Mild, Redox-Neutral Alkylation of Imines Enabled by an Organic Photocatalyst

Niki R. Patel, Christopher B. Kelly, Allison P. Siegenfeld, and Gary A. Molander

Roy and Diana Vagelos Laboratories, Department of Chemistry, University of Pennsylvania,
231 South 34th Street, Philadelphia, Pennsylvania 19104-6323

*To whom correspondence should be addressed. E-mail: gmolandr@sas.upenn.edu

Supporting Information

| Key to Abbreviated Terms |   |
|--------------------------|---|
| General Considerations   | S2 |
| Comments regarding origins of starting materials, purification of solvents, and spectroscopic techniques. |
| Synthesis of Alkylbis(catecholato)silicates | S3 |
| Procedures for the preparation of alkylsilicates and their spectral characterization information. |
| Synthesis of the organic photocatalyst 4CzIPN | S6 |
| Procedure for photocatalyst synthesis and spectral characterization information. |
| Synthesis of Imines | S7 |
| Procedures for the preparation of imines and spectral characterization information. |
| Cyclic Voltammogram of Representative Imines | S16 |
| Graphs of CVs of N-Sulfonyl and N-Aryl imines |
| Optimization & Control Studies for Alkylation | S18 |
| Procedure for photocatalyst synthesis. |
| General Procedure for Alkylation Using Alkylsilicates | S21 |
| General procedure for synthesis and isolation as well as spectral characterization information for alkylated products. |
| Representative Procedure for Large Scale Alkylation | S37 |
| General procedure for the scale up of the described alkylation. |
| Procedure for Ni/Photoredox Cross-Coupling of 4ak | S39 |
| Procedure for the synthesis of 4al. |
| ¹H NMR Spectra of Synthesized Compounds | S41 |
| ¹³C NMR Spectra of Synthesized Compounds | S100 |
| ¹⁹F NMR Spectra of Synthesized Compounds | S159 |
Key to Abbreviated Terms:

4CzIPN: 2,4,5,6-Tetra(9H-carbazol-9-y1)isophthalonitrile
Cz: Carbazole
CV: Cyclic Voltammogram
LED: Light-emitting diode

General Considerations:

General:
All chemical transformations requiring inert atmospheric conditions or vacuum distillation utilized Schlenk line techniques with a 4- or 5-port dual-bank manifold. Argon or nitrogen was used to provide such an atmosphere. LED irradiation was accomplished using the LED reactors described in our previous reports.\(^1\) NMR spectra (\(^1\)H, \(^13\)C, \(^19\)F) were obtained at 298 K. \(^1\)H NMR spectra were referenced to residual non-deuterated chloroform (\(\delta\) 7.26) in CDCl\(_3\) or residual DMSO-\(d_5\) (\(\delta\) 2.50) in DMSO-\(d_6\). \(^13\)C NMR spectra were referenced to CDCl\(_3\) (\(\delta\) 77.3) or DMSO-\(d_6\) (\(\delta\) 39.5). \(^19\)F NMR spectra were referenced to hexafluorobenzene (\(\delta\) –164.9) as an internal standard.\(^2\) Reactions were monitored by HPLC, GC/MS, \(^1\)H NMR, and/or TLC on silica gel plates (60 Å porosity, 250 µm thickness). TLC analysis was performed using hexanes/EtOAc as the eluant and visualized using permanganate stain, Seebach’s stain,\(^3\) ninhydrin stain, and/or UV light. Silica plugs utilized flash silica gel (60 Å porosity, 32-63 µm). Flash chromatography was accomplished using an automated system (monitoring at 254 nm and 280 nm) with silica cartridges (60 Å porosity, 20-40 µm). Solvents were purified with drying cartridges through a solvent delivery system. Melting points (°C) are uncorrected.

Chemicals:
Deuterated NMR solvents were either used as purchased (DMSO-\(d_6\)) or stored over 4Å molecular sieves and/or K\(_2\)CO\(_3\) (CDCl\(_3\)). Na\(_2\)SO\(_4\), MgSO\(_4\), CH\(_2\)Cl\(_2\), CHCl\(_3\), EtOAc, pentane, hexanes, heptane, Et\(_2\)O, and benzene were used as purchased. Et\(_3\)N and \(^4\)Pr\(_2\)NH, were purchased from commercial suppliers and distilled from CaH\(_2\) prior to use. THF was purchased and dried via a solvent delivery system. Catechol was purchased and recrystallized from refluxing hexanes or heptanes. DMF (99.8%, extra dry) was stored over 4 Å molecular sieves. Anhydrous DMSO, aldehydes, sulfonamides, and amines were purchased from commercial suppliers and used

\(^1\) For information on these reactors and their construction see the supporting information of: (a) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. Org. Lett. 2016, 18, 764.; (b) Jouffroy, M.; Kelly, C. B.; Molander, G. Org. Lett. 2016, 18, 876.
\(^2\) Ravikumar, I.; Saha, S.; Ghosh, P. Chem. Commun. 2011, 47, 4721.
\(^3\) Seebach, D.; Imwinkelried, R; Stucky, G. Helv. Chim. Acta 1987, 70, 448.
without further purification. The transition metal photocatalysts Ru(bpy)$_3$(PF$_6$)$_2$ and [Ir{dFCF$_3$ppy}(bpy)]PF$_6$ were prepared in-house by the procedures outlined in our previous publications.$^{1a,4}$ The organic photocatalyst 4CzIPN was prepared using the procedure outlined here. New alkysilicates (3e-f, 3k) were prepared according to the representative procedure outlined below from their corresponding alkytrimethoxysilanes. Information (preparation protocols, characterization, etc.) for all other silicates can be found in our previous reports.$^5$

**Synthesis of Alkylbis(catecholato)silicates**

*Preparation of Diisopropylammonium Bis(catecholato)propylsilicate (3k)*

To an oven-dried, 100 mL round bottom flask equipped with a stir bar, reflux condenser, and gas inlet adapter was added catechol$^6$ (3.01 g, 27.3 mmol, 1.95 equiv) followed by anhydrous THF (28 mL) and anhydrous i-Pr$_2$NH$^7$ (1.70 g, 2.35 mL, 16.8 mmol, 1.2 equiv). The mixture was placed under an argon atmosphere and was allowed to stir at rt for 5 min until the solution became a pale red. After this time, n-PrSi(OMe)$_3$ (2.30 g, 14 mmol, 1.0 equiv) was added. The solution immediately lightened to a golden yellow. The solution was then heated to reflux in an oil bath and allowed to stir overnight at this temperature.$^8$ Once the reaction was judged to be complete by crude $^1$H NMR analysis,$^9$ the solvent was removed *in vacuo* by rotary evaporation. The resulting powder was collected *via* filtration through a medium porosity fritted funnel. The powder was washed with Et$_2$O (~100 mL) and pentane (~150 mL). The solid was collected and

---

$^4$ Tellis, J. C.; Primer, N. P.; Molander, G. A. *Science* **2014**, 345, 433.

$^5$ (a) Jouffroy, M.; Primer, D.; Molander, G. A. *J. Am. Chem. Soc.* **2016**, 138, 475; (b) Patel, N. R.; Kelly, C. B.; Jouffroy, M.; Molander, G. A. *Org. Lett.*, **2016**, 18, 764; (c) Jouffroy, M.; Davies, G. H. M.; Molander, G. A. *Org. Lett.* **2016**, 18, 1606.

$^6$ Recrystallized from hexane or heptane prior to use.

$^7$ A similar protocol can be used to prepare the more organic soluble triethylammonium salt. This salt works equally well for photoredox alkylation.

$^8$ Depending on the nature of the silicate and its solubility in THF, precipitation of the product would occur.

$^9$ For DIPA silicates, it is advisable to use acetone-$d_6$ or DMSO-$d_6$ as the NMR solvent, as these silicates have poor solubility in most other deuterated solvents.
dried further in vacuo to give the propylsilicate 3k (4.20 g, 77%) as a powdery white solid (mp = 194-195 °C) that co-crystallized with ~0.25 equiv THF.\(^\text{10}\)

\(^1\text{H NMR}\) δ 0.44 - 0.52 (m, 2 H), 0.73 (t, \(J = 7.3 \text{ Hz}, 3 \text{ H}\)), 1.13 - 1.26 (m, 2H), 1.18 (d, \(J = 6.4 \text{ Hz}, 12\text{ H}\)), 3.33 (sept, \(J = 6.4 \text{ Hz}, 2\text{ H}\)), 6.35 - 6.46 (m, 4 H), 6.46 - 6.54 (m, 4 H), 7.85 - 8.17 (m, 2 H).

\(^{13}\text{C NMR}\) δ 17.7 (CH\(_3\)), 18.0 (CH\(_2\)), 18.8 (CH\(_3\)), 21.1 (CH\(_2\)), 46.3 (CH), 109.4 (CH), 117.0 (CH), 150.6 (CH).

\(^{\text{FT-IR}}\) (cm\(^{-1}\), neat, ATR) 3046 (w, br), 2865 (w, br), 1484 (s), 1467 (w), 1451 (w), 1393 (vs), 810 (vs).

\(^{\text{HRMS}}\) (ES-) calcd for C\(_{15}\)H\(_{15}\)O\(_4\)Si [M−\(^2\text{PrNH}_2\)^−]: 287.0740, found: 287.0747.

Diisopropylammonium Bis(catecholato)(2-phenylethyl)silicate, 3e (9.30 g, 93%) was prepared according to the general procedure from (2-phenylethyl)trimethoxysilane (5.00 g, 22.1 mmol). The desired silicate 3e was isolated as a off-white solid (mp = 200-201 °C). \(^1\text{H NMR}\) (DMSO-\(d_6\), 500 MHz) δ 0.72 - 0.85 (m, 2H), 1.17 (d, \(J = 6.4 \text{ Hz}, 12\text{ H}\)), 2.36 - 2.57 (m, 2H), 3.32 (s eqpt, \(J = 6.7 \text{ Hz}, 2\text{ H}\)), 6.39 - 6.47 (m, 4H), 6.50 - 6.58 (m, 4H), 6.98 - 7.05 (m, 3H), 7.08 - 7.16 (m, 2H), 8.00 (br s, 2H). \(^{13}\text{C NMR}\) (DMSO-\(d_6\), 125 MHz) δ 18.9 (CH\(_3\)) 20.4 (CH\(_2\)) 30.5 (CH\(_2\)) 46.3 (CH) 109.5 (CH) 117.1 (CH) 124.8 (CH) 127.4 (CH) 127.9 (CH) 146.0 (C) 150.6 (C). \(^{\text{FT-IR}}\) (cm\(^{-1}\), neat, ATR) 3052 (vw, br) 2986 (vw), 2873 (vw), 1593 (w), 1485 (vs), 1239 (vs), 817 (s), 734 (vs), 700 (vs), 674 (vs), 495 (m). \(^{\text{HRMS}}\) (ES-) calcd for C\(_{20}\)H\(_{17}\)O\(_4\)Si [M−\(^2\text{PrNH}_2\)^−]: 349.0896, found: 349.0908.

Diisopropylammonium Bis(catecholato) (3-pentafluorophenylpropyl)silicate, 3f (7.51 g, 89%) was prepared according to the general procedure from (3-pentafluorophenylpropyl)trimethoxysilane (5.02 g, 15.2 mmol). The desired silicate 3f was isolated as a white solid (mp = 174-175 °C). \(^1\text{H NMR}\) (DMSO-\(d_6\), 500 MHz 0.45 - 0.62 (m, 2H), 1.18 (d, \(J = 7.0 \text{ Hz}, 12\text{ H}\)), 1.38 - 1.53 (m, 2H), 2.52 (t, \(J = 7.3 \text{ Hz}, 2\text{ H}\)), 3.33

\(^{10}\) Presence of THF does not impede any photoredox process involving silicates, included alkylation.
(sept, $J = 7.0$ Hz, 2H), 6.37 - 6.44 (m, 4H), 6.46 - 6.53 (m, 4H), 8.00 (br s, 2H). $^{13}$C NMR (DMSO-$d_6$, 125 MHz) $\delta$ 17.9 (CH$_2$), 18.7 (CH$_3$), 18.8 (CH$_3$), 24.5 (CH$_2$), 25.3 (CH$_2$), 46.4 (CH), 109.6 (CH), 116.5 (dt, $J_{C-F} = 192.6$, $J_{C-C-F} = 20.0$ Hz, CF), 117.2 (CH), 136.8 (dt, $J_{C-F} = 243.4$, $J_{C-C-F} = 14.5$ Hz, CF), 139.2 - 139.8 (m, C), 144.4 (dt, $J_{C-F} = 242.5$, $J_{C-C-F} = 11.8$ Hz, CF), 150.5 (C). $^{19}$F NMR (CDCl$_3$, 282 MHz) -165.8 (td, $J = 23.0$, 6.2 Hz, 2F), -161.1 (t, $J = 21.6$ Hz, 1F), -146.7 (dd, $J = 22.7$, 8.3 Hz, 2F). FT-IR (cm$^{-1}$, neat, ATR) 3052 (vw), 1485 (s), 1237 (s), 967 (w), 951 (w), 814 (s), 742 (s). HRMS (ES-) calcd for C$_{21}$H$_{14}$O$_4$F$_5$Si [M$-^{1}$Pr$_2$NH$_2$]: 453.0582, found: 453.0597.

**Diisopropylammonium Bis(catecholato)(3-cyanopropyl)silicate, 3g** (10.34 g, 95%) was prepared according to the general procedure from 3-cyanopropyltrimethoxysilane (4.97 g, 26.3 mmol). The desired silicate 3g was isolated as a light brown solid (mp = 185-186 °C). $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$ 0.54 - 0.66 (m, 2H) 1.17 (d, $J = 6.4$ Hz, 12H) 1.39 - 1.52 (m, 2H) 2.28 (t, $J = 7.0$ Hz, 2H) 3.32 (sept, $J = 6.4$ Hz, 2H) 6.41 - 6.48 (m, 4H) 6.51 - 6.57 (m, 4H) 8.00 (br s, 2H). $^{13}$C NMR (DMSO-$d_6$, 125 MHz) 17.8 (CH$_2$), 19.2 (CH$_3$), 19.5 (CH$_2$), 21.6 (CH$_2$), 46.7 (CH), 110.0 (CH), 117.6 (CH), 121.3 (C), 150.8 (C). FT-IR (cm$^{-1}$, neat, ATR) 3110 (vw), 3052 (vw), 2974 (vw), 2235 (vw), 1485 (vs), 1237 (vs), 810 (vs), 740 (vs), 710 (vs). HRMS (ES-) calcd for C$_{16}$H$_{14}$O$_4$Si [M$-^{1}$Pr$_2$NH$_2$]: 312.0692, found: 312.0692.
Synthesis of 4CzIPN
Preparation of the Organic Photocatalyst

To a 250 mL flame-dried round bottom flask equipped with a stir bar, septum and nitrogen inlet needle was added carbazole (6.43 g, 38.5 mmol, 4.4 equiv). The system was sealed with a rubber septum and evacuated via an inlet needle and purged with Ar. Dry THF (77 mL) was then added, and the solution was cooled to 0 °C in an ice bath. The solution was allowed to cool for 10 min. The flask was then charged with NaHMDS in THF (2 M, 18.4 mL, 36.7 mmol, 4.2 equiv) by syringe, resulting in the solution becoming an orange-brown color. The solution was stirred for five minutes at 0 °C. After this time, the ice bath was removed, and the solution was allowed to stir at rt for 30 min. The flask was then charged with tetrafluoroisophthalonitrile (1.75 g, 8.75 mmol, 1.0 equiv) and equipped with a reflux condenser. The solution was heated at 65 °C under an Ar atmosphere and allowed to stir at this temperature for 72 h. During this time period, the solution became a very dark brown with a voluminous yellow precipitate forming over time. After the 72 h period, the flask was allowed to cool to rt and the contents of the flask were poured into a medium porosity fritted glass funnel. After the solids and liquid were separated, the solids were washed with Et$_2$O (350 mL) to remove residual carbazole. The filtrate was discarded, and the solid was then washed with CHCl$_3$ (600 mL), to which 4CzIPN has partial solubility. The bright yellow filtrate was collected and the solvent was removed in vacuo by rotary evaporation. After removing residual solvent at low pressure (~0.2 mmHg), pure 1 (6.37 g, 92%) was obtained as a bright yellow solid (mp >250 °C). Characterization data for this compound matched that reported in the literature.$^{11}$

$^{11}$ (a) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi C. Nature 2012, 492, 234; (b) Luo, J.; Zhang, J. ACS Catal. 2016, 6, 873.
$^1$H NMR (CDCl$_3$, 500 MHz) δ 6.63 (t, $J = 7.8$ Hz, 2H), 6.82 (t, $J = 8.1$ Hz, 4H), 7.04 - 7.12 (m, 8H), 7.20 - 7.24 (m, 4H), 7.33 (d, $J = 7.6$ Hz, 2H), 7.49 (t, $J = 7.3$ Hz, 2H), 7.66 - 7.73 (m, 8H), 8.22 (d, $J = 7.8$ Hz, 2H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) δ 109.7 (CH), 109.8 (CH), 110.2 (CH), 111.9 (C), 116.7 (C), 119.9 (CH), 120.7 (CH), 121.3 (CH), 121.7 (CH), 122.2 (CH), 122.7 (CH), 124.1 (C), 124.8 (CH), 125.0 (C), 125.3 (C), 126.1 (CH), 127.2 (CH), 135.1 (C), 137.3 (C), 138.5 (C), 140.3 (C), 144.9 (C), 145.5 (C).

