Supplementary Information (SI) for Organic & Biomolecular Chemistry.
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Supporting Information

for

$InCl_3$ Catalyzed Simultaneous Reductive Sulfoximination and *O*-Silylation: Synthesis of Silyloxy Benzylsulfoximine

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1. General information

The starting material sulfoximines were synthesized in the laboratory following the reported method.[1] The arylaldehydes, trialkylsilylhydrides, $InCl_3$ and anhydrous dichloromethane and other chemicals were purchased from various suppliers and used as received. ^1H (400 and 500 MHz) and ^{13}C NMR (101 and 126 MHz) spectra were recorded on BRUKER NMR spectrophotometer. $CDCl_3$ was used as solvent to record NMR spectra. HR Mass spectra were recorded with Agilent QTOF G6545 XT spectrometer at 50,000 resolutions using ESI mode. Melting points were uncorrected. Infrared (IR) spectra were acquired on Perkin Elmer ATR FT-IR Spectrometer. Frequencies are given in wave numbers (cm^{-1}) and only selected peaks were reported.

2. General procedure for synthesis of *ortho*-silyloxy benzylsulfoximine (4a)

A 15 mL sealed tube (1.5 x 8 cm) with a septum containing salicylaldehyde **1a** (15 mg, 0.12 mmol), sulfoximine **2a** (19 mg, 0.12 mmol), trialkylsilane **3a** (43 mg, 0.36 mmol), and $InCl_3$ (5 mol%) was evacuated and backfilled with nitrogen 3 times. The solvent anhydrous DCM (1.5 mL) was added under nitrogen atmosphere to the pressure tube. Then, the rubber septum was replaced by a screw cap and the resulting mixture was stirred at 80 °C for 18 hours. The solvent was evaporated and quenched by water, and further extracted with ethyl acetate (3 x 10 mL). The organic phase was then washed with brine solution (2 x 10 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified through column chromatography (100–200 mesh SiO_2) using 20% of EtOAc in hexane as eluent to give the product **4a**.

Similar protocol was used to synthesize rest of *ortho*-silyloxy benzylsulfoximine (**4b-4t**) and the products were purified using 10-30% of EtOAc in hexane as eluent.

Note: The same procedure was followed for preparing *N*-benzyl sulfoximines (**5a-c**) and *o*-,*m*-disilyloxy benzylsulfoximine (**5d**) with 1 equiv. and 4 equiv. of trialkylsilane respectively.

3. General procedure for the synthesis of 7: Suzuki−Miyaura coupling reaction

A mixture of bromine containing *ortho*-silyloxy benzylsulfoximine (**4e**, 20 mg, 0.0427 mmol), arylboronic acid (6, 19.5 mg, 0.1281 mmol), K_2CO_3 (29.5 mg, 0.2235 mmol), PPh_3 (1.1 mg, 10 mol %) in 1,4-dioxane (2.0 mL), and distilled water (0.8 mL) was degassed with a stream of argon passing through the solution for 15 min. Thereafter, $Pd(PPh_3)_2Cl_2$ (1.5 mg, 5 mol %) was added, and the reaction mixture was stirred under argon atmosphere for 3 h at 80 °C. After

completion, the reaction mixture was cooled, diluted with water (15 mL), and extracted with DCM (3 × 20 mL). The collected organic phase was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with 25% of EtOAc in hexane as eluent to give the product **7**.

Reference:

1. Y. Xie, B. Zhou, S. Zhou, S. Zhou, W. Wei, J. Liu, Y. Zhan, D. Cheng, M. Chen and Y. Li, *ChemistrySelect*, 2017, **2**, 1620

4. H_2 Evolution studies:

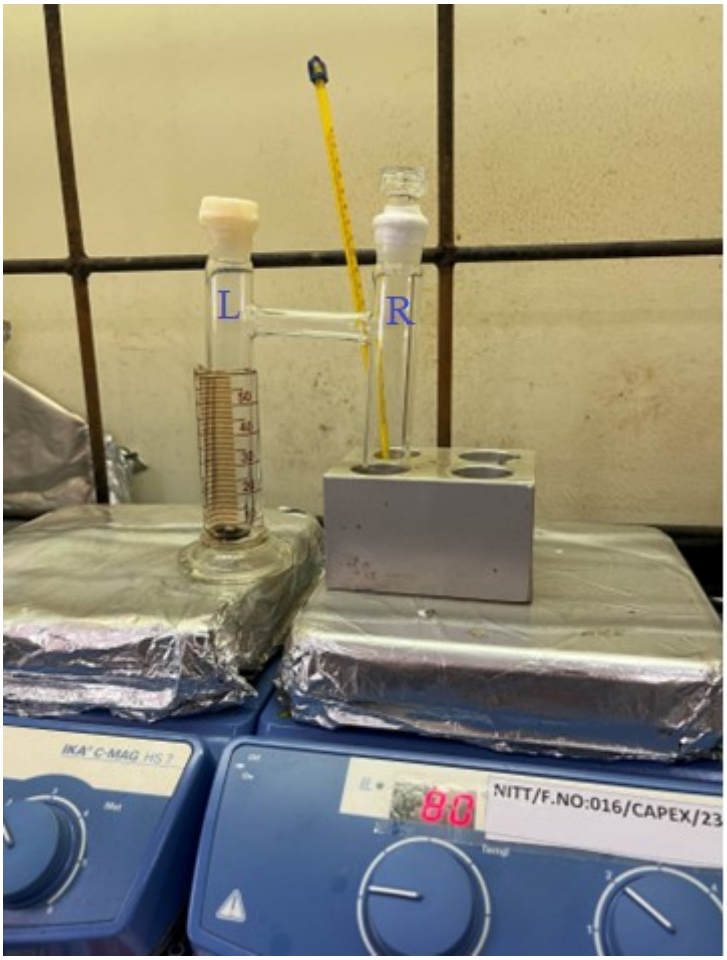
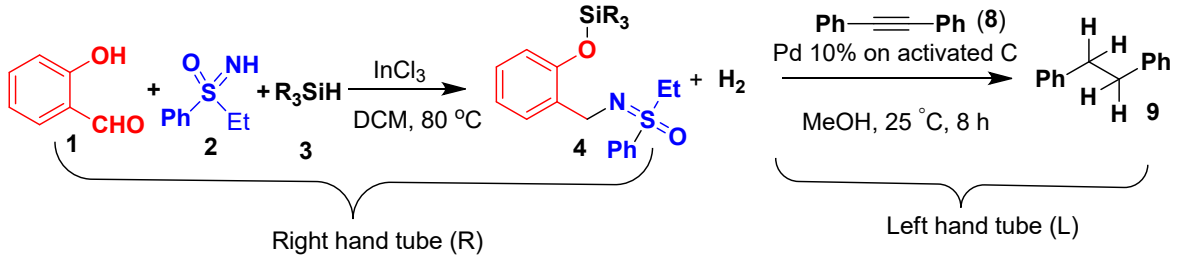


