Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Exploring Different Coordination Modes of the First Tetradentate NHC/1,2,3-Triazole Hybrid Ligand for Group 10 Complexes

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1. Synthesis of 1,1'-Methylenebisimidazole

Imidazole (50 g, 734 mmol, 1.00 eq.) and tetrabutylammonium bromide (7.10 g, 22.0 mmol, 0.03 eq.) are dissolved in 500 mL concentrated NaOH. Subsequently, CH_2Cl_2 (500 mL, 9.53 mol, 10.6 eq.) is added. The mixture is refluxed overnight. $CH_2Cl_2$is removed under reduced pressure. The suspension is filtered to obtain a pale yellow residue. After washing with cold CH_2Cl_2 (-40 °C, 4x50 mL) and drying of the solid at 60 °C it is extracted with 500 mL CH_2Cl_2 using Soxhlet extractor overnight. The resulting suspension is concentrated to 150 mL, cooled to -40 °C and filtered. The filtrate is concentrated to 50 mL, cooled to -40 °C and filtered again. After drying of the combined residues 1,1'-methylenebisimidazole (47.3 g, 319 mmol, 87%) is obtained as a white crystalline solid.

^{1}H-NMR (400 MHz, DMSO-d_6, 296 K): δ 7.92 (t, ^3J = 1.2 Hz, 2H, NC*H*N), 7.39 (d, ^3J = 1.2 Hz, 2H, NC*H*C), 6.90 (t, ^3J = 1.2 Hz, 2H, NC*H*C), 6.21 (s, 2H, CH_2).

^{13}C-NMR (101 MHz, DMSO-d_6, 296 K): δ 137.31 (N*C*HN), 129.16 (N*C*HC), 119.16 (N*C*HC), 54.82 (*C*H_2).

Anal. calcd. for $C_7H_8N_4$: C 56.74; H 5.44; N 37.81. Found: C 56.79; H 5.61; N 37.55.

2. NMR spectroscopy

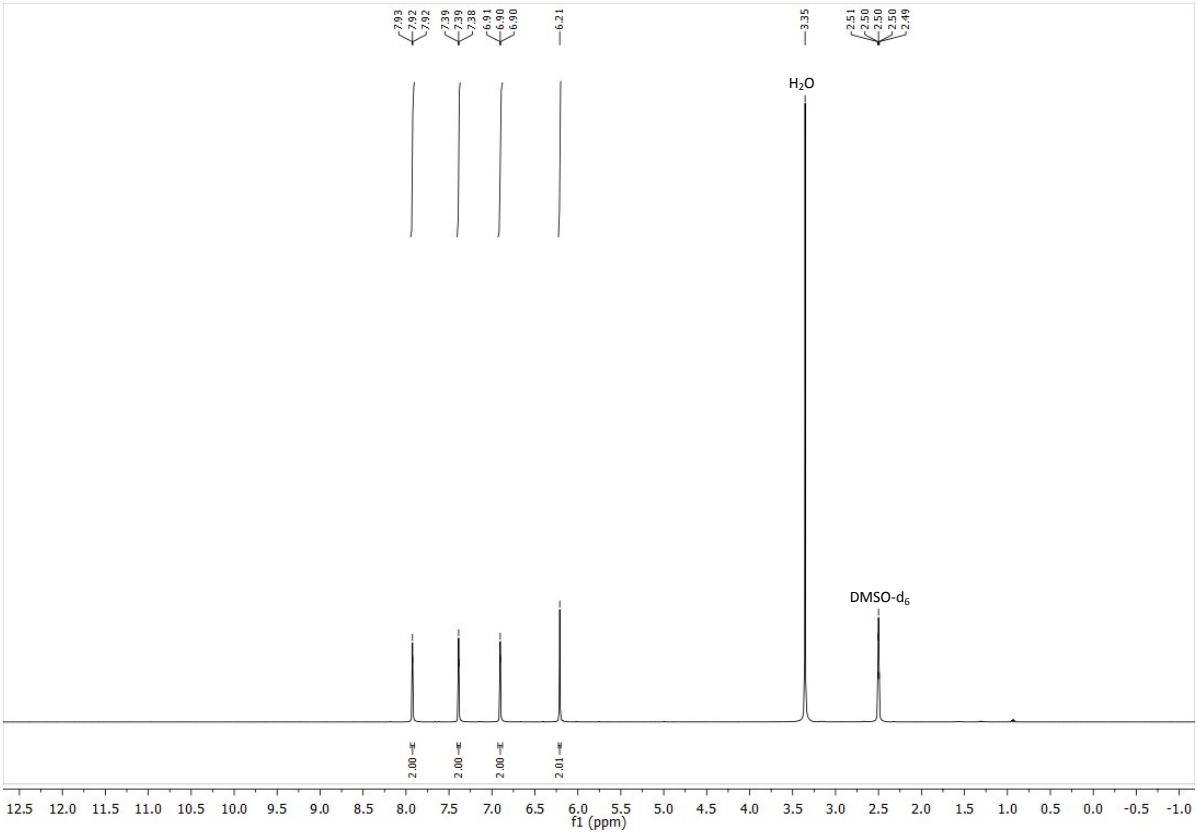

Figure 1. [1]H-NMR of 1,1'-Methylenebisimidazole in DMSO-d_6.

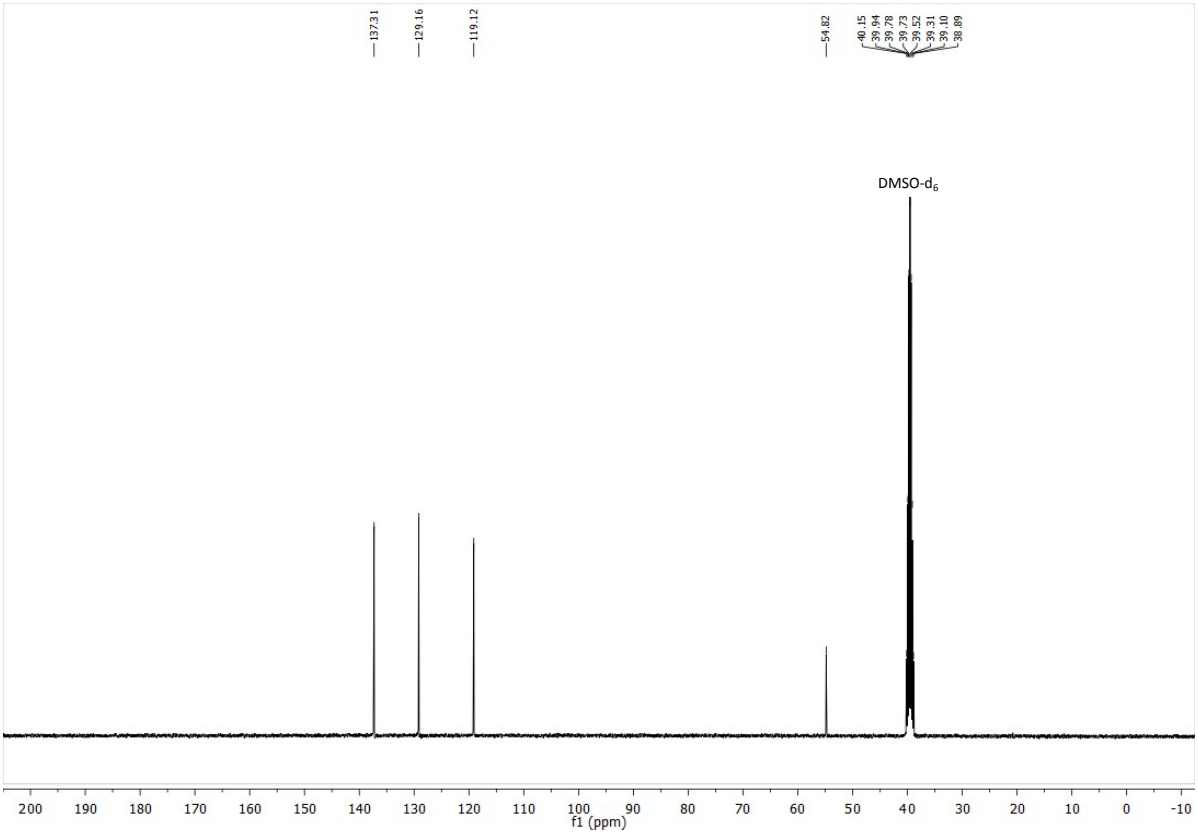

Figure 2. [13]C-NMR of 1,1'-Methylenebisimidazole in DMSO-d_6.

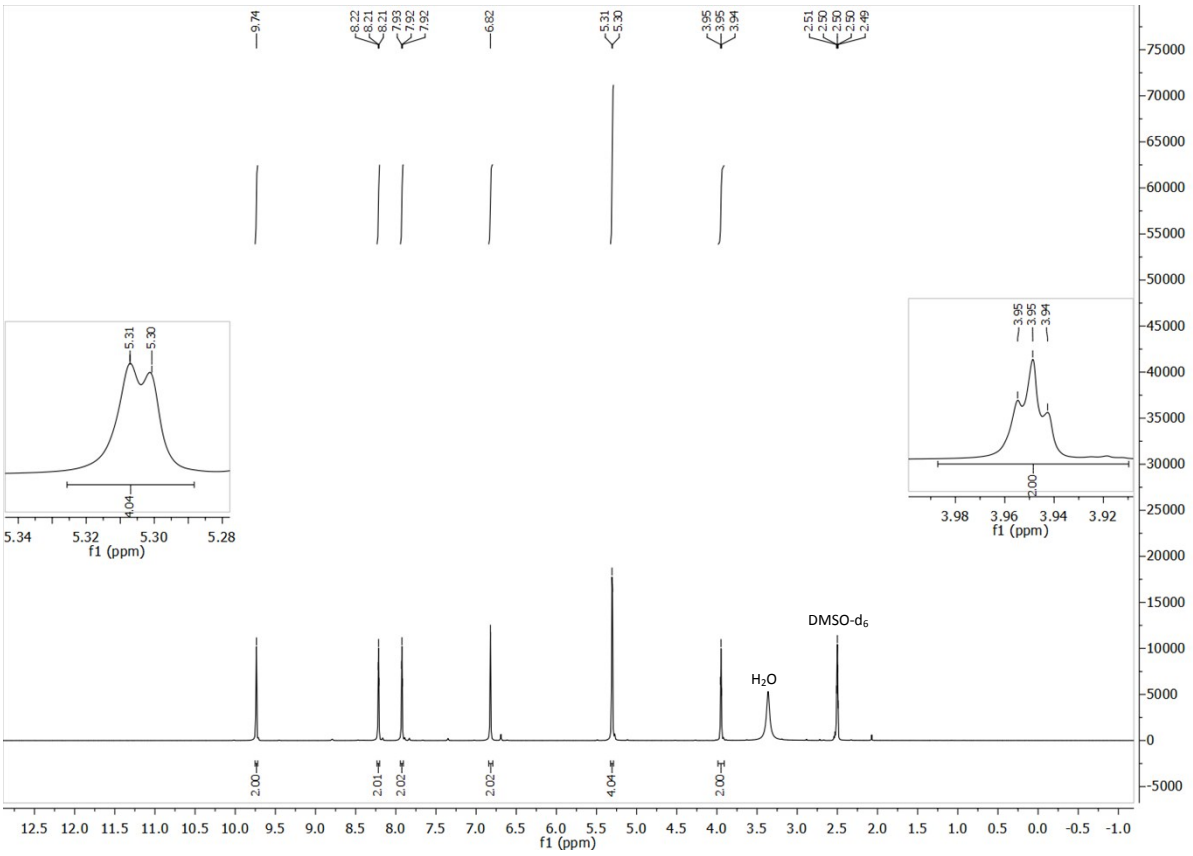

Figure 3. ^{1}H-NMR of **1** in DMSO-d_6.

