Synthesis of Fatty Trichloromethyl-β-diketones and New 1H-Pyrazoles as Unusual FAMEs and FAEEs

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1H and 13C NMR data and spectra for 1,1,1-trichloro-4-methoxy-3-alken-2-ones (2a-e), trichloromethyl-β-diketones (3f,g) and 1H-pyrazole-5-carboxylates (4a-g, 5a-g) are shown. The 1H and 13C spectra were recorded at 298 K on a Bruker DPX 400 spectrometer (1H at 400.13 MHz, 13C at 100.63 MHz) with digital resolution of ± 0.01 ppm. All the chemical shifts are expressed in ppm, 1H and 13C are reported with respect to internal TMS (tetramethylsilane). 0.1 mol L−1 CDCl3 solutions were used except with compounds 2, 0.1 mol L−1 in DMSO-d6. H-H and C-F coupling constants (J) are in Hz. Furthermore, a reaction mechanism for cyclocondensation between 1,1,1-trichloro-4-methoxy-3-alken-2-ones and hydrazine hydrochloride is proposed.

Table S1. 1H NMR data for 1,1,1-trichloro-4-methoxy-3-alken-2-ones 2 and trichloromethyl-β-diketones 3 in CDCl3, δ in ppm, multiplicity, J in Hz

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield / %</th>
<th>H-3</th>
<th>H-5</th>
<th>H-6</th>
<th>Others</th>
<th>Me</th>
<th>OMe</th>
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<tr>
<td>2a, 85</td>
<td></td>
<td>5.96</td>
<td>2.78, t, 8.0</td>
<td>1.57, qui, 8.0</td>
<td>1.28-1.39</td>
<td>0.89, t, 6.8</td>
<td>3.79</td>
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<td>2b, 92</td>
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<td>5.97</td>
<td>2.78, t, 8.0</td>
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<tr>
<td>2c, 95</td>
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<td>5.97</td>
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<td>1.57, qui, 8.0</td>
<td>1.27-1.35</td>
<td>0.88, t, 6.8</td>
<td>3.79</td>
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<tr>
<td>2d, 92</td>
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<td>5.95</td>
<td>2.77, t, 8.0</td>
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<td>1.26-1.34</td>
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<td>3.78</td>
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<td>2e, 90</td>
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<td>5.96</td>
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<td>1.57, qui, 8.0</td>
<td>1.26-1.34</td>
<td>0.88, t, 6.8</td>
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<td>3f, 69</td>
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<td>4.47, q, 7.2</td>
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<td>0.9, 0.88t</td>
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<td>3g, 89</td>
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<td>1.20-1.40</td>
<td>0.89, 0.96, t, t</td>
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*Overlapping signals.

Table S2. 13C NMR data for 1,1,1-trichloro-4-methoxy-3-alken-2-ones 2 and trichloromethyl-β-diketones 3 in CDCl3, δ in ppm

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<thead>
<tr>
<th>Compound</th>
<th>C-1</th>
<th>C-2</th>
<th>C-3</th>
<th>C-4</th>
<th>OMe</th>
<th>Others</th>
</tr>
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<tbody>
<tr>
<td>2a</td>
<td>98.0</td>
<td>179.9</td>
<td>89.7</td>
<td>184.0</td>
<td>56.2</td>
<td>33.4; 31.4; 28.1; 26.9; 22.5; 13.9</td>
</tr>
<tr>
<td>2b</td>
<td>98.0</td>
<td>179.9</td>
<td>89.7</td>
<td>184.0</td>
<td>56.2</td>
<td>33.4; 31.7; 29.4; 28.9; 27.0; 22.5; 14.0</td>
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<tr>
<td>2c</td>
<td>98.0</td>
<td>179.9</td>
<td>89.7</td>
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<td>56.2</td>
<td>33.4; 31.8; 29.4; 29.2; 26.9; 22.6; 14.0</td>
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<tr>
<td>2d</td>
<td>98.0</td>
<td>179.8</td>
<td>89.7</td>
<td>183.9</td>
<td>56.1</td>
<td>33.4; 31.8; 29.4; 29.2; 29.1; 26.9; 22.6; 14.0</td>
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<tr>
<td>2e</td>
<td>98.0</td>
<td>179.9</td>
<td>89.7</td>
<td>184.1</td>
<td>56.2</td>
<td>33.4; 31.9; 29.6; 26.9; 29.5; 29.4; 29.3; 27.0; 22.6; 14.0</td>
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<tr>
<td>3f</td>
<td>96.1</td>
<td>186.7</td>
<td>52.5</td>
<td>203.5</td>
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<td>40.5; 31.1; 23.0; 22.2; 16.3; 13.69</td>
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<tr>
<td>3f'</td>
<td>96.1</td>
<td>185.2</td>
<td>58.6</td>
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<td>3g</td>
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<td>185.2</td>
<td>58.7</td>
<td>203.5</td>
<td>–</td>
<td>40.7; 33.5; 25.4; 22.0; 21.0; 13.8; 13.7</td>
</tr>
</tbody>
</table>