General Procedures of Imines
Preparation of $N$-Sulfonyl Imines

Preparation of Sheppard’s Reagent, Tris(2,2,2-trifluoroethyl)borate

The following procedure is a modification of the procedure described by Sheppard. To a flame-dried 250 mL round bottom flask equipped with a reflux condenser, septum, and stir bar was added boric anhydride (51.04 g, 0.73 mol) and 2,2,2-trifluoroethanol (93 mL, 123.23 g, 1.23 mol). The reaction mixture was heated to 80 °C under argon for 18 h while stirring vigorously. After this time, the thick slurry was cooled to rt and filtered through a coarse fritted funnel. The resulting clear, pale yellow oil was fractionally distilled (bp 119-122 °C @ 760 mmHg) though a 7 cm Vigreux column to give the desired boronate as a clear, colorless oil (46.17 g, 37%).

$^1$H NMR (CDCl$_3$, 500 MHz) δ 4.22 (q, $J = 8.5$ Hz, 6H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) δ 62.2 (q, $J_{C-C-F} = 36.3$ Hz, CH$_2$), 123.7 (q, $J_{C-F} = 277.0$ Hz, CF$_3$).

$^{19}$F NMR (CDCl$_3$, 282 MHz) δ -79.6 (s, 9F).

---

12 Lanigan, R. M.; Starkov, P.; Sheppard, T. D. J. Org. Chem. 2013, 78, 4512
13 2,2,2-Trifluoroethanol can azeotrope with the product, thus it is imperative that multiple fractions be collected.
14 Sheppard’s reagent should be stored in a sealed vial under an inert atmosphere to avoid hydrolysis under atmospheric conditions.
**Representative Procedure for N-Sulfonyl Imine Synthesis**

![Chemical Reaction](image)

**N-(4-Methylbenzylidene)methanesulfonamide**\(^{15}\) (2a)

The following procedure is a modification of the procedure described by Reeves.\(^{16}\) To a 50 mL round bottom flask equipped with a stir bar was added methanesulfonamide (1.71 g, 18 mmol, 1.2 equiv), THF (15 mL), and \(p\)-tolualdehyde (1.80 g, 15 mmol, 1 equiv). The reaction mixture was stirred for 5 min. The flask was then charged with Sheppard’s reagent (4.04 mL, 5.77 g, 18.25 mmol, 1.25 equiv), and was sealed with a rubber septum. The reaction mixture was stirred at rt overnight. After judged to be complete by \(^1\)H NMR analysis,\(^{17}\) the reaction mixture was diluted with \(\sim 20\) mL of EtOAc and transferred to a separatory funnel. Saturated aq NaHCO\(_3\) (\(\sim 50\) mL) and an additional 20 mL of EtOAc were added, and the layers were separated. The aq layer was extracted with additional EtOAc (\(3 \times 30\) mL) and the combined organic layers were washed with saturated aq NaHCO\(_3\) (\(\sim 75\) mL), deionized H\(_2\)O (\(\sim 100\) mL) and finally brine (\(\sim 100\) mL). The organic layer was dried (Na\(_2\)SO\(_4\)), and the solvent was removed \textit{in vacuo} by rotary evaporation. Upon solvent removal, a crude solid was obtained. The solid was washed with pentane (\(5 \times 15\) mL) and dried \textit{in vacuo} to afford pure 2a (2.34 g, 79%) as a white solid (mp = 110-111 °C).

\(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 2.46 (s, 3H), 3.12 (s, 3H), 7.33 (d, \(J = 7.9\) Hz, 2H), 7.85 (d, \(J = 7.9\) Hz, 2H), 8.98 (s, 1H).

\(^13\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 22.3 (CH\(_3\)), 40.6 (CH\(_3\)), 129.9 (C), 130.3 (CH), 131.7 (CH), 147.0 (C), 171.7 (CH).

---

\(^{15}\) Shaghafi, M. B.; Grote, R. E.; Jarvo, E. R. \textit{Org. Lett.} \textbf{2011}, 13, 5188.

\(^{16}\) Reeves, J. T.; Visco, M. D.; Marsini, M. A.; Grinberg, N.; Busacca, C. A.; Mattson, A. E.; Senanayake, C. H. \textit{Org. Lett.} \textbf{2015}, 17, 2442.

\(^{17}\) In several cases with other aldehydes, the reaction required longer reaction times. If the reaction did not reach completion after 24 h, an additional 0.5 equiv of Sheppard’s reagent and 0.25 equiv of the sulfonamide were added. Typically the reaction reached completion within 24 h of this addition. If no progression of the reaction was observed after this time, the reaction was halted and workup commenced.
N-(4-Methylbenzylidene)benzenesulfonamide, 18 2b (2.09 g, 81%) was prepared according to the general procedure from p-tolualdehyde (1.32 g, 11 mmol, 1.1 equiv) with the following modification: Benzenesulfonamide (1.57 g, 10 mmol, 1 equiv) was used in place of methanesulfonamide and served as the limiting reagent. The desired imine 2b was isolated as a white solid (mp = 113-114 °C). 

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, 500 \text{ MHz}) \delta 2.43 (s, 3H), 7.29 (d, J = 8.2 \text{ Hz}, 2H), 7.54 (t, J = 7.9 \text{ Hz}, 2H), 7.62 (tt, J = 7.6, 1.2 \text{ Hz}, 1H), 7.82 (d, J = 8.2 \text{ Hz}, 2H), 8.01 (dd, J = 8.4, 1.1 \text{ Hz}, 2H), 9.02 (s, 1H). \]

\[ \text{\textsuperscript{13}C NMR (CDCl}_3, 125 \text{ MHz}) \delta 22.3 (\text{CH}_3), 128.2 (\text{C}), 129.4 (\text{CH}), 130.1 (\text{C}), 130.2 (\text{CH}), 131.8 (\text{CH}), 133.7 (\text{CH}), 138.8 (\text{C}), 146.8 (\text{C}), 170.7 (\text{CH}). \]

4-Methyl-N-(4-methylbenzylidene)benzenesulfonamide, 19 2c (1.01 g, 74%) was prepared according to the general procedure from p-tolualdehyde (0.721 g, 6 mmol, 1.2 equiv) with the following modification: Benzenesulfonamide (0.856 g, 5 mmol, 1 equiv) was used in place of methanesulfonamide and served as the limiting reagent. The desired imine 2c was isolated as a white solid (mp = 114-115 °C). 

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, 500 \text{ MHz}) \delta 2.43 (s, 3H), 2.44 (s, 3H), 7.29 (d, J = 7.9 \text{ Hz}, 2H), 7.34 (d, J = 8.2 \text{ Hz}, 2H), 7.82 (d, J = 7.9 \text{ Hz}, 2H), 7.88 (d, J = 8.2 \text{ Hz}, 2H), 8.99 (s, 1H). \]

\[ \text{\textsuperscript{13}C NMR (CDCl}_3, 125 \text{ MHz}) \delta 21.9 (\text{CH}_3), 22.3 (\text{CH}_3), 126.8 (\text{CH}), 130.0 (\text{CH}), 130.2 (\text{CH}), 131.7 (\text{CH}), 135.7 (\text{C}), 144.7 (\text{C}), 146.7 (\text{C}), 170.2 (\text{CH}). \]

N-(2-Methylbenzylidene)methanesulfonamide, 20 2d (2.28 g, 71%) was prepared according to the general procedure from o-tolualdehyde (1.80 g, 0.015 mol). The desired imine 2d was obtained as a light yellow solid (mp = 103 °C). 

\[ \text{\textsuperscript{1}H NMR (CDCl}_3, 500 \text{ MHz}) \delta 2.62 (s, 3H), 3.13 (s, 3H), 7.25 - 7.36 (m, 2H), 7.50 (t, J = 7.3 \text{ Hz}, 1H), 8.04 (d, J = 7.6 \text{ Hz}, 1H), 9.32 (s, 1H). \]

\[ \text{\textsuperscript{13}C NMR (CDCl}_3, 125 \text{ MHz}) \delta 19.8 (\text{CH}_3), 40.6 (\text{CH}_3), 126.9 (\text{CH}), 130.3 (\text{C}), 130.7 (\text{CH}), 131.9 (\text{CH}), 135.0 (\text{CH}), 142.7 (\text{C}), 170.3 (\text{CH}). \]

---

18 Cui, X.; Shi, F.; Deng, Y. Chem. Commun. 2012, 48, 7586.
19 Boultwood, T.; Affron, D. P.; Trowbridge, A. D.; Bull, J. A. J. Org. Chem. 2013, 78, 6632.
20 Uraguchi, D.; Kinoshita, N.; Kizu, T.; Ooi, T. J. Am. Chem. Soc. 2015, 137, 13768.
**N-(3-(Trifluoromethyl)benzylidene)methanesulfonamide**,\(^{21}\) 2e (2.67 g, 71%) was prepared according to the general procedure from 3-(trifluoromethyl)benzaldehyde (2.61 g, 0.015 mol). The desired imine 2e was obtained as a white solid (mp = 90-92 °C). \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 3.17 (s, 3H), 7.70 (t, \(J = 7.8\) Hz, 1H), 7.91 (d, \(J = 7.9\) Hz, 1H), 8.13 (d, \(J = 7.9\) Hz, 1H), 8.26 (s, 1H), 9.09 (s, 1H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 40.3 (CH\(_3\)), 123.5 (q, \(J_{\text{C-F}} = 273.4\) Hz, CF\(_3\)), 127.5 (q, \(J_{\text{C-C-F}} = 3.6\) Hz, CH), 130.1 (C), 131.4 (q, \(J_{\text{C-C-C-F}} = 2.7\) Hz, CH), 132.1 (q, \(J_{\text{C-C-F}} = 33.6\) Hz, C), 133.0 (CH), 134.7 (CH), 170.3 (CH). \(^{19}\)F NMR (CDCl\(_3\), 282 MHz) -66.2 (s, 3F). FT-IR (cm\(^{-1}\), neat, ATR) 3072 (vw), 3050 (vw), 2951 (w), 1602 (m), 1301 (vs), 1146 (vs), 968 (m), 802 (vs), 702 (m), 502 (s). HRMS (ES+) calcd for C\(_9\)H\(_9\)F\(_3\)NO\(_2\)S [M+H]\(^+\): 252.0306, found: 252.0298.

**N-(4-Chlorobenzylidene)methanesulfonamide**,\(^{22}\) 2f (2.51 g, 77%) was prepared according to the general procedure from 4-chlorobenzaldehyde (2.11 g, 0.015 mol). The desired imine 2f was obtained as a white solid (mp = 100-102 °C). \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 3.13 (s, 3H), 7.50 (d, \(J = 8.2\) Hz, 2H), 7.89 (d, \(J = 8.5\) Hz, 2H), 8.99 (s, 1H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 40.5 (CH\(_3\)), 130.0 (CH), 130.8 (C), 132.6 (CH), 142.0 (C), 170.5 (CH).

**N-(2,4-Difluorobenzylidene)methanesulfonamide**, 2g (2.63 g, 71%) was prepared according to the general procedure from 2,4-difluorobenzaldehyde (2.61 g, 0.015 mol). The desired imine 2g was obtained as an off-white solid (mp = 119-121 °C). \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 3.14 (s, 3H), 6.95 (ddd, \(J = 10.4, 8.4, 2.3\) Hz, 1H), 7.01 - 7.07 (m, 1H), 8.10 - 8.21 (m, 1H), 9.29 (s, 1H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 40.4 (CH\(_3\)), 105.2 (dd, \(J_{\text{C-C-F}} = 26.0, J_{\text{C-C-C-F}} = 24.0\) Hz, CH), 113.4 (dd, \(J_{\text{C-C-F}} = 22.0, J_{\text{C-C-C-C-F}} = 3.7\) Hz, CH), 117.2 (dd, \(J_{\text{C-C-F}} = 8.7, J_{\text{C-C-C-C-F}} = 3.2\) Hz, C), 131.5 (dd, \(J_{\text{C-C-C-F}} = 11.0, J_{\text{C-C-C-C-F}} = 2.8\) Hz, CH), 165.6 (dd, \(J_{\text{C-F}} = 317.1, J_{\text{C-C-C-F}} = 12.8\) Hz, CF), 164.29 (d, \(J_{\text{C-C-C-F}} = 5.5\) Hz, CH), 167.6 (dd, \(J_{\text{C-F}} = 317.1, J_{\text{C-C-C-F}} = 12.8\) Hz, CF). \(^{19}\)F NMR (CDCl\(_3\), 282 MHz) -114.1 (d, \(J = 12.4\) Hz, 1F), -99.2 (d, \(J = 12.4\) Hz, 1F). FT-IR (cm\(^{-1}\), neat,

\(^{21}\) Marques, C. S.; Burke, A. J. *Eur. J. Org. Chem.* 2012, 4232.

\(^{22}\) Marques, C. S.; Burke, A. J. *Eur. J. Org. Chem.* 2012, 4232.
N-(2-Bromo-5-fluorobenzylidene)methanesulfonamide, 2h (2.69 g, 64%) was prepared according to the general procedure from 2-bromo-5-fluorobenzaldehyde (3.05 g, 0.015 mol). The desired imine 2h was obtained as an off-white white solid (mp = 128-129 °C). $^{1}H$ NMR (CDCl$_3$, 500 MHz) $\delta$ 3.17 (s, 3H), 7.23 (ddd, $J$ = 8.9, 7.5, 3.2 Hz, 1H), 7.68 (dd, $J$ = 8.9, 4.9 Hz, 1H), 7.90 (dd, $J$ = 8.7, 3.2 Hz, 1H), 9.41 (d, $J$ = 2.1 Hz, 1H). $^{13}C$ NMR (CDCl$_3$, 125 MHz) $\delta$ 40.4 (CH$_3$), 117.1 (d, $J_{C-C-F}$ = 24.5 Hz, CH), 123.5 (d, $J_{C-C-C-F}$ = 3.6 Hz, C), 123.6 (d, $J_{C-C-F}$ = 22.7 Hz, CH), 132.8 (d, $J_{C-C-C-F}$ = 7.3 Hz, C), 135.6 (d, $J_{C-C-C-F}$ = 8.2 Hz, CH), 162.1 (d, $J_{C-F}$ = 250.7 Hz, CF), 170.1 (CH). $^{19}F$ NMR (CDCl$_3$, 282 MHz) -115.2 (s, 1F). FT-IR (cm$^{-1}$, neat, ATR) 3062 (vw), 3010 (vw), 2931 (vw), 1596 (vs), 1456 (m), 1411 (w), 1308 (vs), 1137 (vs), 967 (s), 814 (vs), 786 (s), 516 (s), 505 (vs). HRMS (ES+) calcd for C$_8$H$_8$BrFNO$_2$S [M+H]$^+$: 279.9443, found: 279.9429.

N-(4-Methoxybenzylidene)methanesulfonamide, 2i (2.53 g, 79%) was prepared according to the general procedure from p-anisaldehyde (2.04 g, 0.015 mol). The desired imine 2i was obtained as a white solid (mp = 86-87 °C). $^{1}H$ NMR (CDCl$_3$, 500 MHz) $\delta$ 3.11 (s, 3H), 3.91 (s, 3H), 7.01 (d, $J$ = 8.5 Hz, 2H), 7.92 (d, $J$ = 8.5 Hz, 2H), 8.93 (s, 1H). $^{13}C$ NMR (CDCl$_3$, 125 MHz) $\delta$ 40.7 (CH$_3$), 56.0 (CH$_3$), 115.1 (CH), 125.2 (C), 134.0 (CH), 165.7 (C), 170.8 (CH). FT-IR (cm$^{-1}$, neat, ATR) 3032 (vw), 2935 (vs), 2847 (vw), 1594 (s), 1510 (s), 1421 (s), 1294 (s), 1249 (s), 1134 (vs), 1023 (s), 810 (m), 742 (s), 511 (s), 493 (s). HRMS (CI+) calcd for C$_9$H$_{12}$NO$_3$S [M+H]$^+$: 214.0532, found: 214.0534.
N-(4-(Methylthio)benzylidene)methanesulfonamide, 2j (3.05 g, 77%) was prepared according to the general procedure from 4-(methylthio)benzaldehyde (2.28 g, 0.015 mol). The desired imine 2j was obtained as a white solid (mp = 121-123 °C). 1H NMR (CDCl3, 500 MHz) δ 2.55 (s, 3H), 3.12 (s, 3H), 7.32 (d, J = 7.9 Hz, 2H), 7.84 (d, J = 7.9 Hz, 2H), 8.95 (s, 1H). 13C NMR (CDCl3, 125 MHz) δ 14.9 (CH3), 40.7 (CH3), 125.6 (CH), 128.5 (C), 131.7 (CH), 149.7 (C), 170.9 (CH).

