Supporting Information

Rh(II)-Catalyzed Cycloadditions of 1-Tosyl 1,2,3-Triazoles with 2H-Azirines: Switchable Reactivity of Rh-Azavinylcarbene as [2C]- or Aza-[3C]-Synthon

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1. General Information

NMR spectra were recorded on Bruker AV400 instrument. TMS was used as internal standard for $^1$H NMR (0 ppm), and solvent signal was used as reference for $^{13}$C NMR (CDCl$_3$, 77.16 ppm; Acetone-d$_6$, 29.84 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, td = triple doublet, qd = quarter doublet, m = multiplet. Infrared (IR) spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Waters Xevo G2 QTOF MS. Gas chromatography-mass spectra (GC-MS) were recorded on SHIMADZU GC-MS-QP2010SE. Reactions were monitored by Thin Layer Chromatography on plates (GF$_{254}$) supplied by Yantai Chemicals (China) using UV light as visualizing agent and an ethanolic solution of Potassium permanganate, and heat as developing agents. If not specially mentioned, flash column chromatography uses silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China). Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to chromatographically and spectroscopically ($^1$H NMR) homogeneous materials.

2. General Procedures for Preparation of 2H-Azirines

1) Procedure A (for 2a-i and 4a-h)$^1$

![Chemical Reaction Diagram]

To a suspension of NaN$_3$ (452 mg, 7.0 mmol, 2.5 equiv) in acetonitrile (2.2 mL) was added dropwise a solution of iodine monochloride (680 mg, 4.2 mmol, 1.5 equiv) in CH$_2$Cl$_2$ (3.6 mL) at -20°C, and the mixture was stirred at the same temperature. After 30 min, a solution of corresponding alkene (2.8 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (3.6 mL) was added slowly, and the mixture was stirred for 1 h. The reaction was quenched with saturated aqueous Na$_2$S$_2$O$_3$, and the

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organic materials were extracted with Et₂O. The combined extracts were washed with brine and dried over Na₂SO₄. After evaporation of solvents, the resulting crude materials were used immediately for the next step without any further purification.

To a solution of the above obtained compound in Et₂O (8 mL) was added t-BuOK (374 mg, 3.3 mmol, 1.2 equiv) at 0℃, and the mixture was stirred for 1 h at the same temperature. The reaction was quenched by adding ammonium buffer (pH = 9), and the organic materials were extracted with Et₂O. The Et₂O solution was washed with brine and dried over Na₂SO₄. The solvent was removed in vacuo, and the resulting crude materials were purified by flash column chromatography (silica gel; pure hexane) to give the corresponding vinyl azide.

A solution of the obtained vinyl azide in toluene (15 mL) was heated for 1.5 h at 100℃. Evaporation of solvent gave a crude mixture which was purified by flash column chromatography (silica gel, hexanes/EtOAc) to give the 2H-azirines 2a-i/4a-h.

2) Procedure B (for 2j-k)²

![Chemical reaction diagram]

The synthesis of the corresponding vinyl azide was completed by following the procedure described in Procedure A.

A solution of the obtained vinyl azide (4.0 mmol, 1.0 equiv) in dichloromethane (40 mL) was placed in a pressure tube and heated at 150℃ for 0.5 h. Evaporation of the solvent gave a crude mixture which was purified by flash column chromatography (silica gel, hexanes/EtOAc) to give the 2H-azirines 2j-k.

3) Procedure C (for 7a-g)³

![Chemical reaction diagram]

To a mixture of alkene (3.0 mmol, 1.0 equiv), sodium azide (200 mg, 3.0 mmol, 1.0 equiv), and sodium iodide (450 mg, 3.0 mmol, 1.0 equiv) in methanol (4.5 mL) at 0℃ was added a solution

of ceric ammonium nitrate (3.45 g, 6.3 mmol, 2.1 equiv) in methanol (18 mL) dropwise. Upon completion of the reaction as indicated by TLC, saturated aqueous NaHSO₃ (10 mL) was added, and the resulting mixture was extracted with dichloromethane (3×30 mL). The combined organic extracts were washed with distilled water (12 mL) and saturated brine (12 mL) and dried over anhydrous Na₂SO₄, and the solvent was removed under vacuum. The resulting crude materials were used immediately for the next step without any further purification.

To a solution of the above obtained compound in dry Et₂O (10 mL) in an ice bath was added t-BuOK (670 mg, 6.0 mmol, 2.0 equiv). The reaction mixture was stirred for 4h at 0°C and then washed twice with water (25 mL). The organic extract was dried over Na₂SO₄, and the solvent was removed under vacuum. The residue was subjected to chromatography (silica gel, hexanes/EtOAc) to yield the corresponding vinyl azide.

The conversion of above vinyl azides into 8a-g was completed by following the procedure described in Procedure A.

4) Procedure D (for 9a)

To a solution of NH₂OH·HCl (1.08 g, 15.5 mmol, 2.0 equiv) in pyridine (7.5 mL, 93.0 mmol, 12 equiv) was added β-ketoester (1.0 g, 7.75 mmol, 1.0 equiv) dropwise. The solution was stirred for 1 h, and solvent was removed under reduced pressure. The residue was extracted twice with ethyl acetate. The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo to give ketoxime, which was used for the next step without purification.

To the ketoxime was added TsCl (1.77g, 9.3 mmol, 1.2 equiv) and pyridine (7.5 mL, 93.0 mmol, 12 equiv). The solution was stirred for 20 h and quenched with saturated aqueous NH₄Cl. The mixture was extracted three times with DCM. The combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The crude material was purified by column chromatography (hexane/ethyl acetate: 4/1) to yield the ketoximetosylate.

To a solution of ketoximetosylate in DCM (10 mL) was added Et₃N (1.0 mL, 7.75 mmol, 1.0 equiv) dropwise, and the mixture was stirred at room temperature for 3 h. Upon completion of the

reaction as indicated by TLC, the reaction mixture was quenched with water. The aqueous layer was extracted with DCM, and the combined organic layers were washed with water, brine and dried over anhydrous Na₂SO₄. The crude material was purified by column chromatography (hexane/ethyl acetate : 6/1) to yield 2H-azirine 10a.

5) Procedure E (for 9b-d)⁵

To a mixture of β-ketoester (2.2 mmol, 1.0 equiv), NH₂OH·HCl (160 mg, 2.2 mmol, 1.0 equiv) and sodium acetate (210 mg, 2.2 mmol, 1.0 equiv) was added methanol (15 mL) and water (0.7 mL). After stirring at room temperature for 4 h, the solvent was removed in vacuo. The reaction mixture was partitioned between Et₂O and water. After separation, the organic extract was washed with saturated aqueous NaHCO₃, brine and dried over anhydrous Na₂SO₄. The solvents were removed in vacuo, and the resulting crude was used directly in the next reaction.

To an ice cold solution of crude oxime and Et₃N (0.9 mL, 6.6 mmol, 3.0 equiv) in DCM (20 mL) was slowly added TsCl (500 mg, 2.6 mmol, 1.2 equiv), and the mixture was stirred at the same temperature for 2.5 h. The reaction was quenched with water, and the organic material was extracted three times with ethyl acetate. The combined extracts were washed with water, brine, and dried over anhydrous Na₂SO₄. The solvents were removed in vacuo, and the resulting crude materials were used immediately for the next step without further purification.

To an ice cold solution of crude ketoximetosylate in DCM (8 mL) was slowly added DBU (0.4 mL, 2.6 mmol, 1.2 equiv), and the mixture was stirred at the same temperature for 1h. The reaction quenched with water, and the organic materials were extracted with DCM. The combined extracts were washed with brine, and dried over anhydrous Na₂SO₄. After the solvents were removed in vacuo, the residue was purified by column chromatography to give the corresponding 2H-azirines 10b-d.

3. General Procedures for Rh(II)-catalyzed Formal [3+2] and [3+3] Cycloadditions of 1,2,3-Triazoles with 2H-Azirines

1) Procedure A (for 3a-p, 8a-g and 10a-d)
A 10 mL pressure tube, fitted with a rubber septum, was charged with triazole (0.30 mmol, 1.0 equiv), Rh$_2$(esp)$_2$ (3.5 mg, 0.005 mmol, 0.015 equiv) and 2H-azirine (0.60 mmol, 2.0 equiv). The reaction vessel was added freshly distilled 1,2-dichloroethane (0.8 mL), sealed with a teflon screwcap and then placed in an oil bath preheated to 160 °C. The resulting solution was heated at this temperature for 1.0 hour before being cooled to room temperature and concentrated in vacuo. The residue was purified by flash chromatography (SiO$_2$, hexanes/EtOAc) to give the corresponding [3+2] or [3+3] product.

2) Procedure B (for 6a-h)
A 10 mL pressure tube, fitted with a rubber septum, was charged with triazole (0.30 mmol, 1.0 equiv), Rh$_2$(esp)$_2$ (3.5 mg, 0.005 mmol, 0.015 equiv) and 2H-azirine (0.60 mmol, 2.0 equiv). The reaction vessel was added freshly distilled toluene (0.8 mL), sealed with a teflon screwcap and then placed in an oil bath preheated to 160 °C. The resulting solution was heated at this temperature for 1.0 hour before being cooled to room temperature and concentrated in vacuo. The residue was purified by flash chromatography (SiO$_2$, hexanes/EtOAc) to give the corresponding [3+3] product.

3) Procedure C (for 5a-h):
A 10 mL pressure tube, fitted with a rubber septum, was charged with triazole (0.30 mmol, 1.0 equiv), Rh$_2$(esp)$_2$ (3.5 mg, 0.005 mmol, 0.015 equiv) and 2H-azirine (0.60 mmol, 2.0 equiv). The reaction vessel was added freshly distilled 1,2-dichloroethane (0.8 mL) and ClCH$_2$COOH (14.1 mg, 0.15 mmol, 0.5 equiv), sealed with a teflon screwcap and then was placed in an oil bath preheated to 160 °C. The resulting solution was heated at this temperature for 0.5 hour before being cooled to room temperature and concentrated in vacuo. The residue was purified by flash chromatography (SiO$_2$, hexanes/EtOAc) to give the corresponding [3+2] products.
4. Analysis Data of 2H-Azirines

Note: For 2H-azirines 2a-b, 2d-h, 2j, 4a, 4e, 7a and 9a-c which are known compounds\(^6\), the corresponding \(^1\)H-NMR, \(^{13}\)C-NMR and GC-MS data are provided. For 2H-azirines 2c, 2i, 2k, 4b-d, 4f-h, 7b-g and 9d which are new compounds, the corresponding \(^1\)H-NMR, \(^{13}\)C-NMR, and HRMS data are provided.

3-phenyl-2H-azirine (2a): The product was obtained as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) 8 1.79 (s, 2H), 7.54-7.62 (m, 3H), 7.90 (dd, \(J = 7.2\) Hz, 0.4 Hz, 2H); \(^{13}\)C (100 MHz, CDCl\(_3\)) 8 19.8, 125.6, 129.2, 129.7, 133.0, 165.9; GC/MS (EI): m/z 51, 77, 91, 104, 117.

3-(4-bromophenyl)-2H-azirine (2a): The product was obtained as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) 8 1.81 (s, 2H), 7.72 (d, \(J = 8.4\) Hz, 2H), 7.79 (d, \(J = 8.4\) Hz, 2H); \(^{13}\)C (100 MHz, CDCl\(_3\)) 8 20.1, 124.6, 127.9, 131.0, 132.7, 165.4; GC/MS (EI): m/z 89, 116, 155, 157, 195, 197.

