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A green catalyst for green chemistry: Synthesis and application of an olefin metathesis catalyst bearing a quaternary ammonium group

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Contents

1. General

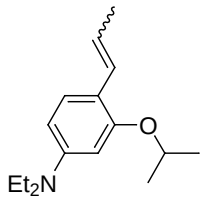
Unless otherwise noted, all reactions were carried out under Ar in the "Radleys Heated Carousel Reaction Station" parallel reactor (www.radleys.com). The solvents were dried by distillation over the following drying agents and were transferred under argon: THF (K/benzophenone), toluene (Na), *n*-pentane, *n*-hexane, CH_2Cl_2 (CaH_2), Et_2O ($LiAlH_4$), MeOH (Mg). Flash column chromatography: Merck silica gel 60 (230–400 mesh). NMR: Spectra were recorded on Bruker AVANCE 500, Varian Gemini 200 and 400 spectrometers in $CDCl_3$; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. IR: Perkin-Elmer Spectrum 2000 FT-IR, wavenumbers in cm^{-1}. MS (EI, LSIMS): AMD 604 Intectra GmbH. MS (ESI): Mariner Perseptive Biosystems, Inc. GC: HP 6890 with HP 5 column. GC/MS: HP 5890 with HP 5 column. Micro-analyses were provided by Institute of Organic Chemistry, PAS, Warsaw. 4-(Diethylamino)-2-hydroxybenzaldehyde (**9**), methyl iodide, 2-propyl iodide, CuCl and carbene **1b** were purchased from Aldrich.

2. Preparation of catalysts 8

2.1. N,N-diethyl-N-3-isopropoxy-4-[(E,Z)-1-propenyl]-phenylamine (10)

K_2CO_3 (1.24 g, 9.0 mmol) and Cs_2CO_3 (410 mg, 1.26 mmol) were placed in a round bottom flask. A solution of 4-(diethylamino)-2-hydroxybenzaldehyde **9** (1.16 g, 6.0 mmol) in dry DMF (15 mL) was added. After stirring for 10 minutes at room temperature 2-iodopropane (0.9 mL, 9.0 mmol) was added. The reaction was carried out for the next 24 hours at room temperature. After pouring onto a saturated aqueous solution of K_2CO_3 the reaction mixture was extracted with MTBE. The combined organic layers were washed with 1M solution of NaOH and then with brine, dried ($MgSO_4$) and the solvent was removed under reduced pressure. Crude 4-(diethylamino)-2-isopropoxybenzaldehyde was obtained as a dark red oil (1.28 g, 5.4 mmol; 91%). IR (film) ν/cm^{-1} 2976, 2930, 2867, 2836, 2758, 1658, 1587, 1547, 1521, 1471, 1146, 1406, 1391, 1356, 1299, 1129, 1238, 1210, 1106, 1076, 1015, 979, 930,; ^{1}H NMR (200 MHz, C_6D_6) δ_H/ppm: 10.72 (s, 1H), 8.10 (d, J = 9.2 Hz, 1H), 6.03 (dd, J = 9.2, 2.1 Hz, 1H), 5.93 (d, J = 2.1 Hz, 1H), 4.30 (septet, J = 6.0 Hz, 1H), 2.87 (q, J = 7.1 Hz, 4H), 1.09 (d, J = 6.0 Hz, 6H), 0.82 (t, J = 7.1 Hz, 6H); ^{13}C NMR (50 MHz, C_6D_6) δ_C/ppm: 186.4, 163.0, 153.6, 130.5, 116.6, 105.1, 95.7, 70.7, 44.6, 22.0, 12.6; MS (EI) *m/z* 235 (32) [$M^{+\cdot}$], 220 (31), 192 (7),178 (100), 162 (9), 150 (14), 148 (8), 136 (2), 122 (4), 106 (2), 94 (4), 77 (5), 65 (9), 41 (9), HRMS (EI) calcd. for $C_{14}H_{21}O_2N$: 235.1572 [$M^{+\cdot}$]; found: 235.1580.

To a solution of dry THF (450 mL) and ethyltriphenylphosphonium bromide (22.08 g, 59.46 mmol) under argon at −78 °C was added dropwise *n*-BuLi (2.5 M in hexane 25.6 ml, 63.7 mmol). After 15 minutes at −78 °C the solution was heated at 30 °C for three hours. After this period the solution was cooled again to −78 °C and 4-(diethylamino)-2-isopropoxybenzaldehyde (10 g, 42.26 mmol) was added. After 30 minutes the reaction mixture was warmed to room temperature and was stirred overnight at this temperature. After pouring onto a saturated aqueous solution of $NaHCO_3$ the reaction mixture was extracted with MTBE. The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography (5% ethyl acetate in hexane with 1.5% triethyl amine) to afford **10** as a yellow oil (10.3 g, 41.6 mmol, 98%; (*E*)/(*Z*)= 2:1).

