**Bis(pyrazolyl)palladium(II) complexes as catalysts for Mizoroki-Heck cross-coupling reactions**

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Supplementary information

**Table SI-1:** Effect of temperature in Mizoroki-Heck cross-coupling reactions.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Cat.** | **Temp (oC)** | **Conv. (%)** | **TON** | **TOF**  **(h-1)** | **Selectivity (%)** | |
| *trans*-stilbene | *cis-*stilbene |
| **1** | **5** | 80 | 21 | 43 | 11 | 88 | 12 |
| **2** | **6** | 80 | 24 | 47 | 12 | 82 | 18 |
| **3** | **7** | 80 | 15 | 29 | 7 | 86 | 14 |
| **4** | **8** | 80 | 20 | 40 | 10 | 86 | 14 |
| **5** | **5** | 100 | 68 | 135 | 34 | 85 | 15 |
| **6** | **6** | 100 | 60 | 121 | 30 | 87 | 13 |
| **7** | **7** | 100 | 69 | 137 | 34 | 85 | 15 |
| **8** | **8** | 100 | 53 | 105 | 26 | 88 | 12 |
| **9** | **5** | 120 | 72 | 144 | 36 | 86 | 14 |
| **10** | **6** | 120 | 72 | 143 | 36 | 86 | 14 |
| **11** | **7** | 120 | 75 | 151 | 38 | 87 | 13 |
| **12** | **8** | 120 | 71 | 142 | 35 | 86 | 14 |
| **13** | **5** | 130 | 100 | 200 | 50 | 87 | 13 |
| **14** | **6** | 130 | 100 | 200 | 50 | 86 | 14 |
| **15** | **7** | 130 | 100 | 200 | 50 | 85 | 15 |
| **16** | **8** | 130 | 100 | 200 | 50 | 87 | 13 |
| **17** | **5** | 140 | 100 | 200 | 50 | 82 | 18 |
| **18** | **6** | 140 | 100 | 200 | 50 | 74 | 26 |
| **19** | **7** | 140 | 100 | 200 | 50 | 78 | 22 |
| **20** | **8** | 140 | 100 | 200 | 50 | 79 | 21 |

Reactions carried out in DMF (1.2 mL) with 0.66 mmol of iodobenzene, 0.73 mmol of styrene, 1.32 mmol of Et3N and 3.3×10-3 mmol Pd catalyst (loading= 0.5 mol%) at various temperatures and 600 rpm for 4 h. Using *n*-decane as internal standard. Cat. = catalyst, Conv. = conversion. Average error estimate; **5** (±0.5724), **6** (±0.5524), **7** (±0.4126), **8** (±0.4413).

**Table SI-2:** Base variation in Mizoroki-Heck cross-coupling reactions.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Cat.** | **Base** | **Conv. (%)** | **TON** | **TOF (h-1)** | **Selectivity (%)** | |
| *trans*-stilbene | *cis-*stilbene |
| **1** | **5** | KOH | 100 | 200 | 50 | 87 | 13 |
| **2** | **6** | KOH | 100 | 200 | 50 | 87 | 13 |
| **3** | **7** | KOH | 100 | 200 | 50 | 86 | 14 |
| **4** | **8** | KOH | 100 | 200 | 50 | 87 | 13 |
| **5** | **5** | K2CO3 | 0 | 0 | 0 | 0 | 0 |
| **6** | **6** | K2CO3 | 0 | 0 | 0 | 0 | 0 |
| **7** | **7** | K2CO3 | 0 | 0 | 0 | 0 | 0 |
| **8** | **8** | K2CO3 | 0 | 0 | 0 | 0 | 0 |
| **9** | **5** | Et3N | 100 | 200 | 50 | 86 | 14 |
| **10** | **6** | Et3N | 100 | 200 | 50 | 86 | 14 |
| **11** | **7** | Et3N | 100 | 200 | 50 | 85 | 15 |
| **12** | **8** | Et3N | 100 | 200 | 50 | 87 | 13 |
| **13** | **5** | C5H5N | 0 | 0 | 0 | 0 | 0 |
| **14** | **6** | C5H5N | 0 | 0 | 0 | 0 | 0 |
| **15** | **7** | C5H5N | 0 | 0 | 0 | 0 | 0 |
| **16** | **8** | C5H5N | 0 | 0 | 0 | 0 | 0 |

Reactions carried out in DMF (1.2 mL) with 0.66 mmol of iodobenzene, 0.73 mmol of styrene, 1.32 mmol of base and 3.3×10-3 mmol Pd catalyst (loading= 0.5 mol%) at 130o C and 600 rpm for 4h. Using *n*-decane as internal standard. Cat. = catalyst, Conv. = conversion. Average error estimate: **5** (±0.0151), **6** (±0.0245), **7** (±0.0173), **8** (±0.0291).

