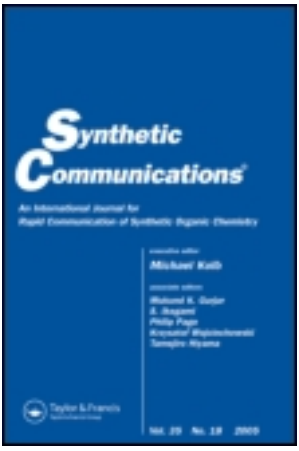

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RAPID AND EFFICIENT SYNTHESIS OF 2-[3-CYANO-4-(2-ARYLIDEN)-5, 5-DIMETHYL-5*H*-FURAN-2-YLIDENE]-MALONONITRILE UNDER FOCUSED MICROWAVE IRRADIATION

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ABSTRACT

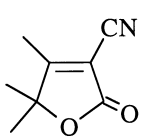
New biological potential furan-2-ylidenemalononitriles (IIIa-j) were synthetised efficiently by one-pot condensation under focused microwave from starting and easy available compounds.

Butenolides are important biologically active compounds.[1] The substitution of oxygen for a carbonyl group by a ylidenemalononitrile group is known to modify biological properties,[2] in particularly benzylidenemalononitriles were studied as cytotoxic agents against tumour and as riot control agents. So we are interested in the furan-2-ylidenemalononitriles (III) derivatives of the butenolid (I) containing a ylidenemalononitrile group.

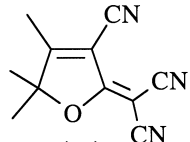
* Corresponding author.

The synthesis and the chemistry of these compounds (III) in spite of their potential biological applications[3] was poorly studied.

Melikian and al[4] has described the synthesis of 2-dicyanomethylen-3-cyano-4,5,5-trimethyl-2,5-dihydrofurane (II), by the reaction of 3-hydroxy-3-methylbutan-2-one with two equivalents of malononitrile in presence of sodium ethoxide. He have described also the condensation with four different aromatic aldehydes into their substituted compounds 2-dicyanomethylen-3-cyano-4,5-dimethyl-4-alkylidene-2,5-dihydrofurans (III).



(I)



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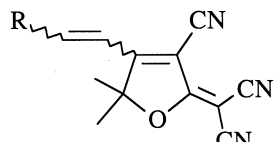
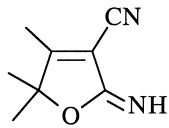


(IIIa-j)

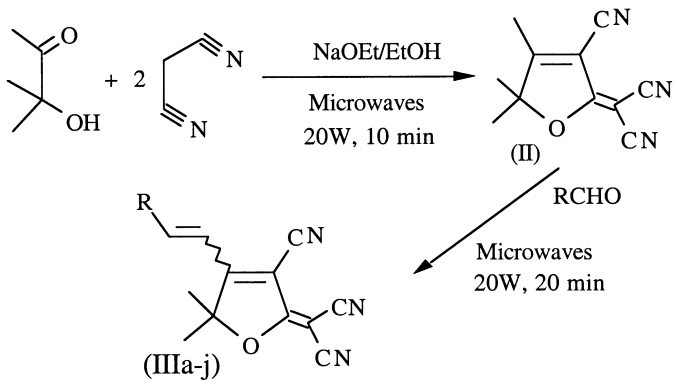
The wide applicability of focused microwave in chemical reaction enhancement is due to high reaction rates with formation of cleaner products and the operational simplicity.[5]

We report herein an efficient and rapid synthesis of dicyanomethylen-dihydrofuran (II) and the one-pot condensation of (II) into their substituted compounds 2-dicyanomethylen-3-cyano-4,5-dimethyl-4-alkylidene-2,5-dihydrofurans (IIIa-j) under focused microwave irradiation.[5] The mixture of 3-hydroxy-3-methyl-butan-2-one (1 eq.), malononitrile[6] (2 eq.) and a solution of sodium ethoxide in a flask was placed in the cavity MES[7] irradiated at 20 W for 10 minutes. Then the corresponding aldehyde (1 eq) was added and the reaction mixture was irradiated again at 20 W for 20 minutes. The overall yields of 2-dicyanomethylen-3-cyano-4,5-dimethyl-4-alkylidene-2,5-dihydrofurans (IIIa-j) were 65–84% according the Scheme I.

