Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Tailor-made N-Heterocyclic Carbenes for Nanoparticle Stabilization

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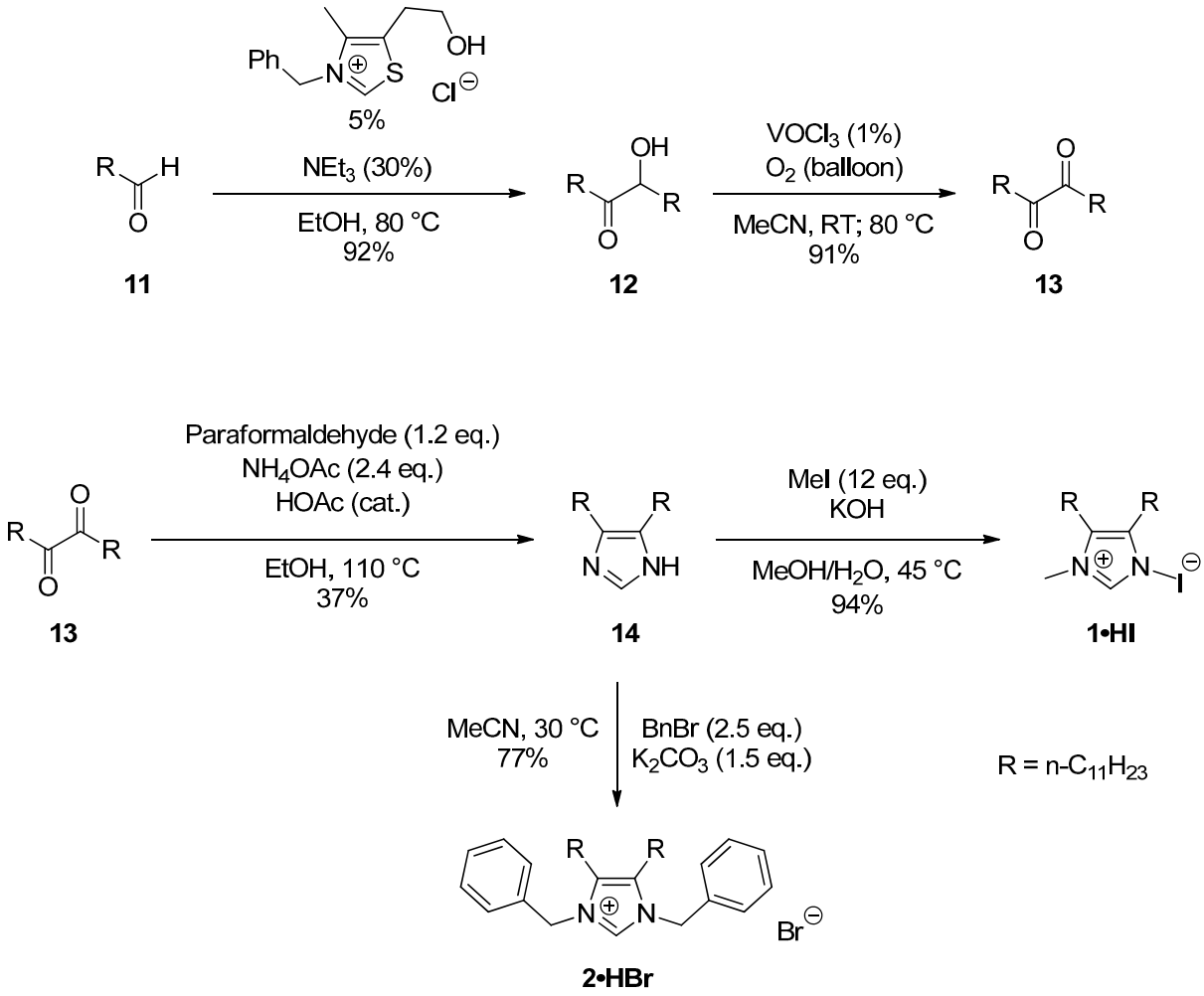
1 Experimental techniques

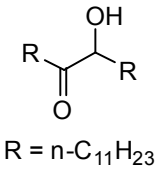
Reactions were performed in oven-dried glassware under an atmosphere of dry argon. Dry solvents (toluene, DCM, hexane) were distilled in a continuous still under an atmosphere of dry argon; anhydrous acetonitrile and ethanol was purchased from Sigma Aldrich and stored over molecular sieves under argon. Solvents for extraction and purification were technical grade and flash-distilled prior to use. All chemicals were obtained from Acros, Aldrich, Strem or Alfa Aesar and used as received unless indicated otherwise. Reactions were monitored by thin layer chromatography on pre-coated aluminium-backed plates (Merck Kieselgel 60 with fluorescent indicator UV_{254}). Flash column chromatography was performed with silica gel (0.040-0.063 mm, Kieselgel 60, Merck), applying head pressure by means of low pressure argon line (0.1-0.3 atm). Brine denotes a saturated aq. solution of NaCl. Infrared spectra were recorded on a Varian Associated FT-IR 3100 Excalibur with ATR unit. The wave numbers (n) of recorded IR-signals are quoted in cm^{-1}. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ or in the solvent indicated using Bruker ARX-300, AV-300 or AV-400 spectrometers. Data are expressed as chemical shifts in parts per million (ppm) relative to residual chloroform and $CDCl_3$ (^{1}H δ7.28, ^{13}C δ77.2, respectively; likewise for other solvents where applicable) as internal standard on the δ scale. ^{1}H coupling constants *J* are given in Hz and rounded to the nearest 0.1 Hz. GC-MS chromatograms were recorded on an Agilent Technologies 7890A GC-system equipped with an Agilent 5975C VL MSD (EI) and a HP-5MS column with helium as carrier gas; the major signals are quoted as ratio of *m*/*z* in Daltons; ESI mass spectra were obtained using a Bruker Daltonics MicroTof and the instrument was calibrated using sodium formicates clusters. TEM analyses were performed by Martin Peterlechner at the Institute of Material Physics using a Zeiss 200 FE electron microscope with schottky emitter and energy Ω filter operating at 200 kV. The microscope is equipped with the CCD camera Gatan USC 4000. ImageJ version 1.39u, Java 1.6.0_02 (NATIONAL INSTITUTES OF HEALTH, USA) was used to measure the size of the NPs. DLS was measured with Zetasizer Nano ZS (MALVERN INSTRUMENTS LTD.). TGA was measured on TGA Q5000 V3.15 from TA INSTRUMENTS under oxygen atmosphere. Elemental analysis was performed using Vario EL III elementar Hanau.

PFG NMR measurements were performed on a DMX400-spektrometer (*Bruker*) in a constant magnetic field of 9.4 T and a diffusion probe (Diff30, *Bruker*). The calibrations of the instrument were determined on the water signal.

2 Synthesis of the imidazolium salts 1•HI, 2•HBr & LC-IPr•HBr



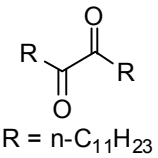
2.1 Synthesis of acyloin 12[1]



A flame dried flask was charged with 3-Benzyl-5-(2-hydroxyethyl)-4-methylthiazol-3-ium chloride (2.90 g, 10.7 mmol, 0.05 eq.). The catalyst was suspended in dry EtOH (100 mL) and dodecanal (**11**) (47.4 mL, 215.0 mmol, 1 eq.)) and NEt_3 (9.0 mL, 64.5 mmol, 0.30 eq.) was added. The mixture was heated to 80 °C for 3 h and subsequently poured on ice (300 mL). The suspension was stirred until all ice was molten. Then the white precipitate was filtered off and the crude product was recrystallized from EtOH to afford the title compound (36.30 g, 98.5 mmol, 92%) as a white solid. $\mathbf{R_f}$ (n-pentane/EtOAc: 95/5): 0.42. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 4.20 – 4.12 (m, 1H, C*H*OH), 3.47 (bs, 1H, OH), 2.57 – 2.30 (m, 2H, $COCH_2$), 1.88 – 1.71 (m, 1H, CH_2), 1.71 – 1.55 (m, 2H, CH_2), 1.57 – 1.38 (m, 3H,

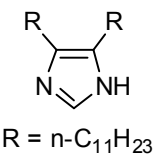
CH_2), 1.38 – 1.17 (m, 32H, CH_2), 0.91 – 0.83 (m, 6H, CH_3). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ = 212.7, 38.0, 33.9, 32.1, 29.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 25.0, 23.8, 22.8, 14.3. **MS-ESI**: calculated for $[C_{24}H_{48}O_2Na]^+$: m/z = 391.3547, found: m/z = 391.3545. **ATR-FTIR (cm^{-1}):** 3336, 2953, 2915, 2849, 1712, 1468, 1375, 1157, 1124, 1102, 1066, 714, 661.

2.2 Synthesis of diketone 13



Following a modified procedure,[2] the acyloin **12** (1.843 g, 5.00 mmol, 1.00 eq.) was suspended in acetonitrile (50 mL) and $VOCl_3$ (8.7 mg, 0.05 mmol, 0.01 eq.) was added dropwise as a solution in acetonitrile (0.1 M). The flask was equipped with an oxygen balloon and the yellow suspension was stirred for 18 h at RT. The mixture was heated for 3 h at 65 °C. Completion of the reaction was monitored by TLC and was indicated by a green color of the reaction mixture. The reaction was quenched by addition of sat. $NaHCO_3$ sol. and extracted with pentane/ethylacetate (1/1). The organic phase was washed with sat. NH_4Cl sol., brine, dried over $MgSO_4$ and the solvent was evaporated. The crude product was recrystallized from EtOH (20 mL) to afford the title compound (1.663 g, 4.69 mmol, 91%) as a pale yellow solid. **R_f** (n-pentane/EtOAc: 95/5): 0.91. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 2.72 (t, *J*=7.4Hz, 4H, $COCH_2$), 1.60 – 1.52 (m, 4H, $COCH_2CH_2$), 1.31 – 1.20 (m, 32H, CH_2), 0.87 (t, *J*=6.9 Hz, 6H, CH_3). **^{13}C{1H} NMR** (101 MHz, $CDCl_3$) δ = 200.4, 36.2, 32.1, 29.8, 29.6, 29.5, 29.3, 23.2, 22.8, 14.3. **MS-ESI**: calculated for $[C_{24}H_{46}O_2Na]^+$: m/z = 389.3390, found: m/z = 389.3388. **ATR-FTIR (cm^{-1}):** 2957, 2916, 2849, 1713, 1467, 1404, 1371, 1290, 1261, 1230, 1160, 1124, 1092.

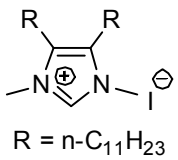
2.3 Synthesis of imidazole 14



Following a modified procedure,[3] a schlenk tube was charged with diketone **13** (6.248 g, 17.04 mmol, 1.00 eq.), paraformaldehyde (0.614 g, 20.45 mmol, 1.20 eq.) and NH_4OAc (3.152 g, 40.90 mmol, 2.40 eq.). The solids were suspended in EtOH (25 mL) and a catalytic amount of HOAc (ca. 5 drops) was added. The mixture was heated for 4h at 110 °C. The reaction was quenched by addition of sat. $NaHCO_3$ sol. and extracted with DCM (3 x 80 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed. The

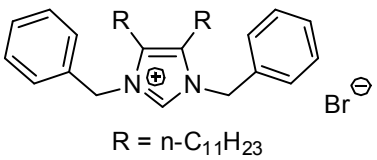
crude product was purified by flash chromatography (DCM/MeOH: 100/5 → 100/10) to afford the title compound (2.394 g, 6.35 mmol, 37%) as a pale yellow solid. **R_f** (DCM/MeOH 9/1): 0.29. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 8.62 (bs, 1H, NH), 7.43 (s, 1H, NCHN), 2.51 (t, *J*=7.6 Hz, 4H, $C_{Ar}CH_2$), 1.69 – 1.47 (m, 4H, CH_2), 1.41 – 1.13 (m, 32H, CH_2), 0.95 – 0.78 (m, 6H, CH_3). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ = 132.7, 131.2, 32.1, 30.3, 29.8, 29.8, 29.7, 29.6, 29.5, 25.6, 22.8, 14.3. **MS-ESI**: calculated for $[C_{25}H_{48}N_2H]^+$: m/z = 377.3890, found: m/z = 377.3895. **ATR-FTIR (cm^{-1}):** 2916, 2851, 1834, 1656, 1471, 1248, 965, 804, 717, 655, 597.

2.4 Synthesis of imidazolium salt 1•HI



Following a modified procedure,[4] imidazole **14** (1.500 g, 3.98 mmol, 1.00 eq.) was suspended in MeOH (3 mL) and mixed with KOH sol. (6 mL, 5 M) and MeI (6.779 g, 47.76 mmol, 12 eq.). The mixture was heated at 45 °C for 2 days. The reaction was quenched by addition of water and extracted with DCM (3 x 50 mL). The combined organic phases were dried over $MgSO_4$ and the solvent was removed. The crude product was purified by flash chromatography (DCM/MeOH: 100/0 → 100/5 → 100/10) to afford the title compound (1.986 g, 3.73 mmol, 94%) as a pale yellow solid. **R_f** (DCM/MeOH 9/1): 0.43. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 10.09 (s, 1H, NCHN), 3.89 (s, 6H, NCH_3), 2.60 – 2.50 (m, 4H, $C_{Ar}CH_2$), 1.54 – 1.43 (m, 4H, CH_2), 1.41 – 1.13 (m, 32H, CH_2), 0.89 – 0.80 (m, 6H, CH_3). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ = 136.5, 131.1, 34.2, 31.9, 29.6, 29.5, 29.4, 29.4, 29.2, 29.1, 23.0, 22.7, 14.2. **MS-ESI**: calculated for $[C_{27}H_{53}N_2]^+$: m/z = 405.4203, found: m/z = 405.4208. **ATR-FTIR (cm^{-1}):** 2921, 2853, 2187, 1668, 1620, 1575, 1463, 1375, 1197, 1128, 1088, 919, 839, 728, 649.

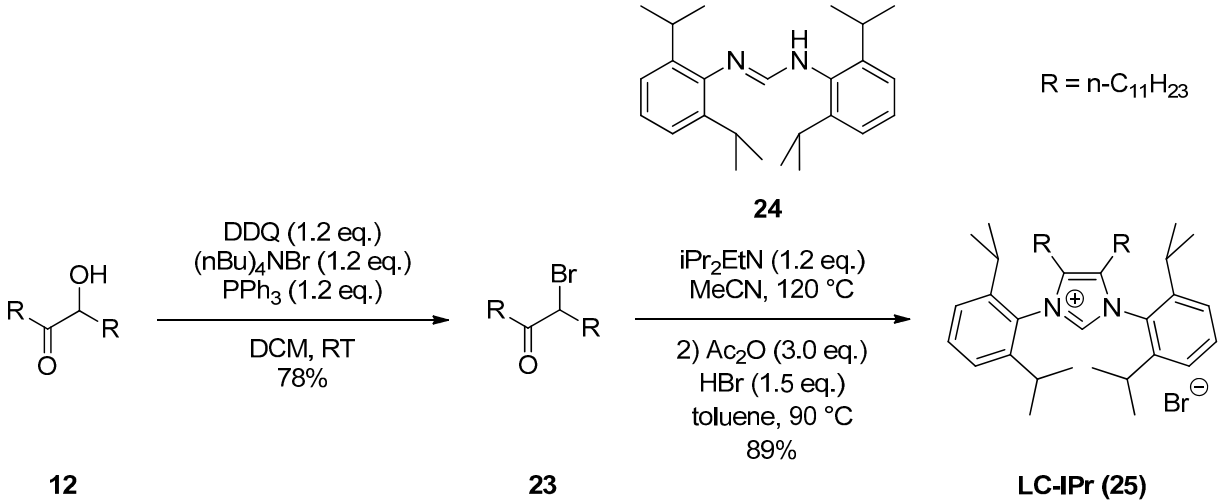
2.5 Synthesis of imidazolium salt 2•HBr



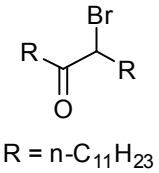
Following a modified procedure,[5] imidazole **14** (0.446 g, 1.18 mmol, 1.00 eq.) and K_2CO_3 (0.245 g, 1.77 mmol, 1.50 eq.) were suspended in acetonitrile (6 mL) for 10 min. Benzyl bromide (0.505 g, 2.95 mmol, 2.50 eq.) was added and the resulting mixture was stirred at 30 °C for 2 days. The reaction was quenched by addition of water and extracted with DCM (3 x 20 mL). The combined organic phases

were dried over $MgSO_4$ and the solvent was removed. The crude product was purified by flash chromatography (DCM/MeOH: 100/5 → 100/10) to afford the title compound (0.581 g, 0.91 mmol, 77%) as a yellow sticky oil, which solidified after some days. **R_f** (DCM/MeOH 9/1): 0.41. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 10.91 (s, 1H, NCHN), 7.43 – 7.34 (m, 6H, H_{Ar}), 7.33 – 7.27 (m, 4H, H_{Ar}), 5.52 (s, 4H, $CH_{2benzylic}$), 2.41 (t, *J*=7.5 Hz, 4H, CH_2), 1.34 – 1.16 (m, 36H, CH_2), 0.92 – 0.84 (m, 6H, CH_3). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ = 137.4, 133.4, 131.5, 129.5, 129.1, 127.7, 51.2, 32.0, 29.6, 29.6, 29.4, 29.4, 29.1, 23.2, 22.8, 14.2. **MS-ESI**: calculated for $[C_{39}H_{61}N_2]^+$: m/z = 557.4829, found: m/z = 557.4836. **ATR-FTIR (cm^{-1}):** 2919, 2850, 1556, 1460, 1369, 1217, 1125, 703.

2.6 Synthesis of LC-IPr•HBr (25)



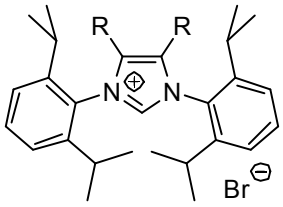
2.7 Synthesis of bromoketone 23



Following a slightly modified procedure,[6] DDQ (2.218 g, 9.77 mmol, 1.20 eq.) and PPh_3 (2.563 g, 9.77 mmol, 1.20 eq.) were suspended in DCM (80 mL). N-butyl ammonium bromide (3.149 g, 9.77 mmol, 1.20 eq) and acyloin **12** (3.000 g, 8.14 mmol, 1.00 eq.) were added afterwards and the dark mixture was stirred at RT for 16 hours. The crude mixture was adsorbed on silica (20 g) and flash chromatography (n-pentane/EtOAc: 100/1) afforded the title compound (2.739 g, 6.35 mmol, 78%) as a white solid. **R_f** (n-pentane/EtOAc 95/5): 0.83. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 4.23 (dd, *J*=8.0 Hz, 6.5 Hz, 1H, CHBr), 2.76 – 2.55 (m, 2H, CH_2CO), 2.05 – 1.86 (m, 2H, CH_2), 1.66 – 1.56 (m, 2H, CH_2), 1.49 – 1.40 (m, 1H,

CH_2), 1.34 – 1.21 (m, 33H, CH_2), 0.87 (t, *J*=6.6 Hz, 6H, CH_3). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ = 204.7, 54.0, 39.1, 33.6, 32.1, 29.8, 29.6, 29.6, 29.5, 29.5, 29.2, 29.1, 27.5, 24.1, 22.8, 14.3. **MS-ESI**: calculated for $[C_{24}H_{47}BrONa]^+$: m/z = 455.2683, found: m/z = 455.2678; calculated for $[(C_{24}H_{47}BrO)_2Na]^+$: m/z = 885.5498, found: m/z = 885.5463. **ATR-FTIR (cm^{-1}):** 2955, 2914, 2848, 1705, 1466, 1456, 1404, 1379, 1132, 1057, 964, 721, 692, 607.

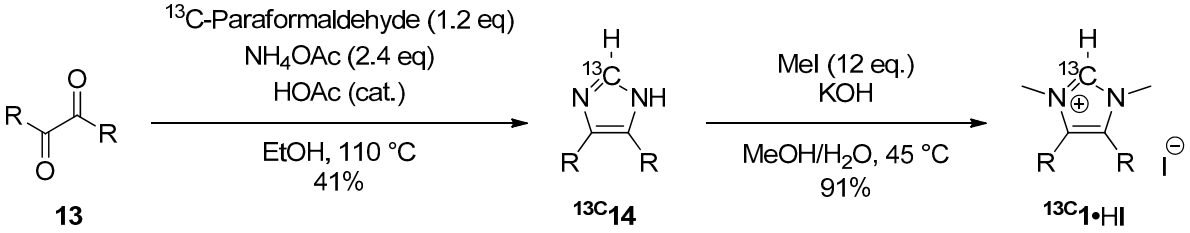
2.8 Synthesis of LC IPr



R = n-$C_{11}H_{23}$

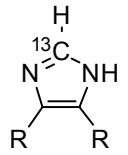
Following a slightly modified procedure,[9] bromoketone **23** (0.500 g, 1.16 mmol, 2.00 eq.) and the formamidine **24**[9] (0.211 g, 0.58 mmol, 1.00 eq.) were suspended in MeCN (1.20 mL), N,N-Diisopropylethylamine (0.33 mL, 0.70 mmol, 1.20 eq.) was added and the reaction mixture was heated at 120 °C for 3 days. The solvent was removed and toluene (1.50 mL) was added followed by Acetic anhydride (163 µL, 1.74 mmol, 3.00 eq.). The mixture was heated at 90 °C for 10 min. Aqueous HBr (110 µL, 0.90 mmol, 1.50 eq., 48%) was added at RT and the mixture was heated at 90 °C for 20 h. The reaction mixture was poured into a separatory funnel containing DCM (10 mL) and H_2O (10 mL). After phase separation the aqueous phase was extracted with DCM (3 x 10 mL) and the combined organic phases were dried over $MgSO_4$ and the solvent was removed. The crude product was purified by flash chromatography (DCM/MeOH: 100/2 → 100/10) to afford the title compound (0.402 g, 0.52 mmol, 89%) as an off-white solid. **R_f** (DCM/MeOH 10/1): 0.43. **1H NMR** (400 MHz, CDCl3) δ = 11.04 (s, 1H, NCHN), 7.54 (t, J=7.8 Hz, 2H, H_{para}), 7.32 (d, J=7.8 Hz, 4H, H_{meta}), 2.40 – 2.34 (m, 4H, $C_{Ar}CH_2$), 2.22 (hept, J=6.5 Hz, 4H, C*H*$(CH_3)_2$), 1.38 – 1.31 (m, 4H, CH_2, overlap), 1.28 (d, J=6.8 Hz, 12H, CH(C*H*$_3)_2$, overlap), 1.27 (d, J=6.8 Hz, 12H, CH(C*H*$_3)_2$, overlap), 1.23 – 1.10 (m, 32H, CH_2, overlap), 0.84 (t, J=7.0, 6H, CH_3). **^{13}C{1H} NMR** (101 MHz, CDCl3) δ = 145.3, 138.5, 132.6, 132.2, 127.8, 124.8, 31.9, 31.9 31.89, 29.6, 29.6, 29.6, 29.5, 29.4, 29.4, 29.4 , 29.3, 29.3, 29.2, 28.9, 28.5, 26.2, 23.3, 22.8, 22.7, 14.1. **MS-ESI**: calculated for $[C_{49}H_{81}N_2]^+$: m/z = 697.6394, found: m/z = 697.6393. **ATR-FTIR (cm^{-1}):** 2958, 2922, 2858, 2754, 1616, 1587, 1533, 1464, 1388, 1367, 1352, 1327, 1300, 1273, 1255, 1230, 1207, 1180, 1103, 1058, 910, 808, 761, 713, 686, 613.

