Supporting Information

Deaminative Ring Contraction for the Synthesis of Polycyclic Heteroaromatics:
A Concise Total Synthesis of Toddaquinoline

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Miscellaneous Synthetic Procedures

2-bromo-3,4-dimethoxybenzaldehyde (S1)

To a solution of KOH (15.6 mmol) in water (10 ml) at 50 °C was added 2-bromo-3-hydroxy-4-methoxybenzaldehyde (8.6 mmol) with aggressive stirring. To this solution, dimethyl sulfate (13.8 mmol) was added dropwise over 10 minutes, followed by an additional 10 minutes of stirring. The reaction mixture was cooled to room temperature and the precipitate was filtered, washed twice with 1 M NaOH, twice with water, then dissolved in dichloromethane. Solvent was removed in vacuo and S1 was isolated as a white solid (1.37 g, 5.62 mmol, 65%). Spectroscopic data for S1 match those previously reported.¹

¹H NMR (500 MHz, Chloroform-d) δ 10.25 (d, J = 0.9 Hz, 1H), 7.74 (d, J = 8.7 Hz, 1H), 6.96 (d, J = 8.7 Hz, 1H), 3.96 (s, 3H), 3.88 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 188.4, 156.1, 143.8, 124.8, 123.9, 120.6, 108.4, 58.1, 53.7.

2-bromo-4,5-dimethoxybenzaldehyde (S2)

To a stirred solution of 3,4-dimethoxybenzaldehyde (18.1 mmol) in methanol (30 mL) was added Br₂ dropwise over the course of 30 minutes, followed by an additional hour of stirring. The reaction mixture was then concentrated under reduced pressure, and the residue was washed with cold water and pet. ether. S2 was isolated as a tan solid (4.01 g, 16.8 mmol, 91%). Spectroscopic data for S2 match those previously reported.²

¹H NMR ¹H NMR (500 MHz, Chloroform-d) δ 10.17 (s, 1H), 7.40 (s, 1H), 7.04 (s, 1H), 3.95 (s, 3H), 3.88 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 190.89, 154.45, 148.83, 126.49, 120.36, 115.41, 110.39, 56.48, 56.13.

HRMS (ESI⁺): Calcd. for C₉H₁₀O₃Br [M+H]+: 244.9813 found 244.9820.
**tert-butyl 3-bromo-4-methylbenzoate (S3)**

Prepared according to a literature procedure used for similar molecules. To a solution of 21.80 mmol t-BuOK in 17.5 mL Et₂O was added a solution of 4.36 mmol methyl 3-bromo-4-methylbenzoate in 1 mL Et₂O, dropwise. The reaction was stirred for 10 minutes, by which time it appeared to be complete based on analysis by TLC. The reaction was quenched by slowly pouring the mixture into ice water. The aqueous layer was extracted with EtOAc (20 mL × 3). Combined organic extracts were washed with brine, dried over anhydrous MgSO₄, filtered, and evaporated to yield S3 as an orange oil (831 mg, 3.06 mmol, 70%). Spectroscopic data for S3 closely match those previously reported.

**TLC** R₄ = 0.61 (9:1 Hex:EtOAc)

**¹H NMR** (500 MHz, Chloroform-d) δ 8.11 (d, J = 1.70 Hz, 1H), 7.79 (dd, J = 7.86, 1.76 Hz, 1H), 7.27 (d, J = 7.87 Hz, 1H), 2.44 (s, 3H), 1.58 (s, 9H).

**10-bromo-9-methylbenzo[h]quinoline (S4)**

To a pressure tube was added palladium(II) acetate (0.029 mmol) and N-bromosuccinimide (0.60 mmol). The tube was purged with nitrogen, followed by addition of 17 (0.57 mmol) dissolved in 4.8 mL acetonitrile. The tube was sealed and heated to 100ºC for 40 hrs. The solution was evaporated, and residue was purified by column chromatography using a gradient of 100% hexanes to 95:5 Hex:EtOAc to yield S4 as white crystals (96 mg, 0.35 mmol, 62%). Spectroscopic data for S4 closely match those previously reported.

**¹H NMR** (500 MHz, Chloroform-d) δ 9.09 (dd, J = 4.3, 1.8 Hz, 1H), 8.17 (dd, J = 8.0, 1.9 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.74 (d, J = 8.7 Hz, 1H), 7.65 (d, J = 8.7 Hz, 1H), 7.54-7.58 (m, 2H), 2.76 (s, 3H).

**¹³C NMR** (126 MHz, Chloroform-d) δ 146.5, 146.2, 140.4, 135.6, 134.5, 130.4, 128.8, 128.0, 127.6, 127.51, 126.0, 121.7, 121.6, 26.1.

**HRMS (ESI⁺):** Calcd. for C₁₄H₁₁NBr [M+H]⁺: 272.0075, found 272.0082.
**General procedure A for the synthesis of secondary amines**

Methylamine hydrochloride (3 equiv.) and potassium carbonate (3 equiv.) were stirred in methanol (0.2 M) in a round bottom flask for 30 min. Aldehyde (1 equiv.) was added to the flask and the mixture stirred for an additional 2 hr. The reaction mixture was cooled to 0 °C and sodium borohydride (1.2 equiv.) was added in portions. The solution was allowed to reach room temperature while stirring for an additional 2 hr. The reaction mixture was filtered, then the solvent was removed under reduced pressure, and the crude material was partitioned into water and EtOAc. The aqueous layer was extracted three times with EtOAc (20 mL), then the combined organic extracts were washed with brine (15 mL) and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure to give the desired secondary amine which was used without further purification.

**1-(6-bromobenzo[d][1,3]dioxol-5-yl)-N-methylmethanamine (31)**

Reaction performed following general procedure A with 10.9 mmol of 6-bromobenzo[d][1,3]dioxol-5-carbaldehyde. 31 was isolated as a colorless oil (2.66 g, 10.9 mmol, 99%). Spectroscopic data for 31 match those previously reported.⁶

**¹H NMR** (500 MHz, Chloroform-d) δ 7.00 (s, 1H), 6.89 (s, 1H), 5.97 (s, 2H), 3.74 (s, 2H), 2.44 (s, 3H).

**¹³C NMR** (126 MHz, Chloroform-d) δ 147.3, 132.4, 114.2, 112.76, 112.75, 110.2, 101.7, 55.6, 35.8.

**HRMS (ESI⁺):** Calcd. for C₉H₁₁NO₂Br [M+H]⁺: 243.9973, found 243.9978.

**1-(2-bromophenyl)-N-methylmethanamine (S5)**

Reaction performed following general procedure A with 16.2 mmol of 2-bromobenzaldehyde. S5 was isolated as a colorless oil (2.617 g, 13.1 mmol, 81%).

**¹H NMR** (500 MHz, Chloroform-d) δ 7.56 (dt, J = 8.0, 1.7 Hz, 1H), 7.38 (dt, J = 7.7, 2.0 Hz, 1H), 7.32–7.27 (m, 1H), 7.16–7.11 (m, 1H), 3.83 (s, 2H), 2.46 (s, 3H).

**¹³C NMR** (126 MHz, Chloroform-d) δ 139.0, 132.7, 130.2, 128.5, 127.3, 123.9, 55.6, 35.8.

**HRMS (ESI⁺):** Calcd. for C₈H₁₁NBr [M+H]⁺: 200.0075, found 200.0078.
1-(1-bromonaphthalen-2-yl)-N-methylmethanamine (S6)

Reaction performed following general procedure A with 12.8 mmol of 1-bromo-2- naphthaldehyde. S6 was isolated as an orange oil (2.943 g, 11.8 mmol, 92%).

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 8.33 (d, \(J = 8.6\) Hz, 1H), 7.84 – 7.76 (m, 2H), 7.59 (ddd, \(J = 8.4, 6.8, 1.3\) Hz, 1H), 7.55 – 7.47 (m, 2H), 4.08 (s, 2H), 2.50 (s, 3H)

\(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 137.0, 133.8, 128.04, 128.03, 127.7, 127.6, 127.4, 127.2, 126.3, 123.9, 56.5, 35.8.

HRMS (ESI\(^+\)): Calcd. for C\(_{12}\)H\(_{12}\)NBr [M+H]\(^+\): 250.0231, found 250.0207

1-(2-bromopyridin-3-yl)-N-methylmethanamine (S7)

Reaction performed following general procedure A with 53.8 mmol of 2-bromonicotinaldehyde. To effectively extract product, extractions were performed 7x with 5:1 CHCl\(_3\):iPrOH instead of 3x with EtOAc. S7 was isolated as a light yellow liquid (10.453 g, 52.0 mmol, 97%). Spectroscopic data for S7 match those previously reported.\(^6\)

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 8.26 (dd, \(J = 4.8, 2.0\) Hz, 1H), 7.71 (ddd, \(J = 7.5, 2.0, 0.9\) Hz, 1H), 7.25 (dd, \(J = 7.4, 4.6\) Hz, 1H), 3.80 (s, 2H), 2.46 (s, 3H).

\(^{13}\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 148.6, 143.7, 138.2, 136.3, 123.0, 54.6, 36.0.

HRMS (ESI\(^+\)): Calcd. for C\(_7\)H\(_{10}\)N\(_2\)Br [M+H]\(^+\): 201.0027, found 201.0029.
1-(2-bromo-3-methylphenyl)-N-methylaniline (S8)

\[
\text{\begin{tikzpicture}
\filldraw[black] (0,0) circle (0.1cm);
\filldraw[black] (1,0) circle (0.1cm);
\filldraw[black] (0,1) circle (0.1cm);
\filldraw[black] (0.5,0.5) circle (0.1cm);
\filldraw[black] (0,0) circle (0.1cm);
\filldraw[black] (1,1) circle (0.1cm);
\filldraw[black] (1,0) circle (0.1cm);
\filldraw[black] (0.5,0.5) circle (0.1cm);
\end{tikzpicture}}
\]

Reaction performed following general procedure A with 2.51 mmol of 2-bromo-3-methylbenzaldehyde. S8 was isolated as an opaque oil (505 mg, 2.36 mmol, 94%).

**TLC** Rf = 0.10 (2:1 Hex:EtOAc)

\(^1\text{H} \text{NMR} \) (500 MHz, Chloroform-\(d\)) \(\delta\) 7.20 – 7.13 (m, 3H), 3.84 (s, 2H), 2.45 (s, 3H), 2.42 (s, 3H).

\(^{13}\text{C} \text{NMR} \) (126 MHz, Chloroform-\(d\)) \(\delta\) 139.4, 138.7, 129.6, 127.8, 126.9, 126.7, 56.5, 35.9, 23.8.

**HRMS (ESI\(^+\)):** Calcd. for C\(_9\)H\(_{13}\)NBr [M+H]\(^+\): 214.0231, found 214.0227.

1-(2-bromo-4-methylphenyl)-N-methylaniline (S9)

\[
\text{\begin{tikzpicture}
\filldraw[black] (0,0) circle (0.1cm);
\filldraw[black] (1,0) circle (0.1cm);
\filldraw[black] (0,1) circle (0.1cm);
\filldraw[black] (0.5,0.5) circle (0.1cm);
\filldraw[black] (0,0) circle (0.1cm);
\filldraw[black] (1,1) circle (0.1cm);
\filldraw[black] (1,0) circle (0.1cm);
\filldraw[black] (0.5,0.5) circle (0.1cm);
\end{tikzpicture}}
\]

Reaction performed following general procedure A with 6.17 mmol of 2-bromo-4-methylbenzaldehyde. S9 was isolated as a colorless oil (1.128 g, 5.26 mmol, 86%).

\(^1\text{H} \text{NMR} \) (500 MHz, Chloroform-\(d\)) \(\delta\) 7.36 (s, 1H), 7.22 (d, \(J = 7.72\) Hz, 1H), 7.06 (d, \(J = 7.64\) Hz, 1H), 3.77 (s, 2H), 2.42 (s, 3H), 2.30 (s, 3H).

\(^{13}\text{C} \text{NMR} \) (126 MHz, Chloroform-\(d\)) \(\delta\) 138.7, 138.0, 133.3, 130.2, 128.2, 123.9, 55.5, 35.9, 20.7.

**HRMS (ESI\(^+\)):** Calcd. for C\(_9\)H\(_{13}\)NBr [M+H]\(^+\): 214.0231, found 214.0235.

1-(2-bromo-5-methylphenyl)-N-methylaniline (S10)

\[
\text{\begin{tikzpicture}
\filldraw[black] (0,0) circle (0.1cm);
\filldraw[black] (1,0) circle (0.1cm);
\filldraw[black] (0,1) circle (0.1cm);
\filldraw[black] (0.5,0.5) circle (0.1cm);
\filldraw[black] (0,0) circle (0.1cm);
\filldraw[black] (1,1) circle (0.1cm);
\filldraw[black] (1,0) circle (0.1cm);
\filldraw[black] (0.5,0.5) circle (0.1cm);
\end{tikzpicture}}
\]

Reaction performed following general procedure A with 2.51 mmol of 2-bromo-5-methylbenzaldehyde. S10 was isolated as an opaque oil (499 mg, 2.33 mmol, 93%).

**TLC** Rf = 0.13 (2:1 Hex:EtOAc)

\(^1\text{H} \text{NMR} \) (500 MHz, Chloroform-\(d\)) \(\delta\) 7.40 (d, \(J = 8.1\) Hz, 1H), 7.18 (d, \(J = 2.3\) Hz, 1H), 6.93 (dd, \(J = 8.2, 2.2\) Hz, 1H), 3.78 (s, 2H), 2.46 (s, 3H), 2.30 (s, 3H).

\(^{13}\text{C} \text{NMR} \) (126 MHz, Chloroform-\(d\)) \(\delta\) 138.6, 137.4, 132.6, 131.3, 129.5, 120.7, 55.8, 36.0, 21.0.

**HRMS (ESI\(^+\)):** Calcd. for C\(_9\)H\(_{13}\)NBr [M+H]\(^+\): 214.0231, found 214.0227.
1-(2-bromo-4-methoxyphenyl)-N-methylmethanamine (S11)

Reaction performed following general procedure A with 9.30 mmol of 2-bromo-5-methoxylphenyl-N-methylmethanamine. S11 was isolated as a tan solid (1.500 g, 6.52 mmol, 70%).

\( ^1H \text{NMR} \) (500 MHz, Chloroform-\( d_2 \)) \( \delta \) 7.31 (d, \( J = 8.45 \) Hz, 1H), 7.11 (d, \( J = 2.60 \) Hz, 1H), 6.83 (dd, \( J = 8.46, 2.60 \) Hz, 1H), 3.82 (s, 2H), 3.79 (s, 3H), 2.44 (s, 3H).

\( ^{13}C \text{NMR} \) (126 MHz, Chloroform-\( d_2 \)) \( \delta \) 159.5, 131.4, 129.9, 124.6, 118.2, 113.5, 55.6, 54.6, 35.2.

HRMS (ESI\(^+\)): Calcd. for C\(_9\)H\(_{13}\)NOBr [M+H]\(^+\): 230.0181, found 230.0186.

1-(2-bromo-5-methoxyphenyl)-N-methylmethanamine (S12)

Reaction performed following general procedure A with 6.98 mmol of 2-bromo-5-methoxylphenyl-N-methylmethanamine. S12 was isolated as a colorless oil (1.093 g, 4.75 mmol, 68%).

\( ^1H \text{NMR} \) (500 MHz, Chloroform-\( d_2 \)) \( \delta \) 7.41 (dd, \( J = 8.68, 1.32 \) Hz, 1H), 6.95 (dd, \( J = 3.19, 1.30 \) Hz, 1H), 6.69 (ddd, \( J = 8.69, 3.13, 1.31 \) Hz, 1H), 3.79 (d, \( J = 1.31 \) Hz, 3H), 3.78 (d, \( J = 1.31 \) Hz, 2H), 2.46 (d, \( J = 1.31 \) Hz, 3H).

\( ^{13}C \text{NMR} \) (126 MHz, Chloroform-\( d_2 \)) \( \delta \) 159.1, 140.1, 133.4, 115.9, 114.44, 114.35, 55.9, 55.6, 36.0.

HRMS (ESI\(^+\)): Calcd. for C\(_9\)H\(_{13}\)NOBr [M+H]\(^+\): 230.0181, found 230.0188.
**1-(2-bromo-3,4-dimethoxyphenyl)-N-methylmethanamine (S13)**

![Chemical Structure](image)

Reaction performed following general procedure A with 5.59 mmol of S1. S13 was isolated as a pale yellow liquid (1.263 g, 4.86 mmol, 87%).

**1H NMR** (500 MHz, Chloroform-d) δ 7.07 (d, J = 8.4 Hz, 1H), 6.83 (d, J = 8.5 Hz, 1H), 3.85 (d, J = 7.0 Hz, 6H), 3.77 (s, 2H), 2.42 (s, 3H), 1.80 (s, 1H).

