Supporting Information for

Unprecedented nucleophile-promoted 1,7-S- or Se-shift reactions under Pummerer reactions of 4-alkenyl-3-sulfinylmethylpyrroles

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Schemes S1 and S2 on the syntheses of compounds 1, 2, and 3a–g; the NMR study for the structure determinations, further DFT calculations, the ORTEP drawing of both sulfone of 5a, 11d and the ¹H and ¹³C NMR charts
## CONTENTS

1. Scheme S1 and S2 for the preparations of allylsulfonylones 3  
   S3
2. NMR study for the structure determinations  
   S2
3. Sample preparation and crystal structure determination of compound 12d  
   and sulfone of 5a  
   S8
4. DFT calculations  
   S13
5. Experimental  
   S16
6. X-ray crystallographic analysis  
   S63
7. References  
   S65
8. DFT computational results, Cartesian coordinates, computed total  
   energies of optimized structures  
   S66
9. $^1$H and $^{13}$C NMR harts  
   S177
1. Preparations of $N$-allyl sulfonamides 3a–f.

Scheme S1: Preparations of sulfonamides 3.

Scheme S2: Synthesis and ytterbium-catalyzed reaction of 9g.
2. NMR study for the structure determinations.

\[ \text{N-(3-Hydroxy-2-(phenylselanyl)propyl)-N-((4-(hydroxymethyl)-1-tosyl-1H-pyrrol-3-yl)methyl)-4-methylbenzenesulfonamide (10a).} \]

Fig S1: NMR study of 10a in CDCl₃.
1,5-Bis(p-toluenesulfonyl)-1,4,5,6,7,8-hexahydro-8-phenyl-7-(phenylthio)pyrrolo[3,2-c]-azepin-3-methanol (11d).

**Fig S2: NMR study of 11d in CDCl₃.**

$^1$H NMR (800 MHz, CDCl₃) δ 2.22 (3H, s, Ts(A)CH₃), 2.38 (3H, s, Ts(B)CH₃), 3.16 (1H, dd, J = 13.6, 2.5 Hz, Hc [quasi-ax]), 3.76 (1H, ddd, J = 5.2, 4.5, 2.5 Hz, Hb), 3.80 (1H, ddd, J = 13.6, 5.2, 1.6 Hz, Hd [quasi-eq]), 3.89 (1H, d, J = 15.6, He [quasi-ax]), 4.53/4.57 (each 1H, d, J = 12.5, Hg and Hh), 4.59 (1H, dd, J = 15.6, 1.6, Hf [quasi-eq]), 5.37 (1H, d, J = 4.5, Ha), 6.74 (2H, dm, J = ca. 7.4 Hz, Ph(C)-ortho), 6.86 (2H, dm, J = ca. 8.4 Hz, Ts(A)-meta), 7.07 (2H, tm, J = ca. 7.4 Hz, Ph(C)-meta), 7.10 (1H, tm-like, J = ca. 7.4, Ph(C)-para), 7.24 (2H, m, Ts(A)-ortho and Ts(B)-metha), 7.30 (1H, tm, J = ca. 7.4, Ph(D)-para), 7.35 (2H, dm, J = ca. 7.4 Hz, Ph(C)-meta), 7.38 (1H, br s-like, Hi), 7.46 (2H, dm, J = ca. 7.4 Hz, Ph(D)-ortho), 7.63 (2H, dm, J = ca. 8.4 Hz, Ts(S)-ortho). $^{13}$C NMR (200 MHz, CDCl₃) δ: 21.4/21.5 (Ts(B)CH₃/Ts(A)CH₃), 44.3 (C-4), 46.6 (C-1), 49.9 (C-3), 54.6 (C-2), 56.8 (C-9), 120.9 (C-7), 124.0 (C-5), 124.1 (C-6), 126.5 (Ph(C)-para), 126.9
(Ts(A)-meta), 127.37 (Ts(B)-meta), 127.38 (Ph(D)-para), 128.0 (Ph(C)-ortho), 128.6 (Ph(C)-meta), 129.1 (Ph(D)-meta), 129.4 (Ts(A)-ortho), 129.7 (Ts(B)-ortho), 130.8 (C-8), 132.2 (Ph(D)-ortho), 135.2 (Ts(A)-ipso), 135.35 (Ts(B)-ipso), 135.42 (Ph(D)-ipso), 138.9 (Ph(C)-ipso), 143.5 (Ts(B)-ipso), 144.5 (Ts(A)-ipso).

Fig S3: NMR study of 11d in Pyridine D₅.

¹H NMR (800 MHz, pyridine-d₅) δ 2.07 (3H, s, Ts(A)CH₃), 2.12 (3H, s, Ts(B)CH₃), 3.41 (1H, dd, J = 13.3, 1.8 Hz, Hc [quasi-ax]), 4.20 (1H, ddd, J = 13.3, 5.3, 1.5 Hz, Hd [quasi-eq]), 4.23 (1H, ddd, J = 5.3, 4.3, 1.8 Hz, Hb), 4.33 (1H, d, J = 15.6, He [quasi-ax]), 4.90/4.92 (each 1H, dd, J = 12.7, 0.8, Hg and Hh), 5.31 (1H, dd, J = 15.6, 1.5, Hf [quasi-eq]), 5.85 (1H, d, J = 4.3, Ha), 6.84 (2H, dm, J = ca. 8.4 Hz, Ts(A)-meta), 7.04 (2H, dm, J = ca. 7.4 Hz, Ph(C)-ortho), 7.06 (2H, tm, J = ca. 7.4 Hz, Ph(C)-meta), 7.08 (1H,
tm-like, $J = \text{ca. } 7.4$, Ph(C)-para), 7.10 (1H, dm, $J = 8.4$, Ts(B)-metha), 7.30 (1H, tm, $J = \text{ca. } 7.4$, Ph(D)-para), 7.40 (2H, dm, $J = \text{ca. } 7.4$ Hz, Ph(C)-meta), 7.49 (2H, dm, $J = \text{ca. } 8.4$ Hz, Ts(A)-ortho), 7.69 (2H, dm, $J = \text{ca. } 7.4$ Hz, Ph(D)-ortho), 7.80 (1H, br s-like, Hi), 7.84 (2H, dm, $J = \text{ca. } 8.4$ Hz, Ts(S)-ortho); $^{13}$C NMR (200 MHz, pyridine-$d_5$) $\delta$: 22.8/22.9 (Ts(B)CH$_3$/Ts(A)CH$_3$), 47.4 (C-4), 49.4 (C-1), 52.6 (C-3), 56.4 (C-2), 58.2 (C-9), 122.7 (C-7), 126.9 (C-5), 128.57 (C-6), 128.64 (Ph(C)-para), 129.1 (Ts(A)-meta), 129.2 (Ph(D)-para), 129.5 (Ts(B)-meta), 130.3 (Ph(C)-ortho), 130.7 (Ph(C)-meta), 131.4 (Ph(D)-meta), 131.7 (Ts(A)-ortho), 131.8 (Ts(B)-ortho), 133.0 (C-8), 133.6 (Ph(D)-ortho), 137.8 (Ts(A)-ipso), 137.9 (Ts(B)-ipso), 138.4 (Ph(D)-ipso), 141.8 (Ph(C)-ipso), 145.4 (Ts(B)-ipso), 146.7 (Ts(A)-ipso).

Fig S4: NMR study of 25g in CDCl$_3$.
3. Sample preparation and crystal structure determination of compound 11d

Perspective drawing of compound 11d, showing the atom-numbering scheme. Displacement ellipsoids are drawn at 50% probability level.

EXPERIMENTAL DETAILS

Sample preparation of compound 11d: Colorless prism-shaped single crystals were obtained by slow evaporation of a solution of 11d in n-hexane/acetone.

Crystal data and structure refinement for compound 11d (CCDC 1824588)

Crystal data

- Empirical Formula: C_{35}H_{34}N_{2}O_{5}S_{3}
- Formula Weight: 658.84
- Crystal Dimensions: 0.30 X 0.20 X 0.10 mm
- Temperature: 123 K
Crystal System | tetragonal
---|---
Space Group | P4₁
Lattice Parameters | a = 14.8202(6) Å  
c = 14.7217(6) Å
Volume | 3233.4(2) Å³
Z value | 4
Dcalc | 1.353 g/cm³
F000 | 1384.00
µ(MoKα) | 2.746 cm⁻¹

**Intensity Measurements**

| Diffractometer | Rigaku RAXIS-RAPID |
| Radiation | MoKα (λ = 0.71075 Å)  
graphite monochromated |
| Detector Aperture | 280 mm x 256 mm |
| Data Images | 44 exposures |
| ω oscillation Range (χ=45.0, φ=90.0) | 130.0 - 190.0° |
| Exposure Rate | 60.0 sec./° |
| ω oscillation Range (χ=45.0, φ=270.0) | 0.0 - 160.0° |
| Exposure Rate | 60.0 sec./° |
| 2θ max | 54.9° |
| No. of Reflections Measured | Total: 30943  
Unique: 7244 (Rint = 0.024) |

**Structure Solution and Refinement**

| Structure Solution | Direct Methods (SIR97) |
| Refinement | Full-matrix least-squares on F |
| Function Minimized | \( \Sigma w (|F_o| - |F_c|)^2 \) |
| Least Squares Weights | 1/[0.0010F_o^2+3.0000σ(F_o)+0.5000] |
| 2θ max cutoff | 54.9° |
| Anomalous Dispersion | All non-hydrogen atoms |
No. Observations (All reflections) 30945  
No. Variables 440  
Reflection/Parameter Ratio 70.33  
Residuals: R (I>2.00σ(I)) 0.0454  
Residuals: R (All reflections) 0.0504  
Residuals: Rw (All reflections) 0.0564  
Goodness of Fit Indicator 0.919  
Max Shift/Error in Final Cycle 0.000  
Maximum peak in Final Diff. Map 13.10 e⁻/Å³  
Minimum peak in Final Diff. Map −3.66 e⁻/Å³

Sample preparation and crystal structure determination of sulfone of 5a.
Perspective drawing of sulfone of 5a, showing the atom-numbering scheme.
Displacement ellipsoids are drawn at 50% probability level.

EXPERIMENTAL DETAILS

Sample preparation of sulfone of 5a: Colorless prism-shaped single crystals were obtained by slow evaporation of a solution of sulfone of 5a in CHCl₃/MeOH.

Crystal data and structure refinement for sulfone of 5a (CCDC 1824587)

Crystal data

| Property            | Value                       |
|---------------------|-----------------------------|
| Empirical Formula   | C₂₉H₃₀N₂O₆S₃               |
| Formula Weight      | 598.75                      |
| Crystal Dimensions  | 0.25 X 0.20 X 0.20 mm       |
| Temperature         | 123 K                       |
| Crystal System      | monoclinic                  |
| Lattice Parameters  | a = 8.8310(3) Å             |
|                     | b = 13.1020(5) Å            |
|                     | c = 25.1669(11) Å           |
|                     | β = 91.4836(13)°            |
| Volume              | 2910.9(2) Å³                |
| Z value             | 4                           |
| D_{calc}            | 1.366 g/cm³                 |
| F_{000}             | 1256.00                     |
| μ(MoKα)             | 2.997 cm⁻¹                  |

Intensity Measurements

| Property      | Value                               |
|---------------|-------------------------------------|
| Diffractometer| Rigaku RAXIS-RAPID                  |
| Radiation     | MoKα (λ = 0.71075 Å)                |
| Detector Aperture | 280 mm x 256 mm                     |
Data Images

44 exposures

ω oscillation Range (χ=45.0, φ=0.0) 130.0 - 190.0°
Exposure Rate 60.0 sec./°

ω oscillation Range (χ=45.0, φ=180.0) 0.0 - 160.0°
Exposure Rate 60.0 sec./°

2θ_{max} 55.0°

No. of Reflections Measured Total: 27881
Unique: 6657 (R_{int} = 0.018)

Structure Solution and Refinement

Structure Solution Direct Methods (SIR92)
Refinement Full-matrix least-squares on F^2
Function Minimized \sum w (Fo^2 - Fc^2)^2
Least Squares Weights 1/[0.0010Fo^2+3.0000\sigma(Fo^2)+0.5000]/(4Fo^2)
2θ_{max} cutoff 55.0°

Anomalous Dispersion All non-hydrogen atoms

No. Observations (All reflections) 27881
No. Variables 391
Reflection/Parameter Ratio 71.31
Residuals: R1 (I>2.00\sigma(I)) 0.0748
Residuals: R (All reflections) 0.0855
Residuals: wR2 (All reflections) 0.1797

Goodness of Fit Indicator 1.474
Max Shift/Error in Final Cycle 0.000
Maximum peak in Final Diff. Map 17.30 e^-/Å^3
Minimum peak in Final Diff. Map -4.66 e^-/Å^3
4. DFT calculations

We performed geometry optimization calculations for all compounds (14a-d, 15a,d, and 21a,d) at the B3LYP/6-31G(d) level. Frequency calculations were also performed to confirm whether the optimized structures were energy minimum structures on the potential energy surface. All DFT calculations were performed with the Gaussian16,\textsuperscript{1} Revision A.03 suite program installed on the Fujitsu PRIMERGY CX400/2550 computer system at the Information Technology Center of Nagoya University.

The energy for each process of both from the sulfonium intermediate 14x to the thioacetylated intermediate 15x and from 14x to azepinium cation 21x were exhibited in Fig. S6. The lower energy of the intermediate 15a of the reaction of N-allylsulfonium intermediate 14a would lead to the formation of diols by treatment with tetrabutylammonium hydroxide (TBAH). On the other hand, the energy of intermediate 21b is lower than that of 15b in the reaction of N-methallyl sulfonium salt 14b because of the stabilizing effect of methyl group on the azepinium cation. The azepinium cation 21b exclusively undergo intra- or intermolecular 1,7-S shift reaction to give the 7-(phenylsulfanyl)pyrrolo[3,2-c]azepin-3-methanol. These calculation data are in good agreement with the experimental results.

The similar tendency was observed in the calculation of the Pummerer reaction of N-2-butenyl 14c and N-cinnamyl derivatives 14d.

Fig S6: Comparing some pathways derived from the Pummerer intermediate 14.
We further investigated the 1,7-S shift reaction from the azepinium cation 21b to the corresponding alcohol. We first predict that the intramolecular 1,7-S shift could occur via the transannular sulfonium intermediate 22b to form the S-shifted pyrroloazepine 23b because the 1,7-S shift reaction proceeded with high diastereoselectivity (11b, 12b, 11d, 12d). The calculation data also supported the intramolecular 1,7-S shift reaction as shown in Fig. S7. The speculation that the diol 17a could be formed by the base-promoted hydrolysis of bis(trifluoroacetate) 16a was ruled out by the DFT-calculation as shown in Fig S8.

Fig S7: 1,7- Sulfur shift on the pyrrolo[2,3-c]azepinium cations 21b.

Fig S8: DFT calculation of 14a to the diol 17a.
Finally, we selected both $N$-allyl and $N$-methalyl derivatives and performed the DFT calculations in the processes from the key intermediates 14x to the final products. The results are shown in Fig S6 and S8, respectively. The energy of $N$-allylsulfonium trifluoroacetate 14aa is lowered at $-18.94$ kcal/mol by moving both the double bond of the $N$-allyl group and the trifluoroacetoxy group to give the cyclic intermediate 14ab. The attack of the trifluoroacetoxy anion to the cyclic intermediate 15a would occur from the back side of the $\alpha$-carbon of the sulfur atom. Treatment of labile bis(trifluoroacetoxy)pyrrole 16a with TBAH would provide the diol 17a. We also calculated the azepine formation from the sulfonium intermediate 14b (Fig. S9). The thionium ion ($\alpha$-sulfur-substituted carbenium ion) 18ba, which was generated from the normal Pummerer reaction, could be stabilized by the bridged intermediate 19b (estimated at $-5.05$ kcal/mol by the DFT calculations), easily undergo intramolecular cyclizat ion to give 20b. The 1,5-hydride shift reaction of 20b forms the azepinium cation 21b. The final 1,7-$S$ shift reaction have been already described above.

Fig S9: DFT calculation of 14b to the azepinopyrrole intermediate 23b.
5. Experimental

General experimental methods.

Analytical thin layer chromatography (TLC) was performed using silica gel precorted glass plates and visualized by ultraviolet radiation (254 nm). Flash column chromatography on silica gel was performed using silica gel (particle size 0.063–0.200 mm) under air pressure. Melting points were determined and uncorrected. $^1$H and $^{13}$C NMR spectra were determined with 600 MHz spectrometer. Chemical shifts are expressed in parts per million (ppm) with respect to tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; q, quartet. IR spectra were determined on a FT-IR infrared spectrometer and are expressed in reciprocal centimeters. EI mass spectra (MS) were obtained with direct-insertion probe at 70 eV. ESI measurements and their high resolution mass were performed using Quadrupole and TOF system.

Preparations of sulfanyl-1 and selanyl diynes 2 and N-alkenylsulfonamides 3a–f.

$N$-(Phenylsulfanylprop-2-ynyl)-$N$-prop-2-ynyl-$p$-toluenesulfonamide (1) and $N$-(phenylselanylprop-2-ynyl)-$N$-prop-2-ynyl-$p$-toluenesulfonamide (2) were prepared according to our previous reports.$^{52,53}$ The substrates in the hydroamination of 1,6-diynes were prepared by the usual methods. $N$-Allyl-$p$-toluenesulfonamide (3a),$^{54}$ $N$-methallyl-$p$-toluenesulfonamide (3b), $N$-(3-methyl-2-butenyl)-$p$-toluenesulfonamide (3c), $N$-cinnamyl-$p$-toluenesulfonamide (3d) were prepared from TsNHBoc and the corresponding alcohols by the Mitsunobu reaction$^{55}$ and the following deprotection as shown in the SI (Scheme S1).$^{56}$ Most of allylic sulfonamides were determined by comparing the spectral data of authentic samples.$^{57}$

$N$-Boc-$p$-toluenesulfonamide.

To a 1,2-dichloroethane (50 mL) solution of $p$-toluenesulfonamide (7.39 g, 43.2 mmol) were added Boc$_2$O (10.8 g, 50.0 mmol), triethylamine (6.60 mL, 47.5 mmol), and dimethylaminopyridines (DMAP) (0.53 g, 4.32 mmol) at room temperature. The reaction mixture was stirred overnight and poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with CHCl$_3$. The combined organic layer was washed with 1 M HCl (50 mL), water (50
mL) and then dried over MgSO₄. The solvent was removed under reduced pressure. The residue was precipitated from n-hexane and filtered off to give the titled compound (11.9 g, quant) as white powders.

\[ ^1 \text{H NMR (400 MHz, CDCl}_3 \delta 1.39 (9H, s, Me×3), 2.45 (3H, s, Me), 7.34 (2H, d, J = 7.8 Hz, ArH), 7.89 (2H, d, J = 7.8 Hz, ArH).} \]

N-Boc-N-methallyl-p-toluenesulfonamide.

To a THF (2.0 mL) solution of N-Boc-N-p-toluenesulfonamide (0.500 g, 1.84 mmol), triphenylphosphine (0.483 g, 1.84 mmol), methallyl alcohol (0.133 g, 1.84 mmol) was added dropwise 2.2 M DEAD (0.80 mL, 1.84 mmol) in THF at room temperature. The reaction mixture was stirred for 10 min and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt-n-hexane (1:10) to give the titled compound (0.547 g, 91%) as white powders.

\[ ^1 \text{H NMR (400 MHz, CDCl}_3 \delta 1.35 (9H, s, Me×3), 1.75 (3H, s, Me), 2.44 (3H, s, Me), 4.40 (2H, brs, CH}_2), 4.90 (1H, brs, olefinic H), 4.93 (1H, brs, olefinic H), 7.29 (2H, d, J = 8.2 Hz, ArH), 7.80 (2H, d, J = 8.2 Hz, ArH). \]

N-Methallyl-p-toluenesulfonamide (3b). To a chloroform (5.0 mL) solution of N-Boc-N-methallyl-p-toluenesulfonamide (0.507 g, 1.56 mmol) was added dropwise trifluoroacetic acid (5.0 mL) at room temperature. The reaction mixture was stirred for 0.5 h and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt-n-hexane (1:5) to give the titled compound 3b (0.446 g, quant) as colorless needles.

mp 36-38 °C, \[ ^1 \text{H NMR (400 MHz, CDCl}_3 \delta 1.68 (3H, s, Me), 2.43 (3H, s, Me), 3.48 (2H, brs, CH}_2), 4.80 (1H, brs, OH), 4.82 (1H, brs, olefinic H), 4.86 (1H, brs, olefinic H), 7.31 (2H, d, J = 8.3 Hz, ArH), 7.75 (2H, d, J = 8.3 Hz, ArH). \]
To a THF (8.0 mL) solution of

\[ \text{N-Boc-N-but-2-enyl-p-toluenesulfonamide}^{27} \]

\[ \text{TsNH} \longrightarrow \text{Boc} \]

\[ \text{N} \]

\[ \text{Me} \]

(\(E\))-2-buten-1-ol (0.53 g, 7.37 mmol) was added dropwise 2.2 M DEAD (3.40 mL, 7.37 mmol) at room temperature. The reaction mixture was stirred for 10 min and then evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt-n-hexane (1:10) to give the titled compound (2.24 g, 94%) as a white solid.

\( ^{1}\text{H NMR (400 MHz, CDCl}_3\text{)}\) \( \delta 1.34 \) (9H, s, Me×3), 1.73 (3H, d, \( J = 6.9 \) Hz, Me), 2.43 (3H, s, Me), 4.37 (2H, d, \( J = 6.2 \) Hz, CH\(_2\)), 5.56-5.61 (1H, m, olefinic H), 5.77-5.82 (1H, m, olefinic H), 7.29 (2H, d, \( J = 6.8 \) Hz, ArH), 7.79 (2H, d, \( J = 6.8 \) Hz, ArH).

\( (E)\)-N-But-2-enyl-p-toluenesulfonamide (3c).^{27}

To a chloroform (11 mL) solution of

\[ \text{TsNH} \longrightarrow \text{Boc} \]

\[ \text{N} \]

\[ \text{Me} \]

\( (E)\)-N-Boc-N-2-butenyl-p-toluenesulfonamide (1.08 g, 3.32 mmol) was added dropwise trifluoroacetic acid (6.0 mL) at room temperature. The reaction mixture was stirred for 0.5 h and evaporated under reduced pressure. The residue was crystallized from n-hexane and filtered off to give the titled compound 3c (0.742 g, 99%) as white powder.

mp 45-47 °C. \( ^{1}\text{H NMR (400 MHz, CDCl}_3\text{)}\) \( \delta 1.59 \) (3H, dd, \( J = 1.4 \) and 6.4 Hz, Me), 2.43 (3H, s, Me), 3.50 (2H, dd, \( J = 1.4 \) and 6.4 Hz, CH\(_2\)), 5.28-5.35 (1H, m, olefinic H), 5.52-5.59 (1H, m, olefinic H), 5.68 (1H, brs, NH), 7.31 (2H, d, \( J = 8.2 \) Hz, ArH), 7.74 (2H, d, \( J = 8.2 \) Hz, ArH).

\( N\)-Boc-N-cinnamyl-p-toluenesulfonamide.^{29}

To a DMF (7.0 mL) solution of

\[ \text{TsNH} \longrightarrow \text{Boc} \]

\[ \text{N} \]

\[ \text{Ph} \]

\( N\)-Boc-p-toluenesulfonamide (1.00 g, 3.69 mmol) was added 60% sodium hydride (0.22 g, 5.53 mmol) at 0 °C. The reaction mixture was stirred for 15 min at room temperature. To the mixture at 0 °C were added cinnamyl chloride (0.675 g, 4.42 mmol) and 15-crown-5-ether (0.22 g, 3.69 mmol) at 0 °C. The mixture was stirred for 12 h and poured into water (50 mL). The
organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was washed with H₂O (50 mL × 2) and dried over MgSO₄. The solvent was removed under reduced pressure. The residue was precipitated from n-hexane and filtered off to give the titled compound (1.35 g, 95%) as white powders.

¹H NMR (400 MHz, CDCl₃) δ 1.35 (9H, s, Me×3), 2.41 (3H, s, Me), 4.60 (2H, dd, J = 1.4 and 6.9 Hz, CH₂), 6.26-6.29 (1H, m, olefinic H), 6.66 (1H, brd, J = 15.8 Hz, olefinic H), 7.26-7.27 (3H, m, ArH), 7.31-7.34 (2H, m, ArH), 7.38 (2H, d, J = 7.8 Hz, ArH), 7.79 (2H, d, J = 8.3 Hz, ArH).

N-Cinnamyl-p-toluenesulfonamide (3d).

To a chloroform (20 mL) solution of N-Boc-N-cinnamyl-p-toluenesulfonamide (0.82 g, 2.17 mmol) was added dropwise trifluoroacetic acid (10 mL) at room temperature. The reaction mixture was stirred for 0.5 h and evaporated to give the titled compound 3d (0.583 g, 96%) as light brown powders.

mp 82-84 °C. ¹H NMR (400 MHz, CDCl₃) δ 2.42 (3H, s, Me), 3.75 (2H, d, J = 6.2 Hz, CH₂), 4.62 (1H, brs, NH), 5.99-6.03 (1H, m, olefinic H), 6.43 (1H, d, J = 15.8 Hz, olefinic H), 7.22 (2H, brd, J = 7.6 Hz, ArH), 7.26 (2H, brd, J = 7.6 Hz, ArH), 7.27-7.29 (1H, m, ArH), 7.30 (2H, d, J = 8.3 Hz, ArH), 7.78 (2H, d, J = 8.3 Hz, ArH).

N-Boc-N-(3-methylbut-2-enyl)-p-toluenesulfonamide.⁷

To a THF (8.0 mL) solution of N-Boc-p-toluenesulfonamide (2.00 g, 7.37 mmol), triphenylphosphine (1.90 g, 7.37 mmol), 3-methylbut-2-en-1-ol (635 mg, 7.37 mmol) was added 2.2 M DEAD (3.40 mL, 7.37 mmol) at room temperature. The reaction mixture was stirred for 0.5 h and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt-n-hexane (1:20 then 1:10) to give the titled compound (2.23 g, 89%) as a white solid.

¹H NMR (400 MHz, CDCl₃) δ 1.33 (9H, s, Me×3), 1.76 (3H, brs, Me), 1.77 (3H, brs, Me), 2.43 (3H, s, Me), 4.45 (2H, d, J = 6.9 Hz, CH₂), 5.30 (1H, brt, J = 6.9 Hz, olefinic H), 7.28 (2H, d, J = 8.3 Hz, ArH), 7.76 (2H, d, J = 8.3 Hz, ArH).

S19
N-3-Methylbut-2-enyl-p-toluenesulfonamide (3e).\textsuperscript{S7}

To a chloroform (5.0 mL) solution of N-Boc-N-(3-methylbut-2-enyl)-p-toluenesulfonamide (0.500 g, 1.47 mmol) was added dropwise trifluoroacetic acid (4.0 mL) at room temperature. The reaction mixture was stirred for 0.5 h and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt-\textit{n}-hexane (1:5) to give the titled compound 3e (0.335 g, quant) as white powders. mp 28-30 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textdelta 1.53 (3H, s, Me), 1.62 (3H, s, Me), 2.43 (3H, s, Me), 3.53 (2H, brt, J = 6.4 Hz, CH\textsubscript{2}), 4.59 (1H, brt, J = 5.5 Hz, NH), 5.03-5.07 (1H, m, olefinic H), 7.30 (2H, d, J = 8.3 Hz, ArH), 7.75 (2H, d, J = 8.3 Hz, ArH).

N-Boc-N-But-3-enyl-p-toluenesulfonamide.\textsuperscript{S10}

To a THF (8.0 mL) solution of N-Boc-p-toluenesulfonamide (2.00 g, 7.37 mmol), 3-butene-1-ol (0.532 g, 7.37 mmol), triphenylphosphine (1.90 g, 7.37 mmol) was added dropwise 2.2 M DEAD (3.40 mL, 7.37 mmol) at room temperature. The reaction mixture was stirred for 0.5 h and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt-\textit{n}-hexane (1:20 then 1:10) to give the tilted compound (2.34 g, 98%) as a yellow oil.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \textdelta 1.34 (9H, s, Me x 3), 2.44 (3H, s, Me), 2.50-2.53 (2H, m, CH\textsubscript{2}), 3.87-3.90 (2H, m, CH\textsubscript{2}), 5.07 (1H, d, J = 10.3 Hz, olefinic H), 5.12-5.15 (1H, m, olefinic H), 5.78-5.84 (1H, m, olefinic H), 7.30 (2H, d, J = 8.3 Hz, ArH), 7.79 (2H, d, J = 8.3 Hz, ArH).

N-But-3-enyl-p-toluenesulfonamide (3f).\textsuperscript{S7}

To a chloroform (24 mL) solution of N-Boc-N-but-3-enyl-p-toluenesulfonamide (2.31 g, 7.10 mmol) was added dropwise trifluoroacetic acid (10 mL) at room temperature. The reaction mixture stirred for 0.5 h and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with
AcOEt-n-hexane (1:10 then 1:5) to give the titled compound 3f (1.55 g, 97%) as colorless oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.20 (2H, q, $J = 6.9$ Hz, CH$_2$), 2.43 (3H, s, Me), 3.01 (2H, t, $J = 6.9$ Hz, CH$_2$), 4.48 (1H, brs, NH), 5.02-5.08 (2H, m, olefinic H), 5.60-5.66 (1H, m, olefinic H), 7.31 (2H, d, $J = 8.2$ Hz, ArH), 7.75 (2H, d, $J = 8.3$ Hz, ArH).

N-Allyl-N-$p$-bromobenzenesulfonamide (3g).

To a dichloroethane (15 mL) solution of allylamine (0.224 g, 3.91 mmol), triethyamine (0.792 g, 7.83 mmol) and DMAP (47.8 mg, 0.39 mmol) was added $p$-bromobenzenesulfonyl bromide (1.00 g, 3.91 mmol) at 0 °C. The reaction mixture was stirred for 1 h at room temperature and then poured into water (100 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was washed with 1 M hydrochloric acid (50 mL) and water (50 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was precipitated from n-hexane and filtrated to give the titled compound (1.04 g, 96%).

mp 50-53 °C, $^1$H NMR (400 MHz, CDCl$_3$) δ 3.61 (2H, t, $J = 5.9$ Hz, CH$_2$), 4.58 (1H, brs, NH), 5.11-5.14 (1H, m, olefinic H), 5.15-5.20 (1H, m, olefinic H), 5.67-5.77 (1H, m, olefinic H), 7.66 (2H, d, $J = 8.7$ Hz, ArH), 7.74 (2H, d, $J = 9.1$ Hz, ArH).

Typical procedure for hydroamination of diynes 1 and 2 with N-alkenylsulfonamides 3.

Preparation of 4-aminomethyl-3-phenylsulfanylpyrrole.

To a DMSO (1.0 mL) solution of $N$-(phenylsulfanyl)prop-2-ynyl)-$N$-prop-2-ynyl-p-toluenesulfonamide (1) (100 mg, 0.28 mmol) were added N-allyl-p-toluenesulfonamide (3a) (178 mg, 0.84 mmol), bis(hexafluoroacetylacetonato)nickel(II) hydrate (13 mg, 0.03 mmol), bis(triphenylphosphine)palladium(II) dichloride (20 mg, 0.03 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (43 mg, 0.28 mmol). The reaction mixture was stirred at room temperature for 6.5 h and then poured into water (50 mL). The organic
layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CHCl₃-n-hexane (5:1) to give N-allyl-N-[(3-(phenylsulfanyl)methyl)-1-tosylpyrrole-4-yl)methyl]-p-toluenesulfonamide (4a) (89 mg, 56%) as white powders.

mp 97–101 °C, IR v 1371, 1344, 1172 (SO₂); ¹H NMR (600 MHz, CDCl₃) δ 2.39 (3H, s, Me), 2.41 (3H, s, Me), 3.67 (2H, d, J = 6.2 Hz, CH₂), 3.87 (2H, s, CH₂), 4.16 (2H, s, CH₂), 4.87 (1H, dd, J = 1.4 and 17.2 Hz, olefinic H), 4.94 (1H, d, J = 11.0 Hz, olefinic H), 5.34–5.41 (1H, m, olefinic H), 6.86 (1H, d, J = 2.1 Hz, ArH), 6.87 (1H, d, J = 2.1 Hz, ArH), 7.17–7.19 (3H, m, ArH), 7.21 (2H, dd, J = 2.1 and 8.3 Hz), 7.24 (2H, d, J = 8.3 Hz, ArH), 7.27 (2H, d, J = 8.3 Hz, ArH), 7.58 (2H, d, J = 8.2 Hz, ArH), 7.66 (2H, d, J = 8.3 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 21.4 (q), 21.5 (q), 29.1 (t), 42.0 (t), 49.5 (t), 118.9 (t), 120.1 (d), 120.7 (d), 122.3 (s), 124.1 (s), 126.5 (d), 126.6 (d × 2), 127.1 (d × 2), 128.6 (d × 2), 129.7 (d × 2), 129.9 (d × 2), 130.5 (d × 2), 132.3 (d), 135.4 (s), 135.7 (s), 136.7 (s), 143.4 (s), 145.0 (s); MS (ESI-TOF) m/z 567 (M⁺+H). Anal. Calcd for C₂₉H₃₀N₂O₄S₃: C, 61.46; H, 5.34; N, 4.94. Found: C, 61.17; H, 5.37; N, 4.91.

