A Three-Component One-Pot Synthesis of Functionalized 5,5-Dicyanocyclopenta-1,3-dienes from Arylidenemalononitriles, Activated Acetylenes, and KCN or KSCN

by **Issa Yavari***, **Mehdi Sirouspour**, and **Sanaz Souri**

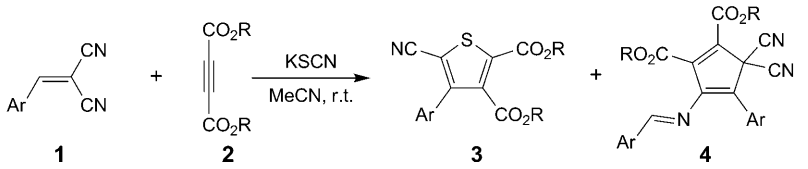
Chemistry Department, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran (phone: +98-21-82883465; fax: +98-21-82883455; e-mail: yavarisa@modares.ac.ir)

The reaction of dialkyl acetylenedicarboxylates with arylidenemalononitriles in the presence of KSCN in MeCN led to a mixture of dialkyl (3*E*)-4-aryl-3-(arylideneamino)-5,5-dicyanocyclopenta-1,3-diene-1,2-dicarboxylates and dialkyl 4-aryl-5-cyanothiophene-2,3-dicarboxylates. When these reactions were performed in the presence of KCN, only the functionalized 5,5-dicyanocyclopenta-1,3-dienes were obtained.

Introduction. – In view of our general interest in reactions involving zwitterionic species [1–4], we report on two three-component reactions involving KSCN or KCN, arylidenemalononitriles (**1**), and dialkyl acetylenedicarboxylates (**2**).

Results and Discussion. – The reaction of **1** and **2** in the presence of KSCN led to dialkyl 4-aryl-5-cyanothiophene-2,3-dicarboxylates (**3**) in 16–30% yields, together with minor amounts (10–15%) of dialkyl 4-aryl-3-[(*E*)-arylideneamino]-5,5-dicyanocyclopenta-1,3-diene-1,2-dicarboxylates (**4**; *Scheme 1*).

Scheme 1



1 **2** **3** **4**

1a Ar = 4-MeO–C_6H_4
1b Ar = 4-Me–C_6H_4
1c Ar = Ph
1d Ar = 4-Cl–C_6H_4
1e Ar = 4-NO_2–C_6H_4

2a R = Me
2b R = Et

	R	Ar	Yield of **3** [%]	Yield of **4** [%]
3a, **4a**	Me	4-MeO–C_6H_4	–	12
3b, **4b**	Et	4-MeO–C_6H_4	–	13
3c, **4c**	Me	4-Me–C_6H_4	30	12
3d, **4d**	Et	4-Me–C_6H_4	24	14
3e, **4e**	Me	Ph	21	15
3f, **4f**	Et	Ph	26	10
3g, **4g**	Me	4-Cl–C_6H_4	22	14
3h, **4h**	Et	4-Cl–C_6H_4	25	10
3i, **4i**	Me	4-NO_2–C_6H_4	16	–
3j, **4j**	Et	4-NO_2–C_6H_4	16	–

The structures of compounds **3** were established by spectroscopic methods. For example, the ^{1}H-NMR spectrum of **3c** exhibited three *singlet*s (at 2.40, 3.81, and 3.93 ppm) for the H-atoms of the Me and MeO groups, together with two characteristic *doublet*s (at 7.26 and 7.37 ppm) for the aromatic H-atoms. The ^{13}C-NMR spectrum of **3c** exhibited 14 signals in agreement with the proposed structure.

The structures of compounds **4a**–**4h** were deduced from their IR, and ^{1}H- and ^{13}C-NMR spectra, and, in case of **4a**, single-crystal X-ray analysis. The ^{1}H-NMR spectrum of **4a** exhibited five *singlet*s of the H-atoms of the MeO (at 3.79, 3.86, 3.87, and 3.95 ppm) and the H-atom of the imino group (at 8.35 ppm), together with four characteristic *doublet*s of the H-atoms of the two aromatic rings. The ^{1}H-decoupled ^{13}C-NMR spectrum of **4a** showed 21 distinct resonances which further confirmed the proposed structure. The ^{1}H- and ^{13}C-NMR spectra of **4b**–**4h** were similar to those for **4a** except for the ester moieties, which exhibited characteristic resonances in the appropriate regions of the spectra.

Unambiguous evidence for the structure of **4a** was obtained from a single-crystal X-ray analysis. An ORTEP [5] diagram of **4a** is displayed in the *Figure*. There are four molecules of **4a** in the unit cell. The structure deduced from the crystallographic experiment, by analogy, can be applied to the other products **4b**–**4h** on account of their NMR-spectroscopic similarities.

