# Electronic Supplementary Information

# Triphenylbismuth(V) di[(iso)nicotinates] - transmetallation agents or divergent organometalloligands? First organobismuth(V)-based silver(I) coordination polymers

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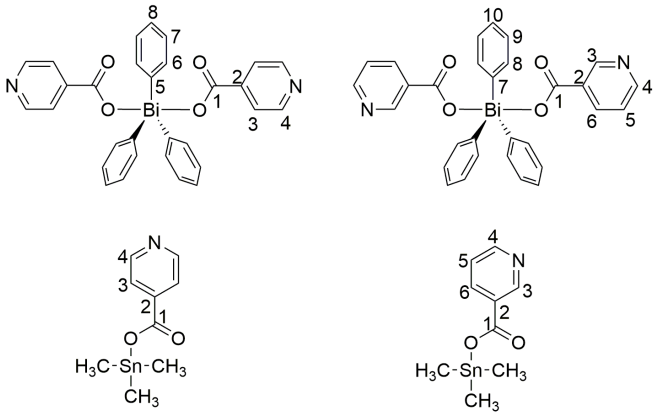
## Content




**Scheme S1.** Numbering schemes for the assignment of resonances in NMR spectra

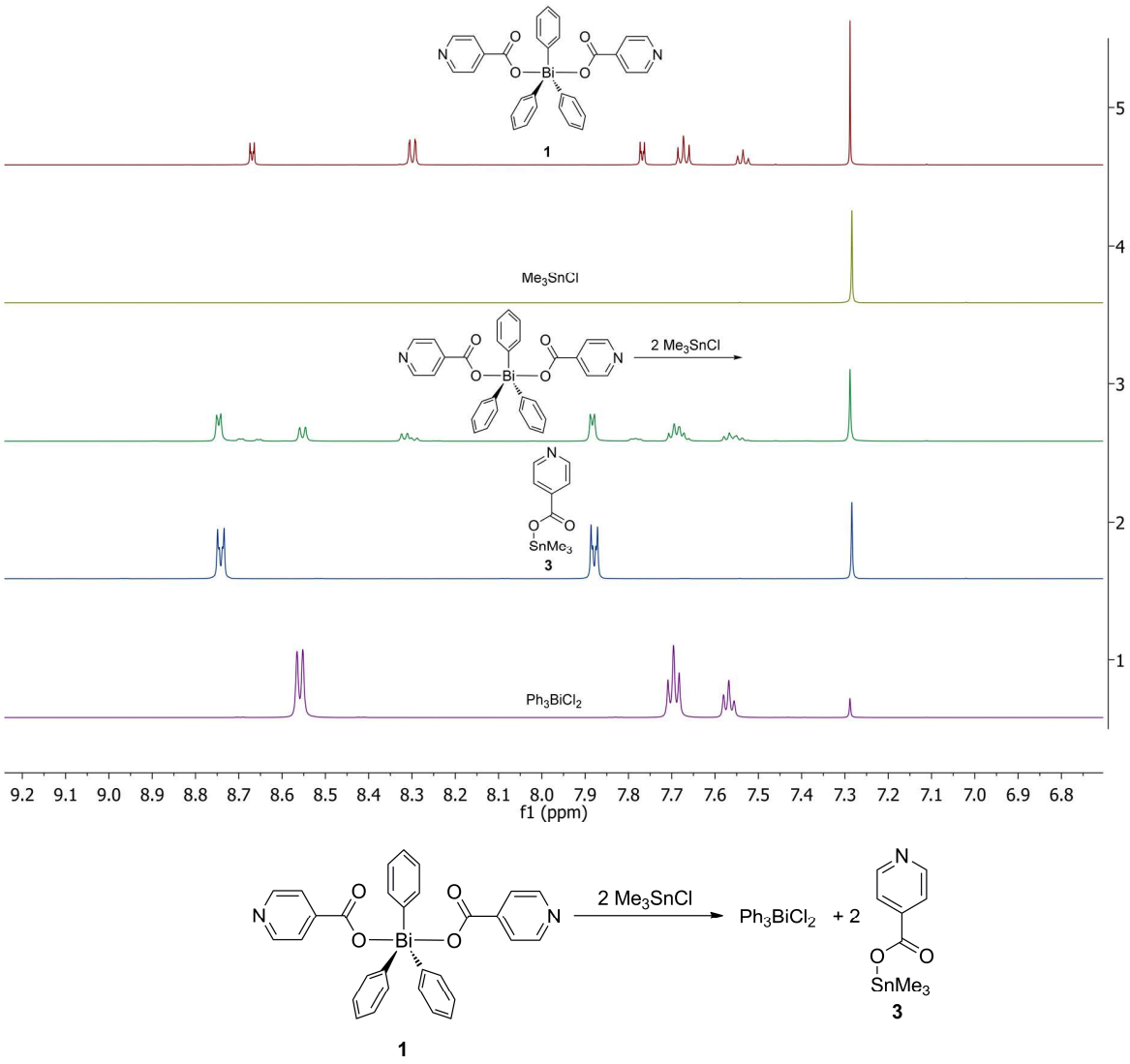



**Figure S1.** Aromatic region of superimposed $^{1}$H NMR spectra ($CDCl_3$, 20 °C) of pure $Ph_3Bi[O(O)CC_5H_4N\text{-}4]_2$ (**1**) (spectrum 5), pure $Me_3SnCl$ (spectrum 4), the crude product isolated from the reaction between these two organometallic species (spectrum 3), pure $Me_3Sn[O(O)CC_5H_4N\text{-}4]$ (**3**) (spectrum 2), and pure $Ph_3BiCl_2$ (spectrum 1), illustrating the transmetallation reaction taking place according to the depicted scheme.

