

## Supporting Information

# Carbodiphosphorane Mediated Synthesis of a Triflyloxyphosphonium Dication and its Reactivity towards Nucleophiles

Sivatmeehan Yogendra,<sup>a</sup> Felix Hennersdorf,<sup>a</sup> Antonio Bauzá,<sup>b</sup> Antonio Frontera,<sup>b</sup> Roland  
Fischer,<sup>c</sup> Jan J. Weigand<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry and Food Chemistry, TU Dresden, 01062 Dresden, Germany; [\*]  
e-mail: jan.weigand@tu-dresden.de

<sup>b</sup>Department of Chemistry, Universitat de les Illes Balears, Palma de Mallorca, Spain

<sup>c</sup>Department of Chemistry, TU Graz, 8010 Graz, Austria

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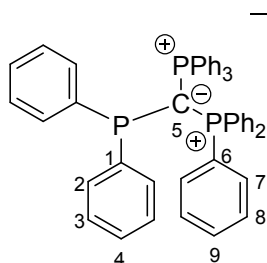
# 1. Material and Method

## 1.1. General remarks

All manipulations were performed in a Glovebox MB Unilab or using Schlenk techniques under an atmosphere of purified Argon. Dry, oxygen-free solvents ( $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_3\text{CN}$ ,  $\text{C}_6\text{H}_5\text{F}$ , *o*- $\text{C}_6\text{H}_4\text{F}_2$  (distilled from  $\text{CaH}_2$ ),  $\text{Et}_2\text{O}$  (distilled from potassium/benzophenone), *n*-hexane, *n*-pentane (distilled from potassium)) were employed. Deuterated benzene ( $\text{C}_6\text{D}_6$ ) was purchased from Sigma-Aldrich and distilled from potassium. Anhydrous deuterated acetonitrile ( $\text{CD}_3\text{CN}$ ) and dichloromethane ( $\text{CD}_2\text{Cl}_2$ ) were purchased from Sigma-Aldrich. All distilled and deuterated solvents were stored over molecular sieves (4 Å:  $\text{CH}_2\text{Cl}_2$ ,  $\text{C}_6\text{H}_5\text{F}$ , *o*- $\text{C}_6\text{H}_4\text{F}_2$ ,  $\text{C}_6\text{D}_6$ ,  $\text{CD}_2\text{Cl}_2$ , *n*-hexane, *n*-pentane,  $\text{Et}_2\text{O}$ ; 3 Å:  $\text{CH}_3\text{CN}$ ,  $\text{CD}_3\text{CN}$ ). All glassware was oven-dried at 160 °C prior to use.  $(\text{Ph}_3\text{P})_2\text{C}^{[1]}$  was prepared according to literature procedure.  $\text{Ph}_2\text{PCl}$ , HOTf,  $\text{Me}_3\text{SiOTf}$ ,  $t\text{BuOOH}$ ,  $\text{Tf}_2\text{O}$ , AgF, 4-(dimethylamino)pyridine (DMAP),  $\text{Ph}_3\text{P}(\text{O})$ , PhOH,  $\text{NH}_4\text{SCN}$  and  $\text{Me}_3\text{SiCN}$ , were purchased from Aldrich, Strem, Apollo Scientific or ABCR Chemicals and used as received. NMR spectra were measured on a Bruker AVANCE III HD Nanobay 400 MHz UltraShield ( $^1\text{H}$  (400.13 MHz),  $^{13}\text{C}$  (100.61 MHz),  $^{31}\text{P}$  (161.98 MHz)  $^{19}\text{F}$  (376.50 MHz)), or on a Bruker AVANCE III HDX, 500 MHz Ascend ( $^1\text{H}$  (500.13 MHz),  $^{13}\text{C}$  (125.75 MHz),  $^{31}\text{P}$  (202.45 MHz)  $^{19}\text{F}$  (470.59 MHz)). All  $^{13}\text{C}$  NMR spectra were exclusively recorded with composite pulse decoupling. Reported numbers assigning atoms in the  $^{13}\text{C}$  spectra were indirectly deduced from the cross-peaks in 2D correlation experiments (HMBC, HSQC). Chemical shifts were referenced to  $\delta_{\text{TMS}} = 0.00$  ppm ( $^1\text{H}$ ,  $^{13}\text{C}$ ) and  $\delta_{\text{H}_3\text{PO}_4(85\%)} = 0.00$  ppm ( $^{31}\text{P}$ , externally). Chemical shifts ( $\delta$ ) are reported in ppm. Coupling constants ( $J$ ) are reported in Hz. The designation of the spin systems is performed by convention.<sup>[2]</sup> The furthest downfield resonance is denoted by the latest letter in the alphabet and the furthest upfield by the earliest letter. Melting points were recorded on an electrothermal melting point apparatus (Büchi Switzerland, Melting point M-560) in sealed capillaries under Nitrogen atmosphere and are uncorrected. Infrared (IR) and Raman spectra were recorded at ambient temperature using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd:YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parenthesis. An ATR unit (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parenthesis using the following abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong. Elemental analyses were performed on a Vario MICRO cube Elemental Analyzer by Elementar Analysatorsysteme GmbH in CHNS modus.

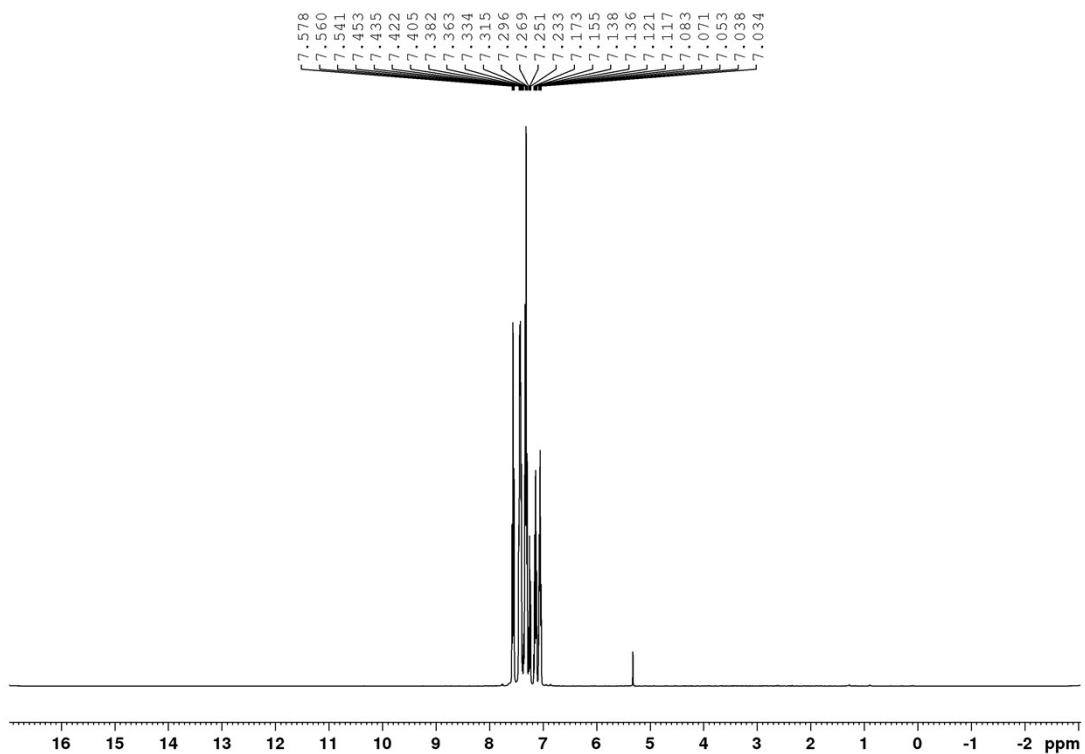
## 2. Synthesis and spectroscopic data

### 2.1. Synthesis of 3[OTf]

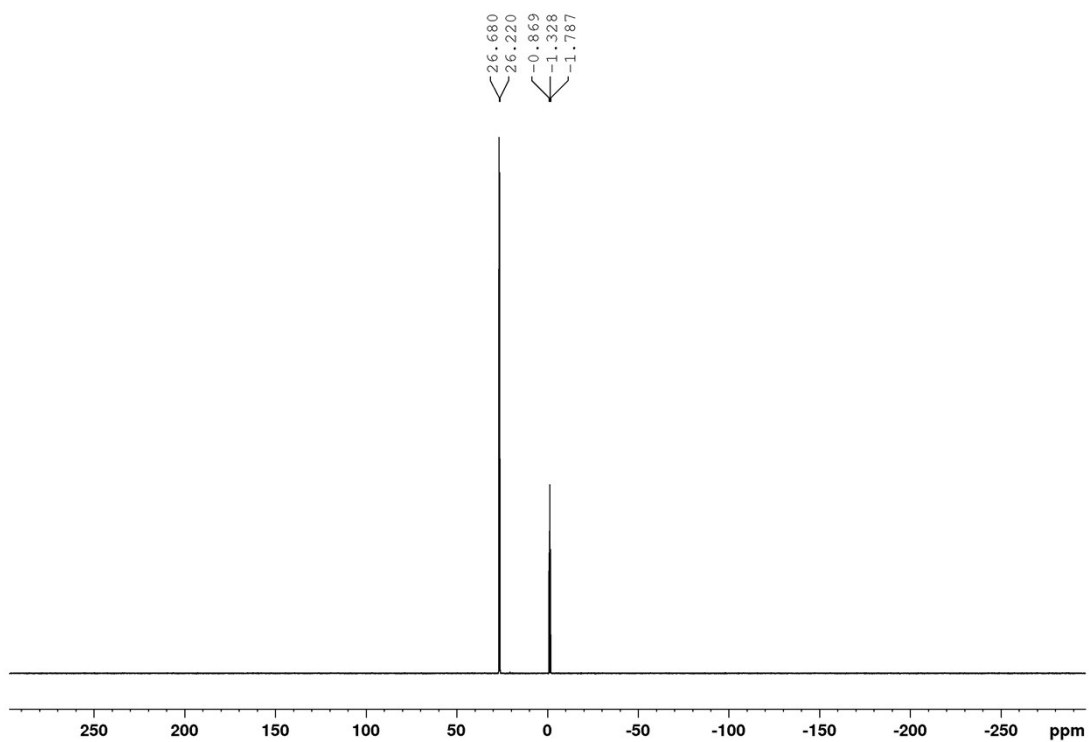


To a suspension of  $(\text{Ph}_3\text{P})_2\text{C}$  (5.37 g, 10.0 mmol) in  $\text{C}_6\text{H}_5\text{F}$  (80 mL),  $\text{Ph}_2\text{PCl}$  (2.21 g, 10.0 mmol) was added and the reaction mixture was stirred for 10 minutes at ambient temperature followed by the addition of  $\text{Me}_3\text{SiOTf}$  (2.45 g, 11.0 mmol). The reaction mixture was stirred for additional 60 minutes after which the colorless suspension was filtered. The residue was washed with  $\text{C}_6\text{H}_5\text{F}$  (10 mL) and *n*-pentane (10 mL) and dried *in vacuo* to give  $3[\text{OTf}]\cdot\text{C}_6\text{H}_5\text{F}$  as colorless and air-stable powder.

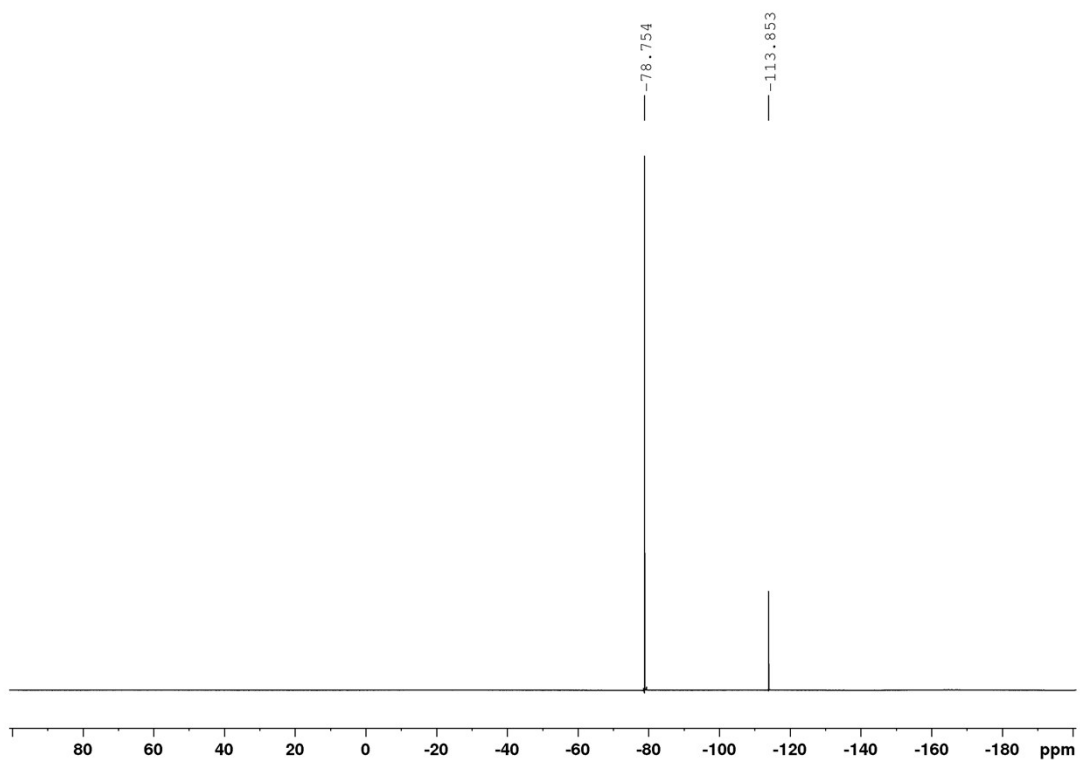
**Yield:** 10.40 g (90%); **mp.:** decomp.:  $>225^\circ\text{C}$ ; **Raman (39 mW, 400 scans, 300 K, in  $\text{cm}^{-1}$ ):**  $\nu = 3066(50), 1586(57), 1224(5), 1188(7), 1163(7), 1099(22), 1032(58), 1002(100), 806(6), 755(7), 697(7), 618(17), 350(5), 313(5), 263(19), 243(16), 204(29)$ ; **IR (300 K, ATR, in  $\text{cm}^{-1}$ ):**  $\nu = 3063(\text{vw}), 1591(\text{w}), 1495(\text{vw}), 1482(\text{w}), 1437(\text{m}), 1281(\text{w}), 1267(\text{s}), 1222(\text{m}), 1188(\text{vw}), 1144(\text{s}), 1097(\text{s}), 1032(\text{s}), 996(\text{vw}), 968(\text{m}), 926(\text{vw}), 880(\text{s}), 805(\text{w}), 755(\text{w}), 743(\text{m}), 714(\text{w}), 686(\text{vs}), 635(\text{vs})$ ;  **$^1\text{H NMR}$  ( $\text{CD}_2\text{Cl}_2$ , 300 K, in ppm):**  $\delta = 7.56$  (6H, t,  $^3J_{\text{HH}} = 7.4$  Hz, C9–H), 7.46–7.39 (12H, m, C7–H), 7.31 (12H, tm,  $^3J_{\text{HH}} = 7.4$  Hz, C8–H), 7.25 (2H, t,  $^3J_{\text{HH}} = 7.25$  Hz, C4–H), 7.14 (4H, t,  $^3J_{\text{HH}} = 7.23$  Hz, C3–H), 7.05 (4H, m, C2–H);  **$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 300 K, in ppm):**  $\delta = 137.4$  (2C, dt,  $^1J_{\text{CP}} = 13.0$  Hz,  $^3J_{\text{CP}} = 5.7$  Hz, C1), 134.8 (12C, dt,  $^2J_{\text{CP}} = 1.8$  Hz,  $^4J_{\text{CP}} = 4.7$  Hz, C7), 133.7 (6C, s, C9), 132.9 (12C, d,  $^2J_{\text{CP}} = 19.9$  Hz, C7), 129.5 (4C, pseudo-t,  $^3J_{\text{CP}} = 6.2$  Hz, C2), 128.8 (6C, s, C9), 128.7 (4C, d,  $^3J_{\text{CP}} = 6.6$  Hz, C3), 126.7 (6C, m, C6), 121.8 (1C,  $^1J_{\text{CF}} = 321.8$  Hz,  $\text{CF}_3$ ), 9.5 (1C, dt,  $^1J_{\text{CP}} = 63.4$  Hz,  $^1J_{\text{CP}} = 82.9$  Hz, C5);  **$^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 300 K, in ppm):**  $\delta = -78.8$  (3F, s,  $^1J_{\text{FC}} = 321.8$  Hz,  $\text{CF}_3$ );  **$^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ , 300 K, in ppm):**  $\delta = 26.4$  (2P, d,  $^2J_{\text{PP}} = 74.2$  Hz),  $-1.3$  (1P, t,  $^2J_{\text{PP}} = 74.2$  Hz); **elemental analysis:** calculated for  $\text{C}_{50}\text{H}_{40}\text{F}_3\text{O}_3\text{P}_3\text{S}\cdot\text{C}_6\text{H}_5\text{F}$ : C: 69.6, H: 4.7, S: 3.3, found: C: 70.0, H: 4.3, S: 3.1.



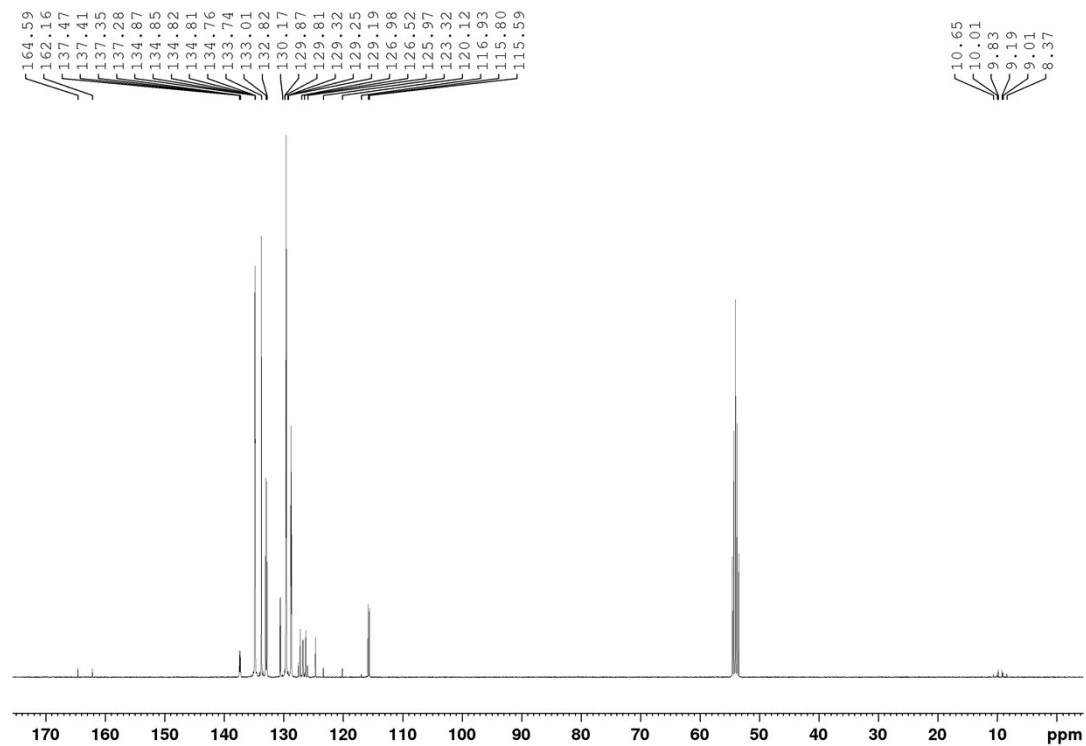
**Figure 2.1.1.**  $^1\text{H}$  NMR spectrum of  $3[\text{OTf}] \cdot \text{C}_6\text{H}_5\text{F}$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).



**Figure 2.1.2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $3[\text{OTf}] \cdot \text{C}_6\text{H}_5\text{F}$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).

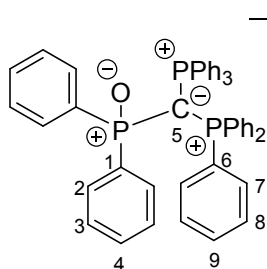


**Figure 2.1.3.**  $^{19}\text{F}$   $\{^1\text{H}\}$  NMR spectrum of  $3[\text{OTf}] \cdot \text{C}_6\text{H}_5\text{F}$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).



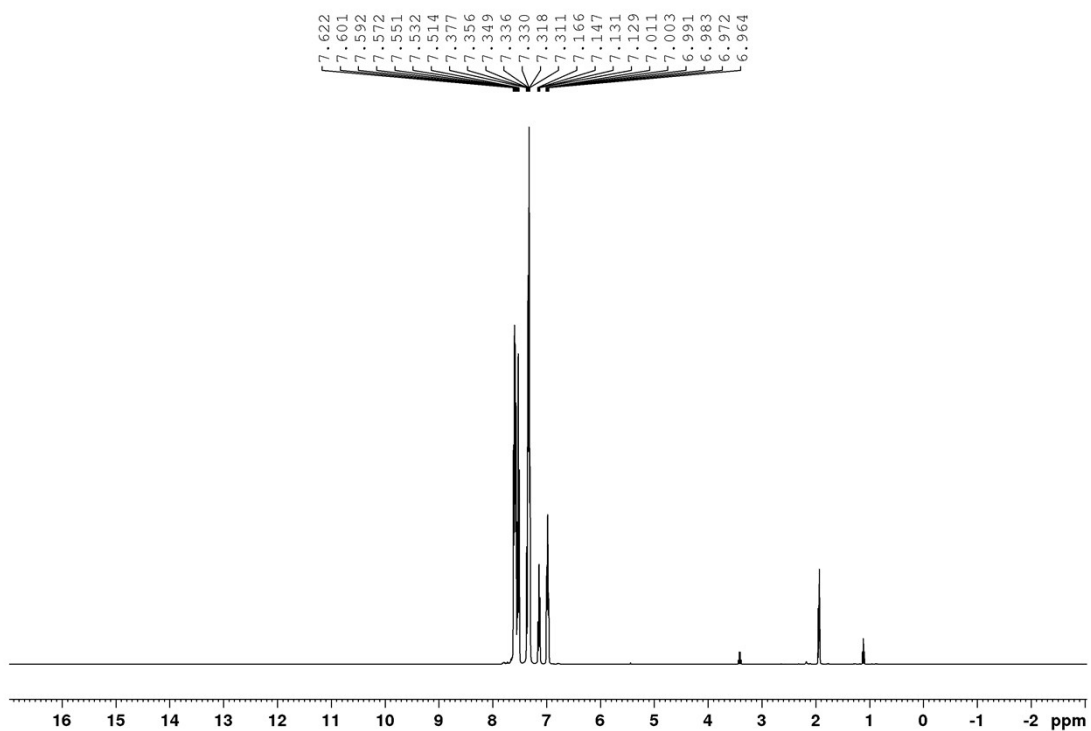
**Figure 2.1.4.**  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectrum of  $3[\text{OTf}] \cdot \text{C}_6\text{H}_5\text{F}$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).

