Influence of Arene Substituents on the Mode and Regiochemistry of Photocycloaddition of Furan to the Benzene Ring

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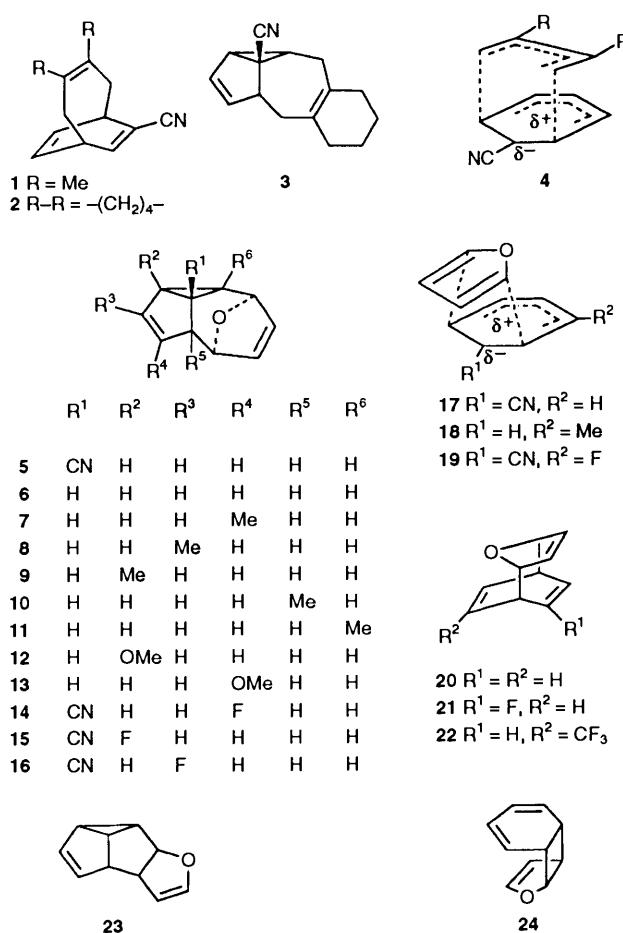[a] Departamento de Quimica, Universidad Politecnica, Apartardo 22012, 46071-Valencia, Spain
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Furan undergoes (2 + 2), (2 + 3), (4 + 3) and (4 + 4) photocycloadditions to the benzene ring. The reaction mode selectivity and regiochemistry of the addition are markedly dependent on the arene substituents, but unlike the photoaddition of ethenes to the benzene ring, the ease of electron transfer between the addends is not the dominant factor which influences the furan reaction. While (4 + 3) and (4 + 4) additions occur with toluene, the (2 + 2) and (2 + 3) processes predominate with anisole, and fluorobenzene and α,α,α-trifluorotoluene yield mainly (2 + 2) and (4 + 2) adducts. The directing influence of the nitrile substituent towards a regio- and stereo-specific (4 + 3) addition of furan is considered to arise from polar and/or secondary orbital interactions. The photoexcited cyanoanisoles are, however, essentially unreactive towards furan, and the benzene–furan non-conjugated bichromophores 41 and 42 do not yield photoisomers.

It is well-known that selectivity between the *ortho* and *meta* modes of photocycloaddition of ethenes to the benzene ring is markedly dependent on the ease of electron transfer between the addends.[1,2] There is, however, no apparent controlling feature which discriminates between the modes of photo-cycloaddition of 1,3-dienes to the benzene ring, although as we have shown, the 1,4-*meta*-mode of reaction does become more significant when the diene has a fixed *cis* geometry.[3,4] Thus, while 2,3-dimethylbuta-1,3-diene undergoes exclusive 1,4-2',5' (*para*)-addition to benzonitrile giving 1, from 1,2-dimethylene-cyclohexane and this arene the *meta*- and the *para*-cyclo-adducts, 3 and 2, are formed in a respective ratio of 1:2.6.[4] The specificity of the *meta*-addition of the diene to the 2,6-positions of benzonitrile is considered to originate from the nitrile substituent directing the addends to the orientation 4 as a result of its stabilising influence on the developing negative charge in the polarised S_1 benzene ring formed on approach of the S_0 1,3-diene:[5] this direction of polarisation is the reverse of that considered to occur on approach of an S_0 ethene to a S_1 benzenoid compound.[6]

As discussed previously, the orientation 4 of the addends may also be the precursor of the regiospecific addition of the diene to the 2,5-positions of the arene, to give *para*-cyclo-adducts such as 1 and 2.[7] For the 1,4-*meta*-addition of 1,3-diene–benzene systems to be the favoured process, it appears that further direction to that provided by the cyano group is necessary, and exclusive formation of this type of adduct has only been observed from the 254 nm irradiation of furan and benzonitrile.[4] In this system, the formation of the *exo*-2,5-2',6'-cycloaddition product 5 reflects alignment by polar interactions of the addends in the ground state. This orientation may be expected to be maintained in the excited state by the attractive interaction between the oxygen and the developing allylic cation moiety in the S_1 benzene ring as shown in 17. Furthermore, since the presence of an ethenyl or ethynyl substituent on the benzene ring has the same controlling influence as the cyano group on the regio- and stereo-chemistries of the furan addition,[4] it is apparent that stabilisation of the developing negative charge in the S_1 arene is not the only role of the substituent and its involvement in secondary orbital interactions with the furan addend is a very important feature in these processes. Indeed, in the absence of this control by the substituent, the photoaddition is non-

1 R = Me
2 R–R = –(CH₂)₄–

3

4

	R¹	R²	R³	R⁴	R⁵	R⁶
5	CN	H	H	H	H	H
6	H	H	H	H	H	H
7	H	H	H	Me	H	H
8	H	H	Me	H	H	H
9	H	Me	H	H	H	H
10	H	H	H	H	Me	H
11	H	H	H	H	H	Me
12	H	OMe	H	H	H	H
13	H	H	H	OMe	H	H
14	CN	H	H	F	H	H
15	CN	F	H	H	H	H
16	CN	H	F	H	H	H

17 R¹ = CN, R² = H
18 R¹ = H, R² = Me
19 R¹ = CN, R² = F

20 R¹ = R² = H
21 R¹ = F, R² = H
22 R¹ = H, R² = CF₃

23

24

selective and from the reaction of parent benzene with furan, the adducts 20, 6, 23, and 24 are formed reflecting (4 + 4), (4 + 3), (3 + 2), and (2 + 2) processes respectively.[8,9] In the present paper, we are concerned with assessing the scope of the photocycloaddition of furan to the benzene ring, and the ability of a variety of substituents to orient the furan and benzene addends by stabilisation of the developing charges in the S_1

benzene ring, and thereby influence the reaction mode selectivity.