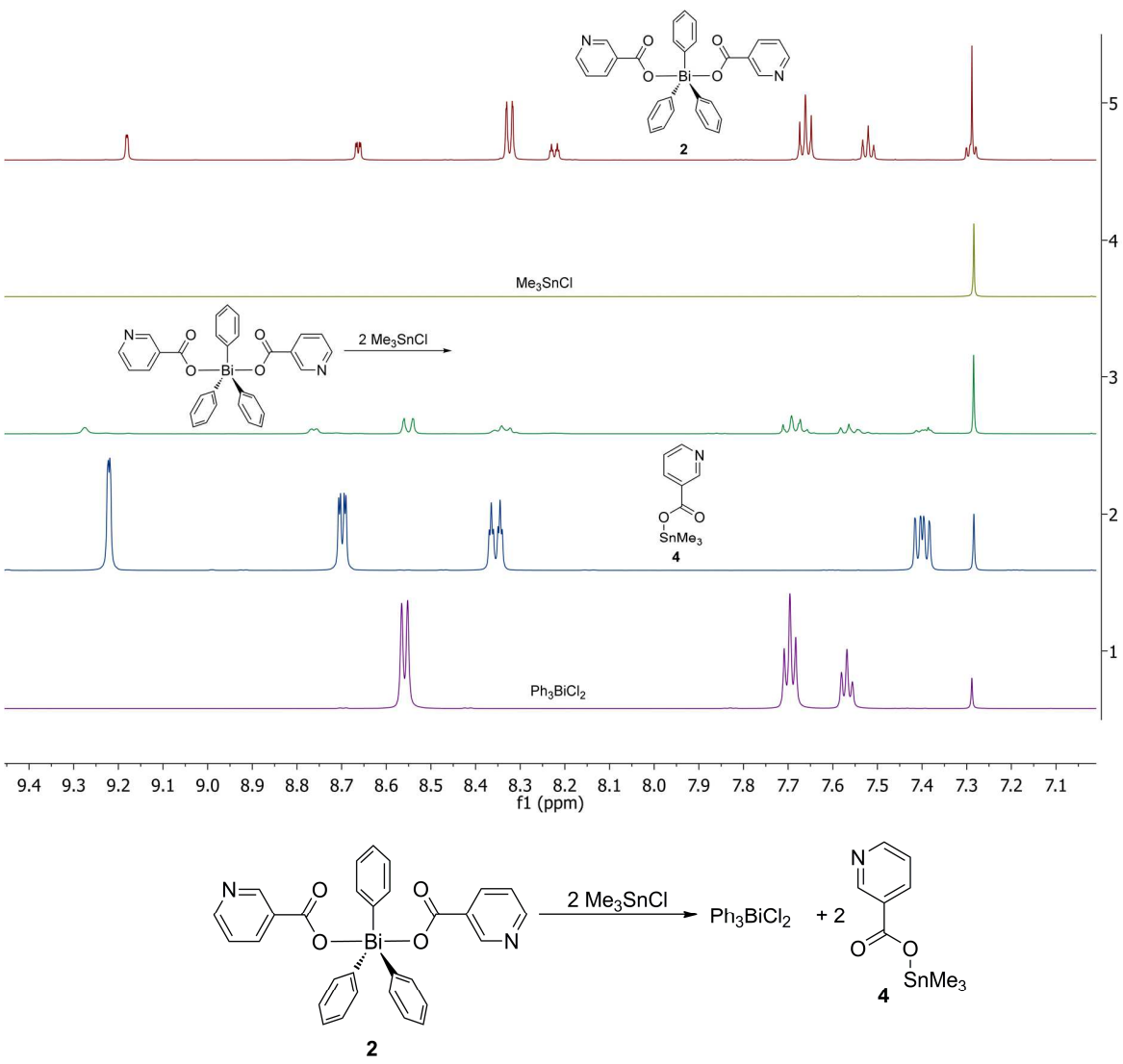



**Figure S2.** Aromatic region of superimposed $^{1}$H NMR spectra ($CDCl_3$, 20 °C) of pure $Ph_3Bi[O(O)CC_5H_4N\text{-}3]_2$ (**2**) (spectrum 5), pure $Me_3SnCl$ (spectrum 4), the crude product isolated from the reaction between these two organometallic species (spectrum 3), pure $Me_3Sn[O(O)CC_5H_4N\text{-}3]$ (**4**) (spectrum 2), and pure $Ph_3BiCl_2$ (spectrum 1), illustrating the transmetallation reaction taking place according to the depicted scheme.