The reaction occurs in two successive steps: formation of (II) and condensation of (II) with aldehyde into (IIIa-j). The mechanism of the formation of (II) is not clear because Melikian and al has proposed two different mechanisms[4,7] for the condensation of 3-hydroxy-3-methylbutan-2-one with nitriles in presence of sodium ethoxide.

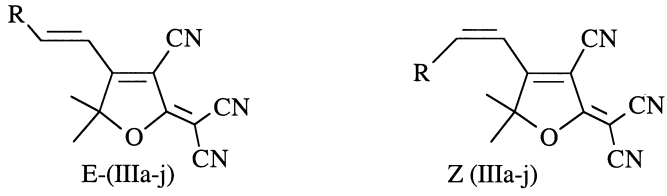


(IV)



Scheme I. One-pot two steps formation of 2-dicyanomethylen-3-cyano-4,5-dimethyl-4-alkylidene-2,5-dihydrofurans (IIIa-j). R = 2-furanyl (a); 2-thiophenyl (b); 3-thiopenyl (c); 3,4-dichlorophenyl (d); s,6-dichlorophenyl (e); 3-nirophenyl (h); E-cinnamyl (i); 3-aminophenyl (j).

We performed the reaction of one molecule of malononitrile with one molecule of 3-hydroxy-3-methylbutan-2-one and we have isolated an iminolactone (IV). This iminolactone (IV) was hydrolysed easily in described lactone (I). The reaction of malononitrile with this iminolactone (IV) conduct to (II). The reaction of imine instead of carbonyl group with nucleophile is well known in particularly in heterocyclic synthesis[9] but the reaction of (IV) is not general and the condensation of the iminolactone (IV) with phenylacetonitrile is not observed perhaps for steric reasons. Although Thorpe reaction type between two molecules of malononitrile yields 2-amino-1,1,3-tricyano-3-propene,[10] this molecule in conditions of reaction with 3-hydroxy-3-methylbutan-2-one does not conduct to (II).[4]



Two isomers of (III) can be obtained in the condensation of (II) with aldehydes. The coupling constant of olefin proton ^{3J}HH between 15 to 17 Hz correspond to a E stereochemistry.

In conclusion, new biologically potential E-furan-2-ylidenemalono-

nitriles (IIIa-j) were conveniently synthesized by one-pot rapid condensations under focused microwave irradiation from starting and easy available compounds.

EXPERIMENTAL

The ^{13}C NMR spectra were recorded with a Bruker AC 250 spectrometer at 62.89 MHz, in $CDCl_3$ using TMS as internal standard (proton decoupled, J_{CP} given in Hz). The IR spectra were recorded as KBr pellets on Perkin Elmer 16 PC FT-IR spectrometer and frequencies are given in cm^{-1}. The mass spectra were obtained on a Nermag Riber R10-10H with a 70 eV electron impact ionization. Uncorrected melting points were determined with a Kofler hot-stage apparatus and are Microwave irradiations were carried out with a focused microwave cavity (cavity EO13 of MES[7]).

2-Imino-4,5,5-trimethyl-2,5-dihydrofurane (IV)

A mixture of 3-hydroxy-3-methylbutan-2-one (3 mmol, 0.306 g), malononitrile (3 mmol, 0.198 g), and sodium ethoxide (0.3 mmol) in ethanol (0.3 mL) was irradiated under focused microwaves 20 W for 8 minutes. The product was chromatographied on silica gel with $EtOH/CH_2Cl_2 = 2/98$. The product obtained after evaporation of the solvent was a yellow oil. Yield 76%. Anal. Found: H 6.82, C 64.01. $C_8H_{10}N_2O$ requires H 6.71 C, 63.98.

