Supporting Information
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SUPPORTING INFORMATION

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General remarks

Solvents (CH₂Cl₂, THF…) were dried by using an MBRAUN solvent purification system. Catalytic reactions with HNTf₂ were performed under an argon atmosphere. All glass apparatus were oven dried and cooled under vacuum before use unless otherwise specified. Commercially available compounds were used without further purification. Thin Layer Chromatography (TLC) was performed on pre-coated plates of silica gel 60 with fluorescent indicator UV254 (Merck). Detection was accomplished by irradiation with a UV lamp and by an ethanolic solution of p-anisaldehyde. Flash chromatography was performed on silica gel (230-400 mesh) typically using a petroleum ether/ethyl acetate eluent system. Melting points were determined on a Wagner & Munz Kofler bench or a Thomas Hoover melting point apparatus in open capillaries and are uncorrected. The infrared spectra (IR) were recorded on a Bruker TENSOR™ 27 (IRTF). NMR spectra were recorded on a Bruker AVANCE 400 instrument. ¹H NMR spectra were recorded at 400 MHz in CDCl₃ and chemical shifts are given in parts per million ppm (δ) from tetramethylsilane TMS as internal reference (TMS δ = 0, CHCl₃ 7.26 ppm), the following abbreviations are used to describe the signal multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, or overlap of non-equivalent resonances, br = broad, app = apparent. Coupling constants J are reported in Hertz (Hz). ¹³C NMR spectra were recorded at 100 MHz in CDCl₃ and chemical shifts are given in ppm (δ) comparatively to the residual solvent signal (CDCl₃ δ = 77.16 ppm). All NMR spectra were recorded at room temperature unless otherwise specified. Mass spectra (MS) were obtained with a Shimadzu (GCMS-QP2010S) gas chromatograph/mass spectrometer. High Resolution Mass Spectra (HRMS) were performed by the Groupe of Mass Spectrometry from Pierre and Marie Curie University (Paris, France).

Synthesis of the N-tosyl alkoxyamines

General procedure A: Synthesis of N-tosyl alkoxyamines 2 and 3:

Compounds 2¹ and 3² were synthesized by treatment of the commercially available aminooxy hydrochloride with p-toluenesulfonyl chloride (1 equiv) in the presence of potassium carbonate (3 equiv) in a MeOH/H₂O solution (3:2) at 0 °C and the solution was stirred at rt. (Scheme 1, eq 1) After 16 h, methanol was removed and the remained aqueous solution was acidified to neutral pH and the products were extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The crude products were purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to obtain the N-tosyl alkoxyamines 2 and 3. (Scheme 1, eq 1).

General procedure B: Synthesis of N-tosyl alkoxyamines 1, 4-8:

The precursor of the N-tosyl alkoxyamines, the alkoxyamines were prepared according to the previously described procedure³ (Scheme 1, eq 2). To a solution of the alkoxyamine (1 equiv)

in CH2Cl2 (c = 0.15 M) at rt was added TsCl (1.2 equiv) followed by pyridine (3 equiv). The reaction mixture was stirred at rt until complete conversion of the starting material (typically 16 h monitored by TLC analysis). Water was added to the reaction medium and the phases were separated. The aqueous layer was extracted with CH2Cl2 and the combined organic layers were washed with 10% aqueous HCl then with brine, dried over MgSO4, filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel to obtain the N-tosyl alkoxyamines.

Scheme 1: Synthesis of N-tosyl alkoxyamines

N-(Hex-5-en-2-yloxy)-4-methylbenzenesulfonamine (1)
Prepared from \( O\)-(hex-5-en-2-yl)hydroxylamine (250 mg, 2.17 mmol) and TsCl (496 mg, 2.60 mmol) according to general procedure B. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate 9:1) afforded 1 as colorless oil (449.3 mg, 1.66 mmol, 76%).

**IR:** \( \nu \) 3224, 1640, 1598, 1446, 1378, 1332, 1166, 1091, 912 cm\(^{-1}\). ¹H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.82-7.79 (m, 2H), 7.36-7.32 (m, 2H), 6.79 (br s, 1H), 5.79 (ddt app, \( J = 16.8, 10.1, 6.5 \) Hz, 1H), 5.01 (dq app, \( J = 17.0, 1.5 \) Hz, 1H), 4.95 (m, 1H), 4.11 (m, 1H), 2.44 (s, 3H), 2.09 (m, 2H), 1.66 (m, 1H), 1.46 (m, 1H), 1.19 (d, \( J = 6.1 \) Hz, 3H). ¹³C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 138.0, 133.8, 129.7 (2C), 128.5 (2C), 114.8, 82.3, 50.6, 33.9, 29.5, 21.6, 18.6. MS (EI) \( m/z \): 270 (M+1\(^+\), 0.02), 156 (7), 155 (19), 92 (9), 91 (32), 83 (72), 82 (45), 67 (18), 65 (13), 55 (100), 53 (3). HRMS (ESI): Calculated for C\(_{13}\)H\(_{19}\)NO\(_3\)SNa [M+Na]\(^+\) : 292.0978, Found: 292.0980.

