**Electronic Supplementary Information**

# Deep Eutectic Solvents: biorenewable reaction media for Au(I)-catalysed cycloisomerisations and one-pot tandem cycloisomerisation/Diels-Alder reactions

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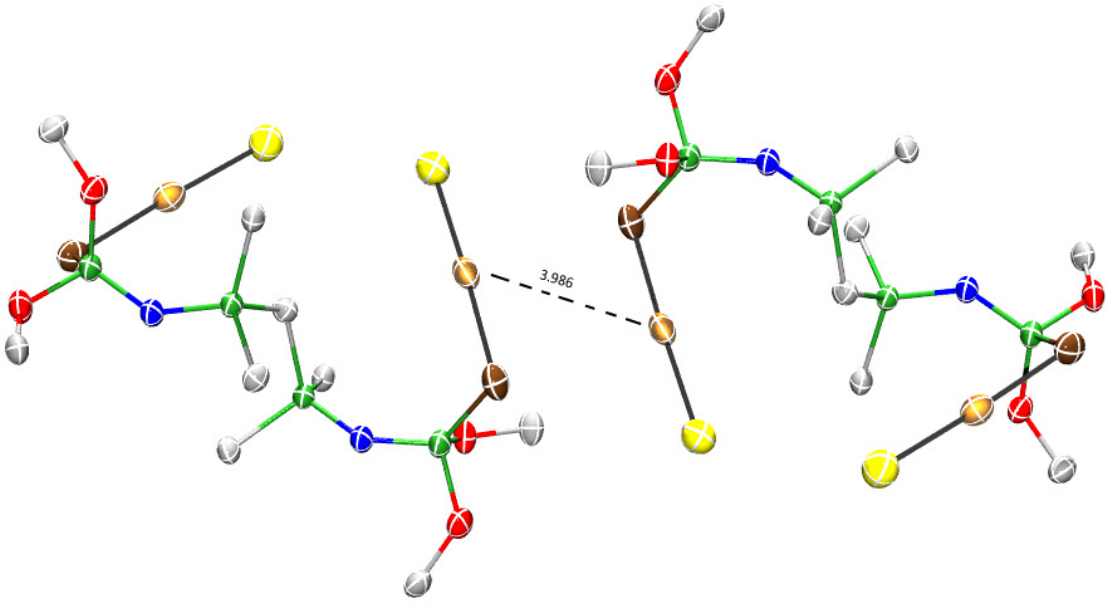



**Figure ESI-1.** Drawing of the crystal structure of complex **3** showing the intermolecular aurophilic Au(I)···Au(I) interaction.

**Crystal data and structure refine for complex 3**

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a saturated solution of complex **3** in dichloromethane. The most relevant crystal and refinement data are collected in Table ESI-1.

Diffraction data were recorded on an Oxford Diffraction Xcalibur Nova (Agilent) single crystal diffractometer, using Cu-Kα radiation (λ= 1.5418 Å). Images were collected at a 63 mm fixed crystal-detector distance, using the oscillation method, with 1º oscillation and variable exposure time per image (2-8 s). Data collection strategy was calculated with the program CryAlis Pro CCD.[1] Data reduction and cell refinement were performed with the programs CryAlis Pro RED.[1] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm as implemented in the program CrysAlis Pro RED.[1]

The software package WINGX[2] was used for space group determination, structure solution and refinement. The structure was solved by direct methods using SHELXL97.[3]

Isotropic least-squares refinement on $F^2$ using SHELXL97 was performed.[3] During the final stages of the refinements, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. The H atoms were

geometrically located and their coordinates were refined riding on their parent atoms. The maximum residual electron density is located near to heavy atoms.

The function minimized was $([\Sigma wF_o^2 - F_c^2)/\Sigma w(F_o^2)]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ (a and b values are collected in Table ESI-1) with $\sigma^2(F_o^2)$ from counting statistics and $P = (Max(F_o^2, 0) + 2F_c^2)/3$.

