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Supporting Information for:

## Green Protection of Pyrazole, Thermal Isomerization and Deprotection of Tetrahydropyranylpyrazoles, and High-Yield, One-Pot Synthesis of 3(5)-Alkylpyrazoles

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<sup>1</sup>H NMR spectrum of 1-(tetrahydropyran-2-yl)pyrazole (1).



<sup>13</sup>C NMR spectrum of 1-(tetrahydropyran-2-yl)pyrazole (1).







<sup>13</sup>C NMR spectrum of 5-methyl-1-(tetrahydropyran-2-yl)pyrazole (2).





<sup>1</sup>H NMR spectrum of 3(5)-methylpyrazole (16).









<sup>13</sup>C NMR spectrum of 5-ethyl-1-(tetrahydropyran-2-yl)pyrazole (3).





<sup>13</sup>C NMR spectrum of 3(5)-ethylpyrazole (17).





<sup>1</sup>H NMR spectrum of 5-*n*-propyl-1-(tetrahydropyran-2-yl)pyrazole (4).

<sup>13</sup>C NMR spectrum of 5-*n*-propyl-1-(tetrahydropyran-2-yl)pyrazole (4).





<sup>1</sup>H NMR spectrum of 3(5)-*n*-propylpyrazole (18).

<sup>13</sup>C NMR spectrum of 3(5)-*n*-propylpyrazole (18).





<sup>1</sup>H NMR spectrum of 5-*n*-butyl-1-(tetrahydropyran-2-yl)pyrazole (5).

<sup>13</sup>C NMR spectrum of 5-*n*-butyl-1-(tetrahydropyran-2-yl)pyrazole (5).



30.0 20.0 ار 0.33 ار 0.33 0.66 0.66 ر 0.66 0.99 10.0 (Millions) 6.082 6.081 6.081 2.0 1.0 (623) (62) 9.0 7.0 8.0 5.0 4.0 3.0 2.0 7.487 7.482 7.253  $2.689 \xrightarrow{2.670}{2.650}$ X : parts per Million : 1H

<sup>1</sup>H NMR spectrum of 3(5)-*n*-butylpyrazole (19).

<sup>13</sup>C NMR spectrum of 3(5)-*n*-butylpyrazole (19).





<sup>13</sup>C NMR spectrum of 5-*n*-pentyl-1-(tetrahydropyran-2-yl)pyrazole (6).





<sup>1</sup>H NMR spectrum of 3(5)-*n*-pentylpyrazole (20).

<sup>13</sup>C NMR spectrum of 3(5)-*n*-pentylpyrazole (20).



30.0 20.0 ار 0.15 87.02m ار 0.15 0.15 0.15 0.15 0.15 0.15 10.0 (Millions) 9.0 8.0 7.0 6.0 5.0 4.0 7.451 7.446 7.251  $\overbrace{6.033}^{6.037} \xrightarrow{}$ 5 256 5 249 5 224 5 224 4.052 4.047 4.042 4.013 3.657 3.601 3.601 3.601 3.601 3.601 X : parts per Million : 1H

<sup>1</sup>H NMR spectrum of 5-*i*-pentyl-1-(tetrahydropyran-2-yl)pyrazole (7).

## <sup>13</sup>C NMR spectrum of 5-*i*-pentyl-1-(tetrahydropyran-2-yl)pyrazole (7).





<sup>1</sup>H NMR spectrum of 3(5)-*i*-pentylpyrazole (21).

<sup>13</sup>C NMR spectrum of 3(5)-*i*-pentylpyrazole (21).



<sup>1</sup>H NMR spectrum of 5-*n*-hexyl-1-(tetrahydropyran-2-yl)pyrazole (8).



<sup>13</sup>C NMR spectrum of 5-*n*-hexyl-1-(tetrahydropyran-2-yl)pyrazole (8).





<sup>1</sup>H NMR spectrum of 3(5)-*n*-hexylpyrazole (22).

<sup>13</sup>C NMR spectrum of 3(5)-*n*-hexylpyrazole (22).



<sup>1</sup>H NMR spectrum of 1,6-bis(1-(tetrahydropyran-2-yl)pyrazol-5-yl)hexane (15).



