

## Supplementary Information

### Microwave Assisted Synthesis of Thiocarbamoylpyrazoles and Application as an Alternative Latent Fingermark Developers

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#### Experimental data for compounds **2a-2h**

##### 1-Thiocarbamoyl-3,5-diphenyl-4,5-dihydro-1*H*-pyrazole (**2a**)

mp 200-203 °C; MW 281.38 g mol<sup>-1</sup>; IR (KBr)  $\nu$  / cm<sup>-1</sup> 3484-3350 (N–H), 1576 (C=N), 1501-1443 (C=C), 1364 (C=S); <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.13 (dd, 1H, *J*<sub>AB</sub> 18.0 Hz, *J*<sub>AX</sub> 3.4 Hz, H<sub>A</sub>), 3.90 (dd, 1H, *J*<sub>AB</sub> 18.0 Hz, *J*<sub>BX</sub> 11.5 Hz, H<sub>B</sub>), 5.94 (dd, 1H, *J*<sub>BX</sub> 11.4 Hz, *J*<sub>AX</sub> 3.3 Hz, H<sub>X</sub>), 7.12-7.89 (m, 10H, aromatic H), 7.92 and 8.06 (two br s, 2H, NH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  42.3 (C-4), 62.8 (C-5), 125.2, 126.8, 127.0, 128.4, 128.6, 130.4, 130.8, 142.9 (12C, Ar), 154.8 (C-3), 176.0 (C(S)NH<sub>2</sub>).

##### 1-Thiocarbamoyl-5-(4-methoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (**2b**)

mp 166-169 °C; MW 311.40 g mol<sup>-1</sup>; IR (KBr)  $\nu$  / cm<sup>-1</sup> 3376-3366 (N–H), 1600 (C=N), 1512-1444 (C=C), 1378 (C=S); <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.11 (dd, 1H, *J*<sub>AB</sub> 18.0 Hz, *J*<sub>AX</sub> 3.3 Hz, H<sub>A</sub>), 3.70 (s, 3H, OCH<sub>3</sub>), 3.86 (dd, 1H, *J*<sub>AB</sub> 18.0 Hz, *J*<sub>BX</sub> 11.3 Hz, H<sub>B</sub>), 5.88 (dd, 1H, *J*<sub>BX</sub> 11.2 Hz, *J*<sub>AX</sub> 3.1 Hz, H<sub>X</sub>), 6.48-7.79 (m, 9H, aromatic H), 7.86 and 8.00 (two br s, 2H, NH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  42.4 (C-4), 55.0 (OCH<sub>3</sub>), 62.3 (C-5), 113.8, 126.6, 127.0, 128.4, 128.6, 130.5, 130.9, 135.0, 158.2 (12C, Ar), 154.9 (C-3), 176.1 (C(S)NH<sub>2</sub>).

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**1-Thiocarbamoyl-5-(4-fluorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (2c)**

mp 235-237 °C; MW 299.37 g mol<sup>-1</sup>; IR (KBr)  $\nu$  / cm<sup>-1</sup> 3477-3355 (N—H), 1575 (C=N), 1507-1421 (C=C), 1365 (C=S); <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.14 (dd, 1H, *J*<sub>AB</sub> 18.1 Hz, *J*<sub>AX</sub> 3.5 Hz, H<sub>A</sub>), 3.90 (dd, 1H, *J*<sub>AB</sub> 18.1 Hz, *J*<sub>BX</sub> 11.5 Hz, H<sub>B</sub>), 5.94 (dd, 1H, *J*<sub>BX</sub> 11.4 Hz, *J*<sub>AX</sub> 3.4 Hz, H<sub>X</sub>), 7.09-7.91 (m, 9H, aromatic H), 7.91 and 8.07 (two br s, 2H, NH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  42.2 (C-4), 62.1 (C-5), 115.1 (d, *J*<sub>CF</sub> 21.5 Hz), 127.0, 127.3 (d, *J*<sub>CF</sub> 8.2 Hz), 128.6, 130.5, 130.7, 139.0 (d, *J*<sub>CF</sub> 2.9 Hz), 162.6 (12C, Ar), 154.8 (C-3), 176.0 (C(S)NH<sub>2</sub>).