**13C NMR** (126 MHz, Chloroform-d) δ 152.6, 146.5, 131.8, 125.2, 119.6, 110.9, 60.4, 56.0, 55.5, 35.6.

**HRMS (ESI+):** Calcd. for C₉H₇NOrsBr [M+H]+: 260.0286, found 260.0291.

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**1-(2-bromo-4,5-dimethoxyphenyl)-N-methylmethanamine (S14)**

![Chemical Structure](image)

Reaction performed following general procedure A with 3.56 mmol of S2. S14 was isolated as a pale yellow liquid (0.907 g, 3.49 mmol, 98%).

**1H NMR** (500 MHz, Chloroform-d) δ 7.00 (s, 1H), 6.92 (s, 1H), 3.86 (d, J = 9.5 Hz, 6H), 3.75 (s, 2H), 2.45 (s, 3H).

**13C NMR** (126 MHz, Chloroform-d) δ 148.5, 148.3, 131.0, 115.4, 113.7, 112.9, 56.1, 56.0, 55.4, 35.9.

**HRMS (ESI+):** Calcd. for C₁₀H₁₄NO₂Br [M+H]+: 260.0286, found 260.0293.
1-(2-bromo-4-fluorophenyl)-N-methylmethanamine (S15)

Reaction performed following general procedure A with 9.85 mmol of 2-bromo-4-fluorobenzaldehyde. S15 was isolated as a yellow oil (1.267 g, 5.81 mmol, 59%).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 7.36 (dd, $J = 8.5, 6.1$ Hz, 1H), 7.30 (dd, $J = 8.2, 2.6$ Hz, 1H), 7.00 (td, $J = 8.3, 2.6$ Hz, 1H), 3.80 (s, 2H), 2.44 (s, 3H), 1.81 (s, 1H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 162.5, 160.5, 131.2 (d, $J_{CF} = 8.5$ Hz), 123.9 (d, $J_{CF} = 9.5$ Hz), 120.1 (dd, $J_{CF} = 24.3, 1.0$ Hz), 114.5 (d, $J_{CF} = 20.6$ Hz), 55.0, 35.9.

**General procedure B for the synthesis of tertiary amines**
To a round bottom flask was added aldehyde (1 equiv.) and benzylamine (1.2 equiv.), dissolved in 1,2-dichloroethane (0.3 M). AcOH (1 equiv.) was added dropwise and stirred at room temperature for 10 min. NaBH(OAc)$_3$ (2 equiv.) was added portion wise and stirred at 40 °C for 18 hr. The reaction mixture was cooled to room temperature, washed with NaHCO$_3$ (10 mL × 3), and brine (10 mL). The organic layer was dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography, using a gradient of 100% hexane to 9:1 Hex:EtOAc to afford the desired tertiary amine.

**General procedure C for the synthesis of tertiary amines**
To a round bottom flask was added secondary amine (1 equiv.), benzyl halide (1.1 equiv.), and Hünig’s base (1.5 equiv.) dissolved in acetonitrile (0.2 M). The reaction mixture was stirred at room temperature for 2 hr. After cooling to room temperature, solvent was removed under reduced pressure. The crude material was purified by flash column chromatography, using a gradient of 100% hexane to 9:1 Hex:EtOAc to afford the desired tertiary amine.

**General procedure D for synthesis of tertiary amines**
To a round bottom flask was added methyl arene (1 equiv.), $N$-bromosuccinimide (1 equiv.), benzoyl peroxide (0.05 equiv.) dissolved in benzene (0.2 M). The reaction mixture was refluxed at 80 °C for 6 hr. The mixture was cooled to room temperature followed by addition of substituted benzylamine (1 equiv.) dissolved in THF (0.6 M). The solution was stirred overnight at room temperature and quenched with 2M NH$_2$OH (10 mL), followed by extraction three times with EtOAc (20 mL). Combined organic layers were washed with brine (15 mL), dried over MgSO$_4$, filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography, using a gradient of 100% hexane to 9:1 Hex:EtOAc to afford the desired tertiary amine.
N-(2-bromo-3-methylbenzyl)-1-(2-bromopyridin-3-yl)-N-methylmethanamine (21a)

Reaction performed following general procedure D with 2.36 mmol of 3-bromo-2-methylpyridine and 2.36 mmol of secondary amine S8. 21a was isolated as a yellow oil (532 mg, 1.39 mmol, 59%).

TLC \( R_f = 0.35 \) (8:2 Hex:EtOAc)

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \( \delta \) 8.23 (dd, \( J = 4.7, 2.3 \) Hz, 1H), 7.89 (d, \( J = 7.6 \) Hz, 1H), 7.33 (d, \( J = 7.4 \) Hz, 1H), 7.24 (dd, \( J = 7.6, 4.7 \) Hz, 1H), 7.21 – 7.11 (m, 2H), 3.73 (s, 2H), 3.69 (s, 2H), 2.42 (s, 3H), 2.27 (s, 3H).

\(^13\)C NMR (126 MHz, Chloroform-\(d\)) \( \delta \) 148.3, 143.8, 138.7, 138.7, 138.3, 136.1, 129.6, 128.0, 127.2, 126.8, 122.9, 62.3, 60.1, 42.4, 23.9.

HRMS (ESI\(^+\)): Calcd. for C\(_{15}\)H\(_{17}\)N\(_2\)Br\(_2\) [M+H]\(^+\): 382.9767, found 382.9752.

N-(2-bromo-4-methylbenzyl)-1-(2-bromopyridin-3-yl)-N-methylmethanamine (21b)

Reaction performed following general procedure D with 3.5 mmol of 3-bromo-2-methylpyridine and 3.5 mmol of secondary amine S9. 21b was isolated as a yellow oil (778 mg, 2.0 mmol, 58%).

Spectroscopic data for 21b match those previously reported.\(^7\)

TLC \( R_f = 0.41 \) (7:3 Hex:EtOAc)

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \( \delta \) 8.23 (dd, \( J = 4.7, 2.0 \) Hz, 1H), 7.88 (dd, \( J = 7.6, 2.0 \) Hz, 1H), 7.39 – 7.34 (m, 2H), 7.24 (dd, \( J = 7.6, 4.7 \) Hz, 1H), 7.08 (dd, \( J = 7.8, 1.8 \) Hz, 1H), 3.68 (s, 2H), 3.66 (s, 2H), 2.30 (s, 3H), 2.25 (s, 3H).

\(^13\)C NMR (126 MHz, Chloroform-\(d\)) \( \delta \) 148.4, 143.9, 138.9, 138.8, 136.2, 134.9, 133.4, 130.7, 128.2, 124.6, 123.0, 61.4, 60.0, 42.4, 20.8.

HRMS (ESI\(^+\)): Calcd. for C\(_{15}\)H\(_{17}\)N\(_2\)Br\(_2\) [M+H]\(^+\): 382.9767, found 382.9764.
\(N-(2\text{-bromo-5-methylbenzyl})-1-(2\text{-bromopyridin-3-yl})-N\text{-methylmethanamine (21c)}\)

\[
\begin{align*}
\text{Me} & \quad \text{N} & \quad \text{Br} & \quad \text{Br} & \quad \text{N} \\
\text{Br} & \quad \text{Br} & \quad \text{N} & \quad \text{Br} & \quad \text{Me}
\end{align*}
\]

Reaction performed following general procedure D with 2.33 mmol of 3-bromo-2-methylpyridine and 2.33 mmol of secondary amine S10. 21c was isolated as a yellow oil (492 mg, 1.28 mmol, 55%).

**TLC** \(R_f = 0.31\) (8:2 Hex:EtOAc)

\(^1\text{H NMR}\) (500 MHz, Chloroform-\(d\)) \(\delta 8.24\) (d, \(J = 4.7\) Hz, 1H), 7.87 (d, \(J = 7.7\) Hz, 1H), 7.40 (d, \(J = 8.1\) Hz, 1H), 7.29 (s, 1H), 7.24 (dd, \(J = 7.5, 4.8\) Hz, 1H), 6.92 (d, \(J = 8.2\) Hz, 1H), 3.67 (s, 4H), 2.30 (s, 3H), 2.27 (s, 3H).

\(^{13}\text{C NMR}\) (126 MHz, Chloroform-\(d\)) \(\delta 148.3, 143.8, 138.8, 137.4, 137.2, 136.0, 132.6, 131.6, 129.5, 122.9, 121.3, 61.5, 60.0, 42.4, 21.0.

**HRMS (ESI\(^+\))**: Calcd. for C\(_{15}\)H\(_{17}\)N\(_2\)Br\(_2\) [M+H]\(^+\): 382.9767, found 382.9752.

\(N-(2\text{-bromo-6-methylbenzyl})-1-(2\text{-bromopyridin-3-yl})-N\text{-methylmethanamine (21d)}\)

\[
\begin{align*}
\text{Me} & \quad \text{N} & \quad \text{Br} & \quad \text{Br} & \quad \text{N} \\
\text{Br} & \quad \text{Br} & \quad \text{N} & \quad \text{Br} & \quad \text{Me}
\end{align*}
\]

Reaction performed following general procedure C with 10.4 mmol of secondary amine S7 and 11.4 mmol of 2-bromo-6-methylbenzyl bromide. 21d was isolated as a yellow oil (2.74 g, 7.6 mmol, 73%). Spectroscopic data for 21d match those previously reported.

\(^1\text{H NMR}\) (500 MHz, Chloroform-\(d\)) \(\delta 8.24\) (dd, \(J = 4.8, 2.0\) Hz, 1H), 7.89 (dd, \(J = 7.6, 2.0\) Hz, 1H), 7.34 (dd, \(J = 7.4, 2.0\) Hz, 1H), 7.24 (dd, \(J = 7.6, 4.7\) Hz, 1H), 7.20 – 7.14 (m, 2H), 3.74 (s, 2H), 3.69 (s, 2H), 2.43 (s, 3H), 2.28 (s, 3H).

**HRMS (ESI\(^+\))**: Calcd. for C\(_{15}\)H\(_{17}\)N\(_2\)Br\(_2\) [M+H]\(^+\): 382.9767, found 382.9765.
\[ N-(2\text{-bromo-3-methoxybenzyl})-1-(2\text{-bromopyridin-3-yl})-N\text{-methylmethanamine (21e)} \]

Reaction performed following general procedure D with 5.00 mmol of 2-bromo-3-methylanisole and 5.00 mmol of secondary amine S7. 21e was isolated as an colorless oil (1.139 g, 2.85 mmol, 57%).

\[^1\text{H NMR}\] (500 MHz, Chloroform-\(d\)) \(\delta\) 8.23 (dd, \(J = 4.70, 1.98\) Hz, 1H), 7.89 (d, \(J = 7.44\) Hz, 1H), 7.23-7.25 (m, 2H), 7.13 (d, \(J = 7.67\) Hz, 1H), 6.82 (dd, \(J = 8.23, 1.49\) Hz, 1H), 3.90 (s, 3H), 3.75 (s, 2H), 3.68 (s, 2H), 2.27 (s, 3H).

\[^{13}\text{C NMR}\] (126 MHz, Chloroform-\(d\)) \(\delta\) 156.1, 148.4, 143.8, 139.8, 138.8, 136.2, 127.8, 123.0, 122.7, 114.1, 110.6, 61.9, 60.1, 56.5, 42.5.

\textbf{HRMS (ESI\(^+\))}: Calcd. for \(\text{C}_{15}\text{H}_{17}\text{N}_{2}\text{OBr}_{2}\) [M+H\(^+\)]: 398.9708, found 398.9716.

\[ N-(2\text{-bromo-4-methoxybenzyl})-1-(2\text{-bromopyridin-3-yl})-N\text{-methylmethanamine (21f)} \]

Reaction performed following general procedure D with 2.91 mmol of 2-bromo-3-methylpyridine and 2.91 mmol of secondary amine S11. 21f was isolated as an colorless oil (550 mg, 1.38 mmol, 47%).

\[^1\text{H NMR}\] (500 MHz, Chloroform-\(d\)) \(\delta\) 8.23 (dd, \(J = 4.7, 2.0\) Hz, 1H), 7.86 (dd, \(J = 7.1, 1.0\) Hz, 1H), 7.36 (d, \(J = 8.5\) Hz, 1H), 7.24 (dd, \(J = 7.6, 4.7\) Hz, 1H), 7.10 (d, \(J = 2.6\) Hz, 1H), 6.83 (dd, \(J = 8.5, 2.6\) Hz, 1H), 3.78 (s, 3H), 3.65 (s, 2H), 3.64 (s, 2H), 2.24 (s, 3H).

\[^{13}\text{C NMR}\] (126 MHz, Chloroform-\(d\)) \(\delta\) 159.2, 148.4, 143.9, 138.9, 136.2, 131.6, 129.9, 125.1, 123.0, 118.1, 113.5, 61.0, 59.9, 55.6, 42.3.

\textbf{HRMS (ESI\(^+\))}: Calcd. for \(\text{C}_{15}\text{H}_{17}\text{N}_{2}\text{OBr}_{2}\) [M+H\(^+\)]: 398.9708, found 398.9713.
N-(2-bromo-5-methoxybenzyl)-1-(2-bromopyridin-3-yl)-N-methylmethanamine (21g)

Reaction performed following general procedure D with 5.00 mmol of 2-bromo-3-methylpyridine and 5.00 mmol of secondary amine S12. 21g was isolated as a pale yellow oil (687 mg, 1.72 mmol, 59%). Spectroscopic data for 21g match those previously reported.6

$^1$H NMR (500 MHz, Chloroform-d) δ 8.24 (dd, J = 4.7, 2.0 Hz, 1H), 7.86 (dd, J = 7.6, 2.0 Hz, 1H), 7.42 (d, J = 8.7 Hz, 1H), 7.25 (dd, J = 7.6, 4.7 Hz, 1H), 7.11 (d, J = 3.1 Hz, 1H), 6.68 (dd, J = 8.7, 3.2 Hz, 1H), 3.78 (s, 3H), 3.68 (s, 2H), 3.67 (s, 2H), 2.29 (s, 3H).

HRMS (ESI⁺): Calcd. for C$_{15}$H$_{17}$N$_2$OBr$_2$ [M+H]$^+$: 398.9708, found 398.9709.

N-(2-bromo-6-methoxybenzyl)-1-(2-bromopyridin-3-yl)-N-methylmethanamine (21h)

Reaction performed following general procedure D with 5.00 mmol of 3-bromo-2-methylanisole and 5.00 mmol of secondary amine S7. 21h was isolated as an orange oil (456 mg, 1.14 mmol, 23%).

$^1$H NMR (500 MHz, Chloroform-d) δ 8.19 (dd, J = 4.80, 2.07 Hz, 1H), 7.83 (d, J = 7.57 Hz, 1H), 7.49 (d, J = 8.87 Hz, 1H), 7.17-7.20 (m, 2H), 6.71 (d, J = 8.92 Hz, 1H), 3.87 (s, 2H), 3.80 (s, 3H), 3.67 (s, 2H), 2.26 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 159.2, 157.8, 148.1, 139.1, 136.3, 132.6, 129.5, 125.3, 122.7, 116.8, 111.0, 109.7, 59.8, 56.0, 42.3.

HRMS (ESI⁺): Calcd. for C$_{15}$H$_{17}$N$_2$OBr$_2$ [M+H]$^+$: 398.9708, found 398.9718.
\[ \text{N-(2-bromobenzyl)-1-(2-bromopyridin-3-yl)-N-methylmethanamine (21i)} \]

Reaction performed following general procedure B with 20.9 mmol of 2-bromonicotinaldehyde and 23 mmol of secondary amine S5. 21i was isolated as a white solid (5.94 g, 16.1 mmol, 77%). Spectroscopic data for 21i match those previously reported.\(^6\)

\text{TLC Rf} = 0.67 (4:6 Hex:EtOAc)

\text{\(^1H\) NMR} (400 MHz, Chloroform-\(d\)) \(\delta\) 8.24 (d, \(J = 4.47\) Hz, 1H), 7.88 (d, \(J = 7.53\) Hz, 1H), 7.55 (d, \(J = 7.95\), 1H), 7.50 (d, \(J = 7.65\), 1H), 7.30 – 7.23 (m, 2H), 7.12 (t, \(J = 7.84\) Hz, 1H), 3.73 (s, 2H), 3.69 (s, 2H), 2.28 (s, 3H).

\text{\(^13C\) NMR} (126 MHz, Chloroform-\(d\)) \(\delta\) 148.5, 143.9, 138.8, 138.0, 136.1, 133.0, 130.8, 128.8, 127.5, 124.8, 123.0, 61.6, 60.2, 42.5.

