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An efficient synthesis of 2-amino-4-aryl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-1,3-dicarbonitriles in THF with DBU as catalyst

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Abstract An efficient and convenient multicomponent reaction for preparation of 2-amino-4-aryl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-1,3-dicarbonitrile derivatives, in THF, with DBU as catalyst is reported. These compounds are typical acceptor–donor–acceptor (A–D–A) systems comprising one electron donor and two electron acceptors with different important chemical properties. Excellent yields and the simplicity of the reaction procedure make this one of the most efficient methods for synthesis of these types of compound.

Keywords 2-Amino-1,3-dicarbonitriles · Optical properties · DBU · Benzo[7]annulene

Introduction

Multifunctionalized benzenes containing the 2-amino-1,3-dicarbonitrile group (**I**), are typical acceptor–donor–acceptor (A–D–A) systems comprising one electron donor and two electron acceptors. These are not only important constituents of a large number of bioactive compounds [1–3], but are also useful as versatile precursors for asymmetric synthesis [4]. They are, furthermore, also very important compounds because of their optical properties [5] and are the basis for artificial photosynthetic systems [6, 7], materials with semiconducting or nonlinear optical properties [8], and molecular electronic devices [9]. Different types 2-amino-1,3-dicarbonitrile compounds have been synthesized. Aromatic aldehydes and aromatic ketones reacted with malononitrile give 4,6-diaryl-2-amino-1,3-dicarbonitriles

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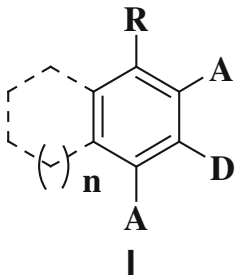
[10, 11]. Acetone, aromatic aldehydes, and malononitrile react together to give similar 2-amino-1,3-dicarbonitrile compounds, for example 5-methyl-4-aryl-2-amino-1,3-dicarbonitriles [12]. Reaction of cyclopentanone [13], cyclohexanone [14], 2,3-dihydroinden-1-one [15], 3,4-dihydronaphthalen-1(2*H*)-one [16], or 6,7,8,9-tetrahydrobenzo[7]annulen-5-one [17] with an aldehyde and malononitrile furnish the corresponding fused polycyclic compounds containing the 2-amino-1,3-dicarbonitriles. However, in literature reports, cycloheptanone has seldom been used for synthesis of the corresponding 2-amino-1,3-dicarbonitrile compounds. In the literature investigated we found only two papers on the synthesis of similar compounds, those by Elgemeie et al. [18] and Kurbatov et al. [19]. Elgemeie et al. reported initial condensation of cycloheptanone and malononitrile to give cycloalkylidenemalononitriles then reaction of these condensation products with an arylmethylenecyanoacetamide, a condensation product from reaction of an aromatic aldehyde and cyanoacetamide, to give four products in moderate yield. Kurbatov reported reaction of an aromatic aldehyde and malononitrile to give the condensation product benzylidenemalononitrile, then reaction of this with malononitrile to give only one product, 2-amino-4-phenyl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-1,3-dicarbonitrile. In these two methods, the condensation products of cycloheptanone and malononitrile or of aromatic aldehyde and malononitrile should be synthesized first, then reacted with another substrate to product 2-amino-1,3-dicarbonitriles, so these are, indeed, multistep reactions.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) [20–22], an efficient organic basic catalyst, is often used in organic synthesis. In continuation of our recent studies on the reaction of multifunctionalized benzenes with 2-amino-1,3-dicarbonitrile compounds [11, 14, 15], herein we report an efficient one-pot synthesis of 2-amino-4-aryl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-1,3-dicarbonitrile derivatives in THF in the presence of DBU as catalyst.



