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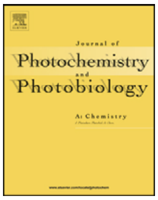

Selective photochemical monoalkylation of active methylene compounds by alkenes. A green pathway for carbon–carbon bond formation

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ABSTRACT

A novel photochemical method for selective α-monoalkylation of active methylene compounds has been developed. Aryl substituted alkenes and an aliphatic diene can be used as alkyl sources for these reactions, which proceed via polycyanoarene sensitized, photoinduced electron transfer pathways that are promoted using very mild conditions (ambient temperature, without noble metals and halogens, and with weak bases such as alkali metal carbonate). The reactions that comprise the new synthetic methods developed in this effort are both safe and environmentally friendly. Especially noteworthy is the fact that photochemical alkylation reactions of β-ketoesters (e.g., acetoacetic and malonic esters) can be used in the place of conventional strong base promoted processes.

1. Introduction

Processes that directly transform carbon–hydrogen bonds into carbon–carbon bonds are important synthetic methods [1–5]. However, from an ecological viewpoint [6,7], most of these reactions are problematic owing to the fact that they rely on the use of noble metal catalysts. Among various substrates explored for these processes, active methylene compounds (**1**) including enolizable β-dicarbonyl compounds are perhaps the most prominent owing to the relatively high acidities of their methylene groups [8–17]. Treatment of these substances with strong bases, such as sodium hydride, results in formation of the corresponding anions, which undergo C–C bond forming reactions with alkyl halides via nucleophilic substitution (Scheme 1a) [18–21]. The use of β-ketoesters in this fashion comprises well-known synthetic methods to obtain methyl ketones (acetoacetic ester synthesis) [11–13] and carboxylic acids (malonic ester synthesis) [14–17].

The alkylation reactions, however, do not always afford the desired products in high yields owing to the intervention of side reactions. For example, over alkylation easily occurs to give undesirable symmetrically disubstituted products (Scheme 1b) [18]. Also, the anions of active methylene compounds tend to oligomerize (Scheme 1c) [8–10]. Highly efficient dimerization of β-dicarbonyl compounds via one-electron oxidation by cerium(IV) ammonium nitrate (CAN) has been reported (Scheme 2) [22].

Methods have been explored to circumvent problems inherent in base promoted alkylation reactions of β-dicarbonyl compounds that are associated with the severe control of reaction conditions [18] and indirect synthetic routes [23–27]. Recently, we have explored a photochemical approach, aimed at solving the problems seen with these reactions [28,29]. This effort led to the development of a novel and facile method for direct α-monoalkylation of propanedinitrile (**1a**, malononitrile) that occurs in the absence of noble metal catalysts via photochemical polar addition (PPA) [30–33] and photo-NOCAS (photochemical nucleophile–olefin combination, aromatic substitution) [34–38] mechanistic pathways. The photoreaction proceeds efficiently under mild and environmentally friendly conditions [28,29]. In further investigations in this area we have observed that the photochemical process can be generally applied to α-monoalkylation reactions of a host of active methylene compounds (**1**) (Schemes 3–5). The results of this recent effort are described below.

2. Experimental

2.1. General

Melting points were taken on YANACO MP-500 apparatus and uncorrected. NMR spectra were recorded on Varian Mercury 300 spectrometer (300 and 75 MHz for ^{1}H and ^{13}C, respectively) using tetramethylsilane as an internal standard. MS (EI$^+$) were measured

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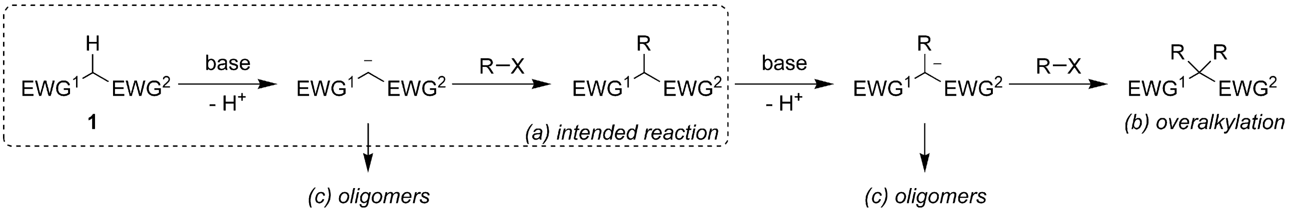
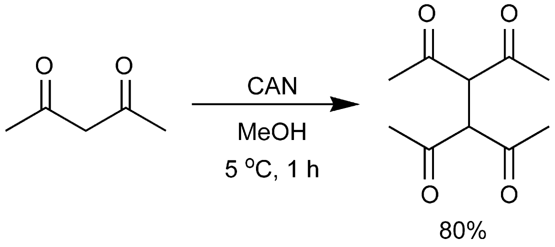


Scheme 1. Conventional monoalkylation reactions of active methylene compounds (**1**). EWG represents electron-withdrawing group.

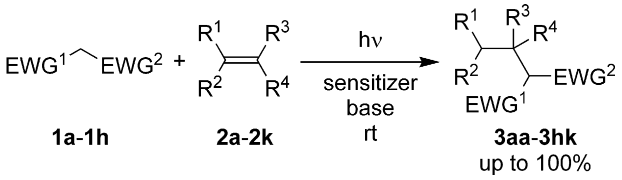


Scheme 2. Dimerization of acetylacetone via CAN oxidation.

by Shimadzu QP-5050 mass spectrometer with Shimadzu GC-17A gas chromatograph. HRMS (EI$^+$ and FAB$^+$) were measured by JEOL JMS-700 mass spectrometer. IR spectra were obtained from JASCO FT/IR-230 spectrophotometer. Elemental analyses were carried out on YANACO MT-6 or J-SCIENCE LAB JM-10 elemental analyzer. X-ray crystallographic analyses were performed on Rigaku RAXIS-RAPID diffractometer. Chiral gas–liquid chromatographic analyses (chiral GC) were performed on Shimadzu GC-2014 gas chromatograph with SPELCO GAMMA DEX 225 column, and recorded on Shimadzu C-R8A data processor. Preparative HPLCs were performed by the use of JASCO Megapak GEL 201C column (GPC), JASCO PU-986 pump, and Shodex RI-72 detector. Photoreactions were conducted under irradiation of Eikohsha EHB-W-300 high-pressure mercury lamp (300 W) through a Pyrex filter.

2.2. Materials

Acetonitrile was distilled over CaH_2 and then P_2O_5 before use. Water was deionized by ion-exchange resin. Benzene was distilled over CaH_2 and then over Na wire. 9-Cyanophenanthrene (9-CP) and di-*l*-menthyl naphthalene-1,4-dicarboxylate (**6**) were prepared by cyanation of 9-bromophenanthrene and esterification of naphthalene-1,4-dicarboxylic acid, respectively. The other materials were purchased and used without further purification.



Scheme 3. Photochemical monoalkylation of **1** using PPA reaction.

2.3. Typical procedure for PPA reactions (Table 1, entry 1)

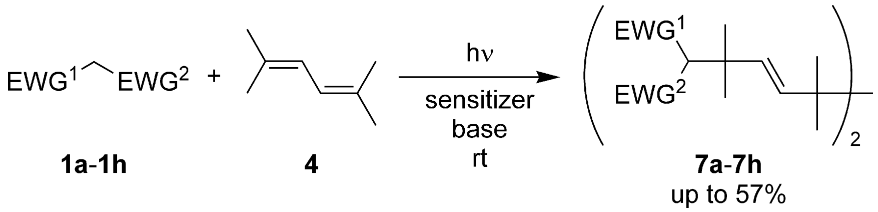
To a Pyrex glass tube (1 cmØ) was added an acetonitrile (4 mL)–water (1 mL) solution containing **1a** (165 mg, 2.5 mmol), **2a** (13.5 mg, 75 µmol), 9-CP (5.1 mg, 25 µmol), and Li_2CO_3 (92.4 mg, 1.25 mmol). Argon gas was then bubbled through the solution for 5 min before it is sealed with a rubber septum and irradiated for 20 h using a 300-W high-pressure mercury lamp. The reaction mixture was then neutralized by addition of aqueous HCl and extracted with ether. The organic extracts were concentrated in vacuo giving a residue, which was subjected to ^1H NMR analysis using CH_2Br_2 as an internal standard to determine the yields of **3aa** as 91%. Purification by silica gel chromatography (ethyl acetate after toluene) followed by HPLC (GPC column, chloroform) gave pure **3aa** as a colourless solid.

