Supporting Information

Gold(III)-Catalyzed Chemoselective Annulations of Anthranils with $N$-Allyynamides for the Synthesis of 3-Azabicyclo[3.1.0]hexan-2-imines

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1. General Remarks

Chemicals were bought from commercial suppliers and were used without further purification. Deuterated solvents were purchased from Euriso-Top. Absolute solvents were dried by an MB-SPS 800 with drying columns. Unless otherwise stated, NMR spectra were recorded at room temperature on the following spectrometers: Bruker Avance III 300, Bruker Avance DRX 300, Bruker Avance III 400, Bruker Avance III 500, Bruker Avance III 600 and Bruker Fourier 300 spectrometers. Chemical shifts were referenced to residual solvent protons and reported in ppm and coupling constants in Hz. The following abbreviations were used for $^1$H NMR spectra to indicate the signal multiplicity: s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). All $^{13}$C NMR spectra were measured with $^1$H-decoupling. The multiplicities mentioned in these spectra [s (singlet, quaternary carbon), d (doublet, CH-group), t (triplet, CH$_2$-group), q (quartet, CH$_3$-group)] were determined by DEPT-135. HRMS were determined at the chemistry department of the University of Heidelberg. For DART-spectra, a Bruker ICR Apex-Qe spectrometer was applied. IR spectra were recorded on a Bruker Vector 22, and the absorption maxima were given in wavelength in cm$^{-1}$ units. X-ray Crystal structure analyses were accomplished on Bruker Smart CCD or Bruker APEX-II CCD instrument using Mo-K$_\alpha$-radiation. Thin-layer chromatography (TLC) was performed on precoated polyester sheets (POLYGRAM SIL G/UV254), and components were visualized by observation under UV light. Melting Points were measured in open glass capillaries in a Büchi melting point apparatus (according to Dr. Tottoli) and were not calibrated. Reagents $^1$[1] and $^2$[2] were prepared according to the previous literatures and characterized in our previous reports.[3]

2. Experiment Procedures

Experiment Procedure 1: Synthesis of substituted anthranils

A round bottom flask equipped with a magnetic stirrer bar was charged with the substituted 2-nitroacylbenzene (3.00 mmol) in EtOAc–MeOH (1:1; 20 mL). SnCl$_2$ · 2H$_2$O (9.00 mmol) was added and the reaction was stirred at room temperature for 12 h. The reaction was quenched by saturated NaHCO$_3$ (20 ml), and filtered. The aqueous phase was extracted with EtOAc (3 × 10 mL) and the organic portions combined, washed with H$_2$O (20 mL), saturated aqueous NaCl (20 mL), dried over Na$_2$SO$_4$, filtered and reduced in vacuo. The residue was purified by column chromatography (using PE and EtOAc as eluent) to provide compound 1. The characterization of unknown compounds has been listed in part 3.

Experiment Procedure 2: Synthesis of substituted allylamides 2

In the dark, to a solution of terminal alkyne (5.5 mmol) in 25 mL acetone was added NBS (1077
mg, 6.05 mmol) and AgNO₃ (94 mg, 0.55 mmol). The resulting mixture was stirred at room temperature for 3 h, filtered, and the filtrate was evaporated. Then 20 mL petroleum ether was added, filtered again and the filtrate was evaporated under vacuum to give the corresponding alkynyl bromide. Amide (5.0 mmol), copper sulfate pentahydrate (187.0 mg, 0.75 mmol), 1,10-phenanthroline (270.0 mg, 1.5 mmol) and K₂CO₃ (1.38 g, 10.0 mmol), toluene (25 mL) were added under a nitrogen atmosphere. The reaction flask was evacuated under vacuum and flushed with nitrogen three times, then sealed under nitrogen and heated to 80 °C. The reaction mixture was stirred overnight, then cooled down to room temperature, filtered through a pad of silica gel, the filtrate was evaporated and purified by flash silica gel column chromatography to give the desired allyynamide 2. Compounds 2 have been characterized in our previous reports.³

**Experiment Procedure 3: Synthesis of 3-azabicyclo[3.1.0]hexan-2-imines 3 from anthranils 1 and ynamides 2**

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

To a mixture of 1 (0.2 mmol, 1 equiv.) and 2 (0.24 mmol, 1.2 equiv.) in 2.0 mL toluene was added NaAuCl₄·2H₂O (5 mol%, 4.0 mg) at room temperature. The reaction mixture was stirred at room temperature until complete consumption of the starting material was observed (TLC). The solvent was removed under reduced pressure, and the residue was purified by column chromatography (using PE and EtOAc as eluent) to afford the desired product 3.

**Experiment Procedure 4: Gram scale synthesis of 3a from anthranil 1a and ynamide 2a**

A round bottom flask equipped with a magnetic stirrer bar was charged with 1a (3.5 mmol, 1 equiv.), 2a (4.2 mmol, 1.2 equiv.), NaAuCl₄·2H₂O (2 mol%, 27.8 mg) and toluene (20 mL). The reaction mixture was stirred at room temperature for 2 h. Then the solvent was reduced in vacuo, and the residue was purified by column chromatography (using PE and EtOAc as eluent) to provide the product 3a (1.41 g, 94%).

**Experiment Procedure 5: The Seyferth-Gilbert homologation of 3a for the synthesis of 6**

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

To the mixture of 3a (86 mg, 0.2 mmol), Cs₂CO₃ (163 mg, 0.5 mmol), MeOH (1.0 mL) and THF (1.0 mL) was added dropwise the dimethyl (1-diazo-2-oxopropyl)phosphonate (78 mg, 0.4 mmol) at 0 °C. After being stirred at room temperature for 6 h, the reaction mixture was added H₂O (10 mL), and extracted with EtOAc (3 × 10 mL). The organic portions were combined and washed with saturated aqueous NaCl (10 mL), dried over Na₂SO₄, filtered and reduced in vacuo. The residue was purified by column chromatography (using PE and EtOAc as eluent) to provide 6 (77 mg, 90%).
3. Characterization Data

**benzo[c]isoxazol-5-ol (1g)**
Yield: 295 mg, 73%; yellow solid, mp 160-162 °C; \( R_f = 0.23 \) (EA/PE = 1/5); \(^1\)H NMR (400 MHz, DMSO-\( \text{d}_6 \)) \( \delta \) 9.88 (s, 1H), 9.39 (d, \( J = 0.8 \) Hz, 1H), 7.55 (d, \( J = 9.2 \) Hz, 1H), 7.06 (dd, \( J = 2.4, 9.6 \) Hz, 1H), 6.73 (dd, \( J = 0.4, 2.0 \) Hz, 1H) ppm; \(^{13}\)C NMR (100 MHz, DMSO-\( \text{d}_6 \)) \( \delta \) 153.8 (s), 153.8 (d), 153.4 (s), 128.6 (d), 119.0 (s), 116.4 (d), 96.5 (d) ppm; IR (reflection) \( \tilde{\nu} = 3100, 3006, 2978, 2877, 2827, 2791, 2742, 2697, 2660, 2484, 2188, 1650, 1569, 1536, 1476, 1448, 1409, 1306, 1227, 1183, 1139, 1100, 957, 936, 917, 819, 804, 739, 697, 614 cm\(^{-1}\)); HRMS (DART) (\( m/z \) [M+H]\(^+\)) \text{C}_\text{7}\text{H}_\text{6}\text{NO}_\text{2} \text{calcd for 136.0393, found 136.0391.}

