Supplementary Information

Grignard Reagents Unlock 3D Nitrogen Heterocycles via Single Carbon Ring Insertion

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2 Experimental Part

2.1 General Information

Oxygen- and moisture-sensitive reactions were carried out under an atmosphere of purified nitrogen using Schlenk line technique. Anhydrous THF, MeOH, toluene, DMF, dioxane, Et_2O, heptane packed under inert gas (argon) were used as purchased. All commercially available reagents were used as received. Analytical thin layer chromatography (TLC) was performed on pre-coated silica gel 60 F-254 plates (particle size 0.040-0.055 mm, 230-400 mesh). NMR spectra were recorded on a Bruker AVII400 (400 MHz) or Bruker Avance NEO 500MHz spectrometers[1] at 296K. All chemical shifts (δ) are reported in parts per million (ppm) and the residual solvent peak was used as an internal standard for $^{1}H/^{13}C$ NMR: $CDCl_3$ δ=7.28/77.0, DMSO-*d*^{6} 2.50/40.0, C_6D_6 δ=7.16/128.0, CD_3CN δ=1.94/1.32. ^{19}F signals were referenced to $CFCl_3$. NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad), coupling constant(s) (Hz) and integration. In some of the NMR spectra, a signal is present at ~1.55 ppm ($CDCl_3$), ~3.33 (DMSO-*d*^{6}) or ~0.40 ppm (C_6D_6) due to water contamination of the deuterated solvent. High resolution mass spectrometry (HRMS) analyses were conducted on Waters HPLC Acquity - Waters LCT Premier system, using an electrospray ionization (ESI TOF) technique (conditions: MeCN/H_2O (80/20), flow rate: 0.2 ml/min), or on Bruker Maxis Impact system, using an atmospheric-pressure chemical ionization ($APCI^+$) solid probe.

[1] The machine used for NMR is stated in the compounds description.

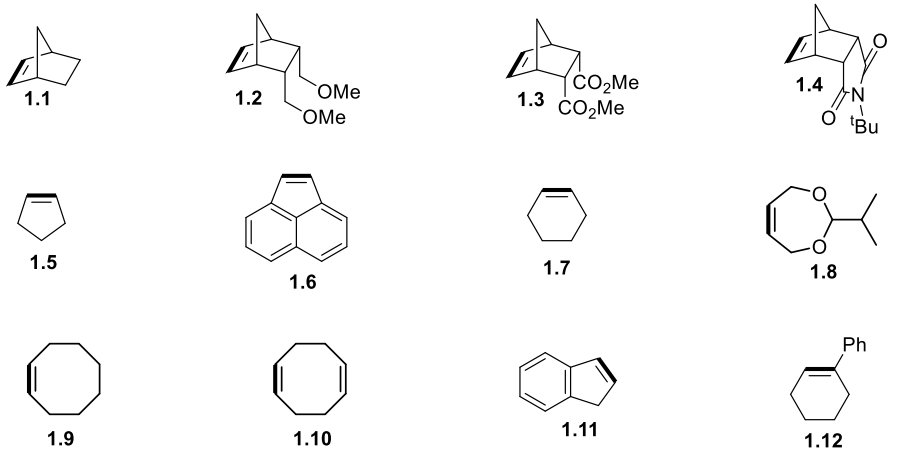
2.2 Synthesis of Starting Materials

*2.2.1 Synthesis of alkenes **1***

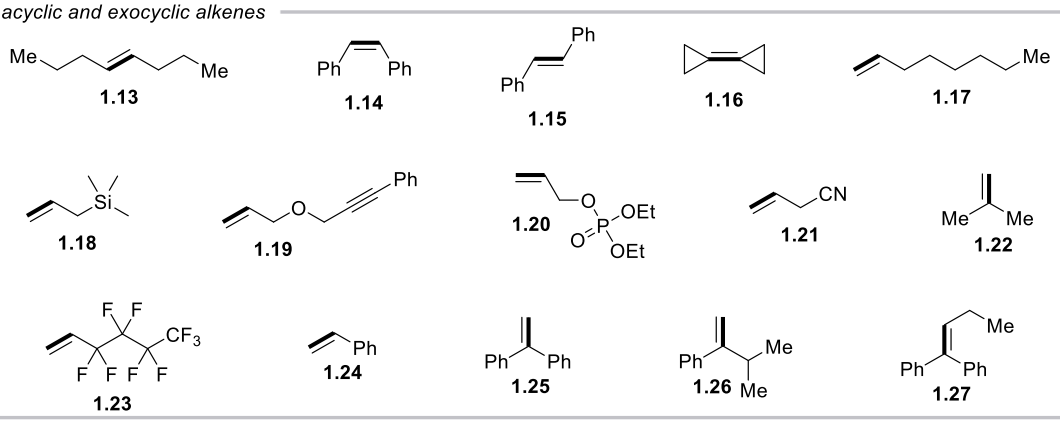
Alkenes **1.1**, **1.5-1.7**, **1.9-1.18**, **1.20-1.26**,**1.37-1.41** were purchased and used as was without further purification.

Compounds **1.2**,[1] **1.3**,[2,3] **1.4**,[4] **1.8**,[5] **1.19**,[6] **1.27**,[7] **1.42**,[8] **1.43**,[9] **1.44**,[10] **1.46**[11] were synthesized according to the reported procedures. Compound **1.45** was synthesized as described below.

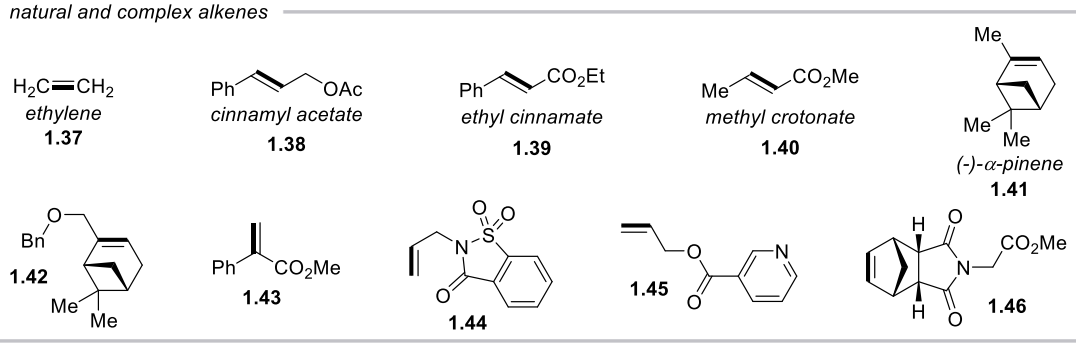
endocyclic alkenes



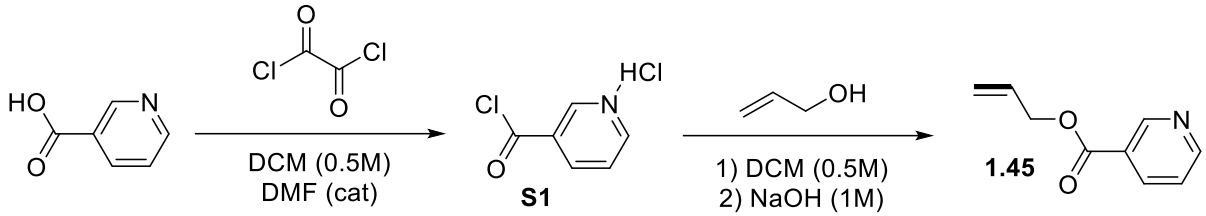
acyclic and exocyclic alkenes



natural and complex alkenes



*2.2.1.1 Synthesis of Allyl nicotinate (**1.45**)*



The literature procedure[12] was modified to synthesize intermediate compound **S1**.

Niacin (50 mmol, 6.16 g) was suspended in DCM (0.5M, 100 ml), DMF (10 drops) was added via Paster pipette, and the suspension was cooled to 0 °C. Oxalyl chloride (2 eq, 100 mmol, 8.6 ml) was added to the suspension dropwise. The reaction mixture was allowed to warm up to room temperature within 1 h and stirred at room temperature overnight. To ensure the complete conversion, the mixture was refluxed for 5 h, then cooled to room temperature. Hexane was added to the mixture, and it was stirred for 10 min. The precipitate was rapidly filtered and washed with hexane (3*50 ml) and dried in vacuo for 30 min. The crude compound **S1** was used without further purification in the next step.

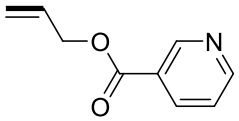
Compound **S1** was suspended in DCM (0.5 M, 100 ml) and the suspension was cooled to 0 °C. Allyl alcohol (1.2 eq, 60 mmol, 4.1 ml) was added dropwise. The reaction mixture was allowed to warm up to room temperature within 1 h and stirred at room temperature overnight. Et_2O (100 ml) was added to the mixture, and it was stirred for 1 min, then hexane was added (50 ml) and the obtained mixture was cooled to 0 °C with stirring until the precipitate is formed. Hexane (100 ml) is added to the obtained suspension, and it was stirred at 0 °C for additional 5 min. The precipitate was filtered and washed with Et_2O (3*50 ml) and hexane (3*50 ml). The solid material was dissolved in cold two-phase mixture of aqueous NaOH (1M, 200 ml) and Et_2O (200 ml). The organic phase was separated and extracted with Et_2O (200 ml). Combined organic phase was washed with aqueous NaOH (3*100 ml, 1M) and brine (100 ml) and dried over anhydrous Na_2SO_4. Filtration of the drying agent and evaporation afforded 2.2 g (26% yield) of the desired compound **1.45**.

If the purity of **1.45** is not sufficient, it can be additionally purified by the following method:

Crude **1.45** (2 g, ~12.3 mmol) is dissolved in Et_2O (5 ml) and EtOAc (5 ml) and the solution is cooled to 0 °C. HCl in EtOAc (1M, 1.5 eq, ~19 ml)[2] is added dropwise at 0 °C. Et_2O (25 ml) is added to the obtained suspension and the precipitate was filtered and washed with Et_2O (5*25 ml). The resulting solid was dissolved in Et_2O (25 ml) and $NaHCO_3$ (saturated, 100 ml). The aqueous phase was extracted with Et_2O (3*25 ml). The combined organic phase was washed with $NaHCO_3$ (saturated, 2*25 ml) and brine (25 ml) and dried over anhydrous Na_2SO_4. The drying agent was filtered off, and the pure **1.45** (1.95 g, 97%) was obtained upon evaporation.

[2] HCl in EtOAc was prepared as follows for the required amount: MeOH (1 ml, 25 mmol) was added to EtOAc (19 ml) and the mixture was cooled to 0 °C. While stirring, acetyl chloride (1.3 ml, 18.5 mmol) was added slowly to the obtained solution (*caution*: the solution may overheat and explosively spill from the reaction flask; thus, it is recommended to maintain the slow rate of addition and keep necessary precautions). The mixture was stirred for additional 5 min and the obtained HCl in EtOAc was used directly.

2.2.1.1.1 Allyl nicotinate (**1.45**)



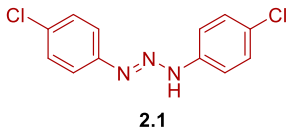
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.80-8.79 (m, 1H), 8.36-8.34 (m, 1H), 7.44-7.42 (m, 1H), 6.04 (ddt, J = 16.5, 10.9, 5.7 Hz, 1H), 5.43 (d, J = 17.2 Hz, 1H), 5.33 (d, J = 10.4 Hz, 1H), 4.87 (d, J = 5.7 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d^6) δ 164.7, 153.1, 150.6, 137.4, 131.6, 126.2, 123.4, 118.9, 66.0.

APCI $[M + H]^+$ calcd for $C_9H_{10}NO_2^+$ 164.0706; found 164.0722.

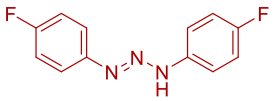
*2.2.2 Synthesis of triazenes **2***

Triazenes **2.1**-**2.5**,[13] **2.6**-**2.8**[14] were synthesized according to the reported procedures.

Symmetrical Triazenes



2.1



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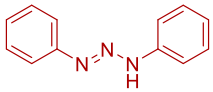
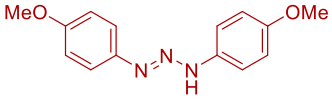
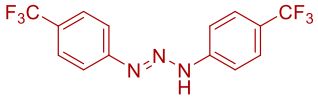


2.3

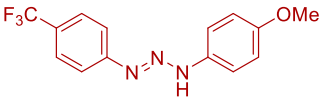


2.4

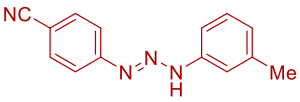


2.5

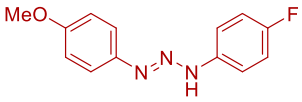
Unsymmetrical Triazenes



2.6



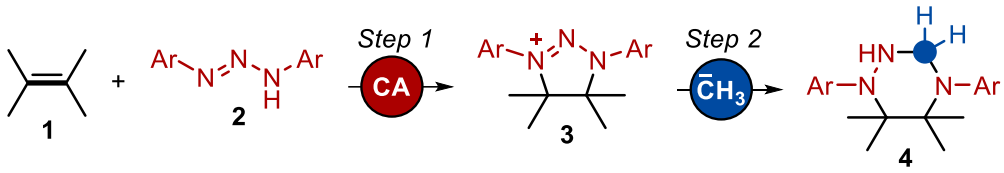
2.7



2.8

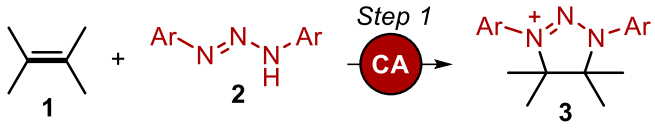
2.3 The Reaction Developed

*2.3.1 Synthesis of compounds **4***



This reaction sequence required two consecutive steps (*Step 1 and 2*) as described below.
Step 1 required small modification of the literature procedure[15] as described previously.[14]
Step 2 was optimized since there has been no precedent of such reaction in the literature.

2.3.2 *Step 1: standard procedure for triazolium salt **3** synthesis*



Previously reported procedure[14] was used which is a modified Jochims cycloaddition.[15,16]

Alkene **1** (4 mmol, 2 eq), triazene **2**[3] (2 mmol, 1 eq), KPF_6 (736 mg, 4 mmol, 2 eq) and acetone (60 ml, 0.033M[4]) were added to the Schlenk flask and nitrogen was bubbled for 10 minutes while the reaction mixture was cooled down to -78 °C[5] with stirring (the reaction flask should be protected from light!). ^{t}BuOCl (0.3 ml[6], 283 mg, 1.3 eq) was added dropwise to the cooled solution and the reaction mixture was allowed to warm up to room temperature during the night in the dark. The reaction mixture was filtered through a sintered funnel, and the precipitate was washed with acetone (until no triazolium was detected by TLC). The solution obtained was evaporated and diethyl ether (50 ml) was added to the solid remaining. The precipitate was triturated with spatula and then was subjected to ultrasound bath for 5 minutes. The precipitate was filtered and washed with Et_2O (3*50 ml) and with toluene or hexane (3*50 ml).[7] The resulting solid was dried in vacuo.

The salts **3** contained remaining KPF_6 left in them (~1 eq); luckily, this "impurity" did not interfere with the desired transformation. Thus, compound **3** did not require additional purification and it was used in the next step as was (the content of the salt was analyzed, and the purity was estimated accordingly).

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[3] The typical loading was 2 mmol relatively to **2**. The reaction may be scaled up to 10 mmol without yield loss (further scaling was not performed).

[4] The concentration of the triazene **2** is stated. The reaction may be concentrated up to 0.1M without yield drop (further concentration options were not checked).

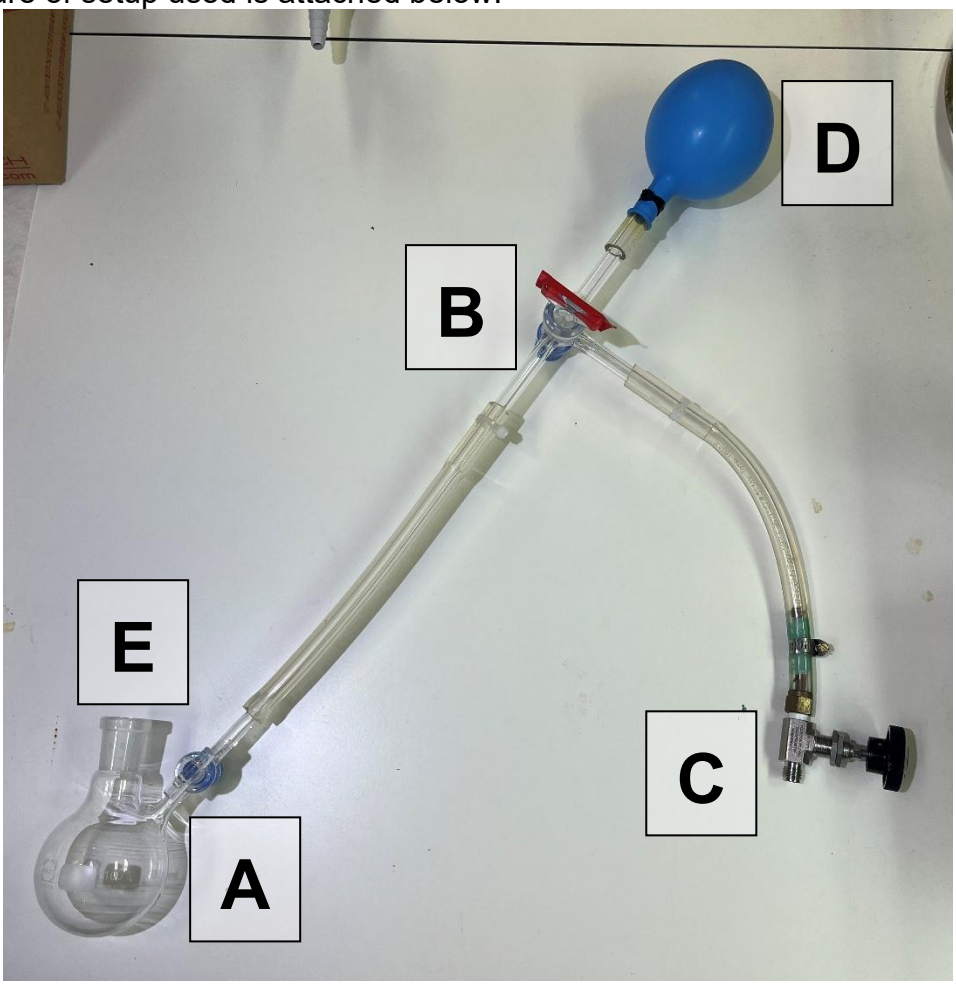
[5] Triazenes (especially asymmetric ones) start to decompose readily in solution, therefore, it is recommended to cool down the solution immediately and proceed with ^{t}BuOCl addition as fast as possible upon cooling.

[6] ^{t}BuOCl density is 0.96 g/ml.

[7] In some cases, the nitrenium cation **3** was soluble in diethyl ether or toluene which has to be checked in advance; if the salt was soluble in a solvent, a mixture with hexane was prepared and used; typical loss during filtration, wash and transfer was measured to be 1-5% of the triazolinium salt **3** yield.

2.3.2.1 Modified procedure for Step 1 with gaseous alkenes

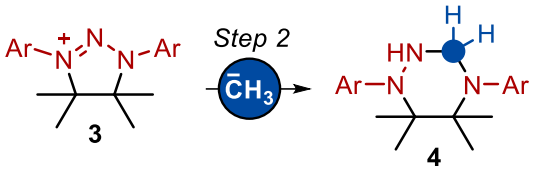
The following protocol was used for cycloaddition reaction with isobutylene (**1.22**) and ethylene (**1.37**) which are gases at room temperature and atmospheric pressure. The picture of setup used is attached below.



The Schlenk flask (**A**) was equipped with 3-way valve (**B**) connected to Swagelok gas valve (**C**) and a rubber balloon (**D**). Source of nitrogen gas was connected through the valve (**C**), an oil bubbler was placed in the joint (**E**) of the flask (**A**), and the system was flushed with nitrogen for 5 min (the balloon was flushed by inflating and deflating 10 times and it was kept inflated afterwards). Then triazene **2** (2 mmol, 1 eq), KPF_6 (736 mg, 4 mmol, 2 eq) and acetone (60 ml, 0.033M) were added to the Schlenk flask (**A**), oil bubbler was placed in the joint (**E**) of the flask (**A**) and the system was flushed with nitrogen gas for 5 min in the dark. The valve (**C**) was closed, and source of nitrogen was switched to the gas cylinder (with isobutylene (**1.22**) and ethylene (**1.37**) correspondingly). The balloon (**D**) was deflated, and three-way valve (**B**) was switched to connect gas valve (**C**) and balloon (**D**). Then the following cycles were repeated 5 times: the balloon was inflated with the corresponding gaseous alkene (**1.22** or **1.37**); the gas-valve (**C**) was closed; the three-way valve (**B**) was switched to connect balloon (**D**) and the flask (**A**); the balloon was deflated through the oil bubbler installed in joint (**E**); the three-way valve (**B**) was switched to connect balloon (**D**) and the gas inlet (**C**). After the last cycle, the balloon (**D**) was inflated again, then the gas valve (**C**) was closed, and the three-way valve (**B**) was switched to connect balloon (**D**) and the flask (**A**). The oil bubbler was changed to the new rubber septum (in joint **E**) under the flow of the alkene gas

from the balloon. Then the balloon was inflated again with the corresponding gaseous alkene. The three-way valve (**B**) was switched to connect balloon (**D**) and the flask (**A**). The gas source was disconnected from the gas valve (**C**), and it was switched to the source of nitrogen gas. The reaction mixture was cooled down to -78 °C with stirring (the reaction flask should be protected from light!). After the cooling the gaseous alkene can be fully dissolved (this might take ~1h) and, thus, the balloon may be fully deflated; in this case we highly recommend inflating balloon with nitrogen (do not inflate the balloon completely as it will inflate again once the reaction will be warming up to room temperature). After cooling to -78 °C, ^{t}BuOCl (0.3 ml, 283 mg, 1.3 eq) was added dropwise to the cooled solution and the reaction mixture was allowed to warm up to room temperature during the night in the dark. The reaction mixture was filtered through a sintered funnel, and the precipitate was washed with acetone (until no triazolium was detected by TLC). The solution obtained was evaporated and diethyl ether (50 ml) was added to the solid remaining. The precipitate was triturated with spatula and then was subjected to ultrasound bath for 5 minutes. The precipitate was filtered and washed with Et_2O (3*50 ml) and with hexane (3*50 ml). The resulting solid was dried in vacuo and used without further purification.

2.3.3 *Step 2: General Procedure A for synthesis of compounds **4** (citric acid quench)*



In the nitrogen atmosphere glove box,[8] the oven dried vial was charged with nitrenium salt **3** (0.2 mmol, 1 eq). THF (0.05 M, 4 ml) was added, and the suspension was cooled down to -10 °C with cooling aluminum block. MeMgBr (1 eq, 3M, 0.067 ml) was added dropwise to the nitrenium suspension with stirring, and the reaction mixture was allowed to reach room temperature overnight. The mixture was filtered through a cotton pad,[9] and the precipitate was washed with THF (2 ml).[10] Anhydrous citric acid (1.5 eq, 58 mg) was added in one portion to the reaction mixture, and it was stirred at room temperature upon completion.[11] The reaction was quenched with aqueous $NaHCO_3$ (sat, 10 ml) and EtOAc (40 ml) was added to extract all the organic materials. Organic phase was separated and washed with aqueous $NaHCO_3$ (sat, 2*10 ml) and brine (10 ml). The organic phase was passed through a pad of Na_2SO_4 for additional drying and evaporated. Et_2O (1-2 ml) was added to the remaining oil and resulting solution/suspension was subjected to flash filtration through neutral aluminum oxide[12] with the eluent specified, and that afforded pure compound **4**. The yield of the reaction is calculated for the two-step sequence.

2.3.4 *Step 2: General Procedure B for synthesis of compounds **4** (NH_4Cl quench)*

The oven dried Schlenk flask was flushed with nitrogen and charged with nitrenium salt **3** (0.2 mmol, 1 eq). THF (0.05 M, 4 ml) was added under N_2 atmosphere, and the suspension was cooled down to 0 °C. MeMgBr (1 eq, 3M, 0.067 ml) was added dropwise, and the reaction mixture was allowed to reach room temperature overnight. The mixture was cooled down to 0 °C and aqueous NH_4Cl (20%, 1 ml) and brine (10 ml) was added to quench the reaction. The aqueous layer was extracted with EtOAc (3*10 ml) and the combined organic layers were washed with brine (10 ml). The organic phase was passed through a pad of Na_2SO_4 for additional drying and evaporated. Et_2O (1-2 ml) was added to the remaining oil and resulting solution/suspension was subjected to flash filtration through neutral aluminum oxide[12] with the eluent specified, and that afforded pure compound **4**. The yield of the reaction is calculated for the two-step sequence.

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[8] The reaction can be run outside the glove box using Schlenk techniques similarly to Step 2: General Procedure B (see below). For example, see Section 2.3.11 “Gram scale synthesis of 4.**9**”.

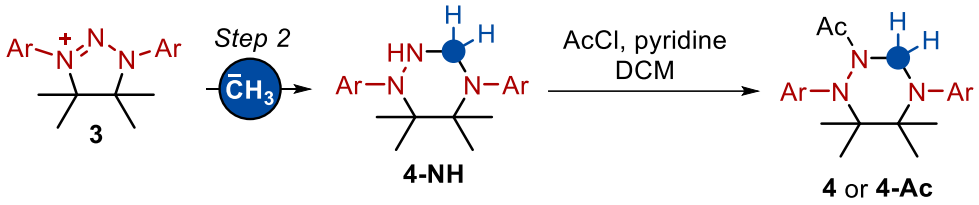
[9] The filtration eliminated side reactions in some cases (such as product **4.4**); thus, it was applied as a standard part of the protocol. For example, it was not applied in “Gram scale synthesis of 4.**9**” and it did not give undesired side reactions (see Section 2.3.11).

[10] It is recommended to take a sample of the reaction mixture at this stage to compare further and look at reaction completeness (for example, see Section 2.3.7).

[11] The TLC analysis was performed to analyze the reaction completeness. For this we recommend comparing the reaction mixture with the sample before addition of acid.

[12] Usually, a Al_2O_3 layer of 3-5 cm was enough to purify the desired compound.

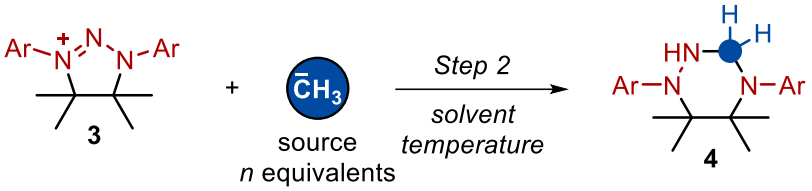
2.3.5 *Step 2: General Procedure C for acylation of compounds **4***



NH-Product **4-NH** can be acylated, if desired, by the following method.
Compound **4-NH** (0.2 mmol) is obtained from step 2 by General Procedure A. The product can be purified as stated via flash filtration through Al_2O_3 pad or the crude sample can be obtained by evaporation of organic layer after extraction and filtration through pad of Na_2SO_4.
The product **4-NH** from step 2 was dissolved in DCM (5 ml, 0.04M). The resulting solution was cooled down to 0 °C and pyridine (6 eq, 1.2 mmol, 95 mg) was added. Acetyl chloride (5 eq, 1 mmol, 79 mg) was dissolved in DCM (0.5 ml) and this solution was added to the cooled mixture of **4** and pyridine with stirring. The reaction mixture was allowed to warm up to room temperature and was stirred overnight. The obtained mixture was diluted with DCM (20 ml) and the resulting organic phase was washed with aqueous solution of HCl (1 M, 3*10 ml), with H_2O (10 ml) and with aqueous solution of $NaHCO_3$ (5% by weight, 2*10 ml). The organic phase was dried over anhydrous Na_2SO_4, the drying agent was filtered off, and the crude product was purified by column chromatography on Si-gel using the eluent specified. The yield of the reaction is calculated for the three-step sequence.

2.3.6 *Step 2: optimization of **4** synthesis*

For optimization, General Procedure B was used with the modifications stated in the table below accordingly. Isolated yield of compound **4** is reported in the table below.



entry	**"CH_3-" source**	***n*** (equiv.)	**solvent** (0.05 M)	**temperature**[13] (°C)	**yield** (%)
1	MeMgBr	4	THF	0 °C -> RT (ovn)	82
2	MeMgBr	4	Et_2O	0 °C -> RT (ovn)	traces[14]
3	MeMgBr	4	Et_2O	0 °C -> RT -> reflux (ovn)[15]	24
4	MeMgBr	4	dioxane	12 °C -> RT (ovn)	76
5	MeMgBr	4	hexane	0 °C -> RT (ovn)	traces[14]
6	MeMgBr	4	hexane	0 °C -> RT -> reflux (24 h)[15]	traces[14]
7	MeMgBr	4	THF	0 °C (2 min) -> RT (40 min)[16]	57
8	MeMgBr	4	THF	RT (ovn)	76
9	MeMgBr	4	THF	-36 °C -> RT (ovn)	74
10	MeLi	4	THF	-78 °C -> RT (ovn)	64
11	$ZnMe_2$	4	THF	0 °C -> RT (ovn)	traces[14]
12	$ZnMe_2$	4	THF	0 °C -> RT -> reflux (ovn)[15]	traces[14]
13	MeMgBr	2	THF	0 °C -> RT (ovn)	94
14	MeMgBr	1	THF	0 °C -> RT (ovn)	98

[13] MeMgBr was added at the first temperature stated, then the reaction mixture was brought to either room temperature overnight. "RT" = room temperature, "ovn" = overnight.

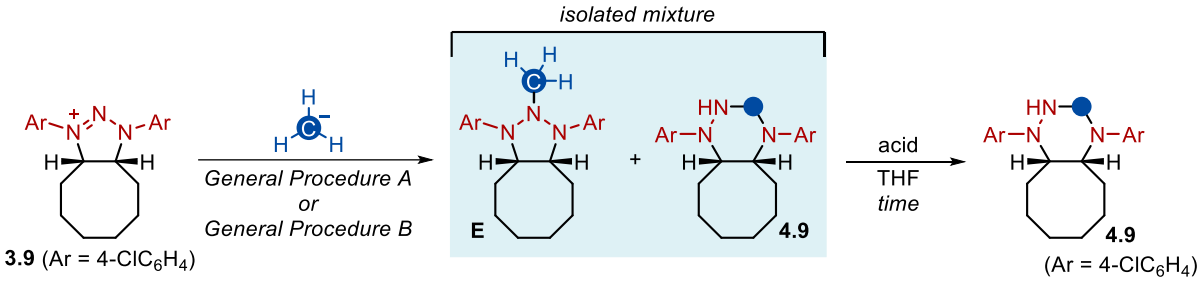
[14] Low conversion of the starting material was detected.

[15] After the reaction mixture reached room temperature (during the period of 1h), it was refluxed for the indicated amount of time.

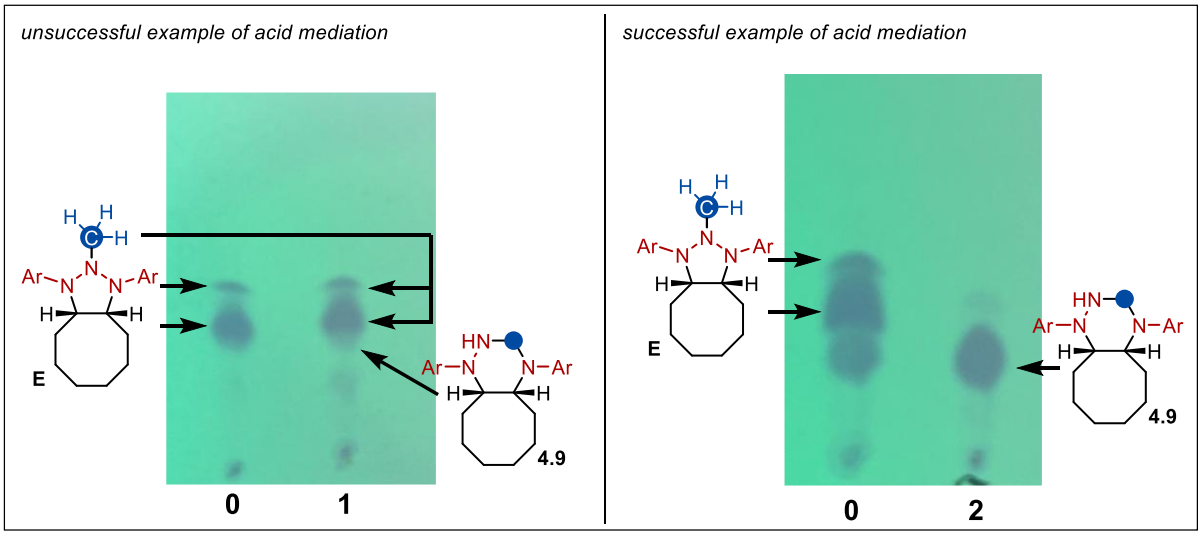
[16] MeMgBr was added at 0 °C, and the cooling bath was removed after 2 min.

