Supporting Information

N_3-ligated Nickel(II) Diketonate Complexes: Synthesis, Characterization and Evaluation of O_2 Reactivity

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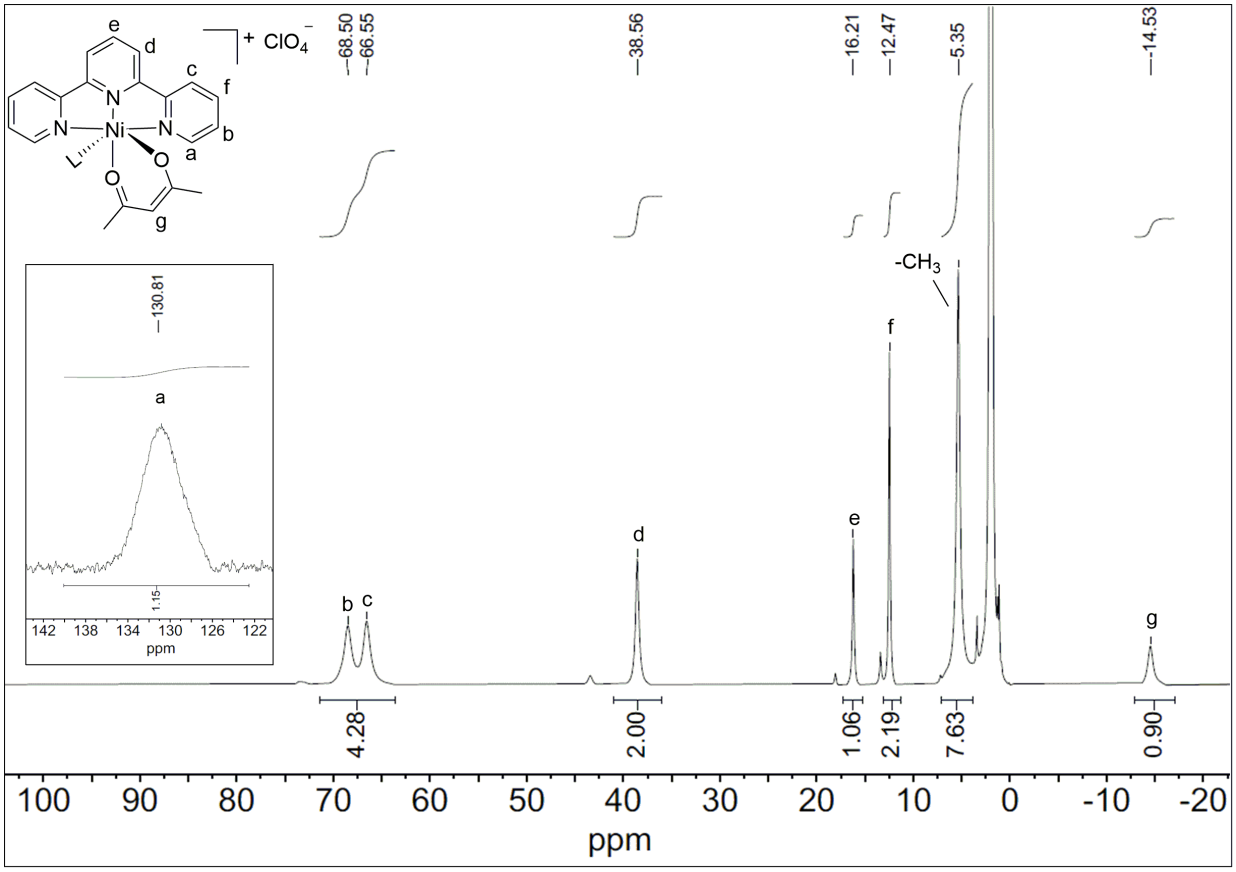


Figure S1: ^{1}H-NMR of **1** in CD_3CN (L= CH_3CN).

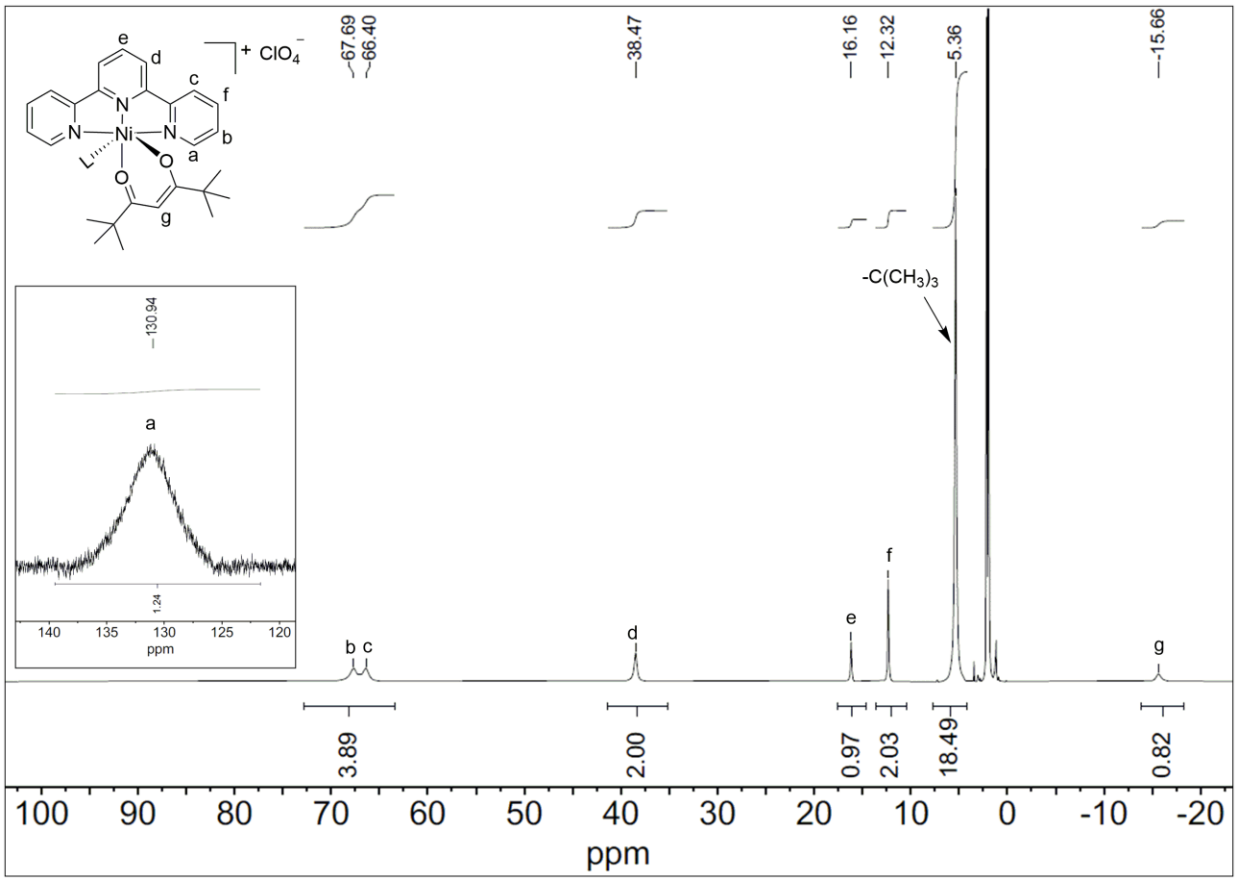


Figure S2: ^{1}H-NMR of **2** in CD_3CN (L= H_2O).

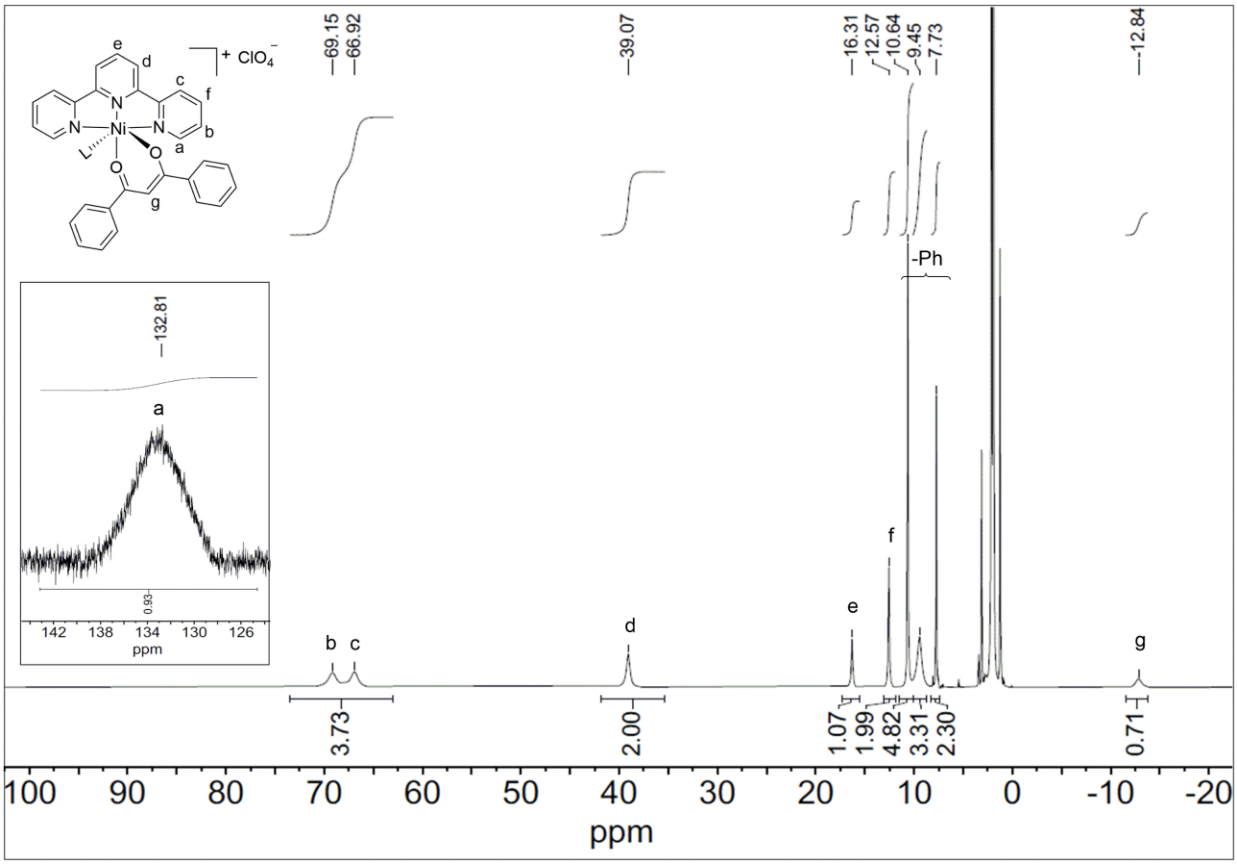


Figure S3: ^{1}H-NMR of **3** in CD_3CN (L= H_2O).

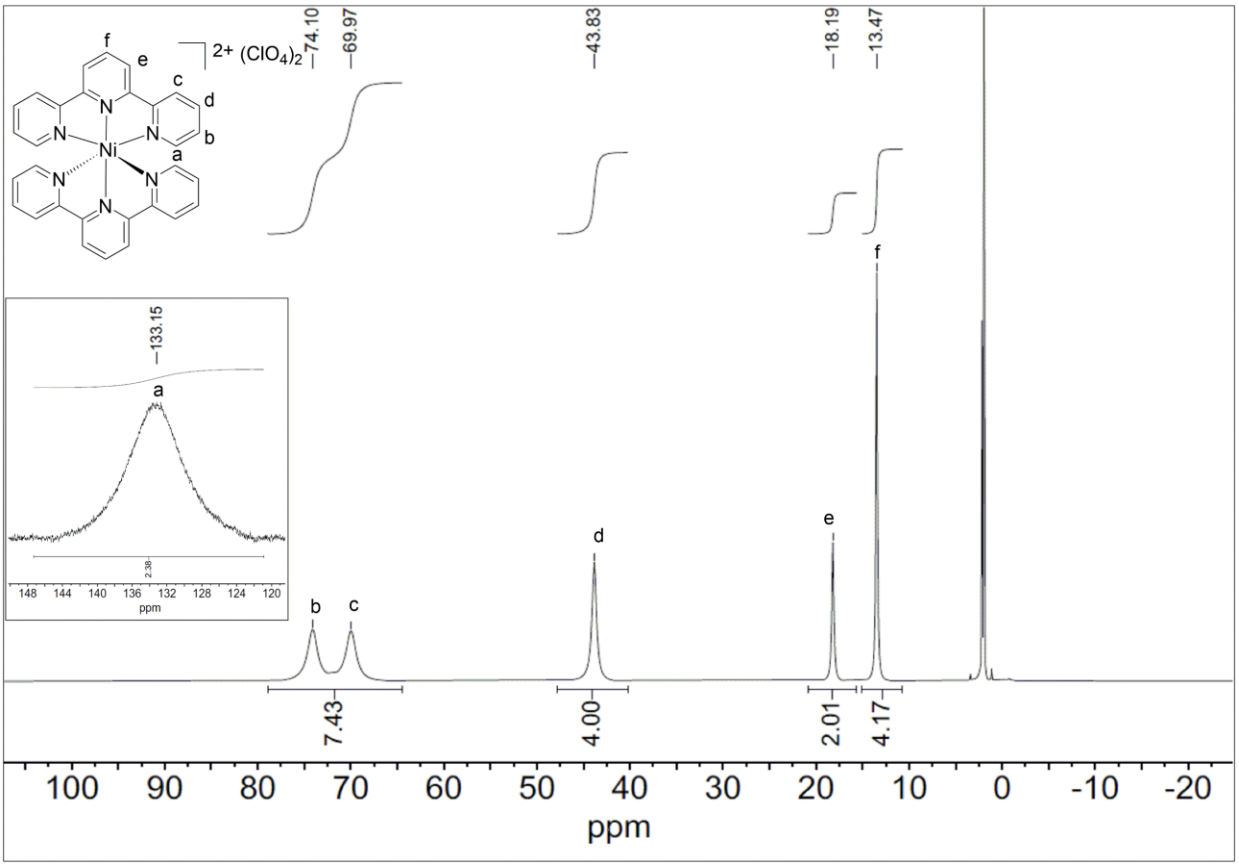


Figure S4: ^{1}H-NMR of **4** in CD_3CN.

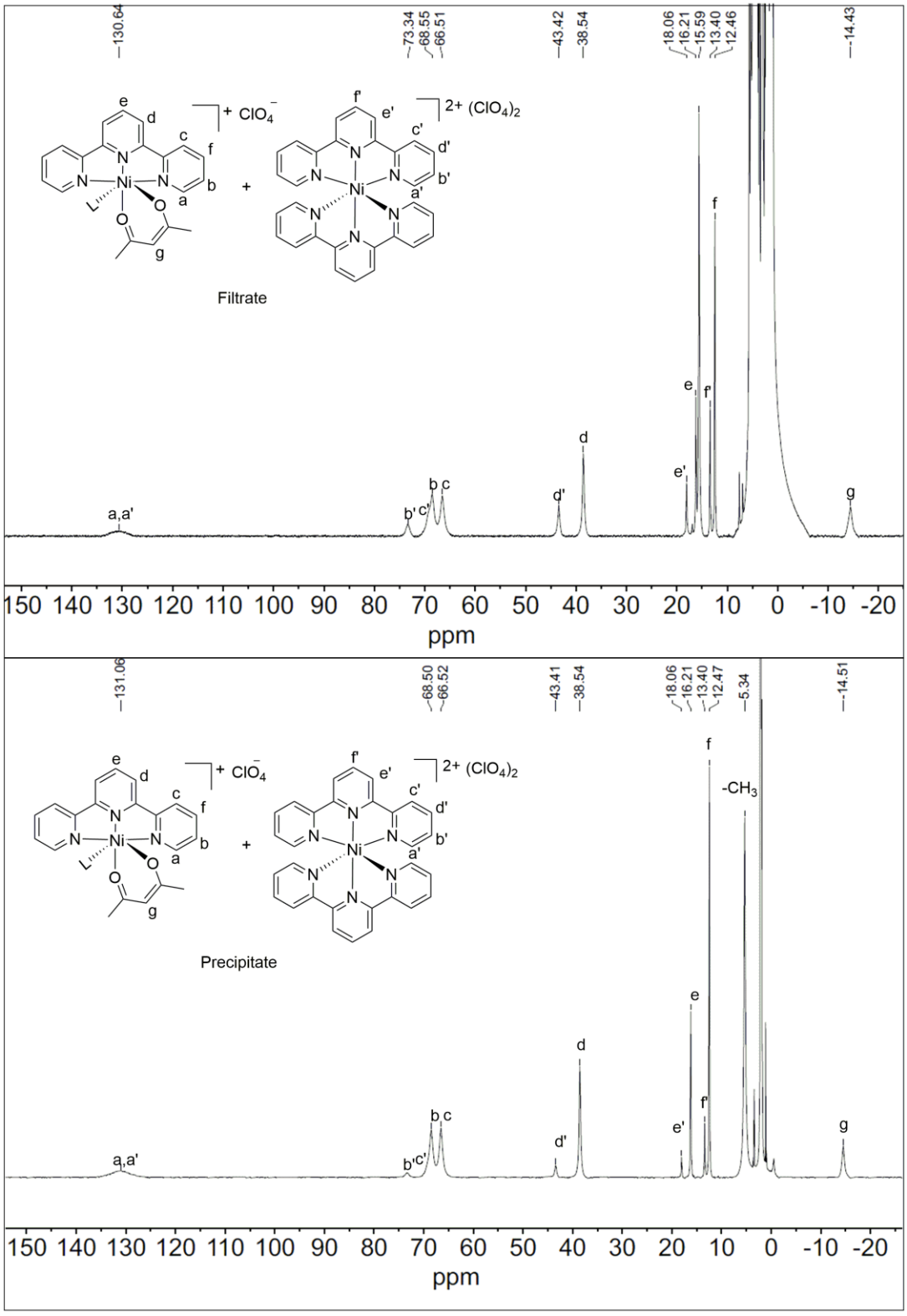


Figure S5: ^{1}H-NMR of filtrate (top) and precipitate (bottom) from the reaction mixture of **1** in CD_3CN.

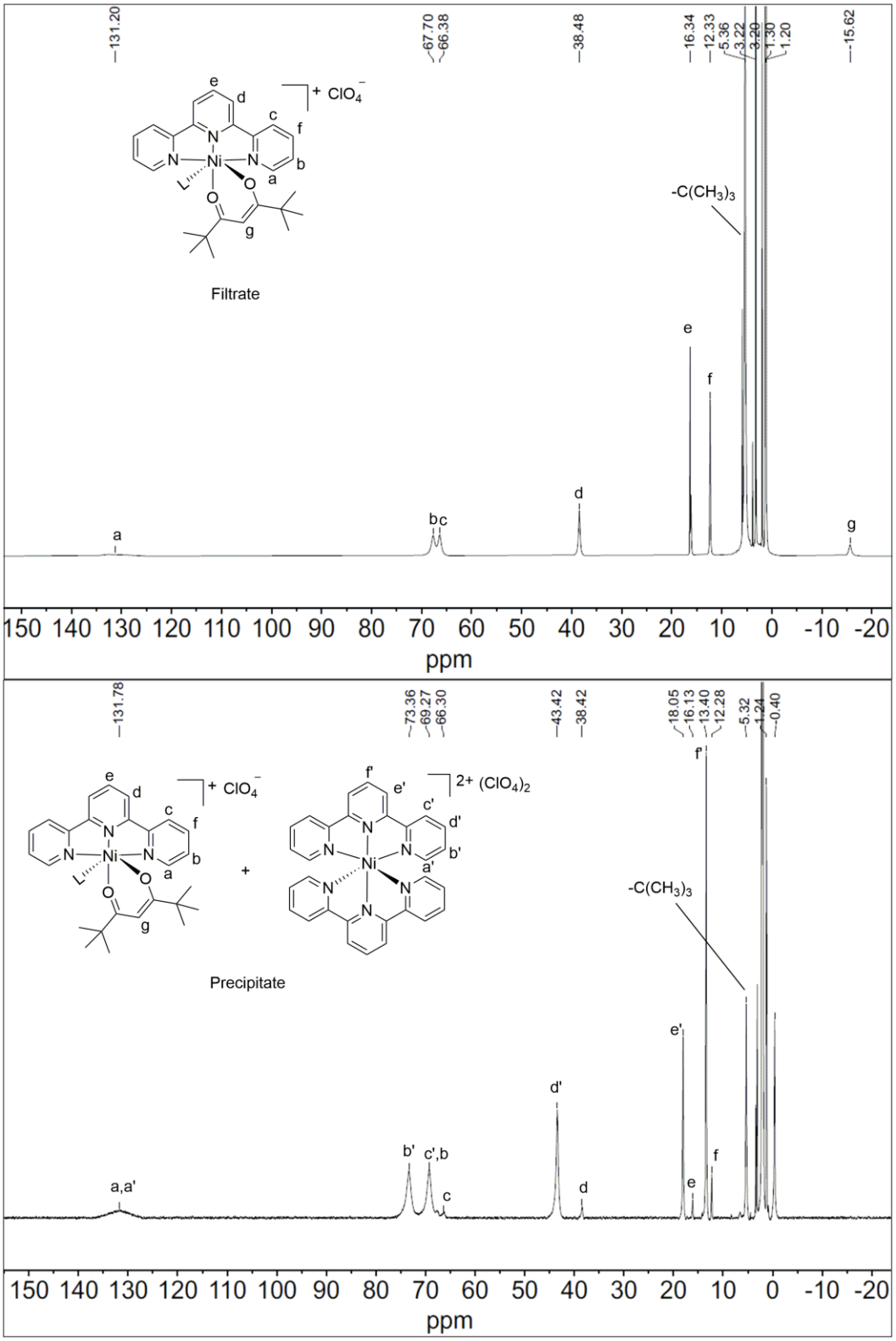


Figure S6: ^{1}H-NMR of filtrate (top) and precipitate (bottom) from the reaction mixture of **2** in CD_3CN.

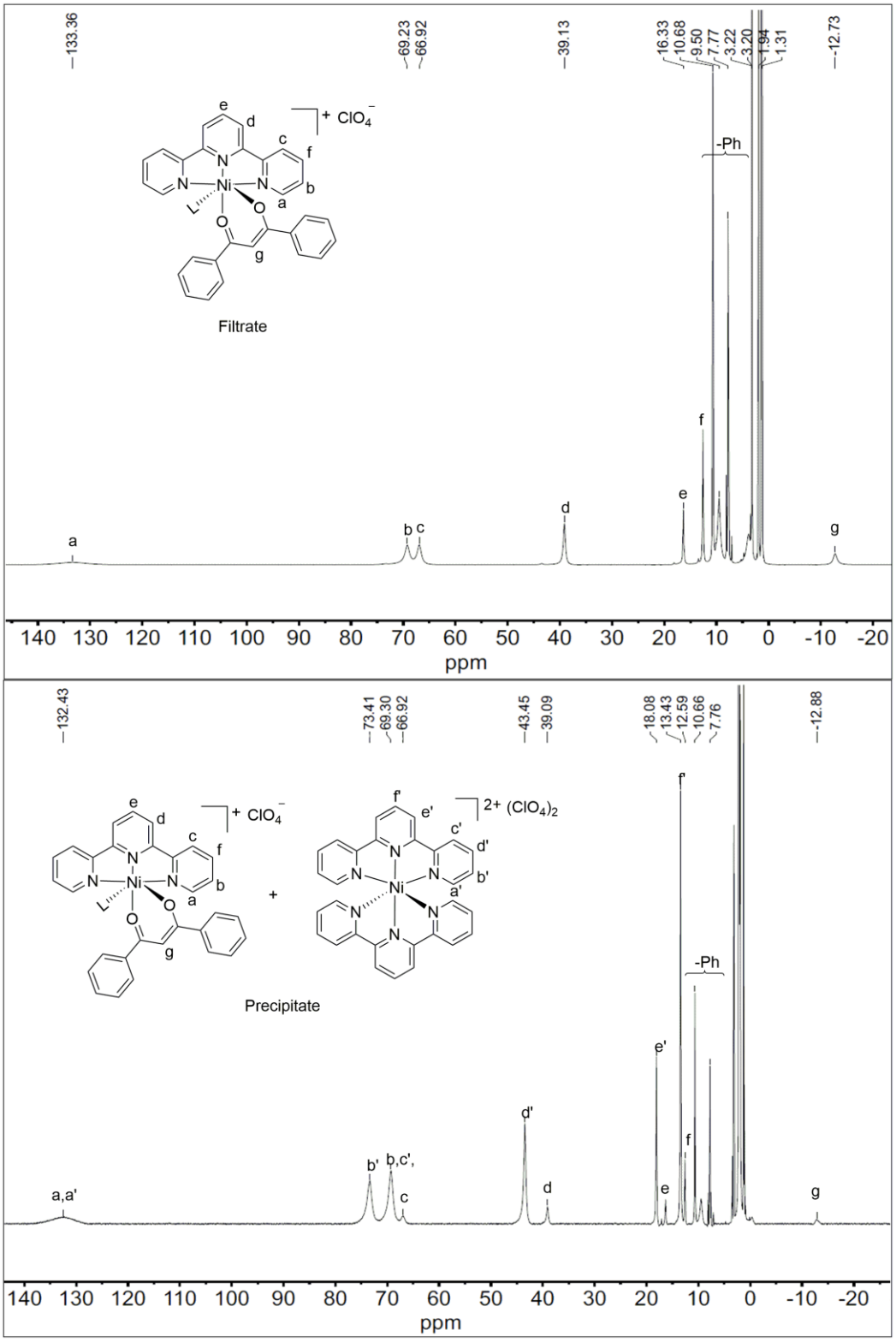


Figure S7: ^{1}H-NMR of filtrate (top) and precipitate (bottom) from the reaction mixture of **3** in CD_3CN.

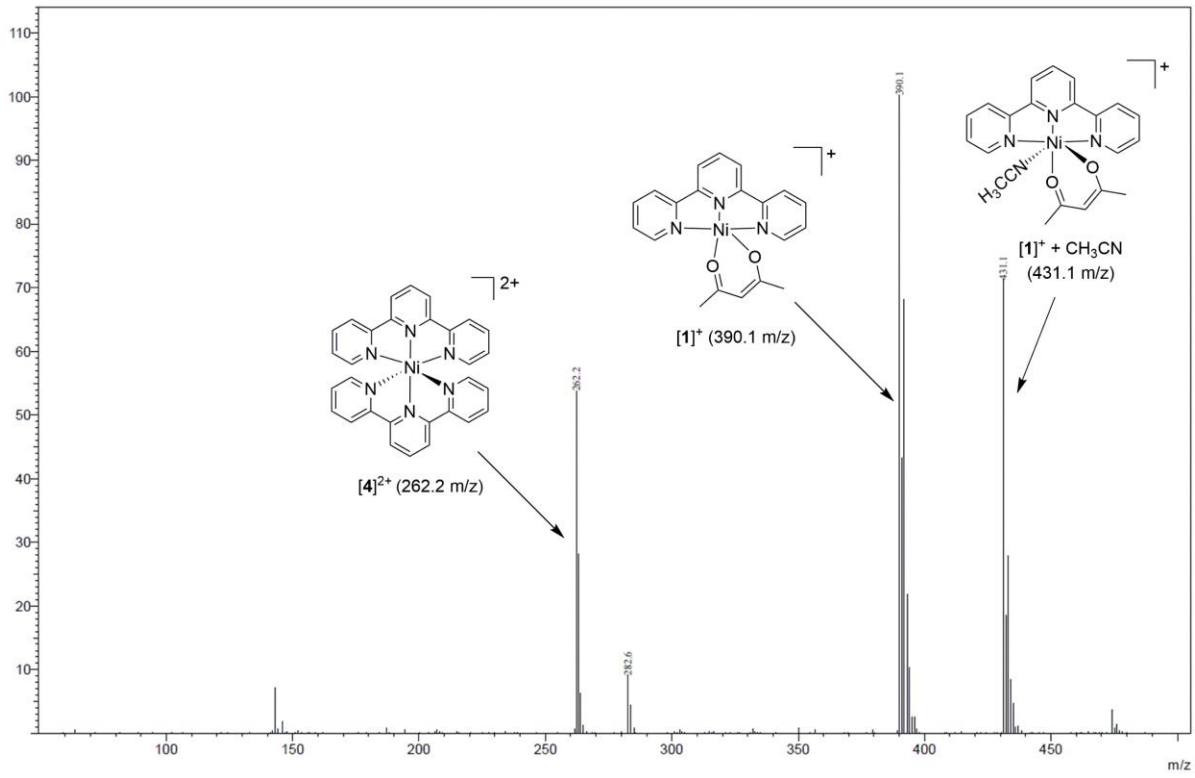


Figure S8: ESI-MS of **1** in CH_3CN.

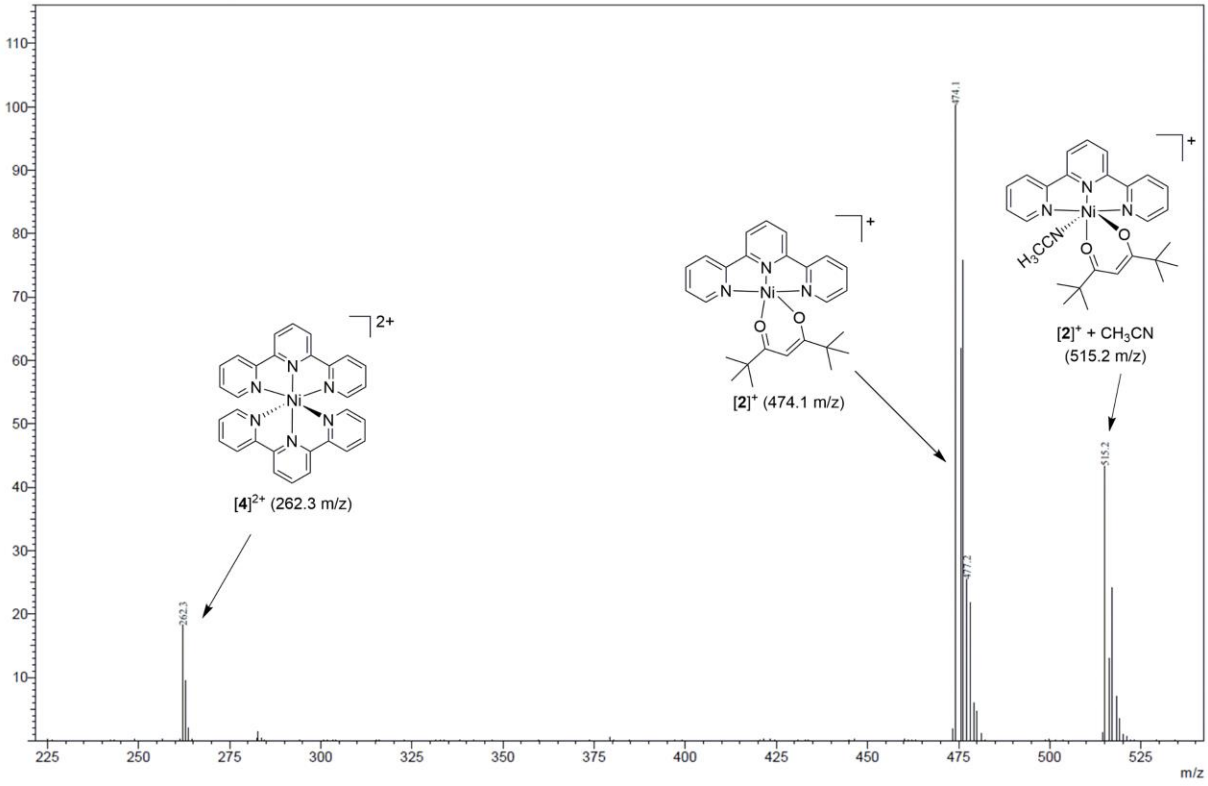


Figure S9: ESI-MS of **2** in CH_3CN.

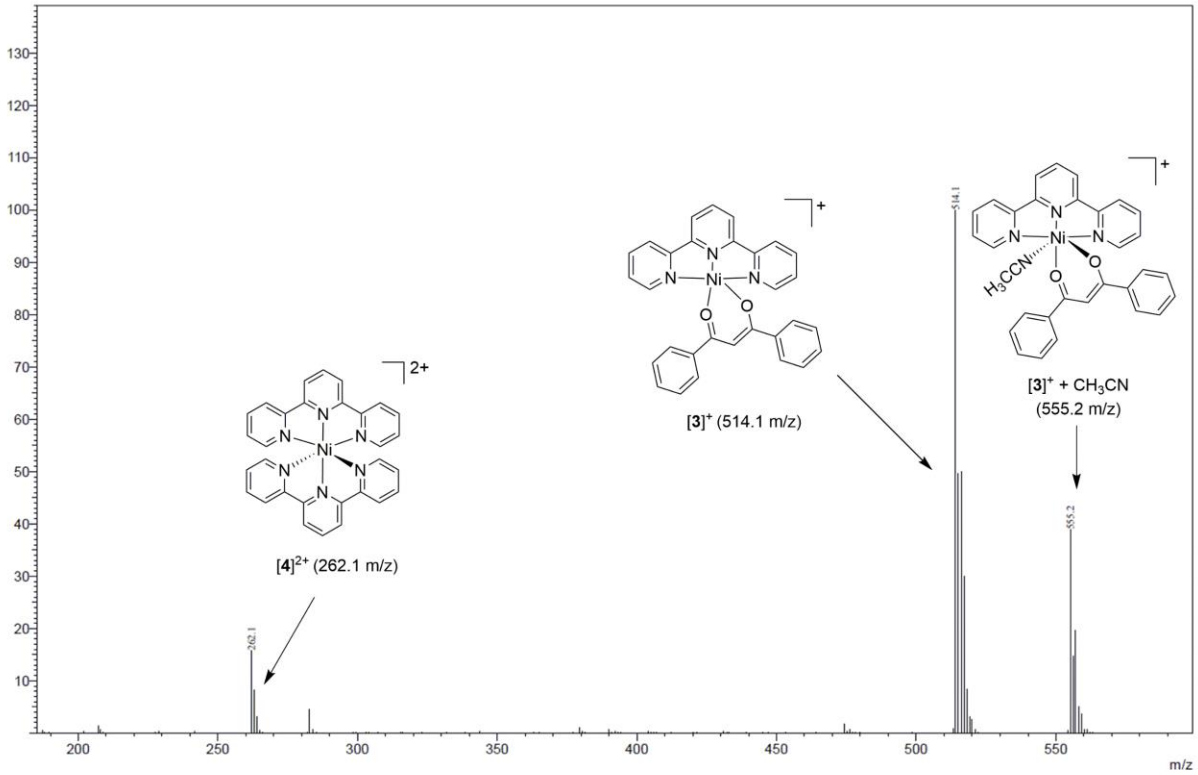


Figure S10: ESI-MS of **3** in CH_3CN.