3-(2-chlorophenyl)-2H-azirine (2c): The product was obtained as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) 8 1.85 (s, 2H), 7.46 (dt, \(J = 7.2\) Hz, 1.6 Hz, 1H), 7.52 (dt, \(J = 7.2\) Hz, 1.6 Hz, 1H), 7.55 (dd, \(J = 8.0\) Hz, 1.6 Hz, 1H), 7.86 (dd, \(J = 7.2\) Hz, 1.6 Hz, 1H); \(^{13}\)C (100 MHz, CDCl\(_3\)) 8 20.3, 124.1, 127.3, 130.8, 132.4, 133.6, 136.3, 165.0; HRMS m/z calcld for C\(_8\)H\(_6\)ClN [M+H]\(^++\): 152.0267; found: 152.0262.

3-(4-fluorophenyl)-2H-azirine (2d): The product was obtained as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) 8 1.79 (s, 2H), 7.26 (t, \(J = 8.8\) Hz, 2H), 7.92 (dd, \(J = 8.8\) Hz, 5.6 Hz, 2H); \(^{13}\)C (100 MHz, CDCl\(_3\)) 8 19.9, 116.6 (d, \(J = 22.3\) Hz).

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Hz), 122.0 (d, \( J = 3.1 \) Hz), 132.0 (d, \( J = 9.2 \) Hz), 164.8, 165.5 (d, \( J = 253.3 \) Hz); GC/MS (EI): m/z 94, 100, 120, 135.

3-(4-nitrophenyl)-2H-azirine (2e): The product was obtained as a yellow oil. 

\[ \text{O}_2\text{N} \]

\( ^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.94 (s, 2H), 8.12 (d, \( J = 8.8 \) Hz, 2H), 8.43 (d, \( J = 8.8 \) Hz, 2H); \( ^{13}\text{C} \) (100 MHz, CDCl\(_3\)) \( \delta \) 20.9, 124.4, 130.4, 131.0, 150.3, 165.7; GC/MS (EI): m/z 50, 63, 89, 116, 162.

3-(p-tolyl)-2H-azirine (2f): The product was obtained as a colorless oil. 

\[ \text{Me} \]

\( ^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.75 (s, 2H), 2.45 (s, 3H), 7.35 (d, \( J = 8.0 \) Hz, 2H), 7.79 (d, \( J = 8.0 \) Hz, 2H); \( ^{13}\text{C} \) (100 MHz, CDCl\(_3\)) \( \delta \) 19.5, 21.9, 122.9, 129.7, 129.9, 143.8, 165.3; GC/MS (EI): m/z 77, 91, 115, 117, 131.

3-(4-methoxyphenyl)-2H-azirine (2g): The product was obtained as a colorless oil. 

\[ \text{MeO} \]

\( ^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.74 (s, 2H), 3.89 (s, 3H), 7.05 (d, \( J = 8.0 \) Hz, 2H), 7.84 (d, \( J = 8.0 \) Hz, 2H); \( ^{13}\text{C} \) (100 MHz, CDCl\(_3\)) \( \delta \) 19.4, 55.6, 114.7, 118.2, 131.6, 163.4, 164.5; GC/MS (EI): m/z 77, 132, 147.

3-(naphthalen-2-yl)-2H-azirine (2h): The product was obtained as a white solid. 

\[ \text{N} \]

\( ^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.89 (s, 2H), 7.61 (m, 2H), 7.92 (d, \( J = 8.0 \) Hz, 1H), 7.98-8.03 (m, 3H), 8.36 (s, 1H); \( ^{13}\text{C} \) (100 MHz, CDCl\(_3\)) \( \delta \) 20.1, 123.1, 124.5, 127.2, 128.2, 128.6, 129.2, 132.0, 133.0, 135.6, 166.0; GC/MS (EI): m/z 127, 139, 167.

3-(2H-azirin-3-yl)-1-tosyl-1H-indole (2i): The product was obtained as a white solid. 

\[ \text{Ts} \]

\( ^1\text{H} \) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.71 (s, 2H), 2.32 (s, 3H), 7.25 (d, \( J = 8.4 \) Hz, 2H), 7.36 (dt, \( J = 7.6 \) Hz, 0.8 Hz, 1H), 7.42 (dt, \( J = 7.6 \) Hz, 0.8 Hz, 1H), 7.85 (d, \( J = 8.4 \) Hz, 2H), 8.01 (d, \( J = 8.0 \) Hz, 1H), 8.08 (d, \( J = 8.0 \) Hz, 1H), 8.13 (s, 1H); \( ^{13}\text{C} \) (100 MHz, CDCl\(_3\)) \( \delta \) 16.9, 21.6, 109.5, 113.6, 121.4, 124.7, 126.2, 127.2, 127.6, 130.3, 131.2, 134.5, 135.2, 146.0, 158.2; HRMS m/z calcd for C\(_{17}\)H\(_{14}\)N\(_2\)O\(_2\)S [M+H]: 311.0854; found:
3-phenethyl-2H-azirine (2j): The product was obtained as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.39 (s, 2H), 3.04-3.13 (m, 4H), 7.22 (d, $J = 7.6$ Hz, 3H), 7.30 (t, $J = 7.6$ Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 19.4, 30.4, 30.4, 126.6, 128.4, 128.7, 140.1, 169.5; GC/MS (EI): m/z 54, 91, 117, 144, 145.

3-(1-phenylethyl)-2H-azirine (2k): The product was obtained as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.48 (d, $J = 1.2$ Hz, 2H), 1.64 (d, $J = 7.2$ Hz, 3H), 4.16 (q, $J = 7.2$ Hz, 1H), 7.24 (d, $J = 7.2$ Hz, 2H), 7.29 (d, $J = 7.2$ Hz, 1H), 7.36 (t, $J = 7.2$ Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 17.8, 20.3, 39.6, 127.5, 127.7, 129.0, 139.2, 172.0; HRMS m/z calcd for C$_{10}$H$_{11}$N [M+H]$^+$: 146.0970; found: 146.0965.

2,3-diphenyl-2H-azirine (4a): The product was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.33 (s, 1H), 7.15 (dd, $J = 8.0$ Hz, 1.6 Hz, 2H), 7.22-7.31 (m, 3H), 7.53-7.63 (m, 3H), 7.91 (dd, $J = 8.0$ Hz, 1.6 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 34.6, 124.2, 126.2, 127.2, 129.4, 130.0, 133.3, 141.0, 163.6; GC/MS (EI): m/z 89, 165, 193.

2,3-bis(4-fluorophenyl)-2H-azirine (4b): The product was obtained as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.31 (s, 1H), 6.97 (t, $J = 8.8$ Hz, 2H), 7.09 (dd, $J = 8.8$ Hz, 5.6 Hz, 2H), 7.25 (t, $J = 8.8$ Hz, 2H), 7.91 (dd, $J = 8.8$ Hz, 5.6 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 34.0, 115.4 (d, $J = 21.6$ Hz), 117.0 (d, $J = 22.2$ Hz), 120.4 (d, $J = 3.2$ Hz), 127.6 (d, $J = 8.0$ Hz), 132.3 (d, $J = 9.3$ Hz), 136.4 (d, $J = 2.9$ Hz), 162.4 (d, $J = 243.9$ Hz), 162.8, 165.8 (d, $J = 254.3$ Hz); HRMS m/z calcd for C$_{14}$H$_8$F$_2$N [M+H]$^+$: 230.0781; found: 230.0784.

2,3-bis(4-chlorophenyl)-2H-azirine (4c): The product was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 3.30 (s, 1H), 7.05 (d, $J =$
8.8 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) δ 34.2, 122.4, 127.4, 128.7, 130.0, 131.2, 133.2, 139.2, 140.0, 162.8; HRMS m/z calcd for C$_{14}$H$_9$Cl$_2$N [M+H]$^+$: 262.0190; found: 262.0187.

2,3-di-p-tolyl-2H-azirine (4d): The product was obtained as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 2.31 (s, 3H), 2.44 (s, 3H), 3.26 (s, 1H), 7.03 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) δ 21.2, 22.0, 34.2, 121.5, 126.1, 129.1, 130.0, 130.1, 136.8, 138.1, 144.1, 163.3; HRMS m/z calcd for C$_{16}$H$_{15}$N [M+H]$^+$: 222.1283; found: 222.1280.

2-methyl-3-phenyl-2H-azirine (4e): The product was obtained as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.36 (d, J = 4.8 Hz, 3H), 2.30 (q, J = 4.8 Hz, 1H), 7.52-7.60 (m, 3H), 7.86 (dd, J = 8.0 Hz, 2.0 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) δ 19.0, 27.6, 125.8, 129.2, 129.4, 132.8, 172.6; GC/MS (EI): m/z 51, 77, 105, 131.

2-phenethyl-3-phenyl-2H-azirine (4f): The product was obtained as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.89-2.03 (m, 2H), 2.30 (t, J = 4.8 Hz, 1H), 2.72-2.83 (m, 2H), 7.19-7.29 (m, 5H), 7.48-7.57 (m, 3H), 7.71 (d, J = 6.8 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) δ 32.1, 33.8, 35.0, 125.8, 126.0, 128.5, 128.6, 129.1, 129.4, 132.9, 141.8, 171.9; HRMS m/z calcd for C$_{16}$H$_{15}$N [M+H]$^+$: 222.1283; found: 222.1275.

2-pentyl-3-phenyl-2H-azirine (4g): The product was obtained as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 0.89 (t, J = 7.2 Hz, 3H), 1.26-1.48 (m, 6H), 1.59-1.64 (m, 2H), 2.27 (t, J = 4.8 Hz, 1H), 7.52-7.59 (m, 3H), 7.86 (dd, J = 8.0 Hz, 2.4 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) δ 14.2, 22.7, 27.4, 31.8, 32.7, 33.2, 126.2, 129.2, 129.3, 132.8, 172.2; HRMS m/z calcd for C$_{17}$H$_{17}$N [M+H]$^+$: 188.1439; found: 188.1434.
The product was obtained as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.18 (d, \(J = 7.2\) Hz, 3H), 1.34 (d, \(J = 7.2\) Hz, 3H), 2.45 (d, \(J = 5.6\) Hz, 1H), 2.51 (d, \(J = 4.4\) Hz, 1H), 2.74 (m, 1H), 3.07 (m, 1H), 7.21-7.26 (m, 2H), 7.33-7.35 (m, 8H), 7.45-7.59 (m, 6H), 7.69 (dd, \(J = 6.8\) Hz, 1.6 Hz, 2H), 7.83 (dd, \(J = 8.0\) Hz, 1.6 Hz, 2H); \(^{13}\)C (100 MHz, CDCl\(_3\)) \(\delta\) 18.7, 19.4, 38.6, 38.8, 42.1, 43.3, 125.8, 126.2, 126.5, 127.5, 127.6, 128.6, 128.7, 129.1, 129.2, 129.4, 129.5, 132.9, 132.9, 144.9, 145.6, 171.3, 171.8; HRMS m/z calcd for C\(_{16}\)H\(_{15}\)N\([M+H]\)^+: 222.1283; found: 222.1285.

The product was obtained as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.52 (s, 3H), 2.89 (s, 1H), 7.05 (d, \(J = 7.2\) Hz, 2H), 7.23-7.31 (m, 3H); \(^{13}\)C (100 MHz, CDCl\(_3\)) \(\delta\) 13.0, 33.5, 125.7, 126.9, 128.4, 141.3, 164.6; GC/MS (EI): m/z 63, 89, 131.

