Supporting Information

Facile Mechanochemical Anion Substitution in Cyclopalladated Azobenzenes

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EXPERIMENTAL DETAILS

General Methods. All chemicals were used as supplied and were not additionally purified or dried. The $^1$H NMR spectra were recorded at 25 °C in CDCl$_3$ and/or in DMSO-$d_6$ with Brucker’s spectrometers AV-600, AV-400 and AV-300. FTIR spectra were recorded with Perkin-Elmer’s spectrometer Spectrum Two. PXRD measurements were performed on a PANalytical Aeris X-ray diffractometer with Ni-filtered CuK$_\alpha$ radiation. Elemental analyses were done on a Perkin-Elmer Series II 2400 CHNS/O analyzer.

Ball-milling reactions

Ball-milling experiments were performed at room temperature of 22±2 °C in the 14 mL poly(methylmetacrylate) (PMMA) jars using one 12 mm (4.3 g) ZrO$_2$ milling ball. An IST500 mixer mill with a built-in fan operating at 30 Hz frequency was used for the synthesis. All reactions were carried out under similar conditions starting with the total weight of reaction mixture of about 220 mg.

Initial compounds

Palladium precursors [(L1)Pd(MeCN)$_2$][BF$_4$] (1), [(L2)Pd(MeCN)$_2$][BF$_4$] (2), [(L2)Pd(µ-OAc)]$_2$ (4), [Pd$_2$(H$_2$O)(µ-Cl)(µ-L1)(Cl)]$_2$ (9), [Pd$_2$(H$_2$O)(µ-Cl)(µ-L2)(Cl)]$_2$ (10) and [Pd(µ-OAc)$_2$(µ-L2)Pd]$_2$ (12), where L1=azobenzene and L2=4-chloro-4′-(N,N-dimethylamino)azobenzene, were prepared by using the ball-milling procedures recently developed by our group. Only the precursor [(L1)Pd(µ-OAc)]$_2$ (3) was prepared by the aging of solid [Pd(OAc)$_2$] and L1 in DMF vapour. Precursors 1 and 9 were prepared for the first time via mechanochemical C–H bond activation.

Mechanosynthesis of mono- and dipalladated complexes via anion substitution

All reactions were performed with one equivalent of mono- and dipalladated L1 or L2 (acetate, chloride or tetrafluoroborate complexes) and 10 equivalents of alkali salts MX (M=Li or Na) of acetate (OAc), acetylacetonate (acac) and chloride (Cl) per one palladium centre using neat grinding (NG). The resulting mixtures were washed with water and dried under vacuum. Reaction times are given in Table 1 of the main manuscript.

Synthesis of acetylacetonate complexes via anion substitution

{[(L1)Pd(acac)]} 7. a) 67.00 mg (0.15 mmol) of [(L1)Pd(MeCN)$_2$][BF$_4$] (1) and 155.63 mg (1.47 mmol) of Li(acac). Isolated yield 85%. Found: C 53.18, H 4.34, N 7.28; Calcd. for C$_{17}$H$_{15}$N$_2$O$_2$Pd: C 52.80, H 4.17, N 7.24. b) 55.00 mg (0.08 mmol) of [(L1)Pd(µ-OAc)]$_2$ (3)
and 168.25 mg (1.58 mmol) of Li(acac). Isolated yield 85%. Found: C 52.48, H 4.28, N 7.39.
e) 52.00 mg (0.08 mmol) of [(L1)Pd(µ-Cl)]2 (5) and 170.68 mg (1.61 mmol) of Li(acac).
Isolated yield 92%. Found: C 52.51, H 4.05, N 7.17.

{(L2)Pd(acac)} 8. a) 75.00 mg (0.14 mmol) of [(L2)Pd(MeCN)]2[BF4] (2) and 148.93 mg (1.40 mmol) of Li(acac). Isolated yield 94%. Found: C 49.51, H 4.64, N 8.95; Calcd. for C10H20ClN2O2Pd: C 49.15, H 4.34, N 9.05. b) 63.00 mg (0.07 mmol) of [(L2)Pd(µ-OAc)]2 (4) and 157.50 mg (1.48 mmol) of Li(acac). Isolated yield 88%. Found: C 48.91, H 4.38, N 8.91.
e) 61.00 mg (0.07 mmol) of [(L2)Pd(µ-Cl)]2 (6) and 161.48 mg (1.52 mmol) of Li(acac).
Isolated yield 89%. Found: C 49.45, H 4.02, N 9.38. Isolated yield 89%. Found: C 49.45, H 4.02, N 9.38.

{(acac)Pd(µ-L1)Pd(acac)} 13. a) 43.00 mg (0.04 mmol) of [Pd(µ-OAc)2(µ-L1)Pd]2 (11) and 178.43 mg (1.68 mmol) of Li(acac). Isolated yield 85%. Found: C 44.35, H 3.61, N 4.93. Calcd. for C22H22N2O4Pd2: C 44.69, H 3.75, N 4.74. b) 33.00 mg (0.04 mmol) of [Pd2(H2O)(µ-Cl)(µ-L1)(Cl)]2 (9) and 186.38 mg (1.76 mmol) of Li(acac). Isolated yield 86%. Found: C 44.37, H 3.53, N 4.88.

{(acac)Pd(µ-L2)Pd(acac)} 14. a) 48.00 mg (0.04 mmol) of [Pd(µ-OAc)2(µ-L2)Pd]2 (12) and 172.95 (1.63 mmol) mg of Li(acac). Isolated yield 92%. Found: C 43.25, H 3.52, N 6.11. Calcd. for C22H22N2O4Pd2: C 43.10, H 3.92, N 6.28. b) 46.00 mg (0.04 mmol) of [Pd2(H2O)(µ-Cl)(µ-L2)(Cl)]2 (10) and 174.38 mg (1.64 mmol) of Li(acac). Isolated yield 86%. Found: C 43.16, H 4.07, N 6.12.

Synthesis of acetate complexes via anion substitution

[(L1)Pd(µ-OAc)]2 (3). a) 80.00 mg (0.17 mmol) of [(L1)Pd(MeCN)]2[BF4] (1) and 143.74 mg (1.75 mmol) of NaOAc. Isolated yield 87%. Found: C 48.25, H 3.68, N 7.85. Calcd. for C28H24NaO8Pd: C 48.50, H 3.49, N 8.08. b) 62.00 mg (0.09 mmol) of [(L1)Pd(µ-Cl)]2 (5) and 157.41 mg (1.92 mmol) of NaOAc. Isolated yield 88%. Found: C 48.82, H 3.56, N 7.77. e) 70.00 mg (0.18 mmol) of [(L1)Pd(acac)] (7) and 148.47 mg (1.81 mmol) of NaOAc. Isolated yield 91%. Found: C 48.15, H 3.58, N 7.74.