## 2.2. Synthesis of 4[OTf]

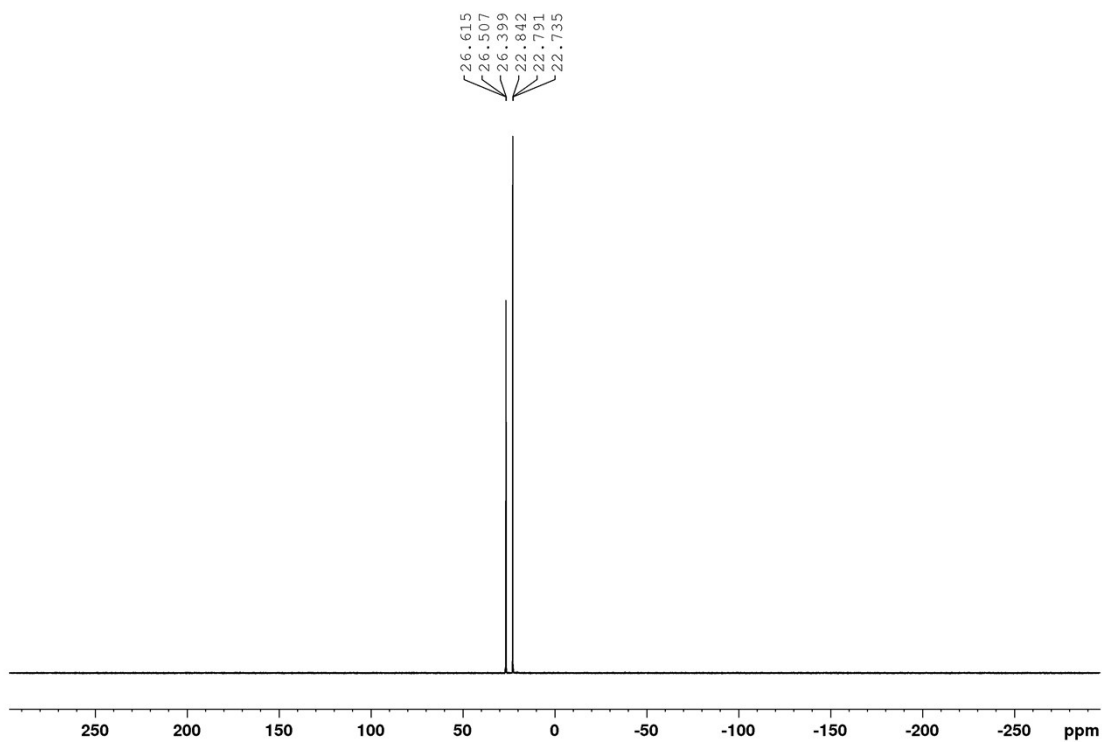


To a solution of **3**[OTf]·C<sub>6</sub>H<sub>5</sub>F (4.57 g, 4.59 mmol) in CH<sub>2</sub>Cl<sub>2</sub>, a solution of <sup>t</sup>BuO<sub>2</sub>H (1.00 mL, 5.50 M in *n*-decane, 5.50 mmol) was added and the reaction mixture was stirred for 30 minutes at ambient temperature. After removing all volatiles *in vacuo* the resulting colorless solid was dissolved in CH<sub>3</sub>CN (6 mL). After the addition of Et<sub>2</sub>O (30 mL) the obtained colorless precipitate was filtered, washed with Et<sub>2</sub>O (20 mL) and dried *in vacuo* to give the product as analytical pure, colorless and air-stable powder.

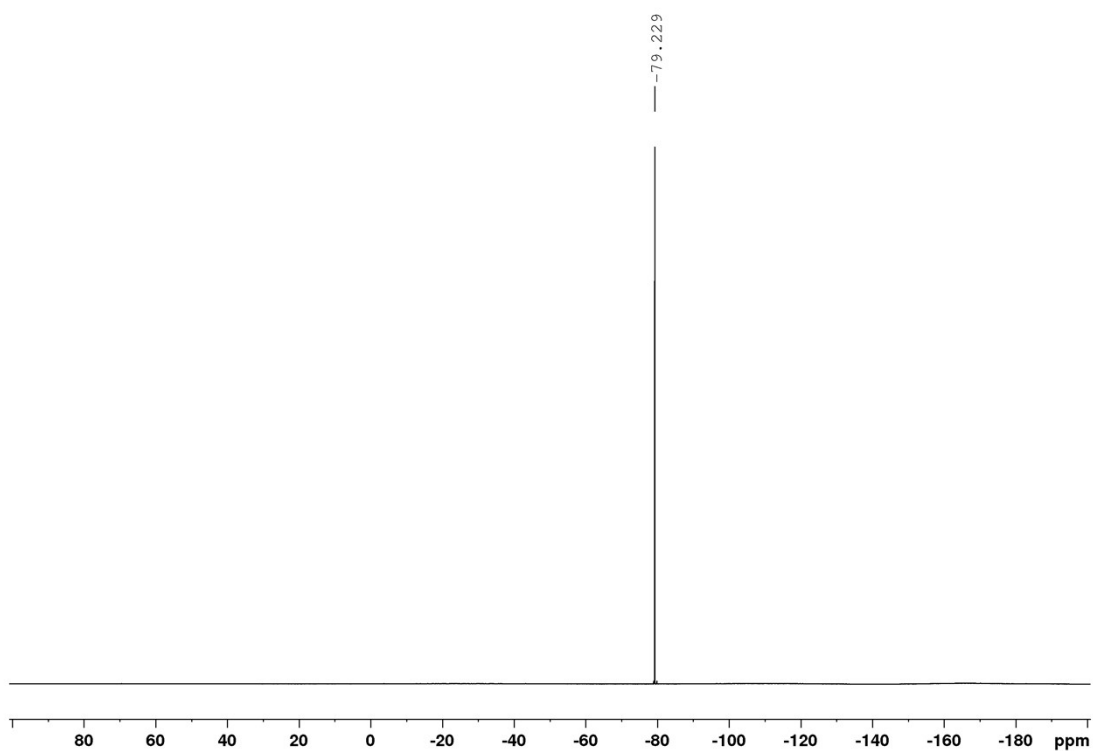
**Yield:** 3.95 g (97%); **mp.:** decomp.: >272 °C; **Raman (39 mW, 400 scans, 300 K, in cm<sup>-1</sup>):**  $\nu = 3069(54), 1588(52), 1164(12), 1098(18), 1032(63), 1003(100), 756(7), 705(8), 618(14), 599(6), 349(8), 315(7), 269(36), 242(5), 225(9), 198(19)$ ; **IR (300 K, ATR, in cm<sup>-1</sup>):**  $\nu = 3070(\text{vw}), 1587(\text{vw}), 1483(\text{vw}), 1438(\text{m}), 1311(\text{vw}), 1278(\text{vw}), 1261(\text{m}), 1224(\text{w}), 1182(\text{vw}), 1149(\text{vs}), 1092(\text{vs}), 1030(\text{s}), 1003(\text{vw}), 984(\text{vw}), 970(\text{w}), 910(\text{vs}), 853(\text{vw}), 760(\text{vw}), 743(\text{m}), 717(\text{w}), 697(\text{vw}), 682(\text{w}), 636(\text{vs})$ ; **<sup>1</sup>H NMR (CD<sub>3</sub>CN, 300 K, in ppm):**  $\delta = 7.60$  (12H, dd, <sup>3</sup>J<sub>HH</sub> = 11.90 Hz, <sup>3</sup>J<sub>HH</sub> = 8.10 Hz, C8–H), 7.53 (6H, t, <sup>3</sup>J<sub>HH</sub> = 7.55 Hz, C9–H), 7.39–7.29 (16H, m, C7–H/ C3H), 7.15 (2H, t, <sup>3</sup>J<sub>HH</sub> = 7.37 Hz, C4–H), 6.99 (4H, td, <sup>3</sup>J<sub>HH</sub> = 7.75 Hz, <sup>3</sup>J<sub>HH</sub> = 3.20 Hz, C2–H); **<sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 300 K, in ppm):**  $\delta = 136.5$  (2C, dt, <sup>1</sup>J<sub>CP</sub> = 108.1 Hz, <sup>3</sup>J<sub>CP</sub> = 2.8 Hz, C1), 135.8 (12C, t, <sup>3</sup>J<sub>CP</sub> = 5.0 Hz, C8), 134.1 (6C, t, <sup>4</sup>J<sub>CP</sub> = 1.4 Hz, C9), 132.8 (4C, d, <sup>3</sup>J<sub>CP</sub> = 9.4 Hz, C3), 131.5 (2C, d, <sup>4</sup>J<sub>CP</sub> = 2.8 Hz, C4), 129.8 (12C, t, <sup>2</sup>J<sub>CP</sub> = 6.4 Hz, C7), 128.9 (4C, d, <sup>2</sup>J<sub>CP</sub> = 12.2 Hz, C2), 126.0 (6C, ddm, <sup>1</sup>J<sub>CP</sub> = 95.8 Hz, <sup>3</sup>J<sub>CP</sub> = 3.0 Hz, C6), 122.2 (1C, s, <sup>1</sup>J<sub>CF</sub> = 320.9 Hz, CF<sub>3</sub>), 19.0 (1C, dt, <sup>1</sup>J<sub>CP</sub> = 78.5 Hz, <sup>1</sup>J<sub>CP</sub> = 77.7 Hz, C5); **<sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 300 K, in ppm):**  $\delta = -79.2$  (3F, s, <sup>1</sup>J<sub>FC</sub> = 320.9 Hz, CF<sub>3</sub>); **<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 300 K, in ppm):**  $\delta = 26.5$  (1P, t, <sup>2</sup>J<sub>PP</sub> = 17.7 Hz), 22.8 (2P, d, <sup>2</sup>J<sub>PP</sub> = 17.7 Hz), **elemental analysis:** calculated for C<sub>50</sub>H<sub>40</sub>F<sub>3</sub>O<sub>4</sub>P<sub>3</sub>S: C: 67.7, H: 4.6, S: 3.6, found: C: 67.7, H: 4.5, S: 3.8.



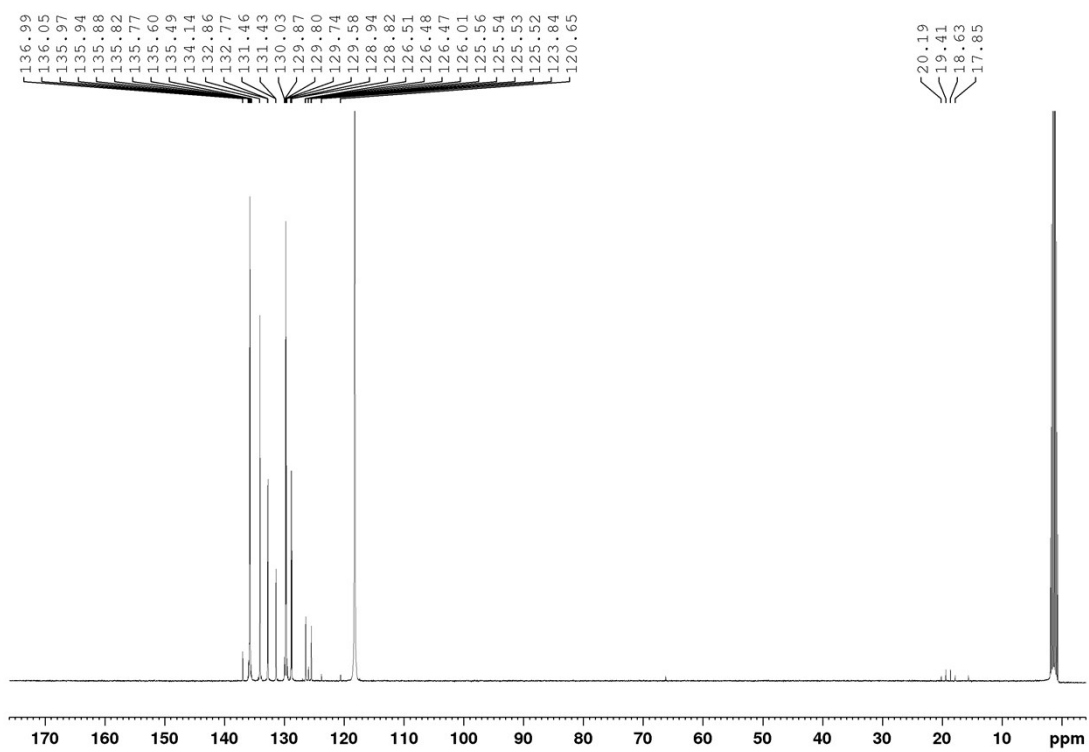
**Figure 2.2.1.**  $^1\text{H}$  NMR spectrum of 4[OTf] ( $\text{CD}_3\text{CN}$ , 300 K).



**Figure 2.2.2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of 4[OTf] ( $\text{CD}_3\text{CN}$ , 300 K).



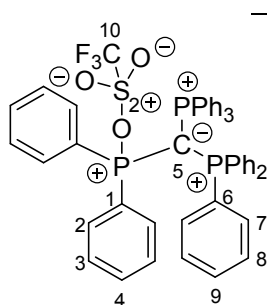
**Figure 2.2.3.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of  $4[\text{OTf}]$  ( $\text{CD}_3\text{CN}$ , 300 K).



**Figure 2.2.4.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $4[\text{OTf}]$  ( $\text{CD}_3\text{CN}$ , 300 K).



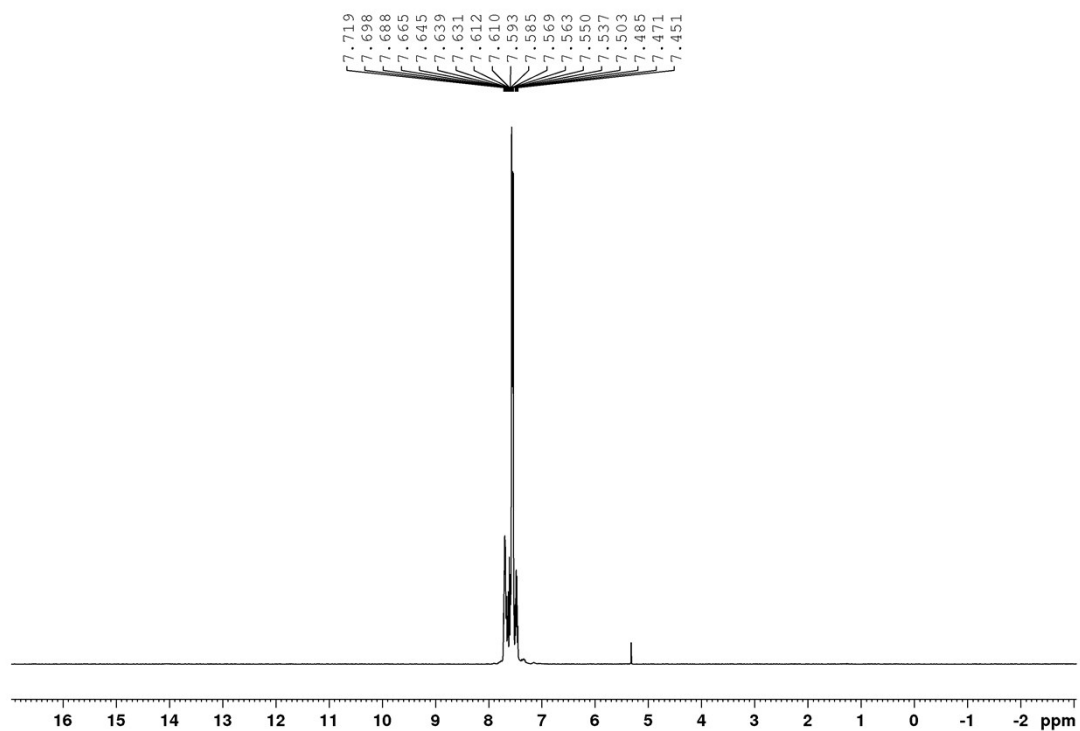
### 2.3. Synthesis of 1[OTf]<sub>2</sub>



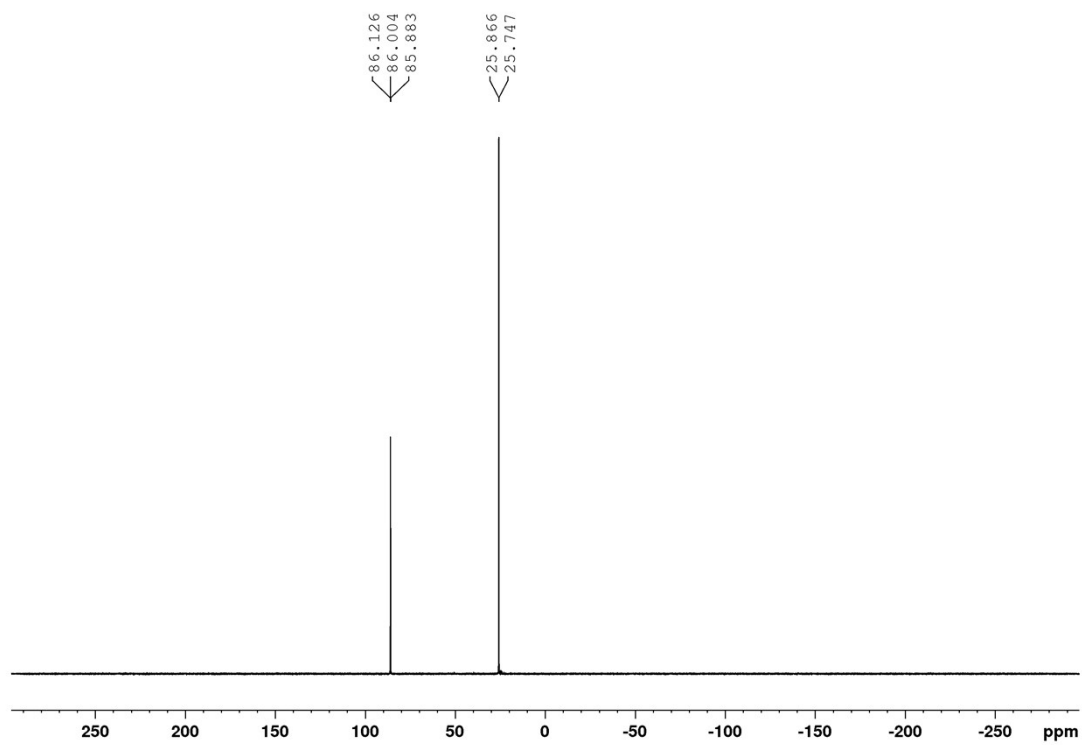
To a suspension of 4[OTf] (7.50 g, 8.46 mmol) in C<sub>6</sub>H<sub>5</sub>F (70 mL), Tf<sub>2</sub>O (1.57 mL, 9.30 mmol) was added and the reaction mixture was stirred for 12 h at ambient temperature. The colorless suspension was filtered and the residue was washed with C<sub>6</sub>H<sub>5</sub>F (2 x 5 mL). After removal of all volatiles *in vacuo*, 1[OTf]<sub>2</sub> was obtained as analytical pure, colorless and moisture

sensitive powder.

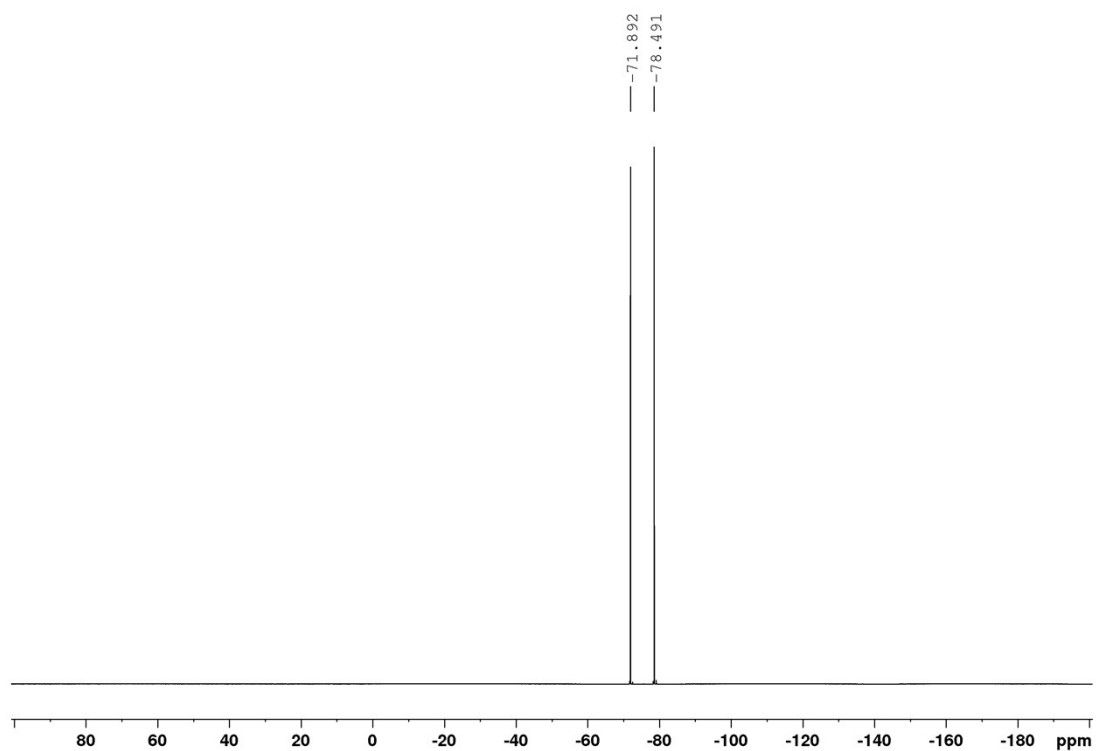
**Yield:** 9.75 g (98%); **mp.:** decomp.: >180 °C; **Raman (35 mW, 400 scans, 300 K, in cm<sup>-1</sup>):**  $\nu = 3080(30), 3068(9), 1586(68), 1242(6), 1224(6), 1192(8), 1168(6), 1098(33), 1032(99), 1004(100), 753(14), 695(6), 616(22), 572(8), 347(15)$ ; **IR (300 K, ATR, in cm<sup>-1</sup>):**  $\nu = 1586(\text{vw}), 1483(\text{w}), 1431(\text{w}), 1276(\text{m}), 1259(\text{w}), 1223(\text{m}), 1159(\text{w}), 1142(\text{vw}), 1124(\text{w}), 1094(\text{m}), 1032(\text{s}), 1002(\text{w}), 982(\text{m}), 922(\text{s}), 800(\text{vs}), 765(\text{w}), 752(\text{w}), 738(\text{vw}), 724(\text{w}), 684(\text{m}), 656(\text{vw}), 636(\text{s})$ ; **<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, in ppm):**  $\delta = 7.76\text{--}7.70$  (6H, m, C9–H),  $7.70\text{--}7.62$  (6H, m, C4–H / C2–H),  $7.62\text{--}7.54$  (24H, m, C7–H / C8–H),  $7.54\text{--}7.48$  (4H, m, C3–H), **<sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, in ppm):**  $\delta = 137.4$  (2C, d, <sup>4</sup>J<sub>CP</sub> = 3.5 Hz, C4), 135.9 (6C, t, <sup>4</sup>J<sub>CP</sub> = 1.4 Hz, C9), 135.3 (12C, t, <sup>2</sup>J<sub>CP</sub> = 5.3 Hz, C7), 133.8 (4C, d, <sup>2</sup>J<sub>CP</sub> = 12.8 Hz, C2), 131.4 (4C, d, <sup>3</sup>J<sub>CP</sub> = 15.3 Hz, C3), 130.8 (12C, t, <sup>3</sup>J<sub>CP</sub> = 6.5 Hz, C8), 121.7 (2C, q, <sup>1</sup>J<sub>CF</sub> = 321.4 Hz, C-OTf), 120.7 (6C, t, <sup>1</sup>J<sub>CP</sub> = 93.5 Hz, <sup>3</sup>J<sub>CP</sub> = 2.0 Hz, C6), 120.6 (2C, t, <sup>1</sup>J<sub>CP</sub> = 110.1 Hz, C1), 118.6 (1C, <sup>1</sup>J<sub>CF</sub> = 322.3 Hz, <sup>3</sup>J<sub>CP</sub> = 1.9 Hz, C10), 22.6 (1C, dt, <sup>1</sup>J<sub>CP</sub> = 97.4 Hz, <sup>1</sup>J<sub>CP</sub> = 72.0 Hz, C5); **<sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, in ppm):**  $\delta = -71.9$  (3F, s, <sup>1</sup>J<sub>FC</sub> = 322.3 Hz, C10),  $-78.5$  (6F, s, <sup>1</sup>J<sub>FC</sub> = 321.4 Hz, CF<sub>3</sub>–OTf); **<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, in ppm):**  $\delta = 86.0$  (1P, t, <sup>2</sup>J<sub>PP</sub> = 20.1 Hz), 25.8 (2P, d, <sup>2</sup>J<sub>PP</sub> = 20.1 Hz); **elemental analysis:** calculated for C<sub>52</sub>H<sub>40</sub>F<sub>9</sub>O<sub>9</sub>P<sub>3</sub>S<sub>3</sub>: C: 53.4, H: 3.5, S: 8.2, found: C: 53.2, H: 3.3, S: 8.5.



