

Supplementary Information

Synthesis of Fatty Trichloromethyl- β -diketones and New 1*H*-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 1*H*-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-*d*₆. 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

Compound, Yield / %	H-3	H-5	H-6	Others	Me	OMe
2a , 85	5.96	2.78, t, 8.0	1.57, qui, 8.0	1.28-1.39	0.89, t, 6.8	3.79
2b , 92	5.97	2.78, t, 8.0	1.58, qui, 8.0	1.29-1.38	0.89, t, 6.8	3.79
2c , 95	5.97	2.78, t, 8.0	1.57, qui, 8.0	1.27-1.35	0.88, t, 6.8	3.79
2d , 92	5.95	2.77, t, 8.0	1.56, qui, 8.0	1.26-1.34	0.87, t, 6.8	3.78
2e , 90	5.96	2.78, t, 8.0	1.57, qui, 8.0	1.26-1.34	0.88, t, 6.8	3.79
3f , 69	4.47, q, 7.2	2.58, m, 6.8	1.58, m, 7.2	1.32, m	0.9, 0.88t	–
3f' , 23	4.42, dd, 8.5, 5.2	– ^a	– ^a	–	–	–
3g , 89	4.43, dd, 8.9, 5.2	2.62, m	1.92, m	1.20-1.40	0.89, 0.96, t, t	–

^aOverlapping 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

Compound	C-1	C-2	C-3	C-4	OMe	Others
2a	98.0	179.9	89.7	184.0	56.2	33.4; 31.4; 28.1; 26.9; 22.5; 13.9
2b	98.0	179.9	89.7	184.0	56.2	33.4; 31.7; 29.4; 28.9; 27.0; 22.5; 14.0
2c	98.0	179.9	89.7	184.0	56.2	33.4; 31.8; 29.4; 29.2; 26.9; 22.6; 14.0
2d	98.0	179.8	89.7	183.9	56.1	33.4; 31.8; 29.4; 29.2; 29.1; 26.9; 22.6; 14.0
2e	98.0	179.9	89.7	184.1	56.2	33.4; 31.9; 29.65; 29.62; 29.59; 29.5; 29.4; 29.3; 27.0; 22.6; 14.0
3f	96.1	186.7	52.5	203.5	–	40.5; 31.1; 23.0; 22.2; 16.3; 13.69
3f'	96.1	185.2	58.6	203.3	–	40.5; 34.3; 31.0; 22.8; 29.6; 7.60
3g	94.4	185.2	58.7	203.5	–	40.7; 33.5; 25.4; 22.0; 21.0; 13.8; 13.7

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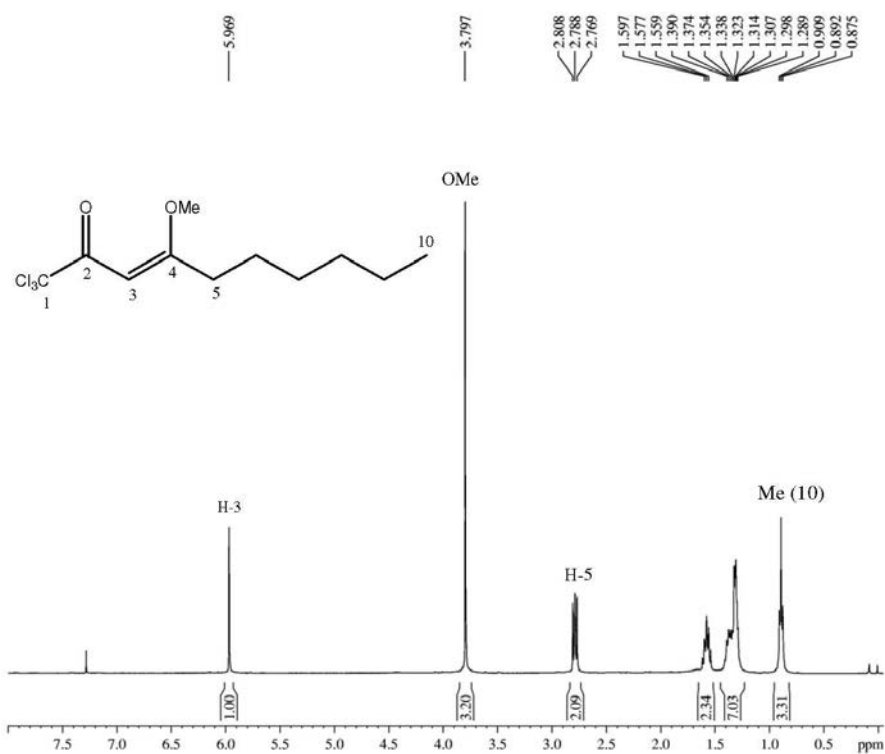


Figure S1. ^1H NMR spectrum (400 MHz, CDCl_3) of 1,1,1-trichloro-4-methoxy-4-decen-2-one.

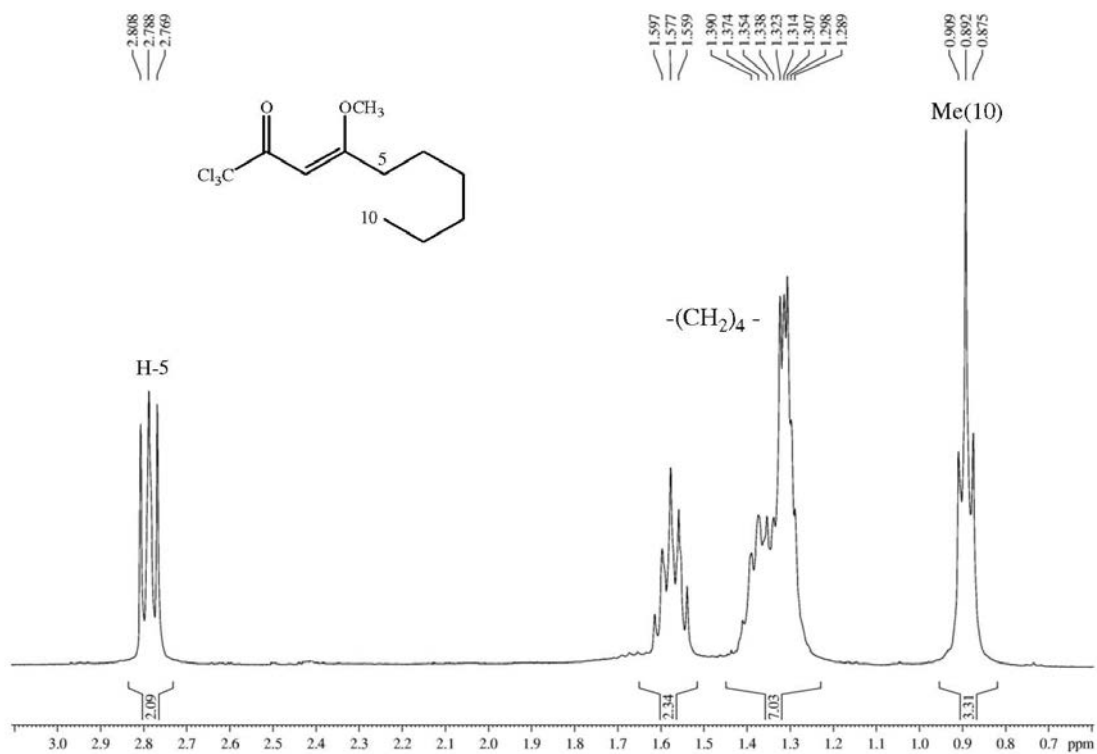


Figure S2. ^1H NMR spectrum (400 MHz, CDCl_3) of 1,1,1-trichloro-4-methoxy-4-decen-2-one, expanded between 0.6-3.1 ppm.

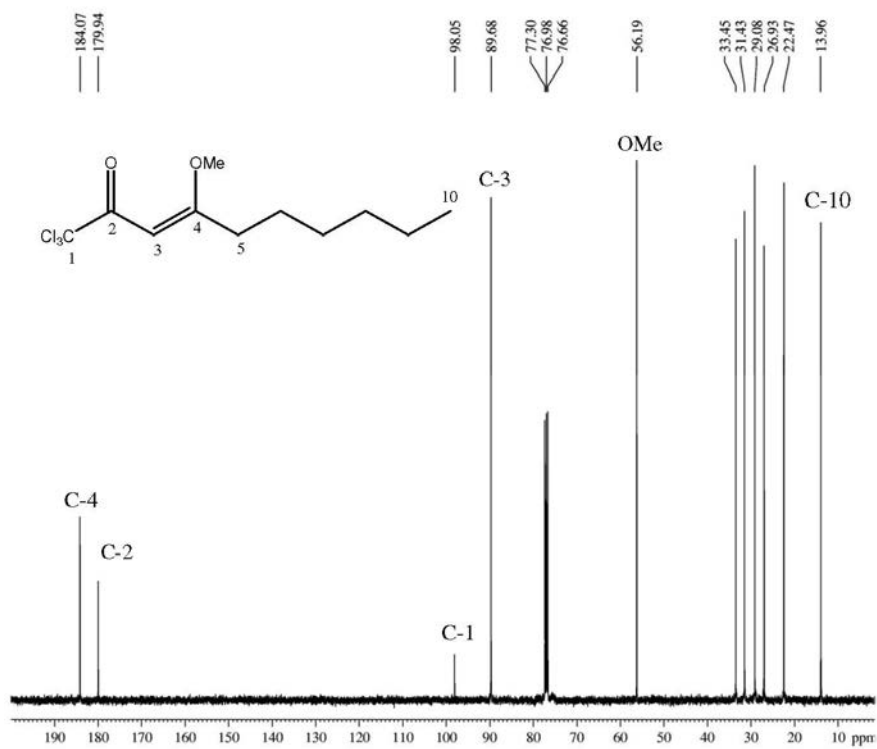


Figure S3. ^{13}C NMR (100 MHz, CDCl_3) spectrum of 1,1,1-trichloro-4-methoxy-4-decen-2-one.

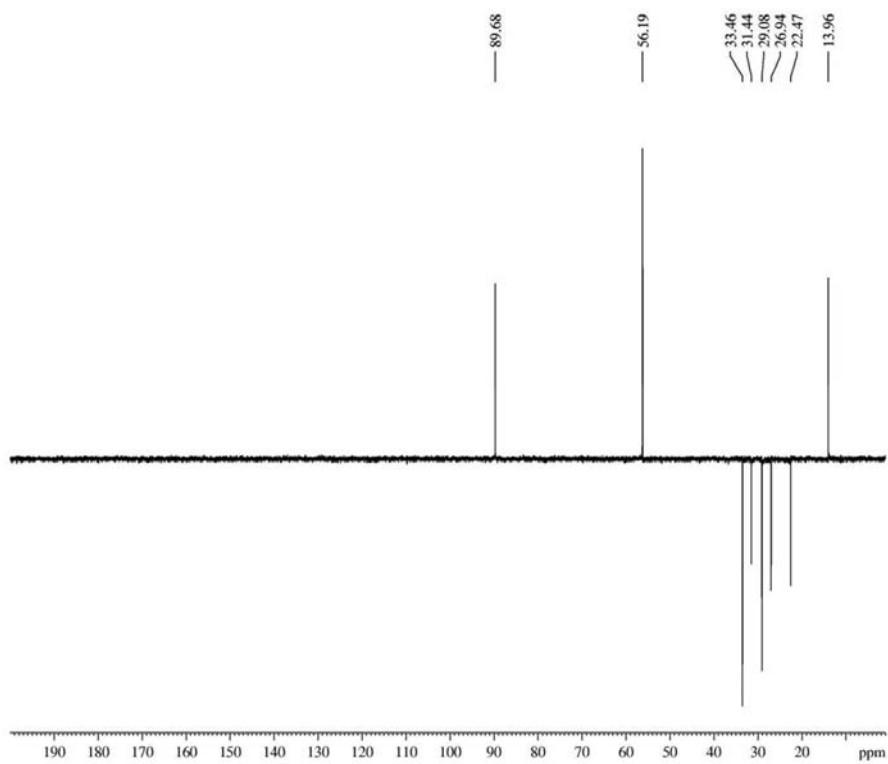


Figure S4. ^{13}C NMR DEPT135 spectrum (100 MHz, CDCl_3) of 1,1,1-trichloro-4-methoxy-4-decen-2-one.

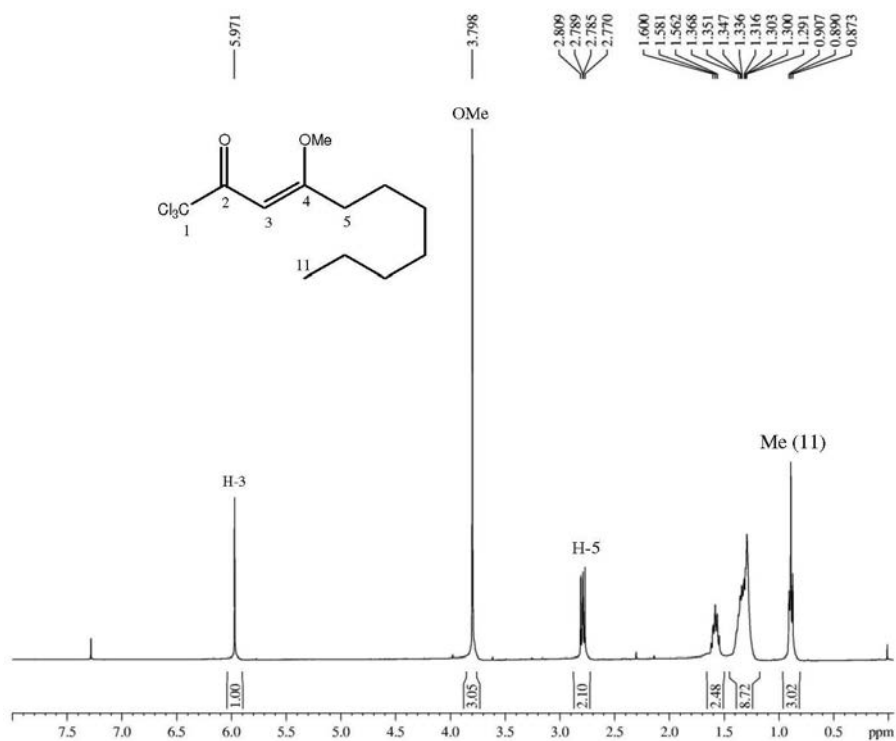


Figure S5. ¹H NMR spectrum (400 MHz, CDCl₃) of 1,1,1-trichloro-4-methoxy-4-undecen-2-one in CDCl₃.

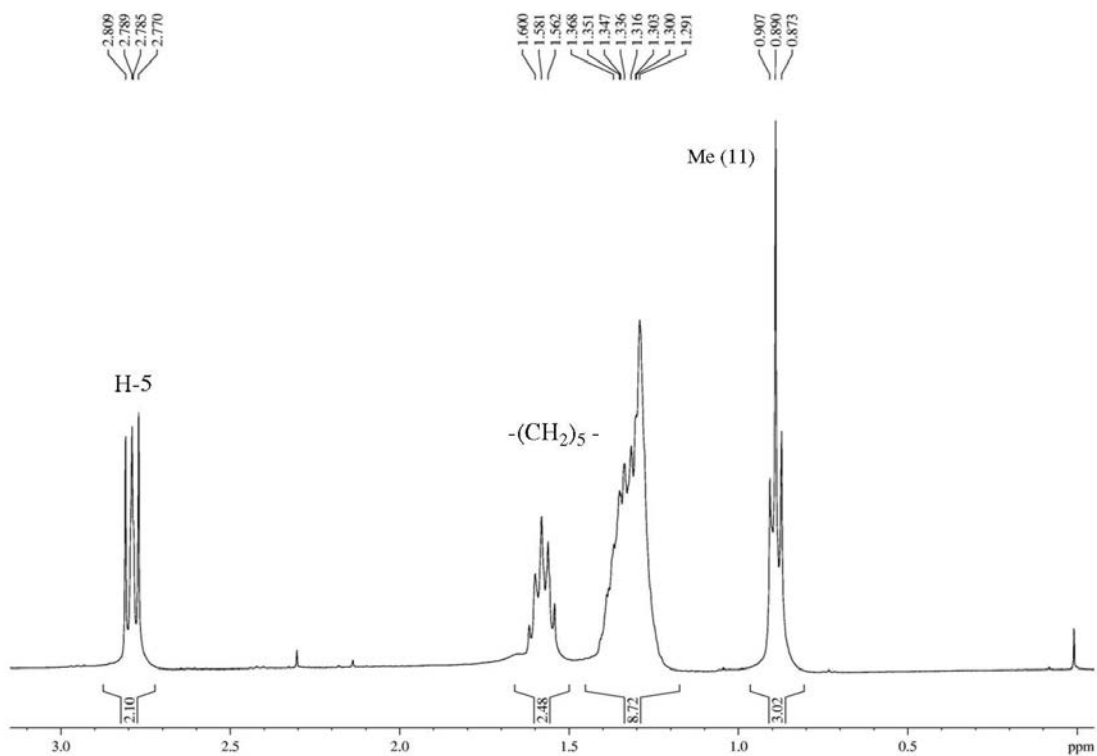


Figure S6. ¹H NMR spectrum (400 MHz, CDCl₃) of 1,1,1-trichloro-4-methoxy-4-undecen-2-one, expanded between 0.3-3.1 ppm.