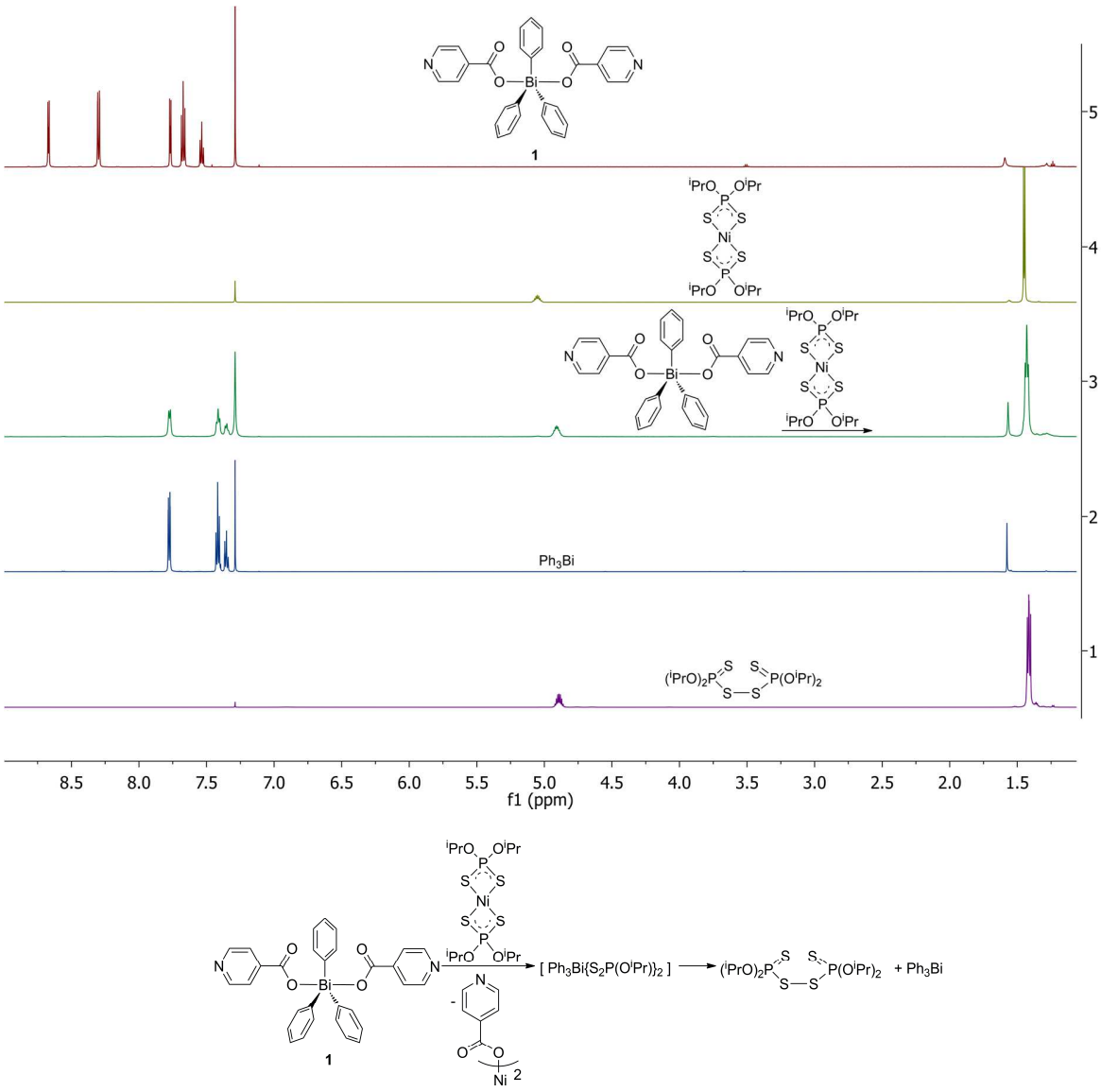
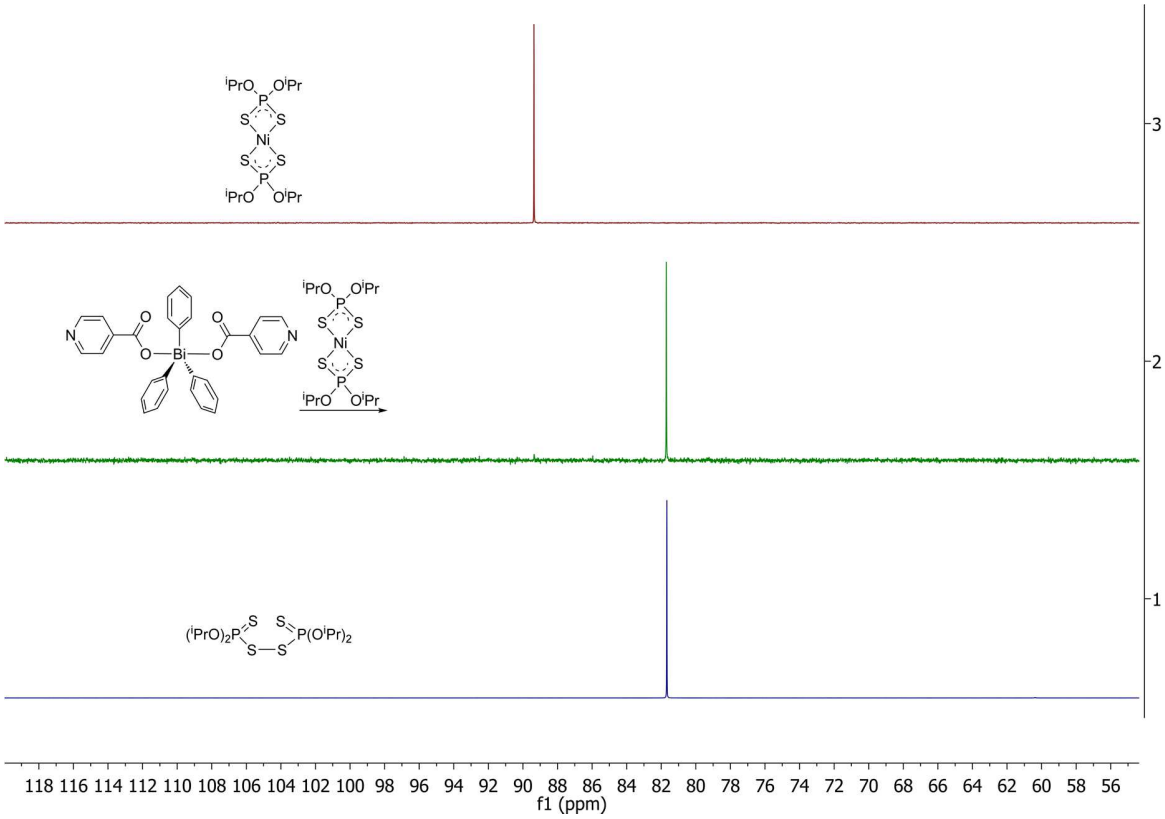



**Figure S3.** Superimposed $^{1}$H NMR spectra ($CDCl_3$, 20 °C) of pure $Ph_3Bi[O(O)CC_5H_4N\text{-}4]_2$ (**1**) (spectrum 5), pure $Ni[S_2P(O^iPr)_2]_2$ (spectrum 4), the crude product isolated from the reaction between these two compounds (spectrum 3), pure $Ph_3Bi$ (spectrum 2), and pure $[(^iPrO)_2P(S)S]_2$ (spectrum 2), illustrating the transmetallation reaction taking place according to the depicted scheme.



