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Efficient palladium-catalyzed synthesis of unsymmetrical donor–acceptor biaryls and polyaryls

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Abstract

4,4′-Unsymmetrically substituted biphenyls can be synthesized by cross-coupling reactions of substituted aromatic organometallic reagents and aromatic halides catalyzed by palladium complexes. This two-step method from commercially available aromatic halides has been used for the synthesis of a series of donor/acceptor *para*-substituted biphenyls, D–C_6H_4–C_6H_4–A, where D is an electron donor group and A an electron acceptor group, which are of interest as liquid crystal precursors and as having potential in non-linear optics. Biaryls in which the donor-phenyl moiety is replaced by a 2-furyl or 2-thienyl can be synthesized similarly. The method can also be used for the convergent synthesis of previously unreported unsymmetrically substituted polyparaphenylenes D-(C_6H_4)$_n$A (n = 3,4).

Introduction

Functionalized unsymmetrical biaryls are important constituents of some pharmaceutical products [1,2] but nowadays their main interest stems from their physical properties in liquid crystals [3]. More recently they have found new applications in the field of non-linear optics. Indeed unsymmetrically substituted biaryls such as D–Ar–Ar′–A, in which D is an electron donor and A an electron acceptor linked by a conjugated polarizable relay Ar–Ar′ have been shown to give rise to second harmonic generation (SHG) with high values of the hyperpolarizability coefficient β [4–11,12*]. These properties, which can be used in the development of new

* Reference number with asterisk indicates a note in the list of references.

electro-optical components, depend on the exact nature of the donor and acceptor moieties as well as on the conjugated relay connecting them. Experimental confirmation and improvement of relevant theories about SHG [4–6,12 *], as well as screening for the best molecular species, clearly requires an easy route to extended families of these derivatives. Moreover chemio- and regio-selective syntheses are highly desirable to avoid possible distortion of SHG measurements arising from contamination by side-products.

Several ways can be envisaged for achieving these goals. One might involve substitutions of polyaryls by the usual electrophilic reactions, but this has to be rejected because of its poor selectivity. A second way involves a convergent synthesis, based on the aryl–aryl coupling of independently substituted aryl moieties. Classical methods for aryl–aryl bond formation [13], mainly the Ullmann [14] and the Gomberg [15] reactions, are not very efficient and selective for the synthesis of highly functionalised donor/acceptor unsymmetrical biaryls. More interesting in this respect are synthesis based on the electrochemically [7,16–18] or photochemically [19] induced $S_{RN}1$-like mechanism. However this reaction is restricted to specific donor groups, since the aryl-donor moiety must behave as a soft nucleophile in the coupling step. More recently unsymmetrical biaryls have been obtained by the reaction of two differently substituted aromatic halides catalyzed by nickel complexes under reducing conditions, involving either chemical [20,21] or electrochemical reduction [22] but with a stoechiometric amount of nickel complexes.

We show below that the palladium-catalyzed cross-coupling reaction [23,24] of readily available organometallic reagents and aromatic halides can be used for the selective convergent synthesis of a wide range of unsymmetrically substituted polyaryls.

Results and discussion

Palladium complexes are well known to be efficient catalysts for cross-coupling reactions of organometallics, RMX (where MX = MgBr, Li), and aromatic halides [23,24]:

$$RMX + ArX' \xrightarrow{[Pd^0(PPh_3)_4]} R{-}Ar + MXX' \qquad (1)$$

Synthesis of donor-acceptor polyparaphenylenes

Since reaction 1 has been shown to be compatible with several organic functions on either the aromatic organometallic reagent [24–27] or the aromatic halide [24–28], we decided to examine its possible extension to the synthesis of unsymmetrical biaryls in which one aryl group bears an electron donor group D, and the other an electron acceptor group A:

$$D{-}Ar{-}MX + X'{-}Ar'{-}A \xrightarrow{[Pd^0(PPh_3)_4]} D{-}Ar{-}Ar'{-}A + MXX' \qquad (2)$$

(M = Mg, Zn; X = Br, Cl; X′ = I, Br)