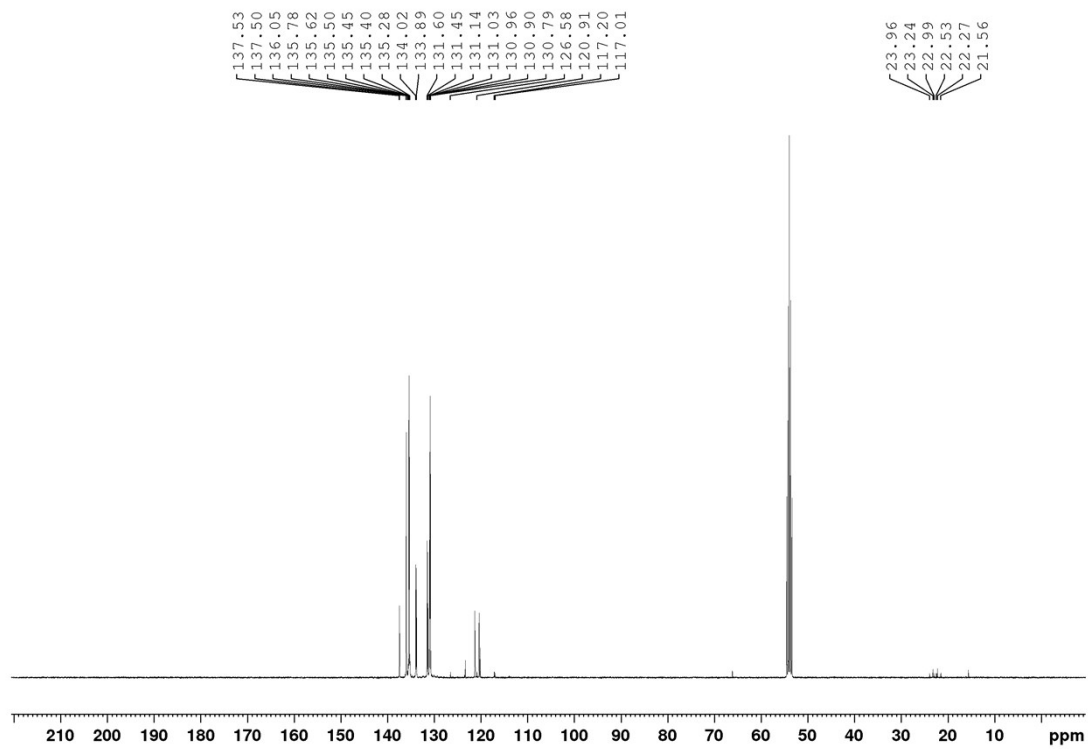
**Figure 2.3.1.**  $^1\text{H}$  NMR spectrum of  $1[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).



**Figure 2.3.2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $1[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).

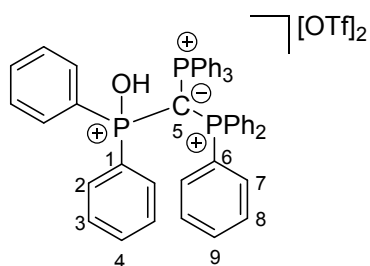


**Figure 2.3.3.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of  $1[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).



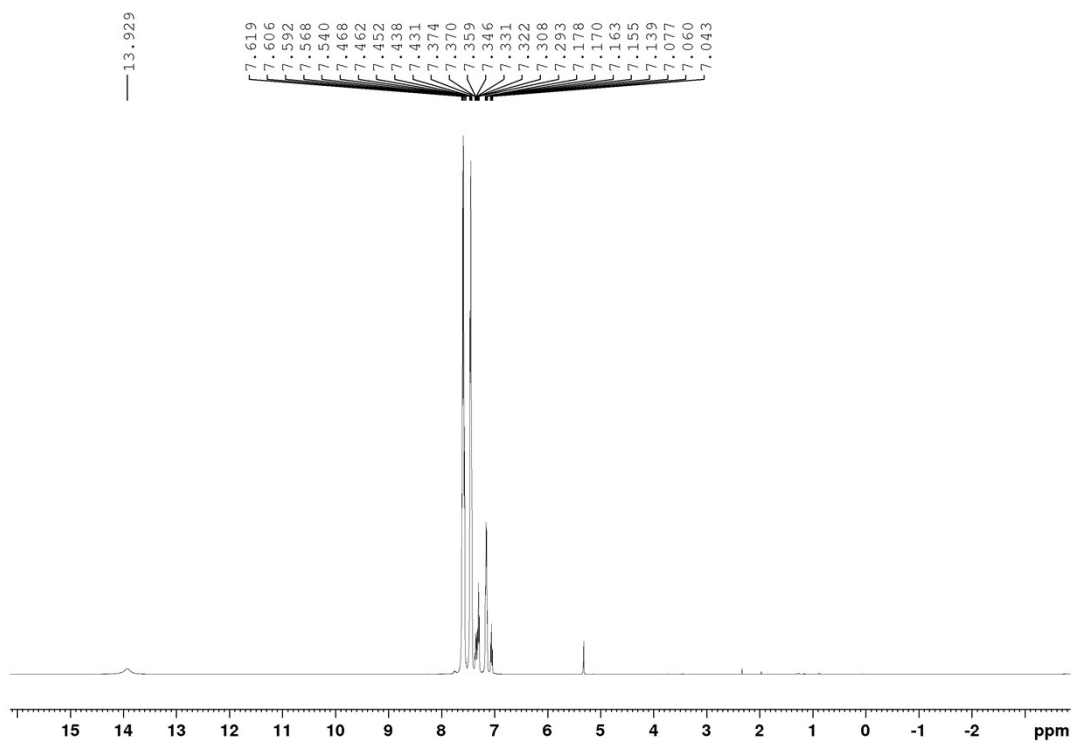
**Figure 2.3.4.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $1[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).

## 2.4. Synthesis of 7[OTf]<sub>2</sub>

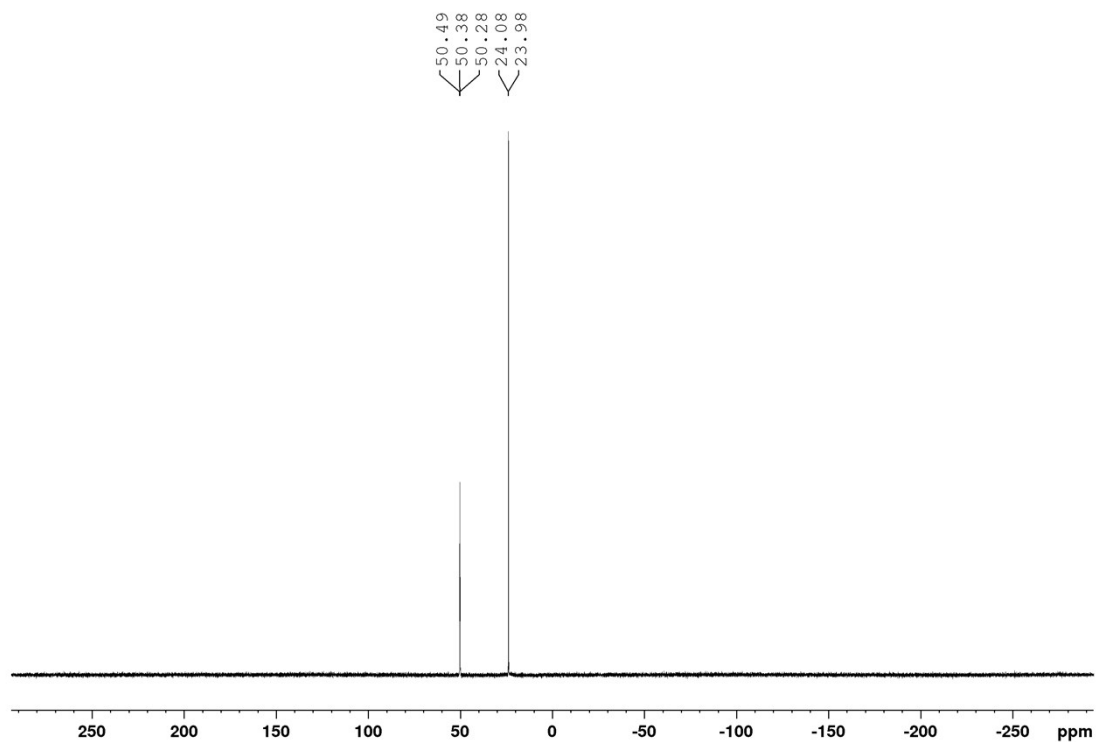


A solution of 4[OTf] (173.8 mg, 0.20 mmol) in C<sub>6</sub>H<sub>5</sub>F (1 mL) was combined with HOTf (17.7 μL, 0.20 mmol) and was stirred for 12 h at ambient temperature. After addition of *n*-hexane (1 mL) the resulting colorless suspension was filtered and the residue was dried *in vacuo* to yield the product as analytically pure, colorless powder.

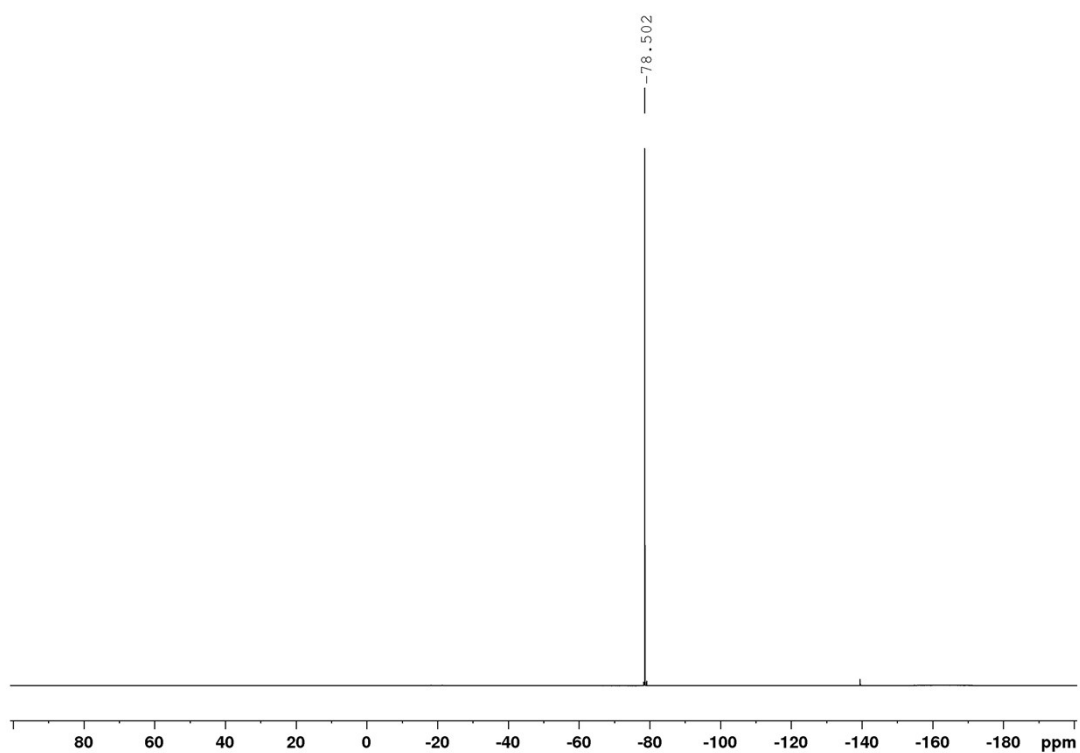
**Yield:** 172 mg (83%); **mp.:** decomp.: >135°C; **Raman (40 mW, 400 scans, 300 K, in cm<sup>-1</sup>):**  $\nu = 3148(5), 3072(80), 1588(59), 1440(5), 1252(5), 1188(7), 1165(7), 1098(17), 1031(63), 1003(100), 763(15), 708(7), 617(12), 345(5)$ ; **IR (300 K, ATR, in cm<sup>-1</sup>):**  $\nu = 1588(\text{vw}), 1484(\text{w}), 1438(\text{m}), 1326(\text{m}), 1266(\text{vw}), 1233(\text{w}), 1190(\text{vw}), 1173(\text{w}), 1155(\text{vw}), 1097(\text{m}), 1030(\text{w}), 1018(\text{vw}), 1001(\text{w}), 974(\text{vs}), 932(\text{vs}), 819(\text{w}), 746(\text{s}), 719(\text{m}), 687(\text{s}), 633(\text{vs})$ ; **<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, in ppm):**  $\delta = 13.93$  (1H, br, OH), 7.62 (6H, t, <sup>3</sup>J<sub>HH</sub> = 7.49 Hz, C9–H), 7.56 (12H, dd, <sup>3</sup>J<sub>HH</sub> = 8.29 Hz, <sup>3</sup>J<sub>HH</sub> = 4.28 Hz, C8–H), 7.47–7.42 (12H, m, C7–H), 7.40 (4H, dm, <sup>3</sup>J<sub>HH</sub> = 8.41 Hz, C2–H), 7.33 (2H, tm, <sup>3</sup>J<sub>HH</sub> = 7.45 Hz, C4–H), 7.15 (4H, dt, <sup>3</sup>J<sub>HH</sub> = 7.88 Hz, <sup>3</sup>J<sub>HH</sub> = 4.00 Hz, C3–H); **<sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, in ppm):**  $\delta = 135.1$  (12C, t, <sup>3</sup>J<sub>CP</sub> = 5.0 Hz, C8), 134.8 (6C, s, C9), 133.7 (2C, d, <sup>4</sup>J<sub>CP</sub> = 3.0 Hz, C4), 132.3 (4C, d, <sup>3</sup>J<sub>CP</sub> = 11.4 Hz, C2), 130.0 (12C, t, <sup>2</sup>J<sub>CP</sub> = 6.6 Hz, C7), 129.7 (4C, d, <sup>3</sup>J<sub>CP</sub> = 13.8 Hz, C3–H), 127.2 (2C, dt, <sup>1</sup>J<sub>CP</sub> = 113.4 Hz, <sup>3</sup>J<sub>CP</sub> = 2.8 Hz, C1), 122.9 (6C, dt, <sup>1</sup>J<sub>CP</sub> = 94.6 Hz, <sup>3</sup>J<sub>CP</sub> = 1.9 Hz, C6), 120.4 (6C, <sup>1</sup>J<sub>CF</sub> = 320.0 Hz, CF<sub>3</sub>), 17.5 (1C, dt, <sup>1</sup>J<sub>CP</sub> = 99.0 Hz, <sup>1</sup>J<sub>CP</sub> = 79.0 Hz, C5); **<sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 300 K, in ppm):**  $\delta = -78.6$  (6F, s, <sup>1</sup>J<sub>FC</sub> = 320.0 Hz, CF<sub>3</sub>); **<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 300 K, in ppm):**  $\delta = 50.3$  (1P, t, <sup>2</sup>J<sub>PP</sub> = 21.0 Hz), 23.9 (2P, d, <sup>2</sup>J<sub>PP</sub> = 21.0 Hz), **elemental analysis:** calculated for C<sub>51</sub>H<sub>41</sub>F<sub>6</sub>O<sub>7</sub>P<sub>3</sub>S<sub>2</sub>: C: 59.1, H: 4.0, S: 6.2, found: C: 59.0, H: 4.0, S: 6.2.



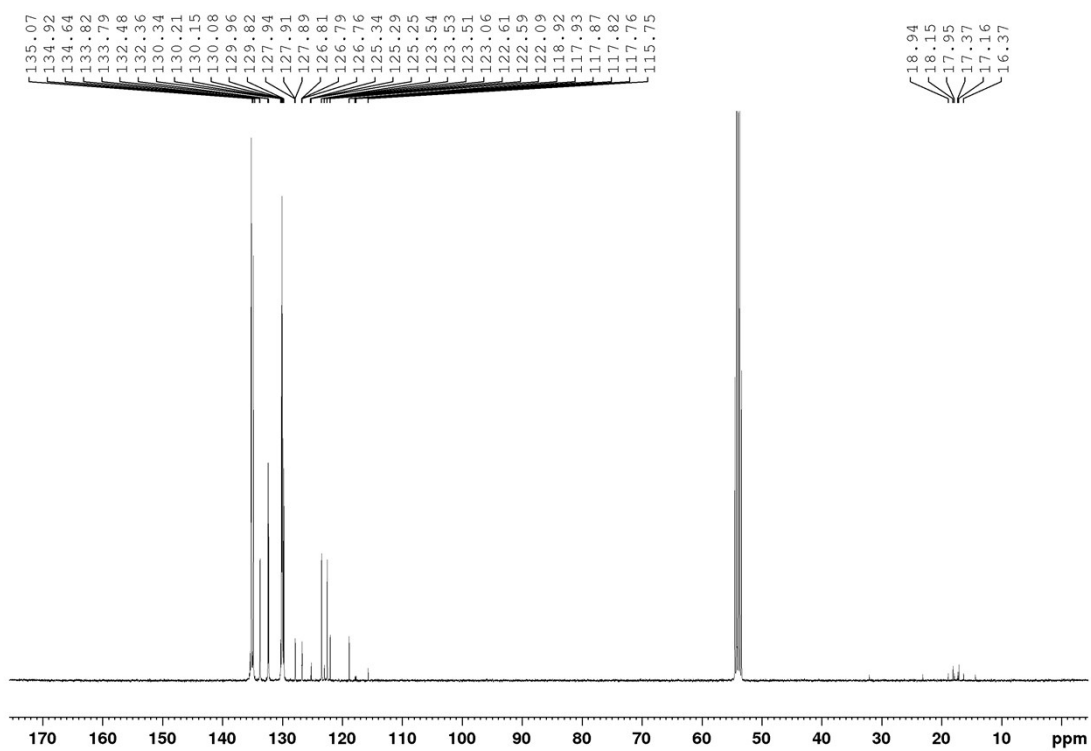
**Figure 2.4.1.**  $^1\text{H}$  NMR spectrum of  $7[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).



**Figure 2.4.2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $7[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).

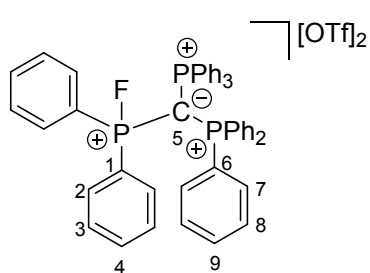


**Figure 2.4.3.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of  $7[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).



**Figure 2.4.4.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $7[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).

## 2.5. Synthesis of 8[OTf]<sub>2</sub>



To a suspension of AgF (37.9 mg, 0.30 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL), a solution of **1**[OTf]<sub>2</sub> (350.7 mg, 0.30 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) was added. The reaction mixture was stirred for 24 h at ambient temperature under the exclusion of light. After removal of all volatiles *in vacuo*, the resulting residue was suspended in *o*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (2 mL) for 20 minutes and was filtered.

The addition of *n*-hexane (4 mL) to the filtrate initially caused the separation of an oily phase which solidified to a colorless precipitate after prolonged stirring (approximately 10 min). After filtration and washing with *n*-hexane (2 mL) the solid was dried *in vacuo*. The product was obtained as analytically pure, colorless and moisture sensitive powder.

**Yield:** 254 mg (82%); **mp.:** decomp.: >242 °C; **IR (300 K, ATR, in cm<sup>-1</sup>):**  $\nu$  = 1586(w), 1506(vw), 1483(w), 1439(m), 1278(w), 1259(s), 1223(w), 1148(m), 1096(m), 1030(s), 1009(vw), 987(m), 938(vw), 925(w), 865(w), 842(vw), 747(m), 719(w), 684(s), 636(vs); **<sup>1</sup>H NMR (CD<sub>3</sub>CN, 300 K, in ppm):**  $\delta$  = 7.71 (6H, t, <sup>3</sup>J<sub>HH</sub> = 7.36 Hz, C9–H), 7.61 (12H, dd, <sup>3</sup>J<sub>HH</sub> = 12.48 Hz, C8–H), 7.53–7.47 (14H, m, C7–H/ C4H), 7.40 (4H, dd, <sup>3</sup>J<sub>HH</sub> = 13.44 Hz, <sup>3</sup>J<sub>HH</sub> = 8.33 Hz, C3–H), 7.27–7.21 (4H, m, C2–H); **<sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 300 K, in ppm):**  $\delta$  = 136.5 (2C, d, <sup>4</sup>J<sub>CP</sub> = 3.2 Hz, C4), 136.0 (6C, s, C9), 135.8 (12C, t, <sup>3</sup>J<sub>CP</sub> = 5.2 Hz, C8), 132.8 (4C, d, <sup>3</sup>J<sub>CP</sub> = 11.8 Hz, C3), 131.1 (2C, dt, <sup>2</sup>J<sub>CP</sub> = 9.4 Hz, <sup>3</sup>J<sub>CF</sub> = 5.0 Hz C2), 131.0 (12C, d, <sup>2</sup>J<sub>CP</sub> = 6.5 Hz, C7), 123.4 (2C, ddt, <sup>1</sup>J<sub>CP</sub> = 118.2 Hz, <sup>2</sup>J<sub>CF</sub> = 17.1 Hz, <sup>3</sup>J<sub>CP</sub> = 2.2 Hz, C1), 121.4 (6C, dm, <sup>1</sup>J<sub>CP</sub> = 93.4 Hz, C6), 122.3 (2C, <sup>1</sup>J<sub>CF</sub> = 321.2 Hz, CF<sub>3</sub>), 22.0 (1C, <sup>1</sup>J<sub>CP(P-F)}</sub> = 98.0 Hz, <sup>1</sup>J<sub>CP(PPh3)}</sub> = 76.1 Hz, <sup>2</sup>J<sub>CF</sub> = 22.9 Hz, C5); **<sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 300 K, in ppm):**  $\delta$  = –79.1 (6F, s, <sup>1</sup>J<sub>FC</sub> = 321.2 Hz, CF<sub>3</sub>), –97.5 (1F, dt, <sup>1</sup>J<sub>FP</sub> = 1012.1 Hz, <sup>3</sup>J<sub>FP</sub> = 15.1 Hz, P–F); **<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>3</sub>CN, 300 K, in ppm):**  $\delta$  = 85.3 (1P, dt, <sup>1</sup>J<sub>PF</sub> = 1012.1 Hz, <sup>2</sup>J<sub>PP</sub> = 20.8 Hz, P–F), 23.8 (2P, dd, <sup>2</sup>J<sub>PP</sub> = 23.80 Hz, <sup>3</sup>J<sub>PF</sub> = 15.0 Hz, PPh<sub>3</sub>); **elemental analysis:** calculated for C<sub>51</sub>H<sub>40</sub>F<sub>7</sub>O<sub>6</sub>P<sub>3</sub>S<sub>2</sub>: C: 59.0, H: 3.9, S: 6.2, found: C: 59.0, H: 3.7, S: 6.2.