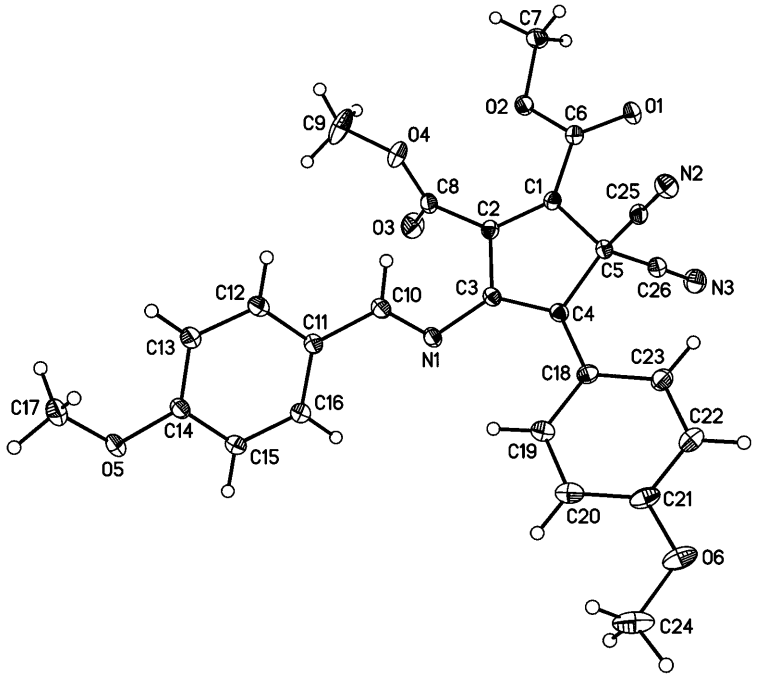
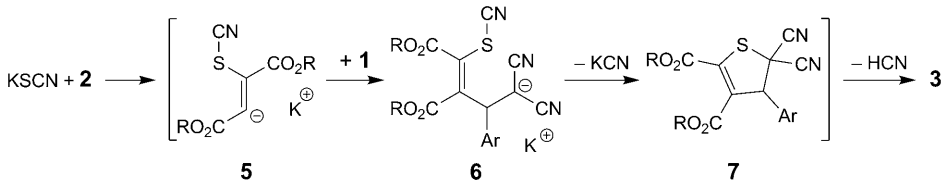


Figure. *X-Ray Crystal Structure of* **4a** (ORTEP-III plot [5], arbitrary atom numbering)

A plausible mechanism for the formation of compound **3** is proposed in *Scheme 2*. It is conceivable that the reaction involves the initial formation of anionic intermediate **5**

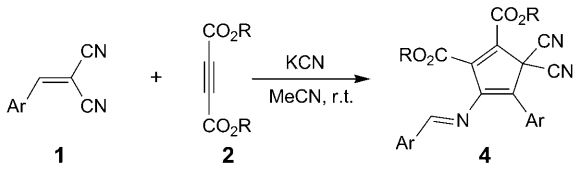
Scheme 2



from SCN^- and **2**, which reacts with **1** to produce **6**. Cyclization of this intermediate, followed by loss of CN^- and HCN, leads to **3**.

The appearance of two geminal CN groups in **4** encouraged us to assume that the formation of **4** involves the addition of a CN^- ion, released during the final steps of the formation of compound **3**. Thus, we repeated the reaction of **1** and **2** in the presence of KCN and obtained, indeed, only compounds **4** (Scheme 3) and as expected in yields higher than those achieved with KSCN.

Scheme 3



1a Ar = 4-MeO–C_6H_4
1b Ar = 4-Me–C_6H_4
1c Ar = Ph
1d Ar = 4-Cl–C_6H_4
1e Ar = 4-NO_2–C_6H_4

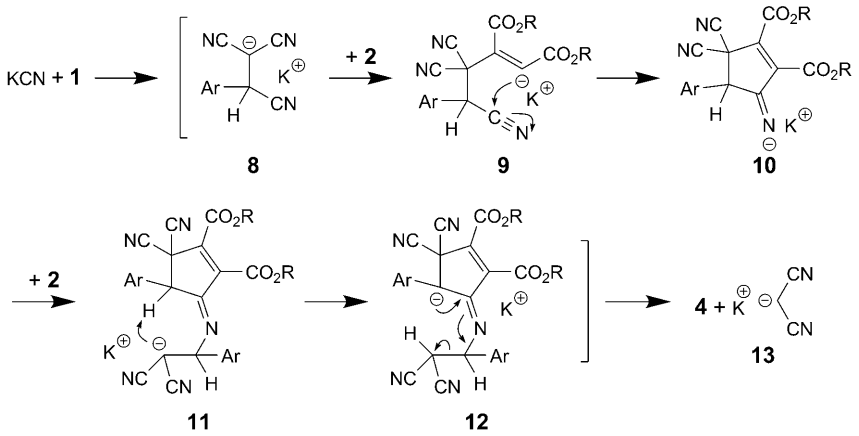
2a R = Me
2b R = Et

	R	Ar	Yield [%]
4a	Me	4-MeO–C_6H_4	24
4b	Et	4-MeO–C_6H_4	25
4c	Me	4-Me–C_6H_4	24
4d	Et	4-Me–C_6H_4	25
4e	Me	Ph	28
4f	Et	Ph	25
4g	Me	4-Cl–C_6H_4	38
4h	Et	4-Cl–C_6H_4	32
4i	Me	4-NO_2–C_6H_4	–
4j	Et	4-NO_2–C_6H_4	–