2.3.7 *Step 2: optimization of acidic quench for compound **4** synthesis*

For additional optimization of acidic quench, compound **3.9** was used as a model substrate since intermediate **E** was quite stable and could be observed by TLC[17] (see example below) analysis as well as NMR. Depending on the method, mixture of **4.9** and **E** or practically pure **E** can be obtained (see below for more information).



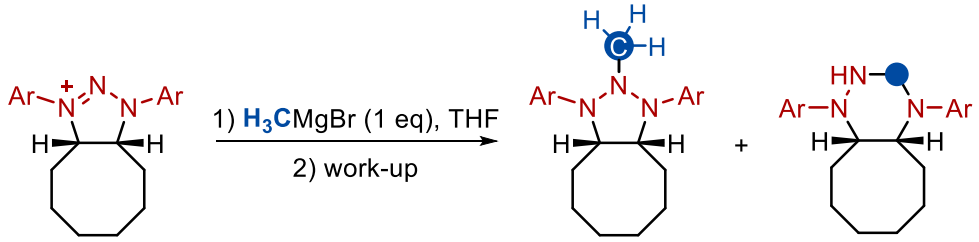
Below, two examples are presented for reaction TLC. The left one is an example of unsuccessful reaction, when an acid did not catalyze the reaction during the period of 24 h (lane **0** is the lane with pure compound **E**, lane **1** is the reaction mixture). The right TLC shows the successful reaction example where almost a complete conversion was achieved within 1 h (lane **0** is the lane with pure compound **E**, lane **2** is the reaction mixture).[18]



[17] The intermediate **E** is not particularly stable on TLC; thus, it is advised to load the samples fast, run the TLC as soon as possible, do not run the plate for more than 3-4 cm and use eluent EtOAc:Hex = 1:10. Additionally, triazane **E** appears as a mixture of two diastereomeric triazanes. Depending on the concentrat

[18] Some decomposition of compound **E** to product **4.9** can be seen due to prolonged storage of the sample **E**.

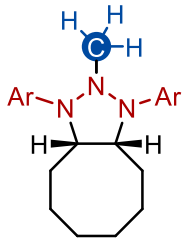
*2.3.7.1 Synthesis, isolation and characterization of intermediate **E***



3.9 (Ar = 4-ClC$_6$H$_4$) **E** **4.9**

In the nitrogen atmosphere glove box, the oven dried vial was charged with nitrenium salt **3.9** (0.2 mmol, 1 eq). THF (0.05 M, 4 ml) was added, and the suspension was cooled down to -10 °C with cooling aluminum block. MeMgBr (1 eq, 3M, 0.06 ml) was added dropwise to the nitrenium suspension with stirring, and the reaction mixture was allowed to reach room temperature during 1 h. The mixture was diluted with hexane (4 ml) and immediately filtered through a small pad of neutral Al_2O_3. Then the pad was then washed with Et_2O/Hexane (1:1, 2 ml). Concentration of the filtrate under reduced pressure afforded a 1:1 mixture of **E** and **4.9** (total: 76 mg, 97%), due to a partially magnesium-catalyzed transformation during the isolation step.

(3aR,9aS)-1,3-bis(4-chlorophenyl)-2-methyldecahydro-1H-cycloocta[d][1,2,3]triazole (**E**)



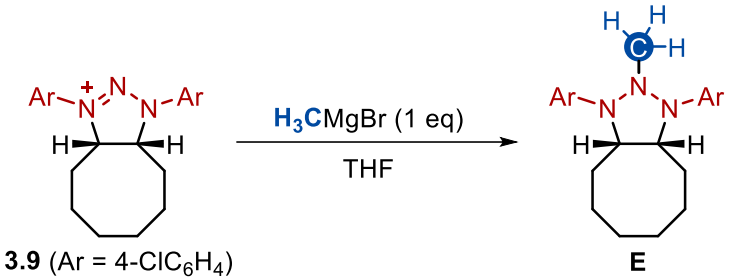
E

(Ar = 4-ClC$_6$H$_4$)

Product **E** was synthesized from alkene **1.9** and triazene **2.1** (0.2 mmol) by the method described above. It was obtained in mixture (1:1) with product **4.9**.

^{1}H NMR (400 MHz, C_6D_6): δ 7.12–7.10 (m, 4H), 6.72- 6.70 (m, 4H), 3.47–3.41 (m, 2H), 2.64 (s, 3H), 1.85–1.81 (m, 4H), 1.39–1.33 (m, 2H), 1.19–1.07 (m, 6H); ^{13}C NMR (101 MHz, C_6D_6): δ 148.7, 129.1, 124.8, 115.6, 69.0, 49.4, 31.1, 28.6, 25.7. APCI $[M+H]^+$ calcd for $C_{21}H_{26}{}^{37}Cl^{35}ClN_3^+$ 392.1469; found 392.1450.

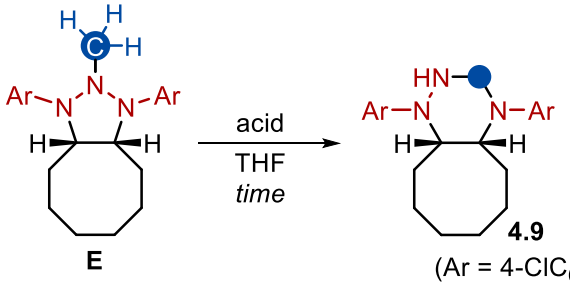
*2.3.7.2 Preparation of **E** stock solution*



3.9 (Ar = 4-ClC_6H_4) **E**

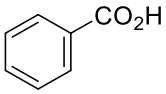
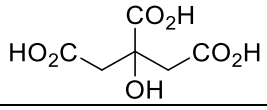
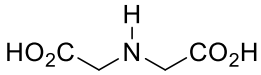
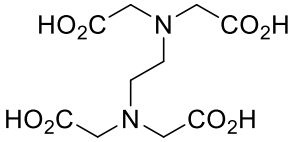
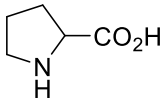
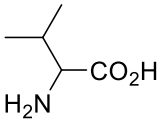
Stock solution of compound **E** was prepared as follows for the optimization study:
In the nitrogen atmosphere glove box, the oven dried vial was charged with nitrenium salt **3.9** (0.4 mmol, 1 eq). THF (0.05 M, 8 ml) was added, and the suspension was cooled down to -10 °C with cooling aluminum block. MeMgBr (1 eq, 3M, 0.133 ml) was added dropwise to the nitrenium suspension with stirring, and the reaction mixture was allowed to reach room temperature during 1 h. The mixture was filtered through a cotton pad, and the precipitate was washed with THF (2 ml). The obtained mixture contained pure compound **E** according to the TLC analysis and it was used without further purification. The stock solution (~10 ml) was split into ten equal portions (~1 ml) and different acids were tested as described below.

*2.3.7.3 Optimization of acidic quench (conversion of **E** to **4.9**)*



E **4.9** (Ar = 4-ClC_6H_4)

Stock solution of **E** was prepared as described above. Then different acids were screened for conversion of **E** to **4.9** as described below.
The acid specified in the table below (1 eq, 0.04 mmol) was added to the stock solution of **E** (0.04 mmol) in THF (~1 ml). The reaction mixture was monitored by TLC analysis.
If reaction was successful and the full completion was achieved within 24-72 h, it was scaled up to 0.2 mmol and the product **4.9** was isolated. The isolated yields of **4.9** are presented in the table below for two step sequence.
The product was isolated in the following manner:
The reaction was quenched with aqueous $NaHCO_3$ (sat, 10 ml) and EtOAc (40 ml) was added to extract all the organic materials. Organic phase was separated and washed with aqueous $NaHCO_3$ (sat, 2*10 ml) and brine (10 ml). The organic phase was passed through a pad of Na_2SO_4 for additional drying and evaporated. Et_2O (1-2 ml) was added to the remaining oil and resulting solution/suspension was subjected to flash filtration through neutral aluminum oxide (2-3 cm) with EtOAc:Hex = 1:10 as eluent. That afforded pure compound **4.9**.

entry	acid	yield (%)[19]
1		90
2	$H-CO_2H$	91
3	$Me-CO_2H$	93
4		97
5	$TsOH \times H_2O$	96[20]
6		0
7		0
8	Bu_4NHSO_4	traces
9		0
10		0

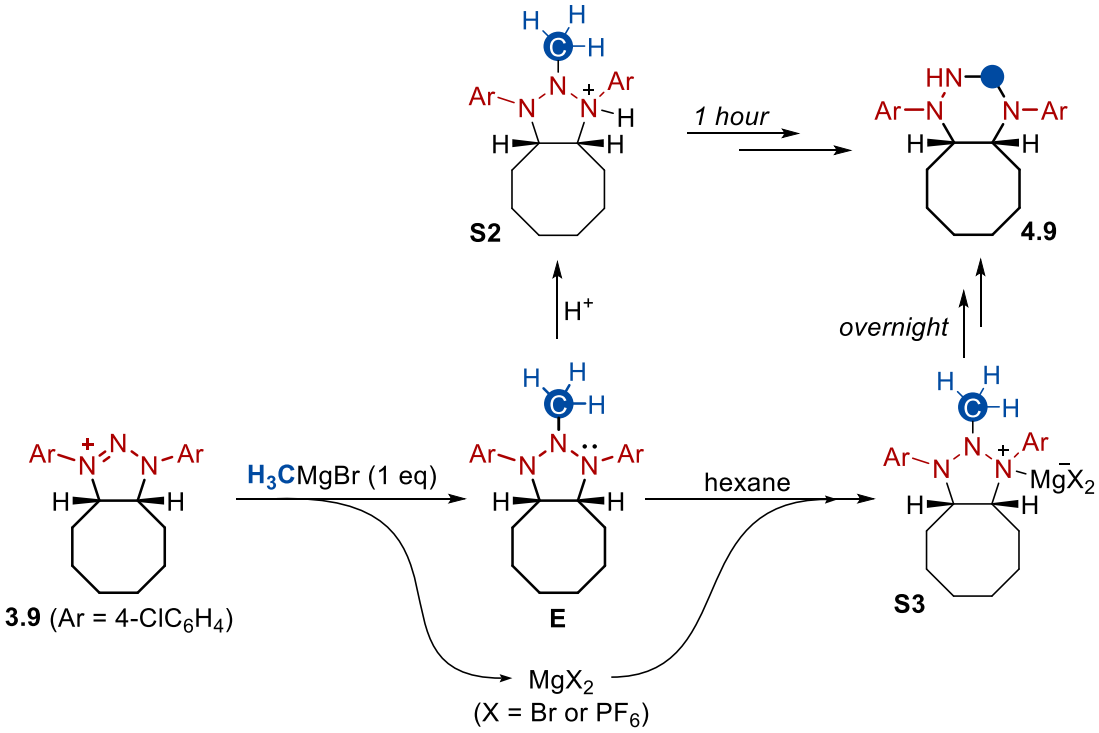
After the tests performed, we chose citric acid (entry 4) as the most suitable reagent to convert triazane intermediates (such as **E**) to final products **4**. This acid can be easily obtained or procured in anhydrous form and did not require any purification upon long storage (it possessed the same activity after the storage period of 6 months in ambient conditions). Additionally, it can be easily removed by basic washing with $NaHCO_3$.
When we screened lower amounts of acid, it led to slow reaction and side products were observed. Thus, it is recommended to use 1-2 equivalents of acid for facile step 2 without any undesired side reactions.

[19] The isolated yield is presented for the scaled-up reaction in case of successful transformation where full conversion was observed in period of 24-72 h. Otherwise, if the reaction did not reach the completion within this period, there had been detected a lot of side products.

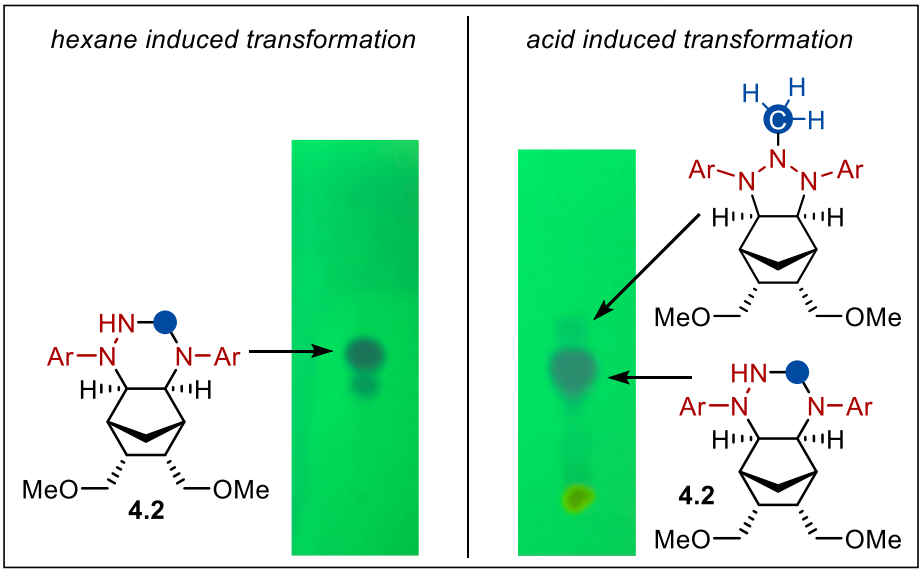
[20] The reaction result depended on the quality of TsOH, since it is hygroscopic.

*2.3.7.4 Hexane as mediator for conversion of intermediates to products **4***

We observed that hexane can alternatively induce the rearrangement step 2 instead of acid. When MeMgBr is added to nitrenium **3.9**, intermediate **E** is formed along with magnesium salts (MgX_2, X = Br or PF_6). After acid is added to the intermediate **E**, lone pair of flanking nitrogen is protonated and **S2** can be formed which can rearrange to the product **4.9** (for more details about H^+-mediation, see section 4.2 "Discussion of the Reaction Mechanism"). MgX_2 species are not well soluble in THF (it is possible to remove them via filtration). Moreover, if MgX_2 is present in the solution, it should be highly solvated and, thus, do not induce the rearrangement. However, once hexane is added, it should induce MgX_2 coordination to flanking nitrogen to produce **S3**, which is similar to Brønsted acid activation via **S2**. This activation can lead to product **4.9** after approximately 12 hours (while the intermediate **E** is stable during this time in THF).

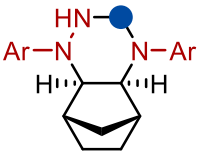


This rearrangement method using hexane proved to be effective only in several instances. However, in some cases the acid mediation was superior.
For instance, when we synthesized compound **4.2** via hexane mediated transformation, side reactions were detected after reaction reached completion after 24 hours (see the left TLC below). However, when we applied acid mediated protocol (General Procedure A), we observed a smooth transformation of triazane to the product **4.2** within several hours (see the right TLC; reaction reached its completion after 5 h).

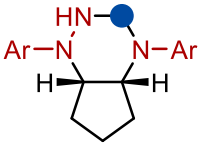


2.3.7.5 Summary of step 2

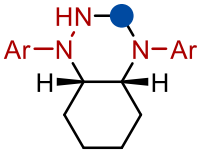
Below are presented the examples that can be obtained without acid mediation and simple work-up with aqueous NH_4Cl (20%) is sufficient. In these cases, intermediate triazane is likely unstable and the rearrangement step 2 is quite fast (except for compound **4.8** which took some time to rearrange).



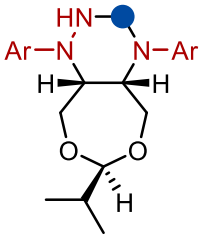
4.1 98%
(Ar = 4-ClC_6H_4)



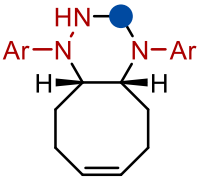
4.5 87%
(Ar = 4-ClC_6H_4)



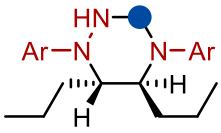
4.7 92%
(Ar = 4-FC_6H_4)



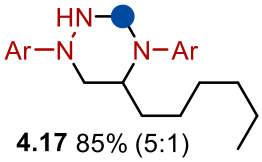
4.8 89%
(Ar = 4-ClC_6H_4)



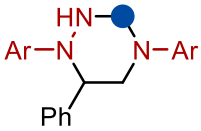
4.10 78%
(Ar = 4-ClC_6H_4)



4.13 98%
(Ar = 4-ClC_6H_4)

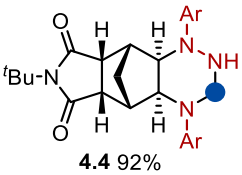


4.17 85% (5:1)
(Ar = 4-ClC_6H_4)

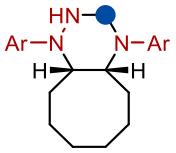


4.24 91% (5:1)
(Ar = 4-ClC_6H_4)

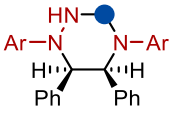
Moreover, the products below require acid mediation, because step 2 does not reach completion without acid addition as we were able to observe intermediate triazane in these cases by NMR and TLC analysis.
Based on our experience, we suggest using General Procedure A with acid mediation for most of the substrates. Once these dependencies had been identified, we applied General Procedure A to all the remaining substrates in the scope.



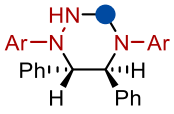
4.4 92%
(Ar = 4-ClC_6H_4)



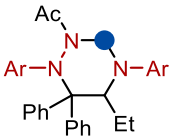
4.9 97%
(Ar = 4-ClC_6H_4)



4.14 91%
(Ar = 4-ClC_6H_4)

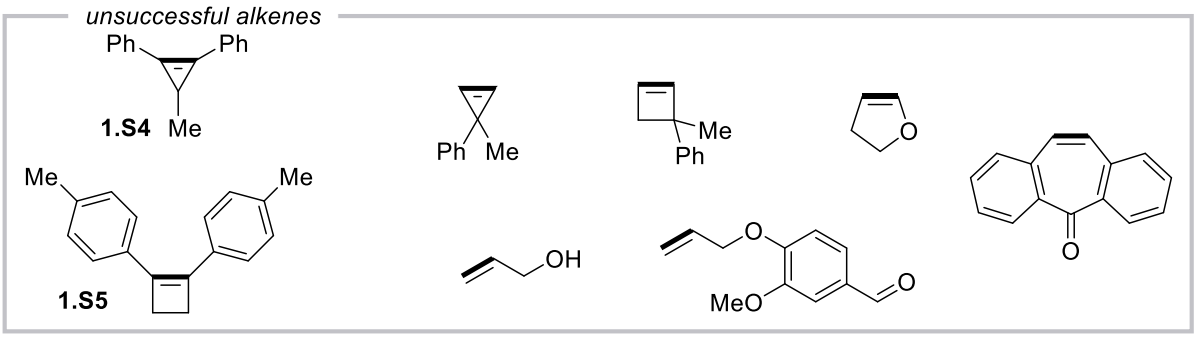


4.15 99%
(Ar = 4-ClC_6H_4)

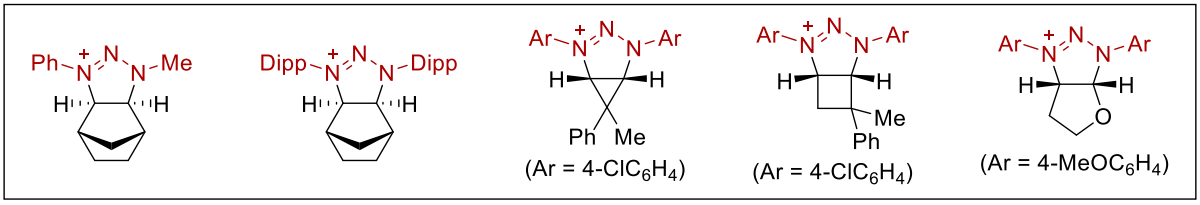


4.27 38%
(Ar = 4-FC_6H_4)

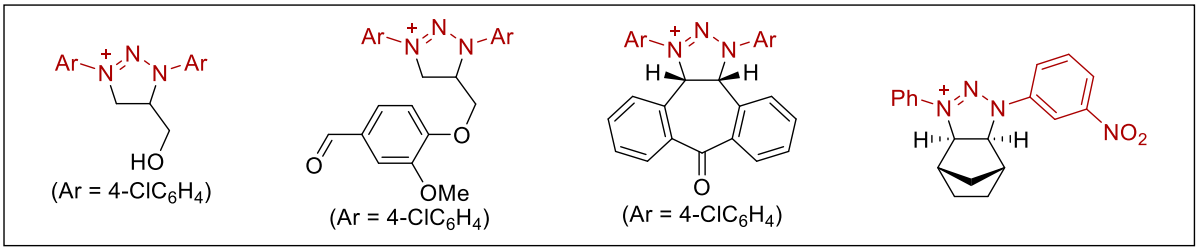
2.3.8 *Step 2: unsuccessful examples*



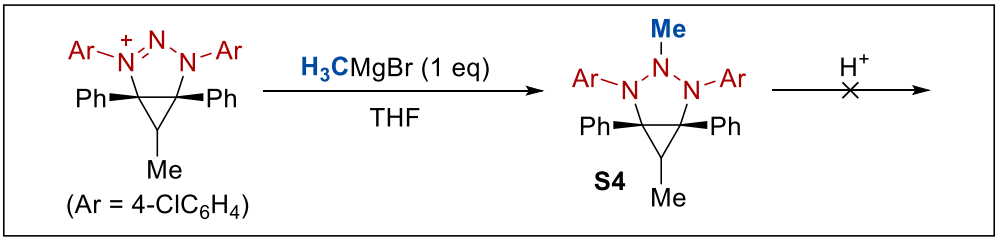
Below are examples of nitrenium cations **3** that provided complex reaction mixture after step 2 by both General Procedure A and B. No desired product was observed in any of these cases.

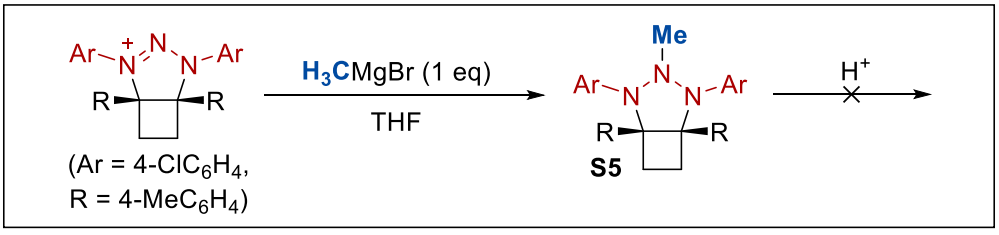


Below are examples of nitrenium cations **3** that clearly gave undesired side reactions on different functional groups and modified nitrenium was observed in the reaction mixture. Accordingly, these functional groups are not suitable for the developed transformation; such groups are unprotected hydroxyl, unprotected aldehyde/ketone and nitro.



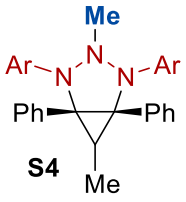
Below are examples of nitrenium cations that provided stable triazanes. These triazanes were inert and did not undergo the developed reaction.





*2.3.8.1 Characterization of triazanes **S4** and **S5***

(1R,5S)-2,4-bis(4-chlorophenyl)-3,6-dimethyl-1,5-diphenyl-2,3,4-triazabicyclo[3.1.0]hexane (**S4**)



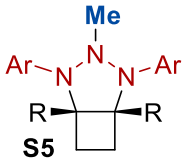
S4

(Ar = 4-ClC_6H_4)

Product **S4** was synthesized from alkene **1.S4** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow solid (97 mg, 71%).

^{1}H NMR (400 MHz, C_6D_6): δ 7.15–7.13 (m, 5H), 7.03–6.97 (m, 8H), 6.93–6.88 (m, 2H), 6.79–6.77 (m, 3H), 2.82 (s, 3H), 2.78 (q, *J* = 6.5 Hz, 1H), 0.70 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6): δ 147.2, 136.7, 129.1, 128.6, 127.7, 127.6, 124.2, 114.2, 64.8, 48.5, 34.8, 12.3. APCI $[M+H]^+$ calcd for $C_{29}H_{26}{}^{35}Cl_2N_3^+$ 486.1498; found 486.1480.

(1R,5S)-2,4-bis(4-fluorophenyl)-3-methyl-1,5-di-p-tolyl-2,3,4-triazabicyclo[3.2.0]heptane (**S5**)



S5

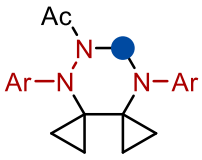
(Ar = 4-ClC_6H_4,
R = 4-MeC_6H_4)

Product **S5** was synthesized from alkene **1.S5** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow solid (96 mg, 29%).

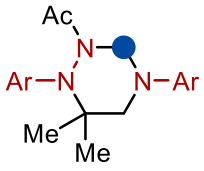
^{1}H NMR (400 MHz, C_6D_6): δ 7.33–7.31 (m, 4H), 7.03–7.01 (m, 4H), 6.95–6.88 (m, 8H), 2.98 (s, 3H), 2.42 (q, *J* = 6.4 Hz, 2H), 2.16 (s, 6H), 2.07 (q, *J* = 6.4 Hz, 2H); ^{13}C NMR (101 MHz, C_6D_6): δ 157.7 (d, *J* = 237.8 Hz), 142.9 (d, *J* =1.8Hz), 138.0, 137.2, 129.1, 128.2, 117.4 (d, *J* = 7.3 Hz), 115.6 (d, *J* = 22.1 Hz), 81.3, 48.8, 26.8, 20.8. ^{19}F NMR (377 MHz, C_6D_6): δ -124.99. APCI $[M-H]^+$ calcd for $C_{31}H_{28}F_2N_3^+$ 480.2246; found 480.2245.

2.3.9 *Step 2: low yielding reactions*

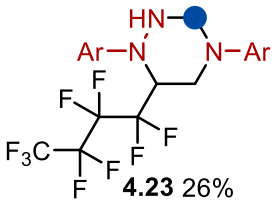
In several cases, we observed non-ideal two-step yields of the desired reaction. In the following examples, cycloaddition Step 1 was giving non-quantitative yields compared to the rest of the cases.



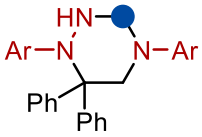
4.16 44%
(Ar = 4-ClC$_6$H$_4$)



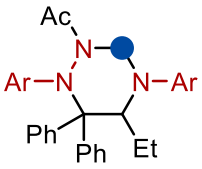
4.22 46%
(Ar = 4-ClC$_6$H$_4$)



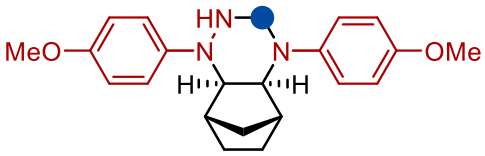
4.23 26%
(Ar = 4-ClC$_6$H$_4$)



4.25 53%
(Ar = 4-ClC$_6$H$_4$)

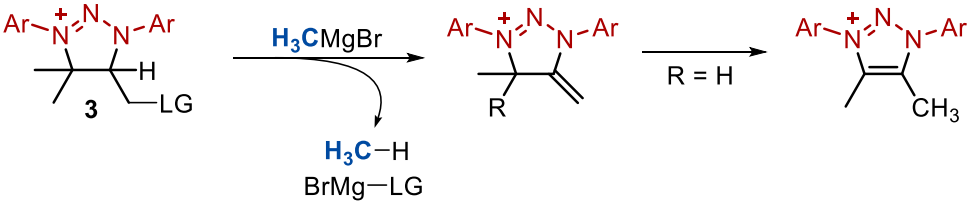


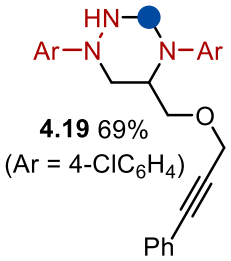
4.27 38%
(Ar = 4-FC$_6$H$_4$)



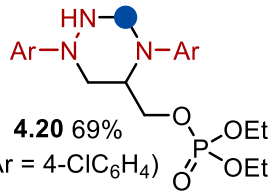
4.29 45% (Ar = 4-MeOC$_6$H$_4$)

Some of the substrates had a possible leaving group at β-carbon which made possible elimination process described below. This can be followed by elimination reaction and isomerization (in case of R = H) similar to triazolium synthesis described in the literature.[17] The described process is likely to cause the yield drop in case of the salts **3** that lead to products mentioned below.

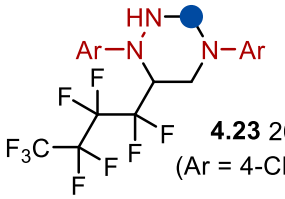




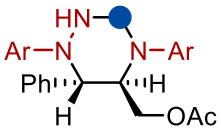
4.19 69%
(Ar = 4-ClC$_6$H$_4$)



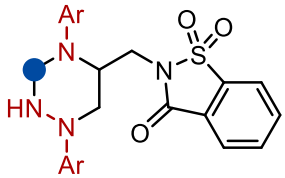
4.20 69%
(Ar = 4-ClC$_6$H$_4$)



4.23 26%
(Ar = 4-ClC$_6$H$_4$)

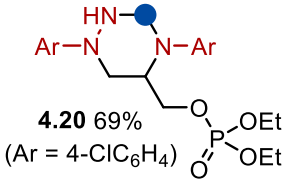


4.40 19%
(Ar = 4-ClC$_6$H$_4$)

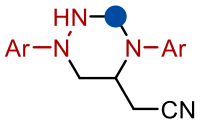


4.44 43% (Ar = 4-ClC$_6$H$_4$)

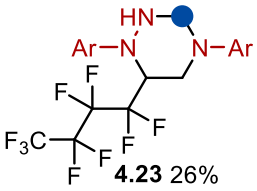
Moreover, some substrates tested contain functional groups that can react with the Grignard reagent (for more information about this see section “2.3.8 Step 2: unsuccessful examples”). We envision that similar reason may be behind the moderate yields for products below.



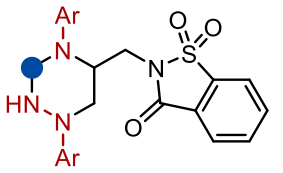
4.20 69%
(Ar = 4-ClC$_6$H$_4$)



4.21 72%
(Ar = 4-ClC$_6$H$_4$)

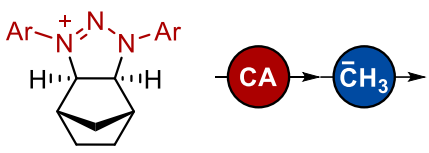


4.23 26%
(Ar = 4-ClC$_6$H$_4$)



4.44 43% (Ar = 4-ClC$_6$H$_4$)

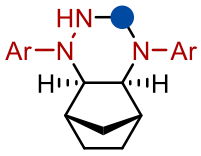
Finaly, nitreniums that are not electrophilic enough provided the lower yields. For instance, when a nitrenium with p-methoxyphenyl substituent was subjected to the standard reaction conditions, we observed a yield drop relatively to other aromatic substituents (compare **4.29** with **4.1** and **4.28**).



4.1 98% (Ar = 4-ClC$_6$H$_4$)
4.28 70% (Ar = Ph)
4.29 45% (Ar = 4-MeOC$_6$H$_4$)

*2.3.10 Characterization of products **4***

(4aRS,5SR,8RS,8aSR)-1,4-bis(4-chlorophenyl)decahydro-5,8-methanobenzo[e][1,2,4]triazine (**4.1**)



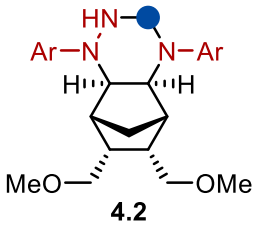
4.1

(Ar = 4-ClC$_6$H$_4$)

Product **4.1** was synthesized from alkene **1.1** and triazene **2.1** (0.2 mmol) by the general procedure B. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:4. Pale yellow solid (75 mg, 98%).

