Electronic Supplementary Information

Interplay of Lewis acidity, intramolecular O→Sn interactions and selectivity: Organotin-functionalized crown ethers as ditopic hosts for sodium and potassium halides

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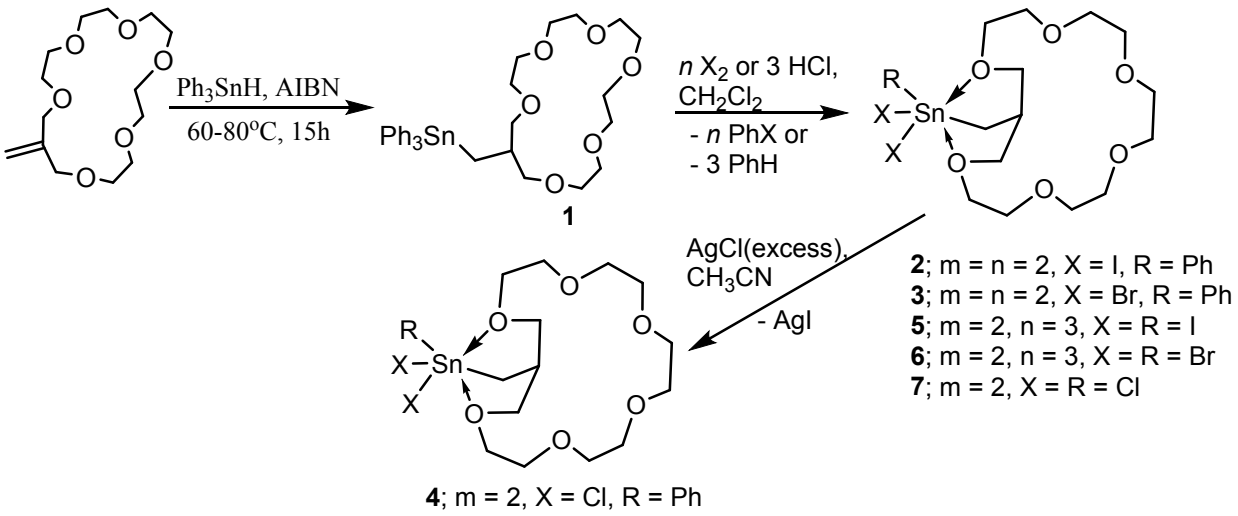


Scheme S1. Synthesis of organotin-functionalized crown ethers **2-7**

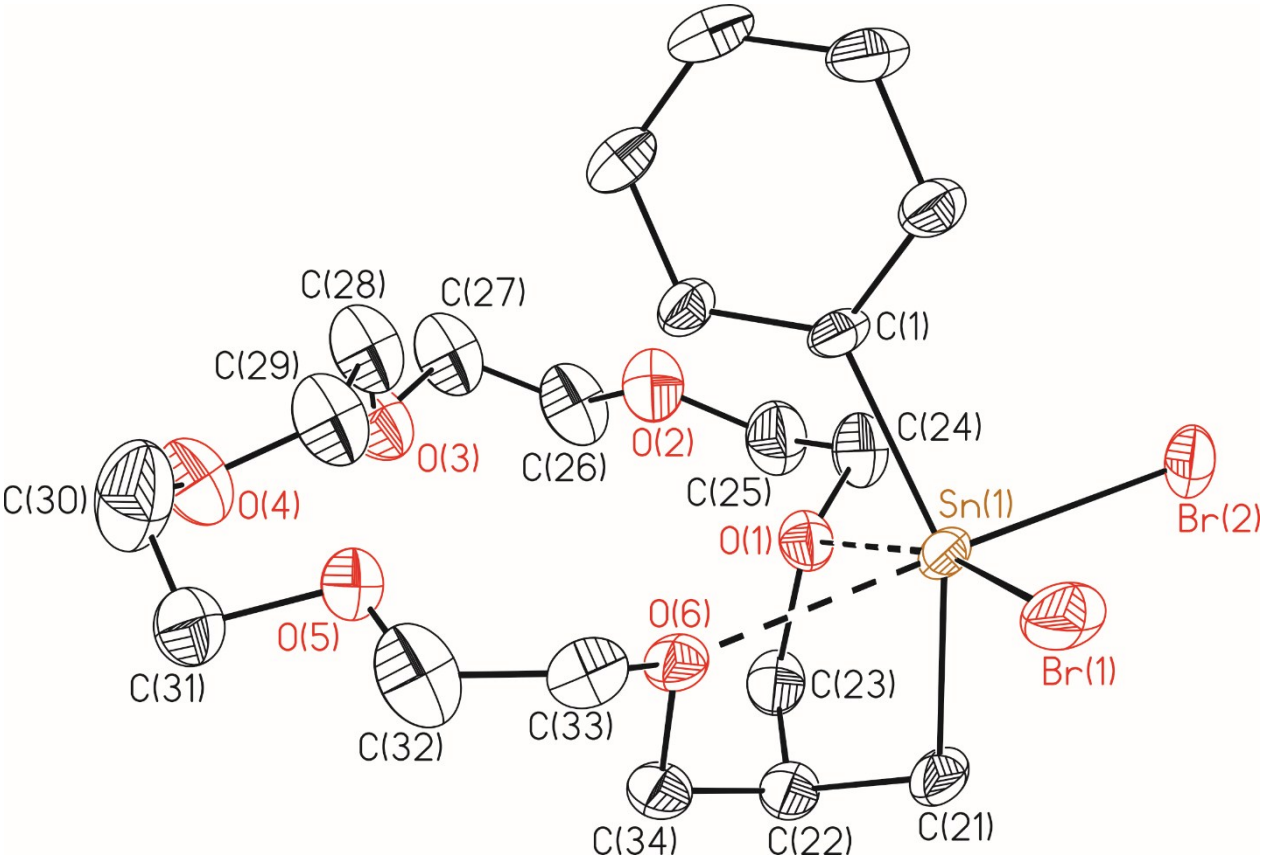


Figure S1. Molecular structure (ORTEP diagram) of **3**

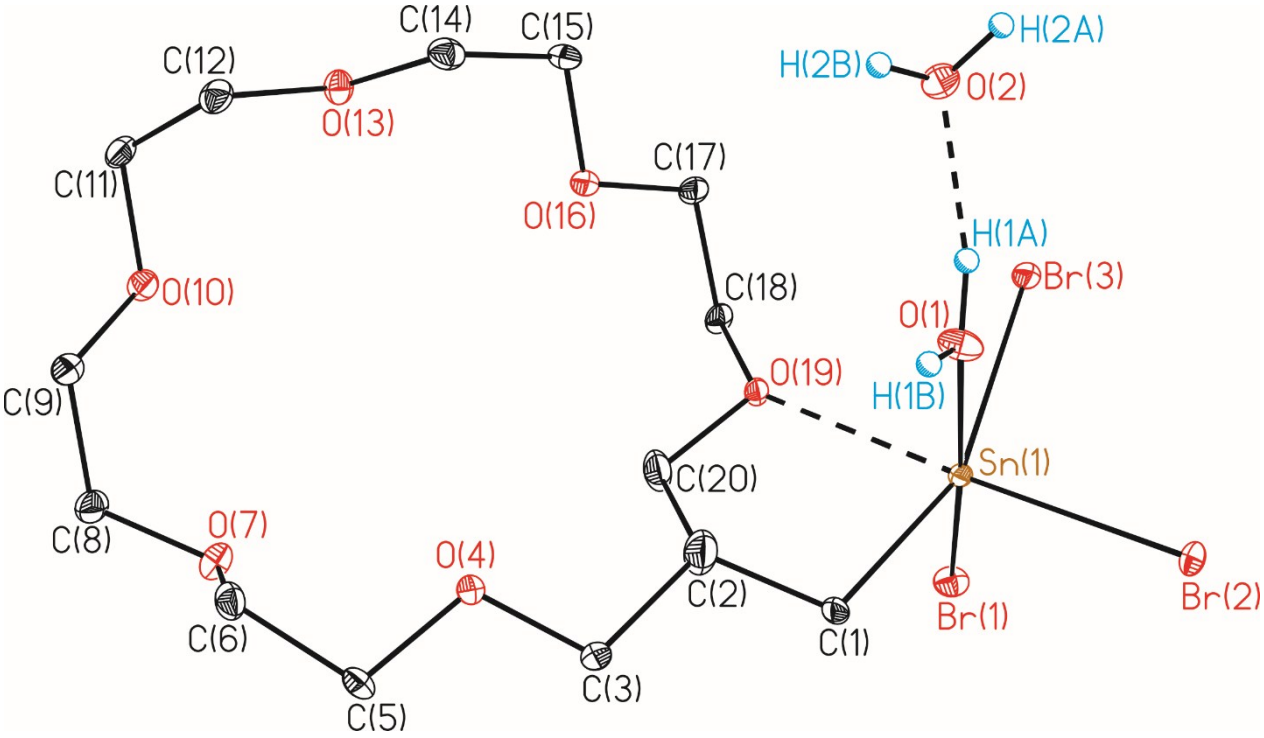


Figure S2. Molecular structure (ORTEP diagram) of [(**6**·H_2O)·H_2O]

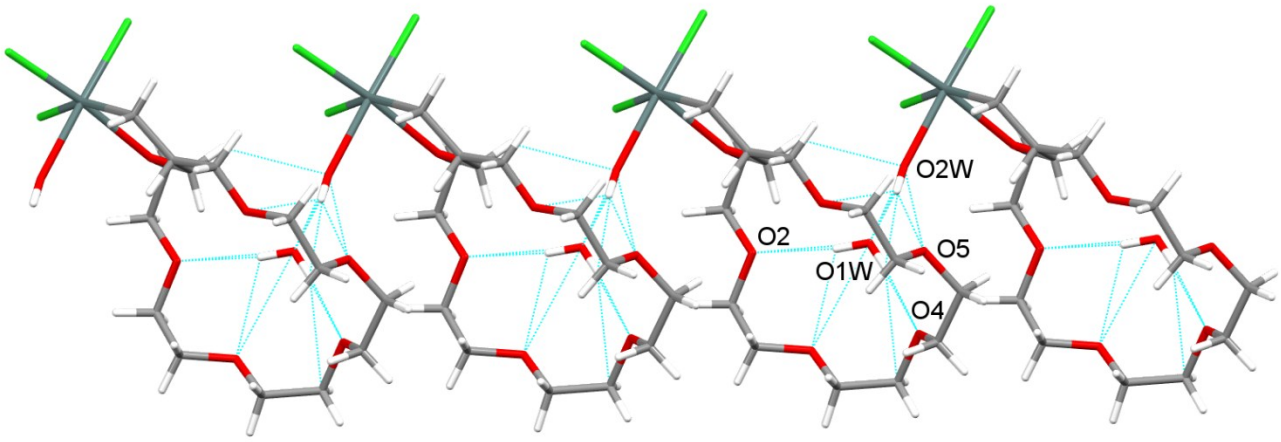


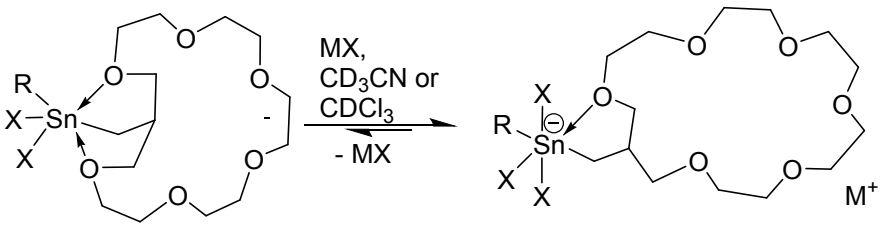
Figure S3. One-dimensional polymeric structure of [(**7**·H_2O)·H_2O] guided by a network of hydrogen bridges.

Table S1. Crystallographic data and structure refinements for compounds **2, 3,** [(**6**·H_2O)·H_2O], [(**7**·H_2O)·H_2O] and $N(Ph_3P)_2$[**4**·Cl]

Compounds	**2**	**3**	[(**6**·H_2O)·H_2O]	[(**7**·H_2O)·H_2O]	$N(Ph_3P)_2$[**4**·Cl]
formula	$C_{20}H_{32}I_2O_6Sn$	$C_{20}H_{32}Br_2O_6Sn$	$C_{14}H_{31}Br_3O_8Sn$	$C_{14}H_{31}Cl_3O_8Sn$	$C_{56.5}H_{63}Cl_4NO_6P_2Sn$
fw	740.94	646.96	685.81	552.43	1174.51
cryst syst	monoclinic	monoclinic	triclinic	triclinic	monoclinic
cryst size, mm	0.20 x 0.20 x 0.18	0.35 x 0.32 x 0.09	0.20 x 0.20 x 0.18	0.20 x 0.20 x 0.18	0.10 x 0.08 x 0.08
space group	*P2(1)/n*	*P2(1)/n*	*P-1*	*P-1*	*P2(1)/c*
a, Å	13.1138(7)	9.4436(4)	7.1137(3)	7.1523(15)	10.8696(8)
b, Å	14.1448(11)	14.3024(7)	10.3359(4)	10.2096(18)	32.808(3)
c, Å	14.5344(11)	18.0530(8)	16.6178(7)	16.569(4)	16.1991(13)
α, deg	90	90	107.749(4)	72.642(11)	90
β, deg	107.462(4)	98.649(2)	100.269(4)	80.828(6)	95.866(4)
γ, deg	90	90	79.071(12)	79.071(12)	90
V, Å^3	2571.8(3)	2410.62(19)	1136.45(9)	1127.0(4)	5746.5(8)
Z	4	4	2	2	4
ρ_{calcd}, Mg/m^3	1.914	1.783	2.004	1.628	1.358
μ, mm^{-1}	3.424	4.406	6.432	1.523	0.734
F(000)	1424	1280	668.0	560	2420
θ range, deg	2.94 to 26.50	1.825 to 26.497	4.19 to 60.082	2.592 to 25.058	2.603 to 25.033
index ranges	-17<=h<=17	-11<=h<=11	-9<=h<=9	-8<=h<=8	$-12 \le h \le 12$
	$-18 \le k \le 18$	-17<=k<=17	-14<=k<=13	-11<=k<=12	$-39 \le k \le 39$
	$-18 \le l \le 17$	-22<=l<=22	-21<=l<=22	-18<=l<=19	$-19 \le l \le 19$
no. of reflns collcd	5327	36293	16664	3980	9996
completeness to θ_{max}	99.8	-	-	99.7	98.5
no. of indep reflns/R_{int}	5327 / 0.054	4989 / 0.0287	5893 / 0.0355	3980 / 0.061	9996 / 0.075
no. of reflns obsd with ($I > 2\sigma(I)$)	2723	4036	5893	1341	3198
no. of refined Params	262	250	260	248	397
GooF (F^2)	0.480		1.046	0.420	0.831
$R1$ (F) ($I > 2\sigma(I)$)	0.0267	0.0452	0.0330	0.0299	0.0545
$wR2$ (F^2) (all data)	0.0563	0.1532	0.0624	0.0729	0.1971
largest diff. peak/hole, e/Å^3	0.652 / -0.724	1.36 / -0.948	1.52 / -0.90	0.476 / -0.362	1.053 / -0.773

