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An efficient synthesis of phthalic acid derivatives *via* three component coupling reaction of ethyl β-arylcrotonate, DMF.DMA and DMAD

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A facile synthesis of biaryl systems has been achieved involving three-component coupling reaction of ethyl β-arylcrotonate, DMF.DMA and electron deficient alkyne. Antibacterial and antifungal activities of a representative biaryl compound are also reported.

Keywords: Multi-component reaction, ethyl β-arylcrotonate, enamine, Diels-Alder reaction, phthalate

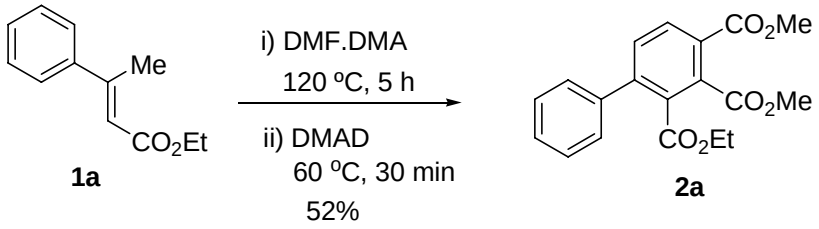
In recent years, research in academic and industry has increasingly emphasized the search for atom-efficient transformation of easily available starting materials into complex organic molecules[1]. In this respect, reactions that provide maximum diversity, i.e. reactions with high exploratory power, are especially desirable. Here, expeditious multi-component reactions (MCR)[2] as well as domino reaction sequences offer significant advantages over step-wise procedures[3]. The Diels-Alder reaction provides one of the most powerful tools for the synthesis of complex organic molecules by virtue of its versatility and stereo control and therefore typifies a favourable transformation in efficient reaction sequences. Consistently, several reported MCRs feature Diels-Alder chemistry with substituted diene building blocks[4].

Results and Discussion

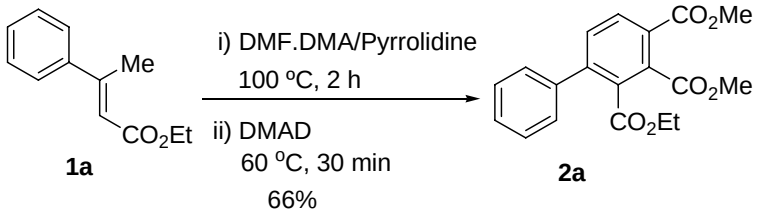
Recently, Beller and coworkers reported a novel preparation of phthalic acid derivatives involving the reaction of α,β-unsaturated aldehyde and dimethyl acetylenedicarboxylate in the presence of acetamide[5]. The one-pot synthesis of *N*-protected carbazoles involving an *in situ* generated enamine intermediate has been reported from our laboratory[6]. These multicomponent coupling reactions take advantage of the intermediacy of push-pull diene which are subjected to *in situ* trapping with electron-deficient dienophiles. The versatility of the Diels-Alder reaction has increased with the advent of new, heteroatom-substituted dienes, which are more reactive but also give highly functionalized and useful products[7].

Very recently, we have reported[8] our preliminary work on the synthesis of phthalic acid derivatives involving a three component coupling reaction of β-arylcrotonate, DMF.DMA and electron deficient alkynes. A mixture of crotonate **1a** (Ref 9) and DMF.DMA are heated at 120°C under nitrogen atmosphere for 5 hr followed by subsequent Diels-Alder reaction with DMAD at 60°C leads to the phthalic acid derivative **2a** in 52% yield (**Scheme I**).