[(L2)Pd(µ-OAc)]2 (4). a) 87.00 mg (0.16 mmol) of [(L2)Pd(MeCN)]2[BF4] (2) and 133.63 mg (1.63 mmol) NaOAc. Isolated yield 93%. Found: C 44.97, H 3.44, N 9.66. Calcd. for C32H32Cl2N6O8Pd2: C 45.30, H 3.80, N 9.91. b) 73.00 mg (0.09 mmol) of [(L2)Pd(µ-Cl)]2 (6) and 149.48 mg (1.82 mmol) of NaOAc. Isolated yield 87%. Found: C 45.67, H 3.64, N 9.97. e) 80.00 mg (0.17 mmol) of [(L2)Pd(acac)]( 8) and 141.35 mg (1.72 mmol) of NaOAc. Isolated yield 90%. Found: C 44.98, H 3.69, N 9.56.

[Pd(µ-OAc)(µ-L1)Pd]2 (11). a) 41.00 mg (0.05 mmol) of [Pd2(H2O)(µ-Cl)(µ-L1)(Cl)]2 (9) and 179.11 mg (2.18 mmol) of NaOAc. Isolated yield 88%. Found: C 37.33, H 2.58, N 5.28. Calcd. for C32H26Na8O18Pd4: C 37.60, H 2.76, N 5.48. b) 60.00 mg (0.10 mmol) of {acac}Pd(µ-L1)Pd(acac) (13) and 166.48 (2.02 mmol) of NaOAc. Isolated yield 90%. Found: C 37.31, H 2.38, N 5.56.

[Pd(µ-OAc)(µ-L2-2H)Pd]2 (12). a) 56.00 mg (0.05 mmol) of [Pd2(H2O)(µ-Cl)(µ-L2)(Cl)]2 (10) and 164.21 mg (2.00 mmol) of NaOAc. Isolated yield 88%. Found: C 36.98, H 2.92, N 7.36. Calcd. for C36H36Cl2N6O8Pd4: C 36.73, H 3.08, N 7.14. b) 65.00 mg (0.10 mmol) of
{(acac)Pd(µ-L2)Pd(acac)}(14) and 159.45 (1.94 mmol) of NaOAc. Isolated yield 92%. Found: C 37.02, H 3.28, N 7.37.

**Synthesis of chloride complexes via anion substitution**

[(L1)Pd(µ-Cl)]2 (5). a) 115.00 mg (0.25 mmol) of [(L1)Pd(MeCN)2][BF4] (1) and 106.78 mg (2.52 mmol) of LiCl. Isolated yield 87%. Found: C 44.88, H 2.89, N 8.33. Calcd. for C24H18Cl2N2Pd2: C 44.61, H 2.81, N 8.67. b) 100.00 mg (0.14 mmol) of [(L1)Pd(µ-OAc)]2 (3) and 122.27 mg (2.88 mmol) of LiCl. Isolated yield 91%. Found: C 44.88, H 2.59, N 8.82. c) 105.00 mg (0.27 mmol) of {(L1)Pd(acac)} (7) and 115.09 mg (2.71 mmol) of LiCl. Isolated yield 88%. Found: C 44.28, H 2.49, N 8.78.

[(L2)Pd(µ-Cl)]2 (6). a) 123.00 mg (0.23 mmol) of [(L2)Pd(MeCN)2][BF4] (2) and 97.63 mg (2.30 mmol) of LiCl. Isolated yield 90%. Found: C 42.09, H 2.96, N 10.19. Calcd. for C28H26Cl4N2Pd2: C 41.97, H 3.27, N 10.49. b) 110.00 mg (0.13 mmol) of [(L2)Pd(µ-OAc)]2 (4) and 109.92 mg (2.59 mmol) of LiCl. Isolated yield 86%. Found: C 41.63, H 3.09, N 10.62. c) 115.00 mg (0.25 mmol) of {(L2)Pd(acac)} (8) and 105.00 mg (2.48 mmol) of LiCl. Isolated yield 91%. Found: C 41.58, H 3.49, N 10.73.

[Pd2(H2O)(µ-Cl)(µ-L1)(Cl)]2 (9). a) 84.00 mg (0.08 mmol) of [Pd(µ-OAc)2(µ-L1)Pd]2 (11) and 139.33 mg (3.29 mmol) of LiCl. Isolated yield 92%. Found: C 38.03, H 2.33, N 7.14; Calcd. for C24H20Cl2N2O2Pd2: C 38.38, H 2.68, N 7.46. b) 90.00 mg (0.15 mmol) of {(acac)Pd(µ-L1)Pd(acac)} (13) and 129.04 (3.04 mmol) of LiCl. Isolated yield 93%. Found: C 38.49, H 2.74, N 7.23.

[Pd2(H2O)(µ-Cl)(µ-L2)(Cl)]2 (10). a) 90.00 mg (0.07 mmol) of [Pd(µ-OAc)2(µ-L2)Pd]2 (12) and 129.62 mg (3.06 mmol) of LiCl. Isolated yield 86%. Found: C 30.42, H 2.33, N 7.62. Calcd. for C28H28Cl6N2O2Pd2: C 30.05, H 2.52, N 7.51. b) 98.00 mg (0.14 mmol) of {(acac)Pd(µ-L2)Pd(acac)}(14) and 124.23 mg (2.93 mmol) of LiCl. Isolated yield 94%. Found: C 30.42, H 2.33, N 7.42.
# NMR SPECTROSCOPY

![Diagram of NMR numbering of protons in azobenzenes and their complexes]

