Transition Metal Free C-N Bond Forming Dearomatizations and Aryl C-H Aminations by In Situ Release of a Hydroxylamine-Based Aminating Agent

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Supporting Information

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**General Experimental Details.** Starting materials were purchased from commercial sources (Acros, Aldrich, Alfa Aesar) and used without further purification unless otherwise stated. Anhydrous 2,2,2-trifluoroethanol was obtained by drying over 4Å molecular sieves while other anhydrous solvents were obtained by passage through drying columns supplied by Anhydrous Engineering Ltd. The removal of solvents *in vacuo* was achieved using both a Büchi rotary evaporator (bath temperatures up to 45 °C) at a pressure of either 15 mmHg (diaphragm pump) or 0.1 mmHg (oil pump), as appropriate, and a high vacuum line at r.t.. Reactions requiring anhydrous conditions were run under a dry atmosphere of nitrogen or argon; glassware was either flame dried immediately prior to use or placed in an oven (200 °C) for at least 2 h and allowed to cool either in a desiccator or under an atmosphere of nitrogen or argon; liquid reagents, solutions or solvents were added via syringe through rubber septa. Flash column chromatography was performed using silica gel (Aldrich 40-63 μm, 230-400 mesh). Thin layer chromatography was performed using aluminium backed 60F254 silica plates. Visualisation was achieved by UV fluorescence or a basic KMnO₄ solution and heat. Proton nuclear magnetic resonance were recorded on a Varian or Jeol spectrometer at 400 MHz or 500 MHz while ¹³C NMR spectra were recorded at 100 MHz. Chemical shifts (δ) are given in parts per million (ppm) and referenced to the appropriate residual solvent peak. Peaks are described as singlets (s), doublets (d), triplets (t), quartets (q), quintets (qn), sextets (s), multiplets (m) and broad (br.). Coupling constants (J) are quoted to the nearest 0.1 Hz. Assignments of ¹H NMR and ¹³C NMR signals were made, where possible, using COSY, HSQC, HMBC, NOE and TOCSY experiments. Mixtures of isomers which could not be separated (e.g. diastereomers and/or rotamers) have been characterized together and are referred to as A and B. Numbering systems for NMR signal assignments are specified on the structure and are not related to those used for the compound names. In situ yields were determined by integration of the ¹H NMR of the crude material employing 1,3,5-trimethoxybenzene or 1,4-dinitrobenzene as internal standard. Mass spectra were determined by the University of Bristol mass spectrometry service using a Bruker Daltonics FT-ICR-MS Apex 4e 7.0T FT-MS. Infrared spectra were recorded on a Perkin Elmer Spectrum Two FTIR spectrometer as either neat films or solids. Abbreviations used are: w (weak), m (medium), s (strong) and br (broad). Melting points were determined using a Reichert melting point table and temperature controller and are uncorrected.
**Experimental procedures and Data**

**General procedure A for TBS protection of phenol**

To a solution of alcohol (1.0 eq.) in DMF (*approx.* 2mL/mmol) at 0 °C was added imidazole (3.3 eq.) and tert-butyldimethylsilyl chloride (2.2 eq.). The reaction was stirred at r.t. and monitored by TLC. Upon completion, the reaction was quenched by addition of H2O and the organic phase extracted with hexane, dried over Na2SO4 and concentrated *in vacuo*. To the crude reaction mixture was added MeOH (1 mL/mmol), THF (1 mL/mmol) and aq. K2CO3 (2.0 eq.) After stirring for 12 h the reaction was quenched with aq. 1 M HCl at 0 °C (until pH *approx.* 3). The mixture was extracted with Et2O (3 × 20 mL), dried over Na2SO4, filtered and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography.

**General procedure B for reduction of carboxylic acid/ester to alcohol using LiAlH4**

To a solution of carboxylic acid/ester (1.0 eq.) in anhydrous THF or Et2O (*approx.* 5 mL/mmol) at 0 °C was added LiAlH4 (*equivalents specified*) dropwise. The reaction was stirred at r.t. and monitored by TLC. Upon completion, the reaction mixture was cooled to 0 °C before addition of water (1 mL/g of LiAlH4), 15% aq. NaOH (1 mL/g LiAlH4) and a final portion of water (3 mL/g of LiAlH4). The mixture was filtered through Celite® and washed with CH2Cl2. The phases were separated and the aqueous phase extracted with CH2Cl2 (2 × 10 mL). The combined organic extracts were dried over Na2SO4, filtered and concentrated *in vacuo* to afford the crude product which was purified by flash column chromatography.

**General procedure C for preparation of hydroxylamine derivatives by Mitsunobu reaction**

Diisopropyl azodicarboxylate (1.2 eq.) was added at 0 °C to a stirring solution of triphenylphosphine (1.2 eq.) in anhydrous THF (*approx.* 2mL/mmol) under a nitrogen atmosphere. After 30 min stirring at this temperature a solution of alcohol (1.0 eq.) and amine nucleophile (1.2 eq.) in anhydrous THF (*approx.* 2mL/mmol) were added. The reaction was stirred at 0 °C for 1 h after which it was stirred at r.t. and monitored by TLC. Upon completion, the reaction mixture was concentrated *in vacuo* and purified by flash column chromatography.
**General procedure D for removal of silyl protecting group with TBAF/AcOH**

To a solution of silyl ether (1.0 eq.) in THF (approx. 20mL/mmol) at 0 °C was added a solution of 1:1 TBAF/AcOH (equivalents specified, 0.1 M in THF). The reaction mixture was stirred at r.t. and monitored by TLC. Upon completion, the reaction mixture was quenched with water (10 mL), extracted with EtOAc (2 × 10 mL), washed with sat. aq. NaHCO₃ (10 mL) and brine (10 mL), dried over Na₂SO₄, filtered and the concentrated in vacuo. The crude product was purified by flash column chromatography.

**General procedure E for intramolecular dearomatizing amination**

To a stirring solution of Boc-protected amino substrate (1.0 eq.) in anhydrous 2,2,2-trifluoroethanol (0.1 M) at 0 °C was added trifluoroacetic acid (2.0 eq.). After stirring for 2 h at 0°C the reaction was warmed to r.t. and monitored by TLC. Upon completion, the reaction mixture was concentrated in vacuo and purified by flash column chromatography, with a small amount of Et₃N (<1%) added to the appropriate eluent. In cases where the product was unstable the TFA salt was obtained by re-acidification with TFA.

**General procedure F for formation of unsaturated esters by Wittig reaction**

Aldehyde (1.0 eq.) and methyl 2-(triphenyl-phosphaneylidene) acetate or ethyl 2-(triphenyl-phosphaneylidene) acetate (1.5 eq.) in CH₂Cl₂ (approx. 1 mL/mmol) were stirred at r.t. overnight and monitored by TLC. Upon completion, the reaction mixture was concentrated in vacuo and purified by flash column chromatography.

**General procedure G for alkene hydrogenation with Pd/C**

A solution of alkene (1.0 eq.) in MeOH or EtOH or EtOAc (approx. 5 mL/mmol) was purged with argon before the addition of 10 wt. % Pd/C (5-10 mol%). The flask was fitted with a balloon of hydrogen and stirred at r.t. overnight and monitored by TLC. Upon completion, the reaction mixture was filtered over a bed of Celite® washing with the appropriate solvent and concentrated in vacuo to afford the product.

**General Procedure H for preparation of Weinreb amides from Carboxylic acids**

To a solution of carboxylic acid (1.0 eq.) in anhydrous CH₂Cl₂ under nitrogen at 0 °C was added \(N,O\)-dimethylhydroxylamine hydrochloride (1.4 eq.), Et₃N (1.4 eq.), 4-dimethylaminopyridine (1.4 eq.), and \(N,N'\)-dicyclohexylcarbodiimide (1.4 eq.). The solution was stirred at r.t. overnight and then filtered through Celite, eluting with EtOAc. The filtrate
was washed sequentially with 1 M aq. HCl (10 mL) and sat. aq. NaHCO₃ (10 mL). The combined organic extracts were dried over MgSO₄, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography.

**General procedure I for reduction of carboxylic acids to alcohols via anhydride**

To a solution of carboxylic acid (1.0 eq.) and triethylamine (1.0 eq.) in THF (10 mL/mmol) at -5 °C was added a solution of ethyl chloroformate (1.0 eq.) in THF (1 mL/mmol) dropwise maintaining a temperature below 0 °C. The reaction was stirred at the same temperature for 1 h and filtered to remove the white precipitate that formed, washing with THF (10 mL). The filtrate was added dropwise to a solution of NaBH₄ (2.5 eq.) in H₂O (approx. 2 mL/mmol) at -5 °C. The reaction was stirred at r.t. overnight and monitored by TLC. Upon completion, the reaction was acidified to approx. pH 3 with aq. 1 M HCl. The layers were separated and the aqueous layer extracted with Et₂O (3 × 10 mL). The combined organic extracts were washed with aq. 1 M NaOH (10 mL) and H₂O (10 mL), dried over MgSO₄, filtered and concentrated in vacuo. The crude product was purified by flash column chromatography.

**tert-Butyl (tosyloxy)carbamate (4)**

![Chemical structure of tert-Butyl (tosyloxy)carbamate (4)]

The title compound was prepared according to a literature procedure.

*The spectroscopic properties were consistent with the data available in the literature.*

**3-(4-((tert-Butyldimethylsilyl)oxy)phenyl)propanoic acid**

![Chemical structure of 3-(4-((tert-Butyldimethylsilyl)oxy)phenyl)propanoic acid]

**General procedure A:** 3-(4-Hydroxyphenyl)propanoic acid (8.30 g, 50.0 mmol), tert-butyldimethylsilyl chloride (16.5 g, 110.0 mmol) and imidazole (11.25 g, 165.0 mmol) in DMF
(100 mL) were employed. Purification by flash column chromatography (25 % EtOAc/hexane) afforded the title compound (10.8 g, 77 %) as a colorless solid; m.p.: 69 - 71 °C (EtOAc/hexane); Rf = 0.2 (20 % EtOAc/hexane); \( \nu_{\text{max}} / \text{cm}^{-1} \) (solid) 2926 (m), 2882 (m), 2855 (m), 1714 (s), 1509 (s), 1249 (s), 1213 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 10.30 (1H, br s, COOH), 7.06 (2H, d, \( J = 8.3 \) Hz, ArCH), 6.77 (2H, d, \( J = 8.3 \) Hz, ArCH), 2.89 (2H, t, \( J = 7.6 \) Hz, C\(_3\)-H\(_2\)), 2.65 (2H, t, \( J = 7.3 \) Hz, C\(_2\)-H\(_2\)), 0.99 (9H, s, TBS (CH\(_3\))\(_3\)), 0.19 (6H, s, TBS (CH\(_3\))\(_2\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 179.4 (C\(_1\)), 154.2 (ArC), 133.0 (ArC), 129.3 (2 x ArCH), 120.2 (2 x ArCH), 36.1 (C2), 30.0 (C3), 25.8 (TBS (CH\(_3\))\(_3\)), 18.3 (TBS SiC(CH\(_3\))\(_3\)), -4.3 (TBS Si(CH\(_3\))\(_2\)). HRMS (ESI\(^+\)) Calculated for C\(_{15}\)H\(_{25}\)O\(_3\)Si: 281.1567. Found [M+H]\(^+\): 281.1580. The title compound has been described only in a patent.\(^3\)

3-(4-((tert-Butyldimethylsilyl)oxy)phenyl)propan-1-ol\(^4\)

\[
\begin{align*}
\begin{array}{c}
\text{CO}_{2}H \\
\text{OTBS} \\
\end{array}
\rightarrow
\begin{array}{c}
\text{OH} \\
\text{OTBS} \\
\end{array}
\end{align*}
\]

**General procedure B:** 3-(4-((tert-Butyldimethylsilyl)oxy)phenyl)propanoic acid (1.40 g, 5.0 mmol) and 2.0 eq. LiAlH\(_4\) (1M in THF) in anhydrous Et\(_2\)O were employed. Purification by flash column chromatography (25 % EtOAc/hexane) afforded the title compound (0.99 g, 74 %) as a colorless oil R\(_f\) = 0.6 (33% EtOAc/hexane); \( \nu_{\text{max}} / \text{cm}^{-1} \) (film) 3339 (br m), 2929 (s), 2885 (s), 2858 (s), 1609 (m), 1508 (s), 1250 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.04 (2H, d, \( J = 8.0 \) Hz), 6.75 (2H, d, \( J = 8.0 \) Hz), 3.64-3.68 (2H, m), 2.64 (2H, t, \( J = 7.4 \) Hz), 1.86 (2H, m), 1.35, (1H, br s), 0.98 (9H, s), 0.18 (6H, s); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 153.7, 134.4, 129.2, 119.9, 62.3, 34.4, 31.2, 25.7, 18.2, -4.4. **Spectroscopic properties were consistent with the data available in the literature.**\(^4\)
**tert-Butyl (3-(4-((tert-butyldimethylsilyl)oxy)phenyl)propyl)(tosyloxy)carbamate (silyl-5a)**

![Chemical structure](attachment:structure.png)

**General procedure C:** 3-(4-((tert-butyldimethylsilyl)oxy)phenyl)propan-1-ol (0.79 g, 3.00 mmol), PPh₃ (0.94 g, 3.60 mmol), DIAD (0.71 mL, 3.60 mmol) and TsONHBoc (1.03 g, 3.60 mmol) in THF (12 mL) were employed. Purification by flash column chromatography (10 % EtOAc/hexane) afforded silyl-5a (1.49 g, 93 %) as a pale yellow oil; Rₖ = 0.5 (20 % EtOAc/hexane); vₓmax / cm⁻¹ (film) 2955 (m), 2930 (m), 2858 (m), 1753 (m), 1720 (s), 1509 (s), 1382 (s), 1368 (s), 1251 (s), 1154 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.84 (2H, d, J = 8.3 Hz, Ts ArC₆H₃), 7.34 (2H, d, J = 8.3 Hz, Ts ArC₆H₃), 7.00 (2H, d, J = 8.4 Hz, C₅H), 6.74 (2H, d, J = 8.4 Hz, C₆H), 3.60 (2H, app. br s, C₁H₂), 2.52 (2H, t, J = 7.8 Hz, C₃H₂), 2.45 (3H, s, Ts C₆H₃), 1.95 - 1.85 (2H, m, C₂H₂), 1.22 (9H, s, Boc (CH₃)₃), 0.98 (9H, s, TBS (CH₃)₃), 0.18 (6H, s, TBS (CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 155.5 (C=O), 153.8 (C₇), 145.6 (Ts ArC), 133.7 (C₄), 131.3 (Ts ArC), 129.6 (2 × Ts ArC₆H₃), 129.5 (2 × Ts ArC₆H₃), 129.1 (C₅), 120.0 (C₆), 83.2 (Boc C(CH₃)₃), 52.6 (C₁), 32.0 (C₃), 27.6 (Boc (CH₃)₃), 27.5 (C₂), 25.7 (TBS (CH₃)₃), 21.7 (Ts CH₃), 18.2 (TBS Si(CH₃)₃), -4.4 (TBS Si(CH₃)₂); HRMS (ESI⁺) Calculated for C₂₇H₄₁NNaO₇Si: 558.2316. Found [M+Na⁺]: 558.2313.

**tert-Butyl (3-(4-hydroxyphenyl)propyl)(tosyloxy)carbamate (5a)**

![Chemical structure](attachment:structure.png)
**General procedure D:** tert-Butyl (3-(4-((tert-butylidimethylsilyl)oxy)phenyl)propyl)(tosyloxy)carbamate (silyl-5a) (0.69 g, 1.28 mmol) and 1:1 TBAF/HOAc solution (0.1 M in THF, 1.28 mmol) in THF (20 mL) were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded 5a (0.35 g, 60 %) as a colorless solid; m.p.: 63 - 65 °C (EtOAc/hexane); Rf = 0.2 (20 % EtOAc/hexane); νmax / cm⁻¹ (solid) 3426 (m, br), 2982 (m), 2934 (m), 1721 (s), 1515 (s), 1369 (s), 1191 (s), 1177 (s), 1152 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.83 (2H, d, J = 8.3 Hz, Ts ArCH), 7.32 (2H, d, J = 8.3 Hz, Ts ArCH), 6.98 (2H, d, J = 8.4 Hz, C₅-H), 6.75 (2H, d, J = 8.4 Hz, C₆-H), 5.75 (1H, br s, OH), 3.60 (2H, app. br s, C₁-H₂), 2.50 (2H, t, J = 7.8 Hz, C₃-H₂), 2.44 (3H, s, Ts CH₃), 1.97 – 1.80 (2H, m, C₂-H₂), 1.23 (9H, s, Boc (CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 155.7 (C=O), 154.1 (C₇), 145.9 (Ts ArC), 132.8 (C₄), 144.5 (C₅), 131.0 (Ts ArC), 129.6 (2× Ts ArC), 129.5 (2× Ts ArCH), 129.3 (C⁵), 115.3 (C₆), 83.6 (Boc C(CH₃)₃), 52.6 (C₁), 31.9 (C₃), 27.7 (C₂), 27.6 (Boc (CH₃)₃), 21.7 (Ts, CH₃); HRMS (ESI⁺) Calculated for C₂₁H₂₇NNaO₆S: 444.1451. Found [M+Na]⁺: 444.1434.

**1-Azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7a)**

![Image of 1-Azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7a) structure]

**General procedure E:** tert-Butyl (3-(4-hydroxyphenyl)propyl)(tosyloxy)carbamate (5a) (60.7 mg, 0.14 mmol) and TFA (22 μL, 0.28 mmol) in TFE (1.4 mL) were stirred at r.t. for 24 h. Purification of the product by flash column chromatography (EtOAc) afforded 7a (29.0 mg, 77 %) as a yellow solid; m.p.: 100 - 102 °C (EtOAc/hexane); Rf = 0.1 (5 % MeOH/CH₂Cl₂); νmax / cm⁻¹ (solid) 1651 (s), 1633 (s), 1426 (m), 1400 (m), 1192 (s), 1175 (s), 1130 (s); ¹H NMR (400 MHz, CD₃OD) δ 7.11 (2H, d, J = 10.3 Hz, C₅-H), 6.43 (2H, d, J = 10.3 Hz, C₆-H), 3.64 (2H, t, J = 7.4 Hz, C₁-H₂), 2.42 - 2.34 (2H, m, C₂-H₂), 2.30 - 2.25 (2H, m, C₃-H₂). The signals corresponding to the NH₂ were not observed. ¹³C NMR (101 MHz, CD₃OD) δ 185.3 (C₇), 144.5 (C₅), 131.7 (C₆), 64.5 (C₄), 46.6 (C₁), 37.8 (C₃), 24.8 (C₂). The signals corresponding
to the trifluoroacetate group could not be resolved due to their weak intensity. HRMS (ESI+) Calculated for C₉H₁₂NO: 150.0913. Found [M+H]⁺: 150.0908.

**Methyl (E)-3-(4-(benzylxy)-3,5-dimethylphenyl)acrylate**

![Chemical Structure]

**General procedure F:** 4-(Benzylxy)-3,5-dimethylbenzaldehyde (2.40 g, 10.0 mmol) and methyl 2-(triphenyl-phosphaneylidene) acetate (5.00 g, 15.0 mmol) in CH₂Cl₂ (15 mL) were employed. Purification by flash column chromatography (gradient, eluent 10 - 20 % EtOAc/hexane) afforded the title compound (2.85 g, 96 %) as a colorless oil; Rᵣ = 0.6 (20 % EtOAc/hexane); ν_max / cm⁻¹ (film) 1713 (s), 1632 (m), 1434 (m), 1265 (s), 1143 (s); ¹H NMR δ 7.63 (1H, d, J = 16.0 Hz, C₃-H), 7.50 - 7.46 (2H, m, ArCH), 7.46 - 7.33 (3H, m, ArCH), 7.23 (2H, s, C₅-H), 6.36 (1H, d, J = 16.0 Hz, C₂-H), 4.83 (2H, s, OCH₂), 3.81 (3H, s, CH₃), 2.32 (6H, s, C₇-H₃); ¹³C NMR (101 MHz, CDCl₃) δ 167.7 (C₁), 157.9 (C₈), 144.8 (C₃), 137.4 (PhC), 131.9 (C₆), 130.2 (C₄), 129.0 (C₅), 128.7 (2 × PhCH), 128.2 (PhCH), 127.9 (2 × PhCH), 116.6 (C₂), 74.2 (OCH₂), 51.7 (OCH₃), 16.6 (C₇); HRMS (ESI⁺) Calculated for C₁₉H₂₀NaO₃: 319.1305. Found [M+Na]⁺: 319.1311.

**Methyl 3-(4-hydroxy-3,5-dimethylphenyl)propanoate⁵**

![Chemical Structure]

**General procedure G:** Methyl (E)-3-(4-(benzylxy)-3,5-dimethylphenyl)acrylate (2.37 g, 8.00 mmol) and 10 wt.% Pd/C (10 mol %) in MeOH (50 mL) were employed to afford the title compound (1.66 g, 99 %) as a colorless solid, which was used without further purification; m.p. 66 - 68 °C (EtOAc/hexane); Rᵣ = 0.4 (20 % EtOAc/hexane); ν_max / cm⁻¹ (solid) 3492 (s,
br), 2952 (m), 2928 (m), 1723 (s), 1277 (s), 1174 (s), 1151 (s); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.81 (2H, s, C$_5$-H), 4.55 (1H, br s, O-H), 3.67 (3H, s, OCH$_3$), 2.82 (2H, t, $J$ = 7.8 Hz, C$_3$-H$_2$), 2.58 (2H, t, $J$ = 7.8 Hz, C$_2$-H$_2$), 2.22 (6H, s, C$_7$-H$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) 173.7, 150.7, 132.2, 128.5, 123.2, 51.7, 36.3, 30.3, 16.0, HRMS. (ESI$^+$) Calculated for C$_{12}$H$_{16}$NaO$_3$: 231.0992. Found [M+Na]$^+$: 231.1002. The title compound has been described only in a patent.

**Methyl 3-((tert-butyldimethylsilyl)oxy)-3,5-dimethylphenylpropanoate**

To a solution of methyl 3-(4-hydroxy-3,5-dimethylphenyl)propanoate (1.33 g, 6.00 mmol) in CH$_2$Cl$_2$ (10 mL) and DMF (12 mL) was added tert-butyldimethylsilyl chloride (1.8 g, 12.0 mmol) and imidazole (0.82 g, 12.0 mmol) at 0 °C. The reaction was stirred at r.t. overnight and quenched with H$_2$O (50 mL) and the organic phase extracted with CH$_2$Cl$_2$ (3 × 15 mL), washed with brine (15 mL), dried over MgSO$_4$, filtered and concentrated in vacuo. Purification by flash column chromatography (10 % EtOAc/hexane) afforded the title compound (1.22 g, 63 %) as a colorless oil; $R_f$ = 0.6 (25 % EtOAc/hexane); $\nu_{max}$/cm$^{-1}$ (film) 2953 (m), 2930 (m), 1740 (s), 1484 (m), 1473 (m), 1253 (s), 1228 (s), 1153 (s); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.79 (2H, s, C$_5$-H), 3.67 (3H, s, OCH$_3$), 2.81 (2H, t, $J$ = 7.8 Hz, C$_3$-H$_2$), 2.58 (2H, t, $J$ = 7.8 Hz, C$_2$-H$_2$), 2.18 (6H, s, C$_7$-H$_3$), 1.03 (9H, s, TBS (C$_3$H$_3$)$_3$), 0.18 (6H, s, TBS (C$_3$H$_3$)$_2$); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.7 (C$_1$), 150.6 (C$_8$), 133.1 (C$_4$), 128.6 (C$_5$), 128.6 (C$_6$), 51.7 (OCH$_3$), 36.2 (C$_2$), 30.3 (C$_3$), 26.3 (TBS (C$_3$H$_3$)$_3$), 18.9 (TBS C(CH$_3$)$_3$), 18.0 (C$_7$), -2.8 (TBS Si(C$_3$H$_3$)$_2$); HRMS (ESI$^+$) Calculated for C$_{18}$H$_{30}$NaO$_3$Si: 345.1856. Found [M+Na]$^+$: 345.1870.
3-(4-((tert-Butyldimethylsilyl)oxy)-3,5-dimethylphenyl)propan-1-ol\(^6\)

![Chemical structure](image)

**General procedure B:** Methyl 3-(4-((tert-butyl dimethylsilyl)oxy)-3,5-dimethylphenyl)propanoate (0.96 mg, 3.0 mmol) and 2.0 eq. LiAlH\(_4\) (1 M in THF) in anhydrous Et\(_2\)O were employed. The crude product was filtered through a plug of silica and washed with EtOAc to afford the title compound (0.69 mg, 80\%) as a pale yellow oil; \(R_f = 0.2\) (25\% EtOAc/hexane); \(\nu_{\text{max}}/\text{cm}^{-1}\) (film) 3345 (br m), 2929 (m), 2858 (m), 1483 (s), 1472 (s), 1252 (s), 1227 (s), 1152 (s); \(1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.79 (2H, s), 3.66 (2H, t, \(J = 6.4\) Hz), 2.57 (2H, t, \(J = 7.5\) Hz), 2.18 (6H, s), 1.89-1.81 (2H, m), 1.29 (1H, br s), 1.03 (9H, s), 0.18 (6H, s); \(13^C\) NMR (101 MHz, CDCl\(_3\)) \(\delta\) 150.1, 134.2, 128.6, 128.3, 62.5, 34.3, 31.2, 26.1, 18.7, 17.8, -3.0. Spectroscopic properties were consistent with the data available in the literature.\(^6\)

tert-Butyl (3-(4-((tert-butyl dimethylsilyl)oxy)-3,5-dimethylphenyl)propyl)(tosyloxy) carbamate

![Chemical structure](image)

**General procedure C:** 3-(4-((tert-Butyldimethylsilyl)oxy)-3,5-dimethylphenyl)propan-1-ol (0.53 g, 1.80 mmol), PPh\(_3\) (0.58 g, 2.20 mmol), DIAD (0.43 mL, 2.20 mmol) and TsONHBoc (0.63 g, 2.20 mmol) in anhydrous THF (8 mL) were employed. Purification by flash column chromatography (10\% EtOAc/hexane) afforded the title compound (0.88 g, 87\%) as a colorless oil; \(R_f = 0.55\) (20\% EtOAc/hexane); \(\nu_{\text{max}}/\text{cm}^{-1}\) (film) 2955 (m), 2930 (m), 1722 (s), 1473 (m), 1483 (m), 1383 (s), 1369 (s), 1230 (s), 1191 (s), 1179 (s), 1154 (s); \(1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 (2H, d, \(J = 8.3\) Hz, Ts ArC\(_H\)), 7.32 (2H, d, \(J = 8.3\) Hz, Ts ArC\(_H\)), 6.75 (2H, s, C5-H), 3.61 (2H, app. br s, C1-H), 2.46-2.42 (5H, m, overlapping C3-H\(_2\) and Ts C\(_H_3\)),

S11
2.18 (6H, s, C7-H3) 1.93-1.81 (2H, m, C2-H2), 1.21 (9H, s, Boc (CH3)3), 1.03 (9H, s, TBS (CH3)2), 0.17 (6H, s, TBS Si(CH3)2); 13C NMR (101 MHz, CDCl3) δ 155.6 (Boc C=O), 150.4 (C8), 145.7 (Ts ArC), 133.7 (C4), 131.4 (Ts ArC), 129.8 (2 × Ts ArCH), 129.6 (2 × Ts ArCH), 128.7 (C5), 128.5 (C6), 83.2 (Boc C(CH3)3), 52.9 (C1), 32.1 (C3), 27.8 (C2), 27.7 (Boc (CH3)3), 26.3 (TBS (CH3)3), 21.9 (Ts CH3), 18.9 (TBS C(CH3)3), 18.0 (C7), -2.8 (TBS (CH3)2); HRMS (ESI+) Calculated for C29H45NNaO6Si: 586.2629. Found [M+Na]+: 586.2648.

tert-Butyl (3-(4-hydroxy-3,5-dimethylphenyl)propyl)(tosyloxy)carbamate (5b)

General procedure D: tert-Butyl (3-(4-(((tert-butyldimethylsilyl)oxy)-3,5-dimethylphenyl)propyl) (tosyloxy)carbamate (0.45 g, 0.80 mmol) and 1:1 TBAF/HOAc solution (0.1 M in THF, 0.88 mmol) in THF (16 mL) were employed. Purification by flash column chromatography (gradient, eluent 20 - 33 % EtOAc/hexane) afforded 5b (0.31 g, 87 %) as a colorless, viscous oil; Rf = 0.3 (20 % EtOAc/hexane); νmax / cm⁻¹ (film) 3530 (br m), 2979 (m), 2930 (m), 1721 (s), 1597 (m), 1489 (m), 1370 (s), 1192 (s), 1177 (s), 1152 (s); 1H NMR (400 MHz, CDCl3) δ 7.84 (2H, d, J = 8.3 Hz, Ts ArC-H), 7.32 (2H, d, J = 8.3 Hz, Ts ArC-H), 6.77 (2H, s, C5-H), 4.49 (1H, s, OH), 3.62 (2H, app. br s, C1-H2), 2.44 (5H, m, overlapping C3-H2 and Ts CH3), 2.21 (6H, s, C7-H3), 1.93-1.85 (2H, m, C2-H2), 1.20 (9H, s, Boc (CH3)3); 13C NMR (101 MHz, CDCl3) δ 155.6 (Boc C=O), 150.5 (C8), 145.8 (Ts ArC), 132.8 (C4), 131.4 (Ts ArC), 129.8 (2 × Ts ArC-H), 129.6 (2 × Ts ArC-H), 128.5 (C5), 123.0 (C6), 83.3 (Boc C(CH3)3), 52.8 (C1), 32.1 (C3), 27.9 (C2), 27.7 (Boc (CH3)3), 21.8 (Ts CH3), 16.0 (C7); HRMS (ESI+) Calculated for C23H31NNaO6S: 472.1764. Found [M+Na]+: 472.1767.
7,9-Dimethyl-1-azaspiro[4.5]deca-6,9-dien-8-one (7b)

General procedure E: tert-Butyl (3-(4-hydroxy-3,5-dimethylphenyl)propyl)(tosyloxy) carbamate (5b) (89.8 mg, 0.20 mmol) and TFA (31.0 μL, 0.40 mmol) in TFE (2 mL) were employed. After stirring at r.t. for 22 h, purification by flash column chromatography (EtOAc) afforded 7b (30.0 mg, 85%) as a pale yellow/orange solid; m.p.: 110 - 113 °C (EtOAc/hexane); Rf = 0.1 (EtOAc); νmax / cm⁻¹ (film) 3318 (m), 2970 (m), 2946 (m), 2917 (m), 2882 (m), 1664 (s), 1623 (s), 1369 (m), 1222 (m); ¹H NMR (400 MHz, CDCl₃) δ 6.60 (2H, s, C₅-H), 3.19 (2H, t, J = 6.9 Hz, C₁-H₂), 2.04-1.96 (2H, m, C₂-H₂), 1.87-1.84 (9H, m, overlapping C₃-H₂, C₇-H₃ and NH); ¹³C NMR (101 MHz, CDCl₃) δ 187.2 (C₈), 147.7 (C₅), 132.7 (C₆), 60.4 (C₄), 46.1 (C₁), 36.7 (C₃), 25.5 (C₂), 16.0 (C₇); HRMS (ESI⁺) Calculated for C₁₁H₁₆NO: 178.1226. Found [M+H]⁺: 178.1228.

Ethyl 3-(3-bromo-4-hydroxyphenyl)propanoate

A solution of bromine (0.25 mL, 4.75 mmol) in acetic acid (20 mL) was slowly added to a stirring solution of ethyl 3-(4-hydroxyphenyl)propionate (1.84 g, 9.50 mmol) at r.t. The
reaction mixture was stirred for 6 h then diluted with EtOAc (80 mL) and washed with brine (2 × 30 mL). The organic extracts were dried over anhydrous MgSO₄, filtered and concentrated in vacuo. Purification by flash column chromatography (5 % EtOAc/PhMe) afforded the title compound (1.14 g, 44 %) as a pale yellow solid; Rf = 0.3 (5 % EtOAc/PhMe); νmax / cm⁻¹ (solid) 3357 (br m), 2977 (m), 2936 (m), 1727 (s), 1704 (s), 1496 (s), 1289 (s), 1254 (s), 1180 (s), 1156 (s), 1039 (s); ¹H NMR (400 MHz, CDCl³) δ 7.29 (1H, d, J = 2.0 Hz), 7.03 (1H, dd, J = 8.2, 2.0 Hz), 6.91 (1H, d, J = 8.2 Hz), 4.11 (2H, q, J = 7.2 Hz), 2.85 (2H, t, J = 8.5 Hz), 2.56 (2H, t, J = 7.6 Hz), 1.22 (3H, t, J = 7.2 Hz); ¹³C NMR (101 MHz, CDCl³) δ 172.7, 150.7, 134.2, 131.6, 129.1, 116.0, 110.0, 60.5, 36.0, 29.8, 14.2. Spectroscopic properties are consistent the data available in the literature.⁷

Ethyl 3-(3-bromo-4-((tert-butyldimethylsilyl)oxy)phenyl)propanoate

To a solution of ethyl 3-(3-bromo-4-hydroxyphenyl)propanoate (1.08 g, 3.95 mmol) in DMF (5 mL) was added tert-butyldimethylsilyl chloride (0.71 g, 4.74 mmol) and imidazole (0.67 g, 9.88 mmol) and the reaction was stirred at r.t. overnight. To the reaction was added water (25 mL) and the organic phase extracted with CH₂Cl₂ (2 x 20 mL). The combined organic extracts were washed with brine (20 mL), dried over MgSO₄, filtered and concentrated in vacuo. Purification by flash column chromatography (5% EtOAc/hexane) afforded the title compound (1.43 g, 93 %) as a colorless oil; Rf = 0.6 (5 % EtOAc/hexane); νmax / cm⁻¹ (film) 2956 (m), 2930 (m), 1734 (s), 151.1 (C7), 134.9 (C4), 133.2 (C9), 128.2 (C5), 120.2 (C6), 115.2 (C8), 60.6 (OCH₂CH₃), 36.1 (C2), 29.9 (C3), 25.9 (TBS (CH₃)₃), 18.5 (TBS Si(C(CH₃)₃), 14.4 (OCH₂CH₃), -4.11 (TBS Si(CH₃)₂); HRMS (ESI⁺) Calculated for C_{17}H_{27}³⁷⁶BrNaO₃Si: 409.0805. Found [M+Na]⁺: 409.0816.
3-(3-Bromo-4-((tert-butyldimethylsilyl)oxy)phenyl)propan-1-ol

To a solution of ethyl 3-(3-bromo-4-((tert-butyldimethylsilyl)oxy)phenyl)propanoate (1.03 g, 2.66 mmol) in anhydrous THF (15 mL) at -15 °C was added 0.75 eq. LiAlH₄ (1M in THF) and the reaction was stirred at the same temperature for 25 min. Then to the reaction mixture was added water (0.5 mL), aq. 1 M NaOH (0.2 mL) and water (1 mL). The reaction mixture was warmed to r.t., filtered through Celite® and washed with CH₂Cl₂. The filtrate was dried over Na₂SO₄, filtered and concentrated in vacuo. Purification by flash column chromatography (20 % EtOAc/hexane) afforded the title compound (0.80 g, 87 %) as a colorless oil; Rᵣ = 0.2 (20 % EtOAc/hexane); νₓ/max/ cm⁻¹ (film) 3327 (br s), 2930 (m), 2858 (m), 1492 (s), 1280 (s), 1253 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.34 (1H, d, J = 2.2 Hz, C₉-H), 6.97 (1H, dd, J = 8.2, 2.2 Hz, C₅-H), 6.77 (1H, dd, J = 8.2, 0.8 Hz, C₆-H), 3.63 (2H, t, J = 6.5 Hz, C₁-H₂), 2.60 (2H, t, J = 7.5 Hz, C₃-H₂), 1.87-1.80 (2H, m, C₂-H₂), 1.51 (1H, br s, OH), 1.03 (9H, s, TBS (CH₃)₃), 0.22 (6H, s, TBS (CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 150.7 (C₇), 136.1 (C₄), 133.2 (C₉), 128.3 (C₅), 120.2 (C₆), 115.2 (C₈), 62.1 (C₁), 34.2 (C₂), 31.0 (C₃), 25.9 (TBS (CH₃)₃), 18.5 (TBS C(CH₃)₃), -4.1 (TBS Si(CH₃)₂); HRMS (ESI⁺) Calculated for C₁₅H₂₅BrNaO₂Si: 367.0699. Found [M+Na]⁺: 367.0701.

