Supporting Information

A Synthesis of Novel Perinaphthenones from Acetylenic Esters and Acenaphthoquinone-Malononitrile Adducts in the Presence of Triphenylphosphine

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1. Experimental analysis

**General remarks:** All purchased solvents and chemicals were of analytical grade and used without further purification. Compound 1 and 2 were prepared from acenaphthoquinone and malononitrile (or ethyl cyanoacetate) according to the literature[1] The melting points of the products were determined in open capillary tubes by using Electrothermal-9100 apparatus. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker DRX-500Avance spectrometer at 500 and 125 MHz, respectively. NMR spectra were obtained in solution of DMSO-$_d_6$ and CDCl$_3$ using tetramethysilane (TMS) as internal standard. The abbreviations used for NMR signals: s = singlet, d = doublet, t = triplet, and m = multiplet. FT-IR spectra were recorded on a Shimadzu IR-460 instrument using the KBr self-supported pellet technique. Mass spectra were obtained on a Finnigan-MAT-8430EI-MS apparatus at ionization potential of 70 eV. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Column chromatography was performed using silica (Merck #60).

**General procedure for synthesis of Knoevenagel adducts (1 and 2)**

A mixture of acenaphthylene-1,2-dione (1.820 g, 10 mmol) and malononitrile (0.600 g, 10 mmol) and or ethyl cyanoacetate (1.131 g, 10 mmol) in absolute ethanol (20 mL) was refluxed for 1 h. The cooled mixture was filtered and the precipitate was washed with cold ethanol (10 mL) to afford compound 1 and or 2.

**General procedure for synthesis of compounds (4a-j)**

To a stirred solution of 1 and or 2 (1 mmol) and acetylenic ester 2 (1 mmol) in CH$_2$Cl$_2$ (5 mL) was added dropwise a mixture of PPh$_3$ (0.026 gr, 0.1 mmol) in 5 mL
CH$_2$Cl$_2$ at 0 °C in 10 min. The mixture was then allowed to warm to rt, and stirred for 12 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (SiO$_2$; $n$-hexane/EtOAc, 2:1) to afford the pure adducts.

2. Characterization data of the new compounds

**Dimethyl 2-cyano-3-(2-cyano-1-oxo-1H-phenalen-3-yl)maleate (4a)**

Yellow solid; mp 185-190 °C; yield: 0.31 g (84 %). IR (KBr) ($v_{\text{max}}$, cm$^{-1}$): 3057, 2952, 2194, 1728, 1654, 1571, 1437, 1255, 1008, 778. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$H 3.95 (3 H, s, MeO), 4.03 (3 H, s, MeO), 7.71 (1 H, t, $^3J = 7.5$ Hz, Ar-H), 7.92 (1 H, t, $^3J = 7.5$ Hz, Ar-H), 8.14 (1 H, d, $^3J = 7.5$ Hz, Ar-H), 8.27 (1 H, d, $^3J = 8.0$ Hz, Ar-H), 8.30 (1 H, d, $^3J = 8.0$ Hz, Ar-H), 8.78 (1 H, d, $^3J = 7.5$ Hz, Ar-H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$C 53.9 (2 MeO), 111.1 (CN), 111.8 (CN), 112.3 (C), 113.0 (C), 122.5 (C), 126.7 (CH), 126.8 (C), 127.9 (CH), 131.2 (C), 131.9 (C), 132.5 (CH), 133.6 (CH), 136.3 (CH), 136.7 (CH), 150.5 (C), 153.1 (C), 158.6 (C=O), 162.1 (C=O), 177.7 (C=O). EI-MS: $m/z$ (%) = 372 (M$^+$, 82), 313 (53), 299 (48), 272 (51), 255 (100), 226 (50), 200 (32). Anal. Calcd for C$_{21}$H$_{12}$N$_2$O$_5$ (372.34): C, 67.74; H, 3.25; N, 7.52. Found: C, 67.95; H, 3.32; N, 7.61%.