Figure 1: Reaction setup

Reaction Procedure

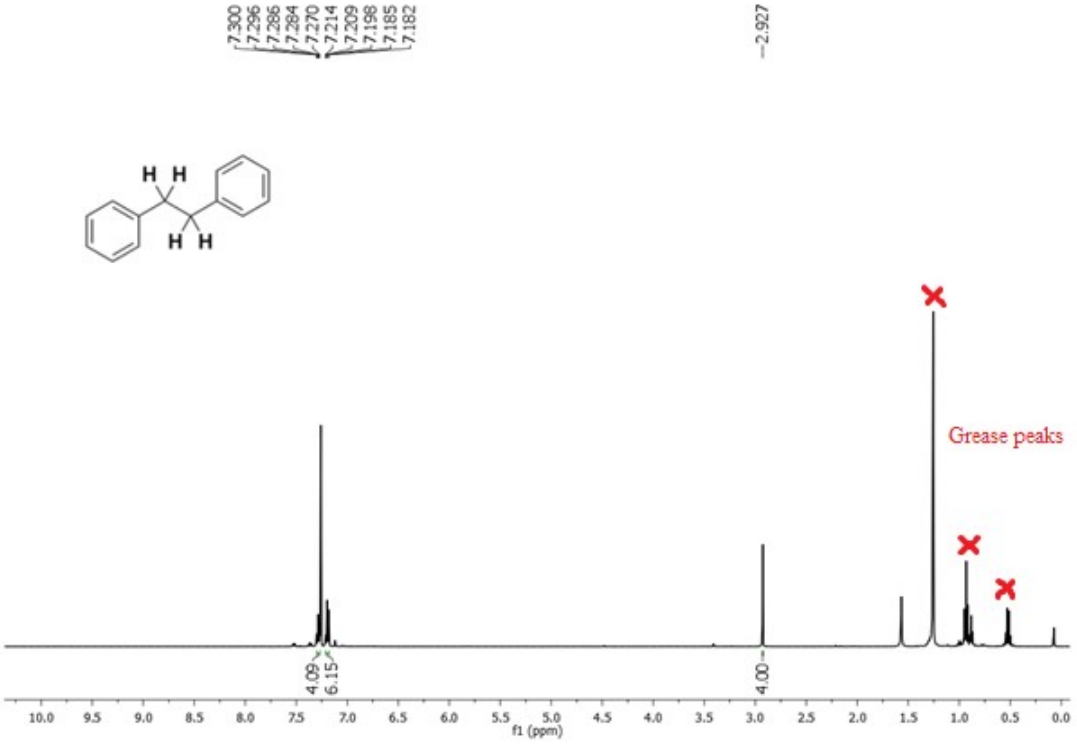


A 20 mL H-shape tube (2.5 x 17 cm) was taken for the reaction. Left side tube (**L**) with septum was charged with diphenylacetylene (**8**, 0.1 mmol), Pd/C, and MeOH (1.5 mL) at room temperature (25 °C). The **L**-tube is linked with the right side tube (**R**) containing salicylaldehyde **1a** (15 mg, 0.12 mmol), sulfoximine **2a** (19 mg, 0.12 mmol), trialkyl silane **3a** (43 mg, 0.36 mmol), and $InCl_3$ (5 mol%). The solvent DCM (1.5 mL) was added and closed tightly with lid (ensured there is no contact with atmospheric air). The resulting mixture was stirred at 80 °C for 8 hours. Simultaneously, The **L**-tube mixture too stirred for 8 h at room temp. After 8 h, the reaction mixture of L-tube was filtered and the filtrate was concentrated under reduced pressure, followed by triturated with hexane twice. The NMR of reaction mixture (without purification) proves the formation of **9**. It is possible only if diphenyl acetylene **8** is reduced (by hydrogen). The experiment proves the formation of H_2 in the reaction.