**tert-Butyl** (3-(3-bromo-4-((tert-butyldimethylsilyl)oxy)phenyl)propyl) (tosyloxy) carbamate

**General procedure C**: 3-(3-Bromo-4-((tert-butyldimethylsilyl)oxy)phenyl)propan-1-ol (0.69 g, 2.00 mmol), PPh₃ (0.63 g, 2.40 mmol), DIAD (0.47 mL, 2.40 mmol) and TsONHBoc (0.69
g, 2.40 mmol) in anhydrous THF were employed. Purification by flash column chromatography (gradient eluent 5% - 10% EtOAc/hexane) afforded the title compound (1.12 g, 91%) as a colorless oil; Rf = 0.6 (20% EtOAc/hexane); νmax/cm⁻¹ (film) 2955 (m), 2930 (m), 2858 (m), 1720 (s), 1493 (s), 1381 (s), 1288 (s), 1254 (s), 1178 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.83 (2H, d, J = 8.2 Hz, Ts ArCH), 7.32 (2H, d, J = 8.0 Hz, Ts ArCH), 7.29 (1H, d, J = 2.1 Hz, C9-H), 6.94 (1H, dd, J = 8.3, 2.2 Hz, C5-H), 6.77 (1H, d, J = 8.6 Hz, C6-H), 3.58 (2H, app. br s, C1-H2), 2.49 (2H, t, J = 7.8 Hz, C3-H2), 2.44 (3H, s, Ts C6-H3), 1.95 - 1.82 (2H, m, C2-H2), 1.22 (9H, s, Boc (CH₃)₃), 1.03 (9H, s, TBS (CH₃)₃), 0.23 (6H, s, Si(CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 155.6 (C=O), 150.9 (C7), 145.8 (Ts ArC), 135.4 (C4), 133.1 (C9), 131.4 (Ts ArC), 129.8 (2 × Ts ArCH), 129.5 (2 × Ts ArCH), 128.2 (C5), 120.2 (C6), 115.2 (C8), 83.4 (Boc C(CH₃)₃), 52.6 (C1), 31.8 (C3), 27.8 (Boc (CH₃)₃), 27.5 (C2), 25.9 (TBS (CH₃)₃), 21.8 (Ts CH₃), 18.5 (TBS Si(CH₃)₃), -4.1 (TBS Si(CH₃)₂); HRMS (ESI⁺) Calculated for C₂₇H₄₀⁷⁹BrNNaO₆Si: 636.1421. Found [M+Na]⁺: 636.1422.

tert-Butyl (3-(3-bromo-4-hydroxyphenyl)propyl)(tosyloxy)carbamate (5c)

**General procedure D:** tert-Butyl (3-(3-bromo-4-((tert-butyldimethylsilyl)oxy)phenyl)propyl)(tosyloxy)carbamate (0.61 g, 1.00 mmol) and 1:1 solution of TBAF/AcOH (0.1 M in THF, 1.00 mmol) in THF (20 mL) were employed. Purification by flash column chromatography (20% EtOAc/hexane) afforded 5c (0.48 g, 96%) as a colorless solid; m.p.: 93 - 95 °C (EtOAc/hexane); Rf = 0.25 (20% EtOAc/hexane); νmax/cm⁻¹ (solid) 3416 (br s), 3146 (br s), 2945 (m), 1682 (s), 1371 (s), 1361 (s), 1180 (s), 1158 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.83 (2H, d, J = 8.3 Hz, Ts ArCH), 7.32 (2H, d, J = 8.1 Hz, Ts ArCH), 7.25 (1H, d, J = 2.2 Hz, C9-H), 7.00 (1H, dd, J = 8.3, 2.1 Hz, C5-H), 6.91 (1H, d, J = 8.3 Hz, C6-H), 5.43 (1H, s, OH), 3.59 (2H, app. br s, C1-H2), 2.50 (2H, t, J = 7.8 Hz, C3-H2), 2.44 (3H, s, Ts C6-H3), 1.91-1.87 (2H, m, C2-H2), 1.21 (9H, s, Boc (CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 155.6 (C=O), 150.6 (C7), 145.9...
(Ts ArC), 134.9 (C4), 131.6 (C9), 131.3 (Ts ArC), 129.8 (2 × Ts ArCH), 129.7 (2 × Ts ArCH), 129.2 (C5), 116.1 (C6), 110.1 (C8), 83.5 (Boc C(CH3)3), 52.5 (C1), 31.7 (C3), 27.8 (Boc (CH3)3), 27.6 (C2), 21.8 (Ts CH3); HRMS (ESI+) Calculated for C21H26BrNO6S: 522.0556. Found [M+Na]+: 522.0555.

7-bromo-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7c) and 6-Bromo-1,2,3,4-tetrahydroquinolin-7-ol (8c)

**General procedure E:** tert-Butyl (3-(3-bromo-4-hydroxyphenyl)propyl)(tosyloxy)carbamate (5c) (75.06 mg, 0.15 mmol) and TFA (22.9 μL, 0.30 mmol) in TFE (1.5 mL) were employed. After stirring at r.t. for 45 h, purification by flash column chromatography (EtOAc) afforded the title compounds 7c (22.0 mg, 43%) as a red/brown oil and 8c (8.8 mg, 19%) as a brown oil. Data for 7c; Rf = 0.1 (EtOAc); νmax / cm⁻¹ (film, CDCl3) 2924 (m), 1675 (s), 1407 (w), 1200 (s), 1134 (m), 1066 (m); ¹H NMR (400 MHz, CD3OD) δ 7.63 (1H, d, J = 3.0 Hz, C9-H), 7.14 (1H, dd, J = 10.0, 3.0 Hz, C5-H), 6.55 (1H, d, J = 10.1 Hz, C6-H), 3.64 (2H, t, J = 6.9 Hz, C1-H2), 2.41-2.30 (4H, m, C2-H2, C3-H2). The signals corresponding to the NH2 were not observed. ¹³C NMR (101 MHz, CD3OD) δ 178.1 (C7), 144.7 (C9), 144.6 (C5), 130.3 (C6), 128.3 (C8), 66.9 (C4), 46.7 (C1), 37.4 (C3), 24.8 (C2). The signals corresponding to the trifluoroacetate group could not be resolved due to their weak intensity. HRMS (ESI⁺) Calculated for C9H11BrNO: 228.0019. Found [M]+: 228.0019.

Data for 8c; Rf = 0.7 (EtOAc); νmax / cm⁻¹ (film) 3389 (m), 3197 (m), 2957 (m), 2918 (m), 2850 (m); ¹H NMR (400 MHz, CDCl3) δ 6.97 (1H, s, C5-H), 6.16 (1H, s, C8-H), 3.27-3.24 (2H, m, C1-H2), 2.66 (2H, t, J = 6.4 Hz, C3-H2), 1.91-1.85 (2H, m, C2-H2); ¹³C NMR (101 MHz, CDCl3) δ 150.8 (C7), 145.1 (C9), 131.7 (C5), 115.8 (C4), 100.8 (C8), 96.6 (C6), 41.7 (C1), 31.7 (C3).
26.1 (C3), 21.9 (C2). HRMS (ESI⁺) Calculated for C₉H₁₁BrNO: 228.0018. Found [M]⁺: 228.0029.

Methyl 3-(3-bromo-4-hydroxyphenyl)propanoate

To a solution of methyl 3-(4-hydroxyphenyl)propanoate (4.50 g, 25.0 mmol) in AcOH (20 mL) was slowly added a solution of Br₂ (1.3 mL, 25.0 mmol) in AcOH (15 mL). The reaction was stirred at r.t. until completion by TLC analysis. The reaction was diluted with EtOAc (20 mL) and washed with brine (20 mL), dried over Na₂SO₄, filtered, and the solvent removed in vacuo. Purification by flash column chromatography (20 % EtOAc/hexane) afforded the title compound (2.98 g, 46 %) as a colorless solid; Rf = 0.2 (20% EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.30 (1H, d, J = 2.1 Hz), 7.05 (1H, dd, J = 8.3, 2.0 Hz), 6.93 (1H, d, J = 8.3 Hz), 3.67 (3H, s), 2.86 (2H, t, J = 7.7 Hz), 2.59 (2H, dd, J = 8.6, 6.7 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 173.2, 150.8, 134.3, 131.7, 129.2, 116.1, 110.1, 51.8, 35.8, 29.7. Spectroscopic properties were consistent with the data available in the literature.

Methyl 3-(3-bromo-4-((tert-butyldimethylsilyl)oxy)phenyl)propanoate

To a solution of methyl 3-(3-bromo-4-hydroxyphenyl)propanoate (2.94 g, 11.3 mmol) in DMF (5 mL) was added tert-butyldimethylsilyl chloride (2.05 g, 13.6 mmol) and imidazole (1.93 g, 28.4 mmol) and the reaction was stirred at r.t. overnight. To the reaction was added water (25
mL) and the organic phase was extracted with CH$_2$Cl$_2$ (2 × 20 mL). The combined organic phases were washed with brine (20 mL), dried over MgSO$_4$, filtered and concentrated in vacuo. Purification by flash column chromatography (20 % EtOAc/hexane) afforded the title compound (3.53 g, 84 %) as a colorless oil; R$_f$ = 0.4 (20 % EtOAc/hexane); $\nu_{\text{max}}$ / cm$^{-1}$ (film) 2952 (m), 2930 (m), 2858 (m), 1738 (s), 1492 (s), 1253 (s); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (1H, d, $J$ = 2.2 Hz, C$_{10}$-H), 7.04-6.93 (1H, m, C$_6$-H), 6.78 (1H, d, $J$ = 8.2 Hz, C$_7$-H), 3.67 (3H, s, C$_1$-H$_3$), 2.85 (2H, t, $J$ = 7.8 Hz, C$_4$-H$_2$), 2.58 (2H, t, $J$ = 7.8 Hz, C$_3$-H$_2$), 1.03 (9H, s, TBS (C$_{3}$H$_3$)$_3$), 0.23 (6H, s, TBS Si(C$_{3}$H$_3$)$_2$); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.3 (C$_2$), 151.1 (C$_8$), 134.8 (C$_5$), 133.2 (C$_{10}$), 128.2 (C$_6$), 120.2 (C$_7$), 115.3 (C$_9$), 51.8 (C$_1$), 35.8 (C$_4$), 29.9 (C$_3$), 25.9 (TBS (C$_{3}$H$_3$)$_3$), 18.5 (TBS C(C$_{3}$H$_3$)$_3$), -4.1 (TBS Si(C$_{3}$H$_3$)$_2$). HRMS (ESI$^+$) Calculated for C$_{16}$H$_{25}$BrNaO$_3$Si: 395.0648. Found [M+Na]$^+$: 395.0647.

**Methyl 3-(4-((tert-butyldimethylsilyl)oxy)-3-cyclopropylphenyl)propanoate**

Methyl 3-(3-bromo-4-((tert-butyldimethylsilyl)oxy)phenyl)propanoate (1.12 g, 3.00 mmol), cyclopropylboronic acid (0.77 g, 9.00 mmol), K$_3$PO$_4$ (3.82 g, 18.0 mmol) and tetrakis(triphenylphosphine)palladium (0) (Pd(PPh$_3$)$_4$) (346 mg, 0.30 mmol) in 20:1 toluene/H$_2$O (0.1 M) were heated at 95 ºC overnight, under an atmosphere of N$_2$, and monitored by GC-MS. Upon completion, the reaction was cooled to r.t. and filtered through Celite® washing with EtOAc. The crude reaction mixture was then washed with water and the organic layer was dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. Purification by flash column chromatography (5 % EtOAc/hexane) afforded the title compound (0.81 g, 80 %) as a pale yellow oil; R$_f$ = 0.5 (20 % EtOAc/hexane); $\nu_{\text{max}}$ / cm$^{-1}$ (film) 2953 (m), 2930 (m), 2897 (m), 2858 (m), 1739 (s), 1498 (s), 1255 (s); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.85 (1H, dd, $J$ = 8.2, 2.3 Hz, C$_6$-H), 6.70 (1H, d, $J$ = 8.2 Hz, C$_7$-H), 6.62 (1H, d, $J$ = 2.2 Hz, C$_{10}$-H), 3.67 (3H, s, C$_1$-H$_3$), 2.84 (2H, t, $J$ = 8.0 Hz, C$_4$-H$_2$), 2.57 (2H, t, $J$ = 8.0 Hz, C$_3$-H$_2$), 2.13 (1H, tt, $J$ = 8.7, 5.4 Hz, C$_{11}$-H), 1.03, (9H, s, TBS (C$_{3}$H$_3$)$_3$), 0.93 - 0.87 (2H, m, C$_{12}$/C$_{13}$-H$_2$), 0.64 - 0.60 (2H, m, C$_{12}$/C$_{13}$-H$_2$), 0.23 (6H, s, TBS Si(C$_{3}$H$_3$)$_2$); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.6 (C$_2$), 152.9
(C8), 134.2 (C9), 133.2 (C5), 125.7 (C6), 124.8 (C10), 118.7 (C7), 51.7 (C1), 36.2 (C3), 30.6 (C4), 25.9 (TBS (CH₃)₃), 18.4 (TBS C(CH₃)₃), 10.1 (C11), 8.2 (C12,C13), -4.1 (TBS Si(CH₃)₂).

HRMS (ESI⁺) Calculated for C₁₉H₃₀NaO₃Si: 357.1856. Found [M+Na]⁺: 357.1862.

3-((tert-Butyldimethylsilyl)oxy)-3-cyclopropylphenyl)propan-1-ol

General procedure B: Methyl 3-((tert-butyldimethylsilyl)oxy)-3-cyclopropylphenyl)propanoate (0.67 g, 2.00 mmol) and 2.0 eq. LiAlH₄ (1 M in THF) in anhydrous Et₂O were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded the title compound (0.48 g, 78 %) as a colorless oil; Rf = 0.2 (20 % EtOAc/hexane); νmax / cm⁻¹ (film) 3334 (m, br), 2953 (m), 2929 (m), 2885 (m), 2857 (m), 1496 (s), 1254 (s); ¹H NMR (400 MHz, CDCl₃) δ 6.84 (1H, dd, J = 8.1, 2.3 Hz, C₅-H), 6.70 (1H, d, J = 8.1 Hz, C₆-H), 6.61 (1H, d, J = 2.2 Hz, C₉-H), 3.65 (2H, t, J = 6.4 Hz, C₁-H₂), 2.59 (2H, dd, J = 8.6, 6.8 Hz, C₃-H₂), 2.12 (1H, tt, J = 8.7, 5.4 Hz, C₁₀-H), 1.88 - 1.79 (2H, m, C₂-H₂), 1.40 (1H, br s, OH), 1.03 (9H, s, TBS (CH₃)₃), 0.92 - 0.88 (2H, m, C₁₁/C₁₂-H₂), 0.64 - 0.60 (2H, m, C₁₁/C₁₂-H₂), 0.23 (6H, s, TBS Si(CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 152.6 (C₇), 134.4 (C₄), 134.1 (C₈), 125.8 (C₅), 124.9 (C₉), 118.6 (C₆), 62.5 (C₁), 34.6 (C₂), 31.6 (C₃), 26.0 (TBS (CH₃)₃), 18.4 (TBS C(CH₃)₃), 10.1 (C₁₀), 8.2 (C₁₁,C₁₂), -4.1 (TBS Si(CH₃)₂). HRMS (ESI⁺) Calculated for C₁₈H₃₀NaO₂Si: 329.1907. Found [M+Na]⁺: 329.1940.

tert-Butyl (3-((tert-butyldimethylsilyl)oxy)-3-cyclopropylphenyl)propyl)(tosyloxy) carbamate

S20
**General procedure C:** 3-(4-((tert-Butyldimethylsilyl)oxy)-3-cyclopropylphenyl)propan-1-ol (0.43 g, 1.40 mmol), PPh$_3$ (0.44 g, 1.68 mmol), DIAD (0.33 mL, 1.68 mmol) and TsONHBoc (0.48 g, 1.68 mmol) in anhydrous THF (6 mL) were employed. Purification by flash column chromatography (5 % EtOAc/hexane) afforded the title compound (0.77 g, 96 %) as a colorless solid; R$_f$ = 0.5 (20 % EtOAc/hexane); v$_{max}$ / cm$^{-1}$ (solid) 2949 (m), 2928 (m), 2883 (m), 2857 (m), 1712 (s), 1504 (m); ¹H NMR (400 MHz, CDCl$_3$) δ 7.84 (2H, d, J = 8.3 Hz, Ts ArC$_6$H), 7.33 (2H, d, J = 8.1 Hz, Ts ArC$_6$H), 6.80 (1H, dd, J = 8.1, 2.1 Hz, C$_5$H), 6.68 (1H, d, J = 8.2 Hz, C$_6$H), 6.57 (1H, d, J = 2.2 Hz, C$_9$H), 3.60 (2H, app. br s, C$_1$H$_2$), 2.49 - 2.44 (5H, m, C$_3$H$_2$ and Ts C$_6$H$_3$), 2.15 - 2.08 (1H, m, C$_{10}$H), 1.94 - 1.83 (2H, m, C$_2$H$_2$), 1.22 (9H, s, Boc (C$_4$H$_3$)$_3$), 1.03 (9H, s, TBS (C$_4$H$_3$)$_3$), 0.92 - 0.86 (2H, m, C$_{11}$/C$_{12}$), 0.69 - 0.60 (2H, m, C$_{11}$/C$_{12}$), 0.22 (6H, s, TBS Si(CH$_3$)$_3$); ¹³C NMR (101 MHz, CDCl$_3$) δ 155.6 (C=O), 152.7 (C$_7$), 145.7 (Ts ArC), 134.1 (C$_8$), 133.7 (C$_4$), 131.4 (Ts ArC), 129.8 (2 × Ts CH), 129.6 (2 × Ts CH), 125.7 (C$_5$), 124.8 (C$_9$), 118.6 (C$_6$), 83.2 (Boc C(CH$_3$)$_3$), 52.8 (C$_1$), 32.3 (C$_3$), 27.7 (C$_2$), 27.7 (Boc (CH$_3$)$_3$) 26.0 (TBS (CH$_3$)$_3$), 21.8 (Ts CH$_3$), 18.4 (TBS C(CH$_3$)$_3$), 10.1 (C$_{10}$), 8.2 (C$_{11}$/C$_{12}$), -4.1 (TBS Si(CH$_3$)$_2$). HRMS (ESI$^+$) Calculated for C$_{30}$H$_{45}$NNaO$_6$Si: 598.2629. Found [M+Na]$^+$: 598.2615.

**tert-Butyl (3-(3-cyclopropyl-4-hydroxyphenyl)propyl)(tosyloxy)carbamate (5d)**

![Diagram of 5d](image)

**General procedure D:** *tert-Butyl* (3-(4-((tert-butyldimethylsilyl)oxy)-3-cyclopropylphenyl)propyl) (tosyloxy)carbamate (0.58 g, 1.00 mmol) and 1:1 TBAF/AcOH solution (0.1 M in THF, 1.00 mmol) in THF (20 mL) were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded 5d (0.37 g, 81 % yield) as a colorless solid; m.p.: 82 - 83 °C (EtOAc/hexane); R$_f$ = 0.2 (20 % EtOAc/hexane); v$_{max}$ / cm$^{-1}$ (solid) 3472 (m, br), 2988 (m), 2930 (m), 1693 (s); ¹H NMR (400 MHz, CDCl$_3$) δ 7.84 (2H, d, J = 8.1 Hz, Ts ArC$_6$H), 7.33 (2H, d, J = 8.0 Hz, Ts ArC$_6$H), 6.90 (1H, dd, J = 8.2, 2.1 Hz, C$_5$H), 6.86 (1H,
d, $J = 2.2$ Hz, C9-H), 6.76 (1H, d, $J = 8.1$ Hz, C6-H), 5.35 (1H, s, O-H), 3.61 (2H, app. br s, C1-H2), 2.48 (2H, t, $J = 7.8$ Hz, C3-H2), 2.45 (3H, s, Ts CH3), 1.95 - 1.84 (2H, m, C2-H2), 1.83 - 1.76 (1H, m, C10-H), 1.21 (9H, s, Boc (CH3)3), 0.98 - 0.93 (2H, m, C11/C12-H2), 0.66 - 0.63 (2H, m, C11/C12-H2); $^{13}$C NMR (101 MHz, CDCl3) δ 155.6 (C=O), 153.7 (C7), 145.8 (Ts Ar), 132.9 (C4), 131.4 (Ts, ArC), 129.8 (2 × Ts, ArCH), 129.6 (2 × Ts, ArCH), 128.5 (C9), 127.5 (C5), 127.5 (C8), 114.6 (C6), 83.3 (Boc (CH3)3), 52.8 (C1), 32.2 (C3), 27.8 (C2), 27.7 (Boc (CH3)3), 21.8 (Ts CH3), 9.5 (C10), 5.6 (C11,C12). HRMS (ESI+) Calculated for C24H31NNaO6S: 484.1764. Found [M+Na]+: 484.1750.

7-Cyclopropyl-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7d) and 6-cyclopropyl-1,2,3,4-tetrahydroquinolin-7-ol (8d)

General procedure E: tert-Butyl (3-(3-cyclopropyl-4-hydroxyphenyl)propyl)(tosyloxy) carbamate (5d) (92.3 mg, 0.20 mmol) and TFA (31.0 μL, 0.40 mmol) in TFE (2 mL) were employed. After stirring at r.t. for 24 h, purification by flash column chromatography (EtOAc) afforded the title compounds 7d (32.1 mg, 53 %) and 8d (12.8 mg, 34 %) as yellow solids.

Data for 7d: m.p.: 99 - 101 °C (EtOAc/hexane); Rf = 0.1 (EtOAc); $\nu_{\text{max}}$ / cm$^{-1}$ (solid) 2962 (m), 1667 (s), 1643 (s); $^1$H NMR (400 MHz, CD3OD) δ 7.07 (1H, dd, $J = 10.0, 3.1$ Hz, C5-H), 6.49 (1H, d, $J = 3.0$ Hz, C9-H), 6.43 (1H, dd, $J = 10.1, 1.3$ Hz, C6-H), 3.66 - 3.56 (2H, m, C1-H2), 2.38 - 2.31 (2H, m, C2-H2), 2.23 - 2.19 (2H, m, C3-H2), 1.94 - 1.88 (1H, m, C10-H), 0.91 - 0.87 (2H, m, C11/C12-H2), 0.65 - 0.62 (2H, m, C11/C12-H2). The signals corresponding to the NH2 were not observed. $^{13}$C NMR (101 MHz, CD3OD) δ 185.4 (C7), 144.5 (C8), 143.9 (C5), 134.6 (C9), 131.7 (C6), 64.9 (C4), 46.3 (C1), 37.8 (C3), 24.8 (C2), 10.0 (C10), 8.0 (C11,C12), 7.9 (C11,C12). The signals corresponding to the trifluoroacetate group could not be resolved due to their weak intensity. HRMS (ESI+) Calculated for C12H16NO: 190.1226. Found [M]+ 190.1230.
Data for 8d: m.p.: 108 - 110 °C (EtOAc/hexane); Rf = 0.4 (EtOAc); νmax / cm⁻¹ (solid) 3306 (m), 2932 (m), 1614 (m); ¹H NMR (400 MHz, CDCl₃) δ 6.68 (1H, s, C₅-H), 6.04 (1H, s, C₈-H), 5.10 (1H, br s, OH), 3.27 - 3.22 (2H, m, C₁₁-H₂), 2.66 (2H, t, J = 6.4 Hz, C₃-H₂), 1.93 - 1.87 (2H, m, C₂-H₂), 1.69 - 1.62 (1H, m, C₁₀-H), 0.89 - 0.84 (2H, m, C₁₁/C₁₂-H₂), 0.57 - 0.53 (2H, m, C₁₁/C₁₂-H₂). ¹³C NMR (101 MHz, CDCl₃) 154.4 (C₇), 144.5 (C₉), 130.1 (C₅), 116.3 (C₆), 113.4 (C₄), 100.1 (C₄), 26.4 (C₃), 22.7 (C₂), 8.7 (C₁₀), 5.2 (C₁₁/C₁₂). HRMS (ESI⁺) Calculated for C₁₂H₁₆NO: 190.1226. Found [M+H]⁺: 190.1228.

**Methyl 3-(6-((tert-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)propanoate**

Methyl 3-(3-bromo-4-((tert-butyldimethylsilyl)oxy)phenyl)propanoate (1.12 g, 3.00 mmol), phenylboronic acid (1.09 g, 9.00 mmol), K₂CO₃ (1.40 g, 10.2 mmol) and dichloro[1,1’-bis(ditertbutylphosphino)ferrocene] palladium(II) (Pd(dtbpf)Cl₂) (97.8 mg, 0.15 mmol) in 5:1 PhMe/MeOH (0.12 M) were heated at 110 °C overnight, under an atmosphere of N₂, and monitored by GC-MS. Upon completion, the reaction was cooled to r.t. and filtered through Celite® washing with EtOAc. The crude reaction mixture was then washed with water and the organic layer dried over Na₂SO₄, filtered and concentrated in vacuo. Purification by flash column chromatography (5 % EtOAc/hexane) afforded the title compound (0.93 g, 84 %) as a pale yellow oil; Rf = 0.5 (20 % EtOAc/hexane); νmax / cm⁻¹ (film) 2952 (m), 2929 (m), 2896 (m), 2857 (m), 1737 (s), 1486 (s), 1253 (s); ¹H NMR (440 MHz, CDCl₃) δ 7.49 - 7.45 (2H, m, PhC₆H), 7.39 - 7.33 (2H, m, PhC₆H), 7.31 - 7.26 (1H, m, PhC₆H), 7.13 (1H, d, J = 2.3 Hz, C₉-H), 7.03 (1H, dd, J = 8.3, 2.4 Hz, C₅-H₂), 6.82 (1H, d, J = 8.2 Hz, C₆-H₂), 3.67 (3H, s, OC₃H₃), 2.93 (2H, t, J = 7.9 Hz, C₃-H₂), 2.63 (2H, t, J = 7.9 Hz, C₂-H₂), 0.81 (9H, s, TBS (CH₃)₃), -0.07 (6H, s, TBS Si(CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 173.6 (C₁), 151.1 (C₇), 139.2 (C₈), 133.6 (PhC), 133.5 (C₄), 130.8 (C₉), 129.9 (2 × PhCH), 128.1 (C₅), 127.9 (2 × PhCH), 126.9 (PhCH₂), 120.5 (C₆), 51.7 (OCH₃), 36.1 (C₂), 30.4 (C₃), 25.7 (TBS (CH₃)₃), 18.2 (TBS Si(CH₃)₃), -4.5 (TBS Si(CH₃)₂); HRMS (ESI⁺) Calculated for C₂₂H₃₀NaO₅Si: 393.1856. Found [M+Na]⁺: 393.1856.
3-(6-((tert-Butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)propan-1-ol

**General procedure B:** Methyl 3-(6-((tert-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)propanoate (0.74 g, 2.00 mmol) and 2.0 eq. LiAlH₄ (1 M in THF) in anhydrous Et₂O were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded the title compound (0.60 g, 87 %) as a colorless oil; Rₜ = 0.2 (20 % EtOAc/hexane); υ_max/ cm⁻¹ (film) 3338 (m, br), 2929 (m), 2857 (m), 2884 (m), 1485 (s), 1256 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.52 - 7.47 (2H, m, PhCH₃), 7.40 - 7.34 (2H, m, PhCH₃), 7.32 - 7.26 (1H, m, PhCH₃), 7.14 (1H, d, J = 2.3 Hz, C₉-H), 7.04 (1H, dd, J = 8.2, 2.4 Hz, C₅-H), 6.84 (1H, d, J = 8.2 Hz, C₆-H), 3.69 (2H, t, J = 6.4 Hz, C₁-H₂), 2.69 (2H, t, J = 7.7 Hz, C₃-H₂), 1.94 - 1.87 (2H, m, C₃-H₂), 1.38 (1H, br s, OH), 0.82 (9H, s, TBS (CH₃)₃), -0.06 (6H, s, TBS Si(CH₃)₂). ¹³C NMR (101 MHz, CDCl₃) δ 150.8 (C₇), 139.3 (C₈), 134.9 (C₄), 133.4 (PhC), 130.9 (C₉), 129.9 (2 × PhCH₃), 128.2 (C₅), 127.9 (2 × PhCH₃), 126.8 (PhCH₃), 120.4 (C₆), 62.5 (C₁), 34.5 (C₂), 31.4 (C₃), 25.7 (TBS (CH₃)₃), 18.2 (TBS Si(CH₃)₂), -4.5 (TBS Si(CH₃)₂); HRMS (ESI⁺) Calculated for C₂₁H₃₀NaO₄Si: 365.1907. Found [M+Na⁺]: 365.1924.

tert-Butyl(3-(6-((tert-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)propyl)(tosyloxy) carbamate

**General procedure C:** 3-(6-((tert-Butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)propan-1-ol (54a) (0.48 g, 1.40 mmol), PPh₃ (0.44 g, 1.68 mmol), DIAD (0.33 ml, 1.68 mmol) and TsONHBoc (0.48 g, 1.68 mmol) in anhydrous THF (6 mL) were employed. Purification by flash column chromatography (5 % EtOAc/hexane) afforded the title compound (0.74 g, 87%)
as a colorless solid; m.p.: 95 - 96 °C (EtOAc/hexane); Rf = 0.5 (EtOAc/hexane); νmax / cm⁻¹ (solid) 2985 (m), 2955 (m), 2937 (m), 1715 (s), 1365 (s); ¹H NMR (400 MHz, CDCl3) δ 7.85 (2H, d, J = 8.2 Hz, Ts ArCH), 7.50-7.47 (2H, m, PhCH), 7.40 - 7.26 (5H, m, 3 × PhCH, 2 × Ts ArCH), 7.09 (1H, d, J = 2.3 Hz, C9-H), 7.01 (1H, dd, J = 8.2, 2.3 Hz, C5-H), 6.82 (1H, d, J = 8.2 Hz, C6-H), 3.64 (2H, app. br s, C1-H2), 2.57 (2H, t, J = 7.8 Hz, C3-H2), 2.44 (3H, s, Ts CH3), 2.01 - 1.88 (2H, m, C2-H2), 1.21 (9H, s, Boc (CH3)3), 0.81 (9H, s, TBS (CH3)3), -0.08 (6H, s, TBS Si(CH3)2). ¹³C NMR (101 MHz, CDCl3) δ 155.5 (C=O), 150.9 (C7), 145.8 (Ts ArC), 139.3 (PhC), 134.2 (C4), 133.4 (C8), 131.4 (Ts ArC), 130.8 (C9), 129.9 (2 × PhCH), 129.8 (2 × Ts ArCH), 129.6 (2 × Ts ArCH), 128.1 (C5), 127.9 (2 × PhCH), 126.8 (PhCH), 120.4 (C6), 83.3 (Boc (CH3)3), 52.8 (C1), 32.2 (C3), 27.8 (Boc (CH3)3), 27.7 (C2), 25.7 (TBS (CH3)3), 21.8 (Ts CH3), 18.2 (TBS Si(CH3)3), -4.5 (TBS Si(CH3)2); HRMS (ESI⁺) Calculated for C33H45NNaO6Si: 634.2629. Found [M+Na]⁺: 634.2609.

tert-Butyl (3-(6-hydroxy-[1,1'-biphenyl]-3-yl)propyl)(tosyloxy)carbamate (5e)

**General procedure D**: tert-Butyl(3-(6-((tert-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)propyl) (tosyloxy)carbamate (0.61 g, 1.00 mmol) and 1:1 TBAF/AcOH solution (0.1 M in THF, 1.00 mmol) in THF (20 mL) were employed. Purification by flash column chromatography (20 % EtOAc/petroleum ether) afforded 5e (0.41 g, 82 %) as a colorless solid; m.p.: 108 - 110 °C (EtOAc/hexane); Rf = 0.2 (20 % EtOAc/hexane); νmax / cm⁻¹ (film) 3467 (m, br), 2980 (m), 2930 (m), 1719 (s), 1368 (s), 1176 (s), 1151 (s); ¹H NMR (400 MHz, CDCl3) δ 7.84 (2H, d, J = 8.4 Hz, Ts ArCH), 7.51 - 7.46 (4H, m, PhCH), 7.42 - 7.36 (1H, m, PhCH), 7.32 (2H, d, J = 8.0 Hz, Ts ArCH), 7.07 - 7.03 (2H, m C5, C9-H), 6.90 (1H, d, J = 8.2 Hz, C6-H), 5.17 (1H, s, OH), 3.65 (2H, app. br s, C1-H2), 2.57 (2H, t, J = 7.8 Hz, C3-H2), 2.44 (3H, s, Ts CH3), 2.01 - 1.87 (2H, m, C2-H2), 1.22 (9H, s, Boc (CH3)3). ¹³C NMR (101 MHz, CDCl3) δ 155.6 (C=O), 150.8 (C7), 145.8 (Ts ArC), 137.3 (PhC), 133.5 (C4), 131.4 (Ts ArC), 130.1 (C9), 129.8 (2 × PhCH), 129.7 (2 × Ts ArCH), 129.4 (2 × Ts ArCH), 129.2 (2 × PhCH), 129.0
(C5), 128.1 (C8), 127.9 (PhCH), 115.9 (C6), 83.4 (Boc C(CH3)3), 52.7 (C1), 32.1 (C3), 27.7 (Boc (CH3)3), 27.7 (C2), 21.8 (Ts CH3); HRMS (ESI+) Calculated for C27H31NNaO6S: 520.1764. Found [M+Na]+: 520.1766.

7-Phenyl-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7e) and 6-Phenyl-1,2,3,4-tetrahydroquinolin-7-ol (8e)

**General procedure E:** tert-Butyl (3-(6-hydroxy-[1,1'-biphenyl]-3-yl)propyl)(tosyloxy) carbamate (5e) (74.6 mg, 0.15 mmol) and TFA (23 μL, 0.30 mmol) in anhydrous TFE (1.5 mL) were employed. After stirring at r.t. for 46 h, purification by flash column chromatography (EtOAc) afforded the title compounds 7e (26.0 mg, 51%) and 8e (11.7 mg, 35%) as yellow solids.

