Advanced Synthesis & Catalysis

First Application of Secondary Phosphines as Supporting Ligands for the Palladium-Catalyzed Heck Reaction: Efficient Activation of Aryl - Chlorides

Anita Schnyder, Thomas Aemmer, Adriano F. Indolese, Ulrich Pittelkow, Martin Studer *
[a] Solvias AG, Klybeckstrasse 191, Postfach, 4002 Basel, Switzerland.

Fax: +41-61-686-6100

E-mail: martin.studer@solvias.com

Experimental Section

General. All experiments were carried out in a 50 mL Schlenk - tubes equipped with a magnet-driven stirrer. Solvents were degassed prior to use by purging them 15 minutes with argon.

Aryl halides, ligands, reagents and solvents were purchased from Fluka Chemical Co. The 20% Pd (w/w) solution in concentrated HCl was obtained from Degussa, $Pd(OAc)_2$ was purchased from Fluka and $PdCl_2(PPh_3)_2$ from Avocado. Diethyleneglycol di-n-butylether (internal GC standard) was purchased from Fluka Chemical Co.

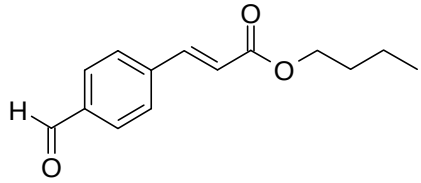
The catalysts were generally added as solution in DMA. The catalyst solutions were prepared by dissolving $Pd(OAc)_2$ or diluting a $PdCl_2$ solution (20% Pd w/w in conc. HCl) with DMA to obtain a 0.25 M catalyst solution. The $PdCl_2$ solution was stable for several month whereas the $Pd(OAc)_2$ must be prepared afresh before each experiment.

^1H and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker dpx 300 spectrometer. Chemical shifts (d) are given in ppm and refer to TMS as internal standard. IR spectra

were recorded on a Perkin Elmer 1710 spectrometer. Gas chromatography was performed on a Fisons GC 8000 with a DB-17 column and helium as the carrier gas using di(ethyleneglycol) di-*n*-butyl ether as internal standard. The combustion analyses were carried out by Solvias AG, Switzerland.

All experiments were carried out according to the general procedure given in the main paper.

Table 2, Entry 1



Butyl *p*-formylcinnamate. The reaction of 4-chlorobenzaldehyde (0.70 g, 5.0 mmol) was effected using the general procedure to afford 0.86 g (3.57 mmol, 71%) of the title compound as an orange oil. R_f = 0.38 (EtOAc:hexane 1 : 4);

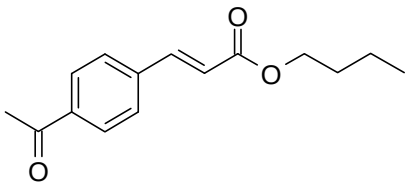
^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 10.05 (s, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 16.1 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 6.58 (d, *J* = 16.1 Hz, 1H), 4.25 (t, *J* = 6.7 Hz, 2H), 1.72 (quintett, *J* = 7.2 Hz, 2H), 1.46 (sextett, *J* = 7.6 Hz, 2H), 0.99 (t, *J* = 7.4 Hz, 3H);

^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 297 K) *d* 191.8, 166.8, 143.2, 140.6, 137.5, 130.5 (2C), 128.9 (2C), 121.9, 65.1, 31.1, 19.6, 14.1;

IR (KBr, cm^{-1}) 2957, 1704, 1639, 1314;

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.27; H, 6.85.

Table 2, Entry 2



Butyl *p*-acetylcinnamate. The reaction of 4-chloroacetophenone (0.77 g, 5.0 mmol) was effected using the general procedure to afford 0.74 g (3.28 mmol, 66%) of the title compound as a yellow oil. R_f = 0.19 (EtOAc:hexane 1 : 20);

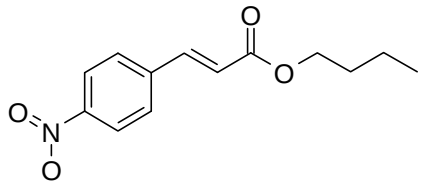
^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) δ 7.99 (d, J = 8.4 Hz, 2H), 7.71 (d, J = 16.1 Hz, 1H), 7.63 (d, J = 8.5 Hz, 2H), 6.55 (d, J = 16.04 Hz, 1H), 4.25 (t, J = 6.7 Hz, 2H), 2.64 (s, 3H), 1.94 (quintett, J = 7.5 Hz, 2H), 1.46 (sextett, J = 7.6 Hz, 2H), 0.99 (t, J = 7.4 Hz, 3H);

^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 297 K) δ 197.7, 167.0, 143.4, 139.2, 138.4, 129.2 (2C), 128.5 (2C), 121.2, 65.1, 31.1, 27.1, 19.8, 14.1;

IR (neat, cm^{-1}) 2957, 1711, 1635, 1310, 1263;

Anal. Calcd for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37; O, 19.49. Found: C, 72.80; H, 7.35 ; O, 19.60.

