Lewis Acid Induced Toggle From Ir(II) to Ir(IV) Pathways in Photocatalytic Reactions: Synthesis of Thiomorpholines and Thiazepanes from Aldehydes and SLAP Reagents

Supporting Information

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1. General information

Reactions with anhydrous solvents were carried out in oven-dried glassware under N_2 using standard manifold techniques.[1]

1.1 Materials

Compounds that are not described in the experimental part were synthesized according to literature procedures. Unless otherwise stated, chemicals were purchased from ABCR, Acros, Alfa Aesar, Apollo Scientific, Fluorochem, Maybridge, Merck, Sigma-Aldrich, Strem, or TCI, and were used without further purification. Common organic solvents were used as supplied (ACS or HPLC grade). Anhydrous MeCN, CH_2Cl_2, and THF (HPLC grade) were freshly dried by passage over activated alumina under an inert atmosphere of N_2. 1,1,1,3,3,3-Hexafluoro-2-propanol is abbreviated to HFIP, and 2,2,2-trifluoroethanol to TFE. BF_3•MeCN (15.2–16.8%, 0.87–0.88 g/mL) was purchased from Sigma-Aldrich and used directly (using 15.2% and 0.87 g/mL for calculating the stoichiometry).

All the synthesized SLAP reagents were stored under 4 °C to avoid the decomposition.

1.2 Blue light reactor and the photocatalytic reaction

Nichia LumiFlex LED strip (blue light, λ_{max} = 467 nm, 6 W for 30 LEDs) were purchased from Lumitronix® LED-Technik (http://www.leds.de/) and assembled in a 15×12×12 cm^3 metal case with total 150 blue LEDs (**maximum power: 30 W**). The case was also equipped with a cooling fan (12×12 cm^2) to maintain the temperature at room temperature. Detailed specification of the blue LEDs can be found in this webpage: http://www.leds.de/en/LED-strips-modules-oxid-oxid-oxid/Flexible-LED-strips/LumiFlex-LED-Leiste-30-LEDs-50cm-24V-blue.html.

Photocatalytic reactions were carried out in closed glass vials (sizes depended on reaction scales), neither degassed beforehand nor conducted under dry conditions. The vials were exposed next to the blue LEDs as shown in Figure S1.

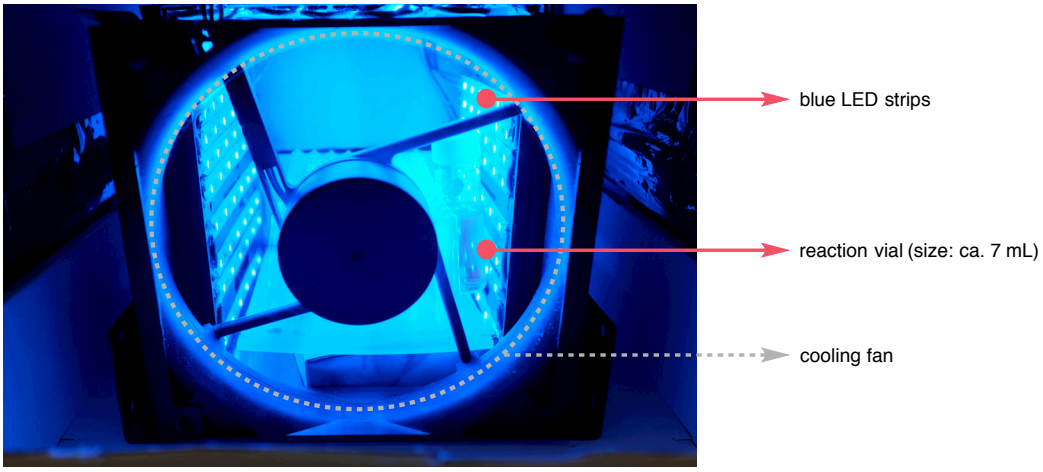


Figure S1. Blue light reactor/reaction setup. We thank Dr. Benedikt Wanner from the Bode group of Laboratorium für Organische Chemie at ETH Zürich for the construction of this blue reactor.

1.3 Reaction monitoring and purification

Thin layer chromatography (TLC) was performed on glass-backed plates pre-coated with silica gel (*Merck*, Silica Gel 60 F254), and visualized by UV quenching and by staining with basic $KMnO_4$, ninhydrin solution, or phosphomolybdic acid.

Flash column chromatography[2] was performed on silica gel (*Silicycle* SiliaFlash F60, 230–400 mesh) using a forced flow of eluent at 0.4–0.5 bar.

1.4 Characterization instruments

NMR spectra were recorded on *Bruker* Avance 400 MHz, and Varian Mercury 300 MHz spectrometers using $CDCl_3$ as the solvent unless indicated otherwise. The residual signal of the $CDCl_3$ was used as the internal standard (7.26 ppm in ^1H and 77.160 ppm in ^{13}C NMR). No additional internal standard was used in the measurement of ^{19}F NMR. Peaks of ^{13}C NMR from the major isomers were marked with asterisks if able to be recognized.

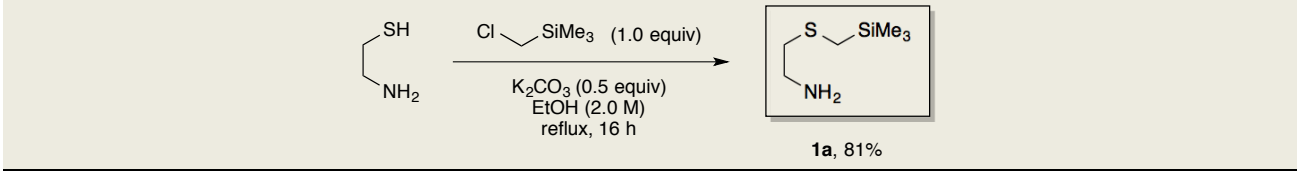
Infrared (IR) data was obtained on a *JASCO* FT-IR-4100 spectrometer with only major peaks being reported.

Melting points (m.p.) were measured on an *Electrothermal Mel-Temp* melting point apparatus and were uncorrected.

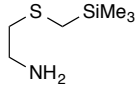
High resolution mass spectra were measured by the Mass Spectrometry Service Facility of Laboratorium für Organische Chemie at ETH Zürich on a Bruker Daltonics maXis for ESI-Qq-TOF spectrometer (ESI-MS) or Micromass (Waters) AutoSpec Ultima for EI spectrometer (EI-MS).

2. Preparation of SLAP reagents

2.1 Synthesis of SLAP TM reagent 1a



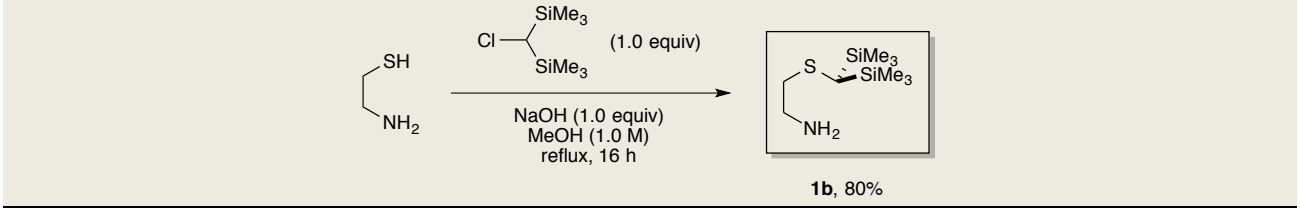
2-(((Trimethylsilyl)methyl)thio)ethanamine (1a)



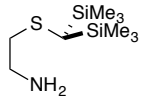
A mixture of 2-aminoethanethiol (3.1 g, 40.0 mmol, 1.0 equiv), (chloromethyl)trimethylsilane (5.5 mL, 40.0 mmol, 1.0 equiv), and K_2CO_3 (2.8 g, 20.0 mmol, 0.5 equiv) in EtOH (20 mL, 2.0 M) was heated to reflux under N_2 for 16 h. The reaction was cooled to room temperature and filtered through a sintered glass funnel. The filtrate was condensed under *vacuo* and the residue was purified by distillation at reduced pressure to afford the desired product (5.4 g, 82%) as colorless oil.

b.p.: 58–60 °C at 1.5×10^{-2} mbar; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 2.84 (td, J = 6.2, 1.0 Hz, 2 H), 2.56 (td, J = 6.2, 1.0 Hz, 2 H), 1.71 (d, J = 1.0 Hz, 2 H), 1.33 (br, 2 H), 0.05 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 40.3, 40.3, 17.9, –1.7; **HRMS** (ESI): calculated for $[C_6H_{18}NSSi]^+$: m/z = 164.0924, found: m/z = 164.0926; **IR** (ν/cm^{-1}, neat): 3353, 3287, 2954, 2898, 1575, 1471, 1390, 1320, 1249, 845, 696.

2.2 Synthesis of SLAP TM reagent 1b



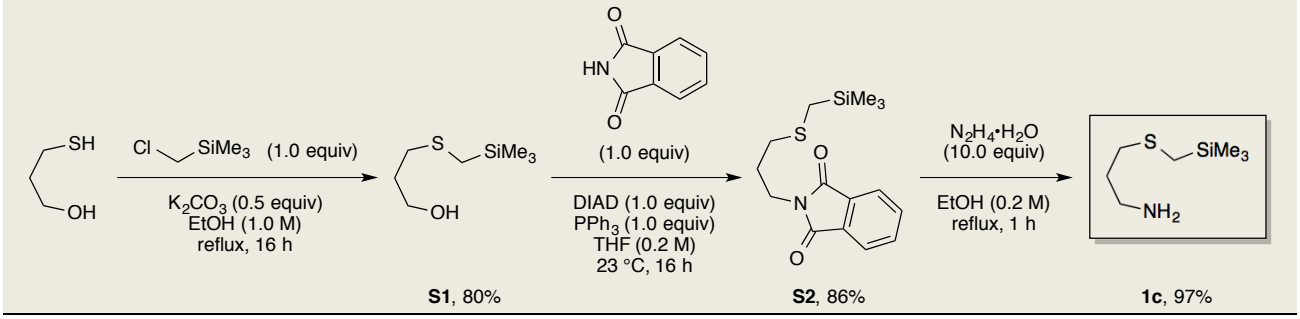
2-((Bis(trimethylsilyl)methyl)thio)ethanamine (1b)



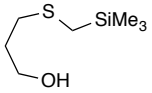
The procedure was modified from the literature.[3] To a stirred solution of NaOH (0.6 g, 16.0 mmol, 1.0 equiv) in MeOH (16 mL, 1.0 M), 2-aminoethanethiol (1.2 g, 16.0 mmol, 1.0 equiv) and bis(trimethylsilyl)chloromethane (3.5 mL, 16.0 mmol, 1.0 equiv) were added. The reaction was refluxed under N_2 for 16 h before cooled to room temerature. Water (10 mL) was added and the mixture was condensed under *vacuo*. The residue was extracted with CH_2Cl_2 (3×20 mL), and the collected organic extracts were combined, washed with brine, dried over Na_2SO_4, filtered, and evaporated under *vacuo*. The residue was purified by distillation at reduced pressure to afford the desired product (3.0 g, 80%) as colorless oil.

b.p.: 89–91 °C at 1.5 × 10^{-2} mbar; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 2.83–2.80 (m, 2 H), 2.56 (ddd, *J* = 7.1, 5.8, 1.1 Hz, 2 H), 1.57 (br, 1 H), 0.61 (d, *J* = 1.1 Hz, 2 H), 0.10 (s, 18 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 41.0, 40.9, 17.0, –0.1; **HRMS** (ESI): calculated for $[C_9H_{26}NSSi]^+$: m/z = 236.1319, found: m/z = 236.1321; **IR** (ν/cm^{-1}, neat): 3361, 3287, 2952, 2898, 2859, 1582, 1464, 1427, 1249, 1001, 842, 770, 683.

2.3 Synthesis of SLAP TM reagent 1c



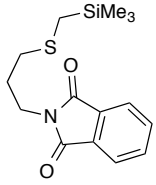
3-(((Trimethylsilyl)methyl)thio)propan-1-ol (S1)



A mixture of 1-mercapto-2-propanol (2.6 mL, 30.0 mmol, 1.0 equiv), (chloromethyl)trimethylsilane (4.1 mL, 30.0 mmol, 1.0 equiv), and K_2CO_3 (2.1 g, 15.0 mmol, 1.0 equiv) in EtOH (30 mL, 1.0 M) was heated to reflux under N_2 for 16 h. The reaction was cooled to room temperature and filtered through a sintered glass funnel. The filtrate was condensed under *vacuo* and the residue was purified by distillation at reduced pressure to afford the desired product (4.3 g, 80%) as colorless oil.

b.p.: 80–82 °C at 1.5×10^{-2} mbar; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 3.74–3.71 (m, 2 H), 2.61 (td, *J* = 7.1, 1.2 Hz, 2 H), 2.02 (br, 1 H), 1.88–1.81 (m, 2 H), 1.77 (s, 2 H), 0.07 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 62.1, 33.1, 31.2, 18.4, –1.6; **HRMS** (EI): calculated for $[C_7H_{18}OSSi]^+$: m/z = 178.0848, found: m/z = 178.0852; **IR** (ν/cm^{-1}, neat): 3357, 2953, 2879, 1416, 1391, 1249, 1062, 846, 773, 753, 697.

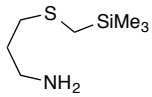
2-(3-(((Trimethylsilyl)methyl)thio)propyl)isoindoline-1,3-dione (S2)



S1 (1.8 g, 10.0 mmol, 1.0 equiv), phthalimide (1.5 g, 10.0 mmol, 1.0 equiv), and PPh_3 (2.6 g, 10.0 mmol, 1.0 equiv) were dissolved in anhydrous THF (50 mL, 0.2 M) under N_2. This clear solution was cooled to 0 °C and diisopropyl azodicarboxylate (DIAD, 2.0 mL, 10.0 mmol, 1.0 equiv) was added dropwise. The reaction was allowed to warm to room temperature and stirred under N_2 for 16 h. After the solvent was removed under *vacuo*, the residue was purified by flash column chromatography (5% to 10% hexanes in EtOAc) to afford the product (2.6 g, 86%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.81 (dd, *J* = 5.5, 3.0 Hz, 2 H), 7.68 (dd, *J* = 5.5, 3.0 Hz, 2 H), 3.76 (dd, *J* = 7.6, 6.7 Hz, 2 H), 2.55–2.51 (m, 2 H), 1.95 (qd, *J* = 7.4, 6.3 Hz, 2 H), 1.74 (s, 2 H), 0.04 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 168.4, 134.0, 132.2, 123.3, 37.3, 33.4, 27.7, 18.2, –1.6; **HRMS** (ESI): calculated for $[C_{15}H_{21}NNaO_3SSi]^+$: m/z = 330.0954, found: m/z = 330.0955; **IR** (ν/cm^{-1}, neat): 2952, 1773, 1714, 1438, 1395, 1365, 1248, 1087, 1011, 847, 719.

3-(((Trimethylsilyl)methyl)thio)propan-1-amine (1c)

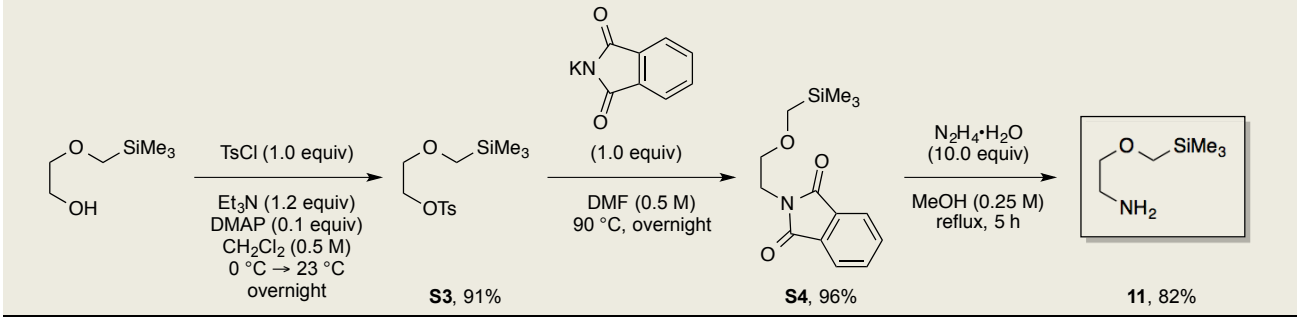


Hydrazine monohydrate (4.0 mL, 81.3 mmol, 10.0 equiv) was added to a solution of **S2** (2.5 g, 8.1 mmol, 1.0 equiv) in EtOH (41 mL, 0.2 M). The mixture was heated under reflux for 1 h and the white solids precipitated during the reaction. The reaction was cooled to room temperature and sufficient amount of 5% $NaOH_{(aq)}$ was added to dissolved the white precipitates. EtOH was removed under *vacuo* and the remained aqueous layer was extracted by CH_2Cl_2 (3×20 mL). The combined extracts were washed with brine, dried over Na_2SO_4, filtered, and condensed under *vacuo* to afford the desired product (1.4 g, 97%) as colorless oil without further purification.

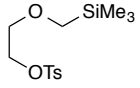
^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.78 (t, *J* = 6.9 Hz, 2 H), 2.54 (td, *J* = 7.2, 1.0 Hz, 2 H), 2.11 (br, 2 H), 1.77–1.70 (m, 4 H), 0.06 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 41.0, 33.6, 32.3, 18.5, –1.6;

HRMS (ESI): calculated for $[C_7H_{20}NSSi]^+$: m/z = 178.1080, found: m/z = 178.1081; **IR** (ν/cm^{-1}, neat): 3354, 2953, 1574, 1485, 1471, 1436, 1390, 1324, 1249, 1132, 844, 773, 753, 696.

2.4 Synthesis of SLAP M reagent 11



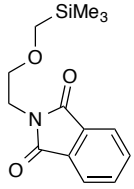
2-((Trimethylsilyl)methoxy)ethyl 4-methylbenzenesulfonate (S3)



2-((trimethylsilyl)methoxy)ethan-1-ol (5.9 g, 40.0 mmol, 1.0 equiv),[4,5] 4-toluenesulfonyl chloride (TsCl, 7.6 g, 40.0 mmol, 1.0 equiv) and 4-dimethylaminopyridine (DMAP, 0.5 g, 4.0 mmol, 0.1 equiv) were dissolved and stirred in anhydrous CH_2Cl_2 (80.0 mL, 0.5 M) under N_2. The solution was cooled in an ice bath and Et_3N (6.7 mL, 48.0 mmol, 1.2 equiv) was added slowly. After the completion of addition, the mixture was gradually warmed to room temperature and remained stirred overnight. The reaction was washed with 5% $HCl_{(aq)}$ (3×30 mL), water (30 mL), and brine (30 mL). The organic layer was dried over Na_2SO_4, filtered, and evaporated under *vacuo* to afford the desired product (11.1 g, 91%) as colorless oil without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.78 (d, *J* = 8.3 Hz, 2 H), 7.33–7.31 (m, 2 H), 4.13–4.10 (m, 2 H), 3.58–3.55 (m, 2 H), 3.05 (s, 2 H), 2.43 (s, 3 H), –0.02 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 144.8, 133.2, 129.9, 128.0, 72.3, 69.3, 65.7, 21.7, -3.1; **HRMS** (ESI): calculated for $[C_{13}H_{23}O_4SSi]^+$: m/z = 303.1081, found: m/z = 303.1085; **IR** (ν/cm^{-1}, neat): 2956, 2896, 2855, 2807, 1599, 1369, 1359, 1248, 1189, 1177, 1120, 1098, 1017, 925, 862, 816, 778, 664.

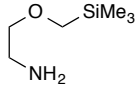
2-(2-((Trimethylsilyl)methoxy)ethyl)isoindoline-1,3-dione (S4)



To a stirred solution of **S3** (9.1 g, 30.0 mmol, 1.0 equiv) in DMF (60.0 mL, 0.5 M), potassium phthalimide (5.6 g, 30.0 mmol, 1.0 equiv) was added in one potion at room temperature. The reaction was heated to 90 °C overnight prior to the addition of H_2O (10 mL). The mixture was cooled to room temperature and DMF was removed under *vacuo*. The residue was suspended with additional brine and extracted with EtOAc (3×50 mL). The organic extracts were combined, washed with water (twice) and brine, dried over Na_2SO_4, filtered, and evaporated under *vacuo* to afford the desired product (8.0 g, 96%) as colorless oil without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.82 (ddd, *J* = 5.6, 3.1, 1.3 Hz, 2 H), 7.68 (ddd, *J* = 5.6, 3.1, 1.3 Hz, 2 H), 3.87 (td, *J* = 5.8, 1.3 Hz, 2 H), 3.63–3.60 (m, 2 H), 3.12 (s, 2 H), –0.07 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 168.3, 133.9, 132.3, 123.2, 71.6, 64.9, 37.1, –3.1; **HRMS** (ESI): calculated for $[C_{14}H_{19}NNaO_3SSi]^+$: m/z = 300.1026, found: m/z = 300.1027; **IR** (ν/cm^{-1}, neat): 2954, 2896, 2856, 2804, 1775, 1714, 1469, 1428, 1392, 1359, 1248, 1189, 1106, 1040, 891, 720.

2-((Trimethylsilyl)methoxy)ethan-1-amine (11)



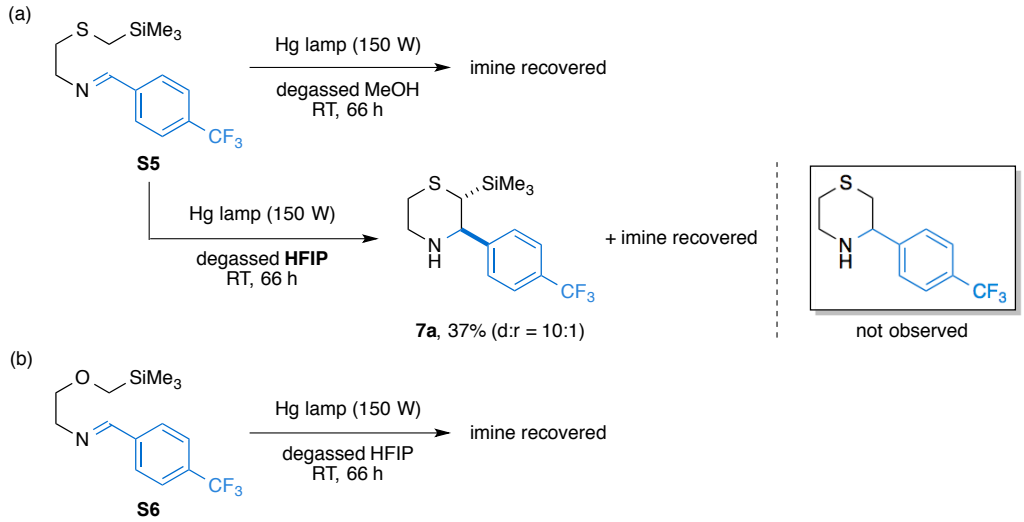
ATTENTION: The title product is volatile! Hydrazine monohydrate (12.2 mL, 250.0 mmol, 10.0 equiv) was added to a solution of **S4** (6.9 g, 25.0 mmol, 1.0 equiv) in MeOH (100 mL, 0.25 M). The mixture was heated under reflux for 5 h and the white solids precipitated during the reaction. The reaction was cooled to room temperature and sufficient amount of 2 N $NaOH_{(aq)}$ was added to dissolved the white precipitates. MeOH was removed under *vacuo* carefully and the residue was extracted by Et_2O (4×30 mL). The combined extracts were washed with 2 N $NaOH_{(aq)}$ and brine, dried over Na_2SO_4, filtered, and condensed under *vacuo* carefully to remove Et_2O. The residue was purified by distillation at reduced pressure to afford the desired product (3.0 g, 82%) as colorless oil.

b.p.: 66–68 °C at 40 mbar; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 3.41 (t, *J* = 5.1 Hz, 2 H), 3.11 (s, 2 H), 2.81 (t, *J* = 5.1 Hz, 2 H), 1.41 (br, 2 H), 0.04 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 77.5, 65.2, 41.9, –2.9; **HRMS** (ESI): calculated for $[C_6H_{18}NOSi]^+$: m/z = 148.1152, found: m/z = 148.1152; **IR** (ν/cm^{-1}, neat): 3369, 2956, 2845, 1575, 1479, 1434, 1309, 1249, 1105, 861, 701.

3. Photocatalytic synthesis of thiomorpholines and thiazepanes with SLAP reagents

3.1 Early examinations for imine cyclization condition

Initially, the radical desilylation was inspired from the Yoon and Mariano groups, and we wondered if the imine **S5** from the **SLAP TM** reagent **1a** could perform cyclization under UV-irradiation (Scheme S1).[6–8] However, we didn't observe the cyclization of imine **S5** in degassed MeOH under the exposure of UV while alternation to the degassed solvent HFIP allowed the formation of a non-desilylated thiomorpholine **7c** with unreacted imine recovered. In addition, this condition was not effective for the imine **S6** from morpholine forming **SLAP M** reagent **11**, and the reaction under strong UV light in long reaction time was neither pleasant. As the consequence of these preliminary findings, we decided to re-examine the feasibility of SLAP reagents using different potential photoredox catalysts under visible-light mediated conditions.



Scheme S1. UV-irradiated cyclization of imines from (a) **SLAP TM** reagent **1a** and (b) SLAP reagent **11**. (preliminary results from Dr. Jiang Tuo, ETH Zürich).

Different electrochemical values of several photocatalysts for their reductive quenching cycles (PC* → PC^{-}) are illustrated in the Figure S2, with the comparison of the oxidation potentials of different SLAP reagents and the reduction potentials of the formed N-centered radicals. According to this information, several photocatalysts ($Ir^{III}[dF(CF_3)ppy]_2(dtbbpy)PF_6$,[9,10] 2CzIPN,[11,12] 4DAIPN[11,12]) seemed appropriate to our thiomorpholine forming **SLAP TM** reagents.

The corresponding imine **2a** from the **SLAP TM** reagent **1a** was first subject to the photocatalytic cyclization using $Ir^{III}[dF(CF_3)ppy]_2(dtbbpy)PF_6$ as the catalyst, but only the imine was recovered (Scheme S2). This was probably because the reducing ability of forming $Ir^{II}[dF(CF3)ppy]_2$dtbbpy was not sufficient to reduce the N-centered radical despite high oxidizing ability of photoexcited $*Ir^{III}[dF(CF_3)ppy]_2(dtbbpy)^{+}$ species. The other two organic photocatalysts were also applied to the cyclization with the imine but not successful. In the case with 2CzIPN trace amount of product was observed, combined with the imine recovered majorly and unidentified side products. While the condition with photocatalyst 2CzIPN could be promising if optimization is applied, the unreliable preparation protocol of this catalyst and the unexpected formation of side products hampered further investigations.

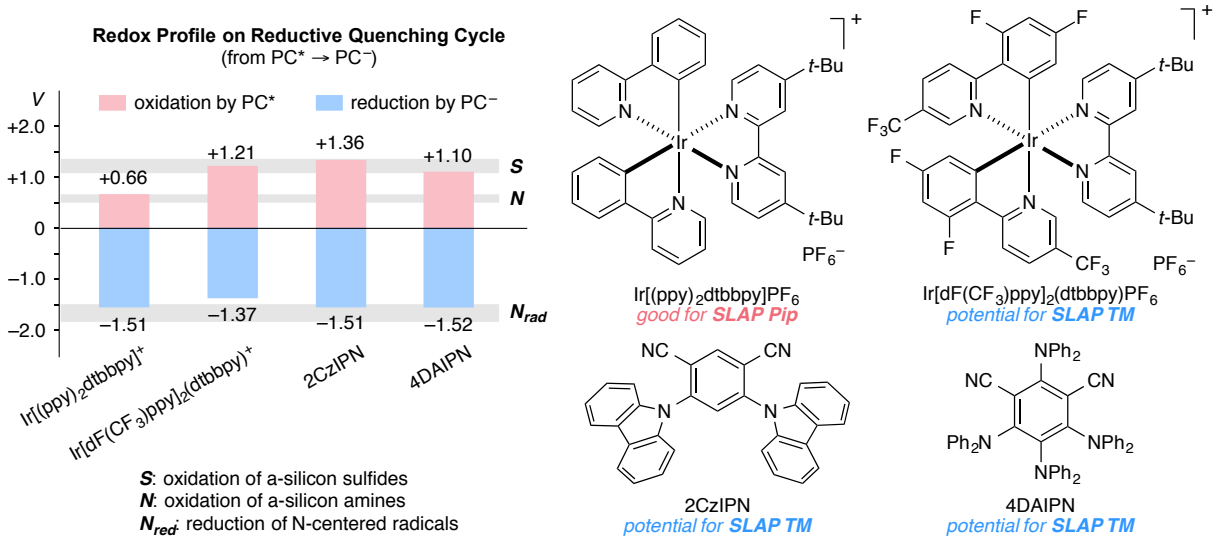
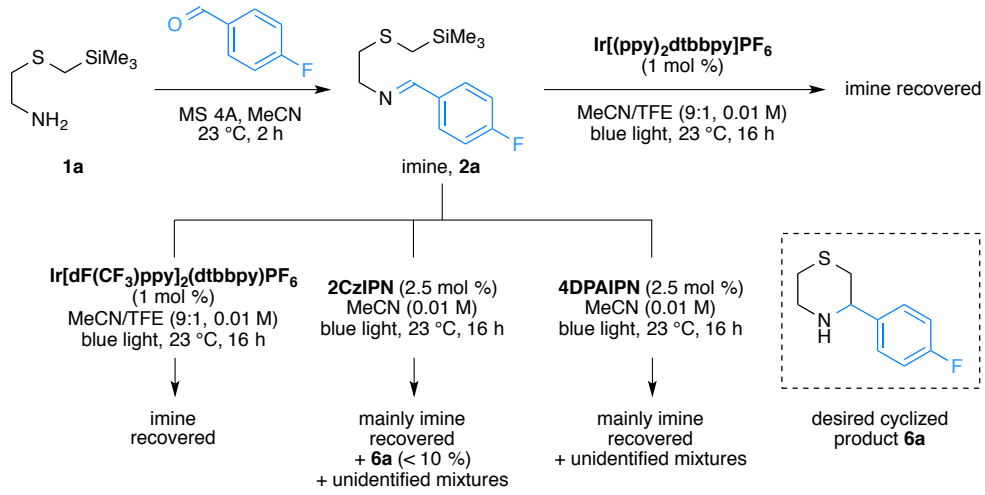


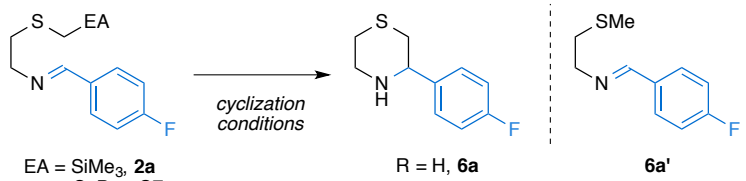
Figure S2. Evaluation of potential photocatalysts. PC = photocatalyst.



Scheme S2. Photocyclization of imine **2a** with potential catalysts.

3.2 Screening of cyclization conditions

Table S1. Screening of cyclization conditions.

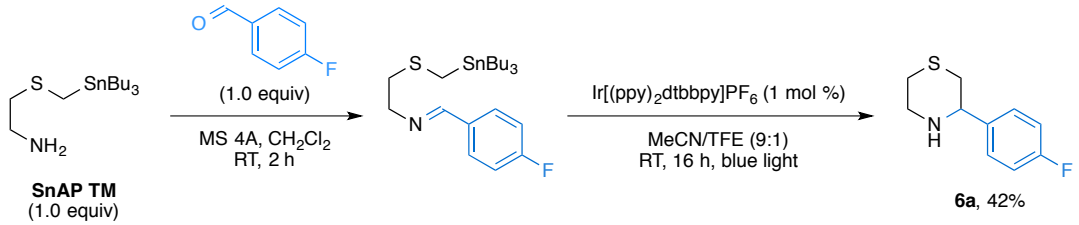


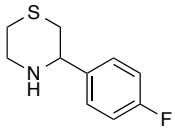
EA = $SiMe_3$, **2a**; $SnBu_3$, **S7** | R = H, **6a** | **6a'**

entry	imine[a]	condition	result
1	**2a**	**SnAP conditions:** $Cu(OTf)_2$ (1.0 equiv), 2,6-lutidine (1.0 equiv), CH_2Cl_2/HFIP (4:1, 0.10 M), 23 °C, 16 h	imine recovered
2	**2a**	**SLAP *N*-Bn conditions:** $Ir[(ppy)_2dtbbpy]PF_6$ (1 mol %), MeCN/TFE (9:1, 0.05 M), 23 °C, blue light, 16 h	imine recovered
3	**S7**	$Ir[(ppy)_2dtbbpy]PF_6$ (1 mol %), MeCN/TFE (9:1, 0.05 M), 23 °C, blue light, 16 h	**6a**, 42%[b]
4	**2a**	*n*-Bu_3NF (2.0 equiv), MS 4A, THF (0.10 M), 60 °C, 16 h	**6a'**, full desilylation
5	**2a**	CsF (2.0 equiv), MeCN, 60 °C	**6a'**, full desilylation
6	**2a**	KOTMS (2.0 equiv), MeCN (0.10 M), 23 °C, 16 h	**6a'**, full desilylation
7	**2a**	CsF (2.0 equiv), $Ir[(ppy)_2dtbbpy]PF_6$ (1 mol %), MeCN/TFE (9:1, 0.05 M), 23 °C, blue light, 16 h	imine + partial desilylation
8	**2a**	KOTMS (2.0 equiv), $Ir[(ppy)_2dtbbpy]PF_6$ (1 mol %), MeCN/TFE (9:1, 0.05 M), 23 °C, blue light, 16 h	**6a'**, full desilylation
9	**2a**	TMSOTf (1.0 equiv), $Ir[(ppy)_2dtbbpy]PF_6$ (1 mol %), MeCN (0.10 M), 23 °C, blue light, 16 h	mostly imine recovered
10	**2a**	TMSOTf (2.0 equiv), $Ir[(ppy)_2dtbbpy]PF_6$ (1 mol %), MeCN (0.10 M), 23 °C, blue light, 16 h	**6a**, 34%[c]
11	**2a**	BF_3•MeCN (2.0 equiv), $Ir[(ppy)_2dtbbpy]PF_6$ (1 mol %), MeCN (0.10 M), 23 °C, blue light, 16 h	**6a**, 36%[c]
12	**2a**	$Bi(OTf)_3$ (2.0 equiv), $Ir[(ppy)_2dtbbpy]PF_6$ (1 mol %), MeCN (0.10 M), 23 °C, blue light, 16 h	**6a**, 56%[c]
13	**2a**	$Cu(OTf)_2$ (2.0 equiv), $Ir[(ppy)_2dtbbpy]PF_6$ (1 mol %), MeCN (0.10 M), 23 °C, blue light, 16 h	**6a**, 42%[c]
14	**2a**	$Bi(OTf)_3$ (1.0 equiv), $Cu(OTf)_2$ (1.0 equiv), $Ir[(ppy)_2dtbbpy]PF_6$ (1 mol %), MeCN (0.10 M), 23 °C, blue light, 16 h	**6a**, 47%[c]
15	**2a**	$Bi(OTf)_3$ (0.5 equiv), $Cu(OTf)_2$ (1.0 equiv), $Ir[(ppy)_2dtbbpy]PF_6$ (1 mol %), MeCN (0.10 M), 23 °C, blue light, 16 h	**6a**, 46%[c]
16	**2a**	$Cu(OTf)_2$ (2.0 equiv), MeCN (0.10 M), 60 °C, 16 h	**6a**, 45%[c]
17	**2a**	Other Lewis acids (TMSOTf, BF_3•MeCN, or $Bi(OTf)_3$, 2.0 equiv), MeCN (0.10 M), 60 °C, 16 h	imine + hydrolysis
18	**2a**	$Cu(OTf)_2$ (2.0 equiv), MeCN (0.10 M), 23 °C, blue light, 16 h	**6a**, 40%[c]
19	**2a**	$(Cu^{I}OTf)_2$•toluene (2.0 equiv), MeCN (0.10 M), 23 °C, blue light, 16 h	imine recovered

[a]Imine formation was performed with 4-fluorobenzaldehyde and MS 4A in CH_2Cl_2. [b]Isolated yield under 0.5 mmol scale. [c]Calculated yield from ^1H NMR measurement of unpurified reaction mixture under 0.1 mmol scale with 1,3,5-trimethoxybenzene as an additional internal standard. BL = blue light; dtbbpy = 4,4′-di-*tert*-butyl-2,2′-bipyridine; $dF(CF_3)ppy$ = 2-(2,4-difluorophenyl)-5-(trifluoromethyl)pyridine; HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol; ppy = 2-phenylpyridine; TFE = 2,2,2-trifluoroethanol.

3-(4-Fluorophenyl)thiomorpholine (6a) (Table S1, entry 4)

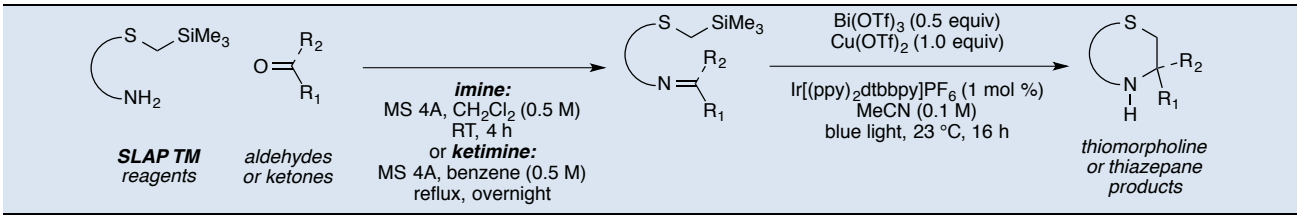




A mixture of the SnAP reagent **SnAP TM** (190.1 mg, 0.5 mmol, 1.0 equiv), 4-fluorobenzaldehyde (54.0 mL, 0.5 mmol, 1.0 equiv), and MS 4A (100.0 mg) in CH_2Cl_2 (1.0 mL, 0.5 M) under N_2 was stirred 2 h at room temperature. The reaction was filtered through Celite and washed with CH_2Cl_2. The filtrate was condensed under *vacuo* and the residue was re-dissolved in MeCN/TFE (9:1, 10 mL, 0.05 M) in a vial (20 mL), followed by the addition of $Ir[(ppy)_2dtbbpy]PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv). The vial was closed, and the reaction was stirred for 16 h at room temperature under the exposure of blue LEDs with a cooling fan to maintain the temperature. H_2O (0.1 mL) was added and the reaction was stirred for another 5 min. After the solvents were removed under *vacuo*, the residue was dissolved in CH_2Cl_2, dried over Na_2SO_4, filtered, and condensed under *vacuo*. The residue was purified by flash column chromatography (10–50% EtOAc in hexanes) to afford the desired product (41.3 mg, 42%) with spectral characteristics identical to those previously reported.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.38–7.28 (m, 2 H), 7.08–6.94 (m, 2 H), 3.90 (dd, *J* = 10.6, 2.3 Hz, 1 H), 3.42 (dt, *J* = 12.5, 3.0 Hz, 1 H), 3.15 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.88 (ddd, *J* = 13.4, 11.7, 3.0 Hz, 1 H), 2.78 (dd, *J* = 13.3, 10.5 Hz, 1 H), 2.42 (dddd, *J* = 9.4, 8.0, 4.8, 2.4 Hz, 2 H), 1.91 (br, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 162.2 (d, *J* = 245.8 Hz), 140.1 (d, *J* = 3.2 Hz), 128.2 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 21.2 Hz), 62.3, 49.2, 35.0, 27.5.

3.3 General procedure



General condition for imine formation:

A mixture of a SLAP reagent (0.5 mmol), an aldehyde (0.5 mmol), and MS 4A (100.0 mg) in CH_2Cl_2 (1.0 mL, 0.5 M) under N_2 was stirred at room temperature 4 h. The reaction was filtered through Celite and washed with CH_2Cl_2. The filtrate was condensed under *vacuo* and used directly for cyclization.

General condition for ketimine formation:

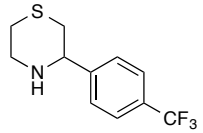
A mixture of a SLAP reagent (0.5 mmol), a ketone (0.5 mmol), and MS 4A (100.0 mg) in benzene (1.0 mL, 0.5 M) under N_2 was stirred at reflux overnight. The reaction was filtered through Celite and washed with CH_2Cl_2. The filtrate was condensed under *vacuo* and used directly for cyclization.

General condition for photo-cyclization:

The reaction was carried out in a closed vial (7 mL) with no need to be degased beforehand or under dry conditions. To a solution of the corresponding imine or ketimine (0.5 mmol, 1.00 equiv) in MeCN (5.0 mL, 0.05 M), $Cu(OTf)_2$ (180.8 mg, 0.50 mmol, 1.00 equiv), $Bi(OTf)_3$ (160.4 mg, 0.25 mmol, 0.5 equiv), and $Ir[(ppy)_2dtbbpy]PF_6$ (4.6 mg, 5.00 μmol, 0.01 equiv) were added. The reaction was stirred for 16 or 48 h at room temperature under the exposure of blue LEDs (30 W) with a cooling fan to maintain the temperature. $NH_{3(aq)}$ (1 mL, ca. 12 M) was added and the reaction was stirred for another 10 min. After the solvents were removed under *vacuo*, the residue was re-dissolved in $CH_2Cl_2/NH_{3(aq)}$ and filtered through Celite. The filtrate was extracted with CH_2Cl_2 and the combined organic layers were washed with $NH_{3(aq)}$. The final organic extracts were dried over Na_2SO_4, filtered, and condensed under *vacuo*. The residue was purified by flash column chromatography to afford the desired thiomorpholine product.

3.4 Substrate scope with non-heterocyclic aldehydes and ketones (Scheme 2)

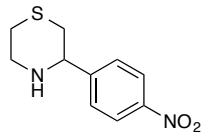
3-(4-(Trifluoromethyl)phenyl)thiomorpholine (6b) (Scheme 2)



The photomediated synthesis of **6b** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv) and 4-(trifluoromethyl)benzaldehyde (68.3 μL, 0.5 mmol, 1.0 equiv) for 16 h. The desired product (83.3 mg, 67%) was obtained by flash column chromatography (10–50% EtOAc in hexanes) with spectral characteristics identical to those previously reported.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.66–7.54 (m, 1 H), 7.54–7.43 (m, 1 H), 3.99 (dd, *J* = 10.5, 2.2 Hz, 1 H), 3.57–3.33 (m, 1 H), 3.16 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.89 (ddd, *J* = 12.9, 11.7, 3.0 Hz, 1 H), 2.78 (dd, *J* = 13.3, 10.6 Hz, 1 H), 2.45 (ddt, *J* = 11.9, 10.9, 2.4 Hz, 1 H), 1.82 (br, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 148.2 (q, *J* = 1.4 Hz), 130.0 (q, *J* = 32.4 Hz), 127.1, 125.7 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.0 Hz), 62.6, 49.0, 35.0, 27.5; **^{19}F NMR** (377 MHz, $CDCl_3$): δ [ppm] = –62.5.

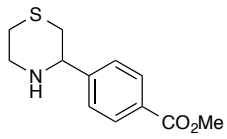
3-(4-Nitrophenyl)thiomorpholine (6c) (Scheme 2)



The photomediated synthesis of **6c** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv) and 4-nitrobenzaldehyde (75.6 mg, 0.5 mmol, 1.0 equiv) for 16 h. The desired product (83.5 mg, 74%) was obtained by flash column chromatography (30–70% EtOAc in hexanes) as yellowish solids.

m.p.: 125–126 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 8.23–8.02 (m, 2 H), 7.69–7.43 (m, 2 H), 4.02 (dd, *J* = 10.4, 2.3 Hz, 1 H), 3.43 (dt, *J* = 11.8, 3.0 Hz, 1 H), 3.14 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.86 (ddd, *J* = 13.3, 11.7, 3.0 Hz, 1 H), 2.73 (dd, *J* = 13.2, 10.5 Hz, 1 H), 2.52–2.32 (m, 2 H), 1.84 (br, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 151.4, 147.4, 127.5, 123.9, 62.2, 48.7, 34.8, 27.4; **HRMS** (ESI): calculated for $[C_{10}H_{13}N_2O_2S]^+$: m/z = 225.0692, found: m/z = 225.0693; **IR** (ν/cm^{-1}, neat): 3325, 2940, 2901, 2815, 1596, 1516, 1350, 1310, 1109, 985, 856, 845, 735.

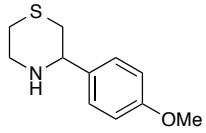
Methyl 4-(thiomorpholin-3-yl)benzoate (6d) (Scheme 2)



The photomediated synthesis of **6d** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv) and methyl 4-formylbenzoate (82.1 mg, 0.5 mmol, 1.0 equiv) for 16 h. The desired product (84.6 mg, 71%) was obtained by flash column chromatography (30–70% EtOAc in hexanes) with spectral characteristics identical to those previously reported.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.99–7.92 (m, 2 H), 7.42–7.38 (m, 2 H), 3.95 (dd, *J* = 10.5, 2.2 Hz, 1 H), 3.87 (s, 3 H), 3.46–3.38 (m, 1 H), 3.13 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.92–2.82 (m, 1 H), 2.80–2.71 (m, 1 H), 2.42 (ddt, *J* = 13.2, 12.4, 2.3 Hz, 2 H), 1.83 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 166.8, 149.2, 130.0, 129.6, 126.6, 62.6, 52.1, 49.0, 34.8, 27.5.

3-(4-Methoxyphenyl)thiomorpholine (6e) (Scheme 2)

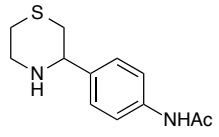


The photomediated synthesis of **6e** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv) and 4-methoxybenzaldehyde (60.8 μL, 0.5 mmol, 1.0 equiv) for 16 h. The desired product (51.7 mg, 49%) was obtained by flash column chromatography (30–70% EtOAc in hexanes) with spectral characteristics identical to those previously reported.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.34–7.23 (m, 2 H), 6.91–6.81 (m, 2 H), 3.87 (dd, *J* = 10.6, 2.2 Hz, 1 H), 3.79 (s, 3 H), 3.43 (dt, *J* = 12.3, 3.2 Hz, 1 H), 3.16 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.89 (ddd, *J* = 12.9, 11.6,

3.0 Hz, 1 H), 2.81 (dd, *J* = 13.2, 10.7 Hz, 1 H), 2.43 (ddt, *J* = 13.1, 11.9, 2.3 Hz, 2 H), 1.81 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 159.0, 136.6, 127.6, 113.9, 62.4, 55.3, 49.3, 35.0, 27.5.

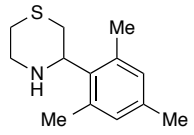
N-(4-(Thiomorpholin-3-yl)phenyl)acetamide (6f) (Scheme 2)



The photomediated synthesis of **6f** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv) and *N*-(4-formylphenyl)acetamide (86.1 mg, 0.5 mmol, 1.0 equiv) for 16 h. The desired product (71.2 mg, 60%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 2:1 to EtOAc:CH_2Cl_2:MeOH = 2:1:0.3) with spectral characteristics identical to those previously reported.[14]

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.67 (br, 1 H), 7.46–7.40 (m, 2 H), 7.30–7.24 (m, 2 H), 3.87 (dd, *J* = 10.6, 2.2 Hz, 1 H), 3.42 (dt, *J* = 12.1, 3.0 Hz, 1 H), 3.14 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.87 (ddd, *J* = 13.4, 11.7, 3.0 Hz, 1 H), 2.77 (dd, *J* = 13.4, 10.6 Hz, 1 H), 2.46–2.36 (m, 2 H), 2.13 (s, 3 H), 1.94 (br, 1 H) **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 168.7, 140.2, 137.4, 127.2, 120.3, 62.5, 49.2, 34.9, 27.5, 24.6.

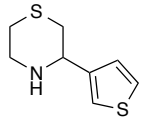
3-Mesitylthiomorpholine (6g) (Scheme 2)



The photomediated synthesis of **6g** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv) and 2,4,6-trimethylbenzaldehyde (73.7 µL, 0.5 mmol, 1.0 equiv) for 16 h. The desired product (26.2 mg, 24%) was obtained by flash column chromatography (hexanes to 20% EtOAc in hexanes) as pale yellow solids.

m.p.: 58–59 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 6.84 (s, 2 H), 4.41 (dd, *J* = 10.9, 2.5 Hz, 1 H), 3.47 (dt, *J* = 11.7, 3.1 Hz, 1 H), 3.30 (dd, *J* = 13.1, 10.9 Hz, 1 H), 3.14 (td, *J* = 11.7, 2.2 Hz, 1 H), 2.94 (ddd, *J* = 13.0, 11.7, 2.9 Hz, 1 H), 2.51 (br, 6 H), 2.42 (dq, *J* = 12.9, 2.4 Hz, 1 H), 2.29 (dd, *J* = 13.2, 2.3 Hz, 1 H), 2.26 (s, 3 H), 1.62 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 136.8, 136.7, 136.6, 130.3, 60.3, 50.2, 30.2, 27.8, 21.6, 20.8; **HRMS** (ESI): calculated for $[C_{13}H_{20}NS]^+$: m/z = 222.1311, found: m/z = 222.1315; **IR** (ν/cm^{-1}, neat): 3321, 2921, 2822, 1610, 1445, 1416, 1317, 1290, 1115, 984, 852, 712.

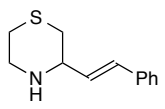
3-(Thiophen-3-yl)thiomorpholine (6h) (Scheme 2)



The photomediated synthesis of **6h** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv) and thiophene-3-carbaldehyde (45.7 µL, 0.5 mmol, 1.0 equiv) for 16 h. The desired product (49.7 mg, 54%) was obtained by flash column chromatography (10–50% EtOAc in hexanes) with spectral characteristics identical to those previously reported.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.29 (dd, *J* = 5.0, 3.0 Hz, 1 H), 7.20 (dt, *J* = 2.8, 1.2 Hz, 1 H), 7.08 (dd, *J* = 4.9, 1.3 Hz, 1 H), 4.07 (dd, *J* = 10.5, 2.4 Hz, 1 H), 3.43 (dt, *J* = 12.3, 3.1 Hz, 1 H), 3.15 (td, *J* = 11.9, 2.4 Hz, 1 H), 2.94–2.73 (m, 2 H), 2.56 (dt, *J* = 13.1, 2.3 Hz, 1 H), 2.42 (dq, *J* = 13.2, 2.5 Hz, 1H), 1.90 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 145.3, 126.1, 126.0, 120.6, 58.3, 49.0, 34.5, 27.5.

(*E*)-3-Styrylthiomorpholine (6i) (Scheme 2)

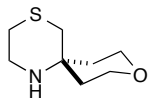


The photomediated synthesis of **6i** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv) and 3-methyl-2-butenal (62.9 µL, 0.5 mmol, 1.0 equiv) for 16 h. The desired product (32.8 mg, 32%) was obtained by flash column chromatography (50–80% EtOAc in hexanes) as pale yellow solids.

m.p.: 93–94 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.38–7.27 (m, 4 H), 7.26–7.21 (m, 1 H), 6.57 (dd, *J* = 16.0, 1.1 Hz, 1 H), 6.18 (dd, *J* = 16.0, 7.0 Hz, 1 H), 3.62–3.52 (m, 1 H), 3.40 (dt, *J* = 12.2, 3.1 Hz, 1 H), 3.10 (td, *J* = 11.9, 2.4 Hz, 1 H), 2.80 (ddd, *J* = 13.2, 11.5, 3.0 Hz, 1 H), 2.67 (dd, *J* = 13.1, 10.2 Hz, 1 H), 2.50 (dt, *J* = 13.0, 2.2 Hz, 1 H), 2.45–2.38 (m, 1 H), 1.77 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] =

136.8, 131.7, 130.7, 128.7, 127.8, 126.5, 59.8, 48.2, 33.1, 27.6; **HRMS** (ESI): calculated for $[C_{12}H_{16}NS]^+$: m/z = 206.0998, found: m/z = 206.1002; **IR** (ν/cm^{-1}, neat): 3308, 3025, 2906, 2820, 1494, 1448, 1415, 1312, 1121, 1016, 967, 761, 736, 693.

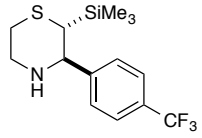
9-Oxa-4-thia-1-azaspiro[5.5]undecane (6j) (Scheme 2)



The photomediated synthesis of **6j** was modified from the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv), dihydro-2*H*-pyran-4(3*H*)-one (46.2 μL, 0.5 mmol, 1.0 equiv), and additional BF_3•MeCN (0.8 mL, 1.0 mmol, 2.0 equiv) for 48 h. The desired product (20.1 mg, 23%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 2:1 to EtOAc:CH_2Cl_2:MeOH = 2:1:0.3) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 3.74 (ddd, *J* = 11.6, 7.1, 4.5 Hz, 2 H), 3.58 (dt, *J* = 12.1, 4.9 Hz, 2 H), 3.15–3.02 (m, 2 H), 2.54 (s, 2 H), 2.53–2.44 (m, 2 H), 1.86–1.68 (m, 5 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 63.5, 47.8, 41.2, 37.4, 36.1, 28.4; **HRMS** (ESI): calculated for $[C_8H_{16}NOS]^+$: m/z = 174.0947, found: m/z = 174.0950; **IR** (ν/cm^{-1}, neat): 3418, 3302, 2946, 2859, 1660, 1462, 1431, 1298, 1237, 1101, 1028, 1015, 841, 734, 703.

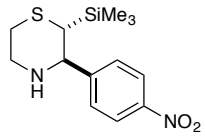
***trans*-3-(4-(Trifluoromethyl)phenyl)-2-(trimethylsilyl)thiomorpholine (7a) (Scheme 2)**



The photomediated synthesis of **7a** followed the general procedure with **1b** (117.8 mg, 0.5 mmol, 1.0 equiv) and 4-(trifluoromethyl)benzaldehyde (68.3 μL, 0.5 mmol, 1.0 equiv) for 16 h. The desired product (72.8 mg, 46%, dr > 10:1) was obtained by flash column chromatography (10–30% EtOAc in hexanes) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.64–7.52 (m, 2 H), 7.45 (d, *J* = 8.1 Hz, 2 H), 3.89 (d, *J* = 10.2 Hz, 1 H), 3.38 (dt, *J* = 12.0, 3.1 Hz, 1 H), 3.14 (td, *J* = 11.9, 2.4 Hz, 1 H), 2.93 (ddd, *J* = 12.9, 11.8, 3.2 Hz, 1 H), 2.55 (d, *J* = 10.2 Hz, 1 H), 2.42 (dt, *J* = 12.8, 2.6 Hz, 1 H), 1.68 (s, 1 H), –0.28 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 147.9 (q, *J* = 1.4 Hz), 130.5 (q, *J* = 32.4 Hz), 128.4, 125.6 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.1 Hz), 65.5, 49.0, 34.5, 28.8, –2.2; **^{19}F NMR** (377 MHz, $CDCl_3$): δ [ppm] = –62.5; **HRMS** (ESI): calculated for $[C_{14}H_{21}F_3NSSi]^+$: m/z = 320.1111, found: m/z = 320.1111; **IR** (ν/cm^{-1}, neat): 3297, 2954, 2911, 2826, 1675, 1619, 1417, 1326, 1251, 1166, 1126, 1068, 1017, 932, 853, 840, 699.