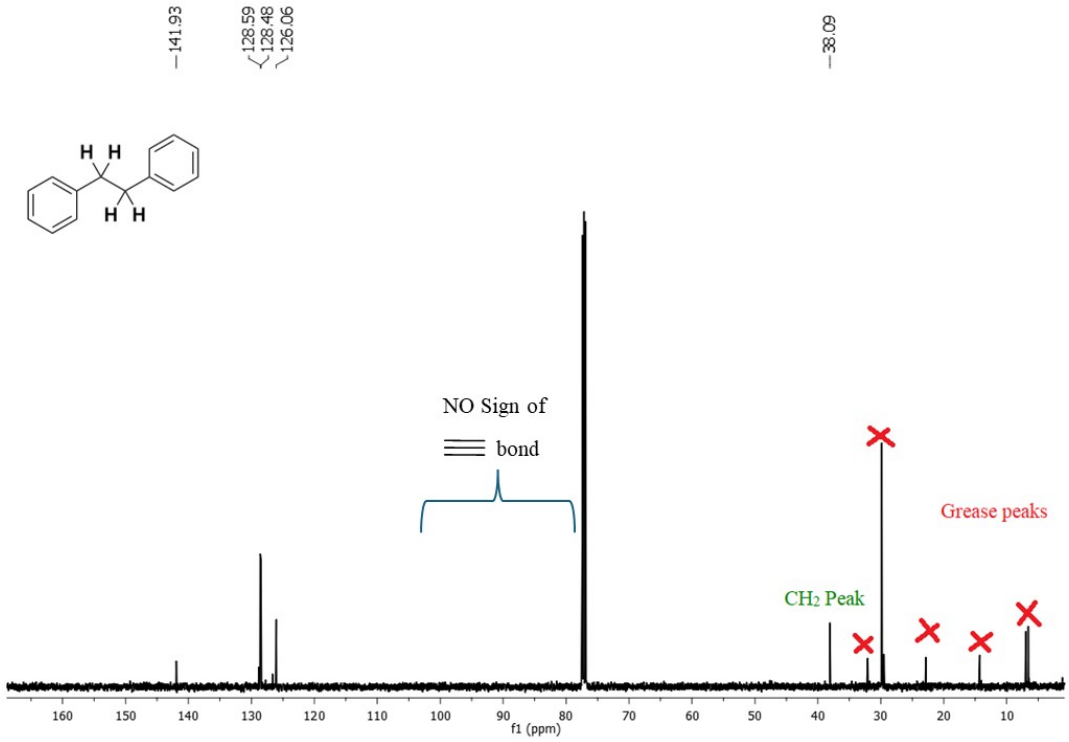
Analytical data of 9 (crude)

Yellowish sticky liquid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 - 7.27 (m, 4H), 7.21 - 7.18 (m, 6H), 2.92 (s, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.9, 128.5, 128.4, 126.0, 38.0.

^{1}H NMR of **9-crude** (500 MHz, $CDCl_3$)

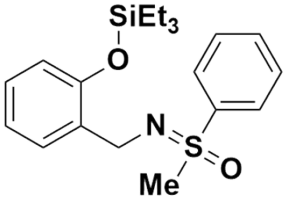


^{13}C {^{1}H} NMR of **9-Crude** (126 MHz, $CDCl_3$)



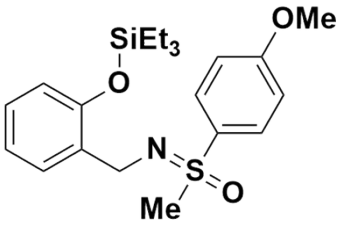
5. Analytical Data of the Synthesized Compounds

Compound 4a



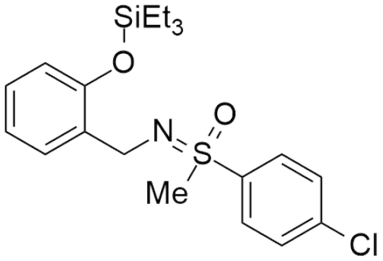
Yellowish sticky liquid, Yield: 69% (32 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.92 (d, J = 8.5 Hz, 2H), 7.63 – 7.57 (m, 2H), 7.52 (t, J = 7.5 Hz, 2H), 7.06 (t, J = 7.5 Hz, 1H), 6.96 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 4.20 (d, J = 16.0 Hz, 1H), 4.04 (d, J = 15.5 Hz, 1H), 3.15 (s, 3H), 0.88 (t, J = 7.5 Hz, 9H), 0.66 (q, J = 8.5 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 152.8, 139.7, 132.8, 131.9, 129.4, 128.8, 128.7, 127.1, 121.3, 118.1, 45.4, 42.1, 6.7, 5.3. **HRMS** (ESI) calcd for $C_{20}H_{30}NO_2SSi^+$ $[M+H]^+$ 376.1761; found 376.1761. **IR** (**cm^{-1}**): ν = 3062, 2926, 1587, 1489, 1455, 1211, 1124, 1083.

Compound 4b



Yellowish sticky liquid, Yield: 56% (28 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.83 (d, J = 9.0 Hz, 2H), 7.63 (d, J = 7.5 Hz, 1H), 7.06 (t, J = 8.0 Hz, 1H), 6.98 (d, J = 9.0 Hz, 2H), 6.95 (d, J = 7.5 Hz, 1H), 6.70 (d, J = 7.5 Hz, 1H), 4.17 (d, J = 16.0 Hz, 1H), 4.03 (d, J = 16.0 Hz, 1H), 3.85 (s, 3H), 3.13 (s, 3H), 0.89 (t, J = 8.0 Hz, 9H), 0.66 (t, J = 8.5 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 163.2, 152.7, 132.0, 130.9, 130.7, 128.6, 127.1, 121.2, 118.0, 114.6, 55.7, 45.6, 42.0, 6.7, 5.3. **HRMS** (ESI) calcd for $C_{21}H_{32}NO_3SSi^+$ $[M+H]^+$ 406.1867; found 406.1879. **IR (cm^{-1})**: ν = 3061, 2924, 2851, 1592, 1577, 1493, 1456, 1120, 1086.