Results and Discussion

The regiochemistry of *meta*-photocycloaddition of ethenes to the benzene ring is directed by electron donor (alkyl and alkoxy) and by electron acceptor (cyano and trifluoromethyl) groups to the 2,6- and 2,4-positions of the arene respectively, reflecting their abilities to stabilise the positive and negative charges developing in the S_1 benzene ring.[10] The direction of polarity in the excited arene is deduced to be reversed for the approach of 1,3-dienes but control of the regiochemistry in the addition using this feature has only been assessed for the cyano substituent.[4,7] The methyl group does seemingly induce some reaction mode selectivity since it has been reported that the furan–toluene system yields a mixture of 2,5-*meta*- and 2,5-*para*-cycloadducts in a respective ratio of 4.7:2.0.[9] However, the assigned structures **7** and **8** to the *meta*-adducts show that, uncharacteristically, these do not arise from a common regio-chemistry of attack. A 2,5–2′,4′-attack of the addends and the formation of **7** is expected from preferential orientation of the addends by the methyl group stabilising the developing allylic cationic moiety in the S_1 benzene ring. The second isomer would then be expected to have structure **9** arising from the alternative direction of formation of the cyclopropane ring. In private corespondence, Professor Cantrell kindly informed us that the previously described[8] structural assignments of **7** and **8** were tentative as the spectral data were extracted from product mixtures. We have repeated the photoreaction of the toluene–furan system and confirm the ratio of *meta* to *para*-cyclo-addition, but from spectral analysis of the products, the two major *meta*-photocycloadducts, formed in a ratio of 2.0:1.7 are deduced to have the structures **7** and **9** respectively, arising from the common intermediate orientation **18**. A further *meta*-cycloadduct (*ca*. 20% of the total *meta*-adducts) was identified as **10** but its isomer **11** arising from the same 1,3-orientation of attack was not isolated. Thus the methyl group does induce some selectivity into the *meta*-addition and the preferred orientaton of the attack substantiates the 'reversed' direction of polarity in the S_1 benzene on approach of the 1,3-diene.[5]

The methoxy group exerts a more powerful directing in-fluence than the methyl group in *meta*-photocycloadditions of ethenes to the benzene ring,[11] and thus it may be expected that the addition of furan to anisole should be more selective than that to toluene. The earlier assignment of structures **12** and **13** to the two 2,5-*meta*-adducts from anisole and furan[9] are consistent with the proposals outlined above concerning the features which may direct the regiochemistry of 1,3-diene additions, but since there was also some doubt about these structural assignments, this system was re-examined. Irradia-tion produced a multicomponent mixture in which three 1:1 adducts (M^+, m/z 176) in a ratio of 1:1:2 together comprised *ca*. 70%. One of the more minor of these adducts had mass spectrometric properties characteristic of an *ortho*- or *para*-cycloadduct of the benzene ring. This adduct could not be totally freed from the other two isomers but from spectral data of an enriched sample (*ca*. 75%), the *exo*-2,3–1′2′-adduct structure **25** was assigned. The other two isomers had abundant parent ions characteristic of *meta*-cycloadducts and unambiguous structural assignments were made from extensive NMR spectroscopic investigations. In particular, since both isomers have resonances for an enol ether moiety, and only one proton on an sp³ carbon adjacent to the oxygen atom, each isomer is deduced to have a 2,3- and not the expected 2,5-dihydrofuran unit. Detailed analysis of the spectral data allowed the isomers to be assigned the *exo*-2,3-*meta*-cycloadduct structures **26** and **27** (formed in relative yields of

2:1 respectively). Thus in contrast to the previous report,[9] 2,5-*meta* cycloaddition does not occur in this system but instead, in its photoreaction with photoexcited anisole, furan behaves as an enol ether. The specific formation of the 1-methoxy-substituted dihydrosemibullvalene skeleton and the *exo* stereochemistry of both **26** and **27** can be accounted for by the arguments outlined to rationalise these features in the *meta* photocycloaddition of enol ethers to anisole:[12] these respec-tively involve preferential orientation of the addends as in **28** by the methoxy group stabilisation of the developing positive charge in the S_1 arene, and the attractive interaction between this charge and the oxygen lone pair on approach of the enol ether. From **28** the two possible directions of intramolecular cyclisation to give the cyclopropane ring in the adduct then yield the regioisomers **26** and **27**.
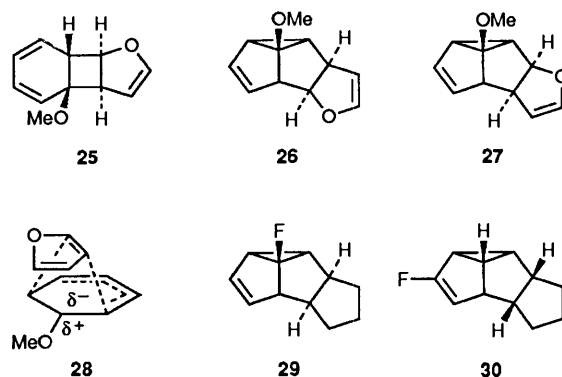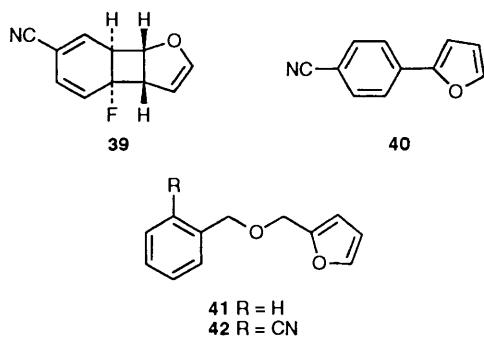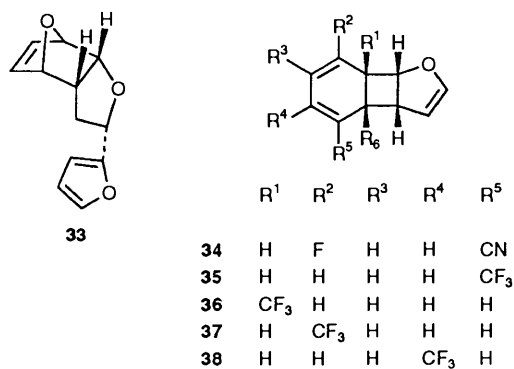

The directing influences of the methoxy and cyano groups on the mode of addition of the furan to the benzene ring thus differ markedly and there is, of course, confliction between these influences in the cyanoanisoles. In the 1,3-arene isomer, however, the charge stabilising abilities of the two substituents do reinforce one another for both the 2,3-*meta*- and 2,5-*meta*-cycloadditions of furan to the benzene ring. Despite this directing feature, however, 254 nm irradiation of furan with each of the three cyanoanisoles produced only minor amounts of multicomponent mixtures and thus the competition between the directing influences of the cyano and methoxy groups on the reaction mode results in inefficiency and low selectivity.