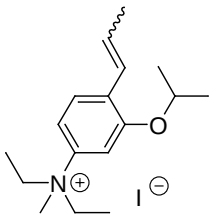


IR (film) ν/cm^{-1} 3025, 2973, 2931, 1611, 1555, 1511, 1467, 1449, 1396, 1374, 1356, 1275, 1222, 1115, 1020, 969, isomer (*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H/ppm: 1.19 (t, J = 7.0 Hz, 6H), 1.38 (d, J = 6.0 Hz, 6H), 1.89 (dd, J = 6.6, 1,7 Hz, 3H), 3.36 (q, J = 7.0 Hz, 4H), 4.50 (heptet, J = 6.0 Hz, 1H), 6.03 (dq, J = 17,8, 6,6 Hz, 1H), 6.26 (d, 2.5 Hz, 1H), 6.31–6.34 (m, 1H), 6.60 (dd, J = 17.8, 1,7 Hz, 1H), 7.33 (d, J = 11.0 Hz, 1H), isomer (*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H/ppm: 1.17 (t, J = 7.0 Hz, 6H), 1.35 (d, J = 6.0 Hz, 6H), 1.86 (dd, J = 7.1, 1.7 Hz, 3H), 3.34 (q, J = 7.0 Hz, 4H), 4.50 (heptet, J = 6.0 Hz, 1H), 5.63 (dq, J = 11.1, 7.1 Hz, 1H), 6.21 (d, J = 2.5 Hz, 1H), 6.25–6,30 (m, 1H), 6.54 (dq, J = 11.1, 1.7 Hz, 1H), 7.21 (d, J = 8.5 Hz, 1H), isomer (*E*): ^{13}C NMR (125 MHz, $CDCl_3$) δ_C/ppm: 13.0, 15.2, 22.6, 44.8, 71.4, 99.8, 104.6, 116.9, 121.4, 125.6, 127.4, 148.2, 156.1, isomer (*Z*): ^{13}C NMR (125 MHz, $CDCl_3$) δ_C/ppm: 13.0, 19.2, 44.8, 71.4, 99.7, 105.8, 116.2, 123.2, 126.2, 131.0, 148.2, 157.1, HRMS (ESI (+)): calcd for $[M+H]^+$ ($C_{16}H_{25}NO$): 248.1936. found 248.1939.[a]

[a] Michrowska, A. *PhD Thesis*, Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland, 2006.

2.2. Diethyl(methyl)[3-izopropoxy-4-[(E/Z)-prop-1-en-1-yl]phenyl]ammonium iodide (11)

Amine **10** (0.074 g, 0.3 mmol) and neat MeI (0.23 mL, 3.6 mmol) were placed in a round bottom flask and stirred at room temperature for 2 days. Excess of MeI was evaporated to dryness to give **11** (0.116 g, 0.3 mmol, 100 %) as a colourless solid ((*E*):(*Z*) = 4:1).