**1-Thiocarbamoyl-5-(4-chlorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (2d)**

mp 174-178 °C; MW 315.82 g mol<sup>-1</sup>; IR (KBr)  $\nu$  / cm<sup>-1</sup> 3388-3300 (N—H), 1576 (C=N), 1500-1470 (C=C), 1374 (C=S); <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.14 (dd, 1H, *J*<sub>AB</sub> 18.1 Hz, *J*<sub>AX</sub> 3.6 Hz, H<sub>A</sub>), 3.90, (dd, 1H, *J*<sub>AB</sub> 18.1 Hz, *J*<sub>BX</sub> 11.6 Hz, H<sub>B</sub>), 5.93 (dd, 1H, *J*<sub>BX</sub> 11.5 Hz, *J*<sub>AX</sub> 3.5 Hz, H<sub>X</sub>), 7.09-7.91 (m, 9H, aromatic H), 7.91 and 8.07 (two br s, 2H, NH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  42.1 (C-4), 62.2 (C-5), 127.0, 127.2, 128.4, 128.6, 130.5, 130.7, 131.3, 141.9 (12C, Ar), 154.8 (C-3), 176.0 (C(S)NH<sub>2</sub>).

**1-Thiocarbamoyl-5-(4-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (2e)**

mp 195-197 °C; MW 360.27 g mol<sup>-1</sup>; IR (KBr)  $\nu$  / cm<sup>-1</sup> 3392-3271 (N—H), 1580 (C=N), 1503-1446 (C=C), 1376 (C=S); <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.15 (dd, 1H, *J*<sub>AB</sub> 18.0 Hz, *J*<sub>AX</sub> 3.6 Hz, H<sub>A</sub>), 3.90, (dd, 1H, *J*<sub>AB</sub> 18.0 Hz, *J*<sub>BX</sub> 11.4 Hz, H<sub>B</sub>), 5.91 (dd, 1H, *J*<sub>BX</sub> 11.4 Hz, *J*<sub>AX</sub> 3.3 Hz, H<sub>X</sub>), 7.08-7.89 (m, 9H, aromatic H), 7.94 and 8.11 (two br s, 2H, NH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  42.0 (C-4), 62.3 (C-5), 119.8, 127.0, 127.6, 128.6, 130.5, 130.7, 131.3, 142.3 (12C, Ar), 154.8 (C-3), 176.0 (C(S)NH<sub>2</sub>).

**1-Thiocarbamoyl-5-(3-bromophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (2f)**

mp 211-216 °C; MW 360.27 g mol<sup>-1</sup>; IR (KBr)  $\nu$  / cm<sup>-1</sup> 3392-3271 (N—H), 1580 (C=N), 1503-1446 (C=C), 1376 (C=S); <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.18 (dd, 1H, *J*<sub>AB</sub> 18.0 Hz, *J*<sub>AX</sub> 3.7 Hz, H<sub>A</sub>), 3.90 (dd, 1H, *J*<sub>AB</sub> 18.2 Hz, *J*<sub>BX</sub> 11.6 Hz, H<sub>B</sub>), 5.93 (dd, 1H, *J*<sub>BX</sub> 11.5 Hz, *J*<sub>AX</sub> 3.6 Hz, H<sub>X</sub>), 7.12-7.89 (m, 9H, aromatic H), 7.94 and 8.11 (two br s, 2H, NH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  42.1 (C-4), 62.3 (C-5), 121.6, 124.3, 127.1, 128.0, 128.6, 129.7, 130.6, 130.8, 145.6 (12C, Ar), 154.9 (C-3), 176.1 (C(S)NH<sub>2</sub>).