To a DMSO (3.0 mL) solution of N-(phenylselanylprop-2-ynyl) -N-prop-2-ynyl-p-toluenesulfonamide (2) (300 mg, 0.75 mmol) were added N-allyl-p-toluenesulfonamide (3a) (315 mg, 1.49 mmol), bis(hexafluoroacetylacetonato)nickel (II) hydrate (35 mg, 0.07 mmol), bis(triphenylphosphine)palladium (II) dichloride (52 mg0.07 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.11 g, 0.75 mmol). The reaction mixture was stirred at room temperature for 3.5 h and then poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined
organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CHCl₃-n-hexane (4:1) to give N-allyl-N-[3-(phenylselenymethyl)-1-tosylpyrrolo-4-yl)methyl]-p-toluenesulfonamide (6a) (0.325 mg, 71%) as white powders. mp 74–76 °C, IR ν 1371, 1344, 1172 (SO₂); 'H NMR (600 MHz, CDCl₃) δ 2.41 (3H, s, Me), 2.43 (3H, s, Me), 3.68 (2H, d, J = 6.2 Hz, CH₂), 3.83 (2H, s, CH₂), 4.15 (2H, s, CH₂), 4.89 (1H, d, J = 17.2 Hz, olefinic H), 4.95 (1H, d, J = 10.3 Hz, olefinic H), 5.36-5.42 (1H, m, olefinic H), 6.71 (1H, d, J = 2.1 Hz, ArH), 6.84 (1H, d, J = 2.1 Hz, ArH), 7.13-7.19 (2H, m, ArH), 7.25-7.33 (7H, m, ArH), 7.58 (2H, d, J = 8.2 Hz, ArH), 7.69 (2H, d, J = 7.6 Hz, ArH); 13C NMR (150 MHz, CDCl₃) δ 21.3 (t), 21.5 (q), 21.6 (q), 41.9 (t), 49.5 (t), 119.0 (t), 119.7 (d), 120.6 (d), 122.1 (s), 124.9 (s), 126.7 (d × 2), 127.2 (d × 2), 127.3 (d), 128.8 (d × 2), 129.6 (s), 129.7 (d × 2), 129.9 (d × 2), 132.3 (d), 134.0 (d × 2), 135.7 (s), 136.7 (s), 143.4 (s), 145.0 (s); MS (EI) m/z 614 (M⁺), 457 (M⁺-SePh). HRMS (ESI-TOF) m/z: [M+Na⁺] Calcd for C_{29}H_{30}N_{2}O_{4}S_{2}SeNa 637.0710, found 637.0727. Anal. Calcd for C_{29}H_{30}N_{2}O_{4}S_{2}Se: C, 56.76; H, 4.93; N, 4.56. Found: C, 56.48; H, 4.75; N, 4.36. Oxidation of 3-(phenylsulfanylmethyl)-4-(N-alkenyl-N-tosylaminomethyl)pyrroles. N-allyl-N-[3-(phenylsulfanyl)methyl]-4-tosylpyrrolo-4-yl)methyl]-p-toluenesulfonamide (5a). To a 1,2-dichloroethane (5.0 mL) solution of N-allyl-N-[3-(phenylsulfanyl)methyl]-1-tosylpyrrolo-4-methyl]-p-toluene sulfonamide (4a) (144 mg, 0.25 mmol) was added portionwise m-chloroperbenzoic acid (44 mg, 0.25 mmol) over 1 h at 0 °C. The reaction mixture was stirred for 5 min and poured into a sat. NaHCO₃ (50 mL). The whole was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give
N-allyl-N-[(3-(phenylsulfinylmethyl)-1-tosylpyrrole-4-yl)methyl]-p-toluenesulfonamide (5a) (139 mg, 94%) as white powders.

mp 119–122 °C, IR ν 1372, 1334, 1171 (SO₂); ¹H NMR (600 MHz, CDCl₃) δ 2.42 (3H, s, Me), 2.43 (3H, s, Me), 3.61 (2H, dt, J = 6.2 and 15.8 Hz, CH × 2), 3.79 (1H, d, J = 14.5 Hz, CH), 3.83 (1H, d, J = 14.4 Hz, CH), 3.85 (1H, d, J = 13.7 Hz, CH), 4.12 (1H, d, J = 13.7 Hz, CH), 4.84 (1H, d, J = 17.2 Hz, olefinic H), 4.93 (1H, d, J = 10.3 Hz, olefinic H), 5.21–5.28 (1H, m, olefinic H), 6.87 (1H, d, J = 2.0 Hz, ArH), 7.07 (1H, d, J = 2.1 Hz, ArH), 7.28–7.35 (6H, m, ArH), 7.41–7.44 (3H, m, ArH), 7.64 (2H, d, J = 8.3 Hz, ArH), 7.73 (2H, d, J = 8.2 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 21.5 (q), 21.6 (q), 41.7 (t), 49.3 (t), 52.7 (t), 116.1 (s), 119.2 (t), 120.5 (d), 122.37 (d), 122.40 (s), 124.3 (d × 2), 127.0 (d × 2), 127.1 (d × 2), 128.7 (d × 2), 129.8 (d × 2), 130.0 (d × 2), 131.8 (d), 135.6 (s), 136.5 (s), 143.0 (s), 143.6 (s), 145.3 (s); MS (EI) m/z 457 (M⁺–SO₂Ph). Anal. Calcd for C₂₉H₃₀N₂O₅S₃+1/2H₂O: C, 58.86; H, 5.28; N, 4.73. Found: C, 58.98; H, 5.08; N, 4.73.

N-Adlyl-N-[(3-(phenylsulfonylmethyl)-1-tosylpyrrole-4-yl)methyl]-p-toluenesulfonamide.

m-Chloroperbenzoic acid (0.44 g, 2.58 mmol) was added portion wise to the dichloroethane (66 mL) solution of 4a (1.46 g, 2.58 mmol) at 0 °C. The reaction mixture was stirred for 0.5 h and poured into sat. NaHCO₃ (50 mL). The mixture was vigorously stirred for 0.5 h. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt-n-hexane (1:2 then 1:1) to give 5a (0.464 g, 31%) and the corresponding sulfone (0.398 g, 26%).

mp 166-169 °C, IR (KBr, cm⁻¹) 1374, 1334, 1158 (SO₂), 1091 (SO); ¹H NMR (600 MHz, CDCl₃) δ 2.44 (3H, s, Me), 2.45 (3H, s, Me), 3.59 (2H, d, J = 6.9 Hz, NCH₂), 3.97 (2H, s, CH₂), 4.32 (2H, s, CH₂), 4.88 (2H, brd, J = 16.5 Hz, olefinic H), 4.95 (2H, d, J = 9.0 Hz, ...
olefinic H), 5.24-5.30 (1H, m, olefinic H), 6.91 (1H, d, J = 2.0 Hz, ArH), 7.10 (1H, d, J = 2.1 Hz, ArH), 7.30-7.34 (4H, m, ArH), 7.43 (2H, t, J = 8.3 Hz, ArH), 7.60 (1H, t, J = 7.6 Hz, ArH), 7.66 (2H, d, J = 8.2 Hz, ArH), 7.71 (2H, d, J = 8.2 Hz, ArH), 7.75 (2H, d, J = 8.5 Hz, ArH), 7.80-7.84 (4H, m, ArH), 7.93 (2H, t, J = 8.3 Hz, ArH), 7.98 (2H, d, J = 8.2 Hz, ArH), 8.03 (2H, d, J = 8.2 Hz, ArH); ^13^C NMR (150 MHz, CDCl_3) δ 21.5 (q), 21.6 (q), 41.7 (t), 49.6 (t), 52.5 (t), 114.7 (s), 119.2 (t), 120.8 (d), 122.8 (s), 122.9 (d), 127.0 (dx2), 127.2 (dx2), 128.6 (dx2), 128.9 (dx2), 129.8 (dx2), 130.1 (dx2), 132.0 (d), 133.7 (d), 135.5 (s), 136.4 (s), 138.2 (s), 143.6 (s), 145.5 (s); MS (ESI-TOF) m/z 621 [M + Na]^+. HRMS (ESI-TOF) m/z: [M+Na]^+ Calcd for C_{29}H_{30}N_{2}O_{6}S_{3}BrNa 621.1164; found 621.1149.

Single X-ray analysis of sulfone was described in the CIF format.

N-[3-(Phenylsulfanylmethyl)-1-tosylpyrrole-4-yl)methyl]-N-methallyl-p-toluenesulfonamide (4b).

To a DMSO (0.5 mL) solution of N-(phenylsulfanylprop-2-ynyl)-N-prop-2-ynyl-p-toluenesulfonamide (1) (50 mg, 0.14 mmol) were added N-methallyl-p-toluenesulfonamide (3b) (63 mg, 0.28 mmol), bis(triphenylphosphine)nickel (II) dichloride (9.2 mg, 0.014 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (21 mg, 0.14 mmol). The reaction mixture was stirred at room temperature for 2 h and then poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was washed with water (50 mL) and dried over MgSO_4. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with chloroform-n-hexane (5:1) to give N-[3-(phenylsulfanylmethyl)-1-tosylpyrrole-4-yl)methyl]-N-methallyl-p-toluenesulfonamide (4b) (37 mg, 45%) as white powders.

mp 96‒99 °C, IR ν 1371, 1336, 1172 (SO_2); ^1^H NMR (600 MHz, CDCl_3) δ 1.46 (3H, s, Me), 2.40 (3H, s, Me), 2.41 (3H, s, Me), 3.61 (2H, s, CH_2), 3.82 (2H, s, CH_2), 4.15 (2H, s, CH_2), 4.61 (1H, s, olefinic H), 4.69 (1H, s, olefinic H), 6.73 (1H, d, J = 2.8 Hz, ArH), 6.82 (1H, d, J = 2.0 Hz, ArH), 7.16–7.21 (5H, m, ArH), 7.24 (2H, brd, J =8.9 Hz, ArH), 7.26 (2H,
d, J = 8.2 Hz, ArH), 7.56 (2H, d, J = 8.9 Hz, ArH), 7.66 (2H, d, J = 8.2 Hz, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 19.7 (q), 21.4 (q), 21.5 (q), 29.2 (t), 42.3 (t), 53.6 (t), 114.0 (t), 119.6 (d), 120.7 (d), 122.4 (s), 123.9 (s), 126.5 (d), 126.7 (d × 2), 127.1 (d × 2), 128.7 (d × 2), 129.6 (d × 2), 129.9 (d × 2), 130.5 (d × 2), 135.4 (s), 135.7 (s), 136.6 (s), 140.2 (s), 143.4 (s), 144.9 (s); MS (EI) 580 ($\text{M}^+_{\text{small}}$), 471, ($\text{M}^+_{\text{small}}$– SPh), 425 ($\text{M}^+_{\text{small}}$– Ts). Anal. Calcd for C$_{30}$H$_{32}$N$_2$O$_4$S$_3$+1/4H$_2$O: C, 61.57; H, 5.60; N, 4.79. Found: C, 61.76; H, 5.63; N, 4.51.

$N$-[3-(Phenylsulfanylmethyl)-1-tosylpyrrole-4-yl)methyl]-$N$-(but-2-yl)-p-toluenesulfonamide (4c).

To a DMSO (1.0 mL) solution of $N$-(phenylsulfanylprop-2-ynyl)-$N$-prop-2-ynyl-p-toluenesulfonamide (1) (50 mg, 0.14 mmol) were added $N$-but-2-ynyl-p-toluenesulfonamide (3c) (63.4 mg, 0.28 mmol), bis(hexafluoroacetylacetonato)nickel(II) hydrate (6.7 mg, 0.014 mmol), bis(triphenylphosphine)palladium(II) dichloride (9.9 mg, 0.014 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (21 mg, 0.14 mmol). The reaction mixture was stirred at room temperature for 10 h and then poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was washed with water (50 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CHCl$_3$-n-hexane (5:1) to give $N$-[3-(phenylsulfanylmethyl)-1-tosylpyrrole-4-yl)methyl]-$N$-(but-2-ynyl)-p-toluenesulfonamide (4c) (66 mg, 80%) as white powder.

Procedure for large scale preparation of 4c: To a DMSO (5.0 mL) solution of $N$-(phenylsulfanylprop-2-ynyl)-$N$-prop-2-ynyl-p-toluenesulfonamide (1) (481 mg, 1.35 mmol) were added $N$-but-2-ynyl-p-toluenesulfonamide (3c) (610 mg, 2.71 mmol), bis(hexafluoroacetylacetonato)nickel(II) hydrate (64 mg, 0.14 mmol), bis(triphenylphosphine)palladium(II) dichloride (95 mg, 0.14 mmol), and
1,8-diazabicyclo[5.4.0]undec-7-ene (0.21 g, 1.35 mmol). The workup procedure gave 4c (341 mg, 43%).

mp 63–65 °C, IR ν 1371, 1337, 1172 (SO$_2$); $^1$H NMR (600 MHz, CDCl$_3$) δ 1.50 (3H, d, $J$ = 6.9 Hz, Me), 2.41 (3H, s, Me), 2.42 (3H, s, Me), 3.62 (2H, d, $J$ = 6.9 Hz, CH$_2$), 3.86 (2H, s, CH$_2$), 4.15 (2H, s, CH$_2$), 5.01–5.07 (1H, m, olefinic H), 5.26–5.32 (1H, m, olefinic H), 6.85 (1H, brs, ArH), 6.86 (1H, brs, ArH), 7.16–7.22 (5H, m, ArH), 7.25 (2H, d, $J$ = 9.6 Hz, ArH), 7.27 (2H, d, $J$ = 7.6 Hz, ArH), 7.59 (2H, d, $J$ = 8.3 Hz, ArH), 7.67 (2H, d, $J$ = 8.2 Hz, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 17.6 (q), 21.5 (q), 21.6 (q), 29.2 (t), 41.7 (t), 48.9 (t), 120.0 (d), 120.5 (d), 122.6 (s), 124.1 (s), 124.8 (d), 126.5 (d), 126.7 (d × 2), 127.2 (d × 2), 128.7 (d × 2), 129.6 (d × 2), 129.9 (d × 2), 130.5 (d × 2), 130.7 (d), 135.5 (s), 135.8 (s), 136.9 (s), 143.3 (s), 145.0 (s); MS (EI) m/z 580 (small M$^+$), 471 (M$^+$–SPh), 425 (M$^+$–Ts). Anal. Calcd for C$_{30}$H$_{32}$N$_2$O$_4$S$_3$+1/4H$_2$O: C, 61.57; H, 5.60; N, 4.79. Found: C, 61.56; H, 5.57; N, 4.84.

N-[(3-(Phenylsulfanylmethyl)-1-tosylpyrrole-4-methyl]-N-cinnamyl-p-toluenesulfonamide (4d).

To a DMSO (1.0 mL) solution of N-(phenylsulfanylprop-2-ynyl)-N-prop-2-ynyl-p-toluenesulfonamide (1) (50 mg, 0.14 mmol) were added N-cinnamyl-p-toluenesulfonamide (3d)$^{28}$ (81 mg, 0.28 mmol), bis(hexafluoroacetylacetonato)-nickel(II) hydrate (6.7 mg, 0.014 mmol), bis(triphenylphosphine)palladium(II) dichloride (9.9 mg, 0.014 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (21 mg, 0.14 mmol). The reaction mixture was stirred at room temperature for 1.5 h and then poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CHCl$_3$-n-hexane (5:1) to give N-[(3-(phenylsulfanylmethyl)-1-tosyl-
N-(3-methyl-2-butenyl)-p-toluenesulfonamide (3e) (67 mg, 0.28 mmol), bis(hexafluoroacetylacetonato)nickel(II) hydrate (7 mg, 0.01 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.12 g, 0.78 mmol). The workup procedure gave 4d (351 mg, 70%).
bis(triphenylphosphine)palladium(II) dichloride (10 mg, 0.01 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (21 mg, 0.14 mmol). The reaction mixture was stirred at room temperature for 17 h and then poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with chloroform-n-hexane (4:1) to give N-[(3-phenylsulfanylmethyl)-1-tosylpyrrole-4-yl)methyl]-N-(3-methyl-2-but enyl)-p-toluene sulfonamide (4e) (62 mg, 74%) as white powders.

mp 42–45 °C, IR ν 1371, 1339, 1173 (SO₂); ¹H NMR (600 MHz, CDCl₃) δ 1.34 (3H, s, Me), 1.53 (3H, s, Me), 2.41 (3H, s, Me), 2.43 (3H, s, Me), 3.70 (2H, d, J = 6.9 Hz, CH₂), 3.88 (2H, s, CH₂), 4.15 (2H, s, CH₂), 4.75-4.77 (1H, m, olefinic H), 6.84 (1H, d, J = 2.1 Hz, ArH), 6.87 (1H, d, J = 2.1 Hz, ArH), 7.17-7.20 (3H, m, ArH), 7.21-7.25 (4H, m, ArH), 7.28 (2H, d, J = 7.5 Hz, ArH), 7.59 (2H, d, J = 8.2 Hz, ArH), 7.67 (2H, d, J = 8.3 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 17.5 (q), 21.5 (q), 21.6 (q), 25.6 (q), 29.2 (t), 41.9 (t), 44.6 (t), 118.2 (d), 120.0 (d), 120.3 (d), 122.6 (s), 124.0 (s), 126.5 (d), 126.7 (d × 2), 127.2 (d × 2), 128.7 (d × 2), 129.6 (d × 2), 129.9 (d × 2), 130.5 (d × 2), 135.5 (s), 135.7 (s), 136.7 (s), 136.8 (s), 143.3 (s), 145.0 (s); MS (ESI-TOF) m/z 617 [M + Na]⁺; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₃₁H₃₄N₂O₄S₃Na 617.1578; found 617.1552. Anal. Calcd for C₃₁H₃₄N₂O₄S₃+1/6H₂O: C, 62.28; H, 5.79; N, 4.69. Found: C, 62.53; H, 5.85; N, 4.39.

To a DMSO (0.5 mL) solution of N-(phenylsulfanylmethyl)-1-tosylpyrrole-4-yl)methyl]-N-(3-butenyl)-p-toluenesulfonamide (4f) added N-(3-butenyl)-p-toluenesulfonamide (3f) (67 mg, 0.28 mmol), bis(hexafluoroacetylacetonato)nickel(II) hydrate (7 mg, 0.01 mmol), bis(triphenylphosphine)palladium(II) dichloride (10 mg, 0.01 mmol), and
1,8-diazabicyclo[5.4.0]undec-7-ene (21 mg, 0.14 mmol). The reaction mixture was stirred at room temperature for 17 h and then poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with chloroform-$n$-hexane (5:1) to give N-[3-(phenylsulfanylmethyl)-1-tosylpyrrole-4-yl)methyl]-N-(3-buteny)-p-toluenesulfonamide (4f) (50 mg, 61%) as white powders.

mp 78–80 °C, IR $\nu$ 1372, 1338, 1173 (SO$_2$); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.99 (2H, dd, $J$=6.9 and 15.1 Hz, CH$_2$), 2.41 (3H, s, Me), 2.43 (3H, s, Me), 3.04 (2H, br t, $J$ = 8.3 Hz, CH$_2$), 3.89 (2H, s, CH$_2$), 4.14 (2H, s, CH$_2$), 4.81 (1H, dd, $J$ = 1.4 and 17.2 Hz, olefinic H), 4.88 (1H, dd, $J$ = 2.1 and 10.3 Hz, olefinic H), 5.41-5.48 (1H, m, olefinic H), 6.88 (1H, d, $J$ = 2.0 Hz, ArH), 6.89 (1H, d, $J$ = 2.7 Hz, ArH), 7.18–7.25 (7H, m, ArH), 7.29 (2H, d, $J$ = 8.3 Hz, ArH), 7.58 (2H, d, $J$ = 8.2 Hz, ArH), 7.68 (2H, d, $J$ = 8.2 Hz, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 21.5 (q), 21.6 (q), 29.2 (t), 33.0 (t), 43.7 (t), 47.4 (t), 116.8 (t), 120.2 (d), 120.4 (d), 122.8 (s), 124.0 (s), 126.6 (d), 126.7 (d × 2), 127.2 (d × 2), 128.7 (d × 2), 129.7 (d × 2), 129.9 (d × 2), 130.6 (d × 2), 134.5 (d), 135.4 (s), 135.7 (s), 136.2 (s), 143.4 (s), 145.0 (s); MS (EI) m/z 580 (small M$^+$), 471 (M$^+$–SPh), 425 (M$^+$–Ts). Anal. Calcd for C$_{30}$H$_{32}$N$_2$O$_4$S$_3$: C, 62.04; H, 5.55; N, 4.82. Found: C, 61.75; H, 5.62; N, 4.74.

N-[3-(Phenylselanylmethyl)-1-tosylpyrrole-4-yl)methyl]-N-methallyl-p-toluenesulfonamide (6b).

To a DMSO (3.0 mL) solution of N-(phenylselanyl)prop-2-ynyl)-N-prop-2-ynyl-p-toluenesulfonamide (2) (300 mg, 0.75 mmol) were added N-methallyl-p-toluenesulfonamide (3b) (336 mg, 1.49 mmol), bis(hexafluoroacetylacetonato)nickel(II) hydrate (35 mg, 0.07 mmol), bis(triphenylphosphine)palladium(II) dichloride (52 mg, 0.07 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.11 g, 0.75 mmol). The reaction mixture was...
stirred at room temperature for 9 h and then poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was washed with water (50 mL) and then dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with chloroform-n-hexane (4:1) to give N-[(3-(phenylselanyl)methyl)-1-tosylpyrrole-4-yl)methyl]-N-methallyl-p-toluenesulfonamide (6b) (0.347 mg, 74%) as white needle crystals. 

mp 98‒102 °C, IR ν 1370, 1335, 1172 (SO$_2$); $^1$H NMR (600 MHz, CDCl$_3$) δ 1.46 (3H, s, Me), 2.42 (3H, s, Me), 2.43 (3H, s, Me), 3.61 (2H, s, CH$_2$), 3.79 (2H, s, CH$_2$), 4.13 (2H, s, CH$_2$), 4.61 (1H, s, olefinic H), 4.69 (1H, s, olefinic H), 6.68 (1H, d, $J$ = 2.0 Hz, ArH), 6.71 (1H, d, $J$ = 2.1 Hz, ArH), 7.15 (2H, t, $J$ = 7.6 Hz, ArH), 7.22-7.24 (1H, m, ArH), 7.26-7.28 (4H, m, ArH), 7.31 (2H, br d, $J$ = 6.9 Hz, ArH), 7.58 (2H, d, $J$ = 8.2 Hz, ArH), 7.67 (2H, d, $J$ = 8.2 Hz, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 19.7 (q), 21.3 (t), 21.5 (q), 21.6 (q), 42.3 (t), 53.6 (t), 113.9 (t), 119.2 (d), 120.7 (d), 122.3 (s), 124.7 (s), 126.7 (d × 2), 127.1 (d × 2), 127.4 (d), 128.8 (d × 2), 129.58 (s), 129.60 (d × 2), 129.8 (d × 2), 133.9 (d × 2), 135.7 (s), 136.6 (s), 140.2 (s), 143.4 (s), 144.9 (s); MS (EI) m/z 471 (M$^+$-SePh), 316 (M$^+$-SePh-Ts). MS (ESI-TOF) m/z 651 [M + Na]$^+$. HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{30}$H$_{32}$N$_2$O$_4$S$_2$SeNa 651.0866; found 651.0871. Anal. Calcd for C$_{30}$H$_{32}$N$_2$O$_4$S$_2$Se+1/4H$_2$O: C, 57.00; H, 5.18; N, 4.43. Found: C, 57.02; H, 4.98; N, 4.19.

N-[(3-Phenylselanyl)methyl]-1-tosylpyrrole-4-yl)methyl]-N-but-2-enyl-p-toluenesulfonamide (6c).

To a DMSO (3.5 mL) solution of N-(phenylselanylprop-2-ynyl)-N-prop-2-ynyl-p-toluenesulfonamide (2) (356 mg, 1.00 mmol) were added N-but-2-enyl-p-toluenesulfonamide (3c) (339 mg, 1.50 mmol), bis(hexafluoroacetylacetonato)nickel(II) hydrate (47 mg, 0.10 mmol), bis(triphenylphosphine)palladium(II) dichloride (70 mg, 0.10 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.15 g, 1.00 mmol). The reaction mixture was
stirred at room temperature for 5.5 h and then poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was washed with water (50 mL) and dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with chloroform-n-hexane (5:1) gave N-[(3-(phenylselanyl)methyl)-1-tosylpyrrole-4-yl)methyl]-N-but-2-enyl-p-toluenesulfonamide (6c) (0.226 mg, 35%) as white powders.

mp 69–72 °C, IR ν 1371, 1334, 1161 (SO₂); ¹H NMR (600 MHz, CDCl₃) δ 1.51 (3H, dd, J=6.9 and 1.4 Hz, Me), 2.42 (3H, s, Me), 2.43 (3H, s, Me), 3.62 (2H, d, J=6.9 Hz, CH₂), 3.82 (2H, s, CH₂), 4.14 (2H, s, CH₂), 5.02-5.07 (1H, m, olefinic H), 5.28-5.34 (1H, m, olefinic H), 6.70 (1H, d, J=2.1 Hz, ArH), 6.84 (1H, d, J=2.1 Hz, ArH), 7.14-7.17 (2H, m, ArH), 7.22-7.24 (1H, m, ArH), 7.26-7.29 (4H, m, ArH), 7.32-7.33 (2H, m, ArH), 7.59 (2H, d, J=8.3 Hz, ArH), 7.68 (2H, d, J=8.2 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 17.6 (q), 21.4 (t), 21.5 (q), 21.6 (q), 41.6 (t), 48.9 (t), 119.6 (d), 120.5 (d), 122.5 (s), 124.8 (d), 124.9 (s), 126.7 (d × 2), 127.2 (d × 2), 127.4 (d), 128.8 (d × 2), 129.6 (d × 2), 129.7 (s), 129.9 (d × 2), 130.7 (d), 133.9 (d × 2), 135.8 (s), 136.9 (s), 143.3 (s), 145.0 (s); MS (EI) m/z 628 (small M⁺), 471 (M⁺-SePh). Anal. Calcd for C₃₀H₃₂N₂O₄S₂Se+1/2H₂O: C, 56.59; H, 5.22; N, 4.40. Found: C, 56.32; H, 5.38; N, 4.45.

N-[(3-(Phenylselanyl)methyl)-1-tosylpyrrole-4-ly)methyl]-N-cinnamyl-p-toluenesulfonamide (6d).

To a DMSO (3.0 mL) solution of N-(phenylselanylprop-2-ynyl)-N-prop-2-ynyl-p-toluenesulfonamide (2) (300 mg, 0.75 mmol) were added N-cinnamyl-p-toluenesulfonamide (3d) (429 mg, 1.49 mmol), bis(hexafluoroacetylacetonato)nickel(II) hydrate (35 mg, 0.07 mmol), bis(triphenylphosphine)palladium(II) dichloride (52 mg, 0.07 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (0.11 g, 0.75 mmol). The reaction mixture was stirred at room temperature for 2.5 h and then poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was washed with water (50 mL) and then dried over MgSO₄. The solvent
was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with chloroform-n-hexane (5:1) to give \( N-[(3\text{-}(\text{phenylselanyl)methyl})-1\text{-tosylpyrrole}-4\text{-yl}]\text{-methyl}]\text{-N-cinnamyl-p-toluenesulfonamide} \) (6d) (0.314 mg, 78%) as white powders.

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\text{mp } 91\text{-}93^\circ C, \text{IR } \nu \text{ 1371, 1341, 1161 (SO}_2\text{);} \quad \text{^1H NMR (600 MHz, CDCl}_3\text{) } \delta 2.39 (3H, s, Me), 2.42 (3H, s, Me), 3.81 (2H, s, CH}_2\text{), 3.85 (2H, d, } J = 6.8 \text{ Hz, CH}_2\text{), 4.19 (2H, s, CH}_2\text{), 5.72 (1H, dt, } J = 15.8 \text{ and 6.9 Hz, olefinic H), 6.20 (1H, d, } J = 15.8 \text{ Hz, olefinic H), 6.71 (1H, d, } J = 2.1 \text{ Hz, ArH), 6.89 (1H, d, } J = 2.1 \text{ Hz, ArH), 7.10\text{-}7.12 (4H, m, ArH), 7.20 (1H, t, } J = 6.8 \text{ Hz, ArH), 7.22\text{-}7.25 (4H, m, ArH), 7.26\text{-}7.30 (5H, m, ArH), 7.58 (2H, d, } J = 8.2 \text{ Hz, ArH), 7.72 (2H, d, } J = 8.2 \text{ Hz, ArH);} \quad \text{^13C NMR (150 MHz, CDCl}_3\text{) } \delta 21.3 (q), 21.5 (q), 21.6 (q), 41.9 (t), 48.9 (t), 119.7 (d), 120.5 (d), 122.2 (s), 123.2 (d), 124.8 (s), 126.3 (d \times 2), 126.7 (d \times 2), 127.2 (d \times 2), 127.3 (d), 127.8 (d), 128.5 (d \times 2), 128.8 (d \times 2), 129.6 (s), 129.7 (d \times 2), 129.9 (d \times 2), 133.9 (d \times 2), 134.2 (d), 135.7 (s), 136.0 (s), 136.7 (s), 143.5 (s), 145.0 (s); \text{ MS (EI) m/z 535 (M}^+\text{-Ts).} \quad \text{Anal. Calcd for C}_{35}H_{34}N_2O_4S_2Se+1/2H_2O: C, 60.16; H, 5.05; N, 4.01. \quad \text{Found: C, 59.86; H, 5.07; N, 3.80.}
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\( N-[(3\text{-}(\text{phenylselanyl)methyl})-1\text{-tosylpyrrole}-4\text{-yl}]\text{-methyl}]\text{-N-(3-methyl-2-butenyl)-p-toluene sulfonamide} \) (6e).

To a DMSO (0.5 mL) solution of \( \text{N-(phenylselanylprop-2-ynyl)} \text{-N-prop-2-ynyl-p-toluenesulfonamide} \) (2) (50 mg, 0.12 mmol) were added \( \text{N-(3-methyl-2-butenyl)-p-tolu} \text{enesulfonamide} \) (3e) (53 mg, 0.25 mmol), bis(hexamfluoroacetyleacetonato)nickel(II) hydrate (6 mg, 0.01 mmol), bis(triphenylphosphine)palladium(II) dichloride (9 mg, 0.01 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (19 mg, 0.12 mmol). The reaction mixture was stirred at room temperature for 14 h and then poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was washed with water (50 mL) and then dried over MgSO\(_4\). The solvent
was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CHCl₃-n-hexane (5:1) to give N-[(3-(phenylselanyl)methyl)-1-tosylpyrrole-4-yl)methyl]-N-(3-methyl-2-butenyl)-p-toluenesulfonamide (6e) (46 mg, 58%) as yellow oil.

IR ν 1371, 1339, 1172 (SO₂); ¹H NMR (600 MHz, CDCl₃) δ 1.35 (3H, s, Me), 1.53 (3H, s, Me), 2.41 (3H, s, Me), 2.43 (3H, s, Me), 3.70 (2H, d, J = 6.9 Hz, CH₂), 3.84 (2H, s, CH₂), 4.14 (2H, s, CH₂), 4.71 (1H, t, J = 6.9 Hz, olefinic H), 6.51 (1H, d, J = 2.0 Hz, ArH), 6.63 (1H, d, J = 2.1 Hz, ArH), 7.15 (2H, t, J = 7.6 Hz, ArH), 7.22 (1H, t, J = 7.6 Hz, ArH), 7.25 (2H, d, J = 6.2 Hz, ArH), 7.28 (2H, d, J = 8.3 Hz, ArH), 7.33 (2H, d, J = 6.9 Hz, ArH), 7.59 (2H, d, J = 8.3 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 17.5 (q), 21.4 (t), 21.5 (q), 21.6 (q), 25.7 (q), 41.9 (t), 44.6 (t), 118.3 (d), 119.6 (d), 120.3 (d), 122.5 (s), 124.9 (s), 126.8 (d × 2), 127.2 (d × 2), 127.4 (d), 128.8 (d × 2), 129.6 (d × 2), 129.8 (s), 129.9 (d × 2), 134.0 (d × 2), 135.8 (s), 136.7 (s), 136.9 (s), 143.2 (s), 145.0 (s); MS (ESI-TOF) m/z 665 [M + Na]+. HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for C₃₁H₃₄N₂O₄S₂SeNa 665.1023; found 665.1025.