^{1}H NMR (400 MHz, C_6D_6): δ 7.27–7.25 (m, 2H), 7.20–7.18 (m, 2H), 6.89–6.87 (m, 2H), 6.30–6.28 (m, 2H), 3.93 (d, *J* = 10.9 Hz, 1H), 3.59 (d, *J* = 10.9 Hz, 1H), 3.30–2.94 (m, 2H), 2.11–2.02 (m, 2H), 1.40 (d, *J* = 10.4 Hz, 1H), 1.23–1.12 (m, 2H), 0.90 (d, *J* = 9.3 Hz, 2H), 0.79 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (101 MHz, C_6D_6): δ 148.3, 146.4, 129.2, 129.0, 124.0, 123.2, 115.7, 114.9, 62.1, 60.9, 59.6, 41.1, 40.5, 35.5, 27.0, 25.1. APCI [M-H]$^+$ calcd for $C_{20}H_{20}{}^{35}Cl_2N_3{}^+$ 372.1029; found 372.1028.

(4aRS,5RS,6RS,7SR,8SR,8aSR)-1,4-bis(4-chlorophenyl)-6,7-bis(methoxymethyl)decahydro-5,8-methanobenzo[e][1,2,4]triazine (**4.2**)



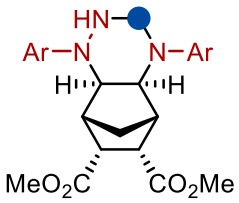
4.2

(Ar = 4-ClC$_6$H$_4$)

Product **4.2** was synthesized from alkene **1.2** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:4 to 1:3. Pale yellow solid (92 mg, 90%).

^{1}H NMR (500 MHz, C_6D_6/DMSO-d_6): δ 7.14–7.08 (m, 6H), 6.83–6.82 (m, 2H), 4.87–4.83 (m, 1H), 4.44–4.41 (m, 1H), 3.83–3.80 (m, 2H), 3.66–3.64 (m, 1H), 3.37–3.30 (m, 2H), 3.27–3.24 (m, 2H), 3.20 (s, 3H), 3.18 (s, 3H), 2.27–2.22 (m, 2H), 2.18–2.08 (m, 2H), 2.01 (d, *J* = 10.2 Hz, 1H), 1.04 (d, *J* = 10.4 Hz, 1H); ^{13}C NMR (126 MHz, C_6D_6/DMSO-d_6): δ 148.9, 147.1, 128.7, 128.4, 121.8, 121.4, 115.2, 114.6, 69.0, 68.9, 61.8, 58.25, 58.22, 54.3, 53.9, 44.4, 43.9, 39.9, 38.4, 36.8. APCI [M-H]$^+$ calcd for $C_{24}H_{28}{}^{35}Cl_2N_3O_2{}^+$ 460.1553; found 460.1550.

dimethyl (4aRS,5RS,6RS,7SR,8SR,8aSR)-1,4-bis(4-chlorophenyl)decahydro-5,8-methanobenzo[e][1,2,4]triazine-6,7-dicarboxylate (**4.3**)



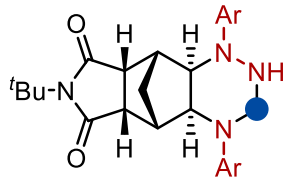
4.3

(Ar = 4-ClC$_6$H$_4$)

Product **4.3** was synthesized from alkene **1.3** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:6 to 1:3. Pale yellow solid (98 mg, 83%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.45–7.44 (m, 2H), 7.34–7.32 (m, 2H), 7.23–7.21 (m, 2H), 6.57–6.56 (m, 2H), 4.23 (d, *J* = 7.5 Hz, 1H), 3.97 (dd, *J* = 10.9, 6.9 Hz, 1H), 3.88–3.87 (m, 1H), 3.58–3.54 (m, 1H), 3.45 (s, 3H), 3.39 (s, 3H), 2.96–2.93 (m, 1H), 2.67 (dd, *J* = 11.9, 4.6 Hz, 1H), 2.46 (dd, *J* = 12.0, 4.0 Hz, 1H), 2.33–2.32 (m, 1H), 2.28–2.27 (m, 1H), 1.56 (d, *J* = 10.8 Hz, 1H), 0.62 (d, *J* = 11.0 Hz, 1H); ^{13}C NMR (126 MHz, C_6D_6): δ 172.2, 172.1, 148.6, 146.6, 129.2, 128.9, 124.5, 123.2, 116.7, 115.1, 62.3, 55.6, 54.3, 51.3, 51.2, 45.5, 45.1, 44.7, 44.4, 37.2. APCI [M-H]$^+$ calcd for $C_{24}H_{24}{}^{35}Cl_2N_3O_4^+$ 488.1138; found 488.1124.

(4aRS,5RS,5aRS,8aSR,9SR,9aSR)-7-(tert-butyl)-1,4-bis(4-chlorophenyl)decahydro-6H-5,9-methano[1,2,4]triazino[5,6-f]isoindole-6,8(7H)-dione (**4.4**)



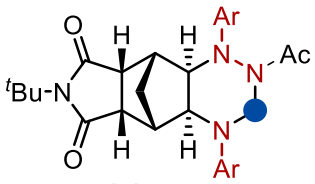
4.4

(Ar = 4-ClC$_6$H$_4$)

Product **4.4** was synthesized from alkene **1.4** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:4 to 1:3. Colorless solid (100 mg, 92%).

^{1}H NMR (400 MHz, C_6D_6/DMSO-d_6): δ 7.29–7.27 (m, 2H), 7.21–7.19 (m, 4H), 6.76–6.74 (m, 2H), 4.87–4.84 (m, 1H), 4.41–4.37 (m, 1H), 3.98–3.94 (m, 1H), 3.75 (br s, 2H), 2.79–2.73 (m, 2H), 2.62 (br s, 2H), 2.00 (d, *J* = 10.3 Hz, 1H), 1.58 (s, 9H), 1.07 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (101 MHz, C_6D_6/DMSO-d_6): δ 178.9, 178.8, 149.2, 146.5, 129.2, 128.8, 124.1, 122.4, 116.8, 114.6, 62.7, 58.5, 57.2, 54.9, 46.7, 45.9, 44.5, 44.4, 38.8, 28.5. APCI [M-H]$^+$ calcd for $C_{26}H_{27}{}^{35}Cl_2N_4O_2^+$ 497.1506; found 497.1494.

(4aRS,5RS,5aRS,8aSR,9SR,9aSR)-2-acetyl-7-(tert-butyl)-1,4-bis(4-chlorophenyl)decahydro-6H-5,9-methano[1,2,4]triazino[5,6-f]isoindole-6,8(7H)-dione (**4.4-Ac**)



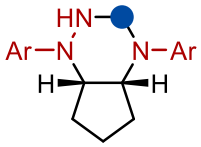
4.4-Ac

(Ar = 4-ClC$_6$H$_4$)

Product **4.4-Ac** was synthesized from alkene **1.4** and triazene **2.1** (0.2 mmol) by the general procedure C. Eluent for chromatography EtOAc:Hexane = from 1:2 to 1:1. Pale yellow oil (108 mg, 99%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29–7.26 (m, 4H), 6.92–6.90 (m, 2H), 6.77–6.75 (m, 2H), 3.93 (d, *J* = 10.7 Hz, 1H), 3.91–3.89 (m, 1H), 3.17 (dd, *J* = 10.1, 5.1 Hz, 1H), 3.12 (dd, *J* = 10.1, 5.4 Hz, 1H), 3.03 (br d, *J* = 4.3 Hz, 2H), 2.82 (br d, *J* = 4.4 Hz, 2H), 2.14 (s, 3H), 2.02 (d, *J* = 11.1 Hz, 1H), 1.65–1.64 (m, 10H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 178.5, 178.1, 173.5, 146.5, 144.9, 129.7, 129.3, 126.3, 125.1, 116.2, 114.2, 61.4, 59.2, 54.7, 54.2, 47.2, 46.6, 45.2, 43.8, 38.6, 28.5, 20.2. APCI $[M+H]^+$ calcd for $C_{28}H_{31}{}^{35}Cl_2N_4O_3^+$ 541.1768; found 541.1800.

(4aSR,7aRS)-1,4-bis(4-chlorophenyl)octahydro-1H-cyclopenta[e][1,2,4]triazine (**4.5**)



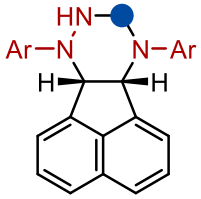
4.5

(Ar = 4-ClC$_6$H$_4$)

Product **4.5** was synthesized from alkene **1.5** and triazene **2.1** (0.2 mmol) by the general procedure B. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow oil (70 mg, 87%).

^{1}H NMR (400 MHz, C_6D_6): δ 7.24–7.22 (m, 2H), 7.13–7.10 (m, 2H), 6.88–6.86 (m, 2H), 6.48–6.46 (m, 2H), 3.81 (d, *J* = 11.5 Hz, 1H), 3.62–3.51 (m, 2H), 3.28 (br d, *J* = 8.3 Hz, 1H), 3.08–3.07 (m, 1H), 1.59–1.52 (m, 1H), 1.47–1.40 (m, 3H), 1.30–1.24 (m, 2H); ^{13}C NMR (101 MHz, C_6D_6): δ 148.5, 147.0, 129.3, 129.1, 127.4, 124.3, 122.3, 116.2, 68.1, 58.5, 57.5, 28.5, 22.1, 20.9. APCI $[M-H]^+$ calcd for $C_{18}H_{18}{}^{35}Cl_2N_3^+$ 346.0872; found 346.0897.

(6bSR,10aRS)-7,10-bis(4-chlorophenyl)-6b,7,8,9,10,10a-hexahydroacenaphtho[1,2-e][1,2,4]triazine (**4.6**)



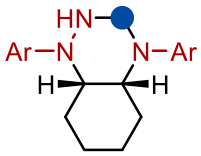
4.6

(Ar = 4-ClC$_6$H$_4$)

Product **4.6** was synthesized from alkene **1.6** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow solid (86 mg, 82%).

^{1}H NMR (500 MHz, DMSO-d$_6$): δ 7.84–7.83 (m, 1H), 7.79–7.78 (m, 1H), 7.51–7.48 (m, 2H), 7.30–7.21 (m, 8H), 7.09–7.07 (m, 2H), 6.52 (d, *J* = 7.7 Hz, 1H), 6.17 (d, *J* = 7.7 Hz, 1H), 4.52–4.48 (m, 1H), 4.12–4.06 (m, 2H); ^{13}C NMR (126 MHz, DMSO-d$_6$): δ 148.2, 147.6, 143.0, 140.3, 138.3, 131.2, 129.4, 129.1, 128.7 (2C), 125.4, 124.5, 122.2, 121.7 (2C), 120.6, 115.7, 115.6, 62.1, 61.9, 56.2. APCI [M+H]$^+$ calcd for $C_{25}H_{20}{}^{35}Cl_2N_3^+$ 432.1029; found 432.1053.

(4aRS,8aSR)-1,4-bis(4-fluorophenyl)decahydrobenzo[e][1,2,4]triazine (**4.7**)



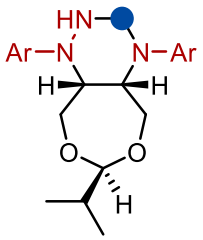
4.7

(Ar = 4-FC$_6$H$_4$)

Product **4.7** was synthesized from alkene **1.7** and triazene **2.2** (0.2 mmol) by the general procedure B. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow oil (66 mg, 92%).

^{1}H NMR (500 MHz, C$_6$D$_6$): δ 6.97–6.91 (m, 4H), 6.81–6.73 (m, 4H), 3.73–3.62 (m, 2H), 3.52–3.42 (m, 2H), 3.07–3.06 (br m, 1H), 1.85–1.78 (m, 1H), 1.63–1.61 (m, 2H), 1.42–1.34 (m, 1H), 1.27–1.24 (m, 1H), 1.13–0.94 (m, 3H); ^{13}C NMR (126 MHz, C$_6$D$_6$): δ 160.7 (d, *J* = 236.7 Hz), 157.0 (d, *J* = 237.4 Hz), 145.8 (d, *J* = 2.1 Hz), 144.7 (d, *J* = 3.0 Hz), 127.7–127.6 (br m), 116.1 (d, *J* = 22.0 Hz), 115.7 (d, *J* = 22.0 Hz), 115.2–115.1 (br m), 71.9, 56.9, 56.5, 28.9, 25.3, 20.0, 19.1. ^{19}F NMR (471 MHz, C$_6$D$_6$): δ -117.03, -126.89. APCI [M-H]$^+$ calcd for $C_{19}H_{20}F_2N_3^+$ 328.1620; found 328.1625.

(4aSR,7RS,9aRS)-1,4-bis(4-chlorophenyl)-7-isopropyloctahydro-[1,3]dioxepino[5,6-e][1,2,4]triazine (**4.8**)



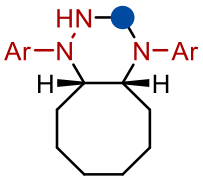
4.8

(Ar = 4-ClC$_6$H$_4$)

Product **4.8** was synthesized from alkene **1.8** and triazene **2.1** (0.2 mmol) by the general procedure B. Eluent for chromatography EtOAc:Hexane = from 1:6 to 1:4. Pale yellow oil (84 mg, 89%).

^{1}H NMR (400 MHz, C_6D_6): δ 7.21–7.19 (m, 2H), 7.13–7.10 (m, 2H), 6.89–6.86 (m, 2H), 6.53–6.51 (m, 2H), 4.12–4.06 (m, 2H), 3.94–3.79 (m, 2H), 3.63–3.49 (m, 3H), 3.14–3.09 (m, 2H), 3.00 (br s, 1H), 1.86–1.75 (m, 1H), 0.96 (t, *J* = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, C_6D_6): δ 147.4, 146.1, 129.5, 129.3, 127.4, 123.7, 121.5, 115.0, 108.9, 66.8, 65.5, 61.1, 59.4, 57.0, 32.4, 17.9 (2C). APCI $[M+H]^+$ calcd for $C_{21}H_{26}{}^{35}Cl_2N_3O_2^+$ 422.1397; found 422.1377.

(4aRS,10aSR)-1,4-bis(4-chlorophenyl)dodecahydrocycloocta[e][1,2,4]triazine (**4.9**)



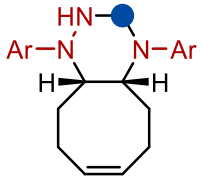
4.9

(Ar = 4-ClC$_6$H$_4$)

Product **4.9** was synthesized from alkene **1.9** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:4. Pale yellow solid (78 mg, 97%).

^{1}H NMR (400 MHz, C_6D_6): δ 7.25–7.23 (m, 2H), 7.11–7.09 (m, 2H), 7.01–6.99 (m, 2H), 6.70–6.68 (m, 2H), 3.83–3.72 (m, 2H), 3.55 (d, *J* = 10.8 Hz, 1H), 3.32 (d, *J* = 10.8 Hz, 1H), 3.02–3.00 (m, 1H), 1.97–1.92 (m, 1H), 1.55–1.12 (m, 11H); ^{13}C NMR (101 MHz, C_6D_6): δ 148.6, 147.8, 130.4, 129.5, 129.2, 127.1, 124.1, 116.2, 70.6, 61.0, 56.6, 28.5, 27.5, 26.8, 25.5, 24.4, 22.7. APCI $[M-H]^+$ calcd for $C_{21}H_{24}{}^{35}Cl_2N_3^+$ 388.1342; found 388.1353.

(4aSR,10aRS,Z)-1,4-bis(4-chlorophenyl)-1,2,3,4,4a,5,6,9,10,10a-decahydrocycloocta[e][1,2,4]triazine (**4.10**)

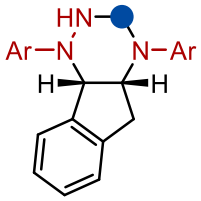


4.10
(Ar = 4-ClC$_6$H$_4$)

Product **4.10** was synthesized from alkene **1.10** and triazene **2.1** (0.2 mmol) by the general procedure B. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow oil (78 mg, 78%).

^{1}H NMR (400 MHz, C_6D_6): δ 7.25–7.22 (m, 2H), 7.09–7.07 (m, 2H), 7.00–6.98 (m, 2H), 6.65–6.62 (m, 2H), 5.52–5.44 (m, 2H), 4.02 (br d, *J* = 7.5 Hz, 1H), 3.78 (d, *J* = 10.9 Hz, 1H), 3.57 (d, *J* = 10.8 Hz, 1H), 3.02 (br s, 1H), 2.59–2.51 (m, 1H), 2.24–2.08 (m, 2H), 1.83–1.73 (m, 3H), 1.23–1.13 (m, 2H); ^{13}C NMR (101 MHz, C_6D_6): δ 148.1, 147.5, 131.1, 130.7, 129.4, 129.3, 127.5, 125.4, 123.7, 115.5, 70.8, 63.8, 55.0, 27.6, 27.4, 23.7, 20.5. APCI [M-H]$^+$ calcd for $C_{21}H_{22}{}^{35}Cl_2N_3^+$ 386.1185; found 386.1187.

(4aRS,9bSR)-1,4-bis(4-chlorophenyl)-2,3,4,4a,5,9b-hexahydro-1H-indeno[2,1-e][1,2,4]triazine (**4.11**)

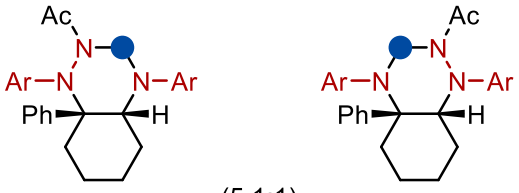


4.11
(Ar = 4-ClC$_6$H$_4$)

Product **4.11** was synthesized from alkene **1.11** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:4. Pale yellow solid (79 mg, 91%).

^{1}H NMR (500 MHz, C_6D_6/DMSO-d_6): δ 7.20–7.15 (m, 4H), 7.13–7.11 (m, 2H), 7.04–7.01 (m, 1H), 6.98–6.96 (m, 1H), 6.94–6.89 (m, 2H), 6.77–6.75 (m, 2H), 5.31 (d, *J* = 5.3 Hz, 1H), 4.40 (dd, *J* = 12.0, 2.4 Hz, 1H), 4.12 (dd, *J* = 11.3, 2.5 Hz, 1H), 3.88–3.86 (m, 1H), 3.69–3.64 (m, 1H), 2.83 (dd, *J* = 16.1, 4.9 Hz, 1H), 2.68 (d, *J* = 16.1 Hz, 1H); ^{13}C NMR (126 MHz, C_6D_6/DMSO-d_6): δ 148.9, 147.0, 143.0, 140.3, 129.2, 129.1, 128.0, 126.6, 125.9, 125.8, 124.1, 122.7, 121.7, 115.2, 67.2, 61.6, 57.4, 36.3. APCI [M-H]$^+$ calcd for $C_{22}H_{18}{}^{35}Cl_2N_3^+$ 394.0872; found 394.0882.

1-((4aSR,8aSR)-1,4-bis(4-fluorophenyl)-8a-phenyloctahydrobenzo[e][1,2,4]triazin-2(1H)-yl)ethan-1-one (**4.12**)

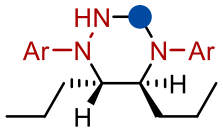


4.12a (Ar = 4-FC_6H_4) **4.12b** (Ar = 4-FC_6H_4)

Product **4.12** (as a mixture of **4.12a** and **4.12b**) was synthesized from alkene **1.12** and triazene **2.2** (0.2 mmol) by the general procedure C. Eluent for chromatography EtOAc:Hexane = 1:4. Pale yellow oil (90 mg, 91%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.63 (m, 8H), 7.36–7.20 (m, 55H), 7.10–7.03 (m, 34H), 6.76–6.73 (m, 10H), 6.70–6.67 (m, 10H), 6.10 (d, *J* = 11.4 Hz, 4H), 5.63 (d, *J* = 11.0 Hz, 5H), 4.62 (br d, *J* = 10.2 Hz, 4H), 4.30–4.27 (m, 9H), 4.23–4.22 (m, 5H), 2.93 (td, *J* = 13.2, 3.8 Hz, 5H), 2.62 (d, *J* = 15.9 Hz, 4H), 2.31–2.28 (m, 5H), 2.24 (s, 5 * 3H), 1.94–1.89 (m, 4H), 1.80–1.61 (m, 35H), 1.53–1.41 (m, 9H), 1.36–1.32 (m, 5H), 1.28–1.24 (m, 4H), 1.15–1.13 (m, 5H), 0.90–0.73 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.5, 172.7, 159.5 (d, *J* = 243.3 Hz), 159.1 (d, *J* = 244.3 Hz), 145.6, 144.4, 143.3, 143.2 (d, *J* = 2.4 Hz), 143.1 (d, *J* = 2.9 Hz), 139.3, 128.8, 128.2, 127.6, 127.3, 127.0, 126.2 (d, *J* = 8.0 Hz), 124.6 (d, *J* = 7.8 Hz), 123.7, 117.0, 116.14 (d, *J* = 22.1 Hz), 116.09 (d, *J* = 22.2 Hz), 116.0 (d, *J* = 22.0 Hz), 114.8 (d, *J* = 22.2 Hz), 67.2, 65.8, 60.2, 58.0, 57.1, 52.5, 38.1, 31.6, 25.9, 23.6, 22.9, 22.0, 21.5, 21.2, 20.7, 19.8. ^{19}F NMR (471 MHz, $CDCl_3$): δ -118.49 (2F), -118.69 (br s), -124.5 (br s). APCI $[M+H]^+$ calcd for $C_{27}H_{28}F_2N_3O^+$ 448.2195; found 448.2210.

(5SR,6SR)-1,4-bis(4-chlorophenyl)-5,6-dipropyl-1,2,4-triazinane (**4.13**)

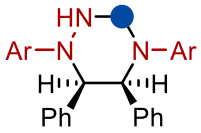


4.13 (Ar = 4-ClC_6H_4)

Product **4.13** was synthesized from alkene **1.13** and triazene **2.1** (0.2 mmol) by the general procedure B. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow oil (78 mg, 98%).

^{1}H NMR (400 MHz, C_6D_6): δ 7.24–7.21 (m, 2H), 7.15–7.13 (m, 2H), 6.91–6.89 (m, 2H), 6.32–6.30 (m, 2H), 3.90–3.84 (m, 1H), 3.73 (d, *J* = 12.0 Hz, 1H), 3.43–3.40 (m, 1H), 3.36 (dd, *J* = 8.9, 5.1 Hz, 1H), 3.15 (d, *J* = 12.3 Hz, 1H), 1.55–1.45 (m, 1H), 1.36–1.30 (m, 3H), 1.16–0.97 (m, 4H), 0.78 (t, *J* = 7.3 Hz, 3H), 0.69 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6): δ 149.2, 148.0, 129.5, 129.3, 123.6, 123.1, 116.5, 114.5, 58.2, 57.6, 55.8, 29.8, 29.1, 20.5 (2C), 14.3, 14.1. APCI $[M-H]^+$ calcd for $C_{21}H_{26}{}^{35}Cl_2N_3^+$ 390.1498; found 390.1499.

(5RS,6SR)-1,4-bis(4-chlorophenyl)-5,6-diphenyl-1,2,4-triazinane (**4.14**)



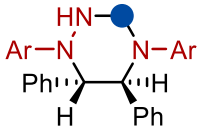
4.14

(Ar = 4-ClC$_6$H$_4$)

Product **4.14** was synthesized from alkene **1.14** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:20 to 1:15. Pale yellow oil (92 mg, 91%).

^{1}H NMR (400 MHz, C_6D_6): δ 7.17–7.16 (m, 2H), 7.12–7.09 (m, 2H), 7.01–6.98 (m, 4H), 6.95–6.92 (m, 2H), 6.84–6.79 (m, 4H), 6.67–6.65 (m, 2H), 6.34–6.31 (m, 2H), 4.73 (d, *J* = 4.5 Hz, 1H), 4.67 (d, *J* = 4.5 Hz, 1H), 4.39–4.37 (m, 1H), 4.13–4.10 (m, 1H), 4.04–3.99 (m, 1H); ^{13}C NMR (101 MHz, C_6D_6): δ 148.2, 146.4, 139.2, 137.6, 129.3 (2C), 128.9, 128.5, 128.4, 128.1, 128.0, 127.3, 125.9, 124.8, 119.5, 116.9, 66.8, 66.7, 63.8. APCI $[M\text{-}H]^+$ calcd for $C_{27}H_{22}{}^{35}Cl_2N_3^+$ 458.1185; found 458.1163.

(5RS,6RS)-1,4-bis(4-chlorophenyl)-5,6-diphenyl-1,2,4-triazinane (**4.15**)



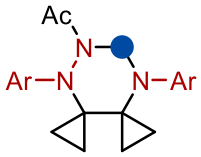
4.15

(Ar = 4-ClC$_6$H$_4$)

Product **4.15** was synthesized from alkene **1.15** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:8. Pale yellow oil (92 mg, 99%).

^{1}H NMR (400 MHz, C_6D_6): δ 7.18–7.16 (m, 2H), 7.10–7.08 (m, 2H), 7.07–7.05 (m, 2H), 7.02–6.95 (m, 8H), 6.83–6.80 (m, 2H), 6.33–6.30 (m, 2H), 4.87–4.86 (m, 2H), 4.36–4.31 (m, 1H), 4.08–4.05 (m, 1H), 3.67–3.65 (m, 1H); ^{13}C NMR (101 MHz, C_6D_6): δ 148.4, 146.6, 140.2, 138.5, 129.4, 129.1, 128.8, 128.6, 128.5, 128.3, 128.1, 127.7, 125.2, 125.1, 118.1, 117.5, 64.7, 63.2, 62.6. APCI $[M\text{-}H]^+$ calcd for $C_{27}H_{22}{}^{35}Cl_2N_3^+$ 458.1185; found 458.1171.

1-(7,10-bis(4-chlorophenyl)-7,8,10-triazadispiro[2.0.24.43]decan-8-yl)ethan-1-one (**4.16**)



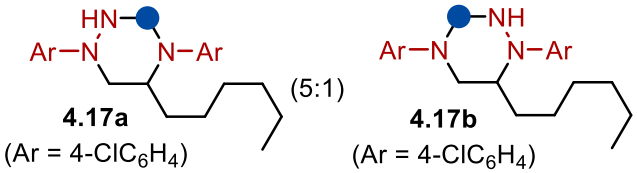
4.16

(Ar = 4-ClC_6H_4)

Product **4.16** was synthesized from alkene **1.16** and triazene **2.1** (0.2 mmol) by the general procedure C. Eluent for chromatography EtOAc:Hexane = from 1:6 to 1:3. Pale yellow oil (80 mg, 44%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.13–7.11 (m, 2H), 7.06–7.04 (m, 2H), 6.99–6.97 (m, 2H), 6.59–6.57 (m, 2H), 6.20 (d, *J* = 13.4 Hz, 1H), 4.10 (d, *J* = 13.3 Hz, 1H), 1.73 (s, 3H), 0.64–0.52 (m, 5H), 0.41–0.39 (m, 1H), 0.24–0.21 (m, 1H), 0.16–0.11 (m, 1H); ^{13}C NMR (126 MHz, C_6D_6): δ 171.6, 146.3 (2C), 129.5, 129.0, 126.5, 125.7, 119.9, 117.0, 55.7, 44.3, 41.3, 19.1, 14.8, 12.4, 12.1, 11.4. APCI $[M+H]^+$ calcd for $C_{21}H_{22}{}^{35}Cl_2N_3O^+$ 402.1134; found 402.1127.

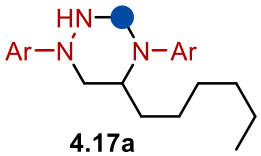
Synthesis of **4.17**



4.17a (Ar = 4-ClC$_6$H$_4$) **4.17b** (Ar = 4-ClC$_6$H$_4$)

Products **4.17a** and **4.17b** were synthesized as a mixture of isomers and characterized accordingly.

1,4-bis(4-chlorophenyl)-5-hexyl-1,2,4-triazinane (**4.17a**)

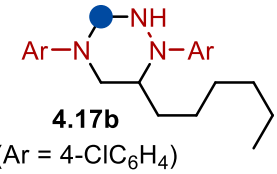


4.17a
(Ar = 4-ClC$_6$H$_4$)

Product **4.17a** was synthesized from alkene **1.17** and triazene **2.1** (0.2 mmol) by the general procedure B. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:4. Pale yellow oil (78 mg, 85%).

^{1}H NMR (400 MHz, C_6D_6): δ 7.22–7.19 (m, 2H), 7.14–7.11 (m, 2H), 6.92–6.90 (m, 2H), 6.39–6.36 (m, 2H), 3.96–3.89 (m, 1H), 3.86–3.81 (m, 1H), 3.30–3.26 (m, 1H), 3.12–3.09 (m, 1H), 2.65–2.62 (m, 1H), 1.65–1.45 (m, 1H), 1.40–1.33 (m, 1H), 1.26–1.03 (m, 8H), 0.86 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6): δ 149.8, 147.2, 129.5, 129.1, 125.2, 124.8, 118.7, 115.9, 61.8, 55.5, 51.9, 32.0, 29.5, 28.0, 26.8, 22.9, 14.2. APCI [M-H]$^+$ calcd for $C_{21}H_{26}{}^{35}Cl_2N_3^+$ 390.1498; found 390.1502.

1,4-bis(4-chlorophenyl)-6-hexyl-1,2,4-triazinane (**4.17b**)

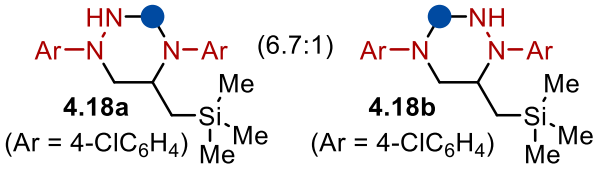


4.17b
(Ar = 4-ClC$_6$H$_4$)

Product **4.17b** was synthesized from alkene **1.7** and triazene **2.1** (0.2 mmol) by the general procedure B. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:4. Pale yellow oil (78 mg, 85%).

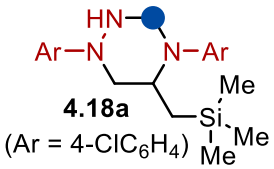
^{1}H NMR (400 MHz, C_6D_6): δ 7.24–7.22 (m, 2H), 7.14–7.11 (m, 2H), 6.88–6.86 (m, 2H), 6.39–6.36 (m, 2H), 3.91–3.89 (m, 1H), 3.54–3.49 (m, 1H), 3.35–3.33 (m, 1H), 3.01–2.98 (m, 1H), 2.64–2.62 (m, 1H), 1.56–1.47 (m, 1H), 1.40–1.36 (m, 1H), 1.24–1.07 (m, 8H), 0.90 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6): δ 148.5, 148.1, 129.4, 129.3, 125.4, 123.5, 117.8, 115.2, 65.1, 54.3, 49.8, 32.0, 29.6, 27.1, 26.3, 23.0, 14.3. APCI [M-H]$^+$ calcd for $C_{21}H_{26}{}^{35}Cl_2N_3^+$ 390.1498; found 390.1502.

Synthesis of **4.18**



Products **4.18a** and **4.18b** were synthesized as a mixture of isomers and characterized accordingly.

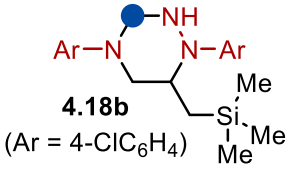
1,4-bis(4-chlorophenyl)-5-((trimethylsilyl)methyl)-1,2,4-triazinane (**4.18a**)



Product **4.18a** was synthesized from alkene **1.18** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:6 to 1:4. Pale yellow solid (79 mg, 95%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.21–7.18 (m, 2H), 7.13–7.10 (m, 2H), 6.97–6.94 (m, 2H), 6.38–6.36 (m, 2H), 4.02 (t, *J* = 11.7 Hz, 1H), 3.84 (dd, *J* = 12.3, 3.2 Hz, 1H), 3.64–3.55 (br m, 1H), 3.12–3.10 (br m, 1H), 2.78–2.64 (m, 2H), 1.00–0.92 (m, 1H), 0.74 (dd, *J* = 14.8, 4.1 Hz, 1H), -0.11 (s, 9H); ^{13}C NMR (126 MHz, C_6D_6): δ 149.9, 146.9, 129.5, 129.1, 124.8, 118.8, 117.7, 115.8, 61.0, 54.0, 52.4, 16.2, -1.0; ^{31}Si (99 MHz, C_6D_6): δ -0.5. APCI $[M+H]^+$ calcd for $C_{19}H_{26}{}^{35}Cl_2N_3Si^+$ 394.1268; found 394.1286.

