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Highly convenient regioselective synthesis of functionalized arylated benzene from ketene-*S*,*S*-acetal under mild conditions at room temperature ☆

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ABSTRACT

A general, highly efficient synthesis of arylated benzenes from simple stitching of α-oxo-ketene-*S*,*S*-acetals and functionalized deoxybenzoins via a 'lactone intermediate' is described. This procedure offers easy access to highly functionalized arylated benzenes containing sterically demanding groups in good to excellent yields. The advantage of the procedure lies in the fabrication of arylated benzenes with desired conformational flexibility along the molecular axis at room temperature and in a transition metal-free environment through easily accessible precursors.

Over the last few decades, polyarylated propeller systems have received a great deal of attention owing to their unique photophysical and optical properties associated with them.[1] These propeller systems exhibit a geared rotation about a central, planar unit such as a phenyl ring, which can perform as molecular rotors,[1] and thus have shown great relevance to modern carbon-nanotechnology.[2] The inherent rotational isomerism associated with sterically crowded arylated benzenes has further enhanced the importance of these propellers with a desired degree of rotational freedom for the development of new chiral ligands or auxiliaries for asymmetric synthesis.[3] Recently, a current interest has been focused to fabricate useful quateraryl or quinquearyl building blocks with electron-donor and -acceptor groups for preparing advanced electroluminescent materials such as organic light emitting diodes.[4]

Highly arylated benzenes are difficult to be synthesized by palladium-catalyzed iterative aryl–aryl cross-coupling between the electrophilic aromatic polyhalides and organometallic species.[5] Although there are numerous synthetic strategies for di- and/or triarylated benzenes,[6] methods for polyarylated benzene such as quater- or quinquephenyls remain sparse. Limited procedures are known for the synthesis of such arylated benzene, in which one of the phenyl rings is tagged with three or more aromatic rings in a juxtaposed manner. The most common and popular approach for the introduction of polyaryl groups onto the benzene skeleton is based on the [4+2]-cycloaddition of arylated cyclopentadienones or 2*H*-pyran-2-ones with functionalized alkynes at elevated temperatures.[7] The notable examples of various types of cycloaddition processes involve copper-mediated cycloaddition of zirconacyclopentadienes with fumaronitrile,[8] through flash vacuum pyrolysis of cyclobutane-fused sulfolanes,[9] reaction of tetraphenylcyclopentadienones either with allyl phenyl sulfone[10] or with 7-oxanorbornadienes[11] or with acrylonitriles[12] at high temperature. Some of these mentioned reactions, however, are relatively limited in scope particularly towards the tolerance of electron-donor or -acceptor substituents or involve high reaction temperature and/or formation of undesirable side products.

The wide-ranging applications and high demand of arylated benzenes and paucity of mild synthetic methodologies prompted us to develop a simple, general and efficient route that could offer flexibility of substituent variations on benzene scaffold. In this Letter, we report a highly convenient and commercially viable synthetic route for arylated benzenes through simple stitching of α-oxo-ketene-*S*,*S*-acetals and deoxybenzoin in just two steps via six-membered lactone intermediate. The versatility and generality of the procedure lies in the creation of a central benzene ring with optionally functionalized tetraaryl moieties in a controlled fashion at room temperature.

During our recent studies[13] on the chemistry of arylated 2*H*-pyran-2-ones, we observed that the nature of an electron-withdrawing group such as nitrile or ester group at position 3 of 2*H*-pyran-2-one dictates the Michael addition of a conjugate base of

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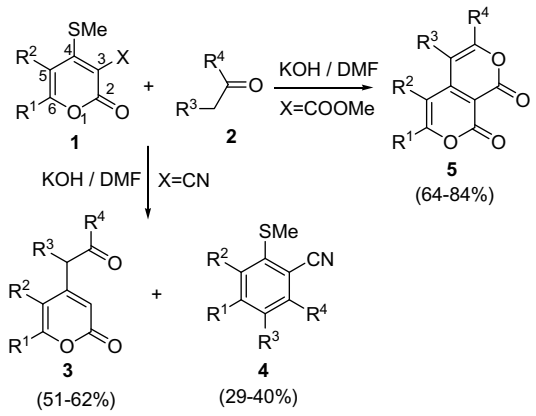


