Supplementary Material for Organic & Biomolecular Chemistry

Tandem Hydroformylation / Fischer Indole Synthesis A Novel Approach To Tryptamides

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Supplementary material

2-(2-Methyl-allyl)-isoindole-1,3-dione (14a). Potassium phthalimide (44.1 g, 300 mmol) and Methyltrioctylammoniumchloride (5 ml) are dissolved in anhydrous DMF (160 ml). Methallylic chloride (29.9 g, 330 mmol) is added dropwise. The mixture is stirred at room temperature over night and then poured into water (150 ml). The solid is filtrated and washed with water. The crude product is purified by recrystallization from hexane to give 2-(2-Methyl-allyl)-isoindole-1,3-dione (59.9 g, 99 %).^{1}H-NMR: ($CDCl_3$, 400 MHz) δ = 1.77 (s, 3H, CH_3); 4.21 (s, 2H, NCH_2); 4.80 (s, 1H, CH_2); 4.88 (s, 1H, CH_2); 7.71-7.73 (2H, CH); 7.84-7.86 (2H, CH).^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 20.4 (CH_3); 43.2 (CH_2); 111.9 (CH_2); 123.3 (2xCH); 132.0 (2xC); 134.0 (2xC); 139.3 (C); 167.7 (2xC). NMR data fits with literature[1]

General procedure for the protection of allyic amines. A typical procedure is described. Ehyl-(2-methyl-allyl)-amine (3.9 g, 39 mmol), triethylamine (4.4 g, 43 mmol), DMAP (0.24 g, 2.0 mmol) are dissolved in dry THF (100 ml). Tosyl chloride (7.5 g, 39 mmol) is dissolved in dry THF (50 ml) and is added dropwise at 0°C. The mixture is stirred for 2h at ambient temperature. The precipitate is filtered and the solvent is removed to give *N*-Ethyl-4-methyl-*N*-(2-methyl-allyl)-benzenesulfonamide (9.2 g, 92 %) without further purification.

***N*-Ethyl-4-methyl-*N*-(2-methyl-allyl)-benzenesulfonamide (14b).** ^{1}H-NMR: ($CDCl_3$, 400 MHz) δ = 0.94 (t, 3H, J = 7.1 Hz, CH_3); 1.65 (s, 3H, CH_3); 2.33 (s, 3H, CH_3); 3.09 (q, 2H, J = 7.1 Hz, CH_2); 3.61 (s, 2H, CH_2); 4.82 (s, 2H, CH_2); 7.21 (d, 2H, J = 8.1 Hz, 2xCH); 7.61 (d, 2H, J = 8.1 Hz, 2xCH). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 13.1 (CH_3); 19.5 (CH_3); 21.2 (CH_3); 42.0 (CH_2); 53.5 (CH_2); 114.0 (CH_2); 126.8 (2xCH); 129.4 (2xCH); 137.0 (C); 140.6 (C); 142.9 (C). IR: $\tilde{\nu}$ [cm^{-1}] = 2975 (vs); 1654 (vs); 1448 (s); 1354 (vs); 1288 (s); 1092 (vs); 710 (s). HRMS found $[M+Na]^+$ 276.1031, $C_{13}H_{19}NO_2S$ requires $[M+Na]^+$, 276.1034. Elementary analysis found C 61.73%, H 7.85%, N 5.69%, $C_{13}H_{19}NO_2S$ requires C 61.63%, H 7.56%, N 5.53%.

[1] Stille, J.K.; Becker, Y.; *J. Org. Chem.*; 45, *11*, **1980**, 2139-2145.

***N*-Ethyl-*N*-(2-methyl-allyl)-benzamide (14c).** The general procedure is followed with ethyl-(2-methyl-allyl)-amine (4.9 g, 49 mmol), triethylamine (5.5 g, 54 mmol), DMAP (0.3 g, 2.5 mmol) and benzoyl chloride (6.9 g, 49 mmol) to give *N*-Ethyl-*N*-(2-methyl-allyl)-benzamide (9.7 g, 97 %) without further purification. ^{1}H-NMR: ($CDCl_3$, 400 MHz) δ = 0.87, 1.04 (2bs, 3H, CH_3); 1.40, 1.61 (2s, 3H, CH_3); 3.03, 3.34 (2bs, 2H, CH_2); 3.57, 3.97 (2s, 2H, CH_2); 4.73, 4.77 (2s, 2H, CH_2); 7.19-7.21 (5H, 5xCH). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 11.8, 13.1 (CH_3); 19.5 (*CH_3*); 39.3, 42.2 (CH_2); 48.4, 53.7 (CH_2); 111.6 (CH_2); 125.7, 125.9 (2xCH); 127.7, 127.9 (2xCH); 128.8 (CH); 136.0, 136.3 (C); 140.1, 140.3 (C); 171.1 (C). IR: $\tilde{\nu}$ [cm^{-1}] = 3082 (w); 2973 (m); 1637 (vs); 1425 (s); 1286 (m); 1095 (m); 702 (s). HRMS found $[M+H]^+$ 204.1403, $C_{13}H_{17}NO$ requires $[M+H]^+$, 204.1388. Elementary analysis found C 76.10%, H 8.78%, N 6.86%, $C_{13}H_{17}NO$ requires C 76.81%, H 8.43%, N 6.89%.

***N*-Ethyl-*N*-(2-methyl-allyl)-acetamide (14d).** The general procedure is followed with ethyl-(2-methyl-allyl)-amine (7.0 g, 71 mmol), tiethylamine (7.9 g, 78 mmol), DMAP (0.4 g, 3.5 mmol) and atyl chloride (5.6 g, 71 mmol) to give *N*-Ethyl-*N*-(2-methyl-allyl)-acetamide (9.6 g, 96 %) without further purification. ^{1}H-NMR: ($CDCl_3$, 400 MHz) δ = 0.90, 0.96 (2t, 3H, *J* = 7.1 Hz, CH_3); 1.47, 1.53 (2s, 3H, CH_3); 1.84, 1.95 (2s, 3H, CH_3); 3.09, 3.16 (2q, 2H, *J* = 7.1 Hz, CH_2); 3.57, 3.75 (2s, 2H, CH_2); 4.56, 4.60 (2s, 1H, C*H*H); 4.65, 4.71(2s, 1H, CH*H*). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 12.3, 13.1 (CH_3); 19.6 (CH_3); 20.8, 21.0 (CH_3); 40.3, 41.7 (CH_2); 49.3, 53.3 (CH_2); 110.7, 111.4 (CH_2); 139.9, 140.6 (C); 169.6, 170.2 (C). NMR data fits with literature[2].