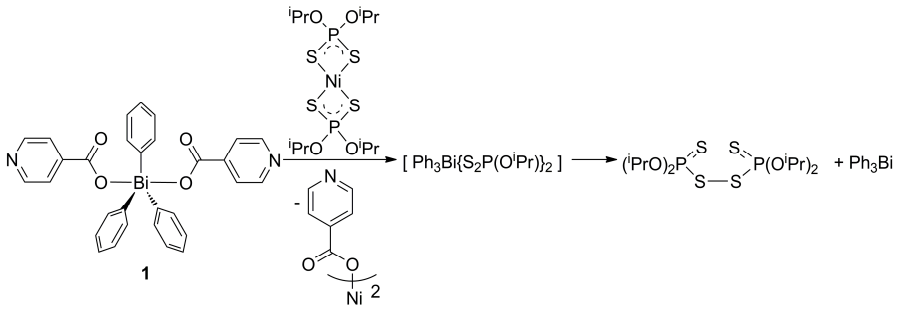




**Figure S4.** Superimposed $^{31}P$ NMR spectra ($CDCl_3$, 20 °C) of pure $Ni[S_2P(O^iPr)_2]_2$ (spectrum 3), the crude product isolated from the reaction between **1** and $Ni[S_2P(O^iPr)_2]_2$ (spectrum 2), and pure $[(^iPrO)_2P(S)S]_2$ (spectrum 1), illustrating the transmetallation reaction taking place according to the depicted scheme.

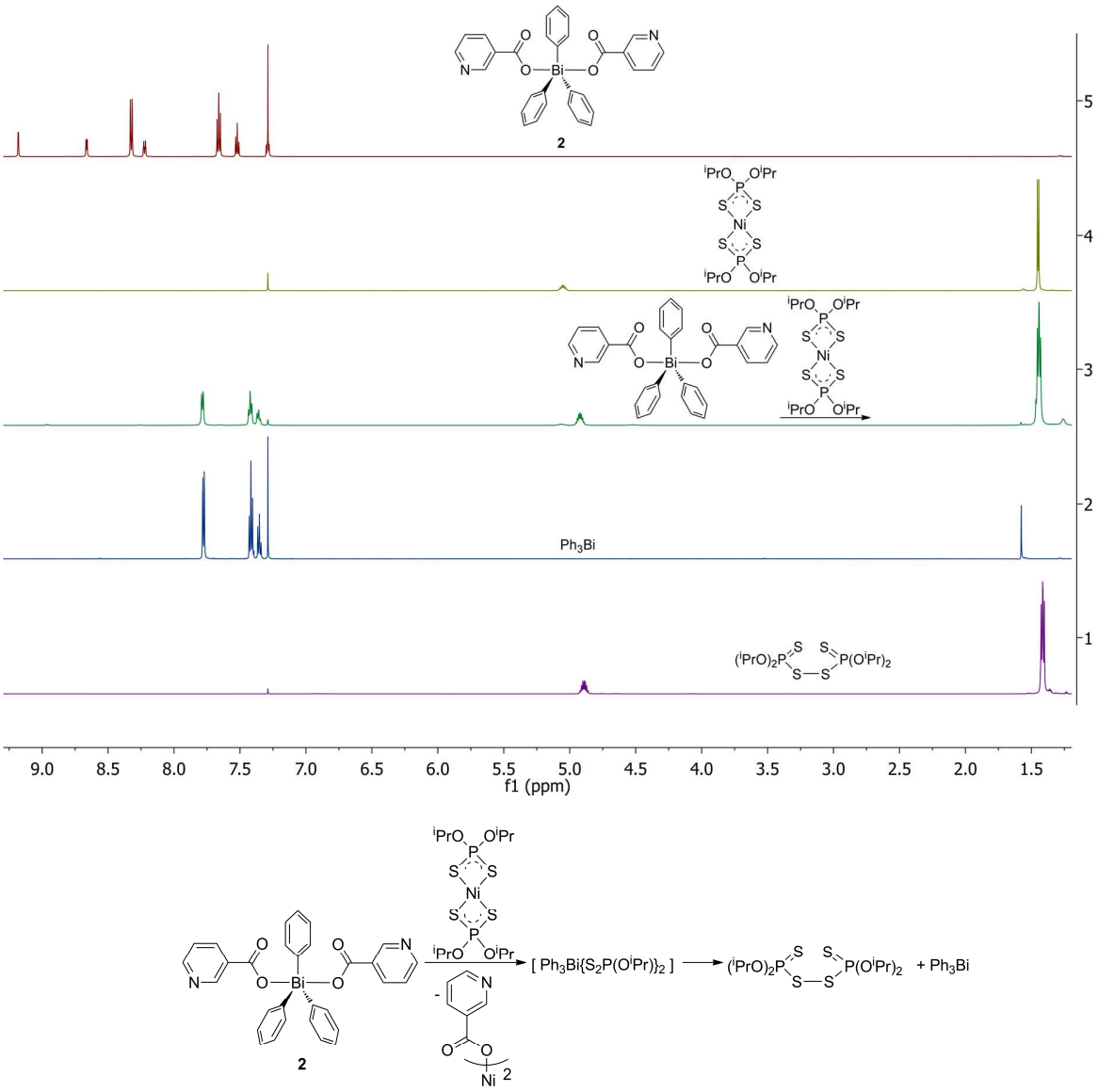






**Figure S5.** Superimposed $^{1}$H NMR spectra ($CDCl_3$, 20 °C) of pure $Ph_3Bi[O(O)CC_5H_4N\text{-}3]_2$ (**2**) (spectrum 5), pure $Ni[S_2P(O^iPr)_2]_2$ (spectrum 4), the crude product isolated from the reaction between these two compounds (spectrum 3), pure $Ph_3Bi$ (spectrum 2), and pure $[(^iPrO)_2P(S)S]_2$ (spectrum 2), illustrating the transmetallation reaction taking place according to the depicted scheme.