Table 2, Entry 3



Butyl *p*-nitrocinnamate. The reaction of 4-chloronitrobenzene (0.79 g, 5.0 mmol) was effected using the general procedure to afford 1.03 g (4.10 mmol, 82%) of the title compound as yellow crystals. R_f = 0.37 (EtOAc:hexane 1 : 20);

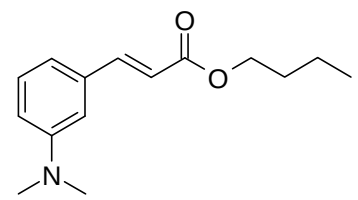
^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) δ 8.27 (d, J = 8.9 Hz, 2H), 7.72 (d, J = 16.0 Hz, 1H), 7.69 (d, J = 8.8 Hz, 2H), 6.58 (d, J = 16.1 Hz, 1H), 4.26 (t, J = 6.7 Hz, 2H), 1.77-1.67 (m, 2H), 1.50-1.40 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H);

^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 297 K) δ 166.5, 148.9, 142.0, 141.2, 129.0 (2C), 124.6 (2C), 123.0, 65.3, 31.1, 19.6, 14.1;

IR (KBr, cm^{-1}) 2957, 1708, 1639, 1599, 1516, 1342;

Anal. Calcd for $C_{13}H_{15}NO_4$: C, 62.64; H, 6.07; N, 5.62. Found: C, 62.57; H, 6.04; N, 5.72.

Table 2, Entry 4



Butyl *m*-*N*,*N*-dimetylaminocinnamate. The reaction of 3-*N*,*N*-dimethylchloroaniline (0.78 g, 5.0 mmol) was effected using the general procedure to afford 1.06 g (4.5 mmol, 90%) of the title compound as yellow crystals. R_f = 0.20 (EtOAc:hexane 1 : 10);

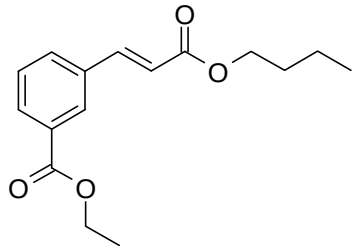
^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 7.71 (d, *J* = 16.0 Hz, 1H), 7.27 (t, *J* = 7.9 Hz, 1H), 6.93 (d, *J* = 7.6 Hz, 1H), 6.86 (t, *J* = 1.9 Hz, 1H), 6.79 (dd, *J* = 8.2 Hz, 2.4 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 3.00 (s, 6H), 1.77-1.67 (m, 2H), 1.53-1.43 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H);

^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 297 K) *d* 167.7, 151.2, 146.1, 135.6, 129.8, 118.2, 116.8, 114.9, 112.3, 64.8 (2C), 40.9, 31.2, 19.6, 14.2;

IR (KBr, cm^{-1}) 2956, 1717, 1638, 1597, 1175;

Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66; O, 12.94. Found: C, 72.92; H, 8.60; N, 5.64; O, 12.90.

Table 2, Entry 5



Butyl *m*-ethyloxycarbonyl-cinnamate. The reaction of ethyl 3-chlorobenzoate (0.86 g, 5.0 mmol) was effected using the general procedure to afford 0.75 g (2.73 mmol, 55%) of the title compound as a brown oil. R_f = 0.38 (EtOAc:hexane 1 : 4);