The fluorine substituent can stabilise a positive charge or a negative charge on the vicinal carbon atom by mesomeric and inductive effects.[13] Indeed, although the principal mode of photoaddition of cyclopentene to fluorobenzene is the rarely observed *para*-process,[14] the two major *meta*-cycloadducts **29** and **30** from this system respectively reflect these two stabilising features.[15] For the photoaddition of furan, the fluorine substituent does not improve on the low selectivity observed for the reaction with benzene,[8] and from MS–GC analysis several 1:1 adducts and 1:1 adducts from which HF has been eliminated are detected. The four major adducts fragment readily in the mass spectrometer indicative of *ortho*- and *para*-products, but the only adduct isolated with acceptable analytical purity was the 2,5–2′,5′-product **21**. To determine whether the cyano substituent could induce selectivity into this system as in the case of benzene,[4] the photoreactions of the fluorobenzonitriles with furan were examined. Unlike the cyanoanisoles, for both the 2- and 3-fluorobenzonitriles, the orienting influences of the substituents can act in concert. Irradiation of furan with the 2-isomer did indeed give a single product by GC, but this had a mass of 169 (*i.e.* a 1:1 adduct minus HF) and was shown to be 2-(2′-furyl)benzonitrile **32**. The likely origin of **32** is considered to be anti-periplanar elimination of HF from the *exo-ortho*-cycloadduct **31** and ring opening of the resulting cyclobutene, but no evidence for either

intermediate was obtained. During the purification of **32** by flash chromatography, a trimer of furan (M$^+$, m/z 204), not detected in the irradiation mixture, was eluted from the column: this appears to be formed on the silica either from a furan photoproduct which is too labile for GC detection or from furan itself. The latter is discounted as it is only from this particular system that the trimer was isolated despite the use of flash chromatography for other separations. From extensive NMR data, the trimer was assigned structure **33** but its origin remains unknown.

31   **32**
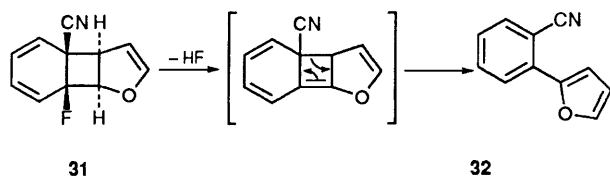
Irradiation of 3-fluorobenzonitrile in the presence of furan gave three 1:1 adducts in a ratio of 1.0:0.2:0.1 (order of GC elution). The minor isomer was assigned the *endo-ortho-*cycloadduct structure **34** arising from 2,3-addition of the furan to the 1,2-positions of the benzonitrile. The other two isomers were deduced to be the 2,5-*meta*-cycloadducts **14** and **15** arising from the same precursor orientation **19** of the addends in which the stabilising effects of the cyano and fluoro substituents on the developing polarity in the S$_1$ arene act in concert. For 4-fluorobenzonitrile where this reinforcing feature of the substituents is not present, the reaction is not so selective and while the major adduct isomer has the *meta*-structure **16** (48%), the *ortho*-adduct **39** (24%) and the substituted product **40** (28%) possibly derived from an isomer of **39**, are also formed. Thus again, for the mode of addition of furan to the benzene ring to be selective, the presence of the cyano substituent is essential.

	R^1	R^2	R^3	R^4	R^5
34	H	F	H	H	CN
35	H	H	H	H	CF$_3$
36	CF$_3$	H	H	H	H
37	H	CF$_3$	H	H	H
38	H	H	H	CF$_3$	H

39   **40**

41 R = H
42 R = CN

In the *meta*-photocycloaddition of ethenes to the benzene ring, the trifluoromethyl group has the same directing influence as the cyano substituent.[16] Thus both substituents orient the

addends so that they reside on the S$_1$ arene carbon atom at which the negative charge is developing on the approach of the ethene. Substituent-directed orientation of the addends is also clearly important in the furan photoadditions (*cf.* reaction mode selectivity between benzene and toluene), but it is evident from our studies with benzonitrile, phenylacetylene, and styrene[4] that secondary orbital interactions have a considerable influence in aligning the molecules and thus determining the selectivity of the reaction. In order to assess further the relative importance of these directing features, the photoreaction of furan with α,α,α-trifluorotoluene was examined. The 254 nm irradiation of this system produced a mixture comprising of at least seven 1:1 adducts (GC–MS, M$^+$, m/z 214), and under electron impact all readily fragmented to the starting materials. Only the five major adduct isomers could realistically be separated with purities > 80% and these in order of elution sequence from capillary column GC were assigned the structures **35**, **36**, **37**, **38** and **22**. From the nature of these products, it is apparent that the function of the trifluoromethyl group in this system is simply to increase the electron acceptability of the benzene ring and thereby its potential for *ortho*-cycloaddition:[1,2] the ΔG° value for this system is 1.34(1.24^{17}) eV compared to 1.91(1.80^{17}) eV for the benzene–furan case. Thus the ability of the trifluoromethyl substituent to orient the addends and direct the regiochemistry of the reaction is not significant in the 1,4-addition of 1,3-dienes. The effect of the cyano group on the benzene ring is to increase still further the thermodynamic driving force for electron transfer [ΔG° value of 1.06(0.96^{17}) eV] between the arene and furan. It may, therefore have been expected that the 2,3-*ortho*-attack of the furan would be promoted but evidently the ability of the nitrile substituent to orient the molecules by polar effects and/or to be involved in secondary orbital interactions, greatly predominates over the electron transfer considerations and 2,5-*meta*-addition is essentially the exclusive process.