**2-((1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3a)**
Yield: 77 mg, 90%; white solid, mp 161-164 °C; \( R_f = 0.24 \) (EA/PE = 1/4); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.14 (s, 1H), 7.87 (d, \( J = 8.4 \) Hz, 2H), 7.27 (d, \( J = 0.8 \) Hz, 2H), 6.85-6.74 (m, 3H), 6.69 (t, \( J = 8.0 \) Hz, 1H), 6.65-6.61 (m, 2H), 6.34 (d, \( J = 8.0 \) Hz, 1H), 4.21-4.13 (m, 2H), 2.40 (s, 3H), 1.83-1.77 (m, 1H), 1.67 (dd, \( J = 5.6, 8.0 \) Hz, 1H), 1.13 (t, \( J = 5.2 \) Hz, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 190.9 (d), 158.1 (s), 151.6 (s), 145.0 (s), 135.6 (s), 134.8 (s), 133.9 (d), 129.7 (d, 2C), 129.4 (d, 2C), 128.6 (d, 2C), 128.1 (d, 2C), 127.2 (d, 126.4 (d), 126.3 (s), 122.8 (d), 122.7 (d), 49.8 (t), 35.2 (s), 22.7 (d), 21.7 (q), 17.3 (t) ppm; IR (reflection) \( \tilde{\nu} = 3053, 2905, 2845, 1687, 1649, 1593, 1570, 1494, 1475, 1448, 1359, 1304, 1275, 1250, 1187, 1169, 1146, 1123, 1091, 1074, 1054, 1023, 1009, 947, 928, 910, 876, 845, 812, 761, 731, 717, 703, 688, 662, 624 cm\(^{-1}\)); HRMS (ESI) (\( m/z \) [M+H]\(^+\)) \text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_3\text{S} \text{calcd for 431.1424, found 431.1409.}

**2-bromo-6-((1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3b)**
Yield: 100 mg, 98%; white solid, mp 135-138 °C; \( R_f = 0.21 \) (EA/PE = 1/4); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 9.37 (s, 1H), 7.87 (d, \( J = 7.8 \) Hz, 2H), 7.27 (d, \( J = 0.8 \) Hz, 2H), 6.92-6.88 (m, 2H), 6.84-6.78 (m, 3H), 6.67 (d, \( J = 7.8 \) Hz, 2H), 6.33 (d, \( J = 7.2 \) Hz, 1H), 4.16-4.11 (m, 2H), 2.41 (s, 3H), 1.85-1.80 (m, 1H), 1.62 (t, \( J = 5.4 \) Hz, 1H), 1.20 (t, \( J = 4.8 \) Hz, 1H) ppm; \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \( \delta \) 190.6 (d), 158.0 (s), 152.6 (s), 145.1 (s), 135.9 (s), 134.8 (s), 133.3 (d), 130.4 (d, 2C), 129.7 (d, 2C), 128.9 (d, 2C), 128.6 (d, 2C), 128.1 (d, 2C), 127.7 (d), 124.4 (s), 123.5 (s), 122.5 (d), 50.1 (t), 35.7 (s), 22.8 (d), 22.1 (q), 17.8 (t) ppm; IR (reflection) \( \tilde{\nu} = 1699, 1653, 1599, 1579, 1551, 1499, 1441, 1399, 1347, 1304, 1282, 1259, 1206, 1189, 1166, 1132, 1097, 1053, 1008, 954, 894, 856, 831, 814, 775, 753, 729, 697, 664 cm\(^{-1}\)); HRMS (DART) (\( m/z \) [M+H]\(^+\)) \text{C}_{25}\text{H}_{22}\text{BrN}_2\text{O}_3\text{S} \text{calcd for 511.0509, found 511.0509,}

found 511.0496.
5-fluoro-2-((1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3e)
Yield: 89 mg, 99%; light yellow solid, mp 161-164 °C; Rf = 0.29 (EA/PE = 1/5); 1H NMR (500 MHz, CDCl_3) δ 9.03 (d, J = 3.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 6.92-6.85 (m, 2H), 6.85-6.80 (m, 2H), 6.71 (td, J = 8.0, 3.0 Hz, 1H), 6.63 (d, J = 7.0 Hz, 2H), 6.31 (dd, J = 4.5, 8.5 Hz, 1H), 4.22-4.14 (m, 2H), 2.41 (s, 3H), 1.85-1.80 (m, 1H), 1.71-1.66 (m, 1H), 1.10 (t, J = 5.0 Hz, 1H) ppm; 13C NMR (125 MHz, CDCl_3) δ 189.9 (d, J_C-F = 1.8 Hz), 158.7 (d, J_C-F = 242.0 Hz), 159.1 (d, J_C-F = 1.3 Hz), 148.0 (d, J_C-F = 2.4 Hz), 145.1 (s), 135.5 (s), 134.8 (s), 129.6 (d, 2C), 129.4 (d, 2C), 128.6 (d, 2C), 128.2 (d, 2C), 127.4 (d), 127.1 (d, J_C-F = 6.3 Hz), 124.3 (d, J_C-F = 7.1 Hz), 121.0 (d, J_C-F = 23.3 Hz), 111.8 (d, J_C-F = 22.6 Hz), 49.9 (t), 35.2 (s), 22.7 (d), 21.7 (q), 17.3 (t) ppm; IR (reflection) ν = 3064, 2860, 1682, 1598, 1478, 1449, 1422, 1365, 1351, 1305, 1263, 1248, 1188, 1172, 1159, 1137, 1122, 1099, 1089, 1074, 1056, 1024, 1010, 968, 946, 908, 888, 870, 831, 794, 757, 744, 730, 703, 675, 661, 622, 610 cm⁻¹; HRMS (DART) (m/z) [M+H]^+ C_{25}H_{24}FN_{2}O_S calcd for 449.1330, found 449.1314.

5-chloro-2-((1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3d)
Yield: 92 mg, 99%; white solid, mp 207-208 °C; Rf = 0.35 (EA/PE = 1/5); 1H NMR (500 MHz, CDCl_3) δ 9.02 (s, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 2.5 Hz, 1H), 6.93 (dd, J = 2.0, 8.5 Hz, 1H), 6.90 (t, J = 7.0 Hz, 1H), 6.83 (t, J = 7.5 Hz, 2H), 6.63 (d, J = 7.5 Hz, 2H), 6.27 (d, J = 8.5 Hz, 1H), 4.22-4.14 (m, 2H), 2.40 (s, 3H), 1.88-1.81 (m, 1H), 1.70-1.64 (m, 1H), 1.11-1.09 (t, J = 5.0 Hz, 1H) ppm; 13C NMR (125 MHz, CDCl_3) δ 189.6 (d), 158.9 (s), 150.2 (s), 145.2 (s), 135.4 (s), 134.6 (s), 133.5 (d), 129.7 (d, 2C), 129.5 (d, 2C), 128.60 (d, 2C), 128.58 (s), 128.2 (d, 2C), 127.5 (d), 127.2 (s), 125.9 (d), 124.3 (d), 50.0 (t), 35.3 (s), 22.6 (d), 21.7 (q), 17.3 (t) ppm; IR (reflection) ν = 3056, 2900, 2872, 1683, 1644, 1587, 1561, 1495, 1469, 1450, 1430, 1406, 1388, 1362, 1305, 1263, 1248, 1187, 1170, 1123, 1095, 1073, 1054, 1023, 1009, 945, 928, 908, 896, 868, 841, 828, 815, 792, 757, 733, 702, 663, 622, 608 cm⁻¹; HRMS (DART) (m/z) [M+H]^+ C_{25}H_{24}ClN_{2}O_S calcd for 465.1034, found 465.1021.

5-bromo-2-((1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3e)
Yield: 101 mg, 99%; light yellow solid, mp 207-209 °C; Rf = 0.33 (EA/PE = 1/5); 1H NMR (500 MHz, CDCl_3) δ 9.00 (s, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 2.0 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.06 (dd, J = 2.0, 8.5 Hz, 1H), 6.91 (t, J = 7.5 Hz, 1H), 6.83 (t, J = 7.5 Hz, 2H), 6.63 (d, J = 7.5 Hz, 2H), 6.21 (d, J = 8.5 Hz, 1H), 4.23-4.14 (m, 2H), 2.40 (s, 3H), 1.88-1.81 (m, 1H), 1.70-1.63 (m, 1H), 1.10 (t, J = 4.5 Hz, 1H) ppm; 13C NMR (125 MHz, CDCl_3) δ 189.5 (d), 158.9 (s), 150.6 (s), 145.2 (s), 136.3 (d), 135.4 (s), 134.6 (s), 129.7 (d, 2C), 129.5 (d, 2C), 129.0 (d), 128.6 (d, 2C), 128.3 (d, 2C), 127.53 (s), 127.51 (d), 124.6 (d), 116.0 (s), 50.0 (t), 35.4 (s), 22.5 (d), 21.7 (q), 17.3 (t) ppm; IR (reflection) ν = 3068, 3055, 2903, 2875, 1682, 1644, 1597, 1582, 1496, 1467, 1450, 1431, 1401, 1388, 1359, 1304, 1264, 1247, 1169, 1154, 1123, 1092, 1071, 1054, 1023, 1009, 944,
5-Methyl-2-((1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3f)