NMR ^{1}H ($CDCl_3$) δ_H : 1.50 (6 H, s, $2 \times CH_3$), 2.15 (3 H, s, $C=CCH_3$), 6.75 (1H, s, NH). **NMR ^{13}C ($CDCl_3$)** δ_C : 13.3 (CH_3), 25.2 ($2 \times CH_3$), 89.3 (C-O), 110.7 (–CN), 127. 4, 165.5 (NC–C=C), 170.2 (C=N). **MS** m/z (rel. int.) : 277 (M^+., 96.9), 262 (100), 229 (10.9), 220 (10.9), 185 (17.2), 179 (17.2), 143 (12.5), 115 (10.9), 88 (25), 81 (21.9), 43 (34.4). **IR (film** ν_{max} cm^{-1} : 2230 (CN), 1664 (νC=N), 1074, 980, 894

4,5,5-Trimethyl-2-oxo-2,5-dihydro-furan-3-carbonitrile (I)

The product (IV) was hydrolysed by a solution of hydrochloric acid (3N). After extraction with ether, drying of magnesium sulfate and evaporation of ether, we have obtained a white solid, yield 95%.

Anal.Found: H 6.10, C 63.48. $C_8H_9NO_2$ requires: H 6.0, C 63.57. MP 62°–63°C (lit.[11] 61.5–62.5°C). **NMR ^{1}H ($CDCl_3$)** δ_H : 1.55 (6 H, s, $2 \times CH_3$), 2.32 (3 H, s, $C=CCH_3$). **NMR ^{13}C ($CDCl_3$)** δ_C : 13.91 (CH_3), 24.42

($2 \times CH_3$), 88.37 (C-O), 104.62, 110.74 (–CN), 165.50 (NC–C = C), 184.84 (C = O). **IR (KBr)** ν_{max} cm^{-1} : 2240 (CN), 1764 (C = O), 1738 (C = C), 1654, 1648.

2-Dicyanomethylen-3-cyano-4,5,5-trimethyl-2, 5-dihydrofurane (II)

A mixture of 3-hydroxy-3-methylbutan-2-one (3 mmol, 0.306 g), malononitrile (6 mmol, 0.396 g), and sodium ethoxide (0.45 mmol) in ethanol (0.3 mL) was irradiated under focused microwaves 20 W for 8 minutes. The solid obtained was crystallised in the ethanol (526 mg, 88%).

Yield: 88%, yellow solid, MP 196–198°C.

Anal.Found: H 4.42, C 66.23. $C_{11}H_9N_3O$ requires: H 4.55, C 66.32. **IR (KBr)** ν_{max} cm^{-1} : 3084, 3056, 2992, 2228 (CN), 1620, 1588, 1560, 1432, 1394, 1340, 1210, 1104, 988, 782.

Synthesis of 2-[3-cyano-4-(R-vinyl)-5,5-dimethyl-5*H*-furan-2-ylidene]-malononitriles (III) from α-Cetols and Malononitrile in One-Pot Under Microwave Irradiation

In a typical experiment a mixture of 3-hydroxy-3-methylbutan-2-one (3 mmol), malononitrile (6 mmol, 0.396 g), and a solution of sodium ethoxide (0.4 mmol) in ethanol (0.25 mL) was irradiated by focused microwave at 20 W for 20 minutes. Then furan-2-carboxaldehyde (3 mmol) was added, and the mixture was irradiated by focused microwave at 20 W for another 20 minutes. After cooling, the product was obtained after filtration and then recrystallised in ethanol (1.1 g, 75%).

2-[3-Cyano-4-(2-furan-2-yl-vinyl)-5,5-dimethyl-5*H*-furan-2-ylidene]-malononitrile (IIIa)

Obtained from 3-hydroxy-3-methylbutan-2-one (1 eq.), malononitrile (2 eq.) and furan-2-carboxaldehyde (1 eq.).

Yield 76%, brown solid, MP: 248–249°C (lit.[4] 245–246°C).

Anal.Found: H 4.31, C 69.14. $C_{16}H_{12}N_3O_2$ requires: H 4.35, C 69.06. **NMR ^{1}H ($CDCl_3$)** δ_H : 1.75 (6 **H**, s, 2 CH_3), 6.64–6.66 (1 H, m, **H**arom), 6.85 (1 H, d, $^3J_{HH} = 16.1$ Hz, *trans* HC = C**H**), 6.97 (1 H, m, **H**arom), 7.55 (1 H, d, $^3J_{HH} = 16.1$ Hz, *trans* C**H** = CH), 7.69 (1 H, s, **H**arom). **NMR ^{13}C ($CDCl_3$)** δ_C : 26.4 (2 CH_3), 97.7 (–$OC(CH_3)_2$), 98.3 (NC–C = C), 110.7

