Electronic Supplementary Information

Liquid membrane transport of potassium fluoride by the organotin-based ditopic host Ph_2FSnCH_2SnFPh-CH_2-[19]-crown-6

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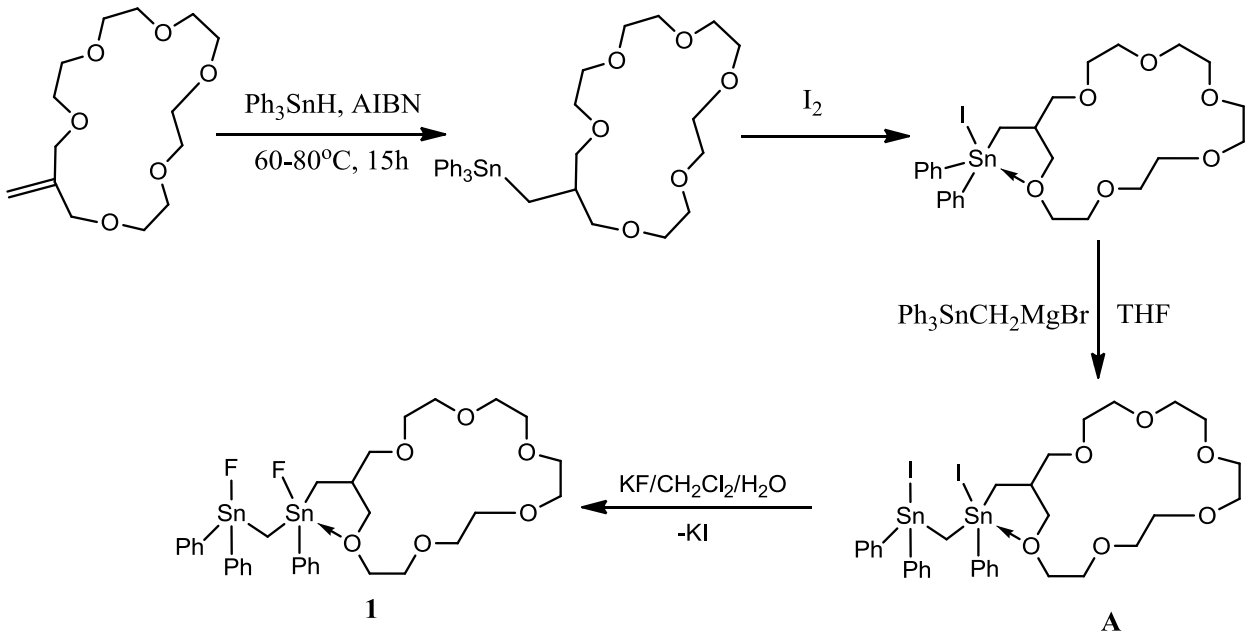


Scheme S1. Synthesis of organotin-based receptor **1**

General Information

NMR Spectroscopy. NMR spectra were recorded on DRX 400, DPX 300, Varian Nova 600 spectrometers with broad band decoupling of ^{119}Sn at 111.92 MHz, ^{19}F at 282.4 MHz, ^{13}C at 100.61 MHz and ^{1}H at 300 or 400 MHz. Chemical shifts δ are given in ppm and referenced to tetramethylstannane (^{119}Sn), $CFCl_3$ (^{19}F), and the deuterated solvent (^{1}H, ^{13}C). The following abbreviations are used for signals assignments: br (broad), brs (broad singlet), s (singlet), d (doublet), dd (doublet of doublet), q (quadruplet), m (multiplet), brm (broad multiplet).

Complexation Studies. The samples for NMR analyses were prepared by dissolving ca. 50 mg of compound **1** and four equiv. KF in CD_3CN. Potassium fluoride 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.

Transport experiments. The conductivity was determined with an apparatus of the type LF530 from the company Wissenschaftlich-Technische Werkstätten. The cell was calibrated at 25°C with a KCl standard solution.

Synthesis of ditopic receptor A.

The ditopic receptor **A** in Scheme S1 was prepared according to our previously reported procedure [Organometallics **2008**, *27*, 5577-5587].

Synthesis of ditopic receptor 1.

A solution of 18-({iodophenyl[(iododiphenylphenylstannyl)methyl]-stannyl}methyl)-1,4,7,10,13,16-hexaoxanonadecane **A** (0.5 g, 0.478 mmol) in CH_2Cl_2 (20 mL) was mixed with a solution of KF (0.85 g, 14.631 mmol) in water (25 mL). The biphasic mixture was stirred at room temperature for ten days. The organic phase was then separated and dried over $MgSO_4$. Removal of the solvent in vacuo afforded 0.31 g (80%) of pure **1** as white solid.

18-({fluorophenyl[(fluorodiphenylstannyl)methyl]-stannyl}methyl)-1,4,7,10,13,16-hexaoxanonadecane (1): m. p. 130 °C. ^{1}H-NMR ($CDCl_3$, 300.13 MHz, 293K) δ: 1.13 (br, 2H, SnCH_2), 2.24 (br, 2H, SnCH_2-Sn), 3.13 (br, 1H, C*H*), 3.52-3.62 (24H, CH_2-O-CH_2), 7.31-7.79

(brm, 15H, Ph). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 100.63 MHz, 293K) δ: 16.1 (Sn-*C*H_2-Sn), 30.0 (Sn-*C*H_2), 36.9 (*C*H), 74.5 (O-*C*H_2-CH), 77.3 (complex broad, *C*H_2-O-*C*H_2), 128.6-143.6 (*o,m,p*-Ph). $^{19}F\{^{1}H\}$-NMR ($CDCl_3$, 282.4 MHz) at 293 K, δ –176.2 (br); at 233 K, δ –173.2 ($^{1}J(^{19}F\text{-}^{117}Sn)$ = 2045 Hz, $^{1}J(^{19}F\text{-}^{119}Sn)$ = 2127 Hz, $^{3}J(^{19}F\text{-}^{117/119}Sn)$ = 236 Hz, $SnFPh_2$ and SnFPh). Elemental Anal. for $C_{33}H_{44}F_2O_6Sn_2\cdot 2H_2O$ (848.16), Cacld : C 46.7, H 5.7; Found: C 46.5, H 5.3.