\text{HRMS (ESI\(^+\))}: \text{Calcd. for} \text{C}_{14}\text{H}_{15}\text{N}_2\text{Br}_2 \text{[M+H]}^+: 368.9602, \text{found 368.9607}.

\[ \text{N-(2-bromobenzyl)-1-(3-bromopyridin-4-yl)-N-methylmethanamine (21j)} \]

Reaction performed following general procedure B with 4.0 mmol of 3-bromopyridine-4-carbaldehyde and 4.8 mmol of secondary amine S5. 21j was isolated as a light tan oil (979 mg, 2.6 mmol, 66%).

\text{\(^1H\) NMR} (500 MHz, Chloroform-\(d\)) \(\delta\) 8.64 (s, 1H), 8.46 (d, \(J = 5.0\) Hz, 1H), 7.59 – 7.53 (m, 2H), 7.51 (dd, \(J = 7.7, 1.7\) Hz, 1H), 7.29 (td, \(J = 7.6, 1.2\) Hz, 1H), 7.12 (td, \(J = 7.7, 1.8\) Hz, 1H), 3.73 (s, 2H), 3.68 (s, 2H), 2.29 (s, 3H).

\text{\(^13C\) NMR} (126 MHz, Chloroform-\(d\)) \(\delta\) 151.8, 148.4, 147.8, 137.9, 133.0, 130.7, 128.8, 127.5, 125.0, 124.8, 122.6, 61.7, 60.2, 42.7.

\text{HRMS (ESI\(^+\))}: \text{Calcd. for} \text{C}_{14}\text{H}_{15}\text{N}_2\text{Br}_2 \text{[M+H]}^+: 368.9602, \text{found 368.9611}.
\[ \text{N-(2-bromobenzyl)-I-(4-bromopyridin-3-yl)-N-methylmethanamine (21k)} \]

Reaction performed following general procedure B with 4.0 mmol of 4-bromonicotinaldehyde and 4.8 mmol of secondary amine S5. 21k was isolated as a light tan oil (793 mg, 2.1 mmol, 53%).

\(^1\text{H NMR}\) (500 MHz, Chloroform-\(d\)) \(\delta\) 8.67 (s, 1H), 8.27 (d, \(J = 5.3\) Hz, 1H), 7.53 (d, \(J = 7.9\) Hz, 2H), 7.48 (d, \(J = 5.3\) Hz, 1H), 7.28 (t, \(J = 7.6\) Hz, 1H), 7.11 (td, \(J = 7.7, 1.7\) Hz, 1H), 3.72 (s, 4H), 2.27 (s, 3H).

\(^{13}\text{C NMR}\) (126 MHz, Chloroform-\(d\)) \(\delta\) 152.0, 149.0, 138.0, 135.2, 134.5, 132.9, 131.0, 128.7, 127.9, 127.5, 124.7, 61.4, 59.0, 42.3.

\text{HRMS (ESI\(^+\))}: \text{Calcd. for C}_{14}\text{H}_{15}\text{N}_2\text{Br}_2 \text{[M+H]}^+: 368.9602, \text{found 368.9610.}

\[ \text{N-(2-bromobenzyl)-I-(3-bromopyridin-2-yl)-N-methylmethanamine (2II)} \]

Reaction performed following general procedure D with 17.4 mmol of 3-bromo-2-methylpyridine and 17.4 mmol of secondary amine S5. 2II was isolated as a white solid (2.088 g, 8.7 mmol, 50%).

\text{TLC} \text{R}_{f} = 0.28 (8:2 \text{Hex:EtOAc})

\(^1\text{H NMR}\) (500 MHz, Chloroform-\(d\)) \(\delta\) 8.53 (dd, \(J = 4.7, 1.5\) Hz, 1H), 7.85 (dd, \(J = 8.1, 1.5\) Hz, 1H), 7.57 (d, \(J = 7.7\) Hz, 1H), 7.50 (dd, \(J = 8.0, 1.3\) Hz, 1H), 7.26 (td, \(J = 8.0, 1.3\) Hz, 1H), 7.10 – 7.06 (m, 2H), 3.91 (s, 2H), 3.77 (s, 2H), 2.34 (s, 3H).

\(^{13}\text{C NMR}\) (126 MHz, Chloroform-\(d\)) \(\delta\) 156.8, 147.6, 140.7, 138.1, 132.6, 131.2, 128.4, 127.2, 124.6, 123.5, 122.6, 62.5, 60.9, 42.4.

\text{HRMS (ESI\(^+\))}: \text{Calcd. for C}_{16}\text{H}_{15}\text{N}_2\text{Br}_2 \text{[M+H]}^+: 368.9602, \text{found 368.9596.}
1-(6-bromobenzo[d][1,3]dioxol-5-yl)-N-((2-bromopyridin-3-yl)methyl)-N-methylmethanamine (21m)

Reaction performed following general procedure D with 2.9 mmol of 2-bromo-3-methylpyridine and 2.9 mmol of secondary amine 31. 21m was isolated as a colorless oil (756 mg, 1.8 mmol, 63%). Spectroscopic data for 21m match those previously reported.6

TLC Rf = 0.27 (8:2 Hex:EtOAc)

1H NMR (500 MHz, Chloroform-d) δ 8.24 (dd, J = 4.8, 2.0 Hz, 1H), 7.85 (dd, J = 7.6, 2.1 Hz, 1H), 7.25 (dd, J = 7.4, 4.6 Hz, 1H), 7.02 (s, 1H), 6.99 (d, J = 1.3 Hz, 1H), 5.96 (d, J = 1.2 Hz, 2H), 3.65 (s, 1H), 3.62 (s, 1H), 2.25 (s, 3H).

13C NMR (126 MHz, Chloroform-d) δ 148.5, 147.53, 147.50, 144.0, 138.8, 136.1, 131.3, 123.0, 114.8, 112.8, 110.4, 101.8, 61.3, 60.1, 42.3.


1-(6-bromobenzo[d][1,3]dioxol-5-yl)-N-((3-bromopyridin-4-yl)methyl)-N-methylmethanamine (21n)

Reaction performed following general procedure B with 4.03 mmol of 3-bromopyridine-4-carbaldehyde and 4.84 mmol of secondary amine 31. 21n was isolated as a white solid (1.510 g, 3.65 mmol, 90%).

1H NMR (500 MHz, Chloroform-d) δ 8.64 (s, 1H), 8.46 (d, J = 4.9 Hz, 1H) 7.52 (d, J = 5.2 Hz, 1H), 7.03 (s, 1H), 6.99 (s, 1H), 5.96 (s, 2H), 3.64 (s, 2H), 3.62 (s, 2H), 2.26 (s, 3H).

13C NMR (126 MHz, Chloroform-d) δ 151.8, 148.4, 147.7, 147.6, 147.5, 131.1, 124.9, 122.6, 114.8, 112.8, 110.3, 101.8, 61.4, 60.0, 42.5.

N-(2-bromo-3,4-dimethoxybenzyl)-1-(3-bromopyridin-4-yl)-N-methylmethanamine (21o)

Reaction performed following general procedure B with 4.05 mmol of 3-bromopyridine-4-carbaldehyde and 4.85 mmol of secondary amine S13. 21o was isolated as a white solid (1.292 g, 3.00 mmol, 74%).

**TLC** Rf = 0.56 (1:1 Hex:EtOAc)

**1H NMR** (500 MHz, Chloroform-d) δ 8.62 (s, 1H), 8.44 (d, J = 4.9 Hz, 1H), 7.54 (d, J = 5.0 Hz, 1H), 7.19 (d, J = 8.5 Hz, 1H), 6.84 (d, J = 8.5 Hz, 1H), 3.85 (d, J = 6.9 Hz, 6H), 3.66 (d, J = 13.3 Hz, 4H), 2.27 (s, 3H).

**13C NMR** (126 MHz, Chloroform-d) δ 152.6, 151.6, 148.2, 147.8, 146.4, 130.6, 125.5, 124.8, 122.5, 120.4, 110.9, 61.4, 60.4, 59.8, 56.0, 42.5.

**HRMS (ESI+):** Calcd. for C_{16}H_{18}N_{2}O_{2}Br_{2} [M+H]^+: 428.9813, found 428.9823.

N-(2-bromo-4,5-dimethoxybenzyl)-1-(3-bromopyridin-4-yl)-N-methylmethanamine (21p)

Reaction performed following general procedure B with 7.03 mmol of 3-bromopyridine-4-carbaldehyde and 8.44 mmol of secondary amine S14. 21p was isolated as a white solid (1.740 g, 4.05 mmol, 58%).

**TLC** Rf = 0.44 (1:1 Hex:EtOAc)

**1H NMR** (500 MHz, Chloroform-d) δ 8.63 (s, 1H), 8.45 (d, J = 4.9 Hz, 1H), 7.50 (d, J = 4.9 Hz, 1H), 7.04 (s, 1H), 6.98 (s, 1H), 3.84 (d, J = 1.6 Hz, 6H), 3.64 (d, J = 11.2 Hz, 4H), 2.27 (s, 3H).

**13C NMR** (126 MHz, Chloroform-d) δ 151.7, 148.5, 148.3, 148.1, 147.6, 129.7, 124.7, 122.5, 115.3, 114.2, 113.0, 61.0, 59.8, 56.1, 56.0, 42.4.

**HRMS (ESI+):** Calcd. for C_{16}H_{18}N_{2}O_{2}Br_{2} [M+H]^+: 428.9813, found 428.9822.
1-(2-bromo-5-chloropyridin-3-yl)-N-((6-bromobenzo[d][1,3]dioxol-5-yl)methyl)-N-methylmethanamine (25a)

Reaction performed following general procedure D with 3.8 mmol of 2-bromo-5-chloro-3-methylpyridine and 3.8 mmol of secondary amine 31. 25a was isolated as a colorless oil (995 mg, 2.2 mmol, 59%).

TLC Rf = 0.50 (8:2 Hex:EtOAc)

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.21 (d, $J = 2.7$ Hz, 1H), 7.85 (d, $J = 2.3$ Hz, 1H), 6.99 (s, 1H), 6.97 (s, 1H), 5.96 (s, 2H), 3.63 (s, 2H), 3.61 (s, 2H), 2.26 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 147.6, 147.5, 147.0, 140.9, 138.2, 137.5, 131.8, 130.9, 115.0, 112.9, 110.5, 101.8, 61.5, 59.6, 42.5.

HRMS (ESI$^+$): Calcd. for C$_{15}$H$_{14}$N$_2$O$_2$ClBr$_2$ [M+H]$^+$: 446.9111, found 446.9124.

1-(2-bromo-5-fluoropyridin-3-yl)-N-((6-bromobenzo[d][1,3]dioxol-5-yl)methyl)-N-methylmethanamine (25b)

Reaction performed following general procedure D with 3.4 mmol of 2-bromo-5-fluoro-3-methylpyridine and 3.5 mmol of secondary amine 31. 25b was isolated as a white solid (820 mg, 1.90 mmol, 56%).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.14 (d, $J = 3.01$ Hz, 1H), 7.68 (dd, $J = 8.81$, 3.01 Hz, 1H), 7.01 (s, 1H), 6.98 (s, 1H), 3.64 (s, 2H), 3.62 (s, 2H), 2.27 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 147.6, 158.7, 147.6 (d, $J_{CF} = 10.5$ Hz), 138.2 (d, $J_{CF} = 3.5$ Hz), 136.9 (d, $J_{CF} = 1.9$ Hz), 136.4 (d, $J_{CF} = 25.3$ Hz), 130.9, 125.8 (d, $J_{CF} = 20.4$ Hz), 115.0, 112.9, 110.4, 101.9, 61.5, 59.5, 42.5.

HRMS (ESI$^+$): Calcd. for C$_{15}$H$_{14}$N$_2$O$_2$FBr$_2$ [M+H]$^+$: 430.9406, found 430.9408.
9-(pyrrolidin-1-ylmethyl)benzo[h]quinoline (35)

Reaction performed following general procedure D with 0.26 mmol of 17 and 0.39 mmol of pyrrolidine. The crude material was purified by flash column chromatography, using Et3N neutralized silica using a gradient of 100% CHCl₃ to 96:4 CHCl₃:MeOH. 35 was isolated as a light yellow semisolid (50 mg, 0.19 mmol, 74%).

**TLC** Rₑₐₜ = 0.45 (9:1 CHCl₃:MeOH, Et3N treated plate)

**¹H NMR** (500 MHz, Chloroform-­d) δ 9.17 (dt, J = 1.7, 0.9 Hz, 1H), 9.00 (dd, J = 4.4, 1.7 Hz, 1H), 8.19 (dd, J = 8.0, 1.7 Hz, 1H), 7.91 (d, J = 7.9 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.67 (dd, J = 8.8, 1.6 Hz, 1H), 7.55 – 7.50 (m, 1H), 3.99 (s, 2H), 2.68 (s, 4H), 1.84 (d, J = 4.0 Hz, 4H).

**¹³C NMR** (126 MHz, Chloroform-­d) δ 146.2, 143.9, 133.4, 130.3, 128.7, 127.0, 125.6, 125.0, 124.0, 122.6, 121.8, 119.2, 58.2, 51.5, 20.9.

**HRMS (ESI⁺):** Calcd. for C₁₈H₁₉N₂ [M+H]⁺: 263.1548, found 263.1555.

*N-(2-bromobenzyl)-1-(2-bromophenyl)-N-methylmethanamine (S₁₆)*

Reaction performed following general procedure C with 10 mmol of secondary amine S₅. S₁₆ was isolated as a colorless oil (3.08 g, 8.3 mmol, 83%). Spectroscopic data for S₁₆ match those previously reported.⁶

**¹H NMR** (500 MHz, Chloroform-­d) δ 7.59 (d, J = 7.7 Hz, 2H), 7.55 (dt, J = 8.0, 1.4 Hz, 2H) 7.30 (tt, J = 7.6, 1.6 Hz, 2H), 7.11 (tt, J = 7.6, 2.0 Hz, 2H), 3.74 (s, 4H), 2.29 (s, 3H).
**N-(2-bromobenzyl)-1-(1-bromonaphthalen-2-yl)-N-methylmethanamine (S17)**

![N-(2-bromobenzyl)-1-(1-bromonaphthalen-2-yl)-N-methylmethanamine](image)

Reaction performed following general procedure C with 1.72 mmol 2-bromobenzylbromide and 1.57 mmol of secondary amine S6. S17 was isolated as a yellow oil (340 mg, 0.81 mmol, 54%).

**TLC** \( R_f = 0.51 \) (8:1 Hex:EtOAc)

\(^1\text{H NMR}\) (400 MHz, Chloroform-\(d\)) \( \delta \) 8.31 (d, \( J = 8.6 \) Hz, 1H), 7.86 – 7.67 (m, 3H), 7.66 – 7.33 (m, 5H), 7.33 – 7.20 (m, 1H), 7.07 (td, \( J = 7.7, 2.0 \) Hz, 1H), 3.94 (s, 1H), 3.73 (s, 2H), 2.26 (s, 3H).

\(^{13}\text{C NMR}\) (125 MHz, Chloroform-\(d\)) \( \delta \) 138.5, 136.9, 134.0, 132.9, 132.5, 131.0, 128.6, 128.2, 128.1, 127.6, 127.5, 127.39, 127.35, 126.4, 124.8, 124.3, 62.2, 61.6, 42.4.

**HRMS (ESI\(^+\)):** Calcd. for C\(_{19}\)H\(_{18}\)NBr\(_2\) [M+H]\(^+\)\( : 417.9806\), found 417.9812.

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**1-(1-bromonaphthalen-2-yl)-N-((1-bromonaphthalen-2-yl)methyl)-N-methylmethanamine (S18)**

![1-(1-bromonaphthalen-2-yl)-N-((1-bromonaphthalen-2-yl)methyl)-N-methylmethanamine](image)

Reaction performed following general procedure D with 1.54 mmol of 1-bromo-2-methylnaphthalene and 1.54 mmol of secondary amine S6. S18 was isolated as a yellow oil (448 mg, 0.95 mmol, 62%). Spectroscopic data for S18 match those previously reported.\(^8\)

**TLC** \( R_f = 0.49 \) (9:1 Hex:EtOAc)

\(^1\text{H NMR}\) (500 MHz, Chloroform-\(d\)) \( \delta \) 8.36 (d, \( J = 8.5 \) Hz, 2H), 7.83 – 7.73 (m, 6H), 7.62 – 7.57 (m, 2H), 7.53 – 7.47 (m, 2H), 4.02 (s, 4H), 2.34 (s, 3H).

\(^{13}\text{C NMR}\) (126 MHz, Chloroform-\(d\)) \( \delta \) 136.7, 134.0, 132.5, 128.2, 127.6, 127.5, 127.4, 126.4, 124.4, 62.2, 42.5.

