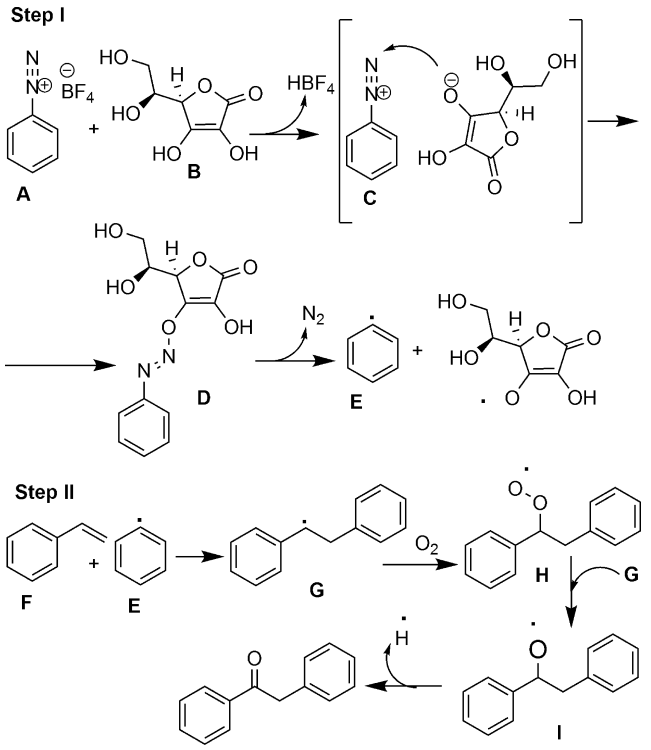
The complete arrest of the reaction in the presence of TEMPO (2,2,6,6-tetramethylpiperidine-1-oxy radical) (Table 1, entry 17) suggests a radical mechanistic pathway. Thus, a probable radical mechanism is proposed in Scheme 6 in

Scheme 6. Plausible Mechanism



accordance with the reported reaction pathway for similar reactions.[3−5] In the first step the aryl diazonium salt **A** interacts with ascorbic acid **B** to generate an intermediate diazoether **D** via nucleophilic attack of ascorbate anion to diazonium ion.[17] Subsequently this diazoether **D** undergoes a homolytic cleavage to produce an aryl radical **E**. In the next step the aryl radical attacks at the β-position of vinyl arene **F** to form a relatively stable benzyl radical **G**, which captures O_2 from air to produce the peroxy radical **H**. This peroxy radical then reacts with another molecule of **G** to provide an oxyl radical **I**, which leads to 2-phenyl acetophenone by abstraction of a hydrogen radical.[18]

To ascertain the source of O_2 either from air or from trace of moisture (H_2O) we performed two experiments by carrying out a representative reaction of styrene and phenyl diazonium fluoroborate with addition of labeled H_2O (H_2O^{18}) in argon atmosphere and in atmospheric condition separately. No product was formed in the reaction in argon atmosphere whereas the corresponding product, 2-phenyl acetophenone, was obtained without any O^{18}-incorporation (HRMS) in the second experiment. This observation confirms the participation of atmospheric O_2 in the reaction.

To conclude, we have developed a convenient protocol for oxidative arylation of vinyl arenes by aryl radicals, generated in situ from aryl diazonium fluoroborates promoted by ascorbic acid under air at room temperature in the absence of any additive and ligand leading to the synthesis of 2-aryl acetophenones. The significant improvement in this procedure over the reported one under photocatalysis[7] is its applicability to reactions with more challenging electron-donating substituted and unsubstituted aryl diazonium fluoroborates. These substrates are reported to remain inert in earlier procedure.[7] The other advantages offered by this procedure are reaction at room temperature, use of inexpensive ascorbic acid in place of expensive photosensitizer in photocatalytic procedure, tolerance to a wide range of functionalities, applicability to vinyl heteroarene, and considerably good yield of products. Certainly, this procedure is of much potential, and it provides an easy access to a library of diversely substituted aryl acetophenones.

EXPERIMENTAL SECTION

General. NMR spectra were recorded on 500, 400, 300 MHz instruments for ^{1}H spectra and 125, 100, 75 MHz instrument for ^{13}C spectra. HRMS analysis was performed in a Qtof mass analyzer using the ESI ionization method. Elemental analyses are done at our Institute using an autoanalyzer.