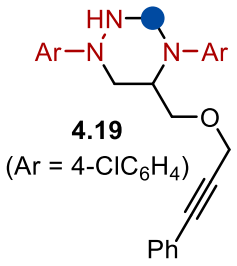
1,4-bis(4-chlorophenyl)-6-((trimethylsilyl)methyl)-1,2,4-triazinane (**4.18b**)



Product **4.18b** was synthesized from alkene **1.18** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:6 to 1:4. Pale yellow solid (79 mg, 95%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.21–7.18 (m, 2H), 7.13–7.10 (m, 2H), 6.91–6.89 (m, 2H), 6.43–6.41 (m, 2H), 3.99–3.95 (m, 1H), 3.69–3.67 (m, 1H), 3.60–3.55 (m, 1H), 3.48 (d, *J* = 12.5 Hz, 1H), 3.01–2.99 (m, 1H), 2.78–2.75 (m, 1H), 1.00–0.96 (m, 1H), 0.56–0.53 (m, 1H), -0.08 (s, 9H); ^{13}C NMR (126 MHz, C_6D_6): δ 148.5, 147.7, 129.4, 129.3, 125.1, 124.0, 117.6, 115.9, 65.4, 53.4, 51.3, 13.5, -1.1; ^{31}Si (99 MHz, C_6D_6): δ 0.1. APCI $[M+H]^+$ calcd for $C_{19}H_{26}{}^{35}Cl_2N_3Si^+$ 394.1268; found 394.1286.

1,4-bis(4-chlorophenyl)-5-(((3-phenylprop-2-yn-1-yl)oxy)methyl)-1,2,4-triazinane (**4.19**)

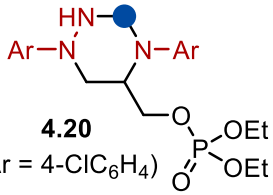


4.19
(Ar = 4-ClC$_6$H$_4$)

Product **4.19** was synthesized from alkene **1.19** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:5. Pale yellow solid (90 mg, 69%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.30–7.28 (m, 2H), 7.15–7.13 (m, 2H), 7.10–7.08 (m, 2H), 6.98–6.95 (m, 5H), 6.37–6.36 (m, 2H), 4.03 and 3.96 (AB-q, *J* = 15.9 Hz, 2H), 3.80–3.78 (m, 2H), 3.72–3.71 (m, 3H), 3.32–3.31 (m, 1H), 2.63–2.55 (m, 2H); ^{13}C NMR (126 MHz, C_6D_6): δ 149.6, 146.4, 131.9, 129.5, 129.1, 128.7, 128.6, 128.5, 125.0, 122.8, 117.3, 116.1, 87.0, 85.6, 65.4, 61.5, 59.1, 54.2, 50.1. APCI $[M+H]^+$ calcd for $C_{25}H_{24}{}^{35}Cl_2N_3O^+$ 452.1291; found 452.1266.

(1,4-bis(4-chlorophenyl)-1,2,4-triazinan-6-yl)methyl diethyl phosphate (**4.20**)

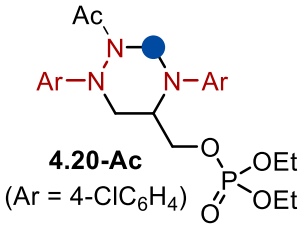


4.20
(Ar = 4-ClC$_6$H$_4$)

Product **4.20** was synthesized from alkene **1.20** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:1 to 3:1. Pale yellow oil (95 mg, 69%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.21–7.17 (m, 2H), 7.12–7.09 (m, 2H), 7.01–6.99 (m, 2H), 6.41–6.40 (m, 2H), 4.24–4.18 (m, 1H), 4.03–3.99 (m, 1H), 3.86–3.79 (m, 6H), 3.69–3.62 (m, 1H), 2.61–2.57 (m, 2H), 0.964 (t, *J* = 7.1 Hz, 3H), 0.956 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, C_6D_6): δ 149.6, 146.1, 129.6, 129.1, 125.5, 125.0, 117.2, 116.5, 63.8 (d, *J* = 5.6 Hz), 63.7 (d, *J* = 5.6 Hz), 63.0 (d, *J* = 5.2 Hz), 61.2, 54.1 (d, *J* = 6.7 Hz), 49.7, 16.1 (d, *J* = 6.4 Hz, 2C); ^{31}P NMR (203 MHz, C_6D_6): δ 0.0. APCI $[M+H]^+$ calcd for $C_{20}H_{27}{}^{35}Cl_2N_3O_4P^+$ 474.1111; found 474.1088.

(2-acetyl-1,4-bis(4-chlorophenyl)-1,2,4-triazinan-5-yl)methyl diethyl phosphate (**4.20-Ac**)

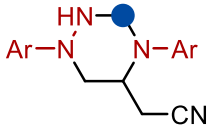


4.20-Ac
(Ar = 4-ClC$_6$H$_4$)

Product **4.20-Ac** was synthesized from alkene **1.20** and triazene **2.1** (0.2 mmol) by the general procedure C as a mixture of two rotamers. Eluent for chromatography EtOAc:Hexane = from 1:1 to 2:1. Pale yellow oil (95 mg, 64%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.27 (m, 8H), 7.24–7.22 (m, 4H), 7.08–7.06 (m, 2H), 7.01–6.99 (m, 4H), 6.84–6.82 (m, 6H), 5.88 (d, *J* = 13.4 Hz, 2 * 1H), 5.32 (d, *J* = 11.3 Hz, 1H), 4.35–4.32 (m, 1H), 4.26 (d, *J* = 13.4 Hz, 2 * 1H), 4.19 (d, *J* = 14.8 Hz, 2 * 1H), 4.14–3.99 (m, 15H), 3.96–3.86 (m, 4H), 3.83–3.80 (m, 1H), 3.78–3.74 (m, 1H), 3.67–3.64 (m, 1H + 2 * 1H), 3.51 (dd, *J* = 13.6, 10.3 Hz, 1H), 2.19 (s, 3H), 2.07 (s, 2 * 3H), 1.36–1.26 (m, 6H + 2 * 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.7, 173.3, 146.3, 145.5, 144.7, 144.4, 130.6, 129.9, 129.8, 129.6, 129.4, 126.2, 125.7, 125.4, 124.4, 117.7, 115.4, 114.0, 65.7 (d, *J* = 5.2 Hz), 64.14 (d, *J* = 6.1 Hz, 2C), 64.07 (d, *J* = 5.8 Hz, 2C), 62.7 (d, *J* = 6.0 Hz), 58.8, 56.0 (d, *J* = 7.0 Hz), 52.7 (d, *J* = 6.6 Hz), 50.7, 49.6, 46.4, 20.3, 20.0, 16.09 (d, *J* = 7.1 Hz), 16.07 (d, *J* = 6.8 Hz), 16.04 (d, *J* = 6.8 Hz), 16.01 (d, *J* = 6.7 Hz); ^{31}P NMR (203 MHz, C_6D_6): δ -1.0. APCI $[M+H]^+$ calcd for $C_{22}H_{29}{}^{35}Cl_2N_3O_5P^+$ 516.1216; found 516.1233.

2-(1,4-bis(4-chlorophenyl)-1,2,4-triazinan-5-yl)acetonitrile (**4.21**)

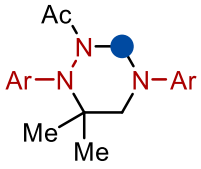


4.21
(Ar = 4-ClC$_6$H$_4$)

Product **4.21** was synthesized from alkene **1.21** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:4 to 1:1. Pale yellow solid (69 mg, 72%).

^{1}H NMR (500 MHz, DMSO-d_6): δ 7.92–7.25 (m, 4H), 7.12–7.10 (m, 2H), 7.04–7.02 (m, 2H), 4.78 (d, *J* = 9.6 Hz, 1H), 4.43 (d, *J* = 11.1 Hz, 2H), 4.18 (t, *J* = 11.9 Hz, 1H), 3.76 (d, *J* = 11.6 Hz, 1H), 2.94 (dd, *J* = 17.1, 7.6 Hz, 1H), 2.74 (dd, *J* = 17.1, 5.7 Hz, 1H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 149.6, 145.9, 129.0, 128.4, 123.4, 122.7, 119.0, 117.8, 115.8, 59.6, 51.1, 50.6, 16.0. APCI $[M-H]^+$ calcd for $C_{17}H_{15}{}^{35}Cl_2N_4^+$ 345.0668; found 345.0675.

1-(1,4-bis(4-fluorophenyl)-6,6-dimethyl-1,2,4-triazinan-2-yl)ethan-1-one (**4.22**)



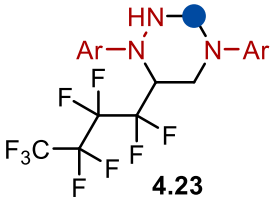
4.22

(Ar = 4-FC_6H_4)

Product **4.22** was synthesized from alkene **1.22** and triazene **2.1** (0.2 mmol) by the general procedure C. Eluent for chromatography EtOAc:Hexane = 1:4. Pale yellow solid (69 mg, 46%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23–7.21 (m, 2H), 7.02–6.98 (m, 4H), 6.96–6.92 (m, 2H), 6.08 (d, *J* = 11.6 Hz, 1H), 4.29 (d, *J* = 11.6 Hz, 1H), 3.15 (q, *J* = 12.2 Hz, 2H), 2.16 (s, 3H), 1.44 (s, 3H), 1.09 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 173.8, 160.0 (d, *J* = 245.1 Hz), 157.1 (d, *J* = 239.1 Hz), 145.2 (d, *J* = 2.3 Hz), 142.1 (d, *J* = 3.2 Hz), 126.4 (d, *J* = 8.0 Hz), 117.3 (d, *J* = 7.6 Hz), 115.8 (d, *J* = 22.3 Hz), 115.5 (d, *J* = 22.2 Hz), 58.8, 56.8, 55.9, 26.7, 26.1, 21.0. ^{19}F NMR (471 MHz, $CDCl_3$): δ -117.29, -124.14. APCI $[M+H]^+$ calcd for $C_{19}H_{22}F_2N_3O^+$ 346.1725; found 346.1755.

1,4-bis(4-chlorophenyl)-6-(perfluorobutyl)-1,2,4-triazinane (**4.23**)



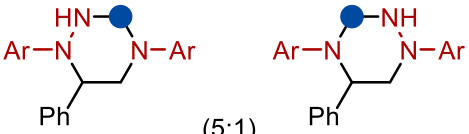
4.23

(Ar = 4-ClC_6H_4)

Product **4.23** was synthesized from alkene **1.23** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow oil (105 mg, 26%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.17–7.15 (m, 2H), 7.10–7.09 (m, 2H), 6.75–6.73 (m, 2H), 6.26–6.24 (m, 2H), 3.94–3.87 (m, 1H), 3.85–3.82 (m, 1H), 3.48–3.45 (m, 1H), 3.28 (dd, *J* = 13.1, 1.8 Hz, 1H), 3.18–3.12 (m, 1H), 2.34 (ddd, *J* = 13.0, 5.3, 1.9 Hz, 1H); ^{13}C NMR (126 MHz, C_6D_6): δ 147.3, 146.5, 129.5, 129.4, 126.5, 125.0, 118.2, 115.2, 62.8, 53.3 (dd, *J* = 26.7, 18.2 Hz), 43.9. Signals for carbons of the perfluoroalkyl group were not observed. ^{19}F NMR (471 MHz, C_6D_6): δ -80.99–(-81.03) (m, 3F), -111.45–(-112.11) (m, 1F), -115.20–(-115.87) (m, 1F), -122.73–(-122.77) (m, 2F), -124.93–(-126.98) (m, 2F). APCI $[M+H]^+$ calcd for $C_{19}H_{15}{}^{35}Cl_2F_9N_3^+$ 526.0494; found 526.0516.

Synthesis of **4.24**

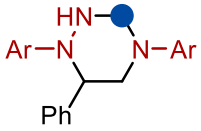


4.24a (5:1) **4.24b**

(Ar = 4-ClC$_6$H$_4$) (Ar = 4-ClC$_6$H$_4$)

Products **4.24a** and **4.24b** were synthesized as a mixture of isomers and characterized accordingly.

1,4-bis(4-chlorophenyl)-6-phenyl-1,2,4-triazinane (**4.24a**)



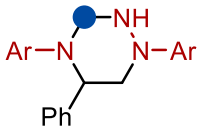
4.24a

(Ar = 4-ClC$_6$H$_4$)

Product **4.24a** was synthesized from alkene **1.24** and triazene **2.1** (0.2 mmol) by the general procedure B. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:4. Pale yellow oil (77 mg, 91%).

^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.16–7.04 (m, 9H), 6.87–6.84 (m, 2H), 6.19–6.17 (m, 2H), 4.25 (t, *J* = 4.8 Hz, 1H), 3.79–3.68 (m, 2H), 3.08 (dd, *J* = 12.3, 6.6 Hz, 1H), 2.96 (dd, *J* = 12.3, 4.1 Hz, 1H); ^{13}C NMR (101 MHz, C$_6$D$_6$): δ 148.4, 147.4, 139.8, 129.4, 129.03, 129.01, 127.9, 127.3, 124.7, 124.5, 116.9, 116.2, 64.3, 60.5, 50.1. APCI [M-H]$^+$ calcd for C$_{21}$H$_{18}$^{35}Cl$_2$N$_3^+$ 382.0872; found 382.0856.

1,4-bis(4-chlorophenyl)-5-phenyl-1,2,4-triazinane (**4.24b**)



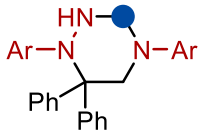
4.24b

(Ar = 4-ClC$_6$H$_4$)

Product **4.24b** was synthesized from alkene **1.24** and triazene **2.1** (0.2 mmol) by the general procedure B. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:4. Pale yellow oil (77 mg, 91%).

^{1}H NMR (400 MHz, C$_6$D$_6$): δ 7.20–7.18 (m, 2H), 7.16–7.03 (m, 3H), 7.01–6.96 (m, 2H), 6.92–6.90 (m, 2H), 6.81–6.79 (m, 2H), 6.50–6.48 (m, 2H), 4.00–3.95 (m, 2H), 3.79–3.77 (m, 1H), 3.38–3.34 (m, 1H), 2.56–2.51 (m, 1H); ^{13}C NMR (101 MHz, C$_6$D$_6$): δ 148.8, 147.0, 140.5, 129.14, 129.09, 128.8, 127.81, 127.78, 125.0, 124.6, 124.1, 116.0, 70.2, 60.8, 56.4. APCI [M-H]$^+$ calcd for C$_{21}$H$_{18}$^{35}Cl$_2$N$_3^+$ 382.0872; found 382.0856.

1,4-bis(4-chlorophenyl)-6,6-diphenyl-1,2,4-triazinane (**4.25**)



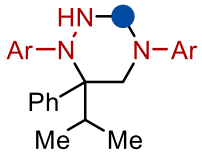
4.25

(Ar = 4-ClC$_6$H$_4$)

Product **4.25** was synthesized from alkene **1.25** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:3. Pale yellow solid (92 mg, 53%).

^{1}H NMR (500 MHz, C$_6$D$_6$/DMSO-d$_6$): δ 7.33–7.31 (m, 4H), 7.12–7.02 (m, 6H), 6.95–6.93 (m, 2H), 6.70–6.69 (m, 2H), 6.56–6.55 (m, 2H), 6.50–6.48 (m, 2H), 5.60 (br t, *J* = 7.4 Hz, 1H), 4.23 (br d, *J* = 6.5 Hz, 2H), 3.94 (br s, 2H); ^{13}C NMR (126 MHz, C$_6$D$_6$/DMSO-d$_6$): δ 147.8, 146.8, 140.8, 128.8, 128.6, 128.5, 127.6, 127.4, 121.5, 121.4, 118.1, 114.8, 71.8, 64.3, 57.6. APCI [M-H]$^+$ calcd for C$_{27}$H$_{22}$^{35}Cl$_2$N$_3^+$ 458.1185; found 458.1213.

1,4-bis(4-fluorophenyl)-6-isopropyl-6-phenyl-1,2,4-triazinane (**4.26**)



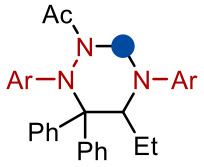
4.26

(Ar = 4-FC$_6$H$_4$)

Product **4.26** was synthesized from alkene **1.26** and triazene **2.2** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:8. Colorless solid (79 mg, 95%).

^{1}H NMR (500 MHz, C$_6$D$_6$): δ 6.95–6.94 (m, 2H), 6.86–6.85 (m, 3H), 6.69–6.65 (m, 2H), 6.60–6.57 (m, 2H), 6.54–6.50 (m, 2H), 6.30–6.28 (m, 2H), 3.73–3.71 (m, 1H), 3.62–3.56 (m, 2H), 3.47–3.46 (m, 1H), 3.11–3.09 (m, 1H), 2.29–2.28 (m, 1H), 0.77–0.76 (m, 3H), 0.41–0.40 (m, 3H); ^{13}C NMR (126 MHz, C$_6$D$_6$): δ 159.2 (d, *J* = 239.8 Hz), 157.7 (d, *J* = 238.7 Hz), 146.1, 144.9 (d, *J* = 2.8 Hz), 138.8, 129.0, 127.8, 127.3, 126.3, 117.5 (d, *J* = 7.3 Hz), 116.0 (d, *J* = 22.0 Hz), 114.5 (d, J = 21.9 Hz), 67.1, 64.4, 50.7, 32.5, 18.8, 17.4. ^{19}F NMR (471 MHz, C$_6$D$_6$): δ -119.39 (br s), -124.03. APCI [M+H]$^+$ calcd for C$_{24}$H$_{26}$F$_2$N$_3^+$ 394.2089; found 394.2102.

1-(5-ethyl-1,4-bis(4-fluorophenyl)-6,6-diphenyl-1,2,4-triazinan-2-yl)ethan-1-one (**4.27**)



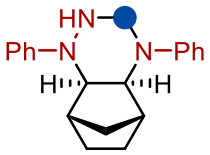
4.27

(Ar = 4-FC_6H_4)

Product **4.27** was synthesized from alkene **1.27** and triazene **2.2** (0.2 mmol) by the general procedure C. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:4. Pale yellow oil (100 mg, 38%).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61–7.60 (br m, 2H), 7.56–7.53 (m, 2H), 7.47–7.45 (m, 1H), 7.05–7.02 (m, 1H), 6.99–6.98 (m, 2H), 6.94–6.91 (m, 2H), 6.84–6.81 (m, 2H), 6.71–6.67 (br m, 2H), 6.44–6.41 (br m, 2H), 6.33–6.31 (m, 2H), 6.19 (d, *J* = 9.2 Hz, 1H), 4.82 (d, *J* = 9.2 Hz, 1H), 4.36 (dd, *J* = 9.8, 3.3 Hz, 1H), 2.24 (s, 3H), 1.70 (dqd, *J* = 14.9, 7.5, 3.1 Hz, 1H), 1.46 (ddq, *J* = 14.7, 10.0, 7.4 Hz, 1H), 0.73 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 174.2, 156.8 (d, *J* = 239.8 Hz), 155.3 (d, *J* = 236.0 Hz), 143.4 (d, *J* = 1.6 Hz), 142.9 (d, *J* = 2.2 Hz), 140.8, 140.7, 129.5, 129.3, 127.9, 127.8, 127.5, 127.2, 116.7 (br), 115.5 (d, *J* = 22.5 Hz), 114.9 (d, *J* = 22.3 Hz), 112.0 (d, *J* = 7.4 Hz), 80.1, 64.0, 55.0, 26.7, 22.3, 13.1. ^{19}F NMR (471 MHz, $CDCl_3$): δ -124.45, -128.06. APCI $[M+H]^+$ calcd for $C_{31}H_{30}F_2N_3O^+$ 498.2351; found 498.2323.

(4aRS,5SR,8RS,8aSR)-1,4-diphenyldecahydro-5,8-methanobenzo[e][1,2,4]triazine (**4.28**)

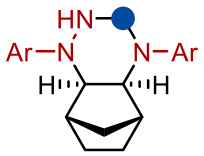


4.28

Product **4.28** was synthesized from alkene **1.1** and triazene **2.3** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:8. Pale yellow oil (61 mg, 70%).

^{1}H NMR (400 MHz, C_6D_6): δ 7.34–7.30 (m, 2H), 7.27–7.23 (m, 2H), 7.19–7.17 (m, 2H), 6.91–6.83 (m, 2H), 6.63–6.31 (m, 2H), 4.24 (d, *J* = 10.9 Hz, 1H), 3.91–3.88 (m, 1H), 3.23–3.19 (m, 2H), 2.26–2.25 (m, 1H), 2.18 (br s, 1H), 1.56 (d, *J* = 10.5 Hz, 1H), 1.25–1.20 (m, 2H), 1.02–0.99 (m, 2H), 0.83 (d, *J* = 10.5 Hz, 1H); ^{13}C NMR (101 MHz, C_6D_6): δ 150.0, 148.1, 129.3, 129.0, 119.2, 118.2, 114.8, 114.0, 62.5, 61.2, 59.8, 41.3, 40.7, 35.6, 27.2, 25.3. APCI $[M+H]^+$ calcd for $C_{20}H_{24}N_3^+$ 306.1965; found 306.1956.

(4aRS,5SR,8RS,8aSR)-1,4-bis(4-methoxyphenyl)decahydro-5,8-methanobenzo[e][1,2,4]triazine (**4.29**)

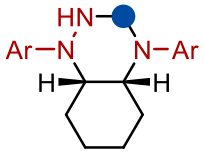


4.29 (Ar = 4-$MeOC_6H_4$)

Product **4.29** was synthesized from alkene **1.1** and triazene **2.4** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:4. Pale yellow oil (73 mg, 45%).

^{1}H NMR (400 MHz, C_6D_6): δ 7.18–7.16 (m, 2H), 6.97–6.95 (m, 2H), 6.90–6.88 (m, 2H), 6.67–6.65 (m, 2H), 4.32 (d, *J* = 10.7 Hz, 1H), 3.98 (d, *J* = 10.7 Hz, 1H), 3.44 (s, 6H), 3.27–3.25 (m, 1H), 3.21–3.19 (m, 1H), 2.33–2.31 (m, 1H), 2.26–2.23 (m, 1H), 1.84 (d, *J* = 10.2 Hz, 1H), 1.33–1.25 (m, 2H), 1.12–1.02 (m, 2H), 0.91 (d, *J* = 10.2 Hz, 1H); ^{13}C NMR (101 MHz, C_6D_6): δ 154.0, 153.4, 144.5, 142.7, 116.8, 116.7, 115.0, 114.5, 64.3, 62.5, 60.7, 55.2 (2C), 41.2, 40.5, 35.6, 27.5, 25.5. APCI $[M+H]^+$ calcd for $C_{22}H_{28}N_3O_2^+$ 366.2176; found 366.2185.

(4aRS,8aSR)-1,4-bis(4-(trifluoromethyl)phenyl)decahydrobenzo[e][1,2,4]triazine (**4.30**)

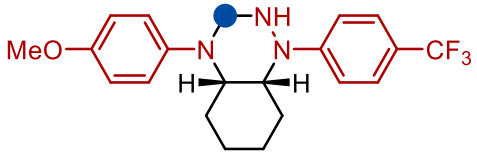


4.30 (Ar = 4-$F_3CC_6H_4$)

Product **4.30** was synthesized from alkene **1.7** and triazene **2.5** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow oil (86 mg, 92%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.53–7.51 (m, 2H), 7.39–7.37 (m, 2H), 6.95–6.94 (m, 2H), 6.65–6.63 (m, 2H), 3.58–3.50 (m, 3H), 3.42–3.40 (m, 1H), 2.98–2.97 (m, 1H), 1.78–1.71 (m, 1H), 1.52–1.50 (m, 2H), 1.29–1.24 (m, 1H), 1.15–0.98 (m, 4H); ^{13}C NMR (126 MHz, C_6D_6): δ 151.8, 151.4, 126.9–126.6 (m, 2C), 125.9 (q, *J* = 270.5 Hz), 125.7 (q, *J* = 32.6 Hz), 125.2 (q, *J* = 271.5 Hz), 123.6, 120.4 (q, *J* = 31.7 Hz), 113.4, 69.8, 55.4, 55.2, 28.9, 24.5, 21.5, 20.5. ^{19}F NMR (471 MHz, C_6D_6): δ -60.60, -61.53. APCI $[M+H]^+$ calcd for $C_{21}H_{22}F_6N_3^+$ 430.1712; found 430.1749.

(4aSR,8aRS)-4-(4-methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)decahydrobenzo[e][1,2,4]triazine (**4.31**)

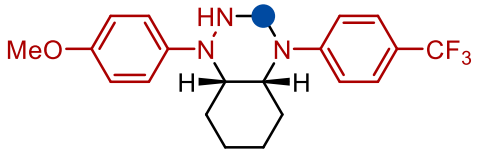


4.31

Product **4.31** was synthesized from alkene **1.7** and triazene **2.6** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow solid (78 mg, 55%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.53–7.51 (m, 2H), 6.98–6.93 (m, 4H), 6.79–6.77 (m, 2H), 3.69–3.68 (m, 2H), 3.61–3.60 (m, 1H), 3.53–3.51 (m, 1H), 3.33 (s, 3H), 3.01–3.00 (m, 1H), 1.94–1.85 (m, 1H), 1.72–1.65 (m, 2H), 1.53–1.45 (m, 1H), 1.25–1.21 (m, 1H), 1.15–1.05 (m, 2H), 0.98–0.92 (m, 1H); ^{13}C NMR (126 MHz, C_6D_6): δ 158.0, 151.8, 141.2, 127.3, 126.7 (q, *J* = 3.7 Hz), 126.0 (q, *J* = 270.3 Hz), 119.6 (q, *J* = 32.3 Hz), 114.8, 112.7, 72.0, 57.2, 55.5, 54.9, 29.0, 25.5, 20.0, 19.8. ^{19}F NMR (471 MHz, C_6D_6): δ -65.09. APCI $[M+H]^+$ calcd for $C_{21}H_{25}F_3N_3O^+$ 392.1944; found 392.1943.

(4aRS,8aSR)-1-(4-methoxyphenyl)-4-(4-(trifluoromethyl)phenyl)decahydrobenzo[e][1,2,4]triazine (**4.32**)

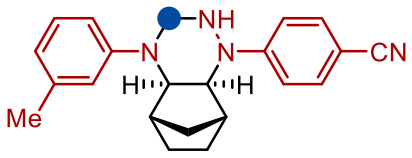


4.32

Product **4.32** was synthesized from alkene **1.7** and triazene **2.6** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow solid (78 mg, 20%).

^{1}H NMR (500 MHz, C_6D_6/DMSO-d_6): δ 7.57–7.56 (m, 2H), 7.29–7.28 (m, 2H), 7.04–7.02 (m, 2H), 6.94–6.92 (m, 2H), 4.59–4.58 (m, 1H), 4.40–4.39 (m, 1H), 4.30–4.25 (m, 1H), 3.98–3.97 (m, 1H), 3.74 (s, 3H), 3.48–3.47 (m, 1H), 2.13–2.11 (m, 1H), 1.70–1.67 (m, 2H), 1.56–1.52 (m, 2H), 1.40–1.34 (m, 2H), 1.25–1.24 (m, 1H); ^{13}C NMR (126 MHz, C_6D_6/DMSO-d_6): δ 156.4, 150.7, 143.5, 126.7 (q, *J* = 3.3 Hz), 125.6 (q, *J* = 270.3 Hz), 118.1 (br m), 114.3 (3C), 60.5, 60.2, 55.5, 55.1, 27.8, 24.3 (2C), 20.9. ^{19}F NMR (471 MHz, C_6D_6/DMSO-d_6): δ -59.56. APCI $[M-H]^+$ calcd for $C_{21}H_{23}F_3N_3O^+$ 390.1788; found 390.1778.

4-((4aRS,5SR,8RS,8aSR)-4-(m-tolyl)octahydro-5,8-methanobenzo[e][1,2,4]triazin-1(2H)-yl)benzonitrile (**4.33**)

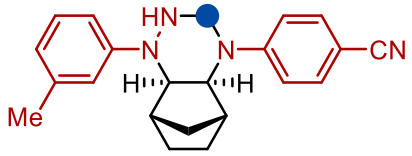


4.33

Product **4.33** was synthesized from alkene **1.1** and triazene **2.7** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:4. Pale yellow solid (69 mg, 98% 1:2.5).

^{1}H NMR (500 MHz, C_6D_6): δ 7.27–7.26 (m, 2H), 7.21–7.16 (m, 1H), 6.74–6.72 (m, 3H), 6.53–6.52 (m, 2H), 4.05–4.01 (m, 1H), 3.50–3.46 (m, 1H), 3.27–3.24 (m, 1H), 3.09–3.07 (m, 1H), 3.01–3.00 (m, 1H), 2.26 (s, 3H), 2.21–2.20 (m, 1H), 1.91–1.90 (m, 1H), 1.47–1.44 (m, 1H), 1.27–1.15 (m, 2H), 1.00–0.88 (m, 2H), 0.85–0.83 (m, 1H); ^{13}C NMR (126 MHz, C_6D_6): δ 151.8, 148.1, 138.8, 133.2, 129.3, 120.6, 120.4, 116.5, 112.9, 112.4, 100.2, 62.8, 60.4, 59.5, 41.5, 40.8, 35.6, 27.4, 24.7, 22.0. APCI $[M\text{-}H_2]^+$ calcd for $C_{22}H_{22}N_4^+$ 342.1839; found 342.1863.

4-((4aSR,5RS,8SR,8aRS)-1-(m-tolyl)octahydro-5,8-methanobenzo[e][1,2,4]triazin-4(1H)-yl)benzonitrile (**4.34**)

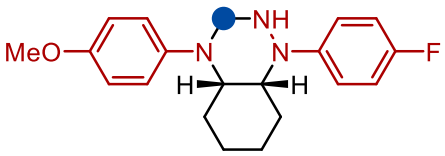


4.34

Product **4.34** was synthesized from alkene **1.1** and triazene **2.7** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:4. Pale yellow solid (69 mg, 98% 1:2.5).

^{1}H NMR (500 MHz, C_6D_6): δ 7.26–7.23 (m, 1H), 7.20–7.18 (m, 2H), 7.11–7.10 (m, 1H), 6.93–6.92 (m, 1H), 6.77–6.76 (m, 1H), 6.11–6.09 (m, 2H), 3.95–3.93 (m, 1H), 3.74–3.72 (m, 1H), 3.16–3.15 (m, 1H), 2.98–2.95 (m, 2H), 2.30 (s, 3H), 2.19–2.18 (m, 1H), 1.99–1.98 (m, 1H), 1.42–1.39 (m, 1H), 1.20–1.18 (m, 2H), 1.00–0.87 (m, 2H), 0.79–0.76 (m, 1H); ^{13}C NMR (126 MHz, C_6D_6): δ 149.8 (2C), 138.5, 133.2, 128.9, 121.2, 120.2, 117.0, 112.7, 112.2, 99.7, 61.7, 61.5, 59.0, 41.0, 40.7, 35.4, 26.5, 25.6, 22.0. APCI $[M\text{-}H_2]^+$ calcd for $C_{22}H_{22}N_4^+$ 342.1839; found 342.1863.

(4aSR,8aRS)-1-(4-fluorophenyl)-4-(4-methoxyphenyl)decahydrobenzo[e][1,2,4]triazine (**4.35**)

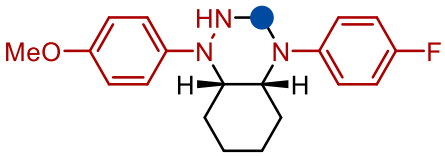


4.35

Product **4.35** was synthesized from alkene **1.7** and triazene **2.8** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow solid (68 mg, 26%).