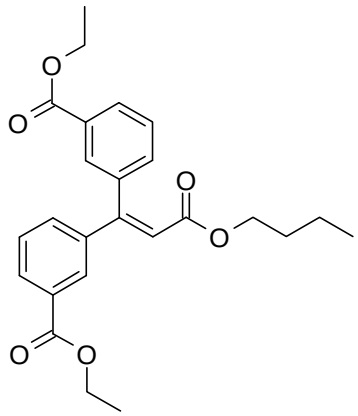
^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 8.22 (t, *J* = 1.7 Hz, 1H), 8.07 (dt, *J* = 7.7 Hz, 1.4 Hz, 1H), 7.75-7.69 (m, 2H), 7.48 (t, *J* = 7.8 Hz, 1H), 6.54 (d, *J* = 16.1 Hz, 1H), 4.42 (q, *J* = 7.1 Hz, 2H), 4.24 (t, *J* = 6.7 Hz, 2H), 1.77-1.67 (m, 2H), 1.50-1.41 (m, 5H), 0.99 (t, *J* = 7.4 Hz, 3H);

^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 297 K) *d* 167.2, 166.4, 143.8, 135.2, 132.5, 131.7, 131.4, 129.4, 129.3, 120.0, 65.0, 61.7, 31.2, 19.6, 14.7, 14.1;

IR (neat, cm^{-1}) 2957, 1718, 1639, 1303, 1194;

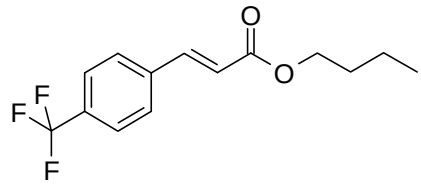
Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30; O, 23.16. Found: C, 69.33; H, 7.34; O, 23.15.

In addition, 0.19 g (0.45 mmol, 9%) **Butyl 3,3-bis-(*m*-ethyloxycarbonyl-phenyl)-acrylate.** were isolated. R_f = 0.09 (EtOAc:hexane 1 : 10):



^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 8.12-8.04 (m, 3H), 7.90 (td, *J* = 1.7 Hz, *J* = 0.5 Hz, 1H), 7.50 (dt, *J* = 7.7 Hz, 0.6 Hz, 1H), 7.44-7.38 (m, 3H), 6.48 (s, 1H), 4.44-4.35 (m, 4H), 4.02 (t, *J* = 6.6 Hz, 2H), 1.50-1.36 (m, 8H), 1.30-1.20 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

Table 2, Entry 6



Butyl *p*-trifluoromethylcinnamate. The reaction of 1-chloro-4-(trifluoromethyl)-benzene (0.90 g, 5.0 mmol) was effected using the general procedure to afford 1.03 g (3.8 mmol, 76%) of the title compound as an orange oil. R_f = 0.48 (EtOAc:hexane 1 : 10);

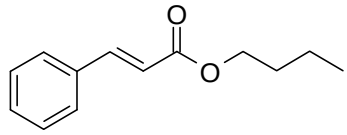
^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 7.71 (d, *J* = 16.1 Hz, 1H), 6.67-6.63 (m, 4H), 6.53 (d, *J* = 16.1 Hz, 1H), 4.25 (t, *J* = 6.7 Hz, 2H), 1.78-1.68 (m, 2H), 1.53-1.40 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H);

^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 297 K) *d* 166.7, 142.9, 131.9 (q, *J* = 33 Hz, 1C), 128.4 (2C), 126.1 (q, *J* = 11.4 Hz, 2C), 124.1 (q, *J* = 272 Hz, 1C), 121.1, 65.0, 31.0, 19.4, 14.0;

IR (neat, cm^{-1}) 2957, 1718, 1642, 1324, 1172;

Anal. Calcd for $C_{14}H_{15}F_3O_2$: C, 61.76; H, 5.55; O, 11.75. Found: C, 61.71; H, 5.73; O, 12.02.

Table 2, Entry 7



Butyl cinnamate. The reaction of chlorobenzene (0.56 g, 5.0 mmol) was effected using the general procedure to afford 0.77 g (3.75 mmol, 75%) of the title compound as a yellow oil. R_f = 0.32 (EtOAc:hexane 1 : 10);

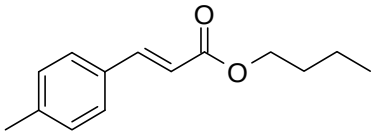
^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) δ 7.71 (d, J = 16.0 Hz, 1H), 7.57-7.53 (m, 2H), 7.42-7.38 (m, 3H), 6.47 (d, J = 16.0 Hz, 1H), 4.24 (t, J = 6.7 Hz, 2H), 1.76-1.67 (m, 2H), 1.50-1.43 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H);

^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 297 K) δ 167.5, 144.9, 134.9, 130.6, 129.3 (2C), 128.4 (2C), 118.7, 64.8, 31.2, 19.6, 14.2;

IR (neat, cm^{-1}) 2956, 1711, 1635, 1310, 1169;

Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90; O, 15.67. Found: C, 76.13; H, 7.96; O, 15.79.

