**Electronic Supplementary Information to**

# INSIGHTS INTO THE CHEMISTRY OF BISMUTH NANOPARTICLES

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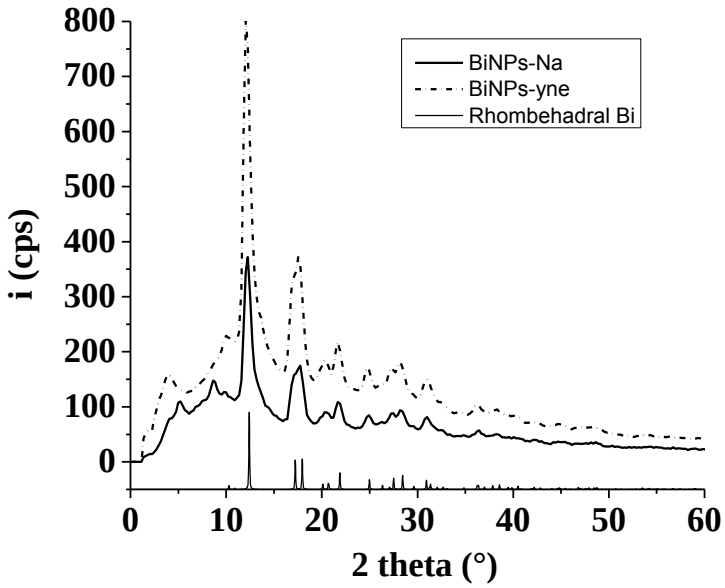
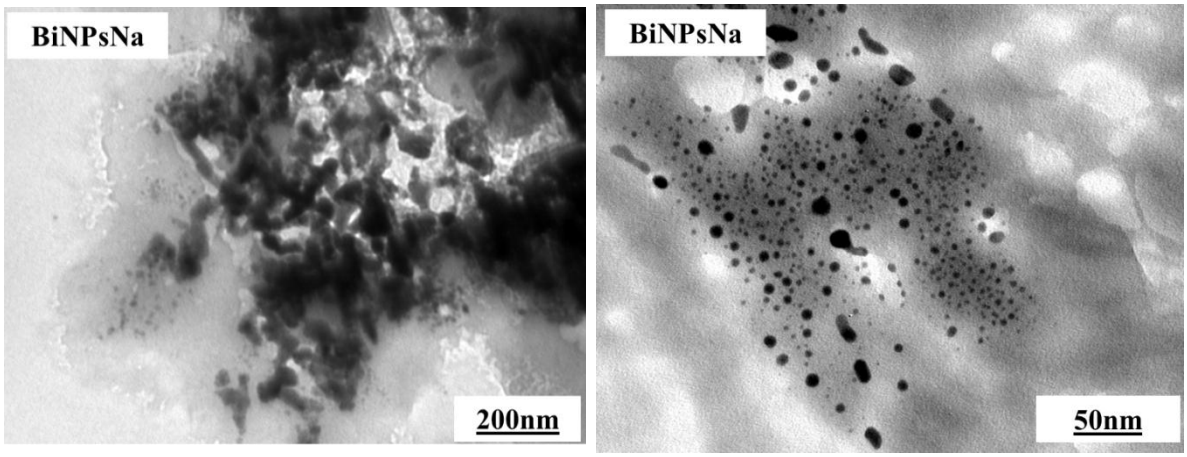
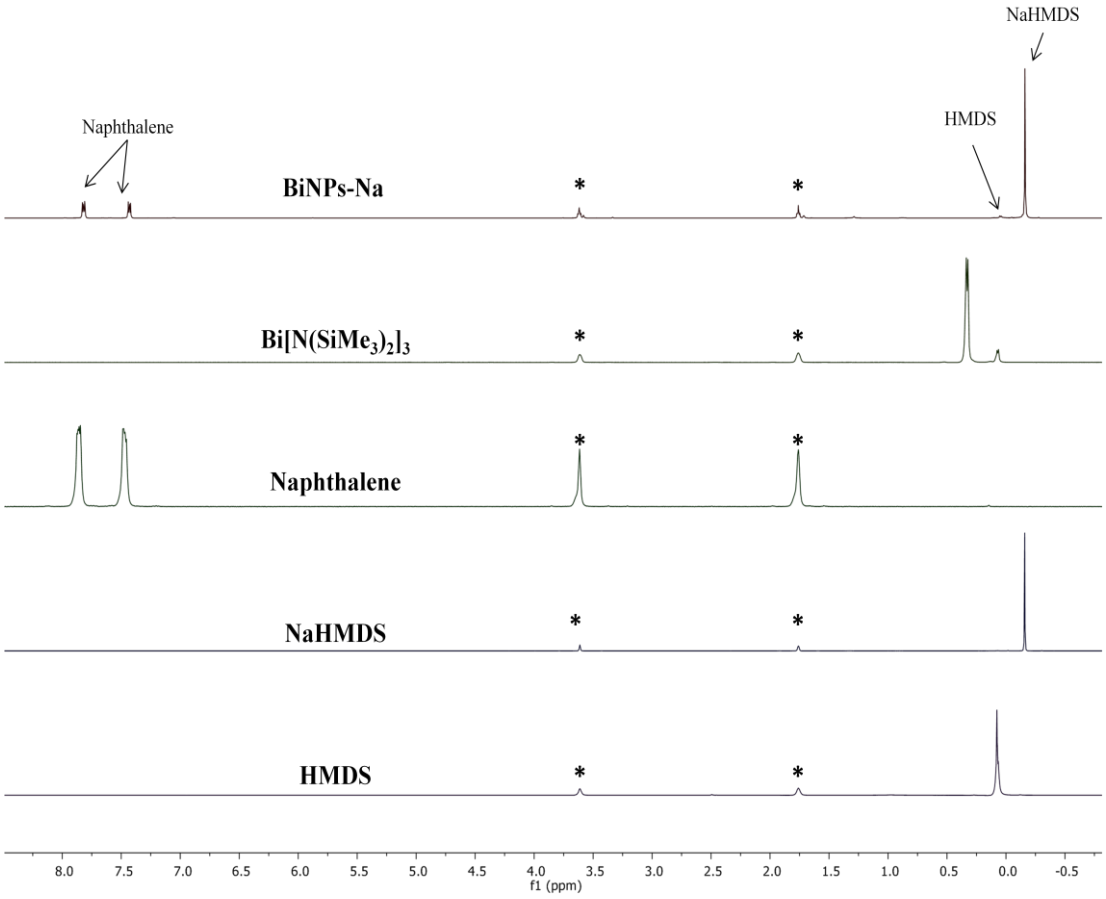
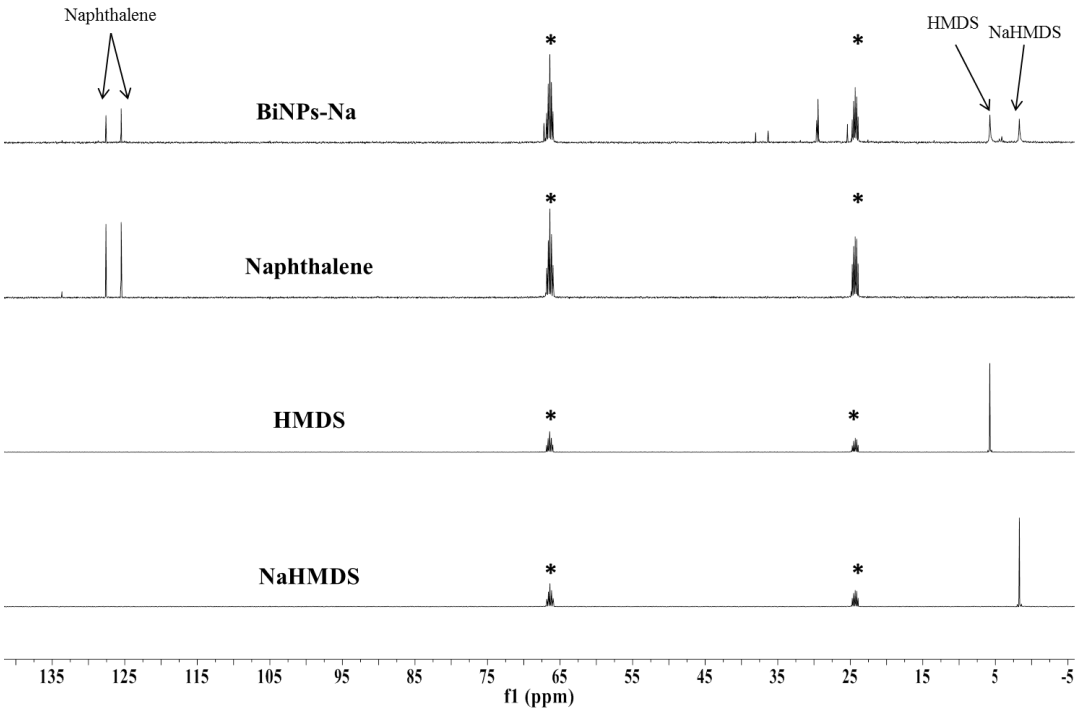