^{1}H NMR (500 MHz, C_6D_6): δ 6.98–6.95 (m, 6H), 6.79–6.77 (m, 2H), 3.87–3.85 (m, 1H), 3.78–3.76 (m, 1H), 3.60–3.59 (m, 1H), 3.51–3.49 (m, 1H), 3.33 (s, 3H), 3.19–3.18 (m, 1H), 1.95–1.87 (m, 1H), 1.78–1.75 (m, 1H), 1.68–1.66 (m, 1H), 1.57–1.49 (m, 1H), 1.31–1.28 (m, 1H), 1.16–0.99 (m, 3H); ^{13}C NMR (126 MHz, C_6D_6): δ 157.8 , 156.9 (d, *J* = 236.8 Hz), 146.0 (d, *J* = 2.0 Hz), 141.6, 127.2, 115.7 (d, *J* = 21.9 Hz), 115.1, 114.8, 72.1, 57.4, 56.6, 54.9, 29.2, 25.6, 20.1, 19.0. ^{19}F NMR (471 MHz, C_6D_6): δ -127.17. APCI $[M-H]^+$ calcd for $C_{20}H_{23}FN_3O^+$ 340.1820; found 340.1804.

(4aRS,8aSR)-4-(4-fluorophenyl)-1-(4-methoxyphenyl)decahydrobenzo[e][1,2,4]triazine (**4.36**)

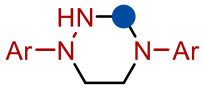


4.36

Product **4.36** was synthesized from alkene **1.7** and triazene **2.8** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow solid (68 mg, 19%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.14–7.13 (m, 2H), 6.94–6.92 (m, 2H), 6.81–6.74 (m, 4H), 3.86–3.84 (m, 1H), 3.78–3.74 (m, 1H), 3.58–3.51 (m, 2H), 3.41 (s, 3H), 3.22–3.21 (m, 1H), 1.90–1.87 (m, 1H), 1.66–1.63 (m, 1H), 1.45–1.34 (m, 3H), 1.17–1.01 (m, 3H); ^{13}C NMR (126 MHz, C_6D_6): δ 157.7, 153.8 (br m), 144.9 (d, *J* = 2.8 Hz), 143.6, 126.7, 116.0 (d, *J* = 22.1 Hz), 115.6, 114.8, 71.9, 57.3, 57.2, 55.1, 28.8, 25.2, 20.0, 18.8. ^{19}F NMR (471 MHz, C_6D_6): δ -117.32. APCI $[M]^+$ calcd for $C_{20}H_{24}FN_3O^+$ 341.1898; found 341.1922.

1,4-bis(4-(trifluoromethyl)phenyl)-1,2,4-triazinane (**4.37**)



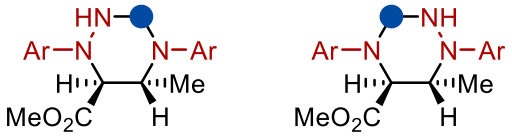
4.37

(Ar = 4-$CF_3C_6H_4$)

Product **4.37** was synthesized from alkene **1.37** and triazene **2.5** (0.2 mmol) by the general procedure B. Eluent for chromatography EtOAc:Hexane = from 1:6 to 1:2. Pale yellow solid (75 mg, 83%).

^{1}H NMR (400 MHz, C_6D_6/DMSO-d_6): δ 7.50–7.44 (m, 4H), 7.12–7.10 (m, 2H), 6.67–6.64 (m, 2H), 4.42 (t, *J* = 7.4 Hz, 1H), 4.11 (br d, *J* = 5.1 Hz, 2H), 3.23 (br s, 2H), 3.07 (br s, 2H); ^{13}C NMR (101 MHz, C_6D_6/DMSO-d_6): δ 153.2, 151.6, 126.6 (q, *J* = 3.7 Hz), 126.4 (q, *J* = 3.7 Hz), 125.8 (q, *J* = 270.2 Hz), 125.7 (q, *J* = 270.5 Hz), 120.2 (q, *J* = 30.6 Hz), 120.1 (q, *J* = 31.3 Hz), 114.8, 113.6, 64.1, 47.3, 45.7. ^{19}F NMR (377 MHz, C_6D_6/DMSO-d_6): δ -60.36, -60.60. APCI $[M+H]^+$ calcd for $C_{17}H_{16}F_6N_3^+$ 376.1243; found 376.1262.

Synthesis of **4.38**

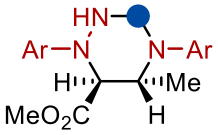


4.38a (3:1) **4.38b**

(Ar = 4-ClC$_6$H$_4$) (Ar = 4-ClC$_6$H$_4$)

Products **4.38a** and **4.38b** were synthesized as a mixture of isomers and characterized accordingly.

methyl (5RS,6SR)-1,4-bis(4-chlorophenyl)-5-methyl-1,2,4-triazinane-6-carboxylate (**4.38a**)



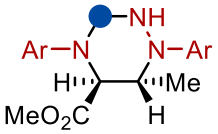
4.38a

(Ar = 4-ClC$_6$H$_4$)

Product **4.38a** was synthesized from alkene **1.38** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:4 to 1:2. Pale yellow oil (57 mg, 54%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.19–7.05 (m, 4H), 6.86–6.85 (m, 2H), 6.33–6.31 (m, 2H), 4.47 (d, *J* = 12.9 Hz, 1H), 4.33 (q, *J* = 6.4 Hz, 1H), 3.96–3.89 (m, 2H), 3.72 (d, *J* = 11.7 Hz, 1H), 3.20 (s, 3H), 0.91 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, C_6D_6): δ 170.6, 149.1, 146.7, 129.5, 129.2, 125.1, 124.6, 117.8, 115.0, 61.8, 58.2, 53.5, 51.8, 12.1. APCI [M-H]$^+$ calcd for $C_{18}H_{18}{}^{35}Cl_2N_3O_2^+$ 378.0771; found 378.0756.

methyl (5SR,6RS)-1,4-bis(4-chlorophenyl)-6-methyl-1,2,4-triazinane-5-carboxylate (**4.38b**)



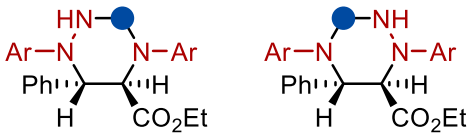
4.38b

(Ar = 4-ClC$_6$H$_4$)

Product **4.38b** was synthesized from alkene **1.38** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:4 to 1:2. Pale yellow oil (19 mg, 18%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.19–7.05 (m, 4H), 6.89–6.85 (m, 2H), 6.33–6.30 (m, 2H), 4.44–4.40 (m, 2H), 3.94–3.89 (m, 2H), 3.12 (s, 3H), 0.83 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, C_6D_6): δ 170.7, 147.9, 147.8, 129.4, 129.2, 124.8, 124.7, 116.8, 116.0, 62.8, 61.1, 51.9, 51.6, 10.3. APCI [M-H]$^+$ calcd for $C_{18}H_{18}{}^{35}Cl_2N_3O_2^+$ 378.0771; found 378.0756.

ethyl (5RS,6SR)-1,4-bis(4-chlorophenyl)-5-phenyl-1,2,4-triazinane-6-carboxylate (**4.39**)

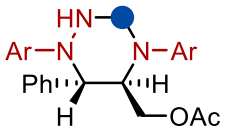


4.39a (Ar = 4-ClC$_6$H$_4$) (1:1) **4.39b** (Ar = 4-ClC$_6$H$_4$)

Product **4.39** was synthesized as a mixture of **4.39a** and **4.39b** from alkene **1.39** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:6 to 1:4. Pale yellow oil (91 mg, 99%).

^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.25–7.22 (m, 2H), 7.17–7.14 (m, 6H), 7.12–7.10 (m, 2H), 7.05–7.01 (m, 8H), 6.98–6.97 (m, 2H, B), 6.89–6.88 (m, 2H, A), 6.40–6.38 (m, 2H, A), 6.34–6.32 (m, 2H, B), 5.68 (s, 1H, B), 5.48 (s, 1H, A), 4.74 (s, 1H), 4.73 (s, 1H), 4.59 (d, *J* = 12.9 Hz, 1H, A), 4.48 (t, *J* = 11.9 Hz, 1H, B), 4.20 (t, *J* = 12.7 Hz, 1H, A), 3.89 (t, *J* = 12.3 Hz, 2H), 3.85–3.78 (m, 2H, A+B), 3.77–3.70 (m, 2H, A+B), 3.55 (d, *J* = 12.3 Hz, 1H, B), 0.78 (t, *J* = 7.1 Hz, 3H), 0.72 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, C$_6$D$_6$): δ 170.4, 170.1, 148.7, 148.2, 147.19, 147.18, 138.2, 136.6, 129.5, 129.4, 129.34, 129.29, 129.0, 128.7, 128.5, 128.4, 128.3, 128.0, 125.0, 124.77, 124.75, 124.4, 118.0, 116.1, 115.7, 114.8, 61.5, 61.4, 60.9, 60.5, 60.4, 59.9, 59.1, 59.0, 14.1 (2C). APCI [M-H]$^+$ calcd for C$_{24}$H$_{22}$^{35}Cl$_2$N$_3$O$_2^+$ 454.1084; found 454.1049.

((5RS,6SR)-1,4-bis(4-chlorophenyl)-6-phenyl-1,2,4-triazinan-5-yl)methyl acetate (**4.40**)



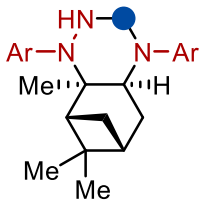
4.40

(Ar = 4-ClC$_6$H$_4$)

Product **4.40** was synthesized from alkene **1.40** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:10 to 1:6. Pale yellow oil (91 mg, 19%).

^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.02–6.82 (m, 9H), 6.70–6.68 (m, 2H), 6.16–6.14 (m, 2H), 4.63–4.62 (m, 1H), 4.27–4.24 (m, 1H), 4.17–4.13 (m, 1H), 4.02–3.98 (m, 1H), 3.77–3.73 (m, 1H), 3.47–3.45 (m, 1H), 3.25–3.22 (m, 1H), 1.25 (s, 3H); ^{13}C NMR (126 MHz, C$_6$D$_6$): δ 170.0, 148.7, 146.5, 137.0, 129.5, 129.4, 129.0, 128.3, 128.2, 124.34, 124.29, 116.1, 115.5, 61.0, 59.3, 57.1, 55.7, 20.0. APCI [M+H]$^+$ calcd for C$_{24}$H$_{24}$^{35}Cl$_2$N$_3$O$_2^+$ 456.1240; found 456.1240.

(4aS,6R,8R,8aR)-1,4-bis(4-fluorophenyl)-7,7,8a-trimethyldecahydro-6,8-methanobenzo[e][1,2,4]triazine (**4.41**)

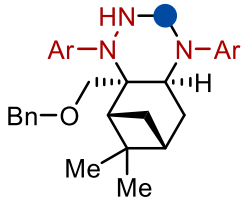


4.41 (Ar = 4-FC_6H_4)

Product **4.41** was synthesized from alkene **1.41** and triazene **2.2** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:8 to 1:4. Pale yellow solid (77 mg, 74%).

^{1}H NMR (500 MHz, C_6D_6): δ 6.89–6.80 (m, 6H), 6.43–6.39 (m, 2H), 4.22 (t, *J* = 9.2 Hz, 1H), 4.10 (d, *J* = 11.4 Hz, 1H), 3.99 (d, *J* = 11.4 Hz, 1H), 3.54 (br s, 1H), 2.23 (d, *J* = 9.5 Hz, 1H), 2.15–2.10 (m, 1H), 2.00–1.95 (m, 1H), 1.86 (t, *J* = 5.8 Hz, 1H), 1.81–1.78 (m, 1H), 1.51 (dd, *J* = 12.9, 10.1 Hz, 1H), 1.12 (s, 3H), 0.97 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (126 MHz, C_6D_6): δ 159.6 (d, *J* = 242.3 Hz), 156.7 (d, *J* = 237.2 Hz), 145.14 (d, *J* = 1.8 Hz), 145.10 (d, *J* = 2.8 Hz), 125.2 (d, *J* = 7.6 Hz), 116.6 (d, *J* = 7.3 Hz), 116.1 (d, *J* = 22.0 Hz), 114.6 (d, *J* = 21.9 Hz), 61.7, 60.1, 56.4, 54.4, 40.6, 38.5, 32.1, 30.9, 29.9, 23.8, 17.9. ^{19}F NMR (471 MHz, C_6D_6): δ -119.94, -125.88. APCI $[M-H]^+$ calcd for $C_{23}H_{26}F_2N_3^+$ 382.2089; found 382.2083.

(4aSR,6RS,8RS,8aRS)-8a-((benzyloxy)methyl)-1,4-bis(4-chlorophenyl)-7,7-dimethyldecahydro-6,8-methanobenzo[e][1,2,4]triazine (**4.42**)

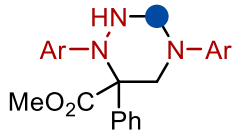


4.42 (Ar = 4-ClC_6H_4)

Product **4.42** was synthesized from alkene **1.42** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:4 to 1:2. Pale yellow oil (104 mg, 76%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.18–7.11 (m, 6H), 7.09–7.05 (m, 1H), 7.03–7.00 (m, 2H), 6.96–6.94 (m, 2H), 6.44–6.41 (m, 2H), 5.09 (br s, 1H), 4.49 (t, *J* = 9.1 Hz, 1H), 4.28 (d, *J* = 12.4 Hz, 1H), 4.19 (d, *J* = 12.7 Hz, 1H), 4.09 (d, *J* = 11.9 Hz, 1H), 3.84 (d, *J* = 11.9 Hz, 1H), 3.20 (s, 2H), 2.27–2.22 (m, 1H), 2.15–2.07 (m, 2H), 1.78–1.76 (m, 1H), 1.77 (q, *J* = 4.6 Hz, 1H), 1.68 (t, *J* = 5.5 Hz, 1H), 1.61 (ddd, *J* = 13.7, 9.1, 1.6 Hz, 1H), 1.05 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (126 MHz, C_6D_6): δ 147.7, 147.4, 137.8, 129.5, 128.6, 128.5, 128.3, 128.12, 128.08, 125.2, 122.3, 115.3, 76.8, 73.6, 63.5, 59.2, 53.4, 50.7, 40.5, 38.2, 33.5, 31.6, 29.3, 24.3. APCI $[M-H]^+$ calcd for $C_{30}H_{32}{}^{35}Cl_2N_3O^+$ 520.1917; found 520.1906.

methyl 1,4-bis(4-chlorophenyl)-6-phenyl-1,2,4-triazinane-6-carboxylate (**4.43**)

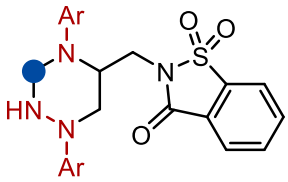


4.43 (Ar = 4-ClC$_6$H$_4$)

Product **4.43** was synthesized from alkene **1.43** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = 1:4. Pale yellow solid (88 mg, 98%).

^{1}H NMR (500 MHz, C_6D_6): δ 7.44–7.42 (m, 2H), 7.08–7.01 (m, 5H), 6.95–6.91 (m, 4H), 6.31–6.29 (m, 2H), 4.57 (d, *J* = 12.4 Hz, 1H), 4.04 (d, *J* = 11.9 Hz, 2H), 3.80 (t, *J* = 12.1 Hz, 1H), 3.27 (s, 3H), 2.94 (d, *J* = 12.1 Hz, 1H); ^{13}C NMR (126 MHz, C_6D_6): δ 171.1, 147.4, 147.1, 138.2, 129.3, 129.0, 128.5, 127.6, 127.2, 126.3, 125.9, 123.1, 118.2, 72.0, 66.0, 61.9, 51.9. APCI $[M+H]^+$ calcd for $C_{23}H_{22}{}^{35}Cl_2N_3O_2^+$ 442.1084; found 442.1110.

2-((1,4-bis(4-chlorophenyl)-1,2,4-triazinan-5-yl)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide (**4.44**)

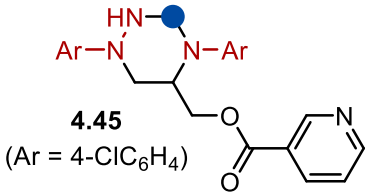


4.44 (Ar = 4-ClC$_6$H$_4$)

Product **4.44** was synthesized from alkene **1.44** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:5 to 1:1. Colorless solid (101 mg, 43%).

^{1}H NMR (500 MHz, DMSO-d_6): δ 8.30–8.28 (m, 1H), 8.08–7.97 (m, 3H), 7.25–7.18 (m, 6H), 7.01–6.99 (m, 2H), 4.68–4.66 (m, 1H), 4.57–4.55 (m, 1H), 4.51–4.50 (m, 1H), 4.42–4.37 (m, 1H), 4.22 (dd, *J* = 14.7, 8.5 Hz, 1H) , 4.00–3.98 (m, 1H), 3.76 (dd, *J* = 14.7, 5.2 Hz, 1H). 3.16–3.13 (m, 1H); ^{13}C NMR (126 MHz, DMSO-d_6): δ 159.6, 150.6, 146.5, 137.0, 136.2, 135.7, 129.1, 128.7, 126.9, 125.6, 123.3, 122.5, 122.0, 117.0, 116.8, 59.5, 52.1, 50.2, 36.8. APCI $[M-H]^+$ calcd for $C_{23}H_{19}{}^{35}Cl_2N_4O_3S^+$ 501.0549; found 501.0565.

(1,4-bis(4-chlorophenyl)-1,2,4-triazinan-5-yl)methyl nicotinate (**4.45**)

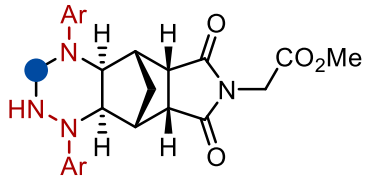


4.45
(Ar = 4-ClC$_6$H$_4$)

Product **4.45** was synthesized from alkene **1.45** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:1 to 2:1. Pale yellow solid (89 mg, 94%).

^{1}H NMR (500 MHz, C$_6$D$_6$/DMSO-d$_6$): δ 8.85 (s, 1H), 8.77–8.76 (m, 1H), 7.95–7.93 (m, 1H), 7.46–7.44 (m, 1H), 7.25–7.23 (m, 2H), 7.18–7.14 (m, 4H), 6.97–6.95 (m, 2H), 4.77–4.70 (m, 2H), 4.57–4.54 (br m, 1H), 4.51–4.44 (m, 2H), 4.29 (t, *J* = 12.1 Hz, 1H), 4.01 (d, *J* = 12.4 Hz, 1H), 3.30–3.28 (m, 1H); ^{13}C NMR (126 MHz, C$_6$D$_6$/DMSO-d$_6$): δ 165.1, 154.0, 150.5, 150.2, 147.5, 137.2, 129.2, 128.9, 125.6, 124.0, 122.9, 122.4, 117.0, 116.2, 62.3, 59.4, 52.5, 49.6. APCI [M+H]$^+$ calcd for C$_{22}$H$_{21}$^{35}Cl$_2$N$_4$O$_2^+$ 443.1036; found 443.1030.

methyl 2-((4aSR,5SR,5aSR,8aRS,9RS,9aRS)-1,4-bis(4-chlorophenyl)-6,8-dioxododecahydro-7H-5,9-methano[1,2,4]triazino[5,6-f]isoindol-7-yl)acetate (**4.46**)

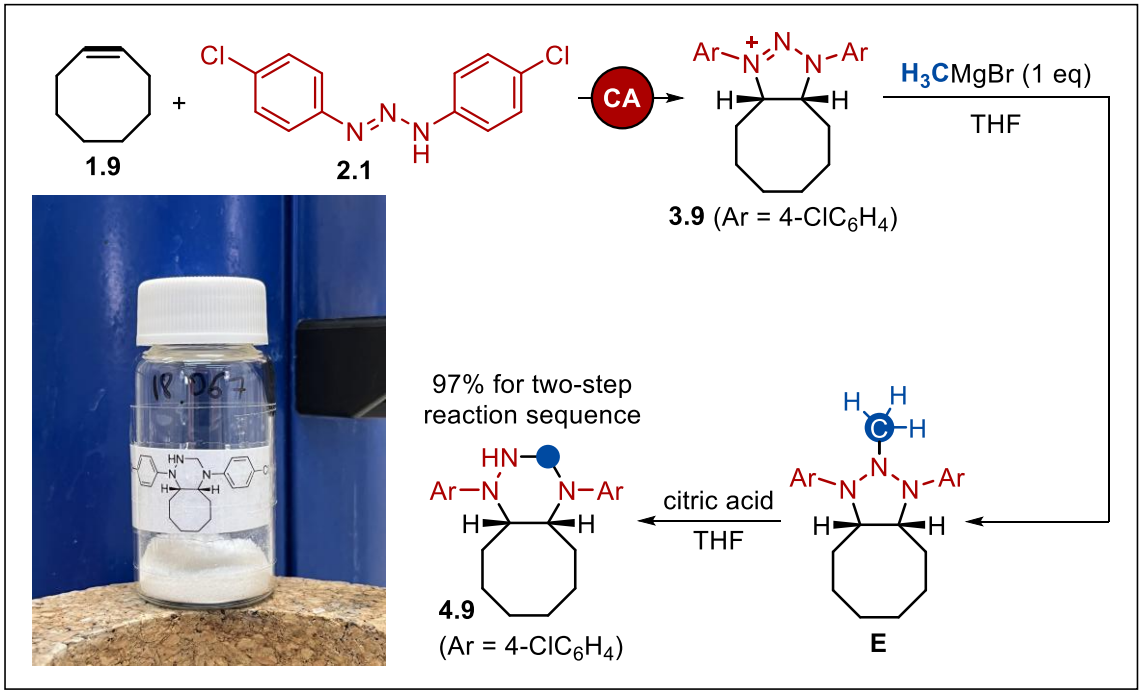


4.46 (Ar = 4-ClC$_6$H$_4$)

Product **4.46** was synthesized from alkene **1.46** and triazene **2.1** (0.2 mmol) by the general procedure A. Eluent for chromatography EtOAc:Hexane = from 1:1 to 2:1. Pale yellow solid (103 mg, 96%).

^{1}H NMR (500 MHz, C$_6$D$_6$): δ 7.28–7.12 (m, 6H), 6.61–6.59 (m, 2H), 4.05–3.97 (m, 5H), 3.60 (dd, *J* = 11.1, 7.1 Hz, 1H), 2.99 (s, 3H), 2.96 (t, *J* = 7.6 Hz, 1H), 2.52–2.49 (m, 2H), 2.46–2.40 (m, 2H), 1.66 (d, *J* = 10.9 Hz, 1H), 0.80 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (126 MHz, C$_6$D$_6$): δ 176.0 (2C), 167.7, 148.3, 146.0, 129.4, 129.1, 125.2, 123.4, 116.8, 114.8, 62.4, 56.8, 54.6, 52.2, 47.1, 46.5, 44.2, 44.0, 39.7, 39.4. APCI [M+H]$^+$ calcd for C$_{25}$H$_{25}$^{35}Cl$_2$N$_4$O$_4^+$ 515.1247; found 515.1212.

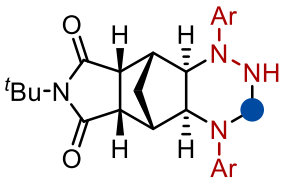
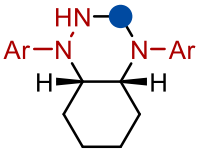
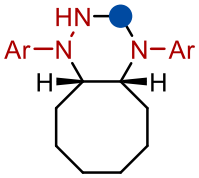
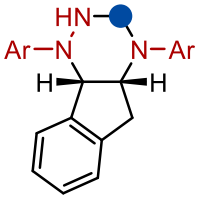
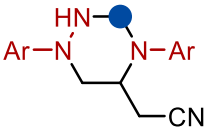
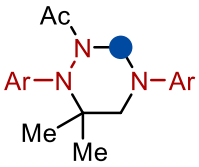
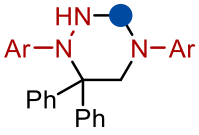
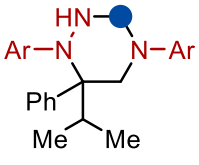
*2.3.11 Gram scale synthesis of **4.9***

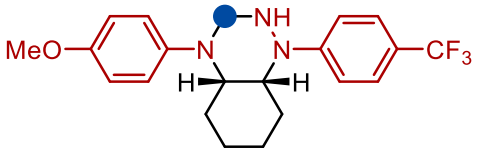
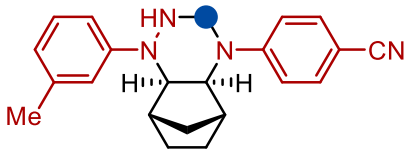
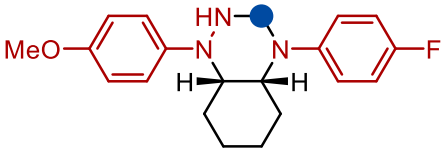
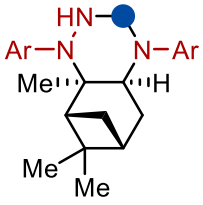
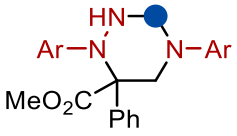
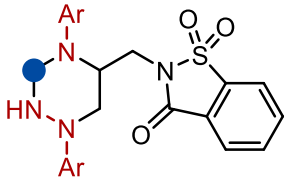
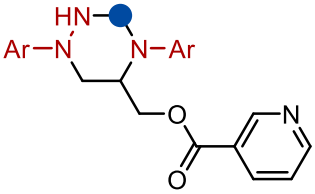


The oven dried Schlenk flask was flushed with nitrogen and charged with nitrenium salt **3.9** (2.69 mmol, 1 eq, 74.2% purity, 1.89 g). THF (0.05 M, 54 ml) was added, and the suspension was cooled down to -5 °C using ice/NaCl cooling bath. MeMgBr (1 eq, 3M, 0.9 ml) was added dropwise to the nitrenium suspension with stirring, and the reaction mixture was allowed to reach room temperature during 18 h. The mixture was cooled to 0 °C using ice bath. Anhydrous citric acid (1.5 eq, 777 mg) was added in one portion to the reaction mixture, and it was stirred at 0 °C for 2 min and the cooling bath was removed. The reaction was stirred at room temperature upon completion (80 min). The reaction was quenched with aqueous $NaHCO_3$ (sat, 100 ml) and EtOAc (100 ml) was added to extract all the organic materials. Organic phase was separated and the aqueous phase was extracted with EtOAc (50 ml). The combined organic layer was washed with aqueous $NaHCO_3$ (sat, 2*50 ml) and brine (50 ml). The organic phase was passed through a pad of Na_2SO_4 for additional drying and evaporated. Et_2O (2 ml) was added to the remaining oil and resulting suspension was subjected to flash filtration through neutral aluminum oxide (5 cm) with the eluent EtOAc:Hex = 1:10 -> 1:6, and that afforded pure compound **4.9** (1.02 g, 2.61 mmol) in 97% yield.

3 Crystallography

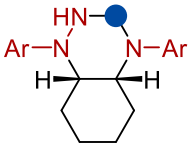
In all the X-ray pictures, CH-hydrogens are omitted for clarity.

compound	structure	Sample name	CCDC code
4.4		Gandelman230R	2505614
4.7		Gandelman211R	2505615
4.9		Gandelman232R	2505616
4.11		Gandelman247R	2505617
4.21		Gandelman242R	2505618
4.22		Gandelman240R	2505619
4.25		Gandelman239R	2505620
4.26		Gandelman269R	2505621

compound	structure	Sample name	CCDC code
4.31		Gandelman268R	2505622
4.34		Gandelman264R	2505623
4.36		Gandelman267R	2505624
4.41		Gandelman255R	2505625
4.43		Gandelman245R	2505626
4.44		Gandelman271R	2505627
4.45		Gandelman258R	2505628

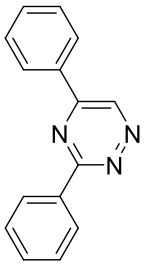
*3.1.1 Structural comparison of structure **4.7** and aromatic triazine*

Below we provided some general structural description of the obtained heterocyclic framework on the example of **4.7**. We compare it with the known structure of 3,5-diphenyl-1,2,4-triazine (CCDC 1415846[18]).

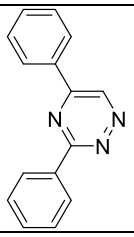


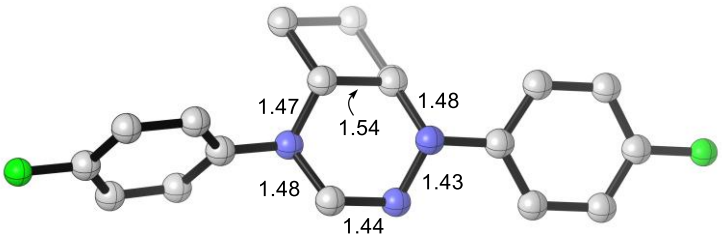
4.7

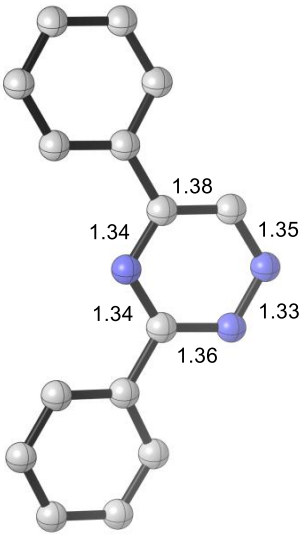
(Ar = 4-FC_6H_4)



As can be seen from the pictures below, bond distances in **4.7** are greater than the similar bonds in 1,2,4-triazine which correspond to compounds **4** being fully saturated analogs of 1,2,4-triazines.[21]

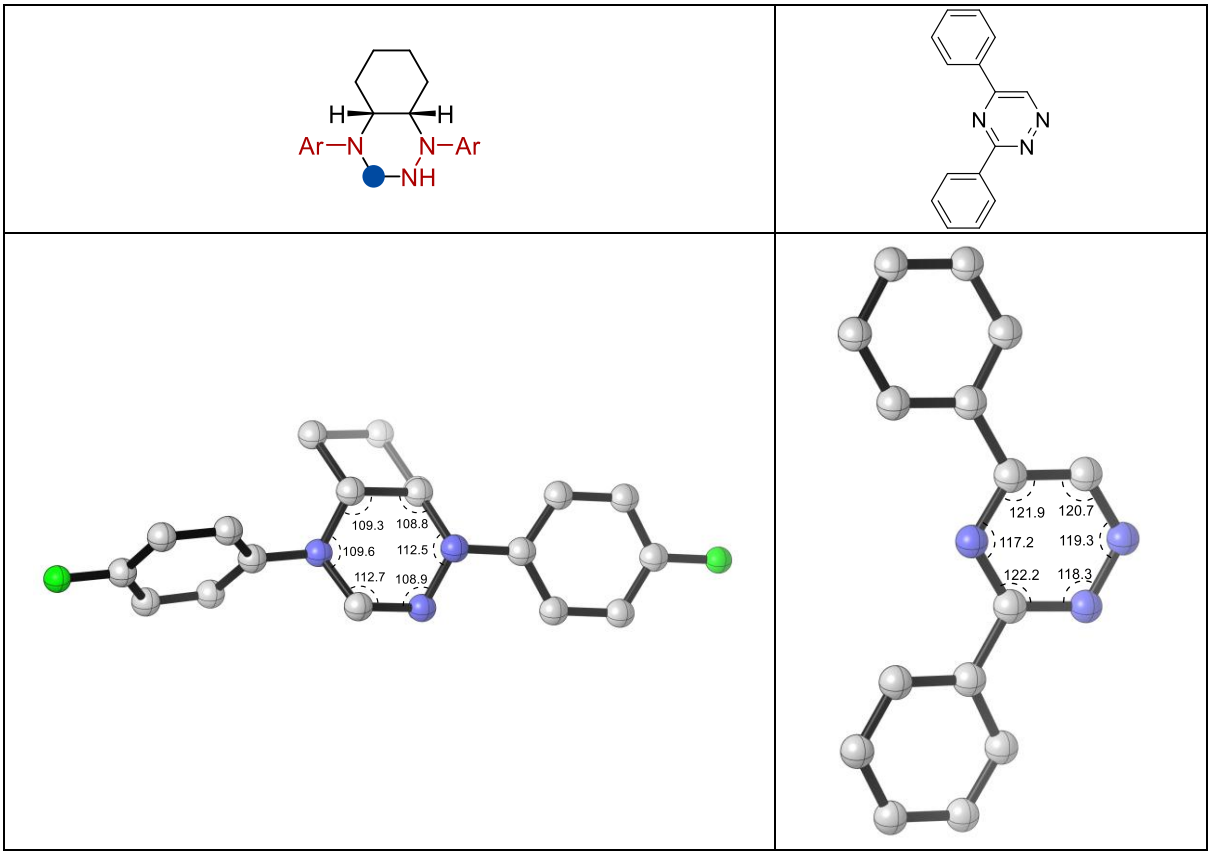






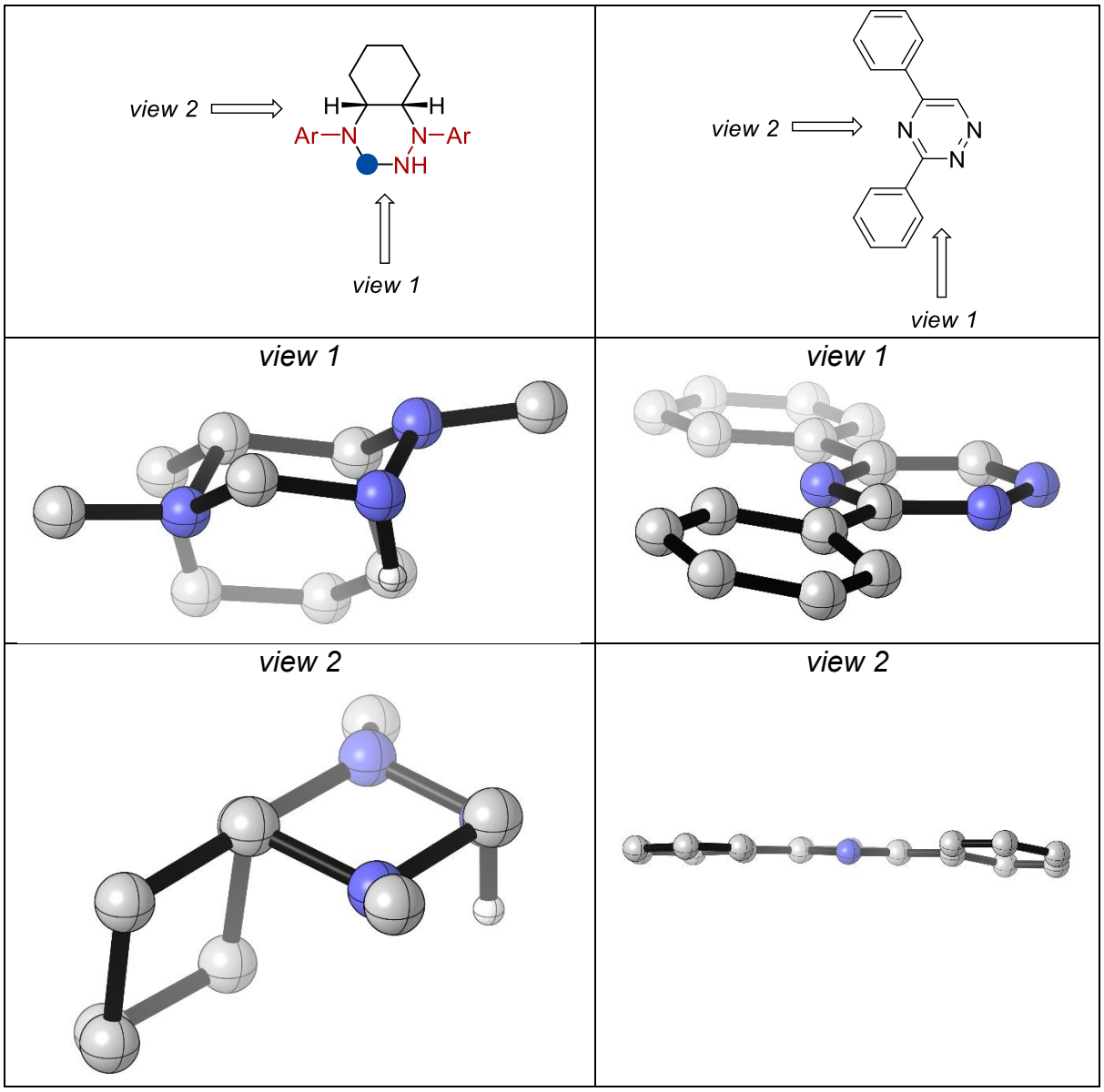
[21] C-H hydrogens are omitted for clarity.