N-(Benzo[d][1,3]dioxol-5-ylmethylene)methanesulfonamide, 2k (2.49 g, 73%) was prepared according to the general procedure from piperonal (2.25 g, 0.015 mol). The desired imine 2k was obtained as a light brown solid (mp = 102-104 °C). 1H NMR (CDCl3, 500 MHz) δ 3.09 (s, 3H), 6.09 (s, 2H), 6.91 (d, J = 7.9 Hz, 1H), 7.40 (dd, J = 8.1, 1.7 Hz, 1H), 7.46 (d, J = 1.5 Hz, 1H), 8.85 (s, 1H). 13C NMR (CDCl3, 125 MHz) δ 40.6 (CH3), 102.6 (CH2), 108.1 (CH), 108.9 (CH), 127.1 (C), 131.1 (CH), 149.1 (C), 154.3 (C), 170.6 (CH). FT-IR (cm⁻¹, neat, ATR) 3021 (vw), 2915 (vw), 1579 (m), 1452 (s), 1262 (vs), 1140 (vs), 929 (m), 810 (vs), 487 (m). HRMS (Cl+) calcd for C9H10NO4S [M+H]+: 228.0331, found: 228.0334.

N-(4-Cyanobenzylidene)methanesulfonamide, 2l (1.04 g, 62%) was prepared according to the general procedure from 4-formylbenzonitrile (1.05 g, 0.015 mol). The desired imine 2l was obtained as white solid (mp = 170-171 °C). 1H NMR (CDCl3, 500 MHz) δ 3.18 (s, 3H), 7.84 (d, J = 8.24 Hz, 2H), 8.08 (d, J = 8.24 Hz, 2H), 9.08 (s, 1H). 13C NMR (CDCl3, 125 MHz) δ 40.5 (CH3), 117.8 (C), 118.3 (C), 131.6 (CH), 133.2 (CH), 135.9 (C), 169.8 (CH). FT-IR (cm⁻¹, neat, ATR) 3025 (vw), 3007 (vw), 2931 (vw), 2226 (m), 1604 (m), 1557 (m), 1301 (s), 1142 (s), 840 (m), 771 (s), 526 (vs). HRMS (Cl+) calcd for C9H6N2O2S [M+H]+: 209.0385, found: 209.0409.

23 Uraguchi, D.; Kinoshita, N.; Kizu, T.; Ooi, T. J. Am. Chem. Soc. 2015, 137, 13768.
24 Marques, C. S.; Burke, A. J. Eur. J. Org. Chem., 2012, 4232.
Methyl 4-(((Methylsulfonyl)imino)methyl)benzoate, 2m (2.83 g, 78%) was prepared according to the general procedure from methyl 4-formylbenzoate (2.46 g, 0.015 mol). The desired imine 2m was obtained as a white solid (mp = 136-137 °C). \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta \) 3.16 (s, 3H), 3.96 (s, 3H), 8.03 (d, \(J = 8.5 \) Hz, 2H), 8.18 (d, \(J = 8.5 \) Hz, 2H), 9.08 (s, 1H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta \) 40.5 (CH\(_3\)), 52.9 (CH\(_3\)), 130.5 (CH), 131.3 (CH), 135.9 (C \(\times 2\)), 166.1 (C), 170.8 (CH). FT-IR (cm\(^{-1}\), neat, ATR) 3023 (vw), 2951 (vw), 2916 (m), 1612 (m), 1298 (s), 1142 (vs), 1106 (m), 972 (m), 809 (m), 695 (m), 490 (m). HRMS (ES+) calcd for C\(_{10}\)H\(_{12}\)NO\(_4\)S [M+H]\(^+\): 242.0487, found: 242.0488.

\(N'\)-(4-Bromobenzylidene)-N,N-dimethylsulfamide, 2n (1.94 g, 89%) was prepared according to the general procedure from 4-bromobenzaldehyde (1.39 g, 7.5 mmol) with the following modification: N,N-dimethylsulfamide (1.12 g, 10 mmol) was used in place of methanesulfonamide. The desired imine 2n was isolated as a white solid (mp = 119-120 °C). \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta \) 2.89 (s, 6H), 7.67 (d, \(J = 8.5 \) Hz, 2H), 7.80 (d, \(J = 8.5 \) Hz, 2H), 8.85 (s, 1H). \(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta \) 38.6 (CH\(_3\)), 130.0 (C), 131.6 (C), 132.3 (CH), 132.8 (CH), 169.5 (CH).

**Representative Procedure for N-Aryl/N-Heteroaryl Imine Synthesis**

\(N\)-(4-Methylbenzylidene)aniline\(^{26}\), 2o

The following procedure is a modification of the procedure outlined by Leadbeater and Tilley.\(^{27}\) To a 100 mL flask equipped with a stir bar was added \(p\)-tolualdehyde (6.01 g, 50 mmol, 1 equiv),
aniline (4.89 g, 52.5 mmol, 1.05 equiv), and benzene (50 mL). The solution was allowed to stir for 5 min at rt and p-TsOH • H2O (0.095 g, 0.5 mmol, 0.01 equiv) was then added all at once. The flask was equipped with a graduated Dean-Stark trap along with a reflux condenser. The Dean-Stark trap was back-filled with ~15 mL of benzene to ensure constant volume throughout the reaction. The reaction mixture was heated to reflux in a 120 °C oil bath and stirred via a magnetic stir plate. To ensure that the vapor made it to the condenser, the arm of the Dean-Stark trap was insulated with a layer of glass wool. The reaction mixture was allowed to reflux until ~1 equivalent of H2O was observed in the trap (~0.9 mL). Upon completion the reaction mixture was cooled to room temperature and the benzene was removed in vacuo by rotatory evaporation. To remove p-TsOH, pentane (~ 50 mL) was added resulting in the precipitation of a white powder. The fine precipitate was filtered and discarded. The filtrate was dried by rotatory evaporation. The resulting crude imine was then purified via vacuum distillation (bp 118-120 °C @ 0.1 mmHg) giving the pure imine 2o (8.09 g, 83%) as a clear, pale yellow oil that solidified on standing (mp = 45-47 °C).

\[ ^1H \text{ NMR (CDCl}_3, 500 \text{ MHz)} \delta 2.44 (s, 3H), 7.21 - 7.27 (m, 3H), 7.30 (d, J = 7.9 Hz, 2H), 7.38 - 7.44 (m, 2H), 7.83 (d, J = 8.2 Hz, 2H), 8.44 (s, 1H). \]

\[ ^{13}C \text{ NMR (DMSO-}d_6, 125 \text{ MHz)} \delta 21.9 (\text{CH}_3), 121.1 (\text{CH}), 126.0 (\text{CH}), 129.1 (\text{CH}), 129.4 (\text{CH}), 129.8 (\text{CH}), 134.0 (\text{C}), 142.1 (\text{C}), 152.5 (\text{C}), 160.6 (\text{CH}). \]

\[ \text{N-(4-Methylbenzylidene)pyridin-2-amine},^{28} 2p (4.40 g, 89\%) \] was prepared according to the general procedure from p-tolualdehyde (3.15 g, 26.25 mmol, 1.05 equiv) with the following modifications: 1) 2-aminopyridine (2.35 g, 25 mmol, 1 equiv) was used in place of aniline and was the limiting reagent; 2) The crude product was washed twice with pentane; 3) The crude material was washed with a minimal amount of Et\textsubscript{2}O in addition to the pentane washes. The desired imine 2p was isolated as a light brown solid (mp = 79-81 °C).

\[ ^1H \text{ NMR (CDCl}_3, 500 \text{ MHz)} \delta 2.43 (s, 3H), 7.16 (ddd, J = 7.3, 4.9, 0.9 Hz, 1H), 7.29 (d, J = 7.9 Hz, 2H), 7.31 (dt, J = 7.9, 1.2 Hz, 1H), 7.74 (td, J = 7.6, 1.8 Hz, 1H), 7.89 (d, J = 8.2 Hz, 2H), 8.49 (ddd, J = 4.9, 1.8, 0.9 Hz, 1H), 9.11 (s, 1H). \]

\[ ^{13}C \text{ NMR (CDCl}_3, 125 \text{ MHz)} \delta 21.9 (\text{CH}_3), \]

\[ ^{28} \text{Meiswinkel, A.; Werner, H. Inorg. Chim. Acta} \textbf{2004}, \textit{357}, 2855. \]
119.8 (CH), 121.8 (C), 129.7 (2 × CH), 133.6 (CH), 138.2 (CH), 142.7 (CH), 149.0 (C), 161.6 (C), 163.0 (CH).

\(N-(\text{Pyridin-2-ylmethylene})\text{aniline,}^{29} \text{2q}\) (3.53 g, 77%) was prepared according to the general procedure from 2-pyridinecarboxaldehyde (2.68 g, 0.025 mol) \textit{with the following modifications:} 1) No \(p\)-TsOH \(\cdot\) \(\text{H}_2\text{O}\) was utilized; 2) Further purification was accomplished by vacuum distillation (100-103 °C @ 0.1 mmHg). The desired imine 2q was isolated as a clear, pale yellow oil. \(^{1}H\) NMR (CDCl\(_3\), 500 MHz) \(\delta\) 7.23 - 7.30 (m, 3 H), 7.33 (dd, \(J = 7.0, 5.2\) Hz, 1H), 7.40 (t, \(J = 7.6\) Hz, 2H), 7.77 (td, \(J = 7.7, 1.1\) Hz, 1H), 8.19 (d, \(J = 7.9\) Hz, 1H), 8.60 (s, 1H), 8.69 (d, \(J = 4.6\) Hz, 1H). \(^{13}C\) NMR (CDCl\(_3\), 125 MHz) \(\delta\) 121.3 (CH), 122.1 (CH), 125.3 (CH), 126.9 (CH), 129.4 (CH), 136.8 (CH), 149.9 (CH), 151.2 (C), 154.8 (C), 160.8 (CH).

\(\text{Methyl 4-((Phenylimino)methyl)benzoate,}^{30} \text{2r}\) (4.58 g, 77%) was prepared according to the general procedure from methyl 4-formylbenzoate (4.10 g, 0.025 mol) \textit{with the following modifications:} 1) The crude product was washed twice with pentane; 2) The crude material was washed with a minimal amount of Et\(_2\)O in addition to the pentane washes. The desired imine 2r was isolated as a pale yellow solid (mp = 126-127 °C). \(^{1}H\) NMR (CDCl\(_3\), 500 MHz) \(\delta\) 3.96 (s, 3H), 7.22 - 7.26 (m, 2H), 7.27 (dt, \(J = 7.3, 1.4\) Hz, 1H), 7.39 - 7.44 (m, 2H), 7.98 (d, \(J = 8.5\) Hz, 2H), 8.14 (d, \(J = 8.5\) Hz, 2H), 8.51 (s, 1H). \(^{13}C\) NMR (CDCl\(_3\), 125 MHz) \(\delta\) 52.6 (CH\(_3\)), 121.2 (CH), 126.8 (CH), 128.9 (CH), 129.5 (CH), 130.3 (s, 6 C), 132.6 (C), 140.3 (C), 151.8 (C), 159.3 (CH), 166.9 (C).

\(^{29}\) Fan, M.; Zhou, W.; Jiang, Y.; Ma, D. \textit{Angew. Chem., Int. Ed.} \textbf{2016}, \textit{55}, 6211.

\(^{30}\) Naka, H.; Koseki, D.; Kondo, Y. \textit{Adv. Synth. Catal.} \textbf{2008}, \textit{350}, 1901.
Cyclic Voltammogram of Representative Imines
Voltammetric measurements were recorded on a CH Instruments: Model 600E Series Electrochemical Analyzer using a standard three electrodes setup in dry and degassed MeCN (10 mL), with ferrocene as an internal reference ($E^0_{1/2} = +0.40$ V vs SCE) and Bu$_4$NPF$_6$ as the electrolyte (0.10 mmol). Cyclic voltammograms were recorded with a step potential of 0.002 V at a scan rate of 0.1 V/s.
Control and Optimization Studies

Procedure for optimization and control studies:

To a 4 mL reaction vial equipped with a stir bar, was added diisopropylammonium bis(catecholato)cyclohexylsilicate 2a (0.0473 g, 0.11 mmol, 1.1 equiv), N-(4-methylbenzylidene)methanesulfonamide, 2a (0.0197 g, 0.1 mmol, 1 equiv) and the appropriate photocatalyst (0.002 mmol, 0.02 equiv). The vial was sealed with a cap containing a TFE lined silicone septa and was evacuated and purged with argon three times via an inlet needle. The vial was then charged with the appropriate anhydrous solvent (1 mL). After this, the cap was sealed with Parafilm® and the vial was irradiated in the aforementioned LED reactor for 18 h. The temperature of the reaction was maintained at approximately 27 °C via a fan. After 18 h, reaction progress was evaluated by GC/MS.

Table S1: Solvent Screen of Photoredox-Mediated Alkylation of Imines

| Entry | Solvent  | Conversion to 4a |
|-------|----------|------------------|
| 1     | Toluene  | 4%               |
| 2     | MeCN     | 10%              |
| 3     | THF      | 28%              |
| 4     | Dioxane  | 39%              |
| 5     | DMF      | 90%              |
| 6     | DMSO     | 97%              |

a Percent conversion was approximated based upon relative areas from the GC/MS trace of a given run. Conversion = 100 × (area of alkylated product)/( area of imine 2a + area of alkylated product)
Table S2: Assessment of Various Photoredox Catalysts$^a$

![Diagram of photocatalyst 3a (1.1 equiv) and product 4a with photocatalyst (2 mol%), DMSO (0.1 M), 18 h, hv]

| Entry | Photocatalyst | Conversion to 4a |
|-------|---------------|------------------|
| 1     | Ru(bpy)$_3$(PF$_6$)$_2$ | 94% |
| 2     | Ru(bpm)$_3$(PF$_6$)$_2$ | 48% |
| 3     | Ru(bpz)$_3$(PF$_6$)$_2$ | 62% |
| 4     | [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ | 97% |
| 5     | Ir(ppy)$_3$ | 98% |
| 6     | MesAcr$^-$ClO$_4^-$ | 8% |
| 7     | Eosin Y | 74% |
| 8     | TPP$^+$BF$_4^-$ | Trace |
| 9     | PTh | 0% |
| 10    | 4CzIPN | 100% |

$^a$ Percent conversion was approximated based upon relative areas from the GC/MS trace of a given run. Conversion = 100 × (area of alkylated product)/(area of imine 2a + area of alkylated product)

---

Structures of Photocatalysts Assessed:

![Structures of various photocatalysts including Ru(bpy)$_3$(PF$_6$)$_2$, Ru(bpm)$_3$(PF$_6$)$_2$, Ru(bpz)$_3$(PF$_6$)$_2$, [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$, Ir(ppy)$_3$, MesAcr$^-$ClO$_4^-$, 4CzIPN, Eosin Y, TPP$^+$BF$_4^-$, and PTh]
Table S3: Control Studies using Imine 2a

![Chemical Diagram](image)

| Entry | Deviation from procedure | Conversion to 4a<sup>a</sup> |
|-------|--------------------------|-----------------------------|
| 1     | None                     | 100%                        |
| 2     | No photocatalyst (4CzIPN)| 0%                          |
| 3     | No light                 | 0%                          |
| 4<sup>b</sup> | No Silicate             | 0%                          |

<sup>a</sup>Percent conversion was approximated based upon relative areas from the GC/MS trace of a given run. Conversion = 100 × (area of alkylated product)/(area of imine 2a + area of alkylated product).

<sup>b</sup>No consumption or hydrolysis of the imine was observed.
General Procedure for Imine Alkylation Mediated by 4CzIPN

\[
\begin{align*}
N-(\text{Cyclohexyl}(p\text{-tolyl})\text{methyl})\text{methanesulfonamide (4a)}
\end{align*}
\]

To an 8 mL reaction vial equipped with a stir bar were added 4CzIPN (4 mg, 0.005 mmol, 0.01 equiv), imine 2a (99 mg, 0.5 mmol, 1 equiv), and alkylsilicate 3a (257 mg, 0.6 mmol, 1.1 equiv). The vial was sealed with a cap containing a TFE lined silicone septa and placed under an argon atmosphere via an inlet needle. The vial was evacuated three times via an inlet needle then purged with argon. The vial was then charged with anhyd DMSO (5 mL) via a syringe. The cap was sealed with Parafilm®, and the now bright yellow solution was irradiated by blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 °C via a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by HPLC and/or GC/MS. Once judged to be complete, the now yellow-brown solution was transferred to a separatory funnel and diluted with deionized H$_2$O (20 mL) and EtOAc (~20 mL). The layers were separated, and the aq layer was extracted with EtOAc (3 × ~20 mL). The combined organic layers were washed with aq 2 M NaOH (2 × ~100 mL) followed by brine (~100 mL). The combined organic layers were dried (Na$_2$SO$_4$), and the solvent was removed in vacuo by rotary evaporation. Further purification was accomplished by SiO$_2$ column chromatography (gradient hexane/EtOAc containing 1% Et$_3$N) to give the desired sulfonylamine, 4a, (110 mg, 78%) as an off-white solid (mp = 143-142 °C).

$^1$H NMR (CDCl$_3$, 500 MHz) δ 0.88 - 0.98 (m, 1H), 1.04 (qd, $J = 12.5, 3.2$ Hz, 1H), 1.09 - 1.28 (m, 3H), 1.34 - 1.42 (m, 1H), 1.55 - 1.71 (m, 3H), 1.74 - 1.82 (m, 1H), 1.99 - 2.06 (m, 1H), 2.35 (s, 3 H), 2.52 (s, 3H), 4.14 (t, $J = 8.4$ Hz, 1H), 5.15 (d, $J = 8.8$ Hz, 1H), 7.12 (d, $J = 8.3$ Hz, 2H), 7.17 (d, $J = 8.1$ Hz, 2H).