**N-(Benzyloxy)-4-methylbenzenesulfonamine (2)**

Prepared from \( O\)-benzylhydroxylamine hydrochloride (1.59 g, 10 mmol) and TsCl (1.90 g, 10 mmol) according to general procedure A. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 85:15) afforded 2 as a white solid (1.40 g, 5.05 mmol, 50%).

**mp** 72-73 °C, **IR:** \( \nu \) 3222, 1597, 1495, 1454, 1369, 1332, 1212, 1165, 1019 cm\(^{-1}\). ¹H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.83 (d, \( J = 8.2 \) Hz, 2H), 7.35 (m, 7H), 6.89 (br s, 1H), 4.99 (s, 2H), 2.45 (s, 3H). ¹³C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 144.9, 135.2, 133.6, 129.7 (2C), 129.3 (2C), 128.6, 128.57 (2C), 128.53 (2C), 79.4, 21.6. MS (EI) \( m/z \): 277 (M\(^+\), 0.3), 106 (4), 91 (100), 77 (13), 65 (20), 51 (6).

**N-(Allyloxy)-4-methylbenzenesulfonamine (3)**

Prepared from \( O\)-Allylhydroxylamine hydrochloride (1.09 g, 10 mmol) and TsCl (1.90 g, 10 mmol) according to general procedure A. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 90:10) afforded 3 as a white solid (1.32 g, 5.8 mmol, 58%).

**mp** 93-94 °C, **IR:** \( \nu \) 3218, 1597, 1492, 1440, 1404, 1329, 1304, 1164, 1089, 1033, 999, 938 cm\(^{-1}\). ¹H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 7.81 (d, \( J = 8.3 \) Hz, 2H), 7.33 (d, \( J = 8.0 \) Hz, 2H), 7.15 (br s, 1H), 5.89 (m, 1H), 5.28-5.20 (m, 2H), 4.45 (dt app, \( J = 6.2, 1.2 \) Hz, 2H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 144.9, 133.5, 132.0, 129.7 (2C), 128.6 (2C), 120.0, 78.1, 21.7.
MS (EI) m/z: 227 (M⁺, 0.8), 155 (54), 139 (8), 132 (15), 131 (14), 118 (4), 117 (6), 92 (10), 91 (100), 65 (24), 51 (3).

\( (E)\)-\( N\)\-[(2,2-Dimethyl-5-phenylpent-4-en-1-yl)oxy]-4-methylbenzenesulfonamine (4)\(^3 \)

Prepared from \( (E)\)-\( O\)-(2,2-dimethyl-5-phenylpent-4-en-1-yl)hydroxylamine (1.23 g, 6.00 mmol) and TsCl (1.37 g, 7.18 mmol) according to general procedure B. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 9:1) afforded 4 (1.72 g, 4.8 mmol, 80%) as a colorless oil. IR: ν 3223, 2960, 1610, 1597, 1390, 1185, 1174, 1092, 1040, 968 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.85-7.81 (m, 2H), 7.60-7.52 (m, 6H), 7.30 (m, 1H), 7.05 (br s, 1H), 6.35 (dABsyst, \( J = 15.7 \) Hz, 1H), 6.20 (dABsyst, \( J = 15.6, 7.5 \) Hz, 1H), 3.80 (s, 2H), 2.43 (s, 3H), 2.10 (dd, \( J = 7.4, 1.1 \) Hz, 2H), 1.16 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 144.8, 137.6, 133.7, 129.7 (2C), 128.6 (2C), 128.5 (2C), 127.0, 126.4, 126.0 (2C), 85.5, 42.6, 35.1, 24.5 (2C), 21.6. MS (EI) m/z: 204 [(M-Ts)⁺, 44], 158 (8), 143 (14), 117 (100), 115 (32), 106 (12), 104 (17), 91 (71), 65 (13), 55 (13).

\( N\)\-[(1-Allylcyclohexyl)methoxy]-4-methylbenzenesulfonamine (5)\(^3 \)

