Electronic Supplementary Information

Hydrostannylation of Carbon Dioxide by a Hydridostannylene Molybdenum Complex

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Computational details.

The structure was subjected to refinement at the DFT level of theory, with the B3LYP hybrid exchange functional[1-4] using Ahlrichs polarized basis set def2-TZVP[5]. For Sn, the effective core potential (ECP) basis set[6] with similar valence quality was used. In addition, dispersion correction with Becke-Johnson damping (D3BJ)[7, 8] was used. The resolution of identity approximation was employed with auxiliary basis set def2-TZVP/C[9, 10] in order to speed up the calculations. Phenyl was used in substitution of Ar^{iPr6} in the calculation of IR frequencies to speed up calculation. The reported IR frequencies are scaled by 0.986 as suggested by Truhlar. All calculations were carried out using the ORCA 4.2.1 quantum chemistry package.[11]

Table S1. Experimental and Calculated Bond Lengths and Bond Angles of **1**

Compound **1**	Bond lengths (Å) Expt.	Bond lengths (Å) Calc.	Compound **1**	Bond angles (°) Expt.	Bond angles (°) Calc.
Sn(1)-C(1)	2.158(2)	2.16853	Mo(1)-Sn(1)-C(1)	140.11(6)	135.0253
Sn(1)-Mo(1)	2.7157(4)	2.72286	H(1)-Sn(1)-C(1)	108.3(6)	100.3012
Sn(1)-H(1)	1.93(2)	1.74977	H(1)-Sn(1)-Mo(1)	111.4(6)	124.6165
Mo(1)-C(38)	2.050(3)	2.04503	Sn(1)-Mo(1)-C(40)	176.48(9)	179.1233
Mo(1)-C(39)	2.053(3)	2.05207	C(38)-Mo(1)-C(40)	91.25(12)	92.8569
Mo(1)-C(40)	2.018(3)	2.00717	Sn(1)-Mo(1)-C(38)	86.08(8)	86.5436
Mo(1)-C(41)	2.050(3)	2.04461	Mo(1)-C(40)-O(40)	179.5(4)	179.8013

Table S2. Scaled CO stretching frequencies (scaled by 0.986).

1 (cm^{-1})

607	
1762	
1998	
2013	
2104	
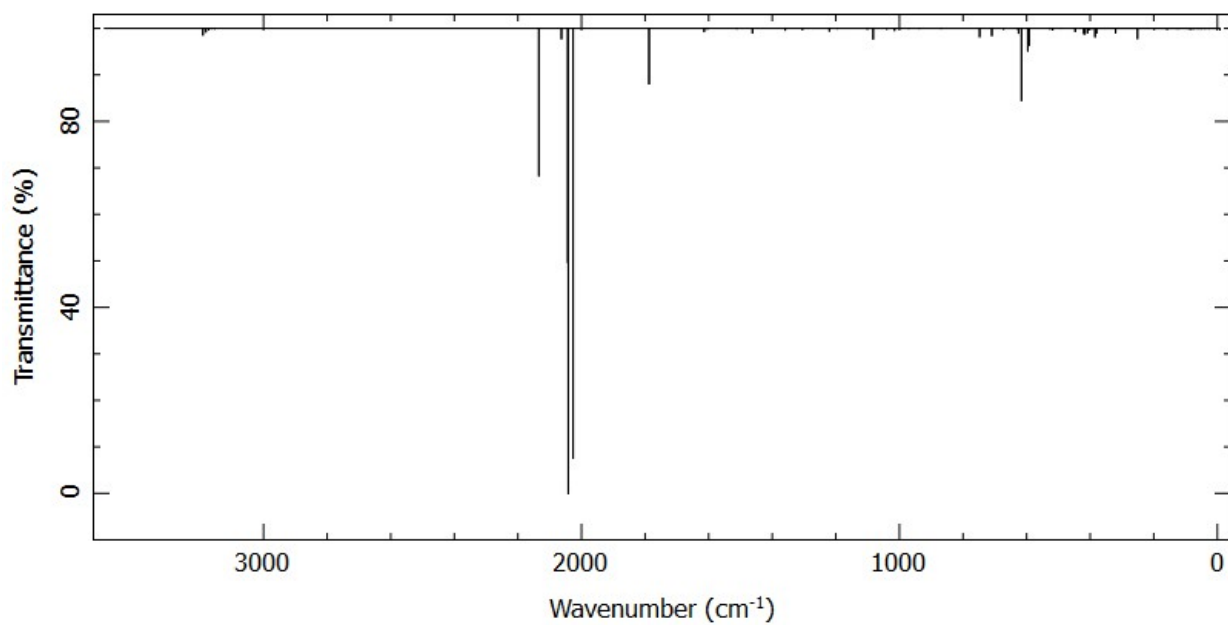
Figure S1. Calculated IR spectrum of **1**.

Table S3. Selected X-ray Crystallographic data for **1-3.**

Compound	**1**	**2**	**2**
Empirical formula	$C_{41}H_{50}MoO_5Sn$	$C_{39}H_{46}MoO_6Sn$	$C_{42}H_{50}MoO_7Sn$
Formula weight	837.44	825.39	881.45
Temperature	90(2) K	90(2) K	90(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Monoclinic

| Space group	P-1	P2$_1$/c	P2$_1$/m
Crystal color and habit	Yellow block	Yellow plate	Colorless block
a(Å)	10.0036(9)	14.7682(5)	8.6205(6)
b(Å)	13.2565(12)	10.7848(4)	18.6744(13)
c(Å)	15.0972(13)	23.6781(10)	12.8381(9)
α(°)	94.4823(14)	90	90
β(°)	92.9268(14)	95.0100(10)	90.8178(10)
γ(°)	96.3788(14)	90	90
Density (calculated) (Mg/m^3)	1.405	1.459	1.417
F(000)	856	1680	900
Crystal size(mm^3)	0.522 x 0.368 x 0.354	0.334 x 0.288 x 0.285	0.476 x 0.456 x 0.268
θ range(°)	1.972 to 27.487°	2.076 to 25.249°	1.925 to 30.631°
Reflections collected	17915	16327	24632
Independent reflections	9055 [R(int) = 0.0163]	6802 [R(int) = 0.0549]	6555 [R(int) = 0.0281]
Observed reflections (I > 2σ(I))	7878	4769	5706
Completeness to 2θ= 25.242°	99.9 %	100.0 %	100.0 %
Goodness-of-fit on F^2	1.045	1.018	1.078
Final R indices (I>2σ(I))	R1 = 0.0313, wR2 = 0.0794	R1 = 0.0417, wR2 = 0.0829	R1 = 0.0248, wR2 = 0.0607
R indices (all data)	R1 = 0.0368,	R1 = 0.0702,	R1 = 0.0313,