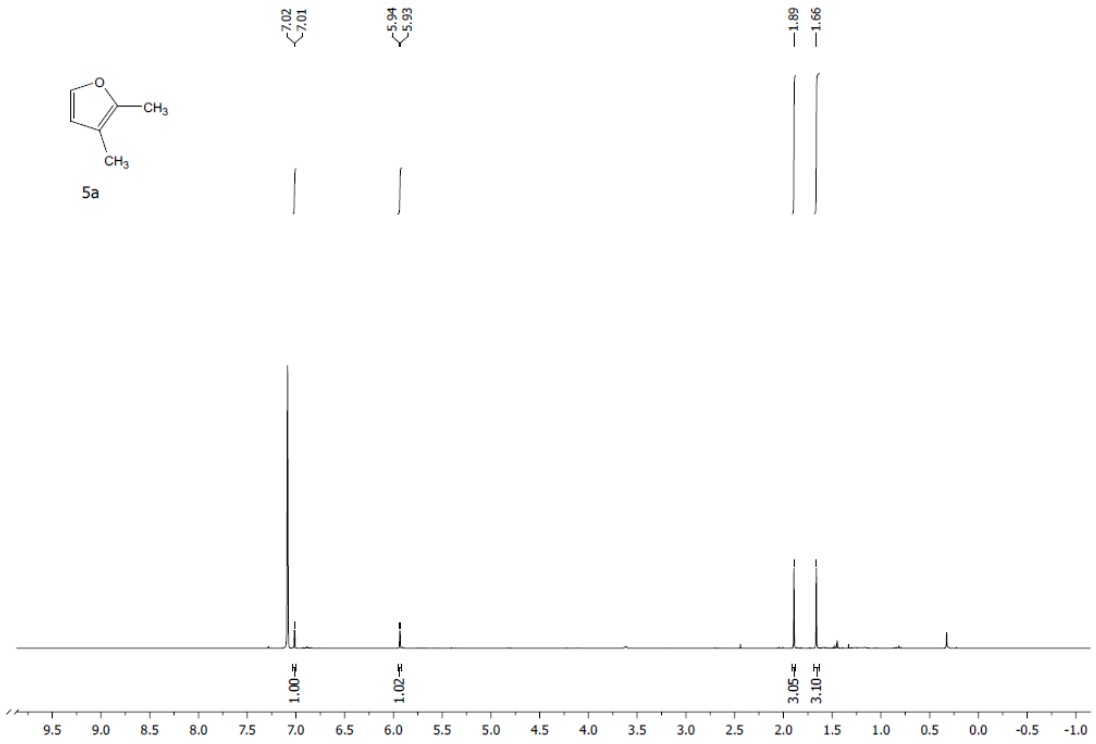
Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[4] The crystallographic plots were made with ORTEP.[5]

**Table ESI-1** Crystal data and structure refine for compound **3**

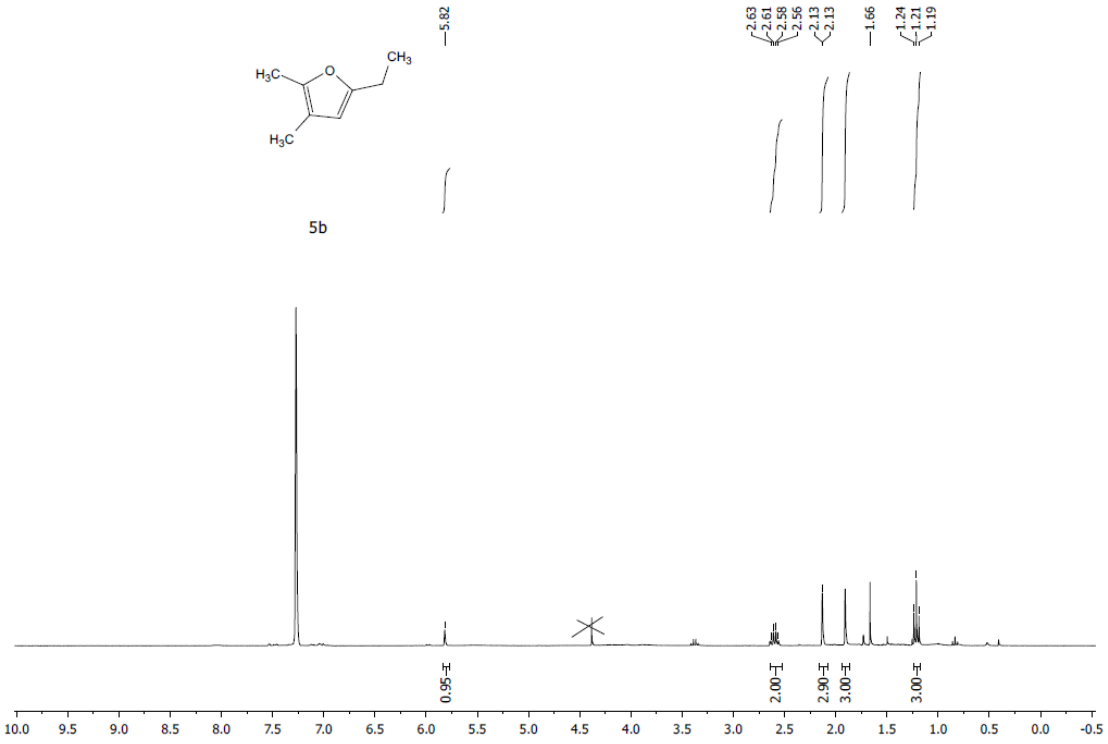
| | **3** |
|---|---|
| Empirical formula | $C_{49}H_{42}Au_2Cl_2N_2O_4P_4S_2$ |
| Formula weight | 1375.37 |
| Temperature/K | 297(4) |
| Wavelength/Å | 1.54180 |
| Crystal system | monoclinic |
| Space group | $C2/_c$ |
| *a*/Å; $\alpha$/º | 25.848(2); 90.0 |
| *b*/Å; $\beta$/º | 1.2564(5); 122.413(11) |
| *c*/Å; $\gamma$/ | 20.6909(16); 90.0 |
| *Z* | 4 |
| Volume/Å$^3$ | 5082.2(6) |
| Calculated density/Mg m$^{-3}$ | 1.494 |
| $\mu$/mm$^{-1}$ | 8.23 |
| *F*(000) | 2279 |
| Crystal size/mm | 0.04 x 0.08 x 0.31 |
| $\theta$ range/º | 43.15 to 94.50 |
| Index ranges | $-25 \leq h \leq 31$<br>$-9 \leq k \leq 13$<br>$-25 \leq l \leq 18$ |
| No. of reflns. collected | 12034 |
| No. of unique reflns. | 4673 [(R(int) = 0.0352] |
| Completeness to $\theta_{max}$ | 97.6 |
| No. of parameters/restraints | 298/0 |
| Goodness-of-fit on $F^2$ | 1.129 |
| Weight function (a, b) | 0.0544, 24.1639 |
| $R_1$ $[I > 2\sigma(I)]^a$ | 0.0428 |
| $wR_2$ $[I > 2\sigma(I)]^a$ | 0.1171 |
| Largest diff. peak and hole/e Å$^{-3}$ | 0.970 and -1.960 |