**HRMS (ESI\(^+\)):** Calcd. for C\(_{23}\)H\(_{20}\)NBr\(_2\) [M+H]\(^+\)\( : 467.9963\), found 467.9973.
1-(1-bromonaphthalen-2-yl)-N-((2-bromopyridin-3-yl)methyl)-N-methylmethanamine (S19)

Reaction performed following general procedure D with 3.0 mmol of 2-bromo-3-methylpyridine and 3.0 mmol of secondary amine S6. S19 was isolated as an orange oil (634 mg, 1.5 mmol, 50%). Spectroscopic data for S19 match those previously reported.⁶

TLC Rf = 0.40 (7:3 Hex:EtOAc)

¹H NMR (500 MHz, Chloroform-d) δ 8.34 (d, J = 8.6 Hz, 1H), 8.25 (dd, J = 4.8, 2.0 Hz, 1H), 7.89 (dd, J = 7.6, 1.9 Hz, 1H), 7.81 (d, J = 8.1 Hz, 1H), 7.78 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 8.4 Hz, 1H), 7.59 (t, J = 7.7 Hz, 1H), 7.51 (t, J = 7.4 Hz, 1H), 7.24 (dd, J = 7.4, 4.5 Hz, 1H), 3.99 (s, 2H), 3.73 (s, 2H), 2.31 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 148.5, 144.0, 138.9, 136.3, 136.1, 134.0, 132.6, 128.2, 127.9, 127.7, 127.5, 126.5, 124.5, 123.0, 62.4, 60.3, 42.6.


tert-butyl 3-bromo-4-(((2-bromopyridin-3-yl)methyl)(methyl)amino)methyl)benzoate (S20)

Reaction performed following general procedure D with 3.06 mmol of S3 and 3.06 mmol of secondary amine S7. S20 was isolated as a yellow oil (803 mg, 1.71 mmol, 56%).

TLC Rf = 0.11 (9:1 Hex:EtOAc)

¹H NMR (500 MHz, Chloroform-d) δ 8.25 (dd, J = 4.8, 2.1 Hz, 1H), 8.14 (d, J = 1.7 Hz, 1H), 7.90 (dd, J = 8.0, 1.7 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.58 (d, J = 8.0 Hz, 1H), 7.25 (dd, J = 7.2, 5.1 Hz, 1H), 3.75 (s, 2H), 3.68 (s, 2H), 2.28 (s, 3H), 1.58 (s, 9H).

¹³C NMR (126 MHz, Chloroform-d) δ 164.5, 148.6, 143.9, 142.6, 138.7, 135.8, 133.9, 132.6, 130.3, 128.4, 124.3, 123.1, 81.8, 61.5, 60.2, 42.5, 28.3.

**N-(2-bromo-4-fluorobenzyl)-1-(2-bromopyridin-3-yl)-N-methylmethanamine (S21)**

Reaction performed following general procedure D with 2.75 mmol of 2-bromo-3-methylpyridine and 2.75 mmol of secondary amine S15. S21 was isolated as a yellow oil (526 mg, 1.36 mmol, 49%). Spectroscopic data for S21 match those previously reported.³

\[ ^1H\text{ NMR} (500 \text{ MHz, Chloroform-}d) \delta 8.25 (dd, J = 4.8, 2.0 \text{ Hz, 1H}), 7.84 (dd, J = 7.6, 2.0 \text{ Hz, 1H}), 7.46 (dd, J = 8.6, 6.2 \text{ Hz, 1H}), 7.32 – 7.22 (m, 2H), 7.01 (d, J = 2.6 \text{ Hz, 0H}), 3.67 (d, J = 4.9 \text{ Hz, 4H}), 2.25 (s, 3H). \]
\[ ^{13}\text{C NMR} (126 \text{ MHz, Chloroform-}d) \delta 162.5, 160.5, 148.4, 146.6, 140.8, 138.6, 135.4, 132.9, 130.9, 129.6, 128.8, 128.5, 128.1, 127.9, 127.8, 127.4, 126.3, 124.7, 121.8, 121.3, 63.0, 61.8, 42.7. \]

**HRMS (ESI⁺): Calculated for C₁₄H₁₃N₂F₂Br₂ [M+H]⁺: 386.9515, found 386.9508.**

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**1-(10-bromobenzo[h]quinolin-9-yl)-N-(2-bromobenzyl)-N-methylmethanamine (S22)**

Reaction performed following general procedure D with 2.0 mmol of 10-bromo-9-methylbenzo[h]quinoline S4 and 2.0 mmol of secondary amine S5. S22 was isolated as a pale yellow oil (422 mg, 0.90 mmol, 45%).

\[ ^1H\text{ NMR} (500 \text{ MHz, Chloroform-}d) \delta 9.09 (dd, J = 4.3, 1.8 \text{ Hz, 1H}), 8.17 (dd, J = 8.0, 1.5 \text{ Hz, 1H}), 8.02 (d, J = 8.1 \text{ Hz, 1H}), 7.85 (d, J = 8.2 \text{ Hz, 1H}), 7.75 (d, J = 8.7 \text{ Hz, 1H}), 7.67 (d, J = 8.7 \text{ Hz, 1H}), 7.63 (d, J = 8.7 \text{ Hz, 1H}), 7.56 (d, J = 3.8 \text{ Hz, 1H}), 7.54 (d, J = 3.8 \text{ Hz, 1H}), 7.30 (t, J = 7.4 \text{ Hz, 1H}), 7.11 (t, J = 7.4 \text{ Hz, 1H}), 4.11 (s, 2H), 3.82 (s, 2H), 2.35 (s, 3H). \]
\[ ^{13}\text{C NMR} (126 \text{ MHz, Chloroform-}d) \delta 146.6, 140.9, 138.6, 135.8, 135.4, 132.9, 130.9, 129.6, 128.8, 128.5, 128.1, 127.9, 127.8, 127.4, 126.3, 124.7, 121.8, 121.3, 63.0, 61.8, 42.7. \]

**HRMS (ESI⁺): Calculated for C₂₂H₁₉N₂Br₂ [M+H]⁺: 468.9915, found 468.9909.**
General procedure E for the synthesis of biaryl-linked dihydroazepines
To a flame dried round bottom flask charged with a magnetic stir bar was added Et₄NI (1 equiv), activated Zn powder (10 equiv.) and NiBr₂(PPh₃)₂ (1 equiv.). The flask was evacuated and back filled with N₂ three times, followed by the addition of anhydrous THF (0.05 M). The green reaction solution was allowed to stir for ten minutes in which time the color changed to a dark red. Tertiary amine (1 equiv) dissolved in anhydrous THF was added and the resulting mixture was stirred at 50 °C for 30 minutes to 24 hours, followed by TLC. Following complete consumption of starting material, the reaction was cooled to room temperature and quenched with 2M NH₃ (aq.) (10 mL). After stirring for 15 minutes, the crude reaction mixture was filtered through a pad of Celite and transferred to a separatory funnel. The solution was extracted with EtOAc (20 mL x 3). The combined organic extracts were washed with brine (20 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude material was purified by flash column chromatography using a gradient of 1:1 Hex:EtOAc to 1:1 EtOAc:MeOH to afford the desired biaryl-linked dihydroazepine.

6-methyl-6,7-dihydro-5H-dibenzo[c,e]azepine (7)

|  
\[ \text{N–Me} \]

Reaction performed following general procedure E with 1.35 mmol of tertiary amine S16. The reaction required 18 hours to go to completion instead of the standard 30 minutes. 7 was isolated as a viscous, pale yellow oil (204 mg, 0.98 mmol, 72%). Spectroscopic data for 7 match those previously reported.⁶

TLC Rᵣ= 0.50 (9:1 EtOAc:MeOH)

¹H NMR (500 MHz, Chloroform-d) δ 7.52 – 7.50 (m, 2H), 7.45 (ddd, J = 8.75, 5.94, 2.84 Hz, 2H), 7.37 – 7.36 (m, 4H), 3.38 (s, 4H), 2.46 (s, 3H).

¹³C NMR (126 MHz, Chloroform-d) δ 141.2, 134.5, 129.9, 128.2, 127.82, 127.81 57.3, 43.1.

6-methyl-6,7-dihydro-5H-benzo[c]pyrido[2,3-e]azepine (11)

![Chemical Structure](image)

Reaction performed following general procedure E with 8.1 mmol of tertiary amine 21i. 11 was isolated as a yellow oil (1.569 g, 7.5 mmol, 92%). Spectroscopic data for 11 match those previously reported.6

TLC Rf = 0.20 (9:1 CHCl3:MeOH)

^1H NMR (500 MHz, Chloroform-d) δ 8.61 (dd, J = 5.0, 1.8 Hz, 1H), 7.80 (dd, J = 7.7, 1.5 Hz, 1H), 7.57 (dd, J = 7.6, 1.8 Hz, 1H), 7.41 (td, J = 7.5, 1.4 Hz, 1H), 7.33 (td, J = 7.4, 1.4 Hz, 1H), 7.25 (dd, J = 7.4, 1.4 Hz, 1H), 7.16 (dd, J = 7.6, 4.8 Hz, 1H), 3.36 (s, 2H), 3.27 (s, 2H), 2.39 (s, 3H).

^13C NMR (126 MHz, Chloroform-d) δ 158.4, 149.0, 140.0, 137.4, 134.0, 130.0, 129.6, 128.9, 128.2, 128.1, 122.1, 56.7, 56.0, 42.7.

HRMS(ESI^+): Calcd. for C_{14}H_{15}N_{2} [M+H]^+: 211.1235, found 211.1234.

6,11-dimethyl-6,7-dihydro-5H-benzo[c]pyrido[2,3-e]azepine (22a)

![Chemical Structure](image)

Reaction performed following general procedure E with 1.4 mmol of tertiary amine 21a. 22a was isolated as a brown oil (217 mg, 0.97 mmol, 69%).

TLC Rf = 0.29 (6:4 EtOAc:MeOH)

^1H NMR (500 MHz, Chloroform-d) δ 8.67 (dd, J = 4.9, 1.7 Hz, 1H), 7.66 (dd, J = 7.6, 1.8 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.23 (dt, J = 7.5, 4.3 Hz, 1H), 7.13 (dd, J = 6.8, 1.9 Hz, 1H), 3.49 (d, J = 12.5 Hz, 1H), 3.46 (d, J = 12.5 Hz, 1H), 3.16 (d, J = 12.5 Hz, 1H), 3.07 (d, J = 12.5 Hz, 1H), 2.48 (s, 3H), 2.40 (s, 3H).

^13C NMR (126 MHz, Chloroform-d) δ 158.7, 148.1, 137.8, 137.0, 136.9, 134.0, 130.93, 130.90, 128.4, 127.2, 121.9, 57.0, 55.8, 42.8, 20.5.

HRMS (ESI^+): Calcd. for C_{15}H_{17}N_{2} [M+H]^+: 225.1392, found 225.1394.
6,10-dimethyl-6,7-dihydro-5H-benzo[c]pyrido[2,3-e]azepine (22b)

Reaction performed following general procedure E with 1.93 mmol of tertiary amine 21a. 22b was isolated as a light brown oil (320 mg, 1.43 mmol, 74%). Spectroscopic data for 22b match those previously reported.6

**TLC** \( R_f = 0.36 \) (9:1 CHCl3:MeOH)

**\(^1\)H NMR** (500 MHz, Chloroform-\(d\)) \( \delta \) 8.72 – 8.71 (m, 1H), 7.72 (s, 1H), 7.68 (d, \( J = 7.6 \) Hz, 1H), 7.30 – 7.25 (m, 3H), 3.43 (d, \( J = 2.1 \) Hz, 2H), 3.37 (d, \( J = 2.2 \) Hz, 2H), 2.49 (s, 3H), 2.47 (s, 3H).

**\(^{13}\)C NMR** (126 MHz, Chloroform-\(d\)) \( \delta \) 159.0, 149.1, 140.1, 138.1, 137.6, 131.7, 130.5, 129.84, 129.80, 128.8, 122.3, 56.8, 56.6, 43.2, 21.4.

**HRMS (ESI\(^+\))**: Calcd. for C\(_{15}\)H\(_{17}\)N\(_2\) [M+H]\(^+\): 225.1392, found 225.1397.

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6,9-dimethyl-6,7-dihydro-5H-benzo[c]pyrido[2,3-e]azepine (22c)

Reaction performed following general procedure E with 1.3 mmol of tertiary amine 21c. 22c was isolated as a pale orange solid (175 mg, 0.79 mmol, 61%).

**TLC** \( R_f = 0.27 \) (6:4 EtOAc:MeOH)

**\(^1\)H NMR** (500 MHz, Chloroform-\(d\)) \( \delta \) 8.69 (dd, \( J = 4.9 \), 1.6 Hz, 1H), 7.77 (d, \( J = 7.8 \) Hz, 1H), 7.67 (dd, \( J = 7.4 \), 1.7 Hz, 1H), 7.32 (d, \( J = 7.8 \) Hz, 1H), 7.26 – 7.23 (m, 1H), 7.16 (s, 1H), 3.43 (s, 2H), 3.37 (s, 2H), 2.50 (s, 3H), 2.43 (s, 3H).

**\(^{13}\)C NMR** (126 MHz, Chloroform-\(d\)) \( \delta \) 158.7, 149.1, 139.1, 137.6, 137.4, 133.9, 130.5, 130.0, 129.1, 128.2, 122.0, 57.0, 56.4, 43.0, 21.4.

**HRMS (ESI\(^+\))**: Calcd. for C\(_{15}\)H\(_{17}\)N\(_2\) [M+H]\(^+\): 225.1392, found 225.1397.
6,8-dimethyl-6,7-dihydro-5H-benzo[c]pyrido[2,3-e]azepine (22d)

Reaction performed following general procedure E with 1.76 mmol of tertiary amine 21d. 22d was isolated as a light tan oil (316 mg, 1.41 mmol, 80%). Spectroscopic data for 22d match those previously reported.6

TLC Rf = 0.22 (9:1 CHCl3:MeOH)

1H NMR (500 MHz, Chloroform-d) δ 8.63 (dd, J = 4.9, 1.8 Hz, 1H), 7.61 (dd, J = 7.6, 1.8 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.19 (dd, J = 7.6, 4.9 Hz, 1H), 7.10 (dd, J = 6.9, 1.9 Hz, 1H), 3.43 (t, J = 13.8 Hz, 2H), 3.11 (d, J = 12.9 Hz, 1H), 3.04 (d, J = 12.3 Hz, 1H), 2.45 (s, 3H), 2.35 (s, 3H).

13C NMR (126 MHz, Chloroform-d) δ 158.6, 148.0, 148.0, 137.1, 135.7, 135.7, 131.1, 130.9, 130.9, 128.3, 127.2, 121.8, 57.0, 55.8, 42.8, 20.5.


11-methoxy-6-methyl-6,7-dihydro-5H-benzo[c]pyrido[2,3-e]azepine (22e)

Reaction performed following general procedure E with 1.25 mmol of tertiary amine 21e. 22e was isolated as an off-white solid (170 mg, 0.71 mmol, 57%).

1H NMR (500 MHz, Chloroform-d) δ 8.74 (dd, J = 4.9, 1.74 Hz, 1H), 7.68 (dd, J = 7.6, 1.75 Hz, 1H), 7.37-7.41 (m, 1H), 7.24-7.27 (m, 1H), 7.06 (d, J = 8.5 Hz, 1H), 6.94 (d, J = 7.3 Hz, 1H), 3.87 (s, 3H), 3.52 (d, J = 12.2 Hz, 1H), 3.47 (d, J = 12.8 Hz, 1H), 3.19 (d, J = 12.9 Hz, 1H), 3.12 (d, J = 12.1 Hz, 1H), 2.42 (s, 3H).

13C NMR (126 MHz, Chloroform-d) δ 156.8, 156.5, 148.4, 137.1, 135.7, 131.1, 129.8, 127.4, 122.1, 111.4, 56.7, 56.2, 56.1, 43.0.

10-methoxy-6-methyl-6,7-dihydro-5H-benzo[c]pyrido[2,3-e]azepine (22f)

Reaction performed following general procedure E with 2.50 mmol of tertiary amine 21f. 22f was isolated as a clear oil (250 mg, 1.89 mmol, 42%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.70 (dt, $J = 4.9$, 1.7 Hz, 1H), 7.67 (dt, $J = 7.5$, 1.6 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.29 – 7.24 (m, 2H), 6.97 (dt, $J = 8.2$, 2.0 Hz, 1H), 3.89 (d, $J = 1.3$ Hz, 3H), 3.37 (d, $J = 12.0$ Hz, 4H), 2.46 (d, $J = 1.3$ Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 159.7, 158.6, 149.0, 141.4, 137.6, 130.9, 130.3, 126.8, 122.3, 115.6, 112.6, 56.3, 56.2, 55.5, 42.8.

