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One-Pot Reaction

Stereoselective One-Pot Synthesis of *cis*-1,2-Dicyanoalkenes from 1,1-Bis(benzenesulfonyl)alkenes and KCN

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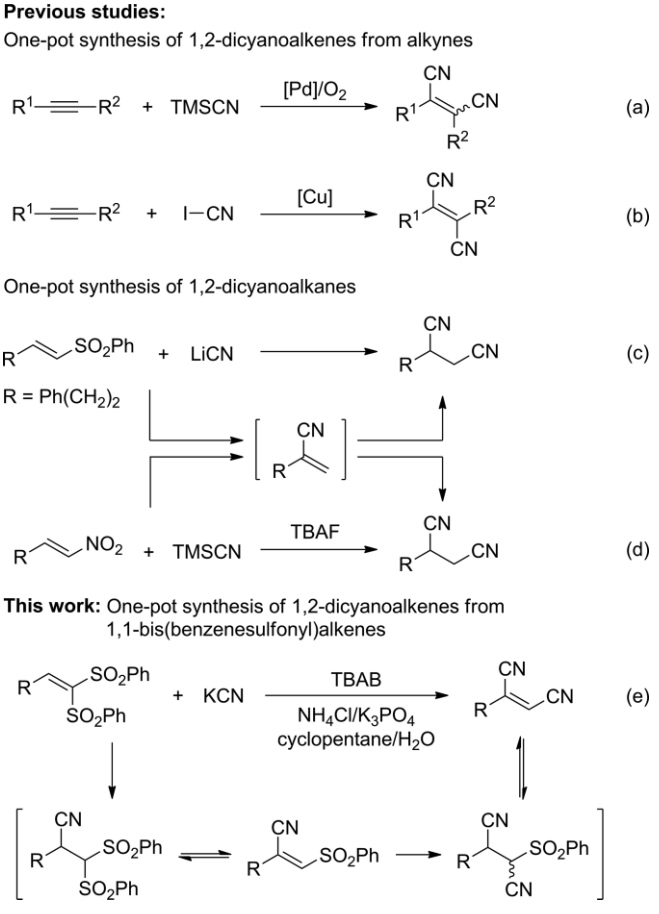
Abstract: An efficient synthesis of *cis*-1,2-dicyanoalkenes by the reaction of 1,1-bis(benzenesulfonyl)alkenes with KCN was developed. This reaction was conducted in the presence of tetrabutylammonium bromide and NH_4Cl/K_3PO_4 under phase-transfer conditions. A series of *cis*-1,2-dicyanoalkenes were obtained in good to high yields. Further transformation of the obtained product allows for access to imide and dicarboxylic acid compounds.

Introduction

1,2-Dicyanoalkenes have found versatile applications in organic synthesis.[1] They can serve not only as key intermediates for the preparation of compounds with great value such as 1,2-dicarboxylic acids,[2] 1,2-diamides[3] and 1,4-diamines,[4] but also as 2π partners in cycloaddition reactions to build complex cyclic structures.[5] In addition, the use of 1,2-dicyanoalkenes in asymmetric catalysis has been described.[6] Despite their synthetic utility, to date, only a limited number of methods are available for the preparation of 1,2-dicyanoalkenes, and most of them rely on multi-step synthesis.[6,7] In 2009, a significant advance was achieved by Arai et al., who reported a palladium-catalyzed dicyanation of alkynes under aerobic conditions to access 1,2-dicyanoalkenes in two stereoisomers (Scheme 1, Eq. a).[8] Very recently, Okamoto and Ohe et al. developed a copper-catalyzed *anti*-selective dicyanation of alkynes (Scheme 1, Eq. b).[9] However, certain drawbacks, such as the requirement for transition-metal catalysts, limited scope of the starting materials, and low stereoselectivity, cannot be completely overcome with these reported methods. The development of an efficient and general protocol for the preparation of 1,2-dicyanoalkenes under mild conditions is highly desired.