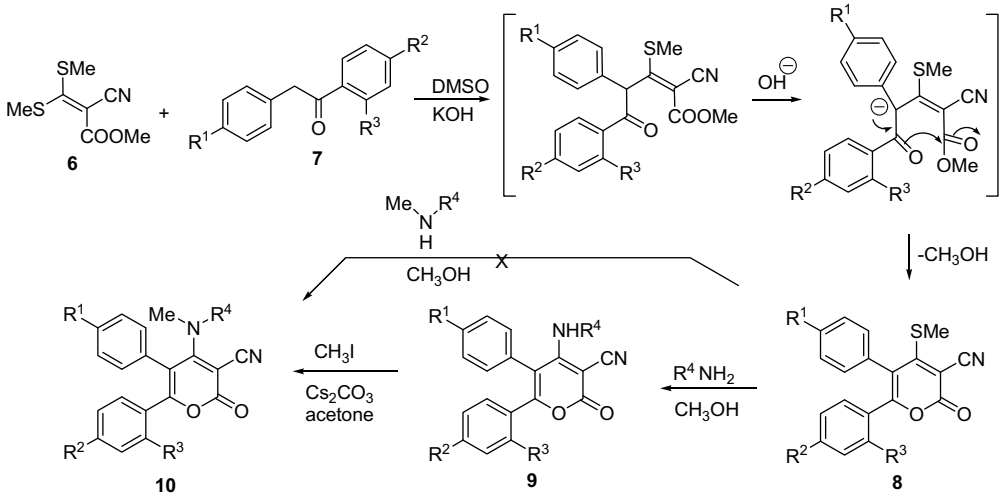
Scheme 1.

deoxybenzoin onto the lactone either at position 4 and/or position 6 of 5,6-diaryl-2*H*-pyran-2-ones (Scheme 1). The reaction of 3-cyano-5,6-diaryl-2*H*-pyran-2-ones (**1**, X = CN) with functionalized deoxybenzoins (**2**) led to the formation of 4-(2-oxo-1,2-diarylethyl)-5,6-diaryl-pyran-2-ones (**3**) through an unusual decyanation as a major product and tetraarylbenzene (**4**) as a minor product. A characteristic feature of 3-cyano-5,6-diaryl-2*H*-pyran-2-ones **1** revealed that C4 and C6 positions are susceptible to nucleophilic attack in a competitive manner depending upon the nature of nucleophile used. In order to prepare donor–acceptor arylated benzene exclusively, the change of electron density at position 4 of 2*H*-pyran-2-one **1** was desirable.

Our aim to prepare 5,6-diaryl-2*H*-pyran-2-ones **8a–d** was achieved by preparing a key intermediate α-cyano-ketene-*S,S*-acetal **6** from easily accessible precursors methyl cyanoacetate, carbon disulfide and methyl iodide through modified procedure.[4e,14] The α-cyano-ketene-*S,S*-acetal **6** on Michael addition–cyclization reaction with various substituted deoxybenzoins[15] **7a–d** under alkaline conditions furnished 5,6-diaryl-2*H*-pyran-2-ones[4e,13] **8a–d** in excellent yields (Scheme 2). The 5,6-diaryllactones **8a–d** generated from α-cyano-ketene-*S,S*-acetal **6** possess a methylsulfanyl group, which may be replaced by a secondary amine. In general, when a secondary amine reacts with 4-methylsulfanyl-2*H*-pyran-2-ones in the presence of methanol at reflux temperature, the corresponding 4-amino-2*H*-pyran-2-ones are formed very easily with excellent yields. Accordingly when we performed a reaction of 3-cyano-5,6-diaryl-4-methylsulfanyl-2*H*-pyran-2-ones and a secondary amine such as dimethyl amine or piperidine under similar conditions, to our surprise, no desired lactone **10** was obtained (Scheme 2).