Table 2, Entry 8



Butyl *p*-methylcinnamate. The reaction of 4-chlorotoluene (0.63 g, 5.0 mmol) was effected using the general procedure to afford 0.95 g (4.35 mmol, 87%) of the title compound as an orange oil. R_f = 0.40 (EtOAc:hexane 1 : 10);

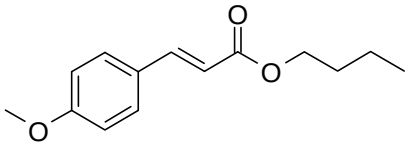
^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) δ 7.68 (d, J = 16.0 Hz, 1H), 7.44 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 6.42 (d, J = 16.0 Hz, 1H), 4.22 (t, J = 6.7 Hz, 2H), 2.39 (s, 3H), 1.74-1.68 (m, 2H), 1.50-1.42 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H);

^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 297 K) δ 167.7, 144.9, 141.0, 132.2, 130.0 (2C), 128.4 (2C), 117.6, 64.7, 31.2, 21.9, 19.6, 14.2;

IR (neat, cm^{-1}) 2957, 1711, 1635, 1310, 1169;

Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31; O, 14.66. Found: C, 76.98; H, 8.43; O, 14.41.

Table 2, Entry 9



Butyl *p*-methoxycinnamate. The reaction of 4-chloroanisole (0.71 g, 5.0 mmol) was effected using the general procedure to afford 0.83 g (3.55 mmol, 71%) of the title compound as a colorless oil.

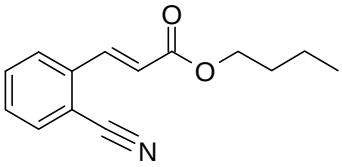
^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 7.66 (d, *J* = 16.0 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 6.33 (d, *J* = 16.0 Hz, 1H), 4.22 (t, *J* = 6.7 Hz, 2H), 3.86 (s, 3H), 1.73-1.68 (m, 2H), 1.51-1.42 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H);

^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 297 K) *d* 167.8, 161.7, 144.6, 130.1 (2C), 127.6, 116.2, 114.7 (2C), 64.7, 55.8, 31.2, 19.2, 14.2;

IR (neat, cm^{-1}) 2957, 1707, 1635, 1602, 1512, 1252;

Anal. Calcd for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74; O, 20.49. Found: C, 71.65; H, 7.84; O, 20.39.

Table 2, Entry 10



Butyl *o*-cyanocinnamate. The reaction of chlorobenzonitrile (0.69 g, 5.0 mmol) was effected using the general procedure but with 4 mol-% catalyst to afford 0.57 g (2.5 mmol, 50%) of the title compound as an orange oil. R_f = 0.15 (EtOAc:hexane 1 : 10);

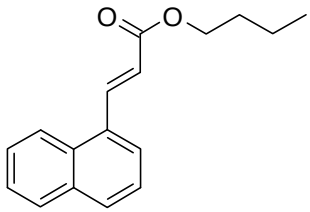
^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 7.99 (d, *J* = 16.0 Hz, 1H), 7.74 (t, *J* = 7.5 Hz, 2H), 7.64 (t, *J* = 7.1 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 1H), 6.63 (d, *J* = 16.0 Hz, 1H), 4.26 (t, *J* = 6.7 Hz, 2H), 1.73 (quint, *J* = 7.6 Hz, 2H), 1.46 (sextett, *J* = 7.6 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H);

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 297 K) *d* 166.3, 139.7, 137.8, 133.9, 133.4, 130.4, 127.4, 123.6, 117.5, 113.1, 65.3, 31.1, 19.6, 14.1;

IR (neat, cm^{-1}) 2957, 2225, 1715, 1639, 1480, 1317;

Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59; N, 6.11; O, 13.96. Found: C, 73.12; H, 6.72; N, 5.96; O, 13.96.

