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Novel combinatorial approach to the synthesis of dihydropyridine (quinoline) based merocyanine dyes

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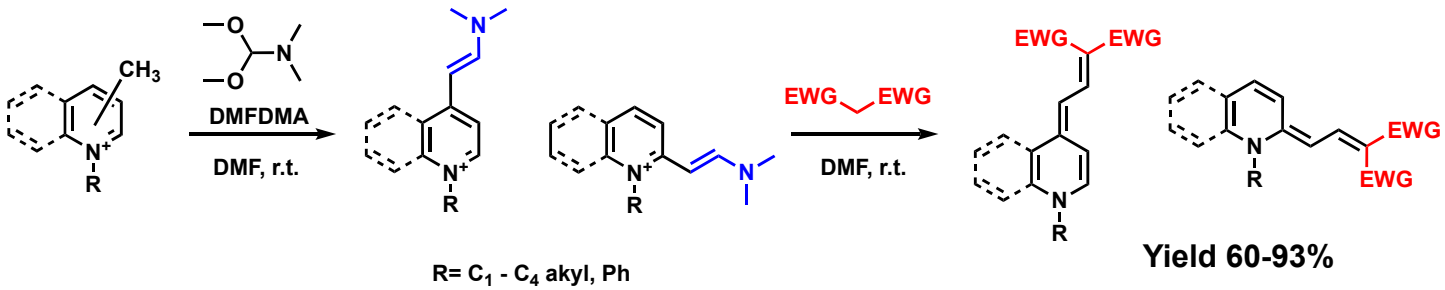
Abstract

A novel, efficient, two-step approach to the synthesis of merocyanine dyes was developed. Initially, N-substituted picolinium salts were formylated with *N,N*-dimethylformamide dimethyl acetal to produce enamine derivatives. Then a series of merocyanine dyes were obtained by the high-yield reaction between the enamines and various active methylene compounds. The described reactions, carried out in mild conditions, provide access to the synthesis of a wide range of dyes. This innovative method enabled the synthesis of a number of new merocyanine dyes and increased the yields of the known compounds.



Keywords: Merocyanines; azinium salts; enamines; protonation

Introduction

Merocyanines are important class of dyes. Both theoretical studies and practical applications of merocyanines are well illustrated in reviews.[1-5] In spite of significant attention to merocyanine dyes, based on azoheterocycles, such as pyridine and quinoline, these compounds have not been studied as well as other classes. The most common structure of merocyanine dyes includes an electron-withdrawing group linked to a cyclic electron-donor fragment via two methine groups. The maJor approach to the synthesis of these merocyanine systems involves the interaction between a methyl group of N-alkylazinium salts and the acetaldehyde derivatives $(EWG)_2CHCHO$ and their analogs.[6-17] The disubstituted acetaldehyde derivatives can be obtained by the formylation of methylene active compounds. According to this synthetic protocol, the selected heterocyclic substrate generally reacts with a set of methylene active compounds, each of which must be previously formylated. Following this synthetic protocol we synthesized a series of dyes[18,19] utilizing 2- and 4-picoline as substrates. The products were purified by column chromatography. Despite the fact that this approach is quite simple and provides good yields, this method requires time-consuming purification techniques, making it inefficient for the synthesis of large dye libraries. An interesting variation of this method is formylation of an active methylene compound by DMF/Ac_2O mixture with heating and condensation with azinium salt (2 examples in 54 – 60% yield) without isolation of intermediate.[20] Thus, there are gaps in the published data for pyridine- or quinoline-containing merocyanine dyes.

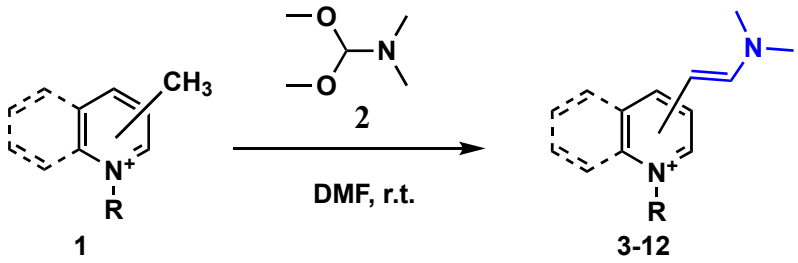
Another synthetic approach appears to be more practical. A methyl group from an azinium salt is formylated to produce (N-phenyl-N-acetyl)enamines.[21-24] Next, the enamine derivatives react with active methylene compounds to form cyanine cationic dyes. However, this approach is less common for the synthesis of merocyanine dyes because enamine formation requires extreme conditions and the yields of the reaction are small.

In this paper we describe a novel and facile approach to the synthesis of merocyanine dyes. The reactions are based on mild formylation of a methyl group in the heterocyclic substrate by *N,N*-dimethylformamide dimethyl acetal (DMFDMA). This leads to the formation of enamine derivatives with high yields. The obtained enamines can be reacted with a series of readily accessible active methylene compounds, providing the capacity to quickly create compound libraries containing a wide range of desired merocyanine dyes.

Results and Discussion

As starting materials we chose quaternary azinium salts **1** (R C_1 – C_4 alkyl, Ph) prepared from picolines and methyl quinolines according to previously described procedures.[25-28]

In the first step, the condensation reaction between the salts **1** and DMFDMA (**2**) was carried out in mild conditions in DMF at room temperature and without any catalyst. This resulted in the formation of enamines **3-12** with high yields (Scheme 1, Table 1, Figure 1).



Scheme 1. Synthesis of enamine**s 3-12.**

Table 1. Enamines **3-12**

Entry	Product	R	Ring structure	Yield, (*) %
1	**3**	Me	lepidine	95
2	**4**	Me	4-picoline	98 (34) [29,30]
3	**5**	Et	4-picoline	99 (78) [29]
4	**6**	*n*-Pr	4-picoline	96
5	**7**	*n*-Bu	4-picoline	97
6	**8**	Ph	4-picoline	93
7	**9**	Me	quinaldine	93 (60) [31]
8	**10**	Me	2-picoline	98 (82) [29]
9	**11**	Et	2-picoline	98 (62) [29]
10	**12**	*n*-Pr	2-picoline	96

***** *the yield reported in the literature*

In the second step, enamines **3-12** reacted in DMF with a series of commercially available methylene active compounds **13-18** (Figure 2) to form merocyanine dyes **19-45**. This approach can be efficiently applied to the synthesis of dyes **19-45** based on the enamine derivatives of 4-methylazines (Scheme 2, Table 2), as well as the 2-methylazines (Scheme 3, Table 3).