**S1:** Experimental WAXS data collected from the black powders obtained by evaporation of crude solutions together with a simulation from the crystalline structure (ICSD 64703) From top to bottom: BiNPs-Na, BiNPs-yne, rhombohedral Bi. NB: The crystallite size couldn't be determined with precision.

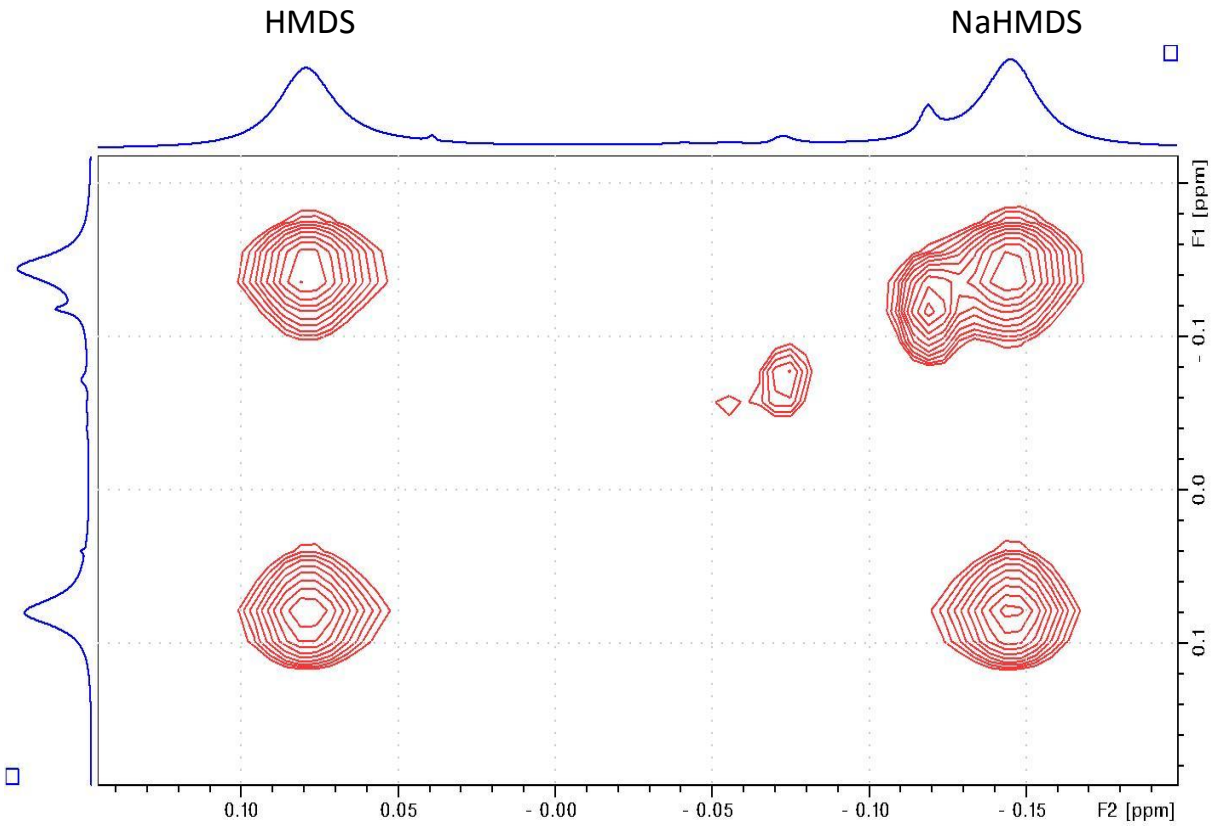



**S2 :** TEM image of the BiNPs-Na spontaneously precipitating from the crude solution (left) and redispersed after evaporation to dryness of the crude solution and naphtalene sublimation (right)

