Supporting Information

for the

Communication

A MolecularComplex with a Formally Neutral Iron Germanide Motif (Fe_2Ge_2)

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Synthesis of 5: Dry and degassed THF (45 mL) was added to the Schlenk flask containing $NHC^{iPr_2Me_2}$•$GeCl_2$ (3.23 g, 9.97 mmol) and $Fe_2(CO)_9$ (3.99 g, 10.97 mmol) at room temperature and the reaction mixture was stirred overnight. All volatiles were removed under vaccum and the crude reaction mixture extracted with warm toluene (60 mL) and filtered. After distilling off the solvent compound **5** was isolated (3.96 g, 8.05 mmol 81 % with respect to the $NHC^{iPr_2Me_2}$•$GeCl_2$). Single crystals suitable for X-ray diffraction were obtained from hot saturated hexane solution after keeping at room temperature for overnight as an orange needles. Mp: 155-157 °C. ^{1}H NMR (300 MHz, [D_6]benzene, 300K): δ = 5.88 (hept, 2H, ^{i}Pr-C*H*), 1.34 (s, 6H, CH_3), 1.06 (d, 12H, *i*Pr-CH_3) ppm. ^{13}C NMR (75.4 MHz, [D_6]benzene, 300 K): δ = 214.61 (*C*O), 154.66 (NCN), 127.76 (N*C*CN), 52.56 (^{i}Pr-*C*H), 20.95 (^{i}Pr-*C*H_3), 9.72 (*C*H_3) ppm. IR (KBr, cm^{-1}): $\bar{\upsilon}$ = 2040 (s), 1961 (s), 1941 (s), 1923 (s), 1913 (s). Elemental Analysis: Calcd. for $C_{15}H_{20}Cl_2FeGeN_2O_4$ (491.71): C, 36.64; H, 4.10; N, 5.70. Found: C, 36.75; H, 3.86, N, 5.88.

Synthesis of 7: Dry and degassed THF (40 mL) was added to the Schlenk flask containing **1** (1.18 g, 2.39 mmol) and KC_8 (0.74 g, 5.51 mmol) at −78 °C, and the reaction mixture was slowly warmed to room temperature and stirred for another 4 hours. All volatiles were removed in vacuum and the crude reaction mixtured was extracted with 40 mL of toluene. After filtration and removal of toluene, the residue was washed with 30 mL of hexane and dried in vacuum. Compound **7** (0.46 g, 0.54 mmol 46 %) was isolated as a red amorphous powder. Single crystals suitable for X-ray diffraction were obtained from warm toluene solution after keeping at 0 °C for two days as red needles. Mp: 131-133 °C. ^{1}H NMR (300 MHz, [D_6]benzene, 300K): δ = 6.13 (hept, 4H, ^{i}Pr-C*H*), 1.51 (s, 12H, CH_3), 1.40 (d, 24H, *i*Pr-CH_3) ppm. ^{13}C NMR (75.4 MHz, [D_6]benzene, 300 K): δ = 216.50 (*C*O), 126.89 (N*C*CN), 53.45 (^{i}Pr-*C*H), 21.45 (^{i}Pr-*C*H_3), 9.99 (*C*H_3) ppm. ^{1}H NMR (300 MHz, [D_8]toluene, 300K): δ = 6.14 (hept, 4H, ^{i}Pr-C*H*), 1.64 (s, 12H, CH_3), 1.45 (d, 24H, *i*Pr-CH_3) ppm. ^{13}C NMR (75.4 MHz, [D_8]toluene, 300 K): δ = 216.52 (*C*O), 126.97 (N*C*CN), 53.57 (^{i}Pr-*C*H), 21.52 (^{i}Pr-*C*H_3), 10.07 (*C*H_3) ppm. UV/Vis (THF): λ_{max} (ε) = 469 (sh, 1080) nm ($Lmol^{-1}cm^{-1}$). IR (KBr, cm^{-1}): $\bar{\upsilon}$ = 2023 (s), 1996 (s), 1958 (m), 1947 (s), 1941 (s), 1936 (s), 1918 (s), 1898 (m), 1882 (s). Elemental Analysis: Calcd. for $C_{30}H_{40}Fe_2Ge_2N_4O_8$ (841.62): C, 42.81; H, 4.79; N, 6.66. Found: C, 42.34; H, 4.51, N, 6.81.

Synthesis of 8: Propylene sulfide (0.035 g, 0.47 mmol) was added to a toluene (20 mL) solution of **7** (0.160 g, 0.19 mmol) at room temperature and stirred for 4 hrs. The solution was filtered and the filtrate concentrated to about 10 mL and kept at 0 °C for two days, afforded compound **5** as a yellow crystalline material (0.069 g, 42 %). Single crystals suitable for X-ray diffraction were obtained either from saturated toluene solution or warm hexane solution after keeping at 0 °C for overnight as a yellow blocks. Mp: 147-149 °C. ^{1}H NMR (300 MHz, [D_6]benzene, 300K): δ = 5.75 (hept, 4H, ^{i}Pr-C*H*), 1.49-1.40 (s & br, altogether 24H, CH_3 & *i*Pr-CH_3), 1.38 (d, 12H, *i*Pr-CH_3) ppm. ^{1}H NMR (300 MHz, [D_8]toluene, 300K): δ = 5.74 (hept, 4H, ^{i}Pr-C*H*), 1.59 (s 12H, CH_3), 1.56-1.44 (br, altogether 12H, *i*Pr-CH_3), 1.41 (d, 12H, *i*Pr-CH_3) ppm. ^{13}C NMR (75.4 MHz, [D_8]toluene, 300 K): δ = 216.73 (*C*O), 53.69 (^{i}Pr-*C*H), 21.61 (^{i}Pr-*C*H_3), 9.79 (*C*H_3) ppm (^{13}C resonance of N*C*CN are overlap with the residual peak of toluene-d_8). UV/Vis (THF): λ_{max} (ε) = 434 (4820) nm ($Lmol^{-1}cm^{-1}$). IR (KBr, cm^{-1}): $\bar{\upsilon}$ = 2014 (m), 2008 (m), 1914 (m), 1906 (m). Despite the NMR spectroscopically clean product, we were unable to obtain a satisfactory elemental analysis.