The product was obtained as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.51(s, 3H), 2.91 (s, 1H), 7.15 (d, \(J = 8.0\) Hz, 2H), 7.53 (d, \(J = 8.0\) Hz, 2H); \(^{13}\)C (100 MHz, CDCl\(_3\)) \(\delta\) 12.6, 32.9, 124.3 (q, \(J = 270.1\) Hz), 125.2 (q, \(J = 3.8\) Hz), 125.8, 128.9 (q, \(J = 32.2\) Hz), 145.6, 163.8; HRMS m/z calcd for C\(_{10}\)H\(_{8}\)F\(_{3}\)N\([M+H]\)^+: 200.0687; found: 200.0686.

The product was obtained as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.52 (s, 3H), 3.27 (s, 1H), 6.73 (dd, \(J = 6.8\) Hz, 2.4 Hz, 1H), 7.12-7.19 (m, 2H), 7.32 (dd, \(J = 6.8\) Hz, 2.4 Hz, 1H); \(^{13}\)C (100 MHz, CDCl\(_3\)) \(\delta\) 13.2, 30.3, 125.7, 126.7, 127.7, 129.5, 133.7, 138.4, 165.0; HRMS m/z calcd for C\(_{9}\)H\(_{8}\)Cl\(_{2}\)N\([M+H]\)^+: 166.0424; found: 166.0419.

The product was obtained as a colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.32 (s, 3H), 2.51 (s, 3H), 2.86
(s, 1H), 6.95 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) δ 13.0, 21.2, 33.4, 125.6, 129.1, 136.6, 138.3, 164.9; HRMS m/z calcd for C$_{10}$H$_{11}$N [M+H]$^+$: 146.0970; found: 146.0965.

3-methyl-2-(naphthalen-2-yl)-2$H$-azirine (7e): The product was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) δ 2.57 (s, 3H), 3.05 (s, 1H), 7.16 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 7.44 (m, 2H), 7.52 (s, 1H), 7.77 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.0 Hz, 1H); $^{13}$C (100 MHz, CDCl$_3$) δ 13.1, 33.8, 123.9, 124.4, 125.6, 126.4, 127.6, 128.1, 132.8, 133.4, 138.9, 164.8; HRMS m/z calcd for C$_{13}$H$_{15}$N [M+H]$^+$: 182.0970; found: 182.0970.

3-phenethyl-2-phenyl-2$H$-azirine (7f): The product was obtained as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 2.89 (s, 1H), 3.09-3.16 (m, 4H), 6.98 (d, J = 6.4 Hz, 2H), 7.00-7.32 (m, 8H); $^{13}$C (100 MHz, CDCl$_3$) δ 29.1, 30.6, 34.0, 125.7, 126.7, 126.9, 128.3, 128.5, 128.8, 140.0, 141.4, 167.3; HRMS m/z calcd for C$_{16}$H$_{15}$N [M+H]$^+$: 222.1283; found: 222.1279.

3-pentyl-2-phenyl-2$H$-azirine (7g): The product was obtained as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 0.90 (t, J = 7.2 Hz, 3H), 1.32-1.44 (m, 4H), 1.73-1.79 (m, 2H), 2.81 (t, J = 7.2 Hz, 2H), 2.88 (s, 1H), 7.05 (d, J = 7.2 Hz, 2H), 7.22 (t, J = 7.2 Hz, 1H), 7.28 (t, J = 7.2 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) δ 14.0, 22.4, 24.2, 27.1, 31.5, 33.5, 125.6, 126.8, 128.3, 141.7, 167.6; HRMS m/z calcd for C$_{13}$H$_{17}$N [M+H]$^+$: 188.1439; found: 188.1432.

Ethyl 3-methyl-2$H$-azirine-2-carboxylate (9a): The product was obtained as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 1.28 (t, J = 7.2 Hz, 3H), 2.44 (s, 1H), 2.54 (s, 3H), 4.19 (m, 2H); $^{13}$C (100 MHz, CDCl$_3$) δ 12.7, 14.3, 28.9, 61.2, 159.3, 172.1; GC/MS (EI): m/z 54, 67, 81, 106, 108.
Ethyl 3-phenyl-2H-azirine-2-carboxylate (9b): The product was obtained as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.27 (dt, J = 7.2 Hz, 0.8 Hz, 3H), 2.84 (d, J = 0.8 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 7.56-7.65 (m, 3H), 7.89 (d, J = 8.0 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) 14.4, 29.8, 61.4, 122.5, 129.5, 130.6, 134.0, 158.7, 171.8; GC/MS (EI): m/z 77, 105, 133, 161.

Ethyl 3-(4-methoxyphenyl)-2H-azirine-2-carboxylate (9c): The product was obtained as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.27 (t, J = 7.2 Hz, 3H), 2.79 (s, 1H), 3.90 (s, 3H), 4.20 (q, J = 7.2 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 14.4, 29.6, 55.8, 61.3, 114.7, 115.0, 132.7, 157.3, 164.2, 172.2; GC/MS (EI): m/z 107, 146, 219.

Ethyl 3-(4-fluorophenyl)-2H-azirine-2-carboxylate (9d): The product was obtained as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.28 (t, J = 7.2 Hz, 3H), 2.85 (s, 1H), 4.22 (qd, J = 7.2 Hz, 2.0 Hz, 2H), 7.26-7.30 (m, 2H), 7.91 (dd, J = 7.6 Hz, 5.6 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 14.4, 29.9, 61.5, 117.1 (d, J = 22.4 Hz), 118.9 (d, J = 3.2 Hz), 133.0 (d, J = 9.5 Hz.), 157.8, 166.2 (d, J = 255.4 Hz), 171.7; HRMS m/z calcd for C$_{11}$H$_{10}$FNO$_2$ [M+H]$^+$: 208.0774; found: 208.0777.

5. Analysis Data of [3+2]/[3+3] Cycloaddition Products

$N$-(2,5-diphenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3a): The product was obtained as a yellow solid. Yield: 81%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.35 (s, 3H), 6.15 (s, 1H), 6.45 (d, J = 2.8 Hz, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 7.2 Hz, 2H), 7.22-7.29 (m, 3H), 7.36 (t, J = 7.6 Hz, 2H), 7.43 (d, J = 7.6 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H), 8.29 (s, 1H); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 21.6, 106.2, 118.1, 123.9, 126.5, 127.0, 127.4, 127.6, 129.0, 129.1, 129.4, 130.8, 130.9, 131.9, 136.3, 143.6; IR $\nu_{max}$ (film): 2336.01, 1717.38, 1699.23, 1157.64, 761.66, 758.50, 711.76, 700.54, 691.14 cm$^{-1}$; HRMS m/z calcd for C$_{25}$H$_{20}$N$_2$O$_2$S [M+H]$^+$: 389.1324; found: 389.1317.
N-(5-(4-bromophenyl)-2-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3b): The product was obtained as a yellow solid. Yield: 65%;

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 2.36 (s, 3H), 6.32 (d, $J = 2.4$ Hz, 1H), 7.20-7.24 (m, 3H), 7.28 (t, $J = 7.2$ Hz, 2H), 7.50-7.62 (m, 8H), 8.11 (s, 1H), 10.49 (s, 1H); $^{13}$C (100 MHz, Acetone-$d_6$) δ 21.4, 108.2, 119.2, 120.0, 126.5, 127.5, 127.7, 128.1, 129.0, 130.0, 130.1, 130.3, 132.1, 132.5, 132.5, 138.8, 143.8; IR $\nu_{\text{max}}$ (film): 1490.40, 1303.64, 1156.99, 1092.95, 697.79, 689.94, 685.75, 681.14, 679.92 cm$^{-1}$; HRMS m/z calcd for C$_{23}$H$_{19}$BrN$_2$O$_2$S [M+H]$^+$: 467.0429; found: 467.0432.

N-(5-(2-chlorophenyl)-2-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3c): The product was obtained as a yellow solid. Yield: 57%; $^1$H NMR (400 MHz, Acetone-$d_6$) δ 2.38 (s, 3H), 6.27 (d, $J = 3.2$ Hz, 1H), 7.22-7.36 (m, 7H), 7.46 (dd, $J = 8.0$ Hz, $J = 1.2$ Hz, 1H), 7.63 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 7.66-7.71 (m, 4H), 7.99 (s, 1H), 10.40 (s, 1H); $^{13}$C (100 MHz, Acetone-$d_6$) δ 21.4, 112.0, 118.4, 127.5, 127.6, 127.7, 128.0, 128.3, 128.7, 129.0, 130.0, 130.1, 130.3, 131.3, 131.6, 132.0, 132.2, 139.0, 143.8; IR $\nu_{\text{max}}$ (film): 1699.86, 1303.67, 1158.57, 1092.54, 764.78, 756.38, 758.43, 688.20, 681.53 cm$^{-1}$; HRMS m/z calcd for C$_{23}$H$_{19}$ClN$_2$O$_2$S [M+H]$^+$: 423.0934; found: 423.0921.

N-(5-(4-fluorophenyl)-2-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3d): The product was obtained as a yellow solid. Yield: 79%; $^1$H NMR (400 MHz, Acetone-$d_6$) δ 2.37 (s, 3H), 6.23 (d, $J = 2.4$ Hz, 1H), 7.12 (t, $J = 8.8$ Hz, 2H), 7.19-7.30 (m, 5H), 7.55 (d, $J = 7.6$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 7.66 (dd, $J = 6.0$ Hz, $J = 8.8$ Hz, 2H), 8.09 (s, 1H), 10.41 (s, 1H); $^{13}$C (100 MHz, Acetone-$d_6$) δ 21.4, 107.6, 116.3 (d, $J = 21.7$ Hz), 119.1, 126.7 (d, $J = 7.9$ Hz), 127.4, 127.7, 128.2, 129.0, 129.8, 130.0 (d, $J = 3.2$ Hz), 130.0, 130.5, 132.3, 138.9, 143.8, 162.3 (d, $J = 242.2$ Hz); IR $\nu_{\text{max}}$ (film): 2988.93, 2970.72, 1498.68, 1158.03, 1090.63, 705.45, 694.03, 690.66, 679.43, 677.81 cm$^{-1}$; HRMS m/z calcd for C$_{23}$H$_{19}$FN$_2$O$_2$S [M+H]$^+$: 407.1230; found: 407.1227.

4-methyl-N-(5-(4-nitrophenyl)-2-phenyl-1H-pyrrol-3-yl)benzenesulfonamide (3e): The product was obtained as an orange solid. Yield: 64%;
**4-methyl-N-(2-phenyl-5-(p-tolyl)-1H-pyrrol-3-yl)benzenesulfonamide (3f):** The product was obtained as a yellow solid. Yield: 74%; $^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 2.30 (s, 3H), 2.37 (s, 3H), 6.19 (s, 1H), 7.16 (d, $J = 8.0$ Hz, 2H), 7.19-7.30 (m, 5H), 7.51 (d, $J = 8.0$ Hz, 2H), 7.57 (d, $J = 7.6$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 8.05 (s, 1H), 10.34 (s, 1H); $^{13}$C (100 MHz, Acetone-$d_6$) $\delta$ 21.1, 21.4, 107.0, 118.9, 124.7, 127.2, 127.6, 128.2, 128.9, 129.3, 130.0, 130.1, 131.5, 132.4, 136.6, 138.9, 143.7; IR $\nu_{max}$ (film): 1576.10, 1559.66, 1157.06, 948.69, 943.92, 692.71, 688.11, 679.16, 675.48 cm$^{-1}$; HRMS m/z calcd for C$_{24}$H$_{22}$N$_2$O$_2$S [M+H]$^+$: 419.1429; found: 419.1421.