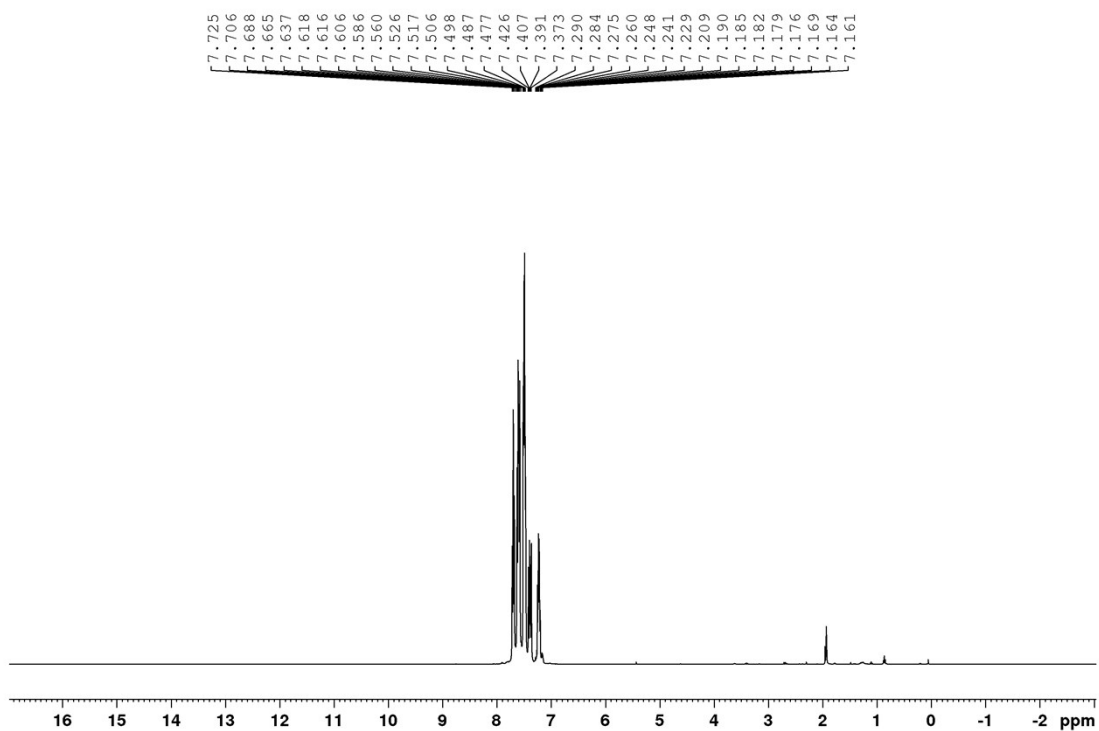


Figure 2.5.1.  $^1\text{H}$  NMR spectrum of  $\mathbf{8}[\text{OTf}]_2$  ( $\text{CD}_3\text{CN}$ , 300 K).

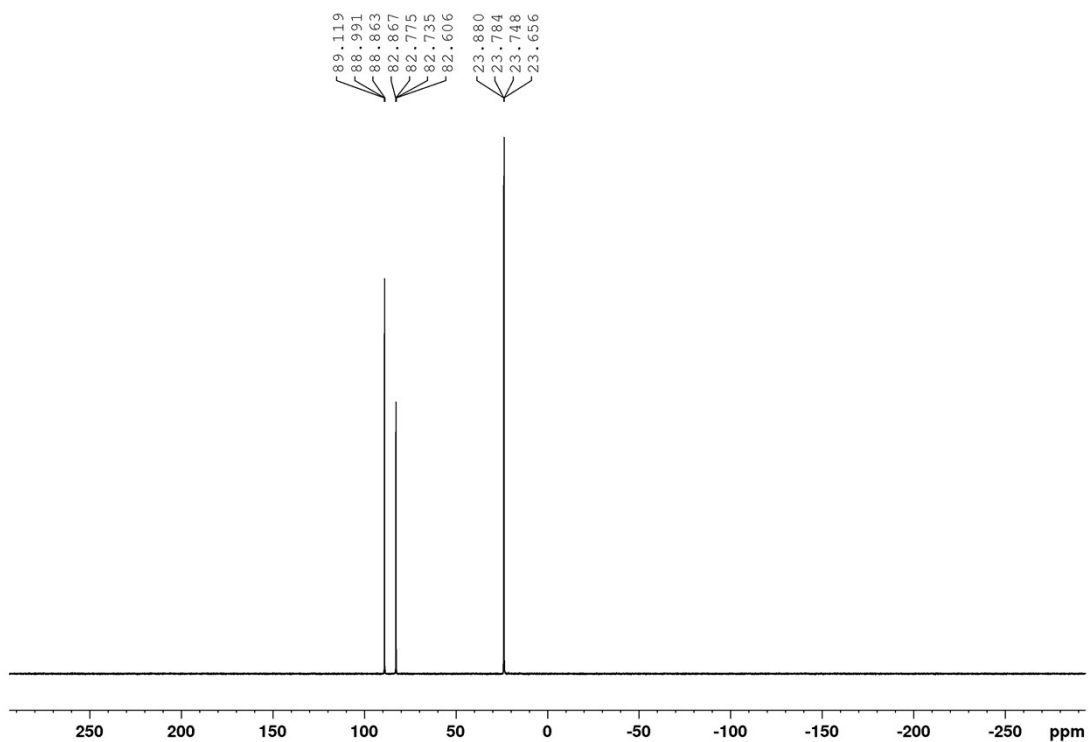
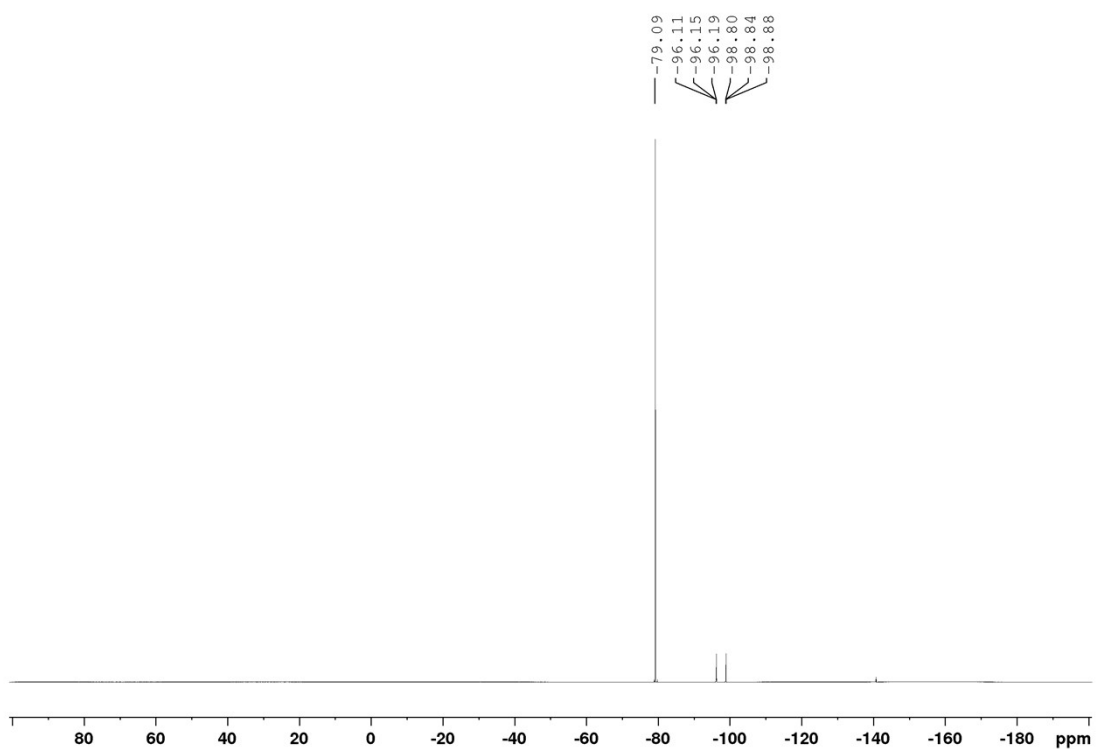
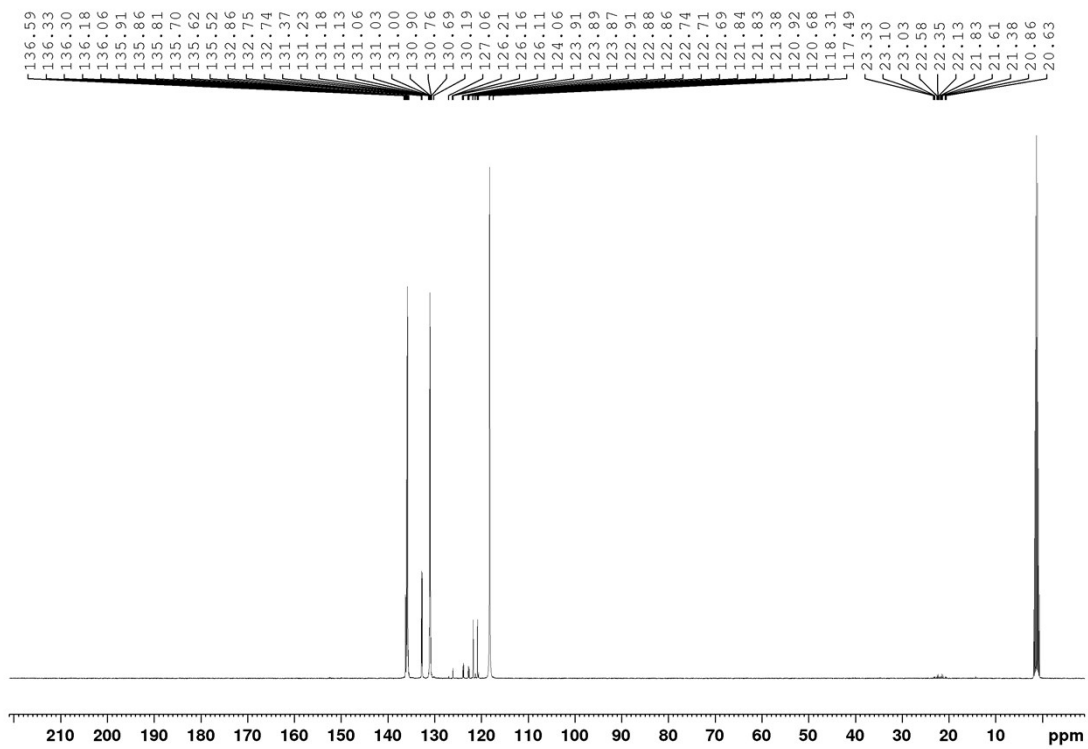


Figure 2.5.2.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\mathbf{8}[\text{OTf}]_2$  ( $\text{CD}_3\text{CN}$ , 300 K).



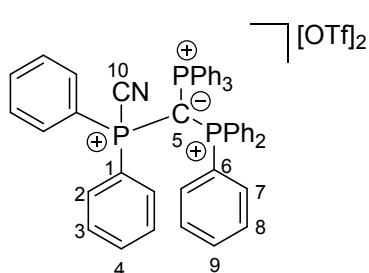


**Figure 2.5.3.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of  $8[\text{OTf}]_2$  ( $\text{CD}_3\text{CN}$ , 300 K).



**Figure 2.5.4.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $8[\text{OTf}]_2$  ( $\text{CD}_3\text{CN}$ , 300 K).

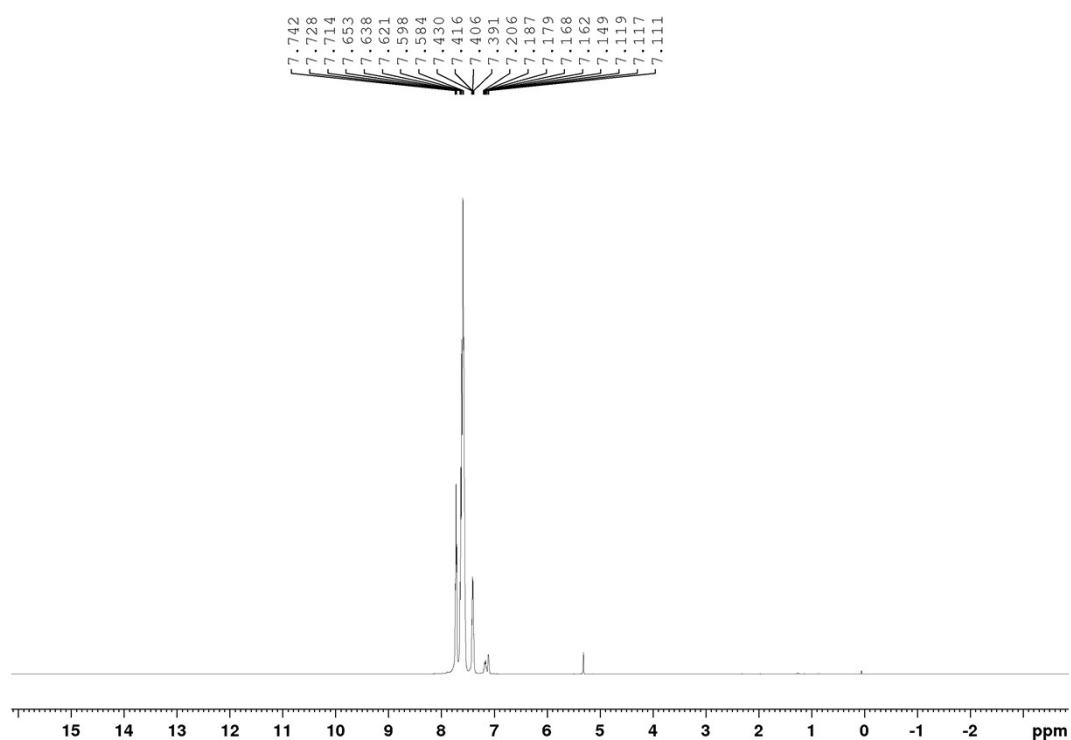
## 2.6. Synthesis of 9[OTf]<sub>2</sub>



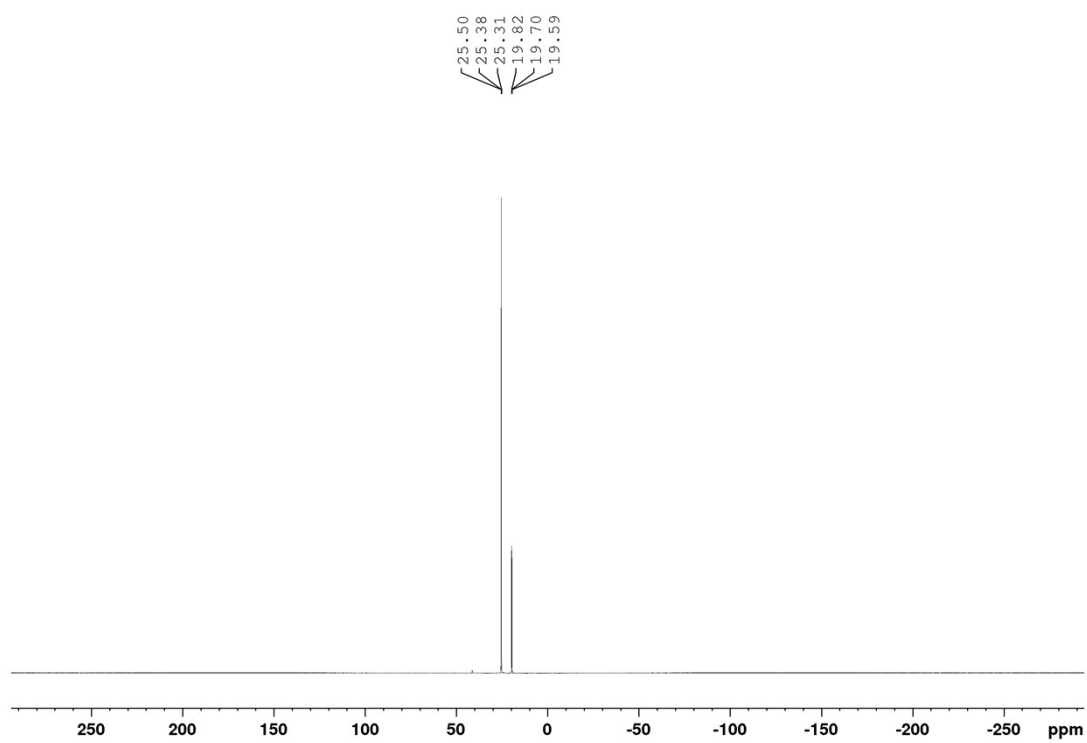
A suspension of **1**[OTf]<sub>2</sub> (584 mg, 0.50 mmol) in *o*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (3 mL) was combined with Me<sub>3</sub>SiCN (55 mg, 0.55 mmol) and the reaction mixture was stirred for 12 h at ambient temperature. After filtration and washing with *o*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (3 x 1 mL) and *n*-pentane (2 x 1 mL), the colorless solid was dried *in vacuo*. The product was obtained as analytical pure, colorless and moisture

sensitive powder.

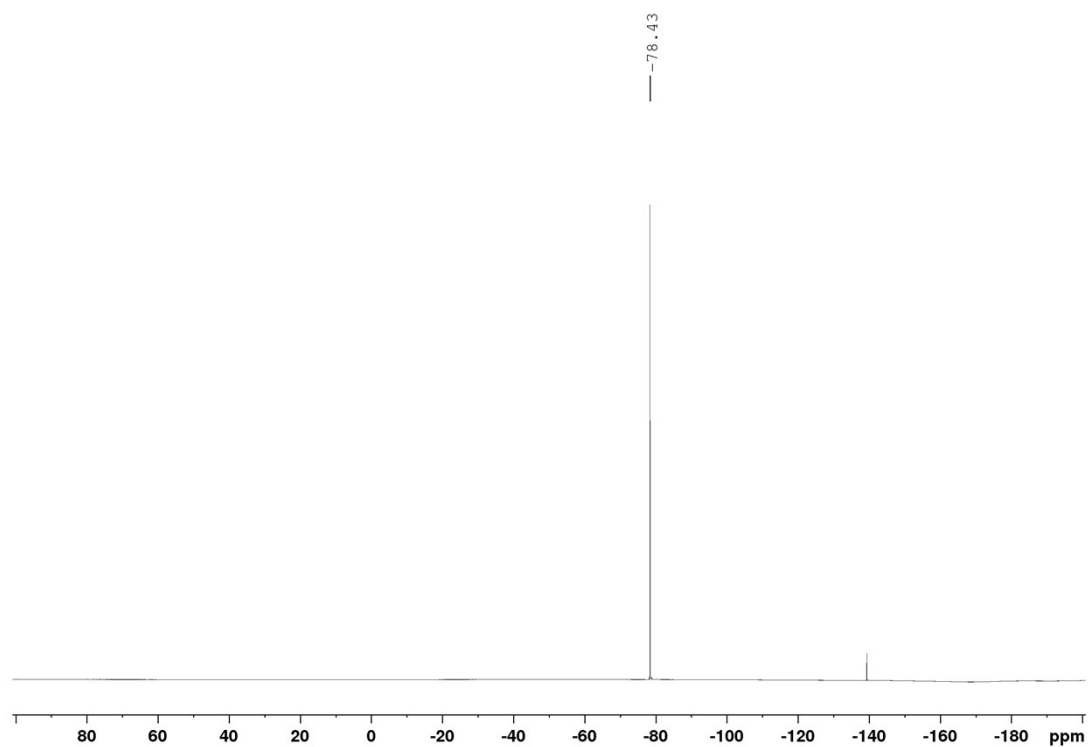
**Yield:** 459 mg (88%); **mp.:** 231 °C; **Raman (34 mW, 450 scans, 300 K, in cm<sup>-1</sup>):**  $\nu = 3084(8), 3067(100), 2192(28), 1585(86), 1440(6), 1262(6), 1223(8), 1188(14), 1165(17), 1097(33), 1031(50), 1024(6), 1003(92), 756(17), 705(11), 615(22), 573(8), 348(14), 313(11), 269(25), 240(11), 217(11)$ ; **IR (300 K, ATR, in cm<sup>-1</sup>):**  $\nu = 2191(w), 1585(w), 1504(w), 1482(w), 1438(m), 1286(w), 1275(vw), 1259(m), 1223(w), 1191(w), 1150(m), 1099(m), 1031(vs), 1001(w), 955(s), 925(vs), 762(vw), 745(m), 718(m), 686(m), 636(vs), 614(vw), 573(w), 532(m), 516(vw), 493(s), 466(vw), 419(w)$ ; **<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, in ppm):**  $\delta = 7.73$  (6H, t, <sup>3</sup>J<sub>HH</sub> = 7.15 Hz, C9–H), 7.66–7.55 (30H, m, C4–H / C2–H / C7–H, C8–H), 7.44–7.39 (4H, m, C3–H); **<sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, in ppm):**  $\delta = 136.5$  (2C, d, <sup>4</sup>J<sub>CP</sub> = 3.4 Hz, C4), 136.0 (6C, s, C9), 135.4 (12C, t, <sup>2</sup>J<sub>CP</sub> = 5.4 Hz, C7), 133.2 (12C, d, <sup>3</sup>J<sub>CP</sub> = 12.7 Hz, C8), 131.7 (4C, d, <sup>3</sup>J<sub>CP</sub> = 15.0 Hz, C3), 131.0 (4C, t, <sup>2</sup>J<sub>CP</sub> = 6.4 Hz, C2) 121.8 (2C, q, <sup>1</sup>J<sub>CF</sub> = 321.4 Hz, C-OTf), 120.8 (6C, dt, <sup>1</sup>J<sub>CP</sub> = 93.6 Hz, <sup>3</sup>J<sub>CP</sub> = 1.7 Hz, C6), 118.5 (2C, dt, <sup>1</sup>J<sub>CP</sub> = 102.9 Hz, <sup>3</sup>J<sub>CP</sub> = 1.7 Hz C1), 113.7 (1C, d, <sup>1</sup>J<sub>CP</sub> = 85.0 Hz, CN), 8.7 (1C, dt, <sup>1</sup>J<sub>CP</sub> = 87.7 Hz, <sup>1</sup>J<sub>CP</sub> = 75.6 Hz, C5); **<sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, in ppm):**  $\delta = -78.4$  (6F, s, <sup>1</sup>J<sub>FC</sub> = 321.7 Hz, CF<sub>3</sub>–OTf); **<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300K, in ppm):**  $\delta = 25.5$  (2P, d, <sup>2</sup>J<sub>PP</sub> = 23.4 Hz), 19.7 (1P, t, <sup>2</sup>J<sub>PP</sub> = 23.4 Hz); **elemental analysis:** calculated for C<sub>52</sub>H<sub>40</sub>F<sub>6</sub>O<sub>6</sub>P<sub>3</sub>S<sub>3</sub>: C: 59.7, H: 3.9, N: 1.3, S: 6.1, found: C: 60.1, H: 3.9, N: 1.3, S: 5.8.



