# 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**

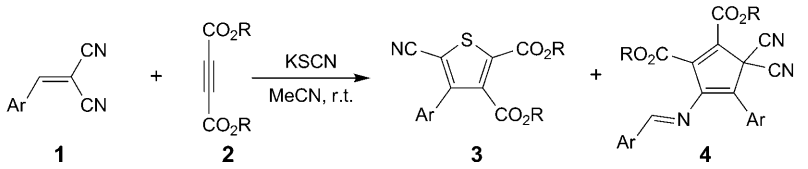
Chemistry Department, Tarbiat Modares University, P.O. Box 14115-175, Tehran, Iran (phone: +98-21-82883465; fax: +98-21-82883455; e-mail: yavarisa@modares.ac.ir)

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*




**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 | – |

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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.

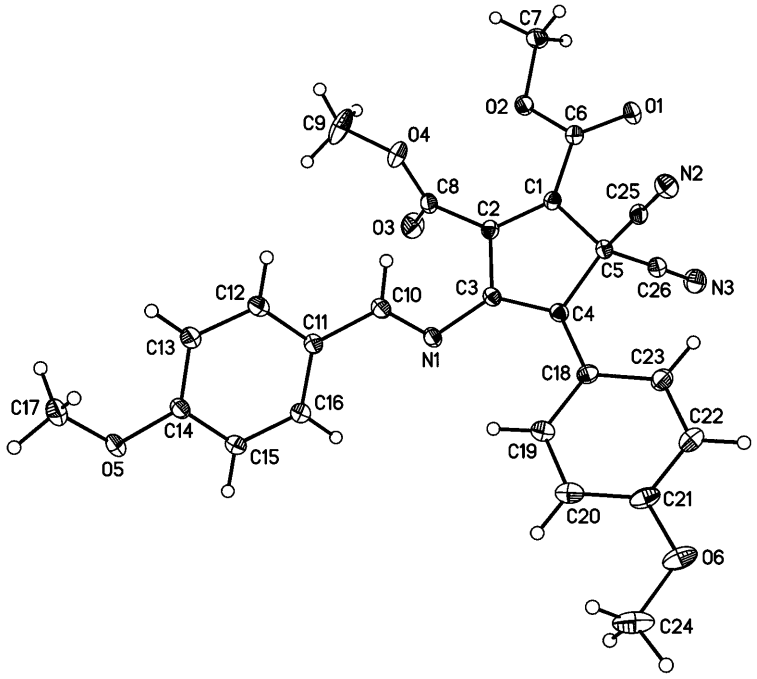
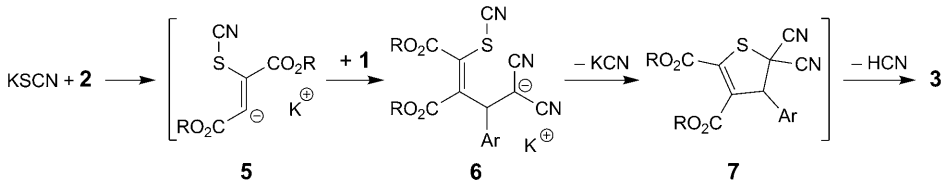



Figure. *X-Ray Crystal Structure of* **4a** (ORTEP-III plot [5], arbitrary atom numbering)

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**

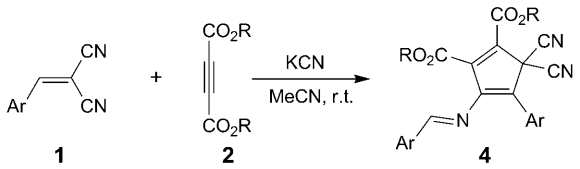
*Scheme 2*




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-$NO_2$–$C_6H_4$

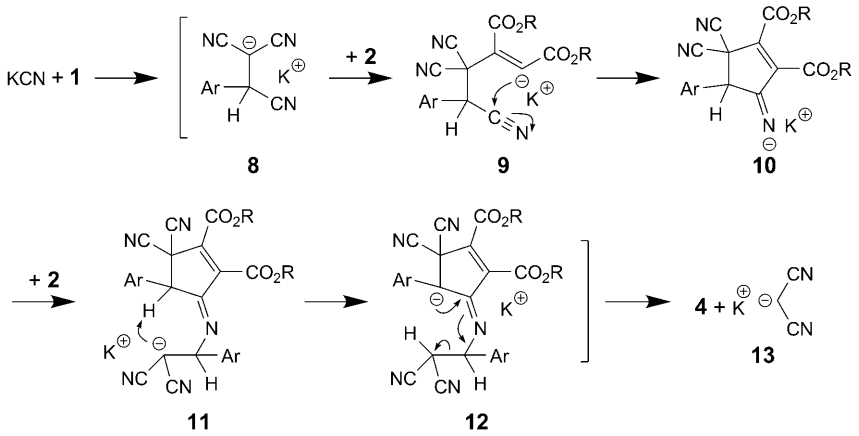
**2a** R = Me
**2b** R = Et

| | 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.; $\delta$ 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); $R_w = 0.0676$; $-21 \le h \le 22$; $-13 \le k \le 13$; $-29 \le l \le 29°$; Mo$K_\alpha$ 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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