2.4. Typical procedure for oxidative photodimerization reactions (Table 3, entry 1)

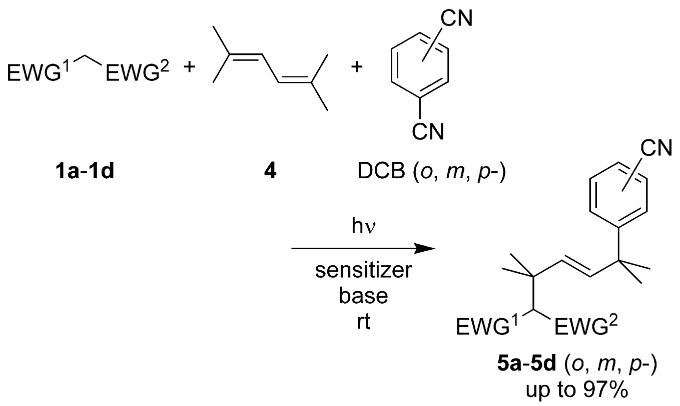
To a Pyrex glass tube (1 cmØ) was added an acetonitrile (4 mL)–water (1 mL) solution containing **1a** (165 mg, 2.5 mmol), **4** (8.3 mg, 75 µmol), Li_2CO_3 (92.4 mg, 1.25 mmol), and 9-CP (5.1 mg, 25 µmol). Argon gas was bubbled through the solution for 5 min before it is sealed with a rubber septum and irradiated for 20 h using a 300-W high-pressure mercury lamp. The reaction mixture was then neutralized by addition of aqueous HCl and extracted with toluene–ether. The organic extracts were concentrated in vacuo giving a residue (52% yield, determined by ^1H NMR analysis using CH_2Br_2 as an internal standard), which was subjected to column chromatography on silica gel (ethyl acetate after toluene) to give a crude product mixture. Further purification by HPLC (GPC column, chloroform) gave **7a** as a colourless solid.

2.5. Typical procedure for three-component coupling reactions (Table 4, entry 1)

To a Pyrex glass tube (1 cmØ) was added an acetonitrile (4 mL)–water (1 mL) solution containing **1a** (165 mg, 2.5 mmol), **4** (10.7 µL, 75 µmol), *p*-DCB (3.2 mg, 25 µmol), Phen (4.5 mg, 25 µmol), and Na_2CO_3 (132 mg, 1.25 mmol). Argon gas was bubbled through the solution for 5 min before it is sealed with a rubber septum and irradiated for 20 h using a 300-W high-pressure mercury lamp. The reaction mixture was then neutralized by addition of aqueous HCl and extracted with toluene–ether. The organic extracts were concentrated in vacuo giving a residue that contained



Scheme 4. Photochemical monoalkylation of **1** using oxidative photodimerization reaction.



Scheme 5. Photochemical monoalkylation of **1** using photo-NOCAS reaction.

87% and 25% yield of *p*-**5a** (based on the amount of *p*-DCB used) and **7a** (based on the amount of **4** used), respectively, as determined by ^{1}H NMR using CH_2Br_2 as an internal standard. Column chromatography on silica gel (ethyl acetate after toluene) gave a crude product mixture, which was purified by HPLC (GPC column, chloroform) to yield pure *p*-**5a** and **7a** as colourless oils.

2.6. Spectral data of photoproducts

2-(2,2-Diphenylethyl)propanedinitrile (3aa) [28,39]: colourless blocks, mp 92–94 °C, ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 2.76$ (dd, *J* = 8.1, 8.1 Hz, 2H), 3.44 (t, *J* = 8.1 Hz, 1H), 4.22 (t, *J* = 8.1 Hz, 1H), 7.22–7.43 (m, 10H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 21.8$, 37.0, 48.4, 112.5 (2C, CN), 127.7 (4C), 127.8 (2C), 129.4 (4C), 140.7 (2C, *ipso*) ppm; MS (EI$^+$) *m*/*z* = 246 (18, M$^+$), 168 (15), 167 (100, Ph_2CH^+), 165 (10); HRMS (EI$^+$) calcd for $C_{17}H_{14}N_2$ 246.1157, found 246.1165; IR (NaCl) 703, 1451, 1496, 2255 (m, C≡N), 2900, 3029 cm^{-1}.

2-(1-Methyl-2,2-diphenylethyl)propanedinitrile (3ab) [28]: pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 1.30$ (d, *J* = 6.7 Hz, 3H), 2.97–3.04 (m, 1H), 3.64 (d, *J* = 3.4 Hz, 1H), 3.80 (d, *J* = 11.8 Hz, 1H), 7.21–7.37 (m, 10H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 16.1$, 28.5, 40.4, 56.4, 111.0 (–CN), 113.0 (–CN), 127.5 (2C + 1C), 127.8 (2C), 128.1, 129.2 (2C), 129.8 (2C), 140.7, 140.8 ppm; MS (EI$^+$) *m*/*z* = 260 (4, M$^+$), 167 (100, Ph_2CH^+); HRMS (EI$^+$) calcd for $C_{18}H_{16}N_2$ 260.1313, found 260.1290; IR (NaCl) $\nu = 2253$ (C≡N) cm^{-1}.

2-(1-Ethyl-2,2-diphenylethyl)propanedinitrile (3ac): MS (EI$^+$) *m*/*z* = 274 (3, M$^+$), 167 (100, Ph_2CH^+), 165 (18), 152 (12).

2-[2,2-Bis(4-methoxyphenyl)ethyl]propanedinitrile (3ae) [28]: pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 2.67$ (dd, *J* = 8.3, 8.0 Hz, 2H), 3.44 (t, *J* = 8.0 Hz, 1H), 3.77 (s, 6H), 4.11 (d, *J* = 8.3 Hz, 1H), 6.86 (AA′XX′, *J* = 8.8 Hz, 4H), 7.13 (AA′XX′, *J* = 8.8 Hz, 4H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 21.8$, 37.4, 46.9, 55.7 (2C), 112.7 (2C, –CN), 114.8 (4C), 128.6 (4C), 133.2 (2C), 158.9 (2C) ppm; MS (EI$^+$) *m*/*z* = 306 (17, M$^+$), 240 (1, $M^+-CH_2(CN)_2$), 228 (18), 227 (100, $(MeOC_6H_4)_2CH^+$); HRMS (EI$^+$) calcd for $C_{19}H_{18}N_2O_2$ 306.1368, found 306.1378; IR (NaCl) $\nu = 579$, 833, 1033, 1179, 1249 (C–O–C), 1509, 1609, 2255 (m, C≡N), 2838, 2905 cm^{-1}.

2-(2-Phenylethyl)propanedinitrile (3af) [28,40,41]: pale yellow powder, mp 42–43 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 2.35$ (dt, *J* = 7.3, 7.3 Hz, 2H), 2.94 (t, *J* = 7.3 Hz, 2H), 3.57 (t, *J* = 7.3 Hz, 1H), 7.18–7.38 (m, 5H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 22.1$, 32.7, 33.0, 112.6 (2C, –CN), 127.5, 128.6 (2C), 129.3 (2C), 137.4 ppm; MS (EI$^+$) *m*/*z* = 170 (36, M$^+$), 91 (100, $PhCH_2^+$); IR (NaCl) $\nu = 2257$ (C≡N) cm^{-1}.

2-(2-Phenylpropyl)propanedinitrile (3ag) [28]: colourless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 1.38$ (d, *J* = 6.9 Hz, 3H), 2.15–2.42 (m, 2H), 3.00–3.05 (m, 1H), 3.20–3.33 (m, 1H), 7.19–7.39 (m, 10H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 21.6$, 22.4, 38.0, 39.4, 112.5 (2C, –CN), 127.0 (2C), 127.9, 129.5 (2C), 142.2 ppm; MS (EI$^+$) *m*/*z* = 184 (27, M$^+$), 118 (11), 105 (100, Ph(Me)CH$^+$); HRMS (EI$^+$) calcd for $C_{12}H_{12}N_2$ 184.1000, found 184.0974; IR (NaCl) $\nu = 2255$ (C≡N) cm^{-1}.

2-{2-[4-(1,1-Dimethylethyl)phenyl]ethyl}propanedinitrile (3ah) [28]: pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 1.36$ (s, 9H), 2.34 (dt, *J* = 7.3, 7.3 Hz, 2H), 2.90 (t, *J* = 7.3 Hz, 2H), 3.56 (t, *J* = 7.3 Hz, 1H), 7.12 (AA′XX′, *J* = 8.5 Hz, 2H), 7.36 (AA′XX′, *J* = 8.5 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 22.0$, 31.8 (3C), 32.1, 33.0, 35.0, 112.7 (2C, –CN), 126.2 (2C), 128.3 (2C), 134.2, 150.5 ppm; MS (EI$^+$) *m*/*z* = 226 (10, M$^+$), 211 (100, M$^+$–Me); HRMS (EI$^+$) calcd for $C_{15}H_{18}N_2$ 226.1470, found 226.1448; IR (NaCl) $\nu = 2218$ (C≡N) cm^{-1}.