Although the mechanistic details of the formation of compounds **4** are not known, a plausible rationalization is proposed in *Scheme 4*. It is conceivable that the reaction starts with the formation of intermediate **8**, followed by addition of **2**, to generate **9**. Cyclization of this intermediate leads to **10**, which reacts with another molecule of **1** to form **11**. Intermediate **11** may undergo an intramolecular H-atom transfer, followed by elimination of dicyanomethanide, to give **4**.

In conclusion, we have described the use of KSCN and KCN as anionic nucleophiles in a reaction involving arylidenemalononitriles and acetylenedicarboxylates to produce dialkyl 4-aryl-5-cyanothiophene-2,3-dicarboxylates and dialkyl 4-aryl-3-[(*E*)-arylideneamino]-5,5-dicyanocyclopenta-1,3-diene-1,2-dicarboxylates. When the reaction was performed in the presence of KCN alone, only the latter products were obtained.

Scheme 4



Simple mixing of the starting materials and the potential diversity of the reaction are the advantages of this procedure.

Experimental Part

General. Dialkyl acetylenedicarboxylates, aldehydes, malononitrile, KSCN, and KCN were obtained from *Merck* and were used without further purification. Arylidenemalononitriles were prepared according to [6]. M.p.: *Electrothermal-9100* apparatus. IR Spectra (KBr, cm^{-1}): *Shimadzu IR-460* spectrometer. ^{1}H- and ^{13}C-NMR spectra: *Bruker DRX-500 Avance* instrument; in $CDCl_3$; at 500.1 and 125.7 MHz, resp.; δ in ppm, J in Hz. MS: *Finnigan-MAT-8430* mass spectrometer; at 70 eV; in m/z (rel. %). Elemental analyses (C, H, N): *Heraeus CHN-O-Rapid* analyzer.

Compounds **3** *and* **4**: *General Procedure.* To a stirred soln. of **1** (5 mmol) and **2** (2 mmol) in 10 ml of MeCN was added KSCN or KCN (2 mmol) at r.t. After completion of the reaction (2 h), as indicated by TLC (hexane/AcOEt, 5:1), the solvent was removed under reduced pressure, and the light brown residue was separated by column chromatography (SiO_2, 230–400 mesh, *Merck*; hexane/AcOEt) to afford the pure products.

Dimethyl 5-Cyano-4-(4-methylphenyl)thiophene-2,3-dicarboxylate (**3c**). Yield: 0.19 g (30%). Colorless crystals. M.p. 140–142°. IR: 1725, 1716, 1580, 1531, 1512, 1432, 1311, 1283, 1243, 1193, 1165, 1078, 991, 831. ^{1}H-NMR: 2.40 (*s*, Me); 3.81 (*s*, MeO); 3.93 (*s*, MeO); 7.26 (*d*, J = 7.9, 2 arom. H); 7.37 (*d*, J = 7.9, 2 arom. H). ^{13}C-NMR: 21.3 (Me); 53.2 (MeO); 53.3 (MeO); 110.7 (C); 112.9 (C); 128.2 (C); 128.3 (2 CH); 129.8 (2 CH); 135.4 (C); 138.9 (C); 140.2 (C); 150.5 (C); 159.8 (C=O); 164.3 (C=O). EI-MS: 317 (4, $[M + 2]^+$), 315 (100, M^+), 284 (90), 252 (85), 224 (50), 91 (5), 59 (40), 39 (36). Anal. calc. for $C_{16}H_{13}NO_4S$ (315.34): C 60.94, H 4.16, N 4.44; found: C 61.23, H 4.24, N 4.30.

Diethyl 5-Cyano-4-(4-methylphenyl)thiophene-2,3-dicarboxylate (**3d**). Yield: 0.16 g (24%.). Colorless crystals. M.p. 145–147°. IR: 1727, 1718, 1585, 1532, 1432, 1314, 1281, 1240, 1196, 1166, 1077, 995, 829. ^{1}H-NMR: 1.40 (*t*, J = 7.2, Me); 1.49 (*t*, J = 7.2, Me); 2.40 (*s*, Me); 4.38 (*q*, J = 7.2, CH_2O); 4.44 (*q*, J = 7.2, CH_2O); 7.30 (*d*, J = 7.7, 2 arom. H); 7.52 (*d*, J = 7.7, 2 arom. H). ^{13}C-NMR: 13.9 (Me); 14.1 (Me); 21.3 (Me); 62.6 (CH_2O); 63.1 (CH_2O); 109.5 (C); 111.1 (C); 127.2 (C); 127.4 (2 CH); 130.4 (2 CH); 135.4 (C); 138.8 (C); 140.6 (C); 150.4 (C); 158.5 (C=O); 162.3 (C=O). EI-MS: 345 (3, $[M + 2]^+$), 343 (100, M^+), 298 (95), 197 (50), 196 (65), 91 (10), 59 (52), 39 (45). Anal. calc. for $C_{18}H_{17}NO_4S$ (343.39): C 62.96, H 4.99, N 4.08; found: C 63.19, H 5.11, N 4.19.