NMR Spectra:

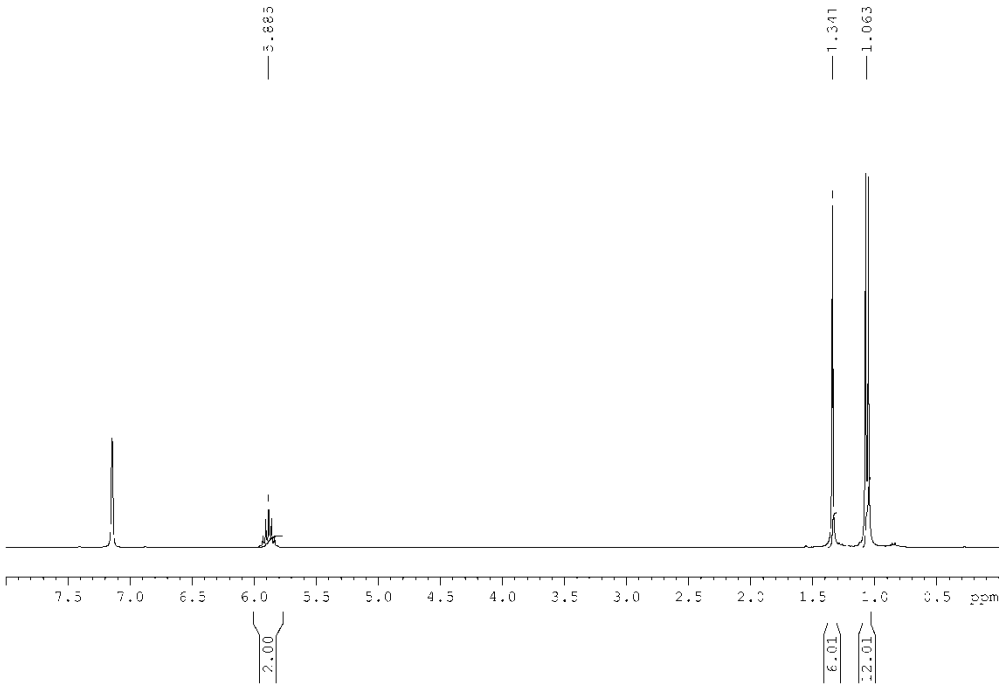

Figure S1: ^{1}H NMR of **5** in [D_6]benzene at 300 K.

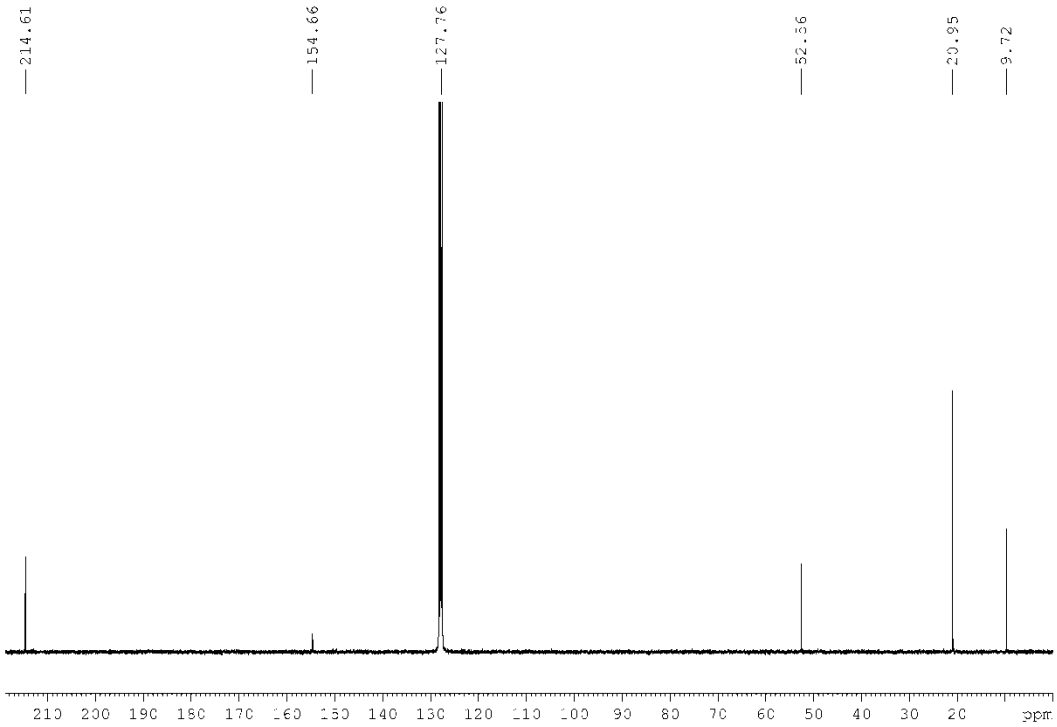

Figure S2: ^{13}C{^{1}H} NMR of **5** in [D_6]benzene at 300 K.

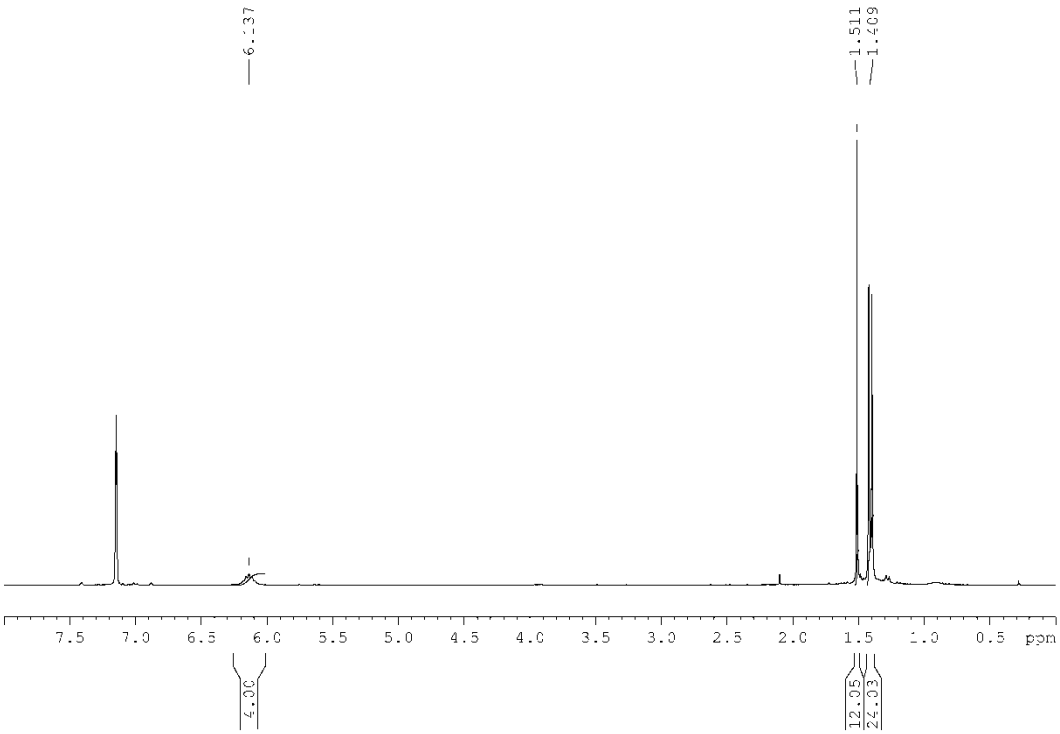

Figure S3: ^{1}H NMR of **7** in [D$_6$]benzene at 300 K.