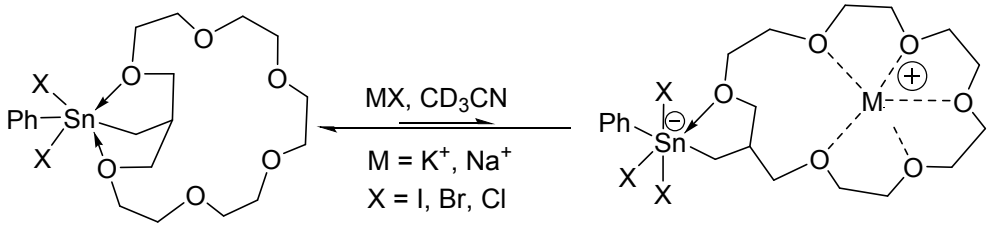
Table S2. Selected interatomic distances (Å) and angles (°) for compounds **2**, **3,** [(**6**·H_2O)·H_2O], [(**7**·H_2O)·H_2O] and $N(Ph_3P)_2$[**4**·Cl]

Compounds	**2**	**3**	[(**6**·H_2O)·H_2O]	[(**7**·H_2O)·H_2O]	$N(Ph_3P)_2$[**4**·Cl]
	X = I	X = Br	X = Br	X = Cl	X = Cl
Sn(1)-X(1)	2.7868(4)	2.5703(7)	2.5824(4)	2.3828(14)	2.461(3)
Sn(1)-X(2)	2.8060(5)	2.5797(7)	2.5409(4)	2.4186(17)	2.564(2)
Sn(1)-X(3)	-	-	2.5313(4)	2.3694(17)	2.590(2)
Sn(1)-C(1)/C(41)	2.134(4)	2.125(5)	2.141(3)	-	2.161(9)
Sn(1)-C(21)	2.139(4)	2.135(5)	-	2.119(5)	2.157(9)
Sn(1)-O(1)	2.528(3)	2.516(3)	2.215(3)	2.363(3)	2.515(6)
Sn(1)- O(6)/ O(2W)/O(19)	2.558(3)	2.511(3)	2.363(2)	2.220(4)	-
C(1)/C(41)-Sn(1)-C(21)	149.54(16)	151.7(2)	-	-	163.8(4)
O(1)-Sn(1)-X(1)	87.55(7)	167.46(8)	172.14(8)	174.78(11)	173.84(16)
O(1)-Sn(1)-X(2)	169.43(7)	93.26(8)	91.09(8)	90.68(10)	88.14(15)
O(1)-Sn(1)-X(3)	-	-	81.44(8)	83.01(11)	84.56(15)
O(6)-Sn(1)-X(1)	157.67(7)	95.62(8)	-	-	-
O(6)/O(2W)/ O(19)-Sn(1)-X(2)	104.22(7)	164.86(8)	175.13(6)	171.74(13)	-
O(1)-Sn(1)-O(6)	70.19(1)	72.47(11)	-	-	-
X(1)-Sn(1)-X(2)	97.494(14)	98.20(3)	93.901(14)	94.53(6)	92.75(9)
C(21)/C(1)-Sn(1)-X(3)	-	-	158.15(9)	157.99(15)	90.2(3)
X(2)-Sn(1)-X(3)	-	-	96.407(13)	91.37(6)	172.62(9)



[**4**.$(Ph_3P)_2NCl$]; X = Cl, R = Ph, M = $[(Ph_3P)_2N]$
[**5**.Bu_4NI]; X = R = I, M = $[Bu_4N]$
[**6**.Ph_4PBr]; X = R = Br, M = $[Ph_4P]$
[**7**.Ph_4PCl]; X = R = Cl, M = $[Ph_4P]$

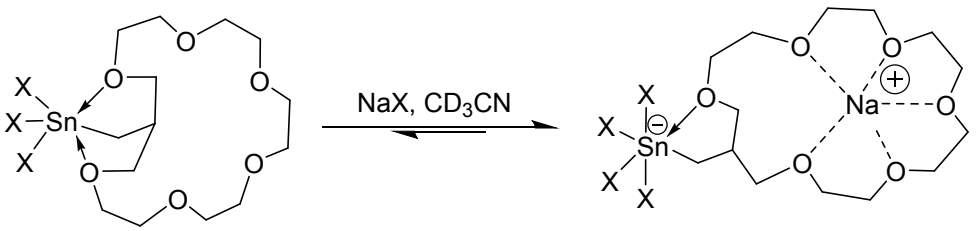
Scheme S2



2, X = I
3, X = Br
4, X = Cl

[**2**·MX], X = I
[**3**·MX], X = Br
[**4**·MX], X = Cl

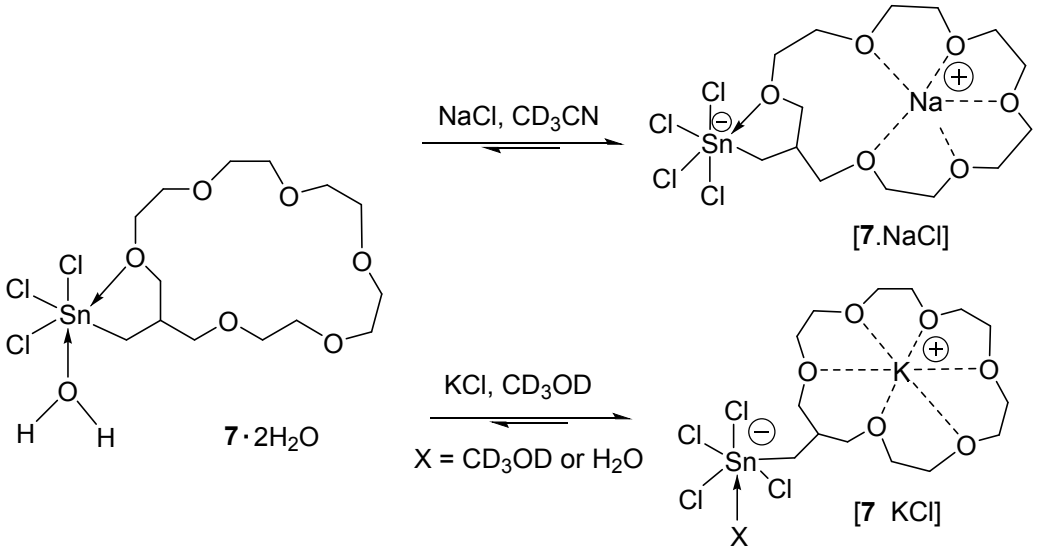
Scheme S3



5, X = I
6, X = Br

[**5**·NaI], X = I
[**6**·NaBr], X = Br

Scheme S4



7·2H_2O

[**7**.NaCl]

[**7** KCl]

Scheme S5

Experimental section

General methods. Solvents were dried and distilled from the appropriate desiccants prior to use. All manipulations were performed under an inert atmosphere of nitrogen or argon. The atom numbering of the [19]-crown-6 fragment is shown in Chart 1.

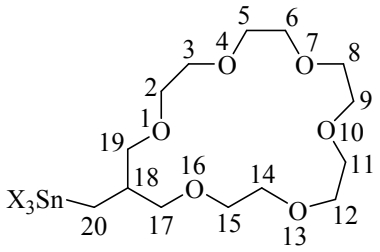


Chart 1

NMR Spectroscopy. NMR spectra were recorded on Bruker DRX 500, DRX 400, DPX 300, Varian Nova 600 and Varian Mercury 200 spectrometers with broad band decoupling of ^{119}Sn at 111.92 MHz, ^{19}F at 282.4 MHz, ^{13}C at 100.61 MHz. Chemical shifts δ are given in ppm and referenced to tetramethylstannane (^{119}Sn), $CFCl_3$ (^{19}F), and tetramethylsilane (^{1}H, ^{13}C). Solid state ^{119}Sn-NMR spectra were recorded on a Bruker AVANCE III 400 spectrometer equiped with a double-bearing CP/MAS probe at room temperature. CP/MAS (cross-olarization/magic angle spinning) experiments were used with a repetition delay of 10s and the contact time was set at 2 ms. Two spinning rates (5000 and 7000 Hz) were used to identify the isotropic chemical shift. The number of scans was set at 1000. The ^{119}Sn chemical shifts were calibrated using tetracyclohexyltin (δ = –97.35).

Complexation Studies. The samples for NMR analyses were prepared by dissolving ca. 50 mg of the compound and the corresponding amounts of the alkali salt in deuterated solvents. The

alkali salts used for the complexation studies were dried in vacuo (10^{-6} mbar) at 100°C for one day and stored under nitrogen.

Electrospray mass spectra were recorded on a Thermoquest-Finnigan instrument using CH_3CN as the mobile phase. The samples were introduced as solution in CH_3CN via a syringe pump operating at 0.5 µL/min. The capillary voltage was 4.5 kV while the cone skimmer voltage varied between 50 and 250 kV. Identification of the expected ions was assisted by comparison of experimental and calculated isotope distribution patterns. The m/*z* values reported correspond to those of the most intense peak in the corresponding isotope pattern.

Crystallography

Intensity data for compounds **2**, **3**, [**4**·Cl]$^-$[$(Ph_3P)_2N]^+$·0.5CH_2Cl_2 and [(**7**·H_2O)·H_2O] were collected on a Nonius Kappa CCD diffractometer (Bruker Corporation) using Mo-Kα radiation at 173 K. Intensity data for compound [(**6**·H_2O)·H_2O] were collected on an XcaliburS CCD diffractometer (Oxford Diffraction) using Mo-Kα radiation at 173(1) K with an Oxford Cryostream.

The structures were solved with direct methods using SHELXS-97[1] (compound **2** and [(**7**·H_2O)·H_2O]) or SHELXT[2] (compound **3**, [**4**·Cl]$^-$[$(Ph_3P)_2N]^+$·0.5CH_2Cl_2 and [(**6**·H_2O)·H_2O]) and refinements were carried out against *F*2 by using SHELXL-2014/7[1] (**2**, **3**, [**4**·Cl]$^-$[$(Ph_3P)_2N]^+$·0.5CH_2Cl_2 and [(**7**·H_2O)·H_2O]) or SHELXL-2017/1[1] (compound [(**6**·H_2O)·H_2O]). The C–H hydrogen atoms were positioned with idealized geometry and refined using a riding model. All non-hydrogen atoms were refined using anisotropic displacement parameters.

Due to weak reflection data the least squares goodness of fit parameter of compound **2** lies outside the range 0.60 <> 4.00. The atoms C28, C29, O4 and O5 in compound **3** are affected by

disorder and refined by a split model over two positions (occupancy values 67:33). Several atoms in the crown ether fragment of compound **3** are constraint with the EADP instruction and restrained with SADI and ISOR instructions. The data of compound [**4**·Cl]$^-$ [$(Ph_3P)_2N]^+\cdot 0.5CH_2Cl_2$ have a low observed / unique reflections ratio which is caused by weak data beyond sin(theta)/lambda > 0.5. Several carbon atoms of the crown ether fragment of compound [**4**·Cl]$^-$[$(Ph_3P)_2N]^+\cdot 0.5CH_2Cl_2$ are restrained with the ISOR instruction. The carbon atoms of the cation are constrained with the EADP instruction and restrained with FLAT and SADI instructions. The atoms of the solvent molecule are restrained with the ISOR instruction. Due to weak reflection data the least squares goodness of fit parameter of compound **7**·H_2O lies outside the range 0.60 <> 4.00. The data of the latter have a low observed / unique reflections ratio which is caused by weak data beyond sin(theta)/lambda > 0.5. The OH protons of compounds [(**6**·H_2O)·H_2O] and [(**7**·H_2O)·H_2O] are located in the difference Fourier map and refined freely, OH distances are restrained to a fix value. The oxygen atom O6 is restrained with the ISOR instruction.

CCDC-780582 (**2**), CCDC-780589 (**3**), CCDC-780583 ([$(Ph_3P)_2N$][**4**·Cl]·$0.5CH_2Cl_2$), CCDC-1588509 [(**6**·H_2O)·H_2O] and CCDC-780588 ([(**7**·H_2O).H_2O]) contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. For decimal rounding of numerical parameters and su values the rules of IUCr have been employed.[3] All figures were generated using ORTEP III[4] visualization software.

Synthesis of Diiodo-(1,4,7,10,13,16-hexaoxa-cyclononadec-18-ylmethyl)-phenylstannane (2).

Over a period of three hours, iodine (0.40g, 1.56 mmol) was added in small portion at 0°C to a stirred solution of (1,4,7,10,13,16-hexaoxa-cyclononadec-18-ylmethyl)-triphenylstannane[5] **1** (0.50g, 0.78 mmol) in CH_2Cl_2 (30 mL). Stirring was continued and the reaction mixture was warmed to room temperature overnight. Dichloromethane and iodobenzene were removed in vacuum (10^{-3} Torr). The yellow residue was recrystallized from ethanol at –5°C to give 0.39g (67%) of pure **2** as yellow crystals, m.p. 172-175°C.

^{1}H-NMR ($CDCl_3$, 400.13 MHz) δ: 2.20 (d, $^3J(^1H\text{-}^1H)$ = 7.0 Hz, $^2J(^1H\text{-}^{117}Sn)$ = 66.0Hz, $^2J(^1H\text{-}^{119}Sn)$ = 79.5 Hz, 2H, Sn-CH_2), 2.55 (m, 1H, CH), 3.45-3.75 (m, 24H, CH_2-O-CH_2), 7.31-7.77 (m, 5H, Ph). $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100.63 MHz) δ : 29.8 ($^1J(^{13}C\text{-}^{117}Sn)$ = 540 Hz, $^1J(^{13}C\text{-}^{119}Sn)$ = 565 Hz, C20), 38.1 ($^2J(^{13}C\text{-}^{117/119}Sn)$ = 40 Hz, C18), 70.3-70.8 (C2-C15), 73.3 ($^3J(^{13}C\text{-}^{117/119}Sn)$ = 71 Hz, C17/C19), 128.5 ($^3J(^{13}C\text{-}^{117/119}Sn)$ = 84 Hz, C_m), 130.1 ($^4J(^{13}C\text{-}^{117/119}Sn)$ = 18 Hz, C_p), 134.1 ($^2J(^{13}C\text{-}^{117/119}Sn)$ = 63 Hz, C_o), 140.7 (C_i). ^{119}Sn $\{^1H\}$-NMR ($CDCl_3$, 111.93 MHz) δ: –261. Elemental Anal. for $C_{20}H_{32}I_2O_6Sn$ (740.98), Cacld : C 32.4; H 4.3. Found: C 32.4; H 4.1 %.

Synthesis of Dibromo-(1,4,7,10,13,16-hexaoxa-cyclononadec-18-ylmethyl)-phenylstannane (3).

To a cooled solution (–55°C) of (1,4,7,10,13,16-hexaoxa-cyclononadec-18-ylmethyl)-triphenylstannane[5] **1** (0.50g, 0.78 mmol) in dichloromethane (30 mL) was added drop-wise a solution of bromide (0.25g, 1.56 mmol) in dichloromethane (10 mL). After the addition had been completed, the mixture was stirred and warmed to room temperature overnight. From the slightly yellow solution obtained, the solvent and the formed bromobenzene were removed in vacuum (10^{-3} Torr) to afford a yellow solid, which was recrystallized from ethanol at –5°C to give 0.28g (55%) of pure **3** as colorless crystals, mp 92°C.