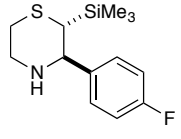
***trans*-3-(4-Nitrophenyl)-2-(trimethylsilyl)thiomorpholine (7b) (Scheme 2)**



The photomediated synthesis of **7b** followed the general procedure with **1b** (117.8 mg, 0.5 mmol, 1.0 equiv) and 4-nitrobenzaldehyde (75.6 mg, 0.5 mmol, 1.0 equiv) for 16 h. The desired product (64.9 mg, 44%, dr > 10:1) was obtained by flash column chromatography (10–50% EtOAc in hexanes) as yellowish solids.

m.p.: 110–111 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 8.16 (d, *J* = 8.8 Hz, 2 H), 7.52 (d, *J* = 8.8 Hz, 2 H), 3.95 (d, *J* = 10.2 Hz, 1 H), 3.50–3.33 (m, 1 H), 3.14 (td, *J* = 11.9, 2.4 Hz, 1 H), 2.93 (ddd, *J* = 13.0, 11.8, 3.2 Hz, 1 H), 2.54 (d, *J* = 10.2 Hz, 1 H), 2.43 (dt, *J* = 12.9, 2.7 Hz, 1 H), 1.71 (s, 1 H), –0.27 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 151.1, 147.7, 129.0, 123.9, 65.1, 48.8, 34.6, 28.8, –2.1; **HRMS** (ESI): calculated for $[C_{13}H_{21}N_2O_2SSi]^+$: m/z = 297.1088, found: m/z = 297.1087; **IR** (ν/cm^{-1}, neat): 2952, 1604, 1520, 1347, 1313, 1250, 1108, 1014, 932, 841, 698.

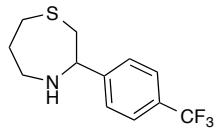
***trans*-3-(4-Fluorophenyl)-2-(trimethylsilyl)thiomorpholine (7c) (Scheme 2)**



The photomediated synthesis of **7c** followed the general procedure with **1b** (117.8 mg, 0.5 mmol, 1.0 equiv) and 4-fluorobenzaldehyde (54.0 μL, 0.5 mmol, 1.0 equiv) for 16 h. The desired product (51.9 mg, 39%, dr > 10:1) was obtained by flash column chromatography (10–30% EtOAc in hexanes) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.35–7.20 (m, 2 H), 7.03–6.92 (m, 2 H), 3.80 (d, *J* = 10.3 Hz, 1 H), 3.36 (ddd, *J* = 12.0, 3.7, 2.4 Hz, 1 H), 3.19–3.07 (m, 1 H), 2.98–2.80 (m, 1 H), 2.50 (dd, *J* = 10.4, 1.1 Hz, 1 H), 2.40 (dt, *J* = 13.0, 2.7 Hz, 1 H), 1.73 (br, 1 H), -0.27 (d, *J* = 1.0 Hz, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 162.5 (d, *J* = 246.4 Hz), 140.0 (d, *J* = 3.3 Hz), 129.5 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 21.1 Hz), , 65.0, 49.2, 34.6, 28.8, -2.2; **HRMS** (ESI): calculated for $[C_{13}H_{21}FNSSi]^+$: m/z = 270.1143, found: m/z = 270.1144; **IR** (ν/cm^{-1}, neat): 3295, 2952, 2924, 2822, 1604, 1509, 1250, 1224, 1156, 1122, 1015, 930, 856, 837.

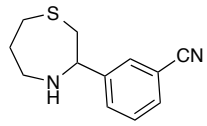
3-(4-(Trifluoromethyl)phenyl)-1,4-thiazepane (8a) (Scheme 2)



The photomediated synthesis of **8a** followed the general procedure with **1c** (88.7 mg, 0.5 mmol, 1.0 equiv) and 4-(trifluoromethyl)benzaldehyde (68.3 µL, 0.5 mmol, 1.0 equiv) for 48 h. The desired product (56.5 mg, 43%) was obtained by flash column chromatography (10–50% EtOAc in hexanes) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.57 (d, *J* = 8.1 Hz, 2 H), 7.48 (d, *J* = 8.1 Hz, 2 H), 4.03 (dd, *J* = 9.0, 3.9 Hz, 1 H), 3.24–3.05 (m, 2 H), 3.02–2.68 (m, 4 H), 2.06 (ddt, *J* = 14.4, 10.1, 5.1 Hz, 1 H), 1.97–1.78 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 148.6 (q, *J* = 1.4 Hz), 129.7 (q, *J* = 32.4 Hz), 127.1, 125.6 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 271.9 Hz), 66.8, 47.0, 43.3, 33.7, 33.0; **^{19}F NMR** (377 MHz, $CDCl_3$): δ [ppm] = –62.5; **HRMS** (ESI): calculated for $[C_{12}H_{15}F_3NS]^+$: m/z = 262.0872, found: m/z = 262.0875; **IR** (ν/cm^{-1}, neat): 2922, 2846, 1618, 1416, 1326, 1164, 1124, 1067, 1017, 845, 723.

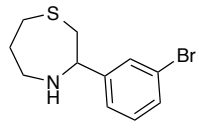
3-(1,4-Thiazepan-3-yl)benzonitrile (8b) (Scheme 2)



The photomediated synthesis of **8b** followed the general procedure with **1c** (88.7 mg, 0.5 mmol, 1.0 equiv) and 3-cyanobenzaldehyde (65.6 mg, 0.5 mmol, 1.0 equiv) for 48 h. The desired product (54.6 mg, 50%) was obtained by flash column chromatography (10–50% EtOAc in hexanes) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.69 (d, *J* = 1.7 Hz, 1 H), 7.59 (dt, *J* = 7.8, 1.6 Hz, 1 H), 7.52 (dt, *J* = 7.7, 1.4 Hz, 1 H), 7.41 (t, *J* = 7.8 Hz, 1 H), 4.01 (dd, *J* = 8.7, 4.0 Hz, 1 H), 3.19–3.01 (m, 2 H), 2.95 (ddd, *J* = 14.5, 4.1, 0.9 Hz, 1 H), 2.91–2.67 (m, 3 H), 2.04 (ddq, *J* = 14.7, 10.2, 5.2 Hz, 1 H), 1.97–1.79 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 146.1, 131.3, 131.1, 130.5, 129.4, 118.9, 112.7, 65.7, 46.7, 43.0, 33.8, 33.1; **HRMS** (ESI): calculated for $[C_{12}H_{15}N_2S]^+$: m/z = 219.0950, found: m/z = 219.0953; **IR** (ν/cm^{-1}, neat): 3342, 2918, 2846, 2228, 1668, 1581, 1479, 1429, 1335, 1130, 900, 808, 692.

3-(3-Bromophenyl)-1,4-thiazepane (8c) (Scheme 2)

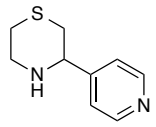


The photomediated synthesis of **8c** followed the general procedure with **1c** (88.7 mg, 0.5 mmol, 1.0 equiv) and 3-bromobenzaldehyde (58.3 µL, 0.5 mmol, 1.0 equiv) for 48 h. The desired product (61.3 mg, 45%) was obtained by flash column chromatography (10–30% EtOAc in hexanes) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.53 (t, *J* = 1.9 Hz, 1 H), 7.37 (ddd, *J* = 7.9, 2.1, 1.1 Hz, 1 H), 7.33–7.23 (m, 1 H), 7.18 (t, *J* = 7.8 Hz, 1 H), 3.92 (dd, *J* = 9.2, 3.8 Hz, 1 H), 3.23–3.03 (m, 2 H), 2.96–2.70 (m, 4 H), 2.13–1.97 (m, 1 H), 1.87 (dddt, *J* = 13.8, 10.1, 6.2, 4.0 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 146.9, 130.5, 130.3, 129.8, 125.4, 122.8, 66.9, 47.1, 43.4, 33.5, 32.9; **HRMS** (ESI): calculated for $[C_{11}H_{15}BrNS]^+$: m/z = 272.0103, found: m/z = 272.0104; **IR** (ν/cm^{-1}, neat): 3311, 2920, 2844, 1593, 1567, 1473, 1422, 1333, 1130, 1070, 997, 878, 789, 754, 694.

3.5 Substrate scope with heterocyclic aldehydes (Scheme 3)

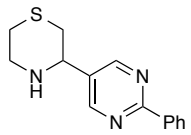
3-(Pyridin-4-yl)thiomorpholine (6k) (Scheme 3)



The photomediated synthesis of **6k** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv), 4-pyridinecarboxaldehyde (47.1 μL, 0.5 mmol, 1.0 equiv), and additional BF_3•MeCN (0.8 mL, 1.0 mmol, 2.0 equiv) for 16 h. The desired product (83.3 mg, 67%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 1:1 to EtOAc:CH_2Cl_2:MeOH = 1:1:0.5) with spectral characteristics identical to those previously reported.[13]

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.79–8.36 (m, 2 H), 7.39–7.10 (m, 2 H), 3.94 (dd, *J* = 10.5, 2.3 Hz, 1 H), 3.45 (dt, *J* = 12.2, 3.1 Hz, 1 H), 3.15 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.89 (ddd, *J* = 13.1, 11.7, 3.0 Hz, 1 H), 2.76 (dd, *J* = 13.1, 10.5 Hz, 1 H), 2.46 (ddt, *J* = 17.8, 10.7, 2.4 Hz, 2 H), 2.08 (br, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 152.4, 150.3, 121.7, 61.7, 48.7, 34.5, 27.4.

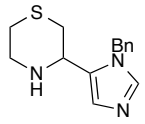
3-(2-Phenylpyrimidin-5-yl)thiomorpholine (6l) (Scheme 3)



The photomediated synthesis of **6l** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv), 2-phenylpyrimidine-5-carbaldehyde (92.1 mg, 0.5 mmol, 1.0 equiv), and additional BF_3•MeCN (1.2 mL, 1.5 mmol, 3.0 equiv) for 16 h. The desired product (96.0 mg, 75%) was obtained by flash column chromatography (30–70% EtOAc in hexanes) as pale yellow solids.

m.p.: 138–139 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 8.75 (s, 2 H), 8.51–8.31 (m, 2 H), 7.58–7.38 (m, 3 H), 3.95 (dd, *J* = 10.6, 2.3 Hz, 1 H), 3.42 (dt, *J* = 12.2, 3.1 Hz, 1 H), 3.12 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.98–2.73 (m, 2 H), 2.58–2.34 (m, 2 H), 1.89 (br, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 164.3, 155.9, 137.4, 134.5, 130.8, 128.7, 128.2, 58.3, 48.8, 34.6, 27.4; **HRMS** (ESI): calculated for $[C_{14}H_{16}N_3S]^+$: m/z = 258.1059, found: m/z = 258.1063; **IR** (ν/cm^{-1}, neat): 3302, 2932, 2900, 1582, 1545, 1430, 1315, 1120, 785, 748, 693.

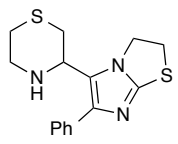
3-(1-Benzyl-1*H*-imidazol-5-yl)thiomorpholine (6m) (Scheme 3)



The photomediated synthesis of **6m** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv), 1-benzyl-1*H*-imidazole-5-carboxaldehyde (93.1 mg, 0.5 mmol, 1.0 equiv), and additional BF_3•MeCN (1.2 mL, 1.5 mmol, 3.0 equiv). The desired product (108.6 mg, 84%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 1:1 to EtOAc:CH_2Cl_2:MeOH = 1:1:0.5) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.47 (d, *J* = 1.1 Hz, 1 H), 7.38–7.26 (m, 3 H), 7.12–7.06 (m, 2 H), 6.99 (s, 1 H), 5.29 (d, *J* = 15.7 Hz, 1 H), 5.18 (d, *J* = 15.7 Hz, 1 H), 3.85 (dd, *J* = 10.5, 2.3 Hz, 1 H), 3.31 (dt, *J* = 13.0, 3.0 Hz, 1 H), 2.97 (ddd, *J* = 12.9, 11.6, 2.5 Hz, 1 H), 2.80 (dd, *J* = 13.2, 10.5 Hz, 1 H), 2.71 (ddd, *J* = 13.4, 11.7, 3.0 Hz, 1 H), 2.40 (dt, *J* = 13.2, 2.1 Hz, 1 H), 2.32 (dq, *J* = 13.3, 2.5 Hz, 1 H), 2.03 (br, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 138.4, 136.5, 133.5, 129.1, 128.2, 126.8, 126.7, 52.8, 48.9, 48.1, 31.9, 27.3; **HRMS** (ESI): calculated for $[C_{14}H_{18}N_3S]^+$: m/z = 260.1216, found: m/z = 260.1219; **IR** (ν/cm^{-1}, neat): 3291, 2911, 1667, 1496, 1454, 1418, 1359, 1245, 1227, 1114, 1028, 929, 734, 713.

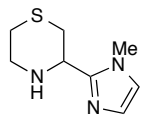
6-Phenyl-5-(thiomorpholin-3-yl)-2,3-dihydroimidazo[2,1-*b*]thiazole (6n) (Scheme 3)



The photomediated synthesis of **6n** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv), 6-phenyl-2,3-dihydroimidazo[2,1-*b*]thiazole-5-carbaldehyde (115.1 mg, 0.5 mmol, 1.0 equiv), and additional BF_3•MeCN (1.2 mL, 1.5 mmol, 3.0 equiv) for 16 h. The desired product (83.3 mg, 55%) was obtained by flash column chromatography (30% EtOAc in hexanes to EtOAc) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.54–7.45 (m, 2 H), 7.39 (dd, *J* = 8.5, 6.9 Hz, 2 H), 7.32–7.22 (m, 1 H), 4.58 (ddd, *J* = 11.1, 7.5, 6.1 Hz, 1 H), 4.32 (dd, *J* = 11.0, 2.4 Hz, 1 H), 4.23 (dt, *J* = 11.1, 7.6 Hz, 1 H), 3.87–3.70 (m, 2 H), 3.35 (dt, *J* = 11.8, 3.1 Hz, 1 H), 3.05 (td, *J* = 11.7, 2.2 Hz, 1 H), 2.98 (dd, *J* = 13.1, 10.9 Hz, 1 H), 2.85 (ddd, *J* = 13.1, 11.7, 2.9 Hz, 1 H), 2.53 (dt, *J* = 13.1, 2.3 Hz, 1 H), 2.40 (dq, *J* = 13.2, 2.5 Hz, 1 H), 1.99 (br, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 149.9, 143.7, 134.6, 128.6, 128.3, 127.9, 127.1, 53.9, 49.2, 47.8, 35.1, 32.2, 27.6; **HRMS** (ESI): calculated for $[C_{15}H_{18}N_3S_2]^+$: m/z = 304.0937, found: m/z = 304.0938; **IR** (ν/cm^{-1}, neat): 3056, 2922, 2850, 1716, 1671, 1603, 1577, 1550, 1493, 1461, 1443, 1407, 1344, 1278, 1115, 1023, 910, 773, 731, 701, 671.

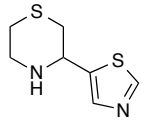
3-(1-Methyl-1*H*-imidazol-2-yl)thiomorpholine (6o) (Scheme 3)



The photomediated synthesis of **6o** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv), 1-methylimidazole-2-carboxaldehyde (55.1 mg, 0.5 mmol, 1.0 equiv), and additional BF_3•MeCN (1.2 mL, 1.5 mmol, 3.0 equiv) for 16 h. The desired product (33.4 mg, 36%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 1:1 to EtOAc:CH_2Cl_2:MeOH = 1:1:0.5) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 6.92 (d, *J* = 1.3 Hz, 1 H), 6.79 (d, *J* = 1.3 Hz, 1 H), 4.12 (dd, *J* = 10.8, 2.5 Hz, 1 H), 3.69 (s, 3 H), 3.44 (dtd, *J* = 13.6, 2.9, 0.9 Hz, 1 H), 3.26–2.98 (m, 2 H), 2.74 (ddd, *J* = 13.4, 11.9, 3.1 Hz, 1 H), 2.59 (dt, *J* = 13.7, 2.4 Hz, 1 H), 2.36 (dq, *J* = 13.5, 2.4 Hz, 1 H), 1.81 (br, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 148.5, 127.4, 121.3, 53.8, 48.0, 32.9, 31.2, 27.6; **HRMS** (ESI): calculated for $[C_8H_{14}N_3S]^+$: m/z = 184.0903, found: m/z = 184.0903; **IR** (ν/cm^{-1}, neat): 3383, 2917, 1661, 1492, 1455, 1417, 1282, 1135, 1021, 932, 739.

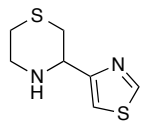
3-(Thiazol-5-yl)thiomorpholine (6p) (Scheme 3)



The photomediated synthesis of **6p** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv), 1,3-thiazole-5-carbaldehyde (43.4 μL, 0.5 mmol, 1.0 equiv), and additional BF_3•MeCN (1.2 mL, 1.5 mmol, 3.0 equiv) for 16 h. The desired product (66.9 mg, 72%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 1:1 to EtOAc:CH_2Cl_2:MeOH = 1:1:0.2) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.65 (d, *J* = 0.7 Hz, 1 H), 7.78 – 7.64 (m, 1 H), 4.28 (dd, *J* = 10.2, 2.5 Hz, 1 H), 3.35 (dt, *J* = 12.4, 3.2 Hz, 1 H), 3.10 (ddd, *J* = 12.5, 11.4, 2.5 Hz, 1 H), 2.86–2.68 (m, 2 H), 2.57 (dt, *J* = 13.1, 2.2 Hz, 1 H), 2.38 (ddt, *J* = 13.3, 3.3, 2.2 Hz, 1 H), 1.97 (br, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 152.4, 142.1, 139.5, 55.2, 48.5, 35.4, 27.3; **HRMS** (ESI): calculated for $[C_7H_{11}N_2S_2]^+$: m/z = 187.0358, found: m/z = 187.0360; **IR** (ν/cm^{-1}, neat): 3405, 3281, 3077, 2909, 2818, 1665, 1448, 1405, 1308, 1294, 1244, 1107, 1018, 876, 802.

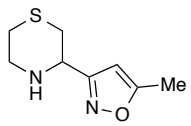
3-(Thiazol-4-yl)thiomorpholine (6q) (Scheme 3)



The photomediated synthesis of **6q** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv), 4-thiazolecarboxaldehyde (56.6 mg, 0.5 mmol, 1.0 equiv), and additional BF_3•MeCN (1.2 mL, 1.5 mmol, 3.0 equiv) for 16 h. The desired product (43.0 mg, 46%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 1:1 to EtOAc:CH_2Cl_2:MeOH = 1:1:0.2) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.76 (d, *J* = 2.0 Hz, 1 H), 7.21 (dd, *J* = 2.0, 0.8 Hz, 1 H), 4.24 (ddd, *J* = 10.1, 2.7, 0.8 Hz, 1 H), 3.45 (dt, *J* = 12.6, 3.2 Hz, 1 H), 3.19 (ddd, *J* = 12.5, 11.5, 2.5 Hz, 1 H), 2.99–2.71 (m, 4 H), 2.45 (ddt, *J* = 13.3, 3.1, 2.2 Hz, 1 H), 2.22 (br, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 159.4, 153.1, 113.5, 58.0, 48.4, 32.9, 27.7; **HRMS** (ESI): calculated for $[C_7H_{11}N_2S_2]^+$: m/z = 187.0358, found: m/z = 187.0361; **IR** (ν/cm^{-1}, neat): 3415, 3082, 2919, 1666, 1443, 1415, 1309, 1289, 1147, 1035, 1018, 878, 827, 732.

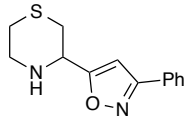
5-Methyl-3-(thiomorpholin-3-yl)isoxazole (6r) (Scheme 3)



The photomediated synthesis of **6r** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv), 5-methylisoxazole-3-carboxaldehyde (55.6 mg, 0.5 mmol, 1.0 equiv), and additional BF_3•MeCN (1.2 mL, 1.5 mmol, 3.0 equiv) for 16 h. The desired product (73.7 mg, 80%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 1:1 to EtOAc:CH_2Cl_2:MeOH = 1:1:0.2) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 5.92 (s, 1 H), 4.08 (dt, *J* = 10.4, 2.1 Hz, 1 H), 3.34 (dt, *J* = 12.5, 3.1 Hz, 1 H), 3.14–3.01 (m, 1 H), 2.77 (tdd, *J* = 14.4, 10.8, 2.3 Hz, 2 H), 2.58 (dq, *J* = 13.2, 2.0 Hz, 1 H), 2.37 (ddd, *J* = 11.4, 3.9, 1.9 Hz, 1 H), 2.34 (s, 2 H), 2.01 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 169.6, 165.5, 99.6, 54.2, 47.8, 32.1, 27.4, 12.3; **HRMS** (ESI): calculated for $[C_8H_{13}N_2OS]^+$: m/z = 185.0743, found: m/z = 185.0743; **IR** (ν/cm^{-1}, neat): 3306, 3128, 2912, 2835, 1673, 1604, 1479, 1448, 1419, 1313, 1257, 1121, 1017, 898, 807, 748.

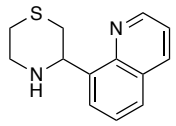
3-Phenyl-5-(thiomorpholin-3-yl)isoxazole (6s) (Scheme 3)



The photomediated synthesis of **5.3s** followed the general procedure with **5.1** (81.7 mg, 0.5 mmol, 1.0 equiv), 3-phenyl-1,2-oxazole-5-carbaldehyde (86.6 mg, 0.5 mmol, 1.0 equiv), and additional BF_3•MeCN (1.2 mL, 1.5 mmol, 3.0 equiv) for 16 h. The desired product (101.9 mg, 83%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 1:1 to EtOAc:CH_2Cl_2:MeOH = 1:1:0.2) as pale yellow solids.

m.p.: 117–118 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.83–7.67 (m, 1 H), 7.49–7.36 (m, 1 H), 6.48 (d, *J* = 0.8 Hz, 1 H), 4.25 (ddd, *J* = 9.2, 3.3, 0.7 Hz, 1 H), 3.39 (dt, *J* = 12.6, 3.4 Hz, 1 H), 3.12 (ddd, *J* = 12.6, 10.8, 2.5 Hz, 1 H), 2.93–2.72 (m, 2 H), 2.46 (dddd, *J* = 13.3, 4.0, 2.5, 1.5 Hz, 1 H), 1.99 (s, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 173.7, 162.3, 130.1, 129.0, 128.9, 126.8, 98.6, 54.2, 47.5, 31.6, 27.6; **HRMS** (ESI): calculated for $[C_{13}H_{15}N_2OS]^+$: m/z = 247.0900, found: m/z = 247.0901; **IR** (ν/cm^{-1}, neat): 3241, 3116, 2912, 2818, 1597, 1577, 1468, 1441, 1405, 1312, 1010, 967, 950, 915, 826, 769, 692.

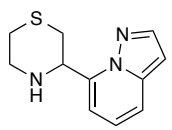
3-(Quinolin-8-yl)thiomorpholine (6t) (Scheme 3)



The photomediated synthesis of **6t** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv), quinoline-8-carboxaldehyde (78.6 mg, 1.0 equiv), and additional BF_3•MeCN (0.8 mL, 1.0 mmol, 2.0 equiv). The desired product (72.6 mg, 63%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 1:1 to EtOAc:CH_2Cl_2:MeOH = 1:1:0.2) as brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.87 (dd, *J* = 4.2, 1.8 Hz, 1 H), 8.09 (dd, *J* = 8.3, 1.8 Hz, 1 H), 7.73 (dd, *J* = 7.1, 1.5 Hz, 1 H), 7.68 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.50–7.45 (m, 1 H), 7.38–7.34 (m, 1 H), 5.00 (dd, *J* = 10.5, 2.3 Hz, 1 H), 3.49–3.43 (m, 1 H), 3.25–3.18 (m, 1 H), 3.11–3.04 (m, 2 H), 2.97–2.89 (m, 1 H), 2.74–2.68 (m, 1 H), 2.45–2.41 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 149.4, 145.7, 141.4, 136.4, 128.4, 127.4, 126.7, 126.4, 121.1, 58.2, 48.9, 33.3, 27.5; **HRMS** (ESI): calculated for $[C_{13}H_{15}N_2S]^+$: m/z = 231.0950, found: m/z = 231.0954; **IR** (ν/cm^{-1}, neat): 3300, 2907, 1596, 1576, 1498, 1465, 1447, 1365, 1318, 1309, 1152, 1119, 1030, 973, 884, 798.

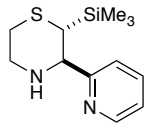
3-(Pyrazolo[1,5-*a*]pyridin-7-yl)thiomorpholine (6u) (Scheme 3)



The photomediated synthesis of **6u** followed the general procedure with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv), pyrazolo[1,5-*a*]pyridine-7-carbaldehyde (73.1 mg, 1.0 equiv), and additional BF_3•MeCN (1.2 mL, 1.5 mmol, 3.0 equiv). The desired product (82.4 mg, 75%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 1:1 to EtOAc:CH_2Cl_2:MeOH = 1:1:0.2) as brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.95 (d, *J* = 2.2 Hz, 1 H), 7.45 (dt, *J* = 8.8, 1.8 Hz, 1 H), 7.07 (ddt, *J* = 8.8, 6.8, 1.8 Hz, 1 H), 6.81 (dd, *J* = 7.1, 2.3 Hz, 1 H), 6.51 (q, *J* = 2.1 Hz, 1 H), 4.77 (dt, *J* = 9.2, 2.9 Hz, 1 H), 3.44 (dt, *J* = 12.4, 3.3 Hz, 1 H), 3.24 (tq, *J* = 12.2, 2.3 Hz, 1 H), 3.09–2.80 (m, 3 H), 2.64 (br, 1 H), 2.48 (ddt, *J* = 14.9, 3.7, 1.9 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 142.0, 141.2, 140.6, 123.2, 117.0, 108.4, 97.1, 57.0, 48.5, 30.7, 27.8; **HRMS** (ESI): calculated for $[C_{11}H_{14}N_3S]^+$: m/z = 220.0903, found: m/z = 220.0904; **IR** (ν/cm^{-1}, neat): 3411, 2917, 2712, 2634, 1635, 1547, 1524, 1455, 1417, 1310, 1215, 1181, 1152, 1039, 916, 796, 780, 730.

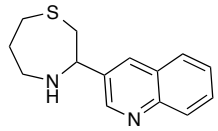
trans-3-(Pyridin-2-yl)-2-(trimethylsilyl)thiomorpholine (7d) (Scheme 3)



The photomediated synthesis of **7d** followed the general procedure with **1b** (117.8 mg, 0.5 mmol, 1.0 equiv), 2-pyridinecarboxaldehyde (47.1 μL, 0.5 mmol, 1.0 equiv), and additional BF_3•MeCN (0.8 mL, 1.0 mmol, 2.0 equiv) for 16 h. The desired product (39.3 mg, 31%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 1:1 to EtOAc:CH_2Cl_2:MeOH = 1:1:0.5) as brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.54 (ddd, *J* = 4.8, 1.8, 1.1 Hz, 1 H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1 H), 7.29 (dt, *J* = 7.7, 1.1 Hz, 1 H), 7.19 (ddd, *J* = 7.7, 4.8, 1.1 Hz, 1 H), 4.01 (d, *J* = 10.3 Hz, 1 H), 3.44 (dt, *J* = 13.1, 3.0 Hz, 1 H), 3.15 (ddd, *J* = 13.1, 12.1, 2.6 Hz, 1 H), 2.86 (ddd, *J* = 13.1, 12.1, 3.0 Hz, 1 H), 2.72 (d, *J* = 10.3 Hz, 1 H), 2.39 (dt, *J* = 13.1, 2.6 Hz, 1 H), 2.27 (br, 1 H), –0.28 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 149.7, 137.0, 123.2, 123.0, 65.4, 47.9, 32.9, 28.5, –2.5; **HRMS** (ESI): calculated for $[C_{12}H_{21}N_2SSi]^+$: m/z = 253.1189, found: m/z = 253.1189; **IR** (ν/cm^{-1}, neat): 3288, 2918, 2849, 1589, 1472, 1434, 1249, 1154, 1121, 1109, 996, 936, 851, 838.

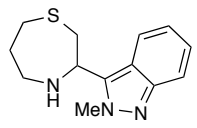
3-(Quinolin-3-yl)-1,4-thiazepane (8d) (Scheme 3)



The photomediated synthesis of **8d** followed the general procedure with **1c** (88.7 mg, 0.5 mmol, 1.0 equiv), 3-quinolinecarboxaldehyde (78.6 mg, 1.0 equiv), and additional BF_3•MeCN (0.8 mL, 1.0 mmol, 2.0 equiv) for 48 h. The desired product (83.2 mg, 68%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 1:1 to EtOAc:CH_2Cl_2:MeOH = 1:1:0.2) as brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 8.87 (d, *J* = 2.2 Hz, 1 H), 8.10 (d, *J* = 2.1 Hz, 1 H), 8.05 (dq, *J* = 8.5, 0.9 Hz, 1 H), 7.76 (dd, *J* = 8.2, 1.4 Hz, 1 H), 7.65 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1 H), 7.49 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1 H), 4.16 (ddd, *J* = 8.9, 3.9, 0.7 Hz, 1 H), 3.23–3.07 (m, 2 H), 3.01 (ddd, *J* = 14.5, 4.0, 1.0 Hz, 1 H), 2.95–2.73 (m, 3 H), 2.06 (dtd, *J* = 19.7, 10.3, 9.2, 4.3 Hz, 2 H), 1.96–1.81 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 150.4, 147.7, 137.1, 132.9, 129.3, 129.2, 128.0, 127.8, 126.8, 64.5, 46.9, 43.1, 33.5, 33.0; **HRMS** (ESI): calculated for $[C_{14}H_{17}N_2S]^+$: m/z = 245.1107, found: m/z = 245.1107; **IR** (ν/cm^{-1}, neat): 3313, 3053, 2921, 2846, 1619, 1572, 1495, 1419, 1326, 1121, 1016, 914, 788, 754, 734.

3-(2-Methyl-2*H*-indazol-3-yl)-1,4-thiazepane (8e) (Scheme 3)

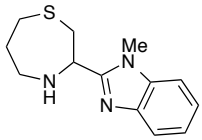


The photomediated synthesis of **8e** followed the general procedure with **1c** (88.7 mg, 0.5 mmol, 1.0 equiv), 2-methyl-2*H*-indazole-3-carbaldehyde (80.1 mg, 1.0 equiv), and additional BF_3•MeCN (1.2 mL, 1.5 mmol, 3.0 equiv). The desired product (38.8 mg, 31%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 1:1 to EtOAc:CH_2Cl_2:MeOH = 1:1:0.1) as yellowish solids.

m.p.: 139–140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.83 (dt, *J* = 8.5, 1.1 Hz, 1 H), 7.61 (dt, *J* = 8.7, 1.0 Hz, 1 H), 7.24 (ddd, *J* = 8.8, 6.6, 1.1 Hz, 1 H), 7.02 (ddd, *J* = 8.5, 6.6, 0.9 Hz, 1 H), 4.48 (dd, *J* = 9.6, 3.5 Hz, 1 H), 4.21 (s, 3 H), 3.30 (ddd, *J* = 14.3, 5.6, 3.1 Hz, 1 H), 3.22–2.97 (m, 3 H), 2.90 (ddtd, *J* = 14.4, 11.1, 3.8, 1.2 Hz, 2 H), 2.12 (ddtd, *J* = 16.3, 11.0, 5.6, 4.0 Hz, 1 H), 2.02–1.84 (m, 2 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 147.9, 136.3, 126.0, 121.2, 120.6, 119.8, 117.2, 61.1, 47.9, 41.0, 38.9, 32.9, 32.8; **HRMS**

(ESI): calculated for $[C_{13}H_{18}N_3S]^+$: m/z = 248.1216, found: m/z = 248.1217; **IR** (ν/cm^{-1}, neat): 3299, 3056, 2923, 2942, 1495, 1436, 1372, 1319, 1282, 1131, 1046, 999, 975, 889, 748, 741.

3-(1-Methyl-1*H*-benzo[*d*]imidazol-2-yl)-1,4-thiazepane (8f) (Scheme 3)

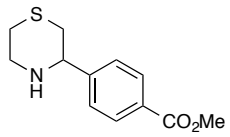


The photomediated synthesis of **8f** followed the general procedure with **1c** (88.7 mg, 0.5 mmol, 1.0 equiv), 1-methyl-1*H*-benzoimidazole-2-carbaldehyde (80.1 mg, 1.0 equiv), and additional BF_3•MeCN (1.2 mL, 1.5 mmol, 3.0 equiv). The desired product (61.7 mg, 50%) was obtained by flash column chromatography (EtOAc:CH_2Cl_2 = 1:1 to EtOAc:CH_2Cl_2:MeOH = 1:1:0.2) as brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.87–7.70 (m, 1 H), 7.47–7.11 (m, 3 H), 4.27 (dd, *J* = 9.8, 4.8 Hz, 1 H), 3.84 (s, 3 H), 3.54 (dd, *J* = 15.0, 9.8 Hz, 1 H), 3.21 (ddd, *J* = 15.0, 4.8, 1.0 Hz, 1 H), 3.09–2.90 (m, 2 H), 2.89–2.76 (m, 2 H), 2.21 (br, 1 H), 2.11 (ddq, *J* = 15.1, 6.9, 4.2 Hz, 1 H), 1.84 (dtdd, *J* = 13.1, 6.0, 4.8, 3.1 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 155.0, 142.1, 136.1, 122.7, 122.0, 119.7, 109.2, 56.8, 44.7, 39.4, 34.8, 33.8, 30.1; **HRMS** (ESI): calculated for $[C_{13}H_{18}N_3S]^+$: m/z = 248.1216, found: m/z = 248.1217; **IR** (ν/cm^{-1}, neat): 3338, 3054, 2916, 1670, 1614, 1470, 1438, 1283, 1236, 1123, 1007, 929, 909, 767, 742.

3.6 Preliminary substrate scope of substituted morpholines and thiomorpholines with organo-photocatalyst 2,4,6-triphenylpyrylium tetrafluoroborate (TPP•BF_4) (Scheme 4)

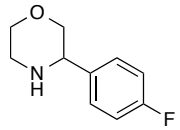
Methyl 4-(thiomorpholin-3-yl)benzoate (6d) (Scheme 4)



A mixture of the SLAP reagent **1a** (81.7 mg, 0.5 mmol, 1.0 equiv), methyl 4-formylbenzoate (82.1 mg, 0.5 mmol, 1.0 equiv), and MS 4A (100.0 mg) in CH_2Cl_2 (1.0 mL, 0.5 M) under N_2 was stirred 4 h at room temperature. The reaction was filtered through Celite and washed with CH_2Cl_2. The filtrate was condensed under *vacuo* and the residue (imine product) was re-dissolved in MeCN (5.0 mL, 0.1 M) in a vial (7 mL), followed by the addition of $Bi(OTf)_3$ (656.2 mg, 1.0 mmol, 2.0 equiv) and photocatalyst TPP•BF_4 (9.9 mg, 25.0 μmol, 0.05 equiv). The reaction was stirred for 24 h at room temperature under the exposure of blue LEDs with a cooling fan to maintain the temperature. **WORKUP:** $NH_{3(aq)}$ (ca. 1.0 mL, ca. 12 M) and sat. $Na_2CO_{3(aq)}$ (ca. 0.5 mL) were added, and the reaction was stirred for another 5 min to allow the formation of salt precipitates. After the mixture was filtered through Celite, the filtrate was evaporated under *vacuo* and the residue was extracted with CH_2Cl_2/water. The organic extracts were combined, dried over Na_2SO_4, filtered, and condensed under *vacuo*. The desired product (85.4 mg, 72%) was obtained by flash column chromatography (30–70% EtOAc in hexanes) with spectral characteristics identical to those previously mentioned.

*This preliminary condition was also applied to the following synthesis of morpholine substrate **12a** and **12b**. Please note this reaction system was not optimized.*

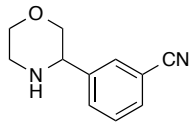
3-(4-Fluorophenyl)morpholine (12a)



The photomediated synthesis of **12a** using $Bi(OTf)_3$ and TPP•BF_4 followed the previous procedure with SLAP reagent **11** (73.6 mg, 0.5 mmol, 1.0 equiv) and 4-fluorobenzaldehyde (54.0 mL, 0.5 mmol, 1.0 equiv) for 24 h. The desired product (56.6 mg, 62%) was obtained by flash column chromatography (30% EtOAc in hexanes to EtOAc) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.37–7.32 (m, 2 H), 7.03–6.97 (m, 2 H), 3.90–3.83 (m, 2 H), 3.77 (dd, *J* = 11.0, 3.2 Hz, 1 H), 3.62 (td, *J* = 11.6, 2.7 Hz, 1 H), 3.33 (dd, *J* = 11.0, 10.1 Hz, 1 H), 3.11 (td, *J* = 11.6, 3.3 Hz, 1 H), 2.99–2.95 (m, 1 H), 1.90 (br, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 162.4 (d, *J* = 245.7 Hz), 136.5 (d, *J* = 3.1 Hz), 128.8 (d, *J* = 8.0 Hz), 115.4 (d, *J* = 21.3 Hz), 73.8 (d, *J* = 1.4 Hz), 67.3, 59.9, 46.7; **^{19}F NMR** (377 MHz, $CDCl_3$): δ [ppm] = –114.7; **HRMS** (ESI): calculated for $[C_{10}H_{13}FNO]^+$: m/z = 182.0976, found: m/z = 182.0978; **IR** (ν/cm^{-1}, neat): 2957, 2850, 1604, 1509, 1450, 1333, 1296, 1223, 1157, 1140, 1106, 930, 834.

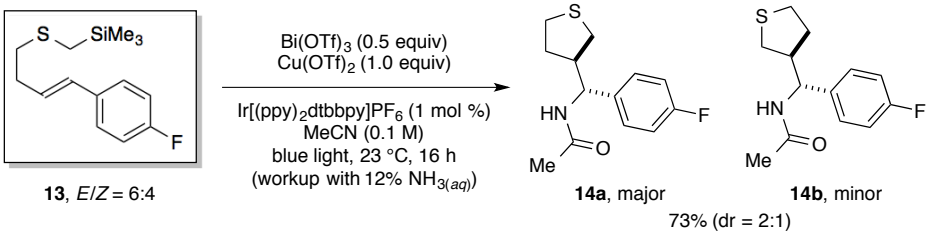
3-(Morpholin-3-yl)benzonitrile (12b)



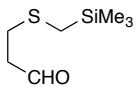
The photomediated synthesis of **12b** using $Bi(OTf)_3$ and TPP•BF_4 followed the previous procedure with SLAP reagent **11** (73.6 mg, 0.5 mmol, 1.0 equiv) and 3-cyanobenzaldehyde (65.6 mg, 0.5 mmol, 1.0 equiv) for 24 h. The desired product (61.7 mg, 66%) was obtained by flash column chromatography (30% EtOAc in hexanes to EtOAc) as yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.72 (t, *J* = 1.6 Hz, 1 H), 7.61 (dt, *J* = 7.7, 1.6 Hz, 1 H), 7.55 (dt, *J* = 7.7, 1.4 Hz, 1 H), 7.42 (t, *J* = 7.7 Hz, 1 H), 3.95 (dd, *J* = 10.0, 3.2 Hz, 1 H), 3.88–3.84 (m, 1 H), 3.78 (apparent dd, *J* = 11.1, 3.2 Hz, 1 H), 3.62 (ddd, *J* = 11.5, 11.3, 2.6 Hz, 1 H), 3.31 (apparent dd, *J* = 11.0, 10.0 Hz, 1 H), 3.11 (td, *J* = 11.5, 3.2 Hz, 1H), 2.99 (ddd, *J* = 11.5, 2.6, 1.6 Hz, 1 H), 1.90 (br, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 142.3, 131.8, 131.5, 130.9, 129.4, 118.8, 112.7, 73.4, 67.3, 59.8, 46.3; **HRMS** (ESI): calculated for $[C_{11}H_{13}N_2O]^+$: m/z = 189.1022, found: m/z = 189.1024; **IR** (ν/cm^{-1}, neat): 3320, 2957, 2850, 2229, 1481, 1451, 1432, 1334, 1293, 1106, 928, 844, 743, 693.

3.7 Photocyclization of alkene mimics (Scheme 5)



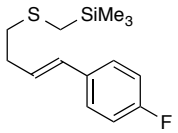
3-(((Trimethylsilyl)methyl)thio)propanal (S8)



To a solution of prop-2-enal (0.74 mL, 11.00 mmol, 1.10 equiv) and Et_3N (0.14 mL, 1.00 mmol, 0.10 equiv) in CH_2Cl_2 (10 mL, 1.00 M), (trimethylsilyl)methanethiol (1.42 mL, 10.00 mmol, 1.00 equiv) was added slowly. The mixture was stirred at room temperature overnight, followed by washing with 5% $HCl_{(aq)}$ (3×5 mL), water, and brine. The organic layer was dried over Na_2SO_4, filtered, and evaporated under *vacuo* to afford the desired product (1.72 g, 98%) as colorless oil without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 9.74 (t, *J* = 1.5 Hz, 1 H), 2.79–2.68 (m, 4 H), 1.76 (s, 2 H), 0.05 (s, 9 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 200.9, 43.2, 28.5, 18.6, –1.7; **HRMS** (EI): calculated for $[C_7H_{16}OSSi]^+$: m/z = 176.0691, found: m/z = 176.0690; **IR** (ν/cm^{-1}, neat): 2955, 2896, 2825, 2724, 1726, 1391, 1362, 1249, 1127, 1055, 846, 697.

(((4-(4-Fluorophenyl)but-3-en-1-yl)thio)methyl)trimethylsilane, mixture of *E*,*Z*-isomers (13)



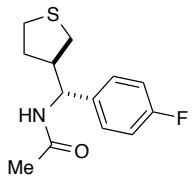
To an ice-cooled solution of (4-fluorobenzyl)triphenylphosphonium bromide (2.2 g, 5.5 mmol, 1.1 equiv) in anhydrous THF (10 mL), *t*BuOK (1.0 M solution in THF, 5.5 mL, 5.5 mmol, 1.1 equiv) was added dropwise. The mixture was warmed to room temperature, stirred for 1 h, and cooled again to 0 °C. A solution of **S8** (881.8 mg, 5.0 mmol, 1.0 equiv) in THF (10 mL) was added dropwise before the reaction was warmed to room temperature. The reaction was stirred for another 5 h and quenched with water. The solvent was removed under *vacuo* and the residue was extracted with EtOAc (3×10 mL). The organic extracts were combined, washed with brine, dried over Na_2SO_4, filtered, and evaporated under *vacuo*. The mixture of pure alkene products (*E*:*Z* = 6:4) was obtained by flash column chromatography as colorless oil (1.1 g, 81%).

The ratio of *E*-isomer:*Z*-isomer was 6:4 as determined by ^{1}H NMR. **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.60–7.56 (m, 1.2 H), 7.54–7.50 (m, 0.8 H), 7.32–7.24 (m, 2 H), 6.74–6.66 (m, 1 H), 6.43 (dt, *J* = 15.8, 6.8 Hz, 0.6 H), 6.00–5.94 (m, 0.4 H), 2.95–2.86 (m, 2.4 H), 2.81–2.75 (m, 1.6 H), 2.10 (s, 1.2 H), 2.03 (s, 0.8 H), 0.39 (s, 5.4 H), 0.37 (s, 3.6 H); **^{13}C NMR** (100 MHz, $CDCl_3$, peaks from the major isomer were marked with asterisks): δ [ppm] = 162.1* (d, *J* = 246.0 Hz), 161.7 (d, *J* = 246.1 Hz), 133.8* (d, *J* = 3.3 Hz), 133.5 (d, *J* = 3.4 Hz), 130.7 (d, *J* = 1.4 Hz), 130.4 (d, *J* = 7.8 Hz), 129.9, 129.0, 128.6* (d, *J* = 2.3 Hz), 127.6* (d, *J* = 7.9 Hz), 115.4* (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.3 Hz), 36.1, 36.0*, 32.8*, 28.1, 18.6*, 18.4, –1.56*, –1.58; **^{19}F NMR** (377 MHz, $CDCl_3$): δ [ppm] = –115.3; **HRMS** (EI): calculated for $[C_{14}H_{21}FSSi]^+$: m/z = 268.1117, found: m/z = 268.1116; **IR** (ν/cm^{-1}, neat): 2954, 2909, 1729, 1602, 1508, 1249, 1227, 1157, 967, 846, 697.

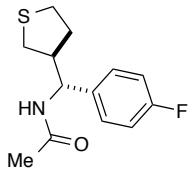
N-((4-Fluorophenyl)(tetrahydrothiophen-3-yl)methyl)acetamide, diastereomers (14)

To a solution of alkene **13** (134.2 mg, 0.5 mmol, 1.0 equiv) in MeCN (5.0 mL, 0.1 M), $Cu(OTf)_2$ (180.8 mg, 0.5 mmol, 1.0 equiv), $Bi(OTf)_3$ (160.4 mg, 0.25 mmol, 0.5 equiv), and $Ir[(ppy)_2dtbbpy]PF_6$ (4.6 mg, 5.0 μmol, 0.01 equiv) were added. The reaction was stirred for 16 h at room temperature under the exposure of blue LEDs (30 W) with a cooling fan to maintain the temperature. $NH_{3(aq)}$ (1 mL, ca. 12 M) was added and the reaction was stirred for another 10 min. After the solvents were removed under *vacuo*, the residue was re-dissolved in $CH_2Cl_2/NH_{3(aq)}$ and filtered. The filtrate was extracted with CH_2Cl_2 and the combined organic

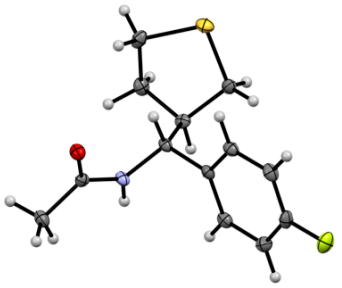
layers were washed with $NH_{3(aq)}$. The final organic extracts were dried over Na_2SO_4, filtered, and condensed under *vacuo* (**14a**:**14b** = 2:1, determined by ^{1}H NMR measurement of unpurified mixtures). The residue was purified by flash column chromatography to obtain white solids, pure **14a** (50.5 mg), pure **14b** (25.9 mg), and mixture of **14a** and **14b** (16.2 mg) (total 92.6 mg, 73%).



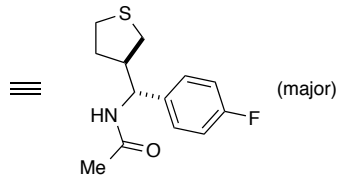
14a. (major) **m.p.**: 155–156 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.31–7.19 (m, 2 H), 7.11–6.94 (m, 2 H), 6.02 (d, *J* = 9.0 Hz, 1 H), 4.96 (t, *J* = 9.0 Hz, 1 H), 2.96 (ddd, *J* = 11.1, 7.3, 4.2 Hz, 1 H), 2.90–2.82 (m, 1 H), 2.59–2.49 (m, 2 H), 2.45–2.36 (m, 1 H), 2.24–2.13 (m, 1 H), 1.96 (s, 3 H), 1.92–1.83 (m, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 169.3, 162.2 (d, *J* = 246.5 Hz), 137.3 (d, *J* = 3.3 Hz), 128.6 (d, *J* = 8.0 Hz), 115.8 (d, *J* = 21.5 Hz), 55.1, 50.1, 34.3, 34.1, 30.5, 23.5; **^{19}F NMR** (377 MHz, $CDCl_3$): δ [ppm] = –114.3; **HRMS** (EI): calculated for $[C_{13}H_{17}FNOS]^+$: m/z = 254.1009, found: m/z = 254.1006; **IR** (ν/cm^{-1}, neat): 3276, 3067, 2931, 2859, 1722, 1651, 1549, 1510, 1373, 1225, 1160, 1015, 835.



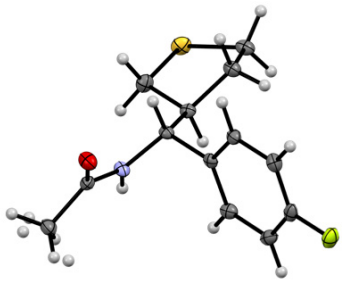
14b. (minor) **m.p.**: 139–140 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ [ppm] = 7.24 (ddd, *J* = 8.7, 4.5, 1.9 Hz, 2 H), 7.09–6.96 (m, 2 H), 6.16 (d, *J* = 8.6 Hz, 1 H), 4.95 (t, *J* = 9.0 Hz, 1 H), 2.93 (dd, *J* = 10.7, 6.5 Hz, 1 H), 2.89–2.78 (m, 2 H), 2.74 (dd, *J* = 10.8, 8.6 Hz, 1 H), 2.63–2.46 (m, 1 H), 1.97 (s, 3 H), 1.85 (dtd, *J* = 12.1, 5.9, 3.7 Hz, 1 H), 1.58 (dtd, *J* = 12.7, 9.6, 7.7 Hz, 1 H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ [ppm] = 169.4, 162.2 (d, *J* = 246.3 Hz), 137.8 (d, *J* = 3.3 Hz), 128.4 (d, *J* = 8.1 Hz), 115.8 (d, *J* = 21.4 Hz), 56.0, 50.3, 34.6, 34.2, 30.7, 23.6; **^{19}F NMR** (377 MHz, $CDCl_3$): δ [ppm] = –114.6; **HRMS** (EI): calculated for $[C_{13}H_{17}FNOS]^+$: m/z = 254.1009, found: m/z = 254.1010; **IR** (ν/cm^{-1}, neat): 3277, 3067, 2931, 2860, 1735, 1651, 1549, 1510, 1373, 1225, 1160, 1014, 838.



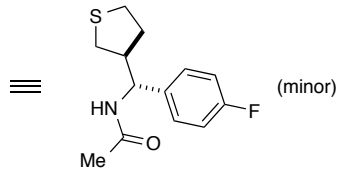
X-ray of **14a**



(major)

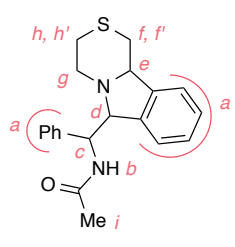


X-ray of **14b**

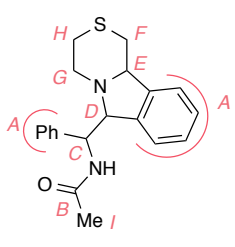


(minor)

_N_-(Phenyl(3,4,6,10b-tetrahydro-1_H_-[1,4]thiazino[3,4-_a_]isoindol-6-yl)methyl)acetamide, mixture of isomers (16) (Scheme 5b)



^{1}H NMR



^{13}C NMR

The photomediated cascade cyclization form imine **15** followed the general procedure (section 3.2) with **1a** (81.7 mg, 0.5 mmol, 1.0 equiv) and (*E*)-2-styrylbenzaldehyde[15] (104.1 mg, 0.5 mmol, 1.0 equiv) for 16 h. The desired product (mixture of isomers, 79.1 mg, 49%) was obtained by flash column chromatography.

^{1}H NMR (400 MHz, $CDCl_3$): δ [ppm] = 7.47–7.18 (m, 8 H, *a*), 7.15 (tdd, *J* = 4.2, 3.2, 0.9 Hz, 1 H, *a*), 6.40 (dd, *J* = 37.7, 7.8 Hz, 1 H, *b*), 5.59 (dd, *J* = 7.8, 1.7 Hz, 1 H, *c*), 4.43 (t, *J* = 2.2 Hz, 1 H,

d), 3.88 (dd, *J* = 10.4, 2.5 Hz, 1 H, *e*), 3.03 (dt, *J* = 12.5, 1.8 Hz, 1 H, *f*), 2.96–2.70 (m, 2 H, *f'* & *h*), 2.55–2.39 (m, 2 H, *g*), 2.23 (dq, *J* = 12.4, 2.1 Hz, 1 H, *h'*), 1.83 (s, 3 H, *i*); **^{13}C NMR** (100 MHz, $CDCl_3$, peaks from the major isomer were marked with asterisks): δ [ppm] = 170.8, 169.9* (B), 143.1, 140.8* (A), 140.5* (A), 138.9* (A), 137.0, 129.2, 129.1, 128.8* (A), 128.7, 128.3, 128.2* (A), 127.9* (A), 127.9, 127.7, 127.4, 127.3, 127.2* (A), 126.5, 125.8, 125.7* (A), 123.5, 122.2* (A), 121.4, 121.1, 120.6* (A), 120.4, 71.5* (D), 70.3, 68.8* (E), 66.9, 53.2* (C), 52.7* (G), 51.8, 50.1, 31.9* (F), 28.7, 28.4* (H), 23.4, 23.2* (I); **HRMS** (EI): calculated for $[C_{20}H_{23}N_2OS]^+$: m/z = 339.1526, found: m/z = 339.1528; **IR** (ν/cm^{-1}, neat): 3342, 3059, 2915, 2809, 1661, 1496, 1460, 1370, 1293, 1263, 1031, 911, 728, 700.

4. Stern-Volmer fluorescence quenching experiments

Fluorescence quenching studies were conducted using Quanta Master 7 (Photon Technology International, USA) of the Hilvert group at ETH Zürich. In each experiment, photocatalyst $Ir[(ppy)_2dtbbpy]PF_6$ (100 μM in degassed MeCN) and varying concentrations of quenchers (100, 200, 300, 400, and 500 μM in degassed MeCN) were added into screw-top 1.0 cm quartz cuvettes. Each sample was irradiated at 460 nm, and the emission spectrum was collected. Plots of intensity of emission (580 nm) *vs.* concentrations of quenchers are shown according to the Stern-Volmer analysis $I_0/I = 1 + k_q\tau_0[Q]$.

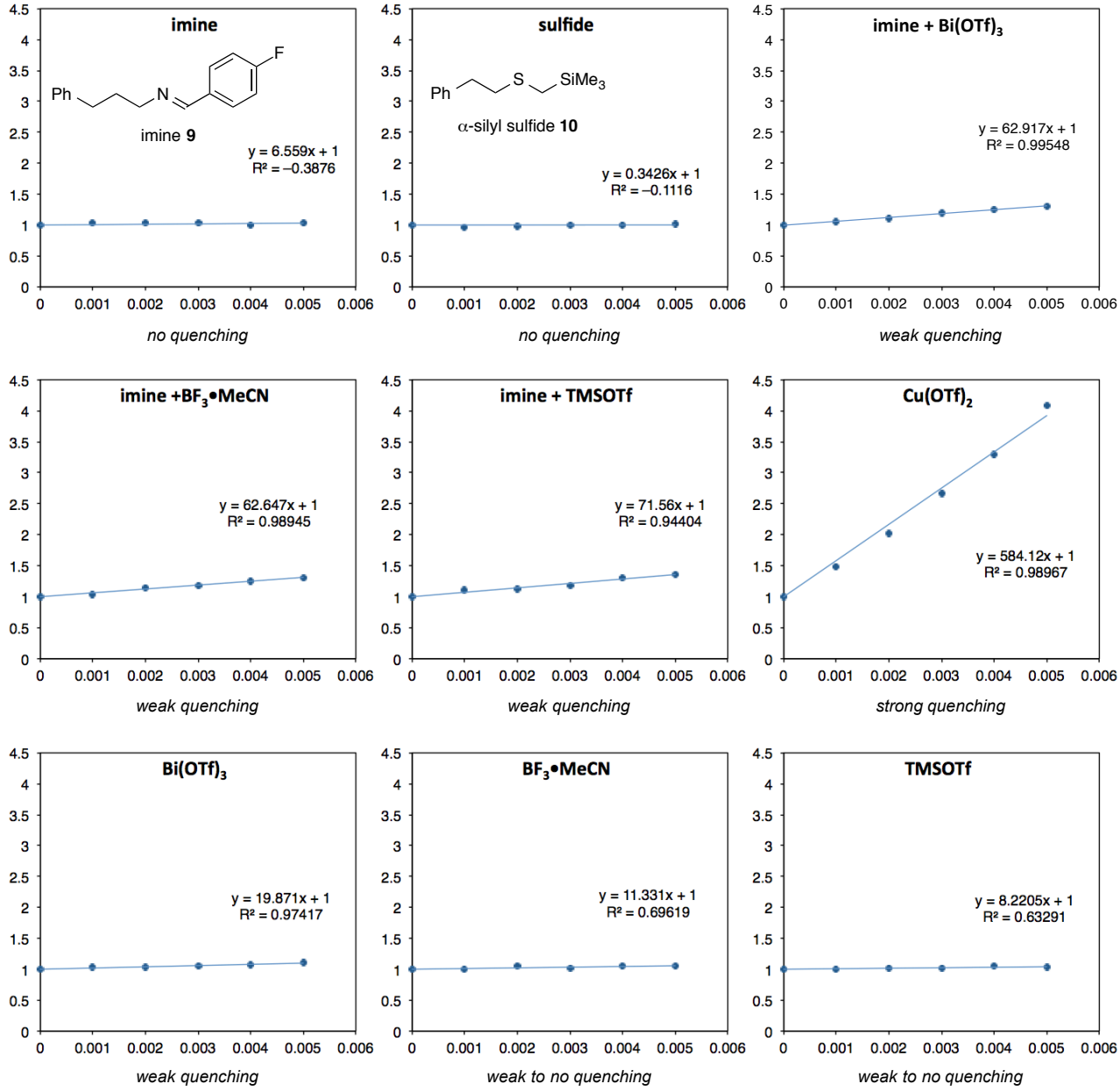


Figure S3. Stern–Volmer relationships of $Ir[(ppy)_2dtbbpy]PF_6$ with different quenchers. The plots were presented as I_0/I (y-axis) *vs.* concentration of quenchers [M] (x-axis).