Dimethyl 5-Cyano-4-phenylthiophene-2,3-dicarboxylate (**3e**). Yield: 0.13 g (21%). Colorless crystals. M.p. 134–136°. IR: 1725, 1715, 1590, 1545, 1430, 1315, 1247, 1199, 1171, 1080, 997, 824, 768. ^{1}H-NMR: 3.79

(*s*, MeO); 3.92 (*s*, MeO); 7.45–7.49 (*m*, 5 arom. H). ^{13}C-NMR: 53.0 (MeO); 53.3 (MeO); 111.0 (C); 112.7 (C); 128.4 (2 CH); 128.9 (2 CH); 129.6 (CH); 129.8 (C); 130.6 (C); 138.9 (C); 150.3 (C); 159.8 (C=O); 164.2 (C=O). EI-MS: 303 (5), 301 (100, M^+), 272 (85), 185 (40), 184 (60), 77 (60), 80 (10), 39 (55). Anal. calc. for $C_{15}H_{11}NO_4S$ (301.31): C 59.79, H 3.68, N 4.65; found: C 59.45, H 3.60, N 4.76.

Diethyl 5-Cyano-4-phenylthiophene-2,3-dicarboxylate (**3f**). Yield: 0.17 g (26%). Colorless crystals. M.p. 139–140°. IR: 1727, 1716, 1591, 1549, 1430, 1315, 1241, 1203, 1179, 1080, 995, 741. ^{1}H-NMR: 1.35 (*t*, *J* = 7.0, Me); 1.40 (*t*, *J* = 7.1, Me); 4.37 (*q*, *J* = 7.0, CH_2O); 4.41 (*q*, *J* = 7.1, CH_2O); 7.43–7.47 (*m*, 5 arom. H). ^{13}C-NMR: 13.9 (Me); 14.0 (Me); 62.5 (CH_2O); 62.9 (CH_2O); 111.1 (C); 112.8 (C); 128.0 (2 CH); 128.6 (2 CH); 129.7 (CH); 129.8 (C); 130.8 (C); 138.7 (C); 150.2 (C); 159.8 (C=O); 164.2 (C=O). EI-MS: 331 (7, $[M+2]^+$), 329 (100, M^+), 284 (85), 199 (40), 77 (64), 39 (50). Anal. calc. for $C_{17}H_{15}NO_4S$ (329.42): C 61.99, H 4.59, N 4.25; found: C 59.95, H 4.61, N 4.66.

Dimethyl 4-(4-Chlorophenyl)-5-cyanothiophene-2,3-dicarboxylate (**3g**). Yield: 0.15 g (22%). Colorless crystals. M.p. 144–146°. IR: 1729, 1717, 1590, 1521, 1437, 1284, 1249, 1194, 1165, 1007, 993, 960, 899, 848, 816. ^{1}H-NMR: 3.80 (*s*, MeO); 3.93 (*s*, MeO); 7.41 (*d*, *J* = 7.5, 2 arom. H); 7.45 (*d*, *J* = 7.5, 2 arom. H). ^{13}C-NMR: 53.3 (MeO); 53.4 (MeO); 111.3 (C); 112.5 (C); 129.4 (C); 129.5 (2 CH); 129.8 (2 CH); 135.8 (C); 136.3 (C); 138.7 (C); 148.9 (C); 159.6 (C=O); 163.9 (C=O). EI-MS: 338 (6, $[M+2]^+$), 336 (100, M^+), 304 (90), 217 (40), 216 (60), 111 (10), 80 (5), 77 (50), 59 (35), 39 (38). Anal. calc. for $C_{15}H_{10}ClNO_4S$ (335.76): C 53.66, H 3.00, N 4.17; found: C 53.50, H 2.95, N 4.16.