The results reported in Table 1 show that the palladium-catalyzed coupling reaction provides a convenient two-step route to unsymmetrical biphenyl derivatives

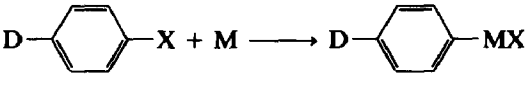
Table 1

Synthesis of unsymmetrical biphenyls from p-D-C_6H_4-MX and p-X′-C_6H_4-A (see eq. 4) [a]

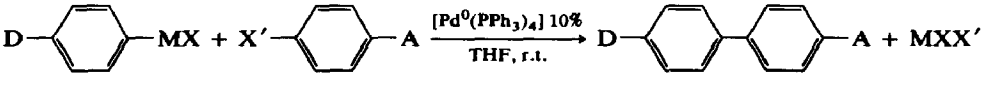
D	MX	X′	A	t [b]	D–⟨⟩–⟨⟩–A	This work [c] (%)	Lit. [d] (%)	Cpd
$(CH_3)_2N$	MgBr	I	CN	2	$(CH_3)_2N$–⟨⟩–⟨⟩–CN	71 (38)		1
$(CH_3)_2N$	ZnCl	Br	CN	12	$(CH_3)_2N$–⟨⟩–⟨⟩–CN	91 (78)	22 [29]	1
CH_3O	MgBr	I	CN	2	CH_3O–⟨⟩–⟨⟩–CN	–(55)		2
CH_3O	ZnCl	Br	CN	24	CH_3O–⟨⟩–⟨⟩–CN	100 (81)	50 [7]	2
CH_3S	MgBr	I	CN	2	CH_3S–⟨⟩–⟨⟩–CN	85 (60)		3
$(CH_3)_2N$	ZnCl	I	NO_2	2	$(CH_3)_2N$–⟨⟩–⟨⟩–NO_2	92 (70)	12 [30]	4
$(CH_3)_2N$	ZnCl	Br	NO_2	12	$(CH_3)_2N$–⟨⟩–⟨⟩–NO_2	58 (46)		4
CH_3O	ZnCl	Br	NO_2	12	CH_3O–⟨⟩–⟨⟩–NO_2	76 (71)	74 [31]	5
CH_3S	ZnCl	Br	NO_2	12	CH_3S–⟨⟩–⟨⟩–NO_2	– (42)		6

[a] All reactions were performed at room temperature, 20 °C. [b] Reaction time in h. [c] Yield determined by ^1H NMR spectroscopy with $Cl_2HCCHCl_2$ as internal standard and isolated yields between parenthesis. Yields are relative to the initial amount of the aryl halide p-X′C_6H_4A. [d] Best reported yield with reference.

from commercially available aryl halides and reagents.



(3)

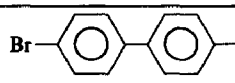
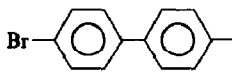
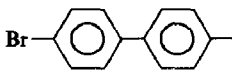


(4)

The use of Grignard reagents in the cross-coupling step requires the carbon–halogen bond in the acceptor aryl halide to be considerably more reactive than the

Table 2

Synthesis of the precursors from p-Br$\{C_6H_4\}_{n_1}$ZnCl and p-Br$\{C_6H_4\}_{n_2}$CN (see eq. 5)

n_1	n_2	Br$\{C_6H_4\}_{n_1+n_2}$CN	This work [a]	Lit. [b,c]	Cpd
1	1	 [d]	53	50 [33]	7
1	2	 [e]	31		8
2	1	 [f]	74		8

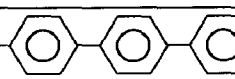
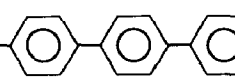
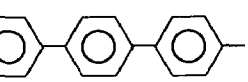
[a] Isolated yields relative to the initial amount of the aryl halide p-Br$(C_6H_4)_{n2}$CN in %. [b] Best reported yield in %. [c] Reference. [d] $[Pd^0L_4]$ 2.5%, 12 h at 20 °C + 2h at 60 °C. [e] $[Pd^0L_4]$ 10%, 24 h at 20 °C. [f] $[Pd^0L_4]$ 2%, 24 h at 20 °C.

