Supporting Information

Synthesis of Functionalized Cyclopentenes through Allenic Ketone-based Multicomponent Reactions

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Table of Contents

| I | General Experimental Information | S2 |
| II | Experimental Procedures and Spectroscopic Data | S3-11 |
| III | Control Experiments | S11-13 |
| IV | Copies of 1H and 13C NMR Spectra of 4a-4t, 5a-5d, 7, 9, A and 4u | S14-41 |
| V | X-ray Crystal Structure and Data of 4n | S42-43 |
| VI | References | S44 |
I. General Experimental Information

Reagents and solvents were purchased from commercial suppliers and used without further purification. 1-Aryl or 1-alkyl substituted allenic ketones were prepared through oxidation of the corresponding homopropargyl alcohols,\(^1\) which were prepared through zinc promoted propargylation of aldehydes.\(^2\) 1,4-Disubstituted allenic ketones were prepared from the reaction of 1-(triphenylphosphoranylidene)-2-propanone or 2-(triphenylphosphoranylidene)acetophenone with phenylacetyl chloride based on a literature procedure.\(^3\) The \(^1\)H and \(^13\)C NMR spectra were recorded at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm from the internal standard tetramethylsilane. Multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); m (multiplet); dd (doublet of doublets); td (triplet of doublets); br s (broad singlet), etc. Coupling constants were given in hertz. High-resolution mass spectra (HRMS) were obtained \textit{via} ESI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 60 F254 0.25 mm), and components were visualized by observation under UV light (254 and 365 nm).
II. Experimental Procedures and Spectroscopic Data

1. Typical procedure for the synthesis of 4a and spectroscopic data of 4a–4u, and 5a-5d.

To a flask containing malononitrile (2a, 33.0 mg, 0.5 mmol) and K$_2$CO$_3$ (82.8 mg, 0.6 mmol) in CH$_3$CN (5 mL) were added ethyl 4-chloroacetoacetate (1, 82.3 mg, 0.5 mmol). The mixture was stirred at room temperature for 20 min. Then 1-phenylbuta-2,3-dien-1-one (3a, 72.0 mg, 0.5 mmol) was added. The resulting mixture was stirred at 80 °C for another 1.5 h. Upon completion as determined by TLC analysis, it was allowed to cool to room temperature and quenched with saturated ammonium chloride. The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO$_2$) using EtOAc/petroleum ether (v/v =1/5) as eluent to give 4a (133.5 mg, 79%). Other cyclopentene derivatives (4b-4t and 5a-5d) were obtained in a similar manner.

Ethyl 2-(2-benzoyl-4,4-dicyano-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4a)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (133.5 mg, 79%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.17 (t, $J$ = 7.6 Hz, 3H), 1.87 (s, 3H), 2.82 (d, AB syst., $J$ = 16.4 Hz, 1H), 2.98 (d, AB syst., $J$ = 16.8 Hz, 1H), 2.99 (s, 2H), 4.12-4.02 (m, 2H), 2.99 (s, 2H), 4.12-4.02 (m, 2H), 2.99 (s, 2H), 7.52 (t, $J$ = 8.0 Hz, 2H), 7.66 (t, $J$ = 8.0 Hz, 1H), 7.88 (d, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ: 13.6, 14.0, 41.9, 42.2, 48.1, 61.4, 83.8, 113.9, 114.1, 129.2, 129.8, 134.8, 136.3, 136.7, 145.4, 170.9, 194.6. HRMS (ESI): calcd for C$_{19}$H$_{19}$N$_2$O$_4$ [M+H]$^+$: 339.1345; found: 339.1351.

Ethyl 2-(2-(1-naphthoyl)-4,4-dicyano-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4b)

Eluent: ethyl acetate/petroleum ether (1/8). Yellow oil (135.8 mg, 70%). $^1$H NMR (400 MHz, CDCl$_3$) δ: 1.21 (t, $J$ = 7.6 Hz, 3H), 1.76 (s, 3H), 3.14-2.94 (m, 4H), 4.16-4.11 (m, 2H), 4.53 (s, 1H), 7.66 (t, $J$ = 8.0 Hz, 1H), 8.11 (d, $J$ = 8.4 Hz, 1H). $^{13}$CNMR (100 MHz, CDCl$_3$) δ: 13.7, 14.0, 42.1, 42.3, 47.7, 61.3, 83.9, 113.9, 114.0, 124.7, 125.3, 127.1, 128.8, 129.1, 130.1, 132.9, 133.4, 134.0, 135.1, 138.5, 146.7, 170.9, 195.9. HRMS (ESI): calcd for C$_{23}$H$_{21}$N$_2$O$_4$ [M+H]$^+$: 389.1501; found: 389.1504.

Ethyl 2-(2-(3-chlorobenzoyl)-4,4-dicyano-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4c)

Eluent: ethyl acetate/petroleum ether (1/3). Yellow oil (141.4 mg, 76%). $^1$H NMR (400 MHz, CDCl$_3$) δ:
1.19 (t, $J = 7.6$ Hz, 3H), 1.87 (s, 3H), 3.02-2.80 (m, 4H), 4.16-4.02 (m, 2H), 4.42 (s, 1H), 7.47 (t, $J = 8.0$ Hz, 1H), 7.61 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H), 7.75 (t, $J = 7.6$ Hz, 1H), 7.87 (s, 3H). $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$: 13.6, 14.0, 41.9, 42.0, 48.2, 61.5, 83.7, 113.8, 113.9, 128.3, 129.1, 130.5, 134.7, 135.5, 137.1, 137.8, 145.2, 171.0, 193.3. HRMS (ESI): calced for C$_{19}$H$_{18}$ClN$_2$O$_4$ [M+H]$^+$: 373.0955; found: 373.0961.