It is worth noting that the λ_{max} of photoexcited $Ir[(ppy)_2dtbbpy]PF_6$ species is not affected by the additional Lewis acids.

5. Cyclic voltammogram of several reaction components

Cyclic voltammetry experiment was performed at room temperature using Metrohm Autolab PGSTAT128N of the Copéret group at ETH Zürich, with a Metrohm 3 mm glassy carbon disk or a Metrohm 3 mm Pt disk as the working electrode, a Pt sheet as counter electrode, and a 0.1 M Ag^+/Ag reference electrode in 0.1 M NBu_4PF_6 in MeCN. Ferrocenium/ferrocene redox couple was used as an internal standard for the reference at +0.40 V vs. SCE in MeCN,[16] unless otherwise stated.

(a) Cyclic voltammograms of α-silyl sulfide **10** with Lewis acids display no significant changes for oxidation on the sulfur of the sulfide substrate.

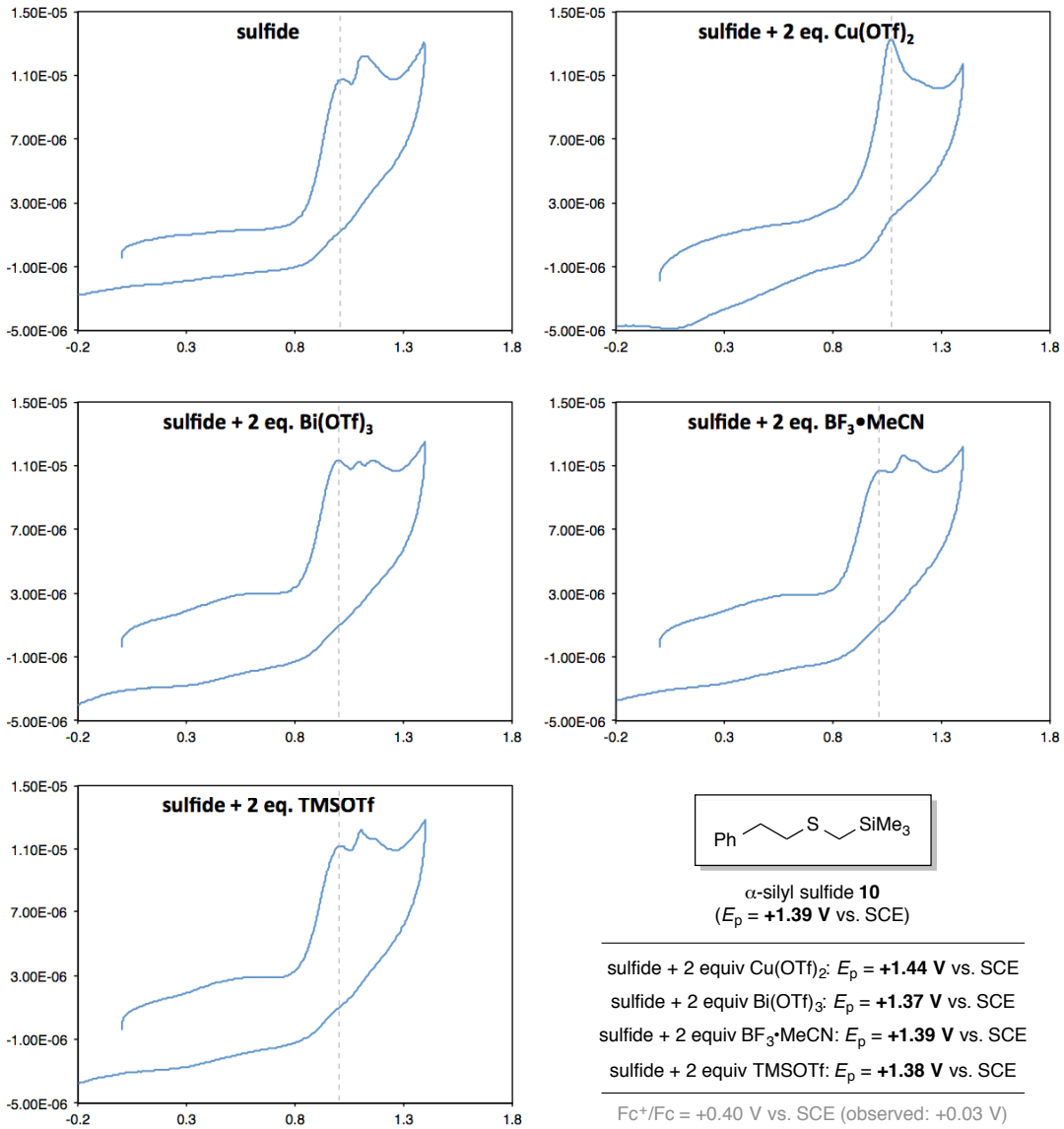


Figure S4. Cyclic voltammograms of α-silyl sulfide **10** with Lewis acids. The cyclic voltammetry experiments were conducted using a glassy carbon electrode under 0.1 M $LiCO_4$ in MeCN. Values of peak potential were shown corrected.

(b) The peak potential for the reduction of BF_3•MeCN was measured below –0.3 V vs. SCE.

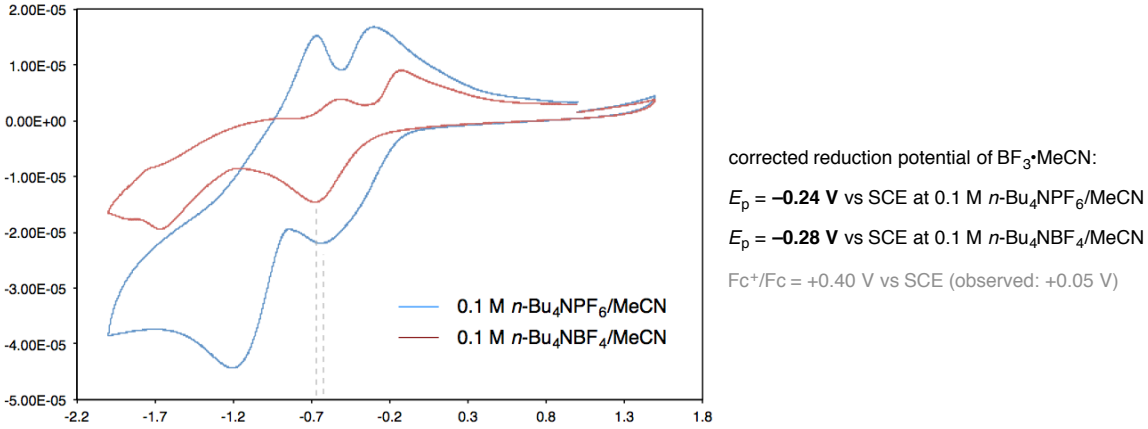


Figure S5. Cyclic voltammograms of BF_3•MeCN. The cyclic voltammetry experiments were conducted using a Pt electrode under 0.1 M *n*-Bu_4NPF_6 or *n*-Bu_4BF_4 in MeCN. Values of peak potential were shown corrected.

(c) The additional TMSOTf affects the redox abilities of iridium complex only in its reductive quenching cycle (decrease of oxidation potential and increase of reduction ability). The reduction of TMSOTf was also observed (*E*p = –0.18 V vs. SCE).

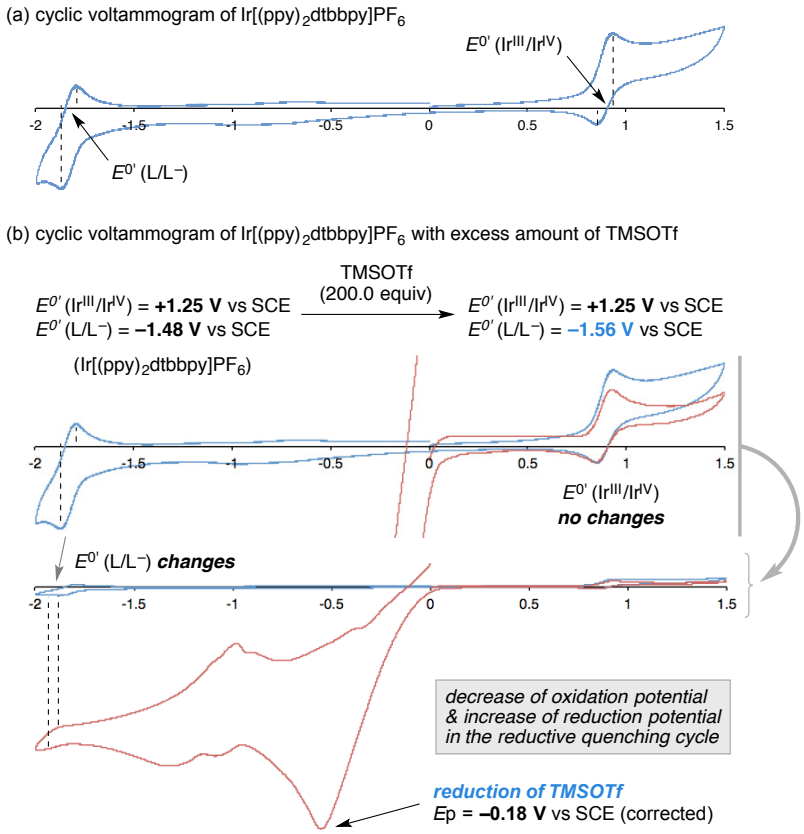


Figure S6. Cyclic voltammograms of (a) Ir[(ppy)$_2$dtbbpy]PF_6 and (b) Ir[(ppy)$_2$dtbbpy]PF_6 with excess amount of TMSOTf. The cyclic voltammetry experiments were conducted using a Pt electrode at 0.1 M *n*-Bu_4NPF_6 in MeCN. Values of peak potential were shown corrected. (Fc^+/Fc = +0.40 V vs. SCE; observed: +0.05 V)

6. X-ray crystallography

6.1 Crystal structure of 14a

Crystals of **14a** were obtained by recrystallization from EtOAc. The X-ray data was collected to confirm the relative stereochemistry.

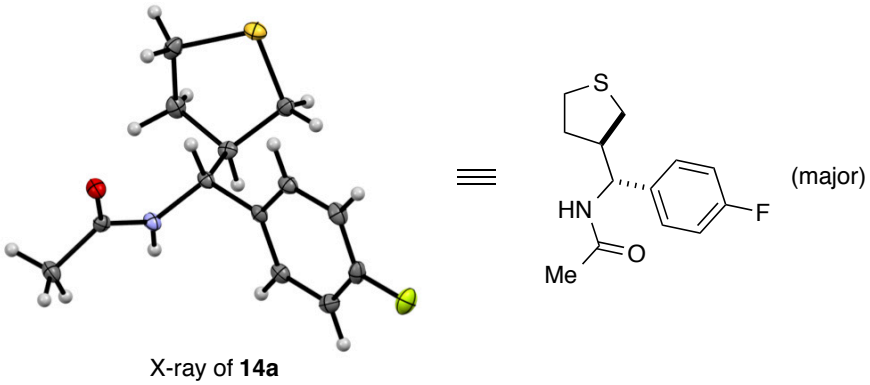


Figure S7. ORTEP representation of **14a**. Ellipsoids include 50% of the electron density. We thank Dr. Nils Trapp from the X-ray crystallographic service of the Laboratorium für Organische Chemie at ETH Zürich for performing the experiments.

Experimental

A suitable single crystal of **14a** [$C_{13}H_{16}FNOS$, code: cu_jb221115_1_1_0ma] was selected and measured on a Bruker Apex2 Duo (Cu) diffractometer. The crystal was kept at 100.0(2) K during data collection. Using Olex2,[17] the structure was solved with the XT[18] structure solution program using Direct Methods and refined with the XL[19] refinement package using Least Squares minimization.

Crystal structure determination of 14a

Crystal Data for $C_{13}H_{16}FNOS$ (M =253.33 g/mol): orthorhombic, space group Fdd2 (no. 43), a = 26.3399(8) Å, b = 35.7236(11) Å, c = 5.1728(2) Å, V = 4867.4(3) Å^3, Z = 16, T = 100.0(2) K, μ(CuKα) = 2.342 mm^{-1}, *Dcalc* = 1.383 g/cm^3, 15523 reflections measured (8.342° ≤ 2Θ ≤ 133.346°), 2111 unique (R_{int} = 0.0288, R_{sigma} = 0.0165) which were used in all calculations. The final R_1 was 0.0231 (I > 2σ(I)) and wR_2 was 0.0595 (all data).

Table S2. Crystal data and structure refinement for **14a**.

Identification code	cu_jb221115_1_1_0ma
Empirical formula	$C_{13}H_{16}FNOS$
Formula weight	253.33
Temperature/K	100.0(2)
Crystal system	orthorhombic
Space group	Fdd2
a/Å	26.3399(8)
b/Å	35.7236(11)
c/Å	5.1728(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4867.4(3)
Z	16
ρ_{calc}g/cm^3	1.383
μ/mm^{-1}	2.342
F(000)	2144.0
Crystal size/mm^3	0.24 × 0.23 × 0.11
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.342 to 133.346
Index ranges	-25 ≤ h ≤ 30, -41 ≤ k ≤ 41, -6 ≤ l ≤ 6
Reflections collected	15523
Independent reflections	2111 [R_{int} = 0.0288, R_{sigma} = 0.0165]
Data/restraints/parameters	2111/2/158
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0231, wR_2 = 0.0595
Final R indexes [all data]	R_1 = 0.0231, wR_2 = 0.0595
Largest diff. peak/hole / e Å^{-3}	0.17/-0.22
Flack parameter	0.013(4)

Table S3. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **14a**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S1	4281.2(2)	2810.0(2)	2121.6(9)	19.87(15)
F2	7015.0(4)	2739.8(3)	4713(3)	26.8(3)
O3	5251.3(5)	4004.9(4)	-682(3)	17.8(3)
C4	6271.5(7)	2830.0(5)	2265(5)	18.7(4)
N5	5187.1(6)	3887.8(5)	3602(4)	14.4(4)
C6	5812.3(7)	3017.6(5)	1940(4)	16.6(4)
C7	5145.4(7)	3481.6(5)	3288(4)	13.6(4)
C8	5309.4(8)	4528.1(5)	2214(5)	20.2(4)
C9	4666.6(7)	2908.4(6)	4985(4)	17.1(4)
C10	6567.3(7)	2924.4(5)	4351(5)	18.1(4)
C11	5246.7(6)	4117.6(6)	1570(4)	13.6(4)
C12	6430.2(8)	3195.4(6)	6113(4)	18.4(4)
C13	4726.2(7)	3334.2(5)	5110(4)	14.8(4)
C14	4053.6(7)	3291.5(6)	1819(5)	19.5(4)
C15	5966.5(8)	3376.8(6)	5783(4)	16.1(4)
C16	5654.7(7)	3289.1(5)	3686(4)	13.9(4)
C17	4202.5(7)	3486.4(5)	4326(5)	18.7(4)

Table S4. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **14a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	22.0(2)	19.8(2)	17.8(3)	-4.4(2)	-0.3(2)	-2.94(18)
F2	19.3(6)	29.8(6)	31.2(8)	1.6(7)	0.0(6)	9.4(5)
O3	24.6(7)	16.1(7)	12.8(8)	-0.5(6)	1.8(6)	-0.5(5)
C4	22.6(10)	15.6(9)	17.8(11)	-2.1(9)	5.6(10)	1.7(7)
N5	19.1(8)	12.1(8)	11.9(9)	-2.2(7)	1.2(7)	0.1(6)
C6	19.3(9)	15.5(9)	15(1)	-1.6(9)	1.3(9)	-1.6(7)
C7	16.8(10)	11.8(9)	12.2(10)	-1.3(8)	1.8(7)	-0.5(7)
C8	26.4(10)	12.9(9)	21.2(11)	-0.4(10)	1.3(9)	-1.3(7)
C9	16(1)	17.7(9)	17.6(11)	3.5(8)	-0.5(8)	-1.5(7)
C10	14.3(9)	17.8(9)	22.1(11)	5.7(9)	3.6(8)	2.7(7)
C11	10.6(8)	14.3(9)	15.9(11)	-1.2(7)	0.6(7)	1.1(6)
C12	17.8(10)	21.6(10)	15.9(11)	1.5(8)	-0.2(8)	-3.1(8)
C13	16.5(10)	17.2(9)	10.8(10)	-0.7(8)	1.3(8)	-1.0(7)
C14	14.9(9)	25.6(10)	18.1(10)	4.3(9)	0.7(8)	2.4(7)
C15	19.2(9)	14.5(9)	14.7(10)	-0.8(8)	3.3(8)	-1.9(8)
C16	15.5(10)	12.1(9)	13.9(11)	1.7(7)	2.7(7)	-2.3(7)
C17	17.0(9)	17.4(9)	21.8(12)	-0.1(9)	5.8(9)	2.0(7)

Table S5. Bond Lengths for **14a**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C9	1.830(2)	C7	C13	1.544(3)
S1	C14	1.828(2)	C7	C16	1.522(3)
F2	C10	1.364(2)	C8	C11	1.513(3)
O3	C11	1.233(3)	C9	C13	1.530(3)
C4	C6	1.393(3)	C10	C12	1.378(3)
C4	C10	1.373(3)	C12	C15	1.393(3)
N5	C7	1.464(2)	C13	C17	1.537(3)
N5	C11	1.343(3)	C14	C17	1.524(3)
C6	C16	1.389(3)	C15	C16	1.396(3)

Table S6. Bond Angles for **14a**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C14	S1	C9	94.04(10)	O3	C11	C8	121.58(19)
C10	C4	C6	118.00(19)	N5	C11	C8	115.65(19)
C11	N5	C7	121.85(18)	C10	C12	C15	118.40(19)
C16	C6	C4	121.1(2)	C9	C13	C7	112.74(16)
N5	C7	C13	108.91(16)	C9	C13	C17	104.39(15)
N5	C7	C16	111.51(15)	C17	C13	C7	111.10(16)
C16	C7	C13	113.18(16)	C17	C14	S1	105.82(14)
C13	C9	S1	106.38(14)	C12	C15	C16	120.4(2)
F2	C10	C4	118.66(18)	C6	C16	C7	119.40(18)
F2	C10	C12	118.40(19)	C6	C16	C15	119.09(19)
C4	C10	C12	122.93(18)	C15	C16	C7	121.50(18)
O3	C11	N5	122.77(18)	C14	C17	C13	107.09(16)

Table S7. Torsion Angles for **14a**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C9	C13	C7	-80.84(18)	C7	C13	C17	C14	71.34(19)
S1	C9	C13	C17	39.85(18)	C9	S1	C14	C17	-11.91(15)
S1	C14	C17	C13	37.47(18)	C9	C13	C17	C14	-50.4(2)
F2	C10	C12	C15	-178.29(17)	C10	C4	C6	C16	-0.7(3)
C4	C6	C16	C7	-178.76(17)	C10	C12	C15	C16	-1.1(3)
C4	C6	C16	C15	0.7(3)	C11	N5	C7	C13	-138.17(18)
C4	C10	C12	C15	1.1(3)	C11	N5	C7	C16	96.2(2)
N5	C7	C13	C9	-178.05(17)	C12	C15	C16	C6	0.2(3)
N5	C7	C13	C17	65.2(2)	C12	C15	C16	C7	179.69(18)
N5	C7	C16	C6	-133.87(19)	C13	C7	C16	C6	102.9(2)
N5	C7	C16	C15	46.7(3)	C13	C7	C16	C15	-76.5(2)
C6	C4	C10	F2	179.21(17)	C14	S1	C9	C13	-16.49(15)
C6	C4	C10	C12	-0.2(3)	C16	C7	C13	C9	-53.4(2)
C7	N5	C11	O3	2.7(3)	C16	C7	C13	C17	-170.21(16)
C7	N5	C11	C8	-177.16(17)					

Table S8. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **14a**.

Atom	*x*	*y*	*z*	U(eq)
H4	6377	2642	1079	22
H6	5603	2959	499	20
H7	5035	3431	1472	16
H8A	5629	4620	1481	30
H8B	5315	4560	4096	30
H8C	5025	4670	1483	30
H9A	4496	2814	6561	21
H9B	5003	2786	4838	21
H12	6647	3257	7519	22
H13	4804	3411	6926	18
H14A	4214	3416	318	23
H14B	3681	3296	1586	23
H15	5862	3561	6993	19
H17A	3950	3433	5694	22
H17B	4219	3761	4064	22
H5	5208(10)	3984(8)	5150(50)	28

6.2 Crystal structure of 14b

Crystals of **14b** were obtained by recrystallization from EtOAc. The X-ray data was collected to confirm the relative stereochemistry.

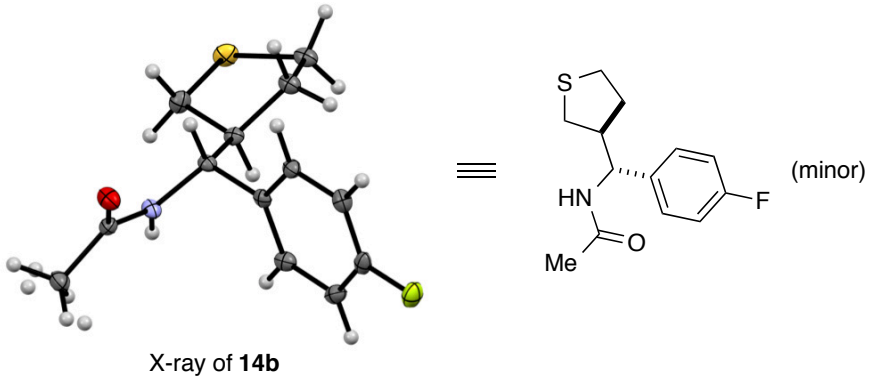


Figure S8. ORTEP representation of **14b**. Ellipsoids include 50% of the electron density. We thank Dr. Nils Trapp from the X-ray crystallographic service of the Laboratorium für Organische Chemie at ETH Zürich for performing the experiments.

Experimental

A suitable single crystal of **14b** [$C_{13}H_{16}FNOS$, code: cu_jb221115_2_1_0m] was selected and measured on a Bruker Apex2 Duo (Cu) diffractometer. The crystal was kept at 100.0(2) K during data collection. Using Olex2,[17] the structure was solved with the XT[18] structure solution program using Direct Methods and refined with the XL[19] refinement package using Least Squares minimization.

Crystal structure determination of 14b

Crystal Data for $C_{13}H_{16}FNOS$ (M =253.33 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 5.11580(10) Å, b = 17.1099(3) Å, c = 14.2535(2) Å, β = 99.9200(10)°, V = 1228.97(4) Å^3, Z = 4, T = 100.0(2) K, μ(CuKα) = 2.319 mm^{-1}, $Dcalc$ = 1.369 g/cm^3, 11653 reflections measured (8.146° ≤ 2Θ ≤ 133.388°), 2146 unique (R_{int} = 0.0283, R_{sigma} = 0.0209) which were used in all calculations. The final R_1 was 0.0281 (I > 2σ(I)) and wR_2 was 0.0711 (all data).

Table S9. Crystal data and structure refinement for **14b**.

Identification code	cu_jb221115_2_1_0m
Empirical formula	$C_{13}H_{16}FNOS$
Formula weight	253.33
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.11580(10)
b/Å	17.1099(3)
c/Å	14.2535(2)
α/°	90
β/°	99.9200(10)
γ/°	90
Volume/Å^3	1228.97(4)
Z	4
ρ_{calc}g/cm^3	1.369
μ/mm^{-1}	2.319
F(000)	536.0
Crystal size/mm^3	0.24 × 0.12 × 0.08
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.146 to 133.388
Index ranges	-5 ≤ h ≤ 6, -20 ≤ k ≤ 15, -15 ≤ l ≤ 16
Reflections collected	11653
Independent reflections	2146 [R_{int} = 0.0283, R_{sigma} = 0.0209]
Data/restraints/parameters	2146/1/159
Goodness-of-fit on F^2	1.057
Final R indexes [I>=2σ (I)]	R_1 = 0.0281, wR_2 = 0.0706
Final R indexes [all data]	R_1 = 0.0287, wR_2 = 0.0711
Largest diff. peak/hole / e Å^{-3}	0.26/-0.27
Identification code	cu_jb221115_2_1_0m

Table S10. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **14b**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
S1	-409.9(6)	4197.8(2)	3369.7(2)	21.63(12)
F2	6760.3(16)	-74.0(5)	6092.3(6)	24.0(2)
O3	10021.3(18)	3548.0(6)	6519.3(7)	20.5(2)
N4	5549(2)	3591.2(6)	6149.2(8)	14.9(2)
C5	7860(3)	3719.8(7)	6737.4(9)	14.7(3)
C6	6443(3)	702.4(8)	5895.6(9)	17.4(3)
C7	5824(2)	2276.2(7)	5490.6(8)	13.2(3)
C8	4366(2)	1914.0(8)	6108.6(9)	16.7(3)
C9	5452(2)	3143.5(7)	5269.1(9)	13.2(3)
C10	2805(2)	3301.4(7)	4608.8(9)	13.9(3)
C11	-2(3)	3177.3(8)	3037.3(9)	18.1(3)
C12	7916(3)	1032.4(8)	5277.8(9)	18.0(3)
C13	7642(3)	4080.9(8)	7682(1)	20.2(3)
C14	2594(2)	2901.6(8)	3639.0(9)	16.6(3)
C15	2313(3)	4168.0(8)	4388.5(10)	19.3(3)
C16	7586(2)	1824.9(8)	5077.8(9)	15.5(3)
C17	4663(3)	1123.7(8)	6318.4(9)	18.6(3)

Table S11. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **14b**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S1	19.12(19)	21.30(19)	22.96(19)	5.38(13)	-0.59(13)	4.22(13)
F2	27.8(4)	14.7(4)	27.4(4)	3.3(3)	-1.0(3)	-0.8(3)
O3	12.3(5)	29.9(5)	19.7(5)	-4.9(4)	3.5(4)	-1.5(4)
N4	11.3(5)	18.4(6)	15.8(5)	-3.6(4)	5.0(4)	-0.1(4)
C5	14.9(6)	13.7(6)	15.8(6)	0.0(5)	3.8(5)	-2.5(5)
C6	17.4(6)	14.3(6)	17.6(6)	1.0(5)	-5.5(5)	-2.1(5)
C7	9.7(6)	17.4(6)	11.2(6)	-0.7(5)	-1.8(5)	-1.3(5)
C8	12.8(6)	22.2(7)	14.9(6)	0.7(5)	2.0(5)	0.7(5)
C9	11.0(6)	16.6(6)	12.6(6)	-1.4(5)	3.3(5)	-0.4(5)
C10	10.8(6)	16.5(6)	14.9(6)	0.3(5)	3.2(5)	0.5(5)
C11	13.6(6)	25.5(7)	15.3(6)	-0.1(5)	2.9(5)	1.7(5)
C12	16.2(6)	18.1(7)	19.2(7)	-3.8(5)	1.3(5)	0.7(5)
C13	22.4(7)	21.8(7)	17.2(7)	-4.9(5)	5.5(5)	-2.5(6)
C14	12.8(6)	21.9(7)	14.9(6)	-0.9(5)	2.2(5)	1.5(5)
C15	17.6(7)	17.4(7)	22.0(7)	1.8(5)	0.6(5)	1.1(5)
C16	14.1(6)	17.9(7)	14.9(6)	-1.7(5)	3.1(5)	-2.5(5)
C17	16.4(6)	22.7(7)	16.1(6)	4.2(5)	0.8(5)	-3.8(5)

Table S12. Bond Lengths for **14b**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
S1	C11	1.8305(14)	C7	C8	1.3940(18)
S1	C15	1.8316(14)	C7	C9	1.5223(17)
F2	C6	1.3616(15)	C7	C16	1.3918(18)
O3	C5	1.2345(16)	C8	C17	1.388(2)
N4	C5	1.3446(17)	C9	C10	1.5341(17)
N4	C9	1.4634(16)	C10	C14	1.5294(17)
C5	C13	1.5028(18)	C10	C15	1.5276(18)
C6	C12	1.375(2)	C11	C14	1.5263(18)
C6	C17	1.379(2)	C12	C16	1.3899(19)

Table S13. Bond Angles for **14b**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	S1	C15	94.22(6)	N4	C9	C7	110.37(10)
C5	N4	C9	121.10(10)	N4	C9	C10	109.25(10)
O3	C5	N4	122.24(12)	C7	C9	C10	111.39(10)
O3	C5	C13	122.09(12)	C14	C10	C9	113.14(10)
N4	C5	C13	115.66(11)	C15	C10	C9	113.19(10)
F2	C6	C12	118.26(12)	C15	C10	C14	105.36(10)
F2	C6	C17	118.97(12)	C14	C11	S1	106.05(9)
C12	C6	C17	122.77(12)	C6	C12	C16	118.12(12)
C8	C7	C9	120.19(11)	C11	C14	C10	106.78(10)
C16	C7	C8	118.46(12)	C10	C15	S1	105.41(9)
C16	C7	C9	121.34(11)	C12	C16	C7	121.28(12)
C17	C8	C7	121.24(12)	C6	C17	C8	118.13(12)

Table S14. Torsion Angles for **14b**.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
S1	C11	C14	C10	35.73(12)	C9	N4	C5	C13	-171.19(11)
F2	C6	C12	C16	179.94(11)	C9	C7	C8	C17	179.74(11)
F2	C6	C17	C8	-179.95(11)	C9	C7	C16	C12	-179.74(11)
N4	C9	C10	C14	176.05(10)	C9	C10	C14	C11	-174.55(10)
N4	C9	C10	C15	56.28(14)	C9	C10	C15	S1	165.27(8)
C5	N4	C9	C7	74.48(14)	C11	S1	C15	C10	-18.00(10)
C5	N4	C9	C10	-162.73(11)	C12	C6	C17	C8	-0.16(19)
C6	C12	C16	C7	0.20(19)	C14	C10	C15	S1	41.14(11)
C7	C8	C17	C6	-0.18(19)	C15	S1	C11	C14	-10.03(10)
C7	C9	C10	C14	-61.76(13)	C15	C10	C14	C11	-50.39(13)
C7	C9	C10	C15	178.46(10)	C16	C7	C8	C17	0.51(18)
C8	C7	C9	N4	48.09(15)	C16	C7	C9	N4	-132.70(12)
C8	C7	C9	C10	-73.44(14)	C16	C7	C9	C10	105.76(13)
C8	C7	C16	C12	-0.52(19)	C17	C6	C12	C16	0.15(19)
C9	N4	C5	O3	8.36(19)					

Table S15. Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **14b**.

Atom	*x*	*y*	*z*	U(eq)
H8	3145	2214	6392	20
H9	6928	3324	4944	16
H10	1339	3102	4926	17
H11A	-1506	2857	3171	22
H11B	85	3136	2351	22
H12	9125	727	4996	22
H13A	5770	4172	7716	30
H13B	8415	3727	8196	30
H13C	8600	4579	7750	30
H13D	6752	3715	8052	30
H13E	6611	4565	7578	30
H13F	9422	4197	8031	30
H14A	4118	3048	3332	20
H14B	2585	2326	3714	20
H15A	3923	4418	4227	23
H15B	1811	4443	4943	23

Table S16. Atomic Occupancy for **14b**.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
H13A	0.650(18)	H13B	0.650(18)	H13C	0.650(18)
H13D	0.350(18)	H13E	0.350(18)	H13F	0.350(18)

7. References

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8. NMR spectra

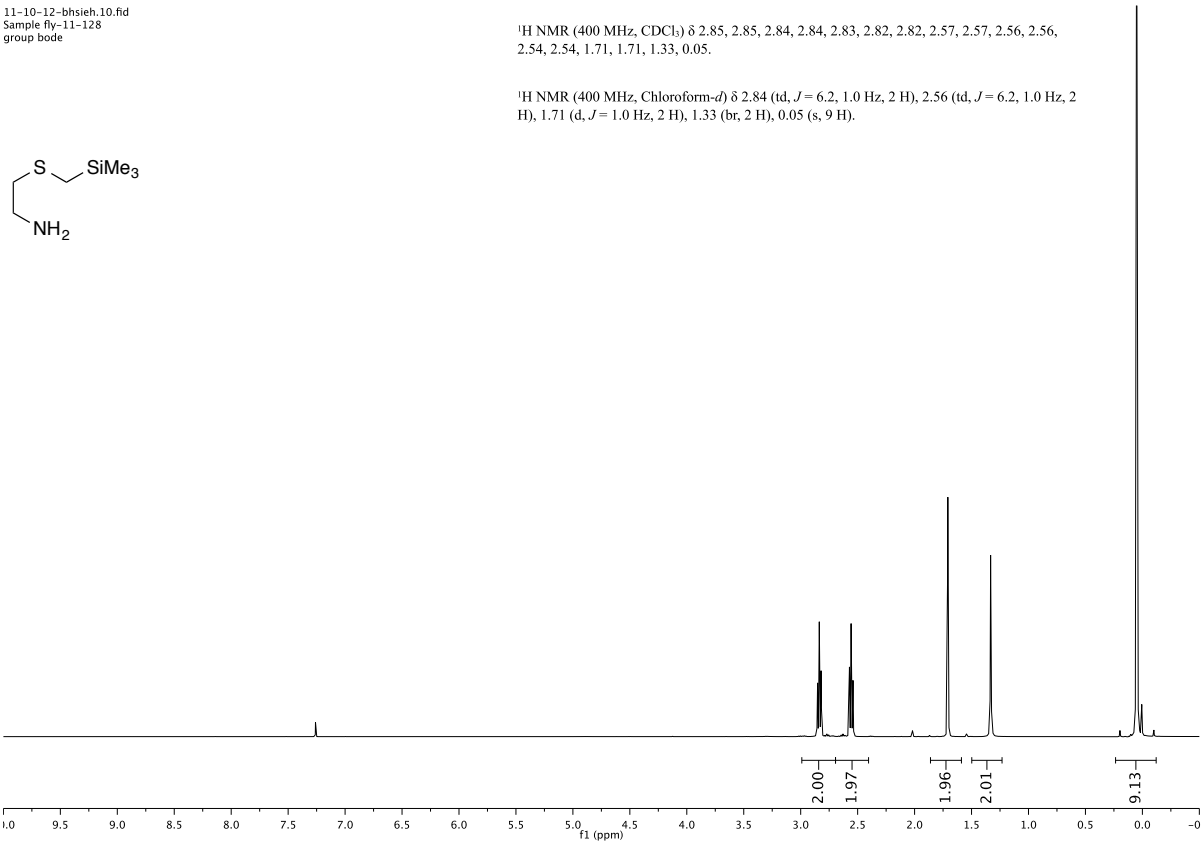
Table of contents

2-(((Trimethylsilyl)methyl)thio)ethanamine (1a)

11-10-12-bhsieh.10.fid
Sample fly-11-128
group bode

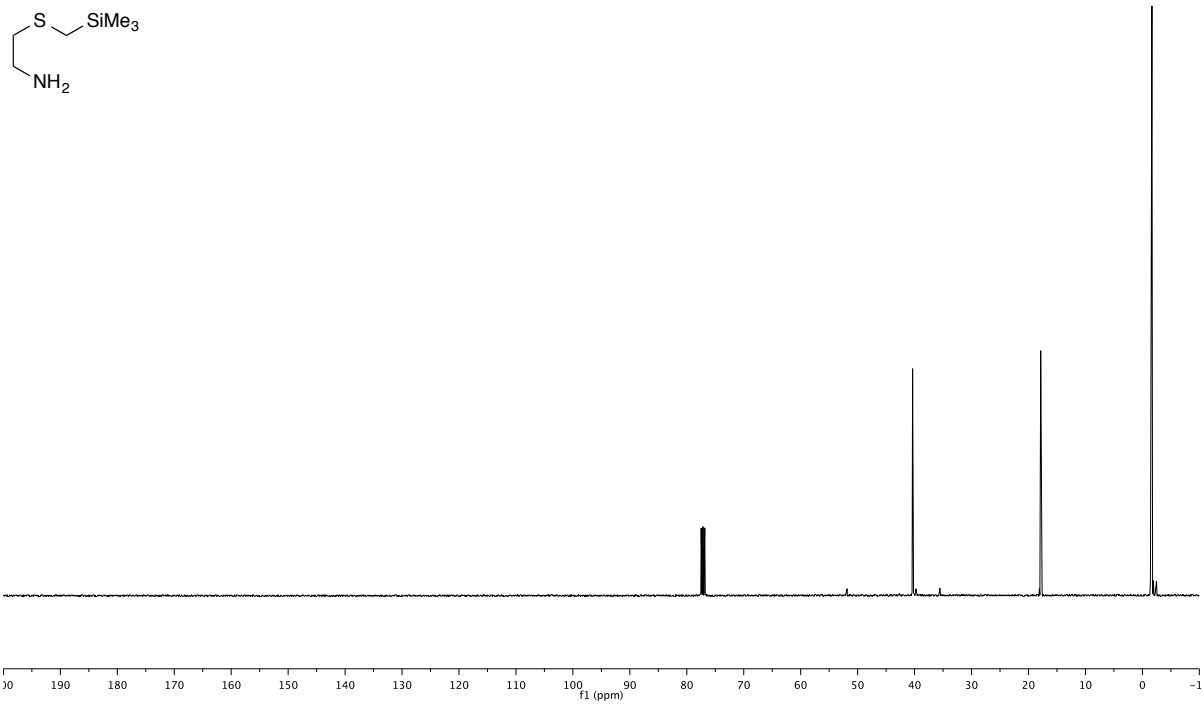
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.85, 2.85, 2.84, 2.84, 2.83, 2.82, 2.82, 2.57, 2.57, 2.56, 2.56, 2.54, 2.54, 1.71, 1.71, 1.33, 0.05.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.84 (td, *J* = 6.2, 1.0 Hz, 2 H), 2.56 (td, *J* = 6.2, 1.0 Hz, 2 H), 1.71 (d, *J* = 1.0 Hz, 2 H), 1.33 (br, 2 H), 0.05 (s, 9 H).



11-10-12-bhsieh.11.fid
Sample fly-11-128
group bode

^{13}C NMR (101 MHz, $CDCl_3$) δ 40.3, 40.3, 17.9, -1.7.

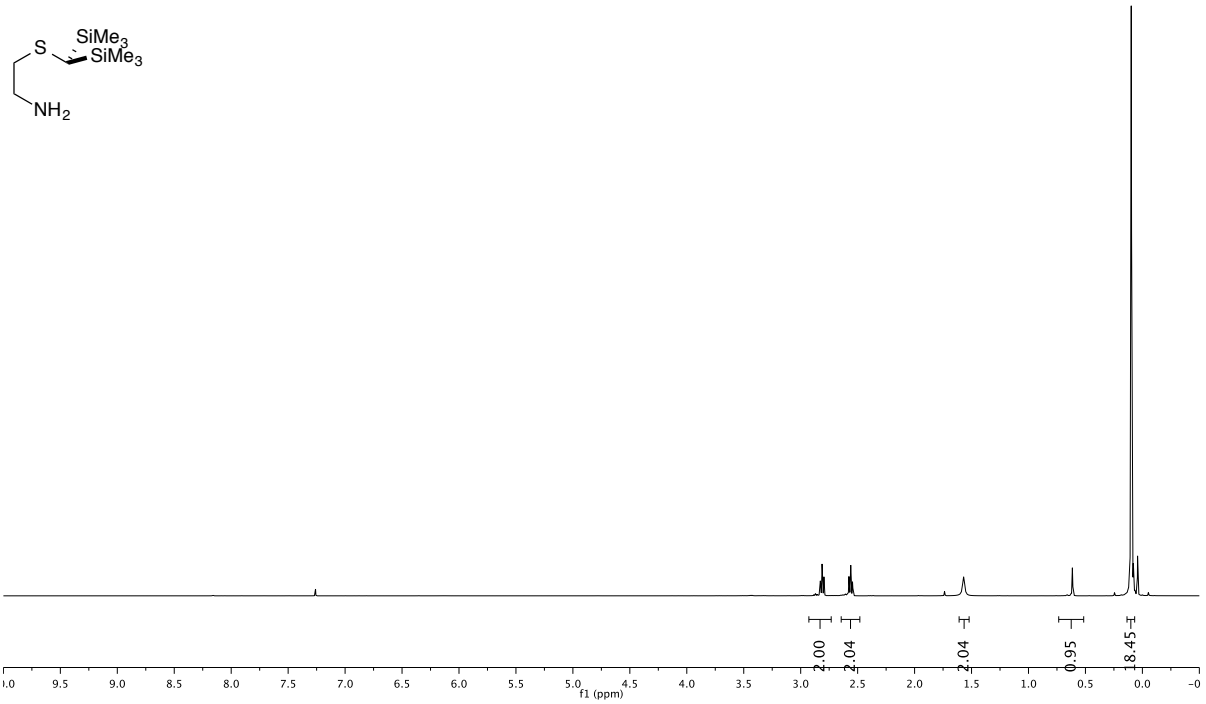


2-((Bis(trimethylsilyl)methyl)thio)ethanamine (1b)

23-25-07-bhsieh.10.fid
Sample fly-08-057
group bode
PRO CDCl3 /opt/v bhsieh 23

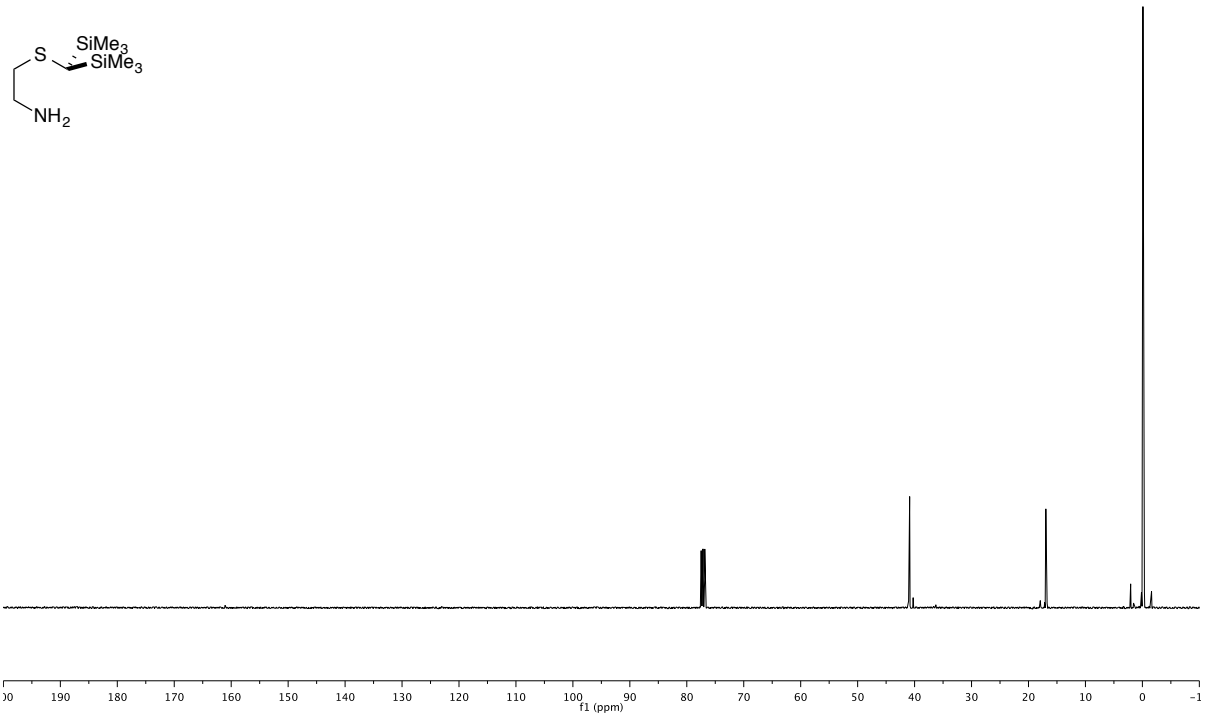
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.83, 2.81, 2.81, 2.81, 2.81, 2.80, 2.58, 2.57, 2.56, 2.56, 2.56, 2.55, 2.54, 1.57, 0.61, 0.61, 0.10.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.83–2.80 (m, 2 H), 2.56 (ddd, *J* = 7.1, 5.8, 1.1 Hz, 2 H), 1.57 (br, 1 H), 0.61 (d, *J* = 1.1 Hz, 2 H), 0.10 (s, 18 H).



23-25-07-bhsieh.11.fid
Sample fly-08-057
group bode
CAR CDCl3 /opt/v bhsieh 23

^{13}C NMR (101 MHz, $CDCl_3$) δ 41.0, 40.9, 17.0, -0.1.

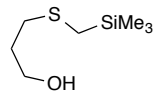


3-(((Trimethylsilyl)methyl)thio)propan-1-ol (S1)

43-25-07-bhsieh.10.fid
Sample fly-07-148
group bode

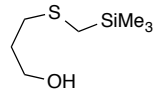
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.74, 3.74, 3.74, 3.73, 3.73, 3.72, 3.71, 3.71, 2.63, 2.62, 2.61, 2.60, 2.59, 2.59, 2.02, 1.88, 1.87, 1.87, 1.86, 1.86, 1.86, 1.85, 1.84, 1.84, 1.84, 1.83, 1.83, 1.82, 1.82, 1.81, 1.81, 1.81, 1.77, 0.07.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.74–3.71 (m, 2 H), 2.61 (td, *J* = 7.1, 1.2 Hz, 2 H), 2.02 (br, 1 H), 1.88–1.81 (m, 2 H), 1.77 (s, 2 H), 0.07 (s, 9 H).



43-25-07-bhsieh.11.fid
Sample fly-07-148
group bode

^{13}C NMR (101 MHz, $CDCl_3$) δ 62.1, 33.1, 31.2, 18.4, -1.6.

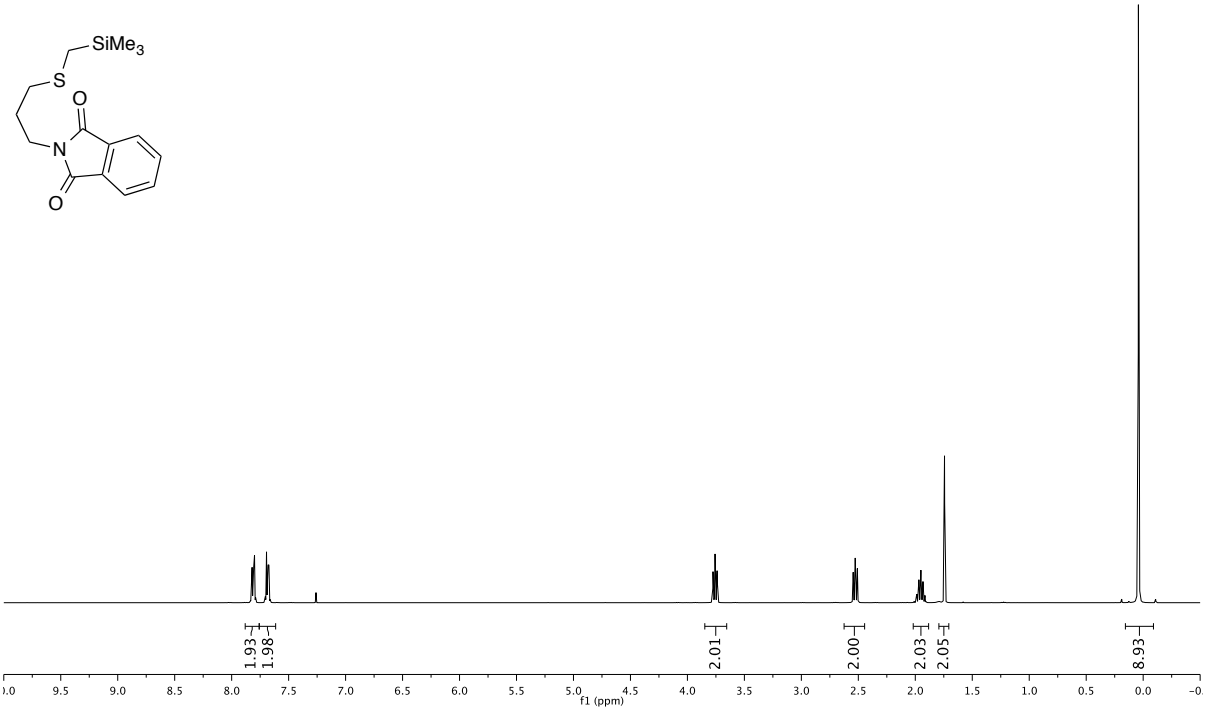


2-(3-(((Trimethylsilyl)methyl)thio)propyl)isoindoline-1,3-dione (S2)

44-25-07-bhsieh.10.fid
Sample fly-07-153
group bode

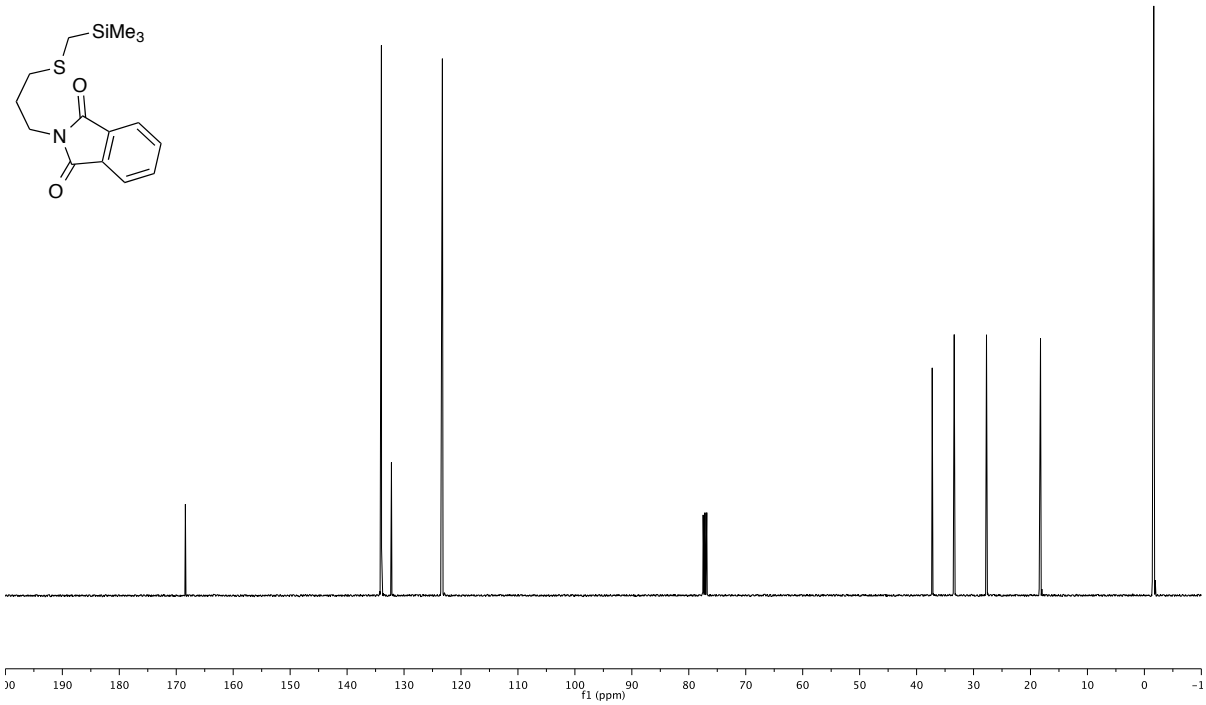
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82, 7.81, 7.81, 7.80, 7.69, 7.69, 7.68, 7.67, 3.78, 3.76, 3.76, 3.74, 2.55, 2.53, 2.51, 1.99, 1.97, 1.97, 1.95, 1.95, 1.94, 1.93, 1.93, 1.91, 1.74, 0.04.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (dd, *J* = 5.5, 3.0 Hz, 2 H), 7.68 (dd, *J* = 5.5, 3.0 Hz, 2 H), 3.76 (dd, *J* = 7.6, 6.7 Hz, 2 H), 2.55–2.51 (m, 2 H), 1.95 (qd, *J* = 7.4, 6.3 Hz, 2 H), 1.74 (s, 2 H), 0.04 (s, 9 H).



44-25-07-bhsieh.11.fid
Sample fly-07-153
group bode

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 134.0, 132.2, 123.3, 37.3, 33.4, 27.7, 18.2, -1.6.

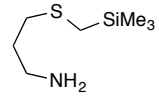


3-(((Trimethylsilyl)methyl)thio)propan-1-amine (1c)

45-25-07-bhsieh.10.fid
Sample fly-08-078
group bode

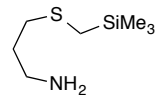
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.80, 2.78, 2.76, 2.56, 2.55, 2.54, 2.54, 2.52, 2.52, 2.52, 2.11, 1.77, 1.75, 1.75, 1.74, 1.74, 1.74, 1.72, 1.70, 0.06.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.78 (t, *J* = 6.9 Hz, 2 H), 2.54 (td, *J* = 7.2, 1.0 Hz, 2 H), 2.11 (br, 2 H), 1.77–1.70 (m, 4 H), 0.06 (s, 9 H).



45-25-07-bhsieh.11.fid
Sample fly-08-078
group bode

^{13}C NMR (101 MHz, $CDCl_3$) δ 41.0, 33.6, 32.3, 18.5, -1.6.