Dimethyl 2-(2,2-diphenylethyl)malonate (3ba): pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 2.67$ (dd, *J* = 8.1, 7.4 Hz, 2H, $-CH_2-$), 3.28 (t, *J* = 7.4 Hz, 1H, $-CH(CO_2Me)_2$), 3.94 (t, *J* = 8.1 Hz, 1H, $-CHPh_2$), 7.15–7.31 (m, 10H, aromatic) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 34.7$, 48.9, 50.2, 52.8 (2C, $-CO_2Me$), 126.5 (2C), 127.8 (4C), 128.6 (4C), 143.0 (2C), 169.5 (2C, C=O) ppm; MS (EI$^+$) *m*/*z* = 312 (2, M$^+$), 180 (100), 167 (23, Ph_2CH^+); IR (NaCl) $\nu = 1736$ (C=O) cm^{-1}.

Dimethyl 2-(2-phenylethyl)malonate (3bf) [42]: colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 2.23$ (td, *J* = 7.7, 7.5 Hz, 2H, $-CH_2-$), 2.65 (t, *J* = 7.7 Hz, 2H, $-CH_2Ph$), 3.38 (t, *J* = 7.5 Hz, 1H, $-CH(CO_2Me)_2$), 3.73 (s, 6H, $-CO_2Me$), 7.14–7.23 (m, 3H, aromatic), 7.23–7.32 (m, 2H, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 30.9$ (2°), 33.8 ($-CHPh_2$), 51.3 ($-CH(CO_2Me)_2$), 53.0 (2C, $-CO_2Me$), 126.4, 128.6 (2C), 128.7 (2C), 140.6 (*ipso*), 169.8 (2C, C=O) ppm.

Dimethyl 2-(2-phenylpropyl)malonate (3bg) [43]: pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.28$ (dd, *J* = 7.0, 0.4 Hz, 3H, –CH*Me*Ph), 2.10–2.30 (m, 2H, $-CH_2-$), 2.64–2.78 (m, 1H, –C*H*MePh), 3.21 (dd, *J* = 8.9, 6.2 Hz, 1H, $-CH(CO_2Me)_2$), 3.63 (s, 3H, $-CO_2Me$), 3.74 (s, 3H, $-CO_2Me$), 7.13–7.23 (m, 3H, aromatic), 7.25–7.33 (m, 2H, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) $\delta = 23.0$ (–CH*Me*Ph), 37.5 ($-CH_2-$), 38.4 (–*C*HMePh), 50.5 ($-CH(CO_2Me)_2$), 52.8 (2C, $-CO_2Me$), 126.6, 127.2 (2C), 128.7 (2C), 145.3 (*ipso*), 169.77 ($-CO_2Me$), 169.85 ($-CO_2Me$) ppm; MS (EI$^+$) *m*/*z* = 250 (3, M$^+$), 132 (91, $CH_2(CO_2Me)_2^{\bullet+}$), 118 (100, $PhCHMe{=}CH_2^{\bullet+}$), 105 (51, PhC$^+$HMe); IR (NaCl) $\nu = 702$, 1154, 1237, 1436, 1739 (C=O), 2956 cm^{-1}.

Ethyl 2-(2,2-diphenylethyl)-3-oxobutyrate (3ca): colourless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 1.26$ (t, *J* = 7.1 Hz, 3H, $-OCH_2Me$), 2.15 (s, 3H, –Ac), 2.55–2.71 (m, 2H, $-CH_2-$), 3.36 (dd, *J* = 7.1, 7.1 Hz, 1H, $-CH(Ac)CO_2Et$), 3.94 (dd, *J* = 8.1, 8.1 Hz, 1H, $-CHPh_2$), 4.17 (q, *J* = 7.1 Hz, 2H, $-OCH_2Me$), 7.15–7.38 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.7$ ($-OCH_2Me$), 29.8 (–C(=O)*Me*), 34.1 ($-CH_2-$), 49.2 ($-CHPh_2$), 58.2 ($-CH(Ac)CO_2Et$), 61.9 ($-OCH_2Me$), 126.7, 126.8, 128.0 (2C), 128.1 (2C), 128.7 (2C), 128.8 (2C), 143.56 (*ipso*), 143.62 (*ipso*), 169.6 ($-CO_2Et$), 202.7 (–*C*(=O)Me) ppm; MS (EI$^+$) *m*/*z* = 292 (1), 265 (1, M$^+$–OEt), 180 (100, $Ph_2C{=}CH_2^{\bullet+}$), 167 (16, Ph_2CH^+), 165 (38); IR (NaCl) $\nu = 702$, 1718 (C=O), 1736 (C=O), 2981 (C≡N) cm^{-1}.

Ethyl 2-cyano-4,4-diphenylbutyrate (3da): pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 1.28$ (t, *J* = 7.1 Hz, 3H, $-OCH_2Me$), 2.53–2.62 (m, 1H, $-CH_2-$), 2.72–2.81 (m, 1H, $-CH_2-$), 3.29 (dd, *J* = 10.0, 5.5 Hz, 1H, $-CH(CN)CO_2Et$), 4.19 (q, 2H, *J* = 7.1 Hz, $-OCH_2Me$), 4.19–4.25 (m, 1H, $-CHPh_2$), 7.18–7.35 (m, 10H, aromatic) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 14.1$, 35.4, 36.3, 48.4, 62.9 ($-OCH_2Me$), 116.1, 126.7, 127.0, 127.3 (2C), 127.6 (2C), 128.5 (2C), 128.8 (2C), 141.2, 142.3, 165.5 (C=O) ppm; MS (EI$^+$) *m*/*z* = 293 (6, M$^+$), 180 (100, $Ph_2C{=}CH_2^{\bullet+}$), 167 (29, Ph_2CH^+); IR (NaCl) $\nu = 2249$ (C≡N) cm^{-1}.

Ethyl 2-cyano-3-methyl-4,4-diphenylbutyrate (3db): mixture (86:14) of diastereomers, pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) $\delta = 1.03$ (d, *J* = 6.6 Hz, 3H, –CH*Me*–, major isomer), 1.12 (d, *J* = 6.7 Hz, 3H, –CH*Me*–, minor isomer), 1.31 (t, *J* = 7.1 Hz, 3H,

$-CH_2\mathit{Me}$), 3.10–3.24 (m, 1H, $-C\mathit{H}Me-$), 3.49 (d, *J* = 3.0 Hz, 1H, $-C\mathit{H}(CN)CO_2Et$, major isomer), 3.54 (d, *J* = 3 Hz, 1H, $-C\mathit{H}(CN)CO_2Et$, minor isomer), 3.83 (d, *J* = 12.1 Hz, 1H, $-C\mathit{H}Ph_2$, major isomer), 4.08 (d, *J* = 12 Hz, 1H, $-C\mathit{H}Ph_2$, minor isomer), 4.26 (q, *J* = 7.1 Hz, 2H, $-CO_2C\mathit{H_2}Me$), 7.12–7.42 (m, 10H) ppm; MS (EI$^+$) *m*/*z* = 307 (0.4, M$^+$), 194 (65, $Ph_2C{=}CHMe^{\bullet+}$), 167 (100, Ph_2CH^+). HRMS (FAB$^+$) calcd for $C_{20}H_{22}NO_2$ ([M+H]$^+$) 308.1651, found 308.1616.

2-(2,2-Diphenylethyl)-2-methylpropanedinitrile (3ha): pale yellow powder, mp 96–97 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.67 (s, 3H, –Me), 2.64 (d, *J* = 7.5 Hz, 2H, $-CH_2-$), 4.28 (t, *J* = 7.5 Hz, 1H, $-C\mathit{H}Ph_2$), 7.16–7.29 (m, 10H, aromatic) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 26.7 (–Me), 31.2 ($-\mathit{C}Me(CN)_2$), 44.3 ($-CH_2-$), 48.9 ($-CHPh_2$), 115.5 (2C, –CN), 127.4, 127.7, 128.9, 141.7 ppm; MS (EI$^+$) *m*/*z* = 260 (14, M$^+$), 167 (100, Ph_2CH^+); IR (NaCl) ν = 2248 (C≡N) cm^{-1}.

2-[*trans*-4-(4-Cyanophenyl)-1,1,4-trimethylpent-2-enyl]propanedinitrile (*p*-5a) [29]: colourless oil, ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.39 (s, 6H), 1.44 (s, 6H), 3.56 (s, 1H), 5.50 (d, *J* = 15.9 Hz, 1H), 5.87 (d, *J* = 15.9 Hz, 1H), 7.42 (AA′XX′, *J* = 8.7 Hz, 2H), 7.60 (AA′XX′, *J* = 8.7 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 25.6 (2C), 28.9 (2C), 36.1, 40.6, 41.6, 110.3, 111.9 (2C), 119.1, 127.2 (2C), 129.6, 132.3 (2C), 141.4, 153.3 ppm; MS (EI$^+$) *m*/*z* = 277 (4, M$^+$), 212 (18, $M^+-CH(CN)_2$), 182 (14), 170 (100, $M^+-CMe_2CH(CN)_2$), 156 (18); HRMS (EI$^+$) calcd for $C_{18}H_{19}N_3$ 277.1579, found 277.1572; IR (NaCl) 840, 2228 (C≡N), 2252 (w, C≡N), 2972 cm^{-1}.