Finally, we attempted to use the molecular constraints of tethered systems to induce selectivity into the photocycloaddition of furan to the benzene ring. We have recently noted the beneficial directing influence of oxygen in the 2-position of the 3-unit tether[18] and hence have synthesised the two furyl systems **41** and **42**. Molecular models of these two bichromophores suggest that the furan and benzene rings may preferentially align in the orientation required for 2,5-*meta*-addition and the cyano group in **42** resides in the position which, as evidenced from the present study, is greatly favoured in the intermolecular reaction for stabilisation of the developing negative charge. However, 254 nm irradiation did not yield any voltatile products from either **41** or **42**: the latter appeared to be largely photostable while **41** underwent fragmentation processes.

Experimental

The photochemical and analytical methods employed in this study are the same as those documented in ref. 7. All NMR spectra were recorded in CDCl$_3$ solution with tetramethylsilane as the standard, and coupling constants are given in Hz. IR spectra were of liquid films unless otherwise stated. Accurate mass data were provided by the SERC Mass Spectrometry Service Centre, Swansea after chromatographic assurance of the homogeneity of the adducts by TLC (one spot) and capillary column GC.

The present study was designed to determine the factors which influence the modes of reaction and direct the regiochemistry of the photoaddition of furan to the benzene ring, and so reaction conditions were not optimised for product formation. In general, the irradiations (254 nm) were of 20%

v/v solutions of the arene in furan. Degassing under nitrogen had no detectable effect on the reaction efficiency within the monitoring period, and while solvent polarity likewise did not have a significant influence, reactions carried out in methanol involving benzonitrile gave evidence for addition of the furan at the cyano substituent: illustrative data for this system are given below.

Photoproducts: Benzonitrile–Furan in Methanol Solution.— Irradiation of a solution (180 cm^3) of benzonitrile (37 g, 2 mol dm^{-3}), and furan (24.5 g, 2 mol dm^{-3}) in methanol for 24 h gave a pale yellow oil (1.45 g) after rotary evaporation and vacuum distillation (0.1 mmHg, 140–150 °C) of the residue. Analysis of the product mixture by GC showed the presence of three components in a relative ratio 1.0:1.0:0.9 (respective GC retention times 1.0:1.1:1.3; OV101, 120 °C). The products were isolated with >99% purity by flash chromatography (5% diethyl ether in 40–60 light petroleum). The product of intermediate retention time had spectroscopic properties and m.p. identical to those of the 1:1 adduct, *exo*-3-cyano-11-oxatetracyclo[6.2.1.0^{2,4}.0^{3,7}]undeca-5,9-diene, **5** which we have described previously. The other two products were identified as the 2- and 3-benzoylfurans from their analytical and spectroscopic data. These substitution products are considered to arise from the two regioisomers of cyano group addition to the 2,3-positions of furan[19] followed by hydrolysis of the azetine in the non-dried methanol.

Toluene–Furan.—The adducts were separated and purified by preparative gas chromatography.

exo-6-*Methyl*-11-*oxatetracyclo*[6.2.1.0^{2,4}.0^{3,7}]*undeca*-5,9-*diene* **7**. M.p. 33–34 °C; δ_H(250 MHz) 6.47 (ddd, $J_{10,9}$ 6.0, $J_{10,1}$ 1.4, $J_{10,8}$ 0.5, 10-H), 6.18 (dd, $J_{9,8}$ 2.0, 9-H), 5.62 (m, $J_{5,4}$ 2.5, $J_{5,CH}$ 1.5, 5-H), 5.01 (br s, 1-H), 4.53 (overlapping dd, $J_{8,7}$ 2.0, 8-H), 2.64 (dd, $J_{7,3}$ 7.5, $J_{7,CH}$ 0.9, 7-H), 2.14 (m, $J_{4,2}$, $J_{4,3}$ 7.5, $J_{4,CH}$ 0.8, 4-H), 1.67 (m, CH$_3$), 1.56 (q, $J_{3,2}$ 7.5, 3-H) and 0.75 (ddd, $J_{2,1}$ 1.6, 2-H); δ_C(62.9 MHz) 143.7 (C-6), 136.2 (C-10), 129.4 (C-9), 123.6 (C-5), 77.99 (C-1), 76.53 (C-8), 45.82 (C-7), 34.49 (C-4), 22.83 (C-2), 22.61 (CH$_3$) and 14.76 (C-1); ν_{max}/cm^{-1} 3407m, 3040m, 2947s, 2863m, 1705m, 1681m, 1651m, 1454m, 1316m, 1066s, 1052s, 765s, 753s and 703s (Found: M$^+$, 160.0888. Calc. for C$_{11}$H$_{12}$O, *M*, 160.0888).

exo-4-*Methyl*-11-*oxatetracyclo*[6.2.1.0^{2,4}.0^{3,7}]*undeca*-5,9-*diene* **9**. δ_H(250 MHz) 6.42 (ddd, $J_{10,9}$ 6.0, $J_{10,1}$ 1.5, $J_{10,8}$ 0.5, 10-H), 6.11 (dd, $J_{9,8}$ 1.8, 9-H), 5.89 (d, $J_{5,6}$ 5.2, 5-H), 5.34 (d of m, 6-H), 5.00 (br s, 1-H), 4.37 (overlapping dd, $J_{8,7}$ 2.0, 8-H), 2.95 (d of overlapping dd, $J_{7,3}$ 7.3, $J_{7,6}$ 2.0, 7-H), 1.26 (s, CH$_3$), 1.23 (dd, $J_{3,2}$ 8.4, 3-H) and 0.67 (d of overlapping dd, $J_{2,1}$ 1.5, $J_{2,6}$ 1.2, 2-H); ν_{max}/cm^{-1} 3013s, 2956m, 1722m, 1618s, 1445w, 1378w, 1313m, 1217s, 1055m, 924m, 869m, 719s and 667s (Found: M$^+$, 160.0888. Calc. for C$_{11}$H$_{12}$O, *M*, 160.0888).

exo-7-*Methyl*-11-*oxatetracyclo*[6.2.1.0^{2,4}.0^{3,7}]*undeca*-5,9-*diene* **10**. Isolated as an enriched mixture with **9**; δ_H(250 MHz) 6.47 (ddd, $J_{10,9}$ 6.0, $J_{10,1}$ 1.5, $J_{10,8}$ 0.5, 10-H), 6.19 (dd, $J_{9,8}$ 1.8, 9-H), 5.95 (dd, $J_{5,6}$ 5.2, $J_{5,4}$ 2.5, 5-H), 5.28 (d of overlapping dd, $J_{6,4}$ 1.5, 6-H), 5.04 (br s, 1-H), 4.11 (d, 8-H), 2.24 (ddd, $J_{4,2}$ 7.0, $J_{4,3}$ 7.1, 4-H), 1.23 (dd, $J_{3,2}$ 7.5, 3-H), 1.18 (s, CH$_3$) and 0.83 (dddd, $J_{2,1}$ 1.5, 2-H); *m/z* 160 (M$^+$).