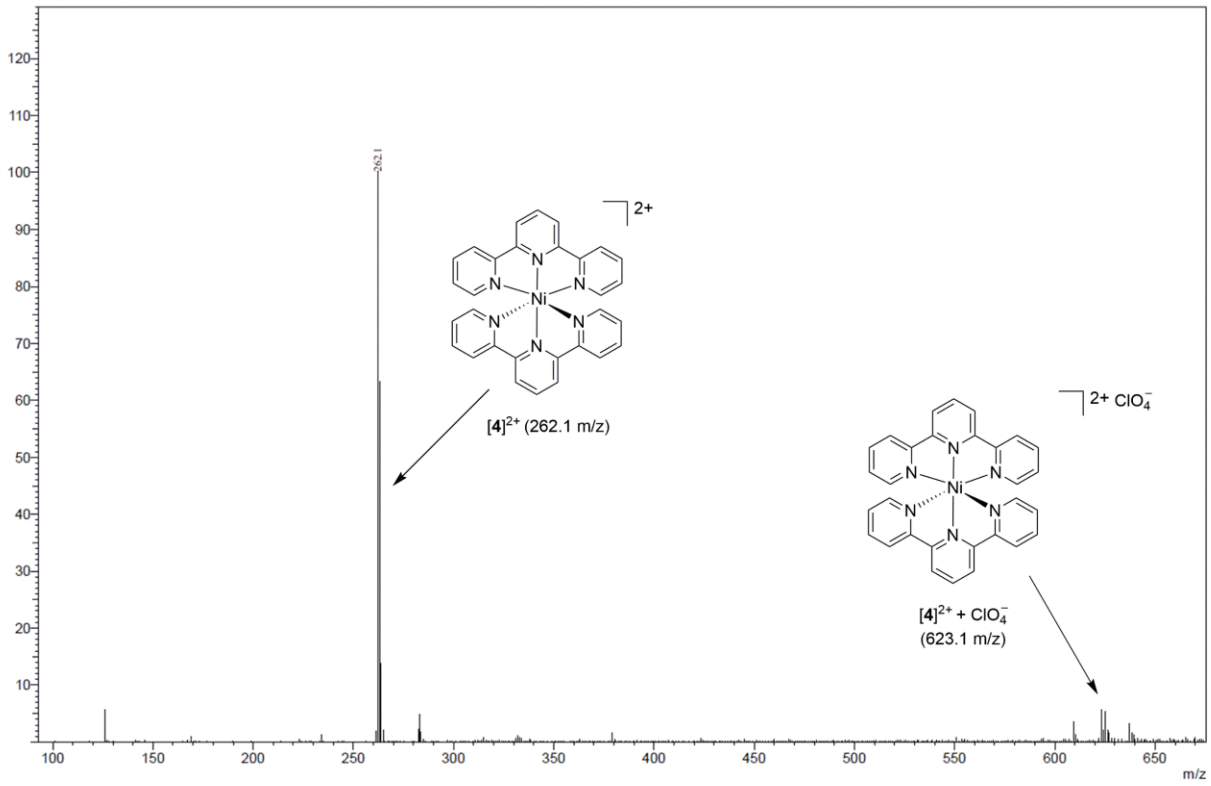


Figure S11: ESI-MS of **4** in CH_3CN.

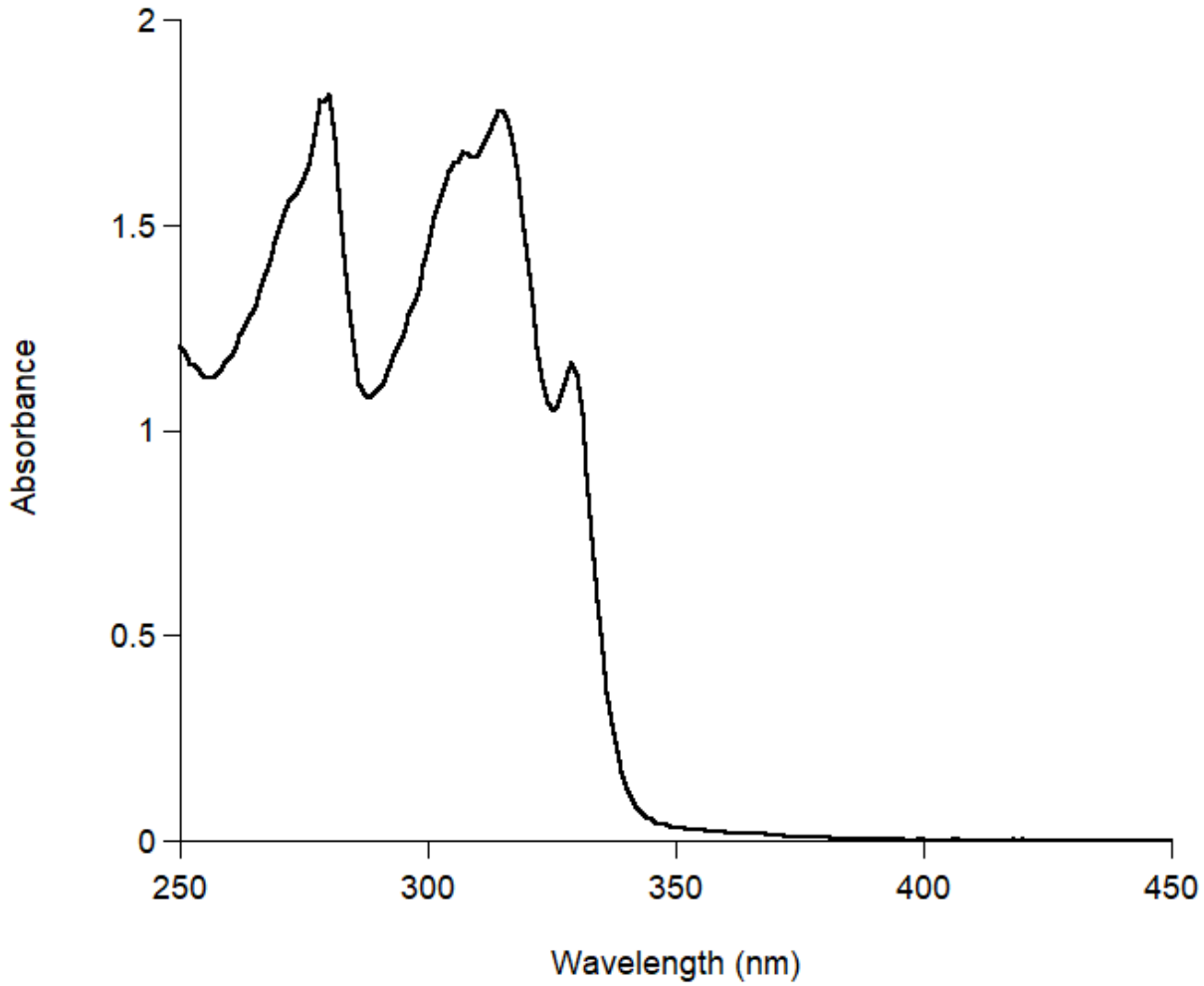


Figure S12: UV-Vis spectrum of **1** in CH_3CN (9.20×10^{-5} M)

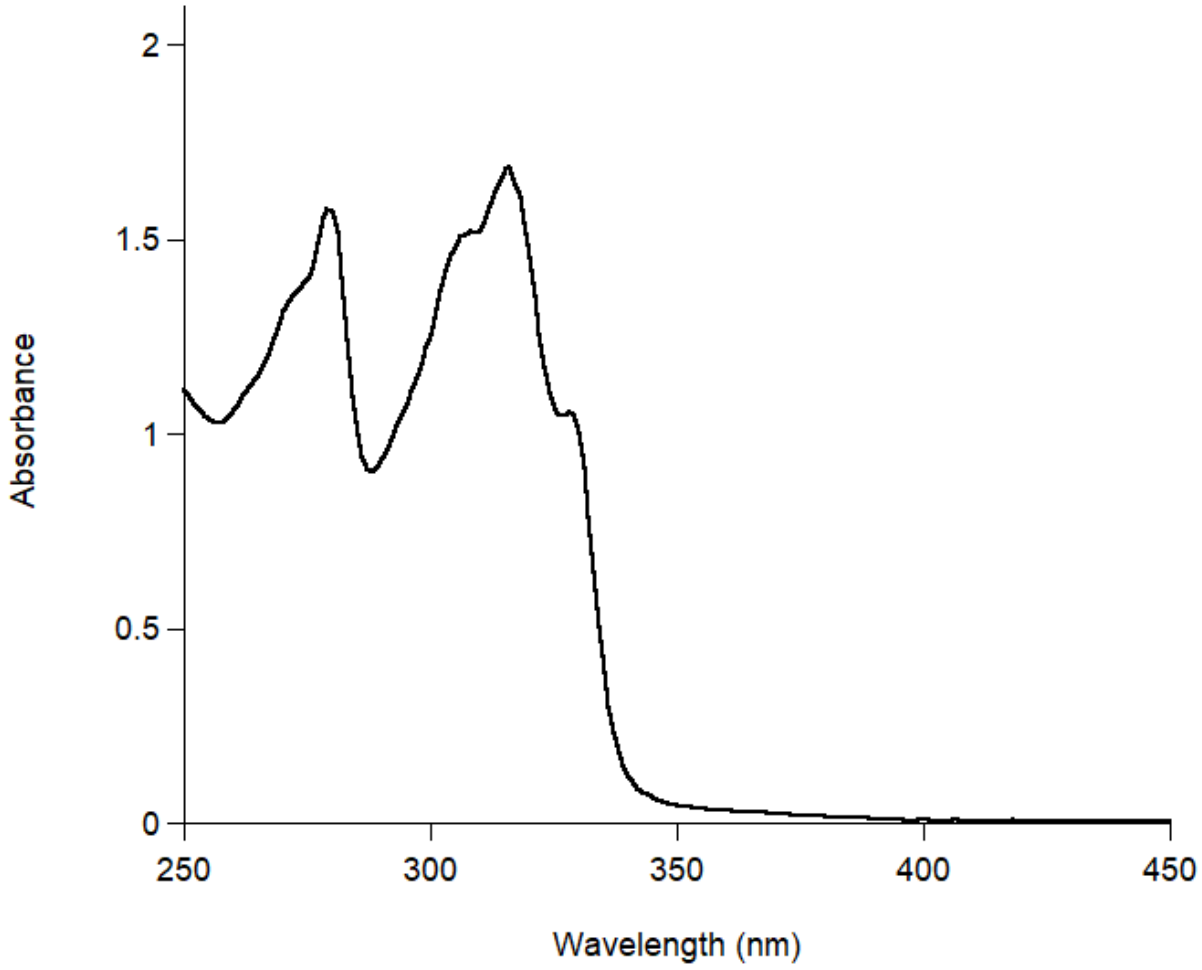


Figure S13: UV-Vis spectrum of **2** in CH_3CN ($7.24x10^{-5}$ M)

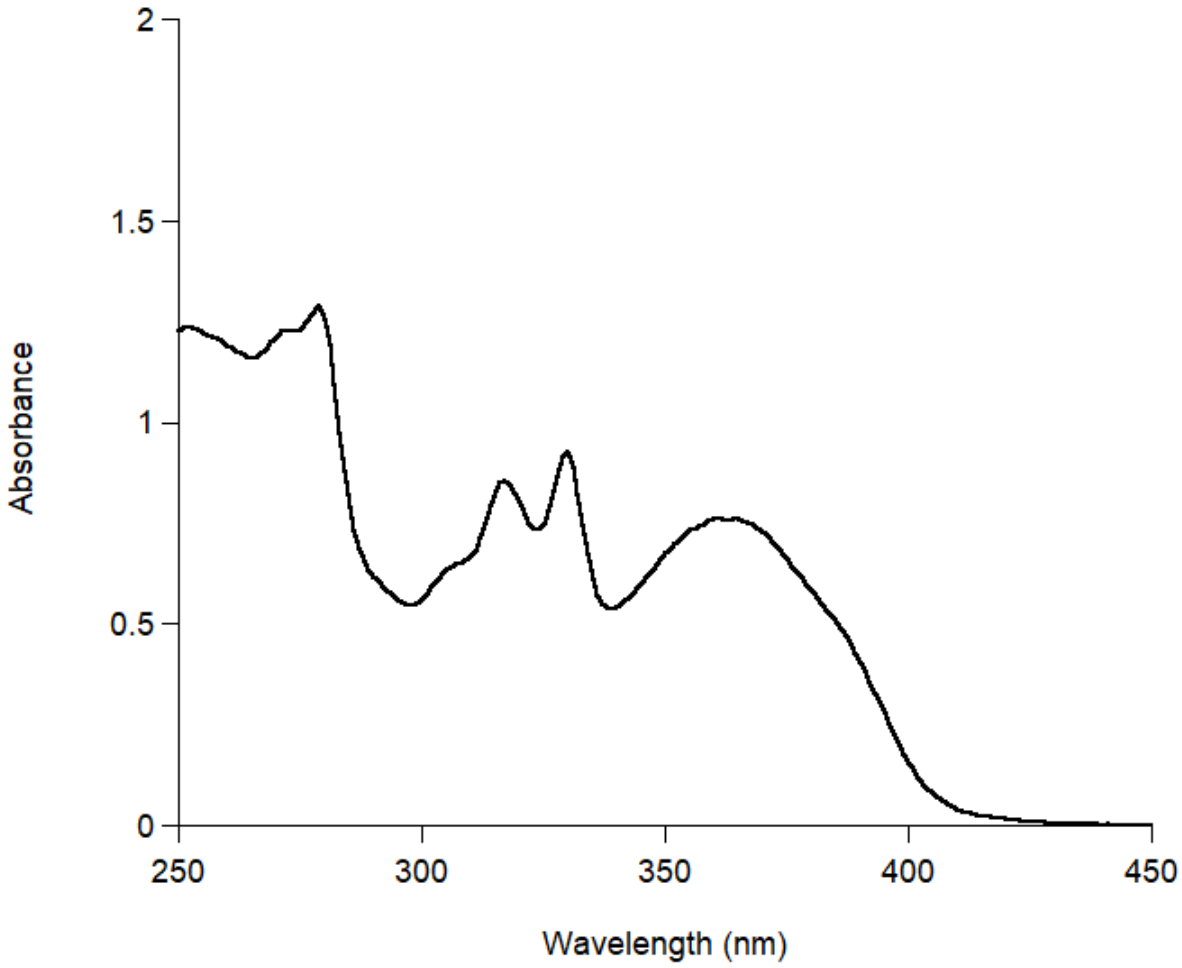


Figure S14: UV-Vis spectrum of **3** in CH_3CN ($6.79x10^{-5}$ M)

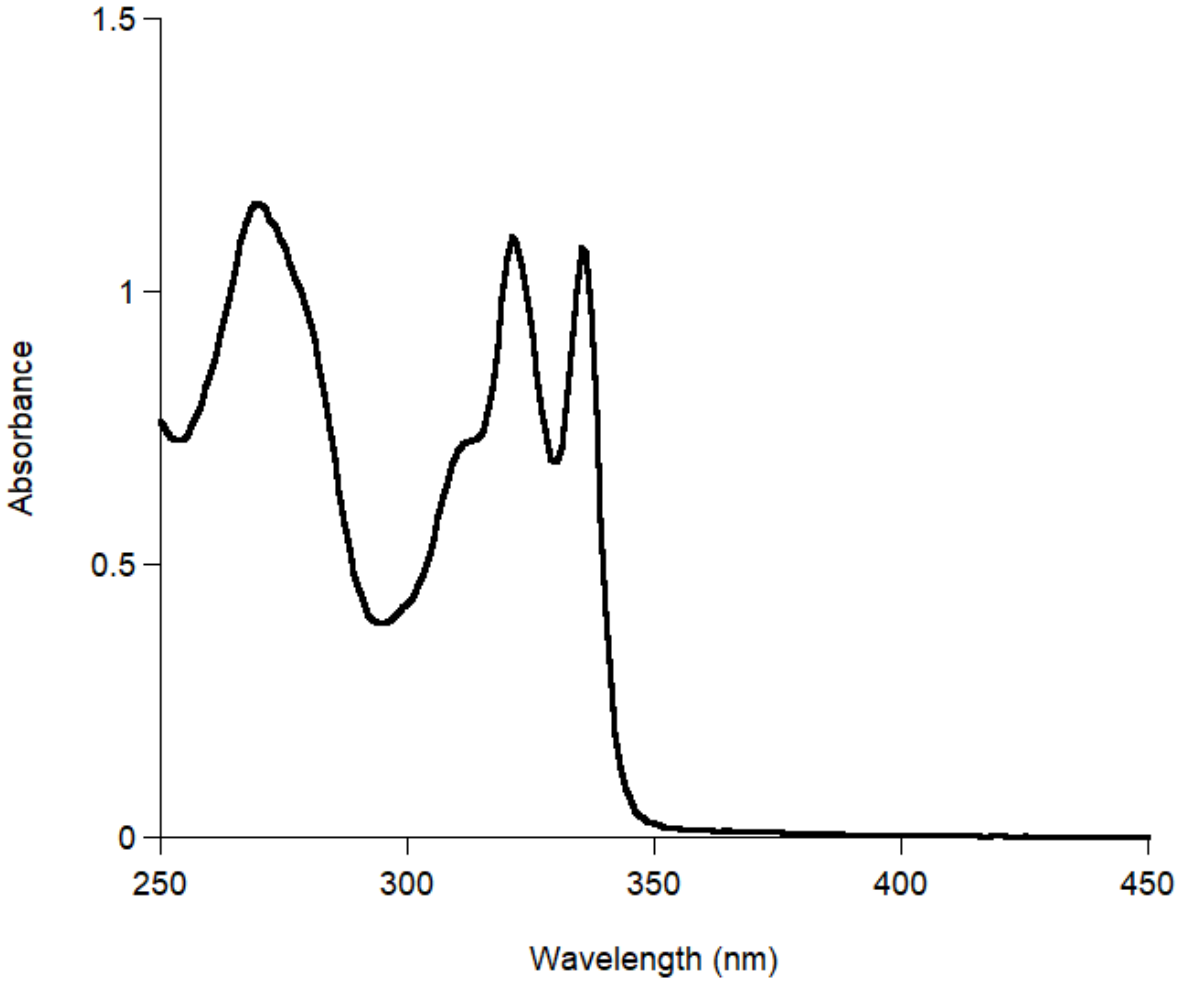


Figure S15: UV-Vis spectrum of **4** in CH_3CN ($3.85x10^{-5}$ M)

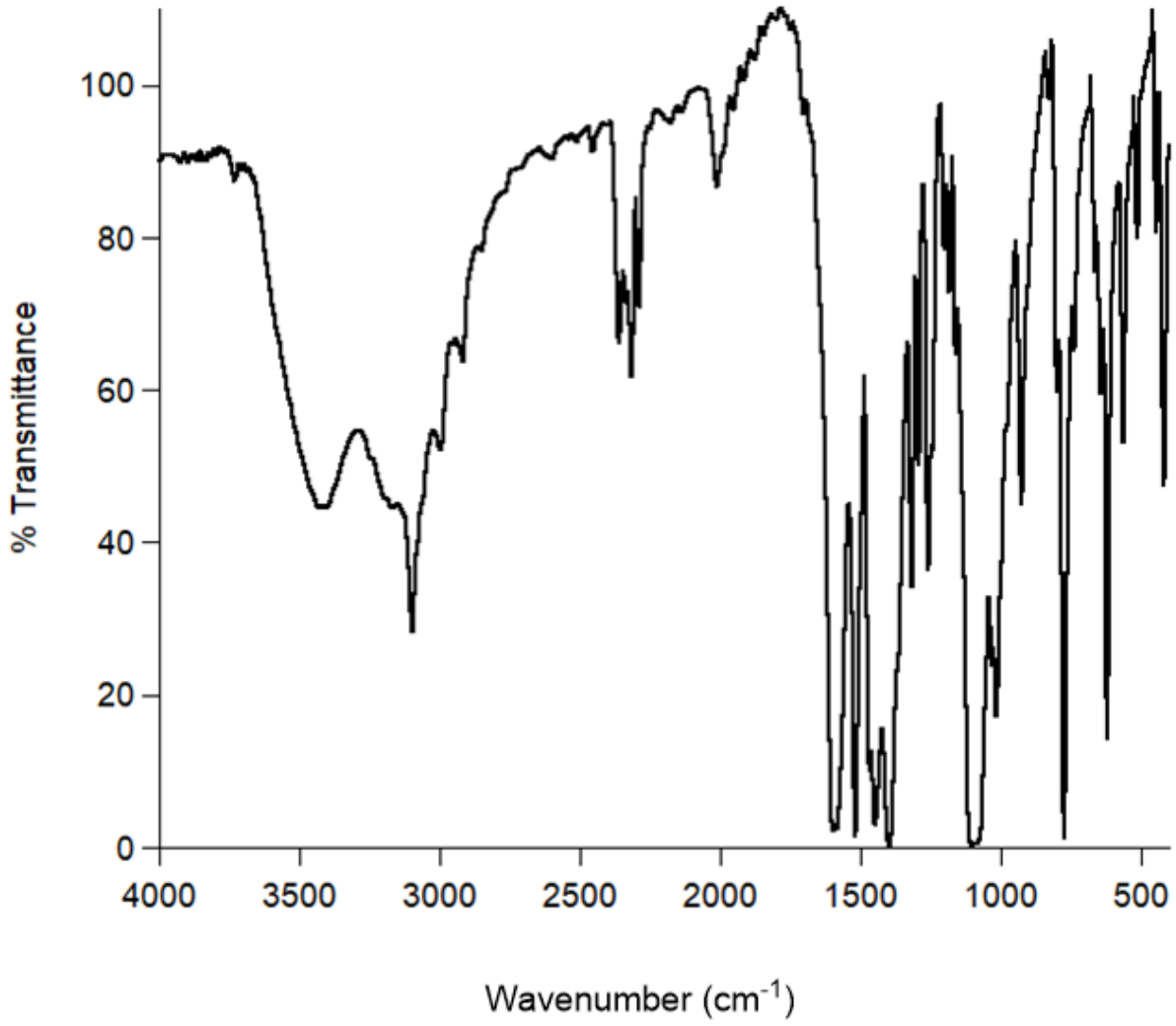


Figure S16: IR spectrum of **1**

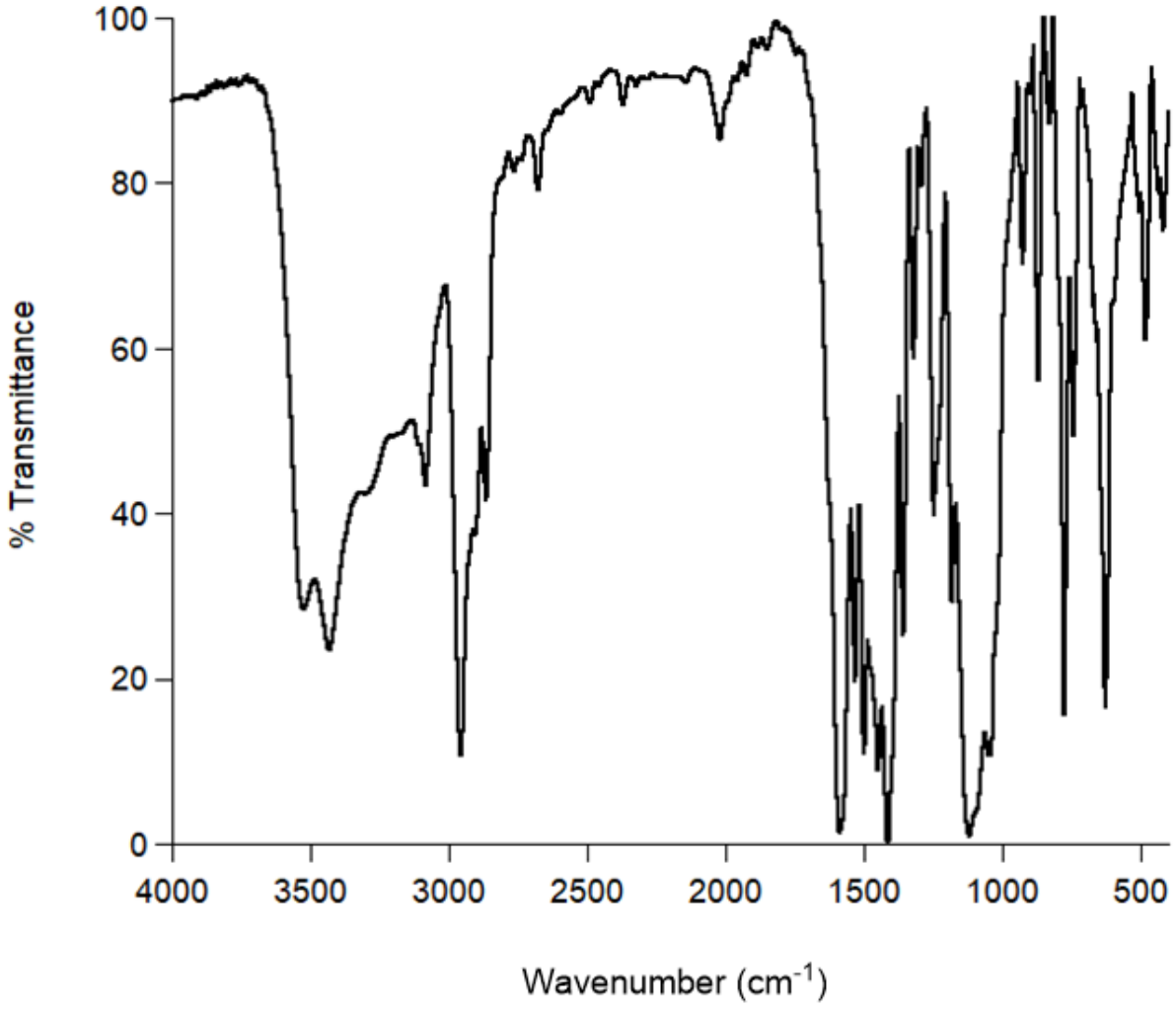
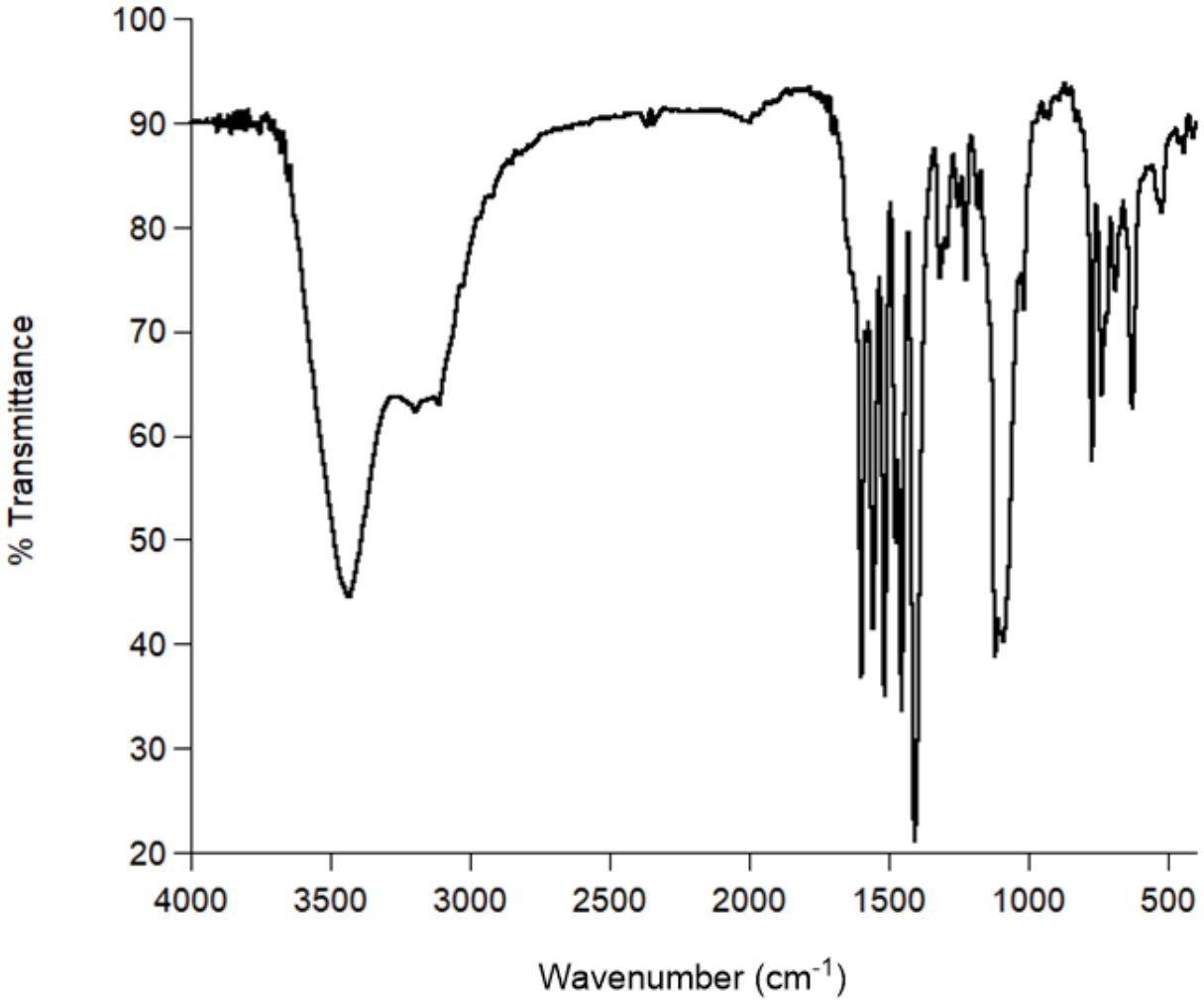


Figure S17: IR spectrum of **2**



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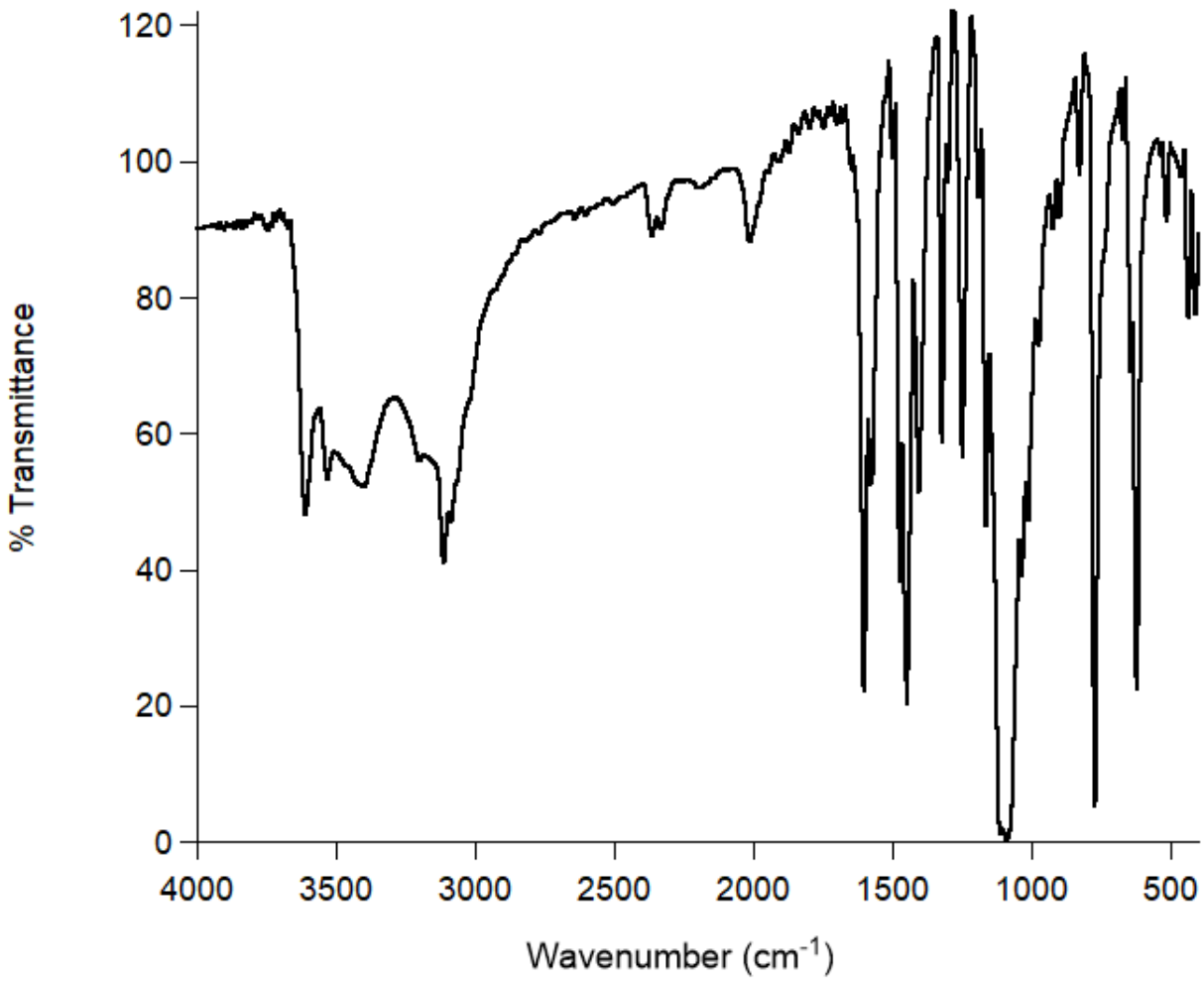