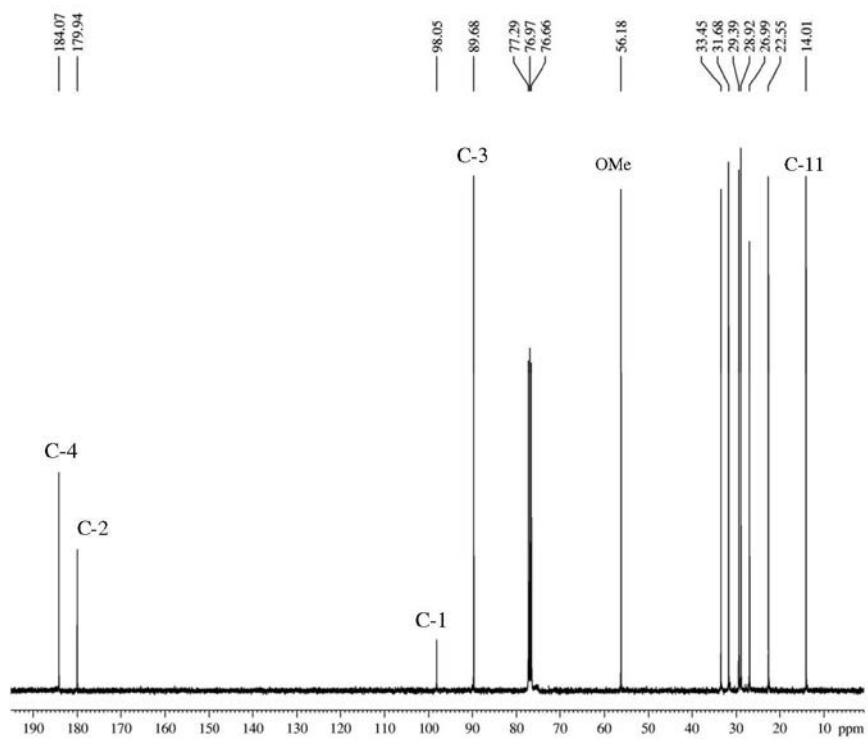


Figure S7. ^{13}C NMR spectrum (100 MHz, CDCl_3) of 1,1,1-trichloro-4-methoxy-4-undecen-2-one.

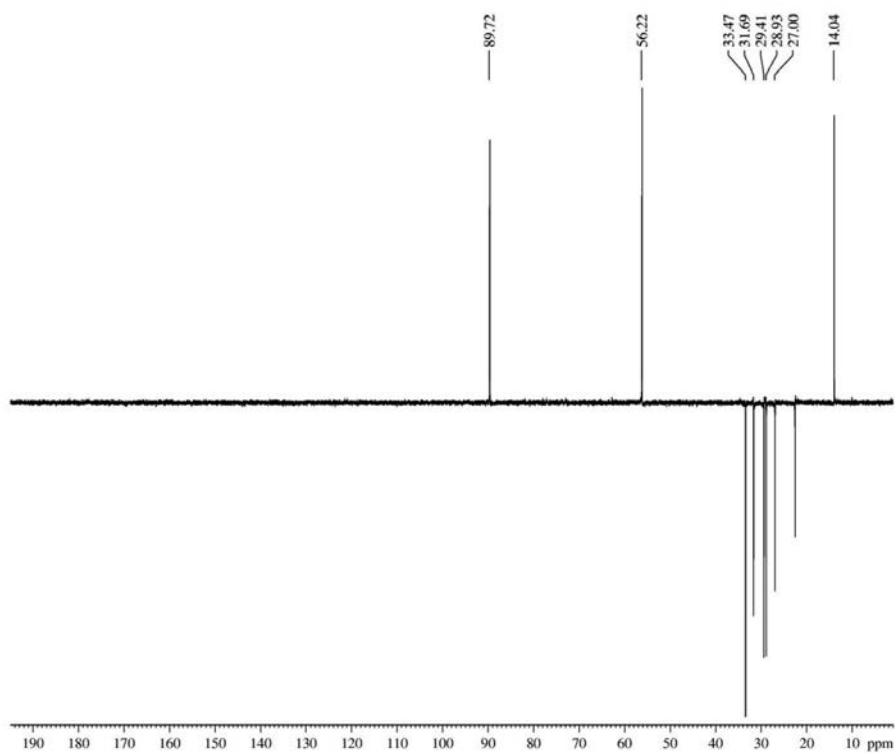


Figure S8. ^{13}C NMR DEPT135 spectrum (100 MHz, CDCl_3) of 1,1,1-trichloro-4-methoxy-4-undecen-2-one.

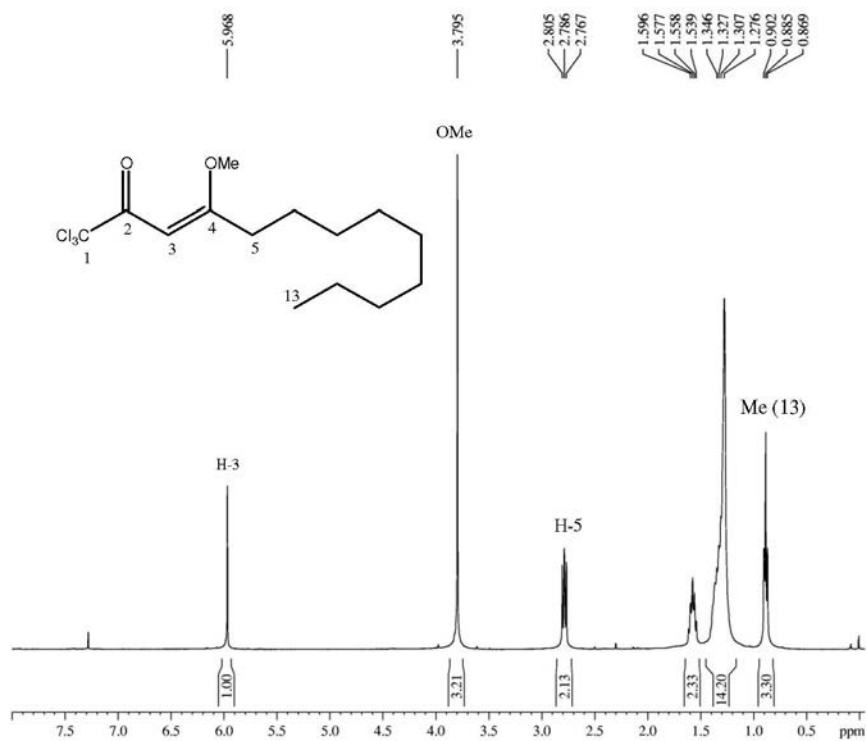


Figure S9. ^1H NMR spectrum (400 MHz, CDCl_3) of 1,1,1-trichloro-4-methoxy-4-tridecen-2-one.

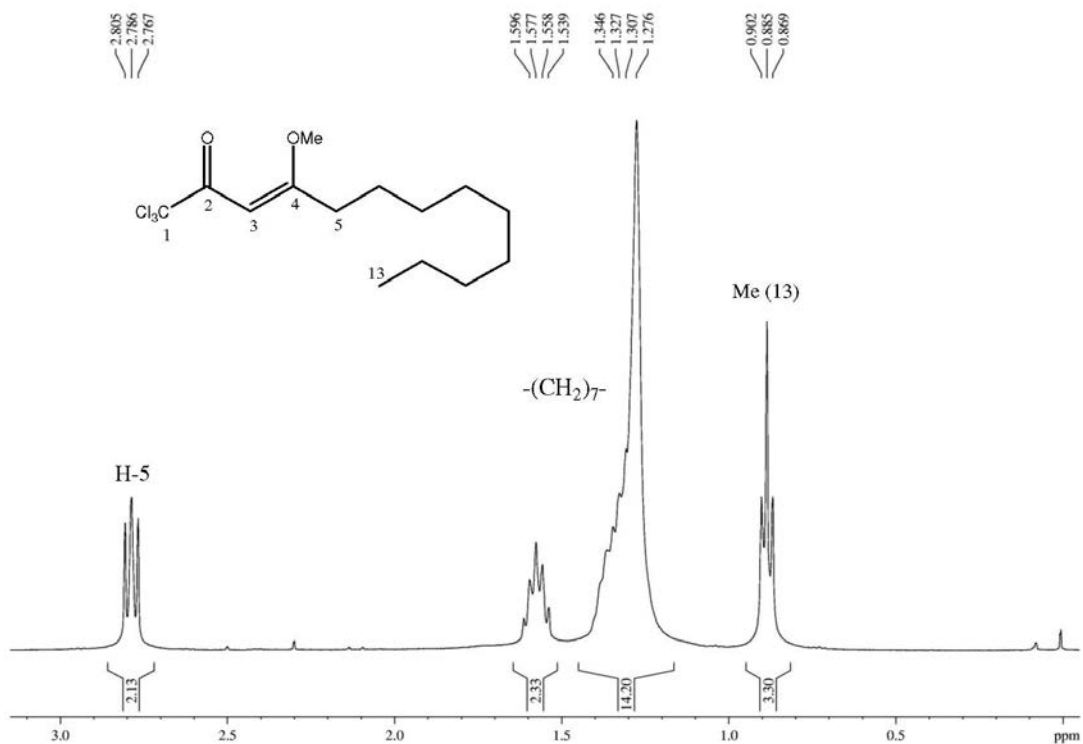


Figure S10. ^1H NMR spectrum (400 MHz, CDCl_3) of 1,1,1-trichloro-4-methoxy-4-tridecen-2-one, expanded between 0 -3,15 ppm.

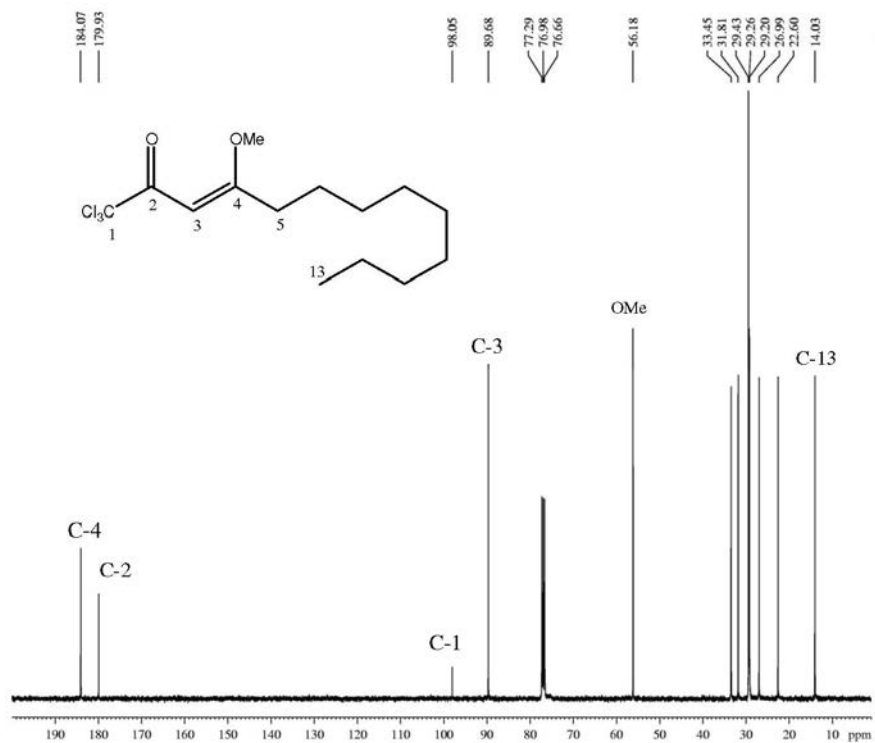


Figure S11. ¹³C NMR spectrum (100 MHz, CDCl₃) of 1,1,1-trichloro-4-methoxy-4-tridecen-2-one.

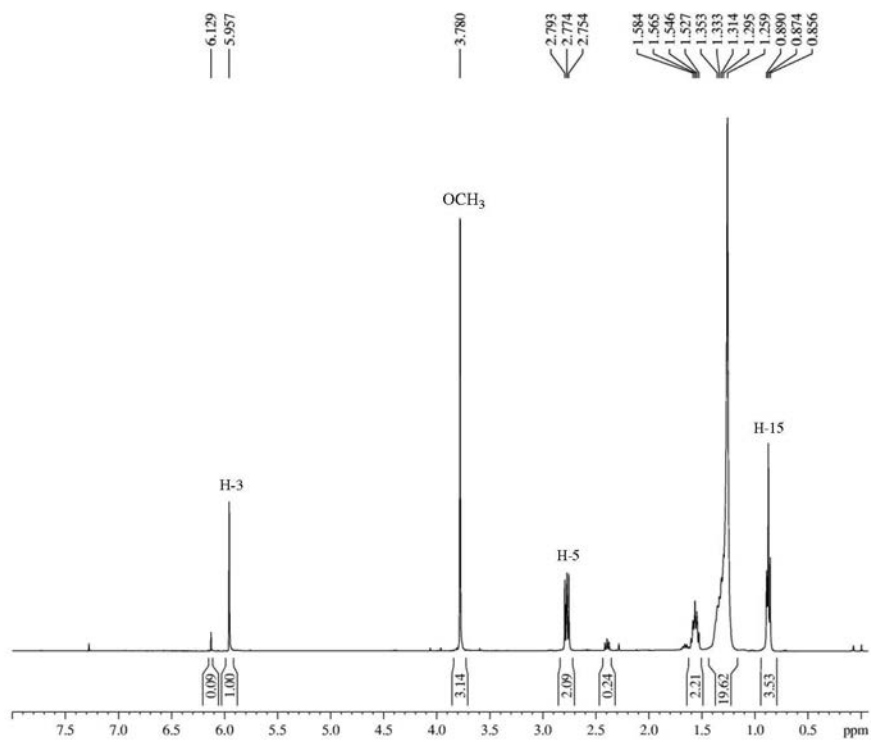


Figure S12. ¹H NMR spectrum (400 MHz, CDCl₃) of 1,1,1-trichloro-4-methoxy-3-pentadecen-2-one.

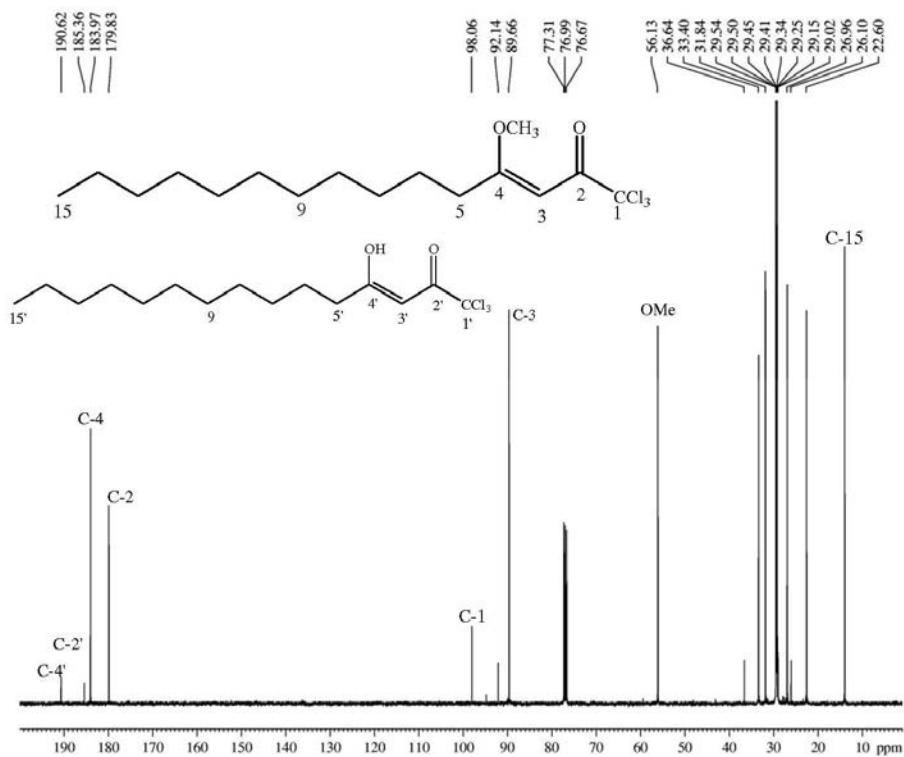


Figure S13. ^{13}C NMR spectrum (100 MHz, CDCl_3) of 1,1,1-trichloro-4-methoxy-3-pentadecen-2-one (91%) + 1,1,1-trichloropentadecan-2-one (9%).



Figure S14. ^{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%).

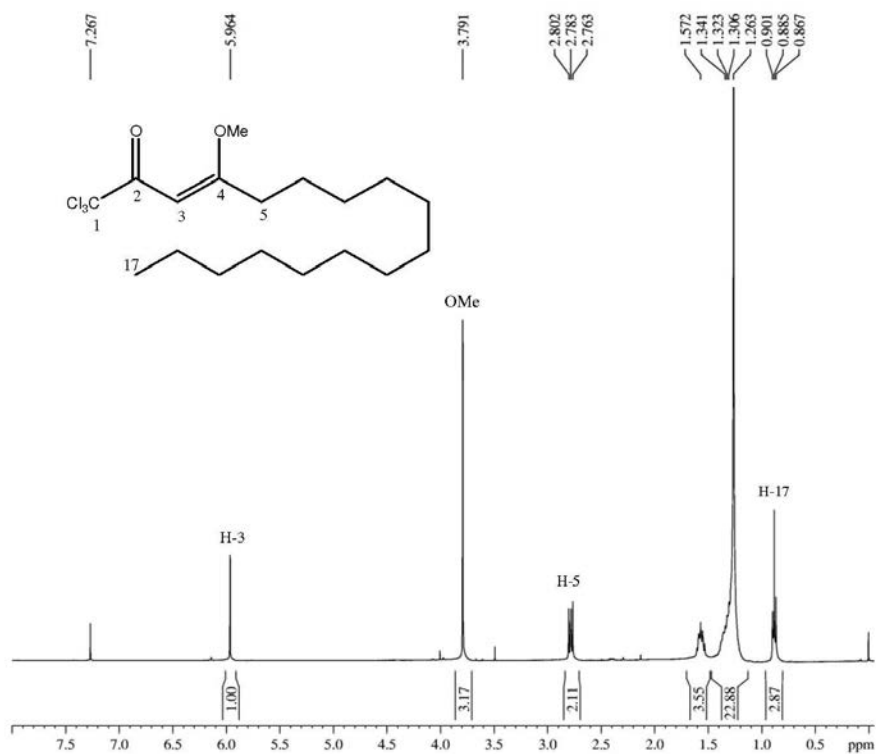


Figure S15. ¹H NMR spectrum (400 MHz, CDCl₃) of 1,1,1-trichloro-4-methoxy-3-heptadecen-2-one.