3 Synthesis of ^{13}C labeled compounds ^{13C}1•HI & ^{13C}2•HBr



R = n-$C_{11}H_{23}$

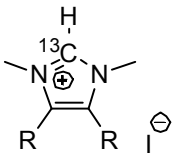
3.1 Synthesis of imidazole ^{13C}14



R = n-$C_{11}H_{23}$

Imidazole ^{13C}**14** was prepared in analogy to **14** ^{13}C labeled paraformaldehyde instead of normal paraformaldehyde. The title compound (0.452 g, 1.20 mmol, 41%) was obtained as a pale yellow solid. **R_f** (DCM/MeOH 9/1): 0.31. **^{1}H NMR** (600 MHz, $CDCl_3$) δ = 7.47 (d, *J*=206.2 Hz, 1H, NCHN), 2.52 (t, *J*=7.6 Hz, 4H, $C_{Ar}CH_2$), 1.63 – 1.54 (m, 4H, CH_2), 1.32 – 1.22 (m, 32H, CH_2), 0.87 (t, *J*=7.0 Hz, 6H, CH_3). **^{13}C{1H} NMR** (151 MHz, $CDCl_3$) δ = 132.4, 32.1, 30.2, 29.8, 29.8, 29.8, 29.6, 29.5, 29.5, 22.8, 14.3. **MS-ESI**: calculated for $[C_{24}{}^{13}CH_{48}N_2H]^+$: m/z = 378.3924, found: m/z = 378.3920. **ATR-FTIR (cm^{-1}):** 2916, 2850, 2623, 1839, 1464, 1376, 1240, 956, 797, 716, 651, 580.

3.2 Synthesis of imidazolium salt ^{13C}1•HI

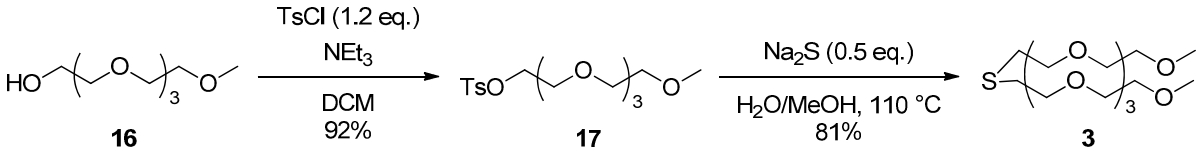


R = n-$C_{11}H_{23}$

Imidazolium salt ^{13C}**1**•HI was prepared in analogy to **1**•HI. The title compound (0.384 g, 0.72 mmol, 91%) was obtained as a pale yellow solid. **R_f** (DCM/MeOH 10/1): 0.37. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 10.10 (d, *J*=220.8 Hz, 1H, NCHN), 3.89 (d, *J*=4.1 Hz, 6H, NCH_3), 2.61 – 2.49 (m, 4H, $C_{Ar}CH_2$), 1.54 – 1.43 (m, 4H, CH_2), 1.32 – 1.20 (m, 32H, CH_2), 0.88 – 0.82 (m, 6H, CH_3). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ = 136.5, 131.1, 34.2, 34.2, 31.9, 29.6, 29.5, 29.4, 29.2, 29.1, 23.0, 22.7, 14.2. **MS-ESI**: calculated for $[C_{26}{}^{13}CH_{53}N_2]^+$: m/z = 406.4237, found: m/z = 406.4239. **ATR-FTIR (cm^{-1}):** 2996, 2954, 2919, 2852, 1620, 1548, 1465, 1130, 807, 723.

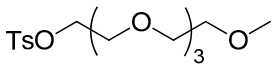
4 Synthesis of thioether 3 and thiol 15

4.1 Synthesis of the thioether 3



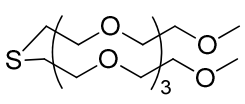
16 **17** **3**

4.1.1 Tetraethylene glycol monomethyl ether tosylate (17)[8]



The tosylation was performed using a method from KOHOMO et al.[8] Briefly, tetraethylene glycol mononmethyl ether (**16**) (4.53 mL, 4.85 g, 23.3 mmol, 1.0 eq.) was dissolved in dry DCM (25 mL) and triethylamine (7.8 mL, 5.7 mg, 56 mmol, 2.4 eq.) and p-toluenesulfonyl chloride (5.33 g, 28.0 mmol, 1.2 eq.) was added. After stirring overnight the reaction mixture was washed with aq. $NaHSO_4$ (100 mL) and aq. $NaHCO_3$ solution (100 mL). The aqueous phases were extracted with DCM (3x20 mL). The combined organic phases were dried over $MgSO_4$, filtrated and concentrated under vacuum. After column chromatography (EtOAc/CH: 3/1) the desired product could be isolated as colorless oil (7.79 g, 21.5 mmol, 92%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 7.82 – 7.76 (m, 2H, H_{Ar}), 7.36 – 7.33 (m, 2H, H_{Ar}), 4.19 – 4.12 (m, 2H, 1-H), 3.72 – 3.51 (m, 14H), 3.37 (s, 3H, OCH_3), 2.45 (s, 3H, $CH_{3benzylic}$). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ = 144.8, 133.0, 129.9, 128.0, 71.9, 70.7, 70.6, 70.6, 70.5, 70.5, 69.3, 68.7, 59.0, 21.7. **MS-ESI**: calculated for $[C_{16}H_{26}O_7SNa]^+$ 385.1291, found 385.1291.

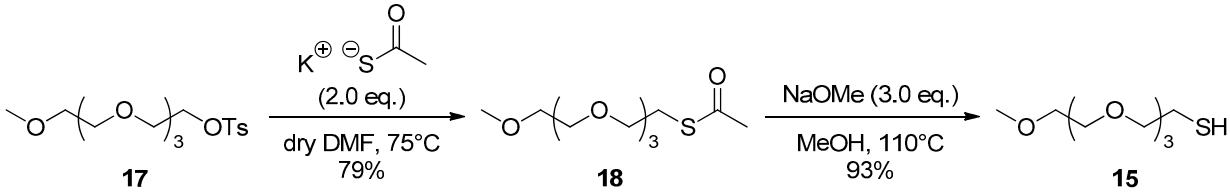
4.1.2 Bis(tetraethylene glycol monomethyl ether)sulfide (3)



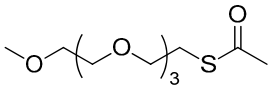
To a solution of sodium sulfide nonahydrate (1.51 g, 6.3 mmol, 0.5 eq.) in dist. Water (8 mL) and MeOH (5 mL) tetraethylene glycol monomethylether tosylate (**17**) (4.53 g, 12.5 mmol, 0.5 eq.) was added. The resulting

mixture was heated to reflux for 5 h. The water phase was extracted with ethyl acetate (5x10 mL). The combined organic layers were dried over $MgSO_4$, filtrated and concentrated under reduced pressure. After column chromatography (EtOAc/MeOH: 40/1) the title compound could be isolated as a colorless oil (2.10 g, 5.07 mmol, 81%). $\mathbf{R_f}$ (EtOAc/MeOH 40/1): 0.14. **^{1}H NMR** (300 MHz, C_6D_6) δ = 3.49 – 3.32 (m, 28H, CH_2), 3.12 (s, 6H, OCH_3), 2.60 (t, *J* = 6.8 Hz, 4H, SCH_2). **^{13}C{1H} NMR** (75 MHz, C_6D_6) δ = 72.4, 71.8, 71.1, 71.0, 70.9, 70.7, 58.7, 32.4. **MS-ESI**: calculated for $[C_{18}H_{38}O_8SNa]^+$: m/z = 437.2180, found: m/z = 437.2180. **ATR-FTIR (cm^{-1}):** 3736, 2873, 2266, 1457, 1350, 1291, 1247, 1198, 1110, 1037, 943, 543.

4.2 Synthesis of tetraethylene glycol monomethylether thiol (15)



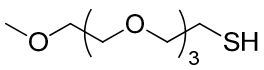
4.2.1 Tetraethylene glycol monomethyl ether thioacetate (18)[9]



Tosylate **17** (5.40 g, 15.0 mmol, 1.0 eq.) was dissolved in dry DMF (25 mL). After the addition of potassium thioacetate (3.36 g, 30 mmol, 2.0 eq.) the reaction mixture was stirred for 3 h at 75°C and the solution was concentrated by rotary evaporator. The residue was dissolved in EtOAc (80 mL) and dist. Water (80 mL). After phase separation the aq. layer was extracted with EtOAc (3x80 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under vacuum. After column chromatography (EtOAc/CH: 3/1) the title compound could be isolated (3.42 g, 11.8 mmol, 79%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 3.64 – 3.52 (m, 14H, CH_2), 3.36 (s, 3H, OCH_3), 3.07 (t, *J* = 6.5 Hz, 2H, SCH_2), 2.32 (s, 3H, $COCH_3$). **^{13}C{1H} NMR** (75 MHz, C_6D_6) δ = 195.4, 72.0, 70.7, 70.6, 70.6, 70.6,

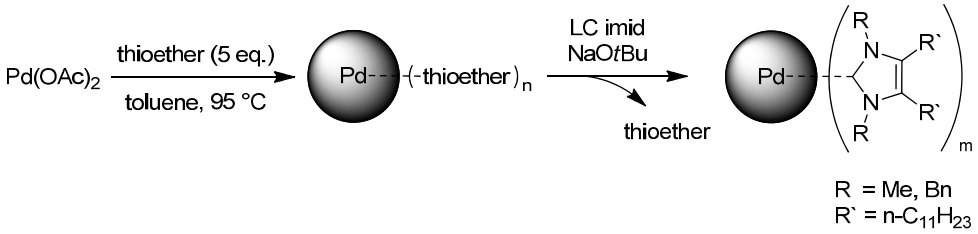
70.3, 69.8, 59.0, 30.6, 28.9. **MS-ESI**: calculated for $[C_{18}H_{38}O_8SNa]^+$: m/z = 289.1080, found: m/z = 289.1085.

4.2.2 Tetraethylene glycol monomethyl ether thiol (15)[9]

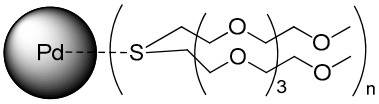


Under Argon atmosphere thioacetate **18** (1.83 g, 6.9 mmol, 1.0 eq.) was dissolved in oxygen free MeOH (10 mL) and NaOMe (810 mg, 15 mmol, 3.0 eq.) was added. The resulting mixture was stirred for 1 h at room temperature. Then aq. HCl (1 M, 50 mL) was added. The aq. layer was extracted with EtOAc (4x50 mL) and the resulting organic phases were dried over $MgSO_4$ and filtrated. After drying under reduced pressure the title compound could be isolated as colorless liquid (1.57 g, 6.4 mmol, 93%). **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 3.66 – 3.53 (m, 14H, CH_2), 3.38 (s, 3H, OCH_3), 2.69 (dt, *J* = 13.1 Hz, *J* = 6.5 Hz, 2H, SCH_2), 1.60 (t, *J* = 8.2 Hz, 3H, SH). **^{13}C{1H} NMR** (75 MHz, C_6D_6) δ = 73.0, 72.0, 70.7, 70.6, 70.3, 59.1, 24.4. **MS-ESI**: calculated for $[C_9H_{20}O_4SNa]^+$: m/z = 247.0975, found: m/z = 247.0975.

5 Synthesis of LC-NHC Pd-NP

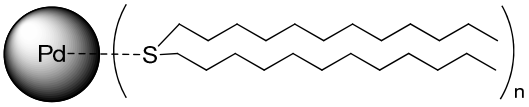


5.1 Synthesis of 3@Pd-NP



The procedure was adopted form OBARE et al.[10] and slightly modified. Under Argon atmosphere bis(tetraethylene glycol monomethylether)thioether (**3**) (357.0 mg, 0.86 mmol, 5.0 eq.) and $Pd(OAc)_2$ (38.2 mg, 0.17 mmol, 1.0 eq.) were dissolved in dry toluene (4 mL) and heated for 1 h at 95 °C. Then the solvent was removed to a minimum and the formed NPs were transferred into centrifugation tubes. After precipitation with cyclohexane (3 mL) the NPs were centrifuged at 1000 rpm for 20 min. This procedure was repeated two times to give the NPs as a brown oil (54.3 mg). **^{1}H NMR** (300 MHz, C_6D_6) δ = 3.49 – 3.32 (m, 28H, CH_2), 3.12 (s, 6H, OCH_3), 2.60 (t, *J* = 6.8 Hz, 4H, SCH_2). **^{13}C{1H} NMR** (75 MHz, C_6D_6) δ = 72.4, 71.8, 71.1, 71.0, 70.9, 70.7, 58.7, 32.4. **DLS**: 5.7 nm. **TEM**: mean particle diameter: 4.5 (0.4) nm (205 measured particles). **TGA**: 24% Pd and 76% organic fraction. Note: Compound contains excess of thioether. If removed the NPs suffer from fast aggregation.

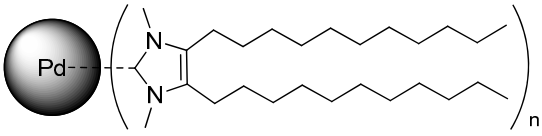
5.2 Synthesis of 4@Pd-NP[10]



Following a procedure from OBARE et al.[10], $Pd(OAc)_2$ (13.5 mg, 0.06 mmol, 1.0 eq.) and didodecylsulfide (**4**) (111.2 mg, 0.30 mmol, 5.0 eq.) were dissolved in dry toluene (5 mL). The reaction mixture was heated to 95° C for 3 h under an argon atmosphere. Then the solvent was evaporated under reduced pressure. The solid was transferred into centrifugation tubes and washed with acetone p.a. (3x6 mL) and centrifuged at 500 rpm for 20 min. The purified NPs were transferred to a flask and dried under vacuum to give a brown powder (21.1 mg).

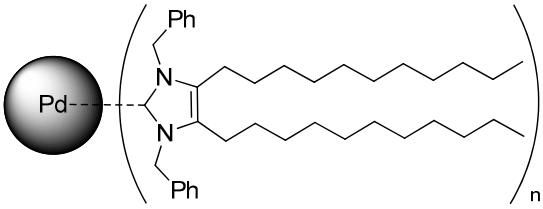
^{1}H-NMR (300 MHz, C_6D_6) δ = 2.44 (t, *J* = 6.9 Hz, 4H, SCH_2), 1.59 (t, *J* = 7.3 Hz , 4H, SCH_2CH_2), 1.39 – 1.29 (m, 36H, 9xCH_2), 0.92 (t, *J* = 6.4 Hz, 6H, CH_3). **^{13}C{1H} NMR** (75 MHz, C_6D_6) δ = 32.5, 32.4, 30.2, 30.1, 30.1, 29.9, 29.8, 29.3, 23.2, 14.4. **DLS**: 4.0 nm. **TEM**: mean particle diameter: 4.0 (0.5) nm (198 measured particles). **TGA**: 31% Pd and 69% organic fraction. Note: Compound contains excess of thioether. If removed the NPs suffer from fast aggregation.

5.3 Synthesis of 1@Pd-NP



In a flame dried schlenk tube **1**•HI (95.9 mg; 0.18 mmol, 1.0 eq.) and NaO*t*Bu (17.3 mg, 0.18 mmol, 1.0 eq.) were dissolved in dry acetonitrile (1 mL) and dry hexane (1.5 mL) and stirred for ½ h under an Argon atmosphere. **3**@Pd-NP (30 mg), dissolved in dry acetonitrile (0.5 mL) were added and stirred overnight at room temperature. The phase transfer of the NPs from the acetonitrile to the hexane phase indicates the ligand exchange. The acetonitrile layer was discarded. To remove excess ligand the hexane phase was extracted with dry acetonitrile (5x1.5 mL). After drying the LC NHC protected Pd-NPs could be obtained as brown solid (23.4 mg). For TGA and elemental analysis the NPs were further purificated by reprecipitation from toluene by addition with acetonitrile (3x3 mL). After each precipitation step the NPs were centrifugated at 1000 rpm for 20 min. (This additional purification did not lead to changes in the catalytically activity or selectivity of the Pd-NP.) **^{1}H-NMR** (300 MHz, C_6D_6) δ = 3.36 – 3.32 (m, 21H, CH_2), 0.98 – 0.91 (m, 6H, CH_3). **^{13}C{1H} NMR** (75 MHz, C_6D_6) δ = 32.4, 30.2, 30.1, 30.0, 29.9, 23.2, 14.4. **DLS**: 5.5 nm. **TEM**: mean particle diameter: 4.5 (0.4) nm (191 measured particles). **TGA**: 66% Pd and 34% organic fraction. **EA**: found: 22.0% C, 3.96% H, 1.6% N; calculated: 22.1% C, 3.70% H, 1.9% N, 72.3% Pd.

5.4 Synthesis of 2@Pd-NPs



2•HBr (95.9 mg; 0.18 mmol, 1.0 eq.) and NaO*t*Bu (17.3 mg, 0.18 mmol, 1.0 eq.) were dissolved in dry acetonitrile (1 mL) and dry hexane (1.5 mL) and stirred for ½ h under an Argon atmosphere. **3**@Pd-NPs (30 mg), dissolved in dry acetonitrile (0.5 mL), were added. After workup according to 5.3 the **2**@Pd-NP (16 mg) could be isolated. For TGA and elemental analysis the NPs were further purificated by reprecipitation and centrifugation (see 5.3). (This additional purification did not lead to changes in the catalytically activity or selectivity of the Pd-NP.) **^{1}H-NMR** (300 MHz, C_6D_6) δ = 3.36 – 3.32 (m, 23H, CH_2), 0.93 – 0.91 (m, 6H, CH_3). **^{13}C{1H} NMR** (75 MHz, C_6D_6) δ = 32.4, 30.2, 30.1, 30.0, 29.9, 23.2, 14.4. **DLS**: 5.7 nm. **TGA**: 62% Pd and 38% organic fraction. **EA**: found: 37.3% C, 5.2% H, 2.5% N; calculated: 37.5% C, 4.8% H, 2.2% N, 55.4 % Pd.

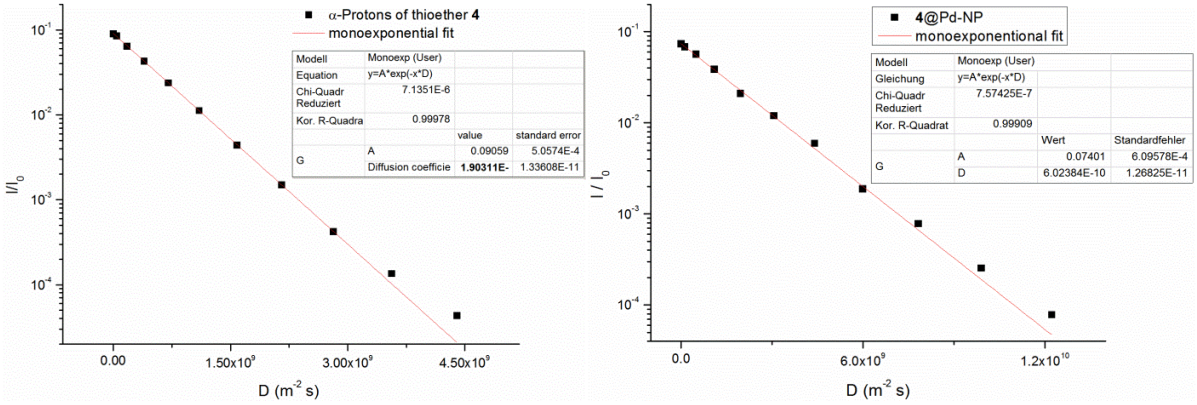
5.5 Synthesis of 1•4@Pd-NP

Under Argon atmosphere **1**•HI (32.0 mg, 0.06 mmol, 1.0 eq.) and NaO*t*Bu (5.5 mg, 0.06 mmol, 1.0 eq.) were dissolved in dry toluene (2 mL) and stirred for ½ h. **4**@Pd-NPs (28.5 mg) dissolved in dry toluene (1 mL) were added. After stirring over night the solvent was reduced to a minimum and the NPs were washed with dry acetonitrile (3x3 mL). **^{1}H-NMR** (300 MHz, C_6D_6) δ = 3.91 (s, 6H, NCH_3), 2.13 (t, *J* = 7.5 Hz, 4H, $C_{Ar}CH_2$), 1.36 – 1.28 (m, 36H, CH_2), 0.93 – 0.91 (m, 6H, CH_3). **^{13}C{1H} NMR** (75 MHz, C_6D_6) δ = 128.4, 32.6, 32.4, 30.2, 30.2, 30.1, 30.1, 30.1, 29.9, 29.8, 29.3, 23.2, 14.4. **DLS**: 4.2 nm.

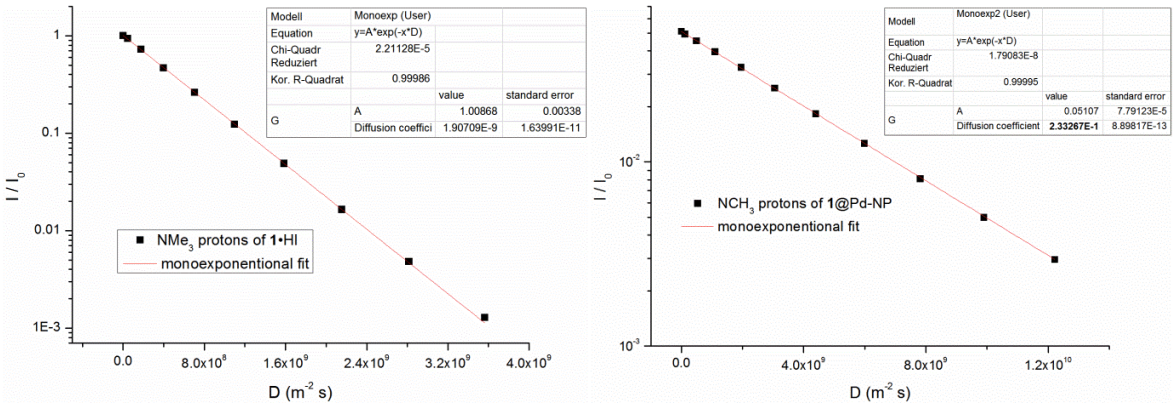
5.5.1 PFG-NMR spectroscopy

PFG-NMR spectroscopy was performed in order to determine whether the NHCs are indeed bound to the NP surface. As the diffusion coefficient (D) is anti-proportional to the radius of the examined substrate, D should decrease when the ligand is coordinated to the NP surface. As expected the diffusion coefficients of the free ligands compared to the NP samples decreases by nearly one order of magnitude for both samples (table 1). As the free NHCs are not stable the imidazolium salts were used to compare the diffusion coefficients of free and bound ligands. The results indicate that the NHC binds to the metal surface even if excess thioether is present in the sample.

sample	diffusion coefficient / 10^{-10} m^2/s
Thioether **4**	19.031
1•HI	20.719
4@Pd-NP	6.0238
1•**4**@Pd-NP	2.3326



graph 1. PFG NMR measurements of the free thioether **4** (right) and **4**@Pd-NPs (left) measured in benzene-d_6.