One-pot multi-step transformation[10] is considered to be one of the most attractive procedures in organic synthesis due to its high efficiency and avoidance of isolation or purification steps. In 1991, Bailey and Jackson reported a one-pot synthesis of 1,2-dicyanoalkane from a (benzenesulfonyl)alkene and LiCN (Scheme 1, Eq. c).[11] This reaction was believed to proceed through a sequential conjugate cyanation of (benzenesulfonyl)alkene, desulphonylation, and conjugate cyanation of in situ generated cyanoalkenes. Recently, Minakata et al. observed similar results in the reaction of nitroalkenes with TMSCN (Scheme 1, Eq. d).[12] Inspired by the above examples and our previous work on the (benzenesulfonyl)alkene chemistry,[13] herein, we reported our finding of the one-pot synthesis of 1,2-dicyanoalkenes. The reaction of 1,1-bis(benzenesulfonyl)alkenes with a cyanation reagent proceeds smoothly through a double



Scheme 1. Relevant previous studies and concept of this study.

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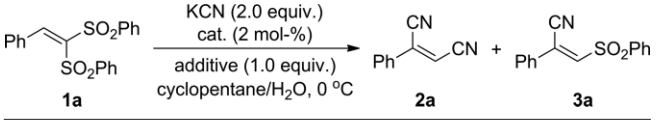
conjugate addition-elimination pathway under the mild conditions (Scheme 1, Eq. e). This method has the advantages of substrate availability,[14] transition-metal free reaction conditions, good functional group compatibility, as well as high stereoselectivity, and may provide a complementary to the reported routes to 1,2-dicyanoalkenes.

Results and Discussion

Our study began with the model reaction of 1,1-bis(benzenesulfonyl)alkenes **1a** with KCN in a biphasic solution of cyclopentane and H_2O at 0 °C in the presence of a catalytic amount of tetrabutylammonium bromide (TBAB). After stirring for 29 h, the desired product **2a** was obtained in 39 % yield as a single stereoisomer, along with 26 % yield of **3a** (Table 1, entry 1). The stereochemistry of **2a** was confirmed by comparison with the ^{1}H NMR spectra of literature,[8a] and the structure of **3a** was determined by X-ray crystallographic analysis.[15] It was reported that in a phase-transfer catalyzed conjugate cyanation with KCN as the cyanide source, Maruoka et al. observed that the addition of a Brønsted acid additive, such as NH_4Cl as the proton source, is helpful for the acceleration of the reaction rate.[16] To improve the efficiency of the model reaction, an equimolar amount of NH_4Cl was employed, and the yield of **2a** was dramatically increased to 72 % (Table 1, entry 2). Next, the roles of TBAB and water in this reaction were examined. No reaction occurred in the absence of TBAB or water (Table 1, entries 3 and 4), which indicated that TBAB behaved as a phase-transfer catalyst to promote the reaction via the extraction of a cyanide anion from the aqueous phase. To our delight, we found that the addition of a weak base could facilitate the elimination of $PhSO_2H$, hence a higher yield of **2a** was achieved within a shorten period when an equimolar amount of K_3PO_4 was added together with NH_4Cl (Table 1, entry 5). Other quaternary ammonium salts, such as tetramethylammonium bromide (TMAB) and tetraethyl-ammonium bromide (TEAB) were evaluated (Table 1, entries 6 and 7), and TBAB was still found to be the best catalyst. Screening of the organic solvent was also conducted, with cyclopentane proving to be more suitable than toluene, petroleum ether (60–90 °C), *n*-hexane and *n*-pentane (Table 1, entries 8–11). Finally, elevating the temperature to 23 °C resulted in lower yield (Table 1, entry 12). Therefore, the reaction conditions as shown in Table 1, entry 5 were selected as the optimized conditions.

