Electronic Supplementary Information

Insertion Reactions of NH_3 and H_2O with the Ferriogermylenes $ArGeFeCp(CO)_2$ (Ar = Ar^{Me6} ($–C_6H_3$-$(C_6H_2$-2,4,6-$Me_3)_2$) or Ar^{iPr4} ($–C_6H_3$-$(C_6H_3$-2,6-$^iPr_2)_2$); Cp = η^5-C_5H_5): Structural Isomerism and Polymorphism in a Metallogermylene

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X-ray Crystallography

Crystals of **1a**, **2ab**, and **3** were removed from a Schlenk flask under a stream of nitrogen and immediately covered with a layer of hydrocarbon oil. A suitable crystal was selected, attached to a glass fiber on a copper pin and quickly placed in the cold N_2 stream on the diffractometer. Data was collected at 100 K on a Bruker APEX DUO diffractometer with Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were applied using SADABS.[S1] The crystal structures were solved by direct methods and refined by full matrix least-squares procedures in SHELXTL.[S2] All non-H atoms were refined anisotropically.

Table S1. Selected X-ray Crystallographic data for **1a**: green, red, and dichroic polymorphs

1a polymorph	**green**	**red**	**dichroic**
formula		$C_{31}H_{30}FeGeO_2$	
fw		562.99	
color, habit	green, block	red, block	green & red, plate
space group	*$P2_1/c$*	*$P2_1/c$*	*P-1*
***a*, å**	15.7808(7)	16.2036(3)	8.915(3)
***b*, å**	9.6448(4)	8.8948(2)	16.229(6)
***c*, å**	16.9149(8)	37.0650(8)	18.739(7)
***α*, °**	90	90	76.499(10)
***β*, °**	90.657(2)	101.5790(10)	86.019(10)
***γ*, °**	90	90	89.859(11)
***V*, å^3**	2574.3(2)	5233.38(19)	2629.7(16)
Z	4	8	4
crystal size, mm	0.149 × 0.113 × 0.039	0.383 × 0.192 × 0.183	0.233 × 0.203 × 0.075
d_{calc}, g cm^{-3}	1.453	1.429	1.442
abs. μ, mm^{-1}	1.757	1.729	1.721
***2θ*, °**	4.816 to 55.064	2.566 to 57.542	3.794 to 55.634
R(int)	0.0419	0.0497	0.2672
obs. reflns. [I>2σ(I)]	5928	13458	155382
data/restraints/parameters	5928/0/322	13458/0/644	12237/0/643
***R_1*, obsd. reflns.**	0.0400	0.0503	0.1063

Table S2. Selected X-ray Crystallographic data for 2-3.

compound	2a	2b	3
formula	$C_{31}H_{33}FeGeNO_2$	$C_{37}H_{45}FeGeNO_2$	$C_{31}H_{32}FeGeO_3$
fw	580.02	664.18	581.00
color, habit	colorless, block	colorless, block	colorless, block
space group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
***a*, å**	11.2499(2)	8.1224(4)	15.7736(14)
***b*, å**	14.6309(2)	18.5737(9)	9.8287(9)
***c*, å**	16.4228(3)	22.0779(11)	17.272(2)
***α*, °**	90	90	90
***β*, °**	96.4474(6)	90	90.304(10)
***γ*, °**	90	90	90
***V*, å^3**	2686.03(8)	3330.7(3)	2677.7(5)
Z	4	4	4
crystal size, mm	0.357 × 0.257 × 0.168	0.365 × 0.269 × 0.241	0.558 × 0.48 × 0.408
d_{calc}, g cm^{-3}	1.434	1.325	1.441
abs. μ, mm^{-1}	5.924	1.370	1.695
***2θ*, °**	8.116 to 137.16	4.292 to 61.262	4.768 to 59.998
R(int)	0.0277	0.0378	0.0149
obs. reflns. [I>2σ(I)]	4902	10275	7798
data/restraints/parameters	4902/0/457	10275/58/463	7798/8/350
***R*$_1$, obsd. reflns.**	0.0277	0.0378	0.0328

Figure S1. Photograph of **1a**, green polymorph

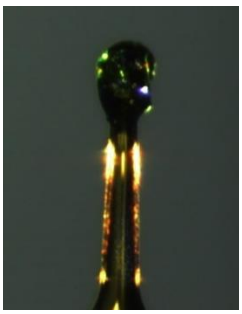


Figure S2. Photograph of **1a**, red polymorph.

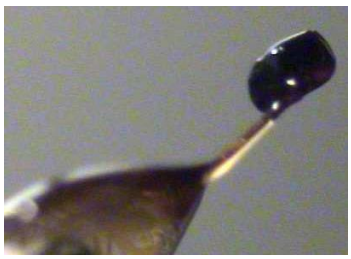
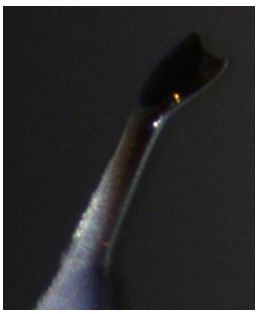
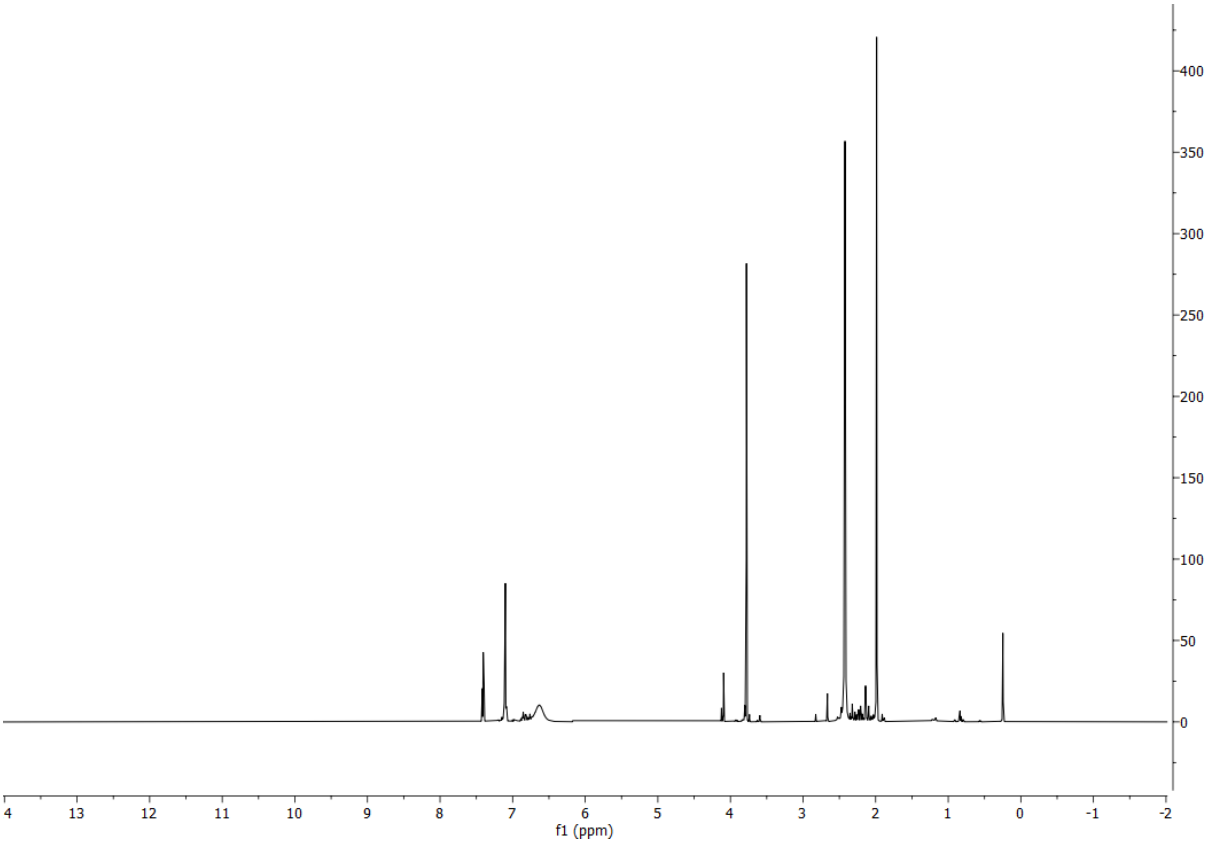