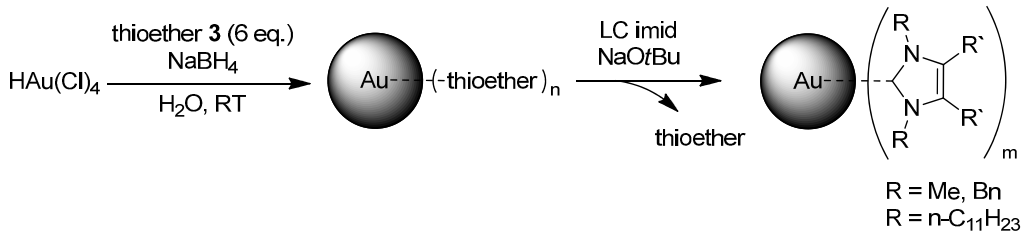


graph 2. PFG NMR measurements of **1**•HI (right, measured in DMSO-d_6) and 1@Pd-NPs (left, measured in benzene)

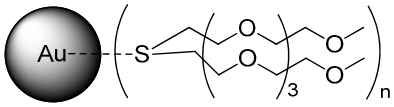
5.6 Synthesis of ^{13C}1•4@Pd-NP

According to 5.5 ^{13C}**1**•HI (32.0 mg, 0.06 mmol, 1.0 eq.) and NaO*t*Bu (5.5 mg, 0.06 mmol, 1.0 eq.) were reacted with **4**@Pd-NPs (28.5 mg) in dry toluene (3 mL) were added. After the descripted workup the NPs could be isolated as brown powder. **^{1}H-NMR** (300 MHz, C_6D_6) δ = 3.91 (s, 6H, NCH_3), 2.13 (t, *J* = 7.8 Hz, 4H, $C_{Ar}CH_2$), 1.36 – 1.28 (m, 36H, CH_2), 0.93 – 0.91 (m, 6H, CH_3). **^{13}C{1H} NMR** (75 MHz, C_6D_6) δ = 168.2, 128.4, 32.6, 32.4, 30.2, 30.2, 30.1, 30.1, 30.1, 29.9, 29.8, 29.3, 23.2, 14.4.

6 Synthesis of LC-NHC Au-NP



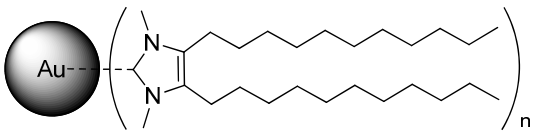
6.1 Synthesis of 3@Au-NP



The **3**@Au-NPs were synthesized using a modified Brust methode. To an aq. solution of $HAuCl_4$ (40% in bidistilled water, 10 mL, 0.10 mmol, 1.0 eq) tetraoctylammonium bromide (109.4 mg, 0.20 mmol, 2.0 eq.) and toluene (2.5 mL) were added and stirred for 20 min. After removing the aq. phase thioether 3 (248.5 mg, 1.2 mmol, 6.0 eq.) was added. Under vigorous stirring $NaBH_4$ (454.0 mg, 12 mmol, 10.0 eq) dissolved in bidistilled water (4.5 mL) was added. After 30 min the aq. phase was discarded and the solvent was removed under reduced pressure. The NPs were purified by three precipitation steps from toluene with pentane and centrifugation at 500 rpm for 10 min. The desired NPs could be obtained as dark solid (52.7 mg).

^{1}H-NMR (300 MHz, C_6D_6) δ = 3.49 - 3.33 (m, 29H, OCH2), 3.13 (s, 6H, CH3), 2.61 (br, *J* = 6.8 Hz, 2H, SCH2). **^{13}C{1H} NMR** (75 MHz, C_6D_6): δ = 72.4, 71.8, 71.1, 71.0, 70.9, 70.7, 58.7. **DLS**: 6.1 nm. **TEM**: mean particle diameter: 5.0 (1.6) nm (202 measured particles). **UV-Vis** max. at 520 nm.

6.2 Synthesis of 1@Au-NP

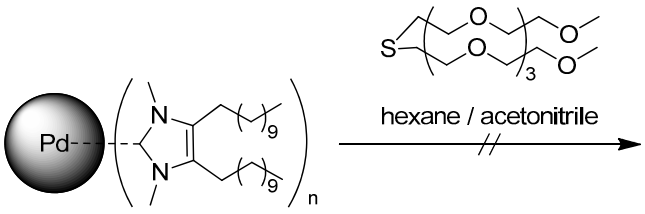


According to 5.3 **1**•HI (32.0 mg, 0.06 mmol, 1.0 eq.) and NaO*t*Bu (5.5 mg, 0.06 mmol, 1.0 eq.) were reacted with **3**@Au-NPs (28.5 mg) in an two phase system of acetonitrile (2 mL) and hexane (2 mL). After the described workup the NPs could be isolated as red solid (19.7 mg). **^{1}H-NMR** (300 MHz, C_6D_6) δ = 3.12 – 2.92 (m, 16H, CCH_2), 1.86 – 1.18 (m, 14H, CH_2CH_2), 1.09 – 0.52 (m,

6H, CH_2CH_3). **^{13}C{1H} NMR** (75 MHz, C_6D_6): δ = 32.0, 29.9, 22.8, 14.1. **DLS**: 5.5 nm. **TEM**: mean particle diameter: 3.9 (0.7) nm (236 measured particles). **UV-Vis** max. at 511 nm.

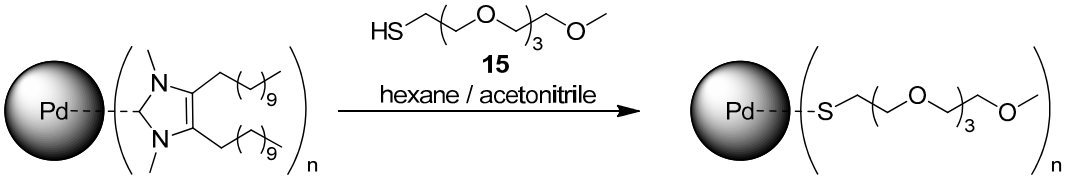
7 Ligand reexchange experiments

7.1 1@Pd-NP and thioether 3



1@Pd-NPs (20 mg) were dissolved in a dry hexane (1 mL) and dry acetonitrile (1 mL) two phase system. After the addition of thioether **3** (26.9 mg, 0.12 mmol, excess) no phase transfer of the NPs appeared. After washing with acetonitrile (3x2 mL) no changes in the NMR spectra were observed, showing that the NHCs could not be removed by excess thioether. **^{1}H-NMR** (300 MHz, C_6D_6) δ = 3.36 – 3.32 (m, 21H, CH_2), 0.93 (m, 6H, CH_3). **^{13}C{1H} NMR** (75 MHz, C_6D_6): δ = 32.4, 30.2, 30.1, 30.0, 29.9, 23.2, 14.4.

7.2 1@Pd-NP and thiol 15

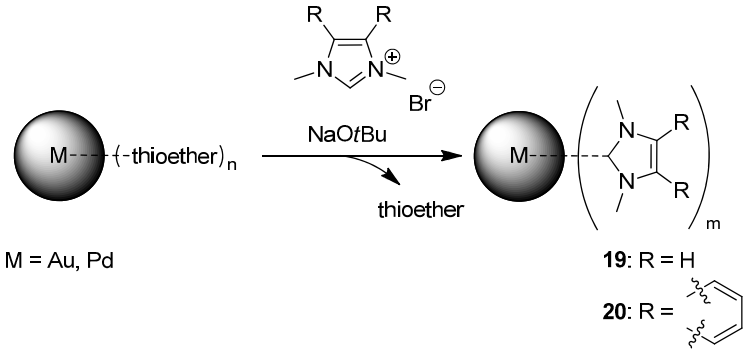


1@Pd-NPs (20 mg) were dissolved in a dry hexane (1 mL) and dry acetonitrile (1 mL) two phase system. After the addition of thiol **15** (26.9 mg, 0.12 mmol, excess) a phase transfer of the NPs from the hexane to the acetonitrile phase could be observed, indicating the exchange of the NHC ligands by the thiol **15**. After washing with hexane

(3x2 mL) the NMR spectra analysis confirmed the ligand exchange. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 3.47 – 3.32 (m, 14H, CH_2), 3.12 (s, 3H, OCH_3), 2.34 (dt, *J* = 7.8 Hz, *J* = 6.2 Hz, 2H, SCH_2), 1.53 – 1.48 (m, 3H, SH). **^{13}C{1H} NMR** (75 MHz, C_6D_6) δ = 73.0, 72.0, 70.7, 70.6, 70.3, 59.1, 24.4.

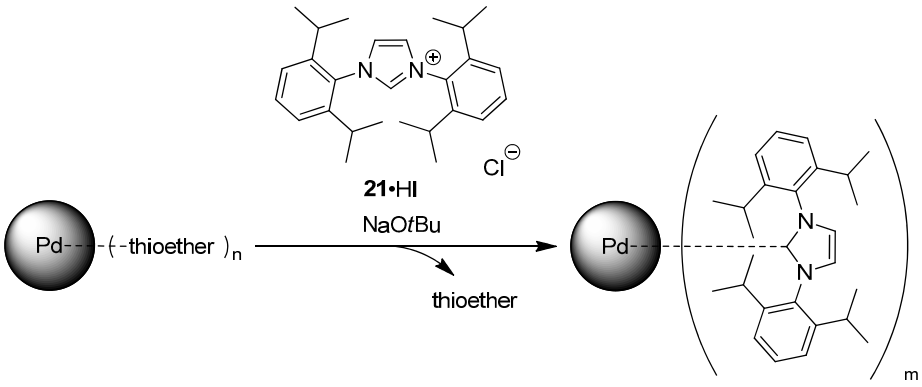
8 Ligand exchange with NHCs without long chains and LC-IPr

8.1 Ligand exchange with 1,3-dimethyl-1*H*-imidazoliumiodide (19) and 1,3-dimethyl-1*H*-benzimidazoliumiodide (20)



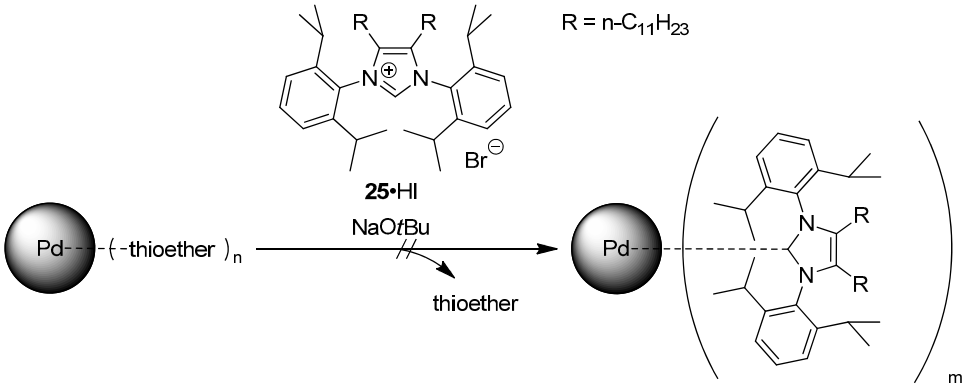
Following a procedure form CHECHIK et al.[11] 1,3-dimethyl-1*H*-imidazoliumiodide (**19**) or 1,3-dimethyl-1*H*-benzimidazoliumiodide (**20**) (0.06 mmol, 1.0 eq.) and NaO*t*Bu (0.06 mmol, 1.0 eq.) were dissolved in dry toluene and stirred for ½ h. **4**@Pd-NPs or **4**@Au-NPs (30 mg) were dissolved in dry toluene (2 mL) and added to the reaction mixture. After ½ h stirring the NPs were left over night without stirring to precipitate out of the solution. The change in solubility indicates the ligand exchange on the surface of the NPs. The NPs were washed with dry toluene (3x5 mL) to remove the thioether and dried under vacuum. NMR-analysis in dry DMSO-d_6 confirmed the full exchange of the thioether by the corresponding NHC but the NPs aggregated and precipitated out of the solution within 12 h or formed a metal mirror on the glass wall. This poor stability was also observed by *Chechik* et al. using 1,3-di-tert-butylimidazol-2-ylidene for the ligand exchange.

8.2 Ligand exchange with 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (21)



As Chaudret et. al[12] were able to stabilize small Ru-NPs (1.7 (0.2) nm) with 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (**21**; IPr) we also wanted to investigate the ligand exchange with this NHC. The corresponding imidazolium salt **21**•HCl (163.0 mg, 0.36 mmol, 1.0 mmol) and NaO*t*Bu (35.0 mg, 0.36 mmol, 1.0 eq.) were dissolved in dry toluene (1 mL) and stirred for ½ h. Then **3**@Pd-NPs (45 mg) were added, dissolved in dry toluene (2 mL). The reaction mixture was stirred overnight. After the reaction the NPs were still soluble in toluene but not in polar solvents like acetonitrile indicating the ligand exchange of the polar thioether **3**. After washing with acetonitrile (3x5 mL) the NPs were dried under vacuum to be analyzed by NMR. Unfortunately the NPs could not be redispersed in any organic solvent. NMR analyses of the washing solution showed beside some other impurities signals that contribute to the protons of the polar thioether **3**. These observations indicate the ligand exchange by IPr but the resulting NP seemed to be very unstable ending up in bulk material.

8.3 Ligand exchange with LC-IPr (25)

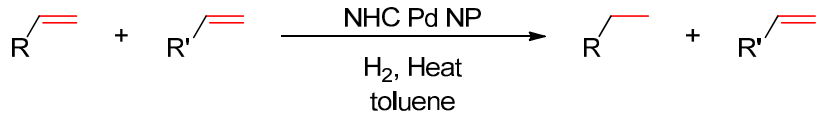


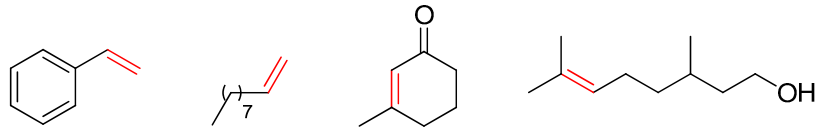
Following the procedure descripted in **8.2**, LC-IPr•HBr (70.0 mg, 0.09 mmol, 1.00 eq.) and NaO*t*Bu (10.1 mg, 0.09 mmol, 1.00 eq.) were reacted with **3**@Pd-NPs (15 mg) in dry toluene (1 mL). After stirring over night a brown suspension was obtained but DLS measurements of the solution revealed that larger aggregates over 200 nm were formed.

The same experiment was repeated in a two phase system of dry hexane (0.8 mL) and dry acetonitrile (0.8 mL). After stirring over night no phase transfer of the Pd-NPs in the hexane phase and no stabilization of the NPs by the NHC could be observed. DLS measurements showed aggregation of the NPs in the acetonitrile phase.

These results confirmed that an interaction of the Pd-NPs with the LC-IPr NHC occurs but leading to unstable and aggregated material.

9 Hydrogenation experiments





S: ?% **P**: ?% | **S**: ?% **P**: ?% | **S**: ?% **P**: ?% | **S**: ?% **P**: ?%

9.1 General procedure

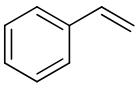
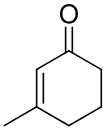
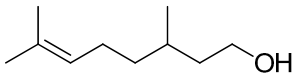
A screw capped glass vial was equipped with a magnetic stirring bar and was filled with toluene (1.00 mL), Styrene (**5**) (46 µL, 0.40 mmol, 1 eq.), 1-decene (**6**) (76 µL, 0.40 mmol, 1 eq.), 3-methylcyclohex-2-enone (**7**) (45 µL, 0.40 mmol, 1 eq) and citronellol (**8**) (73 µL, 0.40 mmol, 1 eq). A solution of the corresponding NP in toluene (0.5 mg in 100 µL) was added to the reaction mixture. The vial was placed in a stainless steel autoclave reactor, which was carefully pressurized/depressurized with hydrogen for three times. Then the indicated pressure was adjusted and the reactor was heated for the indicated time. Afterwards, icosane (56 mg, 0.20 mmol, 0.5 eq.) was added as internal standard to the reaction mixture and an aliquot was analyzed by GC-MS and calibrated GC-FID to evaluate the composition and the ratio between starting materials (**S**) and the corresponding products (**P**).

9.2 Results

9.2.1 Competition experiments

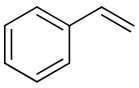
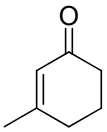
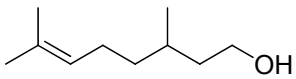
a) Catalyst: **1**@Pd-NP

p: 10 bar T: 40 °C t: 18 h.

			
S: 0% **P**: 97%	**S**: 0% **P**: 69%	**S**: 99% **P**: 0%	**S**: 93% **P**: 0%

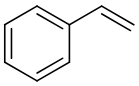
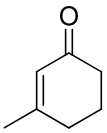
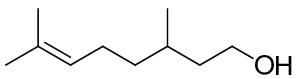
b) Catalyst: **1**@Pd-NP

p: 10 bar T: 80 °C t: 18 h.

			
S: 0% **P**: 90%	**S**: 0% **P**: 47%	**S**: 99% **P**: 0%	**S**: 95% **P**: 0%

c) Catalyst: **1**@Pd-NP

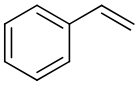
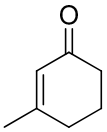
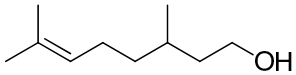
p: 20 bar T: 100 °C t: 18 h.

			
S: 0% **P**: 90%	**S**: 0% **P**: 48%	**S**: 96% **P**: 0%	**S**: 93% **P**: 0%

Note: The residual amount of 1-decene was converted to internal decenes. Main text.

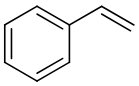
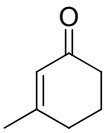
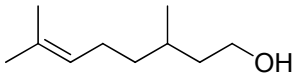
d) Catalyst: **1**@Pd-NP

p: 10 bar T: 40 °C t: 1 h.

			
S: 0% **P**: 95%	**S**: 0% **P**: 57%	**S**: 98% **P**: 0%	**S**: 92% **P**: 0%

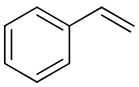
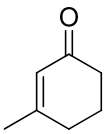
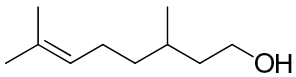
e) Catalyst: **2**@Pd-NP

p: 10 bar T: 40 °C t: 18 h.

			
S: 0% **P**: 99%	**S**: 0% **P**: 60%	**S**: 99% **P**: 0%	**S**: 95% **P**: 0%

f) Catalyst: **1•4**@Pd-NP

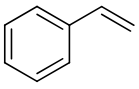
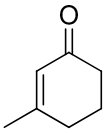
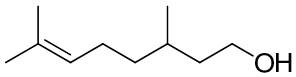
p: 10 bar T: 40 °C t: 18 h.

			
S: 0% **P**: 99%	**S**: 0% **P**: 54%	**S**: 99% **P**: 0%	**S**: 99% **P**: 0%

Note: The residual amount of 1-decene was converted to internal decenes. Main text.

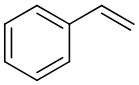
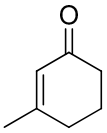
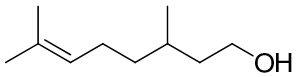
g) Catalyst: **4**@Pd-NP

p: 10 bar T: 40 °C t: 18 h.

			
S: 0% **P**: 91%	**S**: 0% **P**: 93%	**S**: 10% **P**: 82%	**S**: 23% **P**: 70%

h) Catalyst: Pd/C (5% Pd; 18 mg of Pd/C was used)

p: 10 bar T: 40 °C t: 18 h.

			
S: 0% **P**: 93%	**S**: 0% **P**: 96%	**S**: 0% **P**: 94%	**S**: 0% **P**: 96%

Note: The residual amount of 1-decene was converted to internal decenes. Main text.

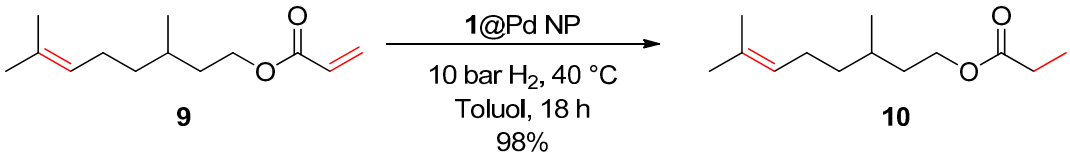
9.2.2 Mercury drop test

Following the general procedure 5.1, a reaction mixture plus internal standard was prepared, pressurized with hydrogen to 10 bar and heated for 5 min at 40 °C. Then an aliquot was analyzed by GC-MS and GC-FID to proof that the active species was formed (remaining styrene (**5**): 44%, remaining 1-decene (**6**): 78%). Afterwards mercury (500 mg, > 500 eq.) was added and the sample was repressurized to 10 bar and heated at 40 °C for 3 days. Another aliquot was analyzed by GC and only a negligible progress of the reaction was detected (styrene (**5**): 44%, 1-decene (**6**): 74%). This experiment indicates that the mode of action is of heterogeneous nature. A control experiment proved that the reaction itself is not harmed by stopping after 5 min and restarting the reaction after 20 min.

9.2.3 Filtration test

Following the general procedure 5.1, a reaction mixture plus internal standard was prepared, pressurized with hydrogen to 10 bar and heated for 5 min at 40 °C. Then an aliquot was analyzed by GC-MS and GC-FID to proof that the active species was formed (remaining styrene (**5**): 48%, remaining 1-decene (**6**): 84%). Afterward, the mixture was filtered through dry Celite in a new screw capped glass tube. The sample repressurized to 10 bar and heated at 40 °C for 3 days. Another aliquot was analyzed by GC and a slow progress of the reaction was detected (styrene (**5**): 0%, 1-decene (**6**): 30%). In case of 1-decene (**6**) the reaction rate was more than 100 times slower. The fact that still a progress was observed can be reasoned by the excellent solubility of the NHC NP in unpolar solvents, which makes it nearly impossible to filter them off completely. Therefore, a filtration test seems to be unsuitable to distinguish between homogeneous and heterogeneous catalysis in this case.

9.2.4 Selective hydrogenation of 3,7-dimethyloct-6-en-1-yl acrylate (9)

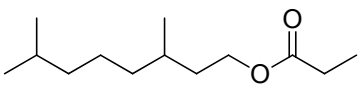


9 **10**

To a screw capped glass vial containing 3,7-dimethyloct-6-en-1-yl acrylate (**9**) (84.1 mg, 0.40 mmol) in toluene (1 mL) a solution of **1**@Pd-NP in toluene (0.5 mg in 100 µL) was added. The vial was placed in a stainless steel autoclave reactor, which was carefully pressurized/depressurized with hydrogen for three times. The pressure was adjusted to 10 bar and the reactor was heated for 18 h at 40 °C. Flash chromatography (n-pentane/EtOAc: 100/2) afforded 3,7-dimethyloct-6-en-1-yl propionate (**9**) (83.0 mg, 0.39 mmol, 98%) as a colorless liquid. $\mathbf{R_f}$ (n-pentane/EtOAc 95/5): 0.65. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 5.08 (ddt, *J*=7.1 Hz, 5.7 Hz, 1.4 Hz, 1H, H_{DB}), 4.18 – 4.03 (m, 2H, CH_2O), 2.31 (q, *J*=7.6 Hz, 2H, CH_2CH_3), 2.07 – 1.89 (m, 2H, CH_2), 1.67 (d, *J*=1.3 Hz, 3H, CH_3C_{DB}), 1.66 – 1.61 (m, 1H, CH), 1.60 (d, *J*=1.3 Hz, 3H, CH_3C_{DB}), 1.57 – 1.17 (m, 4H, CH_2), 1.13 (t, *J*=7.6 Hz, 3H, CH_2CH_3), 0.90 (d, *J*=6.4 Hz, 3H, $CHCH_3$). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ = 174.8, 131.5, 124.7, 63.0, 37.1, 35.6, 29.6, 27.8, 25.9, 25.5, 19.6, 17.8, 9.3. **MS-ESI**: calculated for $[C_{13}H_{24}O_2Na]^+$: m/z = 235.1669, found: m/z =

235.1671. **ATR-FTIR (cm^{-1}):** 2962, 2920, 1739, 1460, 1380, 1351, 1273, 1185, 1082, 1015, 954.

