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Near-Infrared Absorbing Asymmetric Trimethinecyanine Dyes Containing Benz[*c*,*d*]indolium and Pyrylium End Groups

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ABSTRACT

*The synthesis of some new asymmetric trimethinecyanine dyes containing benz[*c,d*]indolium and pyrylium end groups is described. The dyes absorb in the region of 724 to 793 nm and have high molar absorption coefficients. The structure of the compounds was confirmed by elemental analysis, electronic absorption spectra and ^{1}H-NMR spectroscopy.*

1 INTRODUCTION

Dyes absorbing in the near-infrared (IR) region are of interest both from the theoretical and practical viewpoint,[1] and are of interest for application as active media in optical information recording systems,[2–8] and in other fields such as organic photoconductive materials,[9] passive absorbers in the formation of ultrashort light pulses in the near-IR region,[10] and in photochemotherapy.[11]

Among the various dyes absorbing in the near-IR region, four basic types have found practical application:[12] polymethine dyes, phthalocyanine dyes, quinonoid condensed arenes, and some metal complexes. Polymethine

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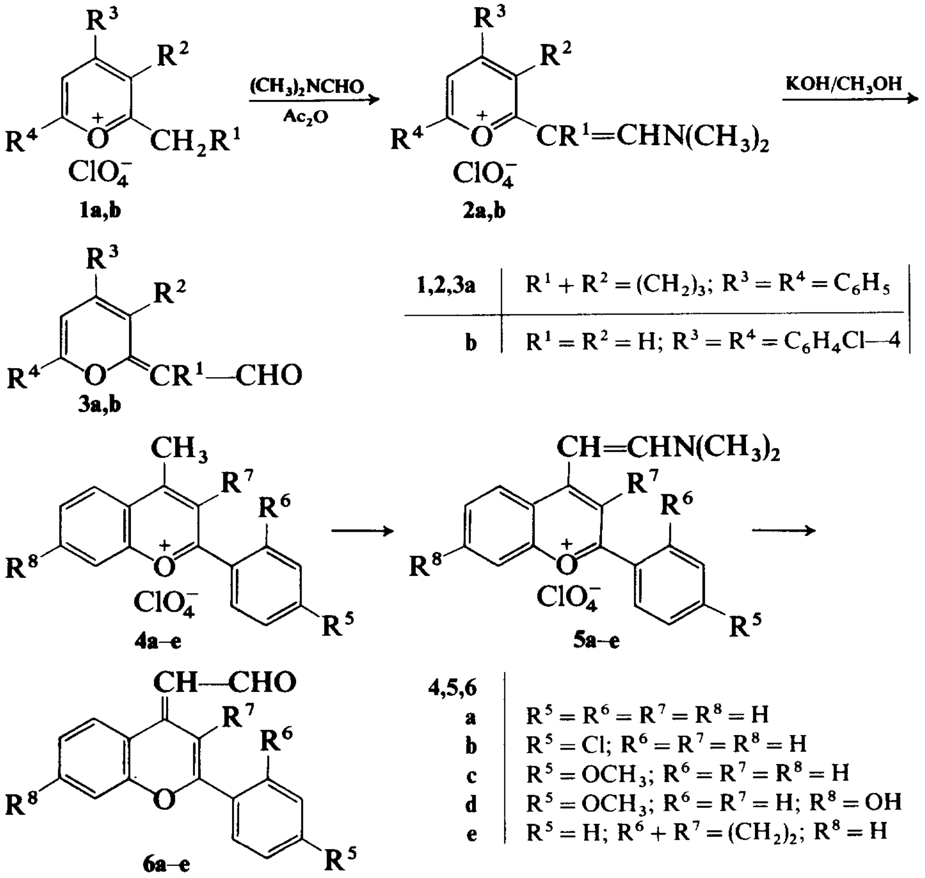
derivatives are the largest group, and among heterocyclic N-containing polymethine dyes, those containing a benz[*c*,*d*]indole mostly show appropriate long wavelength absorption[13] and have been the subject of many investigations.[14–19]

This present paper describes the synthesis of some novel near-IR absorbing asymmetric trimethinecyanine dyes containing benz[*c*,*d*]-indolium and pyrylium end groups.

