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Supporting Information

Tunable porosity of 3D-networks with germanium nodes

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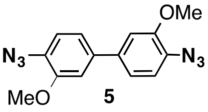
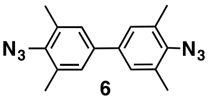
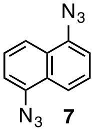
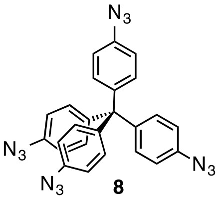
3 1H NMR 13C NMR		**9** DSC TGA
3		**10** DSC TGA
4		**12** DSC TGA
3	 **7**	**13** DSC TGA
4		**14** DSC TGA
3	 **8**	**15** DSC TGA IR
4		**16** DSC TGA IR

Post-functionnalisation

POP	*Route a / with ICl*		*Route b / with TfOH*	
15	**18-ICl**	TGA	**18-TfOH**	TGA
16	/		**19-TfOH**	TGA

General Remarks

NMR. NMR spectra were recorded on a *Bruker* AM 300 (300 MHz) as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to $CHCl_3$ (7.26 ppm), as internal standard. The spectra were analyzed according to first order.

The solid-state NMR spectra were measured on a *Bruker Avance* 400 spectrometer operating at 100.6 MHz for ^{13}C NMR. The ^{13}C CP/MAS (Cross-Polarization with Magic Angle Spinning) experiments were carried out at MAS rates of 14 kHz using densely packed powders of the compounds in 4 mm ZrO_2 rotors. The ^{1}H $\Pi/_2$ pulse was 4 *m*s and decoupling was used during the acquisition. The Hartmann-Hahn condition was optimized with adamantane at a rotational speed of 5 kHz. All spectra were measured using a contact time of 1.5 ms and a relaxation delay of 10.0 s, and 6000 FIDs were accumulated.

ATR. IR spectra were recorded with a *FT-IR Bruker IFS 88* spectrometer with OPUS software using the attenuated total reflection technique (ATR). The deposit of the absorption band was given in wave numbers *v* in cm^{-1}. The forms and intensities of the bands were characterized as follows: vs = very strong 0-10% T, s = strong 11-40% T, m = medium 41-70% T, w = weak 71-90% T, vw = very weak, 91-100% T, br = broad.

MS. MS (EI) (electron impact mass spectrometry) was performed by using a *Finnigan MAT 90* (*70 eV*).

Elemental analysis. The EA measurements were performed on an *Elementar vario MICRO* device using a Sartorius M2P precision balance. The following abbreviations were used: calc. = calculated data, found = measured data.

Scanning Electronic Microscopy. Microstructure of **15** was observed by scanning the polymer microsphere using the field–emission SEM (Zeiss Supra S5) at an accelerating voltage of 15 kV. The polymer was sputter-coated with a thin layer of gold (30 nm) before the measurement.

Thermal properties. The dynamic differential scanning calorimetry (DSC) was measured on a *METTLER Toledo dsc 30*, in a sealed aluminium 40 μL pan under argon atmosphere. The obtained data were analyzed electronically with the software program STAR ^{e}SW 8.10 and plotted in a diagram. The enthalpy changing ΔH [mW] was plotted against the temperature (−50°C to 250 °C) with a heating rate of 10°C/min.

Thermogravimetric analyses (TGA) were performed under N_2 on a Shimadzu TGA-50 Thermogravimetric Analyser, with a heat rate of $10°C.min^{-1}$.

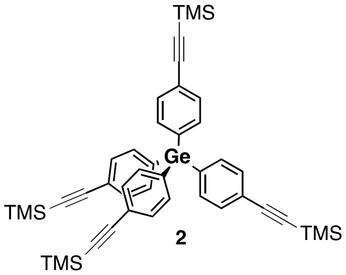
N_2 adsorption. Gas adsorption isotherms were measured volumetrically using a surface analyser ThermoScientific Surfer Gas adsorption Porosimeter. A liquid nitrogen bath (77K) was used and the N_2 gas used was UHP grade. For measurement of the specific surface areas (S_{BET}, $m^2.g^{-1}$) the BET method was applied. For all isotherms plots, closed circles are used for adsorption data points and open circles are used to indicate desorption data points.

Synthesis. Solvents, reagents and chemicals were purchased from Sigma-Aldrich, ABCR and Acros Organics. All solvents, reagents and chemicals were used as purchased unless stated otherwise.

Tetrakis(4-bromophenyl)germanium **1**,[1] tetrakis(4-ethynylphenyl)methane **4**,[2] 4,’4-diazido-3,3’-bismethoxybiphenyl **5**,[3] 4,’4-diazido-3,3’,5,5’-tetramethylbiphenyl **6**,[3] 1,5-naphtalenediazide **7**,[4] tetrakis(4-azidophenyl)methane **8**[5] were obtained according to literature procedures.

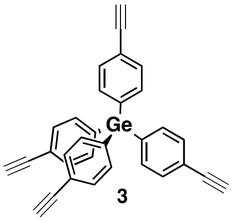
I - Experimental Protocol

II - 1) Synthesis of **2** and **3**



2

In a 100 mL Schlenk flask, tetrakis(4-bromophenyl)germanium (0.750 g, 1.077 mmol, 1 equiv.), copper(I)iodide (0.032g, 0.017 mmol, 0.16 equiv.), [$PdCl_2(PPh_3)_2$] (0.136 g, 0.19 mmol, 0.18 equiv.), and triphenylphosphine (0.102 g, 0.39 mmol, 0.36 equiv.), were dissolved in distillated di-isopropylamine (25 mL), and trimethylsilylacetylene (2.3 mL, 1.586 g, 16.15 mmol, 15.0 equiv.) was added subsequently. The yellow mixture turned rapidly in a dark solution after 30 minutes. The resulting suspension was stirred at 80 °C for 24 h, after which the reaction mixture was allowed to cool to room temperature. The solution was evaporated to dryness, then re-dissolved in a minimum amount of CH_2Cl_2 and purified by column chromatography (SiO_2, 100% pentane) to afford quantitatively tetrakis(4-trimethylsilylethynyl)phenyl)germanium **2** (0.803 g) as a brownish solid. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.25 (s, 36 H), 7.37 (AA'BB', ^{3}J = 8.1 Hz, 8 H), 7.46 (AA'BB', ^{3}J = 8.1 Hz, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 0.1 (CH_3), 95.7 (C_{quart}), 104.9 (C_{quart}), 124.4 (C_{quart}), 131.8 (*C*H), 135.1 (*C*H), 135.9 (C_{quart}). IR (ATR): ν = 2958 (s), 2160 (s), 1589 (vs), 1537 (vs), 1488 (s), 1381 (s), 1306 (vs), 1247 (m), 1223 (vs), 1184 (s), 1083 (s), 1018 (s), 861 (s), 839 (s), 824 (vw), 758 (m), 699 (s), 665 (s), 641 (vs), 611 (s), 542 (w), 424 (s) cm-1. – EA calc. for ($C_{44}H_{52}SiGe$): C 69.01, H 6.84; found C 68.95, H 6.92.



3

To a solution of tetrakis(4-trimethylsilylethynyl)phenyl)germanium (0.767 g, 1.001 mmol, 1 equiv.) in THF (45 mL) was added potassium carbonate in powder (6.643 g, 0.048 mol, 48 equiv.), followed by methanol (50 mL) dropwise. The resulting yellow suspension was stirred at room temperature for 48 h. Solvents were removed in vacuo and the resulting solid was dissolved in a mixture of CH_2Cl_2:H_2O (1:1 v/v, 500 mL). The organic fraction was decantated and separated. The aqueous phase was extracted twice with CH_2Cl_2 (2 x 100 mL). The organic phase were united, washed with brine (70 mL), dried over sodium sulfate and evaporated to dryness. The crude mixture was then passed through a plug of silica (SiO_2, 100% pentane) eluting with 50/50 : pentane/CH_2Cl_2 to afford the desired tetrakis(4-ethynylphenyl)germanium **3** (0.433 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$, δ): 3.13 (s, 4 H), 7.44 (AA'BB', ^{3}J = 8.0 Hz, 8 H), 7.52 (AA'BB', ^{3}J = 8.0 Hz, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 78.5 (C_{quart}), 83.4 (*C*H), 123.5 (C_{quart}), 132.1 (*C*H), 135.2 (*C*H), 136.1 (C_{quart}). IR (ATR): ν = 3250 (s), 1539 (vs), 1485 (s), 1383 (s), 1301 (vs), 1246 (m), 1224 (vs), 1182 (s), 1085 (s), 1019 (s), 863 (s), 837 (s), 825 (vw), 757 (m), 698 (s), 667 (s), 639 (vs), 612 (s), 545 (w), 423 (s) cm^{-1}. – EA calc. for ($C_{32}H_{20}Ge$): C 80.55, H 4.22; found C 80.48, H 4.17.

II - 2) General procedure for the synthesis of **9**-**14**

4,4'-diazidophenyl derivative (2 equiv.), tetrakis(4-ethynylphenyl)derivative (1 equiv.), $CuSO_4.5H_2O$ (10 mol% per azido functional group), sodium ascorbate (10 mol% per azido functional group) were dissolved in abs. DMF (20 mL). The reaction mixture was then heated at 100 °C for 24 h. After that, the reaction mixture was cooled down to room temperature and filtered using a Büchner funnel. The resulting brown solid was successively washed with sat. basic EDTA solution till the washing phase was colourless, followed by subsequent washing with water (3 x 20 mL), methanol (2 x 30 mL), THF (2 x 30 mL). The resulting material was then extracted with hot THF during 24 h before being filtered and washed with dichloromethane. The final brownish product was insoluble in all common solvents. For further analyses, the resulting material was dried at 100 °C at 10^{-6} mbar for 16 h.

HCP 9. Starting from **3** (0.149 g, 0.36 mmol, 1 equiv.), **5** (0.212 g, 0.72 mmol, 2 equiv.), $CuSO_4.5H_2O$ (0.036 g, 0.014 mmol) and sodium ascorbate (0.028 g, 0.014 mmol) and following the general procedure, HCP **9** was obtained in 54% yield (0.195 g). IR (ATR): ν = 1601 (vs), 1503 (m), 1453 (s), 1385 (s), 1240 (s), 1097 (s), 1014 (vw), 985 (s), 800 (vw), 718 (s), 523 (m), 408 (m) cm^{-1}. – EA calc. for ($C_{60}H_{44}O_4N_{12}Ge$): C 67.37, H 4.15, N 15.71; found C 62.88, H 4.18, N 11.48.

HCP 10. Starting from **4** (0.186 g, 0.44 mmol, 1 equiv.) and **5** (0.264 g, 0.89 mmol, 2 equiv.) $CuSO_4.5H_2O$ (0.044 g, 0.018 mmol) and sodium ascorbate (0.035 g, 0.012 mmol) and following the general procedure, HCP **10** was obtained in 68% yield (0.306 g). IR (ATR): ν = 1600 (s), 1487 (m), 1390 (s), 1248 (s), 1015 (w), 986 (vs), 806 (vw), 559 (s), 464 (vs), 411 (vs) cm^{-1}. – EA calc. for ($C_{61}H_{44}O_4N_{12}$): C 72.61, H 4.40, N 16.66; found C 72.65, H 4.52, N 8.51.

HCP 12. Starting from **4** (0.145 g, 0.34 mmol, 1 equiv.) and **6** (0.204 g, 0.69 mmol, 2 equiv.) $CuSO_4.5H_2O$ (0.035 g, 0.014 mmol) and sodium ascorbate (0.028 g, 0.014 mmol) and following the general procedure, HCP **12** was obtained in 54% yield (0.190 g). ^{13}C CP/MAS NMR (400 MHz, δ): 21.4 (br, CH_3), 69.2 (br, C_{quart}, C(Ar)$_4$), 125.9 (br, C_{quart}), 133.3 (br, CH), 139.4 (br), 151.4 (br) ppm. – IR (ATR): ν = 1598 (m), 1477 (m), 1379 (vs), 1216 (s), 1016 (m), 985 (s), 860 (s), 821 (vw), 734 (vs), 545 (s), 448 (s) cm^{-1}. – EA calc. for ($C_{65}H_{52}N_{12}$): C 77.98, H 5.23, N 16.79; found C 71.15, H 4.93, N 8.71.

HCP 13. Starting from **3** (0.098 g, 0.24 mmol, 1 equiv.) and **7** (0.101 g, 0.48 mmol, 2 equiv.) $CuSO_4.5H_2O$ (0.035 g, 0.014 mmol) and sodium ascorbate (0.028 g, 0.014 mmol) and following the general procedure, HCP **13** was obtained in 87 % yield (0.173 g). IR (ATR): ν = 1590 (s), 1512 (vs), 1435 (s), 1223 (s), 1081 (s), 1014 (m), 965 (vs), 820 (vs), 783 (vw), 708 (vs), 666 (s), 519 (m), 466 (vs), 449 (s) cm^{-1}. – EA calc. for ($C_{52}H_{32}N_{12}Ge$): C 69.59, H 3.59, N 18.73; found C 68.29, H 3.60, N 11.59.

HCP 14. Starting from **4** (0.100 g, 0.24 mmol, 1 equiv.) and **7** (0.141 g, 0.48 mmol, 2 equiv.) $CuSO_4.5H_2O$ (0.016 g, 0.08 mmol) and sodium ascorbate (0.020 g, 0.008 mmol) and following the general procedure, HCP **14** was obtained in 58% yield (0.140 g). ^{13}C CP/MAS NMR (400 MHz, δ): 68.8 (br, C_{quart}, C(Ar)$_4$), 131.9 (br), 137.1 (br), 151.2 (br) ppm. – IR (ATR): ν = 2001 (s), 1598 (s), 1492 (s), 1439 (s), 1216 (s), 1014 (m), 821 (vs), 783 (vw), 541 (s), 514 (vs), 449 (s), 424 (s) cm^{-1}. – EA calc. for ($C_{43}H_{26}N_6$): C 82.41, H 4.18, N 13.41; found C 73.83, H 3.94, N 12.50.

II - 3) General procedure for the synthesis of **15**

Tetrakis(4-azidophenyl)methane **8** (0.200 g, 0.41 mmol, 1 equiv.), tetrakis(4-ethynylphenyl)germanium **3** (0.197 g, 0.41 mmol, 1 equiv.), $CuSO_4.5H_2O$ (0.040 g, 0.02 mmol, 10 mol% per azido functional group), sodium ascorbate (0.032 g, 0.02 mmol, 10 mol%) were dissolved in the appropriate solvent (40 mL). The reaction mixture was then heated to 150 °C for 24 h. After that, the reaction mixture was cooled down to room temperature and filtered using a Büchner funnel. The resulting brown solid was successively washed with sat. basic EDTA solution till the washing phase was colourless, followed by subsequent washing with water (3 x 20 mL), methanol (2 x 30 mL), THF (2 x 30 mL). The resulting material was then extracted with hot THF during 24 h during 16 h before being filtered and washed with dichloromethane. The final brownish product **15** was insoluble in all common solvents (0.370 g, 93 %). For further analyses, the resulting material was dried at 100 °C at 10^{-6} mbar during 16 h.

POP 15. ^{13}C CP/MAS NMR (400 MHz, δ): 68.9 (br, C_{quart}, C(Ar)$_4$), 124.0 (br), 130.1 (br), 135.7 (br), 139.6 (br), 152.2 (br) ppm. IR (ATR): v = 3351 (m), 1600 (m), 1507 (vw), 1399 (s), 1225 (s), 1186 (vs), 1041 (m), 1016 (vs), 993 (m), 820 (vw), 705 (s), 824 (vw), 526 (m), 465 (vs), 449 (s) cm^{-1}. – EA calc. for ($C_{57}H_{36}N_{12}Ge$): C 71.19, H 3.77, N 17.48; found C 59.25, H 3.86, N 10.86.

Table S1. Screening of the reaction conditions for the synthesis of **15**.

Entry	Solvent	Base	Temperature	Time	Yield (%)	Specific Surface Area[a]		Total pore volume[b]
						BET	Langmuir	
1	THF	NEt_3	60	5 d.	95	130	227	0.0547
2	DMF	/	100	5 d.	93	660	992	0.3067
3	DMF	/	150	24 h	90	881	1301	0.4293

[a] Surface area calculated over the relative pressure range P/P_0 = 0.05-0.3. Specific surface area is expressed in m^2g^{-1}. [b] Total pore volume for P/P_0 = 0.99 and is expressed in cm^3g^{-1}.

II - 4) General procedure for the synthesis of **16**

Tetrakis(4-azidophenyl)methane **8** (0.279 g, 0.576 mmol, 2 equiv.), tetrakis(4-ethynylphenyl)germanium **3** (0.137 g, 0.28 mmol, 1 equiv.), tetrakis(4-ethynylphenyl)methane **4** (0.120 g, 0.28 mmol, 1 equiv.), $CuSO_4.5H_2O$ (0.056 g, 0.22 mmol, 0.1 equiv. per azido functional group), sodium ascorbate (0.045 g, 0.22 mmol) were dissolved in dist. DMF (40 mL). The reaction mixture was then heated to 150 °C for 24 h. After that, the reaction mixture was cooled down to room temperature and filtered using a Büchner funnel. The resulting brown solid was successively washed with sat. EDTA solution till the washing phase was colourless, followed by subsequent washing with water (3 x 20 mL), methanol (2 x 30 mL), THF (2 x 30 mL). The resulting material was then extracted with hot THF during 24 h before being filtered and washed with dichloromethane. The final brownish product **16** was insoluble in all common solvents (0.376 g, 90 %). For further analyses, the resulting material was dried at 150°C at 10^{-6} mbar for 16 h.

POP 16. ^{13}C CP/MAS NMR (400 MHz, δ): 68.7 (br, C_{quart}, $C(Ar)_4$), 123.8 (br), 129.5 (br), 132.9 (br), 135.5 (br), 139.8 (br), 152.3 (br) ppm. – IR (ATR): ν = 3373 (m), 2120 (s), 1602 (s), 1503 (w), 1402 (vs), 1280 (vs), 1223 (s), 1103 (vs), 1040 (s), 1016 (vs), 993 (m), 916 (vs), 821 (vw), 705 (s), 530 (m), 449 (vs) cm^{-1}. – EA calc. for ($C_{115}H_{72}N_{24}Ge$): C 74.16, H 3.90, N 18.05; found C 65.24, H 4.32, N 14.65.

II - 5) General procedure for the synthesis of **17**

Tetrakis(4-azidophenyl)methane **8** (0.120 g, 0.29 mmol, 1 equiv.), tetrakis(4-ethynylphenyl)methane **4** (0.140 g, 0.29 mmol, 1 equiv.), $CuSO_4.5H_2O$ (0.028 g, 10 mol% per azido functional group), sodium ascorbate (0.023 g, 10 mol%) were dissolved in dist. DMF (22 mL). The reaction mixture was then heated to 150 °C for 24 h. After that, the reaction mixture was cooled down to room temperature and filtered using a Büchner funnel. The resulting brown solid was successively washed with sat. basic EDTA solution till the washing phase was colourless, followed by subsequent washing with water (3 x 20 mL), methanol (2 x 30 mL), THF (2 x 30 mL). The resulting material was then extracted with hot THF during 16 h before being filtered and washed with dichloromethane. The final brownish product **17** was insoluble in all common solvents (0.213 g, 82 %). For further analyses, the resulting material was dried at 100 °C at 10^{-6} mbar during 6 h.