Prepared from \( O\)-[(1-allylcyclohexyl)methyl]hydroxylamine (148.6 mg, 0.88 mmol) and TsCl (202 mg, 1.06 mmol) according to general procedure B. Purification by flash chromatography on silica gel (petroleum ether/Et\(_2\)O = 8:2) afforded 5 as a white solid (226.2 mg, 0.70 mmol, 79%). mp: 67 °C. IR: ν 3220, 2925, 1597, 1452, 1379, 1332, 1185, 1163, 1091, 1036, 914 cm\(^{-1}\). \(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.80-7.78 (m, 2H), 7.34-7.32 (m, 2H), 6.89 (br s, 1H), 5.78 (ddt, \( J = 16.9, 10.2, 7.5 \) Hz, 1H), 5.04-4.96 (m, 2H), 3.86 (s, 2H), 2.45 (s, 3H), 2.01 (dtapp, \( J = 7.5, 1.2, 2H\), 1.46-1.19 (m, 10H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): δ 144.9, 134.5, 133.9, 129.7 (2C), 128.6 (2C), 117.5, 82.4, 40.1, 37.0, 32.6 (2C), 26.2, 21.8, 21.4 (2C). MS (EI) m/z: 323 (M⁺, 0.3), 155 (5), 137 (16), 136 (8), 106 (4), 95 (100), 93 (4), 91 (18), 83 (11), 82 (6), 81 (79), 79 (9), 67 (26), 55 (26).

\( N\)-[3-(Cyclohex-1-en-1-yl)-2,2-dimethylpropoxy]-4-methylbenzenesulfonamine (6)
Prepared from $O$-(3-(cyclohex-1-en-1-yl)-2,2-dimethylpropyl)hydroxylamine (412.6 mg, 2.25 mmol) and TsCl (515 mg, 2.70 mmol) according to general procedure B. Purification by flash chromatography on silica gel (petroleum ether/Et2O = 8:2) afforded 4 (722.2 mg, 2.14 mmol, 95%) as a yellowish oil. IR: $\nu$ 2925, 1597, 1446, 1389, 1335, 1164, 1091, 1039, 919 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.85-7.70 (m, 2H), 7.36-7.32 (m, 2H), 7.08 (br s, 1H), 5.32 (m, 1H), 3.74 (s, 2H), 2.44 (s, 3H), 2.10-1.95 (m, 2H), 1.92-1.87 (m, 2H), 1.80 (br s, 2H), 1.58-1.47 (m, 4H), 0.84 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.7, 134.6, 133.8, 129.6 (2C), 128.6 (2C), 125.5, 86.1, 47.2, 35.3, 31.4, 25.4, 25.0 (2C), 23.2, 22.2, 21.6. MS (EI) $m/z$: 337 (M$^+$. 1.4), 183 (4), 182 (37), 155 (7), 151 (9), 138 (8), 121 (7), 109 (16), 106 (10), 96 (10), 95 (100), 91 (25), 81 (34), 69 (19), 55 (21), 53 (5).

$N$-[2,2-Dimethylhex-5-en-1-yloxy]-4-methylbenzenesulfonamine (7)$^3$

Prepared from $O$-(2,2-dimethylhex-5-en-1-yl)hydroxylamine (402.5 mg, 2.81 mmol) and TsCl (643 mg, 3.37 mmol) according to general procedure B. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 9:1 to 8:2) afforded 7 (785.2 mg, 2.64 mmol, 94%) as a yellowish oil. IR: $\nu$ 2959, 1597, 1474, 1391, 1333, 1185, 1164, 1091, 1038, 995, 952, 909 cm$^{-1}$. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.82-7.78 (m, 2H), 7.36-7.32 (m, 2H), 6.95 (m, 1H), 5.79 (m, 1H), 5.00 (m, 1H), 4.93 (m, 1H), 3.77 (s, 2H), 2.45 (s, 3H), 2.03-1.97 (m, 2H), 1.30-1.25 (m, 2H), 0.86 (s, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.8, 139.2, 133.7, 129.6 (2C), 128.6 (2C), 114.0, 85.5, 38.1, 34.1, 28.1, 24.5 (2C), 21.6. MS (EI) $m/z$: 298 (M+H$^+$, 0.05), 155 (6), 111 (38), 95 (6), 91 (23), 81 (5), 69 (100), 57 (14), 55 (62).

$N$-[2,2-Dimethylhex-4-en-1-yl)oxy]-4-methylbenzenesulfonamine (8)$^3$
Prepared from the mixture of (E) and (Z)-O-(2,2-dimethylhex-4-en-1-yl)hydroxylamine in a 83:17 ratio (291.6 mg, 2.04 mmol) and TsCl (467 mg, 2.45 mmol) according to general procedure B. Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 9:1 to 8:2) afforded 8 as a mixture of E/Z isomers in a 83:17 ratio (582.4 mg, 1.96 mmol, 96%) as a yellowish oil. IR: ν 2960, 1597, 1471, 1389, 1332, 1185, 1163, 1091, 1039, 968 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ (E, major isomer) 7.80-7.78 (m, 2H), 7.34-7.31 (m, 2H), 7.10 (br s, 1H), 5.54-5.33 (m, 2H), 3.72 (s, 2H), 1.86-1.85 (m, 2H), 1.66-1.64 (m, 3H), 0.82 (s, 6H), (Z, minor isomer) 7.82-7.78 (m, 2H), 7.34-7.31 (m, 2H), 7.10 (br s, 1H), 5.42 (m, 1H), 5.38 (m, 1H), 3.75 (s, 2H), 2.44 (s, 3H), 1.93 (d, J = 7.7 Hz, 2H), 1.56-1.54 (m, 3H), 0.85 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ (E, major isomer) 144.7, 133.7, 129.6 (2C), 128.5 (2C), 127.9, 126.8, 85.6, 42.2, 34.6, 24.2 (2C), 21.6, 17.9. δ (Z, minor isomer) 144.7, 133.7, 129.6 (2C), 128.5 (2C), 126.1, 126.0, 85.6, 35.8, 35.1, 24.2 (2C), 21.6, 12.8. MS (EI) m/z: 297 (M⁺, 0.02), 155 (9), 142 (4), 111 (36), 110 (13), 96 (11), 95 (11), 91 (25), 81 (4), 79 (4), 69 (100), 55 (94).