(–CN), 111.1 (–CN), 111.9 (–CN), 112.2, 114.3, 120.7, 132.2, 148.2, 150.9, 173.5 (NC–C = C), 176. **MS** m/z (rel. int.) : 277 ($M^{+\cdot}$, 96.9), 262 (100), 229 (10.9), 220 (10.9), 185 (17.2), 179 (172), 143 (12.5), 115 (10.9), 88 (25), 81 (21.9), 43 (34.4). **IR (KBr)** ν_{max} cm^{-1} : 2234 (CN), 1612, 1586, 1568, 1460, 1378, 1292, 772. **Beilstein** : 7384244.

2-[3-Cyano-4-(2-thiophen-2-yl-vinyl)-5,5-dimethyl-5*H*-furan-2-ylidene]-malononitrile (IIIb)

Obtained from 3-hydroxy-3-methylbutan-2-one (1 eq.), malononitrile (2 eq.) and thiophene-2-carboxaldehyde (1 eq.).

Yield 80%, brown solid, MP: 253–255°C.

Anal.Found: H 4.05, C 65.13. $C_{16}H_{12}N_3OS$ requires: H 4.11, C 65.29 **NMR ^{1}H ($CDCl_3$)** δ_H : 1.78 (6 H, s, 2 C**H**$_3$), 6.74 (1 H, d, $^3J_{HH} = 16.1$ Hz, C**H** = CH), 7.18–7.22 (1 H, m, **H**arom), 7.51 (1 H, d, **H**arom), 7.68 (1 H, d, **H**arom). 7.85 (1 H, d, $^3J_{HH} = 16.1$ Hz, CH = C**H**). **NMR ^{13}C ($CDCl_3$)** δ_C : 26.5 (2 CH_3), 97.6 (–O**C**(CH_3)$_2$), 98.7 (NC–**C** =), 110.5 (N**C**–), 111.1 (–**C**N), 111.6 (–**C**N), 113.6, 129.6, 133.5, 135, 139.7, 140.1, 173.5, 176.5,.5 **MS** EI m/z (rel. int %) : 293 M^+., 24.5), 292 (74.5), 277 (25.5), 276 (66), 266 (4.7), 254 (12), 247 (16), 203(15), 198 (15), 184 (18), 166 (19), 161 (19), 140 (26), 98 (55), 44 (100). **IR (KBr)** n_{max} cm^{-1} : 2228 (CN), 1576, 1546, 1458, 1418, 1396, 1382, 1352, 1292, 1112, 960, 728.

2-[3-Cyano-4-(2-thiophen-3-yl-vinyl)-5,5-dimethyl-5*H*-furan-2-ylidene]-malononitrile (IIIc)

Obtained from 3-hydroxy-3-methylbutan-2-one (1 eq.), malononitrile (2 eq.) and thiophene-3-carboxaldehyde (1 eq.).

Yield 89%, brown solid, MP: 242–243°C.

Anal.Found: H 4.23, C 65.34. $C_{16}H_{12}N_3OS$ requires: H 4.11, C 65.29 **NMR ^{1}H ($CDCl_3$)** δ_H : 1.79 (6 H, s, 2 C**H**$_3$), 6.84 (1 H, d, $^3J_{HH} = 16.3$ Hz, HC = CH*trans*), 7.47–7.48 (2 H, m, **H**arom), 7.68 (1 H, d, $^3J_{HH} = 16.3$ Hz, C**H** = CH), 7.80 (1 H, s, **H**arom). **NMR ^{13}C ($CDCl_3$)** δ_C : 26.6 (2 CH_3), 97.7 (–O**C**(CH_3)$_2$), 100.5, 101.3, 110.6 (NC), 111 (NC–), 111.8 (CN), 114.8, 124.9, 128.6, 133, 137.8, 140.6, 174 (NC–C = **C**), 175.2. **MS** EI m/z (rel. int %) : 293 (M^+, 43), 292 (100), 277 (13), 276 (20), 266 (4.5), 203 (14), 186 (33), 182 (31), 164 (11), 87 (25), 85 (35). **IR (KBr)** ν_{max} cm^{-1} : 2222 (CN), 1570, 1546, 1498, 1374, 1292, 1110, 800, 664.