2 RESULTS AND DISCUSSION

The intermediates used as starting materials were 2-formylmethylidene-2*H*, 4-formylmethylidene-4*H*-pyrane and 1(1H)-ethyl-2-formylmethylidenebenz[*c*,*d*]indole. Pyrane derivatives were obtained according to the method of Reynolds and Van Allan[20] through interaction of pyrylium or

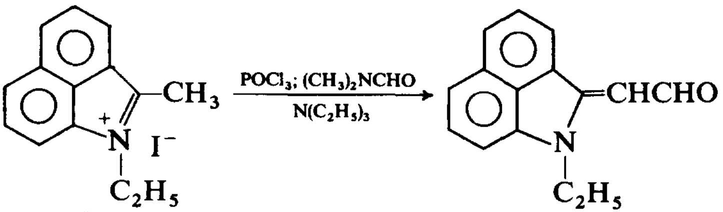


1a,b **2a,b** **3a,b** **4a–e** **5a–e** **6a–e**

1,2,3a	$R^1 + R^2 = (CH_2)_3$; $R^3 = R^4 = C_6H_5$
b	$R^1 = R^2 = H$; $R^3 = R^4 = C_6H_4Cl{-}4$

4,5,6	
a	$R^5 = R^6 = R^7 = R^8 = H$
b	$R^5 = Cl$; $R^6 = R^7 = R^8 = H$
c	$R^5 = OCH_3$; $R^6 = R^7 = R^8 = H$
d	$R^5 = OCH_3$; $R^6 = R^7 = H$; $R^8 = OH$
e	$R^5 = H$; $R^6 + R^7 = (CH_2)_2$; $R^8 = H$

Scheme 1



7 **8**

Scheme 2

flavilium salts and dimethylformamide in acetic anhydride medium (Scheme 1).

1(1H)-ethyl-2-formylmethylidenebenz[*c*,*d*]indole (**8**) was obtained by formylation according to the Vilsmeyer reaction[21] (Scheme 2).

Some characteristics of the intermediates thus obtained are presented in Table 1. The IR spectra of the aldehydes were recorded in nujol; carbonyl absorption for **3a** appears at 1660 cm^{-1} whilst for the other derivatives (**3b**, **6a–e** and **8**) the band was observed in the 1625–1630 cm^{-1} region.

Some of the dyes were obtained by condensation of the aldehydes **3a,b** and **6a–e** with 1-ethyl-2-methylbenz[*c*,*d*]indolium iodide in acetic anhydride (Scheme 3), and other dyes by condensation of 1(1H)-ethyl-2-formylmethylidenebenz[*c*,*d*]indole with pyrylium salts (Scheme 4).

Electronic spectral data of the dyes showed them to absorb within the general range 678–793 nm, λ_{max} being in the range 724–793 nm. In most cases absorption in the visible region was either absent or was of low intensity, at about 400 nm. Table 2 shows the melting points, yields and data on the elemental analysis of dyes **9a–e**, **10a–h** and **12**; their absorption maxima and molar absorptivities are given in Table 3.

