### **Supporting Information**

for

# Hetero-Diels–Alder reactions of hetaryl and aryl thioketones with acetylenic dienophiles

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# Experimental data for selected compounds 4–6, details of the crystal structure determinations, and the original <sup>1</sup>H and <sup>13</sup>C NMR spectra for all products

#### 1. Experimental data for selected compounds 4, 5, and 6

*Dimethyl* 1H-2-*benzothiopyran-3,4-dicarboxylate* (**4a**): Yield: 285.6 mg (84%). Colorles crystals; m.p. 91.0–91.5 °C (MeOH) (lit. [S1] m.p. 90.0-91.0 °C)

*Dimethyl* 7-(N-methylpyrrol-2-yl)-N-methylpyrrolo[2,3-c]thiopyran-4,5-dicarboxylate (4d): Yield: 60.5 mg (35%). Orange solid; m.p. 141.5–142.0 °C (purified chromatographically). IR (KBr): v = 311 (w), 2951 (w), 1730 (s), 1729 (s), 1695 (s), 1572 (w), 1433 (m), 1271 (s), 1251 (s), 1224 (s), 1199 (m), 1164 (w), 726 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\bar{\delta}$  = 6.61-6.58 (m, 2 H<sub>arom</sub>), 6.21 (d, *J* = 6Hz, 1 H<sub>arom</sub>), 5.95-5.93 (m, 1 H<sub>arom</sub>), 5.45-5.43 (m, 1 H<sub>arom</sub>), 5.37 (s, 1 S-CH); 3.92 (d, *J* = 6Hz, 3 H, CH<sub>3</sub>), 3.91 (s, 3H, CH<sub>3</sub>), 3.74, 3.69 (2 s, 6H, 2 OCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\bar{\delta}$  = 164.6, 160.2 (2 C=O), 137.0, 136.1, 134.1, 118.0, 112.5 (5 C(sp<sup>2</sup>)), 124.1, 123.5, 110.3, 107.3, 106.3 (5 CH<sub>arom</sub>), 52.5, 52.4 (2 OCH<sub>3</sub>), 34.1 (CH<sub>3</sub>), 33.5(S-CH), 33.4 (CH<sub>3</sub>) ppm. MS (ESI): *m/z* (%) = 345 (100, [M-1]<sup>+</sup>), 369 (65) [M+Na]<sup>+</sup>. C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>4</sub>S (346.43): calcd. C 58.93, H 5.25, N 8.09, S 9.25; found C 59.33, H 5.25, N 8.24, S 9.21.

*Dimethyl 7-(2-thienyl)-7*H*-thieno[2,3-c]thiopyran-4,5-dicarboxylate* (**4e**): Yield: 123.0 mg (35%). Yellowish crystals, m.p. 94–96 °C (lit. [S2], m.p. 94–95 °C).

*Methyl 1-phenyl-1*H*-2-benzothiopyran-4-carboxylate* (**5a**) [S3]: Yield: 191.8 mg (68%). Yellow oil. IR (film): v = 3059 (w), 2949 (w), 1716 (s), 1578 (w), 1490 (w), 1436 (m), 1239 (s), 1031 (m), 745 (m) cm<sup>-1</sup>.<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 8.10$  (d, J = 7.74 Hz, 1 H<sub>arom</sub>), 7.76 (s, S-CH=), 7.44 (t, J = 7.56 Hz, 1 H<sub>arom</sub>), 7.38-7.25 (m, 6 H<sub>arom</sub>), 7.05 (d, J = 7.62 Hz, 1 H<sub>arom</sub>), 5.21 (s, S-CH), 3.90 (s, 3 H, OCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta = 165.0$  (C=O), 139.9, 131.1, 130.8, 126.9 (4 C(sp<sup>2</sup>)), 135.4, 128.8, 128.6, 128.2, 127.8, 127.7, 127.2, 127.1 (7 CH<sub>arom</sub> + S-CH=); 51.9 (OCH<sub>3</sub>); 47.1 (S-CH) ppm. MS (ESI): m/z (%) = 281 (100, [M–1]<sup>+</sup>), 282 (23, [M]<sup>+</sup>), 283 (48, [M+1]<sup>+</sup>).