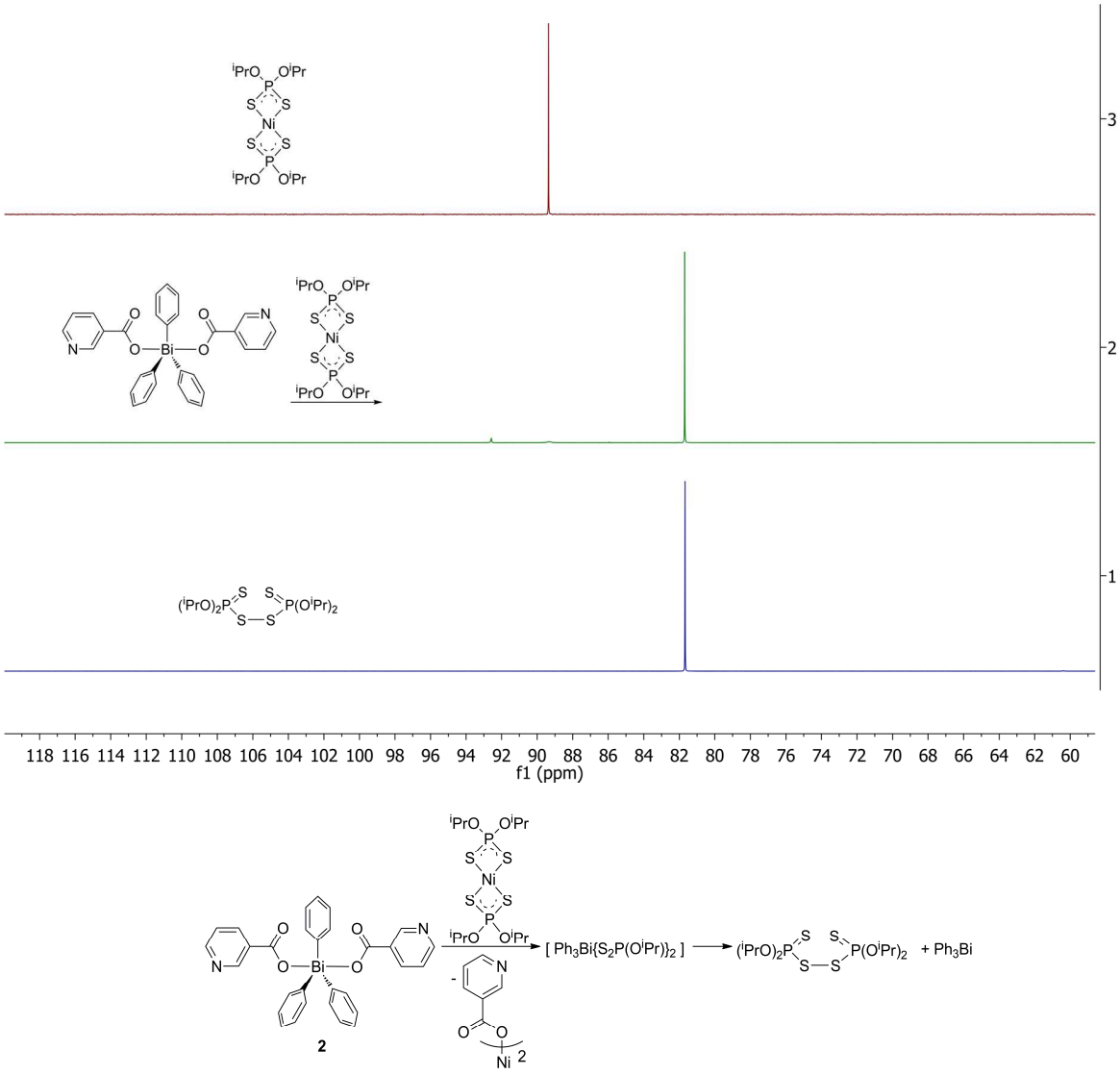



**Figure S6.** Superimposed $^{31}P$ NMR spectra ($CDCl_3$, 20 °C) of pure $Ni[S_2P(O^iPr)_2]_2$ (spectrum 3), the crude product isolated from the reaction between **2** and $Ni[S_2P(O^iPr)_2]_2$ (spectrum 2), and pure $[(^iPrO)_2P(S)S]_2$ (spectrum 1), illustrating the transmetallation reaction taking place according to the depicted scheme.