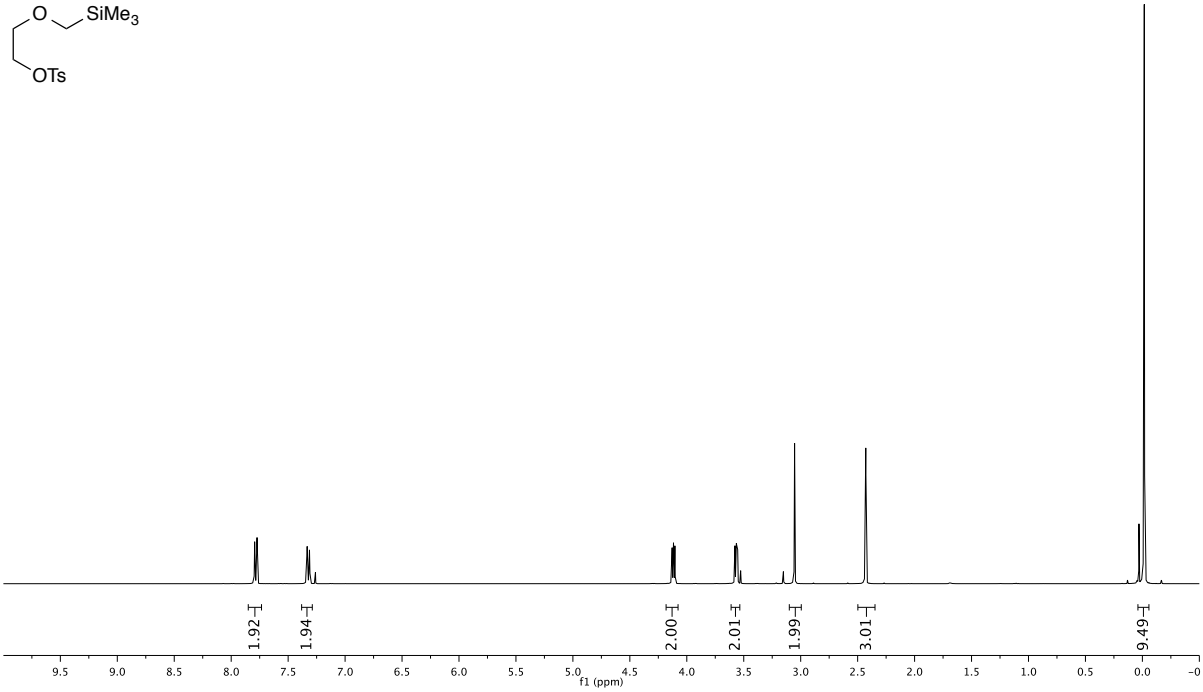


2-((Trimethylsilyl)methoxy)ethyl 4-methylbenzenesulfonate (S3)

35-26-07-bhsieh.10.fid
Sample fly-12-041
group bode
PRO CDCl3 /opt/v bhsieh 35

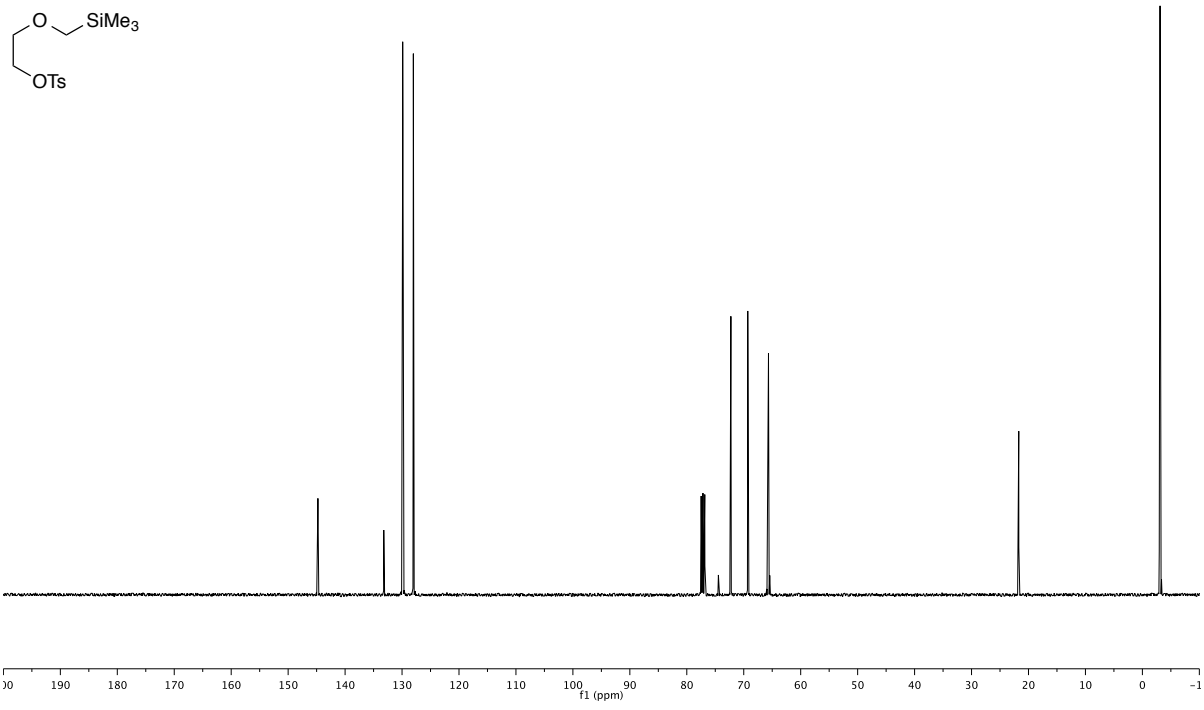
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79, 7.79, 7.78, 7.77, 7.33, 7.33, 7.33, 7.32, 7.31, 7.31, 4.13, 4.12, 4.12, 4.12, 4.11, 4.11, 4.10, 3.58, 3.57, 3.57, 3.56, 3.55, 3.05, 2.43, -0.02.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.3 Hz, 2 H), 7.33–7.31 (m, 2 H), 4.13–4.10 (m, 2 H), 3.58–3.55 (m, 2 H), 3.05 (s, 2 H), 2.43 (s, 3 H), -0.02 (s, 9 H).



35-26-07-bhsieh.11.fid
Sample fly-12-041
group bode
CAR CDCl3 /opt/v bhsieh 35

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 133.2, 129.9, 128.0, 72.3, 69.3, 65.7, 21.7, -3.1.

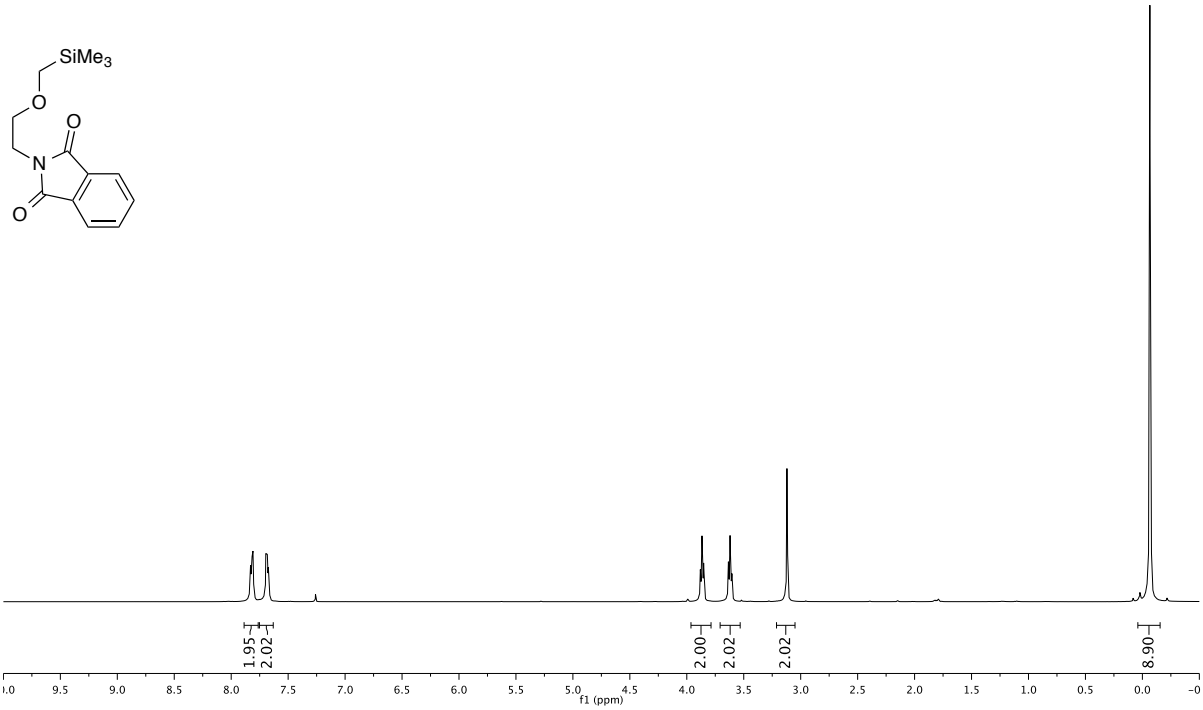


2-(2-((Trimethylsilyl)methoxy)ethyl)isoindoline-1,3-dione (S4)

51-26-07-bhsieh.10.fid
Sample fly-12-042
group bode

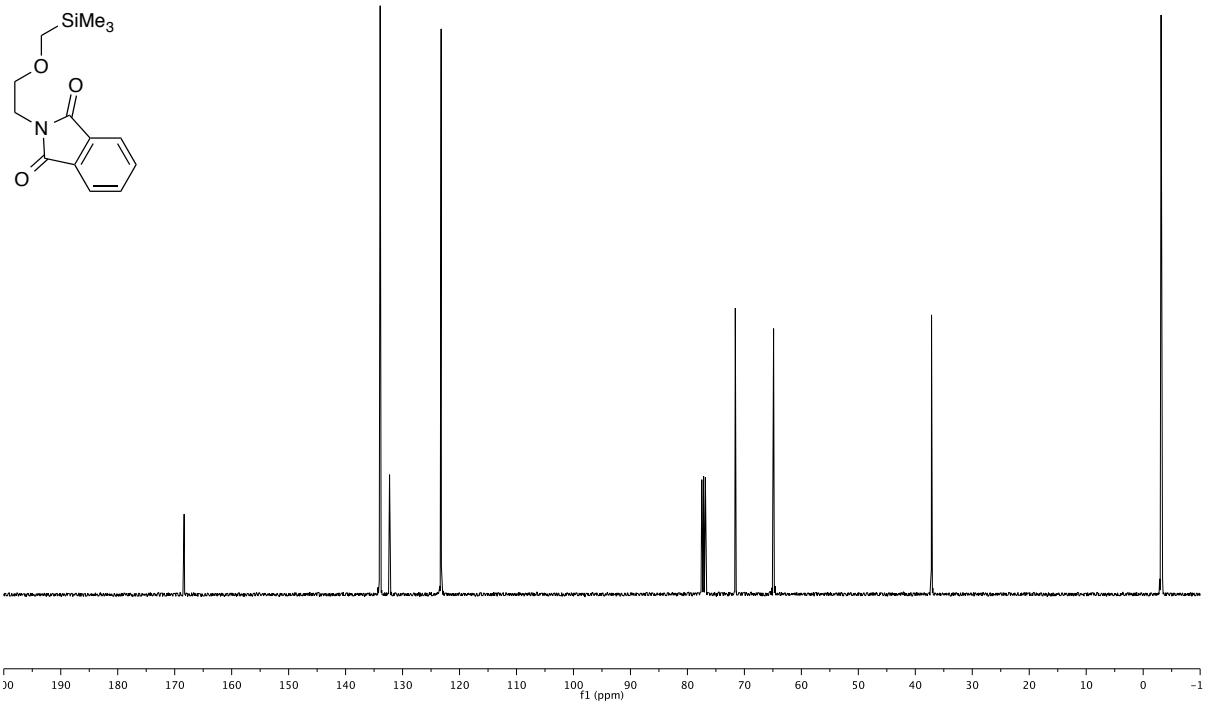
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83, 7.83, 7.82, 7.82, 7.82, 7.81, 7.81, 7.81, 7.70, 7.69, 7.69, 7.69, 7.68, 7.68, 7.68, 7.67, 3.88, 3.88, 3.87, 3.86, 3.85, 3.85, 3.63, 3.63, 3.62, 3.62, 3.61, 3.60, 3.12, -0.07, -0.07.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (ddd, *J* = 5.6, 3.1, 1.3 Hz, 2 H), 7.68 (ddd, *J* = 5.6, 3.1, 1.3 Hz, 2 H), 3.87 (td, *J* = 5.8, 1.3 Hz, 2 H), 3.63–3.60 (m, 2 H), 3.12 (s, 2 H), -0.07 (s, 9 H).



51-26-07-bhsieh.11.fid
Sample fly-12-042
group bode

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 133.9, 132.3, 123.2, 71.6, 64.9, 37.1, -3.1.

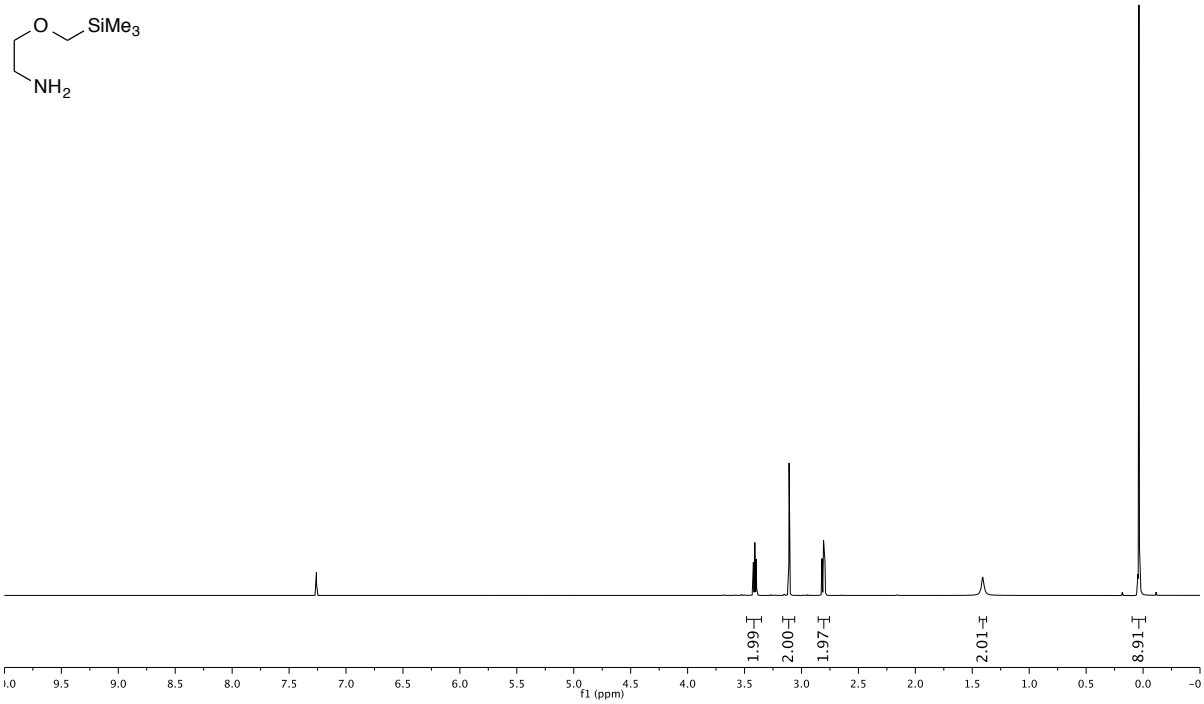


2-((Trimethylsilyl)methoxy)ethan-1-amine (11)

42-25-07-bhsieh.10.fid
Sample fly-12-043
group bode

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.42, 3.41, 3.40, 3.11, 2.82, 2.81, 2.79, 1.41, 0.04.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.41 (t, *J* = 5.1 Hz, 2 H), 3.11 (s, 2 H), 2.81 (t, *J* = 5.1 Hz, 2 H), 1.41 (br, 2 H), 0.04 (s, 9 H).



42-25-07-bhsieh.11.fid
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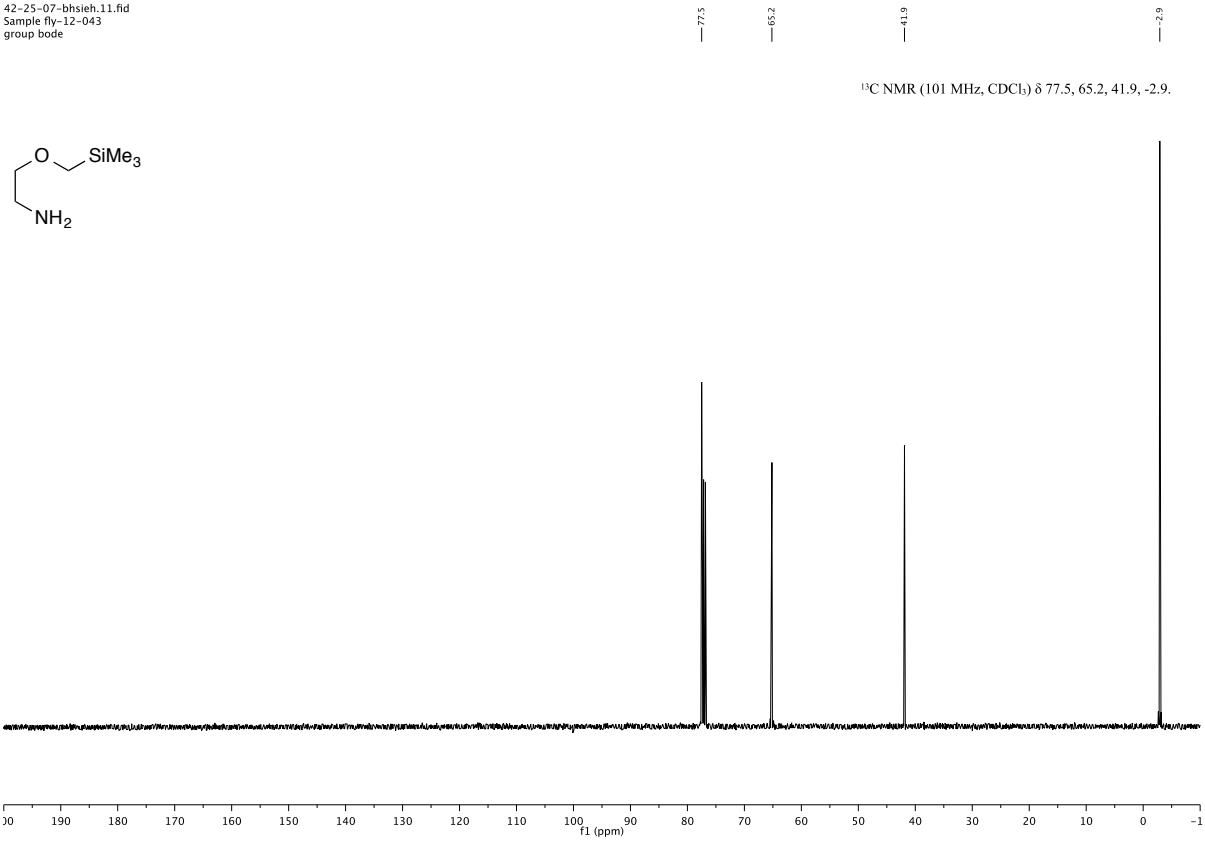
^{13}C NMR (101 MHz, $CDCl_3$) δ 77.5, 65.2, 41.9, -2.9.



3-(4-Fluorophenyl)thiomorpholine (6a) (Table S1, entry 4)

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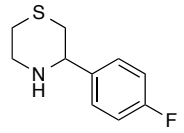
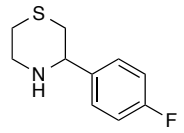
Sample fly-11-130-CC-ab
group bode



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34, 7.34, 7.33, 7.32, 7.31, 7.31, 7.30, 7.29, 7.02, 7.01, 7.01, 7.00, 7.00, 6.99, 6.99, 6.98, 6.97, 6.96, 3.91, 3.91, 3.89, 3.88, 3.45, 3.44, 3.43, 3.43, 3.42, 3.41, 3.40, 3.18, 3.17, 3.15, 3.14, 3.12, 3.11, 2.92, 2.91, 2.89, 2.88, 2.88, 2.87, 2.85, 2.85, 2.81, 2.78, 2.77, 2.75, 2.45, 2.45, 2.44, 2.44, 2.43, 2.43, 2.43, 2.42, 2.42, 2.42, 2.41, 2.41, 2.41, 2.40, 2.40, 2.39, 2.39, 1.91, 1.90.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38–7.28 (m, 2 H), 7.08–6.94 (m, 2 H), 3.90 (dd, *J* = 10.6, 2.3 Hz, 1 H), 3.42 (dt, *J* = 12.5, 3.0 Hz, 1 H), 3.15 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.88 (ddd, *J* = 13.4, 11.7, 3.0 Hz, 1 H), 2.78 (dd, *J* = 13.3, 10.5 Hz, 1 H), 2.42 (dddd, *J* = 9.4, 8.0, 4.8, 2.4 Hz, 2 H), 1.91 (br, 1 H).

13-11-12-bhsieh.11.fid
Sample fly-11-130-CC-ab
group bode

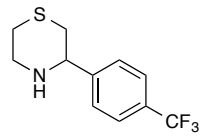


^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2 (d, *J* = 245.8 Hz), 140.1 (d, *J* = 3.2 Hz), 128.2 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 21.2 Hz), 62.3, 49.2, 35.0, 27.5.

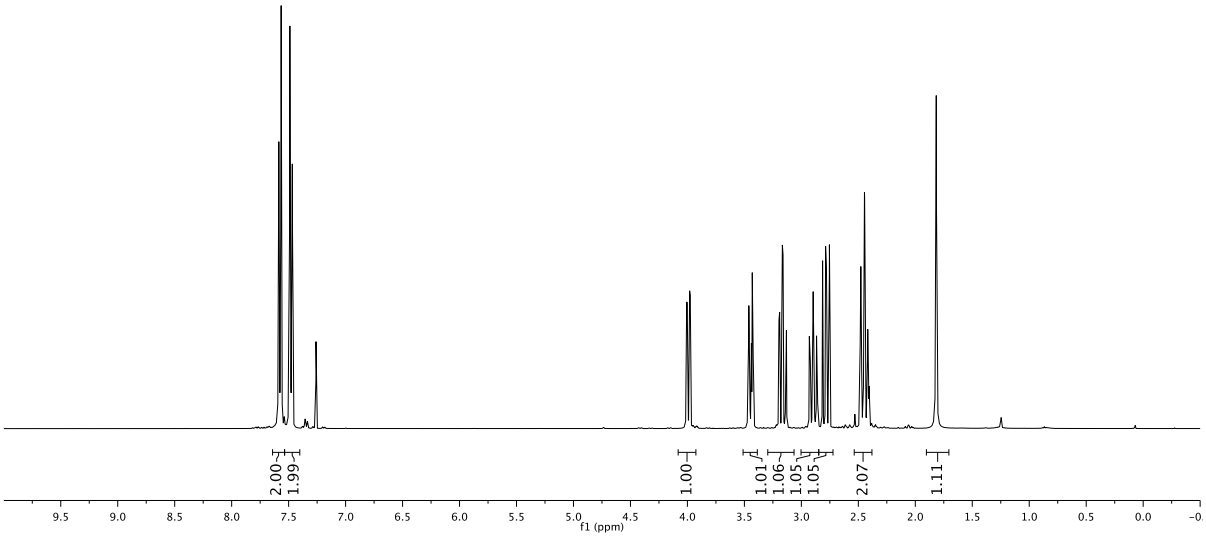
3-(4-(Trifluoromethyl)phenyl)thiomorpholine (6b) (Scheme 2)

28-24-12-bhsieh.10.fid
Sample fly-08-136-CC-6-pCF3
group bode
PRO CDCl3 /opt/v bhsieh 28

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59, 7.59, 7.58, 7.57, 7.49, 7.47, 7.47, 7.47, 4.01, 4.00, 3.98, 3.98, 3.47, 3.47, 3.46, 3.45, 3.45, 3.44, 3.43, 3.43, 3.42, 3.42, 3.20, 3.19, 3.17, 3.16, 3.14, 3.13, 2.93, 2.92, 2.92, 2.90, 2.90, 2.89, 2.89, 2.87, 2.86, 2.81, 2.79, 2.78, 2.76, 2.75, 2.48, 2.48, 2.47, 2.46, 2.45, 2.45, 2.45, 2.44, 2.44, 2.44, 2.42, 2.42, 2.41, 2.41, 1.82.

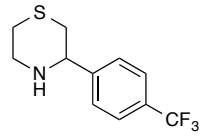


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66–7.54 (m, 1 H), 7.54–7.43 (m, 1 H), 3.99 (dd, *J* = 10.5, 2.2 Hz, 1 H), 3.57–3.33 (m, 1 H), 3.16 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.89 (ddd, *J* = 12.9, 11.7, 3.0 Hz, 1 H), 2.78 (dd, *J* = 13.3, 10.6 Hz, 1 H), 2.45 (ddt, *J* = 11.9, 10.9, 2.4 Hz, 1 H), 1.82 (br, 1 H).



28-24-12-bhsieh.11.fid
Sample fly-08-136-CC-6-pCF3
group bode
CAR CDCl3 /opt/v bhsieh 28

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.2 (q, *J* = 1.4 Hz), 130.0 (q, *J* = 32.4 Hz), 127.1, 125.7 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 272.0 Hz), 62.6, 49.0, 35.0, 27.5.

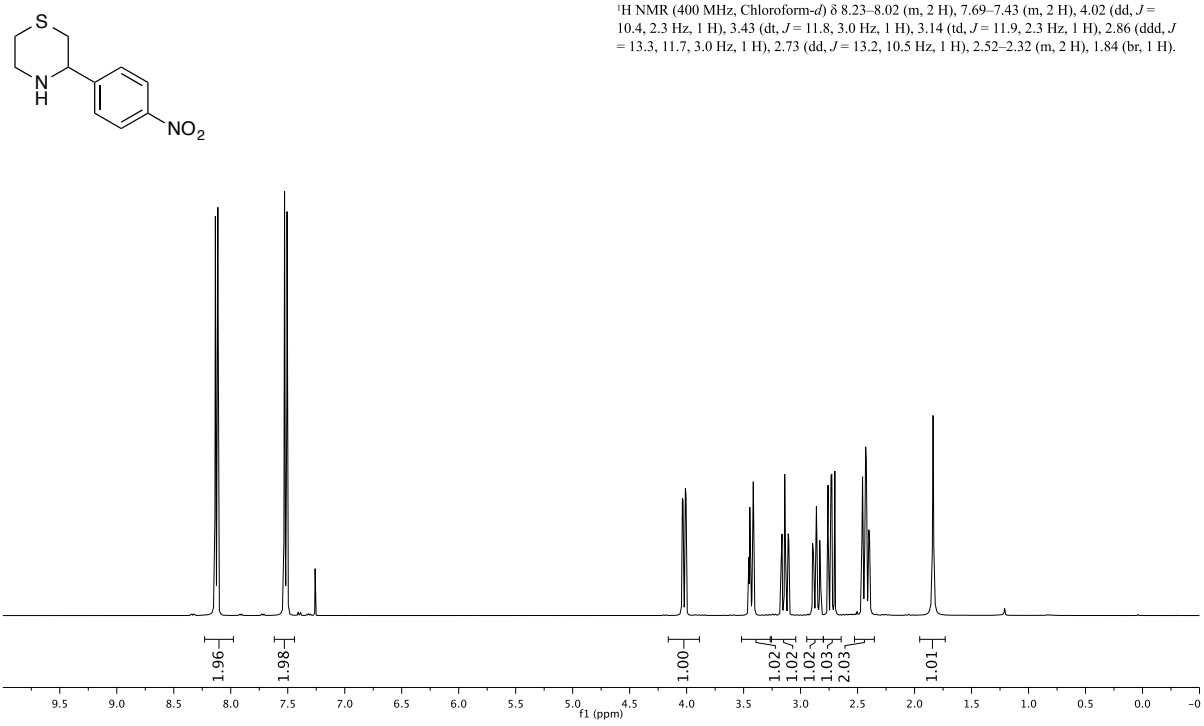


3-(4-Nitrophenyl)thiomorpholine (6c) (Scheme 2)

25-24-12-bhsieh.10.fid
Sample fly-08-092-CC-6-pNO2
group bode
PRO CDCl3 /opt/v bhsieh 25

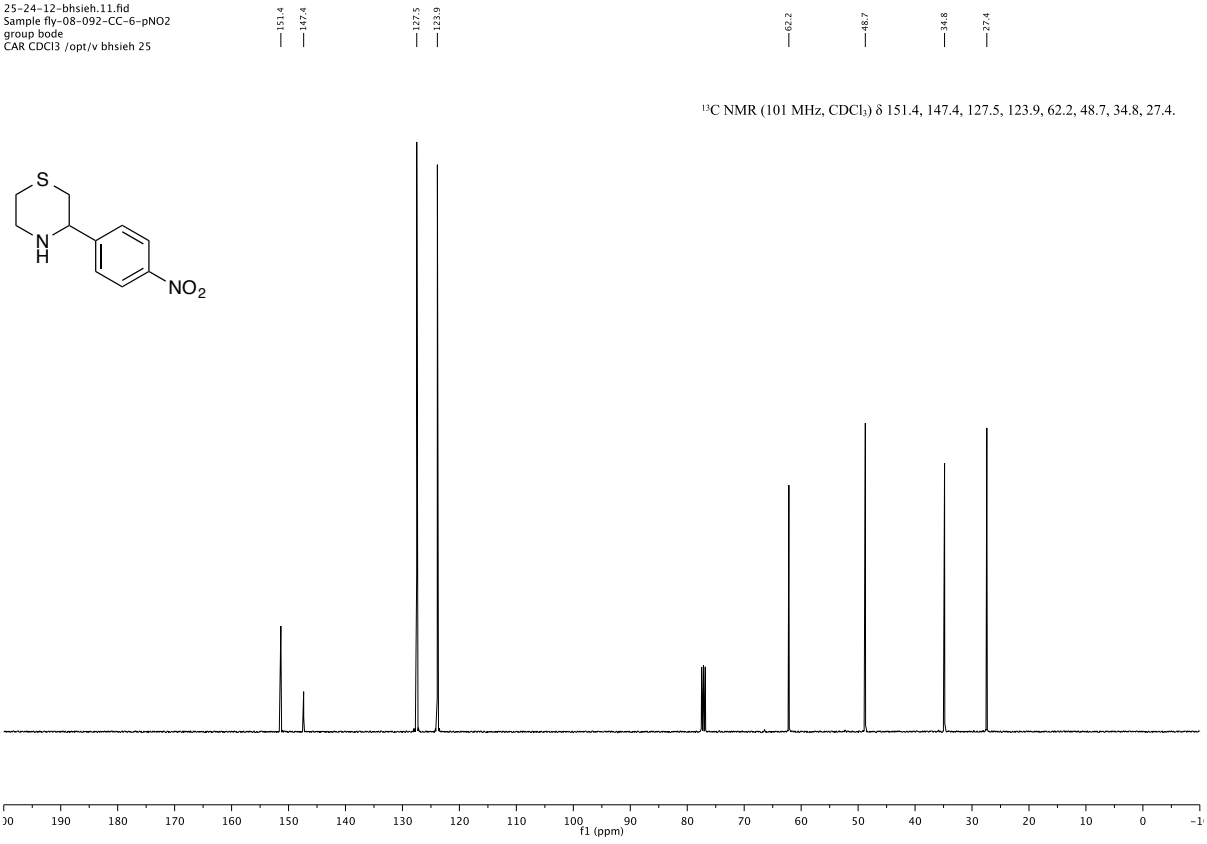
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14, 8.14, 8.13, 8.12, 8.11, 8.11, 7.53, 7.53, 7.52, 7.51, 7.51, 7.50, 4.04, 4.03, 4.01, 4.01, 3.45, 3.45, 3.44, 3.44, 3.42, 3.42, 3.41, 3.17, 3.16, 3.14, 3.13, 3.11, 3.10, 2.89, 2.89, 2.87, 2.86, 2.86, 2.85, 2.83, 2.82, 2.76, 2.73, 2.73, 2.70, 2.46, 2.46, 2.45, 2.44, 2.44, 2.43, 2.43, 2.42, 2.42, 2.42, 2.42, 2.41, 2.40, 2.39, 2.39, 1.84.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23–8.02 (m, 2 H), 7.69–7.43 (m, 2 H), 4.02 (dd, *J* = 10.4, 2.3 Hz, 1 H), 3.43 (dt, *J* = 11.8, 3.0 Hz, 1 H), 3.14 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.86 (ddd, *J* = 13.3, 11.7, 3.0 Hz, 1 H), 2.73 (dd, *J* = 13.2, 10.5 Hz, 1 H), 2.52–2.32 (m, 2 H), 1.84 (br, 1 H).

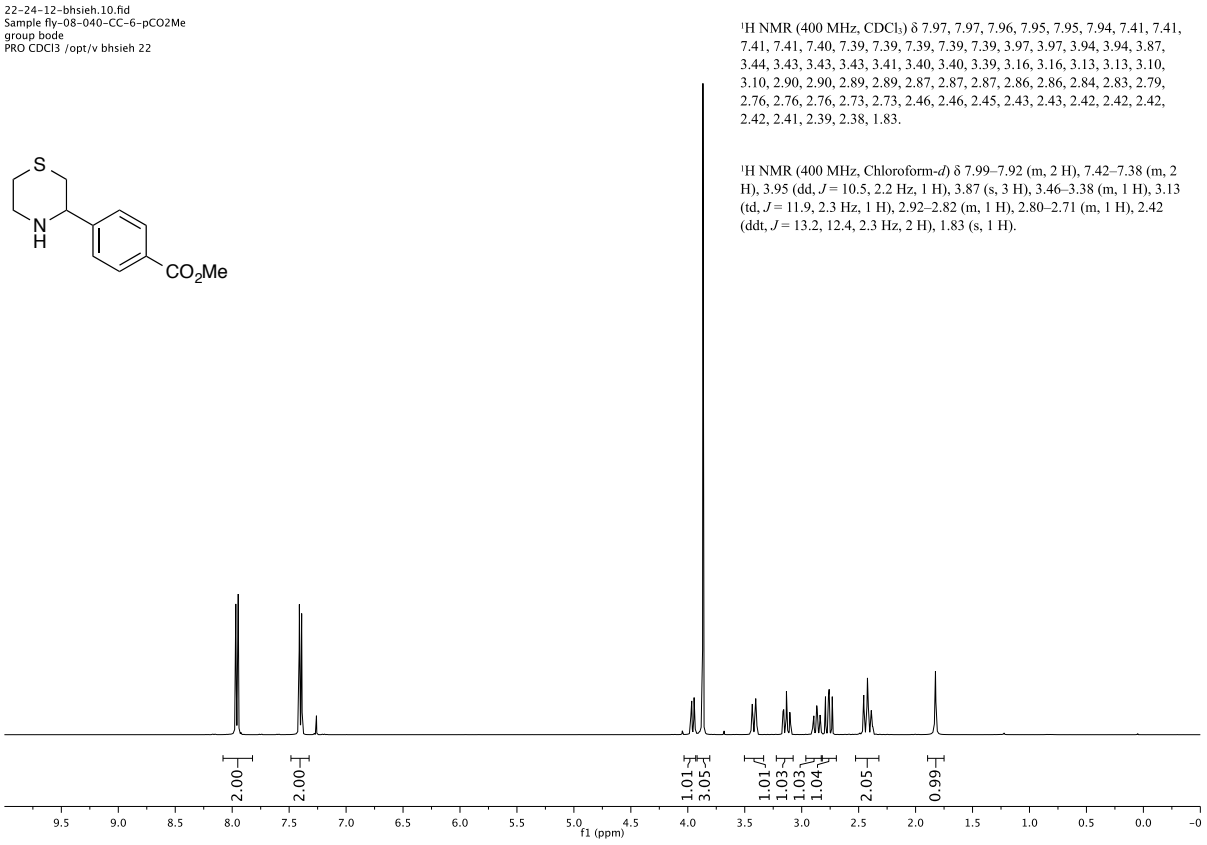


25-24-12-bhsieh.11.fid
Sample fly-08-092-CC-6-pNO2
group bode
CAR CDCl3 /opt/v bhsieh 25

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 147.4, 127.5, 123.9, 62.2, 48.7, 34.8, 27.4.

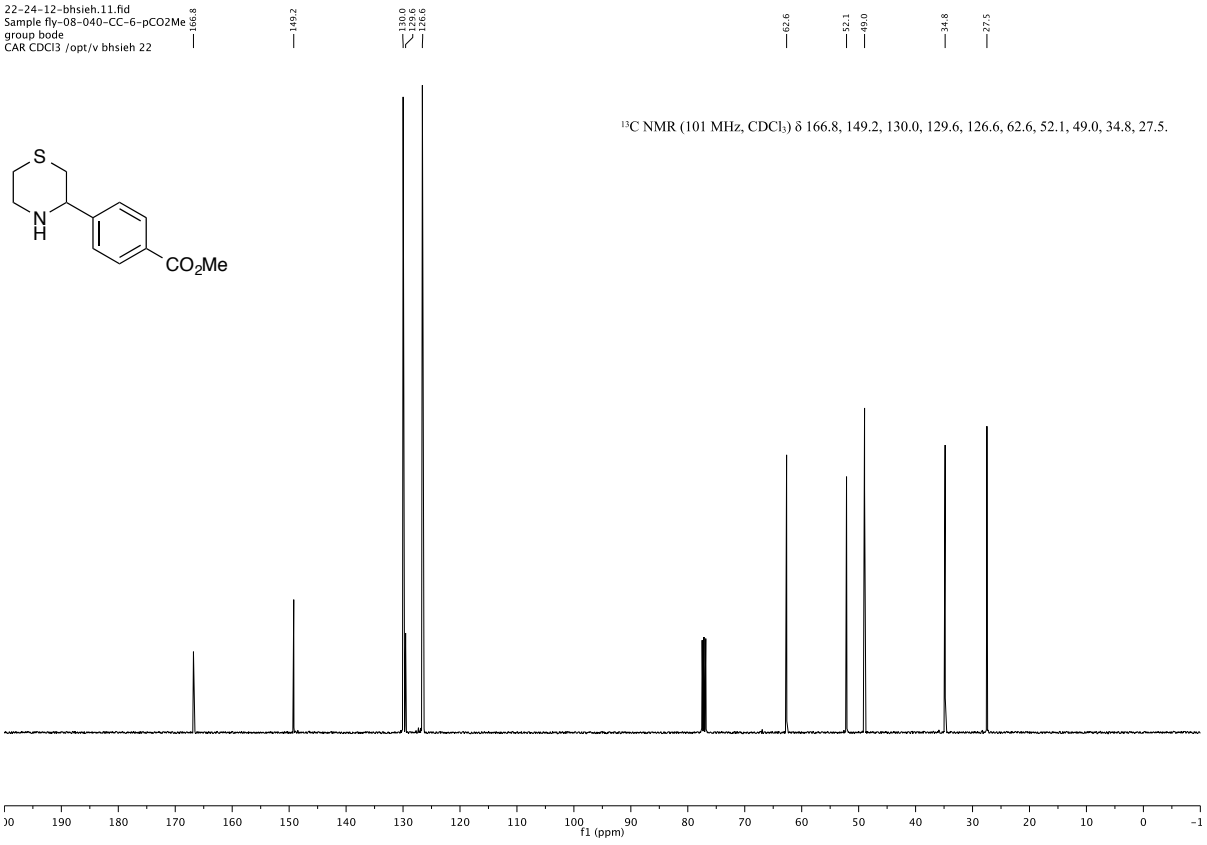


Methyl 4-(thiomorpholin-3-yl)benzoate (6d) (Scheme 2)



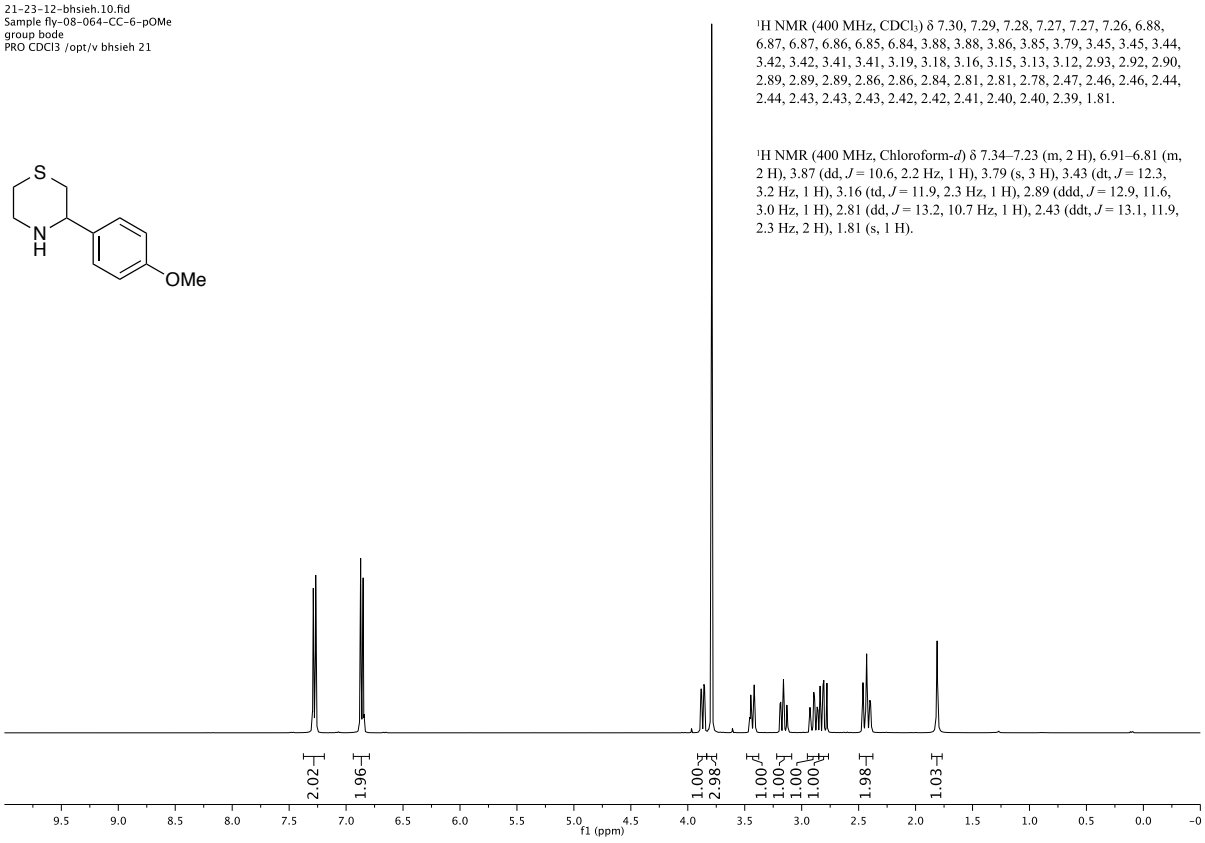
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97, 7.97, 7.96, 7.95, 7.95, 7.94, 7.41, 7.41, 7.41, 7.41, 7.40, 7.39, 7.39, 7.39, 7.39, 7.39, 3.97, 3.97, 3.94, 3.94, 3.87, 3.44, 3.43, 3.43, 3.43, 3.41, 3.40, 3.40, 3.39, 3.16, 3.16, 3.13, 3.13, 3.10, 3.10, 2.90, 2.90, 2.89, 2.89, 2.87, 2.87, 2.87, 2.86, 2.86, 2.84, 2.83, 2.79, 2.76, 2.76, 2.76, 2.73, 2.73, 2.46, 2.46, 2.45, 2.43, 2.43, 2.42, 2.42, 2.42, 2.42, 2.41, 2.39, 2.38, 1.83.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99–7.92 (m, 2 H), 7.42–7.38 (m, 2 H), 3.95 (dd, *J* = 10.5, 2.2 Hz, 1 H), 3.87 (s, 3 H), 3.46–3.38 (m, 1 H), 3.13 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.92–2.82 (m, 1 H), 2.80–2.71 (m, 1 H), 2.42 (ddt, *J* = 13.2, 12.4, 2.3 Hz, 2 H), 1.83 (s, 1 H).



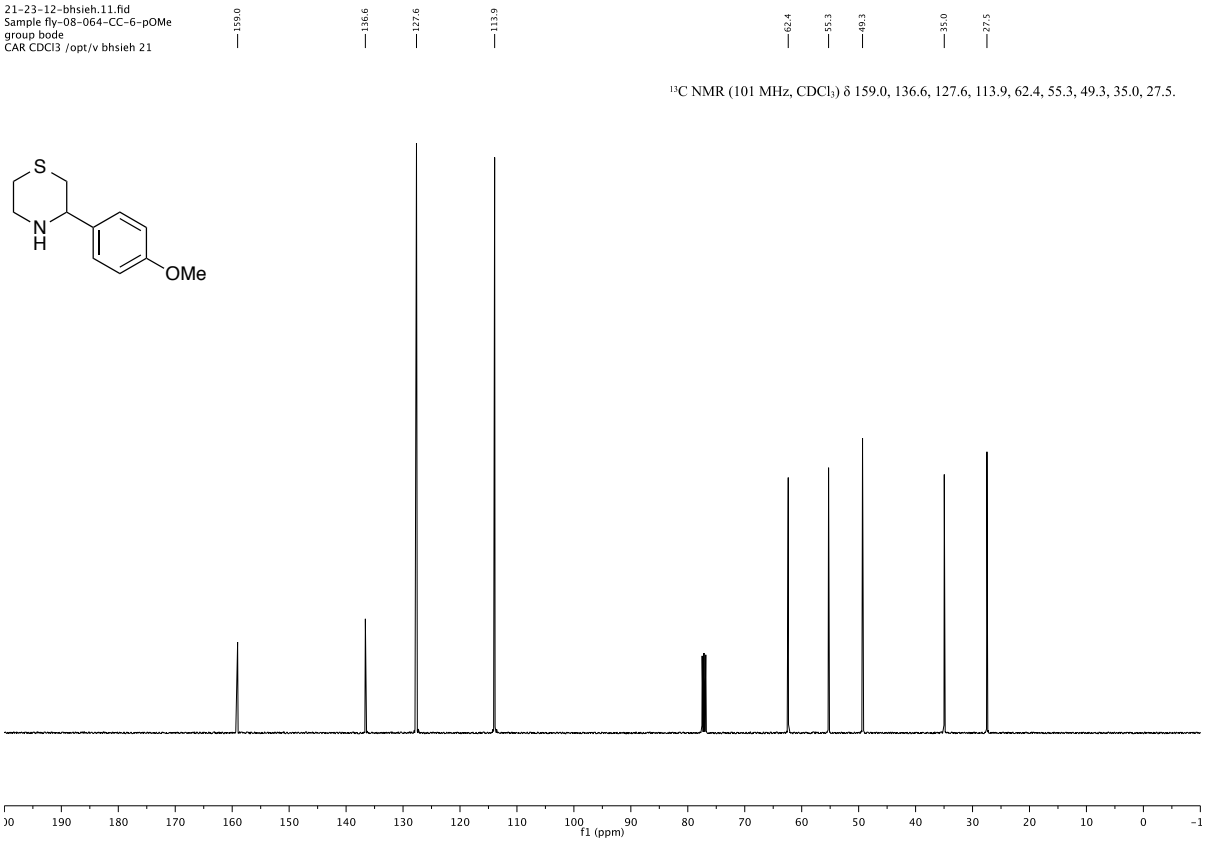
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 149.2, 130.0, 129.6, 126.6, 62.6, 52.1, 49.0, 34.8, 27.5.

3-(4-Methoxyphenyl)thiomorpholine (6e) (Scheme 2)



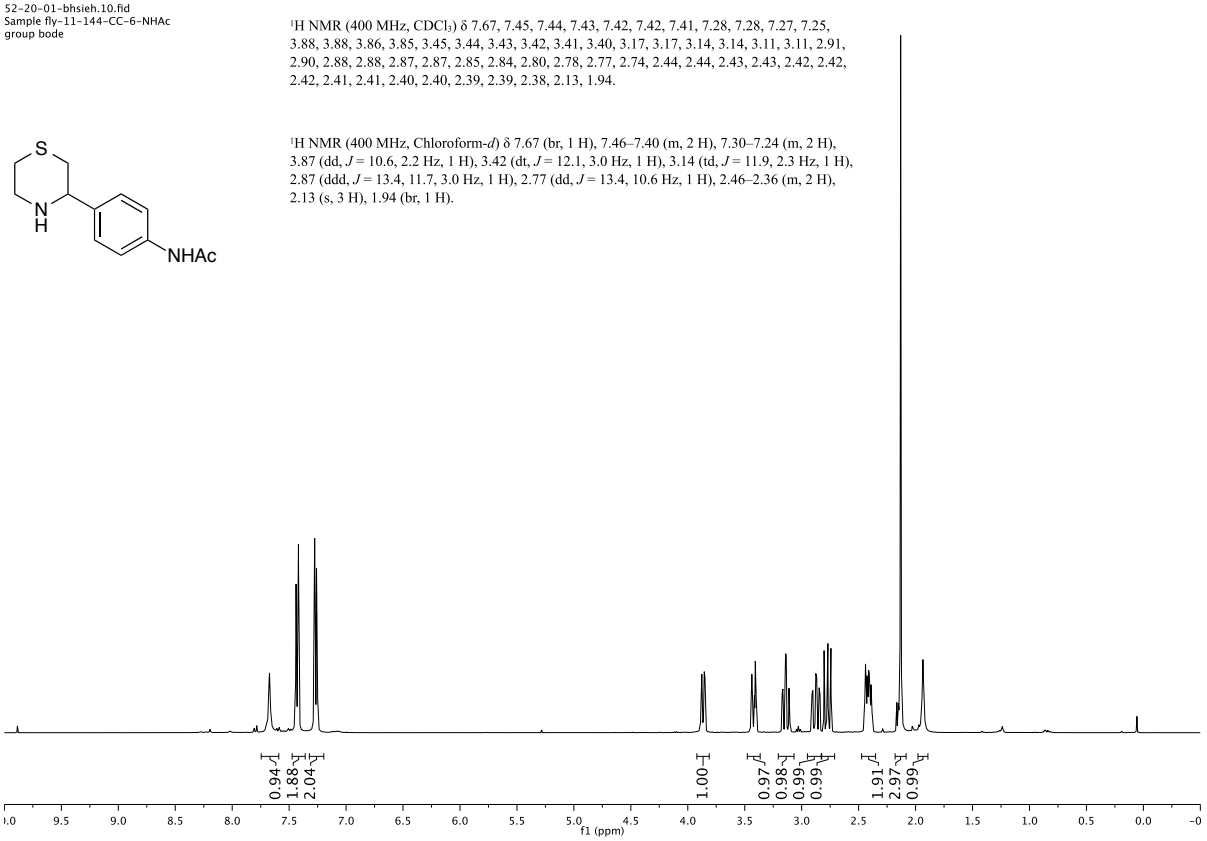
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30, 7.29, 7.28, 7.27, 7.27, 7.26, 6.88, 6.87, 6.87, 6.86, 6.85, 6.84, 3.88, 3.88, 3.86, 3.85, 3.79, 3.45, 3.45, 3.44, 3.42, 3.42, 3.41, 3.41, 3.19, 3.18, 3.16, 3.15, 3.13, 3.12, 2.93, 2.92, 2.90, 2.89, 2.89, 2.89, 2.86, 2.86, 2.84, 2.81, 2.81, 2.78, 2.47, 2.46, 2.46, 2.44, 2.44, 2.43, 2.43, 2.43, 2.42, 2.42, 2.41, 2.40, 2.40, 2.39, 1.81.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34–7.23 (m, 2 H), 6.91–6.81 (m, 2 H), 3.87 (dd, *J* = 10.6, 2.2 Hz, 1 H), 3.79 (s, 3 H), 3.43 (dt, *J* = 12.3, 3.2 Hz, 1 H), 3.16 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.89 (ddd, *J* = 12.9, 11.6, 3.0 Hz, 1 H), 2.81 (dd, *J* = 13.2, 10.7 Hz, 1 H), 2.43 (ddt, *J* = 13.1, 11.9, 2.3 Hz, 2 H), 1.81 (s, 1 H).



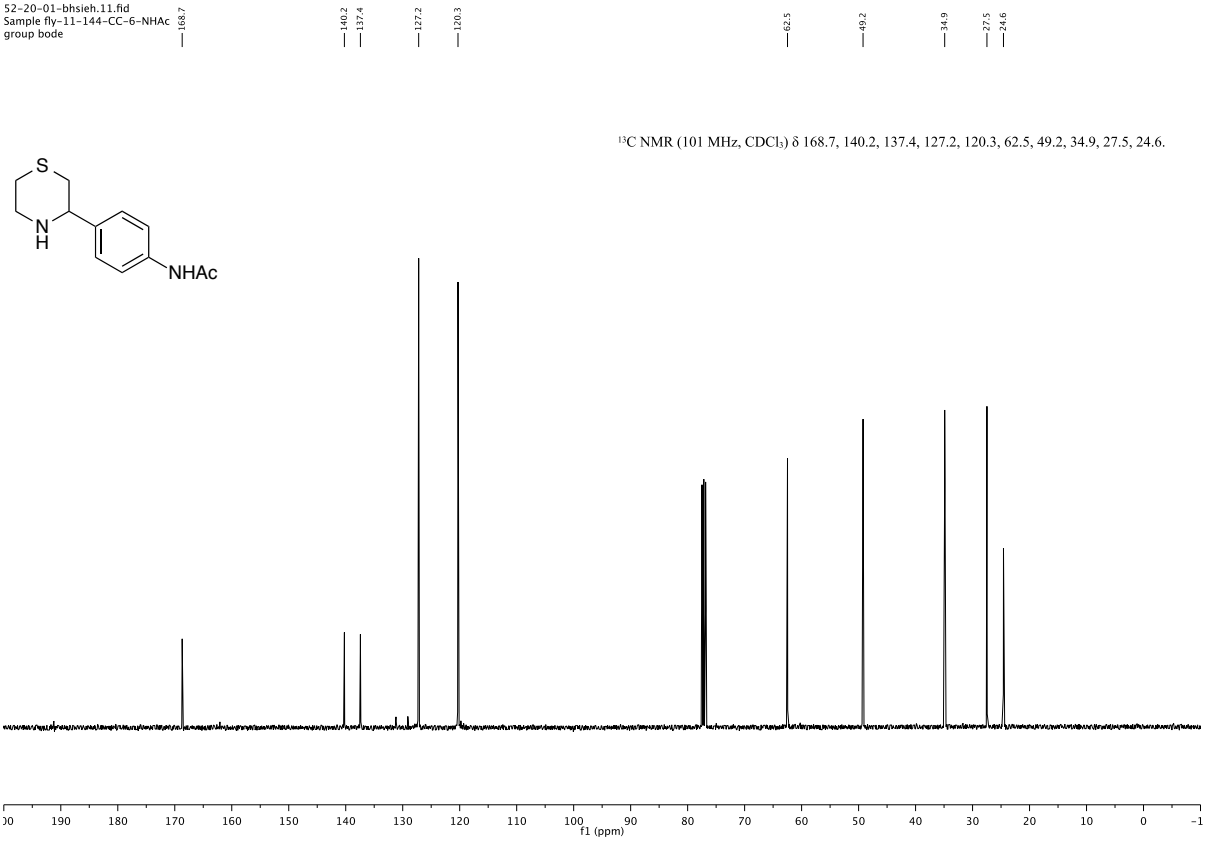
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 136.6, 127.6, 113.9, 62.4, 55.3, 49.3, 35.0, 27.5.

N-(4-(Thiomorpholin-3-yl)phenyl)acetamide (6f) (Scheme 2)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67, 7.45, 7.44, 7.43, 7.42, 7.42, 7.41, 7.28, 7.28, 7.27, 7.25, 3.88, 3.88, 3.86, 3.85, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.17, 3.17, 3.14, 3.14, 3.11, 3.11, 2.91, 2.90, 2.88, 2.88, 2.87, 2.87, 2.85, 2.84, 2.80, 2.78, 2.77, 2.74, 2.44, 2.44, 2.43, 2.43, 2.42, 2.42, 2.42, 2.41, 2.41, 2.40, 2.40, 2.39, 2.39, 2.38, 2.13, 1.94.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (br, 1 H), 7.46–7.40 (m, 2 H), 7.30–7.24 (m, 2 H), 3.87 (dd, *J* = 10.6, 2.2 Hz, 1 H), 3.42 (dt, *J* = 12.1, 3.0 Hz, 1 H), 3.14 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.87 (ddd, *J* = 13.4, 11.7, 3.0 Hz, 1 H), 2.77 (dd, *J* = 13.4, 10.6 Hz, 1 H), 2.46–2.36 (m, 2 H), 2.13 (s, 3 H), 1.94 (br, 1 H).



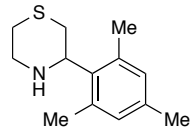
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 140.2, 137.4, 127.2, 120.3, 62.5, 49.2, 34.9, 27.5, 24.6.