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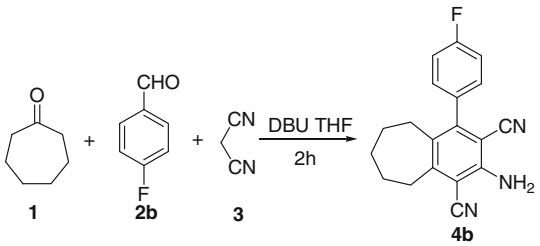
Results and discussion

Before conducting this synthesis, we optimized the reaction conditions. Cycloheptanone (**1**), 4-fluorobenzaldehyde (**2b**) and malononitrile (**3**) were chosen as starting materials for the model reaction (Scheme 1).

The model reaction was examined in different solvents in the presence of DBU. H_2O, CH_3CN, CH_3OH, EtOH, THF, etc., were used under reflux conditions and

Scheme 1 Synthesis of 2-amino-4-(4-fluorophenyl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-1,3-dicarbonitrile



DMF was used at 100 °C to find the best reaction conditions. We found the reaction could not be conducted in H_2O. In the above-mentioned organic solvents, however, the reaction occurred with different yields. Taken into account overall conditions, THF was chosen as optimum solvent of this synthesis. The reaction was then repeated in THF at different temperatures. The results are listed in Table 1. As shown in Table 1, the best results were obtained in THF under reflux (Entry 6). We also found that in the absence of DBU in the THF, the reaction did not occur (Entry 10). Of course, other catalysts were also tested in THF, but these gave the inferior results to DBU.

Having established the optimum conditions for this one-pot reaction, we investigated the reactions (Scheme 2) of cycloheptanone, different aromatic aldehydes, and malononitrile under the chosen conditions as indicated in Table 1 entry 6. The results of the reactions are listed in Table 2. We can see from Table 2 that in all the reactions aromatic aldehydes **2** bearing electron-donating groups (CH_3, CH_3O) and electron-withdrawing groups (F, Cl, Br) give the desired products in good yields. Furthermore, heterocyclic aldehydes, for example picolinaldehyde

Table 1 Synthesis of **4b** under different conditions

Entry	Catalyst	Solvent	Time (h) Temp[a]	Yields (%)
1	DBU	H_2O	3	0
2	DBU	CH_3CN	2	25
3	DBU	CH_3OH	2	32
4	DBU	EtOH	2	35
5	DBU	DMF	2 (100 °C)	16
6	**DBU**	**THT**	**2**	**79**
7	DBU	THF	3	80
8	DBU	THF	2 (0 °C)	10
9	DBU	THT	2 (25 °C)	33
10	–	THT	2	0
11	Et_3N	THF	2	30
12	$C_5H_{11}N$	THF	2	26

Reaction conditions: cycloheptanone (1 mmol), 4-fluorobenzaldehyde (1 mmol), malononitrile (2.5 mmol), catalyst (0.1 mmol), solvent (10 mL), reaction temperature: reflux

The bold characters indicate the optimum conditions

[a] Unless explicitly stated, the reaction was conducted under reflux conditions

Scheme 2 Synthesis of 2-amino-1,3-dicarbonitriles

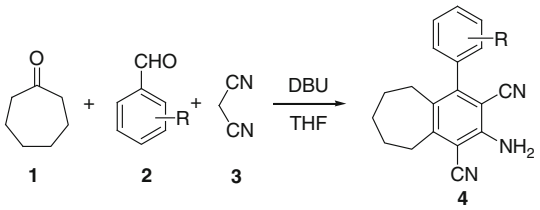


Table 2 Results of synthesis of 2-amino-1,3-dicarbonitriles

Entry	Ar	Products	Time (h)	Yields (%)
1	C_6H_5	**4a**	2	79
2	4-FC_6H_4	**4b**	2	81
3	4-BrC_6H_4	**4c**	2	76
4	4-ClC_6H_4	**4d**	2	75
5	3,4-$Cl_2C_6H_3$	**4e**	2	83
6	4-$CH_3C_6H_4$	**4f**	2.5	85
7	3,4-$(CH_3)_2C_6H_3$	**4g**	2.5	81
8	3,4-$(CH_3O)_2C_6H_3$	**4h**	2.2	77
9	3,4,5-$(CH_3O)_3C_6H_2$	**4i**	2	80
10	Pyridin-3-yl	**4j**	2	77
11	2-Thiophenyl	**4k**	2	71

and thiophene-2-carbaldehyde, could also be used for synthesis of the target products.