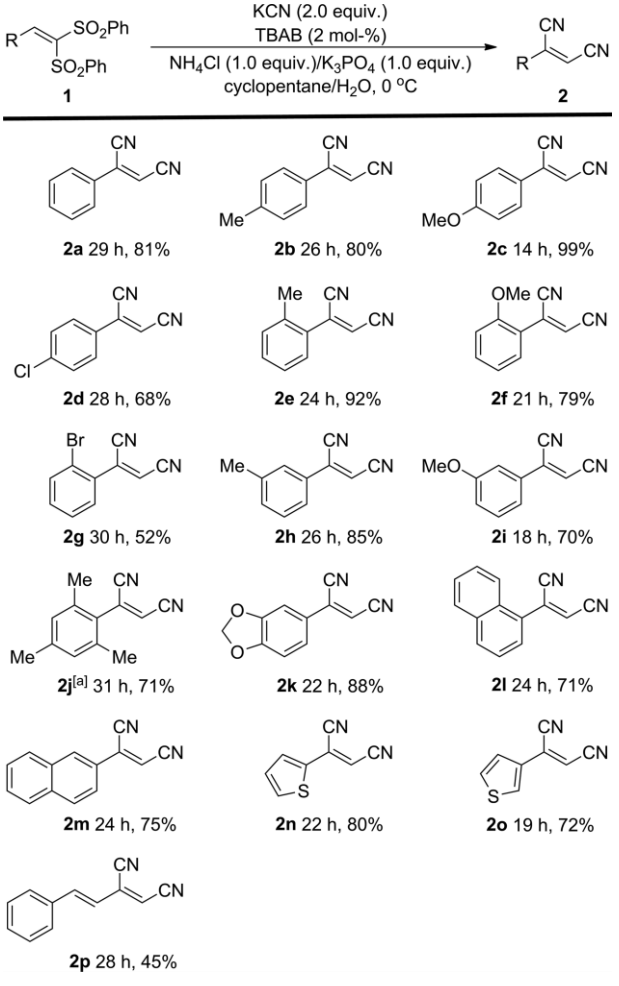
Having established the optimized conditions, the substrate scope was investigated with a variety of 1,1-bis(benzenesulfonyl)alkenes. As revealed in Scheme 2, in the cases of 1,1-bis(benzenesulfonyl)alkenes **1a**–**j** derived from substituted benzaldehydes, all the reactions proceeded smoothly to afford the corresponding 1,2-dicyanoalkenes **2a**–**j** in high yields. Generally, substituents on the phenyl ring at different position are well tolerant. Moreover, 1,1-bis(benzenesulfonyl)alkenes with

Table 1. Condition optimization.[a].



Entry	Cat.	Additives	Time (h)	Yield[b] of **2a** [%]	Yield[b] of **3a** [%]
1	TBAB	–	29	39	26
2	TBAB	NH_4Cl	72	72	–
3	–	NH_4Cl	72	0	–
4[c]	TBAB	NH_4Cl	72	trace	–
5	TBAB	NH_4Cl/K_3PO_4	29	81	–
6	TMAB	NH_4Cl/K_3PO_4	21	19	45
7	TEAB	NH_4Cl/K_3PO_4	21	22	33
8[d]	TBAB	NH_4Cl/K_3PO_4	36	49	–
9[e]	TBAB	NH_4Cl/K_3PO_4	36	61	–
10[f]	TBAB	NH_4Cl/K_3PO_4	12	58	–
11[g]	TBAB	NH_4Cl/K_3PO_4	12	40	–
12[h]	TBAB	NH_4Cl/K_3PO_4	21	45	–

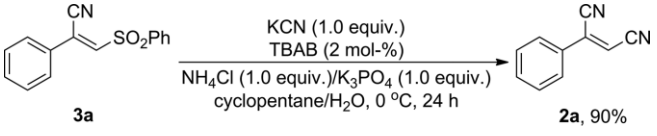
[a] Reaction conditions: **1a** (0.1 mmol), KCN (0.2 mmol), catalyst (0.002 mmol) and additives (0.1 mmol) in cyclopentane (2 mL)/H_2O (0.1 mL) at 0 °C for appropriate time. [b] Isolated yield. [c] Reaction was performed in the absence of H_2O. [d] Toluene was used instead of cyclopentane. [e] Petroleum ether (60–90 °C) was used instead of cyclopentane. [f] *n*-Hexane was used instead of cyclopentane. [g] *n*-Pentane was used instead of cyclopentane. [h] Reaction was conducted at 23 °C.