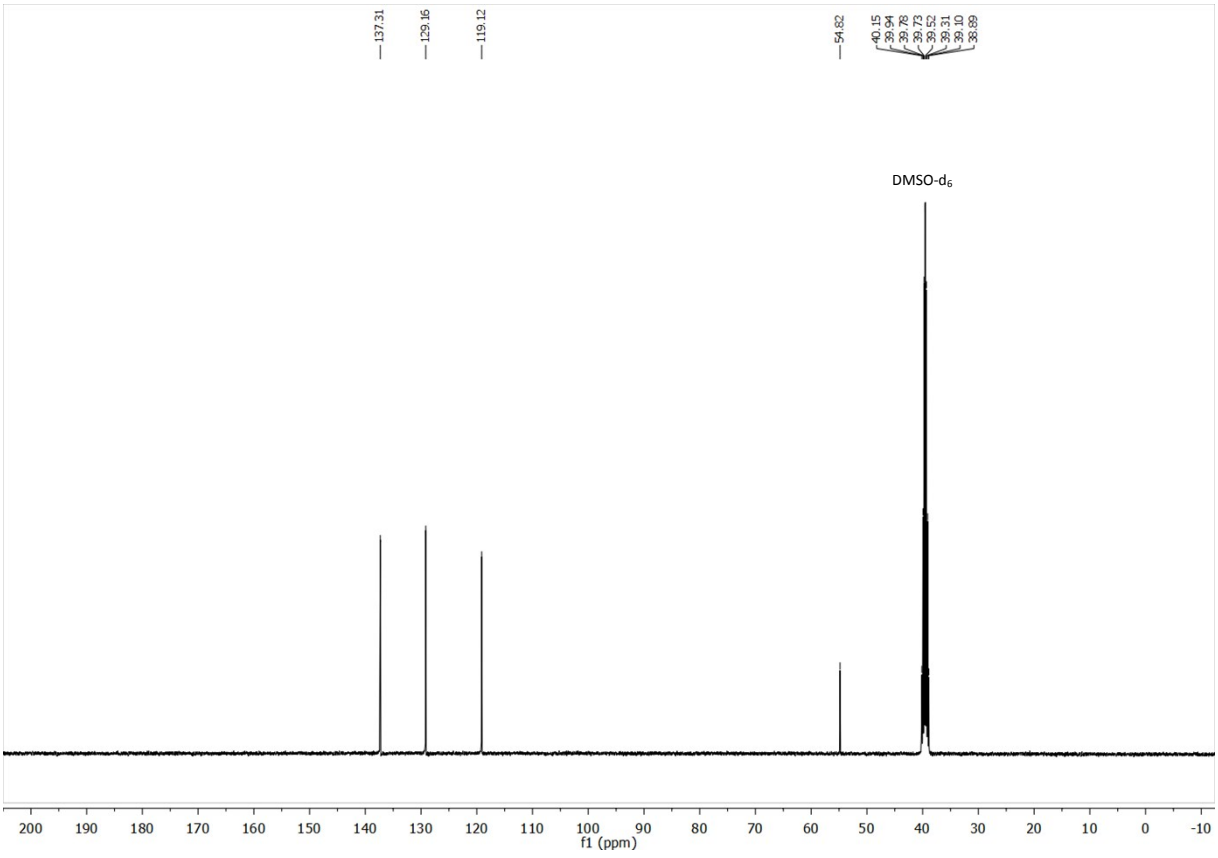

Figure 4. ^{13}C-NMR of **1** in DMSO-d_6.

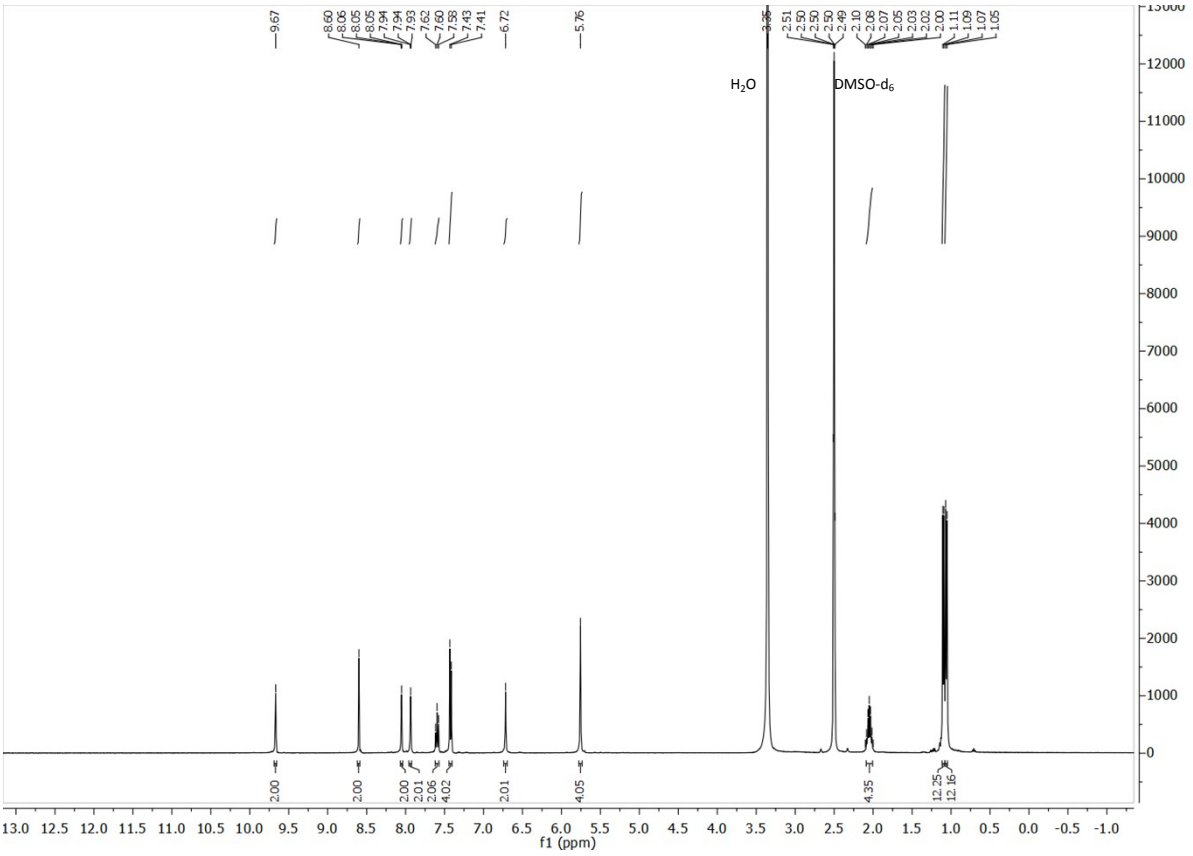

Figure 5. ^{1}H-NMR of **2** in DMSO-d_6.

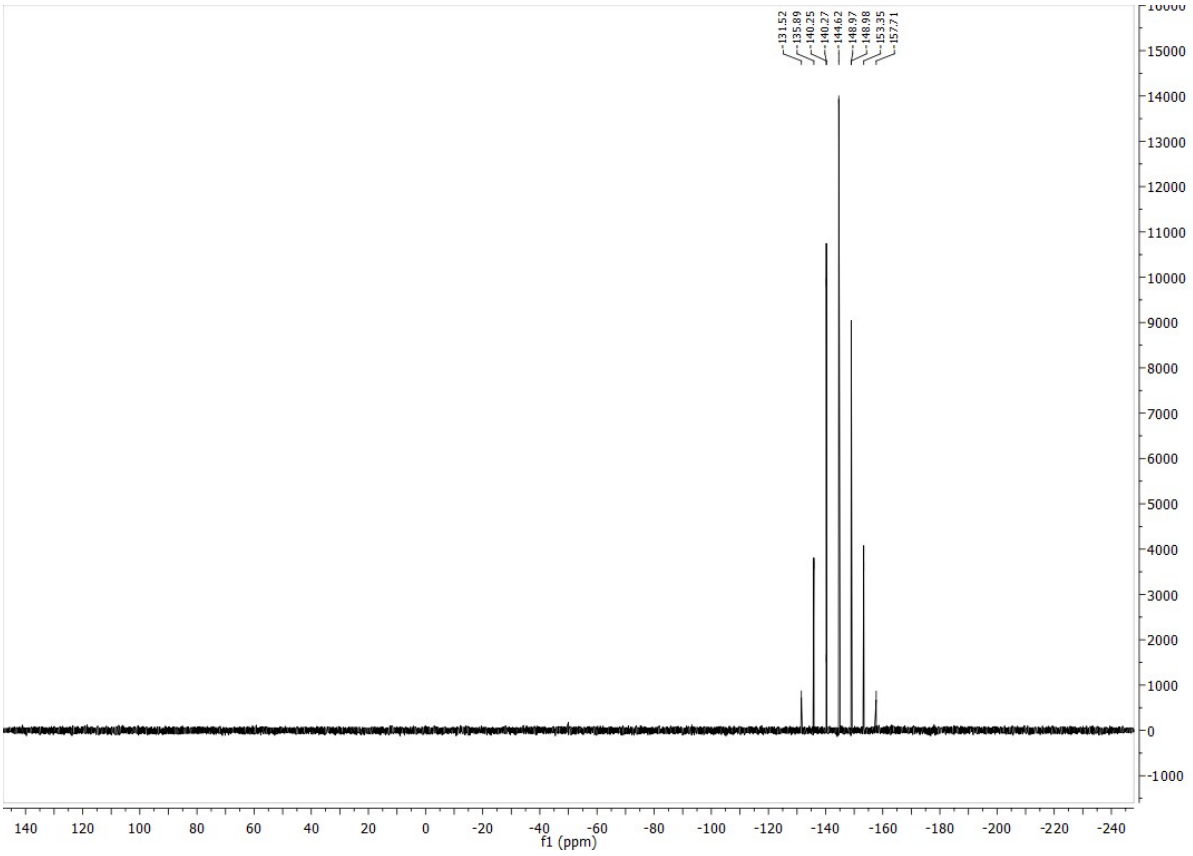

Figure 6. ^{13}P-NMR of **2** in DMSO-d_6.

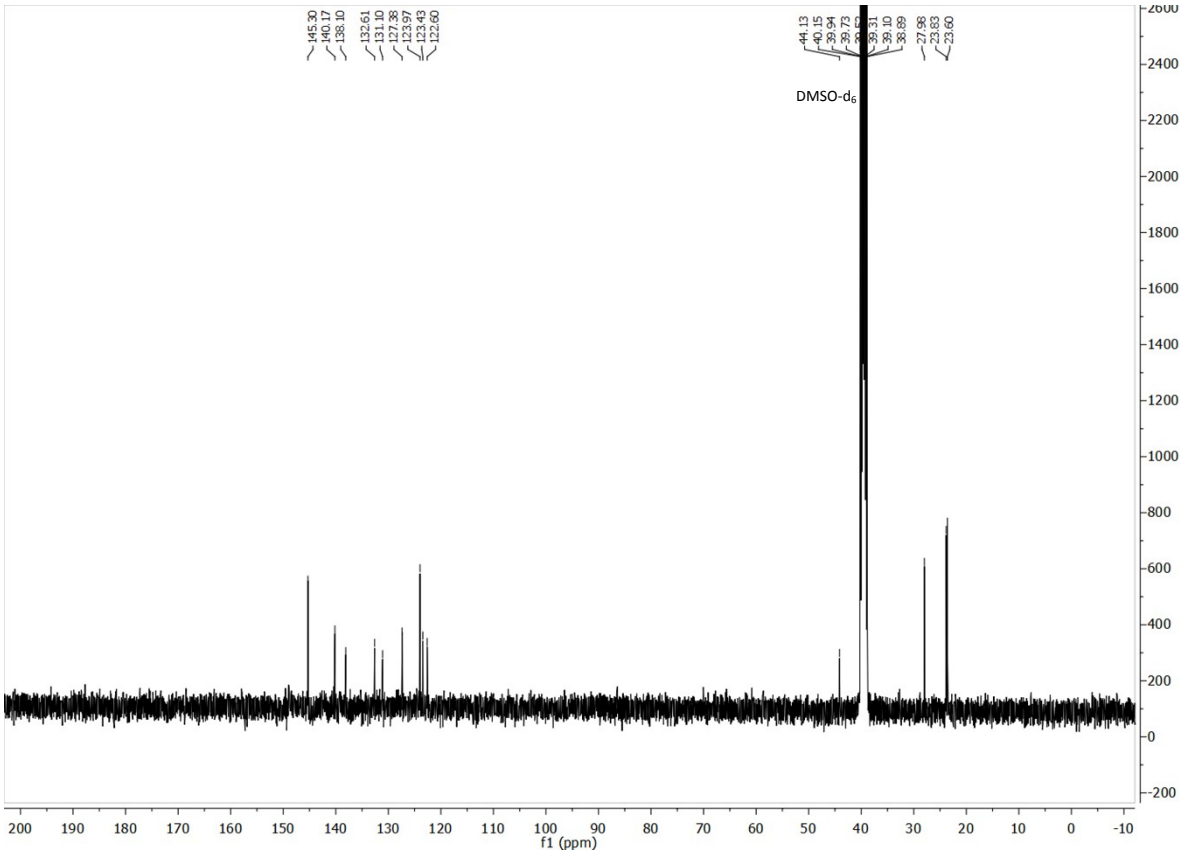

Figure 7. ^{13}C-NMR of **2** in DMSO-d_6.