	wR2 = 0.0817	wR2 = 0.0954	wR2 = 0.0642
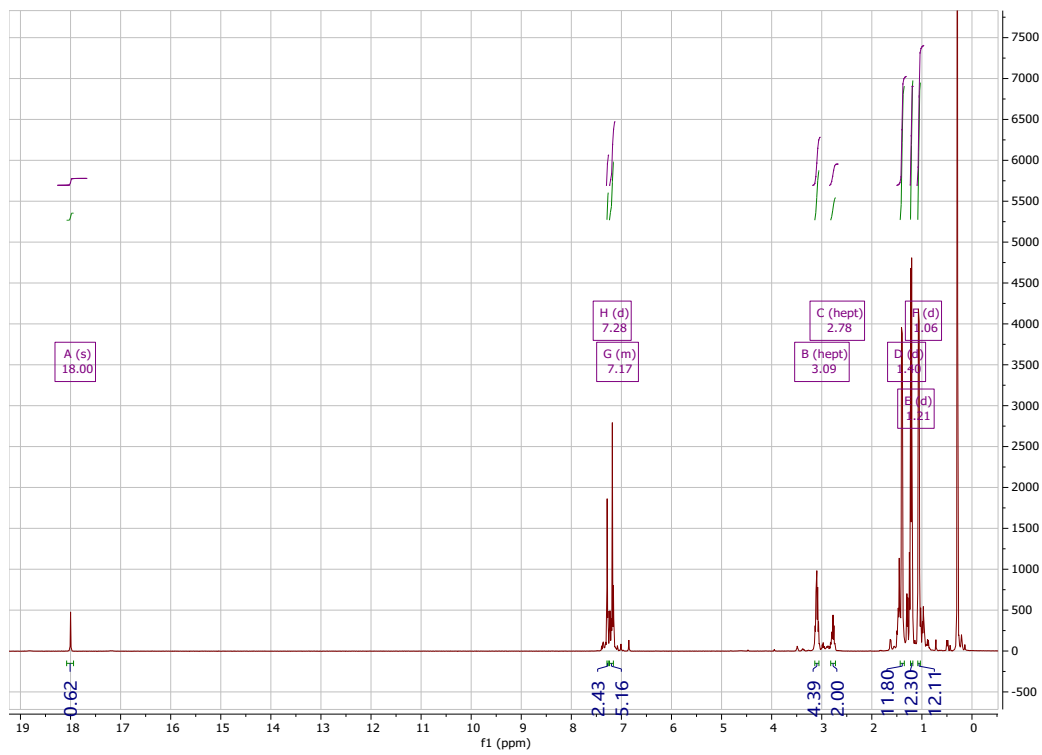
Figure S2. ^{1}H NMR spectrum of **1** in C_6D_6 at 298K.
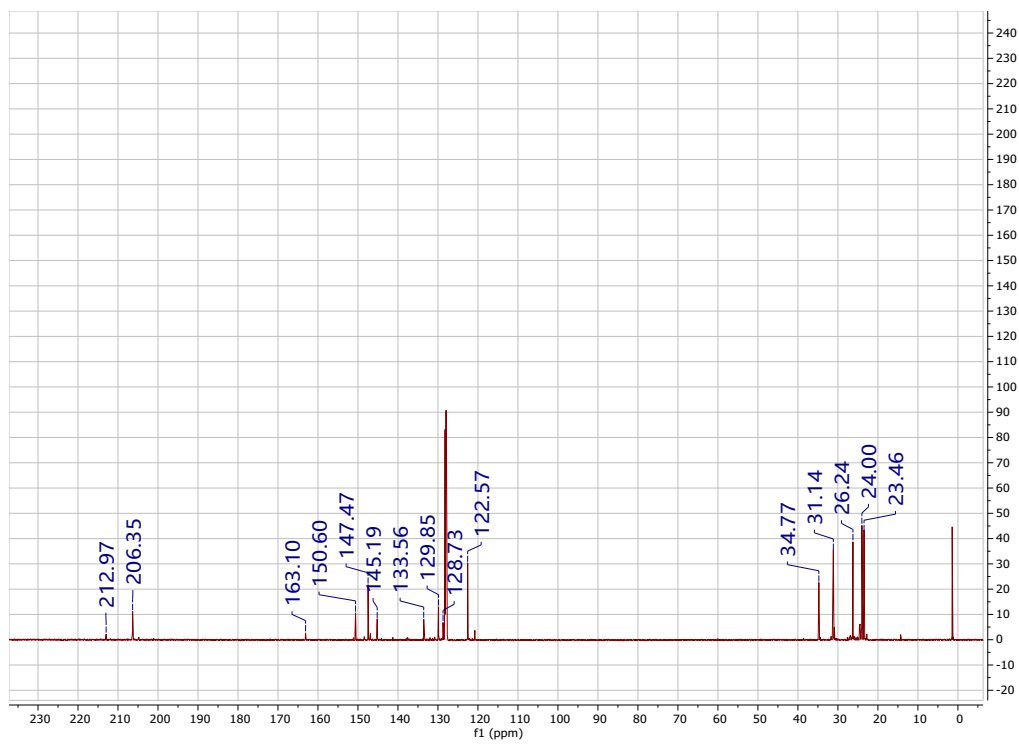
Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6 at 298K.
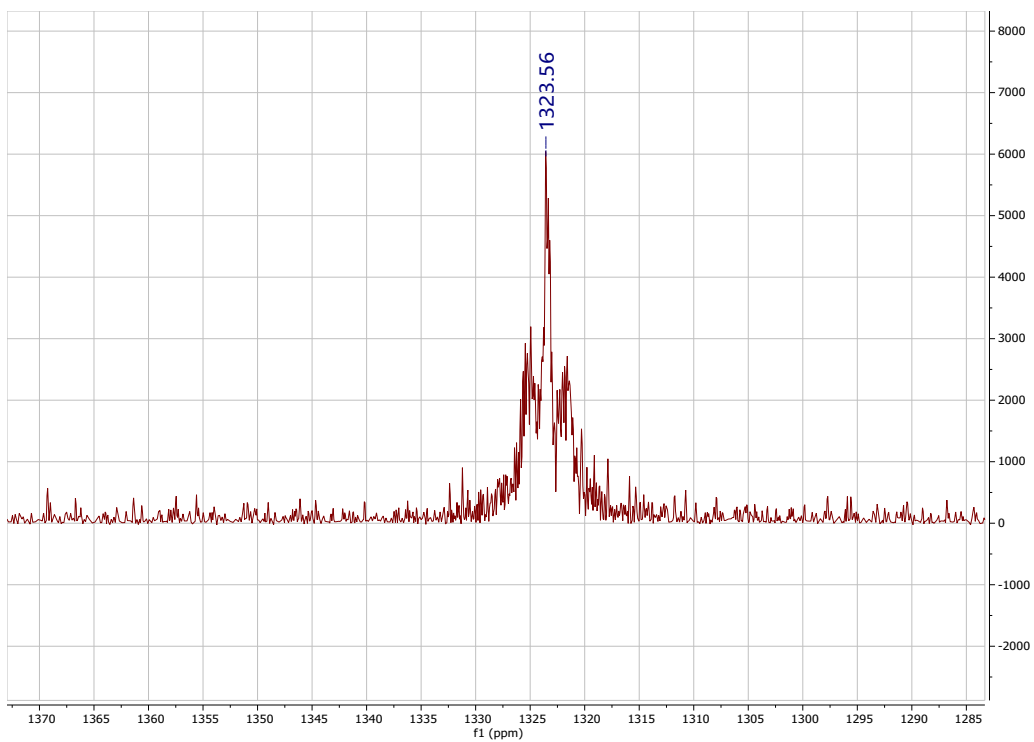
Figure S4. ^{119}Sn{^{1}H} NMR spectrum of **1** in C_6D_6 at 298K.
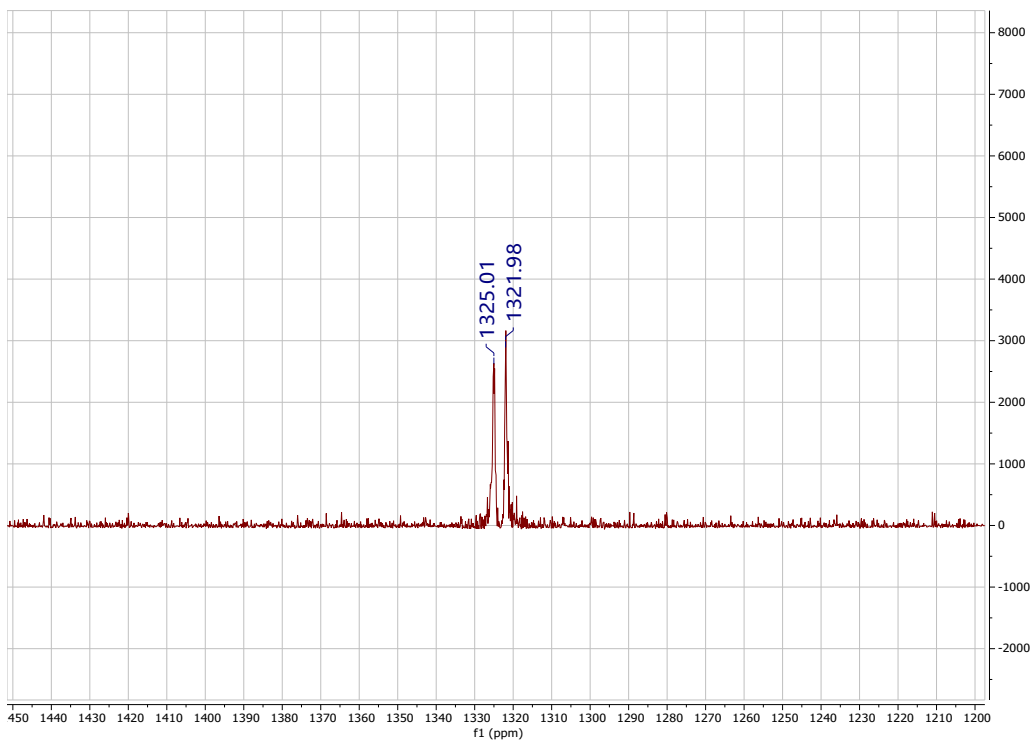
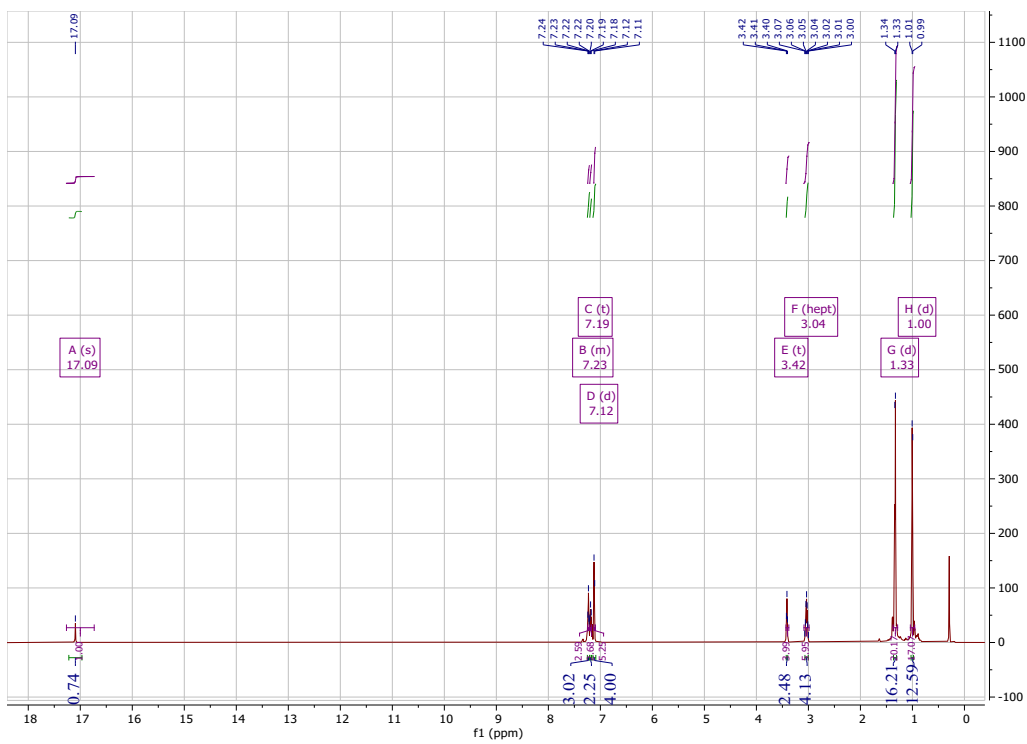**Figure S5.** ^{119}Sn NMR spectrum of **1** in C_6D_6 at 298K.