2-[3-Cyano-4-(3,4-dichloro-styryl)-5,5-dimethyl-5*H*-furan-2-ylidene]-malononitrile (IIId)

Obtained from 3-hydroxy-3-methylbutan-2-one (1 eq.), malononitrile (2 eq.) and 3,4-dichlorobenzaldehyde (1 eq.).

Yield 67 %, orange solid, MP: 253–258°C.

Anal.Found: H 3.01, C 60.43. $C18H_{11}Cl_2N_3O$ requires: H 3.11, C 60.69 **NMR ^{1}H (DMSO-d$_6$)** δ_H : 1.79 (6 H, s, 2 C**H**$_3$), 7.33 (1 H, d, $^3J_{HH} = 16.6$ Hz, HC = C**H**), 7.76 (1 H, d, J = 8.5 Hz, **H**arom), 7.83 (1 H, d, $J = 16.6$ Hz, C**H** = CH), 7.92 (1 H, d, d, $^3J_{HH} = 8.5$ Hz, $^4J_{HH} = 2$ Hz, **H**arom), 8.29 (1 H, d, $^4J_{HH} = 2$ Hz, **H**arom). **NMR ^{13}C (DMSO-d$_6$)** δ_C : 25.1 (2**C**H$_3$), 99.6 (–O**C**(CH$_3$)$_2$), 101.0, 110.6 (–**C**N), 111.8 (–**C**N), 112.6 (–**C**N), 117.5, 129.2, 131.0, 131.3, 132.1, 134.2, 135.1, 144.1, 174.4, 177.1. **MS** EI m/z (rel. int %) : 359 (6.4), 357 (55.3), 355 ($M^{+\cdot}$, 100), 340 (32), 339 (43), 263 (45), 258 (51), 186 (28), 180 (38), 148 (60), 91 (28), 55 (32). **IR (KBr)** ν_{max} cm^{-1} : 2226 (CN), 1618, 1574, 1552, 1468, 1400, 1380, 1210, 1100, 1028, 832, 650.

2-[3-Cyano-4-(2,6-dichloro-styryl)-5,5-dimethyl-5*H*-furan-2-ylidene]-malononitrile (IIIe)

Obtained from 3-hydroxy-3-methylbutan-2-one (1 eq.), malononitrile (2 eq.) and 2,6-dichlorobenzaldehyde (1 eq.).

Yield 66%, yellow solid, MP: 259–260°C.

Anal.Found: H 3.08, C 60.55. $C_{18}H_{11}Cl_2N_3O$ requires: H 3.11, C 60.69 **NMR ^{1}H (CDCl$_3$)** δ_H : 1.85 (6 H, s, 2 CH_3), 7.37 (1 H, d, $^3J_{HH} = 16.9$ Hz, HC = C**H**), 7.44–7.47 (3 H, m, **H**arom), 7.76 (1 H, d, $^3J_{HH} = 16.9$ Hz, C**H** = CH). **NMR ^{13}C (CDCl$_3$)** δ_C : 26.5 (2 CH_3), 98.1 (O**C**(CH$_3$)$_2$), 102.7, 109.6 (**C**N), 110.5 (**C**N), 111.4 (**C**N), 123.3, 129.5, 130.9, 131.7, 135.6, 140.7, 173.4, 175.2. **MS** EI m/z (rel. int %) : 359 (8.6), 357 (45), 355 ($M^{+\cdot}$, 100), 340 (52), 338 (62), 320 (26), 318 (60), 263 (35), 258 (41), 184 (41), 180 (45), 170 (41), 159 (48), 150 (36). 135 (31), 113 (21), 99 (36). **IR (KBr)** ν_{max} cm^{-1} : 2230 (CN), 1588, 1574, 1542, 1376, 1336, 1108, 794.

2-[3-Cyano-4-(3-hydroxy-4-methoxy-styryl)-5,5-dimethyl-5*H*-furan-2-ylidene]-malononitrile (IIIf)

Obtained from 3-hydroxy-3-methylbutan-2-one (1 eq.), malononitrile (2 eq.) and 3-hydroxy-4-methoxybenzaldehyde (1 eq.).

Yield 75%, brown solid, MP > 265°C.