**N-Benzhydryl-4-methylbenzenesulfonamide (19)**⁴

![Chemical Structure](image)

Prepared according to the method described in the literature⁴ by using benzhydrylamine (750.0 mg, 4 mmol) and TsCl (505.0 mg, 2.64 mmol) in the presence of pyridine (645 µl, 8 mmol). Purification by flash chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) afforded 19 (455.6 mg, 1.35 mmol, 51%) as a white solid. mp 153-154 °C. IR: ν 3248, 1598, 1494, 1452, 1314, 1156, 1087, 1054, 1028, 936, 906 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.56-7.52 (m, 2H), 7.21-7.10 (m, 6H), 7.10-7.00 (m, 6H), 5.57 (d, J = 7.0 Hz, 1H), 5.01 (d, J = 7.0 Hz, 1H), 2.37 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 143.2, 140.5 (2C), 137.3, 129.3 (2C), 128.5 (4C), 127.5 (2C), 127.3 (4C), 127.2 (2C), 61.3, 21.5. MS (EI) m/z: 337 (M⁺, 0.03), 260 (5), 182 (100), 180 (22), 167 (16), 165 (11), 155 (12), 104 (19), 91 (31), 77 (14), 65 (7).

**General procedure C: Reaction of N-tosylalkoxyamines with aldehydes in the presence of HNTf₂:**

In a round bottom flask, a solution of N-tosyl alkoxyamine (1 equiv) in anhydrous CH₂Cl₂ (c = 0.25 M), aldehyde (2 equiv) and a solution of HNTf₂ (0.1 equiv) in anhydrous CH₂Cl₂

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were stirred at 40 °C for 18 h. The reaction mixture was cooled down to rt and a saturated aqueous solution of Na₂CO₃ was added. The two phases were separated and the aqueous layer was extracted four times with CH₂Cl₂. The combined organic layers were washed with brine, dried over MgSO₄, filtered and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to obtain the desired oxime ether.

\[ O-(\text{Hex-5-en-2-yl})\text{benzaldoxime (9)} \]

Prepared according to general procedure C from \(N-(\text{hex-5-en-2-yloxy})-4\)-methylbenzenesulfonamine \(1\) (48.4 mg, 0.18 mmol), benzaldehyde (38.1 mg, 0.36 mmol) and HNTf₂ (0.1 equiv). Purification by flash column chromatography (petroleum ether/ethyl acetate = 98:2) afforded \(9\) as a mixture of \(E/Z\) isomers in a 96:4 ratio (24.3 mg, 0.12 mmol, 65%) as a colorless oil. IR: ν 2923, 1640, 1446, 1373, 1335, 1210, 1089, 967, 910, 900 cm⁻¹.

\(E\)-\(9\), major isomer: ¹H NMR (400 MHz, CDCl₃): δ 8.06 (s, 1H), 7.60-7.50 (m, 2H), 7.40-7.30 (m, 3H), 5.85 (m, 1H), 5.04 (dq, \(J = 17.0, 1.8\) Hz, 1H), 4.97 (m, 1H), 4.32 (m, 1H), 2.18 (m, 2H), 1.83 (m, 1H), 1.59 (m, 1H), 1.30 (d, \(J = 6.2\) Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 147.8, 138.4, 130.8, 129.7, 128.4 (2C), 126.9 (2C), 114.6, 79.0, 34.8, 29.7, 19.2.

\(Z\)-\(9\), minor isomer: ¹H NMR (400 MHz, CDCl₃): δ 8.06 (s, 1H), 7.60-7.50 (m, 2H), 7.40-7.30 (m, 3H), 5.85 (m, 1H), 5.04 (dq, \(J = 17.0, 1.8\) Hz, 1H), 4.97 (m, 1H), 4.32 (m, 1H), 2.18 (m, 2H), 1.83 (m, 1H), 1.59 (m, 1H), 1.34 (d, \(J = 6.2\) Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 145.2, 138.4, 132.7, 129.7, 128.4 (2C), 126.9 (2C), 114.6, 79.9, 34.8, 29.7, 19.2.