3-Mesitylthiomorpholine (6g) (Scheme 2)

26-24-12-bhsieh.10.fid
Sample fly-08-095-CC-6-Mes
group bode
PRO CDCl3 /opt/v bhsieh 26

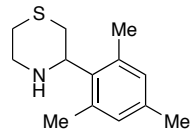
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84, 4.43, 4.42, 4.40, 4.40, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.33, 3.30, 3.29, 3.27, 3.17, 3.16, 3.14, 3.13, 3.11, 3.10, 2.97, 2.96, 2.94, 2.94, 2.93, 2.93, 2.91, 2.90, 2.51, 2.44, 2.44, 2.43, 2.42, 2.41, 2.40, 2.40, 2.39, 2.31, 2.30, 2.30, 2.27, 2.27, 2.26, 1.62.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.84 (s, 2 H), 4.41 (dd, *J* = 10.9, 2.5 Hz, 1 H), 3.47 (dt, *J* = 11.7, 3.1 Hz, 1 H), 3.30 (dd, *J* = 13.1, 10.9 Hz, 1 H), 3.14 (td, *J* = 11.7, 2.2 Hz, 1 H), 2.94 (ddd, *J* = 13.0, 11.7, 2.9 Hz, 1 H), 2.51 (br, 6 H), 2.42 (dq, *J* = 12.9, 2.4 Hz, 1 H), 2.29 (dd, *J* = 13.2, 2.3 Hz, 1 H), 2.26 (s, 3 H), 1.62 (s, 1 H).



26-24-12-bhsieh.11.fid
Sample fly-08-095-CC-6-Mes
group bode
CAR CDCl3 /opt/v bhsieh 26

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 136.7, 136.6, 130.3, 60.3, 50.2, 30.2, 27.8, 21.6, 20.8.

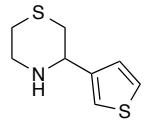


3-(Thiophen-3-yl)thiomorpholine (6h) (Scheme 2)

16-03-10-bhsieh.10.fid
Sample fly-08-048-CC
group bode

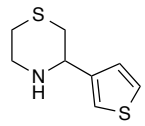
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30, 7.29, 7.28, 7.28, 7.20, 7.20, 7.20, 7.19, 7.19, 7.08, 7.08, 7.07, 7.07, 7.06, 4.08, 4.08, 4.06, 4.05, 3.45, 3.45, 3.44, 3.42, 3.42, 3.41, 3.19, 3.18, 3.16, 3.15, 3.13, 3.12, 2.90, 2.90, 2.87, 2.87, 2.87, 2.86, 2.84, 2.83, 2.82, 2.81, 2.78, 2.59, 2.58, 2.57, 2.55, 2.55, 2.54, 2.45, 2.44, 2.44, 2.43, 2.42, 2.41, 2.40, 2.40, 1.90.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 5.0, 3.0 Hz, 1 H), 7.20 (dt, *J* = 2.8, 1.2 Hz, 1 H), 7.08 (dd, *J* = 4.9, 1.3 Hz, 1 H), 4.07 (dd, *J* = 10.5, 2.4 Hz, 1 H), 3.43 (dt, *J* = 12.3, 3.1 Hz, 1 H), 3.15 (td, *J* = 11.9, 2.4 Hz, 1 H), 2.94–2.73 (m, 2 H), 2.56 (dt, *J* = 13.1, 2.3 Hz, 1 H), 2.42 (dq, *J* = 13.2, 2.5 Hz, 1H), 1.90 (s, 1 H).



16-03-10-bhsieh.11.fid
Sample fly-08-048-CC
group bode

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 126.1, 126.0, 120.6, 58.3, 49.0, 34.5, 27.5.

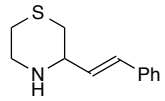


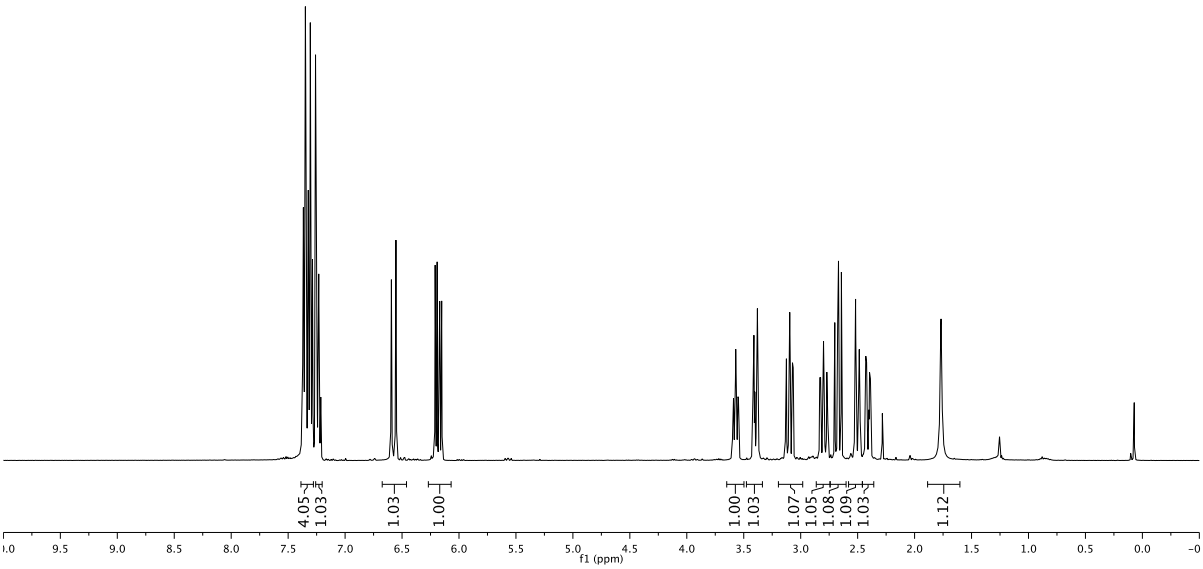
(*E*)-3-Styrylthiomorpholine (6i) (Scheme 2)

23-24-12-bhsieh.10.fid
Sample fly-08-041-CC-6-alkene
group bode
PRO CDCl3 /opt/v bhsieh 23

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37, 7.37, 7.36, 7.35, 7.35, 7.35, 7.34, 7.34, 7.33, 7.32, 7.32, 7.31, 7.31, 7.31, 7.30, 7.29, 7.29, 7.25, 7.25, 7.25, 7.24, 7.23, 7.23, 7.22, 7.21, 7.21, 6.59, 6.59, 6.55, 6.55, 6.21, 6.19, 6.17, 6.15, 3.60, 3.59, 3.59, 3.59, 3.58, 3.58, 3.57, 3.56, 3.56, 3.55, 3.55, 3.55, 3.54, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.13, 3.13, 3.10, 3.10, 3.07, 3.07, 2.83, 2.83, 2.80, 2.80, 2.80, 2.79, 2.77, 2.76, 2.70, 2.68, 2.67, 2.64, 2.52, 2.52, 2.51, 2.49, 2.49, 2.48, 2.43, 2.43, 2.43, 2.42, 2.42, 2.40, 2.40, 2.39, 2.39, 2.39, 2.38, 1.77.

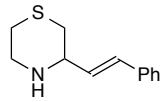
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38–7.27 (m, 4 H), 7.26–7.21 (m, 1 H), 6.57 (dd, *J* = 16.0, 1.1 Hz, 1 H), 6.18 (dd, *J* = 16.0, 7.0 Hz, 1 H), 3.62–3.52 (m, 1 H), 3.40 (dt, *J* = 12.2, 3.1 Hz, 1 H), 3.10 (td, *J* = 11.9, 2.4 Hz, 1 H), 2.80 (ddd, *J* = 13.2, 11.5, 3.0 Hz, 1 H), 2.67 (dd, *J* = 13.1, 10.2 Hz, 1 H), 2.50 (dt, *J* = 13.0, 2.2 Hz, 1 H), 2.45–2.38 (m, 1 H), 1.77 (s, 1 H).





23-24-12-bhsieh.11.fid
Sample fly-08-041-CC-6-alkene
group bode
CAR CDCl3 /opt/v bhsieh 23

^{13}C NMR (101 MHz, $CDCl_3$) δ 136.8, 131.7, 130.7, 128.7, 127.8, 126.5, 59.8, 48.2, 33.1, 27.6.

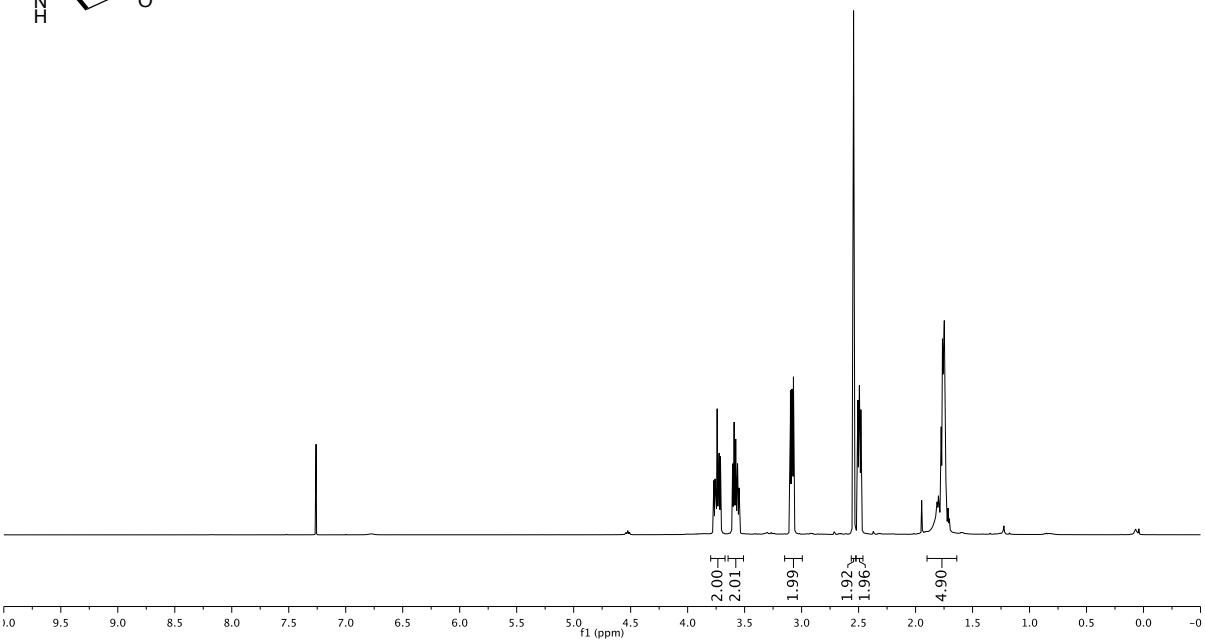


9-Oxa-4-thia-1-azaspiro[5.5]undecane (6j) (Scheme 2)

54-21-01-bhsieh.10.fid
Sample fly-11-125-CC-6-sp-O
group bode

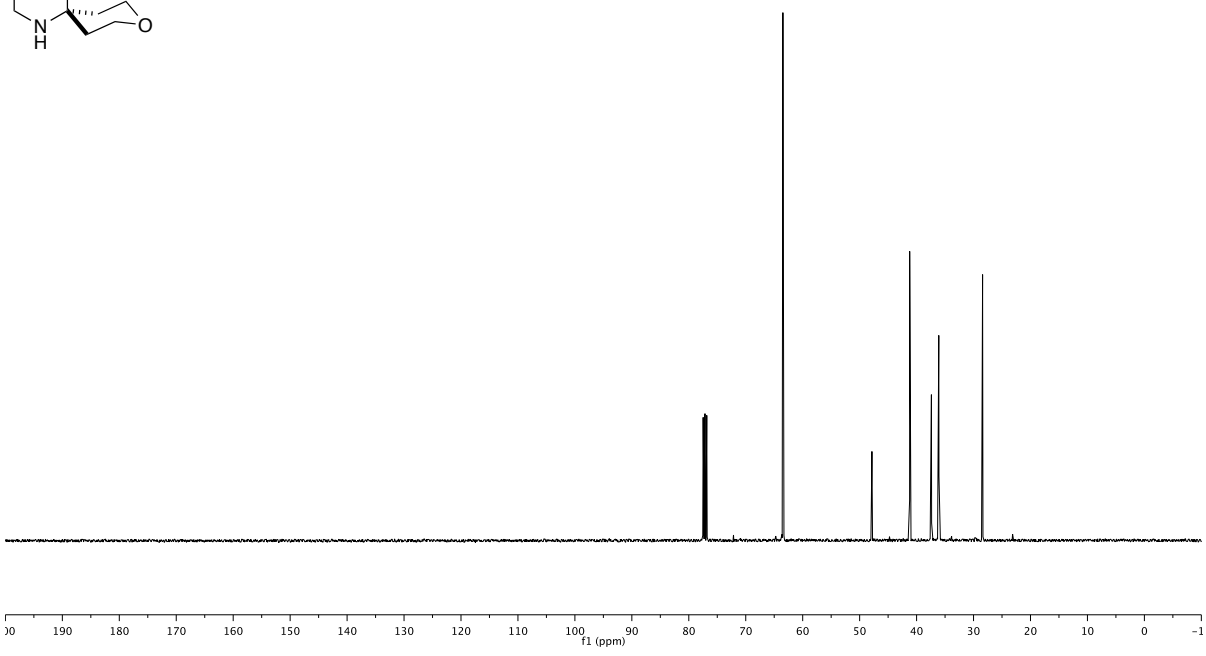
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.61, 3.59, 3.58, 3.58, 3.57, 3.56, 3.55, 3.10, 3.09, 3.08, 3.08, 3.07, 2.54, 2.51, 2.50, 2.49, 2.49, 2.48, 1.81, 1.80, 1.79, 1.78, 1.76, 1.76, 1.75, 1.75, 1.74, 1.73, 1.71, 1.70.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.74 (ddd, *J* = 11.6, 7.1, 4.5 Hz, 2 H), 3.58 (dt, *J* = 12.1, 4.9 Hz, 2 H), 3.15–3.02 (m, 2 H), 2.54 (s, 2 H), 2.53–2.44 (m, 2 H), 1.86–1.68 (m, 5 H).

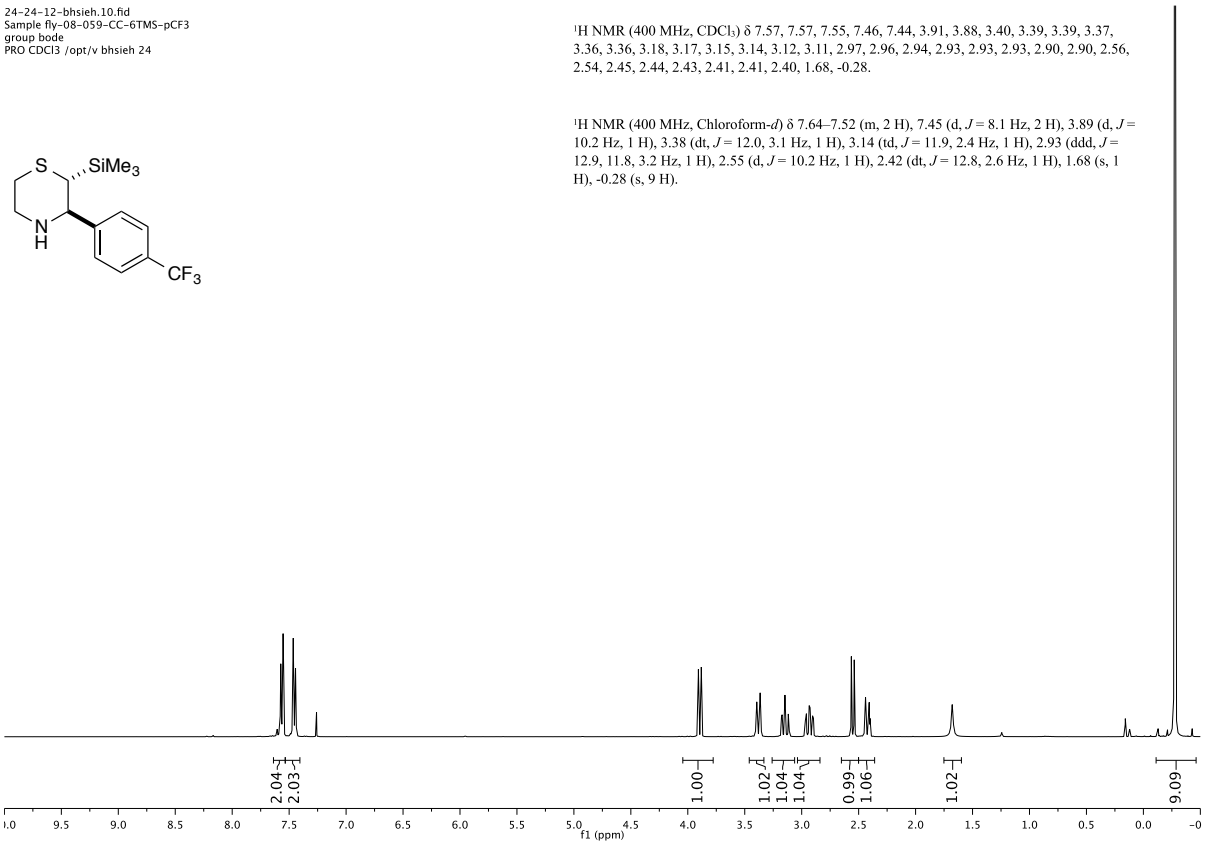


54-21-01-bhsieh.11.fid
Sample fly-11-125-CC-6-sp-O
group bode

^{13}C NMR (101 MHz, $CDCl_3$) δ 63.5, 47.8, 41.2, 37.4, 36.1, 28.4.

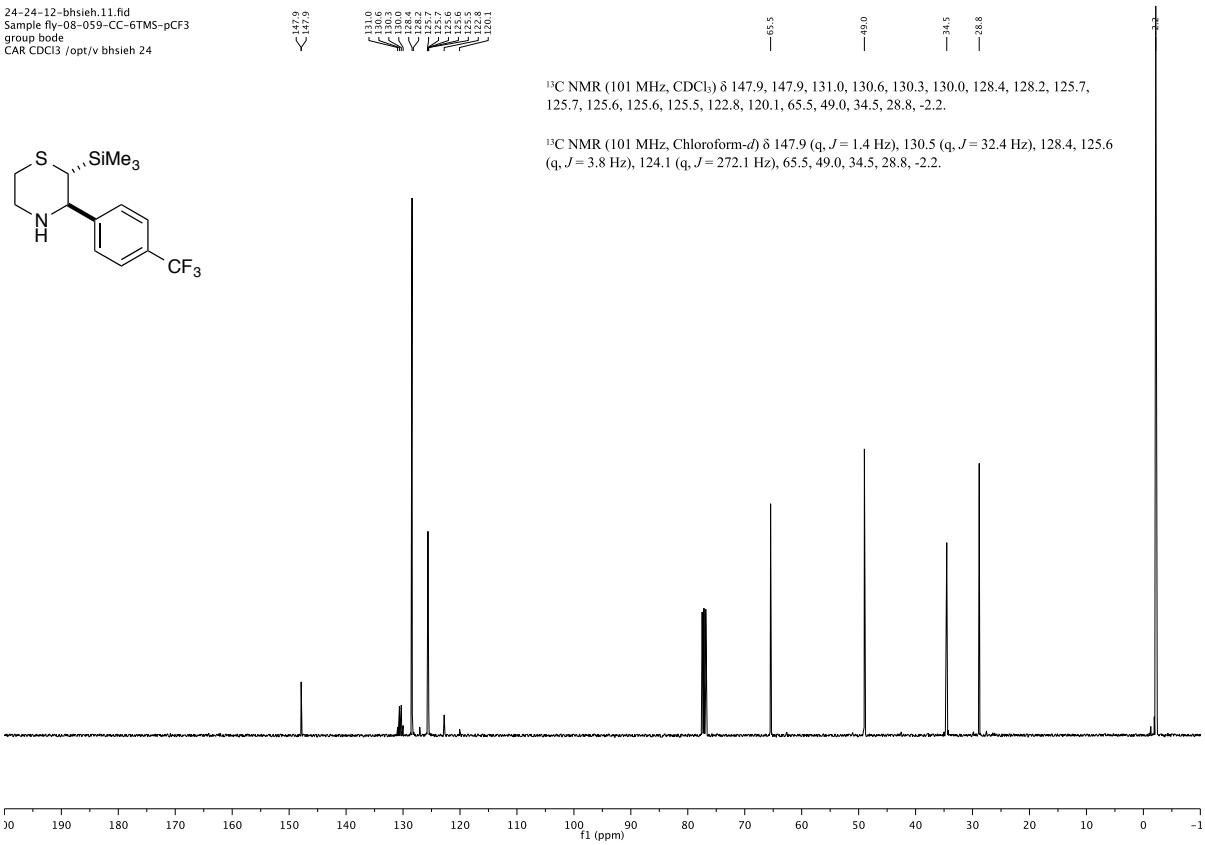


trans-3-(4-(Trifluoromethyl)phenyl)-2-(trimethylsilyl)thiomorpholine (7a) (Scheme 2)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57, 7.57, 7.55, 7.46, 7.44, 3.91, 3.88, 3.40, 3.39, 3.39, 3.37, 3.36, 3.36, 3.18, 3.17, 3.15, 3.14, 3.12, 3.11, 2.97, 2.96, 2.94, 2.93, 2.93, 2.93, 2.90, 2.90, 2.56, 2.54, 2.45, 2.44, 2.43, 2.41, 2.41, 2.40, 1.68, -0.28.

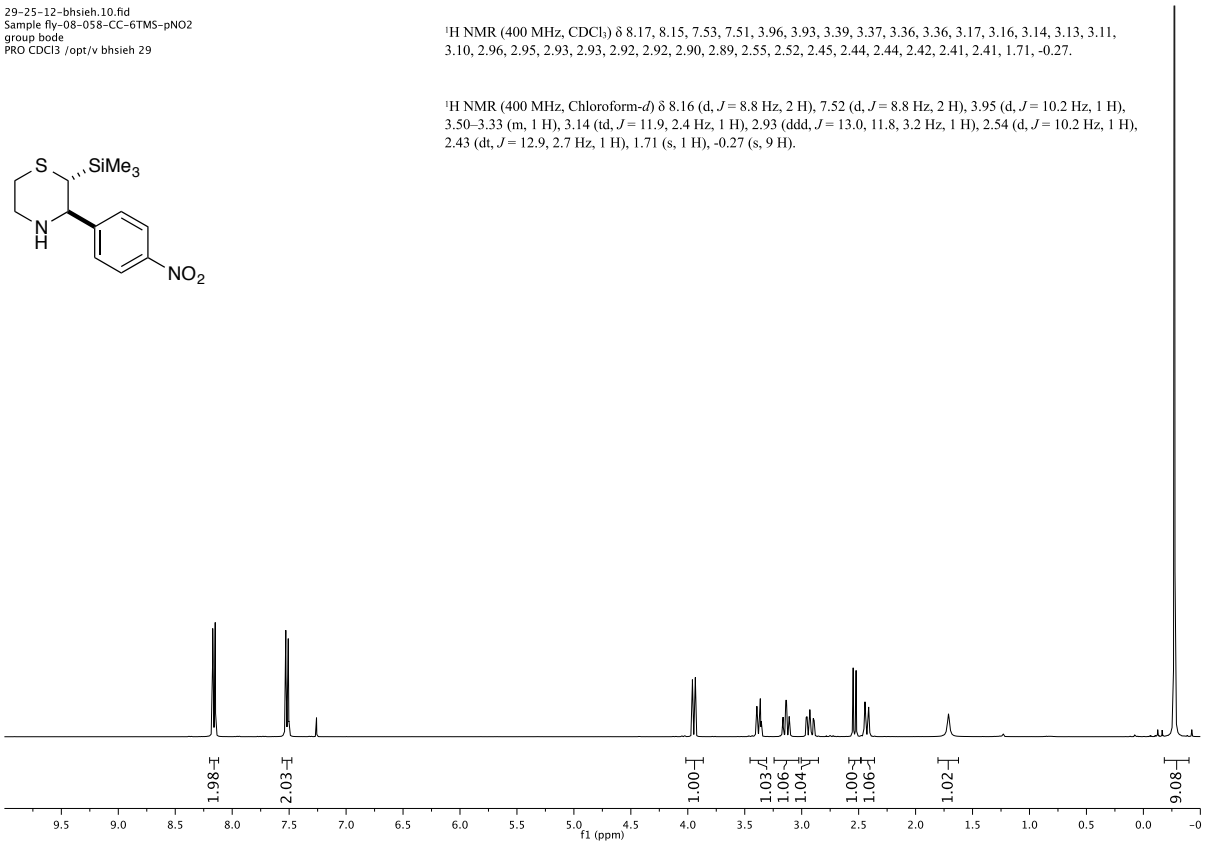
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64–7.52 (m, 2 H), 7.45 (d, *J* = 8.1 Hz, 2 H), 3.89 (d, *J* = 10.2 Hz, 1 H), 3.38 (dt, *J* = 12.0, 3.1 Hz, 1 H), 3.14 (td, *J* = 11.9, 2.4 Hz, 1 H), 2.93 (ddd, *J* = 12.9, 11.8, 3.2 Hz, 1 H), 2.55 (d, *J* = 10.2 Hz, 1 H), 2.42 (dt, *J* = 12.8, 2.6 Hz, 1 H), 1.68 (s, 1 H), -0.28 (s, 9 H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 147.9, 131.0, 130.6, 130.3, 130.0, 128.4, 128.2, 125.7, 125.7, 125.6, 125.6, 125.5, 122.8, 120.1, 65.5, 49.0, 34.5, 28.8, -2.2.

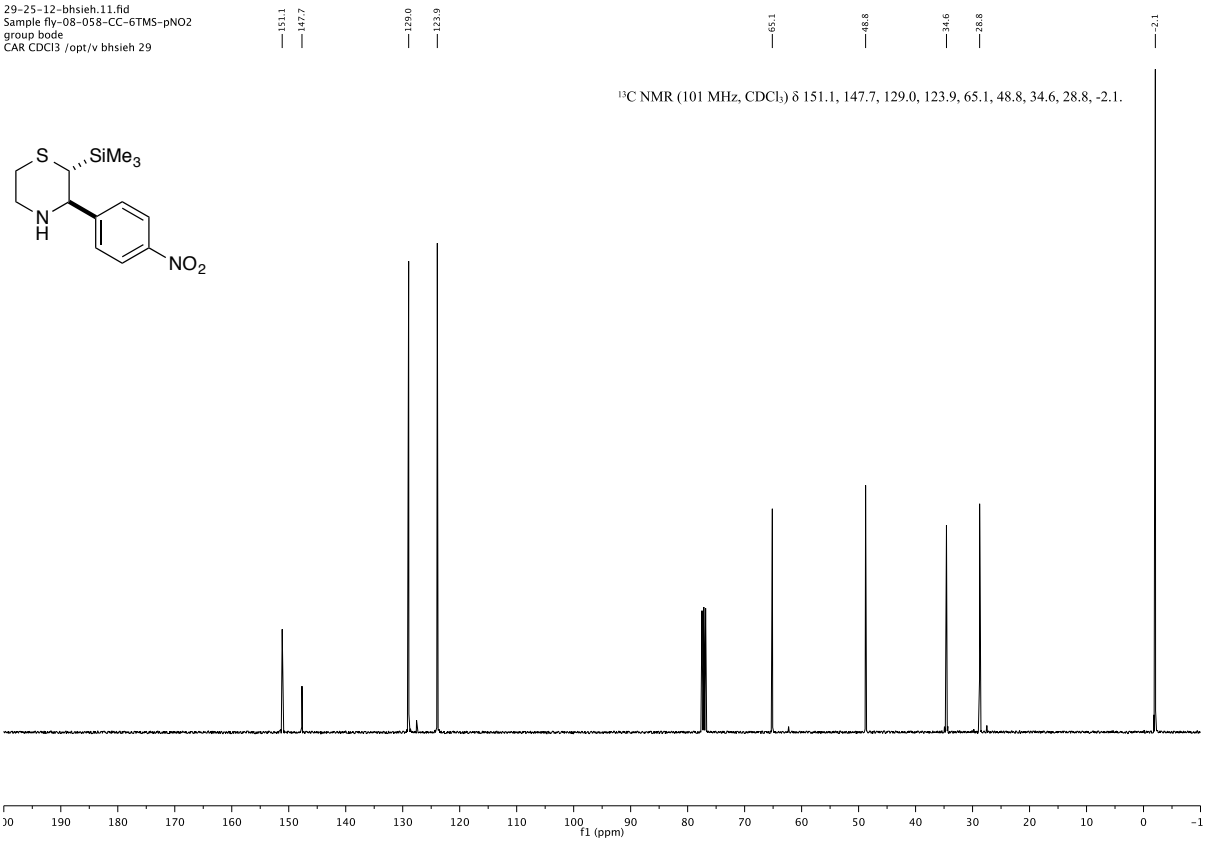
^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.9 (q, *J* = 1.4 Hz), 130.5 (q, *J* = 32.4 Hz), 128.4, 125.6 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.1 Hz), 65.5, 49.0, 34.5, 28.8, -2.2.

trans-3-(4-Nitrophenyl)-2-(trimethylsilyl)thiomorpholine (7b) (Scheme 2)



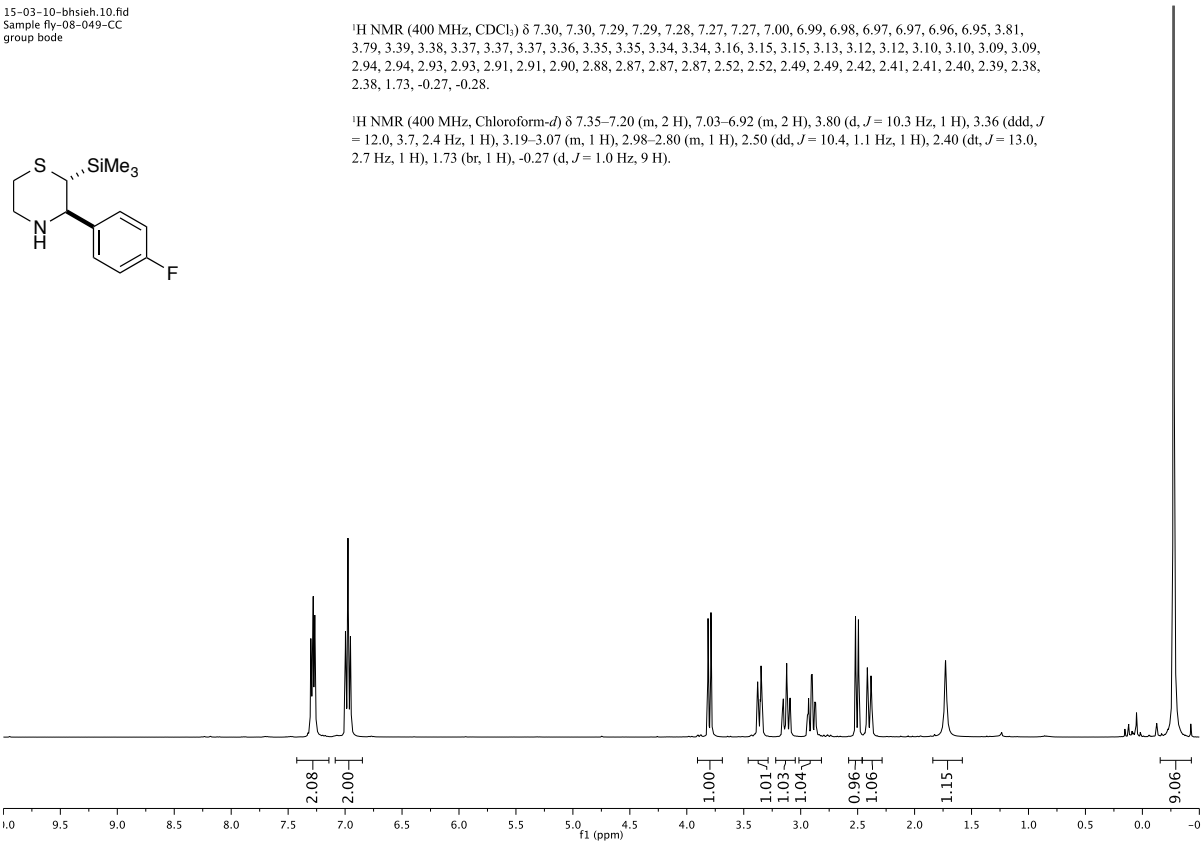
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17, 8.15, 7.53, 7.51, 3.96, 3.93, 3.39, 3.37, 3.36, 3.36, 3.17, 3.16, 3.14, 3.13, 3.11, 3.10, 2.96, 2.95, 2.93, 2.93, 2.92, 2.92, 2.90, 2.89, 2.55, 2.52, 2.45, 2.44, 2.44, 2.42, 2.41, 2.41, 1.71, -0.27.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.16 (d, *J* = 8.8 Hz, 2 H), 7.52 (d, *J* = 8.8 Hz, 2 H), 3.95 (d, *J* = 10.2 Hz, 1 H), 3.50–3.33 (m, 1 H), 3.14 (td, *J* = 11.9, 2.4 Hz, 1 H), 2.93 (ddd, *J* = 13.0, 11.8, 3.2 Hz, 1 H), 2.54 (d, *J* = 10.2 Hz, 1 H), 2.43 (dt, *J* = 12.9, 2.7 Hz, 1 H), 1.71 (s, 1 H), -0.27 (s, 9 H).



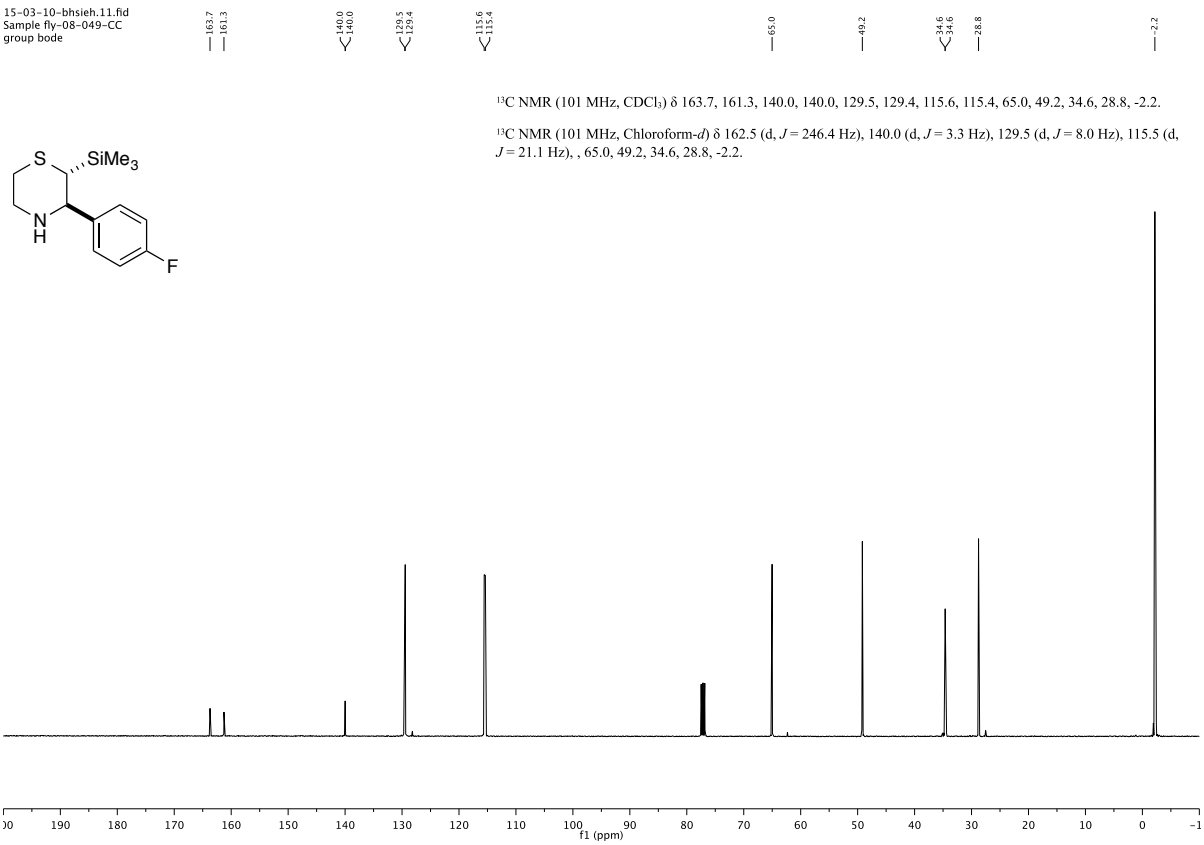
^{13}C NMR (101 MHz, $CDCl_3$) δ 151.1, 147.7, 129.0, 123.9, 65.1, 48.8, 34.6, 28.8, -2.1.

trans-3-(4-Fluorophenyl)-2-(trimethylsilyl)thiomorpholine (7c) (Scheme 2)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30, 7.30, 7.29, 7.29, 7.28, 7.27, 7.27, 7.00, 6.99, 6.98, 6.97, 6.97, 6.96, 6.95, 3.81, 3.79, 3.39, 3.38, 3.37, 3.37, 3.37, 3.36, 3.35, 3.35, 3.34, 3.34, 3.16, 3.15, 3.15, 3.13, 3.12, 3.12, 3.10, 3.10, 3.09, 3.09, 2.94, 2.94, 2.93, 2.93, 2.91, 2.91, 2.90, 2.88, 2.87, 2.87, 2.87, 2.52, 2.52, 2.49, 2.49, 2.42, 2.41, 2.41, 2.40, 2.39, 2.38, 2.38, 1.73, -0.27, -0.28.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35–7.20 (m, 2 H), 7.03–6.92 (m, 2 H), 3.80 (d, *J* = 10.3 Hz, 1 H), 3.36 (ddd, *J* = 12.0, 3.7, 2.4 Hz, 1 H), 3.19–3.07 (m, 1 H), 2.98–2.80 (m, 1 H), 2.50 (dd, *J* = 10.4, 1.1 Hz, 1 H), 2.40 (dt, *J* = 13.0, 2.7 Hz, 1 H), 1.73 (br, 1 H), -0.27 (d, *J* = 1.0 Hz, 9 H).

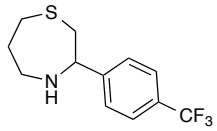


^{13}C NMR (101 MHz, $CDCl_3$) δ 163.7, 161.3, 140.0, 140.0, 129.5, 129.4, 115.6, 115.4, 65.0, 49.2, 34.6, 28.8, -2.2.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.5 (d, *J* = 246.4 Hz), 140.0 (d, *J* = 3.3 Hz), 129.5 (d, *J* = 8.0 Hz), 115.5 (d, *J* = 21.1 Hz), , 65.0, 49.2, 34.6, 28.8, -2.2.

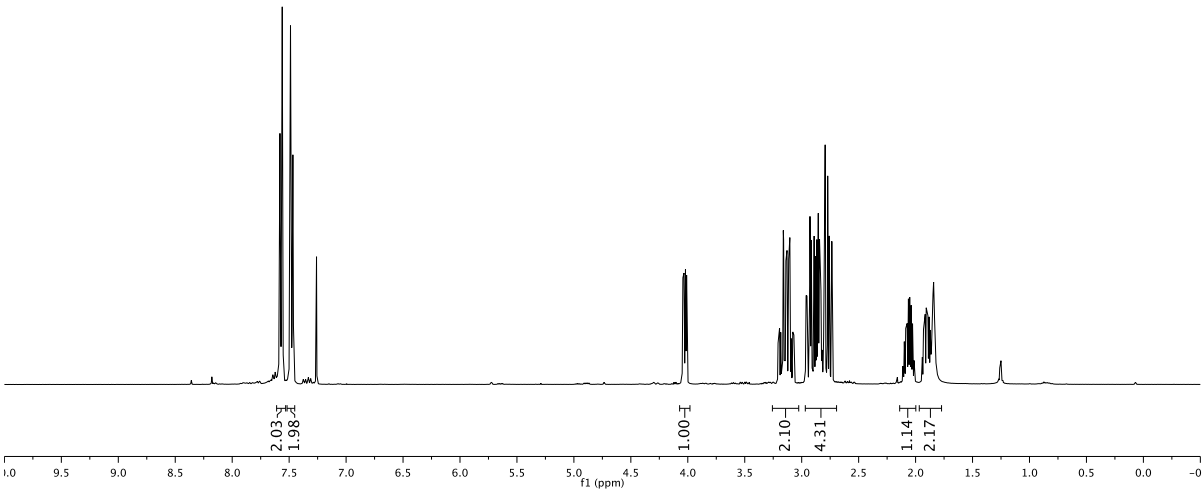
3-(4-(Trifluoromethyl)phenyl)-1,4-thiazepane (8a) (Scheme 2)

27-24-12-bhsieh.10.fid
Sample fly-08-132-CC-7-pCF3
group bode
PRO CDCl3 /opt/v bhsieh 27

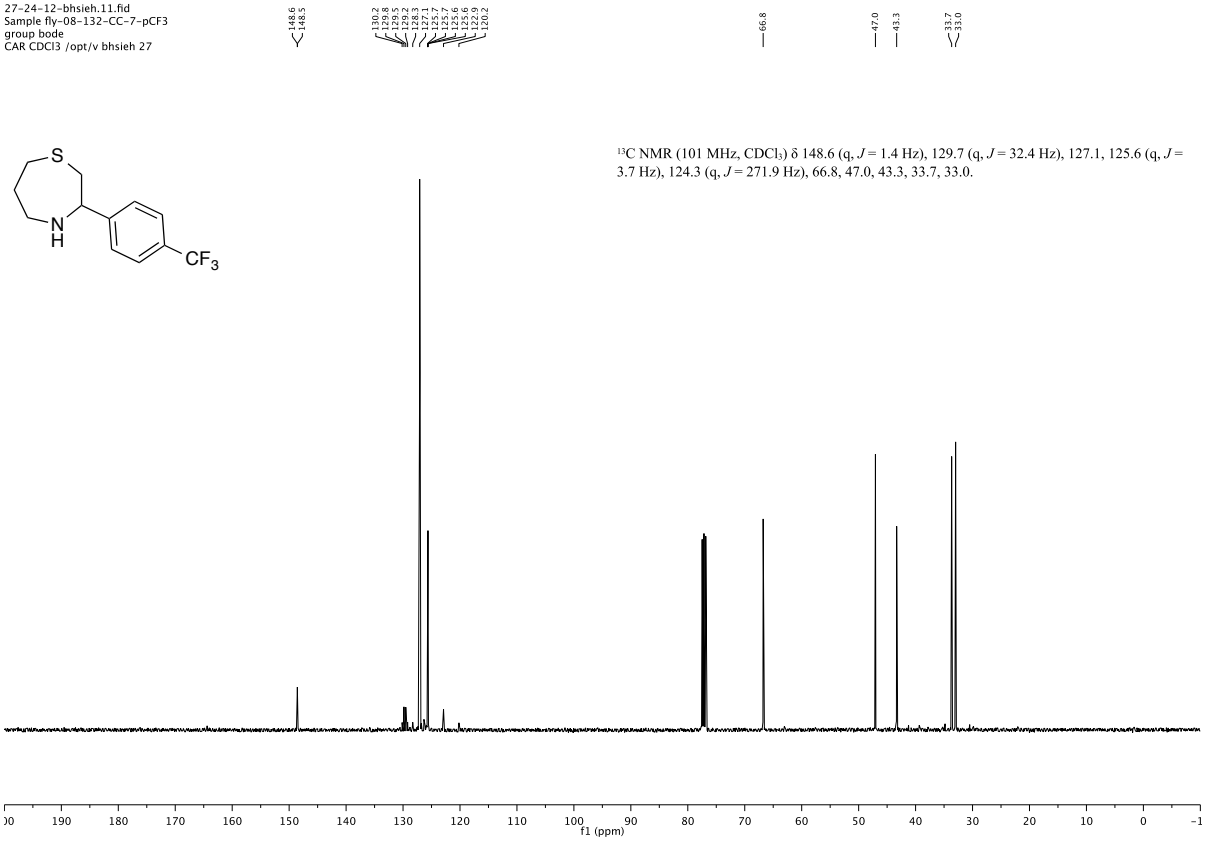


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58, 7.56, 7.49, 7.47, 4.04, 4.03, 4.02, 4.01, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.16, 3.15, 3.14, 3.13, 3.11, 3.10, 3.09, 3.08, 3.07, 2.96, 2.96, 2.95, 2.95, 2.93, 2.93, 2.93, 2.92, 2.92, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.85, 2.84, 2.84, 2.83, 2.83, 2.82, 2.82, 2.81, 2.81, 2.80, 2.79, 2.77, 2.76, 2.74, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.05, 2.04, 2.03, 2.03, 2.01, 1.94, 1.93, 1.93, 1.92, 1.92, 1.91, 1.90, 1.90, 1.89, 1.89, 1.88, 1.87, 1.87, 1.86, 1.86, 1.85, 1.84.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.1 Hz, 2 H), 7.48 (d, *J* = 8.1 Hz, 2 H), 4.03 (dd, *J* = 9.0, 3.9 Hz, 1 H), 3.24–3.05 (m, 2 H), 3.02–2.68 (m, 4 H), 2.06 (ddt, *J* = 14.4, 10.1, 5.1 Hz, 1 H), 1.97–1.78 (m, 2 H).



27-24-12-bhsieh.11.fid
Sample fly-08-132-CC-7-pCF3
group bode
CAR CDCl3 /opt/v bhsieh 27

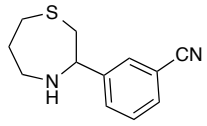


^{13}C NMR (101 MHz, $CDCl_3$) δ 148.6 (q, *J* = 1.4 Hz), 129.7 (q, *J* = 32.4 Hz), 127.1, 125.6 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 271.9 Hz), 66.8, 47.0, 43.3, 33.7, 33.0.

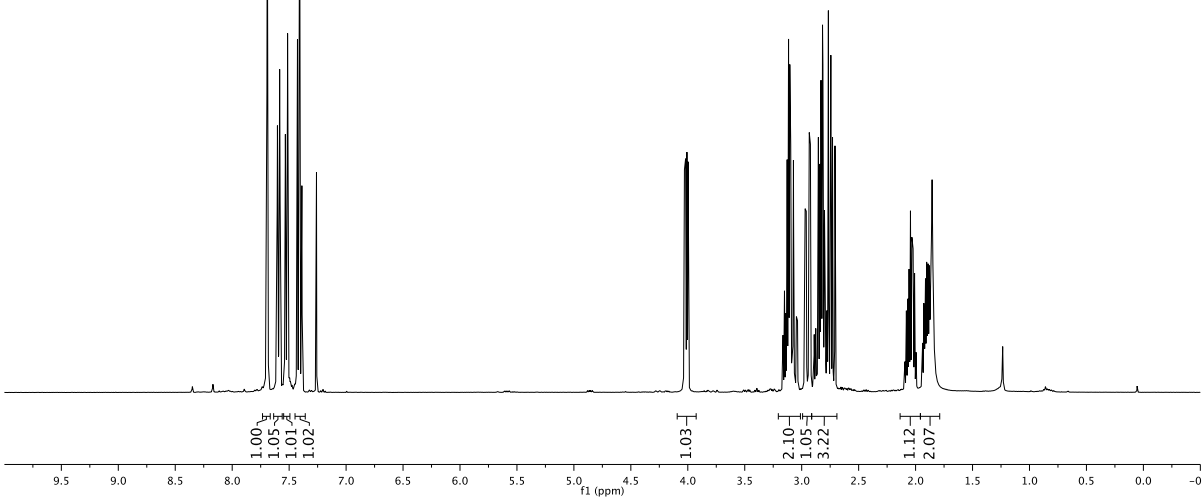
3-(1,4-Thiazepan-3-yl)benzonitrile (8b) (Scheme 2)

32-25-12-bhsieh.10.fid
Sample fly-08-114-CC-7-mCN
group bode
PRO CDCl3 /opt/v bhsieh 32

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70, 7.69, 7.69, 7.61, 7.60, 7.60, 7.59, 7.58, 7.58, 7.54, 7.53, 7.53, 7.52, 7.51, 7.51, 7.43, 7.41, 7.39, 4.03, 4.02, 4.01, 4.00, 3.16, 3.15, 3.15, 3.14, 3.13, 3.12, 3.11, 3.11, 3.10, 3.10, 3.08, 3.07, 3.06, 3.05, 3.04, 2.97, 2.97, 2.96, 2.96, 2.94, 2.93, 2.93, 2.92, 2.89, 2.88, 2.87, 2.85, 2.84, 2.83, 2.83, 2.82, 2.81, 2.81, 2.80, 2.80, 2.79, 2.79, 2.78, 2.78, 2.78, 2.77, 2.74, 2.73, 2.71, 2.09, 2.08, 2.07, 2.06, 2.05, 2.03, 2.02, 2.01, 2.00, 1.94, 1.93, 1.92, 1.92, 1.91, 1.91, 1.90, 1.89, 1.89, 1.88, 1.88, 1.87, 1.87, 1.86, 1.85, 1.84.

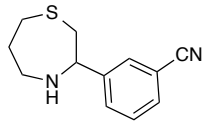


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 1.7 Hz, 1 H), 7.59 (dt, *J* = 7.8, 1.6 Hz, 1 H), 7.52 (dt, *J* = 7.7, 1.4 Hz, 1 H), 7.41 (t, *J* = 7.8 Hz, 1 H), 4.01 (dd, *J* = 8.7, 4.0 Hz, 1 H), 3.19–3.01 (m, 2 H), 2.95 (ddd, *J* = 14.5, 4.1, 0.9 Hz, 1 H), 2.91–2.67 (m, 3 H), 2.04 (ddq, *J* = 14.7, 10.2, 5.2 Hz, 1 H), 1.97–1.79 (m, 2 H).



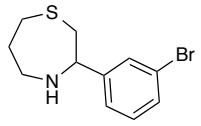
32-25-12-bhsieh.11.fid
Sample fly-08-114-CC-7-mCN
group bode
CAR CDCl3 /opt/v bhsieh 32

^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 131.3, 131.1, 130.5, 129.4, 118.9, 112.7, 65.7, 46.7, 43.0, 33.8, 33.1.



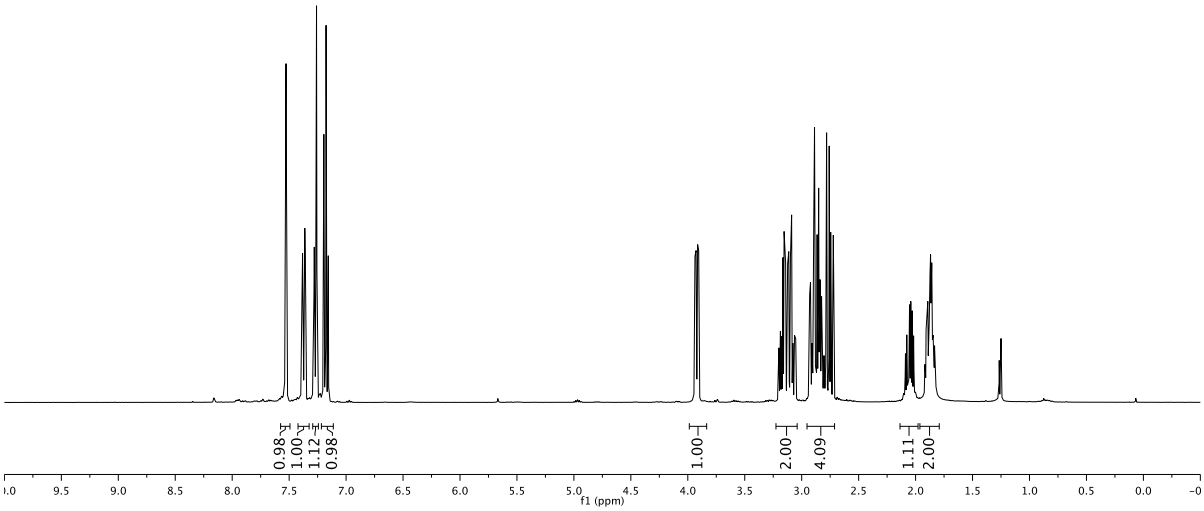
3-(3-Bromophenyl)-1,4-thiazepane (8c) (Scheme 2)

30-25-12-bhsieh.10.fid
Sample fly-08-097-7-mBr
group bode
PRO CDCl3 /opt/v bhsieh 30

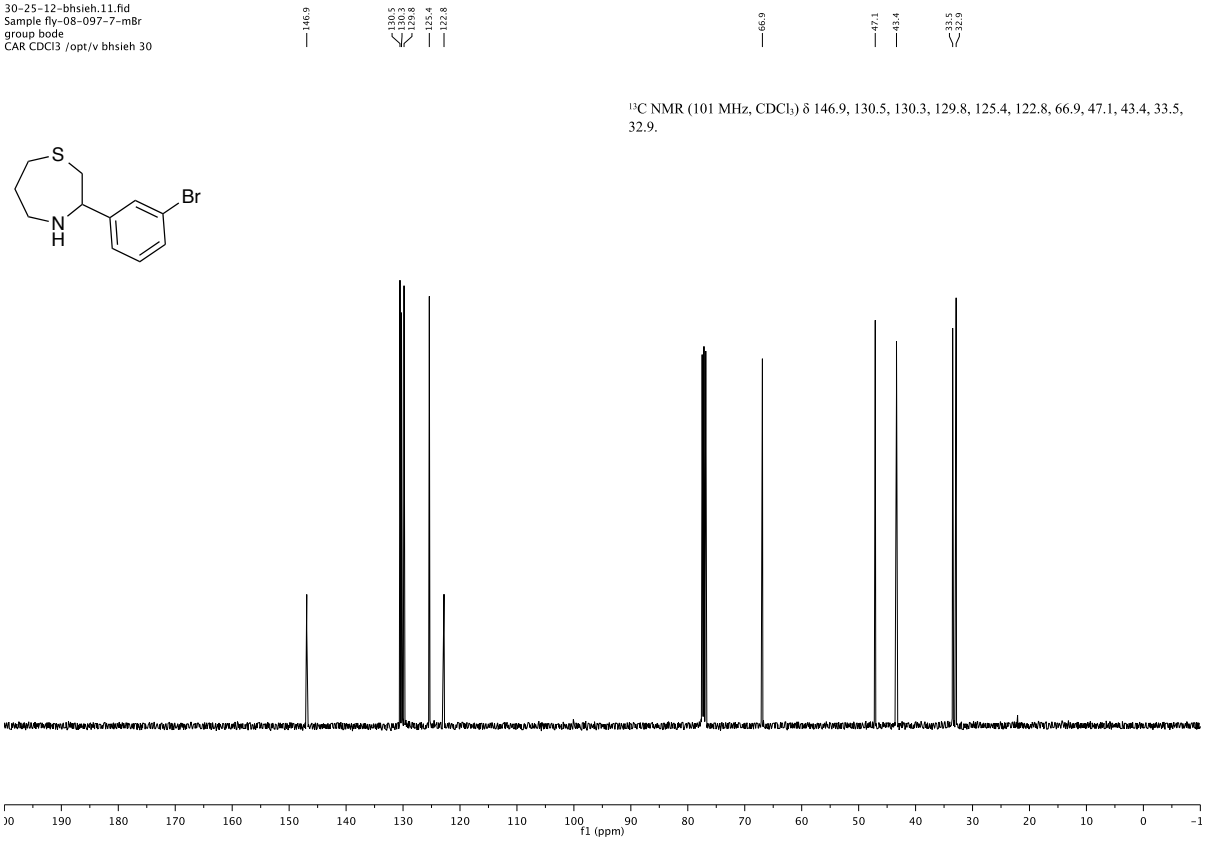


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53, 7.53, 7.52, 7.39, 7.38, 7.38, 7.38, 7.37, 7.36, 7.36, 7.36, 7.28, 7.28, 7.28, 7.26, 7.26, 7.26, 7.20, 7.18, 7.16, 3.94, 3.93, 3.91, 3.90, 3.20, 3.19, 3.19, 3.18, 3.16, 3.15, 3.15, 3.14, 3.12, 3.11, 3.10, 3.09, 3.08, 3.06, 3.05, 2.93, 2.93, 2.92, 2.92, 2.91, 2.90, 2.90, 2.89, 2.89, 2.88, 2.87, 2.86, 2.85, 2.85, 2.84, 2.84, 2.84, 2.83, 2.83, 2.82, 2.82, 2.81, 2.80, 2.80, 2.79, 2.79, 2.78, 2.76, 2.75, 2.72, 2.10, 2.09, 2.09, 2.08, 2.07, 2.06, 2.06, 2.05, 2.04, 2.04, 2.03, 2.03, 2.02, 2.01, 2.00, 1.92, 1.91, 1.90, 1.90, 1.89, 1.88, 1.88, 1.87, 1.87, 1.86, 1.86, 1.85, 1.84, 1.84, 1.83, 1.82.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (t, *J* = 1.9 Hz, 1 H), 7.37 (ddd, *J* = 7.9, 2.1, 1.1 Hz, 1 H), 7.33–7.23 (m, 1 H), 7.18 (t, *J* = 7.8 Hz, 1 H), 3.92 (dd, *J* = 9.2, 3.8 Hz, 1 H), 3.23–3.03 (m, 2 H), 2.96–2.70 (m, 4 H), 2.13–1.97 (m, 1 H), 1.87 (dddt, *J* = 13.8, 10.1, 6.2, 4.0 Hz, 2 H).



