

## Supporting Information

### Catalyst life in imidazolium-based ionic liquids for palladium-catalysed asymmetric allylic alkylation

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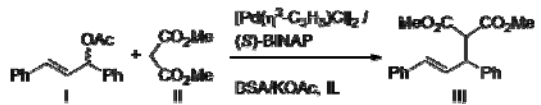
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#### 1. Experimental Part

**General procedure for allylic alkylation of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene (I) in IL and recycling.** A solution of  $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)_2]$  (1.8 mg, 0.005 mmol) and (*S*)-BINAP in the corresponding ratio (L/Pd=1.25 and 2.5) in  $\text{CH}_2\text{Cl}_2$  (1 mL) was stirred for 30 min. Subsequently, IL was added (1mL) and  $\text{CH}_2\text{Cl}_2$  was removed under reduced pressure. Using a micropipette, **I** (126 mg, 0.5 mmol, 117  $\mu\text{L}$ ), dimethyl malonate (**II**) (198 mg, 1.5 mmol, 126  $\mu\text{L}$ ), *N,O*-bis(trimethylsilyl)acetamide (BSA) (305 mg, 1.5 mmol, 366  $\mu\text{L}$ ) were added and solid KOAc (2 mg) was added to start the catalytic reaction. At the end of the reaction the product (**III**) was extracted with dry hexane (8x3mL) and the ionic liquid was dried for 3 h at 60 C and stirring in order to remove solvent traces. The IL-catalytic system was reused for another catalytic reaction by simply adding **I**, **II**, BSA and KOAc in the appropriate amount (see above).

When trapping agents were used the system was charged at the beginning of the reaction with the appropriate reactant 1,5-cyclooctadiene (COD), 2,5-norbornadiene (NBD) or acetonitrile ( $\text{CH}_3\text{CN}$ )(0.011 mmol).

Table S1. Pd/*S*-BINAP catalysed asymmetric allylic alkylation of **I** in IL



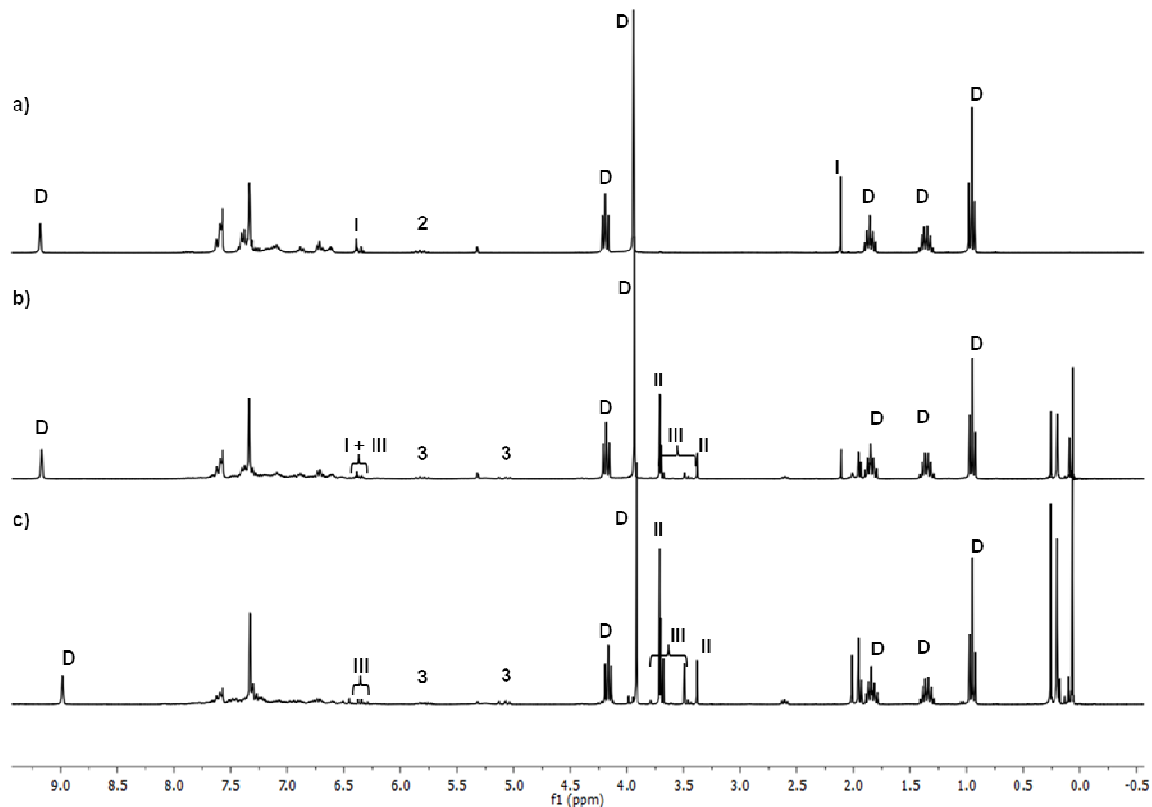
Entry	IL	L*/Pd	1 <sup>st</sup> cycle <sup>[a]</sup>		2 <sup>nd</sup> cycle <sup>[b]</sup>	
			Conv.% <sup>[c]</sup>	ee% <sup>[c]</sup>	Conv.% <sup>[c]</sup>	ee% <sup>[c]</sup>
1	[BMIM][BF <sub>4</sub> ]	1.25	96	80	3	-
2	[BMIM][NTf <sub>2</sub> ]	1.25	91	84	9	65
3	[BMIM][BF <sub>4</sub> ]	1 <sup>[d]</sup>	99	77	5	-
4	[BMIM][NTf <sub>2</sub> ]	1 <sup>[d]</sup>	96	81	5	-
5	[BMIM][BF <sub>4</sub> ]	2.5	93	70	3	-
6	[BMIM][NTf <sub>2</sub> ]	2.5	96	81	5	-
7 <sup>e</sup>	[BMIM][NTf <sub>2</sub> ]	1.25	93	82	2	-
8 <sup>f</sup>	[BMIM][NTf <sub>2</sub> ]	1.25	92	87	3	-
9 <sup>g</sup>	[BMIM][NTf <sub>2</sub> ]	1.25	99	77	4	-

<sup>a</sup> 20°C; 120 min; 1%  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)_2\text{Cl}_2]$ ; **I** (0.5 mmol); **I/II/BSA** 1/3/3 (BSA = *N,O*-bis(trimethylsilyl)acetamide); KOAc (0.005 mmol); IL (1 mL). <sup>b</sup> 2<sup>nd</sup> cycle recharging the system with **I** (0.5 mmol); **I/II/BSA** 1/3/3 after product extraction with hexane (8x3mL). <sup>c</sup> Determined by HPLC. <sup>d</sup> 2%  $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)_2((S)\text{-BINAP})]\text{BF}_4$  (**1**). <sup>e</sup> In presence of COD. <sup>f</sup> In presence of NDB. <sup>g</sup> in presence of  $\text{CH}_3\text{CN}$ .