\text{MS (EI) m/z: 203 (M⁺, 13), 202 (40), 188 (8), 158 (8), 132 (3), 122 (7), 121 (10), 120 (9), 104 (42), 94 (4), 89 (5), 82 (6), 78 (9), 77 (47), 67 (15), 65 (8), 55 (100), 51 (13).}

\(E\)-\(O\)-Benzylbenzaldoxime (10)\(^\text{5}\)

\[ Chemical Formula: C₁₄H₁₃NO \]
\[ Molecular Weight: 211,25912 \]

Prepared according to general procedure C from N-(benzyloxy)-4-methylbenzenesulfonamine 2 (49.8 mg, 0.18 mmol), benzaldehyde (38.1 mg, 0.36 mmol) and HNTf₂ (0.1 equiv). Purification by flash column chromatography (petroleum ether/ethyl acetate = 95:5) afforded 10 as a colorless oil (25.3 mg, 0.12 mmol, 66%). IR: ν 2919, 1604, 1495, 1446, 1365, 1340, 1249, 1210, 1081, 1036, 984, 943, 913 cm⁻¹. \(^1\)H NMR (400 MHz, CDCl₃): δ 8.16 (s, 1H), 7.62-7.55 (m, 2H), 7.45-7.30 (m, 8H), 5.23 (s, 2H). \(^1\)C NMR (100 MHz, CDCl₃): δ 149.0 (2C), 137.5, 132.2, 129.8, 128.6 (2C), 128.5 (2C), 128.4 (2C), 128.0, 127.1, 76.4. MS (EI) \(m/z\): 211 (M⁺, 5), 181 (6), 91 (100), 77 (8), 65 (8), 51 (6).

\((E)-O\)-Allylbenzaldoxime (11)

\[
\overset{\text{O}}{\overset{\text{N}}{\text{C}}} \quad \overset{\text{CH}_3}{\text{C}}
\]

Chemical Formula: C₁₀H₁₁NO
Molecular Weight: 161,20044

Prepared according to general procedure C from N-(allyloxy)-4-methylbenzenesulfonamine 3 (49.9 mg, 0.22 mmol), benzaldehyde (46.6 mg, 0.44 mmol) and HNTf₂ (0.1 equiv). Purification by flash column chromatography (petroleum ether/ethyl acetate = 98:2) afforded 11 as a colorless liquid (25.7 mg, 0.16 mmol, 71%). IR: ν 2919, 2850, 1736, 1463, 1364, 1258, 1082, 1045, 1016 cm⁻¹. \(^1\)H NMR (400 MHz, CDCl₃): δ 8.12 (br s, 1H), 7.60-7.55 (m, 2H), 7.40-7.35 (m, 3H), 6.06 (m, 1H), 5.36 (dqapp, \(J = 17.2, 1.6\) Hz, 1H), 5.26 (dqapp, \(J = 10.4, 1.3\) Hz, 1H), 4.69 (tapp, \(J = 1.3\) Hz, 1H), 4.67 (tapp, \(J = 1.3\) Hz, 1H). \(^1\)C NMR (100 MHz, CDCl₃): δ 147.8, 133.0, 131.2, 128.7, 127.6 (2C), 126.0 (2C), 116.9, 74.1. MS (EI) \(m/z\): 161 (M⁺, 76), 160 (67), 144 (15), 129 (11), 118 (14), 117 (31), 116 (14), 104 (38), 103 (18), 91 (50), 90 (11), 89 (26), 77 (100), 76 (12), 66 (5), 65 (48), 64 (6), 63 (11), 51 (47).

\((E)-O-(\text{E})-2,2\text{-Dimethyl-5-phenylpent-4-en-1-yl})\text{benzaldoxime (12)}

\[
\overset{\text{O}}{\overset{\text{N}}{\text{C}}} \quad \overset{\text{CH}_3}{\text{C}}
\]

Chemical Formula: C₂₀H₂₃NO
Molecular Weight: 293,40272

Prepared according to general procedure C from (E)-N-((2,2-dimethyl-5-phenylpent-4-en-1-yl)oxy)-4-methylbenzenesulfonamine 4 (71.8 mg, 0.20 mmol), benzaldehyde (42.4 mg, 0.40 mmol) and HNTf₂ (0.1 equiv). Purification by flash column chromatography (Petroleum ether/ethyl acetate = 98:2) afforded 12 as a colorless oil (43.9 mg, 0.15 mmol, 73%). IR: ν 3025, 2957, 1598, 1494, 1470, 1446, 1388, 1364, 1338, 1260, 1209, 1045, 1026, 997, 965,

