

Supporting Information

Palladium-Catalyzed Intermolecular [4 + 2] Formal Cycloaddition with (Z)-3-Iodo Allylic Nucleophiles and Allenamides

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Table of Contents

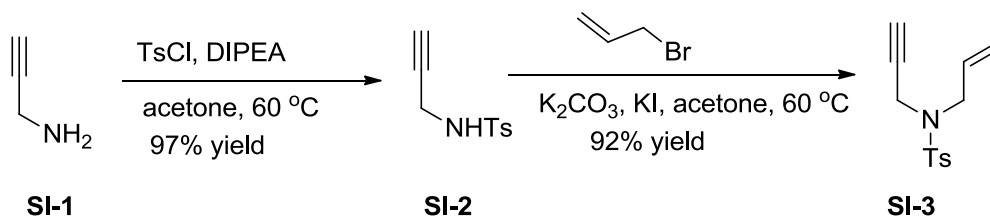
I.	General Information		S3
II.	The Procedure for Substrate Synthesis and Analytical Data for Allenamides 1a -1f, Alkenyl iodide alcohols 2a – 2k and 3-iodide acrylamines 4a – 4e.		S4
III.	The General Synthetic Procedure and Analytical Data for 2-amino-3-methylene-3, 6-dihydro-pyran derivatives.		S20
IV	The General Synthetic Procedure and Analytical Data for 2-amino-3-methylene-1,2,3,6-tetra hydropyridine derivatives.		S33
V	The General Synthetic Procedure and Analytical Data for 2,6,7,7a-tetrahydropyrano[2,3-b]p yrrole derivatives.		S37
VI	Copies of X-Ray Crystal.		S42
VII	Copies of the ¹H NMR, ¹³C NMR, ¹⁹F NMR.		S43

I. General Information

Organic solvents were used without further purification. Purifications of reactions products were carried out by flash chromatography using silica gel (40-63 μm). ^1H NMR (400 MHz), ^{13}C NMR (100 MHz) were measured on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm, δ) downfield from residual solvents peaks and coupling constants are reported as Hertz (Hz). Splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q). Splitting patterns that could not be interpreted or easily visualized are designated as multiplet (m). Electrospray mass spectra were obtained using an ESI/TOF Mariner Mass Spectrometer. Unless otherwise noted, all other commercially available reagents and solvents were used without further purification.

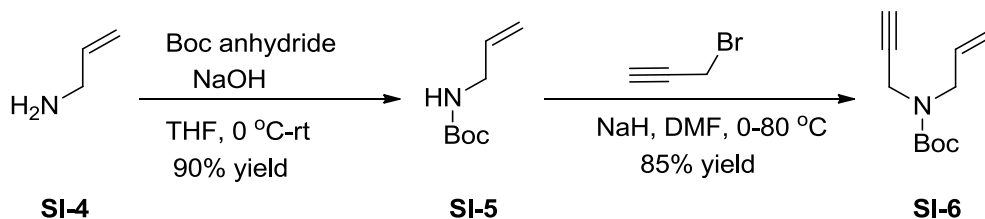
II. The Procedure for Substrate Synthesis

General procedure A: for the synthesis of allenamide (1a-1e)



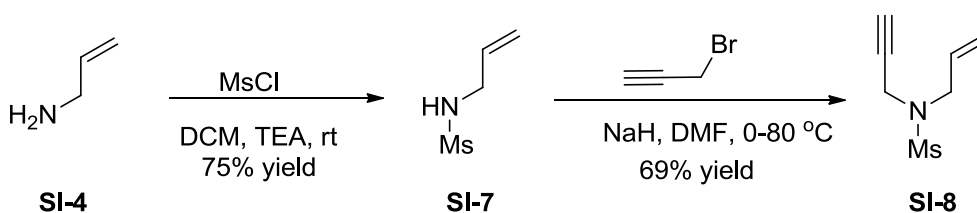
Preparation of Ts-propargylamine SI-2: To a solution of TsCl (30.0 mmol, 1.0 equiv.), DIPEA (60.0 mmol, 2.0 equiv.) in acetone (50 mL) at 60 °C was added propargylamine **SI-1** (60.0 mmol, 2.0 equiv.) after 0.5 h later. The mixture was stirred with reflux at 60 °C for 5 h. After successive filtration and purification by column chromatography (PE:EA, 10:1), **SI-2** was given as white solid.

Preparation of propynylamine SI-3: Dropwise adding 3-Bromopropene (18.46 mmol, 1.3 equiv.) to the mixture of **SI-2** (14.2 mmol, 1.0 equiv.), K₂CO₃ (28.4 mmol, 2.0 equiv.), KI (28.4 mmol, 2.0 equiv.) and acetone (50 mL). The mixture was stirred with reflux at 60 °C for 5 h. The precipitate that had formed was filtered off and then organic layer was dried over Na₂SO₄ and evaporated. The crude product was purified by column chromatography (PE:EA, 15:1) to give the **SI-3** as a white solid.



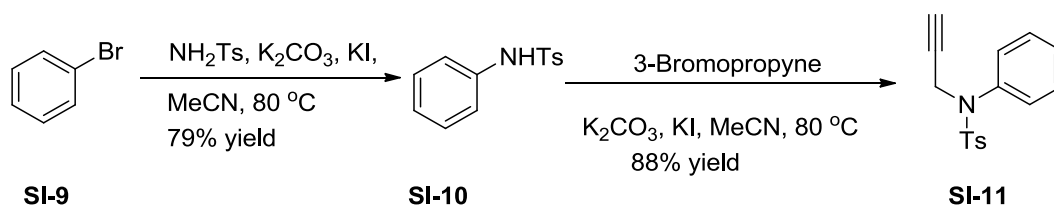
Preparation of allylamins SI-5: To a solution of 3-aminopropylene **SI-4** (35.0 mmol, 1.0 equiv.) in THF (20 mL) at 0 °C was added NaOH aqueous solution (16.00 ml, 35.0 mmol, 2mol/L) for 30 min. Then a solution of di-tert-butyl dicarbonate (35.0 mmol, 1.0 equiv.) in 20 mL THF was added dropwise by constant pressure funnel under vigorous stirring. The mixture was stirred at room temperature over night and then washed with water (50 mL x 3). The organic layer was dried over Na₂SO₄ and concentrated to afford the crude **SI-5**, which was used without further purification.

Preparation of boc-propynylamine SI-6: To a solution of **SI-5** (3.14 g, 20.0 mmol, 1.0 equiv.) in DMF (20 mL) at 0 °C was added NaH (0.92 g, 24.0 mmol, 1.2 equiv.) for 40 min. Then a solution of 3-Bromopropyne (2.06 ml, 30.0 mmol, 1.5 equiv.) in 10 mL DMF was added dropwise by constant pressure funnel under vigorous stirring. Then the mixture was stirred and heated to 80 °C for 5 h. After washed with water (50 mL x 3) and then the organic layer was dried over Na₂SO₄ and purification by column chromatography (PE:EA, 10:1), boc-propynylamine **SI-6** was given as light yellow oil.



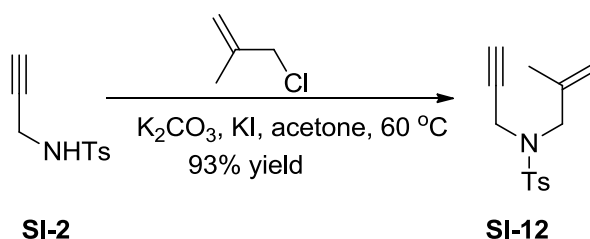
Preparation of ms-allylamin SI-7: To a solution of 3-aminopropylene **SI-4** (50.0 mmol, 1.0 equiv.) in DCM (80 mL) at room temperature was added TEA (200.0 mmol, 4.0 equiv.). Then a solution of methanesulfonyl chloride (50 mmol, 1.0 equiv.) in 20 mL DCM was added dropwise by constant pressure funnel under vigorous stirring. The mixture was stirred at room temperature 30 min and then washed with 1N HCl (50 mL x 3). The organic layer was dried over Na₂SO₄ and concentrated. After successive purification by column chromatography (PE:EA, 2:1), ms-allylamin **SI-7** was given as colorless oil.

Preparation of ms-propynylamine SI-8: To a solution of **SI-7** (27.0 mmol, 1.0 equiv.) in DMF (30 mL) at 0 °C was added NaH (32.4 mmol, 1.2 equiv.) for 50 min. Then a solution of 3-Bromopropyne (32.4 mmol, 1.2 equiv.) in 15 mL DMF was added dropwise by constant pressure funnel under vigorous stirring. Then the mixture was stirred and refluxed at 80 °C for 3 h. After washed with water (50 mL x 3) and then the organic layer was dried over Na₂SO₄ and purification by column chromatography (PE:EA, 5:1), ms-propynylamine **SI-8** was given as light yellow oil.

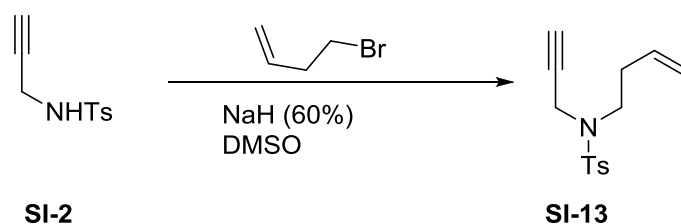


Preparation of SI-10: Dropwise adding bromobenzene **SI-9** (30.0 mmol, 1.2 equiv.) to the mixture of NH_2Ts (25.0 mmol, 1.0 equiv.), K_2CO_3 (50.0 mmol, 2.0 equiv.), KI (50.0 mmol, 2.0 equiv.) and MeCN (80 mL). The mixture was stirred with reflux at 80 °C for 5 h. The precipitate that had formed was filtered off and then organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (PE:EA, 15:1) to give the **SI-10** as a grey solid.

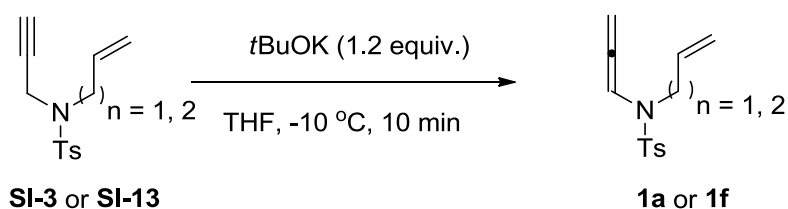
Preparation of SI-11: Dropwise adding 3-bromopropyne (13.0 mmol, 1.3 equiv.) to the mixture of **SI-10** (10.0 mmol, 1.0 equiv.), K_2CO_3 (20.0 mmol, 2.0 equiv.), KI (20.0 mmol, 2.0 equiv.) and MeCN (20 mL). The mixture was stirred with reflux at 80 °C for 5 h. The precipitate that had formed was filtered off and then organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (PE:EA, 10:1) to give the **SI-11** as a white solid.



Preparation of SI-12: Dropwise adding 2-methylallylchloride (26.0 mmol, 1.3 equiv.) to the mixture of **SI-2** (12.0 mmol, 1.0 equiv.), K_2CO_3 (24.0 mmol, 2.0 equiv.), KI (24.0 mmol, 2.0 equiv.) and acetone (50 mL). The mixture was stirred with reflux at 60 °C for 5 h. The precipitate that had formed was filtered off and then organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography (PE:EA, 10:1) to give the **SI-12** as a white solid.

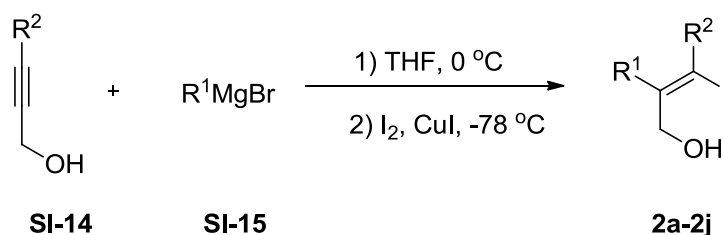


Preparation of SI-13: Under nitrogen, a solution of **SI-2** (2.69 g, 12.85 mmol) in dry DMSO (40 mL) in a 50-mL two-neck round-bottom flask was placed in a 25 °C water bath and then treated with 60% w/w NaH in mineral oil (770.4 mg, 19.26 mmol). After stirring for 1 h, 1-bromo-3-butene (2.0 mL, 19.70 mmol) was added dropwise over 10 minutes. After stirring at 25 °C for 12 h, a saturated aqueous NH_4Cl solution (40 mL) was added to quench the reaction. The deionizer water (200mL) was added and the solution was stirred for a while. The mixture was extracted with dichloromethane (50 mL), which was extracted with brine 4 times. The organic layer were concentrated on a rotary evaporator. Purification of the residue by silica gel flash chromatography (PE/EA 10:1) afforded the desired product (2.83 g, 83.7%) as faint yellow liquid.