Table 2, Entry 11



Butyl 3-(1-naphthyl)-acrylate. The reaction of chloronaphthalene (0.81 g, 5.0 mmol) was effected using the general procedure to afford 0.48 g (1.9 mmol, 38%) of the title compound as a brown oil. R_f = 0.25 (EtOAc:hexane 1 : 20);

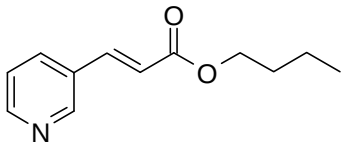
^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 8.55 (d, *J* = 15.8 Hz, 1H), 8.23 (dd, *J* = 8.3 Hz, 1.0 Hz, 1H), 7.93-7.89 (m, 2H), 7.78 (d, *J* = 7.2 Hz, 1H), 7.63-7.48 (m, 3H), 6.56 (d, *J* = 15.8 Hz, 1H), 4.29 (t, *J* = 6.7 Hz, 2H), 1.81-1.71 (m, 2H), 1.54-1.44 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H);

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 297 K) *d* 167.4, 142.0, 134.0, 132.3, 131.8, 130.8, 129.1, 127.2, 126.6, 125.9, 125.4, 123.8, 121.4, 64.9, 31.2, 19.7, 14.2;

IR (neat, cm^{-1}) 2957, 1711, 1631, 1303, 1252,1169;

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.17; H, 7.18.

Table 2, Entry 12



Butyl 3-(3-pyridyl)-acrylate. The reaction of 3-chloropyridine (0.57 g, 5.0 mmol) was effected using the general procedure to afford 0.86 g (4.2 mmol, 84%) of the title compound as a yellow oil. R_f = 0.18 (EtOAc:hexane 1:2);

^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 8.76 (d, *J* = 2.1 Hz, 1H), 8.61 (dd, *J* = 4.8 Hz; 1.6 Hz, 1H), 7.87-7.83 (m, 1H), 7.68 (d, *J* = 16.1 Hz, 1H), 7.36-7.32 (m, 1H), 7.52

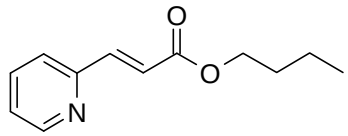
(d, *J* = 16.1 Hz, 1H), 4.24 (t, *J* = 6.7 Hz, 2H), 1.75-1.66 (m, 2H), 1.51-1.39 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H);

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 297 K) *d* 166.8, 151.3, 150.0, 141.2, 134.6, 130.7, 124.1, 120.9, 65.1, 31.1, 19.6, 14.1;

IR (neat, cm^{-1}) 2957, 1711, 1639, 1415, 1310;

Anal. Calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82. Found: C, 69.90; H, 7.38; N, 6.67.

Table 2, Entry 13



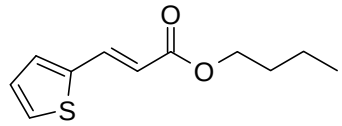
Butyl 3-(2-pyridyl)-acrylate. The reaction of 2-chloropyridine (0.57 g, 5.0 mmol) was effected using the general procedure but with 4 mol-% catalyst to afford 0.10 g (0.5 mmol, 10%) of the title compound as a yellow oil. R_f = 0.32 (EtOAc:hexane 1 : 4 with 1% NEt_3);

^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 8.66 (dt, *J* = 16.0 Hz, 0.7 Hz, 1H), 7.75-7.64 (m, 2H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.30-7.26 (m, 1H), 6.93 (d, *J* = 15.7 Hz, 1H), 4.23 (t, *J* = 6.6 Hz, 2H), 1.75-1.65 (m, 2H), 1.51-1.38 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H);

$^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$, 297 K) *d* 167.2, 153.4, 150.5, 143.6, 137.2, 124.6, 124.5, 122.9, 65.0, 31.1, 19.6, 14.1;

IR (neat, cm^{-1}) 2957, 1715, 1646,1581, 1465, 1432, 1317.

Table 2, Entry 15



Butyl 3-(2-thiophenyl)-acrylate. The reaction of 2-chlorothiophene (0.59 g, 5.0 mmol) was effected using the general procedure but with 4 mol-% catalyst to afford 0.23 g (1.1 mmol, 22%) of the title compound as a brown oil. R_f = 0.30 (EtOAc:hexane 1:10);

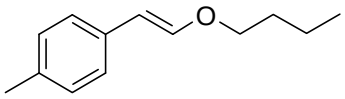
^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 7.79 (d, *J* = 15.7 Hz, 1H), 7.39 (dd, *J* = 5.1 Hz; 0.9 Hz, 1H), 7.28-7.26 (m, 1H), 7.07 (dd, *J* = 5.1 Hz; 3.6 Hz, 1H), 6.26 (d, *J* = 15.7 Hz, 1H), 4.21 (t, *J* = 6.7 Hz, 2H), 1.75-1.65 (m, 2H), 1.51-1.39 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H);