30-25-12-bhsieh.11.fid
Sample fly-08-097-7-mBr
group bode
CAR CDCl3 /opt/v bhsieh 30



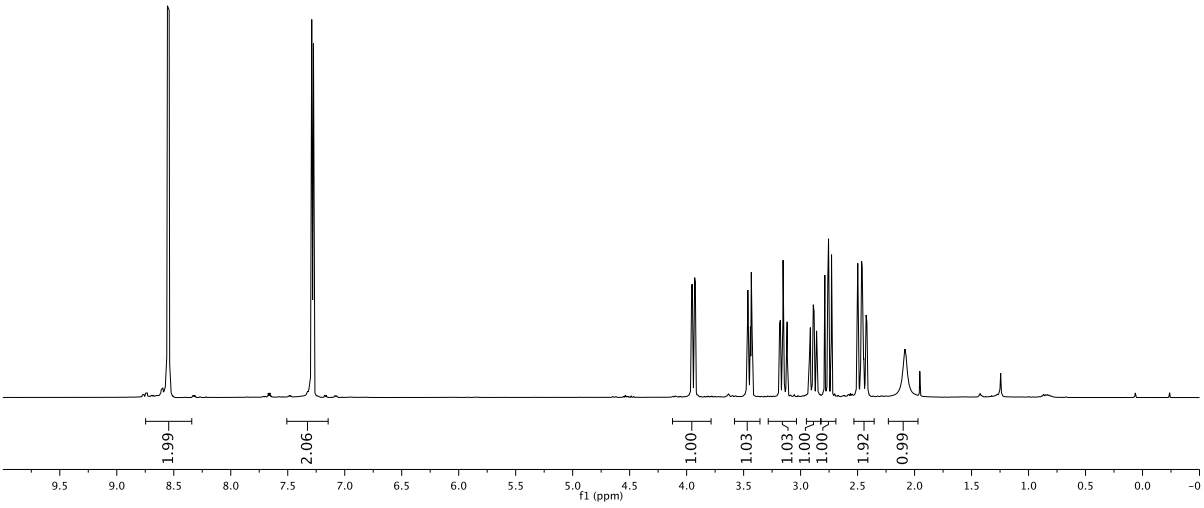
^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 130.5, 130.3, 129.8, 125.4, 122.8, 66.9, 47.1, 43.4, 33.5, 32.9.

3-(Pyridin-4-yl)thiomorpholine (6k) (Scheme 3)

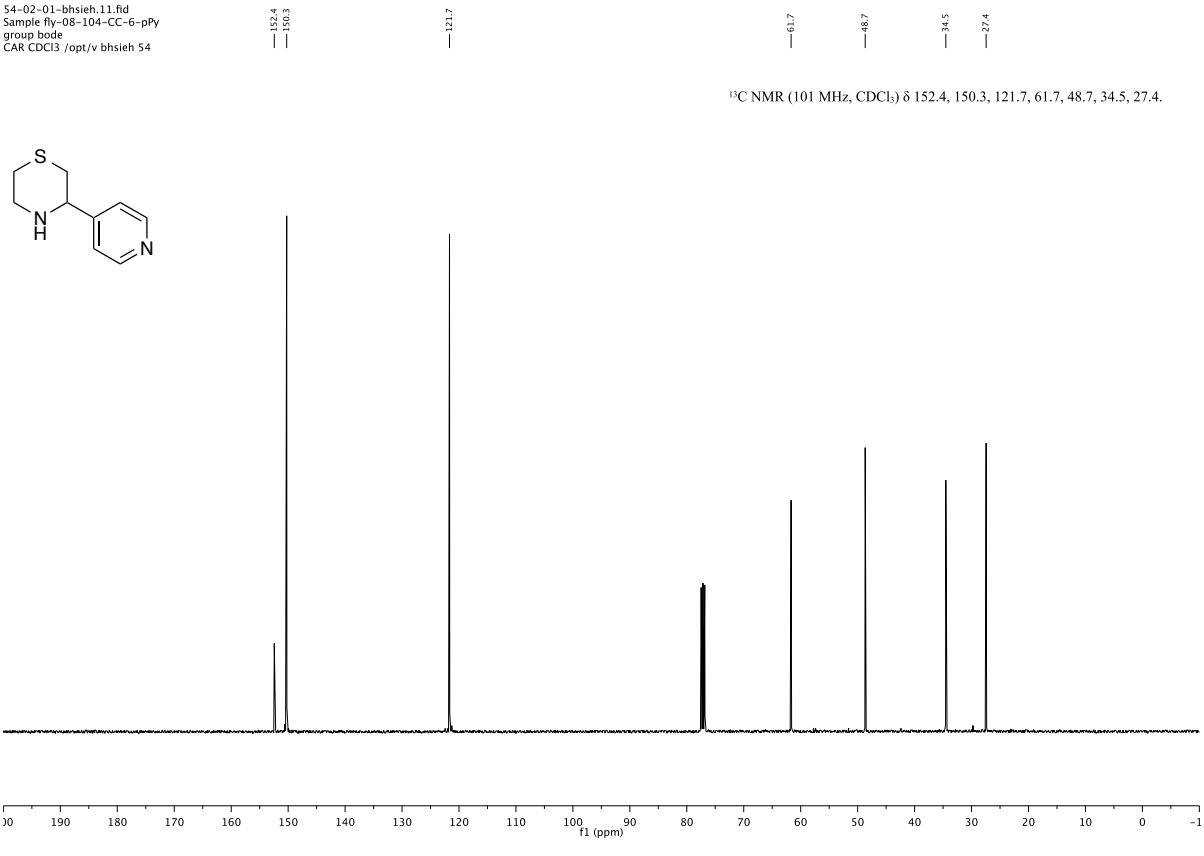
54-02-01-bhsieh.10.fid
Sample fly-08-104-CC-6-pPy
group bode
PRO CDCl3 /opt/v bhsieh 54

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56, 8.55, 8.54, 8.54, 7.29, 7.28, 7.28, 7.27, 3.96, 3.95, 3.93, 3.92, 3.47, 3.46, 3.46, 3.44, 3.43, 3.42, 3.18, 3.18, 3.15, 3.15, 3.12, 3.12, 2.92, 2.91, 2.89, 2.89, 2.88, 2.88, 2.86, 2.85, 2.79, 2.76, 2.75, 2.73, 2.50, 2.50, 2.49, 2.47, 2.47, 2.46, 2.46, 2.45, 2.45, 2.43, 2.42, 2.42, 2.08.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.79–8.36 (m, 2 H), 7.39–7.10 (m, 2 H), 3.94 (dd, *J* = 10.5, 2.3 Hz, 1 H), 3.45 (dt, *J* = 12.2, 3.1 Hz, 1 H), 3.15 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.89 (ddd, *J* = 13.1, 11.7, 3.0 Hz, 1 H), 2.76 (dd, *J* = 13.1, 10.5 Hz, 1 H), 2.46 (ddt, *J* = 17.8, 10.7, 2.4 Hz, 2 H), 2.08 (br, 1 H).

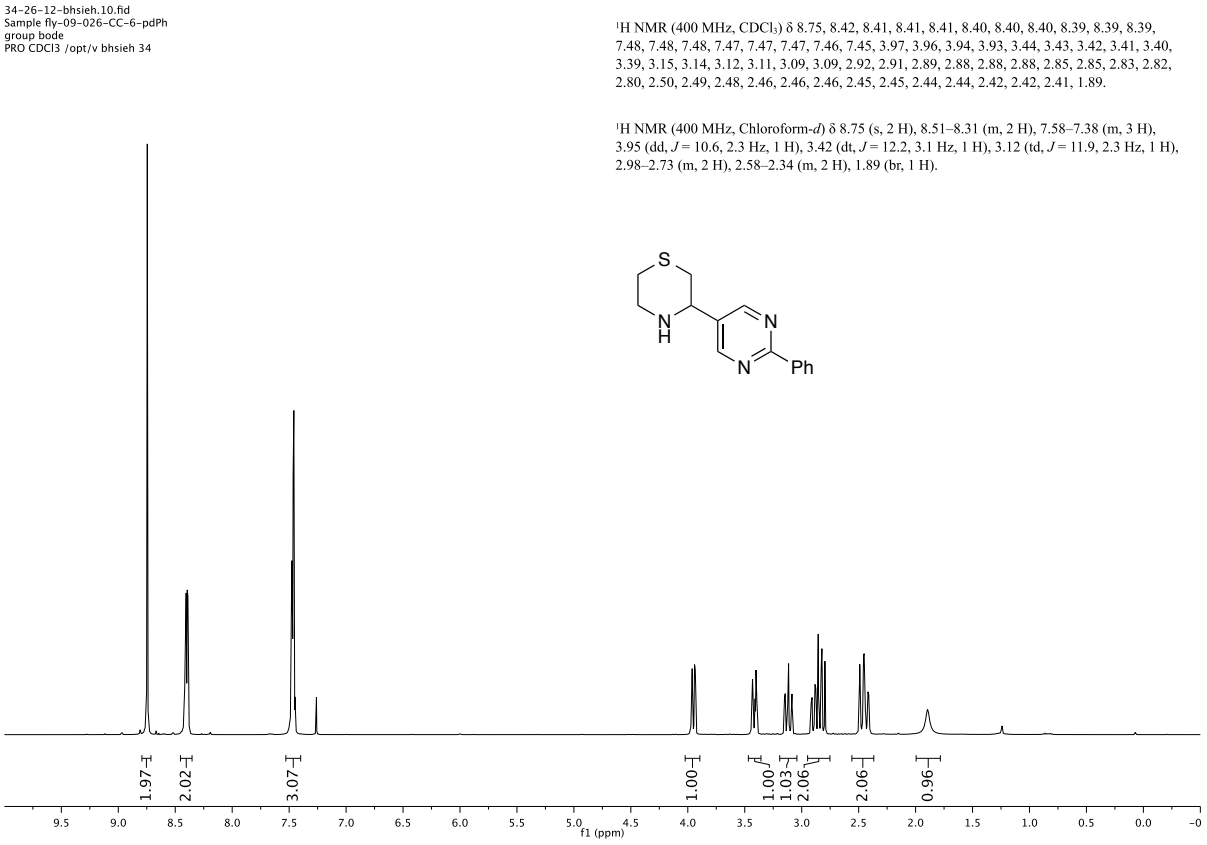


54-02-01-bhsieh.11.fid
Sample fly-08-104-CC-6-pPy
group bode
CAR CDCl3 /opt/v bhsieh 54



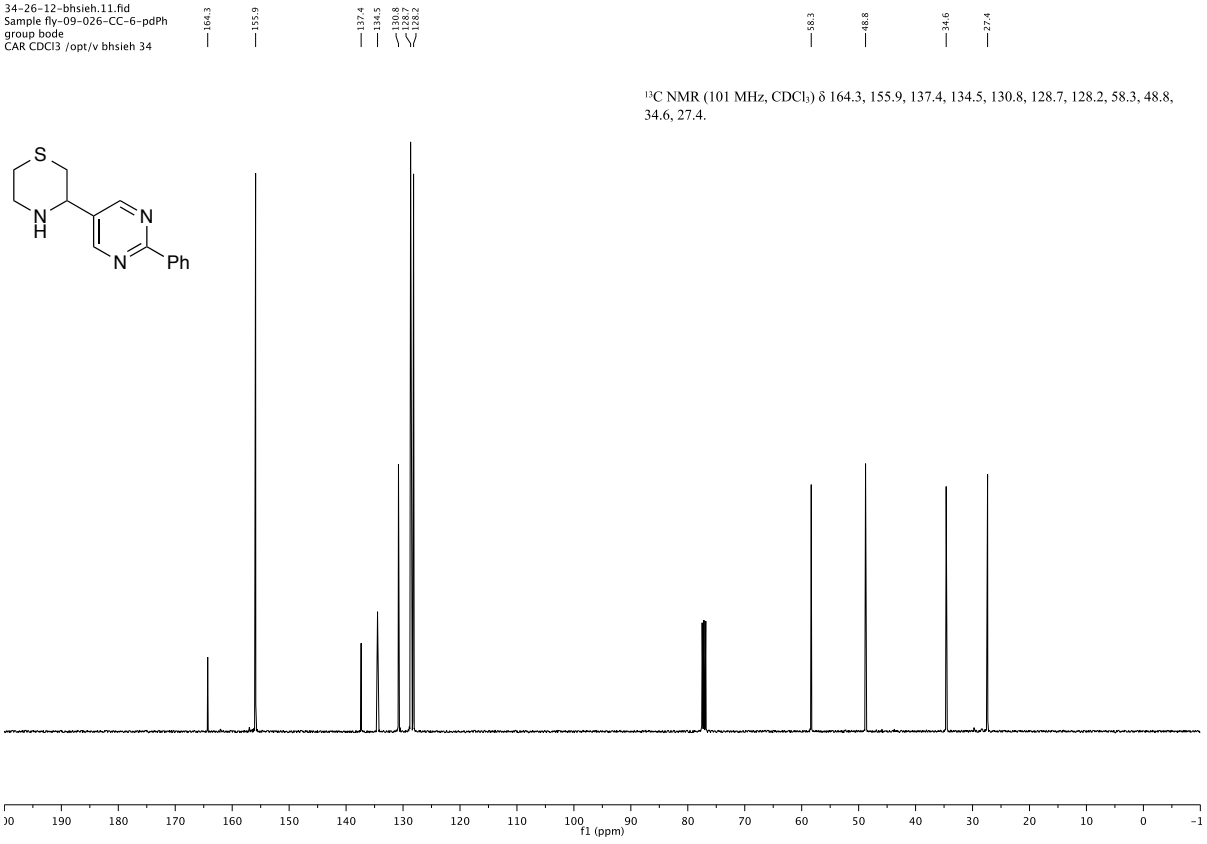
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 150.3, 121.7, 61.7, 48.7, 34.5, 27.4.

3-(2-Phenylpyrimidin-5-yl)thiomorpholine (6l) (Scheme 3)



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75, 8.42, 8.41, 8.41, 8.41, 8.40, 8.40, 8.40, 8.39, 8.39, 8.39, 7.48, 7.48, 7.48, 7.47, 7.47, 7.47, 7.46, 7.45, 3.97, 3.96, 3.94, 3.93, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.15, 3.14, 3.12, 3.11, 3.09, 3.09, 2.92, 2.91, 2.89, 2.88, 2.88, 2.88, 2.85, 2.85, 2.83, 2.82, 2.80, 2.50, 2.49, 2.48, 2.46, 2.46, 2.46, 2.45, 2.45, 2.44, 2.44, 2.42, 2.42, 2.41, 1.89.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (s, 2 H), 8.51–8.31 (m, 2 H), 7.58–7.38 (m, 3 H), 3.95 (dd, *J* = 10.6, 2.3 Hz, 1 H), 3.42 (dt, *J* = 12.2, 3.1 Hz, 1 H), 3.12 (td, *J* = 11.9, 2.3 Hz, 1 H), 2.98–2.73 (m, 2 H), 2.58–2.34 (m, 2 H), 1.89 (br, 1 H).

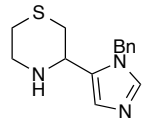


^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 155.9, 137.4, 134.5, 130.8, 128.7, 128.2, 58.3, 48.8, 34.6, 27.4.

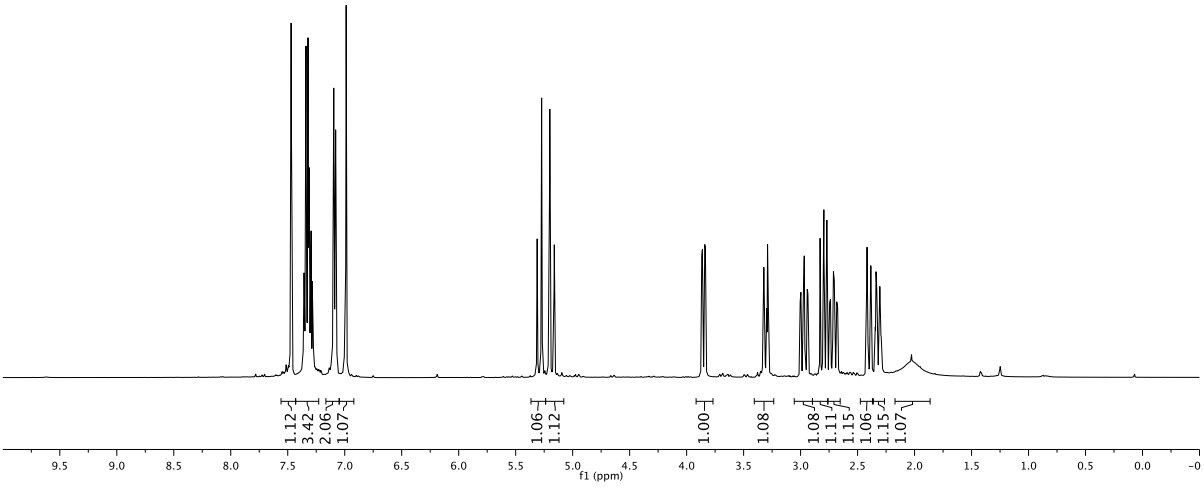
3-(1-Benzyl-1*H*-imidazol-5-yl)thiomorpholine (6m) (Scheme 3)

56-02-01-bhsieh.10.fid
Sample fly-08-144-CC-6-imBn
group bode
PRO CDCl3 /opt/v bhsieh 56

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47, 7.47, 7.36, 7.36, 7.35, 7.35, 7.34, 7.33, 7.33, 7.32, 7.32, 7.31, 7.31, 7.30, 7.29, 7.28, 7.28, 7.28, 7.10, 7.10, 7.09, 7.08, 7.08, 7.08, 6.99, 5.31, 5.27, 5.20, 5.16, 3.87, 3.86, 3.84, 3.84, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.00, 3.00, 2.97, 2.97, 2.97, 2.96, 2.94, 2.94, 2.83, 2.80, 2.80, 2.77, 2.75, 2.74, 2.72, 2.71, 2.71, 2.70, 2.68, 2.68, 2.42, 2.42, 2.41, 2.39, 2.38, 2.38, 2.35, 2.34, 2.33, 2.33, 2.31, 2.31, 2.30, 2.29, 2.03.

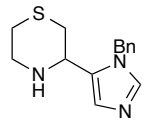


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 1.1 Hz, 1 H), 7.38–7.26 (m, 3 H), 7.12–7.06 (m, 2 H), 6.99 (s, 1 H), 5.29 (d, *J* = 15.7 Hz, 1 H), 5.18 (d, *J* = 15.7 Hz, 1 H), 3.85 (dd, *J* = 10.5, 2.3 Hz, 1 H), 3.31 (dt, *J* = 13.0, 3.0 Hz, 1 H), 2.97 (ddd, *J* = 12.9, 11.6, 2.5 Hz, 1 H), 2.80 (dd, *J* = 13.2, 10.5 Hz, 1 H), 2.71 (ddd, *J* = 13.4, 11.7, 3.0 Hz, 1 H), 2.40 (dt, *J* = 13.2, 2.1 Hz, 1 H), 2.32 (dq, *J* = 13.3, 2.5 Hz, 1 H), 2.03 (br, 1 H).



56-02-01-bhsieh.11.fid
Sample fly-08-144-CC-6-imBn
group bode
CAR CDCl3 /opt/v bhsieh 56

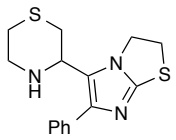
^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 136.5, 133.5, 129.1, 128.2, 126.8, 126.7, 52.8, 48.9, 48.1, 31.9, 27.3.



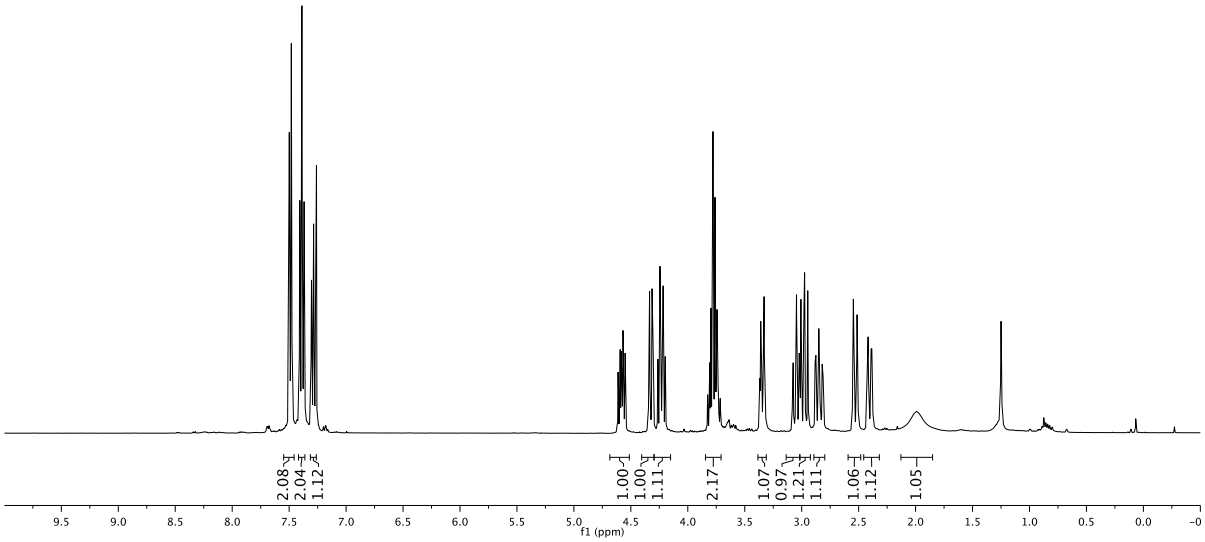
6-Phenyl-5-(thiomorpholin-3-yl)-2,3-dihydroimidazo[2,1-*b*]thiazole (6n) (Scheme 3)

2-03-01-bhsieh.10.fid
Sample fly-08-150-CC-6-Phimidazolethiazole
group bode

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50, 7.50, 7.49, 7.48, 7.48, 7.48, 7.47, 7.41, 7.40, 7.39, 7.38, 7.37, 7.37, 7.36, 7.31, 7.30, 7.30, 7.30, 7.29, 7.29, 7.28, 7.27, 7.27, 4.61, 4.60, 4.59, 4.58, 4.58, 4.57, 4.57, 4.55, 4.34, 4.34, 4.31, 4.31, 4.26, 4.24, 4.24, 4.23, 4.22, 4.20, 3.83, 3.81, 3.80, 3.79, 3.78, 3.76, 3.76, 3.75, 3.74, 3.73, 3.73, 3.72, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.08, 3.07, 3.05, 3.05, 3.02, 3.02, 3.01, 2.98, 2.97, 2.95, 2.88, 2.88, 2.85, 2.85, 2.85, 2.84, 2.82, 2.81, 2.55, 2.55, 2.54, 2.52, 2.51, 2.51, 2.43, 2.42, 2.42, 2.41, 2.40, 2.39, 2.38, 2.38, 1.99.

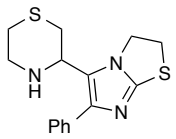


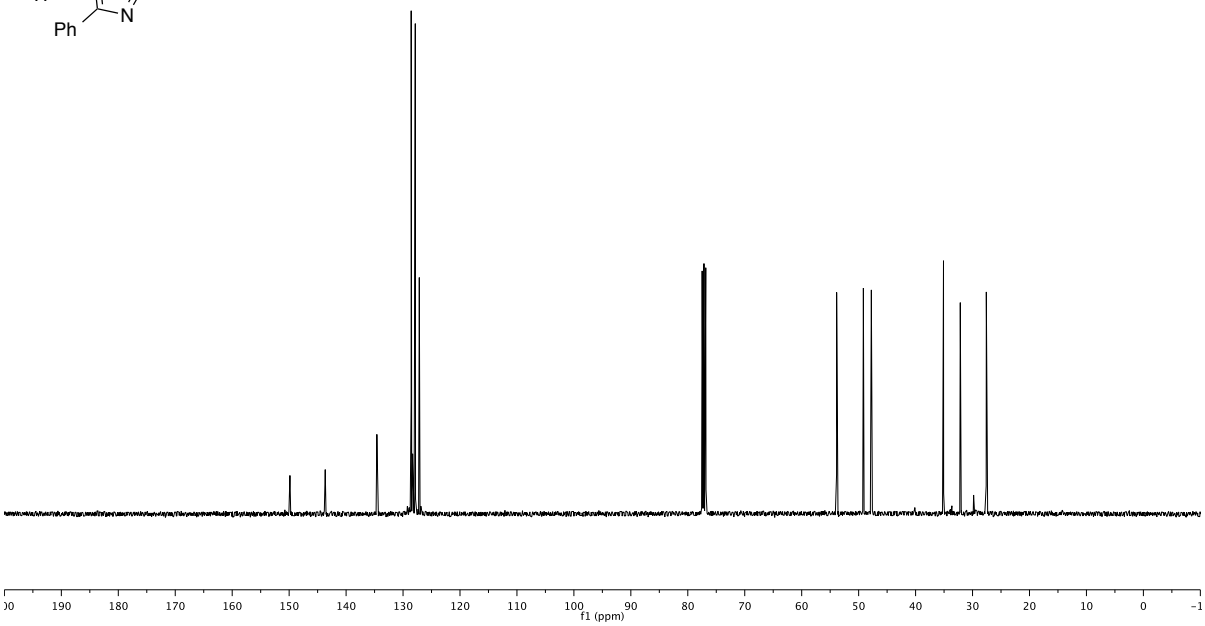
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54–7.45 (m, 2 H), 7.39 (dd, *J* = 8.5, 6.9 Hz, 2 H), 7.32–7.22 (m, 1 H), 4.58 (ddd, *J* = 11.1, 7.5, 6.1 Hz, 1 H), 4.32 (dd, *J* = 11.0, 2.4 Hz, 1 H), 4.23 (dt, *J* = 11.1, 7.6 Hz, 1 H), 3.87–3.70 (m, 2 H), 3.35 (dt, *J* = 11.8, 3.1 Hz, 1 H), 3.05 (td, *J* = 11.7, 2.2 Hz, 1 H), 2.98 (dd, *J* = 13.1, 10.9 Hz, 1 H), 2.85 (ddd, *J* = 13.1, 11.7, 2.9 Hz, 1 H), 2.53 (dt, *J* = 13.1, 2.3 Hz, 1 H), 2.40 (dq, *J* = 13.2, 2.5 Hz, 1 H), 1.99 (br, 1 H).



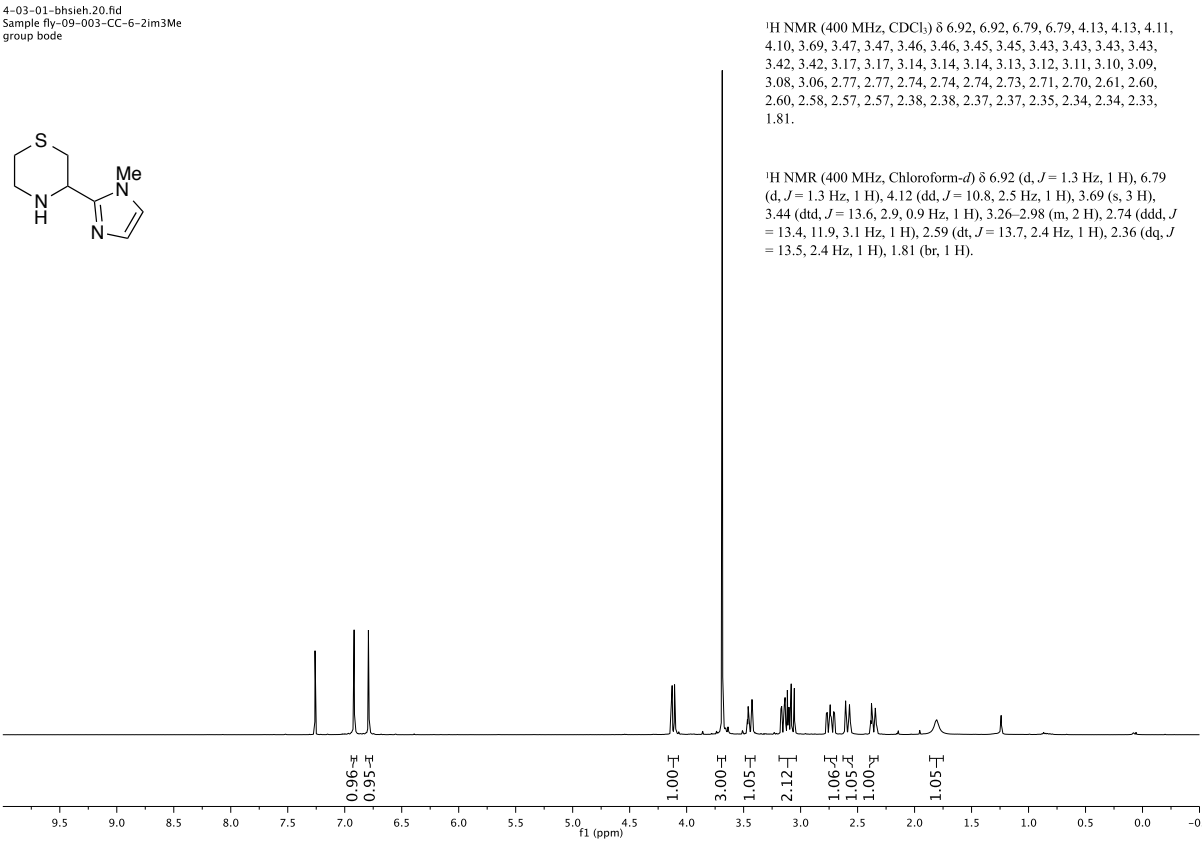
2-03-01-bhsieh.12.fid
Sample fly-08-150-CC-6-Phimidazolethiazole
group bode

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 143.7, 134.6, 128.6, 128.3, 127.9, 127.1, 53.9, 49.2, 47.8, 35.1, 32.2, 27.6.



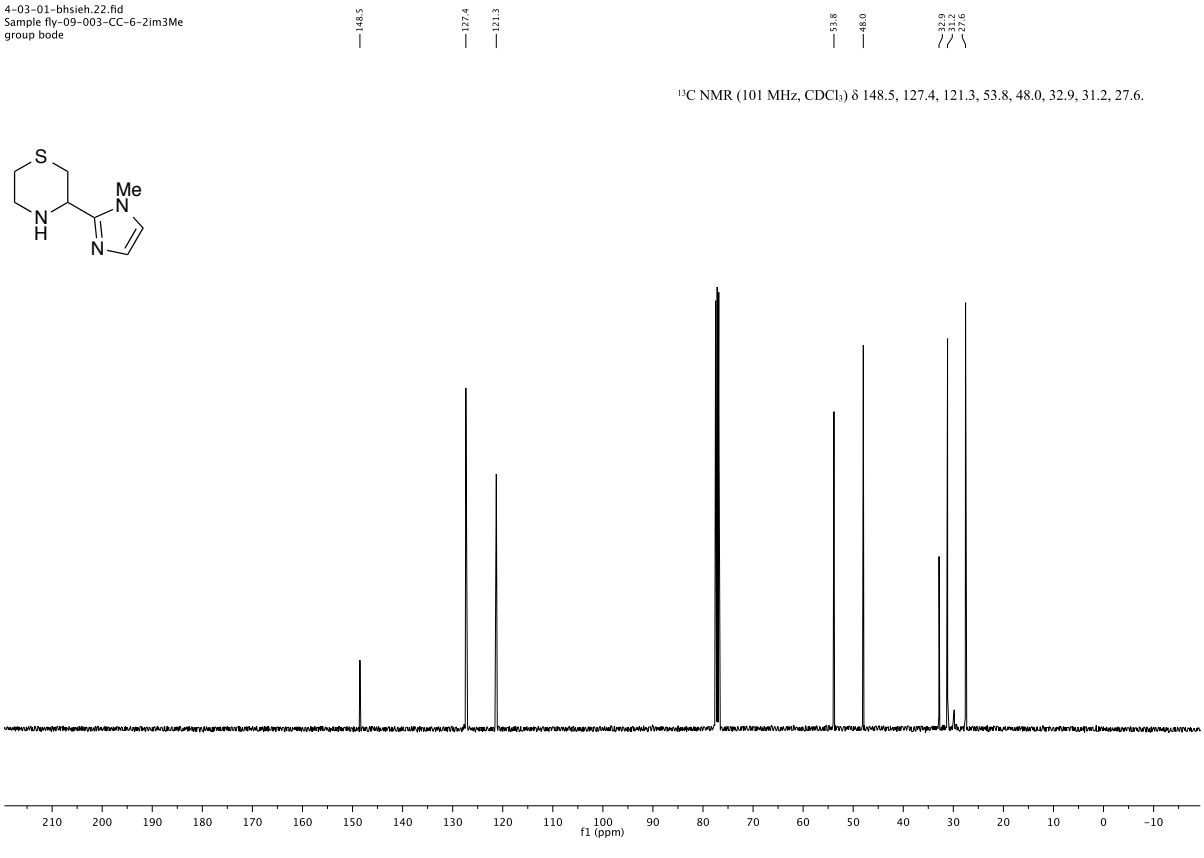


3-(1-Methyl-1*H*-imidazol-2-yl)thiomorpholine (6o) (Scheme 3)



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92, 6.92, 6.79, 6.79, 4.13, 4.13, 4.11, 4.10, 3.69, 3.47, 3.47, 3.46, 3.46, 3.45, 3.45, 3.43, 3.43, 3.43, 3.43, 3.42, 3.42, 3.17, 3.17, 3.14, 3.14, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.06, 2.77, 2.77, 2.74, 2.74, 2.74, 2.73, 2.71, 2.70, 2.61, 2.60, 2.60, 2.58, 2.57, 2.57, 2.38, 2.38, 2.37, 2.37, 2.35, 2.34, 2.34, 2.33, 1.81.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.92 (d, *J* = 1.3 Hz, 1 H), 6.79 (d, *J* = 1.3 Hz, 1 H), 4.12 (dd, *J* = 10.8, 2.5 Hz, 1 H), 3.69 (s, 3 H), 3.44 (dtd, *J* = 13.6, 2.9, 0.9 Hz, 1 H), 3.26–2.98 (m, 2 H), 2.74 (ddd, *J* = 13.4, 11.9, 3.1 Hz, 1 H), 2.59 (dt, *J* = 13.7, 2.4 Hz, 1 H), 2.36 (dq, *J* = 13.5, 2.4 Hz, 1 H), 1.81 (br, 1 H).



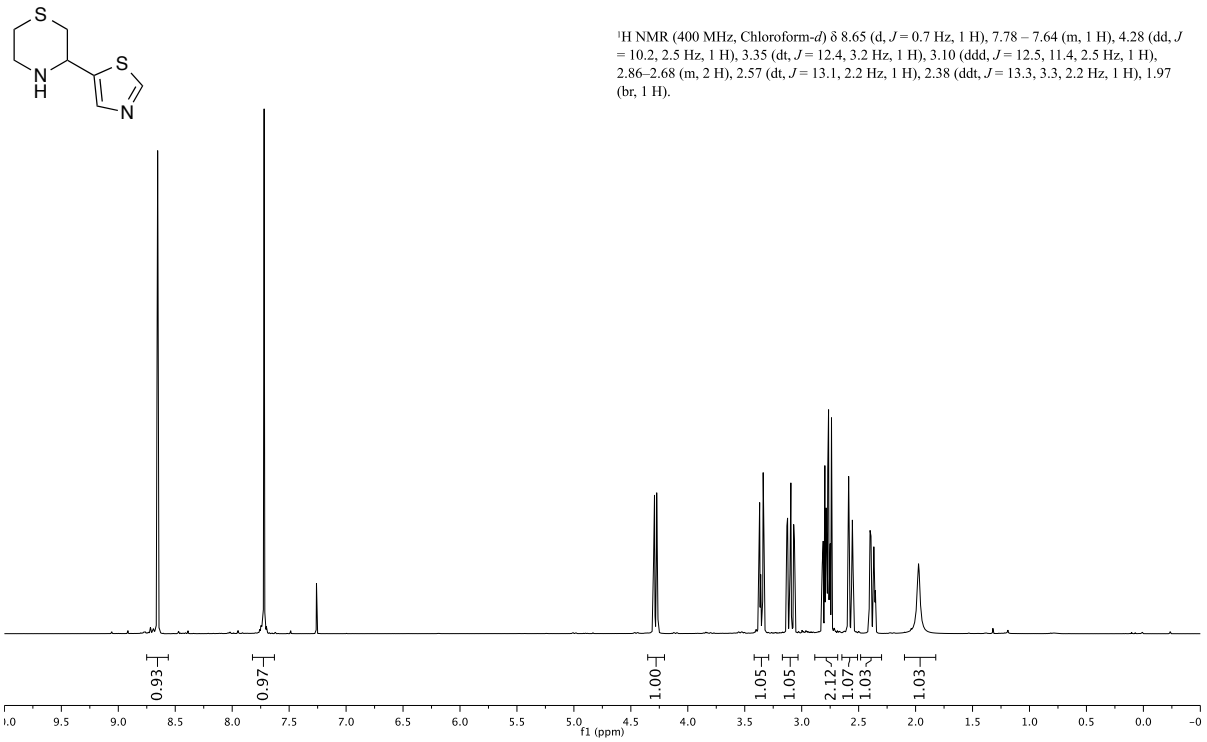
^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 127.4, 121.3, 53.8, 48.0, 32.9, 31.2, 27.6.

3-(Thiazol-5-yl)thiomorpholine (6p) (Scheme 3)

42-16-02-bhsieh.10.fid
Sample fly-08-156-CC
group bode

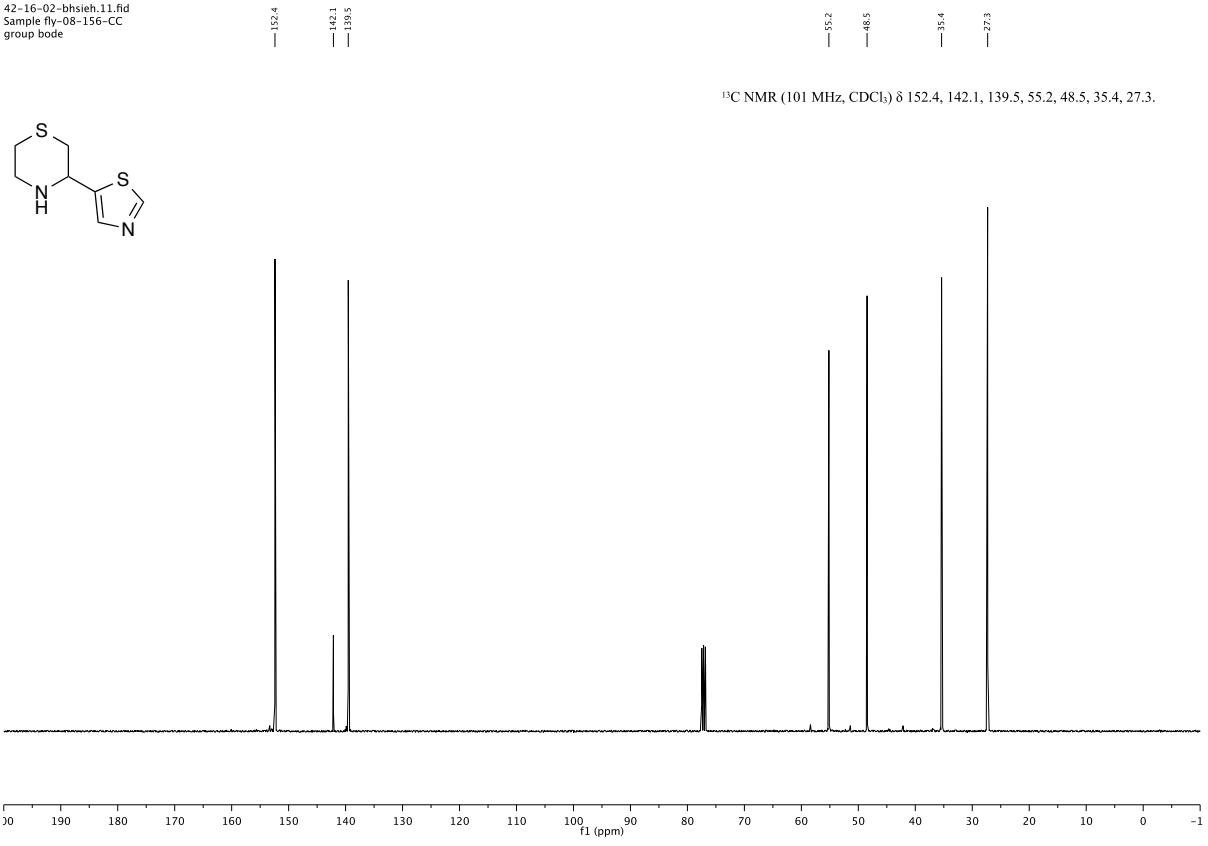
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66, 8.65, 7.72, 7.72, 7.72, 4.30, 4.29, 4.27, 4.27, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.13, 3.12, 3.10, 3.10, 3.10, 3.09, 3.07, 3.06, 2.82, 2.81, 2.80, 2.79, 2.79, 2.78, 2.78, 2.77, 2.76, 2.76, 2.75, 2.74, 2.59, 2.59, 2.58, 2.56, 2.55, 2.55, 2.41, 2.40, 2.40, 2.39, 2.39, 2.39, 2.37, 2.37, 2.36, 2.36, 2.36, 2.35, 1.97.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 0.7 Hz, 1 H), 7.78 – 7.64 (m, 1 H), 4.28 (dd, *J* = 10.2, 2.5 Hz, 1 H), 3.35 (dt, *J* = 12.4, 3.2 Hz, 1 H), 3.10 (ddd, *J* = 12.5, 11.4, 2.5 Hz, 1 H), 2.86–2.68 (m, 2 H), 2.57 (dt, *J* = 13.1, 2.2 Hz, 1 H), 2.38 (ddt, *J* = 13.3, 3.3, 2.2 Hz, 1 H), 1.97 (br, 1 H).



42-16-02-bhsieh.11.fid
Sample fly-08-156-CC
group bode

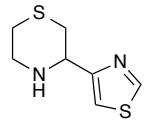
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4, 142.1, 139.5, 55.2, 48.5, 35.4, 27.3.



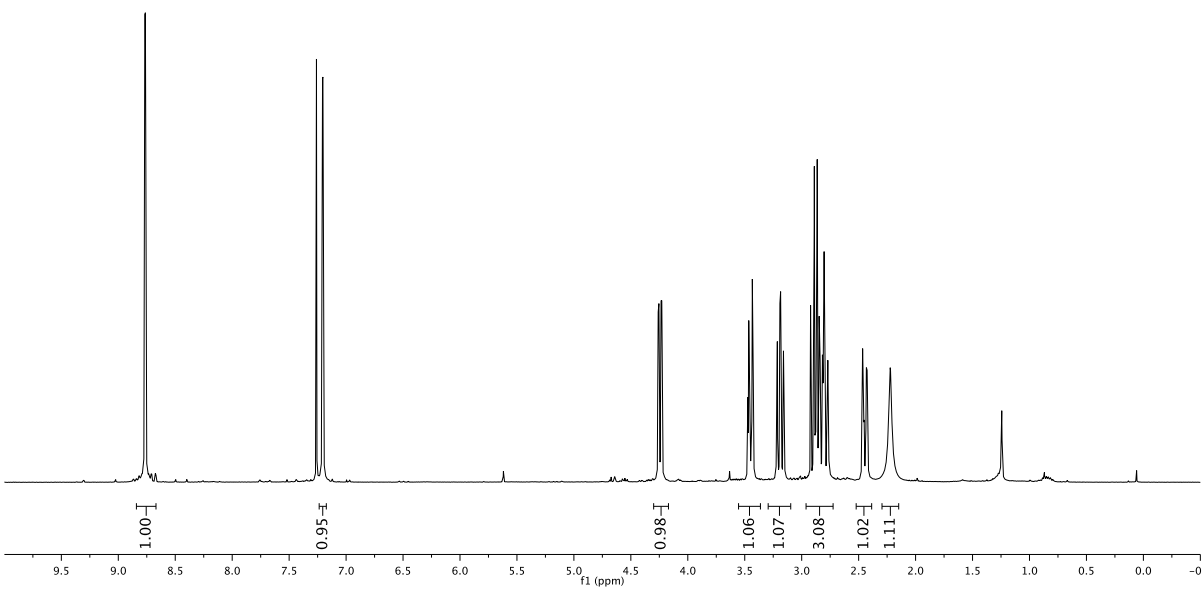
3-(Thiazol-4-yl)thiomorpholine (6q) (Scheme 3)

3-26-12-bhsieh.10.fid
Sample fly-09-011-CC-6-NCSC
group bode

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77, 8.76, 7.21, 7.21, 7.20, 7.20, 4.26, 4.26, 4.25, 4.25, 4.24, 4.23, 4.23, 4.23, 3.47, 3.46, 3.46, 3.44, 3.43, 3.43, 3.22, 3.21, 3.19, 3.19, 3.19, 3.18, 3.16, 3.15, 2.92, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.85, 2.84, 2.84, 2.82, 2.81, 2.80, 2.80, 2.78, 2.77, 2.76, 2.47, 2.47, 2.46, 2.46, 2.46, 2.45, 2.44, 2.43, 2.43, 2.43, 2.42, 2.42, 2.22.



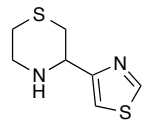
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 (d, *J* = 2.0 Hz, 1 H), 7.21 (dd, *J* = 2.0, 0.8 Hz, 1 H), 4.24 (ddd, *J* = 10.1, 2.7, 0.8 Hz, 1 H), 3.45 (dt, *J* = 12.6, 3.2 Hz, 1 H), 3.19 (ddd, *J* = 12.5, 11.5, 2.5 Hz, 1 H), 2.99–2.71 (m, 4 H), 2.45 (ddt, *J* = 13.3, 3.1, 2.2 Hz, 1 H), 2.22 (br, 1 H).

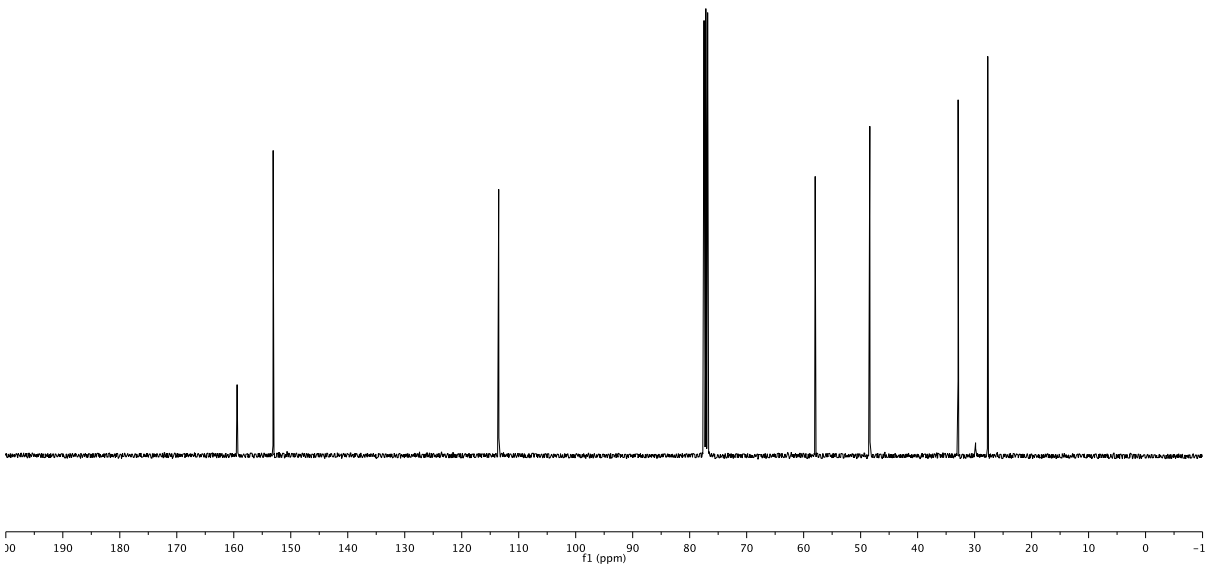


3-26-12-bhsieh.11.fid
Sample fly-09-011-CC-6-NCSC
group bode

159.4
153.1
113.5
58.0
48.4
32.9
27.7

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4, 153.1, 113.5, 58.0, 48.4, 32.9, 27.7.



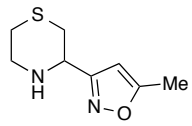


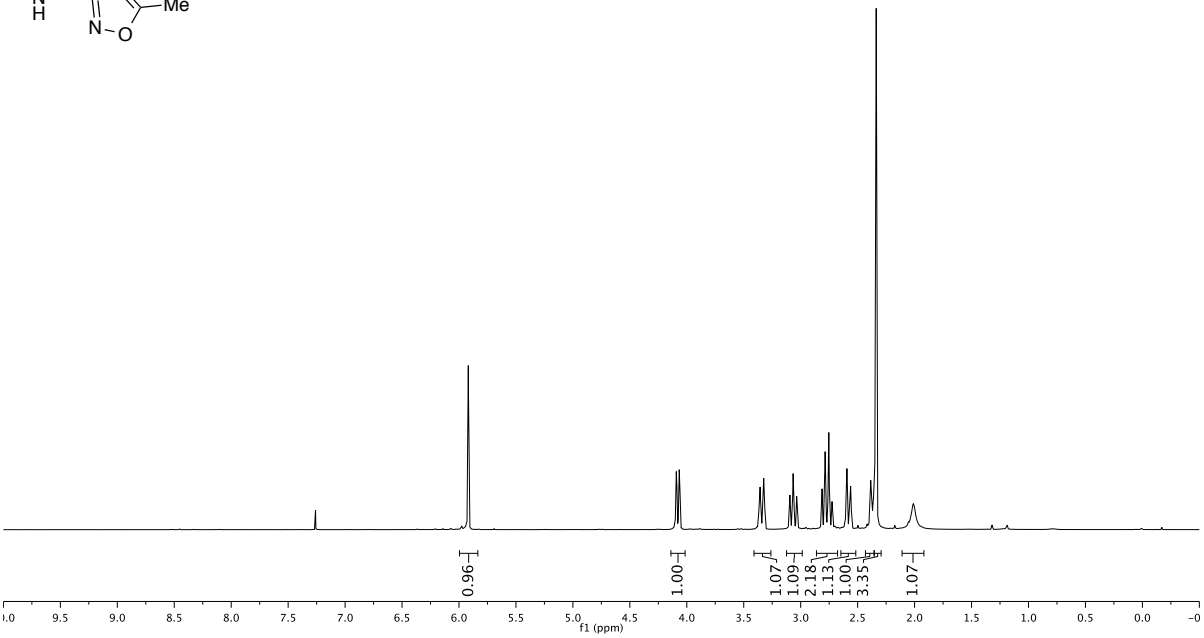
5-Methyl-3-(thiomorpholin-3-yl)isoxazole (6r) (Scheme 3)

35-15-02-bhsieh3.10.fid
Sample fly-08-147-CC
group bode
PRO CDCl3 /opt/v bhsieh 38

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92, 5.92, 5.92, 4.10, 4.09, 4.09, 4.07, 4.07, 4.06, 3.37, 3.36, 3.36, 3.35, 3.34, 3.33, 3.32, 3.32, 3.10, 3.09, 3.09, 3.07, 3.07, 3.06, 3.06, 3.06, 3.04, 3.04, 3.03, 2.82, 2.81, 2.79, 2.79, 2.78, 2.78, 2.76, 2.75, 2.75, 2.75, 2.73, 2.72, 2.72, 2.72, 2.60, 2.60, 2.59, 2.59, 2.57, 2.57, 2.56, 2.56, 2.40, 2.39, 2.39, 2.38, 2.38, 2.37, 2.36, 2.36, 2.35, 2.35, 2.34, 2.34, 2.33, 2.01.

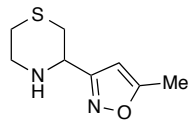
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.92 (s, 1 H), 4.08 (dt, *J* = 10.4, 2.1 Hz, 1 H), 3.34 (dt, *J* = 12.5, 3.1 Hz, 1 H), 3.14–3.01 (m, 1 H), 2.77 (tdd, *J* = 14.4, 10.8, 2.3 Hz, 2 H), 2.58 (dq, *J* = 13.2, 2.0 Hz, 1 H), 2.37 (ddd, *J* = 11.4, 3.9, 1.9 Hz, 1 H), 2.34 (s, 2 H), 2.01 (s, 1 H).



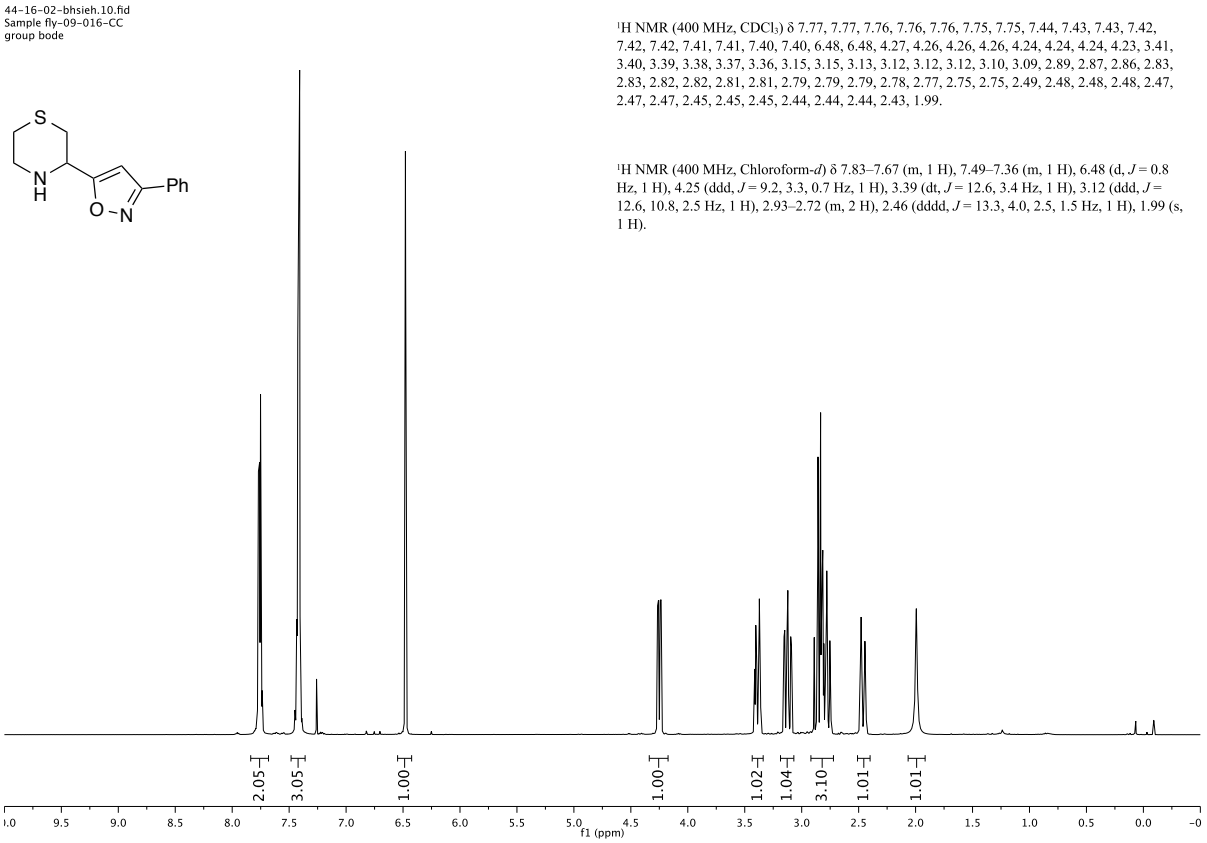


35-15-02-bhsieh3.11.fid
Sample fly-08-147-CC
group bode
CAR CDCl3 /opt/v bhsieh 38

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.6, 165.5, 99.6, 54.2, 47.8, 32.1, 27.4, 12.3.