N-[(3-(Phenylselanyl)methyl)-1-tosylpyrrole-4-yl)methyl]-N-(3-butenyl)-p-toluenesulfonamide (6f).

To a DMSO (0.5 mL) solution of N-(phenylselanyl)prop-2-ynyl-N-prop-2-ynyl-p-toluenesulfonamide (2) (50 mg, 0.12 mmol) were added N-(3-butenyl)-p-toluenesulfonamide (3f) (56 mg, 0.25 mmol), bis(hexafluoroacetylacetonato)nickel(II) hydrate (6 mg, 0.01 mmol), bis(triphenylphosphine)palladium(II) dichloride (9 mg, 0.01 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (19 mg, 0.12 mmol). The reaction mixture was stirred at room temperature for 15 h and then poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was washed with water (50 mL) and then dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CHCl₃-n-hexane (5:1) to give N-[(3-(phenylselanyl)methyl)-1-tosylpyrrole-4-yl)methyl]-N-(3-methyl-2-butenyl)-p-toluenesulfonamide (6e) (46 mg, 58%) as yellow oil.
chromatography on silica gel eluting with chloroform-\textit{n}-hexane (5:1) to give \(N\)-[(3-\textit{phenylselenylmethyl})-1-tosylpyrrole-4-yl)methyl]-\(N\)-(3-but enyl)-\(p\)-toluenesulfonamide (6f) (52 mg, 67%) as white powder.

mp 76–78 °C, IR v 1371, 1339, 1172 (SO\(_2\)); \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 1.99 (2H, dd, \(J = 6.8\) and 15.1 Hz, CH\(_2\)), 2.40 (3H, s, Me), 2.43 (3H, s, Me), 3.04 (2H, brt, \(J = 8.2\) Hz, CH\(_2\)), 3.85 (2H, s, CH\(_2\)), 4.13 (2H, s, CH\(_2\)), 4.81 (1H, dd, \(J = 1.3\) and 17.1 Hz, olefinic H), 4.87 (1H, brd, \(J = 10.3\) Hz, olefinic H), 5.41-5.48 (1H, m, olefinic H), 6.73 (1H, d, \(J = 2.8\) Hz, ArH), 6.88 (1H, d, \(J = 2.7\) Hz, ArH), 7.14-7.17 (2H, m, ArH), 7.21-7.26 (3H, m, ArH), 7.29 (2H, d, \(J = 8.3\) Hz, ArH), 7.33 (2H, brd, \(J = 6.8\) Hz, ArH), 7.58 (2H, d, \(J = 8.3\) Hz, ArH), 7.68 (2H, d, \(J = 8.2\) Hz, ArH); \(^1^3\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 21.4 (t), 21.5 (q), 21.6 (q), 33.0 (t), 43.6 (t), 47.4 (t), 116.7 (t), 119.8 (d), 120.3 (d), 122.7 (s), 124.8 (s), 126.7 (d × 2), 127.2 (d × 2), 127.4 (d), 128.8 (d × 2), 129.6 (s), 129.7 (d × 2), 129.9 (d × 2), 134.0 (d × 2), 134.5 (d), 135.7 (s), 136.2 (s), 143.4 (s), 145.0 (s); MS (ESI-TOF) m/z 651 [M + Na]^+.

HRMS (ESI-TOF) m/z: [M+Na]^+ Calcd for C\(_{30}\)H\(_{32}\)N\(_2\)O\(_4\)S\(_2\)SeNa 651.0866; found 651.0874.

Anal. Calcd for C\(_{30}\)H\(_{32}\)N\(_2\)O\(_4\)S\(_2\)Se: C, 57.41; H, 5.14; N, 4.46. Found: C, 57.17; H, 5.00; N, 4.27.

\(N\)-[(3-\textit{phenylsulfanyl)methyl]-1-tosylpyrrole-4-yl)methyl]-\(N\)-\textit{methallyl}-\(p\)-tolu enesulfonamide (4b). \(m\)-Chloroperbenzoic acid (71 mg, 0.41 mmol) was added over 0.5 h to a 1,2-dichloroethane (10.0 mL) solution of \(N\)-[(3-\textit{phenylsulfanyl)methyl]-1-tosylpyrrole-4-yl)methyl]-\(N\)-\textit{methallyl}-\(p\)-tolu enesulfonamide (4b) (238 mg, 0.41 mmol) at 0 °C. The reaction mixture was further stirred for 10 min and poured into a sat. NaHCO\(_3\) (50 mL). The whole was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was washed with a sat. NaHCO\(_3\) (50 mL) and then dried over MgSO\(_4\). The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-\textit{n}-hexane (1:2) to give
N-[3-(phenylsulfinymethyl)-1-tosylpyrrole-4-yl)methyl]-N-methallyl-p-toluenesulfonamide (5b) (196 mg, 80%) as white powder.

mp 154–158 °C, IR ν 1372, 1335, 1173 (SO₂), 1092 (SO); ¹H NMR (600 MHz, CDCl₃) δ 1.36 (3H, s, Me), 2.43 (6H, s, Me × 2), 3.51 (2H, s, CH₂), 3.73 (1H, d, J = 15.1 Hz, CH), 3.80 (1H, d, J = 15.1 Hz, CH), 3.83 (1H, d, J = 13.8 Hz, CH), 4.08 (1H, d, J = 13.8 Hz, CH), 4.54 (1H, s, olefinic H), 4.62 (1H, s, olefinic H), 6.78 (1H, s, ArH), 6.94 (1H, d, J=2.1 Hz, ArH), 7.28-7.37 (8H, m, ArH), 7.42 (1H, t, J = 6.9 Hz, ArH), 7.61 (2H, d, J = 7.6 Hz, ArH), 7.70 (2H, d, J = 7.5 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 19.8 (q), 21.5 (q), 21.6 (q), 42.6 (t), 52.6 (t), 53.8 (t), 113.9 (t), 115.8 (s), 120.7 (d), 121.7 (d), 122.9 (s), 124.3 (d × 2), 127.0 (d × 2), 127.1 (d × 2), 128.7 (d × 2), 129.7 (d × 2), 130.0 (d × 2), 130.9 (d), 135.6 (s), 136.2 (s), 140.3 (s), 142.8 (s), 143.6 (s), 145.3 (s); MS (EI) m/z 471 (M⁺-PhSO), 316 (M⁺-PhSO-Ts); MS (ESI-TOF) m/z 619 [M + Na⁺]. HRMS (ESI-TOF) m/z: [M+Na⁺]+ Calcd for C₃₀H₃₂N₂O₅S₂S₃Na 619.1371; found 619.1344. Anal. Calcd for C₃₀H₃₂N₂O₅S₃⁺1/2H₂O: C, 59.48; H, 5.49; N, 4.62. Found: C, 59.33; H, 5.55; N, 4.57.

(E)-N-(But-2-enyl)-N-[3-(phenylsulfinymethyl)-1-tosylpyrrol-4-yl)methyl]-N-p-toluene-sulfonamide (5c).

m-Chloroperbenzoic acid (86 mg, 0.50 mmol) was portionwise added over 1 h to a 1,2-dichloroethane (15.0 mL) solution of N-[3-(phenylsulfinylmethyl)-1-tosylpyrrole-4-yl)methyl]-N-(but-2-enyl)-p-toluenesulfonamide (4c) (290 mg, 0.50 mmol) at 0 °C. The reaction mixture was further stirred for 5 min and poured into a sat. NaHCO₃ (50 mL). The whole was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was washed with a sat. NaHCO₃ (50 mL) and then dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give (E)-N-(but-2-enyl)-N-[3-(phenylsulfinylmethyl)-1-tosylpyrrol-4-yl)methyl]-N-p-toluene-sulfonamide (5c) (230 mg, 77%) as white powder.
mp 143–146 °C. IR ν 1372, 1335 (SO₂), 1091 (SO); ¹H NMR (600 MHz, CDCl₃) δ 1.48 (3H, d, J = 6.9 Hz, Me), 2.43 (3H, s, Me), 2.44 (3H, s, Me), 3.51 (1H, dd, J = 6.9 and 15.8 Hz, CH), 3.57 (1H, dd, J = 6.9 and 15.1 Hz, CH), 3.78 (1H, d, J = 15.1 Hz, CH), 3.80 (1H, d, J = 13.8 Hz, CH), 3.84 (1H, d, J = 13.8 Hz, CH), 4.11 (1H, d, J = 13.8 Hz, CH), 4.88–4.93 (1H, m, olefinic H), 5.23–5.29 (1H, m, olefinic H), 6.86 (1H, d, J = 2.1 Hz, ArH), 7.06 (1H, d, J = 2.1 Hz, ArH), 7.30 (2H, d, J = 8.3 Hz, ArH), 7.33–7.36 (4H, m, ArH), 7.42–7.44 (3H, m, ArH), 7.62 (2H, d, J = 8.2 Hz, ArH), 7.74 (2H, d, J = 8.2 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 17.6 (q), 21.5 (q), 21.7 (q), 41.5 (t), 48.7 (t), 52.8 (t), 116.2 (s), 120.4 (d), 122.3 (d), 122.6 (s), 124.2 (d), 124.4 (d × 2), 127.0 (d × 2), 127.2 (d × 2), 128.7 (d × 2), 129.7 (d × 2), 130.1 (d × 2), 130.8 (d), 130.9 (d), 135.6 (s), 136.6 (s), 143.0 (s), 143.5 (s), 145.4 (s); MS (EI) m/z 471 (M⁺-PhSO). MS (ESI-TOF) m/z: [M+Na]⁺. HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₃₀H₃₂N₂O₅S₃Na 619.1371; found 619.1384. Anal. Calcd for C₃₀H₃₂N₂O₅S₃+1/4H₂O: C, 59.93; H, 5.45; N, 4.66. Found: C, 59.85; H, 5.21; N, 4.61.

4-(N-Cinnamyl-N-tosylaminomethyl)-3-(phenylsulfinylmethyl)-N-tosylpyrrole (5d).

![Chemical structure](image)
m-Chloroperbenzoic acid (94 mg, 0.55 mmol) was portionwise added over 1 h to a 1,2-dichloroethane (15.0 mL) solution of 4-(N-cinnamyl-N-tosylaminomethyl)-3-(phenylsulfinylmethyl)-N-tosylpyrrole (4d) (351 mg, 0.55 mmol) at 0 °C. The reaction mixture was further stirred for 5 min and poured into a sat. NaHCO₃ (50 mL). The whole was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was washed with a sat. NaHCO₃ (50 mL) and then dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give 4-(N-cinnamyl-N-tosylaminomethyl)-3-(phenylsulfinylmethyl)-N-tosylpyrrole (5d) (301 mg, 84%) as white powder. mp 50–53 °C, IR ν 1372, 1337, 1171 (SO₂), 1067 (SO); ¹H NMR (600 MHz, CDCl₃) δ 2.42 (3H, s, Me), 2.45 (3H, s, Me), 3.72 (1H, dd, J = 6.9 and 15.8 Hz, CH), 3.79–3.87 (4H, m,
m-Chloroperbenzoic acid (14 mg, 0.08 mmol) was added over 15 min to a 1,2-dichloroethane (3.0 mL) solution of N-[3-(phenylsulfinylmethyl)-1-tosylpyrrole-4-yl)methyl]-N-(3-methyl-2-butenyl)-p-toluene-sulfonamide (4e) (47 mg, 0.08 mmol) at 0 °C. The reaction mixture was further stirred for 15 min and poured into a sat. NaHCO₃ (50 mL). The whole was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was washed with a sat. NaHCO₃ (50 mL) and then dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give N-[3-(phenylsulfinylmethyl)-1-tosylpyrrole-4-yl)-methyl]-N-(3-methyl-2-butenyl)-p-toluene-sulfonamide (5e) (40 mg, 83%) as white powder. mp 62 – 64 °C, IR ν 1373, 1338, 1159 (SO₂), 1068 (SO); ¹H NMR (600 MHz, CDCl₃) δ 1.36 (3H, s, Me), 1.50 (3H, s, Me), 2.43 (3H, s, Me), 2.45 (3H, s, Me), 3.55-3.65 (2H, m, CH₂), 3.76 (1H, d, J = 14.5 Hz, CH), 3.82 (1H, d, J = 14.5 Hz, CH), 3.84 (1H, d, J = 13.7 Hz, CH), 4.13 (1H, d, J = 13.8 Hz, CH), 4.59-4.61 (1H, m, olefinic H), 6.84 (1H, d, J = 2.0 Hz, ArH), 7.08 (1H, d, J = 2.0 Hz, ArH), 7.30 (2H, d, J = 8.3 Hz, ArH), 7.33 (2H, d, J = 8.2
N-[(3-(Phenylsulfinyl)methyl)-1-tosylpyrrole-4-yl)methyl]-N-(3-butenyl)-p-toluenesulfonamide (5f).

m-Chloroperbenzoic acid (54 mg, 0.31 mmol) was added over 0.5 h to a 1,2-dichloroethane (11.0 mL) solution of N-[(3-(phenylsulfinyl)methyl)-1-tosylpyrrole-4-yl)methyl]-N-(3-butenyl)-p-toluenesulfonamide (4f) (181 mg, 0.31 mmol) at 0 °C. The reaction mixture was further stirred for 15 min and poured into a sat. NaHCO₃ (50 mL). The whole was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was washed with a sat. sodium hydrogen carbonate (50 mL) and then dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give N-[(3-(phenylsulfinyl)methyl)-1-tosylpyrrole-4-yl)methyl]-N-(3-butenyl)-p-toluenesulfonamide (5f) (174 mg, 94%) as white powders.

mp 126–129 °C, IR ν 1373, 1334, 1161 (SO₂), 1066 (SO); ¹HNMR (600 MHz, CDCl₃) δ 1.75–1.95 (2H, m, CH₂), 2.42 (3H, s, Me), 2.44 (3H, s, Me), 2.92-2.98 (2H, m, CH₂), 3.73 (1H, d, J = 14.5 Hz, CH), 3.79 (1H, d, J = 14.4 Hz, CH), 3.84 (1H, d, J = 13.8 Hz, CH), 4.14 (1H, d, J = 13.7 Hz, CH), 4.76 (1H, dd, J = 1.4 and 17.2 Hz, olefinic H), 4.85 (1H, d, J = 10.3 Hz, olefinic H), 5.35–5.42 (1H, m, olefinic H), 6.92 (1H, d, J = 2.7 Hz, ArH), 7.08 (1H, d, J = 2.0 Hz, ArH), 7.31 (4H, t, J = 6.9 Hz, ArH), 7.35 (2H, br t, J = 8.3 Hz, ArH), 7.43
(3H, t, J = 8.2 Hz, ArH), 7.63 (2H, d, J = 8.3 Hz, ArH), 7.73 (2H, d, J = 8.2 Hz, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 21.5 (q), 21.6 (q), 32.9 (t), 43.8 (t), 47.4 (t), 52.6 (t), 116.1 (s), 116.8 (t), 120.0 (d), 122.5 (d), 123.1 (s), 124.3 (d × 2), 126.9 (d × 2), 127.1 (d × 2), 128.7 (d × 2), 129.8 (d × 2), 130.1 (d × 2), 130.8 (d × 2), 134.3 (d), 135.5 (s), 135.7 (s), 142.9 (s), 143.6 (s), 145.4 (s); MS (ESI) m/z (ESI-TOF) 619 [M + Na]$^+$; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{30}$H$_{32}$N$_2$O$_5$S$_3$Na 619.1371; found 617.1377. Anal. Calcd for C$_{30}$H$_{32}$N$_2$O$_5$S$_3$+1/3H$_2$O: C, 59.78; H, 5.46; N, 4.65. Found: C, 59.90; H, 5.33; N, 4.71.

Typical procedure for Pummerer reaction of 5a with TFAA and successive treatment with TBAH, synthesis of diol 9a.

Trifluoroacetic anhydride (180 mg, 0.85 mmol) was added dropwise to a dichloromethane (2.0 mL) solution of N-allyl-N-[(3-(phenylsulfinylmethyl)-1-toslypyrrole-4-yl)-methyl]-p-toluenesulfonamide (5a) (50 mg, 0.09 mmol) at −20 °C. The reaction mixture was stirred for 0.5 h and poured into a sat. sodium hydrogen carbonate (50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. To the residue in dichloromethane (2.5 mL) were added tetrabutylammonium hydroxide (0.22 g, 0.86 mmol) in H$_2$O (2 mL) and tetrabutylammonium hydrogensulfate (5.8 mg, 1.7 × 10$^{-2}$ mmol) at room temperature. The mixture was stirred for 10 h and poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give N-(3-hydroxy-2-(phenylthio)propyl)-N-((4-(hydroxymethyl)-1-tosyl-1H-pyrrol-3-yl)methyl)-4-methylbenzenesulfonamide (9a) (48 mg, 93 %) as white powders (entry 10, Table 1).
mp 57–61 °C, IR ν 3432 (OH), 1369, 1338, 1172 (SO₂), 1067 (SO); ¹H NMR (600 MHz, CDCl₃) δ 2.37 (3H, s, Me), 2.43 (3H, s, Me), 2.96 (1H, dd, J = 4.8 and 14.4 Hz, CH), 3.05 (1H, dd, J = 4.8 and 9.6 Hz, CH), 3.47 (1H, dd, J = 9.6 and 14.4 Hz, CH), 3.54 (1H, dd, J = 3.4 and 12.4 Hz, CH), 3.66 (1H, dd, J = 3.4 and 12.4 Hz, CH), 3.87 (1H, d, J = 14.4 Hz, CH), 4.28 (1H, d, J = 14.4 Hz, CH), 4.48 (1H, d, J = 13.1 Hz, CH), 4.53 (1H, d, J = 13.0 Hz, CH), 6.88 (1H, d, J = 2.8 Hz, ArH), 7.09 (1H, d, J = 2.1 Hz, ArH), 7.21 (1H, brd, J = 6.8 Hz, ArH), 7.25-7.27 (3H, m, ArH), 7.29 (4H, brd, J = 7.6 Hz, ArH), 7.60 (2H, d, J = 8.2 Hz, ArH), 7.70 (2H, d, J = 8.3 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 21.5 (q), 21.6 (q), 46.3 (t), 50.2 (t), 50.3 (d), 56.2 (t), 61.4 (t), 119.9 (d), 120.9 (d), 122.1 (s), 126.9 (d × 2), 127.3 (d × 2), 127.4 (d), 128.0 (s), 129.2 (d × 2), 130.0 (d × 2), 131.9 (d × 2), 133.3 (s), 134.4 (s), 135.6 (s), 144.2 (s), 145.4 (s); MS (EI) m/z 600 (small M⁺), 445 (M⁺-Ts).

MS (ESI-TOF) m/z 623 [M + Na⁺]; HRMS (ESI-TOF) m/z: [M+Na⁺] Calcd for C₂₉H₃₂N₂O₆S₃Na 623.13202; found 623.12954. Anal. Calcd for C₂₉H₃₂N₂O₆S₃+1/2H₂O: C, 57.12; H, 5.46; N, 4.59. Found: C, 57.01; H, 5.25; N, 4.41.

3-Acetoxyethyl-4-(N-allyl-N-tosylaminomethyl)-1-(tosyl)pyrrole (7a), entry 1, Table 1.

To an acetic acid (0.50 mL) solution of 5a (20 mg, 0.03 mmol) solution was added acetic anhydride (17.5 mg, 0.17 mmol) at room temperature. The reaction mixture was heated at 120 °C for 6 h and then cooled mixture was poured into water (50 mL). The organic layer was separated and then the aqueous layer was extracted with AcOEt. The combined organic layer was washed with water (50 mL) and then saturated sodium hydrogen carbonate (50 mL) and dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with EtOAc-n-hexane (1:3) to give the tilted compound 7a (14 mg, 86%) as a yellow oil.

IR ν 1739 (CO), 1374, 1172, 1068 (SO₂); ¹H NMR (600 MHz, CDCl₃) δ 2.03 (3H, s, Me), 2.41 (3H, s, Me), 2.44 (3H, s, Me), 3.68 (2H, d, J = 6.8 Hz, CH₂), 4.16 (2H, s, CH₂), 4.86 (1H, dd, J = 1.4 and 17.2 Hz, olefinic H), 4.89 (1H, s, CH₂), 4.96-4.98 (1H, m, olefinic H), 5.35-5.42 (1H, m, olefinic H), 6.91 (1H, d, J = 2.3 Hz, ArH), 7.12 (1H, d, J = 2.3 Hz, ArH), 7.30 (2H, d, J = 7.4 Hz, ArH), 7.30 (2H, d, J = 8.0 Hz, ArH), 7.68 (2H, d, J = 8.3 Hz, ArH), 7.73 (2H, d, J = 8.2 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 20.9 (q), 21.5 (q), 21.6 (q), 41.9 (t), 49.6 (t), 57.7 (t), 119.0 (t), 120.6 (d), 121.0 (d), 122.4 (s), 122.7 (s), 127.0 (d × 2), 127.2 (d × 2), 129.7 (d × 2), 130.1 (d × 2), 132.3 (d), 135.7 (s), 136.8 (s), 143.5 (s), 145.3
4-(N-Allyl-N-tosylaminomethyl)-1-(tosyl)pyrrol-3-carboxaldehyde (8a), entry 7, Table 1.

To a THF (0.50 mL) solution of 5a (20 mg, 0.03 mmol) was added trifluoroacetic anhydride (36 mg, 0.10 mL, 0.17 mmol) at −20 °C. The reaction mixture was stirred for 0.5 h then poured into a saturated sodium hydrogen carbonate (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was dried over MgSO4. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with EtOAc-n-hexane (1:3) to give the titled compound (14 mg, 86%) as colorless prisms (mp 109-110 °C).

IR ν 1683 (CO), 1381, 1344, 1175, 1063 (SO2); 1H NMR (600 MHz, CDCl3) δ 2.43 (3H, s, Me), 2.44 (3H, s, Me), 3.81 (2H, d, J = 6.2 Hz, CH2), 4.42 (2H, s, CH2), 4.94-4.99 (2H, m, olefinic H), 5.48-5.52 (1H, m, olefinic H), 7.18 (1H, s, ArH), 7.28 (2H, d, J = 8.2 Hz, ArH), 7.36 (2H, d, J = 8.2 Hz, ArH), 7.67 (2H, d, J = 8.3 Hz, ArH), 7.69 (1H, d, J = 4.0 Hz, ArH), 7.81 (2H, d, J = 8.3 Hz, ArH), 9.76 (1H, s, CHO); 13C NMR (150 MHz, CDCl3) δ 21.5 (q), 21.7 (q), 43.1 (t), 51.4 (t), 119.1 (t), 121.5 (d), 124.6 (s), 126.8 (s), 127.2 (d × 2), 127.4 (d × 2), 129.7 (d × 2), 129.8 (d), 130.4 (d × 2), 132.3 (d), 134.7 (s), 136.6 (s), 143.5 (s), 146.3 (s), 185.8 (d); MS (ESI-TOF) m/z 495 [M + Na]+; HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for C23H24N2O5S2Na 495.1024; Found 495.1019.
Pummerer reaction of pyrrole 5b with TFAA and successive treatment with TBAH.

Trifluoroacetic anhydride (88 mg (0.10 mL), 0.42 mmol) was added dropwise to a dichloromethane (2.0 mL) solution of N-methallyl-N-[(3-(phenylsulfinyl)methyl)-1-tosylpyrrole-4-yl)methyl]-p-toluenesulfonamide (5b) (50 mg, 0.08 mmol) at −20 °C. The reaction mixture was stirred for 0.5 h and poured into a sat. NaHCO₃ (50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure to give the residue. To the residue in dichloromethane (2.5 mL) were added tetrabutylammonium hydroxide (0.22 g, 0.80 mmol) in H₂O (2.0 mL) and tetrabutylammonium hydrogen sulfate (5.7 mg, 1.6 × 10⁻² mmol) at room temperature. The mixture was stirred for 10 h and poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with CHCl₃. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give 1,5-bis(p-toluenesulfonyl)-1,4,5,6,8-hexahydro-7-methyl-7-(phenylsulfanyl)pyrrolo-[3,2-c]azepin-3-methanol (11b) (29 mg, 58%) as white powder.

mp 61–65 °C, IR ν 3456 (OH), 1363, 1169, 1046 (SO₂), 1091 (SO); ¹H NMR (600 MHz, CDCl₃) δ 1.33 (3H, s, Me), 1.65 (1H, s, OH), 2.36 (3H, s, Me), 2.40 (3H, s, Me), 2.81 (1H, d, J = 11.7 Hz, CH), 3.40 (1H, d, J = 12.4 Hz, CH), 3.45 (1H, d, J = 11.7 Hz, CH), 3.68 (1H, d, J = 13.0 Hz, CH), 3.95 (1H, d, J = 14.5 Hz, CH), 4.01 (1H, d, J = 14.5 Hz, CH), 4.46 (2H, s, CH₂), 7.17 (1H, t, J = 7.5 Hz, ArH), 7.19 (2H, d, J = 8.3 Hz, ArH), 7.23-7.26 (3H, m, ArH), 7.29 (2H, d, J = 8.2 Hz, ArH), 7.34 (2H, d, J = 6.8 Hz, ArH), 7.46 (2H, d, J = 9.0 Hz, ArH), 7.67 (2H, d, J = 8.2 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 21.5 (q), 21.6 (q), 22.5 (q), 40.2 (s), 40.9 (t), 43.7 (t), 54.9 (t), 56.8 (t), 121.4 (s), 123.0 (s), 123.5 (d), 125.8 (d), 126.3 (d × 2), 127.7 (d × 2), 128.7 (d × 2), 129.3 (d × 2), 129.9 (d × 2), 132.9 (s), 134.5 (s), 136.8 (s), 137.1 (s), 143.7 (s), 144.9 (s); MS (El) m/z 596 (M⁺), 441 (M⁺–Ts).
MS (ESI-TOF) m/z 619 [M + Na]^+; HRMS (ESI-TOF) m/z: [M+Na]^+ Calcd for C_{30}H_{32}N_{2}O_{5}S_{3}Na 619.1371; found 619.1351.

Pummerer reaction of pyrrole 5c with TFAA and successive treatment with TBAH.

**Trifluoroacetic anhydride (88 mg, 0.42 mmol) was added dropwise to a dichloromethane (2.0 mL) solution of N-[3-(phenylsulfanyl)methyl]-1-tosyl[pyrrole-4-yl]methyl]-N-(but-2-enyl)-p-toluenesulfonamide (5c) (50 mg, 0.08 mmol) at −20 °C. The reaction mixture was stirred for 0.5 h and poured into a sat. NaHCO₃ (50 mL). The organic layer was separated and the aqueous layer was extracted with CHCl₃. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. To the residue in dichloromethane (2.5 mL) were added tetrabutylammonium hydroxide (0.22 g, 0.80 mmol) in H₂O (2 mL) and tetrabutylammonium hydrogensulfate (5.7 mg, 1.6 × 10⁻² mmol) at room temperature. The mixture was stirred for 10 h and poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with CHCl₃. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give N-(3-hydroxy-2-(phenylthio)butyl)-N-((4-(hydroxymethyl)-1H-pyrrol-3-yl)methyl)-4-methylbenzenesulfonamide (9c) (33 mg, 64%) as white powder.

mp 53–57 °C, IR ν 3431 (OH), 1366, 1342, 1172 (SO₂), 1067 (SO); ¹H NMR (600 MHz, CD₃OD) δ 0.90 (3H, d, J = 6.2 Hz, Me), 2.40 (3H, s, Me), 2.44 (3H, s, Me), 3.03 (1H, dd, J = 6.8 and 14.5 Hz, CH), 3.30 (1H, dd, J = 8.3 and 14.5 Hz, CH), 3.45-3.48 (1H, m, CH), 3.87-3.90 (1H, m, CH), 4.00 (1H, d, J = 15.2 Hz, CH), 4.24 (1H, d, J = 14.4 Hz, CH), 4.45 (1H, d, J = 13.1 Hz, CH), 4.48 (1H, d, J = 13.1 Hz, CH), 6.82 (1H, d, J = 2.1 Hz, ArH), 7.12 (1H, br s, ArH), 7.27–7.33 (8H, m, ArH), 7.51 (2H, d, J = 8.2 Hz, ArH), 7.64 (1H, s, ArH), 7.73 (2H, d, J = 8.2 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 18.6 (q), 21.47 (q), 21.53 (q), 46.1 (t), 49.4 (t), 56.1 (d), 56.2 (t), 66.9 (d), 119.8 (d), 120.6 (d), 121.8 (s), 126.9 (d × 2),
127.3 (d × 3), 128.3 (s), 129.1 (d × 2), 129.8 (d × 2), 130.0 (d × 2), 131.9 (d × 2), 133.7 (s), 134.2 (s), 135.6 (s), 144.0 (s), 145.2 (s); MS (EI) m/z 459 (M⁺–Ts). MS (EI) m/z 637 [M + Na⁺]. HRMS (ESI-TOF) m/z: [M+Na⁺] Calcd for C₃₀H₃₄N₂O₆S₃Na 637.1477; found 637.1466.

Pummerer reaction of pyrrole 5d with TFAA and successive treatment with TBAH.

![Pummerer reaction of pyrrole 5d with TFAA and successive treatment with TBAH.](image)

Trifluoroacetic anhydride (0.24 g, 1.14 mmol) was added dropwise to a dichloromethane (2.0 mL) solution of N-cinnamyl-N-[3-(phenylsulfanyl)methyl]-1-tosylpyrrole-4-methy]-p-toluenesulfonamide (5d) (50 mg, 0.08 mmol) at -20 °C. The reaction mixture was stirred for 0.5 h and poured into a sat. sodium hydrogen carbonate (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. To the residue in dichloromethane (2.5 mL) were added tetrabutylammonium hydroxide (0.22 g, 0.80 mmol) in H₂O (2.0 mL) and tetrabutylammonium hydrogensulfate (5.2 mg, 1.6 × 10⁻² mmol) at room temperature. The whole was stirred for 2 h and poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was washed with water (50 mL) and dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) gave 1,5-bis(p-toluenesulfonyl)-1,4,5,6,7,8-hexahydro-8-phenyl-7-(phenylsulfanyl)pyrrolo-[3,2-c]azepin-3-methanol (11d) (33 mg, 66%) as white powders.

mp 90–94 °C, IR ν 3535 (OH), 1167 (SO₂), 1093 (SO); ¹H NMR (800 MHz, CDCl₃) δ 2.22 (3H, s, Me), 2.38 (3H, s, Me), 3.16 (1H, dd, J = 2.5 and 13.6 Hz, CH), 3.76 (1H, ddd, J = 2.5 and 4.5 and 5.2 Hz, CH), 3.80 (1H, ddd, J = 1.6 and 5.2 and 13.6 Hz, CH), 3.89 (1H, d, J = 15.6 Hz, CH), 4.53/4.57 (each 1H, d, J = 12.5 Hz, CH × 2), 4.59 (1H, dd, J = 1.6 and 15.6 Hz, CH), 5.37 (1H, d, J = 4.5 Hz, CH), 6.74 (2H, dm, J = ca. 7.4 Hz, ArH), 6.86 (2H, dm, J = ca. 8.4 Hz, ArH), 7.07 (2H, tm, J = ca. 7.4 Hz, ArH), 7.10 (1H, tm-like, J = ca. 7.4
Hz, ArH), 7.24 (2H, m, ArH), 7.30 (1H, tm, $J = ca. 7.4$ Hz, ArH), 7.35 (2H, dm, $J = ca. 7.4$ Hz, ArH), 7.38 (1H, br s-like, ArH), 7.46 (2H, dm, $J = ca. 8.4$ Hz, ArH); $^{13}$C NMR (200 MHz, CDCl$_3$) $\delta$ 21.4 (q), 21.5 (q), 44.3 (t), 46.6 (d), 49.9 (t), 54.6 (d), 56.8 (t), 120.9 (d), 124.0 (s), 124.1 (s), 126.5 (d), 126.9 (d $\times$ 2), 127.37 (d $\times$ 2), 127.38 (d), 128.0 (d $\times$ 2), 128.6 (d $\times$ 2), 129.1 (d $\times$ 2), 129.4 (d $\times$ 2), 129.7 (d $\times$ 2), 130.8 (s), 132.2 (d $\times$ 2), 135.2 (s), 135.35 (s), 135.42 (s), 138.9 (s), 143.5 (s), 144.5 (s); MS (EI) m/z 658 (M$^+$), 549 (M$^+$-SPh), 503 (M$^+$-Ts). Anal. Calcd for C$_{35}$H$_{34}$N$_2$O$_5$S$_3$: C, 61.29; H, 5.44; N, 4.08. Found: C, 61.05; H, 5.26; N, 4.04.