POP 17. IR (ATR): ν = 3355 (m), 1598 (m), 1509 (vw), 1403 (s), 1228 (s), 1186 (vs), 1039 (m), 1015 (vs), 991 (m), 822 (vw), 704 (s), 822 (vw), 528 (m), 464 (vs), 451 (s) cm^{-1}. – EA calc. for ($C_{58}H_{36}N_{12}$): C 77.32, H 4.03, N 18.66; found C 65.11, H 3.68, N 14.35.

II - 6) General procedure for the synthesis of **18** and **19**

- *II - 6 - Route a)*: reaction with iodine monochloride (ICl).[6]

General considerations:

This method was adapted from the procedure developed by Bhattacharya and coll..[6] *It has been reported as a very useful one step preparation of Ar_3GeCl and constituted an excellent alternative to the procedure involving heating of Ar_4Ge with $GeCl_4$ in presence of $AlCl_3$.*[7] *Iodine monobromine on the other hand did not react under similar conditions, and when prolonging a refluxing period in ethylene bromide, only 5% of Ph_3GeBr was obtained. Tetrabutylgermanium also failed to react with ICl and IBr. In these reactions, the colour of IX was not discharged and the organo-germanium compounds were recovered quantitatively.*

According to these considerations, a colour change of the reaction mixture could constitute a qualitative method of monitoring the reaction completion.

Moreover, in the original procedure performed on tetraphenylgermanium, no trace of diphenylgermanium dichloride was observed even in presence of an excess of iodine monochloride (1.3 mol, 260 equiv.).

General procedure:

A solution of ICl (Y equiv.) in CCl_4 (5 mL) was slowly added with vigorous stirring to a suspension of germanium based-POP **15** (0.050 g, 0.052 mmol, 1 equiv.) in CCl_4 (5 mL). The blood-red colour of ICl solution slowly changed light pinkish-brown. The reaction mixture was stirred overnight and the resulting solid was filtered and extensively washed with petroleum ether (20 mL), methanol, THF and dichloromethane.

The label **18-Y$_{\mathbf{ICl}}$** corresponds to POP **15** reacted with **Y** equivalents of ICl.

18-1$_{\mathbf{ICl}}$. Starting from **15** and ICl (2.7 μL, 0.008 g, 0.052 mmol, 1 equiv.) and following the general procedure, 0.046 g of **18-1$_{\mathbf{ICl}}$** was obtained. IR (ATR): ν = 3353 (s), 2117 (s), 1601 (s), 1505 (m), 1434 (vs), 1396 (s), 1284 (vs), 1225 (s), 1101 (vs), 1035 (s), 992 (w), 820 (w), 704 (s), 524 (m) cm^{-1}. – EA found C 56.33, H 3.40, N 12.88. – TGA.

18-10$_{\mathbf{ICl}}$. Starting from **15** and ICl (27 μL, 0.084 g, 0.52 mmol, 10 equiv.) and following the general procedure, 0.043 g of **18-10$_{\mathbf{ICl}}$** was obtained. IR (ATR): ν = 3365 (m), 2125 (s), 1602 (s), 1508 (w), 1434 (vs), 1398 (s), 1284 (vs), 1226 (s), 1103 (vs), 1041 (m), 993 (m), 822 (vw), 704 (s), 525 (m) cm^{-1}. – EA found C 58.88, H 3.86, N 13.35. – TGA.

- *II - 6 - Route b)* : reaction with trifluoromethanesulfonic acid (TfOH).[8]

  - *General considerations:*

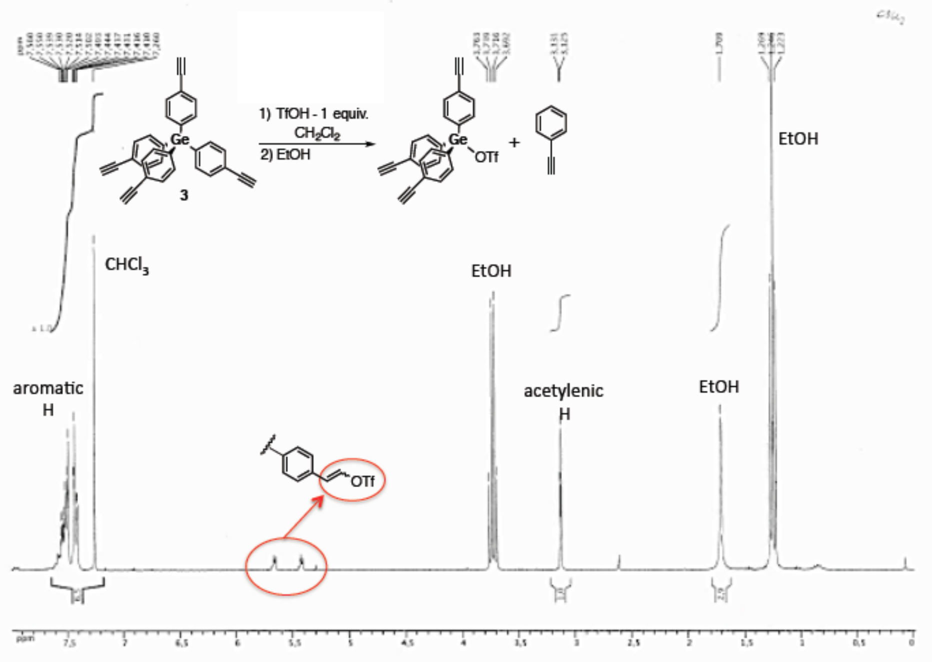
This method was adapted from the procedure developed by Zaitsev and coll.[8]

In the original procedure performed on tetraphenylgermanium, no trace of diphenylgermanium dichloride was observed even in presence of an excess of 2 equivalents of triflic acid.

  - *Control procedure performed on tetrakis(4-ethynylphenyl)germane:*

Trifluoromethanesulfonic acid (4.6 μL, 0.008 g, 0.052 mmol, 1 equiv.) was added at 0 °C to a solution of tetrakis(4-ethynylphenyl)germane **3** (0.025g, 0.052 mmol, 1 equiv.) in CH_2Cl_2 (5 mL). The reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting reaction mixture was hydrolyzed with ethanol, decantated and separated. The organic phase was dried over Na_2SO_4, filtrated and evaporated to dryness.

^{1}H NMR in $CDCl_3$



- *General procedure:*

Trifluoromethanesulfonic acid (Y equiv.) was added at 0 °C to the suspension of the desired germanium based-POP **X** (1 equiv.) in CH_2Cl_2 (5 mL). The reaction mixture was allowed to warm to room temperature and stirred overnight. The resulting solid was filtrated and extensively washed with water, methanol, THF and CH_2Cl_2 to afford **X+3** as a brown solid, insoluble in common solvents.

The label **X+3-Y$_{\text{TfOH}}$** corresponds to POP **X** reacted with **Y** equivalents of TfOH.

18-1$_{\text{TfOH}}$. Starting from **15** (0.050 g, 0.052 mmol, 1 equiv.) and TfOH (4.6 μL, 0.008 g, 0.052 mmol, 1 equiv.) and following the general procedure, 0.037 g of **18-1$_{\text{TfOH}}$** was obtained. IR (ATR): ν = 3412 (s), 2124 (s), 1603 (s), 1508 (m), 1400 (vs), 1224 (m), 1167 (s), 1028 (vw), 993 (s), 822 (m), 761 (s), 694 (vs), 638 (w), 516 (m), 423 (vs) cm^{-1}. – EA found C 53.36, H 3.70, N 12.19, S 2.93. – TGA.
18-10$_{\text{TfOH}}$. Starting from **15** (0.050 g, 0.052 mmol, 1 equiv.) and TfOH (46 μL, 0.078 g, 0.52 mmol, 10 equiv.) and following the general procedure, 0.039 g of **18-10$_{\text{TfOH}}$** was obtained. IR (ATR): ν = 3426 (s), 1621 (s), 1507 (s), 1221 (w), 1168 (s), 1085 (vs), 1023 (vw), 993 (vs), 820 (s), 763(s), 634 (w), 574 (s), 513 (m) cm^{-1}. – EA found C 33.92, H 2.92, N 6.38, S 10.59. – TGA.
18-100$_{\text{TfOH}}$. Starting from **15** (0.050 g, 0.052 mmol, 1 equiv.) and TfOH (0.46 mL, 0.780 g, 0.0052 mol, 100 equiv.) and following the general procedure, 0.042 g of **18-100$_{\text{TfOH}}$** was obtained. IR (ATR): ν = 3427 (s), 1623 (s), 1504 (s), 1222 (w), 1167 (s), 1088 (vs), 1021 (vw), 995 (vs), 821 (s), 761 (s), 635 (w), 573 (s), 512 (m) cm^{-1}. – EA found C 34.78, H 3.01, N 7.55, S 13.21.
19-1$_{\text{TfOH}}$. Starting from **16** (0.050 g, 0.026 mmol, 1 equiv.) and TfOH (2.3 μL, 0.0039 g, 0.026 mmol, 1 equiv.) and following the general procedure, 0.039 g of **19-1$_{\text{TfOH}}$**. IR (ATR): ν = 3412 (s), 2124 (s), 1603 (s), 1509 (m), 1406 (s), 1292 (vs), 1223 (s), 1031 (m), 992 (m), 824 (vw), 718 (s), 532 (m), 417 (vs) cm^{-1}. – EA found C 68.60, H 4.34, N 15.74. – TGA.
19-100$_{\text{TfOH}}$. Starting from **16** (0.050 g, 0.026 mmol, 1 equiv.) and TfOH (0.23 mL, 0.390 g, 2.6 mmol, 100 equiv.) and following the general procedure, 0.035 g of **19-100$_{\text{TfOH}}$** was obtained. IR (ATR): ν = 3363 (s), 2116 (vs), 1602 (s), 1508 (w), 1406 (s), 1222 (m), 1029 (w), 992 (m), 822 (vw), 761 (s), 694 (s), 638 (s), 521 (s) cm^{-1}. – EA found C 64.63, H 4.25, N 13.28, S 1.49. – TGA.

- *II - 6 - Route c)* : reaction with acetic acid (AcOH).

    - *Control procedure performed on tetrakis(4-ethynylphenyl)germane:*

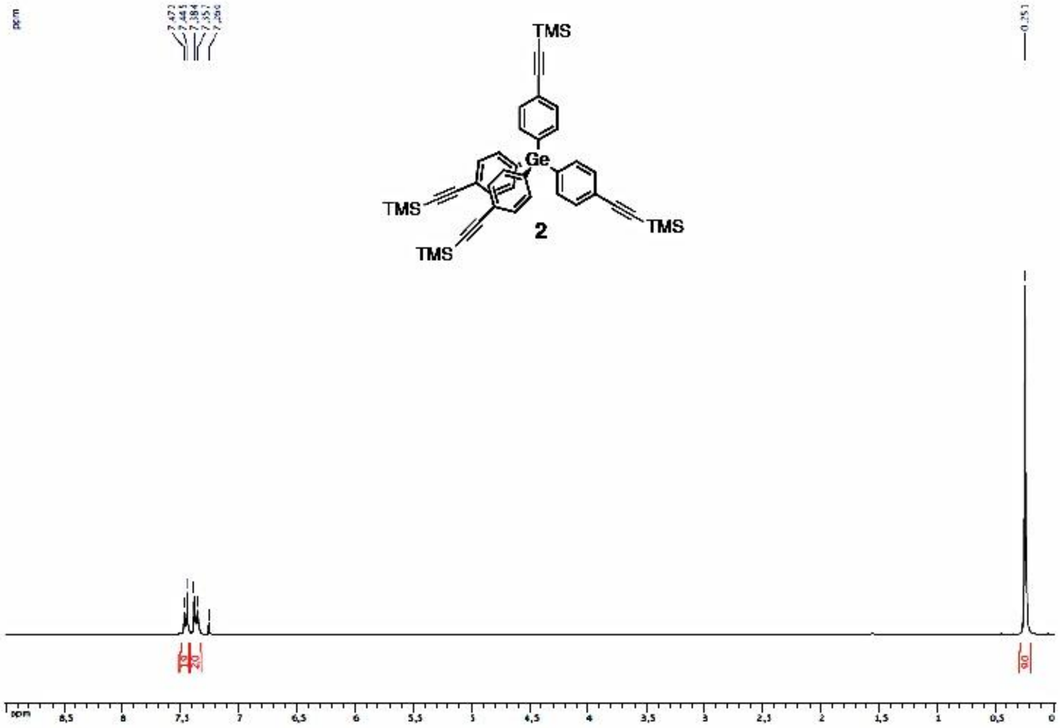
Acetic acid (0.15 mL, 2.6 mmol, 100 equiv.) was added at room temperature to a solution of tetrakis(4-ethynylphenyl)germane **3** (0.046g, 0.052 mmol, 1 equiv.) in methanol (5 mL). The reaction mixture was stirred overnight and subsequently hydrolyzed with water (10 mL), decantated and separated. The organic phase was dried over Na_2SO_4, filtrated and evaporated to dryness before being subjected to ^{1}H NMR analysis. No cleavage of the C-Ge bond was observed as no new signal appeared and only tetrakis(4-ethynylphenyl)germane **3** and acetic acid were detected by ^{1}H NMR (recorded in $CDCl_3$).

    - *General procedure:*

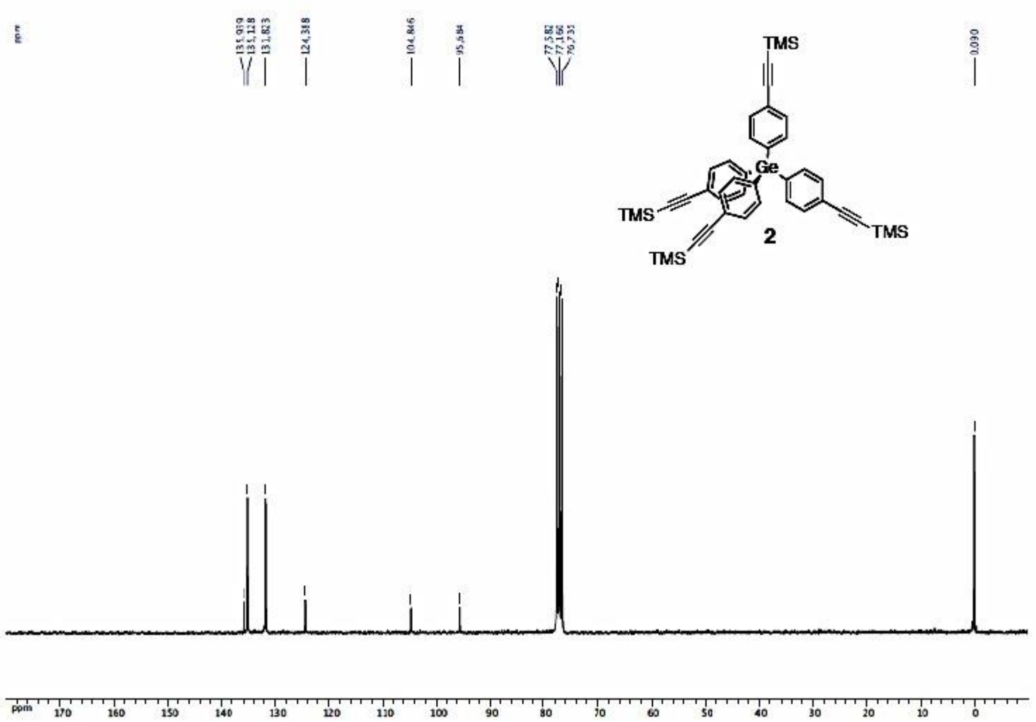
Acetic acid (0.15 mL, 2.6 mmol, 100 equiv.) was added at room temperature to the suspension of **16** (0.050g, 1 equiv.) in methanol (2.5 mL) and the reaction mixture was stirred overnight. The resulting solid was filtrated and extensively washed with water, methanol, THF and CH_2Cl_2 to afford **20** as a brown solid, insoluble in common solvents. The specific surface area of **20** did not changed compared to the one of **16**.