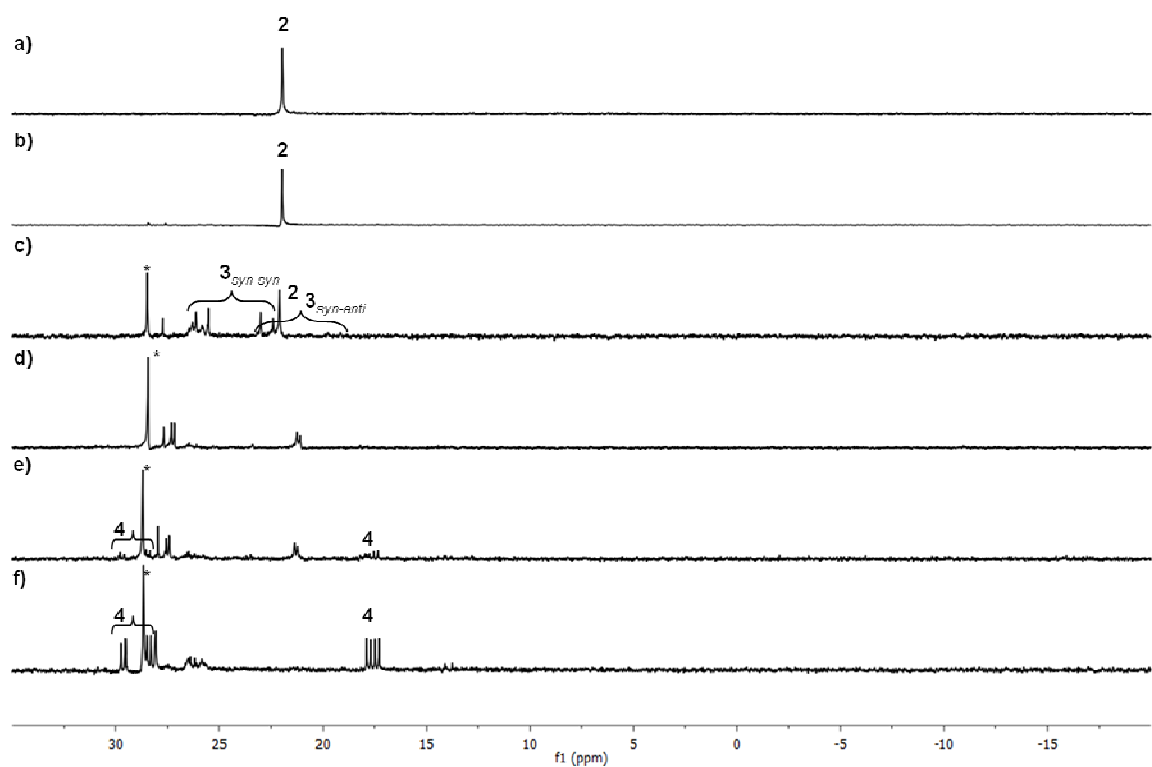
**Modified synthesis of [HDMI][BF<sub>4</sub>]<sup>1</sup> (**B**).** A mixture of 1,2-dimethyl-3-hexylimidazolium methanesulfonate (12.0 g, 43.4 mmol) synthesized as previously described,<sup>2</sup> sodium tetrafluoroborate (5.0 g, 45.6 mmol) and distilled water (50 mL) was vigorously stirred at 50°C for 30 min, resulting in formation of two phases. The aqueous phase was discarded and sodium tetrafluoroborate (0.012 g, 0.1 mmol) in distilled water (5 mL) were added and stirring was continued for 15 min. Addition of dichloromethane (50 mL) allowed separation of two phases. The organic phase was separated, dried with magnesium sulfate and filtered through a short (3 cm) basic alumina column. After removal of solvent under reduced pressure the desired product was obtained as a pale amber liquid (82% yield: 9.5 g, 35.6 mmol).

**Experiment of stoichiometric allylic alkylation of *rac*-1,3-diphenyl-3-acetoxyprop-1-ene (I) in absence of IL.** An NMR tube was charged with  $[\text{PdCl}(\eta^3\text{-C}_3\text{H}_5)_2]$  (4.5 mg, 0.012 mmol), (*S*)-BINAP (9.6 mg, 0.015) and  $\text{CD}_2\text{Cl}_2$  (0.5 mL) was added and stirred manually for 10 min when <sup>1</sup>H and <sup>31</sup>P NMR spectra were recorded. In a similar manner NMR spectra were recorded after addition of **I** (6.2 mg, 0.024 mmol), dimethyl malonate (**II**) (3.2 mg, 0.024 mmol,