Pummerer reaction of pyrrole 5e with TFAA and successive treatment with TBAH.

Trifluoroacetic anhydride (60 mg, 0.29 mmol) was added dropwise to a dichloromethane (2.0 mL) solution of $N$-(3-methyl-2-butenyl)-$N$-[(3-(phenylsulfinylmethyl)-1-tosylpyrrole-4-yl)methyl]$\cdot$p-toluenesulfonamide (5e) (35 mg, 0.06 mmol) at $-20$ °C. The reaction mixture was stirred for 1 h and poured into a sat. sodium hydrogen carbonate (50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure to give the residue. To the residue in dichloromethane (2 mL) were added tetrabutylammonium hydroxide (0.15 g, 0.57 mmol) in H$_2$O (1.5 mL) and tetrabutylammonium hydrogensulfate (3.9 mg, $1 \times 10^{-2}$ mmol) at room temperature. The mixture was stirred for 0.5 h and poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with CHCl$_3$. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-$n$-hexane (1:2) to give $N$-(3-hydroxy-3-methyl-2-(phenylthio)butyl)-$N$-[(4-(hydroxymethyl)-1-tosyl-1H-pyrrol-3-yl)methyl]-4-methylbenzenesulfonamide (9e) (33 mg, 64%) as white powders. mp 53–55 °C, IR $\nu$ 3421 (OH), 1371, 1337 (SO$_2$), 1067 (SO); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.14 (3H, s, Me), 1.15 (3H, s, Me), 2.39 (3H, s, Me), 2.43 (3H, s, Me), 2.61 (1H, brs, OH),
3.00 (1H, dd, J = 9.6 and 15.1 Hz, CH), 3.42 (1H, dd, J = 4.1 and 9.6 Hz, CH), 3.61 (1H, dd, J = 4.1 and 15.1 Hz, CH), 3.98 (1H, d, J = 15.1 Hz, CH), 4.37 (1H, d, J = 15.1 Hz, CH), 4.38 (2H, s, CH$_2$), 6.80 (1H, d, J = 2.1 Hz, ArH), 7.03 (1H, d, J = 2.1 Hz, ArH), 7.17-7.20 (1H, m, ArH), 7.21-7.23 (4H, m, ArH), 7.26 (2H, d, J = 8.2 Hz, ArH), 7.27 (2H, d, J = 9.0 Hz, ArH), 7.61 (2H, d, J = 8.2 Hz, ArH), 7.70 (2H, d, J = 8.3 Hz, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 21.50 (q), 21.53 (q), 25.9 (q), 27.5 (q), 45.4 (t), 49.3 (t), 56.0 (t), 60.6 (d), 73.0 (s), 119.7 (d), 120.8 (d), 121.6 (s), 126.6 (d), 126.9 (d × 2), 127.4 (d × 2), 128.4 (s), 129.0 (d × 2), 129.8 (d × 2), 130.0 (d × 2), 130.1 (d × 2), 135.0 (s), 135.8 (s), 136.1 (s), 143.9 (s), 145.2 (s); MS (ESI-TOF) m/z 651 [M + Na]$^+$; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{31}$H$_{36}$N$_2$O$_6$S$_3$Na 651.1633; found 651.1631.

Pummerer reaction of pyrrole 5f with TFAA and successive treatment with TBAH.

![Chemical structure](image)

Trifluoroacetic anhydride (88 mg, 0.42 mmol) was added dropwise to a dichloromethane (3.5 mL) solution of N-(3-butenyl)-N-[3-(phenylsulfinylmethyl)-1-tosylpyrrole-4-methyl]-p-toluenesulfonamide (5f) (50 mg, 0.08 mmol) at -20 °C. The reaction mixture was stirred for 0.5 h and poured into a sat. sodium hydrogen carbonate (50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure to give the residue. To the residue in dichloromethane (2.5 mL) were added tetrabutylammonium hydroxide (0.22 g, 0.84 mmol) in H$_2$O (2.0 mL) and tetrabutylammonium hydrogensulfate (5.7 mg, 1.7×10$^{-2}$ mmol) at room temperature. The mixture was stirred for 2 h and poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-n-hexane (2:3) to give N-(4-hydroxy-3-phenylthiobutyl)-N-((4-(hydroxymethyl)-1-tosyl-1H-pyrrol-3-yl)methyl)-4-methylbenzenesulfonamide (9f) (12 mg, 23 %) as white powders.
mp 42–45 °C, IR ν 3510, 2923, 1707, 1597, 1370, 1304, 1221, 1172, 1092, 1066, 815, 749, 674, 588, 540; ¹H NMR (600 MHz, CDCl₃) δ 1.24-1.30 (1H, m, CH), 1.45-1.50 (1H, m, CH), 2.37 (3H, s, Me), 2.43 (3H, s, Me), 2.66 (1H, dd, J = 8.3 and 13.8 Hz, CH), 2.80 (1H, dd, J = 4.2 and 13.8 Hz, CH), 3.01-3.05 (1H, m, CH), 3.27-3.32 (1H, m, CH), 3.53 (1H, brs, CH), 3.95 (1H, d, J = 14.5 Hz, CH), 4.23 (1H, d, J = 13.8 Hz, CH), 4.42 (1H, d, J = 13.1 Hz, CH), 4.47 (1H, d, J = 13.1 Hz, CH), 6.95 (1H, brs, ArH), 7.03 (1H, d, J = 1.4 Hz, ArH), 7.22-7.23 (1H, m, ArH), 7.26 (2H, d, J = 7.6 Hz, ArH), 7.30 (6H, brs, ArH), 7.66 (2H, d, J = 7.6 Hz, ArH), 7.71 (2H, d, J = 8.3 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 21.5 (q), 21.6 (q), 35.2 (t), 41.3 (t), 45.0 (t), 45.7 (t), 56.2 (t), 66.6 (d), 119.7 (d), 120.7 (d), 122.3 (s), 126.5 (d), 126.9 (d × 2), 127.1 (d × 2), 128.1 (s), 129.1 (d × 2), 129.6 (d × 2), 129.9 (d × 2), 130.0 (d × 2), 135.2 (s × 2), 135.7 (s), 143.8 (s), 145.3 (s); MS (ESI-TOF) m/z 637 [M + Na]⁺; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₃₀H₃₄N₂O₆S₃Na 637.14767; found 637.14502.

Oxidation-Pummerer reaction of 6a and successive treatment with TBAH.

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\begin{align*}
\text{PhSe} & \quad \text{1) mCPBA} \\
\text{Ts} & \quad \text{2) (CF₃CO)₂O} \\
\text{6a} & \quad \text{3) Bu₄NOH} \\
\text{HO} & \quad \text{HO} \\
\text{N} & \quad \text{N} \\
\text{Ts} & \quad \text{Ts} \\
\text{SePh} & \quad \text{SePh} \\
\text{10a} & \quad \text{10a}
\end{align*}
\]

To a 1,2-dichloroethane (2.0 mL) solution of N-[3-(phenylselanylmethyl)-1-tosylpyrrole-4-methyl]-N-allyl\text{\textit{l}-p-toluenesulfonamide (6a)} (50 mg, 0.08 mmol) was added m-chloroperbenzoic acid (14 mg, 0.08 mmol) over 20 min to at 0 °C. The reaction mixture was stirred for 5 min. Then trifluoroacetic anhydride (85.6 mg, 0.41 mmol) was added dropwise to the reaction mixture. The whole was stirred for 15 min and poured into a sat. sodium hydrogen carbonate (50 mL). The mixture was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. To the residue in dichloromethane (2.5 mL) was added tetrabutylammonium hydroxide (0.21 g, 0.81 mmol) in H₂O (2.0 mL) and tetrabutylammonium hydrogensulfate (5.5 mg, 0.02 mmol). The mixture was stirred for 2 h and poured into water (50 mL). The organic layer was separated and the aqueous
layer was extracted with chloroform. The combined organic layer was washed with water (50 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was purified by the preparative TLC on silica gel eluting with AcOEt-n-hexane to give

$N$-(3-hydroxy-2-(phenylselanyl)propyl)-$N'$-(4-(hydroxymethyl)-1-tosyl-1H-pyrrol-3-yl)methyl)-4-methylbenzenesulfonamide (10a) (48 mg, 91%) as white powders.

mp 37–41 °C, IR $\nu$ 3435, 2924, 2871, 1707, 1597, 1521, 1438, 1372, 1335, 1172, 1092, 1066, 1018, 915, 814, 745, 673, 588, 550; $^1$H NMR (800 MHz, CDCl$_3$) 2.39 (3H, s, Me), 2.44 (3H, s, Me), 2.61 (1H, br s, OH), 2.66 (1H, br s, OH), 3.03 (1H, m, CH), 3.10 (1H, dd, $J = 4.9$ and 13.2 Hz, CH), 3.56-3.59 (1H, m, CH), 3.58 (1H, dd, $J = 9.4$ and 13.2 Hz, CH), 3.77 (1H, br d-like, $J = ca. 12$ Hz, CH), 3.82 (1H, d, $J = 14.4$ Hz, CH), 4.27 (1H, d, $J = 14.4$ Hz, CH), 4.46 (1H, br dd-like, $J = 2.5$ and 13 Hz, CH), 4.52 (1H, br dd-like, $J = 2.5$ and 13 Hz, CH), 6.85 (1H, d, $J = 2.3$ Hz, ArH), 7.07 (1H, d, $J = 2.3$ Hz, ArH), 7.25-7.32 (7H, m, ArH), 7.34-7.36 (2H, m, ArH), 7.50 (2H, d-like, $J = 8.2$ Hz, ArH), 7.70 (2H, d-like, $J = 8.2$ Hz, ArH); $^{13}$C NMR (200 MHz, CDCl$_3$) $\delta$ 21.5 (q), 21.6 (q), 46.1 (t), 46.6 (d), 51.2 (t), 56.2 (t), 61.8 (t), 119.9 (d), 120.8 (d), 122.2 (s), 126.9 (d x 2), 127.3 (d x 2), 127.9 (s), 127.9 (d), 128.7 (s), 129.3 (d x 2), 130.0 (d x 2), 130.1 (d x 2), 133.4 (s), 134.6 (d x 2), 135.6 (s), 144.2 (s), 144.4 (s); MS (EI) m/z 648 (short M$^+$), HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{29}$H$_{32}$N$_2$NaO$_6$S$_2$Se 671.0759; found 671.0740. Anal. Calcd for C$_{29}$H$_{32}$N$_2$O$_6$S$_2$Se+H$_2$O: C, 52.33; H, 5.19; N, 4.21. Found: C, 52.39; H, 5.00; N, 4.19.

Oxidation-Pummerer reaction of 6b and successive treatment with TBAH.

$m$-Chloroperbenzoic acid (14 mg, 0.08 mmol) was added over 20 min to a 1,2-dichloroethane (2.0 mL) solution of N-[3-(phenylselanyl)methyl]-1-tosylpyrrole-4-methyl]-N-allyl-$p$-toluenesulfonamide (6b) (50 mg, 0.08 mmol) at 0 °C. The reaction mixture was stirred for 15 min. To the mixture was added dropwise trifluoroacetic anhydride (85.6 mg, 0.41 mmol). The whole
was stirred for further 25 min and poured into a sat. NaHCO$_3$ (50 mL). Then the mixture was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. To the residue in dichloromethane (2.5 mL) was added tetrabutylammonium hydroxide (0.22 g, 0.81 mmol) in H$_2$O (2.0 mL) and tetrabutylammonium hydrogensulfate (5.7 mg, 0.02 mmol). The whole was stirred for 1 h and then poured into a saturated sodium hydrogen carbonate (50 mL). The whole was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give 1,5-bis(p-toluenesulfonyl)-1,4,5,6,7,8-hexahydro-7-methyl-7-(phenylselanyl)pyrrolo[3,2-c]azepin-3-methanol (12b) (28 mg, 55%) as white powders.

$mp~69–73\ °C,$ IR $\nu$ 3444(OH), 1360, 1169 (SO$_2$), 1091 (SO); $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 1.30 (3H, s, Me), 2.37 (3H, s, Me), 2.41 (3H, s, Me), 3.39 (1H, d, $J = 12.4$ Hz, CH), 3.40 (1H, d, $J = 11.7$ Hz, CH), 3.71 (1H, d, $J = 11.7$ Hz, CH), 3.92 (1H, d, $J = 14.4$ Hz, CH), 4.02 (1H, d, $J = 14.4$ Hz, CH), 4.45 (2H, s, CH$_2$), 7.20 (2H, d, $J = 8.2$ Hz, ArH), 7.22 (2H, d, $J = 10.3$ Hz, ArH), 7.25 (2H, d, $J = 15.0$ Hz, ArH), 7.29 (2H, d, $J = 8.3$ Hz, ArH), 7.45 (2H, d, $J = 8.2$ Hz, ArH), 7.50 (2H, dd, $J = 2.1$ and 7.6 Hz, ArH), 7.65 (2H, d, $J = 8.2$ Hz, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 21.5 (q), 21.6 (q), 23.0 (q), 36.3 (t), 40.1 (s), 43.8 (t), 55.9 (t), 56.8 (t), 121.2 (s), 123.1 (s), 123.5 (d), 126.3 (d $\times$ 2), 126.6 (d), 127.7 (d $\times$ 2), 128.9 (d $\times$ 2), 129.8 (d $\times$ 2), 131.2 (s), 132.5 (d $\times$ 2), 133.0 (s), 134.7 (s), 136.9 (s), 143.7 (s), 144.9 (s); MS (EI) m/z 644 (M$^+$), 489 (M$^+$-Ts). Anal. Calcd for C$_{30}$H$_{32}$N$_2$O$_5$S$_2$Se+1/2H$_2$O: C, 54.46; H, 5.18; N, 4.23. Found: C, 54.71; H, 5.20; N, 3.93.

Oxidation-Pummerer reaction of 6c and successive treatment with TBAH.

$m$-Chloroperbenzoic acid (14 mg, 0.08 mmol) was added over 20 min to a 1,2-dichloroethane (2.0 mL) solution of N-[3-(phenylselanylmethyl)-1-tetra-$n$-butylammonium-$n$-hexane (1:2) to give 1,5-bis(p-toluenesulfonyl)-1,4,5,6,7,8-hexahydro-7-methyl-7-(phenylselanyl)pyrrolo[3,2-c]azepin-3-methanol (12b) (28 mg, 55%) as white powders.
osylpyrrole-4-methyl]-N-but-2-enyl-p-toluenesulfonamide (6c) (50 mg, 0.08 mmol) at 0 °C. After stirring for 10 min, trifluoroacetic anhydride (83.7 mg, 0.39 mmol) was added dropwise to the reaction mixture. The whole was stirred for further 15 min and poured into a sat. sodium hydrogen carbonate (50 mL). Then the mixture was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. To the residue in dichloromethane (2.5 mL) was added tetrabutylammonium hydroxide (0.21 g, 0.81 mmol) in H₂O (2 mL) and tetrabutylammonium hydrogensulfate (5.4 mg, 0.02 mmol). The whole was stirred for 1 h and then poured into a saturated sodium hydrogen carbonate (50 mL). The mixture was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by the preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give N-(3-hydroxy-2-(phenylselanyl)butyl)-N-((4-(hydroxymethyl)-1-tosyl-1H-pyrrol-3-yl)methyl)-4-methylbenzenesulfonamide (10c) (40 mg, 76%) as white powders.

mp 44–47 °C, IR ν 3434 (OH), 1370, 1304, 1172, 1092 (SO₂), 1067 (SO); ¹H NMR (800 MHz, CDCl₃) δ 0.97 (3H, d, J = 6.4 Hz, Me), 2.39 (3H, s, Me), 2.44 (3H, s, Me), 2.44 (1H, br s, OH), 2.83 (1H, brs, OH), 3.15 (1H, dd, J = 5.5 and 13.2 Hz, CH), 3.36 (1H, m, CH), 3.38 (1H, dd, J = 8.2 and 13.2 Hz, CH), 3.77 (1H, m, CH), 4.02 (1H, d, J = 14.4 Hz, CH), 4.06 (1H, dd, J = 14.4 Hz, CH), 4.54 (1H, d, J = 13.2 Hz, CH), 4.60 (1H, d, J = 13.2 Hz, CH), 6.85 (1H, d, J = 2.3 Hz, ArH), 7.11 (1H, d, J = 2.3 Hz, ArH), 7.25–7.29 (6H, m, ArH), 7.30–7.33 (1H, m, ArH), 7.38–7.40 (2H, m, ArH), 7.55 (2H, d-like, J = 8.2 Hz, ArH), 7.71 (2H, d-like, J = 8.2 Hz, ArH); ¹³C NMR (200 MHz, CDCl₃) δ 19.5 (q), 21.5 (q), 21.6 (q), 46.2 (t), 50.6 (t), 53.7 (d), 56.3 (t), 67.2 (d), 120.0 (d), 120.6 (d), 121.9 (s), 127.0 (d × 2), 127.96 (s) 127.98 (d × 2), 128.3 (s), 129.3 (d × 2), 129.9 (d × 2), 130.1 (d × 2), 134.0 (s), 134.6 (d × 2), 135.7 (s), 144.1 (s), 145.3 (s); MS (EI) m/z 662 (M⁺), 507 (M⁺–Ts). HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₃₀H₃₄N₂NaO₆S₂Se 685.0921; found 685.0908.
Oxidation-Pummerer reaction of 6d and successive treatment with TBAH.

$m$-Chloroperbenzoic acid (16.3 mg, 0.09 mmol) was added over 15 min to a 1,2-dichloroethane (2.0 mL) solution of N-[3-(phenylselanylmethyl)-1-tosylpyrrole-4-methyl]-N-cinnamyl-$p$-toluenesulfonamide (6d) (50 mg, 0.07 mmol) at 0 °C. After stirring for 10 min, trifluoroacetic anhydride (76.1 mg, 0.36 mmol) was added dropwise to the reaction mixture. The whole was stirred for further 15 min and poured into a sat. sodium hydrogen carbonate (50 mL). Then the mixture was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. To the residue in dichloromethane (2.5 mL) was added tetrabutylammonium hydroxide (0.19 g, 0.72 mmol) in H$_2$O (2.0 mL) and tetrabutylammonium hydrogensulfate (4.9 mg, 0.01 mmol). The whole was stirred for 1 h and poured into a saturated sodium hydrogen carbonate (50 mL) solution. The mixture was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was washed with a sodium hydrogen carbonate (50 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-$n$-hexane 1:2 to give 1,5-bis(p-toluenesulfonyl)-1,4,5,6,7,8-hexahydro-8-phenyl-7-(phenylselanyl)pyrrolo[3,2-c]azepin-3-methanol (12d) (40 mg, 76%) as white powders.

mp 88–91 °C, IR ν 3445 (OH), 1362, 1270, 1167 (SO$_2$), 1101 (SO); $^1$H NMR (600 MHz, CDCl$_3$) δ 2.21 (3H, s, Me), 2.38 (3H, s, Me), 3.12 (1H, dd, $J = 2.0$ and 13.7 Hz, CH), 3.74 (1H, d, $J = 15.1$ Hz, CH), 3.76-3.78 (1H, m, CH), 3.98-4.01 (1H, m, CH), 4.52 (1H, d, $J = 13.1$ Hz, CH), 4.57 (1H, d, $J = 12.3$ Hz, CH$_2$), 4.67 (1H, dd, $J = 2.0$ and 15.1 Hz, CH), 5.44 (1H, d, $J = 4.1$ Hz, CH), 6.67 (2H, d, $J = 7.6$ Hz, ArH), 6.84 (2H, d, $J = 8.2$ Hz, ArH), 7.02-7.09 (3H, m, ArH), 7.22-7.27 (4H, m, ArH), 7.33-7.35 (3H, m, ArH), 7.38 (1H, s, ArH),

S52
7.63-7.65 (4H, m, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 21.4 (q), 21.5 (q), 44.6 (t), 47.4 (d), 50.2 (d), 50.8 (t), 56.7 (t), 120.7 (d), 124.0 (s), 124.1 (s), 126.4 (d), 126.9 (d × 2), 127.4 (d × 2), 127.7 (d), 127.9 (d × 2), 128.6 (d × 2), 129.2 (d × 2), 129.4 (d × 2), 129.7 (d × 2), 130.4 (s), 131.4 (s), 134.5 (d × 2), 135.06 (s), 135.15 (s), 139.2 (s), 143.6 (s), 144.5 (s); MS (EI) m/z 706 (M$^+$), 549 (M$^+$-SePh). MS (ESI-TOF) m/z 729 [M + Na]$^+$; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{35}$H$_{34}$N$_2$O$_5$S$_2$SeNa 729.0972; found 729.0946.

Single X-ray analysis of 12d was described in the CIF format. Oxidation-Pummerer reaction of 6e and successive treatment with TBAH.

$m$-Chloroperbenzoic acid (60 mg, 0.35 mmol) was added over 1 h to a 1,2-dichloroethane (8.0 mL) solution of N-(3-methyl-2-butenyl)-N-[3-(phenylselanyl)methyl]-1-tosylpyrrole-4-yl)methyl]-p-toluene-sulfonamide (6e) (186 mg, 0.29 mmol) at 0 °C. After stirring for 20 min, trifluoroacetic anhydride (304.4 mg, 1.45 mmol) was added dropwise to the reaction mixture. The whole was stirred for further 45 min and poured into a sat. sodium hydrogen carbonate (50 mL). Then the mixture was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. To the residue in dichloroethane (10.0 mL) was added tetrabutylammonium hydroxide (0.75 g, 2.90 mmol) in H$_2$O (7.0 mL) and tetrabutylammonium hydrogen sulfate (19.7 mg, 0.06 mmol). The whole was stirred for 1 h and then poured into a sodium hydrogen carbonate (50 mL) solution. The mixture was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt-$n$-hexane (1:2) to give N-(3-hydroxy-3-methyl-2-(phenylselanyl)butyl)-N-(4-(hydroxymethyl)-1-tosyl-1H-pyrrol-3-yl)methyl)-4-methylbenzenesulfonamide (10e) (42 mg, 21%) as white powder.
mp 54–56 °C, IR v 3421 (OH), 1371, 1337, 1172 (SO₂), 1067 (SO); ¹HNMR (600 MHz, CDCl₃) δ 1.14 (3H, s, Me), 1.18 (3H, s, Me), 2.40 (3H, s, Me), 2.43 (3H, s, Me), 2.61 (1H, brs, OH), 2.74 (1H, brs, OH), 3.11 (1H, dd, J = 9.0 and 15.1 Hz, CH), 3.44 (1H, dd, J = 5.5 and 8.9 Hz, CH), 3.65 (1H, J = 5.5 and 15.1 Hz, CH), 3.94 (1H, d, J = 15.1 Hz, CH), 4.33 (1H, d, J = 14.4 Hz, CH), 4.42 (2H, s, CH × 2), 6.77 (1H, s, ArH), 7.04 (1H, d, J = 2.1 Hz, ArH), 7.22–7.28 (7H, m, ArH), 7.39 (2H, d, J = 6.1 Hz, ArH), 7.59 (2H, d, J = 8.3 Hz, ArH), 7.70 (2H, d, J = 7.6 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 21.5 (q), 21.6 (q), 26.2 (q), 28.3 (q), 50.2 (t), 56.1 (t), 58.7 (d), 72.9 (s), 119.8 (d), 120.7 (d), 121.7 (s), 126.9 (d × 2), 127.35 (d), 127.42 (d × 2), 128.4 (s), 129.2 (d × 2), 129.8 (d × 2), 130.0 (d × 2), 130.4 (s), 133.1 (d × 2), 134.7 (s), 135.8 (s), 143.9 (s), 145.2 (s); MS (ESI-TOF) m/z 699 [M + Na]⁺; HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for C₃₁H₃₆N₂O₆S₂SeNa 699.1078; found 699.1074. Anal. Calcd for C₃₁H₃₆N₂O₆S₂Se+H₂O: C, 53.67; H, 5.52; N, 4.04. Found: C, 53.75; H, 5.35; N, 4.11.

Oxidation-Pummerer reaction of 6f and successive treatment with TBAH.

\[
\begin{align*}
\text{PhSe} & \quad \text{1) mCPBA} \\
\text{Ts}^- & \quad \text{2) (CF₃CO)₂O} \\
6f & \quad \text{3) Bu₄NOH} \\
\end{align*}
\]

\[
\begin{align*}
\text{HO} & \quad \text{Ts}^- \\
\text{N} & \quad \text{N} \\
\text{SePh} & \quad \text{SePh} \\
10f & \quad \text{10f}
\end{align*}
\]

\[
m\text{-Chloroperbenzoic acid (45 mg, 0.26 mmol) was added over 0.5 h to a 1,2-dichloroethane (8.0 mL) solution of } \] N-[3-(phenylselanylmethyl)-1-tosylpyrrole-4-yl)methyl]-N-(3-butenyl)-p-toluenesulfonylamide (6f) (135 mg, 0.22 mmol) at 0 °C. After stirring for 10 min, trifluoroacetic anhydride (225.9 mg, 1.08 mmol) was added dropwise to the reaction mixture. The whole was stirred for further 15 min and poured into a sat. sodium hydrogen carbonate (50 mL). Then the mixture was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. To the residue in dichloromethane (6.5 mL) was added tetrabutylammonium hydroxide (0.56 g, 2.15 mmol) in H₂O (5 mL) and tetrabutylammonium hydrogensulfate (14.6 mg, 0.04 mmol). The whole was stirred for 1 h and poured into a saturated sodium hydrogen carbonate (50 mL) solution. The mixture was vigorously stirred for 15 min. The organic layer was separated and the aqueous
layer was extracted with chloroform. The combined organic layer was dried over 
MgSO$_4$. The solvent was removed under reduced pressure to give 
N-(4-hydroxy-3-phenylselanylbutyl)-N-(4-(hydroxymethyl)-1-tosyl-1H-pyrrol-3-yl)methyl-
4-methylbenzenesulfonamide (10f) (32 mg, 23%) as white powders.

mp 45‒47 °C, IR ν 3502 (OH), 1370, 1333, 1172 (SO$_2$), 1066 (SO); $^1$HNMR (600 MHz, 
CDCl$_3$) δ 1.25-1.31 (1H, m, CH), 1.44-1.50 (1H, m, CH), 2.38 (3H, s, Me), 2.44 (3H, s, 
Me), 2.66 (1H, brs, OH), 2.67 (1H, dd, J = 8.3 and 13.1 Hz, CH), 2.76 (1H, brs, OH), 2.80  
(1H, dd, J = 4.9 and 13.1 Hz, CH), 3.00-3.05 (1H, m, CH), 3.27-3.32 (1H, m, CH), 3.55  
(1H, brs, CH), 3.95 (1H, d, J = 13.8 Hz, CH), 4.23 (1H, d, J = 14.5 Hz, CH), 4.43 (1H, d, J  
= 13.0 Hz, CH), 4.49 (1H, d, J = 13.7 Hz, CH), 6.94 (1H, d, J = 2.1 Hz, ArH), 7.04 (1H, d, J  
= 2.0 Hz, ArH), 7.25-7.29 (5H, m, ArH), 7.30 (2H, d, J = 8.2 Hz, ArH), 7.45-7.47 (2H, m,  
ArH), 7.66 (2H, d, J = 8.2 Hz, ArH), 7.71 (2H, d, J = 9.0 Hz, ArH); $^{13}$C NMR (150 MHz, 
CDCl$_3$) δ 21.5 (q), 21.6 (q), 35.7 (t), 36.2 (t), 45.0 (t), 45.8 (t), 56.2 (t), 67.1 (d), 119.7 (d),  
dev; 120.7 (d), 122.3 (s), 126.9 (d × 2), 127.2 (d × 2), 127.3 (d), 128.1 (s), 129.26 (d × 2),  
129.32 (s), 129.9 (d × 2), 130.1 (d × 2), 132.8 (d × 2), 135.3 (s), 135.8 (s), 143.9 (s), 145.3  
(s); MS (ESI-TOF) m/z 685 [M + Na]$^+$; HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for  
$^{C_{30}H_{34}N_2O_6S_2SeNa}$ 685.0921; found 685.0912. Anal. Calcd for $^{C_{30}H_{34}N_2O_6S_2Se+1/4H_2O}$:  
C, 54.13; H, 5.35; N, 4.16. Found: C, 54.13; H, 5.35; N, 4.16.

**Pummerer reaction of 5a in the presence of p-methoxybenzenethiol.**

To a dichloroethane (0.50 mL) solution of 5a (20 mg, 0.03 mmol) and 
$p$-methoxybenzenethiol (14.1 mg, 0.10 mmol) was added trifluoroacetic  
anhydride (36 mg, 0.10 mL, 0.17 mmol) at $-20$ °C. The reaction mixture was stirred for  
0.5 h and poured into a saturated sodium hydrogen carbonate (50 mL). The organic  
layer was separated and the aqueous layer was extracted with AcOEt. The combined  
organic layer was dried over MgSO$_4$. The solvent was removed under reduced 
pressure. To the residue in dichloroethane (2.0 mL) was added tetrabutylammonium  
hydroxide (87 mg, 0.34 mmol) in H$_2$O (1 mL) and tetrabutylammonium hydrogensulfate
(2.3 mg, 0.01 mmol) at 0 °C. The whole was stirred for 1 h and then poured into a saturated sodium hydrogen carbonate (50 mL). The mixture was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by the preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give 4a (13 mg, 77%).

Pummerer reaction of 5a and successive treatment with TBAH in the presence of p-methoxybenzenethiol.

To a THF (0.50 mL) solution of 5a (20 mg, 0.03 mmol) was added trifluoroacetic anhydride (36 mg, 0.10 mL, 0.17 mmol) at −20 °C. The reaction mixture was stirred for 0.5 h and poured into a saturated sodium hydrogen carbonate (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. To the residue in dichloromethane (2.0 mL) was added tetrabutylammonium hydroxide (87 mg, 0.34 mmol) in H₂O (1 mL), p-methoxybenzenethiol (14.1 mg, 0.10 mmol) and tetrabutylammonium hydrogensulfate (2.3 mg, 0.01 mmol). The whole was stirred for 1 h and then poured into a saturated sodium carbonate (50 mL) solution. The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by the preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give 9a (13 mg, 77%).

Pummerer reaction of 5a and successive treatment with TBAH in the presence of p-chlorobenzenethiol.
To a dichloroethane (0.50 mL) solution of 5a (20 mg, 0.03 mmol) was added TFAA (36 mg, 0.10 mL, 0.17 mmol) at −20 °C. The reaction mixture was stirred for 0.5 h and poured into a saturated sodium hydrogen carbonate (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. To the residue in dichloromethane (2.0 mL) was added tetrabutylammonium hydroxide (87 mg, 0.34 mmol) in H₂O (1 mL), p-chlorobenzenethiol (15.0 mg, 0.10 mmol) and tetrabutylammonium hydrogensulfate (2.3 mg, 0.01 mmol). The whole was stirred for 1 h and then poured into a saturated sodium carbonate (50 mL) solution. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by the preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give 4a (10 mg, 60%) and 9a (3.0 mg, 17%).

Ytterbium triflate-catalyzed intramolecular cyclization of diol 9a.