[a] $R_1 == \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$: $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$

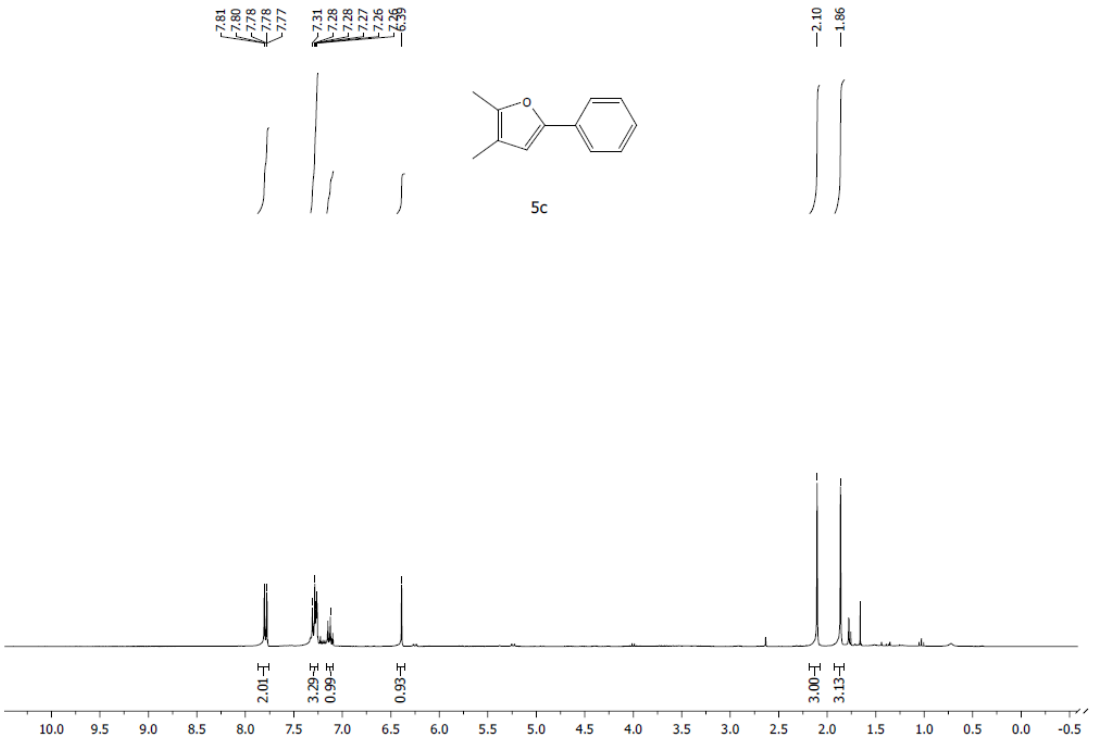
## 2,3-dimethylfuran (5a)