---

31 Occasionally an emulsion would form, thus requiring the addition of a small amount (~ 5 mL) of brine to assist in layer separation.

32 Note that the aq layer will turn dark brown and become warm likely due to the reaction between catechol (or the orthosilicate byproduct) and hydroxide.
$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 21.3 (CH$_3$), 26.1 (CH$_2$), 26.2 (CH$_2$), 26.4 (CH$_2$), 29.9 (CH$_2$), 30.1 (CH$_2$), 41.9 (CH$_3$), 43.9 (CH), 63.4 (CH), 127.3 (CH), 129.6 (CH), 137.6 (C), 137.9 (C).

**FT-IR** (cm$^{-1}$, neat, ATR) 3251 (w, br), 2933 (w), 1448 (m), 1313 (vs), 1159 (vs), 975 (m), 771 (m), 515 (vs).

**HRMS** (ES-) calcd for C$_{13}$H$_{22}$NO$_2$S [M-H]: 280.1377, found: 280.1352.

$N$-(Cyclohexyl($\rho$-tolyl)methyl)benzenesulfonamide, 4b (157 mg, 91%) was prepared according to the general procedure from 2b (130 mg, 0.5 mmol). The desired sulfonylamine 4b was isolated as an off-white semisolid. **$^1$H NMR** (CDCl$_3$, 500 MHz) $\delta$ 0.78 - 0.89 (m, 1H), 0.93 (qd, $J = 12.3$, 3.5 Hz, 1H), 1.00 - 1.19 (m, 3H), 1.22 - 1.34 (m, 1H), 1.48 - 1.63 (m, 3H), 1.65 - 1.76 (m, 1H), 1.90 - 2.00 (m, 1H), 2.22 (s, 3H), 4.01 (t, $J = 7.8$ Hz, 1H), 5.45 (d, $J = 8.2$ Hz, 1H), 6.80 (d, $J = 7.9$ Hz, 2H), 6.88 (d, $J = 7.9$ Hz, 2H), 7.18 - 7.28 (m, 2H), 7.37 (t, $J = 7.3$ Hz, 1H), 7.60 (dd, $J = 8.4$, 1.1 Hz, 2H). **$^{13}$C NMR** (CDCl$_3$, 125 MHz) $\delta$ 21.2 (CH$_3$), 26.2 (CH$_2$), 26.4 (CH$_2$), 29.8 (CH$_2$), 30.0 (CH$_2$), 44.0 (CH), 63.6 (CH), 127.1 (CH), 127.2 (CH), 128.7 (CH), 129.0 (CH), 132.1 (CH), 136.8 (C), 137.1 (C), 141.0 (C). **FT-IR** (cm$^{-1}$, neat, ATR) 3251 (w), 2917 (w), 2849 (w), 1447 (w), 1325 (m), 1261 (s), 1041 (m), 822 (w), 608 (m), 546 (m). **HRMS** (ES+) calcd for C$_{20}$H$_{25}$NNaO$_2$S [M+Na]$^+$: 366.1504, found: 366.1500.

$N$-(Cyclohexyl($\rho$-tolyl)methyl)benzenesulfonamide, 4c (154 mg, 86%) was prepared according to the general procedure from 2c (137 mg, 0.5 mmol). The desired sulfonylamine 4c was isolated as a off-white semisolid. **$^1$H NMR** (CDCl$_3$, 500 MHz) $\delta$ 0.78 - 0.89 (m, 1H), 0.93 (qd, $J = 12.1$, 2.9 Hz, 1H), 1.01 - 1.20 (m, 3H), 1.25 - 1.33 (m, 1H), 1.50 - 1.64 (m, 3H), 1.68 - 1.76 (m, 1H), 1.91 - 1.99 (m, 1H), 2.25 (s, 3H), 2.33 (s, 3H), 3.99 (t, $J = 8.1$ Hz, 1H), 5.32 (d, $J = 8.1$ Hz, 1H), 6.80 (d, $J = 7.8$ Hz, 2H), 6.90 (d, $J = 7.8$ Hz, 2H), 7.04 (d, $J = 8.1$ Hz, 2H), 7.48 (d, $J = 8.1$ Hz, 2H). **$^{13}$C NMR** (CDCl$_3$, 125 MHz) $\delta$ 21.2 (CH$_3$), 21.6 (CH$_3$), 26.2 (CH$_2$), 26.4 (CH$_2$), 29.8 (CH$_2$), 30.0 (CH$_2$), 44.0 (CH), 63.5 (CH), 127.2 (CH), 127.3 (CH), 128.9 (CH), 129.3 (CH), 136.8 (C), 137.2 (C), 138.1 (C), 142.8 (C). **FT-IR** (cm$^{-1}$, neat, ATR) 3249 (w), 2921 (m), 2853 (w), 1440 (m), 1320 (s), 1307 (w), 1158 (vs), 808 (m), 722 (m), 672 (vs), 582 (s) 545 (vs). **HRMS** (ES+) calcd for C$_{21}$H$_{27}$NNaO$_2$S [M+Na]$^+$: 380.1660, found: 380.1657.
N-(Cyclohexyl(o-tolyl)methyl)methanesulfonamide, 4d (90 mg, 64%) was prepared according to the general procedure from 2d (99 mg, 0.5 mmol). The desired sulfonylamine 4d was isolated as an off-white solid (mp = 103-104 °C). \[^1\]H NMR (CDCl\textsubscript{3}, 500 MHz) δ 0.99 - 1.24 (m, 5H), 1.38 (s, 1H), 1.53 - 1.63 (m, 1H), 1.63 - 1.70 (m, 2H), 1.78 - 1.86 (m, 1H), 2.07 - 2.13 (m, 1H), 2.41 (s, 3H), 2.45 (s, 3H), 4.51 (t, \(J = 8.4\) Hz, 1H), 4.96 (d, \(J = 8.3\) Hz, 1H), 7.15 - 7.19 (m, 2H), 7.19 - 7.26 (m, 2H). \[^13\]C NMR (CDCl\textsubscript{3}, 125 MHz) δ 19.9 (CH\textsubscript{3}), 26.2 (CH\textsubscript{2}), 26.4 (CH\textsubscript{2}), 26.5 (CH\textsubscript{2}), 29.9 (CH\textsubscript{2}), 30.0 (CH\textsubscript{2}), 41.9 (CH\textsubscript{3}), 44.0 (CH\textsubscript{2}), 59.1 (br, CH), 126.4 (br, C), 126.9 (CH), 127.6 (CH), 131.0 (CH), 136.0 (CH), 139.7 (C). FT-IR (cm\textsuperscript{-1}, neat, ATR) 3273 (w, br), 2940 (m), 2853 (w), 1427 (m), 1327 (s), 1315 (vs), 1154 (s), 1042 (m), 981 (s), 756 (s), 519 (s). HRMS (ES+) calcd for C\textsubscript{15}H\textsubscript{23}NNaO\textsubscript{2}S [M+Na\textsuperscript{+}]: 304.1347, found: 301.1343.

N-(Cyclohexyl(3-(trifluoromethyl)phenyl)methyl)methanesulfonamide, 4e (114 mg, 68%) was prepared according to the general procedure from 2e (126 mg, 0.5 mmol). The desired sulfonylamine 4e was isolated as a light yellow oil. \[^1\]H NMR (CDCl\textsubscript{3}, 500 MHz) δ 0.92 - 1.08 (m, 2H), 1.09 - 1.24 (m, 3H), 1.34 - 1.42 (m, 1H), 1.58 - 1.73 (m, 3H), 1.75 - 1.82 (m, 1H), 1.91 - 2.01 (m, 1H), 2.60 (s, 3H), 4.29 (t, \(J = 7.9\) Hz, 1H), 5.49 (d, \(J = 8.1\) Hz, 1H), 7.44 - 7.52 (m, 2H), 7.53 (s, 1H), 7.56 (d, \(J = 7.3\) Hz, 1H). \[^13\]C NMR (CDCl\textsubscript{3}, 125 MHz) δ 26.1 (CH\textsubscript{2}), 26.3 (CH\textsubscript{2}), 29.6 (CH\textsubscript{2}), 30.1 (CH\textsubscript{2}), 42.0 (CH\textsubscript{3}), 43.9 (CH), 63.2 (CH), 124.2 (q, \(J_{C-F} = 272.2\) Hz, CF\textsubscript{3}), 124.1 (q, \(J_{C-C-C-F} = 3.8\) Hz, CH), 124.8 (q, \(J_{C-C-C-F} = 3.8\) Hz, CH), 129.5 (CH), 130.9 (CH), 131.3 (q, \(J_{C-C-C-F} = 32.5\) Hz, C), 142.3 (C). \[^{19}\]F NMR (CDCl\textsubscript{3}, 282 MHz) -65.8 (s, 3F). FT-IR (cm\textsuperscript{-1}, neat, ATR) 3283 (w, br), 2929 (m), 2854 (w), 1451 (w), 1326 (vs), 1152 (vs), 1074 (s), 978 (m), 705 (m), 516 (m). HRMS (ES+) calcd for C\textsubscript{15}H\textsubscript{20}F\textsubscript{3}NNaO\textsubscript{2}S [M+Na\textsuperscript{+}]: 358.1065, found: 358.1069.
**N-((4-Chlorophenyl)(cyclohexyl)methyl)methanesulfonamide, 4f** (136 mg, 90%) was prepared according to the general procedure from 2f (109 mg, 0.5 mmol). The desired sulfonylamine 4f was isolated as an off-white solid (mp = 170-171 °C). **\(^1\)H NMR** (CDCl\(_3\), 500 MHz) \(\delta\) 0.88 - 0.97 (m, 1H), 1.01 (qd, \(J = 11.9, 3.4\) Hz, 1H), 1.06 - 1.26 (m, 3H), 1.33 - 1.41 (m, 1H), 1.52 - 1.72 (m, 3H), 1.75 - 1.82 (m, 1H), 1.93 - 1.99 (m, 1H), 2.58 (s, 3H), 4.19 (t, \(J = 7.9\) Hz, 1H), 4.85 (d, \(J = 7.9\) Hz, 1H), 7.18 (d, \(J = 8.2\) Hz, 2H), 7.34 (d, \(J = 8.5\) Hz, 2H). **\(^13\)C NMR** (CDCl\(_3\), 125 MHz) \(\delta\) 26.1 (CH\(_2\)), 26.3 (CH\(_2\)), 26.8 (CH\(_2\)), 30.1 (CH\(_2\)), 42.1 (CH\(_3\)), 43.9 (CH), 63.0 (CH), 128.8 (CH), 129.1 (CH), 133.7 (C), 139.6 (C). **FT-IR** (cm\(^{-1}\), neat, ATR) 3247 (s), 2936 (w), 2856 (w), 1451 (m), 1309 (vs), 1160 (vs), 977 (m), 761 (s), 555 (s), 517 (s). **HRMS** (ES+) calcd for C\(_{14}\)H\(_{20}\)ClNNaO\(_2\)S [M+Na]\(^+\): 324.0801, found: 324.0792.

**N-(Cyclohexyl(2,4-difluorophenyl)methyl)methanesulfonamide, 4g** (130 mg, 85%) was prepared according to the general procedure from 2g (110 mg, 0.5 mmol). The desired sulfonylamine 4g was isolated as an off-white semisolid. **\(^1\)H NMR** (CDCl\(_3\), 500 MHz) \(\delta\) 0.90 - 1.09 (m, 2H), 1.10 - 1.27 (m, 3H), 1.32 - 1.39 (m, 1H), 1.61 - 1.73 (m, 3H), 1.76 - 1.83 (m, 1H), 2.02 - 2.10 (m, 1H), 2.66 (s, 3H), 4.36 (t, \(J = 8.8\) Hz, 1H), 5.18 (d, \(J = 9.0\) Hz, 1H), 6.84 (ddd, \(J = 10.9, 8.7, 2.4\) Hz, 1H), 6.89 (td, \(J = 8.3, 2.4\) Hz, 1H), 7.23 (td, \(J = 8.4, 6.4\) Hz, 1H). **\(^13\)C NMR** (CDCl\(_3\), 125 MHz) \(\delta\) 26.0 (CH\(_2\)), 26.1 (CH\(_2\)), 26.3 (CH\(_2\)), 30.0 (CH\(_2\)), 30.2 (CH\(_2\)), 41.7 (CH\(_3\)), 42.9 (CH), 58.8 (CH), 104.7 (t, \(J_{C-C-F} = 25.7\) Hz, CH), 111.9 (dd, \(J_{C-C-F} = 21.1, J_{C-C-C-C-F} = 2.8\) Hz, 2 C), 124.3 (dd, \(J_{C-C-F} = 12.8, J_{C-C-C-C-F} = 3.7\) Hz, C), 130.3 (dd, \(J_{C-C-C-C-F} = 9.3, 7.3\) Hz, CH), 161.6 (td, \(J_{C-C-F} = 249.3, J_{C-C-C-F} = 11.9\) Hz, 2 \(\times\) CF). **\(^19\)F NMR** (CDCl\(_3\), 282 MHz) -116.6 (d, \(J = 7.2\) Hz, 1F), -113.50 (d, \(J = 8.3\) Hz, 1F). **FT-IR** (cm\(^{-1}\), neat, ATR) 3281 (w, br, 2929 (m), 2854 (w), 1604 (w), 1504 (m), 1449 (w), 1314 (s), 1153 (vs), 1093 (m), 967 (vs), 848 (m), 755 (m), 511 (vs). **HRMS** (ES+) calcd for C\(_{14}\)H\(_{19}\)F\(_2\)NNaO\(_2\)S [M+Na]\(^+\): 326.1002, found: 326.1003.
**N-((2-Bromo-5-fluorophenyl)(cyclohexyl)methyl)methanesulfonamide, 4h** (120 mg, 66%) was prepared according to the general procedure from 2h (140 mg, 0.5 mmol). The desired sulfonylamine 4h was isolated as a powdery white solid (mp = 165-166 °C). **1H NMR** (CDCl₃, 500 MHz) δ 1.02 - 1.25 (m, 5H), 1.34 - 1.47 (m, 1H), 1.60 - 1.76 (m, 3H), 1.77 - 1.86 (m, 1H), 1.96 (br s, 1H), 2.71 (s, 3H), 4.68 (br s, 1H), 5.33 (d, J = 7.6 Hz, 1H), 6.91 (ddd, J = 8.7, 7.6, 2.9 Hz, 1H), 7.04 (dd, J = 9.3, 2.9 Hz, 1H), 7.54 (dd, J = 8.8, 5.1 Hz, 1H). **13C NMR** (CDCl₃, 125 MHz) δ 26.1 (CH₂), 26.2 (CH₂), 26.3 (CH₂), 28.7 (br, CH₂), 30.0 (br, CH₂), 41.7 (CH₃), 43.3 (br, CH), 61.6 (br, CH), 115.4 (br, C), 116.6 (d, J_C-C-F = 21.8 Hz, CH), 117.5 (br, C), 134.7 (br, CH), 143.1 (br, C), 162.4 (d, J_C-F = 248.0 Hz, CF). **19F NMR** (CDCl₃, 282 MHz) -116.3 (s, 1F). **FT-IR** (cm⁻¹, neat, ATR) 3255 (w, br), 2945 (w), 2851 (w), 1471 (w), 1329 (m), 1313 (m), 1153 (vs), 980 (w), 774 (m), 480 (vs). **HRMS** (ES+) calcd for C₁₄H₁₉BrFNNaO₂S [M+Na⁺]: 386.0202, found: 386.0205.