^{1}H-NMR ($CDCl_3$, 400.13 MHz) δ : 1.98 (d, $^{3}J(^{1}H\text{-}^{1}H)$ = 6.3 Hz, $^{2}J(^{1}H\text{-}^{117}Sn)$ = 80.9 Hz, $^{2}J(^{1}H\text{-}^{119}Sn)$ = 91.9 Hz, 2H, Sn-CH_2), 2.59 (m, 1H, CH), 3.48-3.84 (m, 24H, CH_2-O-CH_2), 7.35-7.88 (m, 5H, Ph). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 100.63 MHz) δ : 29.8 (C20), 37.2 (C18), 71.0-71.33 (C2-C15), 74.4 ($^{3}J(^{13}C\text{-}^{117/119}Sn)$ = 64 Hz, C17/C19), 129.2 ($^{3}J(^{13}C\text{-}^{117/119}Sn)$ = 88 Hz, C_m), 130.7 ($^{4}J(^{13}C\text{-}^{117/119}Sn)$ = 18 Hz, C_p), 135.2 ($^{2}J(^{13}C\text{-}^{117/119}Sn)$ = 64 Hz, C_o), 143.8 (C_i). $^{119}Sn\ \{^{1}H\}$-NMR ($CDCl_3$, 111.93 MHz) δ: –147. Elemental Anal. for $C_{20}H_{32}Br_2O_6Sn$ (646.99), Cacld : C 37.1; H 5.0. Found: C 37.1; H 4.7%.

Synthesis of Dichloro-(1,4,7,10,13,16-hexaoxa-cyclononadec-18-ylmethyl)-phenylstannane (4).

To a solution of **2** (0.21g, 0.28 mmol) in CH_3CN (15 mL) was added excess silver chloride, AgCl (0.24g, 1.70 mmol). The resulting mixture was stirred at room temperature and in darkness for 14 days. After the AgI formed and the non-reacted AgCl had been removed by filtration, the solvent was evaporated in vacuum. The slightly yellow oil thus obtained was dissolved in ether and cooled at –5°C to give 0.10g (65%) of pure **4** as colourless crystals, m.p. 82-84°C.

^{1}H-NMR ($CDCl_3$, 400.13 MHz) δ: 1.81 (d, $^{3}J(^{1}H\text{-}^{1}H)$ = 6.0 Hz, $^{2}J(^{1}H\text{-}^{117}Sn)$ = 86.8 Hz, $^{2}J(^{1}H\text{-}^{119}Sn)$ = 96.9 Hz, 2H, Sn-CH_2), 2.59 (m, 1H, CH), 3.50-3.88 (m, 24H, CH_2-O-CH_2), 7.38-7.92 (m, 5H, Ph). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 100.63 MHz) δ : 26.5 ($^{1}J(^{13}C\text{-}^{117}Sn)$ = 697 Hz, $^{1}J(^{13}C\text{-}^{119}Sn)$ = 730 Hz, C20), 36.0 ($^{2}J(^{13}C\text{-}^{117/119}Sn)$ = 43 Hz, C18), 70.4-70.8 (C2-C15), 74.0 ($^{3}J(^{13}C\text{-}^{117/119}Sn)$ = 62 Hz, C17/C19), 128.7 ($^{3}J(^{13}C\text{-}^{117/119}Sn)$ = 93 Hz, C_m), 130.2 ($^{4}J(^{13}C\text{-}^{117/119}Sn)$ = 19 Hz, C_p), 135.0 ($^{2}J(^{13}C\text{-}^{117/119}Sn)$ = 65 Hz, C_o), 143.2 ($^{1}J(^{13}C\text{-}^{117}Sn)$ = 918 Hz, $^{1}J(^{13}C\text{-}^{119}Sn)$ = 960 Hz), C_i). $^{119}Sn\ \{^{1}H\}$-NMR ($CDCl_3$, 111.93 MHz) δ: –118. Elemental Anal. for $C_{20}H_{32}Cl_2O_6Sn$ (558.09), Cacld : C 43.0; H 5.8. Found: C 42.8; H 5.5 %.

Synthesis of Triiodo-(1,4,7,10,13,16-hexaoxa-cyclononadec-18-ylmethyl)-stannane (5).

Over a period of three hours, iodine (1.19g, 4.68 mmol) was added in small portion at 0°C to a stirred solution of (1,4,7,10,13,16-hexaoxa-cyclononadec-18-ylmethyl)-triphenylstannane[5] **1** (1.0g, 1.56 mmol) in CH_2Cl_2 (50 mL). Stirring was continued and the reaction mixture was warmed to room temperature overnight. Dichloromethane and iodobenzene were removed in vacuum (10^{-3} Torr). The red residue was recrystallized from ethanol at –5°C to give 0.63g (51%) of pure **5** as dark yellow crystals, m.p.56°C.

^{1}H-NMR ($CDCl_3$, 400.13 MHz) δ: 2.40 (m, 1H, CH), 2.53 (d, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.0 Hz, $^{2}J(^{1}H\text{-}^{117}Sn)$ = 57.0Hz, $^{2}J(^{1}H\text{-}^{119}Sn)$ = 70.0 Hz, 2H, Sn-CH_2), , 3.60-3.80 (m, 24H, CH_2-O-CH_2). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 100.63 MHz) δ : 34.4 ($^{1}J(^{13}C\text{-}^{117}Sn)$ = 566 Hz, $^{1}J(^{13}C\text{-}^{119}Sn)$ = 593 Hz, C20), 38.8 ($^{2}J(^{13}C\text{-}^{117/119}Sn)$ = 55 Hz, C18), 69.6-71.7 (C2-C15, C17/C19). $^{119}Sn\ \{^{1}H\}$-NMR ($CDCl_3$,CD_3CN, 111.93 MHz) δ: –786 and –793, respectively. Elemental Anal. for $C_{14}H_{27}I_3O_6Sn$ (790.77), Cacld : C 21.3; H 3.4. Found: C 21.3; H 3.5 %.

Synthesis of Tribromo-(1,4,7,10,13,16-hexaoxa-cyclononadec-18-ylmethyl)-stannane (6).

To a cooled solution (–55°C) of (1, 4, 7, 10, 13, 16-hexaoxa-cyclononadec-18-ylmethyl)-triphenylstannane[5] **1** (1.50g, 2.34 mmol) in dichloromethane (50 mL) was added drop-wise a solution of bromide (1.10g, 7.02 mmol) in dichloromethane (20 mL). After the addition had been completed, the mixture was stirred and warmed to room temperature overnight. From the solution obtained, the solvent and the formed bromobenzene were removed in vacuum (10^{-3} Torr) to afford a white yellow solid, which was recrystallized from ethanol at –5°C to give 1.10g (72.8%) of pure **6** as almost colourless crystalline solid, mp 115-118°C.

^{1}H-NMR ($CDCl_3$, 400.13 MHz) δ : 2.08 (d, $^{3}J(^{1}H\text{-}^{1}H)$ = 5.8 Hz, $^{2}J(^{1}H\text{-}^{117}Sn)$ = 68.3 Hz, $^{2}J(^{1}H\text{-}^{119}Sn)$ = 79.8 Hz, 2H, Sn-CH_2), 2.51 (m, 1H, CH), 3.58-4.04 (m, 24H, CH_2-O-CH_2). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 100.63 MHz) δ : 35.0 ($^{1}J(^{13}C\text{-}^{117}Sn)$ = 819 Hz, $^{1}J(^{13}C\text{-}^{119}Sn)$ = 858 Hz, C20), 36.2 ($^{2}J(^{13}C\text{-}^{117/119}Sn)$ = 69 Hz, C18), 70.1-71.4 (C2-C15), 73.2 ($^{3}J(^{13}C\text{-}^{117/119}Sn)$ = 86 Hz, C17/C19). ^{119}Sn $\{^{1}H\}$-NMR ($CDCl_3$,CD_3CN 111.93 MHz) δ: –398 and –448, respectively. Elemental Anal. for $C_{14}H_{27}Br_3O_6Sn$ (649.79), Cacld : C 25.9; H 4.2. Found: C 25.8; H 3.9%.

Synthesis of Trichloro-(1,4,7,10,13,16-hexaoxa-cyclononadec-18-ylmethyl)-stannane (7).

(1, 4, 7, 10, 13, 16-hexaoxa-cyclononadec-18-ylmethyl)-triphenylstannane[5] **1** (2.0g, 3.12 mmol) was mixed with concentred aqueous solution of hydrochloric acid (37%, 25 mL). The mixture was then stirred at 60°C for one day. After cooling at room temperature, the HCl solution was removed under reduced pressure. The brown viscous oil obtained was dissolved in ethanol and cooled at –5°C to give 1.30g (81%) of **7** as almost colourless crystalline solid, m.p. 128°C. Crystals of **7** suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in CH_2Cl_2/*n*-hexane at room temperature.

^{1}H-NMR ($CDCl_3$, 400.13 MHz) δ: 1.71 (d, $^{3}J(^{1}H\text{-}^{1}H)$ = 4.0 Hz, $^{2}J(^{1}H\text{-}^{117}Sn)$ = 96.0 Hz, $^{2}J(^{1}H\text{-}^{119}Sn)$ = 104.0 Hz, 2H, Sn-CH_2), 2.59 (m, 1H, CH), 3.58-4.25 (m, 24H, CH_2-O-CH_2). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 100.63 MHz) δ : 31.5 (C20), 34.5 ($^{2}J(^{13}C\text{-}^{117/119}Sn)$ = 78 Hz, C18), 70.6-71.4 (C2-C15), 74.3 ($^{3}J(^{13}C\text{-}^{117/119}Sn)$ = 76 Hz, C17/C19). ^{119}Sn $\{^{1}H\}$-NMR ($CDCl_3$, CD_3CN, CD_3OD 111.93 MHz) δ: –279, –312, –340, respectively. Elemental Anal. for $C_{14}H_{27}Cl_3O_6Sn\cdot 2H_2O$ (552,46), Cacld : C 30.4; H 5.7. Found: C 30.3; H 5.2 %.

Complexation studies

In situ reaction of 5 with one equivalent Bu_4NI in CD_3CN: Bu_4NI (28.1 mg, 0.08 mmol) was added to a solution of **5** (20.0 mg, 0.03mmol) in CD_3CN (600 μL). ^{119}Sn $\{^1H\}$-NMR (111.92 MHz, 293K) δ: –1033(**5**·I^-).

In situ reaction of 6 with one equivalent Ph_4PBr in CD_3CN: Ph_4PBr (32.3 mg, 0.08 mmol) was added to a solution of **6** (50.0 mg, 0.08 mmol) in CD_3CN (600 μL). ^{119}Sn $\{^1H\}$-NMR (111.92 MHz, 293K) δ: –660 (**6**·Br^-).

In situ reaction of 7 with one equivalent Ph_4PCl in $CDCl_3$: Ph_4PCl (33.9 mg, 0.09 mmol) was added to solution of **7** (50.0 mg, 0.09 mmol) in $CDCl_3$ (600 μL). ^{119}Sn $\{^1H\}$-NMR (111.92 MHz, 293K) δ: –382.

In situ reaction of 2 with four equivalents of NaI in CD_3CN. NaI (40.2 mg, 0.27 mmol) was added to a solution of **2** (50.0 mg, 0.07 mmol) in CD_3CN (600 μL). ^{119}Sn $\{^1H\}$-NMR (111.92 MHz, 293K) δ: –286.

In situ reaction of 3 with four equivalents of NaBr in CD_3CN. NaBr (31.7 mg, 0.31 mmol) was added to a solution of **3** (50.0 mg, 0.08 mmol) in CD_3CN (600 μL). ^{119}Sn $\{^1H\}$-NMR (111.92 MHz, 293K) δ: –228.

In situ reaction of 4 with four equivalents of NaCl in CD_3CN. NaCl (20.8 mg, 0.36 mmol) was added to a solution of **4** (50.0 mg, 0.09 mmol) in CD_3CN (600 μL). ^{119}Sn $\{^1H\}$-NMR (111.92 MHz, 293K) δ: –160.

In situ reaction of 5 with four equivalents of NaI in CD_3CN. NaI (37.8 mg, 0.25) was added to a solution of **5** (50 mg, 0.06 mmol) in CD_3CN (600 μL). ^1H-NMR (400.13 MHz, 293K) δ: 2.13 (m, 1H, CH), 3.15 (d, $^3J(^1H\text{-}^1H)$ = 6.8 Hz, 2H, Sn-CH_2), , 3.52-3.66 (m, 24H, CH_2-O-CH_2).

$^{13}C\{^{1}H\}$-NMR (100.63 MHz, 293K) δ : 4.8 (C20), 40.5 (C18), 68.6-69.5 (C2-C15), 72.0 (C17/C19). ^{119}Sn $\{^{1}H\}$-NMR (111.92 MHz, 293K) δ: –1021 ($\nu_{1/2}$ = 162 Hz). **ESI-MS** (MeCN, m/z, +p): 818.8, $\{I_3Sn\text{-}CH_2\text{-}[19]\text{-crown-6}\cdot Na\}^+$.

In situ reaction of 6 with four equivalents of NaBr in CD_3CN. NaBr (31.7 g, 0.31 mmol) was added to a solution of **6** (50.0 mg, 0.08 mmol) in CD_3CN (600 μL). ^{1}H-NMR (400.13 MHz, 293K) δ: 2.0 (d, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.8 Hz, $^{2}J(^{1}H\text{-}^{117}Sn)$ = 97.4, $^{2}J(^{1}H\text{-}^{117}Sn)$ = 111.7 Hz, Sn-CH_2), 2.78 (m, 1H, CH), 3.58-3.78 (m, 24H, CH_2-O-CH_2). $^{13}C\{^{1}H\}$-NMR (100.63 MHz, 293K) δ : 36.1 ($^{2}J(^{13}C\text{-}^{117/119}Sn)$ = 68 Hz, C18), 50.2 (C20), 69.3-70.1 (C2-C15), 71.5 ($^{3}J(^{13}C\text{-}^{117/119}Sn)$ = 156 Hz, C17/C19). ^{119}Sn $\{^{1}H\}$-NMR (111.92 MHz, 293K) δ: –640 ($\nu_{1/2}$ = 181). **ESI-MS** (MeCN, m/z, +p): 670.8, $\{Br_3Sn\text{-}CH_2\text{-}[19]\text{-crown-6}\cdot Na\}^+$

In situ reaction of 7 with four equivalents of NaCl in CD_3CN. NaCl (21.2 mg, 0.36 mmol) was added to a solution of **7**·$2H_2O$ (50.0 mg, 0.09 mmol) in CD_3CN (600 μL). ^{1}H-NMR (400.13 MHz, 293K) δ: 1.54 (d, $^{3}J(^{1}H\text{-}^{1}H)$ = 7.0 Hz, $^{2}J(^{1}H\text{-}^{117}Sn)$ = 107.2, $^{2}J(^{1}H\text{-}^{117}Sn)$ = 118.7, 2H, Sn-CH_2), 2.69 (m, 1H, CH), , 3.58-3.91 (m, 24H, CH_2-O-CH_2). $^{13}C\{^{1}H\}$-NMR (100.63 MHz, 293K) δ : 34.9 ($^{2}J(^{13}C\text{-}^{117/119}Sn)$ = 69 Hz, C18), 39.9 ($^{1}J(^{13}C\text{-}^{117}Sn)$ = 1097Hz, $^{1}J(^{13}C\text{-}^{119}Sn)$ = 1148 Hz, C20), , 69.5-70.2 (C2-C15), 72.5 ($^{3}J(^{13}C\text{-}^{117}Sn)$ = 133 Hz, $^{3}J(^{13}C\text{-}^{117}Sn)$ = 136 Hz, C17/C19). ^{119}Sn $\{^{1}H\}$-NMR (111.92 MHz, 293K) δ: –350 ($\nu_{1/2}$ = 117 Hz). **ESI-MS** (MeCN, m/z, +p): 538.9, $\{Cl_3Sn\text{-}CH_2\text{-}[19]\text{-crown-5}\cdot Na\}^+$.