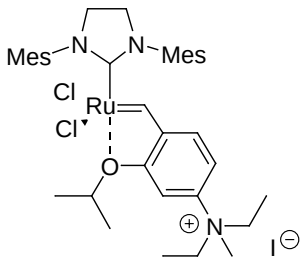


IR (film drom CH_2Cl_2) ν/cm^{-1} 3481, 2977, 2934, 1652, 1601, 1496, 1451, 1425, 1385, 1331, 1295, 1253, 1213, 1170, 1140, 1111, 1028, 973, 904, 881, isomer (*E*): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H/ppm: 1.14 (t, J= 7.1 Hz, 6H), 1.39 (d, J= 5.9 Hz, 6H), 1.93 (dd, J= 6.7, 1.7 Hz, 3H), 3.70 (s, 3H), 4.37–4.59 (m, 4H), 4.99 (heptet, J= 5.9 Hz, 1H), 6.34 (dq, J= 16.0, 6.7 Hz, 1H), 6.66 (dq, J= 16.0, 1.7 Hz, 1H), 7.05 (dd, J= 8.7, 2.6 Hz, 1H), 7.29 (d, J= 2.6 Hz, 1H), 7.53 (d, J= 8.7 Hz, 1H), isomer (*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ_H/ppm: 1.14 (t, J= 7.1 Hz, 6H), 1.39 (d, J= 5.9 Hz, 6H), 1.84 (dd, J= 7.1, 1.8 Hz, 3H), 3.72 (s, 3H), 4.37–4.59 (m, 4H), 4.99 (heptet, J= 5.9 Hz, 1H), 5.92 (dq, J= 11.7, 7.1 Hz, 1H), 6.48 (dq, J= 11.7, 1.8 Hz, 1H), 7.09 (dd, J= 8.7, 2.6 Hz, 1H), 7.33 (d, J= 2.6 Hz, 1H), 7.43 (d, J= 8.7 Hz, 1H), isomer (*Z*): ^{13}C NMR (100 MHz, $CDCl_3$) δ_C/ppm: 8.8, 19.0, 22.0, 46.3, 64.7, 72.0, 107.2, 113.0, 124.1, 127.4, 129.5, 130.5, 139.4, 156.0. MS (ESI (+)) *m/z* 262.2 ($[M-126]^+$), . HRMS (ESI (+)): calcd for $[M-126]^+$ ($C_{17}H_{28}NO$): 262.2165. found 262.2162.[a]

[a] Michrowska, A. *PhD Thesis*, Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland, 2006.

2.3. Quaternary salt 8

Carbene complex **1b** (0.081 g, 0.10 mmol), CuCl (0.014 g, 0.14 mmol) and CH_2Cl_2 (3 mL) were placed in a Schlenk flask equipped with a condenser. A solution of **11** (0.045 g, 0.11 mmol) in CH_2Cl_2 (3 mL) was then added and the resulted solution was stirred under argon at 40 °C for 15 min. From this point forth, all manipulations were carried out in air with reagent-grade solvents. The reaction mixture was concentrated in vacuo and to the residue EtOAc (10 mL) was added. The solution was filtered off and the residue was washed on a Buchner funnel with MeOH (20 mL) and dried under vacuum to give complex **8** as green microcrystalline solid (0.051 g, 63 %).



IR (KBr) ν/cm^{-1} 3431, 2928, 2852, 1629, 1592, 1484, 1448, 1430, 1398, 1384, 1295, 1262, 1214, 1168, 1141, 1098, 1030, 980, 898, 852, 821, ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm: 1.05 (br.s, 6H), 1.34–1.55 (m, 6H), 2.40 (s, 6H), 2.46 (s, 12H), 3.60 (s, 3H), 4.18 (s, 4H), 4.20–4.65 (m, 4H), 5.25–5.45 (m, 1H), 6.90–7.15 (m, 6H), 7.60 (s, 1H), 16.59 (s, 1H), ^{13}C NMR (125 MHz, $CDCl_3$) δ_C/ppm: 8.9, 19.4, 21.1, 22.0, 35.1, 51.5, 64.6, 78.3, 108.0, 115.7, 122.0, 126.8, 128.7, 129.4, 139.1, 139.5, 145.4, 153.5, 208.3, 290.1 HRMS (ESI (+)): calcd for $[M-126]^+$ ($C_{36}H_{50}N_3O^{35}Cl_2{}^{102}Ru$): 712.23744. found 712.2379. [a]

[a] Michrowska, A. *PhD Thesis*, Institute of Organic Chemistry, Polish Academy of Sciences, Warsaw, Poland, 2006.

3. General procedures for metathesis

3.1. Representative procedure of metathesis in CH_2Cl_2

A reaction tube equipped with a magnetic stirring bar was charged with CH_2Cl_2 (10 mL), catalyst **8** (1–5 mol %) and substrate **12** (0.2 mmol). The reaction mixture was stirred at 25 °C. After complete conversion (TLC), the reaction mixture was passed through a cartridge containing silica gel (1–2 g). The cartridge was washed with an additional portion of CH_2Cl_2 (10–20 mL). The CH_2Cl_2 fraction was concentrated under reduced pressure to yield crude product **13**.