**Ethyl 2-(4,4-dicyano-2-(2,4-dichlorobenzoyl)-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4d)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (146.2 mg, 72%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.24 (t, $J = 6.8$ Hz, 3H), 1.79 (s, 3H), 2.78 (d, AB syst., $J = 15.2$ Hz, 1H), 2.88 (d, AB syst., $J = 16.0$ Hz, 1H), 2.98 (d, AB syst., $J = 14.4$ Hz, 1H), 3.09 (d, AB syst., $J = 16.4$ Hz, 1H), 4.19-4.10 (m, 2H), 4.22 (s, 1H), 7.40 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.2$ Hz, 1H), 7.50 (d, $J = 1.6$ Hz, 1H), 7.61 (d, $J = 8.4$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 13.5, 14.1, 42.2, 42.3, 47.6, 61.4, 83.7, 113.5, 113.6, 128.0, 131.2, 132.2, 133.3, 135.1, 139.5, 140.9, 145.0, 170.7, 192.1. HRMS (ESI): calced for C$_{19}$H$_{17}$ClN$_2$O$_4$ [M+H]$^+$: 407.0565; found: 407.0572.

**Ethyl 2-(2-(2-bromobenzoyl)-4,4-dicyano-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4e)**

Eluent: ethyl acetate/petroleum ether (1/5). White solid (156.0 mg, 75%); Mp: 134-136ºC (ethyl acetate/petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.26 (t, $J = 7.2$ Hz, 3H), 1.74 (s, 3H), 2.91 (d, AB syst., $J = 15.2$ Hz, 1H), 2.95 (d, AB syst., $J = 16.4$ Hz, 1H), 3.03 (d, AB syst., $J = 14.8$ Hz, 1H), 3.12 (d, AB syst., $J = 16.0$ Hz, 1H), 4.21-4.13 (m, 3H), 7.49-7.39 (m, 2H), 7.58 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.0$ Hz, 1H), 7.69 (d, $J = 7.6$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 13.5, 14.1, 42.4, 42.5, 47.4, 61.4, 83.8, 113.5, 113.6, 120.0, 128.2, 130.9, 133.5, 134.4, 139.0, 141.7, 144.7, 170.5, 193.9. HRMS (ESI): calced for C$_{19}$H$_{18}$BrN$_2$O$_4$ [M+H]$^+$: 417.0450; found: 417.0457.

**Ethyl 2-(2-(3-bromobenzoyl)-4,4-dicyano-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4f)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (143.5 mg, 69%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.19 (t, $J = 7.2$ Hz, 3H), 1.87 (s, 3H), 3.01-2.80 (m, 4H), 4.14-4.04 (m, 2H), 4.41 (s, 1H), 7.40 (t, $J = 8.0$ Hz, 1H), 7.78 (t, $J = 8.4$ Hz 2H), 8.02 (s, 1H). $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$: 13.5, 14.0, 41.9, 42.1, 48.2, 61.5, 83.7, 113.8, 113.9, 123.5, 128.8, 130.7, 132.0, 137.1, 137.5, 138.0, 145.2, 170.9, 193.2. HRMS (ESI): calced for C$_{19}$H$_{18}$BrN$_2$O$_4$ [M+H]$^+$: 417.0450; found: 417.0458.

**Ethyl 2-(4,4-dicyano-2-(4-cyanobenzoyl)-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4g)**
Eluent: ethyl acetate/petroleum ether (1/10). Yellow oil (128.8 mg, 71%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.20 (t, $J = 7.6$ Hz, 3H), 1.85 (s, 3H), 3.01-2.81 (m, 4H), 4.14-4.04 (m, 2H), 4.39 (s, 1H), 7.82 (d, $J = 8.0$ Hz, 2H), 7.99 (d, $J = 7.6$ Hz, 2H). $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$: 13.6, 14.0, 41.89, 41.91, 48.3, 61.6, 83.7, 113.7, 113.8, 117.6, 130.1, 132.9, 137.6, 139.2, 145.1, 171.1, 193.3. HRMS (ESI): calcd for C$_{20}$H$_{18}$N$_3$O$_4$ [M+H]$^+$: 364.1297; found: 364.1291.

**Ethyl 2-(2-(2-bromo-5-methoxybenzoyl)-4,4-dicyano-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4h)**

Eluent: ethyl acetate/petroleum ether (1/5). Colorless oil (182.8 mg, 82%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.24 (t, $J = 6.8$ Hz, 3H), 1.76 (s, 3H), 2.89 (d, AB syst., $J = 16.4$ Hz, 1H), 2.94 (d, AB syst., $J = 14.4$ Hz, 1H), 3.02 (d, AB syst., $J = 14.0$ Hz, 1H), 3.10 (d, AB syst., $J = 16.0$ Hz, 1H), 3.80 (s, 3H), 4.17-4.07 (m, 3H), 6.94 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.8$ Hz, 1H), 7.11 (d, $J = 3.2$ Hz, 1H), 7.52 (d, $J = 8.8$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$: 13.5, 14.1, 42.4, 42.5, 47.3, 55.8, 61.3, 83.8, 110.0, 113.59, 113.61, 115.7, 119.8, 135.1, 139.6, 141.9, 144.5, 159.4, 170.5, 193.7. HRMS (ESI): calcd for C$_{20}$H$_{20}$BrN$_2$O$_5$ [M+H]$^+$: 447.0506; found: 447.0511.

