Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

A Novel Rhodium-Catalyzed Domino-Hydroformylation-Reaction for the Synthesis of Sulphonamides

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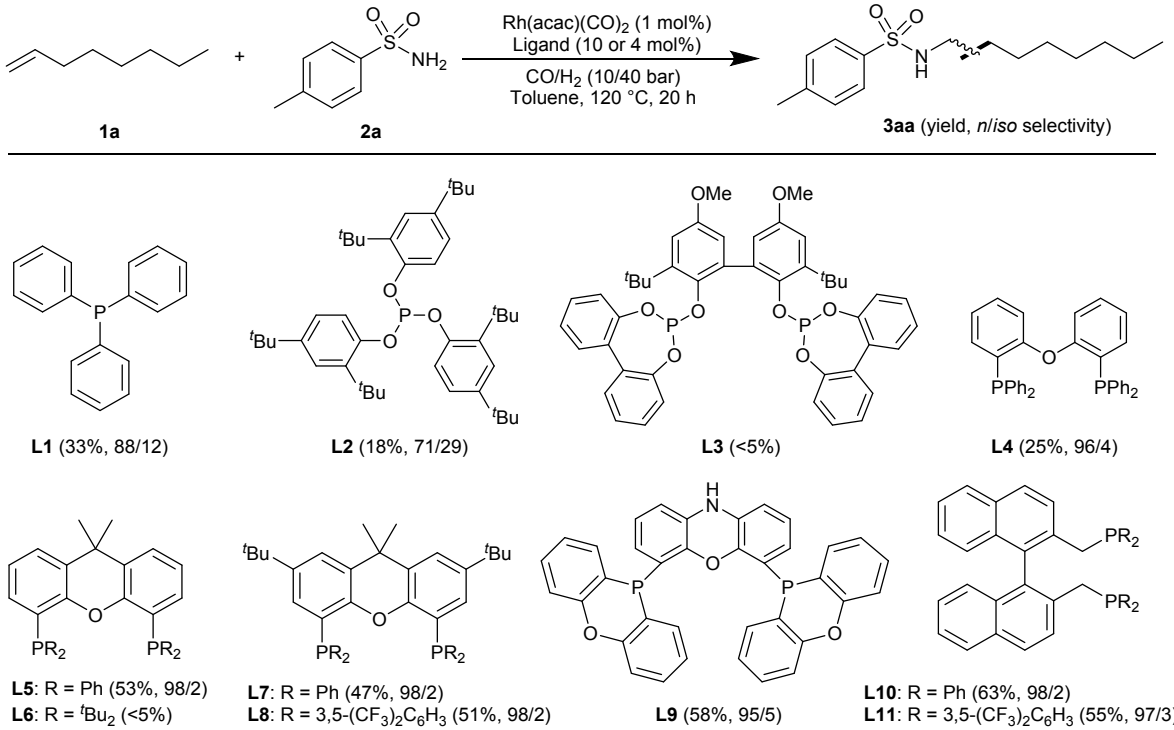
1. General information

Air- and moisture-sensitive syntheses were performed under argon atmosphere in heating gun vacuum dried glassware. Chemicals were purchased from Aldrich, TCI, Alfa, Fluka, Acros or Strem. Unless otherwise noted, all commercial reagents were used without further purification. All compounds were characterized by ^{1}H NMR, ^{13}C NMR, HRMS spectroscopy. ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 300 (300 MHz) NMR spectrometers. Chemical shifts δ (ppm) are given relative to solvent: references for $CDCl_3$ were 7.26 ppm (^{1}H-NMR) and 77.16 ppm (^{13}C-NMR). ^{13}C-NMR spectra were acquired on a broad band decoupled mode. Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet) and br (broad singlet). EI (Electron impact) mass spectra were recorded on an MAT 95XP spectrometer (70 eV, Thermo ELECTRON CORPORATION). ESI (electrospray ionization) high resolution mass spectra were recorded on an Agilent Technologies 6210 TOF LC/MS using H_2O + 0.1% formic acid (10%) and methanol (90%) as eluent. GC analysis was performed on a Agilent 7890A chromatograph with a a 29 m HP5 column. The products were isolated from the reaction mixture by solvent evaporation and further purified by column chromatography on silica gel.

2. Ligands effect on Rh-catalyzed hydrosulphonamidomethylation of 1-octene 1a

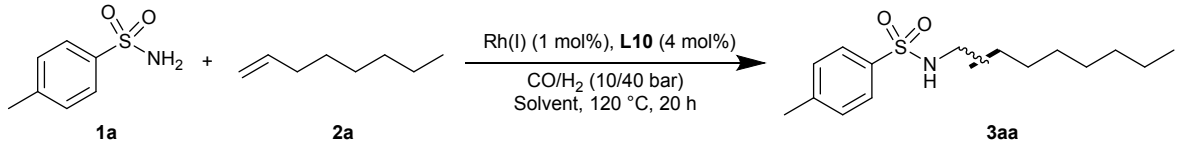


Scheme 2 Rhodium-catalyzed hydrosulphonamidomethylation of **1a** with **2a**: Influence of the ligands. Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), [Rh(acac)$(CO)_2$] (1.0 mol%), monodentate ligand (10.0 mol%), bidentate ligand (4.0 mol%), CO/H_2 (10/40 bar), toluene (2 mL), 120 ºC, 20 h. Yields were determined by GC analysis using isooctane as the internal standard. The ratios of isomers were determined by GC analysis.