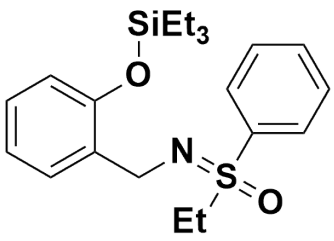
Compound 4c



Yellowish sticky liquid, Yield: 62% (31 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.83 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.0 Hz, 1H), 7.48 (d, J = 8.5 Hz, 2H), 7.06 (t, J = 8.0 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 4.18 (d, J = 15.5 Hz, 1H), 4.03 (d, J = 15.5 Hz, 1H), 3.13 (s, 3H), 0.90 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.5 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 152.8, 139.5, 138.3, 131.5, 130.2, 129.6, 128.7, 127.3, 121.2, 118.1, 45.4, 41.9, 6.7, 5.3. **HRMS** (ESI) calcd for

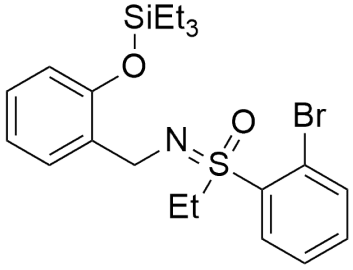
$C_{20}H_{29}ClNO_2SSi^+$ $[M+H]^+$ 410.1371; found 410.1381. IR (cm^{-1}): ν = 3087, 2954, 2875, 1587, 1489, 1456, 1211, 1126, 1083, 733.

Compound 4d



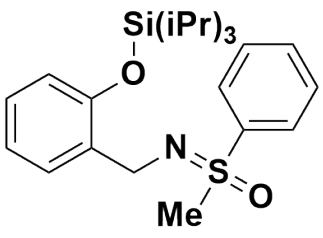
Yellowish sticky liquid, Yield: 71% (34 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.86 (d, J = 7.2 Hz, 2H), 7.66 (d, J = 6.8 Hz, 1H), 7.58 (t, J = 6.8 Hz, 1H), 7.51 (t, J = 7.2 Hz, 2H), 7.06 (t, J = 7.2 Hz, 1H), 6.96 (t, J = 7.2 Hz, 1H), 6.70 (d, J = 7.6 Hz, 1H), 4.20 (d, J = 16.0 Hz, 1H), 4.06 (d, J = 16.0 Hz, 1H), 3.33 – 3.18 (m, 2H), 1.27 (t, J = 7.6 Hz, 3H), 0.87 (t, J = 8.0 Hz, 9H), 0.64 (q, J = 7.6 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 152.8, 137.7, 132.8, 132.2, 129.5, 129.3, 128.6, 127.0, 121.2, 118.0, 51.1, 41.8, 29.8, 7.8, 6.7, 5.3. **HRMS** (ESI) calcd for $C_{21}H_{32}NO_2SSi^+$ $[M+H]^+$ 390.1918; found 390.1918.

Compound 4e



Brown liquid, Yield: 55% (31 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8.5:1.5). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.18 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.47 (t, J = 8.0 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.93 (t, J = 7.0 Hz, 1H), 6.68 (d, J = 8.0 Hz, 1H), 4.15 (d, J = 16.0 Hz, 1H), 4.05 (d, J = 16.0 Hz, 1H), 3.70 – 3.63 (m, 1H), 3.57 – 3.50 (m, 1H), 1.28 (t, J = 7.5 Hz, 3H), 0.88 (t, J = 8.0 Hz, 9H), 0.65 (q, J = 8.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 152.6, 136.7, 135.5, 134.4, 133.8, 131.6, 128.8, 128.0, 127.0, 121.2, 121.1, 117.8, 48.4, 42.2, 7.1, 6.6, 5.2. **HRMS** (ESI) calcd for $C_{21}H_{31}BrNO_2SSi^+$ $[M+H]^+$ 468.1023; found 468.1032. **IR (cm^{-1})**: ν = 3082, 2925, 1587, 1489, 1455, 1210, 1132,1092, 569.

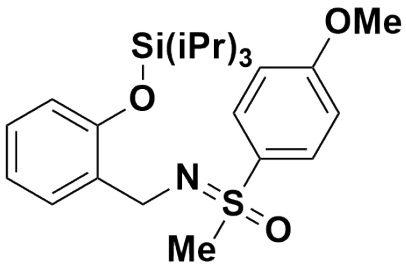
Compound 4f



Yellow sticky liquid, Yield: 65% (33 mg from 0.1289 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.92 (d, J = 7.5 Hz, 2H), 7.66 (d, J = 7.5 Hz, 1H), 7.58 (t, J = 7.5 Hz, 1H), 7.51 (t, J = 7.0 Hz, 2H), 7.05 (t, J = 7.0 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 8.0 Hz, 1H), 4.22 (d, J = 16.0 Hz, 1H), 4.08 (d, J = 16.0 Hz, 1H), 3.16 (s, 3H),

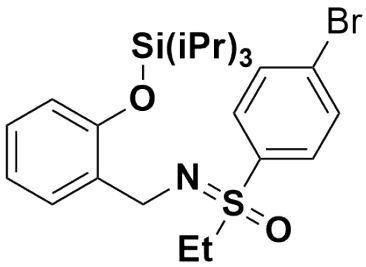
1.21-1.14 (m, 3H), 0.99 (dd, J = 1.5 Hz, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 153.0, 139.7, 132.8, 131.7, 129.4, 128.8, 128.4, 127.0, 120.9, 117.6, 45.3, 42.4, 18.1, 13.1. **HRMS** (ESI) calcd for $C_{23}H_{36}NO_2SSi^+$ $[M+H]^+$ 418.2231; found 418.2236.

Compound 4g



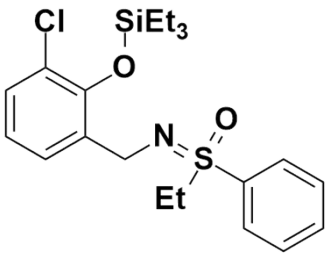
Brown solid, Yield: 68% (37 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 7.5:2.5), mp 102-104 ˚C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.83 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 7.5 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.98 - 6.93 (m, 3H), 6.71 (d, J = 8.0 Hz, 1H), 4.21 (d, J = 16.0 Hz, 1H), 4.09 (d, J = 16.0 Hz, 1H), 3.86 (s, 3H), 3.14 (s, 3H), 1.2 - 1.16 (m, 3H), 1.00 (dd, J = 6.5, 1.0 Hz, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 163.2, 153.0, 131.9, 130.9, 128.4, 126.9, 120.9, 117.6, 114.6, 55.7, 45.6, 42.4, 18.1, 13.1. **HRMS** (ESI) calcd for $C_{24}H_{38}NO_3SSi^+$ $[M+H]^+$ 448.2336; found 448.2354. **IR (cm^{-1})**: ν = 3064, 2943, 2866, 1593, 1485, 1453, 1219, 1135, 1085.