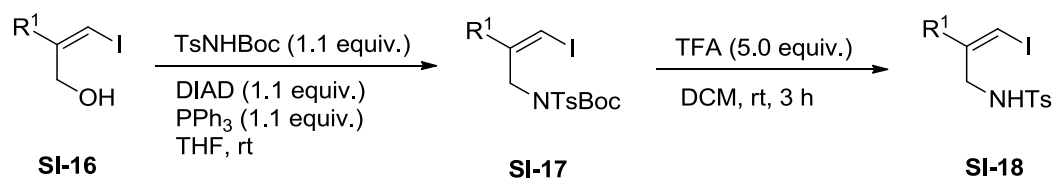
Preparation of allenamide 1a and 1f: To a solution of **SI-3** or **SI-13** (12.0 mmol, 1.0 equiv.) in anhydrous THF (30 mL) at -10 °C was added $t\text{BuOK}$ (14.0 mmol, 1.2 equiv.) for 10 min. After successive purification by column chromatography (PE:EA, 5:1), allenamide **1a** was given as white solid, allenamide **1f** was given as white paste.

General procedure B: synthesis of alkenyl iodide alcohols 2a-2j.



Compounds **2a-2j** were prepared as described in the literature(R. C. Larock, M. J. Doty, X. Han *J. Org. Chem.*, 1999, 64, 8770–8779). To a stirred solution of propargyl alcohol **SI-14** (50 mmol, 1.0 equiv.) in anhydrous THF (100 mL) under N₂ atmosphere was added CuI (5 mmol, 10 mol%) and the mixture was cooled to -78 °C. Freshly prepared Grignard reagent **SI-15** (125 mmol, 2.5 equiv.) in THF (100 mL) was added via constant pressure funnel maintain the temperature below -60 °C for 1 h. Then, the mixture was allowed to warm up to room temperature and vigorously stirred overnight. The reaction was cooled again to -78 °C and treated with I₂ (55 mmol, 1.1 equiv.) in anhydrous THF (100 mL). After warming up to room temperature and stirring at rt for additional 1h, the reaction mixture was kept in refrigerator at about 0-3 °C over 3 hours. The mixture was cooled to 0 °C and was quenched with saturated aqueous NH₄Cl (50 mL). The two phase mixture was poured through a separatory funnel and combined organic layers were washed extracted with saturated aqueous Na₂S₂O₃ (2 x 50 mL) and saturated aqueous NaCl (100 mL), and dried over Na₂SO₄. It was purified by column chromatography to give **2a-2j**.

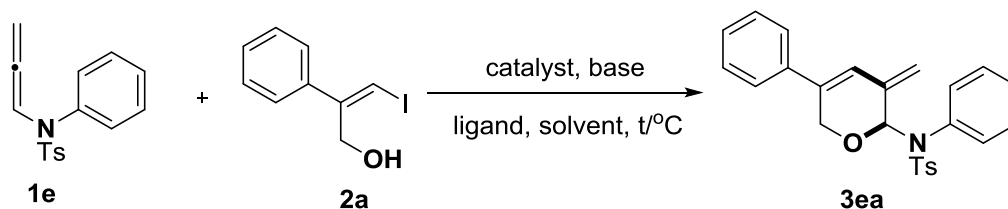
General procedure C: synthesis of 3-iodide acrylamines **SI-18**



To a solution of TsNHBoc (4.4 mmol, 1.1 equiv.) in THF (15 mL) at room temperature was added PPh₃ (4.4 mmol, 1.1 equiv.) and DIAD (4.4 mmol, 1.1 equiv.). Then a solution of **SI-16** (4.0 mmol, 1.0 equiv.) in 10 mL THF was added by constant pressure funnel under moderate stirring. Then the mixture was stirred overnight. After washed with water (50 mL x 3) and 1 N HCl (20 mL), then the organic layer was dried over Na₂SO₄ and purification by column chromatography to give **SI-17**. To a solution of **SI-17** (2.0 mmol, 1.0 equiv.) in anhydrous DCM (15 mL) at room temperature was added TFA (10.0 mmol, 5.0 equiv.) by syringe. Then the

mixture was stirred for 3 h. The mixture was quenched with saturated aqueous NaHCO₃ (30 mL). The organic part was dried over Na₂SO₄, evaporated and purified by column chromatography to give **SI-18**.

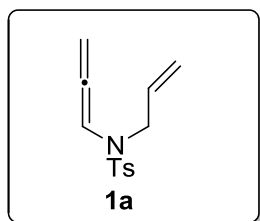
The screening of the reaction conditions for the N-phenyl allenamide.



entry	catalyst	ligand	base	$t(^{\circ}\text{C})$	solvent	yield ^b (%)
1	Pd(OAc) ₂	PPh ₃	Cy ₂ NMe	80	dioxane	22
2	Pd(OAc) ₂	PPh ₃	TEA	80	dioxane	38
3	PdCl ₂ (PPh ₃) ₂	-	K ₂ CO ₃	80	dioxane	35
4	Pd(PPh ₃) ₄	-	DMAP	80	dioxane	40
5	Pd(PPh₃)₄	-	DMAP	50	dioxane	49
6	Pd(PPh ₃) ₄	-	Cy ₂ NMe	50	dioxane	31
7	Pd(PPh ₃) ₄	-	TEA	50	dioxane	34

^a) Reaction Conditions: **1e** (0.2 mmol), **2a** (0.2 mmol), [Pd] (0.02 mmol), base (0.4 mmol), solvent (2.0 mL), N₂, 2.5 h. ^b) Isolated yields.

Analytical Data for Allenamides 1a -1f, Alkenyl iodide alcohols 2a – 2k and 3-iodide acrylamines 4a – 4e.



$C_{13}H_{15}NO_2S$

MW: 249.33 g·mol⁻¹

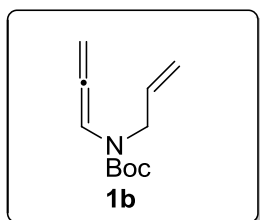
White solid

Isolated Amount: 1.80 g **Yield:** 83%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.70 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.82 (t, *J* = 6.0 Hz, 1H), 5.73-5.63 (m, 1H), 5.27 (d, *J* = 6.4 Hz, 2H), 5.19-5.11 (m, 2H), 3.78 (d, *J* = 5.6 Hz, 2H), 2.45 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 201.9, 143.7, 135.5, 132.4, 129.7, 127.2, 118.1, 99.9, 87.8, 48.8, 21.5.

MS (EI) *m/z* 249 (M⁺); **HRMS (ESI)** Calcd for C₁₃H₁₅NO₂S+H 250.0902, Found 250.0904.



$C_{11}H_{17}NO_2S$

MW: 195.26 g·mol⁻¹

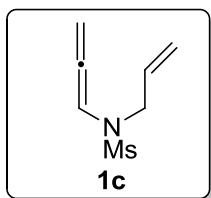
Light-yellow liquid

Isolated Amount: 1.47 g **Yield:** 63%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.15 (s, 0.5H), 6.98 (s, 0.5H), 5.78-5.75 (br, 1H), 5.31 (s, 2H), 5.12 (s, 1H), 5.01 (s, 1H), 3.96 (s, 1H), 3.91 (s, 1H), 1.48 (s, 9H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 210.73, 133.1, 116.2, 100.2, 87.1, 86.5, 81.0, 46.7, 20.2.

MS (EI) *m/z* 195 (M⁺); **HRMS (ESI)** Calcd for C₁₁H₁₇NO₂S+H 196.1338, Found 196.1340.



$C_7H_{11}NO_2S$

MW: 173.23 g·mol⁻¹

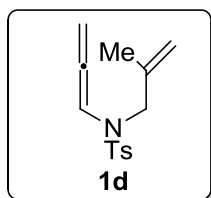
Colourless liquid

Isolated Amount: 1.16 g **Yield:** 56%

¹H NMR (400 MHz, CDCl₃, δ ppm): 6.72-6.65 (m, 1H), 5.81-5.75 (m, 1H), 5.38 (dd, *J* = 6.4, 0.4 Hz, 2H), 5.32-5.28 (m, 1H), 5.25-5.23 (m, 1H), 5.95 (d, *J* = 6.0 Hz, 2H), 2.89 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 201.1, 132.0, 118.7, 99.5, 88.0, 48.8, 38.8.

MS (EI) *m/z* 173 (M⁺); **HRMS (ESI)** Calcd for C₇H₁₁NO₂S+H 174.0589, Found 174.0588.



$C_{14}H_{17}NO_2S$

MW: 263.36 g·mol⁻¹

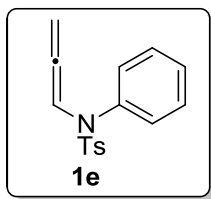
White solid

Isolated Amount: 2.53 g **Yield:** 80%

¹H NMR (400 MHz, CDCl₃, δ ppm): 6.69 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.78 (t, *J* = 6.0 Hz, 1H), 5.32-5.28 (m, 1H), 5.22 (d, *J* = 6.0 Hz, 2H), 4.89-4.88 (m, 2H), 3.65 (s, 2H), 2.43 (s, 3H), 1.72 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 202.3, 143.7, 139.6, 135.3, 129.7, 127.2, 113.3, 99.9, 87.7, 52.1, 21.6, 19.8.

MS (EI) *m/z* 263 (M⁺); **HRMS (ESI)** Calcd for C₁₄H₁₇NO₂S+H 264.1058, Found 264.1055.



$C_{16}H_{15}NO_2S$

MW: 285.36 g·mol⁻¹

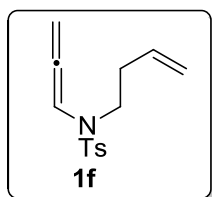
Light yellow solid

Isolated Amount: 2.91 g **Yield:** 85%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.55 (d, *J* = 8.4 Hz, 2H), 7.31-7.28 (m, 5H), 7.11 (t, *J* = 6.0 Hz, 1H), 7.01-6.99 (m, 2H), 5.02 (d, *J* = 6.4 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 201.1, 143.9, 137.2, 135.3, 129.55, 129.50, 128.7, 128.6, 127.7, 102.4, 87.4, 21.6.

MS (EI) m/z 285 (M^+); **HRMS (ESI)** Calcd for $\text{C}_{16}\text{H}_{15}\text{NO}_2\text{S}+\text{H}$ 286.0902, Found 286.0905.



$\text{C}_{14}\text{H}_{17}\text{NO}_2\text{S}$

MW: $263.36\text{ g}\cdot\text{mol}^{-1}$

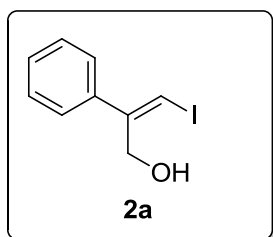
White paste

Isolated Amount: 2.55 g **Yield:** 90%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.66 (d, $J = 8.4$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 6.81 (t, $J = 6.0$ Hz, 1H), 5.76-5.65 (m, 1H), 5.29 (d, $J = 6.0$ Hz, 2H), 5.01-4.98 (m, 2H), 3.15 (t, $J = 7.2$ Hz, 2H), 2.39 (s, 3H), 2.27 (q, $J = 7.2$ Hz, 2H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 201.2, 143.6, 135.2, 134.2, 129.6, 126.9, 116.8, 99.8, 87.5, 45.7, 32.2, 21.4.

MS (EI) m/z 263 (M^+); **HRMS (ESI)** Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_2\text{S}+\text{H}$ 264.1058, Found 264.1060.