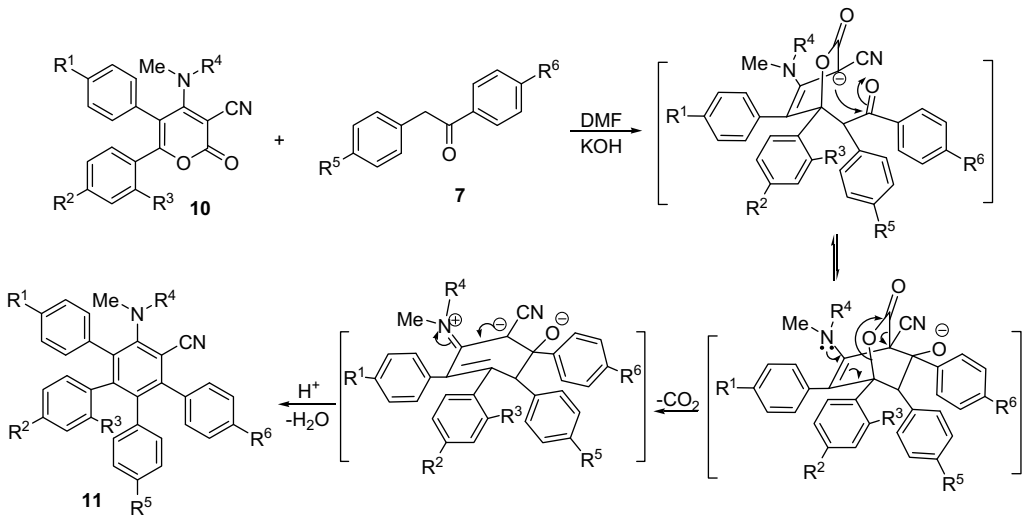
Interestingly, when we tried reaction of **8a–d** with a primary alkyl amine such as methyl amine or isopropyl amine, we observed a clean reaction leading to the formation of 5,6-diaryl-4-alkylamino-2-oxo-2*H*-pyran-3-carbonitriles **9a–e** in good yield.[16] Further, 5,6-diaryl-4-alkylamino-2-oxo-2*H*-pyran-3-carbonitriles **9a–e** were methylated to 5,6-diaryl-4-(*N*-alkyl,*N*-methylamino)-2-oxo-2*H*-pyran-3-carbonitriles **10a–e** by CH_3I in the presence of cesium carbonate in dry acetone under reflux conditions.[17]

Our approach to prepare 6′-(*N*-alkyl,*N*-methylamino)-[1,1′;2′,1″;3′,1‴;4′,1⁗]quinquephenyl-5′-carbonitriles **11a–i** is based on the ring transformation of 5,6-diaryl-4-(*N*-alkyl,*N*-methylamino)-2-oxo-2*H*-pyran-3-carbonitriles **10a–e** using functionalized deoxybenzoins **7a–d** as a carbanion source. Unfortunately, reaction of **10a** with a deoxybenzoin containing an electron-withdrawing nitro group (**7**, $R^5 = NO_2$, R^6 = OMe) resulted in a mixture of decomposed products. The 2*H*-pyran-2-ones **10a–e** have three electrophilic centres; C2, C4 and C6 in which the position C6 is highly susceptible to nucleophilic attack due to the extended conjugation and the presence of an electron-withdrawing substituent at position 3 of the pyranone ring. Thus, stirring an equimolar mixture of 5,6-diaryl-4-(*N*-alkyl,*N*-methylamino)-2-oxo-2*H*-pyran-3-carbonitriles **10a–e** and functionalized deoxybenzoins **7a–d** in the presence of KOH in dry DMF for 2–4 h at room temperature afforded 6′-(*N*-alkyl,*N*-methylamino)-[1,1′;2′,1″;3′,1‴;4′,1⁗]-quin-



Entry	R^1	R^2	R^3	R^4	Yield (%) 9	10
a	H	H	H	Me	71	90
b	H	OMe	H	Me	88	91
c	OMe	OMe	H	Me	90	89
d	Cl	OMe	OMe	Me	83	94
e	H	H	H	*i*-Pr	79	86

Scheme 2.



11	R^1	R^2	R^3	R^4	R^5	R^6	Yield (%)
a	H	H	H	Me	H	H	92
b	H	H	H	Me	H	Cl	89
c	H	OMe	H	Me	H	H	87
d	H	H	H	Me	OMe	OMe	88
e	H	OMe	H	Me	H	OMe	90
f	H	OMe	H	Me	OMe	OMe	92
g	OMe	OMe	H	Me	OMe	OMe	89
h	Cl	OMe	OMe	Me	H	H	56
i	H	H	H	i-Pr	OMe	OMe	73

Scheme 3.

quephenyl-5′-carbonitriles **11a–i** in 56–92% yields (Scheme 3). The reaction was monitored by TLC, which showed an intense blue spot when exposed to short-wave UV radiation at 254 nm. After completion, the reaction mixture was poured into ice water and neutralized with dilute HCl. The precipitate was filtered, dried over $CaCl_2$ and the crude product thus obtained was purified by neutral alumina column chromatography using chloroform/hexane (1:4) as the eluent. All the compounds were characterized by the spectroscopic analysis.[18]