General Experimental Procedure for Oxidative Arylation of Vinyl Arenes. Representative Procedure for the Synthesis of 1-(Naphthalen-2-yl)-2-(4-nitrophenyl)ethanone (3ic, Table 2). To an ice cooled solution of 2- vinylnaphthalene (**1i**, 0.5 mmol, 77 mg), in dry DMF (3 mL), were added 4-nitrophenyl diazonium fluoroborate (**2c**, 1 mmol, 237 mg) and (L)-*threo* ascorbic acid (1 mmol, 176 mg) under air. The resulting mixture was stirred for 5 min at cooled condition, and was then allowed to reach to room temperature and was further stirred for 20 h. After the reaction was complete (TLC), it was extracted with ethyl acetate (60 mL). The extract was washed with water (10 mL) and brine solution (10 mL). The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue (crude product) was purified by column chromatography over silica gel to afford the pure product 1-(naphthalen-6-yl)-2-(4-nitrophenyl)ethanone (**3ic**) as a light yellow solid (124 mg, 85%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.50 (s, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.57−7.65 (m, 2H), 7.88−7.94 (m, 2H), 7.98 (d, J = 8 Hz, 1H), 8.05 (d, J = 8.5 Hz, 1H), 8.20 (d, J = 8.5 Hz, 2H), 8.54 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.1, 123.9 (2C), 124.0, 127.2, 128.0, 128.9, 129.0, 129.7, 130.4, 130.8 (2C), 132.6, 133.6, 135.9, 142.3, 147.2, 196.1; IR (neat) 3016, 1672, 1603, 1524, 1485, 1454, 1217 cm^{-1}. Anal. Calcd for $C_{18}H_{13}NO_3$: C, 74.22, H, 4.50. Found: C, 74.26, H, 4.47. These data are in perfect match with the reported one.[16r]

This procedure was followed for all the reactions listed in Table 2, Scheme 2, Scheme 3, Scheme 4, and Scheme 5. Although this data was obtained based on 1 mmol scale, the reaction was shown to produce a similar result in higher scale too. The known compounds were identified by comparison of their spectroscopic data with those reported (**3aa**,[16h] **3ba**,[16h] **3ca**,[16g] **3db**,[16s] **3da**,[16h] **3ea**,[16t] **3fa**,[16u] **3gb**,[16v] **3ha**,[16w] **3ia**,[16h] **3ja**,[16h] **3bc**,[16g] **3be**,[16g] **3bf**,[16h] **3ic**,[16r] **3kd**,[16s] **3ma**,[16x] and **5aa**[16h]). The unknown products were characterized by ^{1}H NMR, ^{13}C NMR, IR, and HRMS or elemental analysis. These data are given below in the order of their entries in Table 2, Scheme 2, Scheme 3, Scheme 4, and Scheme 5.

*2-(4-Methoxyphenyl)-1-(thiophene-3-yl)ethanone (**3 lb**, Table 2):* colorless gummy liquid (57 mg, 49%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.76 (s, 3H), 4.09 (s, 2H), 6.85−6.88 (m, 2H), 7.17−7.20 (m, 2H), 7.25−7.28 (q, J = 3 Hz, 1H), 7.55 (dd, J_1 = 5.1 Hz, J_2 = 1.2 Hz, 1H), 8.07 (dd, J_1 = 3 Hz, J_2 = 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.9, 55.1, 114.1 (2C), 126.3, 126.4, 127.2, 130.4 (2C), 132.6, 141.8, 158.5, 192.1; IR (KBr) 3080, 1672, 1612, 1512, 1248, 1171 cm^{-1}; HRMS calcd for $C_{13}H_{12}O_2S$ $[M + H]^+$ 233.0631, found 233.0629.

*2-(4-Nitrophenyl)-1-(thiophene-3-yl)ethanone (**3lc**, Table 2):* light yellow solid (76 mg, 61%), mp 132−134 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.31 (s, 2H), 7.34−7.37 (q, J = 2.7 Hz, 1H), 7.41−7.45 (m, 2H), 7.57 (dd, J_1 = 5.1 Hz, J_2 = 1.2 Hz, 1H), 8.14−8.19 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 46.2, 123.8 (2C), 127.0, 127.1, 130.7 (2C), 133.0, 141.5, 141.9, 147.2, 190.2; IR (KBr) 3086, 1678, 1601, 1510, 1348, 1315, 1176 cm^{-1}; HRMS calcd for $C_{12}H_9NO_3S$ $[M + H]^+$ 248.0376, found 248.0374.