Additionally, angles in the cyclic system of **4** correspond to *sp*^{3}-rich heterocycle contrary to that in 1,2,4-triazines where angles are close to *sp*^{2}-hybridized atoms.[22]



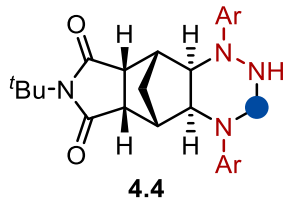
[22] C-H hydrogens are omitted for clarity.

Finally, compounds **4** adopt chair-like configuration contrary to completely flat 1,2,4-triazines. In case of **4.7** its crystal structure resembles the configuration of *cis*-decalin.[23]



[23] C-H hydrogens are omitted for clarity; aryl groups (Ar) are omitted on nitrogen atoms for structure **4.7**.

3.1.2 *(4aRS,5RS,5aRS,8aSR,9SR,9aSR)-7-(tert-butyl)-1,4-bis(4-chlorophenyl)decahydro-6H-5,9-methano[1,2,4]triazino[5,6-f]isoindole-6,8(7H)-dione (4.4)*



4.4

(Ar = 4-ClC_6H_4)

Sample name: Gandelman230R

CCDC number: 2505614

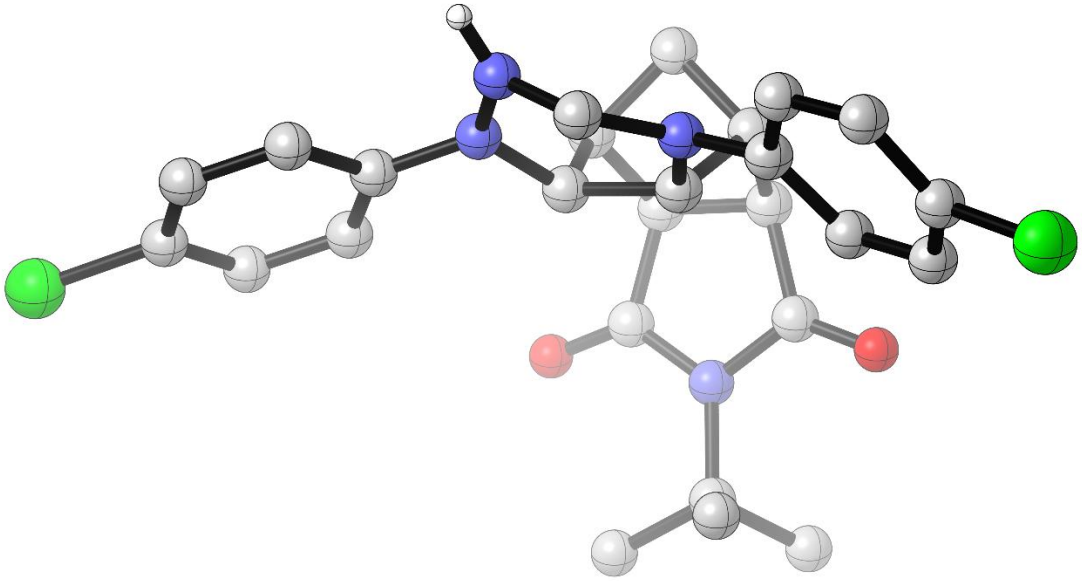


Table 1 Crystal data and structure refinement for Gandelman230R.

Identification code	Gandelman230R
Empirical formula	$C_{26}H_{28}Cl_2N_4O_2$
Formula weight	499.42
Temperature/K	100.15
Crystal system	monoclinic
Space group	C2/c
a/Å	16.0227(6)
b/Å	9.6932(4)
c/Å	31.7914(14)
α/°	90
β/°	108.336(4)
γ/°	90
Volume/Å^3	4686.9(3)
Z	8
ρ_{calc}g/cm^3	1.416
μ/mm^{-1}	0.310
F(000)	2096.0
Crystal size/mm^3	0.3 × 0.3 × 0.24
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.938 to 59.642
Index ranges	-19 ≤ h ≤ 21, -12 ≤ k ≤ 13, -38 ≤ l ≤ 38
Reflections collected	16248
Independent reflections	5255 [R_{int} = 0.0438, R_{sigma} = 0.0405]
Data/restraints/parameters	5255/358/320
Goodness-of-fit on F^2	1.724
Final R indexes [I>=2σ (I)]	R_1 = 0.0682, wR_2 = 0.2316
Final R indexes [all data]	R_1 = 0.0764, wR_2 = 0.2354
Largest diff. peak/hole / e Å^{-3}	0.46/-0.47

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman230R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	9044.1(5)	6972.3(9)	8526.1(2)	30.8(2)
Cl2	3419.2(5)	1371.0(9)	4703.5(3)	30.9(2)
O1	9865.8(15)	2770(2)	6913.6(8)	31.7(6)
O2	7985.0(15)	979(2)	5628.2(8)	31.7(5)
N1	7567.7(17)	5743(3)	6608.2(9)	27.6(6)
N2	6438.5(15)	4698(3)	5800.8(8)	21.8(5)
N3	6234(2)	5888(3)	6012.4(11)	39.7(8)
N4	8913.2(17)	1545(3)	6333.7(9)	23.3(5)
C1	9406.5(18)	2698(3)	6531.4(11)	23.6(6)
C2	8455.4(19)	1776(3)	5886.1(10)	24.2(6)
C3	8639.8(19)	3240(3)	5767.4(11)	24.7(6)
C4	9258.9(19)	3856(3)	6196.3(11)	24.5(6)
C5	8749.1(19)	5121(3)	6283.5(11)	23.9(6)
C6	8325(2)	5615(4)	5802.5(11)	29.1(7)
C7	7850(2)	4240(3)	5638.9(10)	25.1(6)
C8	7301.5(18)	4050(3)	5961.4(9)	19.9(6)
C9	7936.4(18)	4634(3)	6411.7(10)	19.9(6)
C11	8870(2)	285(3)	6609.4(11)	27.7(7)
C12	8471(2)	744(4)	6960.4(13)	36.1(8)
C13	9797(3)	-277(5)	6820.1(19)	59.2(13)
C14	8295(4)	-832(5)	6327.8(15)	70.6(17)
C15	7959.6(19)	6077(3)	7053.6(10)	22.4(6)
C16	7666(2)	7202(3)	7239.1(11)	26.0(7)
C17	8008(2)	7512(3)	7682.4(11)	26.5(7)
C18	8660(2)	6674(3)	7954.1(10)	22.5(6)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman230R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C19	8991.1(19)	5582(3)	7778.0(10)	22.9(6)
C20	8658.6(19)	5290(3)	7330.6(10)	23.3(6)
C21	5729.9(18)	3909(3)	5544.3(9)	19.4(6)
C22	5860.1(19)	2688(3)	5336.8(10)	21.4(6)
C23	5153.6(19)	1920(3)	5080.0(10)	23.7(6)
C24	4303.9(19)	2362(3)	5023.8(10)	23.1(6)
C25	4147(2)	3560(3)	5222.0(10)	23.6(6)
C26	4859.8(18)	4329(3)	5477.5(10)	22.4(6)
C10	6926(4)	6499(6)	6321.2(19)	21.7(18)
C10A	6620(4)	5953(9)	6458(3)	23(2)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for Gandelman230R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	37.4(5)	33.5(5)	23.9(4)	-7.6(3)	13.0(3)	-2.5(3)
Cl2	22.7(4)	36.6(5)	28.2(4)	0.9(3)	0.7(3)	-7.8(3)
O1	27.8(11)	23.7(12)	33.7(13)	3.2(9)	-4.3(10)	-4.8(9)
O2	28.8(11)	32.5(13)	32.0(12)	-10.7(10)	6.9(10)	-0.8(9)
N1	23.3(12)	36.2(15)	21.1(13)	0.6(11)	4.0(10)	10.9(11)
N2	20.6(11)	19.2(13)	23.6(13)	-1.5(9)	4.1(10)	2.0(9)
N3	32.8(15)	32.1(16)	43.5(18)	-13.7(13)	-3.5(13)	12.2(13)
N4	26.0(12)	18.2(12)	27.3(13)	-5.7(10)	10.9(11)	-2.9(10)
C1	19.1(13)	18.3(14)	34.2(17)	-3.9(12)	9.6(12)	-0.8(10)
C2	22.1(13)	26.1(15)	27.9(16)	-6.6(12)	12.8(12)	3.9(12)
C3	23.0(14)	29.5(16)	24.6(15)	-1.5(12)	11.7(12)	0.7(12)
C4	20.1(13)	22.9(15)	32.5(16)	0.0(12)	11.0(12)	-2.3(11)
C5	21.5(13)	19.3(14)	30.8(16)	1.6(11)	8.0(12)	-1.7(11)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman230R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6	28.8(15)	31.1(17)	30.0(17)	7.4(13)	13.1(13)	0.9(13)
C7	27.8(14)	30.3(16)	19.0(14)	4.7(12)	10.0(12)	1.0(12)
C8	20.5(13)	20.7(14)	18.4(14)	-0.8(10)	6.0(11)	-1.5(10)
C9	19.5(12)	18.0(14)	21.2(14)	1.7(10)	4.7(11)	1.4(10)
C11	37.0(16)	17.7(14)	32.2(17)	-4.0(12)	16.0(14)	-3.9(12)
C12	44.7(19)	32.8(18)	38.2(19)	6.1(15)	23.4(16)	6.3(15)
C13	51(2)	37(2)	105(4)	30(2)	47(3)	22.1(19)
C14	134(5)	38(2)	42(2)	-14.3(19)	31(3)	-51(3)
C15	25.2(14)	23.1(15)	21.3(14)	2.2(11)	10.6(12)	1.9(11)
C16	34.5(16)	18.0(14)	29.3(16)	6.5(12)	15.5(13)	7.8(12)
C17	36.6(16)	17.9(14)	31.1(16)	3.6(12)	19.4(14)	5.5(12)
C18	30.5(15)	17.5(14)	23.3(15)	-3.2(11)	13.9(12)	-2.6(11)
C19	22.9(13)	18.5(14)	25.6(15)	-4.2(11)	5.2(12)	1.7(11)
C20	24.0(14)	20.9(15)	25.2(15)	-4.7(11)	8.1(12)	6.3(11)
C21	20.1(13)	22.5(14)	15.6(13)	3.7(10)	5.8(11)	0.0(10)
C22	21.2(13)	22.5(15)	21.4(14)	2.3(11)	7.7(11)	1.3(11)
C23	23.4(14)	25.8(15)	21.4(15)	-0.5(11)	6.3(12)	-0.6(12)
C24	20.2(13)	25.3(15)	22.6(15)	2.5(11)	4.9(11)	-4.5(11)
C25	22.5(13)	27.2(16)	21.0(15)	4.8(11)	6.4(11)	1.3(11)
C26	20.6(13)	24.4(15)	20.6(14)	3.2(11)	4.2(11)	4.9(11)
C10	29(3)	13(3)	18(3)	0(2)	-1(2)	6(2)
C10A	16(3)	31(4)	24(4)	-12(3)	7(3)	1(3)

Table 4 Bond Lengths for Gandelman230R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C18	1.751(3)	C5	C6	1.541(4)

Table 4 Bond Lengths for Gandelman230R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl2	C24	1.750(3)	C5	C9	1.555(4)
O1	C1	1.208(4)	C6	C7	1.542(5)
O2	C2	1.204(4)	C7	C8	1.557(4)
N1	C9	1.459(4)	C8	C9	1.578(4)
N1	C15	1.394(4)	C11	C12	1.517(5)
N1	C10	1.355(5)	C11	C13	1.525(5)
N1	C10A	1.456(7)	C11	C14	1.518(5)
N2	N3	1.424(4)	C15	C16	1.391(4)
N2	C8	1.457(4)	C15	C20	1.411(4)
N2	C21	1.399(4)	C16	C17	1.375(5)
N3	C10	1.363(6)	C17	C18	1.389(4)
N3	C10A	1.357(8)	C18	C19	1.379(4)
N4	C1	1.399(4)	C19	C20	1.382(4)
N4	C2	1.399(4)	C21	C22	1.403(4)
N4	C11	1.517(4)	C21	C26	1.403(4)
C1	C4	1.514(4)	C22	C23	1.386(4)
C2	C3	1.521(4)	C23	C24	1.384(4)
C3	C4	1.532(4)	C24	C25	1.381(5)
C3	C7	1.543(4)	C25	C26	1.391(4)
C4	C5	1.546(4)			

Table 5 Bond Angles for Gandelman230R.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C15	N1	C9	119.5(2)	N2	C8	C9	115.7(2)
C15	N1	C10A	113.0(4)	C7	C8	C9	102.6(2)
C10	N1	C9	115.7(3)	N1	C9	C5	112.0(2)
C10	N1	C15	124.2(3)	N1	C9	C8	114.9(2)

Table 5 Bond Angles for Gandelman230R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C10A	N1	C9	118.9(3)	C5	C9	C8	103.0(2)
N3	N2	C8	121.2(2)	N4	C11	C13	109.0(3)
C21	N2	N3	116.9(2)	N4	C11	C14	111.3(3)
C21	N2	C8	118.4(2)	C12	C11	N4	107.2(3)
C10	N3	N2	115.9(3)	C12	C11	C13	111.0(3)
C10A	N3	N2	115.7(4)	C12	C11	C14	109.0(3)
C1	N4	C11	120.4(3)	C14	C11	C13	109.3(4)
C2	N4	C1	111.7(3)	N1	C15	C20	121.6(3)
C2	N4	C11	127.7(3)	C16	C15	N1	120.5(3)
O1	C1	N4	125.2(3)	C16	C15	C20	117.8(3)
O1	C1	C4	125.2(3)	C17	C16	C15	121.8(3)
N4	C1	C4	109.6(3)	C16	C17	C18	119.3(3)
O2	C2	N4	127.3(3)	C17	C18	Cl1	119.9(2)
O2	C2	C3	124.0(3)	C19	C18	Cl1	119.6(2)
N4	C2	C3	108.7(3)	C19	C18	C17	120.4(3)
C2	C3	C4	105.3(3)	C18	C19	C20	120.1(3)
C2	C3	C7	116.4(2)	C19	C20	C15	120.3(3)
C4	C3	C7	103.8(2)	N2	C21	C22	121.5(3)
C1	C4	C3	104.6(2)	N2	C21	C26	121.0(3)
C1	C4	C5	115.9(3)	C22	C21	C26	117.5(3)
C3	C4	C5	103.8(2)	C23	C22	C21	121.0(3)
C4	C5	C9	109.9(2)	C24	C23	C22	119.9(3)
C6	C5	C4	99.3(3)	C23	C24	Cl2	119.3(2)
C6	C5	C9	102.1(2)	C25	C24	Cl2	119.8(2)
C5	C6	C7	94.7(2)	C25	C24	C23	120.9(3)
C3	C7	C8	109.7(2)	C24	C25	C26	118.9(3)
C6	C7	C3	100.2(2)	C25	C26	C21	121.8(3)

Table 5 Bond Angles for Gandelman230R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	C7	C8	101.6(2)	N1	C10	N3	121.5(5)
N2	C8	C7	112.9(2)	N3	C10A	N1	114.9(6)

Table 6 Torsion Angles for Gandelman230R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C18	C19	C20	176.4(2)	C6	C5	C9	C8	33.6(3)
Cl2	C24	C25	C26	179.6(2)	C6	C7	C8	N2	88.7(3)
O1	C1	C4	C3	179.5(3)	C6	C7	C8	C9	-36.4(3)
O1	C1	C4	C5	-66.9(4)	C7	C3	C4	C1	124.0(2)
O2	C2	C3	C4	179.6(3)	C7	C3	C4	C5	2.1(3)
O2	C2	C3	C7	65.2(4)	C7	C8	C9	N1	123.7(3)
N1	C15	C16	C17	176.5(3)	C7	C8	C9	C5	1.7(3)
N1	C15	C20	C19	-175.2(3)	C8	N2	N3	C10	10.2(6)
N2	N3	C10	N1	-40.1(8)	C8	N2	N3	C10A	-33.8(6)
N2	N3	C10A	N1	51.2(8)	C8	N2	C21	C22	-18.3(4)
N2	C8	C9	N1	0.4(4)	C8	N2	C21	C26	163.1(3)
N2	C8	C9	C5	-121.6(3)	C9	N1	C15	C16	174.7(3)
N2	C21	C22	C23	-179.4(3)	C9	N1	C15	C20	-5.7(4)
N2	C21	C26	C25	179.7(3)	C9	N1	C10	N3	48.5(8)
N3	N2	C8	C7	-110.5(3)	C9	N1	C10A	N3	-43.9(9)
N3	N2	C8	C9	7.3(4)	C9	C5	C6	C7	-55.2(3)
N3	N2	C21	C22	-177.4(3)	C11	N4	C1	O1	4.7(5)
N3	N2	C21	C26	4.0(4)	C11	N4	C1	C4	-173.9(2)
N4	C1	C4	C3	-1.9(3)	C11	N4	C2	O2	-5.4(5)
N4	C1	C4	C5	111.6(3)	C11	N4	C2	C3	174.3(3)
N4	C2	C3	C4	-0.1(3)	C15	N1	C9	C5	-80.4(3)
N4	C2	C3	C7	-114.4(3)	C15	N1	C9	C8	162.6(3)

Table 6 Torsion Angles for Gandelman230R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	N4	C2	O2	179.2(3)	C15	N1	C10	N3	-140.3(5)
C1	N4	C2	C3	-1.1(3)	C15	N1	C10A	N3	168.4(5)
C1	N4	C11	C12	60.6(4)	C15	C16	C17	C18	-0.6(5)
C1	N4	C11	C13	-59.7(4)	C16	C15	C20	C19	4.5(4)
C1	N4	C11	C14	179.6(4)	C16	C17	C18	Cl1	-175.1(2)
C1	C4	C5	C6	-151.5(3)	C16	C17	C18	C19	3.2(5)
C1	C4	C5	C9	-44.9(3)	C17	C18	C19	C20	-1.8(5)
C2	N4	C1	O1	-179.5(3)	C18	C19	C20	C15	-2.1(5)
C2	N4	C1	C4	1.9(3)	C20	C15	C16	C17	-3.2(5)
C2	N4	C11	C12	-114.5(3)	C21	N2	N3	C10	168.7(4)
C2	N4	C11	C13	125.2(4)	C21	N2	N3	C10A	124.7(5)
C2	N4	C11	C14	4.6(5)	C21	N2	C8	C7	91.3(3)
C2	C3	C4	C1	1.2(3)	C21	N2	C8	C9	-150.9(3)
C2	C3	C4	C5	-120.7(2)	C21	C22	C23	C24	0.3(5)
C2	C3	C7	C6	149.3(3)	C22	C21	C26	C25	1.0(4)
C2	C3	C7	C8	42.9(4)	C22	C23	C24	Cl2	-179.3(2)
C3	C4	C5	C6	-37.5(3)	C22	C23	C24	C25	-0.3(5)
C3	C4	C5	C9	69.0(3)	C23	C24	C25	C26	0.6(5)
C3	C7	C8	N2	-165.9(2)	C24	C25	C26	C21	-1.0(4)
C3	C7	C8	C9	69.0(3)	C26	C21	C22	C23	-0.7(4)
C4	C3	C7	C6	34.1(3)	C10	N1	C9	C5	91.3(5)
C4	C3	C7	C8	-72.2(3)	C10	N1	C9	C8	-25.8(5)
C4	C5	C6	C7	57.6(3)	C10	N1	C15	C16	3.8(6)
C4	C5	C9	N1	165.0(2)	C10	N1	C15	C20	-176.5(5)
C4	C5	C9	C8	-71.1(3)	C10A	N1	C9	C5	134.0(5)
C5	C6	C7	C3	-56.5(3)	C10A	N1	C9	C8	17.0(6)
C5	C6	C7	C8	56.3(3)	C10A	N1	C15	C16	-37.8(6)

Table 6 Torsion Angles for Gandelman230R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C6	C5	C9	N1	-90.3(3)	C10A	N1	C15	C20	141.9(5)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman230R.

Atom	*x*	*y*	*z*	U(eq)
H3A	5694.62	6208.38	5947.72	48
H3B	5880.39	6538.79	5863.73	48
H3	8931.56	3227.2	5531.76	30
H4	9826.84	4146.71	6155.02	29
H5	9121.91	5826.19	6487.13	29
H6A	8764.43	5850.32	5653.85	35
H6B	7913.09	6394.21	5779	35
H7	7497.05	4226.73	5317.61	30
H8	7218.25	3040.13	5998.3	24
H9	8117.95	3861.07	6629.74	24
H12A	8863.06	1408.95	7159.07	54
H12B	8391.89	-59.13	7131.51	54
H12C	7898.91	1177.23	6817.39	54
H13A	10000.77	-710.15	6591.64	89
H13B	9791.71	-963.29	7045.77	89
H13C	10192.89	480.53	6958.48	89
H14A	7688.93	-496.53	6209.98	106
H14B	8310.67	-1653.39	6509.82	106
H14C	8514.46	-1067.23	6081.75	106
H16	7216.24	7771.97	7054.63	31
H17	7801.51	8290.75	7801.52	32
H19	9448.8	5029.79	7964.51	27

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman230R.

Atom	*x*	*y*	*z*	U(eq)
H20	8901.85	4555.92	7209.06	28
H22	6441.82	2381.47	5372.96	26
H23	5252.13	1092.41	4942.78	28
H25	3562.45	3853.89	5184.44	28
H26	4754.34	5160.52	5610.45	27
H10A	7215.42	7107.04	6158.9	26
H10B	6676.36	7107.66	6501.49	26
H10C	6347.56	5246.8	6598.28	28
H10D	6492.87	6867.11	6562.47	28

Table 8 Atomic Occupancy for Gandelman230R.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
H3A	0.554(13)	H3B	0.446(13)	C10	0.554(13)
H10A	0.554(13)	H10B	0.554(13)	C10A	0.446(13)
H10C	0.446(13)	H10D	0.446(13)		

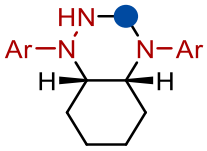
Experimental

Single crystals of $C_{26}H_{28}Cl_2N_4O_2$ **[Gandelman230R]** were obtained by slow evaporation of C_6H_6 solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[19] the structure was solved with the SHELXT[20] structure solution program using Intrinsic Phasing and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman230R]

Crystal Data for $C_{26}H_{28}Cl_2N_4O_2$ (*M* =499.42 g/mol): monoclinic, space group C2/c (no. 15), *a* = 16.0227(6) Å, *b* = 9.6932(4) Å, *c* = 31.7914(14) Å, *β* = 108.336(4)°, *V* = 4686.9(3) Å^3, *Z* = 8, *T* = 100.15 K, μ(MoKα) = 0.310 mm^{-1}, *Dcalc* = 1.416 g/cm^3, 16248 reflections measured (4.938° ≤ 2Θ ≤ 59.642°), 5255 unique (R_{int} = 0.0438, R_{sigma} = 0.0405) which were used in all calculations. The final R_1 was 0.0682 (I > 2σ(I)) and wR_2 was 0.2354 (all data).

3.1.3 (4aRS,8aSR)-1,4-bis(4-fluorophenyl)decahydrobenzo[e][1,2,4]triazine (4.7)



4.7

(Ar = 4-FC_6H_4)

Sample name: Gandelman211R

CCDC number: 2505615

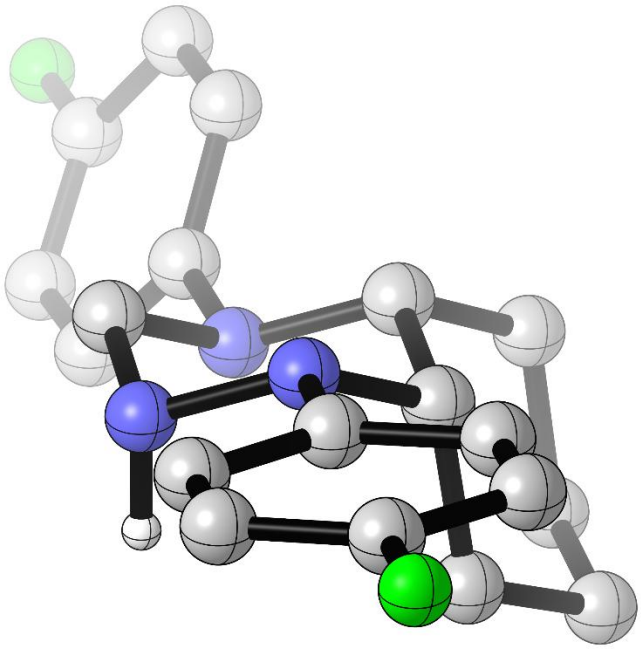


Table 1 Crystal data and structure refinement for Gandelman211R.