$\text{C}_9\text{H}_9\text{IO}$

MW: $260.07\text{ g}\cdot\text{mol}^{-1}$

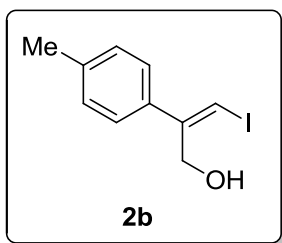
Light yellow liquid

Isolated Amount: 7.15 g **Yield:** 55%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.38-7.29 (m, 5H), 6.59 (s, 1H), 4.63 (s, 2H), 2.11 (s, 1H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 149.6, 138.9, 128.6, 128.2, 126.5, 81.2, 66.7.

MS (EI) m/z 260 (M^+); **HRMS (ESI)** Calcd for $\text{C}_9\text{H}_9\text{IO}+\text{H}$ 260.9776, Found 260.9778.



$C_{10}H_{11}IO$

MW: 274.10 g·mol⁻¹

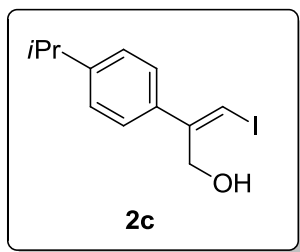
Colourless liquid

Isolated Amount: 8.77 g **Yield:** 64%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.25 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.53 (s, 1H), 4.60 (d, *J* = 5.6 Hz, 2H), 2.31 (s, 3H), 2.15 (t, *J* = 6.0 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 149.4, 138.0, 135.9, 129.2, 126.3, 80.2, 66.6, 21.1.

MS (EI) *m/z* 274 (M⁺); **HRMS (ESI)** Calcd for C₁₀H₁₁IO+H 274.9933, Found 274.9935.



$C_{12}H_{15}IO$

MW: 302.15 g·mol⁻¹

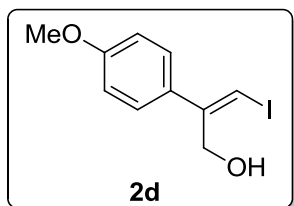
Light yellow solid

Isolated Amount: 4.29 g **Yield:** 57%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.31 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.57 (s, 1H), 4.66 (d, *J* = 5.6 Hz, 2H), 2.93-2.87 (m, 1H), 2.03-1.94 (m, 1H), 1.24 (dd, *J* = 6.8, 1.6 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 149.5, 149.1, 136.3, 127.3, 126.7, 126.5, 80.3, 66.8, 33.8, 23.8.

MS (EI) *m/z* 302 (M⁺); **HRMS (ESI)** Calcd for C₁₂H₁₅IO+H 303.1246, Found 303.1244.



$C_{10}H_{11}IO_2$

MW: 290.10 g·mol⁻¹

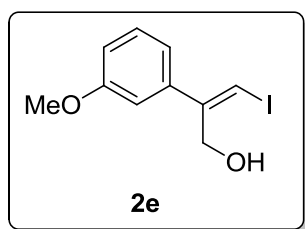
Light gray solid

Isolated Amount: 4.54 g **Yield:** 62%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.32 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.50 (s, 1H), 4.61 (s, 2H), 3.79 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 159.5, 148.9, 131.3, 127.7, 114.0, 79.3, 66.7, 55.2.

MS (EI) m/z 290 (M^+); **HRMS (ESI)** Calcd for $\text{C}_{10}\text{H}_{11}\text{IO}_2 + \text{H}$ 290.9882, Found 290.9879.



$\text{C}_{10}\text{H}_{11}\text{IO}_2$

MW: 290.10 $\text{g}\cdot\text{mol}^{-1}$

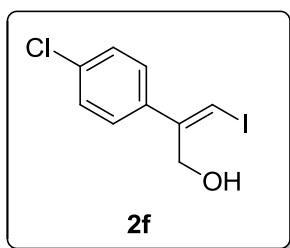
Light gray solid

Isolated Amount: 2.90 g **Yield:** 40%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.26-7.22 (m, 1H), 6.96-6.94 (m, 1H), 6.91 (d, $J = 2.4$ Hz, 1H), 6.86-6.83 (m, 1H), 6.61 (d, $J = 2.4$ Hz, 1H), 4.63 (s, 2H), 3.79-3.78 (m, 3H), 2.02 (d, $J = 1.6$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 159.5, 149.5, 140.3, 129.5, 118.9, 113.6, 112.2, 81.3, 66.7, 55.2.

MS (EI) m/z 290 (M^+); **HRMS (ESI)** Calcd for $\text{C}_{10}\text{H}_{11}\text{IO}_2 + \text{H}$ 290.9882, Found 290.9880.



$\text{C}_9\text{H}_8\text{ClIO}$

MW: 294.52 $\text{g}\cdot\text{mol}^{-1}$

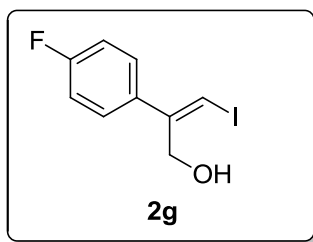
Light gray solid

Isolated Amount: 1.98 g **Yield:** 27%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.31 (s, 3H), 7.16-7.14 (m, 1H), 6.73-6.71 (m, 1H), 6.66 (s, 1H), 4.67 (s, 2H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 154.4, 129.3, 128.8, 127.8, 116.6, 82.1, 66.7.

MS (EI) m/z 294 (M^+); **HRMS (ESI)** Calcd for $\text{C}_9\text{H}_8\text{ClIO} + \text{H}$ 294.9387, Found 294.9389.



C_9H_8FIO

MW: 278.06 g·mol⁻¹

Light yellow solid

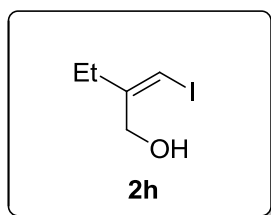
Isolated Amount: 1.90 g **Yield:** 27%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.36-7.33 (m, 2H), 7.00 (t, *J* = 8.4 Hz, 2H), 6.57 (s, 1H), 4.62 (s, 2H), 2.51 (s, 1H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 163.7, 161.2, 148.4, 134.9 (d, *J* = 13.4 Hz), 128.2 (d, *J* = 8.0 Hz), 115.5, 115.3, 81.0 (d, *J* = 1.5 Hz), 66.6.

¹⁹F{¹H} NMR (376 MHz, CDCl₃, δ ppm): -113.1.

MS (EI) *m/z* 278 (M⁺); **HRMS (ESI)** Calcd for C₉H₈FIO+H 278.9682, Found 278.9680.



C_5H_9IO

MW: 212.03 g·mol⁻¹

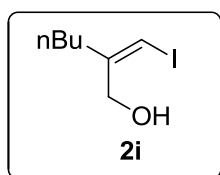
Dark yellow liquid

Isolated Amount: 7.31 g **Yield:** 69%

¹H NMR (400 MHz, CDCl₃, δ ppm): 6.65 (s, 1H), 4.25 (s, 2H), 3.01 (s, 1H), 2.37-2.31 (m, 2H), 1.08 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 151.2, 75.1, 66.7, 28.4, 12.2.

MS (EI) *m/z* 212 (M⁺); **HRMS (ESI)** Calcd for C₅H₉IO+H 212.9776, Found 212.9774.



$C_7H_{13}IO$

MW: 240.08 g·mol⁻¹

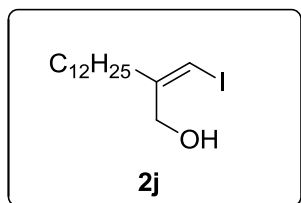
Colourless liquid

Isolated Amount: 3.60 g **Yield:** 60%

¹H NMR (400 MHz, CDCl₃, δ ppm): 5.99 (s, 1H), 4.23 (s, 2H), 2.82 (s, 1H), 2.33-2.92 (m, 2H), 1.49-1.41 (m, 2H), 1.37-1.27 (m, 2H), 0.91 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 150.0, 75.5, 66.6, 35.2, 29.7, 22.1, 13.7.

MS (EI) m/z 240 (M^+); **HRMS (ESI)** Calcd for $\text{C}_7\text{H}_{13}\text{IO}+\text{H}$ 241.0089, Found 241.0091.



$\text{C}_{15}\text{H}_{29}\text{IO}$

MW: 352.29 $\text{g}\cdot\text{mol}^{-1}$

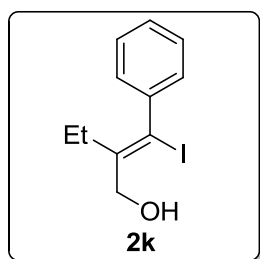
Brown solid

Isolated Amount: 7.06 g **Yield:** 80%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 5.98 (s, 1H), 4.22 (s, 2H), 2.31 (m, 2H), 2.20 (s, 1H), 1.25 (s, 20 H), 0.87 (t, $J = 6.8$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 150.2, 75.7, 66.8, 35.7, 31.9, 29.60, 29.58, 29.5, 29.34, 29.29, 29.2, 27.7, 22.6, 14.1.

MS (EI) m/z 352 (M^+); **HRMS (ESI)** Calcd for $\text{C}_{15}\text{H}_{29}\text{IO}+\text{H}$ 353.1341, Found 353.1343.



$\text{C}_{11}\text{H}_{13}\text{IO}$

MW: 288.12 $\text{g}\cdot\text{mol}^{-1}$

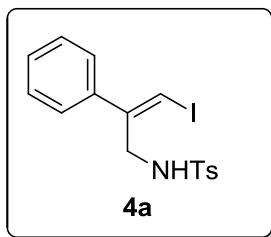
White solid

Isolated Amount: 2.52 g **Yield:** 35%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.36-7.32 (m, 2H), 7.27-7.24 (m, 2H), 7.23-7.22 (m, 1H), 4.45 (s, 2H), 2.19 (dd, $J = 14.8, 7.2$ Hz, 2H), 1.92 (s, 1H), 1.00 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 147.6, 144.0, 128.3, 128.1, 127.8, 97.8, 70.2, 25.0, 13.3.

MS (EI) m/z 288 (M^+); **HRMS (ESI)** Calcd for $\text{C}_{11}\text{H}_{13}\text{IO}+\text{H}$ 289.0089, Found 289.0086.



$C_{16}H_{16}NO_2SI$

MW: 413.27 g·mol⁻¹

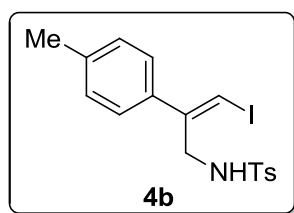
Light yellow solid

Isolated Amount: 0.65 g **Yield:** 78%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.71 (d, *J* = 8.4 Hz, 2H), 7.31-7.28 (m, 5H), 7.16-7.14 (m, 2H), 6.59 (s, 1H), 4.53 (d, *J* = 6.0 Hz, 1H), 4.18 (d, *J* = 6.4 Hz, 2H), 2.45 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 146.2, 143.6, 138.2, 136.4, 129.6, 128.8, 128.6, 127.4, 126.3, 82.8, 49.0, 21.6.

MS (EI) *m/z* 413 (M⁺); **HRMS (ESI)** Calcd for C₁₆H₁₆NO₂SI + H 414.0025, Found 414.0023.



$C_{17}H_{18}INO_2S$

MW: 427.30 g·mol⁻¹

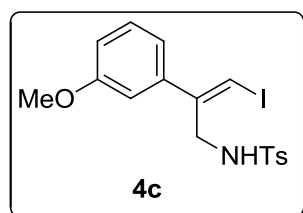
Colorless solid

Isolated Amount: 0.62 g **Yield:** 72%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.71 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.53 (s, 1H), 4.49 (t, *J* = 6.0 Hz, 1H), 4.16 (d, *J* = 6.4 Hz, 2H), 2.45 (s, 3H), 2.33 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 146.0, 143.6, 138.7, 136.4, 135.3, 129.6, 129.5, 126.2, 81.8, 48.9, 21.6, 21.1.

MS (EI) *m/z* 427 (M⁺); **HRMS (ESI)** Calcd for C₁₇H₁₈INO₂S + H 428.0181, Found 428.0183.