Ethyl-(2-methyl-allyl)-carbamic acid ethyl ester (14e). The general procedure is followed with ethyl-(2-methyl-allyl)-amine (2.0 g, 20 mmol), triethylamine (4.3 g, 41 mmol) and ethyl-chlorocarbonate (4.3 g, 39 mmol) to give Ethyl-(2-methyl-allyl)-carbamic acid ethyl ester (3.1 g, 62 %) without further purification. ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 0.99 (bs, 3H, CH_3); 1.15 (bs, 3H, CH_3); 1.59 (s, 3H, CH_3); 3.13-3.17 (2H, CH_2); 3.69-3.73 (2H, CH_2); 4.04 (bs, 2H, CH_2); 4.69, 4.74 (2s, 2H, CH_2). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 13.0, 12.6 (CH_3); 14.5 (CH_3); 19.6 (CH_3); 40.5, 41.1 (CH_2); 52.0, 51.6 (CH_2); 60.8, 60.6 (CH_2); 111.6, 111.2 (CH_2); 141.4 (C), 149.7 (C); 156.0, 156.4 (C). NMR data fits with literature[3].

3-methyl-4-(1,3-dioxoisoindolin-2-yl)butanal (15). 2-(2-methylallyl)isoindoline-1,3-dione (1.00 g, 5.00 mmol) and Rh(acac)$(CO)_2$ (4.0 mg, 0.3 mol-%) were dissolved in anhydrous THF (10 ml) filled in an autoclave and pressurized with 10bar H_2 and 50bar CO. After stirring for 20 hours at 100°C the solvent is removed to give 3-methyl-4-(1,3-dioxoisoindolin-2-

[2] Rische, T.; Baerfacker, L.; Eilbracht, P.; Eur. *J. Org.Chem.*; 3, **1999**, 653-660.
[3] Kleinpeter et. al. ; *J. Prakt. Chem.*; 17, **1977**, 133-139.

yl)butanal (1.16 g, 100 %) without further purification. ^{1}H-NMR (500 MHz, $CDCl_3$): $\delta = 1.01$ (d, J=6.8 Hz, 3H, CH_3); 2.21-2.66 (3H, CH, CH_2); 3.58-3.65 (2H, CH_2); 7.68-7.88 (4H, 4xCH); 9.72 (s, 1H, CH); ^{13}C-NMR (125 MHz, $CDCl_3$): $\delta = 17.8$ (CH_3); 30.0 (CH); 43.3 (CH_2); 48.5 (CH_2); 123.3 (2xCH); 131.9 (2xCH); 134.0 (2xC); 168.6 (2xC); 201.2 (CH). NMR data fits with literature[4]

2-[2-Methyl-4-(phenyl-hydrazono)-butyl]-isoindole-1,3-dione (16). A typical procedure is described. 2-(2-methylallyl)isoindoline-1,3-dione (3.131 mg, 15.56 mmol), phenyl hydrazine (1.682 mg, 15.56 mmol) and Rh(acac)$(CO)_2$ (40 mg, 1.0 mol%) are dissolved in anhydrous THF (100 g); filled in an autoclave and pressurized with 10bar H_2 and 50bar CO. After stirring for 68 hours at 100°C the solvent is removed and the crude product is analyzed by NMR. The product was obtained as an inseparable mixture of E/Z isomers. Analytical data was obtained from the mixture of E/Z isomers. ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ= 0.98, 1.05 (d, 3H, J = 6.6 Hz, CH_3); 2.18-2.37 (3H, CH_2, CH); 3.56 (dd, 1H, J = 7.0 Hz, J = 13.7 Hz, C*H*H); 3.63 (dd, 1H, J = 6.7 Hz, J = 13.7 Hz, CH*H*); 6.76, 6.82 (dd, 1H, J = 8.0 Hz, J = 8.0 Hz, CH); 6.90, 7.00 (d, 2H, J = 8.3 Hz, CH); 7.02 (t, 1H, J = 5.0 Hz, CH); 7.16, 7.20 (dd, 2H, J = 8.0 Hz, J = 8.3 Hz, 2xCH); 7.32, 7.44 (s, 1H, NH); 7.64, 7.67 (d, 2H, J = 5.5 Hz, 2xCH); 7.77, 7.80 (d, 2H, J = 5.5 Hz, 2xCH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ= 17.8, 18.0 (CH_3); 31.0, 31.1 (CH); 36.9 (CH_2); 43.5 (CH_2); 112.3, 112.9 (2xCH); 119.3 (CH); 123.1 (2xCH); 129.0 (2xCH); 131.8 (2xC); 133.8, 134.0 (2xCH); 138.6, 138.3 (CH); 145.1 (C); 168.5 (2xC). IR: $\tilde{\nu}$ [cm^{-1}] = 3315 (s); 2964 (vs); 2873 (s); 1772 (vs); 1600 (s); 1497 (vs); 1257 (vs); 1058 (s); 912 (s). HRMS found $[M]^+$ 321.1472, $C_{19}H_{19}N_3O_2$ requires $[M]^+$ 321.1477.

Ethyl 4-methylenepiperidine-1-carboxylate (20). Methyl triphenyl phosphonium bromide (45.98 g, 128.7 mmol) is suspended in THF (400 ml). n-Butyl lithium (solution in Hexan, 49.14 ml, 122.9 mmol) is added dropwise at -80°C. After stirring for 1h at ambient temperatures Ethyloxy carbonyl piperidone (15.53 g, 95.7 mmol) is added. After stirring for 1h under reflux the mixture is quenched with water (200 ml) and is extracted with cyclohexane. The solution is dried over magnesia and the solvent is removed. The residue is taken up in cyclohexane (50 ml) and is filtered. The solvent is removed to give Ethyl 4-methylenepiperidine-1-carboxylate (12.37 g, 81 %) without further purification. ^{1}H-NMR: ($CDCl_3$, 400 MHz) δ= 1.19 (t, 3H, J = 7.0 Hz, CH_3); 2.11 (t, 4H, J = 5.8 Hz, 2xCH_2); 3.39 (t, 4H, J = 5.8 Hz, 2xCH_2); 4.06 (q, 2H, J = 7.0 Hz, CH_2); 4.67 (s, 2H, CH_2). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ= 14.5 (CH_3); 34.3 (2xCH_2); 45.2 (2xCH_2); 61.1 (CH_2); 109.1 (CH_2); 144.8 (C);

[4] Ahman, J.; Somfai, P.; *Tetrahedron*; *48*, 43, **1992**, 9537-9544.

153.2 (C). IR: $\tilde{\nu}$ [cm^{-1}] = 2982 (s); 2942 (s); 2866 (s); 1700 (s); 1698 (s); 1115 (s); 991 (m); 768 (m). HRMS found $[M]^+$ 169.1130, $C_9H_{15}NO_2$ requires $[M]^+$ 169.1103.