**Diethyl 2-cyano-3-(2-cyano-1-oxo-1H-phenalen-3-yl)maleate (4b)**
Yellow solid; mp 137-140 °C; yield: 0.32 g (80 %). IR (KBr) ($\nu_{\text{max}}$, cm$^{-1}$): 3030, 2985, 2227, 1736, 1643, 1572, 1370, 1256, 1012, 782. $^1$H NMR (500 MHz, CDCl$_3$): \( \delta \)H 1.34 (3 H, t, \( ^3J = 8.5 \) Hz, Me), 1.44 (3 H, t, \( ^3J = 8.5 \) Hz, Me), 4.42 (2 H, q, \( ^3J = 7.5 \) Hz, CH$_2$O), 4.45 (2 H, q, \( ^3J = 7.5 \) Hz, CH$_2$O), 7.76 (1 H, t, \( ^3J = 7.5 \) Hz, Ar-H), 7.91 (1 H, t, \( ^3J = 7.5 \) Hz, Ar-H), 8.14 (1 H, d, \( ^3J = 7.5 \) Hz, Ar-H), 8.29 (1 H, d, \( ^3J = 8.0 \) Hz, Ar-H), 8.37 (1 H, d, \( ^3J = 8.0 \) Hz, Ar-H), 8.77 (1 H, d, \( ^3J = 7.5 \) Hz, Ar-H).

$^{13}$C NMR (125 MHz, CDCl$_3$): \( \delta \)C 12.7 (Me), 12.9 (Me), 63.2 (2 CH$_2$O), 110.8 (CN), 111.9 (CN), 112.5 (C), 113.7 (C), 122.1 (C), 126.1 (C), 126.2 (CH), 127.2 (C), 127.3 (CH), 130.9 (C), 131.9 (CH), 133.2 (CH), 135.8 (CH), 136.3 (CH), 150.4 (C), 151.2 (C), 157.6 (C=O), 161.2 (C=O), 177.3 (C=O). EI-MS: \( m/z \) (%) = 400 (M$^+$, 98), 355 (10), 327 (55), 299 (44), 283 (43), 272 (53), 255 (100), 226 (50), 200 (40), 175 (10).

Anal. Calcd for C$_{23}$H$_{16}$N$_2$O$_5$ (400.11): C, 69.00; H, 4.03; N, 7.00. Found: C, 69.19; H, 4.10; N, 7.08%.

**Di-tert-butyl 2-cyano-3-(2-cyano-1-oxo-1H-phenalen-3-yl)maleate (4c)**

Yellow solid; mp 133-138 °C; yield: 0.34 g (75 %). IR (KBr) ($\nu_{\text{max}}$, cm$^{-1}$): 3052, 2984, 2227, 1729 (C=O), 1643, 1571, 1371, 1285, 1149, 780. $^1$H NMR (500 MHz, CDCl$_3$): \( \delta \)H 1.54 and 1.55 (9 H, s, 3 Me), 1.64 (9 H, s, 3 Me), 7.77 (1 H, t, \( ^3J = 7.7 \) Hz, Ar-H), 7.92 (1 H, t, \( ^3J = 7.7 \) Hz, Ar-H), 8.14 (1 H, d, \( ^3J = 7.5 \) Hz, Ar-H), 8.29
(1 H, d, $^3J = 8.0$ Hz, Ar-H), 8.38 (1 H, d, $^3J = 8.0$ Hz, Ar-H), 8.80 (1 H, d, $^3J = 7.5$ Hz, Ar-H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$C 27.5 (6 Me), 85.7(C), 86.3 (C), 111.8 (CN), 112.4 (CN), 113.1 (C), 114.6 (C), 122.8 (C), 126.7 (CH), 127.0 (C), 127.3 (C), 127.7 (CH), 131.9 (C), 132.3 (CH), 133.8 (CH), 136.1 (CH), 136.6 (CH), 151.5 (C), 151.7 (C), 156.9 (C=O), 160.5 (C=O), 178.0 (C=O). EIMS: $m/\ell$ (%) = 456 (M$^+$, 87), 355 (58), 299 (53), 272 (47), 255 (100), 226 (43), 200 (30). Anal. Calcd for C$_{27}$H$_{24}$N$_2$O$_5$ (456.17): C, 71.04; H, 5.30; N, 6.14. Found: C, 71.17; H, 5.37; N, 6.20%.