acceptor group itself. This would restrict the above method to the functionalization of aryl iodides except when the acceptor group, A in p-X′–C_6H_4–A, is unreactive. This rules out the use of e.g. nitro, nitriles, and esters, that is of the best electron-withdrawing groups from the point of view of SHG. A simple variant on the method is to use organozinc reagents, which are known to be considerably less reactive towards such groups than the corresponding Grignard reagents, although they show a comparable reactivity in palladium catalyzed aromatic halide substitutions [26,28]. This is evident from the results reported in Table 1, which demonstrate that bromide derivatives can be used.

The $Pd^0(PPh_3)_4$ catalyst was found to be compatible with all the the electron acceptor groups investigated in this study. Although zerovalent nickel complexes are

Table 3

Synthesis of unsymmetrical polyphenyls from p-D–C_6H_4–ZnCl and p-Br$\{C_6H_4\}_{n-1}$CN (see eq. 6)

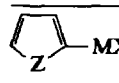
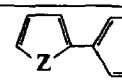
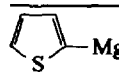
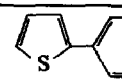
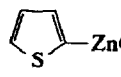
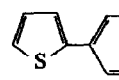
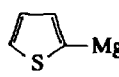
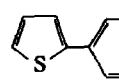
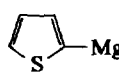
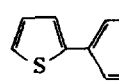
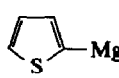
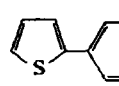
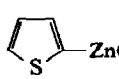
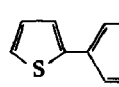
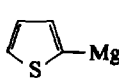
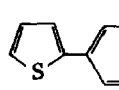
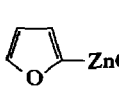
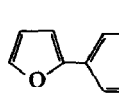
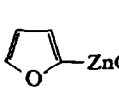
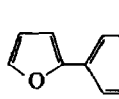
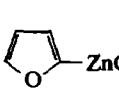
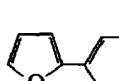
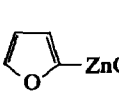
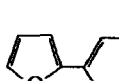
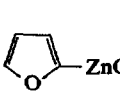
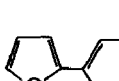
D	$n-1$	D$\{C_6H_4\}_n$CN	Yield [a] (%)	Cpd
$(CH_3)_2N$	2	$(CH_3)_2N$  [b]	54	9
$(CH_3)_2N$	3	$(CH_3)_2N$  [c]	55	10
CH_3S	2	CH_3S  [c]	69	11

[a] Isolated yield based on the initial amount of aryl halide p-Br$\{C_6H_4\}_{n-1}$CN. [b] 12 h at 20 °C. [c] 12 h at 20 °C + 2 h at 60 °C.

The reactions have not been optimized.

Table 4

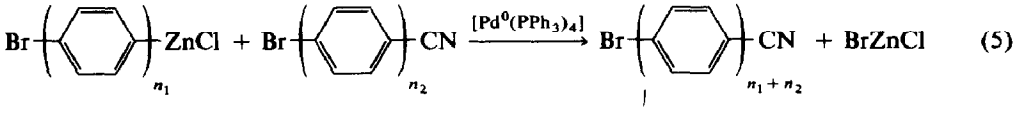
Synthesis of unsymmetrical biaryls from 2-thienyl–MX or 2-furyl–MX and *p*-X′–C_6H_4–A (see eq. 8) [a]