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*2-(2,4-Difluorophenyl)-1-(naphthalen-3-yl)ethanone (**3ig**, Table 2):* white solid (105 mg, 74%), mp 126−128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.41 (s, 2H), 6.83−6.90 (m, 1H), 7.24 (q, J = 8.1 Hz, 1H), 7.54−7.65 (m, 2H), 7.86−7.91 (m, 2H), 7.97 (d, J = 8.1 Hz, 1H), 8.07 (dd, J_1 = 8.7 Hz, J_2 = 1.8 Hz, 1H), 8.56 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.1 (d, J_{C-F} = 1.5 Hz, 1C), 103.92 (d, J_{C-F} = 51.7 Hz, 1C), 103.93, 111.4 (dd, J_1 = 21 Hz, J_2 = 3.8 Hz, 1C), 117.9 (dd, J_1 = 16.5 Hz, J_2 = 3.7 Hz, 1C), 123.9, 127.0, 127.9, 128.7 (d, J_{C-F} = 6 Hz, 1C), 129.7, 130.2, 132.4 (q, J_{C-F} = 3.7 Hz, 1C), 132.6, 133.7, 135.8, 161.1 (dd, J_1 = 246.7 Hz, J_2 = 12 Hz, 1C), 162.3 (dd, J_1 = 246.7 Hz, J_2 = 12 Hz, 1C), 196.0; IR (neat) 2926, 1666, 1591, 1485, 1283, 1246 cm^{-1}. Anal. Calcd for $C_{18}H_{12}F_2O$: C, 76.59, H, 4.28. Found: C, 76.63, H, 4.29.

*2-(2-Methoxyphenyl)-1-(4-(trifluoromethoxy)phenyl)ethanone (**3nh**, Table 2):* white solid (93 mg, 60%), mp 52−54 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.79 (s, 3H), 4.27 (s, 2H), 6.89−6.97 (m, 2H), 7.18−7.21 (m, 1H), 7.25−7.31 (m, 3H), 8.08−8.11 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.1, 55.5, 110.7, 120.40 (2C), 120.42 (q, J_{C-F} = 257.3 Hz, 1C), 123.4, 125.4, 128.7, 130.6 (2C), 131.1, 135.3, 152.6, 157.2, 196.6; IR (KBr) 2945, 1688, 1603, 1497, 1261, 1161 cm^{-1}; HRMS calcd for $C_{16}H_{13}F_3O_3$ $[M + H]^+$ 311.0890, found 311.0891.

*1-(4-Nitrophenyl)-2-(4-(trifluoromethoxy)phenyl)ethanone (**3oi**, Table 2):* light yellow solid (62 mg, 38%), mp 74−76 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.41 (s, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.41 (d, J = 8.7 Hz, 2H), 8.04−8.09 (m, 2H), 8.13 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 44.9, 120.3 (q, J_{C-F} = 257.3 Hz, 1C), 120.6, 123.8, 130.6 (2C), 130.7 (2C), 134.4, 141.7, 147.2, 153.1 (d, J_{C-F} = 2.3 Hz, 1C), 194.6; IR (neat) 3061, 1666, 1579, 1519, 1433, 1304, 1026 cm^{-1}. Anal. Calcd for $C_{15}H_{10}F_3NO_4$: C, 55.39, H, 3.10, N 4.31. Found: C, 55.41, H, 3.15, N, 4.29.

*3-(2-Phenylacetyl)benzaldehyde (**3pa**, Table 2):* light yellow gummy liquid (76 mg, 68%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.34 (s, 2H), 7.26−7.34 (m, 5H), 7.63 (t, J = 7.5 Hz, 1H), 8.04−8.08 (m, 1H), 8.24−8.28 (m, 1H), 8.50 (t, J = 1.5 Hz, 1H), 10.07 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.7, 127.2, 128.7, 128.9 (2C), 129.5 (2C), 129.7, 129.9, 133.7, 134.2, 136.7, 137.4, 191.6, 196.7; IR (neat) 3018, 1734, 1701, 1684, 1506, 1456, 1215 cm^{-1}. Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34, H, 5.39. Found: C, 80.31, H, 5.36.