**Methyl (E)-3-cyano-2-(2-cyano-1-oxo-1H-phenalen-3-yl)acrylate (4d)**

Yellow solid; mp 215-220 °C; yield: 0.27 g (85 %). IR (KBr) ($\nu_{\text{max}}, \text{cm}^{-1}$): 3063, 2926, 2228, 1735, 1642, 1571, 1369, 1254, 1015, 765. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$H 3.89 (3 H, s, MeO), 7.11 (1 H, s, HC=C), 7.72 (2 H, m, 2 Ar-H), 7.93 (1 H, t, $^3J = 7.5$ Hz, Ar-H), 8.28 (1 H, d, $^3J = 8.0$ Hz, Ar-H), 8.37 (1 H, d, $^3J = 8.0$ Hz, Ar-H), 8.81 (1 H, d, $^3J = 7.5$ Hz, Ar-H). $^{13}$C NMR (125 MHz, CDCl$_3$): $\delta$C 53.7 (MeO), 112.8 (CN), 112.9 (CN), 114.0 (CH), 123.7 (C), 126.5 (CH), 127.0 (C), 127.8 (CH), 128.3 (C), 130.3 (C), 131.9 (CH), 132.0 (C), 132.3 (CH), 135.8 (CH), 136.5 (CH), 145.3 (C), 152.0 (C), 161.6 (C=O), 178.0 (C=O). EIMS: $m/\ell$ (%) = 314 (M$^+$, 80), 299 (40), 272 (46), 255 (100), 226 (48), 200 (27). Anal. Calcd for C$_{19}$H$_{10}$N$_2$O$_3$ (314.07): C, 72.61; H, 3.21; N, 8.91. Found: C, 72.77; H, 3.29; N, 8.99%.

**Ethyl (E)-3-cyano-2-(2-cyano-1-oxo-1H-phenalen-3-yl)acrylate (4e)**
Dimethyl 2-cyano-3-(2-(ethoxycarbonyl)-1-oxo-1H-phenalen-3-yl)maleate (4f)

Yellow solid; mp 180-185 °C; yield: 0.36 g (86 %). IR (KBr) (ν max, cm -1): 3055, 2988, 2214, 1727, 1625, 1588, 1370, 1269, 780. 1 H NMR (500 MHz, DMSO-d 6): δ H 1.25 (3 H, t, 3 J = 7.0 Hz, Me), 3.28 (3 H, s, MeO), 3.52 (3 H, s, MeO), 4.48 (2 H, q, 3 J = 7.0 Hz, CH 2 O), 7.73 (1 H, t, 3 J = 7.5 Hz, Ar-H), 7.89 (1 H, t, 3 J = 7.5 Hz, Ar-H), 8.10 (1 H, d, 3 J = 8.0 Hz, Ar-H), 8.31 (1 H, d, 3 J = 8.0 Hz, Ar-H), 8.33 (1 H, d, 3 J = 8.0 Hz, Ar-H), 8.64 (1 H, d, 3 J = 7.5 Hz, Ar-H). 13 C NMR (125 MHz, CDCl 3):