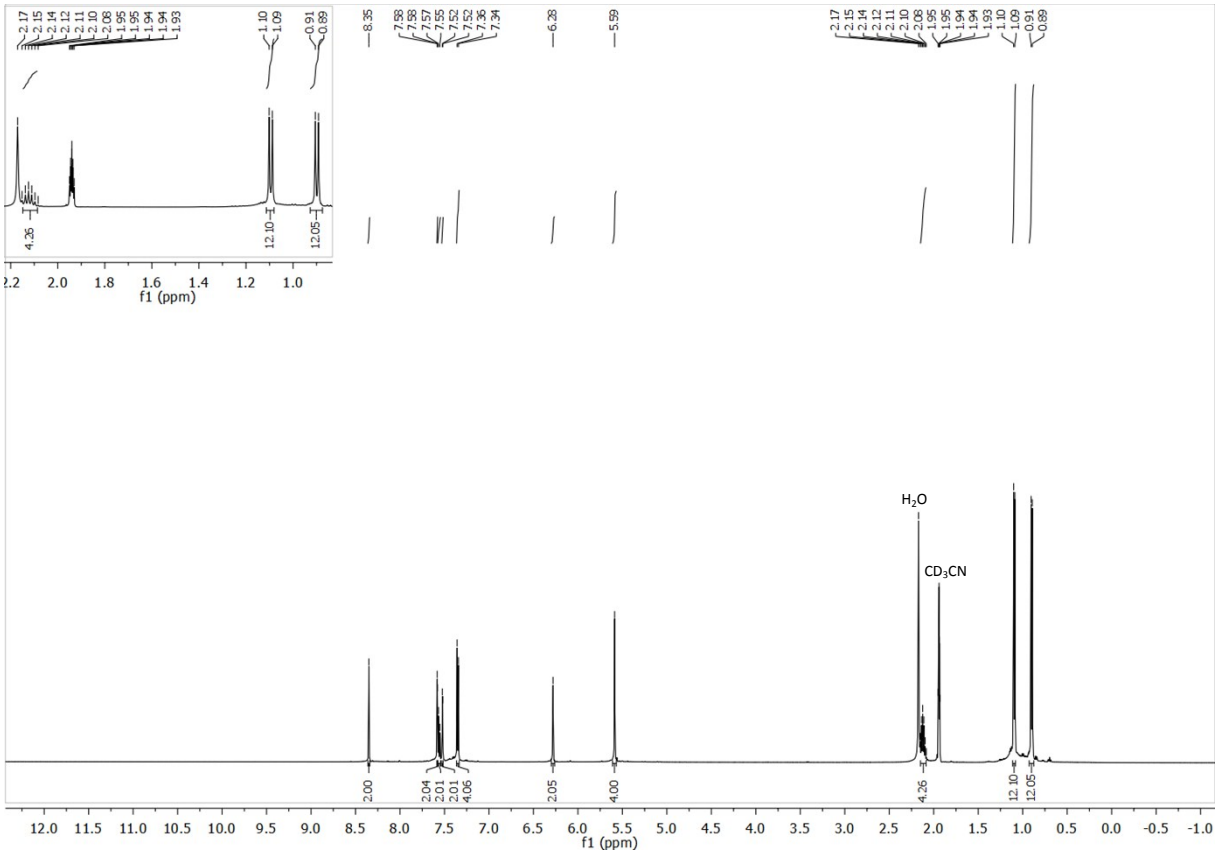

Figure 8. ^{1}H-NMR of **3** in CD_3CN.

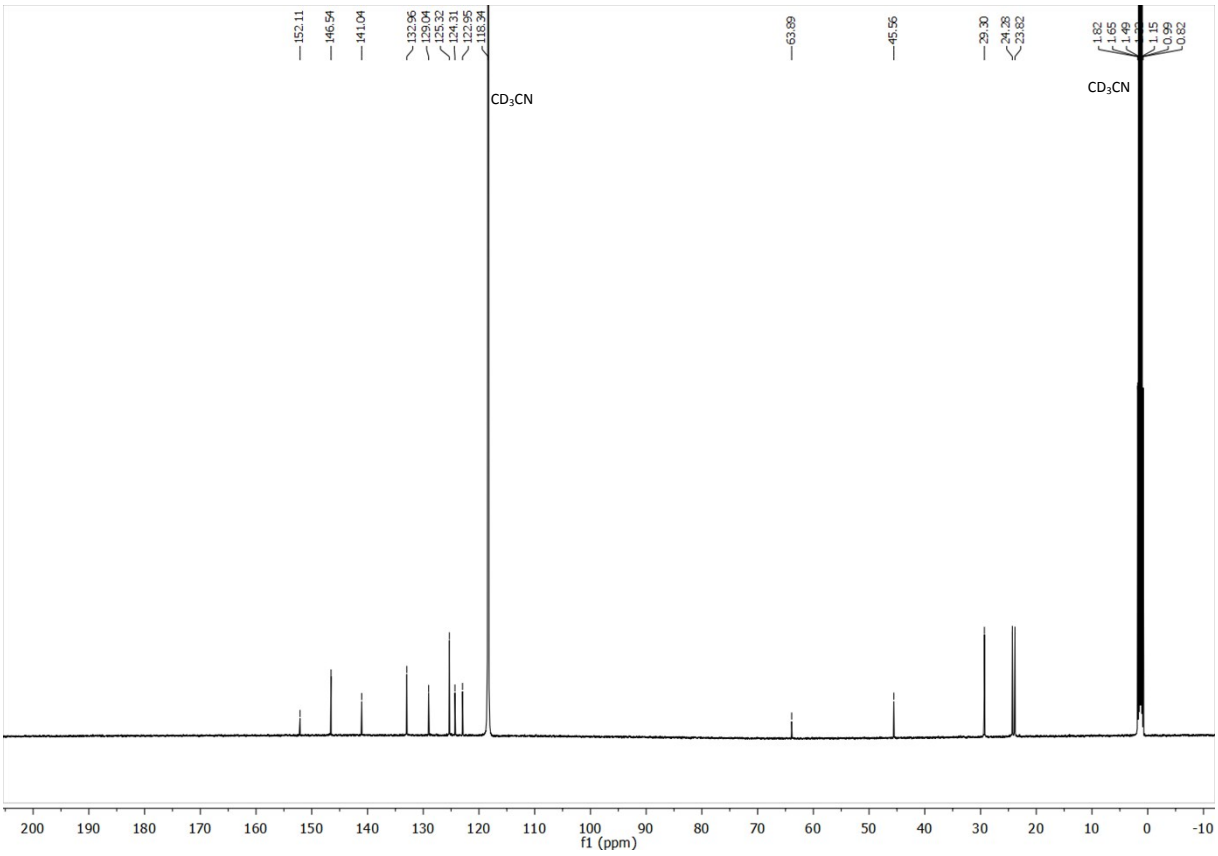

Figure 9. ^{13}C-NMR of **3** in CD_3CN.

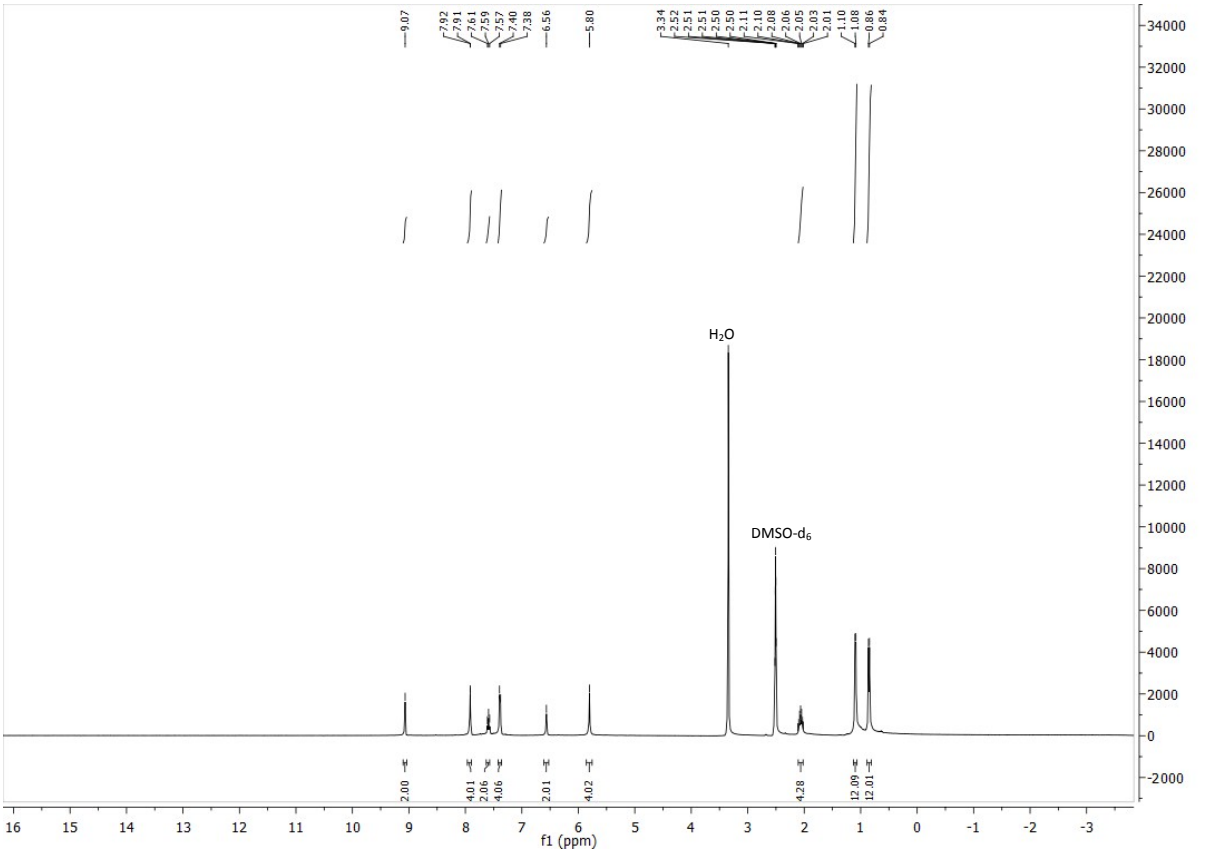

Figure 10. ^{1}H-NMR of **3** in DMSO-d_6.

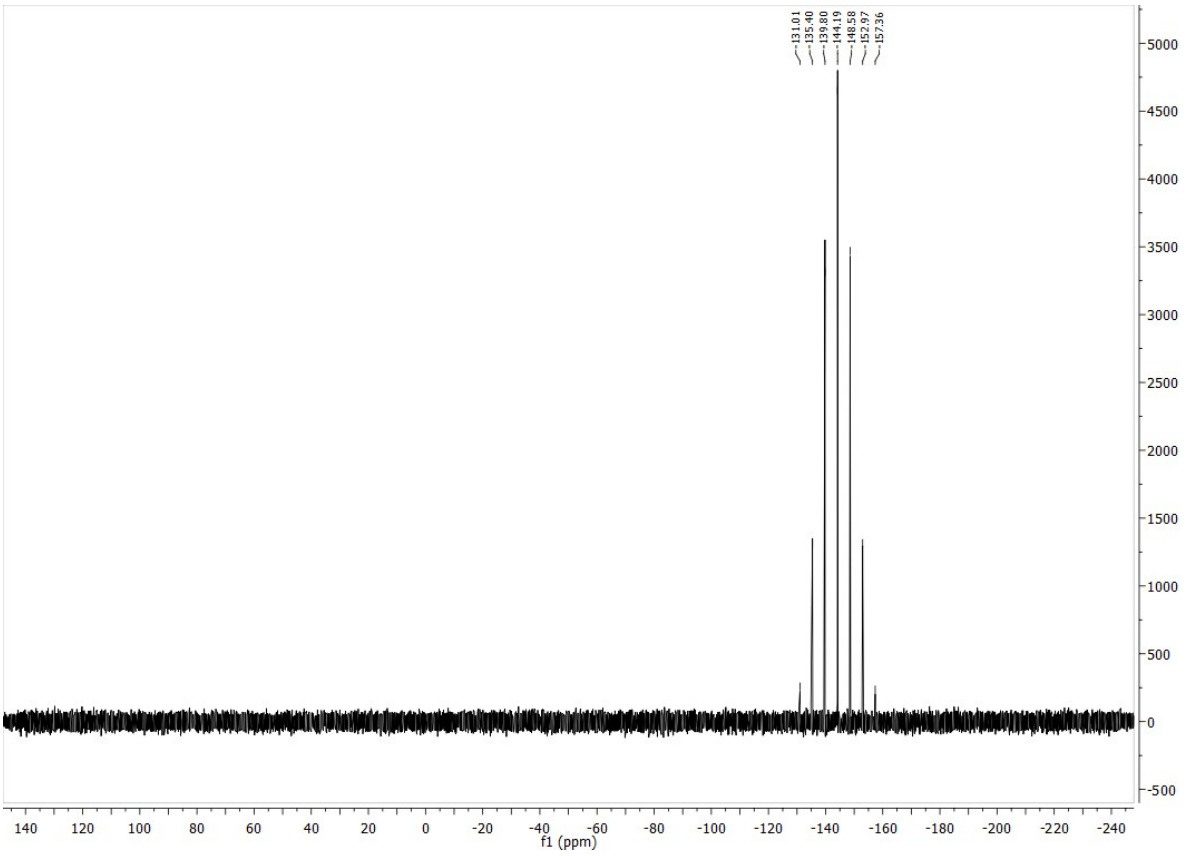

Figure 11. ^{31}P-NMR of **3** in DMSO-d_6.