**N-(5-(4-methoxyphenyl)-2-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3g):** The product was obtained as a yellow solid. Yield: 70%; $^1$H NMR (400 MHz, Acetone-$d_6$) $\delta$ 2.37 (s, 3H), 3.79 (s, 3H), 6.11 (d, $J = 2.8$ Hz, 1H), 6.92 (d, $J = 8.8$ Hz, 2H), 7.18 (t, $J = 7.2$ Hz, 1H), 7.23-7.29 (m, 4H), 7.56 (t, $J = 8.8$Hz, 4H), 7.62 (d, $J = 8.0$ Hz, 2H), 8.05 (s, 1H), 10.28 (s, 1H); $^{13}$C (100 MHz, Acetone-$d_6$) $\delta$ 21.4, 55.6, 106.4, 115.0, 118.9, 126.2, 127.1, 127.5, 128.2, 128.8, 128.9, 130.0, 131.4, 131.5, 132.5, 139.0, 143.7, 159.4; IR $\nu_{max}$ (film): 2918.62, 2854.24, 1499.22, 1457.41, 1447.90, 1250.58, 1180.40, 1159.66, 948.69, 943.92, 692.71, 688.11, 679.16, 675.48 cm$^{-1}$; HRMS m/z calcd for C$_{24}$H$_{22}$N$_2$O$_3$S [M+H]$^+$: 403.1480; found: 403.1474.

**4-methyl-N-(5-(naphthalen-2-yl)-2-phenyl-1H-pyrrol-3-yl)benzenesulfonamide (3h):** The product was obtained as a yellow solid. Yield: 85%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.37 (s, 3H), 6.15 (s, 1H), 6.61 (d, $J = 2.8$ Hz, 1H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.22 (d, $J = 7.2$ Hz, 2H), 7.30 (m, 3H), 7.46 (m, 2H), 7.60 (m,
4-methyl-N-(2-phenyl-5-(1-tosyl-1H-indol-2-yl)-1H-pyrrol-3-yl)benzenesulfonamide (3i): The product was obtained as a yellow solid. Yield: 72%; \(^1H\) NMR (400 MHz, Acetone-\(d_6\)) \(\delta\) 2.30 (s, 3H), 2.41 (s, 3H), 6.14 (d, \(J = 2.4\) Hz, 1H), 7.24 (t, \(J = 7.2\) Hz, 1H), 7.30-7.36 (m, 7H), 7.41 (t, \(J = 7.6\) Hz, 1H), 7.55 (d, \(J = 8.0\) Hz, 1H), 7.69-7.73 (m, 4H), 7.86 (d, \(J = 8.0\) Hz, 2H), 8.05 (d, \(J = 8.4\) Hz, 1H), 8.12 (d, \(J = 6.4\) Hz, 2H), 10.55 (s, 1H); \(^13C\) (100 MHz, Acetone-\(d_6\)) \(\delta\) 21.4, 21.5, 109.2, 114.7, 116.5, 118.6, 121.4, 122.3, 123.6, 124.6, 125.9, 127.5, 127.6, 127.7, 128.5, 129.1, 129.4, 129.5, 130.1, 130.9, 132.2, 135.7, 136.2, 139.0, 144.0, 146.4; IR \(\nu_{\text{max}}\) (film): 1700.58, 1560.11, 1158.53, 724.72, 713.02, 688.62 cm\(^{-1}\); HRMS m/z calcd for \(C_{17}H_{23}O_2S\) [M+H]\(^+\): 439.1480; found: 439.1476.

4-methyl-N-(5-phenethyl-2-phenyl-1H-pyrrol-3-yl)benzenesulfonamide (3j): The product was obtained as a yellow solid. Yield: 65%; \(^1H\) NMR (400 MHz, Acetone-\(d_6\)) \(\delta\) 2.38 (s, 3H), 2.86 (m, 4H), 5.56 (d, \(J = 2.8\) Hz, 1H), 7.14 (t, \(J = 7.2\) Hz, 1H), 7.17-7.30 (m, 9H), 7.52 (d, \(J = 7.6\) Hz, 2H), 7.58 (d, \(J = 8.4\) Hz, 2H), 7.86 (s, 1H), 10.00 (s, 1H); \(^13C\) (100 MHz, Acetone-\(d_6\)) \(\delta\) 21.4, 30.3, 36.7, 107.3, 117.2, 126.6, 126.7, 126.8, 128.2, 128.9, 129.1, 129.2, 129.9, 131.8, 133.0, 139.1, 142.6, 143.5; IR \(\nu_{\text{max}}\) (film): 1700.55, 1559.86, 1160.26, 718.06, 681.30, 677.37 cm\(^{-1}\); HRMS m/z calcd for \(C_{25}H_{32}N_2O_2S\) [M+H]\(^+\): 582.1521; found: 582.1509.

4-methyl-N-(2-phenyl-5-(1-phenylethyl-1H-pyrrol-3-yl)benzenesulfonamide (3k): The product was obtained as a yellow solid. Yield: 72%; \(^1H\) NMR (400 MHz, Acetone-\(d_6\)) \(\delta\) 1.47 (d, \(J = 7.2\) Hz, 3H), 2.38 (s, 3H), 4.07 (q, \(J = 6.8\) Hz, 1H), 5.49 (dd, \(J = 3.2\) Hz, \(J= 0.8\) Hz, 1H), 7.10-7.36 (m, 10H), 7.55-7.61 (m, 4H), 7.86 (s, 1H), 9.97 (s, 1H); \(^13C\) (100 MHz, Acetone-\(d_6\)) \(\delta\) 21.4, 22.0, 39.3, 107.0, 117.1, 126.7, 126.9, 127.5, 128.1, 128.3, 128.9, 129.1, 129.9, 132.9, 136.0, 138.9, 143.7, 146.7; IR \(\nu_{\text{max}}\) (film): 1700.39,
4-methyl-N-(5-phenyl-2-(p-tolyl)-1H-pyrrol-3-yl)benzenesulfonamide (3l): The product was obtained as a yellow solid. Yield: 71%; ¹H NMR (400 MHz, Acetone-d₆) δ 2.32 (s, 3H), 2.37 (s, 3H), 6.25 (d, J = 2.8 Hz, 1H), 7.10 (d, J = 8.0 Hz, 2H), 7.18 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 4H), 7.99 (s, 1H), 10.36 (s, 1H); ¹³C (100 MHz, Acetone-d₆) δ 21.2, 21.4, 107.5, 118.7, 124.7, 127.6, 128.2, 129.5, 129.9, 130.0, 131.0, 133.4, 137.0, 139.0, 143.7; IR ν max (film): 3360.51, 1501.98, 1317.32, 1158.46, 1090.58, 679.31, 676.83 cm⁻¹; HRMS m/z calcd for C₂₅H₂₄N₂O₂S [M+H]⁺: 417.1637; found: 417.1620.

N-(2-(4-(tert-butyl)phenyl)-5-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3m): The product was obtained as a yellow solid. Yield: 70%; ¹H NMR (400 MHz, Acetone-d₆) δ 1.33 (s, 9H), 2.37 (s, 3H), 6.28 (d, J = 2.8 Hz, 1H), 7.17-7.23 (m, 3H), 7.32-7.36 (m, 4H), 7.48 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 8.03 (s, 1H), 10.33 (s, 1H); ¹³C (100 MHz, Acetone-d₆) δ 21.5, 31.6, 35.0, 107.5, 118.7, 124.6, 125.7, 126.9, 127.5, 128.2, 129.4, 129.5, 129.9, 130.0, 131.0, 133.4, 138.8, 143.6, 150.2; IR ν max (film): 2958.45, 1501.52, 1320.22, 1303.27, 1157.78, 1092.67, 760.19, 694.28, 686.61, 676.82 cm⁻¹; HRMS m/z calcd for C₂₇H₂₈N₂O₂S [M+H]⁺: 445.1950; found: 445.1938.

N-(2-(4-methoxyphenyl)-5-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3n): The product was obtained as a yellow solid. Yield: 72%; ¹H NMR (400 MHz, Acetone-d₆) δ 2.36 (s, 3H), 3.80 (s, 3H), 6.22 (d, J = 2.8 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 7.16 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.59-7.62 (m, 4H), 7.99 (s, 1H), 10.31 (s, 1H); ¹³C (100 MHz, Acetone-d₆) δ 21.4, 55.5, 107.4, 114.4, 118.1, 124.5, 124.9, 126.8, 128.2, 129.1, 129.5, 130.0, 130.6, 133.4, 139.0, 143.7, 159.6; IR ν max (film): 3362.88, 1700.19, 1606.34, 1501.78, 1303.13, 1249.40, 1156.59, 1091.52, 762.86, 760.19, 756.37, 707.89 cm⁻¹; HRMS m/z
calcd for C_{23}H_{22}N_{2}O_{3}S [M+H]^+; 419.1429; found: 419.1421.

**N-(2-(4-bromophenyl)-5-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3o):** The product was obtained as a yellow solid. Yield: 67%; 

$^1$H NMR (400 MHz, Acetone-$d_6$) δ 2.39 (s, 3H), 6.27 (t, $J = 2.8$ Hz, 1H), 7.20-7.25 (m, 3H), 7.36 (t, $J = 7.6$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 7.53 (dd, $J = 8.8$ Hz, $J = 2.0$ Hz, 2H), 7.59 (d, $J = 8.4$ Hz, 2H), 7.62 (d, $J = 8.0$ Hz, 2H), 8.18 (s, 1H), 10.54 (s, 1H); $^{13}$C (100 MHz, Acetone-$d_6$) δ 21.5, 108.1, 119.5, 120.6, 124.8, 127.3, 128.2, 128.6, 129.4, 129.6, 130.0, 131.5, 131.9, 131.9, 133.1, 138.8, 143.9; IR $\nu_{\text{max}}$ (film): 3359.79, 1699.99, 1489.63, 1303.83, 1156.74, 1091.64, 761.86, 759.73, 677.42, 675.98 cm$^{-1}$; HRMS m/z calcd for C_{23}H_{19}BrN_{2}O_{2}S [M+H]^+; 467.0429; found: 467.0420.

**N-(2-(4-fluorophenyl)-5-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (3p):** The product was obtained as a yellow solid. Yield: 70%; $^1$H NMR (400 MHz, Acetone-$d_6$) δ 2.36 (s, 3H), 6.24 (d, $J = 2.8$ Hz, 1H), 7.05 (t, $J = 8.8$ Hz, 2H), 7.18 (t, $J = 7.2$ Hz, 1H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.33 (t, $J = 8.0$ Hz, 2H), 7.58-7.61 (m, 6H), 8.08 (s, 1H), 10.45 (s, 1H); $^{13}$C (100 MHz, Acetone-$d_6$) δ 21.4, 107.6, 115.6 (d, $J = 21.4$ Hz), 118.8, 124.7, 127.1, 128.1, 128.7 (d, $J = 3.2$ Hz) 129.1, 129.5, 129.7 (d, $J = 7.9$ Hz), 130.0, 131.3, 133.2, 138.8, 143.8, 162.5 (d, $J = 243.0$ Hz); IR $\nu_{\text{max}}$ (film): 3369.50, 1700.09, 1500.76, 1304.10, 1227.48, 1159.50, 1092.02, 693.66, 687.11, 680.68, 677.92 cm$^{-1}$; HRMS m/z calcd for C_{23}H_{19}FN_{2}O_{2}S [M+H]^+; 407.1230; found: 407.1217.