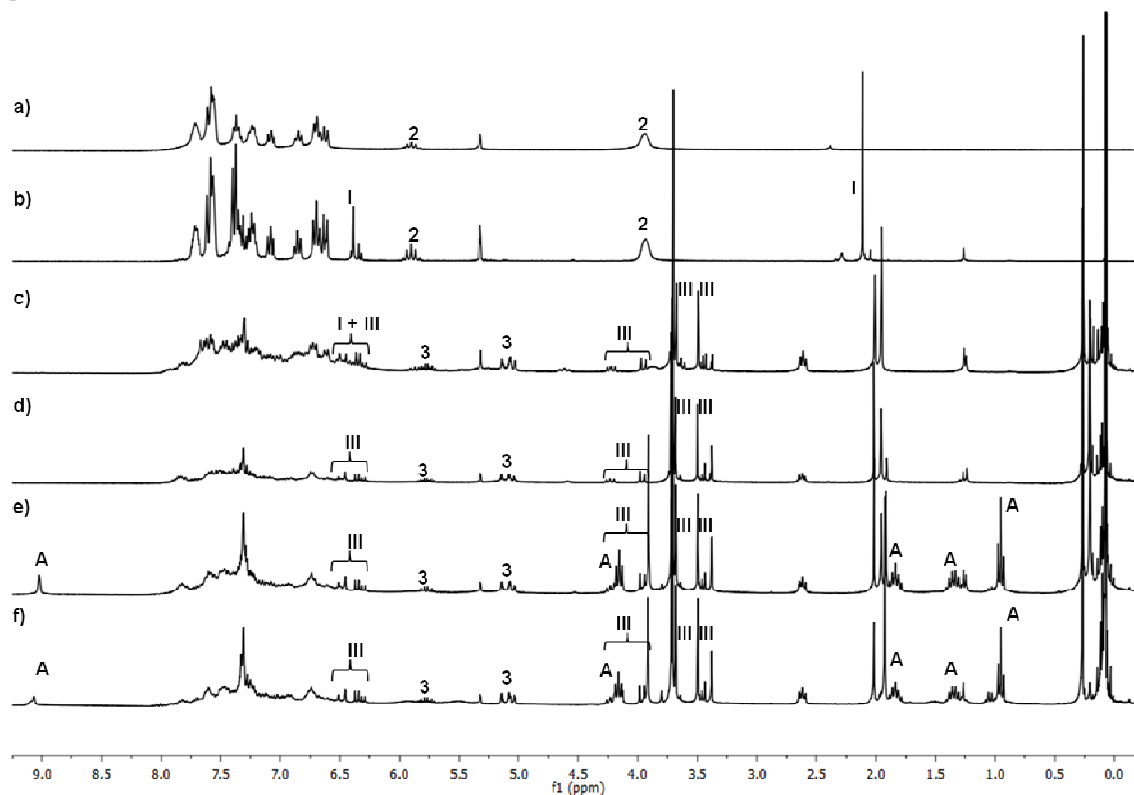
2.8  $\mu\text{L}$ ), *N,O*-bis(trimethylsilyl)acetamide (BSA) (24.8 mg, 0.024 mmol, 6.0  $\mu\text{L}$ ) and solid KOAc (1 mg) and finally, after addition of **II** (3.2 mg, 0.024 mmol, 2.8  $\mu\text{L}$ ) and BSA (24.8 mg, 0.024 mmol, 6.0  $\mu\text{L}$ ). When **I** was completely consumed according to  $^1\text{H}$  NMR, [BMIM][BF<sub>4</sub>] (**A**) (0.123 mmol), was added and NMR were recorded after 10 and 120 min.



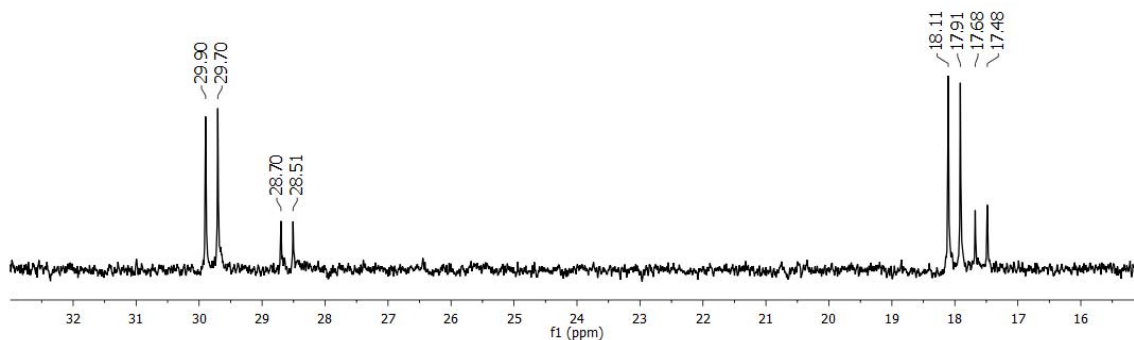
**Fig. S1.**  $^1\text{H}$  NMR spectra for stoichiometric AAA reaction using **2** (*S*)-BINAP: Pd = 1.25) in  $\text{CD}_2\text{Cl}_2$ . a) **2** in presence of [BMIM][NTf<sub>2</sub>] (**D**) and 1 equiv. of **I**; b) Addition of 1 equiv of **II** and BSA; c) Addition of another equivalent of **II** and BSA.



**Fig. S2.**  $^{31}\text{P}$  NMR spectra for stoichiometric AAA reaction using **2** ((*S*)-BINAP:Pd = 1.25) in  $\text{CD}_2\text{Cl}_2$  in absence of IL: a) **2**; b) Addition of 1 equiv of **I**; c) Addition of 1 equivalent of **II** and 1 of BSA; d) Addition of 1 equivalent of **II** and 1 of BSA (spectra recorded after 10 min); e) Spectra recorded after 1 hr; f) Addition of [BMIM][BF<sub>4</sub>] (A) (spectra recorded after 10 min); g) spectra recorded after 2 hr. (\*) Unidentified species



**Fig. S3.**  $^1\text{H}$  NMR spectra for stoichiometric AAA reaction using **2** ((*S*)-BINAP:Pd = 1.25) in  $\text{CD}_2\text{Cl}_2$  in absence of IL: a) **2**; b) Addition of 1 equiv of **I**; c) Addition of 1 equivalent of **II** and 1 of BSA; d) Addition of 1 equivalent of **II** and 1 of BSA (spectra recorded after 10 min); e) Spectra recorded after 1 hr; f) Addition of [BMIM][BF<sub>4</sub>] (A) (spectra recorded after 10 min); g) spectra recorded after 2 hr.