1·KF. Potassium fluoride, KF, (14.1 mg, 0.242 mmol) was added to a solution of **1** (50.0 mg, 0.061 mmol) in CD_3CN. ^{1}H-NMR (CD_3CN, 400.13 MHz, 293K) δ: 1.00 (d, $^{3}J(^{1}H\text{-}^{1}H)$ = 6.8 Hz, $^{2}J(^{1}H\text{-}^{117}Sn)$ =67.6 Hz, $^{2}J(^{1}H\text{-}^{119}Sn)$ =76.8 Hz, 2H SnC*H2*), 1.22 (s, $^{2}J(^{1}H–^{117/119}Sn)$ = 76.8 Hz, SnC*H2*-Sn), 2.22 (m, 1H, C*H*), 3.29-3.54 (complex pattern, 24H, CH_2-O-CH_2), 7.27-7.33 (m, 8H, Ph), 7.61 (m, 2H, Ph), 7.77-7.94 (m, $J_{H,Sn}$ = 56.0/67.6 Hz, 5H, Ph). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 100.63 MHz, 293K) δ: 5.8 (q, $^{2}J(^{13}C\text{-}^{19}F)$ = 26.3 Hz, Sn-*C*H_2-Sn), 20.2 (d, $^{2}J(^{13}C\text{-}^{19}F)$ = 8.7 Hz, Sn-*C*H_2), 37.1 (*C*H), 70.6-71.5 (complex pattern, *C*H_2-O-*C*H_2), 75.9 and 79.2 ($^{3}J(^{13}C\text{-}^{117/119}Sn$ = 65.1 Hz, CH-*C*H_2-O), 128.3-146.7 (*o,m,p*-Ph). $^{19}F\{^{1}H\}$-NMR (CD_3CN, 282.4 MHz) at 296 K δ: –164.9 (br, $\nu_{1/2}$ = 6908 Hz); at 233 K δ: – 90.3 (br, $\nu_{1/2}$ = 1891 Hz, Sn–F–Sn), –163.5 (brs, $\nu_{1/2}$ = 707 Hz, $^{1}J(^{19}F\text{-}^{117/119}Sn)$ = 2056 Hz, $SnFPh_2$ or SnFPh), -167.4 (br, $\nu_{1/2}$ = 978 Hz, $^{1}J(^{19}F\text{-}^{117/119}Sn)$ = 2253 Hz, $SnFPh_2$ or SnFPh). $^{119}Sn\{^{1}H\}$-NMR (CD_3CN, 111.93 MHz) at 296 K δ: –116.3 (br, $\nu_{1/2}$ = 2684 Hz), –194.2 (br, $\nu_{1/2}$ = 1814 Hz); at 233 K δ: –112.2 (dd, $^{1}J(^{119}Sn\text{-}^{19}F_t)$ = 2132.7 Hz, $^{1}J(^{119}Sn\text{-}^{19}F_b)$ = 596.6 Hz, SnF_2Ph_2), –191.6 (dd, $^{1}J(^{119}Sn\text{-}^{19}F_t)$ = 3119.9 Hz, $^{1}J(^{119}Sn\text{-}^{19}F_b)$ = 150.1 Hz, SnF_2Ph).

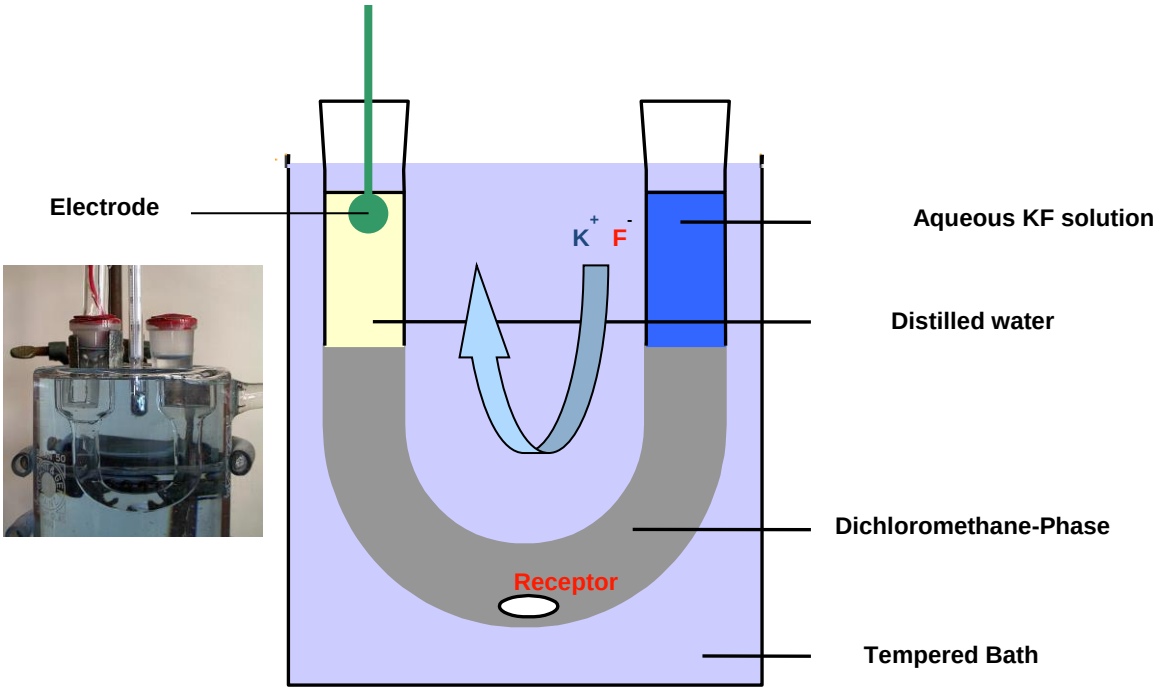


Figure S1. Schematic drawing of the apparatus used for the transport experiments

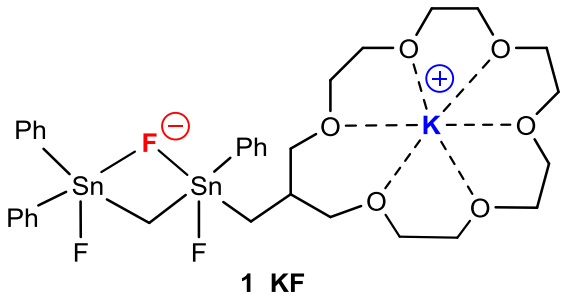


Figure S2. Showing ditopic complexation of KF by host **1**.

Table S1: Electrical conductivity data showing transport activity of the ditopic receptor **1** for 0.37 M salt concentration in the source phase

Receptor (R_1): **1** C_{R1} = 0.03 M , C_{KF} = 0.37 M; V_{sol} = 6 mL					
t/h	cond (µS/cm)	t/h	cond (µS/cm)	t/h	cond (µS/cm)
0	23.1	148	1406	265	2290
63	701	159.5	1496	280	2420
75.5	794	169	1572	288.5	2490
88	912	186.5	1688	304.5	2580
95.5	993	231	2030	312	2620
111.5	1135	240.5	2160	375.5	3330
120.5	1205	255.5	2240	386	3450
135	1316				
Receptors: 18-crown-6 (R_2) **2**, $Ph_2FSnCH_2SnFPh_2$ (R_3) **3**, (18-crown-6 + $Ph_2FSnCH_2SnFPh_2$) (R_2 + R_3) (**2** + **3**) C_{R2} = C_{R3} = 0.03 M , C_{KF} = 0.37 M; V_{sol} = 6 mL					
2		**3**		**Dual host 2 + 3**	
t/h	cond (µS/cm)	t/h	cond (µS/cm)	t/h	cond (µS/cm)
0	14.2	0	17.5	0	19
63	35.1	63	22.1	63	204
75.5	44.1	75.5	30.2	75.5	280
88	51.9	88	34.1	88	301
95.5	52	95.5	65.5	95.5	313
111.5	52	111.5	102	111.5	332
120.5	51.3	120.5	120	120.5	343
135	51	135	150	135	358
148	50	148	160	148	371
159.5	50	159.5	170	159.5	387
169	50	169	180	169	399
186.5	50	186.5	200	186.5	426
231	50	231	210	231	467