2-Allyl-isoindole-1,3-dione (23a). Potassium phthalimide (10.2 g, 54 mmol) and Methyltrioctylammoniumchloride (1 ml) are dissolved in anhydrous DMF (50 ml). Allylbromide (6.5 g, 54 mmol) is added dropwise. The mixture is stirred at room temperature over night and then poured into water (50 ml). The solid is filtered and washed with water. The crude product is purified by recrystallization from hexane to yield 2-Allyl-isoindole-1,3-dione (7.2 g, 72 %) ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 4.23 (d, 2H, J = 5.5 Hz, CH_2); 5.16 (dd, 2H, J = 10.2 Hz, J = 17.4 Hz, CH_2); 5.82 (ddt, 1H, J = 5.5 Hz, J = 10.2 Hz, J = 17.4 Hz, CH); 7.66-7.67 (2H, 2xCH); 7.78-7.80 (2H, 2xCH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 39.9 (CH_2); 117.5 (CH_2); 123.1 (2xCH); 131.4 (CH); 131.9 (2xC); 133.8 (2xCH); 167.7 (2xC). NMR data fits with literature[5].

***N*-Allyl-acetamide (23b).** Allylamine (11.5 g, 201 mmol) and Triethylamine (22.4 g, 222 mmol) are dissolved in anhydrous THF (200 ml). Acetyl chloride (15.8 g, 201 mmol) is added dropwise at 0°C. The mixture is stirred over night at room temperature. The precipitate is filtered and the solvent is removed. The residue is distilled (105°C, 15 mbar) to give *N*-Allyl-acetamide (11.0 g, 55 %). ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.86 (s, 3H, CH_3); 3.68 (t, 2H, J = 5.2 Hz, CH_2); 4.95 (d, 1H, J = 10.2 Hz, C*H*H); 5.02 (d, 1H, J = 17.0 Hz, CH*H*); 5.66 (ddt, 1H, J = 5.2 Hz, J = 10.2 Hz, J = 17.0 Hz, CH); 7.06 (bs, 1H, NH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 21.2, 22.5 (CH_3); 41.7, 45.0 (CH_2); 115.7 (CH_2); 133.8 (CH); 170.7, 174.4 (C). NMR data fits with literature[6].

Allyl-carbamic acid tert-butyl ester (23c). Allylamine (3.6 g, 64 mmol); Triethylamine (7.0 g, 70 mmol) and Di-*tert*-butyl-dicarbonate (13.9 g, 64.0 mmol) are dissolved in dry dichloromethane (75 ml). The mixture is stirred over night at room temperature. The reaction is quenched with saturated NH_4Cl solution (50 ml). The aqueous layer is washed with dichloromethane (3x50 ml) and dried over $MgSO_4$. The solvent is removed and the residue is purified by chromatography (ethyl acetate/cyclohexane, silica) to give Allyl-carbamic acid *tert*-butyl ester (4.2 g, 42 %). ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.40 (s, 9H, 3xCH_3); 3.69 (bs, 2H, CH_2); 4.70 (bs, 1H, NH); 5.05 (d, 1H, J = 10.2 Hz, CHH); 17.2 (d, 1H, J = 17.2 Hz, CHH); 5.79 (ddt, 1H, J = 5.2 Hz, J = 10.2 Hz, J = 17.2 Hz, CH). ^{13}C-NMR: ($CDCl_3$,

[5] Bower, J.F.; Jumnah, R.; Williams, A.C.; Williams, J.M.J.; *J. Chem. Soc., Perkin Trans.1*; *9*, **1997**, 1411-1420.
[6] Rische, T.; Eilbracht, P.; *Eur. J. Org. Chem.*; *3*, **1999**, 653-660.

125 MHz) δ = 28.3 (3xCH_3); 43.0 (CH_2); 79.2 (C); 115.5 (CH_2); 134.9 (CH); 155.7 (C). NMR data fits with literature[7].

***N*-Allyl-4-methyl-benzenesulfonamide (23d).** Allylamine (1.4 g, 24 mmol) and Triethylamine (2.4 g, 24 mmol) are dissolved in anhydrous Diethylether (25 ml).Tosyl chloride (4.5 g, 24 mmol) is dissolved in anhydrous Diethylether (25 ml) and is added dropwise at 0°C. The mixture is stirred over night at room temperature. The precipitate is filtered and the solvent is removed. The residue is purified by chromatography (MTBE/cyclohexane, Silica) to give *N*-Allyl-4-methyl-benzenesulfonamide (4.4 g, 83 %). ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 2.43 (s, 3H, CH_3); 3.58 (d, 2H, *J* = 5.5 Hz, CH_2); 5.07 (d, 1H, *J* = 10.2 Hz, C*H*H); 5.16 (d, 1H, *J* = 17.2 Hz, CH*H*); 5.23 (bs, 1H, NH); 5.71 (ddt, 1H, *J* = 5.5 Hz, *J* = 10.2 Hz, *J* = 17.2 Hz, CH); 7.31 (d, 2H, *J* = xxx Hz, 2xCH); 7.77 (d, 2H, *J* = xxx Hz, 2xCH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 21.9 (CH_3); 46.1 (CH_2); 118.0 (CH_2); 127.6 (2xCH); 130.1 (2xCH); 133.4 (CH); 137.4 (C); 143.9 (C). NMR data fits with literature[8].

General procedure for the allylation of Amides. A typical procedure is described. Sodium hydride (60 wt% in mineral oil, 0.46 g, 12 mmol) is suspended in dry THF (25 ml). N-Ethyl-4-methyl-benzenesulfonamide (2.1 g, 10 mmol) in dry THF (25 ml) is added. 3-Bromo-propene (1.3 g, 10 mmol) in dry THF (25 ml) is added. The mixture is stirred for 1h under reflux. The solvent is removed and the residue is dissolved in Ether (50 ml). The mixture is filtrated through a pad of alumina and the solvent is removed. The residue is purified by chromatography (ethyl acetate/cyclohexane, silica) to give *N*-Allyl-*N*-ethyl-4-methyl-benzenesulfonamide (1.8 g, 72 %).

***N*-Allyl-*N*-ethyl-4-methyl-benzenesulfonamide (23e).** ^{1}H-NMR: ($CDCl_3$, 400 MHz) δ = 1.01 (t, 3H, *J* = 7.0 Hz, CH_3); 2.35 (s, 3H, CH_3); 3.14 (q, 2H, *J* = 7.0 Hz, CH_2); 3.74 (d, 2H, *J* = 6.3 Hz, CH_2); 5.06 (d, 1H, *J* = 10.0 Hz, C*H*H); 5.12 (d, 1H, *J* = 17.1 Hz, CH*H*); 5.59 (ddt, 1H, *J* = 6.3 Hz, *J* = 10.0 Hz, *J* = 17.1 Hz, CH); 7.23 (d, 2H, *J* = 8.3 Hz, 2xCH); 7.63 (d, 2H, *J* = 8.3 Hz, 2xCH). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 13.5 (CH_3); 21.3 (CH_3); 41.8 (CH_2); 49.8 (CH_2); 118.3 (CH_2); 126.9 (2xCH); 129.5 (2xCH); 133.2 (CH); 137.1 (C); 142.9 (C). IR: $\tilde{\nu}$ [cm^{-1}] = 2929 (m); 1599 (m); 1452 (m); 1340 (s); 1306 (m); 1092 (s); 741 (s). HRMS found $[M]^+$ 239.0985, $C_{12}H_{17}NO_2S$ requires $[M]^+$, 239.0980. Elementary analysis found C 60.40%, H 7.20%, N 5.86%, $C_{12}H_{17}NO_2S$ requires C 60.22%, H 7.16%, N 5.85%.