**Fig. S4.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of enriched diastereoisomer **4a**.

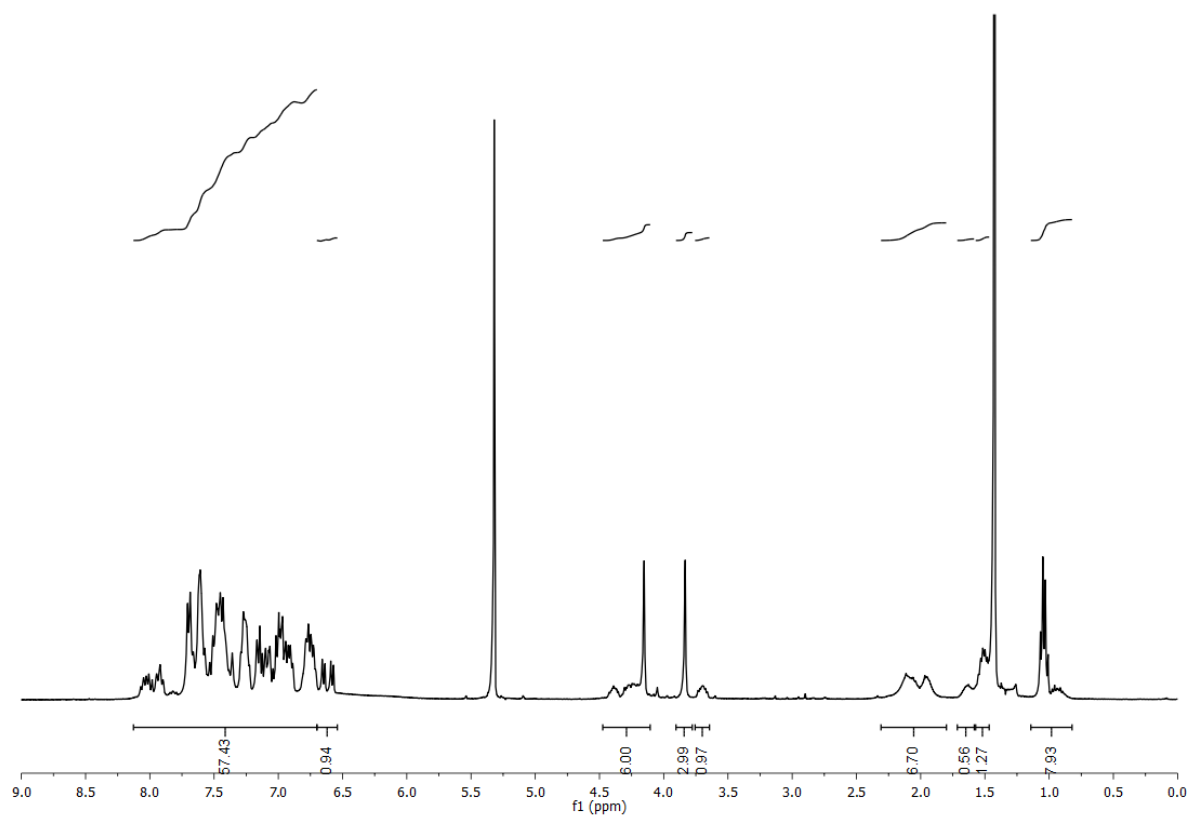