240.5	50	240.5	220	240.5	479
255.5	40	255.5	230	255.5	490
265	40	265	250	265	498
280	40	280	320	280	515
288.5	40	288.5	240	288.5	528
304.5	40	304.5	380	304.5	543
312	40	312	390	312	550
375.5	40	375.5	400	375.5	608
386	40	386	410	386	620

Table S2: Electrical conductivity data showing transport activity of the ditopic receptor **1** for 8.0 M salt concentration in the source phase

Receptors (R_1): **1** C_{R1} = 0.03 M , C_{KF} = 8.0 M; V_{sol} = 6 mL					
t/h	cond (µS/cm)	t/h	cond (µS/cm)	t/h	cond (µS/cm)
0	31.5	97.5	2150	223	4350
22	322	103.5	2270	239	4540
33	1125	120	2500	249	4640
47	1486	128.5	2620	291	5260
55.5	1639	143.5	2830	198	5340
71.5	1814	152	2940	310.5	5430
79.5	1921	216	4180	322	5510

Receptors: 18-crown-6 (R_2) **2**, $Ph_2FSnCH_2SnFPh_2$ (R_3) **3**, (18-crown-6 + $Ph_2FSnCH_2SnFPh_2$) (R_2 + R_3) (**2** + **3**) C_{R2} = C_{R3} = 0.03 M , C_{KF} = 8.0 M; V_{sol} = 6 mL					
2		**3**		**Dual host 2 + 3**	
t/h	cond (µS/cm)	t/h	cond (µS/cm)	t/h	cond (µS/cm)
0	14.2	0	18.5	0	14.3
7	44.1	22	25.1	22	120.7
21	51.9	33	32.3	33	408
27	52	47	37.8	47	541
56	52	55.5	69.4	55.5	613
73	51.3	71.5	108	71.5	717
101.5	51	79.5	140	79.5	769
118	50	97.5	170	97.5	850
126	50	103.5	180	103.5	890
142	50	120	190	120	980
149.5	50	128.5	200	128.5	1050
166	50	143.5	210	143.5	1130
174	50	152	220	152	1180
190	40	216	230	216	1560

199.5	40	223	240	223	1610
215.5	40	239	250	239	1670
286.5	40	249	320	249	1740
295.5	40	291	240	291	2010
310.5	40	198	380	198	2050
318.5	40	310.5	390	310.5	2090
335	40	322	400	322	2130
341			410		
359.5			420		

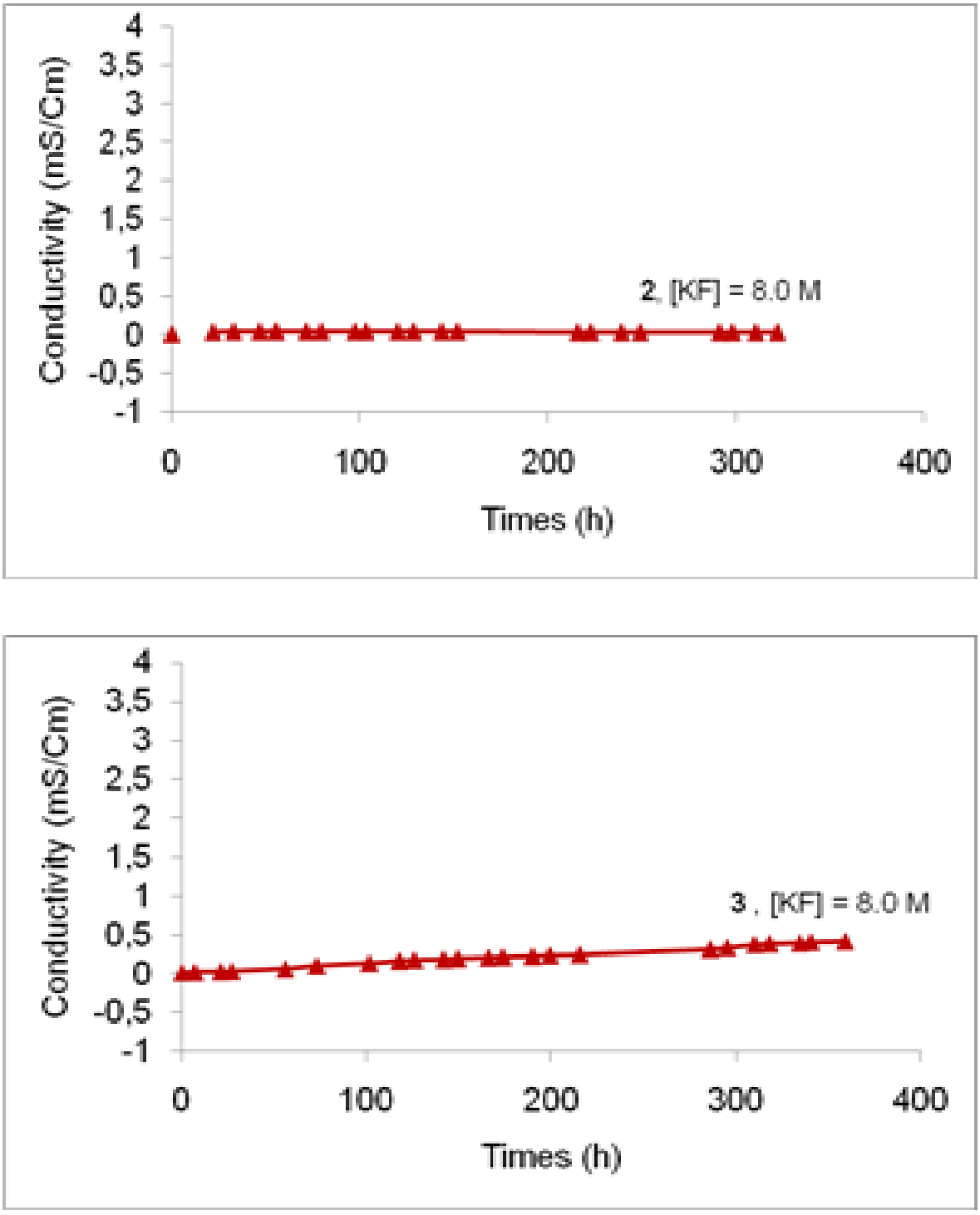


Figure S3. Plot of the electric conductivity vs time when the monotopic receptor **2** (top) or **3** (bottom) were independently used as transporter