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[7] Kawamoto, A.M.; Wills, M.; *J. Chem. Soc. Perkin Trans. 1*; 16, **2001**, 1916-1928.
[8] Dang, H.-S.; Roberts, B.P.; *J. Chem. Soc. Perkin Trans. 1*; 13, **1996**, 1493-1498.

***N*-Allyl-*N*-ethyl-acetamide (23f).** The general procedure is followed with sodium hydride (60 wt% in mineral oil, 1.0 g, 26 mmol), *N*-ethyl-acetamide (2.1 g, 24 mmol) and 3-Bromo-propene (2.9 g, 24 mmol) to give *N*-Allyl-N-Ethyl-acetamide (1.7 g, 55 %) without further purification. ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 0.68, 0.75 (2t, 3H, J = 7.2 Hz, CH_3); 1.62, 1.69 (2s, 3H, CH_3); 2.90, 2.95 (2q, 2H, J = 7.2 Hz, CH_2); 3.48, 3.56 (2d, 2H, J = 6.0 Hz, CH_2); 4.69-4.79 (2H, CH_2); 5.30-5.43 (1H, CH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 12.0, 12.9 (CH_3); 20.2, 20.5 (CH_3); 41.6, 40.0 (CH_2); 46.4, 49.6 (CH_2); 115.2, 115.7 (CH_2); 132.9, 132.5 (CH); 168.7, 169.2 (C). IR: $\tilde{\nu}$ [cm^{-1}] = 2977 (s); 1650 (vs); 1644 (vs); 1635 (vs); 1479 (s); 1455 (s); 1425 (s); 1361 (s); 1270 (s); 1257 (s).

Allyl-ethyl-carbamic acid ethyl ester (23g). The general procedure is followed with sodium hydride (60 wt% in mineral oil, 0.56 g, 14 mmol), ethyl-carbamic acid ethyl ester (1.5 g, 13 mmol) and 3-Bromo-propene (1.5 g, 13 mmol) to give Allyl-ethyl-carbamic acid ethyl ester (1.6 g, 80 %) without further purification. ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 0.97 (t, 3H, J = 7.1 Hz, CH_3); 1.12 (t, 3H, J = 7.0 Hz, CH_3); 3.14 (bs, 2H, CH_2); 3.73 (bs, 2H, CH_2); 4.00 (q, 2H, J = 7.0 Hz, CH_2); 4.98 (d, 1H, J = 10.2 Hz, C*H*H); 5.01 (d, 1H, J = 17.0 Hz, CH*H*); 5.65 (ddt, 1H, J = 5.5 Hz, J = 10.2 Hz, J = 17.0 Hz, CH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 13.8 (CH_3); 14.4 (CH_3); 29.4 (CH_2); 49.0 (CH_2); 60.7 (CH_2); 116.1 (CH_2); 134.0 (CH); 155.4 (C). IR: $\tilde{\nu}$ [cm^{-1}] = 2954 (vs); 2925 (vs); 2854 (vs); 1708 (s); 1463 (s); 1415 (m); 1376 (m); 1263 (m); 1162 (m).

***N*-Allyl-*N*-ethyl-benzamide (23j)** The general procedure is followed with Sodium hydride (60 wt% in mineral oil, 0.7 g, 17 mmol), *N*-ethyl-4-methyl-benzamide (2.4 g, 16 mmol) and 3-Bromo-propene (1.9 g, 16 mmol) to give *N*-Allyl-*N*-ethyl-benzamide (2.0 g, 65 %) without further purification. ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.17, 1.03 (2bs, 3H, CH_3); 3.48, 3.21 (2bs, 2H, CH_2); 3.78, 4.10 (2bs, 2H, CH_2); 5.15, 5.18 (2bs, 2H, CH_2); 5.69, 5.84 (2bs, 1H, CH); 7.24 (s, 5H, 5xCH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 12.3, 13.7 (CH_3); 39.5, 42.9 (CH_2); 51.0, 46.4 (CH_2); 117.1 (CH_2); 126.2 (2xCH); 128.2 (2xCH); 129.2 (CH); 171.3 (C). IR: $\tilde{\nu}$ [cm^{-1}] = 2975 (vs); 1635 (vs); 1602 (s); 1455 (s); 1415 (vs); 1311 (vs); 1284 (s); 1095 (s); 796 (s); 719 (s). HRMS found $[M+Na]^+$ 212.1055, $C_{12}H_{15}NO$ requires $[M+Na]^+$, 212.1051. Elementary analysis found C 75.75%, H 8.10%, N 7.32%, $C_{12}H_{15}NO$ requires C 76.16%, H 7.99%, N 7.40%.

***N*-But-3-enyl-*N*-ethyl-4-methyl-benzenesulfonamide (23h).** Portassium carbonate (6.1 g, 44 mmol) is suspended in dry Acetonitril (30 ml). *N*-Ethyl-4-methyl-benzenesulfonamide (5.9 g, 30 mmol) and 4-Bromo-but-1-ene (4.0 g, 30 mmol) are added. The mixture is stirred

for 12h under reflux. Then the mixture is filtrated through a pad of alumina and the solvent is removed. The residue is purified by chromatography (ethyl acetate/cyclohexane, silica) to give *N*-But-3-enyl-*N*-ethyl-4-methyl-benzenesulfonamide (2.3 g, 31 %). ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.06 (t, 3H, *J* = 7.1 Hz, CH_3); 2.25 (q, 2H, *J* = 7.3 Hz, CH_2); 2.36 (s, 3H, CH_3); 3.12-3.20 (4H, 2xCH_2); 4.97 (d, 1H, *J* = 10.3 Hz, C*H*H); 5.01 (d, 1H, *J* = 17.1 Hz, CH*H*); 5.68 (ddt, 1H, *J* = 6.9 Hz, *J* = 10.3 Hz, *J* = 17.1 Hz, CH); 7.24 (d, 2H, *J* = 8.3 Hz, 2xCH); 7.64 (d, 2H, *J* = 8.3 Hz, 2xCH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 13.9 (CH_3); 21.3 (CH_3); 33.2 (CH_2); 42.7 (CH_2); 46.8 (CH_2); 116.9 (CH); 126.9 (2xCH); 129.5 (2xCH); 134.6 (CH); 137.0 (C); 142.9 (C). HRMS found $[M+H]^+$ 254.1225, $C_{13}H_{19}NO_2S$ requires $[M+H]^+$, 254.1215. Elementary analysis found C 61.70%, H 7.84%, N 5.50%, $C_{13}H_{19}NO_2S$ requires C 61.63%, H 7.56%, N 5.53%.