In situ reaction of 7 with four equivalents of KCl in CD_3OD. KCl (26.9 mg, 0.36 mmol) was added to a solution of **7**·$2H_2O$ (50.0 mg, 0.09 mmol) in CD_3OD (600 μL). ^{1}H-NMR (400.13 MHz, 293K) δ: 1.62 (d, $^{3}J(^{1}H\text{-}^{1}H)$ = 6.5 Hz, $^{2}J(^{1}H\text{-}^{117}Sn)$ = 117.9, $^{2}J(^{1}H\text{-}^{117}Sn)$ = 128.5, 2H, Sn-CH_2), 2.51 (m, 1H, CH), , 3.54-3.72 (m, 24H, CH_2-O-CH_2). $^{13}C\{^{1}H\}$-NMR (100.63 MHz, 293K) δ : 35.8 ($^{2}J(^{13}C\text{-}^{117/119}Sn)$ = 51 Hz, C18), 40.0 ($^{1}J(^{13}C\text{-}^{117}Sn)$ = 1115 Hz, $^{1}J(^{13}C\text{-}^{119}Sn)$ = 1168 Hz,

C20), , 69.7-70.8 (C2-C15), 72.5 ($^{3}J(^{13}C\text{-}^{117}Sn)$ = 143 Hz, $^{3}J(^{13}C\text{-}^{117}Sn)$ = 136 Hz, C17/C19). ^{119}Sn {^{1}H}-NMR (111.92 MHz, 293K) δ: –390 ($\nu_{1/2}$ = 137 Hz). **ESI-MS** (MeOH, m/z, +p): 555.0, $\{Cl_3Sn\text{-}CH_2\text{-}[19]\text{-crown-}5\cdot K\}^{+}$.

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2. G. M. Sheldrick, *Acta Cryst.,* 2015, **C71**, 3.
3. W. Clegg, *Acta Cryst.,* 2003, **E59**, e2-e5.
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5. A. C. T. Kuate, G. Reeske, M. Schurmann, B. Costisella and K. Jurkschat, Organometallics, 2008, 27, 5577-5587.

NMR spectra

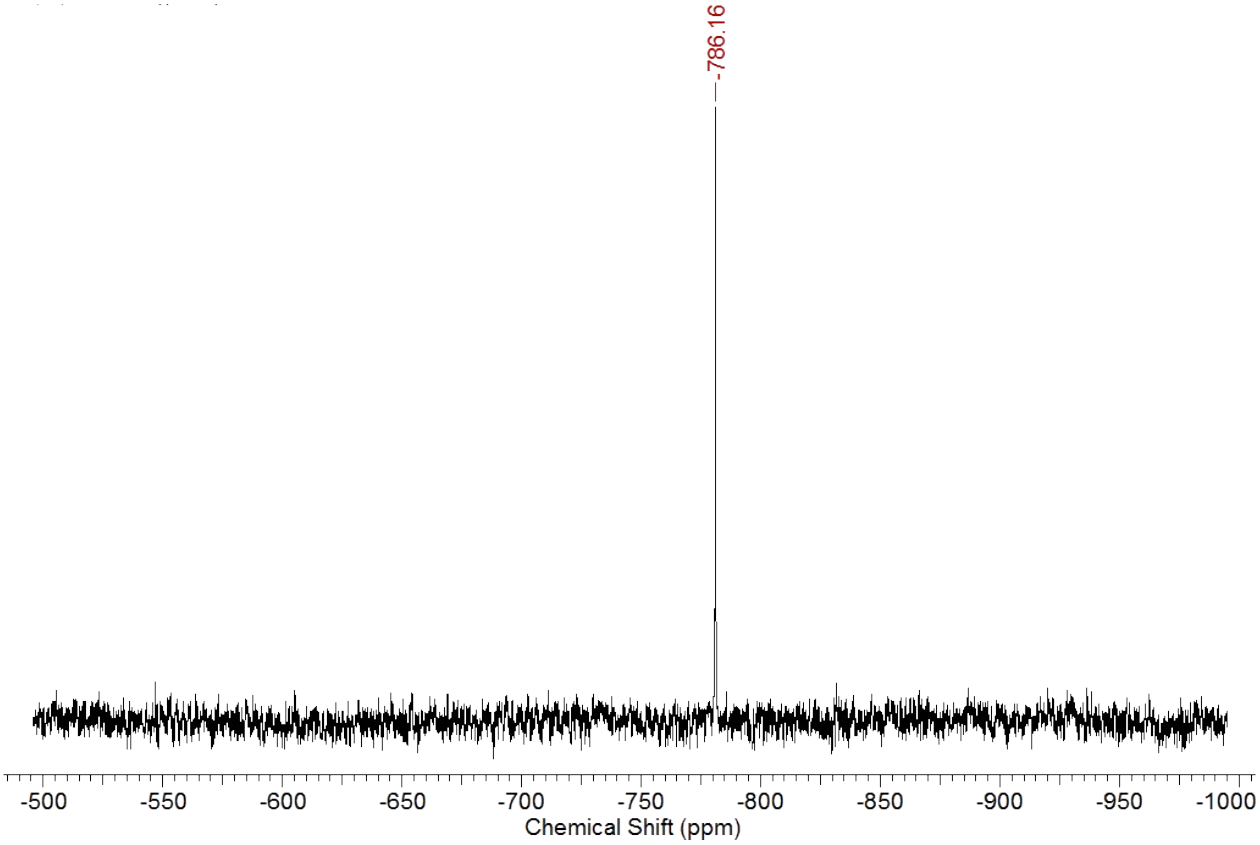

Figure S4. ^{119}Sn NMR spectrum of a solution of compound **5** in $CDCl_3$.

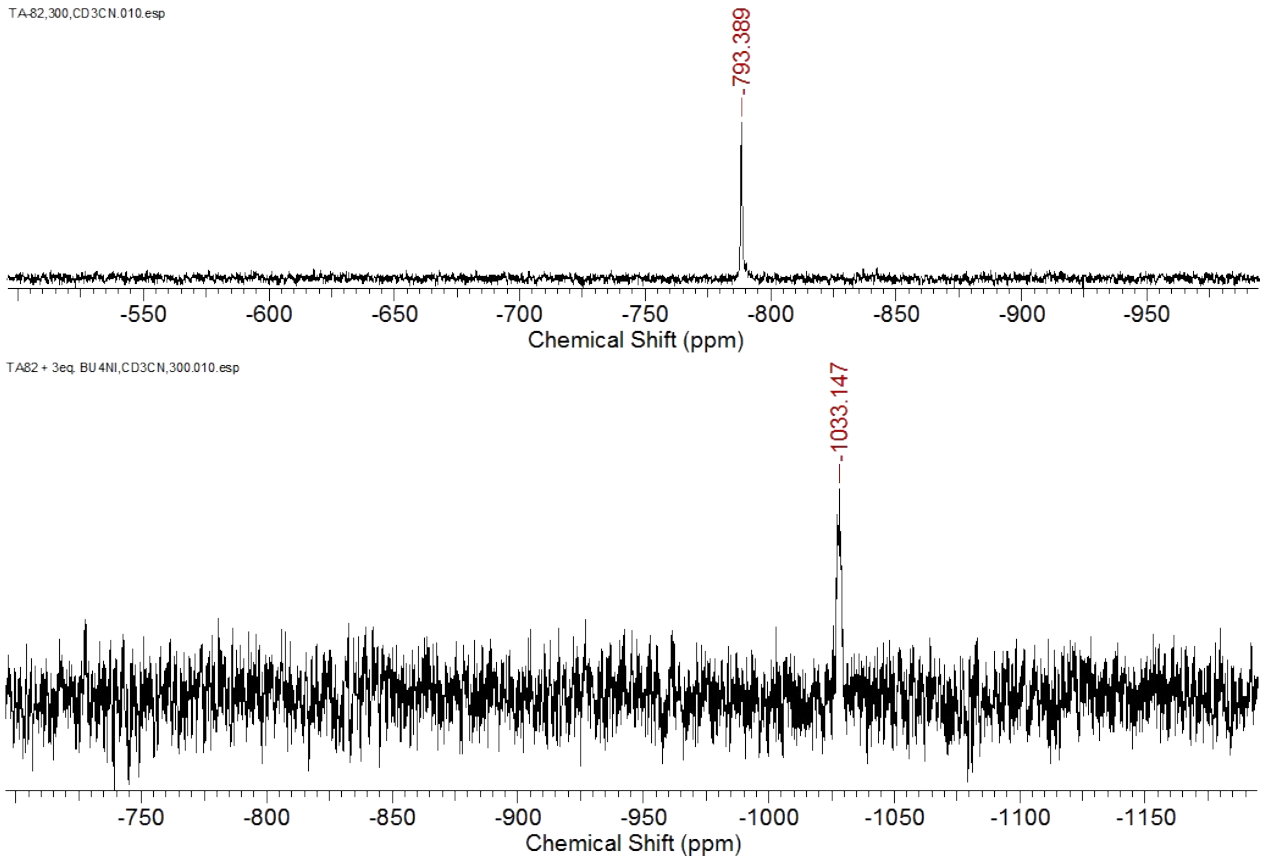

Figure S5. ^{119}Sn NMR spectra of solutions of compound **5** in CD_3CN (top) and of **5** + NBu_4I (bottom).

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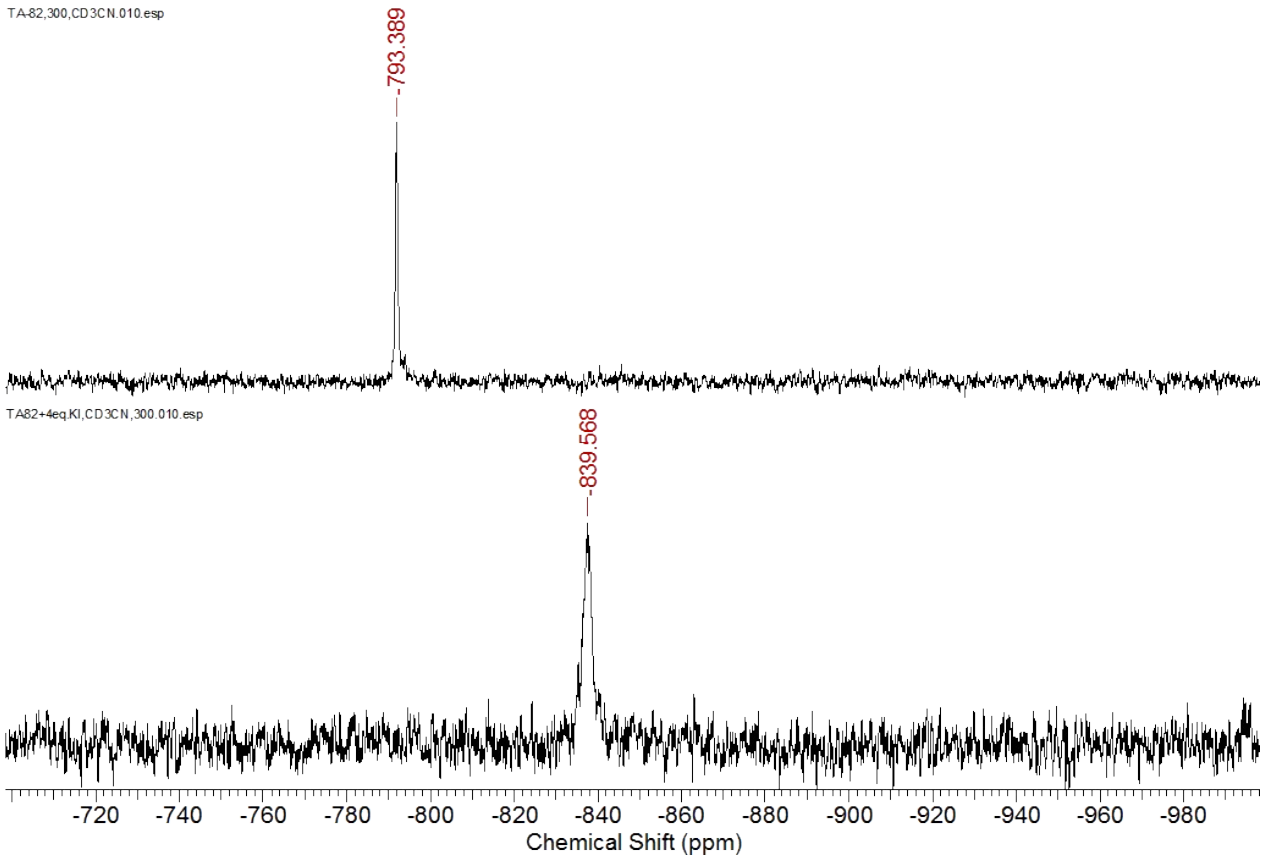

Figure S6. ^{119}Sn NMR spectra of solutions of compound **5** in CD_3CN (top) and of **5** + KI (bottom).

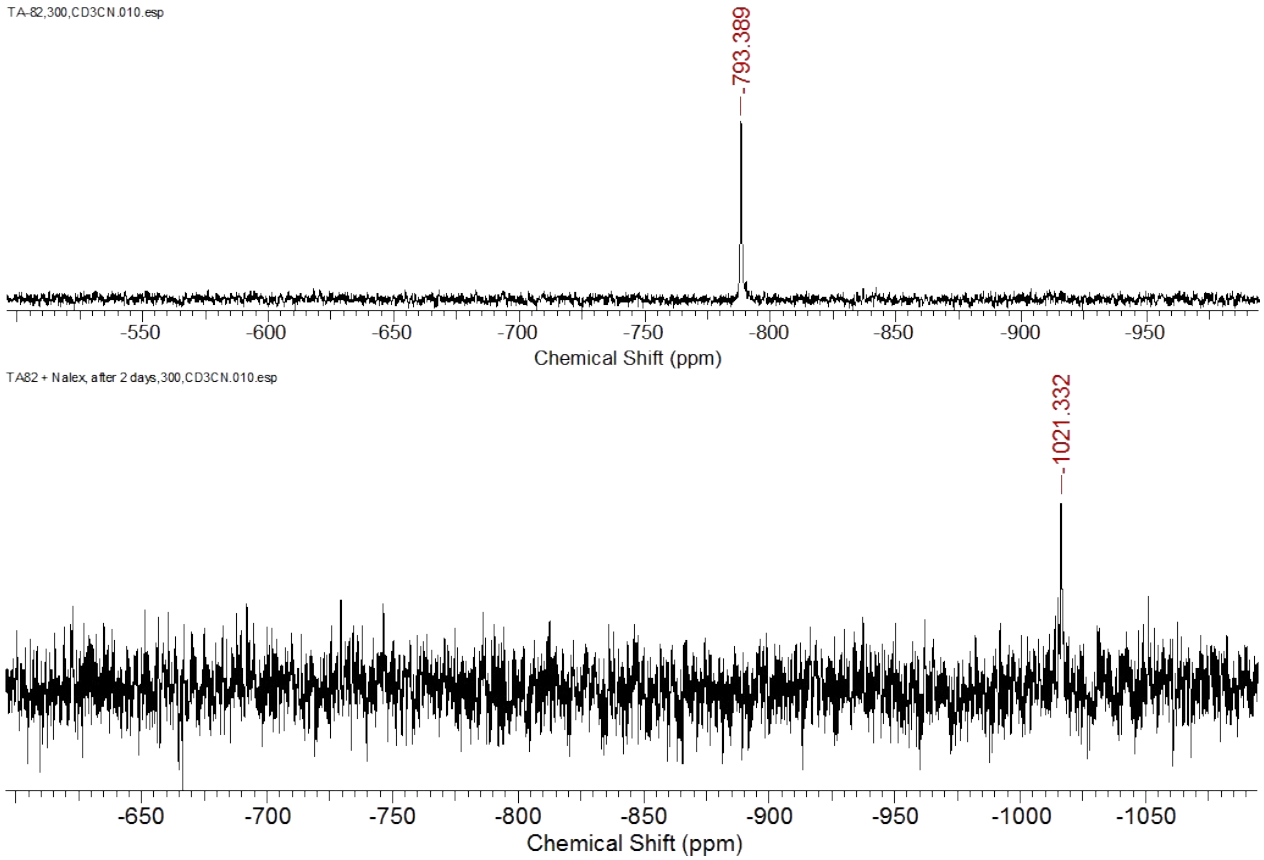

Figure S7. ^{119}Sn NMR spectra of solutions of compound **5** in CD_3CN (top) and of **5** + NaI (bottom).