*1-(1,2-Dihydroacenaphthylen-5-yl)-2-phenylethanone (**3qa**, Table 2):* white solid (77 mg, 71%), mp 112−114 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.26−3.33 (m, 4H), 4.40 (s, 2H), 7.22 (d, J = 7.5 Hz, 1H), 7.30−7.36 (m, 2H), 7.40 (d, J = 4.5 Hz, 4H), 7.60−7.65 (m, 1H), 8.12 (d, J = 7.2 Hz, 1H), 8.85 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.1, 30.3, 47.3, 117.9, 120.2, 122.3, 126.6, 128.5 (2C), 129.2, 129.3 (2C), 129.5, 130.3, 132.5, 135.4, 139.5, 145.9, 153.0, 199.5; IR (KBr) 3026, 2901, 1687, 1595, 1497, 1309, 1155 cm^{-1}; HRMS calcd for $C_{20}H_{17}O$ $[M + H]^+$ 273.1274, found 273.1277.

*1-(Phenanthren-9-yl)-2-phenylethanone (**3ra**, Table 2):* light yellow solid (94 mg, 63%), mp 127−129 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.46 (s, 2H), 7.31−7.42 (m, 5H), 7.60−7.74 (m, 4H), 7.91 (d, J = 7.8 Hz, 1H), 8.19 (s, 1H), 8.60−8.68 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.9, 122.6, 122.8, 126.6, 126.9, 127.0, 127.1, 127.5, 128.5, 128.7 (2C), 128.8, 129.3, 129.6 (2C), 129.7, 129.8, 130.7, 131.7, 134.5, 134.8, 201.5; IR (KBr) 2891, 1686, 1495, 1450, 1309, 1117 cm^{-1}; HRMS calcd for $C_{22}H_{16}O$ $[M + H]^+$ 297.1274, found 297.1272.

*1-(Naphthalen-1-yl)-2-(4-nitrophenyl)ethanone (**3sc**, Table 2):* light yellow solid (96 mg, 66%), mp 123−125 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.45 (s, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.48−7.60 (m, 3H), 7.85−7.88 (m, 1H), 7.96−8.02 (m, 2H), 8.13 (d, J = 8.1 Hz, 2H), 8.62 (d, J = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 48.1, 123.7 (2C), 124.3, 125.6, 126.7, 128.3 (2C), 128.6, 130.3, 130.6 (2C), 133.5, 134.0, 134.6, 142.2, 146.9, 199.6; IR (KBr) 3078, 1670, 1510, 1346, 1301, 1090 cm^{-1}; HRMS calcd for $C_{18}H_{13}NO_3$ $[M + H]^+$ 292.0968, found 292.0969.

*2-(2,4-Difluorophenyl)-1-(2-fluorophenyl)ethanone (**3tg**, Table 2):* colorless solid (97 mg, 77%), mp 95−97 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.29 (d, J = 2.4 Hz, 2H), 6.79−6.89 (m, 2H), 7.13−7.27 (m, 3H), 7.51−7.59 (m, 1H), 7.87−7.92 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 43.2 (dd, J_1 = 9 Hz, J_2 = 1.5 Hz, 1C), 103.93, 103.94 (d, J_{C-F} = 51 Hz, 1C), 111.3 (dd, J_{1C-F} = 21 Hz, J_2 = 3.8 Hz, 1C), 116.8 (d, J_{C-F} = 24 Hz, 1C), 124.8 (d, J_{C-F} = 3 Hz, 1C), 125.2 (d, J_{C-F} = 12.7 Hz, 1C), 131.0 (d, J_{C-F} = 2.3 Hz, 1C), 132.5 (q, J_{C-F} = 6 Hz, 1C), 135.1 (d, J_{C-F} = 9 Hz, 1C), 161.3 (dd, J_1 = 246.7 Hz, J_2 = 12 Hz, 1C), 162.1 (d, J_{C-F} = 252.7 Hz, 1C), 162.4 (dd, J_{1C-F} = 234.7 Hz, J_2 = 12 Hz, 1C), 194.4 (d, J_{C-F} = 4.5 Hz, 1C); IR (KBr) 1688, 1608, 1508, 1452, 1275, 1213, 1089 cm^{-1}. Anal. Calcd for $C_{14}H_9F_3O$: C, 67.20, H, 3.63. Found: C, 67.23, H, 3.67.