The plausible reaction mechanism for the formation of donor–acceptor arylated benzenes **11a–i** from 2*H*-pyran-2-ones **10a–e** is depicted in Scheme 3. The transformation of 5,6-diaryl-2-oxo-2*H*-pyran-3-carbonitriles **10a–e** into quinquephenyls **11a–i** is possibly initiated by Michael addition of conjugate base of deoxybenzoin **7** at position C6 of lactone **10**, followed by intramolecular cyclization involving the carbonyl functionality of **7** and C3 of the pyranone ring followed by elimination of carbon dioxide and water to yield quinquephenyls **11a–i** in excellent yields.

In summary, we have demonstrated highly convenient ring transformation approach to access functionally congested arylated benzenes at room temperature in excellent yields. This protocol offers in a transition metal-free environment, the flexibility of introducing the electron-donor or -acceptor groups in the molecular architecture of arylated benzene scaffolds.

Acknowledgements

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16. *General procedure for the synthesis of 5,6-diaryl-4-alkylamino-2-oxo-2H-pyran-3-carbonitrile* (**9a–e**): A mixture of a respective compound **8a–d** (1 mmol) and methyl amine or isopropyl amine (1.2 mmol) was refluxed in methanol (10 mL) for 1–2 h. After completion, the solvent was evaporated under vacuum, and the residue was treated with water and extracted with chloroform. The crude product was purified on a silica gel column using chloroform as the eluent. Compound **9a**: White solid; mp 160–162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.41 (d, J = 5.6 Hz, 3H, NMe), 5.25 (br s, 1H, NH), 7.10–7.31 (m, 7H, ArH), 7.42–7.48 (m, 3H, ArH); IR (KBr) 1716 (CO), 2218 cm^{-1} (CN); MS (FAB) 303 (M^++1); HRMS calcd for $C_{19}H_{14}O_2N_2$: 302.1055, found: 302.1042. Compound **9b**: Yellow solid; mp 224–226 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.35 (d, J = 5.6 Hz, 3H, NMe), 3.75 (s, 3H, OMe), 5.18 (br s, 1H, NH), 6.66 (d, J = 9.0 Hz, 2H, ArH), 7.14 (d, J = 9.0 Hz, 2H, ArH), 7.16–7.24 (m, 2H, ArH), 7.43–7.51 (m, 3H, ArH); IR (KBr) 1702 (CO), 2215 cm^{-1} (CN); MS (ESI) 333 (M^++1). Compound **9c**: Yellow solid; mp 176–178 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.35 (d, J = 5.6 Hz, 3H, Me), 3.75 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 5.32 (br s, 1H, NH), 6.67 (d, J = 9.0 Hz, 2H, ArH), 6.99 (d, J = 9.0 Hz, 2H, ArH), 7.07–7.19 (m, 4H, ArH); IR (KBr) 1707 (CO), 2210 cm^{-1} (CN); MS (FAB) 363 (M^++1); ^{13}C NMR (50.0 MHz) 32.56, 55.69, 55.82, 110.41, 113.85, 116.21, 117.39, 122.06, 124.14, 131.31, 133.24, 158.14, 160.73, 160.91, 161.40. Compound **9d**: Yellow solid; mp 240–242 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.36 (d, J = 5.6 Hz, 3H, NMe), 3.57 (s, 3H, OMe), 3.75 (s, 3H, OMe), 5.31 (br s, 1H, NH), 6.21 (d, J = 2.0 Hz, 1H, ArH), 6.32 (dd, J = 2.0, 8.8 Hz, 1H, ArH), 6.97–7.08 (m, 3H, ArH), 7.31 (d, J = 8.3 Hz, 2H, ArH); IR (KBr) 1717 (CO), 2215 cm^{-1} (CN); MS (ESI) 397 (M^++1). Compound **9e**: White solid; mp 174–176 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 1.17 (d, J = 6.6 Hz, 6H, 2Me), 4.46–4.61 (m, 1H, CH), 5.82 (d, J = 8.2 Hz, 1H, NH), 7.13–7.34 (m, 7H, ArH), 7.38–7.48 (m, 3H, ArH); IR (KBr) 1712 (CO), 2208 cm^{-1} (CN); MS (ESI) 331 (M^++1); HRMS calcd for $C_{21}H_{18}O_2N_2$: 330.1368, found: 330.1374.