Even though the push-pull diene based annulation methodology was found to be facile with variety of ethyl β-arylcrotonates, phthalates could be obtained only in moderate yields[8]. Hence, in order to increase the yields of the phthalates, different reaction parameters including solvent and concentration were varied. The formation of enamine with ethyl β-arylcrotonate and DMF.DMA using DMF as solvent was also found to be of no use. Finally, use of pyrrolidine was proved pivotal for the formation of desired products in good yields. Thus, the reaction of crotonate **1a** with DMF.DMA in the presence of pyrrolidine at 100°C for 2 hr followed by Diels-Alder reaction with DMAD at 60°C for 30 min led to the isolation of **2a** in 66% yield (**Scheme II**).



Scheme I



Scheme II

Either, the use of highly reactive pyrrolidine acetal or *in situ* generation of the same via addition of pyrrolidine with DMF.DMA has significantly enhanced the rate of enamine formation[10]. Hence, we reasoned that the better yield of **2a** obtained in the presence of pyrrolidine might be due to the enhanced rate of formation of the required enamine. The net reaction for the synthesis of **2a** in the presence of pyrrolidine is outlined in **Scheme III**. The reaction of pyrrolidine with DMF.DMA **3** *in situ* generated the relatively more reactive pyrrolidine acetal, which led to the formation of carbanion **4** and iminium ion **5**. Reaction between these two species produced the required enamine **7**. Diels-Alder reaction of **7** with DMAD followed by elimination of pyrrolidine unit furnished product **2a**.

The results for the three component assembly of various ethyl β-arylcrotonates **1a-f**, DMF.DMA and DMAD/methyl propiolate in the absence/presence of pyrrolidine (Method A and B) are summarized in **Table I**. In all cases, the reactions smoothly proceeded to afford phthalic acid derivatives. Always enhanced yields of phthalates **2a-f** were obtained when the reaction was performed in the presence of pyrrolidine.

The *p*-substituted ethyl β-arylcrotonates **1a-e** reacted equally well with DMF.DMA and DMAD to furnish the corresponding phthalic acid derivatives **2a-e** in both the conditions. The methodology has also been extended to ethyl β-naphthylcrotonate and ethyl β-2-thienylcrotonate systems **1f** and **1g** (entries 2 and 3). Terminal alkyne was also compatible for the present reaction. Thus, the reaction of methyl propiolate with corresponding enamines also led to disubstituted phthalates **2c', 2d'** and **2f'** in reasonable yields (entries 4 and 5). The formation of diene with DMA.DMA was found to be very slow and its subsequent Diels-Alder reaction with DMAD afforded trisubstituted phthalate **2d''** in 30% and 47% yields using conditions A and B, respectively (entry 6).

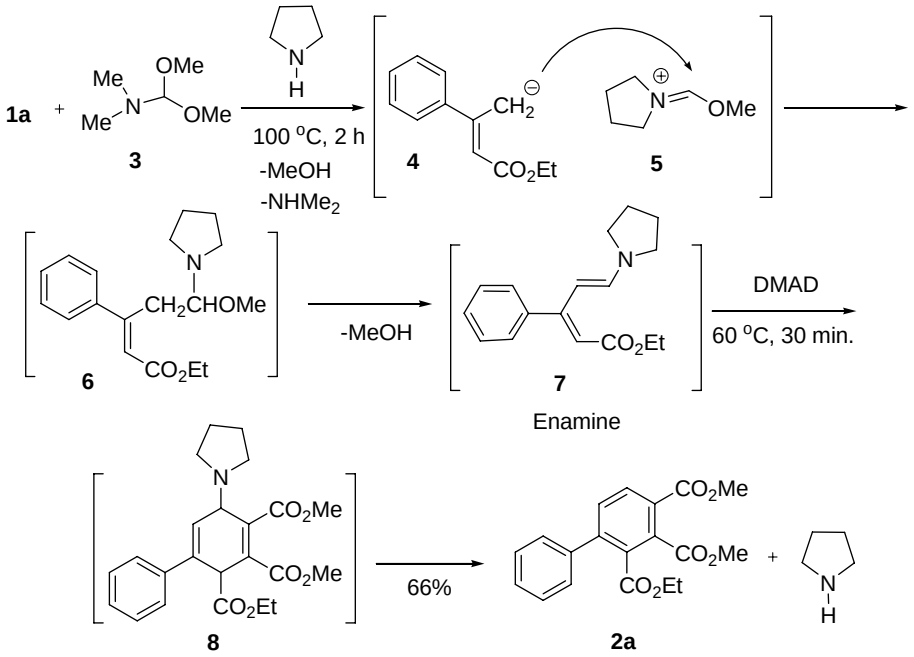
All attempts to carry out a similar three component coupling reaction of crotonates **1a/1c** with double bonded dienophiles, nitrostyrene **9** didn't afford the expected product **11** (**Scheme IV**). Similarly, an attempt was also made to carry out Diels-Alder reaction of *in situ* generated diene with ethyl cinnamate **10** without any success.