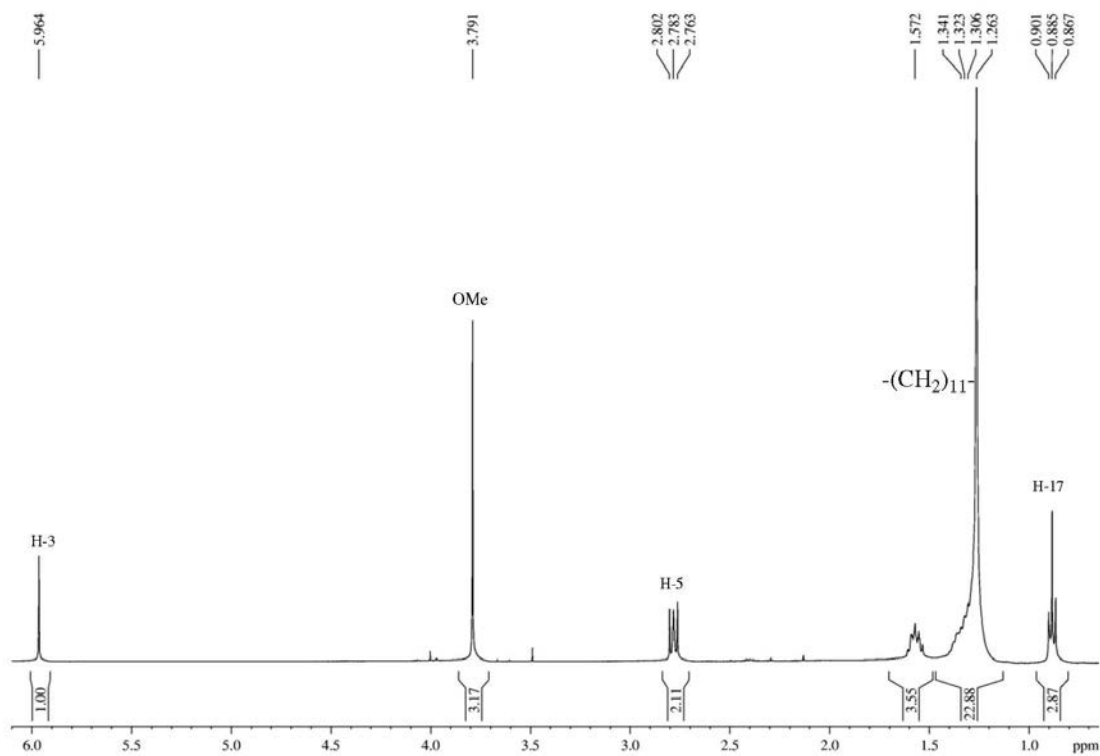


Figure S16. ¹H NMR spectrum (400 MHz, CDCl₃) of 1,1,1-trichloro-4-methoxy-3-heptadecen-2-one, expanded between 0.5-6.1 ppm.

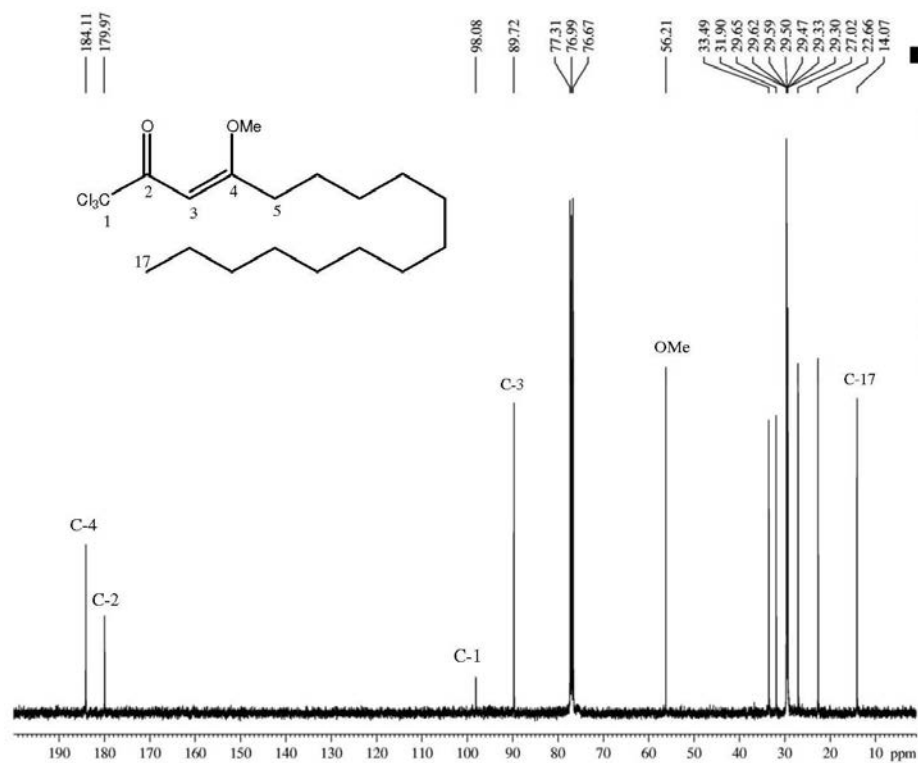


Figure S17. ¹³C NMR spectrum (100 MHz, CDCl₃) of 1,1,1-trichloro-4-methoxy-3-heptadecen-2-one.

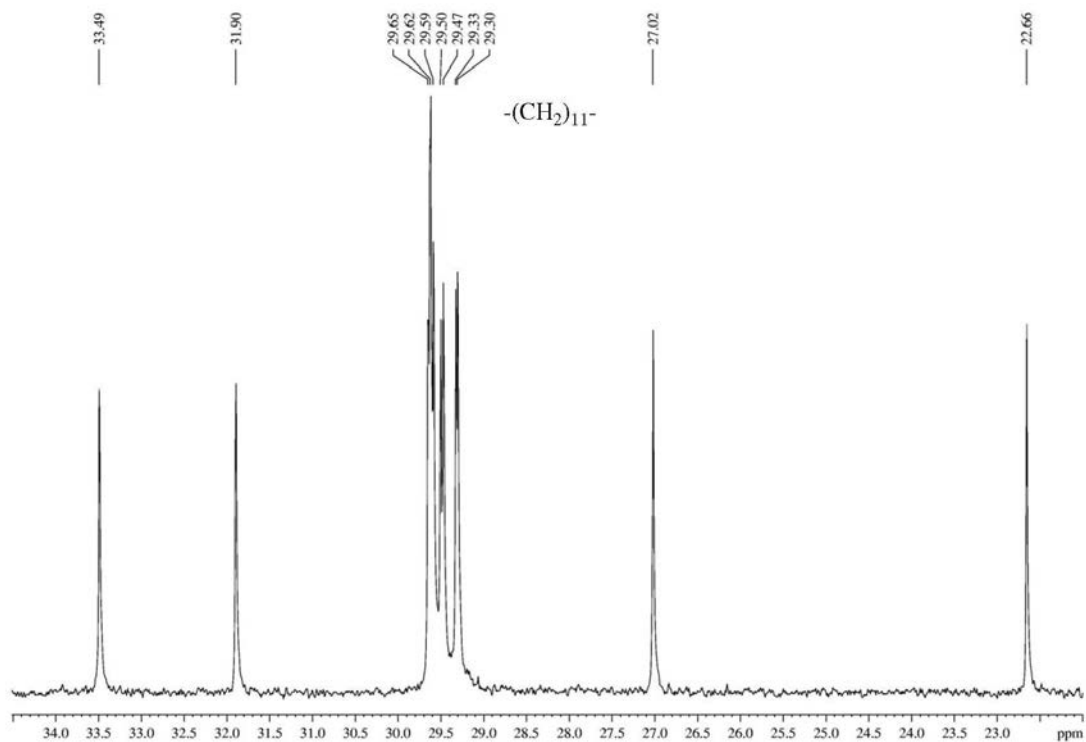


Figure S18. ¹³C NMR spectrum (100 MHz, CDCl₃) of 1,1,1-trichloro-4-methoxy-3-heptadecen-2-one, expanded between 22-35 ppm.

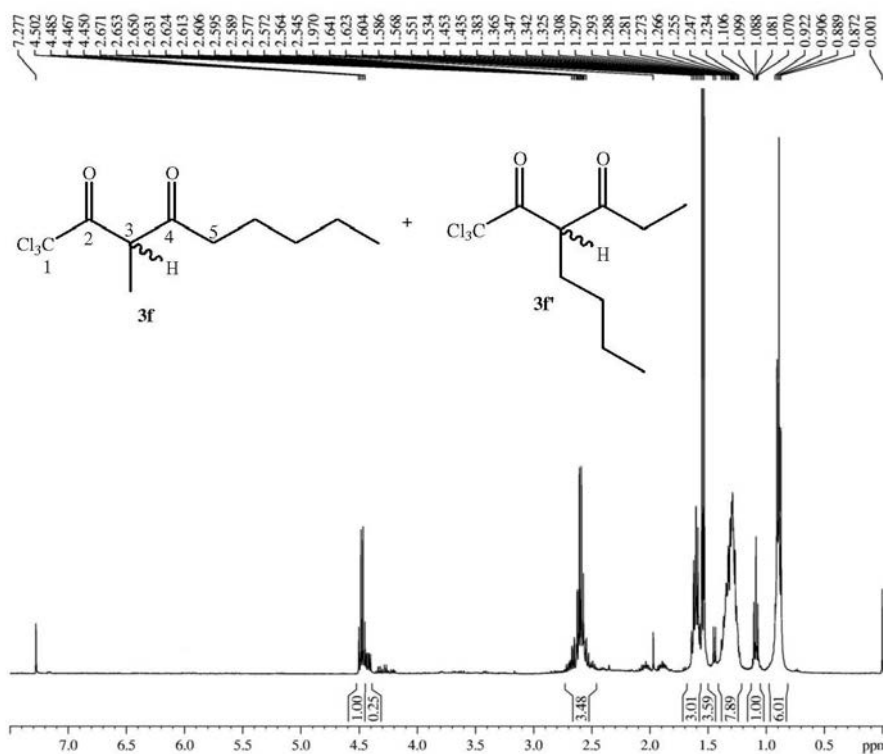


Figure S19. ^1H NMR spectrum (400 MHz, CDCl_3) of 1,1,1-trichloro-3-methylnonan-2,4-dione (ca. 75%) + 1,1,1-trichloro-3-butylhexan-2,4-dione (ca. 25%).

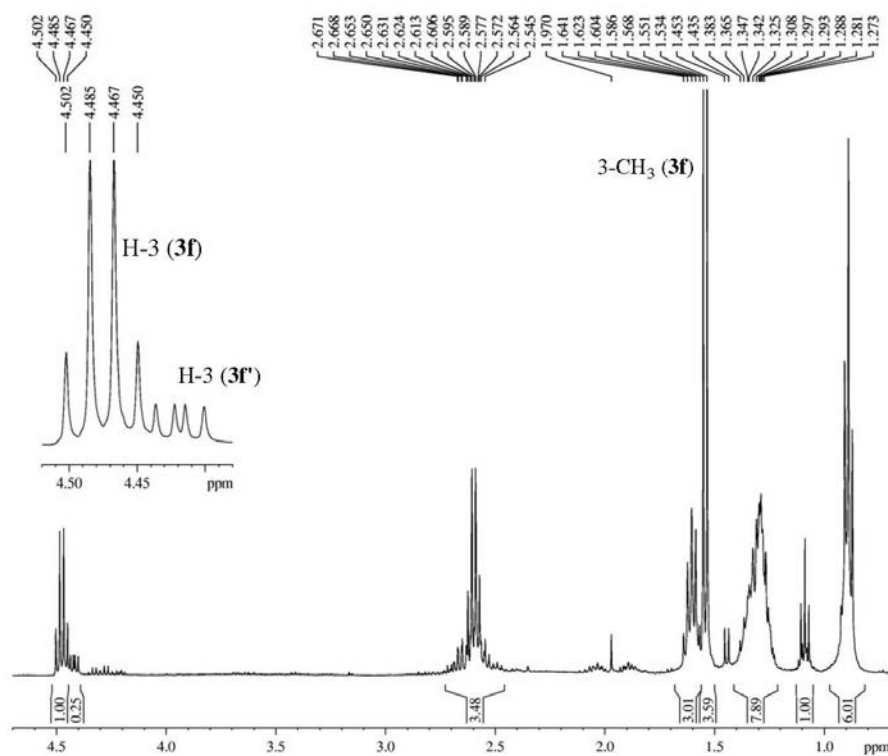


Figure S20. ^1H NMR spectrum (400 MHz, CDCl_3) of 1,1,1-trichloro-3-methylnonan-2,4-dione + 1,1,1-trichloro-3-butylhexan-2,4-dione, expanded between 0.5-4.7 ppm.

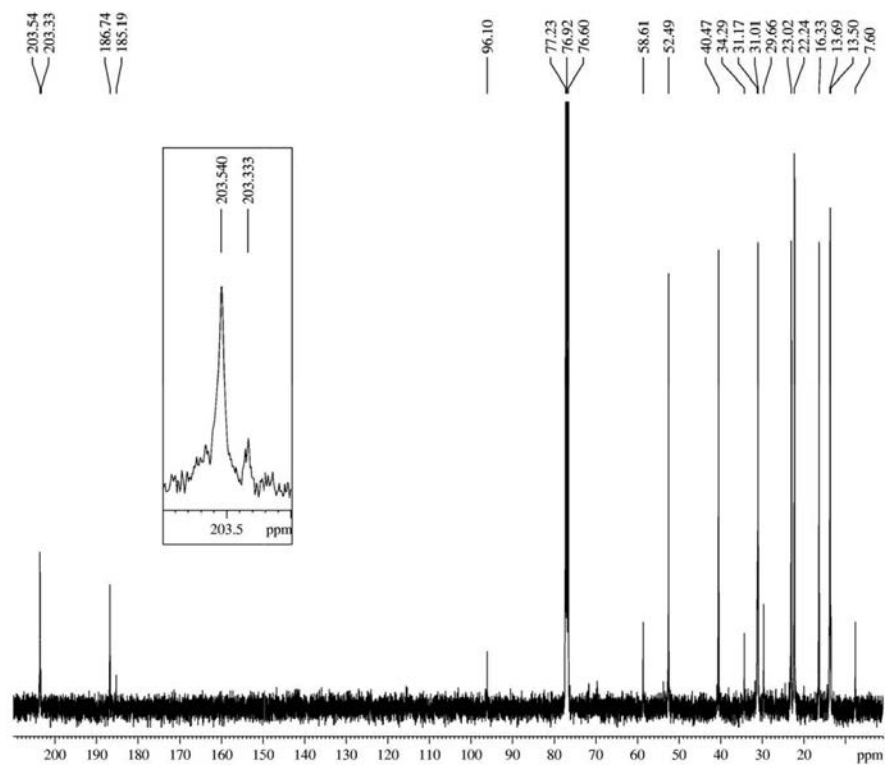


Figure S21. ^{13}C NMR spectrum (100 MHz, CDCl_3) of 1,1,1-trichloro-3-methyl-2,4-nonan-2,4-dione (**3f**) + 1,1,1-trichloro-3-butylhexan-2,4-dione (**3f'**).

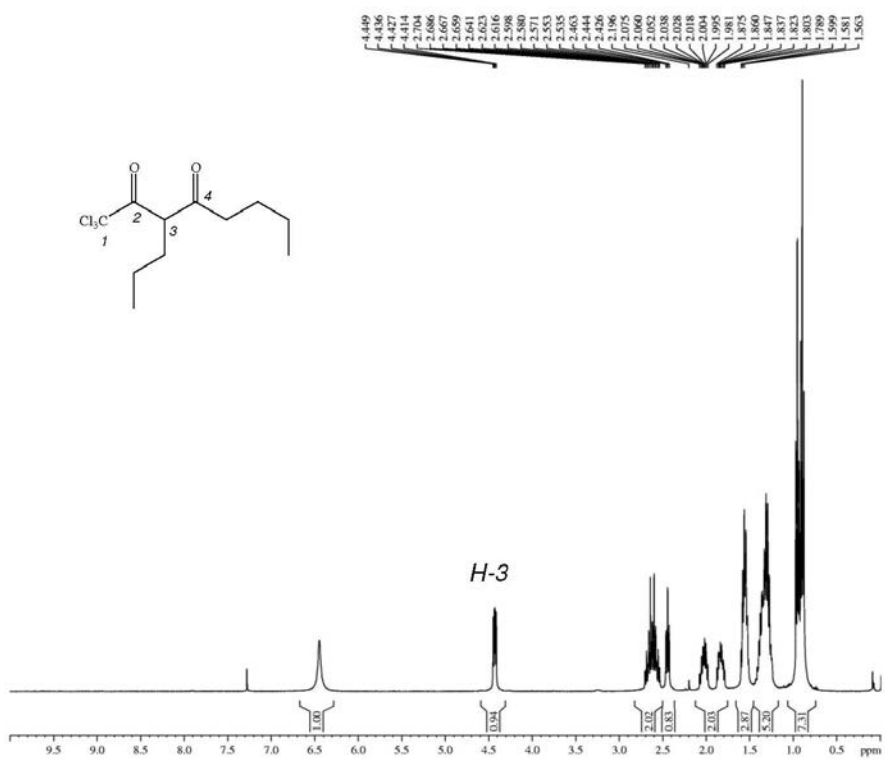


Figure S22. ^1H NMR spectrum (400 MHz, CDCl_3) of 1,1,1-trichloro-3-propyloctan-2,4-dione.