Data for 7e: m.p.: 136 - 138 °C (EtOAc/hexane); Rf = 0.1 (5% MeOH/CH2Cl2); ʋmax / cm\(^{-1}\) (film) 3374 (m, br), 2975 (m), 1665 (s), 1640 (s); 1H NMR (400 MHz, CD3OD) δ 7.46 - 7.37 (5H, m, PhC\(_{H}\)), 7.14 (1H, dd, J = 10.0, 3.3 Hz, C5-H), 7.09 (1H, d, J = 3.2 Hz, C9-H), 6.52 (1H, d, J = 10.0 Hz, C6-H), 3.70 - 3.63 (2H, m, C1-H2), 2.45 - 2.30 (4H, m, C2-H2, C3-H2). The signals corresponding to the NH\(_2\) were not observed. 13C NMR (101 MHz, CD3OD) δ 184.4 (C7), 143.6 (C5), 142.1 (C8), 141.0 (C6), 135.6 (PhC), 132.2 (C6), 130.0 (2 × PhCH), 129.9 (PhCH), 129.2 (2 × PhCH), 65.2 (C4), 46.5 (C1), 37.9 (C3), 24.9 (C2). The signals corresponding to the trifluoroacetate group could not be resolved due to their weak intensity. HRMS (ESI+) Calculated for C15H16NO: 226.1226. Found [M]+: 226.1229.

Data for 8e: m.p.: 91 - 94 °C (EtOAc/hexane); Rf = 0.4 (5% MeOH/CH2Cl2); ʋmax / cm\(^{-1}\) (solid) 3405 (br m), 2925 (m), 2852 (m), 1622 (s), 1488 (s), 1160 (s); 1H NMR (400 MHz, CDCl3) δ 7.46 - 7.40 (4H, m, PhC\(_{H}\)), 7.33 - 7.28 (1H, m, PhCH), 6.84 (1H, s, C5-H), 6.11 (1H, s, C8-H), 4.98 (1H, br s), 4.04 (1H, br s), 3.32 - 3.29 (2H, m, C1-H2), 2.73 (2H, t, J = 6.4 Hz, C3-H2), 1.97 - 1.91 (2H, m, C2-H2); 13C NMR (101 MHz, CDCl3) δ 151.3 (C7), 145.4 (C9), 137.7
Ethyl (E)-3-(4-hydroxy-2-methoxyphenyl)acrylate

**General procedure F:** 4-Hydroxy-2-methoxybenzaldehyde (3.04 g, 20.0 mmol) and ethyl 2-(triphenyl-phosphaneylidene) acetate (10.5 g, 30.0 mmol) in CH$_2$Cl$_2$ (20 mL) were employed. Purification by flash column chromatography (20 % EtOAc/pentane) afforded the title compound (3.54 g, 80%) as a colorless solid; m.p.: 144 - 146 °C (EtOAc/hexane); R$_f$ = 0.2 (20 % EtOAc/hexane); $\nu_{\text{max}}$/ cm$^{-1}$ (solid) 3322 (br m), 1675 (s); $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) $\delta$ 7.88 (1H, d, $J$ = 16.0 Hz, C$_3$-H), 7.50 (1H, d, $J$ = 8.4 Hz, C$_{10}$-H), 6.53 (1H, d, $J$ = 2.3 Hz, C$_7$-H), 6.49 (1H, dd, $J$ = 8.4, 2.3 Hz, C$_9$-H), 6.39 (1H, d, $J$ = 16.0 Hz, C$_2$-H) 4.18 (2H, q, $J$ = 7.1 Hz, OCH$_2$), 3.88 (3H, s, C$_6$), 1.27 (3H, t, $J$ = 7.1 Hz, CH$_2$C$_6$); $^{13}$C NMR (101 MHz, (CD$_3$)$_2$CO) $\delta$ 168.0 (C$_1$), 162.1 (C$_8$), 161.0 (C$_6$), 140.5 (C$_3$), 131.2 (C$_{10}$), 115.8 (C$_4$), 115.8 (C$_2$), 108.9 (C$_9$), 100.0 (C$_7$), 60.4 (OCH$_3$), 56.0 (C$_6$), 14.8 (CH$_2$C$_6$); HRMS (ESI$^+$) Calculated for C$_{12}$H$_{14}$NaO$_4$: 245.0784. Found [M+Na]$^+$: 245.0784.

Ethyl 3-(4-hydroxy-2-methoxyphenyl)propanoate

**General procedure G:** Ethyl (E)-3-(4-hydroxy-2-methoxyphenyl)acrylate (2.22 g, 10.0 mmol) and 10 wt.% Pd/C (5 mol%) in EtOH (30 mL) were employed. Purification by Flash column chromatography (20% EtOAc/hexane) afforded the title compound (1.80 g, 80%) as a colorless solid; R$_f$ = 0.2 (20 % EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.94 (2H, d, $J$ =
Ethyl 3-(4-((tert-butyldimethylsilyl)oxy)-2-methoxyphenyl)propanoate

![Chemical structure](image)

Ethyl 3-(4-hydroxy-2-methoxyphenyl)propanoate (1.68 g, 7.50 mmol), tert-butyldimethylsilyl chloride (1.36 g, 9.00 mmol), and imidazole (1.28 g, 18.75 mmol) in DMF (15 mL) were employed. Purification by flash column chromatography (20 % EtOAc/pentane) afforded the title compound (1.31 g, 52 %) as a colorless oil; R_f = 0.4 (20 % EtOAc/hexane); ^1H NMR (400 MHz, CDCl_3) δ 6.95 (1H, d, J = 8.7 Hz, C^{10}-H), 6.36 - 6.32 (2H, m, C^{7,9}-H), 4.11 (2H, q, J = 7.1 Hz, OC\_H\_2), 3.77 (3H, s, C^{6}-H\_3), 2.85 (2H, t, J = 7.8 Hz, C^{3}-H\_2), 2.55 (2H, t, J = 7.8 Hz, C^{2}-H\_2), 1.23 (3H, t, J = 7.1 Hz, CH\_2CH\_3), 0.98 (9H, s, TBS (CH\_3)_3), 0.20 (6H, s, TBS Si(CH\_3)_2); ^13C NMR (101 MHz, CDCl_3) δ 173.6 (C^{1}), 158.3 (C^{5}), 155.4 (C^{8}), 130.1 (C^{10}), 121.8 (C^{4}), 111.3 (C^{9}), 103.4 (C^{7}), 60.3 (OCH\_2), 55.3 (C\_6), 34.7 (C\_2), 25.9 (TBS (CH\_3)_3), 25.7 (C\_3), 18.3 (TBS Si(CH\_3)_3), 14.4 (CH\_2CH\_3), -4.3 (TBS Si(CH\_3)_2); HRMS (ESI^+): Calculated for C\_{18}H\_{30}NaO\_4Si: 361.1806. Found [M+Na]^+: 361.1821.

3-(4-((tert-Butyldimethylsilyl)oxy)-2-methoxyphenyl)propan-1-ol

![Chemical structure](image)

General procedure B: Ethyl 3-(4-((tert-butyldimethylsilyl)oxy)-2-methoxyphenyl)propanoate (1.01 g, 3.00 mmol) and 1.5 eq. LiAlH\_4 (1M in THF) in anhydrous Et\_2O (15 mL) were employed. Purification by flash column chromatography (33 %
EtOAc/hexane) afforded the title compound (0.65 mg, 73 %) as a colorless oil; Rf = 0.3 (33 % EtOAc/hexane); νmax / cm⁻¹ (film) 3351 (br m), 2952 (m), 2930 (m), 2857 (m), 1607 (m), 1503 (s); ¹H NMR (400 MHz, CDCl₃) δ 6.95 (1H, d, J = 8.4 Hz, C₁₀-H), 6.40 - 6.36 (2H, m, C₇-H, C₉-H), 3.79 (3H, s, C₆-H₃), 3.58 (2H, t, J = 6.2 Hz, C₁-H₂), 2.64 (2H, t, J = 7.3 Hz, C₃-H₂), 1.84 - 1.74 (3H, m, C₂-H₂, OH), 0.99 (9H, s, TBS (CH₃)₃), 0.20 (6H, s, TBS Si(CH₃)₂; ¹³C NMR (101 MHz, CDCl₃) δ 158.2 (C₅), 155.1 (C₈), 130.3 (C₁₀), 122.8 (C₄), 111.8 (C₉), 103.5 (C₇), 62.1 (C₁), 55.5 (C₆), 33.2 (C₂), 25.8 (TBS (CH₃)₃) 25.4 (C₃), 18.3 (TBS C(CH₃)₃) - 4.3 (TBS Si(CH₃)₂); HRMS (ESI⁺) Calculated for C₁₆H₂₈NaO₃Si: 319.1700. Found [M+Na]⁺: 319.1707.

tert-Butyl (3-(4-((tert-butyldimethylsilyl)oxy)-2-methoxyphenyl)propyl)(tosyloxy) carbamate

![Diagram]

General procedure C: 3-(4-((tert-Butylidemethylsilyl)oxy)-2-methoxyphenyl)propan-1-ol (0.53 g, 1.80 mmol), PPh₃ (0.56 g, 2.16 mmol), DIAD (0.42 mL, 2.16 mmol) and TsONHBoc (0.62 g, 2.16 mmol) in anhydrous THF (10 mL) were employed. Purification by flash column chromatography afforded the title compound (0.94 g, 92 %) as a colorless oil; Rf = 0.5 (33 % EtOAc/hexane); νmax / cm⁻¹ (film) 2955 (m), 2930 (m), 1721 (s), 1504 (s), 1158 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.84 (2H, d, J = 8.3 Hz, Ts ArC-H), 7.32 (2H, d, J = 8.3 Hz, Ts ArC-H), 6.90 (1H, d, J = 8.0 Hz, C₁₀-H), 6.36 - 6.33 (2H, m, C₇, C₉-H), 3.75 (3H, s, C₆-H₃), 3.69 - 3.48 (2H, m, C₁-H₂), 2.49 (2H, t, J = 8.0 Hz, C₃-H₂), 2.44 (3H, s, Ts CH₃), 1.94 - 1.78 (2H, m, C₂-H₂), 1.22 (9H, s, Boc (CH₃)₃), 0.99 (9H, s, TBS (CH₃)₃), 0.20 (6H, s, TBS Si(CH₃)₂; ¹³C NMR (101 MHz, CDCl₃) δ 158.2 (C₅), 155.6 (C=O), 155.2 (C₈), 145.7 (Ts ArC), 131.5 (Ts ArC), 129.8 (2 × Ts ArCH), 129.6 (2 × Ts ArCH), 122.4 (C₄), 11.4 (C₉), 103.5 (C₇), 83.2 (Boc C(CH₃)₃), 55.3 (C₆), 53.1 (C₁), 27.8 (Boc (CH₃)₃), 26.7 (C₃), 26.1 (C₂), 25.9 (TBS (CH₃)₃), 21.8 (Ts CH₃), 18.4 (TBS SiC(CH₃)₃), -4.2 (TBS Si(CH₃)₂); HRMS (ESI⁺) Calculated for C₂₈H₄₃NNaO₅Si: 588.2422. Found [M+Na]⁺: 588.2419.
**General procedure D:** tert-Butyl (3-(4-hydroxy-2-methoxyphenyl)propyl)(tosyloxy)carbamate (5f) (0.56 g, 1.00 mmol) and 1:1 TBAF/AcOH solution (0.1 M in THF, 1.00 mmol) in THF (20 mL) were employed. Purification by flash column chromatography (33% EtOAc/hexane) afforded 5f (0.38 g, 84%) as a colorless viscous oil; R_f = 0.25 (33% EtOAc/hexane); \( \nu_{\text{max}} / \text{cm}^{-1} \) (film) 3422 (br m), 2936 (m), 1720 (m), 1368 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.84 (2H, d, \( J = 8.3 \) Hz, Ts ArCH), 7.32 (2H, d, \( J = 8.3 \) Hz, Ts ArCH), 6.90 (1H, d, \( J = 8.0 \) Hz, C\(_{10}\)-H), 6.38 (1H, d, \( J = 2.4 \) Hz, C\(_7\)-H), 6.32 (1H, dd, \( J = 8.0, 2.4 \) Hz, C\(_9\)-H\(_2\)), 4.67 (1H, br s, OH), 3.76 (3H, s, C\(_6\)-H\(_3\)), 3.70 - 3.48 (2H, m, C\(_1\)-H\(_2\)), 2.48 (2H, t, \( J = 7.7 \) Hz, C\(_3\)-H\(_2\)), 2.43 (3H, s, Ts CH\(_3\)), 1.94 - 1.78 (2H, m, C\(_2\)-H\(_2\)), 1.22 (9H, s, Boc (CH\(_3\))\(_3\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 158.5 (C\(_5\)), 155.7 (C=O), 155.3 (C\(_8\)), 145.7 (Ts ArC), 153.1 (Ts ArC), 129.8 (2 x Ts ArCH), 129.6 (2 x Ts ArCH), 121.7 (C\(_4\)), 106.6 (C\(_9\)), 98.9 (C\(_7\)), 83.3 (Boc C(CH\(_3\))\(_3\)), 55.4 (C\(_6\)), 53.1 (C\(_1\)), 27.8 (Boc (CH\(_3\))\(_3\)), 26.7 (C\(_3\)), 26.1 (C\(_2\)), 21.8 (Ts CH\(_3\)); HRMS (ESI\(^+\)) Calculated for C\(_{32}\)H\(_{39}\)NNaO\(_7\): 474.1557. Found [M+Na]\(^+\): 474.1566.

**6-Methoxy-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7f)**

**General procedure E:** tert-Butyl (3-(4-hydroxy-2-methoxyphenyl)propyl)(tosyloxy)carbamate (5f) (67.7 mg, 0.15 mmol) and TFA (23 \( \mu \)L) in TFE (1.5 mL) were stirred at r.t. for 39 h until completion by TLC analysis. Purification by flash column chromatography (EtOAc)
afforded 7f (32.6 mg, 74 %) as a viscous yellow oil; $R_f = 0.1$ (5 % MeOH/CH$_2$Cl$_2$); $\nu_{max}$ / cm$^{-1}$ (film) 2987 (m), 2901 (m), 1665 (s), 1636 (m), 1602 (s); $^1$H NMR (400 MHz, CD$_3$OD) $\delta$ 6.93 (1H, d, $J = 10.0$ Hz, C10-H), 6.29 (1H, dd, $J = 10.0$, 1.6 Hz, C9-H) 5.79 (1H, d, $J = 1.6$ Hz, C7-H), 3.89 (3H, s, C6-H$_3$), 3.66 - 3.54 (2H, m, C1-H$_2$), 2.53 - 2.46 (1H, m, C3-H), 2.40 - 2.22 (3H, m, C3-H', C2-H$_2$). The signals corresponding to the NH$_2$ were not observed. $^{13}$C NMR (400 MHz, CD$_3$OD) $\delta$ 187.4 (C8), 171.2 (C5), 141.4 (C10), 130.0 (C9), 104.2 (C7), 65.6 (C4), 57.6 (C6), 48.7 (C1), 38.0 (C3), 26.0 (C2). The signals corresponding to the trifluoroacetate group could not be resolved due to their weak intensity. HRMS (ESI$^+$) Calculated for C$_{10}$H$_{14}$NO$_2$: 180.1019. Found [M+H]$^+$: 180.1021.

**Ethyl (E)-3-(4-hydroxyphenyl)acrylate**

**General procedure F:** 4-Hydroxybenzaldehyde (4.88 g, 40.0 mmol) and ethyl (triphenylphosphoranylidene)acetate (20.9 g, 60.0 mmol) in CH$_2$Cl$_2$ (40 mL) were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded the title compound (6.56 g, 85 %) as a colorless solid; $R_f = 0.5$ (33 % EtOAc/hexane); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.64 (1H, d, $J = 16.0$ Hz), 7.42 (2H, d, $J = 8.6$ Hz), 6.86 (2H, d, $J = 8.3$ Hz), 6.30 (1H, d, $J = 16.0$ Hz), 6.14 (1H, br s), 4.27 (2H, q, $J = 7.1$ Hz), 1.34 (3H, t, $J = 7.1$ Hz); $^{13}$C NMR (101 MHz) $\delta$ 168.1, 158.1, 144.9, 132.4, 130.1, 127.2, 116.1, 115.5, 115.1, 60.8, 14.5. Spectroscopic properties were consistent with the data available in the literature.$^{10}$

**Ethyl (E)-3-(4-((tert-butyldimethylsilyl)oxy)phenyl)acrylate**

S31
To a solution of Ethyl \((E)-3-(4\text{-hydroxyphenyl})\text{acrylate}\) \((3.84 \text{ g, 20.0 mmol})\) in DMF \((20 \text{ mL})\) were added \textit{tert}-butyldimethylsilyl chloride \((3.60 \text{ g, 24.0 mmol})\) and imidazole \((3.40 \text{ g, 50.0 mmol})\) and the reaction was stirred overnight at r.t. until completion by TLC analysis. Purification by flash column chromatography \((20 \% \text{ EtOAc/ hexane})\) afforded the title compound \((5.13 \text{ g, 84 \%})\) as a colorless oil; \(R_f = 0.4 (10 \% \text{ EtOAc/hexane})\); \(^1\text{H} \text{ NMR} \text{ (400 MHz, CDCl}_3\text{)} \delta 7.63 \text{ (1H, d, } J = 16.0 \text{ Hz)}, 7.41 \text{ (2H, d, } J = 8.6 \text{ Hz)}, 6.83 \text{ (2H, d, } J = 8.5 \text{ Hz)}, 6.30 \text{ (1H, d, } J = 16.0 \text{ Hz)}, 4.25 \text{ (2H, q, } J = 7.3 \text{ Hz)}, 1.33 \text{ (3H, t, } J = 7.3 \text{ Hz)}, 0.98 \text{ (9H, s, TBS (CH}_3)_3\text{)}, 0.22 \text{ (6H, s, TBS Si(CH}_3)_2\text{)}; \(^{13}\text{C} \text{ NMR} \text{ (101 MHz, CDCl}_3\text{)} \delta 167.5, 157.9, 144.4, 129.8, 127.9, 120.6, 116.1, 60.4, 25.8, 18.4, 14.5, -4.2. \text{ Spectroscopic properties were consistent with the data available in the literature.}^{11}

**Ethyl 3-(4-((tert-butyldimethylsilyl)oxy)phenyl)pentanoate**

\[
\text{CuI (2.86 g, 15.0 mmol) in anhydrous Et}_2\text{O (60 mL) was stirred under nitrogen at room temperature until a suspension was observed. The mixture was cooled to -20 \text{\degree C}} \text{ and EtMgBr (3.0 M solution in Et}_2\text{O, 37.5 mmol) was added. After stirring for 5 min, a solution of ethyl (E)-3-(4-((tert-butyldimethylsilyl)oxy)phenyl)acrylate (4.6 g, 15.0 mmol) in anhydrous Et}_2\text{O (15 mL) was added dropwise over 1 h. After stirring at -20 \text{\degree C for 4 h, MeOH (15 mL)} \text{ and sat. aq. NH}_4\text{Cl (60 mL)} \text{ were sequentially added and the mixture was warmed to r.t. After extracting with Et}_2\text{O (3 \times 20 mL)}, \text{the combined organic extracts were dried over anhydrous Na}_2\text{SO}_4, \text{filtered and concentrated in vacuo. Purification by flash column chromatography (20 \% EtOAc/hexane) afforded the title compound (4.36 g, 86 \%) as a pale yellow oil; } R_f = 0.5 (10 \% \text{ EtOAc/hexane}); \nu_{\text{max}} / \text{cm}^{-1} \text{ (film) 2958 (m), 2930 (m), 2858 (m), 1735 (s), 1509 (s), 1252 (s), 1165 (m); } ^1\text{H} \text{ NMR} \text{ (400 MHz, CDCl}_3\text{)} \delta 7.02 \text{ (2H, d, } J = 8.4 \text{ Hz, C}_7\text{-H}), 6.75 \text{ (2H, d, } J = 8.6 \text{ Hz, C}_8\text{-H}), 4.02 \text{ (2H, q, } J = 7.1 \text{ Hz, OCH}_2\text{CH}_3\text{), 2.97 - 2.89 (1H, dd, } J = 8.6 \text{ Hz, C}_8\text{-H}), 4.02 \text{ (2H, q, } J = 7.1 \text{ Hz, OCH}_2\text{CH}_3\text{), 2.97 - 2.89 (1H, m, C}_7\text{-H), 2.59 (1H, dd, } J = 14.9, 7.0 \text{ Hz, C}_2\text{-H}), 2.50 (1H, dd, } J = 14.8, 8.3 \text{ Hz, C}_2\text{-H'), 1.73 - 1.61 (1H, m, C}_4\text{-H), 1.59 - 1.49 (1H, m, C}_4\text{-H'), 1.12 (3H, t, } J = 7.1 \text{ Hz, OCH}_2\text{CH}_3\text{), 0.97 (9H, s, TBS (CH}_3)_3\text{)}, 0.77 (3H, } t J = 7.3 \text{ Hz, C}_5\text{-H}_3\text{), 0.18 (6H, s, TBS Si(CH}_3)_2\text{); } ^{13}\text{C} \text{ NMR} \text{ (101 MHz, CDCl}_3\text{)} \delta 172.7 (\text{C}_1),
3-(4-((tert-Butyldimethylsilyl)oxy)phenyl)pentan-1-ol

**General procedure B:** Ethyl 3-(4-((tert-butyldimethylsilyl)oxy)phenyl)pentanoate (4.10 g, 12.2 mmol), 1.0 eq. LiAlH₄ (1M in THF) and anhydrous Et₂O were employed. The title compound (3.03 g, 84%) was obtained as a colorless oil which was used without further purification; Rₓ = 0.3 (20% EtOAc/hexane); νₓ max / cm⁻¹ (film) 3354 (br m), 2956 (m), 2929 (m), 2858 (m), 1607 (m), 1508 (s), 1253 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.00 (2H, d, J = 8.4 Hz, C₇-H), 6.76 (2H, d, J = 8.5 Hz, C₈-H), 3.55 - 3.43 (2H, m, C₁⁻H₂), 2.55 - 2.47 (1H, m, C₃-H), 1.94 - 1.87 (1H, m, C₂⁻H), 1.79 - 1.72 (1H, m, C₂⁻H'), 1.70 - 1.61 (1H, m, C₄⁻H), 1.57 - 1.49 (1H, m, C₄⁻H'), 0.98 (9H, s, TBS (CH₃)₃), 0.77 (3H, t, J = 7.4 Hz, C₅⁻H₃), 0.19 (6H, s, TBS Si(CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 154.0 (C₉), 137.6 (C₆), 128.6 (C₇-H), 120.0 (C₈-H), 61.5 (C₁), 43.7 (C₃), 39.6 (C₂), 30.1 (C₄), 25.8 (TBS C(CH₃)₃), 18.3 (TBS C(CH₃)₃), 12.2 (C₅), -4.3 (TBS Si(CH₃)₂); HRMS (ESI⁺) Calculated for C₁₉H₃₂NaO₃Si: 359.2013. Found [M+Na]⁺: 359.2016.

**tert-Butyl (3-(4-((tert-butyldimethylsilyl)oxy)phenyl)pentyl)(tosyloxy)carbamate**

**General procedure C:** 3-(4-((tert-Butyldimethylsilyl)oxy)phenyl)pentan-1-ol (2.94 g, 10.0 mmol), PPh₃ (3.15 g, 12.0 mmol mmol), DIAD (2.36 mL, 12.0 mmol) and TsONHBoc (3.44
g, 12.0 mmol) in anhydrous THF (40 mL) were employed. Purification by flash column chromatography (5 % EtOAc/hexane) afforded the title compound (5.35 g, 95 %) as a colorless oil; Rf = 0.6 (20 % EtOAc/hexane); \( \nu_{\text{max}} / \text{cm}^{-1} \) (film) 2962 (m), 2931 (m), 1721 (s), 1509 (s), 1382 (s), 1369 (s), 1253 (s), 1191 (s), 1155 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.78 (2H, d, \( J = 8.2 \) Hz, Ts ArCH\(_2\)), 7.28 (2H, d, \( J = 8.2 \) Hz, Ts ArCH\(_2\)), 6.93 (2H, d, \( J = 8.4 \) Hz, C7-H), 6.74 (2H, d, \( J = 8.4 \) Hz, C8-H), 3.48 - 3.19 (2H, m, C1-H\(_2\)), 2.42 (3H, s, Ts CH\(_3\)), 2.33 - 2.26 (1H, m, C3-H), 1.94 (1H, app. br s, C2-H), 1.66 - 1.57 (1H, m, C4-H), 1.53 - 1.43 (1H, m, C4'-H'), 1.22 (9H, s, Boc (CH\(_3\))\(_3\)), 0.98 (9H, s, TBS (CH\(_3\))\(_3\)), 0.73 (3H, t, \( J = 7.3 \) Hz, C5-H\(_3\)), 0.18 (6H, s, TBS Si(CH\(_3\))\(_2\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) 155.5 (Boc C=O), 154.0 (C9), 145.7 (Ts ArC), 136.9 (C6), 131.4 (Ts ArC), 129.7 (2 × Ts ArCH), 129.6 (2 × Ts ArCH), 128.4 (C7), 120.0 (C8) 83.2 (Boc C(CH\(_3\))\(_3\)), 52.0 (C1), 44.6 (C3), 32.0 (C2), 30.1 (C4), 27.8 (Boc (CH\(_3\))\(_3\)), 25.8 (TBS C(CH\(_3\))\(_3\)), 21.8 (Ts CH\(_3\)), 18.3 (TBS C(CH\(_3\))\(_3\)), 12.1 (C5), -4.3 (TBS (CH\(_3\))\(_2\)); HRMS (ESI\(^+\)) Calculated for C\(_{29}\)H\(_{45}\)NO\(_6\)Si: 586.2629. Found [M+Na]\(^+\): 586.2628.

tert-Butyl (3-(4-hydroxyphenyl)pentyl)(tosyloxy)carbamate (5g)

\[
\begin{align*}
\text{Me} & \quad \text{N} \quad \text{Boc} \\
\text{OTBS} & \quad \text{OH} \\
\text{Me} & \quad \text{N} \quad \text{Boc}
\end{align*}
\]

**General procedure D:** tert-Butyl (3-(4-((tert-butyldimethylsilyl)oxy)phenyl)pentyl)(tosyloxy)carbamate (2.82 g, 5.0 mmol) and 1:1 TBAF/HOAc (0.1 M in THF, 5.0 mmol) in THF (50 mL) were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded 5g (1.80 g, 80 %) as a colorless solid; m.p.: 93 - 95 °C (EtOAc/hexane); Rf = 0.4 (33 % EtOAc/hexane); \( \nu_{\text{max}} / \text{cm}^{-1} \) (film) 3436 (br m), 2965 (m), 2930 (m), 1720 (s), 1514 (s), 1368 (s), 1191 (s), 1177 (s), 1153 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.77 (2H, d, \( J = 8.0 \) Hz, Ts ArCH), 7.28 (2H, d, \( J = 8.1 \) Hz, Ts ArCH), 6.95 (2H, d, \( J = 8.5 \) Hz C7-H), 6.74 (2H, d, \( J = 8.5 \) Hz, C8-H), 4.93 (1H, br s, OH), 3.51 - 3.16 (2H, app. br s, C1-H\(_2\)), 2.42 (3H, s, Ts CH\(_3\)), 2.34 - 2.27 (1H, m, C3-H), 1.95 (1H, app. br s, C2-H), 1.77 (1H, app. br
s, C2-H'), 1.66 - 1.54 (1H, m, C4-H), 1.52 - 1.43 (1H, m, C4-H'), 1.22 (9H, s, Boc (CH3)3), 0.73 (3H, t, J = 7.3 Hz, C5-H3); 13C NMR (101 MHz, CDCl3) δ 155.6 (C=O), 154.1 (C9), 145.8 (Ts ArC), 136.3 (C6), 131.3 (Ts ArC), 129.7 (2 × Ts ArCH), 129.6 (2 × Ts ArCH), 128.7 (C7), 115.4 (C8), 83.4 (Boc C(CH3)3), 51.9 (C1), 44.5 (C3), 32.0 (C2), 27.8 (Boc (CH3)3), 21.8 (Ts CH3), 12.05 (C5); HRMS (ESI+) Calculated for C23H31NNaO6S: 472.1764. Found [M+H]+: 472.1763.

4-Ethyl-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7g)

General procedure E: tert-Butyl (3-(4-hydroxyphenyl)pentyl)(tosyloxy)carbamate (5g) (89.9 mg, 0.20 mmol) and TFA (31 μL, 0.40 mmol) in anhydrous TFE (2 mL) were employed. Purification by flash column chromatography (EtOAc) afforded 7g (40.0 mg, 69%) as a red/brown oil; Rf = 0.1 (5% MeOH/CH2Cl2); νmax / cm−1 2966 (m), 1673 (s), 1636 (m), 1404 (m), 1201 (s), 1134 (s); 1H NMR (400 MHz, CDCl3) δ 6.93 (1H, dd, J = 10.3, 3.2 Hz, C7-H), 6.78 (1H, dd, J = 10.6, 3.2 Hz, C7-H'), 6.43 - 6.36 (2H, m, C8-H2), 6.32 - 3.45 (2H, m, C1-H2), 2.53 - 2.44 (1H, m, C3-H), 2.40 - 2.31 (1H, m, C2-H), 1.93 - 1.81 (1H, m, C2-H'), 1.31 - 1.23 (1H, m, C4-H), 1.14 - 1.05 (1H, m, C4-H'), 0.91 (3H, J = 7.4 Hz, C5-H3); The signals corresponding to the NH2 were not observed. 13C (101 MHz, CDCl3) δ 183.5 (C=O), 143.7 (C7), 139.6 (C7'), 132.4 (C8), 132.0 (C8'), 65.5 (C6), 50.8 (C3), 43.4 (C1), 29.3 (C2), 21.5 (C4), 12.5 (C5); The signals corresponding to the trifluoroacetate group could not be resolved due to their weak intensity. HRMS (ESI+) Calculated for C11H16NO+: 178.1226. Found [M+H]+: 178.1225.
4-Ethyl-1,2,3,4-tetrahydroquinolin-7-ol (8g)

To a solution of tert-Butyl (3-(4-hydroxyphenyl)pentyl)(tosyloxy)carbamate (5g) (67.4 mg, 0.15 mmol) in anhydrous TFE (2.3 mL, 0.067 M) at r.t. was added TFA (1.7 μL, 0.022 mmol). The reaction was heated to 60 °C and stirred overnight monitoring by TLC analysis. Purification by flash column chromatography (gradient, eluent 33% EtOAc/hexane – 100% EtOAc (a small amount < 1% Et3N was added to the eluent)) afforded 8g (20.4 mg, 77%) as a yellow oil; Rf = 0.5 (EtOAc); νmax/cm⁻¹ (film) 3145 (m, br), 2971 (m), 1618 (m), 1467 (m), 1238 (m); ¹H NMR (400 MHz, CDCl3) δ 6.55 (1H, s, C₁₀-H), 6.49 (1H, d, J = 8.0 Hz, C₈-H), 6.41 (1H, d, J = 8.5 Hz, C₇-H), 4.20 (2H, br s), 3.28 - 3.16 (2H, m, C₅-H), 2.62 - 2.56 (1H, m, C₃-H'), 1.95 - 1.87 (1H, m, C₄-H), 1.80 - 1.67 (2H, m, C₄-H', C₂-H), 1.56 - 1.45 (1H, m, C₂-H'), 0.96 (3H, t, J = 7.4 Hz, C₁-H₃); ¹³C NMR (101 MHz, CDCl₃) δ 147.7 (C₉), 138.1 (C₆), 127.9 (C₁₁), 116.0 (C₇), 115.9 (C₁₀), 114.2 (C₈), 39.3 (C₅), 37.2 (C₃), 29.4 (C₂), 26.2 (C₄), 11.7 (C₁). HRMS (ESI⁺) Calculated for C₁₁H₁₅NO: 178.1226. Found [M+H]⁺: 178.1227.

The regiochemistry of the compound was confirmed by nOe analysis as shown on the compound structure. nOes were observed between C₁₀-H and C₃-H and C₁₀-H and C₂-H₂.