Fig. S5.  $^1\text{H}$  NMR spectrum of complex 4

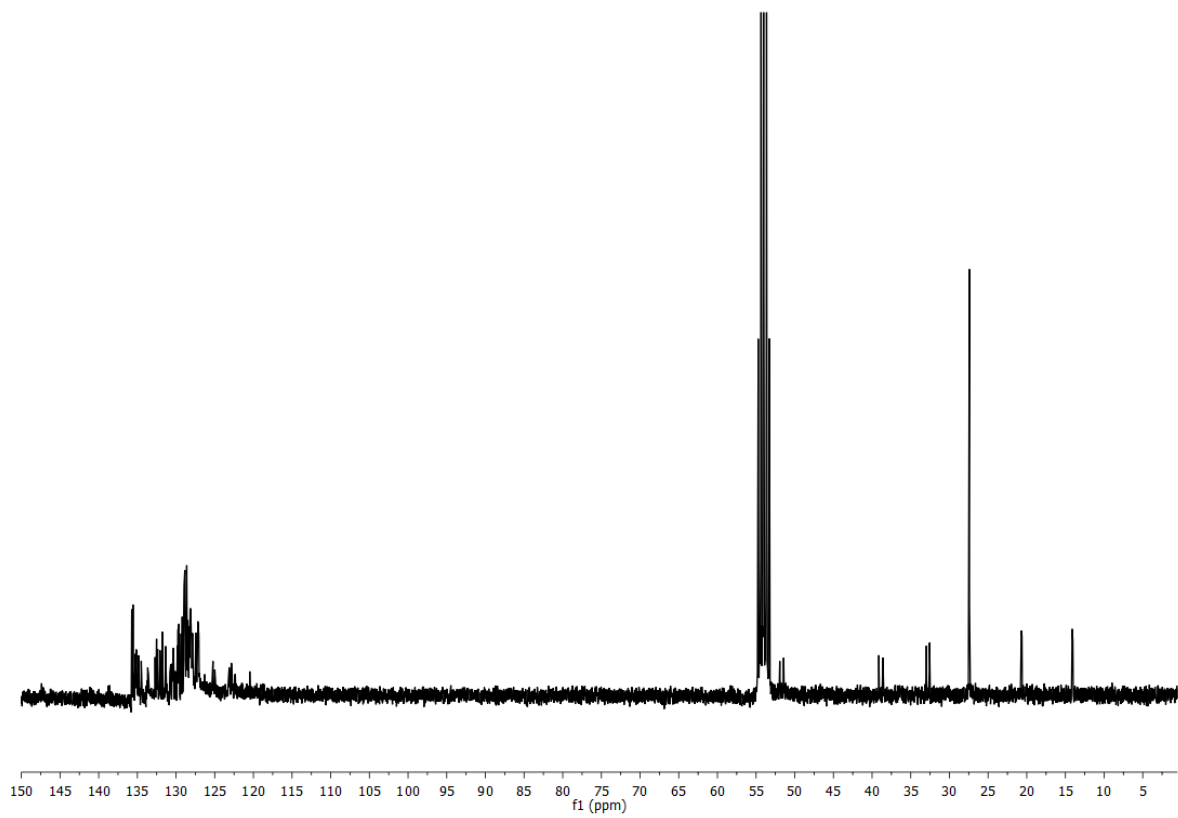
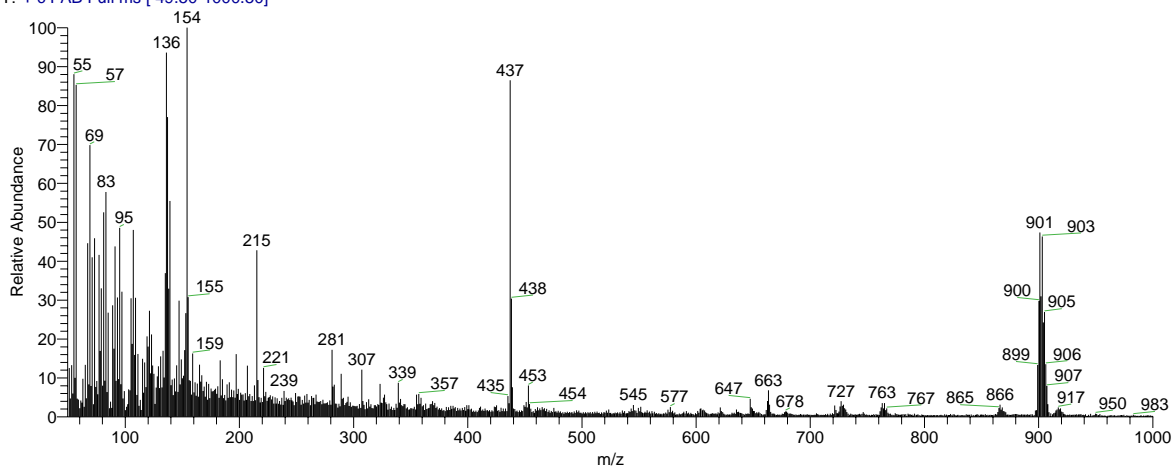
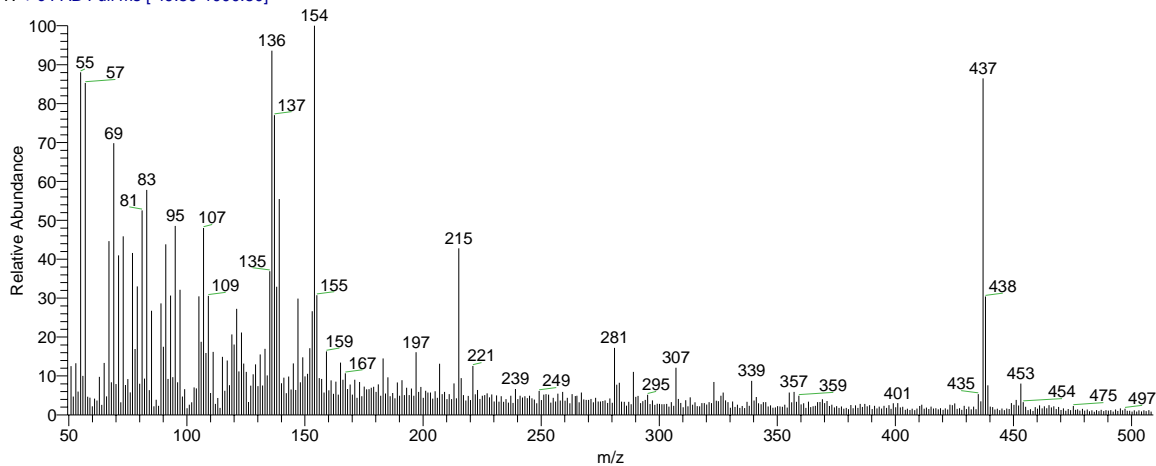