Yield: 71 mg, 80%; white solid, mp 204-206 °C; R_f = 0.38 (EA/PE = 1/3); ^1H NMR (300 MHz, CDCl_3) δ 9.08 (s, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.03 (s, 1H), 6.86-6.74 (m, 4H), 6.66-6.58 (m, 2H), 6.23 (d, J = 8.1 Hz, 1H), 4.21-4.10 (m, 2H), 2.40 (s, 3H), 2.05 (s, 3H), 1.84-1.74 (m, 1H), 1.67-1.61 (m, 1H), 1.09 (t, J = 5.1 Hz, 1H) ppm; ^13C NMR (75 MHz, CDCl_3) δ 191.1 (d), 158.2 (s), 149.5 (s), 144.9 (s), 135.6 (s), 135.0 (s), 134.8 (d), 132.4 (s), 129.6 (d, 2C), 129.4 (d, 2C), 128.6 (d, 2C), 127.9 (d, 2C), 127.1 (d), 126.2 (d), 126.1 (d), 125.9 (t), 22.6 (d), 21.7 (q), 17.2 (t) ppm; IR (reflection) ν = 3069, 3029, 2922, 2858, 1682, 1642, 1606, 1567, 1485, 1449, 1433, 1415, 1358, 1350, 1304, 1282, 1250, 1220, 1188, 1169, 1147, 1124, 1093, 1074, 1051, 1023, 1009, 946, 909, 870, 840, 827, 811, 793, 758, 738, 716, 701, 676, 661, 623, 612 cm⁻¹; HRMS (DART) (m/z) [M+H]^+ C_{26}H_{25}N_2O_3S calcd for 511.0509, found 511.0495.

5-hydroxy-2-((1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3g)

Yield: 38 mg, 43%; yellow solid, mp 245-248 °C; R_f = 0.19 (EA/PE = 1/2); ^1H NMR (400 MHz, DMSO-d_6) δ 9.20 (s, 1H), 8.89 (s, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 6.94-6.84 (m, 3H), 6.80-6.74 (m, 2H), 6.60 (dd, J = 8.4, 2.8 Hz, 1H), 6.53 (d, J = 2.4 Hz, 1H), 6.26 (d, J = 8.4 Hz, 1H), 4.38 (dd, J = 10.4, 5.6 Hz, 1H), 4.12 (d, J = 10.0 Hz, 1H), 2.43 (d, 3H, 1H), 2.00-1.93 (m, 1H), 1.92-1.87 (m, 1H), 1.14 (t, J = 4.8 Hz, 1H) ppm; ^13C NMR (100 MHz, DMSO-d_6) δ 190.7 (d), 159.1 (s), 153.3 (s), 144.9 (s), 144.4 (s), 136.3 (s), 135.8 (s), 129.9 (d, 2C), 129.6 (d, 2C), 128.5 (d, 2C), 128.1 (d, 2C), 127.0 (d), 126.7 (s), 124.1 (d), 122.5 (d), 110.5 (d), 50.2 (t), 34.9 (s), 23.9 (d), 21.6 (q), 17.1 (t) ppm; IR (reflection) ν = 3451, 3037, 2914, 2849, 2752, 1922, 1682, 1638, 1599, 1581, 1491, 1478, 1435, 1389, 1351, 1321, 1302, 1258, 1192, 1161, 1149, 1122, 1101, 1090, 1074, 1051, 1021, 1009, 971, 949, 928, 911, 876, 834, 815, 800, 755, 731, 712, 702, 678, 664, 635, 622, 612 cm⁻¹; HRMS (DART) (m/z) [M+H]^+ C_{25}H_{23}N_2O_4S calcd for 447.1373, found 447.1369.

4-chloro-2-((1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3h)

Yield: 92 mg, 99%; white solid, mp 227-228 °C; R_f = 0.36 (EA/PE = 1/5); ^1H NMR (500 MHz, CDCl_3) δ 9.09 (s, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.17 (d, J = 8.5 Hz, 1H), 6.89-6.82 (m, 3H), 6.72-6.67 (m, 2H), 6.65 (dd, J = 8.5, 1.0 Hz, 1H), 6.31 (d, J = 1.5 Hz, 1H), 4.24-4.12 (m, 2H), 2.41 (s, 3H), 1.89-1.83 (m, 1H), 1.72 (dd, J = 8.0, 5.5 Hz, 1H), 1.15 (t, J = 5.0 Hz, 1H) ppm; ^13C NMR (125 MHz, CDCl_3) δ 189.8 (d), 158.9 (s), 152.3 (s), 145.2 (s), 139.8 (s), 135.4 (s), 134.4 (s), 129.7 (d, 2C), 129.5 (d, 2C), 128.6 (d, 2C), 128.2 (d, 2C), 127.8 (d), 127.6 (d), 124.9 (s), 123.2 (d), 122.7 (d), 50.0 (t), 35.4 (s), 22.6 (d), 21.7 (q), 17.3 (t) ppm; IR (reflection) ν = 3054, 2990, 2914, 2869, 1686, 1664, 1589, 1562, 1445, 1397, 1355, 1303, 1251, 1217, 1184, 1169, 1151, 926, 908, 892, 867, 842, 815, 791, 756, 733, 715, 702, 662, 622, 609 cm⁻¹; HRMS (DART) (m/z) [M+H]^+ C_{25}H_{33}BrN_2O_3S calcd for 511.0509, found 511.0495.
4-bromo-2-((1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3i)
Yield: 98 mg, 96%; white solid, mp 194-196 °C; Rf = 0.34 (EA/PE = 1/4); 1H NMR (500 MHz, CDCl3) δ 9.09 (s, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 1H), 6.89-6.83 (m, 3H), 6.81 (d, J = 8.5 Hz, 1H), 6.69 (d, J = 6.5 Hz, 2H), 6.49 (s, 1H), 4.22-4.15 (m, 2H), 2.41 (s, 3H), 1.89-1.84 (m, 1H), 1.72 (dd, J = 5.0, 7.5 Hz, 1H), 1.15 (t, J = 4.5 Hz, 1H) ppm; 13C NMR (125 MHz, CDCl3) δ 190.0 (d), 159.0 (s), 152.2 (s), 145.2 (s), 135.4 (s), 134.4 (s), 129.8 (d, 2C), 129.5 (d, 2C), 128.7 (s), 128.6 (d, 2C), 128.2 (d, 2C), 127.72 (d), 127.66 (d), 126.0 (d), 125.7 (d), 125.3 (s), 50.0 (t), 35.4 (s), 22.6 (d), 21.8 (q), 17.3 (t) ppm; IR (reflection) ν = 3058, 2902, 1672, 1638, 1598, 1554, 1495, 1448, 1398, 1379, 1348, 1306, 1261, 1247, 1185, 1166, 1127, 1101, 1076, 1051, 1030, 1012, 953, 893, 856, 828, 813, 754, 736, 701, 663, 635, 615 cm⁻¹; HRMS (DART) (m/z) [M+H]⁺ C₂₅H₂₂₃BrClN₂O₃S calcd for 511.0509, found 511.0498.

1-(2-((1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)phenyl)ethan-1-one (3j)
Yield: 77 mg, 87%; light yellow solid, mp 145-146 °C; Rf = 0.24 (EA/PE = 1/4); 1H NMR (500 MHz, CDCl3) δ 7.86 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 7.19-7.16 (m, 1H), 6.92 (s, 1H), 6.84 (d, J = 8.0 Hz, 2H), 6.78 (t, J = 7.5 Hz, 3H), 6.13 (d, J = 7.0 Hz, 1H), 4.23-4.15 (m, 1H), 4.11 (d, J = 10.0 Hz, 1H), 2.38 (s, 3H), 2.18 (s, 3H), 1.81-1.74 (m, 1H), 1.64-1.58 (m, 1H), 1.02 (d, J = 5.0 Hz, 1H) ppm; 13C NMR (125 MHz, CDCl3) δ 157.0 (s), 147.7 (s), 144.5 (s), 135.9 (s), 134.8 (s), 131.6 (d), 130.7 (s), 129.6 (d, 2C), 129.3 (d, 2C), 128.8 (d), 128.6 (d, 2C), 127.9 (d, 2C), 127.1 (d), 122.7 (d), 122.6 (d), 49.8 (t), 35.0 (s), 30.3 (q), 22.5 (d), 21.7 (q), 17.5 (t) ppm; IR (reflection) ν = 3026, 2896, 1669, 1596, 1566, 1499, 1474, 1447, 1349, 1309, 1288, 1251, 1164, 1131, 1099, 1056, 1033, 1010, 978, 951, 919, 840, 814, 763, 719, 695, 683, 661, 627 cm⁻¹; HRMS (DART) (m/z) [M+H]⁺ C₂₆H₂₅ClN₂O₃S calcd for 445.1580, found 445.1566.