Identification code	Gandelman211R
Empirical formula	$C_{19}H_{21}F_2N_3$
Formula weight	329.39
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.7585(3)
b/Å	9.3302(3)
c/Å	17.9229(7)
α/°	90
β/°	96.734(3)
γ/°	90
Volume/Å^3	1620.59(10)
Z	4
ρ_{calc}g/cm^3	1.350
μ/mm^{-1}	0.097
F(000)	696.0
Crystal size/mm^3	0.24 × 0.18 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.93 to 60.076
Index ranges	-13 ≤ h ≤ 13, -12 ≤ k ≤ 12, -21 ≤ l ≤ 24
Reflections collected	14418
Independent reflections	3774 [R_{int} = 0.0363, R_{sigma} = 0.0315]
Data/restraints/parameters	3774/0/221
Goodness-of-fit on F^2	1.080
Final R indexes [I>=2σ (I)]	R_1 = 0.0401, wR_2 = 0.1091
Final R indexes [all data]	R_1 = 0.0489, wR_2 = 0.1150
Largest diff. peak/hole / e Å^{-3}	0.33/-0.24

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman211R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	9234.0(8)	6631.3(10)	3874.3(5)	40.8(2)
F2	2035.9(7)	6215.2(9)	10039.1(4)	31.4(2)
N1	6842.2(9)	5752.4(10)	6501.1(5)	18.1(2)
N2	4654.0(10)	5685.9(13)	7023.2(6)	25.5(2)
N3	5301.2(9)	6322.0(10)	7702.7(5)	19.6(2)
C1	5369.1(11)	6150.2(15)	6404.3(7)	25.0(3)
C2	6776.6(10)	5931.0(11)	7861.4(6)	16.0(2)
C3	7526.6(11)	6400.6(11)	7194.2(6)	16.6(2)
C4	9046.4(10)	5961.1(11)	7339.3(6)	17.1(2)
C5	9243.6(11)	4373.6(11)	7529.0(6)	19.0(2)
C6	8531.5(11)	3986.1(12)	8213.3(7)	20.4(2)
C7	6996.7(11)	4348.4(12)	8072.8(6)	18.6(2)
C8	7463.2(11)	6040.5(12)	5828.7(6)	17.6(2)
C9	7421.0(13)	4964.6(13)	5290.2(7)	27.7(3)
C10	7995.4(15)	5154.5(14)	4628.4(8)	32.1(3)
C11	8641.3(12)	6441.5(14)	4516.4(7)	26.8(3)
C12	8697.5(13)	7532.6(14)	5028.9(8)	30.1(3)
C13	8094.9(13)	7331.9(13)	5685.1(7)	26.5(3)
C14	4477.8(11)	6254.2(11)	8297.0(6)	17.8(2)
C15	3049.3(11)	6018.4(12)	8158.0(7)	20.0(2)
C16	2236.5(11)	6020.3(12)	8743.1(7)	22.0(3)
C17	2839.5(12)	6227.8(12)	9465.1(7)	21.1(2)
C18	4237.0(12)	6469.1(12)	9626.5(7)	21.5(2)
C19	5049.4(11)	6487.1(12)	9043.0(7)	21.6(2)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman211R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	38.9(5)	59.9(6)	27.1(4)	13.5(4)	19.0(4)	9.7(4)
F2	26.2(4)	46.7(5)	23.5(4)	1.2(3)	12.0(3)	1.2(3)
N1	14.5(4)	25.1(5)	14.9(5)	-0.2(4)	2.0(3)	-1.9(4)
N2	16.7(4)	43.8(6)	15.7(5)	-3.0(4)	0.7(4)	-3.8(4)
N3	12.6(4)	31.3(5)	14.6(5)	-0.2(4)	0.1(4)	1.5(4)
C1	15.2(5)	43.9(7)	15.4(6)	0.9(5)	-0.2(4)	1.1(5)
C2	12.3(4)	20.0(5)	15.7(5)	-0.6(4)	1.5(4)	0.0(4)
C3	15.4(5)	17.6(5)	16.5(5)	0.6(4)	0.9(4)	-0.1(4)
C4	14.3(5)	19.6(5)	17.7(5)	0.7(4)	2.8(4)	-1.6(4)
C5	17.0(5)	19.1(5)	21.2(6)	-0.6(4)	3.9(4)	1.8(4)
C6	20.3(5)	20.1(5)	21.3(6)	3.3(4)	4.4(4)	3.4(4)
C7	17.6(5)	19.5(5)	19.4(6)	0.8(4)	5.4(4)	-1.9(4)
C8	15.1(5)	21.9(5)	15.5(5)	2.8(4)	1.3(4)	1.4(4)
C9	36.0(7)	23.9(6)	24.3(7)	-1.9(5)	8.4(5)	-3.2(5)
C10	43.0(7)	31.7(7)	23.6(7)	-3.7(5)	12.0(6)	4.2(6)
C11	22.2(5)	40.8(7)	18.6(6)	9.4(5)	7.5(5)	8.1(5)
C12	31.9(6)	31.8(6)	27.1(7)	8.1(5)	5.5(5)	-7.0(5)
C13	34.7(6)	23.9(6)	21.4(6)	0.2(5)	4.9(5)	-4.8(5)
C14	16.5(5)	19.1(5)	18.2(6)	2.3(4)	2.8(4)	2.6(4)
C15	16.6(5)	25.0(5)	18.0(6)	3.4(4)	0.4(4)	0.9(4)
C16	15.2(5)	26.2(6)	24.9(6)	4.7(5)	3.2(4)	0.9(4)
C17	21.9(5)	21.9(5)	21.3(6)	2.2(4)	9.3(5)	3.4(4)
C18	21.6(5)	24.9(6)	17.9(6)	-2.7(4)	1.8(4)	3.2(4)
C19	16.2(5)	27.4(6)	21.1(6)	-2.7(5)	1.9(4)	2.0(4)

Table 4 Bond Lengths for Gandelman211R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C11	1.3588(14)	C6	C7	1.5272(15)
F2	C17	1.3647(13)	C8	C9	1.3899(17)
N1	C1	1.4751(14)	C8	C13	1.3912(16)
N1	C3	1.4699(14)	C9	C10	1.3815(18)
N1	C8	1.4363(14)	C10	C11	1.3817(19)
N2	N3	1.4332(14)	C11	C12	1.3679(19)
N2	C1	1.4444(15)	C12	C13	1.3879(18)
N3	C2	1.4802(13)	C14	C15	1.4044(15)
N3	C14	1.4090(14)	C14	C19	1.4039(17)
C2	C3	1.5372(15)	C15	C16	1.3870(16)
C2	C7	1.5332(15)	C16	C17	1.3710(18)
C3	C4	1.5314(14)	C17	C18	1.3790(16)
C4	C5	1.5268(15)	C18	C19	1.3846(16)
C5	C6	1.5223(15)			

Table 5 Bond Angles for Gandelman211R.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C3	N1	C1	109.62(9)	C9	C8	C13	118.35(11)
C8	N1	C1	110.82(9)	C13	C8	N1	123.85(10)
C8	N1	C3	115.94(8)	C10	C9	C8	121.44(11)
N3	N2	C1	108.90(9)	C9	C10	C11	118.30(12)
N2	N3	C2	112.52(8)	F1	C11	C10	118.88(12)
C14	N3	N2	112.97(8)	F1	C11	C12	118.95(12)
C14	N3	C2	118.14(9)	C12	C11	C10	122.17(12)
N2	C1	N1	112.72(10)	C11	C12	C13	118.75(11)
N3	C2	C3	108.74(9)	C12	C13	C8	120.97(12)
N3	C2	C7	112.94(9)	C15	C14	N3	121.01(10)

Table 5 Bond Angles for Gandelman211R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	C2	C3	113.64(9)	C19	C14	N3	120.99(10)
N1	C3	C2	109.25(8)	C19	C14	C15	117.93(11)
N1	C3	C4	111.62(9)	C16	C15	C14	120.62(11)
C4	C3	C2	109.36(9)	C17	C16	C15	119.58(10)
C5	C4	C3	113.07(9)	F2	C17	C16	119.30(10)
C6	C5	C4	110.63(9)	F2	C17	C18	119.00(11)
C5	C6	C7	110.24(9)	C16	C17	C18	121.70(11)
C6	C7	C2	111.11(9)	C17	C18	C19	118.90(11)
C9	C8	N1	117.80(10)	C18	C19	C14	121.25(10)

Table 6 Torsion Angles for Gandelman211R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F1	C11	C12	C13	-179.78(11)	C3	N1	C8	C13	-35.10(15)
F2	C17	C18	C19	-179.75(10)	C3	C2	C7	C6	54.17(12)
N1	C3	C4	C5	-67.86(12)	C3	C4	C5	C6	-57.54(12)
N1	C8	C9	C10	-179.92(11)	C4	C5	C6	C7	57.72(12)
N1	C8	C13	C12	178.86(11)	C5	C6	C7	C2	-56.08(12)
N2	N3	C2	C3	58.00(12)	C7	C2	C3	N1	70.90(11)
N2	N3	C2	C7	-69.12(12)	C7	C2	C3	C4	-51.53(12)
N2	N3	C14	C15	-19.02(14)	C8	N1	C1	N2	171.40(10)
N2	N3	C14	C19	164.00(10)	C8	N1	C3	C2	-177.35(8)
N3	N2	C1	N1	59.19(13)	C8	N1	C3	C4	-56.28(12)
N3	C2	C3	N1	-55.82(11)	C8	C9	C10	C11	1.1(2)
N3	C2	C3	C4	-178.25(8)	C9	C8	C13	C12	-1.49(18)
N3	C2	C7	C6	178.66(9)	C9	C10	C11	F1	178.73(11)
N3	C14	C15	C16	-176.95(10)	C9	C10	C11	C12	-1.6(2)
N3	C14	C19	C18	177.82(10)	C10	C11	C12	C13	0.5(2)

Table 6 Torsion Angles for Gandelman211R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	N1	C3	C2	56.27(11)	C11	C12	C13	C8	1.03(19)
C1	N1	C3	C4	177.34(9)	C13	C8	C9	C10	0.41(18)
C1	N1	C8	C9	-88.97(12)	C14	N3	C2	C3	-167.49(9)
C1	N1	C8	C13	90.67(13)	C14	N3	C2	C7	65.39(12)
C1	N2	N3	C2	-59.07(12)	C14	C15	C16	C17	-1.23(17)
C1	N2	N3	C14	164.00(9)	C15	C14	C19	C18	0.75(16)
C2	N3	C14	C15	-153.34(10)	C15	C16	C17	F2	-179.39(10)
C2	N3	C14	C19	29.68(15)	C15	C16	C17	C18	1.51(17)
C2	C3	C4	C5	53.14(12)	C16	C17	C18	C19	-0.65(17)
C3	N1	C1	N2	-59.37(13)	C17	C18	C19	C14	-0.50(17)
C3	N1	C8	C9	145.26(10)	C19	C14	C15	C16	0.13(16)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman211R.

Atom	*x*	*y*	*z*	U(eq)
H2	4744(16)	4674(18)	7058(9)	33(4)
H1A	5288.85	7204.58	6354.93	30
H1B	4919.26	5718.14	5933.61	30
H2A	7168.91	6508.94	8305.74	19
H3	7470.55	7467.49	7147.02	20
H4A	9502.27	6179.55	6887.34	21
H4B	9504.24	6539.14	7760.04	21
H5A	8855.69	3787.41	7094.42	23
H5B	10241.19	4157.76	7631.45	23
H6A	8961.61	4523.18	8656.53	24
H6B	8647.18	2949.34	8320.25	24
H7A	6556.38	4139.96	8531.13	22

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman211R.

Atom	*x*	*y*	*z*	U(eq)
H7B	6551.1	3739.27	7661.61	22
H9	6987.55	4079.19	5379.09	33
H10	7947.67	4418.96	4259.69	39
H12	9140.72	8411.14	4937.37	36
H13	8114.12	8087.61	6041.42	32
H15	2635.74	5855.99	7658.52	24
H16	1268.18	5878.77	8644.17	26
H18	4635.7	6620.41	10129.73	26
H19	6011.75	6660.25	9149.38	26

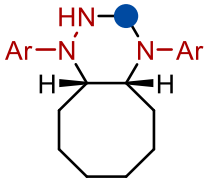
Experimental

Single crystals of $C_{19}H_{21}F_2N_3$ **[Gandelman211R]** were obtained by slow evaporation of Et_2O/Hexane solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman211R]

Crystal Data for $C_{19}H_{21}F_2N_3$ (*M* =329.39 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 9.7585(3) Å, *b* = 9.3302(3) Å, *c* = 17.9229(7) Å, *β* = 96.734(3)°, *V* = 1620.59(10) Å^3, *Z* = 4, *T* = 100.15 K, μ(MoKα) = 0.097 mm^{-1}, *Dcalc* = 1.350 g/cm^3, 14418 reflections measured (4.93° ≤ 2Θ ≤ 60.076°), 3774 unique (R_{int} = 0.0363, R_{sigma} = 0.0315) which were used in all calculations. The final R_1 was 0.0401 (I > 2σ(I)) and wR_2 was 0.1150 (all data).

3.1.4 *(4aRS,10aSR)-1,4-bis(4-chlorophenyl)dodecahydrocycloocta[e][1,2,4]triazine (4.9)*



4.9

(Ar = 4-ClC_6H_4)

Sample name: Gandelman232R

CCDC number: 2505616

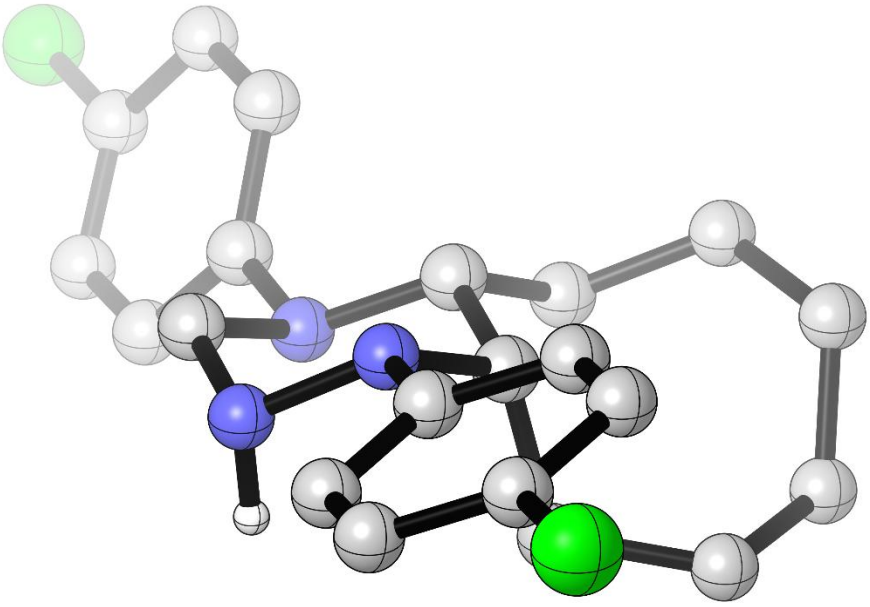


Table 1 Crystal data and structure refinement for Gandelman232R.

Identification code	Gandelman232R
Empirical formula	$C_{21}H_{25}Cl_2N_3$
Formula weight	390.34
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.33771(15)
b/Å	8.72849(9)
c/Å	13.67083(14)
α/°	90
β/°	100.0796(9)
γ/°	90
Volume/Å^3	1919.42(3)
Z	4
ρ_{calc}g/cm^3	1.351
μ/mm^{-1}	3.106
F(000)	824.0
Crystal size/mm^3	0.21 × 0.21 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.494 to 160.178
Index ranges	-20 ≤ h ≤ 14, -10 ≤ k ≤ 11, -16 ≤ l ≤ 17
Reflections collected	16318
Independent reflections	4094 [R_{int} = 0.0479, R_{sigma} = 0.0387]
Data/restraints/parameters	4094/0/239
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0380, wR_2 = 0.1042
Final R indexes [all data]	R_1 = 0.0398, wR_2 = 0.1064
Largest diff. peak/hole / e Å^{-3}	0.33/-0.44

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman232R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	335.0(2)	4533.6(4)	1189.5(2)	23.55(12)
Cl2	3367.6(2)	6510.2(4)	11740.0(2)	21.14(11)
N1	1784.8(7)	4131.0(13)	5494.5(8)	14.4(2)
N2	1495.8(7)	4724.3(15)	7142.0(9)	17.0(2)
N3	2330.6(6)	5260.5(13)	7420.2(8)	13.6(2)
C1	1245.0(8)	4952.2(17)	6088.4(10)	18.1(3)
C2	2919.6(8)	4387.0(15)	6925.7(10)	12.9(3)
C3	2665.4(8)	4582.4(15)	5796.1(10)	13.1(3)
C4	3205.8(8)	3609.3(16)	5225.9(10)	15.5(3)
C5	4132.7(8)	4026.1(17)	5380.5(10)	17.1(3)
C6	4685.4(8)	3653.4(16)	6382.9(10)	16.5(3)
C7	4500.4(8)	2134.7(16)	6868.3(10)	18.0(3)
C8	3931.0(8)	2235.6(16)	7651.7(10)	16.6(3)
C9	3021.3(8)	2709.3(15)	7290.1(10)	14.9(3)
C10	2565.9(8)	5522.4(15)	8444.8(10)	14.0(3)
C11	3382.5(8)	5981.6(17)	8836.7(10)	17.9(3)
C12	3629.0(9)	6279.9(17)	9839.5(11)	19.0(3)
C13	3056.8(9)	6131.5(16)	10474.2(10)	16.7(3)
C14	2247.3(9)	5695.2(17)	10111.2(11)	19.3(3)
C15	2003.5(8)	5388.0(16)	9106.3(11)	17.6(3)
C16	1452.6(8)	4292.3(16)	4457.6(10)	14.7(3)
C17	827.3(8)	3277.2(16)	4041.5(10)	16.7(3)
C18	472.6(8)	3360.1(17)	3043.6(11)	18.3(3)
C19	755.7(8)	4465.9(17)	2457.5(10)	17.6(3)
C20	1365.9(9)	5504.7(17)	2847.3(11)	20.4(3)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman232R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C21	1707.5(9)	5420.3(16)	3849.1(11)	19.2(3)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for Gandelman232R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	19.81(18)	36.2(2)	12.63(18)	-0.21(13)	-2.71(12)	4.96(13)
Cl2	30.9(2)	19.07(19)	11.78(18)	-1.93(11)	-0.88(13)	4.25(12)
N1	12.9(5)	16.9(6)	12.5(5)	-0.5(4)	-0.5(4)	-0.5(4)
N2	11.4(5)	22.7(6)	16.2(6)	-0.6(5)	0.6(4)	-3.0(4)
N3	10.9(5)	16.8(5)	12.8(5)	-2.3(4)	1.1(4)	-1.3(4)
C1	13.5(6)	23.5(7)	16.1(7)	-2.3(5)	-0.4(5)	1.3(5)
C2	12.6(5)	12.8(6)	13.1(6)	-1.0(5)	1.9(5)	-0.8(4)
C3	13.8(6)	13.4(6)	11.5(6)	0.0(5)	0.3(5)	-1.0(4)
C4	15.4(6)	19.1(7)	11.3(6)	-1.7(5)	0.2(5)	0.3(5)
C5	16.3(6)	21.0(7)	14.1(6)	1.9(5)	2.9(5)	-0.4(5)
C6	14.2(6)	17.5(7)	17.3(7)	-0.9(5)	1.2(5)	-0.8(5)
C7	17.7(6)	17.2(7)	18.8(7)	1.3(5)	2.3(5)	2.3(5)
C8	19.0(6)	15.1(6)	14.8(6)	2.6(5)	0.3(5)	1.5(5)
C9	16.8(6)	13.5(6)	14.3(6)	1.1(5)	2.5(5)	-0.7(5)
C10	17.0(6)	11.7(6)	13.0(6)	0.3(5)	1.3(5)	1.2(5)
C11	17.8(6)	21.2(7)	14.9(6)	-2.5(5)	3.1(5)	-4.2(5)
C12	18.2(6)	18.6(7)	18.8(7)	-2.5(5)	-0.4(5)	-2.1(5)
C13	24.8(7)	12.3(6)	11.8(6)	-1.5(5)	-0.2(5)	2.5(5)
C14	21.2(7)	21.3(7)	16.5(7)	-1.1(5)	6.5(5)	2.1(5)
C15	16.3(6)	19.5(7)	17.0(7)	-1.3(5)	3.2(5)	-0.2(5)
C16	14.1(6)	15.3(6)	13.7(6)	-0.2(5)	-0.7(5)	2.5(5)
C17	16.2(6)	16.6(6)	16.6(7)	-0.7(5)	0.9(5)	-0.5(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman232R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C18	14.7(6)	20.6(7)	18.4(7)	-4.0(5)	-1.1(5)	-0.5(5)
C19	14.9(6)	23.5(7)	13.0(6)	-1.5(5)	-1.5(5)	6.6(5)
C20	21.2(7)	21.1(7)	17.7(7)	3.3(5)	0.2(5)	0.9(5)
C21	19.8(6)	17.6(7)	18.2(7)	1.1(5)	-2.0(5)	-1.9(5)

Table 4 Bond Lengths for Gandelman232R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C19	1.7503(14)	C7	C8	1.5391(18)
Cl2	C13	1.7475(14)	C8	C9	1.5386(18)
N1	C1	1.4837(17)	C10	C11	1.4063(19)
N1	C3	1.4791(16)	C10	C15	1.4022(18)
N1	C16	1.4332(17)	C11	C12	1.384(2)
N2	N3	1.4292(15)	C12	C13	1.3884(19)
N2	C1	1.4407(18)	C13	C14	1.382(2)
N3	C2	1.4805(16)	C14	C15	1.388(2)
N3	C10	1.4048(17)	C16	C17	1.3960(19)
C2	C3	1.5369(18)	C16	C21	1.3986(19)
C2	C9	1.5464(18)	C17	C18	1.3876(19)
C3	C4	1.5328(17)	C18	C19	1.385(2)
C4	C5	1.5357(18)	C19	C20	1.383(2)
C5	C6	1.5380(18)	C20	C21	1.387(2)
C6	C7	1.5359(19)			

Table 5 Bond Angles for Gandelman232R.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C3	N1	C1	111.17(10)	N3	C10	C11	120.13(11)

Table 5 Bond Angles for Gandelman232R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C16	N1	C1	109.59(10)	C15	C10	N3	122.25(12)
C16	N1	C3	115.53(10)	C15	C10	C11	117.59(12)
N3	N2	C1	108.19(10)	C12	C11	C10	121.54(12)
N2	N3	C2	112.09(10)	C11	C12	C13	119.36(13)
C10	N3	N2	113.61(10)	C12	C13	Cl2	119.37(11)
C10	N3	C2	116.93(10)	C14	C13	Cl2	120.10(10)
N2	C1	N1	112.84(11)	C14	C13	C12	120.53(13)
N3	C2	C3	108.59(10)	C13	C14	C15	119.96(12)
N3	C2	C9	112.48(10)	C14	C15	C10	121.02(13)
C3	C2	C9	115.06(10)	C17	C16	N1	117.65(12)
N1	C3	C2	109.22(10)	C17	C16	C21	118.50(13)
N1	C3	C4	109.23(10)	C21	C16	N1	123.84(12)
C4	C3	C2	111.79(10)	C18	C17	C16	121.17(13)
C3	C4	C5	116.15(11)	C19	C18	C17	118.74(13)
C4	C5	C6	118.91(11)	C18	C19	Cl1	118.91(11)
C7	C6	C5	115.99(11)	C20	C19	Cl1	119.41(11)
C6	C7	C8	116.10(11)	C20	C19	C18	121.68(13)
C9	C8	C7	117.34(11)	C19	C20	C21	118.93(13)
C8	C9	C2	113.66(10)	C20	C21	C16	120.95(13)

Table 6 Torsion Angles for Gandelman232R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C19	C20	C21	-178.66(10)	C3	C2	C9	C8	108.16(12)
Cl2	C13	C14	C15	-179.69(11)	C3	C4	C5	C6	71.57(16)
N1	C3	C4	C5	174.76(11)	C4	C5	C6	C7	37.92(17)
N1	C16	C17	C18	179.87(12)	C5	C6	C7	C8	-95.90(14)
N1	C16	C21	C20	179.38(13)	C6	C7	C8	C9	66.29(16)

Table 6 Torsion Angles for Gandelman232R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N2	N3	C2	C3	60.80(13)	C7	C8	C9	C2	-67.58(15)
N2	N3	C2	C9	-67.73(14)	C9	C2	C3	N1	72.48(13)
N2	N3	C10	C11	176.92(12)	C9	C2	C3	C4	-48.52(14)
N2	N3	C10	C15	-5.07(18)	C10	N3	C2	C3	-165.50(11)
N3	N2	C1	N1	59.21(14)	C10	N3	C2	C9	65.97(14)
N3	C2	C3	N1	-54.58(13)	C10	C11	C12	C13	-0.4(2)
N3	C2	C3	C4	-175.58(10)	C11	C10	C15	C14	-0.1(2)
N3	C2	C9	C8	-126.78(11)	C11	C12	C13	Cl2	-179.93(11)
N3	C10	C11	C12	178.62(13)	C11	C12	C13	C14	-0.2(2)
N3	C10	C15	C14	-178.18(13)	C12	C13	C14	C15	0.6(2)
C1	N1	C3	C2	52.74(14)	C13	C14	C15	C10	-0.4(2)
C1	N1	C3	C4	175.28(11)	C15	C10	C11	C12	0.5(2)
C1	N1	C16	C17	-83.90(14)	C16	N1	C1	N2	174.60(11)
C1	N1	C16	C21	94.84(15)	C16	N1	C3	C2	178.43(10)
C1	N2	N3	C2	-62.32(14)	C16	N1	C3	C4	-59.03(14)
C1	N2	N3	C10	162.38(11)	C16	C17	C18	C19	0.6(2)
C2	N3	C10	C11	43.89(17)	C17	C16	C21	C20	-1.9(2)
C2	N3	C10	C15	-138.10(13)	C17	C18	C19	Cl1	177.86(10)
C2	C3	C4	C5	-64.25(15)	C17	C18	C19	C20	-1.6(2)
C3	N1	C1	N2	-56.47(15)	C18	C19	C20	C21	0.7(2)
C3	N1	C16	C17	149.60(12)	C19	C20	C21	C16	1.0(2)
C3	N1	C16	C21	-31.66(18)	C21	C16	C17	C18	1.1(2)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman232R.

Atom	*x*	*y*	*z*	U(eq)
H2	1461(12)	3700(20)	7273(14)	22(5)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman232R.

Atom	*x*	*y*	*z*	U(eq)
H1A	1257.52	6061.66	5941.14	22
H1B	665.17	4593.36	5886.44	22
H2A	3475.11	4887.62	7117.36	15
H3	2726.6	5684.93	5623.63	16
H4A	2976.25	3689.24	4507.93	19
H4B	3157.13	2524.82	5419.87	19
H5A	4172.86	5141.92	5267.89	21
H5B	4375.61	3505.33	4854.97	21
H6A	5271.57	3636.75	6285.13	20
H6B	4629.71	4495.64	6851.83	20
H7A	5035.43	1675.31	7185.4	22
H7B	4241.81	1426.27	6337.53	22
H8A	3931	1221.83	7976.48	20
H8B	4181.05	2975.54	8167.31	20
H9A	2706.82	2566.84	7840.11	18
H9B	2774.81	2022.22	6740.66	18
H11	3774.21	6089.59	8403.12	22
H12	4184.45	6583.17	10091.05	23
H14	1858.09	5605.59	10549.33	23
H15	1447.17	5081.95	8862.86	21
H17	641.42	2516.26	4448.65	20
H18	43.55	2671.2	2767.76	22
H20	1548.02	6263.56	2435.72	24
H21	2120.42	6139.14	4125.67	23

Experimental

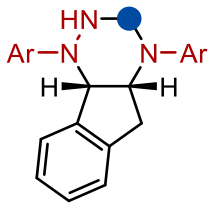
Single crystals of $C_{21}H_{25}Cl_2N_3$ **[Gandelman232R]** were obtained by slow evaporation of Et_2O/Hexane solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution

program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman232R]

Crystal Data for $C_{21}H_{25}Cl_2N_3$ (*M* =390.34 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 16.33771(15) Å, *b* = 8.72849(9) Å, *c* = 13.67083(14) Å, *β* = 100.0796(9)°, *V* = 1919.42(3) Å^3, *Z* = 4, *T* = 100.15 K, μ(CuKα) = 3.106 mm^{-1}, *Dcalc* = 1.351 g/cm^3, 16318 reflections measured (5.494° ≤ 2Θ ≤ 160.178°), 4094 unique (R_{int} = 0.0479, R_{sigma} = 0.0387) which were used in all calculations. The final R_1 was 0.0380 (I > 2σ(I)) and wR_2 was 0.1064 (all data).

3.1.5 *(4aRS,9bSR)-1,4-bis(4-chlorophenyl)-2,3,4,4a,5,9b-hexahydro-1H-indeno[2,1-e][1,2,4]triazine (4.11)*



4.11

(Ar = 4-ClC_6H_4)

Sample name: Gandelman247R

CCDC number: 2505617

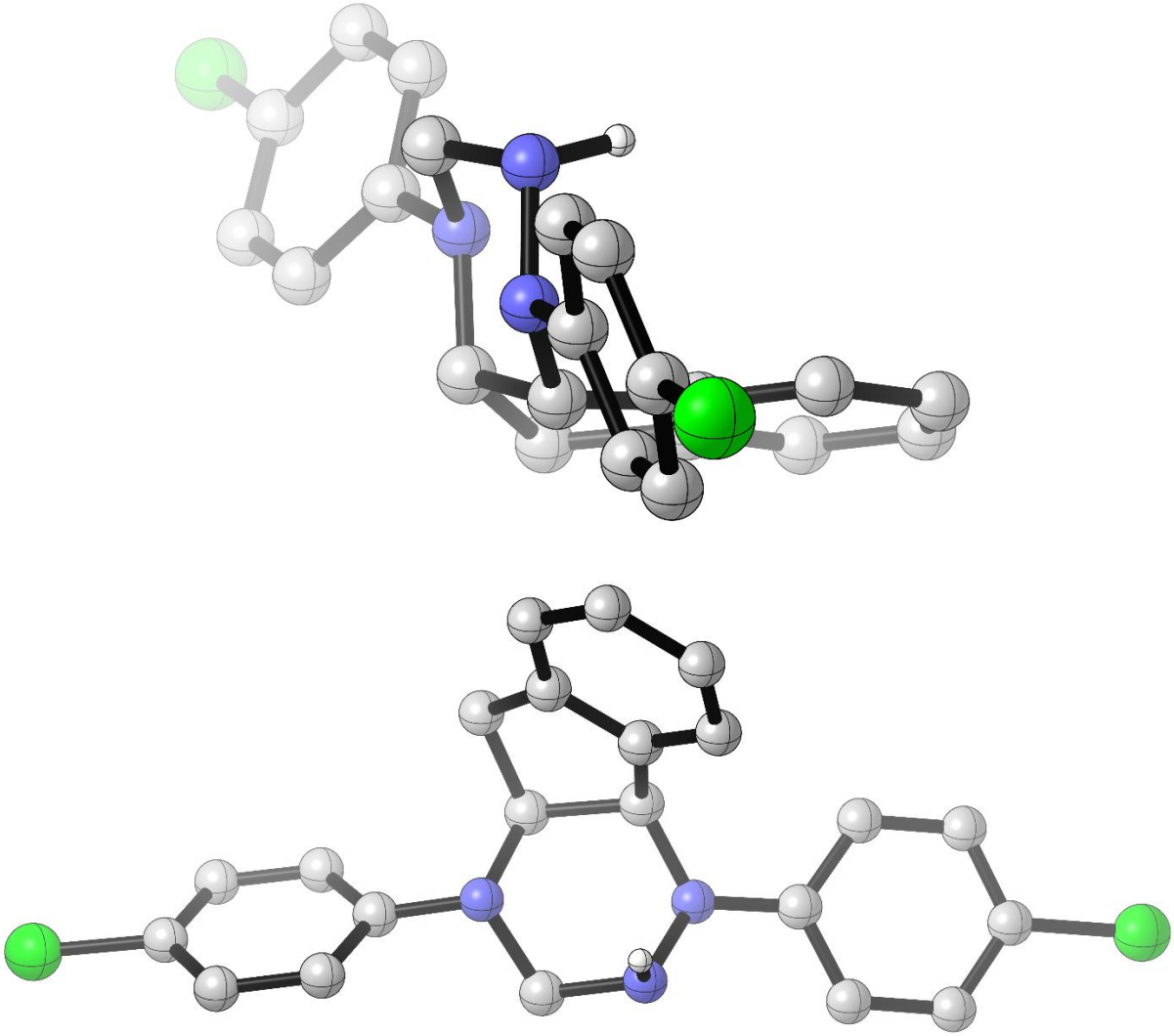


Table 1 Crystal data and structure refinement for Gandelman247R.