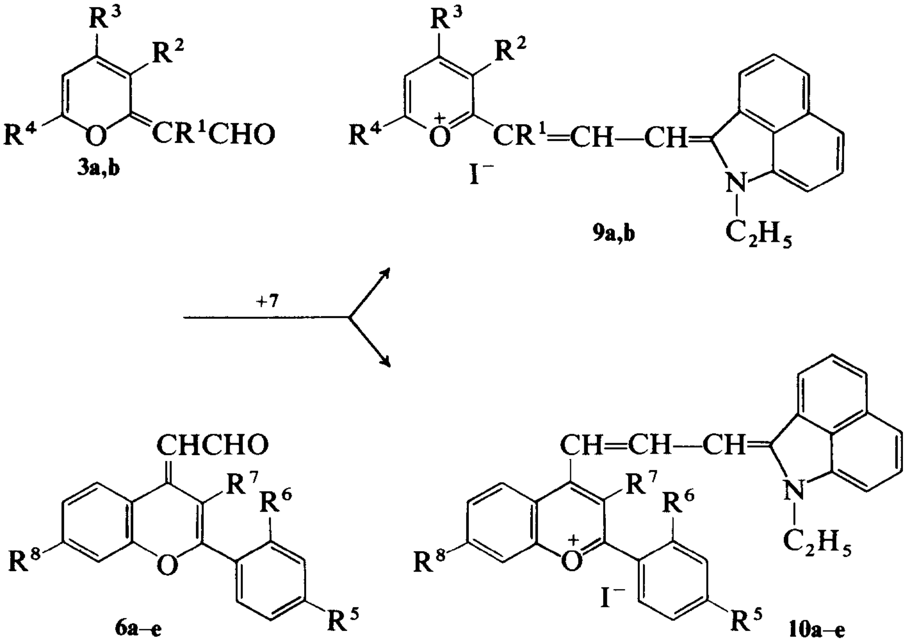
The 2*H*-pyran derivatives **9b**, **9c** and **9d** show absorption maxima in the

TABLE 1

Melting Points,[a] Yields and Elemental Analysis Data for **3a**, **b** and **6a–e**

Compound	*m.p. (°C) (found/reported)*	*Yield (%)*	*Molecular formula*	*Analysis (%) (found/calculated)*	
				C	*H*
3a	164–166/165–166[20]	90	$C_{22}H_{18}O_2$	—	—
3b	172–174	88	$C_{19}H_{12}Cl_2O_2$	66·8/66·5	3·85/3·5
6a	113–115/110–111[20]	83	$C_{17}H_{12}O_2$	—	—
6b	212–213	91	$C_{17}H_{11}ClO_2.1/3\ CH_3OH$	71·4/70·95	4·4/4·2
6c	130–131	89	$C_{18}H_{14}O_3$	77·5/77·7	4·7/5·0
6d	221–223	43	$C_{18}H_{14}O_4.2/3\ CH_3OH$	70·8/71·0	5·3/5·3
6e	133–135	94	$C_{19}H_{14}O_2$	83·3/83·2	4·9/5·1

[a] All compounds were recrystallized from CH_3OH; **6e** from C_2H_5OH.



Scheme 3

TABLE 2

Melting Points,[a] Yields and Elemental Analysis Data for **9a–e**, **10a–h** and **12**

Dye	*m.p.* (°*C*)	*Yield* (%)	*Molecular formula*	*Analysis* (%) (*found/calculated*) *C*	*H*	*N*
9a	278–280	91	$C_{36}H_{30}INO$	69·6/69·8	4·8/4·85	1·8/2·2
9b	301–302	75	$C_{33}H_{24}Cl_3NO_5$	63·8/63·8	4·4/3·8	2·6/2·3
9c	320–321	95	$C_{35}H_{30}ClNO_5$	72·7/72·5	4·8/5·2	2·4/2·4
9d	290–292	93	$C_{35}H_{30}ClNO_7$	68·6/68·7	4·85/4·9	2·05/2·3
9e	236–238	84	$C_{35}H_{28}ClNO_5$	72·7/72·7	4·9/4·8	2·35/2·4
10a	253–255	81	$C_{31}H_{24}INO.0{\cdot}5H_2O$	65·8/66·2	4·7/4·45	1·9/2·5
10b	263–265	90	$C_{31}H_{23}ClINO.H_2O$	61·35/61·45	4·2/4·1	2·0/2·3
10c	272–274	88	$C_{32}H_{26}INO_2.H_2O$	64·4/63·9	4·8/4·7	2·2/2·3
10d	265–267	49	$C_{32}H_{26}INO_3.0{\cdot}5H_2O$	62·9/63·2	4·75/4·4	1·8/2·3
10e	261–263	87	$C_{33}H_{26}INO$	68·3/68·4	4·8/4·5	2·5/2·4
10f	282–284	88	$C_{31}H_{24}ClNO_4S$	68·4/68·7	4·7/4·4	2·3/2·6
10g	272–273	97	$C_{34}H_{28}ClNO_7$	68·0/68·3	4·85/4·7	2·1/2·3
10h	261–263	96	$C_{34}H_{28}ClNO_6.0{\cdot}5CH_3CN$	70·0/69·8	5·05/4·9	3·4/3·5
12	324–327	94	$C_{37}H_{30}ClNO_5$	73·3/73·6	5·2/5·0	2·5/2·3