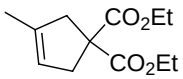
3.2. Representative procedure of metathesis in EtOH–H_2O and MeOH–H_2O

A reaction tube equipped with a magnetic stirring bar was charged with catalyst **8** (6 mg, 0.007 mmol, 5 mol %) and non-degassed water (2 mL). To the resulting suspension a solution of substrate **12** (0.14 mmol) in MeOH or EtOH (5 mL) was added. The reaction mixture was stirred at 25 °C. After complete conversion (TLC), the reaction mixture was evaporated to dryness, dissolved in CH_2Cl_2 (5 mL) and passed through a cartridge containing silica gel (1–2 g). The cartridge was washed with an additional portion of CH_2Cl_2 (15–25 mL). The CH_2Cl_2 fraction was concentrated under reduced pressure to yield crude product **13**.

4. General procedure for residual ruthenium analyses

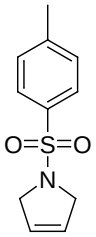
Samples of the crude metathesis product were digested with subboiled HNO_3 (4 mL) and H_2O_2 (1 mL, p.a.; Merck), and diluted with dist. water (to 250 mL). The Ru determination was carried out with an inductively coupled plasma mass spectrometer (ICP-MS) Thermo X7 ICP-MS (Thermo Electron GmbH, Dreieich, Germany, www.thermo.com). This quadrupole instrument had a power of 1200W throughout the measurement. The gas flow rates were 1.0 ml/min (Nebuliser), 1.2 mL/min (Auxiliary) and 13 mL/min (Cool) argon 4.8, respectively. Quantification was performed with liquid Ru standards from 0.01–50μg/L. For drift corrections during the measurements a standard of 1μg/L Ru was interspaced after every second sample measurement.

5. Analytical data of isolated products



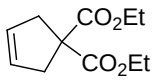
Diethyl 3-methylcyclopent-3-ene-1,1-dicarboxylate (13a)
Colourless oil.[a] IR (film) ν/cm^{-1} 2982, 2937, 1733, 1446, 1367, 1252, 1184, 1161, 1097, 1022, 861, ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm: 1.24 (t, J= 7.0 Hz, 6H), 1.70 (d, J= 1.5 Hz, 3H), 2.93 (s, 2H), 2.96 (br.s, 2H), 4.19 (q, J= 7.0 Hz, 4H), 5.18 (d, J= 1.5 Hz, 1H), ^{13}C NMR (100 MHz, $CDCl_3$) δ_C/ppm: 14.0 16.0, 40.8, 44.6, 59.4, 61.4, 121.2, 137.4, 172.3, , MS (EI) *m/z* 226 (24, $[M]^{+\cdot}$), 181 (17), 180 (15), 153 (49), 152 (100), 136 (2), 134 (3), 125 (25), 124 (25), 107 (44), 97 (8), 93 (35), 81 (25), 80 (47), 79 (64), 77 (21), 67 (9), 55 (3), 53 (7), 39 (9), HRMS (EI): calcd for $[M]^{+\cdot}$ ($C_{12}H_{18}O_4$): 226.1205. found 226.1210.

[a] Taber, D. F.; Frankowski, K. J. *J. Org. Chem.* **2003**, *68*, 6047.



2,5-Dihydro-1-tosyl-1*H*-pyrrole (13b)
Colourless crystals,[a] IR (film) ν/cm^{-1} 3048, 2910, 2854, 1928, 1595, 1492, 1476, 1450, 1336, 1305, 1288, 1161, 1103, 1070, 1017, 1001, 947, 819, ^{1}H NMR (200 MHz, $CDCl_3$) δ_H/ppm: 2.42 (s, 3H), 4.12 (d, J= 4.5 Hz, 4H), 5.65 (d, J= 4.5 Hz, 2H), 7.32 (d, J= 8.3 Hz, 2H), 7.72 (d, J= 8.3 Hz, 2H), ^{13}C NMR (50 MHz, $CDCl_3$) δ_C/ppm: 21.8 55.1, 125.7, 127.7, 130.0, 134.6, 143.7, MS (EI) *m/z* 223 (20, $[M]^{+\cdot}$), 155 (25), 91 (100), 68 (80), 65 (52), 51 (12), 41 (44), 39 (52),

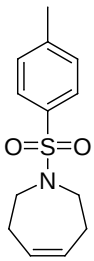
[a] Fürstner, A.; Liebl, M.; Lehmann, C.; Piquet, M.; Kunz, R.; Bruneau, C.; Touchard, D.; Dixneuf, P. H. *Chem. Eur. J.* **2000**, *6*, 1847.