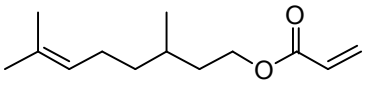
Control experiments: Under identical conditions, **4**@Pd-NPs (0.5 mg) and Pd/C (5% Pd content, 18.0 mg) were used as catalysts instead of **1**@Pd-NPs. Pd/C completely converted the substrate to the fully saturated ester **22**. GC-Yield: 95%. Isolated yield after flash chromatography: 89%. When **4**@Pd-NPs were used as catalyst, the hydrogenation processed with low chemoselectivity giving an inseparable reaction mixture of the starting material (**9**), the desired product (**10**) and the saturated ester (**22**). The composition was determined by calibrated GC. **9**: 5%, **10**: 68%, **22**: 26%.



22

Colorless liquid. $\mathbf{R_f}$ (n-pentane/EtOAc 95/5): 0.66. **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 4.15 – 4.03 (m, 2H, CH_2O), 2.31 (q, *J*=7.6 Hz, 2H, CH_2CO), 1.70 – 1.60 (m, 1H, CH), 1.56 – 1.47 (m, 2H, CH_2), 1.46 – 1.37 (m, 1H, CH), 1.33 – 1.20 (m, 3H, CH_2), 1.18 – 1.08 (m, 6H, CH_3CH_2, CH_2), 0.89 (d, *J*=6.6 Hz, 3H, CH_3CH), 0. 85 (d, *J*=6.7 Hz, 6H, CH_3CHCH_3). **^{13}C{1H} NMR** (101 MHz, $CDCl_3$) δ = 174.7, 63.1, 39.3, 37.3, 35.7, 30.0, 28.1, 27.8, 24.7, 22.8, 22.7, 19.7, 9.3. **MS-ESI**: calculated for $[C_{13}H_{24}O_2Na]^+$: m/z = 237.1825, found: m/z = 237.1831. **ATR-FTIR (cm^{-1}):** 2956, 2928, 2871, 1742, 1464, 1383, 1352, 1275, 1186, 1084.

9.2.5 Synthesis of 3,7-dimethyloct-6-en-1-yl acrylate (9)[13]

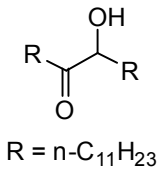


Citronellol (**8**) (1.000 g, 6.40 mmol, 1.00 eq.) and NEt_3 (1.295 g, 12.80 mmol, 2.00 eq.) were dissolved in DCM (30 mL) and cooled to 0 °C. Acryloyl chloride (0.868 g, 9.59 mmol, 1.50 eq.) was added dropwise and the resulting mixture was stirred for 3 h. The reaction was quenched by addition of water (30 mL) and the phases were separated. The aqueous phase was extracted with DCM (2 x 20 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was removed and the crude product was purified by flash chromatography (n-pentane/EtOAc: 100/2) to afford the title compound (0.864 g, 4.11 mmol, 64%) as a colorless liquid. $\mathbf{R_f}$ (n-pentane/EtOAc 95/5): 0.62. **^{1}H NMR** (300 MHz, $CDCl_3$) δ = 6.39 (dd, *J*=17.3, 1.6, 1H, $CH_{2\ gem,cis}$), 6.11 (dd, *J*=17.3, 10.4, 1H, COCH), 5.81 (dd, *J*=10.4, 1.6, 1H, $CH_{2\ gem,trans}$), 5.13 – 5.03 (m, 1H, H_{DB}), 4.26 – 4.12

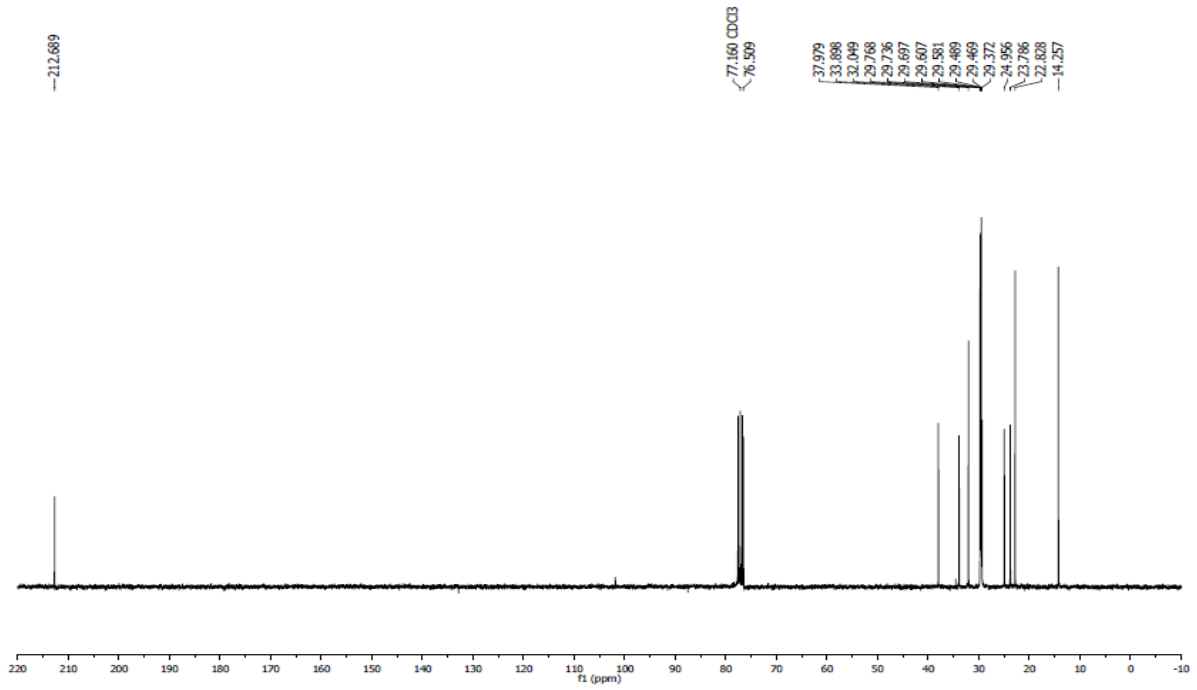
(m, 2H, CH_2O), 2.06 – 1.88 (m, 2H, CH_2), 1.80 – 1.69 (m, 1H, CH_2), 1.71 – 1.64 (m, 3H, CH_3C_{DB}), 1.60 (s, 3H), 1.56 – 1.29 (m, 3H, CH_3C_{DB}), 1.24 – 1.12 (m, 1H, CH_2), 0.92 (d, *J*=6.4 Hz, 3H, CHC*H*$_3$). **^{13}C{1H} NMR** (75 MHz, $CDCl_3$) δ = 166.5, 131.5, 130.6, 128.8, 124.7, 63.2, 37.1, 35.5, 29.6, 25.9, 25.5, 19.7, 17.8. **MS-ESI**: calculated for $[C_{13}H_{22}O_2Na]^+$: m/z = 233.1512, found: m/z = 233.1528. **ATR-FTIR (cm^{-1}):** 2962, 2918, 2872, 1726, 1635, 1456, 1408, 1381, 1294, 1271, 1189, 1063, 984, 630.