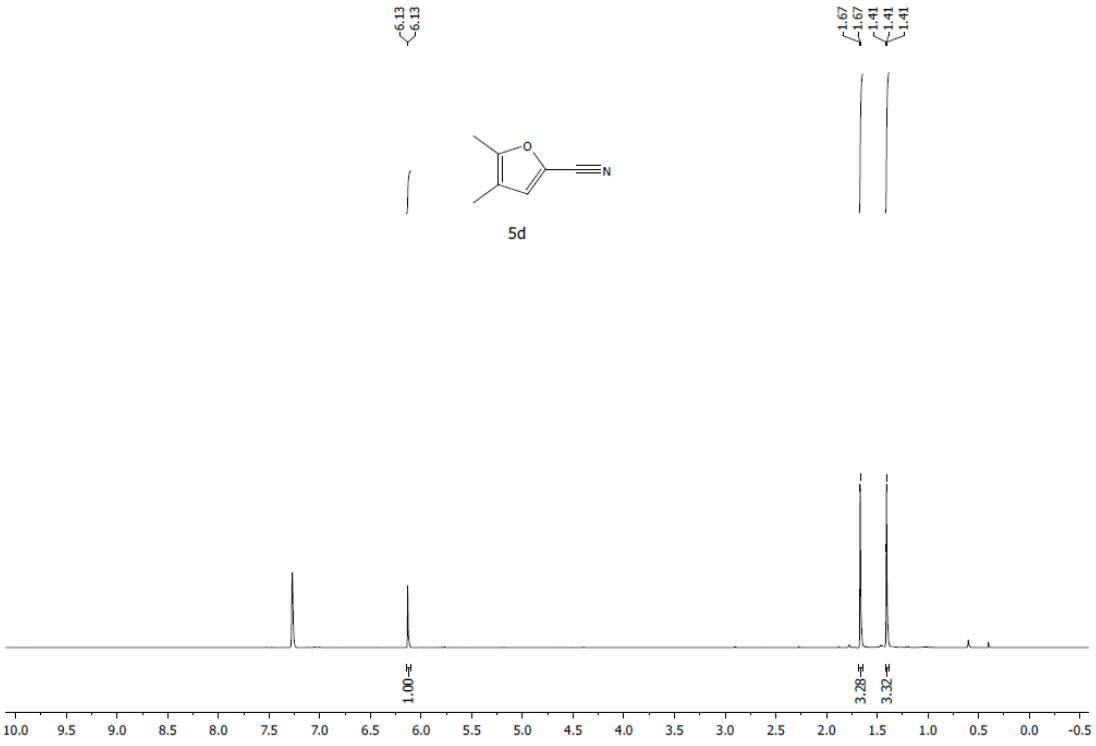

## 5-ethyl-2,3-dimethylfuran (5b)



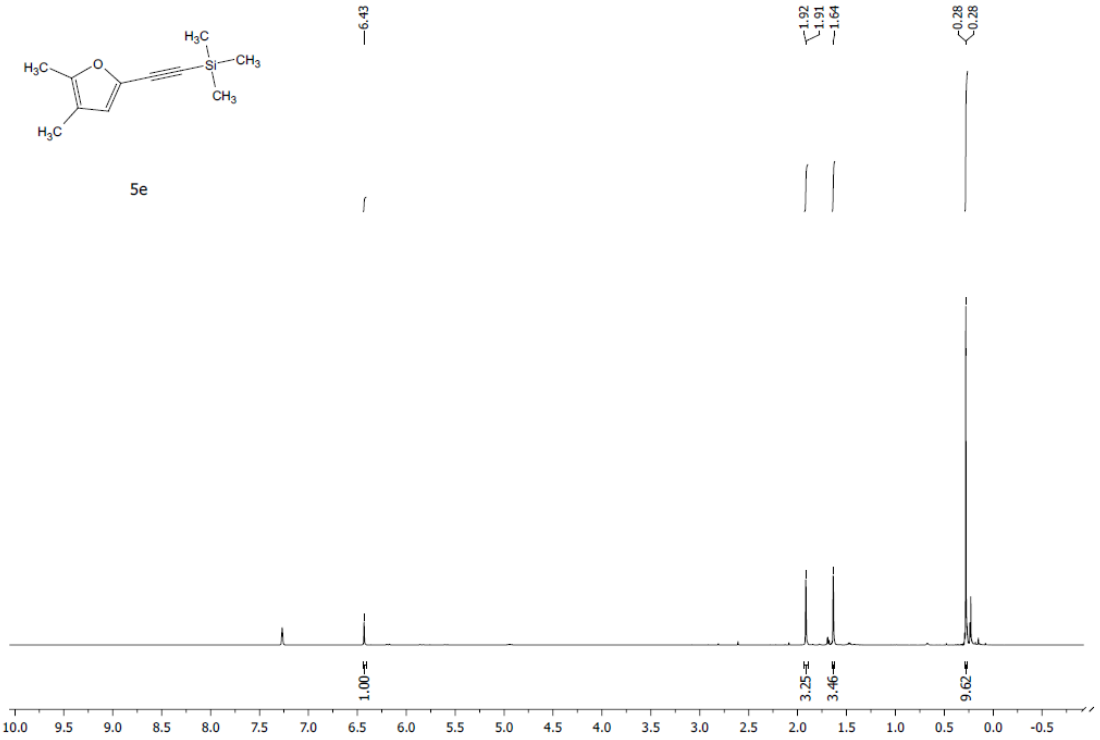
## 5-phenyl-2,3-dimethylfuran (5c)