General procedure: Under argon atmosphere, vial (4 mL) was charged with [Rh(acac)$(CO)_2$] (2.5 mg, 1.0 mol%), monodentate ligand (10 mol%) or bidentate ligand (4 mol%), **2a** (171 mg, 1.0 mmol) and a stirring bar was added. Then, toluene (2 mL) and **1a** (0.16 mL, 1.0 mmol) were injected by syringe. The vial was placed in an alloyed plate, which was then transferred into an autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave was flushed with syngas (CO/H_2: 1/1) three times, then pressurized with syngas to 20 bar, and finally the pressure was increased to 50 bar by introducing H_2. The reaction was performed at 120 ^oC for 20 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. After isooctane (150 uL) (internal standard) was added into the solution, the yield and selectivity were measured by GC analysis.

3. Rh sources, solvents, and additives effects on Rh-catalyzed hydrosulphonamidomethylation of 1a

Table S1 Rhodium-catalyzed hydrosulphonamidomethylation of 1-octene **1a** with 4-methylbenzenesulphonamide **2a**: Investigation of reaction conditions.[a]



Entry	Rh(I)	Solvent	Yield (%)[b]	*n*/*iso*[c]
1	$Rh(acac)(CO)_2$	Toluene	63	98/2
2	$Rh(cod)_2BF_4$	Toluene	28	98/2
3	$[Rh(cod)(OMe)]_2$	Toluene	49	99/1

4	$[Rh(cod)Cl]_2$	Toluene	11	100/0
5	$Rh(acac)(CO)_2$	THF	23	100/0
6	$Rh(acac)(CO)_2$	MeOH	45	98/2
7	$Rh(acac)(CO)_2$	NMP	5	100/0
8	$Rh(acac)(CO)_2$	DME	20	100/0
9	$Rh(acac)(CO)_2$	Ethyl acetate	28	100/0
10	$Rh(acac)(CO)_2$	Toluene/MeOH (9/1)	71	99/1
11	$Rh(acac)(CO)_2$	Toluene/MeOH (3/1)	72	98/2
12	$Rh(acac)(CO)_2$	Toluene/MeOH (1/1)	82	98/2
13	$Rh(acac)(CO)_2$	Toluene/MeOH (1/3)	82	97/3
14	$Rh(acac)(CO)_2$	Toluene/MeOH (1/9)	70	98/2
15[d]	$Rh(acac)(CO)_2$	Toluene/MeOH (1/1)	0	--
16[e]	$Rh(acac)(CO)_2$	Toluene/MeOH (1/1)	84	97/3
17[f]	$Rh(acac)(CO)_2$	Toluene/MeOH (1/1)	89	98/2
18[g]	$Rh(acac)(CO)_2$	Toluene/MeOH (1/1)	24	99/1
19[f,h]	$Rh(acac)(CO)_2$	Toluene/MeOH (1/1)	76	99/1
20[f,i]	$Rh(acac)(CO)_2$	Toluene/MeOH (1/1)	81	96/4
21[f,j]	$Rh(acac)(CO)_2$	Toluene/MeOH (1/1)	61	96/4
21[f,j,k]	$Rh(acac)(CO)_2$	Toluene/MeOH (1/1)	89	98/2

[a] Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), [Rh] (1.0 mol%), **L10** (4.0 mol%), CO/H_2 (10/40 bar), Solvent (2 mL), 120 ºC, 20 h. [b] Yields were determined by GC analysis using isooctane as the internal standard. [c] The ratios of isomers were determined by GC analysis. [d] Pyridinium *p*-toluenesulphonate (12 mg, 5 mol%). [e] 4 Å molecular sieve (20 mg). [f] silica gel (25 mg). [g] $MgSO_4$ (20 mg). [h] $[Rh(acac)(CO)_2]$ (0.5% mol), **L10** (2.0 mol%). [i] CO/H_2 (5/20 bar). [j] Reaction temperature: 100 ºC. [k] **1a** (1. 2 mmol). NMP = *N*-Methyl-2-pyrrolidon. DME = Ethylene glycol dimethyl ether.

3.1 General procedure for Rh sources effect: Under argon atmosphere, vial (4 mL) was charged with [Rh] (1.0 mol%), Naphos (**L10**) (25.6 mg, 4.0 mol%), **2a** (1.0 mmol) and a stirring bar was added. Then, toluene (2 mL) and **1a** (0.16 mL, 1.0 mmol) were injected by syringe. The vial was placed in an alloyed plate, which was then transferred into an autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave was flushed with syngas (CO/H_2: 1/1) three times, then pressurized with syngas to 20 bar, and finally the pressure was increased to 50 bar by introducing H_2. The reaction was performed at 120 ºC for 20 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. After isooctane (150 uL) (internal standard) was added to the solution, the yield and selectivity were measured by GC analysis.