(5-chloro-2-((1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)(phenyl)methanone (3k)
Yield: 90 mg, 83%; white solid, mp 210-213 °C; Rf = 0.38 (EA/PE = 1/4); 1H NMR (500 MHz, CDCl3) δ 7.59 (d, J = 8.0 Hz, 2H), 7.56-7.53 (m, 2H), 7.51 (d, J = 7.0 Hz, 1H), 7.39 (t, J = 7.5 Hz, 2H), 6.93-6.89 (m, 1H), 6.87 (d, J = 4.5 Hz, 4H), 6.82-6.78 (m, 3H), 6.71 (d, J = 8.5 Hz, 1H), 6.21 (d, J = 8.0 Hz, 1H), 4.07-4.02 (m, 2H), 2.08 (s, 3H), 1.82-1.76 (m, 1H), 1.69 (dd, J = 5.0, 7.5 Hz, 1H), 1.29 (t, J = 5.0 Hz, 1H) ppm; 13C NMR (125 MHz, CDCl3) δ 194.4 (s), 157.5 (s), 145.7 (s), 144.0 (s), 137.4 (s), 135.5 (s), 135.2 (s), 132.9 (d), 131.1 (s), 130.2 (d, 2C), 130.1 (d, 2C), 129.6 (d),
128.9 (d, 2C), 128.4 (d, 2C), 128.3 (d, 2C), 128.0 (d), 127.8 (d, 2C), 127.1 (d), 126.7 (s), 124.2 (d),
49.5 (t), 35.1 (s), 23.0 (d), 21.5 (q), 17.9 (t) ppm; IR (reflection) \( \nu = 3060, 3027, 2905, 1681, 1596,
1469, 1448, 1346, 1306, 1270, 1252, 1236, 1205, 1187, 1171, 1129, 1114, 1097, 1076, 1041, 998,
946, 925, 880, 824, 802, 792, 774, 757, 739, 715, 700, 691, 666, 652, 626 \text{ cm}^{-1}; \) HRMS (DART)
\((m/z) [M+H]^+ C_{31}H_{2635}ClN_2O_3S \text{ calcd for } 541.1347, \text{ found } 541.1345.

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5-bromo-2-((1-(2-bromophenyl)-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3l)

Yield: 116 mg, 99%; white solid, mp 213-217 °C; \( R_f = 0.31 \) (EA/PE = 1/5); \(^1\)H NMR (500 MHz,
CDCl\(_3\)) \( \delta \) 9.23 (s, 1H), 7.88 (d, \( J = 8.0 \) Hz, 2H), 7.34 (s, 1H), 7.28 (d, \( J = 8.0 \) Hz, 2H), 7.09 (d, \( J = 8.0 \) Hz, 2H), 6.84-6.71 (m, 2H), 6.46 (d, \( J = 7.5 \) Hz, 1H), 6.34 (d, \( J = 8.0 \) Hz, 1H), 4.30-4.25 (m,
1H), 4.22 (d, \( J = 10.0 \) Hz, 1H), 2.42 (s, 3H), 1.84-1.75 (m, 1H), 1.62 (dd, \( J = 5.0, 7.5 \) Hz, 1H), 1.37
(t, \( J = 5.0 \) Hz, 1H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 189.5 (d), 157.3 (s), 150.9 (s),
145.2 (s), 136.3 (d), 134.9 (s), 134.6 (s), 132.6 (d), 132.1 (d), 129.2 (d, 3C), 129.0 (d), 128.8 (d, 2C), 128.1
(s), 127.1 (d), 125.8 (s), 124.4 (d), 116.1 (s), 49.9 (t), 36.1 (s), 22.5 (d), 18.2 (t) ppm; IR (reflection)
\( \nu = 3067, 2976, 2928, 2890, 2876, 1681, 1649, 1596, 1584, 1561, 1492, 1470, 1429, 1401, 1386,
1369, 1356, 1310, 1262, 1211, 1186, 1171, 1125, 1095, 1063, 1049, 1021, 950, 906, 888, 869, 845,
831, 815, 804, 765, 733, 722, 707, 662, 638, 618 \text{ cm}^{-1}; \) HRMS (DART) \((m/z) [M+H]^+
C_{25}H_{2179}Br_2N_2O_3S \text{ calcd for } 586.9634, \text{ found } 586.9623.

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5-bromo-2-((1-(3-chlorophenyl)-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3m)

Yield: 73 mg, 67%; light yellow solid, mp 219-220 °C; \( R_f = 0.26 \) (EA/PE = 1/5); \(^1\)H NMR (500 MHz,
CDCl\(_3\)) \( \delta \) 9.01 (s, 1H), 7.85 (d, \( J = 8.0 \) Hz, 2H), 7.39 (d, \( J = 1.5 \) Hz, 1H), 7.27 (d, \( J = 8.0 \)
Hz, 2H), 7.14 (d, \( J = 7.0 \) Hz, 1H), 6.90 (d, \( J = 8.0 \) Hz, 1H), 6.79 (t, \( J = 8.0 \) Hz, 1H), 6.61-6.54 (m,
2H), 6.23 (d, \( J = 8.5 \) Hz, 1H), 4.23-4.14 (m, 2H), 2.41 (s, 3H), 1.90-1.83 (m, 1H), 1.62 (dd, \( J = 5.5,
8.0 \) Hz, 1H), 1.12 (t, \( J = 5.0 \) Hz, 1H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 189.1 (d), 158.2
(s), 150.4 (s), 145.3 (s), 136.5 (s), 136.4 (d), 135.2 (s), 134.2 (s), 130.2 (d), 129.6 (d), 129.5 (d, 2C), 129.2
(d, 2C), 128.6 (d, 2C), 127.8 (d), 127.7 (d), 127.6 (s), 124.6 (d), 116.5 (s), 49.9 (t), 35.0 (s), 22.5 (d),
21.8 (q), 17.5 (t) ppm; IR (reflection) \( \nu = 3068, 3054, 2924, 2891, 2853, 1681, 1649, 1596, 1581,
1467, 1434, 1401, 1388, 1360, 1348, 1308, 1261, 1247, 1187, 1169, 1155, 1124, 1088, 1071, 1055, 1019,
969, 946, 921, 895, 863, 841, 811, 785, 729, 712, 696, 679, 662, 642, 612 \text{ cm}^{-1}; \) HRMS (DART)
\((m/z) [M+H]^+ C_{25}H_{2179}Br_2ClN_2O_3S \text{ calcd for } 543.0139, \text{ found } 543.0128.

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2-((1-(m-tolyl)-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3n)

Yield: 88 mg, 99%; light yellow solid, mp 151-154 °C; R_f = 0.31 (EA/PE = 1/5); 1H NMR (500 MHz, CDCl_3) δ 9.11 (s, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 7.23 (d, J = 7.5 Hz, 1H), 7.02 (t, J = 7.5 Hz, 1H), 6.72-6.65 (m, 2H), 6.62 (d, J = 7.5 Hz, 1H), 6.45 (d, J = 7.5 Hz, 1H), 6.38 (s, 1H), 6.33 (d, J = 8.0 Hz, 1H), 4.21-4.12 (m, 2H), 2.40 (s, 3H), 1.92 (s, 3H), 1.83-1.77 (m, 1H), 1.62 (dd, J = 7.5, 5.0 Hz, 1H), 1.09 (t, J = 5.0 Hz, 1H) ppm; 13C NMR (125 MHz, CDCl_3) δ 190.8 (d), 158.2 (s), 151.7 (s), 145.0 (s), 137.8 (s), 135.6 (s), 133.7 (d), 130.7 (d), 129.4 (d, 2C), 128.6 (d, 2C), 128.1 (d), 128.0 (d), 126.6 (d), 126.3 (s), 126.2 (d), 122.73 (d), 122.68 (d), 49.9 (t), 35.2 (s), 22.4 (d), 21.7 (q), 20.8 (q), 17.3 (t) ppm; IR (reflection) ν = 2889, 2853, 1684, 1650, 1593, 1570, 1493, 1474, 1451, 1359, 1347, 1310, 1276, 1251, 1187, 1170, 1143, 1121, 1106, 1090, 1074, 1056, 1036, 1021, 1008, 950, 944, 894, 887, 859, 844, 828, 812, 777, 753, 730, 717, 705, 682, 667, cm⁻¹; HRMS (DART) (m/z) [M+H]^+ C_{26}H_{25}N_2O_3S calcd for 445.1580, found 445.1565.