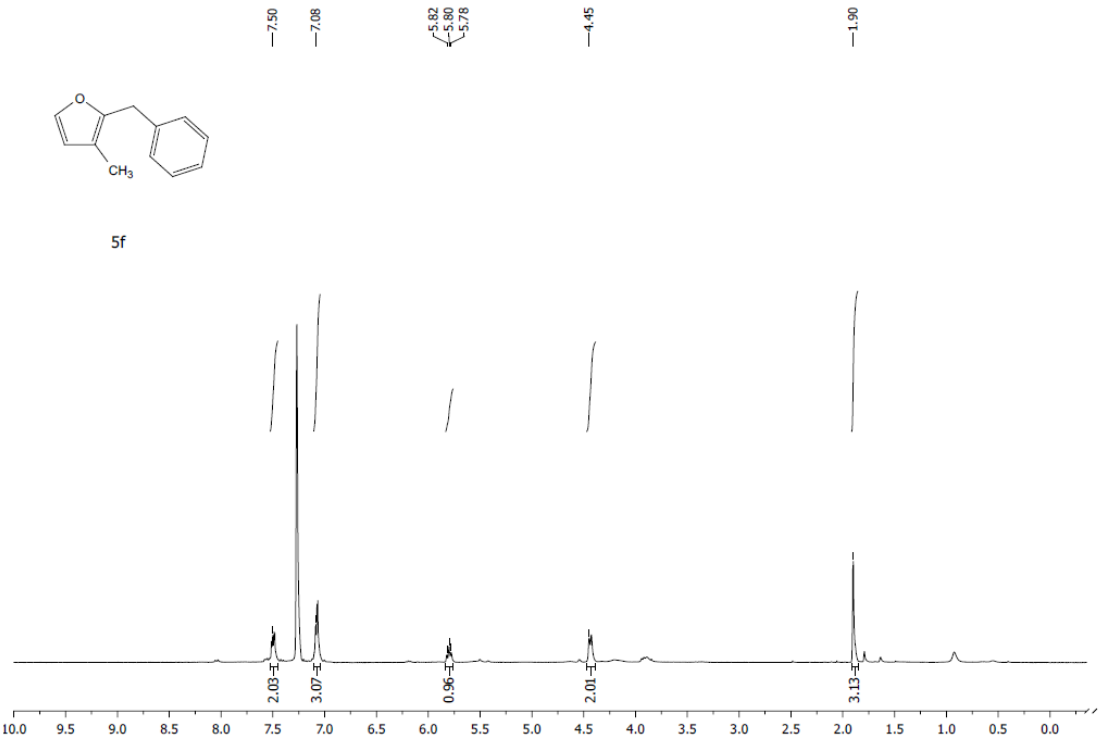

## 4,5-dimethylfuran-2-carbonitrile (5d)



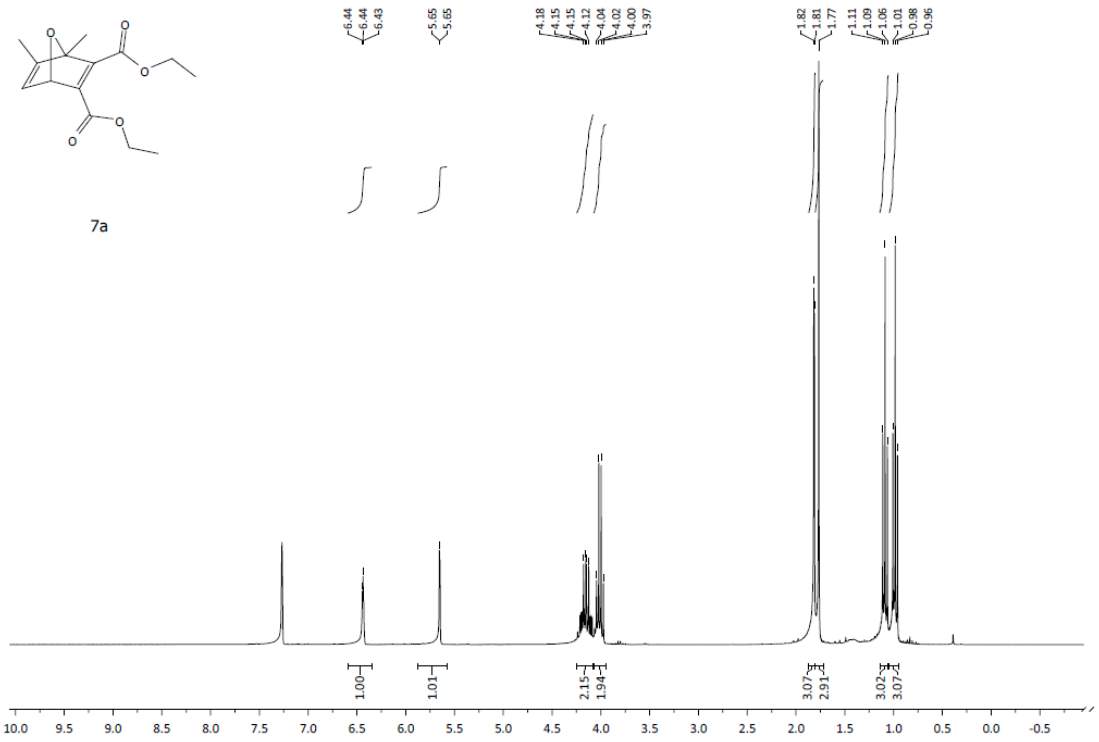
## ((4,5-dimethylfuran-2-yl)ethynyl)trimethylsilane (5e)