**Scheme S1.** NMR numbering of protons in azobenzenes and their complexes.

<table>
<thead>
<tr>
<th>Proton</th>
<th>L1</th>
<th>L2</th>
<th>7</th>
<th>7′</th>
<th>8</th>
<th>8′</th>
<th>13</th>
<th>14</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me (acac)</td>
<td>-</td>
<td>-</td>
<td>2.02 s, 3H</td>
<td>2.01 s, 3H</td>
<td>1.98 br s, 3H</td>
<td>2.14 s, 6H</td>
<td>2.09 s, 9H</td>
<td>2.13 s, 3H</td>
</tr>
<tr>
<td>CH (acac)</td>
<td>-</td>
<td>-</td>
<td>2.13 s, 3H</td>
<td>2.03 s, 3H</td>
<td>2.06, br s, 3H</td>
<td>2.16 s, 6H</td>
<td>5.43 s, 1H</td>
<td>5.44 s, 1H</td>
</tr>
<tr>
<td>NMe₂</td>
<td>-</td>
<td>-</td>
<td>5.43 s, 1H</td>
<td>5.40 s, 1H</td>
<td>5.50 s, 1H</td>
<td>5.49 s, 2H</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H-2</td>
<td>7.92 d, 1H</td>
<td>7.87 d, 1H</td>
<td>2.00 br s, 3H</td>
<td>2.08, br s, 3H</td>
<td>5.55, s, 1H</td>
<td>2.01 s, 3H</td>
<td>2.03 s, 3H</td>
<td>2.06, br s, 3H</td>
</tr>
<tr>
<td>H-3</td>
<td>7.37-7 64, m</td>
<td>6.76 d, 1H</td>
<td>7.43 d, 1H</td>
<td>7.45-7 52 m</td>
<td>7.55-7 62 m</td>
<td>7.92 d, 1H</td>
<td>7.92 d, 1H</td>
<td>7.92 d, 1H</td>
</tr>
<tr>
<td>H-4</td>
<td>7.37-7 64, m</td>
<td>7.29 t, 1H</td>
<td>7.32-7 39 m</td>
<td>-</td>
<td>-</td>
<td>7.67 dd, 1H</td>
<td>7.67 dd, 1H</td>
<td>7.67 dd, 1H</td>
</tr>
<tr>
<td>H-5</td>
<td>7.37-7 64, m</td>
<td>7.26 t, 1H</td>
<td>7.32-7 39 m</td>
<td>-</td>
<td>-</td>
<td>7.20-7 32, overlapped with CDCl₃</td>
<td>7.11 dd, 1H</td>
<td>7.11 dd, 1H</td>
</tr>
<tr>
<td>H-6</td>
<td>7.92, d, 1H</td>
<td>7.87 d, 1H</td>
<td>7.94 d, 1H</td>
<td>8.00 d, 1H</td>
<td>7.68 d, 1H</td>
<td>7.66 d, 1H</td>
<td>7.36 d, 1H</td>
<td>7.36 d, 1H</td>
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<tr>
<td>H-8</td>
<td>7.92, d, 1H</td>
<td>7.79 d, 1H</td>
<td>8.00-8.07 m</td>
<td>7.94-7 98 m</td>
<td>7.36 d, 1H</td>
<td>7.67 dd, 1H</td>
<td>7.67 dd, 1H</td>
<td>7.67 dd, 1H</td>
</tr>
<tr>
<td>H-9</td>
<td>7.37-7 64, m</td>
<td>7.43 d, 1H</td>
<td>7.55-7 62 m</td>
<td>7.92 d, 1H</td>
<td>7.92 d, 1H</td>
<td>7.67 dd, 1H</td>
<td>7.67 dd, 1H</td>
<td>7.67 dd, 1H</td>
</tr>
<tr>
<td>H-10</td>
<td>7.37-7 64, m</td>
<td>7.45-7 52 m</td>
<td>7.55-7 62 m</td>
<td>-</td>
<td>-</td>
<td>7.20-7 32, overlapped with CDCl₃</td>
<td>7.20-7 32, overlapped with CDCl₃</td>
<td>7.20-7 32, overlapped with CDCl₃</td>
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<tr>
<td>H-11</td>
<td>7.37-7 64, m</td>
<td>7.43 d, 1H</td>
<td>7.55-7 62 m</td>
<td>7.92 d, 1H</td>
<td>7.92 d, 1H</td>
<td>7.67 dd, 1H</td>
<td>7.67 dd, 1H</td>
<td>7.67 dd, 1H</td>
</tr>
<tr>
<td>H-12</td>
<td>7.92, d, 1H</td>
<td>7.79 d, 1H</td>
<td>8.00-8.07 m</td>
<td>7.94-7 98 m</td>
<td>7.36 d, 1H</td>
<td>7.67 dd, 1H</td>
<td>7.67 dd, 1H</td>
<td>7.67 dd, 1H</td>
</tr>
</tbody>
</table>

*a s – singlet, d – doublet, t – triplet, m – multiplet, br broad. †Spectra of 7 and 8 recorded in DMSO-d₆*
Table S2

$^1$H NMR data (δ / ppm, J / Hz, CDCl$_3$) for L1, L2 and their acetate complexes$^a$

<table>
<thead>
<tr>
<th>Proton</th>
<th>L1</th>
<th>L2</th>
<th>L2$^a$</th>
<th>3$^c$</th>
<th>4$^d$</th>
<th>11$^c$</th>
<th>12$^{c,d}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>OAc</td>
<td>-</td>
<td>-</td>
<td>2.08 s, 3H</td>
<td>2.1 s, 3H</td>
<td>2.19 s, 3H</td>
<td>2.20 s, 3H</td>
<td>2.07 s, 3H</td>
</tr>
<tr>
<td>NMe$_2$</td>
<td>-</td>
<td>3.10 s, 6H</td>
<td>3.08 s, 6H</td>
<td>-</td>
<td>2.97 s, 6H</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H-2</td>
<td>7.92, d, 1H</td>
<td>7.87 d, 1H</td>
<td>7.80 d, 2H</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>H-3</td>
<td>7.37-7.64, m</td>
<td>6.76 d, 1H</td>
<td>6.84 d, 2H</td>
<td>6.49 dd, 1H</td>
<td>5.59 ds, 1H</td>
<td>6.68-6.88 m</td>
<td>5.87 ds, 1H</td>
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<tr>
<td>H-4</td>
<td>7.37-7.64, m</td>
<td>-</td>
<td>-</td>
<td>6.80 dt, 1H</td>
<td>-</td>
<td>6.68-6.88 m</td>
<td>-</td>
</tr>
<tr>
<td>H-5</td>
<td>7.37-7.64, m</td>
<td>6.76 d, 1H</td>
<td>6.84 d, 2H</td>
<td>7.14 dt, 1H</td>
<td>6.31 dd, 1H</td>
<td>6.68-6.88 m</td>
<td>6.29 dd, 1H</td>
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<td>H-6</td>
<td>7.92, d, 1H</td>
<td>7.87 d, 1H</td>
<td>7.80 d, 2H</td>
<td>7.70 dd, 1H</td>
<td>7.50 d, 1H</td>
<td>8.03, d 1H</td>
<td>7.60 d, 1H</td>
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<td>H-8</td>
<td>7.92, d, 1H</td>
<td>7.79 d, 2H</td>
<td>7.78 d, 2H</td>
<td>7.34, d 1H</td>
<td>7.03 d, 1H</td>
<td>-</td>
<td>-</td>
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<tr>
<td>H-9</td>
<td>7.37-7.64, m</td>
<td>7.43 d, 1H</td>
<td>7.57 d, 2H</td>
<td>7.25 t, 1H</td>
<td>7.27 d, 1H</td>
<td>6.68-6.88 m</td>
<td>6.46 ds, 1H</td>
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<td>H-10</td>
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<td>7.37 t, 1H</td>
<td>-</td>
<td>6.68-6.88 m</td>
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<td>H-11</td>
<td>7.37-7.64, m</td>
<td>7.43 d, 1H</td>
<td>7.57 d, 2H</td>
<td>7.25 t, 1H</td>
<td>7.27 d, 1H</td>
<td>6.68-6.88 m</td>
<td>6.83 dd, 1H</td>
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<tr>
<td>H-12</td>
<td>7.92, d, 1H</td>
<td>7.79 d, 2H</td>
<td>7.78 d, 2H</td>
<td>7.34, d 1H</td>
<td>7.03 d, 1H</td>
<td>8.03, d 1H</td>
<td>7.44 d, 1H</td>
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$^a$ s – singlet, d – doublet, t – triplet, m – multiplet. $^b$ Spectra of L2 and 12 recorded in DMSO-$d_6$. $^c$ Data for anti-transoid isomer. $^d$ Data for anti-cisoid isomer.
Table S3