Figure S6. ^{1}H NMR spectrum of **2** in C$_6$D$_6$ at 298K.
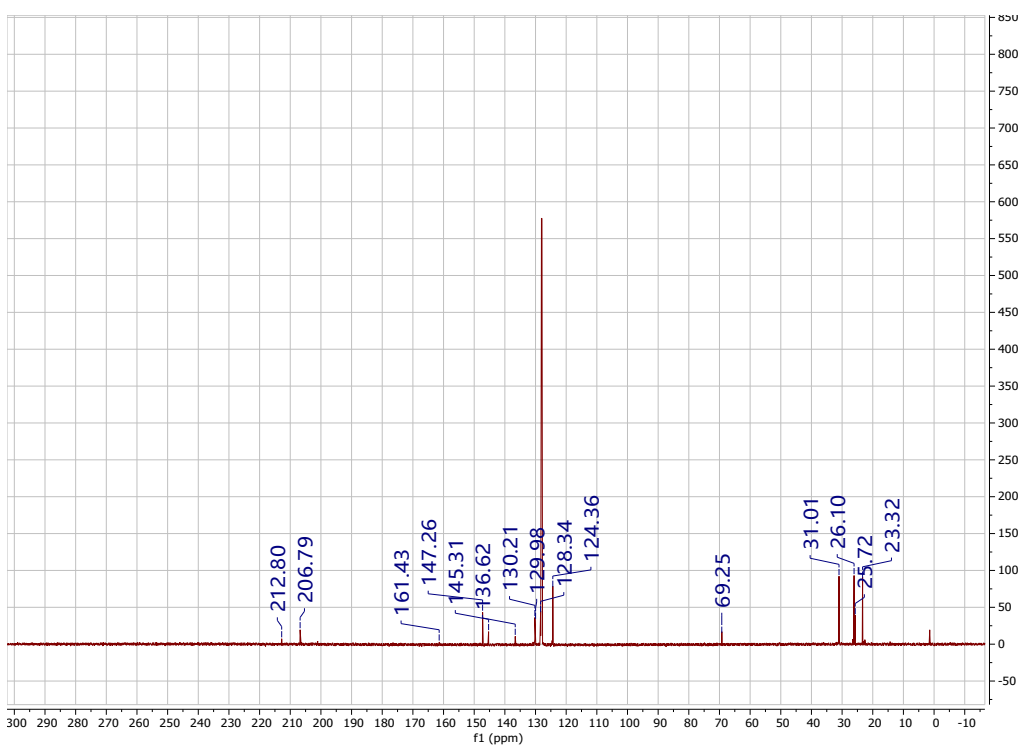
Figure S7. ^{13}C{^{1}H} NMR spectrum of **2** in C$_6$D$_6$ at 298K.
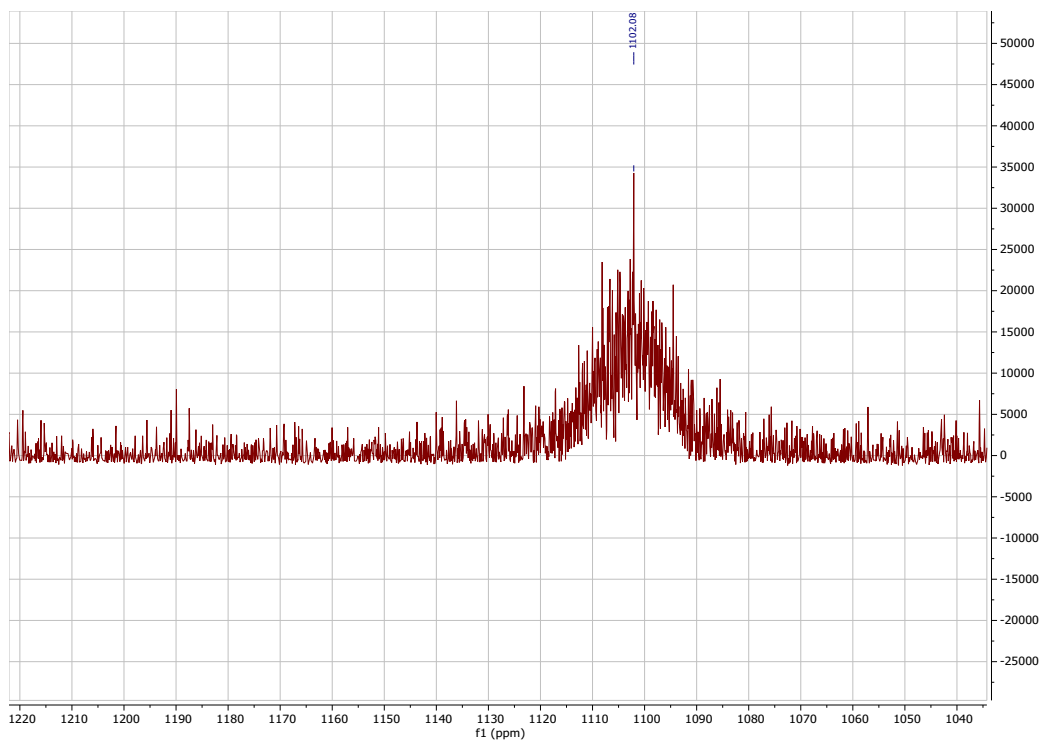
Figure S8. $^{119}Sn\{^1H\}$ NMR spectrum of **2** in C_6D_6 at 298K.