Dimethyl 2-cyano-3-(2-(ethoxycarbonyl)-1-oxo-1H-phenalen-3-yl)maleate (4f)
\[ \delta_C 13.8 \text{ (Me), 52.0 (MeO), 52.7 (MeO), 64.6 (CH}_2\text{O), 114.6 (CN), 122.9 (C), 126.1 \text{ (CH), 126.5 (CH), 127.1 (C), 127.6 (C), 128.4 (C), 128.5 (CH), 128.7 (CH), 129.2 (C), 131.9 (C), 133.3 (CH), 134.4 (CH), 149.1 (C), 150.7 (C), 158.3 (C=O), 161.8 (C=O), 162.3 (C=O), 187.2 (C=O). EI-MS: } m/z \% = 419 (M^+, 91), 360 (62), 345 (53), 318 (52), 301 (100), 275 (42), 246 (25), 202 (34). \text{ Anal. Calcd for C}_{23}\text{H}_{17}\text{NO}_7 \text{ (419.10): C, 65.87; H, 4.09; N, 3.34. Found: C, 65.99; H, 4.16; N, 3.41\%.} \\

**Diethyl 2-cyano-3-(2-(ethoxycarbonyl)-1-oxo-1H-phenalen-3-yl)maleate (4g)**

Yellow solid; mp 170-175 °C; yield: 0.37 g (83 %). IR (KBr) \( (v_{\text{max}}, \text{cm}^{-1}) \): 3107, 2989, 2217, 1728, 1626, 1579, 1372, 1267, 780. \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta_H \) 0.84 (3 H, t, \( ^3J = 7.5 \text{ Hz, Me} \)), 1.42-1.48 (6 H, m, 2 Me), 3.93 (2 H, q, \( ^3J = 7.5 \text{ Hz, CH}_2\text{O} \)), 4.52 (4 H, q, \( ^3J = 7.5 \text{ Hz, 2 CH}_2\text{O} \)), 7.80-7.82 (2 H, m, 2 Ar-H), 8.11 (1 H, d, \( ^3J = 8.0 \text{ Hz, Ar-H} \)), 8.19 (1 H, d, \( ^3J = 8.0 \text{ Hz, Ar-H} \)), 8.48 (1 H, d, \( ^3J = 7.5 \text{ Hz, Ar-H} \)), 8.86 (1 H, d, \( ^3J = 7.5 \text{ Hz, Ar-H} \)). \(^{13}\)C NMR (125 MHz, CDCl\(_3\)): \( \delta_C \) 13.2 (Me), 13.8 (Me), 14.0 (Me), 62.2 (CH\(_2\)O), 63.0 (CH\(_2\)O), 63.6 (CH\(_2\)O), 114.4 (CN), 119.5 (C), 122.8 (CH), 127.2 (C), 128.2 (C), 128.4 (CH), 128.7 (C), 128.8 (CH), 129.1 (CH), 129.7 (CH), 130.5 (C), 130.9 (C), 132.2 (CH), 153.7 (C), 156.4 (C), 159.2 (C=O), 161.1 (C=O), 161.3 (C=O), 178.1 (C=O). EI-MS: \( m/z \% \) = 447 (M\(^+\), 87), 374 (58), 345 (54), 318 (48), 301 (100), 275 (38), 246 (23), 202 (36). Anal. Calcd for C\(_{25}\)H\(_{21}\)NO\(_7\) (447.13): C, 67.11; H, 4.73; N, 3.13. Found: C, 67.25; H, 4.81; N, 3.20\%.}
Di-tert-butyl 2-cyano-3-(2-(ethoxycarbonyl)-1-oxo-1H-phenalen-3-yl)maleate (4h)