3.2 General procedure for solvents effect: Under argon atmosphere, vial (4 mL) was charged with $[Rh(acac)(CO)_2]$ (2.5 mg, 1.0 mol%), Naphos (**L10**) (25.6 mg, 4.0 mol%), **2a** (1.0 mmol) and a stirring bar was added. Then, solvent (2 mL, 2 mL is the total volume for the mixture of toluene and MeOH) and **1a** (0.16 mL, 1.0 mmol) were injected by syringe. The vial was placed in an alloyed plate, which was then transferred into an autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave was flushed with syngas (CO/H_2: 1/1) three times, then pressurized with syngas to 20 bar, and finally the pressure was increased to 50 bar by introducing H_2. The reaction was performed at 120 ºC for 20 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. After isooctane (150 uL) (internal standard) was added to the solution, the yield and selectivity were measured by GC analysis.

3.3 General procedure for additives effect: Under argon atmosphere, vial (4 mL) was charged with

[Rh(acac)$(CO)_2$] (2.5 mg, 1.0 mol%), Naphos (**L10**) (25.6 mg, 4.0 mol%), **2a** (1.0 mmol), additives (pyridinium p-toluenesulphonate 12 mg, 4 Å molecular sieve 20 mg, silica gel 25 mg, or MgSO4 20 mg), and a stirring bar was added. Then, toluene (1 mL), MeOH (1 mL) and **1a** (0.16 mL, 1.0 mmol) were injected by syringe. The vial was placed in an alloyed plate, which was then transferred into an autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave was flushed with syngas (CO/H_2: 1/1) three times, then pressurized with syngas to 20 bar, and finally the pressure was increased to 50 bar by introducing H_2. The reaction was performed at 120 ^oC for 20 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. After isooctane (150 uL) (internal standard) was added to the solution, the yield and selectivity were measured by GC analysis.

4. Compound distribution in Rh-catalyzed hydrosulphonamidomethylation of 1-octene 1a

Table S2 Compound distribution in the hydrosulphonamidomethylation of 1-octene **1a**

Entry	Time/h	1-octene **1a** and its isomers (yield/%)	1-nonanal (yield/%)	Product **3aa** (yield/%)
1	0.3	76	20	1
2	0.6	47	42	6
3	2	18	49	26
4	3	2	45	48
5	4	0	41	52
6	6	0	33	61
7	10	0	22	70
8	12	0	13	78
9	17	0	8	82
10	20	0	4	85

Reaction conditions: **1a** (1.0 mmol), **2a** (1.0 mmol), [Rh(acac)$(CO)_2$] (1.0 mol%), **L10** (4.0 mol%), CO/H_2 (10/40 bar), Toluene/Methanol (1/1 mL), silica gel (25 mg), 120 ºC. Yields were determined by GC analysis using isooctane as the internal standard.

Experiment procedure for entry 1: Under argon atmosphere, vial (4 mL) was charged with [Rh(acac)$(CO)_2$] (2.5 mg, 1.0 mol%), Naphos (**L10**) (25.6 mg, 4.0 mol%), **2a** (1.0 mmol), silica gel (25 mg) and a stirring bar was added. Then, toluene (1 mL), MeOH (1 mL) and **1a** (0.16 mL, 1.0 mmol) were injected by syringe. The vial was placed in an alloyed plate, which was then transferred into an autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave was flushed with syngas (CO/H_2: 1/1) three times, then pressurized with syngas to 20 bar, and finally the pressure was increased to 50 bar by introducing H_2. The reaction was performed at 120 ^oC for 0.3 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. After isooctane (150 uL) (internal standard) was added to the solution, the compound distribution were measured by GC analysis.

The experiment procedures for entries 2-10 are the same as described in entry 1 except the reaction time.

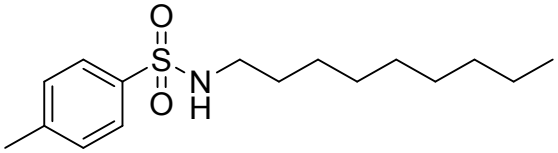
5. Rh-catalyzed hydrosulphonamidomethylation of olefins 1 with sulphonamides 2

General procedure: Under argon atmosphere, vial (4 mL) was charged with [Rh(acac)$(CO)_2$] (2.5 mg, 1.0

mol%), Naphos (**L10**) (25.6 mg, 4.0 mol%), **2** (1.0 mmol), silica gel (25 mg) and a stirring bar was added. Then, toluene (1 mL), MeOH (1 mL) and **1** (**1a** or **1c-n**, 1.2 mmol) were injected by syringe. The vial was placed in an alloyed plate, which was then transferred into an autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave was flushed with syngas (CO/H_2: 1/1) three times, then pressurized with syngas to 20 bar, and finally the pressure was increased to 50 bar by introducing H_2. The reaction was performed at 120 ^oC for 20 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. After isooctane (150 uL) (internal standard) was added to the solution, the yield and selectivity were measured by GC analysis. After removing the solvent under vacuum, the residue was directly purified by flash chromatography on silica gel (eluent: heptane/ethyl acetate = 5/1) to give the desired product **3**.