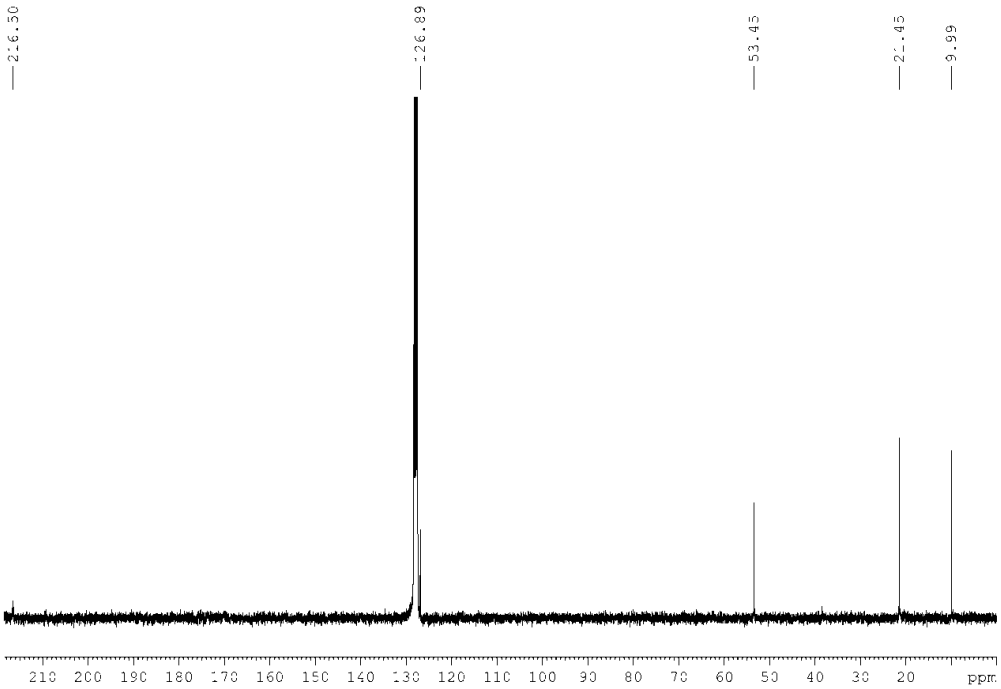

Figure S4: ^{13}C{^{1}H} NMR of **7** in [D$_6$]benzene at 300 K.

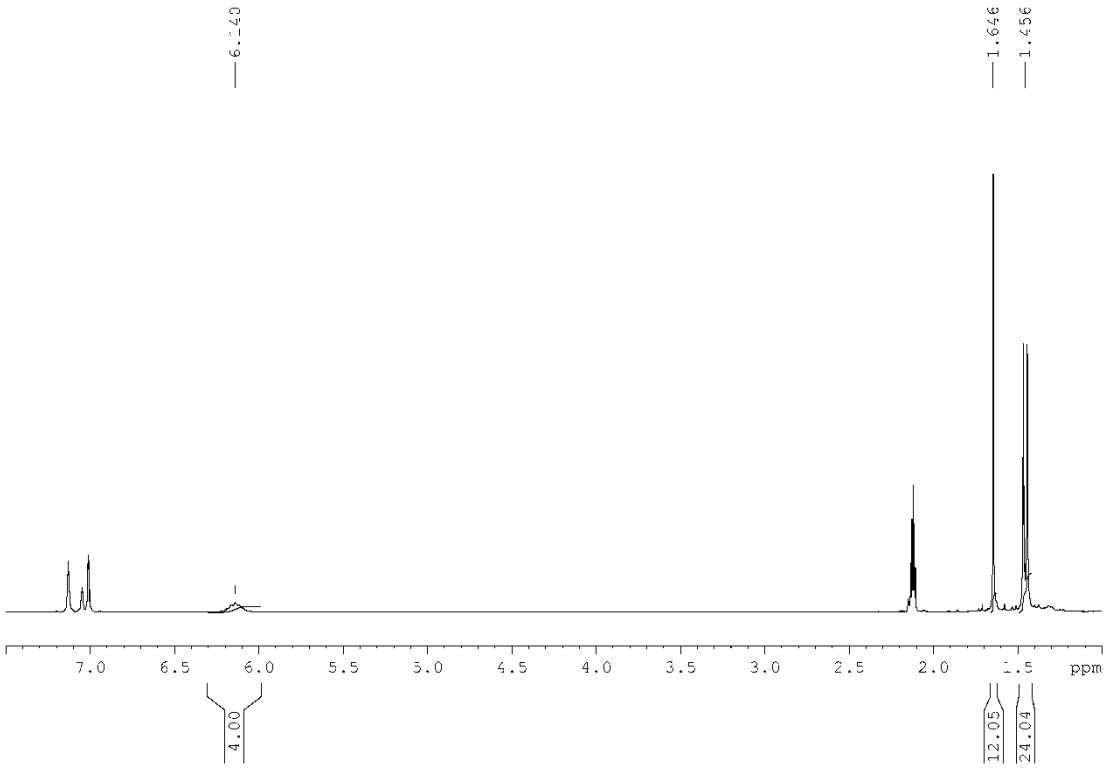

Figure S5: ^{1}H NMR of **7** in [D$_8$]toluene at 300 K.