2-[*trans*-4-(2-Cyanophenyl)-1,1,4-trimethylpent-2-enyl]propanedinitrile (*o*-5a) [29]: pale brown oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.40 (s, 6H), 1.58 (s, 6H), 3.66 (s, 1H), 5.49 (d, *J* = 15.9 Hz, 1H), 5.94 (d, *J* = 15.9 Hz, 1H), 7.32 (ddd, *J* = 7, 7, 2 Hz, 1H), 7.50–7.60 (m, 2H), 7.66 (dd, *J* = 7, 2 Hz, 1H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 25.1 (2C), 29.1 (2C), 35.8, 40.4, 41.6, 111.98, 112.01 (2C), 120.0, 126.8, 127.1, 131.3, 133.0, 135.7, 140.1, 150.9 ppm; MS (EI$^+$) *m*/*z* = 277 (2, M$^+$), 262 (10), 212 (58, $M^+-CH(CN)_2$), 197 (20, $M^+-MeCH(CN)_2$), 182 (19), 170 (100, $M^+-CMe_2CH(CN)_2$); HRMS (EI$^+$) calcd for $C_{18}H_{19}N_3$ 277.1579, found 277.1573; IR (NaCl) 766, 1467, 2221 (C≡N), 2252 (w, C≡N), 2972 cm^{-1}.

Dimethyl 2-[*trans*-4-(4-cyanophenyl)-1,1,4-trimethylpent-2-enyl]-malonate (*p*-5b): colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.25 (s, 6H, –Me), 1.38 (s, 6H, –Me), 3.39 (s, 1H, $-C\mathit{H}(CO_2Me)_2$), 3.69 (s, 6H, $-CO_2\mathit{Me}$), 5.57 (d, *J* = 15.9 Hz, 1H, olefin), 5.70 (d, *J* = 15.9 Hz, 1H, olefin), 7.43 (AA′XX′, *J* = 8.2 Hz, 2H, aromatic), 7.58 (AA′XX′, *J* = 8.2 Hz, 2H, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 26.3 (2C, –Me), 29.1 (2C, –Me), 38.6 (4°), 41.2 (4°), 52.4 (2C, $-CO_2\mathit{Me}$), 61.3 ($-\mathit{C}H(CO_2Me)_2$), 109.8 (4°), 119.2 (–CN), 127.2 (2C), 132.0 (2C), 134.1 (olefin), 136.4 (olefin), 154.8 (*ipso*), 168.2 (2C, $-\mathit{C}O_2Me$) ppm; MS (EI$^+$) *m*/*z* = 343 (5, M$^+$), 264 (24), 212 (40, $M^+-CH(CO_2Me)_2$), 211 (34, $M^+-CH_2(CO_2Me)_2$), 196 (69), 173 (49), 170 (100, $NC-C_6H_4-CMe_2CH{=}CH^+$); HRMS (EI$^+$) calcd for $C_{20}H_{25}NO_4$ 343.1784, found 343.1783; IR (NaCl) ν = 1146, 1245, 1735 (C=O), 1756 (C=O), 2227 (C≡N), 2966 cm^{-1}.

Dimethyl 2-[*trans*-4-(2-cyanophenyl)-1,1,4-trimethylpent-2-enyl]-malonate (*o*-5b): colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.27 (s, 6H, –Me), 1.53 (s, 6H, –Me), 3.38 (s, 1H, $-C\mathit{H}(CO_2Me)_2$), 3.66 (s, 6H, $-CO_2\mathit{Me}$), 5.58 (d, *J* = 16.1 Hz, 1H, olefin), 5.74 (d, *J* = 16.1 Hz, 1H, olefin), 7.25–7.32 (m, 1H, aromatic), 7.45–7.55 (m, 2H, aromatic), 7.61–7.67 (m, 2H, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 25.8 (2C, –Me), 29.2 (2C, –Me), 38.8 (4°), 41.2 (4°), 52.3 (2C, $-CO_2\mathit{Me}$), 61.2 ($-\mathit{C}H(CO_2Me)_2$), 112.1 (4°), 119.9 (4°), 126.5, 127.0, 132.6, 135.5, 135.8 (olefin), 136.2 (olefin), 152.4 (*ipso*), 168.3 (2C, $-\mathit{C}O_2Me$) ppm; MS (EI$^+$) *m*/*z* = 343 (12, M$^+$), 328 (60), 284 (44), 212 (100, $M^+-CH(CO_2Me)_2$), 196 (80), 170 (63, $NC-C_6H_4-CMe_2CH{=}CH^+$); HRMS (EI$^+$) calcd for $C_{20}H_{25}NO_4$ 343.1784, found 343.1785; IR (NaCl) ν = 1146, 1244, 1437, 1735 (C=O), 1757 (C=O), 2221 (C≡N), 2968 cm^{-1}.

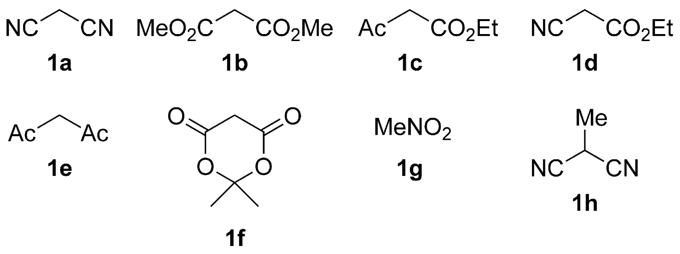
Dimethyl 2-[*trans*-4-(3-cyanophenyl)-1,1,4-trimethylpent-2-enyl]-malonate (*m*-5b): pale yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.25 (s, 6H, –Me), 1.38 (s, 6H, –Me), 3.38 (s, 1H, $-C\mathit{H}(CO_2Me)_2$), 3.70 (s, 6H, $-CO_2\mathit{Me}$), 5.56 (d, *J* = 16.0 Hz, 1H, olefin), 5.69 (d, *J* = 16.0 Hz, 1H, olefin), 7.39 (dd, *J* = 7.8, 7.7 Hz, 1H, 5-position), 7.47 (ddd, *J* = 7.7, 1.4, 1.4 Hz, 1H), 7.56 (ddd, *J* = 7.8, 1.4, 1.4 Hz, 1H), 7.61 (dd, *J* = 1.4, 1.4 Hz, 1H, 2-position) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 26.3 (2C, –Me), 29.2 (2C, –Me), 38.6 (4°), 40.8 (4°), 52.4 (2C, $-CO_2\mathit{Me}$), 61.3 ($-\mathit{C}H(CO_2Me)_2$), 112.3 (4°), 119.4 (–CN), 129.0, 129.6, 130.2, 131.0, 134.2, 136.5, 150.7 (*ipso*), 168.2 (2C, $-\mathit{C}O_2Me$) ppm; MS (EI$^+$) *m*/*z* = 343 (8, M$^+$), 212 (47, $M^+-CH(CO_2Me)_2$), 196 (43), 173 (47), 170 (100, $NC-C_6H_4-CMe_2CH{=}CH^+$), 141 (44); HRMS (EI$^+$) calcd for $C_{20}H_{25}NO_4$ 343.1784, found 343.1781; IR (NaCl) ν = 1145, 1243, 1735 (C=O), 2228 (C≡N), 2964 cm^{-1}.

Ethyl 2-acetyl-6-(4-cyanophenyl)-3,3,6-trimethylhept-4-enoate (*p*-5c): ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.21 (s, 3H, –Me), 1.22 (s, 3H, –Me), 1.26 (t, *J* = 7.3 Hz, 3H, $-CO_2CH_2\mathit{Me}$), 1.39 (s, 6H, –Me), 2.19 (s, 3H, –Ac), 3.43 (s, 1H, $-C\mathit{H}(Ac)CO_2Et$), 4.15 (q, *J* = 7.3 Hz, 2H, $-CO_2C\mathit{H_2}Me$), 5.55 (d, *J* = 16.1 Hz, 1H, olefin), 5.71 (d, *J* = 16.1 Hz, 1H, olefin), 7.43 (AA′XX′, *J* = 8.2 Hz, 2H, aromatic), 7.58 (AA′XX′, *J* = 8.2 Hz, 2H, aromatic) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 14.7 ($-CO_2CH_2\mathit{Me}$), 26.4 (–Me), 26.6 (–Me), 29.0 (–Me), 29.1 (–Me), 31.8, 39.0, 41.2, 61.3 ($-CO_2\mathit{C}H_2Me$), 68.7 ($-\mathit{C}H(Ac)CO_2Et$), 109.9 (4°), 119.2 (–CN), 127.2 (2C), 132.0 (2C), 132.0 (olefin), 134.4 (olefin), 136.2 (olefin), 154.7 (*ipso*), 168.6 (2C, $-\mathit{C}O_2Et$), 202.2 ($-\mathit{C}({=}O)Me$) ppm; MS (EI$^+$) *m*/*z* = 341 (0.5, M$^+$), 196 (14), 170 (20, $NC-C_6H_4-CMe_2CH{=}CH^+$), 129 (16, $^+CH(Ac)CO_2Et$), 116 (11), 43 (100, Ac$^+$); IR (NaCl) ν = 1145, 1365, 1717 (C=O), 2227 (C≡N), 2969 cm^{-1}.