Figure S3. Photograph of **1a**, red-green dichroic polymorph.



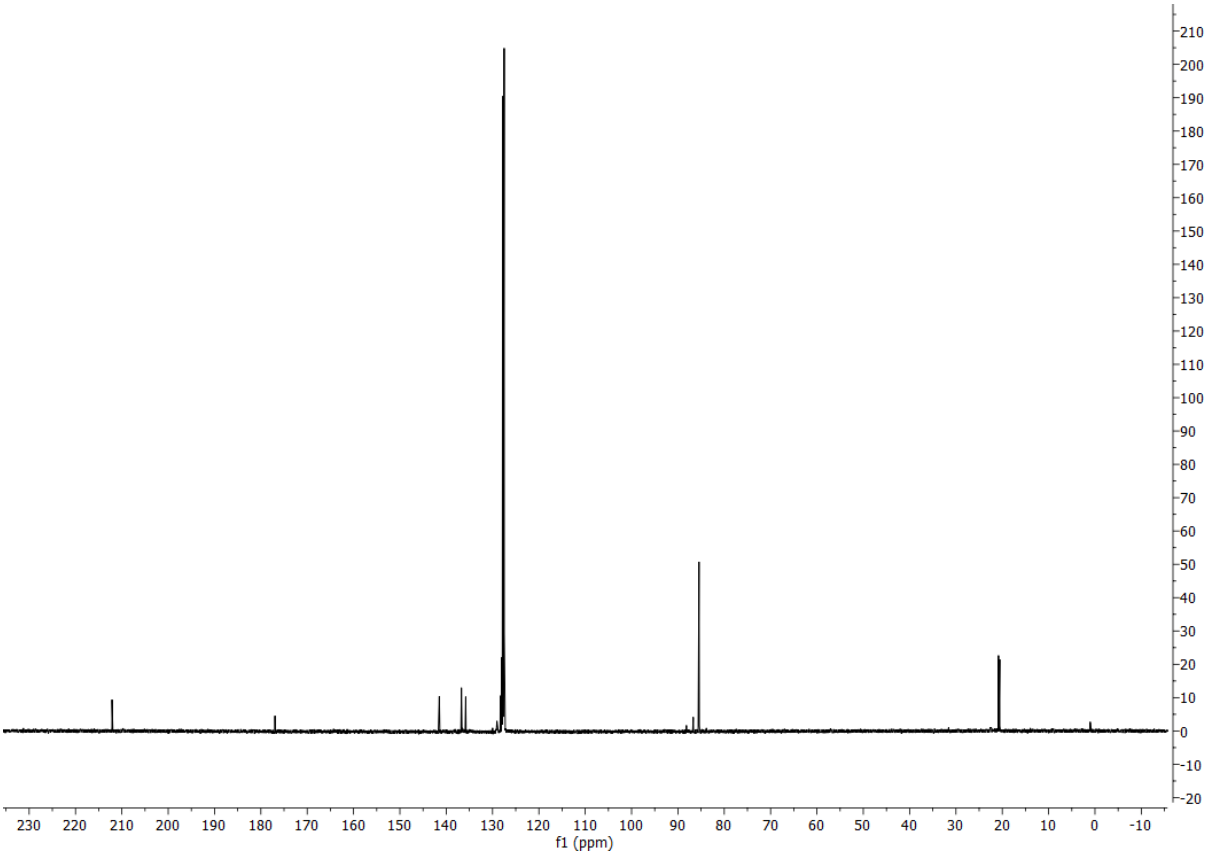
NMR Spectra

Figure S4. ^{1}H NMR spectrum of **1a** in C_6D_6 at 298K.