Spectroscopic characterization of phthalates **2a-g** was achieved by NMR and mass spectra. The latter exhibited the parent ions and expected fragmentation patterns involving cleavage of the methoxide, ethoxide and alkyl moieties. Further, the structure of phthalates was confirmed by ^{13}C NMR analysis. In addition, the structures of **2b** and **2d** were also confirmed by single crystal X-ray analysis[10].

Biological studies of phthalate 2b

Antimicrobial assay

Test pathogenic microorganisms employed for *in vitro* antimicrobial assay were obtained from Indian



Scheme III

Microbial Type Culture Collection Centre (IMTCC), New Delhi. The antimicrobial assay of the phthalate **2b** was performed by standard disc diffusion technique[11,12]. A total of five bacterial strains (two Gram positive and three Gram negative) were used in this antimicrobial screening (**Table II**). The solution of phthalate **2b** (60mg/disc and 30mg/disc) was prepared by dissolving in ethyl acetate. To compare the antibacterial and antifungal activity, kanamycin (30mg/disc) and nystatin (20mg/disc) were used as standard antibiotics. As a negative control, a blank disc impregnated with solvent followed by drying off was used.

Briefly, the test discs, standard discs and blank discs placed in a petridish with particular bacteria and then left in a refrigerator at 4°C for 12-18 hr in order to diffuse the material from the discs to the surrounding media. The petridishes were then incubated at 37°C for overnight to allow the bacterial growth. The antibacterial activity of the phthalate **2b** then determined by measuring the respective zones of inhibition in mm.

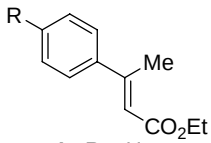
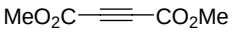
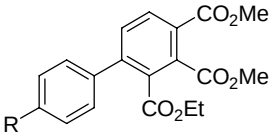
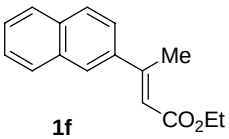
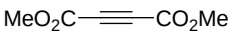
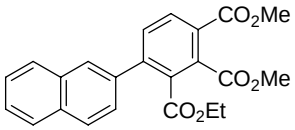
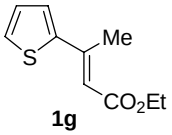
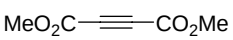
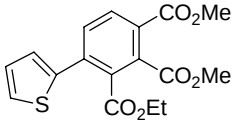
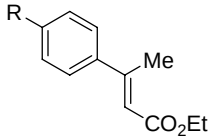
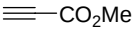
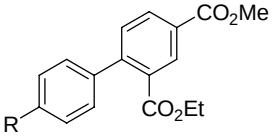
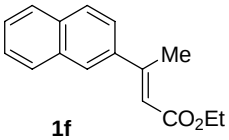
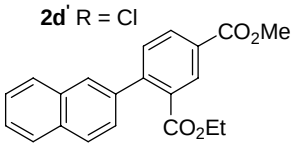
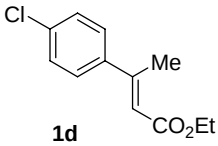
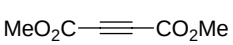
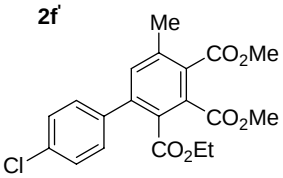
The minimum inhibitory concentrations (MICs) of phthalate **2b** against *Proteus vulgaris, Escherichia coli, Staphylococcus aureus, Aspergillus flaves, Aspergillus niger* and *Trichoderma* sp. were determined by serial dilution technique[11,13] in the presence of a standard amoxicillin trihydrate (for bacteria) and nystatin (for fungi).