*1-(1-Hydroxynaphthalen-6-yl)-2-phenylethanone (**3ua**, Table 2):* colorless gummy liquid (93 mg, 71%); ^{1}H NMR (500 MHz, DMSO-d_6) δ 4.39 (s, 2H), 6.81 (d, J = 8 Hz, 2H), 7.18 (d, J = 7.5 Hz, 2H), 7.58−7.65 (m, 2H), 7.94−7.98 (m, 2H), 8.04 (d, J = 9 Hz, 1H), 8.12 (d, J = 8 Hz, 1H), 8.78 (s, 1H), 9.39 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 43.9, 115.3 (2C), 124.0, 125.2, 126.9, 127.6, 128.3, 128.6, 129.6, 130.3, 130.6 (2C), 132.2, 133.7, 135.0, 156.1, 198.0; IR (KBr) 1659, 1589, 1485, 1283, 1248, 1013 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42, H, 5.38. Found: C, 82.45, H, 5.39.

*1-(4-Isopropoxyphenyl)-2-(3,4-dimethoxyphenyl)ethanone (**3fj**, Table 2):* white solid (76 mg, 48%), mp 126−128 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (d, J = 6 Hz, 6H), 3.77 (s, 3H), 3.78 (s, 3H), 4.10 (s, 2H), 4.49−4.62 (m, 1H), 6.75 (s, 3H), 6.83 (d, J = 9 Hz, 2H), 7.92 (dd, J_1 = 6.9 Hz, J_2 = 1.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7 (2C), 44.6, 55.6, 55.7, 69.9, 111.2, 112.4, 114.9 (2C), 121.4, 127.4, 129.0, 130.8 (2C), 147.7, 148.8, 161.9, 196.2; IR (KBr) 2899, 1678, 1599, 1518, 1268, 1163 cm^{-1}; HRMS calcd for $C_{19}H_{22}O_4$ $[M + H]^+$ 315.1591, found 315.1593.

*2-(2-Chlorophenyl)-1-o-tolylethanone (**3ek**, Table 2):* colorless viscous liquid (68 mg, 55%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.55 (s, 3H), 4.38 (s, 2H), 7.24−7.33 (m, 5H), 7.38−7.44 (m, 2H), 7.81−7.83 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 46.2, 125.7, 126.9, 128.6 (2C), 129.5, 131.5, 131.9, 132.1, 133.4, 134.5, 137.5, 138.6, 199.9; IR (neat) 3020, 2928, 1693, 1681, 1574, 1445, 1323, 1217 cm^{-1}. Anal. Calcd for $C_{15}H_{13}ClO$: C, 73.62, H, 5.35. Found: C, 73.60, H, 5.38.

*1-(3-Chlorophenyl)-2-(4-isopropoxyphenyl)ethanone (**3vl**, Table 2):* white solid (88 mg, 61%), mp 83−85 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.33 (d, J = 6.3 Hz, 6H), 4.16 (s, 2H), 4.56−4.64 (m, 1H), 6.88 (dd, J_1 = 7.2 Hz, J_2 = 1.8 Hz, 2H), 7.12−7.14 (m, 1H), 7.18−7.20 (m, 2H), 7.25 (s, 1H), 7.95 (dd, J_1 = 6.9 Hz, J_2 = 1.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.7 (2C), 44.3, 70.1, 115.1 (2C), 126.8, 127.7, 128.8, 129.5, 129.7, 130.8 (2C), 134.1, 136.9, 162.2, 195.3; IR (neat) 3018, 2979, 1676, 1599, 1261 cm^{-1}; HRMS calcd for $C_{17}H_{18}ClO_2$ $[M + H]^+$ 289.0990, found 289.0992.

*1-(2-Methoxyphenyl)-2-o-tolylethanone (**3wm**, Table 2):* colorless viscous liquid (75 mg, 62%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.56 (s, 3H), 3.79 (s, 3H), 4.24 (s, 2H), 6.91 (d, J = 8.4 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 7.23−7.34 (m, 4H), 7.37−7.42 (m, 1H), 7.80 (d, J = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.9, 43.4, 55.2, 110.4, 120.6, 123.8, 125.5, 128.4, 128.5, 131.0, 131.2, 131.7, 137.9, 138.2, 157.2, 202.5; IR (neat) 2964, 1691, 1601, 1495, 1248 cm^{-1}; HRMS calcd for $C_{16}H_{16}O_2$ $[M + H]^+$ 241.1223, found 241.1225.