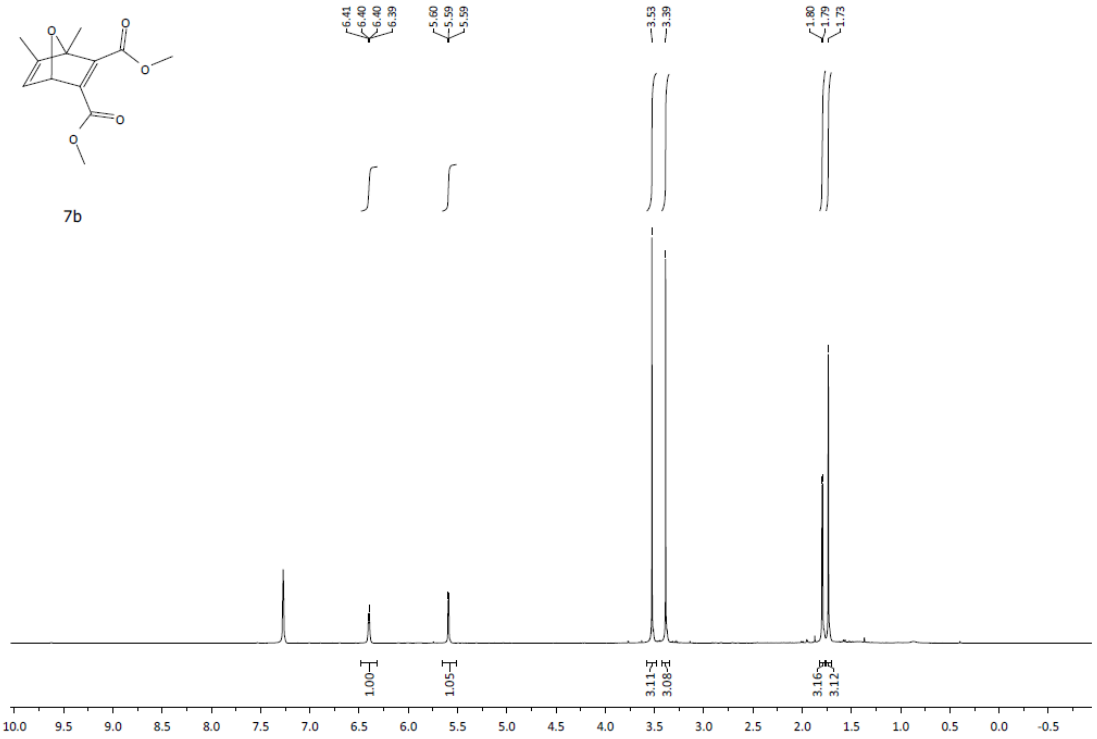

## 2-benzyl-3-methylfuran (5f)



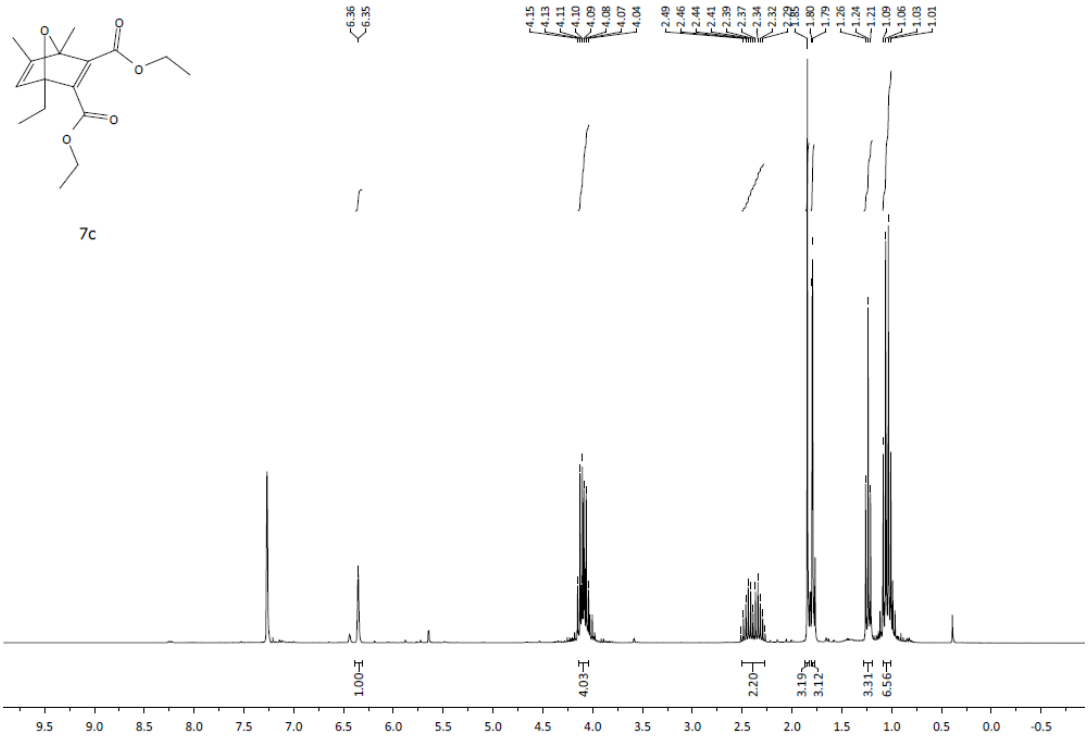
**Diethyl 1,6-dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (7a)**