^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 297 K) *d* 167.3, 140.0, 137.4, 131.2, 128.7, 128.4, 117.5, 64.8, 31.2, 19.6, 14.1;

IR (neat, cm^{-1}) 2957, 1708, 1624, 1306;

Anal. Calcd for $C_{11}H_{14}O_2S$: C, 62.83; H, 6.71; O, 15.25; S, 15.22. Found: C, 62.71; H, 6.62; O, 15.16; S, 15.41.

Table 2, Entry 16



1-Butoxy-2-(*p*-tolyl)-ethene. The reaction of 4-chlorotoluene (0.63 g, 5.0 mmol) and butylvinylether (0.55 g, 5.5 mmol) was effected using the general procedure to afford 0.75 g (2.73 mmol, 55%) of the title compound as a mixture of *E/Z*-isomers. R_f = 0.38 (EtOAc:hexane 1 : 4);

^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) signals for the *E*-isomer *d* 7.16-7.10 (m, 4H), 6.98 (d, *J* = 13.0 Hz, 1H), 5.84 (d, *J* = 12.9 Hz, 1H), 3.85 (t, *J* = 6.5 Hz, 2H), 2.33 (s, 3H), 1.76-1.69 (m, 2H), 1.53-1.43 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H);

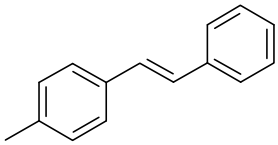
additional signals for the *Z*-isomer *d* 6.18 (d, *J* = 7.0 Hz, 1H), 5.20 (d, *J* = 7.0 Hz, 1H), 3.94 (t, *J* = 6.5 Hz, 2H), 2.34 (s, 3H);

IR (neat, cm^{-1}) 2957, 1653, 1639, 1512, 1158, 1093;

In addition, 0.13 g (0.45 mmol, 19%) ***p*-methyl-acetophenone** were isolated. R_f = 0.09 (EtOAc:hexane 1 : 10):

^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 7.88 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 2.60 (s, 3H), 2.43 (s, 3H);

Table 2, Entry 17



***p*-Methyl-stilbene.** The reaction of 4-chlorotoluene (0.63 g, 5.0 mmol) and styrene (0.57 g, 5.5 mmol) was effected using the general procedure to afford 0.77 g (3.95 mmol, 79%) of the title compound as a colorless solid. R_f = 0.56 (EtOAc:hexane 1 : 10);

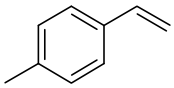
^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 7.58-7.14 (m, 11H), 2.42 (s, 3H);

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 297 K) *d* 138.0, 137.9, 135.0, 129.8, 129.1, 128.2, 127.8, 126.9, 126.8, 21.7;

IR (neat, cm^{-1}) 3022, 1592, 1509, 1447;

Anal. Calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 92.51; H, 7.31.

Table 2, Entry 18



***p*-Methylstyrene.** The reaction of 4-chlorotoluene (6.33 g, 50 mmol) and ethylene (30 bar, ca. 8g), Na_2CO_3 (8.1 g, 76 mmol), diadamantylphosphine (606 mg, 2.0 mmol), the catalyst solution (1 mmol Pd(II) in 4 mL DMA prepared by diluting 530 mg of a 20% Pd (w/w) solution in concentrated HCl with 3.5 mL DMA) and *N,N*-dimethylacetamide (DMA) (40 mL), in a 100 mL autoclave under argon was effected to afford 70% (4.13 g, 35 mmol) of the title compound as a colorless oil by distillation (bp: 80 °C at 70 mbar);

^{1}H NMR (300.1 MHz, $CDCl_3$, 297 K) *d* 7.35 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.73 (dd, *J* = 17.6 Hz; 10.9 Hz, 1H), 5.73 (dd, *J* = 17.6 Hz; 0.9 Hz, 1H), 5.22 (dd, *J* = 10.9 Hz; 0.9 Hz, 1H), 3.37 (s, 3H).

$^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$, 297 K) *d* 138.0, 137.1, 135.2, 129.6 (2C), 126.5 (2C), 113.2, 21.6;

IR (neat, cm^{-1}) 3007, 1628, 1512.