$^1$H NMR data (δ / ppm, J / Hz, DMSO-$d_6$) for L1, L2, and their chloride and tetrafluoroborate complexes.*

<table>
<thead>
<tr>
<th>Proton</th>
<th>L1</th>
<th>L2</th>
<th>5$^a$</th>
<th>6$^b$</th>
<th>9</th>
<th>10</th>
<th>1</th>
<th>2$^b$</th>
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<tbody>
<tr>
<td>NMe$_2$-</td>
<td>-</td>
<td>-</td>
<td>3.08 s, 6H</td>
<td>-</td>
<td>-</td>
<td>3.14 s, 6H</td>
<td>-</td>
<td>3.19 s, 1H</td>
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<tr>
<td>H-2</td>
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<td>7.80 d, 1H</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>J=6.9</td>
<td>J=9.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H-3</td>
<td>7.60 t, 1H</td>
<td>6.84 d, 1H</td>
<td>7.72 dd, 1H</td>
<td>J=7.7, 1.5</td>
<td>7.01 br s, 1H</td>
<td>8.75 br d, 1H</td>
<td>J=7.2</td>
<td>7.24 ds, 1H</td>
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<td>J=9.3</td>
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<td></td>
</tr>
<tr>
<td>H-4</td>
<td>7.58 t, 1H</td>
<td>6.84 d, 1H</td>
<td>7.21 dt, 1H</td>
<td>J=7.6, 1.6</td>
<td>6.59 br d, 1H</td>
<td>7.18-7.28 m</td>
<td>-</td>
<td>7.25-7.45 m</td>
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<td>J=7.0</td>
<td>J=9.3</td>
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<td></td>
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</tr>
<tr>
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*5$^a$ – singlet, d – doublet, t – triplet, m – multiplet, br – broad. 
$^b$Data for alpha isomer.
Figure S1. $^1$H-NMR (DMSO-$d_6$) spectra of: a) L1, b) crude product 1 prepared by IAG using NaOAc and NaBF$_4$ as additives$^1$ c) pure product 1 after washing with water.

Figure S2. $^1$H-NMR (DMSO-$d_6$) spectra of: a) L1, b) 9 prepared by ILAG using NaOAc and H$_2$O as additives$^1$ and c) pure product 9 after washing with water.

Figure S3. $^1$H-NMR (CDCl$_3$) spectra of: a) precursor 3 and b) product 7 obtained from 3 by anion substitution using Li(acac).

Figure S4. $^1$H-NMR (CDCl$_3$) spectra of: a) 4 and b) product 8 obtained from 4 by anion substitution using Li(acac).

Figure S5. $^1$H-NMR (CDCl$_3$) spectra of: a) precursor 11 and b) product 13 obtained from 11 by anion substitution using Li(acac).

Figure S6. $^1$H-NMR spectra of: a) precursor 12 (DMSO-$d_6$) and b) product 14 (CDCl$_3$) obtained from 12 by anion substitution using Li(acac).
Figure S7. $^1$H-NMR (DMSO-$d_6$) spectra of: a) precursor 5 and b) product 7 obtained from 5 by anion substitution using Li(acac).

Figure S8. $^1$H-NMR (DMSO-$d_6$) spectra of: a) precursor 6 and b) product 8 obtained from 6 by anion substitution using Li(acac).

Figure S9. $^1$H-NMR spectra of: a) precursor 9 (DMSO-$d_6$) and b) product 13 (CDCl$_3$) obtained from 9 anion substitution using Li(acac).

Figure S10. $^1$H-NMR (DMSO-$d_6$) spectra of: a) precursor 10 and b) product 14 (CDCl$_3$) obtained from 10 by anion substitution using Li(acac).

Figure S11. $^1$H-NMR (DMSO-$d_6$) spectra of: a) precursor 1 and b) product 7 obtained from 1 by anion substitution using Li(acac).

Figure S12. $^1$H-NMR (DMSO-$d_6$) spectra of: a) precursor 2 and b) product 8 obtained from 2 by anion substitution using Li(acac).
Figure S13. $^1$H-NMR (CDCl$_3$) spectra of product 7 obtained by anion substitution using Li(acac) from precursors: a) 1, b) 3, and c) 5.

Figure S14. $^1$H-NMR (CDCl$_3$) spectra of product 8 obtained by anion substitution using Li(acac) from precursors: a) 2, b) 4 and c) 6.

Figure S15. $^1$H-NMR (CDCl$_3$) spectra of product 13 obtained by anion substitution using Li(acac) from precursors: a) 9 and b) 11.

Figure S16. $^1$H-NMR (CDCl$_3$) spectra of product 14 obtained by anion substitution using Li(acac) from precursors: a) 10 and b) 12.

Figure S17. $^1$H-NMR (CDCl$_3$) spectra of: a) precursor 7 and b) product 3 obtained from 7 by anion substitution using NaOAc.

Figure S18. $^1$H-NMR (CDCl$_3$) spectra of: a) precursor 8 and b) product 4 obtained from 8 by anion substitution using NaOAc.
Figure S19. $^1$H-NMR (CDCl$_3$) spectra of a) precursor 13 and b) product 11 obtained from 13 by anion substitution using NaOAc.