**1-Thiocarbamoyl-5-(3,4-dimethoxyphenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (2g)**

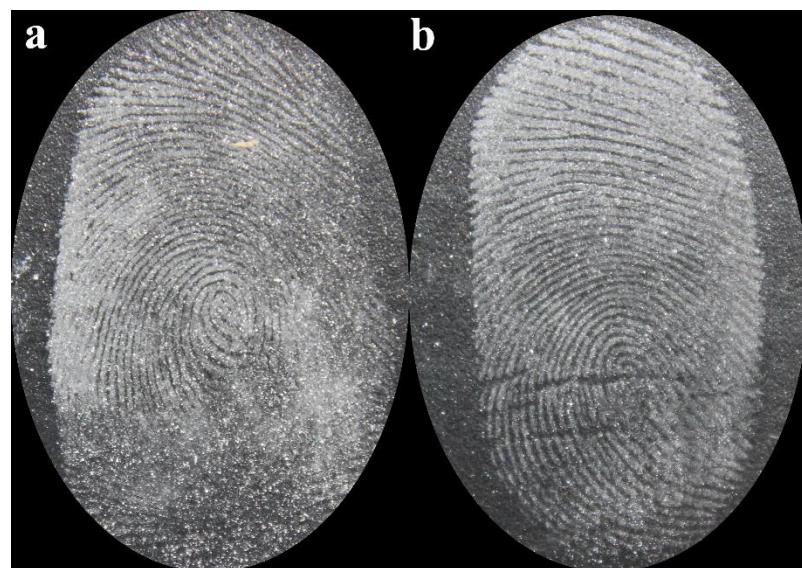
mp 159-160 °C; MW 341.43 g mol<sup>-1</sup>; IR (KBr)  $\nu$  / cm<sup>-1</sup> 3421-3262 (N—H), 1597 (C=N), 1505-1448 (C=C), 1373 (C=S); <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.16 (dd, 1H, *J*<sub>AB</sub> 18.0 Hz, *J*<sub>AX</sub> 3.3 Hz, H<sub>A</sub>), 3.70 (OCH<sub>3</sub>), 3.71 (OCH<sub>3</sub>), 3.86 (dd, 1H, *J*<sub>AB</sub> 18.0 Hz, *J*<sub>BX</sub> 11.3 Hz, H<sub>B</sub>), 5.88 (dd, 1H, *J*<sub>BX</sub> 11.2 Hz, *J*<sub>AX</sub> 3.2 Hz, H<sub>X</sub>), 6.58-7.89 (m, 14H, aromatic H), 7.89 and 8.04 (two br s, 2H, NH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  42.3, 55.4 (OCH<sub>3</sub>), 55.4 (OCH<sub>3</sub>), 42.3 (C-4), 62.5 (C-5), 109.6, 111.8, 116.9, 128.6, 130.4, 130.9, 135.3, 147.7 (12C, Ar), 154.9 (C-3), 176.1 (C(S)NH<sub>2</sub>).

**1-Thiocarbamoyl-5-(2,4-dichlorophenyl)-3-phenyl-4,5-dihydro-1*H*-pyrazole (2h)**

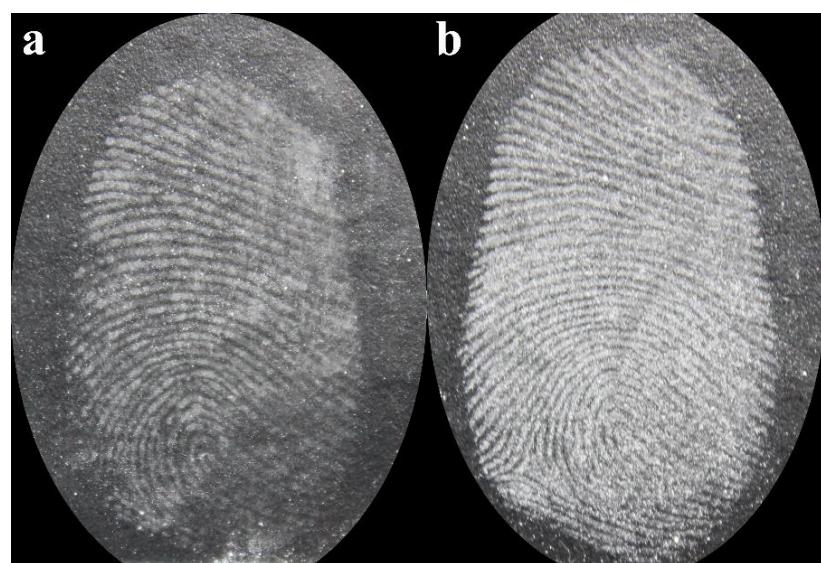
mp 217-220 °C; MW 350.27 g mol<sup>-1</sup>; IR (KBr)  $\nu$  / cm<sup>-1</sup> 3424-3274 (N—H), 1592 (C=N), 1503-1430 (C=C), 1371 (C=S); <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  3.11 (dd, 1H, *J*<sub>AB</sub> 18.1 Hz, *J*<sub>AX</sub> 4.1 Hz, H<sub>A</sub>), 3.99 (dd, 1H, *J*<sub>AB</sub> 18.1 Hz, *J*<sub>BX</sub> 11.7 Hz, H<sub>B</sub>), 6.11 (dd, 1H, *J*<sub>BX</sub> 11.7 Hz, *J*<sub>AX</sub> 4.0 Hz, H<sub>X</sub>), 6.94-7.88 (m, 8H, aromatic H), 8.02 and 8.21 (two br s, 2H, NH<sub>2</sub>); <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  40.7 (C-4), 60.3 (C-5), 127.0, 127.5, 128.5, 128.9, 130.5,

131.3, 132.1, 138.9 (12C, Ar), 154.9 (C-3), 175.9 (C(S)NH<sub>2</sub>).