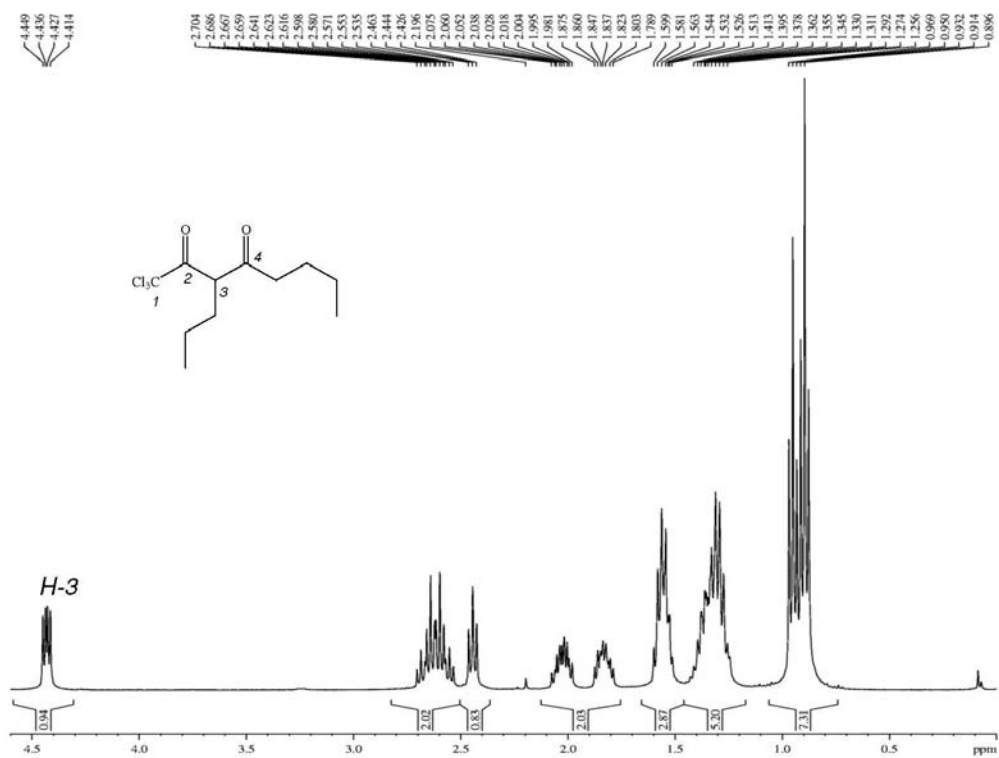


Figure S23. ¹H NMR spectrum (400 MHz, CDCl₃) of 1,1,1-trichloro-3-propyloctan-2,4-dione, expanded between 0-4.6 ppm.

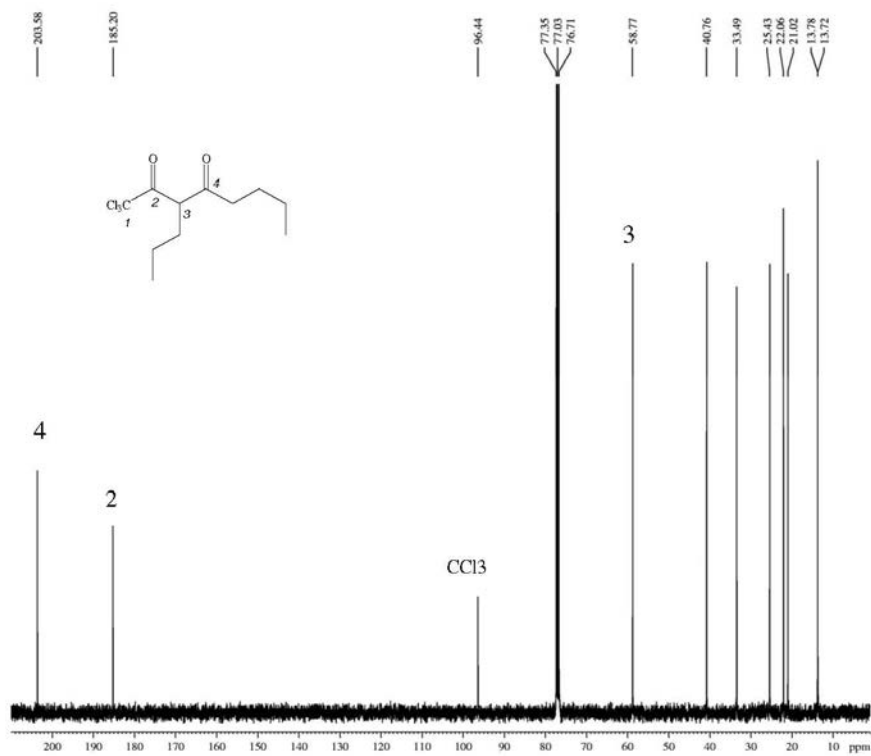


Figure S24. ¹³C NMR spectrum (400 MHz, CDCl₃) of 1,1,1-trichloro-3-propyloctan-2,4-dione.

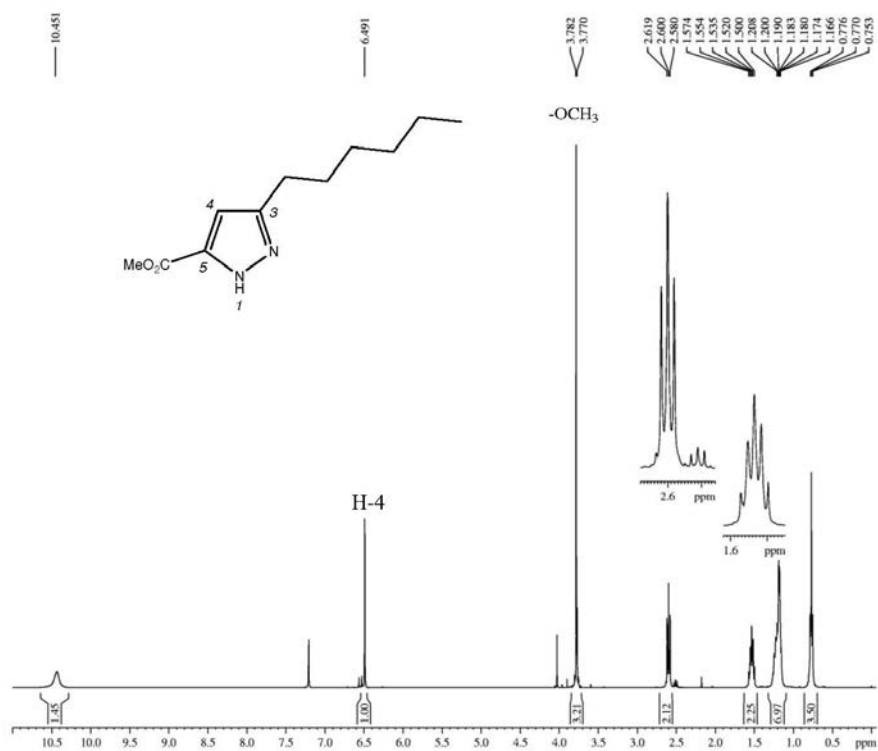


Figure S25. ¹H NMR spectrum (400 MHz, CDCl₃) of methyl 3-hexyl-1*H*-pyrazole-5-carboxylate.

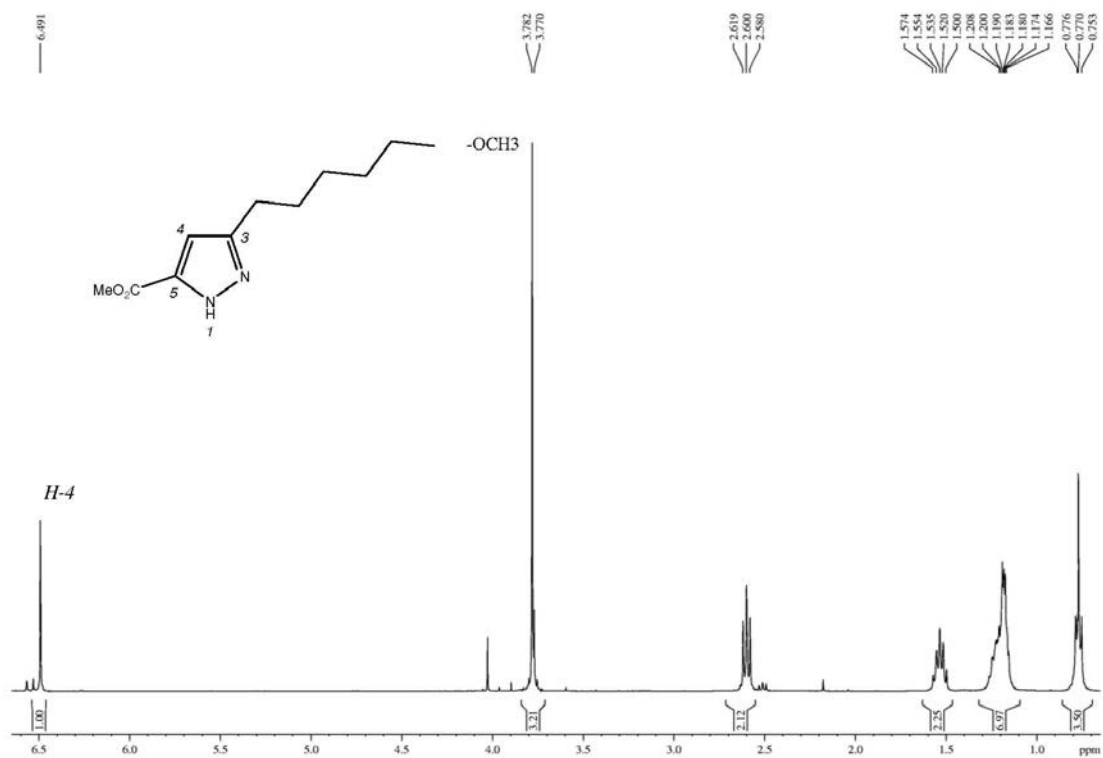


Figure S26. ¹H NMR spectrum (400 MHz, CDCl₃) of methyl 3-hexyl-1*H*-pyrazole-5-carboxylate, expanded between 0.5-6.6 ppm.

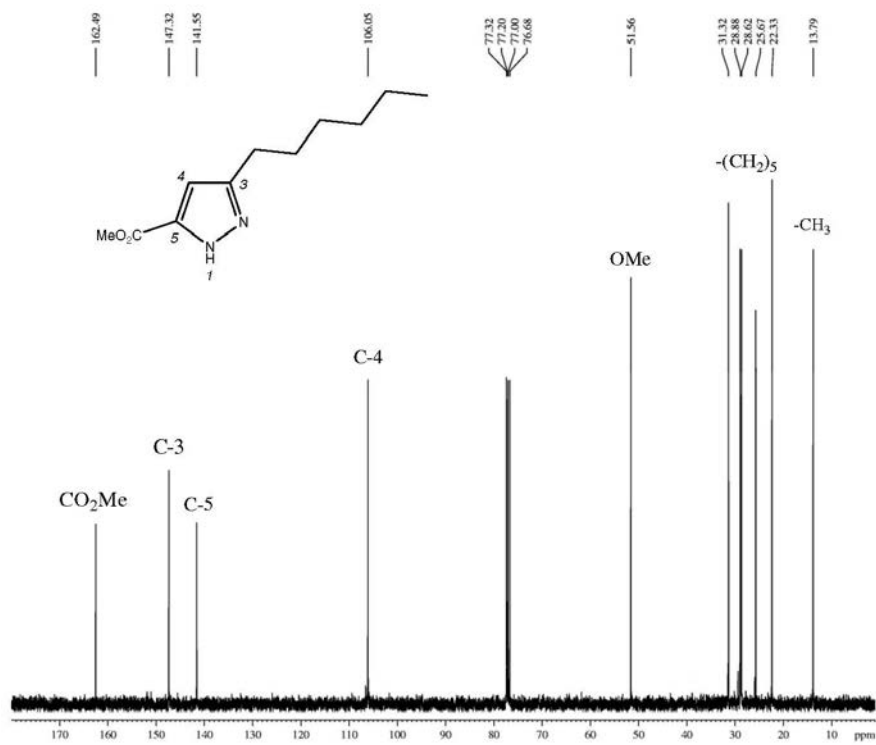


Figure S27. ¹³C NMR spectrum (100 MHz, CDCl₃) of methyl 3-hexyl-1H-pyrazole-5-carboxylate.

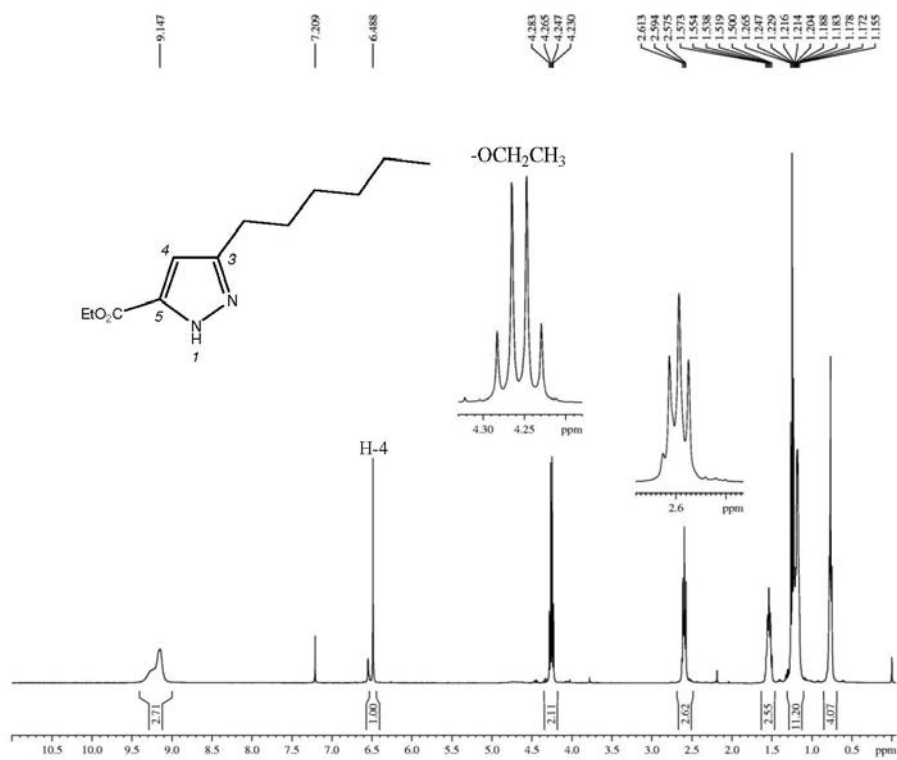


Figure S28. ¹H NMR spectrum (400 MHz, CDCl₃) of ethyl 3-hexyl-1H-pyrazole-5-carboxylate.

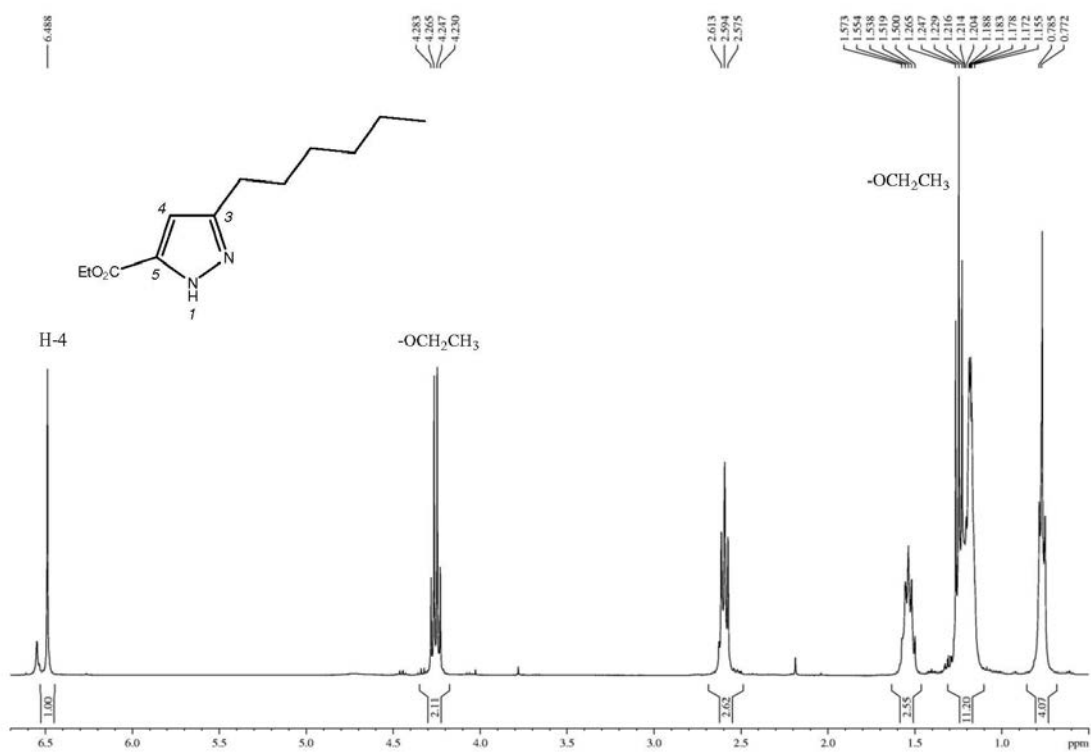


Figure S29. ¹H NMR spectrum (400 MHz, CDCl₃) of ethyl 3-hexyl-1*H*-pyrazole-5-carboxylate, expanded between 0.5-6.7 ppm.

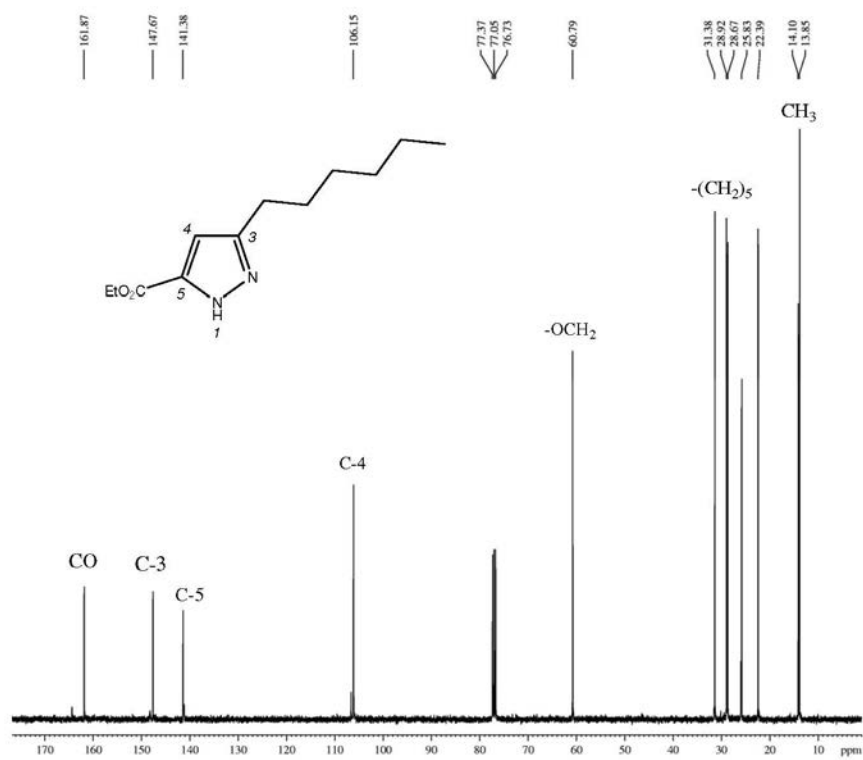


Figure S30. ¹³C NMR spectrum (100 MHz, CDCl₃) of ethyl 3-hexyl-1*H*-pyrazole-5-carboxylate.