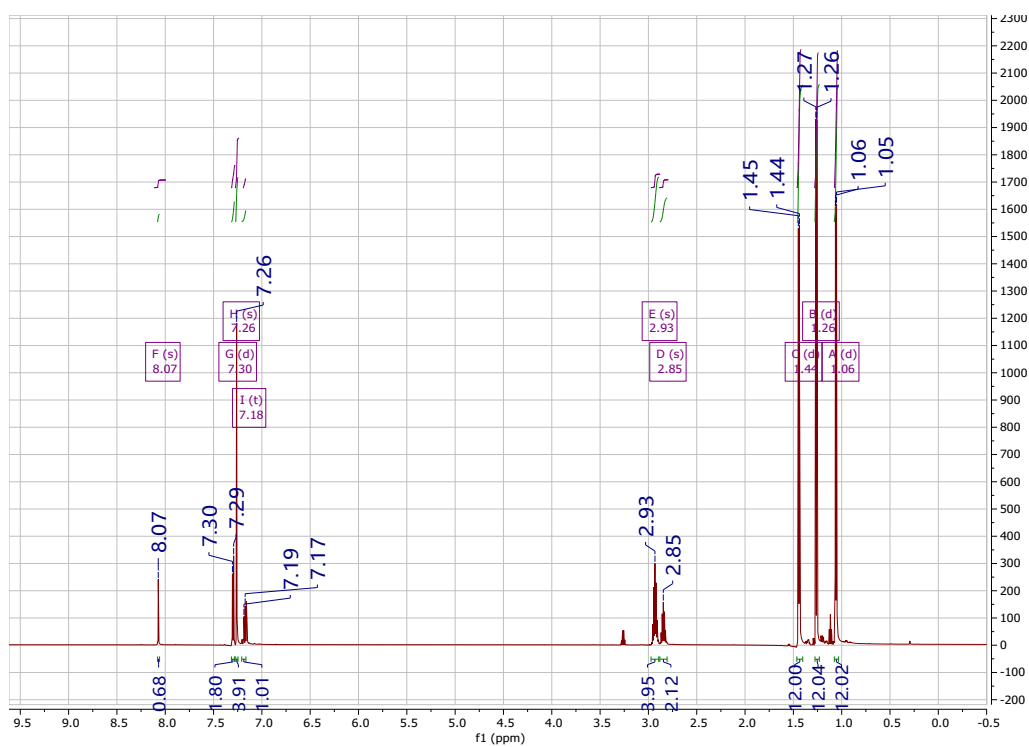
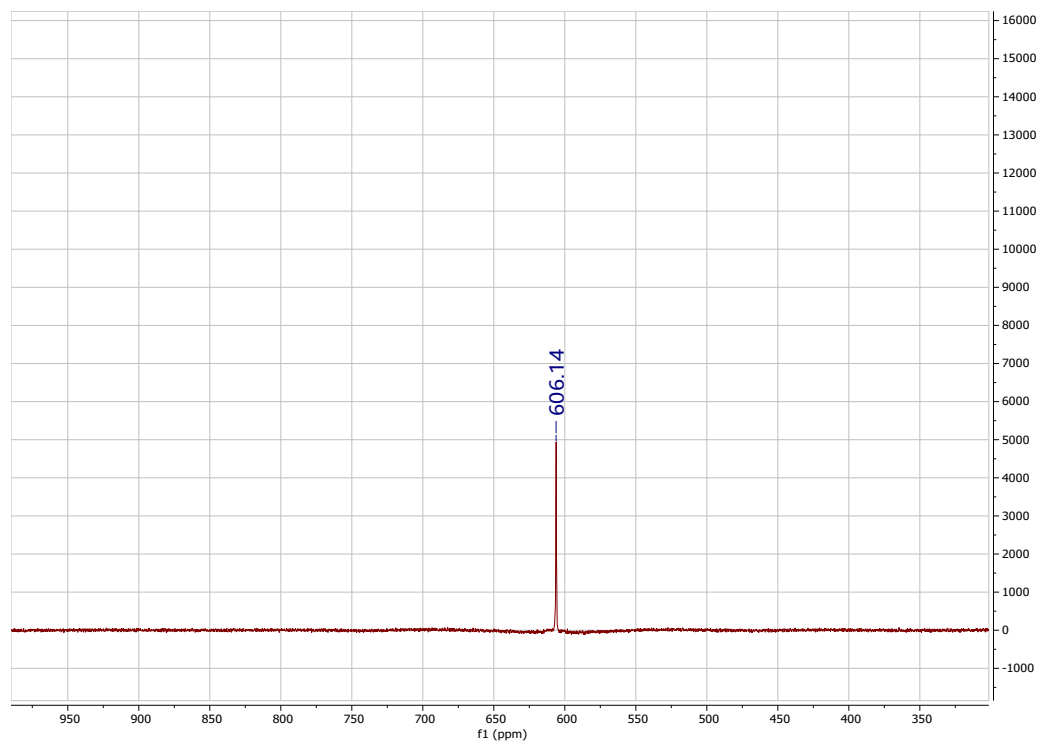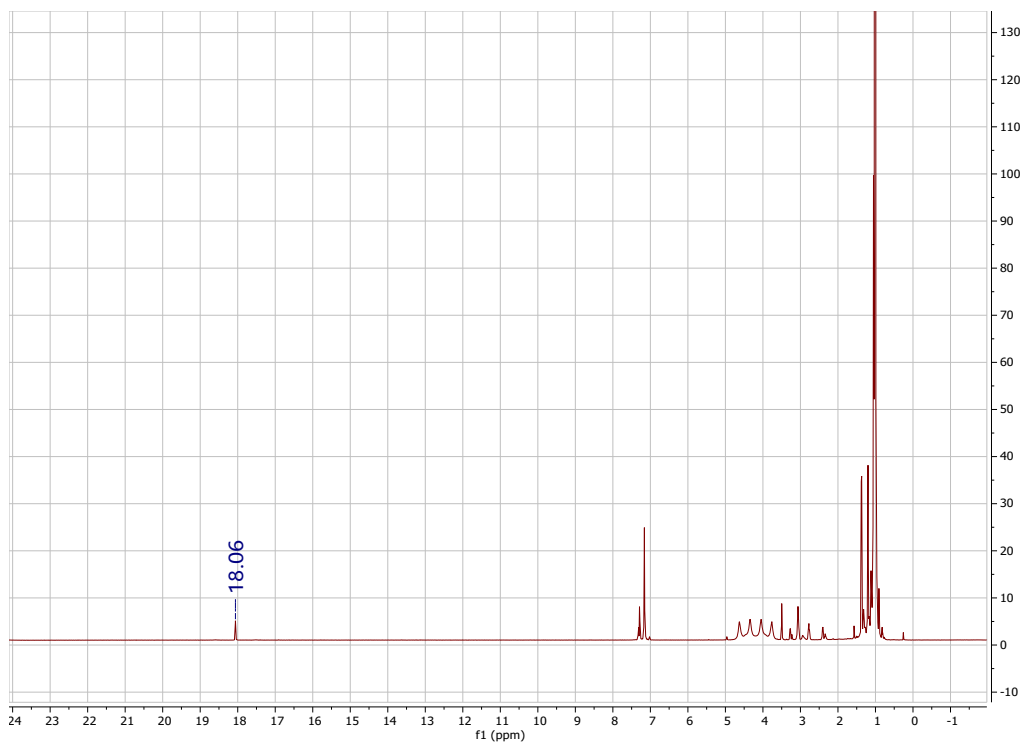**Figure S9.** ^1H NMR spectrum of **3** in C_6D_6 at 298K.
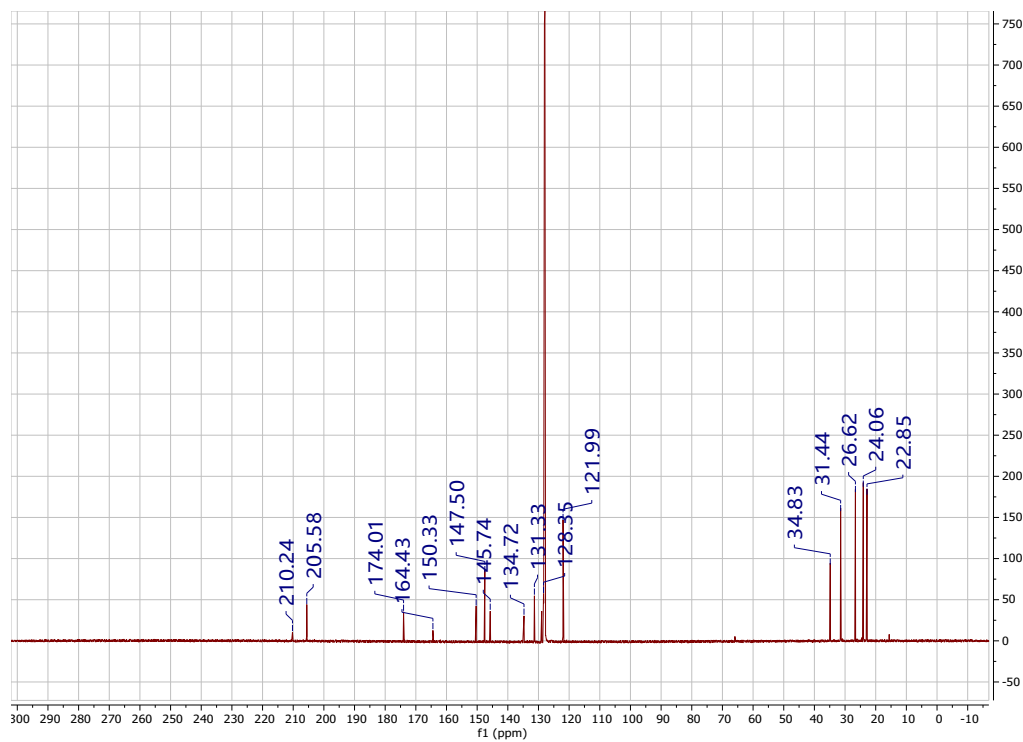
Figure S10. $^{13}C\{^1H\}$ NMR spectrum of **3** in C_6D_6 at 298K.