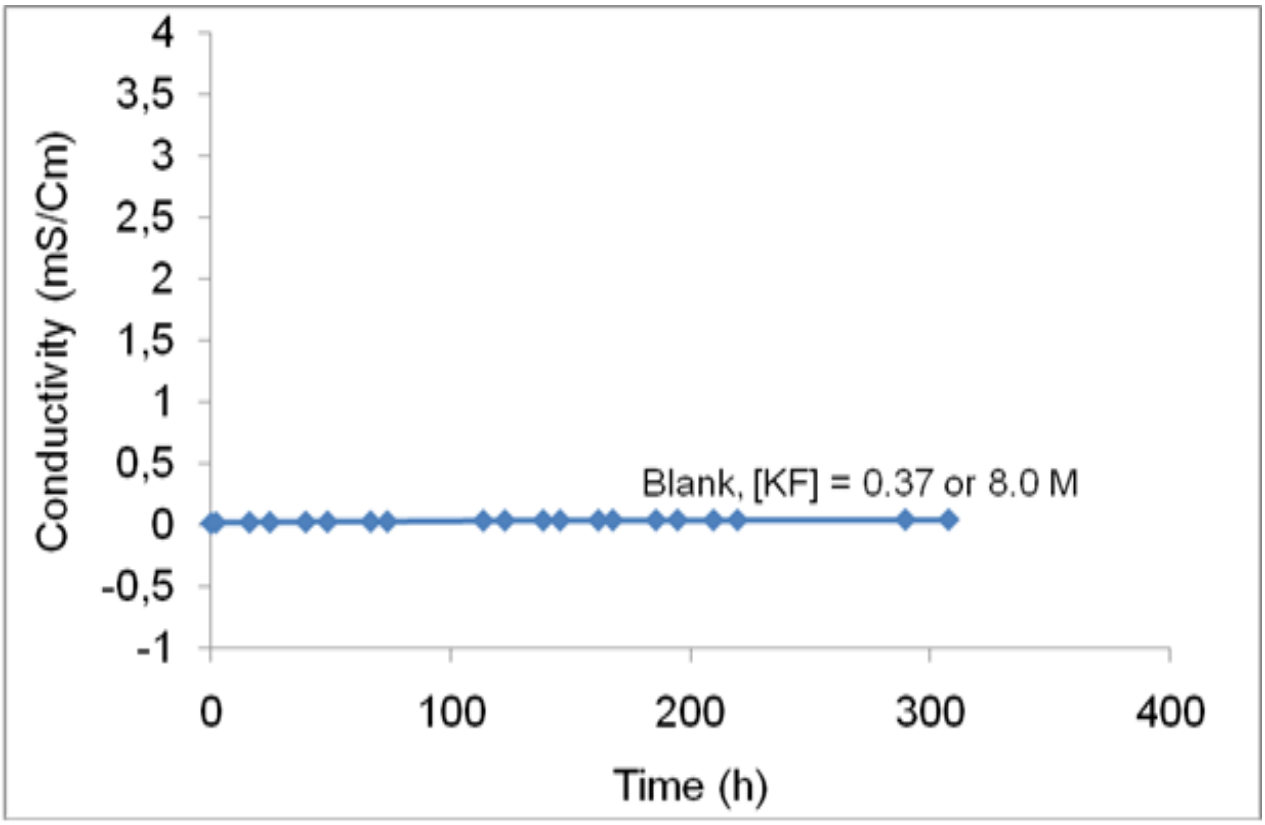
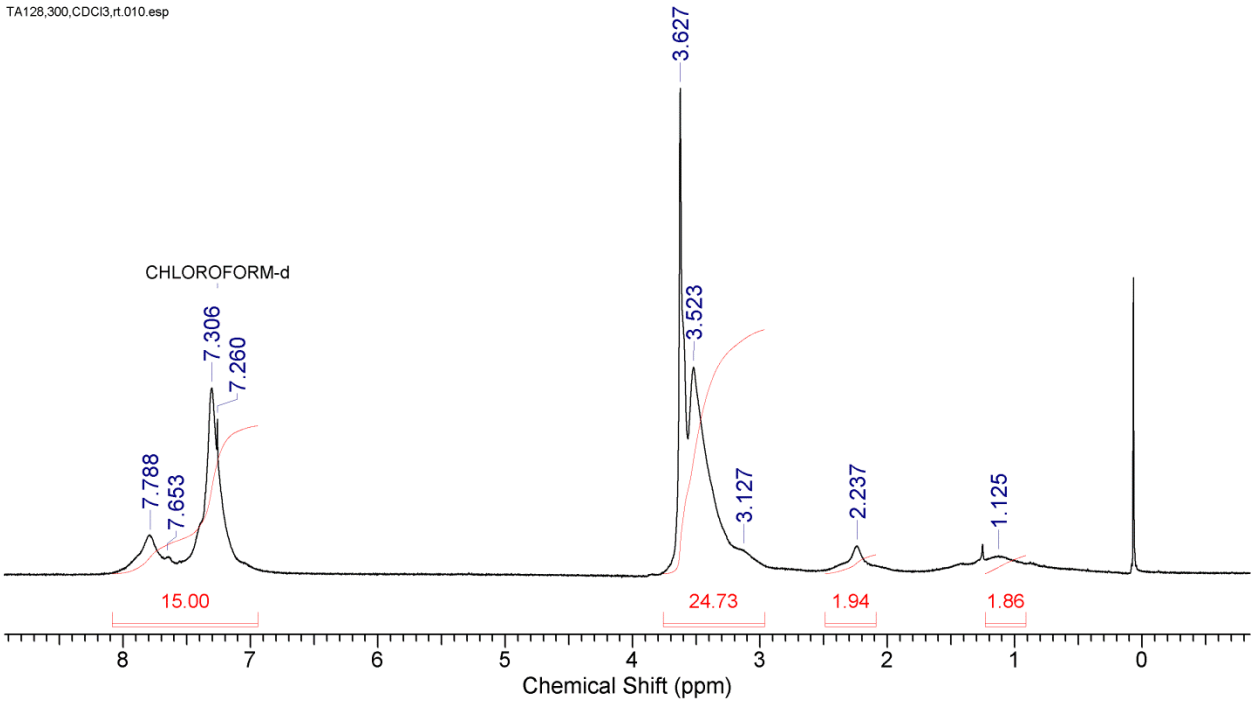


Figure S4. Plot of the electric conductivity vs time for a blank experiment where no receptor had been dissolved in the organic layer.

Copies of NMR spectra

^{1}H NMR spectrum of the ditopic receptor 1

(300MHz, $CDCl_3$, RT)



^{13}C NMR spectrum of the ditopic receptor 1

($CDCl_3$, RT)