Figure S19: IR spectrum of **4**

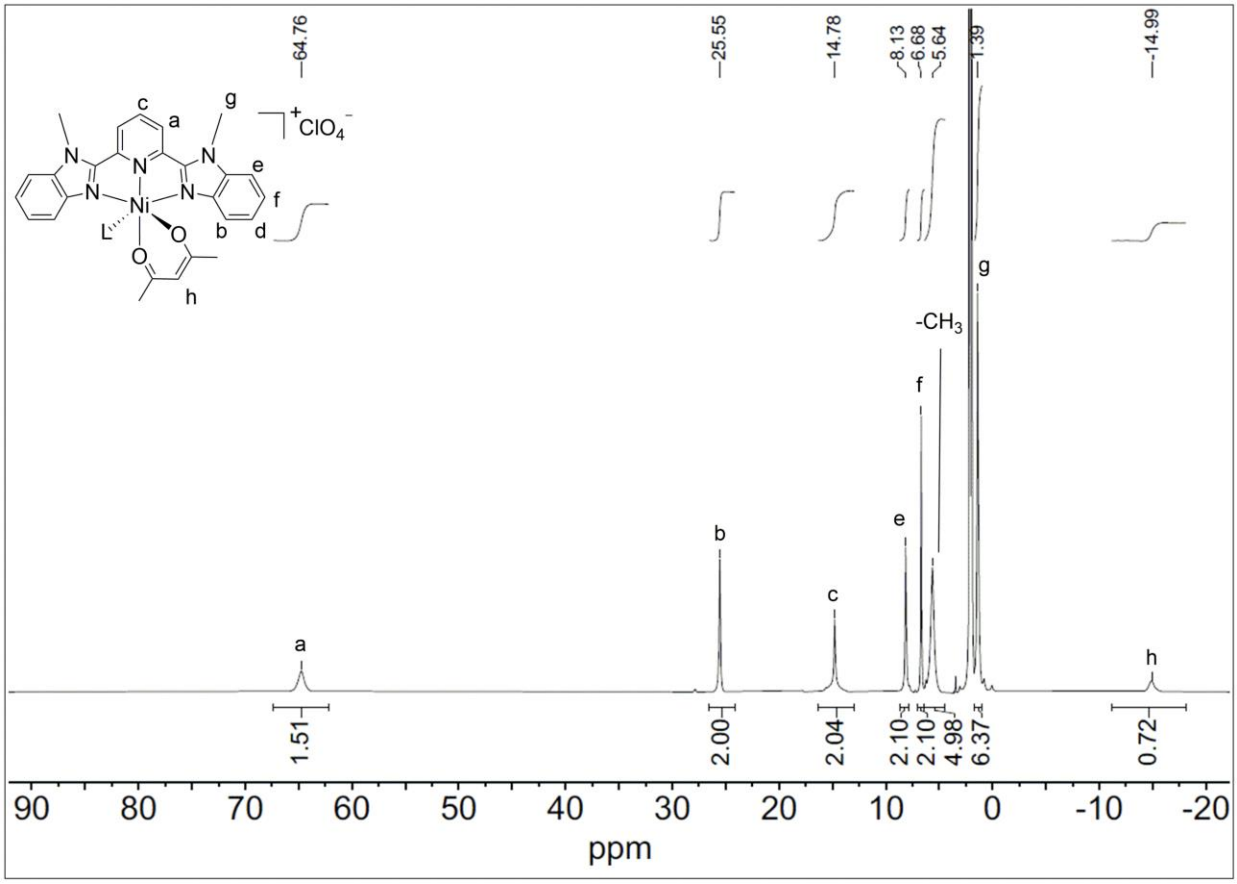

Figure S20: ^{1}H-NMR of **5** in CD_3CN (L= H_2O or CH_3CN). The hydrogen labelled "d" could not be labelled because the peak could not be found

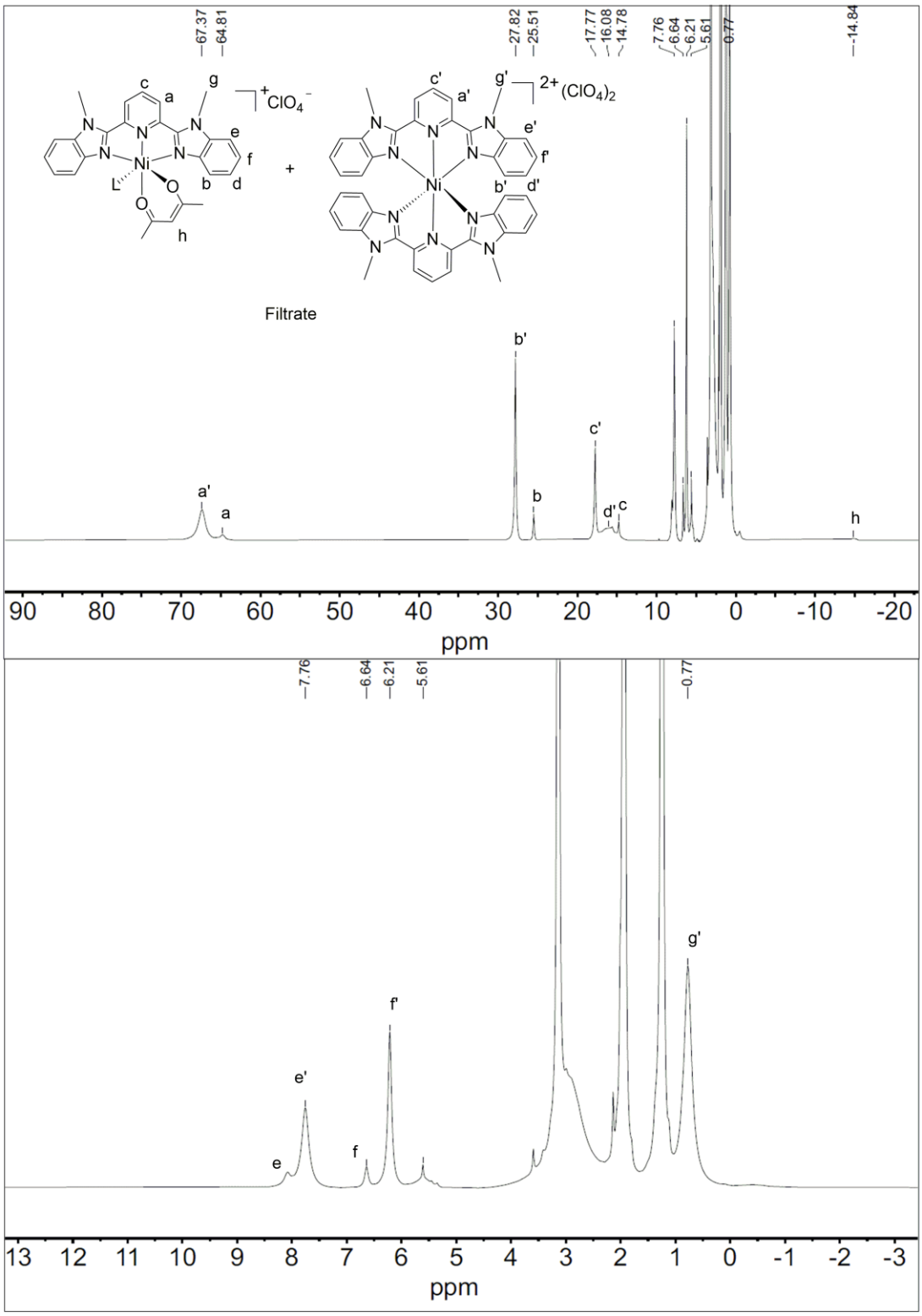

Figure S21: ^{1}H-NMR of the filtrate (top) and a zoomed in diamagnetic region (bottom) from the reaction mixture of **5** in CD_3CN. The hydrogens labelled "d" and "g" could not be labelled because the peak could not be found (d) or due to overlap (g).

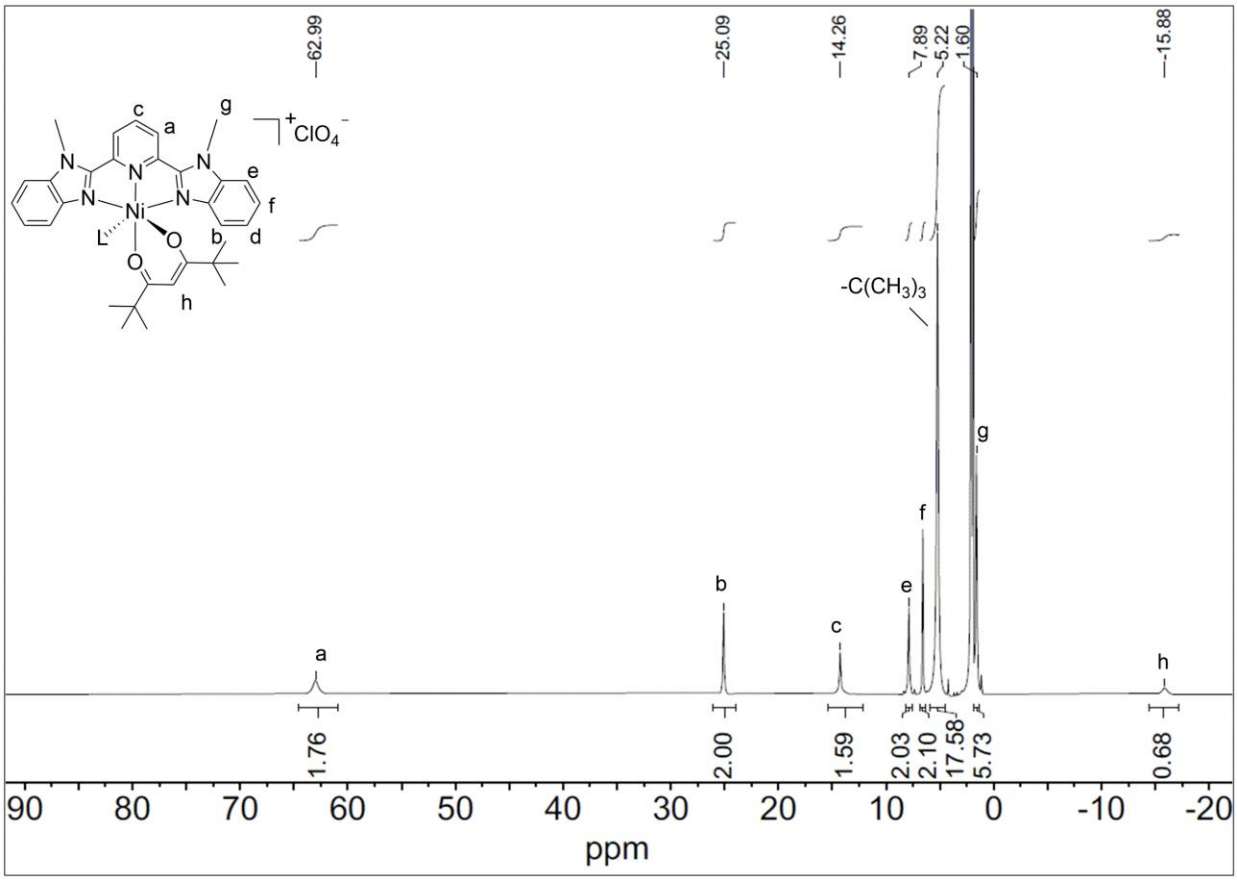

Figure S22: ^{1}H-NMR of **6** in CD_3CN (L= H_2O or CH_3CN). The hydrogens labelled "d" could not be labelled because the peak could not be found

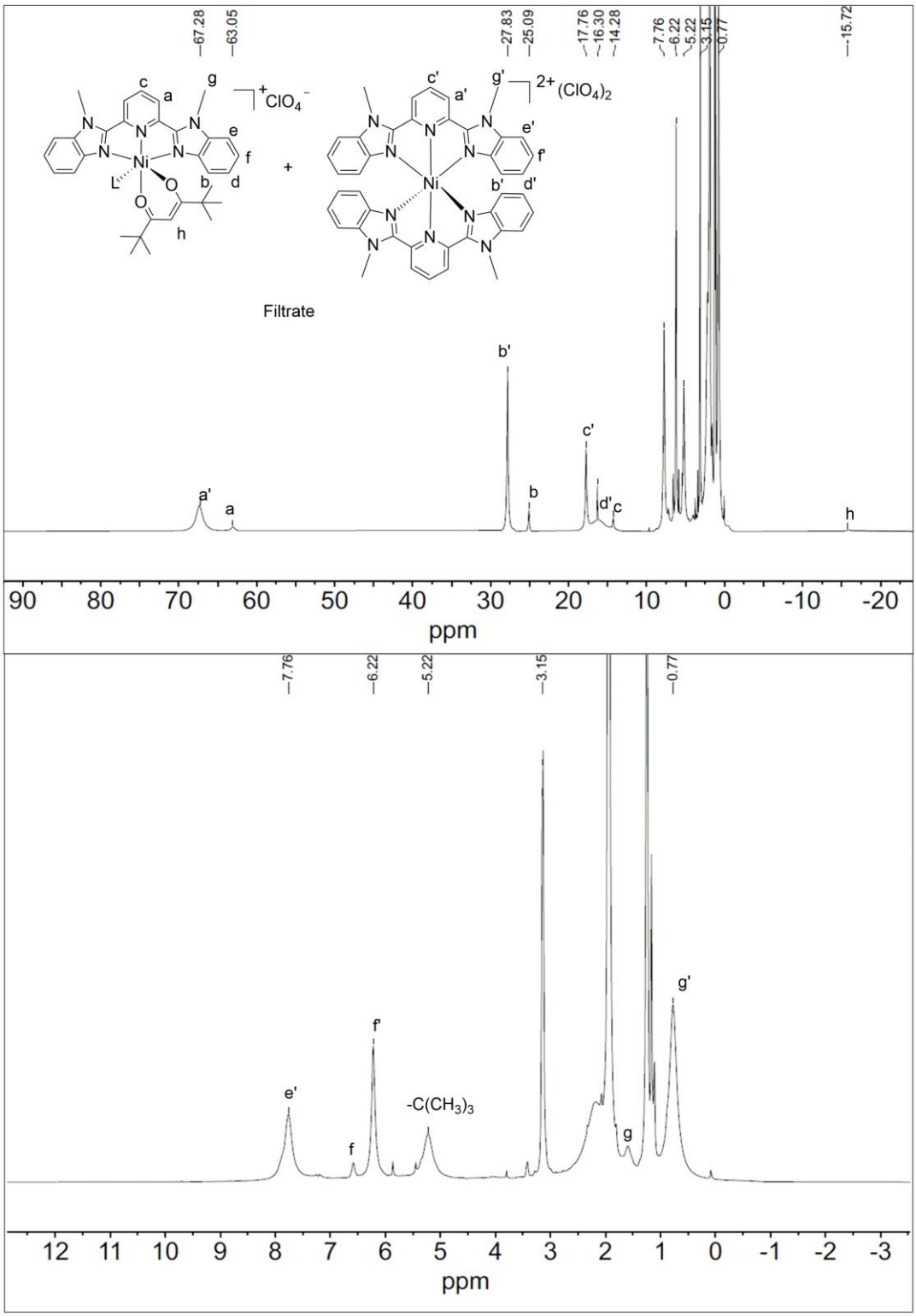

Figure S23: ^{1}H-NMR of the filtrate (top) and a zoomed in diamagnetic region (bottom) from the reaction mixture of **6** in CD_3CN. The hydrogens labelled "d" and "e" could not be labelled because the peak could not be found (d) or due to overlap (e).

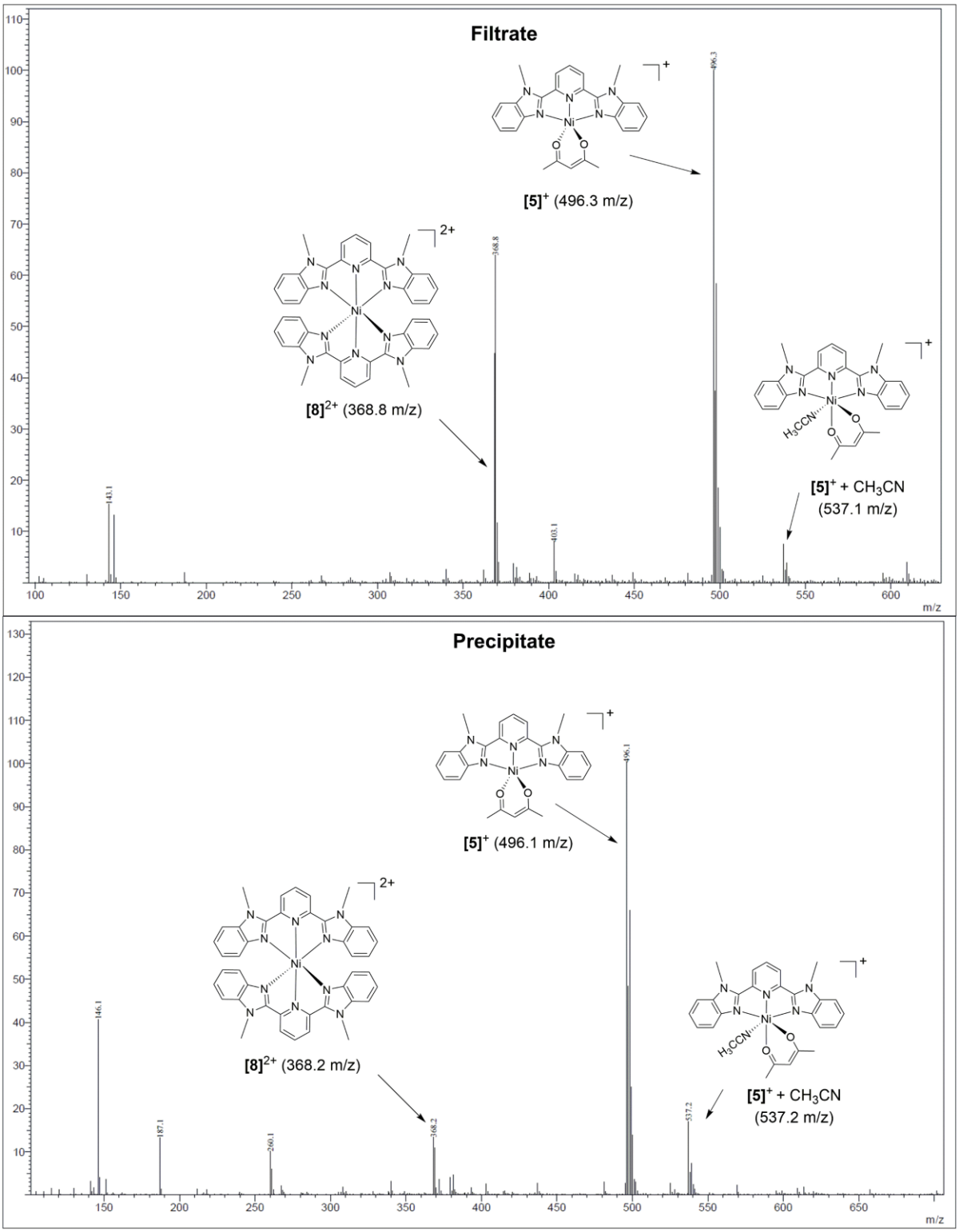

Figure S24: ESI-MS of the filtrate (top) and precipitate (bottom) from the reaction mixture of **5** in CH_3CN.

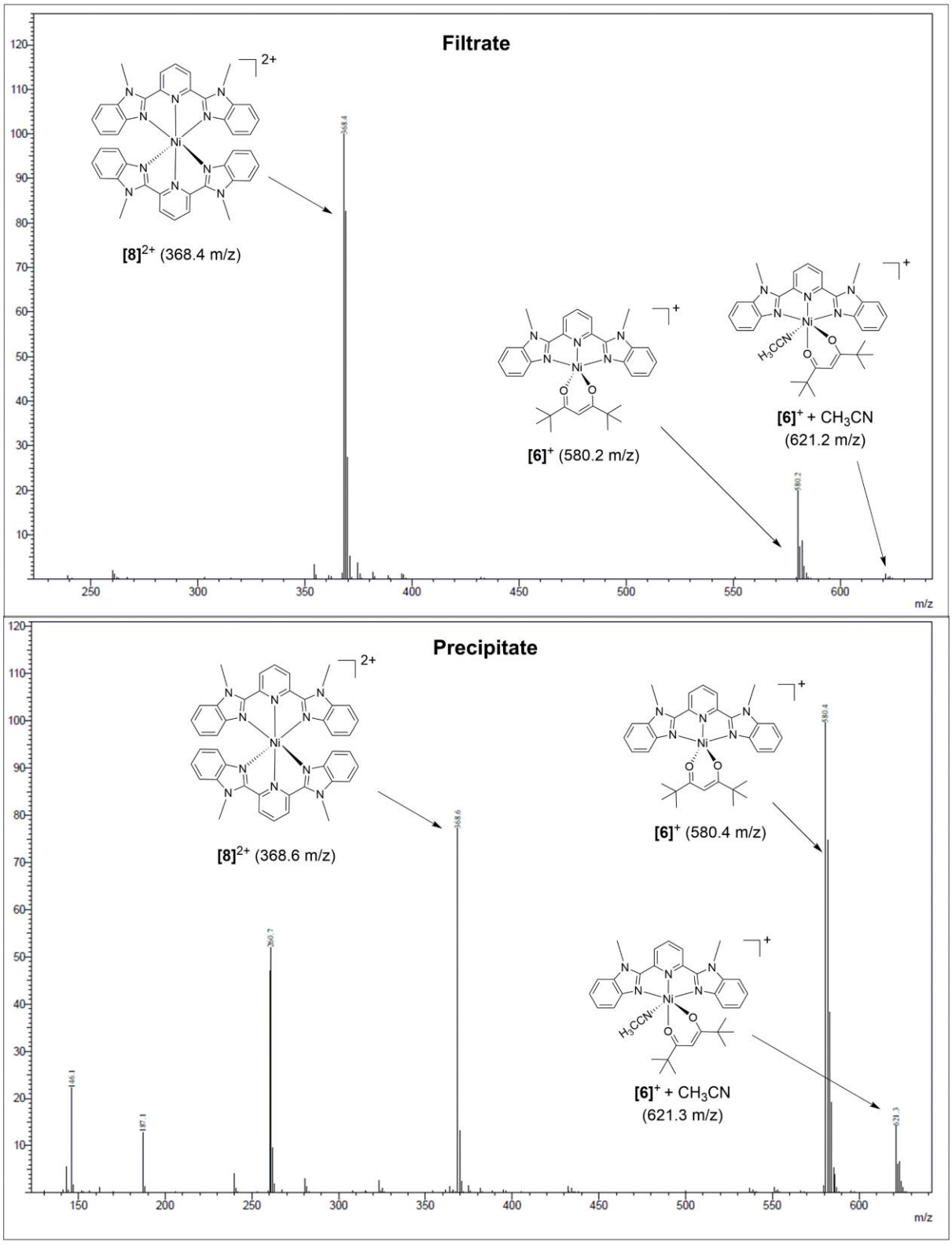

Figure S25: ESI-MS of the filtrate (top) and precipitate (bottom) from the reaction mixture of **6** in CH_3CN.

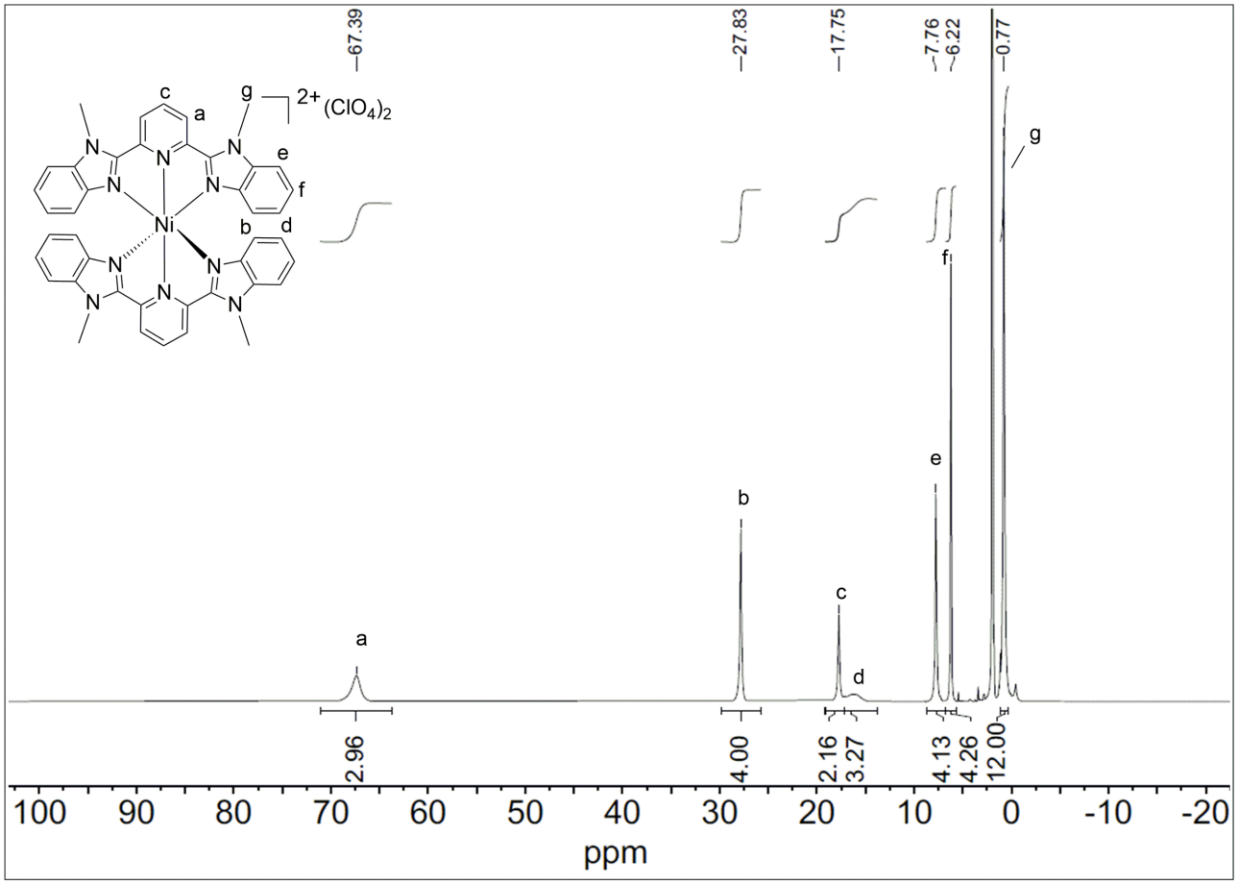

Figure S26: ^{1}H-NMR of **8** in CD_3CN.

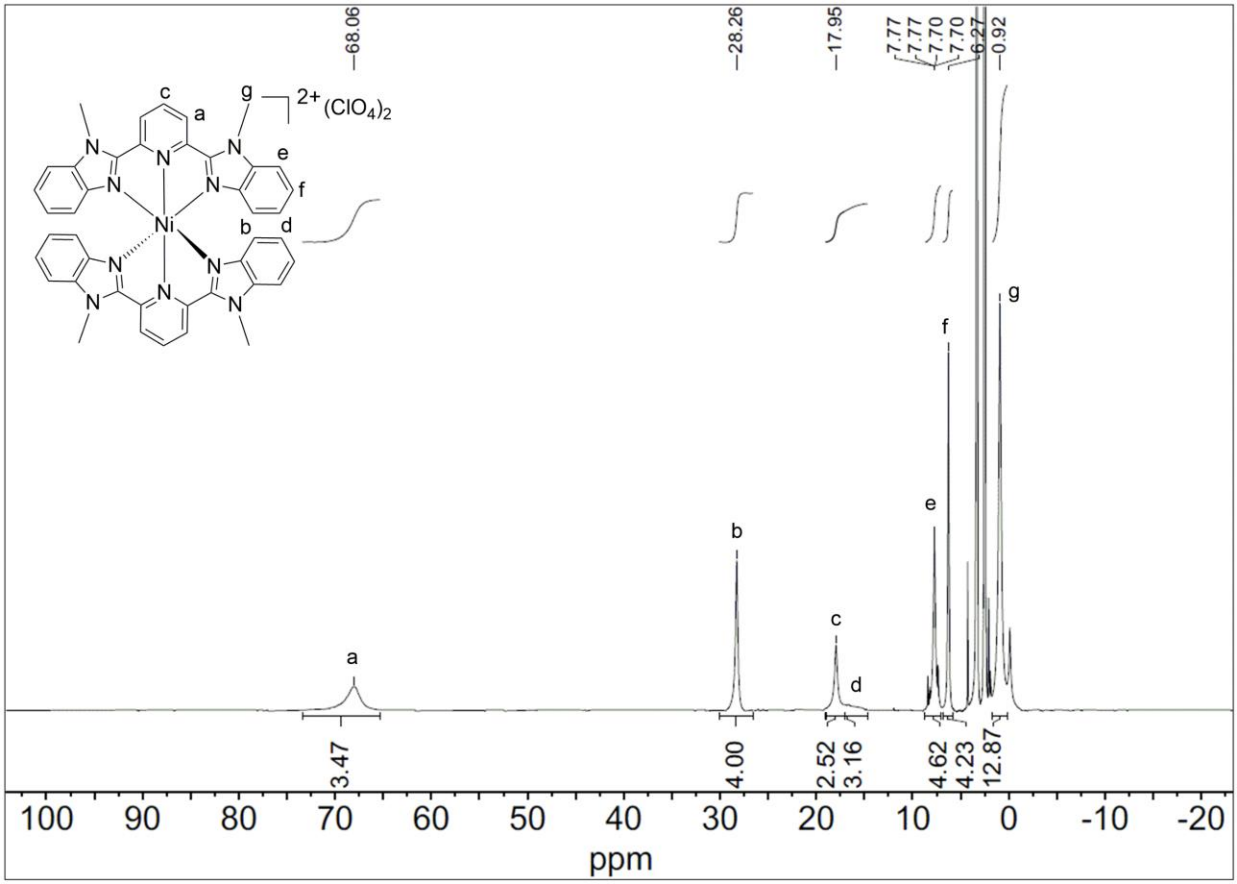

Figure S27: ^{1}H-NMR of **8** in DMSO-d_6.

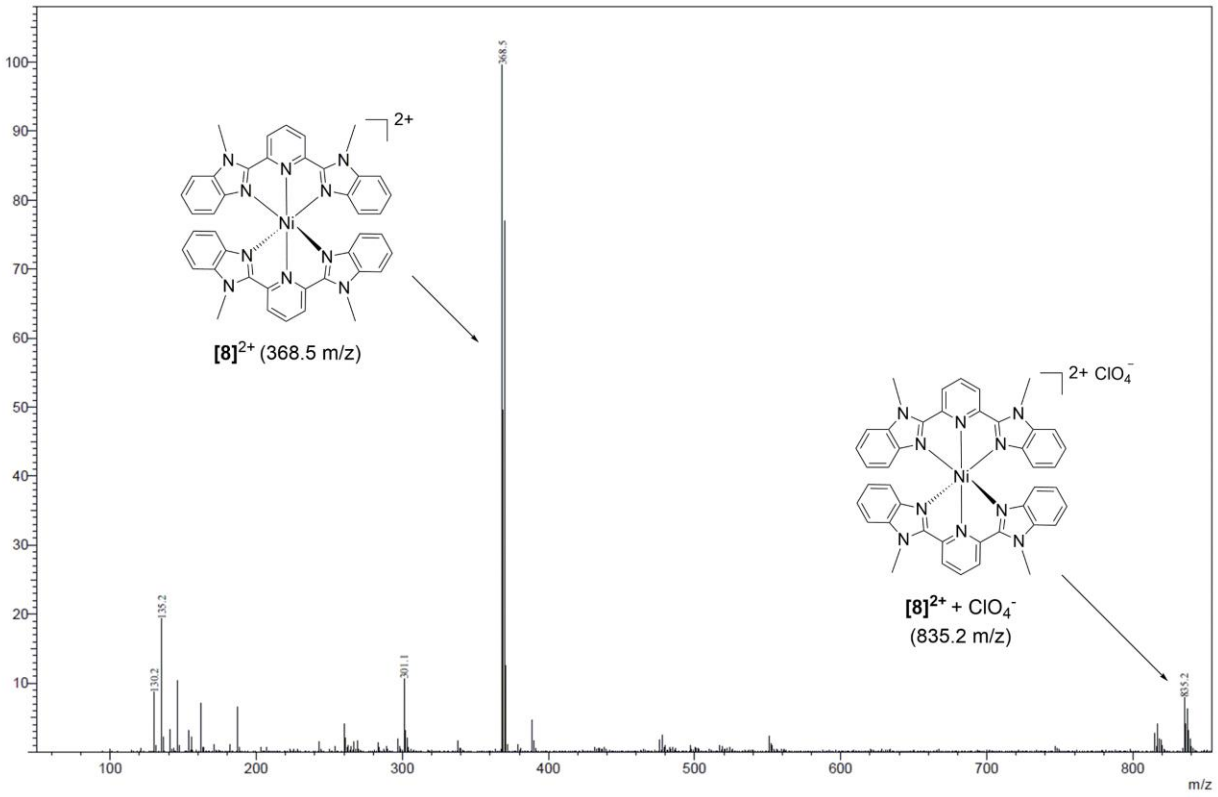

Figure S28: ESI-MS of **8** in CH_3CN.