Figure S20. $^1$H-NMR (DMSO-d$_6$) spectra of a) precursor 14 and b) product 12 obtained from 14 by anion substitution using NaOAc.

Figure S21. $^1$H-NMR (DMSO-d$_6$) spectra of a) precursor 7 and b) product 5 obtained from 7 by anion substitution using LiCl.

Figure S22. $^1$H-NMR (DMSO-d$_6$) spectra of a) precursor 8 and b) product 6 obtained from 8 by anion substitution using LiCl.

Figure S23. $^1$H-NMR spectra of a) precursor 13 (CDCl$_3$) and b) product 9 (DMSO-d$_6$) obtained from 13 by anion substitution using LiCl.

Figure S24. $^1$H-NMR spectra of a) precursor 14 (CDCl$_3$) and b) product 10 (DMSO-d$_6$) obtained from 14 by anion substitution using LiCl.
Figure S25. $^1$H-NMR spectra of: a) precursor 1 (DMSO-$d_6$) and b) product 3 (CDCl$_3$) obtained from 1 by anion substitution using NaOAc.

Figure S26. $^1$H-NMR (DMSO-$d_6$) spectra of: a) precursor 2 and b) product 4 obtained from 2 by anion substitution using NaOAc.

Figure S27. $^1$H-NMR (DMSO-$d_6$) spectra of a) precursor 5 and b) product 3 obtained from 5 (CDCl$_3$) by anion substitution using NaOAc.

Figure S28. $^1$H-NMR (DMSO-$d_6$) spectra of a) precursor 6 and b) product 4 obtained from 6 by anion substitution using NaOAc.

Figure S29. $^1$H-NMR spectra of a) precursor 9 (DMSO-$d_6$) and b) product 11 (CDCl$_3$) obtained from 9 by anion substitution using NaOAc.

Figure S30. $^1$H-NMR (DMSO-$d_6$) spectra of a) precursor 10 and b) product 12 obtained from 10 by anion substitution using NaOAc.
Figure S31. $^1$H-NMR (DMSO-d$_6$) spectra of a) precursor 1 and b) product 5 obtained from 1 by anion substitution using LiCl.

Figure S32. $^1$H-NMR (DMSO-d$_6$) spectra of a) precursor 2 and b) product 6 obtained from 2 by anion substitution using LiCl.

Figure S33. $^1$H-NMR spectra of a) precursor 3 (CDCl$_3$) and b) product 5 (DMSO-d$_6$) obtained from 3 by anion substitution using LiCl.

Figure S34. $^1$H-NMR (DMSO-d$_6$) spectra of: a) precursor 4 and b) product 6 obtained from 4 by anion substitution using LiCl.

Figure S35. $^1$H-NMR spectra of a) precursor 11 (CDCl$_3$) and b) product 9 (DMSO-d$_6$) obtained from 11 by anion substitution using LiCl.

Figure S36. $^1$H-NMR (DMSO-d$_6$) spectra of a) precursor 12 and b) product 10 obtained from 12 by anion substitution using LiCl.
Figure S37. $^1$H-NMR (CDCl$_3$) spectra of product 3 obtained by anion substitution using NaOAc from: a) 1, b) 5 and c) 7.

Figure S38. $^1$H-NMR (CDCl$_3$) spectra of product 4 obtained by anion substitution using NaOAc from: a) 2, b) 6 and c) 8.

Figure S39. $^1$H-NMR (CDCl$_3$) spectra of product 11 obtained by anion substitution using NaOAc from: a) 9 and b) 13.

Figure S40. $^1$H-NMR (DMSO-d$_6$) spectra of product 12 obtained by anion substitution using NaOAc from: a) 10 and b) 14.

Figure S41. $^1$H-NMR (DMSO-d$_6$) spectra of product 5 obtained by anion substitution using LiCl from: a) 1, b) 3 and c) 7.

Figure S42. $^1$H-NMR (DMSO-d$_6$) spectra of product 6 obtained by anion substitution using LiCl from: a) 2, b) 4 and c) 8.
Figure S43. $^1$H-NMR (DMSO-d$_6$) spectra of product 9 obtained by anion substitution using LiCl from: a) 11 and b) 13.

Figure S44. $^1$H-NMR (DMSO-d$_6$) spectra of product 10 obtained by anion substitution using LiCl from: a) 12 and b) 14.
**IR SPECTROSCOPY**

**Table S4.** IR vibrations of select groups of acetate and acetylacetonate complexes

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**Figure S45.** FTIR spectra of: a) L1, b) [Pd(MeCN)$_4$][BF$_4$], c) NaOAc, d) crude product 1 synthesised by IAG using NaOAc and NaBF$_4$ as additives, e) pure product 1 after washing with water and f) recrystallized from MeCN.

**Figure S46.** FTIR spectra of: a) L1, b) NaOAc, c) crude product 9 synthesised by ILAG using NaOAc and H$_2$O as additives and d) pure product 9 after washing with water.
Figure S47. FTIR spectra of: a) precursor 3, b) Li(acac), c) byproduct LiOAc, d) resulting mixture of product 7, Li(acac), LiOAc and e) pure product 7 after washing with water.

Figure S48. FTIR spectra of: a) precursor 4, b) Li(acac), c) byproduct LiOAc, d) resulting mixture of product 8, Li(acac), LiOAc and e) pure product 8 after washing with water.

Figure S49. FTIR spectra of: a) precursor 11, b) Li(acac), c) byproduct LiOAc, d) resulting mixture of product 13, Li(acac), LiOAc and e) pure product 13 after washing with water.

Figure S50. FTIR spectra of: a) precursor 12, b) Li(acac), c) byproduct LiOAc, d) resulting mixture of product 14, Li(acac), LiOAc and e) pure product 14 after washing with water.
Figure S51. FTIR spectra of: a) precursor 5, b) Li(acac), c) resulting mixture of product 7, Li(acac), LiCl and d) pure product 7 after washing with water.

Figure S52. FTIR spectra of: a) precursor 6, b) Li(acac), c) resulting mixture of product 8, Li(acac), LiCl and d) pure product 8 after washing with water.

Figure S53. FTIR spectra of: a) precursor 9, b) Li(acac), c) resulting mixture of product 13, Li(acac), LiCl and d) pure product 13 after washing with water.