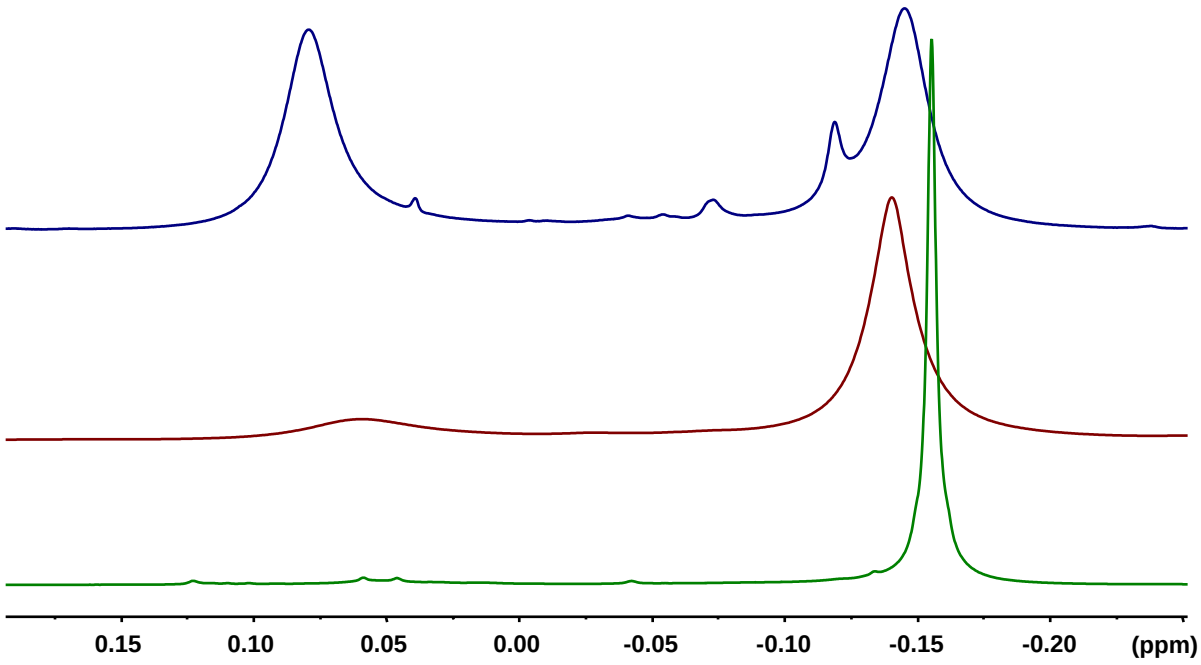

NaHMDS
HMDS
Naphthalene
BiNPs-Na
Bi[N(SiMe3)2]3
Naphthalene
NaHMDS
HMDS
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


Naphthalene
HMDS
NaHMDS
BiNPs-Na
Naphthalene
HMDS
NaHMDS
135 125 115 105 95 85 75 65 55 45 35 25 15 5 -5
f1 (ppm)