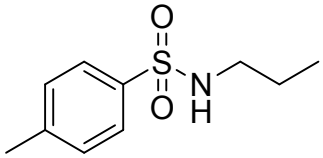
Procedure for 1b with 2a: Under argon atmosphere, An autoclave (25 mL) was charged with $[Rh(acac)(CO)_2]$ (15.5 mg, 6 mol%), Naphos (**L10**) (156.0 mg, 24 mol%), **2a** (2.05 g, 12.0 mmol) and silica gel (300 mg). Then, toluene (3 mL) and MeOH (3 mL) were added. At room temperature, the autoclave was introduced ethylene **1b** (0.7 g, 24.0 mmol). Then pressurized with syngas to 20 bar, and finally the pressure was increased to 50 bar by introducing H_2. The reaction was performed at 120 ^oC for 40 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. Removing the solvent under vacuum, then the residue was directly purified by flash chromatography on silica gel (eluent: heptane/ethyl acetate = 5/1) to give the product **3ab**, 82% yield.

4-methyl-*N*-nonylbenzenesulfonamide, 3aa[1]



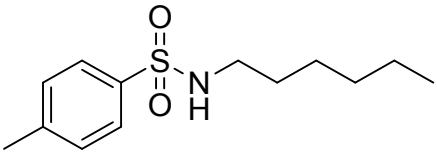
81% yield, *n*/*iso* = 97/3; Colorless oil; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 6.0 Hz, 2H), 7.1 (d, *J* = 9.0 Hz, 2H), 4.48 (s, br, 1H), 2.93 (t, *J* = 6.0 Hz, 2H), 2.44 (s, 3H), 1.49-1.40 (m, 2H), 1.32-1.22 (m, 12H), 0.88 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 142. 83, 136.84, 129.35, 126.86, 42.94, 31.58, 29.19, 29.16, 28.95, 28.84, 26.28, 22.38, 21.18, 13.83; HRMS (EI): Calcd. for $C_{16}H_{27}NO_2S$ $[M]^+$: 297.17570, Found: 297.17550.

4-methyl-*N*-propylbenzenesulfonamide, 3ab[2]



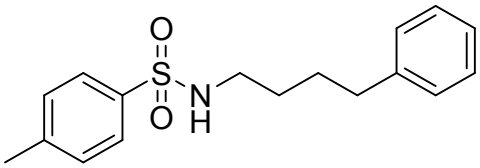
82% yield; Yellowish oil; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 6.0 Hz, 2H), 7.29 (d, *J* = 6.0 Hz, 2H), 5.45 (s, br, 1H), 2.86 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 1.53-1.41 (m, 2H), 0.84 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 142.96, 136.75, 129.40, 126.82, 44.70, 22.55, 21.22, 10.88; HRMS (EI): Calcd. for $C_{10}H_{15}NO_2S$ $[M]^+$: 213.08180, Found: 213.08148.

4-methyl-*N*-hexylbenzenesulfonamide, 3ac[3]



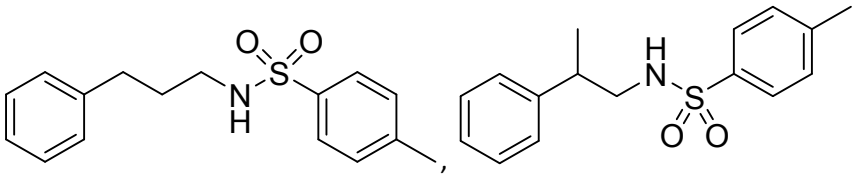
60% yield, *n*/*iso* = 97/3; White solid, M.P. 65 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.78-7.75 (m, 2H), 7.29 (d, *J* = 6.0 Hz, 2H), 4.78 (s, br, 1H), 2.90 (t, *J* = 6.0 Hz, 2H), 2.42 (s, 3H), 1.48-1.39 (m, 2H), 1.28-1.20 (m, 6H), 0.83 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.18, 136.93, 129.48, 127.03, 43.14, 31.15, 29.39, 26.10, 22.37, 21.41, 13.86; HRMS (EI): Calcd. for $C_{13}H_{21}NO_2S$ $[M]^+$: 255.12875, Found: 255.12869.

4-methyl-*N*-(4-phenylbutyl)benzenesulfonamide, 3ad[4]



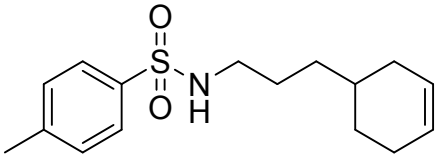
80% yield, *n*/*iso* = 93/7; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 9.0 Hz, 2H), 7.32-7.05 (m, 7H), 2.96 (t, *J* = 6.0 Hz, 2H), 2.57 (t, *J* = 6.0 Hz, 2H), 2.44 (s, 3H), 1.66-1.45 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.04, 141.70, 136.75, 129.47, 128.13, 128.07, 126.87, 125.55, 42.79, 35.02, 28.80, 27.99, 21.30; HRMS (EI): Calcd. for $C_{17}H_{21}NO_2S$ $[M]^+$: 303.12875, Found: 303.12885.