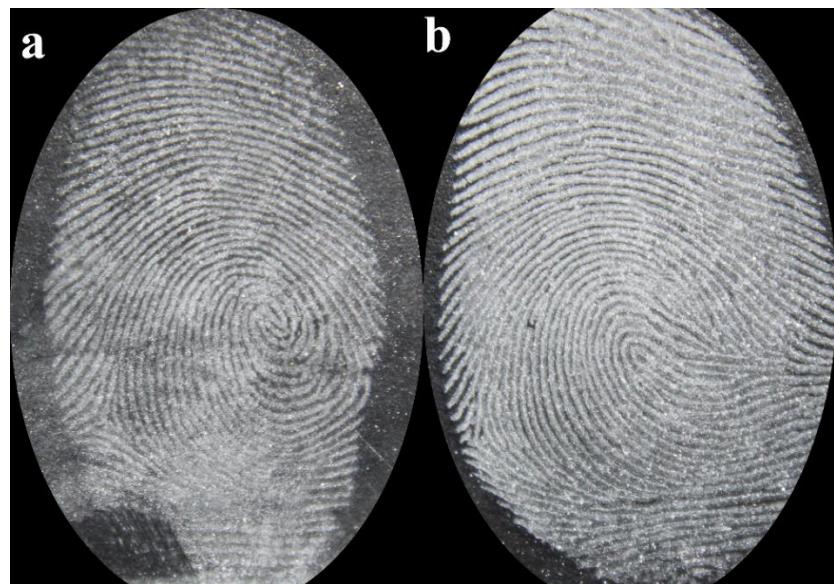
Latent fingerprint developed using 1-thiocarbamoyl-3,5-diaryl-4,5-dihydro-1*H*-pyrazoles **2a-2h**



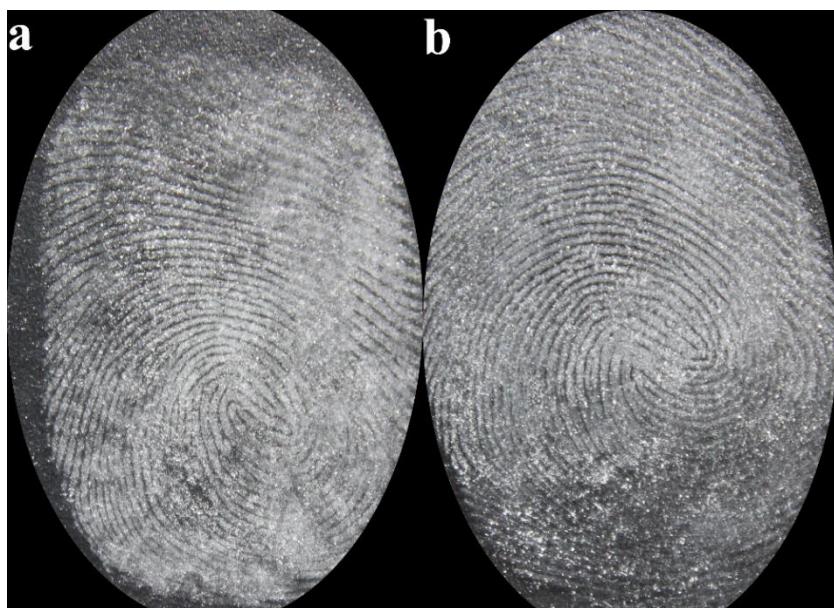
**Figure S1.** Latent fingerprint developed using pyrazole **2a**: (a) natural fingermark; (b) sebaceous fingermark.