Compound 4h



Brown solid, Yield: 66% (41 mg from 0.1289 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8:2), mp 104-106 ˚C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.69 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.5 Hz, 3H), 7.05 (t, J = 7.5 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 8.0 Hz, 1H), 4.22 (d, J = 16.0 Hz, 1H), 4.11 (d, J = 15.5 Hz, 1H), 3.29 – 3.18 (m, 2H), 1.28 (t, J = 7.5 Hz, 3H), 1.22 - 1.15 (m, 3H), 1.00 (dd, J = 6.5, 1.0 Hz, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 153.0, 137.0, 132.6, 131.7, 131.1, 128.4, 128.0, 127.0, 120.9, 117.6, 51.2, 42.1, 18.1, 13.1, 7.7. **HRMS** (ESI) calcd for $C_{24}H_{37}BrNO_2SSi^+$ $[M+H]^+$ 510.1492 ; found 510.1507. **IR (cm^{-1})**: ν = 3065, 2943, 1599, 1485, 1453, 1218, 1138, 1082, 584.

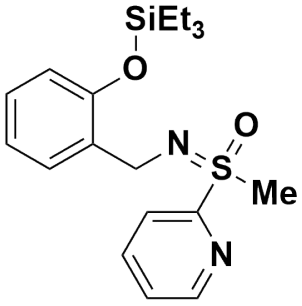
Compound 4i



Yellowish sticky liquid, Yield: 55% (41 mg from 0.1755 mmol of corresponding salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.85 (d, J = 8.0 Hz, 2H), 7.62 – 7.56 (m, 2H), 7.53 (t, J = 7.0 Hz, 2H), 7.17 (d, J = 7.5 Hz, 1H), 6.91 (t, J = 8.0 Hz, 1H), 4.16 (d, J = 16.0 Hz, 1H), 4.04 (d, J = 16.0 Hz, 1H), 3.33 – 3.20 (m, 2H), 1.29 (t, J = 7.5 Hz,

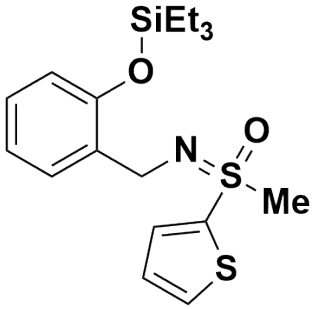
3H), 0.85 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 7.5 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 149.2, 137.7, 134.5, 132.9, 129.5, 129.4, 127.9, 126.9, 124.5, 122.0, 51.1, 42.7, 7.7, 6.7, 5.7. **HRMS** (ESI) calcd for $C_{21}H_{31}ClNO_2SSi^+$ $[M+H]^+$ 424.1528; found 424.1540. **IR (cm^{-1})**: ν = 3061, 2955, 2876, 1579, 1456, 1126, 1085, 764.

Compound 4j



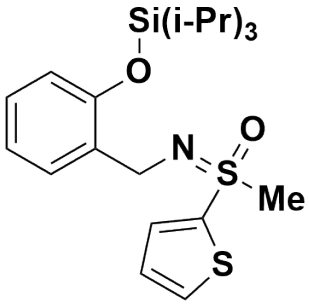
Pale yellow solid, Yield: 53% (24 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8:2), mp 112-114 ˚C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.71- 8.70 (m, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.87 (t, J = 7.5 Hz, 1H), 7.56 (d, J = 7.5 Hz, 1H), 7.46 - 7.43 (m, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.66 (d, J = 8.0 Hz, 1H), 4.26 (d, J = 16.0 Hz, 1H), 4.08 (d, J = 15.5 Hz, 1H), 3.33 (s, 3H), 0.90 (t, J = 7.5 Hz, 9H), 0.71 – 0.65 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 158.2, 152.6, 150.3, 137.7, 131.5, 128.8, 127.1, 126.4, 123.1, 121.2, 117.8, 41.9, 41.2, 6.7, 5.3. **HRMS** (ESI) calcd for $C_{19}H_{29}N_2O_2SSi^+$ $[M+H]^+$ 377.1714; found 377.1704. **IR (cm^{-1})**: ν = 3060, 2927, 2851, 1600, 1450, 1262, 1110, 1073.

Compound 4k



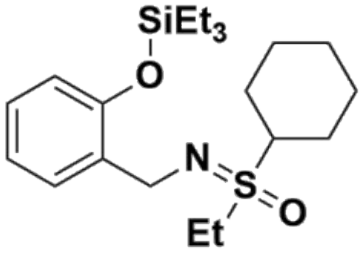
Yellowish sticky liquid, Yield: 60% (28 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 7.5:2.5). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.65 (dd, J = 5.0, 1.5 Hz, 1H), 7.59 – 7.57 (m, 1H), 7.56 (dd, J = 4.0, 1.5 Hz, 1H), 7.15 – 7.06 (m, 2H), 6.96 (t, J = 7.5 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 4.28 (d, J = 15.5 Hz, 1H), 4.17 (d, J = 15.5 Hz, 1H), 3.29 (s, 3H), 0.91 (t, J = 7.5 Hz, 9H), 0.71 – 0.66 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 152.8, 141.5, 133.7, 133.6, 131.6, 128.6, 128.1, 127.2, 121.2, 118.1, 47.2, 42.2, 6.7, 5.3. **HRMS** (ESI) calcd for $C_{18}H_{28}NO_2S_2Si^+$ $[M+H]^+$ 382.1325; found 382.1324.