	X′	A	*t* [b]		This work [c]	Lit. [d]	Cpd
	I	NO_2	2		32 –		**12**
 [e]	I	NO_2	2		72 (67)	98 [34]	**12**
	I	CN	2		83 (73)	85 [34]	**13**
 [f]	I	CO_2H	2		(52)	25 [35]	**14**
	I	CO_2Bu	2		60 (59)		**15**
	Br	CO_2Bu	24		98 (84)		**15**
	I	$CON(Et)_2$	2		97 (80)		**16**
 [g]	I	NO_2	2		98 (71)	75 [34]	**17**
	Br	CN	24		98 (74)	57 [36]	**18**
 [f]	I	CO_2H	2		89 (47)	42 [37]	**19**
	I	CO_2Bu	2		92 (72)		**20**
	I	$CON(Et)_2$	2		99 (80)		**21**

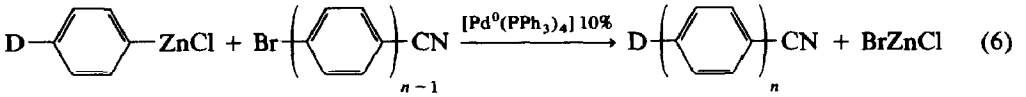
[a] All experiments were performed at room temperature, 20 °C. [b] Reaction time in h. [c] Yield determined by ^1H NMR with $Cl_2HCCHCl_2$ as internal standard and isolated yield between parenthesis. Yields are relative to the initial amount of and halide *p*-X′–C_6H_4–A which was entirely converted at the end of the reaction. [d] Best reported yield with reference. [e] 2-Thienylzinc chloride was prepared via zinc chloride treatment of 2-thienylmagnesium bromide [38]. [f] 2 Equivalents. [g] 2-Furylzinc chloride was prepared via zinc chloride treatment of 2-furyllithium which was synthesized from furan and butyllithium [38].

thought to be more efficient catalysts in nucleophilic aromatic substitutions [32], they proved to be less satisfactory for our purposes because of competitive reactions involving the electron acceptor substituent. For example, when A was CN we observed that replacement of cyanide competed with that of the bromide. Similarly zerovalent nickel complexes reacted with the nitro group for A = NO_2, presumably by an oxidation process [27,28].

Table 2 shows that the same method gives good yields when the donor substituent is replaced by a bromide. This can be used linearly to give substituted polyphenyl bromides (eq. 5) which can be converted via the cross-coupling reaction 6 into unsymmetrically substituted donor–acceptor polyphenyls, $D\text{-}(C_6H_4)\text{-}_nA$. This method was successfully applied to the synthesis of unsymmetrically substituted polyparaphenylenes, as can be seen from the results in Table 3, its only limitation arising from insolubility of the precursors ($n \leq 4$).



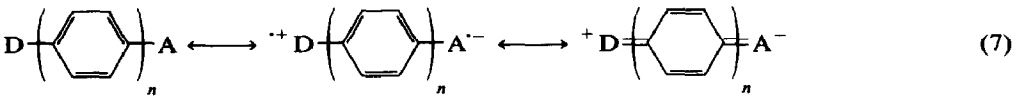
(5)



(6)

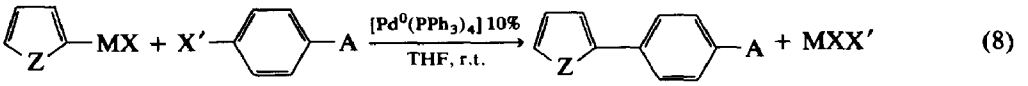
Synthesis of donor–acceptor biaryls containing heterocyclic donor aryl groups

In the above section we were concerned with the synthesis of species in which the donor and acceptor moieties consisted of classical electron donating and withdrawing groups. However the SHG molecular efficiency is related to the ability of these groups to stabilize charge transfer mesomeric forms in the ground state:



(7)

From a chemical point of view these delocalized ionic forms appear to be favored when the donor or acceptor substituent is included in a π-aromatic system. We thus decided to examine the synthetic potential of our method (eq. 4) in cases in which the donor is an heterocycle, viz. a furyl or thienyl moiety (Z = O, S):



(8)

The results presented in Table 4 show that the palladium catalyzed coupling reaction affords unsymmetrical biaryl derivatives in good yields. Indeed, in most cases the yields are quantitative, and always larger than those usually obtained by the the Gomberg–Bachmann method [15,39] or most other previously reported procedures [35–37] (see however Ref. 34, for the synthesis of 4-(2-thienyl)nitrobenzene (**12**), and 4-(2-thienyl)cyanobenzene (**13**), by use of organomercuric reagents). As observed for the biphenyls and polyphenyls cases, organozinc reagents appear to give better yields than the corresponding Grignard reagents owing to their lower reactivity towards electron acceptor groups.