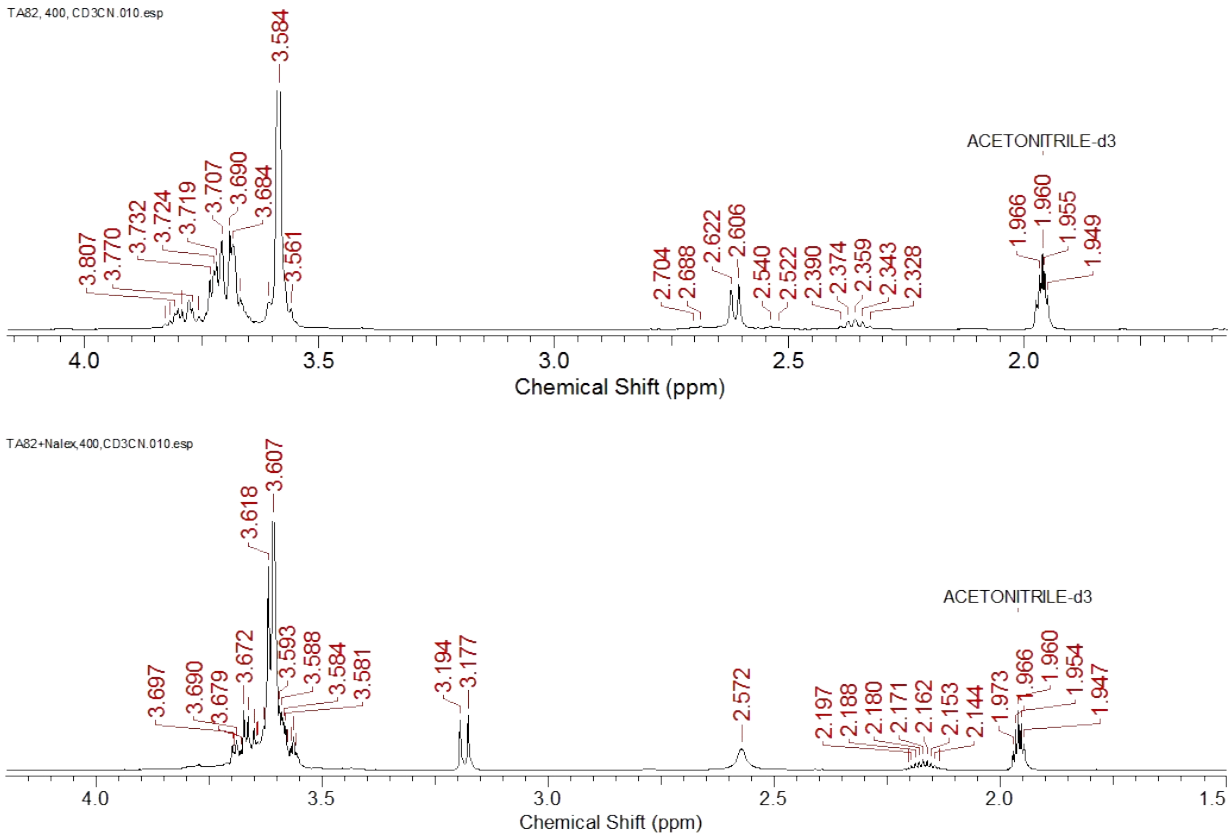

Figure S8. ^{1}H NMR spectra of solutions of compound **5** in CD_3CN (top) and of **5** + NaI (bottom).

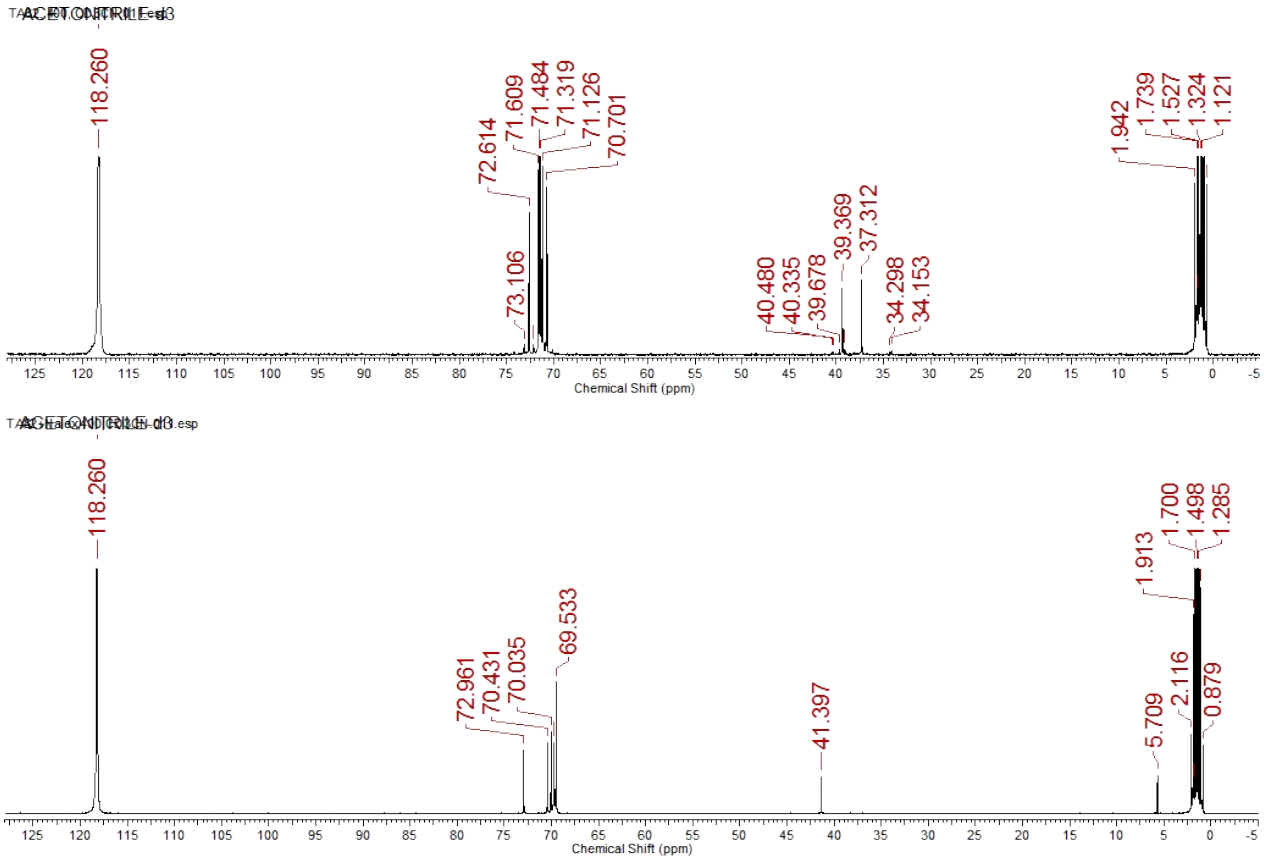

Figure S9. ^{13}C NMR spectra of solutions of compound **5** in CD_3CN (top) and of **5** + NaI (bottom).

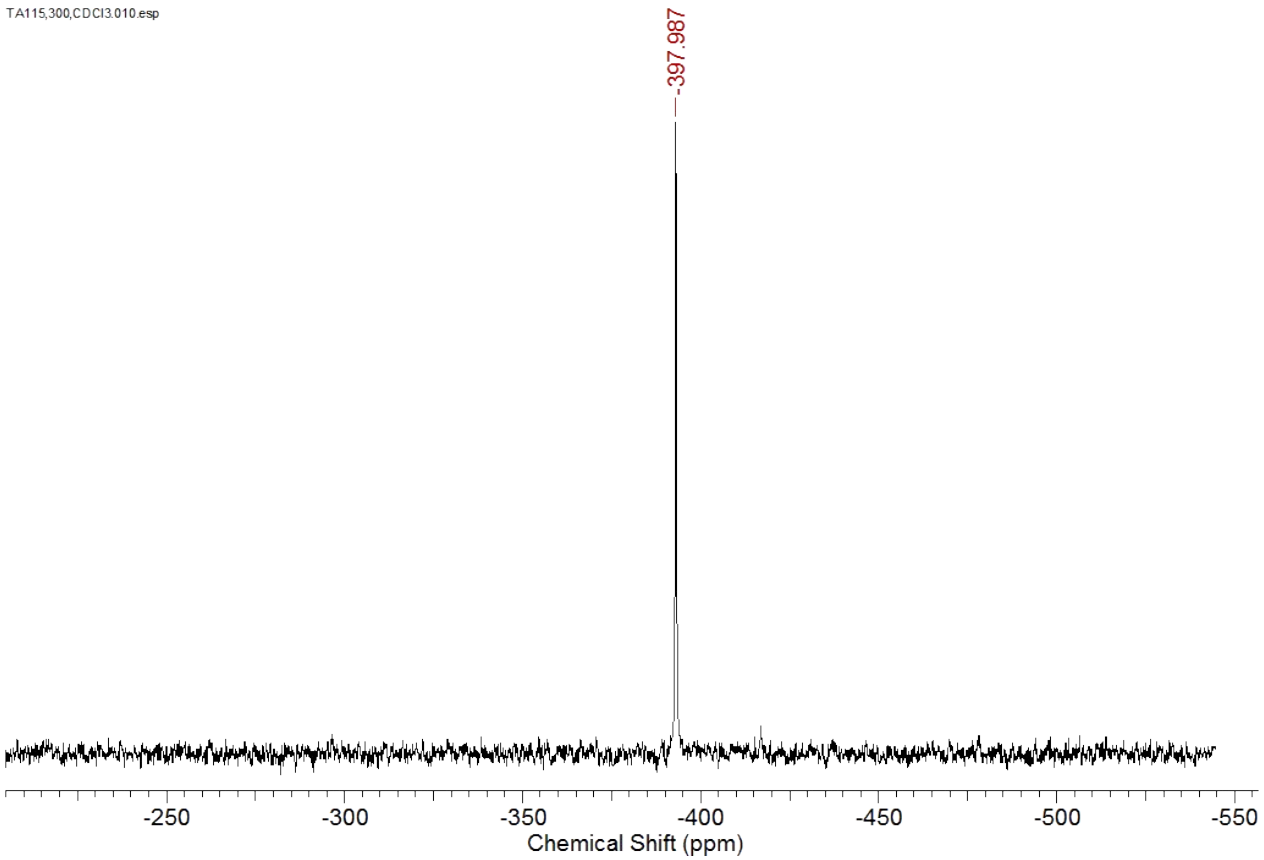

Figure S10. ^{119}Sn NMR spectrum a solution of compound **6** in $CDCl_3$.

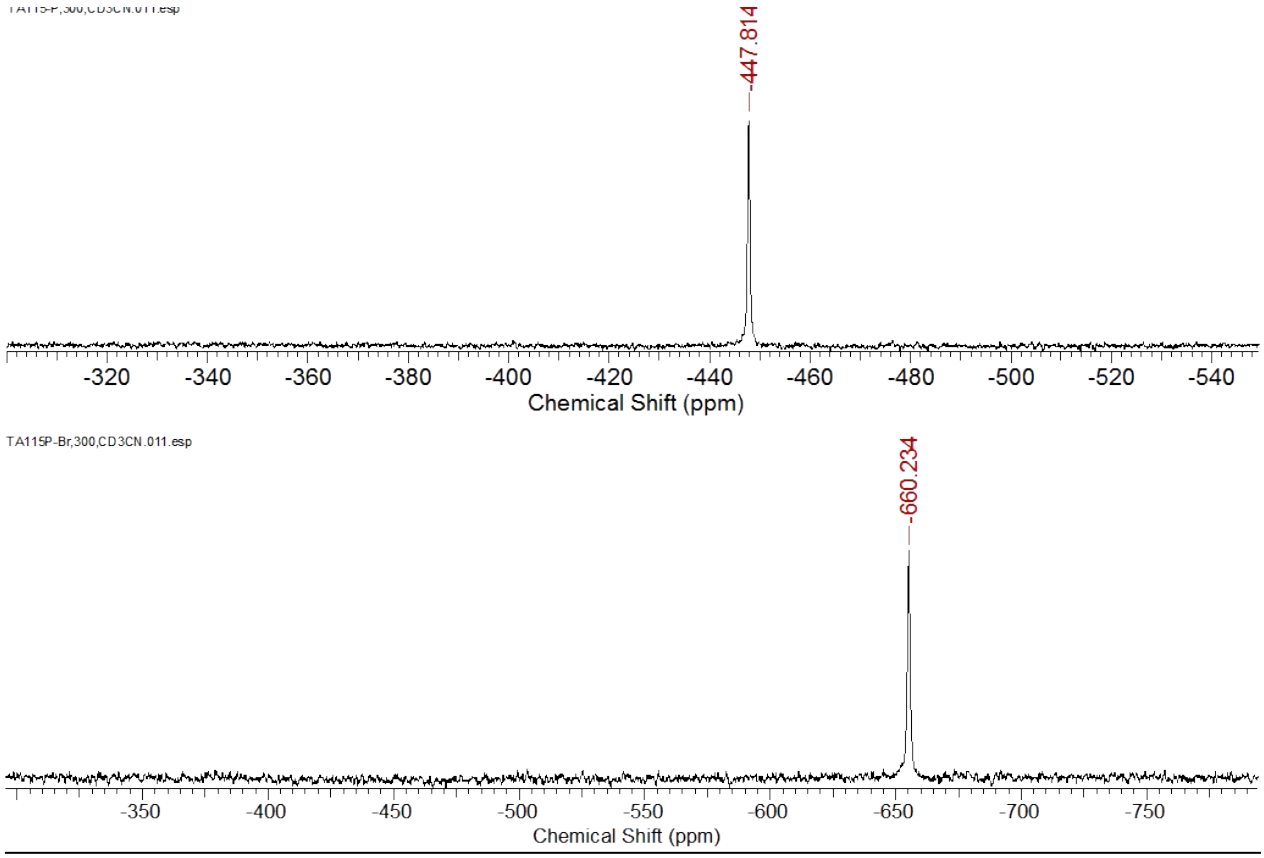

Figure S11. ^{119}Sn NMR spectra of solutions of compound **6** in CD_3CN (top) and of **6** + PPh_4Br (bottom).