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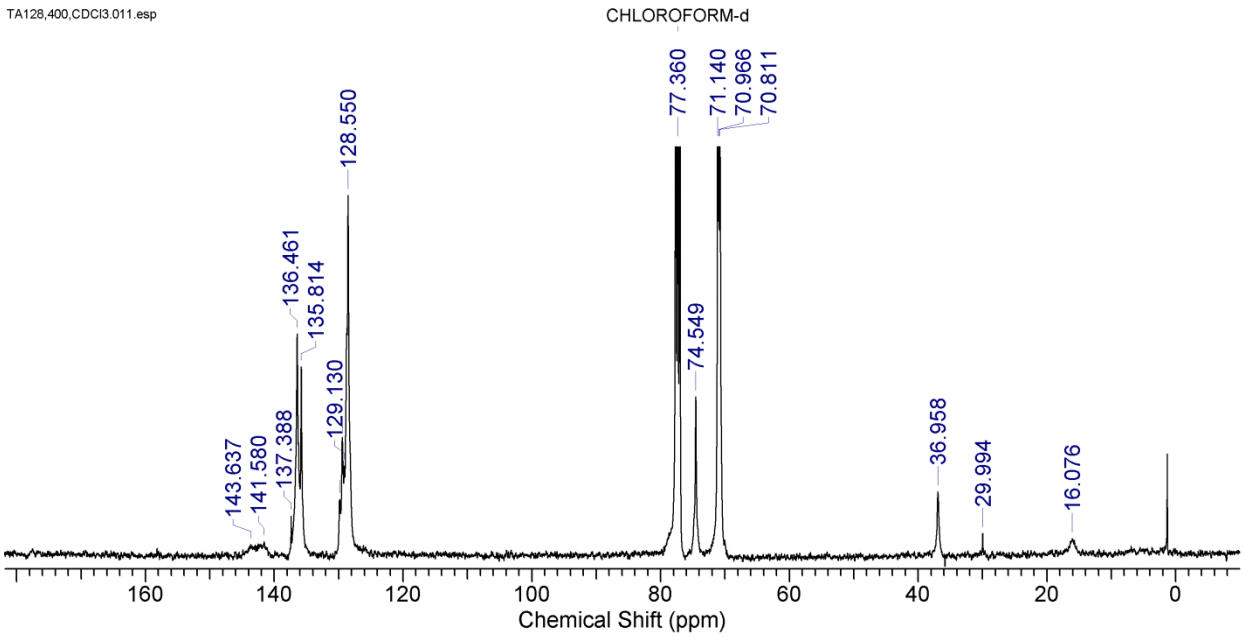

^{19}F NMR spectrum of the ditopic receptor 1

($CDCl_3$, RT)

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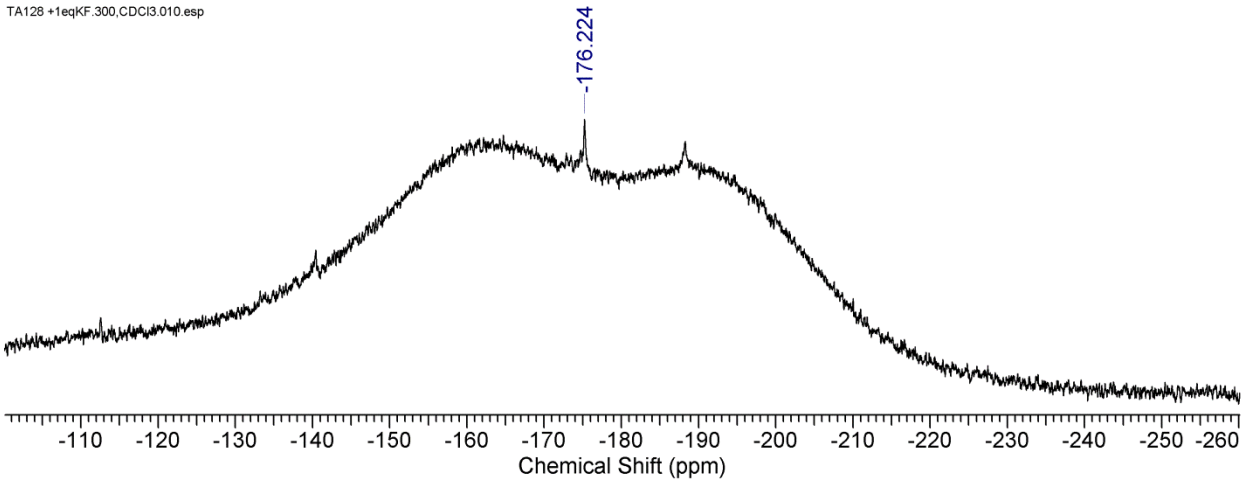
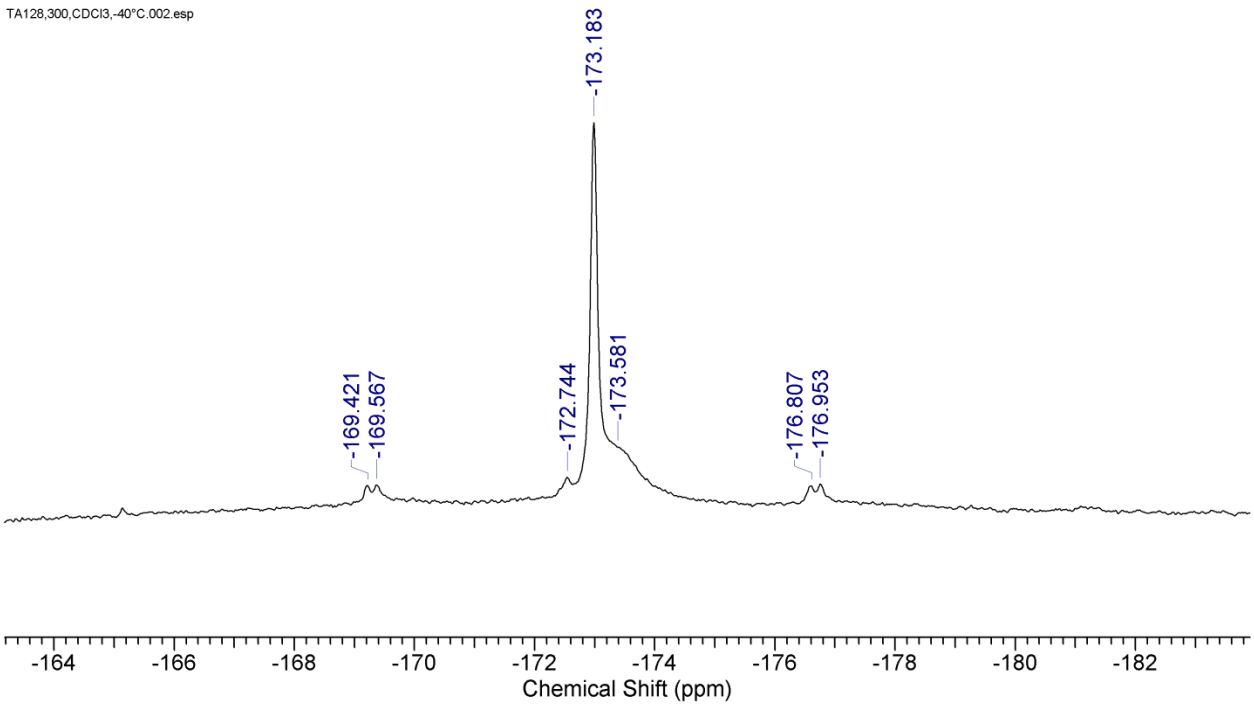