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942 cm\(^{-1}\). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.13 (s, 1H), 7.60-7.57 (m, 2H), 7.40-7.18 (m, 8H), 6.41 (d\(_{AB}\)syst, \(J = 15.7\) Hz, 1H), 6.31 (m, 1H), 3.99 (s, 2H), 2.25 (dd, \(J = 7.3, 1.1\) Hz, 2H), 1.02 (s, 6H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 147.8 (2C), 137.8, 132.5, 132.4, 129.6, 128.6 (2C), 128.5 (2C), 127.0, 126.9 (2C), 126.0 (2C), 82.7, 42.8, 35.6, 24.6 (2C). MS (EI) \(m/z\): 293 (M\(^{+}\), 2), 220 (4), 159 (14), 158 (100), 144 (10), 143 (74), 129 (32), 128 (10), 122 (20), 117 (47), 104 (47), 103 (14), 91 (43), 77 (67). HRMS (ESI) Calculated for C\(_{20}\)H\(_{23}\)NNaO [M+Na\(^{+}\)]: 316.1672, Found: 316.1896.

\((E)-O-\)((1-Allylcyclohexyl)methyl)benzaldoxime (13)

\[
\text{Chemical Formula: } \text{C}_{17}\text{H}_{23}\text{NO} \\
\text{Molecular Weight: } 257,37082
\]

Prepared according to general procedure C from \(N\)-((1-allylcyclohexyl)methoxy)-4-methylbenzenesulfonamine 5 (64.6 mg, 0.20 mmol), benzaldehyde (42.4 mg, 0.40 mmol) and HNTf\(_2\) (0.1 equiv). Purification by flash column chromatography (petroleum ether/ethyl acetate 98:2) afforded 13 as a colorless oil (30.8 mg, 0.12 mmol, 60\%). IR: \(\nu\) 3073, 2925, 1573, 1448, 1340, 1273, 1210, 1046, 944, 913 cm\(^{-1}\). \(^{1}\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 8.09 (s, 1H), 7.60-7.55 (m, 2H), 7.40-7.30 (m, 3H), 5.87 (m, 1H), 5.06-5.00 (m, 2H), 4.04 (s, 2H), 2.17 (ddapp, \(J = 7.5\) Hz, 0.9 Hz, 2H), 1.43 (m, 10H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 147.7, 134.8, 132.5, 129.5, 128.6 (2C), 126.8 (2C), 117.3, 79.5, 40.1, 37.2, 32.7 (2C), 26.2, 21.4 (2C). MS (EI) \(m/z\): 257 (14), 256 (36), 132 (5), 122 (62), 106 (100), 104 (58), 95 (30), 93 (12), 81 (64), 79 (20), 69 (13), 55 (30), 51 (13); HRMS (ESI) Calculated for C\(_{17}\)H\(_{23}\)NNaO [M+Na\(^{+}\)]: 280.1672, Found: 280.1915.

\((E)-O-\)\((3-(Cyclohex-1-en-1-yl)-2,2-dimethylpropyl)benzaldoxime (14)

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\text{Chemical Formula: } \text{C}_{18}\text{H}_{26}\text{NO} \\
\text{Molecular Weight: } 271,39720
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Prepared according to general procedure C \(N\)-\((3-(cyclohex-1-en-1-yl)-2,2-dimethylpropoxy)-4-methylbenzenesulfonamine 6 (67.4 mg, 0.20 mmol), benzaldehyde (42.4 mg, 0.40 mmol) and HNTf\(_2\) (0.1 equiv). Purification by flash column chromatography (petroleum ether/ethyl acetate = 98:2) afforded 14 as a colorless oil (37.9 mg, 0.14 mmol, 69\%). IR: \(\nu\) 2923, 1471, 1446, 1387, 1362, 1338, 1268, 1210, 1046, 1026, 996, 942 cm\(^{-1}\). \(^{1}\)H NMR (400 MHz,
CDCl₃): δ 8.11 (s, 1H), 7.60-7.53 (m, 2H), 7.37-7.32 (m, 3H), 5.42 (m, 1H), 3.93 (s, 2H), 2.01 (m, 6H), 1.57 (m, 4H), 0.96 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 147.7, 135.0, 132.5, 129.5, 128.6 (2C), 126.9 (2C), 125.3, 83.01, 47.3, 35.6, 31.4, 25.4, 25.2 (2C), 23.3, 22.3. MS (EI) m/z: 271 (M⁺, 6), 198 (8), 185 (11), 146 (6), 138 (10), 137 (15), 136 (100), 121 (62), 106 (65), 95 (43), 91 (11), 81 (36), 77 (93), 72 (18), 67 (34), 65 (13), 55 (39). HRMS (ESI): Calculated for C₁₈H₂₆NO [M+H]⁺: 272.2009, Found: 272.2206.