Figure S11. $^{119}Sn\{^1H\}$ NMR spectrum of **3** in C_6D_6 at 298K.

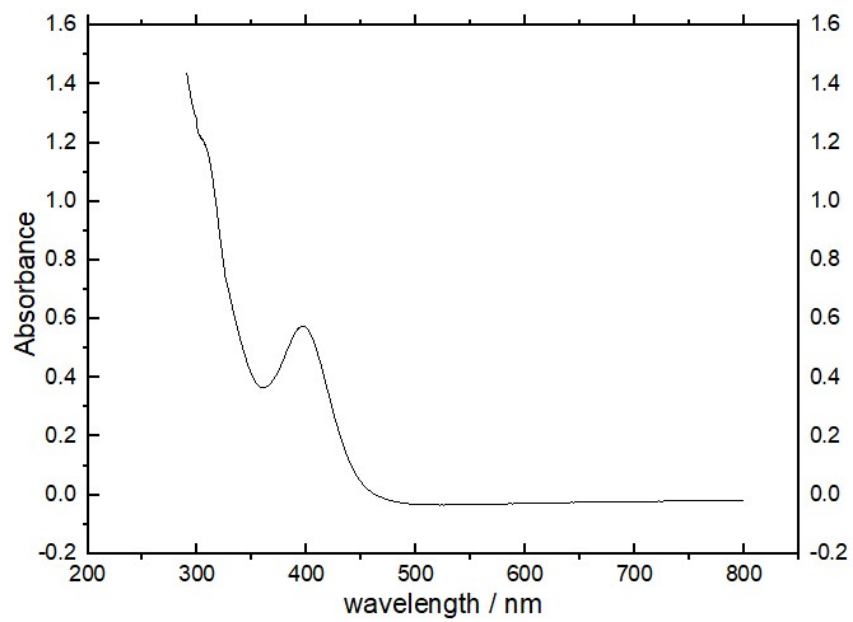**Figure S12.** ¹H NMR spectrum of **3** with HBpin (3 hours after mixing) in C_6D_6 at 298K.
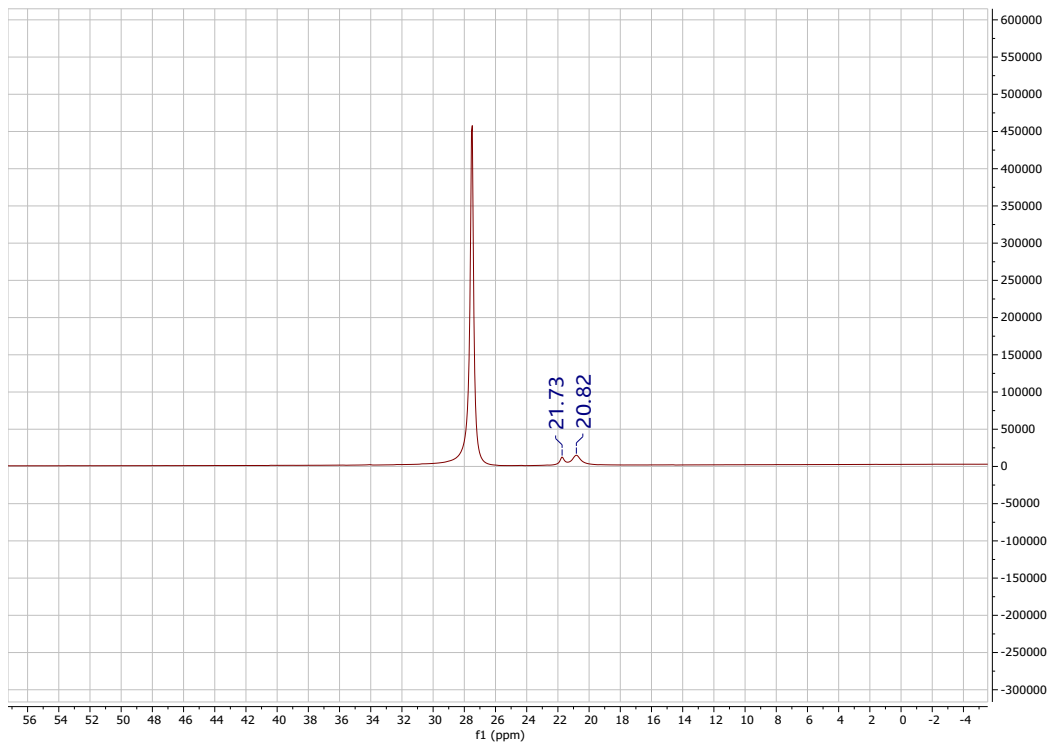
Figure S13. ¹¹B{¹H} NMR spectrum of **3** with HBpin (3 hours after mixing) in C_6D_6 at 298K.
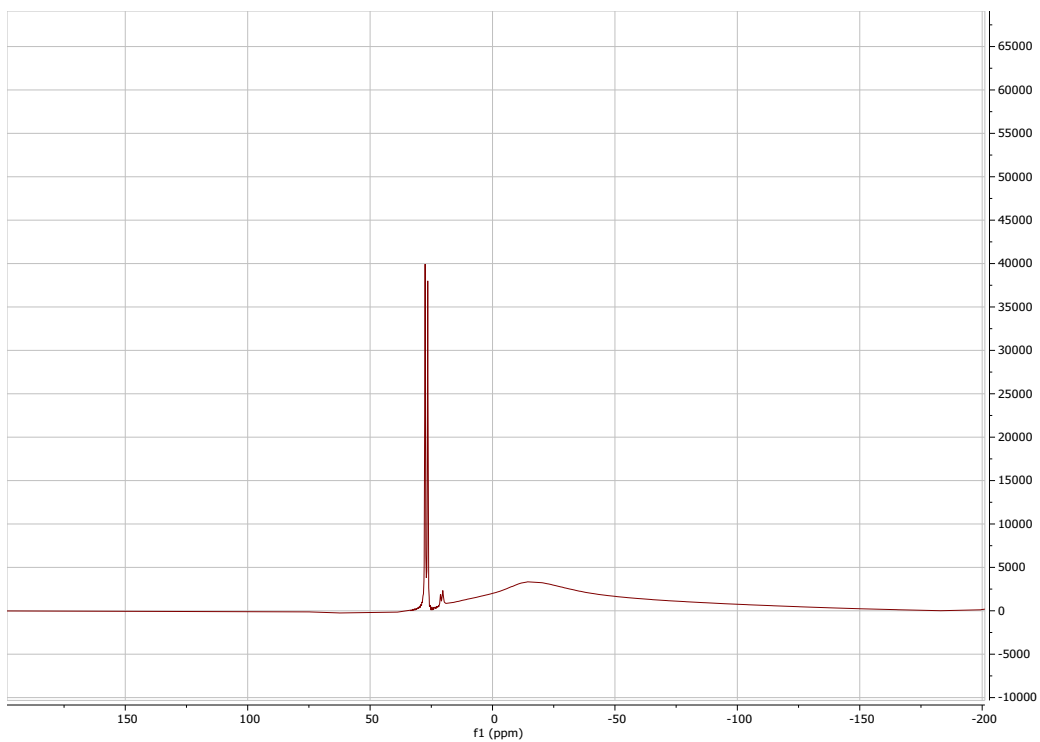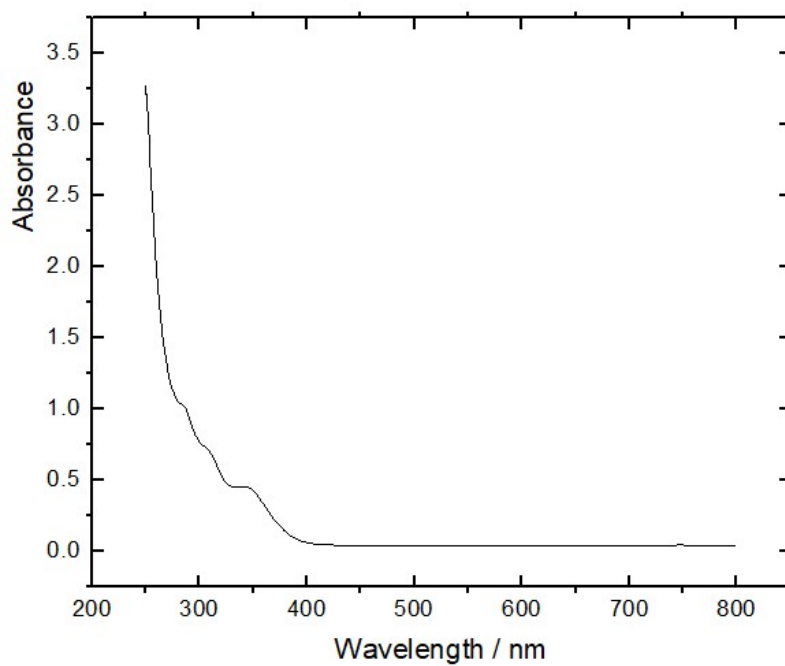
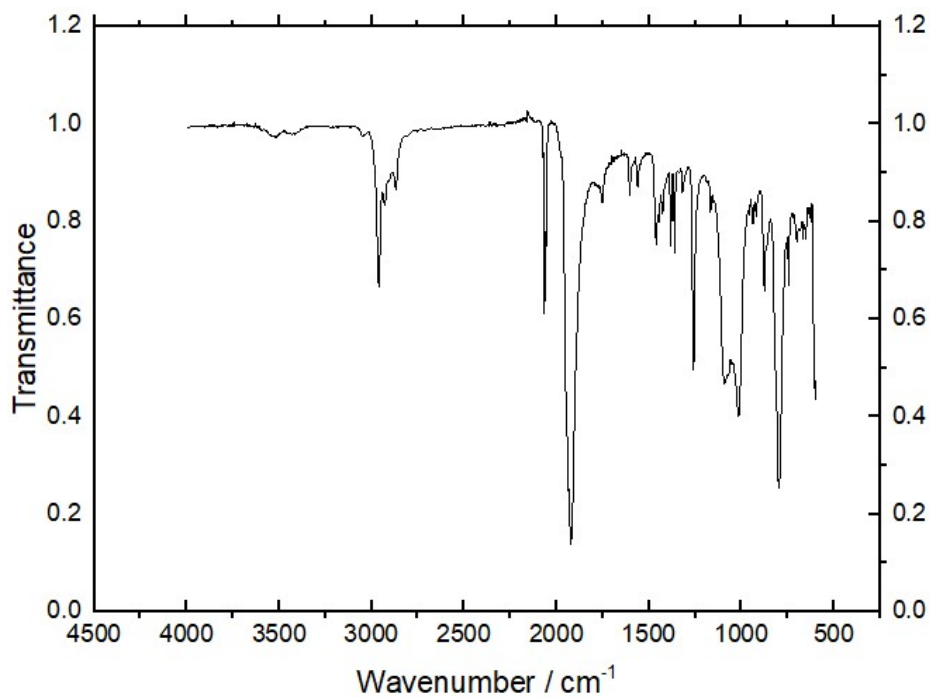**Figure S14.** ^{11}B NMR spectrum of **3** with HBpin (3 hours after mixing) in C$_6$D$_6$ at 298K.