The structures of compounds **4a**–**4k** were determined by consideration of their IR, ^{1}H NMR and high-resolution mass spectra (HRMS). For example, the ^{1}H NMR spectrum of **4a** contains a broad singlet at delta 1.39 (2H), a triplet at delta 1.66 (2H, $J = 0.8$ Hz), 1.73 (2H, $J = 0.8$ Hz), 2.39 (2H, $J = 3.6$ Hz), doublets at delta 3.03 ($J = 7.2$ Hz) due to the CH_2 protons of aliphatic carbon, a singlet at delta 6.42 (2H) due to NH_2 protons, doublets at delta 7.24 (2H, $J = 7.2$ Hz) and a multiplet at delta 7.47-7.52 (3H) due to five phenyl protons. In HRMS, the calculated *m/z* for $C_{19}H_{17}N_3$ $[M + H]^+$ is 288.1501, and we found the experimental *m/z* was 288.1503.

Conclusions

In conclusion, we have developed a facile and efficient method for synthesis of 2-amino-4-aryl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-1,3-dicarbonitriles via a three-component reaction of different aromatic aldehydes, cycloheptanone, and malononitrile in THF with DBU as catalyst. This process has several advantages including excellent yields, simple operation, and mild conditions. Most of the products in the text are newly reported.

Experimental

Melting points were determined on an XT-5 microscopic melting-point apparatus and are uncorrected. IR spectra were recorded on a FT Bruker Tensor 27 spectrometer. ^{1}H NMR spectra were obtained from solution in DMSO-d_6, with Me_4Si as internal standard, using a Bruker-400 spectrometer. HRMS spectra were obtained with a Bruker microTOF-Q 134 instrument.

General procedure for synthesis of 2-amino-4-aryl-6,7,8,9-tetrahydro-5*H*-benzo[7]annulene-1,3-dicarbonitriles

A mixture of cycloheptanone **1** (1 mmol), aromatic aldehyde **2** (1 mmol), malononitrile **3** (2.5 mmol), THF (10 mL), and DBU (0.01 mmol) was placed in a reaction flask under reflux conditions. After completion (monitored by TLC), the reaction mixture was poured into water, filtered, then washed thoroughly with water. The products were dried and recrystallized from 95% ethanol.

*2-amino-4-phenyl-6,7,8,9-tetrahydro-5H-benzo[7]annulene-1,3-dicarbonitrile (**4a**)*

Melting point 209–210 °C (lit [19]. 218 °C); IR (KBr, ν, cm^{-1}): 3,408, 3,348, 3,252, 2,928, 2,856, 2,220, 1,698, 1,684, 1,658, 1,635, 1,559, 1,541, 1,521, 1,507, 1,497, 1,457, 1,444, 1,363, 1,294, 1,249, 1,200, 964, 704, 669 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.39 (2H, br, CH_2), 1.66 (2H, *t*, $J = 0.8$ Hz, CH_2), 1.73 (2H, *t*, $J = 0.8$ Hz, CH_2), 2.39 (2H, *t*, $J = 3.6$ Hz, CH_2), 3.03 (2H, d, $J = 7.2$ Hz, CH_2), 6.42 (2H, s, NH_2), 7.24 (2H, d, $J = 7.2$ Hz, ArH), 7.47–7.52 (3H, m, ArH); HRMS *m/z* calculated for $C_{19}H_{17}N_3$ $[M + H]^+$: 288.1501, Found: 288.1503.

