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Photochemically catalyzed ring opening of oxiranecarbonitriles and [3+2] cycloaddition with olefins: synthesis of polysubstituted tetrahydrofurans

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Abstract—Photoinduced electron transfer catalyzed ring opening of aryl-substituted oxiranecarbonitriles via C_β–O bond cleavage was achieved using 2,4,6-triphenylpyrylium tetrafluoroborate (**TPT**) as a sensitizer and subsequent [3+2] cycloaddition reaction with electron-rich olefins afforded polysubstituted tetrahydrofurans in good to moderate yields.

The synthetic potential of photoinduced electron transfer (PET)-catalyzed reactions has attracted great attention in the past two decades.[1,2] These reactions are often initiated by an electron transfer from the substrate to the excited singlet state of sensitizer. In PET reactions, sensitizer is known to play an important role as an electron carrier which efficiently circulates in the catalytic process. 2,4,6-Triphenylpyrylium tetrafluoroborate (**TPT**) has been widely used as an oxidative sensitizer in many photochemical reactions[1a] offering some advantages over others such as being excited at wavelength >400 nm and having a relatively low reduction potential. Especially, it is salt with no net charge separation associated to the electron transfer step. Therefore the formation of free-radical ion is enhanced, while deactivation through back-electron transfer is reduced.

We are interested in the **TPT**-sensitized electron transfer of aryl-substituted epoxides, especially its ring opening via selective C_β–O bond cleavage and subsequent [3+2] cycloaddition with electron-rich olefins because the authors found no report dealing with the PET-catalyzed [3+2] reaction of epoxides with electron-rich olefins. The PET-catalyzed, for example, 1,4-dicyanophthalene (DCN) or 9,10-dicyanoanthracene (DCA)-sensitized, ring opening of stilbene oxides and subsequent isomerization or rearrangement have been studied intensively;[3] direct photolytic and thermolytic ring opening of aryl-substituted epoxides and subsequent [3+2] reaction with electron-deficient olefins were also documented.[4] Both the 1,4-dicyanophthalene (DCN) or 9,10-dicyanoanthracene (DCA)-catalyzed and directly photolytic or thermolytic ring opening, however, were via C_α–C_β bond cleavage. The sole example reported for photocatalyzed ring opening of epoxides via C_β–O bond cleavage was observed in **TPT**-sensitized methanolysis of chalcone epoxide,[5] but no cycloaddition reaction was attempted. As a part of our ongoing research program on synthetic potential of PET mediated reaction,[6] we report herein a facile synthesis of tetrahydrofurans derivatives by **TPT**-sensitized C_β–O bond cleavage of methoxyphenyl-substituted oxiranecarbonitrile **1a**–**e** and subsequent [3+2] cycloaddition with electron-rich olefins such as styrene (**2a**), α-methylstyrene (**2b**), anethole (**2c**), indene (**2d**), and cyclopentene (**2e**). The synthesis of tetrahydrofuran derivatives is also an area of intense interest for organic chemists due to the presence of these scaffolds within the framework of numerous biologically active natural products and pharmaceutical agents.[7]

We first examined the **TPT**-sensitized cycloaddition reaction of chalcone epoxides with electron-rich olefins and found only 3-(4-methoxyphenyl)- or 3-(3,4-dimethoxyphenyl)-substituted epoxides could react but no

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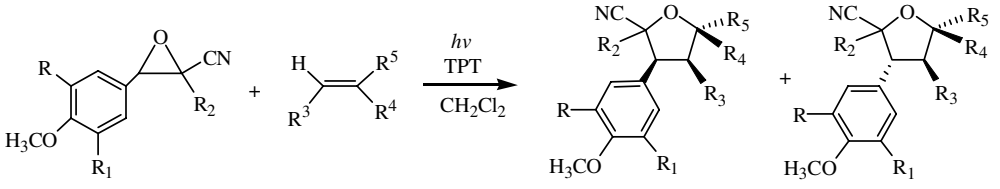
desired adducts were obtained except the rearrangement product 2-benzoyl-2-(4-methoxy)phenylethaldehyde. We then examined the reaction of 3-(4-methoxyphenyl)-substituted oxiranecarbonitriles and found they worked well to give the tetrahydrofuran derivatives. Similarly to the chalcone epoxides, only 4-methoxyphenyl- or 3,4-dimethoxyphenyl-substituted oxiranecarbonitriles could be efficiently oxidized by excited **TPT**. This result is consistent with the reactivity of stilbene oxides under 9,10-dicyanoanthracene (DCA)-sensitization[3e] in which only methoxy-substituted stilbene oxides could be oxidized. The reactivity is also consistent with the prediction by Rehm–Weller equation ($\Delta G_{ET} = E^{ox}_{1/2}(D) - E^{red}_{1/2}(A) - \Delta E_{excit} + E_{coul}$)[8] because the free enthalpy ΔG_{ET} for electron transfer from 4-methoxyphenyl-substituted oxiranecarbonitrile **1a** ($E^{ox}_{1/2} = 1.59$ V vs SCE[5]) to excited **TPT** ($E^{red}_{TPT^*/TPT^{-\cdot}} = E^{red}_{1/2} + \Delta E_{excit} = 2.50$ V vs SCE[2a]), calculated by Rehm–Weller equation, is −0.78 eV ($E_{coul} = 0.13$ eV in CH_2Cl_2) which is largely negative and indicates that the process is feasible.