5-bromo-2-((1-(4-ethylphenyl)-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3o)

Yield: 106 mg, 99%; white solid, mp 160-162 °C; R_f = 0.38 (EA/PE = 1/4); 1H NMR (400 MHz, CDCl_3) δ 8.96 (s, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 2.4 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 7.04 (dd, J = 8.4, 2.4 Hz, 1H), 6.65 (d, J = 8.0 Hz, 2H), 6.52 (d, J = 8.0 Hz, 2H), 6.19 (d, J = 8.8 Hz, 1H), 4.20-4.13 (m, 2H), 2.40 (s, 3H), 2.36 (dd, J = 15.2, 7.6 Hz, 2H), 1.87-1.80 (m, 1H), 1.61 (dd, J = 8.0, 5.2 Hz, 1H), 1.10-1.06 (m, 1H), 1.03 (t, J = 7.6 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl_3) δ 189.4 (d), 158.9 (s), 150.8 (s), 145.1 (s), 144.1 (s), 136.2 (d), 135.5 (s), 131.7 (s), 129.8 (d, 2C), 129.4 (d, 2C), 128.9 (d), 128.6 (d, 2C), 127.8 (d, 2C), 127.5 (s), 124.6 (d), 115.9 (s), 50.0 (t), 35.1 (s), 28.5 (t), 22.3 (d), 21.7 (q), 17.4 (t), 15.9 (q) ppm; IR (reflection) ν = 2897, 2928, 2893, 2868, 1904, 1704, 1684, 1655, 1596, 1584, 1519, 1492, 1469, 1401, 1352, 1310, 1257, 1169, 1125, 1099, 1090, 1046, 1028, 1008, 950, 912, 887, 826, 804, 763, 731, 713, 683, 659, 607 cm⁻¹; HRMS (DART) (m/z) [M+H]^+ C_{26}H_{26}BrN_2O_3S calcd for 539.0822, found 539.0827.

2-((1-(4-(tert-butyl)phenyl)-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3p)

Yield: 96 mg, 99%; white solid, mp 201-204 °C; R_f = 0.41 (EA/PE = 1/4); 1H NMR (500 MHz, CDCl_3) δ 8.97 (s, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 2.4 Hz, 1H), 7.26 (d, J = 8.4 Hz, 2H), 7.04 (dd, J = 8.4, 2.4 Hz, 1H), 6.65 (d, J = 8.0 Hz, 2H), 6.52 (d, J = 8.0 Hz, 2H), 6.19 (d, J = 8.8 Hz, 1H), 4.20-4.13 (m, 2H), 2.40 (s, 3H), 2.36 (dd, J = 15.2, 7.6 Hz, 2H), 1.87-1.80 (m, 1H), 1.61 (dd, J = 8.0, 5.2 Hz, 1H), 1.10-1.06 (m, 1H), 1.03 (t, J = 7.6 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl_3) δ 189.4 (d), 158.9 (s), 150.8 (s), 145.1 (s), 144.1 (s), 136.2 (d), 135.5 (s), 131.7 (s), 129.8 (d, 2C), 129.4 (d, 2C), 128.9 (d), 128.6 (d, 2C), 127.8 (d, 2C), 127.5 (s), 124.6 (d), 115.9 (s), 50.0 (t), 35.1 (s), 28.5 (t), 22.3 (d), 21.7 (q), 17.4 (t), 15.9 (q) ppm; IR (reflection) ν = 2897, 2928, 2893, 2868, 1904, 1704, 1684, 1655, 1596, 1584, 1519, 1492, 1469, 1401, 1352, 1310, 1257, 1169, 1125, 1099, 1090, 1046, 1028, 1008, 950, 912, 887, 826, 804, 763, 731, 713, 683, 659, 607 cm⁻¹; HRMS (DART) (m/z) [M+H]^+ C_{26}H_{26}BrN_2O_3S calcd for 539.0822, found 539.0827.
CDCl$_3$ δ 9.06 (s, 1H), 7.86 (d, $J = 8.5$ Hz, 2H), 7.26 (d, $J = 8.5$ Hz, 2H), 7.19 (d, $J = 5.5$ Hz, 1H), 6.98 (t, $J = 7.0$ Hz, 1H), 6.77 (d, $J = 8.5$ Hz, 2H), 6.66 (t, $J = 7.5$ Hz, 1H), 6.53 (d, $J = 8.0$ Hz, 2H), 6.31 (d, $J = 8.0$ Hz, 1H), 4.20-4.12 (m, 2H), 2.40 (s, 3H), 1.85-1.79 (m, 1H), 1.62 (dd, $J = 8.0$, 5.5 Hz, 1H), 1.14-1.09 (m, 1H), 1.06 (s, 9H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ 190.8 (d), 158.2 (s), 151.8 (s), 150.2 (s), 145.0 (s), 135.6 (s), 133.8 (d), 131.7 (s), 129.6 (d, 2C), 129.4 (d, 2C), 128.6 (d, 2C), 126.3 (d), 126.1 (s), 125.0 (d, 2C), 122.7 (d), 122.6 (d), 49.9 (t), 34.9 (s), 34.3 (s), 31.0 (q, 3C), 22.3 (d), 21.7 (q), 17.3 (t) ppm; IR (reflection) $\tilde{\nu} =$ 3054, 2952, 2907, 2864, 2844, 2753, 1683, 1650, 1593, 1568, 1523, 1474, 1450, 1390, 1362, 1304, 1275, 1256, 1239, 1218, 1194, 1171, 1155, 1113, 1089, 1066, 1048, 1022, 1003, 964, 940, 909, 885, 847, 835, 825, 811, 797, 770, 741, 715, 670, 652, 633, 616 cm$^{-1}$; HRMS (DART) ($m/z$) [M+H]$^+$ C$_{29}$H$_{31}$N$_2$O$_3$S calcd for 487.2050, found 487.2034.

5-bromo-2-((3-tosyl-1-(4-(trifluoromethyl)phenyl)-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3q)

Yield: 100 mg, 87%; white solid, mp 157-158 °C; $R_f = 0.21$ (EA/PE = 1/4); $^1$H NMR (500 MHz, CDCl$_3$) δ 8.98 (s, 1H), 7.85 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 2.0$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 7.03 (d, $J = 7.5$ Hz, 1H), 6.76 (d, $J = 8.0$ Hz, 2H), 6.18 (d, $J = 8.5$ Hz, 1H), 4.24-4.15 (m, 2H), 2.41 (s, 3H), 1.94-1.86 (m, 1H), 1.67 (dd, $J = 5.5$, 8.0 Hz, 1H), 1.19-1.12 (m, 1H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ 189.2 (d), 158.1 (s), 150.3 (s), 145.4 (s), 138.5 (s), 136.3 (d), 135.2 (s), 130.2 (d, 2C), 129.8 (q, $J_{C-F} = 32.6$ Hz), 129.5 (d, 2C), 129.3 (d), 128.7 (d, 2C), 127.8 (s), 125.1 (q, $J_{C-F} = 3.8$ Hz, 2C), 124.7 (d), 124.6 (q, $J_{C-F} = 270.8$ Hz), 116.4 (s), 49.9 (t), 35.0 (s), 22.6 (d), 21.7 (q), 17.4 (t) ppm; IR (reflection) $\tilde{\nu} =$ 2893, 1680, 1643, 1597, 1583, 1494, 1467, 1401, 1382, 1363, 1326, 1262, 1165, 1121, 1092, 1068, 1052, 1022, 1009, 946, 910, 890, 876, 840, 826, 814, 767, 733, 697, 664, 615 cm$^{-1}$; HRMS (DART) ($m/z$) [M+H]$^+$ C$_{20}$H$_{17}$BrF$_3$N$_2$O$_3$S calcd for 577.0403, found 577.0387.