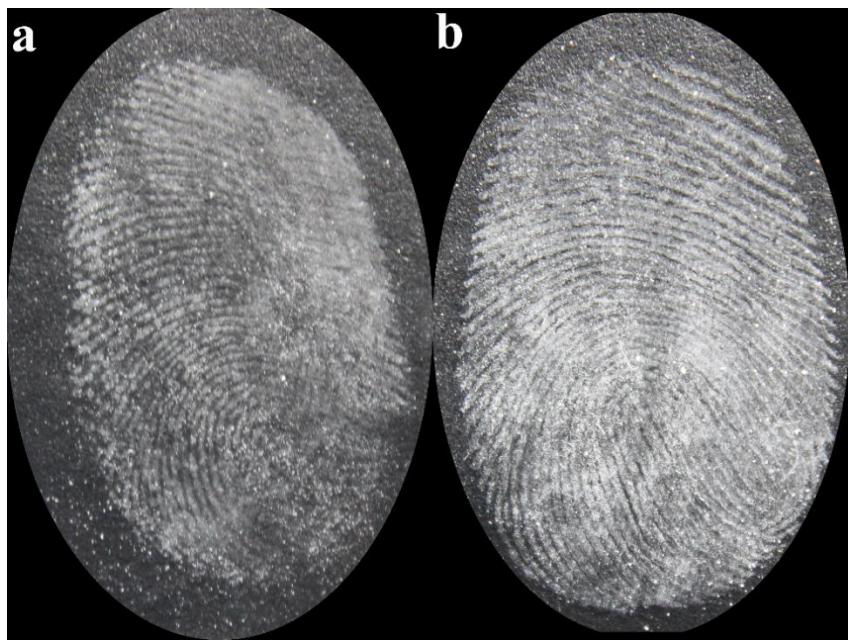
**Figure S2.** Latent fingerprint developed using pyrazole **2b**: (a) natural fingermark; (b) sebaceous fingermark.



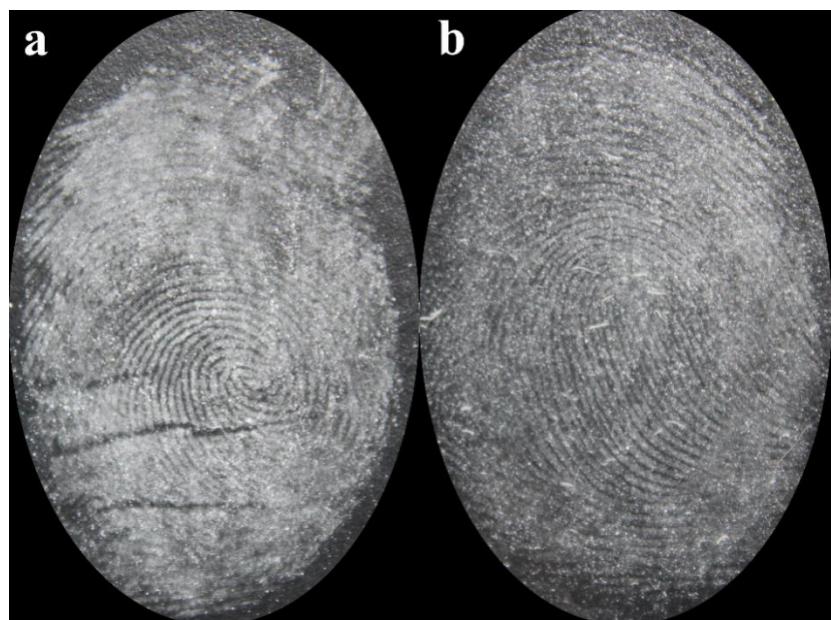
**Figure S3.** Latent fingerprint developed using pyrazole **2c**: (a) natural fingermark; (b) sebaceous fingermark.



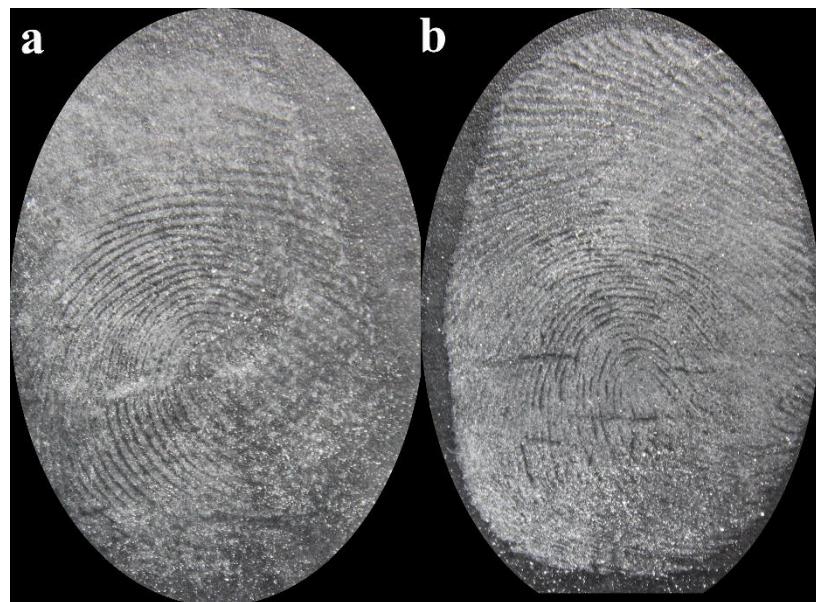
**Figure S4.** Latent fingerprint developed using pyrazole **2d**: (a) natural fingermark; (b) sebaceous fingermark.