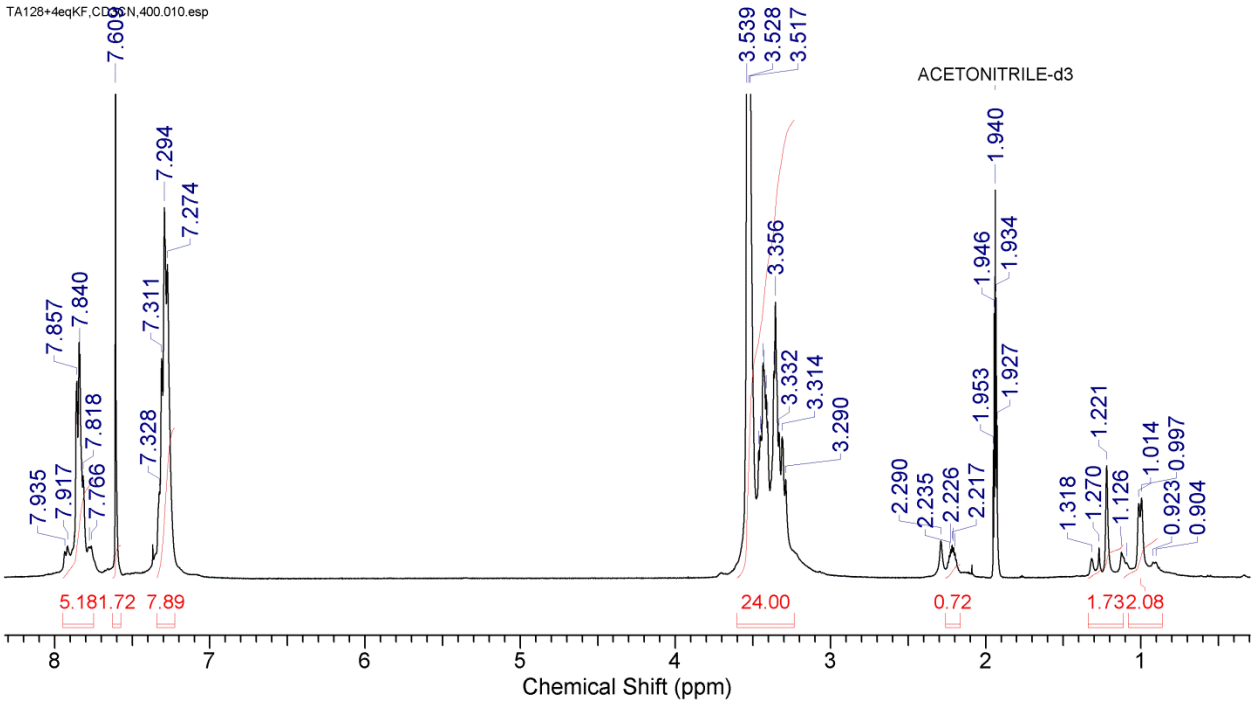
^{19}F NMR spectrum of the ditopic receptor 1

($CDCl_3$, -40°C)



^{1}H NMR spectrum of 1·KF

(400 MHz, CD_3CN, room temperature)



^{13}C NMR spectrum of 1·KF

(CD_3CN, RT)

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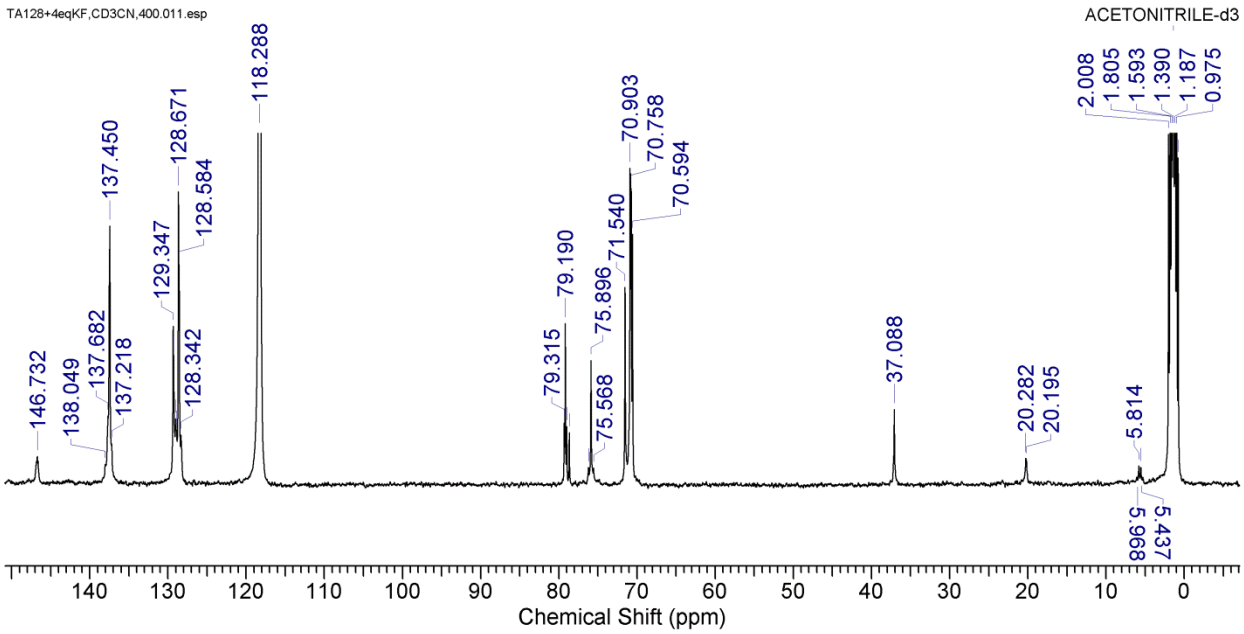
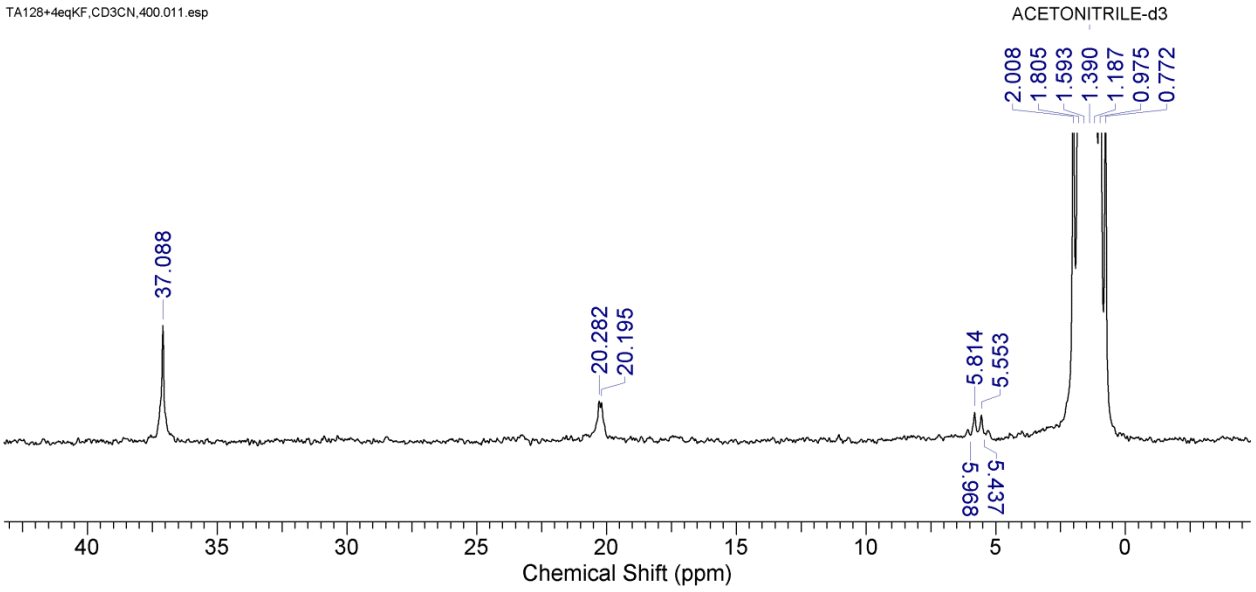