To a dichloroethane (1.5 mL) solution of 9a (30 mg, 0.05 mmol) was added ytterbium(III) trifluoromethanesulfonate hydrate (6.2 mg, 0.01 mmol) at room temperature. The reaction mixture was stirred at reflux for 3.5 h and then poured into a sodium hydrogen carbonate (50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt-n-hexane (1:3) to
give 7-(phenylthio)-2,9-ditosyl-2,6,7,8,9,10-hexahydro-4H-pyrrolo[3,4-g][1,5]oxazonine (25a) (12 mg, 41%) as white powder.

mp 158–160 °C, IR ν 2924, 1374, 1341, 1173 (SO₂), 1067 (SO); ¹H NMR (600 MHz, CDCl₃) δ 2.41 (6H, s, Me × 2), 3.10 (1H, dd, J = 11.0 and 15.1 Hz, CH), 3.54–3.58 (2H, m, CH × 2), 3.67 (1H, dd, J = 5.5 and 15.2 Hz, CH), 3.78 (1H, d, J = 15.1 Hz, CH), 3.89 (1H, dd, J = 3.5 and 10.4 Hz, CH), 4.45 (1H, d, J = 13.8 Hz, CH), 4.56 (1H, d, J = 15.8 Hz, CH), 4.75 (1H, d, J = 13.7 Hz, CH), 6.94 (1H, s, ArH), 7.23 (2H, d, J = 8.3 Hz, ArH), 7.25–7.27 (2H, m, ArH), 7.30 (4H, m, ArH), 7.38 (2H, br d, J = 7.6 Hz, ArH), 7.55 (2H, d, J = 8.3 Hz, ArH), 7.76 (2H, d, J = 8.3 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 21.5 (q), 21.6 (q), 47.5 (d), 48.5 (t), 53.5 (t), 65.0 (t), 66.6 (t), 118.4 (d), 122.9 (d), 123.5 (s), 124.7 (s), 126.9 (d), 127.0 (d × 2), 127.1 (d × 2), 129.1 (d × 2), 129.7 (d × 2), 130.1 (d × 2), 130.7 (d × 2), 134.3 (s), 135.8 (s), 136.0 (s), 143.5 (s), 145.1 (s); MS (ESI-TOF) m/z 605 [M + Na]+; HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for C₂₉H₃₀N₂O₅S₃Na 605.1215; found 605.1187. Anal. Calcd for C₂₉H₃₀N₂O₅S₃: C, 58.88; H, 5.02; N, 4.61. Found: C, 58.88; H, 5.02; N, 4.61.

Ytterbium triflate-catalyzed intramolecular cyclization of diol 9c.

To a 1,2-dichloroethane (1.5 mL) solution of N-(3-hydroxy-2-(phenylthio)butyl)-N-((4-(hydroxymethyl)-1-tosyl-1H-pyrrol-3-yl)methyl)-4-methylbenzene sulfonamide (9c) (30 mg, 0.05 mmol) was added ytterbium(III) trifluoromethanesulfonate hydrate (6.1 mg, 0.01 mmol). The reaction mixture was stirred at reflux for 4.5 h and then poured into a sodium hydrogen carbonate (50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt-n-hexane (1:3) to give 6-methyl-7-(phenylthio)-2,9-ditosyl-2,6,7,8,9,10-hexahydro-4H-pyrrolo[3,4-g][1,5]oxazonine (25c) (10 mg, 34%) as white powder.
mp 185–187 °C, IR ν 2924, 1370, 1300 (SO₂), 1066 (SO); ¹H NMR (600 MHz, CDCl₃) δ 1.44 (3H, d, J = 6.2 Hz, Me), 2.40 (3H, s, Me), 2.41 (3H, s, Me), 2.97 (1H, dd, J = 14.4 Hz, CH), 4.31 (1H, d, J = 15.2 Hz, CH), 4.33 (1H, d, J = 12.3 Hz, CH), 4.59 (1H, d, J = 11.7 Hz, CH), 6.94 (1H, d, J = 2.0 Hz, ArH), 6.98 (1H, brs, ArH), 7.18 (2H, d, J = 8.2 Hz, ArH), 7.28 (2H, d, J = 8.2 Hz, ArH), 7.30–7.38 (5H, m, ArH), 7.51 (2H, brd, J = 7.5 Hz, ArH), 7.69 (2H, d, J = 8.2 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 18.4 (q), 21.5 (q), 21.6 (q), 48.6 (t), 53.3 (d), 54.9 (t), 60.1 (t), 75.6 (d), 118.8 (d), 120.2 (d), 124.4 (s), 125.5 (s), 126.7 (d × 2), 127.3 (d × 2), 127.4 (d), 129.0 (d × 2), 129.5 (d × 2), 130.0 (d × 2), 132.7 (d × 2), 133.5 (s), 134.9 (s), 135.8 (s), 143.3 (s), 145.1 (s); MS (ESI-TOF) m/z 619 [M + Na]⁺; HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₃₀H₃₂N₂O₅S₃Na 619.1371; found 619.1393. Anal. Calcd for C₃₀H₃₂N₂O₅S₃ + 1/3H₂O: C, 59.78; H, 5.46; N, 4.65. Found: C, 59.50; H, 5.41; N, 4.60.

Ytterbium trflate-catalyzed intramolecular cyclization of diol 9e.

To a 1,2-dichloroethane (1.5 mL) solution of N-(3-hydroxy-3-methyl-2-(phenylthio)butyl)-N-((4-(hydroxymethyl)-1-tosyl-1H-pyrrol-3-yl)-methyl)-4-methylbenzenesulfonamide (9e) (30 mg, 0.05 mmol) was added ytterbium(III) trifluoromethanesulfonate hydrate (5.9 mg, 0.01 mmol). The reaction mixture was stirred at reflux for 3.5 h and then poured into a saturated sodium hydrogen carbonate (50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO₄. The residue was purified by column chromatography on silica gel eluting with AcOEt-n-hexane (1:8) to give 6,6-dimethyl-7-(phenylthio)-2,9-ditosyl-2,6,7,8,9,10-hexahydro-4H-pyrrolo[3,4-g][1,5]oxazonine (25e) (14 mg, 48%) as white powder.

mp 86–89 °C, IR ν 2925, 1364, 1173 (SO₂), 1064 (SO); ¹H NMR (600 MHz, CDCl₃) δ 1.20 (3H, s, Me), 1.57 (3H, s, Me), 2.37 (3H, s, Me), 2.38 (3H, s, Me), 3.11 (1H, dd, J = 10.3 and 15.8 Hz, CH), 3.73 (1H, dd, J = 1.4 and 15.8 Hz, CH), 3.90 (1H, d, J = 8.9 Hz, CH), 3.98 (1H, dd, J = 1.4 and 15.8 Hz, CH), 4.28 (1H, d, J = 10.3 Hz, CH), 4.45 (1H, d, J =
15.1 Hz, CH), 4.49 (1H, d, J = 11.0 Hz, CH), 6.93 (1H, br s, ArH), 7.00 (1H, br s, ArH), 7.09 (3H, s, ArH), 7.26 (2H, d, J = 8.2 Hz, ArH), 7.38 (1H, brd, J = 7.5 Hz, ArH), 7.42 (2H, t, J = 6.9 Hz, ArH), 7.62 (2H, d, J = 6.9 Hz, ArH), 7.69 (2H, J = 8.3 Hz, ArH); 13C NMR (150 MHz, CDCl3) δ 21.5 (q), 21.6 (q), 23.5 (q), 24.8 (q), 51.0 (t), 55.6 (t), 56.2 (d), 57.3 (t), 77.7 (s), 117.9 (d), 118.1 (d), 125.0 (s), 126.2 (s), 126.7 (d × 2), 127.2 (d × 2), 127.9 (d), 129.0 (d × 2), 129.4 (d × 2), 129.9 (d × 2), 133.4 (d × 2), 134.1 (s), 135.0 (s), 136.2 (s), 143.2 (s), 144.8 (s); MS (ESI-TOF) m/z 633 [M + Na]+. HRMS (ESI-TOF) m/z: [M+Na]+ Calcd for C31H34N2O5S3Na 633.1528; found 633.1506. Anal. Calcd for C31H34N2O5S3+1/2H2O: C, 60.07; H, 5.69; N, 4.52. Found: C, 59.91; H, 5.71; N, 4.44.

Synthesis of 1,5-Bis(p-toluenesulfonyl)-1,4,5,6,7,8-hexahydro-7-(phenylsulfanyl)pyrrolo[3,2-c]azepin-3-methanol (25g).

Reaction of 1,6-diyne 1 with N-allyl p-bromobenzenesulfonyamide (3g).

To a DMSO (2.0 mL) solution of N-(phenylsulfanylprop-2-ynyl)-N-prop-2-ynyl-p-toluenesulfonyamide (1) (200 mg, 0.56 mmol) were added N-allyl-p-bromobenzenesulfonyamide (3g) (311 mg, 1.13 mmol), bis(hexafluoroacetylacetonato)nicket(II) hydrate (27 mg, 0.06 mmol), bis(triphenylphosphine)palladium(II) dichloride (40 mg, 0.06 mmol), and 1,8-diazabicyclo[5.4.0]undec-7-ene (86 mg, 0.56 mmol). The reaction mixture was stirred at room temperature for overnight and then poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with AcOEt. The combined organic layer was dried over MgSO4. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CHCl3:n-hexane (4:1) to give N-[(3-(phenylsulfanyl)methyl)-1-tosylpyrrole-4-yl)methyl]-N-allyl-4-bromobenzenesulfonamide (4g) (319 mg, 90%) as white powder.
mp 79–81 °C, IR ν 3291, 2926, 1712, 1587, 1444, 1373, 1347, 1306, 1172, 1091, 1067, 903, 813, 749, 704, 672, 588, 540; ¹H NMR (600 MHz, CDCl₃) δ 2.42 (3H, s, Me), 3.70 (2H, d, \( J = 6.2 \) Hz, CH₂), 4.18 (2H, s, CH₂), 4.92 (1H, d, \( J = 17.8 \) Hz, olefinic H), 5.00 (1H, d, \( J = 10.3 \) Hz, olefinic H), 5.36-5.43 (1H, m, olefinic H), 6.87 (1H, d, \( J = 2.0 \) Hz, ArH), 6.89 (1H, d, \( J = 2.0 \) Hz, ArH), 7.18–7.22 (5H, m, ArH), 7.26 (2H, d, \( J = 8.3 \) Hz, ArH), 7.59 (2H, d, \( J = 8.3 \) Hz, ArH), 7.60 (2H, d, \( J = 8.2 \) Hz, ArH), 7.65 (2H, d, \( J = 8.9 \) Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 21.6 (q), 29.2 (t), 41.9 (t), 49.6 (t), 119.5 (t), 120.2 (d), 120.7 (d), 121.9 (s), 123.8 (s), 126.6 (d), 126.7 (d × 2), 127.6 (s), 128.6 (d × 2), 128.7 (d × 2), 130.0 (d × 2), 130.6 (d × 2), 131.8 (d), 132.4 (d × 2), 135.3 (s), 135.6 (s), 138.8 (s), 145.1 (s); MS (ESI-TOF) m/z 653 [M + Na]⁺. HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₂₈H₂₇N₂O₄S₃BrNa 653.0214; found 653.0232. Anal. Calcd for C₂₈H₂₇N₂O₄S₃Br: C, 53.25; H, 4.31; N, 4.44. Found: C, 53.13; H, 4.19; N, 4.45.

Oxidation of N- Allyl-N-[3-(phenylsulfinylmethyl)-1-tosylpyrrole-4-methyl]-4-bromobenzensulfonamide 4g with mCPBA.

To 1,2-dichloroethane (15 mL) solution of N-allyl-N-[3-(phenylsulfanylmethyl)-1-tosylpyrrole-4-methyl]-4-bromobenzene sulfonamide (4g) (264 mg, 0.42 mmol) was added m-chloroperbenzoic acid (72 mg, 0.42 mmol) over 1 h at 0 °C. The reaction mixture was further stirred for 30 min and poured into a sat. NaHCO₃ (50 mL). The whole was vigorously stirred for 15 min. The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was washed with MgSO₄. The solvent was removed under reduced pressure. The residue was purified by the preparative TLC on silica gel eluting with AcOEt-n-hexane (1:2) to give N-allyl-N-[3-(phenylsulfynylmethyl)-1-tosylpyrrole-4-methyl]-4-bromobenzensulfonamide (5g) (250 mg, 92%) as white powders.

mp 116–117 °C, IR ν 3445, 2923, 1711, 1575, 1444, 1373, 1347, 1306, 1172, 1091, 1067, 903, 813, 749, 704, 672, 588, 540; ¹H NMR (600 MHz, CDCl₃) δ 2.44 (3H, s, Me),
3.59 (1H, dd, J = 6.8 and 15.8 Hz, CH), 3.66 (1H, dd, J = 6.2 and 15.8 Hz, CH) 3.82 (1H, d, J = 13.8 Hz, CH), 3.83 (1H, d, J = 4.4 Hz, CH), 3.87 (1H, d, J = 4.4 Hz, CH), 4.11 (1H, d, J = 13.7 Hz, CH), 4.89 (1H, dd, J = 1.4 and 17.2 Hz, olefinic H), 4.98 (1H, d, J = 8.9 Hz, olefinic H), 5.23-5.29 (1H, m, olefinic H), 6.90 (1H, d, J = 2.1 Hz, ArH), 7.04 (1H, d, J = 2.0 Hz, ArH), 7.35 (4H, t, J = 6.9 Hz, ArH), 7.41-7.45 (3H, m, ArH), 7.61 (2H, d, J = 8.9 Hz, ArH), 7.65 (2H, d, J = 8.9 Hz, ArH), (4H, dd, J = 19.9 Hz, ArH), 7.74 (2H, d, J = 8.2 Hz, ArH); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 21.6 (q), 41.7 (t), 49.2 (t), 52.5 (t), 115.9 (s), 119.7 (t), 120.5 (d), 122.1 (s), 122.4 (d), 124.3 (d $\times$ 2), 127.0 (d $\times$ 2), 127.7 (s), 128.5 (d $\times$ 2), 128.7 (d $\times$ 2), 130.0 (d $\times$ 2), 130.9 (d), 131.3 (d), 132.4 (d $\times$ 2), 135.4 (s), 138.5 (s), 142.9 (s), 145.4 (s); MS (ESI-TOF) m/z 669 [M + Na]$^+$. HRMS (ESI-TOF) m/z: [M+Na]$^+$ Calcd for C$_{28}$H$_{27}$N$_2$O$_5$S$_3$BrNa 669.0163; found 669.0179. Anal. Calcd for C$_{28}$H$_{27}$N$_2$O$_5$S$_3$: C, 51.93; H, 4.20; N, 4.33. Found: C, 51.88; H, 4.19; N, 4.25.

Pummerer reaction of sulfoxide 5g with TFAA/TBAH. Trifluoroacetic anhydride (340.5 mg, 1.62 mmol) was added dropwise to a solution of dichloromethane (8 mL) and a solution of N-allyl-N-[3-(phenylsulfinylmethyl)-1-tosylpyrrole-4-yl]methyl]-4-bromobenzenesulfonamide (5g) (210 mg, 0.32 mmol) at −20 °C. The reaction mixture was stirred for 1.5 h and poured into a sat. sodium hydrogen carbonate (50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. To the residue in dichloromethane (10 mL) were added tetrabutylammonium hydroxide (0.84 g, 3.24 mmol) in H$_2$O (8 mL) and tetrabutylammonium hydrogensulfate (22.0 mg, 0.06 mmol) at room temperature. The mixture was stirred for 0.5 h and poured into water (50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO$_4$. The solvent was removed under reduced pressure. The residue was purified by preparative TLC on silica
gel eluting with AcOEt-\(n\)-hexane (1:5:1) to give 
\(N\)-\((3\text{-hydroxy}-2\text{-}-(\text{phenylthio})\text{propyl})\)-\(N\)-\(((4\text{-}-(\text{hydroxymethyl})\text{-}1\text{-tosyl}-1\text{-}H\text{-pyrrol-3-yl})\text{methyl})\)-
\(3\text{-bromobenzenesulfonamide (9g)}\) (100 mg, 46 %) as white powder.

\[\text{mp } 49\text{–}51 \degree C, \text{IR } v 3529, 3409, 2925, 1574, 1520, 1471, 1440, 1400, 1371, 1301, 1171, 1092, 1068, 1010, 917, 814, 753, 703, 673, 588, 540, 422; \] ¹H NMR (600 MHz, CDCl₃) δ 2.37
(3H, s, Me), 2.52 (2H, brs, OH × 2), 2.98 (1H, dd, \(J = 4.8\) and 14.4 Hz, CH), 3.07 (1H, dd, \(J = 4.8\) and 9.0 Hz, CH), 3.44 (1H, dd, \(J = 10.3\) and 15.1 Hz, CH), 3.52 (1H, dd, \(J = 3.4\) and 12.3 Hz, CH), 3.60 (1H, dd, \(J = 3.4\) and 12.4 Hz, CH), 3.94 (1H, d, \(J = 14.4\) Hz, CH), 4.24 (1H, d, \(J = 14.5\) Hz, CH), 4.45 (1H, d, \(J = 13.1\) Hz, CH), 4.49 (1H, d, \(J = 13.1\) Hz, CH), 6.91 (1H, d, \(J = 2.1\) Hz, CH), 7.08 (1H, d, \(J = 2.1\) Hz, ArH), 7.25-7.31 (5H, m, ArH), 7.52 (2H, d, \(J = 8.3\) Hz, ArH), 7.60 (2H, d, \(J = 9.0\) Hz, ArH), 7.70 (2H, d, \(J = 8.2\) Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 21.6 (q), 46.1 (t), 50.1 (t), 50.3 (d), 56.2 (t), 61.3 (t), 119.9 (d), 120.9 (d), 121.8 (s), 126.9 (d × 2), 127.6 (d), 127.7 (s), 128.3 (s), 128.7 (d × 2), 129.2 (d × 2), 130.1 (d × 2), 132.1 (d × 2), 132.6 (d × 2), 133.1 (s), 135.5 (s), 136.4 (s), 145.5 (s); MS (ESI-TOF) m/z 687 [M + Na]⁺. HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₂₉H₂₉N₂O₆S₃BrNa 687.0269; found 687.0244.

Ytterbium-catalyzed cyclization of diol 9g.

Ytterbium(III) trifluoromethane-sulfonate hydrate (18.6 mg, 0.03 mmol) was added dropwise to a dichloroethane (5.0 mL) solution of N-(3-hydroxy-2-(phenylthio)propyl)-N-((4-(hydroxymethyl)-1-tosyl-1H-pyrrol-3-yl)methyl)-
3-bromobenzenesulfonamide (9g) (100 mg, 0.15 mmol). The reaction mixture was stirred at reflux for 4.5 h and then poured into sodium hydrogen carbonate (50 mL). The organic layer was separated and the aqueous layer was extracted with chloroform. The combined organic layer was dried over MgSO₄. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt-\(n\)-hexane (1:2) to give

S63
7-(phenylthio)-2-tosyl-9-p-bromobenzenesulfonamide[2,6,7,8,9,10-hexahydro-4H-pyrrolo[3,4-g][1,5]oxazonine (25g) (54 mg, 56%) as white powders.

mp 188–190 °C, IR ν 3421, 2925, 2856, 1711, 1574, 1470, 1371, 1305, 1173, 1093, 1068, 1009, 963, 813, 766, 674, 595, 539, 421; ¹H NMR (600 MHz, CDCl₃) δ 2.41 (3H, s, Me), 3.15 (1H, dd, J = 11.0 and 14.5 Hz, CH), 3.53 (2H, d, J = 8.9 Hz, CH × 2), 3.62 (1H, d, J = 4.8 and 14.4 Hz, CH), 3.81-3.86 (2H, m, CH × 2), 4.44 (1H, d, J = 13.7 Hz, CH), 4.56 (1H, d, J = 15.2 Hz, CH), 4.74 (1H, d, J = 13.7 Hz, CH), 6.95 (1H, s, ArH), 7.24-7.26 (1H, m, ArH), 7.30-7.32 (5H, m, ArH), 7.38 (2H, d, J = 6.9 Hz, ArH), 7.48 (2H, d, J = 9.0 Hz, ArH), 7.53 (2H, d, J = 8.9 Hz, ArH), 7.77 (2H, d, J = 9.3 Hz, ArH); ¹³C NMR (150 MHz, CDCl₃) δ 21.6 (q), 47.4 (d), 48.6 (t), 53.6 (t), 64.9 (t), 66.4 (t), 118.4 (d), 122.9 (d), 123.2 (s), 124.6 (s), 126.9 (d × 2), 127.0 (d), 127.6 (s), 128.5 (d × 2), 129.1 (d × 2), 130.1 (d × 2), 130.9 (d × 2), 132.3 (d × 2), 134.0 (s), 135.7 (s), 137.9 (s), 145.2 (s); MS (ESI-TOF) m/z 669 [M + Na]⁺. HRMS (ESI-TOF) m/z: [M+Na]⁺ Calcd for C₂₈H₂₇N₂O₅S₃BrNa 669.0163; found 669.0189. Anal. Calcd for C₂₈H₂₇N₂O₅S₃Br+1/4H₂O: C, 51.57; H, 4.25; N, 4.30. Found: C, 51.52; H, 4.10; N, 4.23.

6. X-ray crystallographic analysis

Data of sulfone derivative of 5a and pyrroloazepine 12d were taken on a Rigaku AFC5R diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). The structures of sulfone derivative of 5a and 12d were solved by direct methods with SIR97. Full-matrix least-squares refinement was employed with anisotropic thermal parameters for all non-hydrogen atoms. All calculations were performed using the Crystal Structure (Ver. 3.8) crystallographic software package. ORTEP drawings of sulfone derivative of 5a and 12d are shown in Fig. 2 and Fig. 1, respectively. The data of sulfone derivative of 5a and 12d have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1824587 and CCDC 1824588, respectively.

Crystal data for sulfone derivative of 5a.

Monoclinic, space group P2₁/n, a = 8.8310(3), b = 3.1020(5), c = 25.1669(11) Å, β = 91.4836(13)°, V = 2910.9(2) Å³, Z = 4, μ(Mo-Kα) = 2.997 cm⁻¹, F(000) = 1256, Dc = 1.366 g/cm³, crystal dimensions: 0.25 x 0.20 x 0.20 mm. A total of 27881 reflections (6657 unique) were collected using the ω-2θ scan technique to a maximum 2θ value of 55°, and
all reflections were used in the structure determination. Final $R$ and $R_w$ values were 0.086 and 0.180, respectively. The maximum and minimum peaks in the difference map were $17.3\, e^{-}\AA^{-3}$ and $-4.66\, e^{-}\AA^{-3}$, respectively.

Crystal data for 12d.
Tetragonal, space group $P4_1$, $a = b = 14.8202(6)\,\AA$, $c = 14.7217(6)\,\AA$, $V = 3233.4(2)\,\AA^3$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 2.746\,\text{cm}^{-1}$, $F(000) = 1384$, $D_c = 1.353\,\text{g/cm}^3$, crystal dimensions: 0.30 x 0.20 x 0.10 mm. A total of 30495 reflections (7244 unique) were collected using the $\omega$-2$\theta$ scan technique to a maximum 2$\theta$ value of 55$^\circ$, and all reflections with $I > 2\sigma(I)$ were used in the structure determination. Final $R$ and $R_w$ values were 0.057 and 0.091, respectively. The maximum and minimum peaks in the difference map were $13.1\, e^{-}\AA^{-3}$ and $-3.66\, e^{-}\AA^{-3}$, respectively.
7. References
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8. DFT Computational results, Cartesian coordinates, computed total energies of optimized structures

molecule No.14a

|        |        |        |        |
|--------|--------|--------|--------|
| C      | -2.085560 | -1.053060 | -1.156055 |
| C      | -0.747163  | -0.907943  | -1.019121  |
| C      | -0.172526  | -2.262515  | -1.143344  |
| C      | -1.296247  | -3.159407  | -1.352424  |
| N      | -2.386501  | -2.431771  | -1.343441  |
| S      | -4.071723  | -3.109423  | -1.681604  |
| O      | -4.527180  | -2.286444  | -2.785776  |
| O      | -4.931446  | -2.715809  | -0.194118  |
| C      | -4.977498  | -3.663881  | 0.835338   |
| C      | -5.677060  | -3.347210  | 1.994058   |
| C      | -6.325909  | -2.109054  | 2.139624   |
| C      | -6.256690  | -1.182755  | 1.085465   |
| C      | -5.569460  | -1.472859  | -0.088075  |
| C      | -7.109762  | -1.794739  | 3.387468   |

S67
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 1.110639  | -2.685361 | -1.074038 |
| S       | 5.580326  | -2.546231 | 0.658256  |
| C       | 6.864270  | -1.781486 | -0.284604 |
| C       | 8.177624  | -1.770795 | 0.215713  |
| C       | 9.201898  | -1.218439 | -0.550270 |
| C       | 8.919192  | -0.677297 | -1.807389 |
| C       | 7.613210  | -0.686593 | -2.307550 |
| C       | 6.583089  | -1.239415 | -1.551271 |
| C       | 0.039539  | 0.379107  | -0.872336 |
| N       | -0.651465 | 1.503700  | -0.247686 |
| C       | -0.690693 | 1.583470  | 1.228038  |
| S       | -1.867437 | 2.279685  | -1.134559 |
| O       | -3.191350 | 1.900657  | -0.600422 |
| O       | -1.547401 | 1.997444  | -2.538191 |
| C       | -1.612819 | 4.008331  | -0.773860 |
| C       | -0.470596 | 4.646787  | -1.269379 |
| C       | -0.299155 | 6.003770  | -1.024182 |
| C       | -1.251991 | 6.739730  | -0.298064 |
| C       | -2.387242 | 6.073295  | 0.179832  |
| C       | -2.579784 | 4.711813  | -0.055666 |
| C       | -1.059945 | 8.217810  | -0.064287 |
O 5.009688  -1.154480  1.616813
C 3.928929  -0.509480  1.200924
O 3.249913  -0.709620  0.220056
C 3.551782   0.595852  2.224019
F 2.798874   0.046931  3.199314
F 2.819122   1.540102  1.610373
F 4.619095   1.170150  2.774423
C -1.424991   0.466725  1.924684
C -0.845165  -0.352946  2.802843
H -2.881458  -0.322514  -1.134511
H -1.317856  -4.232488  -1.495043
H -4.494339  -4.628140   0.720147
H -5.728670  -4.076148  2.797789
H -6.756304  -0.223096  1.180692
H -5.540940  -0.759674  -0.905170
H -8.155177  -2.108893  3.270308
H -6.707304  -2.319715  4.258797
H -7.114218  -0.721470  3.599450
H  1.940414  -2.010083  -0.881370
H  1.349702  -3.739043  -1.194365
H  8.382796  -2.195642  1.193042
S69
|   |   |   |   |
|---|---|---|---|
| H | 10.218449 | -1.210027 | -0.168864 |
| H | 9.720776  | -0.249077 | -2.402420 |
| H | 7.402216  | -0.267399 | -3.286869 |
| H | 5.564985  | -1.255578 | -1.926923 |
| H | 0.361933  | 0.691459  | -1.871613 |
| H | 0.946550  | 0.199794  | -0.285696 |
| H | -1.143362 | 2.549278  | 1.479719  |
| H | 0.347852  | 1.625059  | 1.572532  |
| H | 0.264775  | 4.091005  | -1.841888 |
| H | 0.585879  | 6.505909  | -1.406257 |
| H | -3.136429 | 6.626225  | 0.739885  |
| H | -3.466740 | 4.200778  | 0.302219  |
| H | -1.249653 | 8.785178  | -0.984313 |
| H | -0.034006 | 8.442653  | 0.247034  |
| H | -1.740627 | 8.595716  | 0.703813  |
| H | -2.484911 | 0.374427  | 1.693173  |
| H | -1.405118 | -1.126835 | 3.321231  |
| H | 0.210732  | -0.268478 | 3.051789  |

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total energy  -3253.86256444  a.u.

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S70
number of imaginary frequencies  0

molecule No.14b

optimized geometry

|   | x       | y       | z       |
|---|---------|---------|---------|
| C | 1.987391| -0.162176| 1.294311|
| C | 0.837537| -0.089891| 0.550999|
| C | 0.914047| 1.133239 | -0.213471|
| C | 2.112330| 1.747193 | 0.101951|
| N | 2.754520| 0.958738 | 1.019997|
| S | 4.309957| 1.336584 | 1.752616|
| O | 4.223976| 0.742275 | 3.079595|
| O | 4.457390| 2.766408 | 1.508509|
| C | 5.490554| 0.436062 | 0.774352|
| C | 5.864786| -0.850400| 1.171742|

S71
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| C    | 6.80256 | -1.53987 | 0.408059 |
| C    | 7.374765 | -0.964340 | -0.736981 |
| C    | 6.980163 | 0.331927 | -1.104257 |
| C    | 6.044532 | 1.041065 | -0.357188 |
| C    | 8.419407 | -1.705797 | -1.533136 |
| C    | -0.094634 | 1.648183 | -1.165640 |
| S    | -1.151759 | 2.998039 | -0.363700 |
| C    | -2.415722 | 3.424587 | -1.515791 |
| C    | -2.635072 | 4.806027 | -1.663913 |
| C    | -3.578545 | 5.233683 | -2.594244 |
| C    | -4.295032 | 4.294312 | -3.340644 |
| C    | -4.078445 | 2.921808 | -3.165877 |
| C    | -3.132719 | 2.465879 | -2.252631 |
| C    | -0.272241 | -1.104896 | 0.549158 |
| N    | -0.413800 | -1.787977 | -0.754900 |
| C    | 0.545060 | -2.869842 | -1.044944 |
| C    | 1.693749 | -2.502808 | -1.970109 |
| S    | -1.962447 | -1.898691 | -1.417948 |
| O    | -1.792260 | -2.479511 | -2.747994 |
|   | x     | y     | z     |
|---|-------|-------|-------|
| O | -2.535206 | -0.545388 | -1.246757 |
| C | -2.948504 | -3.019202 | -0.432717 |
| C | -3.639298 | -2.550111 | 0.688844 |
| C | -4.366167 | -3.453431 | 1.460636 |
| C | -4.421611 | -4.816079 | 1.131600 |
| C | -3.726208 | -5.255289 | -0.004941 |
| C | -2.993147 | -4.370267 | -0.791231 |
| C | -5.239841 | -5.779069 | 1.955942 |
| O | -1.910440 | 1.937945 | 0.742001 |
| C | -2.532710 | 2.551638 | 1.802314 |
| O | -2.623204 | 3.729302 | 1.970646 |
| C | -3.136474 | 1.454351 | 2.716258 |
| F | -2.208097 | 0.529217 | 3.004979 |
| F | -4.150342 | 0.855780 | 2.068942 |
| F | -3.583993 | 2.002307 | 3.835380 |
| C | 1.648157 | -1.473929 | -2.816544 |
| C | 2.864887 | -3.449433 | -1.891177 |
| H | 2.321628 | -0.894704 | 2.013657 |
| H | 2.551244 | 2.678464 | -0.225623 |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| H       | 5.448210 | -1.289279 | 2.071966 |
| H       | 7.105240 | -2.537798 | 0.713456 |
| H       | 7.420744 | 0.796574  | -1.982181|
| H       | 5.764316 | 2.052251  | -0.632032|
| H       | 8.289038 | -2.789532 | -1.457031|
| H       | 8.390372 | -1.428125 | -2.591282|
| H       | 9.425449 | -1.470909 | -1.161989|
| H       | -0.804055| 0.890831  | -1.507871|
| H       | 0.326250 | 2.191920  | -2.017833|
| H       | -2.084177| 5.523746  | -1.063425|
| H       | -3.759897| 6.295213  | -2.727643|
| H       | -5.034342| 4.632773  | -4.060418|
| H       | -4.650136| 2.202128  | -3.743157|
| H       | -2.978971| 1.401632  | -2.099649|
| H       | -1.220186| -0.617793 | 0.779395 |
| H       | -0.089024| -1.845319 | 1.339382 |
| H       | 0.009804 | -3.720959 | -1.482442|
| H       | 0.946157 | -3.227829 | -0.086294|
| H       | -3.632810| -1.495266 | 0.940005 |
|   |        |        |        |
|---|--------|--------|--------|
| H | -4.909022 | -3.091799 | 2.330036 |
| H | -3.766904 | -6.304644 | -0.284876 |
| H | -2.485256 | -4.713636 | -1.686033 |
| H | -6.252333 | -5.879761 | 1.543885 |
| H | -5.340792 | -5.437704 | 2.990652 |
| H | -4.793034 | -6.778159 | 1.966028 |
| H | 2.471857  | -1.263133 | -3.492705 |
| H | 0.779267  | -0.827982 | -2.879103 |
| H | 3.331894  | -3.423901 | -0.896523 |
| H | 3.629162  | -3.202049 | -2.632748 |
| H | 2.551773  | -4.488197 | -2.064853 |