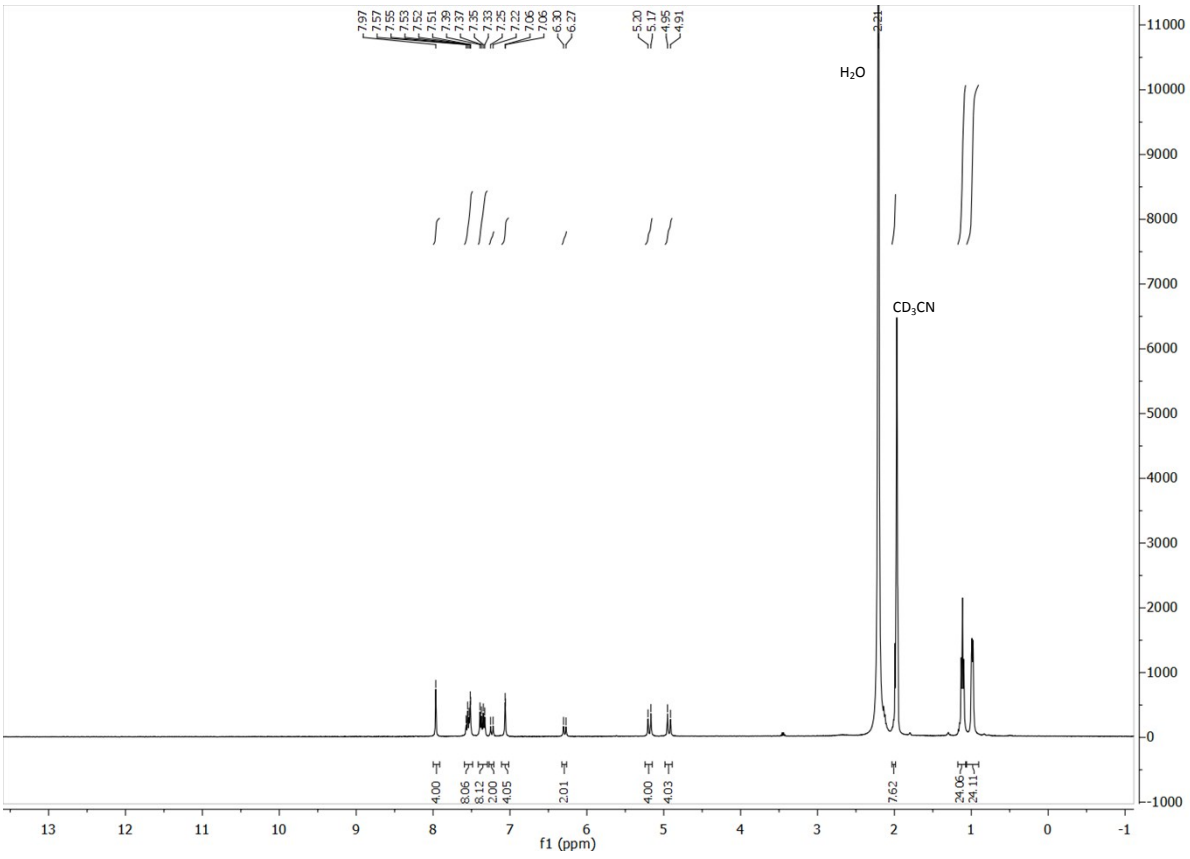

Figure 12. ^{1}H-NMR of **4** in CD_3CN.

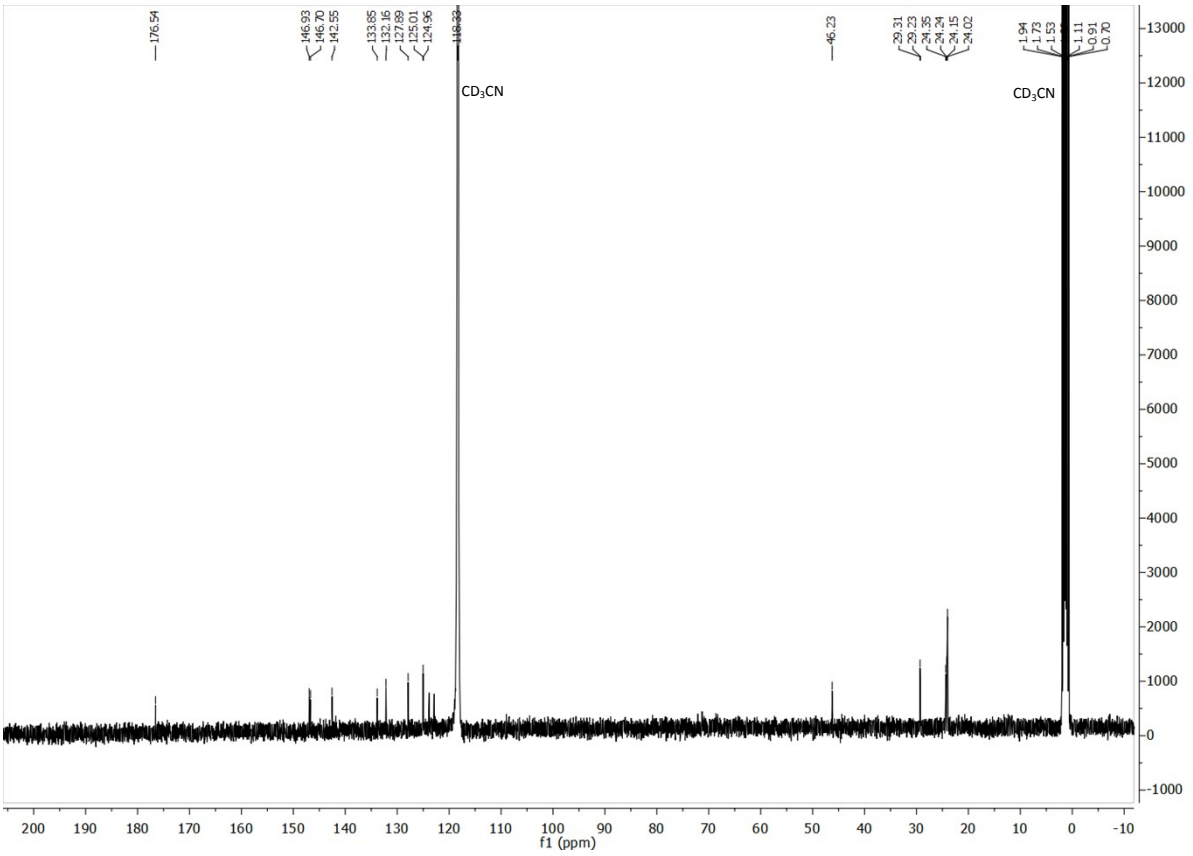

Figure 13. ^{13}C-NMR of **4** in CD_3CN.

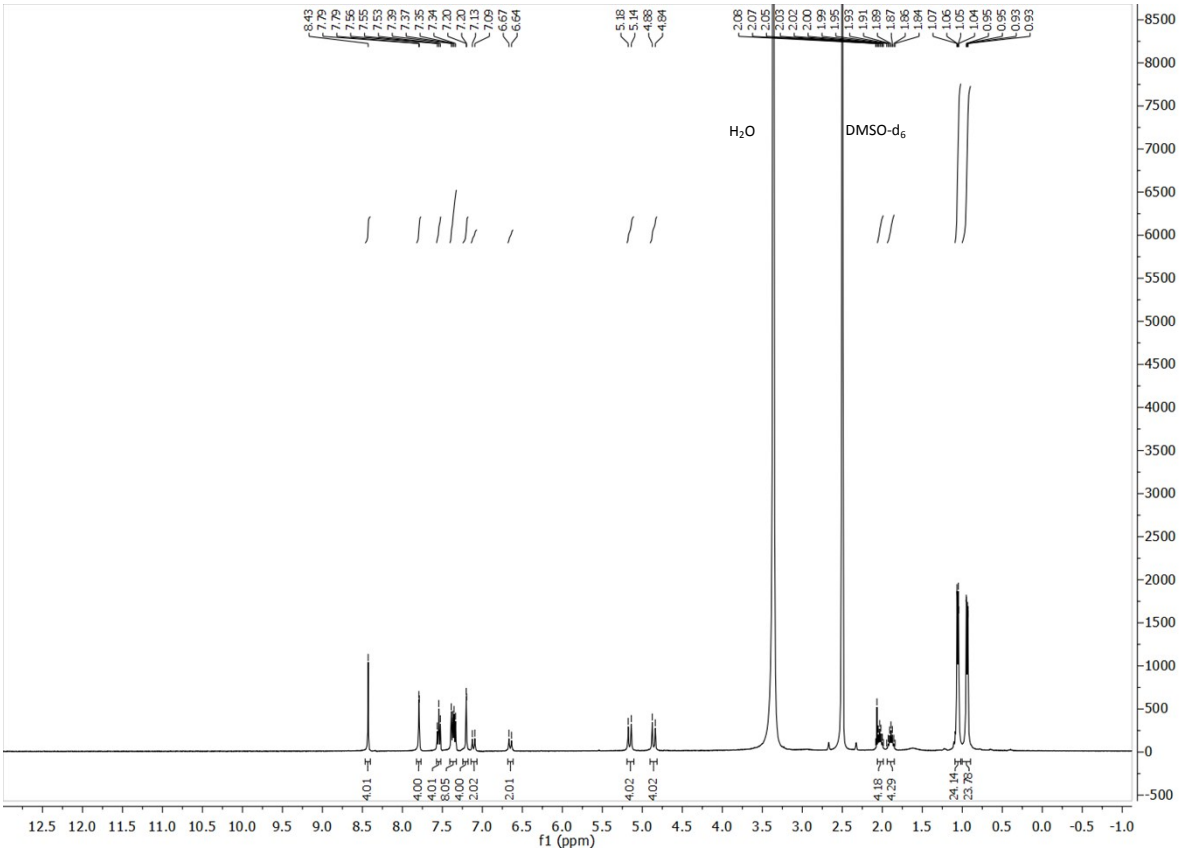

Figure 14. ^{1}H-NMR of **4** in DMSO-d_6.

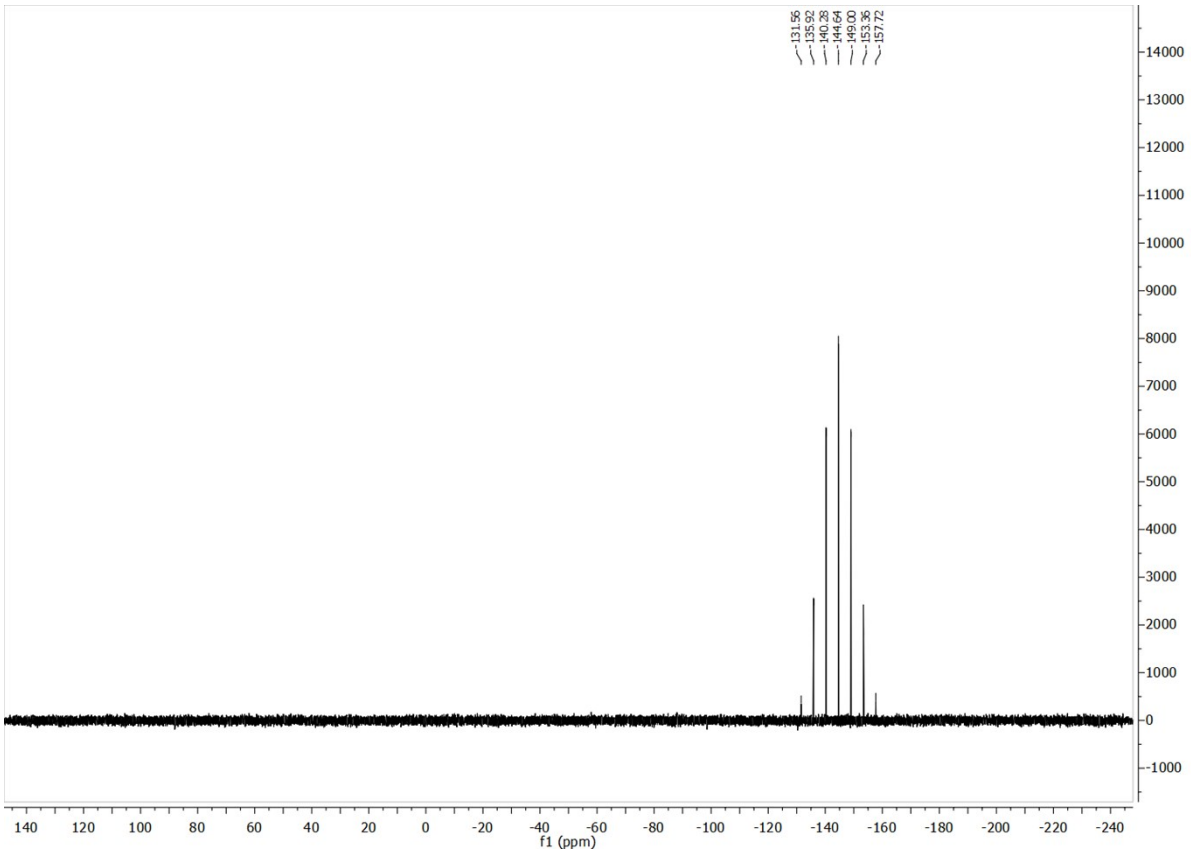

Figure 15. ^{31}P-NMR of **4** in DMSO-d_6.