General procedure for the hydroformylation. A typical procedure is described. 2-Allyl-isoindole-1,3-dione (86 mg, 0.50 mmol), Rh(acac)$(CO)_2$ (0.38 mg, 0.30 mol%) and Xantphos (see table entries) are dissolved in anhydrous THF (0.78 g, 10 wt% olefin), filled in an autoclave and pressurized with 10bar H_2 and 10bar CO. After stirring for 20 hours at 70°C the solvent is removed and the crude product (containing *n*- and *iso*-regioisomers) is analyzed by NMR.

4-(1,3-Dioxo-1,3-dihydro-isoindol-2-yl)-butyraldehyde (24a/25a). *n*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.95 (t, 2H, *J* = 7.2 Hz, CH_2); 2.48 (t, 2H, *J* = 7.2 Hz, CH_2); 3.67 (t, 2H, *J* = 7.0 Hz, CH_2); 7.67 (d, 2H, *J* = 5.2 Hz, 2xCH); 7.77 (d, 2H, *J* = 5.2 Hz, 2xCH); 9.71 (bs, 1H, CH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 21.0 (CH_2); 37.0 (CH_2); 40.9 (CH_2); 123.1 (2xCH); 131.9 (2xC); 133.9 (2xCH); 168.2 (2xC); 200.8 (CH). *Characteristic data for the iso*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.11 (d, 3H, *J* = 7.2 Hz, CH_3); 2.84 (sext*, 1H, *J* = 6.7 Hz, CH); 3.76 (dd, 1H, *J* = 6.5 Hz, *J* = 14.2 Hz, C*H*H); 3.97 (dd, 1H, *J* = 7.1Hz, *J* = 14.2 Hz, CH*H*); 9.68 (d, 1H, *J* = 1.0 Hz, CH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 11.5 (CH_3); 38.0 (CH_2); 45.7 (CH); 123.3 (2xCH); 134.0 (2xCH); 202.1 (CH). NMR data fits with literature[9].

***N*-Ethyl-4-methyl-*N*-(4-oxo-butyl)-benzenesulfonamide (24e/25e).** The general procedure is followed with *N*-Allyl-*N*-ethyl-4-methyl-benzenesulfonamide (222 mg, 0.93 mmol), Rh(acac)$(CO)_2$ (0.72 mg, 0.30 mol%) and Xantphos (see table entries) to give a mixture of *n*-aldehyde and *iso*-aldehyde, which is analyzed by NMR. *n*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 400 MHz) δ = 1.06 (t, 3H, *J* = 7.3 Hz, CH_3); 1.84 (p, 2H, *J* = 7.0 Hz, CH_2); 2.38 (s, 3H, CH_3);

[9] Delugo, G.; Faedda, G.; Gladiali, S.; *J. Organomet. Chem.*; 268, **1984**, 167-174.

2.55 (t, 2H, J = 7.3 Hz, CH_2); 3.10 (t, 2H, J = 7.0 Hz, CH_2); 3.17 (q, 2H, J = 7.0 Hz, CH_2); 7.25 (d, 2H, J = 8.3 Hz, 2xCH); 7.63 (d, 2H, J = 8.3 Hz, 2xCH); 9.76 (bs, 1H, CH). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 13.9 (CH_3); 21.1 (CH_2); 21.4 (CH_3); 40.6 (CH_2); 43.0 (CH_2); 46.6 (CH_2); 127.0 (2xCH); 129.7 (2xCH); 136.8 (C); 143.2 (C); 201.5 (CH). *Characteristic data for the iso*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 400 MHz) δ = 1.03 (t, 3H, J = 7.3 Hz, CH_3); 1.14 (d, 3H, J = 7.3 Hz, CH_3); 2.37 (s, 3H, CH_3); 2.78 (m, 1H, CH); 3.10 (t, 2H, J = 7.0 Hz, CH_2); 3.17 (q, 2H, J = 7.0 Hz, CH_2); 7.19 (d, 2H, J = 8.3 Hz, 2xCH); 7.77 (d, 2H, J = 8.3 Hz, 2xCH); 9.67 (d, 1H, J = 1.8 Hz, CH). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 12.0 (CH_3); 13.9 (CH_3); 21.4 (CH_3); 43.9 (CH_2); 46.1 (CH); 48.1 (CH_2); 127.2 (2xCH); 129.7 (2xCH); 136.8 (C); 143.2 (C). (CH) not detectable. IR: $\tilde{\nu}$ [cm^{-1}] = 2935 (s); 2727 (m); 1724 (vs); 1596 (s); 1336 (vs); 1157 (vs); 1089 (vs); 730 (vs); 549 (vs). HRMS found $[M+H]^+$ 270.1190, $C_{13}H_{19}NO_3S$ requires $[M+H]^+$, 270.1164.

***N*-Ethyl-*N*-(4-oxo-butyl)-acetamide (24f/25f).** The general procedure is followed with *N*-Allyl-*N*-ethyl-4-methyl-acetamide (162 mg, 1.27 mmol), $Rh(acac)(CO)_2$ (0.98 mg, 0.30 mol%) and Xantphos (see table entries) to give a mixture of *n*-aldehyde and *iso*-aldehyde, which is analyzed by NMR. *n*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.03, 0.96 (2t, 3H, J = 7.2 Hz, CH_3); 1.71 (m, 2H, CH_2); 1.93, 1.94 (2s, 3H, CH_3); 2.33, 2.38 (2t, 2H, J = 7.0 Hz, CH_2); 3.10-3.24 (4H, 2xCH_2); 9.62, 9.65 (2bs, 1H, CH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 13.7, 12.7 (CH_3); 20.1, 21.0 (CH_2); 21.1, 21.2 (CH_3); 43.0, 40.9 (CH_2); 44.0, 40.1 (CH_2); 47.1 (CH_2); 170.0 (C); 201.5, 200.6 (CH). *Characteristic data for the iso*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 2.59, 2.64 (2m, 1H, CH); 3.51, 3.54 (2d, 2H, J = 8.5 Hz, CH_2); 9.48, 9.59 (2d, 1H, J = 1.8 Hz, CH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 11.6 (CH_3); 45.8 (CH); 46.1 (CH_2); 202.9 (CH). IR: $\tilde{\nu}$ [cm^{-1}] = 2935 (s); 2726 (m); 1722 (vs); 1644 (vs); 1459 (s); 1425 (vs); 1376 (s); 1278 (s); 1035 (m); 794 (m). HRMS found $[M+H]^+$ 158.1210, $C_8H_{15}NO_2$ requires $[M+H]^+$, 158.1181.