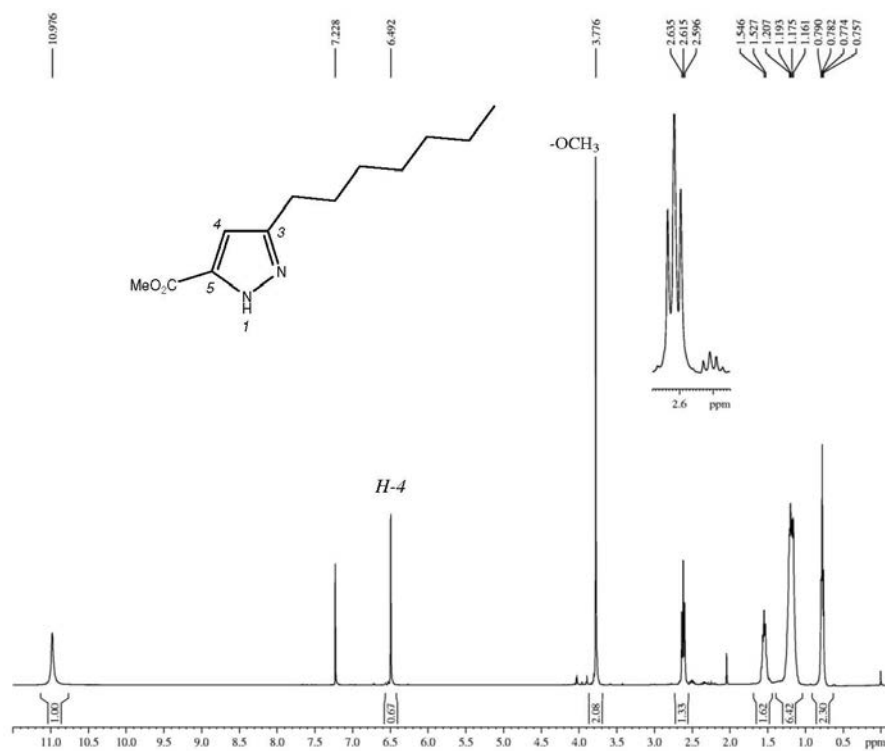


Figure S31. ¹H NMR spectrum (400 MHz, CDCl₃) of methyl 3-heptyl-1H-pyrazole-5-carboxylate.

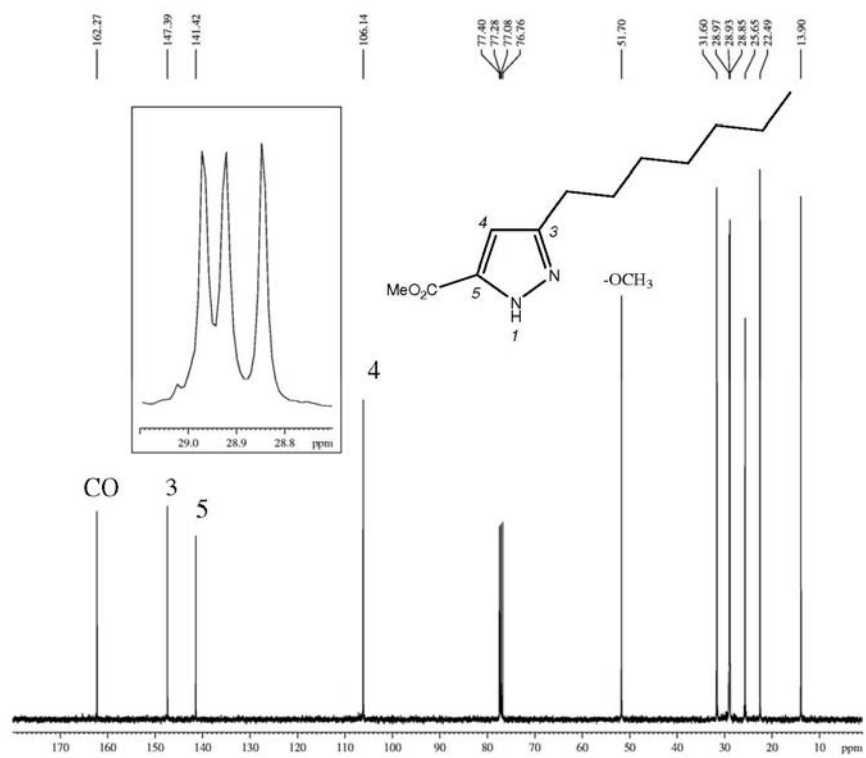


Figure S32. ¹³C NMR spectrum (100 MHz, CDCl₃) of methyl 3-heptyl-1H-pyrazole-5-carboxylate.

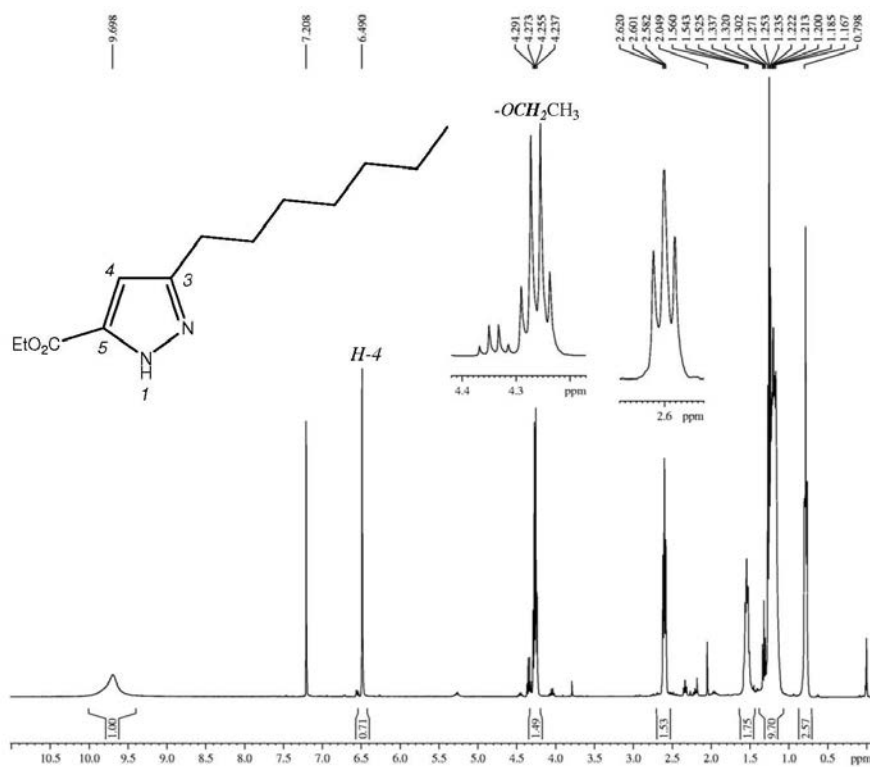


Figure S33. ¹H NMR spectrum (400 MHz, CDCl₃) of ethyl 3-heptyl-1*H*-pyrazole-5-carboxylate in CDCl₃.

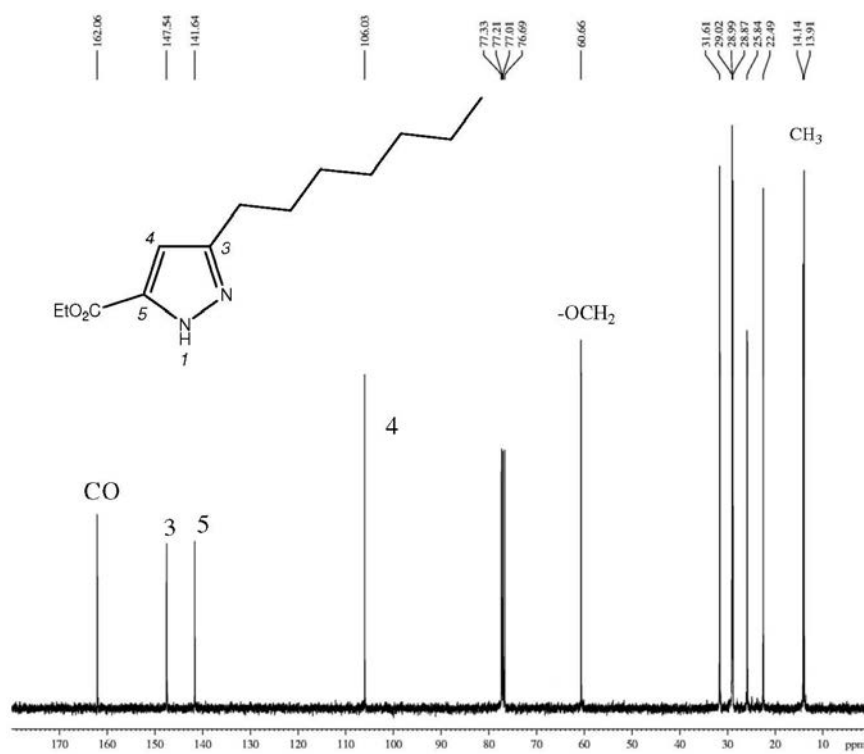


Figure S34. ¹³C NMR spectrum (400 MHz, CDCl₃) of ethyl 3-heptyl-1*H*-pyrazole-5-carboxylate.

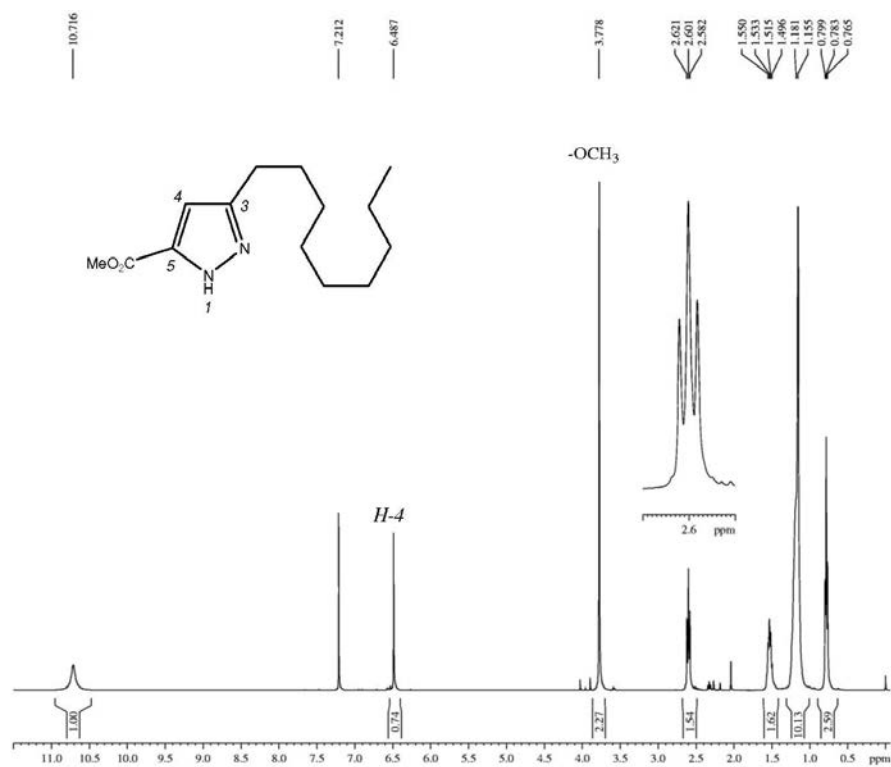


Figure S35. ^1H NMR spectrum (400 MHz, CDCl_3) of methyl 3-nonyl-1H-pyrazole-5-carboxylate.

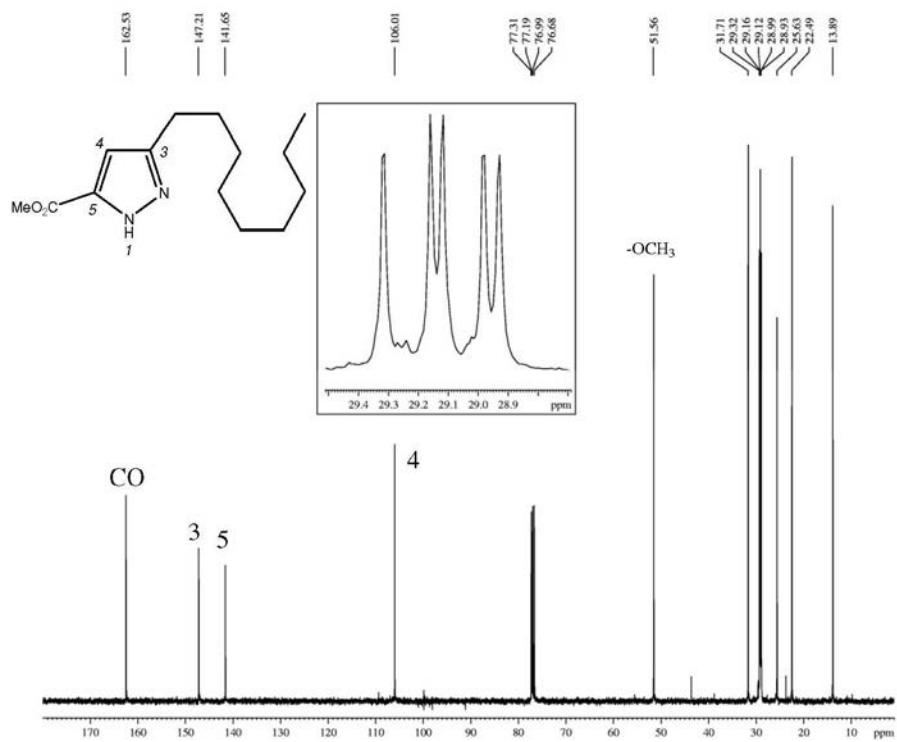


Figure S36. ^{13}C NMR spectrum (100 MHz, CDCl_3) of methyl 3-nonyl-1H-pyrazole-5-carboxylate.

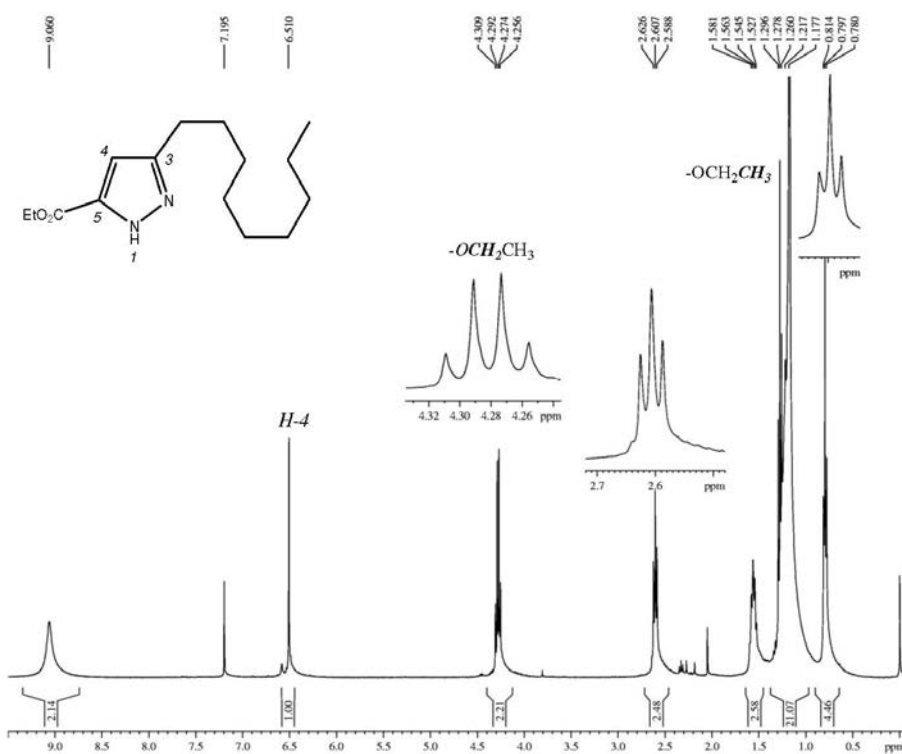


Figure S37. ^1H NMR spectrum (400 MHz, CDCl_3) of ethyl 3-nonyl-1*H*-pyrazole-5-carboxylate.

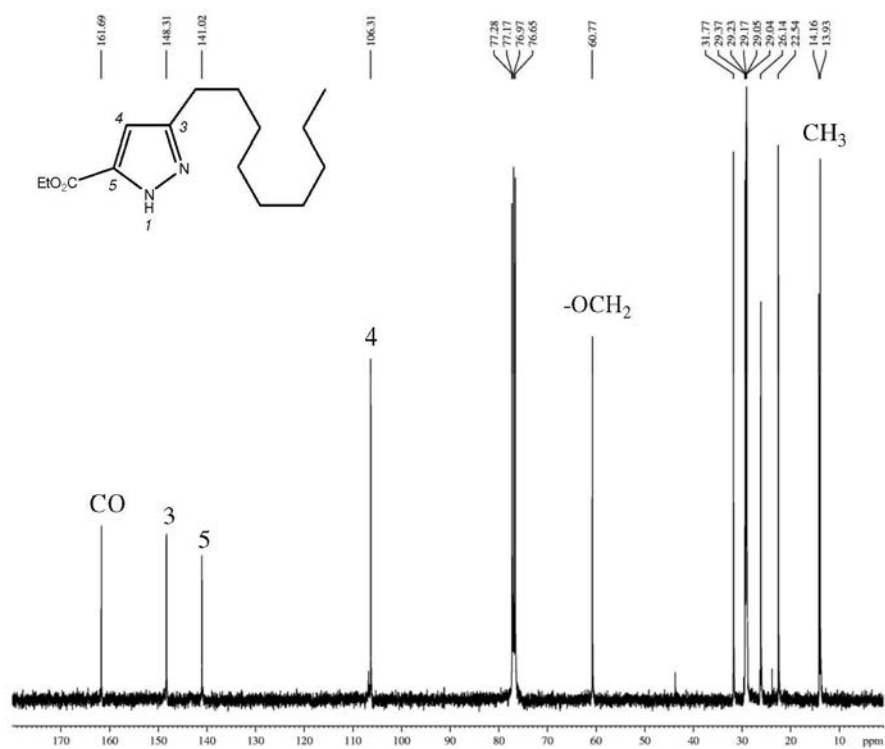


Figure S38. ^{13}C NMR spectrum (100 MHz, CDCl_3) of ethyl 3-nonyl-1*H*-pyrazole-5-carboxylate in CDCl_3 .