$C_{17}H_{18}NO_3SI$

MW: 443.30 g·mol⁻¹

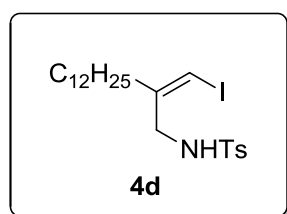
Colorless solid

Isolated Amount: 0.78 g **Yield:** 88%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.68 (d, J = 8.4 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 6.84-6.81 (m, 1H), 6.72-6.70 (m, 1H), 6.65 (t, J = 2.0 Hz, 1H), 6.57 (s, 1H), 4.61 (t, J = 6.4 Hz, 1H), 4.15 (d, J = 6.4 Hz, 1H), 3.76 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 159.7, 146.1, 143.6, 139.6, 136.4, 129.7, 129.6, 127.3, 118.6, 114.2, 112.0, 82.9, 55.3, 49.0, 21.5.

MS (EI) m/z 443 (M^+); **HRMS (ESI)** Calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_3\text{SI} + \text{H}$ 444.0130, Found 444.0128.



$\text{C}_{22}\text{H}_{36}\text{NO}_2\text{SI}$

MW: 505.50 $\text{g}\cdot\text{mol}^{-1}$

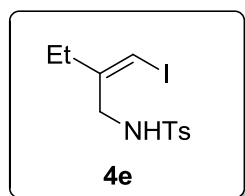
White solid

Isolated Amount: 0.76 g **Yield:** 75%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.78 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.01 (s, 1H), 4.74 (t, J = 6.4 Hz, 1H), 3.65 (d, J = 6.8 Hz, 2H), 2.43 (s, 3H), 2.17 (t, J = 6.8 Hz, 2H), 1.35-1.25 (m, 20H), 0.87 (t, J = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 146.7, 143.5, 136.5, 129.7, 127.2, 78.4, 48.8, 36.2, 31.9, 29.60, 29.58, 29.56, 29.5, 29.29, 29.27, 29.0, 27.4, 22.6, 21.5, 14.1.

MS (EI) m/z 505 (M^+); **HRMS (ESI)** Calcd for $\text{C}_{22}\text{H}_{36}\text{NO}_2\text{SI} + \text{H}$ 506.1590, Found 506.1593.



$\text{C}_{12}\text{H}_{16}\text{NO}_2\text{SI}$

MW: 365.23 $\text{g}\cdot\text{mol}^{-1}$

White solid

Isolated Amount: 0.61 g **Yield:** 83%

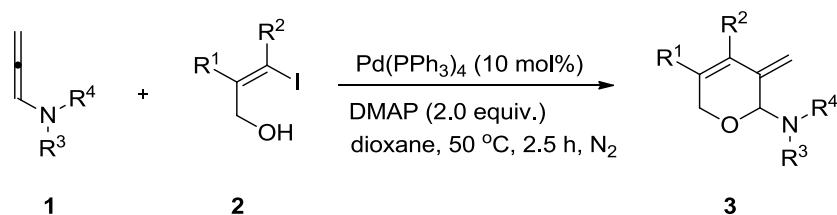
^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.78 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 6.04 (s, 1H), 4.63 (t, J = 6.4 Hz, 1H), 3.67 (d, J = 6.4 Hz, 2H), 2.44 (s, 3H), 3.27-2.21 (m, 2H), 1.00 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 148.0, 143.6, 136.5, 129.7, 127.2, 78.0, 49.1, 29.3, 21.5, 12.1.

MS (EI) m/z 365 (M⁺); **HRMS (ESI)** Calcd for C₁₂H₁₆NO₂SI+H 366.0025, Found 366.0024.

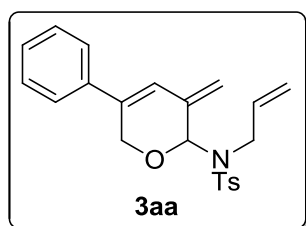
III. The General Synthetic Procedure and Analytical Data for 2-amino-3-methylene-3, 6-dihydro-pyran derivatives.

General Synthetic Procedure:



Drops of allenamide **1** (0.2 mmol, 1.0 equiv.) were added to DMAP (0.4 mmol, 2.0 equiv.) and Pd(PPh₃)₄ (0.02 mmol, 10 mol%) in 2 mL dioxane under N₂ atmosphere, subsequently, the 3-iodo allylic alcohols **2** (0.2 mmol, 1.0 equiv.) was added under stirring. The mixture was stirred at 50 °C for 2.5 h. Then the mixture was extracted by EA (10 mL x 3). The organic part was dried over Na₂SO₄, the solvent was removed under vacuum evaporated and purified by column chromatography to give 2-amino-3-methylene-3,6-dihydro-pyran derivatives **3**.

Analytical Data:



C₂₂H₂₃NO₃S

MW: 381.49 g·mol⁻¹

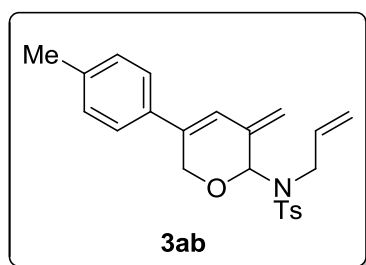
Colourless liquid

Isolated Amount: 74.0 mg Yield: 97%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.78 (d, *J* = 8.0 Hz, 2H), 7.33-7.28 (m, 7H), 6.62 (s, 1H), 6.03 (s, 1H), 5.89-5.79 (m, 1H), 5.20 (s, 1H), 5.16 (s, 1H), 5.05 (d, *J* = 17.2 Hz, 1H), 4.96 (d, *J* = 10.0 Hz, 1H), 4.57-4.47 (m, 2H), 3.86 (dd, *J* = 16.4, 6.8 Hz, 1H), 3.69 (dd, *J* = 16.4, 6.0 Hz, 1H), 2.40 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.4, 137.4, 137.1, 136.8, 136.3, 135.6, 129.3, 128.6, 128.3, 127.9, 124.8, 123.1, 116.9, 114.3, 84.9, 65.6, 47.7, 21.5.

MS (EI) *m/z* 381 (M⁺); **HRMS (ESI)** Calcd for C₂₂H₂₃NO₃S+H 382.1477, Found 382.1475.



$C_{23}H_{25}NO_3S$

MW: 395.51 g·mol⁻¹

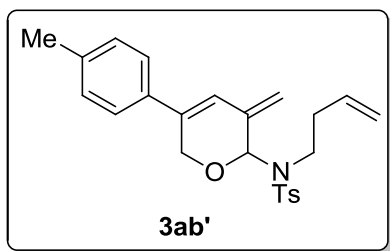
Brown liquid

Isolated Amount: 61.6 mg **Yield:** 78%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.81 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 6.63 (s, 1H), 6.06 (s, 1H), 5.93-5.83 (m, 1H), 5.21 (s, 1H), 5.17 (s, 1H), 5.09 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.00 (dd, *J* = 10.0, 1.2 Hz, 1H), 4.59-4.49 (m, 2H), 3.89 (dd, *J* = 16.4, 6.8 Hz, 1H), 3.73 (dd, *J* = 16.0, 5.6 Hz, 1H), 2.44 (s, 3H), 2.34 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.3, 138.3, 137.4, 137.1, 136.7, 135.6, 133.4, 129.4, 129.3, 127.9, 124.6, 122.3, 116.8, 113.8, 84.9, 65.6, 47.7, 21.5, 21.1.

MS (EI) *m/z* 395 (M⁺); **HRMS (ESI)** Calcd for C₂₃H₂₅NO₃S+H 396.1633, Found 396.1634.



$C_{24}H_{27}NO_3S$

MW: 409.54 g·mol⁻¹

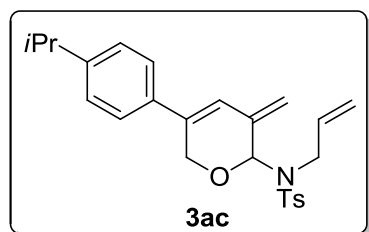
Light green jelly

Isolated Amount: 73.7 mg **Yield:** 90%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.82 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.62 (s, 1H), 6.02 (s, 1H), 5.70-5.60 (m, 1H), 5.21-5.16 (m, 2H), 5.01-4.93 (s, 2H), 4.54-4.44 (m, 2H), 3.31-3.23 (m, 1H), 3.15-3.08 (m, 1H), 2.63-2.54 (m, 1H), 2.43 (m, 4H), 2.30 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.2, 138.1, 137.7, 136.5, 135.0, 133.1, 129.3, 129.2, 127.4, 124.1, 122.0, 116.2, 113.3, 84.7, 65.3, 44.3, 34.8, 21.3, 21.0.

MS (EI) *m/z* 409 (M⁺); **HRMS (ESI)** Calcd for C₂₄H₂₇NO₃S+H 410.1790, Found 410.1788.



$C_{25}H_{29}NO_3S$

MW: 423.57 g·mol⁻¹

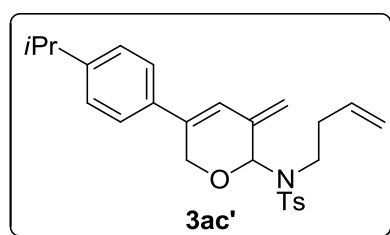
Colourless liquid

Isolated Amount: 74.5 mg **Yield:** 88%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.84 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.66 (s, 1H), 6.10 (s, 1H), 5.95-5.85 (m, 1H), 5.24 (s, 1H), 5.21 (s, 1H), 5.11 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.03 (dd, *J* = 10.0, 1.2 Hz, 1H), 4.62-4.53 (m, 2H), 3.92 (dd, *J* = 16.4, 7.2 Hz, 1H), 3.76 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.96-2.90 (m, 1H), 2.47 (s, 3H), 1.28 (s, 3H), 1.27 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 149.3, 143.4, 137.5, 137.2, 136.8, 135.6, 133.8, 129.3, 127.9, 126.7, 124.8, 122.4, 116.9, 113.9, 84.9, 65.6, 47.7, 33.8, 23.8, 21.5.

MS (EI) *m/z* 423 (M⁺); **HRMS (ESI)** Calcd for $C_{25}H_{29}NO_3S+H$ 424.1946, Found 424.1942.



$C_{26}H_{31}NO_3S$

MW: 437.60 g·mol⁻¹

Brown jelly

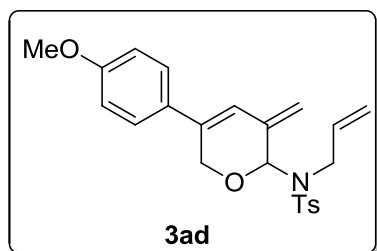
Isolated Amount: 80.5 mg **Yield:** 92%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.83 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.63 (s, 1H), 6.04 (s, 1H), 5.86-5.60 (m, 1H), 5.22-5.17 (m, 2H), 5.01-4.93 (m, 2H), 4.54-4.45 (m, 1H), 3.31-3.23 (m, 1H), 3.16-3.08 (m, 1H), 2.91-2.84 (m, 1H), 2.63-2.54 (m, 1H), 2.40-2.33 (m, 4H), 1.25-1.19 (m, 7H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 149.1, 143.3, 137.8, 136.9, 136.6, 135.1, 133.6, 129.3, 127.5, 126.6, 124.6, 122.2, 116.2, 113.4, 84.8, 65.3, 44.4, 34.9, 33.6, 23.7, 21.4.

IR (neat): ν (cm⁻¹): 3028, 2959, 2870, 2733, 2587, 2254, 1914, 1737, 1641, 1339, 1163, 828, 748, 667.

MS (EI) *m/z* 437 (M⁺); **HRMS (ESI)** Calcd for $C_{26}H_{31}NO_3S+H$ 438.2103, Found 438.2106.