Compound 4l



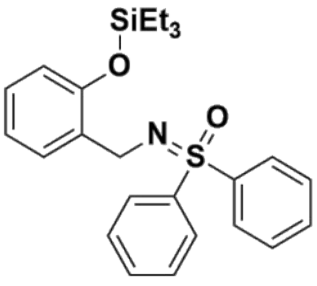
Pale yellow solid, Yield: 62% (32 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 7:3), mp 120-122 ˚C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.64 (d, J = 5.0 Hz, 1H), 7.62 - 7.60 (m, 1H), 7.55 (d, J = 3.5 Hz, 1H), 7.10 - 7.09 (m, 1H), 7.06 (t, J = 8.0 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 4.32 (d, J = 16.0 Hz, 1H), 4.21 (d, J = 16.0 Hz, 1H), 3.30 (s, 3H), 1.25 - 1.17 (m, 3H), 1.02 (d, J = 7.5 Hz, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 153.0, 141.4, 133.6, 133.6, 131.4, 128.4, 128.0, 127.1, 120.9, 117.6, 47.2, 42.5, 18.1, 13.0. **HRMS** (ESI) calcd for $C_{21}H_{34}NO_2S_2Si^+$ $[M+H]^+$ 424.1795; found 424.1799.

Compound 4m



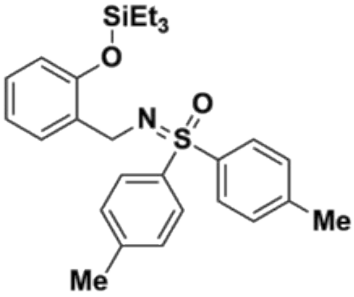
Colourless sticky liquid, Yield: 62% (30 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.56 (d, J = 7.5 Hz, 1H), 7.05 (t, J = 8.0 Hz, 1H), 6.93 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 4.30 (s, 2H), 3.06 - 2.97 (m, 3H), 2.27 - 2.25 (m, 1H), 2.17 - 2.15 (m, 1H), 1.93 - 1.89 (m, 2H), 1.72 - 1.69 (m, 1H), 1.61 – 1.52 (m, 2H), 1.32 (t, J = 7.5 Hz, 3H), 1.28 – 1.18 (m, 3H), 0.98 (t, J = 7.5 Hz, 9H), 0.75 (q, J = 8.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 152.6, 132.6, 128.4, 126.8, 121.0, 117.7, 60.8, 43.2, 40.5, 26.2, 25.8, 25.6, 25.5, 25.3, 7.5, 6.7, 5.3. **HRMS** (ESI) calcd for $C_{21}H_{38}NO_2SSi^+$ $[M+H]^+$ 396.2387; found 396.2406.

Compound 4n



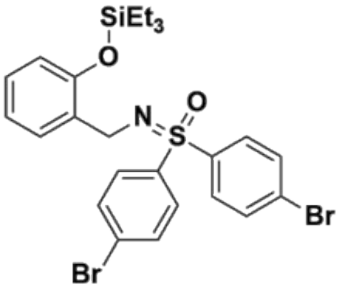
Yellowish sticky liquid, Yield: 40% (21.5 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.02 (d, J = 8.5 Hz, 4H), 7.81 (d, J = 8.5 Hz, 1H), 7.51 - 7.44 (m, 6H), 7.09 (t, J = 7.5 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 4.28 (s, 2H), 0.87 (t, J = 7.5 Hz, 9H), 0.67 – 0.62 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 152.8, 140.9, 132.4, 132.3, 129.2, 128.7, 128.3, 127.0, 121.2, 117.9, 42.1, 6.7, 5.3. **HRMS** (ESI) calcd for $C_{25}H_{32}NO_2SSi^+$ $[M+H]^+$ 438.1918; found 438.1922.

Compound 4o



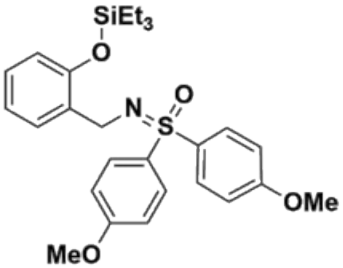
Yellowish sticky liquid, Yield: 66% (37.5 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8.5:1.5). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.88 (d, J = 8.5 Hz, 4H), 7.83 (d, J = 7.5 Hz, 1H), 7.24 (d, J = 8.0 Hz, 4H), 7.09 (t, J = 8.0 Hz, 1H), 7.02 (t, J = 7.0 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 4.26 (s, 2H), 2.36 (s, 6H), 0.88 (t, J = 8.0 Hz, 9H), 0.65 (q, J = 8.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 152.7, 143.0, 138.1, 132.4, 129.8, 128.6, 128.4, 126.9, 121.2, 117.8, 42.1, 21.5, 6.7, 5.3. **HRMS** (ESI) calcd for $C_{27}H_{36}NO_2SSi^+$ $[M+H]^+$ 466.2231; found 466.2249. **IR (cm^{-1})**: ν = 3042, 2956, 1662, 1593, 1488, 1455, 1248, 1126, 1083.

Compound 4p



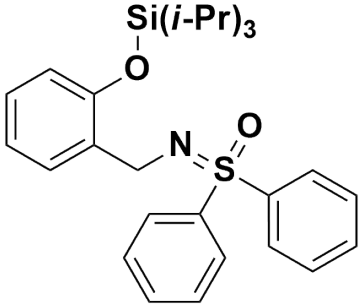
Brown sticky liquid, Yield: 57% (41.5 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 9:1). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.83 (d, J = 8.5 Hz, 4H), 7.70 (d, J = 7.5 Hz, 1H), 7.59 (d, J = 8.5 Hz, 4H), 7.10 (t, J = 8.0 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 4.25 (s, 2H), 0.89 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 152.8, 139.7, 132.6, 131.6, 130.2, 128.4, 127.9, 127.3, 121.2, 118.0, 41.9, 6.7, 5.3. **HRMS** (ESI) calcd for $C_{25}H_{30}$ $Br_2NO_2SSi^+$ $[M+H]^+$ 594.0128; found 594.0136. **IR (cm^{-1})**: ν = 3084, 2955, 2875, 1571, 1486, 1454, 1264, 1139, 1092.