Ethyl 2-cyano-6-(4-cyanophenyl)-3,3,6-trimethylhept-4-enoate (*p*-5d): pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.26–1.33 (m, 3H, $-OCH_2\mathit{Me}$), 1.29 (s, 3H, –Me), 1.30 (s, 3H, –Me), 1.41 (s, 6H, –Me), 3.39 (s, 1H, $-C\mathit{H}(CN)CO_2Et$), 4.15–4.29 (m, 2H, $-OC\mathit{H_2}Me$), 5.55 (d, *J* = 16.0 Hz, 1H, olefin), 5.69 (d, *J* = 16.0 Hz, 1H, olefin), 7.44 (AA′XX′, *J* = 8.8 Hz, 2H, aromatic), 7.59 (AA′XX′, *J* = 8.8 Hz, 2H, aromatic) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 14.6 ($-OCH_2\mathit{Me}$), 26.0 (–Me), 26.3 (–Me), 29.0 (2C, –Me), 39.8 (4°), 41.3 (4°), 49.7 ($-\mathit{C}H(CN)CO_2Et$), 62.9 ($-O\mathit{C}H_2Me$), 110.0 (4°), 115.9 (4°), 119.2 (4°), 127.2 (2C), 131.9 (olefin), 132.2 (2C), 138.5 (olefin), 154.0 (*ipso*), 164.8 (C=O) ppm; MS (EI$^+$) *m*/*z* = 324 (7, M$^+$), 212 (17, $M^+-CH(CN)CO_2Et$), 196 (16), 170 (100, $M^+-CMe_2CH(CN)CO_2Et$), 156 (20), 116 (16); HRMS (EI$^+$) calcd for $C_{20}H_{24}N_2O_2$ 324.1838, found 324.1812; IR (NaCl) ν = 1251, 1741 (C=O), 2227 (C≡N), 2972 cm^{-1}.

***trans*,*trans*-2,11-Dicyano-3,3,6,6,7,7,10,10-octamethyldodeca-4,8-dienedinitrile (7a)** [28,29]: colourless blocks, mp 111–112 °C, ^{1}H NMR ($CDCl_3$, 300 MHz) δ = 1.00 (s, 12H), 1.36 (s, 12H), 3.61 (s, 2H), 5.36 (d, *J* = 15.8 Hz, 2H), 5.80 (d, *J* = 15.8 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) δ = 23.4 (4C), 25.9 (4C), 35.9 (2C), 40.8 (2C), 41.5 (2C), 112.3 (4C), 129.8 (2C), 140.1 (2C) ppm; MS (EI$^+$) *m*/*z* = 175 (39, M$^+$/2), 110 (100, $M^+/2-CH(CN)_2$), 109 (35, $M^+/2-CH_2(CN)_2$), 95 (30, $M^+/2-MeCH(CN)_2$); HRMS (CI$^+$) calcd for $C_{22}H_{31}N_4$ ([M+H]$^+$) 351.2549, found 351.2555; IR (NaCl) 800, 1019, 1093, 1261, 2238 (w, C≡N), 2252 (w, C≡N), 2968 cm^{-1}; Anal. calcd for $C_{22}H_{30}N_4$: C, 75.39; H, 8.63; N, 15.98. Found: C, 75.15; H, 8.47; N, 15.86.

Dimethyl *trans*,*trans*-2,11-Bis(methoxycarbonyl)-3,3,6,6,7,7,10,10-octamethyldodeca-4,8-dienedioate (7b): pale brown oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 0.89 (s, 12H), 1.23 (s, 12H), 3.36 (s, 2H, $-C\mathit{H}(CO_2Me)_2$), 3.68 (s, 12H, $-CO_2\mathit{Me}$), 5.45 (d, *J* = 16.1 Hz, 2H, olefin), 5.49 (d, *J* = 16.1 Hz, 2H, olefin) ppm; ^{13}C NMR (75 MHz, $CDCl_3$) δ = 23.5 (4C, 1°), 26.3 (4C, 1°), 38.9 (2C, 4°), 40.9 (2C, 4°), 52.4 (4C, $-CO_2\mathit{Me}$), 61.4 (2C, $-CH(CO_2Me)_2$), 133.8 (2C, olefin), 135.8 (2C, olefin), 168.4 (4C, C=O) ppm; MS (EI$^+$) *m*/*z* = 241 (41, M$^+$/2), 209 (10, $M^+/2-MeOH$), 183 (17), 177 (26), 149 (13), 121 (28), 110 (19, $M^+/2-CH(CO_2Me)_2$), 109 (100, $M^+/2-CH_2(CO_2Me)_2$), 101 (10), 95 (12, $M^+/2-MeCH(CO_2Me)_2$); HRMS (EI$^+$) calcd for



Scheme 6. Active methylene compounds (**1a**–**1h**).

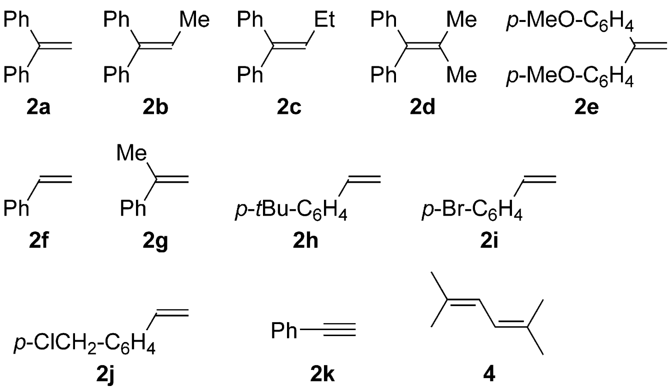
$C_{13}H_{21}O_4$ ($M^+/2$) 241.1440, found 241.1435; IR (NaCl) $\nu = 1142$ (C–O), 1243, 1736 (C=O), 1758 (C=O), 2967 cm^{-1}.

Diethyl *trans,trans*-2,11-diacetyl-3,3,6,6,7,7,10,10-octamethyldodeca-4,8-dienedioate (7c): light yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 0.91$ (s, 12H), 1.19 (s, 6H), 1.20 (s, 6H), 1.26 (t, $J = 7.1$ Hz, 6H, $-CO_2CH_2\mathit{Me}$), 2.19 (d, $J = 0.3$ Hz, 6H, –Ac), 3.41br (s, 2H, $-C\mathit{H}(Ac)CO_2Et$), 4.15 (q, $J = 7.1$ Hz, 4H, $-CO_2C\mathit{H}_2Me$), 5.46 (d, $J = 17$ Hz, olefin), 5.52 (d, $J = 17$ Hz, olefin) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 14.7$ (2C, $-CO_2CH_2\mathit{Me}$), 23.4 (2C), 23.6 (2C), 26.5 (4C), 32.0 (2C), 39.3 (2C), 41.0 (2C), 61.3 (2C), 68.9 (2C), 133.9 (2C, olefin), 135.6 (2C, olefin), 168.8 (2C, $-\mathit{C}O_2Et$), 202.9 (2C, $-\mathit{C}(=O)Me$) ppm; MS (EI$^+$) $m/z = 239$ (42, $M^+/2$), 121 (47), 110 (67, $M^+/2-CH(Ac)CO_2Et$), 109 (100, $M^+/2-CH_2(Ac)CO_2Et$), 95 (77, $M^+/2-MeCH(Ac)CO_2Et$), 67 (99); HRMS (EI$^+$) calcd for $C_{14}H_{23}O_3$ ($M^+/2$) 239.1647, found 239.1649; IR (NaCl) $\nu = 1142$, 1366, 1718 (C=O), 1734 (C=O), 2973 cm^{-1}.