HRMS (ESI$^+$): Calcd. for C$_{15}$H$_{17}$N$_2$O [M+H]$^+$: 241.1341, found 241.1347.

9-methoxy-6-methyl-6,7-dihydro-5H-benzo[c]pyrido[2,3-e]azepine (22g)

Reaction performed following general procedure E with 1.25 mmol of tertiary amine 21g. 22g was isolated as an off-white solid (172 mg, 0.72 mmol, 58%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.67 (d, $J = 4.6$, 1H), 7.83 (d, $J = 8.5$ Hz, 1H), 7.66 (d, $J = 7.5$ Hz, 1H), 7.24 (dd, $J = 7.6$, 5.1 Hz, 1H), 7.04 (dd, $J = 8.6$, 2.5 Hz, 1H), 6.89 (d, $J = 2.5$ Hz, 1H), 3.89 (s, 3H), 3.44 (s, 2H), 3.37 (s, 2H), 2.51 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 160.2, 158.6, 148.9, 137.5, 136.1, 132.8, 130.1, 129.6, 121.7, 115.2, 113.5, 57.4, 56.7, 55.4, 43.3.

HRMS (ESI$^+$): Calcd. for C$_{15}$H$_{17}$N$_2$O [M+H]$^+$: 241.1341, found 241.1343.
8-methoxy-6-methyl-6,7-dihydro-5H-benzo[c]pyrido[2,3-e]azepine (22h)

Reaction performed following general procedure E with 1.14 mmol of tertiary amine 21h. 22h was isolated as an orange solid (138 mg, 0.57 mmol, 50%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.69 (dd, $J = 4.9$, 1.7 Hz, 1H), 7.67 (dd, $J = 7.6$, 1.7 Hz, 1H), 7.42-7.47 (m, 2H), 7.26-7.29 (m, 1H), 7.01 (dd, $J = 7.5$, 1.8 Hz, 1H), 3.89 (s, 3H), 3.57 (s, 2H), 3.35 (s, 2H), 2.48 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 158.7, 157.5, 149.2, 142.0, 137.6, 130.7, 128.9, 122.5, 120.5, 111.0, 56.8, 55.9, 48.3, 43.4.

HRMS (ESI$^+$): Calcd. for C$_{15}$H$_{17}$N$_2$O [M+H]$^+$: 241.1341, found 241.1346.

6-methyl-6,7-dihydro-5H-benzo[c]pyrido[3,4-e]azepine (22j)

Reaction performed following general procedure E with 2.65 mmol of tertiary amine 21j. 22j was isolated as a tan oil (234 mg, 1.11 mmol, 42%).

TLC $R_f$ = 0.28 (9:1 CHCl$_3$:MeOH)

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 8.73 (s, 1H), 8.60 (d, $J = 4.8$ Hz, 1H), 7.52 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.47 (td, $J = 7.3$, 1.7 Hz, 1H), 7.42 (td, $J = 7.2$, 1.5 Hz, 1H), 7.38 (dd, $J = 7.4$, 1.6 Hz, 1H), 7.28 (d, $J = 4.9$ Hz, 1H), 3.37 (s, 4H), 2.46 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 149.2, 148.1, 142.6, 137.5, 136.7, 135.0, 130.2, 128.7, 128.5, 127.6, 124.3, 57.3, 56.5, 43.5.

HRMS (ESI$^+$): Calcd. for C$_{14}$H$_{15}$N$_2$ [M+H]$^+$: 211.1235, found 211.1240.
6-methyl-6,7-dihydro-5H-benzo[c]pyrido[4,3-e]azepine (22k)

![Chemical Structure](image-url)

Reactions performed following general procedure E with 1.34 mmol of tertiary amine 21k. 22k was isolated as a light yellow oil (226 mg, 50%).

**TLC** R_f = 0.28 (9:1 CHCl_3:MeOH)

**^1H NMR** (500 MHz, Chloroform-d) δ 8.68 (d, J = 5.0 Hz, 1H), 8.58 (s, 1H), 7.52 (dd, J = 7.4, 1.7 Hz, 1H), 7.49 (td, J = 7.3, 1.6 Hz, 1H), 7.45 (td, J = 7.2, 1.6 Hz, 1H), 7.42 – 7.39 (m, 2H), 3.39 (s, 2H), 3.38 (s, 2H), 2.47 (s, 3H).

**^13C NMR** (126 MHz, Chloroform-d) δ 150.2, 149.8, 149.0, 138.5, 135.1, 130.3, 129.9, 129.3, 128.5, 127.8, 121.8, 57.2, 54.4, 43.3.

**HRMS (ESI^+):** Calcd. for C_{14}H_{15}N_{2} [M+H]^+: 211.1235, found 211.1239.

6-methyl-6,7-dihydro-5H-benzo[c]pyrido[3,2-e]azepine (22l)

![Chemical Structure](image-url)

Reactions performed following general procedure E with 1.34 mmol of tertiary amine 21l. 22l was isolated as a tan oil (23 mg, 0.1 mmol, 8%).

**TLC** R_f = 0.20 (9:1 CHCl_3:MeOH)

**^1H NMR** (500 MHz, Chloroform-d) δ 8.60 (dd, J = 4.9, 1.6 Hz, 1H), 7.80 (dd, J = 7.7, 1.7 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.44 – 7.40 (m, 2H), 7.38 (dd, J = 5.0, 1.3 Hz, 1H), 3.61 (s, 2H), 3.39 (s, 2H), 2.53 (s, 3H).

**^13C NMR** (126 MHz, Chloroform-d) δ 154.6, 148.7, 139.1, 136.2, 135.2, 135.0, 130.1, 128.6, 128.4, 127.8, 123.2, 59.2, 57.6, 43.8.

**HRMS (ESI^+):** Calcd. for C_{14}H_{15}N_{2} [M+H]^+: 211.1235, found 211.1238.
6-methyl-6,7-dihydro-5H-[1,3]dioxolo[4',5':4,5]benzo[1,2-c]pyrido[2,3-e]azepine (22m)

Reaction performed following general procedure E with 1.81 mmol of tertiary amine 21m. 22m was isolated as a light tan solid (304 mg, 66%). Spectroscopic data for 22m match those previously reported. 6

**TLC** Rf = 0.19 (9:1 CHCl3:MeOH)

**1H NMR** (500 MHz, Chloroform-d) δ 8.66 (d, J = 4.5 Hz, 1H), 7.65 (d, J = 7.5 Hz, 1H), 7.37 (d, J = 1.2 Hz, 1H), 7.24 – 7.22 (m, 1H), 6.82 (s, 1H), 6.03 (s, 2H), 3.33 (s, 2H), 3.32 (s, 2H), 2.46 (s, 3H).

**13C NMR** (126 MHz, Chloroform-d) δ 158.5, 148.9, 148.2, 147.5, 137.5, 134.2, 130.4, 128.9, 121.9, 109.9, 108.6, 101.3, 56.8, 56.5, 43.0.

**HRMS (ESI+):** Calcd. for C15H15N2O2 [M+H]+: 255.1134, found 255.1138.

6-methyl-6,7-dihydro-5H-[1,3]dioxolo[4',5':4,5]benzo[1,2-c]pyrido[3,4-e]azepine (22n)

Reaction performed following general procedure E with 1.45 mmol of tertiary amine 21n. The reaction required 18 hours to go to completion instead of the standard 30 minutes. 22n was isolated as an off-white solid (200 mg, 0.79 mmol, 54%).

**1H NMR** (500 MHz, Chloroform-d) δ 8.62 (s, 1H), 8.52 (d, J = 4.8 Hz, 1H), 7.22 (d, J = 4.9 Hz, 1H), 6.96 (s, 1H), 6.84 (s, 1H), 6.00 (s, 2H), 3.30 (s, 2H), 3.22 (s, 2H), 2.39 (s, 3H).

**13C NMR** (126 MHz, Chloroform-d) δ 148.7, 147.9, 147.7, 147.7, 142.6, 136.6, 131.0, 129.0, 124.2, 110.5, 107.9, 101.5, 57.0, 56.5, 43.3.

10,11-dimethoxy-6-methyl-6,7-dihydro-5H-benzo[c]pyrido[3,4-e]azepine (22o)

Reaction performed following general procedure E with 2.33 mmol of tertiary amine 21o. The reaction required 14 hours to go to completion instead of the standard 30 minutes. 22o was isolated as an off-white solid (443 mg, 1.64 mmol, 70%).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.92 (s, 1H), 8.57 (d, $J = 4.9$ Hz, 1H), 7.27 (d, $J = 7.7$ Hz, 1H), 7.08 (d, $J = 8.2$ Hz, 1H), 6.95 (d, $J = 8.3$ Hz, 1H), 3.93 (s, 3H), 3.64 (s, 3H), 3.46 (dd, $J = 12.5$, 8.0 Hz, 2H), 3.23 (d, $J = 12.2$ Hz, 1H), 3.00 (d, $J = 12.8$ Hz, 1H), 2.40 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 152.8, 150.6, 148.6, 145.8, 142.3, 132.4, 130.3, 128.1, 125.4, 124.1, 111.9, 60.8, 56.6, 56.1, 55.9, 43.0.

HRMS (ESI$^+$): Calcd. for C$_{16}$H$_{18}$N$_2$O$_2$ [M+H]$^+$: 274.1447, found 274.1455.

9,10-dimethoxy-6-methyl-6,7-dihydro-5H-benzo[c]pyrido[3,4-e]azepine (22p)

Reaction performed following general procedure E with 2.33 mmol of tertiary amine 21p. The reaction required 14 hours to go to completion instead of the standard 30 minutes. 22p was isolated as an off-white solid (254 mg, 0.94 mmol, 40%).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.73 (s, 1H), 8.60 – 8.55 (m, 1H), 7.28 (d, $J = 4.8$ Hz, 1H), 7.03 (d, $J = 2.0$ Hz, 1H), 6.94 (d, $J = 1.9$ Hz, 1H), 3.96 (dd, $J = 5.2$, 2.1 Hz, 6H), 3.40 (s, 2H), 3.32 (s, 2H), 2.48 (d, $J = 2.0$ Hz, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 149.0, 148.9, 148.6, 147.8, 142.1, 136.6, 129.6, 127.6, 124.3, 113.1, 110.6, 56.9, 56.4, 56.13, 56.08, 43.2.

HRMS (ESI$^+$): Calcd. for C$_{16}$H$_{18}$N$_2$O$_2$ [M+H]$^+$: 274.1447, found 274.1454.
3-chloro-6-methyl-6,7-dihydro-5H-[1,3]dioxolo[4',5':4,5]benzo[1,2-c]pyrido[2,3-e]azepine (32a)

Reaction performed at 0 °C for 3h following general procedure E with 0.566 mmol of tertiary amine 25a. 32a was isolated as a light yellow oil (74 mg, 45%).

TLC Rf = 0.28 (9:1 CHCl3:MeOH)

1H NMR (500 MHz, Chloroform-d) δ 8.61 (d, J = 2.4 Hz, 1H), 7.65 (d, J = 2.4 Hz, 1H), 7.32 (s, 1H), 6.82 (s, 1H), 6.03 (s, 2H), 3.34 (s, 2H), 2.46 (s, 3H).

13C NMR (126 MHz, Chloroform-d) δ 156.8, 148.6, 148.0, 147.9, 137.2, 133.3, 131.2, 130.2, 128.9, 110.2, 108.7, 101.6, 56.8, 56.1, 42.9.


3-fluoro-6-methyl-6,7-dihydro-5H-[1,3]dioxolo[4',5':4,5]benzo[1,2-c]pyrido[2,3-e]azepine (32b)

Reaction performed following general procedure E with 2.13 mmol of tertiary amine 25b. 32b was isolated as a light brown oil (337 mg, 1.23 mmol, 58%).

1H NMR (500 MHz, Chloroform-d) δ 8.51 (d, J = 2.77 Hz, 1H), 7.40 (dd, J = 8.20, 2.81 Hz, 1H), 7.30 (s, 1H), 6.81 (s, 1H), 6.03 (s, 2H), 3.32 (s, 4H), 2.46 (s, 3H).

13C NMR (126 MHz, Chloroform-d) δ 159.4, 157.4, 154.8 (d, JCF = 4.0 Hz), 148.0 (d, JCF = 57.8 Hz) 137.0 (d, JCF = 23.4 Hz), 133.4, 131.8 (d, JCF = 3.7 Hz), 128.8, 124.3 (d, JCF = 17.7 Hz), 110.0, 108.7, 101.5, 57.0, 56.4, 43.2.

10-methyl-10,11-dihydro-9H-benzo[5',6']azepino[4',3':3,4]benzo[1,2-h]quinoline (38)

Reaction performed following general procedure E with 0.79 mmol of tertiary amine S22. 38 was isolated as a light brown solid (123 mg, 0.40 mmol, 50%).

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.41 (dd, $J = 4.2, 1.8$ Hz, 1H), 8.10 (dd, $J = 7.9, 1.8$ Hz, 1H), 7.93 (d, $J = 7.8$ Hz, 1H), 7.86 (d, $J = 8.7$ Hz, 1H), 7.71 (d, $J = 8.7$ Hz, 1H), 7.66 (d, $J = 7.8$ Hz, 1H), 7.50 (dt, $J = 7.6, 0.7$ Hz, 1H), 7.37 (td, $J = 7.5, 1.2$ Hz, 1H), 7.34 (dd, $J = 7.9, 4.2$ Hz, 1H), 7.22 (td, $J = 7.5, 1.2$ Hz, 1H), 7.12 (dd, $J = 7.6, 1.2$ Hz, 1H), 3.79 (d, $J = 12.4$ Hz, 1H), 3.72 (d, $J = 12.9$ Hz, 1H), 3.64 (d, $J = 11.9$ Hz, 1H), 3.34 (d, $J = 12.9$ Hz, 1H), 2.53 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 147.1, 146.8, 142.9, 138.4, 135.3, 135.2, 134.2, 133.0, 131.1, 129.8, 128.8, 128.5, 128.2, 128.1, 127.5, 126.6, 126.0, 121.4, 57.6, 57.4, 42.8.

HRMS (ESI$^+$): Calcd. for C$_{22}$H$_{19}$N$_2$ [M+H]$^+$: 311.1548, found 311.1552.

6-methyl-6,7-dihydro-5H-naphtho[2,1-c]pyrido[2,3-e]azepine (S23)

Reaction performed following general procedure E with 1.44 mmol of tertiary amine S19. S23 was isolated as a light brown oil (278 mg, 1.07 mmol, 74%). Spectroscopic data for 45 match those previously reported.$^6$

TLC $R_f = 0.36$ (9:1 CHCl$_3$:MeOH)

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.83 – 8.81 (m, 1H), 8.46 – 8.44 (m, 1H), 7.94 – 7.90 (m, 2H), 7.77 (dt, $J = 7.6, 1.7$ Hz, 1H), 7.53 – 7.44 (m, 2H), 7.45 (dd, $J = 8.3, 1.5$ Hz, 1H), 7.34 (dd, $J = 7.6, 4.9, 1.5$ Hz, 1H), 3.64 (dd, $J = 13.0, 1.3$ Hz, 1H), 3.55 (dd, $J = 12.0, 1.4$ Hz, 1H), 3.35 (dd, $J = 13.0, 1.5$ Hz, 1H), 3.30 (d, $J = 12.0$ Hz, 1H), 2.46 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 158.3, 148.5, 137.5, 135.2, 133.9, 132.4, 132.3, 131.0, 129.4, 128.3, 127.8, 126.9, 126.4, 125.9, 122.2, 57.4, 56.2, 43.1.

HRMS (ESI$^+$): Calcd. for C$_{18}$H$_{17}$N$_2$ [M+H]$^+$: 261.1392, found 261.1396.
**6-methyl-6,7-dihydro-5H-benzo[c]naphtho[1,2-e]azepine (S24)**

Reaction performed following general procedure E with 0.67 mmol of tertiary amine S17. S24 was isolated as a yellow oil (0.12 g, 0.46 mmol, 68%).

**TLC** Rf = 0.25 (5:1 EtOAc:MeOH).

**1H NMR** (400 MHz, Chloroform-d) δ 8.14 – 8.09 (m, 1H), 7.91 – 7.88 (m, 1H), 7.84 (d, J = 8.2 Hz, 1H), 7.62 (dd, J = 7.6, 1.5 Hz, 1H), 7.51 – 7.39 (m, 8H), 3.65 (d, J = 12.6 Hz, 1H), 3.59 (d, J = 12.2 Hz, 1H), 3.28 (d, J = 12.6 Hz, 1H), 3.21 (d, J = 12.2 Hz, 1H), 2.44 (s, 3H).