Fig. S6.  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of complex 4

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T: + c FAB Full ms [ 49.50-1000.50]



OT6950\_1 #1-4 RT: 0.00-0.67 AV: 4 NL: 8.00E6  
T: + c FAB Full ms [ 49.50-1000.50]



OT6950\_1 #1-4 RT: 0.00-0.67 AV: 4 NL: 8.00E6  
T: + c FAB Full ms [ 49.50-1000.50]

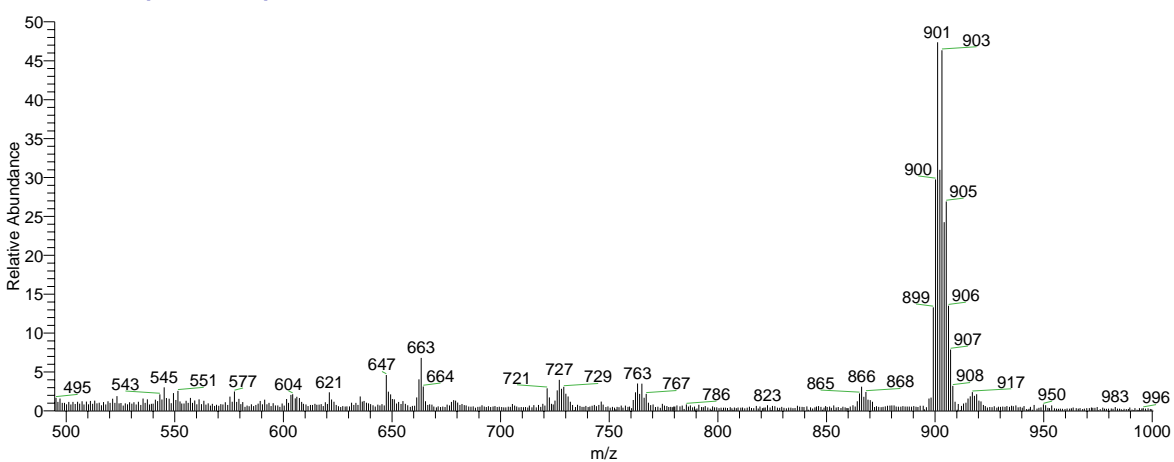


Fig. S7. MS-FAB<sup>+</sup> spectrum of complex 4

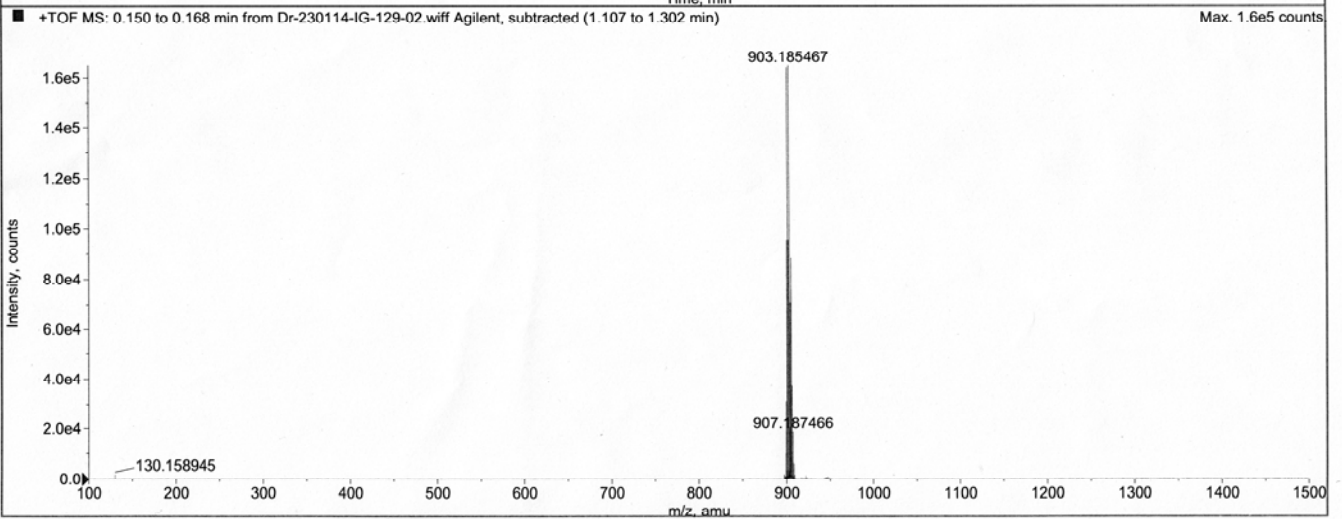
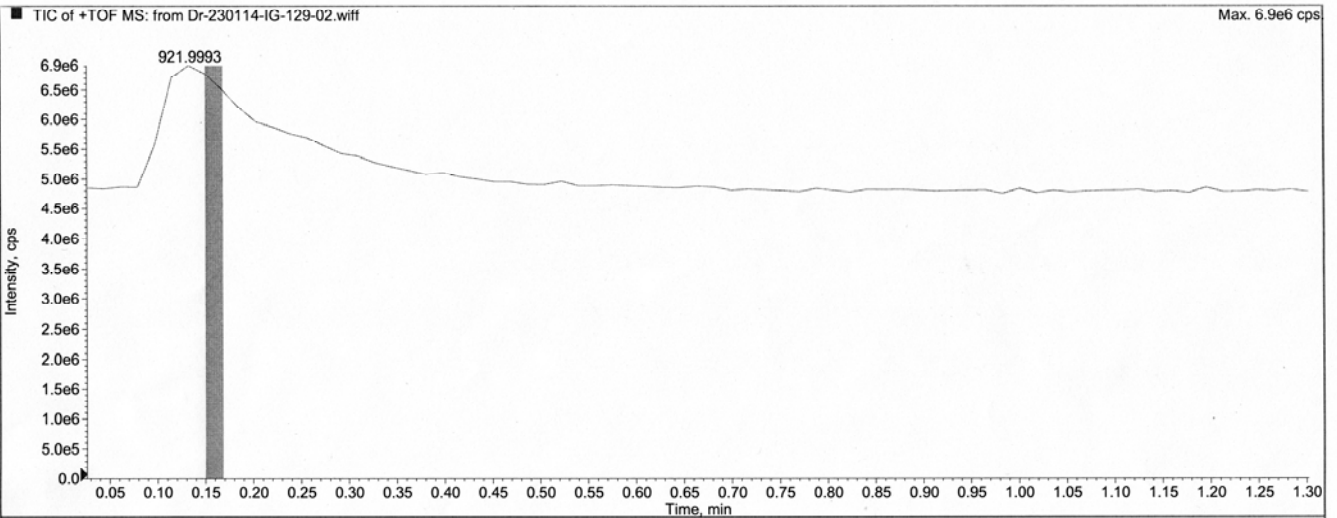
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Elemental composition calculator

Target m/z: +901.1855 amu  
 Tolerance: +5.0000 ppm  
 Result type: Elemental  
 Max num of results: 100  
 Min DBE: -0.5000 Max DBE: +300.0000  
 Electron state: Even  
 Num of charges: 1  
 Add water: N/A  
 Add proton: N/A

	Elements	Min Number	Max Number
1	C	0	60
2	H	0	50
3	N	0	5
4	P	0	3
5	Cl	1	2
6	Pd	1	2

	Formula	Calculated m/z (amu)	mDa Error	PPM Error	DBE
1	C52 H46 N2 F2 Cl Pd	901.185405	0.061195	0.067904	31.5
2	C60 H40 Cl Pd	901.184780	0.686250	0.761497	40.5