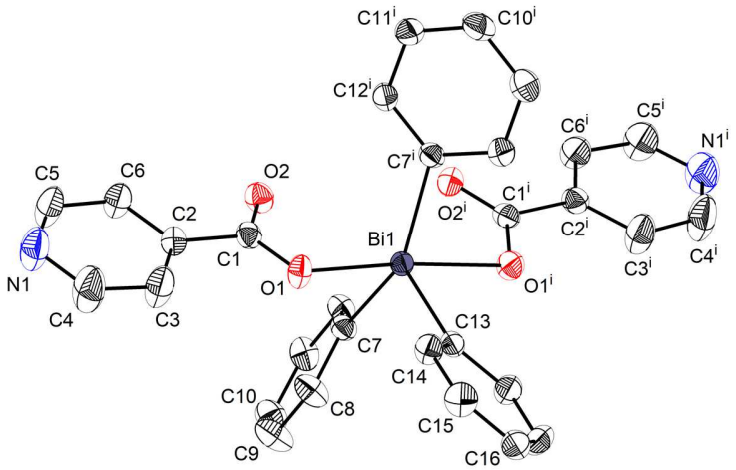



**Figure S7.** Molecular structure of **1**. Thermal ellipsoids are drawn at the 30% probability. Hydrogen atoms are omitted for clarity [symmetry code: (i) *1.5–x*, *y*, *0.5–z*].

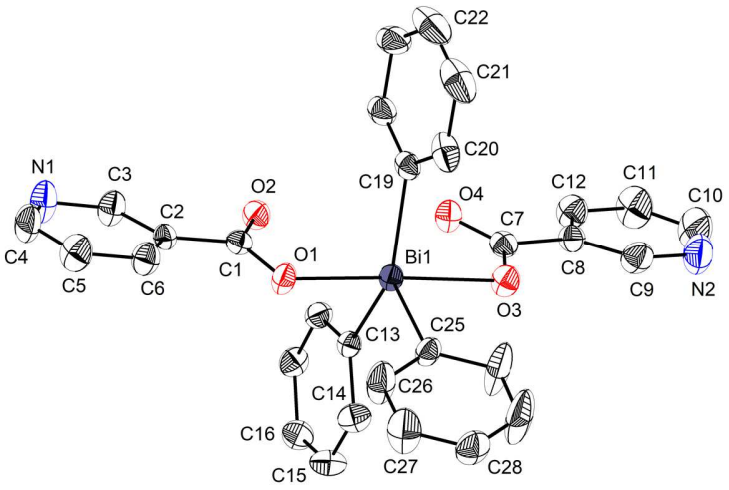



**Figure S8.** Molecular structure of **2**. Thermal ellipsoids are drawn at the 30% probability. Hydrogen atoms are omitted for clarity.

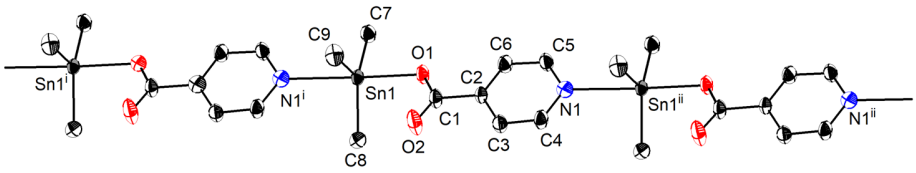



**Figure S9.** Coordination polymer in the crystal of **3**. Thermal ellipsoids are drawn at the 30% probability. Hydrogen atoms are omitted for clarity [symmetry codes: (i) *–1+x*, *1+y*, *z*; (ii) *1+x*, *–1+y*, *z*].

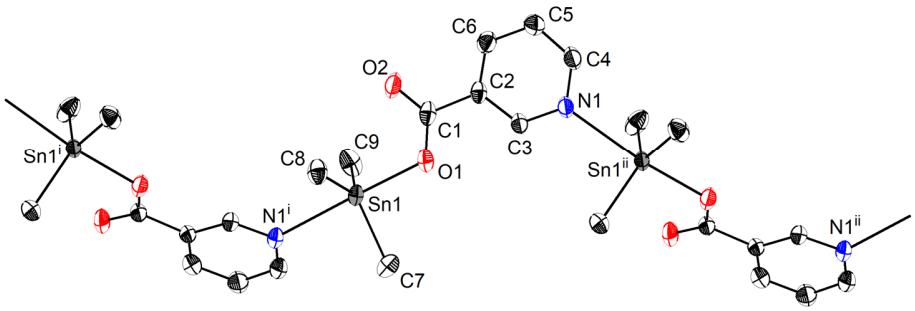



**Figure S10.** Coordination polymer in the crystal of **4**. Thermal ellipsoids are drawn at the 30% probability. Hydrogen atoms are omitted for clarity [symmetry codes: (i) *x*, *–y*, *0.5+z*; (ii) *x*, *–y*, *–0.5+z*].