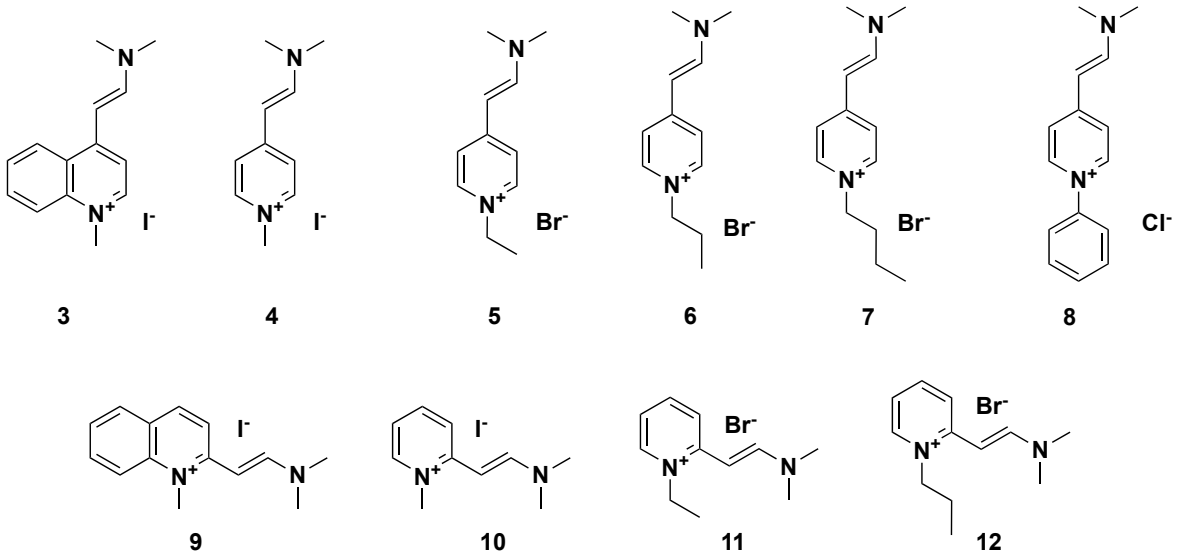


Figure 1. Range of enamines **3-12.**

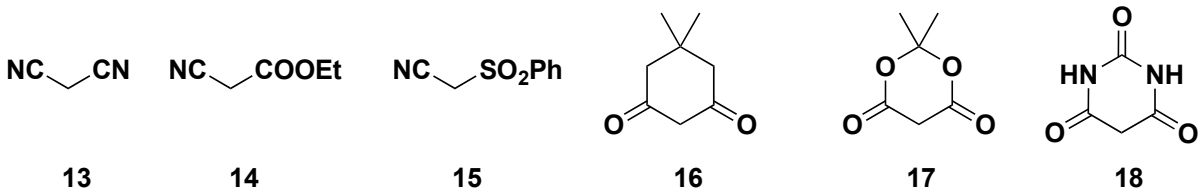
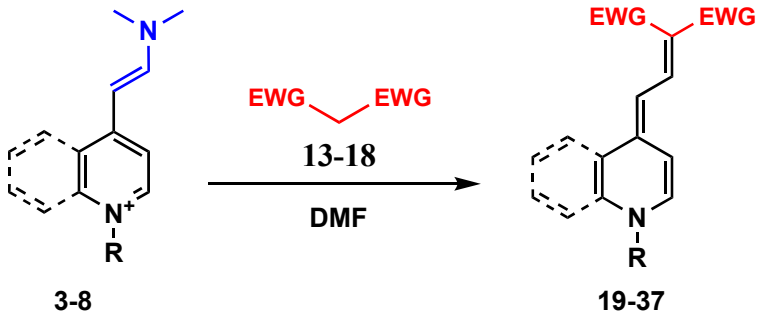
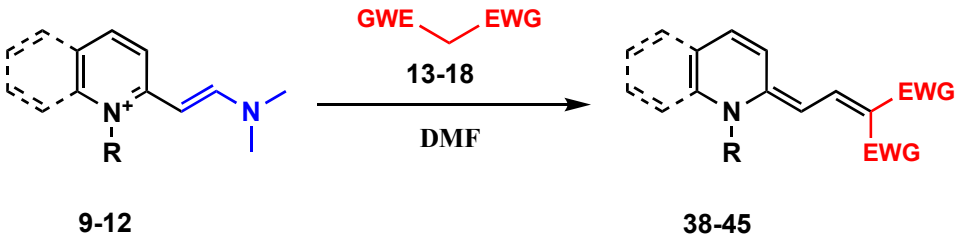


Figure 2. Range of active methylene compounds **13-18.**

For dye syntheses based on methylene components **13**, **17**, **18** the reaction mixture was simply kept at room temperature for 12 h. For the other methylene components used, the best results were achieved by heating reaction mixtures at 60 °C for 5 hours in the presence of sodium acetate. In both cases the products were isolated by diluting reaction mixtures with water followed by filtration after 12 hours (see the Supporting Information for general procedure). The resulting dyes **19-45** were obtained in moderate to high yields. Unlike the previously described method,[18, 19] no further purification was needed.

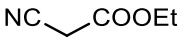
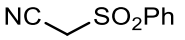
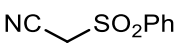
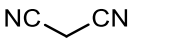
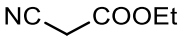
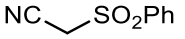
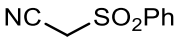
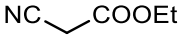


Scheme 2. Synthesis the dyes **19-37.**



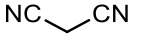
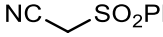
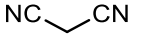
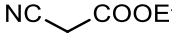
Scheme 3. Synthesis of the dyes **38-45.**

Table 2. Synthesis of merocyanine dyes **19-37**

Entry	Product	Ring structure	R	EWG	Yield, (*) %
1	**19**	lepidine	Me		75
2	**20**	lepidine	Me		86
3	**21**	lepidine	Me	Meldrum's acid	93 (55) [32]
4	**22**	4-picoline	Me		66
5	**23**	4-picoline	Me	Meldrum's acid	62
6	**24**	4-picoline	Et		57 (23) [33]
7	**25**	4-picoline	Et		48 (53) [33]
8	**26**	4-picoline	Et		66
9	**27**	4-picoline	Et	dimedone	47
10	**28**	4-picoline	Et	Meldrum's acid	66
11	**29**	4-picoline	Et	barbituric acid	65
12	**30**	4-picoline	Pr	Meldrum's acid	74
13	**31**	4-picoline	Bu		73
14	**32**	4-picoline	Bu	dimedone	76
15	**33**	4-picoline	Bu	Meldrum's acid	85
16	**34**	4-picoline	Ph		91 (62) [34]
17	**35**	4-picoline	Ph	dimedone	79
18	**36**	4-picoline	Ph	Meldrum's acid	78
19	**37**	4-picoline	Ph	barbituric acid	89

***** *the yield reported in the literature*

Table 3. Synthesis of merocyanine dyes **38-45**

Entry	Product	Ring structure	R	EWG	Yield, (*) %
20	**38**	quinaldine	Me	dimedone	91
21	**39**	2-picoline	Me	barbituric acid	68 (81) [35]
22	**40**	2-picoline	Et		75
23	**41**	2-picoline	Et		70
24	**42**	2-picoline	Et	barbituric acid	87 (52) [35]
25	**43**	2-picoline	Pr		58
26	**44**	2-picoline	Pr		63
27	**45**	2-picoline	Pr	barbituric acid	77

***** *the yield reported in the literature*

The proposed two-step approach will significantly facilitate the practical production of a wide-range merocyanine dyes based on methyl-substituted quaternary azinium salts. For the synthesis of the known merocyanines **21** and **34,** a 30-40% yield increase was achieved in comparison to previously reported methods.[32-35] All other dyes were synthesized by us for the first time.

UV/Vis absorption spectra of all the synthesized dyes **19-45** were recorded in acetone solution. The combined data for the maximum absorption wavelength and the extinction coefficient for each compound are shown in Table 4. Analysis of the UV/Vis absorption spectra of the merocyanines **24-29** with various electron withdrawing groups (Figure 2) shows that the variation of an acceptor group smoothly shifts the absorption maximum within 25 nm.

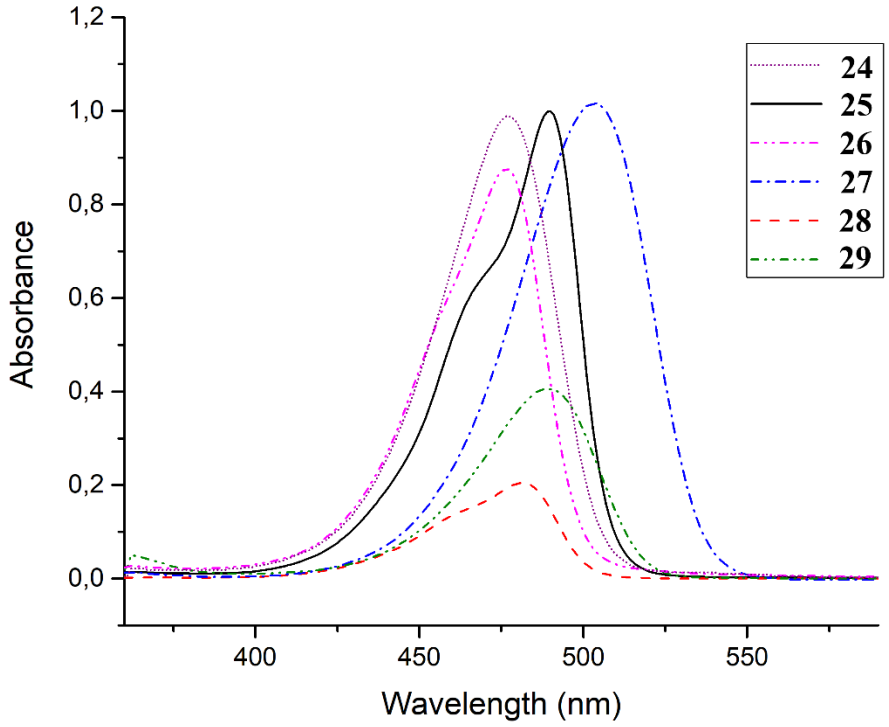


Figure 3. UV/Vis spectra of the merocyanines **24-29**, arranged according to substituent types.