*Methyl* 7-(2-thienyl)-7H-thieno[2,3-c]thiopyran-4-carboxylate (**5d**): Yield: 244 mg (83%). Green colored solid; m.p. 85.0-85.5 °C (chromatographic purification). IR (KBr): v = 3038 (w), 2948 (w), 1701 (s), 1544 (w), 1437 (m), 1255 (s), 1068 (w), 716 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.74 (*d*, *J* = 6 Hz, 1 H<sub>arom</sub>), 7.59 (s, S-CH=), 7.26-7.21 (m, 2 H<sub>arom</sub>), 6.92-6.90 (m, 1 H<sub>arom</sub>), 6.88-6.87 (m, 1 H<sub>arom</sub>), 5.76 (s, S-CH), 3.86 (s, 3 H, OCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  = 164.3 (C=O), 144.5, 131.8, 130.7, 123.1 (4 C(sp<sup>2</sup>)), 131.7, 127.4, 126.9, 126.2, 126.0, 122.9 (5 CH<sub>arom</sub>+ S-CH=), 51.9 (OCH<sub>3</sub>), 38.5 (S-CH) ppm. HRMS (MALDI TOF MS): calcd. for C<sub>13</sub>H<sub>10</sub>NaO<sub>2</sub>S<sub>3</sub> [M+Na]<sup>+</sup> 316.9742; found 316.9741. *Methyl* 7-(*selenophen-2-yl*)-7H-*selenopheno*[2,3-c]*thiopyran-4-carboxylate* (**5e**) and *methyl* 7-(2-*furanyl*)-7H-*thiopyrano*[3,4-b]*furan-4-carboxylate* (**5f**) were identified only in the crude mixtures and could not be isolated in pure form. Yields of **5e** and **5f** were calculated based on the <sup>1</sup>H NMR spectra of crude mixtures recorded using a weighted standard (1,1,2,2-tetrachloroethane).

*Methyl* 7-*phenyl*-7H-*thieno*[2,3-c]*thiopyran*-4-*carboxylate* (**5g**): Yield: 213 mg (74%). Green solid; m.p. 88.5-89.0 °C (chromatographic purification). IR (KBr): v = 3037 (w), 2948 (w), 1701 (s), 1544 (w), 1436 (m), 1254 (s), 1068 (w), 716 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.78 (d, *J* = 5.3 Hz, 1 H<sub>arom</sub>), 7.61 (s, S-CH=), 7.27 (dd, *J* = 1.2, 5.1 Hz, 2 H<sub>arom</sub>), 7.25 (d, *J* = 5.3 Hz, 1 H<sub>arom</sub>,), 6.94-6.92 (m, 1 H<sub>arom</sub>), 6.91-6.88 (m, 2H<sub>arom</sub>), 5.78 (s, S-CH), 3.87 (s, 3 H, OCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  = 164.3 (C=O), 144.5, 130.7, 127.4, 126.0 (4 C(sp<sup>2</sup>)), 131.8, 126.9, 126.2, 123.1, 122.9 (5 CH<sub>arom</sub> + S-CH=), 52.0 (OCH<sub>3</sub>), 38.5 (S-CH) ppm. HRMS (MALDI TOF): calcd. for C<sub>15</sub>H<sub>12</sub>NaO<sub>2</sub>S<sub>2</sub> [M+Na]<sup>+</sup> 311.0180; found 311.0176.