$C_{23}H_{25}NO_4S$

MW: 411.51 g·mol⁻¹

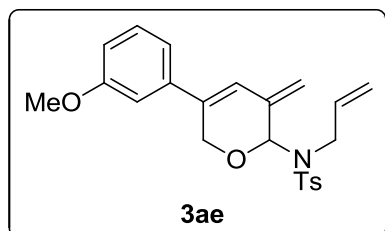
Brown liquid

Isolated Amount: 69.2 mg **Yield:** 82%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.80 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.26-7.24 (m, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.56 (s, 1H), 6.04 (s, 1H), 5.91-5.81 (m, 1H), 5.17 (s, 1H), 5.13 (s, 1H), 5.07 (dd, *J* = 17.2, 1.2 Hz, 1H), 4.98 (dd, *J* = 10.0, 0.8 Hz, 1H), 4.56-4.46 (m, 2H), 3.87 (dd, *J* = 16.0, 6.8 Hz, 1H), 3.79 (s, 3H), 3.71 (dd, *J* = 16.4, 6.0 Hz, 1H), 2.42 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 159.7, 143.4, 137.5, 137.1, 136.3, 135.6, 129.3, 128.7, 127.9, 126.0, 121.4, 116.9, 114.1, 113.4, 84.9, 65.5, 55.3, 47.7, 21.5.

MS (EI) *m/z* 411 (M⁺); **HRMS (ESI)** Calcd for C₂₃H₂₅NO₄S+H 412.1583, Found 412.1585.



$C_{23}H_{25}NO_4S$

MW: 411.51 g·mol⁻¹

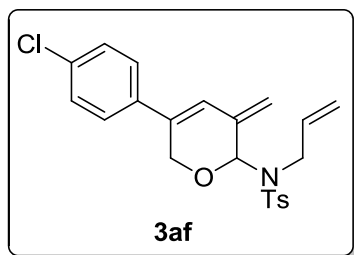
Brown liquid

Isolated Amount: 63.4 mg **Yield:** 77%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.83 (d, *J* = 8.0 Hz, 2H), 7.34-7.28 (m, 3H), 6.94-6.86 (m, 3H), 6.68 (s, 1H), 6.09 (s, 1H), 5.95-5.85 (m, 1H), 5.25 (d, *J* = 19.2 Hz, 2H), 5.11 (d, *J* = 17.2 Hz, 1H), 5.03 (d, *J* = 10.4 Hz, 1H), 4.61-4.50 (m, 2H), 3.92 (dd, *J* = 16.4, 6.8 Hz, 1H), 3.83 (s, 3H), 3.75 (dd, *J* = 16.0, 5.2 Hz, 1H), 2.42 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 159.7, 143.4, 137.7, 137.3, 137.0, 136.7, 135.5, 129.6, 129.3, 127.8, 123.3, 117.3, 116.9, 114.4, 113.4, 110.7, 84.8, 65.6, 55.2, 47.6, 21.5.

MS (EI) *m/z* 411 (M⁺); **HRMS (ESI)** Calcd for C₂₃H₂₅NO₄S+H 412.1583, Found 412.1586.



$C_{22}H_{22}ClNO_3S$

MW: 415.93 g·mol⁻¹

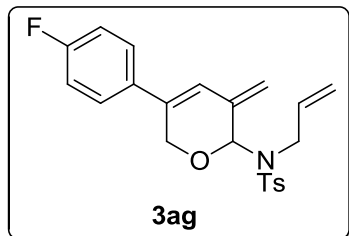
Light brown liquid

Isolated Amount: 60.0 mg **Yield:** 72%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.80 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 4H), 7.24 (d, *J* = 8.8 Hz, 2H), 6.63 (s, 1H), 6.04 (s, 1H), 5.90-5.80 (m, 1H), 5.25 (s, 1H), 5.20 (s, 1H), 5.07 (dd, *J* = 17.2, 1.2 Hz, 1H), 4.99 (dd, *J* = 10.0, 0.8 Hz, 1H), 4.57-4.46 (m, 2H), 3.88 (dd, *J* = 16.4, 7.2 Hz, 1H), 3.71 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.43 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.4, 137.2, 137.1, 135.6, 135.5, 134.8, 134.1, 129.3, 128.9, 127.9, 126.0, 123.6, 117.0, 114.9, 84.9, 65.5, 47.7, 21.5.

MS (EI) *m/z* 415 (M⁺); **HRMS (ESI)** Calcd for C₂₂H₂₂ClNO₃S+H 416.1087, Found 416.1084.



$C_{22}H_{22}FNO_3S$

MW: 399.48 g·mol⁻¹

Colourless liquid

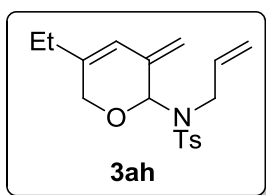
Isolated Amount: 51.9 mg **Yield:** 65%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.80 (d, *J* = 8.4 Hz, 2H), 7.32-7.27 (m, 4H), 7.05-7.01 (m, 2H), 6.59 (s, 1H), 6.06 (s, 1H), 5.90-5.82 (m, 1H), 5.24 (s, 1H), 5.19 (s, 1H), 5.08 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.00 (dd, *J* = 10.0, 1.2 Hz, 1H), 4.58-4.47 (m, 2H), 3.89 (dd, *J* = 16.4, 7.2 Hz, 1H), 3.72 (dd, *J* = 16.4, 6.0 Hz, 1H), 2.43 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 162.7 (d, *J* = 246.9 Hz), 143.4, 137.2, 137.1, 135.8, 135.5, 132.5 (d, *J* = 3.4 Hz), 132.0 (d, *J* = 9.9 Hz), 129.3, 127.9, 126.5 (d, *J* = 8.0 Hz), 123.1 (d, *J* = 1.6 Hz), 117.0, 115.8, 115.5, 114.4, 84.9, 65.6, 47.7, 21.5.

¹⁹F{¹H} NMR (376 MHz, CDCl₃, δ ppm): -113.1.

MS (EI) *m/z* 399 (M⁺); **HRMS (ESI)** Calcd for C₂₂H₂₂FNO₃S+H 400.1383, Found 400.1384.



$C_{18}H_{23}NO_3S$

MW: 333.45 g·mol⁻¹

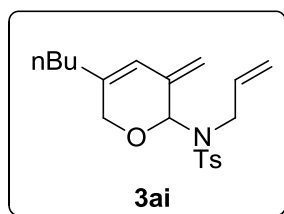
Colourless liquid

Isolated Amount: 43.3 mg **Yield:** 65%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.77 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.02 (s, 1H), 5.95 (s, 1H), 5.90-5.80 (m, 1H), 5.07 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.03 (s, 1H), 4.50-4.96 (m, 2H), 4.17 (d, *J* = 16.4 Hz, 1H), 3.96 (d, *J* = 16.4 Hz, 1H), 3.84 (dd, *J* = 16.4, 6.8 Hz, 1H), 3.67 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.42 (s, 3H), 2.00 (q, *J* = 15.0 Hz, 2H), 1.04 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.3, 141.6, 137.3, 137.2, 135.7, 129.2, 127.8, 120.7, 116.7, 111.4, 85.1, 66.9, 47.6, 25.4, 21.5, 11.5.

MS (EI) *m/z* 333 (M⁺); **HRMS (ESI)** Calcd for C₁₈H₂₃NO₃S+H 334.1477, Found 334.1476.



$C_{20}H_{27}NO_3S$

MW: 361.50 g·mol⁻¹

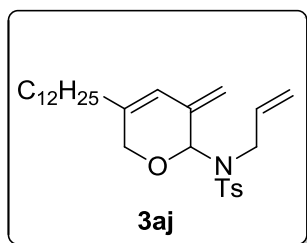
Colourless liquid

Isolated Amount: 42.7 mg **Yield:** 59%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.77 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.02 (s, 1H), 5.95 (s, 1H), 5.90-5.80 (m, 1H), 5.07 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.03 (s, 1H), 4.98 (dd, *J* = 9.2, 1.6 Hz, 1H), 4.94 (s, 1H), 4.17 (d, *J* = 16.4 Hz, 1H), 3.96 (d, *J* = 16.4 Hz, 1H), 3.84 (dd, *J* = 16.4, 6.8 Hz, 1H), 3.67 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.42 (s, 3H), 1.98 (t, *J* = 7.2 Hz, 2H), 1.41-1.27 (m, 4H), 0.90 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.3, 140.3, 137.3, 137.2, 135.7, 129.2, 127.8, 121.7, 116.7, 111.3, 85.1, 66.9, 47.6, 29.4, 22.3, 21.5, 13.7.

MS (EI) *m/z* 361 (M⁺); **HRMS (ESI)** Calcd for C₂₀H₂₇NO₃S+H 362.1790, Found 362.1788.



$C_{28}H_{43}NO_3S$

MW: 473.71 g·mol⁻¹

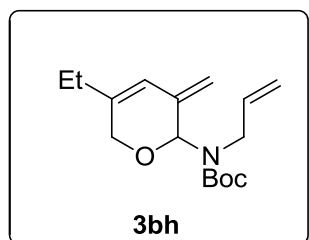
Colourless liquid

Isolated Amount: 68.2 mg **Yield:** 72%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.77 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 6.01 (s, 1H), 5.94 (s, 1H), 5.89-5.79 (m, 1H), 5.06 (dd, *J* = 17.2, 1.2 Hz, 1H), 5.03 (s, 1H), 4.98 (dd, *J* = 10.0, 1.2 Hz, 1H), 4.94 (s, 1H), 4.16 (d, *J* = 16.4 Hz, 1H), 3.95 (d, *J* = 16.4 Hz, 1H), 3.84 (dd, *J* = 16.4, 7.2 Hz, 1H), 3.67 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.42 (s, 3H), 1.97 (t, *J* = 7.2 Hz, 2H), 1.29-1.26 (m, 20H), 0.88 (t, *J* = 6.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.3, 140.4, 137.4, 137.2, 135.7, 129.2, 127.9, 121.8, 116.7, 111.3, 85.1, 66.9, 47.7, 32.9, 31.9, 29.62, 29.59, 29.5, 29.4, 29.3, 27.3, 22.6, 21.5, 14.1.

MS (EI) *m/z* 473 (M⁺); **HRMS (ESI)** Calcd for C₂₈H₄₃NO₃S+H 474.3042, Found 474.3043.



$C_{16}H_{25}NO_3$

MW: 279.37 g·mol⁻¹

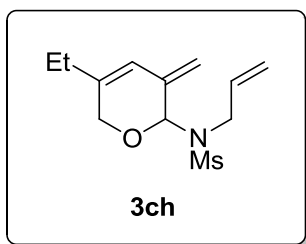
Colourless liquid

Isolated Amount: 37.4 mg **Yield:** 67%

¹H NMR (400 MHz, CDCl₃, δ ppm): 6.05 (s, 2H), 5.92-5.83 (m, 1H), 5.10 (d, *J* = 17.2 Hz, 1H), 5.04 (dd, *J* = 10.0, 1.2 Hz, 1H), 4.90 (s, 1H), 4.80 (s, 1H), 4.28 (d, *J* = 16.4 Hz, 1H), 4.14 (d, *J* = 16.8 Hz, 1H), 3.80 (s, 1H), 3.67 (dd, *J* = 15.6, 5.2 Hz, 1H), 2.05 (q, *J* = 5.8 Hz, 2H), 1.48 (s, 9H), 1.07 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 142.1, 138.3, 120.7, 115.5, 109.8, 80.4, 67.1, 46.7, 28.3, 25.5, 11.6.

MS (EI) *m/z* 279 (M⁺); **HRMS (ESI)** Calcd for C₁₆H₂₅NO₃+H 280.1913, Found 280.1914.



$C_{12}H_{19}NO_3S$

MW: 257.35 g·mol⁻¹

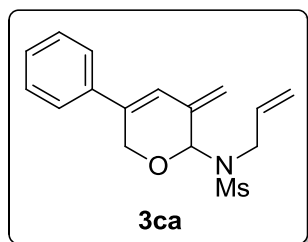
Colourless liquid

Isolated Amount: 28.3 mg **Yield:** 55%

¹H NMR (400 MHz, CDCl₃, δ ppm): 6.04 (s, 1H), 6.03-5.94 (m, 1H), 5.78 (s, 1H), 5.23 (dd, *J* = 17.6, 1.2 Hz, 1H), 5.15 (dd, *J* = 10.4, 1.2 Hz, 1H), 5.07 (s, 1H), 4.99 (s, 1H), 4.29 (d, *J* = 16.4 Hz, 1H), 4.15 (d, *J* = 16.8 Hz, 1H), 3.94 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.84 (dd, *J* = 16.0, 5.2 Hz, 1H), 3.00 (s, 3H), 2.05 (q, *J* = 15.6 Hz, 2H), 1.06 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 141.4, 136.9, 135.4, 120.8, 118.3, 111.4, 85.1, 67.3, 47.9, 41.1, 25.5, 11.6.