Diethyl 4-(4-Chlorophenyl)-5-cyanothiophene-2,3-dicarboxylate (**3h**). Yield: 0.18 g (25%). Colorless crystals. M.p. 151–153°. IR: 1728, 1718, 1592, 1519, 1440, 1280, 1248, 1194, 1163, 1005, 990, 962, 893, 845, 811. ^{1}H-NMR: 1.37 (*t*, *J* = 7.2, Me); 1.43 (*t*, *J* = 7.2, Me); 4.40 (*q*, *J* = 7.2, CH_2O); 4.44 (*q*, *J* = 7.2, CH_2O); 7.47 (*d*, *J* = 7.6, 2 arom. H); 7.57 (*d*, *J* = 7.6, 2 arom. H). ^{13}C-NMR: 13.8 (Me); 13.9 (Me); 62.7 (CH_2O); 63.2 (CH_2O); 110.9 (C); 111.4 (C); 129.4 (C); 129.5 (2 CH); 129.9 (2 CH); 134.7 (C); 142.3 (C); 143.9 (C); 152.1 (C); 158.4 (C=O); 162.0 (C=O). EI-MS: 366 (4, $[M+2]^+$), 364 (100, M^+), 318 (95), 217 (55), 216 (65), 112 (5), 80 (10), 77 (55), 39 (48). Anal. calc. for $C_{17}H_{14}ClNO_4S$ (363.81): C 56.12, H 3.88, N 3.85; found: C 56.15, H 3.85, N 3.80.

Dimethyl 5-Cyano-4-(4-nitrophenyl)thiophene-2,3-dicarboxylate (**3i**). Yield: 0.11 g (16%). Pale yellow crystals. M.p. 161–163°. IR: 1735, 1724, 1593, 1521, 1434, 1346, 1283, 1246, 1200, 1170, 1105, 1107, 1005, 990, 866, 835, 744. ^{1}H-NMR: 3.80 (*s*, MeO); 3.94 (*s*, MeO); 7.65 (*d*, *J* = 7.7, 2 arom. H); 8.31 (*d*, *J* = 7.7, 2 arom. H). ^{13}C-NMR: 53.4 (MeO); 53.5 (MeO); 112.0 (C); 112.3 (C); 124.1 (2 CH); 127.2 (C); 129.7 (2 CH); 136.5 (C); 137.0 (C); 147.5 (C); 148.6 (C); 159.3 (C=O); 163.5 (C=O). EI-MS: 348 (4, $[M+2]^+$), 346 (100, M^+), 315 (61), 287 (40), 77 (20), 39 (10). Anal. calc. for $C_{15}H_{10}N_2O_6S$ (346.31): C 54.02, H 2.91, N 8.09; found: C 54.50, H 3.00, N 8.22.

Diethyl 5-Cyano-4-(4-nitrophenyl)thiophene-2,3-dicarboxylate (**3j**). Yield: 0.12 g (16%). Pale yellow crystals. M.p. 154–156°. IR: 1735, 1724, 1593, 1521, 1434, 1346, 1283, 1246, 1200, 1170, 1105, 1107, 1005, 990, 866, 835, 744. ^{1}H-NMR: 1.40 (*t*, *J* = 7.0, Me); 1.45 (*t*, *J* = 7.1, Me); 4.42 (*q*, *J* = 7.0, CH_2O); 4.46 (*q*, *J* = 7.1, CH_2O); 7.64 (*d*, *J* = 7.7, 2 arom. H); 8.30 (*d*, *J* = 7.7, 2 arom. H). ^{13}C-NMR: 14.2 (Me); 14.6 (Me); 63.0 (CH_2O); 63.3 (CH_2O); 112.1 (C); 112.2 (C); 124.1 (2 CH); 127.0 (C); 129.6 (2 CH); 136.6 (C); 136.8 (C); 147.2 (C); 148.2 (C); 159.4 (C=O); 163.6 (C=O). EI-MS: 376 (6, $[M+2]^+$), 374 (100, M^+), 329 (61), 301 (40), 77 (24), 39 (15). Anal. calc. for $C_{17}H_{14}N_2O_6S$ (374.43): C 54.54, H 3.77, N 7.48; found: C 54.40, H 3.67, N 7.52.

*Dimethyl 5,5-Dicyano-4-(4-methoxyphenyl)-3-{[(*E*)-(4-methoxyphenyl)methylidene]amino}cyclopenta-1,3-diene-1,2-dicarboxylate* (**4a**). Yield: 0.23 g (24%). Orange crystals. M.p. 180–182°. IR (KBr): 1735, 1728, 1593, 1564, 1525, 1501, 1427, 1323, 1297, 1254, 1232, 1181, 1024, 950, 828, 788, 729, 694. ^{1}H-NMR: 3.79 (*s*, MeO); 3.86 (*s*, MeO); 3.87 (*s*, MeO); 3.95 (*s*, MeO); 6.93 (*d*, *J* = 8.4, 2 arom. H); 6.98 (*d*, *J* = 8.3, 2 arom. H); 7.78 (*d*, *J* = 8.4, 2 arom. H); 7.81 (*d*, ^3J = 8.3, 2 arom. H); 8.35 (*s*, CH). ^{13}C-NMR: 29.6 (C); 53.1 (MeO); 53.2 (MeO); 55.3 (MeO); 55.5 (MeO); 110.8 (CN); 114.6 (2 CH); 114.8 (2 CH); 121.9 (C); 124.9 (C); 127.6 (C); 127.8 (C); 129.8 (2 CH); 131.4 (2 CH); 147.9 (C); 150.8 (C); 159.1 (C); 160.6 (C); 162.6 (C=N); 163.9 (C=O); 165.2 (C=O). EI-MS: 471 (82, M^+), 456 (21), 440 (15), 412 (18), 205 (7), 107 (100), 77 (64), 39 (55). Anal. calc. for $C_{26}H_{21}N_3O_6$ (471.47): C 66.24, H 4.49, N 8.91; found: C 66.30, H 4.50, N 8.80.