Irradiation at $\lambda \geqslant 400$ nm of a deaerated anhydrous CH_2Cl_2 solution (50 ml) of the epoxide (**1**, 2 mmol), styrene (**2a**, 2.5 mmol), and a catalytic amount of 2,4,6-triphenylpyrylium tetrafluoroborate (**TPT**, 0.1 mmol) at ambient temperature for 8–15 h as monitored by TLC produced tetrahydrofuran derivative **3a** in moderate to high yields under completely regioselectivity (Scheme 1). The photocatalyzer **TPT** could be recovered. In all cases mixtures of diastereomers were produced but only one or two were dominant. Careful thin layer chromatographic separation by elution with hexane/acetone (10:1 v/v) gave the pure products which were fully identified by ^1H, ^{13}C, and 2D NMR spectroscopy[9] and the stereochemistry was evaluated by chemical shift consideration and NOE correlation as shown in Figure 1.

It is noteworthy that **TPT**-sensitized ring opening of **1a** is via selective C_β–O bond cleavage from structure of **3a**–**d** as determined according to ^1H NMR and 2D NMR. For example, the structure of **3b** which was produced from photoreaction of **1a** and **2b** is 3-(4-methoxyphenyl)-5-methyl-5-phenyl-2-oxiranecarbonitrile (**A**), but not 5-(4-methoxyphenyl)-3-methyl-3-pheny-2-oxiranecarbonitrile (**B**) because a doublet peak at $\delta = 4.49$ ppm (d, $J = 9.6$ Hz) for H-2 is observed in ^1H NMR, instead of singlet peaks which should have appeared for H-2 in **B**. All reciprocal interactions are observed among H-2, H-3, H-4_{ax} or H-4_{equ} and CH_3 in NOE correlations of **3b** as shown in Figure 1.

Other monocyano-substituted and dicyano-substituted epoxide **1b**–**g** were examined and they could all be transformed to tetrahydrofuran derivatives in the **TPT**-sensitized reaction with **2a**–**e**. In most cases only one product was dominant and could be purified by repeated thin



Scheme 1.

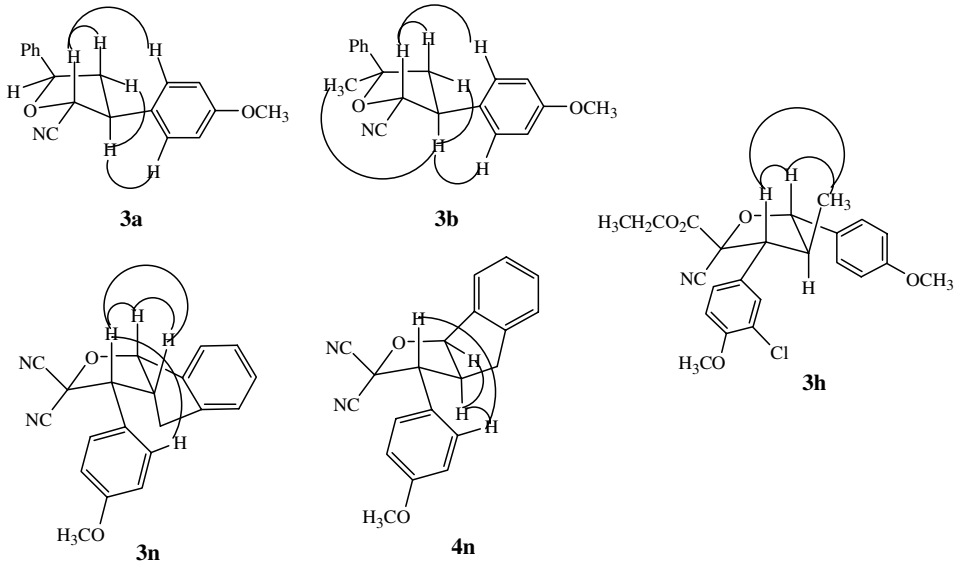


Figure 1. NOESY correlations of *cis*-**3a**, *cis*-**3a**, and *trans*-**4a**.