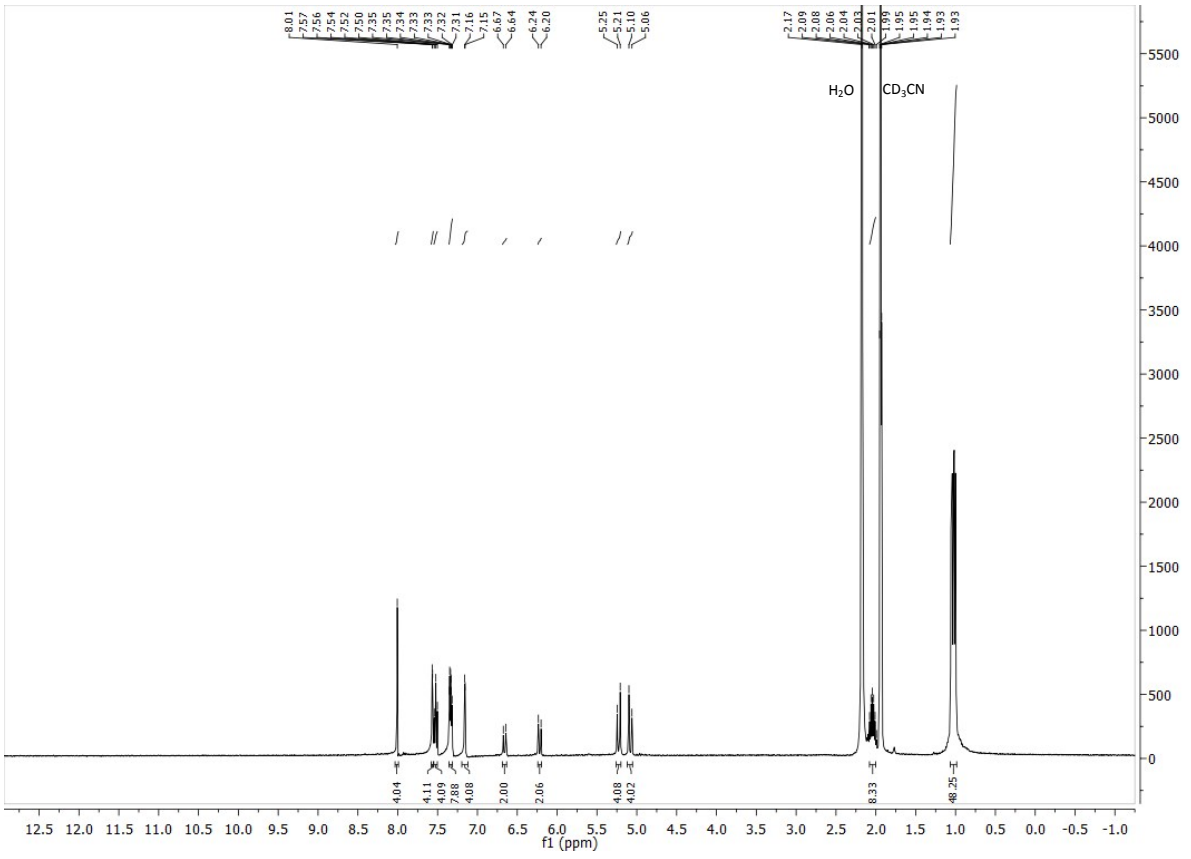

Figure 16. ^{1}H-NMR of **5** in CD_3CN.

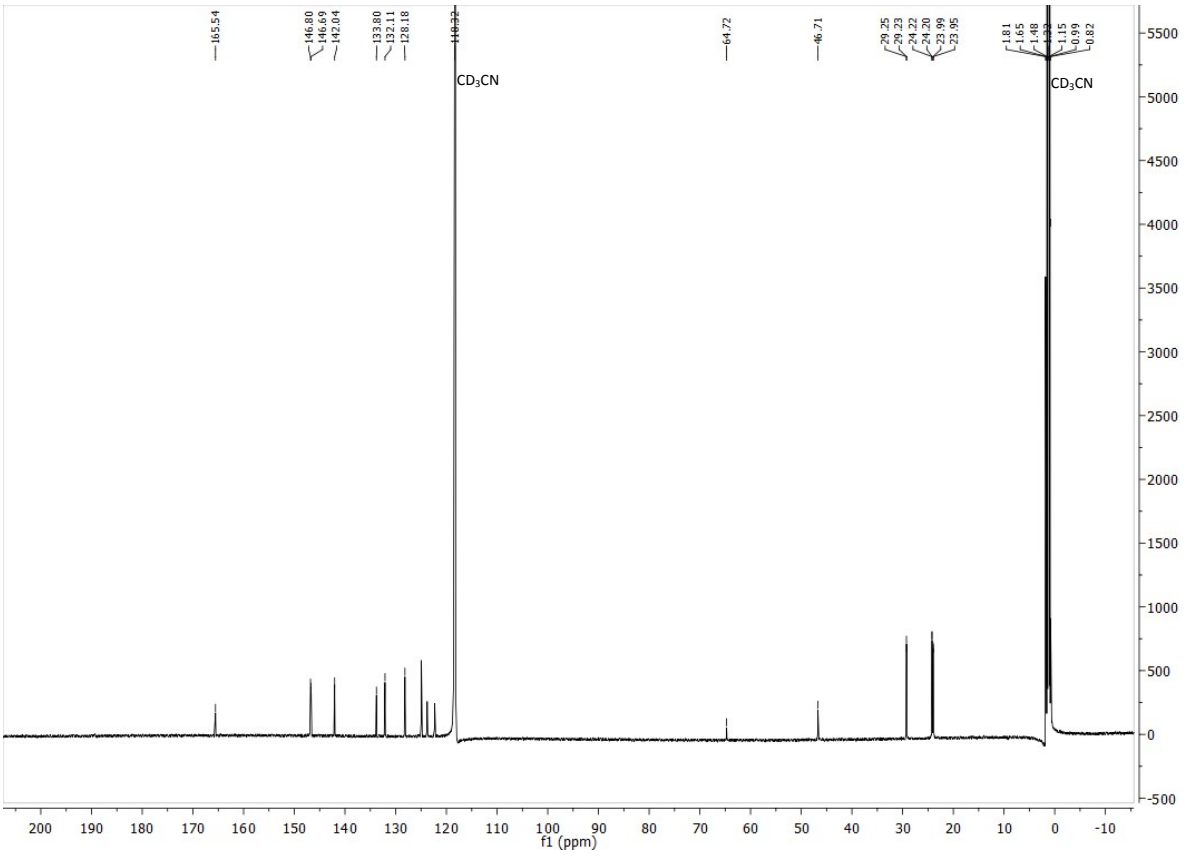

Figure 17. ^{13}C-NMR of **5** in CD_3CN.

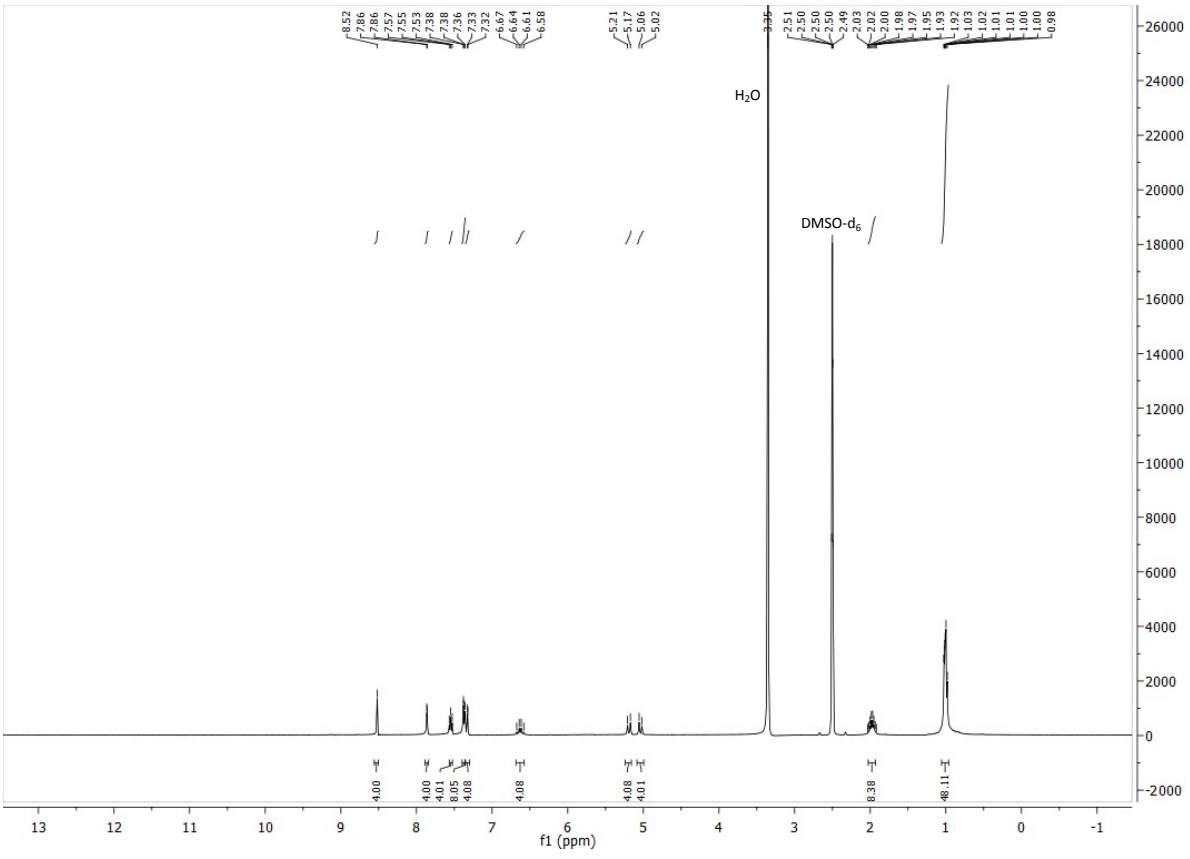

Figure 18. ^{1}H-NMR of **5** in DMSO-d_6.