*e-mail: alex.fcf@ufsm.br
Figure S1. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-4-decen-2-one.

Figure S2. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-4-decen-2-one, expanded between 0.6-3.1 ppm.
Figure S3. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of 1,1,1-trichloro-4-methoxy-4-decen-2-one.

Figure S4. $^{13}$C NMR DEPT135 spectrum (100 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-4-decen-2-one.
Figure S5. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-4-undecen-2-one in CDCl$_3$.

Figure S6. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-4-undecen-2-one, expanded between 0-3.1 ppm.
Figure S7. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-4-undecen-2-one.

Figure S8. $^{13}$C NMR DEPT135 spectrum (100 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-4-undecen-2-one.
Figure S9. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-4-tridecen-2-one.

Figure S10. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-4-tridecen-2-one, expanded between 0 - 3.15 ppm.
Figure S11. $^1$C NMR spectrum (100 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-4-tridecen-2-one.

Figure S12. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-3-pentadecen-2-one.
Figure S13. $\text{^{13}C NMR spectrum (100 MHz, CDCl}_3\) of 1,1,1-trichloro-4-methoxy-3-pentadecen-2-one (91%) + 1,1,1-trichloropentadecan-2-one (9%).}$

Figure S14. $\text{^{13}C NMR DEPT135 spectrum (100 MHz, CDCl}_3\) of 1,1,1-trichloro-4-methoxy-3-pentadecen-2-one (91%) + 1,1,1-trichloropentadecan-2-one (9%).}$
Figure S15. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-3-heptadec-2-one.

Figure S16. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-3-heptadec-2-one, expanded between 0.5-6.1 ppm.
Figure S17. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-3-heptadecen-2-one.

Figure S18. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 1,1,1-trichloro-4-methoxy-3-heptadecen-2-one, expanded between 22-35 ppm.
Figure S19. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-3-methylnonan-2,4-dione (ca. 75%) + 1,1,1-trichloro-3-butylhexan-2,4-dione (ca. 25%).

Figure S20. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-3-methylnonan-2,4-dione + 1,1,1-trichloro-3-butylhexan-2,4-dione, expanded between 0.5-4.7 ppm.
Figure S21. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of 1,1,1-trichloro-3-methyl-2,4-nonan-2,4-dione (3f) + 1,1,1-trichloro-3-butylhexan-2,4-dione (3f').

Figure S22. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-3-propylcycloctan-2,4-dione.
**Figure S23.** $^1$H NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-3-propyloctan-2,4-dione, expanded between 0-4.6 ppm.

**Figure S24.** $^{13}$C NMR spectrum (400 MHz, CDCl$_3$) of 1,1,1-trichloro-3-propyloctan-2,4-dione.
Figure S25. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of methyl 3-hexyl-1H-pyrazole-5-carboxylate.

Figure S26. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of methyl 3-hexyl-1H-pyrazole-5-carboxylate, expanded between 0.5-6.6 ppm.
Figure S27. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of methyl 3-hexyl-1H-pyrazole-5-carboxylate.

Figure S28. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of ethyl 3-hexyl-1H-pyrazole-5-carboxylate.
Figure S29. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of ethyl 3-hexyl-1H-pyrazole-5-carboxylate, expanded between 0.5-6.7 ppm.

Figure S30. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of ethyl 3-hexyl-1H-pyrazole-5-carboxylate.
Figure S31. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of methyl 3-heptyl-$1H$-pyrazole-5-carboxylate.

Figure S32. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of methyl 3-heptyl-$1H$-pyrazole-5-carboxylate.
Figure S33. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of ethyl 3-heptyl-1H-pyrazole-5-carboxylate in CDCl$_3$.