**Ethyl 2-(4,4-dicyano-1-hydroxy-3-methyl-2-(3-methylbenzoyl)cyclopent-2-en-1-yl)acetate (4i)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (112.6 mg, 64%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.17 (t, $J = 7.2$ Hz, 3H), 1.88 (s, 3H), 2.42 (s, 3H), 2.81 (d, AB syst., $J = 16.8$ Hz, 1H), 2.98 (d, AB Syst., $J = 15.6$ Hz, 1H), 2.99 (s, 2H), 4.13-4.02 (m, 2H), 4.42 (s, 1H), 7.48-7.38 (m, 2H), 7.65 (d, $J = 7.2$ Hz, 1H), 7.70 (s, 1H). $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$: 13.5, 14.0, 21.3, 30.9, 41.9, 42.2, 48.1, 61.3, 83.8, 113.9, 114.1, 127.5, 129.0, 129.7, 135.7, 136.3, 136.5, 139.2, 145.5, 170.8, 194.7. HRMS (ESI): calcd for C$_{20}$H$_{21}$N$_2$O$_4$ [M+H]$^+$: 353.1501; found: 353.1505.

**Ethyl 2-(4,4-dicyano-1-hydroxy-3-methyl-2-(4-methylbenzoyl)cyclopent-2-en-1-yl)acetate (4j)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (146.1 mg, 83%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.17 (t, $J = 6.8$ Hz, 3H), 1.87 (s, 3H), 2.43 (s, 3H), 2.80 (d, AB syst., $J = 16.8$ Hz, 1H), 2.96 (d, AB syst., $J = 17.6$ Hz, 1H), 2.99 (s, 2H), 4.12-4.02 (m, 2H), 4.42 (s, 1H), 7.31 (d, $J = 7.6$ Hz, 2H), 7.78 (d, $J = 8.0$Hz, 2H). $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$: 13.5, 14.0, 21.9, 41.9, 42.2, 48.1, 61.3, 83.8, 114.0, 114.2, 129.9, 130.0, 133.8, 136.2, 145.6, 146.2, 170.8, 194.1. HRMS (ESI): calcd for C$_{20}$H$_{21}$N$_2$O$_4$ [M+H]$^+$: 353.1501;
found: 353.1505.

**Ethyl 2-(4,4-dicyano-1-hydroxy-2-(4-methoxybenzoyl)-3-methylcyclopent-2-en-1-yl)acetate (4k)**

Eluent: ethyl acetate/petroleum ether (1/4). Yellow oil (126.9 mg, 69%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.17 (t, $J = 6.8$ Hz, 3H), 1.89 (s, 3H), 2.98–2.76 (m, 4H), 3.88 (s, 3H), 4.12–4.01 (m, 2H), 4.46 (s, 1H), 6.98 (d, $J = 8.8$ Hz, 2H), 7.86 (d, $J = 9.2$ Hz, 2H). $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$: 13.4, 14.0, 41.9, 42.2, 48.1, 55.7, 61.3, 83.8, 114.1, 114.2, 114.4, 129.2, 132.4, 135.6, 145.6, 165.1, 170.8, 192.7. HRMS (ESI): calcd for C$_{20}$H$_{21}$N$_2$O$_5$ [M+H]$^+$: 369.1450; found: 369.1442.

**Ethyl 2-(4,4-dicyano-2-(3,4-dimethoxybenzoyl)-1-hydroxy-3-methylcyclopent-2-en-1-yl)acetate (4l)**

Eluent: ethyl acetate/petroleum ether (1/10). Colorless oil (121.4 mg, 61%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.17 (t, $J = 7.2$ Hz, 3H), 1.89 (s, 3H), 2.77 (d, AB syst., $J = 16.4$ Hz, 1H), 2.93 (d, AB syst., $J = 16.8$ Hz, 1H), 2.97 (s, 2H), 3.91 (s, 3H), 3.94 (s, 3H), 4.11–4.01 (m, 2H), 4.45 (s, 1H), 6.93 (d, $J = 8.8$ Hz, 1H), 7.46 (s, 1H), 7.47 (d, $J = 7.2$ Hz, 1H). $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$: 13.4, 14.0, 41.8, 42.2, 48.3, 56.0, 56.2, 61.3, 83.7, 110.5, 114.1, 114.2, 126.2, 129.3, 135.5, 145.7, 149.5, 155.0, 170.9, 192.7. HRMS (ESI): calcd for C$_{21}$H$_{23}$N$_2$O$_6$ [M+H]$^+$: 399.1556; found: 399.1550.

**Ethyl 3-benzoyl-1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-enecarboxylate (4m)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (128.9 mg, 67%). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.16 (t, $J = 6.4$ Hz, 3H), 1.36 (t, $J = 6.8$ Hz, 3H), 1.69 (s, 3H), 2.82 (d, AB syst., $J = 14.4$ Hz, 1H), 2.85 (d, AB syst., $J = 14.0$ Hz, 1H), 2.96 (d, AB syst., $J = 15.2$ Hz, 1H), 2.97 (d, AB syst., $J = 15.2$ Hz, 1H), 4.10–4.01 (m, 2H), 4.33 (q, $J = 7.2$ Hz, 2H), 4.45 (s, 1H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.62 (t, $J = 7.2$ Hz, 1H), 7.91–7.89 (m, 2H). $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$: 13.8, 14.0, 43.1, 47.5, 55.5, 61.0, 63.8, 84.3, 117.6, 128.9, 129.8, 134.4, 136.8, 139.6, 144.3, 167.2, 171.4, 195.7. HRMS (ESI): calcd for C$_{21}$H$_{24}$NO$_6$ [M+H]$^+$: 386.1604; found: 386.1599.