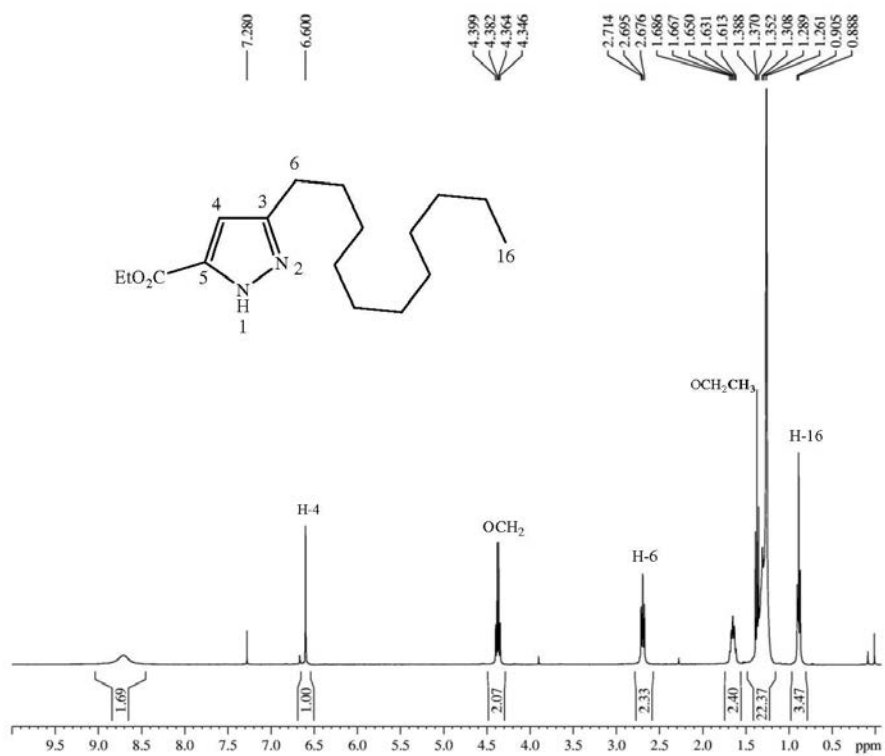


Figure S39. ¹H NMR spectrum (400 MHz, CDCl₃) of ethyl 3-undecyl-1H-pyrazole-5-carboxylate.

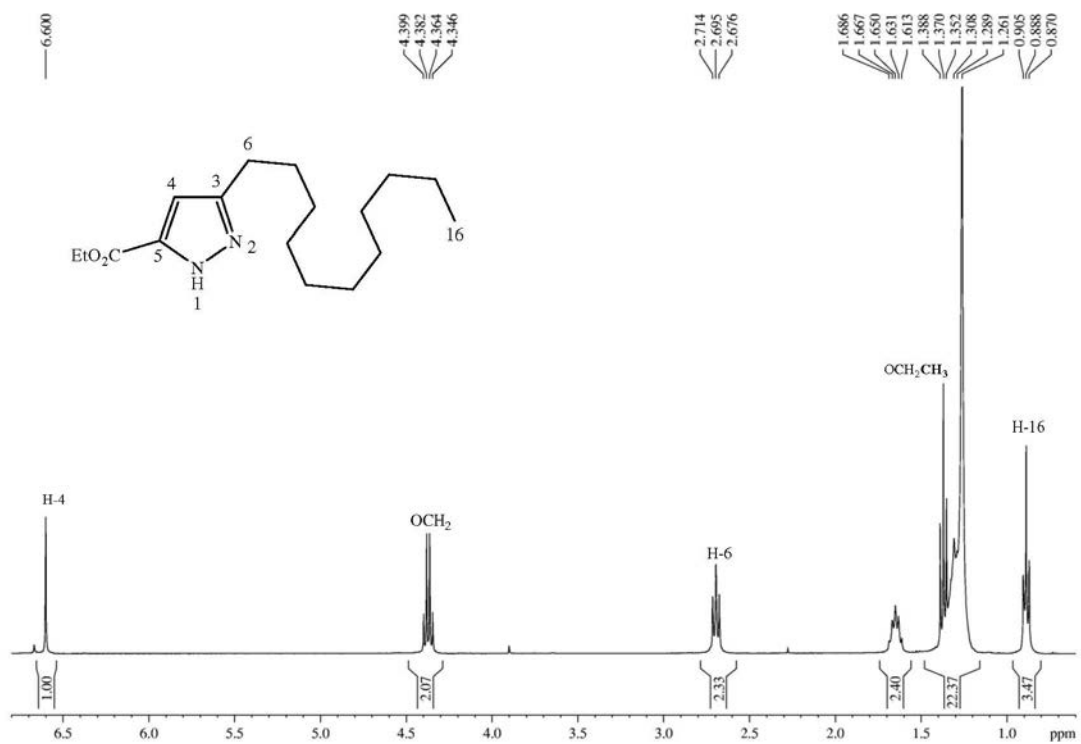


Figure S40. ¹H NMR spectrum (400 MHz, CDCl₃) of ethyl 3-undecyl-1H-pyrazole-5-carboxylate, expanded between 0.5-6.8 ppm.

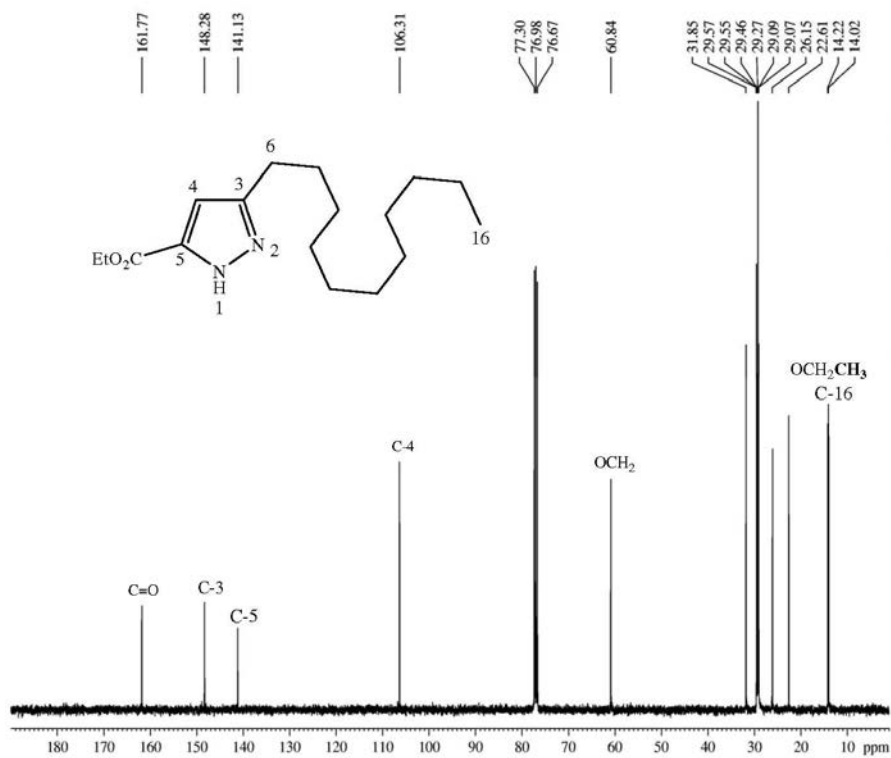


Figure S41. ^{13}C NMR spectrum (100 MHz, CDCl_3) of ethyl 3-undecyl-1*H*-pyrazole-5-carboxylate in CDCl_3 .

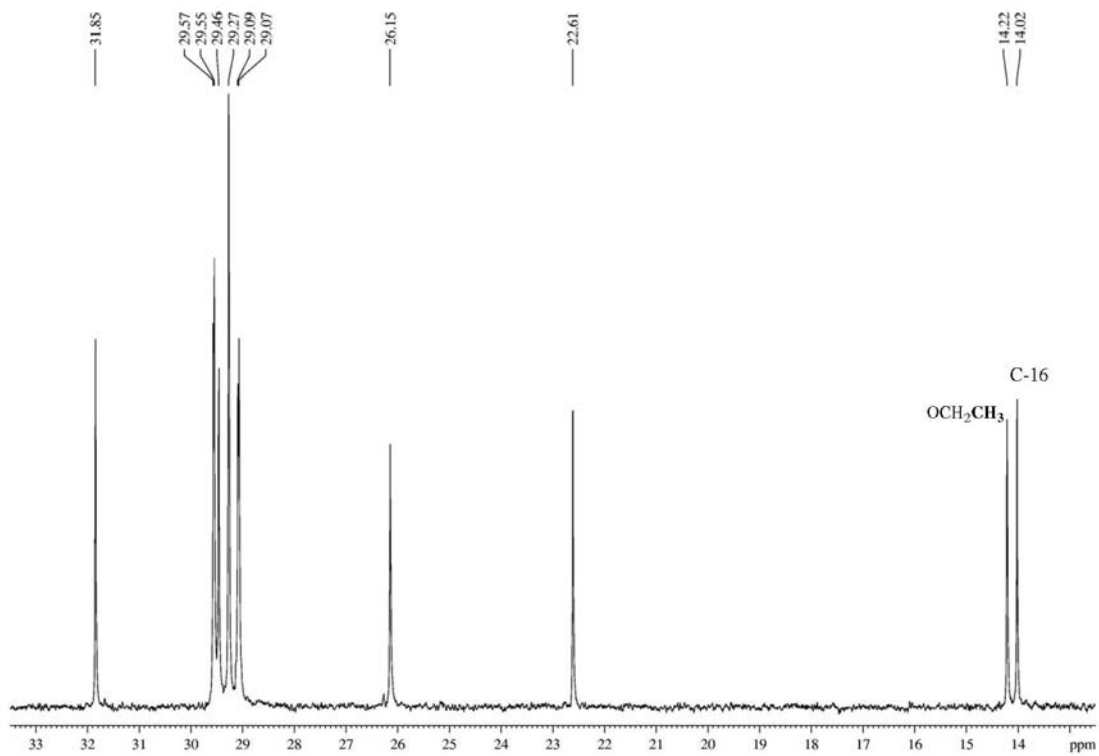


Figure S42. ^{13}C NMR spectrum (100 MHz, CDCl_3) of ethyl 3-undecyl-1*H*-pyrazole-5-carboxylate, expanded between 12.5-33.5 ppm.

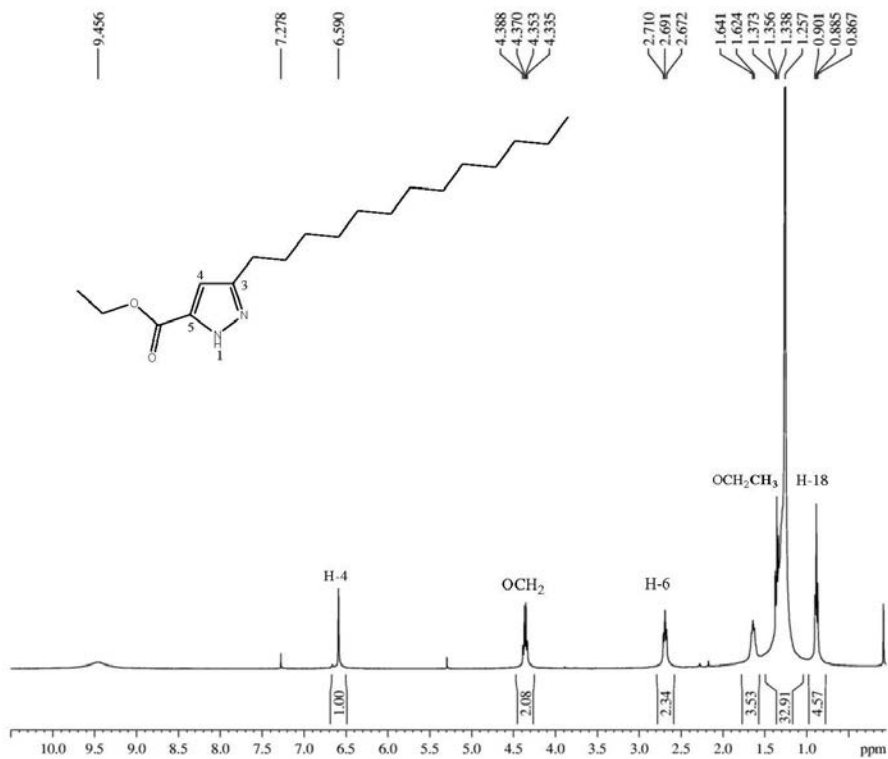


Figure S43. ¹H NMR spectrum (400 MHz, CDCl₃) of ethyl 3-tridecyl-1H-pyrazole-5-carboxylate.

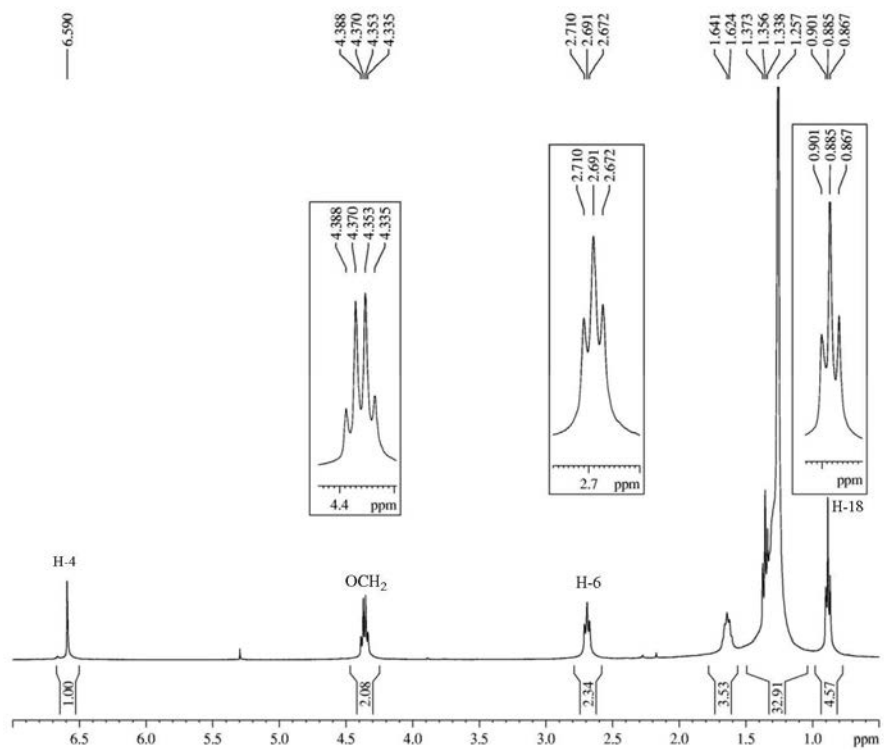


Figure S44. ¹H NMR spectrum (400 MHz, CDCl₃) of ethyl 3-tridecyl-1H-pyrazole-5-carboxylate, expanded between 0.5-7.0 ppm.

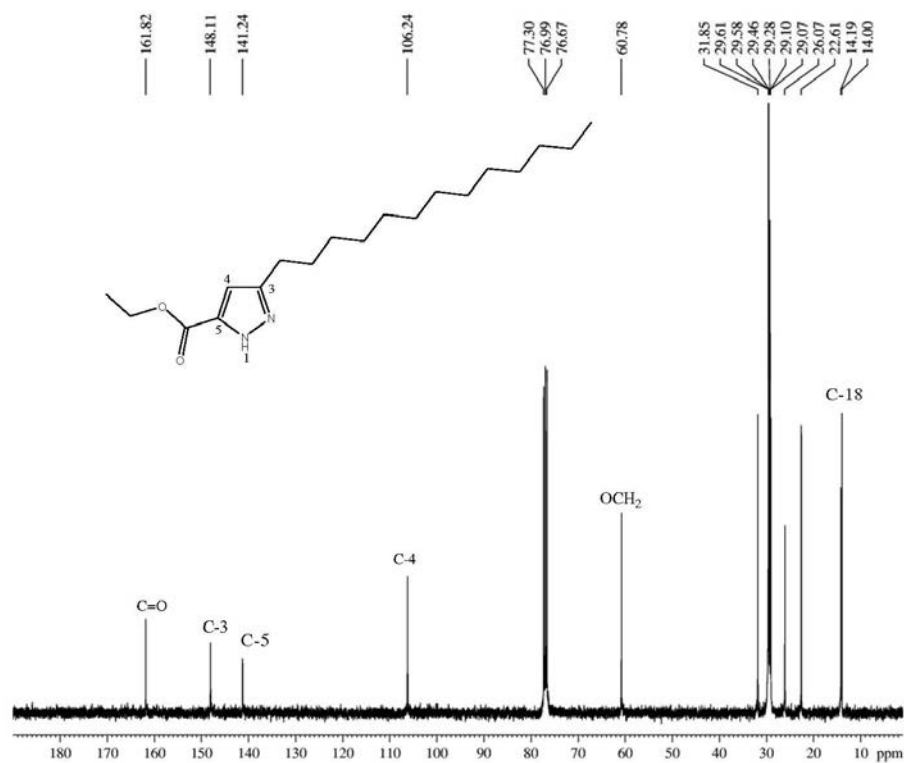


Figure S45. ¹³C NMR spectrum (100 MHz, CDCl₃) of ethyl 3-tridecyl-1*H*-pyrazole-5-carboxylate.