Anal.Found: H 4.63, C 68.61. $C_{19}H_{15}N_3O_3$ requires: H 4.54, C 68.46 **NMR ^{1}H (DMSO-d_6)** δ_H : 1.77 (6 H, s, 2 C**H**$_3$), 3.85 (3 H, OC**H**$_3$), 6.89 (1 H, d, **H**arom), 7.03 (1 H, d, $^3J_{HH} = 16.3$ Hz, HC = C**H**), 7.41 (1 H, d, **H**arom), 7.48 (1 H, s, **H**arom), 7.88 (1 H, d, $^3J_{HH} = 16.3$ Hz, C**H** = CH). **NMR^{13}C (DMSO-d_6)** δ_C : 25.4 (2 **C**H$_3$), 54.9, 55.9 (O**C**H$_3$), 96.3 (O**C**(CH$_3$)$_2$), 99, 111.3, 111.9, 112.2, 112.6, 113, 116.2, 125.6, 126.2, 148.3, 148.9, 152.2, 175.9, 177.3, **MS** EI m/z (rel. int %) : 334 (16), 333 (M^+., 74), 318 (4.7), 317 (8.4), 288 (5.6), 185 (58), 181 (96), 152 (26), 87 (50), 85 (100). **IR (KBr)** ν_{max} cm^{-1} : 3330–3500 (OH), 2246 (CN), 1584, 1548, 1472, 1444, 1418, 1296, 1258, 1202, 1022.

2-[3-Cyano-4-(2-hydroxy-styryl)-5,5-dimethyl-5*H*-furan-2-ylidene]-malononitrile (IIIg)

Obtained from 3-hydroxy-3-methylbutan-2-one (1 eq.), malononitrile (2 eq.) and 3-hydroxybenzaldehyde (1 eq.).

Yield 70 %, brown solid, MP > 265°C.

Anal.Found: H 4.47, C 71.09. $C_{18}H_{13}N_3O_2$ requires: H 4.32, C 71.28, **NMR ^{1}H (DMSO-D$_6$)** δ_H : 1.75 (6 H, s, 2 C**H**$_3$), 2.49 (1 H, s, OH), 6.88–6.96 (2 H, m, **H**arom), 7.33–7.36 (1 H, m, **H**arom), 7.41 (1 H, d, $^3J_{HH} = 16.5$ Hz, HC = CH), 7.83 (1 H, m, **H**arom), 8.16 (1 H, d, $^3J_{HH} = 16.5$ Hz, C**H** = CH). **NMR ^{13}C (DMSO-d_6)** δ_C: 25.2 (2 CH$_3$), 53.8, 97.5, (OC(CH$_3$)$_2$), 99.2, 111.3, 112.1, 112.9, 115.2, 116.6, 119.9, 121.3, 130.6, 134.2, 144, 158.5, 176.3, 177.4. **MS** EI m/z (rel. int %) : 303 (M^+.,23), 302 (14), 220 (22), 215 (24), 186 (99), 185 (63), 182 (66), 106 (49), 92 (74), 78 (44), 65 (74), 59 (100). **IR (KBr)** ν_{max} cm^{-1} : 3150–3300 (OH), 2238 (CN), 2222 (CN), 1730, 1600, 1570, 1536, 1502, 1382, 1264, 1106, 976, 758.

2-[3-Cyano-5,5-dimethyl-4-(3-nitro-styryl)-5*H*-furan-2-ylidene]-malononitrile (IIIh)

Obtained from 3-hydroxy-3-methylbutan-2-one (1 eq.), malononitrile (2 eq.) and 3-nitro-benzaldehyde (1 eq.).

Yield: 73%, yellow solid, MP > 265°C.

Anal.Found: H 3.70, C 64.98. $C_{18}H_{12}N_4O_3$ requires: H 3.64, C 65.06. **NMR ^{1}H (DMSO-d_6)** δ_H : 1.83 (6 H, s, 2 C**H**$_3$), 7.41 (1 H, d, $^3J_{HH} = 16.6$ Hz, HC = C**H**), 7.77 (1 H, m, **H**arom), 7.99 (1 H, d, $^3J_{HH} = 16.6$ Hz, C**H** = CH), 8.31–8.39 (2 H, m, **H**arom), 8.78 (1 H, s, **H**arom). **NMR ^{13}C (DMSO-d_6)** δ_C : 25.1 (2 CH$_3$), 55.3, 99.7, 101.6, 110.5 (CN), 111.7 (CN), 112.6 (CN), 118.0,