*2-amino-4-(4-fluorophenyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-1,3-dicarbonitrile (**4b**)*

Melting point 218–220 °C; IR (KBr, ν, cm^{-1}): 3,408, 3,351, 3,253, 2,964, 2,930, 2,221, 1,660, 1,607, 1,562, 1,466, 1,456, 1,295, 1,249, 1,222, 1,198, 1,160, 965, 836, 535 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.41 (2H, *t*, $J = 2.0$ Hz, CH_2), 1.65–1.67 (2H, m, CH_2), 1.72 (2H, d, $J = 3.6$ Hz, CH_2), 2.37–2.39 (2H, m, CH_2), 3.01-3.03 (2H, m, CH_2), 6.44 (2H, s, NH_2), 7.32 (2H, *t*, $J = 8.8$ Hz, ArH), 7.32 (2H, *t*, $J = 8.8$ Hz, ArH); HRMS *m/z* calculated for $C_{19}H_{16}FN_3$ $[M + Na]^+$: 328.1226, Found: 328.1230.

*2-amino-4-(4-bromophenyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-1,3-dicarbonitrile (**4c**)*

Melting point 234–235 °C; IR (KBr, ν, cm^{-1}): 3,442, 3,345, 3,242, 2,933, 2,854, 2,225, 1,646, 1,598, 1,531, 1,490, 1,473, 1,392, 1,366, 1,349, 1,339, 1,265, 1,231, 1,211, 1,153, 1,128, 1,103, 1,073, 1,010, 965, 906, 825, 786, 765, 671, 512 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.40 (2H, *t*, $J = 4.0$ Hz, CH_2), 1.63 (2H,

d, $J = 4.8$ Hz, CH_2), 1.71 (2H, d, $J = 4.4$ Hz, CH_2), 2.24 (2H, dd, $J = 5.2$ Hz, $J = 5.6$ Hz, CH_2), 2.83 (2H, dd, $J = 5.2$ Hz, $J = 6.4$ Hz, CH_2), 7.26 (2H, d, $J = 8.4$ Hz, ArH), 7.74 (2H, d, $J = 8.4$ Hz, ArH); HRMS *m/z* calculated for $C_{19}H_{16}BrN_3$ $[M + Na]^+$:388.0425, Found: 388.0435.

*2-amino-4-(4-chlorophenyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-1,3-dicarbonitrile (**4d**)*

Melting point 228–230 °C (lit [18]. 230 °C); IR (KBr, *v*, cm^{-1}): 3,291, 3,130, 2,933, 2,856, 2,225, 1,646, 1,599, 1,531, 1,494, 1,473, 1,441, 1,396, 1,363, 1,349, 1,339, 1,299, 1,266, 1,232, 1,211, 1,192, 1,154, 1,129, 1,088, 1,072, 1,014, 965, 906, 890, 861, 841, 828, 787, 766, 709, 671, 628, 562, 526, 515 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.40 (2H, d, $J = 4.4$ Hz, CH_2), 1.63 (2H, d, $J = 4.4$ Hz, CH_2), 1.71 (2H, d, $J = 4.8$ Hz, CH_2), 2.23–2.26 (2H, m, CH_2), 2.82–2.85 (2H, *t*, $J = 5.6$ Hz, CH_2), 7.33 (2H, d, $J = 8.4$ Hz, ArH), 7.60 (2H, d, $J = 8.4$ Hz, ArH); HRMS *m/z* calculated for $C_{19}H_{16}ClN_3$ $[M + Na]^+$: 344.0930, Found: 344.0933.

*2-amino-4-(3,4-dichlorophenyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-1,3-dicarbonitrile (**4e**)*

Melting point 176–178 °C; IR (KBr, *v*, cm^{-1}): 3,257, 3,153, 2,939, 2,911, 2,861, 2,845, 2,184, 2,151, 1,644, 1,608, 1,543, 1,509, 1,490, 1,472, 1,449, 1,407, 1,364, 1,335, 1,319, 1,242, 1,204, 1,159, 1,132, 985, 966, 938, 670 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.32–1.39 (2H, m, CH), 1.43–1.50 (2H, m, CH_2), 1.92 (2H, *t*, $J = 5.6$ Hz, CH), 2.62–2.65 (2H, m, CH_2), 3.25 (2H, br, CH_2), 6.40 (2H, s, NH_2), 7.39 (1H, d, $J = 6.4$ Hz, ArH), 7.53 (1H, d, $J = 8.4$ Hz, ArH); 7.66 (1H, s, ArH)**;** HRMS *m/z* calculated for $C_{19}H_{15}Cl_2N_3$ $[M + H]^+$: 356.0721, Found: 356.0732.