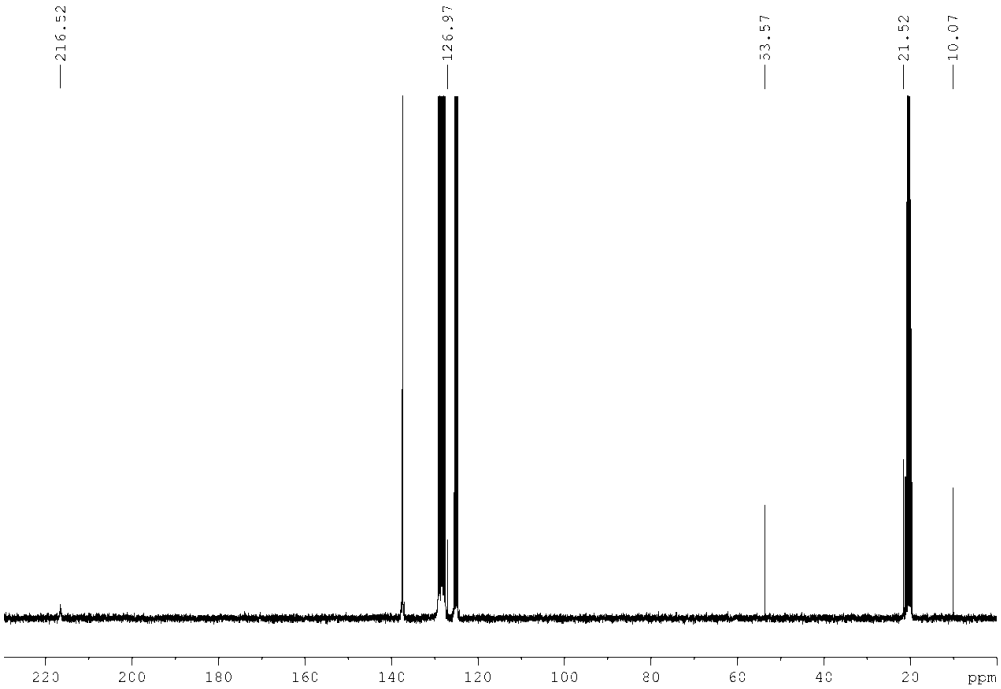

Figure S6: ^{13}C{^{1}H} NMR of **7** in [D$_8$]toluene at 300 K.

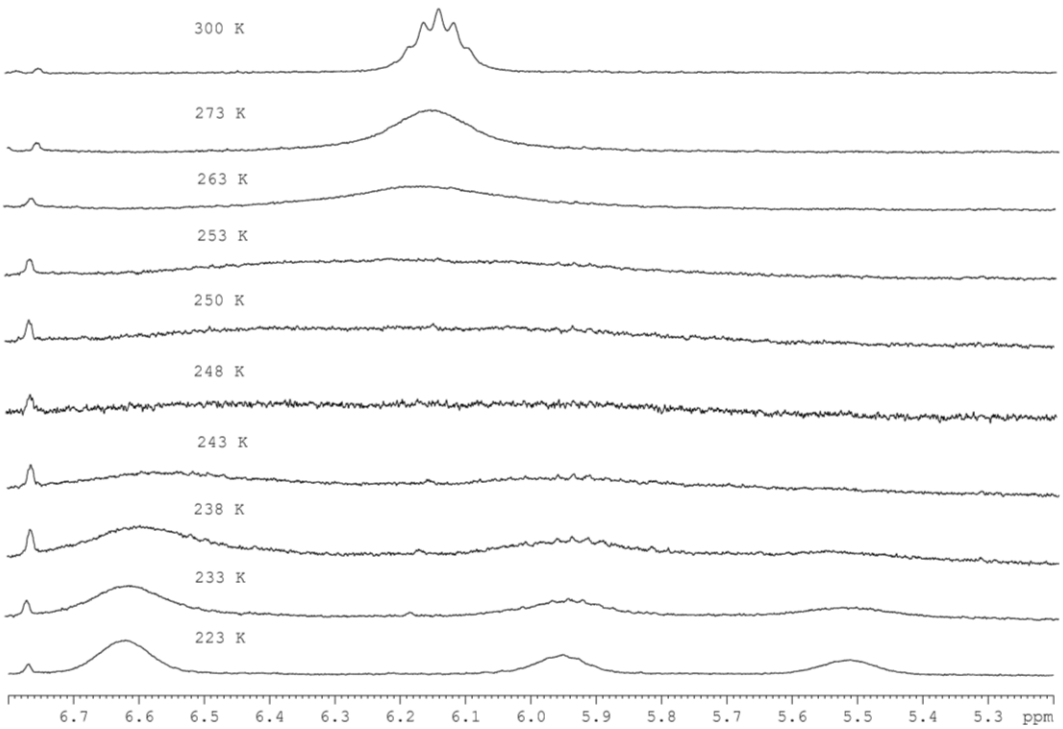

Figure S7: ^{1}H NMR of crude **7** in [D_8]toluene at variable temperatures (Coalescence Temperature, T_c = 248 K, $K_{exchange}$ = 590 Hz, $\Delta G^{\#}$ = -$RT_c \ln K_{exchange}$ = −13.15 kJMol^{-1}). The signal at 6.75 ppm belong to an unidentified impurity, which is completely removed upon crystallization.

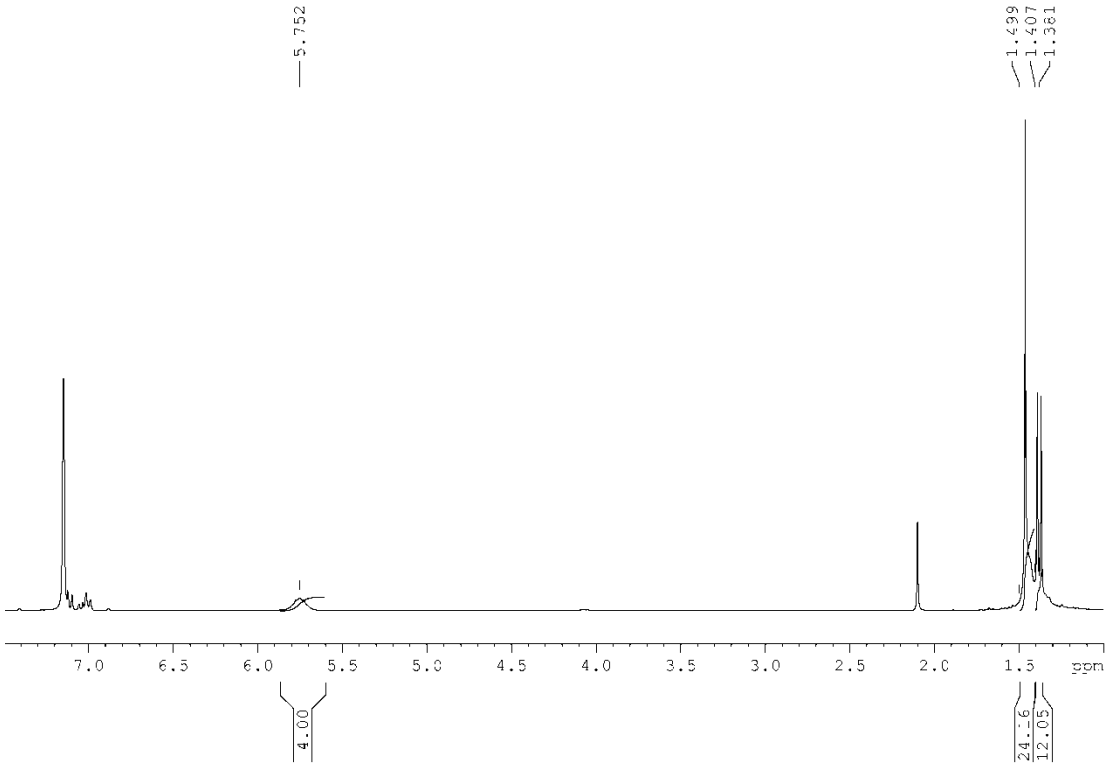

Figure S8: ^{1}H NMR of **8** [D_6]benzene at 300 K.