Dissolving the synthesized dyes in trifluoroacetic acids had interesting results. We previously showed[18] that in trifluoroacetic acid the α-carbon of the polyene chain in dye **25** becomes protonated which, according to ^{1}H NMR data, disrupts the conJugation. This is fully in line with the dye structure, approaching the cyanine limit. This process also occurs in the case of protonation of compound **25** (Figure 4). On the other hand, the protonation of dye **39** occurs without affecting the polyene system. The oxygen atom in the barbituric acid residue is apparently involved in the protonation. This possibly indicates that compound **39** is strongly polarized and that its structure is close to that of a betaine. The X-ray data for **39** (see the Supporting Information for X-ray data) (Figure 5) supports this hypothesis: the values of the determined bond lengths between C(9) – C(8) 1.436A, C(8) – C(7) 1.358A and C(7) – C(4) 1.422A demonstrate that single and double bonds are altered in this molecule, which is consistent with its betaine nature.

Table 4. Absorption spectra of the merocyanine dyes in acetone

Compound	λ_{max} [nm]	$\varepsilon_{max}\times10^{-4}$ [$M^{-1}\times cm^{-1}$]
19	542	7.95
20	531	6.54
21	542	7.29
22	474	2.71
23	474	6.54
24	479	9.88
25	488	10.00
26	475	8.73
27	501	10.24
28	475	1.93
29	487	4.03
30	476	8.24
31	476	7.99
32	507	3.65
33	476	7.90
34	503	8.12
35	523	4.92
36	495	9.11
37	511	3.39
38	574	6.30
39	457	2.67
40	450	6.30
41	448	5.00
42	464	2.37
43	452	3.42
44	456	4.11
45	463	9.43

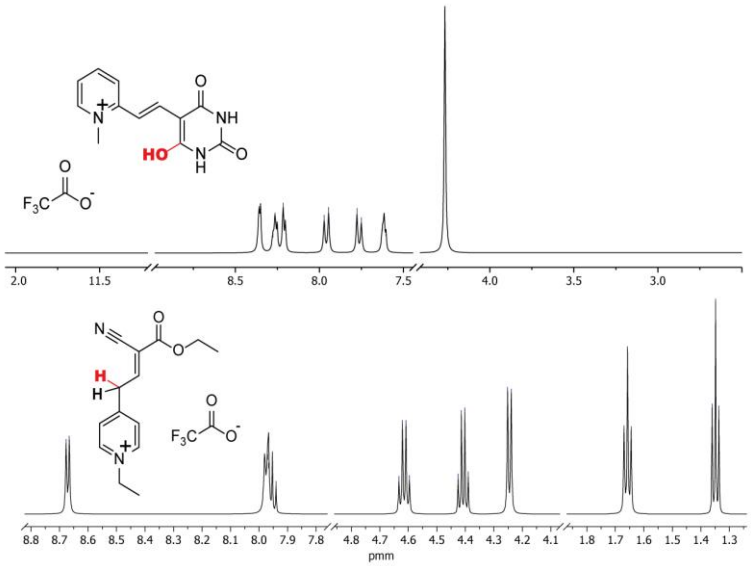


Figure 4. Comparison of ^{1}H NMR spectra for compounds **39** and **25**, protonated by trifluoroacetic acid.

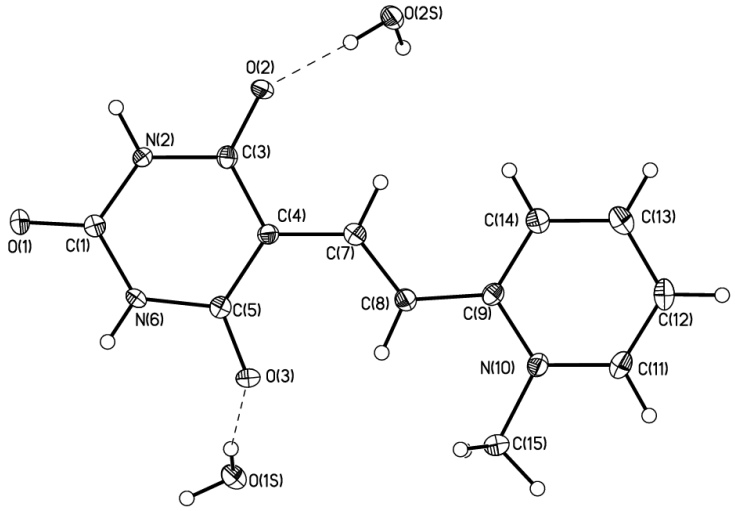


Figure 5. General view of **39** in a crystal, non-hydrogen atoms are represented by probability ellipsoids of atomic displacements (p=50%).

Conclusions

In conclusion, we have reported a new facile approach to the combinatorial synthesis of merocyanine dyes based on readily available starting materials. This promising method for the synthesis of merocyanine dye libraries does not require additional purification of the final products.

Experimental Section

General. ^{1}H NMR spectra were recorded on a Bruker AVANCE 600 spectrometer (600.13 MHz). Chemical shifts are given in ppm relative to $SiMe_4$. The IR spectra recorded on a "Bruker Alpha" in KBr pellets. Melting points were measured on Kofler bench. UV spectra were recorded on a Shimadzu UV-2600 instrument in quartz cells with a light pathlength of 1 cm with the concentration of the substance C_M 10^{-5} [M] (solvent acetone). Reactions were monitored by thin layer chromatography (TLC).

Synthesis of salts 3-12. General Experimental Procedure.
Dimethylformamide dimethyl acetal (5.36 g, 45.0 mmol) was added to a solution of the corresponding picolinium or quinolinium salt **1** (30.0 mmol) in DMF (25 mL), the resulting mixture was stirred at rt for 16 h. The solution was evaporated to near dryness in vacuo. The crude product was purified by precipitation from boiling methanol–diethyl ether to obtain a grey solid **3-12** which was filtered off, washed with diethyl ether and dried.
Synthesis of dyes 23, 24, 28, 29, 30, 33, 36, 37, 39, 40, 42, 43, 45. General Experimental Procedure.
Compounds **13, 17, 18** (1.36 mmol) were added to the solution of the corresponding salts **3-12** (1.46 mmol) in DMF (5-6 mL), the resulting mixture was stirred at rt for 12 h. The reaction mixture was diluted with water (50 mL) and left to stand at room temperature for 12 h. The precipitated product was filtered off, washed with water and air-dried. The products were obtained in good yields without further purification.
Synthesis of dyes 19, 20, 21, 22, 25, 26, 27, 31, 32, 34, 35, 38 41, 44. General Experimental Procedure.
Compounds **14, 15, 16** (1.36 mmol) and NaOAc (1.36 mmol) were added to the solution of the corresponding salts **3-12** (1.46 mmol) in DMF (5-6 mL), the resulting mixture was heated at 60 °C for 5 h and then cooled to rt. The reaction mixture was diluted with water (50 mL). The resulting precipitate was filtered off, washed with water and air-dried. The products were obtained in good yields without further purification.
4-(2-(Dimethylamino)vinyl)-1-methylquinolin-1-ium iodide (3).: Yield**:** 95% *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.66 (d, *J* 8.4 Hz, 1H), 8.56 (d, *J* 12.3 Hz, 1H), 8.41 (d, *J* 7.3 Hz, 1H), 8.04 – 7.99 (m, 2H), 7.75 – 7.71 (m, 1H), 7.62 (d, *J* 7.3 Hz, 1H), 6.27 (d, *J* 12.3 Hz, 1H), 4.14 (s, 3H), 3.44 (s, 3H), 3.28 (s, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 154.6, 153.4, 142.4, 137.9, 132.8, 125.6, 125.2, 122.3, 117.2, 105.8, 90.0, 45.1, 41.2, 37.3. *Anal. calcd* for $C_{14}H_{17}IN_2$ (340,21): C, 49.43; H, 5.04; N, 8.23 Found: C, 49.27; H, 4.93; N, 7.99.
4-(2-(Dimethylamine)vinyl)-1-methylpyridin-1-ium iodide (4). Yield: 98% *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.12 – 8.00 (m, 3H), 7.67 – 7.02 (s, 2H), 5.31 (d, *J* 13.0 Hz, 1H), 3.88 (s, 3H), 3.20 (s, 3H), 2.93 (s, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 155.0, 152.2, 141.7, 127.9, 92.1, 44.7, 44.5, 37.0. *Anal. calcd* for $C_{10}H_{15}IN_2$ (290,15): C, 41.40; H, 5.21; N, 9.66 Found: C, 41.18; H, 5.02; N, 9.51; Spectral data in according with previously described.[29,30]
4-(2-(Dimethylamino)vinyl)-1-ethylpyridin-1-ium bromide (5). Yield: 99% *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.19 (d, *J* 6.9 Hz, 2H), 8.15 (d, *J* 13.0 Hz, 1H), 7.67 – 7.10 (m, 2H), 5.31 (d, *J* 13.0 Hz, 1H), 4.16 (q, *J* 7.4 Hz, 2H), 3.21 (s, 3H), 2.94 (s, 3H), 1.38 (t, *J* 7.4 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 155.2, 152.4, 140.6, 92.2, 52.5, 44.6, 36.9, 34.2, 16.0. *Anal. calcd* for $C_{11}H_{17}BrN_2$ (257,18): C, 51.37; H, 6.66; N, 10.89; Found: C, 51.12; H, 6.49; N, 10.63; Spectral data in according with previously described.[29]
4-**(2-(Dimethylamino)vinyl)-1-propylpyridin-1-ium bromide (6).** Yield*:* 96% *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.32 – 8.23 (m, 3H), 7.47 (s, 2H), 5.41 (d, *J* 12.9 Hz, 1H), 4.19 (t, *J* 7.3 Hz, 2H), 3.29 (s, 3H), 3.01 (s, 3H), 1.85 (q, *J* 7.3 Hz, 2H), 0.90 (t, *J* 7.3 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 154.7, 152.0, 140.3, 115.5, 91.7, 57.8, 44.1, 36.4, 23.1, 9.7. *Anal. calcd* for $C_{12}H_{19}BrN_2$ (271,02): C, 53.15; H, 7.06; N, 10.34 Found: C, 52.92; H, 6.98; N, 9.96;
1-butyl-4-(2-(dimethylamino)vinyl)pyridin-1-ium bromide (7): Yield*:* 97% *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.16 (d, *J* 7.0 Hz, 2H), 8.11 (d, *J* 12.9 Hz, 1H), 7.35 (s, 1H), 5.31 (d, *J* 12.9 Hz, 1H), 4.11 (t, *J* 7.3 Hz, 2H), 3.20 (s,