5-bromo-2-((3-((4-nitrophenyl)sulfonyl)-1-phenyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3r)

Yield: 103 mg, 95%; light yellow solid, mp 194-197 °C; $R_f = 0.20$ (EA/PE = 1/4); $^1$H NMR (500 MHz, CDCl$_3$) δ 9.37 (s, 1H), 8.31 (d, $J = 9.0$ Hz, 2H), 8.20 (d, $J = 9.0$ Hz, 2H), 7.35 (d, $J = 1.5$ Hz, 1H), 7.09 (d, $J = 8.5$ Hz, 1H), 6.93 (t, $J = 7.5$ Hz, 1H), 6.85 (d, $J = 7.5$ Hz, 2H), 6.65 (d, $J = 7.5$ Hz, 2H), 6.17 (d, $J = 8.5$ Hz, 1H), 4.23-4.12 (m, 2H), 1.95-1.89 (m, 1H), 1.71 (dd, $J = 5.5$, 7.5 Hz, 1H), 1.20 (t, $J = 5.0$ Hz, 1H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) δ 188.9 (d), 158.8 (s), 150.7 (s), 149.4 (s), 144.0 (s), 136.4 (d), 134.1 (s), 130.4 (d), 130.1 (d, 2C), 129.9 (d, 2C), 128.3 (d, 2C), 127.8 (d), 127.6 (s), 124.3 (d), 123.9 (d, 2C), 116.4 (s), 49.9 (t), 35.3 (s), 22.7 (d), 17.6 (t) ppm; IR (reflection) $\tilde{\nu} =$ 3109, 2875, 1682, 1666, 1606, 1588, 1525, 1503, 1467, 1401, 1351, 1308, 1252, 1236, 1169, 1154, 1137, 1101, 1057, 1035, 1008, 949, 920, 888, 869, 856, 829, 799, 757, 742, 705, 685, 617
2-((3-(benzylsulfonyl)-1-phenyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3s)
Yield: 82 mg, 95%; light yellow solid, mp 188-190 °C; R_f = 0.31 (EA/PE = 1/4); ^1H NMR (500 MHz, CDCl_3) δ 10.00 (s, 1H), 7.60 (d, J = 7.0 Hz, 2H), 7.46-7.37 (m, 3H), 7.33 (d, J = 7.5 Hz, 1H), 7.11 (t, J = 8.0 Hz, 1H), 6.92-6.84 (m, 3H), 6.81 (t, J = 7.5 Hz, 1H), 6.76 (d, J = 7.0 Hz, 2H), 6.60 (d, J = 8.0 Hz, 1H), 5.16 (d, J = 14.0 Hz, 1H), 4.58 (d, J = 14.0 Hz, 1H), 3.70 (d, J = 10.0 Hz, 1H), 3.22 (dd, J = 10.5, 5.0 Hz, 1H), 1.67-1.61 (m, 2H), 1.16-1.08 (m, 1H) ppm; ^13C NMR (125 MHz, CDCl_3) δ 191.1 (d), 159.7 (s), 150.5 (s), 134.8 (s), 133.9 (d), 131.0 (d, 2C), 129.8 (d, 2C), 129.2 (d), 129.1 (d), 128.9 (d, 2C), 128.8 (s), 128.1 (d, 2C), 127.3 (d), 127.0 (s), 123.2 (d), 122.9 (d), 58.4 (t), 50.1 (t), 35.4 (s), 23.0 (d), 17.4 (t) ppm; IR (reflection) ν = 3056, 3029, 2973, 2929, 2901, 2819, 2723, 1698, 1672, 1653, 1594, 1499, 1479, 1450, 1401, 1380, 1346, 1306, 1278, 1252, 1200, 1170, 1152, 1138, 1126, 1095, 1073, 1057, 1029, 1009, 949, 921, 878, 861, 849, 807, 780, 762, 737, 727, 695, 650, 626 cm⁻¹; HRMS (DART) (m/z) [M+H]^+ C_{25}H_{23}N_2O_3S calcd for 431.1424, found 431.1410.

5-bromo-2-((1-phenyl-3-(propylsulfonyl)-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3t)
Yield: 82 mg, 89%; yellow oil; R_f = 0.32 (EA/PE = 1/4); ^1H NMR (500 MHz, CDCl_3) δ 9.79 (s, 1H), 7.38 (d, J = 2.5 Hz, 1H), 7.14 (dd, J = 2.0, 8.5 Hz, 1H), 6.98-6.95 (m, 1H), 6.91 (t, J = 8.5 Hz, 2H), 6.40 (d, J = 8.5 Hz, 1H), 4.10-4.00 (m, 2H), 3.77-3.67 (m, 1H), 3.57-3.46 (m, 1H), 1.95-1.85 (m, 3H), 1.73 (dd, J = 5.0, 8.0 Hz, 1H), 1.28 (t, J = 5.0 Hz, 1H), 1.08 (t, J = 7.5 Hz, 3H) ppm; ^13C NMR (125 MHz, CDCl_3) δ 189.4 (d), 160.3 (s), 149.8 (s), 136.4 (d), 134.7 (s), 131.1 (d), 129.9 (d, 2C), 128.3 (d, 2C), 127.9 (s), 127.6 (d), 124.8 (d), 116.1 (s), 54.9 (t), 49.5 (t), 35.8 (s), 22.8 (d), 17.5 (t), 17.1 (t), 13.0 (q) ppm; IR (reflection) ν = 3290, 3060, 2935, 2773, 1765, 1672, 1653, 1594, 1499, 1449, 1450, 1401, 1380, 1346, 1306, 1278, 1252, 1200, 1170, 1152, 1138, 1126, 1095, 1073, 1057, 1029, 1009, 949, 921, 878, 861, 849, 807, 780, 762, 737, 727, 695, 650, 626 cm⁻¹; HRMS (DART) (m/z) [M+H]^+ C_{21}H_{22}BrN_2O_3S calcd for 461.0529, found 461.0518.

5-bromo-2-((5-methyl-1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3u)
Yield: 104 mg, 99%; white solid, mp 230-232 °C; R_f = 0.38 (EA/PE = 1/5); ^1H NMR (500 MHz, CDCl_3) δ 9.03 (s, 1H), 7.85 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 2.0 Hz, 1H), 7.26 (d, J = 8.5 Hz, 2H), 7.04 (dd, J = 2.0, 8.5 Hz, 1H), 6.91 (t, J = 7.0 Hz, 1H), 6.88-6.77 (m, 2H), 6.76-6.60 (m, 1H), 6.50-6.30 (m, 1H), 6.20 (d, J = 8.5 Hz, 1H), 4.25 (d, J = 10.5 Hz, 1H), 3.86 (d, J = 10.5 Hz, 1H), 2.40 (s, 3H), 1.41 (d, J = 5.5 Hz, 1H), 1.24-1.20 (m, 1H), 0.89 (s, 3H) ppm; ^13C NMR (125 MHz, CDCl_3) δ
189.6 (d), 159.6 (s), 150.6 (s), 145.1 (s), 136.3 (d), 135.5 (s), 132.2 (s), 129.4 (d, 2C), 128.9 (d), 128.6 (d, 2C), 127.5 (d), 124.7 (d), 115.9 (s), 55.1 (t), 39.2 (s), 27.0 (s), 23.1 (t), 21.7 (q), 16.9 (q) ppm; IR (reflection) \( \nu = 3064, 2968, 2903, 2868, 1678, 1655, 1584, 1502, 1466, 1447, 1403, 1378, 1353, 1293, 1257, 1234, 1220, 1169, 1129, 1105, 1092, 1072, 1045, 1021, 1005, 958, 935, 885, 819, 793, 778, 751, 721, 710, 661, 637 \text{ cm}^{-1} \); HRMS (DART) (m/z) \([M+H]^+\) C\(_{26}\)H\(_{24}\)BrN\(_2\)O\(_3\)S calcd for 523.0686, found 523.0674.