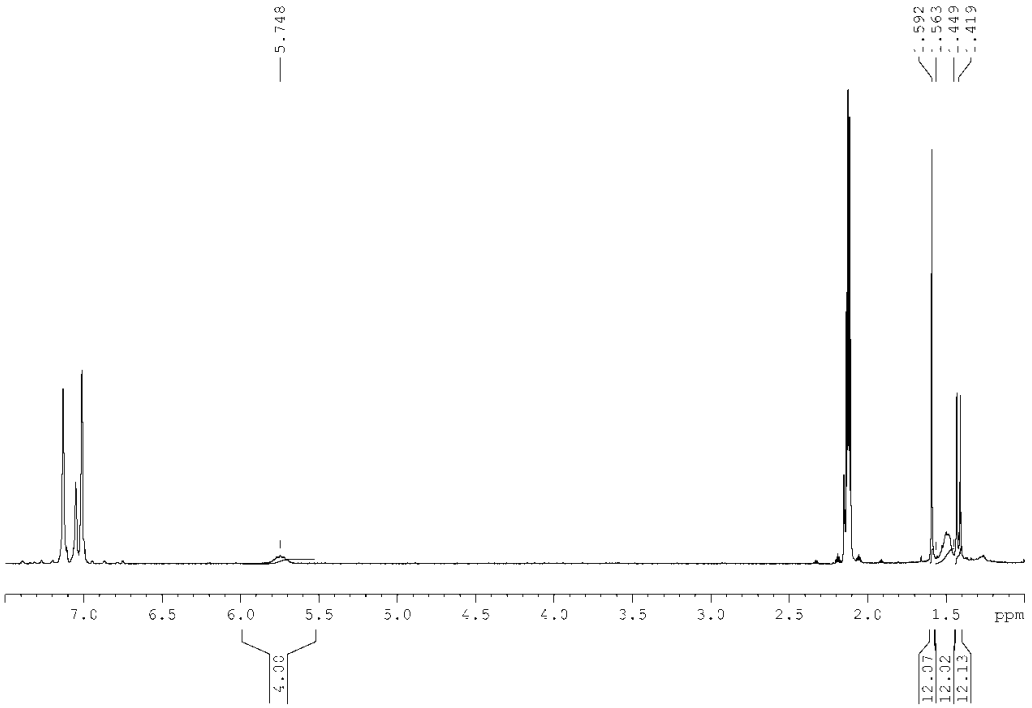

Figure S9: ^{1}H NMR of **8** in [D_8]toluene at 300 K.

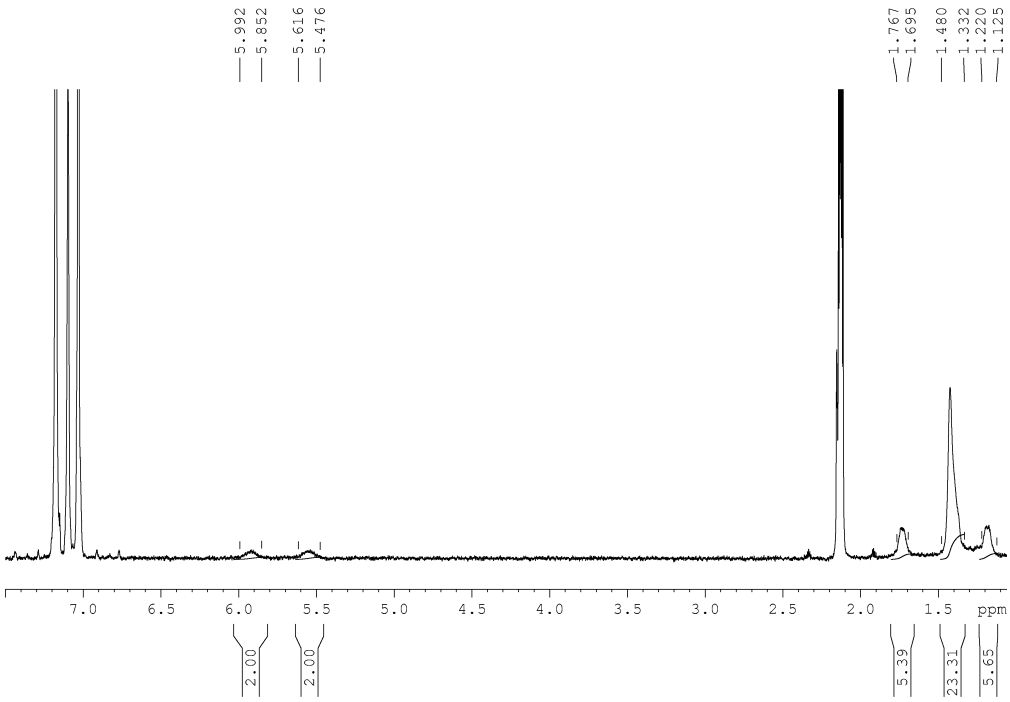

Figure S10: ^{1}H NMR of **8** in [D$_8$]toluene at 233 K.