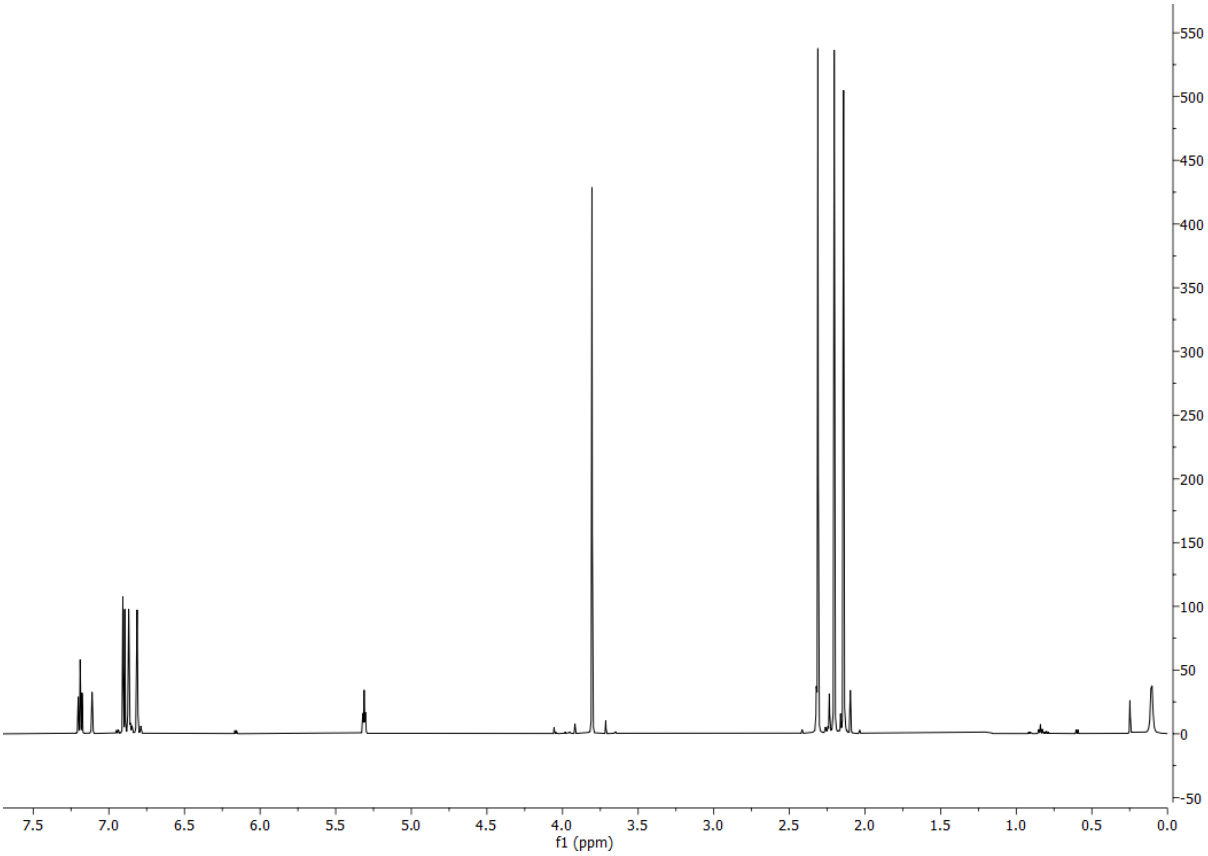
NMR Spectra

Figure S5. $^{13}C\{^{1}H\}$ NMR spectrum of **1a** in C_6D_6 at 298K.



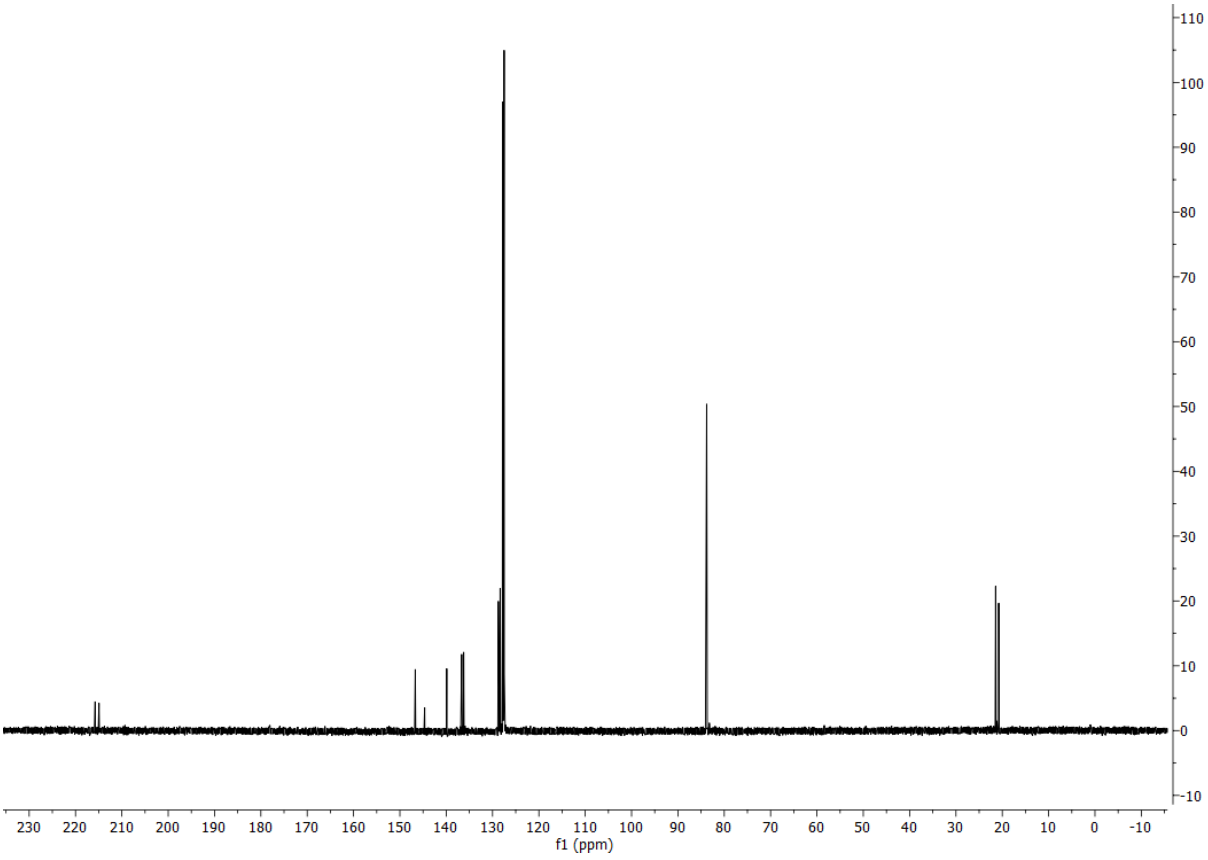
NMR Spectra

Figure S6. ^{1}H NMR spectrum of **2a** in C_6D_6 at 298K.