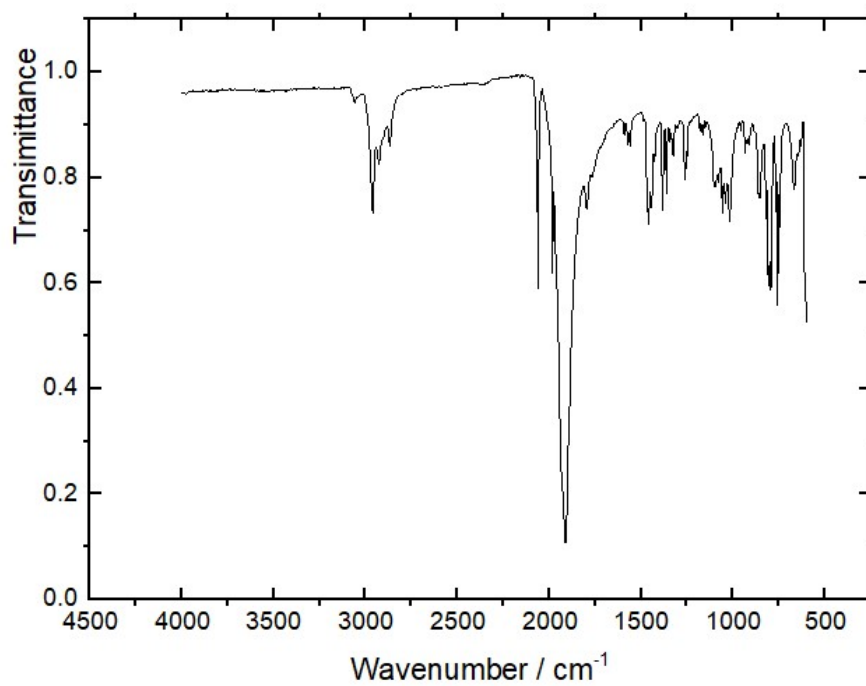**Figure S15.** UV-vis spectrum of **1** in hexanes (2.3*10^{-4} M) at 298K.
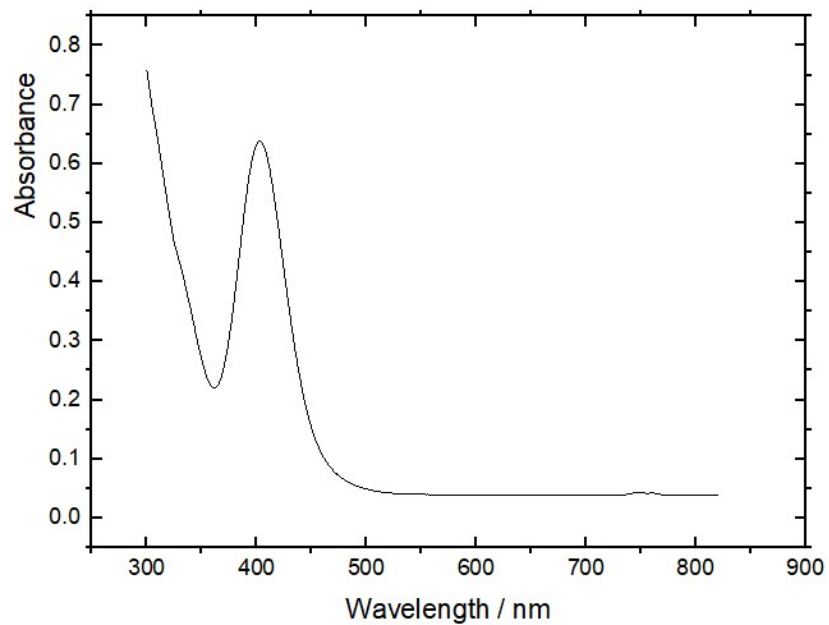
Figure S16. UV-vis spectrum of **2** in hexanes ($6.0*10^{-5}$ M) at 298K.