III - NMR Spectra of 2 and 3

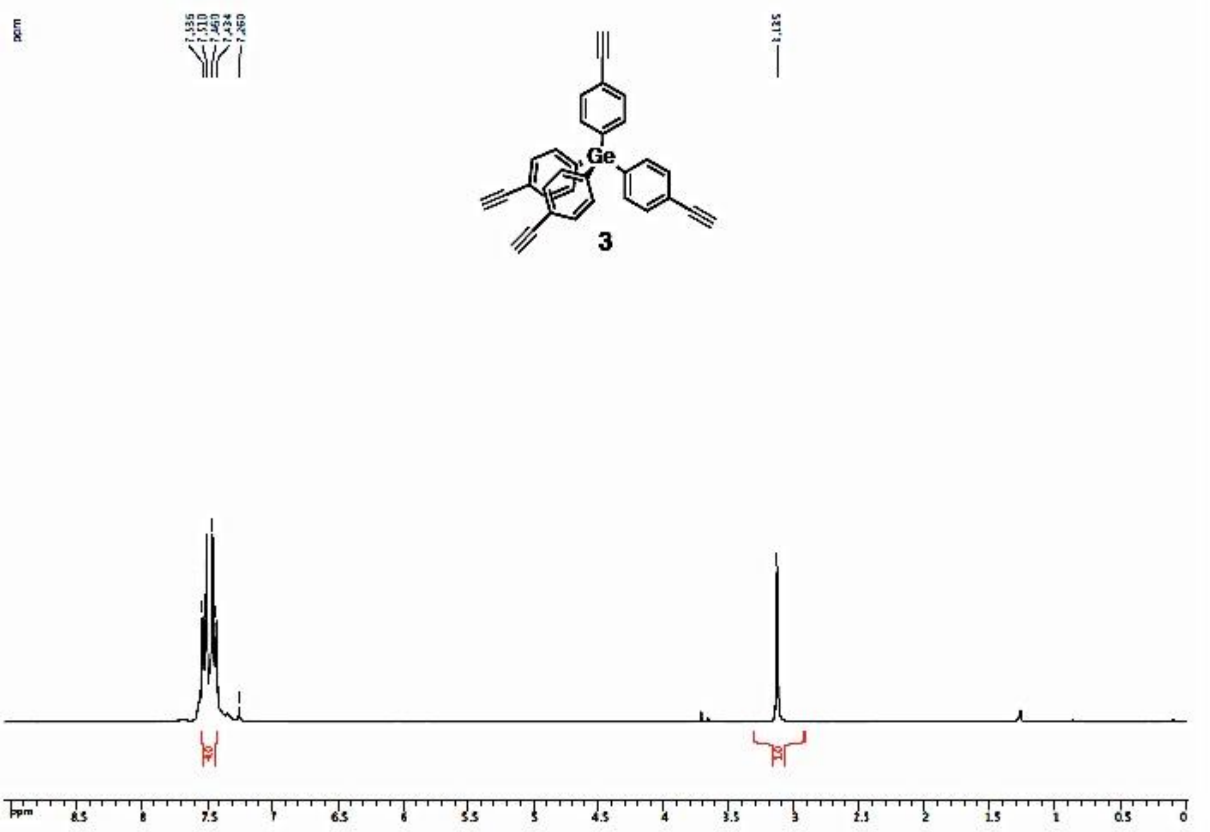
III - 1) ^{1}H NMR of **2** in $CDCl_3$



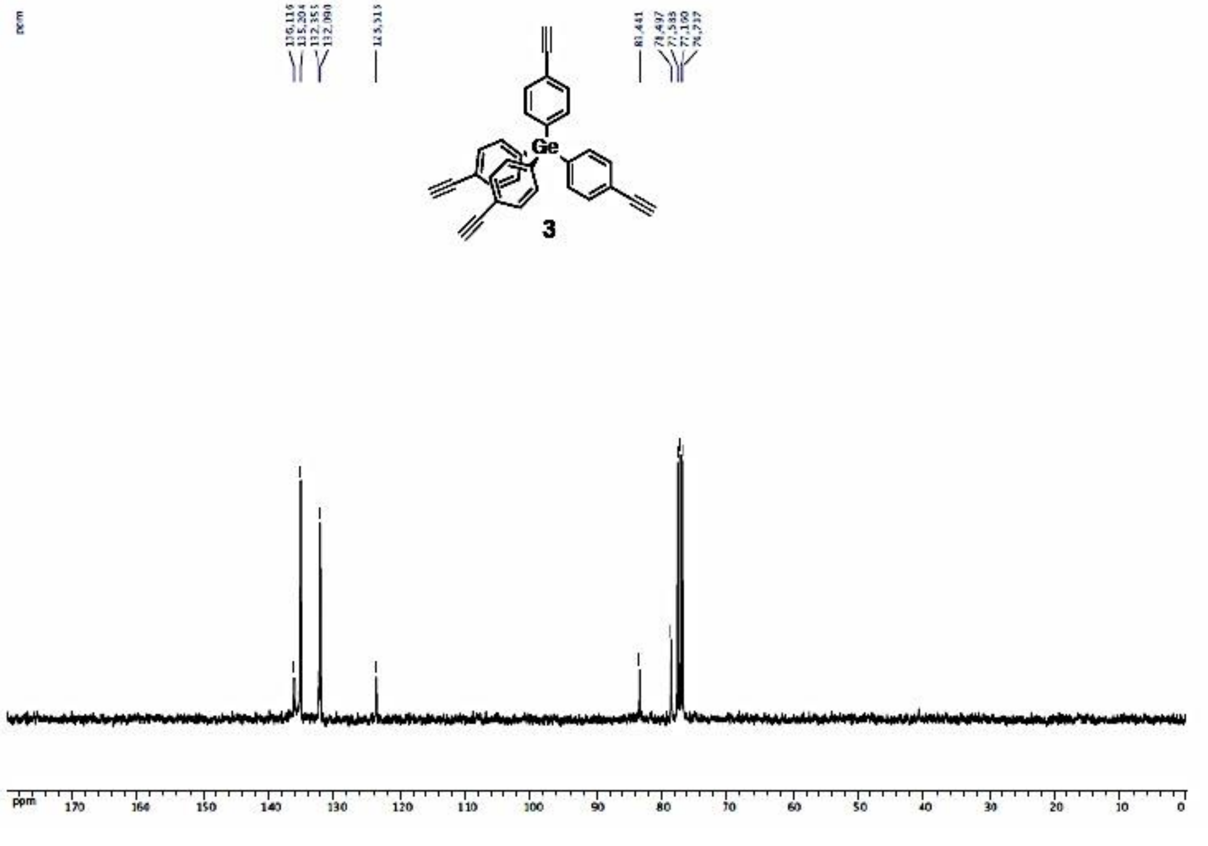
III - 2) ^{13}C NMR of **2** in $CDCl_3$



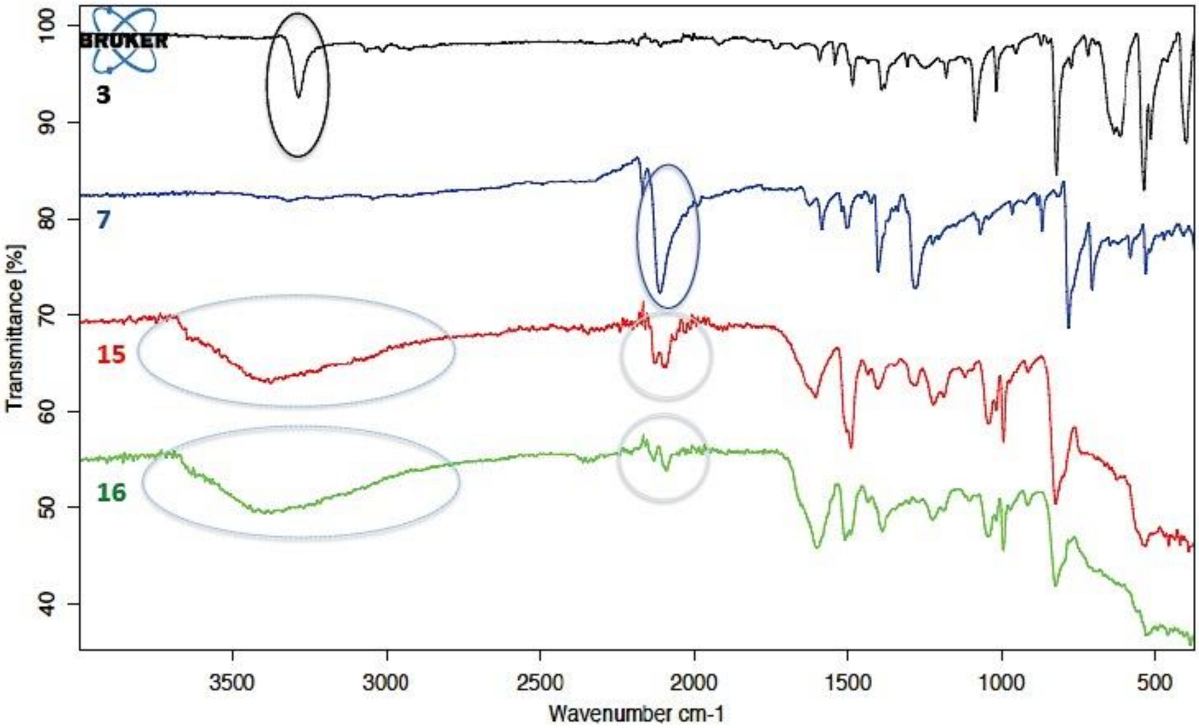
III - 3) ^{1}H NMR of **3** in $CDCl_3$



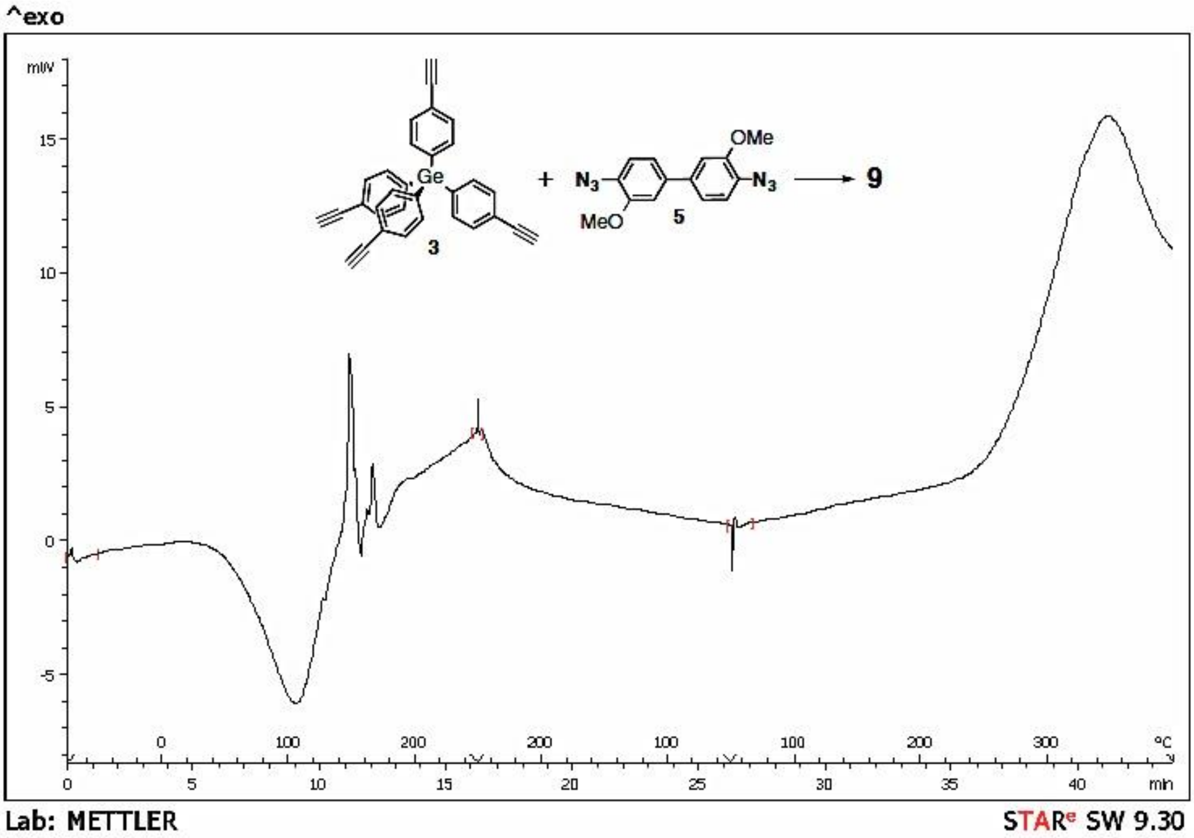
III - 4) ^{13}C NMR of **3** in $CDCl_3$