**Ethyl 3-(1-naphthoyl)-1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-enecarboxylate (4n)**

Eluent: ethyl acetate/petroleum ether (1/8). White solid (165.3 mg, 76%). Mp: 109–111 ºC (ethyl acetate/petroleum ether). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 1.20 (t, $J = 6.8$ Hz, 3H), 1.36 (t, $J = 7.6$ Hz, 3H),
1.57 (s, 3H), 2.85 (d, AB syst., J = 14.4 Hz, 1H), 2.97 (d, AB syst., J = 15.6 Hz, 1H), 3.05 (d, AB syst., J = 14.8 Hz, 1H), 2.12 (d, AB syst., J = 15.6 Hz, 1H), 4.13-4.07 (m, 2H), 4.33 (q, J = 7.2 Hz, 2H), 4.58 (s, 1H), 7.59-7.52 (m, 2H), 7.65 (td, J1 = 7.2 Hz, J2 = 1.2 Hz, 1H), 7.91 (d, J = 8.0 Hz, 1H), 7.98 (td, J1 = 6.8 Hz, J2 = 1.2 Hz, 1H), 8.06 (d, J = 8.0 Hz, 1H), 8.77 (d, J = 8.4 Hz, 1H).

13CNMR (100 MHz, CDCl3) δ: 13.93, 13.99, 14.0, 43.2, 47.0, 55.7, 61.0, 63.7, 84.3, 117.5, 124.8, 125.4, 126.9, 128.6, 128.7, 130.2, 132.4, 133.9, 134.3, 134.5, 142.0, 145.6, 167.1, 171.2, 197.0. HRMS (ESI): calcd for C25H26NO6 [M+H]+: 436.1760; found: 436.1766.

**Ethyl 1-cyano-3-(2,4-dichlorobenzoyl)-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-enecarboxylate (4o)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (183.5 mg, 81%). 1H NMR(400 MHz, CDCl3) δ: 1.22 (t, J = 6.8 Hz, 3H), 1.32 (t, J = 6.4 Hz, 3H), 1.62 (s, 3H), 2.74 (d, AB syst., J = 14.8 Hz, 1H), 2.88 (d, AB syst., J = 15.6 Hz, 1H), 2.98 (d, AB syst., J = 14.8 Hz, 1H), 3.06 (d, AB syst., J = 15.6 Hz, 1H), 4.15-4.09 (m, 2H), 4.32-4.26 (m, 3H), 7.36 (dd, J1 = 8.4 Hz, J2 = 2.0 Hz, 1H), 7.46 (d, J = 2.0 Hz, 1H), 7.58 (d, J = 8.0Hz, 1H). 13CNMR (100 MHz, CDCl3) δ: 13.7, 14.0, 14.1, 43.2, 46.7, 55.9, 61.1, 63.9, 84.2, 117.2, 127.9, 130.9, 132.1, 133.1, 135.9, 138.8, 144.0, 144.7, 166.6, 171.1, 193.1. HRMS (ESI): calcd for C21H22Cl2NO6 [M+H]+: 454.0824; found: 454.0829.

**Ethyl 3-(2-bromobenzoyl)-1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-enecarboxylate (4p)**

Eluent: ethyl acetate/petroleum ether (1/3). Yellow solid (180.5 mg, 78%). Mp: 110-111 ºC (ethyl acetate/petroleum ether). 1H NMR(400 MHz, CDCl3) δ: 1.23 (t, J = 7.2 Hz, 3H), 1.31 (t, J = 7.2 Hz, 3H), 1.55 (s, 3H), 2.73 (d, AB syst., J = 14.0 Hz, 1H), 2.91 (d, AB syst., J = 16.0 Hz, 1H), 3.06 (d, AB syst., J = 14.0 Hz, 1H), 3.13 (d, AB syst., J = 15.6 Hz, 1H), 4.16-4.11 (m, 2H), 4.31-4.24 (m, 3H), 7.35 (td, J1 = 7.6 Hz, J2 = 1.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.53 (dd, J1 = 7.6 Hz, J2 = 1.6 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H). 13CNMR (100 MHz, CDCl3) δ: 13.8, 14.0, 14.1, 43.2, 46.4, 56.2, 61.0, 63.8, 84.3, 117.2, 119.8, 128.0, 130.7, 133.0, 134.1, 139.7, 143.6, 145.7, 166.6, 171.0, 194.9. HRMS (ESI): calcd for C21H23BrNO6 [M+H]+: 464.0709; found: 464.0703.