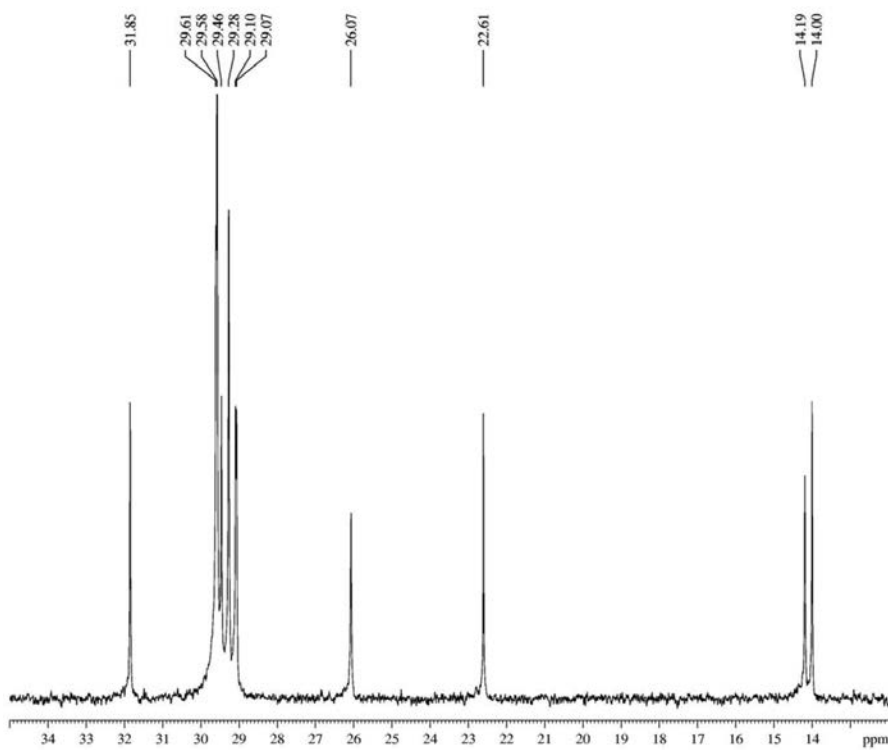


Figure S46. ¹³C NMR spectrum (100 MHz, CDCl₃) of ethyl 3-tridecyl-1*H*-pyrazole-5-carboxylate, expanded between 12-35 ppm.

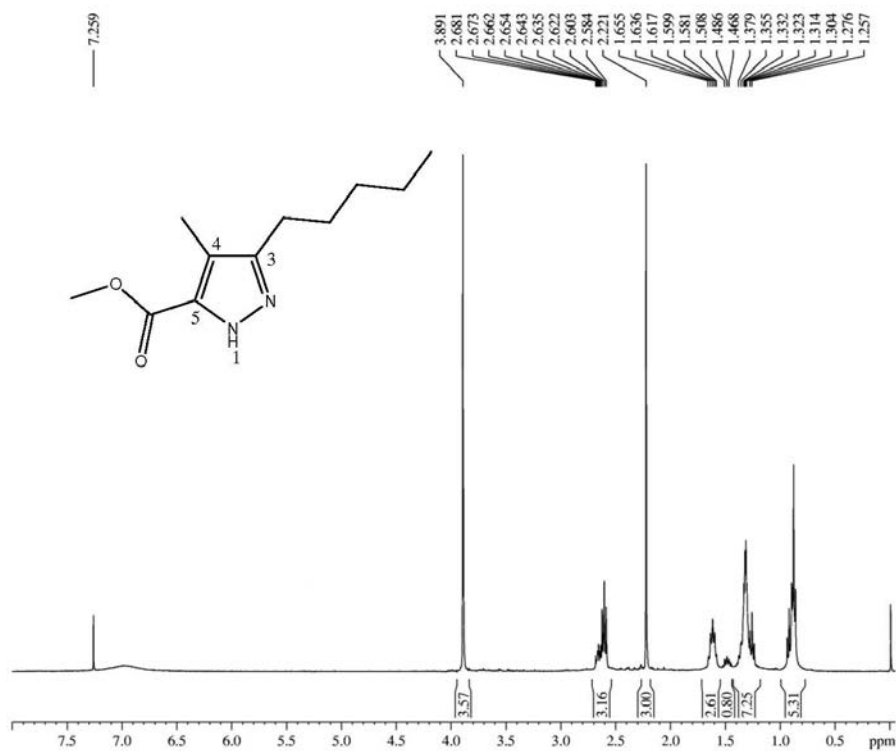


Figure S47. ^1H NMR spectrum (400 MHz, CDCl_3) of methyl 4-methyl-3-pentyl-1H-pyrazole-5-carboxylate + methyl 4-butyl-3-ethyl-1H-pyrazole-5-carboxylate.

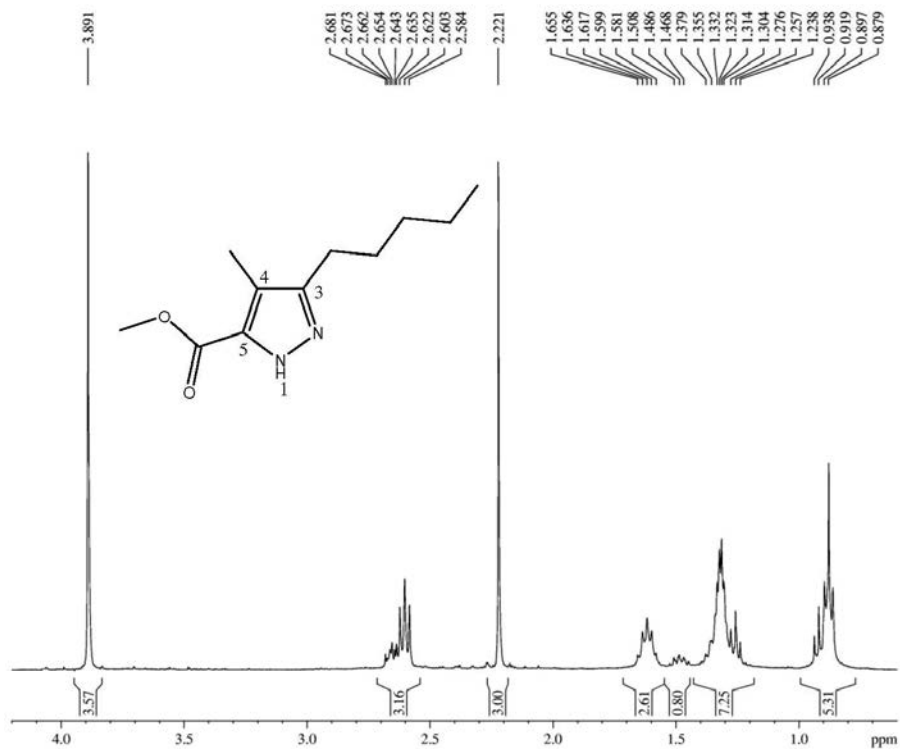


Figure S48. ^1H NMR spectrum (400 MHz, CDCl_3) of methyl 4-methyl-3-pentyl-1H-pyrazole-5-carboxylate + methyl 4-butyl-3-ethyl-1H-pyrazole-5-carboxylate, expanded between 0.6-4.2 ppm.

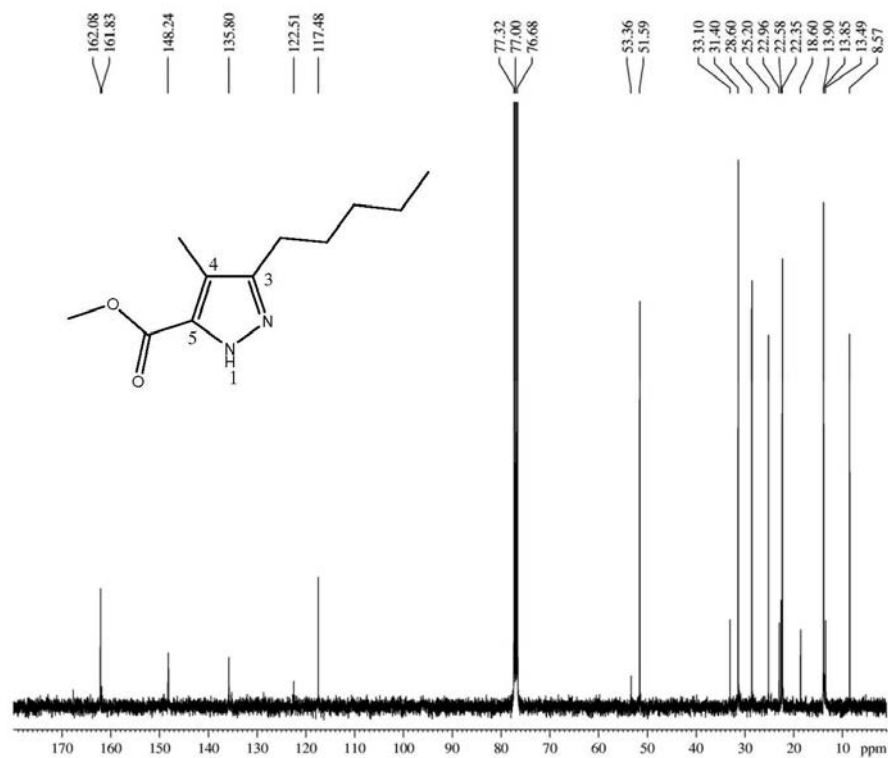


Figure S49. ¹³C NMR spectrum (100 MHz, CDCl₃) of methyl 4-methyl-3-pentyl-1*H*-pyrazole-5-carboxylate + methyl 4-butyl-3-ethyl-1*H*-pyrazole-5-carboxylate.

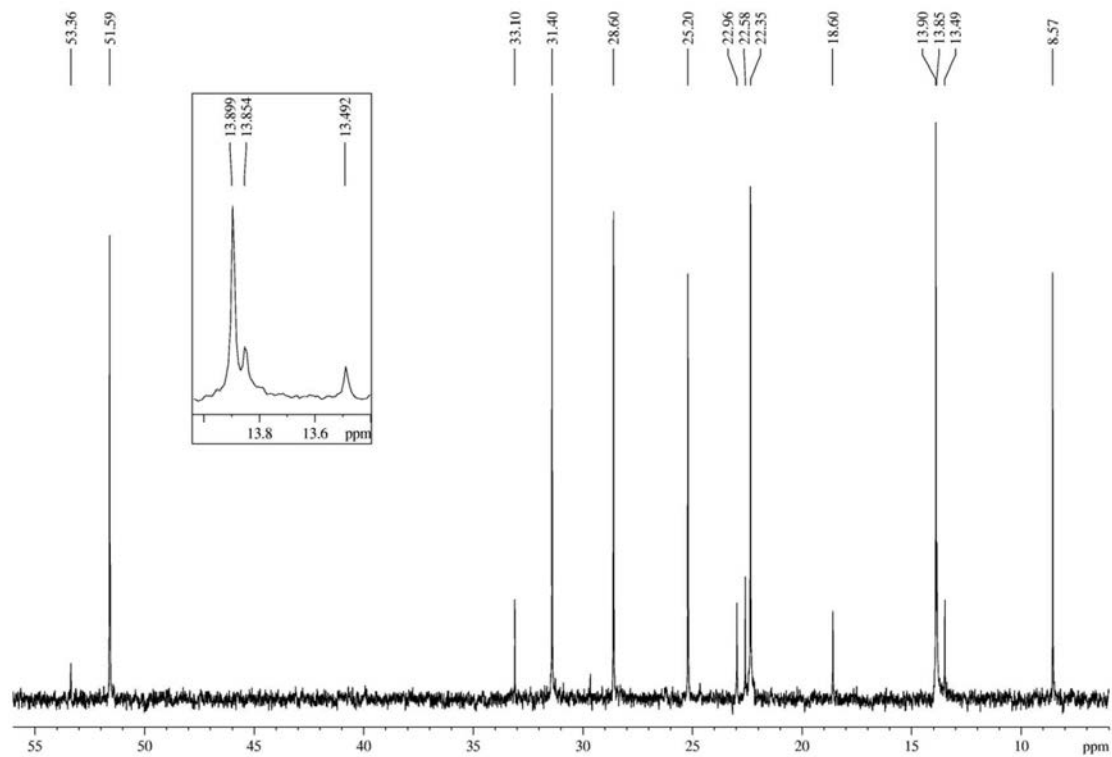


Figure S50. ¹³C NMR spectrum (400 MHz, CDCl₃) of methyl 4-methyl-3-pentyl-1*H*-pyrazole-5-carboxylate + methyl 4-butyl-3-ethyl-1*H*-pyrazole-5-carboxylate, expanded between 6-56 ppm.

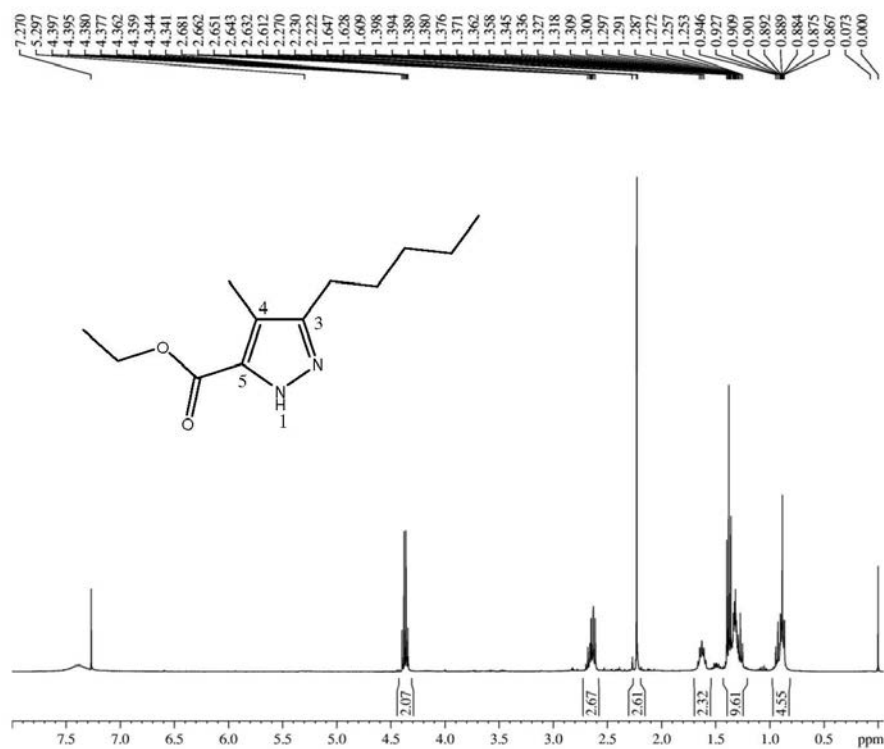


Figure S51. ¹H NMR spectrum (400 MHz, CDCl₃) of ethyl 4-methyl-3-pentyl-1H-pyrazole-5-carboxylate + ethyl 4-butyl-3-ethyl-1H-pyrazole-5-carboxylate.

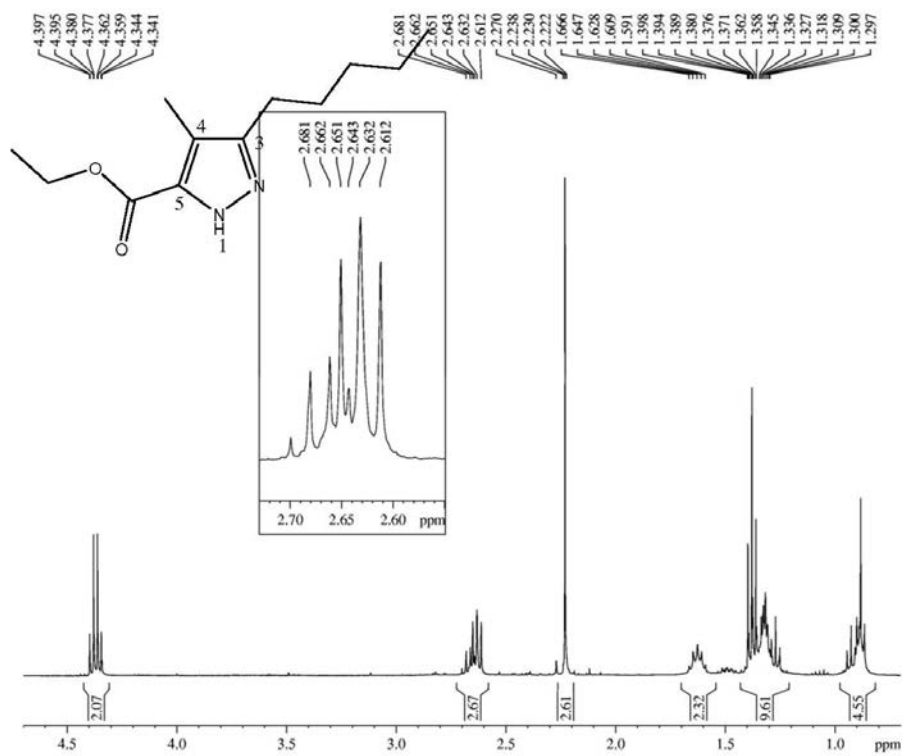


Figure S52. ¹H NMR spectrum (400 MHz, CDCl₃) of ethyl 4-methyl-3-pentyl-1H-pyrazole-5-carboxylate + ethyl 4-butyl-3-ethyl-1H-pyrazole-5-carboxylate, expanded between 0.7- 4.7 ppm.

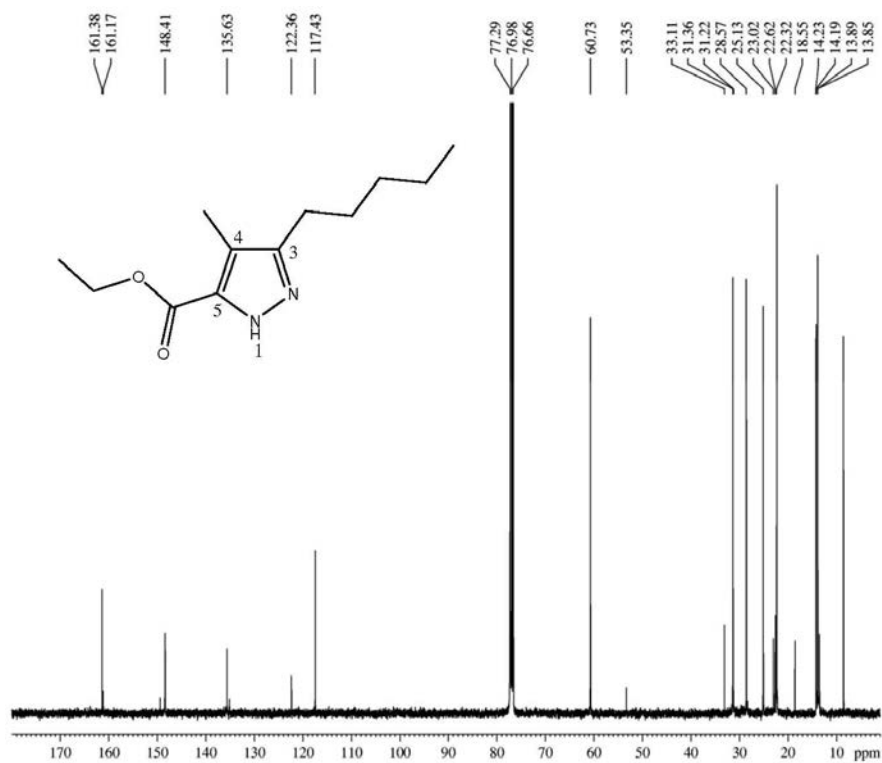


Figure S53. ¹³C NMR spectrum (100 MHz, CDCl₃) of ethyl 4-methyl-3-pentyl-1*H*-pyrazole-5-carboxylate + ethyl 4-butyl-3-ethyl-1*H*-pyrazole-5-carboxylate.