3H), 2.94 (s, 3H), 1.74 (p, *J* 7.4 Hz, 2H), 1.26 (hept, *J* 7.4 Hz, 2H), 0.89 (t, *J* 7.4 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 155.2, 152.5, 140.9, 92.2, 56.9, 44.7, 36.9, 34.2, 32.2, 18.7, 13.3. *Anal. calcd* for $C_{13}H_{21}BrN_2$ (285,23): C, 54.74; H, 7.42; N, 9.82; Found: C, 54.5; H, 7.28; N, 9.53.

4-(2-(dimethylamino)vinyl)-1-phenylpyridin-1-ium chloride (8): Yield: 93% *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.59 (d, *J* 12.8 Hz, 1H), 8.44 (d, *J* 7.4 Hz, 2H), 8.03 – 7.83 (m, 1H), 7.78 (d, *J* 7.8 Hz, 2H), 7.68 (t, *J* 7.8 Hz, 2H), 7.61 (t, *J* 7.3 Hz, 1H), 7.46 – 7.03 (m, 1H), 5.59 (d, *J* 12.8 Hz, 1H), 3.37 (s, 3H), 3.08 (s, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 154.8, 153.8, 141.5, 139.1, 138.6, 129.5, 128.5, 122.4, 118.7, 113.3, 92.8, 44.6, 36.7. *Anal. calcd* for $C_{15}H_{17}ClN_2$ (260,77): C, 69.09; H, 6.57; N, 10.74 Found: C, 68.95; H, 6.46; N, 10.46.

2-(2-(dimethylamino)vinyl)-1-methylquinolin-1-ium iodide (9): Yield: 93% *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.50 (d, *J* 12.2 Hz, 1H), 8.13 (d, *J* 9.5 Hz, 1H), 7.99 (d, *J* 8.8 Hz, 1H), 7.96 (d, *J* 9.6 Hz, 1H), 7.89 (d, *J* 7.8 Hz, 1H), 7.78 (t, *J* 7.9 Hz, 1H), 7.51 (t, *J* 7.4 Hz, 1H), 5.56 (d, *J* 12.2 Hz, 1H), 3.94 (s, 3H), 3.37 (s, 3H), 3.18 (s, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 156.9, 156.2, 139.1, 137.1, 132.4, 129.1, 125.2, 123.9, 118.1, 117.0, 89.1, 54.4, 45.8, 38.0, 36.86. *Anal. calcd* for $C_{14}H_{17}IN_2$ (340,21): C, 49.43; H, 5.04; N, 8.23 Found: C, 49.22; H, 4.91; N, 8.03; Spectral data in according with previously described.[31]

2-(2-(dimethylamino)vinyl)-1-methylpyridin-1-ium iodide (10):Yield**:** 98% *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.21 (d, *J* 6.5 Hz, 1H), 8.18 (d, *J* 12.6 Hz, 1H), 7.94 (d, *J* 8.9 Hz, 1H), 7.79 (t, *J* 7.9 Hz, 1H), 6.99 (t, *J* 6.8 Hz, 1H), 5.13 (d, *J* 12.6 Hz, 1H), 3.86 (s, 3H), 3.25 (s, 3H), 3.02 (s, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 155.1, 153.31, 142.6, 139.2, 119.2, 115.7, 84.8, 54.4, 54.4, 54.4, 45.0, 44.2, 37.4. *Anal. calcd* for $C_{10}H_{15}IN_2$ (290,15): C, 41.40; H, 5.21; N, 9.66 Found: C, 41.22; H, 5.04; N, 9.53; Spectral data in according with previously described.[29]

2-(2-(dimethylamino)vinyl)-1-ethylpyridin-1-ium bromide (11): Yield: 98% *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.30 – 8.21 (m, 2H), 8.00 (d, *J* 8.9 Hz, 1H), 7.78 (t, *J* 7.8 Hz, 1H), 7.03 (t, *J* 6.7 Hz, 1H), 5.21 (d, *J* 12.5 Hz, 1H), 4.35 (q, *J* 7.1 Hz, 2H), 3.26 (s, 3H), 3.03 (s, 3H), 1.33 (t, *J* 7.1 Hz, 3H) *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 154.2, 153.6, 141.7, 139.2, 119.8, 116.3, 84.4, 50.7, 44.9, 37.3, 13.6. *Anal. calcd* for $C_{11}H_{17}BrN_2$ (257,18): C, 51.37; H, 6.66; N, 10.89 Found: C, 51.18; H, 6.46; N, 10.69; Spectral data in according with previously described.[29]

2-(2-(dimethylamino)vinyl)-1-propylpyridin-1-ium bromide (12): Yield: 96% *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.29 – 8.24 (m, 2H), 8.02 (d, *J* 8.8 Hz, 1H), 7.78 (t, *J* 7.9 Hz, 1H), 7.01 (td, *J* 6.9, 1.2 Hz, 1H), 5.19 (d, *J* 12.5 Hz, 1H), 4.30 (t, *J* 7.4 Hz, 2H), 3.25 (s, 3H), 3.02 (s, 3H), 1.78 – 1.71 (m, 2H), 0.90 (t, J 7.4 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 154.4, 153.5, 142.3, 139.2, 119.9, 115.9, 84.6, 56.5, 44.9, 37.3, 20.9, 10.4. *Anal. calcd* for $C_{12}H_{19}BrN_2$ (271,02): C, 53.15; H, 7.06; N, 10.33 Found: C, 52.96; H, 6.9; N, 10.06.