*1-(4-Fluorophenyl)-2-o-tolylethanone (**3dm**, Table 2):* white solid (72 mg, 63%), mp 56−58 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.48 (s, 3H), 4.19 (s, 2H), 6.99−7.05 (m, 2H), 7.19−7.30 (m, 4H), 7.36−7.41 (m, 1H), 7.71−7.74 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.3, 47.4, 115.4 (d, J_{C-F} = 21 Hz, 2C), 125.7, 128.6, 130.2 (d, J_{C-F} = 3 Hz, 1C), 131.1 (d, J_{C-F} = 8.3 Hz, 2C), 131.5, 132.1, 137.4, 138.5, 161.9 (d, J_{C-F} = 243.75 Hz, 1C), 201.1; IR (neat) 3018, 1713, 1693, 1666, 1601, 1504, 1454, 1292, 1219, 1157 cm^{-1}; HRMS calcd for $C_{15}H_{13}FO$ $[M + H]^+$ 229.1023, found 229.1020.

*1-(2,4-Difluorophenyl)-2-m-tolylethanone (**3xn**, Table 2):* white solid (79 mg, 64%), mp 82−84 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 3H), 4.28 (s, 2H), 6.80−6.89 (m, 2H), 7.16−7.24 (m, 1H), 7.35−7.42 (m, 2H), 7.82−7.85 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.4, 38.1 (d, J_{C-F} = 1.5 Hz, 1C), 103.8, 103.9 (d, J_{C-F} = 51.8 Hz, 1C), 111.3 (dd, J_1 = 17.3 Hz, J_2 = 3.8 Hz, 1C), 118.0 (dd, J_1 = 16.5 Hz, J_2 = 3.8 Hz, 1C), 125.6, 128.8 (d, J_{C-F} = 18 Hz, 1C), 132.4 (q, J_{C-F} = 6 Hz, 1C), 134.3, 136.4, 138.6, 161.1 (dd, J_1 = 246.7 Hz, J_2 = 12 Hz, 1C), 162.3 (dd, J_1 = 234 Hz, J_2 = 12 Hz, 1C), 196.2; IR (neat) 3020,

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1686, 1605, 1508, 1217 cm^{-1}. Anal. Calcd for $C_{15}H_{12}F_2O$: C, 73.16, H, 4.91. Found: C, 73.13, H, 4.87.

*1,2-Diphenylpent-4-en-1-one (**5ca**, Scheme 3):* colorless viscous liquid (65 mg, 55%); ^1H NMR (300 MHz, $CDCl_3$) δ 2.41−2.50 (m, 1H), 2.80−2.90 (m, 1H), 4.51 (t, J = 7.2 Hz, 1H), 4.82−4.95 (m, 2H), 5.56−5.70 (m, 1H), 7.01−7.06 (m, 1H), 7.11−7.31 (m, 7H), 7.84 (d, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 38.3, 53.7, 116.8, 127.2, 128.3 (2C), 128.6 (2C), 128.8 (2C), 129.0 (2C), 133.0, 136.1, 136.8, 139.2, 199.2; IR (neat) 1717, 1682, 1597, 1448, 1269 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40, H, 6.82. Found: C, 86.43, H, 6.80.

*1-(2-Hydroxyphenyl)-2-phenylpent-4-en-1-one (**5da**, Scheme 3):* colorless viscous liquid (60 mg, 47%); ^1H NMR (300 MHz, $CDCl_3$) δ 2.56−2.66 (m, 1H), 2.93−3.02 (m, 1H), 4.69 (t, J = 7.2 Hz, 1H), 4.99−5.11 (m, 2H), 5.70−5.84 (m, 1H), 6.80−6.85 (m, 1H), 6.97 (dd, J_1 = 8.4 Hz, J_2 = 0.6 Hz, 1H), 7.22−7.35 (m, 6H), 7.83−7.86 (m, 1H), 12.43 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.9, 53.0, 117.2, 118.8, 118.9, 119.1, 127.5, 128.2 (2C), 129.2 (2C), 130.4, 135.7, 136.4, 138.9, 163.3, 205.4; IR (neat) 3020, 2979, 1643, 1633, 1579, 1485, 1446, 1217, 1155 cm^{-1}. Anal. Calcd for $C_{17}H_{16}O_2$: C, 80.93, H, 6.39. Found: C, 80.95, H, 6.43.