**4-methyl-N-(2,4,5-triphenyl-1H-pyrrol-3-yl)benzenesulfonamide (5a):** The product was obtained as a yellow solid. Yield: 86%; $^1$H NMR (400 MHz, CDCl$_3$) δ 2.26 (s, 3H), 6.27 (s, 1H), 6.81 (d, $J = 8.0$ Hz, 2H), 6.89 (d, $J = 6.8$ Hz, 2H), 7.11-7.22 (m, 9H), 7.26 (t, $J = 6.8$ Hz, 2H), 7.35 (t, $J = 7.6$ Hz, 2H), 7.68 (d, $J = 7.6$ Hz, 2H), 8.29 (s, 1H); $^{13}$C (100 MHz, CDCl$_3$) δ 21.4, 115.5, 121.9, 126.3, 126.4, 126.7, 126.8, 127.0, 127.1, 127.7, 128.3, 128.6, 128.7, 129.0, 129.4, 129.9, 131.4, 131.9, 132.2, 133.2, 142.6; IR $\nu_{\text{max}}$ (film): 1700.53, 1322.43, 1159.46, 1091.59, 700.02, 695.34, 682.59, 678.92, 675.82 cm$^{-1}$; HRMS m/z calcd for C_{29}H_{24}N_{2}O_{3}S [M+H]^+; 465.1637; found: 465.1626.
2,3,5-triphenyl-1-tosyl-1,2-dihydropyrazine (6a): The product was obtained as a yellow solid. Yield: 82%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.24 (s, 3H), 6.39 (s, 1H), 6.84 (s, 1H), 6.97 (d, $J$ = 8.4 Hz, 2H), 7.23-7.44 (m, 11H), 7.51 (d, $J$ = 8.0 Hz, 2H), 7.74 (m, 4H); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 21.6, 53.8, 108.7, 125.2, 126.3, 127.4, 127.7, 128.1, 128.6, 128.7, 128.8, 128.9, 130.9, 135.1, 136.0, 136.4, 137.0, 144.4, 152.5; IR $\nu_{max}$ (film): 2986.03, 2972.19, 2365.34, 1700.08, 1066.74, 718.95, 688.45, 686.25, 683.68 cm$^{-1}$; HRMS m/z calcd for C$_{29}$H$_{24}$N$_2$O$_2$S [M+H]$^+$: 465.1637; found: 465.1624.

$N$-(4,5-bis(4-fluorophenyl)-2-phenyl-1H-pyrrol-3-yl)-4-methylbenzenesulfonamide (5b): The product was obtained as a yellow solid. Yield: 74%; $^1$H NMR (400 MHz, Acetone-d$_6$) $\delta$ 2.27 (s, 3H), 6.85-6.90 (m, 4H), 6.99-7.04 (m, 2H), 7.07-7.11 (m, 2H), 7.19-7.23 (m, 3H), 7.28 (d, $J$ = 5.6 Hz, 2H), 7.29 (d, $J$ = 7.2 Hz, 2H), 7.79 (d, $J$ = 7.6 Hz, 2H), 8.12 (s, 1H), 10.51 (s, 1H); $^{13}$C (100 MHz, Acetone-d$_6$) $\delta$ 21.3, 115.4 (d, $J$ = 21.2 Hz), 115.9 (d, $J$ = 21.6 Hz), 116.4, 122.5, 127.3, 127.5, 127.7, 127.9, 129.6, 129.9 (d, $J$ = 3.3 Hz), 130.3 (d, $J$ = 8.0 Hz), 131.3 (d, $J$ = 3.2 Hz), 131.4, 132.7, 132.9 (d, $J$ = 8.0 Hz), 139.6, 142.9, 162.4 (d, $J$ = 241.4 Hz), 162.4 (d, $J$ = 243.0 Hz); IR $\nu_{max}$ (film): 2984.44, 1495.49, 1221.43, 1159.91, 1065.64, 693.40, 683.98, 680.67, 679.37 cm$^{-1}$; HRMS m/z calcd for C$_{29}$H$_{22}$F$_2$N$_2$O$_2$S [M+H]$^+$: 501.1448; found: 501.1439.

2,3-bis(4-fluorophenyl)-5-phenyl-1-tosyl-1,2-dihydropyrazine (6b): The product was obtained as a yellow solid. Yield: 80%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.27 (s, 3H), 6.30 (s, 1H), 6.83 (d, $J$ = 1.2 Hz, 1H), 6.95 (t, $J$ = 8.4 Hz, 2H), 7.01 (d, $J$ = 8.4 Hz, 2H), 7.06 (t, $J$ = 8.4 Hz, 2H), 7.29-7.40 (m, 5H), 7.50 (d, $J$ = 8.4 Hz, 2H), 7.71-7.77 (m, 4H); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 21.6, 53.0, 108.4, 115.7 (d, $J$ = 4.2 Hz), 116.0 (d, $J$ = 4.0 Hz), 125.1, 126.2, 128.2, 128.7, 129.4 (d, $J$ = 8.6 Hz), 129.5 (d, $J$ = 8.4 Hz), 129.7, 130.5 (d, $J$ = 3.1 Hz), 132.4 (d, $J$ = 3.2 Hz), 135.7, 135.8, 136.9, 144.6, 151.0, 163.1 (d, $J$ = 246.6 Hz), 164.5 (d, $J$ = 251.3 Hz); IR $\nu_{max}$ (film): 2968.33, 2962.30, 2926.02, 1601.16, 1508.48, 1357.22, 1230.01, 1168.96, 1158.00, 1089.22, 1010.04, 757.04, 681.80, 675.48 cm$^{-1}$; HRMS m/z calcd for C$_{29}$H$_{22}$F$_2$N$_2$O$_2$S [M+H]$^+$: 501.1448; found: 501.1443.
N-(4,5-bis(4-chlorophenyl)-2-phenyl-1H-pyrrol-3-yl)-4-methylbenzene sulfonamide (5c): The product was obtained as a yellow solid. Yield: 69%; \(^1\)H NMR (400 MHz, Acetone-\(d_6\)) \(\delta\) 2.30 (s, 3H), 6.89 (d, \(J = 8.0\) Hz, 2H), 7.08 (d, \(J = 8.4\) Hz, 2H), 7.13 (d, \(J = 8.4\) Hz, 2H), 7.20 (d, \(J = 8.4\) Hz, 2H), 7.23-7.33 (m, 7H), 7.81 (d, \(J = 7.6\) Hz, 2H), 8.18 (s, 1H), 10.60 (s, 1H); \(^{13}\)C (100 MHz, Acetone-\(d_6\)) \(\delta\) 21.4, 116.5, 122.7, 127.4, 127.5, 127.6, 128.7, 128.9, 129.0, 129.2, 129.6, 129.9, 132.1, 132.2, 132.5, 132.6, 132.7, 133.8, 139.5, 143.1; IR \(\nu_{\text{max}}\) (film): 3332.27, 1502.20, 1489.77, 1319.09, 1158.93, 1091.06, 690.33, 677.49 cm\(^{-1}\); HRMS m/z calcd for \(\text{C}_{29}\text{H}_{22}\text{Cl}_2\text{N}_2\text{O}_2\text{S}\) [M+H]+: 533.0857; found: 533.0853.

2,3-bis(4-chlorophenyl)-5-phenyl-1-tosyl-1,2-dihydropyrazine (6c): The product was obtained as a yellow solid. Yield: 85%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.26 (s, 3H), 6.28 (s, 1H), 6.84 (d, \(J = 1.2\) Hz, 1H), 7.01 (d, \(J = 8.0\) Hz, 2H), 7.20-7.38 (m, 9H), 7.49 (d, \(J = 8.4\) Hz, 2H), 7.66-7.71 (m, 4H); \(^{13}\)C (100 MHz, CDCl\(_3\)) \(\delta\) 21.6, 52.9, 108.8, 125.1, 126.2, 128.3, 128.5, 128.7, 129.0, 129.1, 129.8, 133.3, 134.5, 135.1, 135.5, 135.8, 136.9, 137.3, 144.7, 150.7; IR \(\nu_{\text{max}}\) (film): 1363.25, 1359.63, 1167.75, 1090.12, 1010.00, 755.02, 681.29, 676.36 cm\(^{-1}\); HRMS m/z calcd for \(\text{C}_{29}\text{H}_{22}\text{Cl}_2\text{N}_2\text{O}_2\text{S}\) [M+H]+: 533.0857; found: 533.0848.

4-methyl-N-(2-phenyl-4,5-di-p-tolyl-1H-pyrrol-3-yl)benzenesulfonamide (5d): The product was obtained as a yellow solid. Yield: 70%; \(^1\)H NMR (400 MHz, Acetone-\(d_6\)) \(\delta\) 2.25 (s, 3H), 2.27 (s, 3H), 2.31 (s, 3H), 6.85 (d, \(J = 8.0\) Hz, 2H), 6.91 (d, \(J = 8.0\) Hz, 2H), 6.96 (d, \(J = 8.0\) Hz, 2H), 7.01 (d, \(J = 8.0\) Hz, 2H), 7.16-7.21 (m, 5H), 7.28 (t, \(J = 7.6\) Hz, 2H), 7.82 (d, \(J = 8.0\) Hz, 2H), 8.00 (s, 1H), 10.33 (s, 1H); \(^{13}\)C (100 MHz, Acetone-\(d_6\)) \(\delta\) 21.1, 21.3, 21.4, 116.5, 123.1, 127.0, 127.4, 127.7, 128.2, 128.7, 128.9, 129.3, 129.5, 129.6, 130.9, 131.0, 131.0, 132.3, 133.0, 135.9, 136.7, 139.7, 142.7; IR \(\nu_{\text{max}}\) (film): 3335.93, 1523.12, 1496.48, 1325.61, 1303.69, 1157.93, 1091.95, 701.50, 687.35, 683.67, 676.91 cm\(^{-1}\); HRMS m/z calcd for \(\text{C}_{31}\text{H}_{28}\text{N}_2\text{O}_2\text{S}\) [M+H]+: 493.1950; found: 493.1945.
5-phenyl-2,3-di-p-tolyl-1-tosyl-1,2-dihydropyrazine (6d): The product was obtained as a yellow solid. Yield: 84%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.26 (s, 3H), 2.27 (s, 3H), 2.38 (s, 3H), 6.34 (s, 1H), 6.80 (d, \(J = 0.8\) Hz, 1H), 6.99 (d, \(J = 8.0\) Hz, 2H), 7.04 (d, \(J = 8.0\) Hz, 2H), 7.16 (d, \(J = 8.0\) Hz, 2H), 7.23 (d, \(J = 8.0\) Hz, 2H), 7.29 (d, \(J = 7.2\) Hz, 1H), 7.35 (t, \(J = 7.2\) Hz, 2H), 7.50 (d, \(J = 8.0\) Hz, 2H), 7.65 (d, \(J = 8.0\) Hz, 2H), 7.73 (d, \(J = 8.0\) Hz, 2H); \(^{13}\)C (100 MHz, CDCl\(_3\)) \(\delta\) 21.3, 21.6, 21.6, 53.6, 108.4, 125.1, 126.3, 127.4, 127.7, 127.9, 128.6, 129.4, 129.5, 129.7, 132.1, 133.8, 136.0, 136.2, 136.9, 138.7, 141.4, 144.2, 152.8; IR \(\nu_{\text{max}}\) (film): 2989.27, 2969.49, 2920.34, 1559.78, 1167.62, 1052.31, 1045.83, 683.16, 678.96 cm\(^{-1}\); HRMS m/z calcd for C\(_{31}\)H\(_{28}\)N\(_2\)O\(_2\)S [M+H]\(^+\): 493.1950; found: 493.1950.