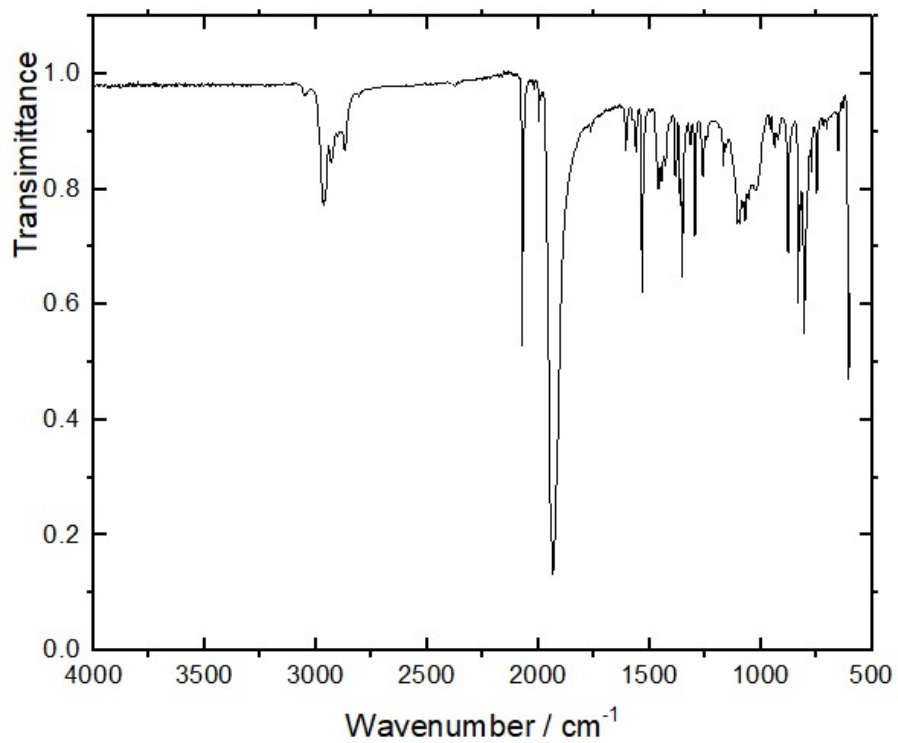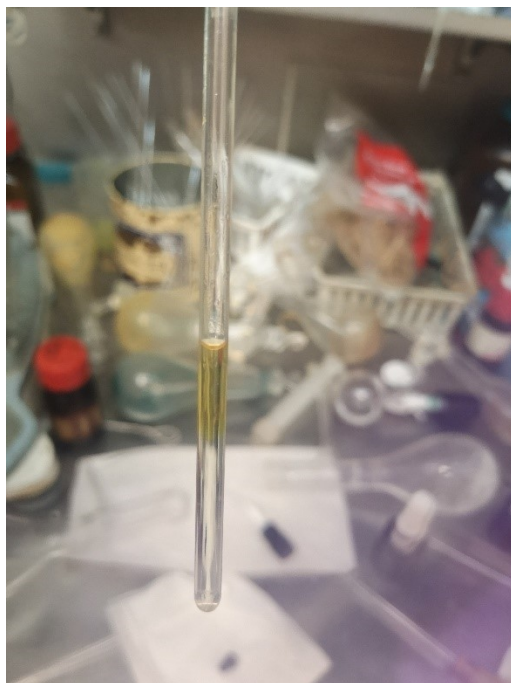**Figure S17.** UV-vis spectrum of **3** in hexanes ($5.4*10^{-5}$ M) at 298K.