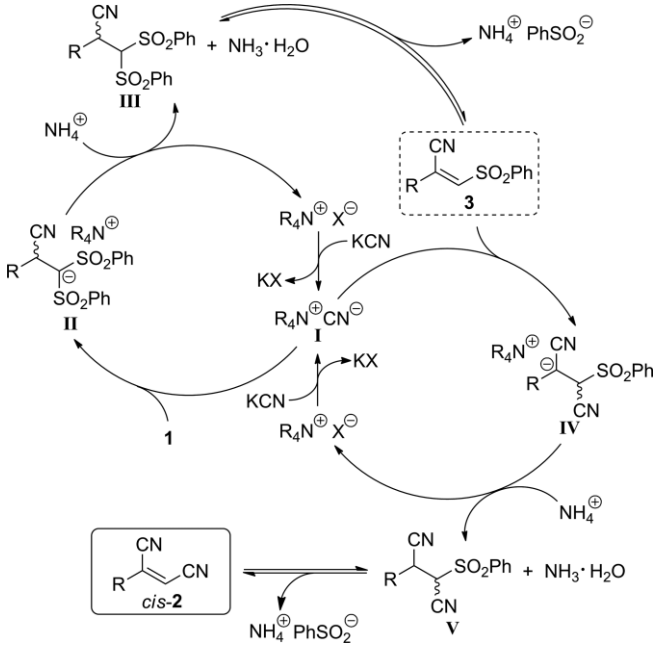
Scheme 2. Reaction scope. Unless otherwise specified, all reactions were carried out with **1** (0.2 mmol), KCN (0.4 mmol), TBAB (0.004 mmol), NH_4Cl (0.2 mmol) and K_3PO_4 (0.2 mmol) in cyclopentane (4 mL)/H_2O (0.2 mL) at 0 °C for appropriate time, yields are given for isolated products. [a] Reaction was conducted at 30 °C.

electron-donating groups (**1b**, **1c**, **1e**, **1f**, **1h**–**j**) exhibited higher activity than those with electron-withdrawing substituents (**1d**, **1g**). Substrates with other aryl or heteroaryl units, including 1,3-benzodioxol-5-yl (**1k**), 1-naphthyl (**1l**), 2-naphthyl (**1m**), 2-thienyl (**1n**), and 3-thienyl (**1o**), were equally reactive under the optimized conditions, providing the desired products **2k**–**o** in good yields ranging from 71 % to 88 %. This transformation also works well with 1,1-bis(benzenesulfonyl)alkene **1p** containing an unsaturated moiety, delivering **2p** in 45 % yield.

To gain the mechanistic information, **3a** was isolated and subjected to standard conditions, the desired product **2a** was obtained in a comparable yield under standard conditions (Scheme 3), thus suggesting the involvement of cyanoalkenes **3** in the reaction pathway. From this result and together with the previous reports,[11,12,16] we proposed a reaction mechanism for the formation of 1,2-dicyanoalkenes **2** as shown in Scheme 4. The quaternary ammonium salt TBAB acts as a phase-transfer catalyst to initiate the reaction via the extraction of a cyanide anion from the aqueous phase. The resulting ammonium cyanide **I** reacts with 1,1-bis(benzenesulfonyl)-alkenes **1** to provide the adduct **II**, which then undergoes protonation by NH_4^+ to give **III**, along with the regeneration of the phase-transfer catalyst. In the presence of a base, elimination of $PhSO_2H$ from **III** leads to the formation of the intermediate **3**. Subsequently, a second conjugate addition of the regenerated ammonium cyanide **I** to cyanoalkenes **3** occurs, followed by protonation and base-induced elimination, yielding the final product **2**. At last, the high stereoselectivity obtained in this reaction could be possibly explained by the difference of steric hindrance between *cis*- and *trans*-isomer, the more stable *cis*-**2** is preferentially formed.

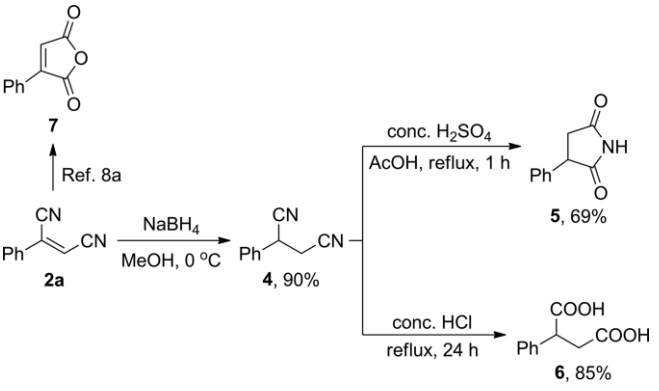


Scheme 3. Mechanistic experiment.



Scheme 4. Proposed reaction pathway.