Yellow solid; mp 167-171 °C; yield: 0.41 g (81 %). IR (KBr) (νmax, cm⁻¹): 3066, 2985, 2215, 1723, 1628, 1577, 1369, 1265, 1149, 778. ¹H NMR (500 MHz, CDCl₃): δH 1.45 (3 H, t, ³J = 7.2 Hz, Me), 1.57, 1.58 (18 H, s, 6 Me), 4.53 (2 H, q, ³J = 7.2 Hz, 2 CH₂O), 7.80-7.83 (2 H, m, 2 Ar-H), 8.06 (1 H, d, ³J = 7.0 Hz, Ar-H), 8.11 (1 H, d, ³J = 8.2 Hz, Ar-H), 8.20 (1 H, d, ³J = 8.2 Hz, Ar-H), 8.49 (1 H, d, ³J = 7.2 Hz, Ar-H). ¹³C NMR (125 MHz, DMSO-d₆): δC 13.6 (Me), 26.8 and 27.2 (6 Me), 64.4 (CH₂O), 86.1 (C), 86.8 (C), 114.4 (CN), 121.9 (C), 126.4 (CH), 126.7 (C), 128.2 (CH), 129.1 (C), 129.4 (C), 129.5 (C), 129.9 (CH), 130.3 (CH), 131.1 (C), 134.2 (CH), 134.6 (CH), 145.8 (C), 154.6 (C), 158.6 (C=O), 160.0 (C=O), 161.3 (C=O), 177.8 (C=O). El-MS: m/z (%) = 503 (M⁺, 84), 402 (55), 345 (49), 318 (46), 301 (100), 275 (40), 246 (29), 202 (35). Anal. Calcd for C₂₉H₂₉NO₇ (503.19): C, 69.17; H, 5.81; N, 2.78. Found: C, 69.30; H, 5.90; N, 2.86%.

Ethyl (E)-3-(1-cyano-3-methoxy-3-oxoprop-1-en-2-yl)-1-oxo-1H-phenalene-2-carboxylate (4i)
Yellow solid; mp 195-199 °C; yield: 0.32 g (88 %). IR (KBr) (νmax, cm⁻¹): 3048, 2922, 2221, 1724, 1572, 1369, 1262, 1017, 778. ¹H NMR (500 MHz, CDCl₃): δH 1.47 (3 H, t, ³J = 7.2 Hz, Me), 3.84 (3 H, s, MeO), 4.54 (2 H, q, ³J = 7.2 Hz, CH₂O), 7.43 (1 H, s, HC=C), 7.82 (2 H, t, ³J = 7.5 Hz, 2 Ar-H), 8.06 (1 H, d, ³J = 7.5 Hz, Ar-H), 8.12 (1 H, d, ³J = 8.0 Hz, Ar-H), 8.20 (1 H, d, ³J = 8.0 Hz, Ar-H), 8.50 (1 H, d, ³J = 7.5 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃): δC 13.3 (Me), 52.5 (MeO), 63.0 (CH₂O), 104.9 (CN), 113.9 (CH), 122.2 (CH), 122.3 (C), 127.9 (C), 128.2 (CH), 128.3 (2 CH), 128.6 (C), 129.2 (CH), 129.7 (C), 130.3 (C), 131.6 (CH), 141.9 (C), 145.4 (C), 160.6 (C=O), 161.5 (C=O), 187.6 (C=O). EI-MS: m/z (%) = 361 (M⁺, 78), 346 (50), 302 (100), 275 (45), 247 (56), 202 (35). Anal. Calcd for C₂₁H₁₅NO₅ (361.10): C, 69.80; H, 4.18; N, 3.88. Found: C, 69.92; H, 4.25; N, 3.96%.