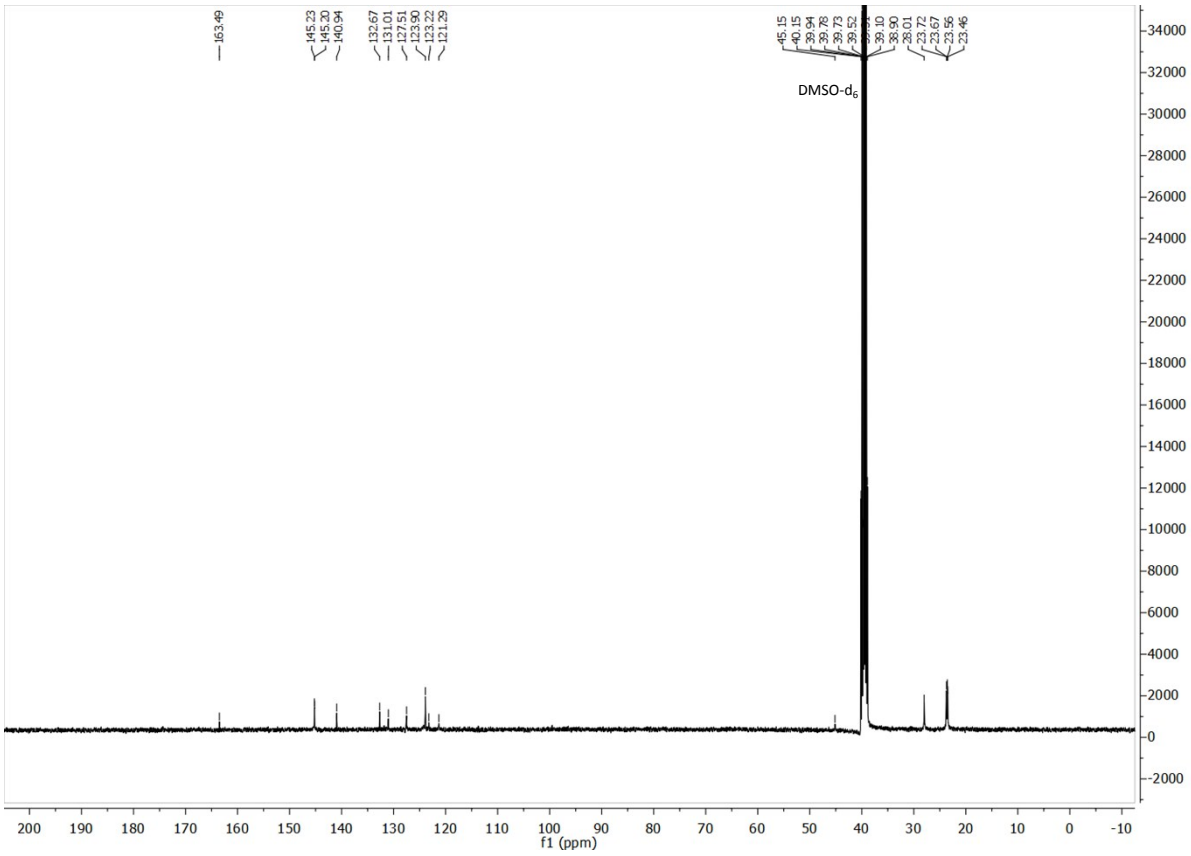

Figure 19. ^{13}C-NMR of **5** in DMSO-d_6.

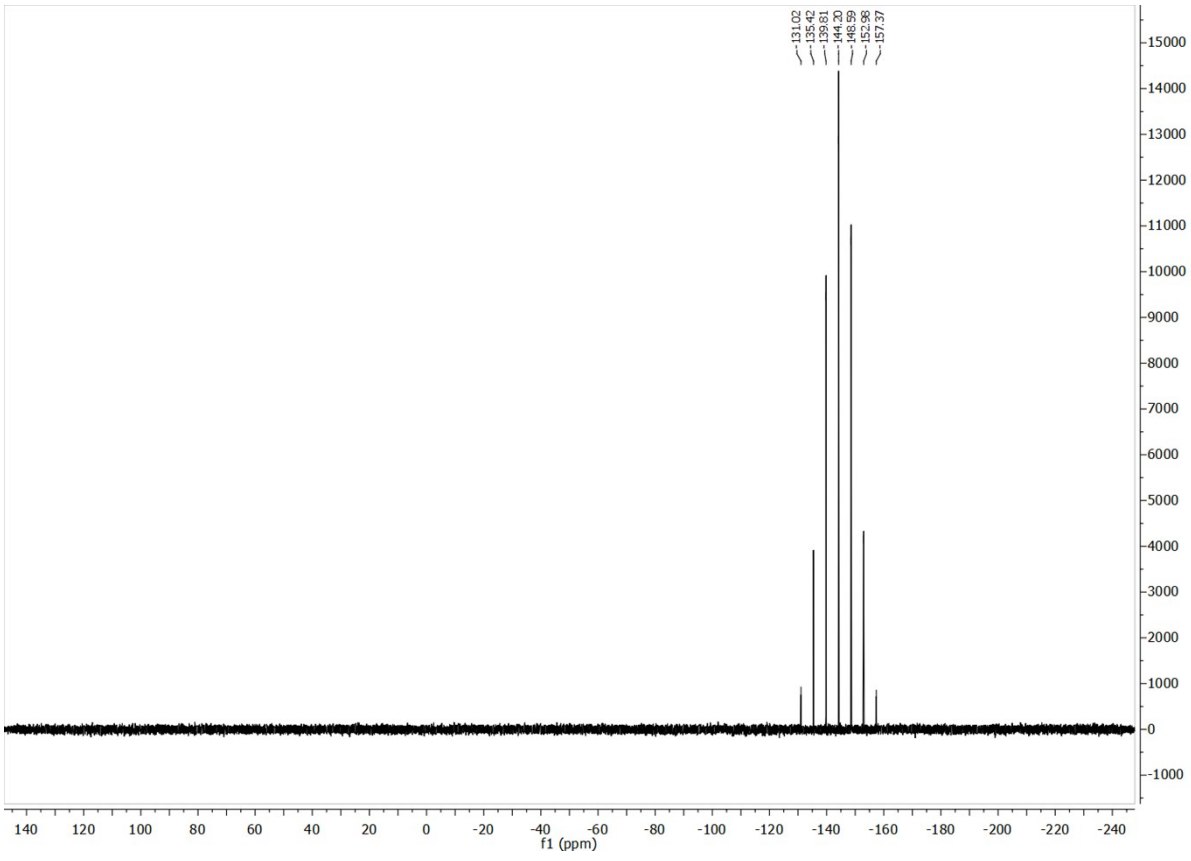

Figure 20. ^{31}P-NMR of **5** in DMSO-d_6.

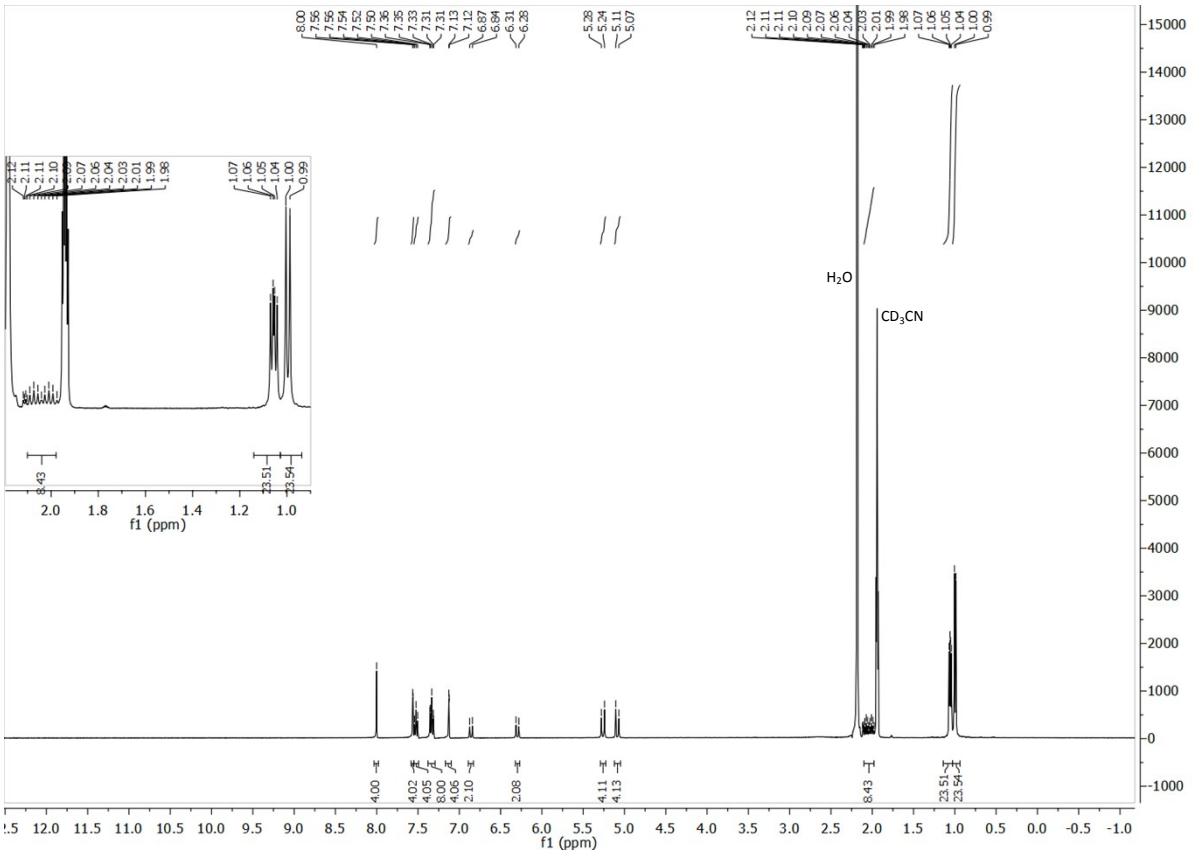

Figure 21. ^{1}H-NMR of **6** in CD_3CN.

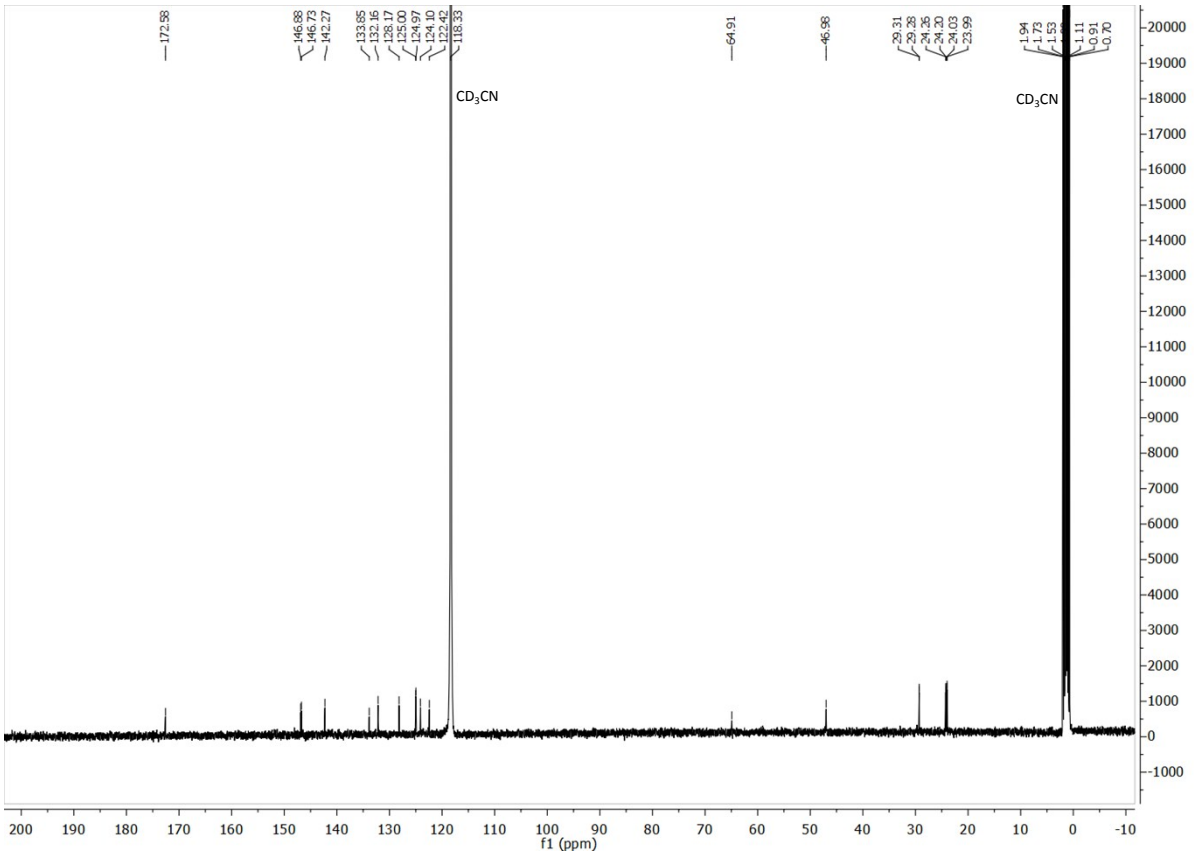

Figure 22. ^{13}C-NMR of **6** in CD_3CN.