Diethyl cyclopent-3-ene-1,1-dicarboxylate (13c)

Colourless oil.[a] IR (film) ν/cm^{-1} 2983, 2934, 1733, 1642, 1446, 1367, 1256, 1182, 1073, 1017, 922, ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm: 1.24 (t, J= 7.1 Hz, 6H), 3.01 (s, 4H), 4.19 (q, J= 7.1 Hz, 4H), 5.61 (s, 2H), ^{13}C NMR (125 MHz, $CDCl_3$) δ_C/ppm: 14.1, 36.7, 61.2, 61.5, 127.8, 172.2, MS (EI) *m/z* 212 (43, $[M]^{+\cdot}$), 199 (12), 195 (6), 173 (2), 167 (58), 166 (80), 153 (48), 149 (12), 139 (70), 138 (100), 127 (4), 125 (18), 111 (52), 110 (35), 94 (11), 93 (45), 83 (9), 79 (55), 67 (44), 66 (59), 65 (26), 55 (7),

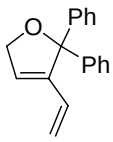
[a] Taber, D. F.; Frankowski, K. J. *J. Org. Chem.* **2003**, *68*, 6047.



1-[(4-Methylphenyl)sulfonyl]-2,3,6,7-tetrahydro-1*H*-azepine (13d)

Colourles solid.[a] IR (KBr) ν/cm^{-1} 3030, 2942, 2899, 2855, 1657, 1596, 1450, 1332, 1286, 1162, 910, 816, 712, ^{1}H NMR (200 MHz, $CDCl_3$) δ_H/ppm: 2.28 (m, 4H), 2.39 (s, 3H), 3.25 (m, 4H), 5.72 (m, 2H), 7.25 (d, J= 8.2 Hz, 2H), 7.64 (d, J= 8.2 Hz, 2H), ^{13}C NMR (50 MHz, $CDCl_3$) δ_C/ppm: 21,5, 29,948,2, 126,9, 129,5, 130,1, 136,2, 142,9, MS (EI) *m/z* 251 (5, $[M]^{+\cdot}$), 223 (2), 184 (6), 155 (4), 105 (2), 91 (19), 96 (16), 77 (1), 65 (13), 42 (100), HRMS (EI): calcd for $[M]^{+\cdot}$ ($C_{13}H_{17}NO_2S$): 251,0980. found 251,0979.

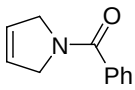
[a] Grela, K.; Kim, M. *Eur. J. Org. Chem.* **2003**, 963.



2,2-Diphenyl-3-vinyl-2,5-dihydrofuran (13e)

Colourless oil.[a] IR (film) ν/cm^{-1} 3427, 3059, 3026, 2925, 1765, 1682, 1598, 1490, 1447, 1226, 1179, 1064, 758, 700, ^{1}H NMR (500 MHz, $CDCl_3$) δ_H/ppm: 4.11 (q, J= 7.1 Hz, 1H), 5.10 (dd, J= 11.2, 0.8 Hz, 1H), 5.31 (dd, J= 17.7, 0.8 Hz, 1H), 6.16–6.18 (m, 1H), 6.20–6.27 (m, 1H), 7.10–7.40 (m, 10H), ^{13}C NMR (125 MHz, $CDCl_3$) δ_C/ppm: 60.3 94.5, 117.5, 124.8, 127.8, 127.9, 129.7, 143.3, 143.6, 171.1, , MS (EI) *m/z* 248 (15, $[M]^{+\cdot}$), 229 (8), 215 (9), 205 (18), 204 (12), 203 (19), 191 (13), 189 (10), 183 (15), 182 (22), 172 (11), 171 (77), 165 (17), 157 (18), 143 (15), 141 (10), 129 (10), 128 (22), 115 (23), 105 (100), 97 (14), 95 (9), 91 (34), 83 (11), 77 (43), 71 (16), 69 (15), 57 (20), 55 (14), 51 (14), 43 (41), 41 (12), 39 (9), HRMS (EI): calcd for $[M]^{+\cdot}$ ($C_{18}H_{16}O$): 248,1201. found 248,1196.

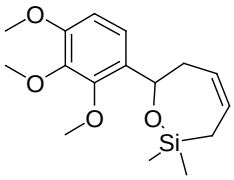
[a] Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F. Thiel, O. R. *Chem. Eur. J.* **2001**, *7*, 3236.