Diethyl *trans,trans*-2,11-dicyano-3,3,6,6,7,7,10,10-octamethyldodeca-4,8-dienedioate (7d): mixture (1:1) of *dl*- and *meso*-isomers, brown oil; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 0.95$ (s, 12H), 1.27 (s, 6H), 1.28 (s, 6H), 1.31 (dd, $J = 7.1$, 7.1 Hz, 6H, $-OCH_2\mathit{Me}$), 3.367 (s, 2H, $-C\mathit{H}(CN)CO_2Et$, one of the isomers), 3.373 (s, 2H, $-C\mathit{H}(CN)CO_2Et$, the other isomer), 4.20 (dq, $J = 10.9$, 7.1 Hz, 2H, $-OC\mathit{H}_2Me$, one of the isomers), 4.23 (dq, $J = 10.9$, 7.1 Hz, 2H, $-OC\mathit{H}_2Me$, the other isomer), 5.37 (d, $J = 16.1$ Hz, 2H, olefin), 5.64 (d, $J = 16.1$ Hz, 2H, olefin) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 14.6$ (2C, $-OCH_2\mathit{Me}$), 23.41 (2C, 1°, isomer A), 23.46 (2C, 1°, isomers A and B), 23.50 (2C, 1°, isomer B), 26.2 (2C, 1°), 26.4 (2C, 1°), 39.9 (2C, 4°), 41.2 (2C, 4°), 49.6 (2C, $-\mathit{C}H(CN)CO_2Et$), 62.7 (2C, $-O\mathit{C}H_2Me$), 116.1 (2C, –CN), 131.7 (2C, olefin), 137.7 (2C, olefin), 165.0 (2C, C=O) ppm; MS (EI$^+$) $m/z = 222$ (45, M^+), 176 (12, M^+-EtOH), 148 (11), 110 (29, $M^+-C^{\bullet}H(CN)CO_2Et$), 109 (100, $M^+-CH_2(CN)CO_2Et$), 95 (13, $M^+-MeCH(CN)CO_2Et$); HRMS (EI$^+$) calcd for $C_{13}H_{20}O_2N$ ($M^+/2$) 222.1494, found 222.1472; IR (NaCl) $\nu = 1037$, 1189 (C–O), 1250 (C–O), 1370, 1467, 1742 (C=O), 2247 (w, C≡N), 2973 cm^{-1}.

***trans,trans*-3,12-Diacetyl-4,4,7,7,8,8,11,11-octamethyltetradeca-5,9-diene-2,13-dione (7e)**: colourless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 0.92$ (s, 12H), 1.16 (s, 12H), 2.18 (d, $J = 0.4$ Hz, 12H, –Ac), 3.72br (s, 2H, $-C\mathit{H}Ac_2$), 5.45 (d, $J = 16.2$ Hz, 2H, olefin), 5.52 (d, $J = 16.2$ Hz, 2H, olefin) ppm; ^{13}C NMR (C_6D_6, 75 MHz) $\delta = 23.2$ (4C), 26.2 (4C), 31.8 (4C, $-C(=O)Me$), 39.4 (2C, 4°), 40.7 (2C, 4°), 75.9 (2C, $-\mathit{C}HAc_2$), 134.0 (2C, olefin), 135.0 (2C, olefin), 202.0 (4C, C=O) ppm; MS (EI$^+$) $m/z = 209$ (69, $M^+/2$), 149 (46, $M^+/2-AcOH$), 110 (24, $M^+/2-Ac_2CH$), 109 (100, $M^+/2-Ac_2CH_2$), 85 (27); HRMS (EI$^+$) calcd for $C_{13}H_{21}O_2$ ($M^+/2$) 209.1541, found 209.1527; IR (NaCl) $\nu = 665$, 986, 1143, 1355, 1696 (C=O), 1719, 2967 cm^{-1}.

2,9-Bis(4,4-dimethyl-3,5-dioxacyclohexa-2,6-dionyl)-2,5,5,6,6,9-hexamethyldeca-3,7-diene (7f): white powder, mp 133–135 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 0.93$ (s, 12H), 1.31 (s, 12H), 1.69 (s, 6H, $-O-C\mathit{Me}_2-O-$), 1.72 (s, 6H, $-O-C\mathit{Me}_2-O-$), 3.25 (s, 2H, 3°), 5.41 (d, $J = 16.1$ Hz, 2H), 5.54 (d, $J = 16.1$ Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 75 MHz) $\delta = 23.4$ (4C), 27.3 (4C), 28.4 (2C, 4°), 29.6 (2C, 4°), 41.2 (2C, $-O-C\mathit{Me}_2-O-$), 41.3 (2C, $-O-C\mathit{Me}_2-O-$), 105.0 (2C, $-O-\mathit{C}Me_2-O-$), 132.6 (2C, olefin), 136.6 (2C, olefin), 164.6 (4C, C=O) ppm; MS (EI$^+$) $m/z = 110$ (100, $(Me_2C{=}CH-)_2^{\bullet+}$), 109 (4), 95; HRMS (FAB$^+$) neither M^+ nor $M^+/2$ was observed; IR (NaCl) $\nu = 1277$, 1752, 2972 cm^{-1}.



Scheme 7. Alkenes (**2a**–**2k** and **4**).

2.7. Crystallographic data of photoproducts

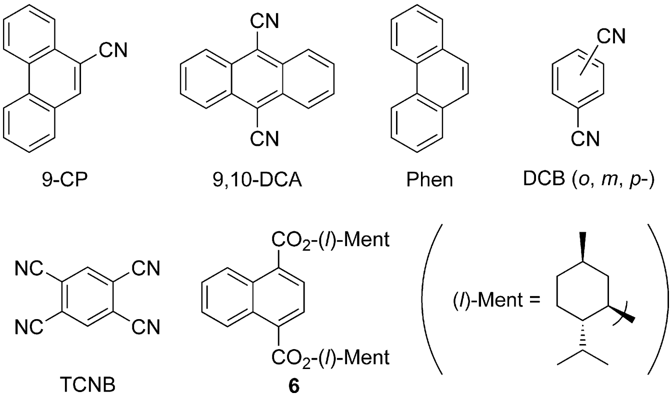
CCDC-702041 and -702042 contains the supplementary crystallographic data for **7a** and **3aa**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

3. Results and discussion

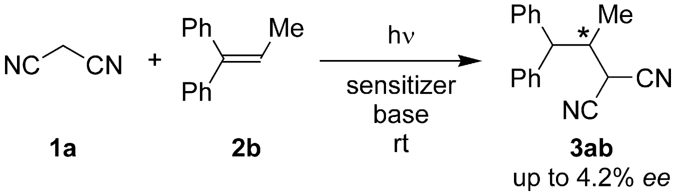
3.1. Monoalkylation of active methylene compounds using photochemical polar addition (PPA) and oxidative photodimerization reactions

3.1.1. PPA reactions

In the earlier effort, we observed that photoirradiation of an aqueous acetonitrile solution containing malononitrile (**1a**), 1,1-diphenylethene (**2a**), lithium carbonate and a catalytic amount of 9-cyanophenanthrene (9-CP) leads to selective high yielding (91%) formation of the *anti*-Markovnikov PPA product, α-monoalkylated propanedinitrile **3aa** (Schemes 3 and 6–8, and Table 1, entry 1) [28]. Importantly, an α,α-dialkylated product is not generated in this process. Most of 9-CP and excess **1a** remain in the product mixture and can be recovered. We believe that this reaction might serve as a useful, safe, and environmentally friendly alkylation methodology that can be carried out under mild conditions (ambient temperatures and weak bases) without the need to employ noble



Scheme 8. Photosensitizers.



Scheme 9. Enantiodifferentiating monoalkylation of **1a** using PPA reaction.

metals or alkyl halide required in conventional alkylation reactions [8–21].

We have found that the efficiency of this reaction strongly depends on the base used. Specifically, lower yields of **3aa** are observed when heavier alkali metal carbonates are used (entries 2–5). In addition, strong bases, such as sodium hydroxide and potassium *tert*-butoxide, are not effective in promoting the reaction (entries 6 and 7). In the absence of a base, the photoreaction does not take place in aqueous acetonitrile (entry 8), but it does proceed in dry dimethyl sulfoxide (DMSO) in the presence of molecular sieves (MS) 4A. We propose that DMSO acts as the "base" in this case (entry 8) [44–46]. While the use of 9-CP results in the highest yield of **3aa** (entry 1), other photosensitizers, including phenanthrene (Phen) which participates as a redox photosensitizer [47], can be used for the reaction (entries 10 and 11).

The results of studies exploring the scope of alkenes that can be employed in the reaction showed that alkyl substituents on the vinylic positions of 1,1-diphenylethene lead to lower yields of the products **3ab**–**3ad** (entries 12–14). The dimethoxy derivative of 1,1-diphenylethene (**2e**), styrene (**2f**) and its alkylated derivatives **2g** and **2h** also participate in reactions that form the corresponding photoproducts **3ae**–**3ah** (entries 15–18). On the other hand, reactions utilizing halogen-containing styrene derivatives (e.g., **2i** and **2j**) afford polymeric mixtures and none of the desired adducts (entries 19 and 20). Finally, alkyne **2k** does not react under the conditions employed (entry 21).