17. *General procedure for the synthesis of 4-(N-alkyl,N-methylamino)-2-oxo-5,6-diaryl-2H-pyran-3-carbonitrile* (**10a–e**): A mixture of a respective compound **9a–e** (1 mmol) and methyl iodide (1.5 mmol) was refluxed in dry acetone (10 mL) in the presence of Cs_2CO_3 (2 mmol) for 1–2 h. After completion, the unreacted Cs_2CO_3 was filtered and washed with acetone. The filtrate was evaporated under vacuum. Crude product was purified on a silica gel column using chloroform as the eluent. Compound **10a**: White solid; mp 216–218 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.89 (s, 6H, NMe_2), 7.05–7.35 (m, 10H, ArH); IR (KBr) 1716 (CO), 2227 cm^{-1} (CN); MS (FAB) 317 (M^++1). Compound **10b**: Yellow solid; mp 232–234 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.87 (s, 6H, NMe_2), 3.75 (s, 3H, OMe), 6.65 (d, J = 9.0 Hz, 2H, ArH), 7.02 (d, J = 9.0 Hz, 2H, ArH), 7.08–7.19 (m, 2H, ArH), 7.29–7.38 (m, 3H, ArH); IR (KBr) 1716 (CO), 2216 cm^{-1} (CN); MS (ESI) 347 (M^++1). Compound **10c**: Yellow solid; mp 212–214 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.88 (s, 6H, NMe_2), 3.76 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 6.67 (d, J = 8.8 Hz, 2H, ArH), 6.87 (d, J = 8.8 Hz, 2H, ArH), 6.97–7.08 (m, 4H, ArH); IR (KBr) 1704 (CO), 2208 cm^{-1} (CN); MS (FAB) 377 (M^++1). Compound **10d**: Yellow solid; mp 226–228 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.90 (s, 6H, NMe_2), 3.59 (s, 3H, OMe), 3.75 (s, 3H, OMe), 6.23 (d, J = 2.0 Hz, 1H, ArH), 6.31 (d, J = 2.0, 8.4 Hz, 1H, ArH), 6.86 (d, J = 8.4 Hz, 2H, ArH), 7.19 (d, J = 8.4 Hz, 2H, Ar); IR (KBr) 1716 (CO), 2214 cm^{-1} (CN); MS (ESI) 411 (M^++1). Compound **10e**: White solid; mp 178–180 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.00 (d, J = 6.6 Hz, 6H, 2Me), 2.78 (s, 3H, NMe), 3.96–4.09 (m, 1H, CH), 7.02–7.25 (m, 7H, ArH), 7.27–7.33 (m, 3H, ArH); IR (KBr) 1709 (CO), 2217 cm^{-1} (CN); MS (ESI) 345 (M^++1).
18. *General procedure for the synthesis of 6′-N-alkyl,N-methylamino-[1,1′;2′,1″;3′,1‴;4′,1⁗]-quinquearyl-5′-carbonitrile* (**11a–i**): A mixture of a respective compound **10a–e** (1 mmol), functionalized deoxybenzoins **7** (1.2 mmol) and powdered KOH (1.2 mmol) in dry DMF (5 mL) was stirred at room temperature for 2–5 h. At the end, reaction mixture was poured into ice water with vigorous stirring and finally neutralized with dilute HCl. The solid thus obtained was filtered and purified on a neutral alumina column using chloroform–hexane (1:4) as the eluent. Compound **11a**: White solid; mp 174–176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.67 (s, 6H, NMe_2), 6.67–6.76 (m, 4H, ArH), 6.80–6.87 (m, 6H, ArH), 6.97–7.04 (m, 2H, ArH), 7.14–7.22 (m, 8H, ArH); IR (KBr) 2215 cm^{-1} (CN); MS (ESI) 451 (M^++1); HRMS calcd for $C_{33}H_{26}N_2$: 450.2096, found: 450.2093. Compound **11b**: White solid; mp 188–190 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.66 (s, 6H, NMe_2), 6.64–6.77 (m, 4H, ArH), 6.79–6.90 (m, 6H, ArH), 6.94–7.03 (m, 2H, ArH), 7.07–7.23 (m, 7H, ArH); IR (KBr) 2218 cm^{-1} (CN); MS (ESI) 485 (M^++1); HRMS calcd for $C_{33}H_{25}ClN_2$: 484.1706, found: 484.1706. Compound **11c**: White solid; mp 224–226 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.66 (s, 6H, NMe_2), 3.59 (s, 3H, OMe), 6.38 (d, J = 8.6 Hz, 2H, ArH), 6.59 (d, J = 8.6 Hz, 2H, ArH), 6.67–6.74 (m, 2H, ArH), 6.81–6.88 (m, 3H, ArH), 7.00 (d, J = 8.6 Hz, 2H, ArH), 7.07–7.18 (m, 8H, ArH); IR (KBr) 2214 cm^{-1} (CN); MS (ESI) 481 (M^++1). Compound **11d**: White solid; mp 182–184 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.65 (s, 6H, NMe_2), 3.60 (s, 3H, OMe), 3.76 (s, 3H, OMe), 6.39 (d, J = 8.6 Hz, 2H, ArH), 6.61 (d, J = 8.6 Hz, 2H, ArH), 6.64–6.80 (m, 4H, ArH), 6.81–6.91 (m, 3H, ArH), 6.93–7.02 (m, 2H, ArH), 7.05–7.20 (m, 5H, ArH); IR (KBr) 2214 cm^{-1} (CN); MS (ESI) 511 (M^++1). Compound **11e**: White solid; mp 144–146 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.65 (s, 6H, NMe_2), 3.59 (s, 3H, OMe), 3.74 (s, 3H, OMe), 6.38 (d, J = 8.8 Hz, 2H, ArH), 6.58 (d, J = 8.8 Hz, 2H, ArH), 6.67–6.76 (m, 4H, ArH), 6.82–6.93 (m, 3H, ArH), 6.95–7.02 (m, 2H, ArH), 7.04–7.22 (m, 5H, ArH); IR (KBr) 2216 cm^{-1} (CN); MS (ESI) 511 (M^++1). Compound **11f**: White solid; mp 138–140 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.60 (s, 6H, NMe_2), 3.56 (s, 3H, OMe), 3.57 (s, 3H, OMe), 3.72 (s, 3H, OMe), 6.32–6.44 (m, 4H, ArH), 6.50–6.62 (m, 4H, ArH), 6.70 (d, J = 8.6 Hz, 2H, ArH), 6.90–6.98 (m, 2H, ArH), 7.00–7.19 (m, 5H, ArH); IR (KBr) 2217 cm^{-1} (CN); MS (ESI) 541 (M^++1); HRMS calcd for $C_{36}H_{32}N_2O_3$: 540.2413, found: 540.2400. Compound **11g**: White solid; mp 214–216 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.65 (s, 6H, NMe_2), 3.62 (s, 6H, 2OMe), 3.76 (s, 6H, 2OMe), 6.41 (d, J = 8.6 Hz, 4H, ArH), 6.54–6.64 (m, 4H, ArH), 6.66–6.78 (m, 4H, ArH), 6.88 (d, J = 8.6 Hz, 2H, ArH), 7.07 (d, J = 8.6 Hz, 2H, ArH); IR (KBr) 2213 cm^{-1} (CN); MS (ESI) 571 (M^++1). Compound **11h**: White solid; mp 140–142 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.68 (s, 6H, NMe_2), 3.46 (s, 3H, OMe), 3.61 (s, 3H, OMe), 5.96 (d, J = 2.2 Hz, 1H, ArH), 6.05 (dd, J = 8.4, 2.2 Hz, 1H, ArH), 6.47 (d, J = 8.4 Hz, 1H, ArH), 6.65–6.68 (m, 1H, ArH), 6.78–6.88 (m, 4H, ArH), 6.89–7.05 (m, 2H, ArH), 7.11–7.22 (m, 7H, ArH); IR (KBr) 2214 cm^{-1} (CN); MS (ESI) 545 (M^++1). Compound **11i**: White solid; mp 136–138 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.82 (d, J = 6.5 Hz, 6H, 2Me), 2.86 (s, 3H, NMe), 3.14–3.22 (m, 1H, CH), 3.60 (s, 3H, OMe), 3.76 (s, 3H, OMe), 6.39 (d, J = 8.8 Hz, 2H, ArH), 6.62 (d, J = 8.5 Hz, 2H, ArH), 6.67–6.71 (m, 2H, ArH), 6.75 (d, J = 8.8 Hz, 2H, ArH), 6.80–6.88 (m, 3H, ArH), 6.96–7.02 (m, 2H, ArH), 7.04–7.15 (m, 5H, ArH); IR (KBr) 2218 cm^{-1} (CN); MS (ESI) 539 (M^++1).