124.3, 125.9, 130.7, 134.5, 136.1, 144.3, 148.4, 174.4, 176.9. **MS** EI m/z (rel. int%) : 333 (26), 332 ($M^{+\cdot}$, 89), 317 (37), 316 (100), 236 (40), 185 (20), 181 (37), 151 (37), 135 (23), 116 (37), 106 (77), 92 (66), 85 (40), 78 (49), **IR (KBr)** ν_{max} cm^{-1} : 2232 (CN), 2212 (CN), 1582, 1546, 1530, 1396, 1384, 1350, 1110, 860, 676.

2-[3-Cyano-4-(4-phenyl-buta-1,3-dienyl)-5,5-dimethyl-5*H*-furan-2-ylidene]-malononitrile (IIIi)

Obtained from 3-hydroxy-3-methylbutan-2-one (1 eq.), malononitrile (2 eq.) and *trans*-cinnamaldehyde (1 eq.).

Yield 81%, brown solid, MP : 221–223°C.

Anal.Found: H 4.83, C 76.72. $C_{20}H_{15}N_3O$ requires: H 4.82, C 76.66.

NMR ^{1}H (CDCl$_3$) δ_H : 1.75 (6 H, s, 2 C**H**$_3$), 6.57 (1 H, d, $^3J_{HH} = 15.5$ Hz, HC = C**H**), 7.00–7.15 (2 H, m), 7.19 (1 H, d, $^3J_{HH} = 15.5$ Hz, C**H** = CH), 7.35–7.75 (5 H, m, **H**arom). **NMR ^{13}C (CDCl$_3$)** δ_C : 26.5 (2 CH_3), 97.6, 98.8, 110.6, 115.1, 118.4, 127.4, 128.3, 128.6, 129.2, 129.3, 129.7, 131.0, 135.2, 146.5, 148.1, 173.7. **MS** EI m/z (rel. int %) : 314 (11), 313 ($M^{+\cdot}$, 30) 298 (8), 286 (19), 275 (23), 270 (36), 196 (29), 192 (33), 180 (47), 116 (52), 106 (30), 92 (100), 78 (52). **IR (KBr)** ν_{max} cm^{-1} : 2228 (CN), 1670, 1560, 1522, 1396, 1380, 1340, 1286, 1168, 1106, 754, 684.

2-[4-(3-Amino-styryl)-3-cyano-5,5-dimethyl-5*H*-furan-2-ylidene]-malononitrile (IIIj)

Obtained from 3-hydroxy-3-methylbutan-2-one (1 eq.), malononitrile (2 eq.) and 3-amino-benzaldehyde (1 eq.).

Yield 78%, brown solid, MP > 265°C.

Anal.Found: H 4.60, C 71.75. $C_{18}H_{14}N_4O$ requires: H 4.67, C 71.51, **NMR ^{1}H (DMSO-d$_6$)** δ_H : 1.72 (6 H, s, 2 CH_3), 6.65 (2 H, d, $^3J_{HH} = 8.5$ Hz, **H**arom), 6.80 (1 H, d, $^3J_{HH} = 16$ Hz, HC = C**H**), 7.66 (2 H, d, $^3J_{HH} = 8.5$ Hz, **H**arom), 7.86 (1 H, d, $^3J_{HH} = 16$ Hz, C**H** = CH). **NMR ^{13}C (DMSO-d$_6$)** δ_C : 25.7 (2 CH_3), 91.5, 98.2, 107.7, 112.2, (CN), 112.8 (CN), 113.6 (CN), 114.3, 122.1, 133.7, 150.0, 155.4, 175.7, 177.5. **MS** EI m/z (rel. int %) : 302 ($M^{+\cdot}$,4.7), 280 (3), 209 (20), 204 (22), 186 (11), 182 (11), 106 (19), 92 (20), 87 (44), 85 (67), 65 (61), 59 (100). **IR (KBr)** ν_{max} cm^{-1} : 3474 (–NH_2), 3364 (–NH_2), 2228 (CN), 1640, 1590, 1564, 1552, 1520, 1496, 1458, 1386, 1266, 1168, 1110, 870, 698, 654.

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