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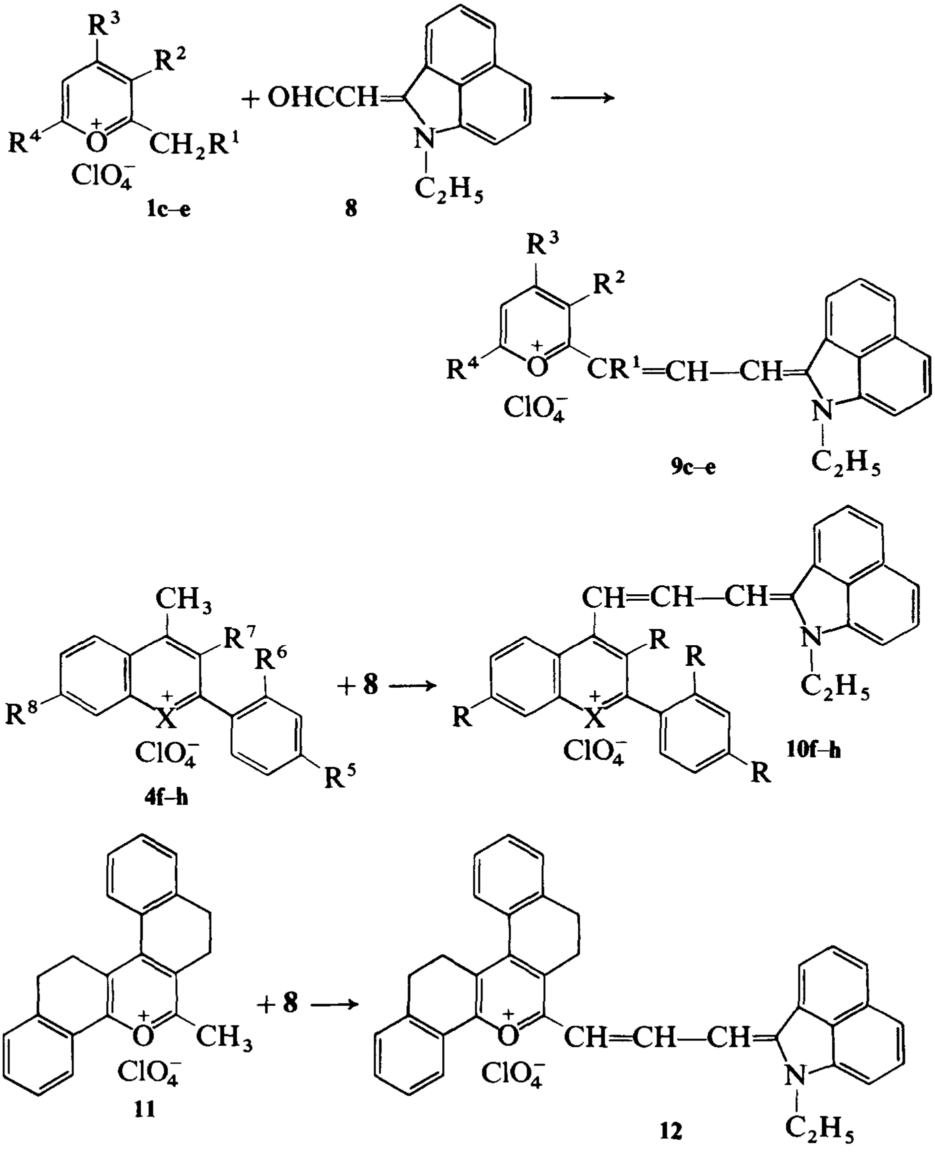
[a] The dyes were recrystallized from CH_3CN.