**Table SI-3:** Catalyst loading optimization for Mizoroki-Heck cross-coupling reactions.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Cat. (loading mol%)** | **Conv. (%)** | **TON** | **TOF (h-1)** | **Selectivity (%)** | |
| *trans*-stilbene | *Cis-*stilbene |
| **1** | **5** (0.38) | 100 | 267 | 67 | 85 | 15 |
| **2** | **6** (0.38) | 100 | 267 | 67 | 87 | 13 |
| **3** | **7** (0.38) | 100 | 267 | 67 | 87 | 13 |
| **4** | **8** (0.38) | 100 | 267 | 67 | 87 | 13 |
| **5** | **5** (0.25) | 100 | 400 | 100 | 86 | 14 |
| **6** | **6** (0.25) | 100 | 400 | 100 | 88 | 12 |
| **7** | **7** (0.25) | 100 | 400 | 100 | 87 | 13 |
| **8** | **8** (0.25) | 100 | 400 | 100 | 86 | 14 |
| **9** | **5** (0.13) | 100 | 800 | 200 | 85 | 15 |
| **10** | **6** (0.13) | 100 | 800 | 200 | 84 | 16 |
| **11** | **7** (0.13) | 100 | 800 | 200 | 85 | 15 |
| **12** | **8** (0.13) | 100 | 800 | 200 | 87 | 13 |
| **13** | **5** (0.0625) | 100 | 1600 | 400 | 89 | 11 |
| **14** | **6** (0.0625) | 100 | 1600 | 400 | 88 | 12 |
| **15** | **7** (0.0625) | 100 | 1600 | 400 | 87 | 13 |
| **16** | **8** (0.0625) | 100 | 1600 | 400 | 88 | 12 |
| **17** | **5** (0.0375) | 97 | 2586 | 646 | 90 | 10 |
| **18** | **6** (0.0375) | 99 | 2629 | 657 | 90 | 10 |
| **19** | **7** (0.0375) | 96 | 2565 | 641 | 90 | 10 |
| **20** | **8** (0.0375) | 94 | 2516 | 629 | 90 | 10 |
| **21** | **5** (0.0094) | 52 | 5605 | 1401 | 89 | 11 |
| **22** | **6** (0.0094) | 53 | 5671 | 1418 | 89 | 11 |
| **23** | **7** (0.0094) | 54 | 5858 | 1464 | 89 | 11 |
| **24** | **8** (0.0094) | 45 | 4891 | 1223 | 89 | 11 |
| **25** | **5** (0.00625) | 20 | 3177 | 794 | 96 | 4 |
| **26** | **6** (0.00625) | 18 | 2910 | 728 | 94 | 6 |
| **27** | **7** (0.00625) | 20 | 3189 | 797 | 94 | 4 |
| **28** | **8** (0.00625) | 23 | 3612 | 903 | 95 | 5 |

Reactions carried out in DMF (1.2 mL) with 1.0 eq of iodobenzene, 1.1 eq of styrene, 2.0 eq of Et3N and varied Pd catalyst loading at 130o C and 600 rpm for 4h. Using *n*-decane as internal standard. Cat. = catalyst, Conv. = conversion. Average error estimate; **5** (±0.3323), **6** (±0.2235), **7** (±0.3855), **8** (±0.3412)