10 ^{1}H and ^{13}C spectra of organic compounds

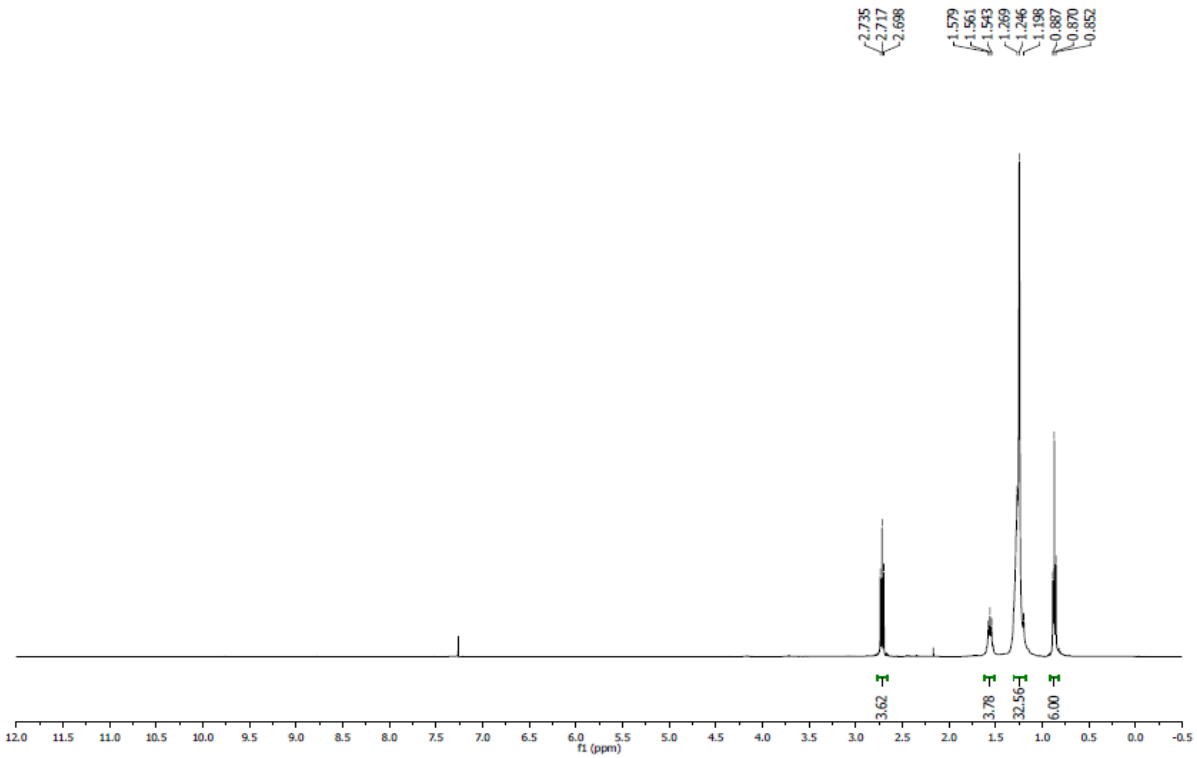
10.1 Aclyoin 12

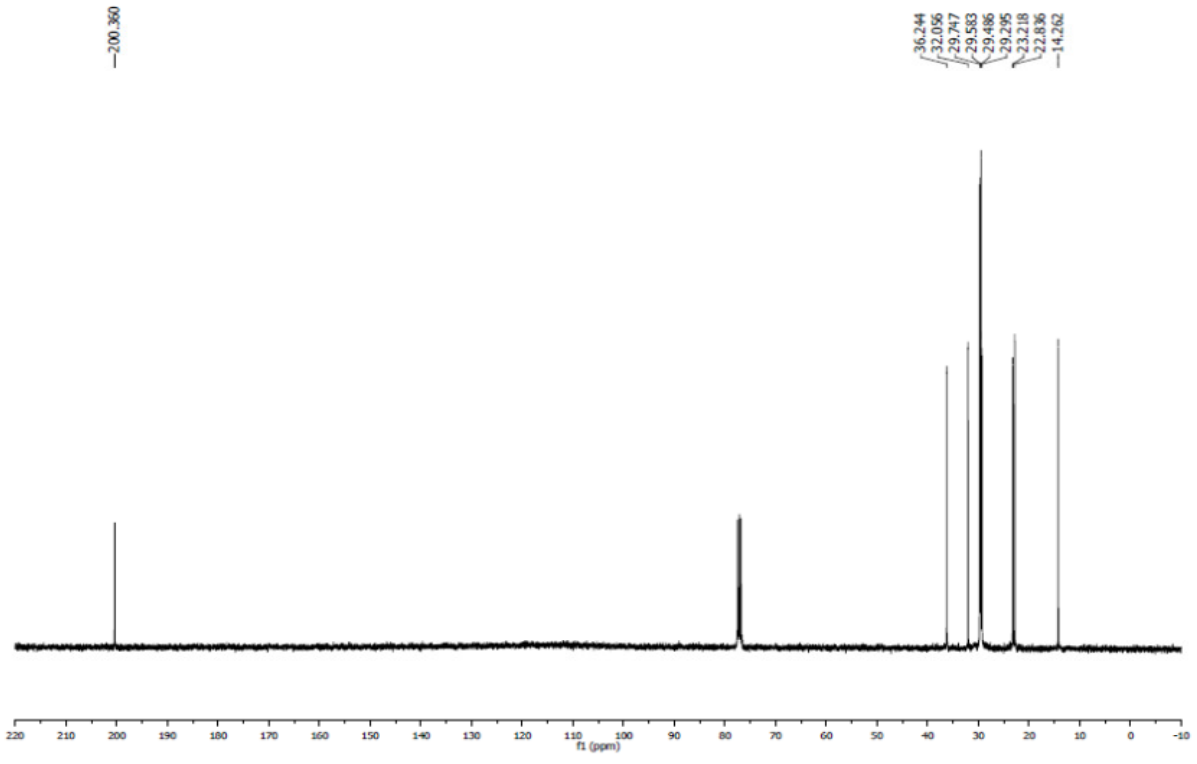


R = n-$C_{11}H_{23}$

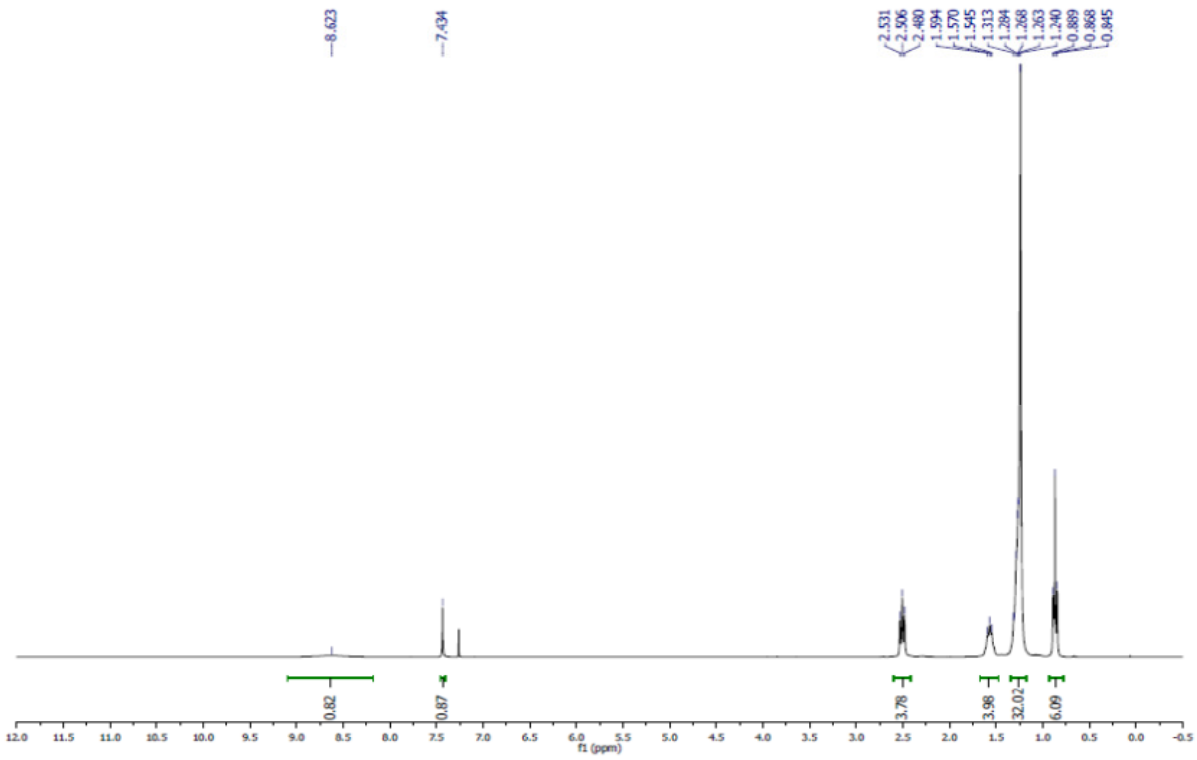


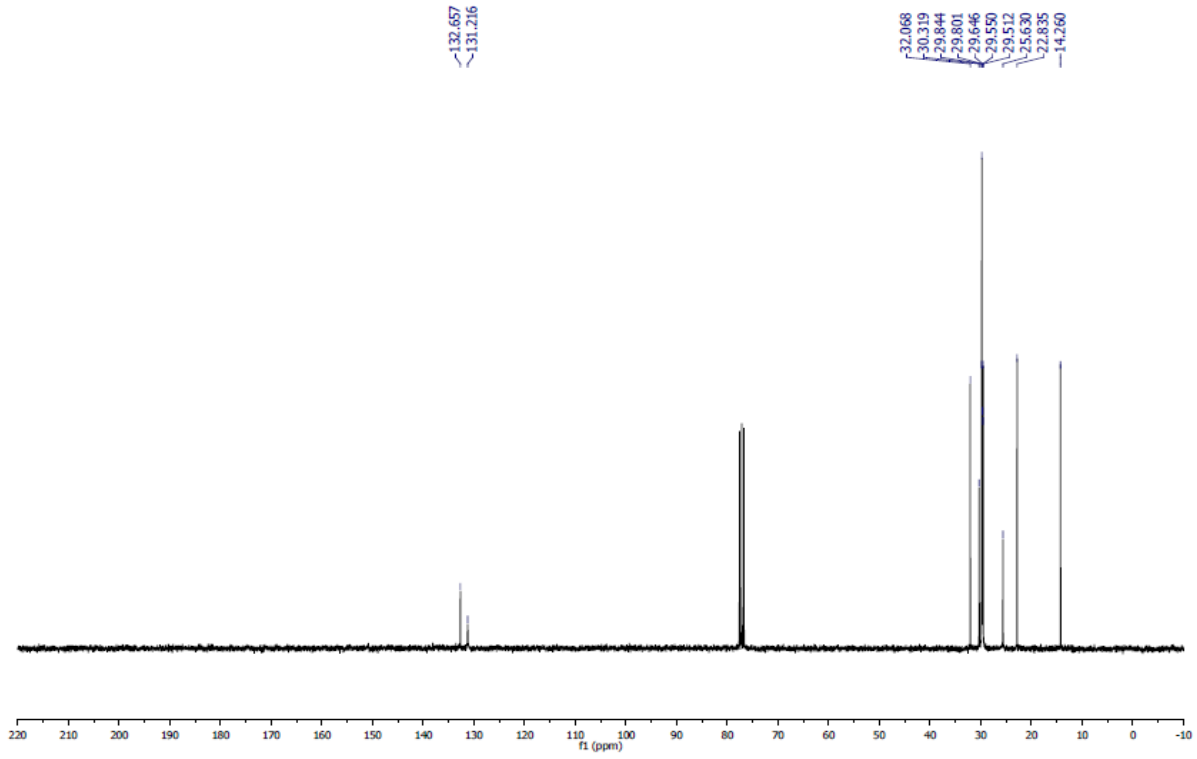
10.2 Diketone 13



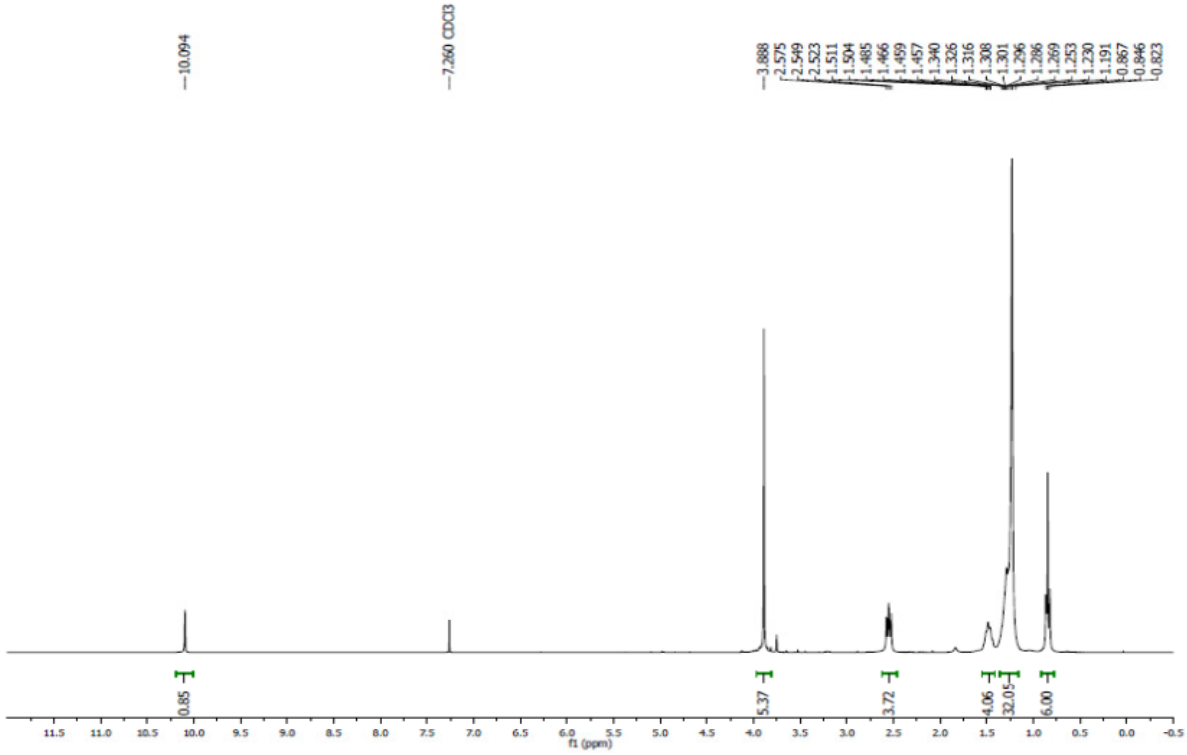


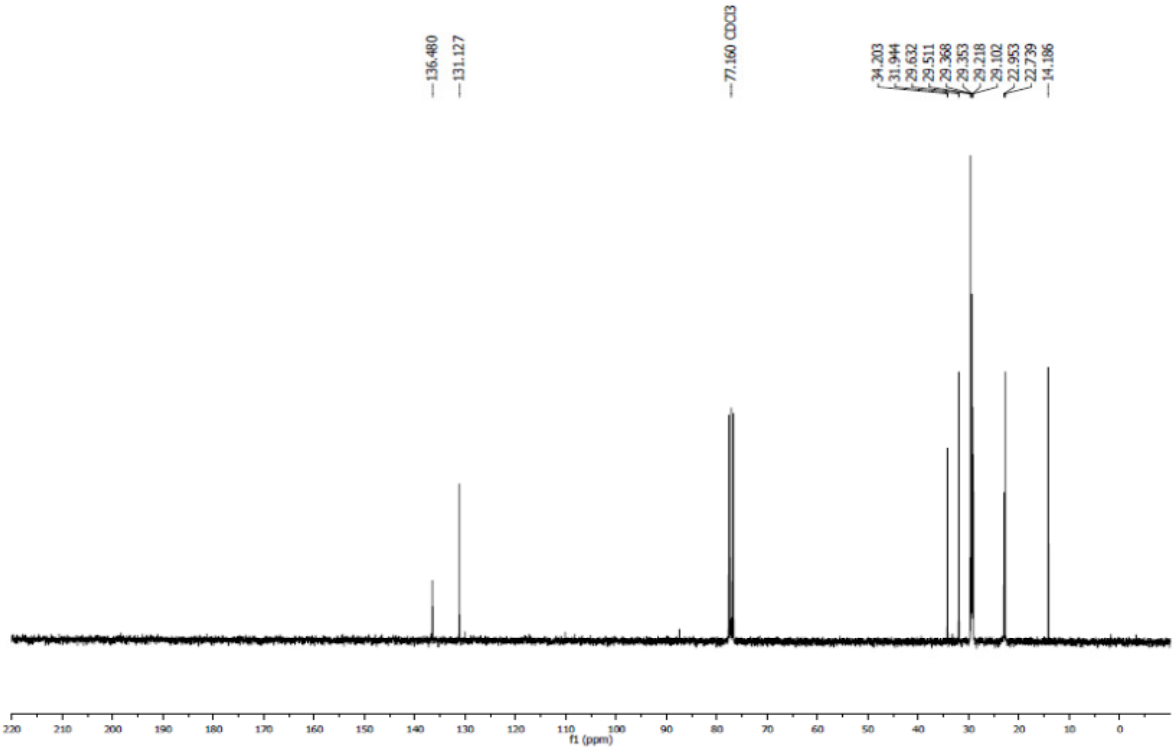
10.3 Imidazole 14



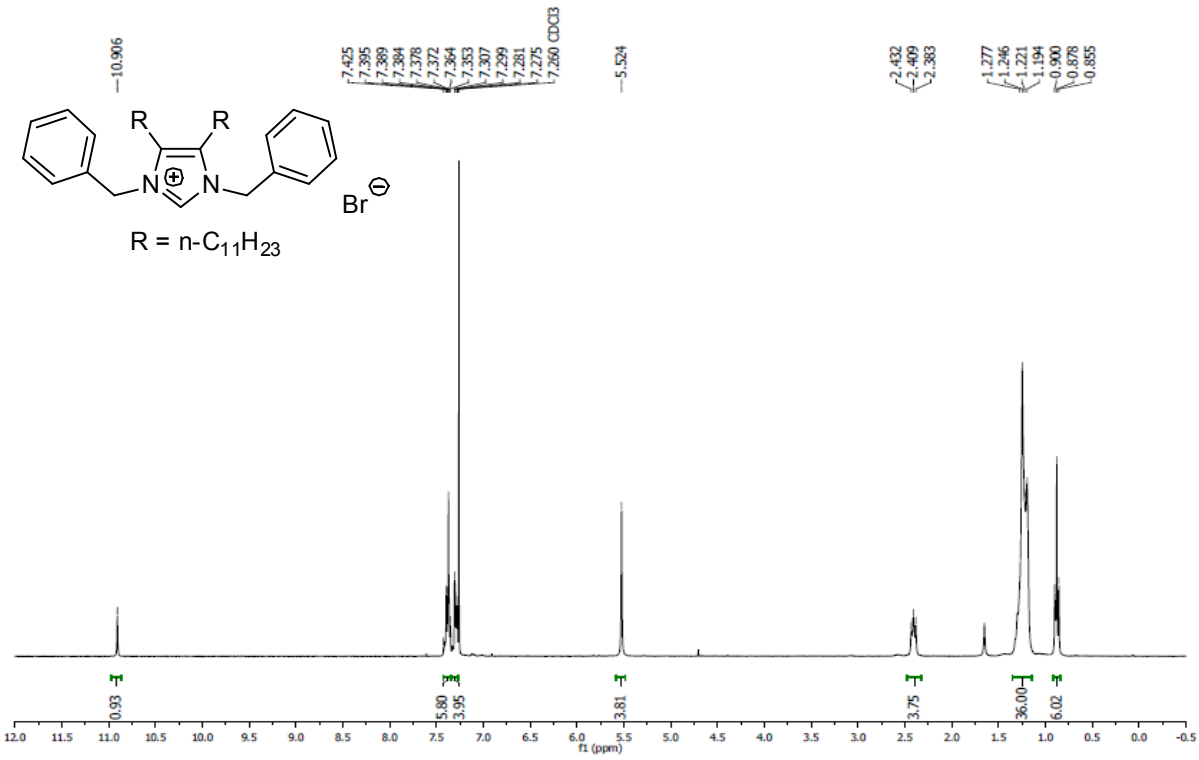


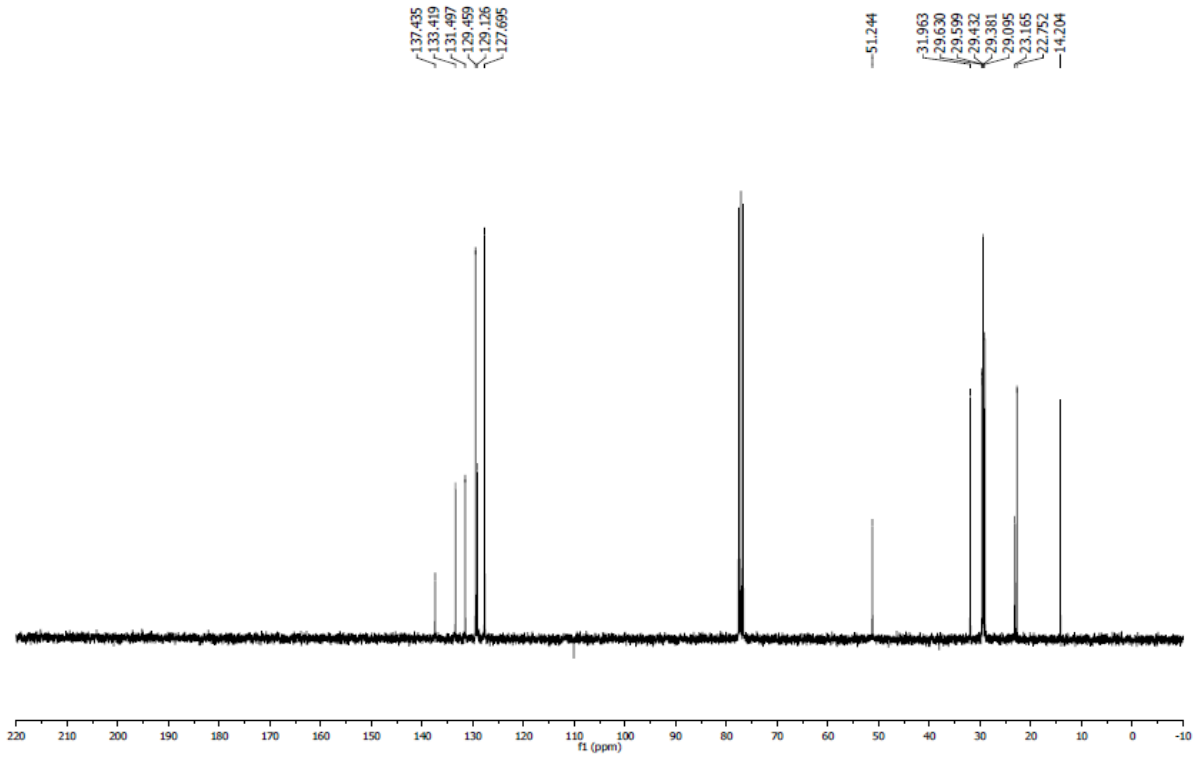
10.4 Imidazolium salt 1•HI



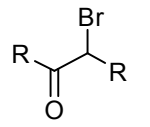


10.5 Imidazolium salt 2•HBr

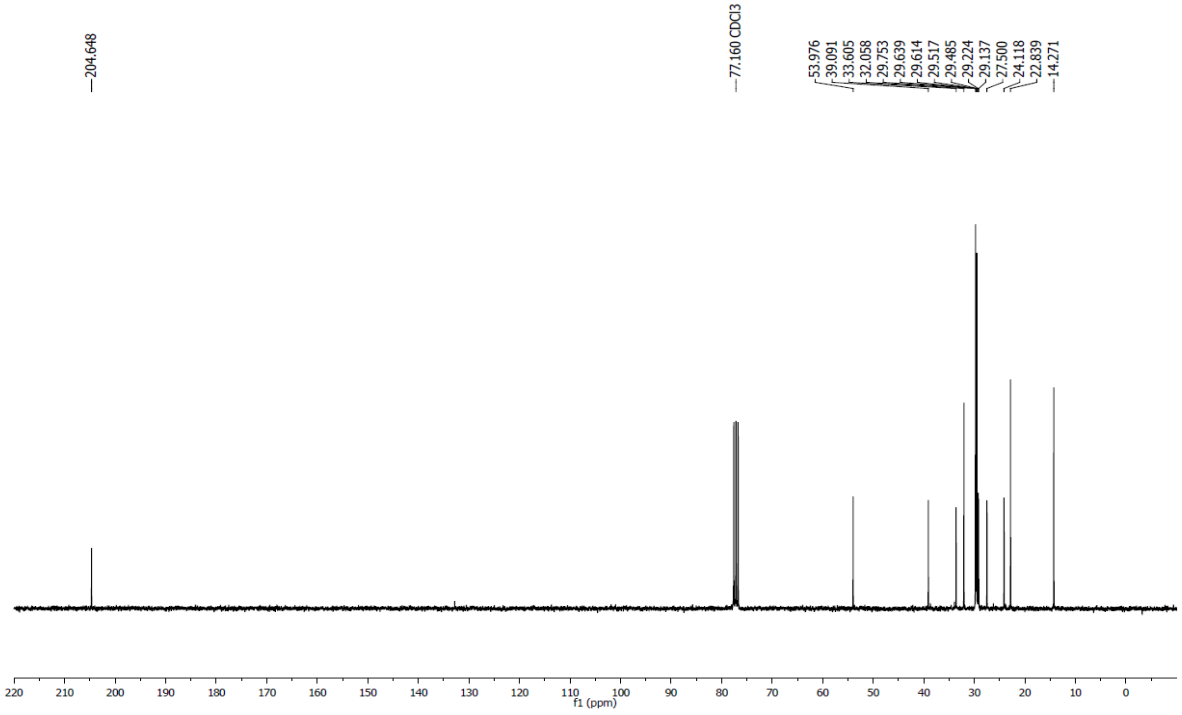




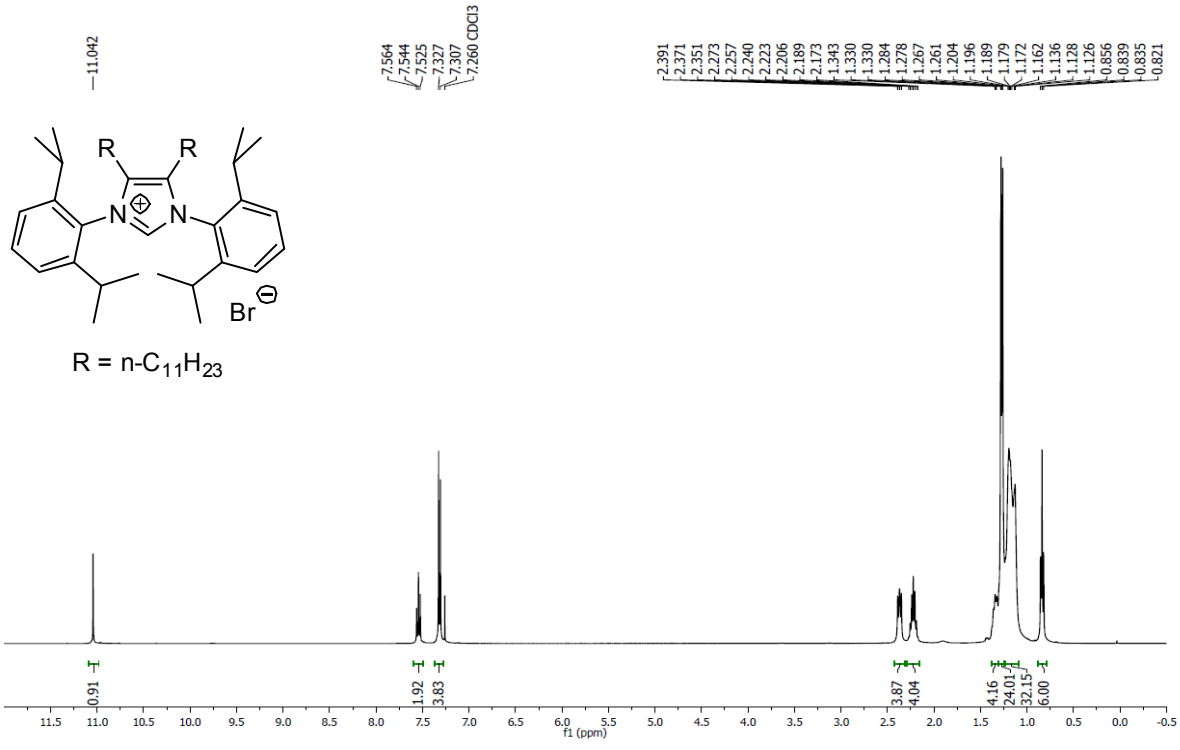
10.6 Bromoketone 23

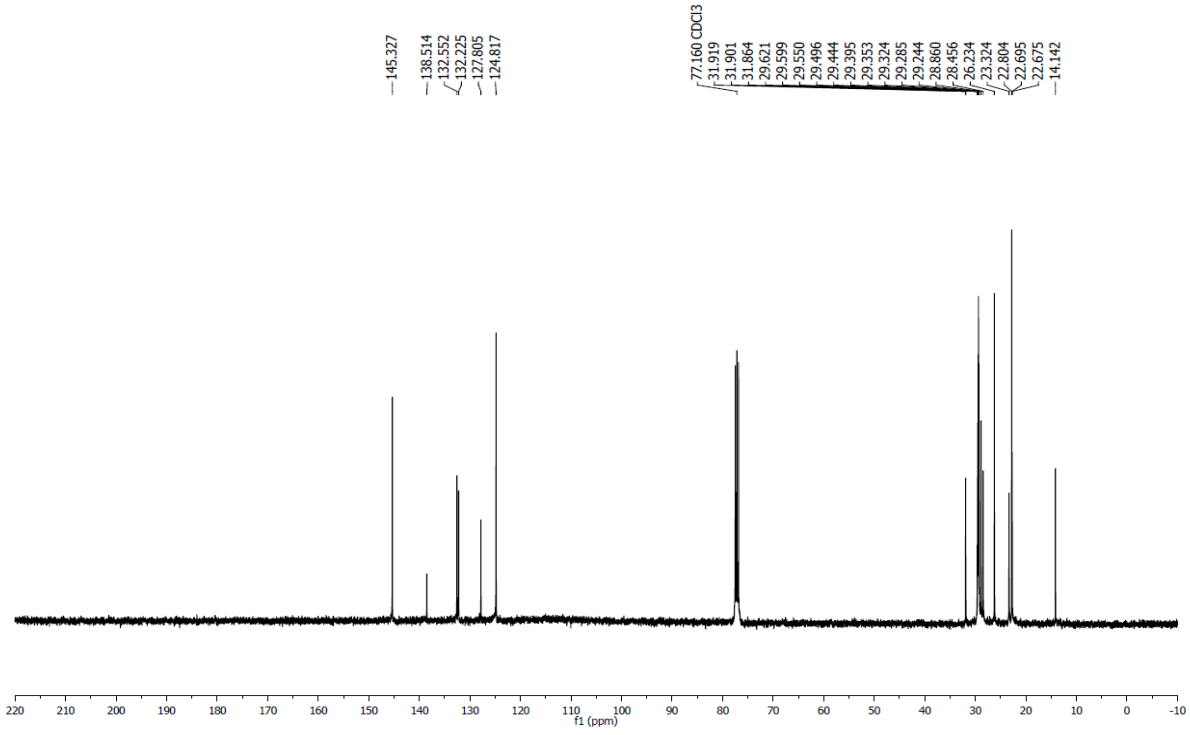


R = n-$C_{11}H_{23}$

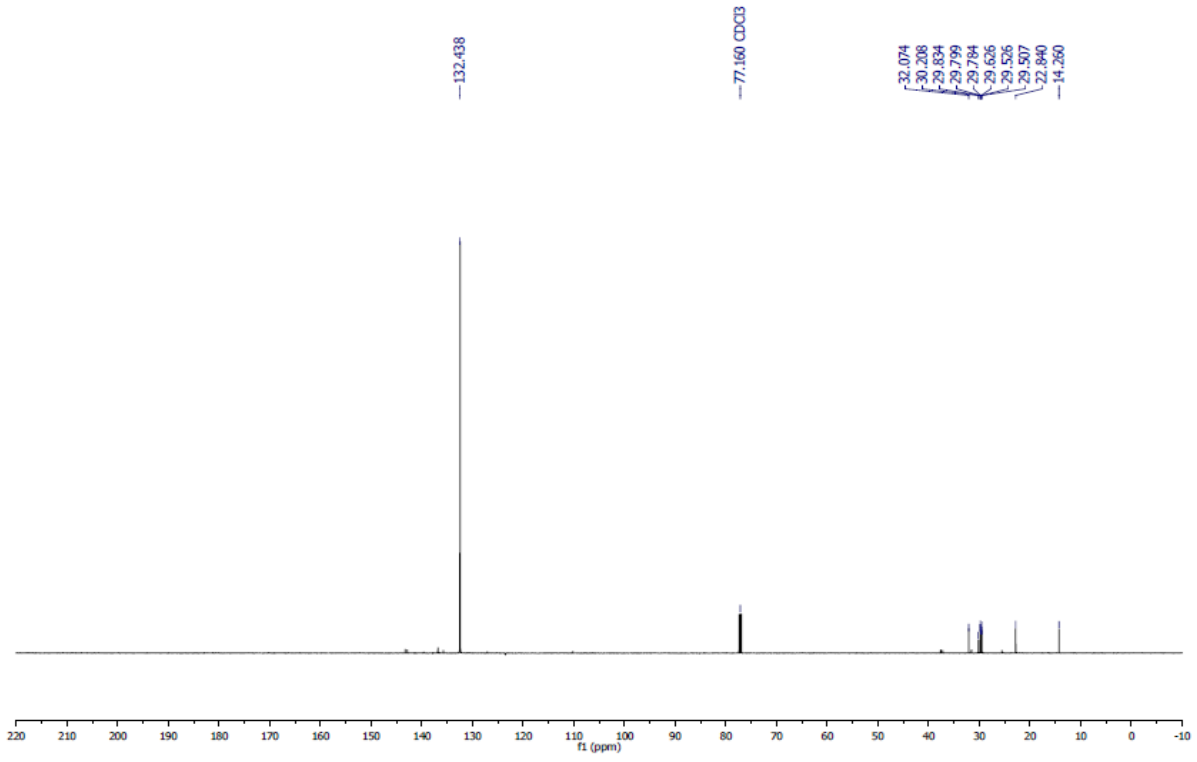


10.7 LC-IPr (25)

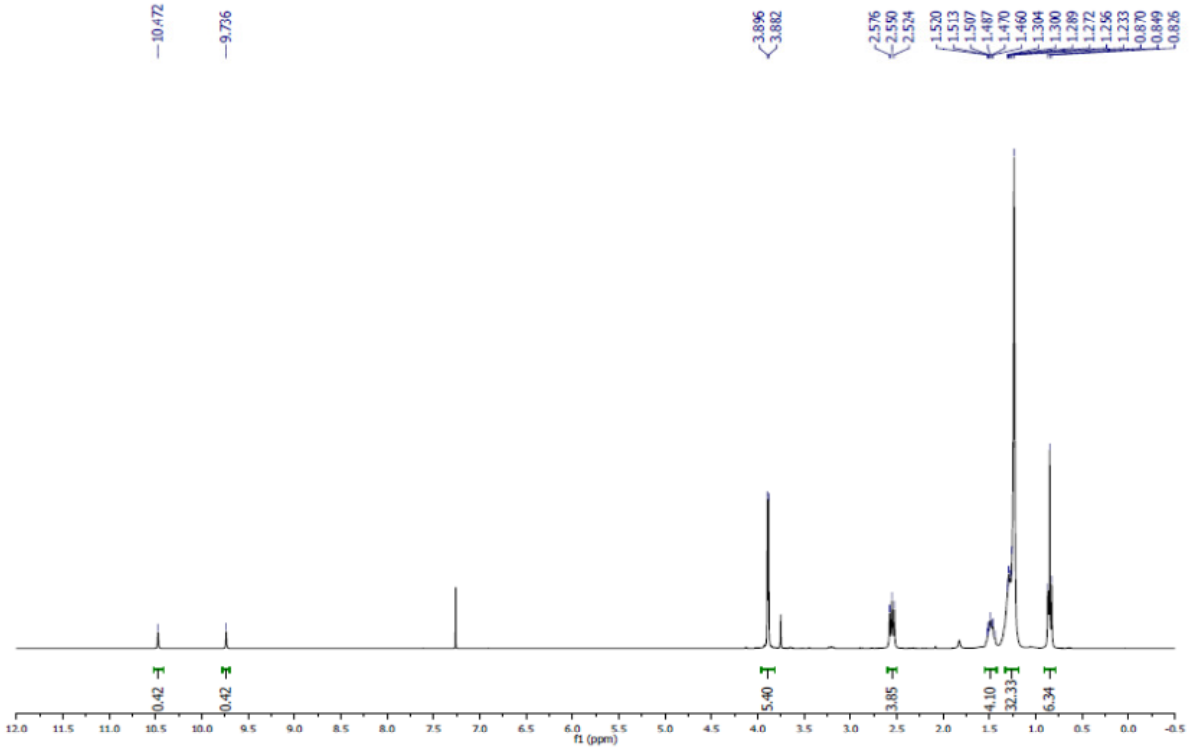

11.042
7.564
7.544
7.525
7.327
7.307
7.260 CDCl3
2.391
2.371
2.351
2.273
2.257
2.240
2.223
2.206
2.189
2.173
1.343
1.330
1.330
1.284
1.278
1.267
1.261
1.204
1.196
1.189
1.179
1.172
1.162
1.136
1.128
1.126
0.856
0.839
0.835
0.821
R
R
N
N
Br
R = n-C11H23
0.91
1.92
3.83
3.87
4.04
4.16
24.01
32.15
6.00
f1 (ppm)


145.327
138.514
132.552
132.225
127.805
124.817
77.160 CDCl3
31.919
31.901
31.864
29.621
29.599
29.550
29.496
29.444
29.395
29.353
29.324
29.285
29.244
28.860
28.456
26.234
23.324
22.804
22.695
22.675
14.142
f1 (ppm)