1,2-Dicyanoalkenes are versatile synthetic intermediates and can be readily transformed into highly functionalized compounds. Some examples are illustrated in Scheme 5. Treatment of **2a** with 2.0 equiv. of $NaBH_4$ in methanol afforded 1,2-dicyanoalkane **4** in 90 % yield. Compound **4** could be converted to cyclic imide **5** or dicarboxylic acid **6** in one step. Our methodology complements Arai's elegant approach to the cyclic anhydride **7**.[8a]



Scheme 5. Synthetic transformation.

Conclusions

In conclusion, we have developed a one-pot, transition-metal free transformation for the synthesis of *cis*-1,2-dicyanoalkenes from 1,1-bis(benzenesulfonyl)alkenes and KCN. This reaction is characterized by the availability of starting materials, transition-metal free reaction conditions, good functional group compatibility, as well as high stereoselectivity. Mechanistic experiments indicated that the reaction proceeds through a double conjugate addition-elimination pathway. In addition, further transformation of the obtained product allows for access to imide and dicarboxylic acid compounds.

Experimental Section

General Methods: NMR spectroscopic data were recorded on Bruker AV 400 MHz instrument at 400 MHz (^{1}H NMR) and 100 MHz (^{13}C NMR), or Bruker AV 600 MHz instrument at 600 MHz (^{1}H NMR) and 150 MHz ^{13}C NMR). Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.2 ppm; [D_4]methanol: δ_H = 3.31 ppm, δ_C = 49.0 ppm; [D_6]DMSO: δ_H = 2.50 ppm, δ_C = 39.5 ppm). High-resolution mass spectrometry (HRMS) spectra were obtained on a Bruker micrOTOF-QII Instrument. Melting points were measured on a WRS-1A digital melting point apparatus and are uncorrected. X-ray structural analyses were conducted on a Rigaku XtaLAB mini (600 W, SHINE, CCD, 75 mm, 0.1 electrons/pixel/sec). Thin layer chromatography (TLC) was performed on 0.20 mm Qingdao Haiyang silica gel plates. Flash column chromatography was performed on silica gel (200–300 mesh, Qingdao Haiyang Chem. Company, Ltd.).

General Procedure for the Synthesis of Compounds 2: To a mixture of 1,1-bis(benzenesulfonyl)alkenes **1** (0.2 mmol), KCN (0.4 mmol), NH_4Cl (0.2 mmol), K_3PO_4 (0.2 mmol) and tetrabutylammonium bromide (0.004 mmol, 2 mol-%) in cyclopentane (4 mL)/H_2O (0.2 mL) was stirred at 0 °C until the starting material disappeared as evidenced by TLC. The reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (PE/EA = 30:1 to 5:1 as eluent) to give the corresponding product **2**.

2-Phenylmaleonitrile[8a] **(2a):** Yellow solid, 24.9 mg, 81 % yield, m.p. 85–86 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (d, J = 7.4 Hz, 2 H), 7.58 (t, J = 7.3 Hz, 1 H), 7.51 (t, J = 7.4 Hz, 2 H), 6.39 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.6, 133.1, 130.0, 129.9, 126.9, 114.9, 114.3, 107.6. HRMS (ESI): m/z calcd. for $C_{10}H_6N_2Na^+$ 177.0423, found 177.0427 [M + Na]$^+$.

2-(*p*-Tolyl)maleonitrile[6] **(2b):** Light yellow solid, 26.9 mg, 80 % yield, m.p. 134–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.55 (d, J = 8.2 Hz, 2 H), 7.31 (d, J = 8.1 Hz, 2 H), 6.32 (s, 1 H), 2.43 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 133.5, 130.6, 127.4, 126.8, 115.1, 114.4, 106.1, 21.8. HRMS (ESI): m/z calcd. for $C_{11}H_8N_2Na^+$ 191.0580, found 191.0585 [M + Na]$^+$.

2-(4-Methoxyphenyl)maleonitrile[6] **(2c):** Yellow solid, 36.4 mg, 99 % yield, m.p. 149–150 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.9 Hz, 2 H), 6.99 (d, J = 8.9 Hz, 2 H), 6.21 (s, 1 H), 3.88 (s, 3 H). ^{13}C NMR (100MHz, $CDCl_3$): δ = 163.6, 132.9, 128.8, 122.7, 115.4, 115.3, 114.5, 104.1, 55.9. HRMS (ESI): m/z calcd. for $C_{11}H_8N_2NaO^+$ 207.0529, found 207.0523 [M + Na]$^+$.