**Table SI-4:** Conversion as a function of time in Mizoroki-Heck cross-coupling reactions.

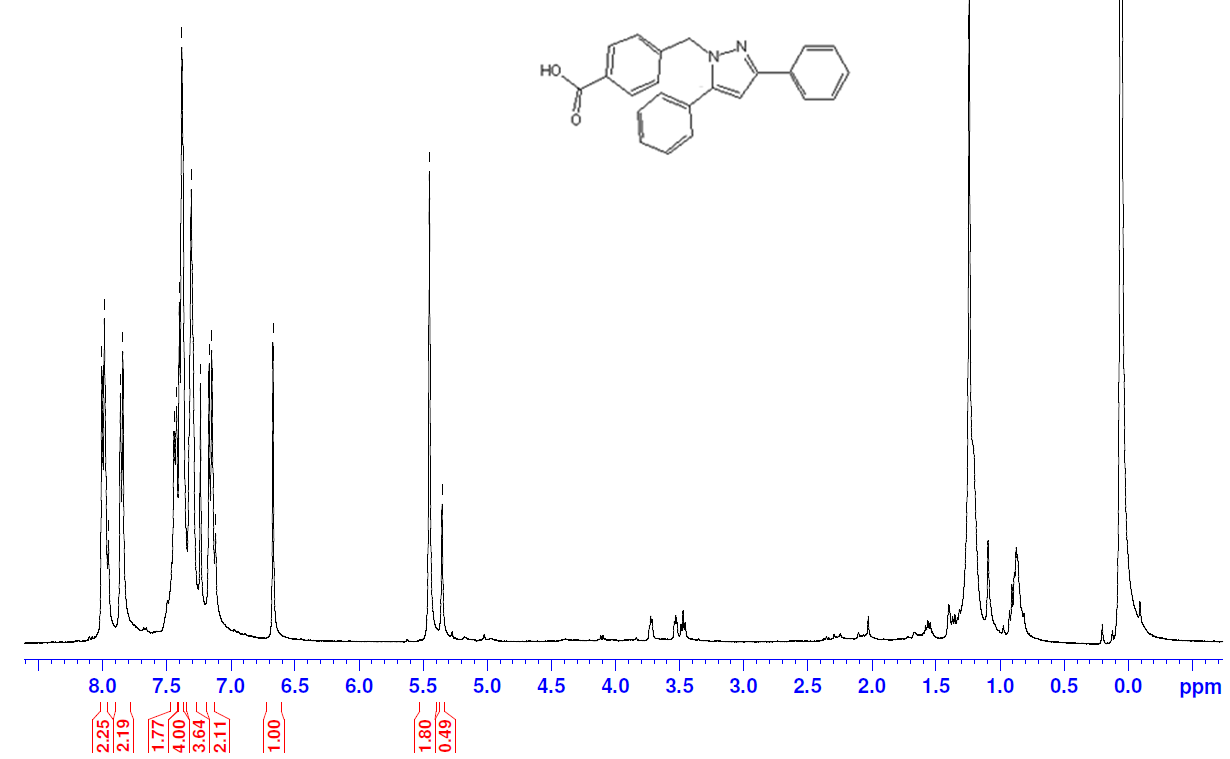
|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Cat.** | **Time (h)** | **Conv. (%)** | **TON** | **TOF**  **(h-1)** | **Selectivity (%)** | |
| *trans-*stilbene | *cis-*stilbene |
| **1** | **5** | 0.5 | 27 | 1437 | 718 | 90 | 10 |
| **2** | **6** | 0.5 | 55 | 2929 | 1465 | 90 | 10 |
| **3** | **7** | 0.5 | 57 | 1507 | 3015 | 89 | 11 |
| **4** | **8** | 0.5 | 74 | 1970 | 3939 | 89 | 11 |
| **5** | **5** | 1 | 72 | 1927 | 1927 | 89 | 11 |
| **6** | **6** | 1 | 80 | 2146 | 2146 | 89 | 11 |
| **7** | **7** | 1 | 85 | 2272 | 2272 | 89 | 11 |
| **8** | **8** | 1 | 90 | 2393 | 2393 | 87 | 13 |
| **9** | **5** | 1.5 | 90 | 2394 | 1596 | 88 | 12 |
| **10** | **6** | 1.5 | 94 | 2497 | 1665 | 88 | 12 |
| **11** | **7** | 1.5 | 94 | 2513 | 1675 | 89 | 11 |
| **12** | **8** | 1.5 | 90 | 2393 | 1596 | 90 | 10 |
| **13** | **5** | 2 | 90 | 2412 | 1206 | 91 | 9 |
| **14** | **6** | 2 | 96 | 2560 | 1280 | 89 | 11 |
| **15** | **7** | 2 | 94 | 2513 | 1257 | 90 | 10 |
| **16** | **8** | 2 | 93 | 2490 | 1245 | 90 | 10 |
| **17** | **5** | 3 | 94 | 2508 | 836 | 88 | 12 |
| **18** | **6** | 3 | 97 | 2597 | 866 | 90 | 10 |
| **19** | **7** | 3 | 98 | 2604 | 868 | 89 | 11 |
| **20** | **8** | 3 | 95 | 2525 | 842 | 87 | 13 |
| **21** | **5** | 4 | 97 | 2586 | 646 | 90 | 10 |
| **22** | **6** | 4 | 99 | 2629 | 657 | 90 | 10 |
| **23** | **7** | 4 | 96 | 2565 | 641 | 90 | 10 |
| **24** | **8** | 4 | 94 | 2516 | 629 | 90 | 10 |