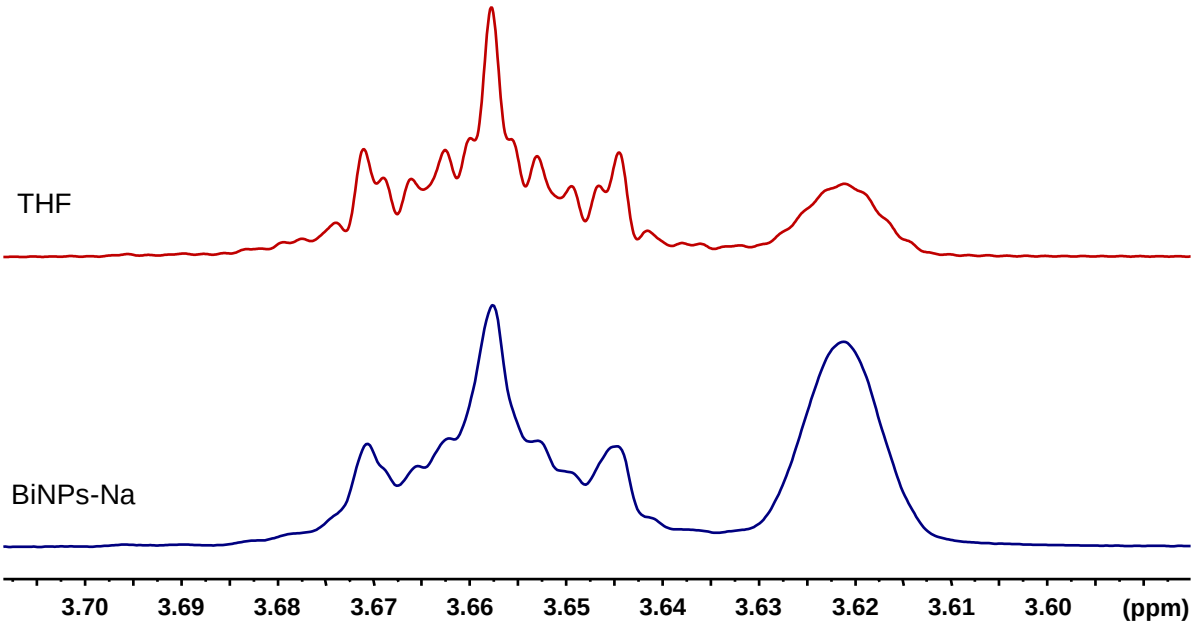
**S3:** $^{1}$H (top) and $^{13}$C{$^{1}$H} (bottom) NMR spectra of BiNPs-Na and comparison to control $^{1}$H NMR spectra of NaHMDS, HMDS and naphtalene ($d^{8}$-THF, *). (signals in the 30-40ppm range, top spectrum : unidentified impurities)



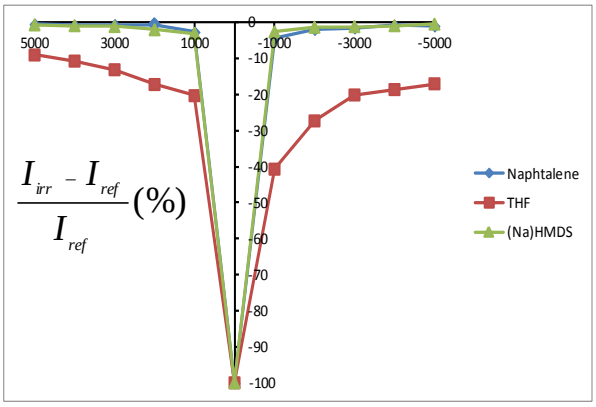

**S4:** $^{1}$H ROESY NMR spectrum (mixing time 100ms) of BiNPs-Na in THF-$d_8$ at 296K.

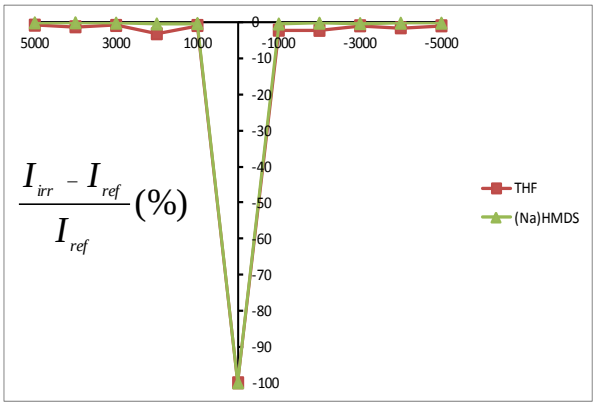


**S5:** $^{1}$H NMR spectra of BiNPs-Na sample in THF-$d_8$ with different ratios of HMDS/NaHMDS molecules. (green line: NaHMDS, red line: + 0.2eq. HMDS, blue line: + 0.8eq. HMDS)