(E)-O-(2,2-Dimethylhex-5-en-1-yl)benzaldoxime (15)

Prepared according to general procedure C from N-((2,2-dimethylhex-5-en-1-yl)oxy)-4-methylbenzenesulfonylamine 7 (51.0 mg, 0.17 mmol), benzaldehyde (36.0 mg, 0.34 mmol) and HNTf₂ (0.1 equiv). Purification by flash column chromatography (petroleum ether/ethyl acetate = 98:2) afforded 15 as a colorless oil (23.1 mg, 0.10 mmol, 62%). IR: ν 3063, 2958, 2927, 2870, 1640, 1574, 1558, 1540, 1472, 1447, 1390, 1364, 1339, 1311, 1210, 1054, 1026, 995, 953, 909 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 8.09 (s, 1H), 7.60-7.56 (m, 2H), 7.40-7.36 (m, 3H), 5.82 (m, 1H), 5.02 (dq, J = 17.1, 1.6 Hz, 1H), 4.92 (m, 1H), 3.94 (s, 2H), 2.15-2.08 (m, 2H), 1.40-1.37 (m, 2H), 0.97 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 147.8, 139.6, 132.5, 129.5, 128.6 (2C), 126.9 (2C), 113.9, 82.8, 38.5, 34.5, 28.4, 24.6 (2C). MS (EI) m/z: 231 (M⁺; 8), 230 (17), 145 (19), 120 (5), 111 (7), 106 (38), 104 (34), 96 (11), 81 (14), 77 (45), 69 (54), 57 (9), 56 (8), 55 (100), 51 (11). HRMS (ESI): Calculated for C₁₅H₂₂NO [M+H]⁺: 232.1696, Found: 232.1888.

O-(2,2-Dimethylhex-4-en-1-yl)benzaldoxime (16)

Prepared according to general procedure C from (E)-N-((2,2-dimethylhex-4-en-1-yl)oxy)-4-methylbenzenesulfonylamine 8 (51.0 mg, 0.17 mmol), benzaldehyde (36.0 mg, 0.34 mmol) and HNTf₂ (0.1 equiv). Purification by flash column chromatography (petroleum ether/ethyl acetate = 98:2) afforded 16 as a colorless oil (22.4 mg, 0.09 mmol, 57%). IR: ν 3025, 2959, 2918, 2870, 1603, 1573, 1471, 1447, 1388, 1364, 1338, 1310, 1290, 1260, 1210, 1174, 1048, 1027, 996, 968, 951, 943 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ (E, major isomer) 8.11 (s, 1H),
7.60-7.57 (m, 2H), 7.40-7.30 (m, 3H), 5.55-5.45 (m, 2H), 3.93 (s, 2H), 2.05-2.00 (m, 2H),
1.70-1.68 (m, 3H), 0.94 (s, 6H). δ (Z, minor isomer) 8.11 (s, 1H), 7.60-7.57 (m, 2H), 7.40-
7.30 (m, 3H), 5.55-5.45 (m, 2H), 3.95 (s, 2H), 2.10-2.06 (m, 2H), 1.63 (dt, J = 6.6, 0.6 Hz,
3H), 0.97 (s, 6H). 13C NMR (100 MHz, CDCl3): δ (E, major isomer) 147.7, 132.5, 129.5,
128.6 (2C), 127.7, 127.2, 126.8 (2C), 82.7, 42,4, 35.0, 24.4 (2C), 18.0. δ (Z, minor isomer)
147.7, 130.8, 128.4 (2C), 127.7, 126.5, 125.9, 82.7, 53.4, 36.0, 35.5, 22.3 (2C), 14.0, 12.9.
MS (EI) m/z: 171 (13), 116 (5), 105 (100), 89 (4), 78 (4), 77 (56), 51 (9). HRMS (ESI):

(E)-O-(Hex-5-en-2-yl)-4-methoxybenzaldoxime (17)

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\text{Chemical Formula: C}_{14}\text{H}_{20}\text{NO}_2
\]
\text{Molecular Weight: 233.30616}