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total energy  -3293.18847015 a.u.
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number of imaginary frequencies  0
molecule No.14c

optimized geometry

|   |   |   |   |
|---|---|---|---|
| C | -2.045835 | -1.009078 | -1.268847 |
| C | -0.708214 | -0.878275 | -1.112185 |
| C | -0.143187 | -2.234790 | -1.258011 |
| C | -1.271877 | -3.118253 | -1.497045 |
| N | -2.355766 | -2.381073 | -1.486547 |
| S | -4.044137 | -3.038649 | -1.841865 |
| O | -3.782159 | -4.467590 | -1.923536 |
| O | -4.478135 | -2.220620 | -2.958273 |
| C | -4.912416 | -2.617718 | -0.366417 |
| C | -4.964759 | -3.546165 | 0.680283 |
| C | -5.665756 | -3.204994 | 1.831553 |
| C | -6.310628 | -1.961802 | 1.951979 |
| C | -6.234863 | -1.055654 | 0.880825 |
| C | -5.545201 | -1.370281 | -0.284946 |
| C | -7.098334 | -1.621338 | 3.190578 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 1.135937  | -2.668891 | -1.184729 |
| S       | 5.660888  | -2.535196 | 0.623007  |
| C       | 6.927746  | -1.745117 | -0.322209 |
| C       | 8.239228  | -1.697962 | 0.180880  |
| C       | 9.251253  | -1.125809 | -0.586861 |
| C       | 8.958189  | -0.601161 | -1.848595 |
| C       | 7.654061  | -0.646763 | -2.351561 |
| C       | 6.636218  | -1.219537 | -1.593477 |
| C       | 0.085386  | 0.399015  | -0.925183 |
| N       | -0.610945 | 1.516857  | -0.295406 |
| C       | -0.690554 | 1.565317  | 1.182558  |
| S       | -1.797463 | 2.318859  | -1.196946 |
| O       | -3.138774 | 1.941545  | -0.706165 |
| O       | -1.444297 | 2.063146  | -2.597996 |
| C       | -1.539551 | 4.038308  | -0.795129 |
| C       | -0.376239 | 4.675409  | -1.240555 |
| C       | -0.201223 | 6.026021  | -0.964331 |
| C       | -1.171153 | 6.757175  | -0.256354 |
| C       | -2.327251 | 6.092435  | 0.171238  |
C   -2.523508  4.737374  -0.096085
C   -0.974616  8.228967   0.011215
O    5.052884 -1.152070  1.571214
C    3.963113 -0.531083  1.142422
O    3.298809 -0.747655  0.155150
C    3.551465  0.568803  2.158085
F    2.789148  0.008940  3.119995
F    2.815531  1.501593  1.530754
F    4.599451  1.159676  2.727706
C   -1.438782  0.435518  1.838920
C   -0.879866 -0.405788  2.714524
C   -1.597927 -1.508465  3.437083
H   -2.835423 -0.271831 -1.240319
H   -1.301302 -4.188528 -1.658088
H   -4.485403 -4.514452  0.584363
H   -5.723374 -3.919036  2.648141
H   -6.730541 -0.092253  0.956711
H   -5.509608 -0.671939 -1.114447
H  -8.148635 -1.916190  3.067264

S78
|   | x         | y         | z         |
|---|-----------|-----------|-----------|
| H | -6.713295 | -2.145680 | 4.070039  |
| H | -7.084073 | -0.546161 | 3.392551  |
| H | 1.968603  | -2.003848 | -0.970395 |
| H | 1.368533  | -3.721595 | -1.324776 |
| H | 8.452612  | -2.110530 | 1.161708  |
| H | 10.266371 | -1.089281 | -0.203285 |
| H | 9.750289  | -0.157489 | -2.445012 |
| H | 7.435043  | -0.240237 | -3.334458 |
| H | 5.619707  | -1.263884 | -1.971111 |
| H | 0.432197  | 0.726735  | -1.911293 |
| H | 0.978102  | 0.201644  | -0.322653 |
| H | -1.149057 | 2.527469  | 1.437638  |
| H | 0.339460  | 1.603126  | 1.552464  |
| H | 0.373208  | 4.123478  | -1.798349 |
| H | 0.700432  | 6.526874  | -1.307257 |
| H | -3.089687 | 6.641721  | 0.716859  |
| H | -3.425756 | 4.227638  | 0.223298  |
| H | -1.139424 | 8.815833  | -0.901386 |
| H | 0.045268  | 8.440428  | 0.350442  |
H  -1.670453  8.596460  0.770791
H  -2.495972  0.348782  1.589165
H   0.179659 -0.288889  2.949977
H  -1.113393 -2.479230  3.265581
H  -2.644453 -1.585581  3.123134
H  -1.580238 -1.342696  4.522274

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total energy  -3293.18300808  a.u.
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number of imaginary frequencies  0

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molecule No.14d

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optimized geometry

|     |       |       |
|-----|-------|-------|
| C   | 1.727902 | -0.297164 | -1.708880 |

S80
|  | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| C | 0.376257  | -0.321027 | -1.662191 |
| C | -0.089485 | 0.774724  | -2.535312 |
| C | 1.107521  | 1.391802  | -3.077553 |
| N | 2.139303  | 0.765871  | -2.567934 |
| S | 3.898792  | 1.183300  | -2.973299 |
| O | 3.752971  | 1.846776  | -4.259147 |
| O | 4.561637  | -0.089606 | -2.766036 |
| C | 4.296632  | 2.346151  | -1.708699 |
| C | 4.274120  | 3.711015  | -2.017417 |
| C | 4.586020  | 4.620956  | -1.012514 |
| C | 4.906667  | 4.191248  | 0.285098  |
| C | 4.918256  | 2.812386  | 0.557963  |
| C | 4.623388  | 1.880347  | -0.428985 |
| C | 5.255505  | 5.181849  | 1.365477  |
| C | -1.342122 | 1.202234  | -2.811888 |
| S | -4.980870 | 3.225897  | -0.707265 |
| C | -6.551412 | 2.418672  | -0.641528 |
| C | -7.636155 | 3.066893  | -0.026180 |
| C | -8.890028 | 2.459626  | -0.023641 |
C  -9.062155  1.211642  -0.628581
C  -7.984328  0.564286  -1.241060
C  -6.728002  1.164398  -1.252369
C  -0.539034  -1.314676  -0.982860
N   0.090379  -2.358673  -0.187707
C   0.266166  -2.187658  1.269449
S   1.007630  -3.531823  -0.991103
O   2.425344  -3.351173  -0.634841
O   0.574943  -3.448477  -2.390695
C   0.466067  -5.078656  -0.280807
C  -0.794515  -5.581579  -0.620072
C  -1.198114  -6.801296  -0.089617
C  -0.362225  -7.534645   0.770218
C   0.896555  -7.008029  1.086289
C   1.321589  -5.786307  0.564171
C  -0.805380  -8.870885  1.313103
O  -4.232467   2.625066  0.795329
C  -3.442393   1.561805  0.718443
O  -3.157644   0.888947  -0.244674

S82
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | -2.819593 | 1.277289  | 2.112675  |
| F    | -3.670421 | 1.506345  | 3.110303  |
| F    | -1.733327 | 2.061120  | 2.274463  |
| F    | -2.419359 | -0.005038 | 2.171040  |
| C    | 1.407875  | -1.317578 | 1.725451  |
| C    | 1.226767  | -0.218035 | 2.473341  |
| C    | 2.263678  | 0.622833  | 3.091755  |
| C    | 3.592787  | 0.191945  | 3.264668  |
| C    | 4.528994  | 1.004880  | 3.900305  |
| C    | 4.159963  | 2.267884  | 4.377479  |
| C    | 2.845302  | 2.709466  | 4.211875  |
| C    | 1.908230  | 1.892558  | 3.580149  |
| H    | 2.467389  | -0.962446 | -1.286620 |
| H    | 1.210286  | 2.217168  | -3.770543 |
| H    | 4.038128  | 4.045428  | -3.021733 |
| H    | 4.582702  | 5.683099  | -1.240207 |
| H    | 5.152663  | 2.464004  | 1.558934  |
| H    | 4.653884  | 0.817877  | -0.212217 |
| H    | 6.344835  | 5.264871  | 1.472875  |
|   | X          | Y          | Z          |
|---|------------|------------|------------|
| H | 4.870246   | 6.179998   | 1.138804   |
| H | 4.856448   | 4.863882   | 2.333772   |
| H | -2.218595  | 0.763242   | -2.345981  |
| H | -1.509188  | 2.030135   | -3.496038  |
| H | -7.488273  | 4.036394   | 0.438545   |
| H | -9.731492  | 2.957820   | 0.448214   |
| H | -10.041651 | 0.742031   | -0.626049  |
| H | -8.127013  | -0.403769  | -1.712019  |
| H | -5.882397  | 0.674689   | -1.724355  |
| H | -1.143943  | -1.787334  | -1.765312  |
| H | -1.235412  | -0.782155  | -0.324952  |
| H | 0.382690   | -3.195379  | 1.687441   |
| H | -0.682047  | -1.801646  | 1.657387   |
| H | -1.439987  | -5.032533  | -1.297855  |
| H | -2.175671  | -7.198273  | -0.351008  |
| H | 1.559210   | -7.563044  | 1.744793   |
| H | 2.304400   | -5.389992  | 0.794676   |
| H | -0.710230  | -9.652289  | 0.548246   |
| H | -1.855799  | -8.848502  | 1.622544   |
### Molecule No. 15a

#### Optimized Geometry

| Atom | X    | Y    | Z    |
|------|------|------|------|
| H    | -0.201866 | -9.176036 | 2.172775 |
| H    | 2.404551  | -1.670228 | 1.467099 |
| H    | 0.203869  | 0.100887  | 2.673418 |
| H    | 3.883952  | -0.802483 | 2.938247 |
| H    | 5.542822  | 0.642461  | 4.049193 |
| H    | 4.885462  | 2.889018  | 4.895747 |
| H    | 2.543918  | 3.681459  | 4.592988 |
| H    | 0.881412  | 2.233037  | 3.467083 |

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**Total Energy**: -3484.92254982 a.u.

**Number of Imaginary Frequencies**: 0
| x   | y       | z       |
|-----|---------|---------|
| C   | -2.201562 | -0.535183 | 0.181536 |
| C   | -1.186017 | -0.069159 | -0.618187 |
| C   | -1.463703 | 1.317978  | -0.877875 |
| C   | -2.638984 | 1.642598  | -0.224839 |
| N   | -3.078195 | 0.510184  | 0.409878  |
| S   | -4.543299 | 0.428691  | 1.400941  |
| O   | -4.846786 | 1.832937  | 1.649244  |
| O   | -4.207854 | -0.529346 | 2.443125  |
| C   | -5.763536 | -0.271265 | 0.315032  |
| C   | -5.957379 | -1.656463 | 0.312793  |
| C   | -6.932841 | -2.192048 | -0.521574 |
| C   | -7.716840 | -1.370449 | -1.348379 |
| C   | -7.503297 | 0.015547  | -1.312183 |
| C   | -6.532911 | 0.576141  | -0.485535 |
| C   | -8.763160 | -1.972449 | -2.252722 |
| C   | -0.603132 | 2.235772  | -1.648659 |
| S   | 0.669343  | 3.052753  | -0.510302 |
| C   | 1.800242  | 3.939283  | -1.586291 |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 2.078323  | 5.260929  | -1.214003 |
| C       | 2.944130  | 6.019173  | -2.002894 |
| C       | 3.512936  | 5.463740  | -3.149910 |
| C       | 3.220595  | 4.146812  | -3.517559 |
| C       | 2.361562  | 3.373664  | -2.738694 |
| C       | -0.006539 | -0.856585 | -1.113058 |
| N       | 1.193935  | -0.710474 | -0.264373 |
| C       | 2.074771  | 0.427423  | -0.468126 |
| S       | 1.903557  | -2.166352 | 0.322211  |
| O       | 0.766855  | -3.026672 | 0.642183  |
| O       | 2.879435  | -1.723767 | 1.321341  |
| C       | 2.811777  | -2.910242 | -1.028247 |
| C       | 2.158157  | -3.790749 | -1.895870 |
| C       | 2.870030  | -4.351675 | -2.953029 |
| C       | 4.227240  | -4.057746 | -3.155135 |
| C       | 4.859267  | -3.180323 | -2.261334 |
| C       | 4.166007  | -2.607131 | -1.197786 |
| C       | 4.998214  | -4.705855 | -4.278488 |
| C       | 1.718102  | 1.718962  | 0.322373  |

S87
| Atom | x         | y         | z         |
|------|-----------|-----------|-----------|
| C    | 1.14447   | 1.470707  | 1.725442  |
| O    | 2.264217  | 1.020112  | 2.499439  |
| C    | 2.009052  | 0.066038  | 3.427881  |
| O    | 0.931961  | -0.385085 | 3.697489  |
| C    | 3.312196  | -0.295645 | 4.172854  |
| F    | 3.510318  | 0.617413  | 5.145172  |
| F    | 4.375987  | -0.277843 | 3.358600  |
| F    | 3.200132  | -1.499254 | 4.726722  |
| H    | -2.359072 | -1.505069 | 0.629743  |
| H    | -3.187821 | 2.569243  | -0.144245 |
| H    | -5.375947 | -2.293058 | 0.971092  |
| H    | -7.099014 | -3.265983 | -0.521385 |
| H    | -8.114989 | 0.667180  | -1.929828 |
| H    | -6.393401 | 1.650931  | -0.441097 |
| H    | -9.371369 | -2.710611 | -1.718955 |
| H    | -9.432181 | -1.208931 | -2.659066 |
| H    | -8.295483 | -2.491347 | -3.099141 |
| H    | -1.128577 | 3.104627  | -2.053475 |
| H    | -0.045514 | 1.748724  | -2.450856 |
| H          | X      | Y      | Z         |
|------------|--------|--------|-----------|
| H          | 1.626845 | 5.690517 | -0.324880 |
| H          | 3.167592 | 7.043079 | -1.720589 |
| H          | 4.183299 | 6.058104 | -3.763060 |
| H          | 3.660900 | 3.719840 | -4.413229 |
| H          | 2.138656 | 2.354554 | -3.036405 |
| H          | 0.243696 | -0.575361 | -2.147736 |
| H          | -0.274386 | -1.912835 | -1.123732 |
| H          | 2.198767 | 0.654160 | -1.536551 |
| H          | 3.060323 | 0.153069 | -0.084264 |
| H          | 1.120861 | -4.058258 | -1.725108 |
| H          | 2.367107 | -5.043281 | -3.623851 |
| H          | 5.914902 | -2.955558 | -2.389367 |
| H          | 4.674798 | -1.964245 | -0.487380 |
| H          | 5.837344 | -4.082766 | -4.602712 |
| H          | 4.358698 | -4.900544 | -5.145132 |
| H          | 5.412815 | -5.669979 | -3.956894 |
| H          | 2.641897 | 2.296562 | 0.438958  |
| H          | 0.358969 | 0.714131 | 1.721008  |
| H          | 0.763039 | 2.394587 | 2.171792  |
total energy  -3253.90585342  a.u.

number of imaginary frequencies  0

molecule No.15b

optimized geometry

|   | x          | y          | z          |
|---|------------|------------|------------|
| C | -1.833045  | -0.424486  | -0.464056  |
| C | -0.694870  | 0.096785   | -1.028049  |
| C | -0.877960  | 1.519776   | -1.105487  |
| C | -2.124633  | 1.814102   | -0.584594  |
| N | -2.695693  | 0.625747   | -0.203575  |
| S | -4.231409  | 0.496065   | 0.663191   |
| O | -4.529495  | 1.881006   | 1.008659   |

S90
| Element | X        | Y        | Z        |
|---------|----------|----------|----------|
| O       | -3.995512| -0.550903| 1.646749 |
| C       | -5.375950| -0.085520| -0.564476|
| C       | -5.607505| -1.458803| -0.681828|
| C       | -6.518170| -1.902719| -1.636541|
| C       | -7.202006| -1.000720| -2.466122|
| C       | -6.949002| 0.372388 | -2.317045|
| C       | -6.043466| 0.841190 | -1.370489|
| C       | -8.214485| -1.492361| -3.470022|
| C       | 0.133410 | 2.475039 | -1.591880|
| S       | 1.310012 | 3.037837 | -0.205756|
| C       | 2.682018 | 3.790584 | -1.083756|
| C       | 3.327741 | 3.176251 | -2.165808|
| C       | 4.363666 | 3.852816 | -2.807612|
| C       | 4.748074 | 5.125854 | -2.376491|
| C       | 4.095541 | 5.732846 | -1.302362|
| C       | 3.055910 | 5.069563 | -0.650063|
| C       | 0.562061 | -0.651989| -1.367390|
| N       | 1.482096 | -0.746326| -0.217282|
| C       | 2.464435 | 0.291122 | 0.034808 |

S91
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | 2.008842  | 1.548369  | 0.842080  |
| C       | 3.231625  | 2.181728  | 1.523704  |
| C       | 0.870580  | 1.275134  | 1.855040  |
| S       | 1.732721  | -2.297648 | 0.468417  |
| O       | 0.469963  | -3.002513 | 0.245153  |
| O       | 2.278205  | -2.039396 | 1.801374  |
| C       | 3.003759  | -3.111401 | -0.492957 |
| C       | 2.648229  | -3.836768 | -1.634220 |
| C       | 3.647843  | -4.451097 | -2.383906 |
| C       | 4.997663  | -4.363266 | -2.009894 |
| C       | 5.322720  | -3.638956 | -0.853478 |
| C       | 4.338544  | -3.015957 | -0.089271 |
| C       | 6.066848  | -5.069208 | -2.806767 |
| O       | 1.484789  | 0.629739  | 2.976699  |
| C       | 0.832367  | -0.170378 | 3.860094  |
| O       | 1.398387  | -0.610624 | 4.815601  |
| C       | -0.670211 | -0.461759 | 3.602637  |
| F       | -0.834278 | -1.168368 | 2.464650  |
| F       | -1.350783 | 0.702120  | 3.468557  |
|   |       |       |       |
|---|-------|-------|-------|
| F | -1.184226 | -1.144508 | 4.612116 |
| H | -2.075171 | -1.436622 | -0.177240 |
| H | -2.646133 | 2.748502 | -0.439518 |
| H | -5.101675 | -2.159030 | -0.025732 |
| H | -6.708762 | -2.968129 | -1.732111 |
| H | -7.477023 | 1.084776 | -2.945058 |
| H | -5.871279 | 1.904651 | -1.243727 |
| H | -9.214749 | -1.533972 | -3.019661 |
| H | -8.275522 | -0.828133 | -4.337541 |
| H | -7.973992 | -2.499778 | -3.822888 |
| H | -0.281743 | 3.433560 | -1.914018 |
| H | 0.765341 | 2.076432 | -2.386744 |
| H | 3.035366 | 2.191534 | -2.514595 |
| H | 4.869104 | 3.385047 | -3.646765 |
| H | 5.554793 | 5.646158 | -2.883575 |
| H | 4.389399 | 6.723994 | -0.971615 |
| H | 2.540192 | 5.540955 | 0.180783 |
| H | 1.092779 | -0.179091 | -2.206177 |
| H | 0.308311 | -1.663587 | -1.683657 |
| H  | 2.949406   | 0.613198   | -0.897469   |
| H  | 3.248895   | -0.150022  | 0.654881    |
| H  | 3.566053   | 1.494228   | 2.304072    |
| H  | 2.993042   | 3.134523   | 2.007335    |
| H  | 4.049988   | 2.339056   | 0.816223    |
| H  | 0.108020   | 0.648558   | 1.398710    |
| H  | 0.424162   | 2.215027   | 2.194786    |
| H  | 1.604937   | -3.946389  | -1.910402   |
| H  | 3.373924   | -5.022762  | -3.266791   |
| H  | 6.360362   | -3.575177  | -0.536464   |
| H  | 4.595406   | -2.494165  | 0.826498    |
| H  | 7.034949   | -4.567488  | -2.714106   |
| H  | 5.807230   | -5.123172  | -3.868680   |
| H  | 6.197851   | -6.099322  | -2.450961   |

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total energy  -3293.20889726  a.u.
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number of imaginary frequencies  0

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S94
molecule No.15c

optimized geometry

|   | x    | y    | z    |
|---|------|------|------|
| C | -2.744599 | -0.892851 | 0.147492 |
| C | -1.502216 | -0.405187 | -0.160534 |
| C | -1.510260 | 0.999684 | 0.153129 |
| C | -2.760764 | 1.307833 | 0.650708 |
| N | -3.507938 | 0.157106 | 0.630477 |
| S | -5.184650 | 0.041381 | 1.145595 |
| O | -5.347327 | 1.181231 | 2.039348 |
| O | -5.328418 | -1.347699 | 1.558940 |
| C | -6.121695 | 0.316171 | -0.342447 |
| C | -6.476749 | -0.776921 | -1.137218 |
| C | -7.222763 | -0.551679 | -2.290616 |
| C | -7.624433 | 0.742113 | -2.657355 |
C  -7.256000   1.816873  -1.833147
C  -6.509971   1.616629  -0.675291
C  -8.466061   0.968339  -3.885503
C  -0.418245   1.967839  -0.042082
S   1.118235   1.675392   1.094112
C   1.655483   3.371613   1.377393
C   1.685838   3.774354   2.718043
C   2.035057   5.091481   3.022789
C   2.348739   5.986741   1.999689
C   2.316249   5.573236   0.663888
C   1.965428   4.263531   0.340684
C  -0.307709  -1.178966  -0.629410
N   0.865734  -0.986798   0.264430
C   2.133549  -0.526560  -0.298243
S   0.958303  -1.989195   1.665107
O  -0.380987  -1.968047   2.242764
O   2.134588  -1.484175   2.381507
C   1.301427  -3.647616   1.097189
C   0.236437  -4.523304   0.863786

S96
C 0.507327  -5.809415  0.401392
C 1.822699  -6.240325  0.175901
C 2.872126  -5.343316  0.431975
C 2.624679  -4.054149  0.894022
C 2.108398  -7.646621  -0.289021
C 2.360201   1.011539  -0.136786
C 3.817796   1.386437  0.233712
O 4.644079   0.778088  -0.806394
C 4.348028   0.897142  1.571048
C 4.707096   1.427095  -1.979754
O 4.133261   2.448700  -2.264248
C 5.584803   0.627227  -2.968704
F 5.784703   1.331756  -4.078127
F 4.937161  -0.514000  -3.281915
F 6.764004   0.313754  -2.419949
H -3.144283  -1.895049  0.124439
H -3.179217   2.234605  1.014300
H -6.193280  -1.782336  -0.845109
H -7.507953  -1.396520  -2.911657

S97
|   |   |   |   |
|---|---|---|---|
| H | -7.567651 | 2.824079 | -2.096351 |
| H | -6.251855 | 2.448196 | -0.028408 |
| H | -9.534195 | 0.915620 | -3.640776 |
| H | -8.281839 | 1.954516 | -4.325659 |
| H | -8.271419 | 0.210378 | -4.653369 |
| H | -0.714233 | 2.986503 | 0.214785 |
| H | 0.010631  | 1.964446 | -1.049013 |
| H | 1.439407  | 3.073109 | 3.509988 |
| H | 2.061174  | 5.412088 | 4.059479 |
| H | 2.621660  | 7.009563 | 2.240724 |
| H | 2.566799  | 6.269964 | -0.130034 |
| H | 1.959357  | 3.949732 | -0.698801 |
| H | 0.011607  | -0.849012 | -1.625999 |
| H | -0.549412 | -2.244354 | -0.726157 |
| H | 2.187880  | -0.770808 | -1.364064 |
| H | 2.956354  | -1.046614 | 0.188883 |
| H | -0.780780 | -4.211067 | 1.074689 |
| H | -0.317465 | -6.494785 | 0.225692 |
| H | 3.899079  | -5.664902 | 0.280096 |

S98
H 3.446706  -3.385510  1.126040
H 2.987408  -7.683175  -0.940248
H 1.259198  -8.070711  -0.832998
H 2.310305  -8.303220  0.567148
H 2.125849  1.528639  -1.071065
H 3.939201  2.467202  0.148231
H 5.415455  1.125928  1.633898
H 4.203491  -0.173566  1.723570
H 3.843502  1.421483  2.388587

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total energy  -3293.22803404  a.u.
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number of imaginary frequencies  0
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molecule No.15d
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optimized geometry

|   | x         | y         | z          |
|---|-----------|-----------|------------|
| C | 3.002657  | -0.116918 | -0.471115  |
| C | 1.904447  | -0.018176 | 0.347669   |
| C | 1.744819  | 1.377587  | 0.668141   |
| C | 2.759597  | 2.072643  | 0.036797   |
| N | 3.518002  | 1.155951  | -0.644545  |
| S | 4.928756  | 1.567476  | -1.625884  |
| O | 4.815459  | 3.013466  | -1.775246  |
| O | 4.875976  | 0.628616  | -2.736321  |
| C | 6.311564  | 1.175153  | -0.579255  |
| C | 6.902337  | -0.087339 | -0.678074  |
| C | 8.000724  | -0.375627 | 0.127335   |
| C | 8.516350  | 0.573225  | 1.023427   |
| C | 7.906125  | 1.836151  | 1.087459   |
| C | 6.807213  | 2.148312  | 0.293065   |
| C | 9.694145  | 0.241739  | 1.905551   |
| C | 0.677946  | 1.965391  | 1.496113   |
| S | -0.962805 | 2.258678  | 0.539957   |

S100
C    0.974801  -1.12932   0.786725
N   -0.154238  -1.387308  -0.138022
C   -1.696373   0.539386   0.241272
C   -0.796049  -0.232278  -0.763770
C   -1.996961   2.987854   1.812329
C   -2.254419   2.341112   3.029255
C   -3.031596   2.990306   3.986604
C   -3.538087   4.268987   3.732737
C   -3.272963   4.904931   2.519333
C   -2.499647   4.267269   1.548226
C   -3.155887   0.726562  -0.241522
S    0.117352  -2.731463  -1.196238
O    1.533695  -2.773641  -1.581847
O   -0.936688  -2.641196  -2.210134
C   -0.194162  -4.120340  -0.115598
C    0.842982  -5.013284   0.155149
C    0.584906  -6.124846   0.957473
C   -0.691980  -6.360445   1.482584
C   -1.716131  -5.444256   1.186837

S101
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | -1.481382 | -4.330056 | 0.389224 |
| C       | -0.973831 | -7.583205 | 2.320562 |
| O       | -3.032585 | 1.290946  | -1.566077 |
| C       | -3.909304 | -0.593342 | -0.235813 |
| C       | -3.994979 | 1.990495  | -2.222736 |
| O       | -3.899674 | 2.212244  | -3.393442 |
| C       | -5.167200 | 2.572105  | -1.390286 |
| F       | -4.668484 | 3.391449  | -0.426845 |
| F       | -5.870692 | 1.603302  | -0.777734 |
| F       | -5.978160 | 3.273918  | -2.164563 |
| C       | -4.014751 | -1.395060 | -1.377560 |
| C       | -4.719955 | -2.599475 | -1.320014 |
| C       | -5.317074 | -3.010654 | -0.127788 |
| C       | -5.211859 | -2.212248 | 1.014825  |
| C       | -4.514432 | -1.007291 | 0.958900  |
| H       | 3.426221  | -0.969561 | -0.979517 |
| H       | 3.000299  | 3.124740  | 0.000909  |
| H       | 6.526805  | -0.814490 | -1.390044 |
| H       | 8.474680  | -1.350146 | 0.048280  |
|     |       |       |       |
|-----|-------|-------|-------|
|     | 8.306956 | 2.590437 | 1.759146 |
| H   |       |       |       |
|     | 6.358769 | 3.135454 | 0.326210 |
| H   |       |       |       |
|     | 9.355923 | -0.153100 | 2.872634 |
| H   |       |       |       |
|     | 10.302995 | 1.127601 | 2.110668 |
| H   |       |       |       |
|     | 10.335929 | -0.517718 | 1.449160 |
| H   |       |       |       |
|     | 0.900950 | 2.980951 | 1.832370 |
| H   |       |       |       |
|     | 0.392316 | 1.359227 | 2.359208 |
| H   |       |       |       |
|     | 0.540858 | -0.860714 | 1.763978 |
| H   |       |       |       |
|     | 1.516234 | -2.048267 | 0.937991 |
| H   |       |       |       |
|     | -1.718099 | 0.034795 | 1.209993 |
| H   |       |       |       |
|     | -1.421840 | -0.606532 | -1.571790 |
| H   |       |       |       |
|     | -0.067410 | 0.443453 | -1.230874 |
| H   |       |       |       |
|     | -1.862015 | 1.350031 | 3.236973 |
| H   |       |       |       |
|     | -3.238748 | 2.498850 | 4.932178 |
| H   |       |       |       |
|     | -4.141404 | 4.768490 | 4.484503 |
| H   |       |       |       |
|     | -3.668800 | 5.896107 | 2.322177 |
| H   |       |       |       |
|     | -2.297960 | 4.753750 | 0.599168 |
| H   |       |       |       |
|     | -3.663466 | 1.430222 | 0.422038 |
| H   |       |       |       |
|     | 1.828199 | -4.841887 | -0.264548 |

S103
|    |    |    |    |
|----|----|----|----|
| H  | 1.389378 | -6.823409 | 1.171294 |
| H  | -2.714214 | -5.612993 | 1.583131 |
| H  | -2.284354 | -3.638160 | 0.157707 |
| H  | -1.675916 | -7.361413 | 3.131135 |
| H  | -0.058447 | -7.988842 | 2.761302 |
| H  | -1.424005 | -8.376613 | 1.710036 |
| H  | -3.562667 | -1.085408 | -2.313655 |
| H  | -4.800142 | -3.212524 | -2.212359 |
| H  | -5.872070 | -3.943520 | -0.090394 |
| H  | -5.688114 | -2.518109 | 1.941802 |
| H  | -4.459031 | -0.376372 | 1.844242 |

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**total energy**  -3484.95217939  a.u.