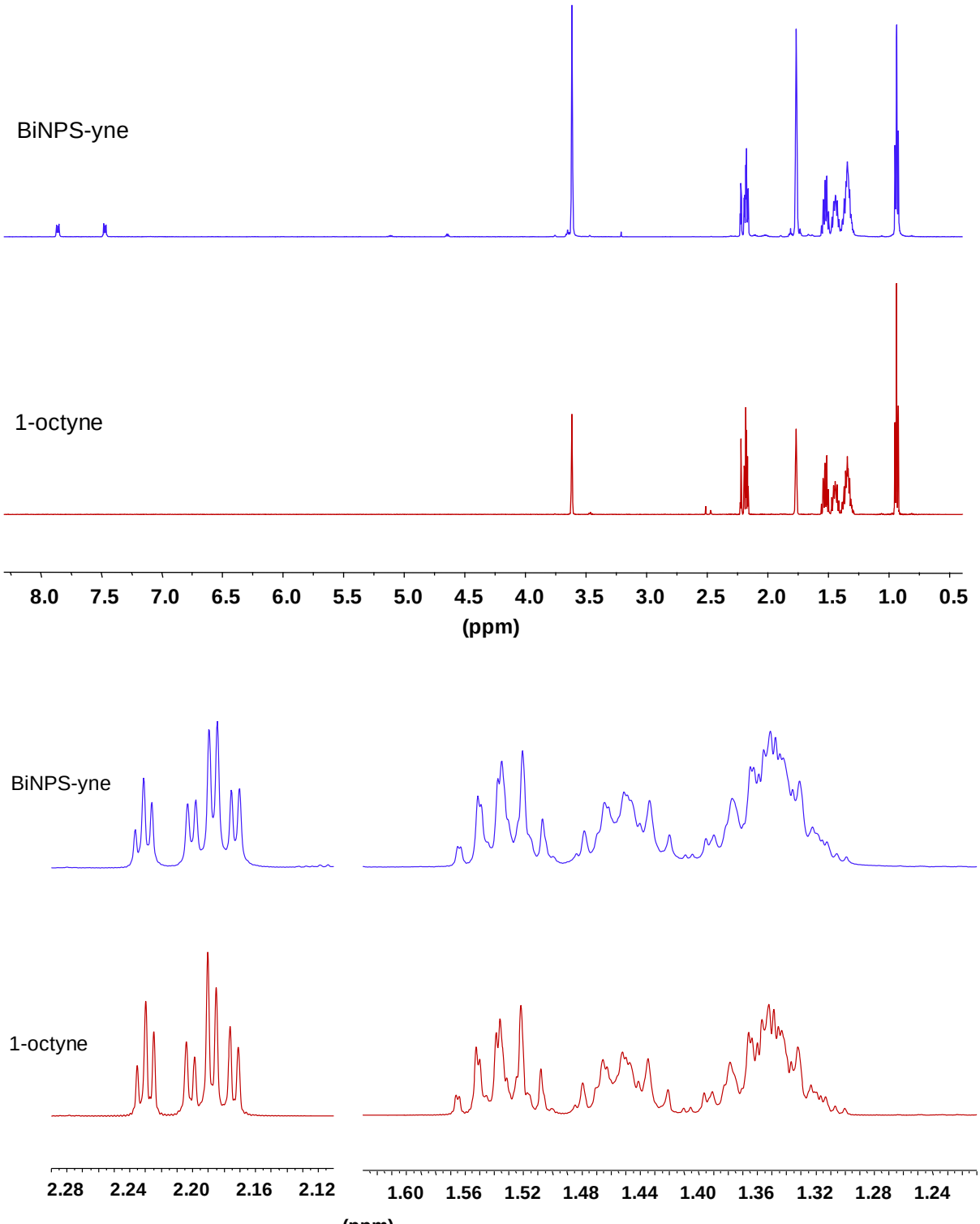



**S6:** Enlargement of the most unshielded THF resonance in the $^{1}$H NMR spectra of the BiNPs-Na sample or of a THF solution (in THF-$d_8$).




**S7:** (left) STD NMR results for BiNPs-Na in THF-$d_8$ obtained by shifting selective irradiation from on-resonance to ± 5000 Hz offsets in increments of 1000 Hz. In each experiment, the intensities of naphthalene, (Na)HMDS and THF resonances were measured ($I_{irr}$) and compared to the ones of an off-resonance reference irradiation at δ=20ppm ($I_{ref}$). (Right) reference STD experiment performed on a (Na)HMDS in THF-$d_8$ solution with exactly the same parameters as for the BiNPs-Na sample.




**S8 :** Top: Full $^{1}$H NMR spectra of 1-octyne and BiNPs-yne in THF (after purification, only limited traces of residual naphtalene can be observed in the 7-8ppm region). Bottom: Enlargement of octyne $^{1}$H resonances.