Ethyl 2-cyano-4-(1-methylquinolin-4(1*H*)-ylidene)but-2-enoate (19): Yield: 75% *mp:* 209-211°C *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.38 (d, *J* 13.6 Hz, 1H), 8.24 (d, *J* 8.1 Hz, 1H), 7.99 (d, *J* 7.3 Hz, 1H), 7.90 (t, *J* 7.8 Hz, 1H), 7.83 (d, *J* 8.6 Hz, 1H), 7.63 (t, *J* 7.6 Hz, 1H), 7.24 (d, *J* 7.4 Hz, 1H), 6.52 (d, *J* 13.6 Hz, 1H), 4.23 (q, *J* 7.1 Hz, 2H), 3.98 (s, 3H), 1.31 (t, *J* 7.1 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 164.7, 148.9, 147.2, 140.6, 138.2, 132.0, 125.1, 123.7, 122.1, 118.4, 116.7, 105.6, 98.6, 81.3, 59.1, 40.5, 13.9. *Anal. calcd* for $C_{17}H_{16}N_2O_2$ (280,12): C, 72.84; H, 5.75; N, 9.99; Found: C, 72.65; H, 5.63; N, 9.82; λ_{max} [nm] (acetone): 542 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 7.95

4-(1-methylquinolin-4(1*H*)-ylidene)-2-(phenylsulfonyl)but-2-enenitrile (20): Yield: 86% *mp:* 253-255 °C *IR* (KBr),ν, cm^{-1}: 3449, 2188, 1621, 1522, 1370, 1276, 1227, 1137, 1081, 1029, 823, 757, 717, 694, 608, 573, 528. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.27 (d, *J* 8.4 Hz, 1H), 8.24 (d, *J* 13.6 Hz, 1H), 8.17 (d, *J* 7.2 Hz, 1H), 7.99 – 7.89 (m, 4H), 7.73 – 7.64 (m, 4H), 7.45 (d, *J* 7.3 Hz, 1H), 6.40 (d, *J* 13.6 Hz, 1H), 4.07 (s, 3H) *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 150.3, 144.6, 142.6, 141.5, 138.1, 132.3, 132.0, 128.9, 125.6, 125.5, 124.0, 122.1, 117.0, 116.3, 106.5, 97.5, 88.8, 40.9. *Anal. calcd* for $C_{20}H_{16}N_2O_2S$ (348,09): C, 68.94; H, 4.63; N, 8.04; Found: C, 68.70; H, 4.43; N, 7.91; λ_{max} [nm] (acetone):531 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 6.54

(E)-2,2-Dimethyl-5-(2-(1-methylquinolin-4(1*H)*-ylidene)ethylidene)-1,3-dioxane-4,6-dione (21). Yield*:* 93% *mp:* 234-237 °C *IR* (KBr),ν, cm^{-1}: 3532, 3471, 1629, 1556, 1519, 1426, 1369, 1360, 1323, 1267, 1220, 1160,

1111, 976, 929. *[1]H NMR:* (600 MHz, DMSO-d_6) δ 8.32 (d, *J* 7.1 Hz, 1H), 8.30 (d, *J* 14.6 Hz, 1H), 8.25 (d, J 8.4 Hz, 1H), 7.99 – 7.93 (m, 2H), 7.91 (d, *J* 14.6 Hz, 1H), 7.71 (t, *J* 6.3 Hz, 1H), 7.55 (d, *J* 7.1 Hz, 1H), 4.10 (s, 3H), 1.59 (s, 6H). *[13]C NMR:* (151 MHz, DMSO-d_6) δ 153.9, 144.7, 143.4, 138.7, 133.3, 126.8, 124.7, 123.8, 118.0, 108.2, 104.3, 101.6, 89.5, 42.1, 26.5. The signal of C(4) is overlapped with CH(beta). *Anal. calcd* for $C_{18}H_{17}NO_4$ (311,12): C, 69.44; H, 5.50; N, 4.50; Found: C, 69.26; H, 5.30; N, 4.25; λ_{max} [nm] (acetone):542,00 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 7.29; Spectral data in according with previously described.[32]

4-(1-Methylpyridin-4(1*H*)-ylidene)-2-(phenylsulfonyl)but-2-enenitrile (22). Yield: 66% mp: 277-280 °C *IR* (KBr),ν, cm^{-1}: 3423, 2170, 1646, 1548, 1480, 1387, 1311, 1269, 1198, 1135, 1088, 1037, 852, 753, 603. *[1]H NMR:* (600 MHz, DMSO-d_6) δ 8.02 (d, *J* 6.8 Hz, 2H), 7.90 – 7.80 (m, 3H), 7.64 (d, *J* 7.4 Hz, 3H), 7.55 – 7.09 (s, 2H), 5.63 (d, *J* 14.4 Hz, 1H), 3.91 (s, 3H). *[13]C NMR:* (151 MHz, DMSO-d_6) δ 152.6, 144.1, 142.2, 141.3, 131.2, 128.6, 125.0, 117.7, 100.3, 80.8, 43.6. The signal of C(CN) is overlapped with hetaryl. *Anal. calcd* for $C_{16}H_{14}N_2O_2S$ (298,08): C, 64.41; H, 4.73; N, 9.39; Found: C, 64.24; H, 4.55; N, 9.21; λ_{max} [nm] (acetone):474 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 2.71

2,2-Dimethyl-5-(2-(1-methylpyridin-4(1*H*)-ylidene)ethylidene)-1,3-dioxane-4,6-dione (23). Yield: 62% *mp:* 281-283 °C *IR* (KBr),ν, cm^{-1}: 3440, 1682, 1638, 1558, 1539, 1479, 1402, 1344, 1263, 1185, 1124 *[1]H NMR:* (600 MHz, DMSO-d_6) δ 8.12 (d, *J* 7.0 Hz, 2H), 7.93 (d, *J* 15.2 Hz, 1H), 7.44 (d, *J* 5.9 Hz, 2H), 7.01 (d, *J* 15.2 Hz, 1H), 3.93 (s, 3H), 1.53 (s, 6H). *[13]C NMR:* (151 MHz, DMSO-d_6) δ 155.6, 142.2, 141.6, 118.4, 108.3, 100.9, 85.1, 44.8, 26.3. The signal of C(4) is overlapped with hetaryl. *Anal. calcd* for $C_{14}H_{15}NO_4$ (261,10): C, 64.36; H, 5.79; N, 5.36; Found: C, 64.12; H, 5.60; N, 5.07; λ_{max} [nm] (acetone):474 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 6.54

2-(2-(1-Ethylpyridin-4(1H)-ylidene)ethylidene)malononitrile (24). Yield: 57% mp: 183-185 °C *IR* (KBr),ν, cm^{-1}: *[1]H NMR:* (600 MHz, DMSO-d_6) δ 7.98 (d, *J* 7.3 Hz, 2H), 7.73 (d, *J* 14.2 Hz, 1H), 7.69 – 6.65 (m, 2H), 5.65 (d, *J* 14.2 Hz, 1H), 4.07 (q, *J* 7.2 Hz, 2H), 1.35 (t, *J* 7.3 Hz, 3H). *[13]C NMR:* (151 MHz, DMSO-d_6) δ 152.6, 147.5, 140.5 (br), 121.2, 119.0, 102.1, 52.2, 47.4, 15.9. *Anal. calcd* for $C_{12}H_{11}N_3$ (197,10): C, 73.07; H, 5.62; N, 21.30 Found: C, 72.94; H, 5.46; N, 21.17; λ_{max} [nm] (acetone):479 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 9,88; Spectral data in according with previously described.[33]

Ethyl-2-cyano-4-(1-ethylpyridin-4(1*H*)-ylidene)-but-2-enoate (25). Yield: 48% mp: 163-166 °C *IR* (KBr),ν, cm^{-1}: 3445, 2186, 1664, 1648, 1542, 1485, 1415, 1326, 1248, 1223, 1180, 1094, 1029, 945 *[1]H NMR:* (600 MHz, DMSO-d_6) δ 7.96 (d, *J* 14.4 Hz, 1H), 7.89 (d, *J* 7.1 Hz, 2H), 7.44 – 6.79 (m, 2H), 5.63 (d, *J* 14.4 Hz, 1H), 4.21 – 3.89 (m, 4H), 1.34 (t, *J* 7.2 Hz, 3H), 1.19 (t, *J* 7.1 Hz, 3H). *[13]C NMR:* (151 MHz, DMSO-d_6) δ 166.2, 152.8, 145.7, 139.7(br), 120.4, 101.4, 74.1, 58.8, 51.9, 15.9, 14.6. *Anal. calcd* for $C_{14}H_{16}N_2O_2$ (244,12): C, 68.83; H, 6.60; N, 11.47; Found: C, 68.61; H, 6.46; N, 11.24; λ_{max} [nm] (acetone):488 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 10,00; Spectral data in according with previously described.[33]