<sup>13</sup>C NMR spectrum of 1,6-bis(1-(tetrahydropyran-2-yl)pyrazol-5-yl)hexane (15).



<sup>1</sup>H NMR spectrum of 1,6-bis(pyrazol-3(5)-yl)hexane (29).



<sup>13</sup>C NMR spectrum of 1,6-bis(pyrazol-3(5)-yl)hexane (29).





<sup>1</sup>H NMR spectrum of 5-*n*-heptyl-1-(tetrahydropyran-2-yl)pyrazole (9).

<sup>13</sup>C NMR spectrum of 5-*n*-heptyl-1-(tetrahydropyran-2-yl)pyrazole (9).





<sup>1</sup>H NMR spectrum of 3(5)-*n*-heptylpyrazole (23).

<sup>13</sup>C NMR spectrum of 3(5)-*n*-heptylpyrazole (23).





<sup>1</sup>H NMR spectrum of 5-*n*-octyl-1-(tetrahydropyran-2-yl)pyrazole (10).

<sup>13</sup>C NMR spectrum of 5-*n*-octyl-1-(tetrahydropyran-2-yl)pyrazole (10).





<sup>1</sup>H NMR spectrum of 3(5)-*n*-octylpyrazole (24).

<sup>13</sup>C NMR spectrum of 3(5)-*n*-octylpyrazole (24).





<sup>1</sup>H NMR spectrum of 5-*n*-nonyl-1-(tetrahydropyran-2-yl)pyrazole (11).

<sup>13</sup>C NMR spectrum of 5-*n*-nonyl-1-(tetrahydropyran-2-yl)pyrazole (11).





<sup>1</sup>H NMR spectrum of 3(5)-*n*-nonylpyrazole (25).

<sup>13</sup>C NMR spectrum of 3(5)-*n*-nonylpyrazole (25).



12.0 11.0 10.0 | 85.02m 73.83m | 85.39m | 85.26m | 85.57m | 85.75m 0.17 85.86m 85.26m 85.26m 85.40m 1.19 0.43 0.25 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 (Millions) 9.0 8.0 7.0 6.0 5.0 4.0 3 5599 3 5599 3 5599 3 5597 3 5597 3 607 3 607 3 607 3 607 3 607 3 607 3 607 3 607 3 607 3 607 3 607 3 607 3 607 3 607 3 607 3 607 3 607 3 607 5  $6.039 \\ 6.036 \\ 6.036$ 5252 5225 5227 5221 X : parts per Million : 1H

<sup>1</sup>H NMR spectrum of 5-*n*-decyl-1-(tetrahydropyran-2-yl)pyrazole (12).







<sup>1</sup>H NMR spectrum of 3(5)-*n*-decylpyrazole (26).

<sup>13</sup>C NMR spectrum of 3(5)-*n*-decylpyrazole (26).





<sup>1</sup>H NMR spectrum of 5-*n*-dodecyl-1-(tetrahydropyran-2-yl)pyrazole (13).

<sup>13</sup>C NMR spectrum of 5-*n*-dodecyl-1-(tetrahydropyran-2-yl)pyrazole (13).





<sup>1</sup>H NMR spectrum of 3(5)-*n*-dodecylpyrazole (27).

<sup>13</sup>C NMR spectrum of 3(5)-*n*-dodecylpyrazole (27).





<sup>1</sup>H NMR spectrum of 5-*n*-hexadecyl-1-(tetrahydropyran-2-yl)pyrazole (14).

<sup>13</sup>C NMR spectrum of 5-*n*-hexadecyl-1-(tetrahydropyran-2-yl)pyrazole (14).



30.0 20.0 41.00m ۱ 82.06m 41.30m 30.57m 82.35m 1.06 0.12 10.0 (Millions) 2.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 1.0 7.481 — 7.251 — 6.082  $2.672 \\ 2.653 \\ 2.63$ X : parts per Million : 1H

<sup>1</sup>H NMR spectrum of 3(5)-*n*-hexadecylpyrazole (28).

<sup>13</sup>C NMR spectrum of 3(5)-*n*-hexadecylpyrazole (28).