**13C NMR** (100 MHz, Chloroform-d) δ 138.3, 136.7, 133.8, 132.7, 132.3, 130.8, 128.4, 128.0, 127.9, 127.4, 127.3, 127.24, 127.20, 126.2, 124.6, 124.1, 62.0, 61.4, 42.2.


**tert-butyl 6-methyl-6,7-dihydro-5H-benzo[c]pyrido[2,3-e]azepine-10-carboxylate (S25)**

Reaction performed following general procedure E with 1.67 mmol of tertiary amine S20. S25 was isolated as a yellow oil (378 mg, 1.22 mmol, 73%).

**TLC** Rf = 0.41 (9:1 EtOAc:MeOH)

**1H NMR** (500 MHz, Chloroform-d) δ 8.73 (dd, J = 4.8, 1.7 Hz, 1H), 8.46 (d, J = 1.8 Hz, 1H), 8.07 (dd, J = 7.8, 1.8 Hz, 1H), 7.69 (dd, J = 7.6, 1.7 Hz, 1H), 7.40 (d, J = 7.8 Hz, 1H), 7.30 (dd, J = 7.5, 4.8 Hz, 1H), 3.48 (s, 2H), 3.36 (s, 2H), 2.49 (s, 3H), 1.61 (s, 9H).

**13C NMR** (126 MHz, Chloroform-d) δ 165.4, 157.9, 149.2, 140.2, 138.4, 137.5, 132.3, 130.3, 129.9, 129.7, 129.3, 122.6, 81.2, 56.8, 56.3, 43.1, 28.2.

**HRMS (ESI+)**: Calcd. for C19H23N2O2 [M+H]+: 311.1760, found 311.1768.
10-fluoro-6-methyl-6,7-dihydro-5H-benzo[c]pyrido[2,3-e]azepine (S26)

Reaction performed following general procedure E with 5.2 mmol of tertiary amine S21. S26 was isolated as a grey oil (500 mg, 2.2 mmol, 42%). Spectroscopic data for S26 match those previously reported.

TLC Rf = 0.28 (9:1 EtOAc:MeOH)

$^1$H NMR (500 MHz, Chloroform-d) δ 8.67 (dd, J = 4.9, 1.7 Hz, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.56 (dd, J = 9.4, 2.7 Hz, 1H), 7.28 (dt, J = 7.7, 5.1 Hz, 2H), 7.09 (dt, J = 8.9, 4.4 Hz, 1H), 3.36 (d, J = 16.7 Hz, 4H), 2.45 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 162.7 (d, $J_{CF} = 246.4$ Hz), 157.6, 149.0 (d, $J_{CF} = 2.8$ Hz), 142.2 (d, $J_{CF} = 7.9$ Hz), 137.6, 131.2 (d, $J_{CF} = 8.2$ Hz), 130.4, 128.6 (d, $J_{CF} = 11.7$ Hz), 122.6, 115.6 (d, $J_{CF} = 21.5$ Hz), 115.1 (d, $J_{CF} = 22.5$ Hz), 56.3, 56.2, 42.9.

HRMS (ESI$^+$): Calcd. for C$_{14}$H$_{14}$N$_2$F [M+H]$^+$: 229.1141, found 229.1145.

4-methyl-4,5-dihydro-3H-dinaphtho[2,1-c:1',2'-e]azepine (S27)

Reaction performed following general procedure E with 1.07 mmol of tertiary amine S18. S27 was isolated as a yellow crystalline solid (162 mg, 0.52 mmol, 49%). Spectroscopic data for S27 closely match those previously reported.

TLC Rf = 0.31 (9:1 CHCl$_3$:MeOH)

$^1$H NMR (500 MHz, Chloroform-d) δ 7.97 (dd, J = 8.2, 2.0 Hz, 4H), 7.59 (d, J = 8.2 Hz, 2H), 7.49 – 7.46 (m, 4H), 7.29 – 7.26 (m, 2H), 3.67 (d, J = 12.3 Hz, 2H), 3.30 (d, J = 12.3 Hz, 2H), 2.46 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-d) δ 135.0, 133.5, 133.3, 131.6, 128.5, 127.9, 127.6, 125.9, 125.6, 57.4, 43.2.

HRMS (ESI$^+$): Calcd. for C$_{23}$H$_{20}$N [M+H]$^+$: 310.1596, found 310.1599.
General procedure F for deaminative contractions
To a round bottom flask was added biaryl-linked dihydroazepine (1 equiv.), trimethyl phosphate (5 equiv.), and lithium iodide (1 equiv.) dissolved in anhydrous THF (0.1M). The reaction mixture was purged with nitrogen and heated to 65 °C for 16 hr. The mixture was allowed to cool to room temperature, followed by addition of 18-crown-6 (3 equiv.) and dropwise 1M t-BuOK in THF (6 equiv.). The mixture was again heated to 65 °C and stirred for an additional 6 hr. After cooling to room temperature, the reaction was quenched with 2M NH₃ (aq.) (5 mL) and extracted with EtOAc (15 mL × 3). Combined organic layers were washed with brine (10 mL), dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude material was purified by column chromatography using a gradient of 100% hexanes to 95:5 Hex:EtOAc to afford the desired polycyclic aromatic.

phenanthrene (8); N,N-dimethyl-9,10-dihydrophenanthren-9-amine (10)
Reaction performed following general procedure F with 0.50 mmol of azepine 7. Purified by column chromatography using a gradient of 100% hexanes to 95:5 Hex:EtOAc, followed by a gradient of 100% EtOAc to 9:1 EtOAc:MeOH. 8 was isolated as a white solid (9 mg, 0.05 mmol, 10%). 10 was isolated as a beige oil (86 mg, 0.39 mmol, 77%). Spectroscopic data for 8 and 10 match those previously reported.⁶

phenanthrene (8)

\[ \text{TLC } R_f = 0.61 \text{ (8:2 Hex:EtOAc)} \]

¹H NMR (500 MHz, Chloroform-d) δ 8.71 (dd, J = 8.3, 1.4 Hz, 2H), 7.91 (dd, J = 7.7, 1.5 Hz, 2H), 7.76 (s, 2H), 7.67 (ddd, J = 8.3, 7.0, 1.5 Hz, 2H), 7.61 (ddd, J = 7.4, 6.9, 1.3 Hz, 2H).

¹³C NMR (126 MHz, Chloroform-d) δ 129.5, 127.7, 126.0, 124.4, 124.0, 120.1.
N,N-dimethyl-9,10-dihydrophenanthren-9-amine (10)

![Image of N,N-dimethyl-9,10-dihydrophenanthren-9-amine (10)]

\(^1^H\) NMR (500 MHz, Chloroform-d)  δ 7.80 (d, J = 7.3 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H) 7.43 (dd, J = 7.5, 1.5 Hz, 1H), 7.39 (td, J = 7.6, 1.5 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.27 – 7.25 (m, 2H), 3.61 (t, J = 5.5 Hz, 1H), 3.12 (dd, J = 15.9, 6.0 Hz, 1H), 3.00 (dd, J = 15.4, 4.8 Hz, 1H), 2.26 (s, 6H).

\(^13^C\) NMR (126 MHz, Chloroform-d)  δ 135.0, 133.8, 129.8, 128.7, 128.6, 128.2, 127.5, 127.4, 126.7, 124.2, 123.7, 122.8, 62.4, 42.1, 30.5.

**HRMS (ESI^+):** Calcd. for C\(_{15}\)H\(_{18}\)N [M+H]^+: 224.1433, found 224.1434.

benzo[h]quinoline (13)

![Image of benzo[h]quinoline (13)]

Reaction performed following general procedure F with 0.50 mmol of azepine 11. Purified by column chromatography using a gradient of 100% hexanes to 95:5 Hex:EtOAc. 13 was isolated as a colorless oil (74 mg, 0.42 mmol, 83%). Spectroscopic data for 13 match those previously reported.\(^6\)

**TLC** R\(_f\) = 0.40 (8:2 Hex:EtOAc)

\(^1^H\) NMR (500 MHz, Chloroform-d)  δ 9.31 (dd, J = 8.1, 1.6 Hz, 1H), 9.01 (dd, J = 4.4, 1.8 Hz, 1H), 8.18 (dd, J = 8.0, 1.8 Hz, 1H), 7.92 (dd, J = 7.8, 1.5 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 7.78 – 7.67 (m, 3H), 7.53 (dd, J = 8.0, 4.4 Hz, 1H).

\(^13^C\) NMR (126 MHz, Chloroform-d)  δ 146.3, 144.0, 133.3, 131.1, 128.9, 125.7, 125.3, 125.2, 124.5, 123.9, 122.8, 121.8, 119.3.
naphtho[2,1-h]quinoline (14)

Reaction performed following general procedure F with 0.50 mmol of azepine S23. Purified by column chromatography using a gradient of 100% Hex to 95:5 Hex:EtOAc. 14 was isolated as a white solid (100 mg, 87%). Spectroscopic data for 14 match those previously reported.\(^6\)

TLC R\(_f\) = 0.50 (8:2 Hex:EtOAc)

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 11.21 (d, \(J = 8.9\) Hz, 1H), 9.23 (dt, \(J = 3.3, 1.6\) Hz, 1H), 8.31 (ddd, \(J = 8.0, 3.4, 1.9\) Hz, 1H), 8.06 – 8.00 (m, 2H), 7.97 (d, \(J = 8.5\) Hz, 1H), 7.93 – 7.82 (m, 3H), 7.69 (ddd, \(J = 8.0, 6.7, 1.3\) Hz, 1H), 7.57 (ddd, \(J = 8.1, 4.2, 1.4\) Hz, 1H).

\(^13\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 148.6, 148.5, 136.6, 134.1, 133.8, 131.8, 130.8, 120.0, 128.8, 128.6, 128.0, 127.5, 127.0, 126.7, 126.5, 126.4, 120.7.

HRMS (ESI\(^+\)): Calcd. for C\(_{17}\)H\(_{12}\)N [M+H]\(^+\): 230.0970, found 230.0973.

[4]helicene (15)

Reaction performed following general procedure F with 0.50 mmol of azepine S24. Purified by column chromatography using 100% hexanes. 15 was isolated as a white solid (67 mg, 0.29 mmol, 59%). Spectroscopic data for 15 match those previously reported.\(^10\)

\(^1\)H NMR (500 MHz, Chloroform-\(d\)) \(\delta\) 9.16 (d, \(J = 8.5\) Hz, 2H), 8.04 (d, \(J = 7.9\) Hz, 2H), 7.92 (d, \(J = 8.5\) Hz, 2H), 7.84 (d, \(J = 8.5\) Hz, 2H), 7.70 (ddd, \(J = 8.4, 6.8, 1.6\) Hz, 2H), 7.64 (ddd, \(J = 7.9, 6.9, 1.2\) Hz, 2H).

\(^13\)C NMR (126 MHz, Chloroform-\(d\)) \(\delta\) 133.6, 131.1, 130.5, 128.7, 128.0, 127.6, 127.5, 127.0, 126.3, 126.0.
[5]helicene (16)

Reaction performed following general procedure F with 0.50 mmol of azepine S27. Purified by column chromatography using a gradient of 100% hex to 99:1 Hex:EtOAc. 16 was isolated as a white solid (121 mg, 0.44 mmol, 87%). Spectroscopic data for 16 match those previously reported.\(^ {10} \)

\( ^1 \)H NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 8.53 (d, \( J = 8.5 \) Hz, 2H), 7.94-7.99 (m, 4H), 7.89-7.91 (m, 4H), 7.52-7.56 (td, \( J = 6.8, 1.2 \) Hz, 2H), 7.27-7.31 (m, 2H).

\( ^{13} \)C NMR (126 MHz, Chloroform-\( d \)) \( \delta \) 132.7, 132.4, 130.9, 129.1, 128.0, 127.6, 127.4, 127.1, 126.5, 126.4, 124.5.

9-methylbenzo[h]quinoline (17)

Reaction performed following general procedure F with 0.50 mmol of azepine 22b. Purified by column chromatography using 1:1 Hex:EtOAc. 17 was isolated as a colorless oil (90 mg, 0.47 mmol, 93%). Spectroscopic data for 17 match those previously reported.\(^ {6} \)

TLC \( R_f = 0.39 \) (8:2 Hex:EtOAc)

\( ^1 \)H NMR (500 MHz, Chloroform-\( d \)) \( \delta \) 9.09 (s, 1H), 9.00 (dt, \( J = 4.1, 1.9 \) Hz, 1H), 8.17 (dd, \( J = 8.0, 2.1 \) Hz, 1H), 7.80 (ddd, \( J = 16.6, 8.5, 1.7 \) Hz, 2H), 7.62 (dd, \( J = 8.9, 1.8 \) Hz, 1H), 7.57 – 7.49 (m, 2H), 2.66 (d, \( J = 1.9 \) Hz, 3H).

\( ^{13} \)C NMR (126 MHz, Chloroform-\( d \)) \( \delta \) 148.7, 146.5, 137.3, 136.0, 131.8, 131.6, 130.1, 127.9, 127.8, 126.7, 124.5, 124.0, 121.8, 22.1.

HRMS (ESI\(^ + \)): \( \text{Calcd. for C}_{14}\text{H}_{12}\text{N} \ [\text{M+H}]^+ : 194.0970, \text{found 194.0973.} \)
9-methoxybenzo[h]quinoline (18)

Reaction performed following general procedure F with 0.50 mmol of azepine 22f. Purified by column chromatography using a gradient of 100% hexanes to 95:5 Hex:EtOAc. 18 was isolated as an opaque oil (85 mg, 0.41 mmol, 81%).

**TLC** $R_f = 0.37$ (8:2 Hex:EtOAc)

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 9.00 (dd, $J = 4.4, 1.7$ Hz, 1H), 8.71 (d, $J = 2.7$ Hz, 1H), 8.16 (dd, $J = 8.1, 1.8$ Hz, 1H), 7.82 (d, $J = 8.7$ Hz, 1H), 7.76 (d, $J = 8.7$ Hz, 1H), 7.55 (d, $J = 8.7$ Hz, 1H), 7.51 (dd, $J = 8.0, 4.3$ Hz, 1H), 7.35 (dd, $J = 8.7, 2.7$ Hz, 1H), 4.11 – 4.08 (m, 3H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 156.4, 145.8, 143.4, 133.4, 130.4, 126.8, 125.8, 124.9, 124.3, 120.2, 119.2, 117.0, 101.3, 53.1.

**HRMS (ESI$^+$):** Calcd. for C$_{14}$H$_{12}$NO [M+H]$^+$: 210.0919, found 210.0921.
9-fluorobenzo[h]quinoline (19); 9-methoxybenzo[h]quinoline (18)

Reaction performed following general procedure F with 0.21 mmol of azepine S26. Purified by column chromatography using a gradient of 100% Hex to 95:5 Hex:EtOAc. 19 was isolated as a white solid (27 mg, 0.14 mmol, 65%). 18 was isolated as an opaque oil (3 mg, 0.04 mmol, 7%). Spectroscopic data for 19 match those previously reported.6

9-fluorobenzo[h]quinoline (19)

\[ \text{TLC } R_f = 0.62 \text{ (8:2 Hex:EtOAc)} \]

\[ ^1\text{H NMR (500 MHz, Chloroform-}d\text{)} \delta 8.99 (dd, J = 4.4, 1.8 Hz, 1H), 8.92 (dd, J = 10.7, 2.7 Hz, 1H), 8.18 (dd, J = 8.0, 1.8 Hz, 1H), 7.89 (dd, J = 8.7, 5.5 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.64 (d, J = 8.8 Hz, 1H), 7.55 (dd, J = 7.9, 4.3 Hz, 1H), 7.44 (td, J = 8.4, 2.7 Hz, 1H).

\[ ^{13}\text{C NMR (126 MHz, Chloroform-}d\text{)} \delta 161.8 \text{ (d, } J_{CF} = 246.6 \text{ Hz), } 148.8, 146.0 \text{ (d, } J_{CF} = 4.7 \text{ Hz), 135.9, 133.3 \text{ (d, } J_{CF} = 8.7 \text{ Hz), 130.3 \text{ (d, } J_{CF} = 2.2 \text{ Hz), 129.9 \text{ (d, } J_{CF} = 8.7 \text{ Hz), 127.1, 126.7, 124.5 \text{ (d, } J_{CF} = 2.8 \text{ Hz), 122.3, 117.3 \text{ (d, } J_{CF} = 24.3 \text{ Hz), 109.3 \text{ (d, } J_{CF} = 22.9 \text{ Hz).}}

\[ ^{19}\text{F NMR (471 MHz, Chloroform-}d\text{)} \delta -112.38. \]

HRMS (ESI\(^+\)): Calcd. for C\(_{13}\)H\(_9\)NF [M+H]\(^+\): 198.0719, found 198.0719.
tert-butyl benzo[h]quinoline-9-carboxylate (20)

\[
\begin{array}{c}
\text{t-BuO} \\
\text{O} \\
\text{N}
\end{array}
\]

Reaction performed following general procedure F with 0.50 mmol of azepine S25. Purified by column chromatography using a gradient of 100% Hex to 95:5 Hex:EtOAc. 20 was isolated as a white solid (63 mg, 0.22 mmol, 45%).