4-(1-Ethylpyridin-4(1*H*)-ylidene)-2-(phenylsulfonyl)but-2-enenitrile (26). Yield: 66% *mp:* 231-234 °C *IR* (KBr),ν, cm^{-1}: 3459, 2172, 1644, 1553, 1478, 1445, 1387, 1311, 1271, 1185, 1134, 1085, 1034, 604, 578 *[1]H NMR:* (600 MHz, DMSO-d_6) δ 8.02 (d, *J* 7.1 Hz, 2H), 7.84 – 7.72 (m, 3H), 7.64 – 7.47 (m, 3H), 7.44 – 7.04 (m, 2H), 5.56 (d, *J* 14.4 Hz, 1H), 4.10 (q, *J* 7.2 Hz, 2H), 1.36 (t, *J* 7.2 Hz, 3H). *[13]C NMR:* (151 MHz, DMSO-d_6) δ 153.4, 144.6, 142.9, 140.2, 131.8, 129.2, 125.5, 118.2, 107,7, 100.9, 81.6, 52.3, 16.0. *Anal. calcd* for $C_{17}H_{16}N_2O_2S$ (312,09): C, 65.36; H, 5.16; N, 8.97; Found: C, 65.11; H, 4.99; N, 8.74; λ_{max} [nm] (acetone):475 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 8.73

2-(2-(1-Ethylpyridin-4(1*H*)-ylidene)ethylidene)-5,5-dimethylcyclohexane-1,3-dione (27). Yield: 47% *mp:* >300°C *IR* (KBr),ν, cm^{-1}: 3443, 2958, 1644, 1635, 1548, 1531, 1508, 1478, 1396, 1354, 1264, 1174, 1120, 989, 886 *[1]H NMR:* (600 MHz, DMSO-d_6) δ 8.14 (d, *J* 7.0 Hz, 2H), 8.01 (d, *J* 15.1 Hz, 1H), 7.46 (d, *J* 15.1 Hz, 1H), 7.37 (d, *J* 5.4 Hz, 2H), 4.17 (q, *J* 7.2 Hz, 2H), 2.15 (s, 4H), 1.39 (t, *J* 7.2 Hz, 3H), 0.94 (s, 6H). *[13]C NMR:* (151 MHz, DMSO-d_6) δ 193.5, 157.0, 140.7, 139.9, 118.3, 111.5, 108.8, 52.6, 51.9, 30.5, 28.4, 16.0. *Anal. calcd* for

$C_{17}H_{21}NO_2$ (271,16): C, 75.25; H, 7.80; N, 5.16; Found: C, 75.04; H, 7.60; N, 4.98; λ_{max} [nm] (acetone):501 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 10.24

5-(2-(1-Ethylpyridin-4(1*H*)-ylidene)ethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (28). Yield: 66% *mp:* 258-261 °C *IR* (KBr),ν, cm^{-1}: 3460, 3052, 2988, 1681, 1642, 1548, 1531, 1476, 1397, 1347, 1261, 1201, 1167, 989, 935, 892, 772. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.22 (d, *J* 7.0 Hz, 2H), 7.95 (d, *J* 15.2 Hz, 1H), 7.45 (d, *J* 5.1 Hz, 2H), 7.02 (d, *J* 15.2 Hz, 1H), 4.21 (q, *J* 7.2 Hz, 2H), 1.53 (s, 6H), 1.40 (t, *J* 7.2 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 155.8, 141.8, 141.1, 118.6, 108.3, 101.0, 85.2, 52.9, 26.3, 16.0. The signal of C(4) is overlapped with hetaryl. *Anal. calcd* for $C_{15}H_{17}NO_4$ (275,12): C, 65.44; H, 6.22; N, 5.09; Found: C, 65.22; H, 6.06; N, 4.92; λ_{max} [nm] (acetone):475 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 1.93

5-(2-(1-Ethylpyridin-4(1*H*)-ylidene)ethylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione hydrate (29). Yield: 65% *mp:* >300 °C *IR (KBr),ν, cm^{-1}:* 3164, 3065, 1718, 1697, 1644, 1601, 1559, 1426, 1333, 1310, 1273, 1170, 1038, 979, 528. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 9.95 – 9.84 (m, 2H), 8.19 (d, *J* 7.1 Hz, 2H), 8.00 (d, *J* 15.2 Hz, 1H), 7.44 (d, *J* 5.7 Hz, 2H), 7.29 (d, *J* 15.2 Hz, 1H), 4.19 (q, *J* 7.3 Hz, 2H), 1.40 (t, *J* 7.3 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 168.7, 155.9, 151.1, 140.9, 140.8, 118.4, 108.3, 92.8, 52.8, 16.0. *Anal. calcd* for $C_{13}H_{15}N_3O_4$ (277,11): C, 56.31; H, 5.45; N, 15.15; Found: C, 56.16; H, 5.31; N, 14.97; λ_{max} [nm] (acetone):487 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 4,03

2,2-Dimethyl-5-(2-(1-propylpyridin-4(1*H*)-ylidene)ethylidene)-1,3-dioxane-4,6-dione (30). Yield: 74% *mp:* 245-247 °C *IR* (KBr),ν,cm–1: 3564, 3491, 3075, 2979, 1687, 1679, 1645, 1632, 1553, 1538, 1409, 1349, 1270, 1181. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.20 (d, *J* 6.9 Hz, 2H), 7.95 (d, *J* 15.2 Hz, 1H), 7.46 (d, *J* 6.5 Hz, 2H), 7.02 (d, *J* 15.2 Hz, 1H), 4.14 (t, *J* 7.3 Hz, 2H), 1.80 (q, *J* 7.3 Hz, 2H), 1.53 (s, 6H), 0.85 (t, *J* 7.3 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6)δ 155.8, 141.9, 141.3, 118.5, 108.3, 100.9, 85.4, 58.9, 40.0, 26.3, 23.7, 10.3. *Anal. calcd* for $C_{16}H_{19}NO_4$ (289,33): C, 66.42; H, 6.62; N, 4.84; Found: C, 66.21; H, 6.5; N, 4.65; λ_{max} [nm] (acetone):476 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 8.24

4-(1-Butylpyridin-4(1*H*)-ylidene)-2-(phenylsulfonyl)but-2-enenitrile (31). Yield: 73% *mp:* 176-178 °C *IR* (KBr),ν, cm^{-1}: 3436, 2172, 1642, 1545, 1539, 1508, 1478, 1390, 1314, 1267, 1181, 1134, 1082, 1029, 843, 759, 713, 607. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.01 (d, *J* 7.1 Hz, 2H), 7.84 – 7.71 (m, 3H), 7.61 – 7.50 (m, 3H), 7.45 – 6.83 (m, 2H), 5.56 (d, *J* 14.4 Hz, 1H), 4.07 (t, *J* 7.2 Hz, 2H), 1.78 – 1.64 (m, 2H), 1.28 – 1.20 (m, 2H), 0.89 (t, *J* 7.3 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 153.4, 144.6, 143.0, 140.5, 131.8, 129.2, 125.5, 118.2, 100.9, 81.8, 56.7, 32.3, 18.7, 13.3. The signal of C(CN) is overlapped with hetaryl. *Anal. calcd* for $C_{19}H_{20}N_2O_2S$ (340,12): C, 67.03; H, 5.92; N, 8.23; Found: C, 66.80; H, 5.75; N, 8.08; λ_{max} [nm] (acetone):476 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 7.99

2-(2-(1-Butylpyridin-4(1*H*)-ylidene)ethylidene)-5,5-dimethylcyclohexane-1,3-dione (32). Yield: 76% *mp:* >300 °C *IR* (KBr),ν, cm^{-1}: 3425, 2955, 1645, 1625, 1555, 1470, 1405, 1359, 1277, 1185, 975, 872. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.12 (d, *J* 7.1 Hz, 2H), 8.00 (d, *J* 15.1 Hz, 1H), 7.46 (d, *J* 15.1 Hz, 1H), 7.40 – 7.33 (m, 2H), 4.14 (t, *J* 7.3 Hz, 2H), 2.15 (s, 4H), 1.78 – 1.72 (m, 2H), 1.30 – 1.23 (m, 2H), 0.94 (s, 6H), 0.90 (t, *J* 7.4 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 193.5, 157.0, 140.9, 139.9, 111.5, 108.9, 57.0, 51.9, 40.4, 32.3, 30.5, 28.4, 18.8, 13.3. *Anal. calcd* for $C_{19}H_{25}NO_2$ (299,19): C, 76.22; H, 8.42; N, 4.68; Found: C, 76.02; H, 8.22; N, 4.53; λ_{max} [nm] (acetone):507 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 3.65