**N-(Cyclohexyl(4-methoxyphenyl)methyl)methanesulfonamide, 4i** (128 mg, 86%) was prepared according to the general procedure from 2i (108 mg, 0.5 mmol). The desired sulfonylamine 4i was isolated as an off-white solid (mp = 126-128 °C). **1H NMR** (CDCl₃, 500 MHz) δ 0.85 - 0.95 (m, 1H), 1.02 (qd, J = 11.9, 2.7 Hz, 1H), 1.08 - 1.27 (m, 3H), 1.32 - 1.40 (m, 1H), 1.50 - 1.70 (m, 3H), 1.72 - 1.80 (m, 1H), 1.96 - 2.06 (m, 1H), 2.51 (s, 3H), 3.80 (s, 3H), 4.12 (t, J = 8.4 Hz, 1H), 4.77 - 5.07 (m, 1H), 6.88 (d, J = 8.2 Hz, 2H), 7.15 (d, J = 8.9 Hz, 2H). **13C NMR** (CDCl₃, 125 MHz) δ 26.1 (CH₂), 26.2 (CH₂), 26.4 (CH₂), 30.0 (CH₂), 30.1 (CH₂), 42.0 (CH₃), 44.0 (CH), 55.5 (CH₃), 63.2 (CH), 114.3 (CH), 128.5 (CH), 132.9 (C), 159.3 (C). **FT-IR** (cm⁻¹, neat, ATR) 3248 (w), 2938 (m), 2851 (w), 1613 (w), 1513 (s), 1443 (m), 1311 (vs), 1249 (s), 1156 (vs), 1132 (s), 1029 (s), 833 (s), 752 (s), 514 (vs). **HRMS** (ES+) calcd for C₁₅H₂₃NNaO₃S [M+Na⁺]: 320.1296, found: 320.1291.
N-(Cyclohexyl(4-(methylthio)phenyl)methyl)methanesulfonamide 4j (125 mg, 80%) was prepared according to the general procedure from 2j (115 mg, 0.5 mmol). The desired sulfonylamine 4j was isolated as an off-white solid (mp = 108-110 °C). \( ^1H \text{NMR} \) (CDCl\(_3\), 500 MHz) \( \delta \) 0.87 - 0.96 (m, 1H), 1.01 (qd, \( J = 12.2, 3.4 \text{ Hz} \), 1H), 1.06 - 1.27 (m, 3H), 1.32 - 1.42 (m, 1H), 1.52 - 1.70 (m, 3H), 1.72 - 1.80 (m, 1H), 1.92 - 2.03 (m, 1H), 2.47 (s, 3H), 2.54 (s, 3H), 4.13 (t, \( J = 8.2 \text{ Hz} \), 1H), 5.28 (d, \( J = 8.5 \text{ Hz} \), 1H), 7.15 (d, \( J = 8.5 \text{ Hz} \), 2H), 7.22 (d, \( J = 8.5 \text{ Hz} \), 2H). \( ^{13}\text{C NMR} \) (CDCl\(_3\), 125 MHz) \( \delta \) 15.8 (CH\(_3\)), 26.1 (CH\(_2\)), 26.4 (CH\(_2\)), 29.8 (CH\(_2\)), 30.1 (CH\(_2\)), 42.0 (CH\(_3\)), 43.9 (CH), 63.2 (CH), 126.8 (CH), 127.9 (CH), 137.6 (C), 138.2 (C). \( \text{FT-IR} \) (cm\(^{-1}\), neat, ATR) 3299 (w), 2932 (w), 1514 (s). \( \text{HRMS} \) (ES\(^+\)) calcd for C\(_{15}\)H\(_{21}\)N\(_2\)O\(_2\)S\(_2\) [M+Na\(^+\)]: 336.1068, found: 336.1068.

N-(Benzo[d][1,3]dioxol-5-yl(cyclohexyl)methyl)methanesulfonamide, 4k (107 mg, 69%) was prepared according to the general procedure from 2k (114 mg, 0.5 mmol). The desired sulfonylamine 4k was isolated as an off-white solid (mp = 137-139 °C). \( ^1H \text{NMR} \) (CDCl\(_3\), 500 MHz) \( \delta \) 0.84 - 0.96 (m, 1H), 1.03 (qd, \( J = 12.0, 2.4 \text{ Hz} \), 1H), 1.09 - 1.28 (m, 3H), 1.34 - 1.40 (m, 1H), 1.47 - 1.58 (m, 1H), 1.59 - 1.71 (m, 2 H), 1.78 (s, 1H), 1.97 - 2.06 (m, 1H), 2.58 (s, 3H), 4.08 (t, \( J = 8.3 \text{ Hz} \), 1H), 5.13 (d, \( J = 8.3 \text{ Hz} \), 1H), 5.97 (s, 2H), 6.70 (d, \( J = 7.8 \text{ Hz} \), 1H), 6.74 (s, 1H), 6.78 (d, \( J = 7.8 \text{ Hz} \), 1H). \( ^{13}\text{C NMR} \) (CDCl\(_3\), 125 MHz) \( \delta \) 26.1 (CH\(_2\)), 26.2 (CH\(_2\)), 26.4 (CH\(_2\)), 30.1 (CH\(_2\)), 30.2 (CH\(_2\)), 42.1 (CH\(_3\)), 43.9 (CH), 63.5 (CH), 101.5 (CH\(_2\)), 107.4 (CH), 108.5 (CH), 121.0 (CH), 135.0 (C), 147.3 (C), 148.4 (C). \( \text{FT-IR} \) (cm\(^{-1}\), neat, ATR) 3246 (w), 2928 (w), 2877 (w), 1487 (m), 1325 (m), 1316 (s), 1240 (s), 1154 (vs), 1037 (s), 982 (m), 785 (m), 763 (s), 506 (s). \( \text{HRMS} \) (ES-) calcd for C\(_{15}\)H\(_{20}\)NO\(_4\)S [M-H\(^-\)]: 310.1119, found: 310.1111.

N-((4-Cyanophenyl)(cyclohexyl)methyl)methanesulfonamide, 4l (100 mg, 68%) was prepared according to the general procedure from 2l (104 mg, 0.5 mmol). The desired sulfonylamine 4l was isolated as an off-white solid (mp = 144-145 °C). \( ^1H \text{NMR} \) (CDCl\(_3\), 500 MHz) \( \delta \) 0.91 - 1.06 (m, 2H), 1.09 - 1.23 (m, 3H), 1.32 - 1.40 (m, 1H), 1.57 - 1.73 (m, 3H), 1.74 - 1.82 (m, 1H), 1.87 - 1.96 (m, 1H), 2.65 (s, 3H), 4.27 (t, \( J = 8.0 \text{ Hz} \), 1H), 5.43 (br s, 1H), 7.39 (d, \( J = 8.3 \text{ Hz} \), 2H), 7.58 - 7.84 (m, 2H).
2H), 7.67 (d, J = 8.3 Hz, 2H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 26.0 (CH$_2$), 26.2 (CH$_2$), 29.5 (CH$_2$), 30.2 (CH$_2$), 42.1 (CH$_3$), 43.8 (CH), 63.2 (CH), 111.9 (C), 118.7 (C), 128.2 (CH), 132.7 (CH), 146.7 (CH). FT-IR (cm$^{-1}$, neat, ATR) 3252 (w, br.), 2932 (w), 2852 (w), 2232 (w), 1451 (m), 1310 (vs), 1159 (vs), 1062 (m), 977 (s), 764 (s), 564 (s), 514 (s). HRMS (ES+) calcd for C$_{15}$H$_{20}$N$_2$NaO$_2$S [M−Na]$^+$: 315.1143, found: 315.1144.

**Methyl 4-(Cyclohexyl(methylsulfonamido)methyl)benzoate, 4m (125 mg, 77%)** was prepared according to the general procedure from 2m (121 mg, 0.5 mmol). The desired sulfonylamine 4m was isolated as an off-white solid (mp = 85-86 °C). $^1$H NMR (CDCl$_3$, 500 MHz) δ 0.90 - 1.08 (m, 2H), 1.08 - 1.27 (m, 3H), 1.31 - 1.40 (m, 1H), 1.57 - 1.71 (m, 3H), 1.73 - 1.82 (m, 1H), 1.93 - 2.02 (m, 1H), 2.56 (s, 3H), 3.92 (s, 3H), 4.26 (t, J = 8.2 Hz, 1H), 5.45 (d, J = 8.3 Hz, 1H), 7.34 (d, J = 8.3 Hz, 2H), 8.04 (d, J = 8.3 Hz, 2H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 26.1 (CH$_2$), 26.3 (CH$_2$), 29.7 (CH$_2$), 30.2 (CH$_2$), 42.1 (CH$_3$), 43.9 (CH), 52.4 (CH$_3$), 63.3 (CH), 127.5 (CH), 129.9 (C), 130.3 (CH), 146.3 (C), 166.9 (C). FT-IR (cm$^{-1}$, neat, ATR) 3297 (w), 2945 (w), 2847 (w), 1722 (s), 1448 (w), 1312 (s), 1260 (vs), 1147 (s), 1113 (s), 1020(vs), 982 (s), 799 (vs), 757 (s), 707 (s), 514 (vs). HRMS (ES−) calcd for C$_{16}$H$_{22}$N$_4$O$_4$S [M−H]$^−$: 324.1275, found: 324.1271.

**N’-((4-Bromophenyl)(cyclohexyl)methyl)-N,N-dimethylsulfamide, 4n (152 mg, 80%)** was prepared according to the general procedure from 2n (131 mg, 0.5 mmol). The desired sulfamide 4n was isolated as a yellow semisolid. $^1$H NMR (CDCl$_3$, 500 MHz) δ 0.89 (qd, J = 12.0, 3.4 Hz, 1H), 1.01 (qd, J = 12.2, 3.4 Hz, 1H), 1.06 - 1.23 (m, 3H), 1.30 - 1.37 (m, 1H), 1.47 - 1.57 (m, 1H), 1.57 - 1.70 (m, 2H), 1.73 - 1.79 (m, 1H), 1.93 - 2.00 (m, 1H), 2.49 (s, 6H), 4.01 (t, J = 7.9 Hz, 1H), 5.15 (d, J = 6.4 Hz, 1H), 7.10 (d, J = 8.5 Hz, 2H), 7.45 (d, J = 8.5 Hz, 2H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 26.1 (CH$_2$), 26.4 (CH$_2$), 29.9 (CH$_2$), 30.1 (CH$_2$), 37.8 (CH$_3$), 44.1 (CH), 63.3 (CH), 121.4 (C), 129.3 (CH), 131.7 (CH), 141.0 (C). FT-IR (cm$^{-1}$, neat, ATR) 3291 (w, br.), 2924 (m), 2852 (w), 1447 (m), 1317 (s), 1147 (vs), 1009 (m), 1062 (m), 954 (s), 826 (m), 706 (s), 572 (vs). HRMS (ES+) calcd for C$_{15}$H$_{24}$BrN$_2$O$_2$S [M+H]$^+$: 375.0742, found: 375.0741.
N-(Cyclohexyl(p-tolyl)methyl)aniline, 4o (72 mg, 51%) was prepared according to the general procedure from 2o (98 mg, 0.5 mmol). The desired amine 4o was isolated as a yellow oil. $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 1.05 - 1.36 (m, 5H), 1.54 - 1.61 (m, 1H), 1.63 - 1.71 (m, 2H), 1.72 - 1.83 (m, 2H), 1.88 - 1.97 (m, 1H), 2.35 (s, 3H), 4.08 - 4.19 (m, 2H), 6.53 (d, $J = 8.3$ Hz, 2H), 6.63 (t, $J = 7.3$ Hz, 1H), 7.09 (t, $J = 8.1$ Hz, 2H), 7.13 (d, $J = 7.8$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 21.3 (CH), 26.6 (CH$_2$), 26.7 (2 × CH$_2$), 29.8 (CH$_2$), 30.5 (CH$_2$), 45.2 (CH), 63.4 (CH), 113.4 (CH), 117.1 (CH), 127.4 (CH), 129.2 (CH), 129.3 (CH), 136.4 (C), 139.9 (C), 148.1 (C). FT-IR (cm$^{-1}$, neat, ATR) 3279 (w), 2918 (w), 2886 (w), 1447 (w), 1323 (m), 1315 (vs), 1156 (s), 1041 (w), 981 (s), 725 (m), 607 (m) 546 (vs). HRMS (CI$^+$) calcd for C$_{20}$H$_{26}$N [M+H]$^+$: 280.2060, found: 280.2055.

N-(Cyclohexyl(pyridin-2-yl)methyl)aniline, 4p (105 mg, 78%) was prepared according to the general procedure from 2p (91 mg, 0.5 mmol). The desired amine 4p was isolated as an off-white powdery solid (mp = 83-84 °C). $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 1.04 - 1.31 (m, 5H), 1.47 - 1.55 (m, 1H), 1.62 - 1.79 (m, 3H), 1.82 - 1.93 (m, 2H), 4.30 (d, $J = 5.2$ Hz, 1H), 4.54 (br. s., 1H), 6.57 (d, $J = 7.9$ Hz, 2H), 6.63 (t, $J = 7.3$ Hz, 1H), 7.06 - 7.14 (m, 3H), 7.25 (d, $J = 7.9$ Hz, 1H), 7.57 (t, $J = 7.6$ Hz, 1H), 8.59 (d, $J = 4.6$ Hz, 1H). $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 26.5 (CH$_2$), 26.6 (CH$_2$), 26.7 (CH$_2$), 29.4 (CH$_2$), 30.5 (CH$_2$), 44.0 (CH), 64.5 (CH), 113.5 (CH), 117.3 (CH), 122.1 (CH), 122.3 (CH), 129.4 (CH), 136.3 (CH), 148.1 (C), 149.5 (CH), 162.3 (C). FT-IR (cm$^{-1}$, neat, ATR) 3267 (w, br), 2927 (m), 2847 (w), 1592 (m), 1498 (m), 1323 (m), 744 (vs), 691 (s), 570 (m). HRMS (ES$^+$) calcd for C$_{18}$H$_{23}$N$_2$ [M+H]$^+$: 267.1856, found: 267.1870.

N-(Cyclohexyl(p-tolyl)methyl)pyridin-2-amine, 4q (108 mg, 76%) was prepared according to the general procedure from 2q (98 mg, 0.5 mmol). The desired amine 4q was isolated as an off-white solid (mp = 93-94 °C). $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 1.01 - 1.26 (m, 5H), 1.50 - 1.58 (m, 1H), 1.60 - 1.78 (m, 4H), 1.85 - 1.93 (m, 1H), 2.31 (s, 3H), 4.29 (t, $J = 6.9$ Hz, 1H), 5.15 (d, $J = 6.7$ Hz, 1H), 6.16 (d, $J = 8.5$ Hz, 1H), 6.49 (dd, $J = 7.0$, 4.9 Hz, 1H), 7.11 (d, $J = 7.9$ Hz, 2H), 7.18 (d, $J = 8.2$ Hz, 2H), 7.25 - 7.29 (m, 1H), 8.04 (d, $J = 3.7$ Hz, 1H). $^{13}$C NMR (CDCl$_3$, 125 MHz)
δ 21.3 (CH₃), 26.5 (CH₂), 26.6 (CH₂), 29.5 (CH₂), 30.4 (CH₂), 44.8 (CH), 61.8 (CH), 106.4 (CH), 113.0 (CH), 127.3 (CH), 129.2 (CH), 136.6 (C), 137.7 (CH), 139.3 (C), 148.4 (CH), 158.8 (C). **FT-IR** (cm⁻¹, neat, ATR) 3237 (w, br), 2916 (m), 2850 (w), 1597 (vs), 1575 (s), 1503 (m), 1440 (vs), 1390 (w), 1381 (m), 1130 (CH), 1081 (m), 768 (s), 3200 (vw), 2925 (m), 2650 (s). **HRMS** (ES+) calcd for C₁₀H₁₂N₂ [M+H]⁺: 281.2012, found: 281.2019.

Methyl 4-(Cyclohexyl(phenylamino)methyl)benzoate, 4r (104 mg, 64%) was prepared according to the general procedure from 2r (120 mg, 0.5 mmol). The desired amine 4r was isolated as a clear, colorless semisolid. **¹H NMR** (CDCl₃, 500 MHz) δ 0.99 - 1.33 (m, 5H), 1.48 - 1.57 (m, 1H), 1.58 - 1.81 (m, 4H), 1.81 - 1.91 (m, 1H), 3.90 (s, 3H), 4.18 (d, J = 3.1 Hz, 2H), 6.47 (d, J = 8.7 Hz, 2H), 6.62 (t, J = 7.3 Hz, 1H), 7.06 (t, J = 8.2 Hz, 2H), 7.38 (d, J = 8.2 Hz, 2H), 7.98 (d, J = 8.2 Hz, 2H). **¹³C NMR** (CDCl₃, 125 MHz) δ 26.5 (CH₂), 26.6 (CH₂), 29.6 (CH₂), 30.4 (CH₂), 45.0 (CH), 52.3 (CH₃), 63.6 (CH), 113.4 (CH), 117.5 (CH), 127.5 (CH), 129.1 (C), 129.4 (CH), 129.9 (CH), 147.6 (C), 148.6 (C), 167.3 (C). **FT-IR** (cm⁻¹, neat, ATR) 3401 (vw, br), 2925 (w), 2852 (w), 1713 (m), 1600 (m), 1503 (m), 1277 (vs), 1103 (m), 747 (m), 691 (m). **HRMS** (ES+) calcd for C₂₁H₂₆NO₂ [M+H]⁺: 324.1958, found: 324.1961.

N-(1-(4-(Methylthio)phenyl)-2-phenylethyl) methanesulfonamide, 4v (116 mg, 72%) was prepared according to the general procedure from 2j (115 mg, 0.5 mmol) with the following modifications: 1) 1.3 equiv of diisopropylammonium bis(catecholato)benzylsilicate 3b (284 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The desired sulfonylamine 4v was isolated as a yellow solid (mp = 119-120 °C). **¹H NMR** (CDCl₃, 500 MHz) δ 2.40 (s, 3H), 2.48 (s, 3H), 3.00 (dd, J = 13.7, 8.2 Hz, 1H), 3.09 (dd, J = 13.4, 6.4 Hz, 1H), 4.69 (q, J = 7.2 Hz, 1H), 4.92 (d, J = 7.0 Hz, 1H), 7.11 (d, J = 7.0 Hz, 2H), 7.18 - 7.25 (m, 4H), 7.25 - 7.30 (m, 3H). **¹³C NMR** (CDCl₃, 125 MHz) δ 15.9 (CH₃), 41.9 (CH₃), 44.1 (CH₂), 59.2 (CH), 126.9 (CH), 127.4 (CH), 127.6 (CH), 129.0 (CH), 129.8 (CH), 136.8 (C), 137.9 (C), 138.7 (C). **FT-IR** (cm⁻¹, neat, ATR) 3326 (w, br), 2924 (vw), 1421 (w), 1311 (s), 1145(vs), 1081 (m), 990 (s), 819 (m), 748 (m), 701 (s), 524 (vs). **HRMS** (ES-) calcd for C₁₆H₁₈NO₂S₂ [M–H]⁻: 320.0777, found: 320.0775.
**N-(1-(4-(Methylthio)phenyl)but-3-en-1-yl)methanesulfonamide, 4w** (99 mg, 73%) was prepared according to the general procedure from 2j (115 mg, 0.5 mmol) with the following modifications: 1) 1.3 equiv of triethylammonium bis(catecholato)allylsilicate 3c (252 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The desired sulfonylamine 4w was isolated as a clear viscous oil that solidified upon standing to give a white powder (mp = 70–71 °C). 