**TLC** R\text{f} = 0.36 (8:2 Hex:EtOAc)

\[^1\text{H NMR}\] (500 MHz, Chloroform-d) \(\delta\) 9.93 (s, 1H), 9.05 (dd, \(J = 4.4, 1.7\) Hz, 1H), 8.28 (dd, \(J = 8.3, 1.8\) Hz, 1H), 8.20 (dd, \(J = 8.0, 1.8\) Hz, 1H), 7.93 (d, \(J = 8.3\) Hz, 1H), 7.84 (d, \(J = 8.8\) Hz, 1H), 7.78 (d, \(J = 8.8\) Hz, 1H), 7.56 (dd, \(J = 8.0, 4.4\) Hz, 1H), 1.69 (s, 9H).

\[^{13}\text{C NMR}\] (126 MHz, Chloroform-d) \(\delta\) 166.2, 149.5, 146.9, 136.08, 136.05, 131.2, 130.6, 128.4, 128.0, 127.7, 127.4, 126.64, 126.60, 122.3, 81.4, 28.5.

**HRMS (ESI\(^+\))**: Calcd. for C\(_{18}\)H\(_{18}\)NO\(_2\) [M+H]\(^+\): 200.1338, found 280.1342.

10-methylbenzo[h]quinoline (23a)

\[
\begin{array}{c}
\text{Me} \\
\text{N}
\end{array}
\]

Reaction performed following general procedure F with 0.50 mmol of azepine 22a. Purified by column chromatography using a gradient of 100% Hex to 95:5 Hex:EtOAc. 23a was isolated as a white solid (56 mg, 58%). Spectroscopic data for 23a match those previously reported.\(^7\)

**TLC** R\text{f} = 0.63 (8:2 Hex:EtOAc)

\[^1\text{H NMR}\] (500 MHz, Chloroform-d) \(\delta\) 9.04 (dd, \(J = 4.3, 1.9\) Hz, 1H), 8.16 (dd, \(J = 8.0, 1.9\) Hz, 1H), 7.80 (dd, \(J = 9.0, 4.3\) Hz, 2H), 7.66 (d, \(J = 8.7\) Hz, 1H), 7.61 – 7.55 (m, 2H), 7.48 (dd, \(J = 8.0, 4.3\) Hz, 1H), 3.37 (s, 3H).

\[^{13}\text{C NMR}\] (126 MHz, Chloroform-d) \(\delta\) 149.1, 147.3, 138.9, 135.5, 135.3, 131.3, 130.1, 128.9, 127.6, 127.4, 126.9, 125.6, 120.7, 27.4.

**HRMS (ESI\(^+\))**: Calcd. for C\(_{18}\)H\(_{12}\)N [M+H]\(^+\): 194.0970, found 194.0973.
8-methylbenzo[h]quinoline (23c)

Reaction performed following general procedure F with 0.50 mmol of azepine 22c. Purified by column chromatography using a gradient of 100% Hex to 95:5 Hex:EtOAc. 23c was isolated as a colorless oil (83 mg, 86%).

**TLC** Rf = 0.44 (8:2 Hex:EtOAc)

**1H NMR** (500 MHz, Chloroform-<i>d</i>) δ 9.18 (d, J = 8.4 Hz, 1H), 8.98 (dd, J = 4.4, 1.7 Hz, 1H), 8.15 (dt, J = 7.9, 1.6 Hz, 1H), 7.74 (d, J = 8.8 Hz, 1H), 7.69 (s, 1H), 7.65 (dd, J = 8.8, 1.3 Hz, 1H), 7.58 (dd, J = 8.5, 1.8 Hz, 1H), 7.49 (ddd, J = 7.9, 4.4, 1.1 Hz, 1H), 2.60 (s, 3H).

**13C NMR** (126 MHz, Chloroform-<i>d</i>) δ 148.9, 146.8, 138.3, 135.9, 133.9, 129.5, 129.1, 127.7, 127.5, 126.2, 125.5, 124.4, 121.5, 21.8.

**HRMS (ESI+):** Calcd. for C<sub>14</sub>H<sub>12</sub>N [M+H]<sup>+</sup>: 194.0970, found 194.0972.

7-methylbenzo[h]quinoline (23d)

Reaction performed following general procedure F with 0.50 mmol of azepine 22d. Purified by column chromatography using a gradient of 100% Hex to 95:5 Hex:EtOAc. 23d was isolated as a white solid (37 mg, 38%). Spectroscopic data for 23d match those previously reported.<sup>6</sup>

**1H NMR** (500 MHz, Chloroform-<i>d</i>) δ 9.04 (dd, J = 4.3, 1.9 Hz, 1H), 8.17 (dd, J = 8.0, 1.9 Hz, 1H), 7.80 (dd, J = 8.9, 5.4 Hz, 2H), 7.66 (d, J = 8.7 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.49 (dd, J = 8.0, 4.3 Hz, 1H), 3.37 (s, 3H).

**13C NMR** (126 MHz, Chloroform-<i>d</i>) δ 149.1, 147.3, 138.9, 135.5, 135.3, 131.3, 130.0, 129.0, 127.6, 127.4, 126.9, 125.6, 120.7, 27.4.

**HRMS (ESI+):** Calcd. for C<sub>14</sub>H<sub>12</sub>N [M+H]<sup>+</sup>: 194.0970, found 194.0967.
10-methoxybenzo[h]quinoline (23e)

![Chemical structure of 23e](image)

Reaction performed following general procedure F with 0.50 mmol of azepine 22e. Purified by column chromatography using 1:1 Hex:EtOAc. 23e was isolated as a brown solid (95 mg, 0.46 mmol, 91%).

**1H NMR** (500 MHz, Chloroform-d) δ 9.16 (br s, 1H), 8.18 (dd, J = 8.0, 1.9 Hz, 1H), 7.79 (d, J = 8.8 Hz, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.64 (t, J = 8.0 Hz, 1H), 7.55 (dd, J = 7.9, 1.2 Hz, 1H), 7.51 (dd, J = 8.0, 4.4 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 4.20 (s, 3H).

**13C NMR** (126 MHz, Chloroform-d) δ 159.3, 148.8, 136.6, 136.1, 128.6, 128.6, 127.4, 126.5, 121.4, 120.9, 109.9, 57.1.

**HRMS (ESI+):** Calcd. for C_{14}H_{12}NO [M+H]^+: 210.0919, found 210.0922.

8-methoxybenzo[h]quinoline (23g)

![Chemical structure of 23g](image)

Reaction performed following general procedure F with 0.50 mmol of azepine 22g. Purified by column chromatography using 1:1 Hex:EtOAc. 23g was isolated as a white solid (80 mg, 0.38 mmol, 77%).

**1H NMR** (500 MHz, Chloroform-d) δ 9.21 (d, J = 9.1 Hz, 1H), 8.97 (dd, J = 4.4, 1.7 Hz, 1H), 8.12-8.16 (m, 1H), 7.72-7.72 (m, 1H), 7.65-7.68 (m, 1H), 7.38 (dd, J = 9.0, 2.6 Hz, 1H), 3.99 (s, 3H).

**13C NMR** (126 MHz, Chloroform-d) δ 159.8, 149.0, 146.7, 136.0, 135.3, 127.4, 126.20, 126.0, 125.4, 121.0, 117.7, 108.0, 55.6.

**HRMS (ESI+):** Calcd. for C_{14}H_{12}NO [M+H]^+: 210.0919, found 210.0925.
7-methoxybenzo[h]quinoline (23h)

Reaction performed following general procedure F with 0.50 mmol of azepine 22h. Purified by column chromatography using 1:1 Hex:EtOAc. 23h was isolated as a white solid (65 mg, 0.31 mmol, 62%).

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 9.00 (dd, $J = 4.4, 1.8$ Hz, 1H), 8.88 (d, $J = 8.3$ Hz, 1H), 8.30 (d, $J = 9.1$ Hz, 1H), 8.20 (dd, $J = 8.1, 1.8$ Hz, 1H), 7.69 (d, $J = 9.3$ Hz, 1H), 7.66 (d, $J = 8.4$ Hz, 1H), 7.53 (dd, $J = 8.1, 4.4$ Hz, 1H), 7.12 (d, $J = 7.9$ Hz, 1H), 4.06 (s, 3H).

$^{13}$C NMR (126 MHz, Chloroform-$d$) $\delta$ 152.9, 146.2, 143.7, 133.4, 130.0, 124.7, 124.0, 122.2, 121.9, 119.3, 118.9, 113.9, 104.8, 53.2.

HRMS (ESI$^+$): Calcd. for C$_{14}$H$_{12}$NO [M+H]$^+$: 210.0919, found 210.0919.

benzo[h]isoquinoline (23j)

Reaction performed following general procedure F with 0.50 mmol of azepine 22j. Purified by column chromatography using 1:1 Hex:EtOAc. 23j was isolated as a yellow solid (87 mg, 0.49 mmol, 97%). Spectroscopic data for 23j match those previously reported.$^{11}$

TLC $R_f$ = 0.29 (2:8 Hex:EtOAc)

$^1$H NMR (500 MHz, Chloroform-$d$) $\delta$ 10.06 (s, 1H), 8.81 (d, $J = 8.1$ Hz, 1H), 8.72 (d, $J = 5.5$ Hz, 1H), 7.98 – 7.91 (m, 2H), 7.78 – 7.65 (m, 4H).

HRMS (ESI$^+$): Calcd. for C$_{13}$H$_{10}$N [M+H]$^+$: 180.0813, found 180.0818.
benzo[f]isoquinoline (23k)

\[ \text{reaction performed following general procedure F with 0.50 mmol of azepine 22k. Purified by column chromatography using 1:1 Hex:EtOAc. 23k was isolated as a tan solid (74 mg, 83%).}

Spectroscopic data for 23k match those previously reported.\(^\text{11}\)

**TLC** R\(_f\) = 0.29 (2:8 Hex:EtOAc)

**\(^1\)H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\) 9.26 (s, 1H), 8.77 (d, \(J = 5.8\) Hz, 1H), 8.73 – 8.66 (m, 1H), 8.44 (d, \(J = 5.8\) Hz, 1H), 8.00 – 7.93 (m, 1H), 7.91 – 7.80 (m, 2H), 7.77 – 7.71 (m, 2H).

**\(^13\)C NMR** (126 MHz, Chloroform-\(d\)) \(\delta\) 151.8, 145.2, 135.1, 133.7, 129.0, 128.9, 128.64, 128.59, 127.4, 127.2, 124.9, 123.4, 116.3.

**HRMS (ESI\(^+\))**: Calcd. for C\(_{13}\)H\(_{10}\)N [M+H]\(^+\): 180.0813, found 180.0816.

benzo[f]quinoline (23l)

\[ \text{reaction performed following general procedure F with 0.10 mmol of azepine 22l. Purified by column chromatography using 1:1 Hex:EtOAc. 23k was isolated as a tan solid (13 mg, 0.07 mmol, 70%).}

**\(^1\)H NMR** (500 MHz, Chloroform-\(d\)) \(\delta\) 8.97-8.94 (m, 2H), 8.62 (d, \(J = 8.2\) Hz, 1H), 8.01 (d, \(J = 9.3\) Hz, 1H), 7.98 (d, \(J = 9.0\) Hz, 1H), 7.94 (d, \(J = 7.8\) Hz, 1H), 7.72-7.64 (m, 2H), 7.56 (dd, 8.27, 4.39 Hz, 1H).

**\(^13\)C NMR** (126 MHz, Chloroform-\(d\)) \(\delta\) 149.8, 148.3, 131.9, 131.1, 130.9, 129.8, 128.9, 128.3, 127.5, 127.3, 125.6, 122.7, 121.5.

**HRMS (ESI\(^+\))**: Calcd. for C\(_{13}\)H\(_{10}\)N [M+H]\(^+\): 180.0813, found 180.0814.
[1,3]dioxolo[4',5':4,5]benzo[1,2-h]quinoline (desoxytoddacquinoline) (23m)

Reaction performed following general procedure F with 0.50 mmol of azepine 22m. Purified by column chromatography using a gradient of 100% Hex to 95:5 Hex:EtOAc. 23m was isolated as a white solid (95 mg, 0.43 mmol, 85%). Spectroscopic data for 23m match those previously reported.6

TLC $R_f$ = 0.48 (8:2 Hex:EtOAc)

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 8.94 (dd, $J = 4.4, 1.8$ Hz, 1H), 8.65 (s, 1H), 8.13 (dd, $J = 8.0, 1.8$ Hz, 1H), 7.68 (d, $J = 8.8$ Hz, 1H), 7.57 (d, $J = 8.8$ Hz, 1H), 7.45 (dd, $J = 8.0, 4.3$ Hz, 1H), 7.23 (s, 1H), 6.13 (s, 2H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 149.1, 148.7, 148.5, 146.2, 136.0, 130.5, 128.3, 127.2, 125.8, 123.9, 121.2, 105.1, 102.5, 101.6.

HRMS (ESI$^+$): Calcd. for C$_{14}$H$_{10}$NO$_2$ [M+H]$^+$: 224.0712, found 224.0712.

[1,3]dioxolo[4',5':4,5]benzo[1,2-h]isoquinoline (23n)

Reaction performed following general procedure F with 0.50 mmol of azepine 22n. Product purified by recrystallization from EtOAc. 23n was isolated as off-white crystals (93 mg, 0.42 mmol, 83%). Spectroscopic data for 23n match those previously reported.12

$^1$H NMR (500 MHz, Chloroform-d) $\delta$ 9.85 (s, 1H), 8.63 (d, $J = 5.4$ Hz, 1H), 8.12 (s, 1H), 7.81 (d, $J = 8.8$ Hz, 1H), 7.66 (d, $J = 5.4$ Hz, 1H), 7.59 (d, $J = 8.8$ Hz, 1H), 7.25 (s, 1H), 6.14 (s, 2H).

$^{13}$C NMR (126 MHz, Chloroform-d) $\delta$ 149.2, 148.4, 146.9, 144.1, 135.1, 131.2, 129.0, 125.9, 125.1, 123.3, 121.2, 106.2, 101.8, 100.3.

HRMS (ESI$^+$): Calcd. for C$_{14}$H$_{10}$NO$_2$ [M+H]$^+$: 224.0712, found 224.0717.
9,10-dimethoxybenzo[h]isoquinoline (23o)

Reaction performed following general procedure F with 0.50 mmol of azepine 22o. Purified by column chromatography using a gradient of 1:1 Hex:EtOAc to 9:1 EtOAc:MeOH. 23o was isolated as an orange oil (33 mg, 0.14 mmol, 28%).

$^1\text{H NMR}$ (500 MHz, Chloroform-$d$) $\delta$ 10.82 (s, 1H), 8.67 (d, $J = 5.3$ Hz, 1H), 7.79 (d, 8.8 Hz, 1H), 7.65 (d, $J = 8.7$ Hz, 1H), 7.64 (d, $J = 5.3$ Hz, 1H), 7.47 (d, $J = 8.8$ Hz, 1H), 7.35 (d, $J = 8.7$ Hz, 1H), 4.03 (s, 3H), 4.01 (s, 3H).

$^{13}\text{C NMR}$ (126 MHz, Chloroform-$d$) $\delta$ 152.4, 151.36, 146.7, 144.9, 137.1, 131.8, 128.3, 125.5, 125.3, 123.8, 123.4, 121.2, 113.6, 59.9, 56.5.

HRMS (ESI$^+$): Calcd. for C$_{15}$H$_{14}$NO$_2$ [M+H]$^+$: 240.1025, found 240.1026.

8,9-dimethoxybenzo[h]isoquinoline (23p)

Reaction performed following general procedure F with 0.50 mmol of azepine 22p. Product purified by recrystallization from EtOAc. 23p was isolated as tan crystals (65 mg, 0.27 mmol, 54%).

$^1\text{H NMR}$ (500 MHz, Chloroform-$d$) $\delta$ 9.92 (s, 1H), 8.64 (d, $J = 5.5$ Hz, 1H), 8.11 (s, 1H), 7.86 (d, $J = 8.7$ Hz, 1H), 7.70 (d, $J = 5.4$ Hz, 1H), 7.61 (d, $J = 8.7$ Hz, 1H), 7.29 (s, 1H), 4.15 (s, 3H), 4.06 (s, 3H).