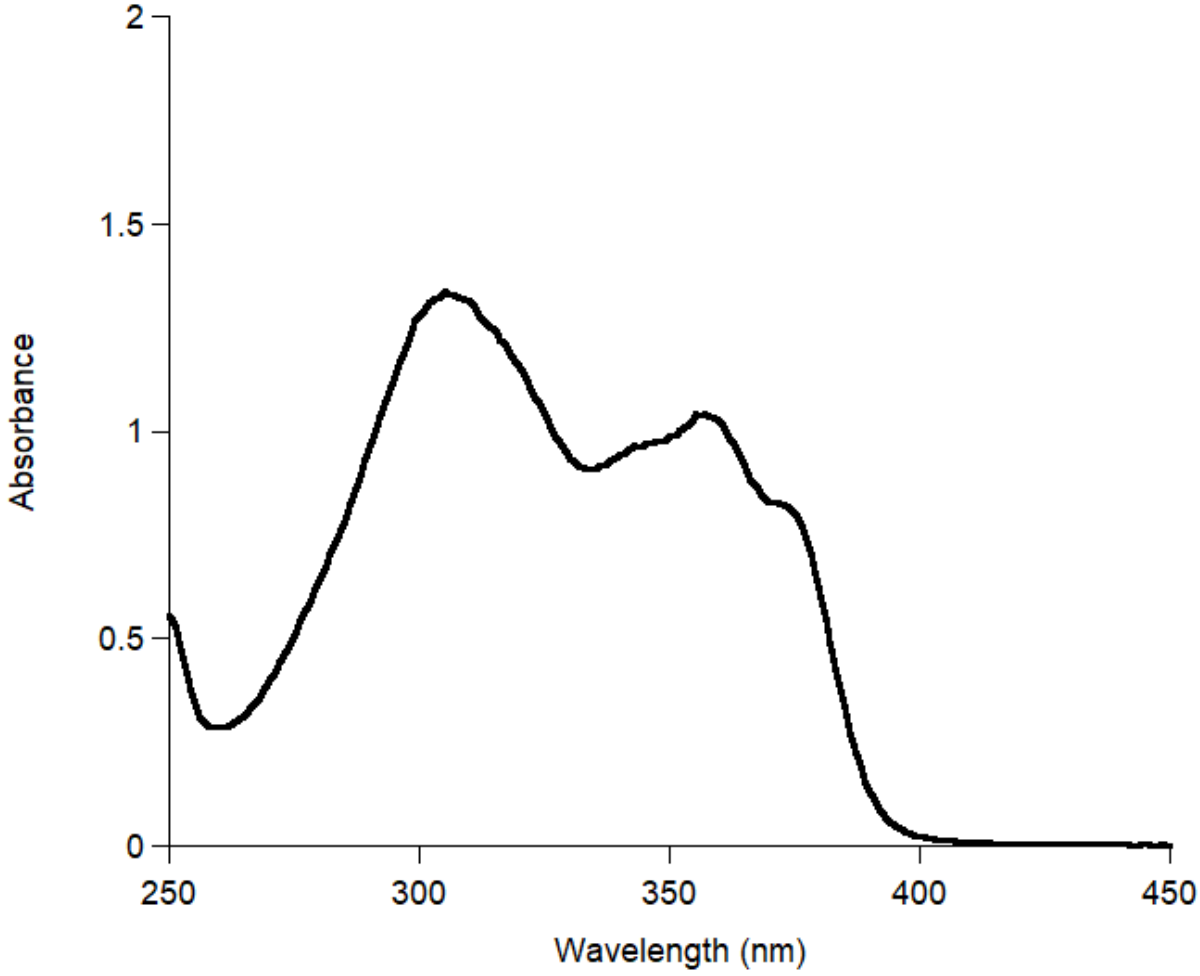

Figure S29: UV-Vis spectrum of **8** in CH_3CN ($5.35x10^{-5}$ M)

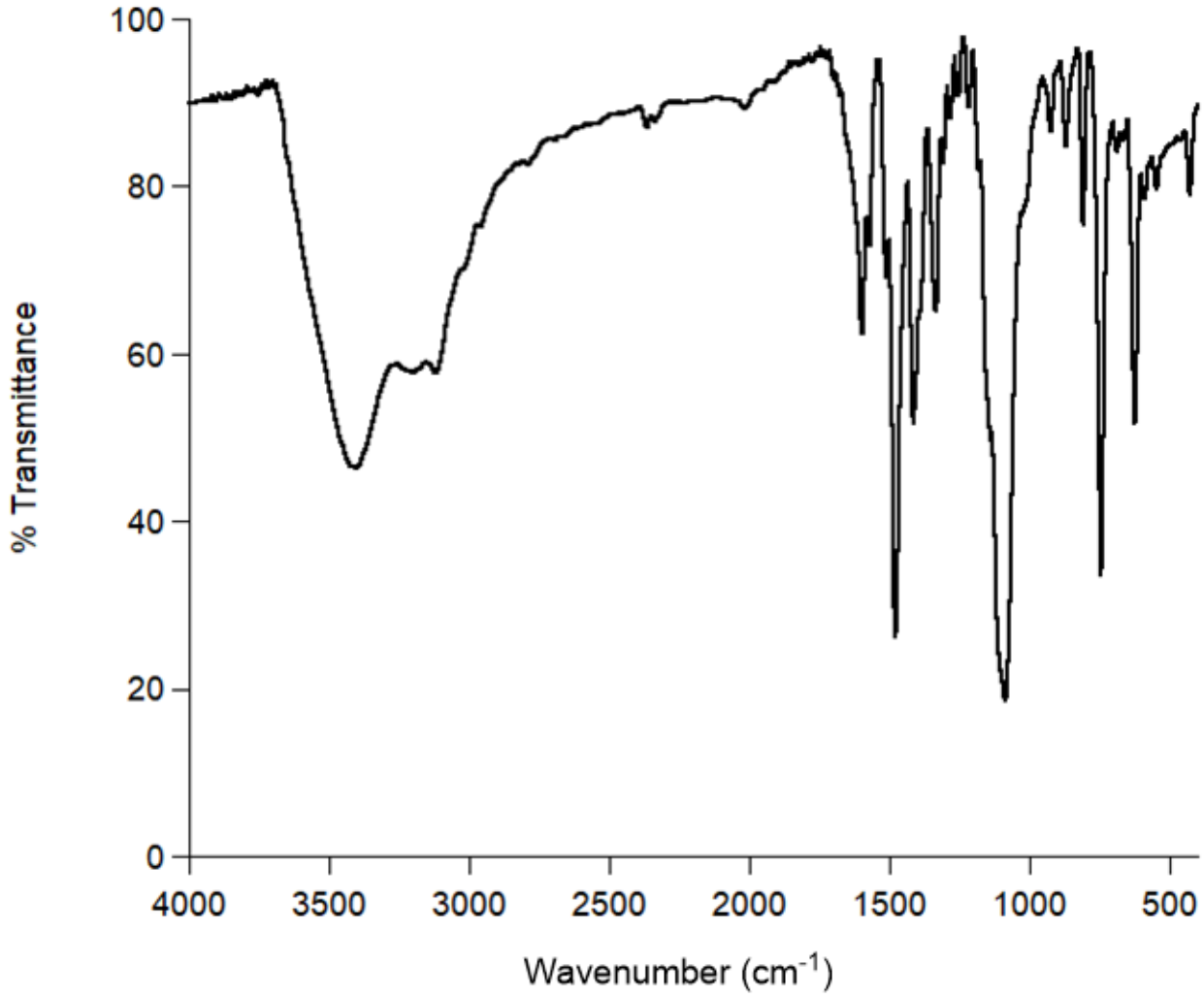

Figure S30: IR spectrum of **8**

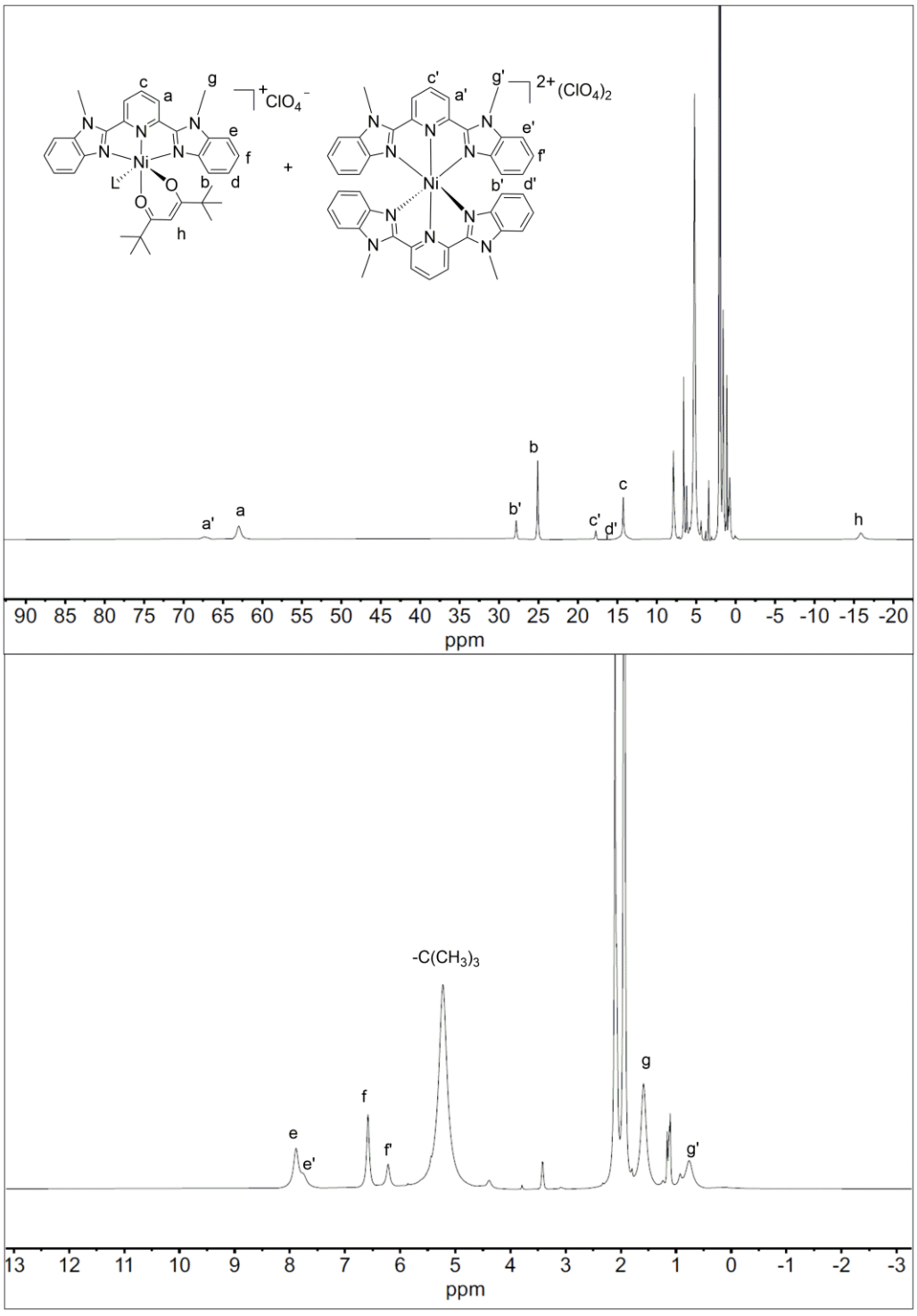

Figure S31: ^{1}H-NMR of the precipitate (top) and a zoomed in diamagnetic region (bottom) isolated during the attempted synthesis of **6** following previously published procedures (i.e. in glovebox with degassed solvents). The hydrogens labelled "d" could not be labelled because the peak could not be found.

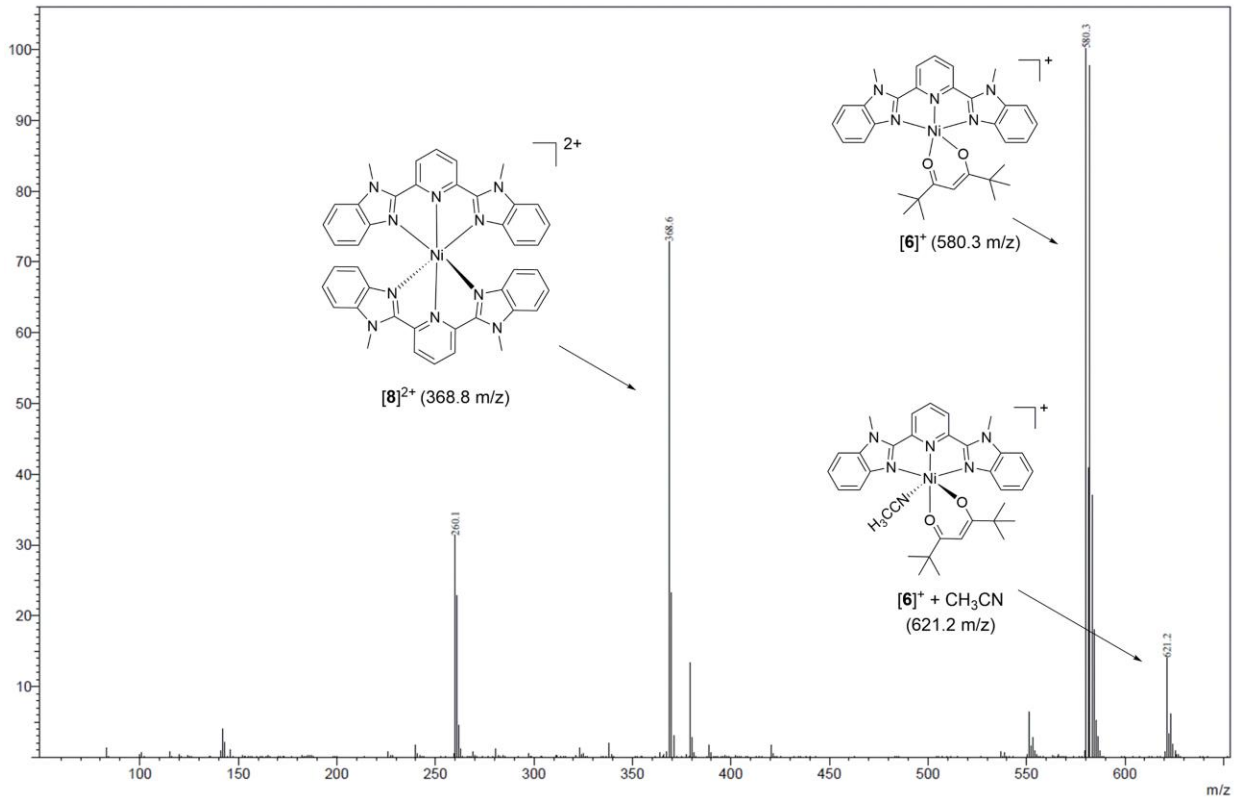

Figure S32: ESI-MS of the isolated precipitate found during synthesis of **6** following previously published procedures (i.e. in glovebox with degassed solvents) in CH_3CN.

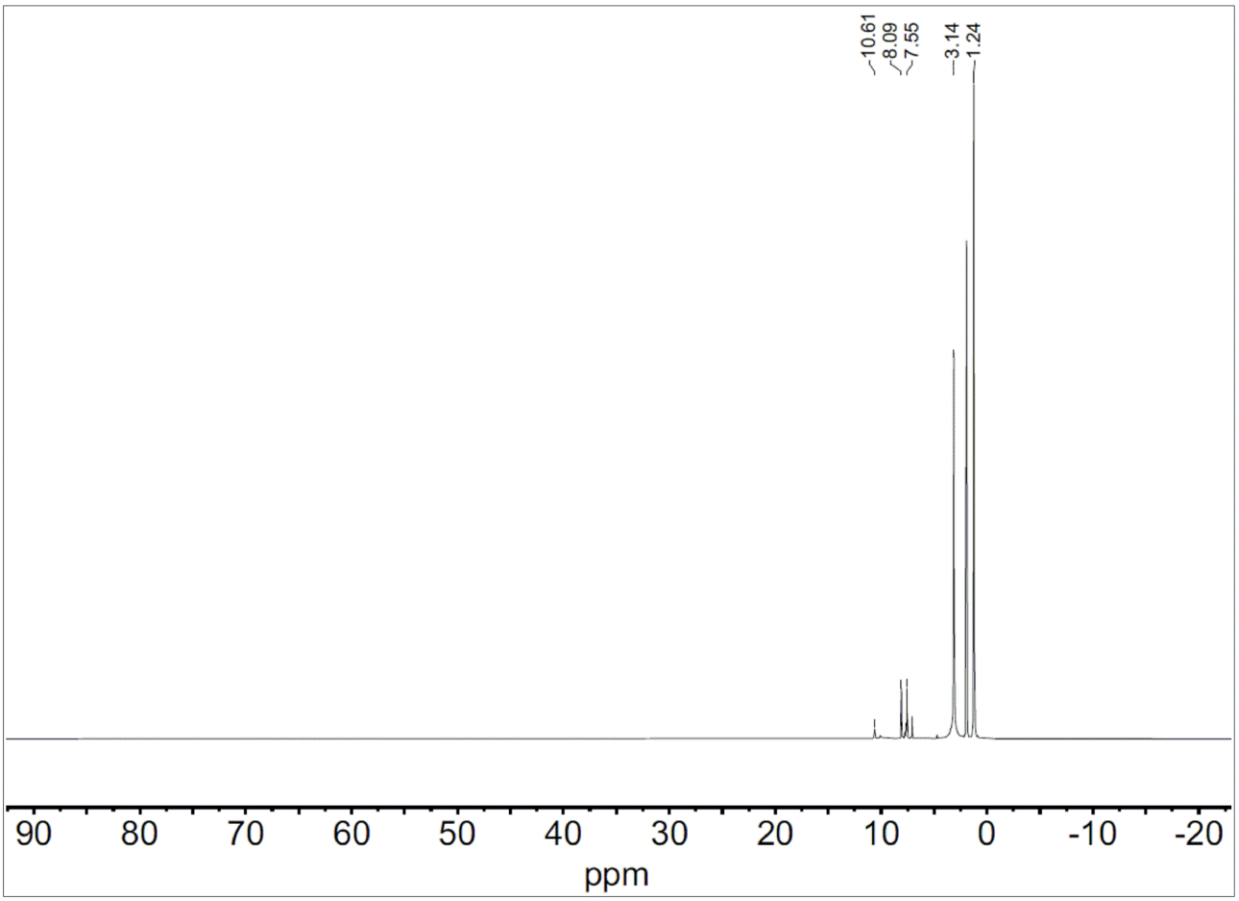

Figure S33: ^{1}H-NMR of the filtrate from the reaction mixture of **7-ClO$_4$** in CD_3CN. Neither **7-ClO$_4$** or **8** were observed.

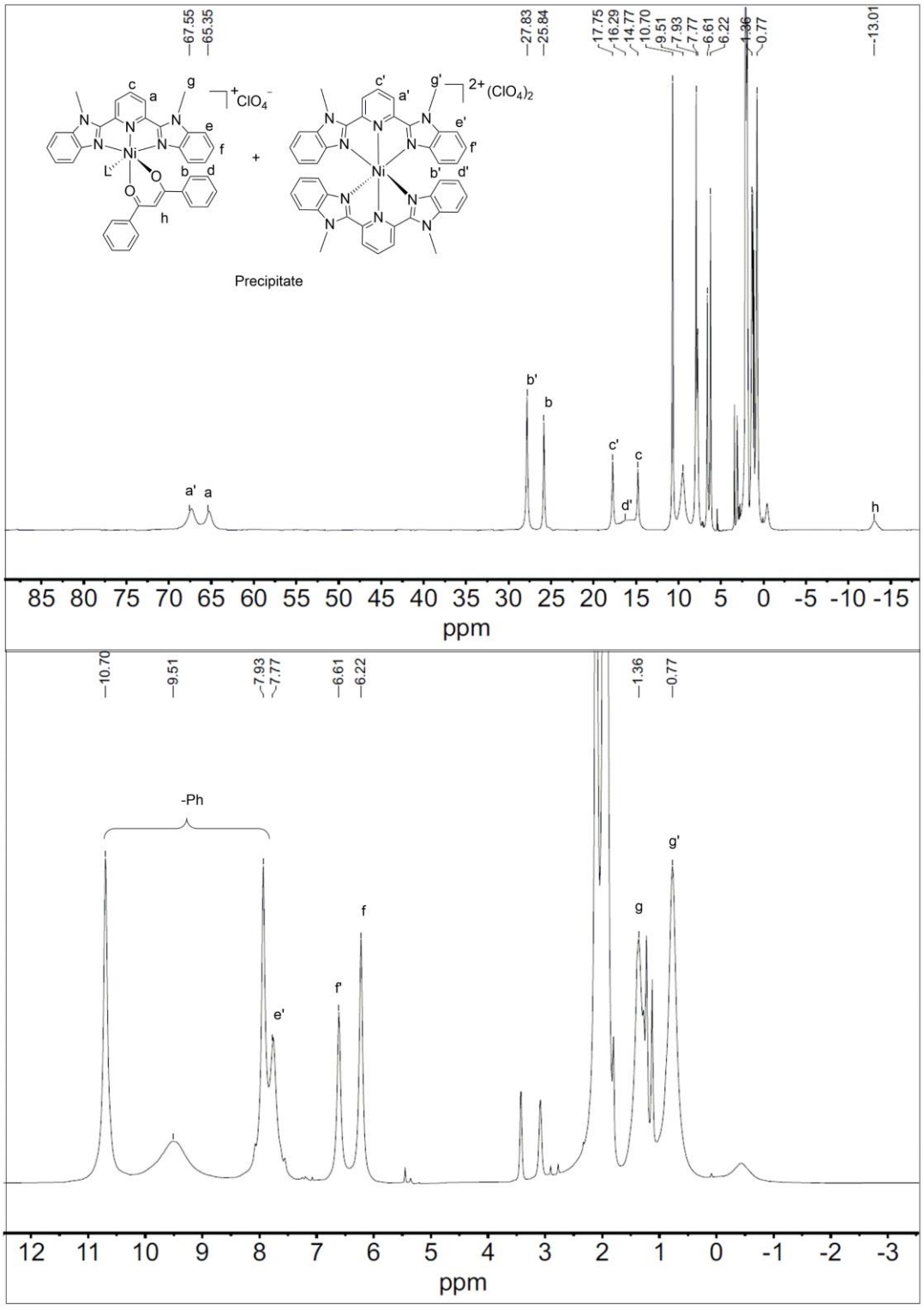

Figure S34: ^{1}H-NMR of the precipitate of **7-ClO$_4$** in CD_3CN (Top, L= H_2O or CH_3CN) and a zoomed in figure of the diamagnetic region (bottom). The hydrogens labelled "d" and "e" could not be labelled because the peak could not be found (d) or due to overlap (e).

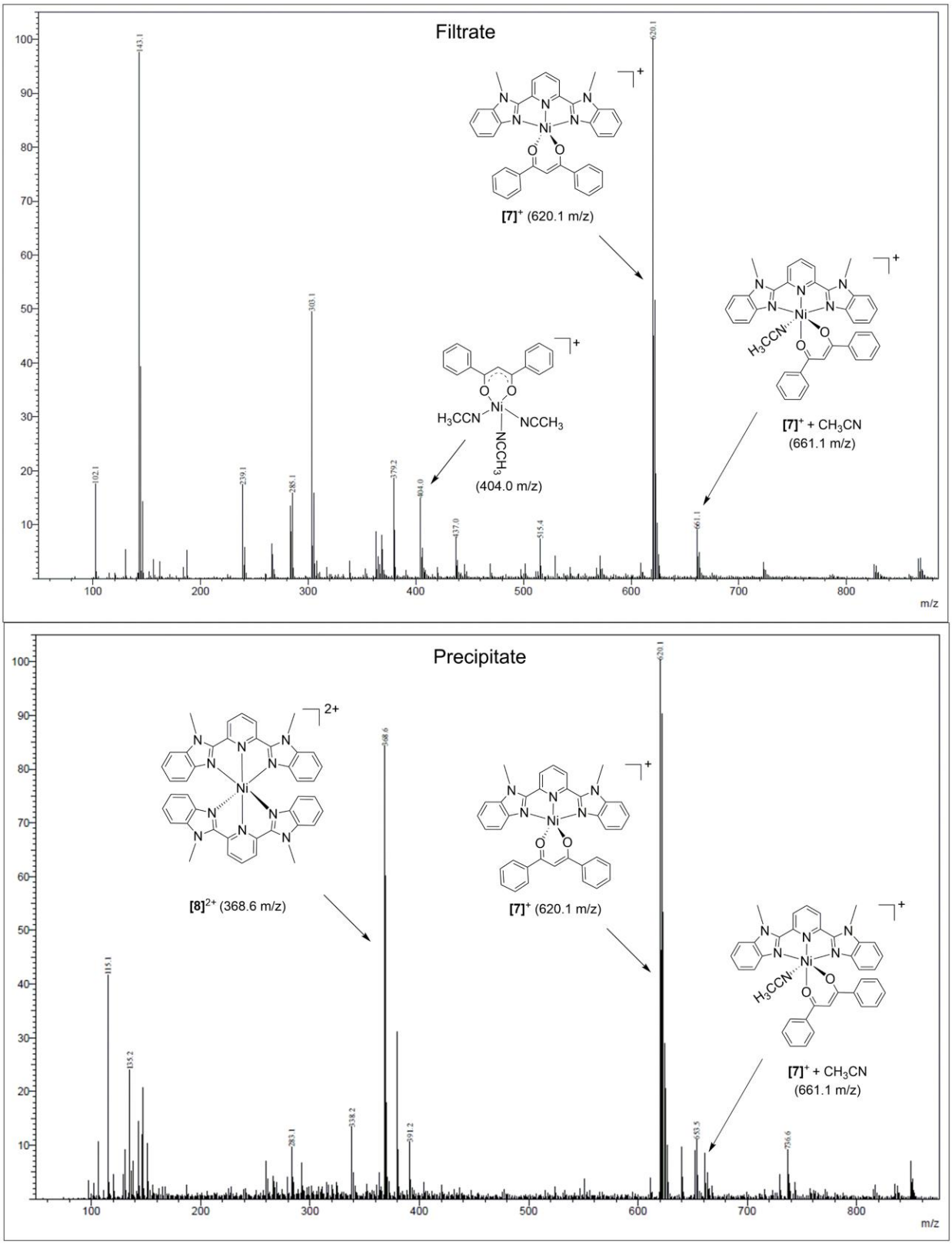

Figure S35: ESI-MS of the filtrate (top) and precipitate (bottom) from the reaction mixture of **7-ClO$_4$** in CH_3CN.

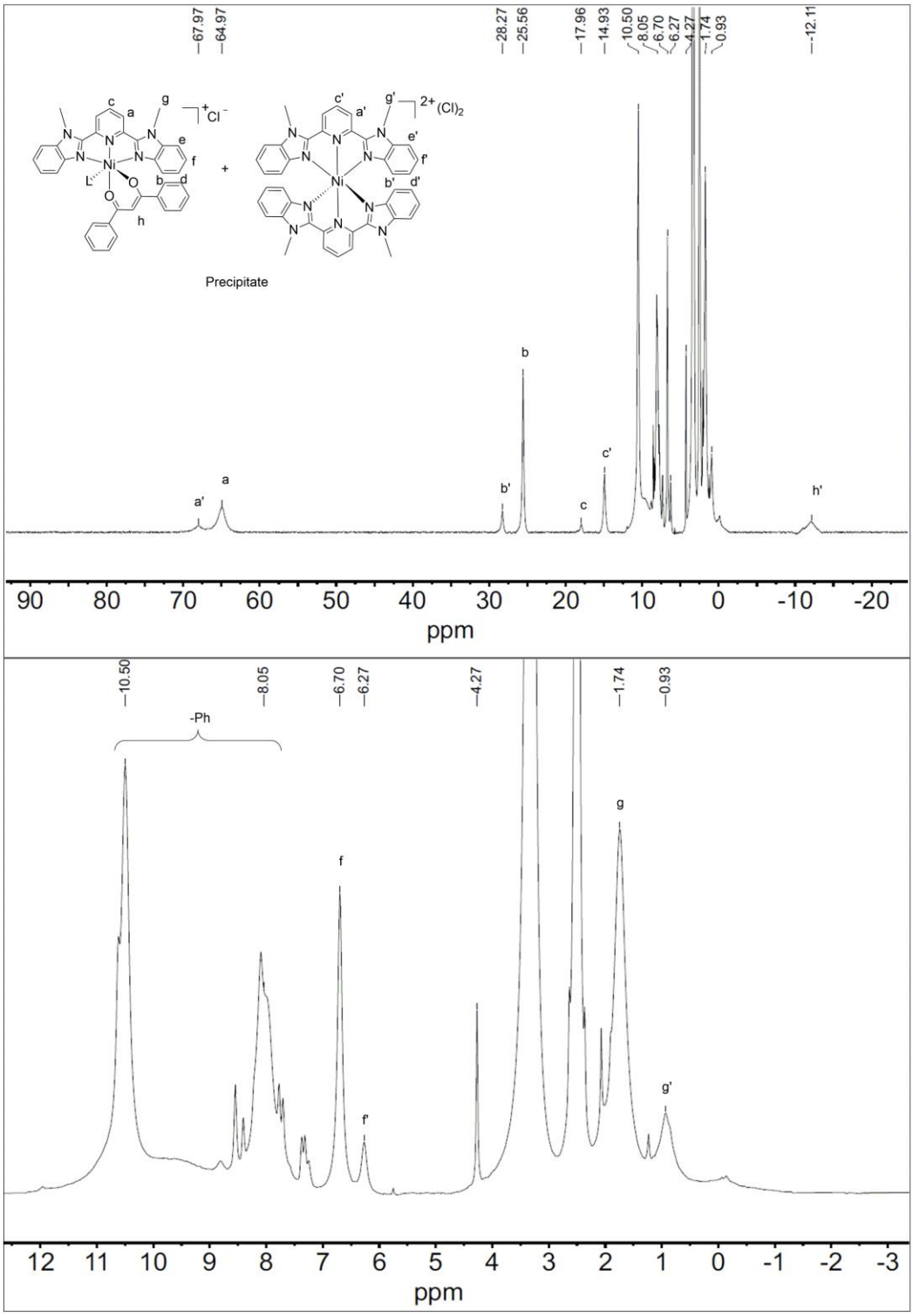

Figure S36: ^{1}H-NMR of the precipitate of **7-Cl** in DMSO (Top, L= H_2O or DMSO) and a zoomed in figure of the diamagnetic region (bottom). This was taken after attempting to separate through a filter a second time. The hydrogens labelled "d" and "e" could not be labelled because the peak could not be found (d) or due to overlap (e).

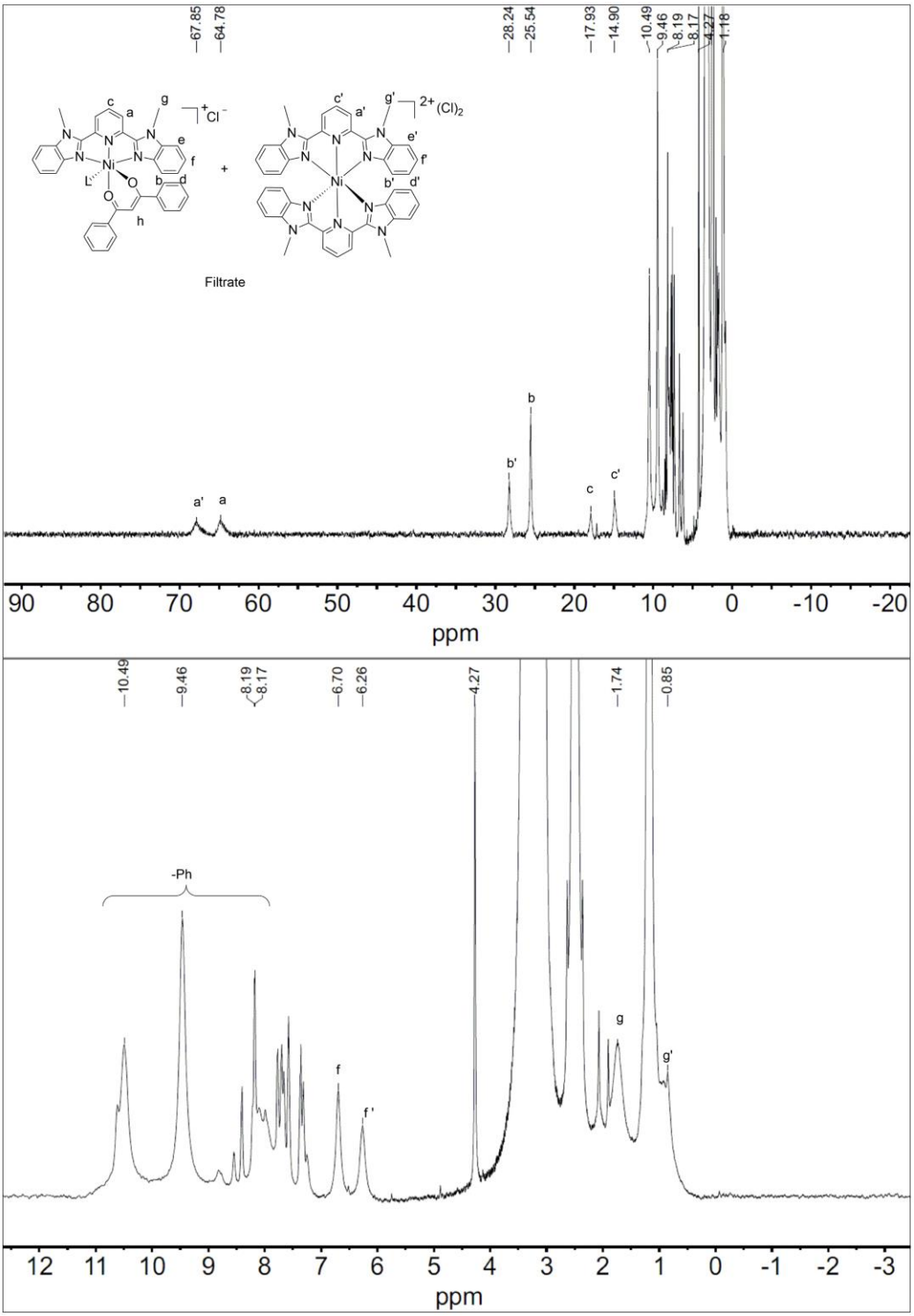

Figure S37: ^{1}H-NMR of the filtrate of **7-Cl** in DMSO (Top, L= H_2O or DMSO) and a zoomed in figure of the diamagnetic region (bottom). This was taken after attempting to separate through a filter a second time. The hydrogens labelled "d" and "e" could not be labelled because the peak could not be found (d) or due to overlap (e). Magnified by 375x (relative to intensity of DMSO peak).

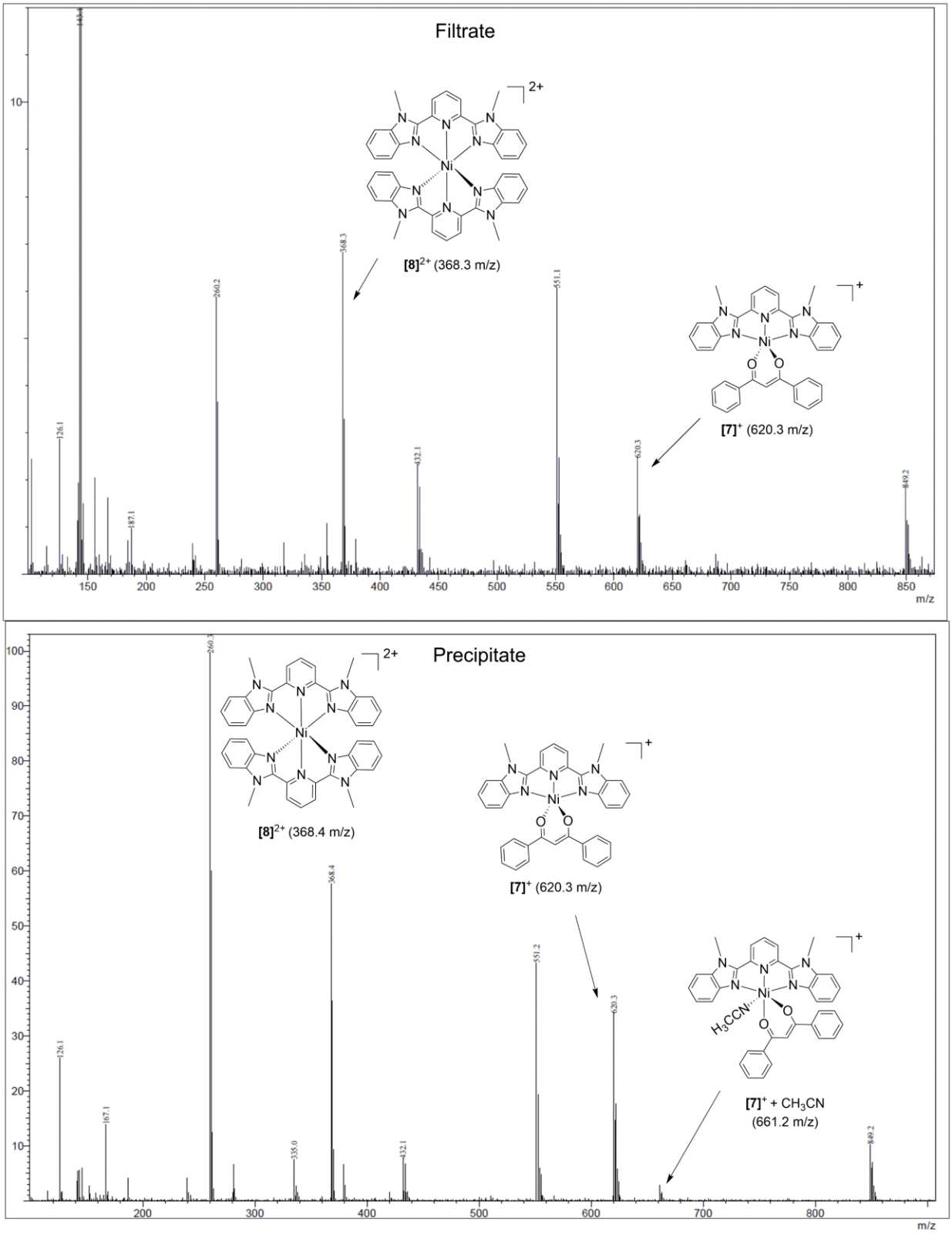

Figure S38: ESI-MS of the filtrate (top) and precipitate (bottom) from the reaction mixture of **7-Cl** in CH_3CN.