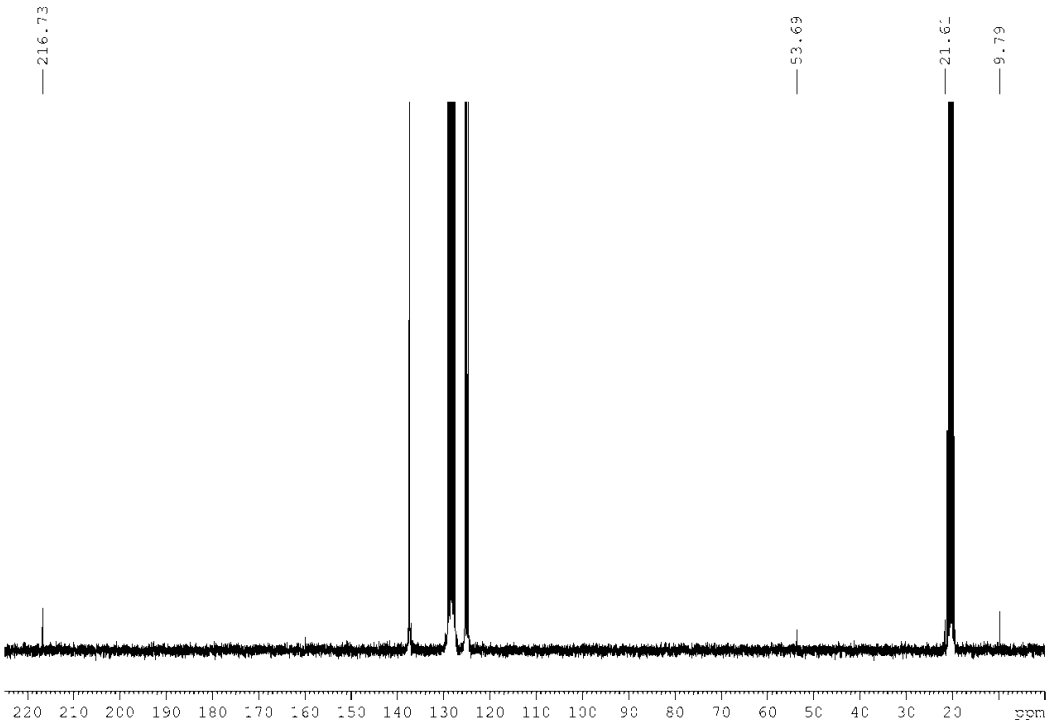

Figure S11: ^{13}C{^{1}H} NMR of **8** in [D$_8$]toluene at 300 K.

Absorption Spectra:

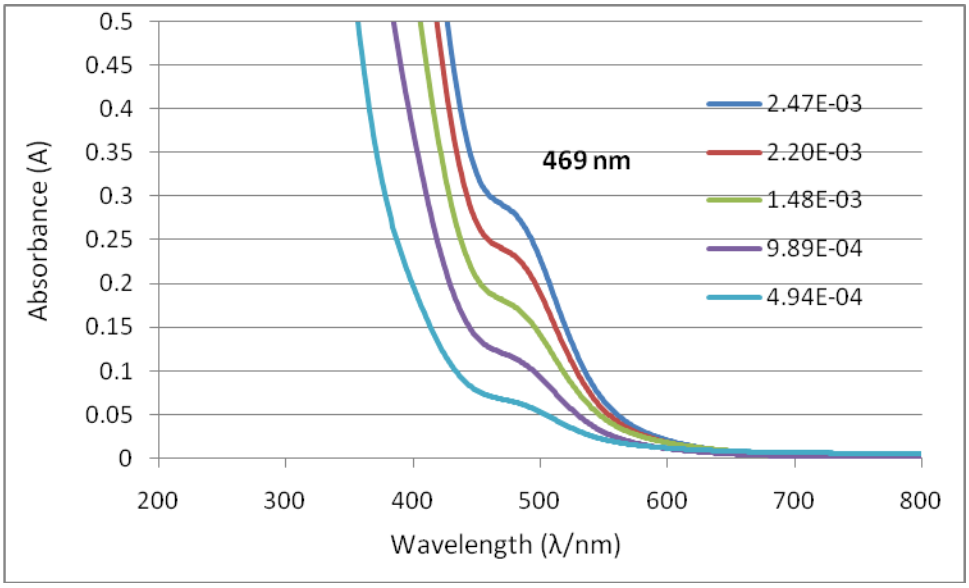

Figure S12: UV/vis Spectra of **7** in THF at different concentrations.

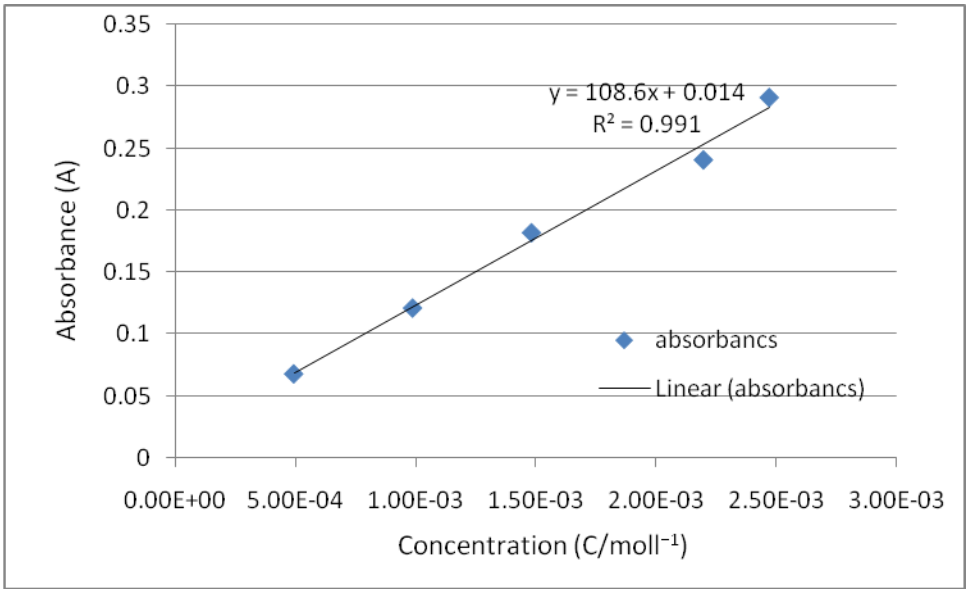

Figure S13: Linear regression of **7** at 469 nm.

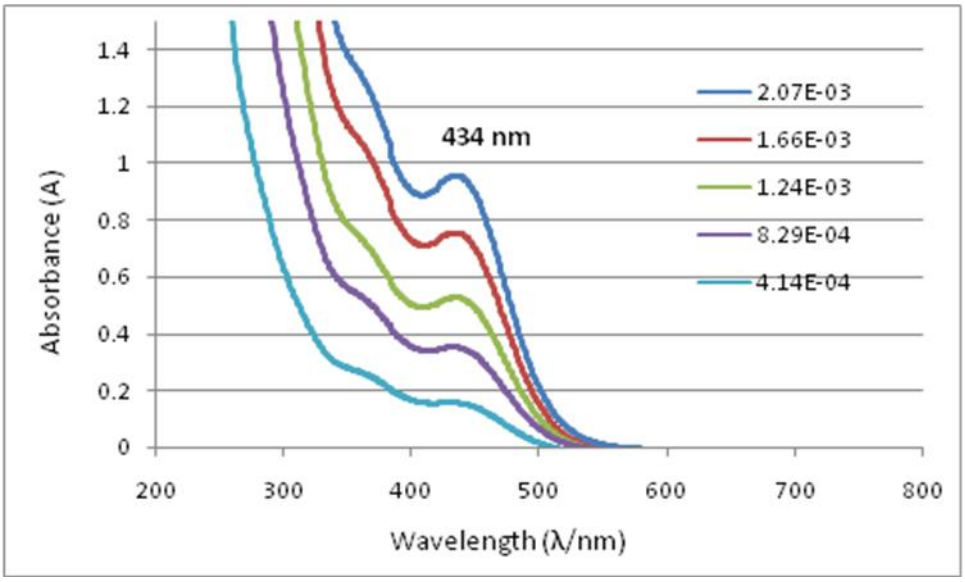

Figure S14: UV/vis Spectra of **8** in THF at different concentrations.