X-Ray Crystal-Structure of **4a**. Structure-determination and refinement data: $C_{26}H_{21}N_3O_6$, M_r 471.46, crystal size, 0.30 × 0.20 × 0.20 mm^3, monoclinic, *a* = 14.5839(7) Å, *b* = 8.9554(4) Å, *c* = 19.7705(10) Å;

$\alpha = 90°, \beta = 111.1520(10)°, \gamma = 90°$; space group $P2_1/n$; $Z = 4$, $V = 2381.3(2)$ Å^3, $D_{calc.} = 1.315$ g cm^{-3}; $R = 0.0456$ (for 6555 reflections); $R_w = 0.0676$; $-21 \le h \le 22$; $-13 \le k \le 13$; $-29 \le l \le 29°$; MoK_α radiation ($\lambda = 0.71073$ Å); $T = 100(2)$ K[1]).

*Diethyl 5,5-Dicyano-4-(4-methoxyphenyl)-3-{[(*E*)-(4-methoxyphenyl)methylidene]amino}cyclopenta-1,3-diene-1,2-dicarboxylate* (**4b**). Yield: 0.25 g (25%). Orange crystals. M.p. 184–186°. IR (KBr): 1735, 1725, 1593, 1560, 1533, 1501, 1428, 1320, 1291, 1254, 1233, 1184, 1020, 950, 827, 785, 730, 697. ^{1}H-NMR: 1.28 (*t*, *J* = 7.1, Me); 1.40 (*t*, *J* = 7.1, Me); 3.81 (*s*, MeO); 3.85 (*s*, MeO); 4.32 (*q*, *J* = 7.1, CH_2O); 4.38 (*q*, *J* = 7.1, CH_2O); 6.92 (*d*, *J* = 8.5, 2 arom. H); 6.97 (*d*, *J* = 8.5, 2 arom. H); 7.75 (*d*, *J* = 8.5, 2 arom. H); 7.87 (*d*, *J* = 8.5, 2 arom. H); 8.37 (*s*, CH). ^{13}C-NMR: 14.0 (Me); 14.1 (Me); 29.5 (C); 55.4 (MeO); 55.6 (MeO); 62.3 (CH_2O); 62.5 (CH_2O); 110.7 (CN); 114.6 (2 CH); 114.9 (2 CH); 121.8 (C); 124.9 (C); 127.7 (C); 127.9 (C); 129.9 (2 CH); 131.5 (2 CH); 147.7 (C); 150.6 (C); 159.2 (C); 160.6 (C); 162.5 (C=N); 163.8 (C=O); 165.3 (C=O). EI-MS: 500 (75, M^+), 471 (19), 430 (14), 402 (26), 393 (45), 107 (100), 77 (59), 39 (51). Anal. calc. for $C_{28}H_{25}N_3O_6$ (499.52): C 67.33, H 5.04, N 8.41; found: C 67.50, H 5.16, N 8.30.

*Dimethyl 5,5-Dicyano-4-(4-methylphenyl)-3-{[(*E*)-(4-methylphenyl)methylidene]amino}cyclopenta-1,3-diene-1,2-dicarboxylate* (**4c**). Yield: 0.21 g (24%). Yellow crystals. M.p. 175–177°. IR (KBr): 1742, 1735, 1623, 1617, 1561, 1493, 1430, 1324, 1294, 1231, 1175, 1054, 1014, 950, 811, 774, 729, 698. ^{1}H-NMR: 2.32 (*s*, Me); 2.42 (*s*, Me); 3.87 (*s*, MeO); 3.97 (*s*, MeO); 7.21 (*d*, *J* = 8.2, 2 arom. H); 7.29 (*d*, *J* = 8.0, 2 arom. H); 7.69 (*d*, *J* = 8.2, 2 arom. H); 7.72 (*d*, *J* = 8.0, 2 arom. H); 8.37 (*s*, CH). ^{13}C-NMR: 21.3 (Me); 21.7 (Me); 29.7 (C); 53.1 (MeO); 53.2 (MeO); 110.6 (CN); 125.7 (C); 126.3 (C); 128.1 (2 CH); 129.0 (C); 129.5 (2 CH); 129.8 (2 CH); 129.9 (2 CH); 132.0 (C); 140.1 (C); 144.3 (C); 149.1 (C); 150.6 (C); 159.0 (C=N); 162.4 (C=O); 166.2 (C=O). EI-MS: 439 (85, M^+), 392 (25), 364 (14), 348 (55), 321 (30), 146 (100), 91 (90), 59 (74). Anal. calc. for $C_{26}H_{21}N_3O_4$ (439.47): C 71.06, H 4.82, N 9.56; found: C 71.01, H 4.94, N 9.65.