5-(2-(1-Butylpyridin-4(1*H*)-ylidene)ethylidene)-2,2-dimethyl-1,3-dioxane-4,6-dione (33). Yield*:* 85% *mp:* 262-265 °C *IR* (KBr),ν, cm^{-1}: 3433, 3067, 2958, 1705, 1649, 1566, 1542, 1479, 1416, 1352, 1277, 1206, 1188, 966, 936, 863. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.20 (d, *J* 7.0 Hz, 2H), 7.95 (d, *J* 15.2 Hz, 1H), 7.45 (d, *J* 5.6 Hz, 2H), 7.02 (d, *J* 15.2 Hz, 1H), 4.17 (t, *J* 7.2 Hz, 2H), 1.80 – 1.72 (m, 2H), 1.53 (s, 6H), 1.30 – 1.21 (m, 2H), 0.89 (t, *J* 7.4 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 155.8, 141.9, 141.3, 118.5, 108.3, 101.0, 85.4, 57.3, 32.3, 26.3, 18.8,

13.3. The signal of C(4) is overlapped with hetaryl. *Anal. calcd* for $C_{17}H_{21}NO_4$ (303,15): C, 67.31; H, 6.98; N, 4.62; Found: C, 67.18; H, 6.85; N, 4.44; λ_{max} [nm] (acetone):476 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 7.90

Ethyl 2-cyano-4-(1-phenylpyridin-4(1*H*)-ylidene)but-2-enoate (34). Yield: 91% *mp:* 205-208 °C *IR* (KBr),ν, cm^{-1}: 3449, 2186, 1671, 1646, 1536, 1505, 1480, 1420, 1246, 1190, 1173, 1087. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.10 (d, *J* 14.1 Hz, 1H), 8.04 (d, *J* 16.7 Hz, 2H), 7.63 (d, *J* 7.5 Hz, 3H), 7.59 (t, *J* 7.8 Hz, 2H), 7.50 (t, *J* 7.2 Hz, 1H), 7.41 – 7.30 (s, 1H), 7.02 – 6.91 (s, 1H), 5.78 (d, *J* 14.1 Hz, 1H), 4.11 (q, *J* 7.1 Hz, 2H), 1.21 (t, *J* 7.1 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 165.6, 151.7, 147.1, 142.2, 138.4, 137.7, 130.0, 128.6, 122.6, 119.4, 118.5, 113.2, 102.3, 78.7, 59.3, 14.5. *Anal. calcd* for $C_{18}H_{16}N_2O_2$ (292,12): C, 73.95; H, 5.52; N, 9.58; Found: C, 73.82; H, 5.37; N, 9.35; λ_{max} [nm] (acetone):503 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 8.12; Spectral data in according with previously described.[34]

5,5-Dimethyl-2-(2-(1-phenylpyridin-4(1*H*)-ylidene)ethylidene)cyclohexane-1,3-dione (35). Yield: 79% mp: >300 °C *IR* (KBr),ν, cm^{-1}: 3423, 3045, 2954, 1642, 1634, 1561, 1528, 1475, 1400, 1354, 1254, 1184, 1165, 976. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.28 (d, *J* 7.3 Hz, 2H), 8.12 (d, *J* 14.9 Hz, 1H), 7.70 (d, *J* 7.6 Hz, 2H), 7.63 (t, *J* 7.8 Hz, 2H), 7.56 (t, *J* 7.3 Hz, 1H), 7.51 (d, *J* 14.9 Hz, 1H), 7.47 – 7.29 (m, 2H), 2.21 (s, 4H), 0.96 (s, 6H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 194.4, 156.7, 142.2, 141.4, 139.4, 130.1, 129.2, 123.1, 113.3, 108.7, 40.0, 30.4, 28.4, 27.9. *Anal. calcd* for $C_{21}H_{21}NO_2$ (319,16): C, 78.97; H, 6.63; N, 4.39; Found: C, 78.74; H, 6.45; N, 4.16; λ_{max} [nm] (acetone):523 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 4.92; Spectral data in according with previously described.[29]

2,2-Dimethyl-5-(2-(1-phenylpyridin-4(1*H*)-ylidene)ethylidene)-1,3-dioxane-4,6-dione (36). Yield: 78% mp: 272-274 °C *IR* (KBr),ν, cm^{-1}: 3443, 3051, 1698, 1649, 1541, 1525, 1509, 1478, 1409, 1349, 1253, 1180, 1125, 931, 762, 511. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.46 (d, *J* 7.4 Hz, 2H), 8.18 (d, *J* 15.0 Hz, 1H), 7.80 (d, *J* 8.1 Hz, 2H), 7.71 (t, *J* 7.8 Hz, 2H), 7.65 (t, *J* 7.4 Hz, 1H), 7.63 – 7.51 (s, 2H), 7.19 (d, *J* 15.0 Hz, 1H), 1.64 (s, 6H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 155.2, 143.2, 141.6, 139.5, 129.5, 128.8, 122.7, 122.7, 107.7, 100.8, 87.2, 25.9. The signal of C(4) is overlapped with hetaryl. *Anal. calcd* for $C_{19}H_{17}NO_4$ (323,12): C, 70.58; H, 5.30; N, 4.33; Found: C, 70.39; H, 5.13; N, 4.08; λ_{max} [nm] (acetone): 495 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 9.11

5-(2-(1-Phenylpyridin-4(1*H*)-ylidene)ethylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (37). Yield: 89% *mp:* >300 °C *IR* (KBr),ν, cm^{-1}: 3433, 2361, 2342, 1699, 1639, 1605, 1542, 1510, 1475, 1423, 1323, 1260, 1227, 1175, 975, 858, 606, 518. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 10.27 – 10.04 (m, 2H), 8.41 (d, *J* 7.2 Hz, 2H), 8.22 (d, *J* 14.9 Hz, 1H), 7.79 (d, *J* 7.9 Hz, 2H), 7.71 (t, *J* 7.7 Hz, 2H), 7.65 (t, *J* 7.4 Hz, 1H), 7.60 – 7.48 (s, 2H), 7.44 (d, *J* 14.9 Hz, 1H). *^{13}C NMR:* (151 MHz, DMSO-d_6) 155.2, 150.4, 142.2, 141.6, 139.2, 129.5, 129.5, 128.7, 122.6, 122.6, 107.6, 94.6. *Anal. calcd* for $C_{17}H_{13}N_3O_3$ (307,10): C, 66.44; H, 4.26; N, 13.67; Found: C, 66.28; H, 4.13; N, 13.43; λ_{max} [nm] (acetone):511 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 3.39

5,5-Dimethyl-2-(2-(1-methylquinolin-2(1*H*)-ylidene)ethylidene)cyclohexane-1,3-dione (38). Yield: 91% *mp:* 257-259 °C *IR* (KBr),ν, cm^{-1}: 3473, 3385, 2951, 2865, 1619, 1541, 1508, 1366, 1269, 1240, 1234, 1224, 966. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.37 (d, *J* 14.4 Hz, 1H), 8.29 (d, *J* 14.3 Hz, 1H), 8.22 (d, *J* 8.3 Hz, 1H), 8.17 (d, *J* 7.1 Hz, 1H), 7.94 – 7.78 (m, 2H), 7.70 – 7.59 (m, 1H), 7.44 (d, *J* 7.3 Hz, 1H), 4.02 (s, 3H), 2.27 (s, 4H), 0.97 (s, 6H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 195.0, 154.7, 142.5, 142.0, 138.7, 133.0, 126.3, 124.6, 124.1, 117.8, 114.6, 107.7, 105.0, 53.4 – 50.2, 41.8, 30.4, 28.3. *Anal. calcd* for $C_{20}H_{21}NO_2$ (307,39): C, 78.15; H, 6.89; N, 4.56; Found: C, 77.90; H, 6.77; N, 4.37; λ_{max} [nm] (acetone):574 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 6.3

5-(2-(1-Methylpyridin-2(1*H*)-ylidene)ethylidene)pyrimidine-2,4,6(1H,3H,5H)-trione dihydrate (39). Yield: 68% *mp:* >300 °C *IR* (KBr),ν, cm^{-1}: 3391, 3185, 2793, 1691, 1648, 1607, 1543, 1427, 1397, 1343, 1271, 1165, 1038, 848, 770, 515. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 10.18 – 9.86 (m, 2H), 8.28 (d, *J* 6.2 Hz, 1H), 8.07 (d, *J* 14.7 Hz, 1H), 7.96 (d, *J* 8.7 Hz, 1H), 7.84 (t, *J* 7.8 Hz, 1H), 7.46 (d, *J* 14.7 Hz, 1H), 7.09 (t, *J* 6.7 Hz, 1H), 3.88 (s, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 164.6 (br), 155.8, 151.1, 143.1, 142.1, 139.8, 120.3, 117.1, 100.1, 93.4, 44.1.