**1H NMR** (CDCl₃, 500 MHz) δ 2.45 - 2.58 (m, 2H), 2.48 - 2.50 (s, 3H), 2.61 (s, 3H), 4.53 (q, J = 7.3 Hz, 1H), 4.66 (d, J = 5.5 Hz, 1H), 5.15 - 5.20 (m, 2H), 5.62 - 5.73 (m, 1H), 7.22 - 7.26 (m, 4H). 

**13C NMR** (CDCl₃, 125 MHz) δ 15.9 (CH₃), 42.2 (CH₃), 42.3 (CH₂), 55.5 (CH₃), 57.1 (CH), 114.4 (CH₂), 119.4 (CH), 128.2 (CH), 133.1 (C), 133.6 (CH), 159.5 (C). 

**FT-IR** (cm⁻¹, neat, ATR) 3268 (w, br), 2931 (vw), 1448 (w), 1317 (s), 1151 (vs), 1081 (m), 980 (m), 817 (m), 759 (m), 516 (vs). 

**HRMS** (ES⁻) calcd for C₁₂H₁₆NO₂S₂ [M⁻H⁻]: 270.0622, found: 270.0614.

**N-(1-(4-(Methylthio)phenyl)but-3-en-1-yl)methanesulfonamide, 4x** (79 mg, 61%) was prepared according to the general procedure from 2i (107 mg, 0.5 mmol) with the following modifications: 1) 1.3 equiv of triethylammonium bis(catecholato)allylsilicate 3c (252 mg, 0.65 mmol) were used; 2) 3 mol % of Ru(bpy)₃(PF₆)₂ (13 mg, 0.015 mol) were used in place of 4CzIPN. The desired sulfonylamine 4x was isolated as a pale brown oil. 

**1H NMR** (CDCl₃, 500 MHz) δ 2.49 - 2.54 (m, 2H), 2.56 (s, 3H), 3.80 (s, 3H), 4.49 (q, J = 6.7 Hz, 1H), 5.02 (d, J = 6.4 Hz, 1H), 5.08 - 5.17 (m, 2H), 5.61 - 5.74 (m, 1H), 6.89 (d, J = 8.9 Hz, 2H), 7.24 (d, J = 8.9 Hz, 2H). 

**13C NMR** (CDCl₃, 125 MHz) δ 42.2 (CH₃), 42.3 (CH₂), 55.5 (CH₃), 57.1 (CH), 114.4 (CH₂), 119.4 (CH), 128.2 (CH), 133.1 (C), 133.6 (CH), 159.5 (C). 

**FT-IR** (cm⁻¹, neat, ATR) 3278 (w, br), 2941 (vw), 1513 (m), 1442 (w), 1311 (s), 1246 (s), 1148 (vs), 980 (s), 831 (s), 516 (vs). 

**HRMS** (Cl⁺) calcd for C₁₂H₁₆NO₂S [M+H⁺]: 256.1007, found: 256.1009.
\( N-(1-(4-(Methylthio)phenyl)but-3-en-1-yl)\)methanesulfonamide, 4y (90 mg, 65\%) was prepared according to the general procedure from 2f (109 mg, 0.5 mmol) \textit{with the following modifications}: 1) 1.3 equiv of diisopropylammonium bis(catecholato)isobutylsilicate 3d (262 mg, 0.65 mmol) were used; 2) 3 mol \% of Ru(bpy)\(_3\)(PF\(_6\))\(_2\) (13 mg, 0.015 mol) were used in place of 4CzIPN. The desired sulfonylamine 4y was isolated as a pale brown oil. \( ^1\text{H NMR} \) (CDCl\(_3\), 500 MHz) \( \delta \) 0.93 (d, \( J = 6.1 \) Hz, 6H), 1.50 - 1.58 (m, 2H), 1.62 - 1.72 (m, 1H), 2.55 (s, 3H), 4.49 (q, \( J = 6.8 \) Hz, 1H), 4.98 (d, \( J = 6.7 \) Hz, 1H), 7.25 (d, \( J = 7.9 \) Hz, 2H), 7.34 (d, \( J = 7.9 \) Hz, 2H). \( ^{13}\text{C NMR} \) (CDCl\(_3\), 125 MHz) \( \delta \) 22.5 (CH\(_3\)), 22.6 (CH\(_3\)), 25.0 (CH), 42.3 (CH\(_3\)), 47.0 (CH), 56.2 (CH), 128.3 (CH), 129.4 (CH), 134.0 (C), 140.7 (C). \( \text{FT-IR (cm}^{-1}, \text{neat, ATR)} \) 3267 (w, br), 2958 (w), 1492 (w), 1311 (s), 1151 (vs), 1135 (s), 1091 (m), 979 (m), 829 (w), 734 (vs), 516 (vs). HRMS (CI+) calcd for C\(_{12}\)H\(_{19}\)ClNO\(_2\)S [M+H]\(^+\): 276.0825, found: 276.0811.

\( N'-(1-(4-Bromophenyl)-3-phenylpropyl)-N,N\)-dimethylsulfamide, 4z (115 mg, 57\%) was prepared according to the general procedure from 2n (146 mg, 0.5 mmol) \textit{with the following modifications}: 1) 1.3 equiv of diisopropylammonium bis(catecholato)(2-phenylethyl)silicate 3e (294 mg, 0.65 mmol) were used; 2) 3 mol \% of 4CzIPN (12 mg, 0.015 mol) were used. The desired sulfamide 4z was isolated as a yellow semisolid. \( ^1\text{H NMR} \) (CDCl\(_3\), 500 MHz) \( \delta \) 1.97 - 2.06 (m, 1H), 2.11 - 2.20 (m, 1H), 2.48 - 2.65 (m, 2H), 2.53 (s, 6H), 4.31 (q, \( J = 7.0 \) Hz, 1H), 4.72 (d, \( J = 7.0 \) Hz, 1H), 7.13 (d, \( J = 7.02 \) Hz, 2H), 7.15 - 7.21 (m, 3H), 7.27 (t, \( J = 7.6 \) Hz, 2H), 7.50 (d, \( J = 8.2 \) Hz, 2 H). \( ^{13}\text{C NMR} \) (CDCl\(_3\), 125 MHz) \( \delta \) 32.5 (CH\(_2\)) 37.8 (CH\(_3\)) 39.3 (CH\(_2\)) 57.9 (CH) 121.9 (C) 126.5 (CH) 128.6 (CH) 128.8 (CH) 128.8 (CH) 132.1 (CH) 140.8 (C) 141.3 (C). \( \text{FT-IR (cm}^{-1}, \text{neat, ATR)} \) 3285 (w, br), 3034 (vw), 2925 (w), 2851 (w), 1454 (m), 1317 (m), 1144 (vs), 1071 (m), 956 (m), 699 (vs), 523 (m). HRMS (ES+) calcd for C\(_{17}\)H\(_{22}\)BrN\(_2\)O\(_2\)S [M+H]\(^+\): 397.0580, found: 397.0588.
N-(4-(Perfluorophenyl)-1-(p-tolyl)butyl)pyridin-2-amine, 4aa (114 mg, 57%) was prepared according to the general procedure from 2p (98 mg, 0.5 mmol) with the following modifications: 1) 1.3 equiv of diisopropylammonium bis(catecholato) (3-pentafluorophenylpropyl)silicate 3f (361 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The desired amine 4aa was isolated as a yellow semisolid. $^1$H NMR (CDCl$_3$, 500 MHz) δ 1.55 - 1.68 (m, 1H), 1.69 - 1.77 (m, 1H), 1.77 - 1.93 (m, 2H), 2.32 (s, 3H), 2.70 (t, $J = 7.3$ Hz, 2H), 4.56 (q, $J = 7.0$ Hz, 1H), 5.07 (d, $J = 6.7$ Hz, 1H), 6.20 (d, $J = 8.5$ Hz, 1H), 6.52 (t, $J = 6.1$ Hz, 1H), 7.12 (d, $J = 7.6$ Hz, 2H), 7.21 (d, $J = 7.9$ Hz, 2H), 7.30 (t, $J = 7.6$ Hz, 1H), 8.04 (d, $J = 4.6$ Hz, 1H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 21.3 (CH$_3$), 22.3 (CH$_2$), 26.2 (CH$_2$), 37.8 (CH$_2$), 56.1 (CH), 106.9 (CH), 114.2 (dt, $J_{C-F} = 207.1$, $J_{C-C-F} = 18.3$ Hz, CF), 113.4 (CH), 126.5 (CH), 129.6 (CH), 137.6 (dt, $J_{C-C-F} = 252.0$, $J_{C-F} = 14.7$ Hz, CF), 137.1 (C), 137.7 (CH), 140.1 - 140.6 (m, C), 140.3 (C), 145.3 (dt, $J_{C-F} = 240.1$, $J_{C-C-F} = 11.9$ Hz, CF), 148.4 (CH), 158.4 (C). $^{19}$F NMR (CDCl$_3$, 282 MHz) -166.0 (td, $J = 21.6$, 8.3 Hz, 2F), -161.0 (t, $J = 20.6$ Hz, 1F), -147.2 (dd, $J = 22.7$, 8.3 Hz, 2F). FT-IR (cm$^{-1}$, neat, ATR) 3255 (vw), 2937 (vw), 2851 (vw), 1600 (m), 1573 (n), 1501 (vs), 1444 (m), 1265 (m), 1121 (m), 962 (m), 734 (vs). HRMS (ES$^+$) calcd for C$_{22}$H$_{26}$F$_5$N$_2$ [M+H]$^+$: 407.1541, found: 407.1531.

Methyl 4-(4-Cyano-1-(phenylamino)butyl)benzoate, 4ab (96 mg, 62%) was prepared according to the general procedure from 2r (120 mg, 0.5 mmol) with the following modifications: 1) 1.3 equiv of diisopropylammonium bis(catecholato)(3-cyanopropyl)silicate 3g (273 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The desired lamine ab was isolated as a clear yellow oil. $^1$H NMR (CDCl$_3$, 500 MHz) δ 1.66 - 1.76 (m, 1H), 1.78 - 1.89 (m, 1H), 1.90 - 2.04 (m, 2H), 2.29 - 2.43 (m, 2H), 3.91 (s, 3H), 4.43 (t, $J = 6.7$ Hz, 1H), 6.51 (d, $J = 7.8$ Hz, 2H), 6.68 (t, $J = 7.2$ Hz, 1H), 7.10 (t, $J = 7.8$ Hz, 2H), 7.42 (d, $J = 8.3$ Hz, 2H), 8.01 (d, $J = 8.3$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 17.3 (CH$_3$), 22.6 (CH$_2$), 37.5 (CH$_2$), 52.3 (CH$_3$), 57.6 (CH), 113.7 (CH), 118.3 (CH), 119.4 (C), 126.6 (CH), 129.5 (CH), 129.6 (C), 130.4 (CH), 146.8 (C), 148.7 (C), 167.0 (C). FT-IR (cm$^{-1}$, neat, ATR) 3281 (w, br.), 3052 (vw) 2949 (w), 2852 (vw), 2242 (w), 1715 (s),...
1601 (m), 1504 (m), 1434 (m), 1278 (vs), 1112 (m), 750 (s), 693 (m). **HRMS** (ES+) calcd for $C_{19}H_{21}N_2O_2$ [M+H]$^+$: 309.1598, found: 309.1609.

**Methyl 4-(4-Methoxy-1-(phenylamino)butyl)benzoate, 4ac** (108 mg, 69%) was prepared according to the general procedure from **2r** (120 mg, 0.5 mmol) with the following modifications: 1) 1.3 equiv of diisopropylammonium bis(catecholato)(3-methoxypropyl)silicate **3h** (291 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The desired amine **4ac** was isolated as a clear yellow oil. $^1$H NMR (CDCl$_3$, 500 MHz) δ 1.57 - 1.76 (m, 2H), 1.89 (q, $J = 7.4$ Hz, 2H), 3.34 (s, 3H), 3.36 - 3.43 (m, 2H), 3.85 - 3.92 (m, 3H), 4.33 (br s, 1H), 4.37 (t, $J = 6.7$ Hz, 1H), 6.47 (d, $J = 8.2$ Hz, 2H), 6.64 (t, $J = 7.3$ Hz, 1H), 7.07 (t, $J = 7.8$ Hz, 2H), 7.43 (d, $J = 8.2$ Hz, 2H), 7.99 (d, $J = 8.2$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 26.7 (CH$_2$), 35.7 (CH$_2$), 52.3 (CH$_3$), 58.9 (CH$_3$), 72.4 (CH$_3$), 113.5 (CH), 117.7 (CH), 126.7 (CH), 129.2 (C), 129.4 (CH), 130.2 (CH), 147.4 (C), 150.0 (C), 167.2 (C). FT-IR (cm$^{-1}$, neat, ATR) 3392 (vw, br), 2925 (w), 2851 (w), 1717 (s), 1504 (m), 1276 (vs), 1111 (s), 735 (s), 707 (m). **HRMS** (ES+) calcd for $C_{19}H_{23}NNaO_3$ [M+Na]$^+$: 336.1576, found: 336.1565.

**Methyl 4-(4-(2-Oxazepane-1-carboxamido)-1-(phenylamino)butyl)benzoate, 4ad** (127 mg, 58%) was prepared according to the general procedure from **2r** (120 mg, 0.5 mmol) with the following modifications: 1) 1.3 equiv of diisopropylammonium bis(catecholato)(2-oxo-propyl-azepanyl-1-carboxamidyl)silicate **3i** (353 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The desired sulfonylamine **4ad** was isolated as a clear yellow oil. $^1$H NMR (CDCl$_3$, 500 MHz) δ 1.70 (m, $J = 0.6$ Hz, 10H), 2.60 - 2.72 (m, 2H), 3.31 (q, $J = 6.2$ Hz, 2H), 3.88 (s, 3H), 3.91 - 4.00 (m, 2H), 4.14 - 4.32 (m, br, 1H), 4.39 (t, $J = 6.7$ Hz, 1H), 6.47 (d, $J = 7.9$ Hz, 2H), 6.63 (t, $J = 7.3$ Hz, 1H), 7.06 (t, $J = 7.6$ Hz, 2H), 7.41 (d, $J = 8.2$ Hz, 2H), 7.97 (d, $J = 8.2$ Hz, 2H), 9.30 (t, $J = 5.2$ Hz, 1H). $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 23.7 (CH$_2$), 26.7 (CH$_2$), 28.5 (CH$_2$), 29.3 (CH$_2$), 36.0 (CH$_2$), 39.9 (CH$_2$), 40.4 (CH$_2$), 44.0 (CH$_2$), 52.2 (CH$_3$), 58.0 (CH), 113.5 (CH), 117.7 (CH), 126.6 (CH), 129.2
(CH), 129.3 (CH), 130.0 (C), 130.2 (CH), 147.2 (C), 149.7 (C), 155.2 (C), 167.1 (C), 179.7 (C). **FT-IR** (cm⁻¹, neat, ATR) 3373 (vw, br), 3262 (vv, br.), 3050 (vv), 2943 (w), 2851 (vv) 1692 (vs), 1601 (m), 1527 (m), 1435 (m), 1277 (vs), 1178 (m), 969 (w), 733 (vs), 693 (s).

**HRMS** (ES+) calcd for C_{25}H_{32}N_{3}O_{4} [M+H]^+: 438.2393, found: 438.2399.

4-(4-Methoxyphenyl)-4-(methylsulfonamido)butyl Acetate, 4ae (68 mg, 43%) was prepared according to the general procedure from 2i (107 mg, 0.5 mmol) with the following modifications: 1) 1.3 equiv of diisopropylammonium bis(catecholato)(3-acetoxypropyl)silicate 3j (291 mg, 0.65 mmol) were used; 2) 3 mol % of Ru(bpy)_3(PF_6)_2 (13 mg, 0.015 mol) were used in place of 4CzIPN. The desired sulfonylamine 4ae was isolated as a pale brown oil. **1H NMR** (CDCl₃, 300 MHz) δ 1.50 - 1.99 (m, 4H), 2.05 (s, 3H), 2.57 (s, 3H), 3.83 (s, 3H), 4.07 (t, J = 6.2 Hz, 2H), 4.42 (q, J = 7.4 Hz, 1H), 4.86 (d, J = 7.6 Hz, 1H), 6.92 (d, J = 8.7 Hz, 2H), 7.24 (d, J = 8.9 Hz, 2H). **13C NMR** (CDCl₃, 125 MHz) δ 21.2 (CH₃), 25.8 (CH₂), 34.4 (CH₂), 42.2 (CH₃), 55.6 (CH₃), 57.9 (CH), 64.0 (CH₂), 114.7 (CH₂), 128.1 (CH₂), 133.2 (C), 159.7 (C), 171.4 (C). **FT-IR** (cm⁻¹, neat, ATR) 3277 (w, br), 2949 (w), 2949 (w), 1732 (s), 1513 (s), 1314(s), 1243 (vs), 1148 (vs), 1031 (vs), 976 (s), 833 (s), 757 (m), 518 (s). **HRMS** (ES-) calcd for C_{14}H_{20}NO_S [M−H]⁻: 314.1062, found: 314.1065.