Prepared according to general procedure C from N-(hex-5-en-2-yloxy)-4-methylbenzenesulfonamine 1 (40.4 mg, 0.15 mmol), 4-methoxybenzaldehyde (41 mg, 0.30
mmol) and HNTf2 (0.1 equiv). Purification by flash column chromatography (petroleum
ether/ethyl acetate = 95:5) afforded 17 as a colorless oil (17.8 mg, 0.07 mmol, 51 %). IR: ν
2973, 2932, 2838, 1640, 1607, 1572, 1513, 1461, 1442, 1418, 1372, 1335, 1305, 1250, 1212,
1170, 1126, 1088, 1033, 967, 920 cm\(^{-1}\). 1H NMR (400 MHz, CDCl3): δ 8.02 (s, 1H),
7.52-7.49 (m, 2H), 6.90-6.70 (m, 2H), 5.85 (m, 1H), 5.04 (dq, J = 17.1, 1.8 Hz, 1H), 4.96
(m, 1H), 4.29 (m, 1H), 3.82 (s, 3H), 2.20-2.15 (m, 2H), 1.81 (m, 1H), 1.60 (m, 1H), 1.29 (d, J =
6.2 Hz, 3H). 13C NMR (100 MHz, CDCl3): δ 160.7, 147.5, 138.5, 128.3 (2C), 125.4, 114.5,
114.1 (2C), 78.7, 55.3, 34.9, 29.7, 19.8. MS (EI) m/z: 233 (M\(^+\), 22), 232 (33), 218 (26), 188
(11), 174 (13), 162 (10), 151 (41), 150 (22), 147 (15), 146 (9), 136 (20), 135 (58), 134 (78),
108 (50), 107 (20), 92 (19), 91 (12), 77 (36), 67 (6), 55 (100), 51 (7). HRMS (ESI):
Calculated for C14H22NO2 [M+H]\(^+\): 234.1489, Found: 234.1485.

O-(Hex-5-en-2-yl)-2,4-dimethoxybenzaldoxime (18)

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\text{O}\quad\text{O}
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\text{Chemical Formula: C}_{15}\text{H}_{21}\text{NO}_3
\text{Molecular Weight: 263.33214}

Prepared according to general procedure C from N-(hex-5-en-2-yloxy)-4-methylbenzenesulfonamine 1 (40.4 mg, 0.15 mmol), 2,4-dimethoxybenzaldehyde (50 mg,
0.30 mmol) and HNTf2 (0.1 equiv). Purification by flash column chromatography (petroleum
ether/ethyl acetate = 95:5) afforded (E)-2,4-dimethoxybenzaldehyde O-hex-5-en-2-yl oxime 18 as a mixture of E/Z isomers in a 90:10 ratio (15.8 mg, 0.06 mmol, 40 %) as a colorless oil. IR: ν 3077, 2969, 2936, 2838, 1607, 1572, 1504, 1463, 1438, 1418, 1372, 1311, 1283, 1270, 1208, 1159, 1120, 1107, 1068, 1034, 993, 965 cm⁻¹.

(E)-18, major isomer:

¹H NMR (400 MHz, CDCl₃): δ 8.37 (s, 1H), 7.72 (d, J = 8.6 Hz, 1H), 6.48 (dd, J = 8.6, 0.5 Hz, 1H), 6.42 (d, J = 2.3 Hz, 1H), 5.85 (m, 1H), 5.03 (dqapp, J = 17.1, 1.8 Hz, 1H), 4.95 (m, 1H), 4.28 (m, 1H), 3.82 (s, 3H), 3.81 (s, 3H), 2.17 (m, 2H), 1.81 (m, 1H), 1.60 (m, 1H), 1.29 (d, J = 6.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 162.1, 158.7, 143.9, 138.6, 127.2, 114.4, 114.3, 105.3, 98.2, 78.5, 55.5, 55.4, 34.9, 29.7, 19.8.

(Z)-18, minor isomer:

¹H NMR (400 MHz, CDCl₃): δ 8.39 (s, 1H), 7.72 (d, J = 8.6 Hz, 1H), 6.44 (dd, J = 8.6, 0.5 Hz, 1H), 6.44 (d, J = 2.3 Hz, 1H), 5.85 (ddt, J = 10.1, 1.9, 1.2 Hz, 1H), 5.03 (dqapp, J = 17.1, 1.8 Hz, 1H), 4.95 (ddt, J = 10.1, 1.9, 1.2 Hz, 1H), 4.28 (m, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 2.17 (m, 2H), 1.81 (m, 1H), 1.60 (m, 1H), 1.33 (d, J = 6.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 162.1, 158.7, 143.9, 139.7, 127.2, 114.4, 114.3, 105.3, 98.2, 79.7, 55.5, 55.4, 34.9, 29.7, 19.8.

MS (EI) m/z: 263 (M⁺, 12), 204 (10), 192 (11), 177 (14), 166 (10), 164 (37), 163 (15), 150 (18), 149 (100), 137 (12), 134 (14), 122 (14), 121 (44), 120 (18), 107 (16), 92 (10), 91 (10), 79 (11), 77 (22), 67 (10), 55 (59). HRMS (ESI): Calculated for C₁₅H₂₂NO₃[M+H]⁺: 264.1594, Found: 264.1591.
20180629.350.1.1r
MSA D19

The image contains a spectrum graph with chemical data points labeled with ppm values. The spectrum is labeled with chemical structures and annotations, indicating specific chemical shifts and peaks. The graph includes a scale for ppm values, ranging from 220 to 20, with tick marks at intervals of 20 ppm.

The chemical structure shows a molecule with a sulfonamide group and a phenyl ring, labeled with chemical shifts such as 129.78, 128.76, 127.92, and 127.22 ppm.