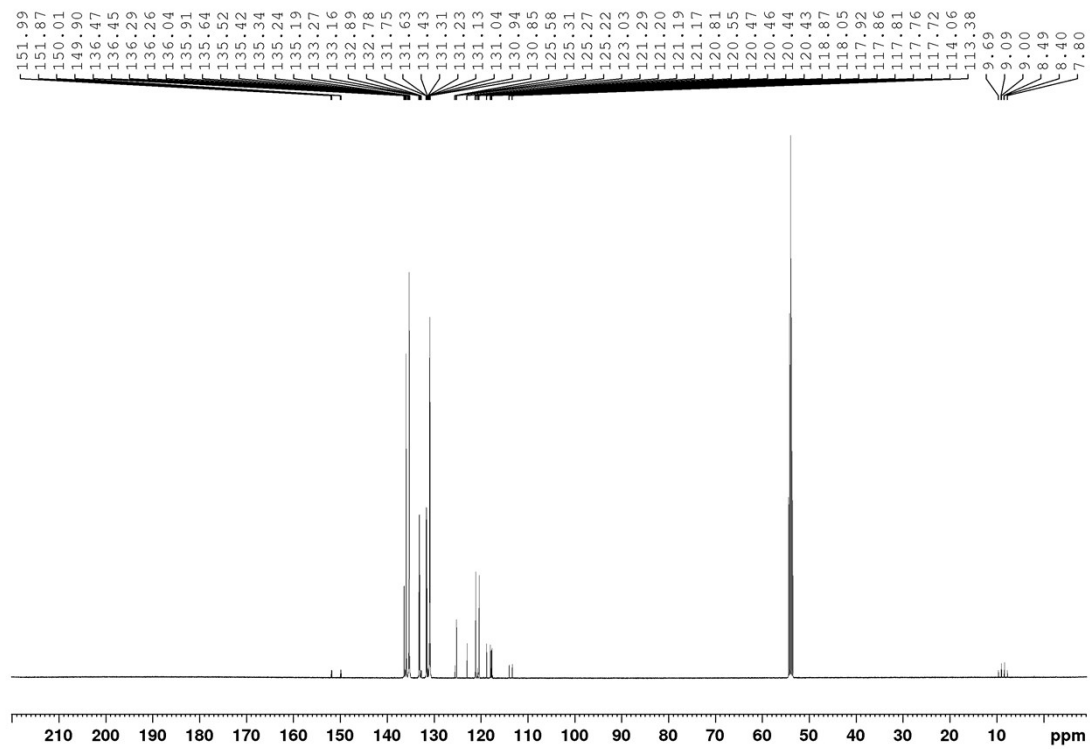
**Figure 2.6.1.**  $^1\text{H}$  NMR spectrum of  $\mathbf{9}[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).



**Figure 2.6.2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $\mathbf{9}[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).

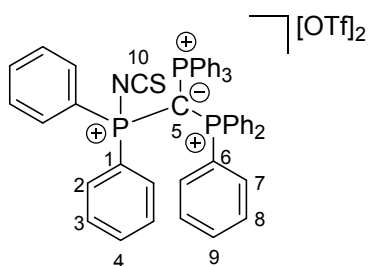


**Figure 2.6.3.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of  $9[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).



**Figure 2.6.4.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $9[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).

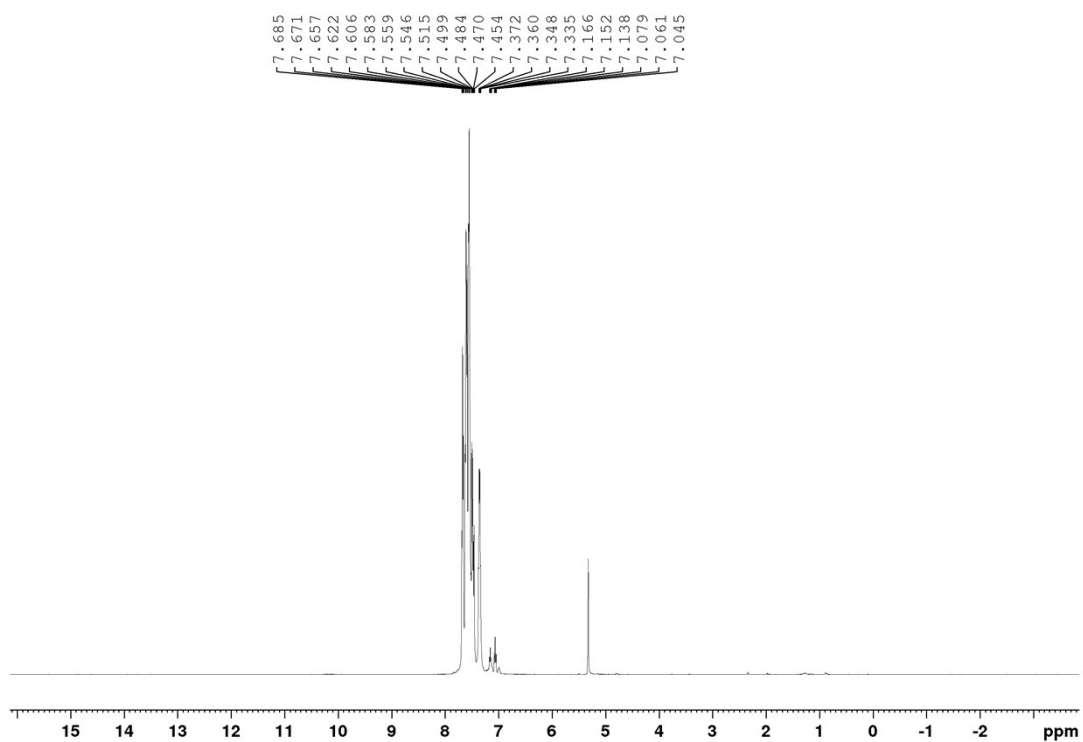
## 2.7. Synthesis of 10[OTf]<sub>2</sub>



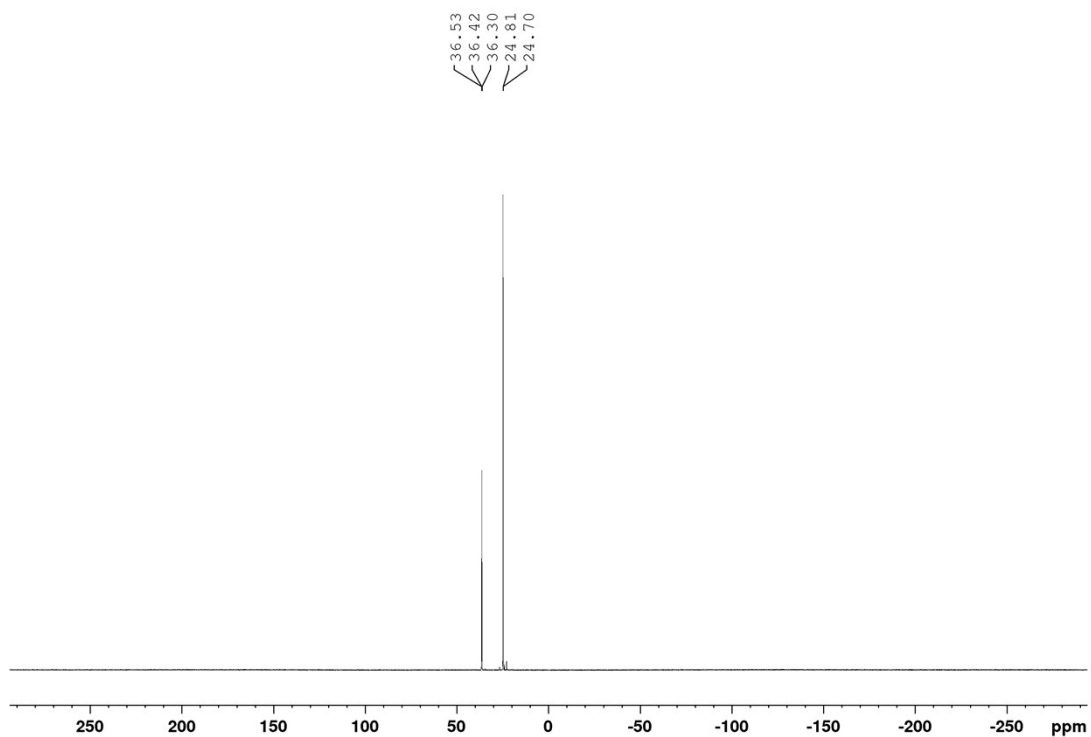
To a solution of **1**[OTf]<sub>2</sub> (350.7 mg, 0.30 mmol) in CH<sub>3</sub>CN (3 mL), solid NH<sub>4</sub>SCN (22.8 mg, 0.30 mmol) was added and the reaction mixture was stirred for 2 h at ambient temperature. After removal of all volatiles *in vacuo*, the residue was suspended in *o*-C<sub>6</sub>H<sub>4</sub>F<sub>2</sub> (2 mL) for 15 minutes and was filtered.

The addition of C<sub>6</sub>H<sub>5</sub>F (2 mL) to the filtrate resulted in the formation of colorless precipitate. After filtration and washing with C<sub>6</sub>H<sub>5</sub>F (2 x 1 mL) the solid was dried *in vacuo*. The product was obtained as analytically pure, colorless powder.

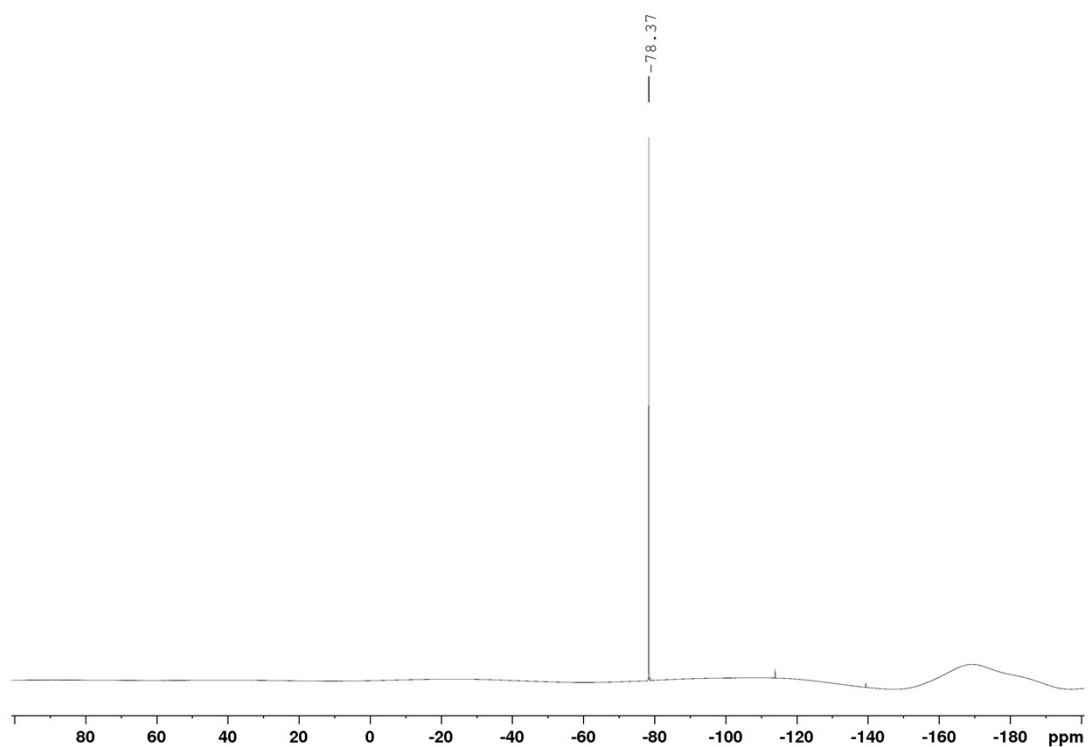
**Yield:** 237 mg (73%); **mp.:** decomp.: >230 °C; **Raman (40 mW, 450 scans, 300 K, in cm<sup>-1</sup>):**  $\nu = 3070(100), 1584(48), 1223(8), 1187(4), 1166(10), 1096(12), 1028(68), 1001(66), 805(8), 753(10), 705(4), 614(8), 347(6), 312(6), 266(10), 243(10)$ ; **IR (300 K, ATR, in cm<sup>-1</sup>):**  $\nu = 3067(\text{vw}), 1956(\text{m}), 1589(\text{w}), 1485(\text{w}), 1438(\text{m}), 1278(\text{w}), 1258(\text{s}), 1222(\text{m}), 1190(\text{vw}), 1142(\text{m}), 1096(\text{s}), 1030(\text{vs}), 999(\text{w}), 963(\text{m}), 938(\text{m}), 846(\text{vw}), 805(\text{w}), 773(\text{w}), 748(\text{s}), 720(\text{w}), 688(\text{s}), 636(\text{s}), 605(\text{w}), 584(\text{w}), 571(\text{w}), 536(\text{vw}), 519(\text{vw}), 494(\text{m}), 463(\text{vw}), 430(\text{vw})$ ; **<sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, in ppm):**  $\delta = 7.67$  (6H, t, <sup>3</sup>J<sub>HH</sub> = 6.72 Hz, C9–H), 7.63–7.57 (12H, m, C7–H / C8–H), 7.57–7.51 (12H, m, C7–H / C8–H), 7.49–7.46 (6H, m, <sup>3</sup>J<sub>HH</sub> = 8.25 Hz, <sup>3</sup>J<sub>HH</sub> = 7.76 Hz, C4–H / C2–H), 7.36 (4H, dt, <sup>3</sup>J<sub>HH</sub> = 6.21 Hz, <sup>3</sup>J<sub>HH</sub> = 5.75 Hz, C3–H); **<sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, in ppm):**  $\delta = 135.5$  (6C, m, C9), 135.5 (2C, m, C4), 135.4 (12C, t, <sup>2</sup>J<sub>CP</sub> = 5.2 Hz, C7 / C8), 132.7 (4C, d, <sup>2</sup>J<sub>CP</sub> = 12.7 Hz, C2), 131.0 (4C, d, <sup>3</sup>J<sub>CP</sub> = 14.8 Hz, C3), 124.2 (2C, dt, <sup>1</sup>J<sub>CP</sub> = 113.7 Hz, <sup>3</sup>J<sub>CP</sub> = 2.2 Hz C1), 121.8 (2C, q, <sup>1</sup>J<sub>CF</sub> = 321.2 Hz, CF<sub>3</sub>), 121.7 (6C, dt, <sup>1</sup>J<sub>CP</sub> = 94.2 Hz, <sup>3</sup>J<sub>CP</sub> = 2.0 Hz, C6), 115.7 (1C, d, <sup>2</sup>J<sub>CP</sub> = 20.8 Hz, NCS), 15.1 (1C, dt, <sup>1</sup>J<sub>CP</sub> = 97.8 Hz, <sup>1</sup>J<sub>CP</sub> = 77.4 Hz, C5); **<sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, in ppm):**  $\delta = -78.4$  (6F, s, <sup>1</sup>J<sub>FC</sub> = 321.8 Hz, CF<sub>3</sub>); **<sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 300 K, in ppm):**  $\delta = 36.4$  (1P, t, <sup>2</sup>J<sub>PP</sub> = 23.6 Hz), 24.8 (2P, d, <sup>2</sup>J<sub>PP</sub> = 23.6 Hz); **elemental analysis:** calculated for C<sub>52</sub>H<sub>40</sub>F<sub>6</sub>O<sub>6</sub>P<sub>3</sub>S<sub>3</sub>·½C<sub>6</sub>H<sub>5</sub>F: C: 58.7, H: 3.8, N: 1.2, S: 8.5, found: C: 58.7, H: 3.8, N: 1.2, S: 8.9.



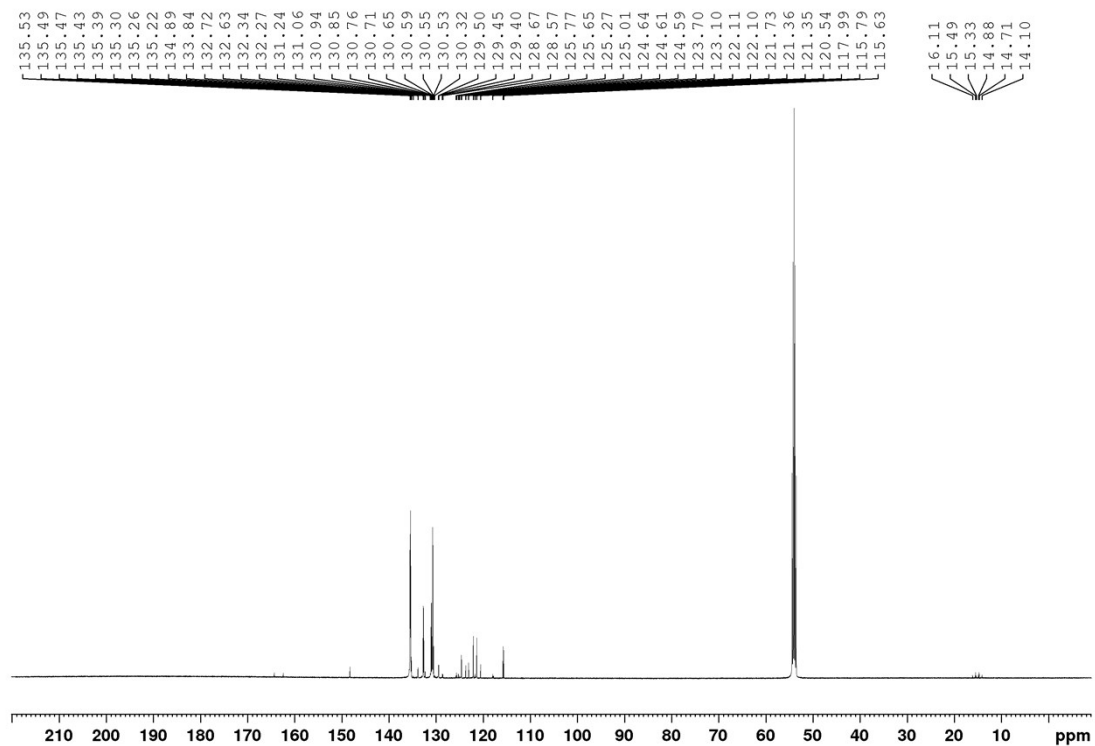
**Figure 2.7.1.**  $^1\text{H}$  NMR spectrum of  $10[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).



**Figure 2.7.2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of  $10[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).



**Figure 2.7.3.**  $^{19}\text{F}$  NMR spectrum of  $10[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).



**Figure 2.7.4.**  $^{13}\text{C}$  NMR spectrum of  $10[\text{OTf}]_2$  ( $\text{CD}_2\text{Cl}_2$ , 300 K).

2.8. Variable temperature  $^{31}\text{P}\{^1\text{H}\}$ - and  $^{19}\text{F}\}$  NMR spectroscopy of  $1[\text{OTf}]_2$

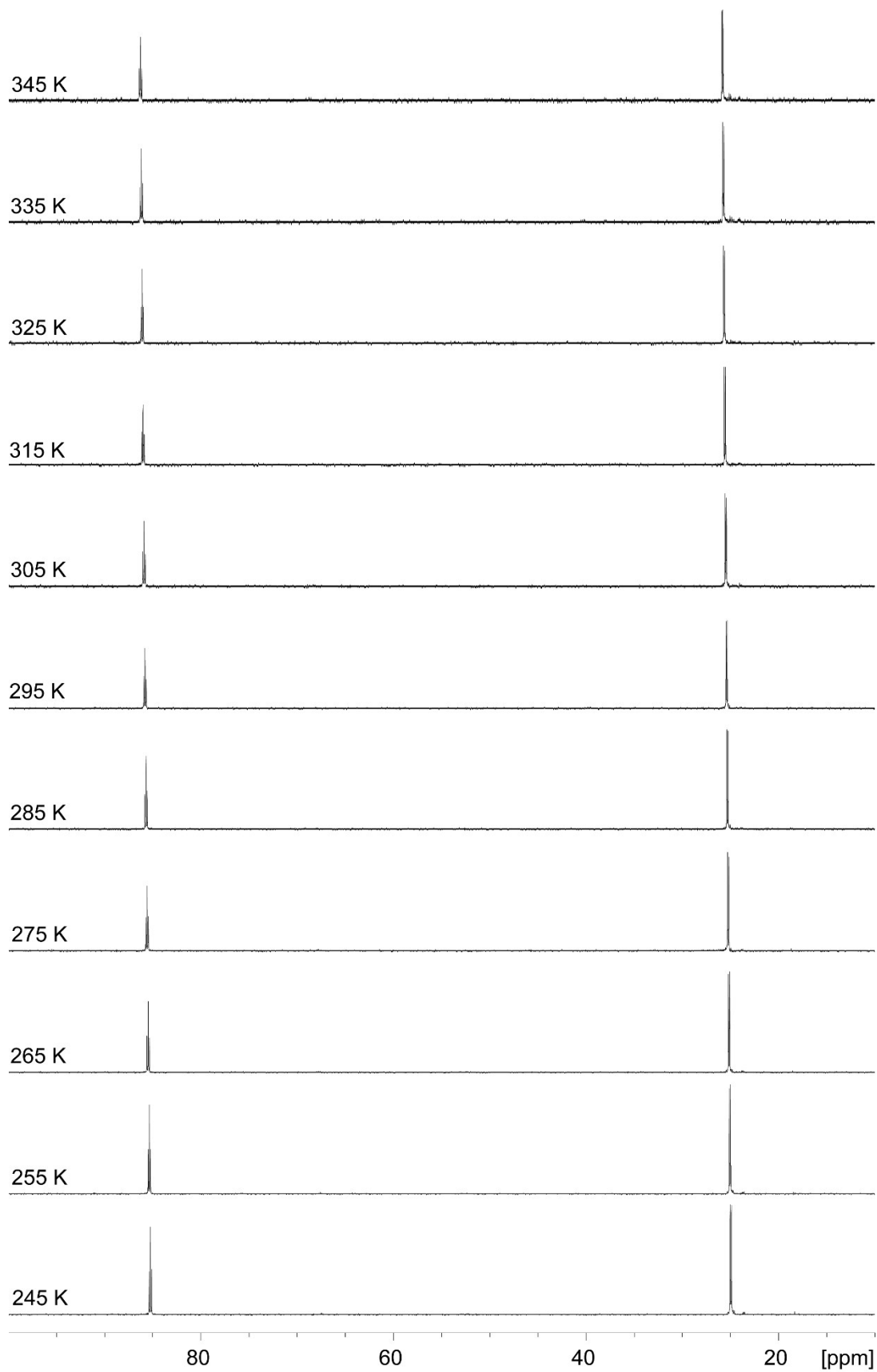


Figure 2.8.1.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of  $1[\text{OTf}]_2$  ( $\text{CH}_2\text{Cl}_2$ , 245 K to 345 K).