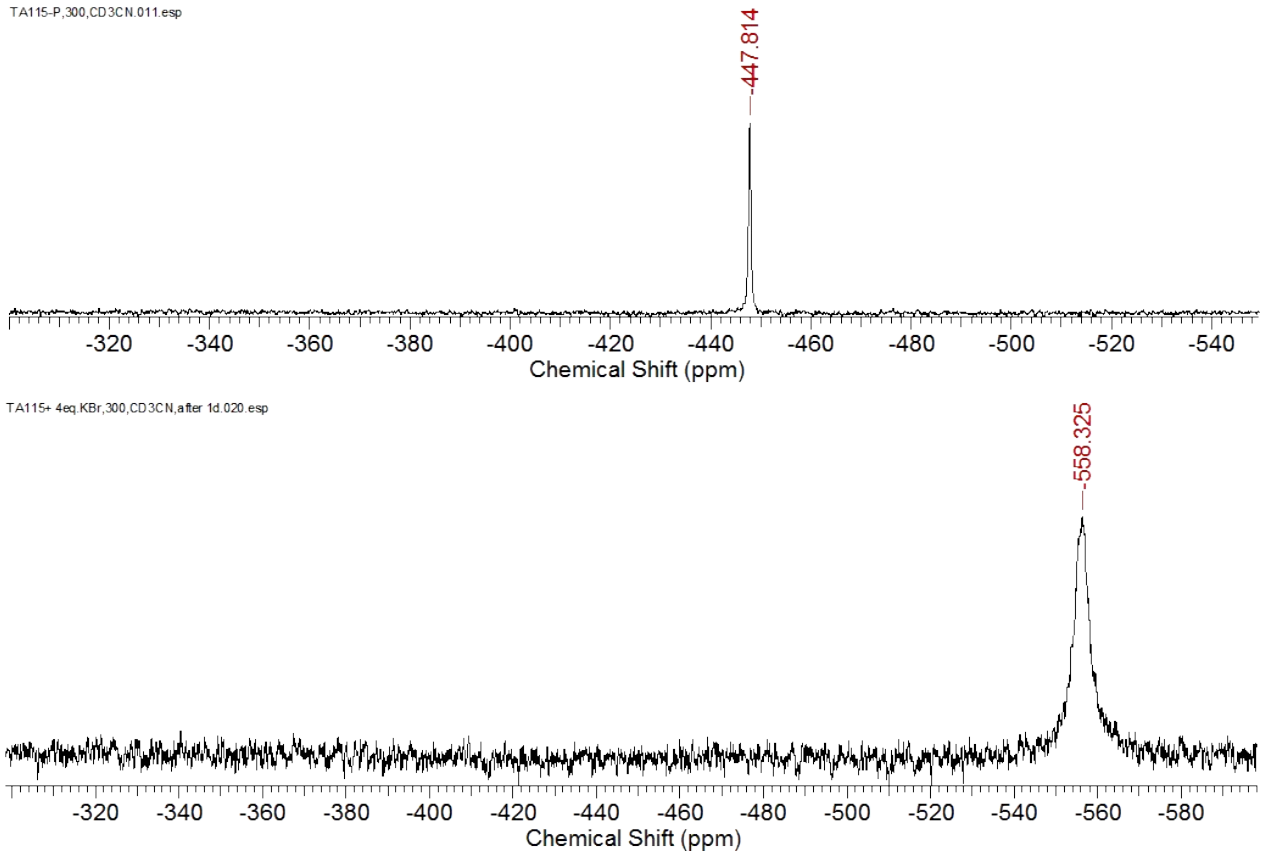

Figure S12. ^{119}Sn NMR spectra of solutions of compound **6** in CD_3CN (top) and of **6** + KBr (bottom).

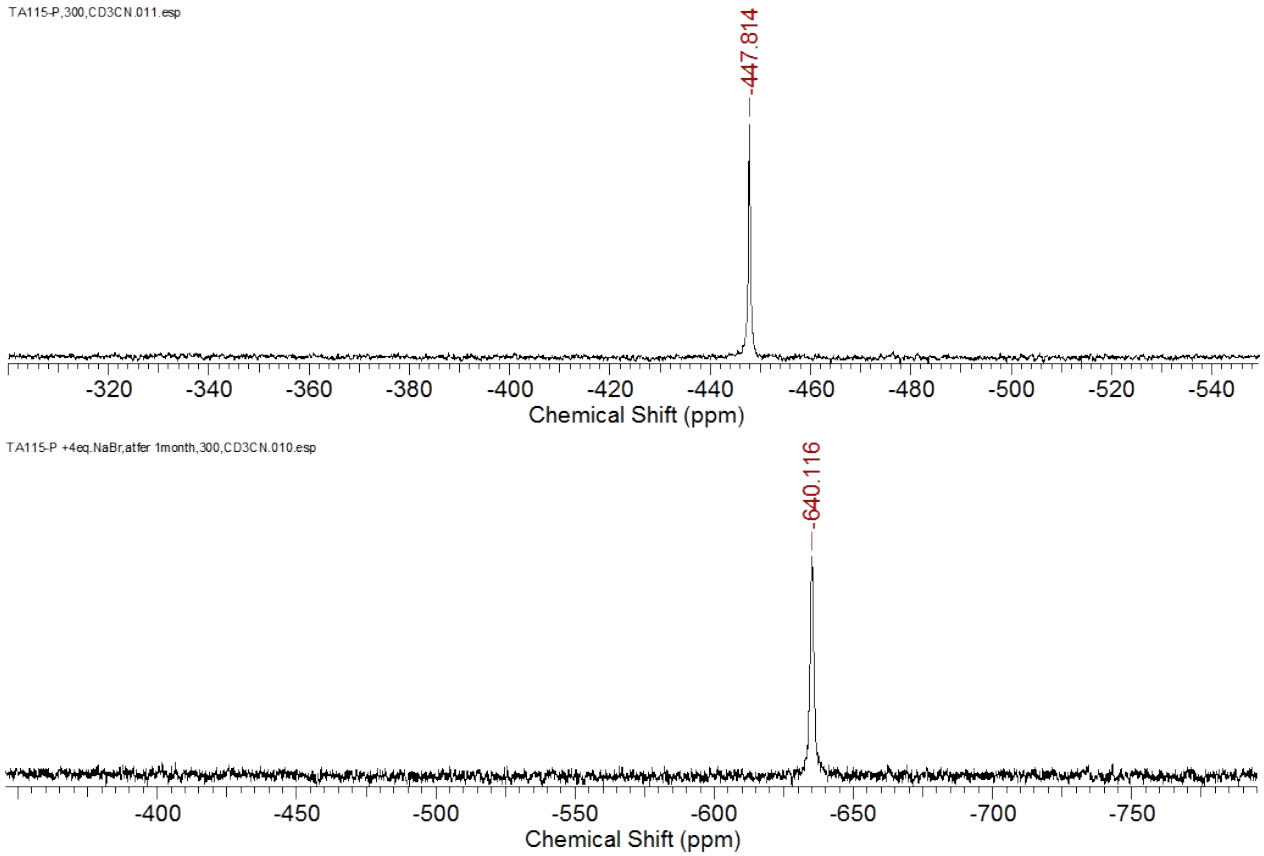

Figure S13. ^{119}Sn NMR spectra of solutions of compound **6** in CD_3CN (top) and of **6** + NaBr (bottom).

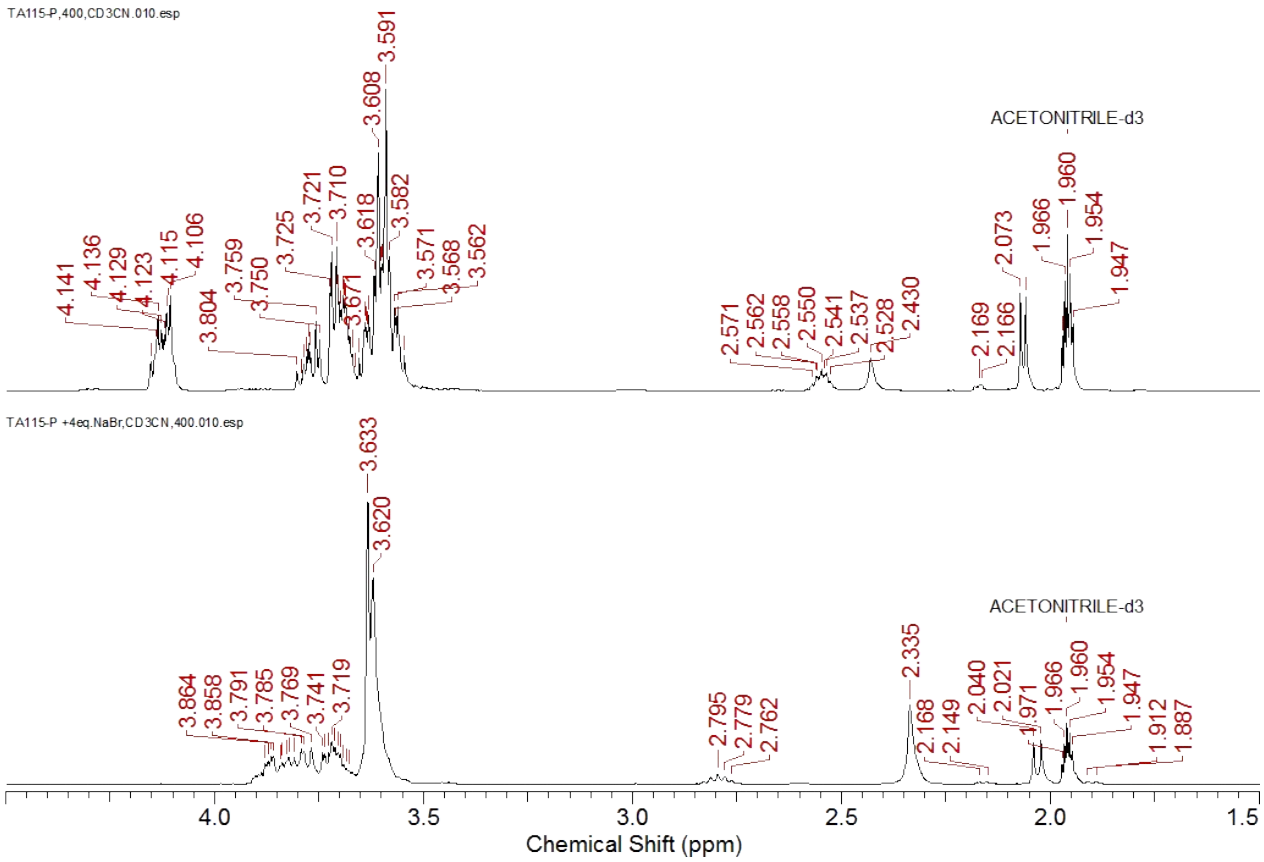

Figure S14. ^{1}H NMR spectra of solutions of compound **6** in CD_3CN (top) and of **6** + NaBr (bottom).

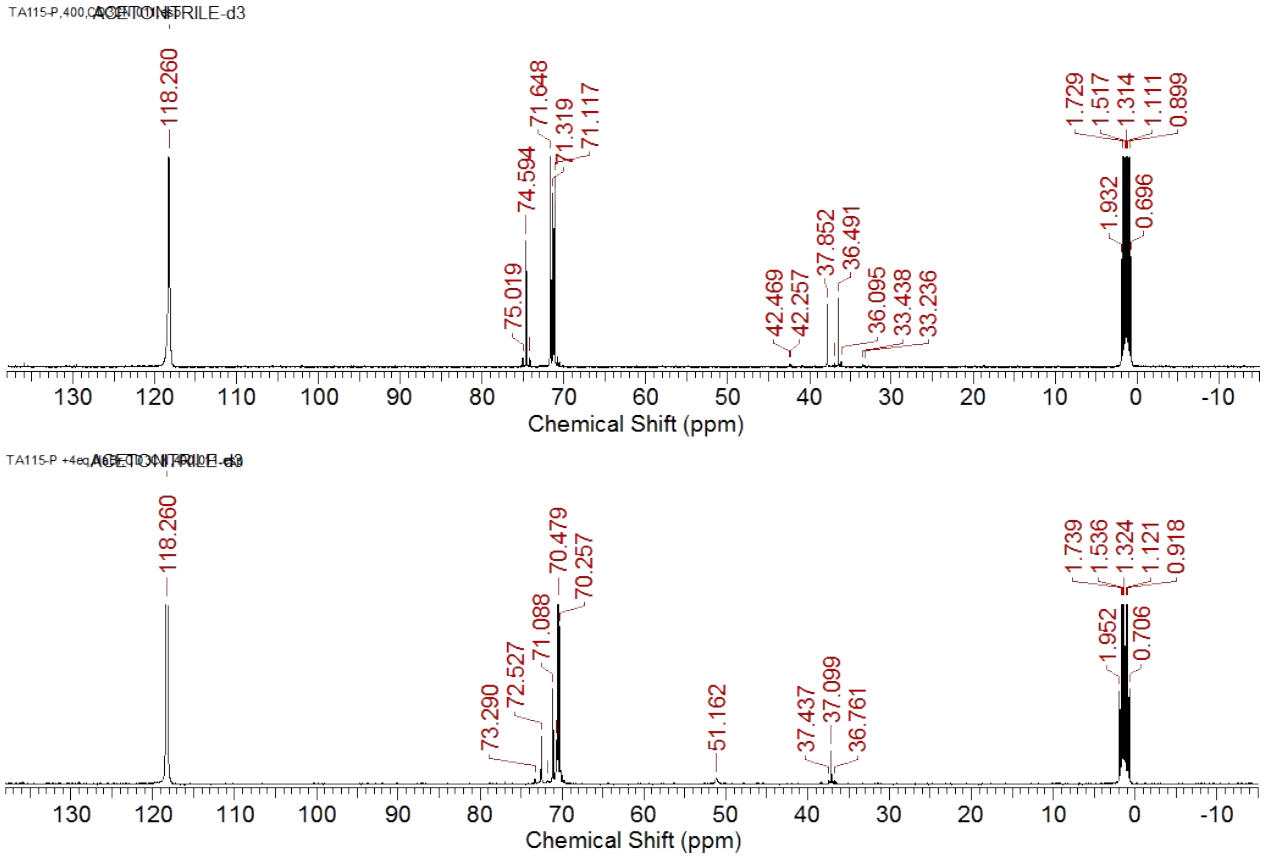

Figure S15. ^{13}C NMR spectra of solutions of compound **6** in CD_3CN (top) and of **6** + NaBr (bottom).