1-Benzoyl-2,5-dihydro-1*H*-pyrrole (13f)

Colourless oil.[a] IR (film) ν/cm^{-1} 3480, 3061, 2862, 1638, 1616, 1575, 1447, 1418, 1355, 1198, 1000, 959, 908, 784, ^{1}H NMR (400 MHz, $CDCl_3$) δ_H/ppm: 4.12–4.25 (m, 2H), 4.41–4.53 (m, 2H), 5.70–5.78 (m, 1H), 5.86–5.96 (m, 1H), 7.36–7.46 (m, 3H), 7.48–7.57 (m, 2H), ^{13}C NMR (100 MHz, $CDCl_3$) δ_C/ppm: 53.3, 55.7, 125.1, 125.9, 126.7, 128.3, 129.8, 136.8, 169.8, MS (EI) *m/z* 173 (55, $[M]^{+\cdot}$), 106 (9), 105 (100), 78 (4), 77 (43), 68 (7), 51 (12), 41 (5), 39 (5), HRMS (EI): calcd for $[M]^{+\cdot}$ ($C_{11}H_{11}NO$): 173.0840. found 173.0832.

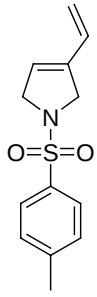
[a] Stille, J. K.; Becker, Y.*J. Org. Chem.* **1980**, *45*, 2139.



(4*Z*)-8,9,10-trimethoxy-2,2-dimethyl-3,6-dihydro-2*H*-1,2-benzoxasilocine (13g)

Colourles oil.[a] IR (film) ν/cm^{-1} 3397, 2957, 2937, 1602, 1494, 1464, 1416, 1304, 1277, 1253, 1198, 1161, 1096, 1045, 1022, 938, 907, 839, 798, ^{1}H NMR (400 MHz, $CDCl_3$) δ_H/ppm: 0.20 (d, J= 3.1 Hz, 6H), 1.43–1.57 (m, 1H), 1.81–1.94 (m, 1H), 2.25–2.35 (m, 1H), 2.54–2.66 (m, 1H), 3.83 (s, 3H), 3.84 (s, 3H), 3.90 (s, 3H), 5.20 (dd, J= 9.3, 1.4 Hz, 1H), 5.62–5.73 (m, 1H), 5.85–5.96 (m, 1H), 6.61–6.72 (m, 1H), 7.20 (dd, J= 8.6, 0.5 Hz, 1H),^{13}C NMR (100 MHz, $CDCl_3$) δ_C/ppm: −2.2, 18.5, 39.0, 56.0, 60.7, 60.9, 69.5, 107.2, 120.5, 126.9, 128.6, 131.6, 141.7, 149.9, 152.6, MS (EI) *m/z* 308 (19, $[M]^{+\cdot}$), 295 (7), 253 (5), 240 (17), 239 (100), 223 (26), 221 (6), 195 (7), 181 (5), 164 (6), 149 (5), 89 (13), 77 (4), 75 (7), 59 (7), 43 (2), 39 (2), HRMS (EI): calcd for $[M]^{+\cdot}$ ($C_{16}H_{24}O_4Si$): 308,1444. found 308,1457.

[a] Michrowska, A.; Gulajski, L.; Grela, K. *Chem. Commun.* **2006**, 841.



1-[(4-Methylphenyl)sulfonyl]-3-vinyl-2,5-dihydro-1*H*-pyrrole (13h)

Colourless solid[a] IR (KBr) ν/cm^{-1} 2918, 2851, 1597, 1493,1450, 1342, 1305, 1162, 1100, 1017, 814, 669, 588, 548, ^{1}H NMR (200 MHz, $CDCl_3$) δ_H/ppm: 2.43 (s, 3H), 4.15–4.23 (m, 4H), 5.04 (d, J= 17.7 Hz, 1H), 5.15 (d, J= 10.2 Hz, 1H), 5.64 (br.s, 1H), 6.35 (dd, J= 17.7, 10.2 Hz, 1H), 7.32 (d, J= 8.0 Hz, 2H), 7.73 (d, J= 8.2 Hz, 2H), ^{13}C NMR (50 MHz, $CDCl_3$) δ_C/ppm: 21.9, 53.8, 55.4, 117.1, 123.7, 127.9, 130.2, 130.3, 134.6, 137.9, 143.9, MS (EI) *m/z* 249 (12, $[M]^{+\cdot}$), 155 (6), 139 (2), 94 (100), 91 (40), 77 (2), 67 (27), 65 (20), 51 (2),

[a] Fürstner, A.; Ackermann, L.; Gabor, B.; Goddard, R.; Lehmann, C. W.; Mynott, R.; Stelzer, F. Thiel, O. R. *Chem. Eur. J.* **2001**, *7*, 3236.