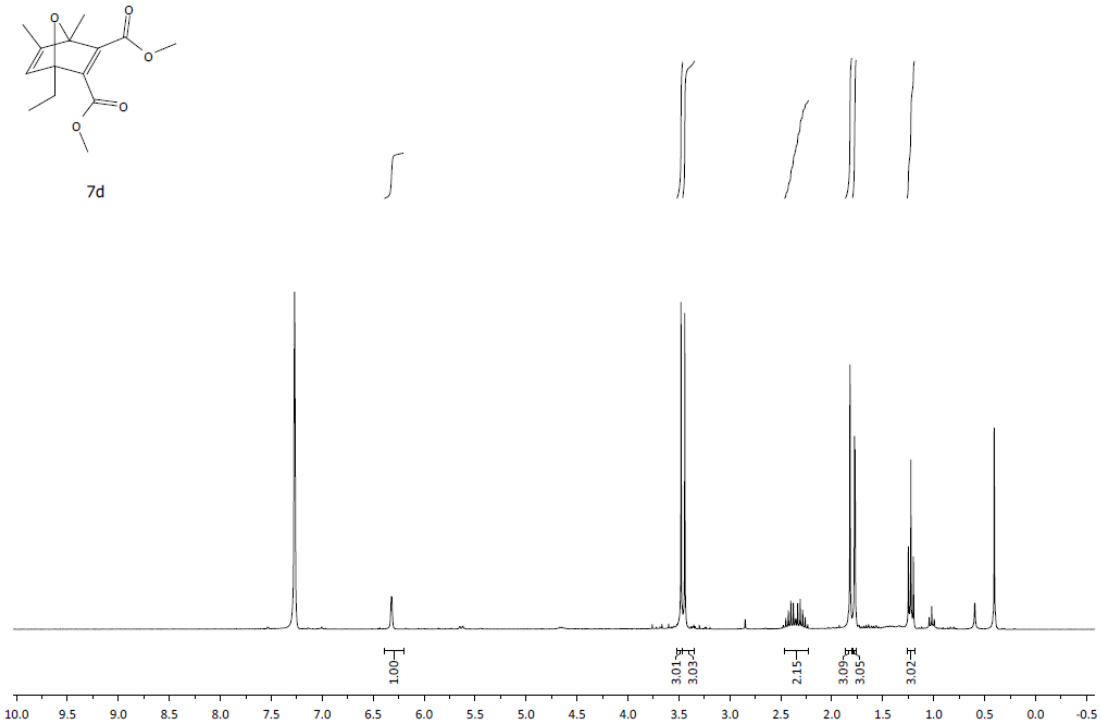

**Dimethyl 1,6-dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (7b)**



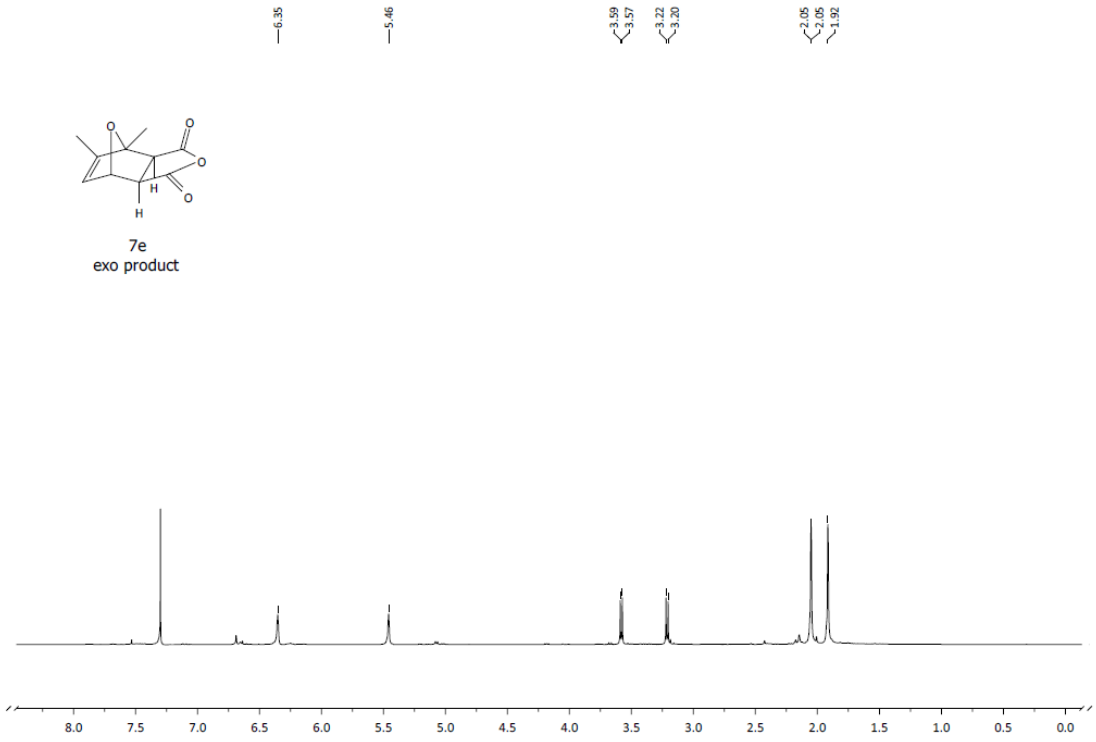
**Diethyl 1-ethyl-4,5-dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (7c)**