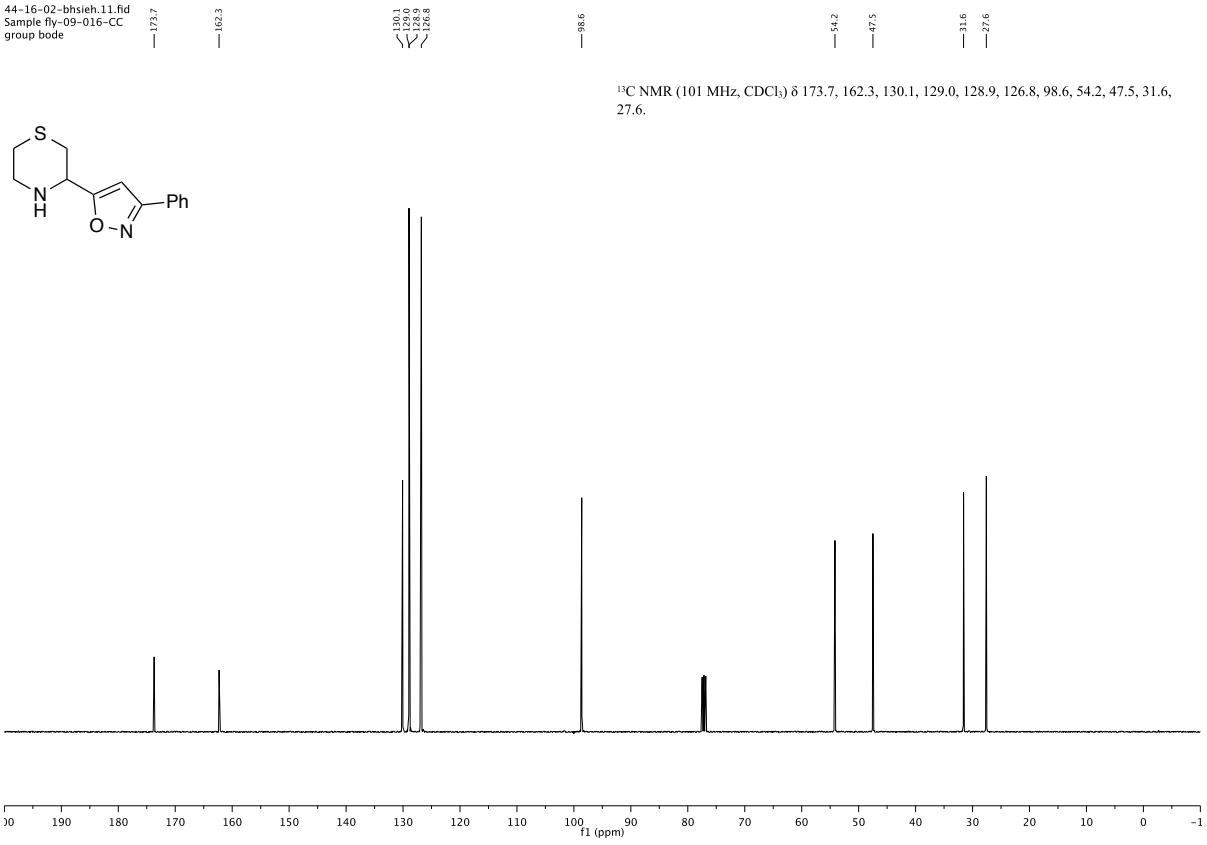


3-Phenyl-5-(thiomorpholin-3-yl)isoxazole (6s) (Scheme 3)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77, 7.77, 7.76, 7.76, 7.76, 7.75, 7.75, 7.44, 7.43, 7.43, 7.42, 7.42, 7.42, 7.41, 7.41, 7.40, 7.40, 6.48, 6.48, 4.27, 4.26, 4.26, 4.26, 4.24, 4.24, 4.24, 4.23, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.15, 3.15, 3.13, 3.12, 3.12, 3.12, 3.10, 3.09, 2.89, 2.87, 2.86, 2.83, 2.83, 2.82, 2.82, 2.81, 2.81, 2.79, 2.79, 2.79, 2.78, 2.77, 2.75, 2.75, 2.49, 2.48, 2.48, 2.48, 2.47, 2.47, 2.47, 2.45, 2.45, 2.45, 2.44, 2.44, 2.44, 2.43, 1.99.

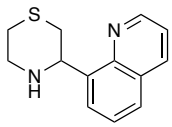
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83–7.67 (m, 1 H), 7.49–7.36 (m, 1 H), 6.48 (d, *J* = 0.8 Hz, 1 H), 4.25 (ddd, *J* = 9.2, 3.3, 0.7 Hz, 1 H), 3.39 (dt, *J* = 12.6, 3.4 Hz, 1 H), 3.12 (ddd, *J* = 12.6, 10.8, 2.5 Hz, 1 H), 2.93–2.72 (m, 2 H), 2.46 (dddd, *J* = 13.3, 4.0, 2.5, 1.5 Hz, 1 H), 1.99 (s, 1 H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 173.7, 162.3, 130.1, 129.0, 128.9, 126.8, 98.6, 54.2, 47.5, 31.6, 27.6.

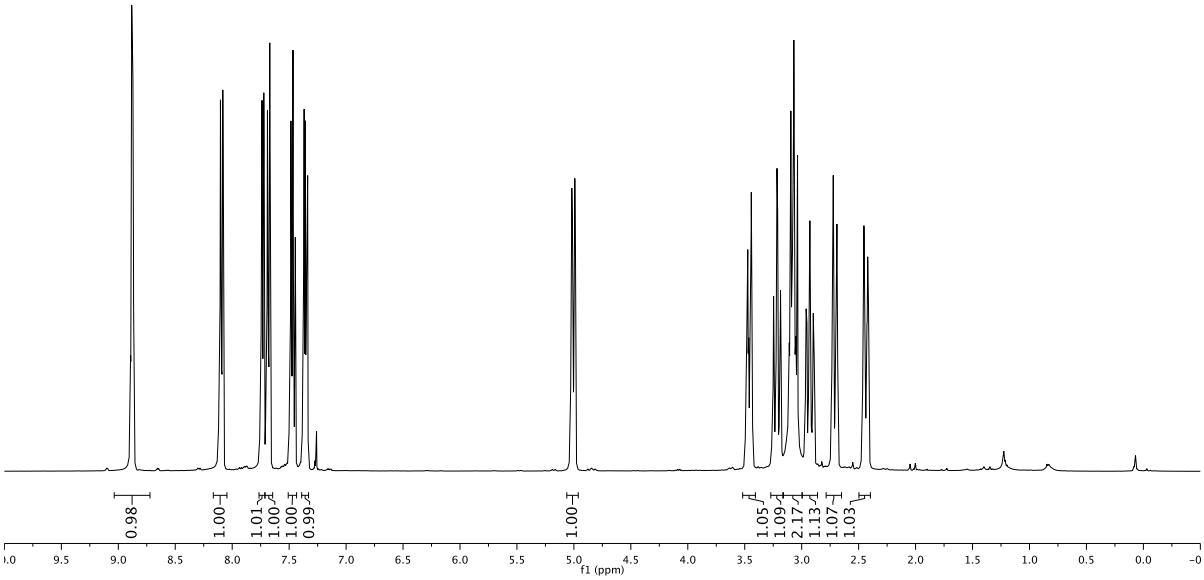
3-(Quinolin-8-yl)thiomorpholine (6t) (Scheme 3)

20-25-07-bhsieh.10.fid
Sample fly-08-141-2-CC
group bode
PRO CDCl3 /opt/v bhsieh 20

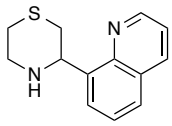


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88, 8.88, 8.87, 8.87, 8.10, 8.10, 8.09, 8.08, 8.08, 7.74, 7.74, 7.72, 7.72, 7.69, 7.69, 7.67, 7.67, 7.50, 7.48, 7.47, 7.46, 7.45, 7.45, 7.38, 7.37, 7.37, 7.36, 7.36, 7.35, 7.34, 5.02, 5.01, 4.99, 4.99, 3.49, 3.48, 3.47, 3.47, 3.46, 3.45, 3.43, 3.25, 3.25, 3.24, 3.23, 3.22, 3.22, 3.21, 3.20, 3.19, 3.19, 3.19, 3.18, 3.11, 3.10, 3.10, 3.08, 3.08, 3.07, 3.07, 3.06, 3.05, 3.04, 3.04, 2.97, 2.96, 2.95, 2.95, 2.94, 2.93, 2.93, 2.92, 2.92, 2.91, 2.90, 2.90, 2.89, 2.74, 2.73, 2.72, 2.72, 2.70, 2.70, 2.69, 2.68, 2.45, 2.45, 2.44, 2.43, 2.43, 2.42, 2.41.

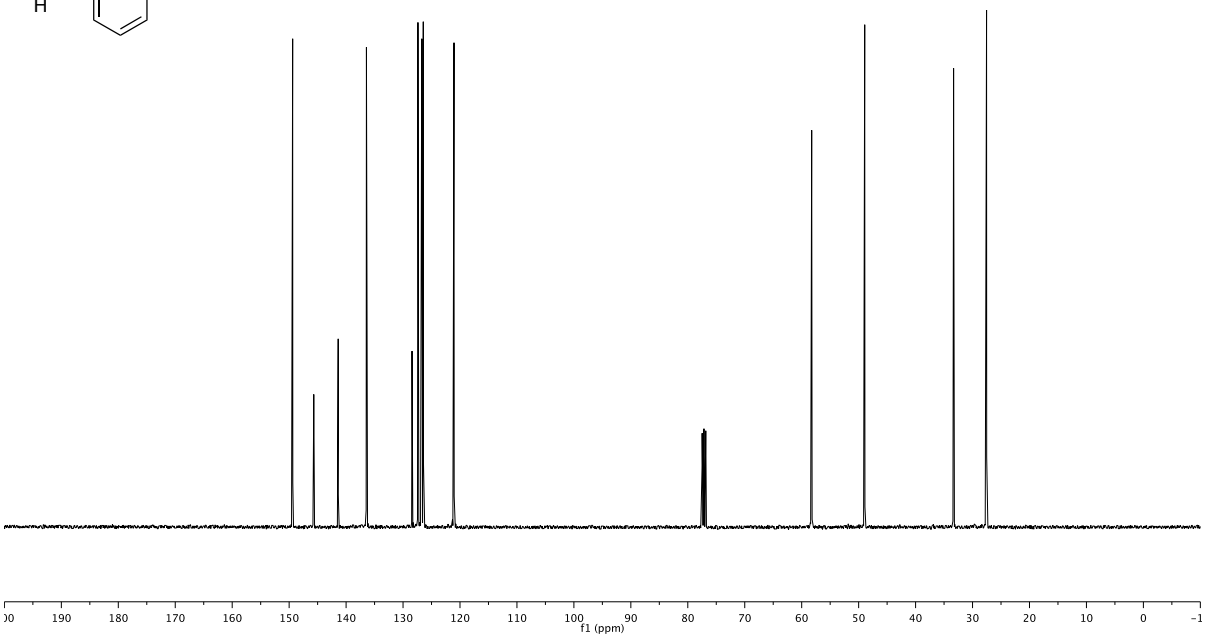
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.87 (dd, *J* = 4.2, 1.8 Hz, 1 H), 8.09 (dd, *J* = 8.3, 1.8 Hz, 1 H), 7.73 (dd, *J* = 7.1, 1.5 Hz, 1 H), 7.68 (dd, *J* = 8.1, 1.5 Hz, 1 H), 7.50–7.45 (m, 1 H), 7.38–7.34 (m, 1 H), 5.00 (dd, *J* = 10.5, 2.3 Hz, 1 H), 3.49–3.43 (m, 1 H), 3.25–3.18 (m, 1 H), 3.11–3.04 (m, 2 H), 2.97–2.89 (m, 1 H), 2.74–2.68 (m, 1 H), 2.45–2.41 (m, 1 H).



20-25-07-bhsieh.11.fid
Sample fly-08-141-2-CC
group bode
CAR CDCl3 /opt/v bhsieh 20

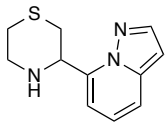


^{13}C NMR (101 MHz, $CDCl_3$) δ 149.4, 145.7, 141.4, 136.4, 128.4, 127.4, 126.7, 126.4, 121.1, 58.2, 48.9, 33.3, 27.5.



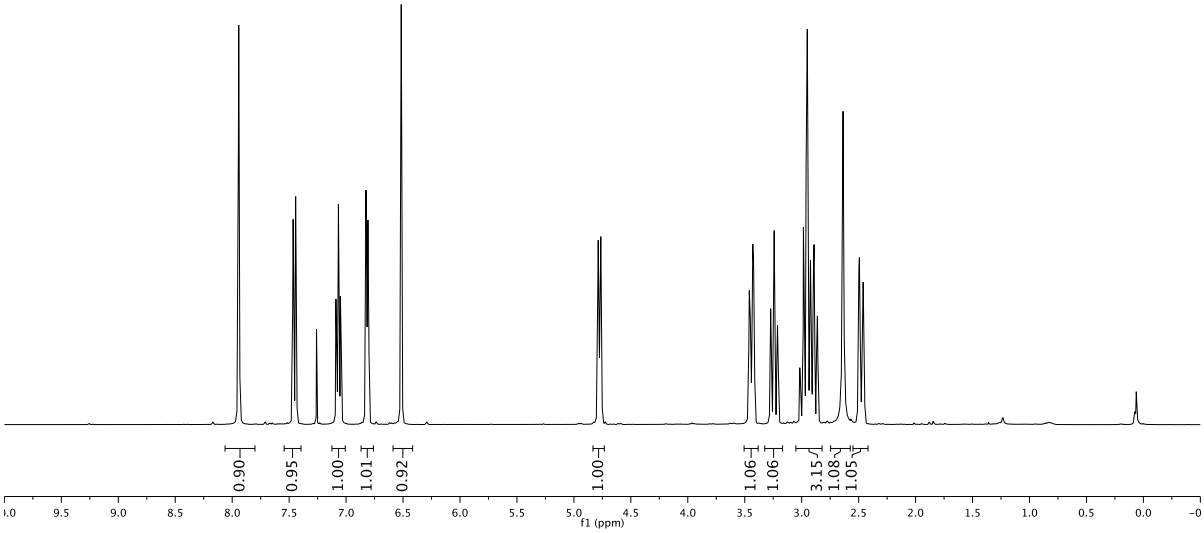
3-(Pyrazolo[1,5-*a*]pyridin-7-yl)thiomorpholine (6u) (Scheme 3)

41-15-02-bhsieh.50.fid
Sample fly-09-032-CC
group bode

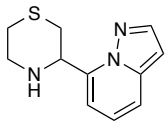


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95, 7.94, 7.94, 7.47, 7.47, 7.46, 7.45, 7.44, 7.44, 7.43, 7.09, 7.09, 7.08, 7.07, 7.07, 7.06, 7.06, 7.05, 7.05, 7.04, 6.83, 6.82, 6.81, 6.80, 6.52, 6.52, 6.51, 6.51, 4.79, 4.79, 4.78, 4.77, 4.76, 4.76, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.28, 3.27, 3.27, 3.26, 3.25, 3.24, 3.24, 3.23, 3.22, 3.21, 3.21, 3.20, 3.02, 3.01, 3.01, 2.99, 2.98, 2.98, 2.97, 2.96, 2.96, 2.95, 2.95, 2.94, 2.93, 2.92, 2.92, 2.90, 2.90, 2.90, 2.89, 2.89, 2.88, 2.87, 2.86, 2.85, 2.64, 2.51, 2.50, 2.50, 2.49, 2.49, 2.47, 2.46, 2.46, 2.46, 2.45, 2.45.

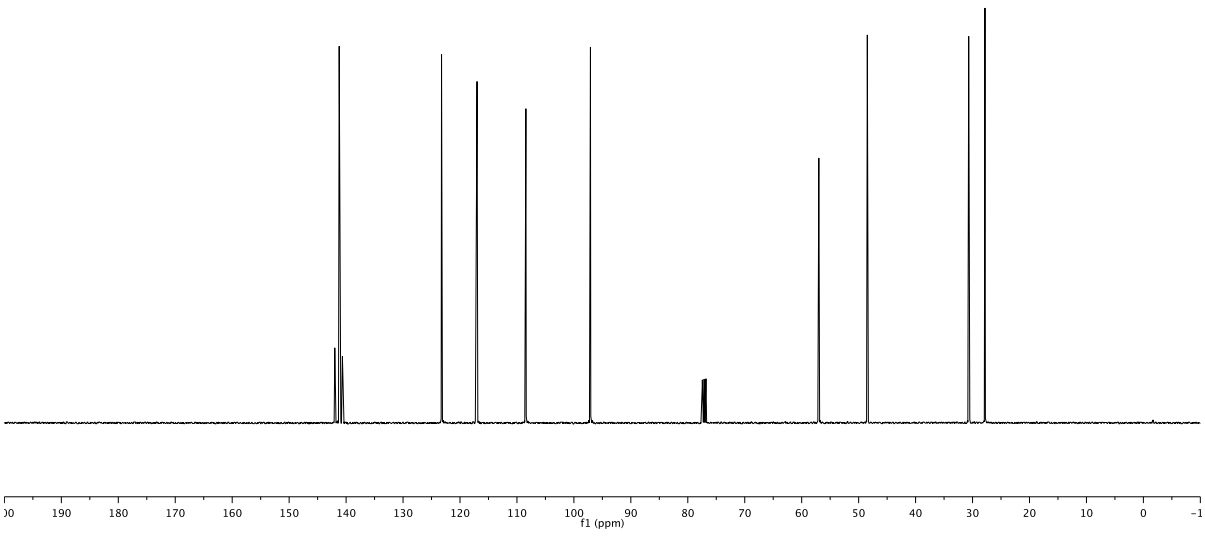
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 2.2 Hz, 1 H), 7.45 (dt, *J* = 8.8, 1.8 Hz, 1 H), 7.07 (ddt, *J* = 8.8, 6.8, 1.8 Hz, 1 H), 6.81 (dd, *J* = 7.1, 2.3 Hz, 1 H), 6.51 (q, *J* = 2.1 Hz, 1 H), 4.77 (dt, *J* = 9.2, 2.9 Hz, 1 H), 3.44 (dt, *J* = 12.4, 3.3 Hz, 1 H), 3.24 (tq, *J* = 12.2, 2.3 Hz, 1 H), 3.09–2.80 (m, 3 H), 2.64 (br, 1 H), 2.48 (ddt, *J* = 14.9, 3.7, 1.9 Hz, 1 H).



41-15-02-bhsieh.51.fid
Sample fly-09-032-CC
group bode

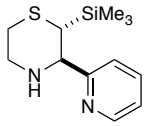


^{13}C NMR (101 MHz, $CDCl_3$) δ 142.0, 141.2, 140.6, 123.2, 117.0, 108.4, 97.1, 57.0, 48.5, 30.7, 27.8.



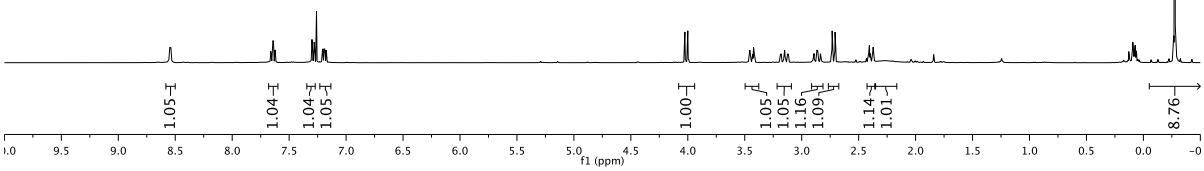
trans-3-(Pyridin-2-yl)-2-(trimethylsilyl)thiomorpholine (7d) (Scheme 3)

51-28-07-bhsieh.10.fid
Sample fly-08-108-CC
group bode



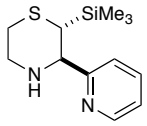
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55, 8.55, 8.55, 8.55, 8.54, 8.54, 8.54, 8.53, 7.66, 7.66, 7.64, 7.64, 7.62, 7.62, 7.30, 7.30, 7.30, 7.28, 7.28, 7.28, 7.21, 7.20, 7.19, 7.19, 7.19, 7.18, 7.17, 7.17, 4.03, 4.00, 3.46, 3.46, 3.45, 3.43, 3.42, 3.42, 3.19, 3.18, 3.16, 3.15, 3.15, 3.15, 3.12, 3.12, 2.90, 2.89, 2.87, 2.87, 2.86, 2.86, 2.84, 2.83, 2.73, 2.71, 2.41, 2.41, 2.40, 2.38, 2.37, 2.37, 2.27, -0.28.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.54 (ddd, *J* = 4.8, 1.8, 1.1 Hz, 1 H), 7.64 (td, *J* = 7.7, 1.8 Hz, 1 H), 7.29 (dt, *J* = 7.7, 1.1 Hz, 1 H), 7.19 (ddd, *J* = 7.7, 4.8, 1.1 Hz, 1 H), 4.01 (d, *J* = 10.3 Hz, 1 H), 3.44 (dt, *J* = 13.1, 3.0 Hz, 1 H), 3.15 (ddd, *J* = 13.1, 12.1, 2.6 Hz, 1 H), 2.86 (ddd, *J* = 13.1, 12.1, 3.0 Hz, 1 H), 2.72 (d, *J* = 10.3 Hz, 1 H), 2.39 (dt, *J* = 13.1, 2.6 Hz, 1 H), 2.27 (br, 1 H), -0.28 (s, 9 H).



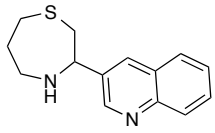
51-28-07-bhsieh.11.fid
Sample fly-08-108-CC
group bode

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.7, 137.0, 123.2, 123.0, 65.4, 47.9, 32.9, 28.5, -2.5.



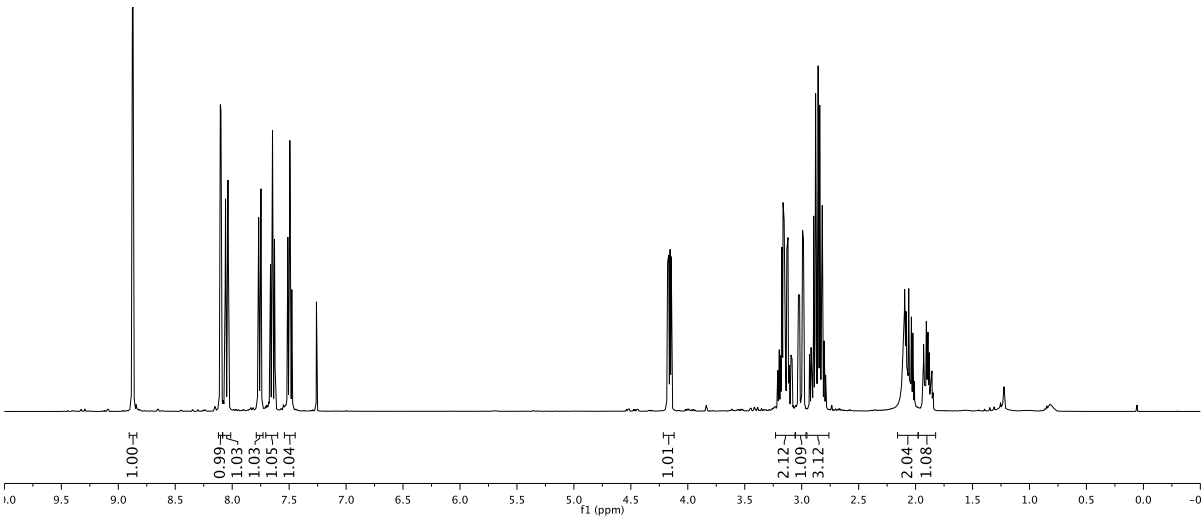
3-(Quinolin-3-yl)-1,4-thiazepane (8d) (Scheme 3)

11-06-01-bhsieh.10.fid
Sample fly-08-118-CC-7-3quinoline
group bode

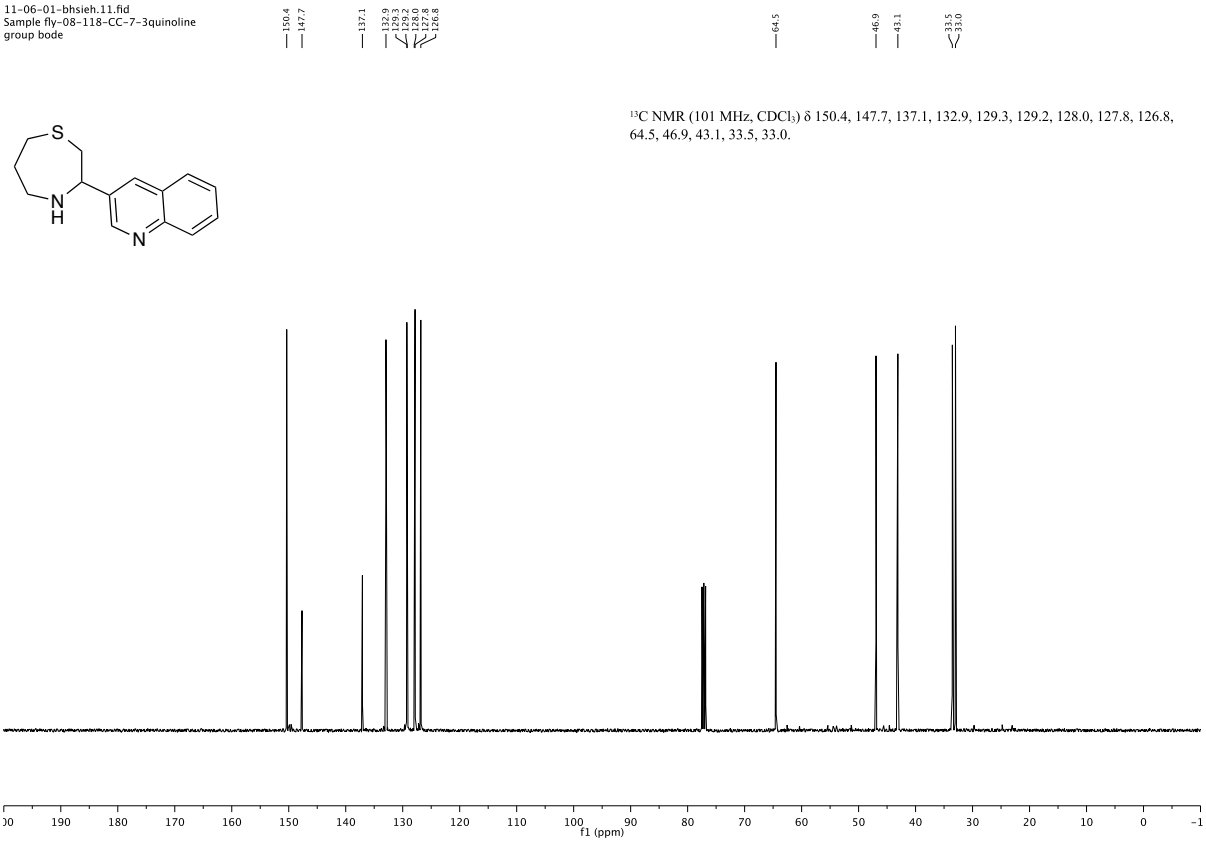


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88, 8.88, 8.87, 8.10, 8.10, 8.10, 8.06, 8.06, 8.06, 8.06, 8.04, 8.04, 8.04, 8.03, 7.77, 7.77, 7.75, 7.75, 7.67, 7.66, 7.65, 7.65, 7.64, 7.63, 7.62, 7.51, 7.51, 7.50, 7.49, 7.49, 7.48, 7.47, 4.18, 4.18, 4.17, 4.17, 4.16, 4.15, 4.15, 4.14, 3.21, 3.20, 3.20, 3.19, 3.17, 3.16, 3.16, 3.15, 3.15, 3.14, 3.13, 3.12, 3.11, 3.09, 3.08, 3.03, 3.03, 3.02, 3.02, 2.99, 2.99, 2.98, 2.98, 2.93, 2.92, 2.91, 2.89, 2.88, 2.88, 2.87, 2.86, 2.86, 2.85, 2.84, 2.84, 2.84, 2.83, 2.82, 2.82, 2.81, 2.81, 2.80, 2.80, 2.79, 2.79, 2.10, 2.10, 2.08, 2.07, 2.07, 2.06, 2.05, 2.04, 2.02, 2.01, 1.94, 1.93, 1.92, 1.92, 1.91, 1.91, 1.90, 1.90, 1.90, 1.89, 1.88, 1.88, 1.88, 1.87, 1.87, 1.87, 1.86, 1.86, 1.85.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.87 (d, *J* = 2.2 Hz, 1 H), 8.10 (d, *J* = 2.1 Hz, 1 H), 8.05 (dq, *J* = 8.5, 0.9 Hz, 1 H), 7.76 (dd, *J* = 8.2, 1.4 Hz, 1 H), 7.65 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1 H), 7.49 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1 H), 4.16 (ddd, *J* = 8.9, 3.9, 0.7 Hz, 1 H), 3.23–3.07 (m, 2 H), 3.01 (ddd, *J* = 14.5, 4.0, 1.0 Hz, 1 H), 2.95–2.73 (m, 3 H), 2.06 (dtd, *J* = 19.7, 10.3, 9.2, 4.3 Hz, 2 H), 1.96–1.81 (m, 1 H).

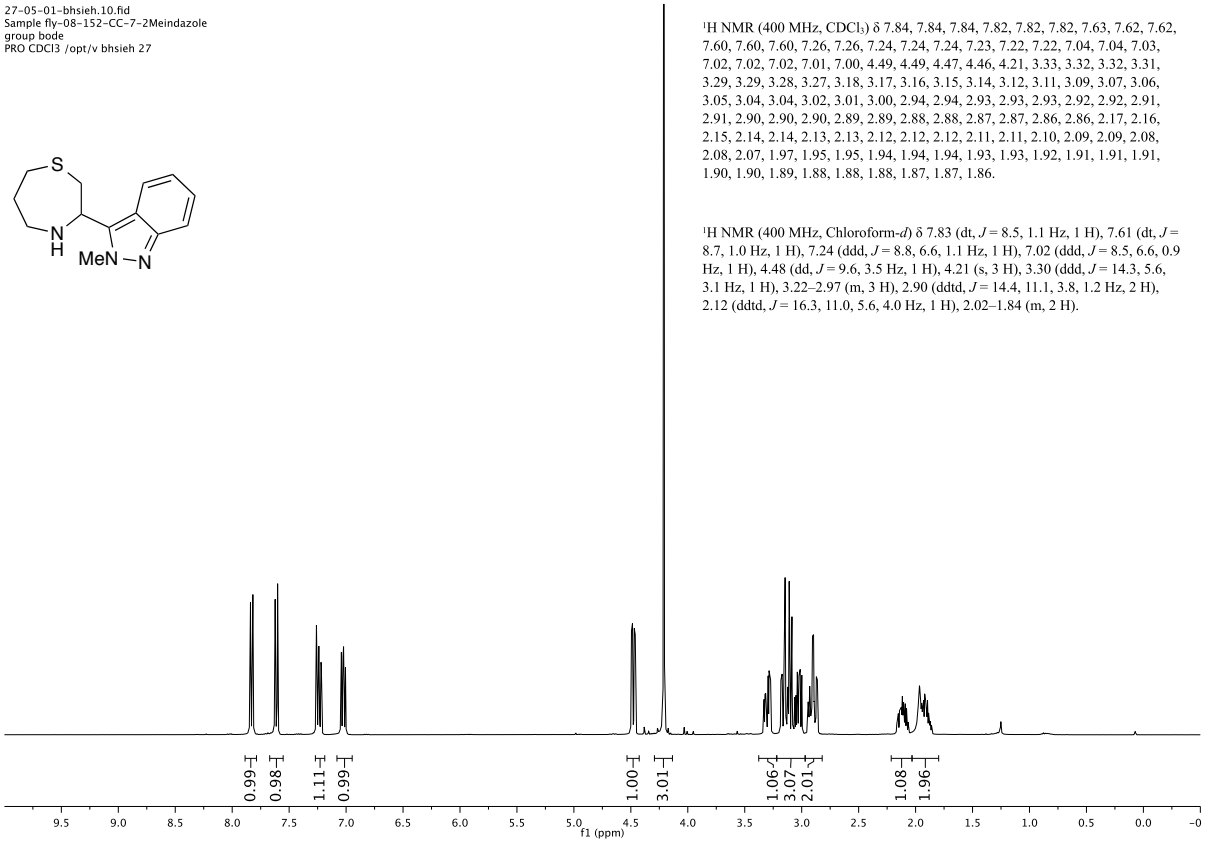


11-06-01-bhsieh.11.fid
Sample fly-08-118-CC-7-3quinoline
group bode



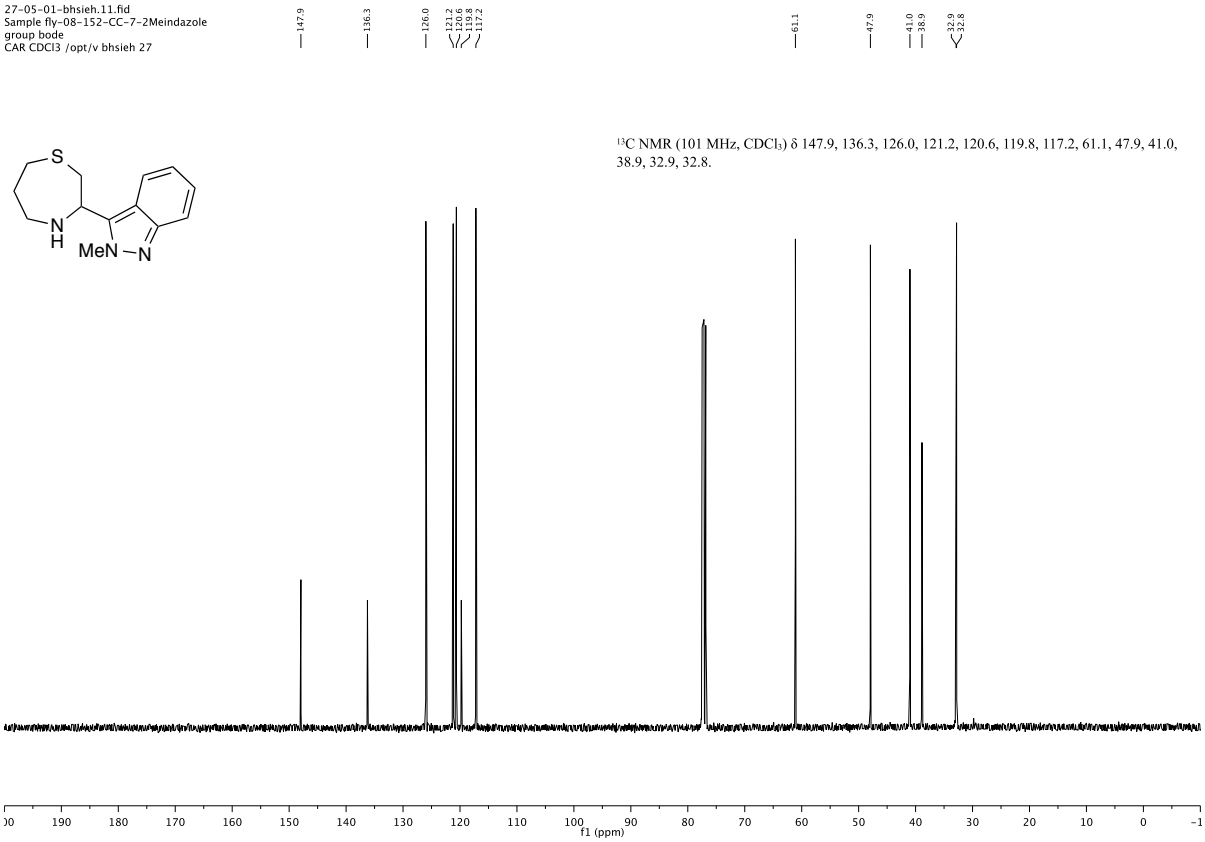
^{13}C NMR (101 MHz, $CDCl_3$) δ 150.4, 147.7, 137.1, 132.9, 129.3, 129.2, 128.0, 127.8, 126.8, 64.5, 46.9, 43.1, 33.5, 33.0.

3-(2-Methyl-2*H*-indazol-3-yl)-1,4-thiazepane (8e) (Scheme 3)



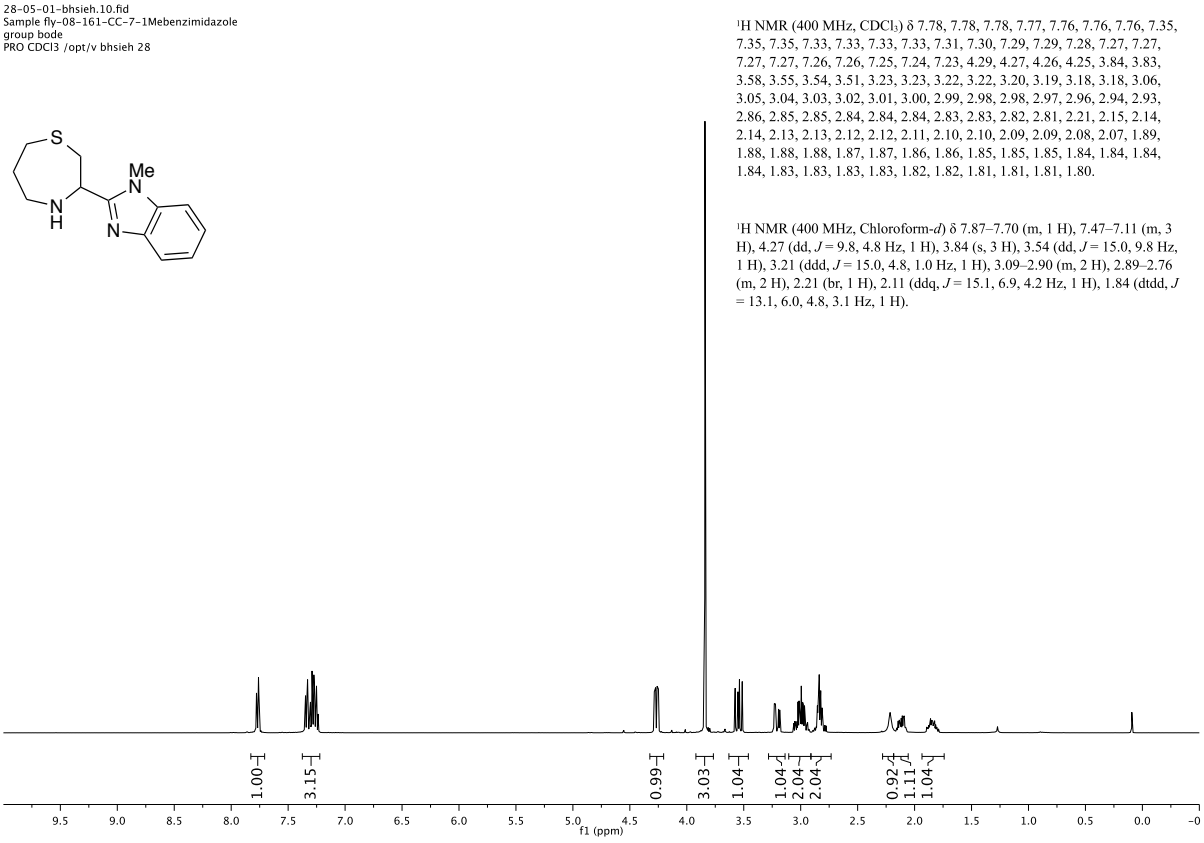
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84, 7.84, 7.84, 7.82, 7.82, 7.82, 7.63, 7.62, 7.62, 7.60, 7.60, 7.60, 7.26, 7.26, 7.24, 7.24, 7.24, 7.23, 7.22, 7.22, 7.04, 7.04, 7.03, 7.02, 7.02, 7.02, 7.01, 7.00, 4.49, 4.49, 4.47, 4.46, 4.21, 3.33, 3.32, 3.32, 3.31, 3.29, 3.29, 3.28, 3.27, 3.18, 3.17, 3.16, 3.15, 3.14, 3.12, 3.11, 3.09, 3.07, 3.06, 3.05, 3.04, 3.04, 3.02, 3.01, 3.00, 2.94, 2.94, 2.93, 2.93, 2.93, 2.92, 2.92, 2.91, 2.91, 2.90, 2.90, 2.90, 2.89, 2.89, 2.88, 2.88, 2.87, 2.87, 2.86, 2.86, 2.17, 2.16, 2.15, 2.14, 2.14, 2.13, 2.13, 2.12, 2.12, 2.12, 2.11, 2.11, 2.10, 2.09, 2.09, 2.08, 2.08, 2.07, 1.97, 1.95, 1.95, 1.94, 1.94, 1.94, 1.93, 1.93, 1.92, 1.91, 1.91, 1.91, 1.90, 1.90, 1.89, 1.88, 1.88, 1.88, 1.87, 1.87, 1.86.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (dt, *J* = 8.5, 1.1 Hz, 1 H), 7.61 (dt, *J* = 8.7, 1.0 Hz, 1 H), 7.24 (ddd, *J* = 8.8, 6.6, 1.1 Hz, 1 H), 7.02 (ddd, *J* = 8.5, 6.6, 0.9 Hz, 1 H), 4.48 (dd, *J* = 9.6, 3.5 Hz, 1 H), 4.21 (s, 3 H), 3.30 (ddd, *J* = 14.3, 5.6, 3.1 Hz, 1 H), 3.22–2.97 (m, 3 H), 2.90 (ddtd, *J* = 14.4, 11.1, 3.8, 1.2 Hz, 2 H), 2.12 (ddtd, *J* = 16.3, 11.0, 5.6, 4.0 Hz, 1 H), 2.02–1.84 (m, 2 H).



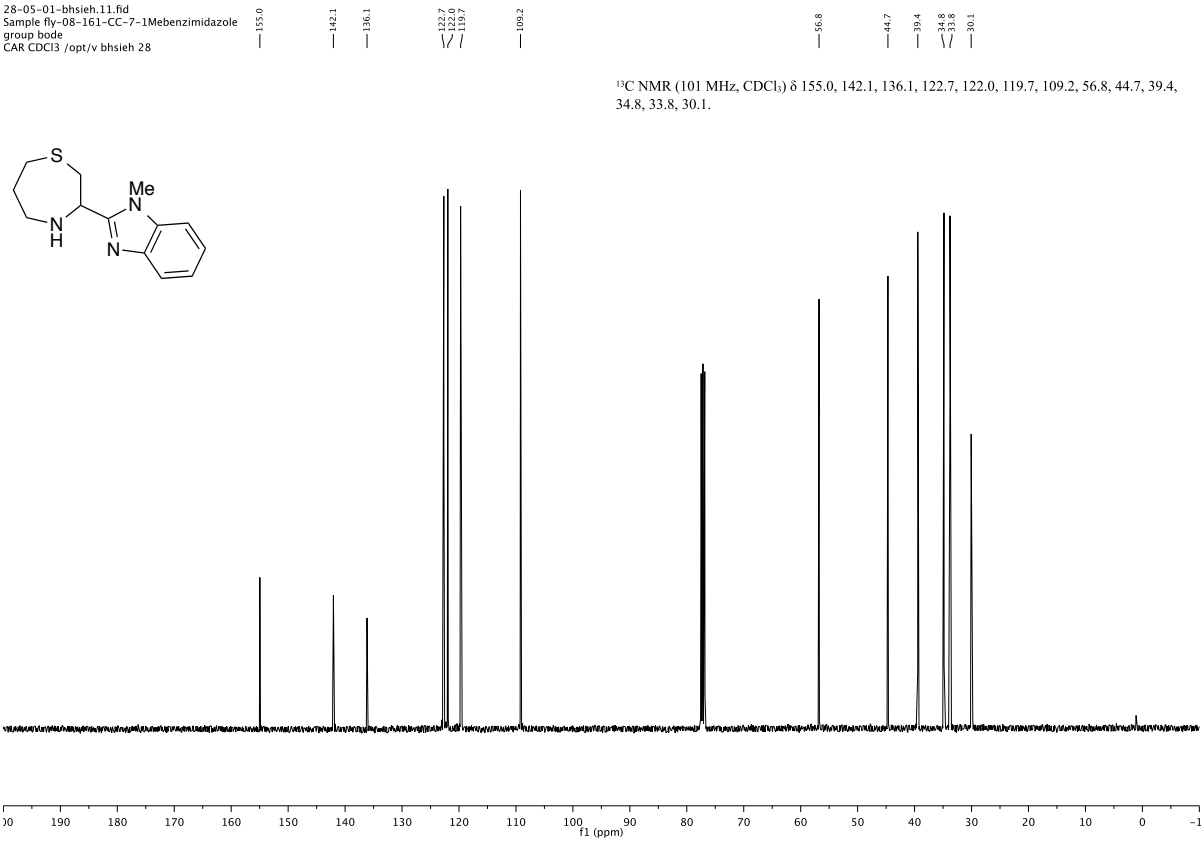
^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 136.3, 126.0, 121.2, 120.6, 119.8, 117.2, 61.1, 47.9, 41.0, 38.9, 32.9, 32.8.

3-(1-Methyl-1*H*-benzo[*d*]imidazol-2-yl)-1,4-thiazepane (8f) (Scheme 3)



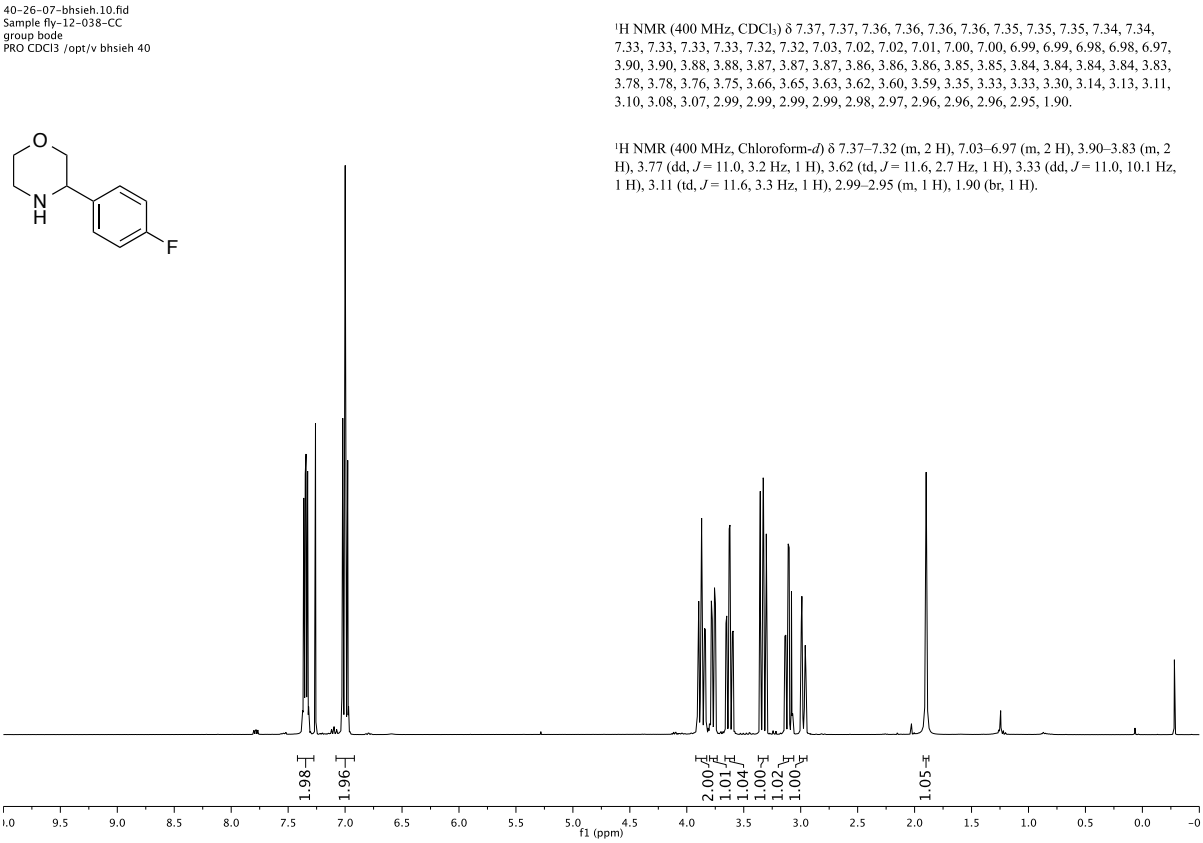
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78, 7.78, 7.78, 7.77, 7.76, 7.76, 7.76, 7.35, 7.35, 7.35, 7.33, 7.33, 7.33, 7.33, 7.31, 7.30, 7.29, 7.29, 7.28, 7.27, 7.27, 7.27, 7.27, 7.26, 7.26, 7.25, 7.24, 7.23, 4.29, 4.27, 4.26, 4.25, 3.84, 3.83, 3.58, 3.55, 3.54, 3.51, 3.23, 3.23, 3.22, 3.22, 3.20, 3.19, 3.18, 3.18, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.98, 2.97, 2.96, 2.94, 2.93, 2.86, 2.85, 2.85, 2.84, 2.84, 2.84, 2.83, 2.83, 2.82, 2.81, 2.21, 2.15, 2.14, 2.14, 2.13, 2.13, 2.12, 2.12, 2.11, 2.10, 2.10, 2.09, 2.09, 2.08, 2.07, 1.89, 1.88, 1.88, 1.88, 1.87, 1.87, 1.86, 1.86, 1.85, 1.85, 1.85, 1.84, 1.84, 1.84, 1.84, 1.83, 1.83, 1.83, 1.83, 1.82, 1.82, 1.81, 1.81, 1.81, 1.80.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87–7.70 (m, 1 H), 7.47–7.11 (m, 3 H), 4.27 (dd, *J* = 9.8, 4.8 Hz, 1 H), 3.84 (s, 3 H), 3.54 (dd, *J* = 15.0, 9.8 Hz, 1 H), 3.21 (ddd, *J* = 15.0, 4.8, 1.0 Hz, 1 H), 3.09–2.90 (m, 2 H), 2.89–2.76 (m, 2 H), 2.21 (br, 1 H), 2.11 (ddq, *J* = 15.1, 6.9, 4.2 Hz, 1 H), 1.84 (dtdd, *J* = 13.1, 6.0, 4.8, 3.1 Hz, 1 H).



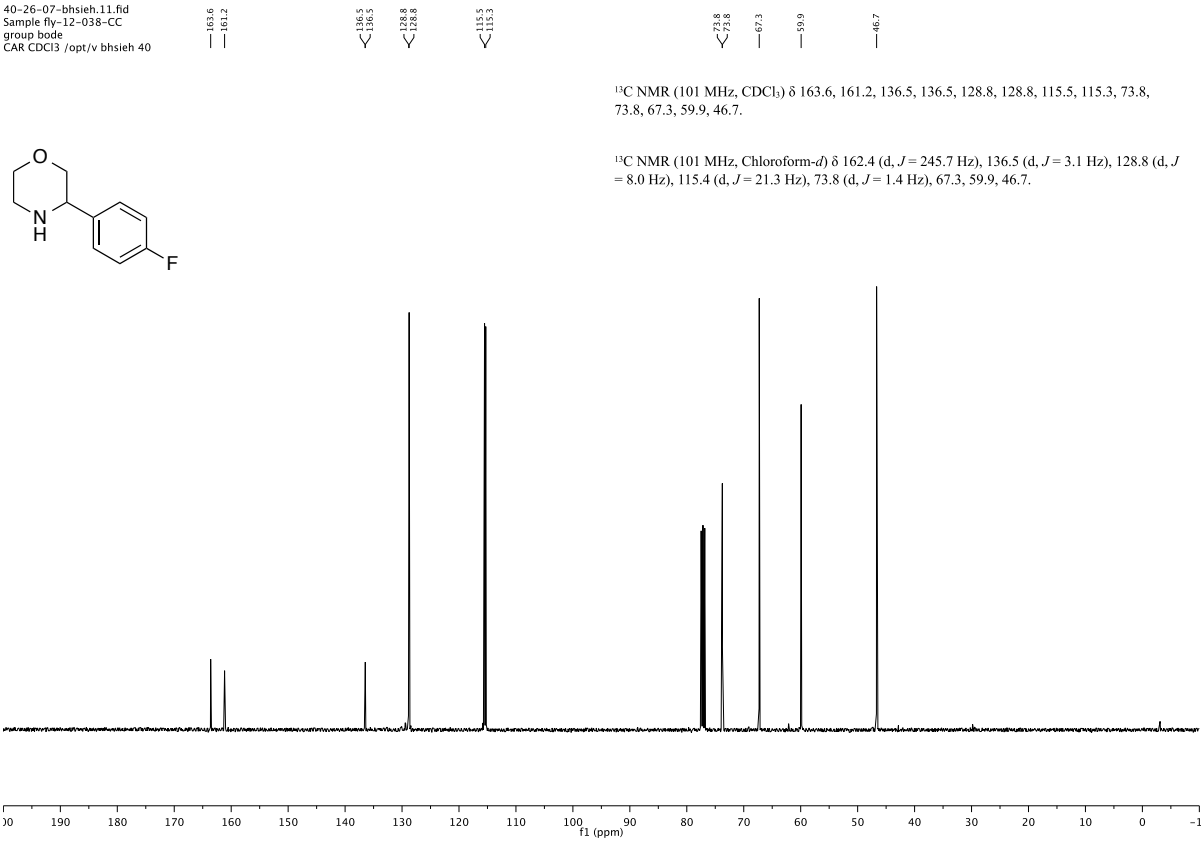
^{13}C NMR (101 MHz, $CDCl_3$) δ 155.0, 142.1, 136.1, 122.7, 122.0, 119.7, 109.2, 56.8, 44.7, 39.4, 34.8, 33.8, 30.1.

3-(4-Fluorophenyl)morpholine (12a)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37, 7.37, 7.36, 7.36, 7.36, 7.36, 7.35, 7.35, 7.35, 7.34, 7.34, 7.33, 7.33, 7.33, 7.33, 7.32, 7.32, 7.03, 7.02, 7.02, 7.01, 7.00, 7.00, 6.99, 6.99, 6.98, 6.98, 6.97, 3.90, 3.90, 3.88, 3.88, 3.87, 3.87, 3.87, 3.86, 3.86, 3.86, 3.85, 3.85, 3.84, 3.84, 3.84, 3.84, 3.83, 3.78, 3.78, 3.76, 3.75, 3.66, 3.65, 3.63, 3.62, 3.60, 3.59, 3.35, 3.33, 3.33, 3.30, 3.14, 3.13, 3.11, 3.10, 3.08, 3.07, 2.99, 2.99, 2.99, 2.99, 2.98, 2.97, 2.96, 2.96, 2.96, 2.95, 1.90.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37–7.32 (m, 2 H), 7.03–6.97 (m, 2 H), 3.90–3.83 (m, 2 H), 3.77 (dd, *J* = 11.0, 3.2 Hz, 1 H), 3.62 (td, *J* = 11.6, 2.7 Hz, 1 H), 3.33 (dd, *J* = 11.0, 10.1 Hz, 1 H), 3.11 (td, *J* = 11.6, 3.3 Hz, 1 H), 2.99–2.95 (m, 1 H), 1.90 (br, 1 H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 163.6, 161.2, 136.5, 136.5, 128.8, 128.8, 115.5, 115.3, 73.8, 73.8, 67.3, 59.9, 46.7.