**Ethyl 3-(3-bromobenzoyl)-1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-enecarboxylate (4p)**

Eluent: ethyl acetate/petroleum ether (1/3). Yellow solid (180.5 mg, 78%). Mp: 110-111 ºC (ethyl acetate/petroleum ether). 1H NMR(400 MHz, CDCl3) δ: 1.23 (t, J = 7.2 Hz, 3H), 1.31 (t, J = 7.2 Hz, 3H), 1.55 (s, 3H), 2.73 (d, AB syst., J = 14.0 Hz, 1H), 2.91 (d, AB syst., J = 16.0 Hz, 1H), 3.06 (d, AB syst., J = 14.0 Hz, 1H), 3.13 (d, AB syst., J = 15.6 Hz, 1H), 4.16-4.11 (m, 2H), 4.31-4.24 (m, 3H), 7.35 (td, J1 = 7.6 Hz, J2 = 1.6 Hz, 1H), 7.41 (t, J = 7.6 Hz, 1H), 7.53 (dd, J1 = 7.6 Hz, J2 = 1.6 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H). 13CNMR (100 MHz, CDCl3) δ: 13.8, 14.0, 14.1, 43.2, 46.4, 56.2, 61.0, 63.8, 84.3, 117.2, 119.8, 128.0, 130.7, 133.0, 134.1, 139.7, 143.6, 145.7, 166.6, 171.0, 194.9. HRMS (ESI): calcd for C21H23BrNO6 [M+H]+: 464.0709; found: 464.0703.
enecarboxylate (4q)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (164.3 mg, 71%). $^1$H NMR(400 MHz, CDCl$_3$) $\delta$: 1.19 (t, $J = 7.6$ Hz, 3H), 1.37 (t, $J = 6.8$ Hz, 3H), 1.71 (s, 3H), 2.99-2.80 (m, 4H), 4.12-4.04 (m, 2H), 4.34 (q, $J = 7.2$ Hz, 2H), 4.42 (s, 1H), 7.39 (t, $J = 8.4$ Hz, 1H), 7.75-7.73 (m, 1H), 7.83 (d, $J = 7.2$ Hz, 1H), 8.04 (s, 1H). $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$: 13.8, 14.0, 43.0, 47.6, 55.5, 61.1, 63.8, 84.3, 117.4, 123.3, 128.7, 130.6, 132.1, 137.1, 138.6, 140.2, 144.0, 167.0, 171.4, 194.2. HRMS (ESI): calcd for C$_{21}$H$_{23}$BrNO$_6$ [M+H]$^+$: 464.0709; found: 464.0713.

Ethyl 1-cyano-3-(4-cyanobenzoyl)-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-enecarboxylate (4r)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (123.3 mg, 60%). $^1$H NMR(400 MHz, CDCl$_3$) $\delta$: 1.19 (t, $J = 7.2$ Hz, 3H), 1.35 (t, $J = 6.8$ Hz, 3H), 1.67 (s, 3H), 2.80 (d, AB syst., $J = 14.0$ Hz, 1H), 2.86 (d, AB syst., $J = 15.6$ Hz, 1H), 2.90 (d, AB syst., $J = 13.6$ Hz, 1H), 2.97 (d, AB syst., $J = 16.0$ Hz, 1H), 4.14-4.03 (m, 2H), 4.35-4.30 (m, 2H), 4.42 (s, 1H), 7.80 (d, $J = 8.8$ Hz, 2H), 8.01 (d, $J = 8.8$ Hz, 2H). $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$: 13.8, 14.0, 42.8, 47.6, 55.4, 61.2, 63.9, 84.3, 117.3, 117.7, 130.1, 132.8, 139.8, 140.5, 143.9, 166.9, 171.6, 194.3. HRMS (ESI): calcd for C$_{22}$H$_{23}$N$_2$O$_6$ [M+H]$^+$: 411.1556; found: 411.1562.

Ethyl 3-(2-bromo-5-methoxybenzoyl)-1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylcyclopent-2-enecarboxylate (4s)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (189.8 mg, 77%). $^1$H NMR(400 MHz, CDCl$_3$) $\delta$: 1.23 (t, $J = 7.2$ Hz, 3H), 1.31 (t, $J = 7.2$ Hz, 3H), 1.60 (s, 3H), 2.73 (d, AB syst., $J = 14.8$ Hz, 1H), 2.91 (d, AB syst., $J = 15.6$ Hz, 1H), 3.04 (d, AB syst., $J = 14.8$ Hz, 1H), 3.09 (d, AB syst., $J = 15.2$ Hz, 1H), 3.79 (s, 3H), 4.14 (q, $J = 7.2$ Hz, 2H), 4.21 (s, 1H), 4.28 (q, $J = 7.2$ Hz, 2H), 6.90 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.8$ Hz, 1H), 7.09 (d, $J = 3.2$ Hz, 1H), 7.48 (d, $J = 8.8$ Hz, 1H). $^{13}$CNMR (100 MHz, CDCl$_3$) $\delta$: 13.8, 14.0, 14.1, 43.2, 46.4, 55.7, 56.2, 60.9, 63.8, 84.3, 109.8, 115.5, 117.2, 119.4, 134.9, 140.4, 143.4, 145.9, 159.3, 166.6, 171.0, 194.7. HRMS (ESI): calcd for C$_{22}$H$_{25}$BrNO$_7$ [M+H]$^+$: 494.0814; found: 494.0820.

Ethyl 2-(4,4-dicyano-1-hydroxy-3-methyl-2-(3-phenylpropanoyl)cyclopent-2-en-1-yl)acetate(4t)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (161.0 mg, 78%). $^1$H NMR(400 MHz, CDCl$_3$) $\delta$: 1.25 (t, $J = 6.8$ Hz, 3H), 1.33 (t, $J = 7.2$ Hz, 3H), 1.95 (s, 3H), 2.90-2.63 (m, 4H), 2.98-2.96 (m, 2H), 3.07-
3.03 (m, 2H), 4.13 (q, \( J = 7.2 \) Hz, 2H), 4.34-4.23 (m, 3H), 7.21-7.19 (m, 3H), 7.29-7.26 (m, 2H). \(^{13}\)CNMR (100 MHz, CDCl\(_3\)): δ: 13.7, 14.0, 14.1, 29.4, 43.2, 45.6, 46.8, 55.7, 61.1, 61.12, 63.8, 83.9, 117.5, 126.2, 126.3, 128.4, 128.5, 128.6, 140.6. HRMS (ESI): calcd for C\(_{23}\)H\(_{28}\)NO\(_6\) \([\text{M+H}]^+\): 414.1917; found: 414.1910.