1,9

c $R^1 = R^2 = H$; $R^3 = R^4 = C_6H_4CH_3$—4

d $R^1 = R^2 = H$; $R^3 = R^4 = C_6H_4OCH_3$—4

e $R^1 + R^2 = (CH_2)_2$; $R^3 = R^4 = C_6H_5$

4,10

f $R^5 = R^6 = R^7 = R^8 = H$; $X = S$

g $R^5 = OCH_3$; $R^6 + R^7 = (CH_2)_2$; $R^8 = OH$; $X = O$

h $R^5 = OCH_3$; $R^6 + R^7 = (CH_2)_2$; $R^8 = H$; $X = O$

Scheme 4

TABLE 3
Absorption Maxima (nm) and Molar Extinction Coefficients (litre mol^{-1} cm^{-1}) of the Dyes **9a–e**, **10a–h** and **12**

Dye	λ_1	E_1	λ_2	E_2	λ_{max}	E_{max}
9a	—	—	720 sh	50 800	781	84 600
9b	—	—	—	—	746	75 800
9c	—	—	—	—	752	85 200
9d	426	32 300	—	—	752	85 800
9e	—	—	726 sh	58 400	793	135 000
10a	—	—	678 sh	67 500	724	89 600
10b	—	—	680 sh	65 300	724	79 800
10c	396	20 200	678 sh	64 000	739	121 650
10d	406	18 800	678 sh	59 100	737	105 000
10e	397	15 100	688 sh	70 700	739	103 100
10f	—	—	718 sh	69 900	759	76 600
10g	437	13 800	692 sh	61 100	755	128 100
10h	427	14 300	686 sh	56 100	754	128 600
12	396	22 300	—	—	785	77 500

746–752 nm region, with E_{max} values from 76 000 to 86 000. Unlike the 4*H*-pyran derivatives, substituent effects are minimal. Dyes **9a** and **9e** are of particular interest, showing the most bathochromic long wavelength absorption maxima (781 and 793 nm, respectively); this possibly arises because of the lack of rotation around the bond at the 2-position in these compounds. Dye **9e** additionally exhibits a very high intensity (E_{max} 135 000), attributable to the planar configuration of the molecule.

In the 4*H*-pyran derivatives **10a** and **10d** the methoxy group has more influence on the absorption maxima. Dye **10c**, for example, shows a bathochromic shift of 15 nm and a marked increase in intensity (E_{max} 121 650) compared to dye **10a** (E_{max} 89 600). The effect is not as pronounced in dye **10d** (E_{max} 105 000), probably due to the influence of the hydroxy group.

The xanthylium derivatives **10e**, **10g** and **10h** also have high intensity absorption, the methoxy group in these dyes also inducing bathochromic shifts of 15–16 nm.

Dyes **10a** and **10f** are analogs demonstrating the influence of the pyrylium and thiopyrylium rings. Replacement of sulfur for oxygen leads to a bathochromic shift of 35 nm, but with lowering of the absorption intensity.

The ^1H-NMR spectra in DMSO-d_6 were recorded for most of the dyes. Dyes **9a–e** show a triplet for the methyl protons of the ethyl group at the nitrogen atom of the benz[*c*,*d*]indole with an intensity for three protons at 1·26 to 1·36 ppm. The signals for the methylene protons of the same group are at 4·12 to 4·34 ppm as a quartet, with an intensity for two protons. The signals for the aromatic protons are within the range 6·18–9·70 ppm, together with the signals for the protons of the polymethine chain.

Dyes **10a–h** showed a different pattern with respect to the chemical shifts. The signals for the methyl group of the ethyl radical at the nitrogen atom of the benz[*c*,*d*]indole ring appear in the range 1·43–1·48 ppm, with an intensity for three protons. The methylene protons of the same radical appear as a quartet at 4·40 to 4·53 ppm, with an intensity for two protons. The aromatic protons appear as multiplets in the range 7·00–9·23 ppm. The signals for the protons of the polymethine chain are within the same range.

A singlet in the range 3·88–3·95 ppm, with an integral intensity for three protons, is observed with all dyes containing a methoxy group, i.e. **9d**, **10c**, **10d**, **10g** and **10h**. In the case of **9d** the two methoxy groups appear at 3·91 and 3·95 ppm, respectively.