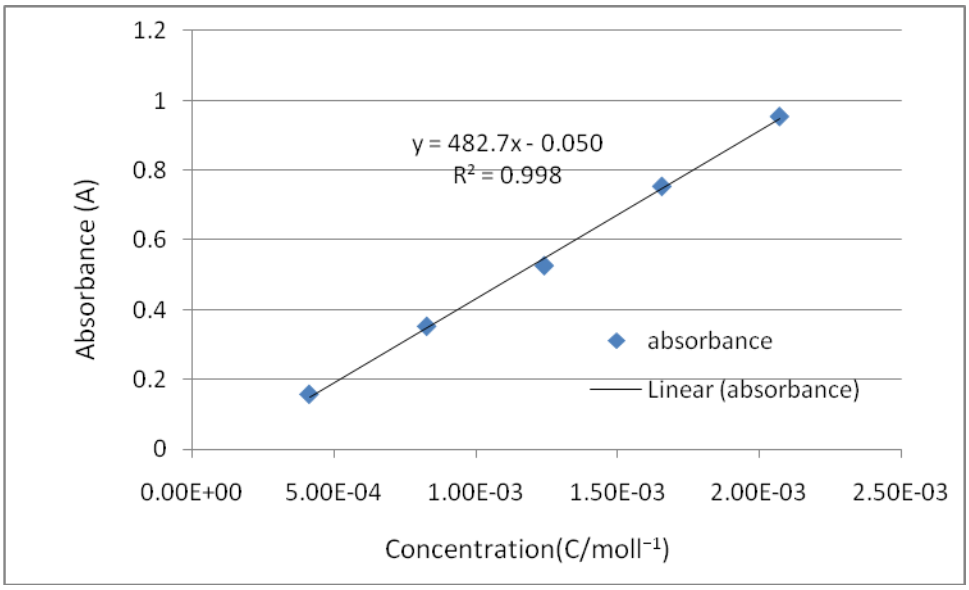

Figure S15: Linear regression of **8** at 434 nm.

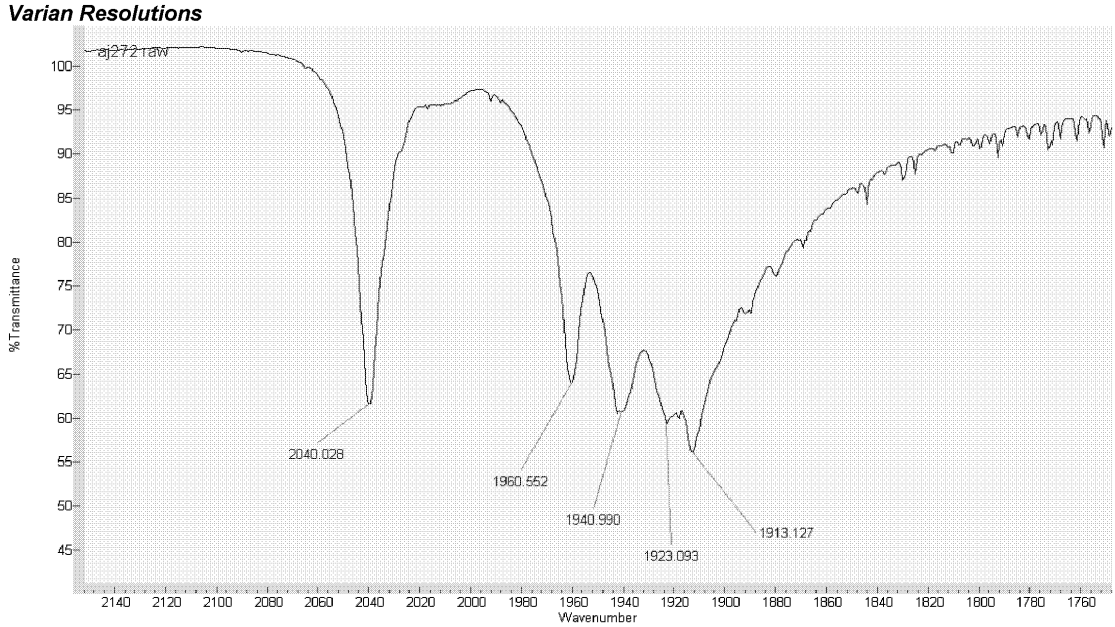

Figure S16: IR spectrum of **5**.

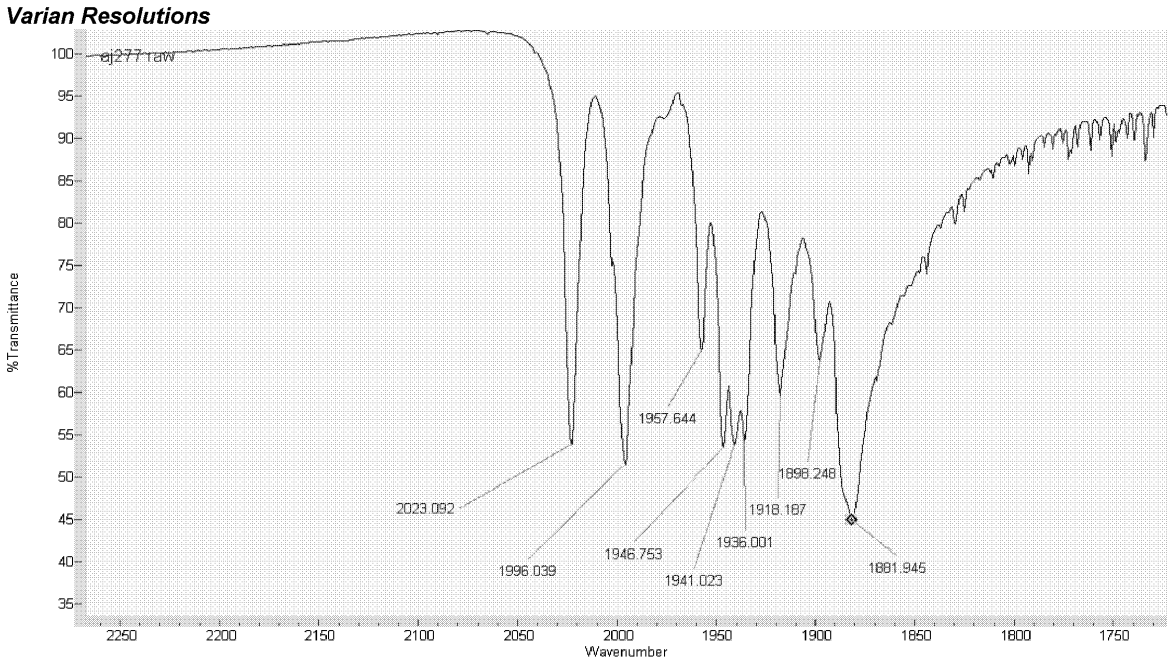

Figure S17: IR spectrum of **7**.