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**number of imaginary frequencies**  0

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S104
molecule No.21a

|    | x          | y          | z          |
|----|------------|------------|------------|
| C  | 0.648543   | -0.534888  | -0.364794  |
| C  | 0.015760   | 0.680710   | -0.557583  |
| C  | -1.388945  | 0.434888   | -0.671886  |
| C  | -1.570115  | -0.927522  | -0.528965  |
| N  | -0.335170  | -1.517809  | -0.347812  |
| S  | 0.003256   | -3.184932  | 0.116631   |
| O  | 0.475561   | -3.105074  | 1.500256   |
| O  | 0.874174   | -3.714506  | -0.931423  |
| C  | -1.589262  | -3.954434  | 0.045164   |
| C  | -2.008420  | -4.535633  | -1.156260  |
| C  | -3.249243  | -5.164167  | -1.193095  |
| C  | -4.067993  | -5.228008  | -0.053654  |
| C  | -3.612312  | -4.638344  | 1.136834   |
| C  | -2.376133  | -4.002756  | 1.200589   |
| C  | -5.393926  | -5.944335  | -0.098739  |

S105
| Element | X  | Y  | Z     |
|---------|----|----|-------|
| C       | 2.108983 | -0.768405 | -0.148481 |
| C       | 2.621007 | -0.123733 | 1.175193 |
| C       | 1.840057 | 1.148730  | 1.577060 |
| N       | 1.788413 | 2.092122  | 0.457523 |
| C       | 0.699373 | 2.023880  | -0.564643 |
| C       | -2.478550 | 1.440760  | -0.861262 |
| S       | -2.779196 | 2.333670  | 0.749714  |
| C       | -3.995605 | 3.555006  | 0.243956  |
| C       | -5.356963 | 3.314946  | 0.473455  |
| C       | -6.304563 | 4.272238  | 0.108404  |
| C       | -5.899178 | 5.468181  | -0.487162 |
| C       | -4.542367 | 5.711542  | -0.712955 |
| C       | -3.590278 | 4.761086  | -0.344426 |
| S       | 3.243910  | 2.834796  | 0.154375  |
| O       | 3.715534  | 3.482345  | 1.374258  |
| O       | 3.174987  | 3.516761  | -1.131619 |
| C       | 4.283305  | 1.373916  | -0.026760 |
| C       | 5.104495  | 1.239107  | -1.120551 |
| C       | 5.896724  | 0.083960  | -1.246488 |

S106
|   |   |   |   |
|---|---|---|---|
| C | 5.865830 | -0.994455 | -0.322742 |
| C | 5.027348 | -0.868019 | 0.762301 |
| C | 4.163650 | 0.304849 | 0.995738 |
| C | 6.738705 | -2.204449 | -0.541090 |
| H | -2.474656 | -1.514770 | -0.555897 |
| H | -1.370677 | -4.504301 | -2.033215 |
| H | -3.585745 | -5.620536 | -2.119836 |
| H | -4.232057 | -4.684232 | 2.027975 |
| H | -2.020272 | -3.562289 | 2.125800 |
| H | -6.103822 | -5.521621 | 0.618494 |
| H | -5.265994 | -7.004888 | 0.154214 |
| H | -5.841463 | -5.899135 | -1.096144 |
| H | 2.649925 | -0.326139 | -0.995344 |
| H | 2.352470 | -1.831485 | -0.159876 |
| H | 2.562496 | -0.849854 | 1.993823 |
| H | 2.299728 | 1.638018 | 2.440222 |
| H | 0.818004 | 0.890629 | 1.854347 |
| H | -0.030781 | 2.805134 | -0.328349 |
| H | 1.143711 | 2.270542 | -1.534730 |

S107
|   |   |   |   |
|---|---|---|---|
| H | -3.407807 | 0.954624 | -1.169263 |
| H | -2.218722 | 2.185041 | -1.619680 |
| H | -5.666598 | 2.385205 | 0.941141 |
| H | -7.358790 | 4.083867 | 0.290884 |
| H | -6.638381 | 6.212419 | -0.769372 |
| H | -4.224101 | 6.645546 | -1.167435 |
| H | -2.533300 | 4.956281 | -0.501194 |
| H | 5.150373  | 2.024357 | -1.868849 |
| H | 6.571182  | 0.014546 | -2.097776 |
| H | 4.977564  | -1.663439| 1.503070 |
| H | 4.421855  | 0.728358 | 1.984318 |
| H | 6.623271  | -2.930789| 0.266928 |
| H | 7.795342  | -1.919183| -0.594747 |
| H | 6.485412  | -2.702748| -1.483713 |

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total energy  -2727.08525279  a.u.
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number of imaginary frequencies  0
molecule No.21b

optimized geometry

| x         | y         | z         |
|-----------|-----------|-----------|
| C         | -1.293990 | -0.981205 | -0.886332 |
| C         | -1.143702 | 0.375289  | -0.765213 |
| C         | -2.442440 | 0.988848  | -0.756558 |
| C         | -3.345450 | -0.037346 | -0.885610 |
| N         | -2.658906 | -1.244956 | -0.934893 |
| S         | -3.392625 | -2.767526 | -1.426741 |
| O         | -2.461266 | -3.781415 | -0.933727 |
| O         | -3.716437 | -2.653044 | -2.843562 |
| C         | -4.890951 | -2.787508 | -0.473683 |
| C         | -6.099755 | -2.483225 | -1.104810 |
| C         | -7.274722 | -2.532295 | -0.357544 |
| C         | -7.259861 | -2.886763 | 0.999224  |
| Element | X         | Y         | Z         |
|---------|-----------|-----------|-----------|
| C       | -6.027097 | -3.194087 | 1.600141  |
| C       | -4.841329 | -3.152746 | 0.875755  |
| C       | -8.540141 | -2.969494 | 1.791921  |
| C       | -2.757637 | 2.439194  | -0.581813 |
| S       | -2.353485 | 2.953569  | 1.165785  |
| C       | -0.156500 | -1.945640 | -0.882633 |
| C       | 1.048836  | -1.428079 | -0.093077 |
| C       | 0.866109  | -0.663052 | 1.165367  |
| N       | 1.232695  | 0.114992  | -0.058237 |
| C       | 0.193775  | 1.028303  | -0.675741 |
| C       | -2.488498 | 4.741473  | 1.041555  |
| C       | -3.734984 | 5.362823  | 1.197335  |
| C       | -3.835685 | 6.752374  | 1.121224  |
| C       | -2.694803 | 7.526873  | 0.900314  |
| C       | -1.450109 | 6.910871  | 0.756059  |
| C       | -1.344268 | 5.521022  | 0.825632  |
| S       | 2.927257  | 1.023127  | 0.020653  |
| O       | 3.644322  | 0.304816  | 1.063516  |
| O       | 2.500441  | 2.407394  | 0.163337  |
|   |   |   |   |
|---|---|---|---|
| C | 3.667303 | 0.756572 | -1.563172 |
| C | 3.314750 | 1.599077 | -2.625967 |
| C | 3.937783 | 1.413190 | -3.854814 |
| C | 4.915259 | 0.419941 | -4.034544 |
| C | 5.260790 | -0.388641 | -2.938882 |
| C | 4.650243 | -0.231661 | -1.698986 |
| C | 5.608832 | 0.254881 | -5.361688 |
| C | 2.276746 | -2.294854 | -0.267516 |
| H | -4.424139 | -0.013503 | -0.924597 |
| H | -6.116059 | -2.228536 | -2.159163 |
| H | -8.219924 | -2.299075 | -0.839773 |
| H | -5.999771 | -3.476948 | 2.648964 |
| H | -3.896085 | -3.409846 | 1.341988 |
| H | -8.395852 | -2.629207 | 2.822368 |
| H | -8.898105 | -4.006083 | 1.839305 |
| H | -9.333761 | -2.368612 | 1.338658 |
| H | -3.815131 | 2.633582 | -0.777517 |
| H | -2.168084 | 3.067584 | -1.257064 |
| H | 0.174535 | -2.189361 | -1.902095 |

S111
|  | x  | y  | z   |
|---|----|----|-----|
| H | -0.441554 | -2.898255 | -0.427070 |
| H | 1.659457  | -0.721280  | 1.906183  |
| H | -0.129915 | -0.440017  | 1.535359  |
| H | 0.160855  | 1.931366   | -0.062642 |
| H | 0.589217  | 1.287353   | -1.664538 |
| H | -4.617216 | 4.758162   | 1.385415  |
| H | -4.803883 | 7.230003   | 1.242278  |
| H | -2.774817 | 8.608910   | 0.847416  |
| H | -0.559939 | 7.512033   | 0.592896  |
| H | -0.376293 | 5.038965   | 0.723006  |
| H | 2.594689  | 2.398029   | -2.486685 |
| H | 3.671773  | 2.059723   | -4.686124 |
| H | 6.029737  | -1.147003  | -3.555457 |
| H | 4.946271  | -0.841339  | -0.853038 |
| H | 6.501042  | 0.892953   | -5.407638 |
| H | 4.959036  | 0.542403   | -6.193421 |
| H | 6.937305  | -0.776754  | -5.517908 |
| H | 3.091346  | -2.023317  | 0.400364  |
| H | 2.617689  | -2.292460  | -1.306801 |

S112
|    | 1.981170   | -3.320511   | -0.020632   |
|----|------------|-------------|-------------|
| F  | 5.357262   | -2.340948   | 1.206254    |
| C  | 5.789242   | -1.849252   | 2.384653    |
| F  | 6.762742   | -2.642867   | 2.839984    |
| F  | 6.286256   | -0.623593   | 2.172329    |
| C  | 4.614985   | -1.781719   | 3.389054    |
| O  | 3.463250   | -1.982589   | 3.090100    |
| O  | 5.073955   | -1.461921   | 4.597698    |
| H  | 4.314683   | -1.414190   | 5.210808    |

total energy  -3293.23088908  a.u.

number of imaginary frequencies  0
optimized geometry

|   | x       | y       | z       |
|---|---------|---------|---------|
| C | 0.252470| -1.496150| -0.486708|
| C | -0.357179| -0.245979| -0.476966|
| C | 0.493142| 0.672216| 0.236733|
| C | 1.599941| -0.030034| 0.626635|
| N | 1.478352| -1.333524| 0.186209|
| S | 2.781601| -2.519239| 0.386127|
| O | 2.768022| -3.297042| -0.852029|
| O | 2.585824| -3.155302| 1.685866|
| C | 4.238103| -1.504408| 0.440978|
| C | 4.843646| -1.255559| 1.675582|
| C | 6.016033| -0.503661| 1.703633|
| C | 6.591387| -0.007875| 0.524150|
| C | 5.958810| -0.283688| -0.700201|
| C | 4.788964| -1.032703| -0.755325|
| C | 7.878920| 0.776081| 0.561356|
| C | 0.264839| 2.133798| 0.457860|
| C | -0.146769| -2.854576| -1.043314|
|   |        x        |        y        |        z        |
|---|----------------|----------------|----------------|
| C | -0.772858      | 7.306399       | -0.011213      |
| C | -1.592332      | 6.458362       | -0.758595      |
| C | -1.160152      | 5.170582       | -1.079331      |
| H | 2.474782       | 0.299963       | 1.164864       |
| H | 4.411146       | -1.654544      | 2.586817       |
| H | 6.496892       | -0.306779      | 2.657752       |
| H | 6.395336       | 0.087890       | -1.623205      |
| H | 4.317457       | -1.257889      | -1.705964      |
| H | 7.884630       | 1.572581       | -0.189541      |
| H | 8.734077       | 0.122008       | 0.347362       |
| H | 8.048082       | 1.226487       | 1.543639       |
| H | 0.895860       | 2.502751       | 1.270471       |
| H | -0.775895      | 2.354483       | 0.716872       |
| H | 0.664562       | -3.178491      | -1.708519      |
| H | -1.407981      | -3.766190      | -2.531992      |
| H | -2.176798      | -1.845374      | -3.724876      |
| H | -0.664092      | -1.127929      | -3.118115      |
| H | -1.311833      | 1.102039       | -1.824681      |
| H | -2.293375      | 0.727322       | -0.434185      |

S116
H   -0.554856  -4.911898  -0.450515
H   -1.114856  -3.717522  0.729320
H    0.603509  -4.105422  0.604946
H   -2.141887  -1.621710  1.295931
H   -2.964615  -0.969944  3.527550
H   -6.786517    0.077197  1.848123
H   -5.992914  -0.594824  -0.399524
H   -6.496424    0.134192  4.245344
H   -4.967033   0.985458  4.503222
H   -5.114086  -0.708261  4.973287
H    1.909952   5.248838  0.394792
H    1.128354   7.530459  0.983060
H   -1.109852   8.309154  0.235525
H   -2.566739   6.800218  -1.096385
H   -1.791107   4.511598  -1.668616

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total energy  -2766.42701572  a.u.

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number of imaginary frequencies   0

S117
molecule No.21d

|     | x          | y          | z          |
|-----|------------|------------|------------|
| C   | -0.060996  | 0.209517   | -1.021328  |
| C   | 1.177243   | 0.017652   | -1.740249  |
| C   | 1.620030   | -1.281110  | -1.547895  |
| C   | 0.682820   | -1.874462  | -0.671284  |
| N   | -0.282015  | -1.013097  | -0.321382  |
| S   | -1.465442  | -1.379535  | 1.019824   |
| O   | -2.393839  | -2.353375  | 0.472056   |
| O   | -1.873476  | -0.051665  | 1.457723   |
| C   | -0.394458  | -2.142729  | 2.206672   |
| C   | -0.640948  | -3.471466  | 2.563272   |
| C   | 0.165979   | -4.056064  | 3.537091   |
C  1.204952  -3.339276  4.147309
C  1.424898  -2.005724  3.756539
C  0.631866  -1.391976  2.795613
C  2.064762  -3.972556  5.211131
C  2.875735  -1.919851  -2.063748
S  3.598110  -3.060848  -0.792580
C  -1.248909  1.022938  -1.829965
C  -0.531306  1.615106  -0.682540
C   0.510014  2.740642  -0.931851
N  1.859372  2.292718  -1.290915
C  1.868170  1.219473  -2.312185
C  5.322499  -3.069222  -1.295375
C  5.866804  -4.218490  -1.880134
C  7.219237  -4.244491  -2.226845
C  8.021816  -3.125210  -2.001737
C  7.475471  -1.978086  -1.419768
C  6.129825  -1.948278  -1.054409
S  2.891470  1.965474  0.064311
O  4.015462  1.210253  -0.501814

S119
O  2.095015  1.401314  1.167667
C  3.416276  3.601525  0.533303
C  4.250542  4.326188 -0.325670
C  4.683700  5.586281  0.067203
C  4.305433  6.135144  1.305720
C  3.474329  5.381745  2.144440
C  3.407981  4.114313  1.771051
C  4.542432  6.715967  1.965244
C  4.270801  6.397443  -0.254534
H  0.705305 -0.257545  2.094471
H  0.016534  -5.087076  3.825941
H  2.233460 -1.440927  4.211965
H  0.824720 -0.366529  2.495508

S120
| H         | 3.124712 | -3.749098 | 5.049754 |
|-----------|----------|-----------|----------|
| H         | 1.942106 | -5.058698 | 5.235622 |
| H         | 1.799828 | -3.584715 | 6.202991 |
| H         | 3.617352 | -1.146566 | -2.276603|
| H         | 2.687697 | -2.476260 | -2.988509|
| H         | -0.850515| 1.274246  | -2.811483|
| H         | -1.080942| 1.677283  | 0.250525 |
| H         | 0.579172 | 3.366549  | -0.040240|
| H         | 0.151541 | 3.377977  | -1.748154|
| H         | 1.358165 | 1.621857  | -3.197343|
| H         | 2.897145 | 0.997883  | -2.592950|
| H         | 5.235406 | -5.083192 | -2.059627|
| H         | 7.641865 | -5.137796 | -2.677870|
| H         | 9.072830 | -3.147038 | -2.275448|
| H         | 8.101427 | -1.109171 | -1.236623|
| H         | 5.704873 | -1.064877 | -0.585569|
| H         | 4.555340 | 3.908628  | -1.279495|
| H         | 5.330398 | 6.156227  | -0.594683|
| H         | 3.174913 | 5.787721  | 3.106687 |
| Atom | X      | Y      | Z      |
|------|--------|--------|--------|
| H    | 2.395074 | 3.527674 | 2.428825 |
| H    | 4.272942 | 7.869563 | 2.600887 |
| H    | 4.685948 | 8.227376 | 0.913891 |
| H    | 5.873216 | 7.460058 | 1.968252 |
| H    | -3.324169 | 1.640967 | -0.112844 |
| H    | -5.673352 | 0.914244 | -0.319899 |
| H    | -6.356897 | -0.581752 | -2.173046 |
| H    | -4.679718 | -1.331928 | -3.852978 |
| H    | -2.326490 | -0.593114 | -3.663289 |
| F    | -7.714512 | -0.812355 | 0.264606 |
| C    | -8.869405 | -0.267841 | -0.141528 |
| F    | -8.904352 | -0.315940 | -1.490035 |
| F    | -9.883403 | -0.989897 | 0.339277 |
| C    | -8.933318 | 1.208429 | 0.310050 |
| O    | -7.947252 | 1.875099 | 0.500217 |
| O    | -10.198894 | 1.621217 | 0.406825 |
| H    | -10.184097 | 2.566833 | 0.652782 |

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total energy  -3484.96161361   a.u.

S122
number of imaginary frequencies  0

molecule No.21ba

optimized geometry

|   | x        | y        | z        |
|---|----------|----------|----------|
| C | -0.628375| -1.303212| 0.201563 |
| C |  0.074326| -0.115131| 0.112924 |
| C | -0.852853|  0.941042| 0.177197 |
| C | -2.096863|  0.363763| 0.255847 |
| N | -1.967159| -0.998445| 0.046796 |
| S | -3.302517| -2.123961| 0.196191 |
| O | -3.474027| -2.250995| 1.643290 |
| O | -2.970992| -3.290392| 0.621732 |
| C | -4.683886| -1.261268| 0.505005 |
C    -4.929023   -1.370835   -1.877663
C     -6.040138   -0.724041   -2.408961
C     -6.910284    0.018513   -1.593654
C     -6.636971    0.102100   -0.219175
C    -5.531639   -0.535483    0.337352
C     -8.131781    0.682336   -2.177723
C     -0.552494    2.398024   -0.331989
S    -0.198755    3.147582    1.340725
C     -0.103733   -2.678415    0.522620
C     0.563807    -2.785083    1.921506
C     1.399074   -1.537453    2.239547
N     2.131245   -1.096696    1.019121
C     1.556489    0.079271    0.300100
C     0.298104    4.809697    0.870227
C     -0.672350    5.804613    0.689107
C    -0.287447    7.101206    0.346364
C     1.064940    7.413456    0.192307
C     2.034686    6.427132    0.382587
C     1.654487    5.127546    0.720454

S124
S   3.763345  -1.330091   1.032036
O   3.870014  -2.864194   1.373473
O   4.557093  -0.516411   1.940282
C   4.321159  -1.155010  -0.631960
C   5.265210  -0.158855  -0.898895
C   5.741373  -0.029890  -2.201041
C   5.297702  -0.876795  -3.227420
C   4.349151  -1.869728  -2.919245
C   3.858277  -2.023149  -1.629555
C   5.844646  -0.750872  -4.625578
C  -0.422514  -3.081050   3.046477
H  -3.057405   0.809506  -0.460898
H  -4.270932  -1.959750  -2.507617
H  -6.242218  -0.803251  -3.473587
H  -7.304029   0.667205   0.425878
H  -5.332295  -0.484368   1.402402
H  -8.426500   1.562814  -1.598995
H  -8.983389  -0.010378  -2.175853
H  -7.965006   0.989955  -3.214551

S125
|   |       |       |       |
|---|-------|-------|-------|
| H | -1.401454 | 2.922284 | -0.778093 |
| H | 0.321020  | 2.571595 | -0.968745 |
| H | 0.654843  | -2.943372 | -0.223253 |
| H | -0.892849 | -3.428169 | 0.437260  |
| H | 2.090847  | -1.751139 | 3.060074  |
| H | 0.759282  | -0.716392 | 2.564471  |
| H | 1.739302  | 1.000197  | 0.869174  |
| H | 2.074603  | 0.164301  | -0.661005 |
| H | -1.721916 | 5.562242  | 0.827149  |
| H | -1.043358 | 7.869187  | 0.208447  |
| H | 1.362716  | 8.425205  | -0.067866 |
| H | 3.087974  | 6.670298  | 0.273127  |
| H | 2.406474  | 4.360216  | 0.879930  |
| H | 5.621115  | 0.488675  | -0.105008 |
| H | 6.475376  | 0.739825  | -2.420538 |
| H | 3.999048  | -2.536295 | -3.702256 |
| H | 3.139660  | -2.803890 | -1.403488 |
| H | 5.074169  | -0.951086 | -5.376697 |
| H | 6.651967  | -1.477047 | -4.786532 |

S126
H  6.256951  0.245134  -4.808693  
H  -1.225859 -2.338943   3.061148  
H   0.082895 -3.087993   4.017420  
H  -0.890217 -4.059731   2.895416  
O   1.569771 -3.852250   1.874323  
H   2.955694 -3.341347   1.506365  
H   1.188358 -4.666605   1.505466  

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total energy  -2842.87569632  a.u.

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number of imaginary frequencies  0

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molecule No.22b

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optimized geometry

          x       y       z

S127
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | -0.986078 | -0.062856 | -0.020549 |
| C       | -0.493531 | -0.328986 | -1.256570 |
| C       | -1.628637 | -0.554206 | -2.151038 |
| C       | -2.813721 | -0.450665 | -1.324591 |
| N       | -2.431158 | -0.166900 | -0.103429 |
| S       | -3.563281 | 0.041196  | 1.362602  |
| O       | -3.496237 | 1.467927  | 1.631071  |
| O       | -3.074455 | -0.973439 | 2.279404  |
| C       | -5.130498 | -0.407804 | 0.688127  |
| C       | -5.530761 | -1.749883 | 0.738565  |
| C       | -6.788584 | -2.082322 | 0.248206  |
| C       | -7.649299 | -1.103692 | -0.279368 |
| C       | -7.214150 | 0.232444  | -0.310286 |
| C       | -5.961466 | 0.595785  | 0.173019  |
| C       | -9.025096 | -1.475558 | -0.767757 |
| C       | -1.655986 | -0.743807 | -3.488442 |
| S       | 0.395461  | 2.715293  | 0.183980  |
| C       | -0.294845 | 0.292402  | 1.264158  |
| C       | 0.979258  | 1.164588  | 1.117991  |
| Element | X       | Y       | Z       |
|---------|---------|---------|---------|
| C       | 2.166966| 0.445996| 0.403884|
| N       | 1.856970| -0.637924| -0.528220|
| C       | 0.960208| -0.386426| -1.647990|
| S       | 1.976640| -2.242735| 0.034913|
| O       | 1.368755| -3.055119| -1.025209|
| O       | 1.478062| -2.314112| 1.417053|
| C       | 3.736922| -2.542661| 0.089621|
| C       | 4.364342| -2.718191| 1.322737|
| C       | 5.734760| -2.979289| 1.352419|
| C       | 6.481763| -3.075715| 0.172154|
| C       | 5.818922| -2.900883| -1.055365|
| C       | 4.455216| -2.638969| -1.107040|
| C       | 7.958195| -3.384985| 0.206843|
| C       | 1.443070| 1.573715| 2.524269|
| C       | 1.851815| 3.757553| 0.054059|
| C       | 2.601021| 3.766647| -1.132979|
| C       | 3.699359| 4.618704| -1.259993|
| C       | 4.053225| 5.467023| -0.209429|
| C       | 3.299204| 5.473597| 0.966279|
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | 2.197066  | 4.628557  | 1.098401  |
| H    | -3.851722 | -0.570550 | -1.604471 |
| H    | -4.879195 | -2.504894 | 1.166009  |
| H    | -7.114694 | -3.117787 | 0.285619  |
| H    | -7.871938 | 1.000386  | -0.707134 |
| H    | -5.638785 | 1.631675  | 0.170518  |
| H    | -9.046156 | -2.489878 | -1.177213 |
| H    | -9.381623 | -0.782465 | -1.535193 |
| H    | -9.743853 | -1.443830 | 0.061475  |
| H    | -2.592610 | -0.869346 | -4.024307 |
| H    | -0.744714 | -0.761314 | -4.077215 |
| H    | -0.012795 | -0.631510 | 1.785597  |
| H    | -0.986873 | 0.832556  | 1.914668  |
| H    | 2.814906  | 0.020031  | 1.174663  |
| H    | 2.771143  | 1.192596  | -0.122811 |
| H    | 1.253054  | 0.556749  | -2.121989 |
| H    | 1.100192  | -1.178317 | -2.387462 |
| H    | 3.785212  | -2.662662 | 2.237894  |
| H    | 6.227757  | -3.116933 | 2.310954  |

S130
|  | x       | y       | z       |
|---|---------|---------|---------|
| H | 6.381739| -2.977557| -1.982152|
| H | 3.952602| -2.520248| -2.061451|
| H | 8.145780| -4.423977| -0.092683|
| H | 8.374140| -3.249837| 1.209305 |
| H | 8.516816| -2.744622| -0.484502|
| H | 0.676731| 2.158036 | 3.041648 |
| H | 2.357652| 2.172456 | 2.478040 |
| H | 1.656335| 0.675728 | 3.117119 |
| H | 2.307958| 3.124592 | -1.958872|
| H | 4.274774| 4.621978 | -2.181441|
| H | 4.907305| 6.130341 | -0.310570|
| H | 3.562070| 6.145023 | 1.778643 |
| H | 1.595845| 4.651266 | 2.001553 |
| O | 0.023790| 2.185081 | -3.208013|
| H | -0.027873| 2.480834 | -2.279309|
| H | 0.137729| 3.001786 | -3.717772|

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total energy  -2842.85305662  a.u.
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S131
number of imaginary frequencies  0

molecule No.23b

optimized geometry

|    | x     | y     | z     |
|----|-------|-------|-------|
| C  | 1.644253 | -0.656925 | -0.188763 |
| C  | 1.001445 | -1.809715 | -0.579725 |
| C  | 1.574566 | -2.917106 | 0.130865  |
| C  | 2.578832 | -2.402729 | 0.919727  |
| N  | 2.620780 | -1.033588 | 0.731339  |
| S  | 3.816247 | -0.028804 | 1.559223  |
| O  | 4.391160 | -0.944362 | 2.536515  |
| O  | 3.108800 | 1.189347  | 1.937586  |
| C  | 5.014619 | 0.346806  | 0.299585  |
| C  | 5.940951 | -0.632665 | -0.074224 |
|   |   |   |   |
|---|---|---|---|
| C | -4.820215 | -1.170855 | 0.845916 |
| C | -8.094455 | -0.618706 | -1.037220 |
| S | -0.281609 | 2.937692 | -0.686692 |
| C | -0.327905 | 1.012113 | 1.383054 |
| C | -1.833741 | 3.545834 | -0.017670 |
| C | -2.985688 | 3.567407 | -0.818705 |
| C | -4.171172 | 4.115859 | -0.326538 |
| C | -4.213841 | 4.649484 | 0.962949 |
| C | -3.066306 | 4.642470 | 1.759010 |
| C | -1.877132 | 4.099905 | 1.270852 |
| H | 3.263848 | -2.878398 | 1.605139 |
| H | 5.927796 | -1.612106 | 0.392240 |
| H | 7.614480 | -1.075163 | -1.336170 |
| H | 6.033598 | 2.910066 | -1.660602 |
| H | 4.335989 | 2.382726 | 0.067883 |
| H | 8.205504 | 0.435200 | -3.306227 |
| H | 8.943971 | 1.548307 | -2.153323 |
| H | 7.708744 | 2.138487 | -3.270365 |
| H | 1.821362 | -5.001468 | 0.603396 |

S134
| H     | 0.901410 | -4.713562 | -0.880547 |
|-------|----------|-----------|-----------|
| H     | 1.339325 | 0.842576  | -1.678104 |
| H     | 1.951407 | 1.466430  | -0.152927 |
| H     | -1.222463| 0.680665  | -1.985980 |
| H     | -2.275919| 0.775831  | -0.582260 |
| H     | -0.479293| -2.783879 | -1.823668 |
| H     | 0.052708 | -1.223040 | -2.418279 |
| H     | -3.732161| -1.693074 | -2.363739 |
| H     | -6.110687| -1.193054 | -2.821213 |
| H     | -6.826899| -0.652653 | 1.386124  |
| H     | -4.447135| -1.165307 | 1.864078  |
| H     | -8.565381| -0.052988 | -0.228570 |
| H     | -8.647871| -1.560399 | -1.146802 |
| H     | -8.219042| -0.059730 | -1.969932 |
| H     | -1.302420| 1.380269  | 1.716252  |
| H     | 0.453476 | 1.587131  | 1.886239  |
| H     | -0.239714| -0.029369 | 1.704079  |
| H     | -2.942757| 3.176354  | -1.830948 |
| H     | -5.056616| 4.138234  | -0.955857 |

S135
H  -5.134833  5.083578  1.341658
H  -3.091871  5.071722  2.756547
H  -0.978027  4.115252  1.878473
O  -0.183880 -4.493133  0.821073
H  -1.316497 -3.861548  0.217810
H  -0.082958 -4.159052  1.730916

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total energy  -2842.87912061  a.u.

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number of imaginary frequencies  0

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molecule No.14aa

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optimized geometry

    x      y      z

C  -7.455061 -1.695813 -1.697723

S136
|  |  |  |  |  |
|---|---|---|---|---|
| C | -8.439767 | -2.367584 | -2.621759 |  |
| C | -6.860515 | -2.407054 | -0.643847 |  |
| C | -5.977468 | -1.789491 | 0.237117 |  |
| C | -5.681308 | -0.436235 | 0.052235 |  |
| C | -6.259794 | 0.303185 | -0.983037 |  |
| C | -7.140013 | -0.336440 | -1.850720 |  |
| S | -4.568814 | 0.370609 | 1.180401 |  |
| O | -4.475439 | -0.404199 | 2.410459 |  |
| O | -4.789033 | 1.811452 | 1.140707 |  |
| N | -2.982289 | 0.181237 | 0.443012 |  |
| C | -2.147638 | -0.909819 | 0.603962 |  |
| C | -0.984953 | -0.671560 | -0.086913 |  |
| C | -1.128377 | 0.628239 | -0.700688 |  |
| C | -2.373753 | 1.117378 | -0.355250 |  |
| C | -0.121401 | 1.312162 | -1.554955 |  |
| S | 0.445528 | 2.920789 | -0.780104 |  |
| C | 1.812980 | 3.496173 | -1.734723 |  |
| C | 1.819388 | 4.882393 | -1.972945 |  |
| C | 2.845165 | 5.420588 | -2.744671 |  |

S137
C  3.848414  4.587247  -3.247035
C  3.836924  3.212087  -2.985050
C  2.817665  2.645095  -2.225801
O  1.126487  2.231452   0.627456
C  1.378562  3.156548  1.615151
O  1.243623  4.337615  1.497086
C  1.850818  2.427505  2.898945
F  0.847821  1.661516  3.359184
F  2.176256  3.327786  3.816964
F  2.905457  1.653182  2.629116
C  0.157611  1.645031  -0.218261
N  1.373902  1.189962  0.484813
S  2.822296  1.096933  -0.357885
O  3.739565  0.322270  0.480305
O  2.444480  0.600862  -1.702096
C  3.521518  2.728063  -0.584621
C  1.398105  1.359625  1.957133
C  1.244630  2.785692  2.420907
C  0.260544  3.202326  3.219082

S138
| Element | X    | Y    | Z    |
|---------|------|------|------|
| C       | 3.125939 | -3.514407 | -1.671988 |
| C       | 3.657722  | -4.792695  | -1.809918  |
| C       | 4.580046  | -5.303467  | -0.881830  |
| C       | 4.966121  | -4.487674  | 0.190587   |
| C       | 4.446389  | -3.203620  | 0.347821   |
| C       | 5.143336  | -6.693317  | -1.048449  |
| H       | -9.460040 | -2.282338  | -2.225726  |
| H       | -8.436553 | -1.908567  | -3.615069  |
| H       | -8.222257 | -3.434136  | -2.733915  |
| H       | -7.100745 | -3.457579  | -0.504699  |
| H       | -5.542623 | -2.338300  | 1.065501   |
| H       | -6.041344 | 1.360141   | -1.091087  |
| H       | -7.599302 | 0.231739   | -2.655053  |
| H       | -2.450288 | -1.753819  | 1.205332   |
| H       | -2.868848 | 2.051503   | -0.578042  |
| H       | -0.514768 | 1.682850   | -2.509359  |
| H       | 0.770958  | 0.705833   | -1.735013  |
| H       | 1.045163  | 5.520111   | -1.557481  |
| H       | 2.866000  | 6.487079   | -2.943867  |
| Atom Position | X      | Y      | Z    |
|--------------|-------|-------|------|
| H            | 4.650484 | 5.012827 | -3.842696 |
| H            | 4.627407 | 2.576677 | -3.371365 |
| H            | 2.819061 | 1.579669 | -2.014570 |
| H            | 0.406585 | -1.788568 | -1.271613 |
| H            | -0.151461 | -2.617570 | 0.181930 |
| H            | 0.588862 | -0.741399 | 2.359813 |
| H            | 2.335572 | -0.922938 | 2.309616 |
| H            | 2.004987 | -3.489654 | 2.084032 |
| H            | 0.197738 | -4.231242 | 3.561886 |
| H            | -0.508389 | -2.522454 | 3.582201 |
| H            | 2.438563 | -3.119809 | -2.412478 |
| H            | 3.360403 | -5.402549 | -2.659278 |
| H            | 5.693242 | -4.856793 | 0.908670 |
| H            | 4.771735 | -2.569405 | 1.165572 |
| H            | 5.613051 | -6.814242 | -2.031487 |
| H            | 4.352900 | -7.450152 | -0.974535 |
| H            | 5.894234 | -6.917239 | -0.285843 |

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total energy  -3253.87273581  a.u.
number of imaginary frequencies  0

molecule No.14ab

optimized geometry

|   | x        | y        | z        |
|---|----------|----------|----------|
| C | -2.963445| -0.070114| -1.167951|
| C | -1.804242| 0.217345 | -0.495012|
| C | -1.569223| -0.872972|  0.421707|
| C | -2.590898| -1.782822|  0.253790|
| N | -3.439738| -1.289755| -0.710415|
| C | -0.414403| -1.098445|  1.319368|
| C | -0.995325|  1.466213| -0.701821|
| N |  0.345740|  1.226812| -1.298282|
| S |  1.016734| -1.812895|  0.326954|
C  2.087928  -0.421355  -0.345790
C  1.427828  0.969763  -0.339429
S  0.753264  2.254526  -2.604797
S -4.966707  -1.995838  -1.143700
O  -4.840379  -3.398548  -0.764110
O  -5.212296  -1.545934  -2.508132
C  -6.135463  -1.200804  -0.053400
C  -6.781015  -0.036924  -0.475695
C  -7.687357  0.578101  0.384364
C  -7.960970  0.047284  1.653451
C  -7.300228  -1.127025  2.044826
C  -6.390726  -1.758808  1.201264
C  -8.968494  0.704672  2.564741
O  -0.418348  2.277898  -3.481036
O  2.064533  1.783940  -3.063499
C  0.971969  3.897417  -1.920539
C  2.212996  4.271418  -1.393084
C  2.346696  5.517177  -0.787793
C  1.265109  6.407125  -0.709285