4-methyl-*N*-(2-phenylpropyl)benzenesulfonamide and 4-methyl-*N*-(3-phenylpropyl)benzenesulfonamide, 3ae[5]



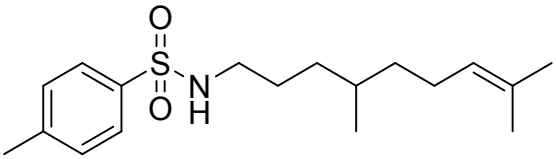
78% yield, *n*/*iso* = 33/67; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.89-7.73 (m, 2H), 7.35-7.12 (m, 7H), 4.93 (s, br, 1H), 3.23-2.89 (m, 2.52H), 2.67-2.62 (m, 0.74), 2.47 (s, 3H), 1.87-1.78 (m, 0.75), 1.28 (d, *J* = 9.0 Hz, 1.98H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.14, 142.95, 140.86, 136.73, 136.67, 129.52, 128.55, 128.20, 126.97, 126.92, 126.86, 126.67, 125.78, 49.53, 42.41, 39.54, 32.49, 30.91, 21.34, 18.97; HRMS (EI): Calcd. for $C_{16}H_{19}NO_2S$ $[M]^+$: 289.11310, Found: 289.11307.

***N*-(3-(cyclohex-3-en-1-yl)propyl)-4-methylbenzenesulfonamide, 3af**



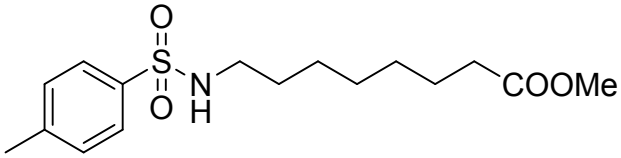
55% yield, *n*/*iso* = 86/14; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.68 (d, *J* = 9.0 Hz, 2H), 7.22 (d, *J* = 6.0 Hz, 2H), 5.52 (t, *J* = 15.0 Hz, 2H), 2.82 (t, *J* = 6.0 Hz, 2H), 2.34 (s, 3H), 1.92-1.88 (m, 3H), 1.57-1.33 (m, 5H), 1.15-1.04 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.11, 136.84, 129.52, 126.95, 126.81, 126.16, 43.31, 33.21, 32.85, 31.50, 28.55, 26.75, 24.95, 21.36; HRMS (EI): Calcd. for $C_{16}H_{23}NO_2S$ $[M]^+$: 293.14440, Found: 293.14430.

***N*-(4,8-dimethylnon-7-en-1-yl)-4-methylbenzenesulfonamide, 3ag**



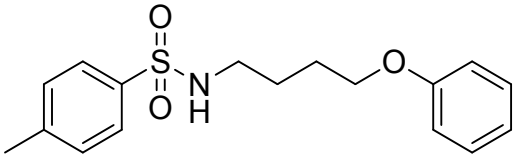
72% yield, *n*/*iso* = 97/3; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.78-7.74 (m, 2H), 7.30 (d, *J* = 6.0 Hz, 2H), 5.12-5.05 (m, 1H), 4.77 (s, br, 1H), 2.90 (t, *J* = 6.0 Hz, 2H), 2.43 (s, 3H), 1.93-1.88 (m, 2H), 1.67 (s, 3H), 1.58 (s, 3H), 1.45-1.39 (m, 2H), 1.29-1.20 (m, 3H), 1.11-1.03 (m, 2H), 0.80 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.03, 136.89, 130.87, 129.49, 126.95, 124.61, 43.41, 36.71, 33.55, 31.81, 26.89, 25.55, 25.28, 21.32, 19.17, 17.47; HRMS (EI): Calcd. for $C_{18}H_{29}NO_2S$ $[M]^+$: 323.19135, Found: 323.19129.

methyl 8-(4-methylphenylsulfonamido)octanoate, 3ah



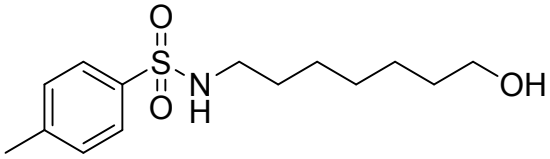
84% yield, *n*/*iso* = 97/3; White solid, 67 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 9.0 Hz, 2H), 7.33 (d, *J* = 6.0 Hz, 2H), 3.68 (s, 3H), 2.92 (t, *J* = 6.0 Hz, 2H), 2.45 (s, 3H), 2.29 (t, *J* = 6.0 Hz, 2H), 1.61-1.57 (m, 2H), 1.49-1.44 (m, 2H), 1.24-1.26 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 174.15, 143.17, 136.87, 129.56, 126.99, 51.39, 43.03, 33.88, 29.31, 28.77, 28.55, 26.18, 24.65, 21.41; HRMS (ESI): Calcd. for $C_{16}H_{25}NO_4S$ $[M + H]^+$: 328.15771, Found: 328.15744.