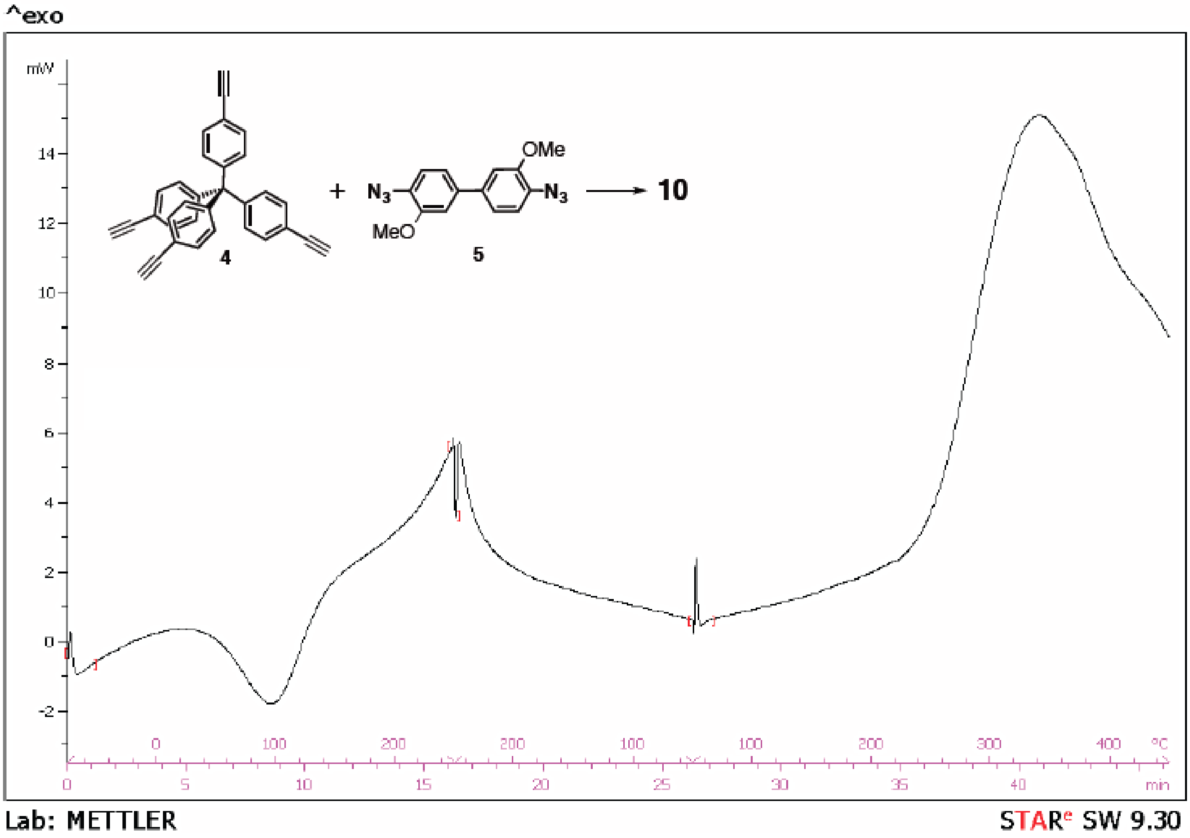


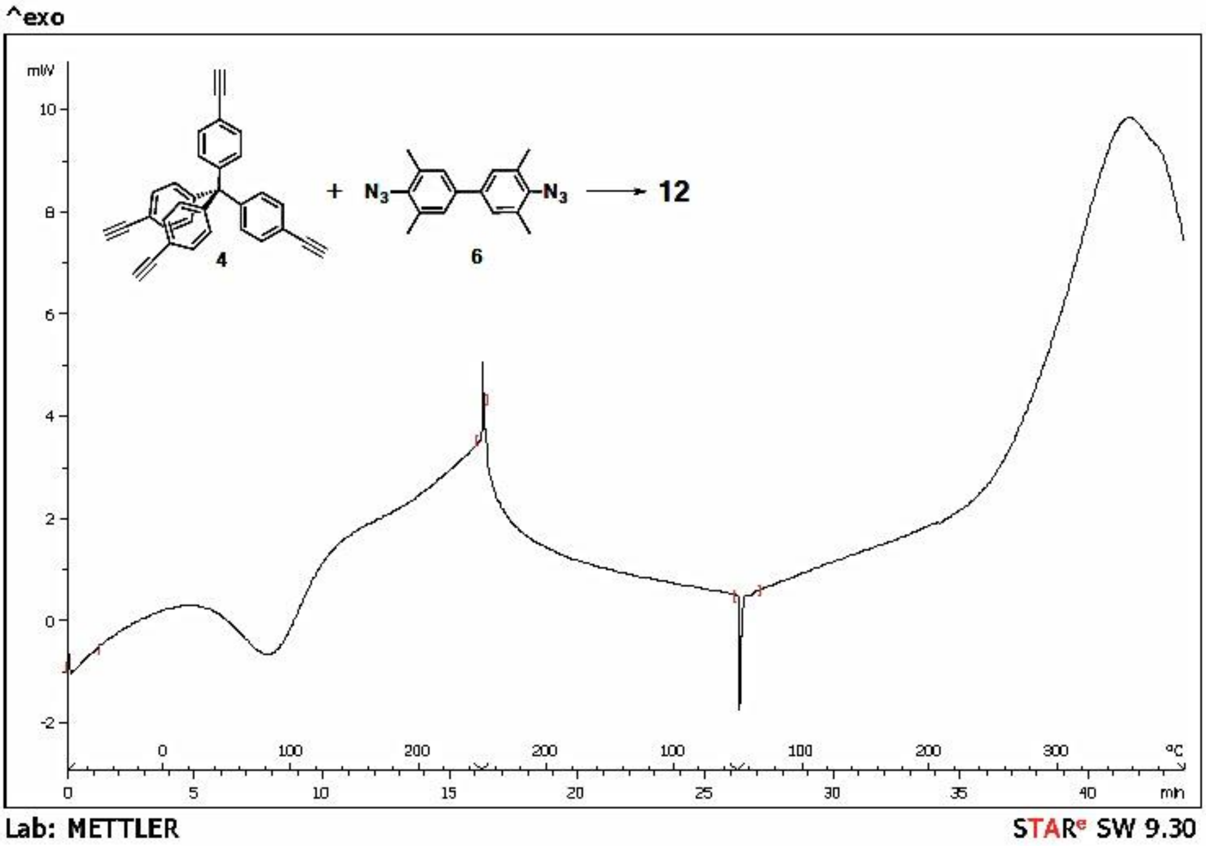
IV - IR Spectra

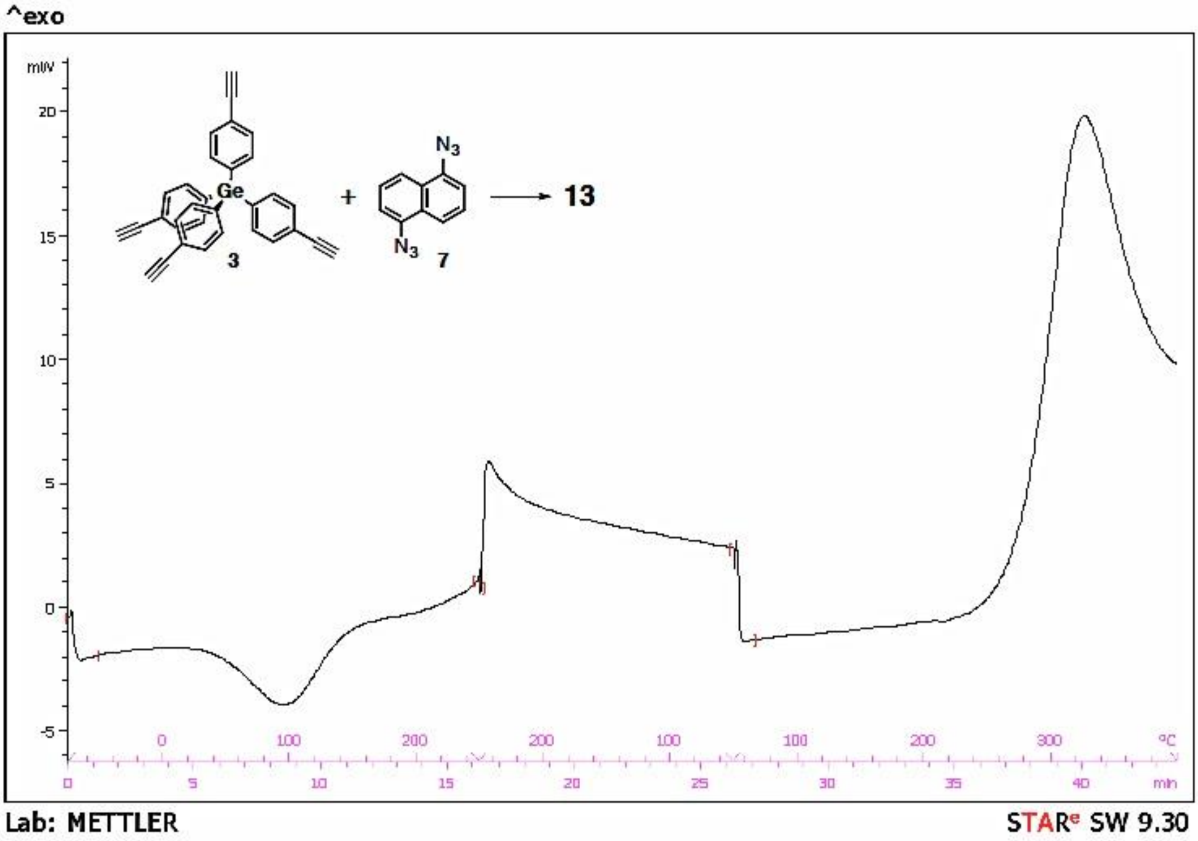


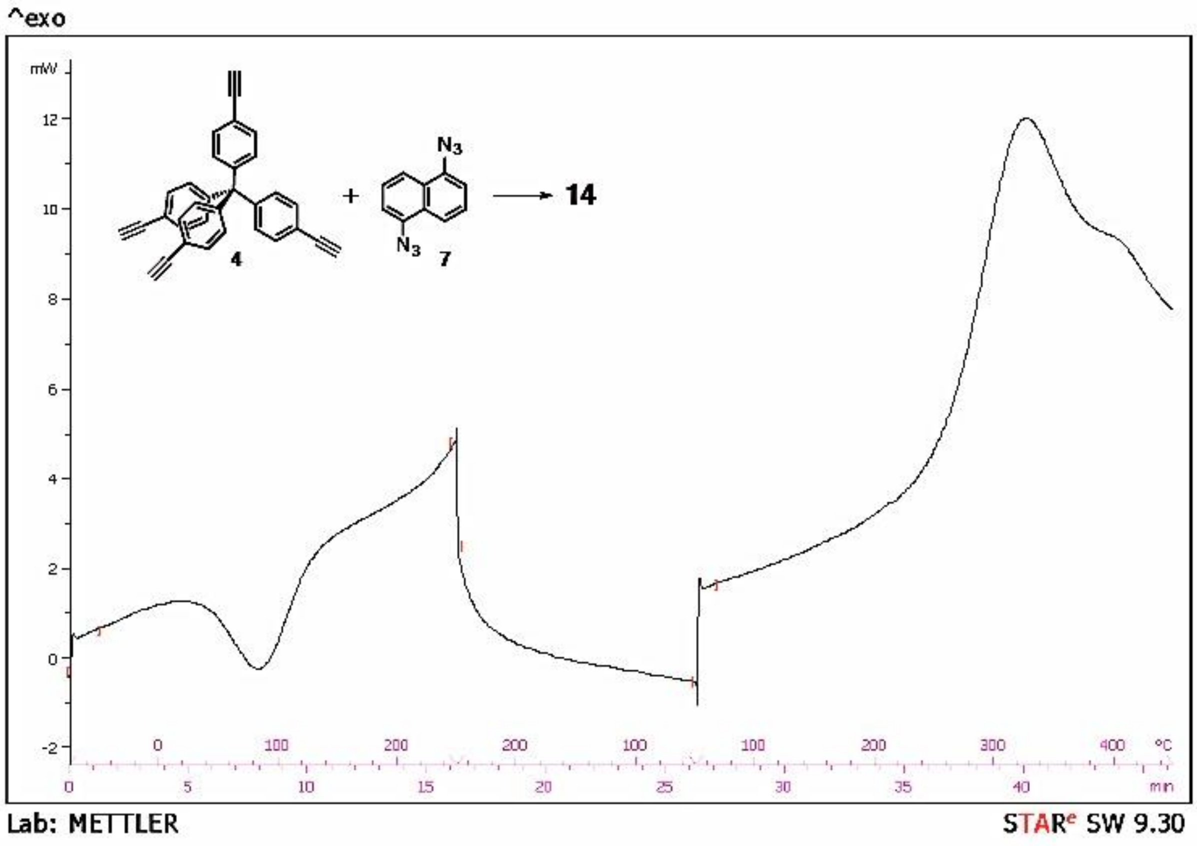
V - DSC Analyses

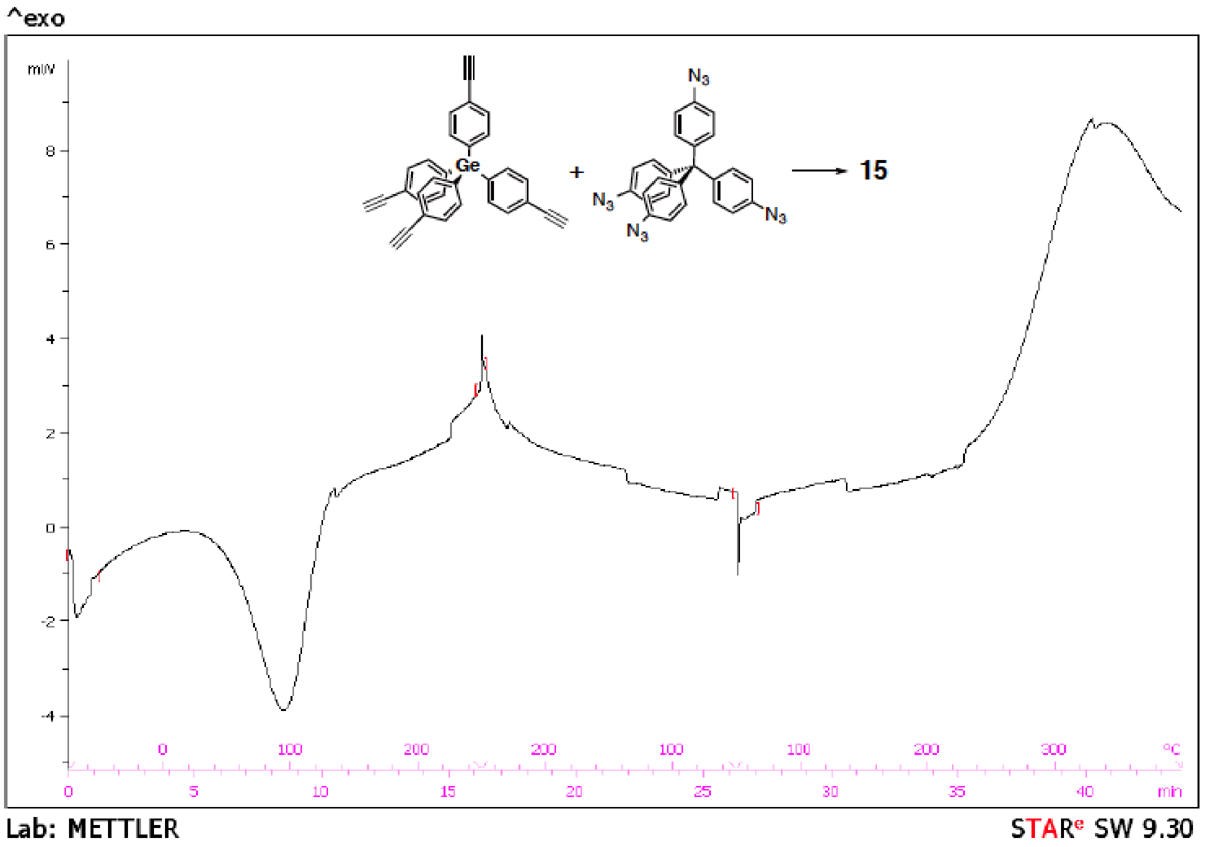





^exo
mW
10
8
6
4
2
0
-2
4
+
N_3
N_3
6
12
0
100
200
200
100
100
200
300
°C
0
5
10
15
20
25
30
35
40
min
Lab: METTLER
STARe SW 9.30


^exo
mW
20
15
10
5
0
-5
Ge
3
+
N_3
N_3
7
13
0
100
200
200
100
100
200
300
°C
0
5
10
15
20
25
30
35
40
min
Lab: METTLER
STARe SW 9.30


^exo
mW
12
10
8
6
4
2
0
-2
4
7
14
0
100
200
200
100
100
200
300
400
°C
0
5
10
15
20
25
30
35
40
min
Lab: METTLER
STARe SW 9.30


^exo
mW
8
6
4
2
0
-2
-4
Ge
15
0
100
200
200
100
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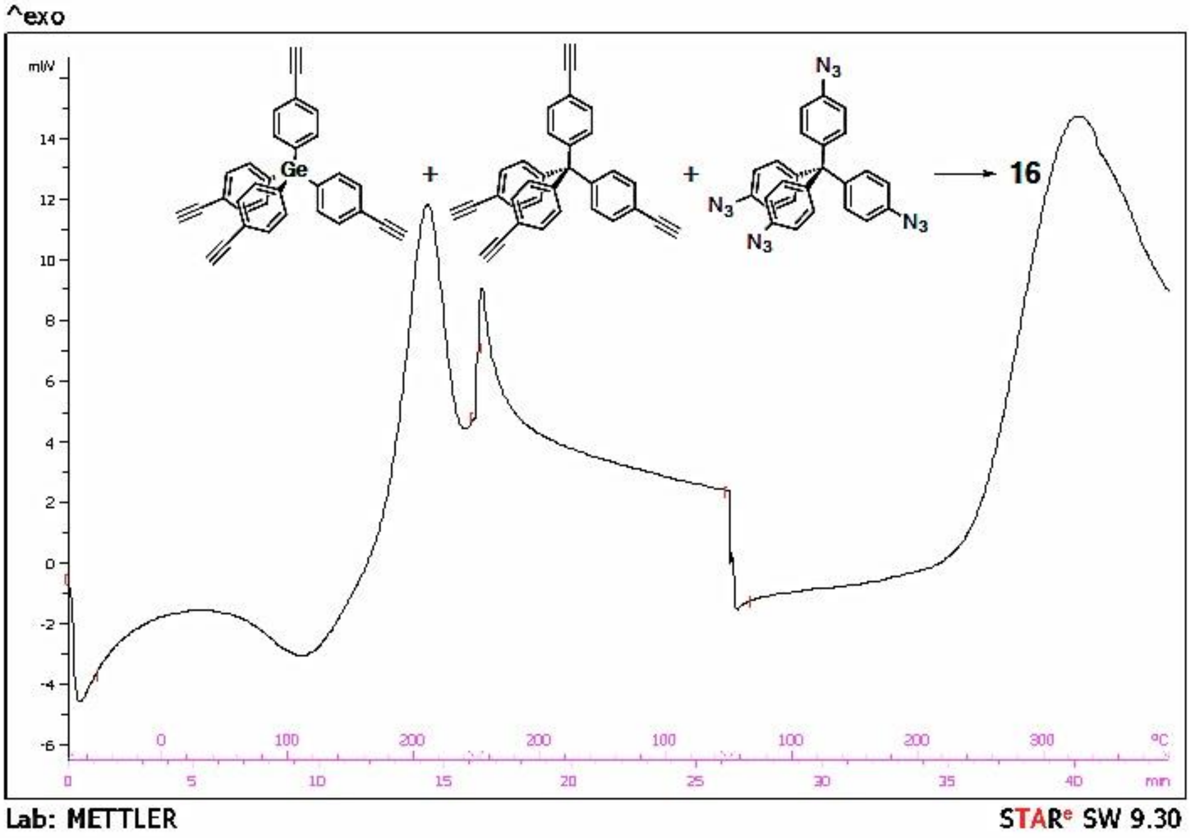
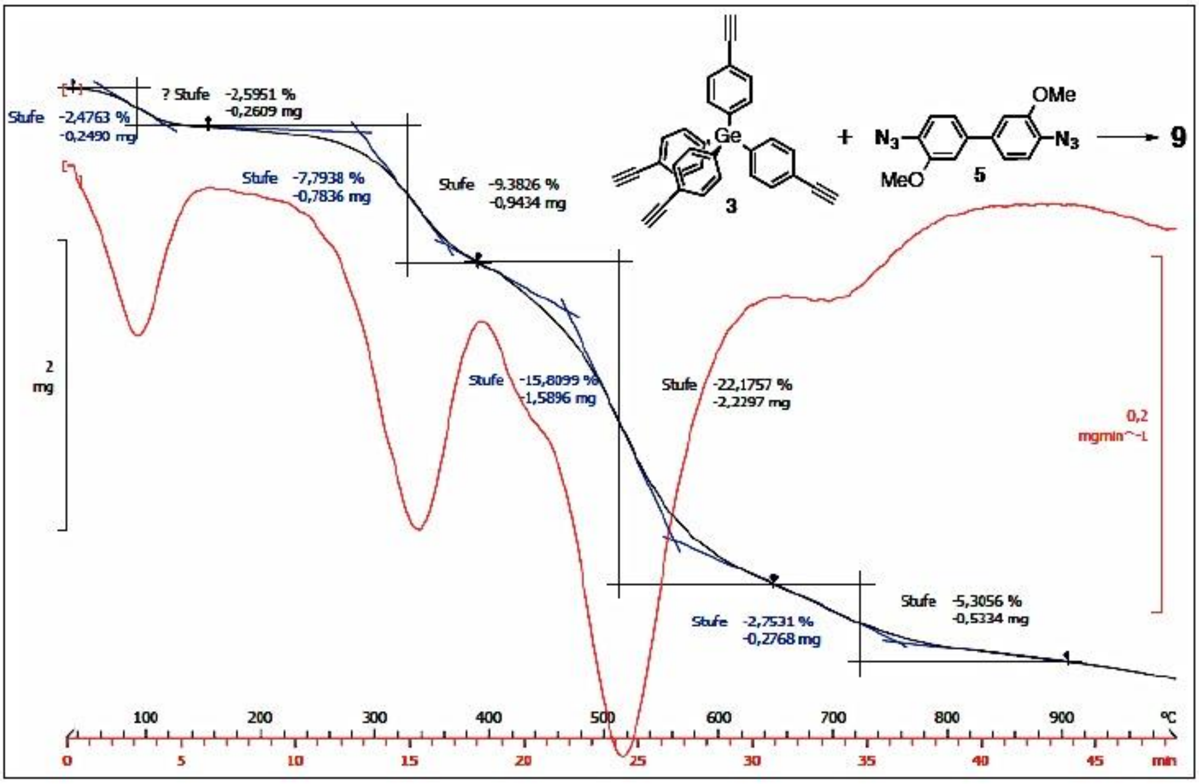
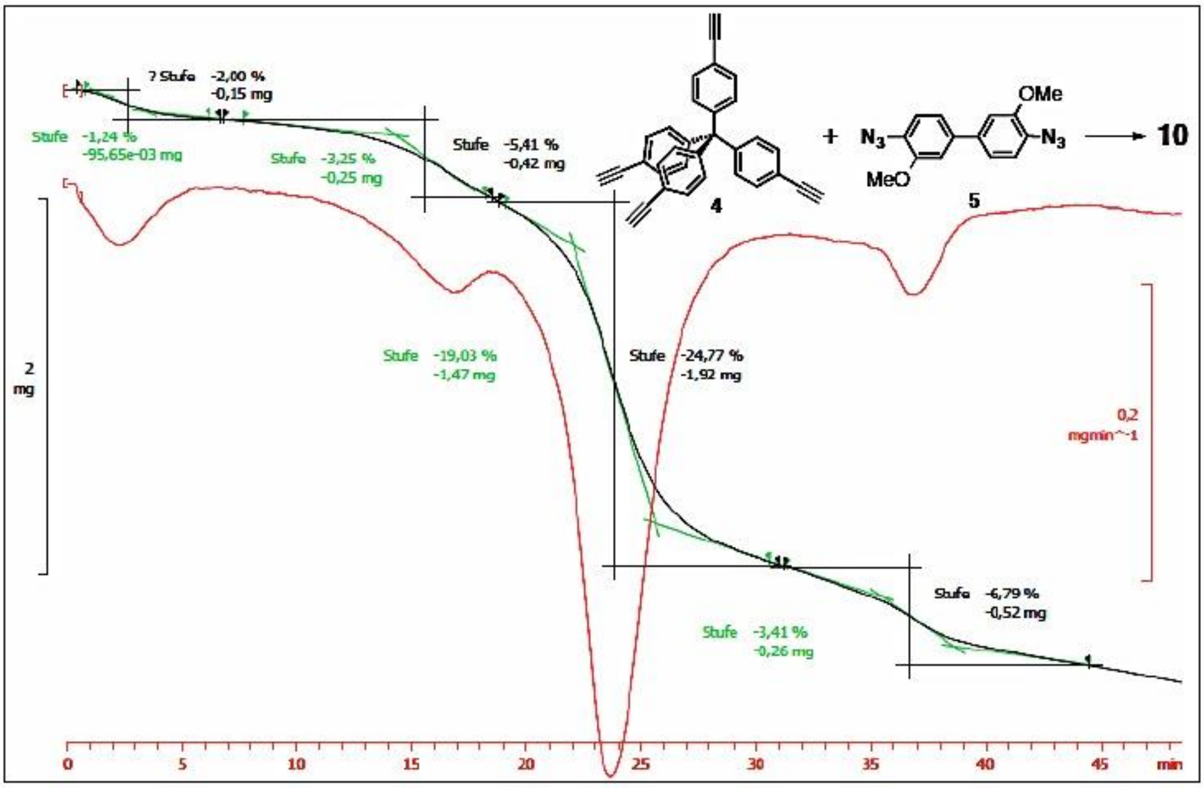
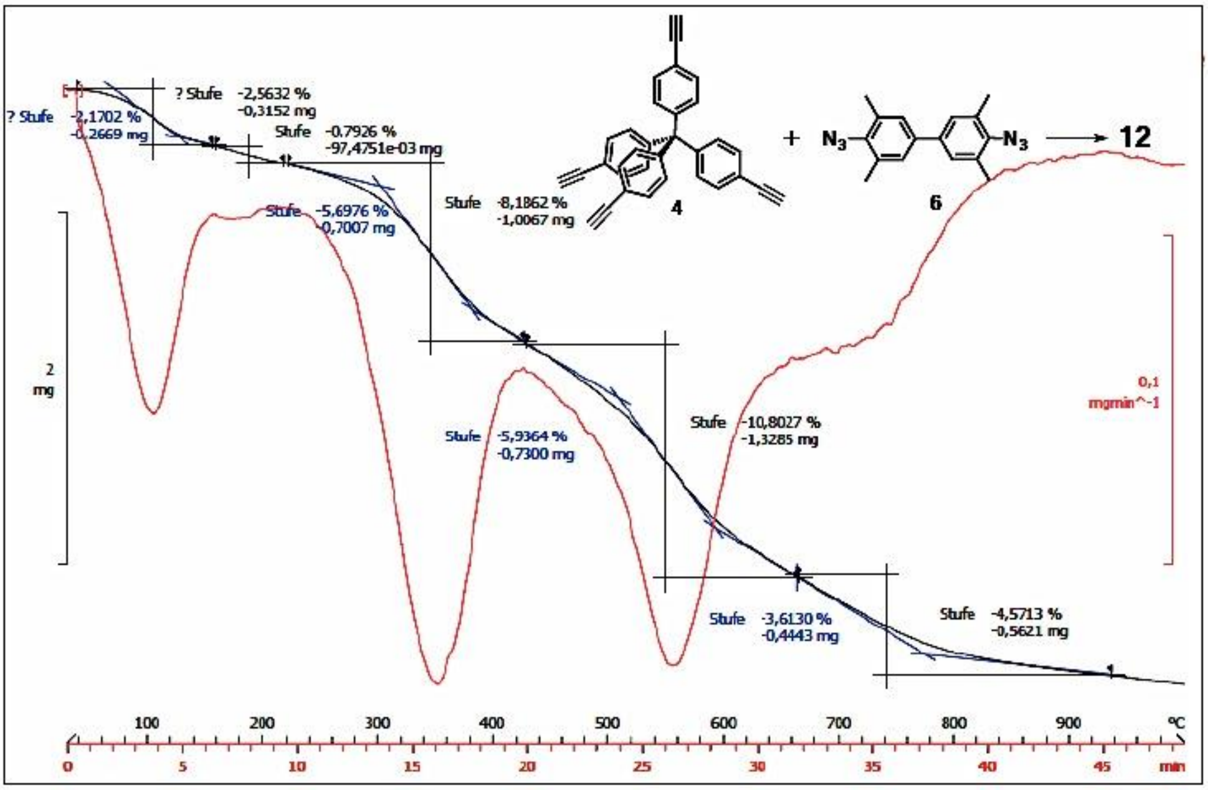
200
300
°C
0
5
10
15
20
25
30
35
40
min
Lab: METTLER
STARe SW 9.30