Reactions carried out in DMF (1.2 mL) with 26.4 mmol of iodobenzene, 29.04 mmol of styrene, 52.8 mmol of Et3N and 3.3×10-3 mmol Pd catalyst (loading= 0.0375 mol%) at 130 oC and 600 rpm for varied reaction periods. Using *n*-decane as internal standard. Cat. = catalyst, Conv. = conversion. Average error estimate; **5** (±0.2276), **6** (±0.3321), **7** (±0.2988), **8** (±0.3231)

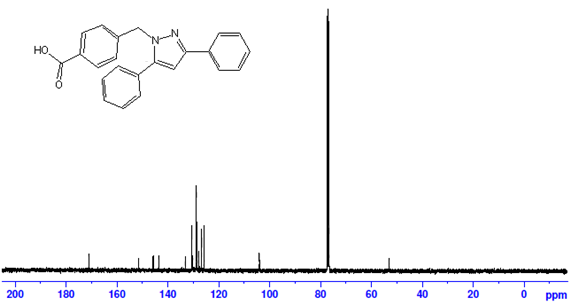
**Table SI-5:** Mercury poisoning test in Mizoroki-Heck cross-coupling reactions with (pre)catalysts **8-11**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Entry** | **Cat.** | **Amount of Hg (mg)** | **Conv.**  **(%)** | **TON** | **TOF**  **(h-1)** | **Selectivity (%)** | |
| *trans-*stilbene | *cis-*stilbene |
| **1** | **5** | 0 | 100 | 200 | 50 | 87 | 13 |
| **2** | **6** | 0 | 100 | 200 | 50 | 86 | 14 |
| **3** | **7** | 0 | 100 | 200 | 50 | 85 | 15 |
| **4** | **8** | 0 | 100 | 200 | 50 | 87 | 13 |
| **5** | **5** | 1 | 100 | 200 | 50 | 89 | 11 |
| **6** | **6** | 1 | 100 | 200 | 50 | 87 | 13 |
| **7** | **7** | 1 | 100 | 200 | 50 | 88 | 12 |
| **8** | **8** | 1 | 100 | 200 | 50 | 86 | 14 |
| **9** | **9** | 0 | 100 | 200 | 50 | 89 | 11 |
| **10** | **9** | 1 | 100 | 200 | 50 | 89 | 11 |