$^{13}\text{C NMR}$ (126 MHz, Chloroform-$d$) $\delta$ 150.5, 150.1, 146.3, 143.7, 137.0, 135.2, 131.0, 127.7, 124.2, 123.2, 121.5, 108.7, 102.4, 56.3, 56.2.

HRMS (ESI$^+$): Calcd. for C$_{15}$H$_{14}$NO$_2$ [M+H]$^+$: 240.1025, found 240.1029.
3-chloro-[1,3]dioxolo[4',5':4,5]benzo[1,2-h]quinoline (33a)

Reaction performed following general procedure F with 0.43 mmol of azepine 32a. After addition of t-BuOK, the reaction was heated to 40 °C. Purified by column chromatography using a gradient of 100% Hex to 95:5 Hex:EtOAc. 72 was isolated as a white solid (57 mg, 51%).

**TLC** Rf = 0.51 (8:2 Hex:EtOAc)

**$^1$H NMR** (500 MHz, Chloroform-d) $\delta$ 8.83 (d, $J = 2.4$ Hz, 1H), 8.57 (s, 1H), 8.11 (d, $J = 2.5$ Hz, 1H), 7.71 (d, $J = 8.8$ Hz, 1H), 7.50 (d, $J = 8.8$ Hz, 1H), 7.22 (s, 1H), 6.14 (s, 2H).

**$^{13}$C NMR** (126 MHz, Chloroform-d) $\delta$ 149.3, 148.8, 147.7, 144.2, 134.2, 130.4, 128.7, 128.6, 128.1, 126.3, 122.9, 105.2, 102.5, 101.7.

**HRMS (ESI$^+$):** Calcd. for C$_{14}$H$_9$NO$_2$Cl [M+H]$^+$: 258.0322, found 258.0329.
3-(tert-butoxy)-[1,3]dioxolo[4',5':4,5]benzo[1,2-h]quinoline (33b); 3-methoxy-[1,3]dioxolo[4',5':4,5]benzo[1,2-h]quinoline (33c); 3-fluoro-[1,3]dioxolo[4',5':4,5]benzo[1,2-h]quinoline (33d)

Reaction performed following general procedure F with 0.37 mmol of azepine 32b. Purified by column chromatography using a gradient of 100% hexanes to 4:1 Hex:EtOAc. In order of elution from the column, 33d was isolated as a white solid (11 mg, 0.05 mmol, 12%), 33b as a colorless oil (33 mg, 0.11 mmol, 30%), and 33c as a white solid (35 mg, 0.14 mmol, 37%).

3-(tert-butoxy)-[1,3]dioxolo[4',5':4,5]benzo[1,2-h]quinoline (33b)

![Chemical structure of 3-(tert-butoxy)-[1,3]dioxolo[4',5':4,5]benzo[1,2-h]quinoline (33b)](image)

\[ ^1H \text{ NMR (500 MHz, Chloroform-}d\text{)} \delta 8.68 (d, J = 2.7 Hz, 1H), 8.56 (s, 1H), 7.70 (d, J = 2.7 Hz, 1H), 7.66 (d, J = 8.8 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.21 (s, 1H), 6.12 (s, 2H), 1.44 (s, 9H). \]

\[ ^{13}C \text{ NMR (126 MHz, Chloroform-}d\text{)} \delta 149.3, 148.6, 148.6, 147.1, 142.2, 129.6, 128.6, 128.0, 127.6, 126.2, 123.6, 105.1, 102.2, 101.5, 80.1, 28.9. \]

HRMS (ESI\textsuperscript{+}): Calcd. for C\textsubscript{18}H\textsubscript{18}NO\textsubscript{3} [M+H]\textsuperscript{+}: 296.1281, found 296.1281.
3-methoxy-[1,3]dioxolo[4',5':4,5]benzo[1,2-h]quinoline (33c)

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{OMe}
\end{array}
\]

\[\text{H NMR (500 MHz, Chloroform-}d\text{) } \delta 8.68 (d, J = 2.9 \text{ Hz, 1H}), 8.54 (s, 1H), 7.67 (d, J = 8.7 \text{ Hz, 1H}), 7.53 (d, J = 8.8 \text{ Hz, 1H}), 7.46 (d, J = 2.9 \text{ Hz, 1H}), 7.21 (s, 1H), 6.11 (s, 2H), 3.98 (s, 3H).\]
\[\text{C NMR (126 MHz, Chloroform-}d\text{) } \delta 153.7, 148.6, 148.2, 141.1, 129.7, 129.0, 127.9, 126.4, 123.4, 116.9, 114.4, 105.0, 102.0, 101.5, 55.8.\]
\[\text{HRMS (ESI}\text{)}: \text{Calcd. for } C_{15}H_{12}NO_3 [M+H]^+: 254.0811, \text{ found 254.0809.}\]

3-fluoro-[1,3]dioxolo[4',5':4,5]benzo[1,2-h]quinoline (33d)

\[
\begin{array}{c}
\text{O} \\
\text{N} \\
\text{F}
\end{array}
\]

\[\text{H NMR (500 MHz, Chloroform-}d\text{) } \delta 8.80 (d, J = 2.9 \text{ Hz, 1H}), 8.56 (s, 1H), 7.76 (dd, J = 8.8, 2.9 \text{ Hz, 1H}), 7.70 (d, J = 8.8 \text{ Hz, 1H}), 7.52 (d, J = 8.8 \text{ Hz, 1H}), 7.21 (s, 1H), 6.12 (s, 2H).\]
\[\text{C NMR (126 MHz, Chloroform-}d\text{) } \delta 158.2, 146.2, 148.8 (d, J_{CF} = 15.4 \text{ Hz}), 143.0 (d, J_{CF} = 2.4 \text{ Hz}), 138.6 (d, J_{CF} = 25.8 \text{ Hz}), 129.8 (d, J_{CF} = 1.7 \text{ Hz}), 128.7, 128.3, 126.4 (d, J_{CF} = 5.1 \text{ Hz}), 123.2 (d, J_{CF} = 3.8 \text{ Hz}), 119.3 (d, J_{CF} = 17.1 \text{ Hz}), 105.1, 102.5, 101.7.\]
\[\text{HRMS (ESI}\text{)}: \text{Calcd. for } C_{14}H_{9}NO_2F [M+H]^+: 242.0611, \text{ found 242.0612.}\]
**From 33a:** To a disposable tube with a Teflon septum screw top cap was added Pd$_2$dba$_3$ (0.0012 mmol, 0.01 equiv.), Me$_4$-ButylXPhos (0.0050 mmol, 0.04 equiv.), and KOH (0.373 mmol, 3 equiv.). The tube was evacuated and backfilled three times with N$_2$, followed by addition of 33a (0.124 mmol, 1 equiv.) dissolved in dioxane and degassed H$_2$O. The reaction was stirred at 100 °C overnight. The mixture was cooled to room temperature, then carefully acidified with dilute HCl, and extracted with EtOAc (5 mL × 3). Combined organics were dried over Na$_2$SO$_4$, filtered, and concentrated under reduced pressure. Crude reaction mixture was purified using preparative TLC (1:1 Hex:EtOAc) to yield 3 as a white solid (6 mg, 21%).

**From 33b:** To a solution of 33b (26 mg) in 1.5 mL CH$_2$Cl$_2$ was added 650 µL trifluoroacetic acid. The reaction mixture was stirred overnight. The solvent was evaporated under a stream of nitrogen to yield 3 as an off-white solid (21 mg, quant.).

Spectroscopic data for 3 closely matches those previously reported.$^{13}$

**TLC** R$_f$ = 0.49 (1:1 Hex:EtOAc)

**$^1$H NMR** (500 MHz, Methanol-$d_4$) δ 8.50 (d, $J = 2.8$ Hz, 1H), 8.13 (s, 1H), 7.94 (d, $J = 8.8$ Hz, 1H), 7.77 (d, $J = 2.8$ Hz, 1H), 7.58 (d, $J = 8.7$ Hz, 1H), 7.30 (s, 1H), 6.13 (s, 2H).

**$^{13}$C NMR** (126 MHz, Methanol-$d_4$) δ 153.6, 151.1, 150.9, 136.4, 135.6, 131.6, 130.8, 129.8, 125.8, 124.0, 123.7, 106.9, 103.7, 101.0.

**HRMS (ESI$^+$):** Calcd. for C$_{14}$H$_{10}$NO$_3$ [M+H]$^+$: 240.0661, found 240.0667.
Reaction performed following general procedure F with 0.39 mmol of azepine 38. Purified by column chromatography using a gradient of 100% hexanes to 9:1 Hex:EtOAc. 39 was isolated as pale yellow crystals (9 mg, 0.03 mmol, 25%). Spectroscopic data for 39 closely match those previously reported.\(^{14}\)

**\(^1H\) NMR** (500 MHz, Chloroform-\(d\)) \(\delta\) 8.71 (dd, \(J = 4.3, 1.8\) Hz, 1H), 8.29 (dd, \(J = 8.0, 1.7\) Hz, 1H), 8.17 (dd, \(J = 8.4, 1.0\) Hz, 1H), 8.00 (d, \(J = 1.1\) Hz, 1H), 7.99 (d, \(J = 1.3\) Hz, 1H), 7.97 (d, \(J = 8.4\) Hz, 1H), 7.94 (dd, \(J = 8.0, 1.4\) Hz, 1H), 7.92 (d, \(J = 8.1\) Hz, 1H), 7.90 (d, \(J = 8.4\) Hz, 1H), 7.87 (d, \(J = 8.4\) Hz, 1H), 7.54 (ddd, \(J = 7.8, 6.8, 1.0\) Hz, 1H), 7.51 (dd, \(J = 8.0, 4.1\) Hz, 1H), 7.27 (ddd, \(J = 8.3, 6.7, 1.3\) Hz, 1H).

**\(^{13}C\) NMR** (126 MHz, Chloroform-\(d\)) \(\delta\) 146.6, 135.9, 134.3, 132.8, 132.7, 131.2, 130.5, 129.0, 128.6, 127.7, 127.4, 126.7, 126.5, 126.3, 126.1, 125.6, 123.3, 121.8.

**HRMS (ESI\(^+\)):** Calcd. for C\(_{21}\)H\(_{14}\)N [M+H]\(^+\): 280.1126, found 280.1128.
References:


Figure S1. $^1$H NMR (500 MHz, CD$_3$OD) spectrum of compound 3.

Figure S2. $^{13}$C NMR (126 MHz, CD$_3$OD) spectrum of compound 3.
Figure S3. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 7.

Figure S4. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 7.
Figure S5. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 8.

Figure S6. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 8.
Figure S7. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 10.

Figure S8. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 10.
Figure S9. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 11.

Figure S10. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 11.
Figure S11. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 13.

Figure S12. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 13.
Figure S13. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 14.

Figure S14. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 14.
Figure S15. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 15.

Figure S16. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 15.
Figure S17. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 16.

Figure S18. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 16.
Figure S19. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 17.

Figure S20. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 17.
Figure S21. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 18.

Figure S22. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 18.
Figure S23. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 19.

Figure S24. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 19.
Figure S25. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 20.

Figure S26. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 20.
Figure S27. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21a.

Figure S28. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 21a.
**Figure S29.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21b.

**Figure S30.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 21b.
Figure S31. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21c.

Figure S32. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 21c.
Figure S33. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21d.
Figure S34. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21e.

Figure S35. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 21e.
Figure S36. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21f.

Figure S37. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 21f.
Figure S38. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21g.
Figure S39. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21h.

Figure S40. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 21h.
**Figure S41.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21h.

**Figure S42.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 21h.
Figure S43. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21j.

Figure S44. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 21j.
Figure S45. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21k.

Figure S46. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 21k.
Figure S47. ¹H NMR (500 MHz, CDCl₃) spectrum of compound 21l.

Figure S48. ¹³C NMR (126 MHz, CDCl₃) spectrum of compound 21l.
Figure S49. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21m.

Figure S50. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 21m.
Figure S51. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21n.

Figure S52. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 21n.
Figure S53. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21o.

Figure S54. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 21o.
Figure S55. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 21p.

Figure S56. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 21p.
Figure S57. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22a.

Figure S58. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22a.
Figure S59. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22b.

Figure S60. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22b.
Figure S61. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22c.

Figure S62. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22c.
**Figure S63.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22d.

**Figure S64.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22d.
Figure S65. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22e.

Figure S66. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22e.
Figure S67. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22f.

Figure S68. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22f.
Figure S69. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22g.

Figure S70. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22g.
**Figure S71.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22h.

**Figure S72.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22h.
Figure S73. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22j.

Figure S74. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22j.
**Figure S75.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22k.

**Figure S76.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22k.
Figure S77. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22l.

Figure S78. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22l.
Figure S79. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22m.

Figure S80. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22m.
Figure S81. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22n.

Figure S82. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22n.
Figure S83. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22o.

Figure S84. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22o.
Figure S85. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 22p.

Figure S86. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 22p.
**Figure S87.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 23a.

**Figure S88.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 23a.
Figure S89. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 23c.

Figure S90. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 23c.
Figure S91. \(^1\)H NMR (500 MHz, CDCl\(_3\)) spectrum of compound 23d.

Figure S92. \(^{13}\)C NMR (126 MHz, CDCl\(_3\)) spectrum of compound 23d.
Figure S93. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 23e.

Figure S94. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 23e.
Figure S95. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 23g.

Figure S96. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 23g.
Figure S97. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 23h.

Figure S98. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 23h.
Figure S99. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 23j.

Figure S100. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 23j.
**Figure S101.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 23k.

**Figure S102.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 23k.
Figure S103. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 23L.

Figure S104. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 23L.
Figure S105. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 23m.

Figure S106. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 23m.
Figure S107. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 23n.

Figure S108. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 23n.
Figure S109. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 23a.

Figure S110. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 23a.
Figure S111. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 23p.

Figure S112. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 23p.
**Figure S113.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 25a.

**Figure S114.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 25a.
Figure S115. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 25b.

Figure S116. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 25b.
Figure S117. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 31.

Figure S118. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 31.
**Figure S119.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 32a.

**Figure S120.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 32a.
Figure S121. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 32b.

Figure S122. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 32b.
Figure S123. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 33a.

Figure S124. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 33a.
Figure S125. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 33b.

Figure S126. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 33b.
Figure S127. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 33c.

Figure S128. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 33c.
Figure S129. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 33d.

Figure S130. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 33d.
**Figure S131.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 35.

**Figure S132.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 35.
Figure S133. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 38.

Figure S134. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 38.
Figure S135. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound 39.

Figure S136. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound 39.
Figure S137. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S1.

Figure S138. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S1.
Figure S139. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S2.

Figure S140. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S2.
Figure S141. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S3.
Figure S142. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S4.

Figure S143. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S4.
**Figure S144.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S5.

**Figure S145.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S5.
Figure S146. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S6.

Figure S147. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S6.
Figure S148. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S7.

Figure S149. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S7.
**Figure S150.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S8.

**Figure S151.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S8.
Figure S152. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S9.

Figure S153. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S9.
Figure S154. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S10.

Figure S155. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S10.
Figure S156. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S11.

Figure S157. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S11.
Figure S158. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S12.

Figure S159. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S12.
Figure S160. $^1\text{H}$ NMR (500 MHz, CDCl$_3$) spectrum of compound S13.

Figure S161. $^{13}\text{C}$ NMR (126 MHz, CDCl$_3$) spectrum of compound S13.
Figure S162. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S14.

Figure S163. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S14.
Figure S164. $^1$H NMR (500 MHz, CDCl₃) spectrum of compound S15.

Figure S165. $^{13}$C NMR (126 MHz, CDCl₃) spectrum of compound S15.
Figure S16. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S16.
Figure S167. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S17.

Figure S168. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S17.
Figure S169. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S18.

Figure S170. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S18.
**Figure S171.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S19.

**Figure S172.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S19.
Figure S173. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S20.

Figure S174. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S20.
Figure S175. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S21.

Figure S176. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S21.
Figure S177. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S22.

Figure S178. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S22.
Figure S179. ^1^H NMR (500 MHz, CDCl$_3$) spectrum of compound S23.

Figure S180. ^1^C NMR (126 MHz, CDCl$_3$) spectrum of compound S23.
Figure S181. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S24.

Figure S182. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S24.
Figure S183. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S25.

Figure S184. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S25.
**Figure S185.** $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S26.

**Figure S186.** $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S26.
Figure S187. $^1$H NMR (500 MHz, CDCl$_3$) spectrum of compound S27.

Figure S188. $^{13}$C NMR (126 MHz, CDCl$_3$) spectrum of compound S27.