**Ethyl 1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-3-(3-methylbenzoyl)-2-methylene cyclopentanecarboxylate (5a)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (137.3 mg, 69%). \(^1\)H NMR(400 MHz, CDCl\(_3\)): δ:

1.11 (t, \( J = 7.6 \) Hz, 3H), 1.34 (t, \( J = 6.8 \) Hz, 3H), 2.40 (s, 3H), 2.83-2.64 (m, 4H), 4.05-4.01 (m, 2H), 4.32 (q, \( J = 7.2 \) Hz, 2H), 4.63 (t, \( J = 2.8 \) Hz, 1H), 4.95 (t, \( J = 2.0 \) Hz, 1H), 5.39 (s, 1H), 5.62 (t, \( J = 2.4 \) Hz, 1H), 7.38 (t, \( J = 7.6 \) Hz, 1H), 7.45 (d, \( J = 7.2 \) Hz, 1H), 7.72 (d, \( J = 8.0 \) Hz, 1H), 7.75 (s, 1H). \(^{13}\)CNMR (100 MHz, CDCl\(_3\)): δ: 13.9, 14.0, 21.8, 43.2, 47.0, 50.0, 54.9, 60.9, 63.7, 80.2, 116.3, 119.0, 126.3, 129.1, 129.12, 136.7, 136.9, 139.1, 147.1, 167.9, 169.9, 201.3. HRMS (ESI): calcd for C\(_{22}\)H\(_{26}\)NO\(_6\) \([\text{M+H}]^+\): 400.1760; found: 400.1768.

**Ethyl 1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-3-(4-methylbenzoyl)-2-methylene cyclopentanecarboxylate (5b)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (141.6 mg, 71%). \(^1\)H NMR(400 MHz, CDCl\(_3\)): δ:

1.10 (t, \( J = 7.2 \) Hz, 3H), 1.32 (t, \( J = 6.8 \) Hz, 3H), 2.40 (s, 3H), 2.82-2.62 (m, 4H), 4.07-3.95 (m, 2H), 4.33 -4.28 (m, 2H), 4.61 (s, 1H), 4.93 (s, 1H), 5.43 (s, 1H), 5.59 (s, 1H), 7.28 (d, \( J = 8.0 \) Hz, 2H), 7.82 (d, \( J = 7.6 \) Hz, 2H). \(^{13}\)CNMR (100 MHz, CDCl\(_3\)): δ: 13.9, 14.0, 21.8, 43.2, 47.0, 50.0, 54.7, 60.8, 63.6, 80.2, 116.1, 119.0, 129.0, 129.9, 134.4, 146.2, 147.2, 167.9, 169.9, 200.6. HRMS (ESI): calcd for C\(_{22}\)H\(_{26}\)NO\(_6\) \([\text{M+H}]^+\): 400.1760; found: 400.1764.

**Ethyl 1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-3-(4-methoxybenzoyl)-2-methylene cyclopentanecarboxylate (5c)**

Eluent: ethyl acetate/petroleum ether (1/3). Yellow oil (151.4 mg, 73%). \(^1\)H NMR(400 MHz, CDCl\(_3\)): δ:

1.11 (t, \( J = 7.2 \) Hz, 3H), 1.32 (t, \( J = 7.6 \) Hz, 3H), 2.81-2.61 (m, 4H), 3.85 (s, 3H), 4.07-3.98 (m, 2H), 4.33 -4.27 (m, 2H), 4.57 (t, \( J = 1.6 \) Hz, 1H), 4.94 (s, 1H), 5.55 (s, 1H), 5.59 (t, \( J = 2.0 \) Hz, 1H), 6.94 (d, \( J = 8.4 \) Hz, 2H), 7.90 (d, \( J = 9.2 \) Hz, 2H). \(^{13}\)CNMR (100 MHz, CDCl\(_3\)): δ: 13.9, 14.0, 43.1, 47.0, 50.0, 54.4, 55.7, 60.8, 63.6, 80.2, 114.4, 116.0, 119.1, 129.8, 131.4, 147.2, 165.0, 168.0, 169.9, 199.2. HRMS (ESI): calcd
for C_{22}H_{26}NO_{7}\ [M+H]^{+}: 416.1709; found: 416.1702.

**Ethyl 1-cyano-3-(3,4-dimethoxybenzoyl)-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methylene cyclopentanecarboxylate (5d)**

Eluent: ethyl acetate/petroleum ether (1/3). White solid (151.3 mg, 68%). Mp: 112-113 °C (ethyl acetate/petroleum ether). \(^{1}\)H NMR(400 MHz, CDCl\(_3\)) \(\delta\): 1.08 (t, \(J = 6.8\) Hz, 3H), 1.25 (t, \(J = 6.4\) Hz, 3H), 2.81-2.58 (m, 4H), 3.81 (s, 3H), 3.86 (s, 3H), 4.03-3.93 (m, 2H), 4.29 -4.24 (m, 2H), 4.81 (s, 1H), 5.43 (s, 1H), 5.49 (s, 1H), 7.13 (d, \(J = 8.4\) Hz, 1H), 7.49 (s, 1H), 7.62 (dd, \(J_1 = 8.4\) Hz, \(J_2 = 1.6\) Hz, 1H). \(^{13}\)CNMR (100 MHz, CDCl\(_3\)) \(\delta\): 14.2, 14.4, 43.4, 46.9, 50.1, 56.0, 56.4, 56.6, 60.5, 63.6, 80.2, 111.0, 111.5, 116.2, 119.9, 124.6, 130.7, 147.4, 149.2, 154.5, 167.8, 170.3, 198.2. HRMS (ESI): calcd for C_{23}H_{28}NO_{8}\ [M+H]^{+}: 446.1815; found: 446.1810.