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\text{N} \\
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5-bromo-2-((6-methyl-1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3v)

Yield: 99 mg, 95%, dr = 6.3:1; white solid, mp 174-177 °C; \( R_f = 0.32 \) (EA/PE = 1/5); \(^1\)H NMR (500 MHz, CDCl\(_3\), *peaks of the minor isomer) \( \delta^\ast 9.00 \) (s, 0.14H), 8.77 (s, 0.86H), \( \ast 7.87 \) (d, \( J = 8.0 \text{ Hz}, 0.3H)\), 7.81 (d, \( J = 8.0 \text{ Hz}, 1.75H), 7.37 (bs, 0.83H), \( \ast 7.27 \) (s, 0.33H), \( \ast 7.25 \) (s, 0.17H), 7.23 (d, \( J = 8.0 \text{ Hz}, 1.75H), 7.18-7.00 \) (m, 1H), 6.95-6.88 (m, 1 H), 6.88 (t, \( J = 8.0 \text{ Hz}, 1H)\), 6.85-6.77 (m, 2H), \( \ast 6.62 \) (d, \( J = 7.5 \text{ Hz}, 0.30H)\), 6.55 (d, \( J = 7.5 \text{ Hz}, 1.72H)\), 6.28-6.04 (m, 1H), \( \ast 4.30-4.25 \) (m, 0.15H), \( \ast 4.22-4.14 \) (m, 1.78 H), \( \ast 4.02 \) (d, \( J = 11.0 \text{ Hz}, 0.16H)\), \( \ast 2.40 \) (s, 0.49H), 2.38 (s, 2.64H), 1.63 (t, \( J = 4.5 \text{ Hz}, 1H)\), 1.39 (bs, 1H), \( \ast 1.22 \) (d, \( J = 10.8 \text{ Hz}, 0.49H)\), 1.00 (d, \( J = 6.2 \text{ Hz}, 2.68H)\) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\), the major isomer) \( \delta 189.1 \) (d), 158.3 (s), 150.9 (s), 145.1 (s), 136.4 (d), 135.3 (s), 132.5 (s), 131.3 (d, 2C), 129.3 (d, 2C), 129.1 (d), 128.7 (d, 2C), 128.1 (d, 2C), 127.4 (d), 127.0 (s), 124.3 (d), 115.7 (s), 49.9 (t), 39.4 (s), 28.5 (d), 25.3 (d), 21.7 (q), 14.6 (q) ppm; IR (reflection) \( \nu = 3070, 2969, 2899, 2870, 1686, 1649, 1582, 1493, 1467, 1449, 1400, 1383, 1364, 1276, 1258, 1244, 1202, 1163, 1116, 1104, 1083, 1039, 1016, 987, 946, 922, 903, 883, 846, 833, 807, 759, 734, 705, 665, 612 \text{ cm}^{-1} \); HRMS (DART) (m/z) \([M+H]^+\) C\(_{26}\)H\(_{24}\)BrN\(_2\)O\(_3\)S calcd for 523.0686, found 523.0673.

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\text{CHO} \quad \begin{array}{c}
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\text{N} \\
\text{Ts}
\end{array}
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5-bromo-2-((3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3w)

Yield: 50 mg, 58%; white solid, mp 161-164 °C; \( R_f = 0.18 \) (EA/PE = 1/4); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \( \delta 9.41 \) (s, 1H), 7.83 (d, \( J = 7.8 \text{ Hz}, 3H)\), 7.49 (dd, \( J = 8.4, 2.1 \text{ Hz}, 1H)\), 7.27 (d, \( J = 7.8 \text{ Hz}, 2H)\), 6.72 (d, \( J = 8.4 \text{ Hz}, 1H)\), 4.09 (d, \( J = 10.2 \text{ Hz}, 1H)\), 3.91 (dd, \( J = 10.2, 5.4 \text{ Hz}, 1H)\), 2.40 (s, 3H), 1.90-1.81 (m, 1H), 1.72-1.63 (m, 1H), 1.15-1.06 (m, 1H), 0.80-0.73 (m, 1H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta 190.3 \) (d), 159.7 (s), 151.5 (s), 145.1 (s), 137.5 (d), 135.3 (s), 130.0 (d), 129.5 (d, 2C), 129.0 (s), 128.5 (d, 2C), 124.4 (d), 117.1 (s), 50.4 (t), 21.7 (q), 18.5 (d), 14.3 (d), 12.8 (t) ppm; IR (reflection) \( \nu = 3070, 2969, 2899, 2870, 1686, 1649, 1582, 1493, 1467, 1449, 1400, 1383, 1364, 1276, 1258, 1244, 1202, 1163, 1116, 1104, 1083, 1039, 1016, 987, 946, 922, 903, 883, 846, 833, 807, 759, 734, 705, 665, 612 \text{ cm}^{-1} \); HRMS (DART) (m/z) \([M+H]^+\) C\(_{19}\)H\(_{18}\)BrN\(_2\)O\(_3\)S calcd for 433.0216, found 433.0204.

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\text{N} \\
\text{Ts}
\end{array}
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5-bromo-2-((1-butyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-ylidene)amino)benzaldehyde (3x)
Yield: 69 mg, 70%; white solid, mp 119-122 °C; Rf = 0.32 (EA/PE = 1/10); 'H NMR (300 MHz, CDCl3) δ 9.22 (brs, 1H), 7.78 (d, J = 2.4 Hz, 1H), 7.75 (d, J = 8.4 Hz, 2H), 7.43 (dd, J = 8.7, 2.4 Hz, 1H), 7.24 (d, J = 8.1 Hz, 2H), 6.60 (d, J = 8.4 Hz, 1H), 4.06-3.93 (m, 2H), 2.39 (s, 3H), 1.61-1.53 (m, 1H), 1.22-1.18 (m, 2H), 0.87-0.75 (m, 6H), 0.53 (t, J = 6.6 Hz, 3H) ppm; 'C NMR (75 MHz, CDCl3) δ 189.8 (d), 158.9 (s), 150.1 (s), 145.0 (s), 137.1 (d), 135.7 (s), 129.8 (d), 129.4 (d, 2C), 128.4 (d, 2C), 128.0 (s), 124.2 (d), 116.5 (s), 49.8 (t), 30.8 (s), 29.8 (t), 29.5 (t), 22.1 (t), 17.7 (q), 19.3 (d), 19.2 (t), 13.6 (q) ppm; IR (reflection) ν = 3446, 3336, 3067, 2958, 2930, 2859, 1665, 1585, 1558, 1466, 1401, 1360, 1325, 1287, 1256, 1238, 1216, 1164, 1127, 1091, 1042, 952, 886, 866, 814, 706, 665, 609 cm⁻¹; HRMS (DART) (m/z) [M+H]+ C23H2679BrN2O3S calcd for 489.0842, found 489.0838.

N-allyl-N-(7-formyl-3-phenyl-1H-indol-2-yl)-4-methylbenzenesulfonamide (4a)

White solid, mp 167-169 °C; Rf = 0.46 (EA/PE = 1/4); 'H NMR (400 MHz, CDCl3) δ 10.06 (s, 1H), 10.04 (brs, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.63 (dd, J = 0.8, 7.2 Hz, 1H), 7.60-7.55 (m, 2H), 7.24-7.17 (m, 6H), 6.96-6.90 (m, 2H), 5.66-5.52 (m, 1H), 4.91-4.85 (m, 1H), 4.84-4.78 (m, 1H), 3.97-3.93 (m, 2H), 2.39 (s, 3H) ppm; 'C NMR (100 MHz, CDCl3) δ 193.00 (d), 144.30 (s), 135.98 (s), 132.37 (d), 131.08 (s), 129.95 (d, 2C), 129.80 (s), 129.60 (d), 129.36 (d, 2C), 128.45 (d, 2C), 127.62 (s, 2C), 127.57 (d, 2C), 127.11 (d), 126.96 (d), 121.4 (d), 119.18 (d), 121.4 (d), 119.44 (t), 113.84 (s), 53.29 (t), 21.61 (q) ppm; IR (reflection) ν = 3324, 3070, 3021, 2918, 2824, 2744, 1857, 1667, 1604, 1567, 1493, 1444, 1423, 1371, 1338, 1308, 1228, 1202, 1155, 1092, 1050, 1028, 981, 923, 875, 844, 811, 793, 749, 705, 660 cm⁻¹; HRMS (DART) (m/z) [M+H]+ C25H23N2O3S calcd for 431.1424, found 431.1413.