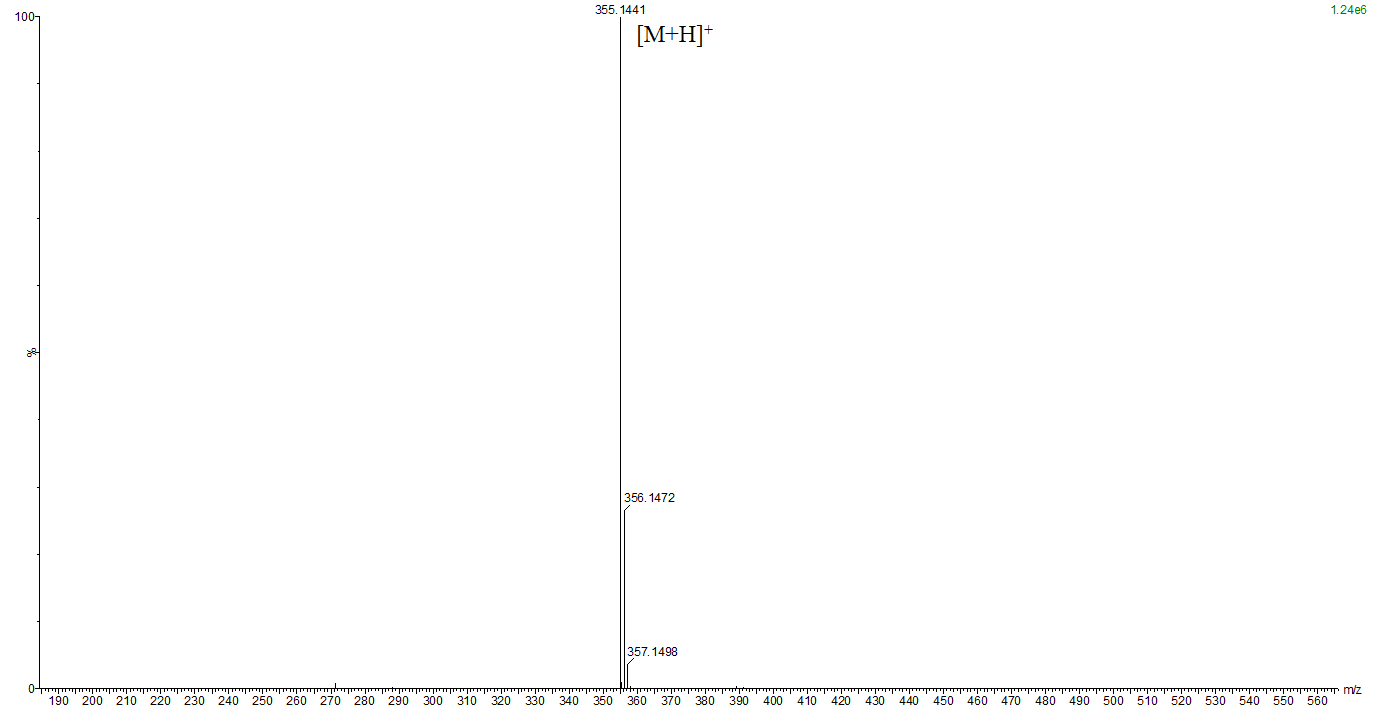
Reactions carried out in DMF (1.2 mL) with 0.66 mmol of iodobenzene, 0.73 mmol of styrene, 1.32 mmol of Et3N and 3.3×10-3 mmol Pd catalyst (loading= 0.5 mol%) at 130 oC and 600 rpm for 4 h. Using *n*-decane as internal standard Cat. = catalyst, Conv. = conversion. Average error estimate; **5** (±0.2264), **6** (±0.2817), **7** (±0.3100), **8** (±0.2977), **9** (±0.3342)



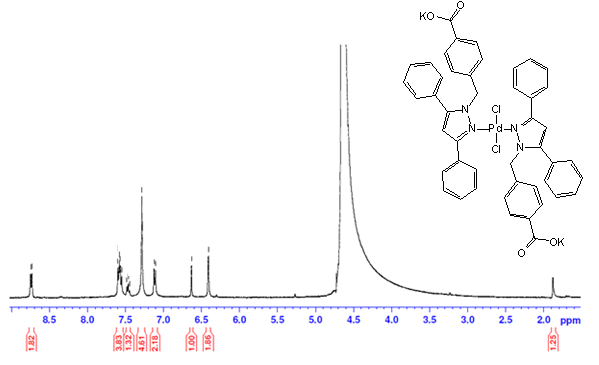
**Figure SI-1:**1HNMR spectrum of **1a**, recorded in CDCl3.