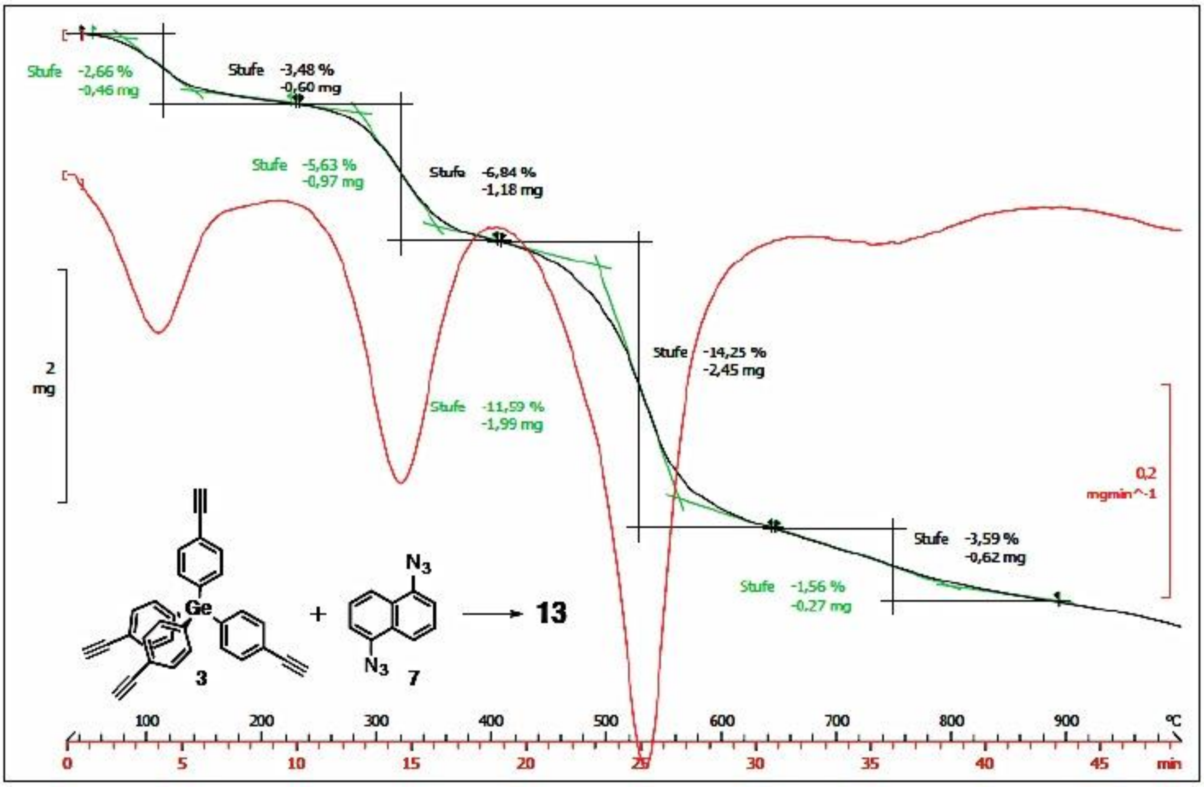

^exo
mW
14
12
10
8
6
4
2
0
-2
-4
-6
Ge
+
+
N3
N3
N3
N3
16
0
100
200
200
100
100
200
300
°C
0
5
10
15
20
25
30
35
40
min
Lab: METTLER
STARe SW 9.30

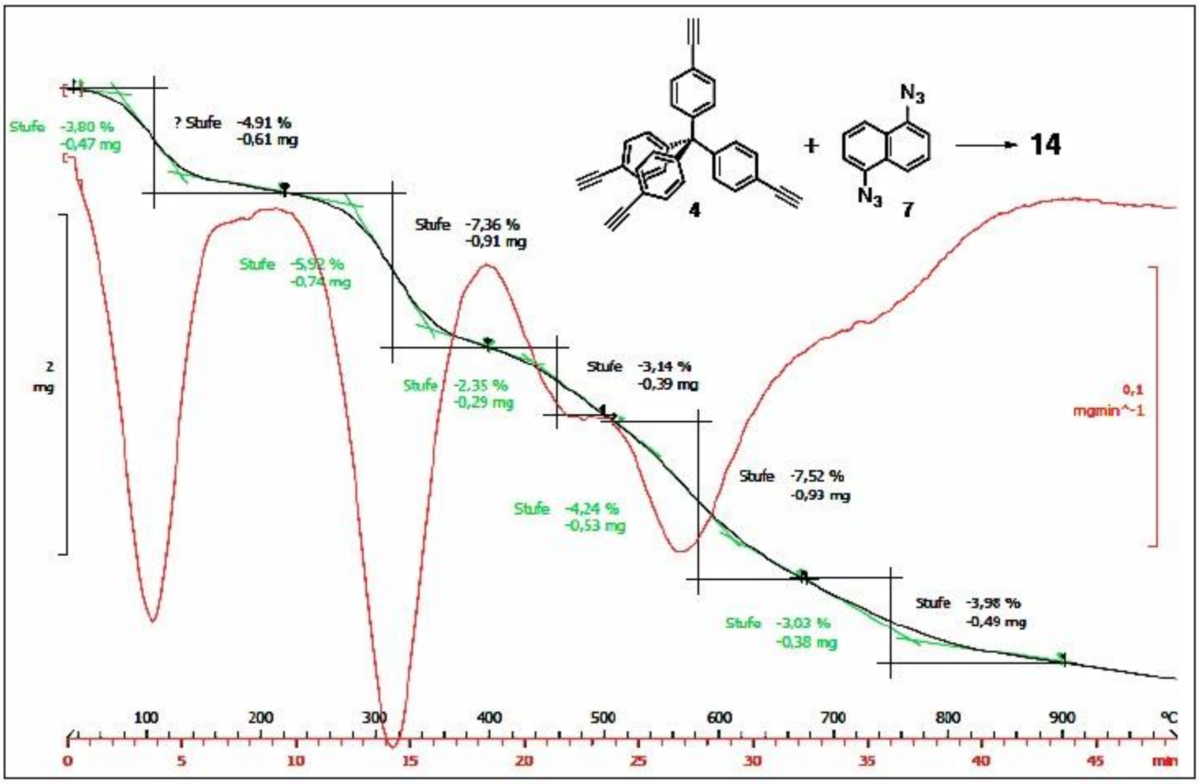
VI - TGA Analyses



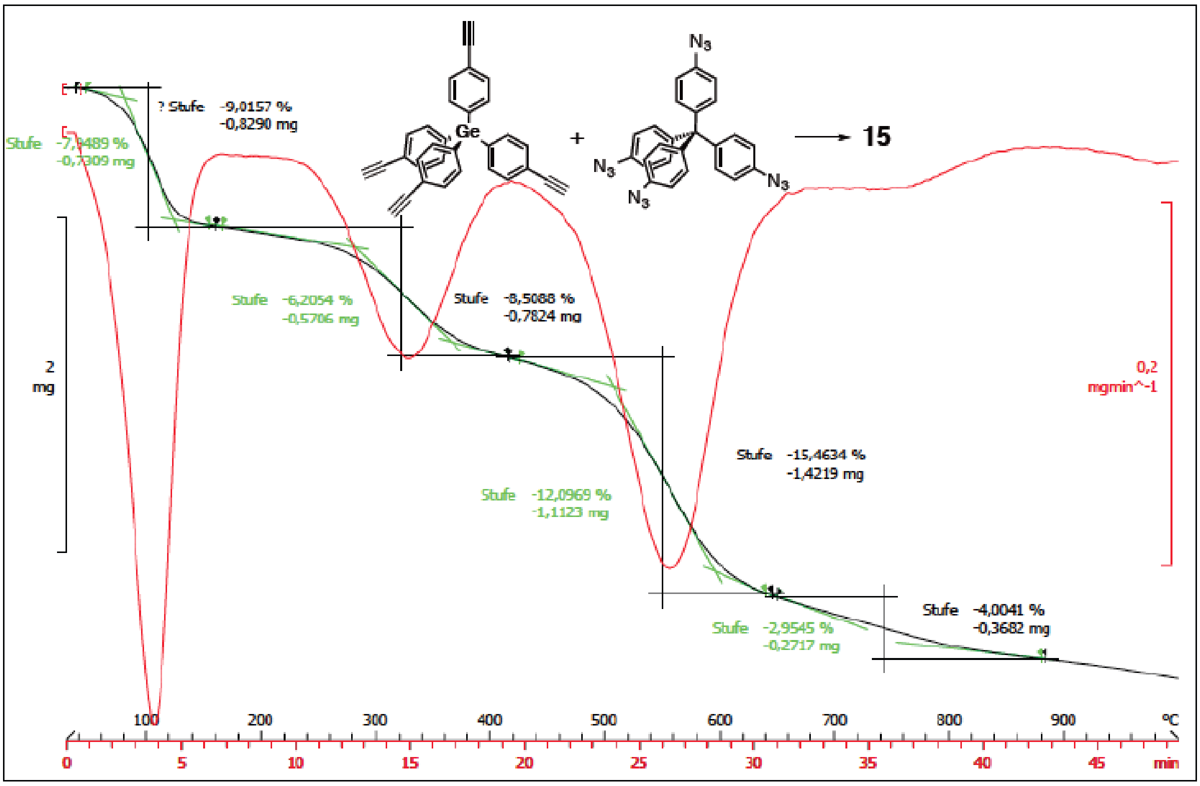



? Stufe -2,5632 %
-0,3152 mg
? Stufe -2,1702 %
-0,2669 mg
Stufe -0.7926 %
-97,4751e-03 mg
Stufe -5,6976 %
-0,7007 mg
Stufe -8,1862 %
-1,0067 mg
Stufe -5,9364 %
-0,7300 mg
Stufe -10,8027 %
-1,3285 mg
Stufe -3,6130 %
-0,4443 mg
Stufe -4,5713 %
-0,5621 mg
2
mg
0,1
mgmin^-1
4
+
N3
N3
6
12
100 200 300 400 500 600 700 800 900 °C
0 5 10 15 20 25 30 35 40 45 min

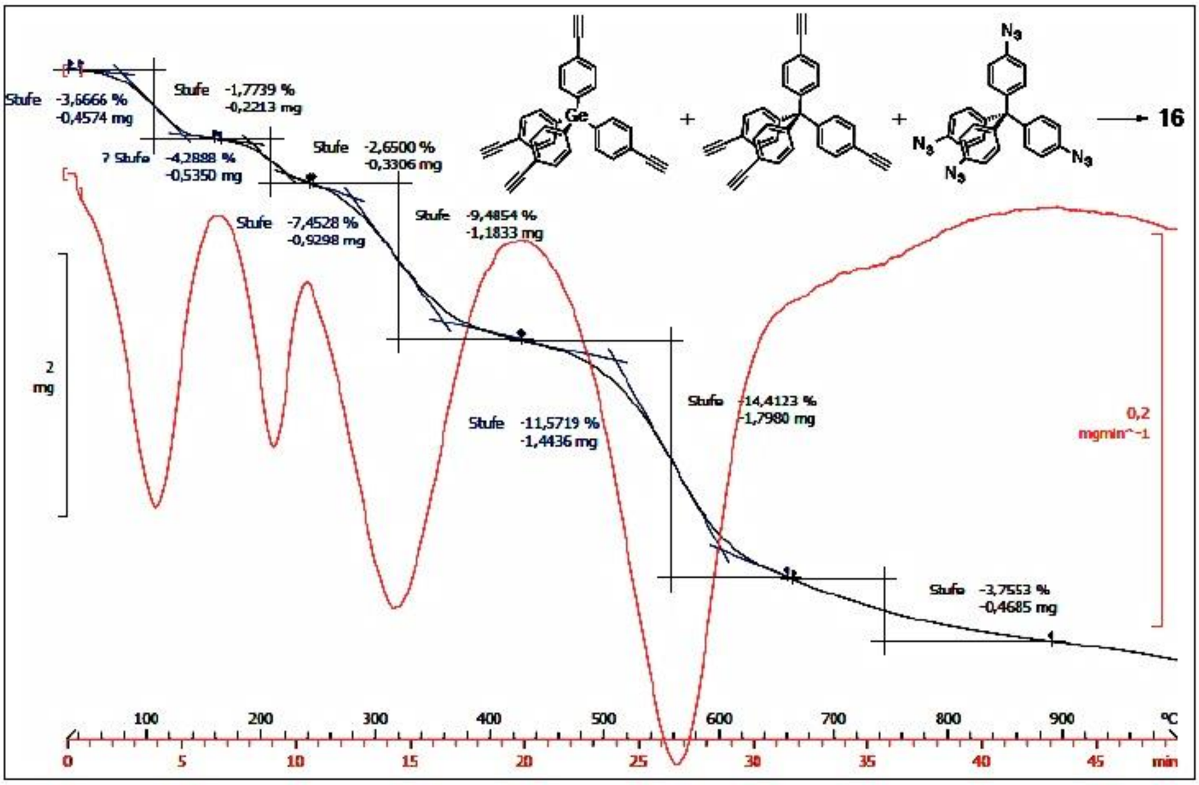

Stufe -2,66 %
-0,46 mg
Stufe -3,48 %
-0,60 mg
Stufe -5,63 %
-0,97 mg
Stufe -6,84 %
-1,18 mg
Stufe -14,25 %
-2,45 mg
Stufe -11,59 %
-1,99 mg
Stufe -3,59 %
-0,62 mg
Stufe -1,56 %
-0.27 mg
2
mg
0,2
mgmin^-1
Ge
3
+
N3
N3
7
13
100 200 300 400 500 600 700 800 900 °C
0 5 10 15 20 25 30 35 40 45 min



4
N3
N3
7
14
Stufe -3,80 % -0,47 mg
? Stufe -4.91 % -0,61 mg
Stufe -5,92 % -0,74 mg
Stufe -7,36 % -0,91 mg
Stufe -2,35 % -0,29 mg
Stufe -3,14 % -0,39 mg
Stufe -4,24 % -0,53 mg
Stufe -7,52 % -0,93 mg
Stufe -3,03 % -0,38 mg
Stufe -3,98 % -0,49 mg
2 mg
0,1 mgmin^-1
100
200
300
400
500
600
700
800
900
°C
0
5
10
15
20
25
30
35
40
45
min



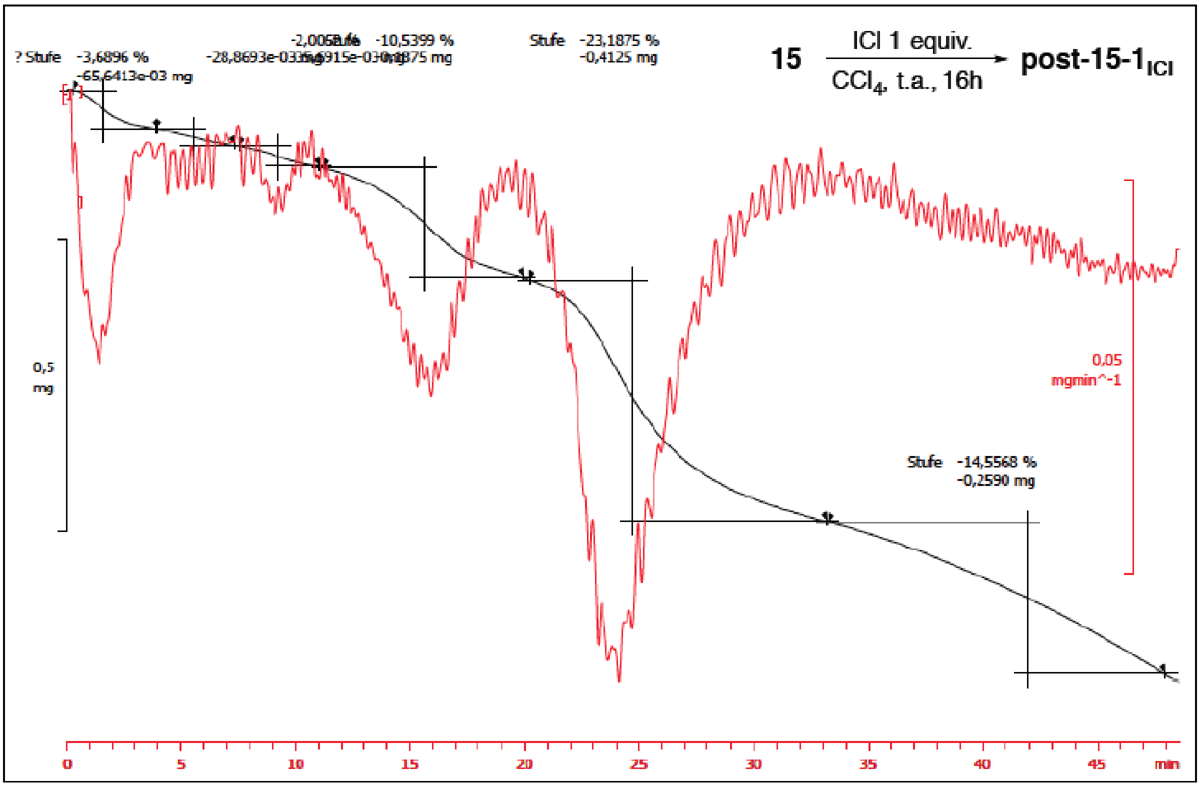
Ge
N3
N3
N3
15
? Stufe -9,0157 % -0,8290 mg
Stufe -7,9489 % -0,7309 mg
Stufe -6,2054 % -0,5706 mg
Stufe -8,5088 % -0,7824 mg
Stufe -12,0969 % -1,1123 mg
Stufe -15,4634 % -1,4219 mg
Stufe -2,9545 % -0,2717 mg
Stufe -4,0041 % -0,3682 mg
2 mg
0,2 mgmin^-1
100
200
300
400
500
600
700
800
900
°C
0
5
10
15
20
25
30
35
40
45
min