Anisole–Furan.—The adducts were separated and purified by flash chromatography using 5% diethyl ether in light petroleum (b.p. 40–60 °C).

exo-2-*Methoxy*-9-*oxatricyclo*[6.3.0.0^{2,7}]*undeca*-3,5,10-*triene* **25**. δ_H(250 MHz) 6.35 (overlapping dd, $J_{10,11}$ 2.8, $J_{10,1}$ 2.5, 10-H), 6.17 (ddd, $J_{4,3}$ 9.7, $J_{4,5}$ 5.2, $J_{4,6}$ 1.4, 4-H), 5.99 (dddd, $J_{6,5}$ 9.4, $J_{6,7}$ 6.0, $J_{6,3}$ 1.4, 6-H), 5.91 (dd, H-5), 5.59 (d of overlapping dd, $J_{3,5}$ 1.0, $J_{3,7}$ 1.5, 3-H), 5.18 (overlapping dd, $J_{11,1}$ 2.8, 11-H), 4.34 (dd, $J_{8,1}$ 7.1, $J_{8,7}$ 4.4, 8-H), 3.73 (m, $J_{1,7}$ 1.5, 1-H),

3.27 (m, 7-H) and 3.10 (s, OCH$_3$); δ_C(62.9 MHz) 147.0, 130.9, 126.9, 126.4, 125.7, 122.7, 104.0, 59.81, 50.36, 47.46, 31.85 and 29.62; *m/z* 176 (M$^+$).

exo-3-*Methoxy*-11-*oxatetracyclo*[6.3.0.0^{2,5}.0^{3,7}]*undeca*-5,9-*diene* **26**. δ_H(250 MHz) 6.33 (overlapping dd, $J_{10,9}$ 2.5, $J_{10,8}$ 2.5, 10-H), 5.73 (dd, $J_{6,5}$ 5.6, $J_{6,7}$ 2.5, 6-H), 5.53 (dd, $J_{5,4}$ 2.3, 5-H), 4.85 (overlapping dd, $J_{9,8}$ 2.5, 9-H), 4.45 (d, $J_{1,8}$ 7.1, 1-H), 3.41 (d of overlapping dd, 8-H), 3.32 (s, OCH$_3$), 3.20 (d, 7-H), 2.25 (br d, $J_{4,2}$ 9.2, 4-H) and 2.20 (d, H-2); δ_C(62.9 MHz) 145.9 (C-10), 135.5 (C-6), 126.4 (C-5), 101.9 (C-9), 84.87 (C-1), 59.31 (C-8), 56.65 (C-7), 54.80 (OMe), 41.15 (C-4), 34.88 (C-2) and 29.54 (C-3) (Found: M$^+$, 176.0837. Calc. for C$_{11}$H$_{12}$O$_2$, *M*, 176.0837).

exo-3-*Methoxy*-9-*oxatetracyclo*[6.3.0.0^{2,4}.0^{3,7}]*undeca*-5,9-*diene* **27**. δ_H(250 MHz) 6.35 (overlapping dd, $J_{10,1}$ 2.7, 10-H), 5.65 (m, $J_{5,6}$ 5.0, 5-H, 6-H), 5.04 (overlapping dd, $J_{11,1}$, $J_{11,10}$ 2.7, 11-H), 4.47 (d, $J_{8,1}$ 6.5, 8-H), 3.46 (d, $J_{7,6}$ 1.5, 7-H), 3.38 (s, OCH$_3$), 2.83 (dd, 1-H), 2.22 (d of overlapping dd, $J_{4,2}$ 8.6, $J_{4,5}$, $J_{4,6}$ 1.8, 4-H) and 1.90 (d, H-2); δ_C(62.9 MHz) 147.0, 129.3, 103.4, 93.4, 88.75, 56.67, 56.43, 46.27, 41.73, 37.62 and 29.29 (Found: M$^+$, 176.0837. Calc. for C$_{11}$H$_{12}$O$_2$, *M*, 176.0837).

Fluorobenzene–Furan.—Separation and isolation of the photoproducts could not be achieved by flash chromatography, preparative gas chromatography or by chemical methods. The major adduct **21** did, however, crystallise from a pentane solution of the mixture at −25 °C.

7-Fluoro-11-*oxatricyclo*[4.2.2.1^{2,5}]*deca*-3,7,9-*triene* **21**. M.p. 69–70 °C; δ_H(250 MHz) 6.49 (m, $J_{9,10}$ 8.2, $J_{9,1}$ 6.3, $J_{9,6}$ 2.5, $J_{9,F}$ 1.4, 9-H), 6.42 (m, $J_{10,6}$ 6.2, $J_{10,1}$, $J_{10,F}$ 2.0, 10-H), 6.09 (d overlapping dd, $J_{3,4}$ 5.6, $J_{3,2}$ 1.7, $J_{3,5}$ 0.5, 3-H), 5.85 (dd, $J_{4,5}$ 1.5, $J_{4,2}$ 0.5, 4-H), 5.19 (ddd, $J_{8,F}$ 7.5, $J_{8,1}$ 5.3, $J_{8,6}$ 3.0, 8-H), 3.96 (dd with fine coupling, $J_{5,6}$ 6.2, 5-H), 3.89 (d of overlapping dd, $J_{2,1}$ 6.3, 2-H), 2.57–2.44 (m, $J_{1,F}$ 3.1, 1-H) and 2.35–2.24 (m, $J_{6,F}$ 14.5, 6-H); δ_C(62.9 MHz) 173.5 (C-7, $J_{C,F}$ 27.7) 134.9 (C-3), 134.2 (C-4), 132.1 (C-9), 131.6 (C-10), 108.6 (C-8, $J_{C,F}$ 12.5), 76.55 (C-2), 75.88 (C-5), 48.51 (C-6, $J_{C,F}$ 22) and 39.57 (C-1, $J_{C,F}$ 10); δ_F(84.25 MHz) −103, relative to C$_6$F$_6$; ν_{max}/cm^{-1} (CCl$_4$ solution) 3059w, 2963s, 1685s, 1619w, 1603w, 1578w, 1546w, 1347s, 1322m, 1307m, 1233w, 1203w, 1151s, 1035m, 933m, 873m, 836s and 702s (Found: M$^+$, 164.0637. Calc. for C$_{10}$H$_9$FO, *M*, 164.0637).