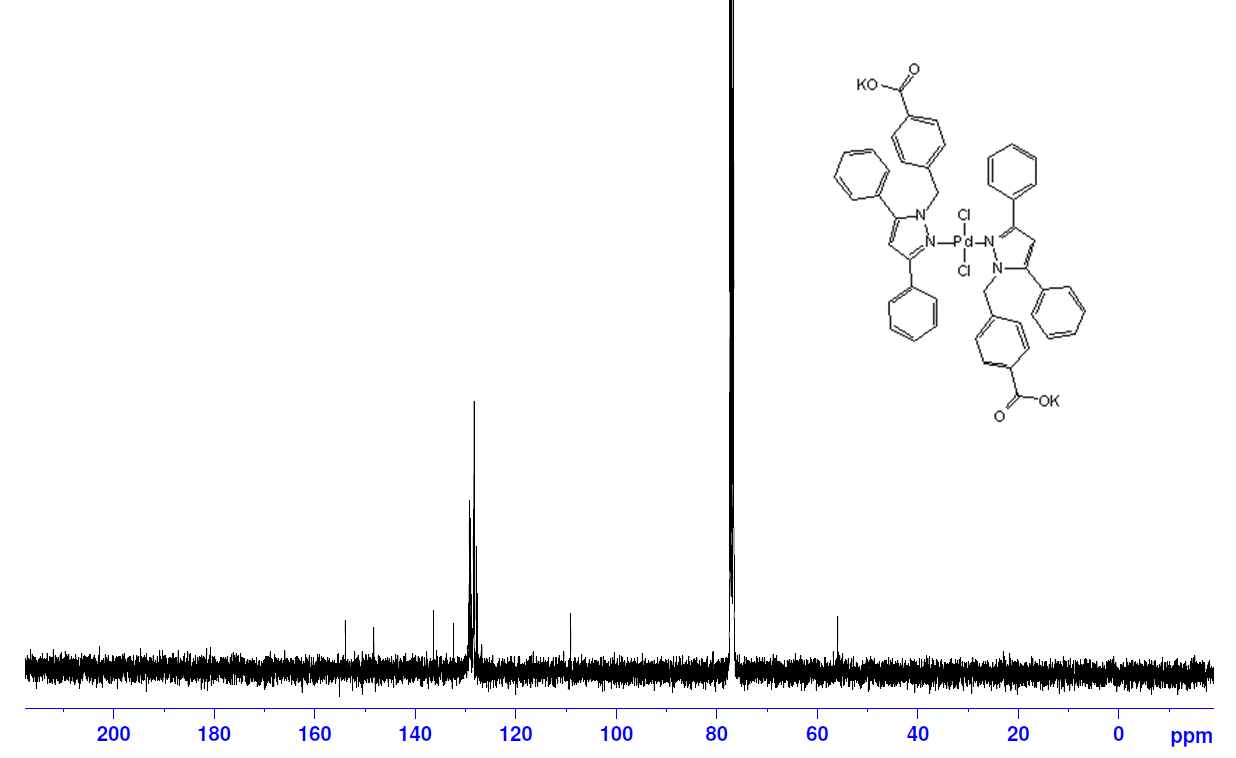
**Figure SI-2:**13C{1H} NMR spectrum of **1a**, recorded in CDCl3.