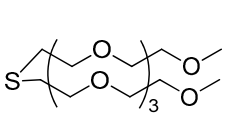
10.8 Imidazole ^{13C}14

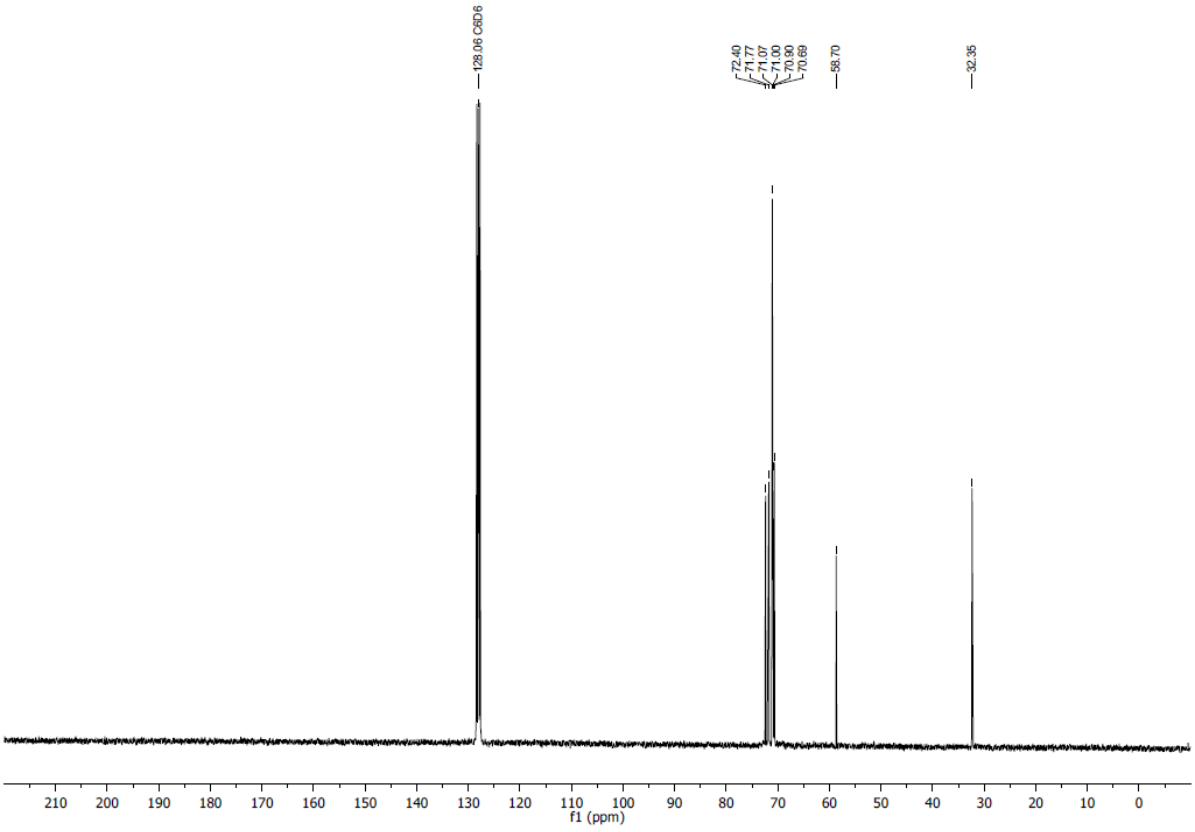


10.9 Imidazoium salt ^{13C}1•HI

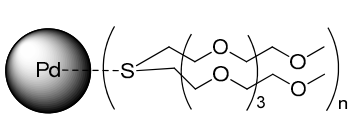


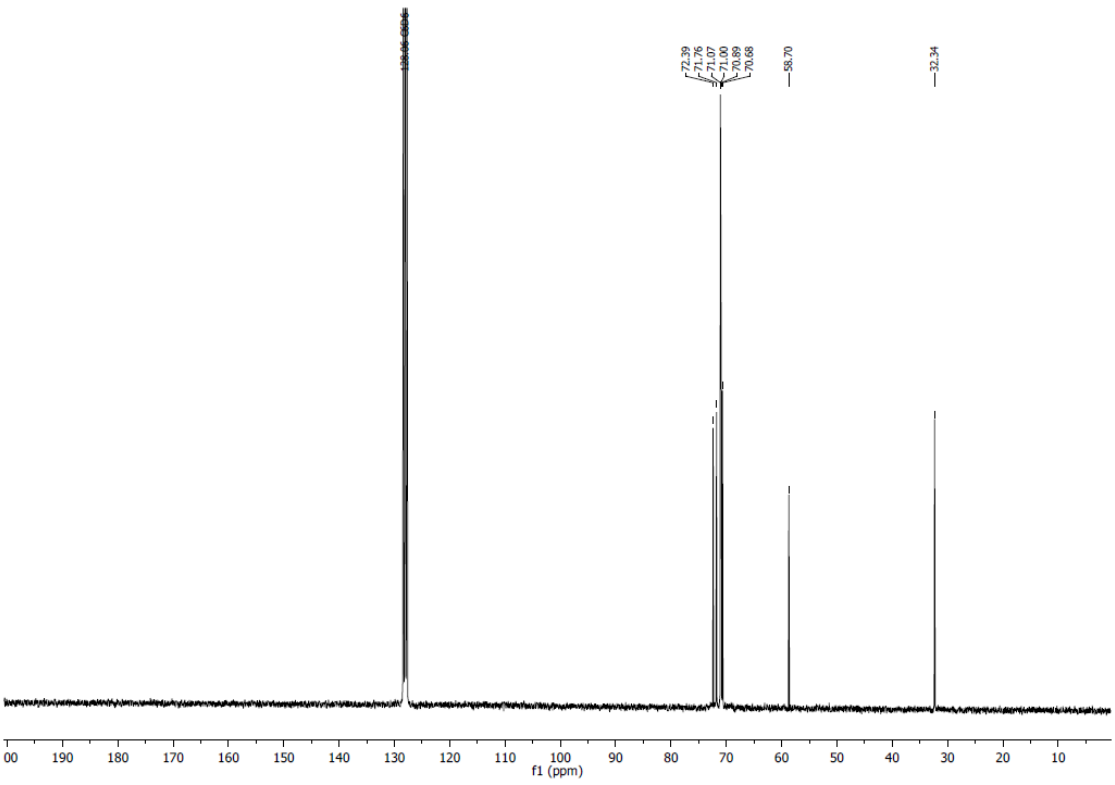
10.10 Bis(tetraehylene glycol monomethyl ether)thioether (3)





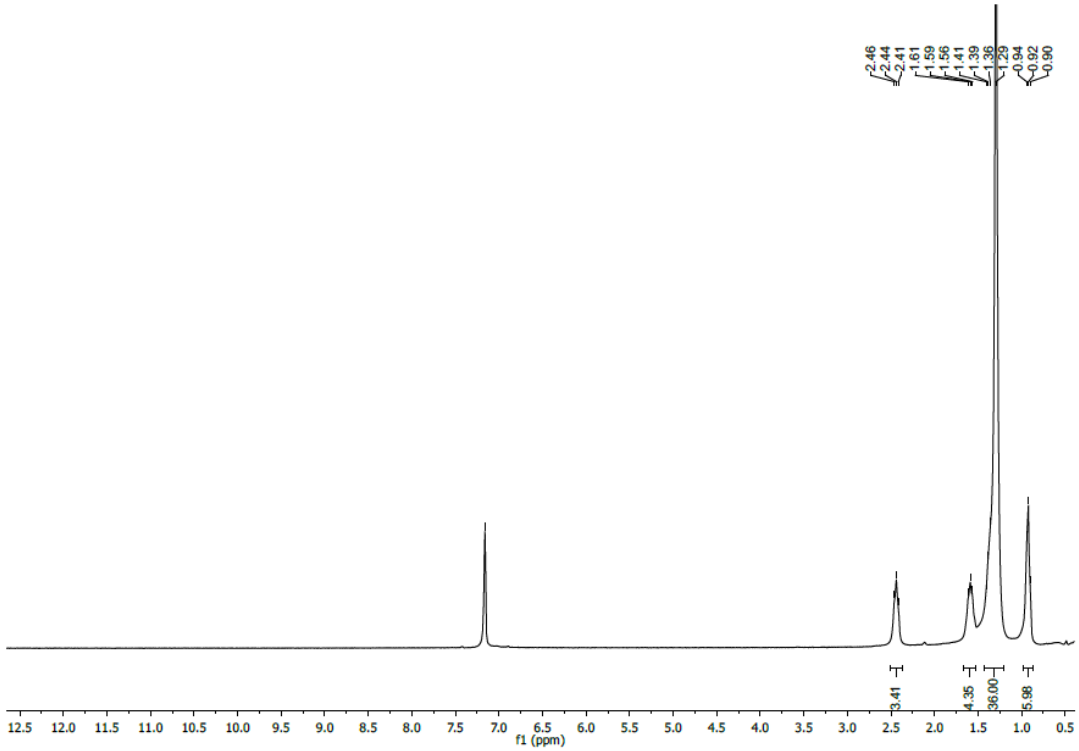
10.11 3@Pd-NP

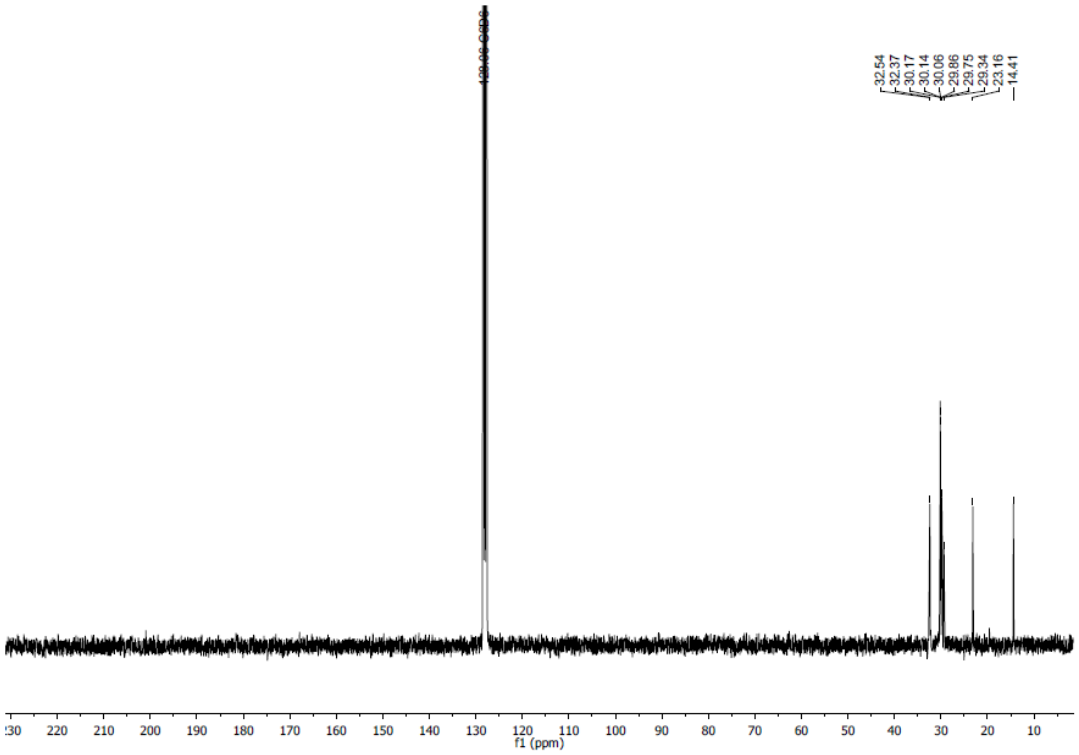




Note: Due to the excess of thioether the spectrum is an overlap of bound and free ligand.

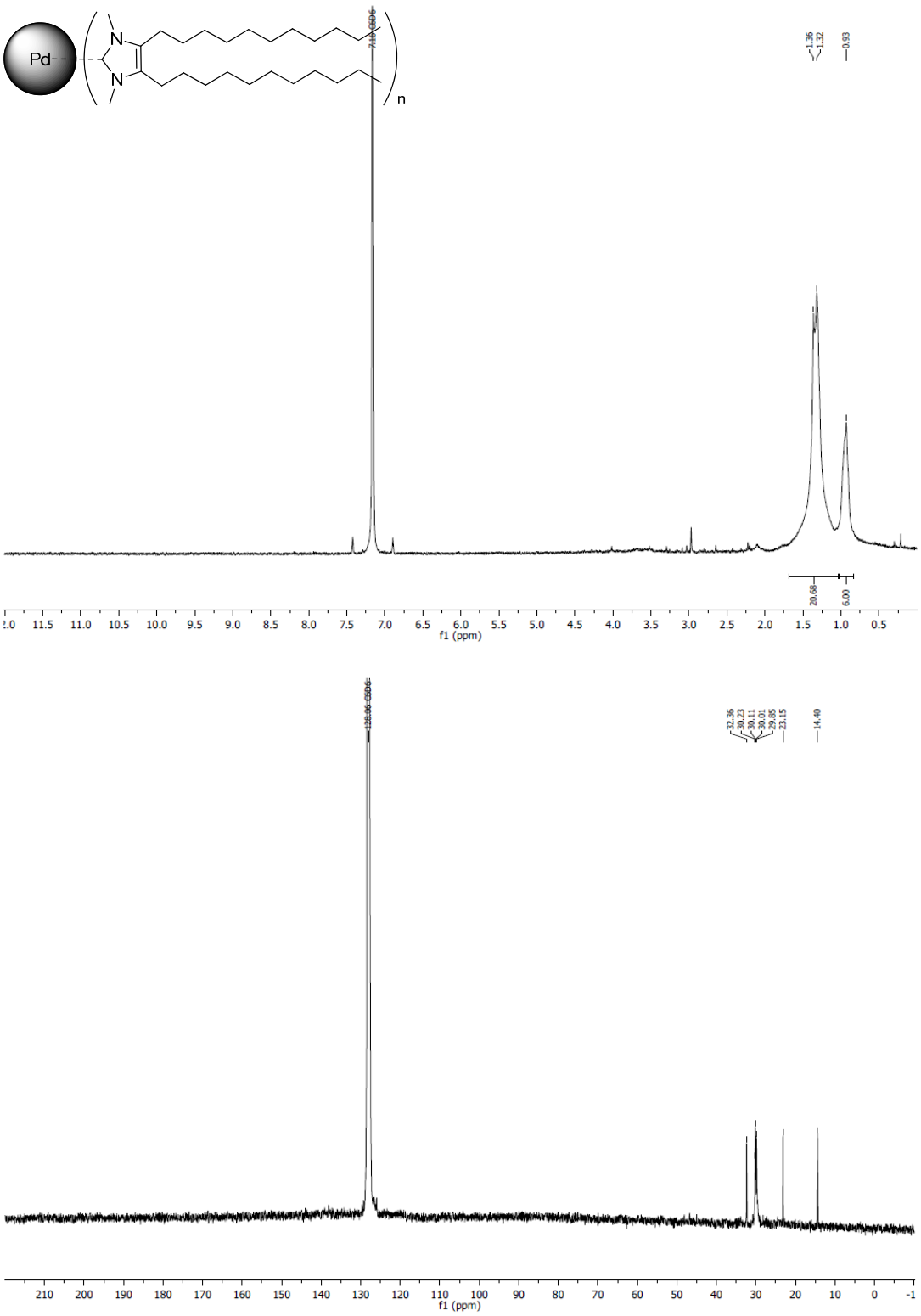
10.12 4@Pd-NP





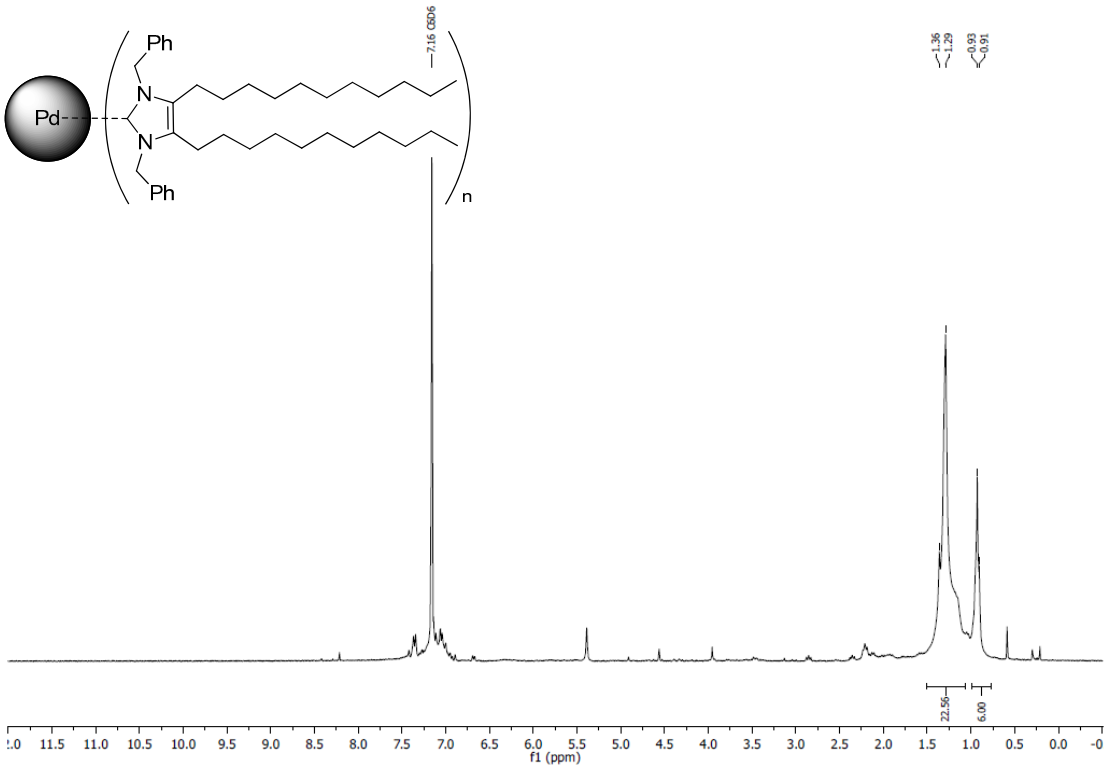
Note: Due to the excess of thioether the spectrum is an overlap of bound and free ligand.

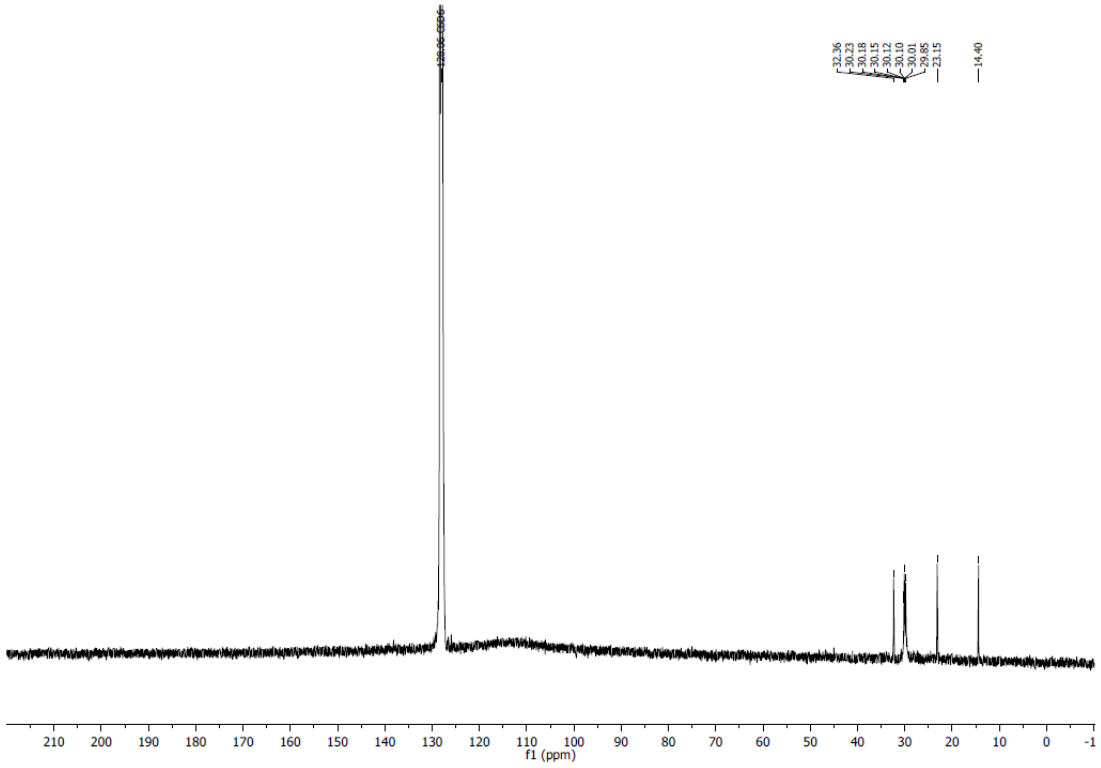
10.13 1@Pd-NP



Signals located at the surface of the particle disappear (see main text).

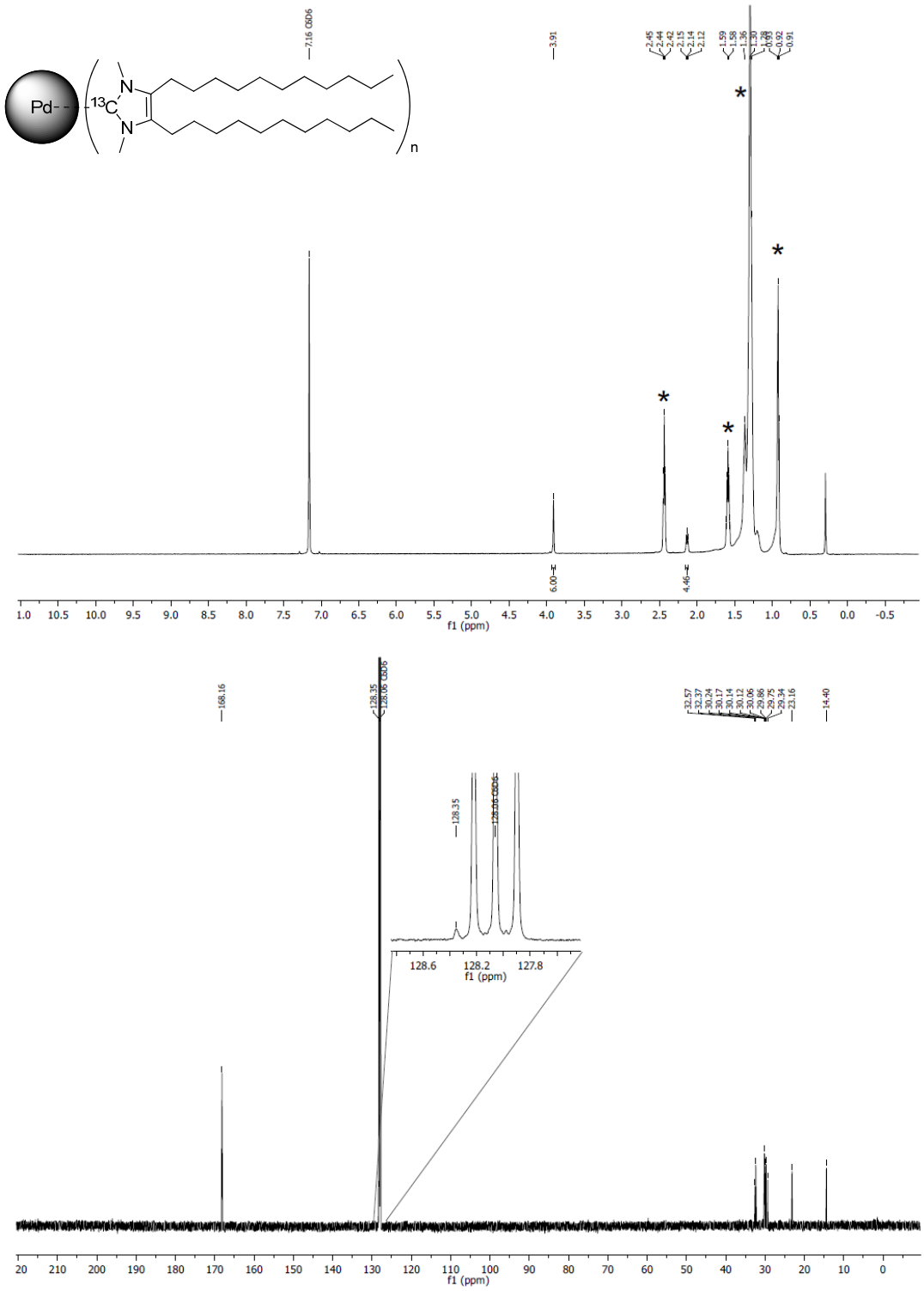
10.14 2@Pd-NP





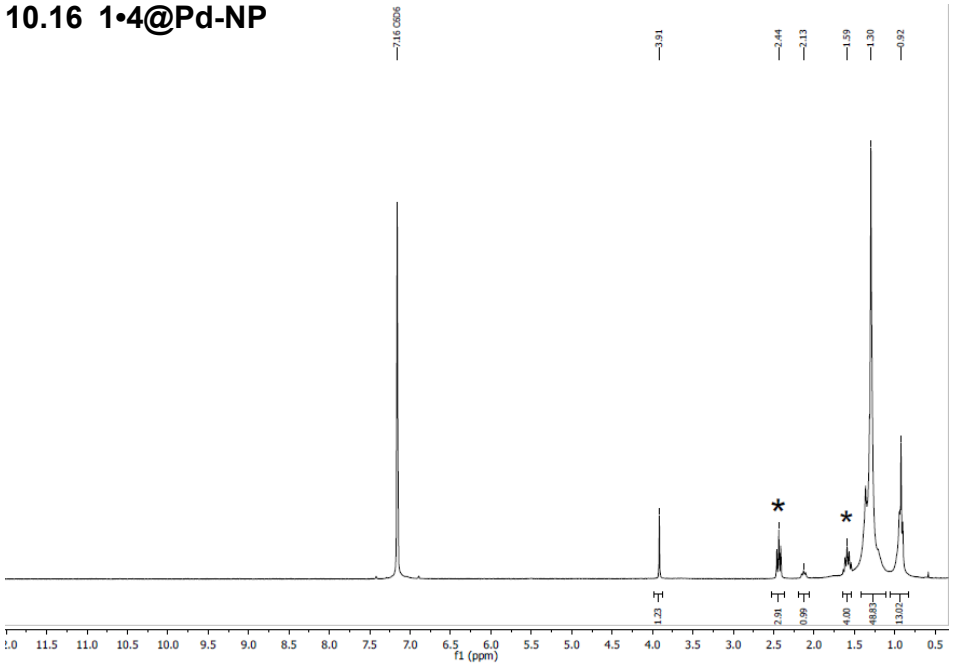
Signals located at the surface of the particle disappear (see main text).