2-(4-Chlorophenyl)maleonitrile (2d): Light yellow solid, 25.7 mg, 68 % yield, m.p. 176–177 °C. ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 7.79 (d, J = 8.5 Hz, 2 H), 7.64 (d, J = 8.5 Hz, 2 H), 7.45 (s, 1 H). ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 137.5, 130.5, 129.7, 128.8, 128.8, 115.9, 114.7, 111.1. HRMS (ESI): m/z calcd. for $C_{10}H_5ClN_2Na^+$ 211.0033, found 211.0031 [M + Na]$^+$.

2-(*o*-Tolyl)maleonitrile[6] **(2e):** Light yellow solid, 30.9 mg, 92 % yield, m.p. 65–66 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.34 (m, 1 H), 7.26–7.19 (m, 3 H), 6.05 (s, 1 H), 2.43 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 136.5, 134.3, 131.8, 130.9, 129.2, 127.2, 114.5, 114.3, 113.6, 20.5. HRMS (ESI): m/z calcd. for $C_{11}H_8N_2Na^+$ 191.0580, found 191.0579 [M + Na]$^+$.

2-(2-Methoxyphenyl)maleonitrile[6] **(2f):** Yellow solid, 29.1 mg, 79 % yield, m.p. 130–131 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.68–7.66 (m, 1 H), 7.50 (t, J = 7.4 Hz, 1 H), 7.09 (t, J = 7.6 Hz, 1 H), 7.03 (d, J = 8.4 Hz, 1 H), 7.00 (s, 1 H), 3.96 (s, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 158.9, 133.9, 131.5, 130.7, 121.6, 119.0, 115.8, 115.0, 112.1, 111.3, 56.1. HRMS (ESI): m/z calcd. for $C_{11}H_8N_2NaO^+$ 207.0529, found 207.0531 [M + Na]$^+$.

2-(2-Bromophenyl)maleonitrile (2g): White solid, 24.2 mg, 52 % yield, m.p. 64–65 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.70 (d, J = 8.1 Hz, 1 H), 7.47–7.44 (m, 1 H), 7.41–7.39 (m, 2 H), 6.34 (s, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 134.5, 133.2, 133.0, 131.8, 130.8, 128.6, 121.8, 115.5, 113.9, 113.8. HRMS (ESI): m/z calcd. for $C_{10}H_5BrN_2Na^+$ 254.9528, found 254.9529 [M + Na]$^+$.

2-(*m*-Tolyl)maleonitrile[6] **(2h):** Light yellow solid, 28.6 mg, 85 % yield, m.p. 81–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (s, 2 H), 7.41–7.38 (m, 2 H), 6.36 (s, 1 H), 2.42 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.0, 134.0, 133.8, 130.0, 129.7, 127.5, 124.0, 115.0, 114.4, 107.2, 21.5. HRMS (ESI): m/z calcd. for $C_{11}H_8N_2Na^+$ 191.0580, found 191.0582 [M + Na]$^+$.

2-(3-Methoxyphenyl)maleonitrile[6] **(2i):** Yellow solid, 25.8 mg, 70 % yield, m.p. 100–101 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42 (t, J = 8.0 Hz, 1 H), 7.26–7.24 (m, 1 H), 7.13–7.09 (m, 2 H), 6.37 (s, 1 H), 3.87 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 160.5, 133.6, 131.3, 131.0, 119.2, 118.7, 114.8, 114.3, 112.2, 107.8, 55.8. HRMS (ESI): m/z calcd. for $C_{11}H_8N_2NaO^+$ 207.0529, found 207.0531 [M + Na]$^+$.

2-Mesitylmaleonitrile (2j): White solid, 27.9 mg, 71 % yield, m.p. 80–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.95 (s, 2 H), 5.94 (s, 1 H), 2.31 (s, 3 H), 2.29 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.9, 136.0, 133.7, 129.5, 127.8, 115.7, 114.3, 113.9, 21.3, 20.2. HRMS (ESI): m/z calcd. for $C_{13}H_{12}N_2Na^+$ 219.0893, found 219.0892 [M + Na]$^+$.