S142
H  -0.603738 -1.895937  2.043160
H   0.009589 -0.234673  1.848796
H  -0.873718  2.009926  0.245560
H  -1.551386  2.111367 -1.382621
H   2.887377 -0.344380  0.408246
H   1.078786  1.183372  0.671941
H   2.266325  1.653463 -0.496741
H  -6.587473  0.366552 -1.463786
H  -8.195045  1.483371  0.061889
H  -7.504941 -1.555964  3.022289
H  -5.897750  2.677314  1.501175
H  -8.712299  0.556706  3.618626
H  -9.969100  0.280276  2.409429
H  -9.037619  1.780584  2.376590
H   3.066893  3.608731 -1.479139
H   3.308647  5.802556 -0.370684
H  -0.800465  6.707243 -1.245454
H  -1.059421  4.490723 -2.328370
H   0.585249  8.411623 -0.251433

S144
| Atom | X   | Y   | Z   |
|------|-----|-----|-----|
| H    | 2.348670 | 8.240688 | -0.325339 |
| H    | 1.460889 | 7.617635 | 1.065849  |
| H    | 3.232574 | -0.078556 | -2.116104 |
| H    | 1.828468 | -1.132567 | -2.417275 |
| H    | 2.068916 | -4.435543 | 0.180967  |
| H    | 3.452742 | -5.775817 | 1.756768  |
| H    | 4.152610 | -4.795680 | 3.930961  |
| H    | 3.487447 | -2.480191 | 4.532186  |
| H    | 2.116280 | -1.117500 | 2.959218  |
| O    | 1.465138 | 0.891685  | 2.815941  |
| C    | 2.601007 | 1.392346  | 2.580812  |
| O    | 3.547241 | 0.933413  | 1.912083  |
| C    | 2.799031 | 2.842661  | 3.110033  |
| F    | 4.081454 | 3.117869  | 3.411322  |
| F    | 2.058281 | 3.114334  | 4.201327  |
| F    | 2.417235 | 3.722150  | 2.138070  |

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total energy  -3780.14046264  a.u.  
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number of imaginary frequencies  0

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molecule No.14ac

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optimized geometry

|     | x     | y     | z     |
|-----|-------|-------|-------|
| C   | -0.732669 | -1.551781 | -2.007363 |
| C   | 0.295673   | -0.651593 | -1.873843 |
| C   | -0.228372  | 0.638322  | -2.240175 |
| C   | -1.558856  | 0.469145  | -2.577298 |
| N   | -1.851753  | -0.862604 | -2.435849 |
| S   | -3.423501  | -1.592099 | -2.791120 |
| O   | -3.088079  | -2.954789 | -3.178156 |
| O   | -4.051617  | -0.621364 | -3.678221 |
| C   | -4.256684  | -1.598708 | -1.221281 |
| C   | -4.069658  | -2.677882 | -0.353032 |

S146
C   -4.738827  -2.676578  0.867236
C   -5.590920  -1.621840  1.230113
C   -5.770119  -0.563000  0.325867
C   -5.109531  -0.539280 -0.898617
C   -6.283592  -1.615090  2.569357
C    1.700394  -0.969825 -1.451220
C    0.520151  1.914192  -2.257881
S    0.389774  2.787806 -0.587572
N    1.996658 -0.588705 -0.054664
C    2.406920  0.770355  0.251308
C    1.273944  1.724604  0.713781
C    0.201197  1.028760  1.546716
O   -0.600117  2.087676  2.112960
C   -1.821358  1.915358  2.667451
O   -2.439786  2.845386  3.099058
C   -2.403737  0.478267  2.698325
F   -1.543070 -0.383521  3.268650
F   -3.545562  0.462048  3.377080
F   -2.645394  0.057452  1.434343

S147
C   1.399502  4.263894  -0.726221
C   0.806197  5.448215  -0.271320
C   1.528788  6.639417  -0.350333
C   2.818702  6.642040  -0.883072
C   3.398502  5.454119  -1.339161
C   2.693337  4.254478  -1.263411
S   2.381671  -1.831719  1.055174
O   1.459042  -2.919375  0.734595
O   2.389560  -1.155445  2.358613
C   4.044827  -2.384195  0.709464
C   4.246848  -3.435575  -0.190080
C   5.548318  -3.842903  -0.471831
C   6.652779  -3.226196  0.135313
C   6.417771  -2.182439  1.043487
C   5.125023  -1.758030  1.339242
C   8.055536  -3.703435  -0.147755
H  -0.759843  -2.621110  -1.861561
H  -2.301819   1.163344  -2.941770
H  -3.435461  -3.510700  -0.637429

S148
H  -4.606743  -3.515529  1.544877
H  -6.445505   0.249304   0.580500
H  -5.270712   0.268430 -1.604442
H  -7.260708  -1.125489  2.513986
H   -5.681908  -1.064685  3.303523
H  -6.427597  -2.629129  2.953618
H   2.431021  -0.476944 -2.109266
H   1.863932  -2.043359 -1.550069
H    0.091935  2.661099 -2.931781
H   1.581194  1.798921 -2.488199
H   2.958660  1.201960 -0.593224
H   3.102292  0.742356  1.094572
H   1.717853  2.521794  1.318355
H    0.693789  0.457365  2.337699
H  -0.398967  0.348468  0.942104
H  -0.198173  5.439020  0.140982
H    1.079276  7.562275  0.002199
H    3.375531  7.571871 -0.946317
H    4.400872  5.460901 -1.755877
| Number         | x    | y    | z    |
|----------------|------|------|------|
| H              | 3.151242 | 3.338616 | -1.623000 |
| H              | 3.399458 | -3.946098 | -0.634990 |
| H              | 5.708443 | -4.664157 | -1.165281 |
| H              | 7.259410 | -1.704806 | 1.538095 |
| H              | 4.953976 | -0.978069 | 2.073539 |
| H              | 8.787394 | -2.900111 | -0.019420 |
| H              | 8.148886 | -4.095165 | -1.165325 |
| H              | 8.334527 | -4.512432 | 0.539718 |

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total energy  -3253.90394330  a.u.
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number of imaginary frequencies  0
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molecule No.15aa
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optimized geometry
| x          | y          | z          |
|------------|------------|------------|
| C 3.156932 | 0.995701   | -0.101517  |
| C 1.952851 | 0.340924   | -0.087539  |
| C 2.061229 | -0.733743  | 0.868198   |
| C 3.329334 | -0.689898  | 1.401076   |
| N 3.994413 | 0.368716   | 0.810707   |
| S 5.681532 | 0.702516   | 1.011760   |
| O 6.012348 | 0.142810   | 2.318839   |
| O 5.829560 | 2.115076   | 0.682091   |
| C 6.472697 | -0.274811  | -0.255559  |
| C 6.686581 | 0.285651   | -1.516518  |
| C 7.297874 | -0.487324  | -2.500222  |
| C 7.696611 | -1.807713  | -2.244768  |
| C 7.480691 | -2.335986  | -0.963254  |
| C 6.871149 | -1.581197  | 0.035356   |
| C 8.327798 | -2.647005  | -3.328626  |
| C 1.043801 | -1.768530  | 1.163233   |
| C 0.708376 | 0.725108   | -0.837868  |
| N -0.229489 | 1.479683  | 0.044506   |

S151
|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| S | -0.518614 | -1.214620 | 2.067066  |
| C | -1.614872 | -0.551461 | 0.707557  |
| C | -1.559074 | 0.940468  | 0.372747  |
| C | -3.045484 | -0.980891 | 1.065453  |
| O | -3.795936 | -0.868323 | -0.167104 |
| C | -4.976440 | -1.503380 | -0.187999 |
| O | -5.500062 | -2.074198 | 0.730480  |
| C | -5.630866 | -1.331368 | -1.576064 |
| F | -6.665316 | -2.162648 | -1.704050 |
| F | -4.762771 | -1.554194 | -2.569816 |
| F | -6.084770 | -0.062042 | -1.691315 |
| C | 0.039317  | 0.238609  | 3.082714  |
| C | -1.023928 | 0.650732  | 4.072595  |
| C | -1.559525 | 1.945193  | 4.022814  |
| C | -2.520648 | 2.343057  | 4.955226  |
| C | -2.958497 | 1.455217  | 5.937804  |
| C | -2.427174 | 0.163963  | 5.993098  |
| C | -1.464135 | -0.234884 | 5.068506  |
| S | -0.160167 | 3.172999  | -0.060216 |
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| O    | 1.233032| 3.504622| -0.362114 |
| O    | -0.832313| 3.673743| 1.145020  |
| C    | -1.155533| 3.651666| -1.472751 |
| C    | -2.530683| 3.852176| -1.319954 |
| C    | -3.297716| 4.179612| -2.435511 |
| C    | -2.715919| 4.312087| -3.704792 |
| C    | -1.331476| 4.125626| -3.825807 |
| C    | -0.547112| 3.796307| -2.722664 |
| C    | -3.562562| 4.633988| -4.912109 |
| H    | 3.471492 | 1.889150| -0.617480 |
| H    | 3.822055 | -1.313084| 2.132056 |
| H    | 6.398460 | 1.312778| -1.712885 |
| H    | 7.474527 | -0.055306| -3.481759 |
| H    | 7.800136 | -3.350969| -0.741840 |
| H    | 6.724985 | -1.987579| 1.030335 |
| H    | 7.562040 | -3.202377| -3.885998 |
| H    | 9.024517 | -3.381599| -2.912627 |
| H    | 8.871694 | -2.028562| -4.049517 |
| H    | 1.424858 | -2.556962| 1.816981  |

S153
H  0.614202  -2.232263  0.264403
H  0.192576  -0.164065  -1.212710
H  0.964829  1.328078  -1.712290
H  -1.294265  -1.161737  -0.144109
H  -2.262273  1.054593  -0.466972
H  -1.945714  1.528246  1.207831
H  -3.503781  -0.335323  1.822510
H  -3.059784  -2.019987  1.393465
H  0.334673  1.047845  2.414296
H  0.938346  -0.145541  3.577812
H  -1.217254  2.645372  3.265213
H  -2.923973  3.350813  4.910356
H  -3.708054  1.766208  6.660168
H  -2.760716  -0.531813  6.757757
H  -1.053262  -1.240564  5.120668
H  -2.984615  3.782963  -0.337234
H  -4.365840  4.342480  -2.316673
H  -0.858244  4.248004  -4.796718
H  0.527364  3.684183  -2.818587

S154
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | -2.982227 | 5.150262 | -5.683241 |
| H    | -4.416687 | 5.265070 | -4.646257 |
| H    | -3.963225 | 3.716438 | -5.362668 |
| O    | -1.439719 | -3.515431 | 0.664871 |
| C    | -1.349639 | -3.471505 | -0.585954 |
| O    | -0.645670 | -2.712370 | -1.297872 |
| C    | -2.321259 | -4.418224 | -1.347018 |
| F    | -3.566535 | -3.855175 | -1.373697 |
| F    | -2.443398 | -5.617138 | -0.748447 |
| F    | -1.958480 | -4.632610 | -2.622844 |

Total energy: -3819.62022273 a.u.

Number of imaginary frequencies: 0

Molecule No.16a
optimized geometry

|   | x     | y     | z     |
|---|-------|-------|-------|
| C | -0.881912 | -1.830166 | -1.533379 |
| C | -0.956832  | -0.515135  | -1.159138 |
| C | 0.353145   | 0.059073   | -1.365963 |
| C | 1.172055   | -0.935676  | -1.856296 |
| N | 0.414723   | -2.080496  | -1.968027 |
| S | 1.087164   | -3.664438  | -2.197276 |
| O | 2.229059   | -3.468381  | -3.084746 |
| O | -0.052860  | -4.507967  | -2.535003 |
| C | 1.682917   | -4.078714  | -0.566197 |
| C | 3.043983   | -3.958146  | -0.286148 |
| C | 3.488595   | -4.219525  | 1.008948  |
| C | 2.594126   | -4.585592  | 2.022859  |
| C | 1.234613   | -4.722826  | 1.700872  |
| C | 0.769138   | -4.473622  | 0.414665  |
| C | 3.063934   | -4.786607  | 3.442333  |
| C | 0.775937   | 1.457793   | -1.095341 |
| Element | X    | Y    | Z    |
|---------|------|------|------|
| C       | -2.198840 | 0.226654 | -0.727668 |
| N       | -3.314038 | -0.663019 | -0.379986 |
| S       | -4.714611 | -0.604362 | -1.308376 |
| O       | -5.456141 | -1.827132 | -0.988809 |
| O       | -4.294014 | -0.274794 | -2.672456 |
| C       | -5.700432 | 0.773754  | -0.706123 |
| C       | -5.493084 | 2.053109  | -1.229579 |
| C       | -6.234799 | 3.121943  | -0.732507 |
| C       | -7.189227 | 2.937171  | 0.278754  |
| C       | -7.386406 | 1.642925  | 0.778498  |
| C       | -6.654573 | 0.560762  | 0.291916  |
| C       | -8.012020 | 4.097369  | 0.786050  |
| C       | -3.438171 | -1.139581 | 1.019704  |
| C       | -3.217140 | -2.622298 | 1.179117  |
| C       | -2.353908 | -3.147695 | 2.049981  |
| S       | 1.970768  | 1.468808  | 0.373945  |
| C       | 2.085542  | 3.157627  | 1.028472  |
| C       | 3.347020  | 3.590695  | 1.447449  |
| C       | 3.471540  | 4.859890  | 2.011968  |
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | 2.352529  | 5.681431  | 2.152518  |
| C    | 1.098796  | 5.231460  | 1.735083  |
| C    | 0.954621  | 3.962405  | 1.175926  |
| O    | 0.369418  | 1.192408  | 1.462843  |
| C    | 0.222857  | 0.213169  | 2.328856  |
| O    | -0.815246 | -0.011257 | 2.915199  |
| C    | 1.452433  | -0.696504 | 2.603721  |
| F    | 1.174774  | -1.602316 | 3.546669  |
| F    | 2.509849  | 0.035446  | 3.022969  |
| F    | 1.822543  | -1.356567 | 1.486491  |
| H    | -1.636332 | -2.599067 | -1.566090 |
| H    | 2.215794  | -0.928062 | -2.133832 |
| H    | 3.736447  | -3.669388 | -1.069422 |
| H    | 4.547384  | -4.126489 | 1.235996  |
| H    | 0.529317  | -5.020298 | 2.472453  |
| H    | -0.284486 | -4.574854 | 0.178613  |
| H    | 2.594744  | -5.663316 | 3.901935  |
| H    | 2.795103  | -3.915340 | 4.053581  |
| H    | 4.149605  | -4.910959 | 3.495971  |
H   -0.051639  2.100092 -0.797077
H   1.330461  1.940583 -1.897076
H   -2.524040  0.877194 -1.545674
H   -1.972545  0.870301  0.132344
H   -4.780862  2.199912 -2.034699
H   -6.077898  4.116155 -1.144219
H   -8.130201  1.476226  1.553859
H   -6.836208 -0.443673  0.658684
H   -8.336927  3.937304  1.819130
H   -8.915481  4.234065  0.177133
H   -7.449415  5.035974  0.746678
H   -4.436693 -0.878404  1.395019
H   -2.720150 -0.580858  1.625823
H   -3.849256 -3.257953  0.562115
H   -2.266130 -4.224526  2.176228
H   -1.717564 -2.524746  2.674974
H    4.221012  2.963526  1.313578
H    4.448744  5.203539  2.337505
H    2.456266  6.670446  2.589115

S159
|   |   |   |   |
|---|---|---|---|
| H | 0.224549 | 5.865790 | 1.846771 |
| H | -0.026240 | 3.604591 | 0.889355 |
| O | 3.548122  | 1.679369 | -0.736961 |
| C | 3.743652  | 2.659441 | -1.596858 |
| O | 2.947627  | 3.473044 | -2.013429 |
| C | 5.233788  | 2.689472 | -2.027356 |
| F | 5.439167  | 3.600329 | -2.981558 |
| F | 5.633278  | 1.490939 | -2.484035 |
| F | 5.999695  | 3.009953 | -0.960459 |

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total energy  -3780.26271065  a.u.
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number of imaginary frequencies  0
-----------------------------------------------------------------------------------------------------
molecule No.17a
-----------------------------------------------------------------------------------------------------
optimized geometry

|   | x       | y       | z       |
|---|---------|---------|---------|
| C | 1.722982| 0.073959| -0.445728|
| C | 0.873811| -0.973764| -0.187561|
| C | 1.554253| -2.188161| -0.571113|
| C | 2.788393| -1.835222| -1.048041|
| N | 2.889494| -0.447343| -0.986867|
| S | 4.313680| 0.457117| -1.293540|
| O | 3.849169| 1.822210| -1.534042|
| O | 5.057462| -0.314202| -2.284667|
| C | 5.214407| 0.423880| 0.249949|
| C | 5.026804| 1.451588| 1.175409|
| C | 5.729895| 1.412190| 2.377421|
| C | 6.613103| 0.362945| 2.668703|
| C | 6.788294| -0.648972| 1.712789|
| C | 6.096707| -0.628343| 0.504807|
| C | 7.347289| 0.312237| 3.986728|
| C | 1.020721| -3.587989| -0.499588|
| O | 2.093216| -4.486983| -0.769317|
C   -0.509042  -0.837619   0.389576
N   -1.558391  -1.363411  -0.504208
S   -2.671633  -2.471793   0.085476
C   -1.598973  -0.937010  -1.903446
O   -1.978978  -3.241631  1.128212
O   -3.262208  -3.127121  -1.086642
C   -3.990933  -1.578525   0.915286
C   -3.839219  -1.207558   2.252356
C   -4.865177  -0.506301   2.884936
C   -6.045812  -0.175918   2.204922
C   -6.178651  -0.579077   0.868269
C   -5.161403  -1.273147   0.218554
C   -7.145703   0.601462   2.887853
C   -1.583861   0.588042  -2.136765
S   -3.080116   1.398873  -1.397872
C   -1.455680   0.878527  -3.644064
O   -1.113475   2.225031  -3.939105
C   -2.382563   2.731813  -0.418432
C   -2.635397   2.760180   0.960378
C  -2.155365  3.816779  1.737607
C  -1.409087  4.839419  1.150266
C  -1.155479  4.810819  -0.223424
C  -1.650121  3.770971  -1.011361
H   1.605103  1.138600  -0.310083
H   3.587251  -2.437091  -1.448886
H   4.358881   2.274792   0.945872
H   5.595153   2.214236   3.098619
H   7.481503  -1.461692   1.914111
H   6.250705  -1.403064  -0.238535
H   8.344807  -0.124697   3.873144
H   6.803000  -0.304976   4.713650
H   7.458694   1.309787   4.422972
H   0.205169  -3.718523  -1.229687
H   0.577405  -3.773099   0.490008
H   1.720845  -5.380568  -0.797563
H  -0.709010   0.216946   0.620389
H  -0.580880  -1.398775   1.324069
H  -2.478491  -1.390114  -2.364740

S163
|   |        |        |        |
|---|--------|--------|--------|
| H | -0.721444 | -1.354614 | -2.417330 |
| H | -2.945163 | -1.490413 | 2.797762 |
| H | -4.752908 | -0.225880 | 3.929508 |
| H | -7.093593 | -0.348564 | 0.327998 |
| H | -5.275948 | -1.593678 | -0.810786 |
| H | -7.117069 | 1.660272  | 2.598825 |
| H | -7.053533 | 0.555267  | 3.977489 |
| H | -8.135063 | 0.219385  | 2.613679 |
| H | -0.715248 | 1.020305  | -1.631670 |
| H | -2.411372 | 0.693685  | -4.143612 |
| H | -0.714146 | 0.190315  | -4.080020 |
| H | -0.179963 | 2.348442  | -3.704798 |
| H | -3.203534 | 1.955181  | 1.417373 |
| H | -2.357306 | 3.833046  | 2.805633 |
| H | -1.030491 | 5.656997  | 1.757932 |
| H | -0.584051 | 5.610368  | -0.688052 |
| H | -1.484553 | 3.754570  | -2.083974 |

-----------------------------------------------

total energy  -2879.59237401  a.u.
number of imaginary frequencies 0

molecule No.18ba

optimized geometry

|   | x      | y      | z      |
|---|--------|--------|--------|
| C | 0.211952 | 0.064306 | 0.098588 |
| C | 0.137897 | -1.055994 | -0.663204 |
| C | 1.460332 | -1.696024 | -0.600315 |
| C | 2.270985 | -0.865524 | 0.231075 |
| N | 1.518348 | 0.161115 | 0.618423 |
| C | 1.775915 | -2.891490 | -1.228646 |
| S | 3.146180 | -3.896918 | -1.296454 |
| C | 4.411383 | -3.157724 | -0.257804 |
| C | 4.454690 | -3.480597 | 1.104541 |
C   5.472096 -2.944574  1.894418
C   6.438447 -2.111370  1.324554
C   6.398687 -1.814326 -0.040146
C   5.385361 -2.339637 -0.843372
C  -1.046779 -1.593314 -1.418237
N  -2.252015 -0.768858 -1.262188
S  -3.730282 -1.709945 -1.292760
C  -2.281972  0.450273 -2.101177
C  -2.613788  1.752305 -1.396718
C  -2.638990  2.941593 -2.325859
C  -2.873849  1.856930  0.849699
S   2.084865  1.450800  1.757260
O   3.400028  0.960940  2.146159
O   0.964267  1.596874  2.670208
C   2.226153  2.870198  0.711507
C   3.452659  3.141265  0.094667
C   3.557947  4.273816 -0.705060
C   2.465800  5.137184 -0.894694
C   1.250936  4.833994 -0.258872

S166
|   |   |   |   |
|---|---|---|---|
| C | 1.117855 | 3.708900 | 0.548575 |
| C | 2.606775  | 6.381263  | -1.733721 |
| O | -3.315420 | -3.085979 | -0.991017 |
| O | -4.451977 | -1.387136 | -2.527642 |
| C | -4.693198 | -1.112393 | 0.085680  |
| C | -5.787364 | -0.281624 | -0.154735 |
| C | -6.555321 | 0.149665  | 0.925611  |
| C | -6.248284 | -0.237341 | 2.237146  |
| C | -5.142174 | -1.077998 | 2.445085  |
| C | -4.366067 | -1.524902 | 1.380472  |
| C | -7.104777 | 0.206916  | 3.397300  |
| H | -0.534297 | 0.808848  | 0.329771  |
| H | 3.295106  | -0.961830 | 0.554815  |
| H | 0.985722  | -3.341846 | -1.830318 |
| H | 3.708451  | -4.138453 | 1.539494  |
| H | 5.512807  | -3.184647 | 2.952316  |
| H | 7.230548  | -1.701847 | 1.943918  |
| H | 7.161156  | -1.181322 | -0.483853 |
| H | 5.355598  | -2.122009 | -1.906741 |
| H    | -1.285065 | -2.596568 | -1.054815 |
|------|-----------|-----------|-----------|
| H    | -0.779656 | -1.703069 | -2.483479 |
| H    | -2.979932 | 0.306811  | -2.936653 |
| H    | -1.289738 | 0.551143  | -2.561743 |
| H    | -2.871831 | 3.864914  | -1.788389 |
| H    | -3.391913 | 2.810057  | -3.114141 |
| H    | -1.674313 | 3.074568  | -2.835487 |
| H    | -3.124956 | 2.816141  | 0.355699  |
| H    | -2.890373 | 0.992207  | 0.564932  |
| H    | 4.305563  | 2.490921  | 0.256004  |
| H    | 4.506882  | 4.499154  | -1.183598 |
| H    | 0.399269  | 5.495495  | -0.389599 |
| H    | 0.181942  | 3.494065  | 1.053000  |
| H    | 1.650461  | 6.682277  | -2.171342 |
| H    | 3.329395  | 6.240585  | -2.543190 |
| H    | 2.963642  | 7.218375  | -1.119675 |
| H    | -6.035524 | 0.009568  | -1.169209 |
| H    | -7.411641 | 0.793700  | 0.744210  |
| H    | -4.894904 | -1.396209 | 3.454563  |

S168
total energy  -2766.42365036  a.u.

number of imaginary frequencies  0

molecule No.19b

optimized geometry

|   |   |   |
|---|---|---|
| N | -2.085033 | -1.089614 | -1.362659 |
| C | -1.316673 | 0.072492 | -1.188622 |
| C | -0.036097 | -0.290614 | -0.905654 |

S169
C    -0.011388  -1.755803  -0.925033
C    -1.337188  -2.182425  -1.221013
S    -3.847434  -1.120047  -1.809243
O    -4.085246  -2.545602  -1.986751
O    -3.932216  -0.138886  -2.877020
C    -4.626305  -0.519573  -0.341863
C    -5.024544  -1.432809   0.639794
C    -5.647950  -0.945700   1.784287
C    -5.874799   0.428304   1.962637
C    -5.469829   1.315171   0.950344
C    -4.848028   0.856655  -0.204819
C    -6.532947   0.950127   3.214052
C    1.087893  -2.571330  -0.699495
S    1.108080  -4.269775  -0.803533
C    2.759583  -4.695669  -0.246064
C    3.257377  -4.218481   0.972474
C    4.531089  -4.614054   1.380729
C    5.281740  -5.492338   0.595407
C    4.764759  -5.977048  -0.607851
S170
| Atom | X          | Y          | Z         |
|------|-----------|-----------|-----------|
| C    | 3.498811  | -5.580070 | -1.039056 |
| C    | 1.127753  | 0.644860  | -0.663383 |
| N    | 1.084427  | 1.348663  | 0.634280  |
| C    | 2.219937  | 1.135977  | 1.542532  |
| S    | 0.403447  | 2.915606  | 0.619498  |
| O    | 0.208977  | 3.275348  | 2.022164  |
| O    | -0.714994 | 2.824616  | -0.328100 |
| C    | 1.612107  | 4.030063  | -0.087532 |
| C    | 2.554223  | 4.644418  | 0.744118  |
| C    | 3.507270  | 5.488377  | 0.180618  |
| C    | 3.535076  | 5.738103  | -1.200325 |
| C    | 2.571274  | 5.118181  | -2.008642 |
| C    | 1.608116  | 4.270693  | -1.465110 |
| C    | 4.550304  | 6.684312  | -1.792369 |
| C    | 2.183167  | -0.171276 | 2.315310  |
| C    | 1.073001  | -0.901427 | 2.458781  |
| C    | 3.492693  | -0.527056 | 2.974314  |
| H    | -1.758147 | 1.053618  | -1.260985 |
| H    | -1.760951 | -3.171647 | -1.327644 |
|   | X         | Y         | Z         |
|---|-----------|-----------|-----------|
| H | -4.871137 | -2.497250 | 0.498336  |
| H | -5.972900 | -1.645081 | 2.549153  |
| H | -5.651508 | 2.379906  | 1.066042  |
| H | -4.560235 | 1.544954  | -0.992121 |
| H | -5.798060 | 1.452373  | 3.855939  |
| H | -6.989957 | 0.145242  | 3.795902  |
| H | -7.308670 | 1.685810  | 2.976412  |
| H |  2.032203 | -2.109916 | -0.422454 |
| H |  2.660300 | -3.558686 |  1.594867 |
| H |  4.928557 | -4.248637 |  2.322798 |
| H |  6.267776 | -5.804782 |  0.925345 |
| H |  5.347748 | -6.659941 | -1.218007 |
| H |  3.098694 | -5.946036 | -1.979731 |
| H |  1.179789 |  1.364546 | -1.487542 |
| H |  2.067578 |  0.085746 | -0.697298 |
| H |  2.219319 |  1.950225 |  2.274477 |
| H |  3.171395 |  1.212694 |  0.990409 |
| H |  2.519479 |  4.488866 |  1.817146 |
| H |  4.235212 |  5.972911 |  0.826129 |
| H     | 2.565154  | 5.312340  | -3.077985 |
|-------|-----------|-----------|-----------|
| H     | 0.841078  | 3.830261  | -2.092932 |
| H     | 4.741306  | 6.461296  | -2.846422 |
| H     | 5.502127  | 6.640158  | -1.253598 |
| H     | 4.193019  | 7.720736  | -1.736430 |
| H     | 1.064119  | -1.795455 | 3.077523  |
| H     | 0.133002  | -0.595332 | 2.012148  |
| H     | 3.400947  | -1.426104 | 3.590521  |
| H     | 3.839813  | 0.287472  | 3.624145  |
| H     | 4.286960  | -0.692317 | 2.233195  |

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总能量 -2766.43168618 a.u.

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想象频率个数 0

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分子 No.20b

S173
optimized geometry

| x          | y          | z          |
|------------|------------|------------|
| N -0.029881 | 0.187788   | 3.352596   |
| C -0.986404 | -0.012058  | 2.254747   |
| C -0.287637 | -0.882015  | 1.251315   |
| C 0.969481  | -1.180699  | 1.773165   |
| C 1.029935  | -0.477393  | 3.074473   |
| C -1.553820 | 1.341223   | 1.712198   |
| C -1.181544 | 1.663158   | 0.253338   |
| C -1.955906 | 0.771332   | -0.745943  |
| N -2.145994 | -0.606497  | -0.272630  |
| C -0.923212 | -1.364577  | 0.000970   |
| S 1.135090  | 1.445692   | -1.256212  |
| O 1.827298  | 0.112358   | -1.285525  |
| O 0.260218  | 1.415783   | 0.227041   |
| C 2.351914  | 2.661189   | -0.753972  |
| C 2.179868  | 3.975280   | -1.193100  |
| C 3.121337  | 4.939644   | -0.835626  |
| C 4.237012  | 4.606541   | -0.055489  |
C   4.389237   3.272257   0.361596
C   3.460973   2.297759   0.013786
C   5.270590   5.644532   0.304973
C   1.950929  -1.899640   1.091125
S   3.492172  -2.231558   1.696354
C   4.350376  -2.937168   0.290641
C   4.266683  -2.350532  -0.979422
C   4.983650  -2.929252  -2.026747
C   5.784172  -4.052058  -1.802469
C   5.873381  -4.610739  -0.525201
C   5.155135  -4.056737   0.533519
S  -3.313506  -1.505236  -1.195462
O  -3.152079  -2.885568  -0.725486
O  -3.171494  -1.161446  -2.613151
C  -4.857948  -0.842608  -0.599020
C  -5.322220  -1.214715   0.667140
C  -6.543702  -0.717732  1.107370
C  -7.316052   0.137488   0.301986
C  -6.827036   0.484902  -0.964356

S175
| C   | -5.604506 | -0.002210 | -1.426444 |
| C   | -8.655940 | 0.638135  | 0.781377  |
| C   | -1.455625 | 3.137703  | -0.061079 |
| H   | -1.831691 | -0.591745 | 2.657976  |
| H   |  1.884127 | -0.495061 | 3.748290  |
| H   | -1.159481 | 2.124833  | 2.364151  |
| H   | -2.643463 | 1.348391  | 1.800166  |
| H   | -1.475745 | 0.803008  | -1.734040 |
| H   | -2.952527 | 1.206931  | -0.864036 |
| H   | -1.215271 | -2.416832 | 0.131931  |
| H   | -0.200625 | -1.333662 | -0.829882 |
| H   |  1.326955 | 4.248414  | -1.809460 |
| H   |  2.991553 | 5.963764  | -1.174545 |
| H   |  5.252163 | 2.998604  | 0.963545  |
| H   |  3.591789 | 1.265047  | 0.320374  |
| H   |  6.147742 | 5.563796  | -0.349939 |
| H   |  5.622832 | 5.517186  | 1.333967  |
| H   |  4.875367 | 6.659079  | 0.201594  |
| H   |  1.751069 | -2.239850 | 0.078884  |

S176
| H   | 3.666895 | -1.460549 | -1.150483 |
|-----|----------|-----------|-----------|
| H   | 4.925321 | -2.489169 | -3.017552 |
| H   | 6.344726 | -4.488944 | -2.623275 |
| H   | 6.495205 | -5.483416 | -0.351453 |
| H   | 5.210774 | -4.496119 | 1.525059  |
| H   | -4.745637| -1.896262 | 1.283978  |
| H   | -6.913349| -1.005717 | 2.088060  |
| H   | -7.414416| 1.137313  | -1.604683 |
| H   | -5.240087| 0.247640  | -2.417202 |
| H   | -8.973708| 1.528343  | 0.230939  |
| H   | -8.634258| 0.882839  | 1.848455  |
| H   | -9.428113| -0.129139 | 0.640968  |
| H   | -2.494865| 3.395992  | 0.167241  |
| H   | -1.283881| 3.352793  | -1.121751 |
| H   | -0.798634| 3.776016  | 0.535968  |

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total energy  -2766.44631352  a.u.
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number of imaginary frequencies  0

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S177
9. $^1$H and $^{13}$C NMR chart

[Diagram of $^1$H and $^{13}$C NMR charts showing spectral peaks for compounds 3a and 3b.]