2-Fluorobenzonitrile–Furan:—Compound **32** was isolated by either flash chromatography or preparative gas chromatography.

2-(2′-Furyl)benzonitrile **32**. δ_H(400 MHz) 7.88 (d, $J_{3,4}$ 8.1, 3-H), 7.69 (dd, $J_{6,5}$ 7.8, $J_{6,4}$ 1.1, 6-H), 7.61 (overlapping dd, $J_{4,5}$ 7.6, 4-H), 7.55 (d, $J_{5′,4′}$ 1.8, 5′-H), 7.32 (overlapping dd, $J_{5,3}$ 1.1, 5-H), 7.32 (d, $J_{3′,4′}$ 3.5, 3′-H) and 6.55 (dd, 4′-H); δ_C(100.6 MHz) 149.6 (C-2), 143.2 (C-5′), 134.0 (C-6), 133.1 (C-2), 132.8 (C-4), 127.0 (C-5), 125.8 (C-3), 118.9 (CN), 112.1 (C-4′), 110.3 (C-3′) and 106.8 (C-1); ν_{max}/cm^{-1} 2217s, 1601, 1500 and 1484 (Found: M$^+$, 169.0527. Calc. for C$_{11}$H$_7$NO, *M*, 169.0528).

endo-(*endo*-2-*Furyl*)-9,10-*dioxatricyclo*[4,2,1,1^{2,5}]*dec*-7-*ene* **33**. δ_H(400 MHz) 7.36 (d, $J_{5′,4′}$ 1.7, 5′-H), 6.44 (dd, $J_{8,9}$ 5.9, $J_{8,7}$ 1.4, 8-H), 6.29 (dd, $J_{4′,3′}$ 3.2, 4′-H), 6.28 (dd, $J_{9,1}$ 1.8, 9-H), 6.24 (d, 3′-H), 5.35 (dd, $J_{4exo,5exo}$ 8.9, $J_{4exo,5endo}$ 6.4, 4$_{exo}$-H), 4.90 (br d, $J_{1,9}$ 1.4, 1-H), 4.78 (br d, 7-H), 4.40 (d, $J_{2,6}$ 5.85, 2-H), 2.57 (ddd, $J_{6,6exo}$ 8.9, $J_{6,5endo}$ 5.8, 6-H), 2.26 (d of overlapping dd, $J_{5exo,5endo}$ 12.8, 5$_{exo}$-H) and 2.07 (ddd, 5$_{endo}$-H); δ_C(100.6 MHz) 142.4, 138.9, 133.8, 130.7, 110.2, 107.3, 84.4, 83.4, 82.8, 77.4, 44.16 and 34.73; ν_{max}/cm^{-1} 3131w, 3116w, 2957m, 2867w, 1606w, 1503m, 1444w, 1348m, 1308m, 1150m, 1072s, 1053s, 1035s, 1012s, 987s, 904s, 878m, 827m, 740s and 689m; *m/z* 204 (M$^+$, 3%), 136(72), 110(70), 107(100), 94(70), 81(71) and 68(23).

3-Fluorobenzonitrile–Furan.—The adducts were separated and isolated by either flash chromatography or preparative gas chromatography.

endo-2-*Cyano*-6-*fluoro*-9-*oxatricyclo*[6.3.0.0^{2,7}]*undeca*-3,5,10-*triene* **34**. δ_H(250 MHz) 6.60 (dd, $J_{10,11}$ 2.8, $J_{10,1}$ 1.4, 10-H), 5.92 (ddd, $J_{4,3}$ 9.6, $J_{4,5}$ 6.7, $J_{4,F}$ 4.7, 4-H), 5.51 (ddd, $J_{5,F}$ 12.8, $J_{5,7}$ 1.1, 5-H), 5.45 (overlapping dd, $J_{8,1}$, $J_{8,7}$ 7.3, 8-H), 5.07 (dd, $J_{3,F}$ 1.9, 3-H), 5.02 (overlapping dd, $J_{11,1}$ 2.8, 11-H), 4.26 (m, $J_{1,7}$ 2.8, 1-H) and 4.11 (m, $J_{7,F}$ 4.7, 7-H); δ_C(62.9 MHz) 161.6 (C-6, $J_{C,F}$ 32.9), 154.7 (C-10), 131.1 (C-4, $J_{C,F}$ 9), 121.9 (CN), 114.6 (C-3, $J_{C,F}$ 6), 102.3 (C-5, $J_{C,F}$ 19.5), 99.25(C-11), 82.92 (C-8, $J_{C,F}$ 3), 76.99 (C-2), 59.71 (C-1) and 45.50 (C-7, $J_{C,F}$ 24); δ_F(84.25 MHz) − 113.8 ($J_{H,F}$ 12.8, 4.7, 4.7 and 1.9) relative to CFCl$_3$ (Found: M$^+$, 189.0591. Calc. for C$_{11}$H$_8$FNO, M, 189.0590).

exo-3-*Cyano*-6-*fluoro*-1-*oxatetracyclo*[6.2.1.0^{2,4}.0^{3,7}]*undeca*-5,9-*diene* **14**. δ_H(250 MHz) 6.26 (dd, $J_{10,9}$ 6.0, $J_{10,1}$ 1.5, 10-H), 6.35 (dd, $J_{9,8}$ 1.8, 9-H), 5.35 (d, $J_{5,4}$ 2.2, 5-H), 5.06 (overlapping dd, $J_{1,2}$ 1.5, 1-H), 4.72 (overlapping dd, $J_{8,7}$ 2.0, 8-H), 3.06 (dd, $J_{7,F}$ 3.7, 7-H), 2.74 (ddd, $J_{4,2}$ 7.2, $J_{4,F}$ 4.7, 4-H) and 1.42 (dd, 2-H); δ_C(62.9 MHz) 158.6 (C-6, $J_{C,F}$ 29.1), 136.4 (C-10), 129.4 (C-9), 120.7 (CN), 101.5 (C-5, $J_{C,F}$ 15.1), 77.11 (C-1), 74.66 (C-8), 42.36 (C-7, $J_{C,F}$ 24), 36.15 (C-4, $J_{C,F}$ 9), 30.19 (C-2) and 28.00 (C-3, $J_{C,F}$ 4); δ_F(84.25 MHz) − 118.2, relative to CFCl$_3$; ν_{max}/cm^{-1} 2233, 1677 and 1662 (Found: M$^+$, 189.0589. Calc. for C$_{11}$H$_8$FNO, M, 189.0590).