Anal. calcd for $C_{12}H_{15}N_3O_5$ (281,27): C, 51.24; H, 5.38; N, 14.94; Found: C, 51.04; H, 5.19; N, 14.76; λ_{max} [nm] (acetone):457 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 2.67 ; Spectral data in according with previously described.[35]

2-(2-(1-Ethylpyridin-2(1*H*)-ylidene)ethylidene)malononitrile (40). Yield: 75% *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.08 (d, *J* 6.4 Hz, 1H), 7.92 (d, *J* 8.9 Hz, 1H), 7.88 (d, *J* 13.8 Hz, 1H), 7.63 (t, *J* 7.9 Hz, 1H), 6.93 – 6.83 (m, 1H), 5.57 (d, *J* 13.8 Hz, 1H), 4.17 (q, *J* 7.1 Hz, 2H), 1.33 (t, *J* 7.2 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 152.2, 149.0, 141.1, 138.2, 120.7, 120.7, 118.6, 115.3, 92.9, 50.4, 48.4, 13.4. *Anal. calcd* for $C_{12}H_{11}N_3$ (197,10): C, 73.07; H, 5.62; N, 21.30 Found: C, 72.84; H, 5.49; N, 21.16; λ_{max} [nm] (acetone):450 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 6.30

4-(1-Ethylpyridin-2(1*H*)-ylidene)-2-(phenylsulfonyl)but-2-enenitrile (41). Yield: 70% *mp:* 184-186 °C *IR* (KBr),ν, cm^{-1}: 3442, 2172, 1634, 1526, 1440, 1397, 1316, 1300, 1273, 1223, 1140, 1085, 1032, 621, 601, 577. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.12 (t, *J* 6.6 Hz, 1H), 7.94 – 7.86 (m, 2H), 7.84 – 7.79 (m, 2H), 7.72 – 7.67 (m, 1H), 7.60 – 7.54 (m, 3H), 6.95 (t, *J* 6.8 Hz, 1H), 5.48 (d, *J* 14.0 Hz, 1H), 4.18 (q, *J* 7.2 Hz, 2H), 1.31 (t, *J* 7.2 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 152.8, 144.4, 144.3, 141.4, 138.7, 131.9, 129.2, 125.7, 120.7, 117.8, 115.8, 91.7, 82.7, 50.4, 13.5. *Anal. calcd* for $C_{17}H_{16}N_2O_2S$ (312,09): C, 65.36; H, 5.16; N, 8.97; Found: C, 65.11; H, 4.98; N, 8.75; λ_{max} [nm] (acetone):448 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 5.00

5-(2-(1-Ethylpyridin-2(1*H*)-ylidene)ethylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione hydrate (**42**). Yield*:* 87% *mp:* >300 °C *IR* (KBr),ν, cm^{-1}: 3450, 3141, 1689, 1636, 1606, 1542, 1433, 1405, 1337, 1293, 1143, 762, 524 *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 10.16 – 9.82 (m, 2H), 8.31 (d, *J* 6.3 Hz, 1H), 8.08 (d, *J* 14.6 Hz, 1H), 7.99 (d, *J* 8.7 Hz, 1H), 7.85 (t, *J* 7.8 Hz, 1H), 7.60 (d, *J* 14.6 Hz, 1H), 7.14 (t, *J* 6.6 Hz, 1H), 4.29 (q, *J* 6.9 Hz, 2H), 1.41 (t, *J* 7.1 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 164.45 (br), 154.9, 151.1, 142.3, 142.1, 139.8, 120.9, 117.6, 99.7, 93.25, 51.2, 13.8. *Anal. calcd* for $C_{13}H_{15}N_3O_4$ (277,28): C, 56.31; H, 5.45; N, 15.15; Found: C, 56.06; H, 5.29; N, 15.01; λ_{max} [nm] (acetone):464 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 2,37; Spectral data in according with previously described.[35]

2-(2-(1-Propylpyridin-2(1*H*)-ylidene)ethylidene)malononitrile (43). Yield: 58% mp: 147-149 °C *IR* (KBr),ν, cm^{-1}: 3432, 2191, 1665, 1624, 1541, 1518, 1462, 1372, 1324, 1284, 1206, 1154, 1090, 825, 766. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.06 (d, *J* 6.2 Hz, 1H), 7.93 (d, *J* 8.9 Hz, 1H), 7.90 (d, *J* 13.8 Hz, 1H), 7.63 (t, *J* 7.7 Hz, 1H), 6.87 (t, *J* 6.4 Hz, 1H), 5.54 (d, *J* 13.8 Hz, 1H), 4.10 (t, *J* 7.0 Hz, 2H), 1.90 – 1.56 (m, 2H), 0.91 (t, *J* 7.2 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 152.3, 149.0, 141.6, 138.2, 120.7, 120.6, 118.5, 114.9, 93.1, 56.4, 48.5, 20.7, 10.4. *Anal. calcd* for $C_{13}H_{13}N_3$ (211,11): C, 73.91; H, 6.20; N, 19.89 Found: C, 73.76; H, 6.03; N, 19.63; λ_{max} [nm] (acetone):452 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 3.42

Ethyl 2-cyano-4-(1-propylpyridin-2(1*H*)-ylidene)but-2-enoate (44). Yield: 63% *mp:* 162-165 °C *IR* (KBr),ν, cm^{-1}: 3450, 2969, 2182, 1669, 1635, 1532, 1449, 1412, 1310, 1241, 1217, 1155, 1100, 1078, 803, 757. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 8.08 (d, *J* 14.0 Hz, 1H), 8.01 (d, *J* 6.4 Hz, 1H), 7.75 (d, *J* 9.0 Hz, 1H), 7.57 (t, *J* 7.9 Hz, 1H), 6.79 (t, *J* 6.6 Hz, 1H), 5.53 (d, *J* 14.0 Hz, 1H), 4.14 – 4.01 (m, 4H), 1.85 – 1.65 (m, 2H), 1.20 (t, *J* 7.1 Hz, 3H), 0.92 (t, *J* 7.4 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 165.9, 152.7, 146.9, 141.6, 137.8, 120.3, 120.0, 114.0, 92.2, 75.1, 58.9, 56.1, 20.6, 14.6, 10.4. *Anal. calcd* for $C_{15}H_{18}N_2O_2$ (258,14): C, 69.74; H, 7.02; N, 10.84; Found: C, 69.53; H, 6.88; N, 10.65; λ_{max} [nm] (acetone):456 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 4.11

5-(2-(1-Propylpyridin-2(1*H*)-ylidene)ethylidene)pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione hydrate (45). Yield*:* 77% *mp:* >300 °C *IR* (KBr),ν, cm^{-1}: 3526, 3410, 3153, 1685, 1636, 1606, 1542, 1432, 1400, 1336, 1300, 1273, 1158, 755, 523. *^{1}H NMR:* (600 MHz, DMSO-d_6) δ 10.14 – 9.81 (m, 2H), 8.29 (d, *J* 6.2 Hz, 1H), 8.08 (d, *J* 14.6 Hz, 1H), 8.00 (d, *J* 8.7 Hz, 1H), 7.84 (t, *J* 7.7 Hz, 1H), 7.61 (d, *J* 14.6 Hz, 1H), 7.12 (t, *J* 6.6 Hz, 1H), 4.21 (t, *J* 7.2 Hz, 2H), 1.83 (q, *J* 7.3 Hz, 2H), 0.95 (t, *J* 7.3 Hz, 3H). *^{13}C NMR:* (151 MHz, DMSO-d_6) δ 164.5 (br), 155.0, 151.1, 142.5, 142.2, 139.8, 120.8, 117.2, 99.9, 93.3, 57.2, 21.2, 10.5. *Anal. calcd* for $C_{14}H_{17}N_3O_4$ (291,31): C, 57.72; H, 5.88; N, 14.42; Found: C, 57.3; H, 5.54; N, 13.93; λ_{max} [nm] (acetone):463 $\varepsilon_{max} \times 10^{-4}$ [$M^{-1} \times cm^{-1}$]: 8.85

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Supplementary Material

The Supporting Information is available free of charge on the website.
Details of experimental, synthetic, and analytical procedures, along with spectroscopic data for synthesized compounds.

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