10.15 ^{13C}1•4@Pd-NP



Signals located at the surface of the particle disappear (see main text). Signals marked with an asterix correspond to thioether **4** which is still present in the sample.

10.16 1•4@Pd-NP



10.17 Replacement experiments with thiol 15

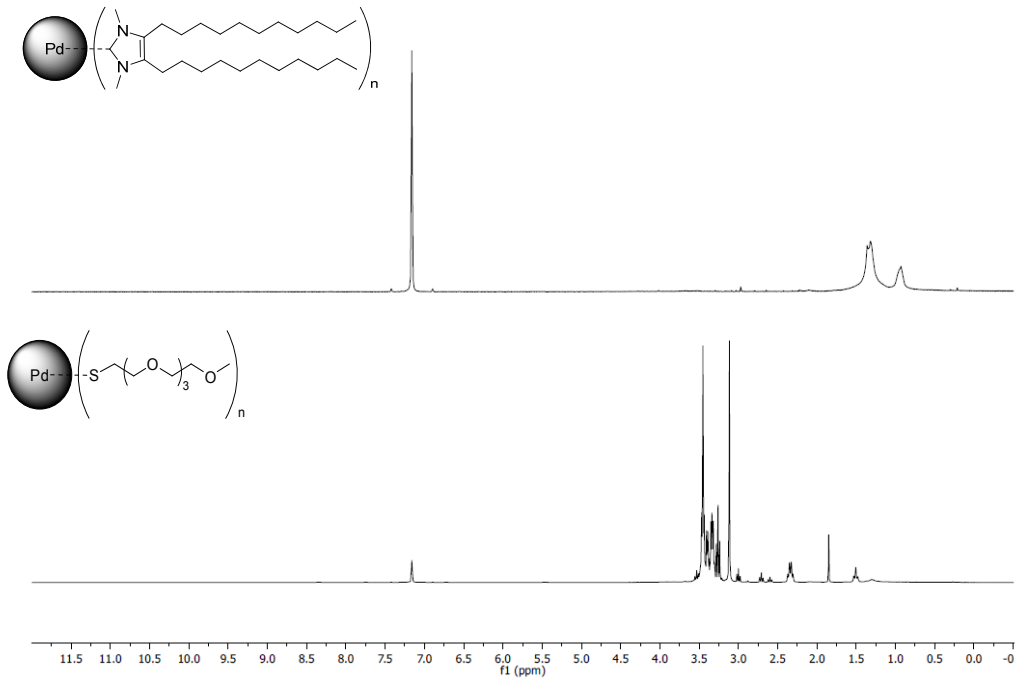
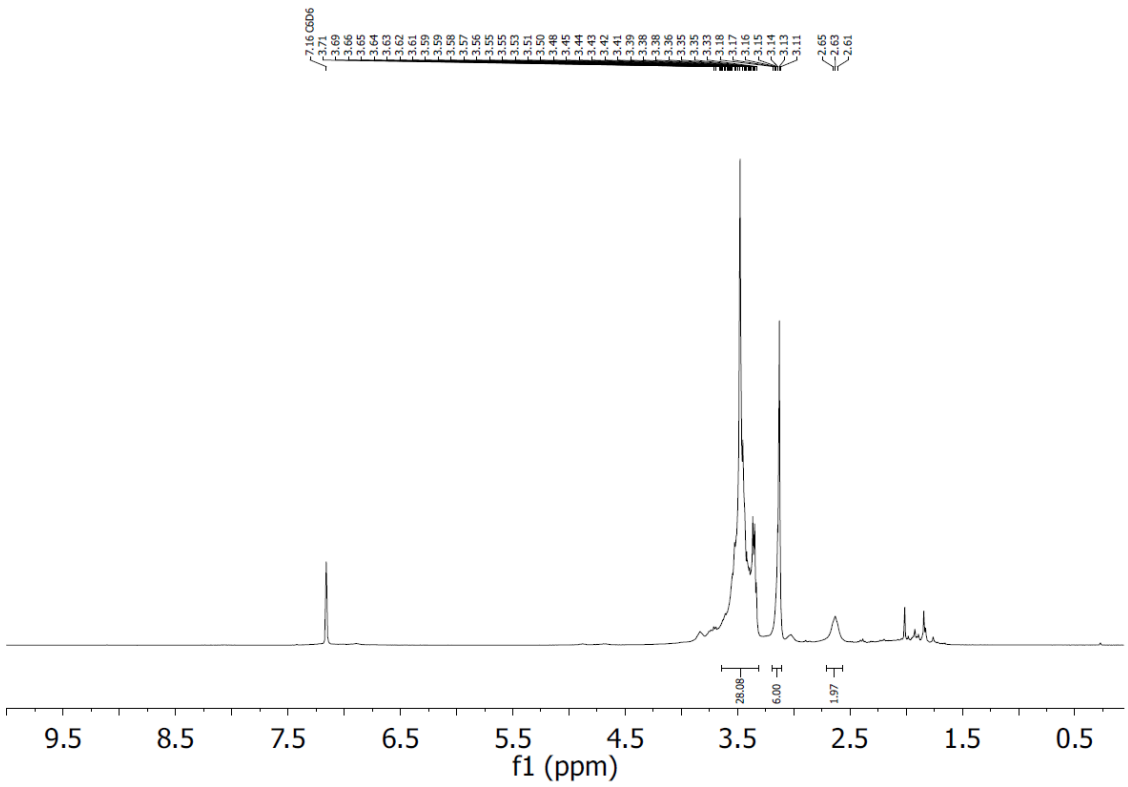
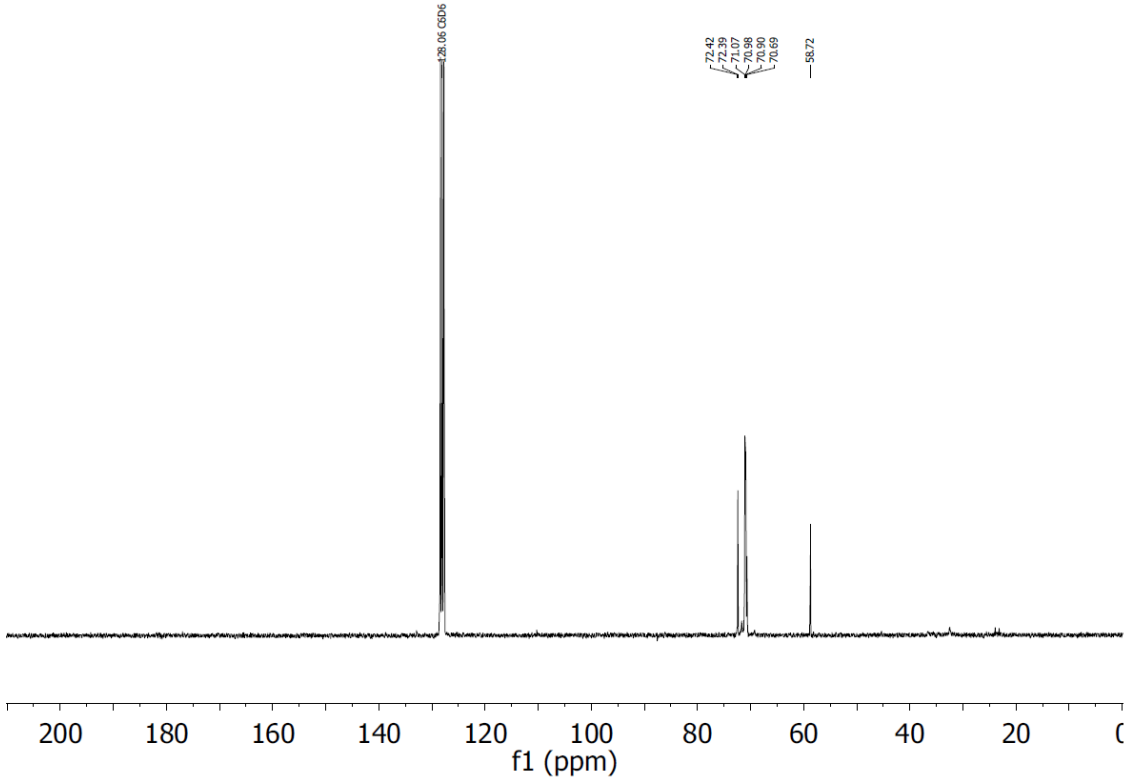


Figure 1: *top: ^{1}H NMR spectra of **1**@Pd-NP; bootom: ^{1}H NMR spectra after ligand exchange with thiol **15**.*

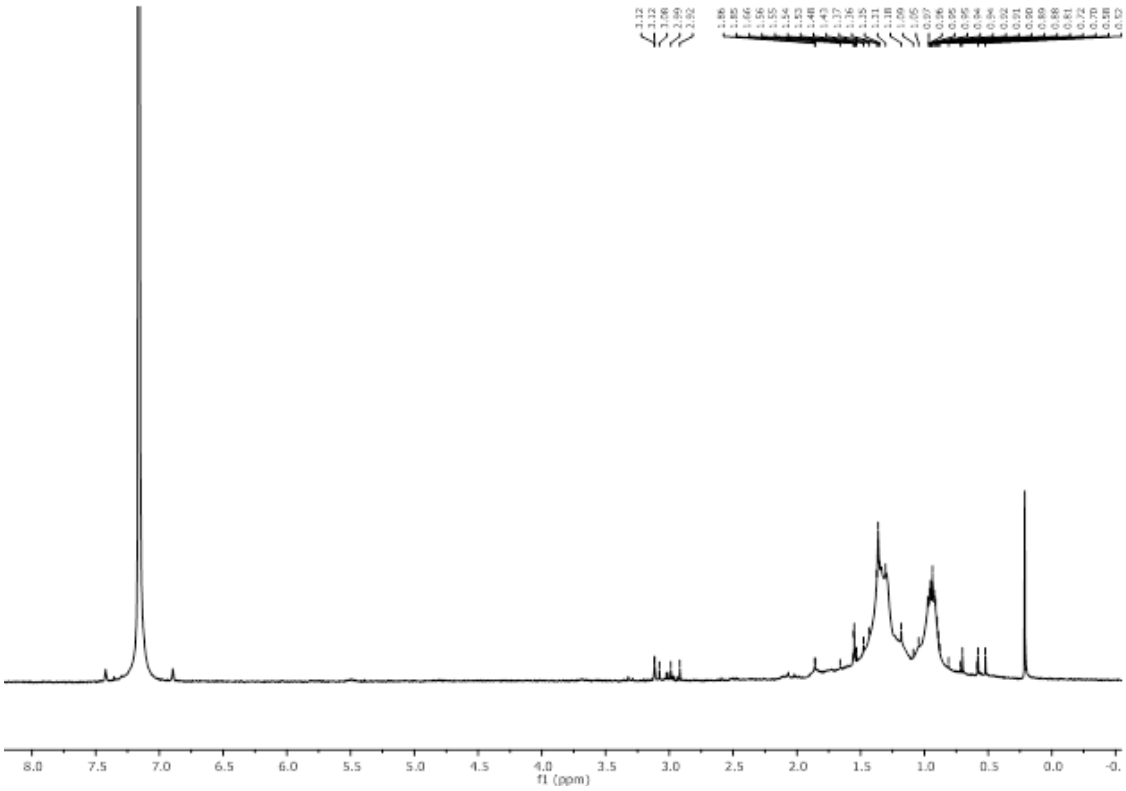
Signals located close to the surface of the particle disappear (see main text). Signals marked with an asterix correspond to thioether **4** which is still present in the sample.

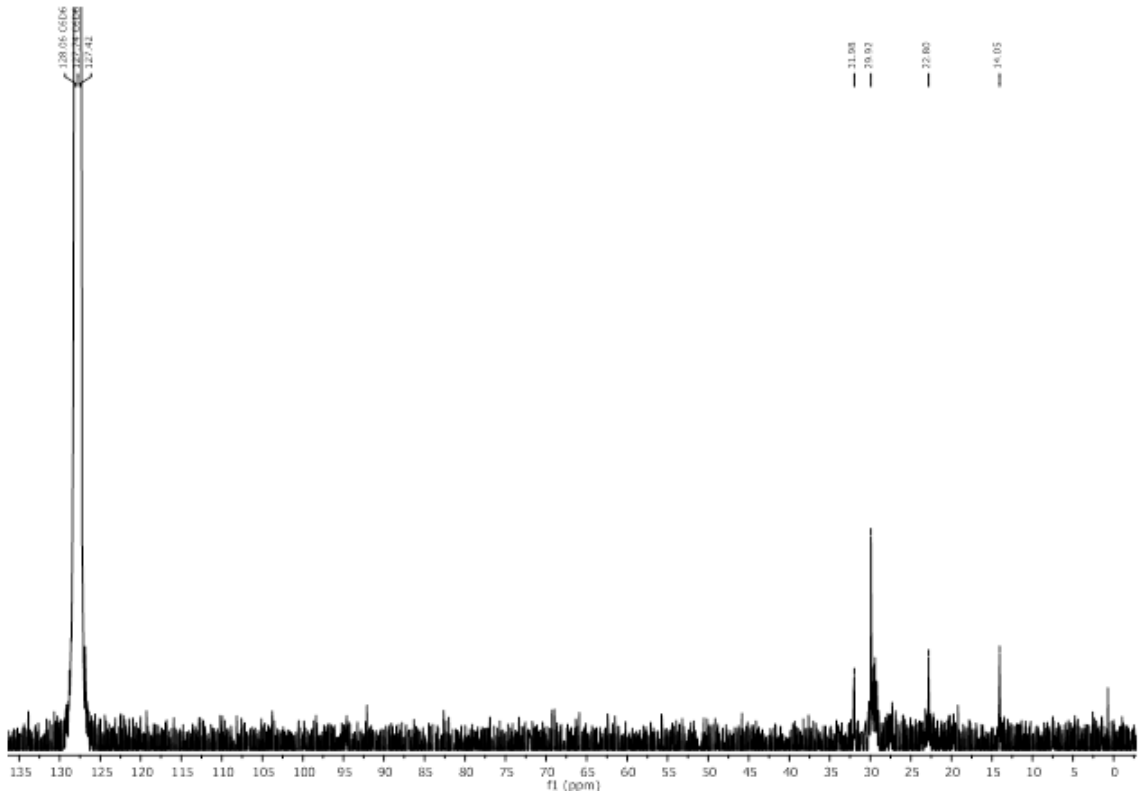
10.18 3@Au-NP


7.16 C6D6
3.71
3.69
3.66
3.65
3.64
3.63
3.62
3.61
3.59
3.59
3.58
3.57
3.55
3.55
3.53
3.51
3.50
3.48
3.45
3.44
3.43
3.42
3.41
3.39
3.38
3.38
3.36
3.35
3.35
3.33
3.18
3.17
3.16
3.15
3.14
3.13
3.11
2.65
2.63
2.61
28.08
6.00
1.97
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


128.06 C6D6
72.42
72.39
71.07
70.98
70.90
70.69
58.72
200
180
160
140
120
100
80
60
40
20
f1 (ppm)

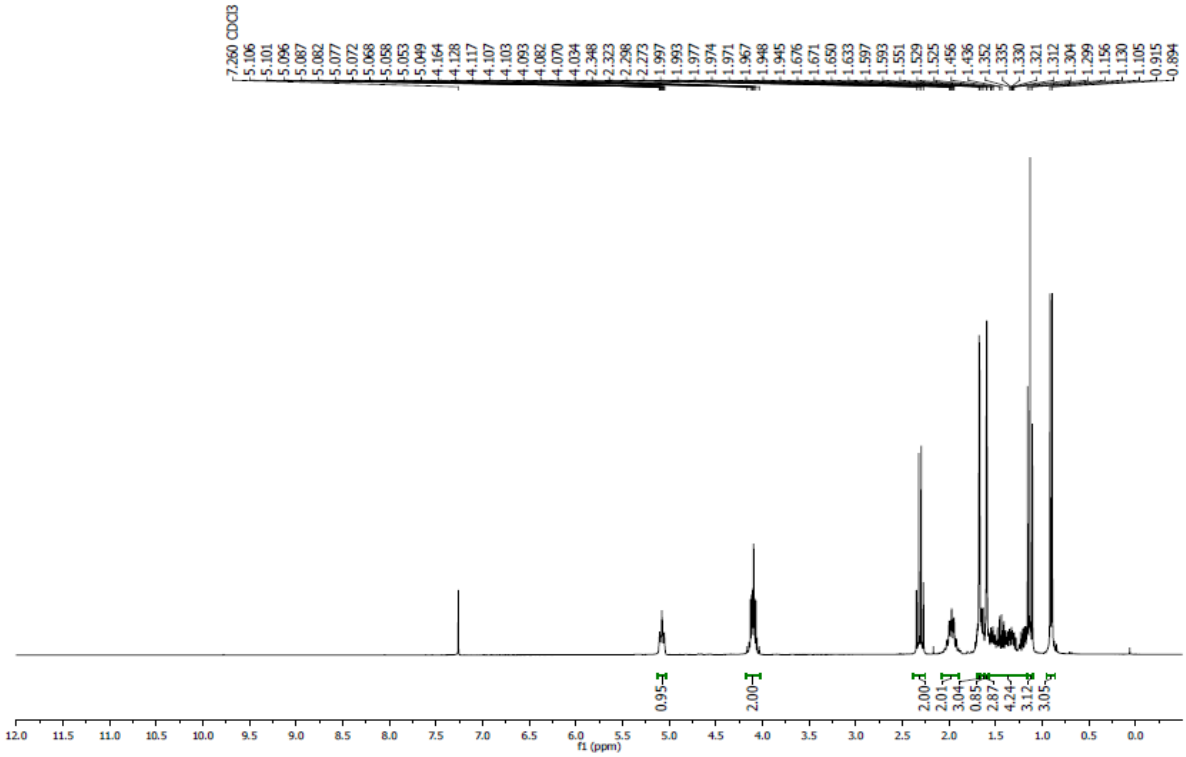
10.19 1@Pd-NP

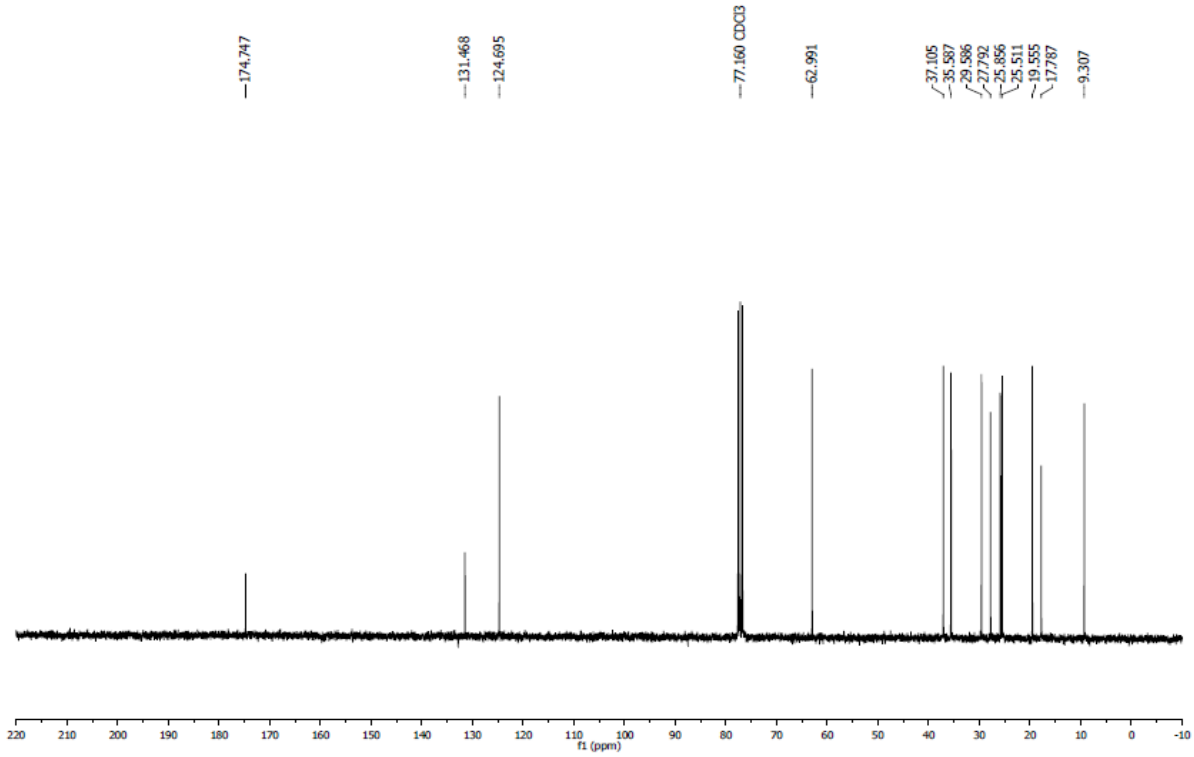




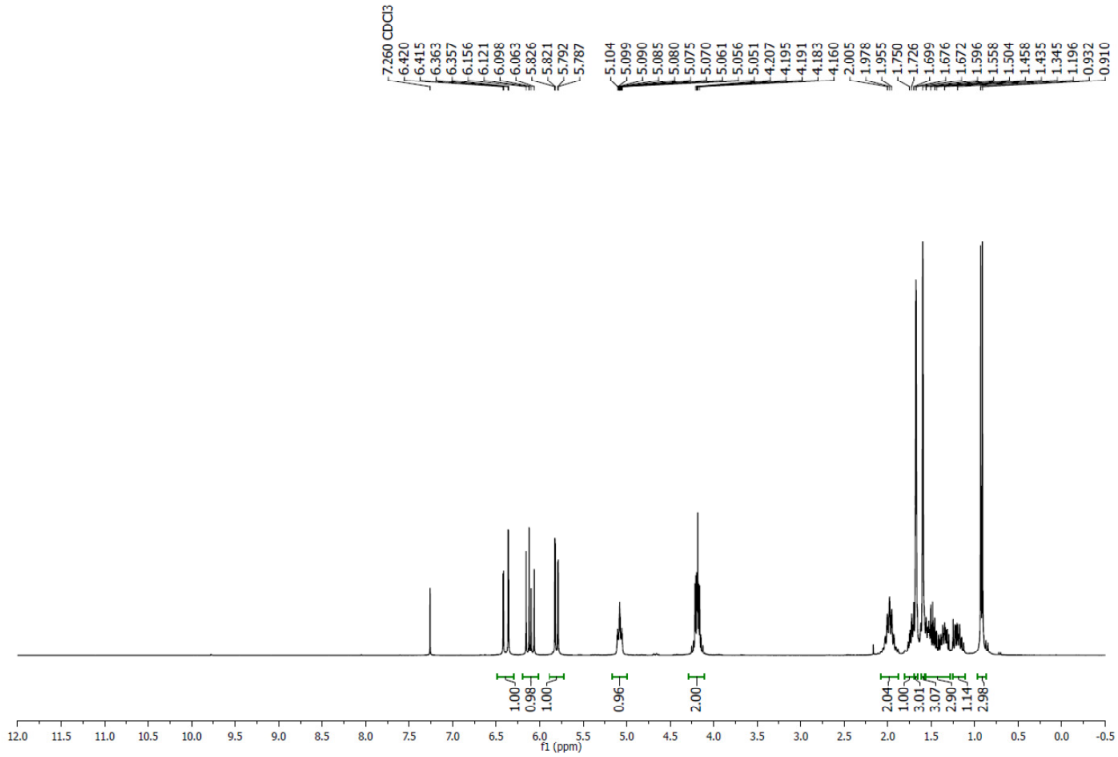
Signals located at the surface of the particle disappear (see main text).