exo-3-*Cyano*-4-*fluoro*-11-*oxatetracyclo*[6.2.1.0^{2,4}.0^{3,7}]-*undeca*-5,9-*diene* **15**. This photocycloadduct readily underwent an ethenylcyclopropane–cyclopentane rearrangement to give **14** and for this reason could only be isolated as an enriched mixture with **14**. Extracted data; δ_H(400 MHz) 6.54 (dd, $J_{10,9}$ 5.9, $J_{10,1}$ 1.5, 10-H), 6.37 (dd, $J_{9,8}$ 1.8, 9-H), 6.18 (dd, $J_{5,6}$ 5.5, $J_{5,F}$ 1.5, 5-H), 5.63 (doublet of overlapping dd, $J_{6,7}$ 2.3, $J_{6,F}$ 2.3, 6-H), 5.05 (overlapping dd, $J_{1,2}$ 1.5, 1-H), 4.41 (overlapping dd, $J_{8,7}$ 2.1, 8-H), 3.22 (overlapping dd, 7-H) and 2.08 (dd, $J_{2,F}$ 15.0, 2-H); m/z 189 (M$^+$, 1%), 160 (2), 140 (4), 133 (10), 121 (9), 108 (2), 94 (5), 81 (100) and 68 (75).

4-Fluorobenzonitrile–Furan.—The photoproducts were isolated and separated by flash chromatography.

exo-3-*Cyano*-5-*fluoro*-11-*oxatetracyclo*[6.2.1.0^{2,4}.0^{3,7}]-*undeca*-5,9-*diene* **16**. δ_H(400 MHz) 6.56 (ddd, $J_{10,9}$ 5.9, $J_{10,1}$ 1.5, $J_{10,8}$ 0.5, 10-H), 6.22 (dd, $J_{9,8}$ 1.8, 9-H), 5.06 (overlapping dd, $J_{1,2}$ 1.5, 1-H), 4.69 (dd, $J_{6,2}$ 2.3, $J_{6,F}$ 1.4, 6-H), 4.43 (overlapping dd, $J_{8,7}$ 1.9, 8-H), 2.96 (d of overlapping dd, $J_{7,F}$ 6.6, 7-H), 2.77 (dd, $J_{4,2}$ 7.6, $J_{4,F}$ 0.8, 4-H) and 1.53 (d of overlapping dd, $J_{2,6}$ 1.5, 2-H); δ_C(22.49 MHz) 158.1 (C-5, $J_{C,F}$ 280), 136.50 (C-10), 129.5 (C-9), 120.2 (CN), 106.0 (C-6, $J_{C,F}$ 15), 78.56 (C-1), 77.70 (C-8, $J_{C,F}$ 9), 37.26 (C-2) and 29.82 (C-7, $J_{C,F}$ 4); δ_F(84.25 MHz) − 120.8 (J 6.6) relative to CFCl$_3$; ν_{max}/cm^{-1} 2234 and 1602 (Found: M$^+$, 189.0590. Calc. for C$_{11}$H$_8$FNO, M, 189.0590).

endo-5-*Cyano*-2-*fluoro*-9-*oxatricyclo*[6.3.0.0^{2,7}]*undeca*-3,5,10-*triene* **39**. δ_H(400 MHz) 6.48 (d, $J_{6,7}$ 6.0, 6-H), 6.28 (overlapping dd, $J_{10,11}$ 2.8, $J_{10,1}$ 1.7, 10-H), 6.14 (ddd, $J_{4,3}$ 10, $J_{4,F}$ 3.4, $J_{4,6}$ 1.1, 4-H), 5.91 (dd, $J_{3,4}$ 10, $J_{3,F}$ 7.6, 3-H), 5.36 (m, $J_{8,1}$, $J_{8,7}$ 8.8, $J_{8,F}$ 1.3, 8-H), 4.93 (overlapping dd, $J_{11,1}$ 2.8, 11-H), 3.89 (m, $J_{1,F}$ 16, 1-H) and 3.62 (m, $J_{7,F}$ 29.2, 7-H); δ_C(100 MHz) 149.6 (C-10), 138.1 (C-4, $J_{C,F}$ 6), 125.9 (C-6, $J_{C,F}$ 11), 123.7 (C-3, $J_{C,F}$ 20), 117.7 (CN), 110.4 (C-5), 100.5 (C-11), 91.85 (C-2, $J_{C,F}$ 217), 89.14 (C-8, $J_{C,F}$ 35), 44.55 (C-1, $J_{C,F}$ 44) and 44.34 (C-7, $J_{C,F}$ 44); δ_F(84.25 MHz) − 30 relative to CFCl$_3$; ν_{max}/cm^{-1} 2210 and 1650 (Found: M$^+$, 189.0591. Calc. for C$_{11}$H$_8$FNO, M, 189.0590).

4-(2′-Furyl)benzonitrile **40**. δ_H(250 MHz) 7.74 (dd, $J_{2,3}$ 8.4, $J_{2,6}$ 0.8, 2-H, 3-H), 7.64 (dd, $J_{5,6}$ 8.4, $J_{5,3}$ 0.8, 5-H, 6-H), 7.52 (dd, $J_{5',4'}$ 1.8, $J_{5',3'}$ 0.7, 5′-H), 6.80 (dd, $J_{3',4'}$ 3.4, 3′-H) and 6.52 (dd, 4′-H); ν_{max}/cm^{-1} 2222, 1599, 1505 and 1490 (Found: M$^+$, 169.0527. Calc. for C$_{11}$H$_7$NO, M, 169.0528).