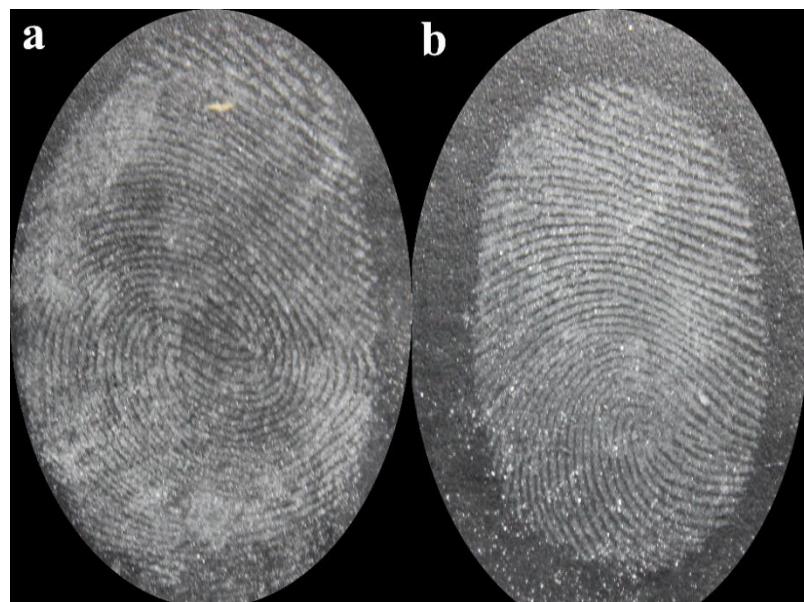
**Figure S5.** Latent fingerprint developed using pyrazole **2e**: (a) natural fingermark; (b) sebaceous fingermark.



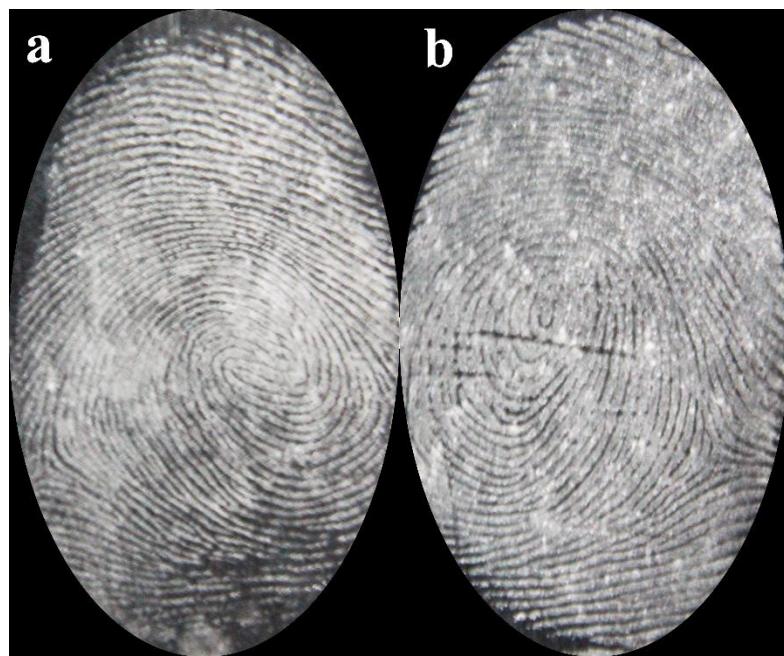
**Figure S6.** Latent fingerprint developed using pyrazole **2f**: (a) natural fingermark; (b) sebaceous fingermark.



**Figure S7.** Latent fingerprint developed using pyrazole **2g**: (a) natural fingermark; (b) sebaceous fingermark.



**Figure S8.** Latent fingerprint developed using pyrazole **2h**: (a) natural fingermark; (b) sebaceous fingermark.



**Figure S9.** Latent fingerprint developed using white standard powder: (a) natural fingermark; (b) sebaceous fingermark.



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