*2-amino-4-p-tolyl-6,7,8,9-tetrahydro-5H-benzo[7]annulene-1,3-dicarbonitrile (**4f**)*

Melting point 230–232 °C; IR (KBr, *v*, cm^{-1}): 3,408, 3,350, 3,252, 2,963, 2,929, 2,858, 2,220, 1,658, 1,606, 1,561, 1,511, 1,466, 1,455, 1,423, 1,365, 1,352, 1,294, 1,248, 1,221, 1,198, 1,159, 1,097, 1,013, 964, 835, 558, 534 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.38–1.40 (2H, m, CH_2), 1.62–1.65 (2H, m, CH_2), 1.71–1.72 (2H, m, CH_2), 2.25–2.27 (2H, m, CH_2), 2.38 (3H, s, CH_3), 2.81–2.83 (2H, m, CH_2), 7.15 (2H, d, $J = 8.0$ Hz, ArH), 7.33 (2H, d, $J = 7.6$ Hz, ArH); Anal. calcd for $C_{20}H_{19}N_3$: C, 79.70; H, 6.35; N, 13.94; found C 79.75 H 6.37, N 13.89; HRMS *m/z* calculated for $C_{20}H_{19}N_3$ $[M + Na]^+$: 324.1477, Found: 324.1485.

*2-amino-4-(3,4-dimethylphenyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-1,3-dicarbonitrile (**4g**)*

Melting point 176.5–177.8 °C; IR (KBr, *v*, cm^{-1}): 3,353, 3,246, 2,931, 2,856, 2,768, 2,214, 1,686, 1,647, 1,559, 1,501, 1,491, 1,459, 1,364, 1,319, 1,293, 1,249, 1,200,

962, 875, 837, 821 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.36–1.40 (2H, m, CH_2), 1.64 (2H, t, $J = 4.0$ Hz, CH_2), 1.69–1.73 (2H, m, CH_2), 2.27 (3H, s, CH_3), 2.28 (3H, s, CH_3), 2.39 (2H, t, $J = 5.6$ Hz, CH_2), 3.01 (2H, t, $J = 5.2$ Hz, CH_2), 6.38 (2H, s, NH_2), 6.94 (1H, d, $J = 7.6$ Hz, ArH), 7.00 (1H, s, ArH), 7.25 (1H, d, $J = 7.6$ Hz, ArH); Anal. calcd for $C_{21}H_{21}N_3$: C, 79.97; H, 6.71; N, 13.32; found C 79.92, H 6.70, N 13.42; HRMS *m/z* calculated for $C_{21}H_{21}N_3$ $[M + Na]^+$: 338.1633, Found: 338.1635.

*2-amino-4-(3,4-dimethoxyphenyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-1,3-dicarbonitrile (**4h**)*

Melting point 226–228 °C; IR (KBr, *v*, cm^{-1}): 3,420, 3,351, 3,252, 2,955, 2,923, 2,854, 2,217, 1,655, 1,605, 1,587, 1,560, 1,518, 1,455, 1,407, 1,319, 1,294, 1,257, 1,236, 1,201, 1,186, 1,156, 1,139, 1,023, 814 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.43–1.44 (2H, m, CH_2), 1.63–1.67 (2H, m, CH_2), 1.73–1.74 (2H, m, CH_2), 2.44 (2H, t, $J = 4.8$ Hz, CH_2), 3.01 (2H, t, $J = 4.8$ Hz, CH_2), 3.74 (3H, s, OCH_3), 3.82 (3H, s, OCH_3), 6.37 (2H, s, NH_2), 6.77 (1H, d, $J = 8.0$ Hz, ArH), 6.82 (1H, d, $J = 1.2$ Hz, ArH), 7.06 (1H, d, $J = 8.0$ Hz, ArH); Anal. calcd for $C_{21}H_{21}N_3O_2$: C, 72.60; H, 6.09; N, 12.10; found C 72.62, H 6.08, N 12.19; HRMS *m/z* calculated for $C_{21}H_{21}N_3O_2$ $[M + H]^+$: 348.1712, Found: 348.1713.