layer chromatography (TLC). Sometimes two main products could be separated by TLC. For example, two diastereoisomer **3n** and **4n** were produced from the reaction of **1e** with **2d** and their configurations were characterized by ^{1}H NMR and NOE correlations as depicted in Figure 1. All results are listed in Table 1. The characterization of configurations by ^{1}H NMR and NOE correlation was further confirmed by the X-ray structure of **3a**[9] as depicted in Figure 2.

The stereoselectivity of reactions according to NOE results is derived from the steric effect of CN and R^5 in the reaction of **1a** and **2a**–**e** as indicated from the transition states (**I**) and (**II**) formed from the cation radical of **1a** with styrene. Obviously (**I**) might be more favorable than (**II**) and thus easily transformed to **3a** because the configuration of CN and Ph is trans in (**I**) as depicted in Figure 3. But a more important effect is derived from the thermomechanical stability of products because the configuration of aryl group at C-3 and another aryl group at C-5 is cis in all main products **3a**–**r** from both monocyano-substituted and dicyano-substituted oxiranes.

Because no reaction was detected in the methylene dichloride solution of **1a** with **2a**–**d** in the absence of sensitizer **TPT** at $\lambda \geqslant 400$ nm after prolonged irradiation (48 h) or in the methylene dichloride solution of **1a** with **2a**–**d** in the presence of **TPT** but without irradiation, it was certain that photoinduced electron transfer was essential for the ring opening of epoxides. It was also found that no adduct was formed in the methylene dichloride solution of **1a** and electron-deficient olefins such as methyl acrylate or diethyl fumarate in the presence of sensitizer **TPT** after prolonged irradiation (48 h). So it could be inferred that the intermediate formed from ring opening of **1a** was radical cation, not carbonyl ylides. A plausible mechanism according to the above results is proposed as follows:

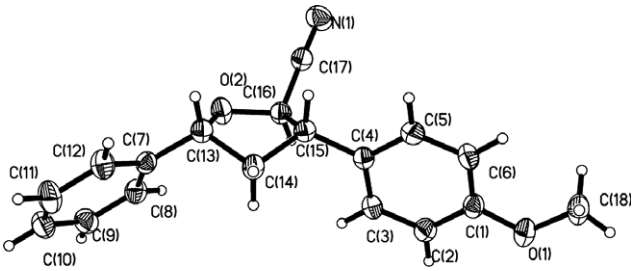


Figure 2. X-ray structure (ORTEP drawing) of *cis*-**3a**.

Table 1. Photochemical reaction of 3-aryloxiranecarbonitriles with olefins

Entry	Epoxides				Olefins				*t* (h)	Conv.[a] (%)	Yield[b] (%)	
		R	R^1	R^2		R^3	R^4	R^5				
1	**1a**	H	H	H	**2a**	H	H	Ph	12	98	**3a**	70
2	**1a**	H	H	H	**2b**	H	CH_3	Ph	12	98	**3b**	76
3	**1a**	H	H	H	**2d**	$CH_2C_6H_4$		H	12	98	**3c**	67
4	**1a**	H	H	H	**2e**	$(CH_2)_3$		H	18	85	**3d**	63
5	**1b**	H	H	CO_2Et	**2b**	H	CH_3	Ph	15	98	**3e**	57
6	**1b**	H	H	CO_2Et	**2d**	$CH_2C_6H_4$		H	15	98	**3f** + **4f**	48 + 23
7	**1c**	H	Cl	CO_2Et	**2b**	H	CH_3	Ph	12	92	**3g**	58
8	**1c**	H	Cl	CO_2Et	**2c**	CH_3	H	PMP	15	95	**3h**	52
9	**1d**	CH_3O	H	CO_2Et	**2a**	H	H	Ph	12	98	**3i** + **4i**	51 + 15
10	**1d**	CH_3O	H	CO_2Et	**2b**	H	CH_3	Ph	12	98	**3j**	62
11	**1d**	CH_3O	H	CO_2Et	**2d**	$CH_2C_6H_4$		H	15	98	**3k**	65
12	**1e**	H	H	CN	**2a**	H	H	Ph	8	90	**3l**	56
13	**1e**	H	H	CN	**2b**	H	CH_3	Ph	8	90	**3m**	67
14	**1e**	H	H	CN	**2d**	$CH_2C_6H_4$		H	10	92	**3n** + **4n**	55 + 23
15	**1e**	H	H	CN	**2c**	CH_3	H	PMP	10	92	**3o**	62
16	**1f**	CH_3O	H	CN	**2b**	H	CH_3	Ph	12	95	**3p** + **4p**	48 + 23
17	**1f**	CH_3O	H	CN	**2e**	$(CH_2)_3$		H	12	98	**3q** + **4q**	48 + 15
18	**1g**	CH_3O	Cl	CN	**2a**	H	H	Ph	12	98	**3r**	57