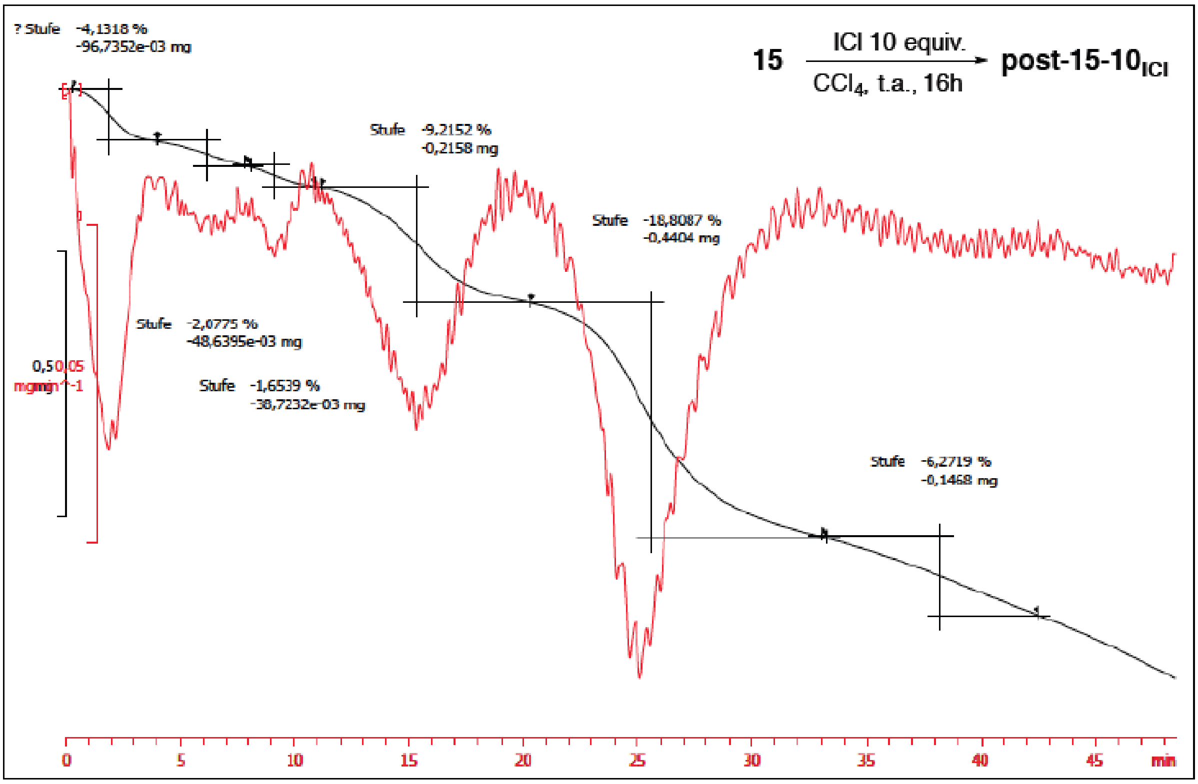
Stufe -3,6666 %
-0,4574 mg
Stufe -1,7739 %
-0,2213 mg
? Stufe -4,2888 %
-0,5350 mg
Stufe -2,6500 %
-0,3306 mg
Stufe -7,4528 %
-0,9298 mg
Stufe -9,4854 %
-1,1833 mg
Stufe -11,5719 %
-1,4436 mg
Stufe -14,4123 %
-1,7980 mg
Stufe -3,7553 %
-0,4685 mg
2
mg
0,2
mgmin^-1
Ge
N3
+
16
100 200 300 400 500 600 700 800 900 °C
0 5 10 15 20 25 30 35 40 45 min

Cleavage of 15 in presence of iodine monochloride (route a)

With 1 equiv. of ICl : **TGA 18-1$_{ICl}$**

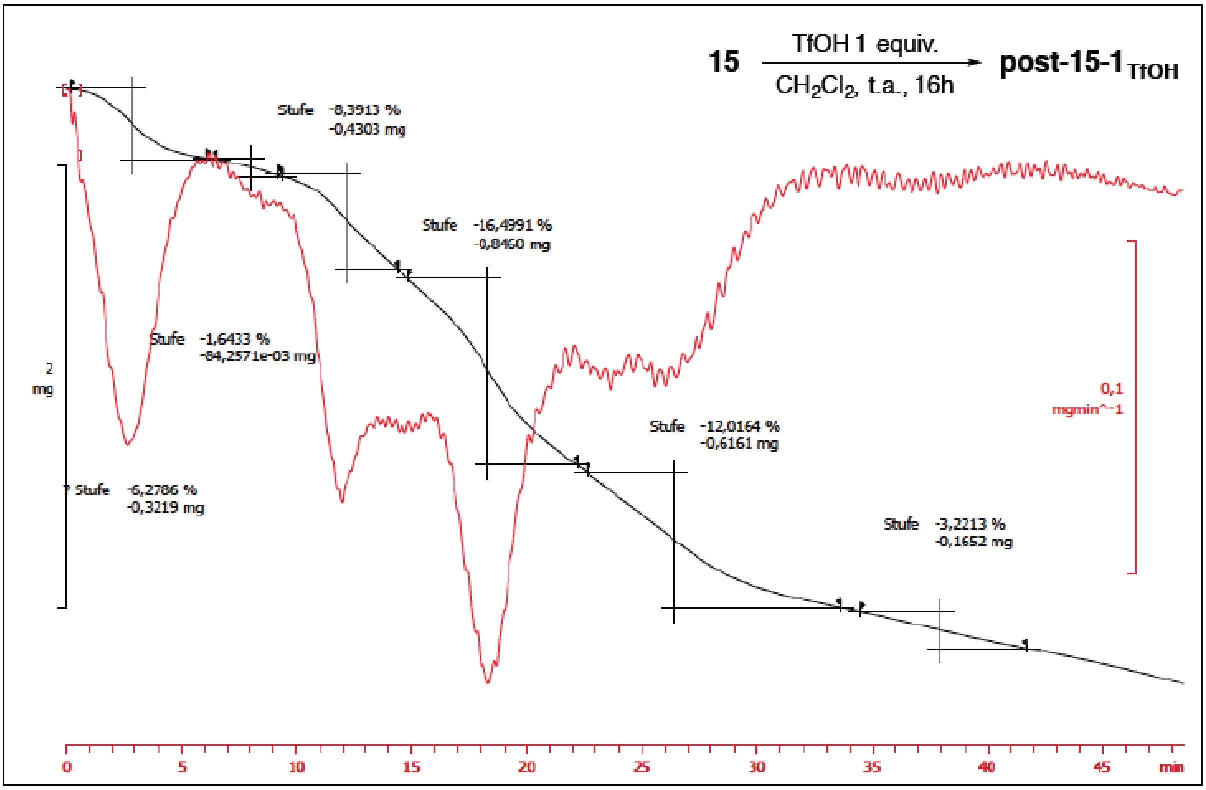


With 10 equiv. of ICl : **TGA 18-10$_{ICl}$**

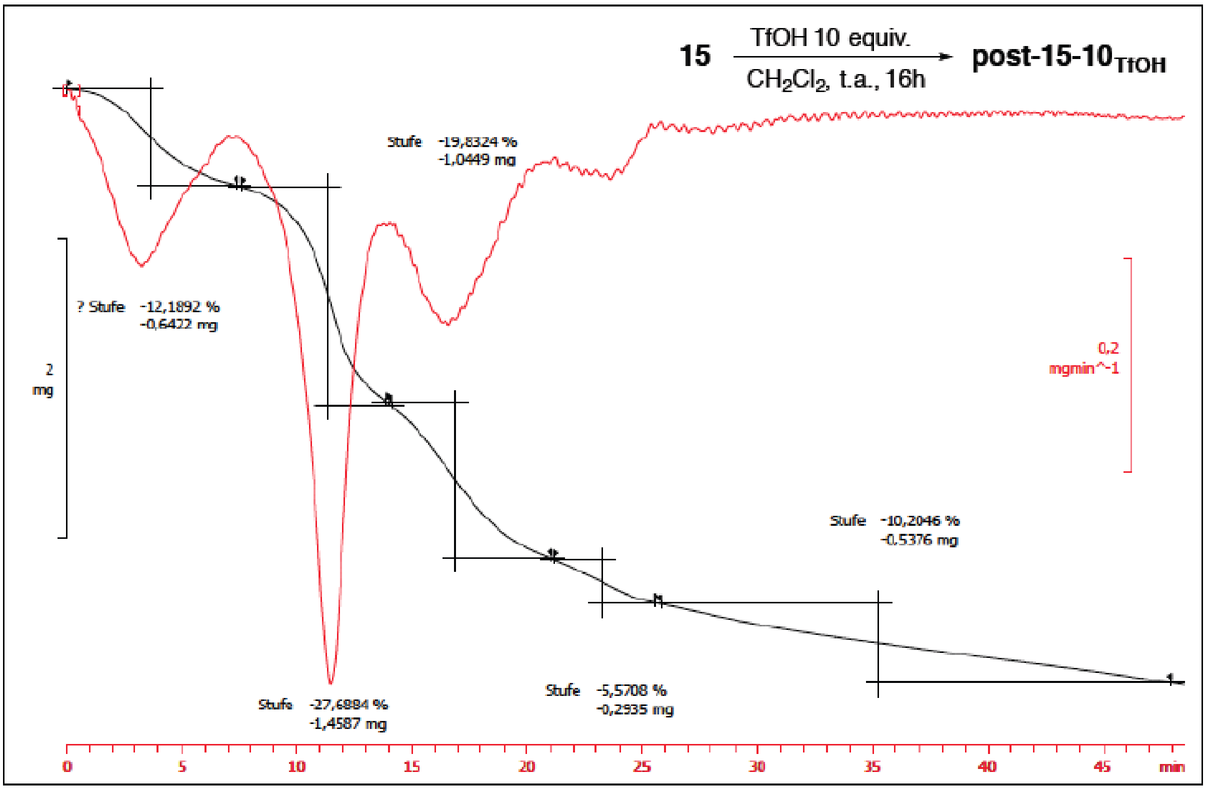


Cleavage of 15 in presence of trifluoromethanesulfonic acid (route b)

With 1 equiv. of TfOH : **TGA 18-1$_{TfOH}$**

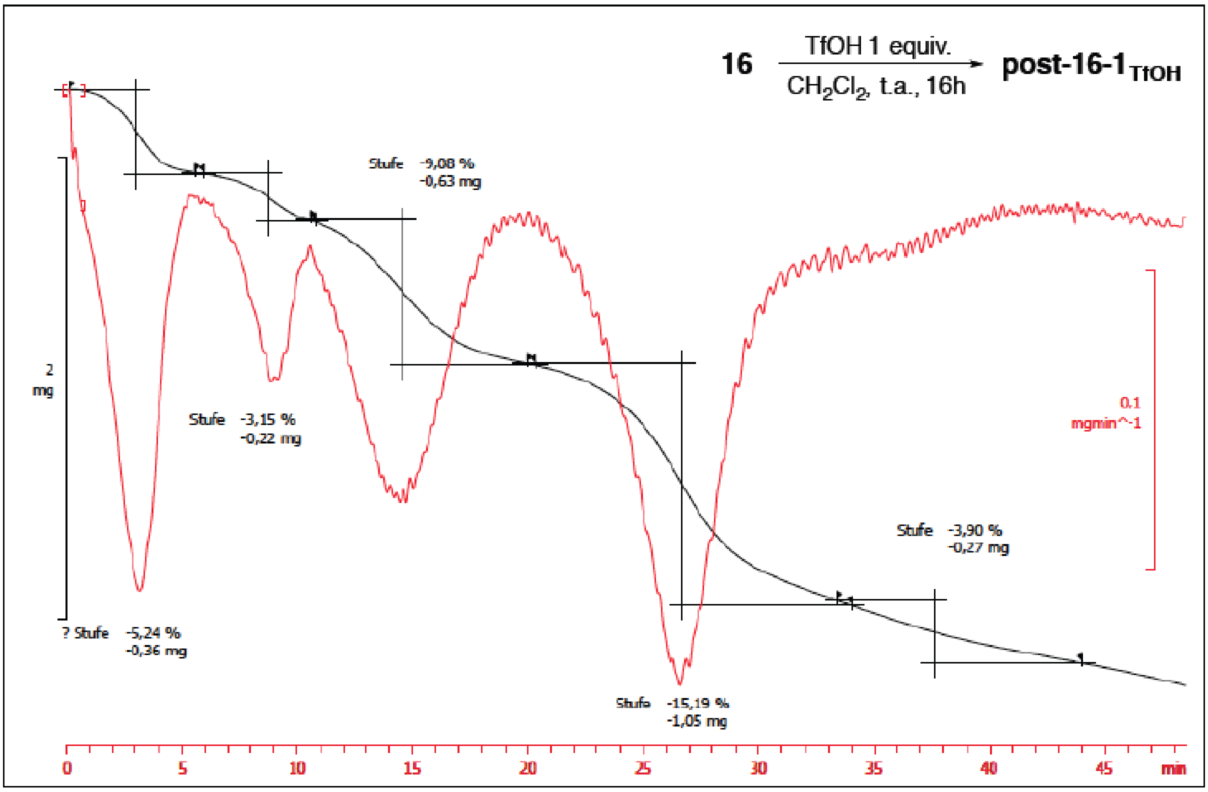


With 10 equiv. of TfOH : **TGA 18-10$_{TfOH}$**

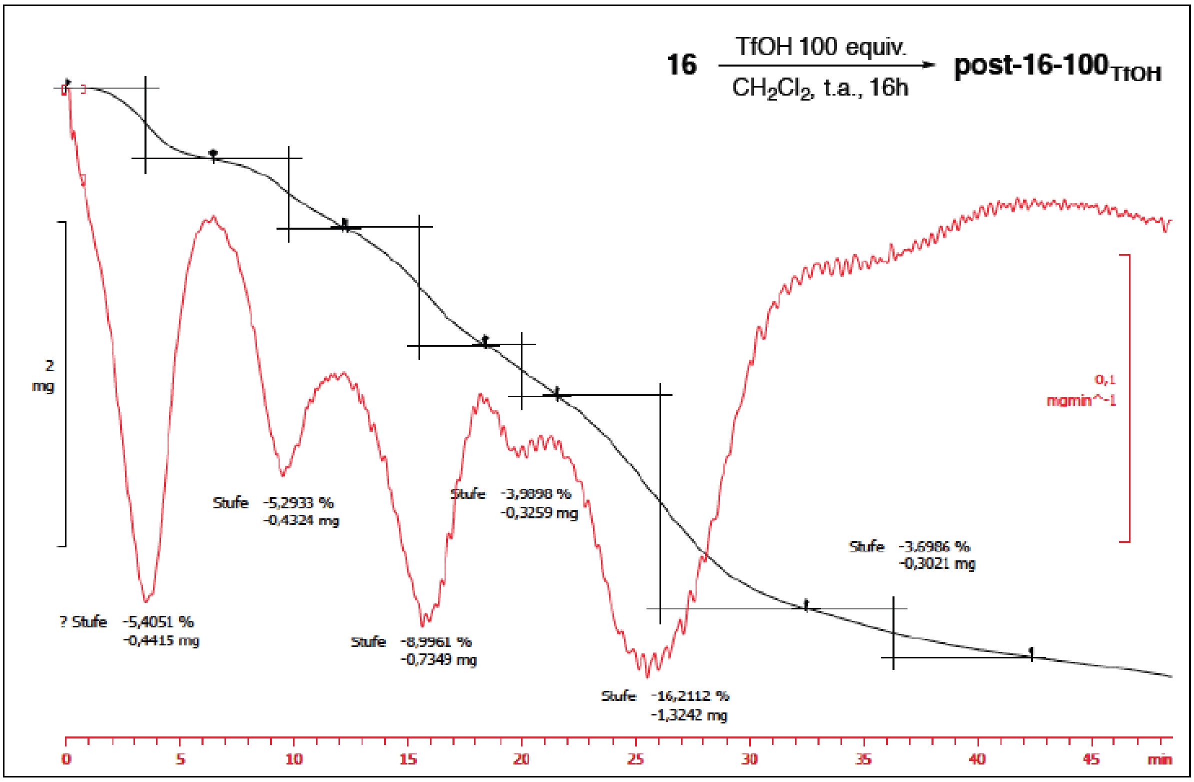


Cleavage of 16 in presence of trifluoromethanesulfonic acid (route b)