The results of antibacterial and anti fungal activities in terms of zone of inhibition in mm are presented in **Table II** and **Table III** respectively. The Gram positive bacteria (*Staphylococcus aureus, Proteus vulgaris)* and Gram negative bacteria (*Escherichia coli and Salmonella typhi)* showed a moderate sensitivity towards the phthalate **2b**. However all the pathogenic fungi also showed a weak sensitivity to the phthalate **2b** *Aspergillus flaves, Trichoderma* sp., *Aspergillus niger, Trichoderma viride and Fusarium* species. In the present study Minimum Inhibitory concentrations (MICs) of phthalate **2b** was found to have good potency against *Escherichia coli, Proteus vulgaris, Staphylococcus aureus, Aspergillus niger and Aspergillus flaves* (**Table IV**).

Summary

The results described above demonstrate that the highly substituted phthalic acid derivatives are easily prepared from the readily available starting materials involving an enamine formation followed by subsequent Diels-Alder reaction and aromatization. The observed one pot synthesis of biaryls **2a-d** could be performed in relatively better yields by the addition of pyrrolidine. The advantage of the present methodology over the previously reported[8] was fully demonstrated by performing the synthesis of the biaryls both in the presence as well as absence of

Table I — One-pot synthesis of phthalic acid derivatives

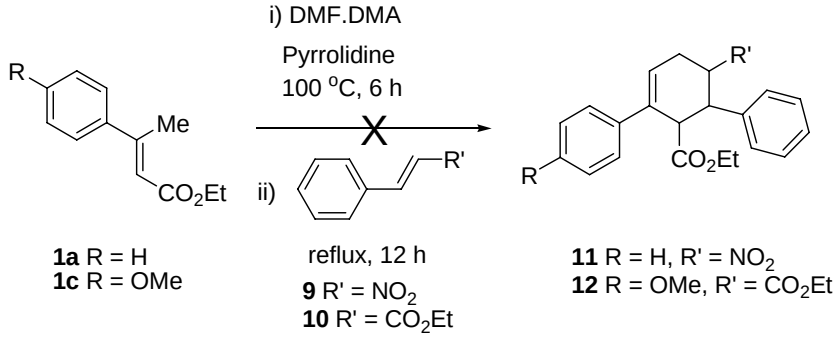
Entry	Ethyl β-arylcrotonates[9]	Dienophile	Products	Yield (%)
1	 **1a** R = H **1b** R = Me **1c** R = OMe **1d** R = Cl **1e** R = Br		 **2a** R = H **2b** R = Me **2c** R = OMe **2d** R = Cl **2e** R = Br	52[a], 66[b] 52[a], 64[b] 54[a], 68[b] 56[a], 70[b] 53[a], 65[b]
2	 **1f**		 **2f**	49[a], 61[b]
3	 **1g**		 **2g**	52[a], 63[b]
4	 **1c** R = OMe **1d** R = Cl		 **2c'** R = OMe **2d'** R = Cl	53[a], 64[b] 52[a], 61[b]
5	 **1f**		 **2f'**	48[a], 58[b]
6[c]	 **1d**		 **2d''**	30[a], 47[b]

[a] Yield of isolated products using method A
[b] Yield of isolated products using method B
[c] For entry 6 DMA.DMA was used instead of DMF.DMA.

pyrrolidine. In all the cases in the presence of pyrrolidine always better yields of the biaryl systems were produced in a shorter reaction time period. As a representative case, the antimicrobial study of phthalate **2b** was carried out and the results are also presented.