[a] Conversion based on **1**.
[b] Isolated yield based on **1**.

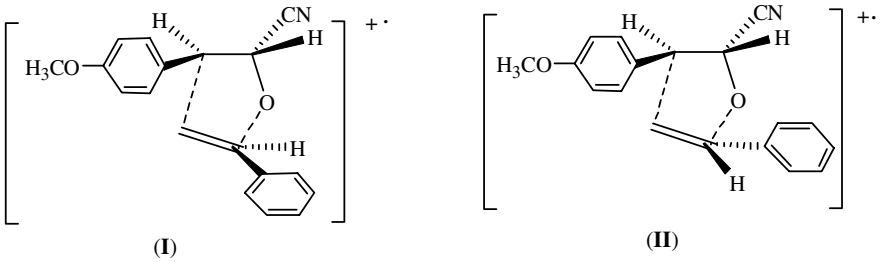
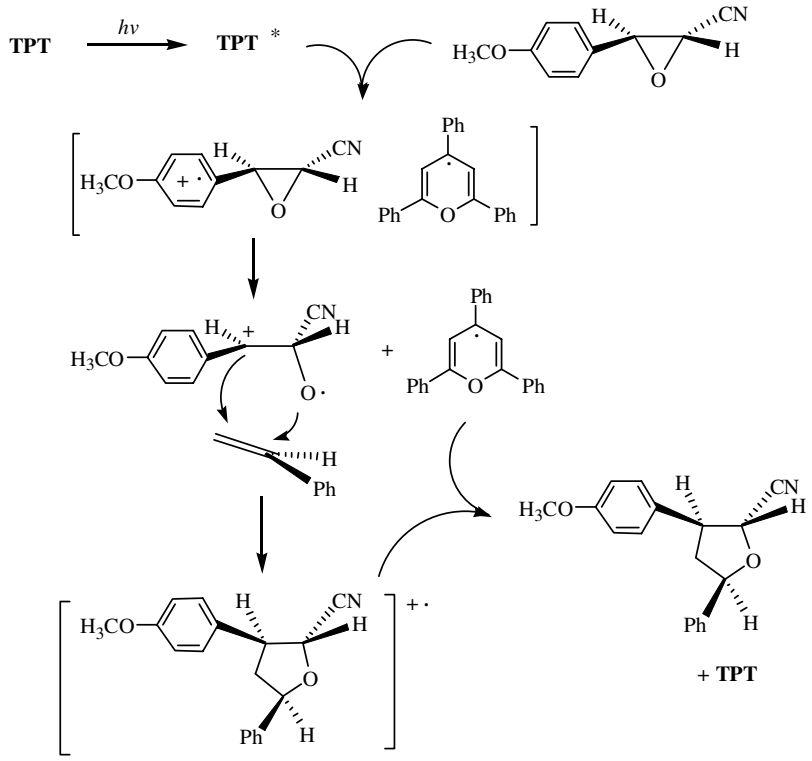


Figure 3. Transition state (**I**) and (**II**) formed from the cation radical of **1a** with styrene.



In summary, an efficient approach for synthesis of a variety of tetrahydrofuran derivatives has been developed. To the best of our knowledge, this is the first report for the synthesis of these compounds via PET-catalyzed C_β–O bond cleavage of aryl-substituted epoxides and subsequent [3+2] reactions with electron-rich olefins.