With 1 equiv. of TfOH : **TGA 19-1$_{\text{TfOH}}$**

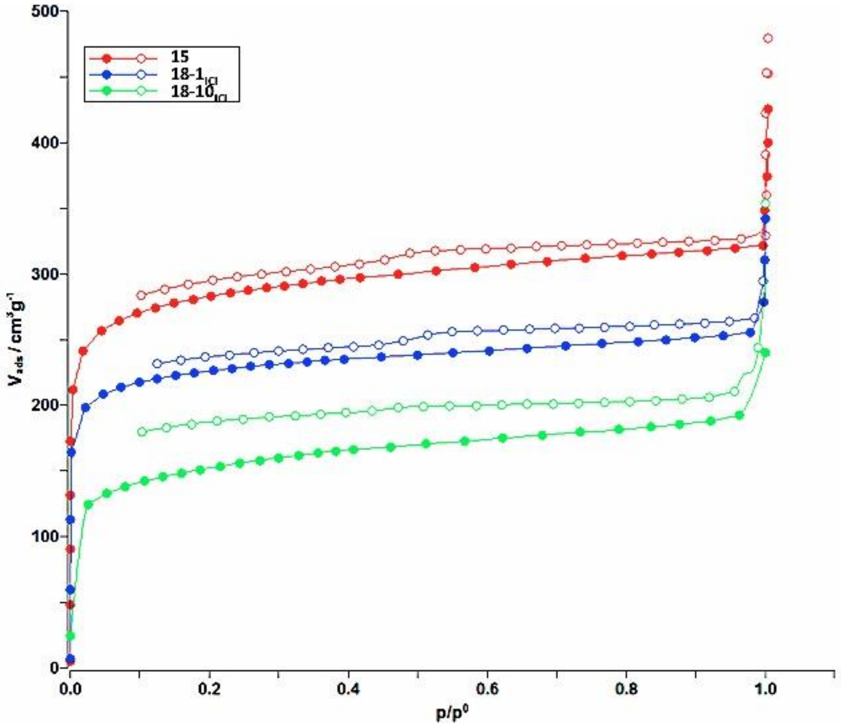


With 100 equiv. of TfOH : **TGA 19-100$_{\text{TfOH}}$**

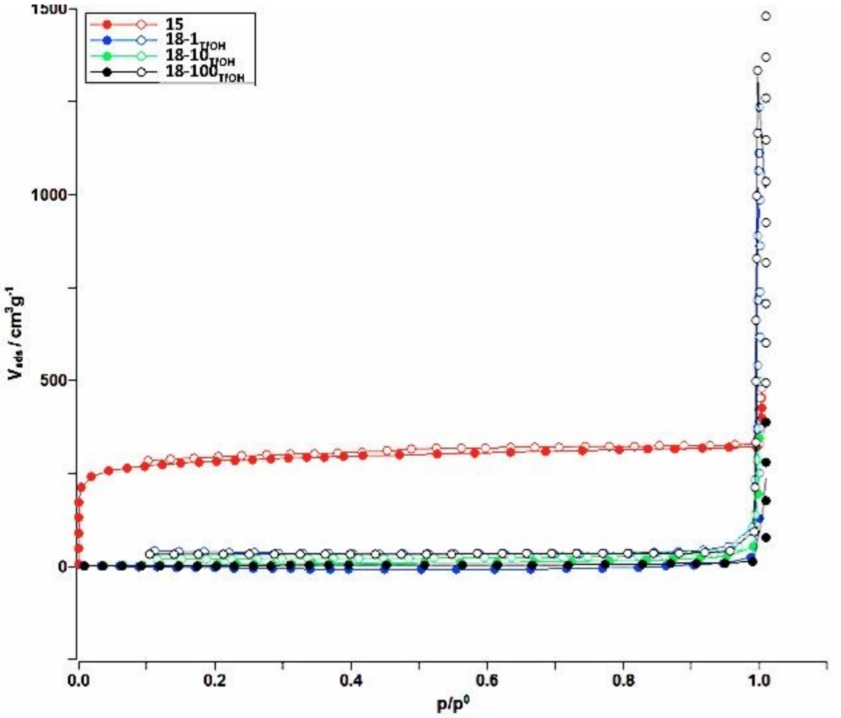


VII - N_2 adsorption data of POPs 9-19

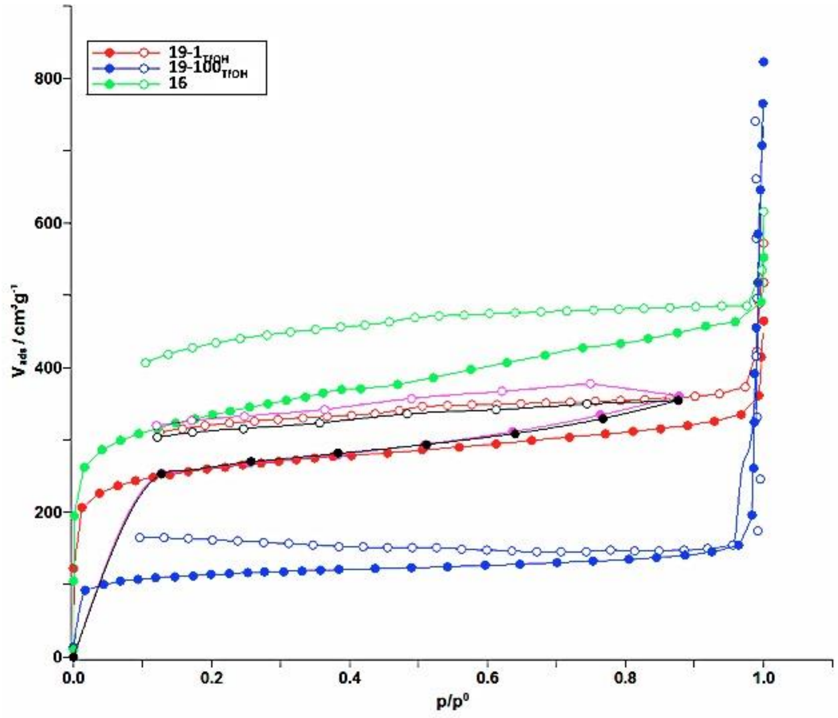
- N_2 adsorption isotherms of POPs **15** and **18-X$_{ICl}$**.



- N_2 adsorption isotherms of POPs **15** and **18-X$_{TfOH}$**.



- N_2 adsorption isotherms of POPs **16** and **19-X$_{\text{TfOH}}$**.



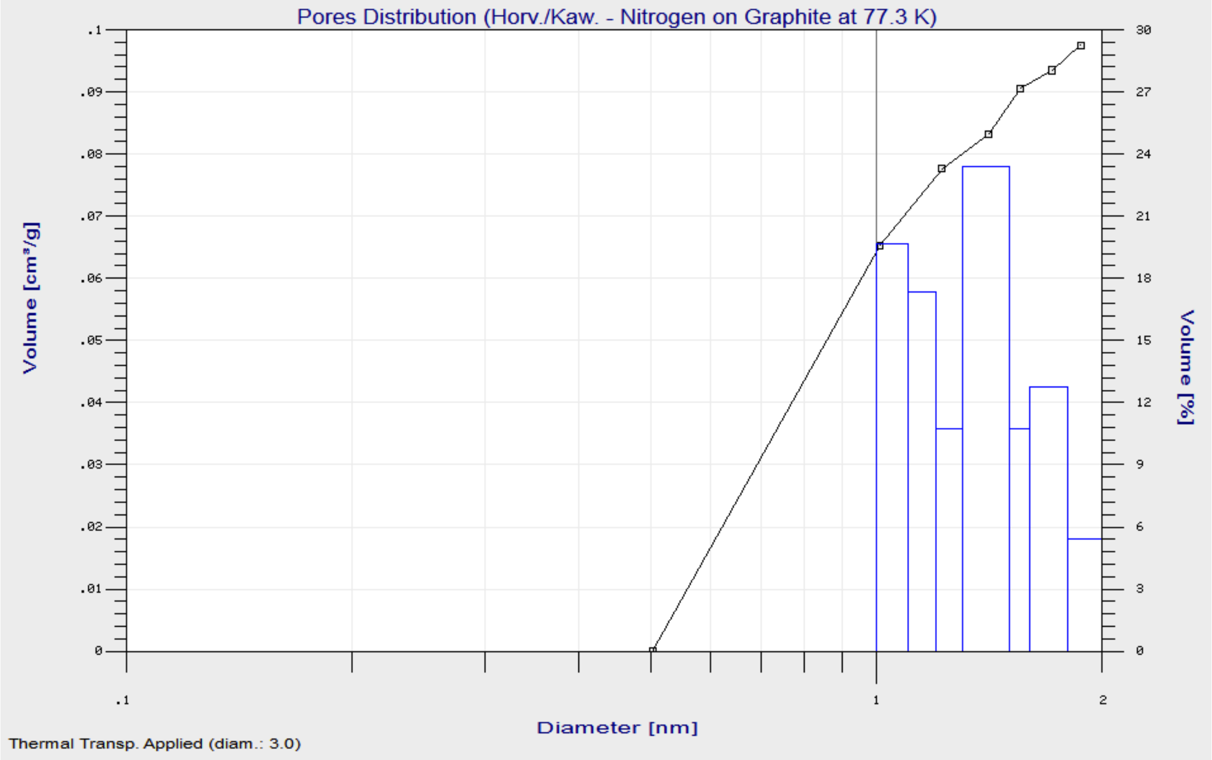
- Adsorption data of POPs **9**-**19**.

Entry	POP	Specific Surface Area[a]		Total Pore volume[b]	Maximum diameter[c]	Average diameter[c]
		BET	Langmuir			
1	**10**	231	351	0.0975	1.10	0.93
2	**12**	123	198	0.0455	1.10	0.99
3	**14**	134	268	0.0365	1.57	1.09
4	**15**	881	1301	0.4293	0.59	0.48
5	**16**	1056	1570	0.4903	0.62	0.44
6	**17**	1080	1614	0.5001	0.69	0.44
7	**18-1$_{\text{ICl}}$**	696	1034	0.3410	0.48	0.01
8	**18-10$_{\text{ICl}}$**	487	731	0.2250	1.21	0.94
9	**18-1$_{\text{TfOH}}$**	3	5	0.0023	/	/
10	**18-10$_{\text{TfOH}}$**	23	45	0.0065	/	/
11	**18-100$_{\text{TfOH}}$**	9	16	0.0030	/	/
12	**19-1$_{\text{TfOH}}$**	815	1227	0.3901	0.58	0.59
13	**19-100$_{\text{TfOH}}$**	361	532	0.1719	1.03	0.88

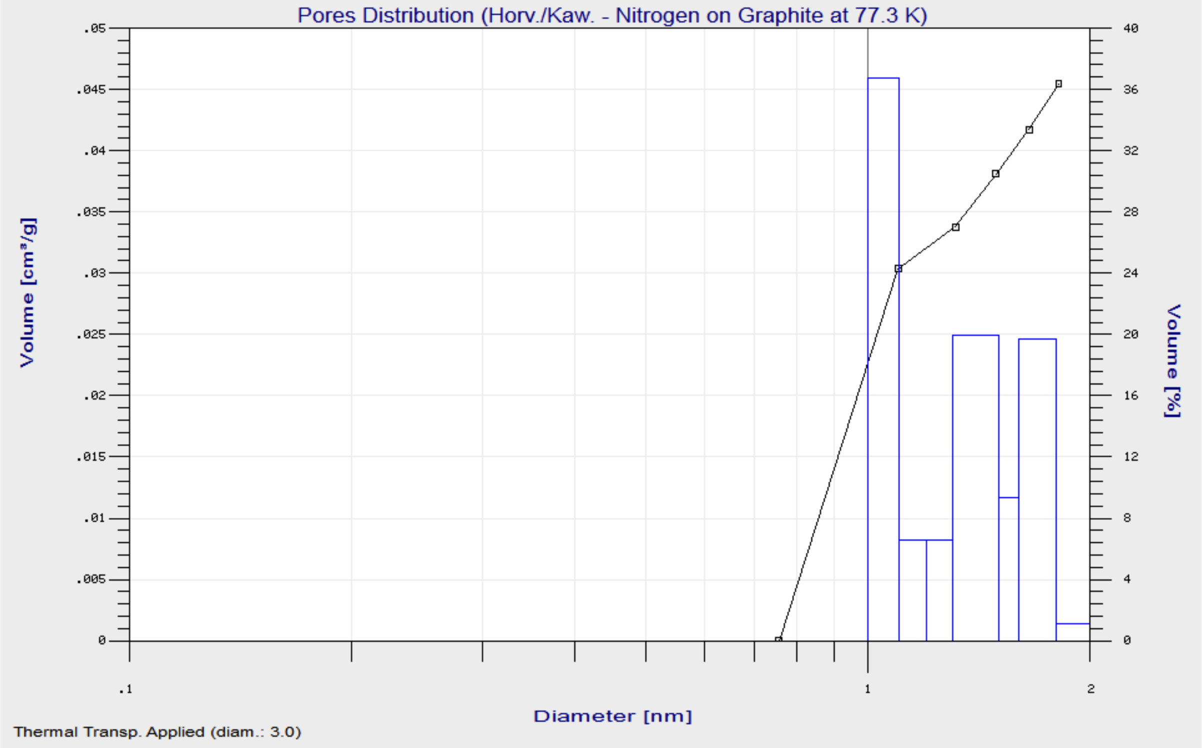
[a] Surface area calculated over the relative pressure range P/P_0 = 0.05-0.3. Specific surface area is expressed in m^2.g^{-1}. [b] Total pore volume for P/P_0 = 0.99 and is expressed in cm^3.g^{-1}. [c] The Saito and Foley method was applied for calculation of the pore characteristics. Maximum and average diameters of pore are expressed in nm.

- Pore size distribution of POPs **10**-**16**, **18** and **19**.