4-(Pyridin-2-ylamino)-4-(p-tolyl)butyl Acetate, 4af (100 mg, 67%) was prepared according to the general procedure from 2f (98 mg, 0.5 mmol) with the following modifications: 1) 1.3 equiv of diisopropylammonium bis(catecholato)(3-acetoxypropyl)silicate 3j (291 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The desired amine 4af was isolated as a clear yellow oil. **1H NMR** (CDCl₃, 500 MHz) δ 1.60 - 1.71 (m, 1H), 1.72 - 1.81 (m, 1H), 1.82 - 1.96 (m, 2H), 2.02 (s, 3H), 2.32 (s, 3H), 4.06 (td, J = 6.4, 1.8 Hz, 2H), 4.57 (q, J = 6.7 Hz, 1H), 5.03 (d, J = 6.7 Hz, 1H), 6.21 (d, J = 8.2 Hz, 1H), 6.52 (dd, J = 6.9, 5.3 Hz, 1H), 7.13 (d, J = 7.9 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 7.30 (ddd, J = 8.5, 7.1, 1.8 Hz, 1H), 8.05 (dd, J = 4.7, 1.4 Hz, 1H). **13C NMR** (CDCl₃, 125 MHz) δ 21.2 (CH₃), 21.3 (CH₃), 25.8 (CH₂), 34.9 (CH₂), 56.1 (CH), 64.3 (CH₂), 106.9 (CH), 113.4 (CH), 126.5 (CH), 129.6 (CH), 137.1 (C), 137.7 (CH), 140.4 (C), 148.4 (CH), 158.4 (C), 171.4
(C). **FT-IR** (cm⁻¹, neat, ATR) 3253 (vw, br), 2951 (w), 2849 (vw), 1734 (s), 1599 (s), 1510 (m), 1443 (m), 1237 (vs), 1040 (m), 771 (m), 734 (m). **HRMS** (ES⁺) calcd for C₁₅H₂₂N₂NaO₂ [M+Na⁺]: 321.1579, found: 321.1589.

**N’-(1-(4-Bromophenyl)butyl)-N,N-dimethylsulfamide, 4ag** (102 mg, 61%) was prepared according to the general procedure from 2n (146 mg, 0.5 mmol) *with the following modifications:* 1) 1.3 equiv of diisopropylammonium bis(catecholato)propylysilicate 3k (253 mg, 0.65 mmol) were used; 2) 3 mol % of 4CzIPN (12 mg, 0.015 mol) were used. The desired sulfamide 4ag was isolated as a pale yellow semisolid. **¹H NMR** (CDCl₃, 500 MHz) δ 0.90 (t, J = 7.3 Hz, 3H), 1.17 - 1.27 (m, 1H), 1.29 - 1.40 (m, 1H), 1.60 - 1.70 (m, 1H), 1.77 (br s, 1H), 2.53 (s, 6H), 4.27 (q, J = 7.3 Hz, 1H), 4.97 (d, J = 6.4 Hz, 1H), 7.17 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H). **¹³C NMR** (CDCl₃, 125 MHz) δ 13.9 (CH₃), 19.5 (CH₂), 37.8 (CH₃), 40.1 (CH₂), 58.0 (CH), 121.6 (C), 128.7 (CH), 131.9 (CH), 141.9 (C). **FT-IR** (cm⁻¹, neat, ATR) 3284 (w, br), 2989 (m), 2856 (w), 1456 (m), 1318 (s), 1448 (vs), 1128 (s), 1071 (s), 1113 (s), 957 (s), 720 (s), 706 (vs), 556 (vs). **HRMS** (ES⁺) calcd for C₁₂H₂₀BrN₂O₂S [M+H⁺]: 335.0423, found: 335.0424.

**N-(1-(4-(Methylthio)phenyl)but-3-en-1-yl)methanesulfonamide, 4ah** (89 mg, 68%) was prepared according to the general procedure from 2f (109 mg, 0.5 mmol) *with the following modifications:* 1) 1.3 equiv of diisopropylammonium bis(catecholato)propylysilicate 3k (253 mg, 0.65 mmol) were used; 2) 3 mol % of Ru(bpy)₃(PF₆)₂ (13 mg, 0.015 mol) were used in place of 4CzIPN. The desired sulfonylamide 4ah was isolated as a pale brown oil. **¹H NMR** (CDCl₃, 500 MHz) δ 0.91 (t, J = 7.5 Hz, 3H), 1.17 - 1.31 (m, 1H), 1.30 - 1.42 (m, 1H), 1.58 - 1.73 (m, 1H), 1.73 - 1.84 (m, 1H), 2.59 (s, 3H), 4.42 (t, J = 7.3 Hz, 1H), 5.04 (br s, 1H), 7.24 (d, J = 8.2 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H). **¹³C NMR** (CDCl₃, 125 MHz) δ 13.8 (CH₃), 19.5 (CH₂), 39.9 (CH₂), 42.2 (CH₃), 57.7 (CH), 128.3 (CH), 129.3 (CH), 133.9 (C), 140.6 (C). **FT-IR** (cm⁻¹, neat, ATR) 3277 (w, br), 2961 (w), 1492 (w), 1311 ν(s), 1151 (vs), 1127 (s), 1090 (s), 976 (s), 732 (vs), 516 (vs). **HRMS** (Cl⁺) calcd for C₁₁H₁₇ClO₂S [M+H⁺]: 262.0669, found: 262.0659.
*N*-((4-Chlorophenyl)(cyclopentyl)methyl)methanesulfonamide, **4aj** (105 mg, 73%) was prepared according to the general procedure from **2f** (109 mg, 0.5 mmol) with the following modifications: 1) 1.3 equiv of diisopropylammonium bis(catecholato)cyclopentylsilicate **3l** (270 mg, 0.65 mmol) were used; 2) 3 mol% of 4CzIPN (12 mg, 0.015 mol) were used. The desired sulfonylamine **4aj** was isolated as a crystalline, pale yellow solid (mp = 94-95 °C). ¹H NMR (CDCl₃, 500 MHz) δ 1.09 (dq, J = 12.9, 8.3 Hz, 1H), 1.29 - 1.39 (m, 1H), 1.41 - 1.52 (m, 2H), 1.52 - 1.62 (m, 2H), 1.63 - 1.71 (m, 1H), 1.85 - 1.94 (m, 1H), 2.09 - 2.20 (m, 1H), 2.51 (s, 3H), 4.15 (t, J = 8.4 Hz, 1H), 5.41 (d, J = 7.3 Hz, 1H), 7.24 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 7.9 Hz, 2H). ¹³C NMR (CDCl₃, 125 MHz) δ 25.4 (2 × CH₂), 30.4 (CH₂), 30.5 (CH₂), 42.1 (CH₃), 46.6 (CH), 62.7 (CH), 128.7 (CH), 129.2 (CH), 133.8 (C), 140.5 (C). FT-IR (cm⁻¹, neat, ATR) 3265 (w, br), 2953 (w), 2868 (w), 1447 (w), 1308 (vs), 1155 (vs), 1090 (m), 978 (m), 517 (s). HRMS (ES⁻) calcd for C₁₃H₁₇ClNO₂S [M-H]⁻: 286.0669, found: 286.0664.
Representative Procedure for Large Scale Alkylation

\[ \text{N-} \text{(Cyclohexyl}(4\text{-methoxyphenyl})\text{methyl)methanesulfonamide (4i)} \]

To an oven dried, 100 mL round bottom flask equipped with a stir bar were added diisopropylammonium bis(catecholato)cyclohexylsilicate 3a (3.07 g, 7.15 mmol, 1.3 equiv), imine 2i (1.07 g, 5 mmol, 1 equiv), and 4CzIPN (0.0394 g, 0.05 mmol, 0.01 equiv). The flask was sealed with a rubber septum and was evacuated and purged with argon three times via an inlet needle. The flask was then charged with anhyd DMSO (50 mL) via a syringe. The now bright yellow solution was irradiated by blue LEDs in the aforementioned photoreactor. The temperature of the reaction was maintained at approximately 27 °C via a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by GC/MS. Once complete (~36 h), the now yellow-brown solution was transferred to a separatory funnel and diluted with deionized H\textsubscript{2}O (~150 mL) and EtOAc (~100 mL). The layers were separated,\textsuperscript{33} and the aq layer was extracted with EtOAc (3 \times ~100 mL). The combined organic layers were washed with 2 M NaOH (2 \times ~150 mL), followed by brine (~150 mL). The organic layer was dried (Na\textsubscript{2}SO\textsubscript{4}), and the solvent was removed \textit{in vacuo} by rotary evaporation. Further purification was accomplished by \textit{SiO\textsubscript{2}} column chromatography (gradient hexane/EtOAc containing 1% Et\textsubscript{3}N) to give the desired sulfonylamine 4a (1.15 g, 77%) as a light brown solid (mp = 126-127 °C).

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 500 MHz) \( \delta \) 0.85 - 0.95 (m, 1H), 1.02 (qd, \( J = 11.9 \), 2.7 Hz, 1H), 1.08 - 1.27 (m, 3H), 1.32 - 1.40 (m, 1H), 1.50 - 1.70 (m, 3H), 1.72 - 1.80 (m, 1H), 1.96 - 2.06 (m, 1H), 2.51 (s, 3H), 3.80 (s, 3H), 4.12 (t, \( J = 8.4 \) Hz, 1H), 4.77 - 5.07 (m, 1H), 6.88 (d, \( J = 8.2 \) Hz, 2H), 7.15 (d, \( J = 8.9 \) Hz, 2H).

\textsuperscript{33} In the event that an emulsion forms, addition of a small amount (~30 mL) of brine can be used to assist in layer separation.
$^{13}$C NMR (CDCl$_3$, 125 MHz) 26.1 (CH$_2$), 26.2 (CH$_2$), 26.4 (CH$_2$), 30.0 (CH$_2$), 30.1 (CH$_2$), 42.0 (CH$_3$), 44.0 (CH), 55.5 (CH$_3$), 63.2 (CH), 114.3 (CH), 128.5 (CH), 132.9 (C), 159.3 (C).

FT-IR (cm$^{-1}$, neat, ATR) 3248 (w), 2938 (m), 1613 (w), 1443 (m), 1311 (vs), 1249 (s), 1156 (vs), 1132 (s), 1029 (s), 833 (s), 752 (s), 514 (vs).

HRMS (ES+) calcd for C$_{15}$H$_{23}$NNaO$_3$S [M+Na]$^+$: 320.1296, found: 320.1291.

$N'$-((4-Bromophenyl)(cyclopentyl)methyl)-$N,N$-dimethylsulfamide 4ak (1.14 g, 63%) was prepared according to the general procedure from 2n (1.46 g, 5 mmol) with the following modifications: 1) 1.2 equiv of diisopropylammonium bis(catecholato)cyclopentylsilicate 3l (2.49 g, 6 mmol) were used; 2) the reaction was complete in 24 h. The desired sulfamide 4ak was isolated as a viscous yellow oil that solidified upon standing to give a yellow solid (mp = 86-87 °C). $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 1.03 - 1.15 (m, 1H), 1.26 - 1.36 (m, 1H), 1.41 - 1.53 (m, 2H), 1.53 - 1.64 (m, 2H), 1.64 - 1.75 (m, 1H), 1.84 - 1.94 (m, 1H), 2.02 - 2.15 (m, 1H), 2.46 (s, 6H), 4.01 (dd, $J = 9.6, 6.6$ Hz, 1H), 4.84 (d, $J = 6.4$ Hz, 1H), 7.14 (d, $J = 8.2$ Hz, 2H), 7.46 (d, $J = 8.2$ Hz, 2H). $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 25.4 (2 $\times$ CH$_2$), 30.4 (CH$_2$), 30.5 (CH$_2$), 37.7 (CH$_3$), 47.0 (CH), 63.0 (CH), 121.5 (C), 129.1 (CH), 131.8 (CH), 141.9 (C). FT-IR (cm$^{-1}$, neat, ATR) 3260 (w, br), 2948 (w), 2856 (w), 1449 (w), 1317 (m), 1142 (vs), 1070 (w), 954 (w), 705 (m), 576 (m). HRMS (ES+) calcd for C$_{14}$H$_{22}$BrN$_2$O$_2$S [M+H]$^+$: 361.0585, found: 361.0590.
Procedure for Ni/Photoredox Cross-Coupling of 4ak

\[ \text{HN-SO}_2\text{NMe}_2 \] \[ \text{H}_2\text{O} \] \[ \text{OMe} \] \[ \text{OMe} \] \[ \text{H}_2\text{O} \] \[ \text{OMe} \] \[ \text{OMe} \] 

\[ 4a_b \] \[ 4a_l \]

\[ \text{HN-SO}_2\text{NMe}_2 \]

\[ \text{N'}-(\text{Cyclopentyl(4-(3-methoxypropyl)phenyl)methyl})-N,N\text{-dimethylsulfamide, 4al} \]

To an 8 mL reaction vial equipped with a stir bar were added the diisopropylammonium bis(catecholato)(3-methoxypropyl)silicate 3h (273 mg, 0.65 mmol, 1.3 equiv), \([\text{Ni(dtbbpy)}(\text{H}_2\text{O})_4]\text{Cl}_2 \) (11.8 mg, 0.025 mmol, 0.05 equiv),\(^{34}\) and \([\text{Ru(bpy)}_3\text{(PF}_6)_2] \) (10.8 mg, 0.0125 mmol, 0.025 equiv). The vial was sealed with a cap containing a TFE-lined silicone septa. The vial was evacuated three times via an inlet needle then purged with argon. The vial was then charged via a syringe with sulfamide 4ak (181 mg, 0.5 mmol, 1 equiv) dissolved in anhyd, degassed DMF (5 mL). The cap was sealed with Parafilm, and the now bright red solution was irradiated in the aforementioned LED reactor. The temperature of the reaction was maintained at approximately 27 °C via a fan. The solution was stirred vigorously while being irradiated. Reaction progress was monitored by HPLC. Once judged to be complete, the now opaque, milky-brown solution was transferred to a separatory funnel and diluted with deionized H\textsubscript{2}O (~20 mL) and EtOAc (~20 mL). The layers were separated,\(^{35}\) and the aq layer was extracted with EtOAc (3 × ~20 mL). The combined organic layers were washed with 2 M NaOH (2 × ~30 mL), 2 M HCl (~30 mL), deionized H\textsubscript{2}O (~30 mL), and brine (~50 mL). The organic layer was dried (Na\textsubscript{2}SO\textsubscript{4}), and the solvent was removed in vacuo by rotary evaporation. Further purification was accomplished by flash column chromatography (gradient hexane/EtOAc containing 1% Et\textsubscript{3}N) to give the desired coupling product, 4al, (129 mg, 73%) as a clear, colorless oil that solidified upon standing (mp = 84-85 °C).

\(^{34}\) In previous reports, we either pre-complexed the dtbbpy ligand to nickel in situ or conducted the reaction without pre-complexation. We recently found that preparation of \([\text{Ni(dtbbpy)}(\text{H}_2\text{O})_4]\text{Cl}_2 \) simplifies the process entirely. This complex can easily be prepared by reacting dtbbpy (1.05 equiv) with NiCl\(_2 \) · 6H\textsubscript{2}O in refluxing ethanol (0.1 M) for 12 h. Once cooled to rt the solvent can be removed in vacuo by rotary evaporation, and the resulting mint green solid can be washed with Et\textsubscript{2}O followed by pentane to remove any residual ligand. This complex can be stored on the bench for an indefinite period of time.

\(^{35}\) Note that a precipitate will often form and rest at the interface between the organic and aq layers. It can be discarded during the washes without compromising yield.
$^1$H NMR (CDCl$_3$, 500 MHz) δ 1.07 - 1.17 (m, 1 H), 1.27 - 1.37 (m, 1 H), 1.41 - 1.52 (m, 2 H), 1.53 - 1.63 (m, 2 H), 1.64 - 1.74 (m, 1 H), 1.82 - 1.94 (m, 3 H), 2.06 - 2.18 (m, 1 H), 2.42 (s, 6 H), 2.63 - 2.70 (m, 2 H), 3.33 (s, 3 H), 3.37 (t, $J$ = 6.4 Hz, 2 H), 4.02 (dd, $J$ = 9.5, 7.0 Hz, 1 H), 4.69 (d, $J$ = 6.4 Hz, 1 H), 7.11 - 7.18 (m, 4 H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) 25.4 (2 × CH$_2$), 30.4 (CH$_2$), 30.5 (CH$_2$), 31.4 (CH$_2$), 32.2 (CH$_2$), 37.6 (CH$_3$), 47.1 (CH), 58.8 (CH$_3$), 63.3 (CH), 72.1 (CH$_2$), 127.3 (CH), 128.7 (CH), 140.2 (C), 141.5 (C).