**Table S1**. X-ray crystal data and structure refinement for compounds **1**–**4**.

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Empirical formula | $C_{30}H_{23}BiN_2O_4$ | $C_{30}H_{23}BiN_2O_4$ | $C_9H_{13}NO_2Sn$ | $C_9H_{13}NO_2Sn$ |
| Formula weight | 684.48 | 684.48 | 285.89 | 285.89 |
| Temperature (K) | 297(2) | 294(2) | 297(2) | 294(2) |
| Crystal system | Monoclinic | Triclinic | Triclinic | Monoclinic |
| Space group | *P*2/*n* | *P*-1 | *P*-1 | *C*2/*c* |
| *a* (Å) | 12.9965(12) | 9.0030(12) | 6.6686(9) | 24.937(10) |
| *b* (Å) | 9.7492(9) | 11.5252(15) | 8.9159(12) | 7.100(3) |
| *c* (Å) | 13.4933(13) | 12.9642(17) | 10.1287(13) | 15.414(6) |
| *α* (º) | 90.00 | 95.401(2) | 79.674(2) | 90.00 |
| *β* (º) | 105.707(2) | 93.536(2) | 72.196(2) | 124.647(5) |
| *γ* (º) | 90.00 | 101.254(2) | 75.429(2) | 90.00 |
| Volume (Å$^3$) | 1645.8(3) | 1309.0(3) | 551.50(13) | 2245.1(16) |
| *Z* | 2 | 2 | 2 | 8 |
| $D_{calc}$ (g cm$^{-3}$) | 1.381 | 1.737 | 1.722 | 1.692 |
| Absorption coefficient (mm$^{-1}$) | 5.387 | 6.773 | 2.287 | 2.247 |
| *F*(000) | 664 | 664 | 280 | 1120 |
| Crystal size (mm) | 0.23x0.25x0.29 | 0.33x0.39x0.40 | 0.28x0.33x0.39 | 0.23x0.28x0.37 |
| *ϑ* range for data collection (º) | 1.93 to 25.01 | 1.58 to 24.99 | 2.12 to 24.99 | 1.98 to 26.37 |
| Reflections collected | 15123 | 12304 | 5081 | 11208 |
| Independent reflections | 2906 | 4564 | 1885 | 2282 |
| | [$R_{int}$ = 0.0565] | [$R_{int}$ = 0.0516] | [$R_{int}$ = 0.0210] | [$R_{int}$ = 0.0324] |
| Absorption correction | Multi-Scan[1] | Multi-Scan[1] | Multi-Scan[1] | Multi-Scan[1] |
| Data / restraints / parameters | 2906 / 0 / 169 | 4564 / 24 / 334 | 1885 / 0 / 118 | 2282 / 0 / 119 |
| Goodness-of-fit on $F^2$ | 1.071 | 0.973 | 1.087 | 1.111 |
| Final *R* indices [$I$>2σ($I$)] | $R_1$ = 0.0270 | $R_1$ = 0.0318 | $R_1$ = 0.0225 | $R_1$ = 0.0266 |
| | $wR_2$ = 0.0641 | $wR_2$ = 0.0572 | $wR_2$ = 0.0569 | $wR_2$ = 0.0619 |
| *R* indices (all data) | $R_1$ = 0.0297 | $R_1$ = 0.0408 | $R_1$ = 0.0243 | $R_1$ = 0.0298 |
| | $wR_2$ = 0.0650 | $wR_2$ = 0.0597 | $wR_2$ = 0.0579 | $wR_2$ = 0.0634 |
| Largest difference peak and hole (e Å$^{-3}$) | 0.35 and −1.44 | 0.92 and −0.95 | 0.41 and −0.38 | 0.32 and −0.45 |
| CCDC No. | 1585633 | 1585634 | 1585635 | 1585636 |

[1] G. M. Sheldrick, *SADABS, Program for area detector adsorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.

**Table S2**. X-ray crystal data and structure refinement for coordination polymers **5**–**9**.

| | **5** | **6**·$CH_2Cl_2$ | **7**·2THF | **8**·$CH_2Cl_2$ | **9**·$CH_2Cl_2$ |
|---|---|---|---|---|---|
| Empirical formula | $C_{31}H_{23}AgBiF_3N_2O_7S$ | $C_{64}H_{50}Ag_2Bi_2Cl_4F_6N_4O_{14}S_2$ | $C_{38}H_{39}AgBiF_6N_2O_6S_2Sb$ | $C_{31}H_{25}AgBiCl_2F_6N_2O_4Sb$ | $C_{31}H_{25}AgBiCl_2N_3O_7$ |
| Formula weight | 941.42 | 2052.70 | 1172.31 | 1113.03 | 939.29 |
| Temperature (K) | 160.0(1) | 130.1(2) | 170(2) | 199.9(1) | 293(2) |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/n$ | $P2_1/n$ | $P$-1 | $P2_1/c$ |
| $a$ (Å) | 13.6678(5) | 12.3800(4) | 16.1795(6) | 10.5410(6) | 11.0075(15) |
| $b$ (Å) | 15.1649(10) | 19.8689(8) | 8.7028(4) | 10.8892(5) | 16.9543(16) |
| $c$ (Å) | 15.0978(6) | 28.0926(9) | 29.2014(12) | 16.7211(7) | 17.883(2) |
| $\alpha$ (º) | 90.00 | 90.00 | 90.00 | 83.744(4) | 90.00 |
| $\beta$ (º) | 102.116(4) | 90.574(3) | 98.001(3) | 71.929(4) | 98.652(11) |
| $\gamma$ (º) | 90.00 | 90.00 | 90.00 | 76.436(4) | 90.00 |
| Volume (Å$^3$) | 3059.6(3) | 6909.8(4) | 4071.7(3) | 1772.38(15) | 3299.5(7) |
| $Z$ | 4 | 4 | 4 | 2 | 4 |
| $D_{calc}$ (g cm$^{-3}$) | 2.044 | 1.973 | 1.912 | 2.086 | 1.891 |
| Absorption coefficient (mm$^{-1}$) | 6.522 | 5.934 | 5.519 | 6.476 | 6.131 |
| $F$(000) | 1808 | 3952 | 2256 | 1052 | 1808 |
| Crystal size (mm) | 0.15x0.20x0.40 | 0.05x0.10x0.15 | 0.10x0.17x0.22 | 0.03x0.10x0.35 | 0.08x0.12x0.17 |
| $\vartheta$ range for data collection (º) | 1.93 to 25.03 | 1.79 to 25.03 | 2.31 to 25.00 | 1.92 to 25.03 | 2.22 to 25.00 |
| Reflections collected | 14322 | 29329 | 23210 | 12588 | 34784 |
| Independent reflections | 5402 | 12047 | 7144 | 6253 | 5798 |
| | [$R_{int}$ = 0.0431] | [$R_{int}$ = 0.0529] | [$R_{int}$ = 0.1492] | [$R_{int}$ = 0.0520] | [$R_{int}$ = 0.2068] |
| Absorption correction | Multi-Scan[1] | Multi-Scan[1] | Multi-Scan[1] | Multi-Scan[1] | Multi-Scan[1] |
| Data / restraints / parameters | 5402 / 0 / 415 | 12047 / 66 / 858 | 7144 / 1 / 496 | 6253 / 30 / 436 | 5798 / 0 / 406 |
| Goodness-of-fit on $F^2$ | 1.034 | 1.097 | 0.962 | 1.035 | 0.765 |
| Final $R$ indices [$I$>2σ($I$)] | $R_1$ = 0.0367 | $R_1$ = 0.0665 | $R_1$ = 0.0524 | $R_1$ = 0.0483 | $R_1$ = 0.0452 |
| | $wR_2$ = 0.0732 | $wR_2$ = 0.1365 | $wR_2$ = 0.0956 | $wR_2$ = 0.0948 | $wR_2$ = 0.0908 |
| $R$ indices (all data) | $R_1$ = 0.0512 | $R_1$ = 0.1017 | $R_1$ = 0.1067 | $R_1$ = 0.0607 | $R_1$ = 0.0992 |
| | $wR_2$ = 0.0794 | $wR_2$ = 0.1531 | $wR_2$ = 0.1130 | $wR_2$ = 0.1013 | $wR_2$ = 0.1034 |
| Largest difference peak and hole (e Å$^{-3}$) | 1.52 and −0.67 | 3.28 and −1.65 | 1.29 and −1.30 | 1.79 and −1.44 | 1.20 and −2.83 |
| CCDC No. | 1585637 | 1585638 | 1585639 | 1585640 | 1585641 |