3-(4-((tert-Butyldimethylsilyl)oxy)phenyl)-N-methoxy-N-methylpropanamide¹²

General procedure H: 3-(4-((tert-Butyldimethylsilyl)oxy)phenyl)propanoic acid (2.40 g, 8.57 mmol), N,O-dimethylhydroxylamine hydrochloride (1.17 g, 12.0 mmol), Et₃N (1.67 mL,
12.0 mmol), 4-dimethylaminopyridine (1.46 g, 12.0 mmol), and \( N,N' \)-dicyclohexylcarbodiimide (2.48 g, 12.0 mmol) were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded the title compound (1.97 g, 71 %) as a colorless oil; \( R_f = 0.2 \) (33 % EtOAc/hexane); \( \nu_{\text{max}} / \text{cm}^{-1} \) 2955 (m), 2930 (m), 2857 (m), 2857 (m), 1665 (s), 1509 (s), 1250 (s), 1169 (m); \( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.06 (2H, d, \( J = 8.0 \) Hz), 6.75 (2H, d, \( J = 8.0 \) Hz), 3.57 (3H, s), 3.16 (3H, s), 2.88 (2H, t, \( J = 7.6 \) Hz), 2.71 - 2.67 (2H, m), 0.97 (9H, s), 0.17 (6H, s); \( ^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 173.7, 153.8, 133.9, 129.2, 119.9, 61.1, 33.9, 32.1, 29.9, 25.6, 18.1, -4.4. Spectroscopic properties were consistent with the data available in the literature.\(^{12}\)

4-(4-((\text{tert-Butyldimethylsilyl})oxy)phenyl)butan-2-one\(^{13}\)

\[
\begin{array}{c}
\text{OTBS} \quad \text{NMe} \\
\text{OMe} \quad \text{Me} \\
\end{array}
\]

To a solution of 3-(4-((\text{tert-Butyldimethylsilyl})oxy)phenyl)-\( N \)-methoxy-\( N \)-methylpropanamide (0.69 g, 2.15 mmol) in anhydrous THF (5 mL) at 0 °C was added methylmagnesium bromide (3 M in Et\(_2\)O, 1.43 mL, 4.30 mmol) dropwise over 5 min. The reaction mixture was stirred at r.t. for 1.5 h and then a solution of sat. aq. NH\(_4\)Cl (5 mL) was added. The aqueous phase was extracted with EtOAc (3 \( \times \) 5mL) and the combined organic layers were washed with brine (10 mL), dried over Na\(_2\)SO\(_4\) and concentrated \textit{in vacuo} to afford the title compound (0.60 g, 99 %) as a colorless oil, which was used without further purification; \( R_f = 0.6 \) (33 % EtOAc/hexane); \( \nu_{\text{max}} / \text{cm}^{-1} \) 2955 (m), 2929 (m), 2888 (m), 2857 (m), 1716 (s), 1610 (m), 1509 (s), 1361 (m), 1251 (s), 1159 (m), 1168 (m); \( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.02 (2H, d, \( J = 8.0 \) Hz), 6.75 (2H, d, \( J = 8.0 \) Hz), 2.85 - 2.68 (4H, m), 2.12 (3H, s), 0.98 (9H, s), 0.18 (6H, s); \( ^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 208.2, 153.9, 133.9, 129.2, 120.1, 45.5, 30.2, 29.1, 25.8, 18.2, -4.3. Spectroscopic properties were consistent with the data available in the literature.\(^{13}\)
4-(4-\((\text{tert-Butyldimethylsilyl})\text{oxy})\text{phenyl})\text{butan-2-ol}\quad 14

To a solution of 4-(4-\((\text{tert-butyldimethylsilyl})\text{oxy})\text{phenyl})\text{butan-2-one} (0.56 g, 2.14 mmol) in MeOH (10 mL) was slowly added NaBH₄ (0.16 g, 4.28 mmol) at 0 °C. After stirring for 45 min at this temperature the reaction was quenched by addition of water (10 mL) and extracted with Et₂O (3 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried over MgSO₄, filtered and concentrated in vacuo to afford the title compound (0.55 g, 92%) as a colorless oil which was used without further purification; Rᵣ = 0.5 (33 % EtOAc/hexane); νₘₐₓ / cm⁻¹ (film) 3339 (m, br), 2957 (m), 2929 (m), 2857 (m), 1609 (m), 1508 (s), 1250 (s), 1168 (m); ¹H NMR (400 MHz, CDCl₃) δ 7.05 (2H, d, J = 8.4 Hz), 6.76 (2H, d, J = 8.4 Hz), 3.86 - 3.77 (1H, m), 2.72 - 2.57 (2H, m), 1.80 - 1.69 (2H, m), 1.65 - 1.54 (1H, br s), 1.22 (3H, d, J = 6.2 Hz), 0.99 (9H, s), 0.19 (6H, s); ¹³C NMR (101 MHz, CDCl₃) δ 153.6, 134.7, 129.2, 119.9, 67.5, 41.0, 31.3, 25.7, 23.6, 18.2, -4.4. Spectroscopic properties were consistent with the data available in the literature. ¹⁴

tert-Butyl (4-(4-\((\text{tert-butylidimethylsilyl})\text{oxy})\text{phenyl})\text{butan-2-yl})(\text{tosyloxy})\text{carbamate}

**General procedure C:** 4-(4-\((\text{tert-Butyldimethylsilyl})\text{oxy})\text{phenyl})\text{butan-2-ol} (0.22 g, 0.77 mmol), PPh₃ (0.24 g, 0.92 mmol), DIAD (0.18 mL, 0.92 mmol) and TsONHBoc (0.26 g, 0.92 mmol) in anhydrous THF (3 mL) were employed. Purification by flash column chromatography (10 % EtOAc/hexane) afforded the title compound (0.34 g, 75 %) as a colorless oil; Rᵣ = 0.6 (20 % EtOAc/hexane); νₘₐₓ / cm⁻¹ (film) 2954 (m), 2930 (m), 2857 (m), 1721 (m), 1509 (s), 1368 (m), 1251 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.32 (2H, d, J = 8.4 Hz, Ts ArCH), 7.01 (2H, d, J = 8.4 Hz, C₆-H), 6.73 (2H, d, J =
8.4 Hz, C7-H), 3.97 (1H, app. sextet, J = 6.8 Hz, C2-H), 2.61 - 2.57 (2H, m, C4-H2), 2.43 (3H, s, Ts CH3), 2.06 - 1.97 (1H, m, C3-H2), 1.74 - 1.66 (1H, m, C3-H'), 1.27 (9H, s, Boc (CH3)3), 1.21 (3H, d, J = 6.8 Hz, C1-H1), 0.97 (9H, s, TBS (CH3)3), 0.17 (6H, s, TBS Si(CH3)2); 13C NMR (101 MHz, CDCl3) δ 156.4 (C=O), 153.8 (C8), 145.6 (Ts ArC), 134.4 (C5), 131.9 (Ts ArC), 129.7 (2 × Ts ArCH), 129.6 (2 × Ts ArCH), 129.3 (C6), 119.9 (C7), 83.4 (Boc C(CH3)3), 60.8 (C2), 32.2 (C3), 29.8 (C4), 27.8 (Boc (CH3)3), 25.8 (TBS (CH3)3), 21.8 (Ts CH3), 18.3 (TBS Si(CH3)3), 17.4 (C1), -4.4 (TBS Si(CH3)2); HRMS (ESI+) Calculated for C28H43NNaO6Si: 572.2473. Found [M+Na]+: 572.2465.

**tert-Butyl (4-(4-hydroxyphenyl)butan-2-yl)(tosyloxy)carbamate (5h)**

![Structure of 5h]

**General procedure D:** tert-Butyl (4-(4-((tert-butyl dimethylsilyl)oxy)phenyl)butan-2-yl)(tosyloxy) carbamate (0.32 g, 0.58 mmol) and 1:1 TBAF/HOAc solution (0.1 M in THF, 0.58 mmol) in THF (20 mL) were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded 5h (0.19 g, 75 %) as a colorless oil; Rf = 0.2 (20% EtOAc/hexane); v\textsubscript{max} / cm\textsuperscript{-1} (film) 3477 (br m), 2979 (m), 1721 (s), 1515 (s), 1369 (s), 1191 (s), 1177 (s), 1156 (s); 1\textsuperscript{H} NMR (400 MHz, CDCl3) δ 7.85 (2H, d, J = 8.5 Hz, Ts ArC), 7.31 (2H, d, J = 8.5 Hz, Ts ArC), 7.01 (2H, d, J = 7.8 Hz, C6-H), 6.74 (2H, d, J = 8.3 Hz, C7-H), 5.14 (1H, br s, OH), 3.97 (1H, app. sextet, J = 7.2 Hz, C2-H), 2.58 (2H, t, J = 7.5 Hz, C4-H2), 2.42 (3H, s, Ts CH3), 2.05 - 1.95 (1H, m, C3-H), 1.73-1.60 (1H, m, C3-H'), 1.27 (9H, s, Boc (CH3)3), 1.20 (3H, d, J = 6.8 Hz, C1-H3); 13C NMR (101 MHz, CDCl3) δ 156.5 (C=O) 153.9 (C8), 145.7 (Ts ArC), 133.7 (C5), 131.8 (Ts ArC), 129.7 (2 × Ts ArCH), 129.6 (2 × Ts ArCH), 129.5 (C6), 115.3 (C7), 83.6 (Boc C(CH3)3), 60.8 (C2), 36.0 (C3) 32.1 (C4), 27.8 (Boc C(CH3)3), 21.8 (Ts CH3), 17.4 (C1); HRMS (ESI+) Calculated for C22H29NNaO6S: 458.1608. Found [M+Na]+: 458.1597.
2-Methyl-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7h)

General procedure E: tert-Butyl (4-(4-hydroxyphenyl)butan-2-yl)(tosyloxy)carbamate (5h) (93.0 mg, 0.21 mmol) and TFA (32 μL, 0.42 mmol) in TFE (2.1 mL) were stirred at r.t. for 24 h. Purification by flash column chromatography (EtOAc) afforded 7h (34.0 mg, 58%) as a yellow/brown oil; R_f = 0.1 (5% MeOH/CH_2Cl_2); ν_max / cm^{-1} (film, CDCl_3) 2922 (m), 1667 (s), 1635 (m), 1393 (m), 1173 (s), 1133 (s); ^1H NMR (400 MHz, CDCl_3) δ 9.80 (2H, br s, NH), 7.04 (1H, dd, J = 10.2, 3.2 Hz, C_5-H), 6.95 (1H, dd, J = 10.3, 3.2 Hz, C_5-H'), 6.33 - 6.32 (1H, m, C_6-H), 6.31 - 6.29 (1H, m, C_6-H'), 4.05 - 3.96 (1H, m, C_1-H), 2.47 - 2.39 (1H, m, C_2-H), 2.36 - 2.29 (1H, m, C_3-H), 2.24 - 2.17 (1H, m, C_3-H'), 2.08 - 1.98 (1H, m, C_2-H'), 1.46 (3H, d, J = 6.6 Hz, CH_3); ^13C NMR (101 MHz, CDCl_3) δ 183.6 (C_7), 143.6 (C_5), 143.0 (C_5), 130.5 (C_6), 130.4 (C_6), 63.2 (C_4), 57.2 (C_1), 37.1 (C_3), 32.0 (C_2), 17.5 (CH_3); HRMS (ESI^+) Calculated for C_{10}H_{14}NO: 164.1070. Found [M+H]^+: 164.1068.

3-(4-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)propan-1-ol

General procedure B: Ethyl (E)-3-(4-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)acrylate (1.64 g, 4.59 mmol, 1.0 eq.) and 2.0 eq. LiAlH_4 (1.0 M in THF) in anhydrous THF (10 mL) were employed. Purification by flash chromatography (gradient, elution 20 - 33 % EtOAc/hexane) afforded the title compound (0.77 g, 53%) as a colorless oil; R_f = 0.6 (33% EtOAc/hexane); ν_max / cm^{-1} (film) 2988 (s), 2901 (s), 1394 (m), 1275 (m), 1260 (m), 1075 (s), 1066 (s), 1057 (s), 750 (s); ^1H NMR (400 MHz, CDCl_3) δ 8.27 – 8.19 (1H, m), 7.99 (1H, dd, J
= 8.1, 1.5 Hz), 7.53 – 7.45 (2H, m), 7.18 (1H, d, J = 7.7 Hz), 6.79 (1H, d, J = 7.7 Hz), 3.74 (2H, t, J = 6.4 Hz), 3.10 (2H, dd, J = 8.6, 6.7 Hz), 2.08 – 1.90 (2H, m), 1.10 (9H, s), 0.29 (6H, s); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 150.4, 133.1, 130.6, 128.4, 126.2, 126.0, 124.9, 123.9, 123.5, 112.2, 62.7, 33.8, 28.9, 26.1, 26.0, 18.6, -4.1; HRMS (ESI\(^{+}\)) Calculated for C\(_{19}\)H\(_{28}\)NaO\(_2\)Si: 339.1751. Found [M+Na\(^{+}\)]: 339.1763.

tert-Butyl (3-(4-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)propyl)(tosyloxy)carbamate

To a solution of alcohol (0.75 g, 2.36 mmol), TsONHBoc (0.82 g, 2.84 mmol, 1.2 eq.) and PPh\(_3\) (0.93 g, 2.84 mmol, 1.2 eq.) in anhydrous THF (16 mL) at 0 °C was added a solution of DIAD (0.70 mL, 2.84 mmol, 1.2 eq.) in anhydrous THF (5 mL) dropwise under Argon atmosphere. The reaction mixture was stirred at r.t. overnight before being concentrated \textit{in vacuo} and loaded directly onto silica gel for purification by flash chromatography (gradient, elution 20 % PhMe/hexane - 100% PhMe) to afford the title compound (1.12 g, 81 %) as a colorless solid; m.p.: 87 - 89 °C (EtOAc/hexane); R\(_f\) = 0.7 (33% EtOAc/hexane); \(\nu_{\text{max}}\) / cm\(^{-1}\) (solid) 2972 (s), 1722 (m), 1393 (s), 1259 (m), 1156 (m), 1075 (s), 750 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.25 – 8.15 (1H, m), 7.95 – 7.87 (1H, m), 7.84 (2H, d, J = 8.4 Hz), 7.48 (2H, dddd, J = 16.6, 8.1, 6.8, 1.5 Hz), 7.30 (2H, d, J = 7.8 Hz), 7.13 (1H, d, J = 7.7 Hz), 6.77 (1H, d, J = 7.7 Hz), 3.70 (2H, s), 2.97 (2H, t, J = 7.8 Hz), 2.43 (3H, s), 2.16 – 1.89 (2H, m), 1.19 (9H, s), 1.10 (9H, s), 0.28 (6H, s); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 155.6, 150.6, 145.8, 133.0, 131.4, 129.8, 129.8, 129.6, 128.4, 126.3, 125.9, 124.9, 123.7, 123.5, 112.1, 83.4, 53.1, 29.7, 27.7, 27.1, 26.1, 21.8, 18.6, -4.1; HRMS (ESI\(^{+}\)) Calculated for C\(_{31}\)H\(_{43}\)NNaO\(_3\)Si: 608.2473. Found [M+Na\(^{+}\)]: 608.2473.
**tert-Butyl (3-(4-hydroxynaphthalen-1-yl)propyl)(tosyloxy)carbamate (5i)**

![Chemical Structure](image)

**General procedure D:** tert-Butyl (3-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)propyl) (tosyloxy)carbamate (0.97 g, 1.66 mmol) and 1:1 TBAF/AcOH solution (1.0 M in THF, 1.66 mmol) in THF (17 mL) were employed. Purification by flash column chromatography (gradient, eluent 20 - 30% EtOAc/hexane) afforded 5i (0.53 g, 67%) as a viscous colorless oil; Rf = 0.4 (33% EtOAc/hexane); \( \nu_{\max} / \text{cm}^{-1} \) (film) 3417 (br, m), 2980 (m), 2871 (m), 1720 (s), 1589 (m), 1370 (s), 1178 (s), 1151 (s), 763 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 8.23 (1H, d, \( J = 7.9 \) Hz), 7.91 (1H, d, \( J = 8.2 \) Hz), 7.83 (2H, d, \( J = 8.1 \) Hz), 7.54 – 7.43 (2H, m), 7.29 (2H, d, \( J = 8.1 \) Hz), 7.08 (1H, d, \( J = 7.6 \) Hz), 6.73 (1H, d, \( J = 7.6 \) Hz), 3.70 (2H, s), 2.95 (2H, t, \( J = 7.9 \) Hz), 2.42 (3H, s), 2.03 (2H, q, \( J = 12.1, 8.4 \) Hz), 1.19 (9H, s); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \): 155.7, 150.5, 145.8, 132.8, 131.3, 129.8, 129.6, 126.5, 125.8, 125.0, 124.9, 123.7, 122.6, 108.2, 83.5, 53.0, 29.6, 27.7, 27.1, 21.8; HRMS (ESI\(^+\)) Calculated for C\(_{25}\)H\(_{30}\)NNaO\(_6\)S: 494.1608. Found [M+Na]\(^+\): 494.1603.

**4H-spiro[naphthalene-1,2'-pyrrolidin]-4-one trifluoroacetate (7i)**

![Chemical Structure](image)

**General procedure E:** tert-Butyl (3-(4-hydroxynaphthalen-1-yl)propyl)(tosyloxy)carbamate (5i) (70.7 mg, 0.150 mmol) and TFA (23 μL, 0.30 mmol) in anhydrous TFE (1.5 mL) were stirred at r.t. for 22 h. Purification by flash column chromatography (EtOAc) afforded 7i (14.3
343 mg, 30 %) as a yellow/brown solid; Rf = 0.1 (5 % MeOH/CH2Cl2); \( \nu_{\text{max}} / \text{cm}^{-1} \) (solid) 2987 (m), 2971 (m), 1665 (s), 1601 (m); \(^1\)H NMR (400 MHz, CD3OD) \( \delta \) 8.19 (1H, d, \( J = 7.7 \) Hz, C9-H), 7.88 - 7.82 (2H, m, C11-H, C12-H), 7.67 (1H, ddd, \( J = 8.1, 6.1, 2.3 \) Hz, C10-H), 7.25 (1H, d, \( J = 10.3 \) Hz, C5-H), 6.61 (1H, d, \( J = 10.3 \) Hz, C6-H), 3.84 - 3.72 (2H, m, C1-H), 2.71 - 2.62 (1H, m, C3-H), 2.57 - 2.48 (3H, m, C3-H', C2-H2). The signals corresponding to the NH2 were not observed. \(^{13}\)C NMR (101 MHz, CDCl3) \( \delta \) 184.0 (C7), 144.5 (C5), 140.5 (C13), 135.4 (C11), 132.1 (C8), 131.1 (C10), 130.7 (C6), 128.1 (C9), 127.7 (C12), 65.9 (C4), 47.7 (C1), 41.2 (C3), 25.8 (C2). The signals corresponding to the trifluoroacetate group could not be resolved due to their weak intensity. HRMS (ESI\(^+\)) Calculated for C13H14NO: 200.1069. Found [M+H]\(^+\): 200.1074.

\( (E)\)-3-(4-Hydroxy-3-methoxyphenyl)acrylic acid\(^{15}\)

Vanillin (3.04 g, 20.0 mmol) and malonic acid (2.30 g, 22.0 mmol) were added to a solution of aniline (0.22 mL, 2.36 mmol) and pyridine (2.43 mL, 30.0 mmol) in toluene (5 mL). The solution was stirred at refluxing temperature for 2 h. The mixture was cooled to r.t. and neutralised with an aq. 25 % solution of K2CO3 (12 mL) followed by careful addition of concentrated HCl (until pH = 3). The resulting precipitate was filtered and washed with ice cold H2O (10 mL) to afford the title compound (3.0 g, 77 %) as a yellow solid which was used without further purification; Rf = 0.5 (33 % EtOAc); \(^1\)H NMR (440 MHz, CD3OD) \( \delta \) 7.60 (1H, d, \( J = 15.8 \) Hz), 7.18 (1H, d, \( J = 2.0 \) Hz), 7.07 (1H, dd, \( J = 8.2, 2.0 \) Hz), 6.81 (1H, d, \( J = 8.2 \) Hz), 6.31 (1H, d, \( J = 15.8 \) Hz), 3.90 (3H, s); \(^{13}\)C NMR (101 MHz, CD3OD) \( \delta \) 171.0, 150.5, 149.4, 146.9, 127.8, 123.9, 116.5, 115.9, 111.7, 56.4. Spectroscopic properties were consistent with the data available in the literature.\(^{15}\)
Methyl 3-(4-hydroxy-3-methoxyphenyl)propanoate\textsuperscript{16}

\[
\begin{align*}
\text{OH} & \quad \text{OH} \quad \text{OMe} \\
\text{O} & \quad \text{O} \quad \text{OMe} \\
\text{COOH} & \quad \text{COOMe}
\end{align*}
\]

General procedure G: (E)-3-(4-Hydroxy-3-methoxyphenyl)acrylic acid (1.94 g, 10.0 mmol) and 10 wt.% Pd/C (5 mol%) in 5:1 EtOAc/MeOH (60 mL) were employed. Purification by flash column chromatography (50 % EtOAc/hexane) afforded the title compound (1.66 g, 80 %) as a yellow oil; \( R_f = 0.4 \) (33 % EtOAc/hexane); \( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 6.83 (1H, d, \( J = 7.9 \) Hz), 6.72 - 6.66 (2H, m), 5.57 (1H, s), 3.86 (3H, s), 3.67 (3H, s), 2.88 (2H, t, \( J = 7.8 \) Hz), 2.60 (2H, t, \( J = 7.8 \) Hz); \( ^{13}C \) NMR (101 MHz, CDCl\textsubscript{3}) \( \delta \) 173.5, 146.4, 144.1, 132.5, 120.9, 114.5, 111.0, 55.9, 51.7, 36.2, 30.7. Spectroscopic properties were consistent with the data available in the literature.\textsuperscript{16}

Methyl 3-(4-((tert-butyldimethylsilyl)oxy)-3-methoxyphenyl)propanoate

Methyl 3-(4-hydroxy-3-methoxyphenyl)propanoate (1.55 g, 7.40 mmol), tert-butyldimethylsilyl chloride (1.34 g, 8.90 mmol) and imidazole (0.65 g, 9.60 mmol) in 2.5:1 CH\textsubscript{2}Cl\textsubscript{2}/DMF (35 mL) were stirred at r.t. overnight and monitored by TLC. Upon completion, the reaction was quenched by addition of H\textsubscript{2}O (50 mL), extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 × 20 mL), washed with brine (20 mL), dried over MgSO\textsubscript{4}, filtered and concentrated \textit{in vacuo}. Purification by flash column chromatography (gradient 20 - 33 % EtOAc/hexane) afforded the title compound (1.85 g, 77 %) as a pale yellow oil; \( R_f = 0.7 \) (33 % EtOAc/hexane); \( \nu_{\text{max}} / \text{cm}^{-1} \) (film) 2952 (m), 2930 (m), 2857 (m), 1738 (s), 1512 (s); \( ^1H \) NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) 6.74 (1H, d, \( J = 8.0 \) Hz, C\textsubscript{6}-H), 6.67 (1H, d, \( J = 2.0 \) Hz, C\textsubscript{9}-H), 6.62 (1H, dd, \( J = 8.0 \) Hz, 2.0 Hz, C\textsubscript{5}-H), 3.77 (3H, s, C\textsubscript{10}-H\textsubscript{3}), 3.65 (3H, s, CO\textsubscript{2}CH\textsubscript{3}), 2.87 (2H, t, \( J = 7.4 \) Hz, C\textsubscript{3}-H\textsubscript{2}), 2.59 (2H, t, \( J = 7.4 \) Hz, C\textsubscript{2}-H\textsubscript{2}), 0.98 (9H, s, TBS (CH\textsubscript{3})\textsubscript{3}), 0.13 (6H, s, TBS Si(CH\textsubscript{3})\textsubscript{2}); \( ^{13}C \) NMR (101 MHz,
CDCl$_3$ $\delta$ 173.5 (C1), 150.9 (C8), 143.5 (C7), 134.1 (C4), 120.9 (C6), 120.4 (C5) 112.5 (C9), 55.5 (C10), 51.6 (CO$_2$CH$_3$), 36.1 (C2), 30.8 (C3), 25.8 (TBS (CH$_3$)$_3$), 18.5 (TBS Si(CH$_3$)$_3$), -4.6 (TBS Si(CH$_3$)$_2$). HRMS (ESI$^+$) Calculated for C$_{17}$H$_{28}$NaO$_4$Si: 347.1649. Found [M+Na]$^+$: 347.1661.

3-(4-((tert-Butyldimethylsilyl)oxy)-3-methoxyphenyl)propan-1-ol

**General procedure B:** Methyl 3-(4-((tert-butyldimethylsilyl)oxy)-3-methoxyphenyl)propanoate (1.71 g, 5.00 mmol) and 2.0 eq. LiAlH$_4$ (1.0 M in THF) in anhydrous Et$_2$O (25 mL) were employed to afford the title compound (1.34 g, 90 %) as a pale yellow oil which was used without further purification; $R_f = 0.3$ (33 % EtOAc/hexane); $\nu_{\max}$ / cm$^{-1}$ (film) 3357 (m br), 2930 (m), 2857 (m), 1511 (s); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.74 (1H, d, $J = 8.0$ Hz, C$_6$-H), 6.67 (1H, d, $J = 2.0$ Hz, C$_9$-H), 6.62 (1H, dd, $J = 8.0$, 2 Hz, C$_5$-H), 3.78 (3H, s, C$_{10}$-H), 3.65 (2H, t, $J = 6.4$ Hz, C$_1$-H), 2.63 (2H, t, $J = 7.4$ Hz, C$_3$-H), 1.89 - 1.82 (2H, m, C$_2$-H), 0.98 (9H, s, TBS (CH$_3$)$_3$), 0.13 (6H, s, TBS Si(CH$_3$)$_2$); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 150.8 (C$_8$), 143.2 (C$_7$), 135.3 (C$_5$), 120.8 (C$_6$), 120.5 (C$_5$), 112.6 (C$_9$), 62.5 (C$_1$), 55.6 (C$_{10}$), 34.4 (C$_2$), 31.9 (C$_3$), 25.8 (TBS (CH$_3$)$_3$), 18.5 (TBS Si(CH$_3$)$_3$), -4.6, (TBS Si(CH$_3$)$_2$). HRMS (ESI$^+$) Calculated for C$_{17}$H$_{28}$NaO$_4$Si: 319.1700. Found [M+Na]$^+$: 319.1710.

**tert-Butyl (3-(4-((tert-butyldimethylsilyl)oxy)-3-methoxyphenyl)propyl)(tosyloxy) carbamate**

**General procedure C:** 3-(4-((tert-butyldimethylsilyl)oxy)-3-methoxyphenyl)propan-1-ol (0.59 g, 2.00 mmol), PPh$_3$ (0.63 g, 2.40 mmol), DIAD (0.47 mL, 2.40 mmol) and TsONH$_2$Boc
(0.69 g, 2.40 mmol) in anhydrous THF (10 mL) were employed. Purification by flash column chromatography (10 % EtOAc/hexane) afforded the title compound (0.94 g, 83 %) as a colorless oil; Rf = 0.5 (20 % EtOAc/hexane); νmax / cm⁻¹ (film) 2954 (m), 2930 (m), 2857 (m), 1720 (m), 1512 (s); ¹H NMR (400 MHz, CDCl₃) 7.84 (2H, d, J = 8.3 Hz, Ts ArÇH), 7.32 (2H, d, J = 8.3 Hz, Ts ArÇH), 6.74 (1H, d, J = 8.0 Hz, C₆-H), 6.66 (1H, d, J = 2.0 Hz, C₉-H), 6.59 (1H, dd, J = 8.0, 2.0 Hz, C₅-H), 3.79 (3H, s, C₁₀-H₃), 3.62 (2H, app. br s, C₁-H₂), 2.52 (2H, t, J = 7.8 Hz, C₃-H₂), 2.45 (3H, s, Ts C₃-H₃), 2.42 (3H, s, Ts C₃-H₃), 1.98 - 1.87 (2H, m, C₂-H₂), 1.22 (9H, s, Boc (CH₃)₃), 0.99 (9H, s, TBS (CH₃)₃), 0.14 (6H, s, TBS Si(CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 155.6 (C=O), 150.9 (C₈), 145.8 (Ts ArÇ), 143.3 (C₇), 134.7 (C₄), 131.4 (Ts ArÇ), 129.8 (2 × Ts ArÇ), 129.7 (2 × Ts ArÇ), 120.8 (C₆), 120.5 (C₅), 122.5 (C₉) 83.3 (Boc C(CH₃)₃), 55.6 (C₁₀), 52.8 (C₁), 32.6 (C₃), 27.8 (Boc (CH₃)₃), 27.6 (C₂), 25.9 (TBS (CH₃)₃), 21.8 (Ts CH₃), 18.6 (TBS Si(CH₃)₃), -4.5 (TBS Si(CH₃)₂). HRMS (ESI⁺) Calculated for C₂₈H₄₃NNaO₇Si: 588.2422. Found [M+Na]⁺: 588.2432.

tert-Butyl (3-(4-hydroxy-3-methoxyphenyl)propyl)(tosyloxy)carbamate (5j)

General procedure D: tert-Butyl (3-(4-(((tert-butyldimethylsilyl)oxy)-3-methoxyphenyl) propyl)(tosyloxy)carbamate (0.57 g, 1.0 mmol), and 1:1 TBAF/AcOH solution (0.1 M in THF, 1.0 mmol) in THF (20 mL) were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded 5j (0.28 g, 62 %) as a colorless solid; m.p.: 82 - 84 °C (EtOAc/hexane); Rf = 0.4 (33 % EtOAc/hexane); νmax / cm⁻¹ (solid) 3505 (m, br), 2989 (m), 2964 (m), 2935 (m), 1749 (s), 1514 (m), 1153 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.84 (2H, d, J = 8.2 Hz, Ts ArÇH), 7.33 (2H, d, J = 8.1 Hz, Ts ArÇH), 6.82 (1H, d, J = 8.0 Hz, C₆-H), 6.69 (1H, d, J = 1.9 Hz, C₉-H), 6.64 (1H, dd, J = 8.0, 1.9 Hz, C₅-H), 5.47 (1H, s, OÇH), 3.89 (3H, s, C₁₀-H₃), 3.60 (2H, app. br s, C₁-H₂), 2.53 (2H, t, J = 7.6 Hz, C₃-H₂), 2.45 (3H, s, Ts CH₃), 1.97 - 1.87 (2H, m, C₂-H₂), 1.22 (9H, s, Boc (CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 155.6 (C=O), 146.5 (C₈) 145.8, (Ts ArÇ), 143.9 (C₇), 133.1 (C₄), 131.3 (Ts ArÇ), 129.8 (2 × Ts ArÇ).
ArCH), 129.6 (2 × Ts ArCH), 120.9 (C5), 114.3 (C6), 110.9 (C9), 83.3 (Boc C(CH3)3), 56.1 (C10), 52.6 (C1), 32.6 (C3), 27.7 (Boc C(CH3)3), 27.7 (C2) 21.8 (Ts CH3). HRMS (ESI+) Calculated for C22H29NNaO7S: 474.1557. Found [M+Na]+: 474.1551.

7-Methoxy-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7j) and 7-methoxy-1,2,3,4-tetrahydroquinolin-6-ol (8j)

General procedure E: tert-Butyl (3-(4-hydroxy-3-methoxyphenyl)propyl)(tosyloxy) carbamate (5j) (67.7 mg, 0.15 mmol) and TFA (23 μL) in TFE (1.5 mL) were stirred at r.t. for 40 h. Upon completion, the reaction mixture was concentrated in vacuo. An in situ yield was obtained by 1H NMR analysis against 1,3,5-trimethoxybenzene as an internal standard; a 27 % yield of 7j and 62 % yield of 8j were observed. Purification by flash column chromatography (EtOAc) afforded 8j (14.9 mg, 55 %) as a yellow solid, however, 7j could not be isolated cleanly.

Data for 7j: from NMR analysis of crude material: 1H NMR (400 MHz, CD3OD) δ 7.11 (1H, dd, J = 10.0, 2.9 Hz, C5-H), 6.46 (1H, d, J = 10.0 Hz, C6-H), 6.03 (1H, d, J = 2.9 Hz, C10-H), 3.75 (3H, s, C9-H2), 3.68 - 3.60 (2H, m, C1-H2), 2.46-2.43 (2H, m, C2-H2), 2.33 - 2.27 (2H, m, C3-H2); 13C NMR (101 MHz, CD3OD) δ 180.8 (C7), 153.5 (C8), 144.8 (C5), 131.3 (C6), 111.5 (C10), 66.6 (C4), 56.0 (C9) 46.1 (C1) 38.2 (C3), 24.7 (C2);

Data for 8j: m.p.: 76 - 78 °C (EtOAc/hexane); Rf = 0.7 (EtOAc); νmax / cm⁻¹ (solid) 3383 (br m), 3324 (br m), 2926 (m), 1508 (s), 1464 (m), 1443 (m); 1H NMR (400 MHz, CDCl3) δ 6.50 (1H, s, C5-H), 6.14 (1H, s, C9-H), 3.79 (3H, s, C8-H3), 3.25 - 3.20 (2H, m, C1-H2), 2.68 (2H, t, J = 6.5 Hz, C3-H2), 1.94-1.88 (2H, m, C2-H2); 13C NMR (101 MHz, CDCl3) δ 144.7 (C6), 139.3 (C10), 139.1 (C7), 113.1 (C5), 112.7 (C4), 101.7 (C9), 57.0 (C8), 42.3 (C1), 26.7 (C3), 22.8 (C2); HRMS (ESI+) Calculated for C10H14NO2: 180.1019. Found [M+H]+:180.1027.
6-Methylchroman-2-one

General procedure G: 6-Methylcoumarin (4.80 g, 30.0 mmol) and 5 mol% Pd/C (10 wt. %, 1.50 mmol), in EtOAc (30 mL) were employed. Purification by flash column chromatography afforded the title compound (3.40 g, 70 %) as a colorless solid; Rf = 0.4 (20 % EtOAc/hexane); 1H NMR (400 MHz, CDCl3) δ 7.04 (1H, dd, J = 8.1, 1.9 Hz), 6.99 (1H, s), 6.93 (1H, d, J = 8.2 Hz), 2.98 - 2.93 (2H, m), 2.79 - 2.73 (2H, m), 2.31 (3H, s); 13C NMR (101 MHz, CDCl3) δ 168.9, 149.9, 134.0, 128.8, 128.5, 122.4, 116.7, 29.4, 23.8, 20.8. Spectroscopic properties were consistent with the data available in the literature.17

3-(2-((tert-Butyldimethylsilyl)oxy)-5-methylphenyl)propanoic acid

To a solution of 6-methylchroman-2-one (1.74 g, 10.0 mmol) in THF (50 mL) was added an aq. 1 M solution of LiOH (33.0 mmol, 58 mL). After stirring at r.t. overnight the pH was acidified to approx. 3 with aq. 1 M HCl. The product was extracted with EtOAc (2 × 20 mL), dried over Na2SO4, filtered and concentrated in vacuo. The crude product was dissolved in DMF (20 mL) and cooled to 0 °C before tert-butyldimethylsilyl chloride (3.32 g, 22.0 mmol) and imidazole (2.24 g, 33.0 mmol) were added. After being stirred at r.t. overnight the reaction was quenched by addition of H2O (50 mL) and the product was extracted with hexane (3 × 20 mL), dried over MgSO4, filtered and concentrated in vacuo. To the crude product in MeOH (10 mL) and THF (10 mL) was added aq. K2CO3 (20.0 mmol, 2.76 g in 30 mL H2O). After stirring at r.t. overnight the reaction was cooled to 0 °C and quenched with aq. 1 M HCl (30 mL). The mixture was extracted with Et2O (3 × 20 mL), dried over Na2SO4, filtered and concentrated in vacuo. Purification by flash column chromatography (20 % EtOAc/hexane) afforded the title compound (1.60 g, 54 %) as a colorless solid; m.p.: 49 - 51 °C (EtOAc/hexane); Rf = 0.4 (20 % EtOAc/hexane); νmax/cm⁻¹ (solid) 2961 (m), 2948 (m), 2948 (m), 2900 (m), 1702 (s), 1499 (m), 1252 (s); 1H NMR (400 MHz, CDCl3) δ 6.97 (1H, d, J = 2.5 Hz, C5-H), 6.89 (1H, dd, J = 8.3, 2.3 Hz, C8-H), 6.69 (1H, d, J = 8.3 Hz, C9-H), 2.89 (2H, t, J = 7.8 Hz, C3-H2), 2.65 (2H, t, J = 7.9 Hz, C2-H2), 2.26 (3H, s, C7-H3), 1.01 (9H, s, TBS (CH3)3), 0.23 (6H, s, TBS
Si(CH$_3$)$_2$; $^{13}$C NMR (101 MHz, CDCl$_3$) δ 179.3 (C1), 151.5 (C10), 130.9 (C5), 130.5 (C4), 130.4 (C6), 128.0, (C8) 118.3 (C9), 34.3 (C2), 26.2 (C3), 25.9 (TBS (CH$_3$)$_3$), 20.7 (C7), 18.4 (TBS C(CH$_3$)$_3$), -4.0 (TBS Si(CH$_3$)$_2$); HRMS (ESI$^+$) Calculated for C$_{16}$H$_{27}$O$_3$Si: 295.1724. Found [M+H]$^+$: 295.1739.