*Diethyl 5,5-Dicyano-4-(4-methylphenyl)-3-{[(*E*)-(4-methylphenyl)methylidene]amino}cyclopenta-1,3-diene-1,2-dicarboxylate* (**4d**). Yield: 0.23 g (25%). Yellow crystals. M.p. 172–174°. IR (KBr): 1737, 1730, 1620, 1612, 1555, 1492, 1435, 1322, 1290, 1225, 1165, 1050, 1014, 956, 810, 777, 730, 700. ^{1}H-NMR: 1.29 (*t*, *J* = 7.1, Me); 1.43 (*t*, *J* = 7.1, Me); 2.36 (*s*, Me); 2.45 (*s*, Me); 4.36 (*q*, *J* = 7.1, CH_2O); 4.45 (*q*, *J* = 7.1, CH_2O); 7.23 (*d*, *J* = 8.1, 2 arom. H); 7.31 (*d*, *J* = 8.1, 2 arom. H); 7.70 (*d*, *J* = 8.1, 2 arom. H); 7.73 (*d*, *J* = 8.1, 2 arom. H); 8.41 (*s*, CH). ^{13}C-NMR: 13.9 (Me); 14.0 (Me); 21.2 (Me); 21.7 (Me); 29.6 (C); 62.5 (CH_2O); 62.7 (CH_2O); 110.8 (CN); 125.6 (C); 126.4 (C); 128.1 (2 CH); 128.8 (C); 129.3 (2 CH); 129.8 (2 CH); 129.9 (2 CH); 132.1 (C); 140.0 (C); 144.2 (C); 149.2 (C); 150.5 (C); 158.5 (C=N); 162.0 (C=O); 166.1 (C=O). EI-MS: 468 (75, M^+), 439 (20), 398 (25), 370 (31), 146 (100), 91 (85), 59 (70). Anal. calc. for $C_{28}H_{25}N_3O_4$ (467.52): C 71.93, H 5.39, N 8.99; found: C 71.45, H 5.44, N 8.88.

*Dimethyl 5,5-Dicyano-4-phenyl-3-{[(*E*)-phenylmethylidene]amino}cyclopenta-1,3-diene-1,2-dicarboxylate* (**4e**). Yield: 0.23 g (28%). Bright yellow crystals. M.p. 165–167°. IR (KBr): 1725, 1717, 1611, 1564, 1523, 1425, 1317, 1265, 1210, 1154, 1040, 763, 678. ^{1}H-NMR: 3.89 (*s*, MeO); 3.99 (*s*, MeO); 7.37 (*t*, *J* = 7.2, CH); 7.42 (*t*, *J* = 7.1, 2 arom. H); 7.49 (*t*, *J* = 7.7, 2 arom. H); 7.58 (*t*, *J* = 7.5, CH); 7.80 (*d*, *J* = 7.6, 2 arom. H); 7.83 (*d*, *J* = 7.1, 2 arom. H); 8.43 (*s*, CH). ^{13}C-NMR: 33.0 (C); 53.2 (MeO); 53.3 (MeO); 110.4 (CN); 125.9 (C); 126.3 (C); 128.2 (CH); 129.0 (C); 129.1 (CH); 129.2 (2 CH); 129.5 (2 CH); 129.7 (2 CH); 133.3 (2 CH); 134.4 (C); 149.7 (C); 150.3 (C); 158.9 (C=N); 162.2 (C=O); 166.7 (C=O). EI-MS: 411 (68, M^+), 396 (25), 365 (22), 337 (30), 334 (46), 77 (100), 39 (57). Anal. calc. for $C_{24}H_{17}N_3O_4$ (411.41): C 70.07, H 4.16, N 10.21; found: C 70.12, H 4.23, N 10.27.

*Diethyl 5,5-Dicyano-4-phenyl-3-{[(*E*)-phenylmethylidene]amino}cyclopenta-1,3-diene-1,2-dicarboxylate* (**4f**). Yield: 0.22 g (25%). Bright yellow crystals. M.p. 173–175°. IR (KBr): 1729, 1721, 1614, 1560, 1522, 1425, 1321, 1265, 1205, 1150, 1040, 764, 678. ^{1}H-NMR: 1.25 (*t*, *J* = 7.1, Me); 1.40 (*t*, *J* = 7.1, Me); 4.34 (*q*, *J* = 7.1, CH_2O); 4.42 (*q*, *J* = 7.1, CH_2O); 7.36 (*t*, *J* = 7.5, CH); 7.42 (*t*, *J* = 7.1, 2 arom. H); 7.49 (*t*, *J* = 7.6, 2 arom. H); 7.59 (*t*, *J* = 7.5, CH); 7.80 (*d*, *J* = 7.6, 2 arom. H); 7.85 (*d*, *J* = 7.1, 2 arom. H); 8.42 (*s*, CH). ^{13}C-NMR: 13.9 (Me); 14.0 (Me); 32.8 (C); 62.8 (CH_2O); 62.9 (CH_2O); 110.5 (CN); 126.2 (C); 126.3 (C);

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[1]) The crystallographic data of **4a** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-753003. Copies of the data can be obtained, free of charge, *via* the internet (http://www.ccdc.cam.ac.uk/data_request/cif), e-mail (data_request@ccdc.cam.ac.uk), or fax (+44-1223-336033).