Conclusion

Palladium cross-coupling reaction between a donor-substituted aromatic organometallic reagent and an acceptor-substituted aromatic halide has been shown to provide an efficient synthesis of a great variety of unsymmetrical biphenyls, polyphenyls and biaryls compounds, in higher yields than those obtained by previous procedures. Moreover, starting from commercially available aromatic halides, it can be used linearly or convergently to make previously unreported compounds with properties important for non-linear optics [12*]. Owing to its regiospecificity it can be extended to make *ortho* or *meta* substituted unsymmetrical biaryls, as well as derivatives bearing several electron donating or withdrawing groups, although in this paper we have focused on the synthesis of *para*-disubstituted polyaryls because of their potential properties for second harmonic generation [4–6,12*].

Experimental

The ^{1}H NMR 250 MHz spectra were recorded on a Bruker AC 250 spectrometer. IR spectra were recorded on a Perkin Elmer Model 599.

Chemicals

THF (Janssen) was distilled over sodium-benzophenone. Most substituted aromatic halides were obtained commercially (Janssen, Aldrich and K & K) and used without further purification. The compound *p*-I–C_6H_4–CO_2Bu was synthesized by esterification of the corresponding acid. *p*-I–C_6H_4–$CON(Et)_2$ was made by the reaction of diethylamine with *p*-I–C_6H_4–COCl.

General procedure

X′–Ar′–A (5 mmol) was added under argon into 5 ml of anhydrous THF, followed by 0.5 mmol of $Pd(PPh_3)_4$ and 6 mmol of a THF solution (ca. 2 *M*) of the organometallic reagents D–ArMgBr or D–ArZnCl in THF (the D–ArZnCl was made by treating the corresponding Grignard reagent with anhydrous zinc chloride in THF at 0 °C). After reaction (for reaction times and at temperatures indicated in footnotes to the relevant tables) the mixture was treated with aqueous HCl 10% or with water alone in the case of compounds **1** and **4**) and the organic products then extracted with methylene chloride. Pure unsymmetrical biphenyls and biaryls were isolated by flash chromatography (eluent: petroleum ether and ethylacetate). Compounds **8**–**11** were isolated by simple filtration, and washed with water then petroleum ether.

Products identification

Products were characterized by their melting points and IR, ^{1}H NMR, and mass spectra. We report here spectroscopic data which were not previously available in the literature.

Compound **1** [29]: ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.05 (s, 6H); 6.86 (d, *J* 9 Hz, 2H); 7.58 (d, *J* 9 Hz, 2H); 7.69 (s, 4H). IR (KBr): ν(C≡N) 2220 cm^{-1}; $\nu(N(CH_3)_2)$ 1360 cm^{-1}. MS: $m/z = 222$.

Compound **2** [7,17].

Compound **3**: m.p. 112–114° C; ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.56 (s, 3H); 7.38 (d, *J* 9 Hz, 2H); 7.56 (d, *J* 9 Hz, 2H); 7.69 (d, *J* 9 Hz, 2H); 7.76 (d, *J* 9Hz, 2H). IR (KBr): ν(C≡N) 2220 cm^{-1}. MS: *m/z* = 225, 210. Anal. Found: C, 73.98; H, 4.69; N 5.88. $C_{14}H_{11}NS$ calcd.: C, 74.56; H, 4.92; N, 6.22%.