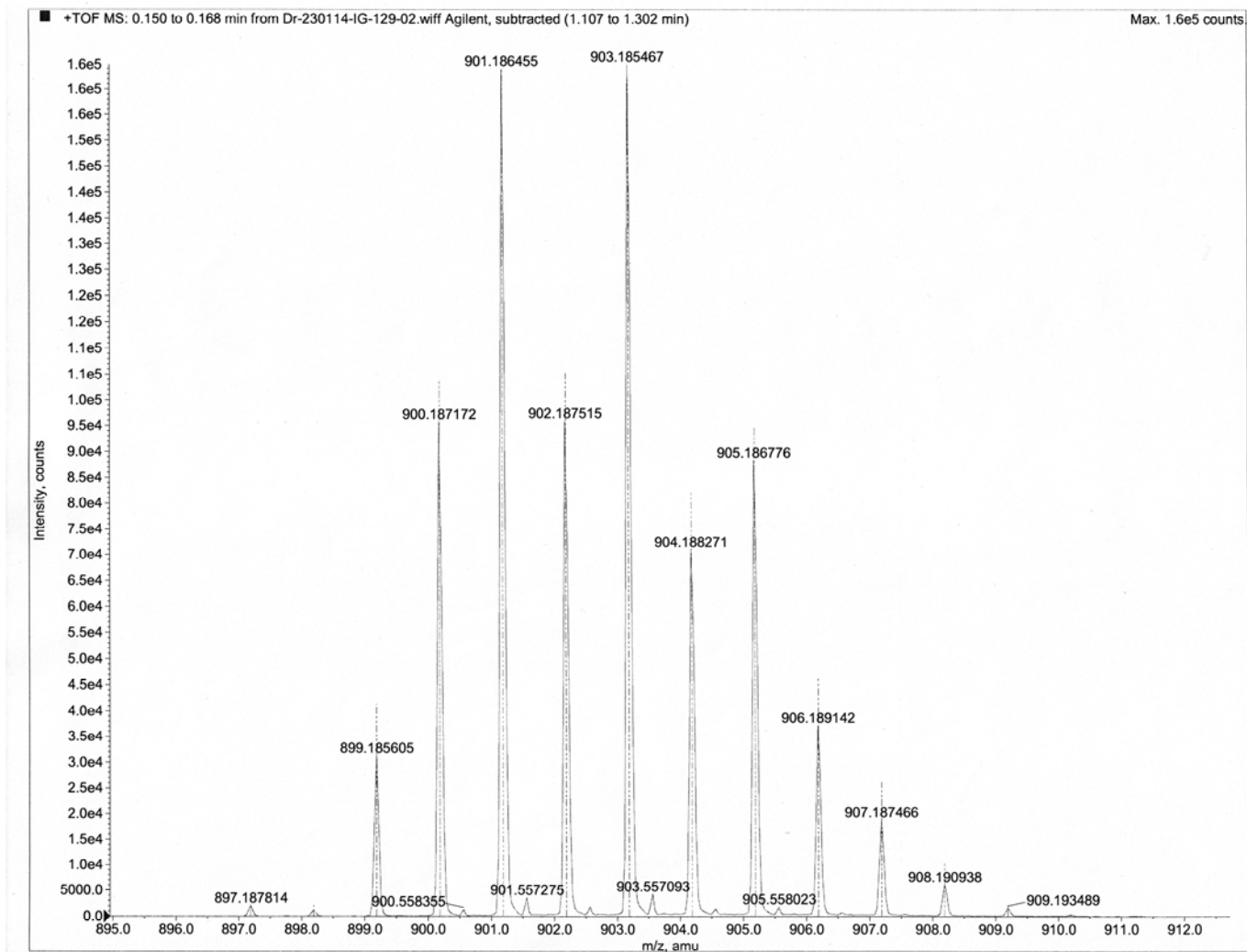
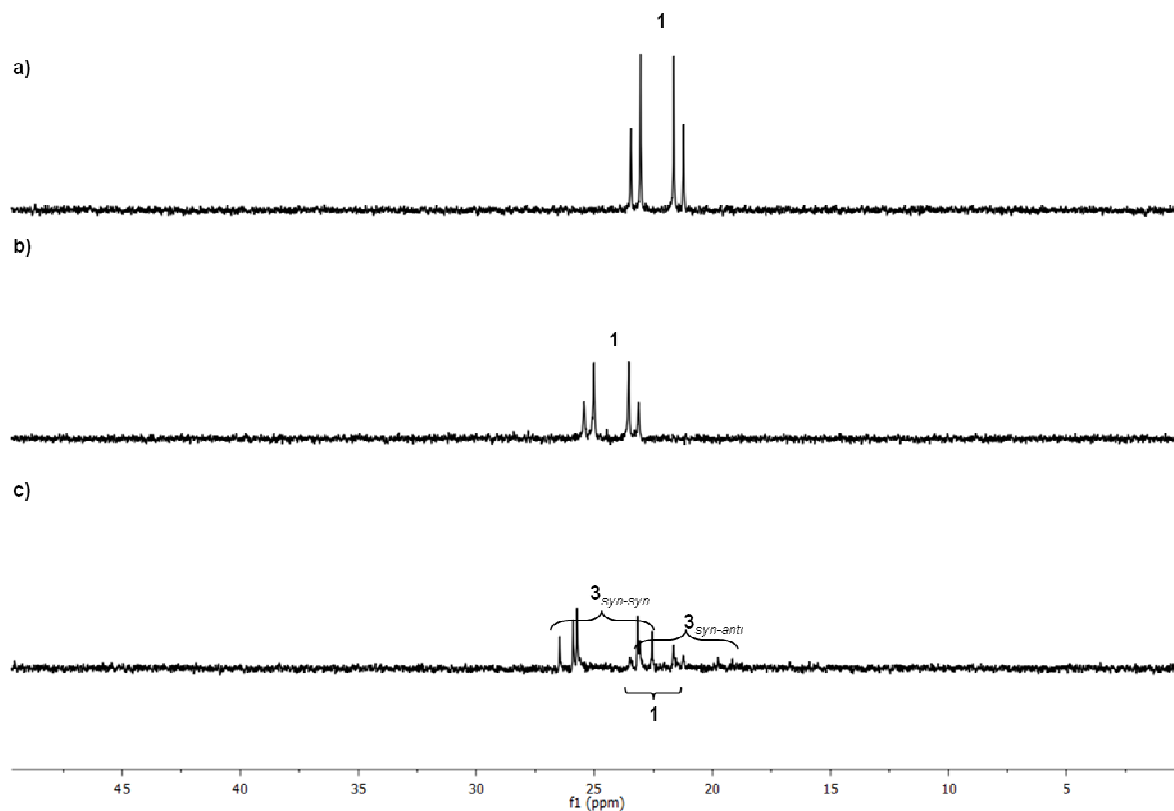
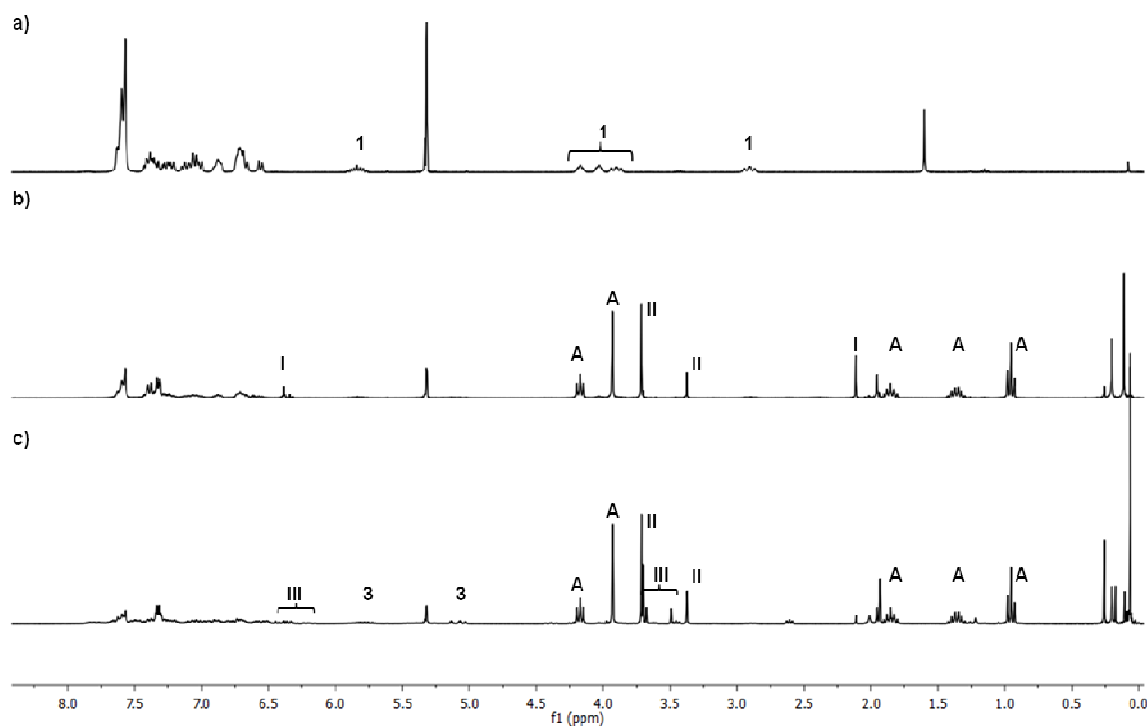