[1] G. M. Sheldrick, *SADABS, Program for area detector adsorption correction*, Institute for Inorganic Chemistry, University of Göttingen, Germany, 1996.

**Table S3**. Summary of the experimental results.

| Reagents | Product | Ligand coordination pattern / tecton conformation | Ag(I) coordination geometry | Network dimensionality and topology | Supramolecular interactions |
|---|---|---|---|---|---|
| Tecton **1** + $Me_3SnCl$ (molar ratio 1:2) | Transmetallation - $Ph_3BiCl_2$ and $Me_3Sn[O(O)CC_5H_4N\text{-}4]$ (**3**) | $\mu_2$-bridging (O1, N1) carboxylate in **3** / - | - | 1-D linear chain in **3** | - |
| Tecton **2** + $Me_3SnCl$ (molar ratio 1:2) | Transmetallation - $Ph_3BiCl_2$ and $Me_3Sn[O(O)CC_5H_4N\text{-}3]$ (**4**) | $\mu_2$-bridging (O1, N1) carboxylate in **4** / - | - | 1-D *zig-zag* chain in **4** | - |
| Tecton **1** + $Ni[S_2P(O^iPr)_2]_2$ (molar ratio 1:1) | Transmetallation - $Ph_3Bi$, $[(^iPrO)_2P(S)S]_2$ and $Ni[O(O)CC_5H_4N\text{-}4]_2$ | - / - | - | - | - |
| Tecton **2** + $Ni[S_2P(O^iPr)_2]_2$ (molar ratio 1:1) | Transmetallation - $Ph_3Bi$, $[(^iPrO)_2P(S)S]_2$ and $Ni[O(O)CC_5H_4N\text{-}3]_2$ | - / - | - | - | - |
| Tecton **1** + AgOTf (molar ratio 1:1) | $[Ag\{Ph_3Bi[O(O)CC_5H_4N\text{-}4]_2\}(OTf)]$ (**5**) | $\mu_2$-bridging (N1, N2) of tecton **1** / - | *see-saw* [$\tau_{4\ Ag(1)}$ 0.63] | 1-D double chain built from near-linear chains | Ag···π contacts (1-D → 2-D) |
| Tecton **2** + AgOTf (molar ratio 1:1) | $[Ag\{Ph_3Bi[O(O)CC_5H_4N\text{-}3]_2\}(OTf)]\cdot CH_2Cl_2$ (**6**·$CH_2Cl_2$) | $\mu_2$-bridging (N1, N2) of tecton **2** / *cis* | *see-saw* [$\tau_{4\ Ag(1A)}$ 0.48, $\tau_{4\ Ag(1AX)}$ 0.24, and $\tau_{4\ Ag(1B)}$ 0.17, $\tau_{4Ag(1BX)}$ 0.40, respectively] | 2-D grid-like layer constructed from corrugated chains | intra-layer offset π···π contacts |
| Tecton **1** + $AgSbF_6$ (molar ratio 1:1) | $[Ag\{Ph_3Bi[O(O)CC_5H_4N\text{-}4]_2\}](SbF_6)\cdot 2THF$ (**7**·2THF) | $\mu_3$-bridging (N1, O2, N2) of tecton **1** / - | distorted trigonal-bipyramid [$\tau_{5\ Ag(1)}$ 90%] | 2-D grid-like network built from linear chains | Ag···O contacts |
| Tecton **2** + $AgSbF_6$ (molar ratio 1:1) | $[Ag\{Ph_3Bi[O(O)CC_5H_4N\text{-}3]_2\}](SbF_6)\cdot CH_2Cl_2$ (**8**·$CH_2Cl_2$) | $\mu_2$-bridging (N1, N2) of tecton **2** / *trans* | Square-planar | 1-D zig-zag chain | offset π···π stacking (1-D → 2-D) |
| Tecton **2** + $AgNO_3$ (molar ratio 1:1) | $[Ag\{Ph_3Bi[O(O)CC_5H_4N\text{-}3]_2\}(NO_3)]\cdot CH_2Cl_2$ (**9**·$CH_2Cl_2$) | $\mu_2$-bridging (N1, N2) of tecton **2** / *trans* | see-saw [$\tau_{4\ Ag(1)}$ 0.67] | 1-D wavy chain | Ag···Ag and π···π contacts (1-D → 3-D) |