Compound 4q



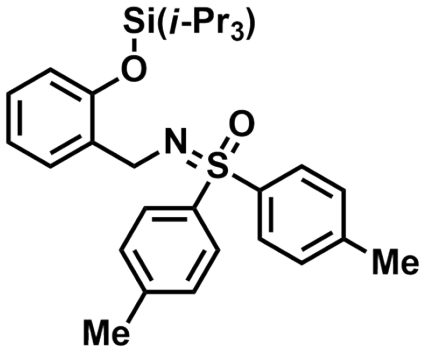
Yellowish sticky liquid, Yield: 64% (39 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 7:3). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.92 (d, J = 9.0 Hz, 4H), 7.84 (d, J = 7.5 Hz, 1H), 7.09 (t, J = 8.0 Hz, 1H), 7.02 (t, J = 7.0 Hz, 1H), 6.91 (d, J = 9.0 Hz, 4H), 6.73 (d, J = 8.0 Hz, 1H), 4.27 (s, 2H), 3.78 (s, 6H), 0.89 (t, J = 8.0 Hz, 9H), 0.66 (q, J = 8.0 Hz, 6H).**^{13}C NMR** (126 MHz, $CDCl_3$): δ 162.6, 152.6, 132.8, 132.5, 130.4, 128.2, 126.8, 121.1, 117.8, 114.3, 55.5, 42.0, 6.6, 5.2. **HRMS** (ESI) calcd for $C_{30}H_{42}NO_4SSi^+$ $[M+H]^+$ 498.2129; found 498.2122.

Compound 4r



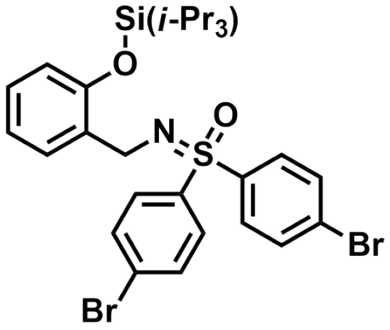
Pale yellow solid, Yield: 42% (24.5 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8.5:1.5), mp 101-103 ˚C. **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.02 (d, J = 8.5 Hz, 4H), 7.83 (d, J = 7.5 Hz, 1H), 7.51 – 7.44 (m, 6H), 7.07 (t, J = 8.0 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 4.31 (s, 2H), 1.21 - 1.15 (m, 3H), 0.98 (d, J = 7.0 Hz, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 153.0, 140.8, 132.4, 132.0, 129.2, 128.8, 128.2, 126.9, 120.9, 117.5, 42.5, 18.1, 13.0. **HRMS** (ESI) calcd for $C_{28}H_{38}NO_2SSi^+$ $[M+H]^+$ 480.2387; found 480.2404.

Compound 4s



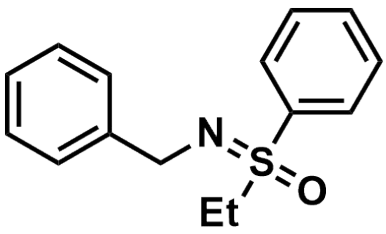
Yellowish sticky liquid, Yield: 40% (25 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.87 (d, J = 8.5 Hz, 4H), 7.83 (d, J = 7.5 Hz, 1H), 7.24 (d, J = 8.5 Hz, 4H), 7.06 (t, J = 8.0 Hz, 1H), 6.99 (t, J = 7.5 Hz, 1H), 6.71 (d, J = 7.5 Hz, 1H), 4.29 (s, 2H), 2.36 (s, 6H), 1.18 – 1.12 (m, 3H), 0.98 (d, J = 7.5 Hz, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 152.9, 143.2, 138.9, 132.1, 129.9, 128.7, 128.3, 126.9, 120.9, 117.5, 41.8, 21.5, 18.1, 13.0. **HRMS** (ESI) calcd for $C_{30}H_{42}NO_2SSi^+$ $[M+H]^+$ 508.2700; found 508.2726.

Compound 4t



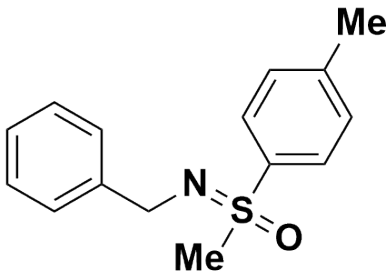
Yellowish sticky liquid, Yield: 40% (31 mg from 0.1228 mmol of salicylaldehyde), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.83 (d, J = 8.5 Hz, 4H), 7.71 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 9.0 Hz, 4H), 7.08 (t, J = 8.0 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 6.73 (d, J = 8.0 Hz, 1H), 4.29 (s, 2H), 1.22 - 1.16 (m, 3H), 1.00 (d, J = 7.0 Hz, 18H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 153.0, 139.6, 132.6, 131.4, 130.3, 128.2, 127.9, 127.2, 120.9, 117.6, 42.3, 18.1, 13.0. **HRMS** (ESI) calcd for $C_{28}H_{36}Br_2NO_2SSi^+$ $[M+H]^+$ 636.0597; found 636.0595