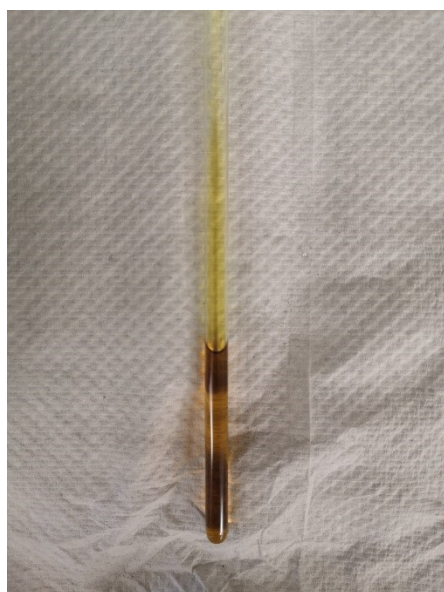**Figure S18.** ATR-FTIR spectrum of **1** at 298K.

Figure S19. ATR-FTIR spectrum of **2** at 298K.

Figure S20. ATR-FTIR spectrum of **3** at 298K.

Figure S21. Photo of addition HBpin into **3** in C_6D_6 at 298K.

Figure S22. Photo of addition HBpin into **3** (3 hours after) in C_6D_6 at 298K.

References

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