4-methyl-*N*-(4-phenoxybutyl)benzenesulfonamide, 3ai[6]



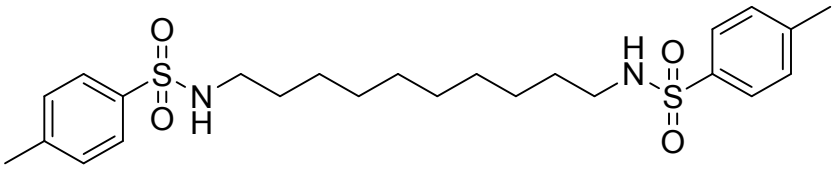
49% yield, *n*/*iso* = 93/7; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.83-7.79 (m, 2H), 7.36-7.29 (m, 4H), 7.01-6.99 (m, 1H), 6.90-6.87 (m, 2H), 5.03 (s, br, 1H), 3.94 (t, *J* = 6.0 Hz, 2H), 3.06 (t, *J* = 6.0 Hz, 2H), 2.46 (s, 3H), 1.87-1.78 (m, 2H), 1.75-1.66 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 158.61, 143.30, 136.80, 129.65, 129.37, 127.01, 120.65, 114.32, 66.96, 42.81, 26.34, 26.18, 21.45; HRMS (EI): Calcd. for $C_{17}H_{21}NO_3S$ $[M]^+$: 319.12367, Found: 319.12358.

***N*-(7-hydroxyheptyl)-4-methylbenzenesulfonamide, 3aj**



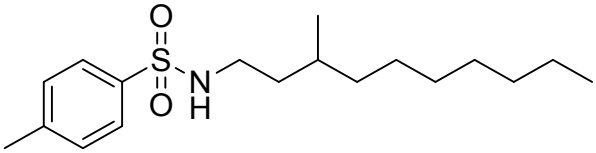
78% yield, *n*/*iso* = 95/5; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.76-7.72 (m, 2H), 7.28 (d, *J* = 9.0 Hz, 2H), 3.58 (t, *J* = 6.0 Hz, 3H), 2.88 (t, *J* = 6.0 Hz, 3H), 2.41 (s, 3H), 1.54-1.39 (m, 4H), 1.32-1.24 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.19, 136.82, 129.57, 126.97, 62.66, 43.01, 32.31, 29.25, 28.64, 26.28, 25.39, 21.42; HRMS (ESI): Calcd. for $C_{14}H_{23}NO_3S$ $[M + H]^+$: 286.14714, Found: 286.14729.

***N*,*N*'-(decane-1,10-diyl)bis(4-methylbenzenesulfonamide), 3ak[7]**



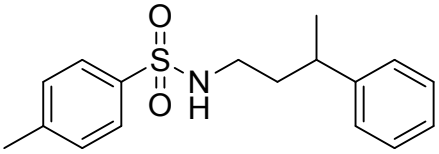
40% yield; White solid, M.P. 126 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 9.0 Hz, 4H), 7.30 (d, *J* = 6.0 Hz, 4H), 4.78 (s, br, 2H), 2.90 (t, *J* = 6.0 Hz, 4H), 2.42 (s, 6H), 1.48-1.38 (m, 4H), 1.21-1.16 (m, 12H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.22, 136.89, 129.61, 127.03, 43.13, 29.40, 29.10, 28.86, 26.35, 21.47; HRMS (ESI): Calcd. for $C_{24}H_{36}N_2O_4S_2$ $[M + H]^+$: 481.21893, Found: 481.21919.

4-methyl-*N*-(3-methyldecyl)benzenesulfonamide, 3am



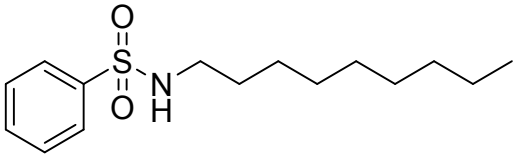
72% yield, *n*/*iso* = 98/2; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.78-7.74 (m, 2H), 7.30 (d, *J* = 6.0 Hz, 2H), 4.54 (s, br, 1H), 3.01-2.86 (m, 2H), 2.43 (s, 3H), 1.49-1.19 (m, 15H), 0.88 (d, *J* = 6.0 Hz, 3H), 0.78 (d, *J* = 9.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 143.21, 136.92, 129.61, 127.07, 41.25, 36.66, 36.51, 31.82, 30.12, 29.77, 29.27, 26.77, 22.62, 21.46, 19.21, 14.06; HRMS (EI): Calcd. for $C_{18}H_{31}NO_2S$ $[M]^+$: 325.20700, Found: 325.20638.

4-methyl-*N*-(3-phenylbutyl)benzenesulfonamide, 3an[5]



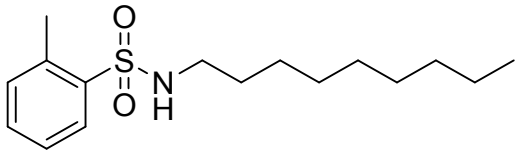
63% yield, *n*/*iso* = 100/0; White solid, M.P. 78 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.70-7.66 (m, 2H), 7.30-7.17 (m, 5H), 7.10-7.08 (m, 2H), 4.24 (s, br, 1H), 2.85 (t, *J* = 6.0 Hz, 2H), 2.76-2.67 (m, 1H), 2.43 (s, 3H), 1.79-1.73 (m, 2H), 1.21 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 145. 81, 143.00, 136.67, 129.44, 128.26, 126.86, 126.65, 125.96, 41.27, 37.50, 36.79, 21.90, 21.27; HRMS (EI): Calcd. for $C_{17}H_{21}NO_2S$ $[M]^+$: 303.12875, Found: 303.12860.