2-(Benzo[*d*][1,3]dioxol-5-yl)maleonitrile (2k): Orange solid, 34.8 mg, 88 % yield, m.p. 170–171 °C. ^{1}H NMR (400 MHz, [D_6]DMSO): δ = 7.44 (s, 1 H), 7.29–7.24 (m, 2 H), 7.10 (d, J = 8.2 Hz, 1 H), 6.17 (s, 2 H). ^{13}C NMR (100 MHz, [D_6]DMSO): δ = 151.4, 148.8, 131.0, 124.2, 124.0, 116.4, 115.0, 109.0, 107.4, 105.5, 102.7. HRMS (ESI): m/z calcd. for $C_{11}H_6N_2NaO_2^+$ 221.0321, found 221.0323 [M + Na]$^+$.

2-(Naphthalen-1-yl)maleonitrile[6] **(2l):** Yellow solid, 29.0 mg, 71 % yield, m.p. 119–120 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.09 (d, J = 8.3 Hz, 1 H), 8.03 (d, J = 6.7 Hz, 1 H), 7.95 (d, J = 7.9 Hz, 1 H), 7.69–7.60 (m, 2 H), 7.55–7.51 (m, 2 H), 6.33 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 133.9, 133.5, 132.8, 129.7, 129.3, 129.1, 128.5, 128.1, 127.5, 125.3, 123.7, 115.1, 114.4, 114.1. HRMS (ESI): m/z calcd. for $C_{14}H_8N_2Na^+$ 227.0580, found 227.0582 [M + Na]$^+$.

2-(Naphthalen-2-yl)maleonitrile[6] **(2m):** Yellow solid, 30.6 mg, 75 % yield, m.p. 145–146 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (s, 1 H), 7.96–7.88 (m, 3 H), 7.66–7.60 (m, 3 H), 6.47 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.1, 133.6, 133.0, 130.1, 129.7, 129.5, 129.3, 128.1, 128.1, 127.4, 121.1, 115.1, 114.4, 107.0. HRMS (ESI): m/z calcd. for $C_{14}H_8N_2Na^+$ 227.0580, found 227.0581 [M + Na]$^+$.

2-(Thiophen-2-yl)maleonitrile[6] **(2n):** Brown solid, 25.6 mg, 80 % yield, m.p. 118–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59–7.56 (m, 2 H), 7.18 (t, J = 4.3 Hz, 1 H), 6.10 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.0, 133.2, 132.0, 129.4, 126.9, 114.8, 113.4, 103.8. HRMS (ESI): m/z calcd. for $C_{11}H_6N_2NaO_2^+$ 182.9987, found 182.9985 [M + Na]$^+$.

2-(Thiophen-3-yl)maleonitrile (2o): Green solid, 23.0 mg, 72 % yield, m.p. 132–133 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.88 (d, J = 1.1 Hz, 1 H), 7.48 (dd, J = 4.9, 2.9 Hz, 1 H), 7.29 (d, J = 4.8 Hz, 1 H), 6.20 (s, 1 H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 133.1, 130.6, 129.5, 127.6, 123.7, 114.9, 114.3, 105.5. HRMS (ESI): m/z calcd. for $C_{11}H_6N_2NaO_2^+$ 182.9987, found 182.9989 [M + Na]$^+$.

2-((*E*)-Styryl)maleonitrile (2p): Yellow solid, 16.2 mg, 45 % yield, m.p. 147–148 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53–7.50 (m, 2 H), 7.44–7.42 (m, 3 H), 7.35 (d, J = 15.8 Hz, 1 H), 6.84 (d, J = 15.8 Hz, 1 H), 5.92 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 143.3, 134.0, 132.4, 131.2, 129.4, 128.3, 121.6, 115.1, 113.0, 107.5. HRMS (ESI): m/z calcd. for $C_{12}H_8N_2Na^+$ 203.0580, found 203.0578 [M + Na]$^+$.

(*Z*)-2-Phenyl-3-(phenylsulfonyl)acrylonitrile (3a): Yellow solid, m.p. 125–126 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, J = 7.5 Hz, 2 H), 7.72 (t, J = 7.3 Hz, 1 H), 7.66–7.61 (m, 4 H), 7.56–7.49 (m, 1 H), 7.46 (t, J = 7.3 Hz, 2 H), 7.35 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 139.4, 134.9, 132.6, 130.7, 129.9, 129.7, 128.6, 127.4, 125.0, 113.1. HRMS (ESI): m/z calcd. for $C_{15}H_{12}NO_2S^+$ 270.0583, found 270.0589 [M + H]$^+$.