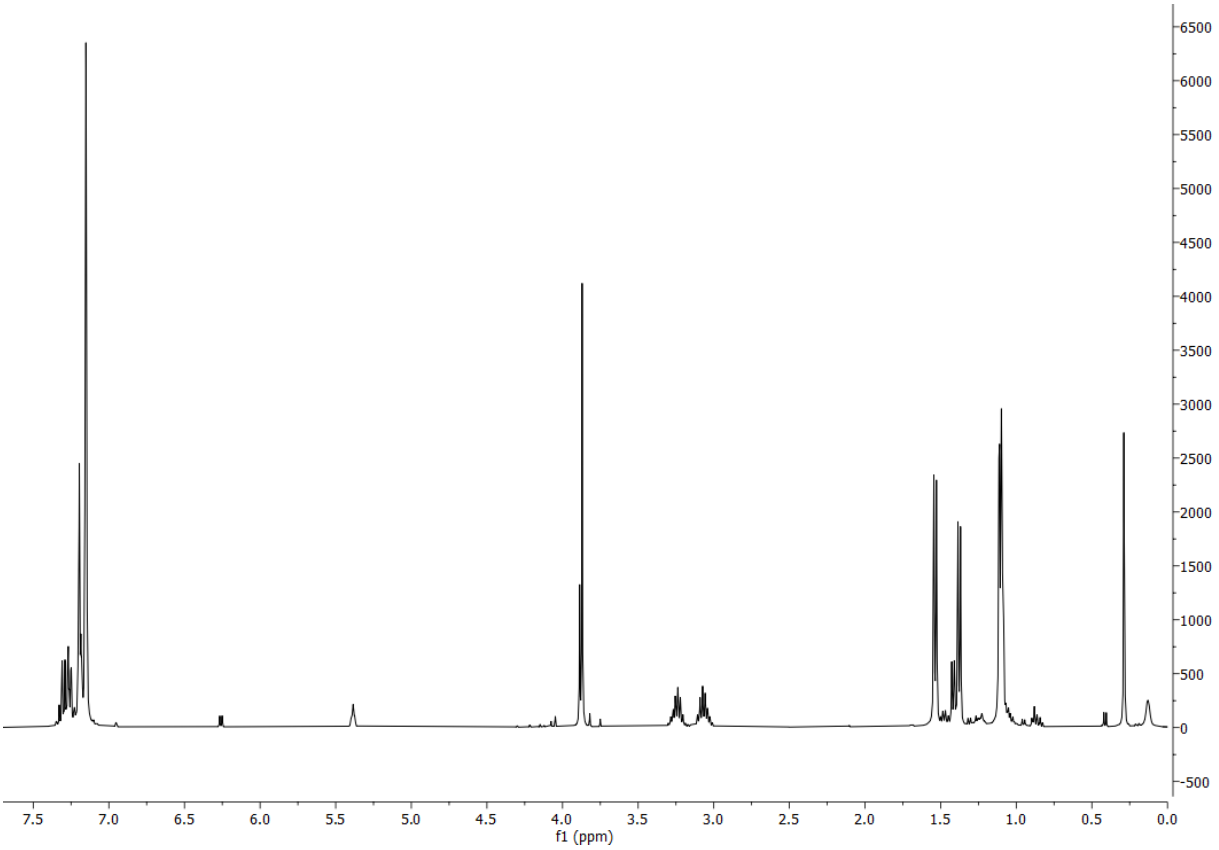
NMR Spectra

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in C_6D_6 at 298K.



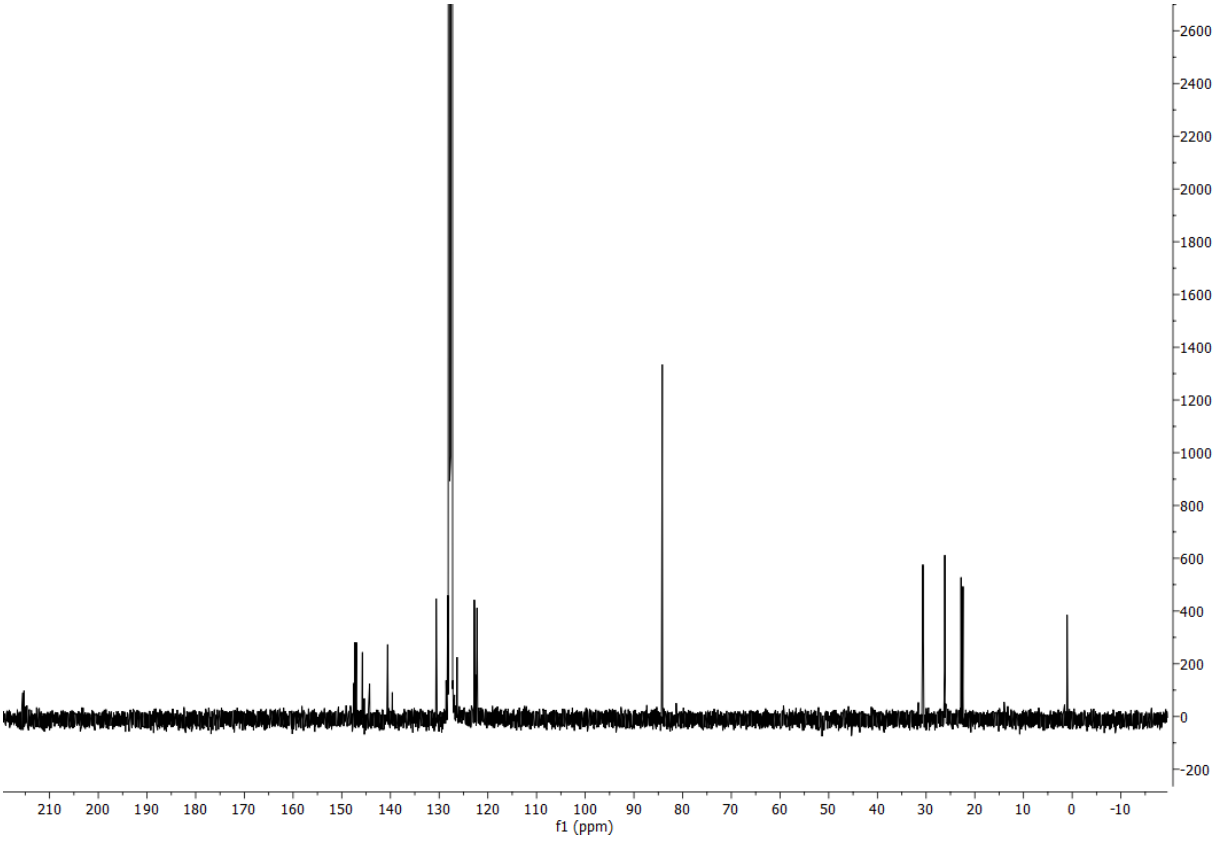
NMR Spectra

Figure S8. ^{1}H NMR spectrum of **2b** in C_6D_6 at 298K.