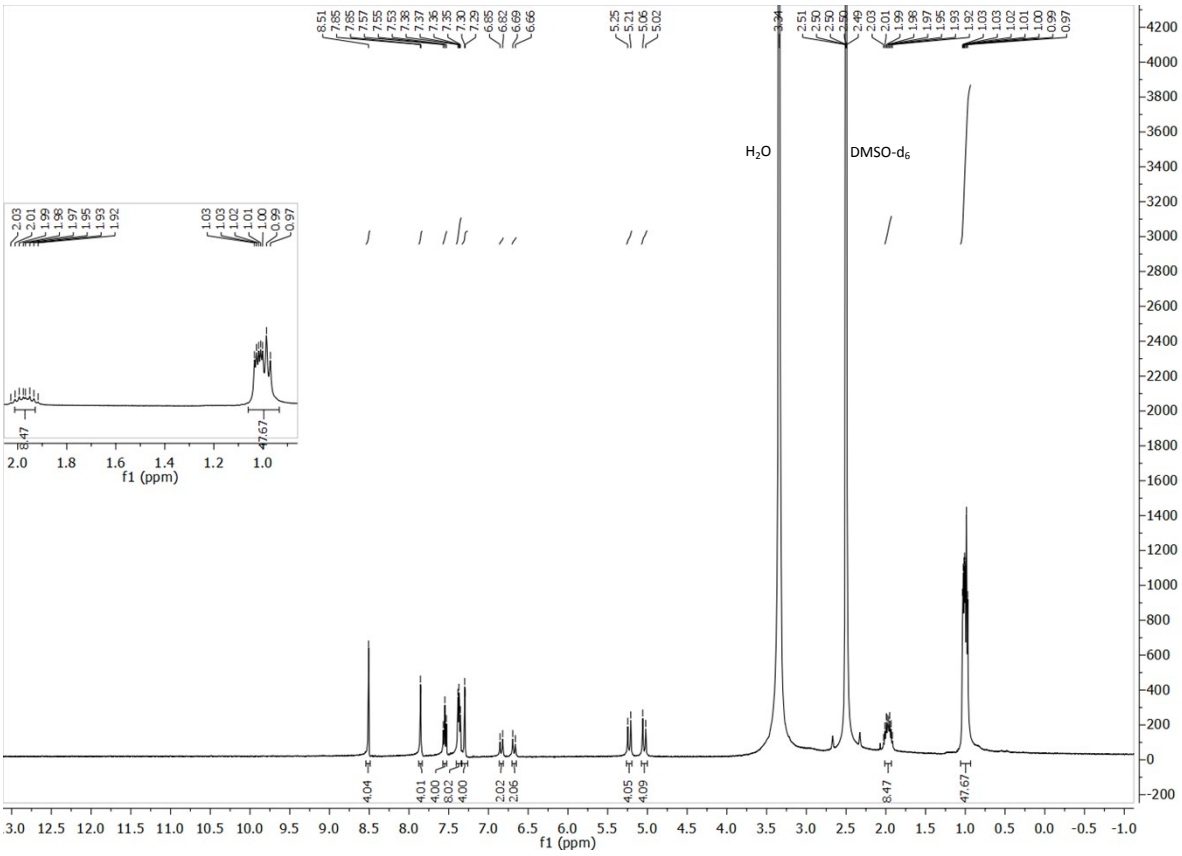

Figure 23. [1]H-NMR of **6** in DMSO-d_6.

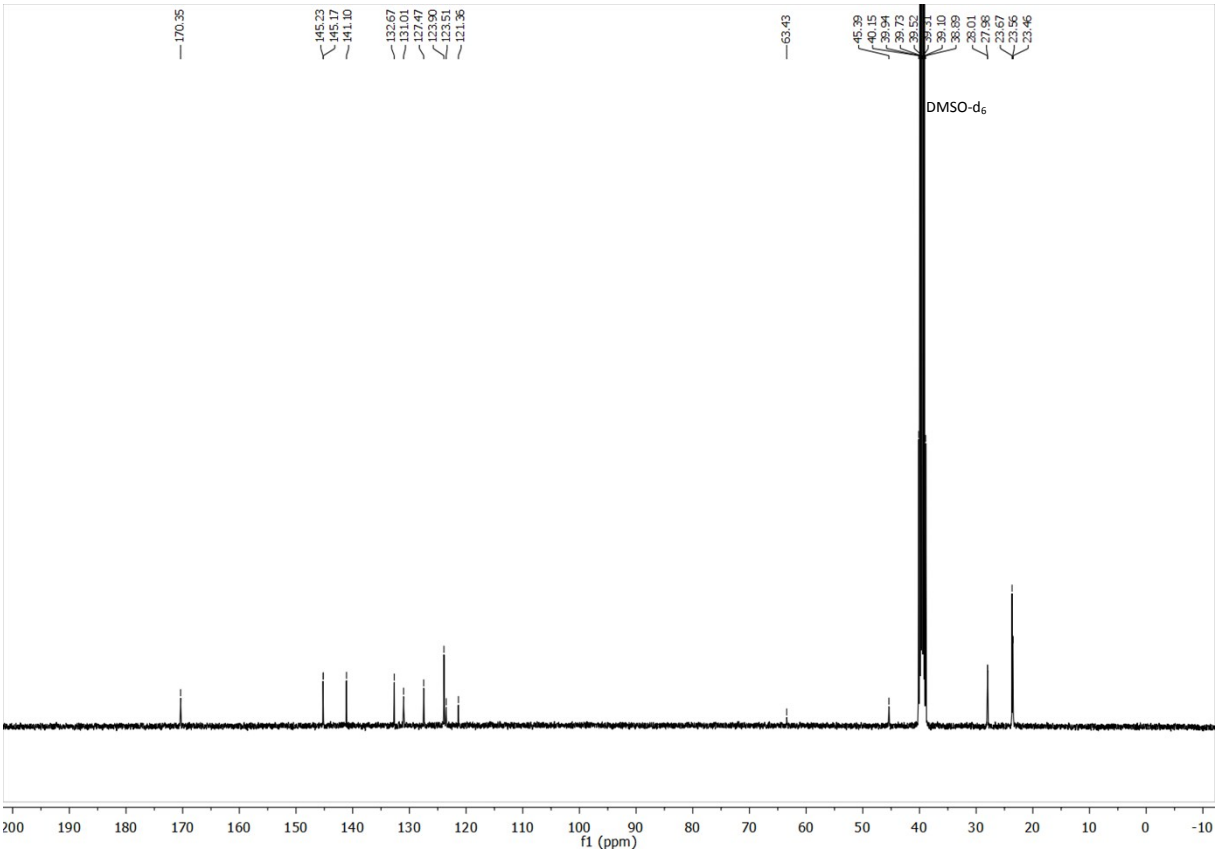

Figure 24. [13]C-NMR of **6** in DMSO-d_6.

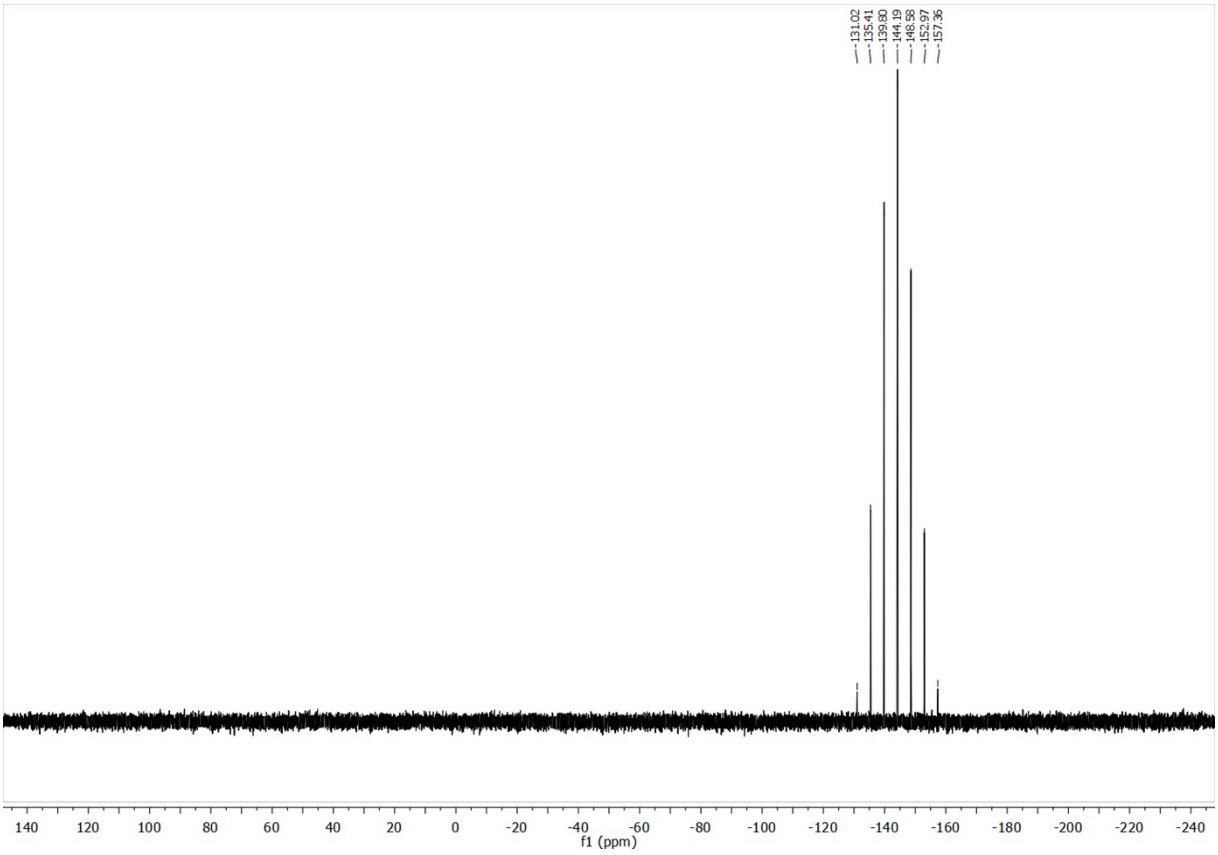

Figure 25. ^{31}P-NMR of **6** in DMSO-d_6.

3. Variable Temperature ^{1}H-NMR Spectroscopy

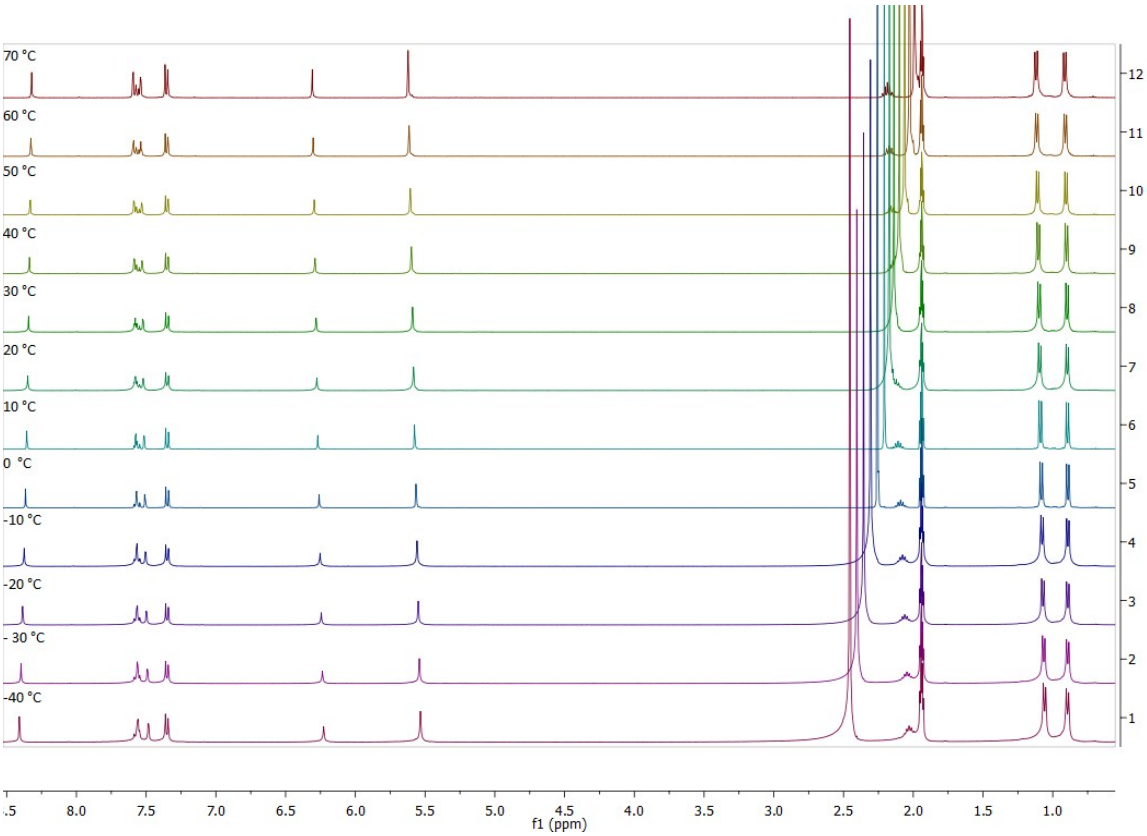

Figure 26. ^{1}H-NMR of **3** in CD_3CN at various temperatures.