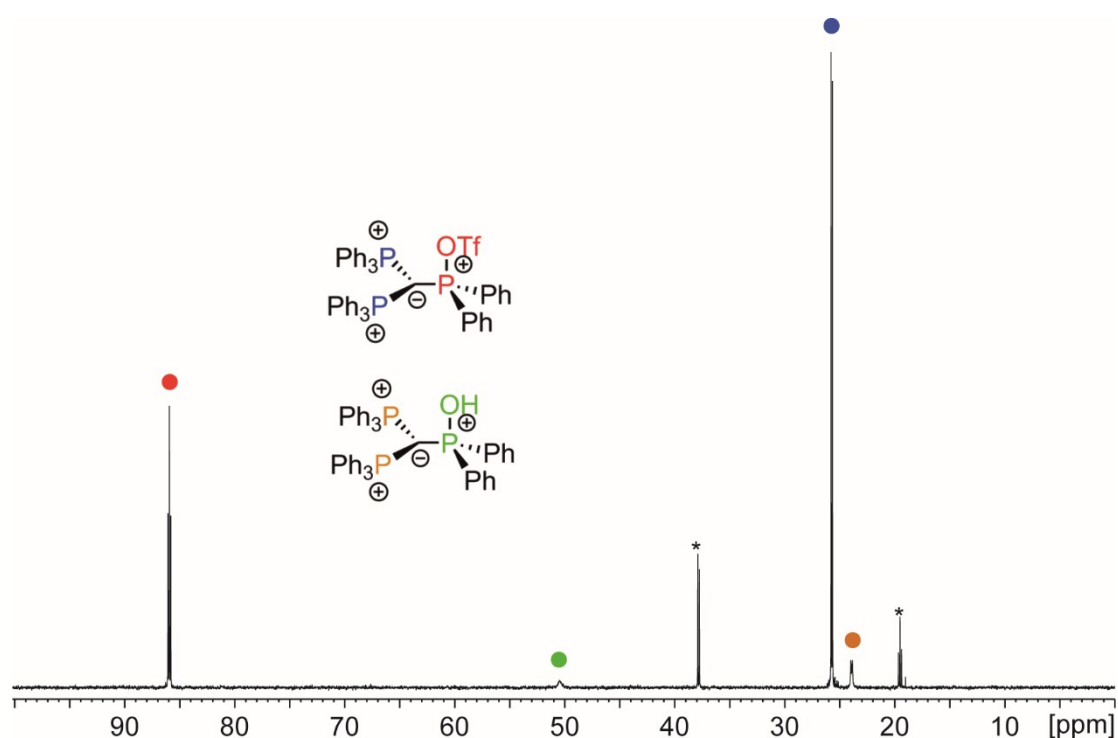




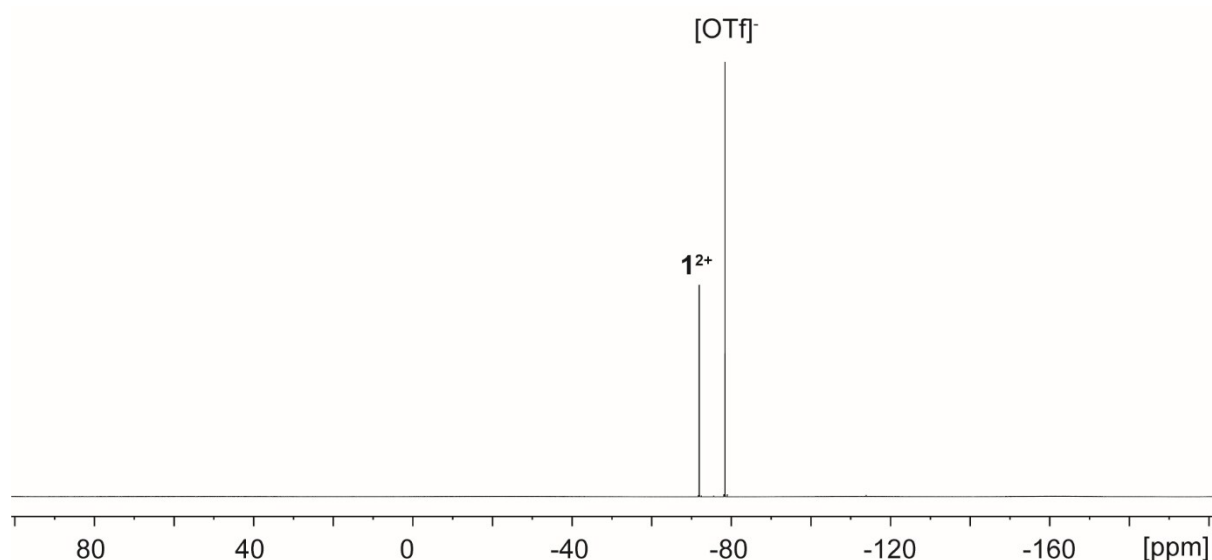
**Figure 2.8.2.**  $^{19}\text{F}$  NMR spectra of  $1[\text{OTf}]_2$  ( $\text{CH}_2\text{Cl}_2$ , 245 K to 345 K).

## 2.9. Reaction of 3[OTf] with *in situ* generated PhI(OTf)

A solution of Me<sub>3</sub>SiOTf (91 mg, 0.10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) was added to a solution of PhI(OAc)<sub>2</sub> (35 mg, 0.10 mmol) followed by the addition of 3[OTf]. The colorless solution was stirred for 45 minutes at ambient temperature. <sup>19</sup>F and <sup>31</sup>P NMR spectrum of the reaction mixture show the formation of 1[OTf]<sub>2</sub> (72%, quantified by <sup>31</sup>P NMR spectroscopy), 8[OTf]<sub>2</sub> (14%, quantified by <sup>31</sup>P NMR spectroscopy) and one unidentified product (A<sub>2</sub>X spin system: δ(P<sub>X</sub>) = 37.8 ppm, δ(P<sub>A</sub>) = 19.5 ppm, <sup>2</sup>J<sub>PP</sub> = 23.5 Hz, 14%, quantified by <sup>31</sup>P NMR spectroscopy).



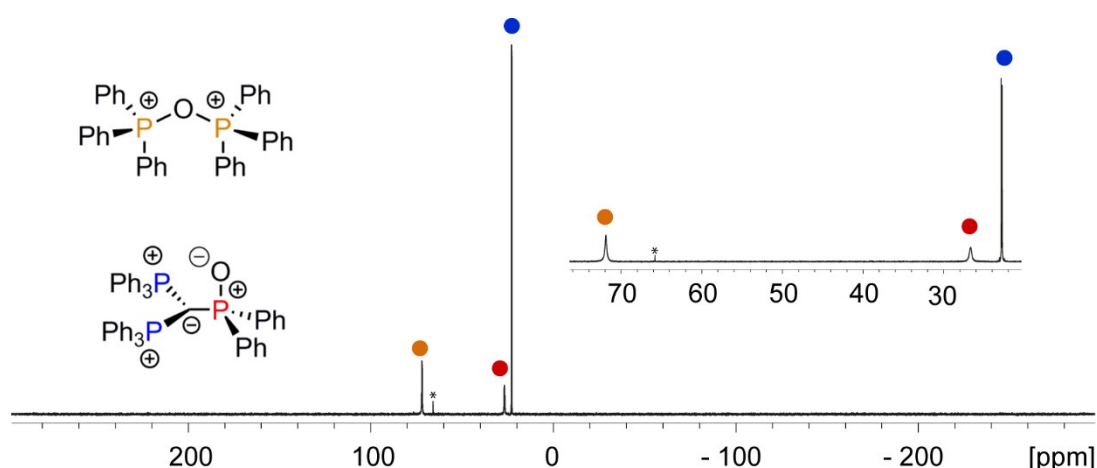
**Figure 2.9.1.** <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction mixture of 3[OTf] with *in situ* generated PhI(OTf)<sub>2</sub> (CH<sub>2</sub>Cl<sub>2</sub> with C<sub>6</sub>D<sub>6</sub>-capillary, 300 K; unidentified side-product is marked with asterisk).



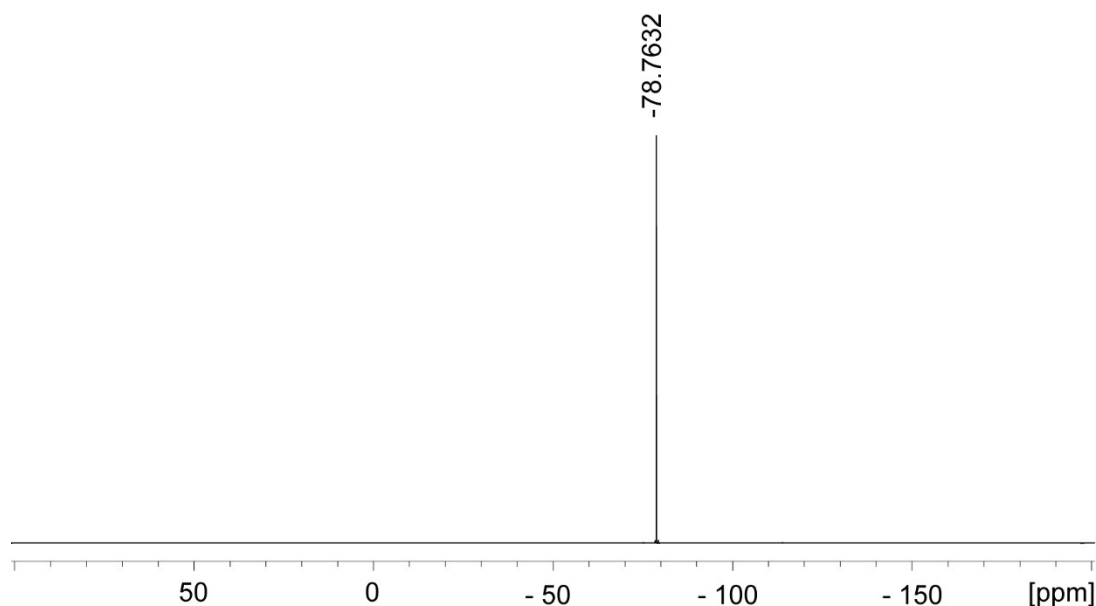
**Figure 2.9.2.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of the reaction mixture of  $3[\text{OTf}]$  with *in situ* generated  $\text{PhI}(\text{OTf})_2$  ( $\text{CH}_2\text{Cl}_2$  with  $\text{C}_6\text{D}_6$ -capillary, 300 K).

## 2.10. Reaction of $1[\text{OTf}]_2$ with $\text{Ph}_3\text{PO}$

To a solution of  $1[\text{OTf}]_2$  (58.4 mg, 0.05 mmol) in  $\text{CH}_2\text{Cl}_2$ , solid  $\text{Ph}_3\text{PO}$  (28 mg, 0.1 mmol) was added and the reaction mixture was stirred for 1 h at ambient temperature.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction mixture shows complete consumption of  $1[\text{OTf}]_2$  and quantitative formation to the HENDRICKSON reagent ( $(\text{Ph}_3\text{P})_2\text{O}(\text{OTf})_2$ :  $\delta = 71.9$  ppm)<sup>[3]</sup> and  $4[\text{OTf}]$  ( $\delta(\text{P}(\text{O})\text{Ph}_2) = 26.7$  ppm;  $\delta(\text{PPh}_3) = 22.8$  ppm).  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum displays only one singlet resonance at  $\delta = -78.8$  ppm for the non-coordinating OTf anion.

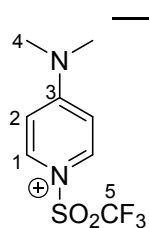


**Figure 2.10.1.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction mixture of  $1[\text{OTf}]_2$  with  $\text{Ph}_3\text{PO}$  ( $\text{CH}_2\text{Cl}_2$  with  $\text{C}_6\text{D}_6$ -capillary, 300 K; unidentified side-product (<1%) is marked with asterisk).



**Figure 2.10.2.**  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum of the reaction mixture of  $1[\text{OTf}]_2$  with  $\text{Ph}_3\text{PO}$  ( $\text{CD}_2\text{Cl}_2$  with  $\text{C}_6\text{D}_6$ -capillary, 300 K).

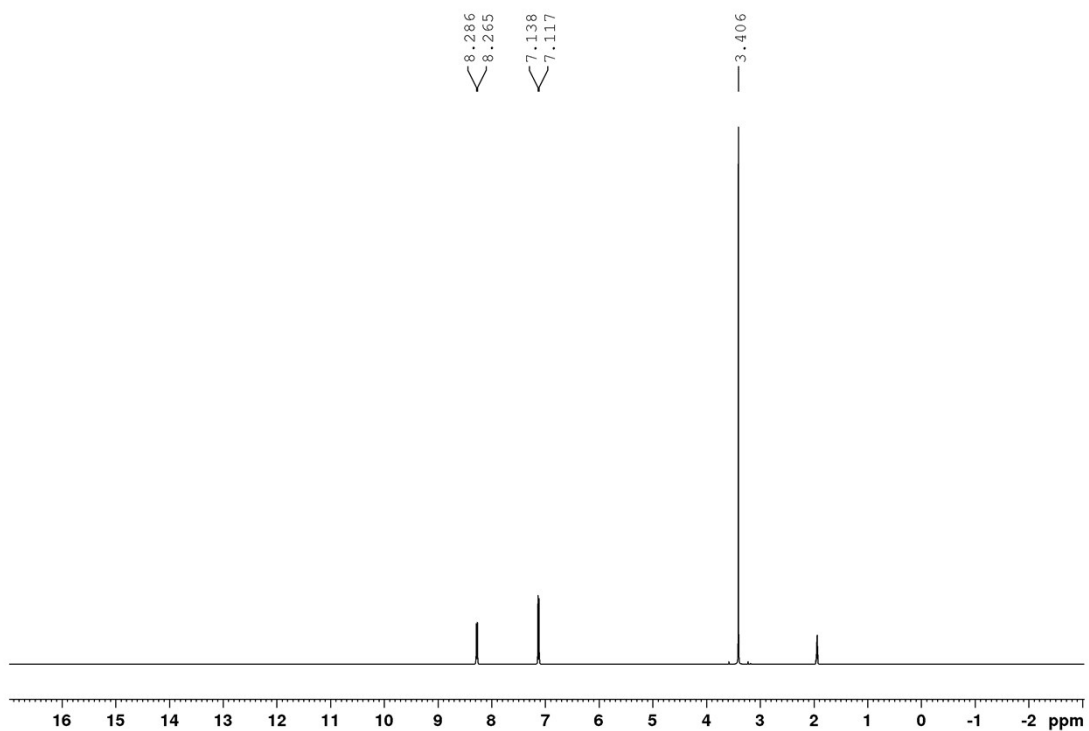
### 2.11. Reaction of $1[\text{OTf}]_2$ with 4-dimethylaminopyridine



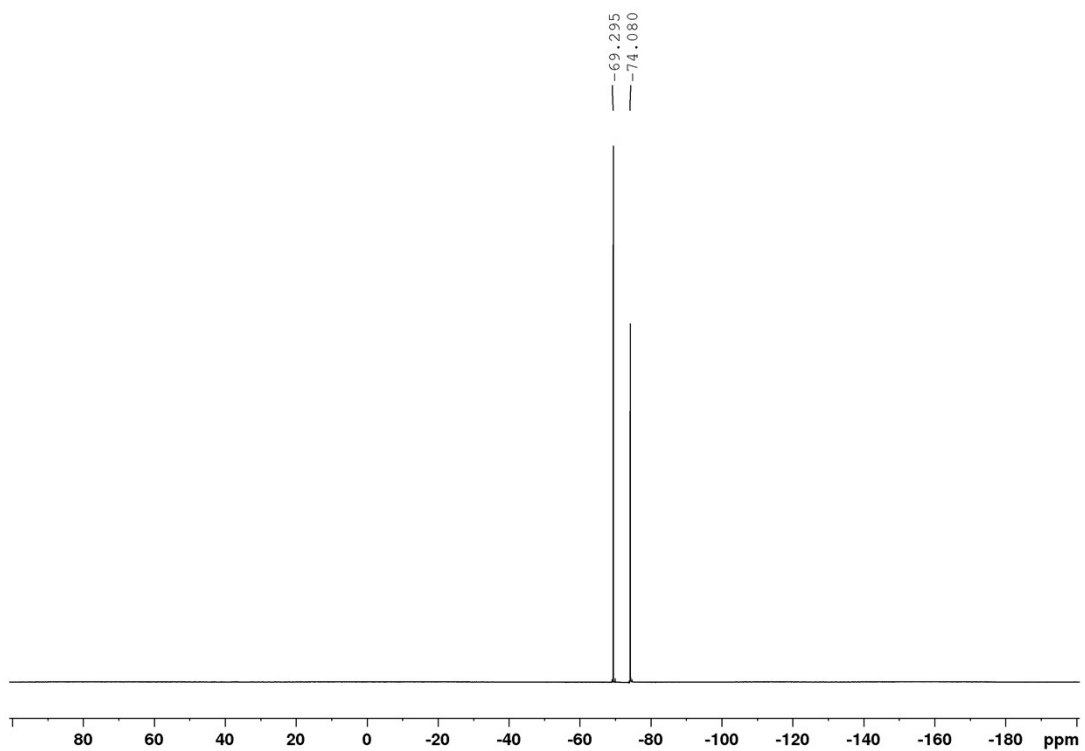
To a solution of 4-dimethylaminopyridine (12.0 mg, 0.1 mmol) in *o*- $\text{C}_6\text{H}_4\text{F}_2$  (0.5 mL), a solution of  $1[\text{OTf}]_2$  (117.0 mg, 0.1 mmol) in *o*- $\text{C}_6\text{H}_4\text{F}_2$  (0.5 mL) was added and the reaction mixture was stirred for 2 h at ambient temperature. After filtration of the resulting suspension and washing with *o*- $\text{C}_6\text{H}_4\text{F}_2$  (1 mL) the colorless solid was dried *in vacuo*. The product was

obtained as analytical pure, colorless and moisture sensitive powder.

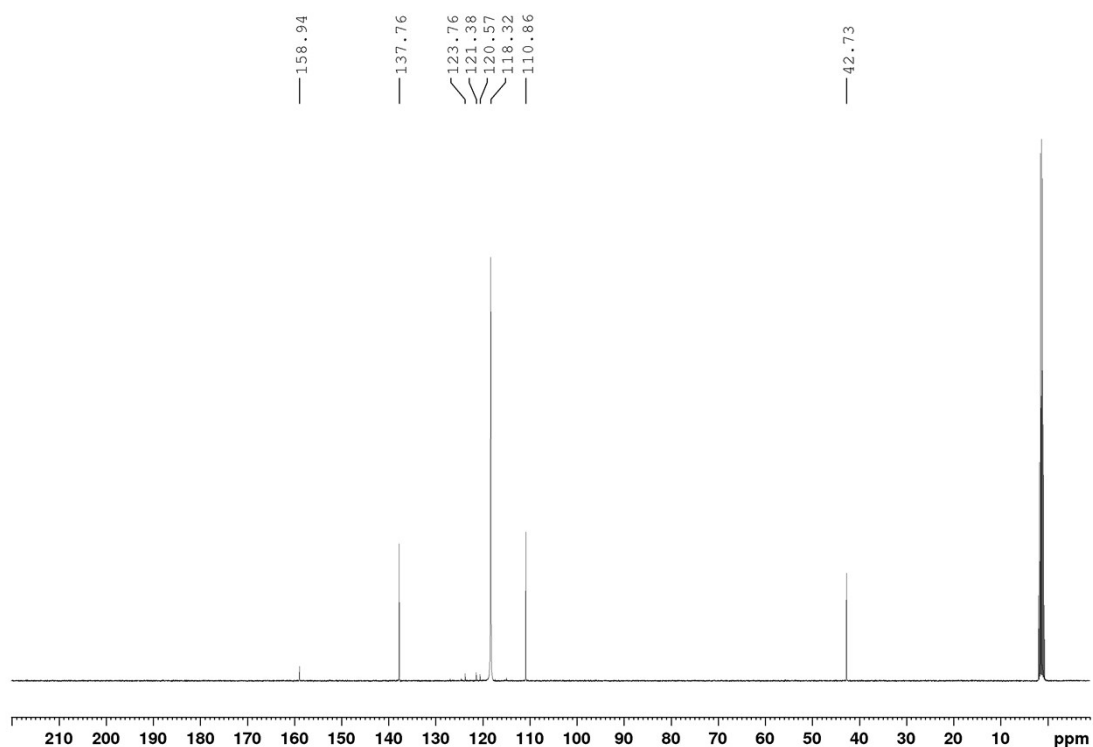
**Yield:** 36 mg (90%); **mp.:** 194°C; **Raman (50 mW, 1100 scans, 300 K, in  $\text{cm}^{-1}$ ):** 3125(7), 2947(27), 2827(7), 1645(100), 1591(60), 1554(13), 1409(13), 1246(23), 1228(10), 1034(37), 1008(20), 936(10), 763(67), 648(13), 562(7), 348(7), 316(10), 252(23); **IR (300 K, ATR, in  $\text{cm}^{-1}$ ):** 3072(vw), 1640(m), 1590(w), 1496(w), 1438(m), 1407(vw), 1345(vw), 1264(w), 1220(s), 1153(w), 1126(m), 1031(vs), 1002(vw), 821(m), 780(w), 756(w), 634(vs), 584(m), 560(vw), 507(m), 480(w);  **$^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , 300 K, in ppm):**  $\delta$  = 8.27 (2H, d,  $^3J_{\text{HH}}$  = 8.20 Hz, C1–H), 7.13 (2H, d,  $^3J_{\text{HH}}$  = 8.20 Hz, C2–H), 3.41 (6H, s, C4–H);  **$^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ , 300 K, in ppm):**  $\delta$  = 158.9 (1C, s, C3), 137.8 (2C, s, C1), 122.2 (1C, q,  $^1J_{\text{CF}}$  = 320.7 Hz,  $\text{CF}_3$ ), 119.8 (1C, q,  $^1J_{\text{CF}}$  = 323.3 Hz, C5), 110.9 (2C, s, C2), 42.7 (2C, s, C4);  **$^{19}\text{F}\{^1\text{H}\}$  NMR ( $\text{CD}_3\text{CN}$ , 300 K, in ppm):**  $\delta$  = -74.5 (3F, s,  $^1J_{\text{FC}}$  = 322.5 Hz,  $\text{CF}_3$ ), -79.3 (3F, s,  $^1J_{\text{FC}}$  = 320.8 Hz,  $\text{CF}_3$ ); **elemental analysis:** calculated for  $\text{C}_9\text{H}_{10}\text{F}_6\text{N}_2\text{O}_5\text{S}_2$ : C 26.7, H: 2.5, N: 6.9; S: 15.9, found: C: 27.0, H: 2.5, N: 6.9; S: 15.7.