**2. Preparation of 3-benzoyl-4-hydroxy-2-methyl-4-phenylcyclopent-2-ene-1,1-dicarbonitrile (7) from the reaction 2a with 3a and 2-bromo-1-phenylethanone (6)**

To a flask containing malononitrile (2a, 33.0 mg, 0.5 mmol) and K_{2}CO_{3} (82.8 mg, 0.6 mmol) in CH_{3}CN (5 mL) were added 2-bromo-1-phenylethanone (6, 99.5 mg, 0.5 mmol). The mixture was stirred at room temperature for 20 min. Then 1-phenylbuta-2,3-dien-1-one (3a, 72 mg, 0.5 mmol) was added. The resulting mixture was stirred at 80 °C for another 1.5 h. Upon completion as determined by TLC analysis, it was allowed to cool to room temperature and quenched with saturated ammonium chloride. The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na_{2}SO_{4} and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO\(_2\)) using EtOAc/petroleum ether (v/v =1/5) as eluent to give 3-benzoyl-4-hydroxy-2-methyl-4-phenylcyclopent-2-ene-1,1-dicarbonitrile (7, 91.8 mg, 56%).

**3-Benzoyl-4-hydroxy-2-methyl-4-phenylcyclopent-2-ene-1,1-dicarbonitrile (7)**

Eluent: ethyl acetate/petroleum ether (1/5). Yellow solid (91.8 mg, 88%). Mp: 116-117°C (ethyl acetate/petroleum ether). \(^{1}\)H NMR(400 MHz, CDCl\(_3\)) \(\delta\): 2.03 (s, 3H), 2.91 (d, AB syst., \(J = 14.0\) Hz, 1H), 3.12 (d, AB syst., \(J = 14.0\) Hz, 1H), 4.33 (s, 1H), 7.22 (t, \(J = 7.2\) Hz, 1H), 7.30 (t, \(J = 8.0\) Hz, 2H), 7.52 (d, \(J = 7.2\) Hz, 2H), 7.53 (d, \(J = 7.2\) Hz, 2H), 7.67 (d, \(J = 8.0\) Hz, 1H), 7.84 (d, \(J = 7.6\) Hz, 2H). \(^{13}\)CNMR (100 MHz, CDCl\(_3\)) \(\delta\): 14.3, 43.2, 51.5, 88.4, 114.0, 114.3, 124.7, 128.3, 128.9, 129.3, 129.6, 134.9, 135.9, 139.3,
142.3, 145.9, 194.7. HRMS (ESI): calcd for C_{14}H_{16}N_{3}O_{3} [M+H]^+: 274.1186; found: 274.1189. HRMS (ESI): calcd for C_{21}H_{17}N_{2}O_{2} [M+H]^+: 329.1290; found: 329.1282.

3. Preparation of ethyl 3,3-dicyano-4-methyl-6-oxo-6-phenylhex-4-enoate (9) from the reaction 2a, 3a and ethyl 2-chloroacetate (8)

To a flask containing malononitrile (2a, 33.0 mg, 0.5 mmol) and K_{2}CO_{3} (82.8 mg, 0.6 mmol) in CH_{3}CN (5 mL) were added ethyl 2-chloroacetate (8, 61.3 mg, 0.5 mmol). The mixture was stirred at room temperature for 20 min. Then 1-phenylbuta-2,3-dien-1-one (3a, 72.0 mg, 0.5 mmol) was added. The resulting mixture was stirred at 80 °C for another 1.5 h. As completion as determined by TLC analysis, it was allowed to cool to room temperature and quenched with saturated ammonium chloride. The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na_{2}SO_{4} and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_{2}) using EtOAc/petroleum ether (v/v =1/5) as eluent to give ethyl 3,3-dicyano-4-methyl-6-oxo-6-phenylhex-4-enoate (9, 91.8 mg, 62%).

Ethyl 3,3-dicyano-4-methyl-6-oxo-6-phenylhex-4-enoate (9)

Eluent: ethyl acetate/petroleum ether (1/5). Yellow oil (91.8 mg, 62%). ^{1}H NMR(400 MHz, CDCl_{3}) δ: 1.32 (t, J = 7.2 Hz, 3H), 2.28 (d, J = 0.8 Hz, 3H), 3.19 (s, 2H), 4.29 (q, J = 6.8 Hz, 2H), 7.40 (d, J = 0.8 Hz, 1H), 7.53-7.49 (m, 2H), 7.64-7.60 (m, 1H), 7.95-7.93 (m, 2H). ^{13}C NMR (100 MHz, CDCl_{3}) δ: 14.0, 15.5, 40.7, 41.2, 62.6, 113.0, 127.3, 128.7, 129.0, 134.0, 137.1, 140.7, 165.8, 190.3. HRMS (ESI): calcd for C_{17}H_{17}N_{2}O_{3} [M+H]^+: 297.1239; found: 297.1235.