***N*-nonylbenzenesulfonamide, 3ba[7]**



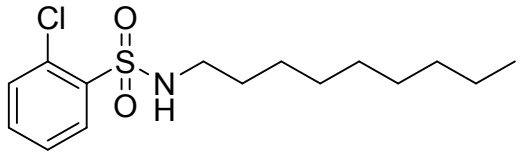
79% yield, *n*/*iso* = 97/3; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 9.0 Hz, 2H), 7.62-7.50 (m, 3H), 4.53 (s, br, 1H), 2.96 (t, *J* = 6.0 Hz, 2H), 1.48-1.41 (m, 2H), 1.32-1.22 (m, 12H), 0.88 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 140.03, 132.48, 129.04, 127.04, 43.24, 31.82, 29.48, 29.39, 29.18, 29.07, 26.51, 22.64, 14.10; HRMS (EI): Calcd. for $C_{15}H_{25}NO_2S$ $[M]^+$: 283.16005, Found: 283.15975.

2-methyl-*N*-nonylbenzenesulfonamide, 3ca



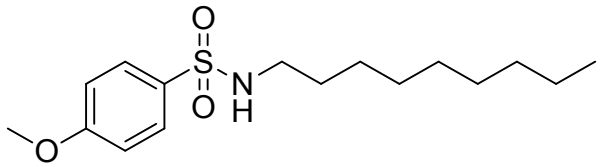
80% yield, *n*/*iso* = 98/2; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.98 (dd, *J* = 9.0, 3.0 Hz, 2H), 7.49-7.44 (m, 1H), 7.35-7.31 (m, 2H), 4.40 (s, br, 1H), 2.94 (q, *J* = 6.0 Hz, 2H), 2.66 (s, 3H), 1.49-1.40 (m, 2H), 1.32-1.21 (m, 12H), 0.88 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.93, 136.87, 132.37, 132.31, 129.13, 125.88, 42.83, 31.63, 29.42, 29.20, 28.99, 28.86, 26.33, 22.45, 20.10, 13.9; HRMS (EI): Calcd. for $C_{16}H_{27}NO_2S$ $[M]^+$: 297.17570, Found: 297.17535.

2-chloro-*N*-nonylbenzenesulfonamide, 3da



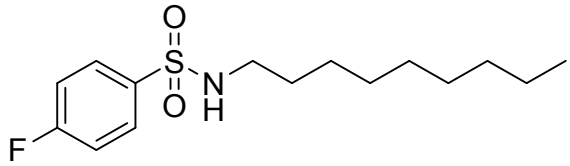
75% yield, *n*/*iso* = 97/3; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.11 (d, *J* = 9.0 Hz, 1H), 7.55-7.41 (m, 3H), 4.99 (s, br, 1H), 2.93 (q, *J* = 6.0 Hz, 2H), 1.51-1.41 (m, 2H), 1.32-1.22 (m, 12H), 0.88 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.08, 133.42, 131.31, 131.09, 130.99, 126.97, 43.09, 31.55, 29.18, 29.11, 28.91, 28.77, 26.21, 22.38, 13.86; HRMS (ESI): Calcd. for $C_{15}H_{24}ClNO_2S$ $[M + H]^+$: 318.1289, Found: 318.1289.

4-methoxy-*N*-nonylbenzenesulfonamide, 3ea



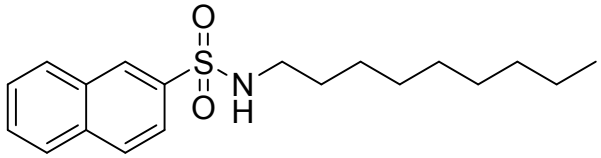
48% yield, *n*/*iso* = 97/3; White solid, M.P. 49 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.83-7.79 (m, 2H), 7.01-6.97 (m, 2H), 4.51 (s, br, 1H), 3.88 (s, 3H), 2.93 (t, *J* = 6.0 Hz, 2H), 1.48-1.41 (m, 2H), 1.32-1.22 (m, 12H), 0.91-0.85 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 162.72, 131.52, 129.14, 114, 13, 55.53, 43.13, 31.76, 29.43, 29.33, 29.12, 29.01, 26.47, 14.03; HRMS (EI): Calcd. for $C_{16}H_{27}NO_3S$ $[M]^+$: 313.17062, Found: 313.17045.