Ethyl-(4-oxo-butyl)-carbamic acid ethyl ester (24g/25g). The general procedure is followed with Allyl-ethyl-carbamic acid ethyl ester (84 mg, 0.53 mmol), $Rh(acac)(CO)_2$ (0.41 mg, 0.30 mol%) and Xantphos (see table entries) to give a mixture of *n*-aldehyde and *iso*-aldehyde, which is analyzed by NMR. *n*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.04 (t, 3H, J = 7.0 Hz, CH_3); 1.17 (t, 3H, J = 7.0 Hz, CH_3); 1.78 (t, 2H, J = 7.1 Hz, CH_2); 2.40 (m, 2H, CH_2); 3.19 (bs, 4H, 2xCH_2); 4.05 (q, 2H, J = 7.0 Hz, CH_2); 9.70 (bs, 1H, CH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 13.9, 13.6 (CH_3); 14.5 (CH_3); 20.8 (CH_2); 40.9 (CH_2); 41.6 (CH_2); 45.9, 45.2 (CH_2); 60.9 (CH_2); 201.5 (CH). (C) not detectable. *Characteristic data for the iso*-

regioisomer: ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 9.59 (d, 1H, J = 2.0 Hz, CH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 11.6 (CH_3). IR: $\tilde{\nu}$ [cm^{-1}] = 2977 (s); 2933 (m); 2722 (w); 1697 (vs); 1479 (s); 1425 (s); 1276 (s); 1189 (s); 1147 (m); 1074 (m); 1025 (m); 771 (m). HRMS found $[M+H]^+$ 188.1290, $C_9H_{18}NO_3$ requires $[M+H]^+$, 188.1287.

General procedure for the hydroformylation of allylic amides. A typical procedure is described. *N*-Allyl-acetamide (115 mg, 1.15 mmol); $Rh(acac)(CO)_2$ (0.90 mg, 0.30 mol%) and Xantphos (see table entries) are dissolved in anhydrous THF (1.04 g, 10 wt% olefin), filled in an autoclave and pressurized with 10bar H_2 and 10bar CO. After stirring for 20 hours at 70°C the solvent is removed and the crude product is analyzed by NMR.

1-(2-Hydroxy-pyrrolidin-1-yl)-ethanone (26a). ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.84-2.13 (7H, 2xCH_2, CH_3); 3.54, 3.33 (t, 2H, J = 9.8 Hz, CH_2); 5.56, 5.33 (bs, 1H, CH); (OH) not detectable. ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 22.4, 21.2 (CH_3); 23.0, 21.0 (CH_2); 32.2, 35.2 (CH_2); 47.0, 45.2 (CH_2); 80.9, 81.9 (CH); 171.1, 170.7 (C). NMR data fits with literature[10].

2-Hydroxy-pyrrolidine-1-carboxylic acid tert-butyl ester (26b). The general procedure is followed with Allyl-carbamic acid tert-butyl ester (168 mg, 1.07 mmol); $Rh(acac)(CO)_2$ (0.83 mg, 0.30 mol%) and Xantphos (see table entries). The crude product is analyzed by NMR. ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.43 (s, 9H, 3xCH_3); 1.79-1.99 (4H, 2xCH_2); 3.20-3.24 (1H, C*H*H); 3.41-3.49 (1H, CH*H*); 5.43, 5.34 (bs, 1H, CH); (OH) not detectable. ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 22.7, 22.0 (CH_2); 28.4 (3xCH_3); 32.6, 33.4 (CH_2); 45.9, 45.7 (CH_2); 80.0 (C); 81.7, 81.4 (CH); (C) not detectable. NMR data fits with literature[11].

1-(Toluene-4-sulfonyl)-pyrrolidin-2-ol (26c). The general procedure is followed with *N*-Allyl-4-methyl-benzenesulfonamide (219 mg, 1.04 mmol); $Rh(acac)(CO)_2$ (0.80 mg, 0.30 mol%) and Xantphos (see table entries). The crude product is analyzed by NMR. ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.68-2.05 (4H, 2xCH_2); 2.37 (s, 3H, CH_3); 2.97-3.04 (1H, C*H*H); 3.41-3.49 (1H, CH*H)*; 5.38, 5.72 (bs, 1H, CH); 7.26 (d, 2H, J = 7.2 Hz, 2xCH); 7.69 (d, 2H, J = 7.2 Hz, 2xCH); (OH) not detectable. ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 21.4 (CH_3); 22.9 (CH_2); 33.8, 33.5 (CH_2); 47.4, 47.7 (CH_2); 83.8, 89.1 (CH); 127.0 (2xCH); 129.7 (2xCH); 135.4 (C); 143.4, 143.5 (C). NMR data fits with literature[12].

General procedure for the tandem hydroformylation / condensation. A typical procedure is described. 2-Allyl-isoindole-1,3-dione (967 mg, 5.17 mmol), phenyl hydrazine (557 mg, 5.17 mmol), $Rh(acac)(CO)_2$ (0.38 mg, 0.30 mol%) and Xantphos (see table entries) are

[10] Mori, M.; Washioka, Z.; Urayama, T.; Yoshiura, K.; Chiba, K.; Ban, Y.; *J. Org. Chem.*; *48*, 13, **1983**, 4058-4067.
[11] Dieter, R.K.; Li, S.J.; *J. Org. Chem.*; 62, **1997**, 7726-7735.
[12] Ahman, J.; Somfai, P.; *Tetrahedron*; *48*, 43, **1992**, 9537-9544.

dissolved in anhydrous THF (8.70 g, 10 wt% olefin); filled in an autoclave and pressurized with 10bar H_2 and 10bar CO. After stirring for 68 hours at 70°C the solvent is removed and the crude product (containing *n*- and *iso*-regioisomers) is analyzed by NMR.

2-[4-(Phenyl-hydrazono)-butyl]-isoindole-1,3-dione (27a/28a). The product was obtained as an inseparable mixture of E/Z & n/iso-isomers. Analytical data was obtained from the mixture. *n*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.96 (m, 2H, J = 7.2 Hz, CH_2); 2.36, 2.27 (dt, 2H, J = 5.2 Hz, J = 7.5 Hz, CH_2); 3.78 (t, 2H, J = 7.0 Hz, CH_2); 6.77, 6.82 (dd, 1H, J = 7.2 Hz, J = 7.5 Hz, CH); 6.91, 7.01 (d, 2H, J = 7.5 Hz, 2xCH); 7.05, 6.45 (t, 1H, J = 5.2 Hz, CH); 7.18 (dd, 1H, J = 8.5 Hz, J = 8.5 Hz, 2xCH); 7.23 (s, 1H, NH); 7.65 (d, 2H, J = 5.3 Hz, 2xCH); 7.81 (d, 2H, J = 5.3 Hz, 2xCH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 25.6 (CH_2); 29.5 (CH_2); 37.4 (CH_2); 112.3 (2xCH); 119.4 (CH); 123.2 (2xCH); 129.0 (CH); 129.1 (CH); 132.0 (2xC); 133.9 (2xCH); 139.2, 141.6 (CH); 144.9 (C); 168.4 (2xC). *Characteristic data for the iso*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.17 (d, 3H, J = 7.0 Hz, CH_3); 2.96 (m, 1H, J = 7.0 Hz, CH); 6.35 (d, 1H, J = 6.5 Hz, CH); 7.47 (s, 1H, NH); 7.71-7.73 (2H, 2xCH_2); 7.86-7.88 (2H, 2xCH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 16.0 (CH_3); 36.2 (CH); 112.9 (2xCH); 120.1 (CH); 123.5 (2xCH). IR: $\tilde{\nu}$ [cm^{-1}] = 3315 (s); 2966 (s); 1770 (vs); 1722 (vs); 1600 (s); 1398 (s); 1259 (s); 1066 (m); 750 (m); 723 (m). HRMS found $[M]^+$ 307.1349, $C_{18}H_{17}N_3O_2$ requires $[M]^+$, 307.1321.