**Figure 2.11.1.** <sup>1</sup>H NMR spectrum of 5[OTf] (CD<sub>3</sub>CN, 300 K).

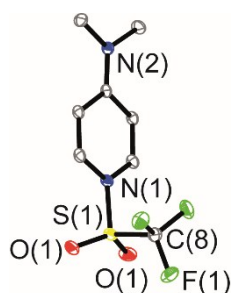


**Figure 2.11.2.** <sup>19</sup>F {<sup>1</sup>H} NMR spectrum of 5[OTf] (CD<sub>3</sub>CN, 300 K).

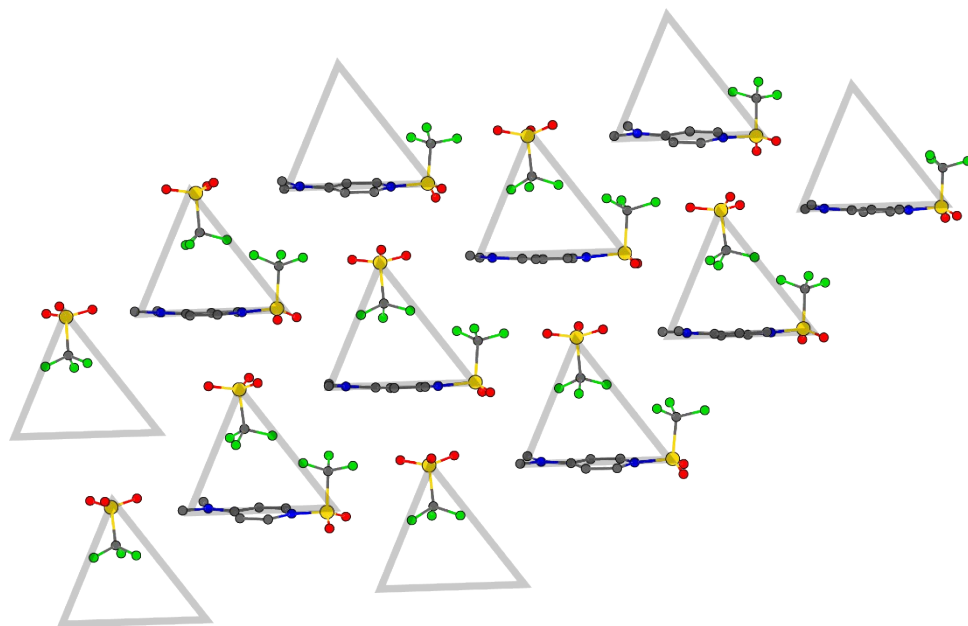


**Figure 2.11.3.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of  $5[\text{OTf}]$  ( $\text{CD}_3\text{CN}$ , 300 K).

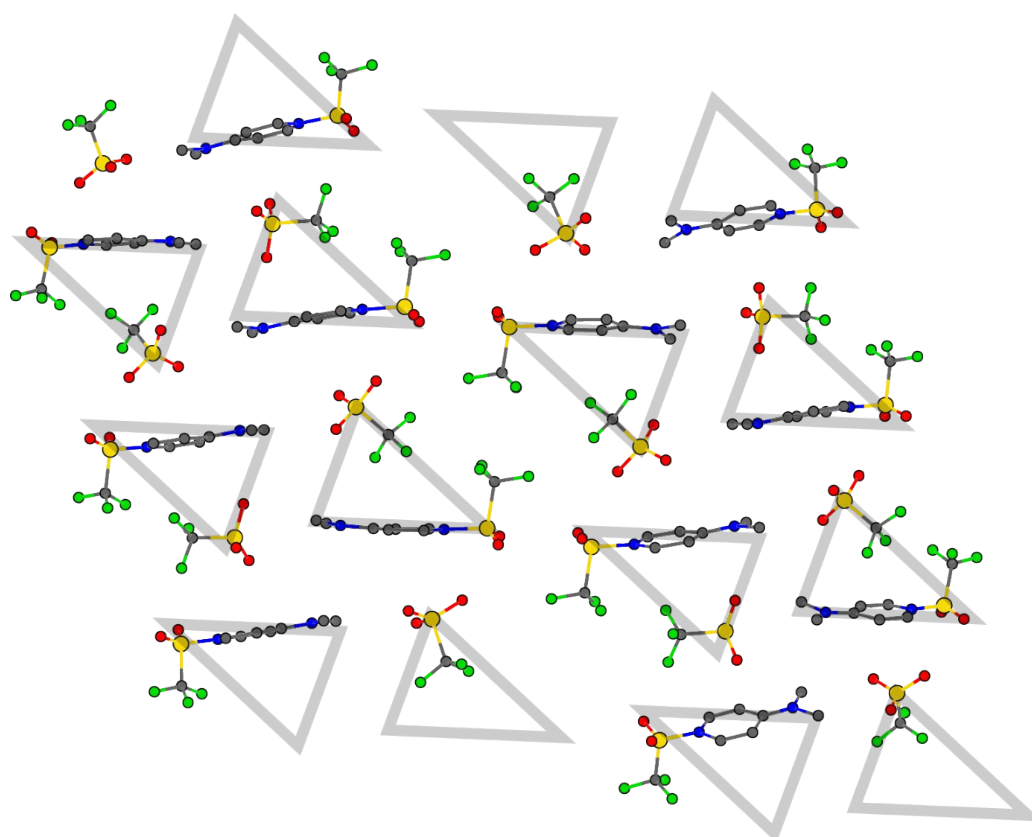
Single crystals suitable for x-ray diffraction were obtained by vapor diffusion of *n*-pentane in a solution of  $\text{CH}_2\text{Cl}_2$  at different temperatures ( $-30\text{ }^\circ\text{C}$  and  $21\text{ }^\circ\text{C}$ ). Colorless needles were observed at  $-30\text{ }^\circ\text{C}$ , whereas colorless blocks were obtained at  $21\text{ }^\circ\text{C}$  (for details, see Table 4.3).



**Figure 2.11.4.** Molecular structure of  $5^+$  in  $5[\text{OTf}]$  ( $P2_1/n$ ) (hydrogen atoms are omitted for clarity and thermal ellipsoids are displayed at 50 % probability); selected bond lengths in Å: S(1)–N(1) 1.679(1), S(1)–O(1) 1.415(1), S(1)–O(2) 1.422(1), S(1)–C(8) 1.852(2), N(2)–C(3) 1.321(2).



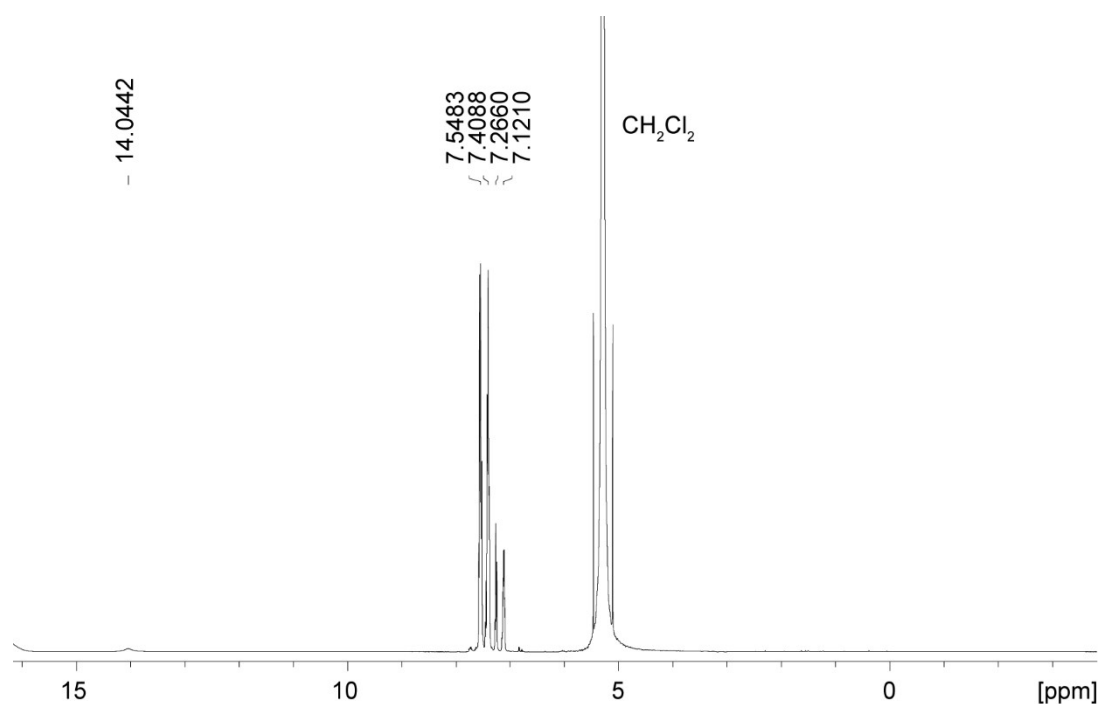
**Figure 2.11.5.** X-Ray structure of one possible polymorph of 5[OTf], which crystallizes in the monoclinic space group  $P2_1/n$  with 4 formula units in the unit cell.



**Figure 2.11.6.** X-Ray structure of a polymorph of 5[OTf], which crystallizes in the monoclinic space group  $C2/c$  with 24 formula units in the unit cell.

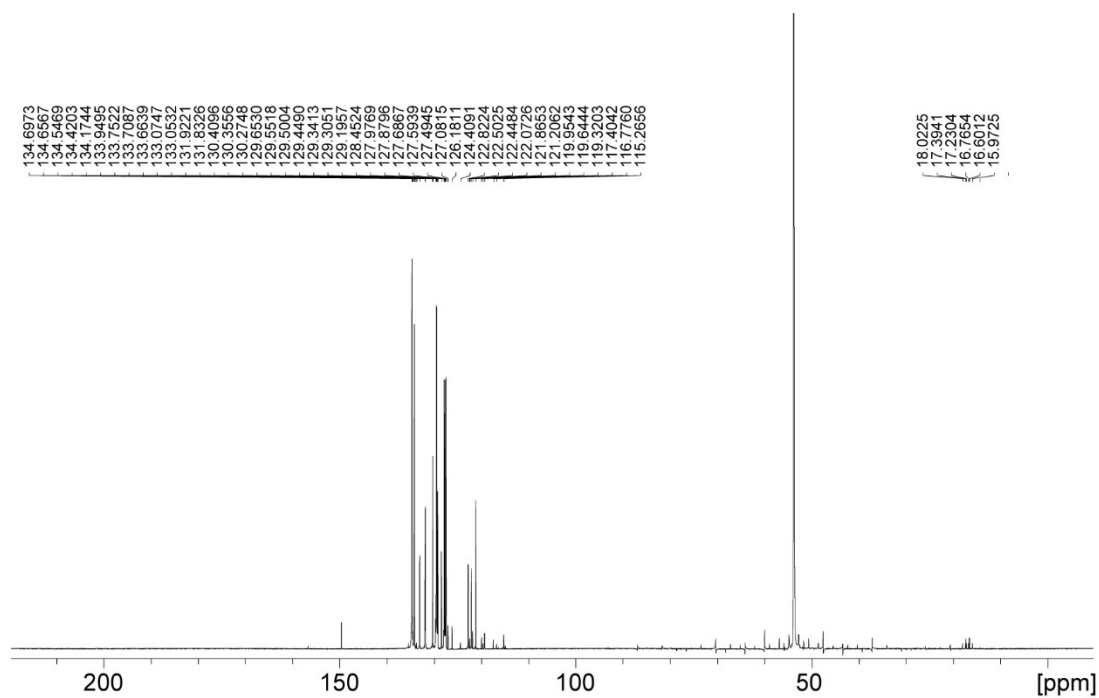
## 2.12. Reaction of $1[\text{OTf}]_2$ with Phenol

To a solution of  $1[\text{OTf}]_2$  (117.0 mg, 0.10 mmol) in  $\text{CH}_2\text{Cl}_2$ , solid Phenol (9.4 mg, 0.10 mmol) was added and the reaction mixture was stirred for 48 h at ambient temperature.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the reaction mixture shows complete consumption of  $1[\text{OTf}]_2$  and quantitative formation to  $8[\text{OTf}]_2$ .  $^{19}\text{F}\{^1\text{H}\}$  NMR spectrum displays a singlet resonance at  $\delta(\text{PhOTf}) = -73.4$  ppm for the PhOTf and a singlet resonance at  $\delta([\text{OTf}]^-) = -78.6$  ppm for the non-coordinating triflate anion.  $^{13}\text{C}\{^1\text{H}\}$  and  $^{19}\text{F}\{\}$  NMR data for PhOTf are consistent with that, presented in ref<sup>[4]</sup>.

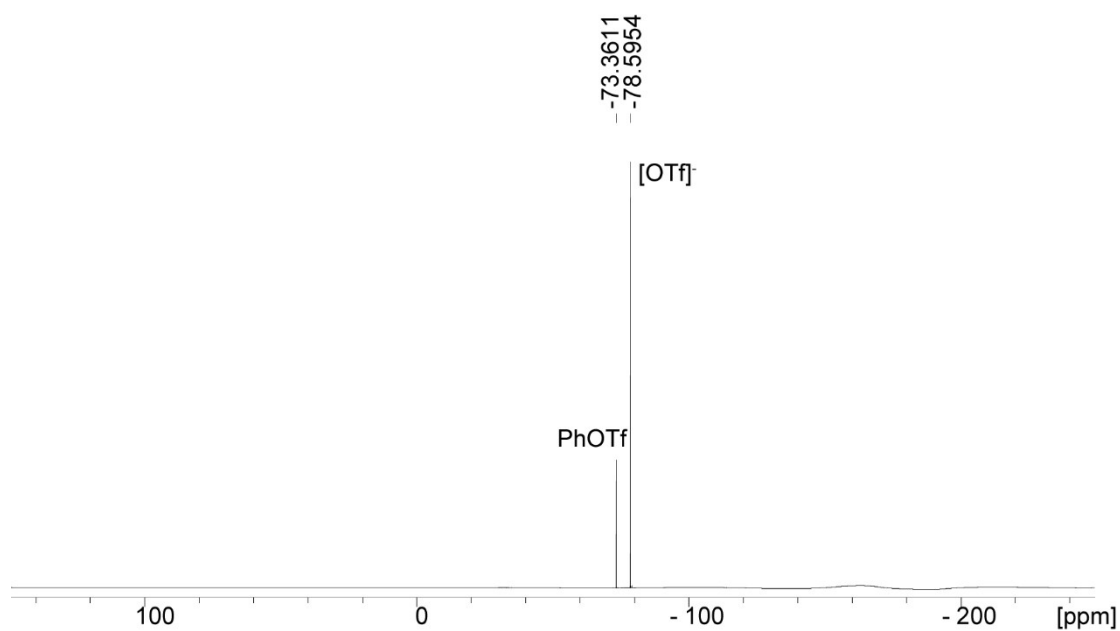


**Figure 2.12.1.**  $^1\text{H}$  NMR spectrum of the reaction mixture of  $1[\text{OTf}]_2$  with Phenol ( $\text{CH}_2\text{Cl}_2$  with  $\text{C}_6\text{D}_6$ -capillary, 300 K).

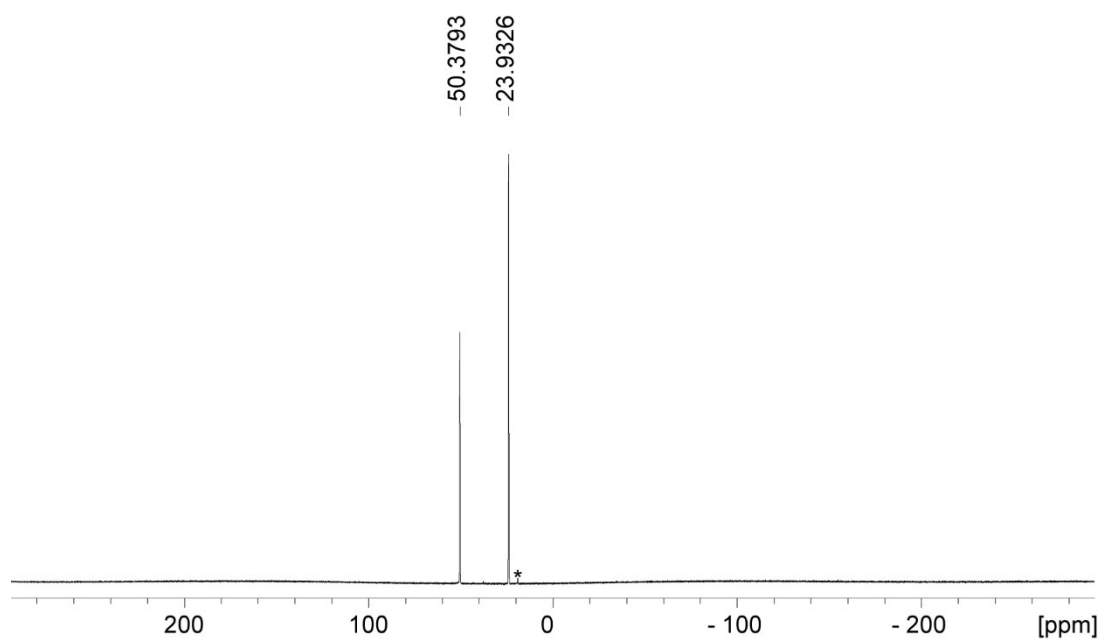




**Figure 2.12.2.**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of the reaction mixture of **1**[OTf] $_2$  and Phenol ( $\text{CH}_2\text{Cl}_2$ ) with  $\text{C}_6\text{D}_6$ -capillary, 300 K).



**Figure 2.12.3.**  $^{19}\text{F}\{\}$  NMR spectrum of the reaction mixture of **1**[OTf] $_2$  and Phenol ( $\text{CH}_2\text{Cl}_2$ ) with  $\text{C}_6\text{D}_6$ -capillary, 300 K).



**Figure 2.12.4.**  $^{31}\text{P}$  NMR spectrum of the reaction mixture of **1**[OTf]<sub>2</sub> with Phenol ( $\text{CH}_2\text{Cl}_2$  with  $\text{C}_6\text{D}_6$ -capillary, 300 K; unidentified side-product is marked with asterisk).

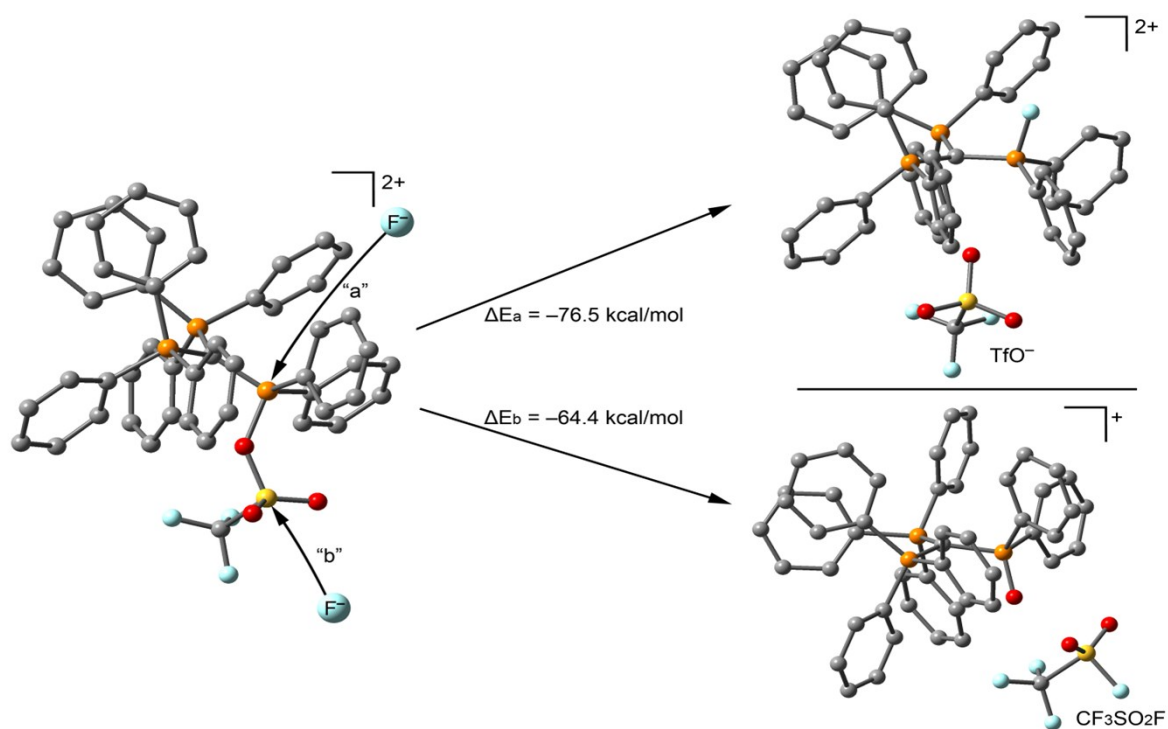
### 3. Computational Methods

#### 3.1. Methods

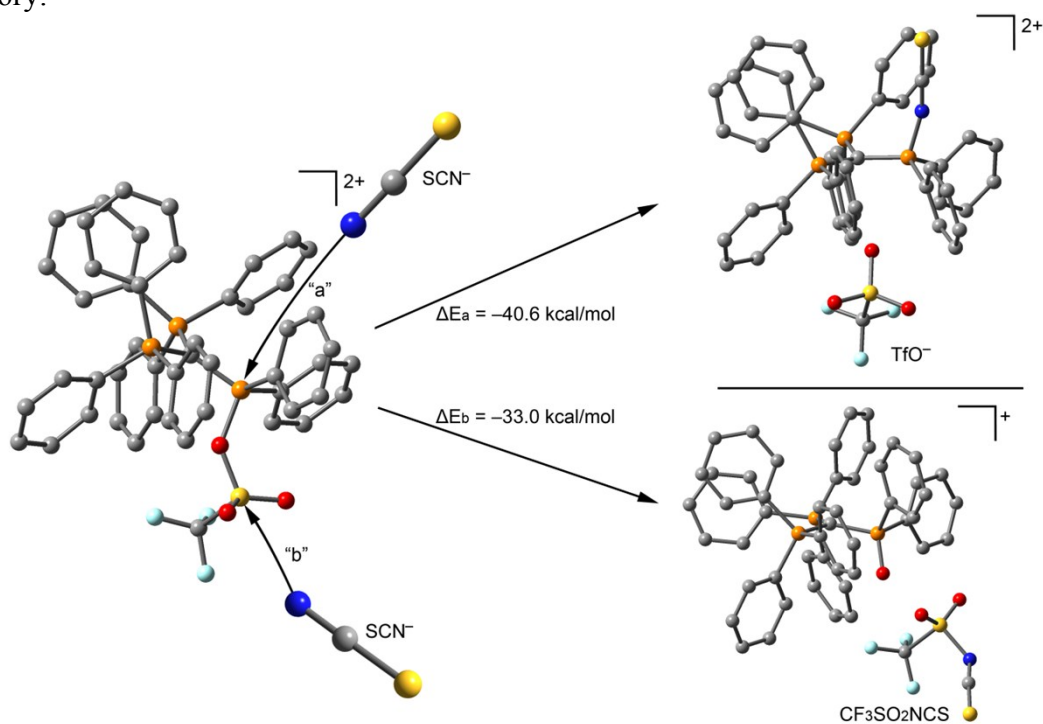
The geometry optimization has been performed at the BP86-D3/def2-TZVP level of theory without symmetry constraints by means of the Turbomole version 7.0 program, unless otherwise noted. Solvent effects have been taken into account using the COSMO continuum model. The minimum nature of the complexes has been checked by using frequency analysis. The molecular charge distribution has been performed at the BP86/def2-TZVP level of theory using the Gaussian-09 and the GaussView program to represent it.