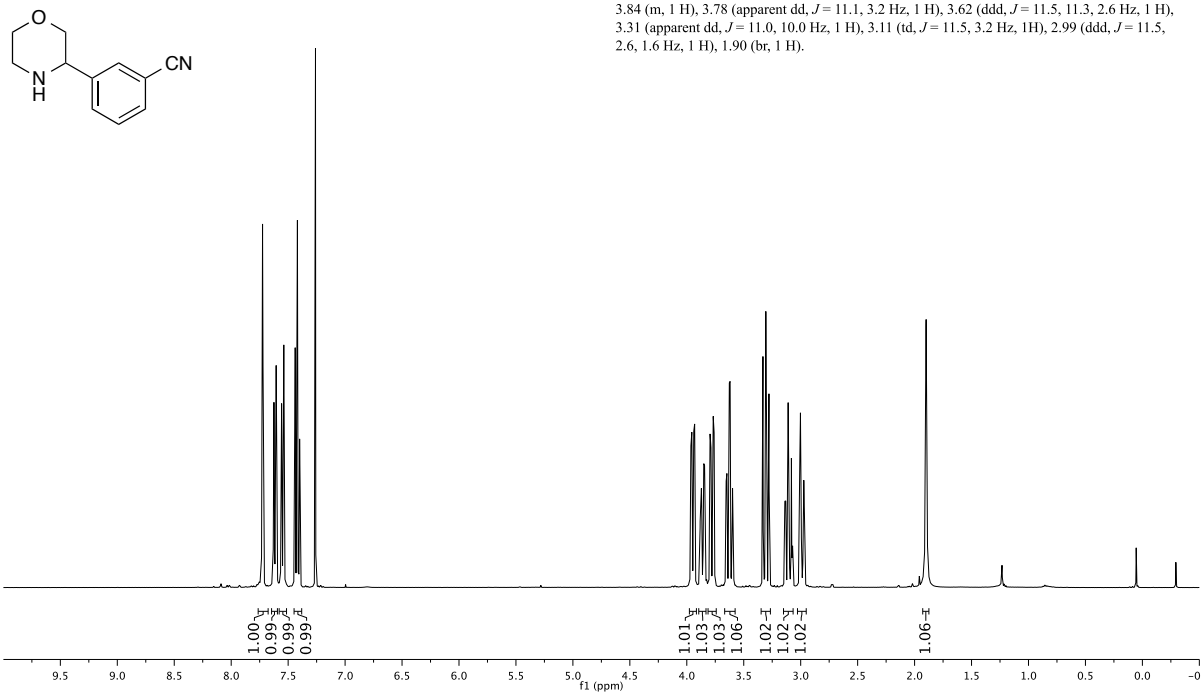
^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.4 (d, *J* = 245.7 Hz), 136.5 (d, *J* = 3.1 Hz), 128.8 (d, *J* = 8.0 Hz), 115.4 (d, *J* = 21.3 Hz), 73.8 (d, *J* = 1.4 Hz), 67.3, 59.9, 46.7.

3-(Morpholin-3-yl)benzonitrile (12b)

41-26-07-bhsieh.10.fid
Sample fly-12-039-CC
group bode
PRO CDCl3 /opt/v bhsieh 41

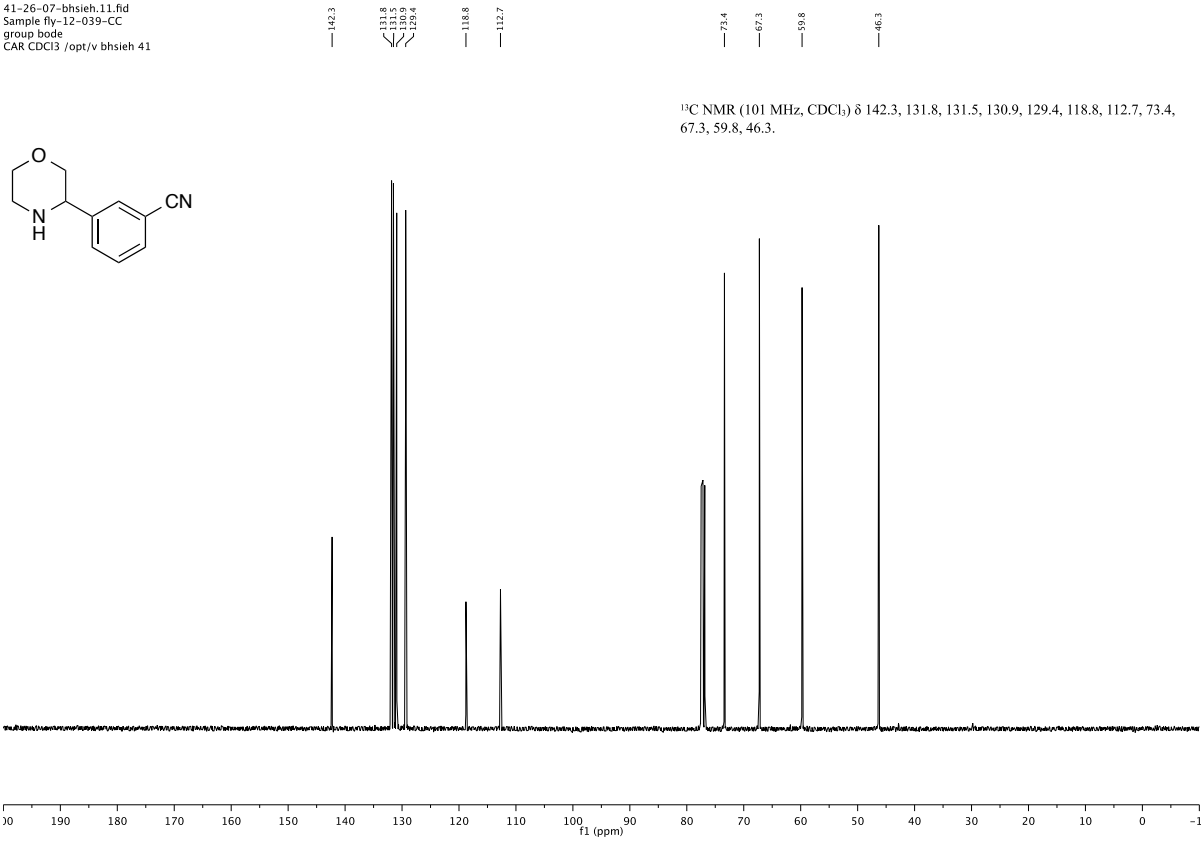
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73, 7.72, 7.72, 7.63, 7.62, 7.62, 7.61, 7.61, 7.60, 7.56, 7.56, 7.55, 7.54, 7.54, 7.53, 7.44, 7.42, 7.40, 3.96, 3.96, 3.94, 3.93, 3.88, 3.88, 3.87, 3.87, 3.85, 3.85, 3.84, 3.84, 3.80, 3.79, 3.77, 3.76, 3.65, 3.65, 3.63, 3.62, 3.60, 3.59, 3.33, 3.31, 3.30, 3.28, 3.14, 3.13, 3.11, 3.10, 3.08, 3.07, 3.01, 3.00, 3.00, 3.00, 2.98, 2.97, 2.97, 2.97, 1.90.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (t, *J* = 1.6 Hz, 1 H), 7.61 (dt, *J* = 7.7, 1.6 Hz, 1 H), 7.55 (dt, *J* = 7.7, 1.4 Hz, 1 H), 7.42 (t, *J* = 7.7 Hz, 1 H), 3.95 (dd, *J* = 10.0, 3.2 Hz, 1 H), 3.88–3.84 (m, 1 H), 3.78 (apparent dd, *J* = 11.1, 3.2 Hz, 1 H), 3.62 (ddd, *J* = 11.5, 11.3, 2.6 Hz, 1 H), 3.31 (apparent dd, *J* = 11.0, 10.0 Hz, 1 H), 3.11 (td, *J* = 11.5, 3.2 Hz, 1H), 2.99 (ddd, *J* = 11.5, 2.6, 1.6 Hz, 1 H), 1.90 (br, 1 H).



41-26-07-bhsieh.11.fid
Sample fly-12-039-CC
group bode
CAR CDCl3 /opt/v bhsieh 41

^{13}C NMR (101 MHz, $CDCl_3$) δ 142.3, 131.8, 131.5, 130.9, 129.4, 118.8, 112.7, 73.4, 67.3, 59.8, 46.3.

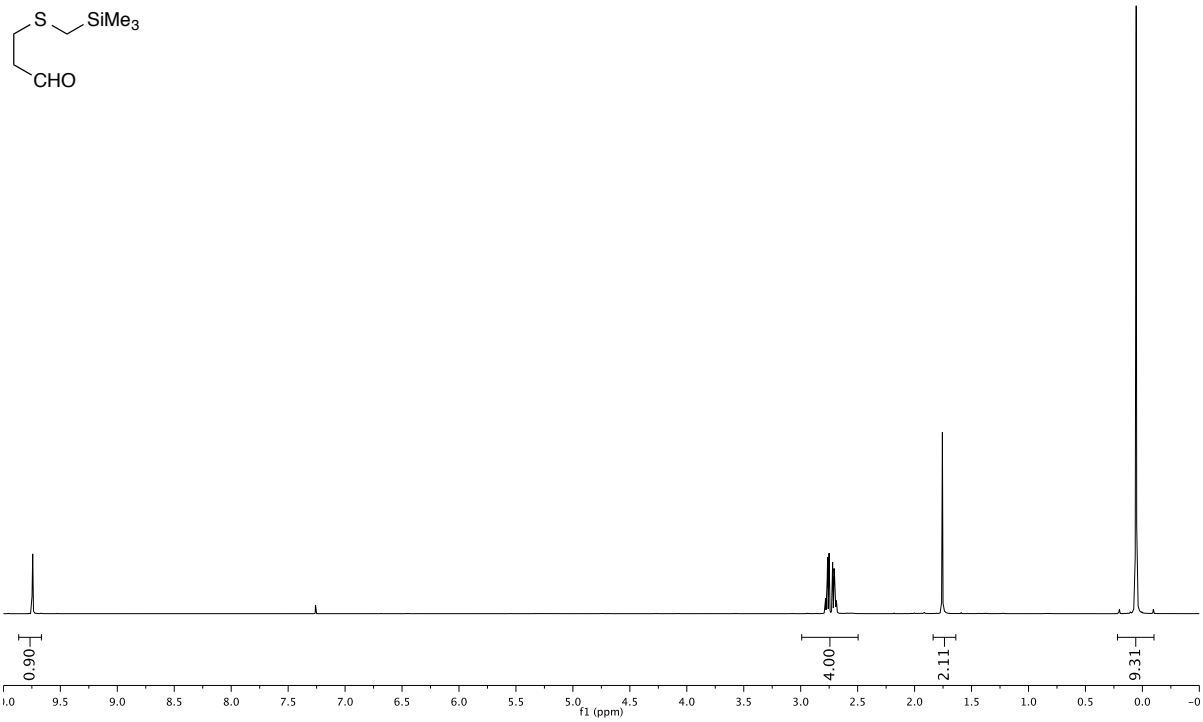


3-(((Trimethylsilyl)methyl)thio)propanal (S8)

41-20-11-bhsieh.10.fid
Sample fly-11-101
group bode

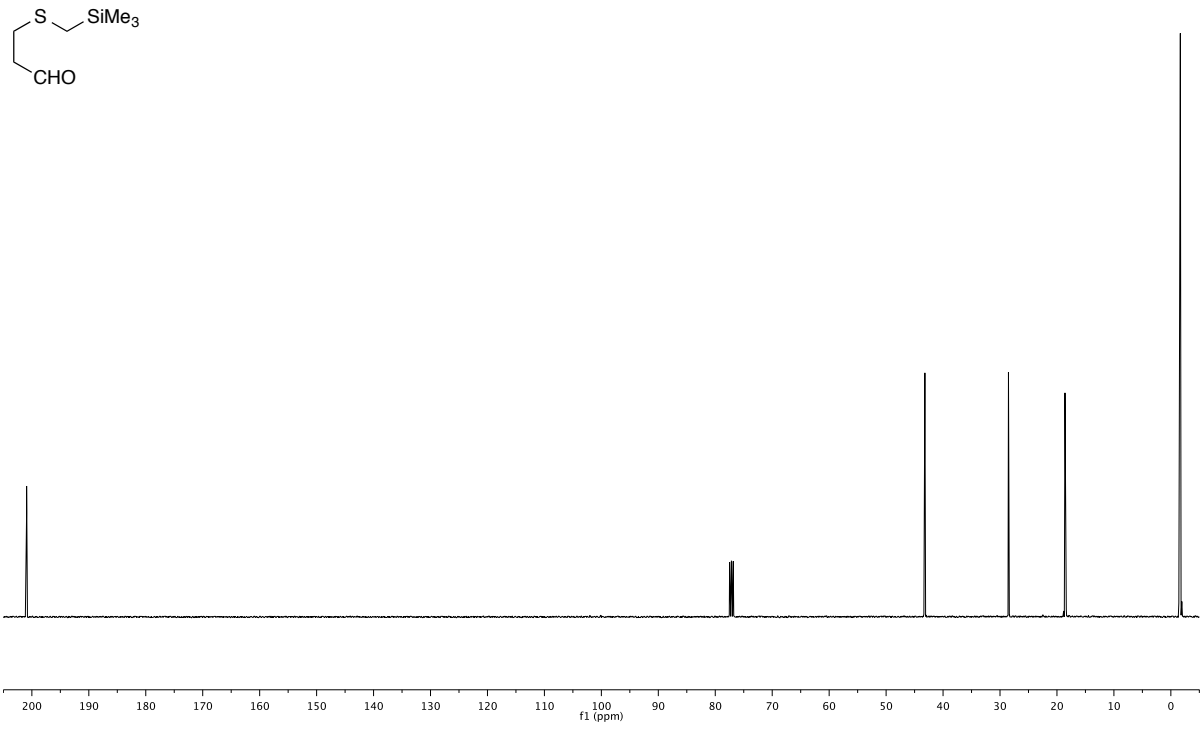
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.75, 9.74, 9.74, 2.79, 2.79, 2.78, 2.78, 2.77, 2.77, 2.77, 2.76, 2.75, 2.75, 2.75, 2.73, 2.72, 2.72, 2.72, 2.71, 2.71, 2.70, 2.70, 2.70, 2.70, 2.69, 2.69, 2.68, 2.68, 1.76, 0.05.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.74 (t, *J* = 1.5 Hz, 1 H), 2.79–2.68 (m, 4 H), 1.76 (s, 2 H), 0.05 (s, 9 H).



41-20-11-bhsieh.11.fid
Sample fly-11-101
group bode

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 43.2, 28.5, 18.6, -1.7.



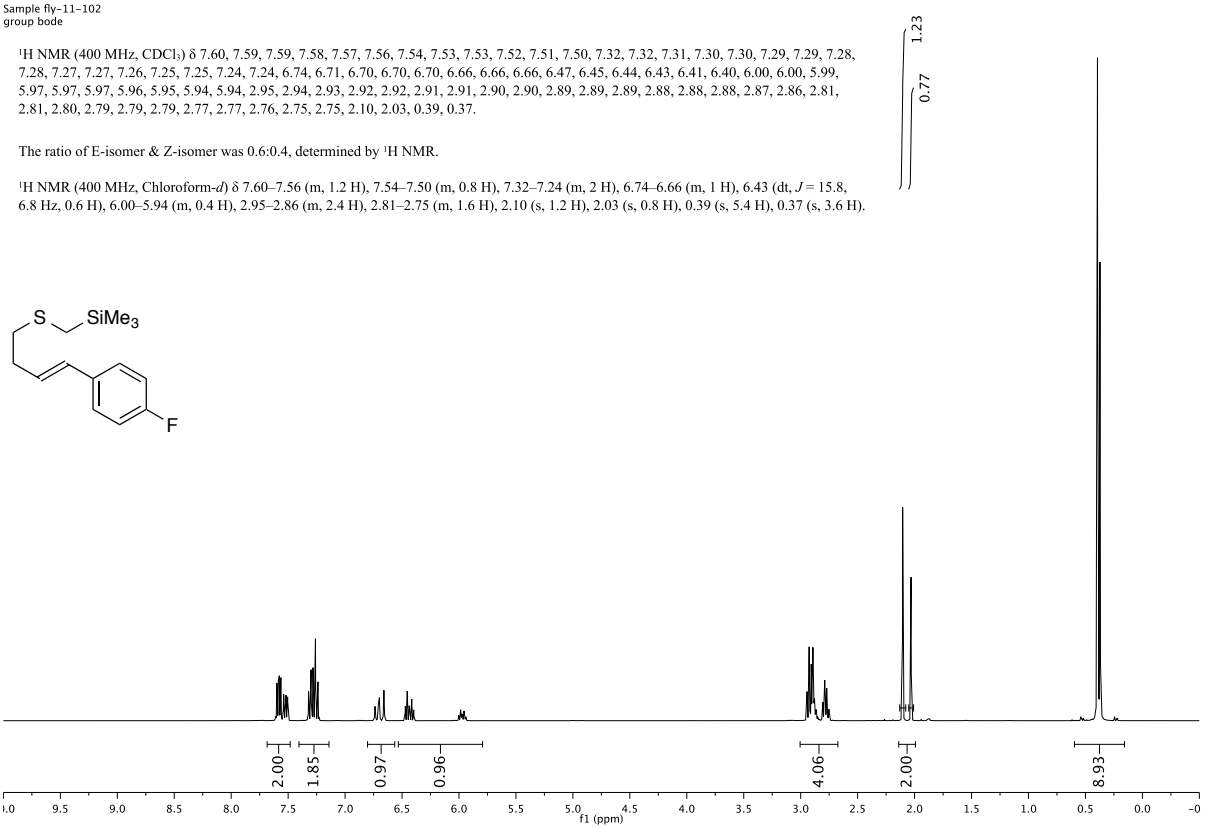
(((4-(4-Fluorophenyl)but-3-en-1-yl)thio)methyl)trimethylsilane, mixture of *E*,*Z*-isomers (13)

41-21-11-bhsieh.10.fid
Sample fly-11-102
group bode

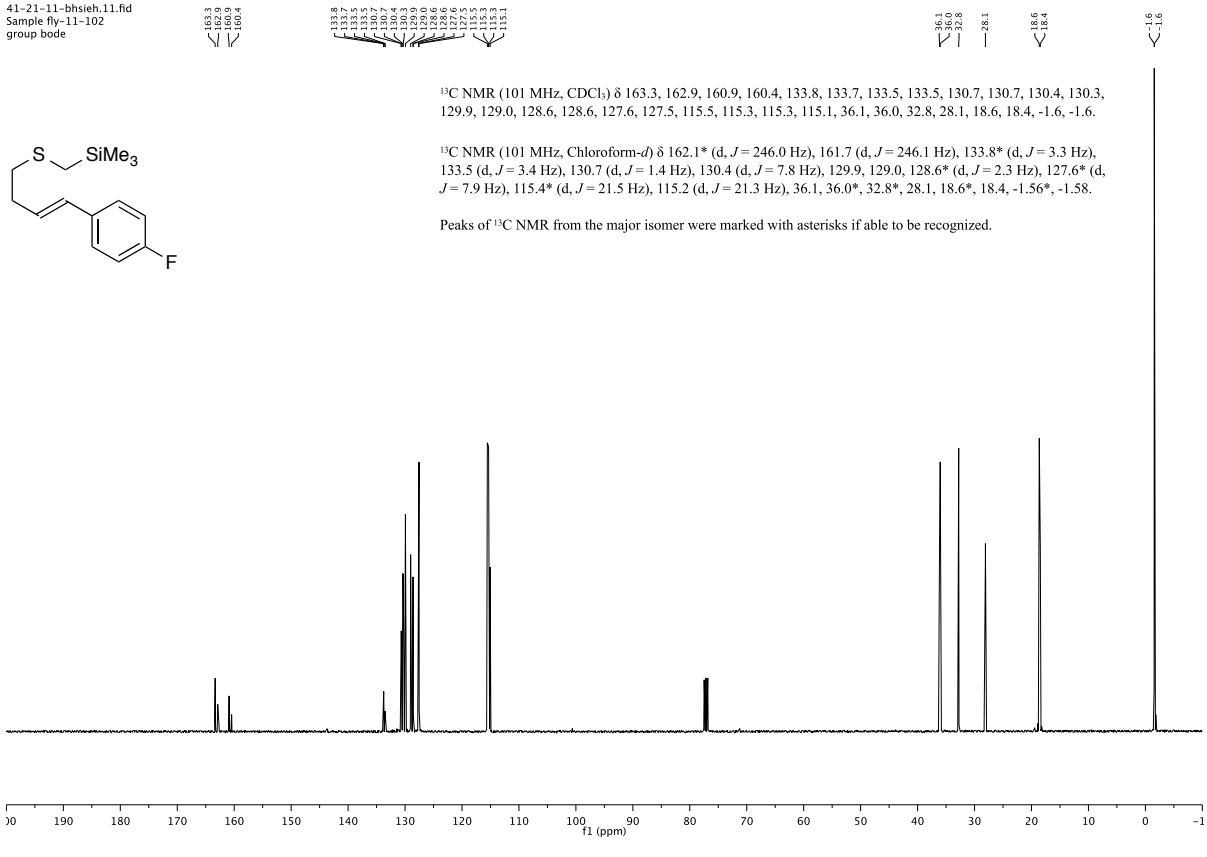
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60, 7.59, 7.59, 7.58, 7.57, 7.56, 7.54, 7.53, 7.53, 7.52, 7.51, 7.50, 7.32, 7.32, 7.31, 7.30, 7.30, 7.29, 7.29, 7.28, 7.28, 7.27, 7.27, 7.26, 7.25, 7.25, 7.24, 7.24, 6.74, 6.71, 6.70, 6.70, 6.70, 6.66, 6.66, 6.66, 6.47, 6.45, 6.44, 6.43, 6.41, 6.40, 6.00, 6.00, 5.99, 5.97, 5.97, 5.97, 5.96, 5.95, 5.94, 5.94, 2.95, 2.94, 2.93, 2.92, 2.92, 2.91, 2.91, 2.90, 2.90, 2.89, 2.89, 2.89, 2.88, 2.88, 2.88, 2.87, 2.86, 2.81, 2.81, 2.80, 2.79, 2.79, 2.79, 2.77, 2.77, 2.76, 2.75, 2.75, 2.10, 2.03, 0.39, 0.37.

The ratio of E-isomer & Z-isomer was 0.6:0.4, determined by ^{1}H NMR.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60–7.56 (m, 1.2 H), 7.54–7.50 (m, 0.8 H), 7.32–7.24 (m, 2 H), 6.74–6.66 (m, 1 H), 6.43 (dt, *J* = 15.8, 6.8 Hz, 0.6 H), 6.00–5.94 (m, 0.4 H), 2.95–2.86 (m, 2.4 H), 2.81–2.75 (m, 1.6 H), 2.10 (s, 1.2 H), 2.03 (s, 0.8 H), 0.39 (s, 5.4 H), 0.37 (s, 3.6 H).



41-21-11-bhsieh.11.fid
Sample fly-11-102
group bode



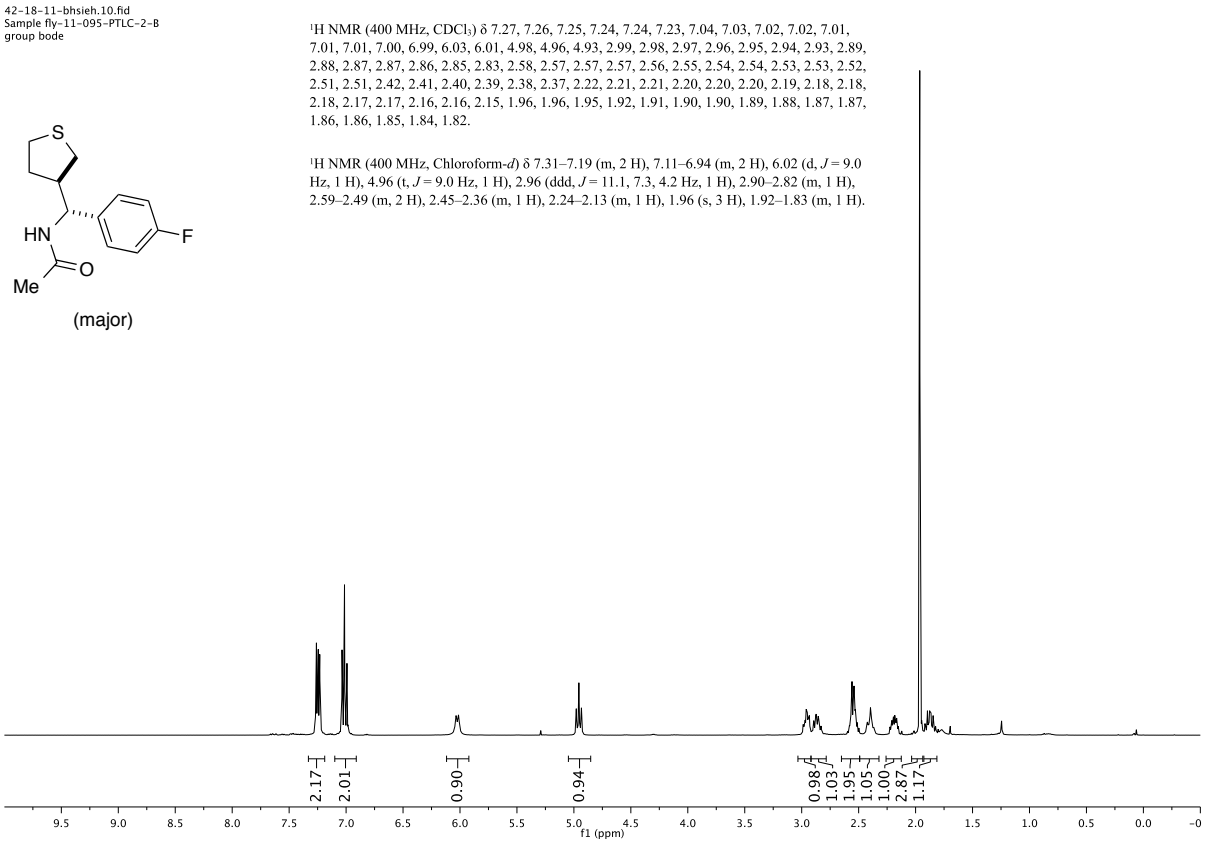
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3, 162.9, 160.9, 160.4, 133.8, 133.7, 133.5, 133.5, 130.7, 130.7, 130.4, 130.3, 129.9, 129.0, 128.6, 128.6, 127.6, 127.5, 115.5, 115.3, 115.3, 115.1, 36.1, 36.0, 32.8, 28.1, 18.6, 18.4, -1.6, -1.6.

^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.1* (d, *J* = 246.0 Hz), 161.7 (d, *J* = 246.1 Hz), 133.8* (d, *J* = 3.3 Hz), 133.5 (d, *J* = 3.4 Hz), 130.7 (d, *J* = 1.4 Hz), 130.4 (d, *J* = 7.8 Hz), 129.9, 129.0, 128.6* (d, *J* = 2.3 Hz), 127.6* (d, *J* = 7.9 Hz), 115.4* (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.3 Hz), 36.1, 36.0*, 32.8*, 28.1, 18.6*, 18.4, -1.56*, -1.58.

Peaks of ^{13}C NMR from the major isomer were marked with asterisks if able to be recognized.

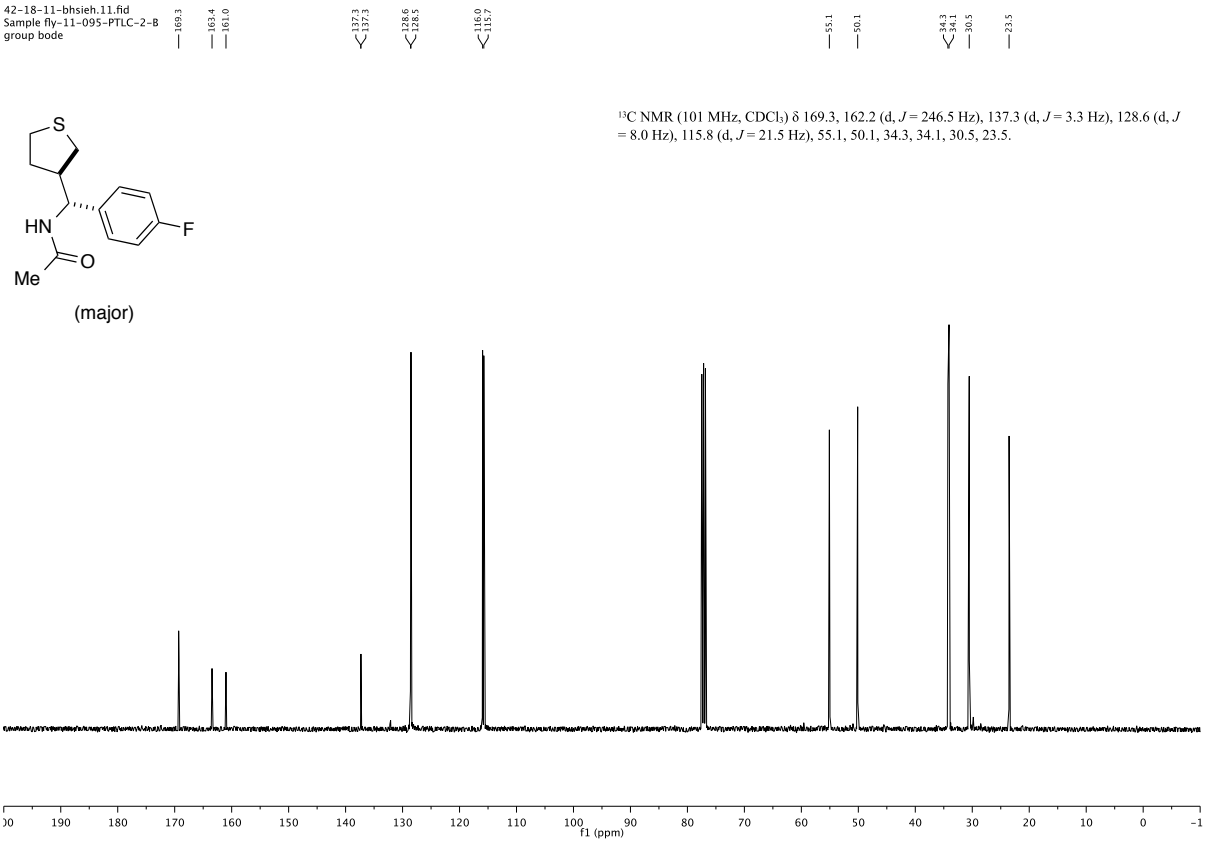
N-((4-Fluorophenyl)(tetrahydrothiophen-3-yl)methyl)acetamide, diastereomers (14)

major diastereomer product: **14a**



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27, 7.26, 7.25, 7.24, 7.24, 7.23, 7.04, 7.03, 7.02, 7.02, 7.01, 7.01, 7.01, 7.00, 6.99, 6.03, 6.01, 4.98, 4.96, 4.93, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.89, 2.88, 2.87, 2.87, 2.86, 2.85, 2.83, 2.58, 2.57, 2.57, 2.57, 2.56, 2.55, 2.54, 2.54, 2.53, 2.53, 2.52, 2.51, 2.51, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.22, 2.21, 2.21, 2.20, 2.20, 2.20, 2.19, 2.18, 2.18, 2.18, 2.17, 2.17, 2.16, 2.16, 2.15, 1.96, 1.96, 1.95, 1.92, 1.91, 1.90, 1.90, 1.89, 1.88, 1.87, 1.87, 1.86, 1.86, 1.85, 1.84, 1.82.

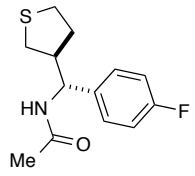
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31–7.19 (m, 2 H), 7.11–6.94 (m, 2 H), 6.02 (d, *J* = 9.0 Hz, 1 H), 4.96 (t, *J* = 9.0 Hz, 1 H), 2.96 (ddd, *J* = 11.1, 7.3, 4.2 Hz, 1 H), 2.90–2.82 (m, 1 H), 2.59–2.49 (m, 2 H), 2.45–2.36 (m, 1 H), 2.24–2.13 (m, 1 H), 1.96 (s, 3 H), 1.92–1.83 (m, 1 H).



^{13}C NMR (101 MHz, $CDCl_3$) δ 169.3, 162.2 (d, *J* = 246.5 Hz), 137.3 (d, *J* = 3.3 Hz), 128.6 (d, *J* = 8.0 Hz), 115.8 (d, *J* = 21.5 Hz), 55.1, 50.1, 34.3, 34.1, 30.5, 23.5.

minor diastereomer product: **14b**

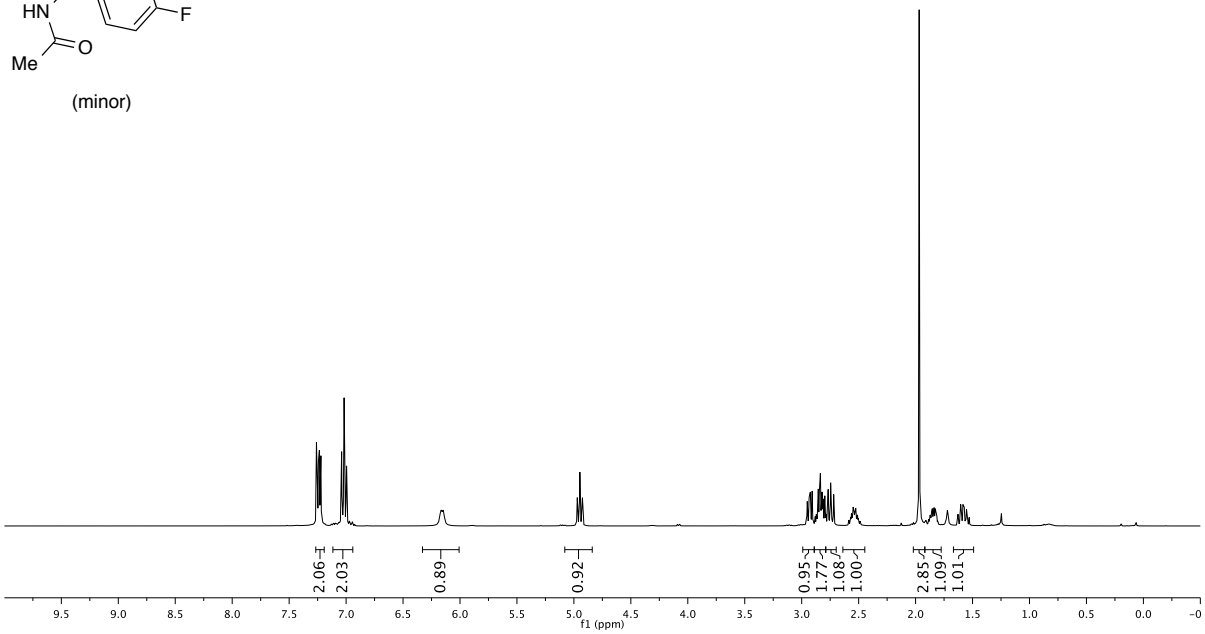
41-18-11-bhsieh.10.fid
Sample fly-11-095-PTLC-2-A
group bode



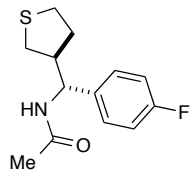
(minor)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26, 7.26, 7.25, 7.24, 7.24, 7.23, 7.23, 7.22, 7.04, 7.03, 7.03, 7.02, 7.02, 7.01, 7.01, 7.00, 7.00, 6.17, 6.15, 4.97, 4.95, 4.93, 2.95, 2.93, 2.92, 2.91, 2.88, 2.87, 2.86, 2.85, 2.85, 2.84, 2.83, 2.82, 2.81, 2.81, 2.80, 2.79, 2.79, 2.77, 2.77, 2.75, 2.74, 2.72, 2.59, 2.57, 2.57, 2.56, 2.56, 2.56, 2.55, 2.54, 2.53, 2.53, 2.52, 2.51, 2.50, 2.50, 2.49, 1.98, 1.97, 1.96, 1.96, 1.88, 1.87, 1.87, 1.86, 1.85, 1.84, 1.84, 1.83, 1.82, 1.81, 1.63, 1.61, 1.60, 1.60, 1.58, 1.58, 1.58, 1.57, 1.56, 1.55, 1.55, 1.53.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.24 (ddd, *J* = 8.7, 4.5, 1.9 Hz, 2 H), 7.09–6.96 (m, 2 H), 6.16 (d, *J* = 8.6 Hz, 1 H), 4.95 (t, *J* = 9.0 Hz, 1 H), 2.93 (dd, *J* = 10.7, 6.5 Hz, 1 H), 2.89–2.78 (m, 2 H), 2.74 (dd, *J* = 10.8, 8.6 Hz, 1 H), 2.63–2.46 (m, 1 H), 1.97 (s, 3 H), 1.85 (dtd, *J* = 12.1, 5.9, 3.7 Hz, 1 H), 1.58 (dtd, *J* = 12.7, 9.6, 7.7 Hz, 1 H).

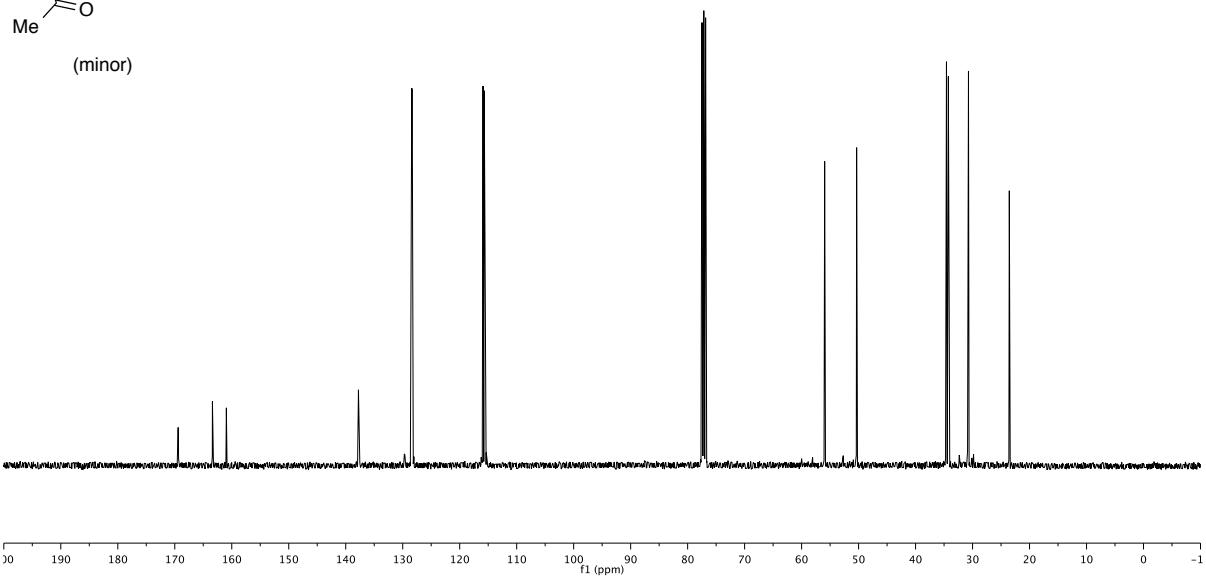


41-18-11-bhsieh.11.fid
Sample fly-11-095-PTLC-2-A
group bode

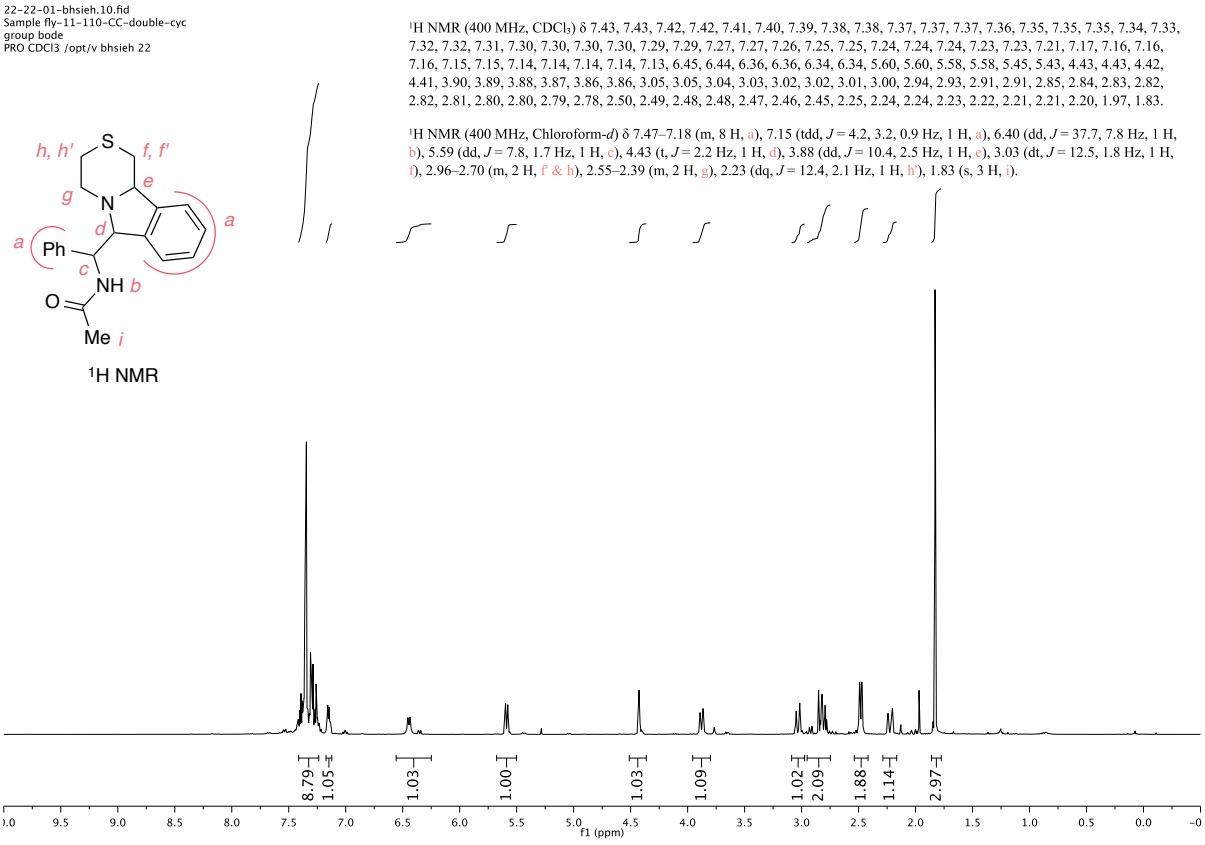


(minor)

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 162.2 (d, *J* = 246.3 Hz), 137.8 (d, *J* = 3.3 Hz), 128.4 (d, *J* = 8.1 Hz), 115.8 (d, *J* = 21.4 Hz), 56.0, 50.3, 34.6, 34.2, 30.7, 23.6.

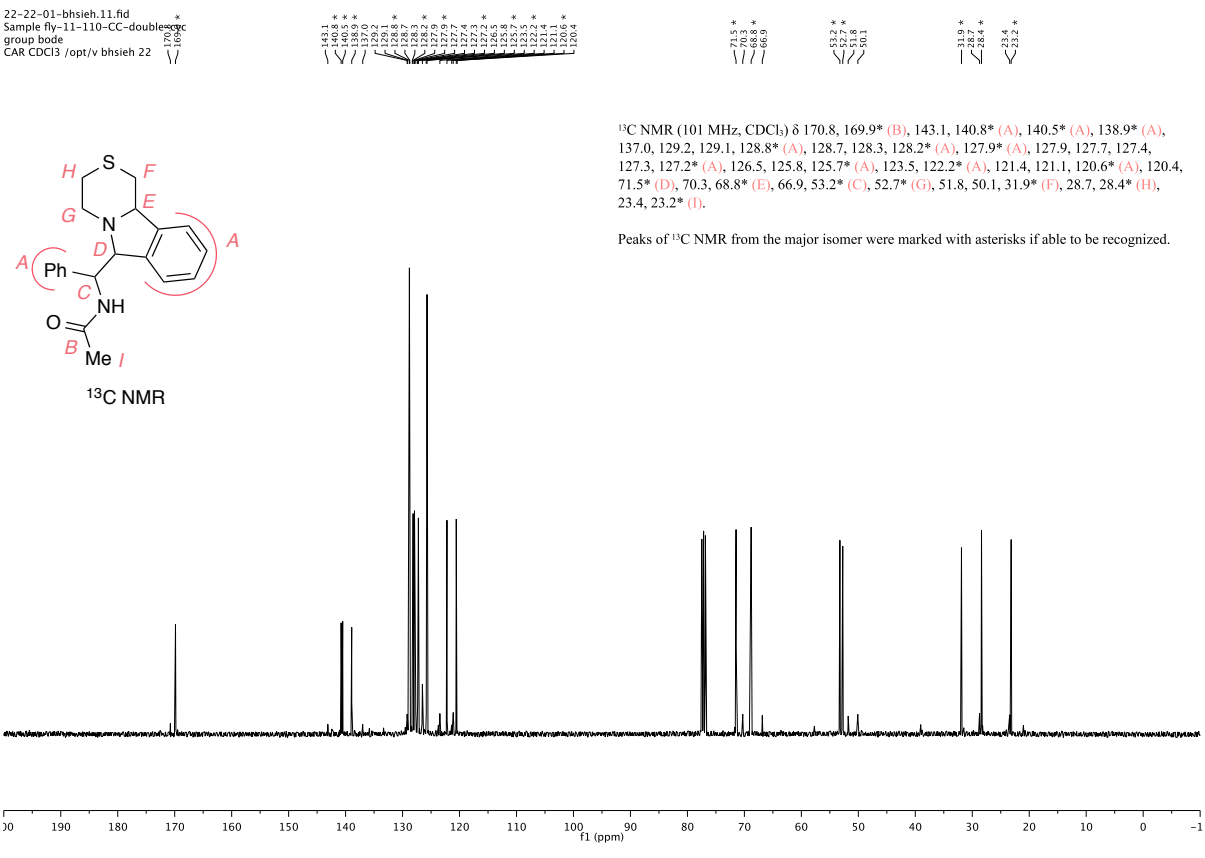


N-(Phenyl(3,4,6,10b-tetrahydro-1*H*-[1,4]thiazino[3,4-*a*]isoindol-6-yl)methyl)acetamide, mixture of isomers (16) (Scheme 5b)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43, 7.43, 7.42, 7.42, 7.41, 7.40, 7.39, 7.38, 7.38, 7.37, 7.37, 7.37, 7.36, 7.35, 7.35, 7.35, 7.34, 7.33, 7.32, 7.32, 7.31, 7.30, 7.30, 7.30, 7.30, 7.29, 7.29, 7.27, 7.27, 7.26, 7.25, 7.25, 7.24, 7.24, 7.24, 7.23, 7.23, 7.21, 7.17, 7.16, 7.16, 7.16, 7.15, 7.15, 7.14, 7.14, 7.14, 7.14, 7.13, 6.45, 6.44, 6.36, 6.36, 6.34, 6.34, 5.60, 5.60, 5.58, 5.58, 5.45, 5.43, 4.43, 4.43, 4.42, 4.41, 3.90, 3.89, 3.88, 3.87, 3.86, 3.86, 3.05, 3.05, 3.04, 3.03, 3.02, 3.02, 3.01, 3.00, 2.94, 2.93, 2.91, 2.91, 2.85, 2.84, 2.83, 2.82, 2.82, 2.81, 2.80, 2.80, 2.79, 2.78, 2.50, 2.49, 2.48, 2.48, 2.47, 2.46, 2.45, 2.25, 2.24, 2.24, 2.23, 2.22, 2.21, 2.21, 2.20, 1.97, 1.83.

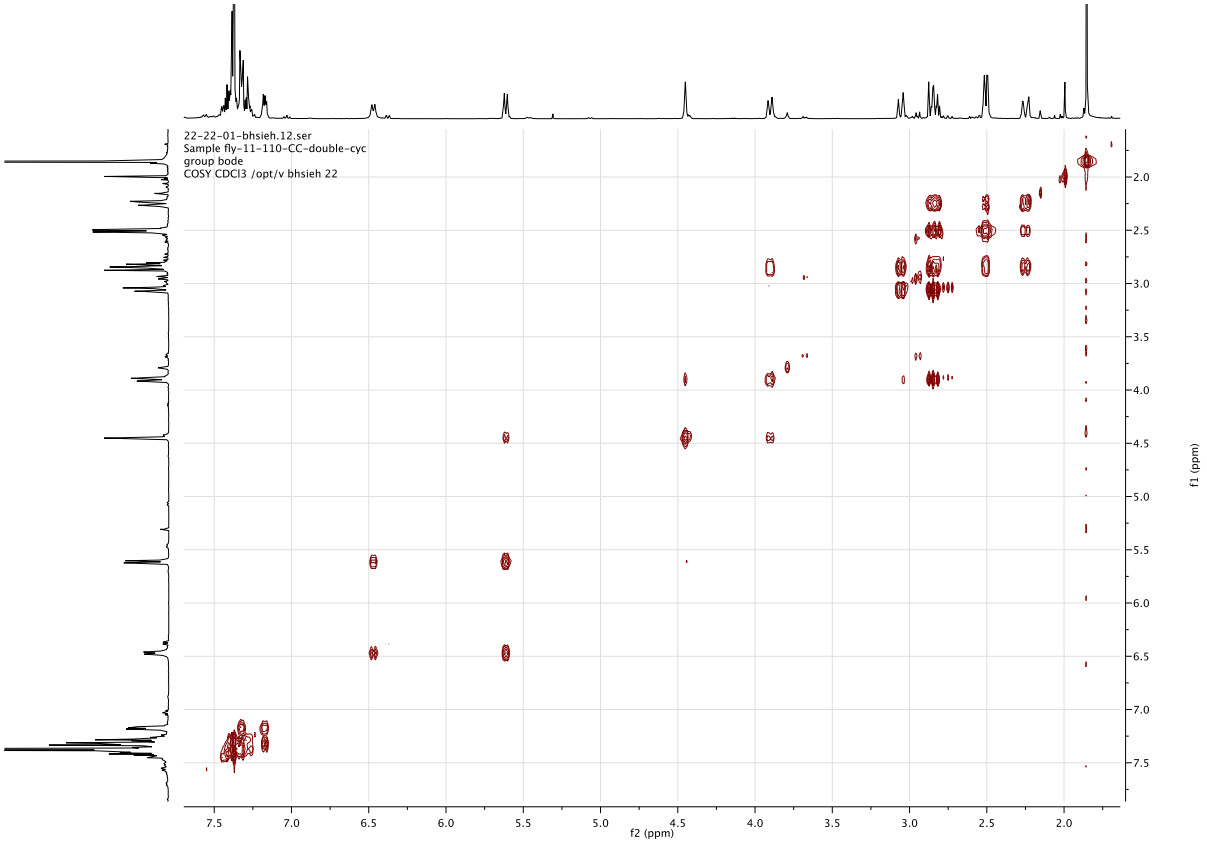
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47–7.18 (m, 8 H, a), 7.15 (tdd, *J* = 4.2, 3.2, 0.9 Hz, 1 H, a), 6.40 (dd, *J* = 37.7, 7.8 Hz, 1 H, b), 5.59 (dd, *J* = 7.8, 1.7 Hz, 1 H, e), 4.43 (t, *J* = 2.2 Hz, 1 H, d), 3.88 (dd, *J* = 10.4, 2.5 Hz, 1 H, e), 3.03 (dt, *J* = 12.5, 1.8 Hz, 1 H, f), 2.96–2.70 (m, 2 H, f' & h), 2.55–2.39 (m, 2 H, g), 2.23 (dq, *J* = 12.4, 2.1 Hz, 1 H, h'), 1.83 (s, 3 H, i).



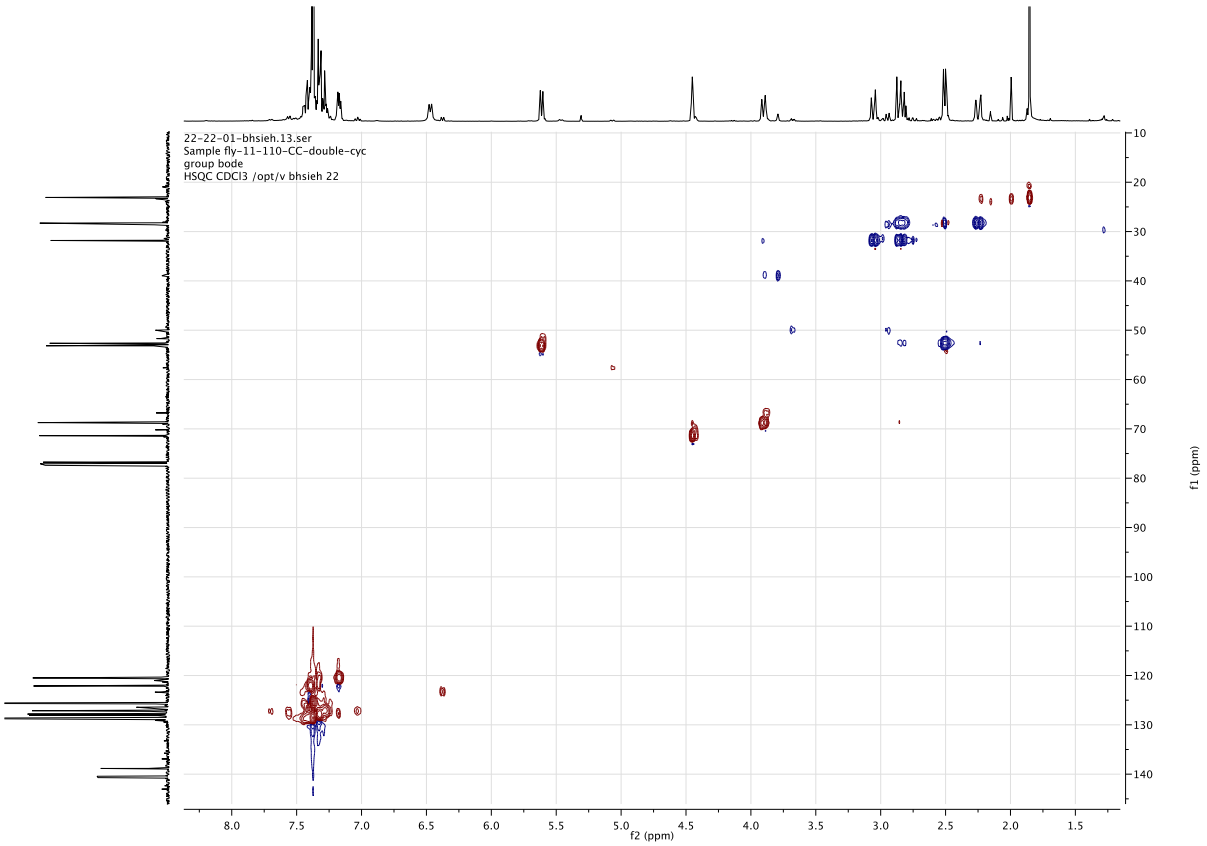
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 169.9* (B), 143.1, 140.8* (A), 140.5* (A), 138.9* (A), 137.0, 129.2, 129.1, 128.8* (A), 128.7, 128.3, 128.2* (A), 127.9* (A), 127.9, 127.7, 127.4, 127.3, 127.2* (A), 126.5, 125.8, 125.7* (A), 123.5, 122.2* (A), 121.4, 121.1, 120.6* (A), 120.4, 71.5* (D), 70.3, 68.8* (E), 66.9, 53.2* (C), 52.7* (G), 51.8, 50.1, 31.9* (F), 28.7, 28.4* (H), 23.4, 23.2* (I).

Peaks of ^{13}C NMR from the major isomer were marked with asterisks if able to be recognized.

* COSY spectra of **16**.



* HSQC spectra of **16**.



* HMBC spectra of **16**.