Table S1. Summary of X-ray data collection and refinement for **1-3** and **8**

	1	**2**	**3**	**8**
empirical formula	$C_{22}H_{21}ClNiN_4O_6$	$C_{26}H_{32}ClNiN_3O_4$	$C_{30}H_{24}ClNiN_3O_7$	$C_{45}H_{38.5}Cl_2N_{11.5}NiO_8$
formula weight	531.59	592.70	632.68	997.98
crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
space group	*C 1 2/c 1*	*P -1*	*P 1 21/c 1*	*P 1*
a (Å)	15.6762(12)	9.9556(2)	18.6814(19)	12.2882(13)
b (Å)	13.2879(9)	11.6346(4)	10.5353(9)	19.219(2)
c (Å)	21.9128(18)	14.2457(4)	14.8709(14)	19.786(2)
α (deg)	90	110.337(3)	90	87.747(3)
β (deg)	91.405(3)	91.439(2)	109.241(3)	77.340(3)
γ (deg)	90	113.304(3)	90	77.490(3)
V (Å^3)	4563.1(6)	1395.42(8)	2763.3(5)	4450.7(8)
Z	8	2	4	4
density (calcd), Mg m^{-3}	1.548	1.411	1.521	1.489
temp (K)	100(1)	102(3)	100	105
crystal size (mm^3)	0.12 x 0.2 x 0.4	0.37 x 0.23 x 0.18	0.02 x 0.09 x 0.38	0.2 x 0.18 x 0.15
diffractometer	Bruker D8 Venture	Rigaku	Bruker D8 Venture	Bruker D8 Venture
Abs. coeff. (mm^{-1})	1.015	0.839	0.983	0.622
2θ max (deg)	62.78	60.72	50.02	49.98
Reflections collected	9996	10275	9888	9194
Indep. reflections	7634	8096	4911	31034
variable parameters	310	355	387	2487
*R*1 / w*R*2[b]	0.0319/0.0722	0.0329/.0774	0.0693/0.1995	0.0371/0.0769
goodness-of-fit (F^2)	1.031	1.053	1.191	1.029
largest diff. (e Å^{-3})	0.519/-0.508	0.413/-0.536	1.56/-0.99	0.651/-0.431

[a]Radiation used: Mo Kα (λ = 0.71073 Å). [b]$R1 = \sum | |F_o| - |F_c| | / \sum |F_o|$;
w$R2 = [\sum[w(F_o^2-F_c^2)^2]/[\sum(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$.

Table S2. Selected bond Distances (Å) and angles (deg) for **1-3**

	1	**2**	**3**
Ni(1)-O(1)	2.0477(9)	2.0023(10)	1.982(4)
Ni(1)-O(2)	1.9947(10)	1.9772(10)	2.018(4)
Ni(1)-O(7)	-	2.1416(11)	2.094(4)
Ni(1)-N(1)	2.0004(11)	1.9982(12)	1.997(5)
Ni(1)-N(2)	2.1078(11)	2.0966(12)	2.107(5)
Ni(1)-N(3)	2.1035(12)	2.1012(12)	2.135(5)
Ni(1)-N(4)	2.4945(17)	-	-
O(1)-C(16)	1.2707(16)	1.2626(17)	1.264(7)
O(2)-C(19)	1.2688(16)	-	-
O(2)-C(22)	-	1.2752(16)	-
O(2)-C(24)	-	-	1.268(7)
Ni(1)-O(7)	-	2.1416(11)	2.094(4)
O(2)- Ni(1)-O(1)	90.59(4)	91.33(4)	89.96(16)
O(2)- Ni(1)-N(1)	178.16(4)	176.30(5)	94.95(17)
O(2)- Ni(1)-N(2)	100.46(4)	105.13(5)	94.55(18)
O(2)- Ni(1)-N(3)	103.46(4)	98.43(5)	88.39(18)
O(2)- Ni(1)-N(4)	86.89(4)	-	-
O(2)- Ni(1)-O(7)		85.19(4)	171.59(16)
O(1)- Ni(1)-N(1)	88.92(4)	90.31(4)	173.43(18)
O(1)- Ni(1)-N(2)	94.41(4)	90.88(5)	96.52(18)
O(1)- Ni(1)-N(3)	89.46(4)	91.52(5)	106.90(18)
O(1)- Ni(1)-N(4)	176.56(4)	-	-
O(1)- Ni(1)-O(7)	-	174.93(4)	83.14(17)
N(1)- Ni(1)-N(2)	77.81(4)	78.16(5)	78.76(18)
N(1)- Ni(1)-N(3)	78.31(4)	78.21(5)	77.67(18)
N(1)- Ni(1)-N(4)	93.68(4)	-	-
N(3)- Ni(1)-N(2)	155.72(4)	156.26(5)	156.41(18)
N(4)- Ni(1)-N(2)	88.36(4)	97.37(15)	-
N(4)- Ni(1)-N(3)	88.85(4)	-	-
N(1)- Ni(1)-O(7)	-	93.38(4)	92.31(18)
N(2)- Ni(1)-O(7)	-	86.49(4)	91.01(17)
N(3)- Ni(1)-O(7)		92.63(5)	89.02(18)

Table S3. Selected bond Distances (Å) and angles (deg) for **8**

	8
Ni(1B)-N(1B)	2.027(4)
Ni(1B)-N(2B)	2.114(4)
Ni(1B)-N(4B)	2.106(4)
Ni(1B)-N(6B)	2.025(4)
Ni(1B)-N(7B)	2.082(4)
Ni(1B)-N(8B)	2.094(4)
N(1B)-Ni(1B)-N(2B)	78.28(15)
N(1B)-Ni(1B)-N(4B)	77.73(15)
N(1B)-Ni(1B)-N(7B)	99.95(15)
N(1B)-Ni(1B)-N(6B)	174.90(16)
N(1B)-Ni(1B)-N(8B)	104.84(15)
N(2B)-Ni(1B)-N(4B)	155.74(15)
N(2B)-Ni(1B)-N(6B)	97.21(15)
N(2B)-Ni(1B)-N(7B)	94.31(15)
N(2B)-Ni(1B)-N(8B)	92.58(14)
N(4B)-Ni(1B)-N(6B)	106.91(15)
N(4B)-Ni(1B)-N(7B)	93.30(15)
N(4B)-Ni(1B)-N(8B)	90.10(15)
N(6B)-Ni(1B)-N(7B)	77.89(15)
N(6B)-Ni(1B)-N(8B)	77.56(15)
N(7B)-Ni(1B)-N(8B)	155.14(15)

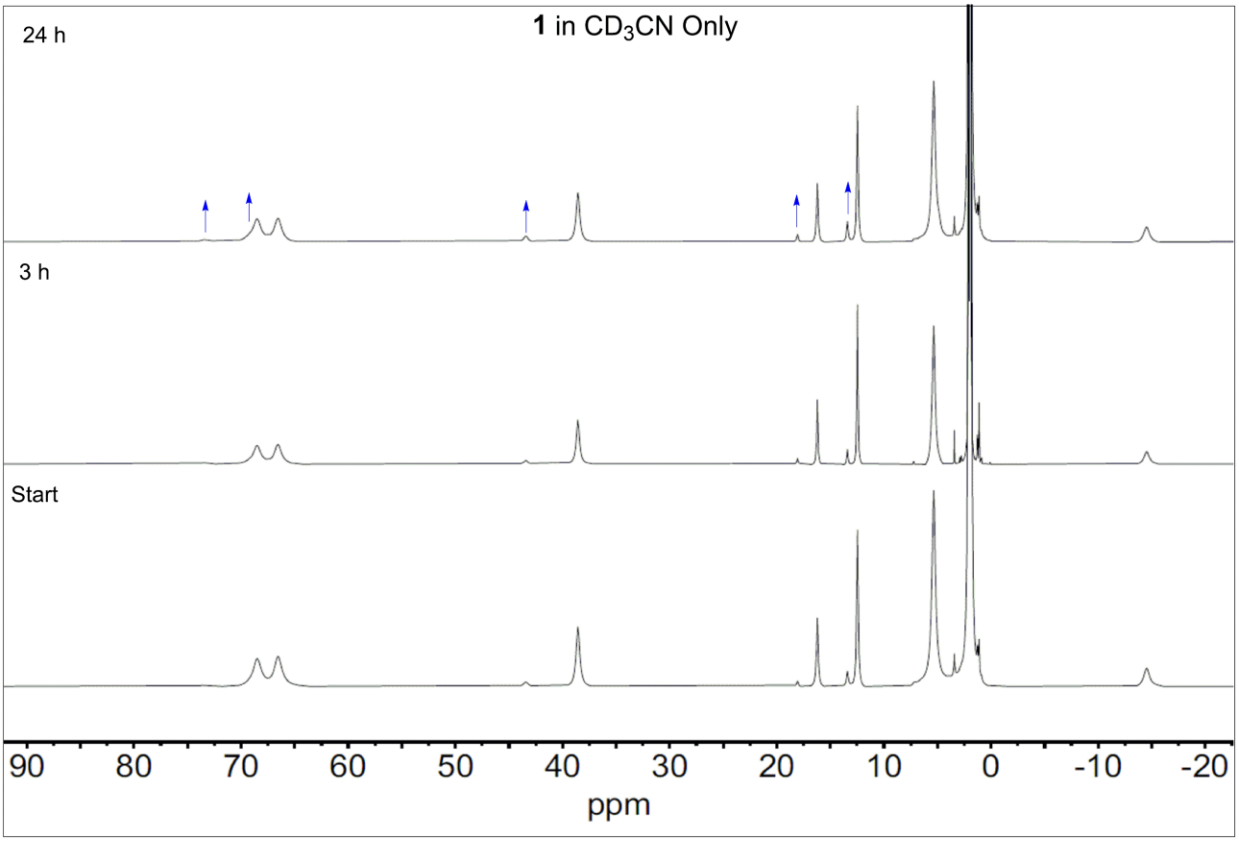

Figure S39: ^{1}H-NMR under paramagnetic conditions for **1** over time in dry CD_3CN only.

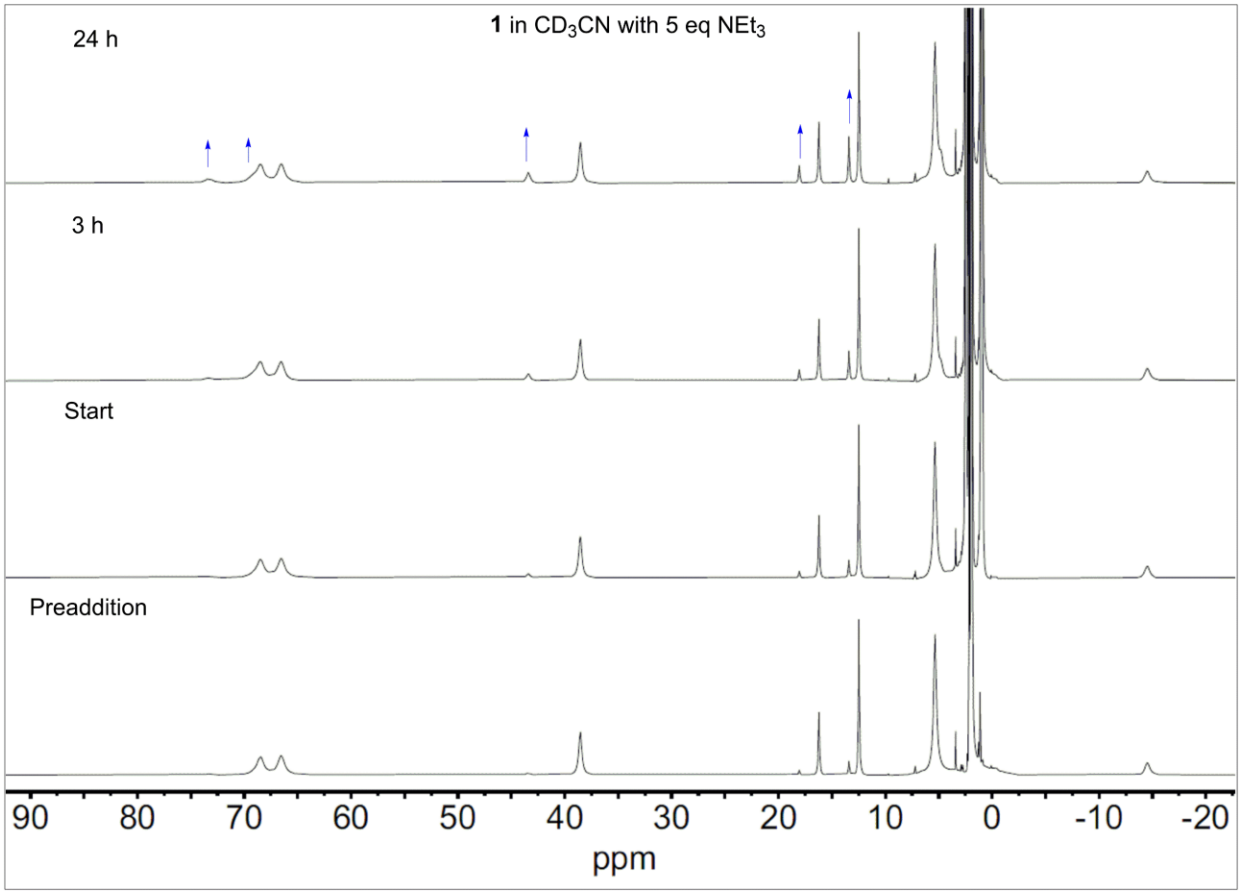

Figure S40: ^{1}H-NMR under paramagnetic conditions for **1** over time in dry CD_3CN with 5 equivalents of NEt_3.

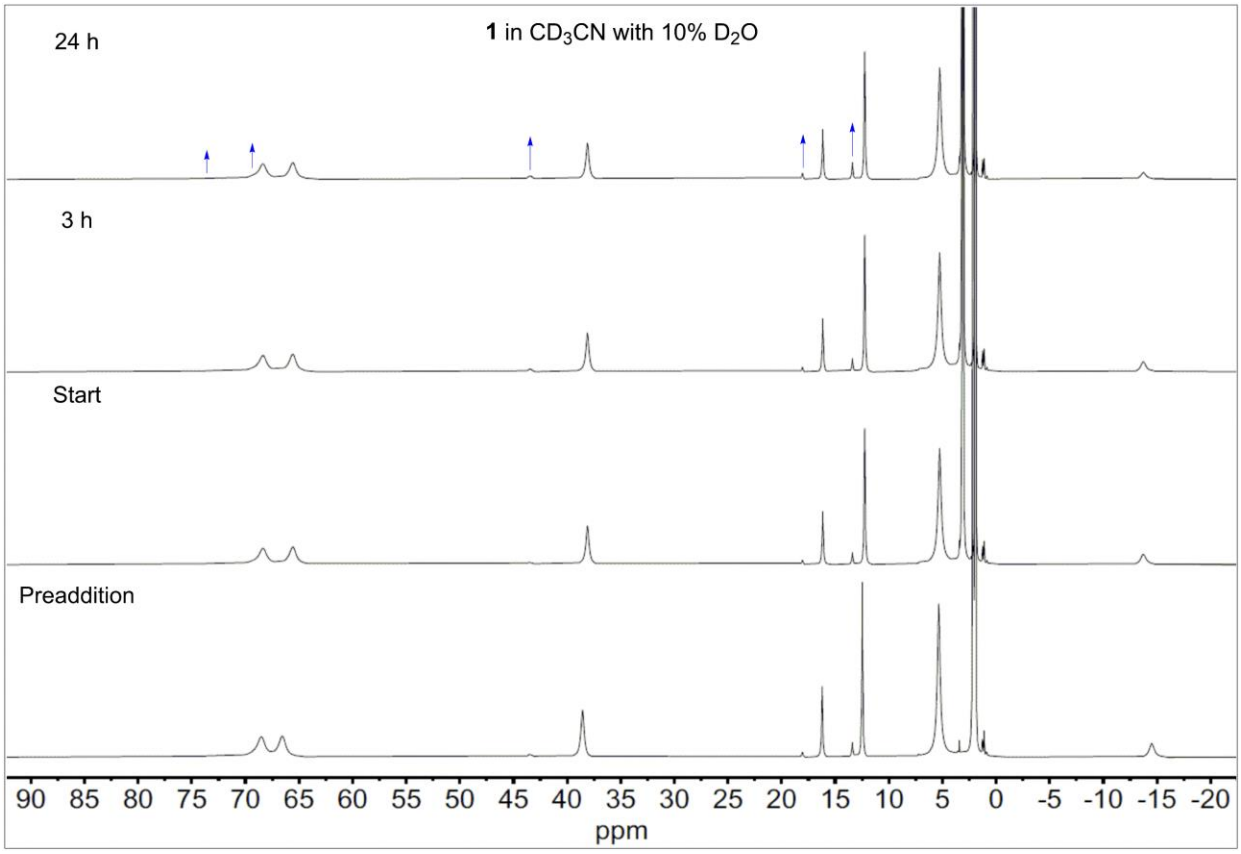

Figure S41: ^{1}H-NMR under paramagnetic conditions for **1** over time in dry CD_3CN with 10% D_2O (v:v).

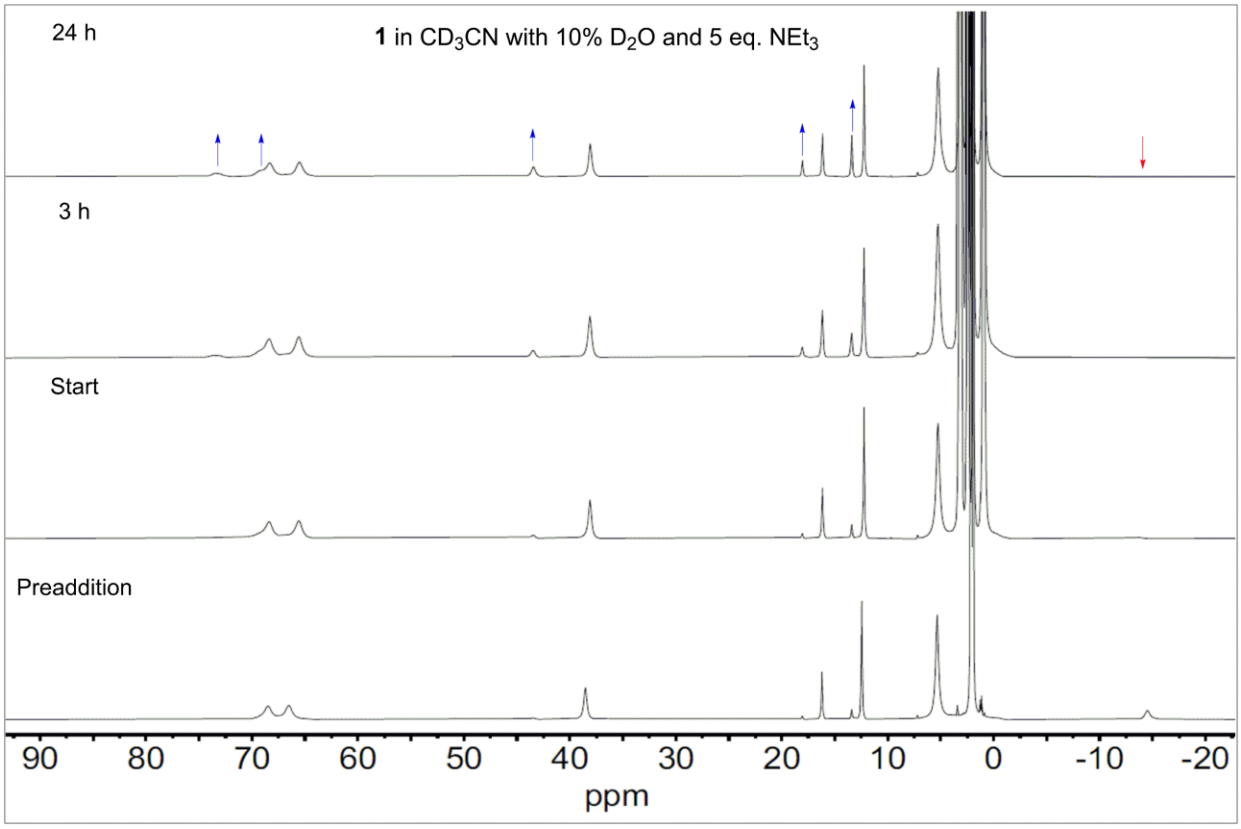

Figure S42: ^{1}H-NMR under paramagnetic conditions for **1** over time in dry CD_3CN with 5 equivalents of NEt_3 and 10% D_2O (v:v).

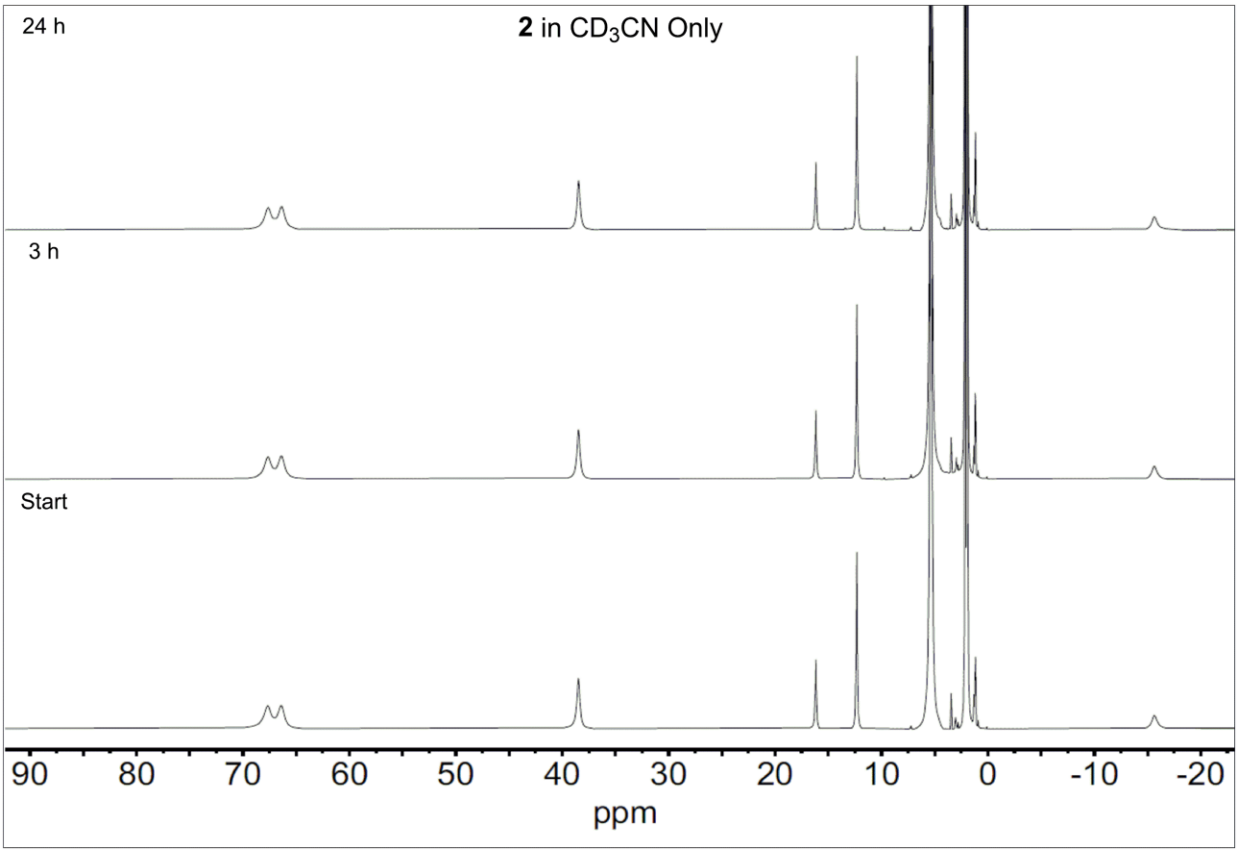

Figure S43: ^{1}H-NMR under paramagnetic conditions for **2** over time in dry CD_3CN only.

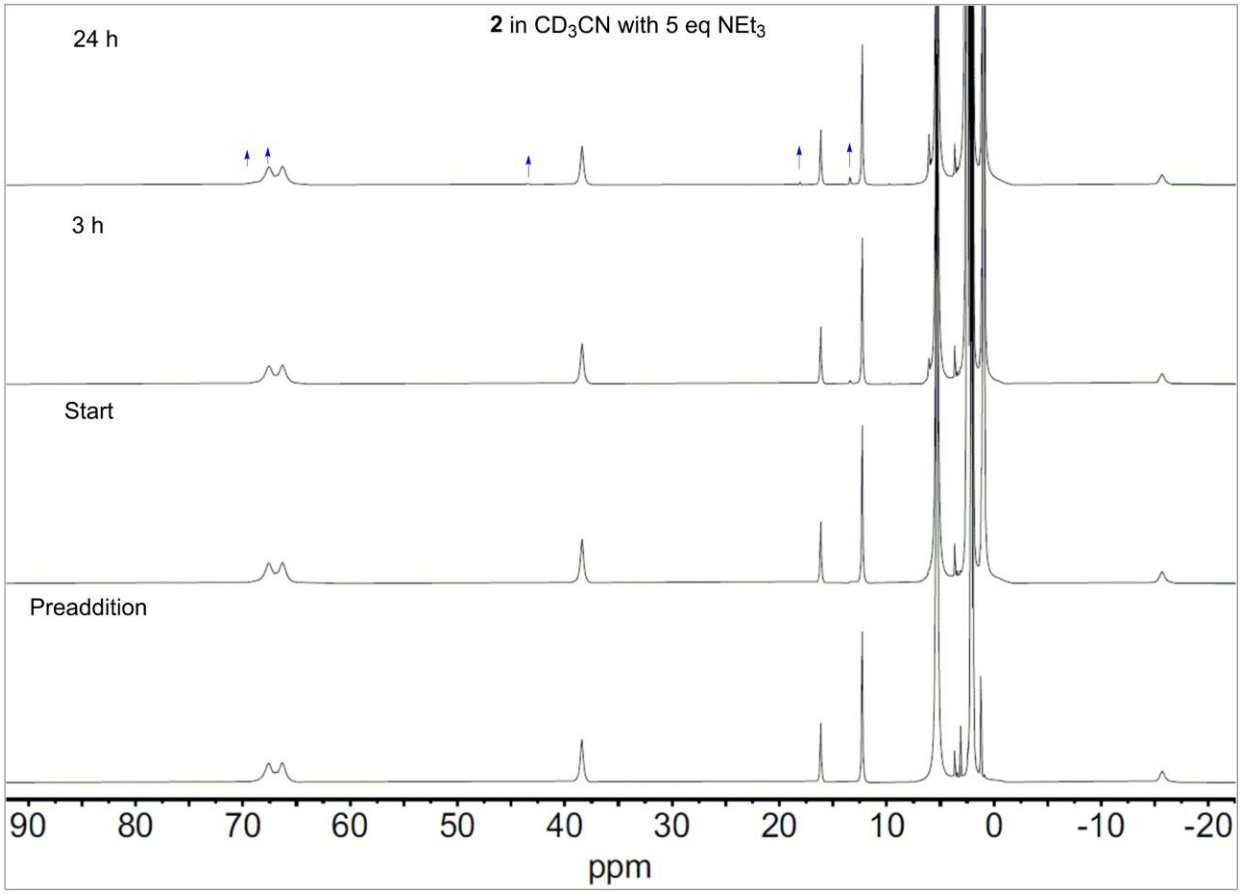

Figure S44: ^{1}H-NMR under paramagnetic conditions for **2** over time in dry CD_3CN with 5 equivalents of NEt_3.

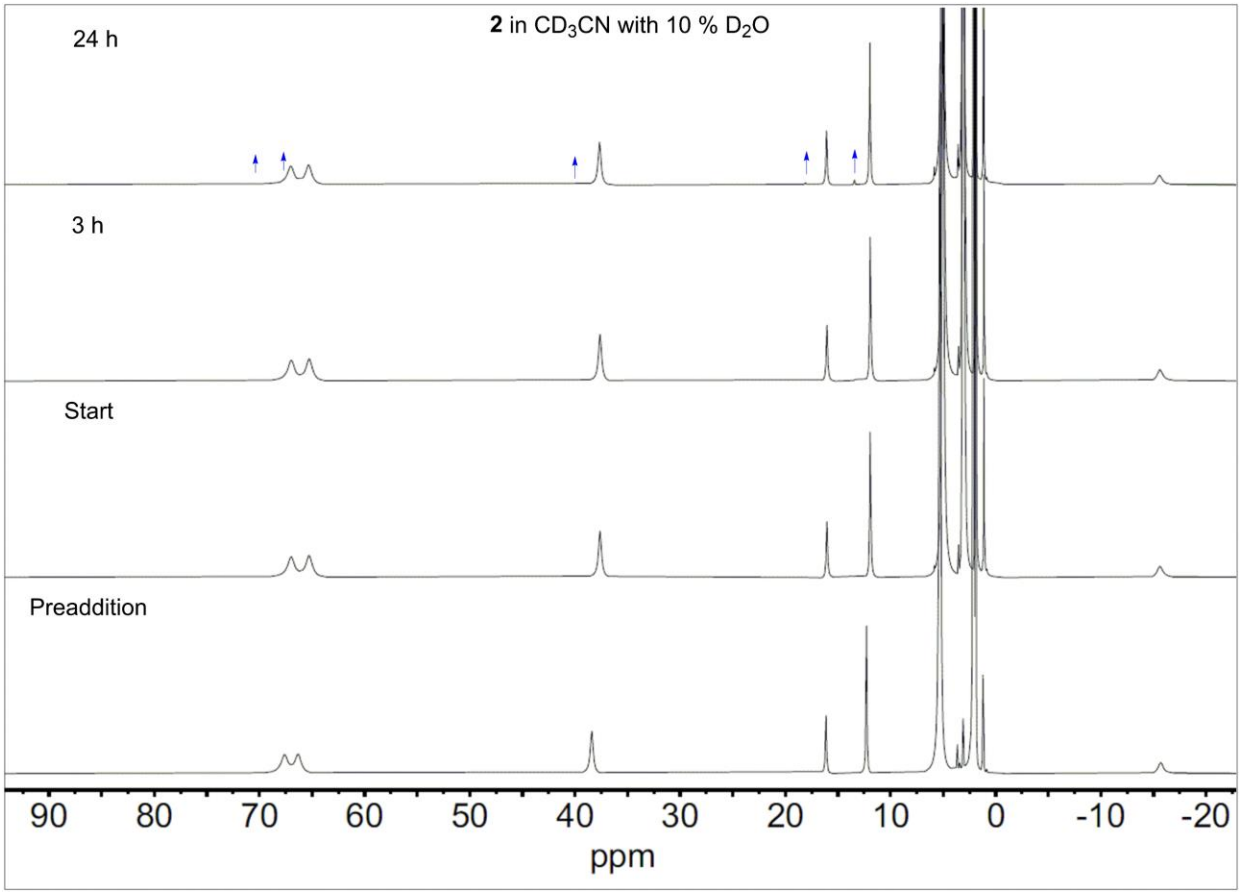

Figure S45: ^{1}H-NMR under paramagnetic conditions for **2** over time in dry CD_3CN with 10% D_2O (v:v).

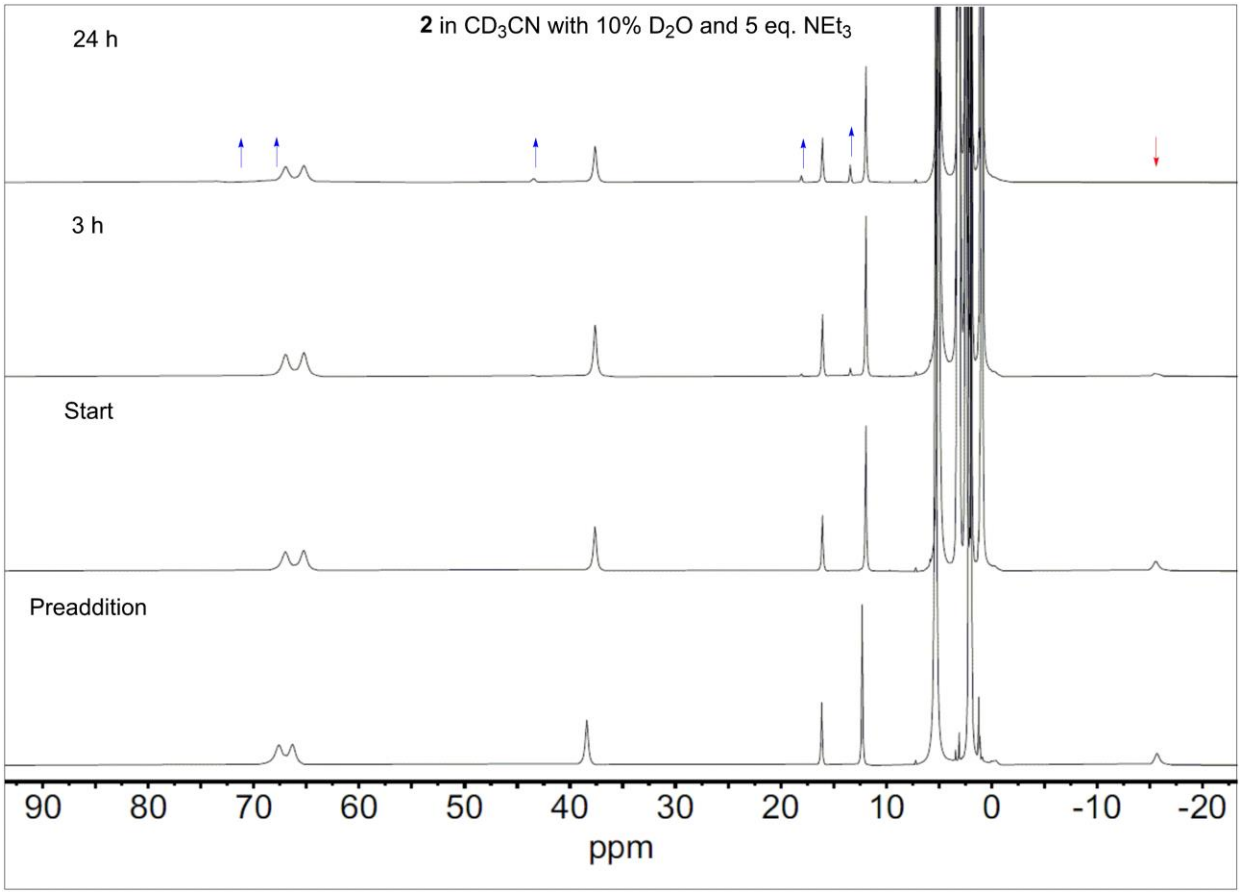

Figure S46: ^{1}H-NMR under paramagnetic conditions for **2** over time in dry CD_3CN with 5 equivalents of NEt_3 and 10% D_2O (v:v).