*1,2-Diphenylpent-4-yn-1-one (**5ea**, Scheme 4):* white solid (66 mg, 56%), mp 76−78 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 1.97 (t, J = 2.4 Hz, 1H), 2.70−2.78 (m, 1H), 3.03−3.12 (m, 1H), 4.82 (t, J = 7.5 Hz, 1H), 7.24−7.29 (m, 1H), 7.31−7.40 (m, 6H), 7.45−7.50 (m, 1H), 7.97−8.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.4, 52.9, 69.9, 82.3, 127.6, 128.2 (2C), 128.6 (2C), 128.9 (2C), 129.1 (2C), 133.1, 136.2, 138.1, 197.9; IR (neat) 1681, 1578, 1491, 1270 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O$: C, 87.15, H, 6.02. Found: C, 87.11, H, 6.00.

*1-(2-Hydroxyphenyl)-2-phenylpent-4-yn-1-one (**5fa**, Scheme 4):* colorless viscous liqud (62 mg, 49%); ^1H NMR (300 MHz, $CDCl_3$) δ 1.95 (t, J = 2.7 Hz, 1H), 2.65−2.73 (m, 1H), 2.99−3.07 (m, 1H), 4.82 (t, J = 7.5 Hz, 1H), 6.75−6.80 (m, 1H), 6.94 (dd, J_1 = 8.4 Hz, J_2 = 0.9 Hz, 1H), 7.22−7.39 (m, 6H), 7.76 (dd, J_1 = 8.1 Hz, J_2 = 1.5 Hz, 1H), 12.26 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 23.2, 52.4, 70.2, 81.9, 118.7, 119.0, 127.9, 128.0 (3C), 129.3 (2C), 130.5, 136.6, 138.0, 163.3, 203.9; IR (neat) 3018, 1640, 1629, 1480, 1441, 1150 cm^{-1}. Anal. Calcd for $C_{17}H_{14}O_2$: C, 81.58, H, 5.64. Found: C, 81.55, H, 5.61.

*1-(2-(Allyloxy)phenyl)-2-phenylpent-4-en-1-one (**5ga**, Scheme 5):* colorless viscous liquid (82 mg, 56%); ^1H NMR (300 MHz, $CDCl_3$) δ 2.54−2.64 (m, 1H), 2.94−3.04 (m, 1H), 4.58−4.61 (m, 2H), 4.80 (t, J = 7.5 Hz, 1H), 4.95−5.10 (m, 2H), 5.31−5.45 (m, 2H), 5.73−5.82 (m, 1H), 6.00−6.10 (m, 1H), 6.85−6.92 (m, 2H), 7.16−7.22 (m, 1H), 7.25 (d, J = 4.5 Hz, 4H), 7.30−7.36 (m, 1H), 7.42 (dd, J_1 = 7.5 Hz, J_2 = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 37.7, 57.5, 69.4, 112.7, 116.4, 118.3, 120.8, 126.9, 128.5 (2C), 128.8 (2C), 129.5, 130.5, 132.7, 132.8, 136.4, 138.9, 156.6, 203.1; IR (neat) 3301, 2918, 2124, 1671, 1479 cm^{-1}. Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16, H, 6.89. Found: C, 82.11, H, 6.91.

*2-Phenyl-1-(2-(prop-2-ynyloxy)phenyl)pent-4-yn-1-one (**5ha**, Scheme 5):* colorless viscous liquid (84 mg, 58%); ^1H NMR (300 MHz, $CDCl_3$) δ 1.89 (t, J = 3 Hz, 1H), 2.54 (t, J = 2.4 Hz, 1H), 2.62−2.72 (m, 1H), 2.97−3.06 (m, 1H), 4.66 (d, J = 2.4 Hz, 2H), 4.86−4.91 (m, 1H), 6.88−6.94 (m, 2H), 7.14−7.24 (m, 5H), 7.32−7.35 (m, 1H), 7.52 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 22.9, 56.1, 56.6, 69.7, 76.4, 77.9, 82.6, 112.9, 121.6, 127.3, 128.5 (2C), 128.7 (2C), 128.8, 130.9, 133.2, 137.9, 155.6, 200.9; IR (neat) 3302, 3028, 2920, 2122, 1674, 1597, 1483, 1452, 1292, 1219 cm^{-1}. Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31, H, 5.59. Found: C, 83.29, H, 5.61.

■ ASSOCIATED CONTENT

Supporting Information

Spectroscopic data of all known products and copies of ^1H NMR and ^{13}C NMR spectra for all synthesized compounds. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b00825.

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Notes

The authors declare no competing financial interest.

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