3 EXPERIMENTAL

3.1 General

Melting points were determined on a Kofler apparatus and were uncorrected. The IR spectra were recorded in nujol or chloroform on a Carl Zeiss 71 IR spectrophotometer. The visible–near-IR spectra were recorded on a Specord 40M spectrophotometer (2×10^{-5} M in acetonitrile). The ^{1}H-NMR spectra were recorded on a Brucker at 250 MHz in DMSO-d_6.

3.2 Preparation of pyran aldehydes[20] (3a,b and 6a–e)

3.2.1 General procedure for the preparation of monoiminium salts

Salts of **1a,b** or **4a–e** (0·13M) with dimethylformamide (3 ml) in acetic anhydride (50 ml) were refluxed with continuous stirring for 15 min. The reaction mixture was then cooled, and in cases where a precipitate was not formed diethyl ether was added. The monoiminium salt was filtered and dried.

3.2.2 General procedure for the preparation of aldehydes

The 0·01M monoiminium salt in 5% methanolic potassium hydroxide (50 ml) was refluxed with stirring for 30 min. After cooling, the precipitate was filtered, dried and recrystallized. Characterization data are shown in Table 1.

3.3 Preparation of 1(1H)-ethyl-2-formylmethylidenebenz-[*c*,*d*]indole[21] (8)

1-Ethyl-2-methylbenz[*c*,*d*]indolium iodide (15 g, 0·046M) was dissolved, with stirring, in dimethylformamide (75 ml). The reaction mixture was cooled to about 10°C and phosphorus oxychloride (23 g, 14 ml, 0·15M) was added dropwise with continuous stirring at such a rate that the reaction temperature was maintained within the range 10–25°C. After completion of the addition, the reaction mixture was heated at 25 to 30°C and stirred for 15 min. It was then cooled to 10°C and triethylamine (19·7 g, 27·2 ml, 0·195M) was added dropwise, with stirring, at this temperature, and stirring was continued for 1 h. The liquor was then heated to 50°C, cooled and poured onto ice-cold 10% aqueous sodium hydroxide (600). The crude product was filtered and washed with water. Yield, 9·5 g (91·8%); m.p. after recrystallization from methanol, 163–165°C (literature m.p. 158–159°C[21]).

Calc. for $C_{15}H_{13}NO$:	C%	H%
Found	80·52	5·97
Calc.	80·72	5·83

3.4 Preparation of the dyes

3.4.1 *Dyes obtained by condensation of 1-ethyl-2-methylbenz[*c,d*]indolium iodide with pyran aldehydes* **9a,b** *and* **10a–e**

A mixture of 1-ethyl-2-methylbenz[*c,d*]indolium iodide (1 g, 0·0031M), the respective aldehyde (**3a,b** and **6a–e**, 0·0031M) and acetic anhydride (15 ml) was refluxed with stirring for 10 min. After cooling in a refrigerator for 24 h, in cases where the product remained in solution, diethyl ether was added to precipitate the product. The dye was filtered, washed with ether and recrystallized. Yields, melting points and elemental analysis data are given in Table 2. The absorption maxima and molar absorptivities are presented in Table 3.

3.4.2 *Dyes obtained from pyrylium salts by condensation with 1(*1H*)-ethyl-2-formylmethylidenebenz[*c,d*]indole (***9c–e, 10f–h** *and* **12***)*

A mixture of 1[1*H*]-ethyl-2-formylmethylidenebenz[*c,d*]indole (1 g, 0·0045M), the respective pyrylium salt (**1c–e, 4f–h** and **11**, 0·0045M) and acetic anhydride (15 ml) was treated under the same conditions as above. Data for these dyes are also given in Tables 2 and 3.

3.5 ^{1}H-NMR δ ppm (DMSO-d_6)

9a—1·34 (t, 3H, $=N—CH_2\underline{CH_3}$), 1·78 (s, br, 2H, $CH_2\underline{CH_2}CH_2$), 2·78 (s, br, 4H, $\underline{CH_2}CH_2\underline{CH_2}$), 4·34 (q, 2H, $=N—\underline{CH_2}CH_3$), 6·60–9·70 (m, 19H, Ar + —CH=CH—CH=).