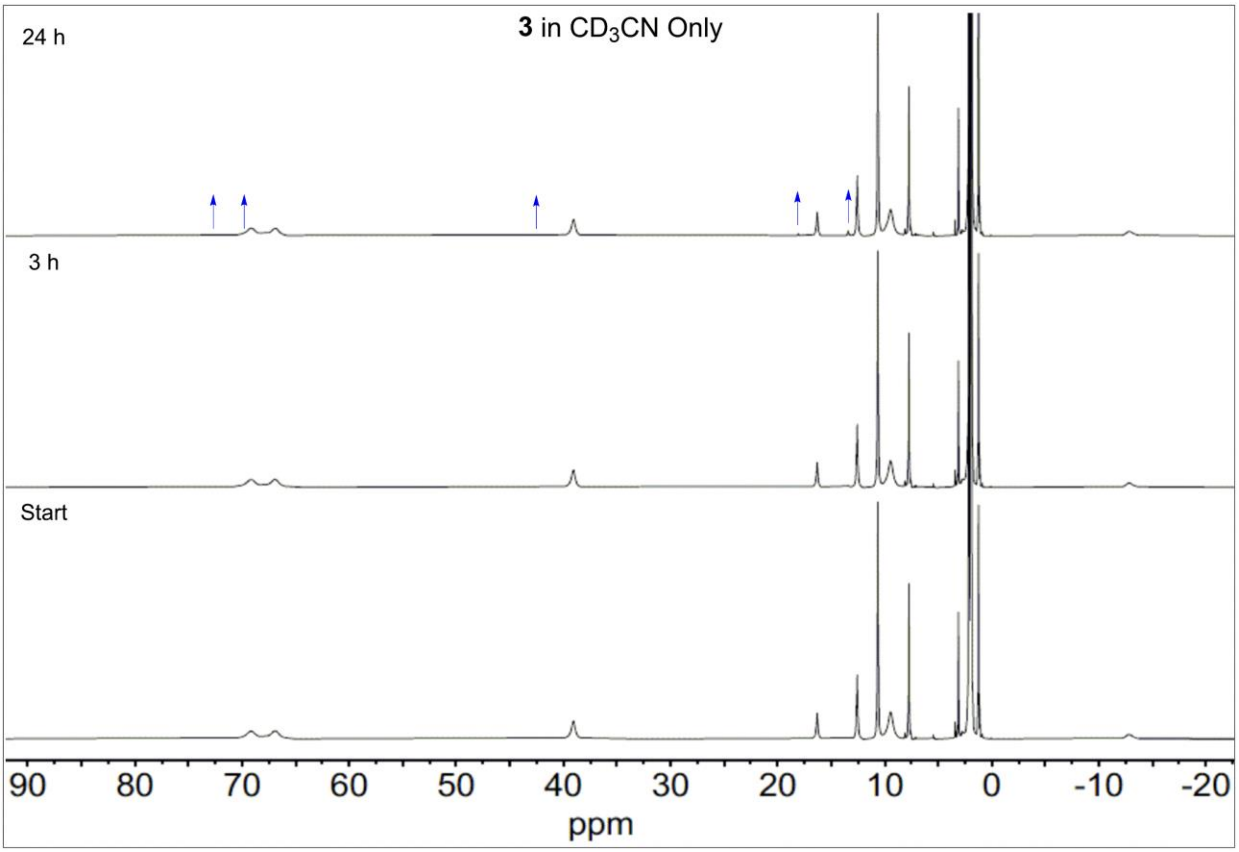

Figure S47: ^{1}H-NMR under paramagnetic conditions for **3** over time in dry CD_3CN only.

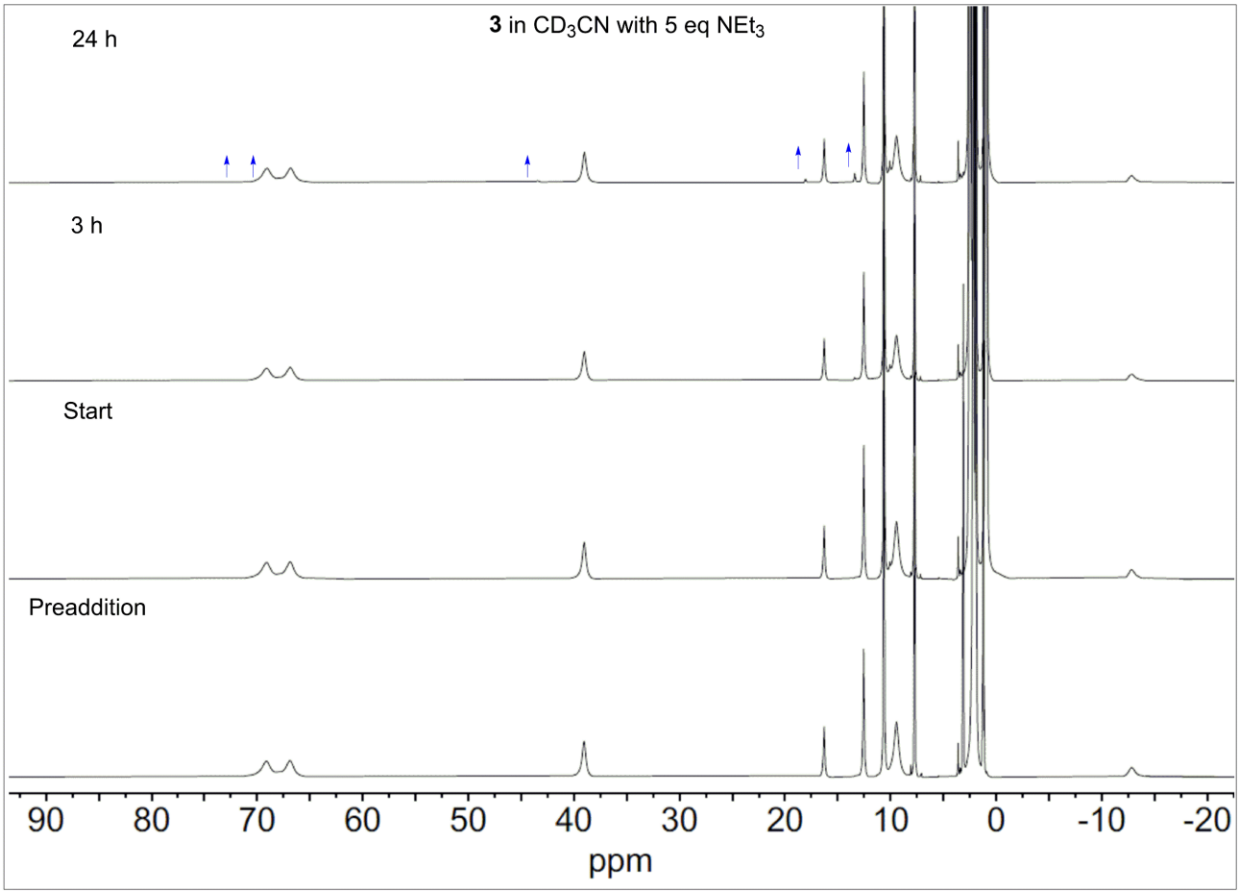

Figure S48: ^{1}H-NMR under paramagnetic conditions for **3** over time in dry CD_3CN with 5 equivalents of NEt_3.

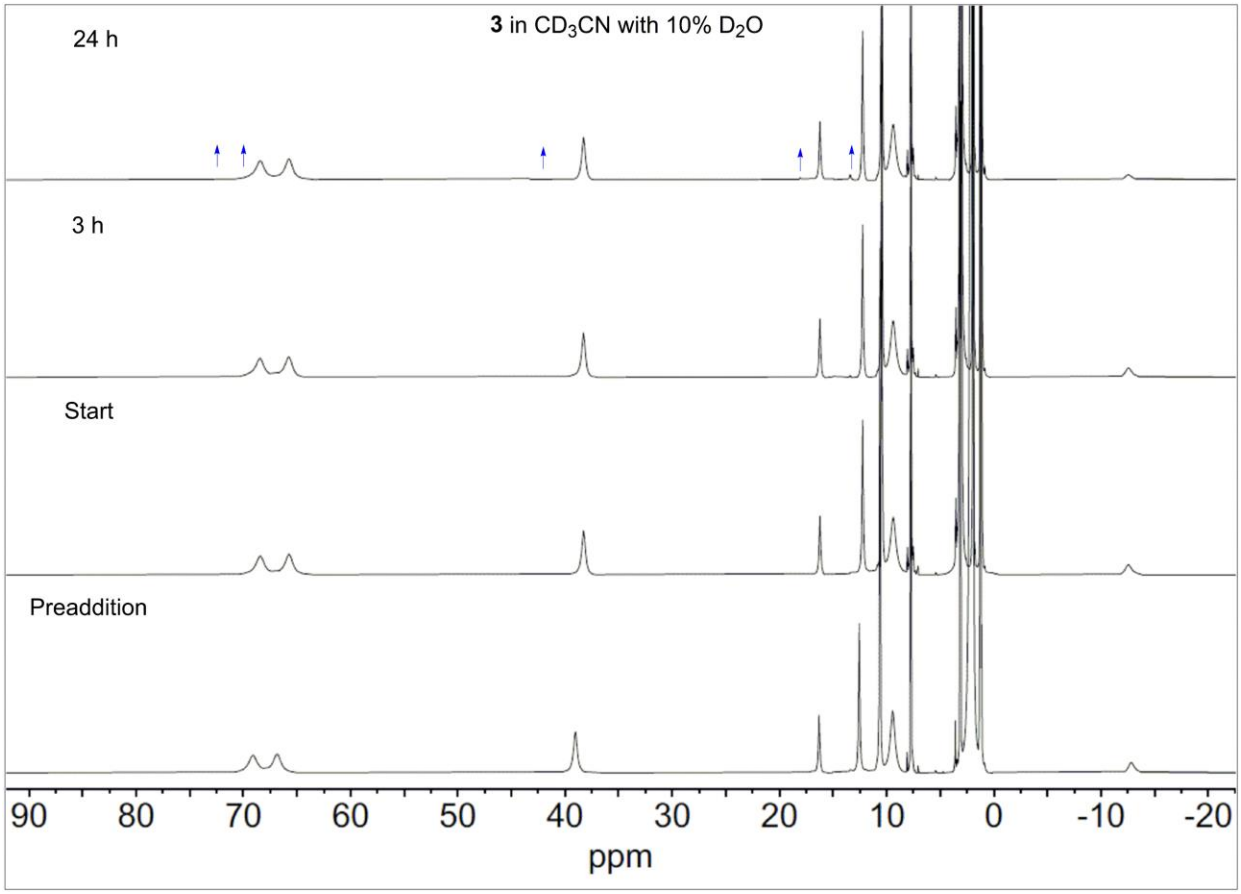

Figure S49: ^{1}H-NMR under paramagnetic conditions for **3** over time in dry CD_3CN with 10% D_2O (v:v).

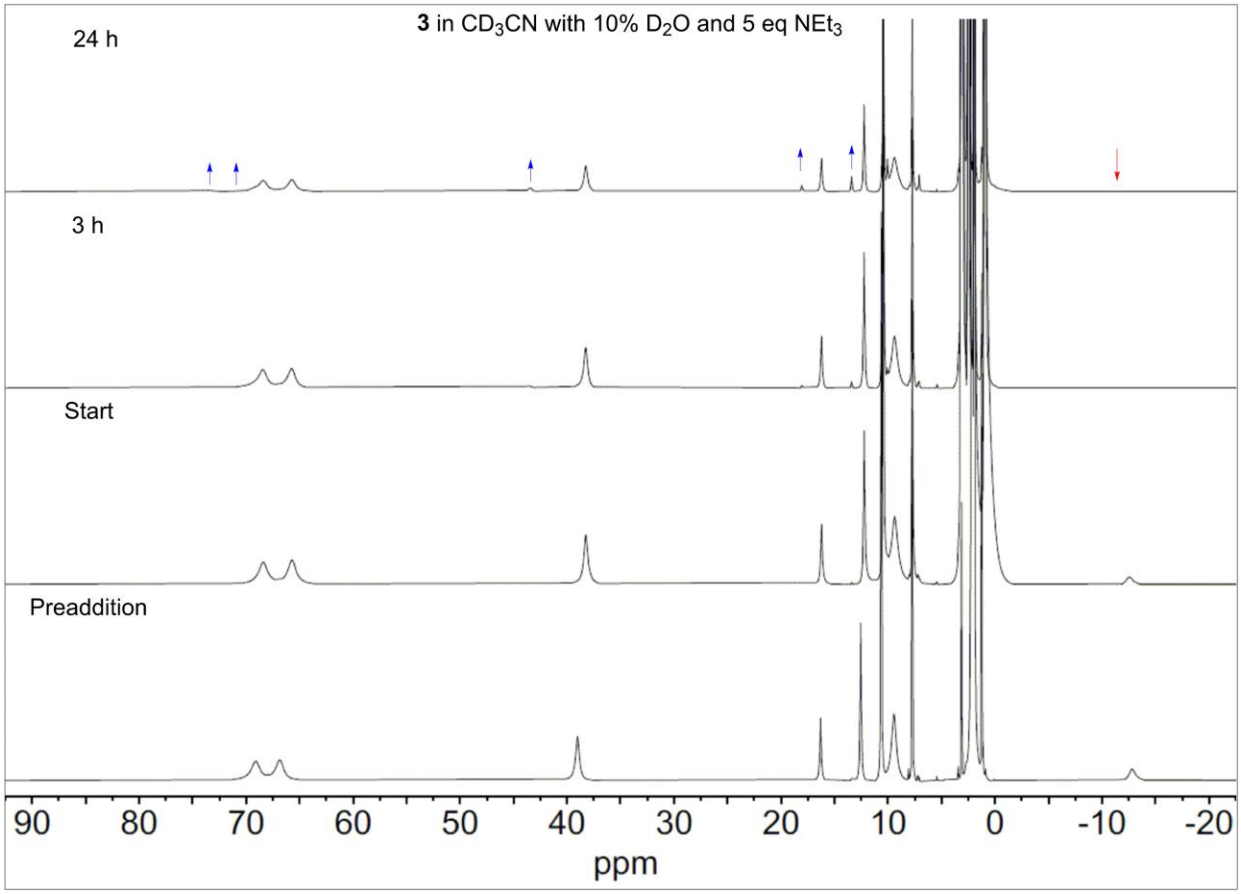

Figure S50: ^{1}H-NMR under paramagnetic conditions for **3** over time in dry CD_3CN with 5 equivalents of NEt_3 and 10% D_2O (v:v).

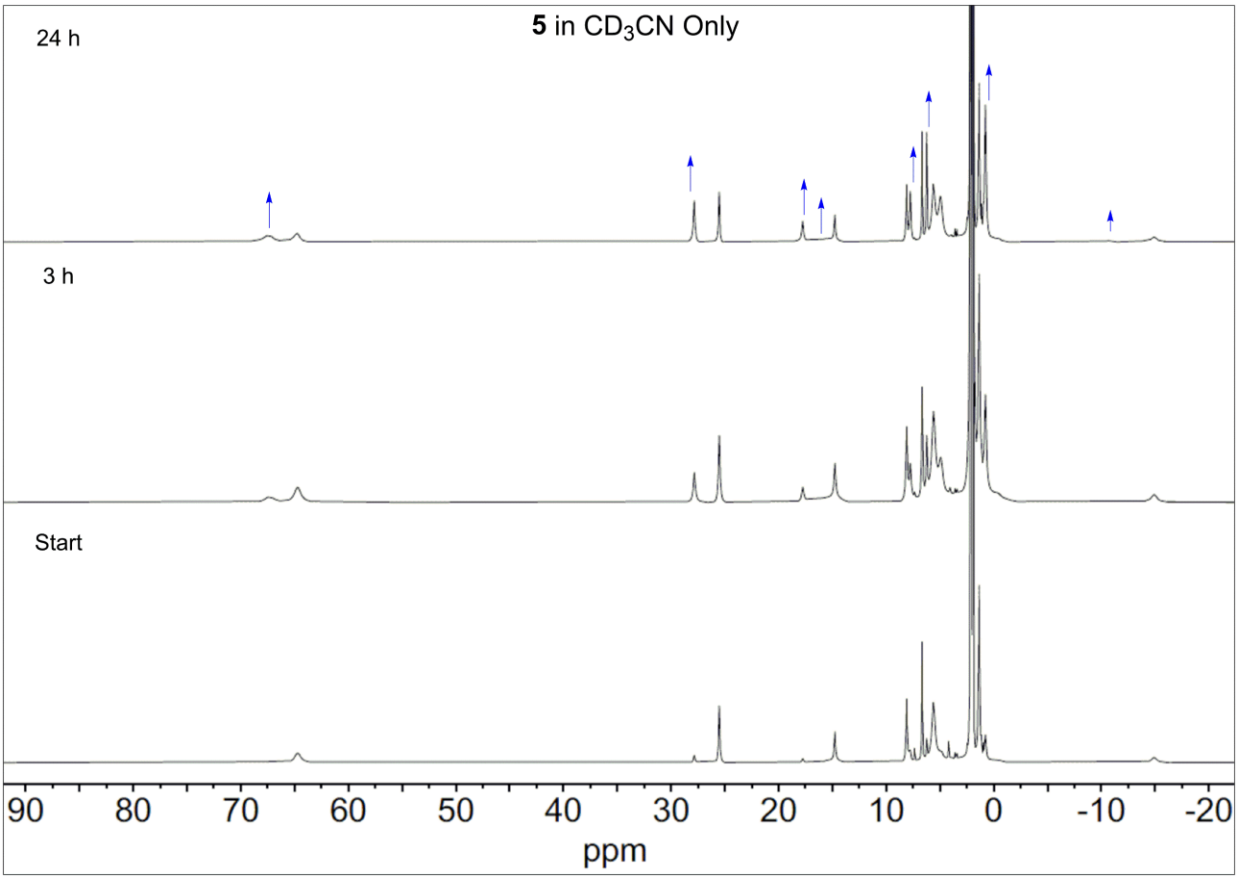

Figure S51: ^{1}H-NMR under paramagnetic conditions for **5** over time in dry CD_3CN only.

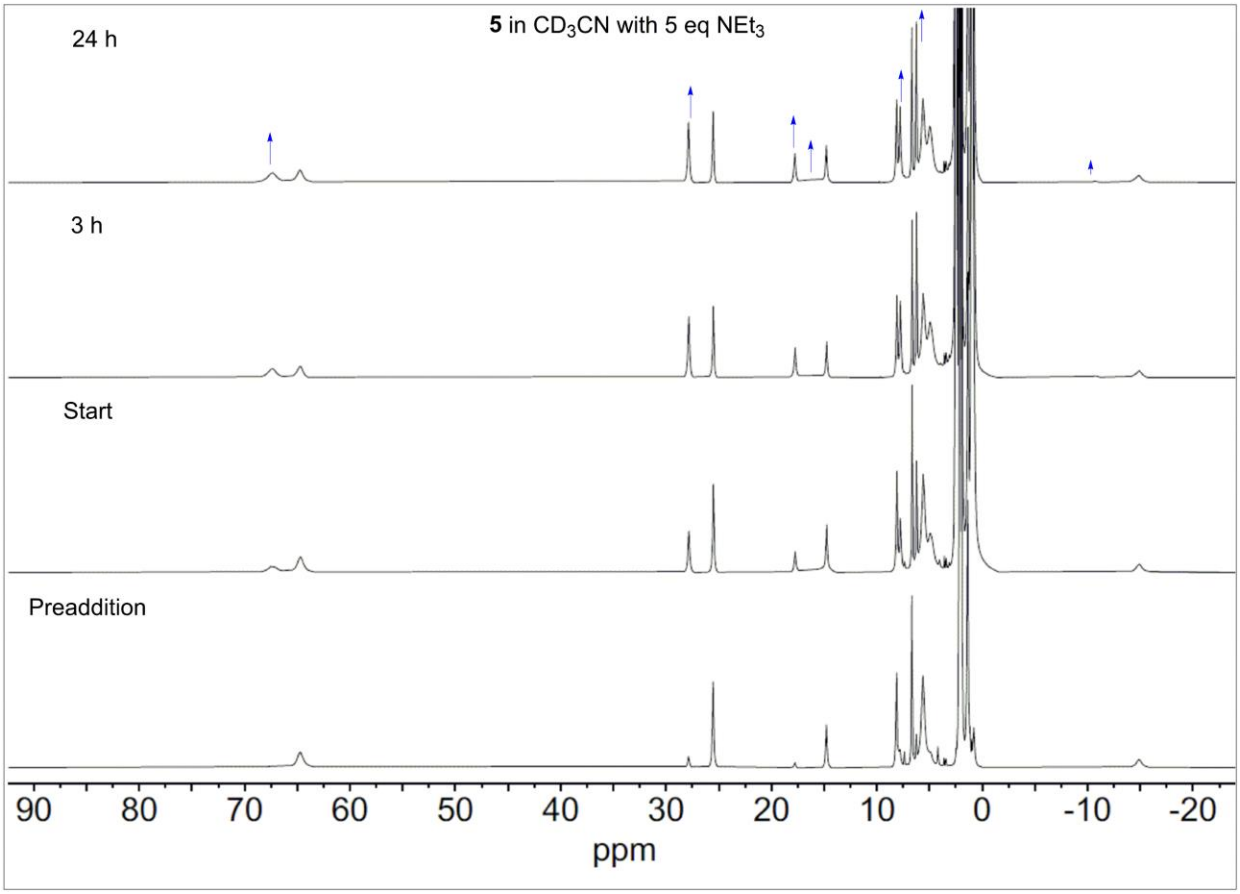

Figure S52: ^{1}H-NMR under paramagnetic conditions for **5** over time in dry CD_3CN with 5 equivalents of NEt_3.

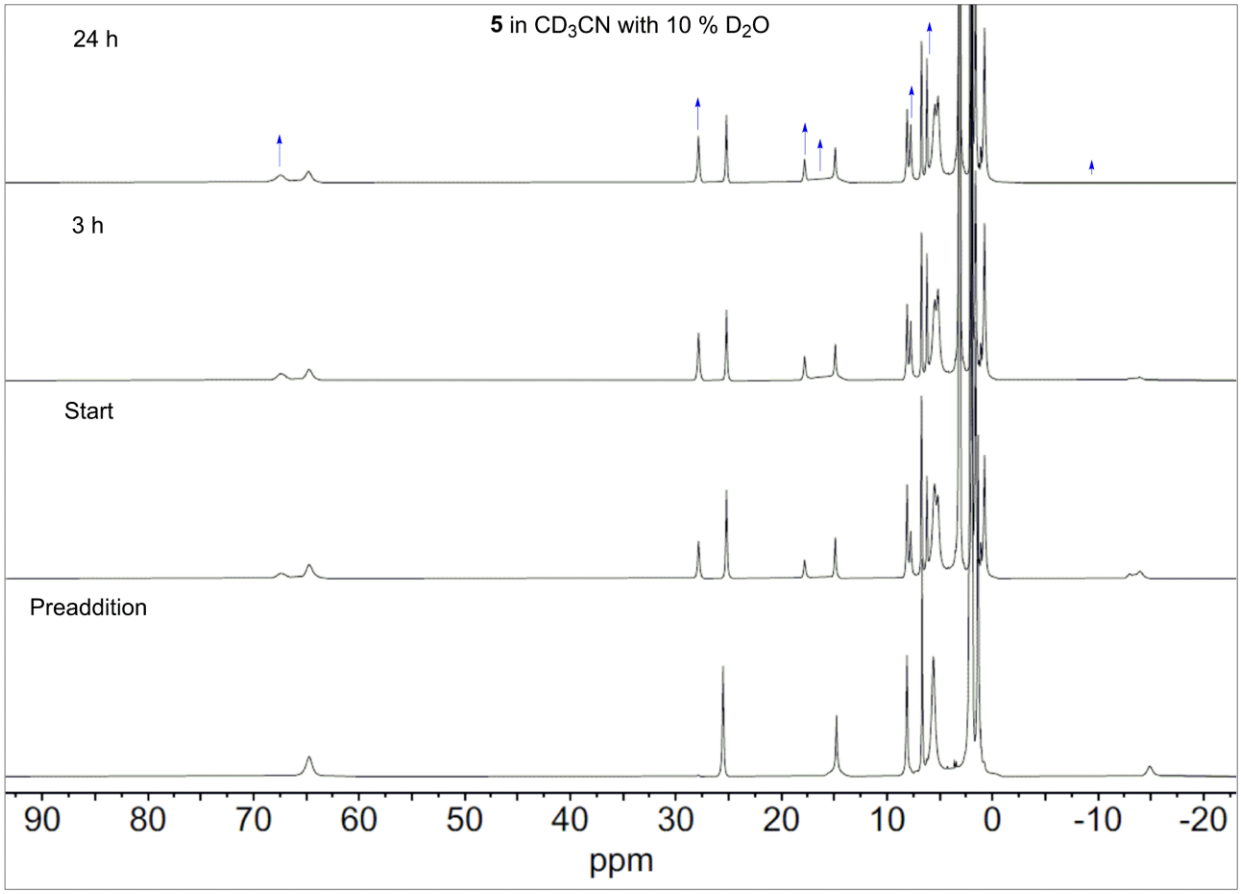

Figure S53: ^{1}H-NMR under paramagnetic conditions for **5** over time in dry CD_3CN with 10% D_2O (v:v).

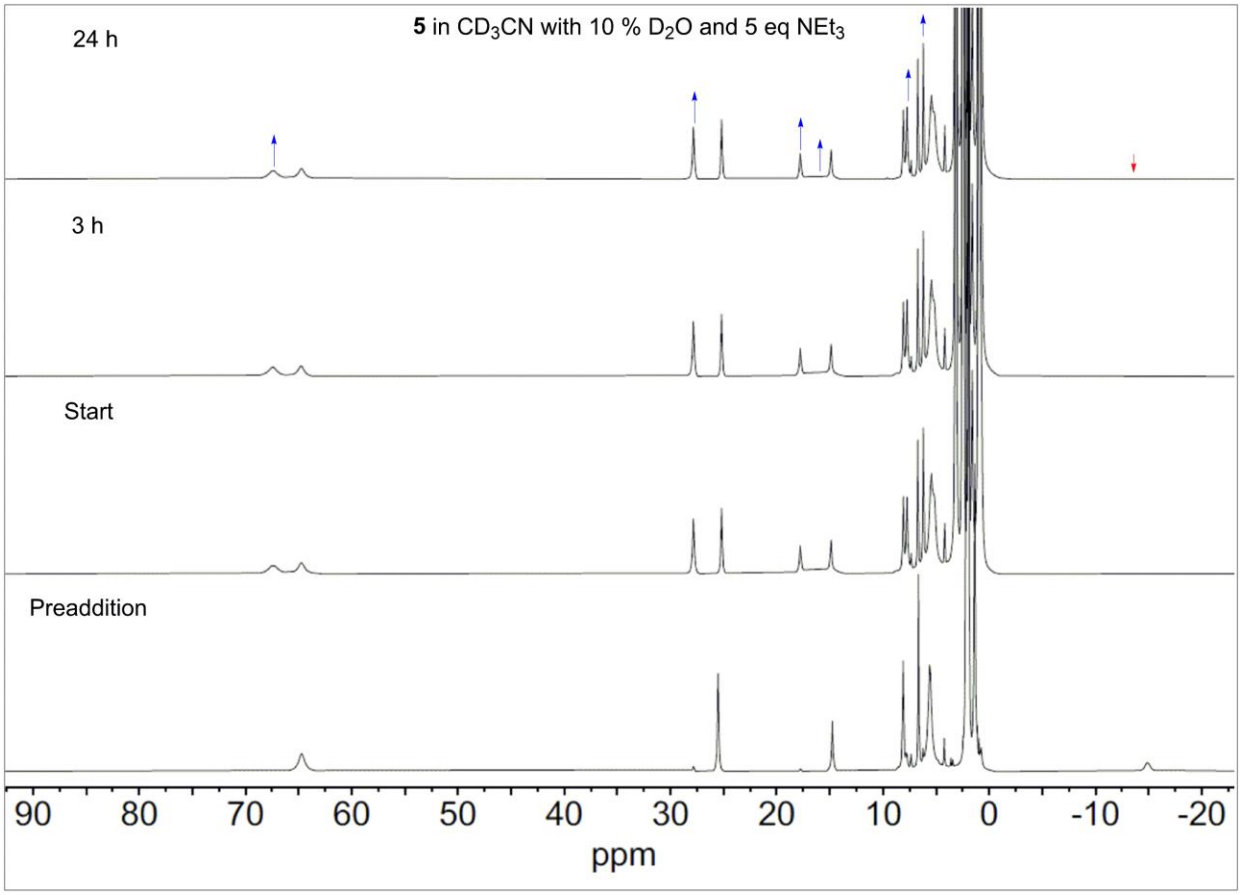

Figure S54: ^{1}H-NMR under paramagnetic conditions for **5** over time in dry CD_3CN with 5 equivalents of NEt_3 and 10% D_2O (v:v).

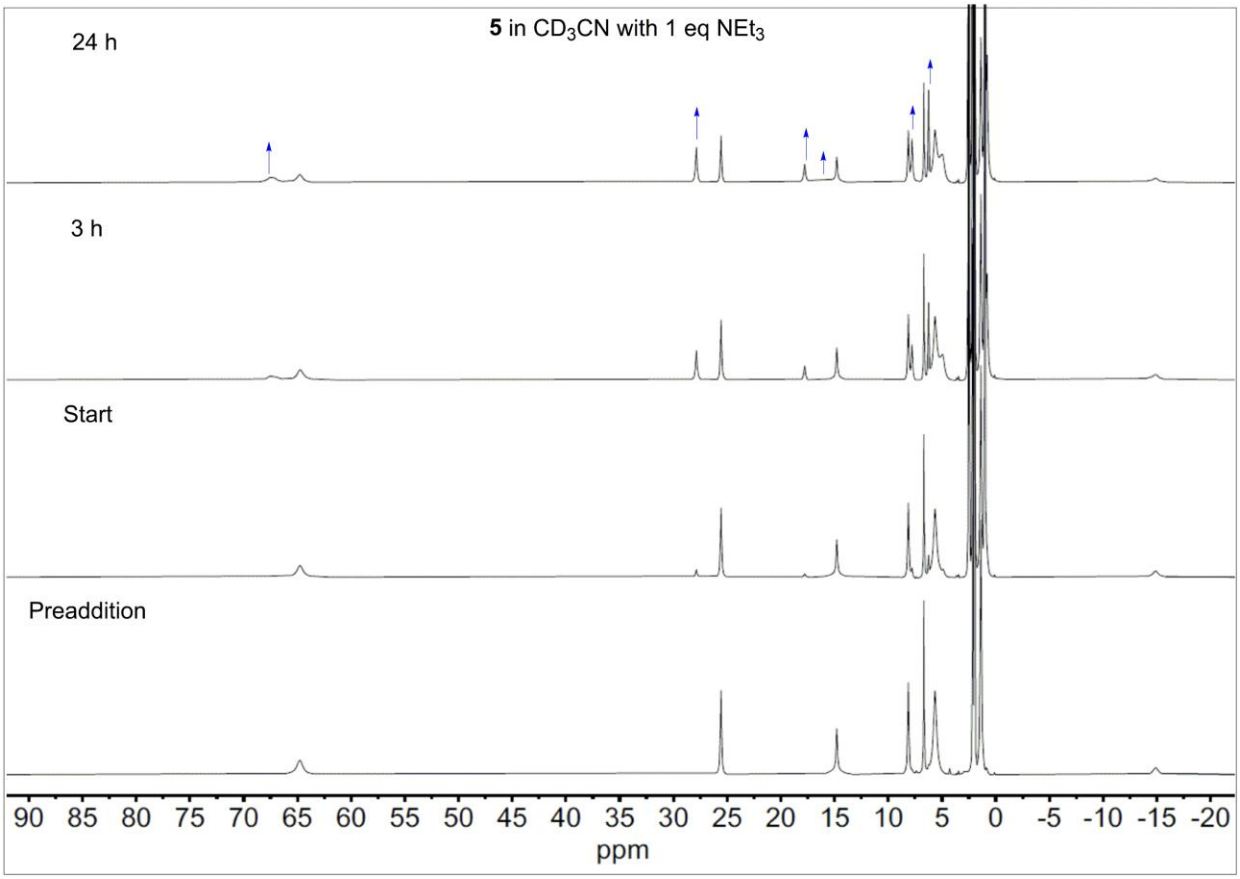

Figure S55: ^{1}H-NMR under paramagnetic conditions for **5** over time in dry CD_3CN with 1 equivalent of NEt_3.