Figure S54. FTIR spectra of: a) precursor 10, b) Li(acac), c) resulting mixture of product 14, Li(acac), LiCl and d) pure product 14 after washing with water.
**Figure S55.** FTIR spectra of: a) precursor 1, b) Li(acac), c) byproduct LiBF₄, d) resulting mixture of 7, Li(acac), LiBF₄ and e) pure product 7 after washing with water.

**Figure S56.** FTIR spectra of: a) 2, b) Li(acac), c) byproduct LiBF₄, d) resulting mixture of product 8, Li(acac), LiBF₄ and e) pure product 8 after washing with water.

**Figure S57.** FTIR spectra of purified product 7 obtained by ion exchange reaction with Li(acac) from: a) 1, b) 3 and c) 5.

**Figure S58.** FTIR spectra of purified product 8 obtained by ion exchange reaction with Li(acac) from: a) 2, b) 4 and c) 6.
Figure S59. FTIR spectra of purified product 13 obtained by ion exchange reaction with Li(acac) from: a) 9 and b) 11.

Figure S60. FTIR spectra of purified product 14 obtained by ion exchange reaction with Li(acac) from: a) 10 and b) 12.

Figure S61. FTIR spectra of: a) precursor 7, b) NaOAc, c) byproduct Na(acac), d) resulting mixture of product 3, NaOAc, Na(acac) and e) pure product 3 after washing with water.

Figure S62. FTIR spectra of: a) precursor 8, b) NaOAc, c) byproduct Na(acac), d) resulting mixture of product 4, NaOAc, Na(acac) and e) pure product 4 after washing with water.
**Figure S63.** FTIR spectra of: a) precursor 13, b) NaOAc, c) byproduct Na(acac), d) resulting mixture of product 11, NaOAc, Na(acac) and e) pure product 11 after washing with water.

**Figure S64.** FTIR spectra of: a) precursor 14, b) NaOAc, c) byproduct Na(acac), d) resulting mixture of 12, NaOAc, Na(acac) and e) pure product 12 after washing with water.

**Figure S65.** FTIR spectra of: a) precursor 7, b) byproduct Li(acac), c) resulting mixture of product 5, LiCl, Li(acac) and d) pure 5 after washing with water.

**Figure S66.** FTIR spectra of: a) precursor 8, b) byproduct Li(acac), c) resulting mixture of product 6, LiCl, Li(acac) and d) pure 6 after washing with water.
Figure S67. FTIR spectra of: a) 13, b) byproduct Li(acac), c) resulting mixture of product 9, LiCl, Li(acac) and d) pure product 9 after washing with water.

Figure S68. FTIR spectra of: a) d precursor 14, b) byproduct Li(acac), c) resulting mixture of product 10, LiCl, Li(acac) and d) pure product 10 after washing with water.

Figure S69. FTIR spectra of: a) precursor 1, b) NaOAc, c) byproduct NaBF₄, d) resulting mixture of product 3, NaOAc, NaBF₄ and e) pure product 3 after washing with water.

Figure S70. FTIR spectra of: a) precursor 2, b) NaOAc, c) byproduct NaBF₄, d) resulting mixture of product 4, NaOAc, NaBF₄ and e) pure product 4 after washing with water.
Figure S71. FTIR spectra of: a) precursor 5, b) NaOAc, c) resulting mixture of 3, NaOAc, byproduct NaCl and d) pure product 3 after washing with water.

Figure S72. FTIR spectra of: a) precursor 6, b) NaOAc, c) resulting mixture of product 4, NaOAc, byproduct NaCl and d) pure product 4 after washing with water.

Figure S73. FTIR spectra of: a) precursor 9, b) NaOAc, c) resulting mixture of product 11, NaOAc, byproduct NaCl and d) pure product 11 after washing with water.

Figure S74. FTIR spectra of: a) precursor 10, b) NaOAc, c) resulting mixture of product 12, NaOAc, byproduct NaCl and d) pure product 12 after washing with water.
Figure S75. FTIR spectra of: a) precursor 1, b) byproduct LiBF$_4$, c) resulting mixture of product 5, LiCl, LiBF$_4$ and d) pure product 5 after washing with water.

Figure S76. FTIR spectra of: a) precursor 2, b) byproduct LiBF$_4$, c) resulting mixture of product 6, LiCl, LiBF$_4$ and d) pure product 6 after washing with water.

Figure S77. FTIR spectra of: a) precursor 3, b) byproduct LiOAc, c) resulting mixture of product 5, LiCl, byproduct LiOAc and d) pure product 5 after washing with water.

Figure S78. FTIR spectra of: a) precursor 4, b) byproduct LiOAc, c) resulting mixture of product 6, LiCl, byproduct LiOAc and d) pure product 6 after washing with water.
Figure S79. FTIR spectra of: a) precursor 11, b) byproduct LiOAc, c) resulting mixture of product 9, LiCl, byproduct LiOAc and d) pure product 9 after washing with water.

Figure S80. FTIR spectra of: a) precursor 12, b) byproduct LiOAc, c) resulting mixture of product 10, LiCl, byproduct LiOAc and d) pure product 10 after washing with water.

Figure S81. FTIR spectra of purified product 3 obtained by ion exchange reaction with NaOAc from: a) 1, b) 5 and c) 7.

Figure S82. FTIR spectra of purified product 4 obtained by ion exchange reaction with NaOAc from: a) 2, b) 6 and c) 8.
Figure S83. FTIR spectra of purified product 11 obtained by ion exchange reaction with NaOAc from: a) 9 and b) 13.

Figure S84. FTIR spectra of purified product 12 obtained by ion exchange reaction with NaOAc from: a) 10 and b) 14.

Figure S85. FTIR spectra of purified monopalladated product 5 obtained by ion exchange reaction with LiCl from: a) 1, b) 3 and c) 7.

Figure S86. FTIR spectra of purified monopalladated product 6 obtained by ion exchange reaction with LiCl from: a) 2, b) 4 and c) 8.
Figure S 87. FTIR spectra of purified dipalladated product 9 obtained by ion exchange reaction with LiCl from: a) 11 and b) 13.

Figure S 88. FTIR spectra of purified dipalladated product 10 obtained by ion exchange reaction with LiCl from: a) 12 and b) 14.
POWDER X-RAY DIFFRACTION

Structure solution from powder diffraction data.

**General remarks.** Crystal structures of 7 and 13 were solved from powder diffraction data collected on a Panalytical Aeris laboratory powder diffractometer using Ni-filtered radiation from a copper anode. Sample was prepared in a thin layer on a silicon zero-background holder and data were collected in Bragg-Brentano geometry. Indexing was performed on selected peaks, positions of which were fitted by general peak fitting. Structure solution for both C1ABacac and C2ABacac was accomplished in direct space by treating expected molecular fragments as rigid bodies. All calculations were performed using the program Topas (version 4.2) from Bruker-AXS (Karlsruhe, Germany).