III. Control experiments

1. Reaction of 1 with 2a leading to the formation of intermediate A

To a flask containing malononitrile (2a, 33.0 mg, 0.5 mmol) and K_{2}CO_{3} (69.0 mg, 0.5 mmol) in CH_{3}CN (5 mL) were added ethyl 4-chloroacetoacetate (1, 82.3 mg, 0.5 mmol). The mixture was stirred at room temperature for 30 min. Upon completion as determined by TLC analysis, it was allowed to cool to room temperature and quenched by saturated ammonium chloride. The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na_{2}SO_{4} and concentrated under reduced pressure. The residue was purified by flash chromatography (SiO_{2}) using EtOAc/petroleum ether
(v/v = 1/3) as eluent to give ethyl 5,5-dicyano-3-oxopentanoate (A, 79.5 mg, 82%).

**Ethyl 5,5-dicyano-3-oxopentanoate (A)**

Eluent: ethyl acetate/petroleum ether (1/3). Yellow oil (79.5 mg, 82%). \(^1\)H NMR (400 MHz, DMSO-d\(_6\)) \(\delta\): 1.19 (t, \(J = 7.2\) Hz, 3H), 3.49 (d, \(J = 6.8\) Hz, 2H), 3.69 (s, 2H), 4.10 (q, \(J = 6.8\) Hz, 2H), 4.91 (t, \(J = 5.6\) Hz, 1H). \(^{13}\)CNMR (100 MHz, DMSO-d\(_6\)) \(\delta\): 14.3, 17.8, 41.6, 48.2, 61.3, 114.4, 167.0, 199.0. HRMS (ESI): calcld for C\(_9\)H\(_{11}\)N\(_2\)O\(_3\) [M+H]^+: 195.0770; found: 195.0777.

2. Reaction of A with 3a leading to the formation of 4a

To a flask containing ethyl 5,5-dicyano-3-oxopentanoate (A, 97.0 mg, 0.5 mmol) and 1-phenylbuta-2,3-dien-1-one (3a, 72.0 mg, 0.5 mmol) in CH\(_3\)CN (5 mL) were added K\(_2\)CO\(_3\) (69.0 mg, 0.5 mmol). The mixture was stirred at 80 °C for 1.5 h. Upon completion as determined by TLC analysis, it was allowed to cool to room temperature and quenched by saturated ammonium chloride. The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (SiO\(_2\)) using EtOAc/petroleum ether (v/v = 1/5) as eluent to give 4a (148.7 mg, 88%).

3. Isomerization reaction of 5a toward 4u

To a flask containing ethyl 1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-3-(3-methylbenzoyl)-2-methylene cyclopentanecarboxylate (5a, 200.1 mg, 0.5 mmol) in DMSO (5 mL) were added NaOH (24.0 mg, 0.6 mmol). The mixture was stirred at 100 °C for 1.0 h. Upon completion as determined by TLC analysis, it was allowed to cool to room temperature and quenched by saturated ammonium chloride. The mixture was extracted with ethyl acetate (3×15 mL). The combined organic layers were dried over anhydrous Na\(_2\)SO\(_4\) and concentrated under reduced pressure. The resulting residue was purified by flash chromatography (SiO\(_2\)) using EtOAc/petroleum ether (v/v = 1/7) as eluent to give 4u (30.0 mg, 15%).

**ethyl 1-cyano-4-(2-ethoxy-2-oxoethyl)-4-hydroxy-2-methyl-3-(3-methylbenzoyl)cyclopent-2-ene carboxylate (4u),** Eluent: ethyl acetate/petroleum ether (1/7). Yellow oil (30.0 mg, 15%). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 1.17 (t, \(J = 6.4\) Hz, 3H), 1.37 (t, \(J = 7.6\) Hz, 3H), 2.42 (s, 3H), 2.99-2.72 (m, 4H), 4.11-4.04 (m, 2H), 4.37-4.30 (m, 2H), 4.46 (s, 1H), 7.44-7.36 (m, 2H), 7.79-7.68 (m, 2H). \(^{13}\)CNMR (100 MHz, CDCl\(_3\)) \(\delta\): 13.8, 14.0, 21.3, 30.9, 43.1, 47.5, 55.5, 61.0, 63.7, 84.3, 117.6, 127.4, 128.8, 129.7, 135.2, 136.9,
138.9, 139.5, 143.4, 167.2, 171.4, 195.8. HRMS (ESI): calcd for C$_{22}$H$_{26}$NO$_6$ [M+H]$^+$: 400.1760; found: 400.1755.
IV. (1) Copies of $^1$H and $^{13}$C NMR spectra of 4a-4t
4e
4k
4o
(2) Copies of $^1$H and $^{13}$C NMR spectra of 5a-5e
(3) Copies of $^1$H and $^{13}$C NMR spectra of 7, 9, A and 4u
V. X-ray crystal structure and data of 4n

![X-ray crystal structure of 4n]

**Figure 1** The X-ray crystal structure of 4n

**X-ray structure determination.** Single crystals suitable for X-ray diffraction were obtained by slow evaporation of the solvent from a EtOAc/petroleum ether (v/v =1/8) solution of 4n. Crystal data collection and refinement parameters of 4n are summarized in Table 1. Intensity data were collected at 290 K on a SuperNova Dual diffractometer using mirror-monochromated Mo Kα radiation, λ = 0.71073 Å. The data were corrected for decay, Lorentz, and polarization effects as well as absorption and beam corrections based on the multi-scan technique. The structure was solved by a combination of direct methods in SHELXTL and the difference Fourier technique, and refined by full-matrix least-squares procedures. Nonhydrogen atoms were refined with anisotropic displacement parameters. The H-atoms were either located or calculated and subsequently treated with a riding model. The crystallographic data (excluding structure factors) for 4n has been deposited at the Cambridge Crystallographic Data Centre. CCDC 1875026 contains the supplementary
crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1 Crystallographic data and structure refinement results of 4n

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VI. References