Acknowledgment

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9. *Representative products*:
cis-2-Cyano-3-(4-methoxyphenyl)-5-phenyl-2,3,4,5-tetrahydrofuran (**3a**) colorless needles, mp: 76–78 °C ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.14 (q, $J = 10.5$ Hz, 1H, H-4ax), 2.76–2.85 (m, 1H, H-4equ), 3.79 (s, 3H, OCH_3), 3.96 (dt, $J = 11.5$, 7.5 Hz, 1H, H-3), 4.70 (d, $J = 7.8$ Hz, 1H, H-2),

5.28 (dd, $J = 10.5$, 4.8 Hz, 1H, H-5), 6.89 (d, $J = 8.7$ Hz, 2H, H-3′), 7.23 (d, $J = 8.7$ Hz, 2H, H-2′), 7.29–7.41 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 42.6 (C-4), 51.0 (C-3), 55.3 (O*C*H$_3$), 73.3 (C-2), 82.8 (C-5), 114.4 (2C, C-3′), 118.9 (*C*N), 125.5 (C-4″), 125.8 (2C, C-2″), 128.2 (2C, C-3″), 128.6 (2C, C-2′), 130.2 (C-1′), 139.4 (C-1″), 159.1 (C-4′). MS m/z 279 (M^+, 52), 224 (93), 209 (12), 193 (16), 159 (23), 121 (27), 105 (100). HRMS (ESI) m/z calcd for $C_{18}H_{17}NO_2$ $(M+Na)^+$: 302.1152. Found: 302.1148. X-ray data for compound **3a**: $C_{18}H_{17}NO_2$, $M = 279.33$, colorless plates, monoclinic, $a = 5.8513(2)$, $b = 9.3655(4)$, $c = 27.1933(9)$ Å, $V = 1490.20(10)$ Å^3, $T = 294(2)$ K, space group $P2(1)/c$, $Z = 4$, μ (MoK$_a$) $= 0.081$ mm^{-1}, $2\theta_{max} = 25.50$, 2767 reflection collected, 1570 unique ($R_{init} = 0.082$) which was used in all calculations. Final $wR(F^2) = 0.0923$ (all data). CCDC file No. 633304.

cis-2-Cyano-3-(4-methoxyphenyl)-5-methyl-5-phenyl-2,3,4,5-tetrahydrofuran (**3b**), dense oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.69 (s, 3H, C*H*$_3$), 2.41 (t, $J = 12.3$ Hz, 1H, H-4ax), 2.71 (dd, $J = 12.3$, 7.8 Hz, 1H, H-4equ), 3.76 (s, 3H, OC*H*$_3$), 3.96 (dt, $J = 10.5$, 8.1 Hz, 1H, H-3), 4.49 (d, $J = 9.6$ Hz, 1H, H-2), 6.84 (d, $J = 8.7$ Hz, 2H, H-3′), 7.14 (d, $J = 8.7$ Hz, 2H, H-2′), 7.27 (t, $J = 8.1$ Hz, 1H, H-4″), 7.34–7.42 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.0 (*C*H$_3$), 46.5 (C-4), 51.3 (C-3), 55.1 (O*C*H$_3$), 72.6 (C-2), 87.4 (C-5), 114.4 (2C,C-3′), 118.9 (*C*N), 124.1 (2C, C-2″), 127.0 (C-4″), 128.2 (C-1′), 128.4 (2C, C-3″), 128.5 (2C, C-2′), 146.1 (C-1″), 159.1 (C-4′). MS m/z 293 (M^+, 33), 278 (8), 238 (21), 223 (81), 115 (34), 105 (82), 84 (100). HRMS (ESI) m/zcalcd for $C_{19}H_{19}NO_2$ $(M+Na)^+$: 316.1308. Found: 316.1305.