**Ethyl (E)-3-(1-cyano-3-ethoxy-3-oxoprop-1-en-2-yi)-1-oxo-1H-phenalene-2-carboxylate (4j)**

Yellow solid; mp 150-158 °C; yield: 0.32 g (86 %). IR (KBr) (νmax, cm⁻¹): 3045, 2987, 2211, 1725, 1624, 1589, 1367, 1272, 1147, 779. ¹H NMR (500 MHz, DMSO-d₆): δH 1.18 (3 H, t, ³J = 7.0 Hz, Me), 1.37 (3 H, t, ³J = 7.0 Hz, Me), 4.42-4.50 (4 H, m, 2 CH₂O), 7.39 (1 H, s, HC=C), 7.87 (1 H, t, ³J = 7.5 Hz, Ar-H), 7.91 (1 H, t, ³J = 7.5 Hz, Ar-H), 8.11 (1 H, d, ³J = 7.5 Hz, Ar-H), 8.31 (1 H, d, ³J = 8.0 Hz, Ar-H), 8.38 (1 H, d, ³J = 8.0 Hz, Ar-H), 8.58 (1 H, d, ³J = 7.5 Hz, Ar-H). ¹³C NMR (125 MHz, CDCl₃): δC 13.7 (Me), 13.8 (Me), 63.2 (2 CH₂O), 103.6 (CN), 114.3 (CH),
124.0 (C), 127.4 (C), 128.6 (CH), 128.7 (CH), 128.8 (CH), 128.9 (C), 129.6 (CH), 130.1 (CH), 130.8 (C), 131.9 (C), 132.4 (CH), 141.8 (C), 150.2 (C), 160.9 (C=O), 161.6 (C=O), 187.9 (C=O). EI-MS: \( m/z \) (%) = 375 (M\(^+\), 81), 348 (55), 304 (100), 275 (48), 247 (53), 202 (37). Anal. Calcd for C\(_{22}\)H\(_{17}\)NO\(_5\) (375.11): C, 70.39; H, 4.56; N, 3.73. Found: C, 70.50; H, 4.64; N, 3.80%.

3. Crystal structure determination and refinement

The X-ray diffraction measurement was carried out on STOE IPDS 2T diffractometer with graphite-monochromated MoK\(\alpha\) radiation. The single crystal suitable for X-ray analysis was obtained from DMSO solution and mounted on a glass fiber and used for data collection. Compound 4c is crystallized at triclinic crystal system. For the unit cell a = 1062.8(2) pm, b = 1862.6(4) pm, c = 1278.5(3) pm, Alpha = 90°, Beta = 109.11°(3), Gamma = 90°, cell volume = 2.3914(10) nm\(^3\) and orientation matrixes for data collection were obtained by least-square refinement of the diffraction data from 12379 for compound 4c. Diffraction data were collected in a series of \(\omega\) scans in 1° oscillations and integrated using the Stoe X-AREA software package. Numerical absorption correction was applied using X-Red32 software. The structure was solved by direct methods and subsequent difference Fourier maps and then refined on F\(^2\) by a full-matrix least-squares procedure using
anisotropic displacement parameters. Atomic factors are from the International Tables for X-ray Crystallography. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. All refinements were performed using the X-STEP32, SHELXL-2014 and WinGX-2013.3 programs.[2] CCDC-1502615 contains the supplementary crystallographic data for this compound 4c. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

4. Reference:


s11
S1: Dimethyl 2-cyano-3-(2-cyano-1-oxo-1H-phenalen-3-yl)maleate (4a)
S2: Diethyl 2-cyano-3-(2-cyano-1-oxo-1H-phenalen-3-yl)maleate (4b)
S3: Di-tert-butyl 2-cyano-3-(2-cyano-1-oxo-1H-phenalen-3-yl)maleate (4c)
S4: Methyl (E)-3-cyano-2-(2-cyano-1-oxo-1H-phenalen-3-yl)acrylate (4d)
S5: Ethyl (E)-3-cyano-2-(2-cyano-1-oxo-1H-phenalen-3-yl)acrylate (4e)
S6: Dimethyl 2-cyano-3-(2-(ethoxycarbonyl)-1-oxo-1H-phenalen-3-yl)maleate (4f)
S7: Diethyl 2-cyano-3-(2-(ethoxycarbonyl)-1-oxo-1H-phenalen-3-yl)maleate (4g)
S8: Di-tert-butyl 2-cyano-3-(2-(ethoxycarbonyl)-1-oxo-1H-phenalen-3-yl)maleate (4h)
S9: Ethyl (E)-3-(1-cyano-3-methoxy-3-oxoprop-1-en-2-yl)-1-oxo-1H-phenalene-2-carboxylate (4i)
S10: Ethyl (E)-3-(1-cyano-3-ethoxy-3-oxoprop-1-en-2-yl)-1-oxo-1H-phenalene-2-carboxylate (4j)