Dimethyl 1H-2-benzothiopyran-3,4-dicarboxylate S,S-dioxide (**6a**) [S4]: Yield: 336 mg (90%). Colorless crystals; m.p. 188.5-188.8 °C (MeOH). IR (KBr): v = 3065 (w), 2926 (w), 1737 (s), 1716 (s), 1602 (m), 1559 (w), 1438 (w), 1325 (s), 1248 (s), 1227 (s), 1132 (s), 1073 (w), 762 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 7.54$ -7.49 (m, 2 H<sub>arom</sub>), 7.48-7.43 (m, 4 H<sub>arom</sub>), 7.42-7.39 (m, 2 H<sub>arom</sub>), 7.25 (*d*, *J* = 6.95 Hz, 1 H<sub>arom</sub>), 5.48 (s, S-CH), 4.05, 3.93 (2 s, 6 H, 2 OCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta = 165.3$ , 161.0 (2 C=O), 146.0, 133.8 130.4, 129.9, 126.9 (5 C(sp<sup>2</sup>)), 134.8, 132.6, 130.8, 129.8, 129.5, 129.1, 128.9 (7 CH<sub>arom</sub>), 70.0 (broad, for 2 OCH<sub>3</sub>), 53.5 (S-CH) ppm. MS (ESI): *m/z* (%) = 373 (20, [M+1]<sup>+</sup>), 395 (100, [M+Na]<sup>+</sup>). C<sub>19</sub>H<sub>16</sub>O<sub>6</sub>S (372.41): calcd. C 61.29, H 4.30, S 8.60; found C 61.34, H 4.27, S 8.91.

*Methyl* 1H-2-*benzothiopyran-4-dicarboxylate S*,*S*-*dioxide* (**6b**): Yield: 104 mg (94%). White solid; m.p. 137.5 – 138.0 °C (isolated crude product). IR (KBr): v = 3061 (w), 2953 (w), 1733 (s), 1602 (w), 1447 (w), 1316 (s), 1236 (s), 1125 (s), 1020 (m), 776 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 7.82$  (d, J = 8.0 Hz, 1 H<sub>arom</sub>), 7.50 (t, J = 7.6 Hz, 1 H<sub>arom</sub>), 7.45-7.40 (m, 4 H<sub>arom</sub>), 7.37-7.34 (m, 2 H<sub>arom</sub>), 7.22 (d, J = 7.6 Hz, 1 H<sub>arom</sub>), 7.15

(s, HC=), 5.42 (s, 1 CH), 3.98 (s, 3 H, OCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  = 164.6 (C=O), 139.6, 133.6, 128.8 (4 C(sp<sup>2</sup>)), 131.1, 130.6 130.4, 130.2, 129.4, 129.0, 128.9, 127.0 (9 CH<sub>arom</sub> + S-CH=), 68.9 (OCH<sub>3</sub>), 53.3 (S-CH) ppm. MS (ESI): *m/z* (%) = 304 (70, [M–10]<sup>+</sup>), 314 (20, [M]<sup>+</sup>), 337 (100, [M+Na]<sup>+</sup>). C<sub>17</sub>H<sub>14</sub>O<sub>4</sub>S (314.36): calcd. C 64.95, H 4.49, S 10.20; found C 65.06, H 4.56, S 10.15.

Dimethyl 11,12-dihydro-4bH-benzo[4,5]cyclohepta[1,2,3-ij]isothiochromene-6,7dicarboxylate 5,5-dioxide (**6c**): Yield: 76 mg (74%). White solid; m.p. 207.5-208.0 °C (isolated crude product). IR (KBr): v = 3014 (w), 2953 (w), 1729 (s), 1717 (s), 1597 (w), 1569 (m), 1439 (m), 1322 (s), 1262 (s), 1231 (s), 1147 (s), 1102 (w), 759 (m) cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>):  $\delta = 7.44$ -7.38 (m, 1 H<sub>arom</sub>), 7.35-7.31 (m, 3 H<sub>arom</sub>), 7.24-7.14 (m, 3 H<sub>arom</sub>), 5.75 (br. s S-CH), 4.00, 3.97 (2 s, 6 H, 2 OCH<sub>3</sub>), 3.59 (br. s, 1 H), 3.13 (br. s, 2 H), 2.92 (br. s, 1 H) ppm. <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta = 169.9$ , 165.4 (2 C=O), 134.6, 132.7, 132.3, 130.6, 130.5, 129.2, 126.2 (7 C(sp<sup>2</sup>)), 133.7, 131.0, 130.2, 129.8, 128.2, 127.9, 126.6 (7 CH<sub>arom</sub>), 65.8, 62.5 (2 OCH<sub>3</sub>), 53.5 (S-CH), 37.2, 34.6 (2 broad signals, 2 CH<sub>2</sub>) ppm. HRMS (MALDI TOF): calcd. for C<sub>21</sub>H<sub>18</sub>NaO<sub>6</sub>S [M+Na]<sup>+</sup> 421.0723; found 421.0722.