*2-amino-4-(3,4,5-trimethoxyphenyl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-1,3-dicarbonitrile (**4i**)*

Melting point 230.0–232.7 °C; IR (KBr, *v*, cm^{-1}): 3,445, 3,355, 3,246, 2,920, 2,846, 2,215, 1,699, 1,685, 1,648, 1,558, 1,542, 1,509, 1,465, 1,412, 1,374, 1,292, 1,244, 1,203, 1,153, 1,125, 1,011, 967 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.47 (2H, s, CH_2), 1.65 (2H, s, CH_2), 1.75 (2H, d, $J = 0.8$ Hz, CH_2), 2.44 (2H, d, $J = 6.8$ Hz, CH_2), 3.02 (2H, t, $J = 4.0$ Hz, CH_2), 3.73 (3H, s, OCH_3), 3.77 (6H, s, $2XOCH_3$), 6.42 (2H, s, NH_2), 6.56 (2H, d, $J = 2.0$ Hz, ArH); Anal. calcd for $C_{22}H_{23}N_3O_3$: C, 70.01; H, 6.14; N, 11.13; found C 70.09, H 6.16, N 11.11; HRMS *m/z* calculated for $C_{22}H_{23}N_3O_3$ $[M + Na]^+$: 400.1637, Found: 400.1642.

*2-amino-4-(pyridin-3-yl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-1,3-dicarbonitrile (**4j**)*

Melting point 216.7–218.7 °C; IR (KBr, *v*, cm^{-1}): 3,444, 3,348, 3,249, 2,925, 2,849, 2,769, 2,219, 1,686, 1,654, 1,632, 1,560, 1,544, 1,524, 1,509, 1,491, 1,460, 1,439, 1,420, 1,365, 1,321, 1,297, 1,250, 1,200, 1,145, 1,090, 1,049, 993, 962 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.40 (2H, s, CH_2), 1.65 (2H, d, $J = 0.4$ Hz, CH_2), 1.72 (2H, s, CH_2), 2.34 (2H, t, $J = 2.4$ Hz, CH_2), 3.04 (2H, d, $J = 0.8$ Hz, CH_2), 6.48 (2H, s, NH_2), 7.43 (1H, d, $J = 7.6$ Hz, ArH), 7.49 (1H, t, $J = 5.6$ Hz, ArH), 7.96 (1H, t, $J = 7.6$ Hz, ArH), 8.71 (1H, d, $J = 3.6$ Hz, ArH); Anal. calcd for $C_{18}H_{16}N_4$: C, 74.98; H, 5.59; N, 19.43; found C 74.82, H 5.56, N 19.49; HRMS *m/z* calculated for $C_{18}H_{16}N_4$ $[M + Na]^+$: 311.1273, Found: 311.1267.

*2-amino-4-(thiophen-2-yl)-6,7,8,9-tetrahydro-5H-benzo[7]annulene-1,3-dicarbonitrile (**4k**)*

Melting point 275–276 °C; IR (KBr, ν, cm^{-1}): 3,425, 2,937, 2,227, 2,193, 1,698, 1,684, 1,654, 1,616, 1,557, 1,541, 1,521, 1,474, 1,457, 1,421, 1,364, 1,251, 1,066, 1,012, 669 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) (δ, ppm): 1.12–1.25 (2H, m, CH_2), 1.34–1.51 (2H, m, CH), 1.65–1.73 (3H, m, CH_2, CH), 2.01–2.12 (1H, m, CH), 2.23–2.27 (1H, m, CH), 3,32 (1H, d, $J = 7.2$ Hz, CH), 7.58 (1H, d, $J = 8.0$ Hz, ArH), 7.81–7.86 (1H, m, ArH), 8.28 (1H, d, $J = 8.0$ Hz, ArH). HRMS *m/z* calculated for $C_{17}H_{15}N_3S$ $[M + Na]^+$: 316.0884, Found: 316,0889.

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