4-fluoro-*N*-nonylbenzenesulfonamide, 3fa



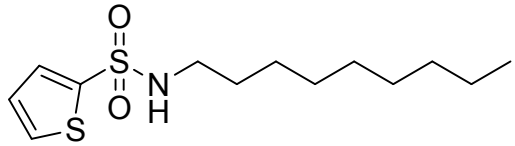
61% yield, *n*/*iso* = 97/3; White solid, 71 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.93-7.86 (m, 2H), 7.23-7.16 (m, 2H), 4.73 (s, br, 1H), 2.94 (t, *J* = 9.0 Hz, 2H), 1.48-1.40 (m, 2H), 1.31-1.21 (m, 12H), 0.87 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 164.97 (d, *J* = 252.7 Hz), 136.07, 129.73 (d, *J* = 9.0 Hz), 116.25 (d, *J* = 22.5 Hz), 43.21, 31.77, 29.49, 29.34, 29.13, 29.01, 26.45, 22.60, 14.06; HRMS (EI): Calcd. for $C_{15}H_{24}FNO_2S$ $[M]^+$: 301.15063, Found: 301.15041.

***N*-nonylnaphthalene-2-sulfonamide, 3ga**



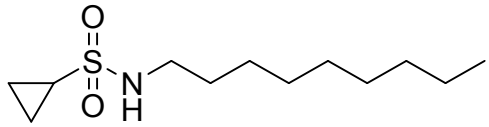
61% yield, *n*/*iso* = 97/3; White solid, M.P. 75 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.46 (s, 1H), 7.99-7.89 (m, 4H), 7.65-7.61 (m, 2H), 4.82 (s, br, 1H), 2.99 (t, *J* = 6.0 Hz, 2H), 1.51-1.41 (m, 2H), 1.28-1.17 (m, 12H), 0.86 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 136.82, 134.78, 132.17, 129.46, 129.21, 128.71, 128.42, 127.89, 127.51, 122.37, 43.30, 31.78, 29.57, 29.35, 29.13, 29.03, 26.49, 22.61, 14.08; HRMS (EI): Calcd. for $C_{19}H_{27}NO_2S$ $[M]^+$: 333.17570, Found: 333.17577.

***N*-nonylthiophene-2-sulfonamide, 3ha**



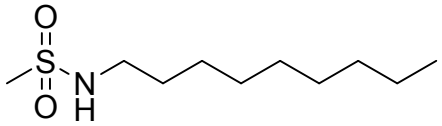
90% yield, *n*/*iso* = 97/3; Colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.63-7.59 (m, 2H),7.11 (dd, *J* = 6.0, 3.0 Hz, 1H), 4.46 (s, br, 1H), 3.05 (t, *J* = 6.0 Hz, 2H), 1.59-1.46 (m, 2H), 1.33-1.25 (m, 12H), 0.89 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 140.75, 131.73, 131.43, 127.20, 43.28, 31.60, 29.18, 29.12, 28.96, 28.86, 26.31, 22.42, 13.88; HRMS (EI): Calcd. for $C_{13}H_{23}NO_2S_2$ $[M]^+$: 289.11647, Found: 289.11608.

***N*-nonylcyclopropanesulfonamide, 3ia**



55% yield, *n*/*iso* = 97/3; White solid, M.P. 46 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.14 (s, br, 1H), 3.16 (t, *J* = 6.0 Hz, 2H), 2.45-2.37 (m, 1H), 1.60-1.53 (m, 2H), 1.37-1.28 (m, 12H), 1.18-1.17 (m, 2H), 1.03-0.98 (m, 2H), 0.89 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 43.40, 31.79, 30.24, 29.89, 29.41, 29.17, 29.13, 26.55, 22.60, 14.05, 5.21; HRMS (EI): Calcd. for $C_{12}H_{25}NO_2S$ $[M]^+$: 247.16005, Found: 247.15958.

***N*-nonylmethanesulfonamide, 3ja**



66% yield, *n*/*iso* = 98/2; White solid, M.P. 71 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 4.50 (s, br, 1H), 3.10 (t, *J* = 6.0 Hz, 2H), 2.94 (s, 3H), 1.60-1.51 (m, 2H), 1.30-1.26 (m, 12H), 0.87 (t, *J* = 6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 43.37, 40.12, 31.84, 30.10, 29.47, 29.22, 29.17, 26.60, 22.66, 14.11; HRMS (EI): Calcd. for $C_{10}H_{23}NO_2S$ $[M]^+$: 221.14440, Found: 221.14403.

6. References

1 A. S. K. Hashmi, M. Rudolph, J. W. Bats, W. Frey, F. Rominger and T. Oeser, *Chem. Eur. J.*, 2008, **14**, 6672-6678.

2 Q. Shen, L. Zhang, Y.-R. Zhou and J.-X. Li, *Tetrahedron Lett.*, 2013, **54**, 6725-6728.

3 V. Valerio, D. Petkova, C. Madelaine and N. Maulide, *Chem. Eur. J.*, 2013, **19**, 2606-2610.

4 M. Mizukami, H. Saito, T. Higuchi, M. Imai, H. Bando, N. Kawahara and S. Nagumo, *Tetrahedron Lett.*, 2007, **48**, 7228-7231.

5 T. Nishikata and H. Nagashima, *Angew. Chem. Int. Ed.*, 2012, **51**, 5363-5366.

6 S. Kim and T. A. Lee, *Synlett*, 1997, 950-952.

7 T. Takematsu, M. Konnai and H. Omokawa, *Ger. Offen.*, DE 2744137 A1 19780406, **1978**.

7. NMR specta of products 3