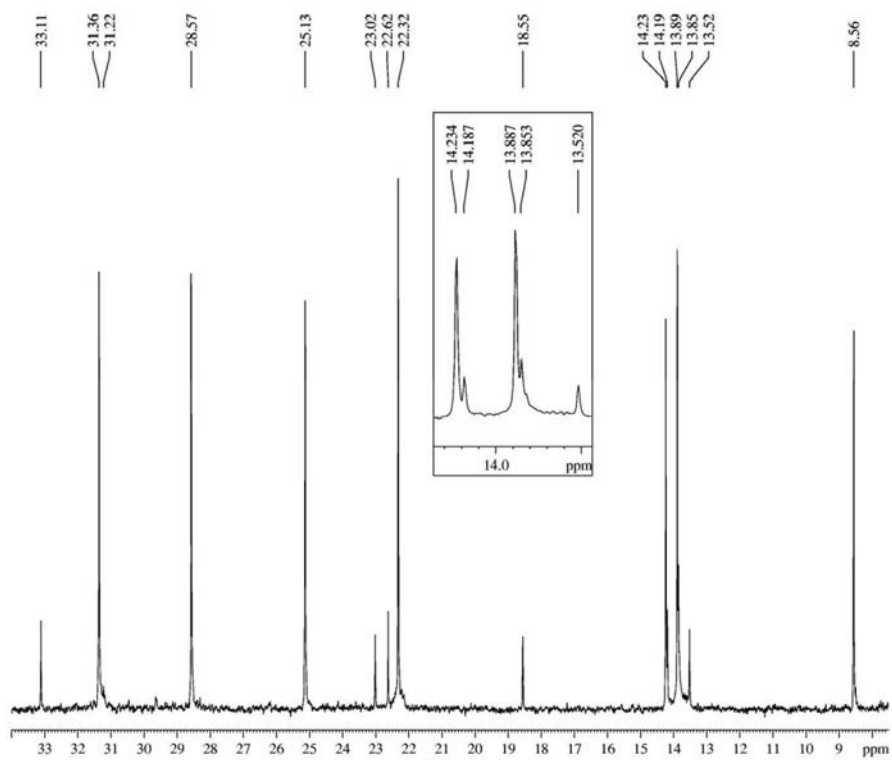


Figure S54. ¹³C NMR spectrum (100 MHz, CDCl₃) of ethyl 4-methyl-3-pentyl-1*H*-pyrazole-5-carboxylate + ethyl 4-butyl-3-ethyl-1*H*-pyrazole-5-carboxylate.

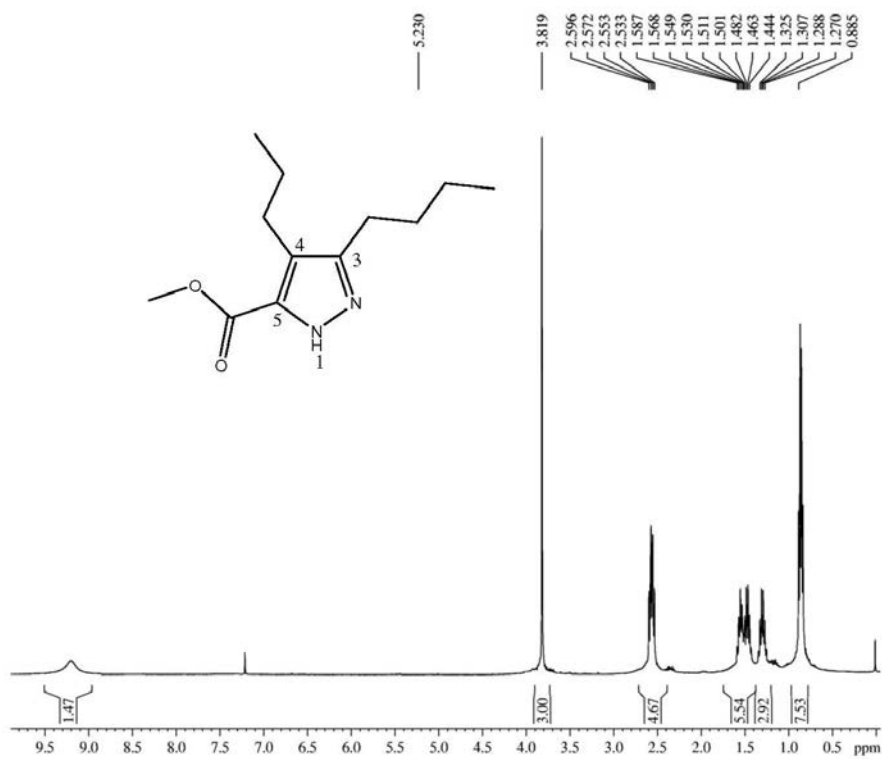


Figure S55. ^1H NMR spectrum (400 MHz, CDCl_3) of methyl 3-butyl-4-propyl-1H-pyrazole-5-carboxylate.

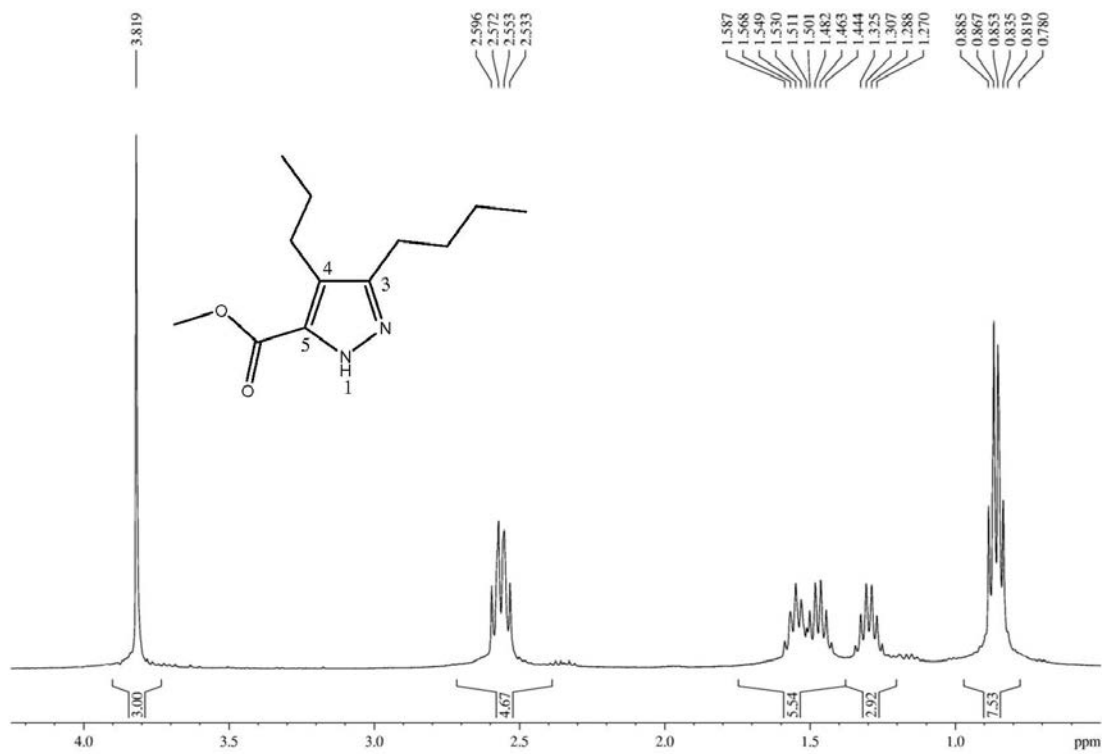


Figure S56. ^1H NMR spectrum (400 MHz, CDCl_3) of methyl 3-butyl-4-propyl-1H-pyrazole-5-carboxylate, expanded between 0.5–4.2 ppm.

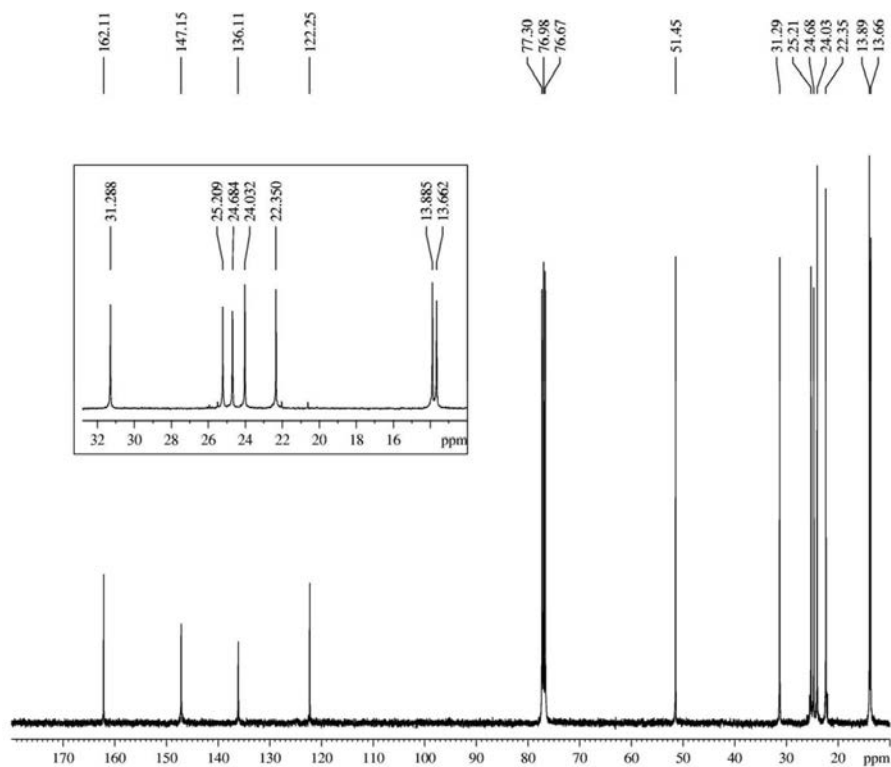


Figure S57. ^{13}C NMR spectrum (100 MHz, CDCl_3) of methyl 3-butyl-4-propyl-1*H*-pyrazole-5-carboxylate in CDCl_3 .

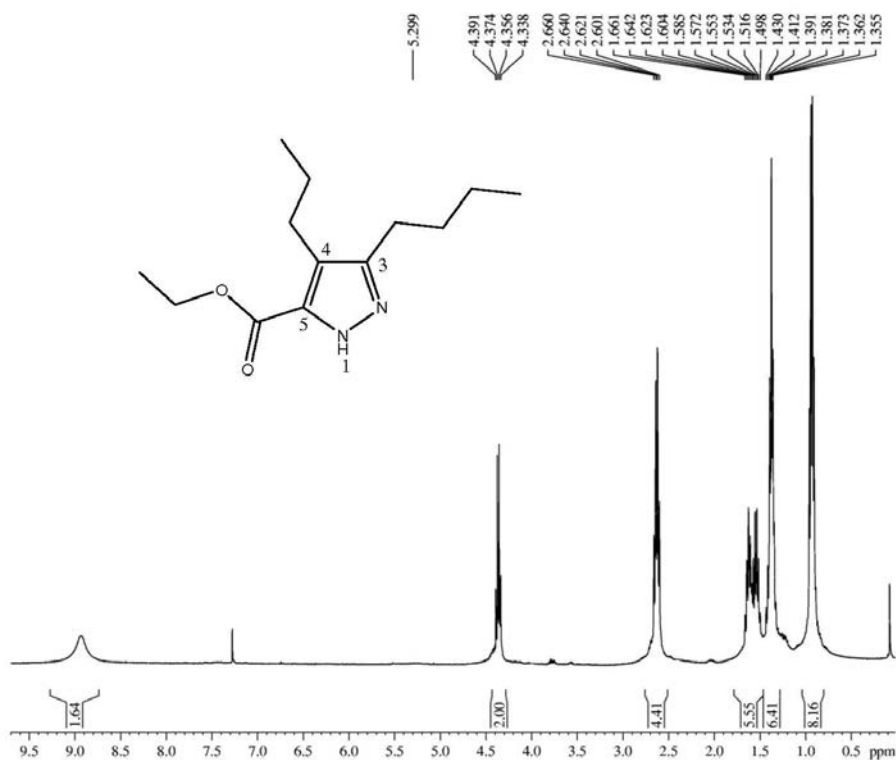


Figure S58. ^1H NMR spectrum (400 MHz, CDCl_3) of ethyl 3-butyl-4-propyl-1*H*-pyrazole-5-carboxylate in CDCl_3 .

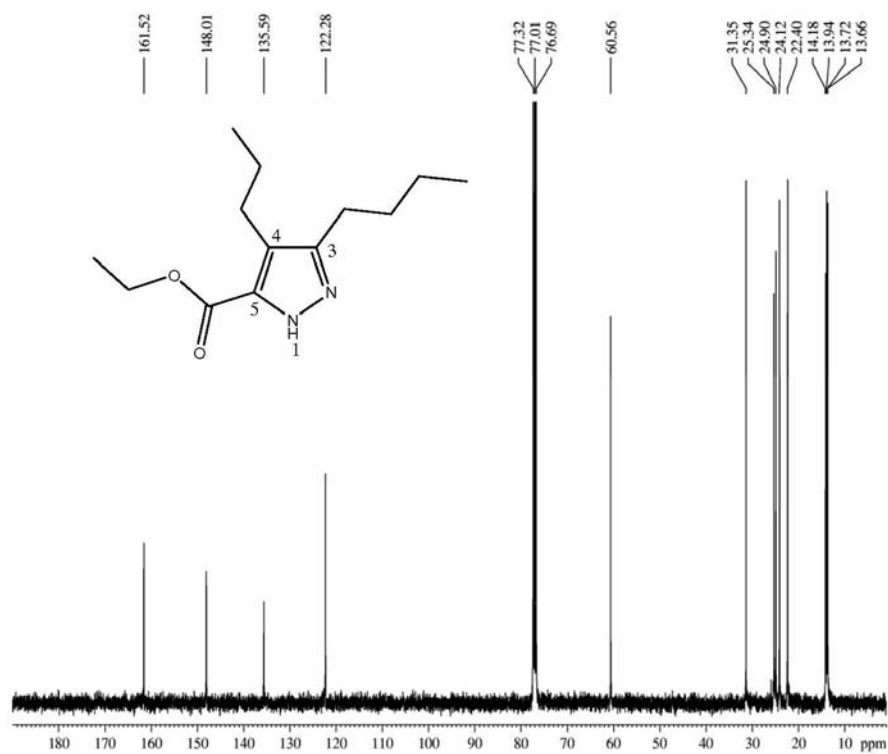


Figure S59. ¹³C NMR spectrum (400 MHz, CDCl₃) of ethyl 3-butyl-4-propyl-1H-pyrazole-5-carboxylate.

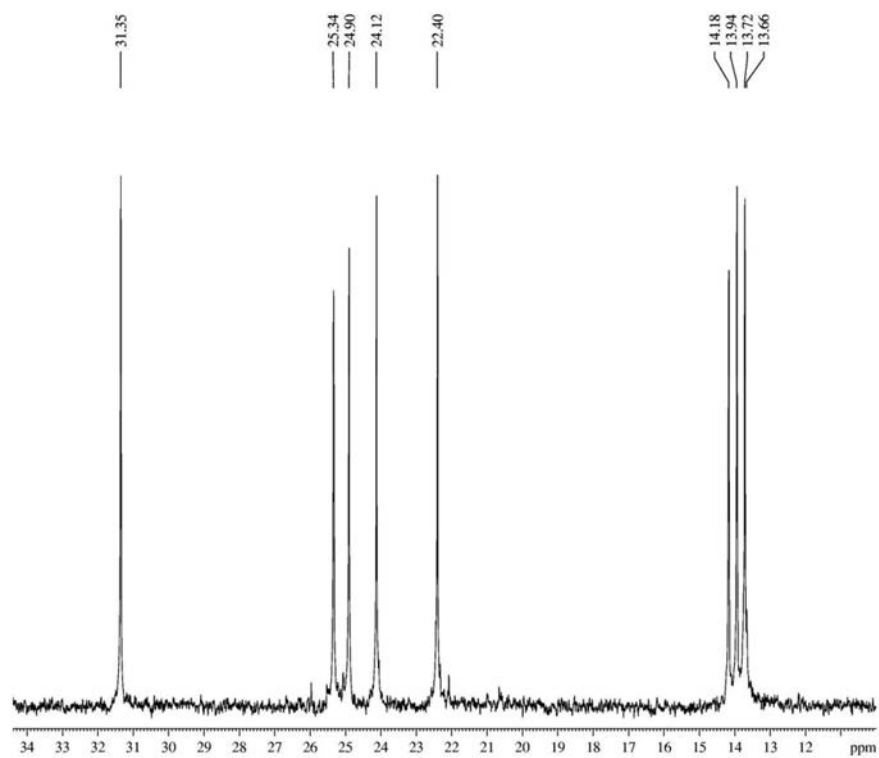


Figure S60. ¹³C NMR spectrum (400 MHz, CDCl₃) of methyl 3-butyl-4-propyl-1H-pyrazole-5-carboxylate, expanded between 10-34 ppm.