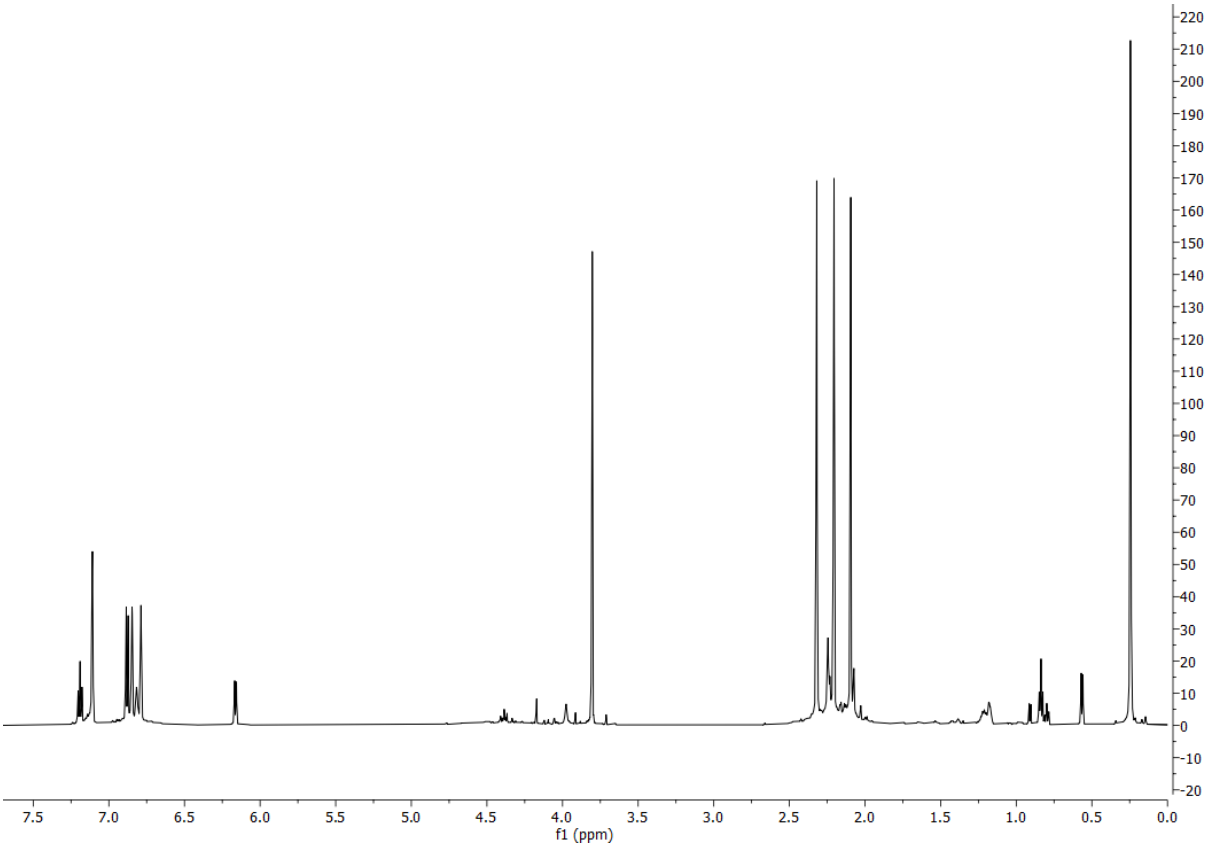
NMR Spectra

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in C_6D_6 at 298K.



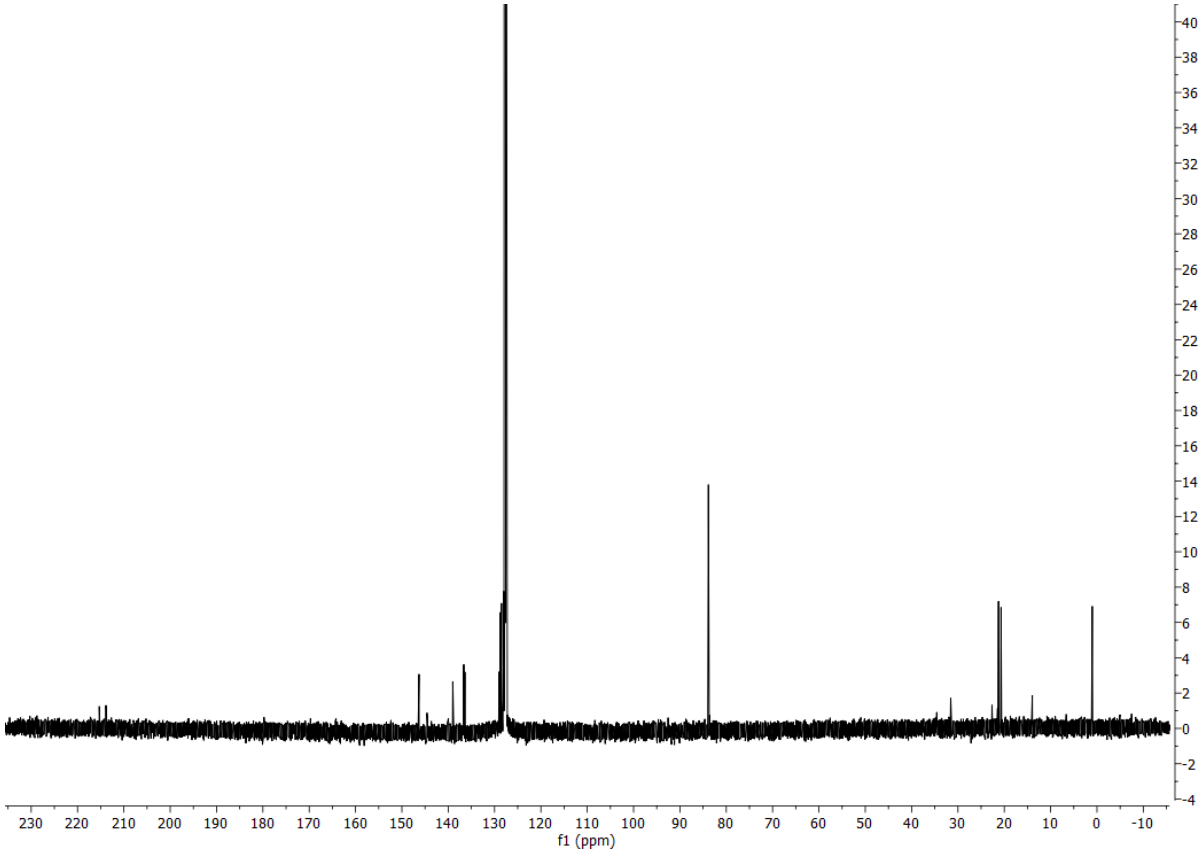
NMR Spectra

Figure S10. ^{1}H NMR spectrum of **3** in C_6D_6 at 298K.