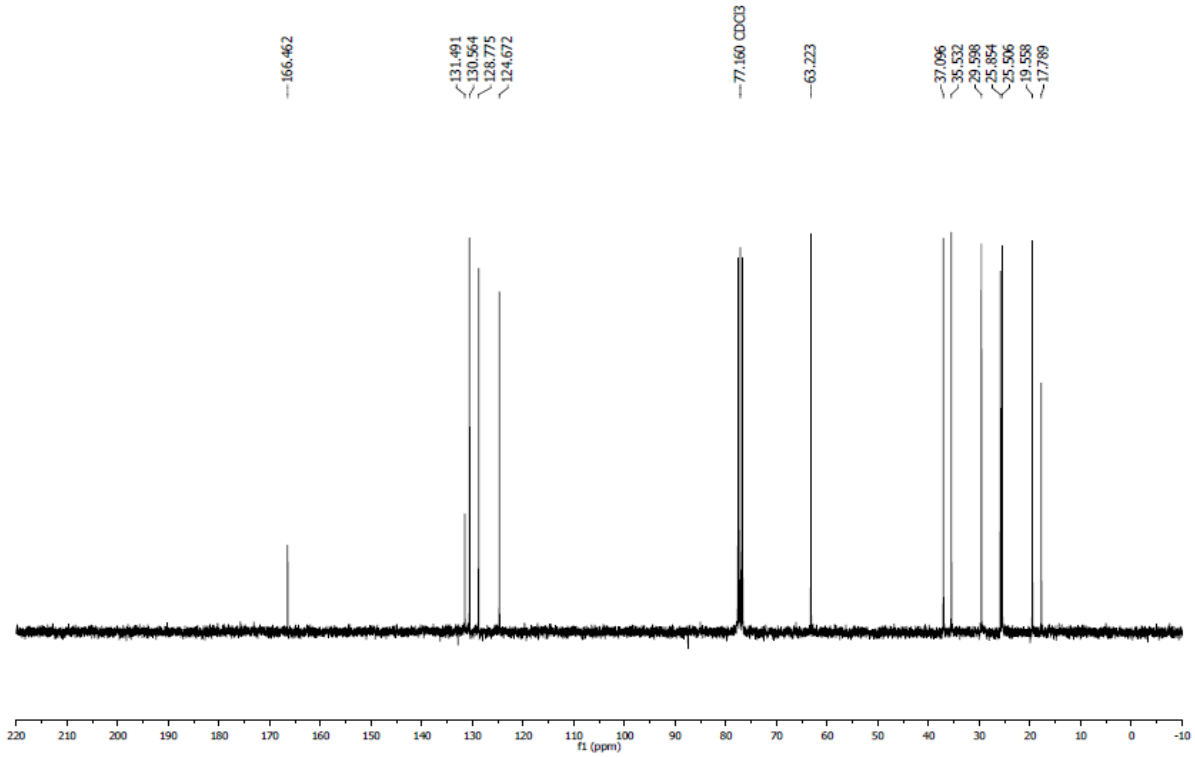
10.20 3,7-Dimethyloct-6-en-1-yl propionate (9)



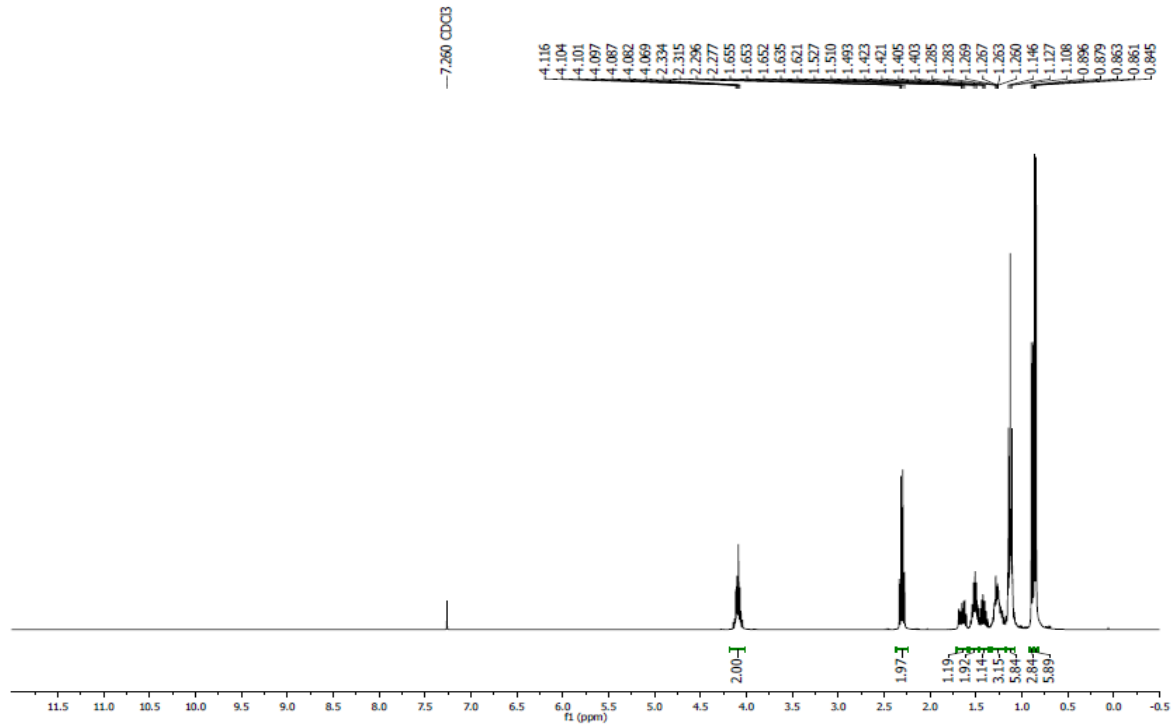


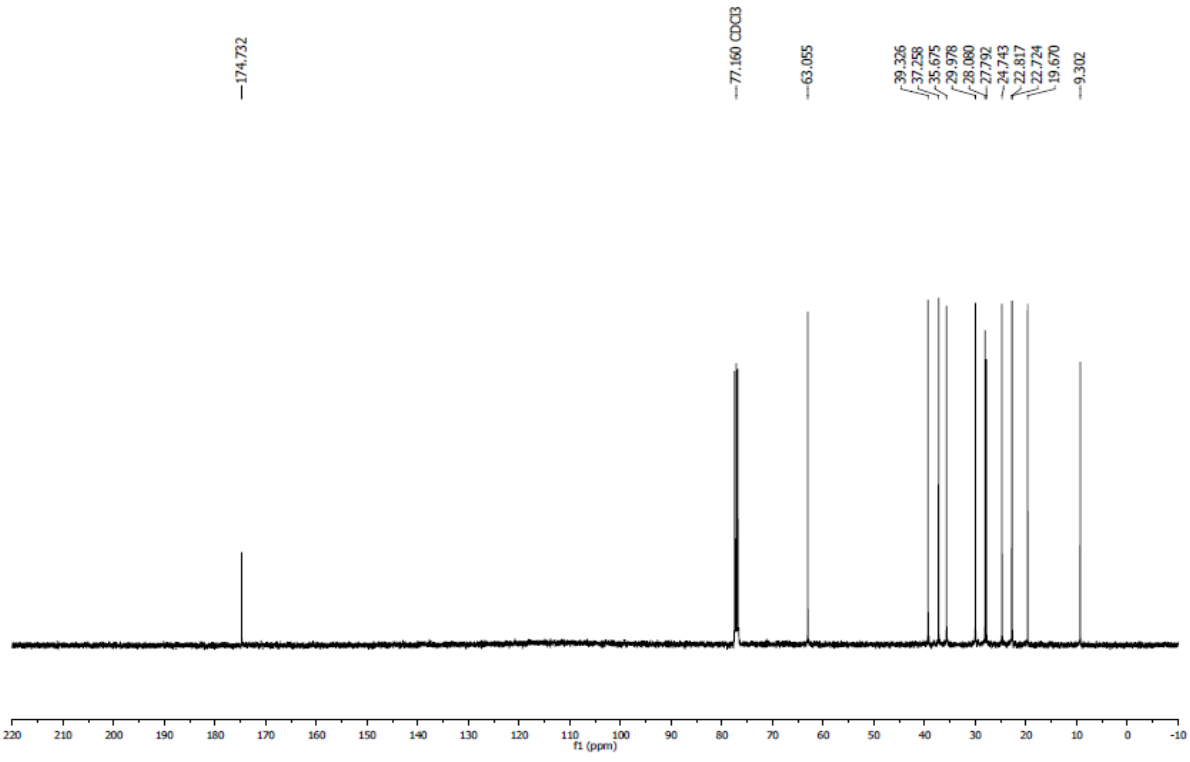
10.21 3,7-dimethyloct-6-en-1-yl acrylate (10)



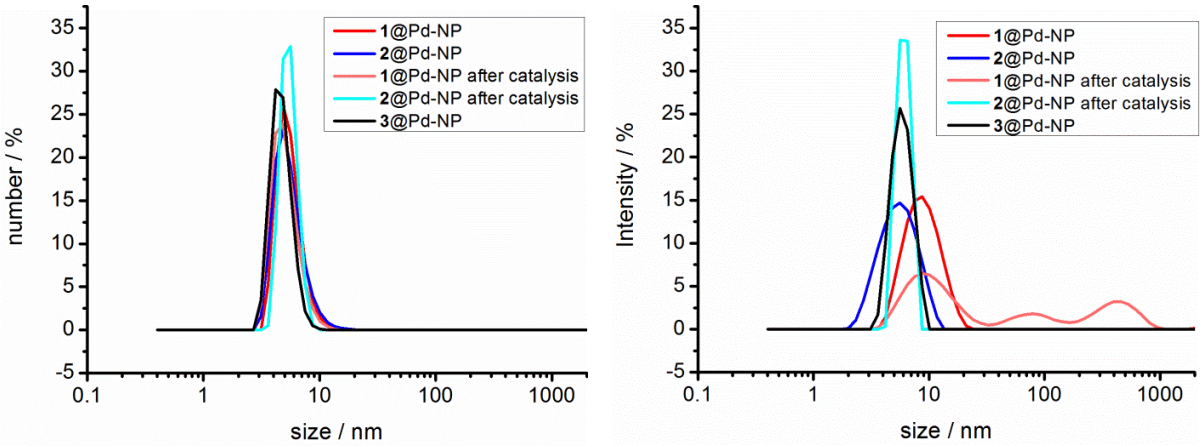


10.22 3,7-dimethyloctyl propionate (22)

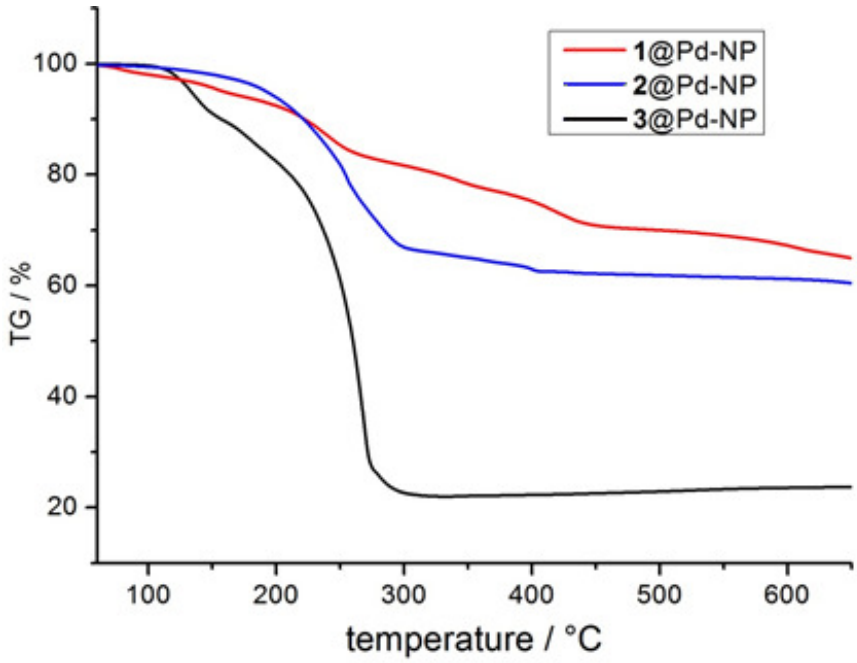




11 DLS measurements



12 TGA measurements



13 TEM images

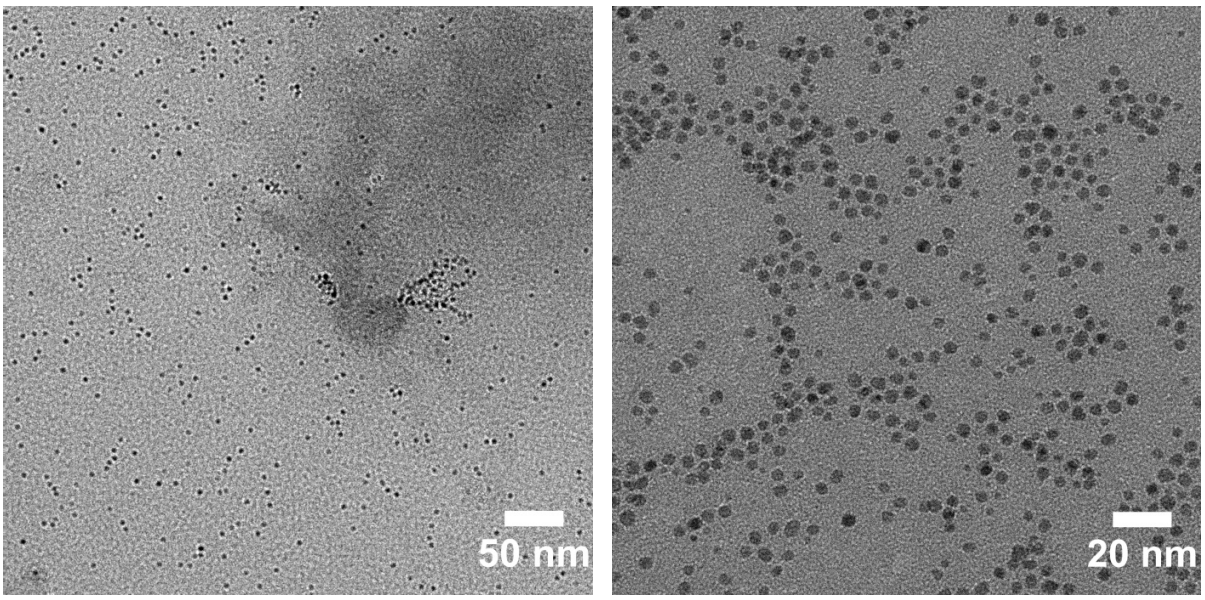


Figure 2. **3**@Pd-NPs (left) and **4**@Pd-NPs (reight).

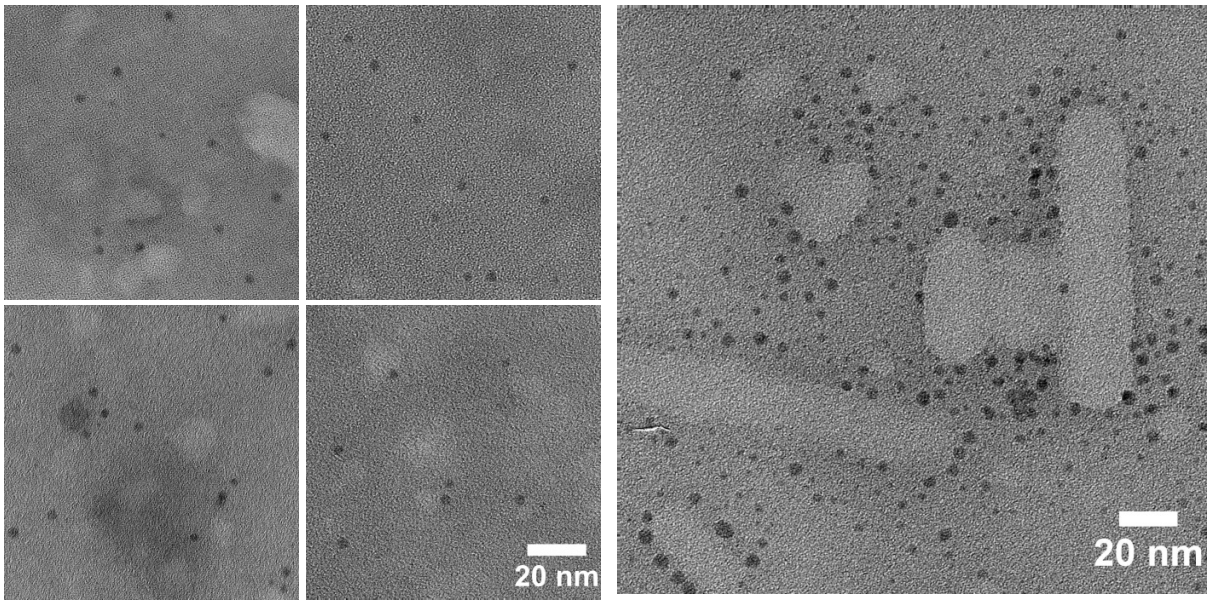


Figure 3. **1**@Pd-NPs (left) and **2**@Pd-NPs (reight).

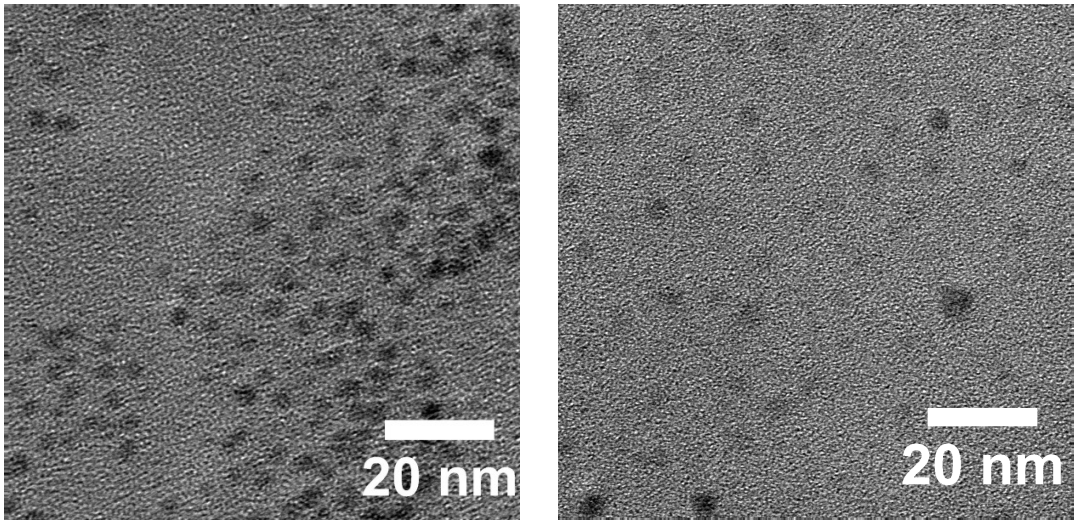


Figure 3. **2**@Pd-NPs for (left) and after catalysis (reight).

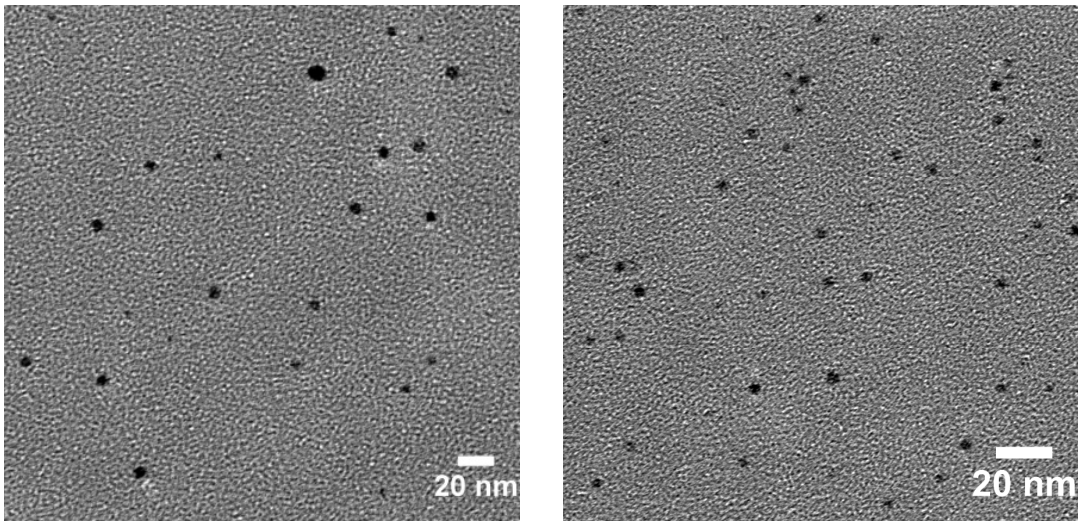
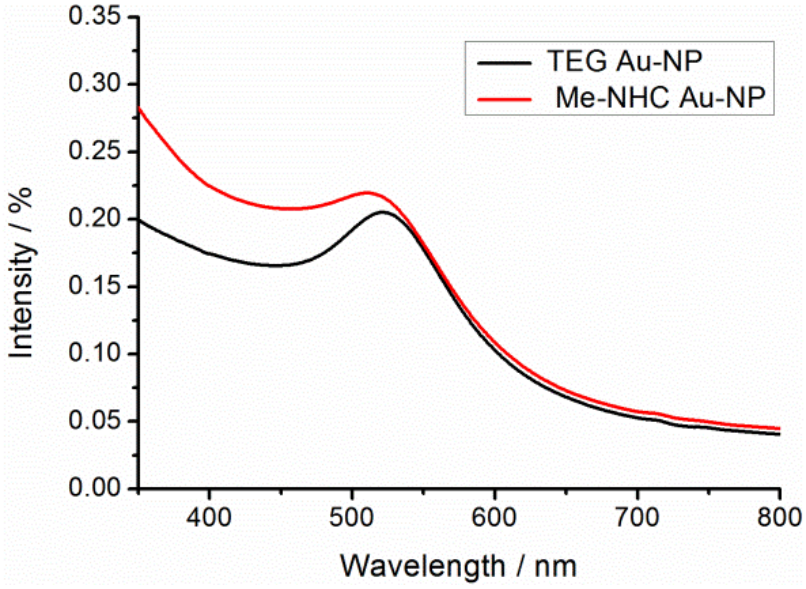


Figure 4. **3**@Au-NPs (left) and **1**@Au-NPs (right).

14 UV/Vis measurements of Au-NPs



15 References

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