3-(2-((tert-Butyldimethylsilyl)oxy)-5-methylphenyl)propan-1-ol\(^{18}\)

![Chemical structure](image)

**General procedure I:** 3-(2-((tert-Butyldimethylsilyl)oxy)-5-methylphenyl)propanoic acid (1.25 g, 4.26 mmol), Et$_3$N (0.59 mL, 4.26 mmol), ethylchloroformate (0.41 mL, 4.26 mmol) and NaBH$_4$ (0.40 g, 10.60 mmol) in THF (30 mL) and H$_2$O (15 mL) were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded the title compound (0.83 mg, 60 %) as a colorless oil; R$_f$ = 0.35 (20 % EtOAc/hexane); $\nu_{\text{max}}$/cm$^{-1}$ (film) 3334 (m, br), 2953 (m), 2929 (m), 2885 (m), 2858 (m), 1498 (s), 1253 (s); $^1$H NMR (400 MHz, CDCl$_3$) δ 6.94 (1H, d, $J$ = 2.3 Hz, C5-H), 6.86 (1H, dd, $J$ = 8.2, 2.3 Hz, C8-H), 6.68 (1H, d, $J$ = 8.1 Hz, C9-H), 3.61 (2H, t, $J$ = 6.4 Hz, C1-H$_2$), 2.65 (2H, t, $J$ = 7.4 Hz, C3-H$_2$), 2.25 (3H, s, C7-H$_3$), 1.99 - 1.70 (2H, m, C2-H$_2$), 1.01 (9H, s, TBS (CH$_3$)$_3$), 0.22 (6H, s, TBS Si(CH$_3$)$_2$); $^{13}$C NMR (400 MHz, CDCl$_3$) δ 151.3 (C10), 131.9 (C4), 131.1 (C5), 130.6 (C6), 127.4 (C8), 118.5 (C9), 62.4 (C1), 33.3 (C2), 26.6 (C3), 26.0 (TBS (CH$_3$)$_3$), 20.7 (C7), 18.4 (TBS C(CH$_3$)$_3$), -4.0 (TBS Si(CH$_3$)$_2$). Spectroscopic properties were consistent with the data available in the literature.$^{18}$

**tert-Butyl(3-(2-((tert-butyldimethylsilyl)oxy)-5-methylphenyl)propyl)(tosyloxy) carbamate**

![Chemical structure](image)

**General procedure C:** 3-(2-((tert-Butyldimethylsilyl)oxy)-5-methylphenyl)propan-1-ol (0.87 g, 1.58 mmol), PPh$_3$ (0.50 g, 1.90 mmol), DIAD (0.37 mL, 1.90 mmol) and TsONHBoc (0.54 g, 1.90 mmol) were employed. Purification by flash column chromatography (10 % EtOAc/hexane) afforded the title compound (0.71 mg, 65 %) as a colorless oil; R$_f$ = 0.6 (20 %
EtOAc/hexane); ν<sub>max</sub> / cm<sup>-1</sup> (film) 2957 (m), 2929 (m), 2901 (m), 2859 (m), 1721 (m), 1499 (m); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (2H, d, J = 8.3 Hz, Ts ArCH), 7.31 (2H, d, J = 8.3 Hz, Ts ArCH), 6.92 (1H, d, J = 2.3 Hz, C<sub>5</sub>-H), 6.85 (1H, dd, J = 8.1, 2.3 Hz, C<sub>8</sub>-H), 6.66 (1H, d, J = 8.1 Hz, C<sub>9</sub>-H), 3.62 (2H, app. br s, C<sub>1</sub>-H<sub>2</sub>), 2.51 (2H, t, J = 7.8 Hz, C<sub>3</sub>-H<sub>2</sub>), 2.43 (3H, s, Ts CH<sub>3</sub>), 2.25 (3H, s, C<sub>7</sub>-H<sub>3</sub>), 1.96 - 1.84 (2H, m, C<sub>2</sub>-H<sub>2</sub>), 1.20 (9H, s, Boc (CH<sub>3</sub>)<sub>3</sub>), 1.01 (9H, s, TBS (CH<sub>3</sub>)<sub>3</sub>), 0.21 (6H, s, TBS Si(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.5 (C=O), 151.3 (C<sub>10</sub>), 145.6 (Ts ArC), 131.5 (Ts ArC), 131.4 (C<sub>4</sub>), 130.8 (C<sub>5</sub>), 130.2 (C<sub>6</sub>), 129.8 (2 × Ts ArCH), 129.6 (2 × Ts ArCH), 127.5 (C<sub>8</sub>), 118.3 (C<sub>9</sub>), 83.1 (Boc (CH<sub>3</sub>)<sub>3</sub>), 52.9 (C<sub>1</sub>), 27.7 (C<sub>3</sub>), 27.7 (Boc (CH<sub>3</sub>)<sub>3</sub>), 26.1 (C<sub>2</sub>), 25.9 (TBS (CH<sub>3</sub>)<sub>3</sub>), 21.8 (Ts CH<sub>3</sub>), 20.6 (C<sub>7</sub>), 18.3 (TBS Si(CH<sub>3</sub>)<sub>3</sub>), -4.1 (TBS Si(CH<sub>3</sub>)<sub>2</sub>); HRMS (ESI<sup>+</sup>) Calculated for C<sub>28</sub>H<sub>43</sub>NNaO<sub>6</sub>S: 572.2473. Found [M+Na]<sup>+</sup>: 572.2477.

tert-Butyl (3-(2-hydroxy-5-methylphenyl)propyl)(tosyloxy)carbamate (5k)

![Structural diagram]

**General procedure D:** tert-Butyl (3-(2-((tert-butyldimethylsilyl)oxy)-5-methylphenyl)propyl) (tosyloxy)carbamate (0.44 g, 0.80 mmol) and 1:1 TBAF/AcOH solution (0.1 M in THF, 0.80 mmol) in THF (16 mL) were employed. Purification by flash column chromatography (gradient, eluent 20 - 33 % EtOAc/hexane) afforded 5k (0.27 g, 77%) as a colorless solid; m.p.: 107 - 108 °C (EtOAc/hexane); R<sub>f</sub> = 0.2 (20 % EtOAc/hexane); ν<sub>max</sub> / cm<sup>-1</sup> (solid) 3447 (m), 2986 (m), 1685 (s), 1509 (m), 1382 (s); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.85 (2H, d, J = 8.3 Hz, Ts ArCH), 7.33 (2H, d, J = 8.1 Hz, Ts ArCH), 7.03 - 6.81 (2H, m, C<sub>8</sub>-H, C<sub>9</sub>-H), 6.64 (1H, d, J = 8.0 Hz, C<sub>5</sub>-H), 4.99 (1H, s, OH), 3.65 (2H, br s, C<sub>1</sub>-H<sub>2</sub>), 2.56 (2H, t, J = 7.8 Hz, C<sub>3</sub>-H<sub>2</sub>), 2.44 (3H, s, Ts CH<sub>3</sub>), 2.24 (3H, s, C<sub>7</sub>-H<sub>3</sub>), 2.0 - 1.89 (2H, m, C<sub>2</sub>-H<sub>2</sub>), 1.21 (9H, s, Boc (CH<sub>3</sub>)<sub>3</sub>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 155.8 (C=O), 151.4 (C<sub>10</sub>), 145.7 (Ts ArC), 131.3 (Ts ArC), 130.8 (C<sub>5</sub>), 129.9 (C<sub>6</sub>) 129.8 (2 × Ts ArCH), 129.6 (2 × Ts ArCH), 127.8 (C<sub>8</sub>), 127.0 (C<sub>4</sub>), 115.4 (C<sub>9</sub>), 83.5 (Boc (CH<sub>3</sub>)<sub>3</sub>), 53.0 (C<sub>1</sub>), 27.7 (Boc (CH<sub>3</sub>)<sub>3</sub>), 27.2 (C<sub>3</sub>), 26.3 (C<sub>2</sub>), 21.8 (Ts CH<sub>3</sub>), 20.6 (C<sub>7</sub>); HRMS (ESI<sup>+</sup>) Calculated for C<sub>22</sub>H<sub>25</sub>NNaO<sub>5</sub>S: 458.1608. Found [M+Na]<sup>+</sup>: 458.1608.
9-Methyl-1-azaspiro[4.5]deca-7,9-dien-6-one tosylate (7k)

**General procedure E**: tert-Butyl (3-(2-hydroxy-5-methylphenyl)propyl)(tosyloxy)carbamate (5k) (25.2 mg, 0.06 mmol) and TFA (8.9 μL, 0.12 mmol) in anhydrous TFE (0.57 mL) were employed. Upon completion, the reaction mixture was concentrated in vacuo to afford 7k as a brown solid. An in situ yield was obtained by $^1$H NMR against 1,4-dinitrobenzene as an internal standard; a yield of 91% was obtained. 

**Rf** = 0.1 (5 % MeOH/CH$_2$Cl$_2$); $\nu_{\text{max}}$/cm$^{-1}$ (solid) 3447 (m, br), 2970 (m), 2923 (m), 1673 (m), 1655 (m), 1606 (m); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.31 (1H, br s, NH), 8.16 (1H, br s, NH), 7.71 (2H, d, $J = 8.0$ Hz, Ts ArC$_H$), 7.18 (2H, d, $J = 7.9$ Hz, Ts ArC$_H$), 6.83 (1H, dd, $J = 10.0, 2.2$ Hz, C$_9$-H), 6.34 (1H, br s, C$_5$-H), 6.07 (1H, d, $J = 10$ Hz, C$_9$-H), 3.72 (2H, br s, C$_1$-H$_2$), 2.36 (3H, s, Ts CH$_3$), 2.24 - 2.05 (4H, m, C$_2$-H$_2$, C$_3$-H$_2$), 1.83 (3H, s, C$_7$-H$_3$); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 197.6 (C$_{10}$), 147.1 (C$_8$), 141.3 (Ts ArC), 140.4 (Ts ArC), 132.6 (C$_6$), 131.4 (C$_5$), 129.2 (Ts ArC$_H$), 126.0 (Ts ArC$_H$), 123.9 (C$_9$), 72.5 (C$_4$), 48.2 (C$_1$), 37.2 (C$_2$/C$_3$), 22.6 (C$_2$/C$_3$), 21.5 (Ts CH$_3$), 20.9 (C$_7$); HRMS (ESI$^+$) Calculated for C$_{10}$H$_{14}$NO: 164.1070. Found [M]$^+$: 164.1071.

**Ethyl (E)-3-(2-hydroxy-4-methoxyphenyl)acrylate**

**General procedure F**: 2-Hydroxy-4-methoxybenzaldehyde (1.80 g, 12.0 mmol) and ethyl 2-(triphenyl-phosphaneylidene) acetate (6.27 g, 18.0 mmol) in CH$_2$Cl$_2$ (15 mL) were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded the title compound (2.73 g, quant.) as a colorless solid; R$_f$ = 0.3 (20 % EtOAc/hexane); $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) $\delta$ 9.13 (1H, s), 7.93 (1H, d, $J = 16.1$ Hz), 7.54 (1H, d, $J = 8.4$ Hz), 6.53 - 6.50 (2H, m), 6.48 (1H, d, $J = 16.1$ Hz), 4.18 (2H, q, $J = 7.1$ Hz), 3.79 (3H, s), 1.27 (3H, t, $J = 7.1$ Hz); $^{13}$C NMR (101 MHz, CDC$_3$) $\delta$ 170.0, 163.6, 158.9, 140.7, 131.2, 116.1, 115.6, 107.2, 102.3, 60.4, 55.7, 14.8. Spectroscopic properties were consistent with the data available in the literature.
**Ethyl 3-(2-hydroxy-4-methoxyphenyl)propanoate**\(^{20}\)

\[
\begin{align*}
\text{MeO} & \quad \text{HO} & \quad \text{Et} \\
& \quad \text{OEt} & \\
& & \quad \text{MeO} & \quad \text{OH} & \quad \text{Et}
\end{align*}
\]

**General procedure G:** Ethyl (E)-3-(2-hydroxy-4-methoxyphenyl)acrylate (2.22 g, 10.0 mmol) and 10 wt.% Pd/C (5 mol%) in EtOH (30 mL) were employed to afford the title compound (2.21 g, 99\%) as an off-white solid; \(R_t = 0.2\) (20 % EtOAc/hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.50\) (1H, s), 6.97 (1H, d, \(J = 8.3\) Hz), 6.48 - 6.40 (2H, m), 4.14 (2H, q, \(J = 7.2\) Hz), 3.75 (3H, s), 2.79 - 2.89 (2H, m), 2.63 - 2.73 (2H, m), 1.24 (3H, t, \(J = 7.2\) Hz); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 176.1, 159.7, 155.4, 131.1, 119.7, 106.9, 102.9, 61.5, 55.4, 35.6, 24.1, 14.2. Spectroscopic properties were consistent with the data available in the literature.\(^{20}\)

**Ethyl 3-(2-((tert-butyldimethylsilyl)oxy)-4-methoxyphenyl)propanoate**

\[
\begin{align*}
\text{MeO} & \quad \text{HO} & \quad \text{Et} \\
& \quad \text{OEt} & \\
& & \quad \text{MeO} & \quad \text{OH} & \quad \text{Et}
\end{align*}
\]

Ethyl 3-(2-hydroxy-4-methoxyphenyl)propanoate (1.68 g, 7.50 mmol), \(\text{tert-butyldimethylsilyl}\) chloride (1.36 g, 9.00 mmol), and imidazole (1.28 g, 18.75 mmol) in DMF (15 mL) were employed. Purification by flash column chromatography (20 % EtOAc/pentane) afforded the title compound (1.59 g, 63\%) as a colorless oil; \(R_t = 0.5\) (20 % EtOAc/hexane); \(\nu_{\text{max}} / \text{cm}^{-1}\) (film) 2955 (m), 2931 (m), 2858 (m), 1733 (s), 1611 (s), 1505 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 7.04\) (1H, d, \(J = 8.3\) Hz, C\(_5\)-H), 6.44 (1H, dd, \(J = 8.3, 2.5\) Hz, C\(_6\)-H), 6.38 (1H, d, \(J = 2.5\) Hz, C\(_9\)-H), 4.12 (2H, q, \(J = 7.1\) Hz, OCH\(_2\)), 3.75 (3H, s, C\(_8\)-H\(_3\)), 2.84 (2H, dd, \(J = 8.9, 7.0\) Hz, C\(_3\)-H\(_2\)), 2.54 (2H, dd, \(J = 8.9, 7.0\) Hz, C\(_2\)-H\(_2\)), 1.23 (3H, t, \(J = 7.1\) Hz, CH\(_2\)CH\(_3\)), 1.02 (9H, s, TBS (CH\(_3\))\(_3\)), 0.25 (6H, s, TBS Si(CH\(_3\))\(_2\)); \(^1\)C NMR (101 MHz, CDCl\(_3\)) \(\delta 173.4\) (C=O), 159.1 (C\(_7\)), 154.5 (CH\(_3\)), 130.4 (C\(_5\)), 123.7 (C\(_4\)), 105.7 (C\(_6/C\_9\)), 105.6 (C\(_6/C\_9\)), 60.3 (OCH\(_2\)), 55.4 (C\(_8\)), 34.9 (C\(_2\)), 25.9 (TBS (CH\(_3\))\(_3\)), 25.8 (C\(_3\)), 18.3 (TBS Si(C(CH\(_3\))\(_3\))), 14.4 (CH\(_2\)CH\(_3\)), -4.0 (TBS Si(CH\(_3\))\(_2\)); HRMS (ESI\(^+\)) Calculated for C\(_{18}\)H\(_{30}\)NaO\(_4\)Si: 361.1806. Found [M+Na\(^+\)]: 361.1820.
3-(2-((tert-Butyldimethylsilyl)oxy)-4-methoxyphenyl)propan-1-ol\textsuperscript{21}

\[
\begin{align*}
\text{MeO} & \quad \text{TBS} \quad \text{OEt} \quad \text{MeO} \\
\text{OH} & \quad \text{TBS}
\end{align*}
\]

A solution of ethyl 3-(2-((tert-butyldimethylsilyl)oxy)-4-methoxyphenyl)propanoate (1.01 g, 3.0 mmol) in anhydrous THF (15 mL) was cooled to -78 °C before 2.0 eq. DIBALH (1 M in CH\(_2\)Cl\(_2\)) was added dropwise to maintain the temperature of the reaction mixture below -75 °C. The reaction was stirred at this temperature for 4 h and then warmed to 0 °C and stirred for an additional 2 h. The reaction mixture was diluted with EtOAc (10 mL) and quenched with Rochelle’s salt (10 mL). The mixture was filtered through Celite® and washed with EtOAc. The phases were separated and the aqueous phase extracted with EtOAc (10 mL). The combined organic extracts were dried over Na\(_2\)SO\(_4\), filtered and concentrated in vacuo. Purification by flash column chromatography (33 % EtOAc/hexane) afforded the title compound (0.44 g, 50 %) as a colorless oil; R\(_f\) = 0.3 (33 % EtOAc/hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.03 (1H, d, \(J = 8.4\) Hz), 6.47 (1H, dd, \(J = 8.4, 2.4\) Hz), 6.39 (1H, d, \(J = 2.4\) Hz), 3.76 (3H, s), 3.61 (2H, t, \(J = 6.4\) Hz), 2.62 (2H, t, \(J = 7.2\) Hz), 1.85 - 1.77 (2H, m), 1.64 (1H, br s), 1.01 (9H, s), 0.25 (6H, s); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 158.8, 154.4, 130.6, 124.7, 106.1, 105.7, 62.4, 55.4, 33.4, 25.9, 25.8, 18.4, -4.0. Spectroscopic properties were consistent with the data available in the literature.\textsuperscript{21}

**tert-Butyl (3-(2-((tert-butyldimethylsilyl)oxy)-4-methoxyphenyl)propyl)(tosyloxy) carbamate**

\[
\begin{align*}
\text{MeO} & \quad \text{TBS} \quad \text{OH} \\
\text{Boc} & \quad \text{Ts} \quad \text{N}
\end{align*}
\]

**General procedure C:** 3-(2-((tert-Butyldimethylsilyl)oxy)-4-methoxyphenyl)propan-1-ol (0.44 g, 1.50 mmol), PPh\(_3\) (0.47 g, 1.80 mmol), DIAD (0.35 mL, 1.80 mmol) and TsONHBoc (0.52 g, 1.80 mmol) in anhydrous THF (6 mL) were employed. Purification by flash column chromatography (10% EtOAc/hexane) afforded the title compound (0.82 g, 96 %) as a colorless oil; R\(_f\) = 0.5 (33 % EtOAc/hexane); \(\nu_{\text{max}}/\text{cm}^{-1}\) (film) 2955 (m), 2931 (m), 1720 (s), 1504 (s), 1160 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 (2H, d, \(J = 8.3\) Hz, Ts ArCH), 7.31 (2H, d, \(J = 8.3\) Hz, Ts ArCH), 7.00 (1H, d, \(J = 8.3\) Hz, C\(_5\)-H), 6.44 (1H, dd, \(J = 8.3, 2.5\) Hz, C\(_6\)-H), 6.36 (1H, d, \(J = 2.5\) Hz, C\(_9\)-H), 3.75 (3H, s, C\(_8\)-H\(_3\)), 3.71 - 3.49 (2H, m, C\(_1\)-H\(_2\)), 2.49 (2H, t, \(J = 7.7\) Hz, C\(_2\)-H\(_2\))...
Hz, C3-H2), 2.43 (3H, s, Ts CH3), 1.95 - 1.81 (2H, m, C2-H2), 1.21 (9H, s, Boc (CH3)3), 1.01 (9H, s, TBS (CH3)3), 0.24 (6H, s, TBS Si(CH3)2); 13C NMR (101 MHz, CDCl3) δ 158.8 (C7), 155.5 (C=O), 154.3 (C10), 145.6 (Ts ArC), 131.4 (Ts ArC), 130.3 (C5), 129.7 (2 × Ts ArCH), 129.6 (2 × Ts ArCH), 124.1 (C4), 105.7 (C6), 105.5 (C9), 83.1 (Boc C(CH3)3), 55.3 (C8), 52.8 (C1), 27.7 (Boc (CH3)3), 27.0 (C3), 26.2 (C2), 25.9 (TBS (CH3)3), 21.8 (Ts CH3), 18.3 (TBS Si(CH3)2); HRMS (ESI+) Calculated for C28H43NNaO7Si: 588.2422. Found [M+Na]+: 588.2426.

tert-Butyl (3-(2-hydroxy-4-methoxyphenyl)propyl)(tosyloxy)carbamate (5l)

\[
\text{MeO} \quad \text{TBS} \quad \text{N}^\text{OTs} \quad \text{Boc} \quad \text{MeO} \quad \text{OH} \quad \text{N}^\text{OTs} \quad \text{Boc} \\
5l
\]

**General procedure D:** tert-Butyl (3-(2-((tert-butyldimethylsilyl)oxy)-4-methoxyphenyl)propyl) (tosyloxy)carbamate (0.56 g, 1.00 mmol) and 1:1 TBAF/AcOH solution (0.1 M in THF, 0.1 mmol) in THF (20 mL) were employed. Purification by flash column chromatography (33 % EtOAc/hexane) afforded 5l (0.30 g, 68 %) as a colorless, viscous oil; Rf = 0.2 (33 % EtOAc/hexane); νmax / cm\(^{-1}\) (film) 3422 (br s), 2936 (m), 1720 (m), 1508 (m), 1368 (s); \(^1\)H NMR (400 MHz, CDCl3) δ 7.85 (2H, d, J = 8.0 Hz, Ts ArC-H), 7.33 (2H, d, J = 8.0 Hz, Ts ArCH), 6.98 (1H, d, J = 8.3 Hz, C5-H), 6.42 (1H, dd, J = 8.3, 2.4 Hz, C6-H), 6.36 (1H, d, J = 2.4 Hz, C9-H), 5.37 (1H, br s, OH), 3.75 (3H, s, C8-H3), 3.72 - 3.53 (2H, m, C1-H2), 2.54 (2H, t, J = 7.7 Hz, C3-H2), 2.44 (3H, s, Ts CH3), 1.98 - 1.85 (2H, m, C2-H2), 1.22 (9H, s, Boc (CH3)3); 13C NMR (101 MHz, CDCl3) δ 159.3 (C7), 156.0 (C=O), 154.6 (C10), 145.9 (Ts ArC), 131.4 (Ts ArC), 130.7 (C5), 130.0 (2 × Ts ArCH), 129.7 (2 × Ts ArCH), 119.6 (C4), 106.1 (C6), 102.1 (C9), 83.6, 55.5 (C8), 53.0 (C1), 27.8 (Boc (CH3)3), 26.6 (C2/C3), 26.5 (C2/C3), 21.8 (Ts CH3); HRMS (ESI+) Calculated for C22H29NNaO7Si: 474.1557. Found [M+Na]+: 474.1560.
8-Methoxy-1-azaspiro[4.5]deca-7,9-dien-6-one trifluoroacetate (7l)

General procedure E: tert-Butyl (3-(2-hydroxy-4-methoxyphenyl)propyl)(tosyloxy) carbamate (5l) (67.7 mg, 0.15 mmol) and TFA (23 μL, 0.30 mmol) in TFE (1.5 mL) were stirred at r.t. for 25 h. Purification by flash column chromatography (EtOAc) afforded 7l (34.1 mg, 78 %) as a yellow oil; Rf = 0.1 (5 % MeOH/CH2Cl2); νmax / cm⁻¹ (film) 2987 (m), 2901 (m), 1672 (s), 1634 (m); ¹H NMR (400 MHz, CD₃OD) δ 6.69 (1H, d, J = 10.1 Hz, C₅-H), 6.36 (1H, dd, J = 10.1, 2.2 Hz, C₆-H), 5.63 (1H, d, J = 2.2 Hz, C₉-H), 3.88 (3H, s, C₈-H), 3.69 - 3.54 (2H, m, C₁-H₂, C₃-H₂). The signals corresponding to the NH₂ were not observed. ¹³C NMR (101 MHz, CD₃OD) δ 196.9 (C₁₀), 173.1 (C₇), 138.5 (C₅), 125.5 (C₆), 98.8 (C₉), 71.4 (C₄), 57.5 (C₈), 48.5 (C₁), 39.4 (C₃), 24.2 (C₂). The signals corresponding to the trifluoroacetate group could not be resolved due to their weak intensity. HRMS (ESI⁺) Calculated for C₁₀H₁₄NO₂: 180.1019. Found [M+H]⁺: 180.1011.

1-(Allyloxy)naphthalene

The title compound was prepared according to a literature procedure. Spectroscopic properties were consistent with the data available in the literature.

2-Allylnaphthalen-1-ol

The title compound was prepared according to a literature procedure.
Spectroscopic properties were consistent with the data available in the literature.\(^{24}\)

\(((2\text{-Allylnaphthalen-1-yl})\text{oxy})(\text{tert-butyl})\text{dimethylsilane}\)^{24}

The title compound was prepared according to a literature procedure.\(^{22}\)

Spectroscopic properties were consistent with the data available in the literature.\(^{24}\)

\(3-(1\text{-}((\text{tert-Butyldimethylsilyl})\text{oxy})\text{naphthalen-2-yl})\text{propan-1-ol}\)^{22}

The title compound was prepared according to a literature procedure.\(^{22}\)

Spectroscopic properties were consistent with the data available in the literature.\(^{22}\)

\(\text{tert-Butyl \(3-(1\text{-}((\text{tert-Butyldimethylsilyl})\text{oxy})\text{naphthalen-2-yl})\text{propyl})(tosyloxy) carbamate}\)

\text{General procedure C:} \(3-(1\text{-}((\text{tert-Butyldimethylsilyl})\text{oxy})\text{naphthalen-2-yl})\text{propan-1-ol} \) (0.47 g, 1.50 mmol), \(\text{PPh}_3\) (0.47 g, 1.80 mmol), \(\text{DIAD} \) (0.35 mL, 1.80 mmol) and \(\text{TsONHBoc}\) (0.52 g, 1.80 mmol) in anhydrous \(\text{THF} \) (8 mL) were employed. Purification by flash column chromatography (10 % EtOAc/hexane) afforded the title compound as a colorless, viscous oil (0.67 g, 76 %); \(R_f = 0.4 \) (20 % EtOAc/hexane); \(\nu_{\text{max}} / \text{cm}^{-1} \) (film) 2955 (m), 2930 (m), 2895 (m), 2858 (m), 1720 (s), 1382 (s), 1369 (s); \(^1\text{H NMR} \) (400 MHz, CDCl\(_3\)\) \(\delta \) 8.06 - 8.02 (1H, m, Ar\(\text{C}_\text{H}\)), 7.80 (2H, d, \(J = 8.4 \text{ Hz, Ts Ar}\text{C}_\text{H}\)), 7.78 - 7.74 (1H, m, Ar\(\text{CH}\)), 7.46 - 7.37 (3H, m, Ar\(\text{CH}\)), 7.28 - 7.22 (3H, m, Ts Ar\(\text{CH}\), Ar\(\text{CH}\)), 3.71 - 3.43 (2H, m, C\(1\text{-H}_2\)), 2.73 (2H, \(t, J = 7.7 \text{ Hz, C3-H}_2\)), 2.39 (3H, s, Ts \(\text{CH}_3\)), 1.99 - 1.88 (2H, m, C\(2\text{-H}_2\)), 1.19 (9H, s, Boc (CH\(_3\))\(_3\)), 1.11 (9H, s, TBS (CH\(_3\))\(_3\)), 0.17 (6H, s, TBS Si(CH\(_3\))\(_2\)); \(^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)\) \(\delta \) 155.6 (C=O),
148.3 (C5), 145.7 (Ts ArC), 133.8 (ArC), 131.4 (Ts ArC), 129.7 (2 × Ts ArCH) 129.6 (2 × Ts ArCH), 128.2 (ArC), 128.1 (ArCH), 127.7 (ArCH), 126.2 (C4), 125.4 (ArCH), 124.9 (ArCH), 123.2 (ArCH), 121.8 (ArCH), 83.3 (Boc C(CH3)3), 52.8 (C1), 27.7 (Boc (CH3)3), 27.6 (C3), 26.4 (C2), 26.3 (TBS (CH3)3), 21.8 (Ts CH3), 18.9 (TBS Si(CH3)3), -3.0 (TBS Si(CH3)2); HRMS (ESI+) Calculated for C31H43NNaO6Si: 608.2472. Found [M+Na]+: 608.2466.

tert-Butyl (3-(1-hydroxynaphthalen-2-yl)propyl)(tosyloxy)carbamate (5m)

General procedure D: tert-Butyl (3-((tert-butyldimethylsilyl)oxy)naphthalen-2-yl)propyl) (tosyloxy)carbamate (0.56 g, 0.97 mmol) and 1:1 TBAF/AcOH solution (0.1 M in THF, 0.97 mmol) in THF (20 mL) were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded 5m (0.31 g, 68 %) as a pale yellow solid; m.p.: 107 - 109 °C (EtOAc/hexane); Rf = 0.2 (20 % EtOAc/hexane); v_max / cm⁻¹ (solid) 3485 (m), 2970 (m), 2942 (m), 2882 (m), 1729 (s), 1385 (s); ¹H NMR (400 MHz, CDCl₃) δ 8.18-8.15 (1H, m, ArC_H), 7.85 (2H, d, J = 8.3 Hz, Ts ArC_H), 7.77 (1H, dd, J = 8.1, 1.4 Hz, ArC_H), 7.49-7.41 (2H, m, ArCH), 7.39 (1H, d, J = 8.4 Hz, ArCH), 7.30 (2H, d, J = 8.3 Hz, Ts ArCH), 7.22 (1H, d, J = 8.4 Hz, ArCH), 6.07 (1H, br s, OH), 3.69 (2H, t, J = 6.5 Hz, C1-H2), 2.81 (2H, t, J = 7.5 Hz, C3-H2), 2.43 (3H, s, Ts CH3), 2.10-2.00 (2H, m, C2-H2), 1.24 (9H, s, Boc (CH3)3); ¹³C NMR (101 MHz, CDCl₃) δ 156.4 (C=O), 148.8 (C5), 146.0 (Ts ArC), 133.6 (ArC), 131.3 (Ts ArC), 129.8 (2 × Ts ArCH), 129.7 (2 × Ts ArCH), 128.8 (ArCH), 127.7 (ArCH), 125.7 (ArCH), 125.4 (ArCH), 125.0 (ArC), 121.5 (ArCH), 120.5 (ArCH), 120.3 (ArC), 84.0 (Boc C(CH3)3), 52.9 (C1), 27.7 (Boc (CH3)3), 27.3 (C3), 27.2 (C2), 21.8 (Ts CH3); HRMS (ESI+) Calculated for C25H29NO6S: 494.1607. Found [M+Na]+: 494.1614.

1H-spiro[naphthalene-2,2'-pyrrolidin]-1-one (7m)
General procedure E: tert-Butyl (3-(1-hydroxynaphthalen-2-yl)propyl)(tosyloxy)carbamate (5m) (70.7 mg, 0.15 mmol) and TFA (23 μL, 0.3 mmol) in 30:1 anhydrous TFE/CH$_2$Cl$_2$ (1.5 mL) were stirred at r.t. for 26 h. Purification by flash column chromatography (gradient eluent 50 % EtOAc/hexane – 100 % EtOAc) afforded 7m (11.4 mg, 38 %) as a yellow/brown solid; m.p.: 57 - 60 °C (EtOAc/hexane); R$_f$ = 0.1 (EtOAc); $\nu_{max}$ / cm$^{-1}$ (solid) 2920 (m), 2851 (m), 1674 (s), 1595 (s), 1371 (s); $^{1}$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (1H, d, $J$ = 7.7 Hz, C$_7$-H), 7.56 - 7.51 (1H, m, C$_9$-H), 7.34 - 7.29 (1H, m, C$_8$-H), 7.17 (1H, d, $J$ = 7.5 Hz, C$_{10}$-H), 6.43 (1H, d, $J$ = 10.0 Hz, C$_{12}$-H), 6.25 (1H, d, $J$ = 10.0 Hz, C$_{13}$-H), 3.41 - 3.33 (1H, m, C$_1$-H), 3.13 - 3.05 (1H, m, C$_1$-H'), 2.40 (1H, br s, NH), 2.11 - 2.06 (1H, m, C$_3$-H), 1.92 - 1.78 (3H, m, C$_3$-H', C$_2$-H$_2$); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 203.7 (C$_5$), 139.8 (C$_{13}$), 138.2 (C$_{11}$), 134.7 (C$_9$), 129.0 (C$_6$), 127.9 (C$_8$), 127.3 (C$_7$), 127.2 (C$_{10}$), 123.3 (C$_{12}$), 70.2 (C$_4$), 48.4 (C$_1$), 38.9 (C$_3$), 25.9 (C$_2$); HRMS (ESI$^+$) Calculated for C$_{13}$H$_{14}$NO: 200.1069. Found [M+H]$^+$: 200.1079.

1,2-Dihydro-3H-naphtho[2,1-b]pyran-3-one$^{25}$

![1,2-Dihydro-3H-naphtho[2,1-b]pyran-3-one](image)

The compound was prepared according to a literature procedure.$^{25}$

Spectroscopic properties were consistent with the data available in the literature.$^{25}$

3-(2-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)propanoic acid

![3-(2-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)propanoic acid](image)

To a solution of 1,2-Dihydro-3H-naphtho[2,1-b]pyran-3-one (7.90 g, 37.0 mmol) in THF (200 mL) was added aq. 1 M LiOH (125 mL). After stirring at r.t. overnight the pH was acidified to approx. 3 with 1 M HCl. The product was extracted with EtOAc (50 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. The crude product was dissolved in DMF (20 mL) and tert-butyldimethylsilyl chloride (12.2 g, 81.4 mmol) and imidazole (8.30 g, 122.1 mmol) were added at 0 °C. After being stirred at r.t. overnight the reaction was quenched by addition of H$_2$O and the product was extracted with hexane, dried over MgSO$_4$, filtered and concentrated.
in vacuo. To the crude product in MeOH (30 mL) and THF (30 mL) was added aq. K$_2$CO$_3$ (74.0 mmol, 10.2 g in 100 mL H$_2$O). After stirring for 5 h the reaction was quenched with aq. 1 M HCl (100 mL) at 0 °C. The mixture was extracted with Et$_2$O, dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. Purification by flash column chromatography (20 % EtOAc/hexane) afforded the title compound (8.10 g, 66 %) as a pale yellow solid; m.p.: 94 - 96 °C (EtOAc/hexane); R$_f$ = 0.3 (33 % EtOAc/hexane); $\nu$_max / cm$^{-1}$ (solid) 2957 (m), 2928 (m), 2900 (m), 2857 (m), 1699 (s); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.97 (1H, d, $J$ = 8.5 Hz, ArC$_H$), 7.79 (1H, d, $J$ = 7.8 Hz, ArCH), 7.65 (1H, d, $J$ = 8.5 Hz, ArCH), 7.51 (1H, t, $J$ = 7.7 Hz, ArCH), 7.36 (1H, t, $J$ = 7.5 Hz, ArCH), 7.11 (1H, d, $J$ = 8.9 Hz, ArCH), 3.43 (2H, t, $J$ = 8.5 Hz, C$_2$H$_2$), 2.67 (2H, t, $J$ = 8.5 Hz, C$_3$H$_2$), 1.08 (9H, s, TBS (C$_3$H$_3$)$_3$), 0.31 (6H, s, TBS Si(C$_3$H$_3$)$_2$); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 179.3 (C=O), 150.8 (ArC), 133.0 (ArC), 129.5 (ArC), 128.6 (ArCH), 127.9 (ArCH), 126.5 (ArCH), 123.4 (ArCH), 123.1 (ArC), 122.8 (ArCH), 120.2 (ArCH), 33.9 (C1), 25.8 (TBS (C$_3$H$_3$)$_3$), 21.0 (C2), 18.3 (TBS Si(C$_3$H$_3$)$_2$), 3.9 (TBS Si(C$_3$H$_3$)$_2$); HRMS (ESI$^+$) Calculated for C$_{19}$H$_{26}$NaO$_3$Si: 353.1543. Found [M+Na]$^+$: 353.1551.