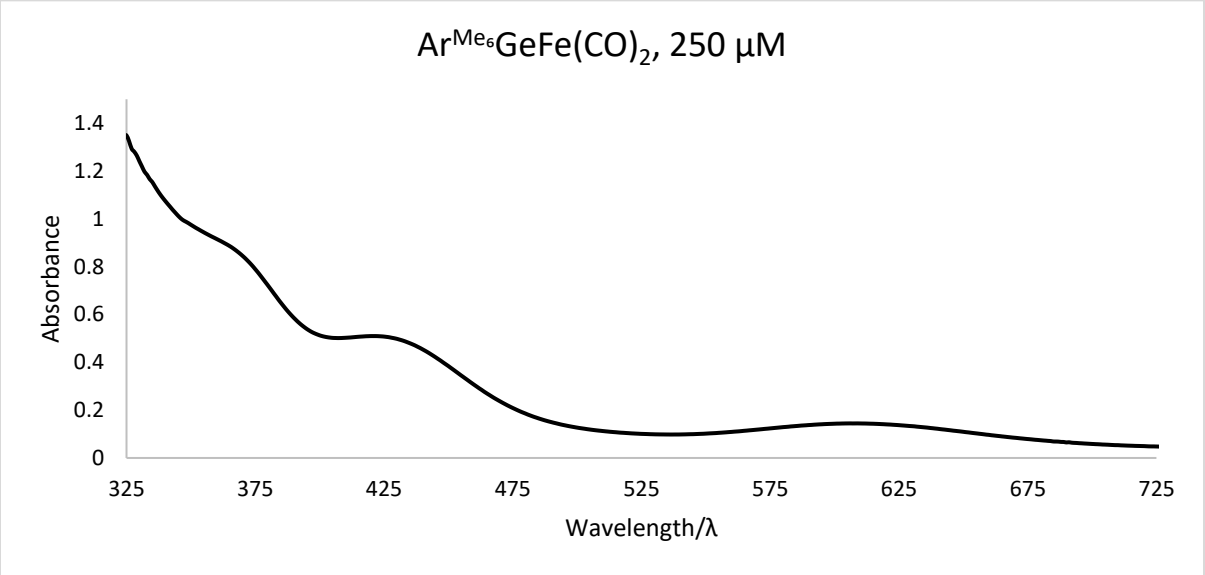
NMR Spectra

Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at 298K.



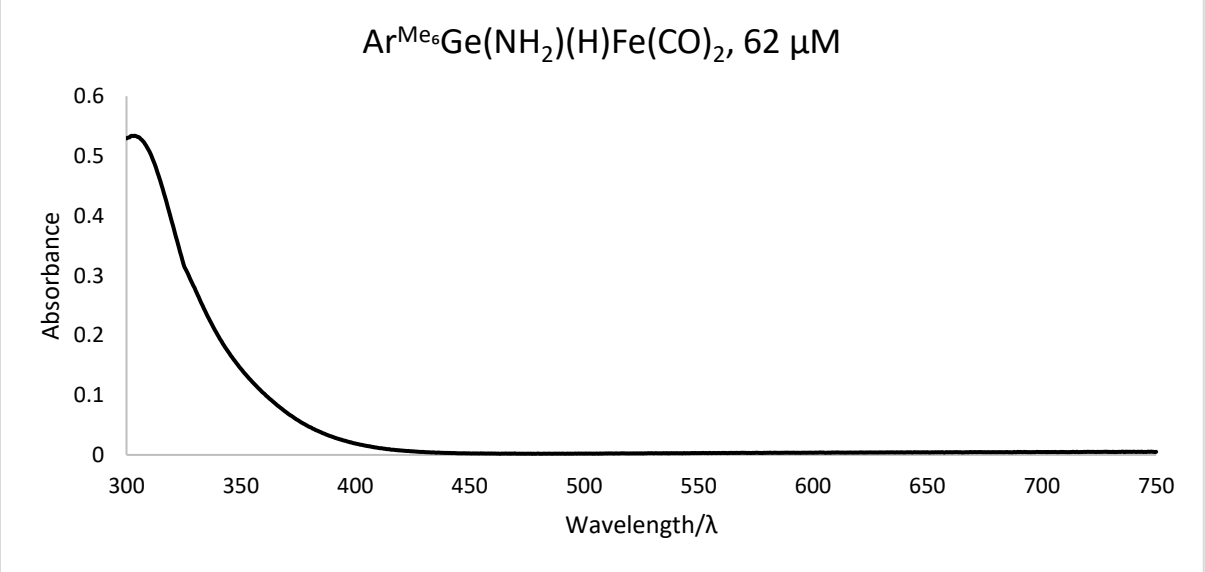
UV-vis Spectra

Figure S12. UV-vis spectrum of **1a** in hexanes at 298K.



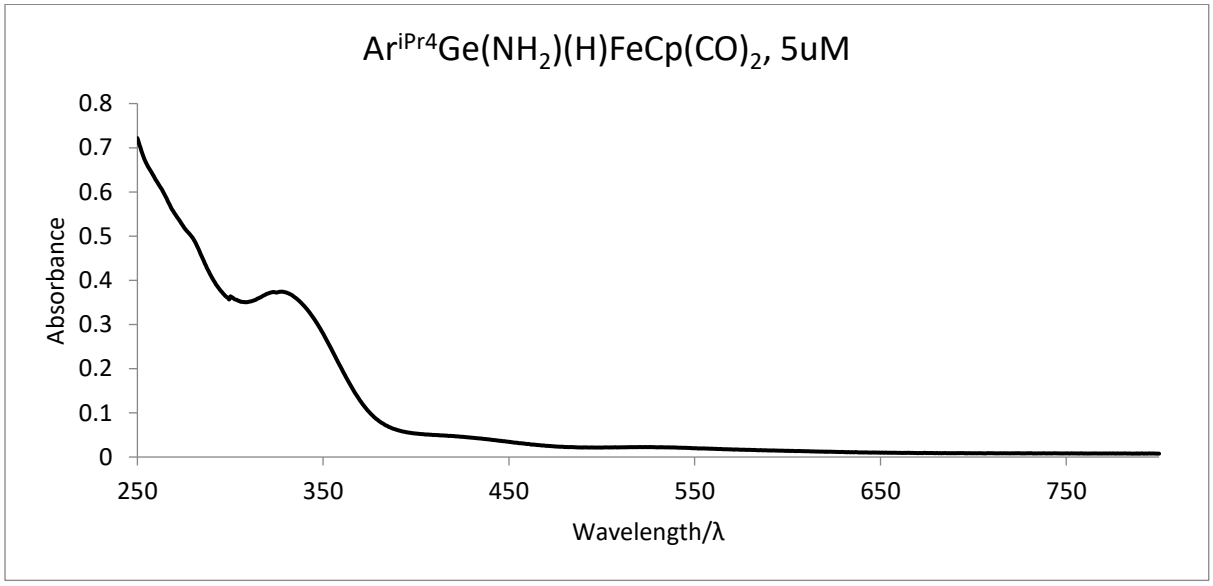
UV-vis Spectra

Figure S13. UV-vis spectrum of **2a** in hexanes at 298K.