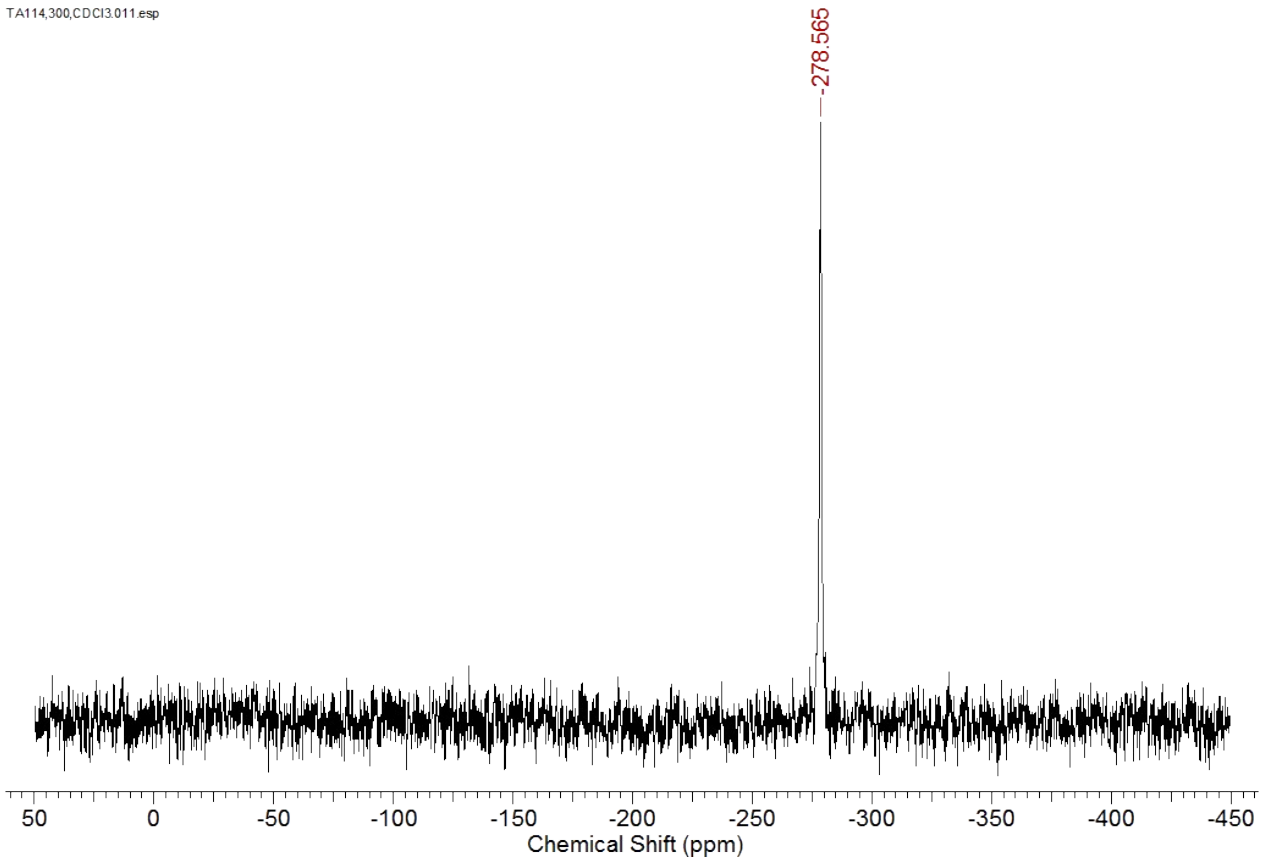

Figure S16. ^{119}Sn NMR spectrum a solution of compound **7** in $CDCl_3$.

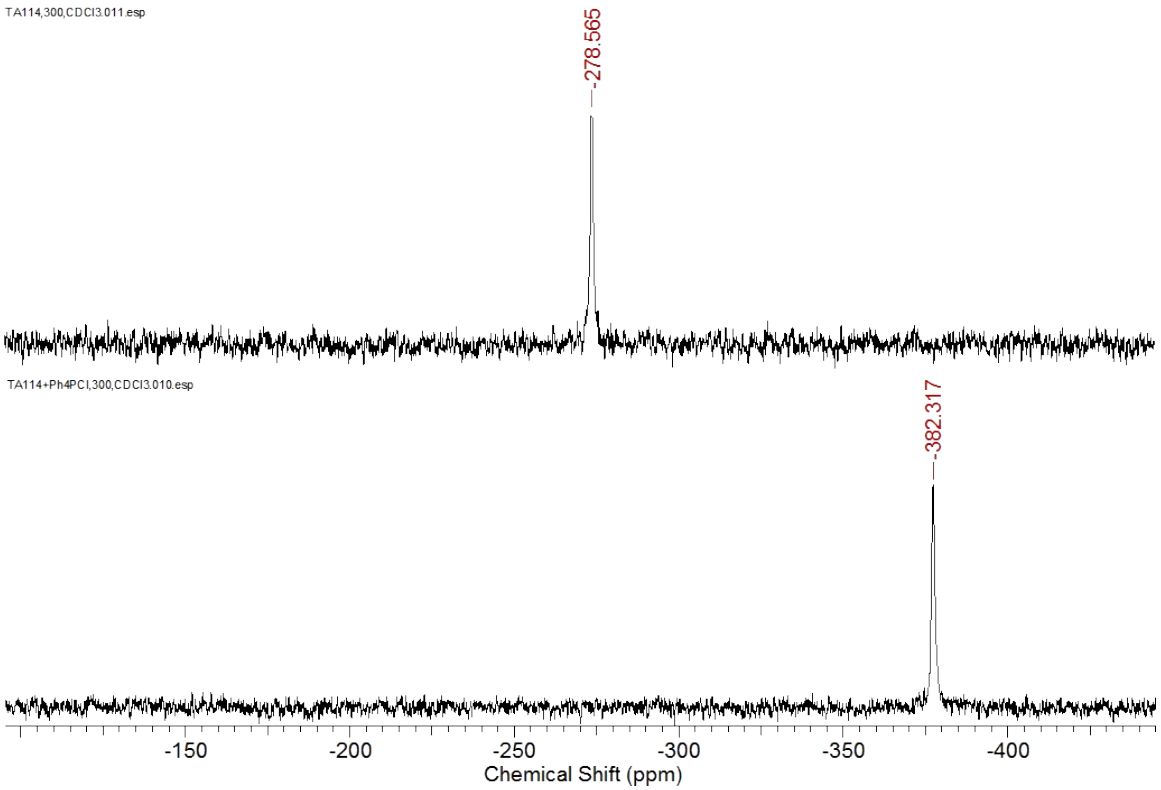

Figure S17. ^{119}Sn NMR spectra of solutions of compound **7** in CD_3CN (top) and of **7** + PPh_4Cl (bottom).

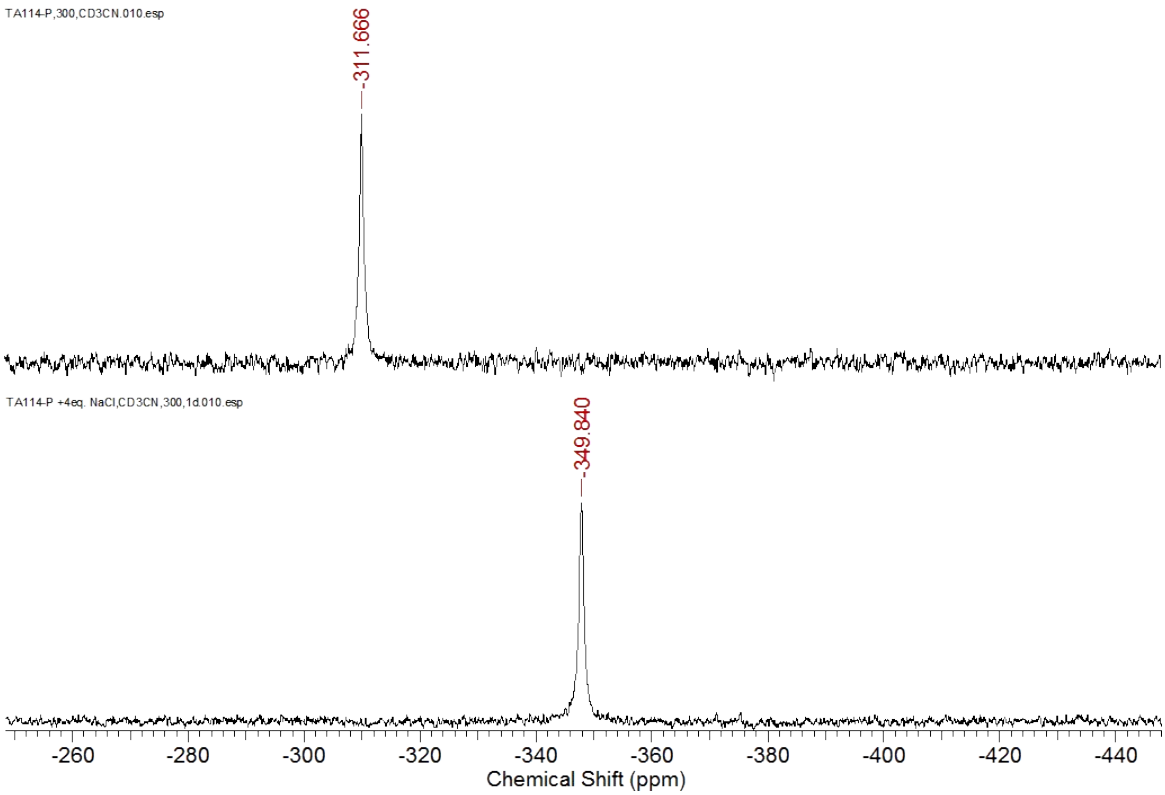

Figure S18. ^{119}Sn NMR spectra of solutions of compound **7** in CD_3CN (top) and of **7** + NaCl (bottom).

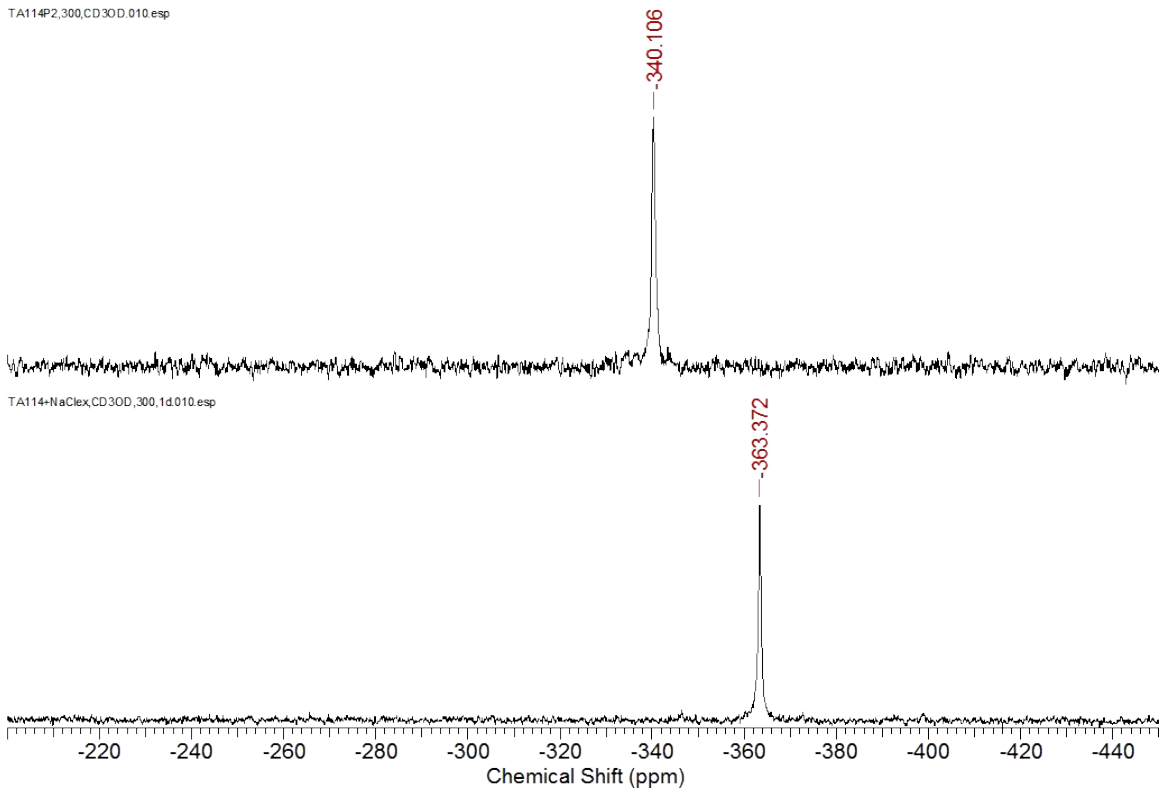

Figure S19. ^{119}Sn NMR spectra of solutions of compound **7** in CD_3OD (top) and of **7** + NaCl (bottom).

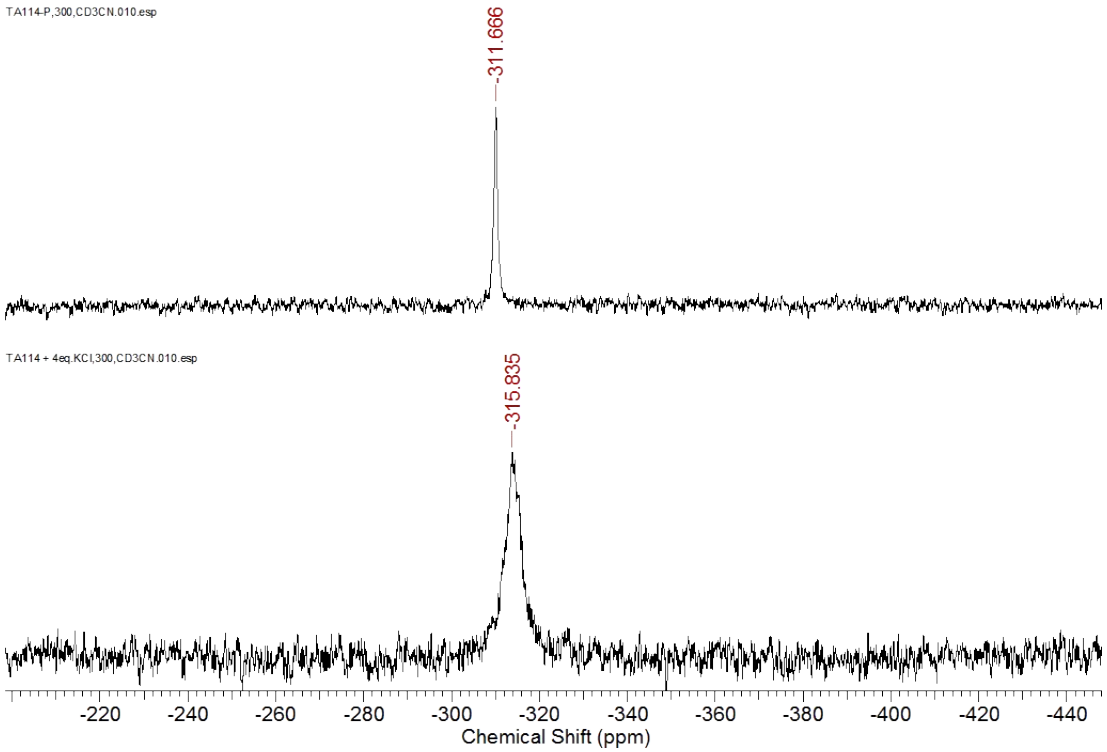

Figure S20. ^{119}Sn NMR spectra of solutions of compound **7** in CD_3CN (top) and of **7** + KCl (bottom).