***N*-Ethyl-4-methyl-*N*-[4-(phenyl-hydrazono)-butyl]-benzenesulfonamide (27b/28b).** The general procedure is followed with *N*-Allyl-*N*-ethyl-4-methyl-benzenesulfonamide (349 mg, 1.46 mmol), phenyl hydrazine (158 mg, 1.46 mmol), $Rh(acac)(CO)_2$ (1.13 mg, 0.30 mol%) and Xantphos (see table entries) to give a mixture of *n*-hydrazone and *iso*-hydrazone, which is analyzed by NMR. The product was obtained as an inseparable mixture of E/Z & *n*/*iso*-isomers. Analytical data was obtained from the mixture. *n*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 400 MHz) δ = 1.08 (t, 3H, J = 7.1 Hz, CH_3); 2.29 (dt, 2H, J = 5.1 Hz, J = 7.3 Hz, CH_2); 2.37 (s, 3H, CH_3); 3.13-3.23 (4H, 2xCH_2); 6.78 (dd, 1H, J = 7.3 Hz, J = 8.3 Hz, CH); 6.93 (d, 2H, J = 9.5 Hz, 2xCH); 7.17, 6.65 (t, 1H, J = 5.1 Hz, CH); 7.19 (dd, 2H, J = 7.3 Hz, J = 8.3 Hz, 2xCH); 7.23 (s, 1H, NH); 7.24 (d, 2H, J = 8.2 Hz, 2xCH); 7.65 (d, 2H, J = 8.2 Hz, 2xCH). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 14.0 (CH_3); 21.4 (CH_3); 26.0 (CH_2); 29.1 (CH_2); 42.9 (CH_2); 47.0 (CH_2); 112.4, 112.9 (2xCH); 119.4, 120.0 (CH); 127.0 (2xCH); 129.1 (2xCH); 129.6 (2xCH); 136.9 (C); 139.6, 142.2 (CH); 143.0 (C); 145.3 (C). *Characteristic data for the iso*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 400 MHz) δ = 1.11 (d, 3H, J = 7.0 Hz, CH_3); 2.76 (m, 1H, J = 7.0 Hz, CH); 3.09 (dd, 1H, J = 6.8 Hz, J = 13.8 Hz, C*H*H); 3.30 (dd, 1H, J = 8.5 Hz, J = 13.8 Hz, CH*H*); 6.24 (d, 1H, J = 7.3 Hz, CH). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 16.2

(CH_3); 35.6 (CH); 43.2 (CH_2); 51.4 (CH_2); 115.1 (2xCH); 136.5 (C); 139.1 (CH). IR: $\tilde{\nu}$ [cm^{-1}] = 3399 (m); 2923 (m); 2856 (m); 1598 (m); 1455 (m); 1332 (m); 1153 (s); 1089 (m); 742 (m). HRMS found $[M]^+$ 359.1689, $C_{19}H_{25}N_3O_2S$ requires $[M]^+$ 359.1667.

***N*-Ethyl-*N*-[4-(phenyl-hydrazono)-butyl]-acetamide (27c/28c).** The general procedure is followed with *N*-Allyl-*N*-ethyl-4-acetamide (276 mg, 2.17 mmol), phenyl hydrazine (235 mg, 2.17 mmol), $Rh(acac)(CO)_2$ (1.68 mg, 0.30 mol%) and Xantphos (see table entries) to give a mixture of *n*-hydrazone and *iso*-hydrazone, which is analyzed by NMR. The product was obtained as an inseparable mixture of E/Z isomers. Analytical data was obtained from the mixture of E/Z isomers. *n*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.15, 1.10 (t, 3H, J = 7.1 Hz, CH_3); 1.79 (m, 2H, J = 7.8 Hz, CH_2); 2.07, 2.08 (s, 3H, CH_3); 2.27 (dt, 2H, J = 5.2 Hz, J = 7.2 Hz, CH_2); 3.29 (t, 2H, J = 7.2 Hz, CH_2); 3.36 (q, 2H, J = 7.2 Hz, CH_2); 6.78 (dd, 1H, J = 7.5 Hz, J = 8.0 Hz, CH); 6.95 (d, 2H, J = 8.0 Hz, 2xCH); 7.05, 6.45 (t, 1H, J = 5.2 Hz, CH); 7.20 (dd, 2H, J = 7.2 Hz, J = 7.5 Hz, 2xCH); 7.53, 7.67 (s, 1H, NH). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 13.9, 12.8 (CH_3); 21.3 (CH_3); 24.9, 25.6 (CH_2); 29.4, 29.0 (CH_2); 43.3, 40.3 (CH_2); 44.6, 47.6 (CH_2); 112.3 (2xCH); 119.1, 119.4 (CH); 129.0, 129.1 (2xCH); 140.1, 138.9 (CH); 145.4 (C); 170.0 (C). *Characteristic data for the iso*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 2.77 (m, 1H, J = 6.7 Hz, CH); 3.16 (dd, 1H, J = 6.2 Hz, J = 13.7 Hz, C*H*H); 3.63 (dd, 1H, J = 9.3 Hz, J = 13.7 Hz, CH*H*); 6.19 (d, 1H, J = 6.7 Hz, CH). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 16.1 (CH_3); 35.8 (CH); 143.0 (CH). HRMS found $[M]^+$ 247.1702, $C_{14}H_{21}N_3O$ requires $[M]^+$ 247.1685.