#### 2. X-ray crystallography

Crystal data for **4b**: C<sub>21</sub>H<sub>18</sub>O<sub>4</sub>S, *M*<sub>r</sub> = 366.43, colorless, prism, 0.15 × 0.15 × 0.22 mm, *T* = 160(1) K, monoclinic, *I*/*a*, *Z* = 8, *a* = 21.68846(14), *b* = 10.06163(5), *c* = 16.63858(12) Å,  $\beta$  = 109.0246(8)°, *V* = 3432.57(4) Å<sup>3</sup>, *D*<sub>x</sub> = 1.418 g cm<sup>-3</sup>,  $\mu$ (Cu *Ka*) = 1.885 mm<sup>-1</sup>,  $\omega$  scans,  $2\theta_{(max)}$  = 148.5°, transmission factors (min; max) = 0.545; 1.000, 31829 reflections measured, 3481 symmetry independent reflections, 3435 reflections with *I* > 2 $\sigma$ (*I*), 3481 reflections used in refinement, 238 parameters, *R*(*F*) [*I* > 2 $\sigma$  (*I*) reflections] = 0.0285, *wR*(*F*<sup>2</sup>) (all data) = 0.0748, *w* = [ $\sigma^2$ (*F*<sub>0</sub><sup>2</sup>) + (0.0357*P*)<sup>2</sup> + 2.8020*P*]<sup>-1</sup> where *P* = (*F*<sub>0</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3, goodness of fit = 1.055, secondary extinction coefficient = 0.00042(6), final  $\Delta_{max}/\sigma$  = 0.001,  $\Delta\rho$ (max; min) = 0.28; -0.22 e Å<sup>-3</sup>. Crystals from methanol. Crystal data for **6d**: C<sub>19</sub>H<sub>16</sub>O<sub>4</sub>S, *M*<sub>r</sub> = 340.39, colorless, prism, 0.15 × 0.17 × 0.24 mm, *T* = 160(1) K triclinic *P*=1, *Z* = 4, *a* = 0.2306(2), *b* = 12.2639(3), *c* = 14.1109(4) Å *a* =

= 160(1) K, triclinic, *P*-1, *Z* = 4, *a* = 9.2396(2), *b* = 12.3639(3), *c* = 14.1109(4) Å, *a* = 89.197(2),  $\beta$  = 73.619(2)°,  $\gamma$  = 88.599(2)°, *V* = 1546.05(7) Å<sup>3</sup>, *D*<sub>x</sub> = 1.462 g cm<sup>-3</sup>,  $\mu$ (Mo *Ka*) = 0.230 mm<sup>-1</sup>,  $\omega$  scans,  $2\theta_{(max)}$  = 56.6°, transmission factors (min; max) = 0.909;

1.000, 40958 reflections measured, 12307 symmetry independent reflections, 8546 reflections with  $l > 2\sigma(l)$ , 12307 reflections used in refinement, 436 parameters, R(F) [ $l > 2\sigma(l)$  reflections] = 0.0371,  $wR(F^2)$  (all data) = 0.1041,  $w = [\sigma^2(F_0^2) + (0.0568P)^2]^{-1}$  where  $P = (F_0^2 + 2F_c^2)/3$ , goodness of fit = 1.042, final  $\Delta_{max}/\sigma = 0.001$ ,  $\Delta\rho(max; min) = 0.37$ ; -0.48 e Å<sup>-3</sup>. Crystals from CH<sub>2</sub>Cl<sub>2</sub>.