3-(2-((tert-Butyldimethylsilyloxy)naphthalen-1-yl)propan-1-ol$^{22}$

![Diagram](image)

**General procedure I**: 3-(2-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)propanoic acid (1.65 g, 5.00 mmol), Et$_3$N (0.70 mL, 5.00 mmol), ethyl chloroformate (0.54 g, 5.00 mmol) and NaBH$_4$ (0.47 g, 12.5 mmol) in THF (50 mL) and H$_2$O (20 mL) were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded the title compound (1.19 g, 75 %) as a colorless oil; R$_f$ = 0.6 (33 % EtOAc/hexane); $\nu$_max / cm$^{-1}$: (film) 3336 (m, br), 2953 (m), 2929 (m), 2882 (m), 2857 (m), 1622 (m), 1594 (m), 1465 (m), 1264 (m), 1241 (s); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.00 (1H, d, $J$ = 8.1 Hz), 7.79 (1H, d, $J$ = 8.4 Hz), 7.63 (1H, d, $J$ = 8.6 Hz), 7.48 (1H, t, $J$ = 7.8 Hz), 7.35 (1H, t, $J$ = 7.2 Hz), 7.12 (1H, d, $J$ = 9.0 Hz), 3.63 (2H, t, $J$ = 5.9 Hz), 3.20 (2H, t, $J$ = 6.7 Hz), 2.53 (1H, br s), 1.95 (2H, qn, $J$ = 7.4 Hz), 1.10 (9H, s), 0.31 (6H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 150.6, 133.4, 129.9, 128.6, 127.4, 126.3, 124.7, 123.6, 123.5, 120.6, 62.2, 32.5, 26.0, 21.5, 18.5, -3.8. Spectroscopic properties were consistent with the data available in the literature.$^{22}$
tert-Butyl (3-(2-((tert-butyldimethylsiloyloxy)naphthalen-1-yl)propyl) (tosyloxy) carbamate

To a solution of 3-(2-((tert-butyldimethylsilyloxy)naphthalen-1-yl)propan-1-ol (0.63 g, 2.00 mmol), tert-butyl (tosyloxy)carbamate (0.56 g, 3.00 mmol) and PPh₃ (1.05 g, 4.00 mmol) in anhydrous PhMe:THF (3:1, 8 mL/mmol) at 0°C was added a solution of DIAD (0.78 mL, 4.00 mmol) in anhydrous PhMe (2 mL/mmol) dropwise. The reaction was stirred at r.t. until completion by TLC analysis (4 h). The reaction mixture was concentrated in vacuo and purification by flash column chromatography (gradient 20 – 25 % EtOAc/hexane) afforded the title compound (0.74 g, 63%) as a colorless solid; m.p. 79 - 80°C (EtOAc/hexane); R_f = 0.7 (33 % EtOAc/hexane); ν_max / cm⁻¹ (solid) 2961 (m), 2927 (m), 2857 (m), 1709 (s), 1596 (m), 1466 (m), 1368 (s), 1240 (s), 1174 (s), 1164 (s), 1153 (s), 1087 (m); ¹H NMR (400 MHz, CDCl₃) δ 7.86 (1H, d, J = 8.6 Hz, ArCH), 7.82 (2H, d, J = 8.3 Hz, ArCH), 7.75 (1H, d, J = 8.2 Hz, ArCH), 7.59 (1H, d, J = 8.8 Hz, ArCH), 7.47 - 7.43 (1H, m, ArCH), 7.33 (1H, ddd, J = 8.1, 6.8, 1.1 Hz, ArCH), 7.27 (2H, d, J = 8.2 Hz, ArCH), 7.05 (1H, d, J = 8.8 Hz, ArCH), 3.71 (2H, br s, C₁-H₂), 3.02 (2H, t, J = 7.9 Hz, C₃-H₂), 2.42 (3H, s, Ts CH₃), 1.98 - 1.89 (2H, m, C₂-H₂), 1.16 (9H, s, Boc (CH₃)₃), 1.07 (9H, s, TBS (CH₃)₃), 0.27 (6H, s, Si(CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 155.5 (C=O), 150.6 (ArC), 145.6 (Ts ArC), 133.3 (ArC), 131.5 (Ts ArC), 129.7 (2 × Ts ArCH), 129.6 (ArC), 129.5 (2 × Ts ArCH), 128.6 (ArCH), 127.5 (ArCH), 126.4 (ArCH), 124.2 (ArC), 123.3 (ArCH), 123.2 (ArCH), 120.3 (ArCH), 83.1 (Boc C(CH₃)₃), 53.1 (C₁), 27.6 (Boc (CH₃)₃), 26.1 (C₂), 26.0 (TBS (CH₃)₃), 22.7 (C₃), 21.8 (Ts CH₃), 18.4 (TBS C(CH₃)₃), -3.8 (TBS Si(CH₃)₂); HRMS (ESI⁺) Calculated for C₃₁H₄₃NNaO₆SSi: 608.2473. Found [M+Na⁺]: 608.2456.

tert-butyl (3-(2-hydroxynaphthalen-1-yl)propyl)(tosyloxy)carbamate (5n)

5n
General procedure D: tert-Butyl (3-(2-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)propyl)(tosyloxy) carbamate (0.16 g, 0.28 mmol) and 1:1 TBAF/AcOH solution (0.1 M in THF, 0.28 mmol) in THF were employed. Purification by flash column chromatography (33 % EtOAc/hexane) afforded 5n (0.11 g, 84 %) as a pale yellow solid; m.p.: 55 - 57 °C (EtOAc/hexane); Rf = 0.35 (33 % EtOAc/hexane); νmax / cm⁻¹ 3359 (m, br), 2931 (m), 1721 (s), 1369 (s), 1191 (s), 1178 (s), 1154 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.88 - 7.83 (3H, m, Ts ArCH, ArCH), 7.77 (1H, d, J = 8.1 Hz, ArCH), 7.62 (1H, d, J = 8.8 Hz, ArCH), 7.47 (1H, ddd, J = 8.3, 6.9, 1.4 Hz, ArCH), 5.60 (1H, br s, OH), 3.79 - 3.70 (2H, m, C1-H₂), 3.07 (2H, t, J = 7.8 Hz, C3-H₂), 2.44 (3H, s, Ts CH₃), 2.08 - 1.97 (2H, m, C2-H₂), 1.20 (9H, s, Boc (CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 156.1 (C=O), 151.1 (ArC), 145.9 (Ts ArC), 133.2 (ArC), 131.3 (Ts ArC), 129.7 (2 × Ts ArCH), 129.7 (2 × Ts ArCH), 129.5 (ArC), 128.8 (ArCH), 128.1 (ArCH), 126.6 (ArCH), 123.1 (ArCH), 118.8 (ArC), 118.1 (ArCH), 83.6 (Boc C(CH₃)₃), 53.2 (C1), 27.7 (Boc (CH₃)₃), 26.4 (C2), 22.2 (C3) 21.8 (Ts CH₃); HRMS (ESI⁺) Calculated for C₂₅H₂₉NNaO₆S: 494.1608. Found [M+Na]⁺: 494.1598.

2H-spiro[naphthalene-1,2'-pyrrolidin]-2-one (7n)

General procedure E: tert-Butyl (3-(2-hydroxynaphthalen-1-yl)propyl)(tosyloxy)carbamate (5n) (117.9 mg, 0.25 mmol), TFA (38 μL, 0.50 mmol) and TFE (2.5 mL) were employed. After stirring at r.t. for 38 h, purification by flash column chromatography (50 % EtOAc/hexane) afforded 7n (38.8 mg, 78 %) as a viscous yellow oil; Rf = 0.25 (33 % EtOAc/hexane); νmax/cm⁻¹ (film) 3339 (m), 2965 (m), 2866 (m), 1671 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.66 (1H, d, J = 9.9 Hz, C6-H), 7.41 - 7.34 (2H, m, C11-H and C7-H), 7.29 - 7.21 (2H, m, C8-H and C9-H), 6.17 (1H, d, J = 9.9 Hz, C12-H), 3.45 (1H, dt, J = 10.3, 6.4 Hz, C1-H), 3.28 (1H, dt, J = 10.2, 6.4 Hz, C1-H'), 2.34 - 2.22 (1H, m, C3-H), 1.96 - 1.69 (3H, m, C2-H₃, C3-H'); ¹³C NMR (101 MHz, CDCl₃) δ 205.1, (C=O), 148.8 (C5), 144.8 (C11), 130.1 (C7), 129.2
(C8), 129.1 (C10), 127.0 (C9), 126.0 (C6), 123.6 (C12), 73.9 (C4), 49.9 (C1), 42.9 (C3), 25.6 (C2); HRMS (ESI+) Calculated for C13H13NNaO: 222.0889. Found [M+Na]+: 222.0883.

1,2-Dihydro-9-methoxy-3H-naphtho[2,1-b]pyran-3-one

The title compound was prepared according to a literature procedure. Spectroscopic properties were consistent with the data available in the literature.

3-(2-((tert-Butyldimethylsilyl) oxy)-7-methoxynaphthalen-1-yl)propanoic acid

To a solution of 1,2-dihydro-9-methoxy-3H-naphtho[2,1-b]pyran-3-one (1.71 g, 7.50 mmol) in THF (75 mL) was added aq. 1 M LiOH (44.0 mL, 24.8 mmol). After stirring at r.t. overnight the pH was acidified to approx. 3 with aq. 1 M HCl. The product was extracted with EtOAc (50 mL), dried over Na2SO4, filtered and concentrated in vacuo. The crude product was dissolved in DMF (15 mL) and tert-butyldimethylsilyl chloride (2.50 g, 16.5 mmol) and imidazole (1.68 g, 24.8 mmol) were added at 0 °C. After being stirred at r.t. overnight the reaction was quenched by addition of H2O and the product was extracted with hexane, dried over MgSO4, filtered and concentrated in vacuo. To the crude product in MeOH (7.5 mL) and THF (7.5 mL) was added aq. K2CO3 (22 mL, 15.0 mmol). After stirring overnight at r.t., the reaction was quenched with aq. 1 M HCl (20 mL) at 0 °C. The organic phase was extracted with Et2O (3 × 10 mL), dried over Na2SO4, filtered and concentrated in vacuo. Purification by flash column chromatography (20 % EtOAc/hexane) afforded the title compound (1.77 g, 65 %) as a yellow solid; m.p.: 113 - 115 °C (EtOAc/hexane); Rf = 0.5 (33 % EtOAc/hexane); νmax / cm⁻¹ (solid) 3675 (w), 2958 (m), 2927 (m), 1703 (s), 1627 (m), 1514 (s), 1264 (s), 1231 (s), 1037 (s); 1H NMR (CDCl3) δ 7.68 (1H, d, J = 8.9 Hz, ArCH), 7.56 (1H, d, J = 8.8 Hz, ArCH), 7.24 (1H, d, J = 2.4 Hz, ArCH), 7.02 (1H, dd, J = 8.9, 2.4 Hz, ArCH), 6.95 (1H, d, J = 8.8 Hz, ArCH), 3.95 (3H, s, OCH3), 3.43 - 3.26 (2H, m, C3-H2), 2.76 - 2.56 (2H, m, C2-H2), 1.97 (9H, s, TBS (CH3)3), 0.29 (6H, s, TBS (Si(CH3)2); 13C NMR (101 MHz, CDCl3) δ 178.9 (C=O),
158.3 (ArC), 151.4 (ArC), 134.3 (ArC), 130.1 (ArCH), 127.6 (ArCH), 124.8 (ArC), 122.1 (ArC), 117.6 (ArCH), 115.7 (ArCH), 101.7 (ArCH), 55.3 (OCH₃), 33.5 (C₂), 25.8 (TBS (CH₃)₃), 21.1 (C₃), 18.3 (TBS Si(CH₃)₃), -3.9 (TBS Si(CH₃)₂); HRMS (-ve ion) Calculated for C₂₀H₂₇O₄Si: 359.1684. Found [M-H]: 359.1685.

3-(2-((tert-Butyldimethylsilyl)oxy)-7-methoxynaphthalen-1-yl)propan-1-ol

![Chemical structure of 3-(2-((tert-Butyldimethylsilyl)oxy)-7-methoxynaphthalen-1-yl)propan-1-ol]

**General procedure I:** 3-(2-((tert-Butyldimethylsilyl)oxy)-7-methoxynaphthalen-1-yl)propanoic acid (1.08 g, 3.00 mmol), ethyl chloroformate (0.29 mL, 3.00 mmol), Et₃N (0.42 mL, 3.00 mmol), and NaBH₄ (0.28 g, 7.50 mmol) were employed. Purification by flash column chromatography (20% EtOAc/hexane) afforded the title compound (0.68 g, 65%) as a pale yellow oil; Rₜ = 0.25 (20% EtOAc/hexane); νmax / cm⁻¹ (film) 3370 (br m), 2953 (m), 2930 (m), 2884 (m), 2857 (m), 1624 (s), 1513 (s), 1461 (s), 1230 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.67 (1H, d, J = 8.9 Hz), 7.53 (1H, d, J = 8.8 Hz), 7.02 (1H, dd, J = 8.9, 2.4 Hz), 6.94 (1H, d, J = 8.8 Hz), 3.93 (3H, s), 3.59 (2H, t, J = 6.1 Hz), 3.14 (2H, t, J = 7.2 Hz), 2.06-1.77 (3H, m), 1.05 (9H, s), 0.27 (6H, s); ¹³C NMR (101 MHz, CDCl₃) δ 158.0, 151.2, 134.5, 130.0, 127.0, 125.1, 123.4, 115.6, 102.5, 62.0, 55.3, 31.9, 25.9, 21.5, 18.4, -3.9; HRMS (ESI⁺) Calculated for C₂₀H₃₀NaO₃Si: 369.1856. Found [M+Na]⁺: 369.1855. Spectroscopic properties were consistent with the data available in the literature.²²

**tert-Butyl (2-(2-((tert-butyldimethylsilyl)oxy)-7-methoxynaphthalen-1-yl)ethyl)(tosyloxy) carbamate**

![Chemical structure of tert-Butyl (2-(2-((tert-butyldimethylsilyl)oxy)-7-methoxynaphthalen-1-yl)ethyl)(tosyloxy) carbamate]

**General procedure C:** 3-(2-((tert-Butyldimethylsilyl)oxy)-7-methoxynaphthalen-1-yl)propan-1-ol (0.40 g, 1.15 mmol), PPh₃ (0.36 g, 1.38 mmol), DIAD (0.27 mL, 1.38 mmol) and TsONHBoc (0.40 mg, 1.38 mmol) in anhydrous THF (5 mL) were employed. Purification by flash column chromatography (10% EtOAc/hexane) afforded the title compound (0.48 g,
68 %) as a colorless oil; Rf = 0.5 (20 % EtOAc/hexane); \( \nu_{\text{max}} / \text{cm}^{-1} \) (film) 2956 (m), 2930 (m), 2900 (m), 2859 (m), 1721 (s), 1623 (s), 1513 (s), 1381 (s), 1368 (s), 1231 (s), 1178 (s), 1152 (s); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.82 (2H, d, \( J = 8.2 \) Hz, Ts ArCH), 7.65 (1H, d, \( J = 8.9 \) Hz, ArCH), 7.51 (1H, d, \( J = 8.8 \) Hz, ArCH), 7.30 (2H, d, \( J = 8.1 \) Hz, Ts ArCH), 7.16 (1H, d, \( J = 2.4 \) Hz, ArCH), 7.00 (1H, dd, \( J = 8.9, 2.4 \) Hz, ArCH), 6.90 (1H, d, \( J = 8.8 \) Hz, ArCH), 3.96 (3H, s, OCH\(_3\)), 3.73 (2H, app. br s, C1-H$_2$), 2.96 (2H, t, \( J = 8.1 \) Hz, C3-H$_2$), 2.42 (3H, s, Ts, CH$_3$), 1.96 (2H, qn, \( J = 7.5 \) Hz, C2-H$_2$), 1.16 (9H, s, Boc (CH$_3$)$_3$), 1.05 (9H, s, TBS (CH$_3$)$_3$), 0.25 (6H, s, TBS (Si(CH$_3$)$_2$)$_3$); \(^{13}\)C NMR (101 MHz, CDCl$_3$) \( \delta \) 158.2 (ArC), 155.4 (C=O), 151.2 (ArC), 145.7 (Ts ArC), 134.5 (ArC), 131.4 (Ts ArC), 13.0 (ArCH), 129.7 (2 \times Ts ArCH), 129.6 (2 \times Ts ArCH), 127.2 (ArCH), 124.9 (ArC), 123.2 (ArC), 117.7 (ArCH), 116.0 (ArCH), 101.9 (ArCH), 83.2 (Boc C(CH$_3$)$_3$), 55.5 (OCH$_3$), 52.9 (C1), 27.6 (Boc (CH$_3$)$_3$), 26.0 (TBS (CH$_3$)$_3$), 25.8 (C2), 22.9 (C3), 21.8 (Ts CH$_3$), 18.4 (TBS C(CH$_3$)$_3$), -3.8 (TBS Si(CH$_3$)$_2$); HRMS (ESI$^+$) Calculate for C$_{32}$H$_{45}$NNaO$_7$SSi: 638.2578. Found [M+Na$^+$]: 638.2560.

tert-Butyl (3-(2-hydroxy-7-methoxynaphthalen-1-yl)propyl)(tosyloxy)carbamate (5o)

**General procedure D:** tert-Butyl (2-(2-((tert-butyldimethylsilyloxy)-7-methoxynaphthalen-1-yl) ethyl)(tosyloxy)carbamate (0.30 g, 0.50 mmol) and 1:1 TBAF/AcOH solution (0.1 M in THF, 0.50 mmol) in THF (10 mL) were employed. Purification by flash column chromatography (gradient, eluent 20 – 33 % EtOAc/hexane) afforded 5o (0.13 g, 51 %) as a pale yellow solid; Rf = 0.2 (20 % EtOAc/hexane); \(^1\)H NMR (400 MHz, CDCl$_3$) \( \delta \) 7.84 (2H, d, \( J = 8.1 \) Hz, Ts ArCH), 7.65 (1H, d, \( J = 8.9 \) Hz, ArCH), 7.54 (1H, d, \( J = 8.7 \) Hz, ArCH), 7.32 (2H, d, \( J = 8.0 \) Hz, Ts ArCH), 7.14 (1H, d, \( J = 2.3 \) Hz, ArCH), 6.99 (1H, dd, \( J = 8.9, 2.4 \) Hz, ArCH), 6.89 (1H, d, \( J = 8.7 \) Hz, ArCH), 5.34 (1H, br s, OH), 3.95 (3H, s, OCH$_3$), 3.76 (2H, br s, C1-H$_2$), 3.00 (2H, t, \( J = 7.8 \) Hz, C3-H$_2$), 2.43 (3H, s, Ts CH$_3$), 2.07 - 2.00 (2H, m, C2-H$_2$), 1.19 (9H, s, Boc (CH$_3$)$_3$); \(^{13}\)C NMR (101 MHz, CDCl$_3$) \( \delta \) 158.4 (ArC), 155.9 (C=O), 151.3 (ArC), 145.7 (Ts ArC), 134.3 (ArC), 131.2 (Ts ArC), 129.6 (2 \times Ts ArCH), 129.5 (2 \times Ts ArCH), 127.7 (ArCH), 124.7 (ArC), 117.7 (ArCH), 115.4 (ArCH), 115.3 (ArCH), 101.7 (ArCH), 83.5 (Boc C(CH$_3$)$_3$), 55.3 (OCH$_3$), 52.9 (C1), 27.5 (Boc (CH$_3$)$_3$), 25.8
(C2), 22.2 (C3), 21.7 (Ts CH3); HRMS (ESI†) Calculated for C26H31NNaO7S: 524.1713. Found [M+Na]+: 524.1708.

7-methoxy-2H-spiro[naphthalene-1,2'-pyrrolidin]-2-one (7o)

![Diagram of the reaction]

**General procedure E:** tert-Butyl (3-(2-hydroxy-7-methoxynaphthalen-1-yl)propyl)(tosyloxy) carbamate (5o) (50.2 mg, 0.10 mmol), TFA (15 μL, 0.20 mmol) and TFE (1 mL) were employed. After stirring at r.t. for 48 h, purification by flash column chromatography (gradient, eluent 50 % EtOAc/hexane – EtOAc) afforded 7o (17.4 mg, 76 %) as a yellow oil; Rf = 0.2 (EtOAc); νmax / cm⁻¹ (film) 3340 (m), 2963 (m), 2942 (m), 2865 (m), 1666 (s), 1601 (s), 1555 (m), 1279 (s), 1224 (s); ¹H NMR (400 MHz, CDCl3) δ 7.32 (1H, d, J = 9.8 Hz, C11-H), 7.23 (1H, d, J = 2.6 Hz, C6-H), 7.19 (1H, d, J = 8.3 Hz, C9-H), 6.75 (1H, dd, J = 8.3, 2.6 Hz, C8-H), 6.03 (1H, d, J = 9.8 Hz, C12-H), 3.85 (3H, s, OCH3), 3.44 (1H, dt, J = 10.2, 6.3 Hz, C1-H), 3.27 (1H, dt, J = 10.2, 6.3 Hz, C1'-H'), 2.92 (1H, br s, NH), 2.30 - 2.23 (1H, m, C3-H), 1.93 - 1.72 (3H, m, C3-H’ and C2-H2); ¹³C NMR (101 MHz, CDCl3) δ 204.9 (C13), 161.5 (C7), 151.2 (C5), 144.7 (C11), 130.9 (C9), 122.4 (C10), 120.8 (C12), 112.2 (C6), 112.0 (C8), 74.1 (C4), 55.4 (CH3), 49.9 (C1), 43.2 (C3), 25.1 (C2); HRMS (ESI†) Calculated for C14H15NNaO2: 252.0995. Found [M+Na]+: 252.1002.

2-(Cinnamyloxy)naphthalene

![Diagram of the reaction]

The title compound was prepared according to a literature procedure.²⁷

*Spectroscopic properties were consistent with the data available in the literature.*²⁷
The title compound was prepared according to a literature procedure.\textsuperscript{27} Spectroscopic properties were consistent with the data available in the literature.\textsuperscript{28}

tert-Butyldimethyl((1-(1-phenylallyl)naphthalen-2-yl)oxy)silane

To a solution of 1-(1-phenylallyl)naphthalen-2-ol (1.40 g, 5.30 mmol), in DMF (10 mL) was added tert-butyldimethylsilyl chloride (0.97 g, 6.45 mmol) and imidazole (0.91 g, 13.4 mmol) and the reaction mixture was stirred at r.t. overnight until completion by TLC analysis. The reaction was quenched with water (50 mL) and extracted with CH$_2$Cl$_2$ (3 × 20 mL). The organic phase was washed with brine (20 mL), dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. Purification by flash column chromatography (4\% EtOAc/hexane) afforded the title compound (1.37 g, 69\%) as a pale-yellow oil; $R_f$ = 0.4 (20\% EtOAc/hexane); $\nu_{\max}$ cm$^{-1}$ (film) 2955 (m), 2928 (m), 1622 (m), 1586 (m), 1463 (m), 1253 (m), 1236 (m); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.75 (1H, d, $J$ = 7.9 Hz, ArCH), 7.70 - 7.63 (2H, m, ArCH), 7.25 - 7.13 (8H, m, ArCH), 6.64 (1H, ddd, $J$ = 17.3, 10.1, 7.5 Hz, C$_2$-H), 5.91 (1H, d, $J$ = 7.6 Hz, C$_3$-H) 5.28 - 5.16 (2H, m, C$_1$-H), 0.99 (9H, s, TBS (CH$_3$)$_3$), 0.23 (6H, d, $J$ = 7.3 Hz, TBS Si(CH$_3$)$_2$); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 151.4 (ArC), 143.7 (ArC), 138.9 (C$_2$), 132.9 (ArC), 130.4 (ArC), 128.7 (ArCH), 128.6 (ArCH), 128.3 (2 × ArCH), 127.6 (2 × ArCH), 126.0 (ArC), 125.7 (2 × ArCH), 125.5 (ArCH), 123.2 (ArCH), 120.6 (ArCH), 117.5 (C1), 45.4 (C3), 26.0 (TBS (CH$_3$)$_3$), 18.5 (TBS SiC(CH$_3$)$_3$), -3.6 (TBS Si(CH$_3$)$_2$); HRMS (ESI$^+$) Calculated for C$_{25}$H$_{31}$NaOSi: 397.1958. Found [M+Na]$^+$: 397.1972.
tert-Butyl (3-(2-hydroxynaphthalen-1-yl)-3-phenylpropyl)(tosyloxy)carbamate (5p)

General procedure C and D: 3-(2-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)-3-phenylpropan-1-ol (0.27 g, 0.69 mmol), PPh₃ (0.22 g, 0.832 mmol), DIAD (0.16 mL, 0.83 mmol) and TsONHBoc (0.24 mg, 0.83 mmol) in anhydrous THF (4 mL) were employed. The product was purified by flash column chromatography (10 % EtOAc/hexane) to afford the desired product (0.40 g) which could not be obtained cleanly so was used crude in the next step using 1:1 TBAF/AcOH solution (0.1 M in THF, 0.60 mmol) in THF (12 mL). Purification by flash column chromatography (33 % EtOAc/hexane) afforded 5p (0.26 g, 71% over 2 steps) as
an off-white solid; m.p.: 75 - 78 °C (EtOAc/hexane); Rf = 0.1 (20% EtOAc/hexane); νmax / cm⁻¹ ¹ (film) 3410 (m, br), 2978 (m), 1721 (m), 1373 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.99 - 7.89 (1H, m, ArCH), 7.79 - 7.70 (3H, m, ArCH), 7.66 (1H, d, J = 8.8 Hz, ArCH), 7.46 - 7.37 (1H, m, ArCH), 7.35 - 7.26 (9H, m, ArCH), 7.00 (1H, d, J = 8.8 Hz, ArCH), 5.11 (1H, br s, OH), 4.99 (1H, t, J = 8.1 Hz, C3-H), 3.73 - 3.61 (1H, m, C1-H), 3.42-3.15 (1H,m, C1-H'), 2.84-2.51 (2H, m, C2-H2), 2.37 (3H, s, Ts CH₃), 1.15 (9H, s, Boc (CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 155.6 (C=O), 151.9 (ArC), 145.7 (Ts ArC), 142.9 (ArC), 133.2 (ArC), 131.3 (Ts ArC), 129.8 (ArC), 129.7 (2 x Ts ArCH), 129.6 (2 x Ts ArCH), 129.2 (ArCH), 129.0 (ArCH), 128.9 (ArCH), 127.5 (ArCH), 126.8 (ArCH), 126.6 (ArCH), 123.3 (ArCH), 121.3 (ArC), 119.2 (ArCH), 83.6 (Boc C(CH₃)₃), 52.3 (C1), 38.4 (C3), 28.0 (C2), 27.7 (Boc (CH₃)₂), 21.8 (Ts CH₃); HRMS (ESI⁺) Calculated for C₃₁H₃₅N₂O₆S: 570.1920. Found [M+Na]⁺: 570.1912.

**3'-phenyl-2H-spiro[naphthalene-1,2'-pyrrolidin]-2-one (7p)**

![Diagram](image)

**General procedure E:** tert-Butyl (3-(2-hydroxynaphthalen-1-yl)-3-phenylpropyl)(tosyloxy) carbamate (5p) (53.2 mg, 0.097 mmol) and TFA (15.0 μL, 0.19 mmol) in anhydrous TFE (1 mL) were employed. After stirring at r.t. for 22 h and purification by flash column chromatography (20% EtOAc/hexane) 7p (19.2 mg, 72%) was obtained as a 1:1 mixture of diastereomers A and B and as a pale-yellow solid. The diastereomers could not be separated by column chromatography.

**Data for mixture of diastereomers A + B:** Rf = 0.5 (50% EtOAc/hexane); νmax / cm⁻¹ (solid) 2961 (m), 2864 (m), 1650 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.85 (1H, d, J = 7.8 Hz, C6-H, B), 7.68 (1H, d, J = 7.8 Hz, C6-H, A), 7.47 (1H, td, J = 7.6, 1.4 Hz, C7-H, B), 7.38 (1H, td, J = 7.6, 1.3 Hz, C7-H, A), 7.30 - 7.25 (1H, m, C8-H, B), 7.18 - 7.09 (5H, m, 3 × PhCH₂, B, C8-H, A, C9-H, B), 7.05 - 7.00 (1H, m, PhCH₂, A), 6.93 - 6.90 (2H, m, 2 × PhCH₂, A), 6.85 - 6.81 (2H, m, C9-H, A, C11-H, A), 6.77 (1H, d, J = 9.9 Hz, C11-H, B), 6.71 - 6.68 (2H, m, 2 × PhCH₂, B), 6.52 - 6.48 (2H, m, 2 × PhCH₂, A), 6.03 (1H, d, J = 9.8 Hz, C12-H, A), 5.44 (1H, d, J = 9.9 Hz, C12-H, B), 3.69 (1H, ddd, J = 10.7, 8.1 Hz, C1-H, B), 3.56 - 3.49 (2H, m, C1-H₂, A), 3.40 -
3.25 (3H, m, C3-H, A+B, C1-H', B), 2.69 (2H, br s, NH, A+B), 2.57 - 2.46 (1H, m, C2-H, B), 2.44 - 2.33 (1H, m, C2-H, A), 2.22 - 1.26 (1H, m, C2-H, A), 2.04 - 1.98 (1H, m, C2-H', B); 13C NMR (101 MHz, CDCl3) δ 205.8 (C13, B), 205.2 (C13, A), 147.7 (C5, B), 145.9 (C11, A), 145.0 (C5, A), 143.8 (C11, B), 137.1 (PhC, B), 136.9 (PhC, A), 130.9 (C10, A), 130.5 (C10, B), 130.5 (C7, B), 129.3 (C7, A), 129.2 (2 × PhCH A), 128.7 (C9, A), 128.6 (PhCH, B), 128.1 (PhCH, B), 128.0 (C6, A), 127.6 (2 × PhCH, B), 127.3 (C8, B), 127.4 (C8, A/C9, B), 127.3 (C8, A/C9, B), 127.0 (PhCH, A), 126.9 (2 × PhCH, A), 126.8 (C6, B), 124.9 (C12, B), 124.1 (C12, A), 78.1 (C4, A), 77.2 (C4, B), 64.5 (C3, A/B), 61.8 (C3, A/B), 48.3 (C1, B), 47.3 (C1, A), 32.0 (C2, A), 30.0 (C2, B); HRMS (ESI+) Calculated for C19H17NNaO: 298.1202. Found [M+Na]+: 298.1200.

3-(2-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)-N-methoxy-N-methylpropanamide

**General procedure H:** 3-(2-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)propanoic acid (2.64 g, 8.00 mmol), N,O-dimethylhydroxylamine hydrochloride (1.09 g, 11.2 mmol), Et3N (1.56 mL, 11.2 mmol), 4-dimethylaminopyridine (1.37 g, 11.2 mmol), and N,N′-dicyclohexylcarbodiimide (2.31 g, 11.2 mmol) were employed. Purification by flash column chromatography (20 % EtOAc/hexane) afforded 3-(2-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)-N-methoxy-N-methylpropanamide (2.20 g, 74 %) as a pale yellow oil; Rf = 0.7 (33 % EtOAc/hexane); νmax / cm⁻¹ 2954 (m), 2930 (m), 2857 (m), 1664 (s), 1594 (m), 1466 (s), 1379 (m), 1242 (s), 1072 (m); 1H NMR (400 MHz, CDCl3) 8.02 (1H, d, J = 8.5 Hz, ArCH) δ 7.78 (1H, d, J = 8.4 Hz, ArCH), 7.64 (1H, d, J = 8.9 Hz, ArCH), 7.51 - 7.47 (1H, m, ArCH), 7.37 - 7.32 (1H, m, ArCH), 7.11 (1H, d, J = 8.8 Hz, ArCH), 3.59 (3H, s, C2-H3), 3.41 (2H, t, J = 8.1 Hz, C5-H2), 3.21 (3H, s, C1-H3), 2.73 (2H, t, J = 8.1 Hz, C4-H2), 1.07 (9H, s, TBS (CH3)3), 0.30 (6H, s, TBS Si(CH3)2); 13C NMR (101 MHz, CDCl3) δ 174.2 (C3) 150.7 (ArC), 133.2 (ArC), 129.5 (ArC), 128.5 (ArCH), 127.5 (ArCH), 126.3 (ArCH), 124.3 (ArC), 123.3 (ArCH), 123.1 (ArCH), 120.3 (ArCH), 61.2 (C2), 32.3 (C4), 31.9 (C1), 25.8 (TBS (CH3)3),
20.7 (C5), 18.3 (TBS C(CH₃)₃), -3.9 (TBS Si(CH₃)₂); HRMS (ESI⁺) Calculated for C₂₁H₃₁NNaO₃Si: 396.1965. Found [M+Na]⁺: 396.1976.

4-(2-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)butan-2-one

To a solution of 3-(2-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)-N-methoxy-N-methyl propanamide (0.94 g, 2.50 mmol) in anhydrous THF (6 mL) at 0 °C was added methylmagnesium bromide (3 M in Et₂O, 1.6 mL, 5.0 mmol) dropwise over 5 min. The reaction mixture was stirred at r.t. for 1 h until completion by TLC analysis. The reaction mixture was quenched by addition of sat. aq. NH₄Cl (5 mL) and the aqueous phase was extracted with EtOAc (3 × 5mL). The combined organic extracts were washed with brine (10 mL), dried over Na₂SO₄ and concentrated in vacuo to afford the title compound (0.61 g, 74 %) as a pale yellow oil which was used without further purification; Rf = 0.8 (33 % EtOAc/hexane); νmax / cm⁻¹ 2954 (m), 2929 (m), 2893 (m), 2857 (m), 1713 (s), 1622 (m), 1594 (m), 1466 (s), 1360 (m), 1242 (s), 1161 (m), 1075 (m); ¹H NMR (400 MHz, CDCl₃) δ 7.91 (1H, d, J = 8.5 Hz, ArCH), 7.79 (1H, d, J = 8.4 Hz, ArCH), 7.64 (1H, d, J = 8.8 Hz, ArCH), 7.49 (1H, ddd, J = 8.4, 6.8, 1.4 Hz, ArCH), 7.35 (1H, ddd, J = 8.0, 6.8, 1.1 Hz, ArCH), 7.10 (1H, d, J = 8.8 Hz, ArCH), 3.33 (2H, t, J = 8.2 Hz, C4-H₂), 2.74 (2H, t, J = 8.2 Hz, C3-H₂), 2.18 (3H, s, C1-H₃), 1.06 (9H, s, TBS (CH₃)₃), 0.29 (6H, s, TBS Si(CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 208.5 (C2), 150.6 (ArC), 133.0 (ArC), 129.5 (ArC), 128.6 (ArCH), 127.5 (ArCH), 126.4 (ArCH), 123.9 (ArC), 123.4 (ArC), 122.9 (ArCH), 120.2 (ArCH), 43.5 (C3), 29.9 (C1), 25.8 (TBS (CH₃)₃), 19.9 (C4), 18.3 (TBS C(CH₃)₃), -3.9 (TBS Si(CH₃)₂); HRMS (ESI⁺) Calculated for C₂₀H₂₈NaO₂Si: 351.1750. Found [M+Na]⁺: 351.1753.