MS (EI) *m/z* 257 (M⁺); **HRMS (ESI)** Calcd for C₁₂H₁₉NO₃S+H 258.1164, Found 258.1161.



$C_{16}H_{19}NO_3S$

MW: 305.39 g·mol⁻¹

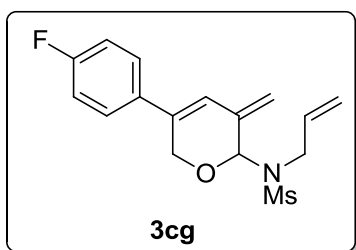
Colourless liquid

Isolated Amount: 35.5 mg **Yield:** 58%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.38-7.35 (m, 5H), 6.69 (s, 1H), 6.08-5.98 (m, 1H), 5.92 (s, 1H), 5.28-5.24 (m, 3H), 5.18 (dd, *J* = 10.0, 0.8 Hz, 1H), 4.77-4.67 (m, 2H), 4.00 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.93-3.87 (m, 1H), 3.06 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 137.0, 136.7, 136.3, 135.3, 128.7, 128.4, 124.8, 123.2, 118.5, 114.3, 85.0, 66.0, 47.9, 41.2.

MS (EI) *m/z* 305 (M⁺); **HRMS (ESI)** Calcd for C₁₆H₁₉NO₃S+H 306.1164, Found 306.1162.



$C_{16}H_{18}FNO_3S$ (*cis:trans* = 8 : 1)

MW: 323.38 g·mol⁻¹

Colourless liquid

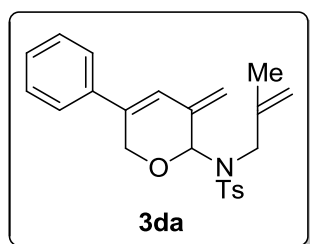
Isolated Amount: 48.5 mg **Yield:** 75%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.34-7.31 (m, 2H), 7.05 (t, *J* = 8.4 Hz, 2H), 6.62 (s, 1H), 6.07-5.98 (m, 1H), 5.90 (s, 1H), 5.27 (s, 1H), 5.22-5.16 (m, 3H), 4.68 (s, 2H), 3.99 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.90-3.86 (m, 1H), 3.05 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 162.7 (d, *J* = 248.6 Hz), 136.9, 135.7, 135.2, 132.45 (d, *J* = 3.4 Hz), 126.5 (d, *J* = 8.0 Hz), 123.2 (d, *J* = 1.2 Hz), 118.6, 115.7 (d, *J* = 21.5 Hz), 114.4, 85.0, 66.0, 47.9, 41.2.

¹⁹F{¹H} NMR (376 MHz, CDCl₃, δ ppm): -112.9., -113.0.

MS (EI) *m/z* 323 (M⁺); **HRMS (ESI)** Calcd for C₁₆H₁₈FNO₃S+H 324.1070, Found 324.1072.



C₂₃H₂₅NO₃S

MW: 395.51 g·mol⁻¹

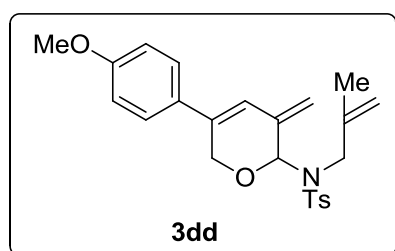
Colourless liquid

Isolated Amount: 55.4 mg **Yield:** 70%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.82 (d, *J* = 8.0 Hz, 2H), 7.36-7.27 (m, 8H), 6.10 (s, 1H), 5.25 (s, 1H), 5.18 (s, 1H), 4.96 (s, 1H), 4.86 (s, 1H), 4.54 (d, *J* = 16.4 Hz, 1H), 4.50 (d, *J* = 16.4 Hz, 1H), 3.81 (d, *J* = 16.4 Hz, 1H), 3.64 (d, *J* = 16.0 Hz, 1H), 2.44 (s, 3H), 1.71 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.3, 141.4, 137.2, 136.8, 136.5, 136.3, 129.2, 128.6, 128.2, 127.9, 124.7, 123.1, 114.5, 113.9, 84.7, 65.0, 51.0, 21.5, 20.3.

MS (EI) *m/z* 395 (M⁺); **HRMS (ESI)** Calcd for C₂₃H₂₅NO₃S+H 396.1633, Found 396.1635.



C₂₄H₂₇NO₄S

MW: 425.54 g·mol⁻¹

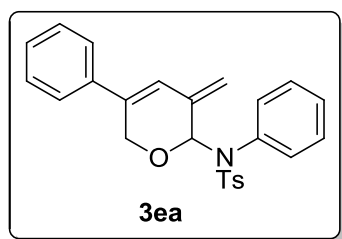
Colourless liquid

Isolated Amount: 58.8 mg **Yield:** 69%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.82 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.56 (s, 1H), 6.08 (s, 1H), 5.20 (s, 1H), 5.13 (s, 1H), 4.95 (s, 1H), 4.85 (s, 1H), 4.51 (d, *J* = 16.4 Hz, 1H), 4.41 (d, *J* = 16.0 Hz, 1H), 3.83-3.79 (m, 4H), 3.63 (d, *J* = 16.4 Hz, 1H), 2.45 (s, 3H), 1.70 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 159.7, 143.3, 141.5, 137.3, 136.9, 136.0, 129.2, 128.7, 128.0, 126.0, 121.4, 114.1, 113.8, 113.6, 84.7, 64.9, 55.2, 51.1, 21.5, 20.3.

MS (EI) *m/z* 425 (M⁺); **HRMS (ESI)** Calcd for C₂₄H₂₇NO₄S+H 426.1739, Found 426.1742.



C₂₅H₂₃NO₃S

MW: 417.52 g·mol⁻¹

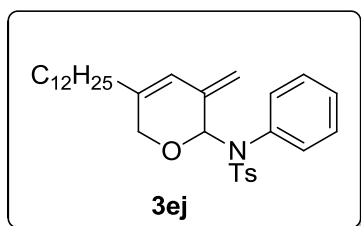
Colourless liquid

Isolated Amount: 41.7 mg **Yield:** 50%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.50 (d, *J* = 8.4 Hz, 2H), 7.23-7.19 (m, 4H), 7.18-7.11 (m, 8H), 6.41 (s, 1H), 6.32 (s, 1H), 5.10 (s, 1H), 4.98 (s, 1H), 4.62-4.51 (m, 2H), 2.32 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.4, 137.1, 136.7, 136.53, 136.45, 136.4, 131.5, 129.0, 128.6, 128.2, 128.1, 128.0, 124.8, 123.5, 115.1, 85.3, 65.3, 21.5.

MS (EI) *m/z* 417 (M⁺); **HRMS (ESI)** Calcd for C₂₅H₂₃NO₃S+H 418.1477, Found 418.1478.



C₃₁H₄₃NO₃S

MW: 509.74 g·mol⁻¹

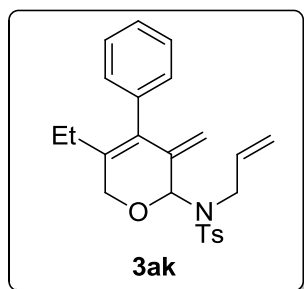
Brown liquid

Isolated Amount: 40.8 mg **Yield:** 40%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.59 (d, *J* = 8.4 Hz, 2H), 7.31-7.28 (m, 2H), 7.25-7.20 (m, 5H), 6.41 (s, 1H), 5.83 (s, 1H), 5.01 (s, 1H), 4.87 (s, 1H), 4.27 (d, *J* = 16.4 Hz, 1H), 4.11 (d, *J* = 16.4 Hz, 1H), 2.44 (s, 3H), 1.94 (t, *J* = 6.8 Hz, 2H), 1.34-1.30 (m, 20H), 0.92 (t, *J* = 6.4 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.2, 139.8, 137.2, 136.8, 136.7, 131.4, 128.9, 128.2, 128.1, 127.9, 121.9, 112.2, 85.3, 66.6, 32.9, 31.9, 29.62, 29.60, 29.5, 29.4, 29.32, 29.28, 27.3, 22.7, 21.5, 14.1.

MS (EI) *m/z* 509 (M⁺); **HRMS (ESI)** Calcd for C₃₁H₄₃NO₃S+H 510.3042, Found 510.3044.



C₂₄H₂₇NO₃S

MW: 409.54 g·mol⁻¹

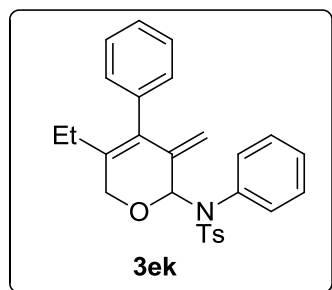
Colorless crystal

Isolated Amount: 51.6 mg **Yield:** 63%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.80 (d, *J* = 8.4 Hz, 2H), 7.38-7.29 (m, 5H), 7.10-7.08 (m, 2H), 6.10 (s, 1H), 5.91-5.81 (m, 1H), 5.13-5.08 (m, 2H), 5.00 (dd, *J* = 10.0, 0.8 Hz, 1H), 4.56 (s, 1H), 4.32 (d, *J* = 16.4 Hz, 1H), 4.16 (d, *J* = 16.8 Hz, 1H), 3.94 (dd, *J* = 16.4, 7.2 Hz, 1H), 3.76 (dd, *J* = 16.4, 5.6 Hz, 1H), 2.44 (s, 3H), 1.82 (q, *J* = 15.0 Hz, 2H), 0.87 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.3, 139.0, 137.7, 137.36, 137.32, 135.7, 132.8, 129.6, 129.3, 128.2, 127.9, 127.0, 116.9, 113.2, 85.7, 66.4, 47.8, 23.9, 21.5, 12.9.

MS (EI) *m/z* 409 (M⁺); **HRMS (ESI)** Calcd for C₂₄H₂₇NO₃S+H 410.1790, Found 410.1788.



C₂₇H₂₇NO₃S

MW: 445.57 g·mol⁻¹

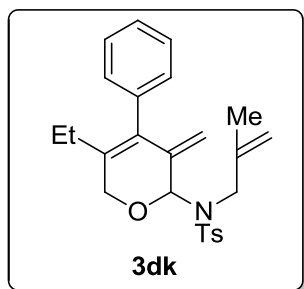
Pale-yellow solid

Isolated Amount: 33.9 mg **Yield:** 38%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.65 (d, *J* = 7.6 Hz, 2H), 7.33-7.21 (m, 8H), 7.14 (d, *J* = 7.6 Hz, 2H), 6.54 (s, 3H), 5.04 (s, 1H), 4.45 (s, 1H), 4.31 (s, 2H), 2.43 (s, 3H), 1.68 (q, *J* = 15.0 Hz, 2H), 0.73 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.3, 138.4, 137.3, 137.0, 136.6, 132.5, 129.4, 129.1, 128.3, 128.1, 128.0, 126.8, 114.7, 86.2, 64.6, 23.8, 21.6, 12.7.

MS (EI) *m/z* 445 (M⁺); **HRMS (ESI)** Calcd for C₂₇H₂₇NO₃S+H 446.1790, Found 446.1792.



C₂₅H₂₉NO₃S

MW: 423.57 g·mol⁻¹

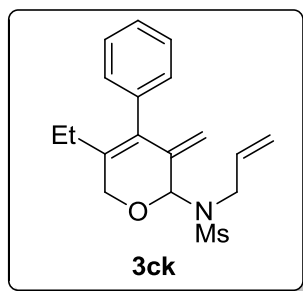
Colorless solid

Isolated Amount: 56.8 mg **Yield:** 67%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.67 (d, *J* = 8.4 Hz, 2H), 7.32-7.30 (m, 3H), 7.24-7.21 (m, 2H), 7.02 (d, *J* = 7.2 Hz, 2H), 6.07 (s, 1H), 5.04 (s, 1H), 4.92 (s, 1H), 4.81 (s, 1H), 4.49 (s, 1H), 4.20 (d, *J* = 16.8 Hz, 1H), 4.03 (d, *J* = 16.8 Hz, 1H), 3.82 (d, *J* = 16.0 Hz, 1H), 3.62 (d, *J* = 16.4 Hz, 1H), 2.39 (s, 3H), 1.76 (dd, *J* = 14.8 Hz, 2H), 1.63 (s, 3H), 0.80 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.3, 141.5, 138.8, 137.5, 137.3, 137.1, 132.7, 129.6, 129.2, 128.2, 127.9, 127.0, 113.9, 113.5, 85.6, 65.9, 51.1, 29.7, 23.9, 20.4, 12.9.