α,α,α-Trifluorotoluene–Furan.—The adducts were separated by preparative gas chromatography.

endo-2-(*Trifluoromethyl*)-9-*oxatricyclo*[6.3.0.0^{2,7}]*undeca*-3,5,10-*triene* **35**. δ_H(400 MHz) 6.49 (dd, $J_{10,11}$ 2.8, $J_{10,1}$ 1.5, 10-H), 6.06 (dd, $J_{4,3}$ 10, $J_{4,5}$ 5.8, 4-H), 5.85 (dd, $J_{5,6}$ 9.9, 5-H), 5.56 (dd, $J_{6,7}$ 5.0, 6-H), 5.32 (overlapping dd, $J_{8,1}$, $J_{8,7}$ 7.4, 8-H), 5.24 (dd, $J_{3,7}$ 1.3, 3-H), 4.99 (dd, $J_{11,1}$ 2.8, 11-H), 3.90 (m, H-1) and 3.71 (m, $J_{7,1}$ 3.0, 7-H); δ_F(376.5 MHz) − 78.98 relative to C$_6$F$_6$; m/z 214 (M$^+$).

endo-7-(*Trifluoromethyl*)-9-*oxatricyclo*[6.3.0.0^{2,7}]*undeca*-3,5,10-*triene* **36**. δ_H(400 MHz) 6.40 (dd, $J_{10,11}$ 2.75, $J_{10,1}$ 1.7, 10-H), 6.06 (dd, $J_{5,6}$ 10.1, $J_{5,4}$ 5.7, 5-H), 5.83 (dd, $J_{4,3}$ 9.9, 4-H), 5.44 (d, 6-H), 5.38 (dd, $J_{3,2}$ 5.5, 3-H), 5.32 (d, $J_{8,1}$ 7.4, 8-H), 5.10 (overlapping dd, $J_{11,1}$ 2.8, 11-H), 3.35 (m, H-1) and 3.48 (br dd, $J_{2,1}$ 7.9, $J_{2,8}$ 2.4, 2-H); δ_F(376.5 MHz) − 79.89 relative to C$_6$F$_6$; m/z 214 (M$^+$).

endo-4-(*Trifluoromethyl*)-9-*oxatricyclo*[6.3.0.0^{2,7}]*undeca*-3,5,10-*triene* **37**. δ_H(220 MHz) 6.25 (dd, $J_{10,11}$ 2.8, $J_{10,1}$ 1.4, 10-H), 5.83 (dd, $J_{5,6}$ 9.8, 5-H), 5.58 (dd, $J_{6,7}$ 4.8, 6-H), 5.47 (br d, $J_{3,2}$ 5.2, $J_{3,7}$ 1.2, 6-H), 4.89 (overlapping dd, $J_{8,7}$, $J_{8,1}$ 6.6, 8-H), 4.76 (overlapping dd, $J_{11,1}$ 1.4, 11-H), 3.35 (m, 1-H), 3.05 (m, 7-H) and 2.79 (m, 2-H); δ_F(84.25 MHz) − 69.40 relative to C$_6$F$_6$; m/z 214 (M$^+$).

endo-6-(*Trifluoromethyl*)-9-*oxatricyclo*[6.3.0.0^{2,7}]*undeca*-3,5,10-*triene* **38**. δ_H(220 MHz) 6.37 (dd, $J_{10,11}$ 2.8, $J_{10,1}$ 1.4, 10-H), 6.14 (br d, $J_{5,4}$ 5.8, 5-H), 5.41 (dd, $J_{4,3}$ 9.8, 4-H), 5.06 (dd, $J_{3,2}$ 2.2, 3-H), 4.84 (overlapping dd, $J_{8,1}$, $J_{8,7}$ 6.6, 8-H), 4.62 (overlapping dd, $J_{11,1}$ 1.4, 11-H), 3.48 (m, 1-H) and 3.12 (m, 2-H, 7-H); δ_F(84.25 MHz) − 78.49 relative to C$_6$F$_6$; m/z 214 (M$^+$).

7-(*Trifluoromethyl*)-11-*oxatricyclo*[4.2.2.1^{2,5}]*undeca*-3,7,9-*triene* **22**. δ_H(60 MHz) 7.15 (m, 8-H), 6.19 (m, 9-H, 10-H), 5.10 (s, 3-H, 4-H), 4.20 (br d, $J_{5,6}$ 6.0, 5-H), 4.35 (br d, $J_{2,3}$ 6.0, 2-H) and 3.18–3.07 (m, 1-H, 6-H); m/z 214 (M$^+$).

1-*Phenyl*-2-*oxa*-3-(2′*furyl*)*propane* **41** *and* 1-(2′-*cyano-phenyl*)-2-*oxa*-(2″-*furyl*)*propane* **42**. The two bichromophore **41** and **42** were synthesised by the same procedure involving dropwise addition of furfuryl alcohol (3.4 g, 0.034 mol dm^{-3}) in dimethyl formamide (DMF; 30 cm^3) to a stirred 40% solution of sodium hydride (60% dispersion in oil, 3.4 g, 0.034 mol dm^{-3} in paraffin) in DMF (30 cm^3) under nitrogen. When effervesence had ceased, the benzyl bromide (0.034 mol dm^{-3}) in DMF (30 cm^3) was added dropwise over 1 h. The mixture was left to stand for a further 1 h, and then refluxed for 4 h. Work up with ethanol and aq. hydrochloric acid (2 mol dm^{-3}) followed by ether extraction of the mixture and purification of the product by flash chromatography and vacuum distillation gave **41** and **42** in respective yields of 72 and 40%. **41**, B.p. 105–110 °C/0.05 mmHg; δ_H(250 MHz) 7.36–7.17 (m, aryl-5,5′-H), 6.26 (m, 3′, 4′-H), 4.48 (s, CH$_2$) and 4.41 (s, CH$_2$); δ_C(62.9 MHz) 151.6, 142.4, 137.7, 128.1, 127.6, 127.4, 110.0, 109.1, 71.55 (CH$_2$) and 63.58 (CH$_2$); ν_{max}/cm^{-1} 1606, 1499, 1455, 1360, 1224, 1151, 1091, 1073, 1017 (Found: M$^+$, 188.0837. Calc. for C$_{12}$H$_{12}$O$_2$, M, 188.0837). **42**, B.p. 145–150 °C; δ_H(400 MHz) 7.63–7.56 (m, aryl-3-H), 7.42 (dd, $J_{5'',4''}$ 1.96, $J_{5'',3''}$ 0.7, 5″-H), 7.38–7.34 (m, aryl-H), 6.39 (d, $J_{3'',4''}$ 3.17, 3″-H), 6.35 (dd, 4″-H), 4.72 (s, CH$_2$) and 4.58 (s, CH$_2$); δ_C(100.4 MHz) 151.0, 143.0, 141.7, 132.9, 132.7, 128.7, 128.3, 117.2 (CN), 111.4, 110.3, 109.9, 69.35 (CH$_2$) and 64.74 (CH$_2$); ν_{max}/cm^{-1} 2225, 1602, 1503, 1451, 1387, 1223, 1151, 1112, 1077, 1017 (Found: M$^+$, 213.0789. Calc. for C$_{13}$H$_{11}$NO$_2$, M, 213.0790).

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