**Structure solution of 7.** For 7 we have first taken the acetylacetonate and the monopalladated L1 moieties as separate rigid bodies. Structure solution was found only when preferred orientation was introduced into global optimisation in parallel. It was modelled using spherical harmonics coefficients of which were reset to zero before starting new optimisation cycles. Simulated annealing runs have positioned the acetylacetonate coordinated to Pd and even the trans influence of the carbon atom was evident since the Pd-O distance with carbon opposite was longer than the Pd-O distance with nitrogen opposite. The acetylacetonate fragment was slightly tilted relative to the plane of the palladacycle. Geometry of the moiety as a whole was then optimised in vacuum and was introduced for the final Rietveld refinement cycles. The acetylacetonate fragment was allowed to rotate around the axis defined by two oxygen atoms and the free phenyl ring of L1 was also allowed to rotate. The final Rietveld fit exhibits serious mismatch between calculated and measured patterns which we attribute to inadequate modelling of preferred orientation. Several short contacts can be recognised involving hydrogen atoms which however originate from longer C−H bonds as the rigid body was optimised in vacuum. For example, C−H bond distances are typically around 1.06 Å in our structure model whereas the usual C−H distance from X-ray diffraction will be around 0.95 Å.

**Figure S89.** Rietveld plot of 7. Pattern collected in Bragg-Brentano geometry using Ni-filtered copper radiation. Blue–measured, red–calculated, grey–difference. Tick marks represent calculated peak position. Preferred orientation accounted for using spherical
harmonics of the 6th order. $a = 13.983(1) \, \text{Å}$, $b = 10.629(1) \, \text{Å}$, $c = 11.426(1) \, \text{Å}$, $\alpha = 90^\circ$, $\beta = 111.303(4)^\circ$, $\gamma = 90^\circ$, $V = 1582.1(2) \, \text{Å}^3$, space group: $P2_1/n$.

**Figure S90.** View of the molecular structure of 7. Palladium-purple, oxygen-red, nitrogen-blue, carbon-grey, hydrogen-white.

**Structure solution of 13.** For 13, indexing afforded triclinic unit cell of approximately 540 Å$^3$ which neatly fits one molecule of 13. In the space group P-1, half of the molecule must comprise the asymmetric unit and the centre of inversion is bisecting the N-N bond. Structure solution was attempted using half of the molecule, previously optimised in vacuum, as a rigid body. A dummy atom was positioned to bisect the N-N bond and the rigid body was positioned with this dummy atom lying on a centre of inversion at (0,0,0). This meant that only the orientation of the rigid body needed to be found. Preferred orientation was modelled using spherical harmonics.

**Figure S91.** Rietveld plot of 13. Pattern collected in Bragg-Brenatano geometry using Ni-filtered copper radiation. Blue—measured, red—calculated, grey—difference. Tick marks represent calculated peak position. Preferred orientation accounted for using spherical harmonics of the 6th order. $a = 5.6613(4) \, \text{Å}$, $b = 11.3428(9) \, \text{Å}$, $c = 9.7569(8) \, \text{Å}$, $\alpha = 111.274(5)^\circ$, $\beta = 96.289(5)^\circ$, $\gamma = 107.464(6)^\circ$, $V = 539.86(8) \, \text{Å}^3$, space group: $P-1$. 
**Figure S92.** View of the molecular structure of 13. Palladium-purple, oxygen-red, nitrogen-blue, carbon-grey, hydrogen-white.

**PXRD OF REACTANTS AND PRODUCT**

**Figure S93.** PXRD patterns of: a) L1, b) NaBF₄, c) NaOAc, d) crude product 1 prepared by IAG using NaOAc and NaBF₄ as additives, e) pure product 1 after washing with water and f) product 1 recrystallized from MeCN.

**Figure S94.** PXRD patterns of: a) L1, b) NaOAc, c) PdCl₂, d) crude product 9 prepared by IAG using NaOAc as additive and e) pure product 9 after washing with water.

**Figure S95.** PXRD patterns of: a) precursor 3, b) Li(acac), c) byproduct LiOAc, d) resulting mixture of product 7, Li(acac), LiOAc and e) pure product 7 after washing with water.

**Figure S96.** PXRD patterns of: a) precursor 4, b) Li(acac), c) byproduct LiOAc, d) resulting mixture of product 8, Li(acac), LiOAc and e) pure product 8 after washing with water.
Figure S97. PXRD patterns of: a) precursor 11, b) Li(acac), c) byproduct LiOAc, d) resulting mixture of product 13, Li(acac), LiOAc and e) pure product 13 after washing with water.

Figure S98. PXRD patterns of: a) precursor 12, b) Li(acac), c) byproduct LiOAc, d) resulting mixture of product 14, Li(acac), LiOAc and e) pure dipalladated 14 after washing with water.

Figure S99. PXRD patterns of: a) precursor 5, b) Li(acac), c) byproduct LiCl, d) resulting mixture of product 7, Li(acac), LiCl and e) pure product 7 after washing with water.

Figure S100. PXRD patterns of: a) precursor 6, b) Li(acac), c) byproduct LiCl, d) resulting mixture of product 8, Li(acac), LiCl and e) pure product 8 after washing with water.

Figure S101. PXRD patterns of: a) precursor 9, b) Li(acac), c) byproduct LiCl, d) resulting mixture of 13, Li(acac), LiCl and d) pure product 13 after washing with water.

Figure S102. PXRD patterns of: a) precursor 10, b) Li(acac), c) byproduct LiCl, d) resulting mixture of product 14, Li(acac), LiCl and d) pure product 14 after washing with water.
Figure S103. PXRD patterns of: a) precursor 1, b) Li(acac), c) byproduct LiBF$_4$, d) resulting mixture of 7, Li(acac), LiBF$_4$ and e) pure product 7 after washing with water.

Figure S104. PXRD patterns of: a) precursor 2, b) Li(acac), c) byproduct LiBF$_4$, d) resulting mixture of product 8, Li(acac), LiBF$_4$ and e) pure product 8 after washing with water.

Figure S105. PXRD patterns of purified product 7 obtained by ion exchange reaction with Li(acac) from: a) 1, b) 3 and c) 5.

Figure S106. FTIR spectra of purified product 8 obtained by ion exchange reaction with Li(acac) from: a) 2, b) 4 and c) 6.