The photoinduced monoalkylation reaction takes place with a variety of active methylene compounds, but in each case a different base-dependence is observed. In general, active methylene compounds with weaker acidities require stronger bases. For example, 2,2-diphenylethylation of dimethyl malonate (**1b**) proceeds efficiently in the presence of stronger bases (entries 22–24), as exemplified by the formation of **3ba** in quantitative yield when potassium *tert*-butoxide is used (entry 24). Other alkenes (**2b**, **2f**–**2h**) also react with **1b** (entries 25–28). Ethyl acetoacetate (**1c**) and ethyl cyanoacetate (**1d**), which react in a manner similar to **1a** and **1b** (entries 29–31), can be applied in mild photochemical β-ketoester (e.g., acetoacetic [11–13] and malonic [14–17] ester) synthetic procedures. However, adducts are not formed in reactions of acetylacetone (**1e**) and Meldrum's acid (**1f**) [48,49] (entries 32 and 33) and the active "methyl" compound nitromethane (**1g**) does not participate in this process (entry 34). While introduction of the second alkyl group into the active "methine" compound, 2-methylpropanedinitrile (**1h**) is accomplished in 22% yield using **2a** as the alkene, reaction of **1h** with the more highly substituted alkene **2b** does not take place (entries 35 and 36).

3.1.2. Enantioselective carbon–carbon bond formation via PPA

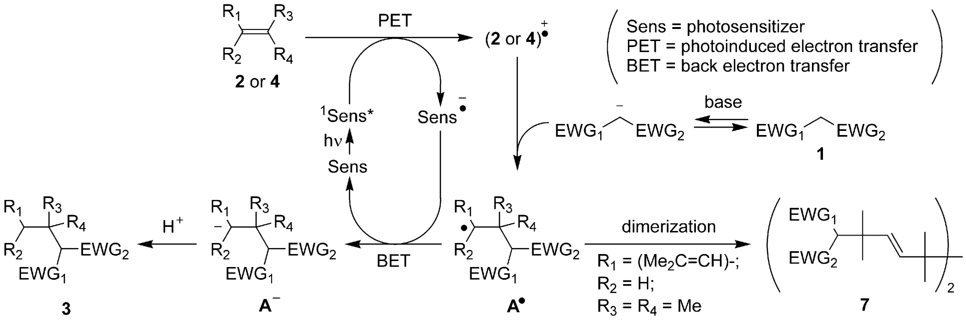
The development of photosensitized (catalytic) stereoselective reactions that proceed via electron transfer pathways is a challenging research topic [27,50–59]. A comprehensive study on enantiodifferentiating PPA reactions of alcohols with 1,1-diphenyl-1-alkenes has been carried out by Inoue and co-workers [53–55], but knowledge is lacking on the use of carbon nucleophiles in these processes.

Our current studies have uncovered the first enantiodifferentiating PPA reaction of a carbon nucleophile. Specifically, a slight enantiomeric excess (*ee*) of 0.7% was observed in the product **3ab** of the PPA reaction of **1a** with **2b** photosensitized by the bis-*l*-menthyl ester of 1,4-naphthalenedicarboxylic acid **6** [53] (Scheme 9, and Table 2, entry 2). A small increase of *ee* and a severe decrease of yield take places when a solvent system with lower polarity is employed (entry 3). This result suggests that lower solvent polarity causes an enhancement in the face selective complexation between the excited chiral photosensitizer **6** and the prochiral alkene **2b**.

3.1.3. Oxidative photodimerization reactions

Nucleophile-incorporated dimers are produced when 2,5-dimethyl-2,4-hexadiene (**4**) is employed in the PPA reactions [32,33]. For example, photoirradiation of an aqueous acetonitrile solution, containing malononitrile (**1a**) and **4** along with lithium carbonate and a catalytic amount of 9-CP, leads to formation of the oxidative dimer **7a** in a 52% yield (Scheme 4, and Table 3, entry 1) [28]. The strength of the base used in this process affects the yield of **7a**. Accordingly, reactions with heavier alkali metal carbonates result in slightly lower yields of **7a** (entries 2–4). The reaction does not proceed in the absence of base (entry 5) unless dry DMSO is used as a solvent (entry 6) [44–46]. Lastly, photosensitizers other than 9-CP can be used to promote the reaction albeit with lower yields (entries 7–11).

Other active methylene compounds undergo monoalkylation as well. Stronger bases, such as potassium *tert*-butoxide, promote alkylation of **1b** with diene **4** (entries 12–14) and similar reactions take place with **1c**–**1f** to form **7c**–**7f** (entries 15–17, 19, and 20). Instead of the acetylacetone (**1e**)–sodium hydroxide pair (entry 17), magnesium acetylacetonate serves as a participant in this reaction in the absence of base (entry 18).



Scheme 10. Plausible mechanism for the formation of **3** and **7**.

Table 1
Photochemical polar addition of **1** into **2**.[a].

Entry	Active methylene compound	Alkene	Sensitizer(s)	Base	Product	Yield[b]/%
1[c]	**1a**	**2a**	9-CP	Li_2CO_3	**3aa**	91
2[c]				Na_2CO_3		66
3[c]				K_2CO_3		68
4[c]				Rb_2CO_3		23
5[c]				Cs_2CO_3		15
6				NaOH		13
7[d]				KO-*t*Bu		Trace
8				None		0
9[e]						31
10[c]			9,10-DCA	Li_2CO_3		27
11[c]			*p*-DCB, Phen			44
12[c]		**2b**	9-CP	Li_2CO_3	**3ab**	52
13		**2c**			**3ac**	19
14		**2d**			**3ad**	0
15[c]		**2e**			**3ae**	46
16[c]		**2f**			**3af**	40
17[c]		**2g**			**3ag**	33
18[c]		**2h**			**3ah**	38
19		**2i**			**3ai**	0
20		**2j**			**3aj**	0
21		**2k**			**3ak**	0
22	**1b**	**2a**	9-CP	Li_2CO_3	**3ba**	0
23				Cs_2CO_3		38
24[d]				KO-*t*Bu		100
25[d]		**2b**		KO-*t*Bu	**3bb**	12
26[d]		**2f**			**3bf**	78
27[d]		**2g**			**3bg**	77
28[d]		**2h**			**3bh**	72
29	**1c**	**2a**	9-CP	NaOH	**3ca**	51
30	**1d**	**2a**	9-CP	Na_2CO_3	**3da**	63
31		**2b**			**3db**	13
32[d]	**1e**	**2a**	9-CP	KO-*t*Bu	**3ea**	0
33[d]	**1f**	**2a**	9-CP	KO-*t*Bu	**3fa**	Complex
34[d]	**1g**	**2a**	9-CP	KO-*t*Bu	**3ga**	0
35	**1h**	**2a**	9-CP	Na_2CO_3	**3ha**	22
36		**2b**			**3hb**	0

[a] *Conditions*: 300-W high-pressure mercury lamp, Pyrex filter, active methylene compound (2.5 mmol), alkene (75 μmol), sensitizer(s) (25 μmol), base (1.25 mmol), in MeCN (4 mL)–H_2O (1 mL), under Ar, rt, 20 h.

[b] Determined by ^1H NMR based on the amount of **2** used.

[c] Ref. [28].

[d] In dry MeCN (5 mL).

[e] In dry DMSO (5 mL) with MS4A (250 mg).

3.1.4. Plausible mechanisms

The mechanism that we have proposed earlier (Scheme 10) [28] appears to be applicable to PPA and oxidative photodimerization reactions of the active methylene compounds. In this pathway, photoinduced electron transfer (PET) from alkene **2** or diene **4** to the singlet excited state of the electron-acceptor photosensitizer (^{1}Sens*) affords cation radicals $\mathbf{2}^{\bullet+}$ or $\mathbf{4}^{\bullet+}$, which react with the anion of active methylene compound **1** to form benzylic or allylic radical intermediates $\mathbf{A}^{\bullet}$. Single electron transfer (SET) from the anion of **1** to ^{1}Sens* also occurs competitively, but it represents only a minor pathway since the concentration of the anion of **1a** is quite low ($\sim 2 \times 10^{-5}$ M) when a weak carbonate base is used, which can be estimated from solubility of lithium carbonate and pK_a values of **1a** and the carbonate [29].

When mono-olefins **2** are used as substrates, back electron transfer (BET) from $\text{Sens}^{\bullet-}$ to $\mathbf{A}^{\bullet}$ followed by protonation gives the *anti*-Markovnikov adduct **3**. On the other hand, allylic radical $\mathbf{A}^{\bullet}$, produced from the diene substrate, dimerizes to form **7**.

In redox-photosensitized processes [47], Phen acts as an electron mediator between the alkene and the photosensitizer since the Phen cation radical arising by SET to the excited state sensitizer serves as the electron acceptor from the alkene and diene.