N-allyl-N'-(4-bromo-2-formylphenyl)-N-tosylhex-2-enimidamide (5)

Yield: 13 mg, 13%; light yellow oil; Rf = 0.31 (EA/PE = 1/5); 'H NMR (400 MHz, CDCl3) δ 9.59 (s, 1H), 7.84 (d, J = 2.4 Hz, 1H), 7.70 (d, J = 8.4 Hz, 2H), 7.48 (dd, J = 8.4, 2.4 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 6.48 (d, J = 8.8 Hz, 1H), 6.43-6.34 (m, 1H), 5.78-5.67 (m, 2H), 5.15-5.11 (m, 1H), 5.11-5.08 (m, 1H), 4.23 (d, J = 6.0 Hz, 2H), 2.38 (s, 3H), 2.04-1.96 (m, 1H), 1.34-1.25 (m, 2H), 0.77 (d, J = 7.2 Hz, 3H) ppm; 'C NMR (100 MHz, CDCl3) δ 189.6 (d), 156.7 (s), 150.0 (s), 149.1 (d), 144.4 (s), 137.4 (d), 135.9 (s), 132.6 (d), 130.5 (d), 129.5 (d, 2C), 128.3 (d, 2C), 127.6 (s), 123.2 (d), 121.4 (d), 119.1 (t), 117.3 (s), 51.3 (t), 34.8 (t), 21.6 (t), 21.4 (q), 13.6 (q) ppm; IR (reflection) ν = 3303, 2960, 2930, 2872, 1686, 1646, 1597, 1495, 1465, 1356, 1291, 1259, 1167, 1120, 1089, 987, 927, 889, 814, 706, 668 cm⁻¹; HRMS (DART) (m/z) [M+H]+ C23H2679BrN2O3S calcd for 489.0842, found 489.0840.

N-(2-ethynylphenyl)-1-phenyl-3-tosyl-3-azabicyclo[3.1.0]hexan-2-imine (6)
Yield: 77 mg, 90%; light yellow oil; R_f = 0.41 (EA/PE = 1/10); ^1H NMR (400 MHz, CDCl_3) \( \delta \) 7.91 (d, \( J = 8.0 \text{ Hz}, 2\text{H} \)), 7.22 (d, \( J = 8.0 \text{ Hz}, 2\text{H} \)), 6.94 (dd, \( J = 0.8, 7.6 \text{ Hz}, 1\text{H} \)), 6.84-6.74 (m, 5H), 6.66 (t, \( J = 7.2 \text{ Hz}, 1\text{H} \)), 6.52 (td, \( J = 7.6, 0.8 \text{ Hz}, 1\text{H} \)), 6.19 (d, \( J = 8.0 \text{ Hz}, 1\text{H} \)), 4.16-4.11 (m, 1H), 4.09-4.04 (m, 1H), 2.62 (s, 1H), 2.37 (s, 3H), 1.77-1.71 (m, 1H), 1.62-1.57 (m, 1H), 1.17 (t, \( J = 4.8 \text{ Hz}, 1\text{H} \)) ppm; ^13C NMR (100 MHz, CDCl_3) \( \delta \) 157.1 (s), 150.8 (s), 144.1 (s), 135.9 (s), 135.3 (s), 132.2 (d), 129.8 (d, 2C), 129.2 (d, 2C), 129.0 (d, 2C), 128.3 (d), 127.7 (d, 2C), 126.8 (d), 121.9 (d, 2C), 113.5 (s), 82.2 (s), 79.3 (d), 49.7 (t), 35.3 (s), 22.8 (d), 21.6 (q), 17.3 (t) ppm; IR (reflection) \( \tilde{\nu} = \) 3248, 3063, 3025, 2898, 1912, 1664, 1594, 1494, 1475, 1439, 1401, 1380, 1359, 1306, 1359, 1306, 1287, 1251, 1187, 1169, 1156, 1125, 1103, 1092, 1070, 1045, 1010, 952, 917, 880, 839, 810, 758, 750, 716, 696, 679, 663, 628, 611 cm\(^{-1}\); HRMS (DART) (m/z) \([\text{M+H}]^+\) C\(_{26}\)H\(_{23}\)N\(_2\)O\(_2\)S calcd for 427.1475, found 427.1470.

4. References


5. NMR Spectra

$^1$H NMR of 1g in DMSO-$d_6$

$^{13}$C NMR of 1g in DMSO-$d_6$
$^1$H NMR of 3a in CDCl$_3$

$^{13}$C NMR of 3a in CDCl$_3$
$^1$H NMR of 3b in CDCl$_3$

$^{13}$C NMR of 3b in CDCl$_3$
$^1$H NMR of 3c in CDCl$_3$

$^{13}$C NMR of 3c in CDCl$_3$
\(^1\)H NMR of \(3d\) in CDCl\(_3\)

\(^{13}\)C NMR of \(3d\) in CDCl\(_3\)
$^1$H NMR of 3e in CDCl$_3$

$^{13}$C NMR of 3e in CDCl$_3$
$^1$H NMR of 3f in CDCl$_3$

$^{13}$C NMR of 3f in CDCl$_3$
$^1$H NMR of 3g in DMSO-$d_6$

$^{13}$C NMR of 3g in DMSO-$d_6$
$^1$H NMR of 3h in CDCl$_3$

$^{13}$C NMR of 3h in CDCl$_3$
$^1$H NMR of 3i in CDCl$_3$  

$^{13}$C NMR of 3i in CDCl$_3$
$^1$H NMR of 3j in CDCl$_3$ 

$^{13}$C NMR of 3i in CDCl$_3$
$^1$H NMR of $3k$ in CDCl$_3$

$^{13}$C NMR of $3k$ in CDCl$_3$
$^1$H NMR of 3I in CDCl$_3$

$^{13}$C NMR of 3I in CDCl$_3$
$^1$H NMR of 3m in CDCl$_3$

$^{13}$C NMR of 3m in CDCl$_3$
$^1$H NMR of 3n in CDCl$_3$

$^{13}$C NMR of 3n in CDCl$_3$
$^1$H NMR of $3\sigma$ in CDCl$_3$

![$^1$H NMR spectrum of $3\sigma$ in CDCl$_3$](image1)

$^{13}$C NMR of $3\sigma$ in CDCl$_3$

![$^{13}$C NMR spectrum of $3\sigma$ in CDCl$_3$](image2)
$^1$H NMR of 3p in CDCl$_3$

$^{13}$C NMR of 3p in CDCl$_3$
$^1$H NMR of 3q in CDCl$_3$

$^{13}$C NMR of 3q in CDCl$_3$
$^1$H NMR of 3r in CDCl$_3$

$^{13}$C NMR of 3r in CDCl$_3$
$^1$H NMR of 3s in CDCl$_3$

![H NMR spectrum of 3s in CDCl$_3$]

$^{13}$C NMR of 3s in CDCl$_3$

![C NMR spectrum of 3s in CDCl$_3$]
$^1$H NMR of 3t in CDCl$_3$

$^{13}$C NMR of 3t in CDCl$_3$
$^1$H NMR of 3u in CDCl$_3$

$^{13}$C NMR of 3u in CDCl$_3$
$^1$H NMR of 3v in CDCl$_3$

$^{13}$C NMR of 3v in CDCl$_3$
$^1$H NMR of $3w$ in CDCl$_3$

$^{13}$C NMR of $3w$ in CDCl$_3$
$^1$H NMR of 3x in CDCl$_3$

$^{13}$C NMR of 3x in CDCl$_3$
$^1$H NMR of 4a in CDCl$_3$

$^{13}$C NMR of 4a in CDCl$_3$
$^1$H NMR of 5 in CDCl$_3$

$^{13}$C NMR of 5 in CDCl$_3$
$^1$H NMR of 6 in CDCl$_3$

$^{13}$C NMR of 6 in CDCl$_3$
6. Solid state molecular structures of 3m and 3p