Compound **4** [30]: ^{1}H NMR (250 MHz, $CDCl_3$): δ 3.06 (s, 6H); 6.89 (d, *J* 9 Hz, 2H); 7.53 (d, *J* 9 Hz, 2H); 7.75 (d, *J* 9 Hz, 2H); 8.3 (d, *J* 9 Hz, 2H). IR (KBr): $\nu(NO_2)$ 1335 cm^{-1}; $\nu(N(CH_3)_2)$ 1375 cm^{-1}. MS: *m/z* = 242, 212, 196.

Compound **5** [31,40]: MS: *m/z* = 229, 214, 199, 183.

Compound **6**: m.p. 128° C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.54 (s, 3H); 7.35 (d, *J* 9 Hz, 2H); 7.56 (d, *J* 9 Hz, 2H); 7.71 (d, *J* 9 Hz, 2H); 8.28 (d, *J* 9 Hz, 2H). IR (KBr): $\nu(NO_2)$ 1340 cm^{-1}. MS: *m/z* = 245, 231. Anal. Found: C, 64.01; H, 4.66; N, 5.52. $C_{13}H_{11}NO_2S$ calcd.: C, 63.69; H, 4.48; N 5.71%.

Compound **7** [33,41]: ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.46 (d, *J* 9 Hz, 2H); 7.63 (d, *J* 9 Hz, 2H); 7.66 (d, *J* 9 Hz, 2H); 7.75 (d, *J* 9 Hz, 2H). MS: *m/z* = 259,257, 177, 151.

Compound **8**: m.p. 260° C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.55 (d, *J* 9 Hz, 2H); 7.64 (d, *J* 9 Hz, 2H); 7.72 (s, 4H); 7.78 (m, 4H). IR (KBr): ν(C≡N) 2220 cm^{-1}. MS: *m/z* = 335,333, 255. Anal. Found: C, 68.19; H, 3.66; N 4.00. $C_{19}H_{12}BrN$ calcd.: C, 68.28, H 3.59, N 4.19%.

Compound **9**: m.p. > 280° C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 6.86 (d, *J* 9 Hz, 2H); 7.6 (d, *J* 9 Hz, 2H); 7.65 (d, *J* 9 Hz, 2H); 7.71 (*d*, *J* 9 Hz, 2H); 7.76 (s, 4H). IR (KBr): ν(C≡N) 2240 cm^{-1}; $\nu(N(CH_3)_2)$ 1360 cm^{-1}. MS: *m/z* = 298, 282, 254. Anal. Found C, 83.97; H, 6.13; N, 9.25. $C_{21}H_{18}N_2$ calcd.: C, 84.56; H, 6.04; N, 9.39%.

Compound **10**: m.p. > 280° C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.88 (d, *J* 9 Hz, 2H); 7.6 (d, *J* 9 Hz, 2H); 7.72 (m, 8 H); 7.8 (s, 4H). IR (KBr): ν(C≡N) 2220 cm^{-1}. MS: *m/z* = 374. Anal. Found: C, 86.01; H, 5.98; N, 7.11. $C_{27}H_{22}N_2$ calcd.: C, 86.64; H, 5.88; N, 7.48%.

Compound **11**: m.p. 202–204° C. ^{1}H NMR (250 MHz, $CDCl_3$): δ 2.54 (s, 3H); 7.35 (d, *J* 9 Hz, 2H); 7.57 (d, *J* 9 Hz, 2H); 7.68 (m, 4H); 7.76 (dd, 4H). IR (KBr): ν(C≡N) 2215 cm^{-1}. MS: *m/z* = 301, 286. Anal. Found: C, 79.55; H, 4.45; N, 5.09. $C_{20}H_{15}NS$ calcd.: C, 79.75; H, 4.98; N, 4.64%.

Compound **12** [34,39]: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.2 (dd, *J* 5, 3.5 Hz, 1H); 7.5 (dd, *J* 5, 1 Hz, 1H); 7.54 (dd *J* 3.5, 1 Hz, 1H); 7.8 (d, *J* 9 Hz, 2H); 8.28 (d, *J* 9 Hz, 2H). MS: *m/z* = 205, 175, 115.