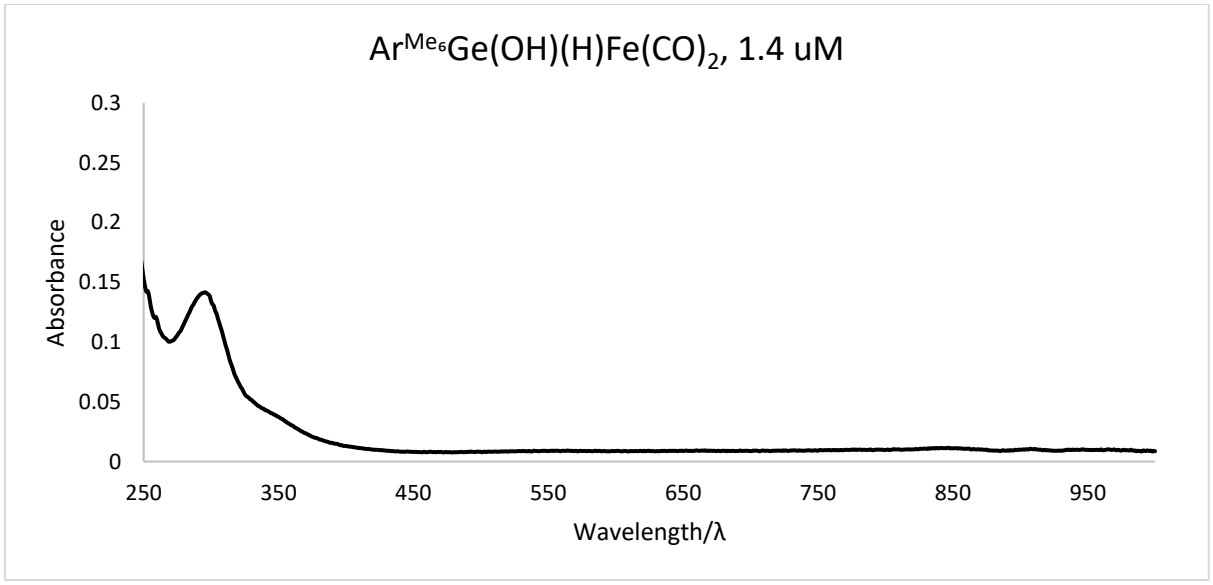
UV-vis Spectra

Figure S14. UV-vis spectrum of **2b** in hexanes at 298K.



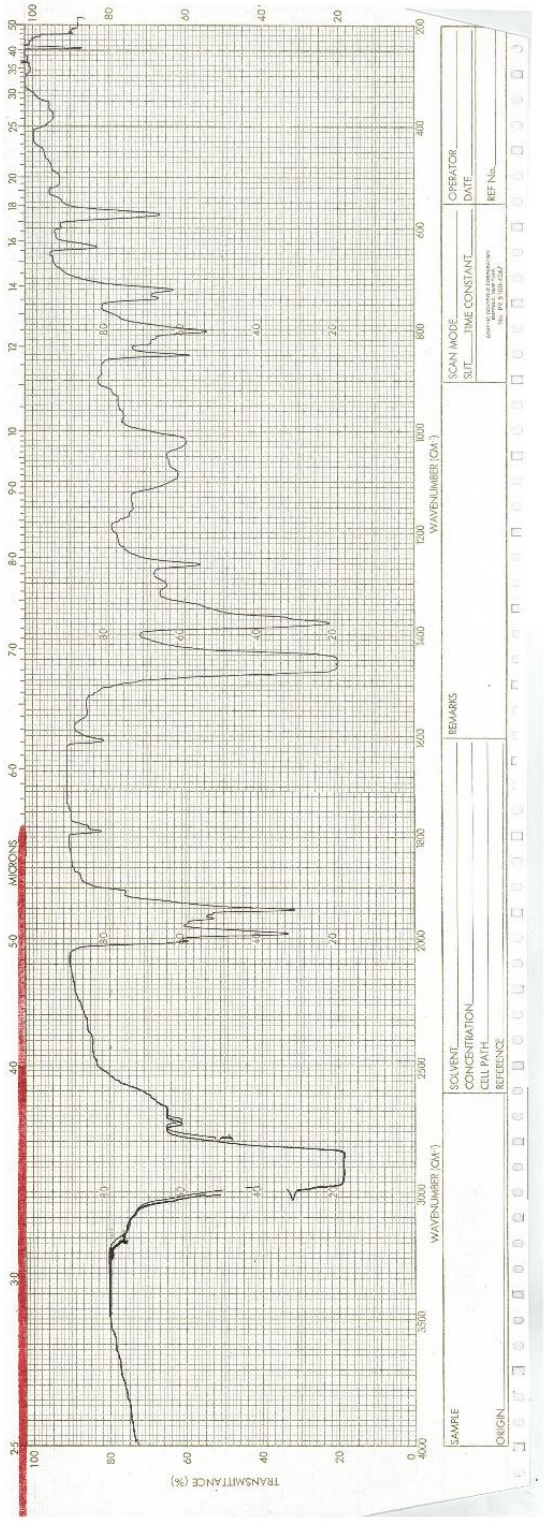
UV-vis Spectra

Figure S15. UV-vis spectrum of **3** in hexanes at 298K.