Figure S107. PXRD patterns of purified product 13 obtained by ion exchange reaction with Li(acac) from: a) 9 and b) 11.

Figure S108. PXRD patterns of purified product 14 obtained by ion exchange reaction with Li(acac) from: a) 10 and b) 12.
Figure S109. PXRD patterns of: a) precursor 7, b) NaOAc, c) byproduct Na(acac), d) resulting mixture of product 3, NaOAc, Na(acac) and e) pure product 3 after washing with water.

Figure S110. PXRD patterns of: a) initial precursor 8, b) NaOAc, c) byproduct Na(acac), d) resulting mixture of product 4, NaOAc, Na(acac) and e) pure product 4 after washing with water.

Figure S111. PXRD patterns of: a) precursor 13, b) NaOAc, c) byproduct Na(acac), d) resulting mixture of 11, NaOAc, Na(acac) and e) pure product 11 after washing with water.

Figure S112. PXRD patterns of: a) precursor 14, b) NaOAc, c) byproduct Na(acac), d) resulting mixture of product 12, NaOAc, Na(acac) and e) pure product 12 after washing with water.

Figure S113. PXRD patterns of: a) precursor 7, b) LiCl, c) byproduct Li(acac), d) resulting mixture of 5, LiCl, Li(acac) and e) pure product 5 after washing with water.

Figure S114. PXRD patterns of: a) precursor 8, b) LiCl, c) byproduct Li(acac), d) resulting mixture of 6, LiCl, Li(acac) and e) pure product 6 after washing with water.
Figure S115. PXRD patterns of: a) precursor 13, b) LiCl, c) byproduct Li(acac), d) resulting mixture of product 9, LiCl, Li(acac) and e) pure product 9 after washing with water.

Figure S116. PXRD patterns of: a) precursor 14, b) LiCl, c) byproduct Li(acac), d) resulting mixture of product 10, LiCl, Li(acac) and e) pure product 10 after washing with water.

Figure S117. PXRD patterns of: a) precursor 1, b) NaOAc, c) byproduct NaBF₄, d) resulting mixture of product 3, NaOAc, NaBF₄ and e) pure product 3 after washing with water.

Figure S118. PXRD patterns of: a) precursor 2, b) NaOAc, c) byproduct NaBF₄, d) resulting mixture of product 4, NaOAc, NaBF₄ and e) pure product 4 after washing with water.

Figure S119. PXRD patterns of: a) precursor 5, b) NaOAc, c) byproduct NaCl, d) resulting mixture of product 3, NaOAc, byproduct NaCl and e) pure product 3 after washing with water.

Figure S120. PXRD patterns of: a) 6, b) NaOAc, c) byproduct NaCl, d) resulting mixture of product 4, NaOAc, byproduct NaCl and e) pure product 4 after washing with water.
**Figure S121.** PXRD patterns of: a) precursor 9, b) NaOAc, c) byproduct NaCl, d) resulting mixture of product 11, NaOAc, byproduct NaCl and e) pure product 11 after washing with water.

**Figure S122.** PXRD patterns of: a) precursor 10, b) NaOAc, c) byproduct NaCl, d) resulting mixture of product 12, NaOAc, byproduct NaCl and e) pure product 12 after washing with water.

**Figure S123.** PXRD patterns of: a) precursor 1, b) LiCl, c) byproduct LiBF₄, d) resulting mixture of product 5, LiCl, LiBF₄ and e) pure product 5 after washing with water.

**Figure S124.** FTIR spectra of: a) precursor 2, b) LiCl, c) byproduct LiBF₄, d) resulting mixture of product 6, LiCl, LiBF₄ and e) pure product 6 after washing with water.

**Figure S125.** PXRD patterns of: a) precursor 3, b) LiCl, c) byproduct LiOAc, d) resulting mixture of product 5, LiCl, byproduct LiOAc and e) pure product 5 after washing with water.

**Figure S126.** PXRD patterns of: a) precursor 4, b) LiCl, c) byproduct LiOAc, d) resulting mixture of product 6, LiCl, byproduct LiOAc and e) pure product 6 after washing with water.
Figure 127. PXRD patterns of: a) precursor 11, b) LiCl, c) byproduct LiOAc, d) resulting mixture of product 9, LiCl, byproduct LiOAc and e) pure product 9 after washing with water.

Figure 128. PXRD patterns of: a) precursor 12, b) LiCl, c) byproduct LiOAc, d) resulting mixture product 10, LiCl, byproduct LiOAc and e) pure product 10 after washing with water.

Figure S129. PXRD patterns of purified product 3 obtained by ion exchange reaction with NaOAc from: a) 1, b) 5 and c) 7.

Figure S130. PXRD patterns of purified product 4 obtained by ion exchange reaction with NaOAc from: a) 2, b) 6 and c) 8.

Figure S131. PXRD patterns of purified product 11 obtained by ion exchange reaction with NaOAc from: a) 9 and b) 13.

Figure S132. PXRD patterns of purified product 12 obtained by ion exchange reaction with NaOAc from: a) 10 and b) 14.
Figure S133. PXRD patterns of purified product 5 obtained by ion exchange reaction with LiCl from: a) 1, b) 3 and c) 7.

Figure S134. PXRD patterns of purified product 6 obtained by ion exchange reaction with LiCl from: a) 2, b) 4 and c) 8.

Figure S135. PXRD patterns of purified product 9 obtained by ion exchange reaction with LiCl from: a) 11 and b) 13.

Figure S136. PXRD patterns of purified product 10 obtained by ion exchange reaction with LiCl from: a) 12 and b) 14.
**RAMAN SPECTROSCOPY**

Table S5. Fluorescence maxima in Raman spectra of products

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<th>7</th>
<th>2</th>
<th>4</th>
<th>6</th>
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<td>13</td>
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<td>~1250</td>
<td>~750</td>
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</tbody>
</table>

Figure S137. Raman spectrum of 1.

Figure S138. Raman spectrum of 2.

Figure S139. Raman spectrum of 3.

Figure S140. Raman spectrum of 4.
Figure S141. Raman spectrum of 5.

Figure S142. Raman spectrum of 6.

Figure S143. Raman spectrum of 7.

Figure S144. Raman spectrum of 8.

Figure S145. Raman spectrum of 9.

Figure S146. Raman spectrum of 10.
**Figure S147.** Raman spectrum of 11.  

**Figure S148.** Raman spectrum of 12.  

**Figure S149.** Raman spectrum of 13.  

**Figure S150.** Raman spectrum of 14.  

**References:**  