Table 2
Enantiodifferentiating PPA of **1a** into **2b**.[a].

Entry	Sensitizer	Solvents	Yield[b]/%	*ee*[c]/%
1[d]	9-CP	MeCN/H_2O = 4/1	38	–
2	**6**	MeCN/H_2O = 4/1	25	0.7
3		PhH/MeCN = 3/1	0.8	4.2

[a] *Conditions*: 300-W high-pressure mercury lamp, Pyrex filter, **1a** (2.5 mmol), **2b** (75 μmol), sensitizer (25 μmol), Na_2CO_3 (1.25 mmol), solvents (5 mL in total), under Ar, rt, 20 h.

[b] Determined by ^1H NMR based on the amount of **2b** used.

[c] Determined by chiral GC.

[d] Ref. [28].

3.2. Tandem monoalkylation of active methylene compounds using three-component coupling reactions

3.2.1. Three-component coupling reactions

Active methylene compounds also participate in photo-NOCAS type, three-component coupling reactions [29]. For example, photoirradiation of an aqueous acetonitrile solution containing **1a**, **4**, *p*-dicyanobenzene (*p*-DCB, terephthalonitrile), lithium carbonate, and Phen, gives rise to generation of the α-monoalkylated

Table 3
Oxidative photodimerization of **4** with **1**.[a].

Entry	Active methylene compound	Sensitizer(s)	Base	Product	Yield[b]/%
1[c]	**1a**	9-CP	Li_2CO_3	**7a**	52
2			Na_2CO_3		50
3			K_2CO_3		46
4			Cs_2CO_3		46
5			None		0
6[d]					31
7		9,10-DCA	Na_2CO_3		43
8		*m*-DCB, Phen			47
9		*o*-DCB, Phen			37
10		*p*-DCB, Phen			25
11		TCNB, Phen			22
12	**1b**	9-CP	Na_2CO_3	**7b**	0
13			NaOH		0
14[e]			KO-*t*Bu		57
15	**1c**	9-CP	NaOH	**7c**	41
16[e]	**1d**	9-CP	KO-*t*Bu	**7d**	41
17	**1e**	9-CP	NaOH	**7e**	45
18	$Mg(acac)_2$		None	**7e**	11
19[e]	**1f**	9-CP	KO-*t*Bu	**7f**	(18)[f]
20[e]	**1g**	9-CP	KO-*t*Bu	**7g**	Complex

[a] *Conditions*: 300-W high-pressure mercury lamp, Pyrex filter, active methylene compound (2.5 mmol), **4** (75 μmol), sensitizer(s) (25 μmol), base (1.25 mmol), in MeCN (4 mL)–H_2O (1 mL), under Ar, rt, 20 h.
[b] Determined by ^{1}H NMR based on the amount of **4** used.
[c] Ref. [28].
[d] In dry DMSO (5 mL) with MS4A (250 mg).
[e] In dry MeCN (5 mL).
[f] Isolated yield (^{1}H NMR spectrum of the crude mixture was too complex to determine the yield).

para-cyanophenyl product *p*-**5a** in high yield (84%) together with the dimer **7a** (23%) (Scheme 5, and Table 4, entry 1) [29]. Much higher yields are obtained when heavier alkali metal carbonates are used in this process (entries 2 and 3). A similar reaction with *o*-dicyanobenzene (*o*-DCB, phthalonitrile) affords *o*-**5a** in modest yield (entry 5), but the *meta* analogue *m*-DCB (isophthalonitrile) does not undergo this NOCAS type reaction to produce *m*-**5a** (entry 7). It should be noted that these reactions occur in the absence of the mediator Phen, but the yield of *o*-**5a** is lower in this case (entries 4, 6, and 8).

When the active methylene compound **1b** is employed as the substrate not only are adducts *o*- and *p*-**5a** formed from reactions of the corresponding dicyanobenzenes, but *m*-DCB also reacts to form *m*-**5a** when potassium *tert*-butoxide is used as the base (entries 9–11). The use of strong bases also enhances the yields of tandem alkylation reactions of **1c**–**1e** (entries 12–14).

Overall, this noble metal-free photoreaction serves as a novel methodology for substitution reactions at aryl–cyano centers, which have precedence but are still challenging tasks [34–38,60–63].

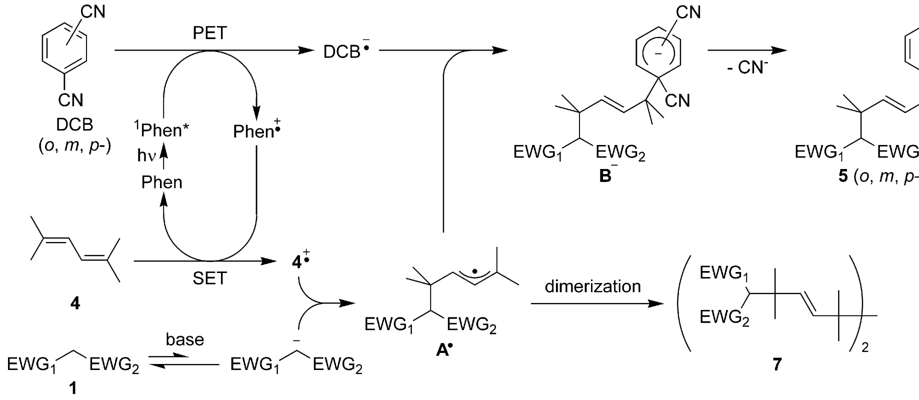
3.2.2. *Plausible mechanism*

The mechanistic route followed in the three-component coupling reaction begins with photoinduced SET to afford **4**$^{\bullet+}$ and DCB$^{\bullet-}$ (Scheme 11) [29,47]. The radical cation **4**$^{\bullet+}$ is trapped by the anion of **1** to form an allylic radical intermediate **A**$^{\bullet}$, which

Table 4
Three-component photoreaction of **1**, **4**, and dicyanobenzenes (DCBs).[a].

Entry	Active methylene compound	Dicyanobenzene	Sensitizer	Base	Products (yields[b]/%)	
1[c]	**1a**	*p*-DCB	Phen	Li_2CO_3	*p*-**5a** (84)	**7a** (23)
2[c]				Na_2CO_3	(87)	(25)
3[c]				K_2CO_3	(96)	(25)
4			None	Na_2CO_3	(87)	(26)
5[c]		*o*-DCB	Phen		*o*-**5a** (52)	(37)
6			None		(38)	(45)
7[c]		*m*-DCB	Phen		*m*-**5a** (0)	(47)
8			None		(0)	(46)
9[d]	**1b**	*p*-DCB	Phen	KO-*t*Bu	*p*-**5b** (76)	**7b** (35)
10[d]		*o*-DCB			*o*-**5b** (47)	(38)
11[d]		*m*-DCB			*m*-**5b** (13)	(30)
12	**1c**	*p*-DCB	Phen	NaOH	*p*-**5c** (97)	**7c** (32)
13[d]	**1d**	*p*-DCB	Phen	KO-*t*Bu	*p*-**5d** (73)	**7d** (31)
14	**1e**	*p*-DCB	Phen	NaOH	*p*-**5e** (76)	**7e** (22)

[a] *Conditions*: 300-W high-pressure mercury lamp, Pyrex filter, active methylene compound (2.5 mmol), **4** (75 μmol), dicyanobenzene (25 μmol), sensitizer (25 μmol), base (1.25 mmol), in MeCN (4 mL)–H_2O (1 mL), under Ar, rt, 20 h.
[b] Determined by ^{1}H NMR based on the amount of dicyanobenzene (for **5**) and **4** (for **7**) used.
[c] Ref. [29].
[d] In dry MeCN (5 mL).



Scheme 11. Plausible mechanism for the formation of **5** and **7**.

couples with DCB$^{\bullet-}$ within a solvent cage to give **B**$^-$. Stabilization of the negative charge in **B**$^-$ by an *ortho*- or *para*-disposed cyano group is crucial in order for the radical coupling process to proceed smoothly. Elimination of cyanide ion from the *ipso*-position of **B**$^-$ then regenerates the aromatic ring and affords the three-component coupling product **5**. When **A**$^\bullet$ diffuses out of the solvent cage, it undergoes dimerization to produce **7**.

4. Conclusion

This study has led to the development of two novel photochemical reactions, which result in α-monoalkylation of active methylene compounds. The first involves the introduction of electron-rich alkenes via a photochemical polar addition (PPA) pathway and the second corresponds to tandem introduction of a diene and cyanoarene groups via a photo-NOCAS mechanism. We believe that these reactions will find utility as safe and environmentally friendly synthetic methods, since they proceed under mild conditions (ambient temperature, without noble metals and alkyl halides, and in the presence of weak bases such as alkali metal carbonate). Of particular interest are photoinduced reactions of β-ketoesters, which can serve as replacements of conventional. acetoacetic and malonic ester synthetic protocols.

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