Procedure for the Synthesis of Compound 4: To a solution of **2a** (92.5 mg, 0.6 mmol) in MeOH (2 mL) was added $NaBH_4$ (27.2 mg, 0.72 mmol) at 0 °C. After 10 min, the reaction was quenched by addition of water (1 mL) and the resulting mixture was extracted with EtOAc (10 mL × 3). The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 and concentrated under

vacuum. The residue was purified by flash chromatography on silica gel to give compound **4**.

2-Phenylsuccinonitrile[12] **(4):** White solid, 84.3 mg, 90 % yield, m.p. 60–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.40 (m, 5 H), 4.19 (t, J = 6.8 Hz, 1 H), 2.96 (d, J = 6.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 132.3, 129.7, 129.6, 127.3, 118.1, 115.6, 34.0, 24.7. HRMS (ESI): m/z calcd. for $C_{10}H_8N_2Na^+$ 179.0580, found 179.0585 [M + Na]$^+$.

Procedure for the Synthesis of Compound 5: To a mixture of **4** (31.2 mg, 0.2 mmol) and acetic acid (0.5 mL), was added concentrated H_2SO_4 (50 μL) under argon atmosphere. The resulting mixture was refluxed for 1 h. After cooling, the reaction was quenched by a saturated $NaHCO_3$ aqueous solution (15 mL) and extracted with EtOAc (10 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (PE/EA = 10:1 to 2:1 as eluent) to give product **5**.

3-Phenylpyrrolidine-2,5-Dione[17] **(5):** White solid, 24.2 mg, 69 % yield, m.p. 78–80 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.02 (br. s, 1 H), 7.32–7.28 (m, 2 H), 7.26–7.22 (m, 1 H), 7.18–7.16 (m, 2 H), 3.99 (dd, J = 9.6, 5.1 Hz, 1 H), 3.15 (dd, J = 18.6, 9.6 Hz, 1 H), 2.78 (dd, J = 18.6, 5.1 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 178.7, 177.0, 136.8, 129.4, 128.2, 127.6, 47.4, 38.4. HRMS (ESI): m/z calcd. for $C_{10}H_{10}NO_2^+$ 176.0706, found 176.0715 [M + H]$^+$.

Procedure for the Synthesis of Compound 6: A mixture of **4** (23.4 mg, 0.15 mmol) and concentrated HCl (1 mL) was refluxed for 24 h. After cooling, NaOH aqueous solution (2 M, 5 mL) was added. The aqueous layer was washed with diethyl ether (10 mL × 1), acidified by HCl (2 M), and extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried with anhydrous Na_2SO_4 and concentrated under vacuum to give compound **6**.

2-Phenylsuccinic Acid[18] **(6):** White solid, 25 mg, 85 % yield, m.p. 161–162 °C. ^{1}H NMR (400 MHz, [D$_4$]methanol): δ = 7.24–7.13 (m, 5 H), 3.91 (dd, J = 10.2, 5.2 Hz, 1 H), 3.00 (dd, J = 17.0, 10.2 Hz, 1 H), 2.51 (dd, J = 17.0, 5.2 Hz, 1 H). ^{13}C NMR (100 MHz, [D$_4$]methanol): δ = 176.4, 175.0, 139.6, 129.6, 128.7, 128.3, 48.4, 38.5. HRMS (ESI): m/z calcd. for $C_{10}H_9O_4^-$ 193.0506, found 193.0506 [M–H]$^-$.

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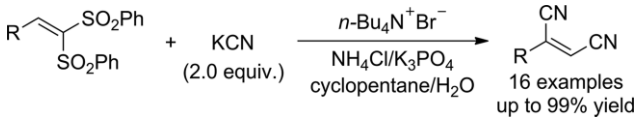
One-Pot Reaction



cis-1,2-Dicyanoalkenes can be synthesized in good to high yields by a transition-metal-free one-pot reaction of 1,1-bis(benzenesulfonyl)alkenes with KCN under phase-transfer conditions.

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