^{13}C NMR spectrum of 1·KF (cutout)

(CD_3CN, RT)



^{13}C NMR spectrum of 1·KF (cutout)

(CD_3CN, RT)

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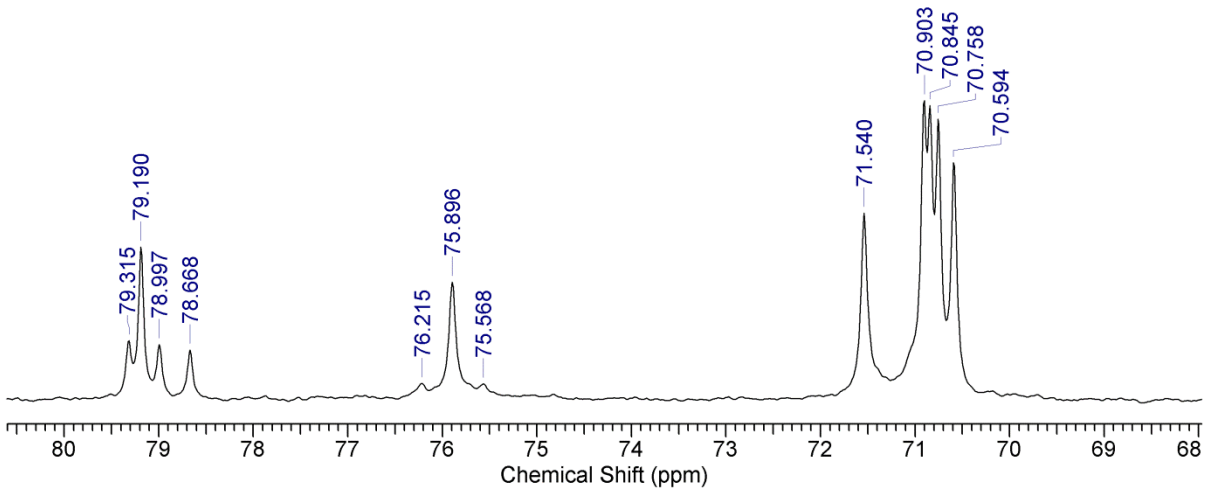
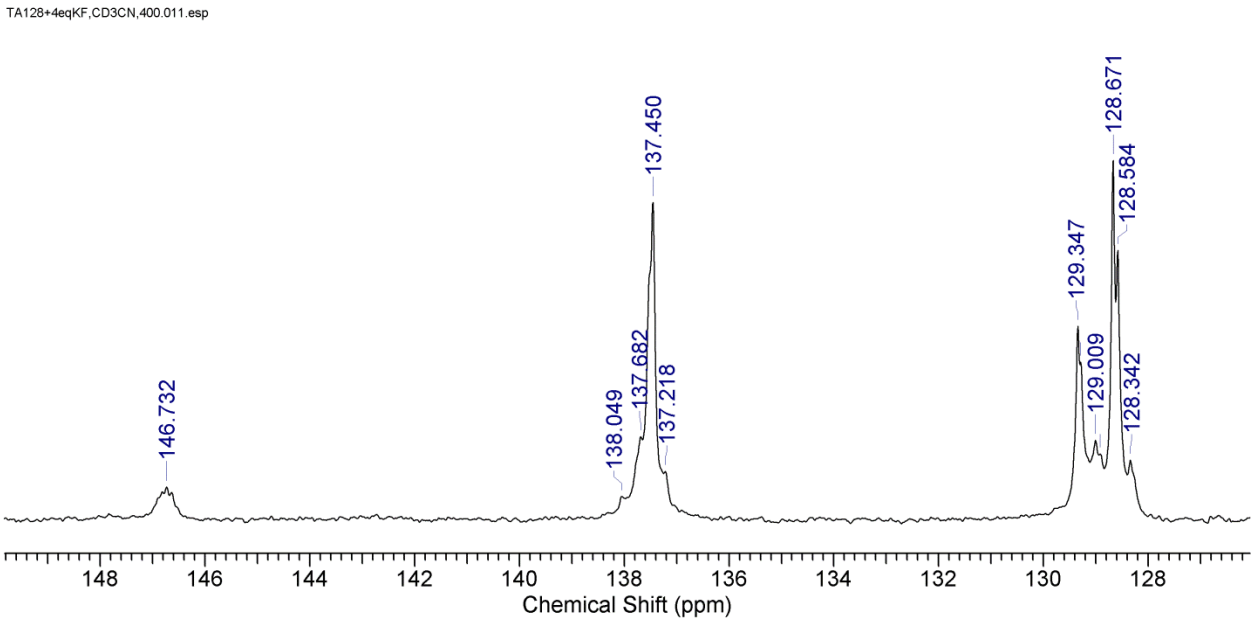


^{13}C NMR spectrum of 1·KF (cutout)

(CD_3CN, RT)



^{119}Sn NMR spectrum of 1·KF

(CD_3CN, RT)

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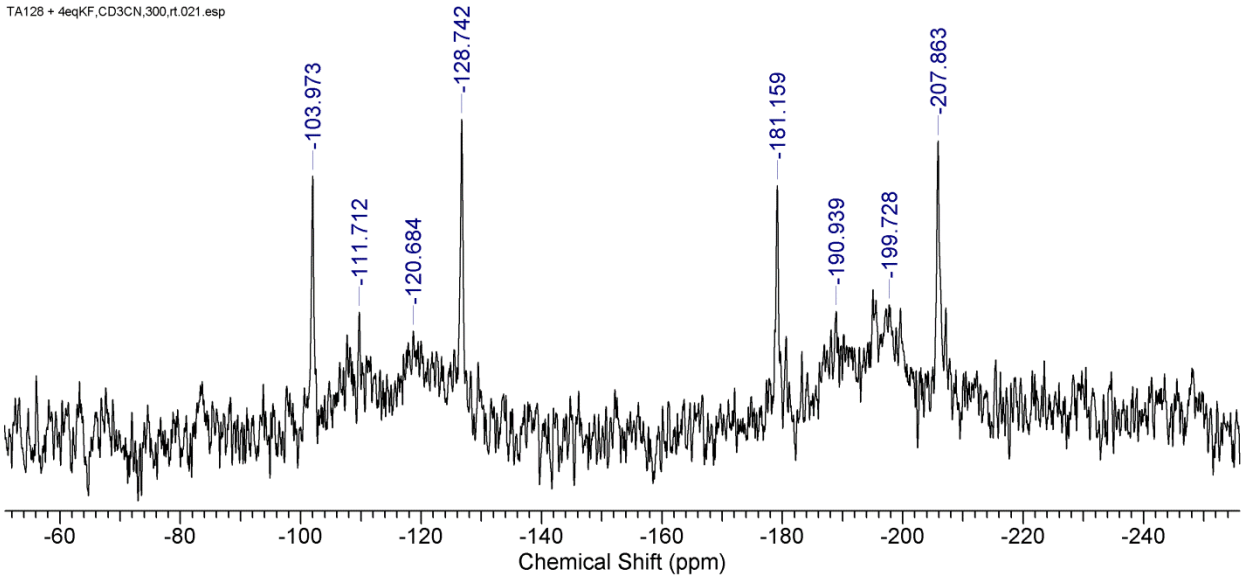