Compound **13** [34]: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.17 (dd, *J* 5, 3.5 Hz, 1H); 7.43 (dd, *J* 5, 1 Hz, 1H); 7.46 (dd, *J* 3.5, 1 Hz, 1H); 7.69 (d, *J* 9 Hz, 2H); 7.74 (d, *J* 9 Hz, 2H). IR (KBr): ν(C≡N) 2240 cm^{-1}. MS: *m/z* = 185.

Compound **14** [35]: ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.21 (dd, *J* 5, 3.5 Hz, 1H); 7.61 (dd, *J* = 5, 1 Hz, 1H); 7.67 (dd, *J* 3.5, 1 Hz, 1H); 7.84 (d, *J* 9 Hz, 2H); 8.10 (d, *J* 9 Hz, 2H). MS: *m/z* = 204, 187, 159.

Compound **15** [42*]: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.00 (t, *J* 6.5 Hz, 3H); 1.49 (m, *J* 6.5 Hz, 2H); 1.77 (m, *J* 6.5 Hz, 2H); 4.35 (t, *J* 6.5 Hz, 2H); 7.12 (dd, *J* 5, 3.5 Hz, 1H); 7.36 (dd, *J* 5, 1 Hz, 1H); 7.43 (dd, *J* 3.5, 1 Hz, 1H); 7.67 (d, *J* 8.5 Hz, 2H); 8.05 (d, *J* 8.5 Hz, 2H). IR (KBr): ν(C–H) 2960 cm^{-1}, ν(C=O) 1715 cm^{-1}, ν(C–O) 1280 cm^{-1}. MS: *m/z* = 260, 204.

Compound **16**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.2 (t, *J* 6.5 Hz, 6H); 3.4 (m, 4H); 7.07 (dd, *J* 5, 3.5 Hz, 1H); 7.29 (dd, *J* 5, 1 Hz, 1H); 7.32 (dd, *J* 3.5, 1 Hz, 1H); 7.36 (d, *J* 8.5 Hz, 2H); 7.6 (d, *J* 8.5 Hz, 2H). MS: *m/z* = 259, 187, 159.

Compound **17** [15,34,37]: ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.62 (dd, J 3.5, 2 Hz, 1H); 6.94 (dd, J 3.5, 0.7 Hz, 1H); 7.64 (dd, J 2, 0.7 Hz, 1H); 7.86 (d, J 9 Hz, 2H); 8.31 (d, J 9 Hz, 2H). MS: m/z = 189, 159, 143.
Compound **18**: [36].
Compound **19** [37,43]: ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.67 (dd, J 3.5, 2 Hz, 1H); 7.13 (dd, J 3.5, 0.7 Hz, 1H); 7.77 (dd, J 2, 0.7 Hz, 1H); 7.90 (d, J 8.5 Hz, 2H); 8.13 (d, J 8.5 Hz, 2H). MS: m/z = 188, 171, 143.
Compound **20**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.00 (t, J 7 Hz, 3H); 1.5 (m, J 7 Hz, 2H); 1.78 (m, J 7 Hz, 2H); 4.35 (t, J 7 Hz, 2H); 6.57 (dd, J 3.5, 2 Hz, 1H); 6.85 (dd, J 3.5, 0.7 Hz, 1H); 7.57 (dd, J 2, 0.7 Hz, 1H); 7.77 (d, J 8.5 Hz, 2H); 8.11(d, J 8.5 Hz, 2H). MS: m/z = 244, 188, 171, 143.
Compound **21**: ^{1}H NMR (250 MHz, $CDCl_3$) δ 1.22 (t, J 7 Hz, 6H); 3.46 (q, J 7 Hz, 4H); 6.55 (dd, J 3.5, 2 Hz, 1H); 6.78 (dd, J 3.5, 0.7 Hz, 1H); 7.46 (d, J 8.5 Hz, 2H); 7.54 (dd J 2, 0.7 Hz, 1H); 7.76 (d, J 8.5 Hz, 2H). IR (KBr): ν(C–H) 2970 cm^{-1}, ν(C=O) 1620 cm^{-1}. MS: m/z = 243, 242, 171, 143.

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