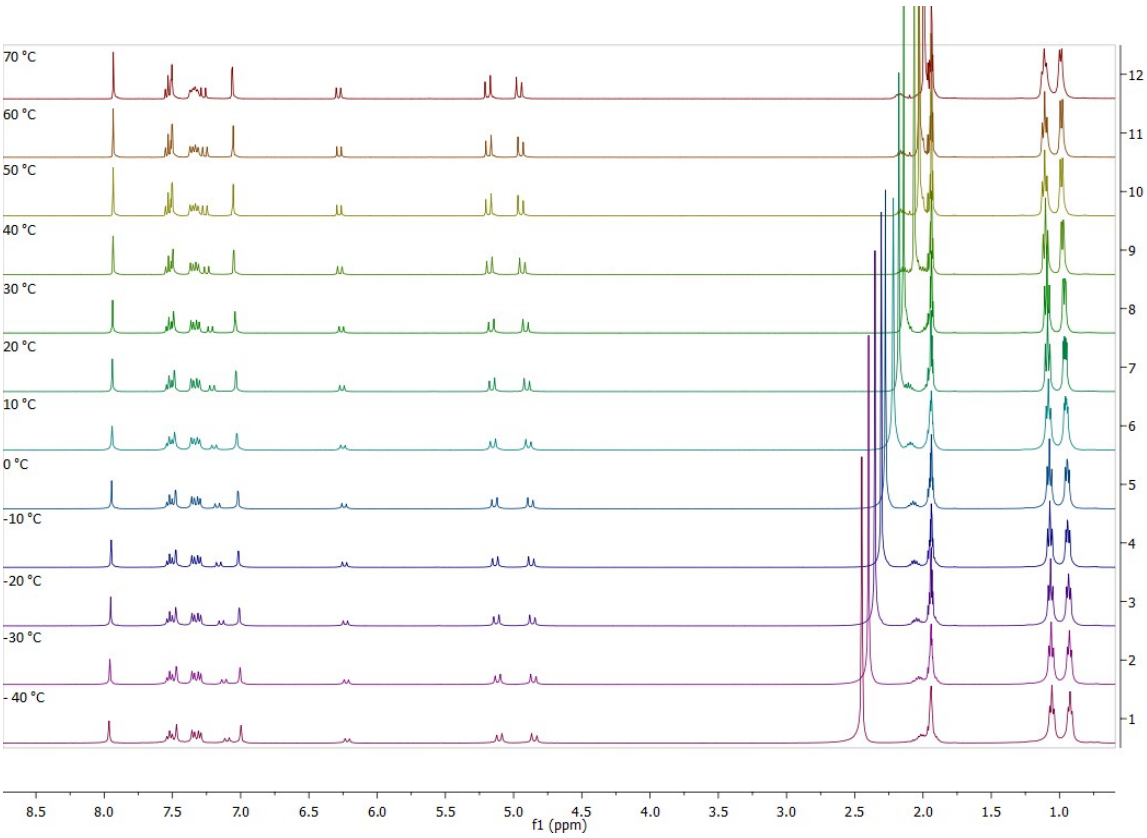

Figure 27. ^{1}H-NMR of **4** in CD_3CN at various temperatures.

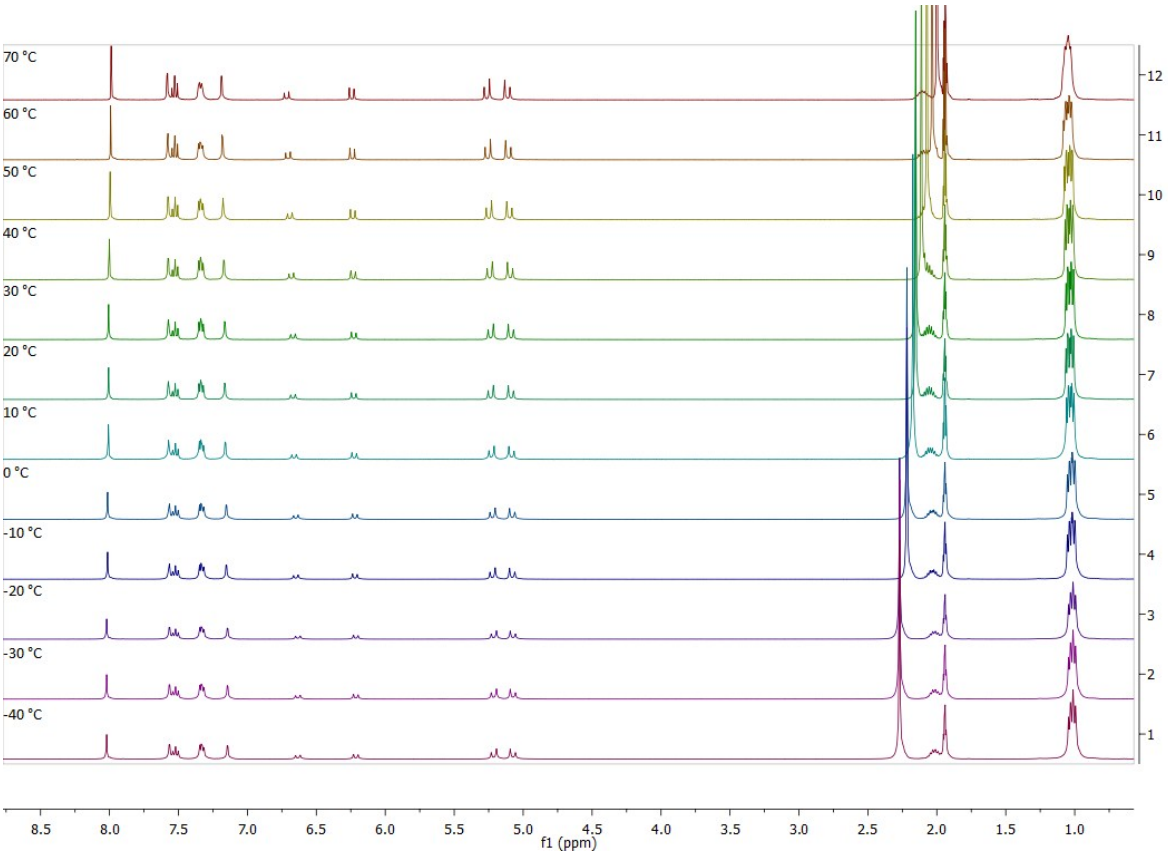

Figure 28. ^{1}H-NMR of **5** in CD_3CN at various temperatures.

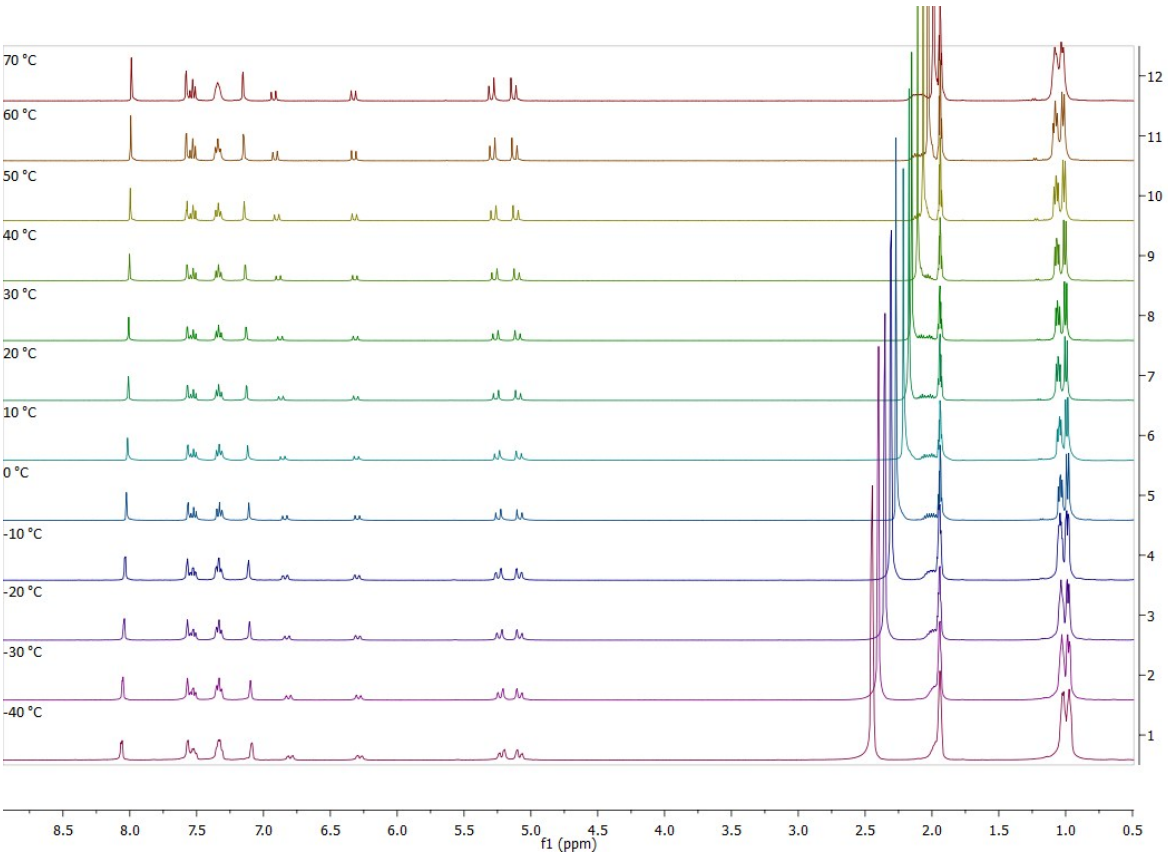

Figure 29. ^{1}H-NMR of **6** in CD_3CN at various temperatures.

4. Crystallographic data

Table 1. Crystallographic data and structure refinement parameters.

Substance identification	**Compound 3**	**Compound 4**	**Compound 6**
CCDC	1923376	1923375	1923374
Chemical formula	$C_{37}H_{46}F_{12}N_{10}P_2Pd$	$C_{74}H_{92}F_{12}N_{20}NiP_2$	$C_{82}H_{112}F_{12}N_{20}O_2P_2Pd$
Fw [g mol^{-1}]	1027.18	1610.31	1806.25
T [K]	100(2)	100(2)	100(2)
Crystal system	triclinic	triclinic	triclinic
Space group	*P* -1	*P* -1	*P* -1
a [Å]	15.1615(18)	9.9082(15)	10.2595(19)
b [Å]	15.3391(19)	11.862(2)	11.748(2)
c [Å]	23.869(3)	19.211(3)	20.722(4)
α [deg]	104.258(3)	97.837(5)	104.056(6)
β [deg]	92.735(3)	93.258(5)	92.793(6)
γ [deg]	116.887(3)	106.980(5)	111.557(5)
V [Å^3]	4716.5(10)	2128.1(6)	2226.8(7)
Z	4	2	1
Density (calcd) [g cm^{-3}]	1.478	1.256	1.347
μ [mm^{-1}]	0.549	0.343	0.326
F (000)	2138	842	944
Crystal size (mm^3)	0.040 × 0.042 × 0.128	0.064 × 0.129 × 0.206	0.095 × 0.131 ×0.345
***θ* range for data collection [deg]**	1.99 to 25.35	2.26 to 25.35	1.93 to 25.35
Reflections collected	120771	73359	65958
Independent reflections	17268	7782	8134
Data/restrains/parameters	17268 / 619 / 1388	7782 / 139 / 561	8134 / 651 / 781
GOF on F^2	1.015	1.024	1.097
Final R1	R1 = 0.0467	R1 = 0.0398	R1 = 0.0851
wR2 [I > 2σ(I)]	wR2 = 0.0982	wR2 = 0.0903	wR2 = 0.2143
Largest diff. peak and hole [eÅ^{-3}]	2.423 and -0.631	0.819 and -0.389	3.078 and -1.480

For the refinement of compound **4** the squeeze function was applied due to large voids within the crystal structure. These voids most likely stem from evaporation of co-crystallized solvent. The crystal structure of compound **6** exhibits slight twinning due to the constitution of the measured crystal. **6** (and **3**) crystallize in adhered plates, therefore, no pristine single-crystal could be used in the measurement.

5. References

[1]Allen, F. H.(2004). ENCIFER. J. Applied Cryst. 37, 335-338.

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[9]Spek, A.L. (2003). J. Appl. Cryst. 36, 7-13.

[10]Wilson, A.J.C. (1992). Ed. International Tables for Crystallography, Volume C, Kluwer Academic Publishers, Dordrecht, The Netherlands.