Experimental Section

The melting points were determined in open capillaries and are uncorrected. Reagent grade chemicals were purchased from commercial source and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz or on a Jeol-GSX 400 (400 MHz) with TMS as internal standard (chemical shift in (δ) ppm). The mass spectra were recorded on a Jeol-JMS-DX 303 HF mass spectrometer. Thin layer chromatography (TLC) was performed using glass plates coated with silica gel (ACME) of 0.25 nm thickness. Spots were visualized using iodine vapour.



Scheme IV

Table II — Antibacterial activity of phthalate **2b** and Kanamycin

Test organisms	Diameter of zone of inhibition (in mm)		
	Phthalate-**2b** (30mg/disc)	Phthalate-**2b** (60mg/disc)	Kanamycin (30mg/disc)
Staphylococcus aureus (Gram positive)	12	18	21
Bacillus sp. (Gram positive)	9	24	26
Proteus vulgaris (Gram negative)	10	19	24
Salmonella typhi (Gram negative)	5	12	20
Escherichia coli (Gram negative)	10	22	26

Table III — Antifungal activity of compound phthalate **2b** and Nystatin

Test organisms	Diameter of zone of inhibition (in (20mg/disc mm)	
	Phthalate-**2b** (30mg/disc)	Nystatin (Standard)
Aspergillus niger	12	22
Aspergillus flaves	14	25
Trichoderma viride	10	32
Trichoderma sp.	13	28
Fusarium sp.	7	24

Table IV — The result of MIC values (in mg/mL)

Test organisms	Diameter of zone of inhibition (in mm)		
	Phthalate-**2b**	Amoxycillin trihydrate	Nystatin
Proteus vulgaris	18	4	-
Escherichia coli	14	2	-
Staphylococcus aureus	30	8	-
Aspergillus flaves	85	-	3
Aspergillus niger	50	-	5
Trichoderma sp.	150	-	8

General procedure for the one-pot synthesis of phthalic acid derivatives (Method A)

The DMF-DMA (1.7 mL, 2.5 mmoles) was added to ethyl β-phenylcrotonate **1a** (1 g, 1 mmole) at rt under N_2. It was refluxed at 120ºC for 5 hr. After completion of the enamine formation (monitored by TLC), the reaction mixture was cooled to 60°C, DMAD (0.97 mL, 1.5 mmole) was added and stirred for 30 min. Then, it was quenched with 5% ice cold HCl (50 mL), extracted with DCM (2 × 25 mL). The combined extracts were washed with brine (2 × 20 mL) and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatographic purification (Silica gel, Hexane: Ethyl acetate, 5:1) afforded **2a** as a pale-yellow liquid (0.94 g, 52 %).

General procedure for the one-pot synthesis of phthalic acid derivatives (Method B)

The DMF.DMA (1.7 mL, 2.5 mmoles) and pyrrolidine (1.5 mL) were added to ethyl β-phenylcrotonate (1.0 g, 1 mmole) at room temperature under nitrogen atmosphere. The reaction mixture was then refluxed at 100°C for 2 hr. After completion of the enamine formation (monitored by TLC), it was cooled to 60°C, DMAD (0.97 mL, 1.5 mmole) was added and stirred for 30 min at the same temperature. The reaction was then quenched by adding with 5% ice cold HCl (50 mL), extracted with DCM (2 × 25 mL). The combined extracts were washed with brine (2 × 20 mL) and dried (Na_2SO_4). Removal of the solvent followed by flash column chromatographic purification (Silica gel, Hexane:Ethyl acetate, 5:1) afforded **2a** as a pale-yellow liquid (1.2 g, 66 %).