Figure S34. $^{13}$C NMR spectrum (400 MHz, CDCl$_3$) of ethyl 3-heptyl-1H-pyrazole-5-carboxylate.
Figure S35. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of methyl 3-nonyl-$1H$-pyrazole-5-carboxylate.

Figure S36. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of methyl 3-nonyl-$1H$-pyrazole-5-carboxylate.
Figure S37. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of ethyl 3-nonyl-1H-pyrazole-5-carboxylate.

Figure S38. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of ethyl 3-nonyl-1H-pyrazole-5-carboxylate in CDCl$_3$. 
Figure S39. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of ethyl 3-undecyl-$1H$-pyrazole-5-carboxylate.

Figure S40. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of ethyl 3-undecyl-$1H$-pyrazole-5-carboxylate, expanded between 0.5-6.8 ppm.
Figure S41. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of ethyl 3-undecyl-1H-pyrazole-5-carboxylate in CDCl$_3$.

Figure S42. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of ethyl 3-undecyl-1H-pyrazole-5-carboxylate, expanded between 12.5-33.5 ppm.
Figure S43. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of ethyl 3-tridecyl-$1H$-pyrazole-5-carboxylate.

Figure S44. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of ethyl 3-tridecyl-$1H$-pyrazole-5-carboxylate, expanded between 0.5-7.0 ppm.
Figure S45. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of ethyl 3-tridecyl-1H-pyrazole-5-carboxylate.

Figure S46. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of ethyl 3-tridecyl-1H-pyrazole-5-carboxylate, expanded between 12-35 ppm.
Figure S47. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of methyl 4-methyl-3-pentyl-1H-pyrazole-5-carboxylate + methyl 4-butyl-3-ethyl-1H-pyrazole-5-carboxylate.

Figure S48. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of methyl 4-methyl-3-pentyl-1H-pyrazole-5-carboxylate + methyl 4-butyl-3-ethyl-1H-pyrazole-5-carboxylate, expanded between 0.6-4.2 ppm.
Figure S49. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of methyl 4-methyl-3-pentyl-1H-pyrazole-5-carboxylate + methyl 4-butyl-3-ethyl-1H-pyrazole-5-carboxylate.

Figure S50. $^{13}$C NMR spectrum (400 MHz, CDCl$_3$) of methyl 4-methyl-3-pentyl-1H-pyrazole-5-carboxylate + methyl 4-butyl-3-ethyl-1H-pyrazole-5-carboxylate, expanded between 6-56 ppm.
Figure S51. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of ethyl 4-methyl-3-pentyl-1H-pyrazole-5-carboxylate + ethyl 4-butyl-3-ethyl-1H-pyrazole-5-carboxylate.

Figure S52. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of ethyl 4-methyl-3-pentyl-1H-pyrazole-5-carboxylate + ethyl 4-butyl-3-ethyl-1H-pyrazole-5-carboxylate, expanded between 0.7-4.7 ppm.
Figure S53. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of ethyl 4-methyl-3-pentyl-$1H$-pyrazole-5-carboxylate + ethyl 4-butyl-3-ethyl-$1H$-pyrazole-5-carboxylate.

Figure S54. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of ethyl 4-methyl-3-pentyl-$1H$-pyrazole-5-carboxylate + ethyl 4-butyl-3-ethyl-$1H$-pyrazole-5-carboxylate.
Figure S55. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of methyl 3-butyl-4-propyl-1H-pyrazole-5-carboxylate.

Figure S56. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of methyl 3-butyl-4-propyl-1H-pyrazole-5-carboxylate, expanded between 0.5-4.2 ppm.
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Figure S57. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of methyl 3-butyl-4-propyl-1H-pyrazole-5-carboxylate in CDCl$_3$.

Figure S58. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of ethyl 3-butyl-4-propyl-1H-pyrazole-5-carboxylate in CDCl$_3$. 
Figure S59. $^{13}$C NMR spectrum (400 MHz, CDCl$_3$) of ethyl 3-butyl-4-propyl-1H-pyrazole-5-carboxylate.

Figure S60. $^{13}$C NMR spectrum (400 MHz, CDCl$_3$) of methyl 3-butyl-4-propyl-1H-pyrazole-5-carboxylate, expanded between 10-34 ppm.