All measurements were made on an Agilent Technologies SuperNova area-detector diffractometer [S5] using Cu Ka radiation ( $\lambda = 1.54184$  Å) in the case of **4b** and Mo Ka radiation ( $\lambda = 0.71073$  Å) in the case of **6d** from a micro-focus X-ray source and an Oxford Instruments Cryojet XL cooler. Data reduction was performed with CrysAlisPro [S5]. The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction using spherical harmonics [S5] was applied. The space groups of **4b** and **6d** were determined by the systematic absences, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure. The chosen crystal of 6d was a non-merohedral twin resulting from a rotation of  $180^{\circ}$  about [0 1 0] with a twin matrix of [-100/010/00-1]and the major twin fraction in the selected crystal is 0.8861(4). All reflections from both twin components were integrated; a total of 11129 and 11104 non-overlapping reflections from twin components 1 and 2, respectively, plus 18725 reflections from both twin components that were overlapping by more than 80%. Equivalent reflections were merged. The data collection and refinement parameters are given above, and views of the molecules are shown in the Figures. The structures were solved by direct methods using SHELXS-2013 [S6], which revealed the positions of all non-H-atoms. In the case of 6d, there are two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group using the program PLATON [S7], but none could be found. The non-H-atoms of 4b and 6d were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 Ueq of its parent C-atom (1.5 Ueq for the methyl groups). The refinement of each structure was carried out on  $F^2$  by using full-matrix least-squares procedures, which minimized the function  $\Sigma w (F_o^2 - F_c^2)^2$ . A correction for secondary extinction was applied for 4b. Neutral atom scattering factors for non-H-atoms were taken from ref.

[S8], and the scattering factors for H-atoms were taken from ref. [S9]. Anomalous dispersion effects were included in  $F_c$ ; [S10] the values for f' and f'' were those of ref. [S11]. The values of the mass attenuation coefficients are those of ref. [S12]. The *SHELXL-2014* program [S13] was used for all calculations. CCDC-1038599 and 1038600 contain 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.

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- Collection of the <sup>1</sup>H- and <sup>13</sup>C-NMR spectra for the described compounds
  *4*, *5*, and *6*



**Figure S1:** The <sup>1</sup>H NMR spectrum of compound **4b**.



Figure S2: The <sup>13</sup>H NMR spectrum of compound 4b.



**Figure S3:** The <sup>1</sup>H NMR spectrum of compound **4c**.



Figure S4: The <sup>13</sup>C NMR spectrum of compound 4c.



**Figure S5**: The <sup>1</sup>H NMR spectrum of compound **4d**.



Figure S6: The <sup>13</sup>C NMR spectrum of compound 4d.



Figure S7: The <sup>1</sup>H NMR spectrum of compound 5a.



Figure S8: The <sup>13</sup>C NMR spectrum of compound 5a.



Figure S9: The <sup>1</sup>H NMR spectrum of compound 5b.



Figure S10. The <sup>13</sup>C NMR spectrum of compound 5b.



Figure S11: The <sup>1</sup>H NMR spectrum of compound 5c.



Figure S12: The <sup>13</sup>C NMR spectrum of compound 5c.



**Figure S13**: The <sup>1</sup>H NMR spectrum of compound **5d**.



Figure S14: The <sup>13</sup>C NMR spectrum of compound 5d.



Figure S15: The <sup>1</sup>H NMR spectrum of compound 5g.



Figure S17: The <sup>1</sup>H NMR spectrum of compound 6a.



Figure S18:. The <sup>13</sup>C NMR spectrum of compound 6a.



Figure S19: The <sup>1</sup>H NMR spectrum of compound 6b.



Figure S20:. The <sup>13</sup>C NMR spectrum of compound 6b.



Figure S21: The <sup>1</sup>H NMR spectrum of compound 6c.



**Figure S22**: The <sup>13</sup>C NMR spectrum of compound **6c**.



Figure S23: The <sup>1</sup>H NMR spectrum of compound 6d.



Figure S24: The <sup>13</sup>C NMR spectrum of compound 6d.