4-methyl-N-(4-methyl-2,5-diphenyl-1H-pyrrol-3-yl)benzenesulfonamide (5e): The product was obtained as a yellow solid. Yield: 60%; \(^1\)H NMR (400 MHz, Acetone-\(d_6\)) \(\delta\) 2.01 (s, 3H), 2.29 (s, 3H), 7.05 (d, \(J = 8.0\) Hz, 2H), 7.11-7.20 (m, 3H), 7.24 (t, \(J = 7.6\) Hz, 1H), 7.38-7.45 (m, 4H), 7.53-7.56 (m, 4H), 8.04 (s, 1H), 10.15 (s, 1H); \(^{13}\)C (100 MHz, Acetone-\(d_6\)) \(\delta\) 10.3, 121.4, 117.7, 118.0, 126.8, 127.4, 127.9, 128.2, 128.7, 129.3, 129.7, 129.9, 132.7, 134.4, 139.2, 143.3; IR \(\nu_{\text{max}}\) (film): 3353.80, 2922.72, 1704.30, 1302.67, 1156.13, 1092.41, 695.31, 681.84, 678.23 cm\(^{-1}\); HRMS m/z calcd for C\(_{24}\)H\(_{22}\)N\(_2\)O\(_2\)S [M+H]\(^+\): 403.1480; found: 403.1477.

2-methyl-3,5-diphenyl-1-tosyl-1,2-dihydropyrazine (6e): The product was obtained as a light yellow oil. Yield: 83%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.27 (d, \(J = 7.2\) Hz, 3H), 2.24 (s, 3H), 5.38 (q, \(J = 7.2\) Hz, 1H), 6.93 (s, 1H), 7.00 (d, \(J = 8.0\) Hz, 2H), 7.32 (t, \(J = 7.2\) Hz, 1H), 7.38-7.43 (m, 5H), 7.51 (d, \(J = 8.4\) Hz, 2H), 7.81 (m, 4H); \(^{13}\)C (100 MHz, CDCl\(_3\)) \(\delta\) 16.4, 21.6, 46.8, 108.4, 125.1, 126.3, 127.0, 127.9, 128.7, 129.7, 130.9, 135.2, 135.4, 136.1, 136.2, 144.3, 154.9; IR \(\nu_{\text{max}}\) (film): 2956.56, 1700.03, 1652.68, 1588.15, 1169.00, 706.35, 686.53, 678.98 cm\(^{-1}\); HRMS m/z calcd for C\(_{24}\)H\(_{22}\)N\(_2\)O\(_2\)S [M+H]\(^+\): 403.1480; found: 403.1475.
4-methyl-N-(4-phenethyl-2,5-diphenyl-1H-pyrrol-3-yl)benzenesulfonamide (5f): The product was obtained as a yellow solid. Yield: 50%; 'H NMR (400 MHz, Acetone-d₆) δ 2.26 (s, 3H), 2.87 (s, 4H), 6.99 (d, J = 8.0 Hz, 2H), 7.11-7.21 (m, 6H), 7.25-7.29 (m, 3H), 7.41-7.48 (m, 4H), 7.49 (dd, J = 8.0 Hz, 1.2 Hz, 2H), 7.59 (dd, J = 8.0 Hz, 1.2 Hz, 2H), 8.00 (s, 1H), 10.17 (s, 1H); 13C (100 MHz, Acetone-d₆) δ 21.3, 27.3, 37.1, 117.3, 122.2, 126.5, 126.8, 127.2, 127.5, 127.8, 128.6, 128.7, 129.1, 129.2, 129.4, 129.8, 130.3, 132.7, 134.5, 139.4, 143.3, 143.6; IR νmax (film): 3346.57, 1160.02, 700.50, 697.41, 693.77, 687.61, 678.46 cm⁻¹; HRMS m/z calcd for C₃₁H₂₈N₂O₂S [M+H]⁺: 493.1950; found: 493.1953.

2-phenethyl-3,5-diphenyl-1-tosyl-1,2-dihydropyrazine (6f): The product was obtained as a light yellow oil. Yield: 79%; 'H NMR (400 MHz, CDCl₃) δ 1.72 (m, 1H), 1.96 (m, 1H), 2.20 (s, 3H), 2.85 (m, 2H), 5.28 (dd, J = 10.0 Hz, 3.6 Hz, 1H), 6.89 (s, 1H), 6.92 (d, J = 8.0 Hz, 2H), 7.18-7.34 (m, 8H), 7.40 (t, J = 7.6 Hz, 3H), 7.45 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 7.6 Hz, 2H), 7.79 (d, J = 7.6 Hz, 2H); 13C (100 MHz, CDCl₃) δ 21.5, 30.5, 31.3, 50.8, 108.1, 125.1, 126.2, 126.2, 127.1, 128.1, 128.6, 128.7, 128.8, 129.6, 130.9, 135.5, 135.9, 136.1, 136.8, 141.1, 144.3, 154.6; IR νmax (film): 2953.18, 2924.79, 1652.76, 1448.25, 1358.75, 1168.44, 1091.45, 1028.37, 699.09, 690.36, 687.49 cm⁻¹; HRMS m/z calcd for C₃₁H₂₈N₂O₂S [M+H]⁺: 493.1950; found: 493.1947.

4-methyl-N-(4-pentyl-2,5-diphenyl-1H-pyrrol-3-yl)benzenesulfonamide (5g): The product was obtained as a yellow solid. Yield: 65%; 'H NMR (400 MHz, Acetone-d₆) δ 0.86 (t, J = 6.8 Hz, 3H), 1.23-1.29 (m, 4H), 1.52 (m, 2H), 2.29 (s, 3H), 2.56 (m, 2H), 2.56 (m, 2H), 7.01 (d, J = 8.0 Hz, 2H), 7.09-7.18 (m, 3H), 7.25 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 8.4 Hz, 4H), 7.50 (dd, J = 8.4 Hz, 1.2 Hz, 2H), 7.56 (dd, J = 8.4 Hz, 1.2 Hz, 2H), 8.03 (s, 1H), 10.09 (s, 1H); 13C (100 MHz, Acetone-d₆) δ 14.4, 21.3, 23.1, 24.6, 30.8, 32.9, 117.3, 123.3, 126.7, 127.0, 127.5, 127.7, 127.8, 128.2, 128.7, 129.3, 129.7, 130.2, 132.8, 134.7, 139.6, 143.2; IR νmax (film): 3358.34, 2928.88, 1601.79, 1493.29, 1316.86, 1304.51, 1158.70, 1094.34, 696.10, 688.93, 678.42, 676.78 cm⁻¹; HRMS m/z calcd for C₂₈H₂₀N₂O₂S [M+H]⁺: 459.2106; found: 459.2091.
2-pentyl-3,5-diphenyl-1-tosyl-1,2-dihydropyrazine (6g): The product was obtained as a light yellow oil. Yield: 80%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.88 (t, \(J = 7.2\) Hz, 3H), 1.26-1.61 (m, 8H), 2.20 (s, 3H), 5.25 (dd, \(J = 8.8\) Hz, 3.2 Hz, 1H), 6.68 (d, \(J = 1.2\) Hz, 1H), 6.94 (d, \(J = 8.0\) Hz, 2H), 7.32 (t, \(J = 7.2\) Hz, 1H), 7.37-7.43 (m, 5H), 7.46 (d, \(J = 8.4\) Hz, 2H), 7.76 (dd, \(J = 8.0\) Hz, 1.2 Hz, 2H), 7.80 (d, \(J = 6.8\) Hz, 2H); \(^13\)C (100 MHz, CDCl\(_3\)) \(\delta\) 14.2, 21.6, 22.6, 24.9, 28.9, 31.4, 51.3, 108.1, 125.0, 126.1, 127.1, 128.0, 128.6, 130.8, 135.8, 136.0, 136.5, 144.2, 154.9; IR \(\nu\)\(_{\text{max}}\) (film): 2921.18, 2848.80, 1357.77, 1168.14, 1089.18, 758.40, 677.23 cm\(^{-1}\); HRMS m/z calcd for C\(_{28}\)H\(_{30}\)N\(_2\)O\(_2\)S\([M+H]^+\): 459.2106; found: 459.2101.

\(N-(2,5\text{-diphenyl-4-(1-phenylethyl)-1H-pyrrol-3-yl})\)-4-methylbenzenesulfonamide (5h): The product was obtained as a yellow solid. Yield: 58%; \(^1\)H NMR (400 MHz, Acetone-d\(_6\)) \(\delta\) 1.48 (d, \(J = 7.2\) Hz, 3H), 2.26 (s, 3H), 4.57 (q, \(J = 7.2\) Hz, 1H), 6.95 (d, \(J = 8.0\) Hz, 2H), 7.09-7.13 (m, 4H), 7.19-7.24 (m, 7H), 7.28 (d, \(J = 7.6\) Hz, 2H), 7.40 (d, \(J = 8.4\) Hz, 2H), 7.48 (dd, \(J = 7.2\) Hz, 2.4 Hz, 2H), 8.07 (s, 1H), 10.11 (s, 1H); \(^13\)C (100 MHz, Acetone-d\(_6\)) \(\delta\) 19.5, 21.3, 34.2, 117.0, 126.0, 126.6, 126.9, 127.5, 127.5, 127.8, 128.3, 128.6, 128.7, 128.8, 129.6, 129.7, 132.8, 135.0, 139.6, 143.1, 147.9; IR \(\nu\)\(_{\text{max}}\) (film): 1699.99, 1158.61, 1559.69, 680.25, 678.21, 676.43 cm\(^{-1}\); HRMS m/z calcd for C\(_{31}\)H\(_{28}\)N\(_2\)O\(_2\)S\([M+H]^+\): 493.1950; found: 493.1949.

3,5-diphenyl-2-(1-phenylethyl)-1-tosyl-1,2-dihydropyrazine (6h): The product was obtained as a light yellow oil. Yield: 84%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.26 (d, \(J = 7.2\) Hz, 3H), 1.50 (d, \(J = 7.2\) Hz, 3H), 2.13 (s, 3H), 2.16 (s, 3H), 2.89 (m, 1H), 2.97 (m, 1H), 5.16 (dd, \(J = 10.0\) Hz, 1.2 Hz, 1H), 5.45 (dd, \(J = 8.8\) Hz, 1.2 Hz, 1H), 6.67 (d, \(J = 1.2\) Hz, 1H), 6.84 (d, \(J = 8.0\) Hz, 2H), 6.87 (d, \(J = 8.0\) Hz, 2H), 6.96 (d, \(J = 1.2\) Hz, 1H), 6.97-7.25 (m, 15H), 7.29 (d, \(J = 7.6\) Hz, 2H), 7.32-7.35 (m, 4H), 7.37-7.45 (m, 10H), 7.73 (d, \(J = 7.2\) Hz, 2H), 7.86 (d, \(J = 7.2\) Hz, 2H), 7.90 (dd, \(J = 7.6\) Hz, 2.0 Hz, 2H); \(^13\)C (100 MHz, CDCl\(_3\)) \(\delta\) 17.7, 18.3, 21.5, 21.5, 38.5, 39.6, 55.9, 56.8, 107.1, 108.6, 125.1, 125.2, 126.0, 126.1, 127.2, 127.2, 127.4, 127.6, 128.1, 128.1, 128.2, 128.3, 128.4, 128.6, 128.6, 128.7, 128.7, 129.5, 129.5, 129.8, 130.7, 135.7, 135.9, 136.0, 136.5, 137.1, 137.3, 137.4, 141.0, 141.8.
3-methyl-2,5-diphenyl-1-tosyl-1,2-dihydropyrazine (8a): The product was obtained as a light yellow oil. Yield: 75%; ¹H NMR (400 MHz, CDCl₃) δ 1.98 (s, 3H), 2.39 (s, 3H), 5.51 (d, J = 1.2 Hz, 1H), 6.79 (d, J = 0.8 Hz, 1H), 7.23-7.30 (m, 8H), 7.35 (t, J = 7.2 Hz, 2H), 7.64-7.66 (m, 4H); ¹³C (100 MHz, CDCl₃) δ 21.7, 25.3, 57.0, 109.0, 124.9, 126.5, 127.7, 127.9, 128.6, 128.9, 130.0, 134.6, 135.1, 135.9, 136.1, 144.5, 157.4; IR νmax (film): 2970.54, 2919.80, 1699.92, 1456.39, 1163.87, 1066.21, 683.60, 676.42 cm⁻¹; HRMS m/z calcd for C₂₅H₂₂N₃O₂S [M+H]^+: 403.1480; found: 403.1469.