FT-IR (cm$^{-1}$, neat, ATR) 3284(w, br), 2942 (w), 2867 (w), 1448 (m), 1338 (s), 1151 (vs), 1116 (s), 953 (s), 705 (vs), 563 (vs).

HRMS (ES$^+$) calcd for C$_{18}$H$_{31}$N$_2$O$_3$S [M+H]$^+$: 355.2050, found: 355.2046.
\(^1\)H NMR Spectra of Synthesized Compounds

Diisopropylammonium Bis(catecholato)propylsilicate
500 MHz, DMSO–d6
Disopropylammonium Bis(catecholato)(2-phenylethyl)silicate
500 MHz, CDCl₃
Diisopropylammonium Bis(catecholato) (3-pentafluorophenylpropyl)silicate

500 MHz, DMSO–d$_6$
Diisopropylammonium Bis(catecholato)(3–cyanopropyl)silicate
500 MHz, DMSO–d6

[Image of NMR spectra and chemical structure]
(4s,6s)--2,4,5,6--tetra(9H--carbazol--9--yl)isophthalonitrile
500 MHz, CDCl3
Tris(2,2,2-trifluoroethyl) borate
500 MHz, CDCl
N-(4-methylbenzylidene)methanesulfonamide
500 MHz, CDCl₃
N-(4-methylbenzyl)benzenesulfonamide
500 MHz, CDCl3
4-methyl-N-(4-methylbenzylidene)benzenesulfonamide
500 MHz, CDCl3
N-(2-methylbenzylidene)methanesulfonamide
500 MHz, CDCl₃

[Chemical structure diagram]

[1H NMR spectrum]

ppm
0.88 0.99 1.00 1.99 3.04 3.03
10 9 8 7 6 5 4 3 2 1 0

2d

S50
N-(3-((trifluoromethyl)benzylidene)methanesulfonamide
500 MHz, CDCl₃
N-(4-chlorobenzylidene)methanesulfonamide
500 MHz, CDCl3
N-(2,4-difluorobenzylidene)methanesulfonamide
500 MHz, CDCl3

![Chemical Structure](image)

- 9.30 ppm
- 8.2 ppm
- 7.1 ppm
- 7.0 ppm
- 6.9 ppm

- 1.00
- 1.00
- 3.06
- 1.01
- 1.02
N-(2-bromo-5-fluorobenzylidene)ethanesulfonamide
500 MHz, CDCl3
N-(4-methoxybenzylidene)methanesulfonamide
500 MHz, CDCl3

[Chemical structure diagram]
N-(4-(methylthio)benzylidene)methanesulfonamide
500 MHz, CDCl3

S56
N-(benzo[d][1,3]dioxol-5-ylmethylene)methanesulfonamide
500 MHz, CDCl3
N-(4-cyanobenzylidene)methanesulfonamide
500 MHz, CDCl₃
methyl 4-(((methylsulfonyl)imino)methyl)benzoate
500 MHz, CDCl₃
N-(4-bromobenzylidene)-N,N-dimethylsulfamide
500 MHz, CDCl3

8.9 ppm
7.8 ppm
7.7 ppm

10 9 8 7 6 5 4 3 2 1 0 ppm

S60
N-(4-methylbenzylidene)aniline
500 MHz, CDCl₃
N-(4-methylbenzylidene)pyridin-2-amine
500 MHz, CDCl₃
N-(pyridin-2-ylmethylene)aniline
500 MHz, CDCl₃
methyl 4-((phenylimino)methyl)benzoate
500 MHz, CDCl₃
N-(cyclohexyl(p-toly)methyl)methanesulfonamide
500 MHz, CDCl3
N-(cyclohexyl(p-tolyl)methyl)benzenesulfonamide
500 MHz, CDCl3
N-(cyclohexyl(p-tolyl)methyl)-4-methylbenzenesulfonamide
500 MHz, CDCl₃
N-(cyclohexyl(o-toly)methyl)methanesulfonamide
500 MHz, CDCl3
N-(cyclohexyl[3-(trifluoromethyl)phenyl)methyl]methanesulfonamide
500 MHz, CDCl3
N-((4-chlorophenyl)(cyclohexyl)methyl)methanesulfonamide
500 MHz, CDCl3
N-(cyclohexyl(2,4-difluorophenyl)methyl)methanesulfonamide
500 MHz, CDCl3

![Chemical Structure]

1H NMR (500 MHz, CDCl3): δ 7.25 ppm (s, 1H), 6.9 ppm (s, 1H), 5.2 ppm (s, 1H), 4.4 ppm (s, 1H), 2.0-1.2 ppm (m, 2H, 2H, 2H, 2H)
N-((2-bromo-5-fluorophenyl)(cyclohexyl)methyl)methanesulfonamide
500 MHz, CDCl3
N-\((\text{cyclohexyl}(4\text{-methoxyphenyl})\text{methyl})\text{methanesulfonamide}\)

500 MHz, CDCl3

![N-(cyclohexyl(4-methoxyphenyl)methyl)methanesulfonamide spectrum]
N-(cyclohexyl[4-(methylthio)phenyl)methyl]methanesulfonamide
500 MHz, CDCl3
N-((benzo[\(d\)][1,3]dioxol-5-yl)cyclohexyl)methanesulfonamide
500 MHz, CDCl3
\textit{N-(14-суаноппенил)(1циклопентилметил)метанесуфамид}

500 MHz, CDCl$_3$
methyl 4-\((\text{cyclohexyl}(\text{methylsulfonamido})\text{methyl})\text{benzoate}\)

500 MHz, CDCl$_3$

![Chemical Structure Image]
N-((4-bromophenyl)(cyclohexyl)methyl)-N,N-dimethylsulfamide
500 MHz, CDCl3
N-(cyclohexyl(p-toly)methyl)aniline
500 MHz, CDCl3
N-(cyclohexyl(pyridin-2-yl)methyl)aniline

500 MHz, CDCl₃
N-(cyclohexyl(p-tolyl)methyl)pyridin-2-amine
500 MHz, CDCl3

[Chemical structure image]
methyl 4-((cyclohexyl(phenylamino)methyl)benzoate
500 MHz, CDCl3
N-[(4-(methylthio)phenyl)-2-phenylethyl]methanesulfonamide
500 MHz, CDCl3
N-(1-((4-(methylthio)phenyl)but-3-en-1-yl)methanesulfonamide
500 MHz, CDCl3
N-((1-(4-methoxyphenyl)but-3-en-1-yl)methanesulfonamide
500 MHz, CDCl₃

HN⁺SO₂Me
MeO
4x
N-(1-(4-chlorophenyl)-3-methylbutyl)methanesulfonamide
500 MHz, CDCl₃
N\textsuperscript{\prime\prime}-(1-(4-bromophenyl)-3-phenylpropyl)-N,N-dimethylsulfamide
500 MHz, CDCl\textsubscript{3}
N-(4-(perfluorophenyl)-1-(p-tolyl)butyl)aniline
500 MHz, CDCl₃
methyl 4-(4-cyano-1-(phenylamino)butyl)benzoate

500 MHz, CDCl3
methyl 4-(4-methoxy-1-phenylamino)butyl)benzoate
500 MHz, CDCl3
methyl 4-(4-[(2-oxazepane-1-carboxamido)-1-(phenylamino)butyl]benzoate
500 MHz, CDCl3
4-(4-methoxyphenyl)-4-(methylsulfonamido)butyl acetate
300 MHz, CDCl3
4-((pyridin-2-ylamino)-4-((p-tolyl)butyl acetate
500 MHz, CDCl3

![NMR spectrum](image)
N’-(1-(4-bromophenyl)-3-phenylpropyl)-N,N-dimethylsulfamide
500 MHz, CDCl₃
N-1-(4-chlorophenyl)butyl)methanesulfonamide
500 MHz, CDCl3
N-(cyclopentyl(4-(methylthio)phenyl)methyl)methanesulfonamide
500 MHz, CDCl3
N-\((4-\text{chlorophenyl})(\text{cyclopentyl})\text{methyl})\text{methanesulfonamide}

500 MHz, CDCl3

Embedded chemical structure and spectra.
N’-((4-bromophenyl)(cyclopentyl)methyl)-N,N-dimethylsulfamide
500 MHZ, CDCl3
N'-(cyclopentyl(4-(3-methoxypropyl)phenyl)methyl)-N,N-dimethylsulfamide
500 MHZ, CDCl3
$^{13}$C NMR Spectra of Synthesized Compounds

Disopropylammonium Bis(catecholato)propylsilicate
125 MHz, DMSO–d$_6$
Diisopropylammonium Bis(catecholato)(3-cyanopropyl)silicate
125 MHz. DMSO–d6
Diusopropylammonium Bis(catecholato)(2-phenylethyl)silicate
125 MHz, DMSO-d6
Diisopropylammonium Bis(catecholato) (3-pentafluorophenylpropyl)silicate

125 MHz, DMSO–d6

---

---
2,4,5,6-Tetra(9H-carbazol-9-yl)isophthalonitrile
125 MHz, CDCl3

148.61 148.91 138.48 137.26 127.24 126.05 125.25 125.82 124.14 122.67 122.21 121.08 119.93 116.67 114.39 110.75

142 140 138 136 134 132 130 128 126 ppm

122 120 118 116 114 112 ppm

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
Tris(2,2,2-trifluoroethyl) borate
125 MHz, CDCl3
N-((4-methylbenzylidene)methanesulfonamide
125 MHz, CDCl3
N-(4-methylbenzylidene)aniline
125 MHz, CDCl$_3$
4-methyl-N-(4-methylbenzylidene)benzenesulfonamide
125 MHz, CDCl3
N-(2-methylbenzylidene)methanesulfonamide
125 MHz, CDCl₃
N-(3-(trifluoromethyl)benzylidene)methanesulfonamide
125 MHz, CDCl3
N-(4-chlorobenzylidene)methanesulfonamide
125 MHz, CDCl₃
N-(2,4-difluorobenzylidene) methanesulfonamide
125 MHz, CDCl3

![N-(2,4-difluorobenzylidene) methanesulfonamide spectrum]
N-(2-bromo-5-fluorobenzylidene) methanesulfonamide
125 MHz, CDCl3

Chemical shifts and spectra.
N-[(4-methoxybenzylidene)methanesulfonamide
125 MHz, CDCl₃
N-(4-(methylthio)benzylidene)methanesulfonamide
125 MHz, CDCl3
N-(benzo[\text{d}]\text{1,3}]-dioxol-5-ylmethylene)methanesulfonamide
125 MHz, CDCl₃
N-(4-cyanobenzylidene) methanesulfonamide
125 MHz, CDCl₃
methyl 4-(((methylsulfonylimino)methyl)benzoate
125 MHz, CDCl₃
$N'-(4\text{-Bromobenzylidene})\text{-}N,N\text{-dimethylsulfamide}$

125 MHz, CDCl3
N-(4-methylbenzylidene)aniline
125 MHz, CDCl₃
N-(4-methylbenzyldiene)pyridin-2-amine
125 MHz, CDCl3
N-(pyridin-2-ylmethylene)aniline
125 MHz, CDCl3

\[
\begin{align*}
160.79 & \\
154.78 & \\
151.18 & \\
149.88 & \\
126.82 & \\
129.41 & \\
126.89 & \\
128.36 & \\
122.06 & \\
121.29 & \\
\end{align*}
\]
methyl 4-((phenylimino)methyl)benzoate
125 MHz, CDCl3
N-(cyclohexyl(p-tolyl)methyl)methanesulfonamide
125 MHz, CDCl3
N-(cyclohexyl(p-tolyl)methyl)benzenesulfonamide
125 MHz, CDCl3
N-(cyclohexyl(p-tolyl)methyl)-4-methylbenzenesulfonamide
125 MHz, CDCl3
N-(cyclobexyl(o-toly)methyl)methanesulfonamide
125 MHz, CDCl3
N-[(cyclohexyl)3-(trifluoromethyl)phenyl)methyl)methanesulfonamide
125 MHz, CDCl₃
N-((4-chlorophenyl)(cyclohexyl)methyl) methanesulfonamide
125 MHz, CDCl3
N-(cyclohexyl[2,4-difluorophenyl)methyl]methanesulfonamide
125 Mhz, CDCl3
N-((2-bromo-5-fluorophenyl)(cyclohexyl)methyl)methanesulfonamide
125 MHz, CDCl3
N-(cyclohexyl(4-methoxyphenyl)methyl)methanesulfonamide
125 MHz, CDCl3
N-(cyclohexyl[4-(methylthio)phenyl)methyl]methanesulfonamide
125 MHz, CDCl3
N-(benzo[d][1,3]dioxol-5-yl(cyclohexyl)methyl)methanesulfonamide
125 MHz, CDCl3
N-(4-cyanophenyl)(cyclohexyl)methyl)methanesulfonamide
125 MHz, CDCl3
methyl 4-[(cyclohexyl(methylsulfonamido)methyl)benzoate
125 MHz, CDCl₃
N'-(4-bromophenyl)(cyclohexyl)methyl)-N,N-dimethylsulfamide
125 MHz, CDCl3

\[ \text{HN-} \text{SO}_2 \text{NMe}_2 \]

\[ \text{Br} \quad \text{4n} \]

\[ \text{HN-} \text{SO}_2 \text{NMe}_2 \]

30 29 28 27 ppm

30 29 28 27 ppm
N-(cyclohexyl(p-toly)methyl)aniline
125 MHz, CDCl3
N-(cyclohexyl(pyridin−2−yl)methyl)aniline
125 MHz, CDCl₃
N-\((\text{cyclohexyl}(p\text{-tolyl})\text{methyl})\)pyridine-2-amine
125 MHz, CDCl$_3$
methyl 4-((cyclohexyl(phenylamino)methyl)benzoate
125 MHz, CDCl3
N-(1-(4-(methylthio)phenyl)-2-phenylethyl)methanesulfonamide
125 MHz, CDCl3
N-(1-(4-(methylthio)phenyl)but-3-en-1-yl)methanesulfonamide
125 MHz, CDCl3
N-(1-(4-methoxyphenyl)but-3-en-1-yl) methanesulfonamide
125 MHz, CDCl₃

HN-SO₂Me
MeO
4x

159.50
133.65
133.10
128.21
119.39
114.44
57.14
56.51
42.23
42.17

42.8  42.6  42.4  42.2  42.0  41.8  ppm

200  190  180  170  160  150  140  130  120  110  100  90  80  70  60  50  40  30  20  10  0  ppm

S144
N-(1-(4-chlorophenyl)-3-methylbutyl)methanesulfonamide
125 MHz, CDCl3
N’-(1-(4-bromophenyl)-3-phenylpropyl)-N,N-dimethylsulfamide
125 MHz, CDCl3
N-(4-(perfluorophenyl)-1-((p-tolyl)butyl)pyridin-2-amine
125 MHz, CDCl3
methyl 4-((4-cyano-1-((phenylamino)butyl)benzoate
125 MHz, CDCl3
methyl 4-((4-methoxy-1-(phenylamino)butyl)benzoate
125 MHz, CDCl₃
methyl 4-(4-(2-oxazepane-1-carboxamido)-1-(phenylamino)butyl)benzoate
125 MHz, CDCl3
4-(4-methoxyphenyl)-4-(methylsulfonamido)butyl acetate
75 MHz, CDCl₃

| 171.34 | 159.68 | 133.19 | 128.03 | 114.70 |
|--------|--------|--------|--------|--------|
| 63.96  | 57.38  | 55.86  | 42.16  | 34.38  | 25.75  | 21.19  |

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
4-(pyridin-2-ylamino)-4-(p-tolyl)butyl acetate
125 MHz, CDCl3
N’-(1-(4-bromophenyl)butyl)-N,N-dimethylsulfamide
125 MHz, CDCl$_3$
N-(1-((4-chlorophenyl)butyl)methanesulfonamide
125 MHz, CDCl₃
N-(cyclopentyl(4-(methylthio)phenyl)methyl)methanesulfonamide
125 MHz, CDCl₃
N-((4-chlorophenyl)(cyclopentyl)methyl)methanesulfonamide
125 MHz, CDCl₃
N'-((4-bromophenyl)(cyclopentyl)methyl)-N,N-dimethylsulfamide
125 MHz, CDCl3
N'-(cyclopentyl(4-(3-methoxypropyl)phenyl)methyl)-N,N-dimethylsulfamide
500 MHZ, CDCl₃

![Chemical Structure Image]
$^{19}$F NMR Spectra of Synthesized Compounds

Disopropylammonium Bis(catecholato) (3-pentafluorophenylpropyl)silicate
282 MHz, CDCl$_3$
Tris(2,2,2-trifluoroethyl)borate
282 MHz, CDCl3
N-(3-(trifluoromethyl)benzylidene)methanesulfonamide
282 MHz, CDCl3
N-(2,4-difluorobenzylidene)methanesulfonamide
282 MHz, CDCl3
N-(2-bromo-5-fluorobenzylidene) methanesulfonamide
282 MHz, CDCl3
N-(cyclohexyl(3-(trifluoromethyl)phenyl)methyl)methanesulfonamide
282 MHz, CDCl3
N-(cyclohexyl(2,4-difluorophenyl)methyl)methanesulfonamide
282 MHz, CDCl3
N-((2-bromo-5-fluorophenyl)(cyclohexyl)methyl)methanesulfonamide
282 MHz, CDCl3
N-(4-(perfluorophenyl)-1-(p-toly)butyl)pyridin-2-amine
282 MHz, CDCl3