^{119}Sn NMR spectrum of 1·KF

(CD_3CN, -40^{o}C)

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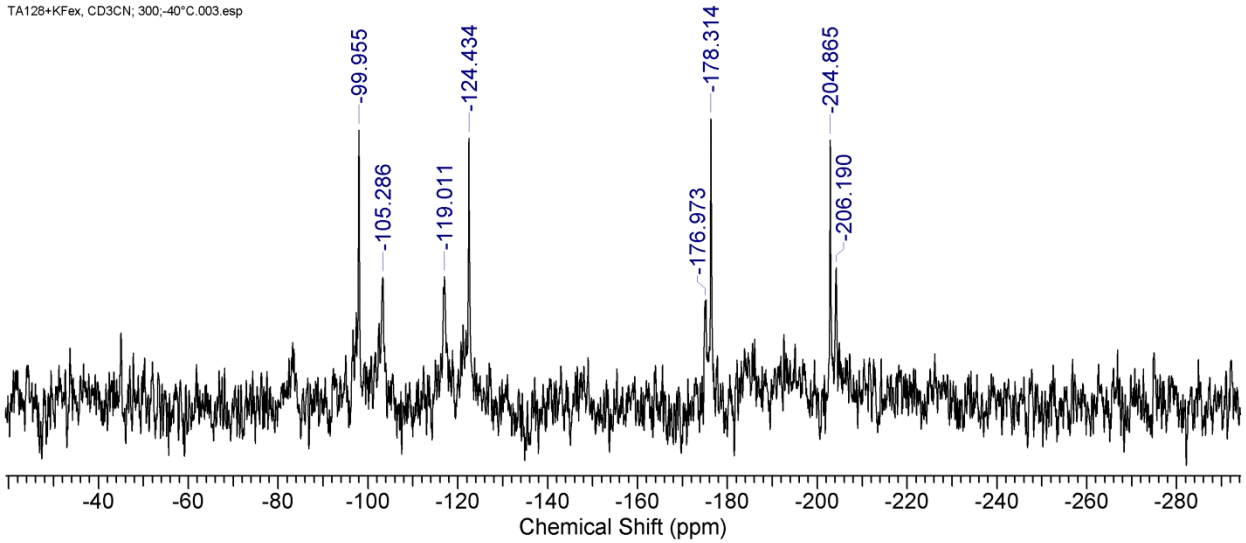

^{19}F NMR spectrum of 1·KF

(CD_3CN, RT)

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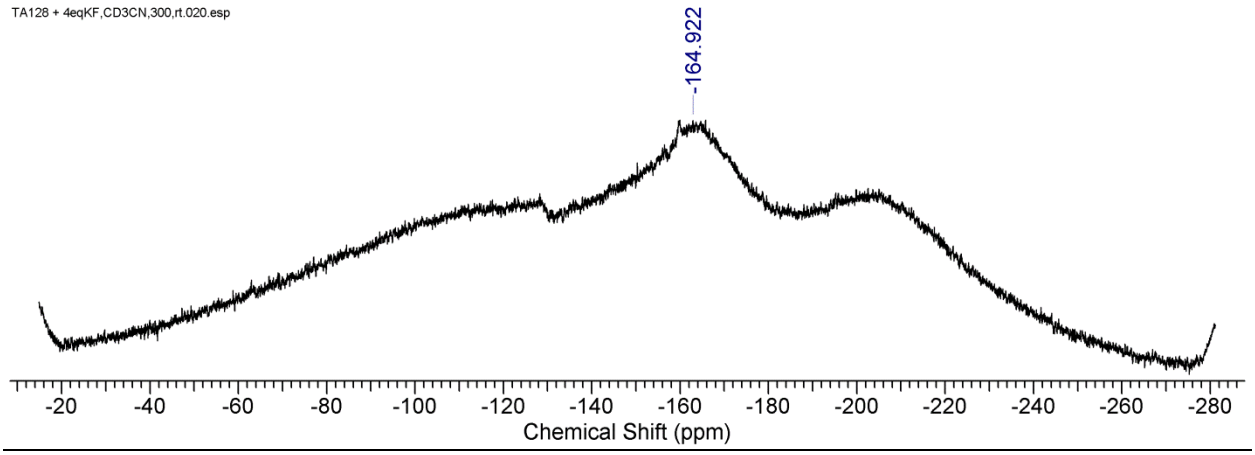
File Name	C:\Users\Alain Charly\Documents\Research Files_Chemistry\Forschung-Tagne\NMR_definitiv\Bisstannylfluorid-crown-6, TA128\TA128 + 4eqKF,CD3CN,300,rt\20\fid						
Frequency (MHz)	282.40	*Nucleus*	19F	*Number of Transients*	128	*Origin*	spect
Original Points Count	32768	*Owner*	guest	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	1024.00	*SW(cyclical) (Hz)*	75187.97	*Solvent*	ACETONITRILE-d3	*Spectrum Offset (Hz)*	-42360.6719
Spectrum Type	STANDARD	*Sweep Width (Hz)*	75185.67	*Temperature (degree C)*	23.160		

VerticalScaleFactor = 1



^{19}F NMR spectrum of 1·KF

(CD_3CN, -40^{o}C)

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Acquisition Time (sec)	0.4358	*Comment*	19F of TA128KF-P T=-40C CD3CN			*Date*	25 Nov 2008 17:17:04
Date Stamp	25 Nov 2008 17:17:04						
File Name	C:\Users\Alain Charly\Documents\Research Files_Chemistry\Forschung-Tagne\NMR_definitiv\Bisstannylfluorid-crown-6, TA128\TA128+KFex, CD3CN; 300;-40°C\2\fid						
Frequency (MHz)	282.40	*Nucleus*	19F	*Number of Transients*	128	*Origin*	spect
Original Points Count	32768	*Owner*	guest	*Points Count*	32768	*Pulse Sequence*	zg30
Receiver Gain	1024.00	*SW(cyclical) (Hz)*	75187.97	*Solvent*	ACETONITRILE-d3	*Spectrum Offset (Hz)*	-27890.6680
Spectrum Type	STANDARD	*Sweep Width (Hz)*	75185.67	*Temperature (degree C)*	-34.840		

VerticalScaleFactor = 1