3-methyl-5-phenyl-1-tosyl-2-(4-(trifluoromethyl)phenyl)-1,2-dihydropyrazine (8b): The product was obtained as a light yellow oil. Yield: 70%; ¹H NMR (400 MHz, CDCl₃) δ 2.00 (s, 3H), 2.40 (s, 3H), 5.55 (s, 1H), 6.81 (s, 1H), 7.24-7.31 (m, 3H), 7.36 (t, J = 7.2 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 7.63-7.65 (m, 4H); ¹³C (100 MHz, CDCl₃) δ 21.6, 25.3, 56.3, 108.7, 123.8 (q, J = 270.7 Hz), 124.8, 125.8 (q, J = 3.8 Hz), 126.4, 127.9, 128.0, 128.6, 130.0, 131.1 (q, J = 32.3 Hz), 135.0, 135.5, 135.8, 138.6, 144.7, 156.2; IR νmax (film): 2970.05, 1652.40, 1325.82, 1164.82, 1123.03, 1067.08, 686.59, 683.65, 675.48 cm⁻¹; HRMS m/z calcd for C₂₅H₂₅F₃N₃O₂S [M+H]^+: 471.1354; found: 471.1354.

2-(2-chlorophenyl)-3-methyl-5-phenyl-1-tosyl-1,2-dihydropyrazine (8c): The product was obtained as a light yellow oil. Yield: 76%; ¹H NMR (400 MHz, CDCl₃) δ 2.00 (s, 3H), 2.37 (s, 3H), 6.03 (d, J = 0.8 Hz, 1H), 7.01 (dt, J = 7.6 Hz, J = 1.2 Hz, 1H), 7.07 (s, 1H), 7.15-7.20 (m, 3H), 7.25-7.41 (m, 5H), 7.63 (dd, J = 6.8 Hz, J = 2.0 Hz, 2H), 7.70-7.73 (m, 2H); ¹³C (100 MHz, CDCl₃) δ 21.7, 24.7, 54.1, 110.9, 124.6, 126.9, 127.7, 127.9, 128.7, 128.9, 129.9, 130.2, 131.8, 132.4, 134.9, 135.4, 136.2, 144.5, 158.1; IR νmax (film): 2926.64, 1161.43, 1126.04, 1035.99, 1010.64, 683.62, 681.65, 678.18 cm⁻¹; HRMS m/z calcd for C₂₃H₂₁ClN₃O₂S [M+H]^+: 437.1091; found: 437.1087.
3-methyl-5-phenyl-2-(p-tolyl)-1-tosyl-1,2-dihydropyrazine (8d): The product was obtained as a light yellow oil. Yield: 96%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.96 (s, 3H), 2.29 (s, 3H), 2.39 (s, 3H), 5.47 (s, 1H), 6.77 (s, 1H), 7.07 (d, $J$ = 8.0 Hz, 2H), 7.16 (d, $J$ = 8.0 Hz, 2H), 7.22-7.29 (m, 3H), 7.35 (t, $J$ = 7.2 Hz, 2H), 7.63-7.66 (m, 4H); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 21.3, 21.7, 25.3, 56.8, 109.0, 124.9, 126.5, 127.7, 127.8, 128.6, 129.6, 130.0, 131.6, 135.1, 136.0, 136.2, 138.9, 144.4, 157.6; IR $\nu_{\text{max}}$ (film): 1700.60, 1160.07, 1124.84, 1034.23, 1009.22, 688.53, 680.42 cm$^{-1}$; HRMS m/z calcd for C$_{25}$H$_{22}$N$_2$O$_2$S [M+H]$^+$: 417.1637; found: 417.1625.

3-methyl-2-(naphthalen-2-yl)-5-phenyl-1-tosyl-1,2-dihydropyrazine (8e): The product was obtained as a light yellow oil. Yield: 83%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.03 (s, 3H), 2.35 (s, 3H), 5.67 (s, 1H), 6.80 (s, 1H), 7.19-7.29 (m, 3H), 7.34 (t, $J$ = 7.6 Hz, 2H), 7.40-7.47 (m, 2H), 7.52 (d, $J$ = 8.8 Hz, 1H), 7.57 (s, 1H), 7.65 (d, $J$ = 8.0 Hz, 4H), 7.69 (d, $J$ = 8.0 Hz, 1H), 7.78 (d, $J$ = 8.0 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 21.7, 25.4, 57.2, 109.1, 125.0, 125.5, 126.5, 126.7, 127.6, 127.7, 127.9, 128.3, 128.6, 129.0, 130.0, 131.8, 133.1, 133.5, 135.3, 136.0, 136.1, 144.5, 157.5; IR $\nu_{\text{max}}$ (film): 1652.11, 1166.33, 1036.20, 812.43, 754.23, 746.71, 683.72 cm$^{-1}$; HRMS m/z calcd for C$_{25}$H$_{22}$N$_2$O$_2$S [M+H]$^+$: 453.1637; found: 453.1631.

3-phenethyl-2,5-diphenyl-1-tosyl-1,2-dihydropyrazine (8f): The product was obtained as a light yellow oil. Yield: 80%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.25 (m, 1H), 2.39 (s, 3H), 2.62-2.81 (m, 3H), 5.47 (d, $J$ = 1.2 Hz, 1H), 6.81 (d, $J$ = 1.2 Hz, 1H), 7.06 (d, $J$ = 7.2 Hz, 2H), 7.14-7.31 (m, 11H), 7.35 (t, $J$ = 7.2 Hz, 2H), 7.63 (d, $J$ = 8.4 Hz, 2H), 7.69 (d, $J$ = 7.2 Hz, 2H); $^{13}$C (100 MHz, CDCl$_3$) $\delta$ 21.7, 31.2, 39.8, 56.7, 109.2, 125.0, 126.2, 126.6, 127.8, 127.9, 128.4, 128.5, 128.6, 128.9, 129.0, 130.0, 134.8, 134.9, 136.1, 136.3, 141.2, 144.5, 159.0; IR $\nu_{\text{max}}$ (film): 1559.72, 1653.81, 684.48, 679.78, 676.84 cm$^{-1}$; HRMS m/z calcd for C$_{31}$H$_{28}$N$_2$O$_2$S [M+H]$^+$: 493.1950; found: 493.1926.

3-pentyl-2,5-diphenyl-1-tosyl-1,2-dihydropyrazine (8g): The product was obtained as a light yellow oil. Yield: 75%; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.84 (t, $J$ = 7.2 Hz, 3H), 1.13-1.36 (m, 6H),
2.02 (m, 1H), 2.32 (m, 1H), 2.39 (s, 3H), 5.46 (s, 1H), 6.81 (s, 1H), 7.23-7.31 (m, 8H), 7.36 (t, \( J = 7.2 \) Hz, 2H), 7.66 (d, \( J = 8.0 \) Hz, 2H), 7.69 (d, \( J = 7.6 \) Hz, 2H); \(^{13}\)C (100 MHz, CDCl\(_3\)) \( \delta \) 14.0, 21.6, 22.4, 24.9, 31.4, 38.2, 56.2, 108.8, 124.8, 126.5, 127.7, 127.8, 128.5, 128.8, 129.9, 134.8, 134.9, 136.1, 136.3, 140.1; IR \( \nu_{\text{max}} \) (film): 2926.43, 1160.57, 1125.32, 1035.51, 1008.98, 685.14, 681.99, 679.48 cm\(^{-1}\); HRMS m/z calcd for C\(_{28}\)H\(_{30}\)N\(_2\)O\(_2\)S [M+H]\(^+\): 459.2106; found: 459.2096.

**Ethyl-2-methyl-4-(4-methylphenylsulfonamido)-5-phenyl-1H-pyrrole-3-carboxylate (10a):** The product was obtained as a colorless oil. Yield: 91%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.21 (t, \( J = 7.2 \) Hz, 3H), 2.33 (s, 3H), 2.36 (s, 3H), 3.95 (q, \( J = 7.2 \) Hz, 2H), 7.06 (s, 1H), 7.08 (d, \( J = 4.4 \) Hz, 2H), 7.19 (t, \( J = 7.2 \) Hz, 1H), 7.25-7.29 (m, 2H), 7.43 (d, \( J = 8.4 \) Hz, 2H), 7.62 (d, \( J = 8.4 \) Hz, 2H), 8.47 (s, 1H); \(^{13}\)C (100 MHz, CDCl\(_3\)) \( \delta \) 13.8, 14.4, 21.6, 59.7, 108.6, 117.1, 126.3, 126.4, 127.1, 127.9, 128.6, 129.0, 131.1, 134.0, 136.0, 143.3, 164.8; IR \( \nu_{\text{max}} \) (film): 1700.42, 1162.51, 687.10, 684.98, 679.28 cm\(^{-1}\); HRMS m/z calcd for C\(_{21}\)H\(_{22}\)N\(_2\)O\(_4\)S [M+H]\(^+\): 399.1379; found: 399.1375.

**Ethyl-4-(4-methylphenylsulfonamido)-2,5-diphenyl-1H-pyrrole-3-carboxylate (10b):** The product was obtained as a colorless oil. Yield: 95%; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 1.04 (t, \( J = 7.2 \) Hz, 3H), 2.32 (s, 3H), 3.81 (q, \( J = 7.2 \) Hz, 2H), 7.08 (d, \( J = 8.0 \) Hz, 2H), 7.19 (s, 1H), 7.24 (t, \( J = 7.2 \) Hz, 1H), 7.31-7.42 (m, 7H), 7.45 (d, \( J = 8.4 \) Hz, 2H), 7.71 (d, \( J = 7.6 \) Hz, 2H), 8.49 (s, 1H); \(^{13}\)C (100 MHz, CDCl\(_3\)) \( \delta \) 13.8, 14.4, 21.6, 59.7, 109.2, 118.3, 126.5, 127.6, 127.9, 128.2, 128.6, 128.7, 129.0, 129.1, 130.8, 131.6, 135.4, 135.9, 143.3, 164.3; IR \( \nu_{\text{max}} \) (film): 3316.35, 1683.30, 1459.85, 1163.73, 690.00, 686.96, 685.09, 677.08 cm\(^{-1}\); HRMS m/z calcd for C\(_{26}\)H\(_{24}\)N\(_2\)O\(_4\)S [M+H]\(^+\): 461.1535; found: 461.1529.