Compound 5a



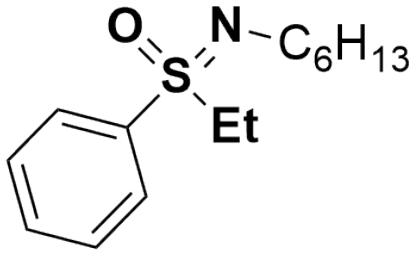
Yellowish sticky liquid, Yield: 76% (28 mg from 0.1413 mmol of corresponding aldehyde), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.89 (d, J = 7.5 Hz, 2H), 7.60 (t, J = 7.5 Hz, 1H), 7.54 (t, J = 7.5 Hz, 2H), 7.38 (d, J = 7.5 Hz, 2H), 7.29 (t, J = 7.0 Hz, 2H), 7.19 (t, J = 7.5 Hz, 1H), 4.25 (d, J = 14.5 Hz, 1H), 4.03 (d, J = 14.5 Hz, 1H), 3.31 – 3.19 (m, 2H), 1.26 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 141.5, 137.5, 133.0, 129.5, 129.4, 128.3, 127.6, 126.5, 51.0, 47.2, 7.5. **HRMS** (ESI) calcd for $C_{15}H_{18}NOS^+$ $[M+H]^+$ 260.1104; found 260.1109.

Compound 5b



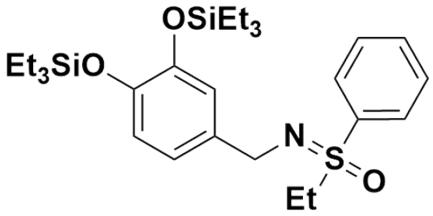
Colourless sticky liquid, Yield: 71% (26 mg from 0.1413 mmol of corresponding aldehyde), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.72 (d, J = 8.5 Hz, 2H), 7.26 - 7.24 (m, 4H), 7.18 (d, J = 8.0 Hz, 2H), 7.09 (t, J = 7.5 Hz, 1H), 4.09 (d, J = 14.5 Hz, 1H), 3.87 (d, J = 14.5 Hz, 1H), 3.03 (s, 3H), 2.34 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$): δ 143.8, 141.2, 136.2, 130.1, 128.7, 128.2, 127.6, 126.4, 47.3, 45.3, 21.5. **HRMS** (ESI) calcd for $C_{15}H_{18}NOS^+$ $[M+H]^+$ 260.1104; found 260.1123.

Compound 5c



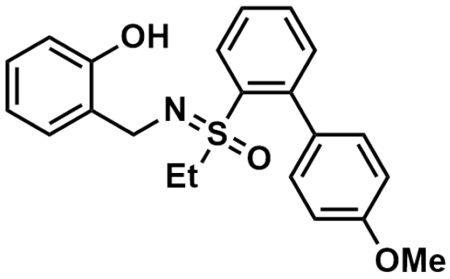
Colourless sticky liquid, Yield: 59% (30 mg from 0.1997 mmol of corresponding aldehyde), purified through column chromatography (Hexane/EtOAc 9:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84 (d, J = 8.5 Hz, 2H), 7.58 (t, J = 7.0 Hz, 1H), 7.53 (t, J = 8.0 Hz, 2H), 3.20 – 3.11 (m, 2H), 2.98 – 2.93 (m, 1H), 2.81 – 2.76 (m, 1H), 1.57 – 1.51 (m, 2H), 1.32 – 1.23 (m, 6H), 1.99 (t, J = 7.5 Hz, 3H), 0.84 (t, J = 7.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 138.0, 132.8, 129.6, 129.3, 50.9, 43.9, 33.0, 31.7, 27.0, 22.7, 14.1, 7.5. **HRMS** (ESI) calcd for $C_{14}H_{24}NOS^+$ $[M+H]^+$ 254.1573; found 254.1569.

Compound 5d



Yellowish sticky liquid, Yield: 48% (27 mg from 0.1086 mmol of corresponding aldehyde), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.86 (d, J = 8.5 Hz, 2H), 7.59 (t, J = 7.0 Hz, 1H), 7.52 (t, J = 7.0 Hz, 2H), 6.85 (d, J = 2.5 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H), 6.71 (d, J = 8.5 Hz, 1H), 4.12 (d, J = 14.5 Hz, 1H), 3.90 (d, J = 14.0 Hz, 1H), 3.27 – 3.15 (m, 2H), 1.24 (t, J = 7.5 Hz, 3H), 0.99 - 0.95 (m, 18H), 0.76 – 0.65 (m, 12H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 146.5, 145.3, 137.8, 134.7, 132.9, 129.5, 129.4, 120.4, 120.2, 119.9, 51.1, 46.6, 7.6, 6.8, 6.8, 5.2, 5.1. **HRMS** (ESI) calcd for $C_{27}H_{46}NO_3SSi_2^+$ $[M+H]^+$ 520.2731; found 520.2739.

Compound 7



Colourless sticky liquid, Yield: 66% (11 mg from 0.0427 mmol of 4e), purified through column chromatography (Hexane/EtOAc 8:2). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.19 (t, J = 8.0 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 7.5 Hz, 1H), 7.18 (d, J = 9.0 Hz, 2H), 7.12 (t, J = 8.0 Hz, 1H), 6.88 – 6.81 (m, 4H), 6.76 – 6.72 (m, 1H), 4.46 (d, J = 14.5 Hz, 1H), 4.11 (d, J = 15.0 Hz, 1H), 3.82 (s, 3H), 2.96 - 2.89 (m, 1H), 2.74 - 2.67 (m, 1H), 1.10 (t, J = 7.5 Hz, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$): δ 159.7, 157.4, 142.1, 135.4, 133.5, 132.9, 131.4, 130.7, 130.4, 128.1, 128.0, 127.7, 124.1, 121.1, 119.2, 113.4, 55.4, 49.1, 46.5, 6.8. **HRMS** (ESI) calcd for $C_{22}H_{24}NO_3S^+$ $[M+H]^+$ 382.1471; found 382.1481.