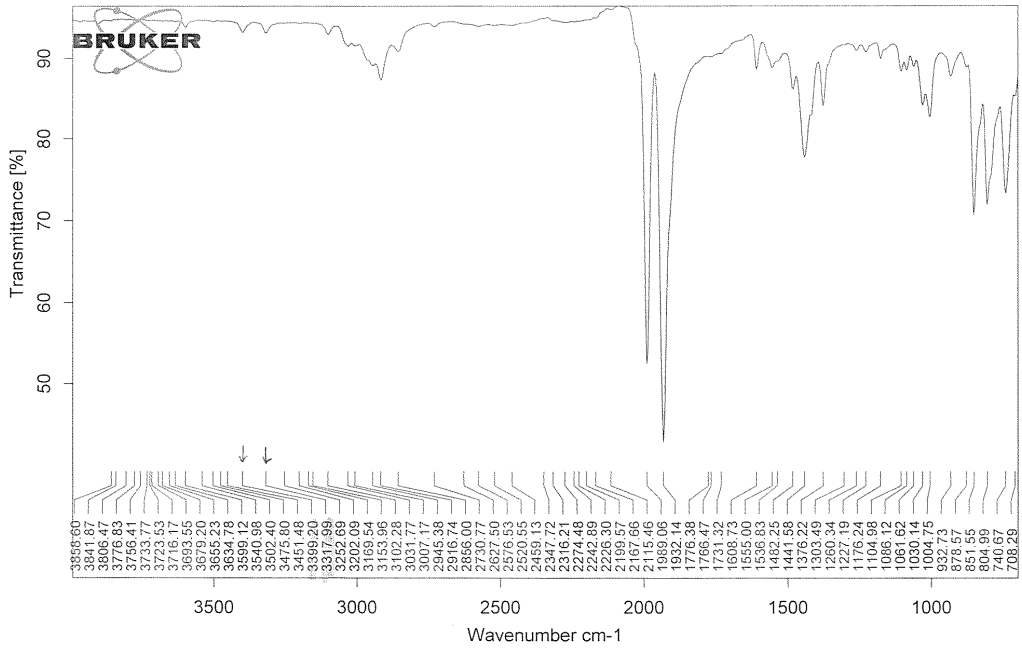
IR spectra

Figure S16. Infrared spectrum of **1a**



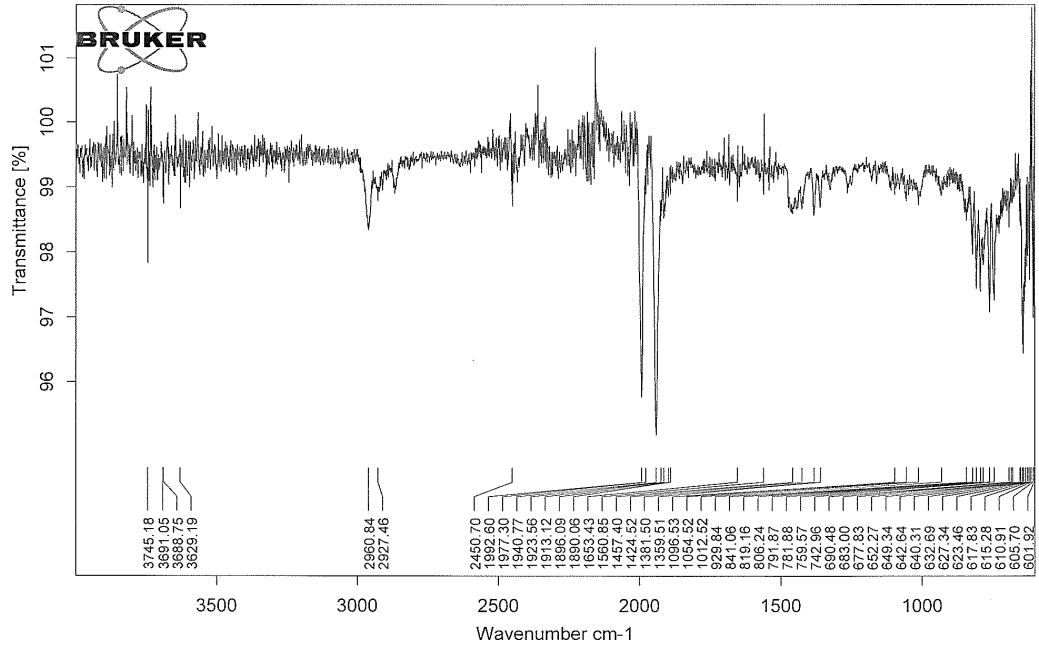
IR spectra

Figure S17. Infrared spectrum of **2a**



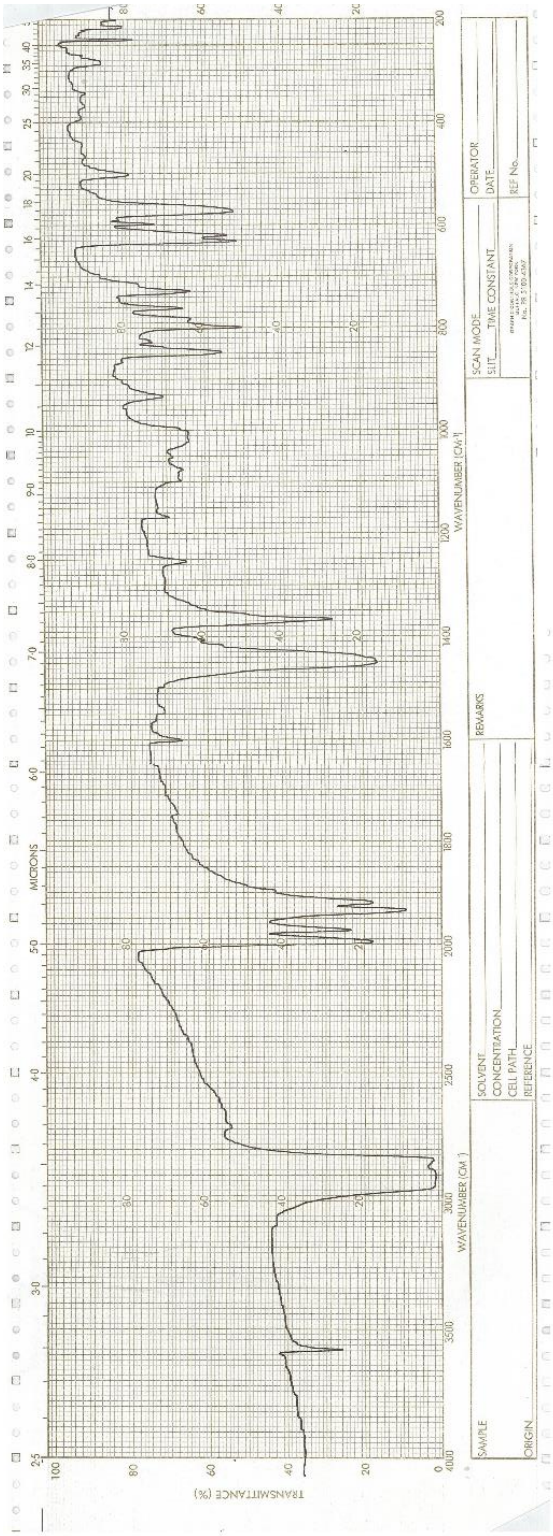
IR spectra

Figure S18. Infrared spectrum of **2b**



IR spectra

Figure S19. Infrared spectrum of **3**.



References

S1 Bruker, Bruker AXS Inc., Madison, Wisconsin, USA, **2001**
S2 G. M. Sheldrick, Acta Cryst. A 2015, 71, 3-8.
S3 Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H.; *OLEX2*: A complete structure solution, refinement and analysis program. J. Appl. Cryst, **2009**, *42*, 339-341.