**Ethyl-2-(4-methoxyphenyl)-4-(4-methylphenylsulfonamido)-5-phenyl-1H-pyrrole-3-carboxylate (10c):** The product was obtained as a colorless oil. Yield: 90%; \(^1\)H NMR (400 MHz, Acetone-\(d_6\)) \( \delta \) 1.08 (t, \( J = 7.2 \) Hz, 3H), 2.35 (s, 3H), 3.83 (s, 3H), 3.85 (q, \( J = 7.2 \) Hz, 2H), 6.95 (d, \( J = 8.8 \) Hz, 2H), 7.18 (d, \( J = 8.0 \) Hz, 2H), 7.24 (t, \( J = 7.2 \) Hz, 1H), 7.33 (t, \( J = 8.0 \) Hz, 2H), 7.42 (d, \( J = 8.0 \) Hz, 2H), 7.47 (d,
$J = 8.8$ Hz, 2H), 7.74 (s, 1H), 7.85 (d, $J = 8.0$ Hz, 2H), 10.67 (s, 1H); $^{13}$C (100 MHz, Acetone-d$_6$) δ 14.3, 21.4, 55.6, 60.1, 113.9, 118.8, 125.0, 127.6, 127.8, 128.5, 128.9, 129.4, 129.7, 131.6, 132.2, 132.2, 136.3, 143.8, 160.7, 165.0; IR $\nu_{\text{max}}$ (film): 1699.90, 1159.19, 691.39, 682.70, 675.84 cm$^{-1}$; HRMS m/z calcd for C$_{27}$H$_{26}$N$_2$O$_5$S [M+H]$^+$: 491.1641; found: 491.1638.

Ethyl-2-(4-fluorophenyl)-4-(4-methylphenylsulfonamido)-5-phenyl-1H-pyrrole-3-carboxylate (10d): The product was obtained as a colorless oil. Yield: 88%; $^1$H NMR (400 MHz, Acetone-d$_6$) δ 1.07 (t, $J = 7.2$ Hz, 3H), 2.34 (s, 3H), 3.85 (q, $J = 7.2$ Hz, 2H), 7.14-7.26 (m, 4H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.33 (t, $J = 7.6$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.59 (dd, $J = 8.8$ Hz, 5.6 Hz, 2H), 7.75 (s, 1H), 7.84 (d, $J = 7.6$ Hz, 2H), 10.82 (s, 1H); $^{13}$C (100 MHz, Acetone-d$_6$) δ 14.2, 21.4, 60.2, 110.9, 115.3 (d, $J = 21.6$ Hz), 118.9, 127.8, 127.8, 128.5, 128.9, 129.1 (d, $J = 3.3$ Hz), 129.7, 130.0, 132.1, 132.5 (d, $J = 8.2$ Hz), 135.1, 137.6, 143.9, 163.5 (d, $J = 244.3$ Hz), 164.8; IR $\nu_{\text{max}}$ (film): 2955.88, 2920.33, 2849.88, 1457.08, 1377.91, 1253.84, 1161.08, 1066.17, 683.41, 676.10 cm$^{-1}$; HRMS m/z calcd for C$_{26}$H$_{23}$FN$_2$O$_4$S [M+H]$^+$: 479.1441; found: 479.1440.
6. NMR Spectra of 2H-Azirines

\[ \text{NMR Spectra of } \text{2H-Azirines} \]

\[ \text{\textsuperscript{1}H NMR Spectrum for 2a (CDCl}_3, \text{ 400 MHz)} \]

\[ \text{\textsuperscript{13}C NMR Spectrum for 2a (CDCl}_3, \text{ 100 MHz)} \]
H NMR Spectrum for 2b (CDCl₃, 400 MHz)

13C NMR Spectrum for 2b (CDCl₃, 100 MHz)
$^1$H NMR Spectrum for 2c (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 2c (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 2d (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 2d (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 2e (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 2e (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 2f (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 2f (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 2g (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 2g (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for $2h$ (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for $2h$ (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 2i (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 2i (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 2j (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 2j (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 2k (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 2k (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 4a (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 4a (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 4b (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 4b (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 4c (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 4c (CDCl$_3$, 100 MHz)
\textbf{H NMR Spectrum for 4d (CDCl$_3$, 400 MHz)}

\textbf{\textsuperscript{13}C NMR Spectrum for 4d (CDCl$_3$, 100 MHz)}
$^1$H NMR Spectrum for 4e (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 4e (CDCl$_3$, 100 MHz)
\( ^1H \) NMR Spectrum for 4f (CDCl\(_3\), 400 MHz)

\( ^13C \) NMR Spectrum for 4f (CDCl\(_3\), 100 MHz)
$^1$H NMR Spectrum for 4g (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 4g (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 4h (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 4h (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 7a (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 7a (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 7b (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 7b (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 7c (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 7c (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 7d (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 7d (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 7e (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 7e (CDCl$_3$, 100 MHz)
$^{1}H$ NMR Spectrum for 7f (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 7f (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 7g (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 7g (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 9a (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 9a (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 9b (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 9b (CDCl$_3$, 100 MHz)
1H NMR Spectrum for 9c (CDCl₃, 400 MHz)

13C NMR Spectrum for 9c (CDCl₃, 100 MHz)
$^1$H NMR Spectrum for 9d (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 9d (CDCl$_3$, 100 MHz)
7. NMR Spectra of [3+2] and [3+3] Products

$^1$H NMR Spectrum for 3a (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 3a (CDCl$_3$, 100 MHz)
**H NMR Spectrum for 3b** (Acetone-d$_6$, 400 MHz)

**C NMR Spectrum for 3b** (Acetone-d$_6$, 100 MHz)
$^1$H NMR Spectrum for 3c (Acetone-\textit{d}_6, 400 MHz)

$^{13}$C NMR Spectrum for 3c (Acetone-\textit{d}_6, 100 MHz)
$^1$H NMR Spectrum for 3d (Acetone-d$_6$, 400 MHz)

$^{13}$C NMR Spectrum for 3d (Acetone-d$_6$, 100 MHz)
$^1$H NMR Spectrum for 3e (Acetone-$d_6$, 400 MHz)

$^{13}$C NMR Spectrum for 3e (Acetone-$d_6$, 100 MHz)
$^1$H NMR Spectrum for 3f (Acetone-\textit{d}_6, 400 MHz)

$^{13}$C NMR Spectrum for 3f (Acetone-\textit{d}_6, 100 MHz)
$^1$H NMR Spectrum for 3g (Acetone-$d_6$, 400 MHz)

$^{13}$C NMR Spectrum for 3g (Acetone-$d_6$, 100 MHz)
$^1$H NMR Spectrum for $3h$ (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for $3h$ (CDCl$_3$, 100 MHz)
H NMR Spectrum for 3i (Acetone-d$_6$, 400 MHz)

$^{13}$C NMR Spectrum for 3i (Acetone-d$_6$, 100 MHz)
$^1$H NMR Spectrum for 3j (Acetone-\(d_6\), 400 MHz)

$^{13}$C NMR Spectrum for 3j (Acetone-\(d_6\), 100 MHz)
$^1$H NMR Spectrum for 3k (Acetone-d$_6$, 400 MHz)

$^{13}$C NMR Spectrum for 3k (Acetone-d$_6$, 100 MHz)
$^1\text{H NMR Spectrum for 3l (Acetone-d$_6$, 400 MHz)}$

$^{13}\text{C NMR Spectrum for 3l (Acetone-d$_6$, 100 MHz)}$
\(^1\)H NMR Spectrum for 3m (Acetone-\(d_6\), 400 MHz)

\(^13\)C NMR Spectrum for 3m (Acetone-\(d_6\), 100 MHz)
$^1$H NMR Spectrum for 3n (Acetone-$d_6$, 400 MHz)

$^{13}$C NMR Spectrum for 3n (Acetone-$d_6$, 100 MHz)
$^1$H NMR Spectrum for 3o (Acetone-$d_6$, 400 MHz)

$^{13}$C NMR Spectrum for 3o (Acetone-$d_6$, 100 MHz)
$^1$H NMR Spectrum for 3p (Acetone-$d_6$, 400 MHz)

$^{13}$C NMR Spectrum for 3p (Acetone-$d_6$, 100 MHz)
$^1$H NMR Spectrum for 5a (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 5a (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 5b (Acetone-$d_6$, 400 MHz)

$^{13}$C NMR Spectrum for 5b (Acetone-$d_6$, 100 MHz)
\(^1\text{H}\) NMR Spectrum for 5c (Acetone-\(d_6\), 400 MHz)

\(^{13}\text{C}\) NMR Spectrum for 5c (Acetone-\(d_6\), 100 MHz)
$^1$H NMR Spectrum for 5d (Acetone-d$_6$, 400 MHz)

$^{13}$C NMR Spectrum for 5d (Acetone-d$_6$, 100 MHz)
H NMR Spectrum for 5e (Acetone-d₆, 400 MHz)

13C NMR Spectrum for 5e (Acetone-d₆, 100 MHz)
$^1$H NMR Spectrum for 5f (Acetone-d$_6$, 400 MHz)

$^{13}$C NMR Spectrum for 5f (Acetone-d$_6$, 100 MHz)
$^1$H NMR Spectrum for 5g (Acetone-$d_6$, 400 MHz)

$^{13}$C NMR Spectrum for 5g (Acetone-$d_6$, 100 MHz)
$^{1}$H NMR Spectrum for 5h (Acetone-d$_6$, 400 MHz)

$^{13}$C NMR Spectrum for 5h (Acetone-d$_6$, 100 MHz)
$^1$H NMR Spectrum for 6a (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 6a (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 6b (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 6b (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 6c (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 6c (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 6d (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 6d (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 6e (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 6e (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 6f (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 6f (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 6g (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 6g (CDCl$_3$, 100 MHz)
**$^1$H NMR Spectrum for 6h (CDCl$_3$, 400 MHz)**

![H NMR Spectrum](image)

**$^{13}$C NMR Spectrum for 6h (CDCl$_3$, 100 MHz)**

![C NMR Spectrum](image)
$^1$H NMR Spectrum for 8a (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 8a (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 8b (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 8b (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 8c (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 8c (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 8d (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 8d (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 8e (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 8e (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 8f (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 8f (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 8g (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 8g (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 10a (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 10a (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for 10b (CDCl$_3$, 400 MHz)

$^{13}$C NMR Spectrum for 10b (CDCl$_3$, 100 MHz)
$^1$H NMR Spectrum for $10c$ (Acetone-$d_6$, 400 MHz)

$^{13}$C NMR Spectrum for $10c$ (Acetone-$d_6$, 100 MHz)
1H NMR Spectrum for 10d (Acetone-d₆, 400 MHz)

13C NMR Spectrum for 10d (Acetone-d₆, 100 MHz)
8. X-ray Crystallographic Structure of 3a’ and 6a

![Chemical structure of 3a']

X-ray Crystallographic structure and data of 3a’

<table>
<thead>
<tr>
<th>Compound</th>
<th>3a’</th>
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<tbody>
<tr>
<td>formula</td>
<td>C_{30}H_{23} Br N_{2} O_{3} S</td>
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<td>space group</td>
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<td>a/Å</td>
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<tr>
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<tr>
<td>β/deg</td>
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<tr>
<td>γ/deg</td>
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<tr>
<td>V/Å³</td>
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<td>D_c/g cm(^{-3})</td>
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<tr>
<td>μ/mm(^{-1})</td>
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<tr>
<td>R(_1) (I &gt; 2σ)</td>
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<tr>
<td>wR(_2) (all data)</td>
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<tr>
<td>GOF</td>
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### Compound 6a

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<tr>
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<tr>
<td>β/deg</td>
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<tr>
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<tr>
<td>wR₂ (all data)</td>
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<td>GOF</td>
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