4-(2-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)butan-2-ol
To a solution of 4-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)butan-2-one (0.56 g, 1.70 mmol) in MeOH (10 mL) was slowly added NaBH₄ (0.13 mg, 3.40 mmol) at 0 °C. The reaction was stirred at this temperature for 1.5 h until complete by TLC analysis. The reaction was quenched by addition of water (10 mL) and extracted with Et₂O (3 × 10 mL). The combined organic extracts were washed with brine (10 mL), dried over MgSO₄, filtered and the solvent removed in vacuo to afford the title compound (0.49 g, 87 %) as a pale yellow oil which was used without further purification.; Rf = 0.6 (33 % EtOAc/hexane); ν max / cm⁻¹ 3360 (m br), 2957 (m), 2928 (m), 2884 (m), 2857 (m), 1622 (m), 1594 (m), 1465 (m), 1241 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.97 (1H, d, J = 8.4 Hz), 7.78 (2H, d, J = 8.3 Hz), 7.62 (1H, d, J = 8.8 Hz), 7.48 (1H, ddd, J = 8.4, 6.8, 1.4 Hz), 7.35 (1H, ddd, J = 8.0, 6.8, 1.1 Hz), 7.10 (1H, d, J = 8.9 Hz), 3.73-3.65 (1H, m, C₂-H), 3.27-3.13 (2H, m, C₄-H₂), 2.29 (1H, br s, OH), 1.87 - 1.74 (2H, m, C₃-H₂), 1.19 (3H, d, J = 6.2 Hz, C₁-H), 1.06 (9H, s, TBS (CH₃)₃), 0.29 (6H, s, TBS Si(CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 150.3 (Ar C), 133.2 (Ar C), 129.8 (Ar C), 128.5 (Ar CH), 127.3 (Ar CH), 126.2 (Ar CH), 124.8 (Ar CH), 123.5 (Ar C), 123.4 (Ar CH), 120.5 (Ar CH), 67.1 (C₂), 38.9 (C₃), 25.9 (TBS (CH₃)₃), 23.1 (C₄), 21.6 (C₁), 18.4 (TBS Si(CH₃)₃), -3.9 (TBS Si(CH₃)₂); HRMS (ESI⁺) Calculated for C₂₀H₂₇NaO₂Si: 353.1907. Found [M+Na]⁺: 353.1894.

**tert-Butyl (4-(2-hydroxynaphthalen-1-yl)butan-2-yl)(tosyloxy)carbamate (5q)**

**General procedure C and D:** 4-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)butan-2-ol (0.22 g, 0.77 mmol), PPh₃ (0.24 g, 0.92 mmol), DIAD (0.18 mL, 0.92 mmol) and TsONHBoc (0.26 g, 0.92 mmol) in anhydrous THF (3 mL) were employed. The desired product could not be obtained pure so to the crude product in THF (5 mL) was added a solution of TBAF (1M in THF, 1.06 mL, 1.06 mmol) at 0 °C. The reaction mixture was stirred at this temperature for 1.5 h until complete by TLC. The reaction mixture was quenched with sat. aq. NH₄Cl (5 mL) and extracted with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine (10 mL), dried over MgSO₄, filtered and concentrated in vacuo. Purification by flash column
chromatography (gradient 20 – 33 % EtOAc/hexane) afforded 5q (0.32 g, 69 %) as a colorless solid; Rf = 0.4 (33 % EtOAc/hexane); \( \nu_{\text{max}} / \text{cm}^{-1} \) (solid) 3461 (m, br) 2975 (m), 1688 (s), 1386 (s); \(^1\)H NMR (400 MHz, CD\(_3\)OD) \( \delta \) 7.83 (3H, d, \( J = 8.3 \) Hz, ArCH), 7.72 (1H, d, \( J = 8.1 \) Hz, ArCH), 7.58 (1H, d, \( J = 8.8 \) Hz, ArCH), 7.42 - 7.33 (3H, m, ArCH), 7.24 (1H, t, \( J = 7.5 \) Hz, ArCH), 7.09 (1H, d, \( J = 8.8 \) Hz, ArCH), 4.00 (1H, sextet, \( J = 6.9 \) Hz, C2-H), 3.03 (2H, dd, \( J = 9.3, 6.6 \) Hz, C4-H\(_2\)), 2.38 (3H, s, Ts C\(_3\)H\(_3\)), 1.94 - 1.83 (1H, m, C3-H'), 1.77 - 1.66 (1H, m, C3-H'), 1.27 (3H, d, \( J = 6.7 \) Hz, C1-H), 1.20 (9H, s, Boc (CH\(_3\))\(_3\)); \(^{13}\)C NMR (101 MHz, CD\(_3\)OD) \( \delta \) 157.9 (C=O), 153.3 (Ar C), 147.4 (Ts ArC), 134.7 (ArC), 132.9 (ArC), 130.8 (2 \times Ts ArCH), 130.7 (2 \times Ts ArCH), 130.4 (ArC), 129.5 (ArCH), 128.5 (ArCH), 127.1 (ArCH), 123.7 (ArCH), 123.4 (ArCH), 120.3 (ArC), 118.6 (ArCH), 84.7 (Boc C(CH\(_3\))\(_3\), 62.8 (C2), 35.2 (C3), 27.9 (Boc (CH\(_3\))\(_3\)), 22.8 (C4), 21.6 (Ts CH\(_3\)), 17.8 (C1); HRMS (ESI\(^+\)) Calculated for C\(_{26}\)H\(_{31}\)NNaO\(_6\)Si: 508.1764. Found [M+Na]\(^+\): 508.1756.

5'-Methyl-2H-spiro[naphthalene-1,2'-pyrrolidin]-2-one (7q)

\[
\text{General procedure E: } \text{tert-Butyl (4-(4-hydroxyphenyl)butan-2-yl)(tosyloxy)carbamate (5q)} \quad (97.1 \text{ mg, 0.20 mmol) and TFA (30 } \mu\text{L, 0.4 mmol) in 5:1 TFE/CH}_2\text{Cl}_2 \text{ (3 mL) were stirred at r.t. for 48 h. Purification by flash column chromatography (20 – 33 % EtOAc/hexane – 100 % EtOAc) afforded 7q (23.0 mg, 54 %) as a 1.5:1 mixture of diastereomers A and B and as a yellow solid.} \\
Rf = 0.5 (2:1 EtOAc/hexane); \( \nu_{\text{max}} / \text{cm}^{-1} \) 3337 (s), 2963 (s), 2916 (s), 2850 (s), 1668 (s), 1084 (s); HRMS (ESI\(^+\)) Calculated for C\(_{14}\)H\(_{15}\)NNaO: 236.1046. Found [M+Na]\(^+\): 236.1046.

Data for the major diastereomer: m.p.: 89 - 90 °C (EtOAc/hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.67 (1H, d, \( J = 7.8 \) Hz, C7-H), 7.41 - 7.35 (2H, m, C8-H, C12-H), 7.26 - 7.24 (2H, m, C9-H, C10-H), 6.18 (1H, d, \( J = 9.9 \) Hz, C13-H), 3.63 - 3.55 (1H, m, C2-H), 2.42 (1H , br s, NH) overlapping 2.45 - 2.39 (1H, ddd, \( J = 12.9, 7.0, 2.8 \) Hz, C4-H), 1.92 - 1.86 (1H, dddd, \( J = 11.5, 6.4, 5.1, 2.8 \) Hz, C3-H), 1.82 - 1.74 (1H, ddd, \( J = 13.0, 10.8, 6.2 \) Hz, C4-H'), 1.42 - 1.35 (1H,
m, C3-H') overlapping 1.39 (3H, d, J = 6.2 Hz, C1-H3); 13C NMR (101 MHz, CDCl3) δ 204.3 (C14), 149.1 (C6), 144.6 (C12), 130.4 (C8), 129.1 (C10), 128.9 (C11), 126.9 (C9), 125.8 (C7), 123.4 (C13), 74.8 (C5), 58.2 (C2), 42.9 (C4), 33.3 (C3), 20.2 (C1).

Data for the minor diastereomer: 1H NMR (400 MHz, CDCl3) δ 7.85 (1H, dd, J = 7.8, 1.0 Hz), 7.42 - 7.32 (2H, m, C8-H, C12-H), 7.28 - 7.22 (2H, m, C9-H, C10-H), 6.15 (1H, d, J = 9.9 Hz, C13-H), 3.76 - 3.67 (1H, m, C2-H), 2.72 (1H, br s, NH2), 2.25 (1H, ddd, J = 12.4, 10.1, 6.8 Hz, C4-H), 1.90 (1H, dddd, J = 12.4, 6.8, 5.7, 3.5 Hz, C3-H), 1.81 (1H, ddd, J = 12.4, 6.8, 5.7 Hz, C3-H'), 1.53 (1H, dddd, J = 11.8, 10.0, 8.9, 6.9 Hz, C3-H'), 1.33 (3H, d, J = 6.2 Hz, C1-H3); 13C NMR (101 MHz, CDCl3) δ 206.5 (C14), 149.2 (C6), 144.4 (C12) 130.0 (C8), 129.5 (C10), 129.2 (C11), 127.1 (C9), 126.6 (C7), 124.0 (C13), 74.0 (C5), 55.9 (C2), 42.7 (C4), 32.6 (C3), 22.3 (C1).

The stereochemistry of the major diastereomer was determined unambiguously by X-ray crystallography.

1-(2-Phenylacetyl)-1-azaspiro[4.5]deca-6,9-dien-8-one (9a)

A solution of 1-Azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7a) (19.2 mg, 0.073 mmol) in anhydrous THF (0.36 mL) under an atmosphere of nitrogen was cooled to 0 °C and phenylacetyl chloride (19.4 μL, 0.147 mmol) and K3PO4 (62.2 mg, 0.293 mmol) were added.
The reaction was warmed to r.t. and stirred overnight and monitored by TLC. Upon completion, the reaction was quenched with water (1 mL) and extracted with EtOAc (3 × 2 mL). The combined organic extracts were dried over Na$_2$SO$_4$, filtered and concentrated in vacuo. Purification by flash column chromatography (gradient, eluent 50 % EtOAc/pentane – 100 % EtOAc) afforded 9a (12.2 mg, 63 %) as a 3:1 mixture of rotamers A+B and as a colorless, viscous oil; R$_f$ = 0.3 (3% MeOH/CH$_2$Cl$_2$); v$_{max}$/cm$^{-1}$ (film) 3029 (m), 2972 (m), 2881 (m), 1659 (s), 1622 (s), 1395 (s); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.35 - 7.10 (5H, m, 5 × PhCH$_2$, A + B), 6.95 (0.50 H, d, J = 10.0 Hz, 0.50 × C$_5$-H$_2$, B), 6.76 (1.50 H, d, J = 10.0 Hz, 1.50 × C$_5$-H$_2$, A), 6.32 (0.50 H, d, J = 10.0 Hz, 0.50 × C$_6$-H$_2$, B), 6.25 (1.50 H, d, J = 10.0 Hz, 1.5 × C$_1$-H$_2$, A), 3.86 (0.5 H, t, J = 6.9 Hz, 0.50 × C$_1$-H$_2$, B), 2.25 (0.50 H, t, J = 6.9 Hz, 0.50 × C$_3$-H$_2$, B), 2.12 - 1.99 (3.5 H, m, 3.5 H × C$_2$ + C$_3$-H$_2$, A + B); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 185.4 (C$_7$, A), 184.4 (C$_7$, B), 170.7 (C$_8$, B), 169.5 (C$_8$, A), 51.2 (C$_5$, B) 150.7 (C$_5$, A), 134.8 (PhC$_2$, B), 134.2 (PhC$_2$, A), 129.4 (PhCH$_2$, B), 129.0 (2 × PhCH$_2$, A), 128.9 (2 × PhCH$_2$, A), 128.7 (PhCH$_2$, B), 128.5 (C$_6$, B), 128.3 (C$_6$, A), 127.1 (PhCH$_2$, A), 126.9 (PhCH$_2$, B), 62.7 (C$_4$, A), 62.0 (C$_4$, B), 49.0 (C$_1$, B), 48.5 (C$_1$, A), 42.8 (C$_9$, A), 42.0 (C$_3$, B), 39.9 (C$_9$, B), 38.9 (C$_3$, A), 24.5 (C$_2$, A), 22.6 (C$_2$, B); HRMS (ESI$^+$) Calculated for C$_{17}$H$_{18}$NO$_2$: 268.1332. Found [M+H]$^+$: 268.1325.

(6$^R$, 6a$^S$, 10a$^S$)-6-Phenyl-2,3,6a,7-tetrahydro-1H,5H-pyrrolo[2,1-i]indole-5,8(6H)-dione (10a)

To a solution of 1-(2-phenylacetyl)-1-azaspiro[4.5]deca-6,9-dien-8-one (9a) (26.7 mg, 0.10 mmol) in anhydrous THF (1 mL) at -78 °C and under an atmosphere of nitrogen was added 1.5 eq. lithium bis(trimethylsilyl)amide (1.0 M in THF, 0.15 mL, 0.15 mmol). The reaction was stirred at this temperature for 2 h and monitored by TLC. Upon completion, the reaction mixture was warmed to 0 °C and quenched with sat. aq. NH$_4$Cl (0.3 mL) and extracted with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine (5 mL), dried over
anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. Purification by flash column chromatography (EtOAc) afforded 10a (17.9 mg, 67 %; > 20:1 d.r.) as a colorless oil; Rf = 0.4 (3 % MeOH/CH₂Cl₂); νₘₐₓ / cm⁻¹ (film) 2920 (m), 1677 (br s), 1395 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.39 - 7.27 (3H, m, PhCH), 7.15 - 7.11 (2H, m, PhCH), 6.64 (1H, dd, J = 10.3, 1.9 Hz, C9-H), 6.13 (1H, dd, J = 10.3, 1.1 Hz, C10-H), 3.97 (1H, ddd, J = 12.4, 7.3, 5.2 Hz, C5-H), 3.68 (1H, d, J = 12.2 Hz, C3-H), 3.28 - 3.20 (1H, m, C5-H'), 2.71 - 2.62 (2H, m, C2-H, C1-H), 2.49 - 2.43 (1H, m, C1-H'), 2.32 - 2.21 (1H, m, C6-H), 2.19 - 2.11 (1H, m, C6-H'), 2.10 - 2.02 (2H, m, C7-H); ¹³C NMR (101 MHz, CDCl₃) δ 196.0 (C11), 173.5 (C4), 146.9 (C9), 135.7 (PhC), 129.2 (2 × PhCH), 129.0 (2 × PhCH), 128.0 (C10), 127.8 (PhCH), 65.3 (C8), 56.3 (C3), 51.5 (C2), 42.7 (C5), 36.3 (C1), 35.6 (C7), 26.3 (C6). HRMS (ESI⁺) Calculated for C₁₇H₁₇NNaO₂: 290.1151. Found [M+Na]⁺: 290.1155.

The relative stereochemistry of this compound was determined by nOe experiments as indicated on the compound structure. nOes were observed between C3-H and C9-H.

4-Ethyl-1-(2-phenylacetyl)-1-azaspiro[4.5]deca-6,9-dien-8-one (9g)

The title compound was prepared using the same procedure as for 9a using 4-Ethyl-1-azaspiro[4.5]deca-6,9-dien-8-one salt (7g) (43.7 mg, 0.15 mmol), 2.5 eq. phenylacetyl chloride (26 μL, 0.2 mmol) and K₃PO₄ (67.9 mg, 0.32 mmol) in anhydrous THF (1 mL). Purification by flash column chromatography (gradient, eluent 50% EtOAc/pentane – 100% EtOAc) afforded 9g (18.7 mg, 79 %) as a 2.3:1 mixture of rotamers A:B and a colorless oil; Rf = 0.3 (3 % MeOH/CH₂Cl₂); νₘₐₓ / cm⁻¹ (film) 2962 (m), 2930 (m), 2876 (m), 1660 (s), 1623 (s), 1454 (m), 1397 (s), 1384 (s), 719 (m); ¹H NMR (400 MHz, CDCl₃) δ 7.33 - 7.17 (4.40 H, m, PhC₉H₅, A+B), 7.13 - 7.10 (0.60 H, m, 2 × PhC₉H₅, B), 6.82 - 6.70 (0.60 H, m, 0.60 × C7-H, B), 6.67 (0.70 H, dd, J = 10.0, 3.0 Hz, 0.70 × C7-H, A), 6.57 (0.70 H, dd, J = 10.0, 3.0 Hz, 0.70 × C7-H, A), 6.40 - 6.34 (0.60 H, m, 0.60 × C8-H, B), 6.34 - 6.26 (1.40 H, m, 1.40 × C8-H, A), 4.09 (0.3 H, dd, J = 12.3, 8.1 Hz, 0.3 × C1-H), 3.82 (0.7 H, t, J = 9.2 Hz, 0.7 × C1-H), 3.65 - 3.52
(2.40 H, m, 2.40 × C1-H, A+B, C11-H2, A), 3.43 (0.6 H, d, J = 4.6 Hz, 0.6 × C11-H2, B), 2.31 - 2.25 (1H, m, C2-H, A+B), 2.23 - 2.14 (0.30 H, m, 0.30 × C3-H, B), 2.02 - 1.95 (0.70 H, m, 0.70 × C3-H, A), 1.76 - 1.64 (0.70 H, m, 0.70 × C2-H’, A), 1.63 - 1.55 (0.3 H, m, 0.30 × C2-H’, B), 1.27 - 1.17 (1H, m, C4-H, A+B), 1.06 - 0.95 (1H, m, C4-H’, A+B), 0.93 - 0.84 (3H, m, C5-H3, A+B); 13C NMR (101 MHz, CDCl3) δ 185.8 (C9, A), 184.7 (C9, B), 170.6 (C10, B), 169.5 (C10, A), 152.1 (C7, A), 152.0 (C7, B), 147.8 (C7, B), 146.4 (C7, A), 134.8 (PhC, B), 134.1 (PhC, A), 130.4 (C8, A), 129.9 (C8, B), 129.6 (C8, B), 129.3 (PhCH, B), 128.9 (PhCH, A + B), 128.7 (PhCH, A + B), 128.3 (PhCH, A + B), 128.2 (C8, A), 126.9 (PhCH, A + B), 126.7 (PhCH, B), 65.7 (C6, A), 65.5 (C6, B), 53.5 (C3, B), 50.6 (C3, A), 47.4 (C1, B), 47.3 (C1, A), 42.5 (C11, A), 40.1 (C11, B), 29.9 (C2, A), 27.8 (C2, B), 21.3 (C4, A + B), 12.5 (C5, A + B); HRMS (ESI⁺) Calculated for C19H21NNaO2: 318.1464. Found [M+Na]⁺: 318.1472.

(1R*, 6R*, 6aS*, 10aS*) and (1S*, 6R*, 6aS*, 10aS*)-1-Ethyl-6-phenyl-2,3,6a,7-tetrahydro-1H,5H-pyrrolo[2,1-i]indole-5,8(6H)-dione (10g)

The title compound was prepared using the same procedure as for 10a employing 4-ethyl-1-(2-phenylacetyl)-1-azaspiro[4.5]deca-6,9-dien-8-one (9g) (29.5 mg, 0.100 mmol) and 1.5 eq. lithium bis(trimethylsilyl)amide (1 M in THF) in anhydrous THF (1 mL). Purification by flash column chromatography (50 % EtOAc/hexane) afforded 10g (16.6 mg, 56 %) as a 3:1 mixture of diastereomers A and B and as a colorless solid.

Rf = 0.6 (3% MeOH/CH2Cl2); νmax / cm⁻¹ (solid) 2963 (m), 2929 (m), 2877 (m), 1693 (s), 1675 (s), 1394 (s); HRMS (ESI⁺) Calculated for C19H21NNaO2: 318.1464. Found [M+Na]⁺: 318.1469.

Data for the major diastereomer A: m.p. 194 °C (EtOAc/hexane); 1H NMR (400 MHz, CDCl3) δ 7.36 - 7.32 (2H, m, PhCH), 7.30 - 7.24 (1H, m, PhCH), 7.15 - 7.12 (2H, m, PhCH), 6.62 (1H,
dd, $J = 10.4, 1.7$ Hz, C10-\(\text{-H}^\text{2}\), 6.22 (1H, d, $J = 10.4$ Hz, C11-\(\text{-H}^\text{2}\)), 3.77 - 3.71 (1H, m, C4-\(\text{-H}^\text{2}\)), 3.68 (1H, d, $J = 12.0$ Hz, C3-\(\text{-H}^\text{2}\)), 3.43 (1H, t, $J = 10.6$ Hz, C4-\(\text{-H}^\text{2}\))’, 2.71 (1H, dd, $J = 12.3, 6.1$ Hz, C2-\(\text{-H}^\text{2}\)), 2.65 - 2.53 (2H, m, C1-\(\text{-H}^\text{2}\), C5-\(\text{-H}^\text{2}\)), 2.50 - 2.43 (1H, m, C1-\(\text{-H}^\text{2}\))’, 2.10 - 1.91 (2H, m, C6-\(\text{-H}^\text{2}\), C5-\(\text{-H}^\text{2}\))’, 1.62 - 1.52 (1H, m, C7-\(\text{-H}^\text{2}\)), 1.37 - 1.23 (1H, m, C7-\(\text{-H}^\text{2}\))’, 0.99 (3H, t, $J = 7.4$ Hz, C8-\(\text{-H}^\text{2}\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) $\delta$ 196.3 (C=O), 171.8 (C=O), 144.1 (C10), 135.8 (PhC), 129.4 (C11), 129.3 (2 × PhCH), 122.9 (2 × PhCH), 127.8 (PhCH), 67.7 (C9), 57.8 (C3), 51.7 (C2), 51.4 (C6), 40.5 (C4), 36.8 (C1), 32.3 (C5), 23.7 (C7), 13.0 (C8).

Data for the minor diastereomer B: \(^1\)H NMR (400 MHz, CDCl\(_3\)) $\delta$ 7.38 - 7.32 (2H, m, PhCH), 7.32 - 7.28 (1H, m, PhCH), 7.14 - 7.10 (2H, m, PhCH), 6.58 (1H, dd, $J = 10.2, 1.9$ Hz, C10-\(\text{-H}^\text{2}\)), 6.16 (1H, dd, $J = 10.2, 0.9$ Hz, C11-\(\text{-H}^\text{2}\)), 4.05 (1H, ddd, $J = 10.8, 7.3, 2.7$ Hz, C4-\(\text{-H}^\text{2}\)), 3.62 (1H, d, $J = 12.3$ Hz, C3-\(\text{-H}^\text{2}\)), 3.14 - 3.06 (1H, m, C4-\(\text{-H}^\text{2}\))’, 2.76 (1H, dd, $J = 12.4, 5.7$ Hz, C2-\(\text{-H}^\text{2}\)), 2.56 - 2.41 (2H, m, C1-\(\text{-H}^\text{2}\)), 2.33 - 2.25 (1H, m, C5-\(\text{-H}^\text{2}\)), 2.17 - 2.08 (1H, m, C6-\(\text{-H}^\text{2}\)), 1.78 - 1.68 (1H, m, C7-\(\text{-H}^\text{2}\)), 1.64 - 1.55 (1H, m, C5-\(\text{-H}^\text{2}\))’, 1.47 - 1.35 (1H, m, C7-\(\text{-H}^\text{2}\))’, 1.03 (3H, t, $J = 7.3$ Hz, C8-\(\text{-H}^\text{2}\)); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) $\delta$ 196.1 (C=O), 174.6 (C=O), 148.8 (C10), 135.8 (PhC), 129.4 (2 × PhCH), 129.0 (2 × PhCH), 128.2 (C11), 127.9 (PhCH), 66.4 (C9), 55.6 (C3), 48.9 (C6), 46.3 (C2), 42.9 (C4), 36.2 (C1), 31.9 (C5), 22.4 (C7), 13.2 (C8).

The relative stereochemistry of the minor diastereomer was determined by nOe experiments as indicated on the compound structure; nOes were observed between C2-\(\text{-H}^\text{2}\) and C7-\(\text{-H}^\text{2}\) and between C6-\(\text{-H}^\text{2}\) and C10-\(\text{-H}^\text{2}\). The major diastereomer was determined unambiguously by X-ray crystallography.
(1R*, 6aR*, 10aS*) and (1S*, 6aR*, 10aS*)-1-Ethyl-6-phenyl-2,3,6a,7-tetrahydro-1H,5H-benzo[4]pyrrolo[1,2-c]imidazole-5,8(6H)-dione (11g)

A solution of 4-ethyl-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (45.0 mg, 0.154 mmol) in anhydrous CH₂Cl₂ (0.77 mL, 0.2 M) was cooled to 0 °C and phenyl isocyanate (34.0 μL, 0.308 mmol) and Et₃N (86.0 μL, 0.618 mmol) was added. The reaction was stirred at this temperature for 2 h before warming to r.t. and stirring overnight, monitoring by TLC. Upon completion, the reaction mixture was quenched with sat. aq. NH₄Cl (1 mL) and extracted with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine (5 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. Purification by flash column chromatography (33 % EtOAc/hexane) afforded 11g (34.1 mg, 75 %) as a colorless solid. A mixture of diastereomers A and B were obtained in a 4:1 ratio.

Rᵣ = 0.6 (3 % MeOH/CH₂Cl₂); νmax / cm⁻¹ (solid) 2965 (m), 2926 (m), 2885 (m), 1692 (s), 1683 (s), 1380 (s), 1309 (s); HRMS (ESI⁺) Calculated for C₁₈H₂₀N₂NaO₂: 319.1417. Found [M+Na]⁺: 319.1426.

Data for the major diastereomer A: m.p.: 148 - 151 °C (EtOAc/hexane); ¹H NMR (400 MHz, CDCl₃) δ 7.37 - 7.30 (4H, m, PhCH), 7.17 - 7.11 (1H, m, PhCH), 6.57 (1H, d, J = 10.3 Hz, C₇-H), 6.21 (1H, d, J = 10.3 Hz, C₈-H), 4.57 (1H, app. t, J = 6.2 Hz, C₁₁-H), 3.87 - 3.78 (1H, m, C₁-H'), 3.43 - 3.35 (1H, m, C₁-H'), 2.84 (1H, dd, J = 16.3, 5.8 Hz, C₁₀-H), 2.66 (1H, dd, J = 16.3, 7.0 Hz, C₁₀-H'), 2.45 - 2.36 (1H, m, C₂-H), 2.08 - 1.98 (1H, m, C₃-H), 1.88 - 1.76 (1H, m, C₂-H'), 1.54 - 1.44 (1H, m, C₄-H'), 1.39 - 1.28 (1H, m, C₄-H'), 0.99 (3H, t, J = 7.4 Hz, C₅-H₃); ¹³C NMR (101 MHz, CDCl₃) δ 195.6 (C₉), 159.4 (C₁₄), 142.4 (C₇), 137.3 (PhC), 129.6
(C8), 129.3 (PhCH), 125.1 (PhCH), 122.2 (PhCH), 64.8 (C6), 58.6 (C12), 50.1 (C3), 43.9 (C1), 39.6 (C11), 30.9 (C2), 25.6 (C4), 13.2 (C5).

The minor diastereomer could not be isolated in a pure form.

Data for minor diastereomer B: Characteristic peaks only: 1H NMR (400 MHz, CDCl3) δ 6.48 (1H, d, J = 10.2 Hz, C7-H), 6.14 (1H, d, J = 10.2 Hz, C8-H), 4.51 - 4.48 (1H, m, C11-H), 3.94 - 3.87 (1H, m, C1-H), 3.20 (1H, td, J = 11.5, 5.0 Hz, C11-H'), 2.78 (1H, dd, J = 17.5, 4.8 Hz, C10-H'), 2.57 (1H, dd, J = 17.7, 2.8 Hz, C10-H

The relative stereochemistry of the major diastereomer of this compound was determined by nOe experiments as indicated on the compound structure. nOes were observed between C3-H and C11-H and between C4-H2 and C7-H.

9-Methyl-1-(2-phenylacetyl)-1-azaspiro[4.5]deca-7,9-dien-6-one

![Chemical structure](image)

The title compound was prepared using the same procedure as for 9a employing 9-Methyl-1-azaspiro[4.5]deca-7,9-dien-6-one tosylate (0.150 mmol), phenylacetyl chloride (40.0 μL, 0.300 mmol) and K3PO4 (127.4 mg, 0.600 mmol) in anhydrous THF (0.75 mL). Purification by flash column chromatography (EtOAc) afforded the title compound (34.0 mg, 81%) as a 9:1 mixture of rotamers A:B and as a yellow oil; Rf = 0.4 (3 % MeOH/CH2Cl2); νmax / cm⁻¹ (film) 2972 (m), 2878 (m), 1675 (s), 1642 (s), 1406 (s); 1H NMR (400 MHz, CDCl3) δ 7.32 - 7.27 (2H, m, PhC-H, A+B), 7.25 - 7.20 (2.90H, m, PhCH, A+B), 7.13 - 7.09 (0.10H, m, 0.10 × PhCH, B), 6.93 (0.10H, dd, J = 9.8, 2.4 Hz, 0.10 × C8-H, B), 6.32 (0.90H, dd, J = 9.9, 2.4 Hz, 0.90 × C8-H, A), 6.18 - 6.09 (1.10H, m, 1.00 × C9-H, A+B, 0.10 × C5-H, B), 5.90 - 5.87 (0.90H, m, 0.90 × C5-H, A), 3.97 - 3.91 (0.10H, m, 0.1 × C1-H, B), 3.78 - 3.69 (0.9H, m, 0.90 × C1-H, A), 3.67 - 3.60 (2.8H, m, 1.00 × C1-H', A+B, 1.80 × C12-H2, A), 3.12 (0.20H, m, 0.20 × C12-H2, B), 2.28 - 2.22 (0.10H, m, 0.10 × C3-H, B), 2.21 - 2.13 (1H, m, 0.90 × C2-H, A, C3-H', B), 2.10 - 1.95 (2.30H, m, 1.00 × C3-H', A+B, 1.00 × C2-H', A+B, 0.30 × C7-H3, B), 1.92 (2.70H, s, C7-H3, A), 1.89 - 1.82 (1H, m, 0.90 × C3-H, A, 0.10 × C2-H, B); 13C NMR (101 MHz, CDCl3) δ
208.6 (C10, B), 200.1 (C11, A), 170.3 (C11, B), 168.6 (C11, A), 145.5 (C8, B), 145.0 (C8, A), 140.3 (C5, B), 137.5 (C5, A), 134.5 (PhC, A+B), 129.6 (2 × PhCH, B), 129.2 (2 × PhCH, A), 128.7 (2 × PhCH, A), 128.3 (2 × PhCH, B), 126.8 (PhCH, A), 126.6 (PhCH, B), 125.8 (C9), 125.1 (C9, B), 70.1 (C4, A), 49.0 (C1, B), 48.8 (C1, A), 41.9 (C12, A), 40.7 (C12, B), 40.3 (C3, B), 37.6 (C3, A+B), 24.0 (C2, A), 21.1 (C7, A), 20.9 (C7, B); HRMS (ESI+) Calculated for C18H19NNaO2: 304.1308. Found [M+Na]+: 304.1318.

(6R*, 6aS*)-6a-Hydroxy-9-methyl-6-phenyl-2,3,6a-tetrahydro-1H,5H-pyrrolo[2,1-i]indol-5-one (12k)

![Chemical Structure](image)

The title compound was prepared using the same procedure as for 10a employing 9-methyl-1-(2-phenylacetyl)-1-azaspiro[4.5]deca-7,9-dien-6-one (28.1 mg, 0.10 mmol) and 1.5 eq. lithium bis(trimethylsilyl)amide (1.0 M in THF) in anhydrous THF (1 mL). Purification by flash column chromatography afforded 12k (18.9 mg, 67 %, > 15:1 d.r.) as a colorless solid; m.p.: 150 - 152 °C (EtOAc/hexane); Rf = 0.5 (3% MeOH/CH2Cl2); νmax / cm⁻¹ (solid) 3356 (br m), 2969 (m), 2942 (m), 2880 (m), 1673 (s), 1402 (s); 1H NMR (400 MHz, CDCl3) δ 7.38 - 7.31 (3H, m, PhC₇H), 7.28 - 7.24 (2H, m, PhC₇H), 5.78 (1H, dd, J = 9.8, 1.5 Hz, C₈-Η), 5.53 (1H, m, C₅-Η), 5.38 (1H, d, J = 9.8 Hz, C₉-Η), 4.27 (1H, s, C₁₁-Η), 3.89 (1H, ddd, J = 12.9, 8.4, 6.1 Hz, C₃-Η), 2.54 (1H, ddd, J = 12.9, 8.4, 6.1 Hz, C₃-Η'), 1.54 (1H, dt, J = 12.9, 7.3 Hz, C₇-Η'), 13C NMR (101 MHz, CDCl3) δ 172.8 (C₁₂), 134.2 (2 × PhCH), 131.3 (C₉), 131.2 (PhC), 128.6 (2 × PhCH), 128.6 (C₆), 128.0 (PhCH), 127.0 (C₅), 126.7 (C₈), 79.1 (C₁₀), 72.7 (C₄), 61.6 (C₁₁), 42.9 (C₁), 30.6 (C₃), 26.2 (C₂), 21.2 (C₇); HRMS (ESI+) Calculated for C_{18}H_{19}NNaO₂: 304.1308. Found [M+Na]⁺: 304.1322.

The relative stereochemistry of this compound was determined unambiguously using X-ray crystallography.
(6aR*, 10aR*)-7-Methyl-6-phenyl-2,3,6a,9-tetrahydro-1H,5H-benzo[d]pyrrolo[1,2-c]imidazole-5,10(6H)-dione (11k)

A solution of 9-Methyl-1-azaspiro[4.5]deca-7,9-dien-6-one tosylate (7k) (0.15 mmol) in anhydrous CH₂Cl₂ (0.2 M) was cooled to 0 °C and 1.1 eq. phenyl isocyanate (18 μL, 0.17 mmol) and Et₃N (84 μL, 0.60 mmol) were added. The reaction was stirred at this temperature for 3 h then heated to 40 °C and stirred overnight, monitoring by TLC analysis. Upon completion, the reaction mixture was cooled to r.t., quenched with sat. aq. NH₄Cl (1 mL) and extracted with EtOAc (3 × 5 mL). The combined organic phases were washed with brine (5 mL), dried over Na₂SO₄, filtered and concentrated in vacuo. Purification by flash column chromatography (1% MeOH/CH₂Cl₂) afforded 11k (28.9 mg, 68 %) as a colorless solid; m.p.: 110 - 113 °C (EtOAc/hexane); Rf = 0.6 (3 % MeOH/CH₂Cl₂); v_max / cm⁻¹ (solid) 2987 (m), 2953 (m), 2916 (m), 1726 (s), 1693 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.40 - 7.35 (4H, m, PhC_H), 7.21 - 7.16 (1H, m, PhC_H), 5.59 - 5.55 (1H, m, C_8-H), 4.74 (1H, s, C_5-H), 3.94 - 3.87 (1H, m, C_1-H), 3.68 - 3.60 (1H, m, C_9-H), 2.88 (1H, ddd, J = 12.2, 9.0, 6.5 Hz, C_1-H'), 2.79 - 2.70 (2H, m, C_9-H', C_3-H), 2.00 - 1.85 (2H, m, C_2-H'), 1.55 - 1.46 (1H, m, C_3-H'), 1.41 (3H, s, C_7-H₃); ¹³C NMR (101 MHz, CDCl₃) δ 204.6 (C_10), 161.5 (C_11), 138.9 (PhC), 134.4 (C_6), 129.3 (2 × PhCH), 125.8 (PhCH), 123.9 (2 × PhCH), 121.6 (C_8), 70.9 (C_4), 66.5 (C_5), 45.9 (C_1), 36.5
(C9), 29.4 (C3), 23.7 (C2), 22.6 (C7); HRMS (ESI+) Calculated for C_{17}H_{18}N_{2}NaO_{2}: 305.1260. Found [M+Na]^+: 305.1273.

The relative stereochemistry was determined using nOe analysis as indicated on the compound structure. An nOe was observed between C5-H and C3-H2.