#### 3.2. Nucleophilic attacks for $F^-$ , $SCN^-$ , $CN^-$ , DMAP and $Ph_3PO$ at $1^+$

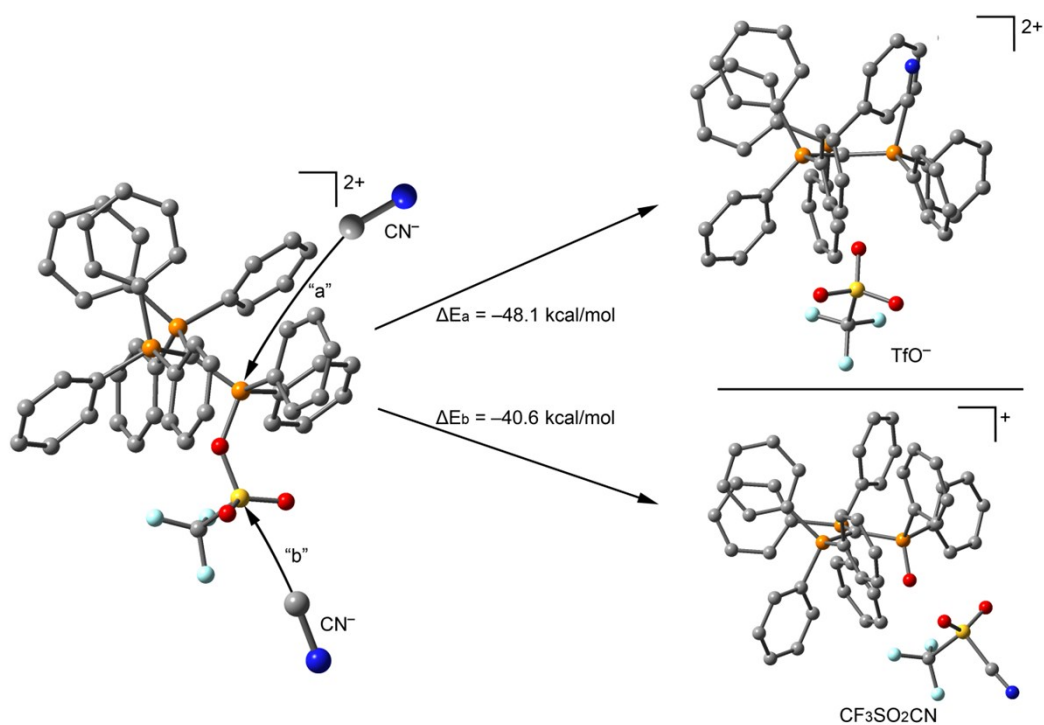
In the following figures we show the energetic features of the two possible nucleophilic attacks for  $F^-$ ,  $SCN^-$ ,  $CN^-$ , DMAP and  $Ph_3PO$ . It can be observed that for linear nucleophiles both attacks are possible, being more favourable the attack to the P atom in 12.1 kcal/mol for  $F^-$ , 7.6 kcal/mol for  $SCN^-$  and 7.5 kcal/mol for  $CN^-$ . In contrast, for the sterically hindered DMAP and  $Ph_3PO$  nucleophiles, only the attack to the S atom is possible. The reaction energies are in these cases less exergonic compared to charged nucleophiles (DMAP: -21.2 kcal/mol,  $Ph_3P(O)$ : -8.3 kcal/mol, ).



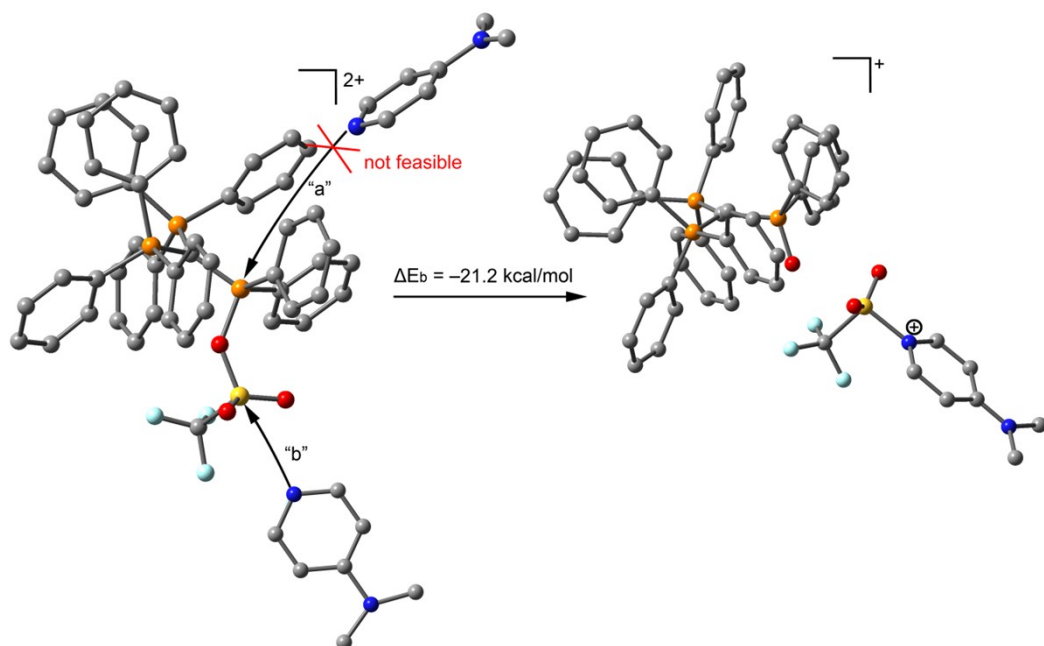
**Figure 3.2.1.** Optimized structures of  $1^{2+}$  and their corresponding products obtained upon the nucleophilic attack of  $F^-$ . The reaction energies are also given at the RI-BP86/def2-TZVP level of theory.



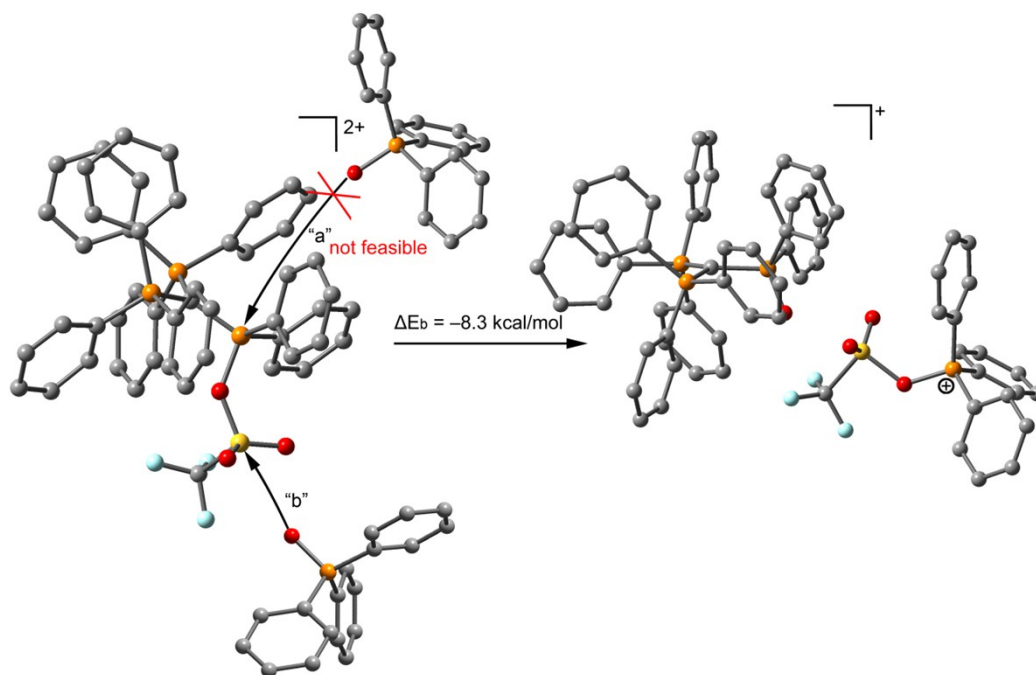
**Figure 3.2.2.** Optimized structures of  $1^{2+}$  and their corresponding products obtained upon the nucleophilic attack of  $SCN^-$ . The reaction energies are also given at the RI-BP86/def2-TZVP level of theory.



**Figure 3.2.3.** Optimized structures of  $1^{2+}$  and their corresponding products obtained upon the nucleophilic attack of  $\text{CN}^-$ . The reaction energies are also given at the RI-BP86/def2-TZVP level of theory.



**Figure 3.2.4.** Optimized structures of  $1^{2+}$  and its corresponding product obtained upon the nucleophilic attack of DMAP. The reaction energy is also given at the RI-BP86/def2-TZVP level of theory.



**Figure 3.2.5.** Optimized structures of  $1^{2+}$  and its corresponding product obtained upon the nucleophilic attack of  $\text{Ph}_3\text{PO}$ . The reaction energy is also given at the RI-BP86/def2-TZVP level of theory.

#### 4. X-ray structure refinements

Suitable single crystals were coated with Paratone-N oil, mounted using either a glass fibre or a nylon loop and frozen in the cold nitrogen stream. Crystals were measured at 100 K on different diffractometers as indicated in tables 4.1 - 4.3. Data of **8**[OTf]<sub>2</sub>, **9**[OTf]<sub>2</sub>, **10**[OTf]<sub>2</sub> and **5**[OTf] (*C2/c*) were collected on a Rigaku Oxford Diffraction SuperNova system using Cu K<sub>α</sub> radiation ( $\lambda = 1.54184 \text{ \AA}$ ) generated by a Nova micro-focus X-ray source. Reflections were collected with an Atlas S2 detector. Data reduction and absorption correction was performed with CrysAlisPro<sup>[5]</sup> software. Data of **1**[OTf]<sub>2</sub>, **3**[OTf], **4**[OTf], **7**[OTf]<sub>2</sub> and **5**[OTf] (*P2<sub>1</sub>/n*), were collected on a Bruker Kappa APEX II system using Mo K<sub>α</sub> radiation ( $\lambda = 0.71073 \text{ \AA}$ ) generated by a fine-focus sealed tube. The data reduction and absorption correction was performed with the Bruker SMART<sup>[6]</sup> and Bruker SADABS<sup>[7]</sup>, respectively. Using Olex2<sup>[8]</sup>, the structures were solved with SHELXT<sup>[9]</sup> by direct methods and refined with SHELXL<sup>[10]</sup> by least-square minimization against  $F^2$  using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions using the riding model. Images of the structures were produced with Olex2<sup>[8]</sup> software.

The solvent molecules in **7**[OTf]<sub>2</sub> are disordered. Therefore SADI, SIMU, DELU and ISOR restraints were applied.

The solvent molecule in **3**[OTf] is disordered over three positions. Therefore SADI, SIMU, DFIX, SUMP and ISOR restraints were applied.

The cation in **10**[OTf]<sub>2</sub> shows disorder of the *isothiocyano* substituted phosphorus atom. In order to get converging refinement SAME, SADI and SIMU restraints were applied. This also causes the moderate figures of merit. Attempts to grow crystals of better quality failed.

The solvent molecules in **8**[OTf]<sub>2</sub> are disordered. Therefore SADI and SAME restraints were applied.

**5**[OTf] (*C2/c*) contains three ion pairs in the asymmetric unit which differentiate basically only in the orientation of the triflate anion. One anion was refined as disordered with the minor component of 8 % showing the orientation of a different anion. Its geometry was restraint by a SAME command. In this way all three units seem to be slightly disordered. The small extent and the weak scattering power of all elements but sulfur render refinement of the disorder without excessive use of constraints impossible. Therefore the figures of merit are only moderate.

**Table 4.1.** Crystallographic data and details of the structure refinements of compounds 3[OTf], 4[OTf] and 1[OTf]<sub>2</sub>.

	3[OTf]·C <sub>6</sub> H <sub>5</sub> F	4[OTf]·C <sub>6</sub> H <sub>4</sub> F <sub>2</sub>	1[OTf] <sub>2</sub>
Formula	C <sub>56</sub> H <sub>45</sub> F <sub>4</sub> O <sub>3</sub> P <sub>3</sub> S	C <sub>56</sub> H <sub>44</sub> F <sub>5</sub> O <sub>4</sub> P <sub>3</sub> S	C <sub>52</sub> H <sub>40</sub> F <sub>9</sub> O <sub>9</sub> P <sub>3</sub> S <sub>3</sub>
M <sub>r</sub> in g mol <sup>-1</sup>	966.89	1000.88	1168.93
Color, habit	colorless, plate	colorless, rod	colorless, block
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
a in Å	14.864(2)	22.6503(8)	11.1377(7)
b in Å	15.907(3)	21.0918(7)	30.8211(15)
c in Å	20.806(3)	19.7027(7)	15.1641(9)
α in °	90	90	90
β in °	104.742(8)	98.320(1)	99.058(2)
γ in °	90	90	90
V in Å <sup>3</sup>	4757.4(13)	9313.6(6)	5140.6(5)
Z	4	8	4
T in K	100.0	100.0	100.0
Crystal size in mm <sup>3</sup>	0.3 x 0.25 x 0.03	0.243 × 0.08 × 0.04	0.07 × 0.06 × 0.05
ρ <sub>c</sub> in g cm <sup>-3</sup>	1.350	1.428	1.510
F(000)	2008.0	4144.0	2392.0
Diffractometer	Bruker APEX II	Bruker APEX II	Bruker APEX II
λ <sub>XKα</sub> in Å	X = Mo 0.71073	X = Mo 0.71073	X = Mo 0.71073
θ <sub>min</sub> in °	2.834	3.208	3.704
θ <sub>max</sub> in °	59.008	61.206	50.7
Index range	-20 ≤ h ≤ 20 -21 ≤ k ≤ 21 -28 ≤ l ≤ 28	-32 ≤ h ≤ 32 -30 ≤ k ≤ 30 -28 ≤ l ≤ 28	-13 ≤ h ≤ 13 -24 ≤ k ≤ 37 -17 ≤ l ≤ 18
μ in mm <sup>-1</sup>	0.230	0.242	0.327
Abs. correction	multi-scan	multi-scan	multi-scan
Reflections collected	76663	98999	41381
Reflections unique	13066	14253	9367
R <sub>int</sub>	0.0446	0.0593	0.0621
Reflections obs. [F > 2σ(F)]	10596	10522	6376
Residual density in e Å <sup>-3</sup>	0.59, -0.43	0.76, -0.65	1.25, -0.99
Parameters	625	622	685
GOOF	1.018	1.022	1.059
R <sub>1</sub> [I > 2σ(I)]	0.0370	0.0472	0.0796
wR <sub>2</sub> (all data)	0.0948	0.1272	0.1997
CCDC	1517445	1517443	1517444



**Table 4.2.** Crystallographic data and details of the structure refinements of **8[OTf]<sub>2</sub>**, **7[OTf]<sub>2</sub>** and **9[OTf]<sub>2</sub>**.

	<b>8[OTf]<sub>2</sub>·2 C<sub>6</sub>H<sub>5</sub>F</b>	<b>7[OTf]<sub>2</sub>·1.727 C<sub>6</sub>H<sub>4</sub>F<sub>2</sub></b>	<b>9[OTf]<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>F<sub>2</sub></b>
Formula	C <sub>63</sub> H <sub>51</sub> F <sub>8</sub> O <sub>7</sub> P <sub>3</sub> S <sub>2</sub>	C <sub>61.36</sub> H <sub>46.91</sub> F <sub>10.45</sub> O <sub>6</sub> P <sub>3</sub> S <sub>2</sub>	C <sub>55</sub> H <sub>42</sub> F <sub>7</sub> O <sub>6</sub> P <sub>3</sub> S <sub>2</sub>
M <sub>r</sub> in g mol <sup>-1</sup>	1229.06	1235.90	1102.92
Color, habit	colorless, block	colorless, block	colorless, block
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	<i>P2<sub>1</sub>/n</i>	<i>P2<sub>1</sub>/c</i>	<i>Pccn</i>
a in Å	19.27568(7)	15.8033(11)	17.93704(9)
b in Å	19.40125(7)	19.1016(11)	30.59463(14)
c in Å	30.87590(13)	19.2535(13)	18.10622(9)
α in °	90	90	90
β in °	100.4701(4)	102.320(4)	90
γ in °	90	90	90
V in Å <sup>3</sup>	11354.48(8)	5678.2(6)	9936.28(9)
Z	8	4	8
T in K	100.0	100.0	100.0
Crystal size in mm <sup>3</sup>	0.315 × 0.192 × 0.051	0.17 × 0.13 × 0.12	0.348 × 0.115 × 0.061
ρ <sub>c</sub> in g cm <sup>-3</sup>	1.438	1.446	1.475
F(000)	5072.0	2536.7	4536.0
Diffractometer	OD SuperNova	Bruker APEX II	OD SuperNova
λ <sub>XKα</sub> in Å	X = Cu 1.54184	X = Mo 0.71073	X = Cu 1.54184
θ <sub>min</sub> in °	5.028	2.638	5.712
θ <sub>max</sub> in °	153.256	55.214	153.256
Index range	-24 ≤ h ≤ 24 -24 ≤ k ≤ 18 -38 ≤ l ≤ 35	-20 ≤ h ≤ 20 -24 ≤ k ≤ 24 -24 ≤ l ≤ 24	-20 ≤ h ≤ 22 -33 ≤ k ≤ 38 -22 ≤ l ≤ 17
μ in mm <sup>-1</sup>	2.352	0.265	2.579
Abs. correction	gaussian	multi-scan	gaussian
Reflections collected	122272	50279	102087
Reflections unique	23737	13072	6596
R <sub>int</sub>	0.0204	0.0558	0.0292
Reflections obs. [F > 2σ(F)]	22830	8661	6136
Residual density in e Å <sup>-3</sup>	1.16, -0.52	0.96, -0.95	0.72, -0.37
Parameters	1542	840	667
GOOF	1.028	1.032	1.027
R <sub>1</sub> [I > 2σ(I)]	0.0368	0.0632	0.0269
wR <sub>2</sub> (all data)	0.1044	0.1868	0.0708
CCDC	1517446	1517447	1517442

**Table 4.3.** Crystallographic data and details of the structure refinements of **10[OTf]<sub>2</sub>·5[C<sub>6</sub>H<sub>5</sub>F]**.

	<b>10[OTf]<sub>2</sub>·1.5 C<sub>6</sub>H<sub>5</sub>F</b>	<b>5[OTf] (C2/c)</b>	<b>5[OTf] (P2<sub>1</sub>/n)</b>
Formula	C <sub>61</sub> H <sub>47.5</sub> F <sub>7.5</sub> N <sub>1</sub> O <sub>6</sub> P <sub>3</sub> S <sub>2</sub>	C <sub>9</sub> H <sub>10</sub> F <sub>6</sub> N <sub>2</sub> O <sub>5</sub> S <sub>2</sub>	C <sub>9</sub> H <sub>10</sub> F <sub>6</sub> N <sub>2</sub> O <sub>5</sub> S <sub>2</sub>
M <sub>r</sub> in g mol <sup>-1</sup>	1222.09	404.31	404.31
Color, habit	colorless, block	colorless, needle	colorless, block
Crystal system	monoclinic	monoclinic	monoclinic
Space group	<i>P2<sub>1</sub>/c</i>	<i>C2/c</i>	<i>P2<sub>1</sub>/n</i>
a in Å	13.3116(2)	23.6628(5)	9.1678(3)
b in Å	21.2851(3)	10.00738(16)	10.6276(4)
c in Å	19.4915(3)	40.5816(8)	15.2706(5)
α in °	90	90	90
β in °	93.0535(14)	108.008(2)	94.576(2)
γ in °	90	90	90
V in Å <sup>3</sup>	5514.87(15)	9139.0(3)	1483.10(9)
Z	4	24	4
T in K	100.0	100.0	99.99
Crystal size in mm <sup>3</sup>	0.215 × 0.148 × 0.092	0.268 × 0.073 × 0.039	0.27 × 0.23 × 0.12
ρ <sub>c</sub> in g cm <sup>-3</sup>	1.472	1.763	1.811
F(000)	2516.0	4896.0	816.0
Diffractometer	OD SuperNova	OD SuperNova	Bruker APEX II
λ <sub>XKα</sub> in Å	X = Cu 1.54184	X = Cu 1.54184	X = Mo 0.71073
θ <sub>min</sub> in °	6.154	7.776	4.674
θ <sub>max</sub> in °	153.134	153.316	52.994
Index range	-16 ≤ h ≤ 16 -26 ≤ k ≤ 26 -24 ≤ l ≤ 20	-29 ≤ h ≤ 28 -11 ≤ k ≤ 12 -51 ≤ l ≤ 47	-11 ≤ h ≤ 11 -13 ≤ k ≤ 13 -19 ≤ l ≤ 19
μ in mm <sup>-1</sup>	2.741	4.099	0.454
Abs. correction	gaussian	gaussian	multi-scan
Reflections collected	51985	23429	40950
Reflections unique	11521	9425	3079
R <sub>int</sub>	0.0264	0.0544	0.0506
Reflections obs. [F > 2σ(F)]	11393	8435	2855
Residual density in e Å <sup>-3</sup>	1.37, -1.12	1.13, -1.01	0.39, -0.37
Parameters	991	680	219
GOOF	1.149	1.028	1.056
R <sub>1</sub> [I > 2σ(I)]	0.0992	0.0603	0.0283
wR <sub>2</sub> (all data)	0.2252	0.1735	0.0716
CCDC	1517448	1518258	1518259

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