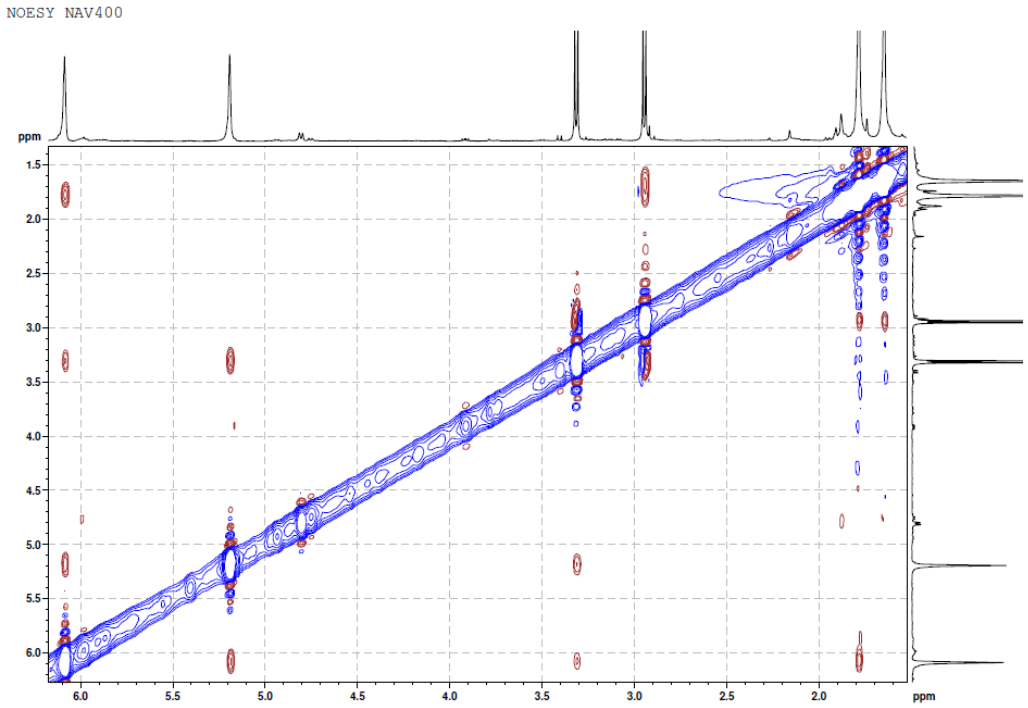



**Dimethyl 1-ethyl-4,5-dimethyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (7d)**

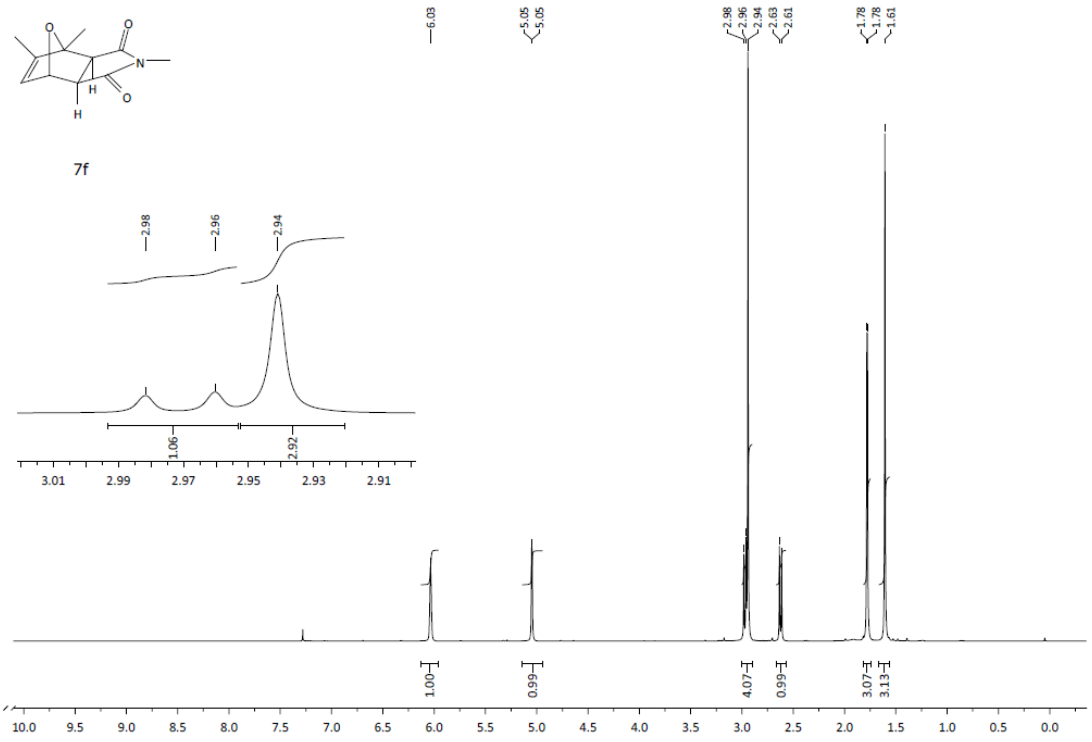


**4,5-dimethyl-3a,4,7,7a-tetrahydro-4,7-epoxyisobenzofuran-1,3-dione (7e)**



**2,4,5-trimethyl-3a,4,7,7a-tetrahydro-1H-4,7-epoxyisoindole-1,3(2H)-dione (7f)**




## References

(1) *CrysAlis*$^{Pro}$ *CCD, CrysAlis*$^{Pro}$ *RED,* Oxford Diffraction Ltd., Abingdon, Oxfordshire, U.K., 2008.

(2) L. J. Farrugia, *J. Appl. Crystallogr.,* 2012, **45**, 849.

(3) G. M. Sheldrick, *SHELXL97: Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen, Germany, 1997.

(4) *Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, U.K., 1974, *Vol. IV* (present distributor: Kluwer Academic Publishers, Dordrecht, The Netherlands).

(5) L. J. Farrugia, *J. Appl. Crystallogr.,* 1997, **30**, 565.