MS (EI) *m/z* 423 (M⁺); **HRMS (ESI)** Calcd for C₂₅H₂₉NO₃S+H 424.1946, Found 424.1943.



$C_{18}H_{23}NO_3S$

MW: 333.45 g·mol⁻¹

Colorless liquid

Isolated Amount: 38.7 mg **Yield:** 58%

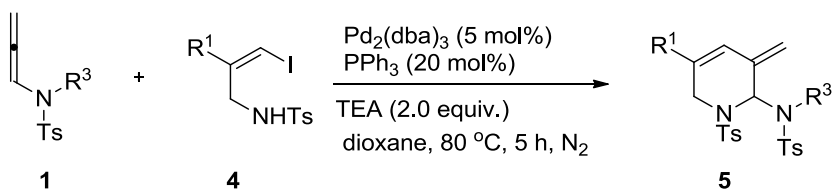
¹H NMR (400 MHz, CDCl₃, δ ppm): 7.36 (d, *J* = 7.2 Hz, 2H), 7.33-7.31 (m, 1H), 7.10 (d, *J* = 6.4 Hz, 2H), 6.09-6.00 (m, 1H), 5.93 (s, 1H), 5.30 (d, *J* = 17.2 Hz, 1H), 5.19-5.15 (m, 2H), 4.59 (s, 1H), 4.46 (d, *J* = 16.8 Hz, 1H), 4.36 (d, *J* = 16.4 Hz, 1H), 4.02-4.00 (m, 1H), 3.93-3.89 (m, 1H), 3.04 (s, 3H), 1.87-1.85 (m, 2H), 0.90 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 138.7, 137.6, 137.3, 135.4, 132.9, 129.6, 128.3, 127.1, 118.5, 113.1, 85.7, 66.9, 48.0, 41.3, 24.0, 13.0.

MS (EI) *m/z* 333 (M⁺); **HRMS (ESI)** Calcd for C₁₈H₂₃NO₃S+H 334.1477, Found 334.1478.

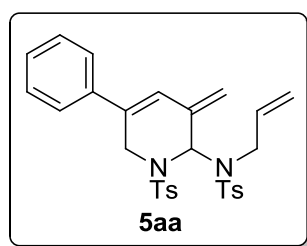
IV. The General Synthetic Procedure and Analytical Data for 2-amino-3-methylene-1,2,3,6-tetrahydropyridine derivatives

General Synthetic Procedure:



Drops of allenamide **1** (0.3 mmol, 1.5 equiv.) were added to **4** (0.2 mmol, 1.0 equiv.) and Pd₂(dba)₃ (0.01 mmol, 5 mol%), PPh₃ (0.04 mmol, 20 mol%) in 2 mL dioxane under N₂ atmosphere, subsequently, the base TEA (0.4 mmol, 2.0 equiv.) was added under stirring. The mixture was stirred at 80 °C for 5 h. The mixture was extracted by EA (10 mL x 3). The organic part was dried over Na₂SO₄, the solvent was removed under vacuum evaporated and purified by column chromatography to give 2-amino-3-methylene-1,2,3,6-tetrahydropyridine derivatives **5**.

Analytical Data:



C₂₉H₃₀N₂O₄S₂

MW: 534.69 g·mol⁻¹

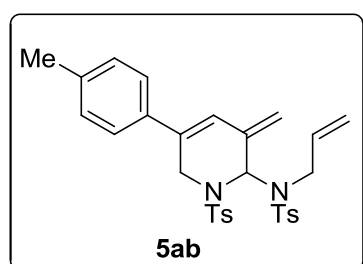
Colourless solid

Isolated Amount: 75.97 mg **Yield:** 71%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.67 (d, *J* = 8.4 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 2H), 7.34-7.27 (m, 9H), 6.89 (s, 1H), 5.70-5.59 (m, 1H), 5.31 (s, 1H), 5.13 (dd, *J* = 11.2, 1.2 Hz, 1H), 5.10-5.09 (m, 1H), 4.14 (s, 2H), 3.88 (d, *J* = 0.8 Hz, 2H), 3.75 (d, *J* = 6.4 Hz, 2H), 2.41 (s, 3H), 2.39 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.9, 143.8, 137.3, 136.9, 134.9, 133.5, 133.1, 132.3, 129.8, 128.7, 128.6, 127.6, 127.5, 125.5, 121.7, 119.1, 119.0, 54.0, 46.8, 46.2, 21.50, 21.48.

MS (EI) *m/z* 534 (M⁺); **HRMS (ESI)** Calcd for C₂₉H₃₀N₂O₄S₂+H 535.1725, Found 535.1722.



C₃₀H₃₂N₂O₄S₂

MW: 548.72 g·mol⁻¹

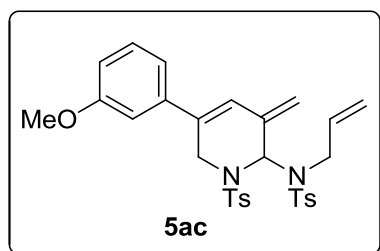
White solid

Isolated Amount: 69.1 mg **Yield:** 63%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.67 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.15 (d, $J = 7.6$ Hz, 2H), 6.85 (s, 1H), 5.70-5.60 (m, 1H), 5.31 (s, 1H), 5.15-5.09 (m, 2H), 4.13 (s, 2H), 3.88 (s, 2H), 3.76 (d, $J = 6.0$ Hz, 2H), 2.42 (s, 3H), 2.39 (m, 3H), 2.35 (m, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 143.9, 143.8, 138.8, 136.9, 135.0, 134.4, 133.6, 133.2, 132.3, 129.7, 129.3, 127.7, 125.4, 121.3, 119.0, 118.3, 54.0, 46.8, 46.2, 21.51, 21.49, 21.2.

MS (EI) m/z 548 (M^+); **HRMS (ESI)** Calcd for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_4\text{S}_2 + \text{H}$ 549.1882, Found 549.1881.



$\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_5\text{S}_2$

MW: 564.72 $\text{g}\cdot\text{mol}^{-1}$

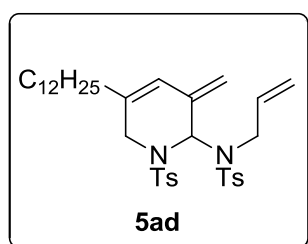
Colourless solid

Isolated Amount: 67.7 mg **Yield:** 60%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.69 (d, $J = 8.4$ Hz, 2H), 7.66 (d, $J = 8.0$ Hz, 2H), 7.34-7.28 (m, 6H), 6.94-6.71 (m, 1H), 6.892-6.886 (m, 1H), 6.85-6.84 (m, 1H), 5.72-5.62 (m, 1H), 5.37 (s, 1H), 5.16 (dd, $J = 10.8, 1.2$ Hz, 1H), 5.13-5.12 (m, 1H), 4.14 (s, 2H), 3.90 (s, 2H), 3.84 (s, 3H), 3.78 (d, $J = 6.4$ Hz, 2H), 2.44 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 159.7, 143.9, 143.8, 138.9, 136.8, 134.9, 133.5, 132.7, 132.3, 132.3, 129.77, 129.75, 127.7, 127.5, 121.8, 119.4, 119.0, 118.1, 113.6, 111.7, 55.3, 54.0, 46.9, 46.3, 21.50, 21.49.

MS (EI) m/z 564 (M^+); **HRMS (ESI)** Calcd for $\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_5\text{S}_2 + \text{H}$ 565.1831, Found 565.1833.



$\text{C}_{35}\text{H}_{50}\text{N}_2\text{O}_4\text{S}_2$

MW: 626.91 $\text{g}\cdot\text{mol}^{-1}$

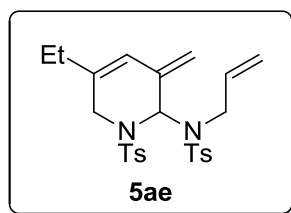
Brown solid

Isolated Amount: 97.8 mg **Yield:** 78%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.64 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.31-7.29 (m, 4H), 6.32 (s, 1H), 5.66-5.56 (m, 1H), 5.14-5.12 (m, 2H), 5.08-5.07 (m, 1H), 3.76 (s, 2H), 3.71 (d, *J* = 6.4 Hz, 2H), 3.63 (s, 2H), 2.42 (d, *J* = 8.0 Hz, 6H), 1.99 (t, *J* = 7.2 Hz, 2H), 1.33-1.26 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.68, 143.67, 140.8, 134.9, 133.7, 133.5, 132.3, 129.7, 127.6, 127.5, 119.3, 118.8, 117.7, 53.9, 47.9, 46.3, 35.0, 31.9, 29.62, 29.60, 29.5, 29.4, 29.31, 29.29, 27.5, 22.6, 21.50, 21.48, 14.1.

MS (EI) *m/z* 626 (M⁺); **HRMS (ESI)** Calcd for C₃₅H₅₀N₂O₄S₂+H 627.3290, Found 627.3289.



C₂₅H₃₀N₂O₄S₂

MW: 486.65 g·mol⁻¹

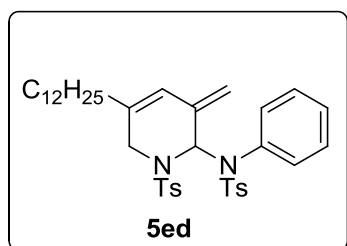
Colourless liquid

Isolated Amount: 76.8 mg **Yield:** 79%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.65 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 4H), 6.32 (s, 1H), 5.67-5.57 (m, 1H), 5.16 (s, 1H), 5.13-5.07 (m, 2H), 3.75 (s, 2H), 3.72 (d, *J* = 6.4 Hz, 2H), 3.63 (s, 2H), 2.43 (s, 3H), 2.41 (s, 3H), 2.03 (q, *J* = 14.8 Hz, 2H), 0.98 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.7, 141.9, 134.9, 133.7, 133.3, 132.3, 129.7, 127.6, 127.5, 119.4, 118.8, 116.7, 53.9, 47.9, 46.3, 27.7, 21.48, 21.46, 11.7.

MS (EI) *m/z* 486 (M⁺); **HRMS (ESI)** Calcd for C₂₅H₃₀N₂O₄S₂+H 487.1725, Found 487.1728.



C₃₈H₅₀N₂O₄S₂

MW: 662.94 g·mol⁻¹

Brown solid

Isolated Amount: 60.9mg **Yield:** 46%

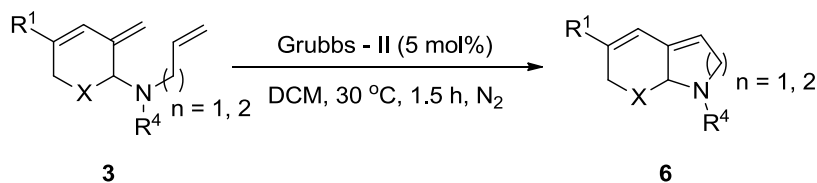
¹H NMR (400 MHz, CDCl₃, δ ppm): 7.59 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.26-7.24 (m, 5H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.02-6.99 (m, 2H), 6.13 (s, 1H), 5.69 (s, 1H), 3.78 (s, 2H), 3.56 (s, 2H), 2.43 (s, 3H), 2.37 (s, 3H), 1.76 (t, *J* = 6.8 Hz, 2H), 1.31-1.18 (m, 20H), 0.89 (t, *J* = 6.8 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 144.0, 143.5, 140.9, 139.2, 134.2, 133.6, 129.5, 129.0, 127.74, 127.71, 127.5, 127.4, 123.9, 120.7, 116.5, 48.0, 47.1, 34.5, 31.8, 29.60, 29.57, 29.4, 29.3, 28.9, 26.9, 22.6, 21.5, 21.4, 14.0.