9b—1·36 (t, 3H, $=N—CH_2\underline{CH_3}$), 4·27 (q, 2H, $=N—\underline{CH_2}CH_3$), 6·50–8·70 (m, 19H, Ar + —CH=CH—CH=).

9c—1·33 (t, 3H, $=N-CH_2\underline{CH_3}$), 2·43 (t, 6H, $2C_6H_4\underline{CH_3}$), 4·19 (q, 2H, $=N-\underline{CH_2}CH_3$), 6·50–8·70 (m, 19H, $Ar + -CH{=}CH-CH{=}$).

9d—1·31 (t, 3H, $=N-CH_2\underline{CH_3}$), 3·91 (s, 3H, $C_6H_4O\underline{CH_3}$), 3·95 (s, 3H, $C_6H_4O\underline{CH_3}$), 4·12 (q, 2H, $=N-\underline{CH_2}CH_3$), 6·50–7·80 (m, 19H, $Ar + -CH{=}CH-CH{=}$).

9e—1·26 (t, 3H, $=N-CH_2\underline{CH_3}$), 2·79 (s, br, 2H, $ArCH_2\underline{CH_2}$), 3·05 (s, br, 2H, $Ar\underline{CH_2}CH_2$), 4·13 (q, 2H, $=N-\underline{CH_2}CH_3$), 6·18–8·12 (m, 19H, $Ar + -CH{=}CH-CH{=}$).

10a—1·48 (t, 3H, $=N-CH_2\underline{CH_3}$), 4·51 (q, 2H, $=N-\underline{CH_2}CH_3$), 7·67–9·21 (m, 19H, $Ar + -CH{=}CH-CH{=}$).

10b—1·47 (t, 3H, $=N-CH_2\underline{CH_3}$), 4·50 (q, 2H, $=N-\underline{CH_2}CH_3$), 7·34–9·20 (m, 18H, $Ar + -CH{=}CH-CH{=}$).

10c—1·47 (t, 3H, $=N-CH_2\underline{CH_3}$), 3·91 (s, 3H, $C_6H_4O\underline{CH_3}$), 4·50 (q, 2H, $=N-\underline{CH_2}CH_3$), 7·18–9·21 (m, 18H, $Ar + -CH{=}CH-CH{=}$).

10d—1·48 (t, 3H, $=N-CH_2\underline{CH_3}$), 3·91 (s, 3H, $C_6H_4O\underline{CH_3}$), 4·51 (q, 2H, $=N-\underline{CH_2}CH_3$), 7·18–9·23 (m, 17H, $Ar + -CH{=}CH-CH{=}$).

10e—1·48 (t, 3H, $=N-CH_2\underline{CH_3}$), 3·04–3·27 (m, 4H, $C_6H_4CH_2CH_2$), 4·53 (q, 2H, $=N-\underline{CH_2}CH_3$), 7·27–9·00 (m, 17H, $Ar + -CH{=}CH-CH{=}$).

10f—1·48 (t, 3H, $=N-CH_2\underline{CH_3}$), 4·52 (q, 2H, $=N-\underline{CH_2}CH_3$), 7·34–8·86 (m, 19H, $Ar + -CH{=}CH-CH{=}$).

10g—1·45 (t, 3H, $=N-CH_2\underline{CH_3}$), 3·04–3·24 (m, 4H, $ArCH_2CH_2$), 4·46 (q, 2H, $=N-\underline{CH_2}CH_3$), 7·03–8·90 (m, 15H, $Ar + -CH{=}CH-CH{=}$).

10h—1·43 (t, 3H, $=N-CH_2\underline{CH_3}$), 3·00–3·28 (m, 4H, $ArCH_2CH_2$), 3·88 (s, 3H, OCH_3), 4·40 (q, 2H, $=N-\underline{CH_2}CH_3$), 7·00–8·83 (m, 16H, $Ar + -CH{=}CH-CH{=}$).

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