***N*-Ethyl-4-methyl-*N*-[5-(phenyl-hydrazono)-pentyl]-benzenesulfonamide (27d/28d).** The general procedure is followed with *N*-But-3-enyl-*N*-ethyl-4-methyl-benzenesulfonamide (355 mg, 1.40 mmol), phenyl hydrazine (152 mg, 1.40 mmol), $Rh(acac)(CO)_2$ (1.09 mg, 0.30 mol%) and Xantphos (see table entries) to give a mixture of *n*-hydrazone and *iso*-hydrazone, which is analyzed by NMR. The product was obtained as an inseparable mixture of E/Z & n/iso-isomers. Analytical data was obtained from the mixture. *n*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 400 MHz) δ = 1.06 (t, 3H, J = 7.1 Hz, CH_3); 1.52-1.62 (4H, 2xCH_2); 2.25 (q, 2H, J = 7.0 Hz, CH_2); 2.37, 2.38 (s, 3H, CH_3); 3.10-3.20 (4H, 2xCH); 6.78, 6.79 (dd, 1H, J = 8.2 Hz, J = 8.5 Hz, CH); 6.94, 7.03 (d, 2H, J = 8.5 Hz, 2xCH); 7.01, 6.44 (t, 1H, J = 5.3 Hz, CH); 7.23 (dd, 2H, J = 8.5 Hz, J = 8.5 Hz, 2xCH); 7.24 (d, 2H, J = 8.4 Hz, 2xCH); 7.26 (bs, 1H, NH); 7.65 (d, 2H, J = 8.4 Hz, 2xCH). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 14.0 (CH_3); 21.4 (CH_3); 23.9, 22.6 (CH_2); 28.1, 28.0 (CH_2); 31.5 (CH_2); 42.6, 42.7 (CH_2); 47.2, 46.7 (CH_2); 112.4, 112.9 (2xCH); 119.4, 119.9 (CH); 127.0 (2xCH); 129.1 (2xCH); 129.6, 129.7 (2xCH); 137.0 (C); 140.6, 139.8 (CH); 143.0 (C); 145.3 (C). *Characteristic data*

for the iso-regioisomer: ^{1}H-NMR: ($CDCl_3$, 400 MHz) δ = 6.30 (d, 1H, J = 8.0 Hz, CH). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 18.4 (CH_3); 33.8 (CH_2); 33.9 (CH); 45.6 (CH_2); 140.5, 139.8 (CH). HRMS found $[M]^+$ 373.1849, $C_{20}H_{27}N_3O_2S$ requires $[M]^+$ 373.1824.

4-methyl-*N*-[4-(phenyl-hydrazono)-butyl]-benzenesulfonamide (27e/28e). The general procedure is followed with *N*-Allyl-4-methyl-benzenesulfonamide (336 mg, 1.59 mmol), phenyl hydrazine (172 mg, 1.59 mmol), $Rh(acac)(CO)_2$ (1.23 mg, 0.30 mol%) and Xantphos (see table entries) to give a mixture of *n*-hydrazone and *iso*-hydrazone, which is analyzed by NMR. The product was obtained as an inseparable mixture of E/Z & n/iso-isomers. Analytical data was obtained from the mixture. *n*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.74 (m, 2H, J = 7.0 Hz, CH_2); 2.29, 2.24 (q, 2H, J = 7.0 Hz, CH_2); 2.39 (s, 3H, CH_3); 2.98 (t, 2H, J = 7.0 Hz, CH2); 5.03, 5.23 (t, 1H, J = 6.0 Hz, NH); 6.83 (dd, 2H, J = 6.2 Hz, J = 7.0 Hz, 2xCH); 6.92, 6.89 (d, 2H, J = 7.0 Hz, 2xCH); 6.99, 6.37 (t, 1H, J = 5.0 Hz, CH); 7.20-7.36 (4H, 3xCH, NH); 7.72 (d, 2H, J = 8.2 Hz, 2xCH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 21.4 (CH_3); 23.7, 23.1 (CH_2); 26.5, 25.5 (CH_2); 42.5, 42.6 (CH_2); 112.4, 113.0 (2xCH); 119.5, 118.9 (CH); 127.0, 127.3 (2xCH); 129.2, 129.0 (2xCH); 129.7, 129.9 (2xCH); 136.7 (C); 139.4, 139.0 (CH); 143.3 (C); 145.1 (C). *Characteristic data for the iso*-regioisomer: ^{1}H-NMR: ($CDCl_3$, x00 MHz) δ = 1.06 (d, 3H, J = 7.3 Hz, CH_3); 2.43 (s, 3H, CH_3); 3.56 (bs, 1H, CH); 5.36 (t, 1H, J = 6.0 Hz, NH); 7.0 (d, 1H, J = 7.3 Hz, CH); 7.76 (d, 2H, J = 8.2 Hz, 2xCH). ^{13}C-NMR: ($CDCl_3$, 100 MHz) δ = 16.2 (CH_3); 36.0 (CH); 42.5, 46.4 (CH_2); 142.0 (CH). IR: $\tilde{\nu}$ [cm^{-1}] = 3318 (s); 2969 (m); 2871 (m); 1600 (vs); 1496 (s); 1324 (s); 1159 (vs); 1093 (s); 750 (m); 424 (m). HRMS found $[M]^+$ 331.1324, $C_{17}H_{21}N_3O_2S$ requires $[M]^+$ 331.1354.

6-(phenyl-hydrazono)-hexanoic acid methyl ester (27f/28f). The general procedure is followed with methyl pent-4-enoate (263 mg, 2.30 mmol), phenyl hydrazine (249 mg, 2.30 mmol), $Rh(acac)(CO)_2$ (1.78 mg, 0.30 mol%) and Xantphos (see table entries) to give a mixture of *n*-hydrazone and *iso*-hydrazone, which is analyzed by NMR.The product was obtained as an inseparable mixture of E/Z & n/iso-isomers. Analytical data was obtained from the mixture. *n*-regioisomer: ^{1}H-NMR: ($CDCl_3$, 500 MHz) δ = 1.53-1.64 (2H, CH_2); 1.70 (m, 2H, J = 7.6 Hz, CH_2); 2.29, 2.18 (dt, 2H, J = 5.5 Hz, J = 7.6 Hz, CH_2); 2.35, 2.36 (t, 2H, J = 7.6 Hz, CH_2); 3.67, 3.68 (s, 3H, CH_3); 6.80, 6.86 (dd, 1H, J = 7.3 Hz, J = 7.6 Hz, CH); 6.97, 7.05 (d, 2H, J = 8.2 Hz, CH); 6.99, 6.48 (t, 1H, J = 5.5 Hz, CH); 7.22, 7.25 (dd, 2H, J = 7.3 Hz, J = 7.6 Hz, 2xCH_2); 7.34, 7.38 (bs, 1H, NH). ^{13}C-NMR: ($CDCl_3$, 125 MHz) δ = 24.3 (CH_2); 26.3 (CH_2); 31.6 (CH_2); 33.6 (CH_2); 51.3 (CH_3); 112.3, 112.8 (2xCH); 119.2, 119.9 (CH); 129.0 (2xCH); 140.5, 104.1 (CH); 145.3 (C); 173.9 (C). *Characteristic data for*

the iso-regioisomer: ^{1}H-NMR: ($CDCl_3$, x00 MHz) $\delta = 1.11$ (d, 3H, $J = 7.0$ Hz, CH_3); IR: $\tilde{\nu}$ [cm^{-1}] = 3315 (w); 2950 (m); 1731 (s); 1600 (s); 1496 (s); 1259 (s); 750 (s); 694 (m). HRMS found $[M]^+$ 234.1389, $C_{13}H_{18}N_2O_2$ requires $[M]^+$ 234.1368.