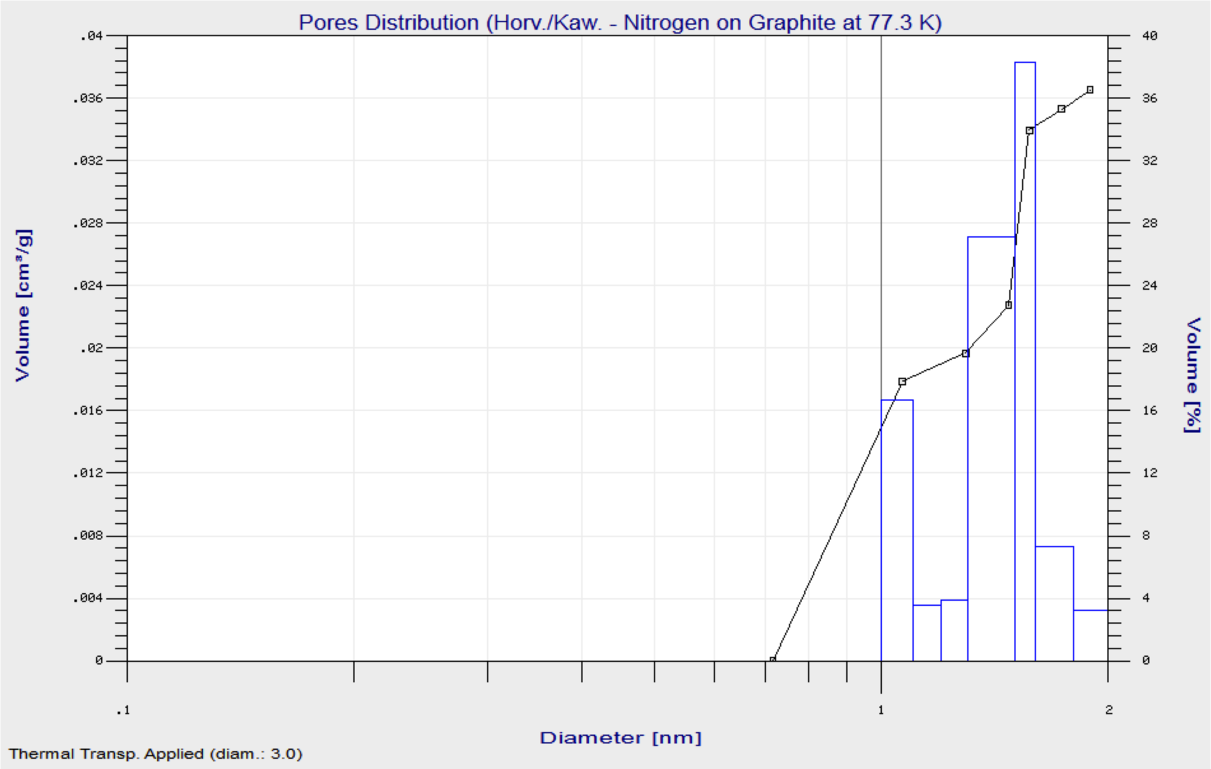
Pore size distribution of POP **10**



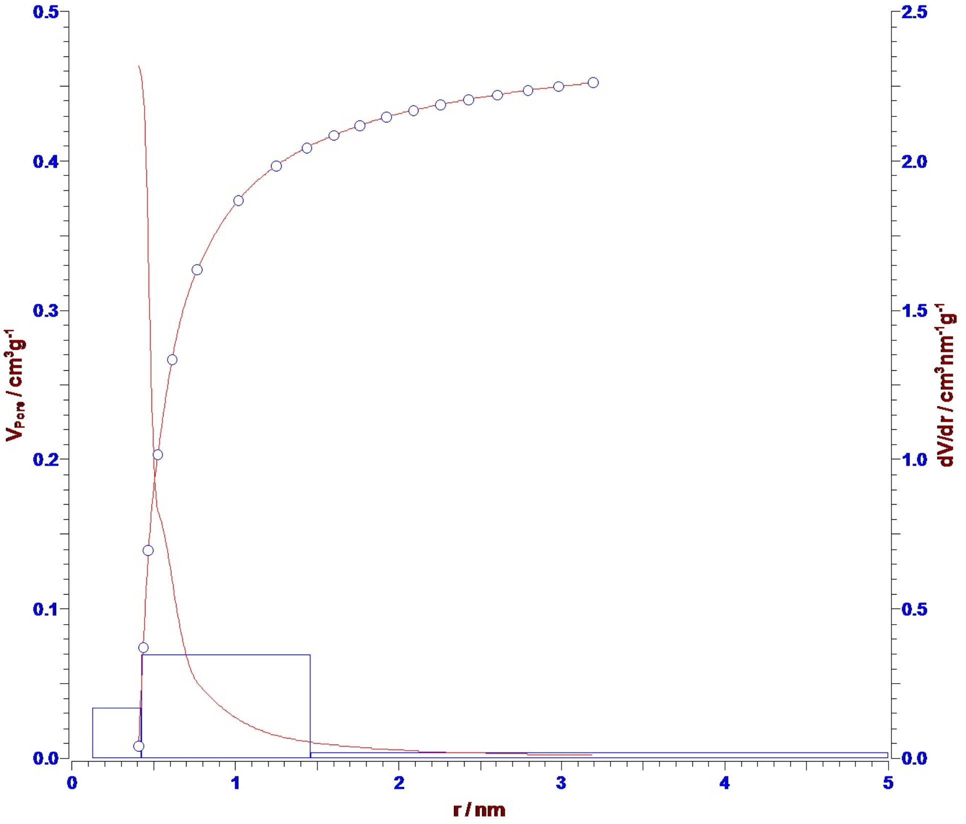
Pore size distribution of POP **12**



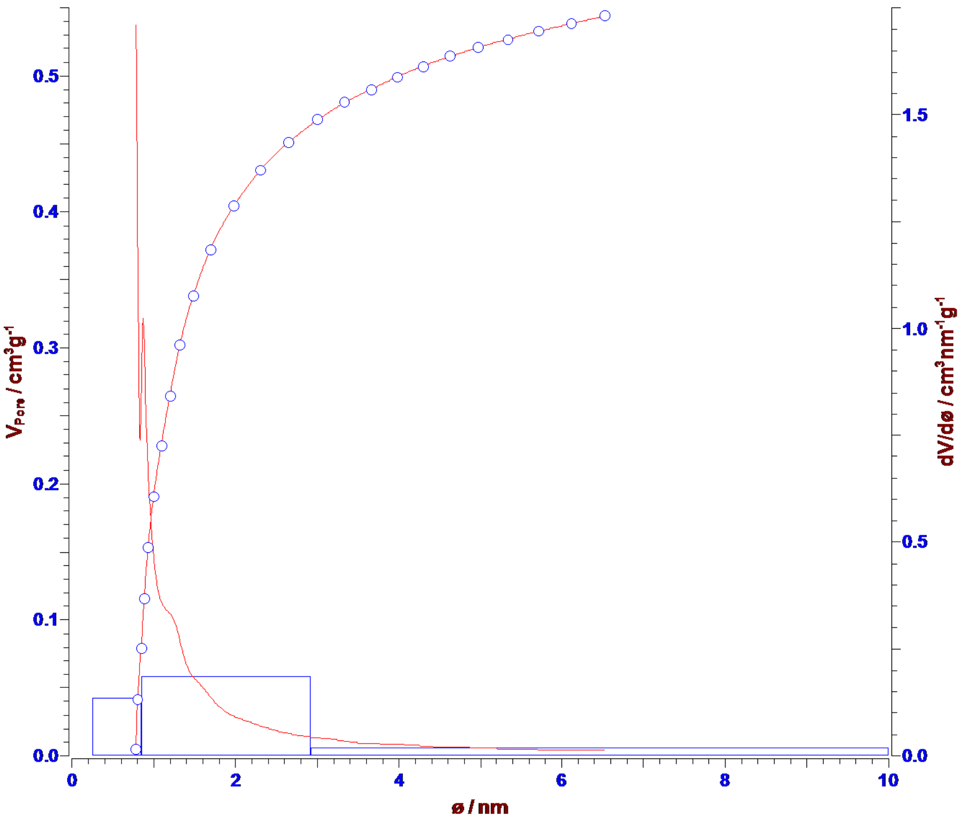
Pore size distribution of POP **14**



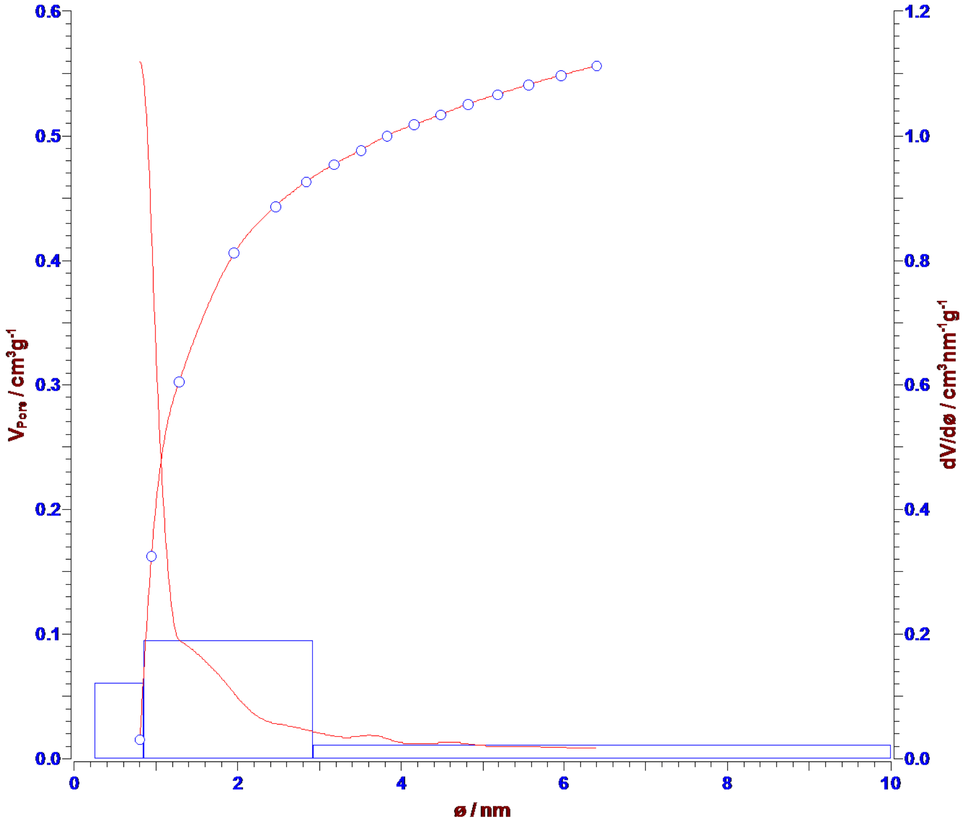
Pore size distribution of **15**



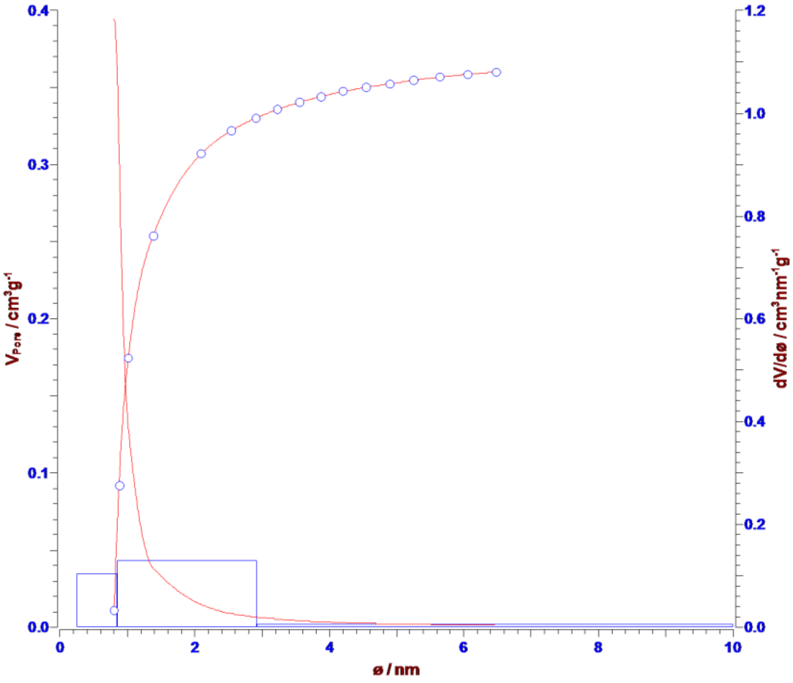
Pore size distribution of **16**



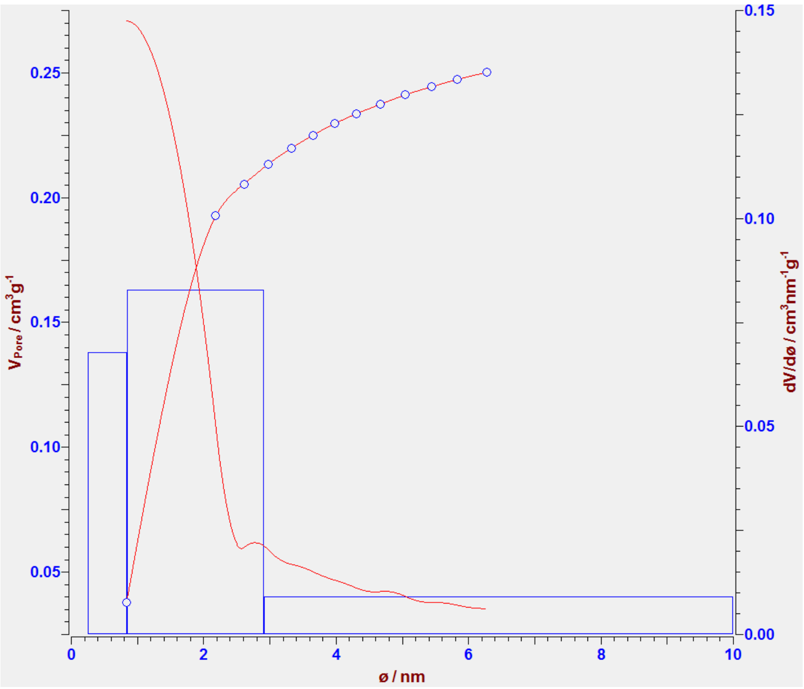
Pore size distribution of **17**



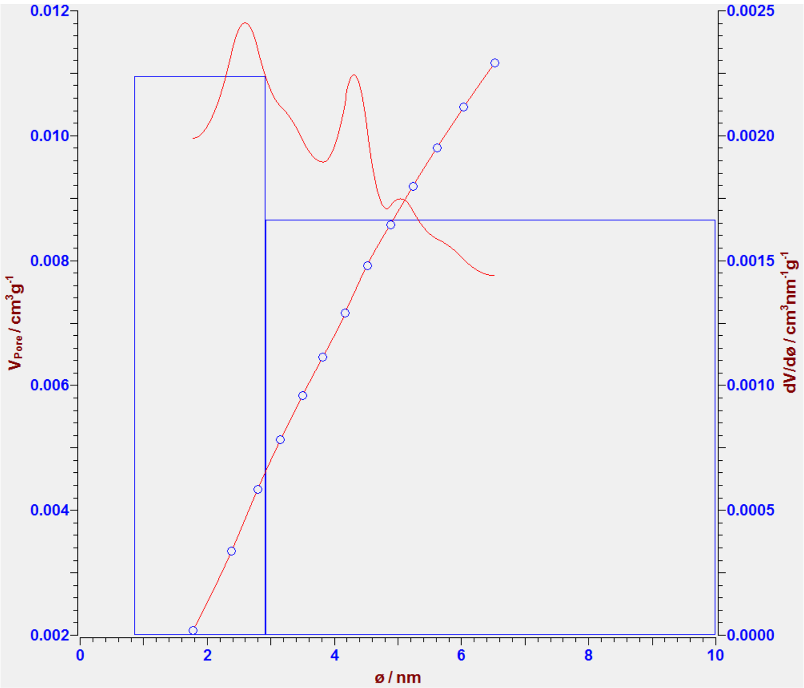
Pore size distribution of **18-1**$_{\mathrm{ICl}}$



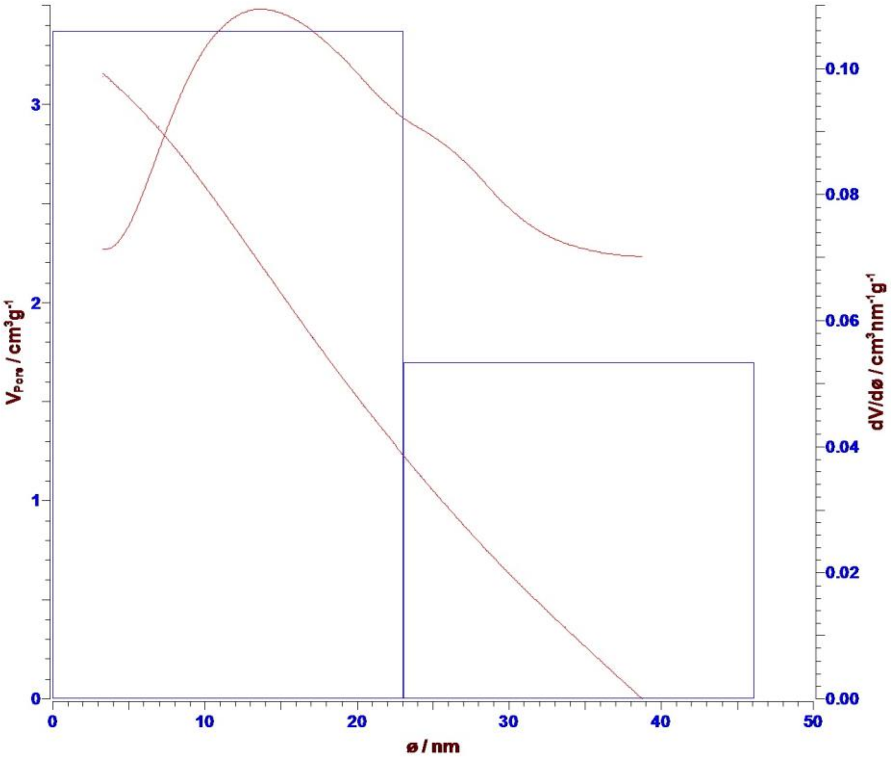
Pore size distribution of **18-10**$_{\mathrm{ICl}}$



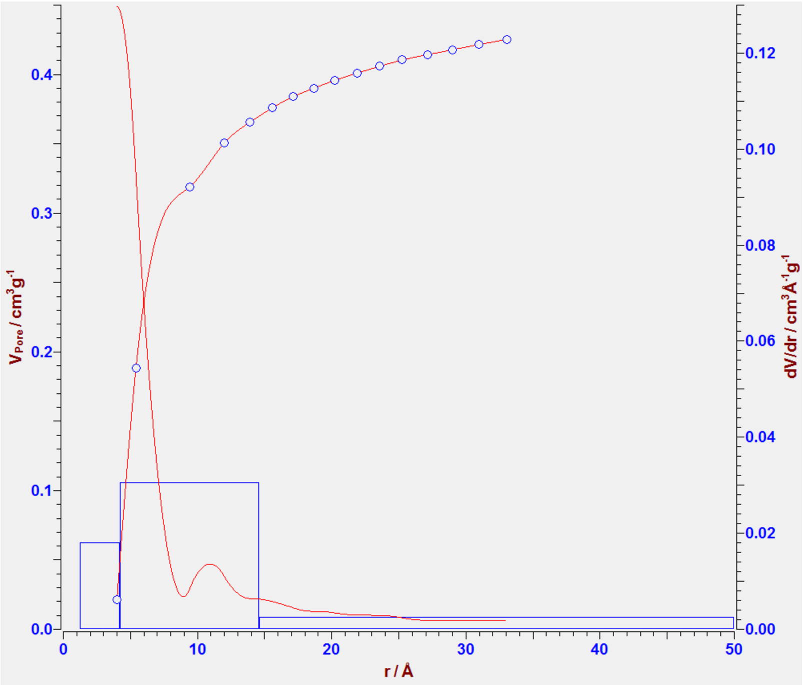
Pore size distribution of **18-10**$_{\mathbf{TfOH}}$



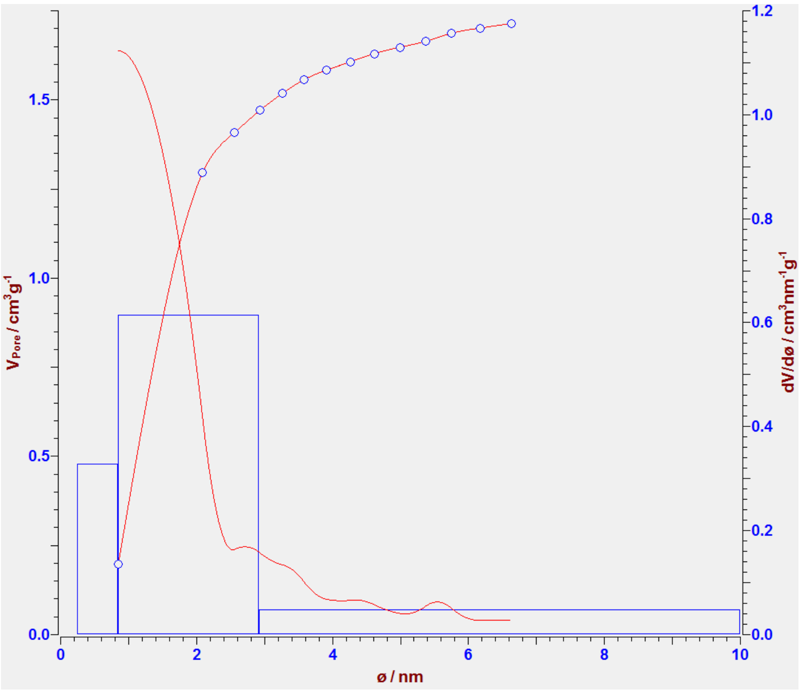
Pore size distribution of **18-100**$_{\mathbf{TfOH}}$



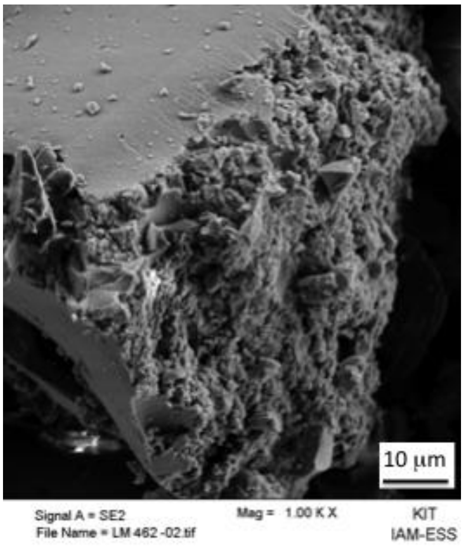
Pore size distribution of **19-1**$_{\mathbf{TfOH}}$

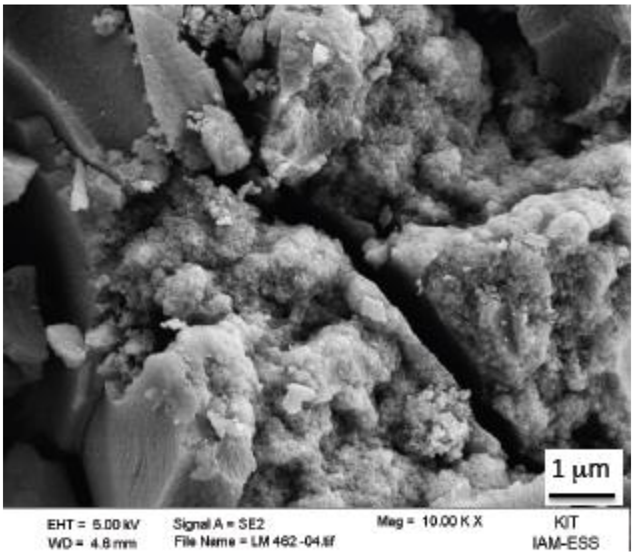


Pore size distribution of **19-100**$_{\mathbf{TfOH}}$



VIII - SEM pictures of POP 15





IX - References

[1] J. B. Lambert, L. Zhongqiang, L. Chunqing, *Organometallics* **2008**, *27*, 1464-1469.

[2] W. Lu, D. Yuan, D. Zhao, I. C. Schiling, O. Plietzsch, T. Muller, S. Bräse, J. Guenther, J. Blümel, R. Krishna, Z. Li, H.-C. Zhou, *Chem. Mater.* **2010**, *22*, 5964-5972.

[3] K. T. Hattori, T. Hattori, S. Uchino, T. Ueno, N. Hayashi, S. Shirai, N. Moriuchi, M. Morita, *Jpn. J. Appl. Phys.* **1992**, *31*, 4307-4311.

[4] P. R. Serwinski, R. Walton, J. A. Sanborn, P. M. Lahti, E. Tomonori, D. Miura, H. Tomioka, A. Nicolaides, *Org. Lett.* **2011**, *3*, 357-360.

[5] O. Plietzsch, I. C. Schiling, M. Tolev, M. Nieger, C. Richert, T. Muller, S. Bräse, *Org. Biomol. Chem.* **2009**, *7*, 4734-4743.

[6] S. N. Bhattachariya, P. Raj, R. C. Srivastava, *J. Organomet. Chem.* **1976**, *105*, 45-49.

[7] S. Konieczny, S. J. Jacobs, J. K. Braddock Wilking, P. P. Gaspar, *J. Organomet. Chem.* **1988**, *341*, C17-C22.

[8] K. V. Zaitsev, A. A. Kapranov, Y. F. Oprunenko, A. V. Churakov, J. A. K. Howard, B. N. Tarasevich, S. S. Karlov, G. S. Zaitseva, *J. Organomet. Chem.* **2012**, *700*, 207-213.