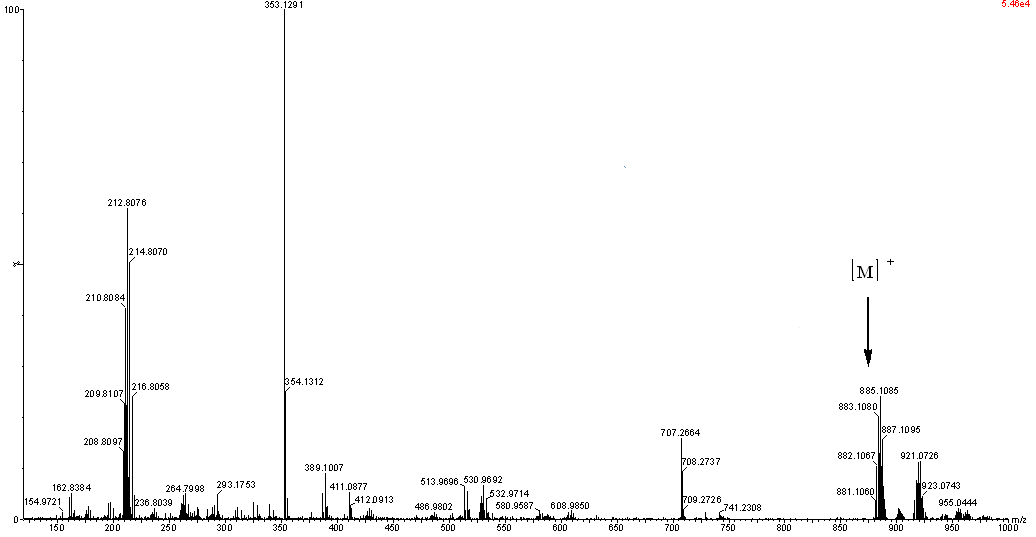
**Figure SI-3:**Mass spectrum of **1a**



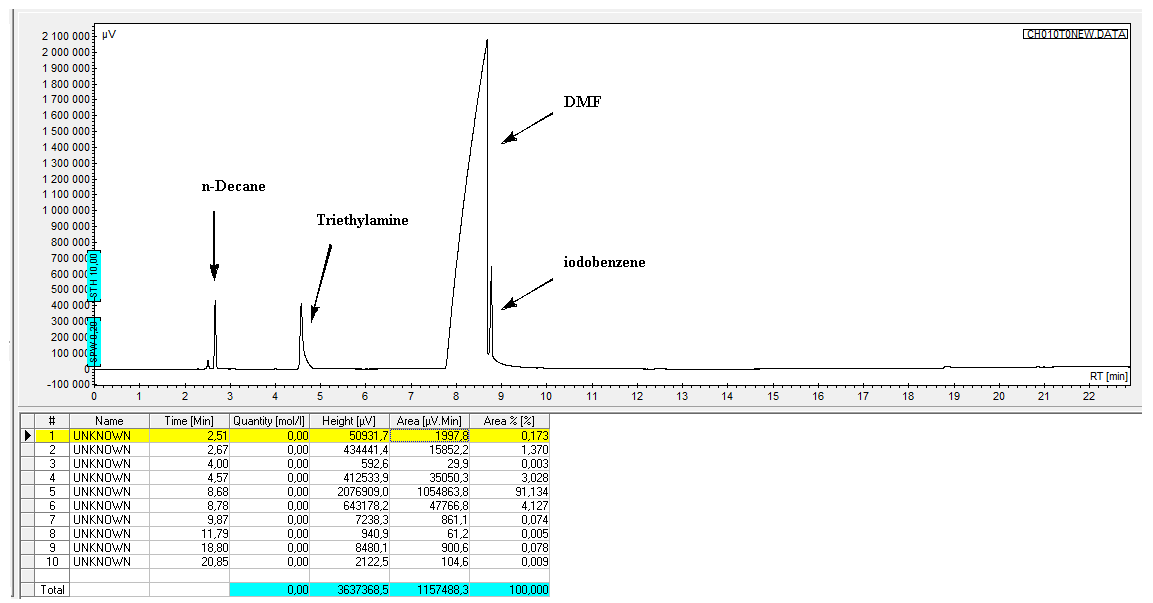
**Figure SI-4:** 1H NMR spectrum of complex **9+**KOH, recorded in D2O.



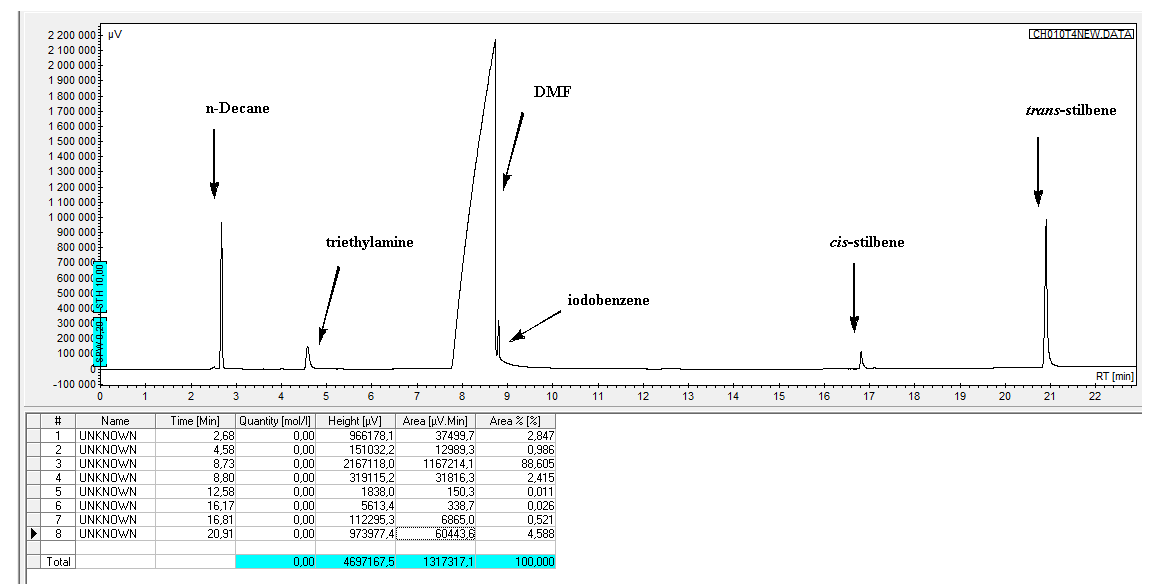
**Figure SI-5:** 13C{1H} spectrum of complex **9+**KOH, recorded in CDCl3.



**Figure SI-6:** Mass spectrum of **9**



**Figure SI-7:** Representative Gas chromatogram before Mizoroki-Heck cross-coupling reaction.

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**Figure SI-8:** Representative gas chromatogram after Mizoroki-Heck cross-coupling reaction