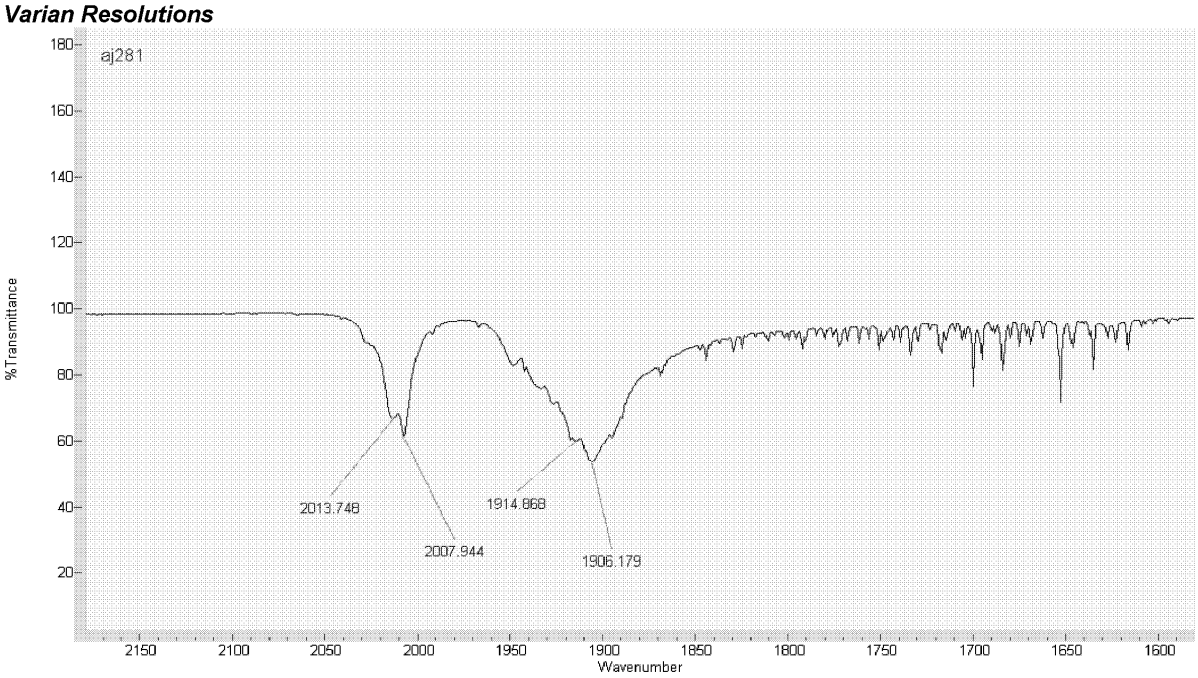

Figure S18: IR spectrum of **8**.

Table S1: Crystal data and structure refinement for **5 (CCDC-986900)**.

Identification code	sh3456	
Empirical formula	C15 H20 Cl2 Fe Ge N2 O4	
Formula weight	491.67	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 9.8194(3) Å	α= 90°.
	b = 12.8753(5) Å	β= 94.829(2)°.
	c = 15.9909(6) Å	γ = 90°.
Volume	2014.52(12) $Å^3$	
Z	4	
Density (calculated)	1.621 Mg/m^3	
Absorption coefficient	2.498 mm^{-1}	
F(000)	992	
Crystal size	0.51 x 0.12 x 0.07 mm^3	
Theta range for data collection	2.03 to 29.63°.	
Index ranges	-13<=h<=11, -16<=k<=17, -22<=l<=19	
Reflections collected	22526	
Independent reflections	5676 [R(int) = 0.0312]	
Completeness to theta = 29.63°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8525 and 0.3606	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5676 / 0 / 306	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0271, wR2 = 0.0583	
R indices (all data)	R1 = 0.0420, wR2 = 0.0632	
Largest diff. peak and hole	0.447 and -0.361 $e.Å^{-3}$	

Table S2: Crystal data and structure refinement for **7 (CCDC-986901)**.

Identification code	sh3457	
Empirical formula	C30 H40 Fe2 Ge2 N4 O8	
Formula weight	841.54	
Temperature	152(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 11.1640(4) Å	α= 90°.
	b = 14.6309(5) Å	β= 90°.
	c = 21.7358(8) Å	γ = 90°.
Volume	3550.3(2) $Å^3$	
Z	4	
Density (calculated)	1.574 Mg/m^3	
Absorption coefficient	2.529 mm^{-1}	
F(000)	1712	
Crystal size	0.38 x 0.12 x 0.06 mm^3	
Theta range for data collection	1.68 to 30.60°.	
Index ranges	-15<=h<=15, -20<=k<=20, -30<=l<=31	
Reflections collected	81348	
Independent reflections	10855 [R(int) = 0.0387]	
Completeness to theta = 30.60°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8549 and 0.4450	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10855 / 0 / 427	
Goodness-of-fit on F^2	0.897	
Final R indices [I>2sigma(I)]	R1 = 0.0227, wR2 = 0.0475	
R indices (all data)	R1 = 0.0297, wR2 = 0.0496	
Absolute structure parameter	0.005(5)	
Largest diff. peak and hole	0.333 and -0.245 $e.Å^{-3}$	

Table S3: Crystal data and structure refinement for **8 (CCDC-986902)**.

Identification code	sh3458	
Empirical formula	C37 H48 Fe2 Ge2 N4 O8 S	
Formula weight	965.73	
Temperature	152(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 11.0226(2) Å	α= 90°.
	b = 17.8671(4) Å	β= 90°.
	c = 21.7025(4) Å	γ = 90°.
Volume	4274.13(15) $Å^3$	
Z	4	
Density (calculated)	1.501 Mg/m^3	
Absorption coefficient	2.159 mm^{-1}	
F(000)	1976	
Crystal size	0.44 x 0.18 x 0.07 mm^3	
Theta range for data collection	1.48 to 27.18°.	
Index ranges	-14<=h<=13, -19<=k<=22, -26<=l<=27	
Reflections collected	58484	
Independent reflections	9253 [R(int) = 0.0520]	
Completeness to theta = 27.18°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8566 and 0.4529	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9253 / 0 / 501	
Goodness-of-fit on F^2	1.046	
Final R indices [I>2sigma(I)]	R1 = 0.0433, wR2 = 0.0866	
R indices (all data)	R1 = 0.0640, wR2 = 0.0926	
Largest diff. peak and hole	1.620 and -0.536 $e.Å^{-3}$	