Compound 2a: Viscous liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.33-7.31 (m, 3H), 7.30-7.19 (m, 2H), 3.97 (q, *J* = 7.2 Hz, 2H), 3.85 (s, 3H), 3.84 (s, 3H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.0, 167.2, 165.6, 144.9, 139.2, 134.4, 132.0, 131.3, 131.2, 128.4, 128.2, 128.0, 127.9, 127.8, 61.8, 52.8, 52.7, 13.4; MS (EI): *m/z* (%) 342 (M^+, 40), 311 (14), 297 (37), 251 (30), 179 (15), 91 (100); HRMS: *m/z* Calcd for $C_{19}H_{18}O_6$ 342.1103, Found 342.1108.

Compound 2b: m.p. 114ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, *J* = 8.0 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 4H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 3.93 (s, 3H), 2.40 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 167.4, 165.7, 144.9, 138.1, 136.2, 134.3, 131.9, 131.2, 129.2, 129.1, 127.9, 127.8, 61.7, 52.8, 52.7, 21.1, 13.4; MS (EI): *m/z* (%) 356 (M^+, 100), 325 (52), 311 (42), 279 (20); Anal. Calcd for $C_{20}H_{20}O_6$: C, 67.41; H, 5.66. Found: C, 67.11; H, 5.98%; HRMS: *m/z* Calcd for $C_{20}H_{20}O_6$ 356.1260, Found 356.1264.

Compound 2c: m.p. 148ºC;^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 4.09 (q, *J* = 7.0 Hz, 2H), 3.92 (s, 3H), 3.84(s, 3H), 3.63 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.1, 167.5, 165.7, 159.7, 144.5, 134.4, 131.9, 131.5, 131.2, 129.3, 129.2, 127.9, 127.3, 61.7, 55.3, 52.8, 52.7, 13.6; MS (EI): *m/z* (%) 372 (M^+, 100), 353 (45), 303 (49), 256 (27); Anal. Calcd for $C_{20}H_{20}O_7$: C, 64.51; H, 5.41. Found: C, 64.28; H, 5.62%; HRMS: *m/z* Calcd for $C_{20}H_{20}O_7$ 372.1209, Found 372.1214.

Compound 2d: m.p. 102ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (d, *J* = 8.2 Hz, 1H), 8.21 (d, *J* = 8.2 Hz, 1H), 7.36 (s, 4H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.89 (s, 3H), 3.74 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.6, 165.9, 165.1, 145.6, 139.3, 137.2, 134.6, 132.7, 132.2, 129.4, 129.2, 128.5, 122.1, 61.4, 52.9, 52.8, 13.7; MS (EI) : *m/z* (%) 376 (M^+, 100), 338 (43), 301 (32), 264 (27); Anal. Calcd for $C_{19}H_{17}ClO_6$: C, 60.57; H, 4.55. Found: C, 60.43; H, 4.65%; HRMS: *m/z* Calcd for $C_{19}H_{17}ClO_6$ 376.0714, Found 376.0720.

Compound 2e: m.p. 105ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.32 (s, 4H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 3. 72 (s, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 165.4, 165.0, 144.8, 139.1, 136.5, 134.3, 132.5, 132.1, 129.6, 129.1, 127.5, 121.8, 61.2, 52.6, 52.4, 13.4; MS (EI): *m/z* (%) 422 (M^{+2}, 73), 420 (M^+, 73), 382 (56), 322 (100); Anal. Calcd for $C_{19}H_{17}BrO_6$: C, 54.17; H, 4.07. Found: C, 53.96; H, 4.28%; HRMS: *m/z* Calcd for $C_{19}H_{17}BrO_6$ 420.0209, Found 420.0214.