3-(3-Methoxyphenyl)propan-1-ol

General procedure 2: 3-(3-Methoxyphenyl)propanoic acid (0.54 g, 3.00 mmol) and 2.0 eq. LiAlH4 (1 M in THF) in anhydrous Et2O were employed to afford the title compound (0.34 mg, 68 %) as a pale yellow oil which was used without further purification; 1H NMR (400 MHz, CDCl3) δ 7.23 - 7.19 (1H, m), 6.82 - 6.79 (1H, m), 6.77 - 6.73 (2H, m), 3.80 (3H, s), 3.66 (2H, t, J = 6.5 Hz), 2.71 - 2.67 (2H, m), 2.14 (1H, br s), 1.92 - 1.85 (2H, m). Spectroscopic properties were consistent with the data available in the literature.

tert-Butyl (3-(3-methoxyphenyl)propyl)(tosyloxy)carbamate (13a)

General procedure C: 3-(3-Methoxyphenyl)propan-1-ol (0.24 mg, 1.50 mmol), PPh3 (0.47 mg, 1.80 mmol), DIAD (0.35 mL, 1.80 mmol) and TsONHBoc (517 mg, 1.80 mmol) in anhydrous THF (8 mL) were employed. Purification by flash column chromatography (gradient, eluent 5 - 10% EtOAc/hexane) afforded 13a (0.53 g, 81 %) as a colorless, viscous oil; Rf = 0.5 (33% EtOAc/hexane); 1H NMR (400 MHz, CDCl3) δ 7.83 (2H, d, J = 8.4 Hz), 7.32 (2H, d, J = 8.4 Hz), 7.19 (1H, t, J = 7.8 Hz), 6.80 - 6.69 (3H, m), 3.79 (3H, s), 3.62 (2H, br s), 2.57 (2H, t, J = 7.8 Hz), 2.44 (3H, s), 1.95 (2H, br s), 1.21 (9H, s); 13C NMR (101 MHz, CDCl3) δ 159.7, 155.4, 145.7, 142.7, 131.2, 129.7, 129.4, 129.5, 129.4, 120.7, 113.9, 111.4, 83.2, 55.1, 52.6, 32.8, 27.6, 27.3, 21.7. Spectroscopic properties were consistent with the data available in the literature.
6-Methoxy-1,2,3,4-tetrahydroquinoline (14a)\(^1\)

![Chemical structure of 14a](image)

**General procedure E:** tert-Butyl (3-(3-methoxyphenyl)propyl)(tosyloxy)carbamate (13a) (87.1 mg, 0.20 mmol), TFA (31.0 μL, 0.40 mmol) in TFE (2 mL) were employed. After stirring at r.t. for 40 h, purification by flash column chromatography (gradient, eluent 10 - 25% EtOAc/hexane) afforded 14a (26.0 mg, 80 %) as a pale yellow oil; \(R_f = 0.45\) (33 % EtOAc/hexane); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.63 - 6.54 (2H, m), 6.46 (1H, d, \(J = 8.5\) Hz), 3.73 (3H, s), 3.37 (1H, br s), 3.27 - 3.24 (2H, m), 2.76 (2H, t, \(J = 6.5\) Hz), 1.97 - 1.89 (2H, m); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 151.9, 138.8, 122.9, 115.6, 114.9, 112.9, 55.8, 42.3, 27.2, 22.4. Spectroscopic properties were consistent with the data available in the literature.\(^1\)

tert-Butyl (3-phenylpropyl)(tosyloxy)carbamate (13b)\(^1\)

![Chemical structure of 13b](image)

**General procedure C:** 3-Phenylpropan-1-ol (0.20 g, 1.50 mmol), PPh\(_3\) (0.47 g, 1.80 mmol), DIAD (0.36 mL, 1.80 mmol) and TsONHBoc (0.52 g, 1.80 mmol) in anhydrous THF (6 mL) were employed. Purification by flash column chromatography (10 % EtOAc/hexane) afforded 13b (0.52 g, 85 %) as a viscous colorless oil; \(R_f = 0.7\) (33% EtOAc/hexane); \(\nu_{\text{max}}/\text{cm}^{-1}\) (film) 2981 (m), 2932 (m), 2865 (m), 1718 (s), 1598 (m), 1454 (m), 1368 (s), 1294 (m), 1191 (s), 1151 (s), 1177 (s), 1089 (m); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (2H, d, \(J = 8.3\) Hz), 7.35 - 7.31 (2H, m), 7.31 - 7.26 (2H, m), 7.22 - 7.15 (3H, m), 3.63 (2H, br s), 2.60 (2H, t, \(J = 7.8\) Hz), 2.45 (3H, s), 2.02 - 1.91 (2H, m), 1.23 (9H, s); \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 155.4, 145.7, 141.1, 131.2, 129.7, 129.5, 128.4, 128.3, 126.0, 83.2, 52.6, 32.8, 27.6, 27.4, 21.7. Spectroscopic properties were consistent with the data available in the literature.\(^1\)
**1,2,3,4-Tetrahydroquinoline (14b)**

\[
\begin{align*}
\text{Boc} & \quad \text{OTs} \\
& \quad \text{N} \\
\begin{array}{c}
\text{Ph} \\
\text{Ph}
\end{array} & \quad \text{H}
\end{align*}
\]

**General procedure E:** tert-Butyl (3-phenylpropyl)(tosyloxy)carbamate (13b) (0.12 g, 0.30 mmol) and TFA (46.0 μL, 0.60 mmol) in TFE (3 mL) were employed. After stirring at r.t. for 24 h, purification by flash column chromatography (33 % Et₂O/hexane) afforded 14b (26.0 mg, 65 %) as a yellow oil; Rf = 0.7 (33% EtOAc/hexane); νmax/cm⁻¹ (film); ¹H NMR (400 MHz, CDCl₃) δ 6.99 - 6.95 (2H, m), 6.62 (1H, t, J = 7.3 Hz), 6.48 (1H, d, J = 7.9 Hz), 3.80 (1H, br s), 3.31 (2H, t, J = 5.4 Hz), 2.78 (2H, t, J = 6.5 Hz), 2.01 - 1.90 (2H, m); ¹³C NMR (101 MHz, CDCl₃) δ 144.8, 129.5, 126.7, 121.4, 116.9, 114.2, 41.9, 26.9, 22.2. Spectroscopic properties were consistent with the data available in the literature.¹

**3-(2-Bromophenyl)propan-1-ol**

To a solution of ethyl 3-(2-bromophenyl)propanoic acid (0.92 g, 4.00 mmol) in anhydrous THF (20 mL) at -10 °C was added 0.75 eq. LiAlH₄ (1 M in THF) and the reaction was stirred at the same temperature for 30 min. To the reaction mixture was added water (0.5 mL), aq. 1 M NaOH (0.2 mL) and a further portion of water (1 mL). The reaction mixture was warmed to room temperature, filtered through Celite® and washed with CH₂Cl₂. The phases were separated and the aqueous phase washed with CH₂Cl₂. The combined organic extracts were dried over Na₂SO₄, filtered and concentrated *in vacuo* to afford the title compound as a colorless oil (0.16 g, 19 %) which was used without further purification; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (1H, d, J = 8.0 Hz), 7.26 - 7.21 (2H, m), 7.09 - 7.02 (1H, m), 3.70 (2H, t, J = 6.4 Hz), 2.83 (2H, t, J = 7.80 Hz), 1.94 - 1.85 (2H, m), 1.54 (1H, br s); ¹³C NMR (101 MHz, CDCl₃) δ 141.1, 132.8, 130.4, 127.6, 127.5, 124.4, 62.1, 32.7, 32.4. Spectroscopic properties were consistent with the data available in the literature.¹
**tert-Butyl(3-(2-bromophenyl)propyl)(tosyloxy)carbamate (13c)**

![Chemical structure](image)

**General procedure C:** 3-(2-Bromophenyl)propan-1-ol (0.16 g, 0.74 mmol), PPh$_3$ (0.23 g, 0.88 mmol), DIAD (0.17 mL, 0.88 mmol) and TsONHBoc (0.25 g, 0.88 mmol) in anhydrous THF (4 mL) were employed. Purification by flash column chromatography (10% EtOAc/hexane) afforded 13c (0.26 g, 72%) as a colorless solid; R$_f$ = 0.6 (20% EtOAc); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (2H, d, $J$ = 8.3 Hz), 7.52 (2H, dd, $J$ = 7.9, 1.1 Hz), 7.33 (2H, d, $J$ = 8.1 Hz), 7.24 - 7.19 (2H, m), 7.06 (1H, ddd, $J$ = 7.9, 6.6, 2.4 Hz), 3.66 (2H, br s), 2.71 (2H, t, $J$ = 7.9 Hz), 2.45 (3H, s), 1.99 - 1.90 (2H, m), 1.23 (9H, s); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.5, 145.8, 140.6, 132.9, 131.4, 130.3, 129.8, 129.7, 127.9, 127.6, 124.5, 83.4, 52.7, 33.3, 27.8, 26.2, 21.9. Spectroscopic properties were consistent with the data available in the literature.$^1$

**3-(2-(Trifluoromethyl)phenyl)propan-1-ol**

![Chemical structure](image)

**General procedure E:** 3-(2-(Trifluoromethyl)phenyl)propanoic acid (0.55 g, 2.50 mmol) and 1.0 eq. LiAlH$_4$ (1.0 M in THF) in anhydrous THF were employed to afford the title compound (0.38 g, 75%) as a colorless oil which was used without further purification; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.61 (1H, d, $J$ = 7.9 Hz), 7.45 (1H, t, $J$ = 7.6 Hz), 7.34 (1H, d, $J$ = 7.7 Hz), 7.27 (1H, t, $J$ = 7.6 Hz), 3.71 (2H, t, $J$ = 6.4 Hz), 2.87 (2H, t, $J$ = 7.9 Hz), 1.93 (1H, br s), 1.92 - 1.85 (2H, m); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 140.7, 131.7, 131.0, 128.5, 125.9, 123.3, 120.6, 62.2, 34.5, 28.9. Spectroscopic properties were consistent with the data available in the literature.$^1$
**tert-Butyl (tosyloxy)(3-(2-(trifluoromethyl)phenyl)propyl)carbamate (13d)**

![Chemical Structure](image)

**General procedure C**: 3-(2-(Trifluoromethyl)phenyl)propan-1-ol (0.20 g, 1.00 mmol), PPh₃ (0.32 g, 1.20 mmol), DIAD (0.24 mL, 1.20 mmol) and TsONHBoc (0.35 mg, 1.20 mmol) in anhydrous THF (5 mL) were employed. Purification by flash column chromatography (10% EtOAc/hexane) afforded 3d (0.45 mg, 95%) as a colorless oil; Rᵣ = 0.5 (20% EtOAc/hexane);

1H NMR (400 MHz, CDCl₃) δ 7.85 (2H, d, J = 8.3 Hz), 7.60 (2H, d, J = 7.9 Hz), 7.47 (1H, t, J = 7.6 Hz), 7.33 (2H, d, J = 8.3 Hz), 7.31 - 7.27 (1H, m), 3.67 (2H, br s), 2.75 (2H, t, J = 8.1 Hz), 2.44 (3H, s), 2.01 - 1.90 (2H, m), 1.23 (9H, s);

13C NMR (101 MHz, CDCl₃) δ 155.5, 145.8, 140.1, 132.0, 131.3, 130.9, 129.8, 129.7, 128.5, 126.3, 126.1, 83.5, 52.9, 29.7, 27.9, 27.7, 21.8. Spectroscopic properties were consistent with the data available in the literature.¹

**Methyl (3-(4-((tert-butyldimethylsilyloxy)phenyl)propyl)(tosyloxy)carbamate**

![Chemical Structure](image)

**General procedure C**: 3-(4-((tert-Butyldimethylsilyloxy)phenyl)propan-1-ol (0.53 g, 2.00 mmol), PPh₃ (0.63 g, 2.40 mmol), DIAD (0.47 mL, 2.40 mmol) and methyl (tosyloxy)carbamate (0.59 g, 2.40 mmol) in anhydrous THF (8 mL) were employed. Purification by flash column chromatography (10% EtOAc/hexane) afforded the title compound (0.93 g, 94%) as a colorless oil; Rᵣ = 0.4 (20% EtOAc/hexane); ν max / cm⁻¹ (film) 2955 (m), 2930 (m), 2858 (m), 1728 (s), 1509 (s), 1253 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.83 (2H, d, J = 8.1 Hz, Ts ArCH), 7.33 (2H, d, J = 8.1 Hz, Ts ArCH), 6.99 (2H, d, J = 8.1 Hz, C5-H), 6.74 (2H, d, J = 8.1 Hz, C6-H), 3.58 (2H, app. br s, C1-H₂), 3.47 (3H, s, OCH₃), 2.51 (2H, t, J = 7.8 Hz, C3-H₂), 2.45 (3H, s, Ts CH₃), 1.94 - 1.85 (2H, m, C2-H₂), 0.98 (9H, s, TBS (CH₃)₃), 0.18 (6H, s, TBS Si(CH₃)₂); ¹³C NMR (101 MHz, CDCl₃) δ 157.2 (C=O), 153.9 (C7), 146.0 (Ts ArC), 133.6 (C4), 131.2 (Ts ArC), 129.7 (2 x Ts ArCH), 129.6 (2 x Ts ArCH), 129.2
(C5), 120.1 (C6), 53.7 (OCH3), 52.7 (C1), 32.0 (C3), 27.7 (C2), 25.8 (TBS CH3), 21.9 (Ts CH3), 18.3 (TBS Si(CH3)3), -4.3 (TBS Si(CH3)2); HRMS (ESI+) Calculated for C24H35NaO6S: 516.1847. Found [M+Na]+: 516.1851.

**Methyl (3-(4-hydroxyphenyl)propyl)(tosyloxy)carbamate (15)**

![Diagram](Image)

**General procedure D**: Methyl (3-(4-((tert-butyldimethylsilyl)oxy)phenyl)propyl)(tosyloxy) carbamate (490 mg, 1.00 mmol) and 1.1 eq. 1:1 TBAF/AcOH solution (0.1 M in THF, 11 mL, 1.1 mmol) in THF (20 mL) were employed. Purification by flash column chromatography (gradient 20 – 33 % EtOAc/hexane) afforded 15 (289 mg, 76 %) as a viscous, colorless oil; Rf = 0.1 (20 % EtOAc/hexane); νmax / cm⁻¹ (film) 3431 (m, br), 3023 (m), 2956 (m), 1726 (m), 1514 (m), 1175 (s); 1H NMR (400 MHz, CDCl3) δ 7.82 (2H, d, J = 8.2 Hz, Ts ArC H), 7.33 (2H, d, J = 8.2 Hz, Ts ArC H), 6.99 (2H, d, J = 8.1 Hz, C5-H), 4.88 (1H, s, OH), 3.59 (2H, br s, C1-H2), 2.51 (2H, t, J = 7.8 Hz, C3-H2), 2.45 (3H, s, OCH3), 1.95 - 1.85 (2H, m, C2-H2); 13C NMR (101 MHz, CDCl3) δ 157.3 (C=O), 154.0 (C7), 146.1 (Ts ArC), 133.0 (C4), 131.1 (Ts ArC), 129.7 (2 x Ts ArC), 129.6 (2 x Ts ArC), 129.5 (C5), 115.4 (C6), 53.8 (OCH3), 52.7 (C1), 31.9 (C3), 27.8 (C2), 21.9 (Ts CH3); HRMS (ESI+) Calculated for C18H21NNaO6S: 402.0982. Found [M+Na]+: 402.0984.

**tert-butyl pent-4-en-1-yl(tosyloxy)carbamate (17)**

![Diagram](Image)

**General procedure C**: 4-Penten-1-ol (0.17 g, 2.00 mmol), PPh3 (0.63 g, 2.40 mmol), DIAD (0.47 mL, 2.40 mmol) and TsONHBoc (0.69 g, 2.40 mmol) in anhydrous THF (15 mL) were
employed. Purification by flash column chromatography (10 % EtOAc/hexane) afforded 17 (0.47 g, 66%) as a colorless crystalline solid; m.p.: 47-50 °C (EtOAc/hexane); Rₜ = 0.5 (33% EtOAc/hexane); νₓ max / cm⁻¹ (film) 2977 (m), 1715 (s), 1365 (s), 1355 (s), 1177 (s), 1154 (s); ¹H NMR (400 MHz, CDCl₃) δ 7.85 (2H, d, J = 8.3 Hz, Ts ArC‐H), 7.34 (2H, d, J = 8.2 Hz, Ts ArCH), 5.81 - 5.71 (1H, m, C₄‐H), 5.05 - 4.93 (2H, m, C₅‐H₂), 3.62 (2H, app. br s, C₁‐H₂), 2.45 (3H, s, Ts CＨ₃), 2.07 - 2.00 (2H, m, C₃‐H₂), 1.77 - 1.66 (2H, m, C₂‐H₂), 1.22 (9H, s, Boc (CH₃)₃); ¹³C NMR (101 MHz, CDCl₃) δ 155.6 (Boc C=O), 145.8 (Ts ArC), 137.4 (C₄), 131.4 (Ts ArC) 129.8 (Ts ArCH), 129.7 (Ts ArC'H), 115.4 (C₅), 52.6 (C₁), 30.7 (C₃), 27.7 (Boc (CH₃)₃), 25.0 (C₂), 21.8 (Ts CＨ₃); HRMS (ESI⁺) Calculated for C₁₇H₂₅NNaO₅S: 378.1346. Found [M+Na]⁺: 378.1346.

Selected control reactions and solvent screen

Table 1. Solvent investigation

| Entry | Solvent (0.1 M) | Time (h) | Yield (%)<sup>a</sup> |
|-------|-----------------|----------|-----------------------|
| 1     | TFE             | 24       | 77                    |
| 2     | EtOH            | 24       | 0                     |
| 3     | Toluene         | 24       | 40                    |
| 4     | THF             | 24       | 0                     |
| 5     | CH₂Cl₂          | 24       | 41                    |
| 6     | EtOAc           | 24       | 0                     |
| 7     | 1,4-Dioxane     | 24       | 0                     |
| 8     | MeCN            | 24       | 8                     |
| 9     | 2-propanol      | 24       | 0                     |
| 10    | MeOH            | 24       | 0                     |

<sup>a</sup>In situ yield determined by ¹H NMR against 1,3,5-trimethoxybenzene internal standard.
Table 2. Effect of increased temperature on the reaction

\[
\begin{align*}
\text{5a} & \quad \text{OH} \\
& \quad \text{Boc} \\
& \quad \text{N} \\
& \quad \text{OTs} \\
\text{7a} & \quad \text{O} \\
& \quad \text{NH} \\
\end{align*}
\]

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Entry} & \text{Temp (°C)} & \text{Time} & \text{Yield (%)}^a \\
\hline
1 & 40 & 15 h & 78 \\
2 & 60 & 10 h & 74 \\
3 & 80 & 8 h & 44 \\
\hline
\end{array}
\]

*aIn situ yield determined by \(^1\)H NMR against 1,3,5-trimethoxybenzene internal standard.

Table 2. Results of investigation into possible radical based mechanism

\[
\begin{align*}
\text{5a} & \quad \text{OH} \\
& \quad \text{Boc} \\
& \quad \text{N} \\
& \quad \text{OTs} \\
\text{7a} & \quad \text{O} \\
& \quad \text{NH} \\
\end{align*}
\]

\[
\begin{array}{|c|c|c|c|c|c|}
\hline
\text{Entry} & \text{TFA (mol%)} & \text{Additive (100 mol%)} & \text{Temp (°C)} & \text{Time (h)} & \text{Yield (%)}^a \\
\hline
1 & 200 & \text{none} & 0 - \text{r.t.} & 24 & 77 \\
2 & 200 & \text{none} & 0 - \text{r.t.} & 24 & 79^b \\
3 & 200 & \text{TEMPO} & 0 - \text{r.t.} & 24 & 14 \\
4 & 300 & \text{TEMPO} & 0 - \text{r.t.} & 24 & 30 \\
5 & 300 & \text{TEMPO} & 40 & 42 & 58 \\
6 & 200 & \text{BHT} & 0 - \text{r.t.} & 24 & 46 \\
7 & 300 & \text{BHT} & 40 & 22 & 69 \\
8 & 200 & \text{none} & 0 - \text{r.t.} & 24 & 78^c \\
\hline
\end{array}
\]

*aIn situ yield determined by \(^1\)H NMR against 1,3,5-trimethoxybenzene internal standard. ^bReaction performed using distilled TFE and TFA. ^cReaction performed in the absence of light.
Table 4. Dienone-phenol rearrangement control reactions

| Entry | TFA (mol%) | TFE (M) | Temp (°C) | Time (h) | Yield (%)<sup>a</sup> |
|-------|------------|---------|-----------|----------|-----------------------|
| 1     | 15         | 0.1     | r.t.      | 48       | 50                    |
| 2     | 0          | 0.1     | 60        | 25       | 57                    |

<sup>a</sup>In situ yield determined by <sup>1</sup>H NMR against 1,3,5-trimethoxybenzene internal standard.
3-(4-((tert-Butyldimethylsilyl)oxy)phenyl)propanoic acid
tert-Butyl (3-(4-((tert-butyldimethylsilyl)oxy)phenyl)propyl)(tosyloxy)carbamate (silyl-5a)
*tert*-Butyl (3-(4-hydroxyphenyl)propyl)(tosyloxy)carbamate (5a)
1-Azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7a)
Methyl (E)-3-(4-(benzyl oxy)-3,5-dimethylphenyl)acrylate
Methyl 3-(4-hydroxy-3,5-dimethylphenyl)propanoate
Methyl 3-(4-((tert-butyldimethylsilyl)oxy)-3,5-dimethylphenyl)propanoate
tert-Butyl(3-(4-((tert-butyldimethylsilyl)oxy)-3,5-dimethylphenyl)propyl)(tosyloxy)carbamate
**tert-Butyl (3-(4-hydroxy-3,5-dimethylphenyl)propyl)(tosyloxy)carbamate (5b)**

![NMR Spectrum]

**1H NMR**
- CH₃ (s, 3H, 2.20 ppm)
- Me (s, 3H, 2.20 ppm)
- OH (s, 1H, 7.55 ppm)
- Boc (s, 1H, 3.78 ppm)
- OTs (s, 1H, 4.00 ppm)

**13C NMR**
- C₅H₁₂O₂ (s, 12.3 ppm)
- C₅H₁₂O₂ (s, 21.6 ppm)
- C₅H₁₂O₂ (s, 26.8 ppm)
7,9-Dimethyl-1-azaspiro[4.5]deca-6,9-dien-8-one (7b)
Ethyl 3-(3-bromo-4-((tert-butyldimethylsilyl)oxy)phenyl)propanoate
3-(3-Bromo-4-((tert-butyldimethylsilyl)oxy)phenyl)propan-1-ol
*tert*-Butyl(3-(3-bromo-4-((*tert*-butyldimethylsilyl)oxygenyl)phenyl)propyl)(tosyloxy) carbamate
**tert-Butyl (3-(3-bromo-4-hydroxyphenyl)propyl)(tosyloxy)carbamate (5c)**
7-Bromo-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7c)
6-Bromo-1,2,3,4-tetrahydroquinolin-7-ol (8c)
Methyl 3-(3-bromo-4-((tert-butylidimethylsilyl)oxy)phenyl)propanoate
Methyl 3-(4-((tert-butyldimethylsilyl)oxy)-3-cyclopropylphenyl)propanoate
3-(4-((tert-Butyldimethylsilyl)oxy)-3-cyclopropylphenyl)propan-1-ol
tert-Butyl (3-(4-((tert-butyldimethylsilyl)oxy)-3-cyclopropylphenyl)propyl)(tosyloxy) carbamate
tert-Butyl (3-(3-cyclopropyl-4-hydroxyphenyl)propyl)(tosyloxy)carbamate (5d)
7-Cyclopropyl-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7d)
6-cyclopropyl-1,2,3,4-tetrahydroquinolin-7-ol (8d)
Methyl3-(6-((tert-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)propanoate
3-(6-((tert-Butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)propan-1-ol
tert-Butyl(3-(6-((tert-butyldimethylsilyl)oxy)-[1,1'-biphenyl]-3-yl)propyl)(tosyloxy)carbamate
tert-Butyl (3-(6-hydroxy-[1,1'-biphenyl]-3-yl)propyl)(tosyloxy)carbamate (5e)
7-Phenyl-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7e)
6-Phenyl-1,2,3,4-tetrahydroquinolin-7-ol (8e)
Ethyl (E)-3-(4-hydroxy-2-methoxyphenyl)acrylate
Ethyl 3-([tert-butyl(dimethyl)silyloxy])-2-methoxyphenyl)propanoate

[Chemical structure image]

S121
3-(4-((tert-Butyldimethylsilyl)oxy)-2-methoxyphenyl)propan-1-ol
**tert-Butyl (3-(4-((tert-butyldimethylsilyl)oxy)-2-methoxyphenyl)propyl)(tosyloxy) carbamate**

![NMR Spectrum](image_url)
*tert*-Butyl (3-(4-hydroxy-2-methoxyphenyl)propyl)(tosyloxy)carbamate (5f)
6-Methoxy-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7f)
Ethyl 3-((tert-butyldimethylsilyl)oxy)phenyl)pentanoate
3-(4-((tert-Butyldimethylsilyl)oxy)phenyl)pentan-1-ol
tert-Butyl (3-(4-((tert-butyldimethylsilyl)oxy)phenyl)pentyl)(tosyloxy)carbamate
**tert-Butyl (3-(4-hydroxyphenyl)pentyl)(tosyloxy)carbamate (5g)**

![Chemical Structure](image)

**NMR Spectra**

- **Proton (1H) NMR**
  - Chemical shifts range from 0.0 to 10.0 ppm.

- **Carbon (13C) NMR**
  - Chemical shifts range from -10 to 200 ppm.

S129
4-Ethyl-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7g)
4-Ethyl-1,2,3,4-tetrahydroquinolin-7-ol (8g)
*tert*-Butyl (4-(4-(tert-butyldimethylsilyl)oxy)phenyl)butan-2-yl)(tosyloxy)carbamate
**tert-Butyl (4-(4-hydroxyphenyl)butan-2-yl)(tosyloxy)carbamate (5h)**

![Chemical Structure](image)

**S133**
2-Methyl-1-azaspiro[4.5]deca-6,9-dien-8-one trifluoroacetate (7h)
3-(4-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)propan-1-ol
**tert-Butyl (3-(4-((tert-butyldimethylsilyl)oxy)naphthalen-1-yl)propyl)(tosyloxy)carbamate**

![Chemical Structure Image]

**NMR Spectra**

- **1H NMR**: 8.50, 7.50, 6.50, 5.50, 4.50, 3.50, 2.50, 1.50, 1.00, 0.50, 0.00 ppm
- **13C NMR**: 200.48, 190.39, 180.30, 170.21, 160.12, 150.03, 140.94, 130.85, 120.76, 110.67 ppm

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S136
tert-Butyl (3-(4-hydroxynaphthalen-1-yl)propyl)(tosyloxy)carbamate (5i)
4H-spiro[naphthalene-1,2'-pyrrolidin]-4-one trifluoroacetate (7i)
Methyl 3-(4-((tert-butyldimethylsilyl)oxy)-3-methoxyphenyl)propanoate
3-(4-((tert-Butyldimethylsilyl)oxy)-3-methoxyphenyl)propan-1-ol
tert-Butyl (3-(4-((tert-butyldimethylsilyl)oxy)-3-methoxyphenyl)propyl)(tosyloxy) carbamate
**tert-Butyl (3-(4-hydroxy-3-methoxyphenyl)propyl)(tosyloxy)carbamate (5j)**
7-methoxy-1,2,3,4-tetrahydroquinolin-6-ol (8j)
3-(2-((tert-Butyldimethylsilyl)oxy)-5-methylphenyl)propanoic acid
 tert-Butyl(3-((tert-butyldimethylsilyloxy)-5-methylphenyl)propyl)(tosyloxy) carbamate

\[
\text{Me} \begin{array}{c}
\underline{\text{Boc}} \\
\text{OTBS} \\
\end{array} \\
\text{N}^+ \text{OTs}
\]

\[
\begin{align*}
10.0 & \quad 9.5 & \quad 9.0 & \quad 8.5 & \quad 8.0 & \quad 7.5 & \quad 7.0 & \quad 6.5 & \quad 6.0 & \quad 5.5 & \quad 5.0 & \quad 4.5 & \quad 4.0 & \quad 3.5 & \quad 3.0 & \quad 2.5 & \quad 2.0 & \quad 1.5 & \quad 1.0 & \quad 0.5 & \quad 0.0 & \quad -0.5 \\
\end{align*}
\]

\[
\begin{align*}
200 & \quad 190 & \quad 180 & \quad 170 & \quad 160 & \quad 150 & \quad 140 & \quad 130 & \quad 120 & \quad 110 & \quad 100 & \quad 90 & \quad 80 & \quad 70 & \quad 60 & \quad 50 & \quad 40 & \quad 30 & \quad 20 & \quad 10 & \quad 0 & \quad -10 \\
\end{align*}
\]
**tert-Butyl (3-(2-hydroxy-5-methylphenyl)propyl)(tosyloxy)carbamate (5k)**

![Chemical Structure](image)

**NMR Spectra**

- **FT (ppm)**
  - 11.0, 9.5, 9.0, 8.5, 8.0, 7.5, 7.0, 6.5, 6.0, 5.5, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, 0.0

- **FT (ppm)**
  - 0.0, 10.0, 15.0, 20.0, 25.0, 30.0, 35.0, 40.0, 45.0, 50.0, 55.0, 60.0, 65.0, 70.0, 75.0, 80.0, 85.0, 90.0, 95.0, 100.0

**Notes:**
- [b][63860][F2B1]
- Single pulse decoupled gated NOE
- 1.10, 2.10, 3.10, 4.10, 5.10, 6.10, 7.10, 8.10, 9.10, 10.10, 11.10, 12.10, 13.10, 14.10, 15.10, 16.10, 17.10, 18.10, 19.10, 20.10, 21.10, 22.10, 23.10, 24.10, 25.10, 26.10, 27.10, 28.10, 29.10, 30.10

S146
9-Methyl-1-azaspiro[4.5]deca-7,9-dien-6-one tosylate (7k)
Ethyl 3-((tert-butyl(dimethyl)silyl)oxy)-4-methoxyphenylpropanoate
**tert-Butyl (3-(2-((tert-butyldimethylsilyl)oxy)-4-methoxyphenyl)propyl)(tosyloxy) carbamate**

![Chemical Structure Image]

**S149**
tert-Butyl (3-(2-hydroxy-4-methoxyphenyl)propyl)(tosyloxy)carbamate (5l)

$\text{MeO} \quad \text{N} \quad \text{OTs}$

$\text{Boc}$
8-Metohoxy-1-azaspiro[4.5]deca-7,9-dien-6-one trifluoroacetate (7l)
 tert-Butyl (3-((tert-butyldimethylsilyl)oxy)naphthalen-2-yl)propyl(tosyloxy) carbamate
tert-Butyl (3-(1-hydroxynaphthalen-2-yl)propyl)(tosyloxy)carbamate (5m)
1H-spiro[naphthalene-2,2’-pyrrolidin]-1-one (7m)
3-(2-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)propanoic acid
\textit{tert-}Butyl(3-(2-((\textit{tert-})butyl(dimethyl)silyl)oxy)naphthalen-1-yl)propyl)(tosyloxy) carbamate

\begin{align*}
\text{Boc} \\
\text{OTs} \\
\text{OTBS}
\end{align*}

\begin{align*}
\text{\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
F1 (ppm) & 10.0 & 9.5 & 9.0 & 8.5 & 8.0 & 7.5 & 7.0 & 6.5 & 6.0 & 5.5 & 5.0 & 4.5 & 4.0 & 3.5 & 3.0 & 2.5 & 2.0 & 1.5 & 1.0 & 0.5 & 0.0 \\
\hline
\text{\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
\text{\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
\end{tabular}}
\end{tabular}}
\end{align*}

\begin{align*}
\text{\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
F1 (ppm) & 200 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0 & -10 \\
\hline
\end{tabular}}
\end{align*}

S156
tert-butyl (3-(2-hydroxynaphthalen-1-yl)propyl)(tosyloxy)carbamate (5n)
2H-spiro[naphthalene-1,2′-pyrrolidin]-2-one (7n)
3-(2-((tert-Butyldimethylsilyl)oxy)-7-methoxynaphthalen-1-yl)propanoic acid
tert-Butyl (2-(2-((tert-butyldimethylsilyl)oxy)-7-methoxynaphthalen-1-yl)ethyl)(tosyloxy)carbamate
*tert*-Butyl (3-(2-hydroxy-7-methoxynaphthalen-1-yl)propyl)(tosyloxy)carbamate (5o)
7-methoxy-2H-spiro[naphthalene-1,2’-pyrrolidin]-2-one (7o)
 tert-Butyldimethyl((1-(1-phenylallyl)naphthalen-2-yl)oxy)silane

[Chemical structure image]

[spectroscopy images]
3-(2-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)-3-phenylpropan-1-ol

![Chemical Structure Image]
**tert-Butyl (3-(2-hydroxynaphthalen-1-yl)-3-phenylpropyl)(tosyloxy)carbamate (5p)**
3'-phenyl-2H-spiro[naphthalene-1,2'-pyrrolidin]-2-one (7p)
3-(2-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)-N-methoxy-N-methylpropanamide
4-(2-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)butan-2-one
4-(2-((tert-Butyldimethylsilyl)oxy)naphthalen-1-yl)butan-2-ol
tert-Butyl (4-(2-hydroxynaphthalen-1-yl)butan-2-yl)(tosyloxy)carbamate (5q)
5'-Methyl-2H-spiro[naphthalene-1,2'-pyrrolidin]-2-one (7q)
1-(2-Phenylacetyl)-1-azaspiro[4.5]deca-6,9-dien-8-one (9a)
$(6R^*, 6aS^*, 10aS^*)$-6-phenyl-2,3,6a,7-tetrahydro-1H,5H-pyrrolo[2,1-i]indole-5,8(6H)-dione (10a)
4-Ethyl-1-(2-phenylacetyl)-1-azaspiro[4.5]deca-6,9-dien-8-one (9g)
(1R*, 6R*, 6aS*, 10aS*)-1-Ethyl-6-phenyl-2,3,6a,7-tetrahydro-1H,5H-pyrrolo[2,1-i]indole-5,8(6H)-dione (10g)
(1R*, 6aR*, 10aS*)-1-Ethyl-6-phenyl-2,3,6a,7-tetrahydro-1H,5H-benzo[d]pyrrolo[1,2-c]imidazole-5,8(6H)-dione (11g)
9-methyl-1-(2-phenylacetyl)-1-azaspiro[4.5]deca-7,9-dien-6-one
(6R,6aS)-6a-Hydroxy-9-methyl-6-phenyl-2,3,6,6a-tetrahydro-1H,5H-pyrrolo[2,1-i]indol-5-one (12k)
7-methyl-6-phenyl-2,3,6a,9-tetrahydro-1H,5H-benzo[d]pyrrolo[1,2-c]imidazole-5,10(6H)-dione (11k)
Methyl (3-(4-((tert-butyl)dimethylsilyl)oxy)phenyl)propyl)(tosyloxy)carbamate
Methyl (3-(4-hydroxyphenyl)propyl)(tosyloxy)carbamate (15)
**tert-Butyl pent-4-en-1-yl(tosyloxy)carbamate (17)**

\[
\text{Boc} \quad \text{OTs}
\]
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