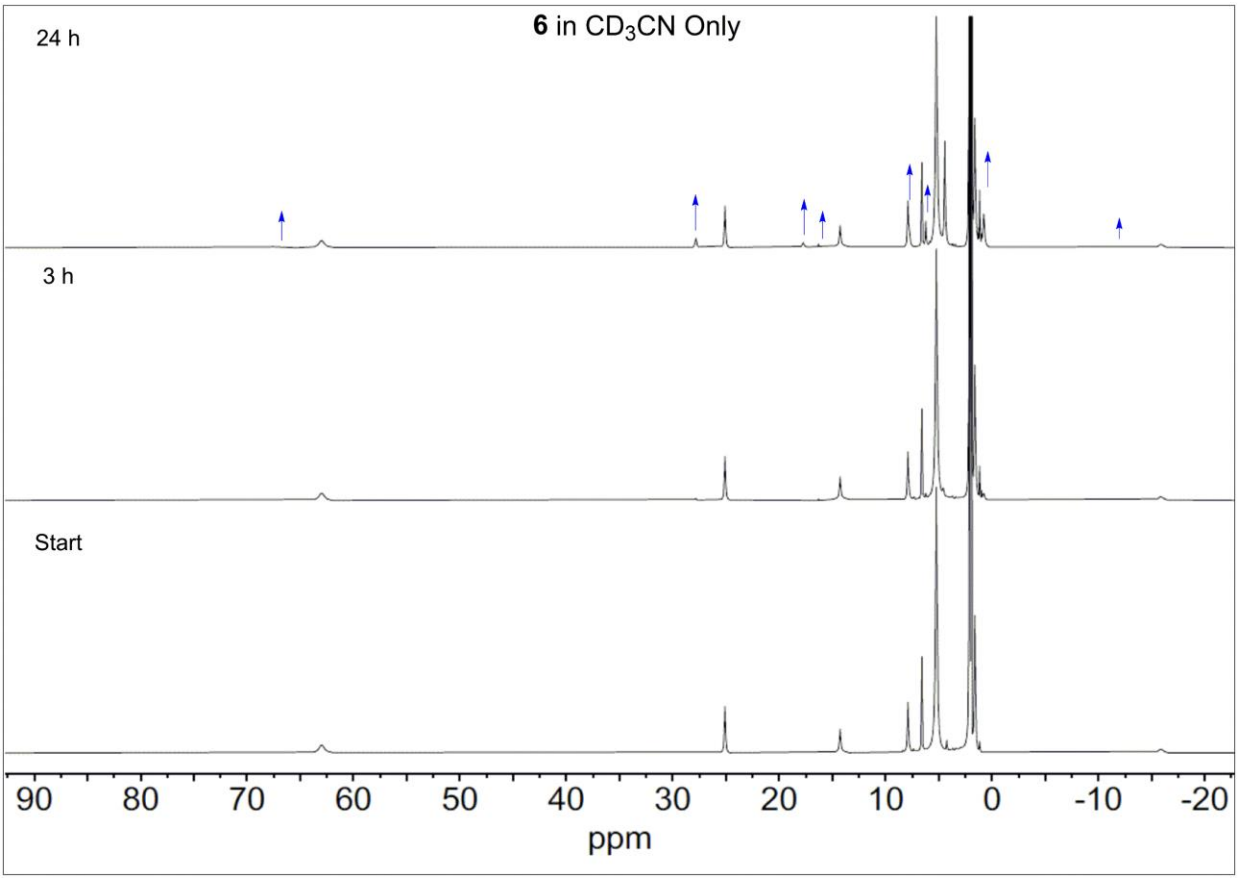

Figure S56: ^{1}H-NMR under paramagnetic conditions for **6** over time in dry CD_3CN only.

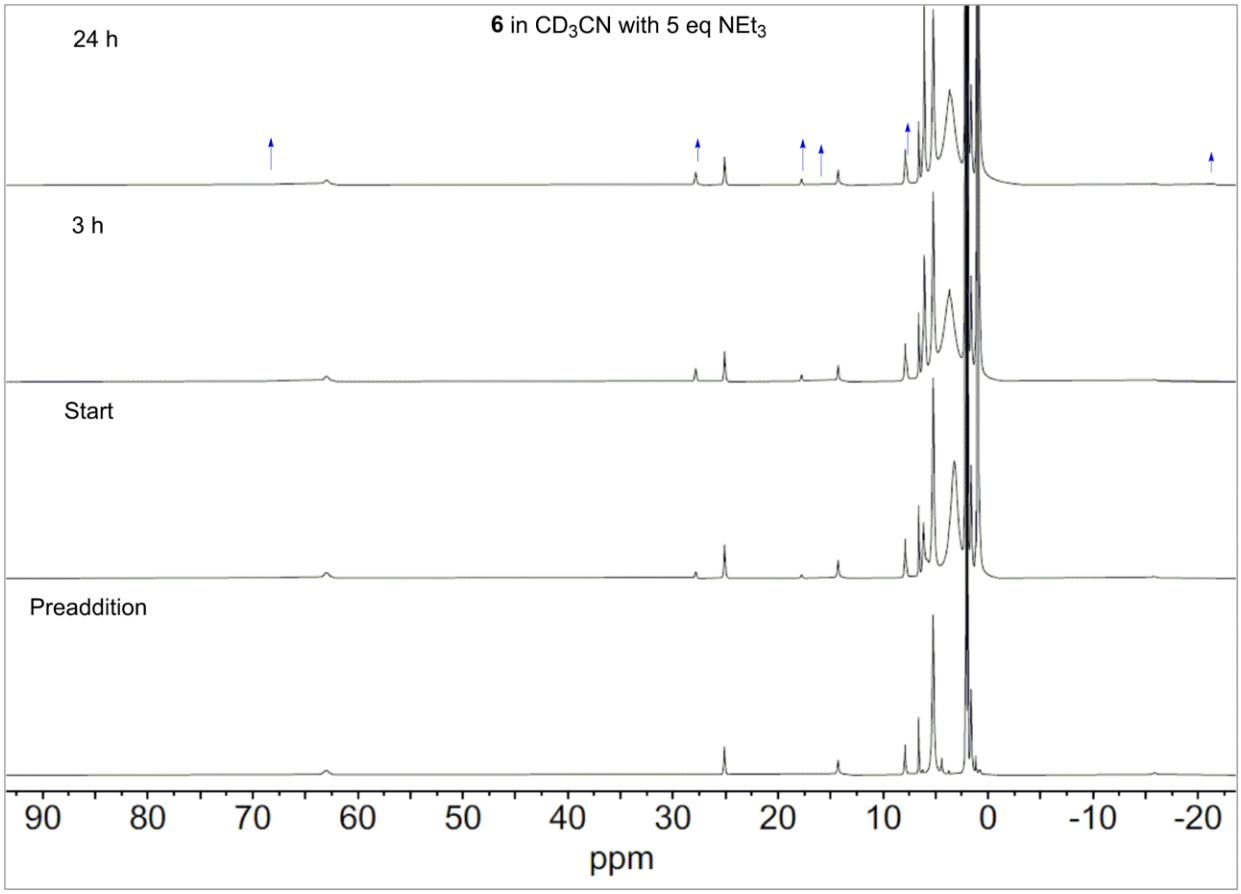

Figure S57: ^{1}H-NMR under paramagnetic conditions for **6** over time in dry CD_3CN with 5 equivalents of NEt_3.

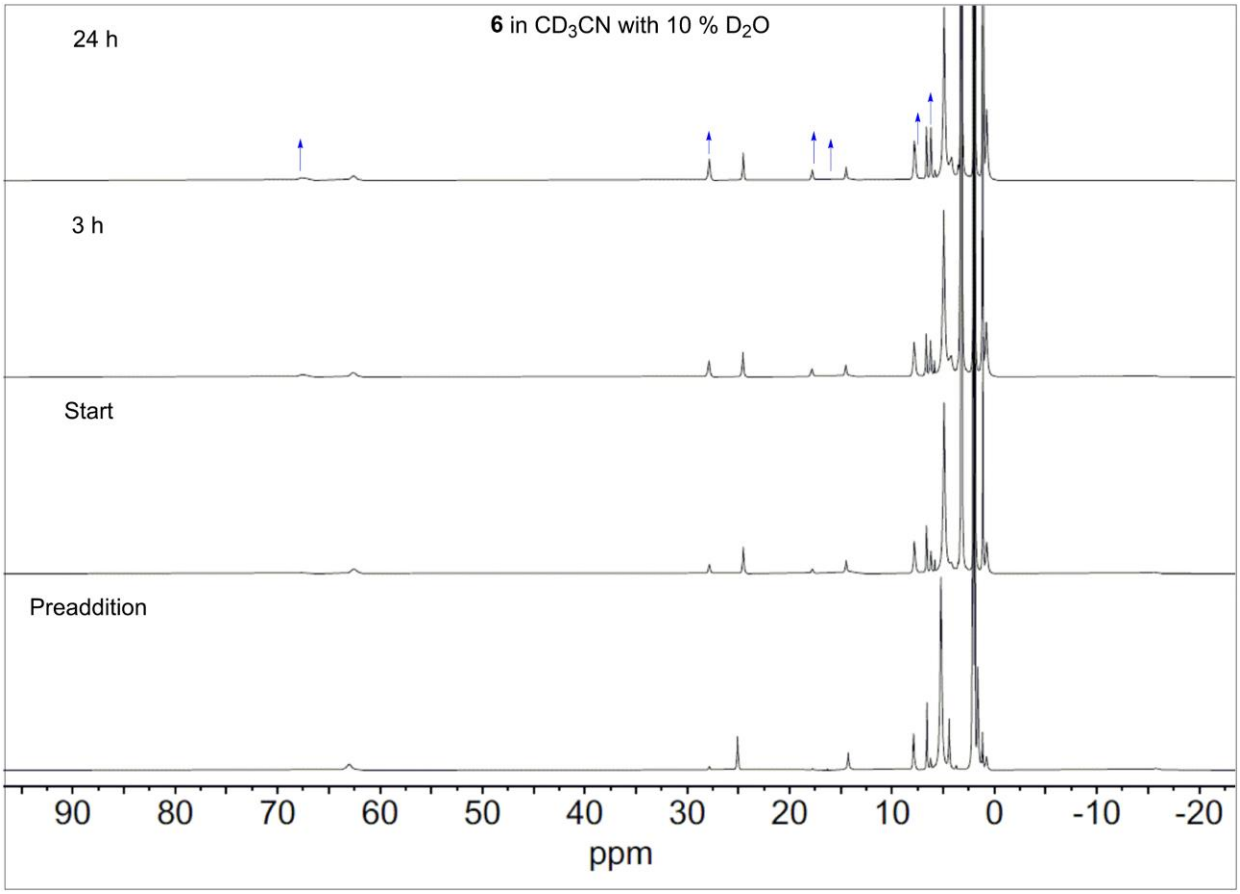

Figure S58: ^{1}H-NMR under paramagnetic conditions for **6** over time in dry CD_3CN with 10% D_2O (v:v).

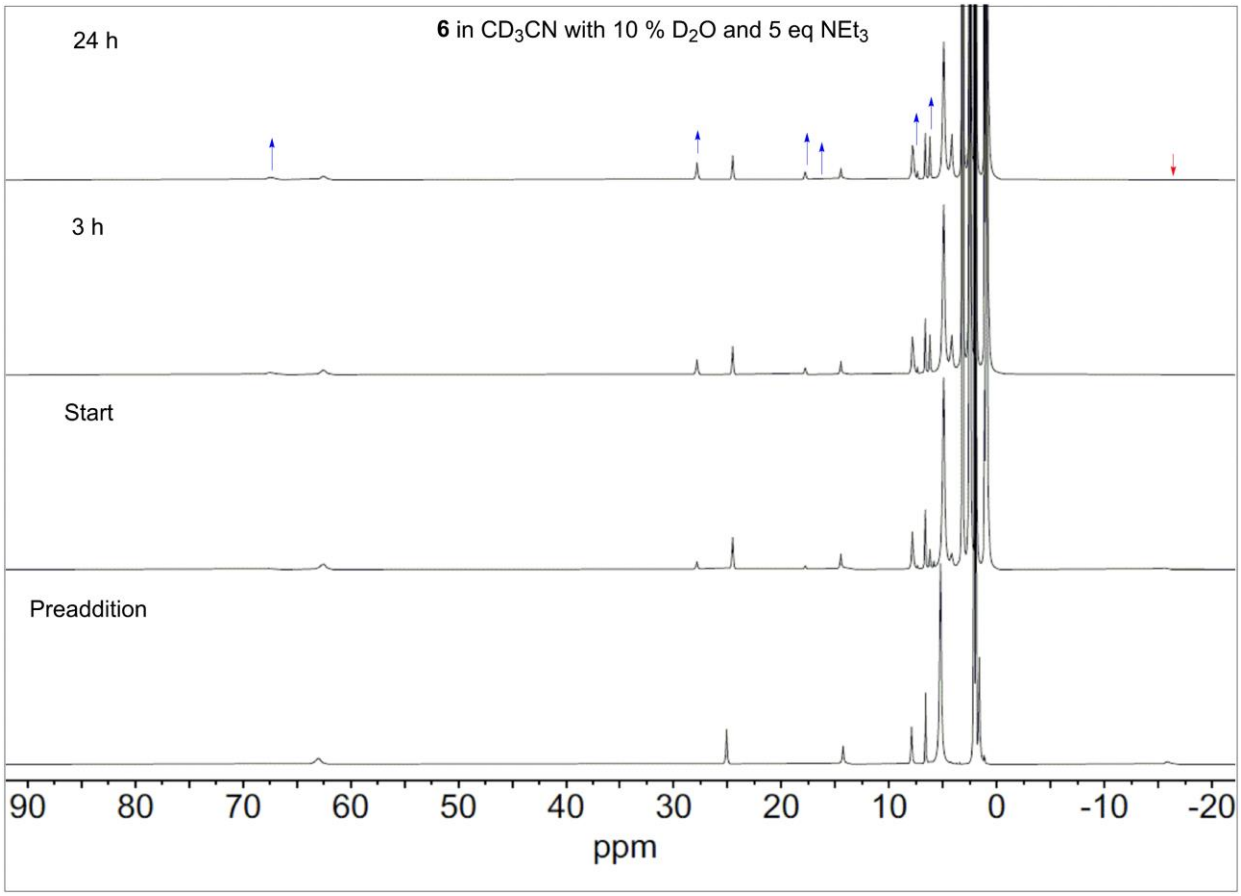

Figure S59: ^{1}H-NMR under paramagnetic conditions for **6** over time in dry CD_3CN with 5 equivalents of NEt_3 and 10% D_2O (v:v).

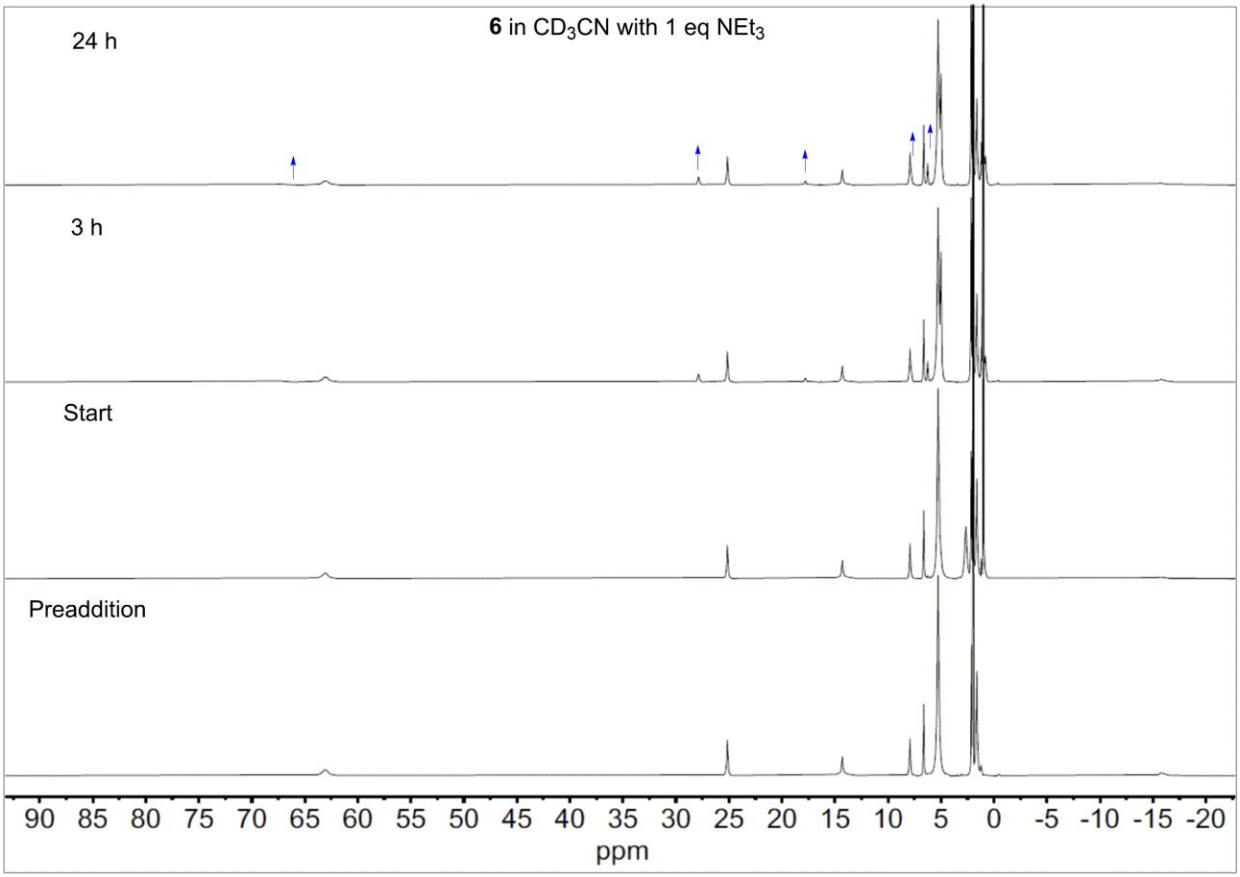

Figure S60: ^{1}H-NMR under paramagnetic conditions for **6** over time in dry CD_3CN with 1 equivalent of NEt_3.

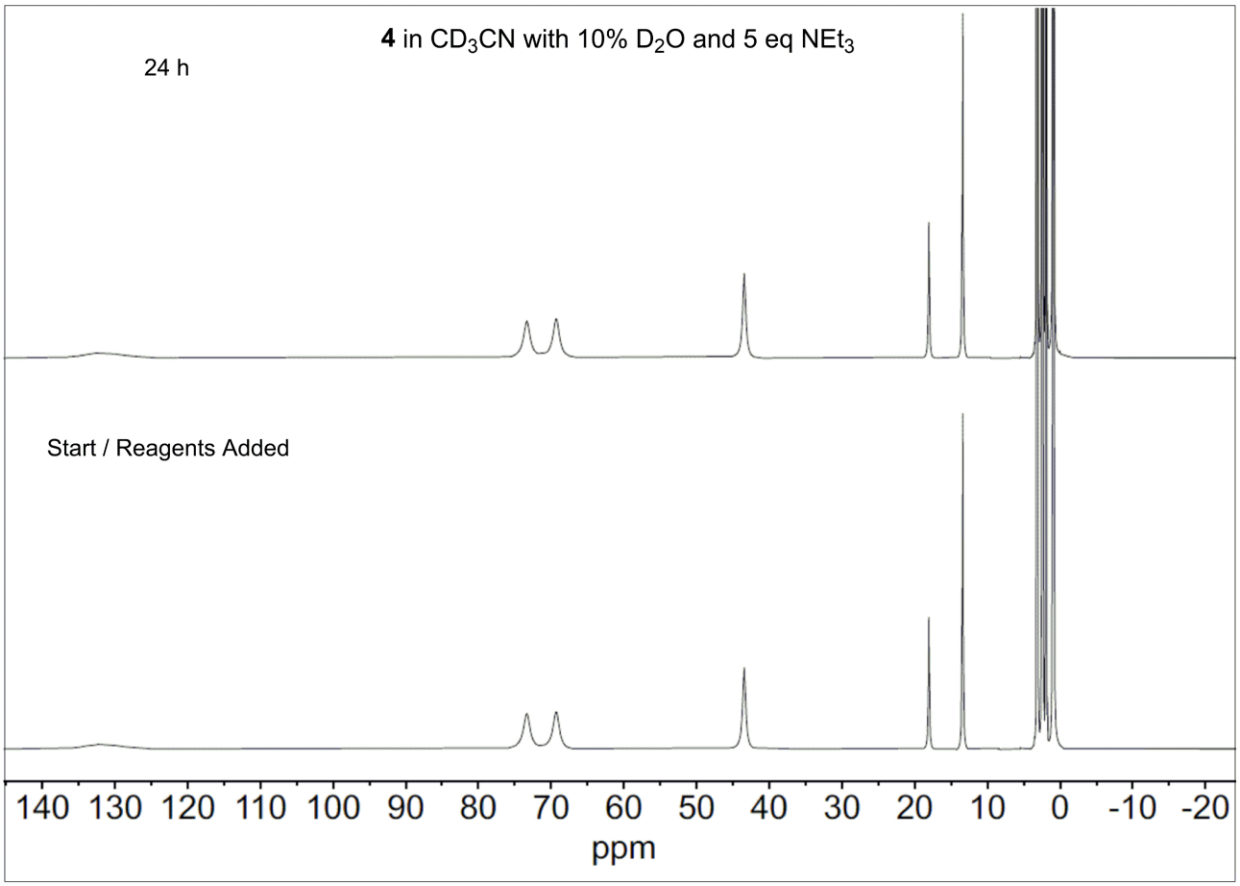

Figure S61: ^{1}H-NMR under paramagnetic conditions for **4** at the start and 24 hours later in dry CD_3CN with 5 equivalents of NEt_3 and 10% D_2O (v:v).

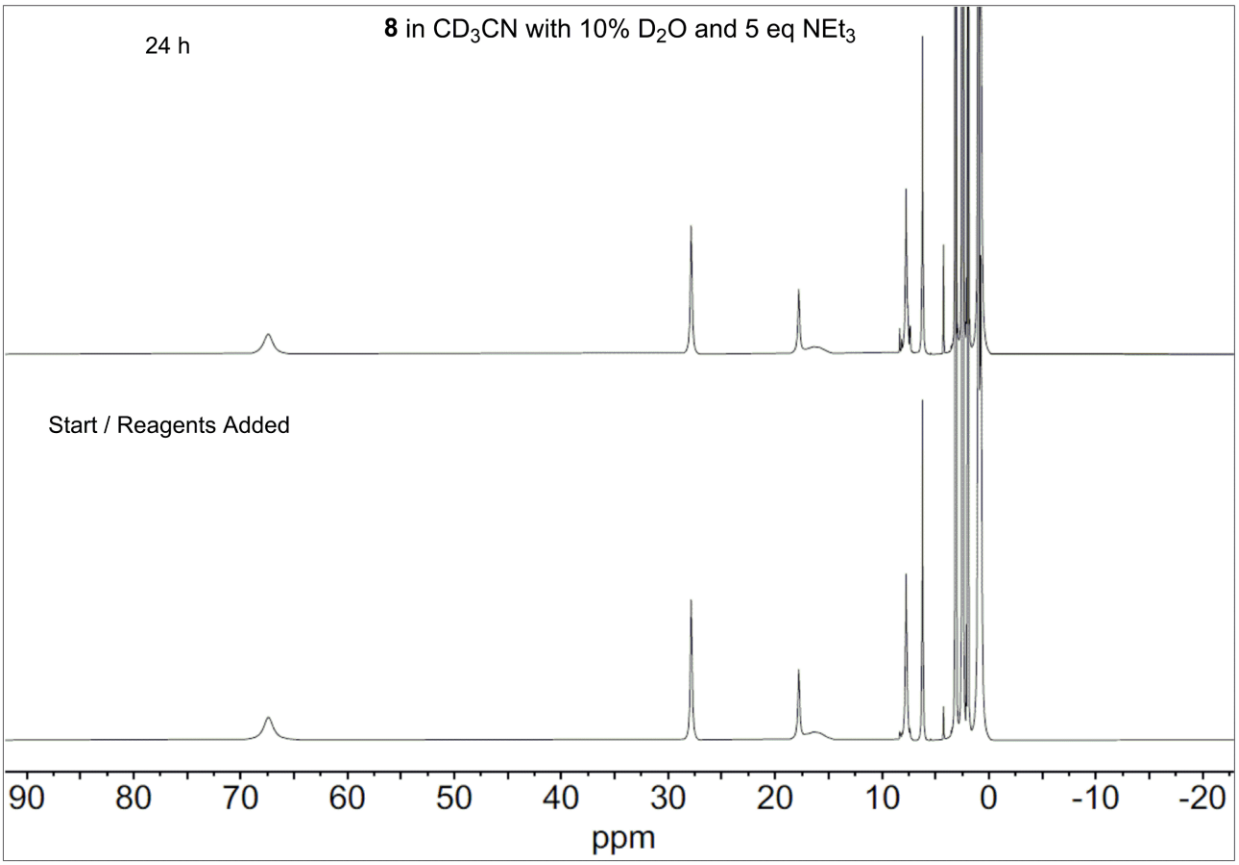

Figure S62: ^{1}H-NMR under paramagnetic conditions for **8** at the start and 24 hours later in dry CD_3CN with 5 equivalents of NEt_3 and 10% D_2O (v:v).

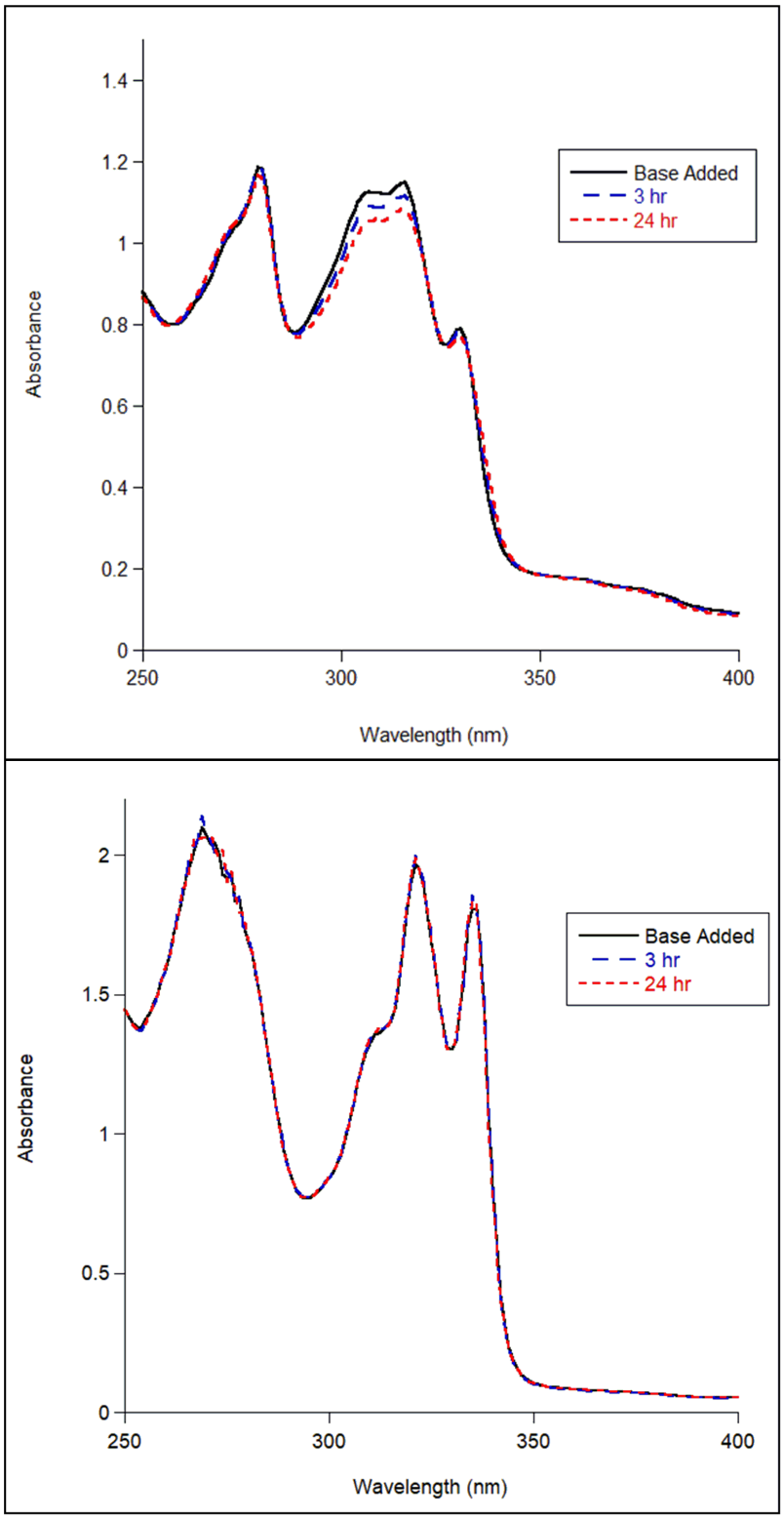

Figure S63: UV-Vis absorption spectra of **1** (top) and **4** (bottom) over time. Concentration: 5.00×10^{-4} M. Conditions: CH_3CN, 10% D_2O (v:v), 5 eq NEt_3, RT.

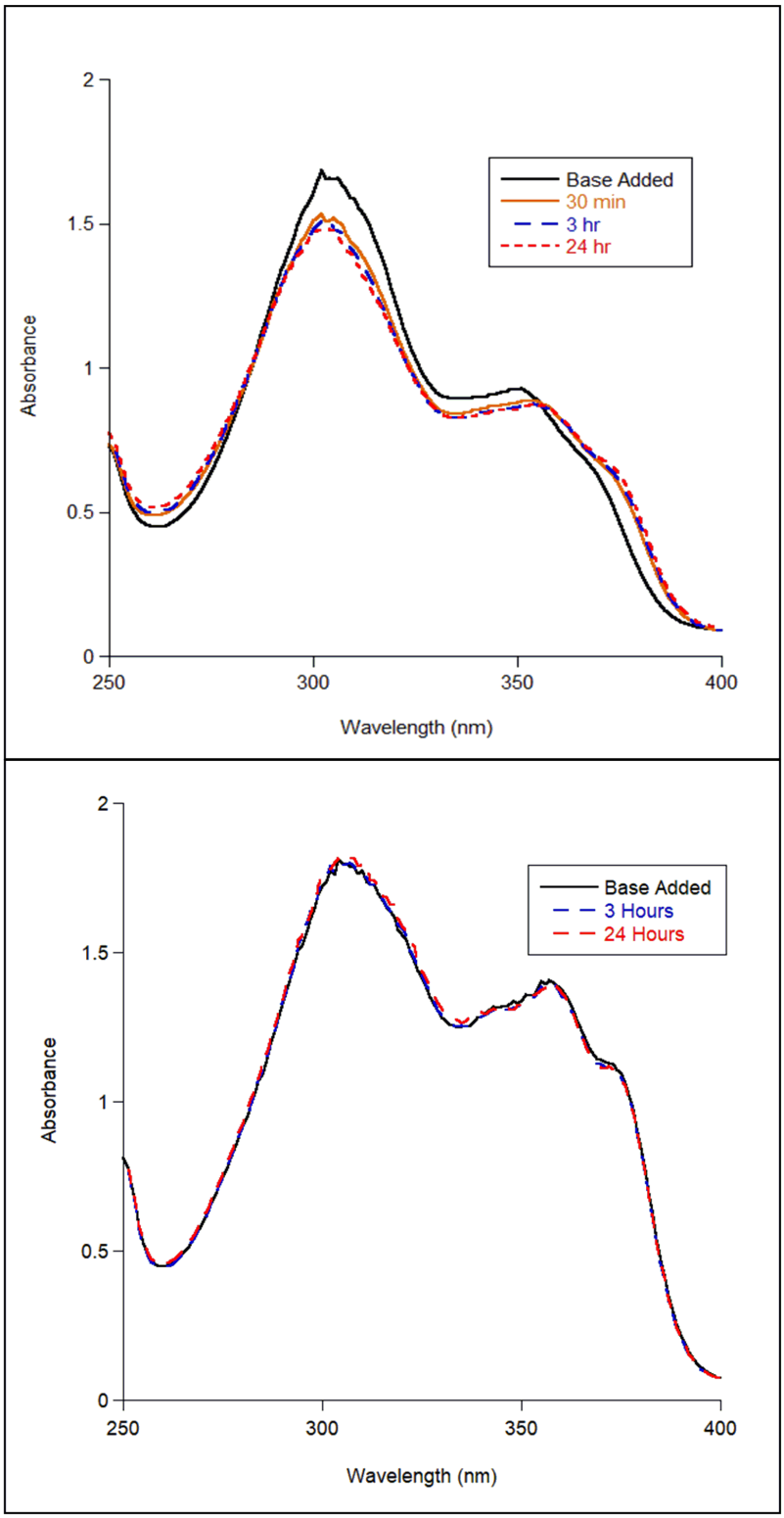

Figure S64: UV-Vis absorption spectra of **5** (top) and **8** (bottom) over time. Concentration: 5.00×10^{-4} M. Conditions: CH_3CN, 10% D_2O (v:v), 5 eq NEt_3, RT.

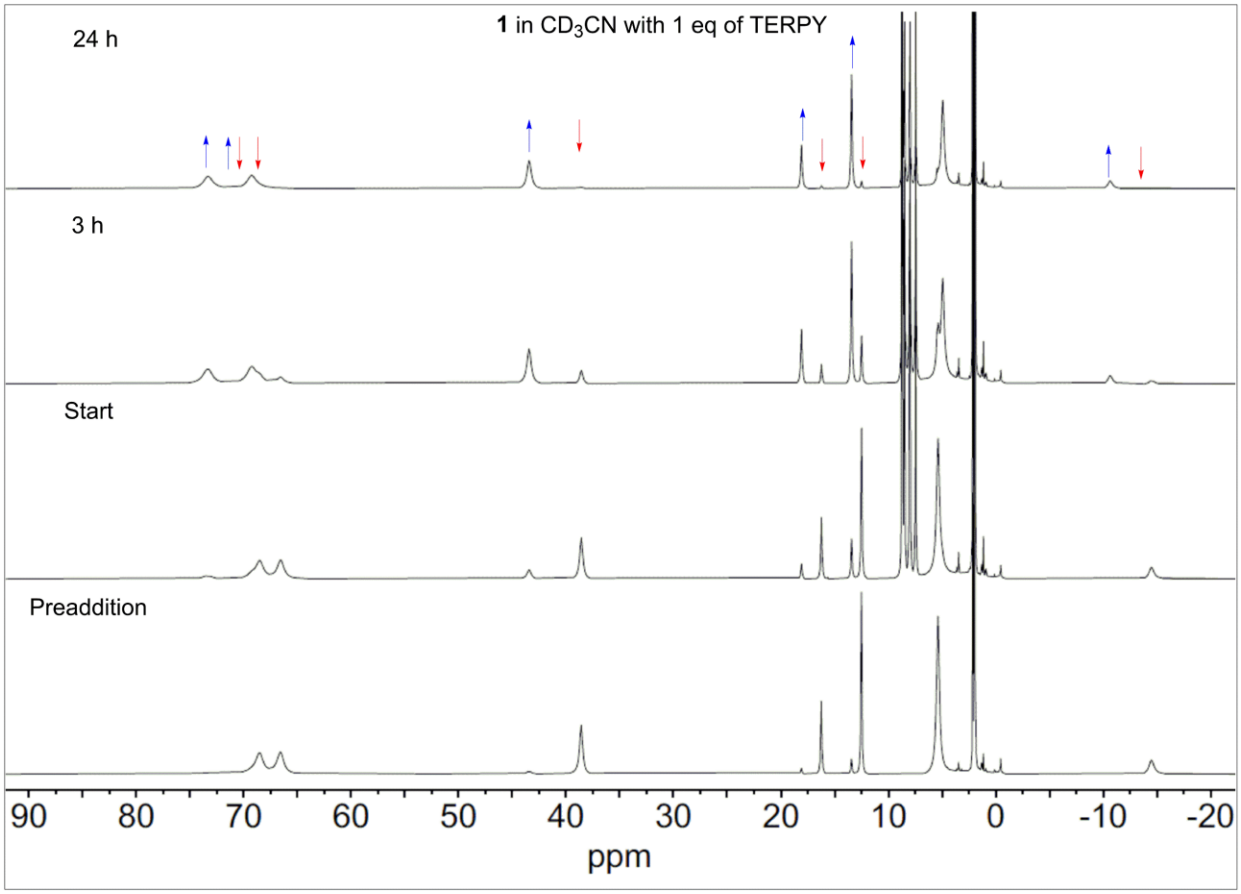

Figure S65: ^{1}H-NMR under paramagnetic conditions for **1** over time in dry CD_3CN only with 1 equivalent of TERPY.