Compound 2f: m.p. 136ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.89-7.82 (m, 4H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.55-7.50 (m, 2H), 7.45-7.43 (m, 1H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.95 (s, 3H), 3.94 (s, 3H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 167.3, 165.7, 144.9, 136.6, 134.5, 133.0, 132.7, 132.2, 131.5, 131.4, 131.2, 128.1, 127.8, 127.6, 127.3, 126.6, 126.5, 125.9, 61.7, 52.9, 52.7, 13.4; MS (EI): *m/z* (%) 392 (M^+, 100), 347 (16), 315 (25), 202 (32); Anal. Calcd for $C_{23}H_{20}O_6$: C, 70.40; H, 5.14. Found: C, 70.18; H, 5.28%; HRMS: *m/z* Calcd for $C_{23}H_{20}O_6$ 392.1259, Found 392.1265.

Compound 2g: Viscous liquid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 5.1 Hz, 1H), 7.04-7.10 (m, 2H), 4.17 (q, *J* = 7.4 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 1.11 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.8, 167.3, 165.6, 139.7, 137.0, 134.2, 132.4, 131.6, 131.1, 128.2, 127.6, 127.5, 62.1, 53.1, 53.0, 52.7, 13.7; MS: (EI): *m/z* (%) 348 (M^+, 100), 303 (61), 257 (58), 186 (26); HRMS: *m/z* Calcd for $C_{17}H_{16}O_6S$ 348.0668, Found 348.0673.

Compound 2c': Viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (s, 1H), 8.02 (d, *J* = 6.9 Hz, 1H), 7.28-7.22 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.88 (s, 3H), 3.73 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 165.3, 144.2, 138.3, 134.6, 133.1, 131.3, 131.5, 131.1, 130.0, 129.4, 129.2, 127.4, 121.1, 61.5, 52.8, 52.3, 13.4; MS (EI): *m/z* (%) 314 (M^+, 100), 283 (28), 264 (72), 182 (26); HRMS: *m/z* Calcd for $C_{18}H_{18}O_5$ 314.1154, Found 314.1158.

Compound 2d': Viscous liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.42 (s, 1H), 8.09 (d, *J* = 6.8 Hz, 1H), 7.35-7.30 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.88 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.3, 165.9, 145.4, 138.9, 135.0, 133.9, 131.9, 131.7, 131.4, 130.7, 129.5, 129.4, 128.2, 121.6, 61.3, 52.8, 13.7; MS (EI): *m/z* (%) 318 (M^+, 100), 348 (45), 287 (18), 273 (85), 186 (21); HRMS: *m/z* Calcd for $C_{17}H_{15}ClO_4$ 318.0659, Found 318.0664.

Compound 2f': Viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (s, 1 H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.91-7.84 (m, 4H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.58-7.53 (m, 2H), 7.48-7.45 (m, 1H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.96 (s, 3H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ 167.6, 166.3, 145.5, 136.8, 135.2, 132.4, 132.9, 132.2, 131.8, 131.5, 131.1, 128.6, 127.9, 127.5, 127.1, 126.6, 126.8, 125.3, 61.8, 52.8, 13.4; MS (EI): *m/z* (%) 334 (M^+, 100), 289 (24), 258 (16), 214 (45); HRMS: *m/z* Calcd for $C_{21}H_{18}O_4$ 334.1205, Found 334.1210.

Compound 2d": Viscous liquid; ^1H NMR (300 MHz, $CDCl_3$): δ 8.44 (s, 1H), 7.34 (s, 4H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 3.78 (s, 3H), 2.38 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.8, 165.8, 165.2, 145.7, 139.6, 138.1, 134.8, 132.8, 132.2, 129.6, 129.1, 127.5, 122.3, 61.2, 52.9, 52.6, 17.9, 13.5; MS (EI) : *m/z* (%) 390 (M^+, 100), 348 (45), 287 (22), 232 (38); HRMS: *m/z* Calcd for $C_{20}H_{19}ClO_6$ 390.0870, Found 390.0875.

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