MS (EI) *m/z* 662 (M⁺); **HRMS (ESI)** Calcd for C₃₈H₅₀N₂O₄S₂+H 663.3290, Found 663.3288.

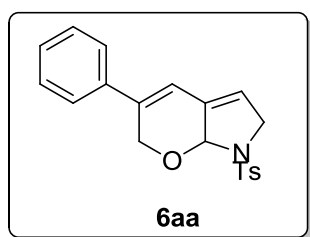
V. The General Synthetic Procedure and Analytical Data for 2,6,7,7a-tetrahydropyrano[2,3-b]pyrrole derivatives

General Synthetic Procedure:



Drops of pyran or yridine derivatives **3** (1.0 equiv.) were added to Grubbs second generation catalysts (G-II) (5 mol%) in 1 mL anhydrous DCM under N₂ atmosphere. The mixture was stirred at 30 °C for 1.5 h. The mixture was removed under vacuum evaporated and purified by column chromatography to give 2,6,7,7a-tetrahydropyrano[2,3-b]pyrrole derivatives **6**.

Analytical Data:



C₂₀H₁₉NO₃S

MW: 353.43 g·mol⁻¹

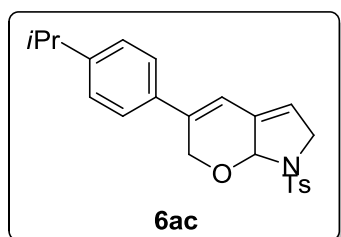
Colourless solid

Isolated Amount: 44.0 mg **Yield:** 83%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.86 (d, *J* = 8.0 Hz, 2H), 7.34-7.32 (m, 7H), 6.61 (s, 1H), 5.71 (s, 1H), 5.64 (s, 1H), 4.86 (s, 2H), 4.34-4.23 (m, 2H), 2.43 (s, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.8, 140.0, 136.2, 135.5, 133.9, 129.7, 128.7, 128.6, 127.6, 125.2, 118.1, 115.8, 90.5, 67.2, 55.8, 21.5.

MS (EI) *m/z* 353 (M⁺); **HRMS (ESI)** Calcd for C₂₀H₁₉NO₃S+H 354.1164, Found 354.1166.



C₂₃H₂₅NO₃S

MW: 395.51 g·mol⁻¹

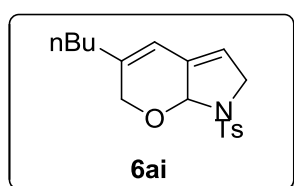
Colourless solid

Isolated Amount: 43.2 mg **Yield:** 73%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.86 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.28 (s, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.57 (s, 1H), 5.70 (s, 1H), 5.61 (s, 1H), 4.90-4.80 (m, 2H), 4.33-4.22 (m, 2H), 2.94-2.87 (m, 1H), 2.42 (s, 3H), 1.25 (s, 6H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 149.7, 143.8, 140.0, 135.7, 134.1, 133.7, 129.7, 127.6, 126.8, 125.2, 117.7, 115.1, 90.5, 67.3, 55.8, 33.8, 29.7, 23.8, 21.6.

MS (EI) *m/z* 395 (M⁺); **HRMS (ESI)** Calcd for C₂₃H₂₅NO₃S+H 396.1633, Found 396.1631.



C₁₈H₂₃NO₃S

MW: 333.45 g·mol⁻¹

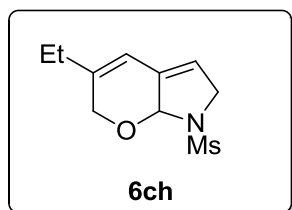
Colourless liquid

Isolated Amount: 47.0 mg **Yield:** 94%

¹H NMR (400 MHz, CDCl₃, δ ppm): 7.75 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 2H), 5.94 (s, 1H), 5.50 (s, 1H), 5.33 (s, 1H), 4.38 (d, *J* = 17.2 Hz, 1H), 4.18 (d, *J* = 16.8 Hz, 1H), 4.13-4.10 (m, 2H), 2.34 (s, 3H), 1.93 (t, *J* = 7.2 Hz, 2H), 1.26-1.18 (m, 4H), 0.82 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.7, 143.6, 135.4, 133.8, 129.6, 127.5, 115.3, 114.6, 90.5, 68.4, 55.5, 32.2, 29.4, 22.3, 21.5, 13.7.

MS (EI) *m/z* 333 (M⁺); **HRMS (ESI)** Calcd for C₁₈H₂₃NO₃S+H 334.1477, Found 334.1475.



C₁₀H₁₅NO₃S

MW: 229.30 g·mol⁻¹

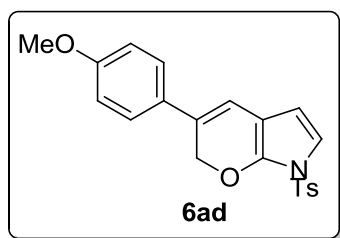
Pale-brown liquid

Isolated Amount: 18.5 mg **Yield:** 54%

¹H NMR (400 MHz, CDCl₃, δ ppm): 6.08 (s, 1H), 5.65 (s, 1H), 5.52 (s, 1H), 4.47-4.41 (m, 2H), 4.24 (d, *J* = 16.8 Hz, 2H), 3.06 (s, 3H), 2.03 (q, *J* = 14.6 Hz, 2H), 1.07 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 144.9, 134.0, 115.5, 113.8, 90.5, 68.3, 55.2, 41.8, 25.3, 11.7.

MS (EI) m/z 229 (M^+); **HRMS (ESI)** Calcd for $\text{C}_{10}\text{H}_{15}\text{NO}_3\text{S}+\text{H}$ 230.0851, Found 230.0852.



$\text{C}_{21}\text{H}_{19}\text{NO}_4\text{S}$

MW: 381.44 $\text{g}\cdot\text{mol}^{-1}$

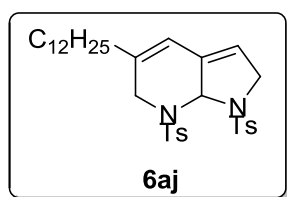
Brown oil

Isolated Amount: 52.0 mg **Yield:** 91%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.77 (d, $J = 7.6$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H), 7.30-7.28 (m, 3H), 7.16 (s, 1H), 6.89 (d, $J = 8.0$ Hz, 1H), 6.57 (s, 1H), 6.46 (s, 1H), 4.65 (s, 2H), 3.81 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 159.1, 145.1, 138.6, 135.8, 133.3, 130.0, 127.4, 126.9, 125.3, 121.5, 121.2, 119.6, 114.7, 114.0, 60.8, 55.3, 21.6.

MS (EI) m/z 381 (M^+); **HRMS (ESI)** Calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_4\text{S}+\text{H}$ 382.1113, Found 382.1115.



$\text{C}_{33}\text{H}_{46}\text{N}_2\text{O}_4\text{S}_2$

MW: 598.86 $\text{g}\cdot\text{mol}^{-1}$

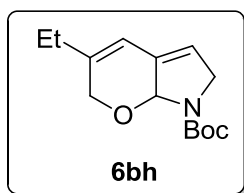
Colourless solid

Isolated Amount: 50.3 mg **Yield:** 56%

^1H NMR (400 MHz, CDCl_3 , δ ppm): 7.67 (d, $J = 7.6$ Hz, 2H), 7.59 (d, $J = 7.6$ Hz, 2H), 7.32-7.30 (m, 4H), 6.28-6.23 (m, 1H), 5.38-5.35 (m, 1H), 5.13 (s, 1H), 3.71 (s, 2H), 3.64 (s, 1H), 3.59 (s, 1H), 2.42 (s, 6H), 1.99-1.98 (m, 2H), 1.33-1.26 (m, 20H), 0.88 (s, 3H).

^{13}C NMR (100 MHz, CDCl_3 , δ ppm): 143.74, 143.71, 141.1, 134.9, 133.9, 133.1, 129.73, 129.70, 128.7, 127.7, 127.5, 119.3, 117.4, 52.6, 48.0, 46.4, 35.1, 31.9, 29.64, 29.57, 29.42, 29.39, 29.3, 27.6, 22.7, 21.5, 14.1.

MS (EI) m/z 598 (M^+); **HRMS (ESI)** Calcd for $\text{C}_{33}\text{H}_{46}\text{N}_2\text{O}_4\text{S}_2+\text{H}$ 599.2977, Found 599.2976.



$C_{14}H_{21}NO_3$

MW: 251.32 g·mol⁻¹

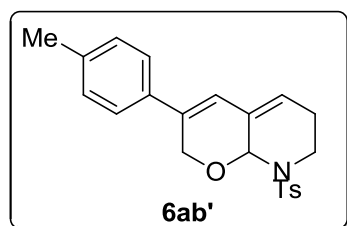
White solid

Isolated Amount: 46.7 mg **Yield:** 93%

¹H NMR (400 MHz, CDCl₃, δ ppm): 6.04 (s, 1H), 5.57-5.45 (m, 2H), 4.48-4.37 (m, 1H), 4.23-4.18 (m, 3H), 2.09 (q, *J* = 7.6 Hz, 2H), 1.47 (s, 9H), 1.04 (t, *J* = 7.6 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 154.7, 144.6, 134.2, 115.9, 113.8, 89.1, 80.4, 68.2, 54.4, 28.3, 25.2, 11.6.

MS (EI) *m/z* 251 (M⁺); **HRMS (ESI)** Calcd for C₁₄H₂₁NO₃+H 252.1600, Found 252.1603.



$C_{22}H_{23}NO_3S$

MW: 381.49 g·mol⁻¹

white crystal

Isolated Amount: 61.0 mg **Yield:** 80%

¹H NMR (600 MHz, CDCl₃, δ ppm): 7.76 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.42 (s, 1H), 5.74 (d, *J* = 6.6 Hz, 1H), 5.46 (s, 1H), 4.72 (d, *J* = 16.2 Hz, 1H), 4.61 (d, *J* = 16.2 Hz, 1H), 3.67 (dd, *J* = 12.0, 4.8 Hz, 1H), 2.80-2.76 (m, 1H), 2.28 (s, 3H), 2.21-2.18 (m, 4H), 1.99 (dd, *J* = 16.8, 6.6 Hz, 1H).

¹³C NMR (100 MHz, CDCl₃, δ ppm): 143.1, 137.8, 137.6, 135.4, 133.4, 131.3, 129.3, 129.2, 127.4, 124.5, 122.9, 121.0, 78.1, 67.2, 39.5, 25.6, 21.3, 21.0.

MS (EI) *m/z* 381 (M⁺); **HRMS (ESI)** Calcd for C₂₂H₂₃NO₃S+H 382.1477, Found 382.1476.

VI. Copies of X-Ray Crystal

Table 1. Crystal data and structure refinement for 3ak.

Identification code	mo_ww1_0m
Empirical formula	C ₂₄ H ₂₇ N O ₃ S
Formula weight	409.53

Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	P-1	
Space group	P-1	
Unit cell dimensions	a = 8.9412(15) Å	a = 92.060(5)°.
	b = 11.6147(19) Å	b = 111.910(5)°.
	c = 11.727(2) Å	g = 102.119(5)°.
Volume	1095.9(3) Å ³	
Z	2	
Density (calculated)	1.241 Mg/m ³	
Absorption coefficient	0.172 mm ⁻¹	
F(000)	436	
Crystal size	0.21 x 0.19 x 0.15 mm ³	
Theta range for data collection	2.44 to 25.01°.	
Index ranges	-10 ≤ h ≤ 10, -13 ≤ k ≤ 13, -13 ≤ l ≤ 13	
Reflections collected	8204	
Independent reflections	3840 [R(int) = 0.0284]	
Completeness to theta = 25.01°	99.0 %	
Absorption correction	None	
Max. and min. transmission	0.9747 and 0.9648	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	3840 / 0 / 264	
Goodness-of-fit on F ²	1.001	
Final R indices [I > 2σ(I)]	R1 = 0.0457, wR2 = 0.1034	
R indices (all data)	R1 = 0.0907, wR2 = 0.1218	
Largest diff. peak and hole	0.361 and -0.268 e.Å ⁻³	

VII. Copies of the ¹H NMR, ¹³C NMR, ¹⁹F NMR