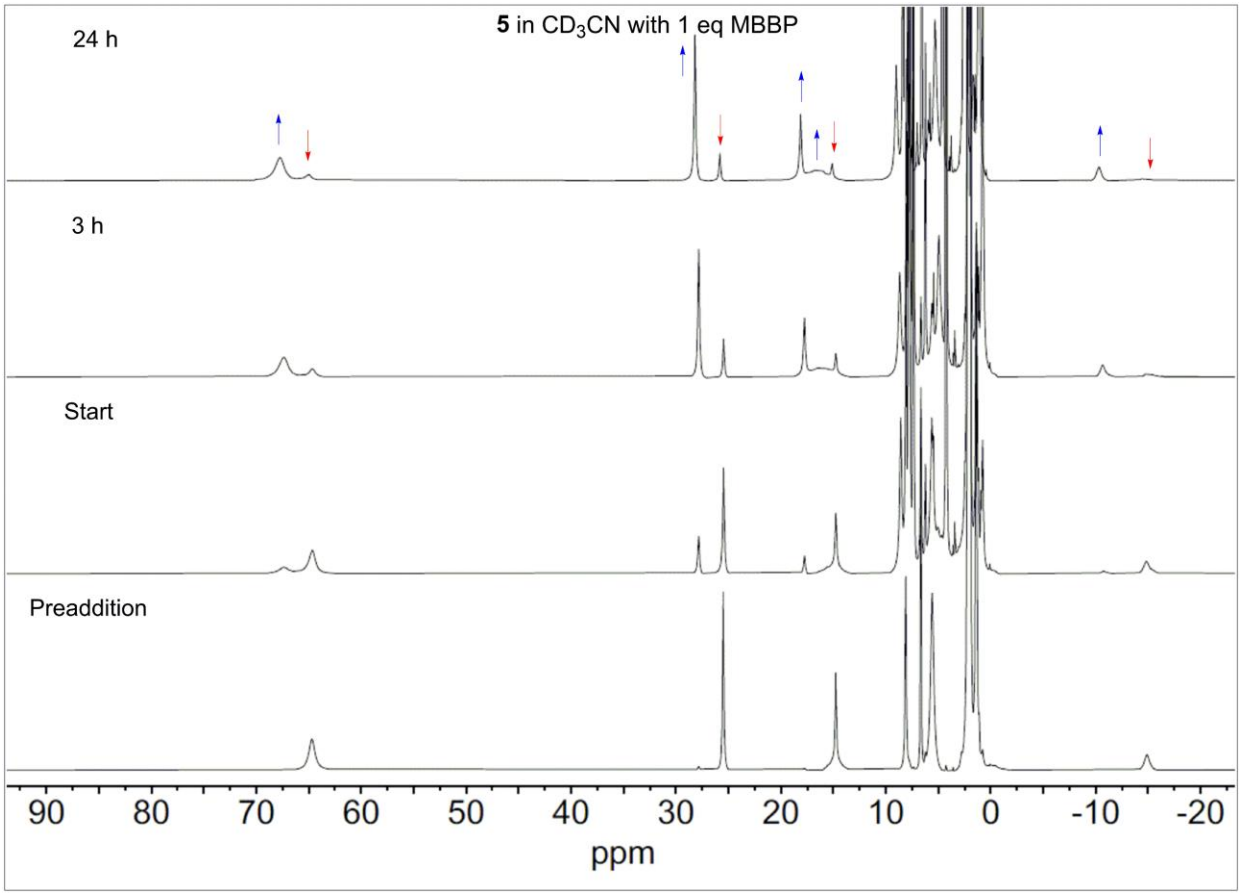

Figure S66: ^{1}H-NMR under paramagnetic conditions for **5** over time in dry CD_3CN only with 1 equivalent of MBBP.

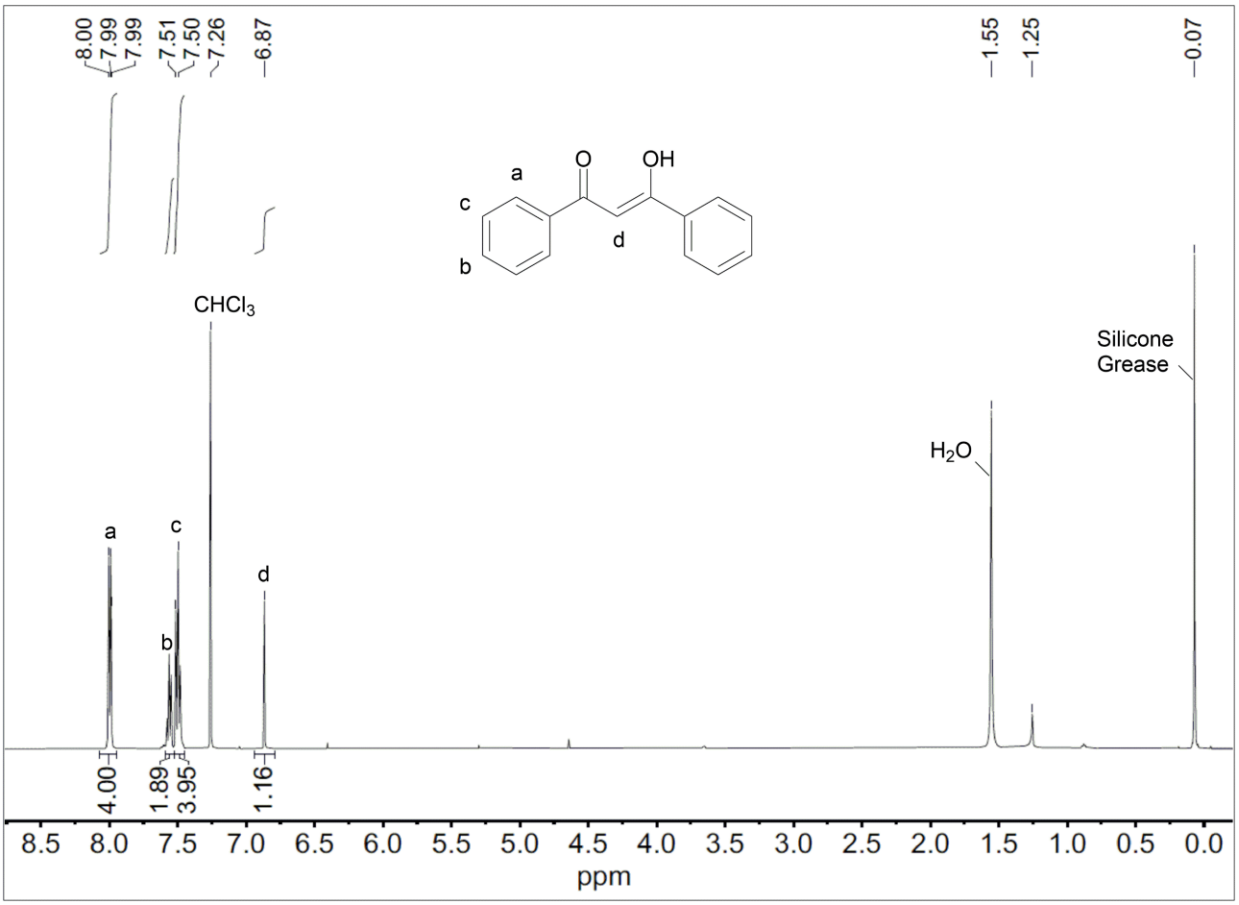

Figure S67: Organic recovery of a reaction mixture of **3** after 24 hours in CH_3CN, 10% H_2O (v:v) and 100 equivalents of NEt_3 with O_2 (Solvent: $CDCl_3$).

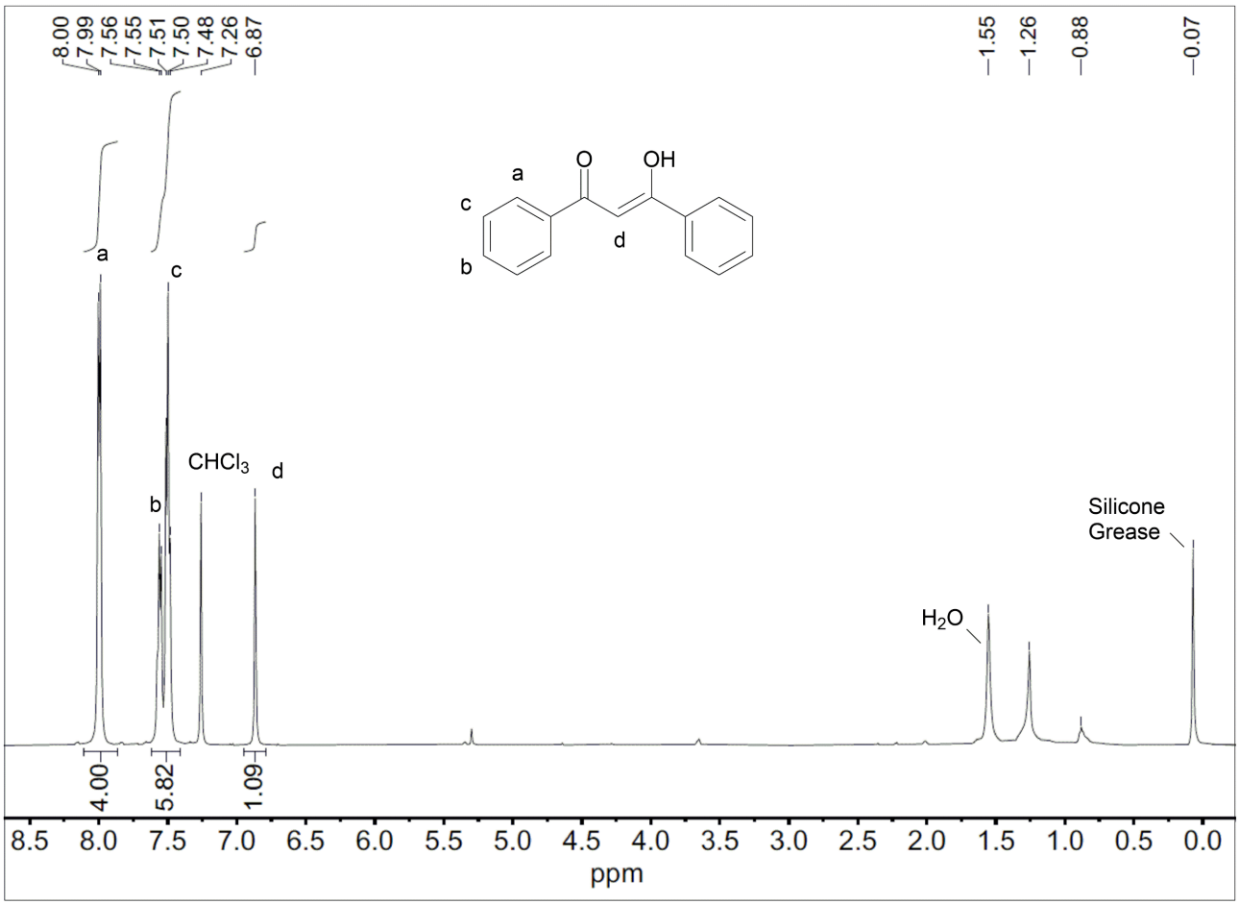

Figure S68: Organic recovery of a reaction mixture of **7** after 24 hours in CH_3CN, 10% H_2O (v:v) and 100 equivalents of NEt_3 with O_2 (Solvent: $CDCl_3$). The reagents of **7** were mixed together first for 30 minutes prior to addition of the other reagents.

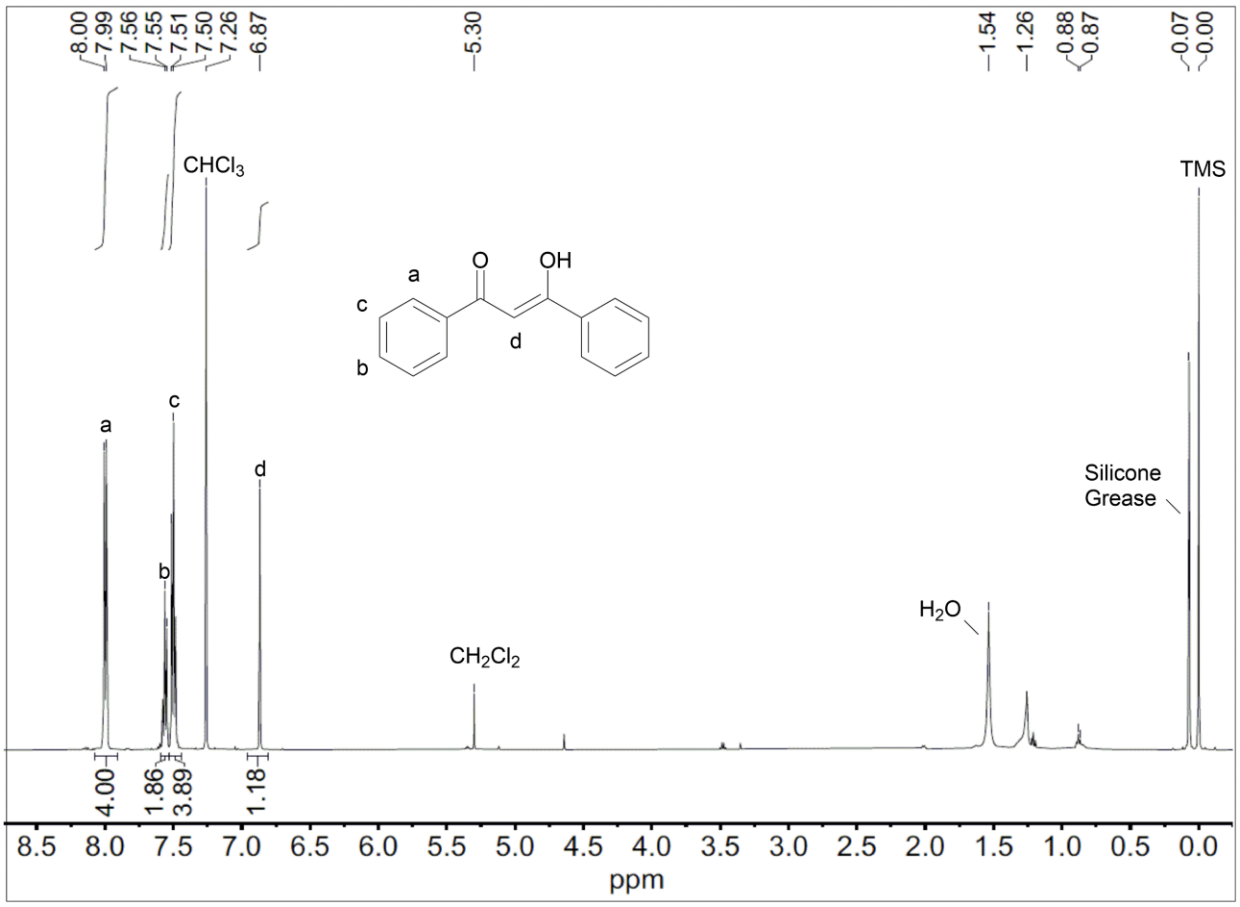

Figure S69: Organic recovery of a reaction mixture of **3** after 24 hours in dry CH_3CN and 1 equivalent of NEt_3 with O_2 (Solvent: $CDCl_3$).

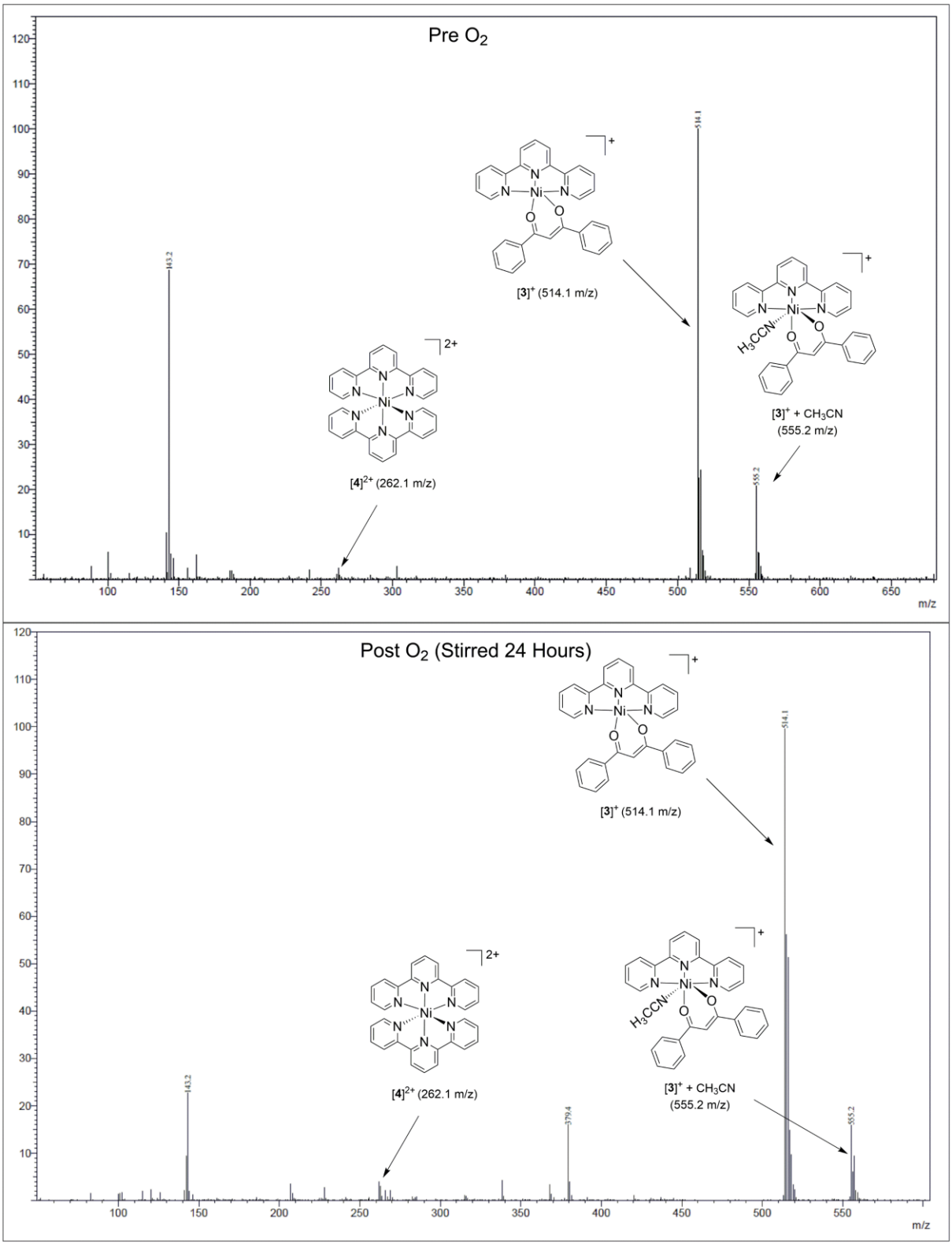

Figure S70: ESI-MS of a reaction mixture of **3** before O_2 purge (top) and O_2 purge and a 24 hour stir period (bottom) in dry CH_3CN and 1 equivalent of NEt_3.

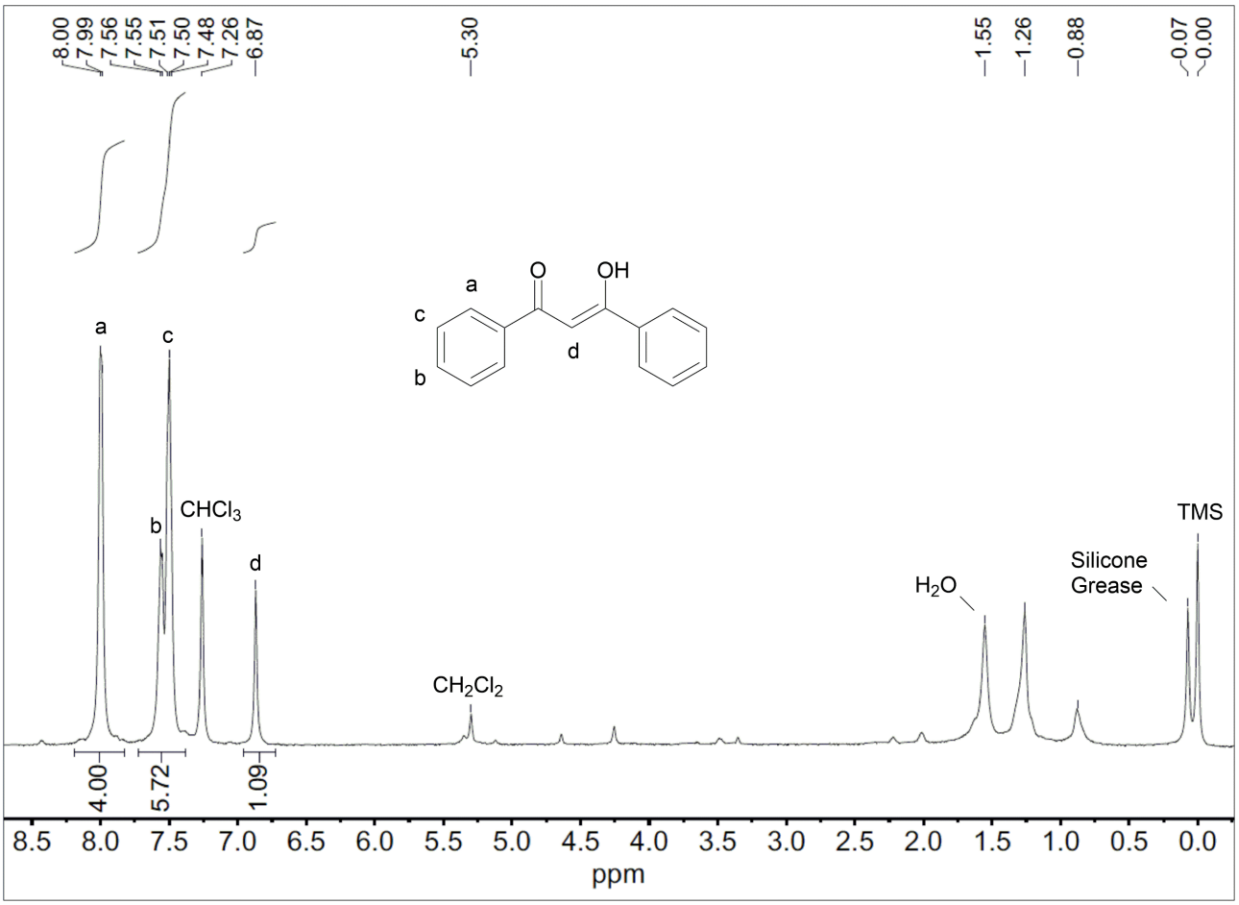

Figure S71: Organic recovery of a reaction mixture of **7-ClO_4** after 24 hours in dry CH_3CN and 1 equivalent of NEt_3 with O_2 (Solvent: $CDCl_3$). The reagents of **7-ClO_4** were mixed together first for 30 minutes prior to addition of the other reagents.

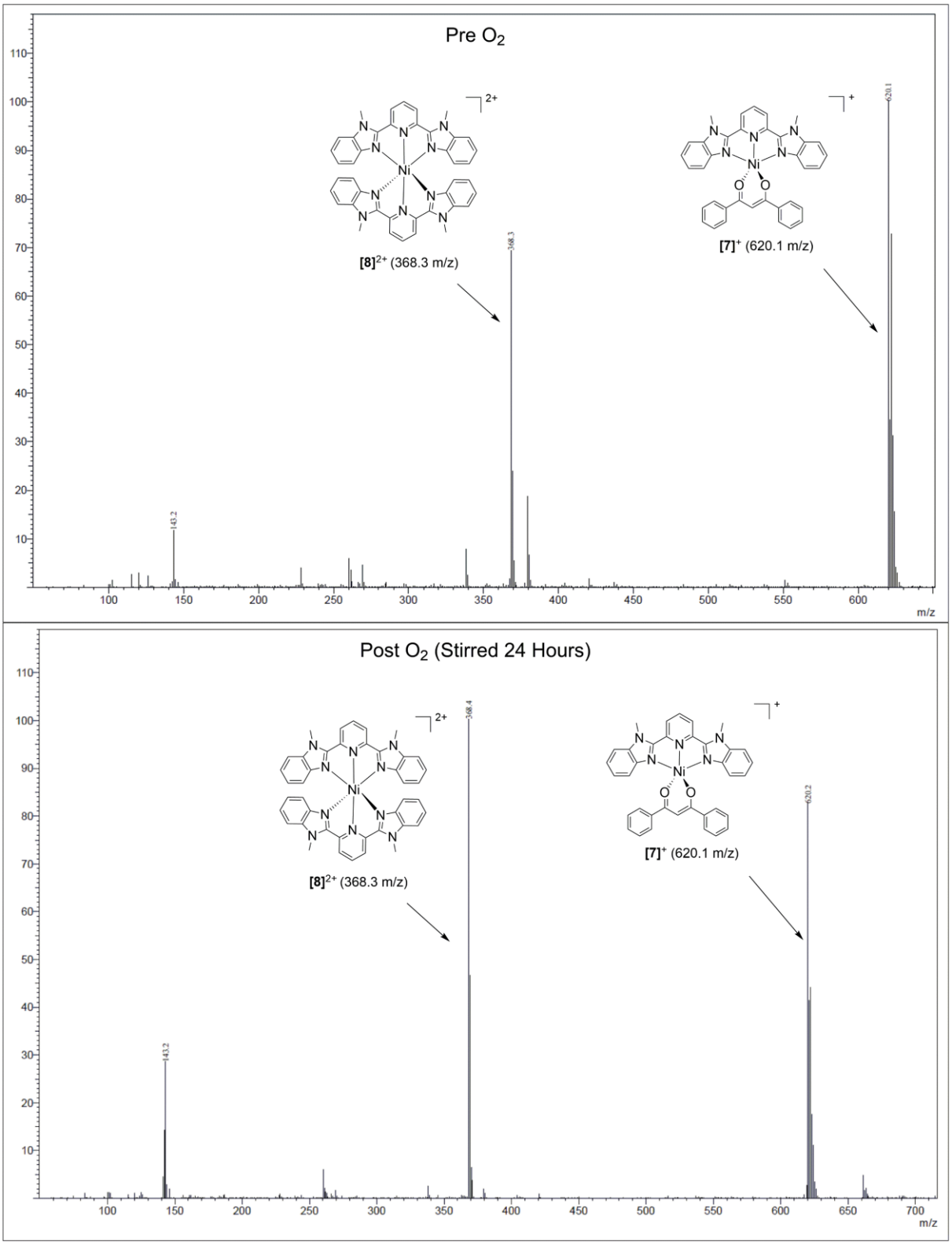

Figure S72: ESI-MS of a reaction mixture of **7-ClO$_4$** before O_2 purge (top) and O_2 purge and a 24 hour stir period (bottom) in dry CH_3CN and 1 equivalent of NEt_3.

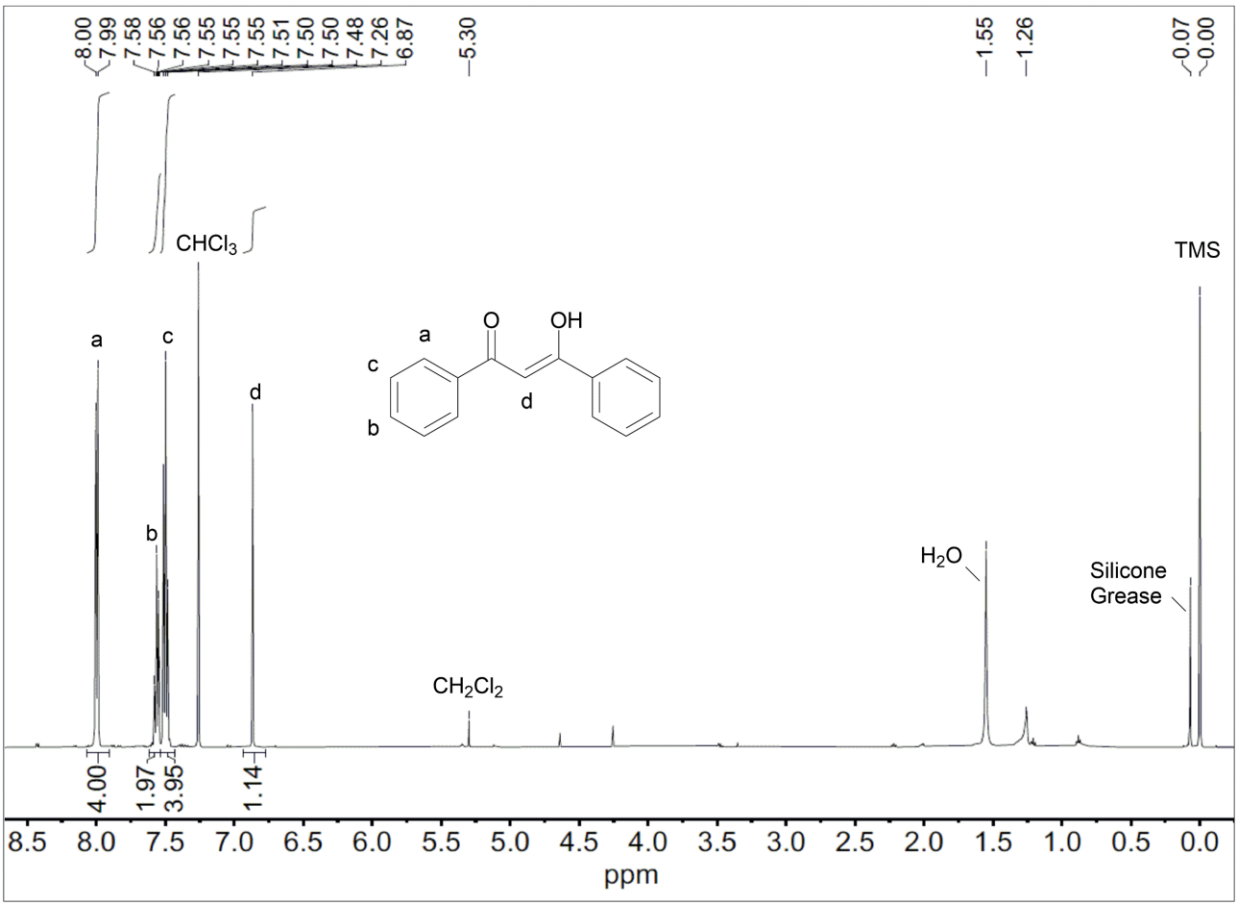

Figure S73: Organic recovery of a reaction mixture of **7-Cl** after 24 hours in dry CH_3CN and 1 equivalent of NEt_3 with O_2 (Solvent: $CDCl_3$). The reagents of **7-Cl** were mixed together first for 30 minutes prior to addition of the other reagents.

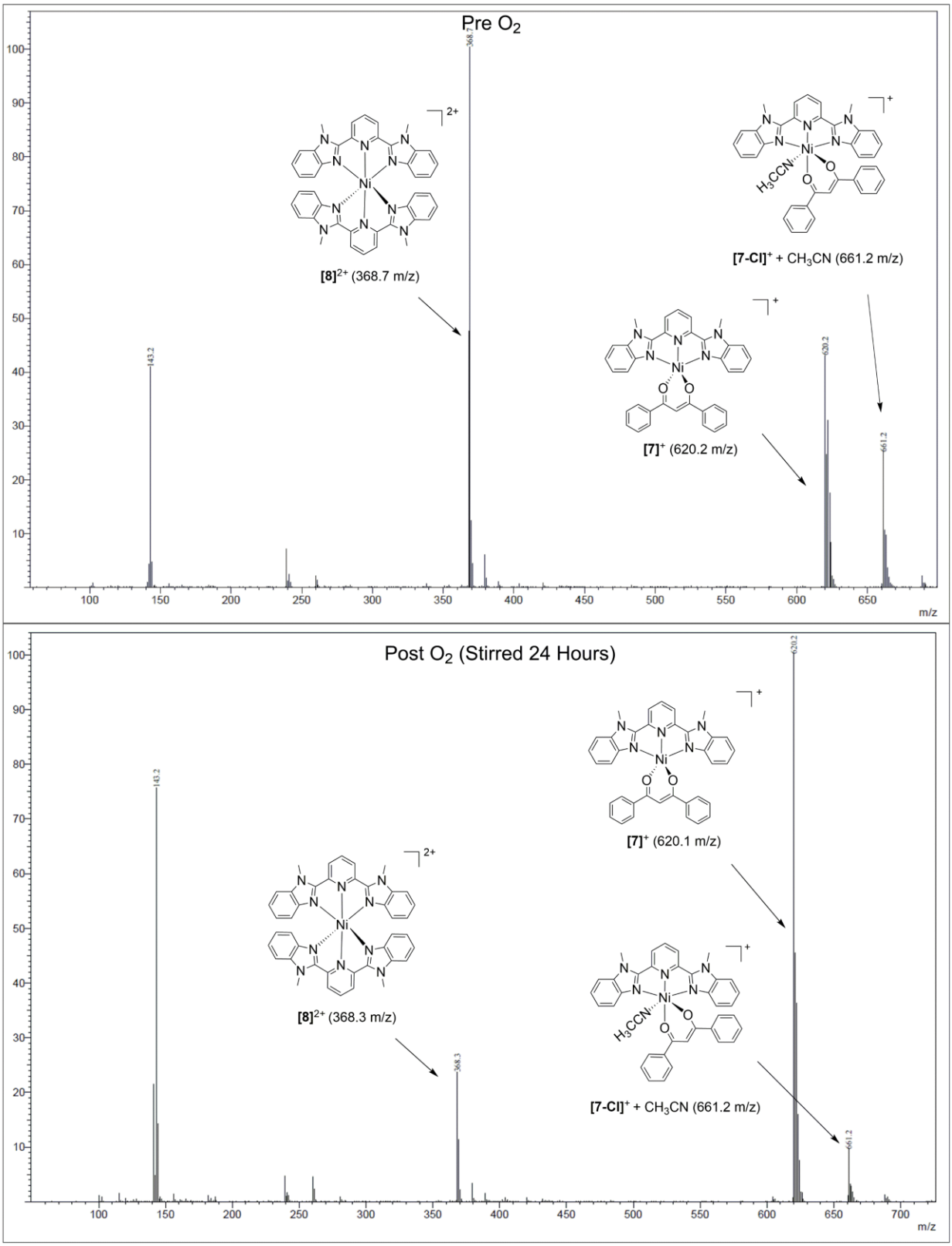

Figure S74: ESI-MS of a reaction mixture of **7-Cl** before O_2 purge (top) and O_2 purge and a 24 hour stir period (bottom) in dry CH_3CN and 1 equivalent of NEt_3.