cis-Ethyl-2-cyano-3-(3,4-dimethoxyphenyl)-5-methyl-5-phenyl-2,3,4,5-tetrahydrofuran-carboxylate (**3j**), dense oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.86 (t, $J = 7.2$ Hz, 3H, CH_3), 1.82 (s, 3H, C*H*$_3$), 2.60 (dd, $J = 12.3$, 7.2 Hz, 1H, H-4equ), 2.86 (t, $J = 12.3$ Hz, 1H, H-4ax), 3.75 (q, $J = 7.2$ Hz, 2H, OCH_2), 3.80 (s, 3H, OC*H*$_3$), 3.86 (s, 3H, OC*H*$_3$), 4.47 (dd, $J = 12.6$, 6.9 Hz, 1H, H-3), 6.76–6.86 (m, 3H), 7.31 (t, $J = 7.8$ Hz, 1H, H-4″), 7.40 (t, $J = 7.8$ Hz, 1H, H-3″), 7.57 (t, $J = 7.5$ Hz, 1H, H-2″); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.4 (*C*H$_3$), 29.1 (*C*H$_3$), 42.6 (C-4), 55.5 (C-3), 55.8 (O*C*H$_3$), 55.9 (O*C*H$_3$), 62.6 (O*C*H$_2$), 81.8 (C-2), 89.2 (C-5), 110.8 (C-2′) 110.9 (C-5′), 119.0 (*C*N), 120.3 (C-6′), 124.6 (2C, C-3″), 125.6 (C-1′), 127.1 (C-4″), 128.2 (2C, C-2′), 145.9 (C-1″), 148.8 (C-3′), 149.1 (C-4′), 165.3 (C=O). MS m/z 395 (M^+, 23), 304 (2), 275 (11), 268 (32), 253 (55), 204 (29), 105 (100). HRMS (ESI) m/z calcd for $C_{23}H_{25}N_2O_5$ $(M+Na)^+$: 418.1623. Found: 418.1618.

cis-2,3,4,10-Tetrahydro-2,2-dicyano-3-(4-methoxyphenyl)-indeno[1,2-*b*]furan (**3n**). Colorless needles, mp: 121–122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.83 (dd, $J = 17.1$, 3.9 Hz, 1H, H-5equ), 3.08 (dd, $J = 17.1$, 9.3 Hz, 1H, H-5ax), 3.76 (s, 3H, C*H*$_3$O), 3.80–3.90 (m, 1H, H-4), 4.21 (d, $J = 8.4$ Hz, 1H, H-3), 5.99 (d, $J = 7.5$ Hz, 1H, H-10), 6.79 (d, $J = 7.5$ Hz, 2H, H-3′), 7.04 (m, 3H, H-6, H-2′), 7.30–7.33 (m, 2H, H-7, H-8), 7.48–7.51 (m, 1H, H-9). ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.4 (C-5), 45.2 (C-4), 55.2 (O*C*H$_3$), 59.1 (C-3), 71.7 (C-2), 91.0 (C-10), 112.4 (*C*N), 114.2 (2C, C-3′), 114.8 (*C*N), 124.7 (C-1′), 124.8 (C-6), 125.7 (C-7), 127.6 (C-9), 129.9 (2C, C-2′), 130.3 (C-8), 138.1 (C-5a), 143.3 (C-9a), 169.8 (C-4′). MS m/z 316 (M^+, 2), 236 (5), 221 (1), 205 (1), 178 (100), 128 (6), 121 (100). HRMS (ESI) m/z calcd for $C_{20}H_{16}N_2O_2$ $(M+Na)^+$: 339.1104. Found: 339.1104.

trans-2,3,4,10-Tetrahydro-2,2-dicyano-3-(4-methoxyphenyl)-indeno[1,2-*b*]furan (**4n**). colorless needles, mp: 183–184 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.86 (dd, $J = 16.8$, 3.2 Hz, 1H, H-5equ), 3.23 (dd, $J = 16.8$, 7.1 Hz, 1H, H-5ax), 3.53 (d, $J = 11.2$ Hz, 1H, H-3), 3.69–3.80 (m, 1H, H-4), 3.85 (s, 3H, C*H*$_3$O), 5.99 (d, $J = 7.6$ Hz, 1H, H-10), 6.99 (d, $J = 8.4$ Hz, 2H, H-3″), 7.26 (d, $J = 7.8$ Hz, 1H, H-6), 7.34–7.39 (m, 2H), 7.44 (d, $J = 8.7$ Hz, 2H, H-2′), 7.49 (d, $J = 7.8$ Hz, 1H, H-9). ^{13}C NMR (75 MHz, $CDCl_3$) δ 34.6 (C-5), 45.0 (C-4), 55.4 (O*C*H$_3$), 61.2 (C-3), 74.2 (C-2), 89.8 (C-10), 112.6 (*C*N), 113.2 (*C*N), 114.8 (2C, C-3′), 122.2 (C-1′), 125.8 (C-6), 126.0 (C-7), 128.0 (C-9), 129.8 (C-8), 130.0 (2C, C-2′), 139.5 (C-5a), 140.3 (C-9a), 160.7 (C-4′). MS m/z 316 (M^+, 4), 221 (1), 205 (2), 178 (3), 128 (7), 121 (100). HRMS (ESI) m/z calcd for $C_{20}H_{16}N_2O_2$ $(M+Na)^+$: 339.1104. Found: 339.1102.