Fig. S8. HR-MS-TOF<sup>+</sup> spectrum of complex 4

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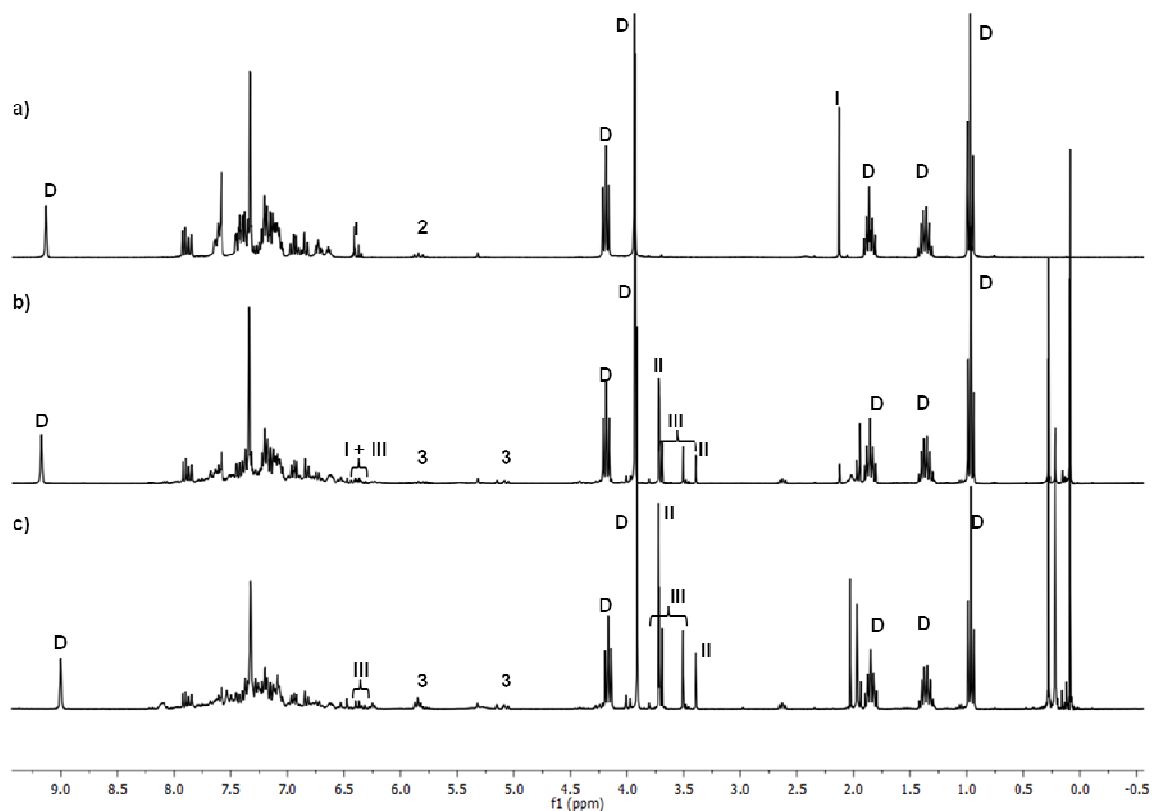


**Fig. S9.**  $^{31}\text{P}$  NMR spectra for stoichiometric AAA reaction using **1** in  $\text{CD}_2\text{Cl}_2$ . a) **1**; b) In presence of  $[\text{BMIM}][\text{BF}_4]$  (**A**) and 1 equiv of **I**, **II** and BSA; c) Addition of another equivalent of **II** and BSA.



**Fig. S10.**  $^1\text{H}$  NMR spectra for stoichiometric AAA reaction using **1** in  $\text{CD}_2\text{Cl}_2$ . a) **1**; b) In presence of  $[\text{BMIM}][\text{BF}_4]$  (**A**) and of 1 equiv of **I**, **II** and BSA; c) Addition of another equivalent of **II** and BSA.





**Fig. S11.**  $^1\text{H}$  NMR spectra for stoichiometric AAA reaction using **2** (*(S)*-BINAP:Pd = 2.5) in  $\text{CD}_2\text{Cl}_2$ . a) **2** in presence of [BMIM][NTf<sub>2</sub>] (**D**) and 1 equiv. of **I**; b) Addition of 1 equiv of **II** and BSA; c) Addition of another equivalent of **II** and BSA.

REFERENCES:

1. Complete characterisation of [HDMIM][BF<sub>4</sub>] in: D.-Q. Xu, B.-Y. Liu, S.-P. Luo, Z.-Y. Xu, Y.-C. Shen, *Synthesis*, 2003, **17**, 2626.
2. C. Betti, D. Landini, A. Maia, *Tetrahedron*, 2008, **64**, 1689.