128.0 (CH); 129.1 (C); 129.3 (CH); 129.4 (2 CH); 129.5 (2 CH); 129.8 (2 CH); 133.3 (2 CH); 134.4 (C); 149.8 (C); 150.1 (C); 159.7 (C=N); 162.3 (C=O); 166.6 (C=O). EI-MS: 439 (80, M^+), 410 (19), 369 (24), 362 (54), 341 (45), 77 (100), 39 (62). Anal. calc. for $C_{26}H_{21}N_3O_4$ (439.47): C 71.06, H 4.82, N 9.56; found: C 70.94, H 4.90, N 9.70.

*Dimethyl 4-(4-Chlorophenyl)-3-{[(*E*)-(4-chlorophenyl)methylidene]amino}-5,5-dicyanocyclopenta-1,3-diene-1,2-dicarboxylate* (**4g**). Yield: 0.36 g (38%). Yellow crystals. M.p. 169–171°. IR (KBr): 1720, 1713, 1609, 1583, 1556, 1521, 1478, 1427, 1322, 1288, 1261, 1209, 1164, 1084, 1054, 1005, 820, 771. ^{1}H-NMR: 3.89 (*s*, MeO); 3.99 (*s*, MeO); 7.40 (*d*, *J* = 8.7, 2 arom. H); 7.48 (*d*, *J* = 8.4, 2 arom. H); 7.71 (*d*, *J* = 8.7, 2 arom. H); 7.77 (*d*, *J* = 8.4, 2 arom. H); 8.39 (*s*, CH). ^{13}C-NMR: 29.7 (C); 53.3 (MeO); 53.4 (MeO); 110.1 (CN); 126.7 (C); 127.4 (C); 129.4 (2 CH); 129.6 (2 CH); 129.7 (2 CH); 130.6 (2 CH); 130.8 (C); 132.7 (C); 136.2 (C); 140.1 (C); 149.6 (C); 149.7 (C); 158.8 (C=N); 162.1 (C=O); 165.5 (C=O). EI-MS: 482 (5, $[M+2]^+$), 480 (78, M^+), 465 (19), 434 (24), 406 (50), 370 (65), 77 (100), 39 (65). Anal. calc. for $C_{24}H_{15}Cl_2N_3O_4$ (480.30): C 60.02, H 3.15, N 8.75; found: C 60.11, H 3.13, N 8.72.

*Diethyl 4-(4-Chlorophenyl)-3-{[(*E*)-(4-chlorophenyl)methylidene]amino}-5,5-dicyanocyclopenta-1,3-diene-1,2-dicarboxylate* (**4h**). Yield: 0.33 g (32%). Bright yellow crystals. M.p. 178–180°. IR (KBr): 1725, 1715, 1602, 1581, 1550, 1520, 1471, 1425, 1321, 1289, 1265, 1205, 1160, 1085, 1050, 1003, 824, 770. ^{1}H-NMR: 1.26 (*t*, *J* = 7.0, Me); 1.43 (*t*, *J* = 7.1, Me); 4.37 (*q*, *J* = 7.0, CH_2O); 4.45 (*q*, *J* = 7.1, CH_2O); 7.42 (*d*, *J* = 8.4, 2 arom. H); 7.50 (*d*, *J* = 8.1, 2 arom. H); 7.74 (*d*, *J* = 8.4, 2 arom. H); 7.79 (*d*, *J* = 8.1, 2 arom. H); 8.42 (*s*, CH). ^{13}C-NMR: 14.0 (Me); 14.1 (Me); 29.7 (C); 62.8 (CH_2O); 62.9 (CH_2O); 110.3 (CN); 126.7 (C); 127.5 (C); 129.4 (2 CH); 129.6 (2 CH); 129.7 (2 CH); 130.6 (2 CH); 131.1 (C); 132.7 (C); 136.1 (C); 139.8 (C); 149.5 (C); 149.7 (C); 158.3 (C=N); 161.7 (C=O); 165.3 (C=O). EI-MS: 510 (4, $[M+2]^+$), 508 (70, M^+), 479 (21), 438 (25), 410 (32), 397 (40), 77 (100), 39 (61). Anal. calc. for $C_{26}H_{19}Cl_2N_3O_4$ (508.36): C 61.43, H 3.77, N 8.27; found: C 61.45, H 3.72, N 8.32.

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