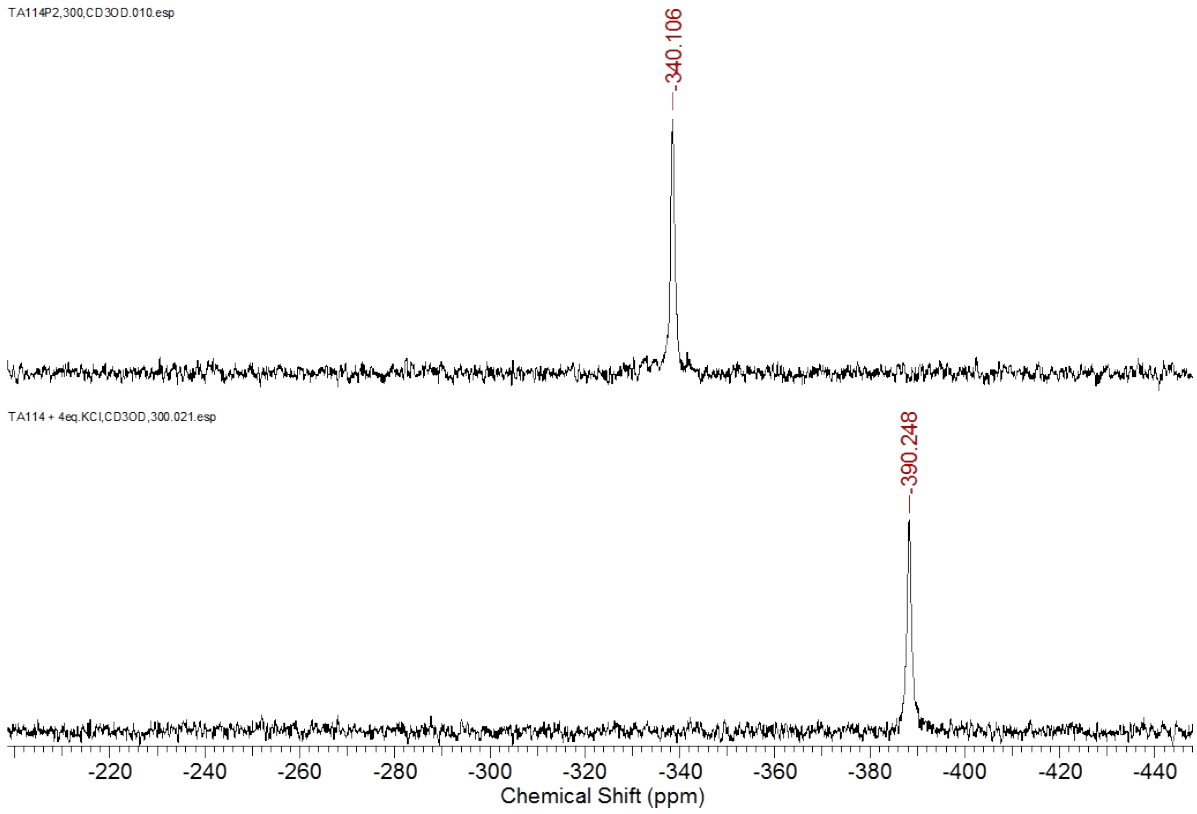

Figure S21. ^{119}Sn NMR spectra of solutions of compound **7** in CD_3OD (top) and of **7** + KCl (bottom).

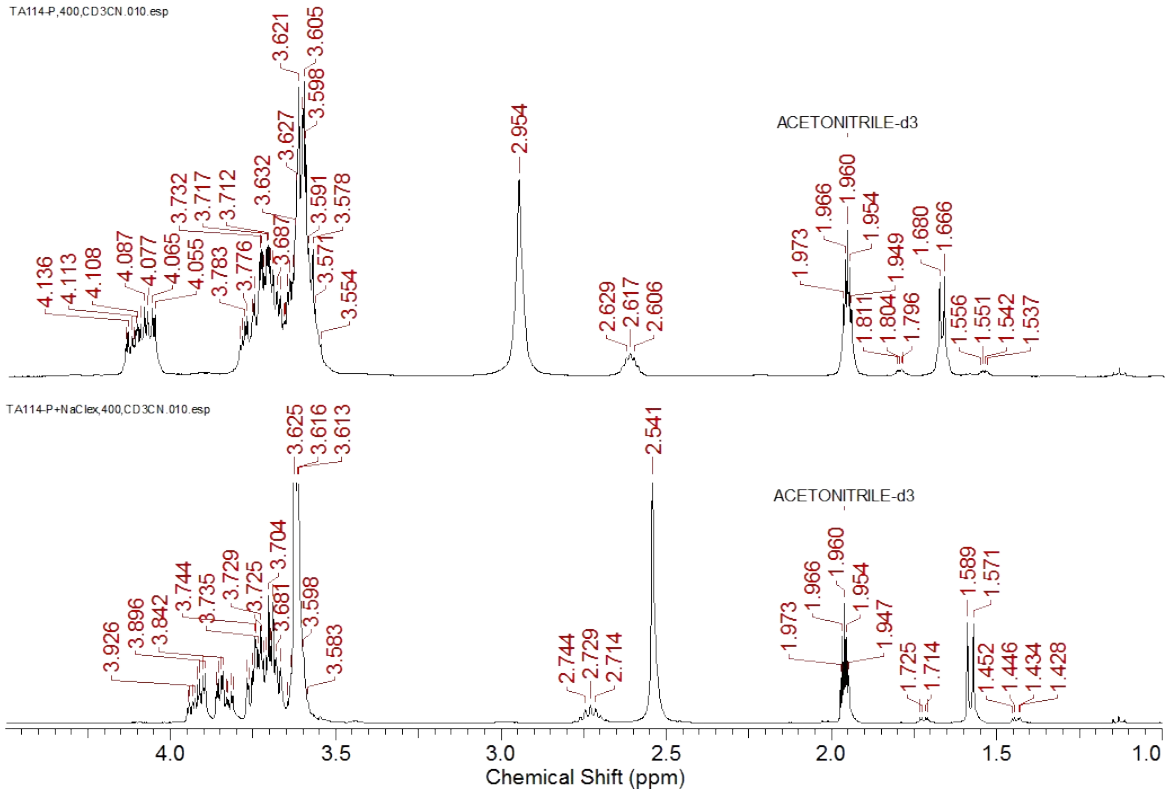

Figure S22. ^{1}H NMR spectra of solutions of compound **7** in CD_3CN (top) and of **7** + NaCl (bottom).

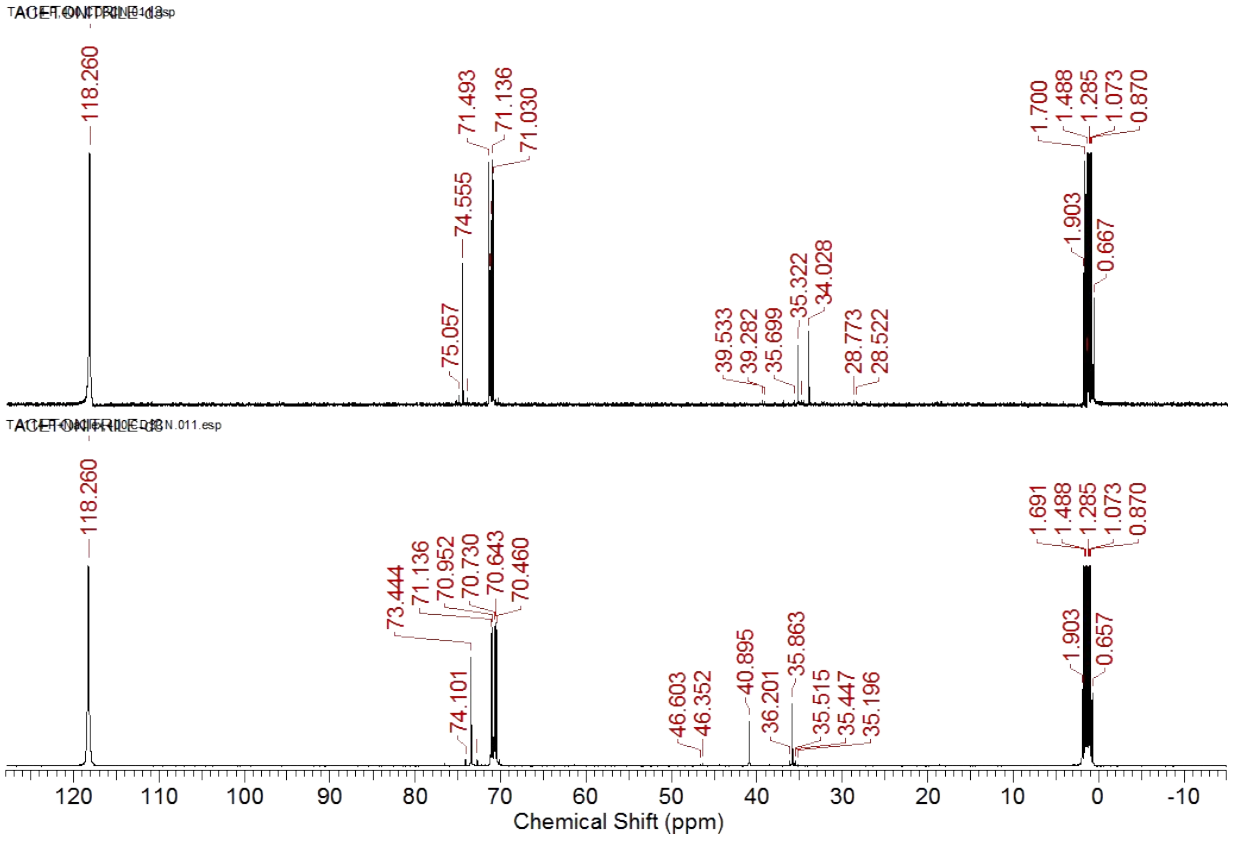

Figure S23. ^{13}C NMR spectra of solutions of compound **7** in CD_3CN (top) and of **7** + NaCl (bottom).

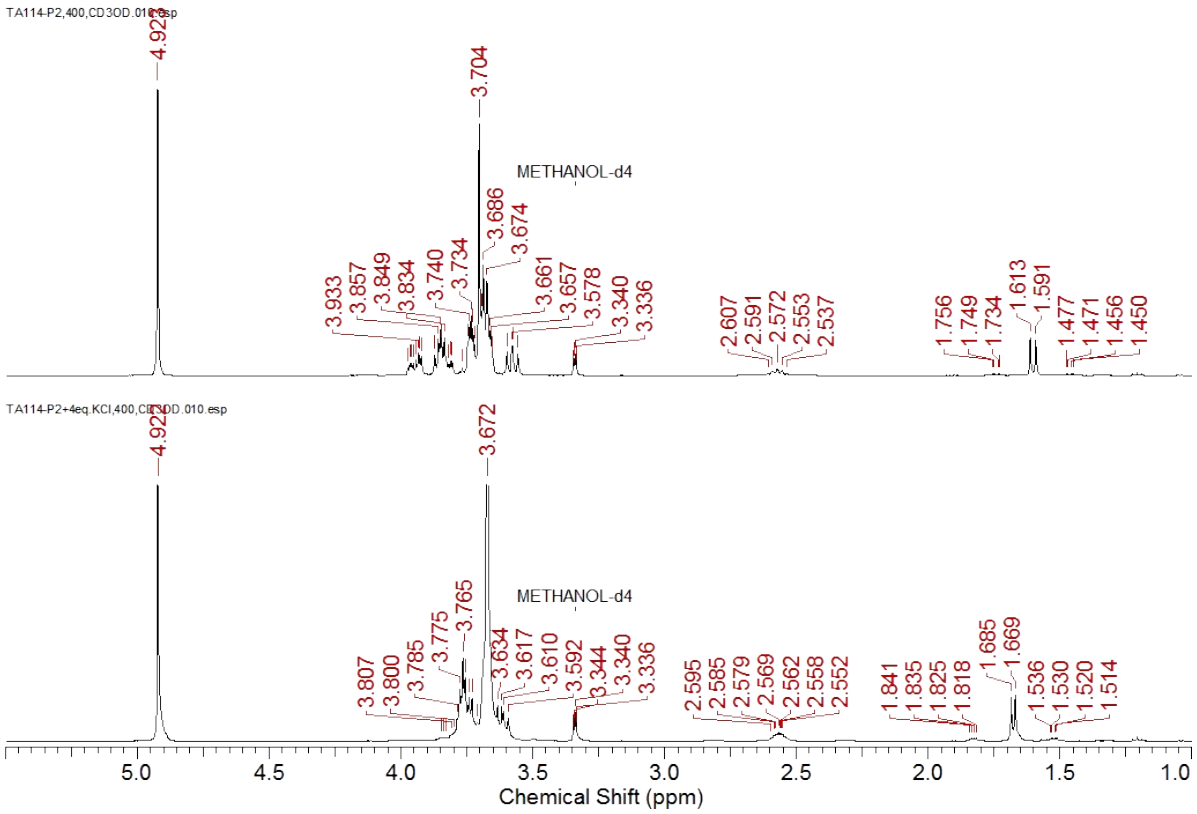

Figure S24. ^{1}H NMR spectra of solutions of compound **7** in CD_3OD (top) and of **7** + KCl (bottom).

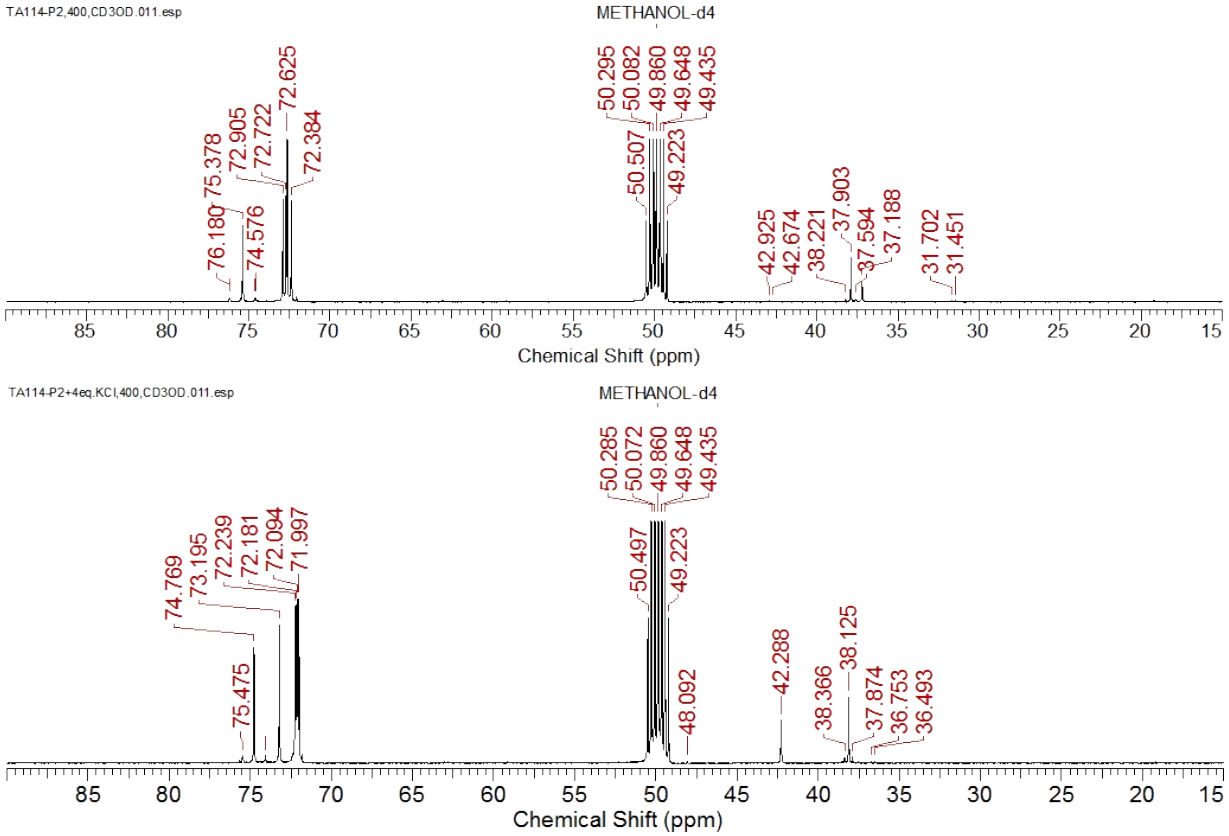

Figure S25. ^{13}C NMR spectra of solutions of compound **7** in CD_3OD (top) and of **7** + KCl (bottom).