Identification code	Gandelman247R
Empirical formula	$C_{22}H_{19}Cl_2N_3$
Formula weight	396.30
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	7.58648(17)
b/Å	10.8739(2)
c/Å	12.5337(2)
α/°	66.0924(17)
β/°	87.9926(16)
γ/°	87.9546(16)
Volume/Å^3	944.41(3)
Z	2
ρ_{calc}g/cm^3	1.394
μ/mm^{-1}	3.174
F(000)	412.0
Crystal size/mm^3	0.24 × 0.18 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.718 to 159.774
Index ranges	-9 ≤ h ≤ 9, -13 ≤ k ≤ 13, -15 ≤ l ≤ 15
Reflections collected	13428
Independent reflections	4008 [R_{int} = 0.0773, R_{sigma} = 0.0664]
Data/restraints/parameters	4008/0/248
Goodness-of-fit on F^2	1.130
Final R indexes [I>=2σ (I)]	R_1 = 0.0598, wR_2 = 0.1794
Final R indexes [all data]	R_1 = 0.0637, wR_2 = 0.1851
Largest diff. peak/hole / e Å^{-3}	0.48/-0.56

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman247R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	-3325.3(7)	959.8(6)	9616.2(5)	36.2(2)
N1	2542(2)	4813.6(16)	7969.1(13)	21.2(3)
C1	3206(3)	5266(2)	8828.6(15)	24.3(4)
Cl2	11879.9(7)	9651.1(5)	7085.4(5)	33.6(2)
N2	5662(2)	6239.5(16)	7652.5(13)	20.4(3)
C2	3944(3)	4562.9(19)	7237.6(15)	21.1(4)
N3	4195(2)	6488.6(16)	8286.9(13)	22.1(4)
C3	5197(3)	5779.6(18)	6760.1(14)	19.7(4)
C4	4246(3)	6769.0(19)	5687.9(14)	20.3(4)
C5	4476(3)	8144(2)	5075.8(15)	23.5(4)
C6	3512(3)	8817(2)	4066.9(17)	28.2(4)
C7	2355(3)	8120(2)	3685.9(17)	30.0(5)
C8	2130(3)	6745(2)	4304.2(17)	28.0(4)
C9	3087(3)	6070(2)	5314.0(15)	22.9(4)
C10	3113(3)	4593(2)	6120.5(16)	23.3(4)
C11	1217(3)	3831.5(19)	8416.8(15)	20.1(4)
C12	-391(3)	4208.3(19)	8796.0(15)	22.9(4)
C13	-1773(3)	3321(2)	9184.0(16)	25.0(4)
C14	-1555(3)	2046(2)	9189.2(16)	25.6(4)
C15	23(3)	1641(2)	8841.1(16)	25.2(4)
C16	1420(3)	2527(2)	8464.0(16)	23.3(4)
C17	7088(3)	7090.6(18)	7474.7(15)	19.7(4)
C18	8323(3)	7333(2)	6548.4(17)	24.6(4)
C19	9791(3)	8106(2)	6433.6(18)	26.4(4)
C20	10051(3)	8646(2)	7247.5(18)	25.2(4)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman247R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C21	8863(3)	8419(2)	8167.2(16)	25.2(4)
C22	7381(3)	7662.7(18)	8274.0(15)	22.1(4)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for Gandelman247R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	29.4(3)	32.7(3)	42.1(3)	-9.8(2)	2.0(2)	-15.2(2)
N1	25.5(8)	17.7(7)	20.7(7)	-8.2(6)	4.7(6)	-5.7(6)
C1	31.3(10)	21.5(9)	19.6(8)	-7.6(7)	2.0(7)	-8.1(8)
Cl2	24.5(3)	29.5(3)	51.1(3)	-20.1(2)	-0.4(2)	-8.1(2)
N2	24.4(8)	18.0(8)	19.3(7)	-7.9(6)	1.0(6)	-4.1(6)
C2	25.2(9)	17.4(8)	20.7(8)	-7.5(7)	1.4(7)	-2.6(7)
N3	27.6(8)	17.7(7)	21.4(7)	-8.3(6)	4.8(6)	-5.3(6)
C3	24.0(9)	17.2(8)	17.7(7)	-6.6(7)	1.3(6)	-4.0(7)
C4	22.1(9)	20.2(9)	17.2(7)	-6.3(7)	1.5(6)	-2.6(7)
C5	27.7(10)	21.0(9)	20.6(8)	-6.8(7)	0.3(7)	-4.9(7)
C6	34.0(11)	22.9(10)	22.1(8)	-3.0(7)	-2.9(7)	-1.8(8)
C7	32.1(11)	33.6(11)	21.9(8)	-8.5(8)	-6.5(7)	2.9(9)
C8	28.6(10)	32.7(11)	25.1(9)	-13.9(8)	-1.7(7)	-3.3(8)
C9	22.8(9)	26.4(10)	20.7(8)	-10.7(7)	3.7(7)	-5.4(7)
C10	26.7(9)	22.1(9)	23.4(8)	-11.1(7)	3.6(7)	-7.3(7)
C11	24.1(9)	17.1(8)	17.0(7)	-4.4(6)	0.2(6)	-4.6(7)
C12	27.3(10)	17.8(8)	21.5(8)	-6.0(7)	0.0(7)	-0.6(7)
C13	23.2(9)	27.9(10)	21.7(8)	-7.6(7)	-0.7(7)	-3.2(8)
C14	26.0(10)	25.1(10)	21.7(8)	-4.8(7)	0.2(7)	-8.5(8)
C15	31.7(10)	18.7(9)	23.7(8)	-6.6(7)	-2.4(7)	-5.4(8)
C16	26.5(10)	18.6(9)	23.2(8)	-6.9(7)	1.2(7)	-3.4(7)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman247R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C17	23.5(9)	12.8(8)	19.5(7)	-2.9(6)	-2.7(6)	-0.9(7)
C18	25.9(10)	23.2(9)	26.5(8)	-11.7(7)	0.0(7)	-3.2(8)
C19	23.9(9)	25.9(10)	30.0(9)	-11.7(8)	1.0(7)	-2.8(8)
C20	21.6(9)	18.9(9)	34.8(9)	-10.0(8)	-4.8(7)	-1.5(7)
C21	32.6(10)	17.2(9)	24.1(8)	-6.0(7)	-6.1(7)	-3.0(8)
C22	29.8(10)	14.6(8)	19.0(8)	-3.4(7)	-2.2(7)	-2.1(7)

Table 4 Bond Lengths for Gandelman247R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C14	1.742(2)	C7	C8	1.391(3)
N1	C1	1.464(2)	C8	C9	1.393(3)
N1	C2	1.470(2)	C9	C10	1.512(3)
N1	C11	1.420(2)	C11	C12	1.401(3)
C1	N3	1.447(2)	C11	C16	1.398(3)
Cl2	C20	1.751(2)	C12	C13	1.387(3)
N2	N3	1.427(2)	C13	C14	1.387(3)
N2	C3	1.456(2)	C14	C15	1.378(3)
N2	C17	1.402(2)	C15	C16	1.394(3)
C2	C3	1.556(2)	C17	C18	1.410(3)
C2	C10	1.544(3)	C17	C22	1.404(3)
C3	C4	1.525(2)	C18	C19	1.387(3)
C4	C5	1.391(3)	C19	C20	1.390(3)
C4	C9	1.391(3)	C20	C21	1.384(3)
C5	C6	1.395(3)	C21	C22	1.387(3)
C6	C7	1.394(3)			

Table 5 Bond Angles for Gandelman247R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C2	113.29(16)	C8	C9	C10	129.23(18)
C11	N1	C1	114.04(14)	C9	C10	C2	103.41(15)
C11	N1	C2	116.62(15)	C12	C11	N1	117.99(17)
N3	C1	N1	112.16(14)	C16	C11	N1	123.31(17)
N3	N2	C3	114.66(15)	C16	C11	C12	118.67(17)
C17	N2	N3	114.99(14)	C13	C12	C11	120.91(18)
C17	N2	C3	120.64(14)	C12	C13	C14	119.26(18)
N1	C2	C3	109.46(15)	C13	C14	Cl1	119.14(16)
N1	C2	C10	108.57(16)	C15	C14	Cl1	119.80(16)
C10	C2	C3	102.98(13)	C15	C14	C13	121.04(18)
N2	N3	C1	108.61(15)	C14	C15	C16	119.70(19)
N2	C3	C2	112.57(13)	C15	C16	C11	120.38(18)
N2	C3	C4	118.18(16)	N2	C17	C18	121.99(17)
C4	C3	C2	102.99(15)	N2	C17	C22	119.87(16)
C5	C4	C3	129.34(18)	C22	C17	C18	118.02(18)
C5	C4	C9	121.42(18)	C19	C18	C17	121.06(18)
C9	C4	C3	109.14(16)	C18	C19	C20	119.44(18)
C4	C5	C6	118.30(18)	C19	C20	Cl2	119.43(16)
C7	C6	C5	120.49(19)	C21	C20	Cl2	119.94(16)
C8	C7	C6	120.84(19)	C21	C20	C19	120.62(19)
C7	C8	C9	118.9(2)	C20	C21	C22	120.05(19)
C4	C9	C8	120.10(19)	C21	C22	C17	120.79(17)
C4	C9	C10	110.66(17)				

Table 6 Torsion Angles for Gandelman247R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C14	C15	C16	177.94(14)	C4	C5	C6	C7	-0.2(3)

Table 6 Torsion Angles for Gandelman247R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C1	N3	N2	-60.0(2)	C4	C9	C10	C2	18.2(2)
N1	C2	C3	N2	44.7(2)	C5	C4	C9	C8	0.3(3)
N1	C2	C3	C4	-83.68(17)	C5	C4	C9	C10	178.98(16)
N1	C2	C10	C9	85.59(17)	C5	C6	C7	C8	0.3(3)
N1	C11	C12	C13	176.53(16)	C6	C7	C8	C9	-0.1(3)
N1	C11	C16	C15	-175.67(17)	C7	C8	C9	C4	-0.2(3)
C1	N1	C2	C3	-48.4(2)	C7	C8	C9	C10	-178.61(19)
C1	N1	C2	C10	-160.11(15)	C8	C9	C10	C2	-163.21(19)
C1	N1	C11	C12	64.4(2)	C9	C4	C5	C6	-0.1(3)
C1	N1	C11	C16	-117.55(19)	C10	C2	C3	N2	160.04(16)
Cl2	C20	C21	C22	177.72(15)	C10	C2	C3	C4	31.67(17)
N2	C3	C4	C5	37.2(3)	C11	N1	C1	N3	-165.11(16)
N2	C3	C4	C9	-146.45(16)	C11	N1	C2	C3	176.22(15)
N2	C17	C18	C19	-175.63(18)	C11	N1	C2	C10	64.5(2)
N2	C17	C22	C21	174.74(17)	C11	C12	C13	C14	-0.3(3)
C2	N1	C1	N3	58.3(2)	C12	C11	C16	C15	2.3(3)
C2	N1	C11	C12	-160.49(17)	C12	C13	C14	Cl1	-177.20(14)
C2	N1	C11	C16	17.5(3)	C12	C13	C14	C15	1.5(3)
C2	C3	C4	C5	162.00(18)	C13	C14	C15	C16	-0.8(3)
C2	C3	C4	C9	-21.66(19)	C14	C15	C16	C11	-1.2(3)
N3	N2	C3	C2	-51.3(2)	C16	C11	C12	C13	-1.6(3)
N3	N2	C3	C4	68.6(2)	C17	N2	N3	C1	-155.81(15)
N3	N2	C17	C18	-156.37(17)	C17	N2	C3	C2	164.36(16)
N3	N2	C17	C22	27.7(2)	C17	N2	C3	C4	-75.7(2)
C3	N2	N3	C1	57.8(2)	C17	C18	C19	C20	0.2(3)
C3	N2	C17	C18	-12.2(3)	C18	C17	C22	C21	-1.4(3)
C3	N2	C17	C22	171.84(16)	C18	C19	C20	Cl2	-178.69(16)

Table 6 Torsion Angles for Gandelman247R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C3	C2	C10	C9	-30.40(18)	C18	C19	C20	C21	0.1(3)
C3	C4	C5	C6	175.88(18)	C19	C20	C21	C22	-1.0(3)
C3	C4	C9	C8	-176.42(17)	C20	C21	C22	C17	1.7(3)
C3	C4	C9	C10	2.3(2)	C22	C17	C18	C19	0.4(3)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman247R.

Atom	*x*	*y*	*z*	U(eq)
H1A	2198.92	5424.67	9284.82	29
H1B	3973.48	4549.42	9376.48	29
H2	4601.21	3696.92	7668.11	25
H3	3410(40)	7170(30)	7750(20)	25(6)
H3A	6312.39	5475.63	6481.59	24
H5	5269.88	8613.4	5338.08	28
H6	3644.89	9756.89	3636.28	34
H7	1710.57	8590.48	2995.29	36
H8	1338.87	6274.32	4042.35	34
H10A	3838.18	4059.91	5780.84	28
H10B	1904.33	4236.92	6283.57	28
H12	-536.53	5083.74	8787.22	27
H13	-2857	3582.88	9443.38	30
H15	158.29	761.13	8857.98	30
H16	2515.33	2243.64	8237.74	28
H18	8147.73	6960.76	5994.06	30
H19	10611.7	8265.08	5804.09	32
H21	9062.63	8780.01	8725.88	30
H22	6554.03	7530.7	8895.45	27

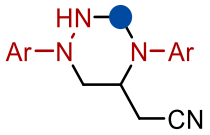
Experimental

Single crystals of $C_{22}H_{19}Cl_2N_3$ **[Gandelman247R]** were obtained by slow evaporation of Et_2O/Hexane solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman247R]

Crystal Data for $C_{22}H_{19}Cl_2N_3$ (M =396.30 g/mol): triclinic, space group P-1 (no. 2), a = 7.58648(17) Å, b = 10.8739(2) Å, c = 12.5337(2) Å, α = 66.0924(17)°, β = 87.9926(16)°, γ = 87.9546(16)°, V = 944.41(3) Å^3, Z = 2, T = 100.15 K, μ(CuKα) = 3.174 mm^{-1}, $Dcalc$ = 1.394 g/cm^3, 13428 reflections measured (7.718° ≤ 2Θ ≤ 159.774°), 4008 unique (R_{int} = 0.0773, R_{sigma} = 0.0664) which were used in all calculations. The final R_1 was 0.0598 (I > 2σ(I)) and wR_2 was 0.1851 (all data).

3.1.6 2-(1,4-bis(4-chlorophenyl)-1,2,4-triazinan-5-yl)acetonitrile (4.21)



4.21

(Ar = 4-ClC_6H_4)

Sample name: Gandelman242R

CCDC number: 2505618

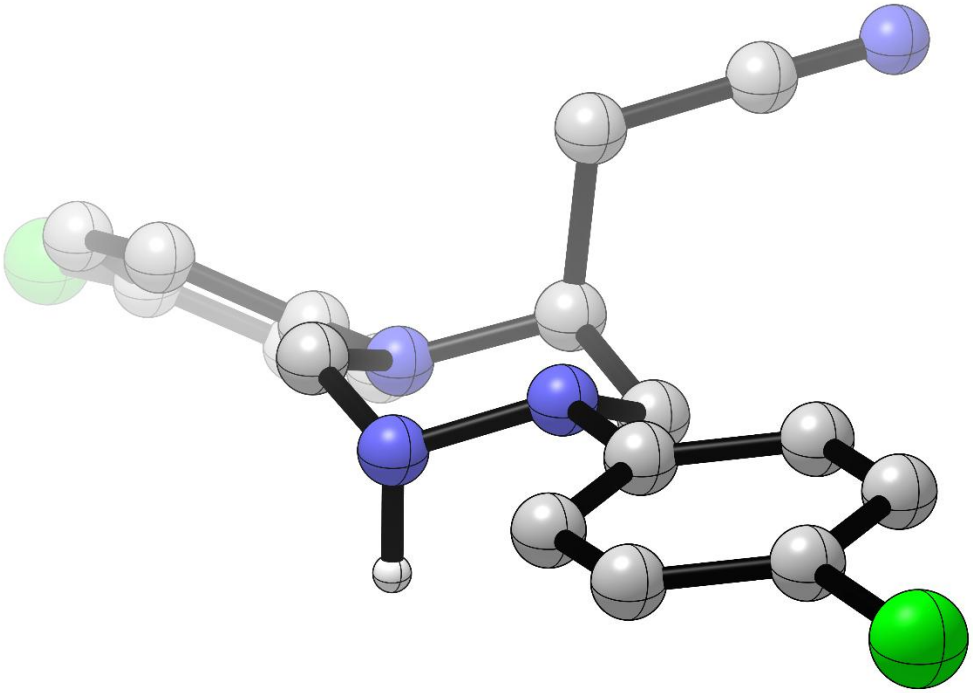


Table 1 Crystal data and structure refinement for Gandelman242R.

Identification code	Gandelman242R
Empirical formula	$C_{17}H_{16}Cl_2N_4$
Formula weight	347.24
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.72600(18)
b/Å	19.9035(4)
c/Å	9.2230(2)
α/°	90
β/°	99.762(2)
γ/°	90
Volume/Å^3	1578.63(6)
Z	4
ρ_{calc}g/cm^3	1.461
μ/mm^{-1}	3.727
F(000)	720.0
Crystal size/mm^3	0.18 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.886 to 160.32
Index ranges	-10 ≤ h ≤ 10, -24 ≤ k ≤ 25, -11 ≤ l ≤ 11
Reflections collected	12287
Independent reflections	3367 [R_{int} = 0.1275, R_{sigma} = 0.0770]
Data/restraints/parameters	3367/224/218
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0744, wR_2 = 0.2085
Final R indexes [all data]	R_1 = 0.0796, wR_2 = 0.2173
Largest diff. peak/hole / e Å^{-3}	0.66/-0.55

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman242R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	5782.9(7)	1403.5(3)	4818.8(8)	40.8(3)
N1	5500(2)	4278.2(10)	3068(2)	29.7(5)
C1	5742(3)	2243.4(12)	4264(3)	30.0(5)
Cl2	4039(5)	8504(4)	774(6)	35.9(9)
Cl2A	4190(30)	8366(18)	600(20)	39(3)
N2	3972(2)	5183.0(10)	1808(3)	31.7(5)
C2	5052(3)	2417.6(12)	2851(3)	30.1(5)
N3	5314(2)	5602.7(10)	2083(2)	27.5(4)
C3	4992(3)	3089.6(11)	2428(3)	27.5(5)
N4	10674(3)	5198.2(13)	3174(3)	44.5(6)
C4	5629(3)	3592.0(11)	3421(3)	26.2(5)
C5	6359(3)	3394.7(12)	4840(3)	29.0(5)
C6	6400(3)	2728.2(12)	5266(3)	29.9(5)
C7	4407(3)	4494.1(12)	1774(3)	35.3(6)
C8	6356(3)	5433.8(12)	3453(3)	31.4(5)
C9	6871(3)	4709.0(12)	3407(3)	31.4(5)
C10	7991(3)	4608.1(13)	2274(3)	35.3(6)
C11	9498(3)	4943.7(14)	2763(3)	37.3(6)
C12	4976(3)	6286.3(12)	1786(3)	26.5(5)
C13	3529(3)	6498.1(12)	1030(3)	27.7(5)
C14	3246(3)	7168.7(12)	689(3)	29.9(5)
C15	4410(3)	7643.9(12)	1127(3)	30.0(5)
C16	5842(3)	7445.1(12)	1880(3)	30.7(5)
C17	6135(3)	6775.8(12)	2201(3)	29.8(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman242R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	26.1(4)	34.1(4)	56.0(5)	8.3(2)	-10.6(3)	-1.5(2)
N1	19.2(10)	31.8(10)	33.2(10)	1.1(8)	-9.7(8)	-4.0(7)
C1	15.5(11)	31.0(12)	40.7(13)	3.1(9)	-3.5(9)	-0.5(8)
Cl2	31.6(8)	24.9(13)	44.8(11)	1.3(8)	-11.7(7)	4.1(7)
Cl2A	37(5)	26(5)	48(5)	-20(6)	-14(3)	17(5)
N2	15.7(9)	35.6(11)	39.6(11)	1.2(8)	-7.3(8)	-3.5(7)
C2	15.5(10)	32.5(11)	39.2(13)	-2.1(9)	-4.1(9)	-0.7(8)
N3	14.3(9)	31.7(10)	32.6(10)	-3.1(7)	-6.7(7)	-0.8(7)
C3	13.6(10)	34.7(11)	31.4(11)	-1.2(9)	-4.2(8)	-1.6(8)
N4	24.0(12)	52.3(14)	54.0(15)	5.5(11)	-2.3(10)	-4.5(9)
C4	13.0(10)	32.2(11)	31.5(12)	-1.1(8)	-2.0(9)	0.1(7)
C5	19.5(11)	35.0(11)	30.1(12)	-3.2(9)	-2.6(9)	0.8(9)
C6	16.7(11)	39.0(12)	31.5(11)	1.8(9)	-3.5(9)	1.2(8)
C7	18.6(12)	33.9(12)	47.0(15)	1.6(10)	-13.2(10)	-1.1(8)
C8	22.4(11)	31.9(11)	34.8(12)	-1.0(9)	-9.6(9)	-3.0(8)
C9	21.0(11)	31.7(11)	36.4(13)	-0.6(9)	-9.8(9)	-1.7(8)
C10	20.6(12)	36.4(12)	45.2(14)	-1.2(10)	-5.1(10)	2.2(9)
C11	21.1(12)	44.0(14)	43.7(14)	3.7(11)	-3.7(10)	1.4(9)
C12	15.2(10)	33.9(11)	28.4(11)	-1.3(8)	-2.0(8)	0.4(8)
C13	14.1(11)	36.7(12)	29.8(12)	-3.9(8)	-3.5(9)	-0.3(8)
C14	16.6(11)	39.1(12)	30.8(11)	-2.2(9)	-5.4(8)	2.9(9)
C15	22.6(12)	33.6(11)	30.8(12)	0.5(9)	-3.6(9)	0.0(9)
C16	20.0(11)	34.3(12)	34.5(12)	2.4(9)	-5.4(9)	-3.4(8)
C17	15.1(10)	36.2(12)	35.2(12)	2.2(9)	-4.1(8)	-1.4(8)

Table 4 Bond Lengths for Gandelman242R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C1	1.747(2)	C3	C4	1.405(3)
N1	C4	1.404(3)	N4	C11	1.150(4)
N1	C7	1.460(3)	C4	C5	1.410(3)
N1	C9	1.462(3)	C5	C6	1.382(4)
C1	C2	1.384(4)	C8	C9	1.514(3)
C1	C6	1.391(3)	C9	C10	1.560(4)
Cl2	C15	1.763(7)	C10	C11	1.475(4)
Cl2A	C15	1.52(3)	C12	C13	1.400(3)
N2	N3	1.426(3)	C12	C17	1.409(3)
N2	C7	1.425(3)	C13	C14	1.384(3)
C2	C3	1.392(3)	C14	C15	1.396(3)
N3	C8	1.465(3)	C15	C16	1.381(3)
N3	C12	1.409(3)	C16	C17	1.379(3)

Table 5 Bond Angles for Gandelman242R.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C4	N1	C7	119.42(19)	N3	C8	C9	109.76(19)
C4	N1	C9	119.38(19)	N1	C9	C8	109.2(2)
C7	N1	C9	113.53(19)	N1	C9	C10	111.4(2)
C2	C1	Cl1	119.98(19)	C8	C9	C10	111.4(2)
C2	C1	C6	121.1(2)	C11	C10	C9	111.4(2)
C6	C1	Cl1	118.93(19)	N4	C11	C10	178.4(3)
C7	N2	N3	110.68(19)	N3	C12	C17	119.8(2)
C1	C2	C3	119.6(2)	C13	C12	N3	121.9(2)
N2	N3	C8	112.93(19)	C13	C12	C17	118.2(2)
C12	N3	N2	113.09(18)	C14	C13	C12	121.0(2)
C12	N3	C8	117.91(18)	C13	C14	C15	119.7(2)

Table 5 Bond Angles for Gandelman242R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C3	C4	120.6(2)	C14	C15	Cl2	120.2(2)
N1	C4	C3	122.3(2)	C14	C15	Cl2A	120.1(9)
N1	C4	C5	119.4(2)	C16	C15	Cl2	119.6(2)
C3	C4	C5	118.2(2)	C16	C15	Cl2A	119.1(9)
C6	C5	C4	121.1(2)	C16	C15	C14	120.2(2)
C5	C6	C1	119.3(2)	C17	C16	C15	120.2(2)
N2	C7	N1	113.9(2)	C16	C17	C12	120.7(2)

Table 6 Torsion Angles for Gandelman242R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C1	C2	C3	178.48(18)	C6	C1	C2	C3	-1.0(4)
Cl1	C1	C6	C5	-179.38(18)	C7	N1	C4	C3	13.3(4)
N1	C4	C5	C6	174.9(2)	C7	N1	C4	C5	-163.8(2)
N1	C9	C10	C11	-169.4(2)	C7	N1	C9	C8	51.0(3)
C1	C2	C3	C4	0.2(4)	C7	N1	C9	C10	-72.4(3)
Cl2	C15	C16	C17	178.2(3)	C7	N2	N3	C8	-57.1(3)
Cl2A	C15	C16	C17	-171.5(12)	C7	N2	N3	C12	165.8(2)
N2	N3	C8	C9	58.3(3)	C8	N3	C12	C13	-146.6(2)
N2	N3	C12	C13	-11.8(3)	C8	N3	C12	C17	36.0(3)
N2	N3	C12	C17	170.8(2)	C8	C9	C10	C11	68.4(3)
C2	C1	C6	C5	0.1(4)	C9	N1	C4	C3	-134.2(2)
C2	C3	C4	N1	-175.7(2)	C9	N1	C4	C5	48.7(3)
C2	C3	C4	C5	1.4(3)	C9	N1	C7	N2	-51.7(3)
N3	N2	C7	N1	52.6(3)	C12	N3	C8	C9	-166.8(2)
N3	C8	C9	N1	-53.7(3)	C12	C13	C14	C15	-1.1(4)
N3	C8	C9	C10	69.7(3)	C13	C12	C17	C16	0.5(4)
N3	C12	C13	C14	-176.9(2)	C13	C14	C15	Cl2	-177.1(3)

Table 6 Torsion Angles for Gandelman242R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N3	C12	C17	C16	178.0(2)	C13	C14	C15	Cl2A	172.4(13)
C3	C4	C5	C6	-2.4(4)	C13	C14	C15	C16	0.8(4)
C4	N1	C7	N2	159.0(2)	C14	C15	C16	C17	0.2(4)
C4	N1	C9	C8	-159.6(2)	C15	C16	C17	C12	-0.9(4)
C4	N1	C9	C10	76.9(3)	C17	C12	C13	C14	0.5(4)
C4	C5	C6	C1	1.6(4)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman242R.

Atom	*x*	*y*	*z*	U(eq)
H2	3376.44	5236.95	2679.8	38
H2A	4622.17	2080.32	2173.57	36
H3	4515.62	3209.77	1459.57	33
H5	6830.93	3725.41	5513.49	35
H6	6871.7	2602.63	6232.37	36
H7A	4881.77	4414.94	887.55	42
H7B	3459.16	4213.72	1686.68	42
H8A	5809.37	5501.6	4299.04	38
H8B	7275.51	5732.78	3582.21	38
H9	7442.05	4584.84	4404.05	38
H10A	8166.26	4121.76	2147.37	42
H10B	7503.48	4792.99	1309.03	42
H13	2729.33	6176.68	746.73	33
H14	2265.71	7305.1	159.84	36
H16	6628.63	7770.59	2179.09	37
H17	7128.44	6643.1	2707.75	36

Table 8 Atomic Occupancy for Gandelman242R.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
Cl2	0.88(4)	Cl2A	0.12(4)		

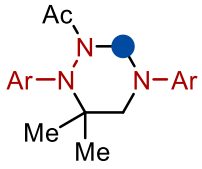
Experimental

Single crystals of $C_{17}H_{16}Cl_2N_4$ **[Gandelman242R]** were obtained by slow evaporation of C_6H_6 solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman242R]

Crystal Data for $C_{17}H_{16}Cl_2N_4$ (M =347.24 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 8.72600(18) Å, b = 19.9035(4) Å, c = 9.2230(2) Å, β = 99.762(2)°, V = 1578.63(6) Å^3, Z = 4, T = 100.15 K, μ(CuKα) = 3.727 mm^{-1}, *Dcalc* = 1.461 g/cm^3, 12287 reflections measured (8.886° ≤ 2Θ ≤ 160.32°), 3367 unique (R_{int} = 0.1275, R_{sigma} = 0.0770) which were used in all calculations. The final R_1 was 0.0744 (I > 2σ(I)) and wR_2 was 0.2173 (all data).

3.1.7 *1-(1,4-bis(4-fluorophenyl)-6,6-dimethyl-1,2,4-triazinan-2-yl)ethan-1-one (4.22)*

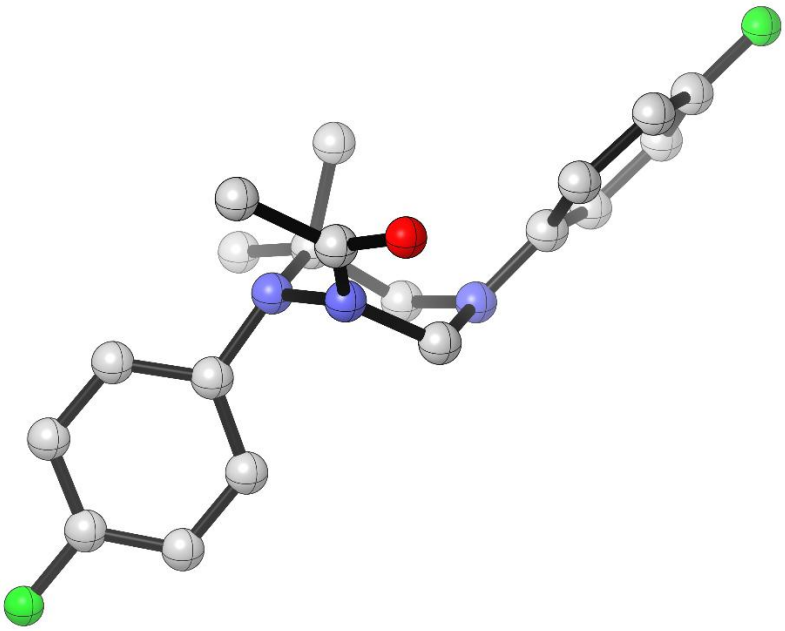


4.22

(Ar = 4-FC_6H_4)

Sample name: Gandelman240R

CCDC number: 2505619



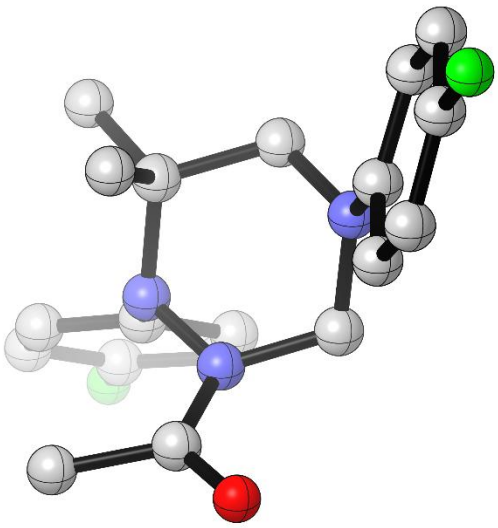


Table 1 Crystal data and structure refinement for Gandelman240R.

Identification code	Gandelman240R
Empirical formula	$C_{19}H_{21}F_2N_3O$
Formula weight	345.39
Temperature/K	100.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	11.83637(14)
b/Å	13.06576(19)
c/Å	21.3083(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3295.35(8)
Z	8
ρ_{calc}g/cm^3	1.392
μ/mm^{-1}	0.860
F(000)	1456.0
Crystal size/mm^3	0.15 × 0.12 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.298 to 160.538
Index ranges	-14 ≤ h ≤ 9, -16 ≤ k ≤ 14, -26 ≤ l ≤ 27
Reflections collected	15259
Independent reflections	3541 [R_{int} = 0.0749, R_{sigma} = 0.0520]
Data/restraints/parameters	3541/0/229
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0647, wR_2 = 0.1816
Final R indexes [all data]	R_1 = 0.0701, wR_2 = 0.1911
Largest diff. peak/hole / e Å^{-3}	0.40/-0.40

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman240R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	9017.5(9)	4611.8(10)	9733.1(5)	35.8(3)
O1	9395.8(9)	8495.1(10)	7568.2(6)	26.6(3)
N1	6990.5(11)	6588.8(12)	7723.7(6)	22.3(3)
C1	7251.1(13)	7633.1(13)	7549.8(8)	22.0(4)
F2	5099.4(9)	8928.2(9)	4640.6(5)	32.5(3)
N2	8024.2(11)	7703.8(11)	7008.2(6)	21.3(3)
C2	7571.3(13)	6010.6(13)	6656.5(8)	22.5(4)
N3	7791.7(11)	7102.5(11)	6471.4(6)	20.4(3)
C3	6658.1(13)	5982.9(14)	7173.5(8)	23.6(4)
C4	8692.4(14)	5567.6(14)	6896.2(8)	26.3(4)
C5	7168.4(14)	5395.5(14)	6092.4(8)	26.0(4)
C6	7542.0(13)	6104.2(14)	8227.7(8)	22.3(4)
C7	7111.8(13)	5170.3(14)	8452.4(8)	24.3(4)
C8	7610.1(14)	4671.9(15)	8954.4(8)	26.3(4)
C9	8533.6(13)	5114.9(16)	9246.4(8)	27.2(4)
C10	8964.5(13)	6040.0(15)	9051.8(8)	26.2(4)
C11	8478.3(13)	6530.1(14)	8537.9(8)	24.1(4)
C12	9088.3(13)	8103.0(13)	7070.9(8)	22.6(4)
C13	9847.5(13)	8068.9(15)	6501.3(8)	27.8(4)
C14	7045.6(13)	7582.1(13)	6021.7(8)	21.3(4)
C15	6038.9(13)	8093.0(13)	6175.6(8)	22.7(4)
C16	5393.9(13)	8556.4(14)	5710.6(8)	24.6(4)
C17	5742.0(14)	8484.9(14)	5095.4(8)	24.9(4)
C18	6721.2(14)	7989.5(15)	4923.0(8)	27.6(4)
C19	7377.3(13)	7547.4(15)	5393.6(8)	25.4(4)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Gandelman240R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	29.6(6)	54.2(7)	23.5(6)	12.1(5)	-8.0(4)	-3.1(5)
O1	20.2(6)	38.2(7)	21.4(6)	-2.4(5)	-4.4(4)	-1.6(5)
N1	19.2(6)	33.4(7)	14.4(7)	0.4(6)	-1.5(5)	-2.1(5)
C1	17.2(7)	32.9(8)	15.9(7)	-0.4(6)	1.3(5)	0.8(6)
F2	29.3(5)	46.5(7)	21.7(6)	5.0(5)	-8.6(4)	5.1(4)
N2	16.6(6)	33.2(7)	14.2(7)	-1.7(5)	-0.5(5)	-0.4(5)
C2	19.7(7)	31.5(8)	16.4(8)	1.1(6)	-1.6(5)	0.5(6)
N3	16.9(6)	31.0(7)	13.3(6)	-2.0(5)	-2.0(4)	0.1(5)
C3	18.8(7)	36.2(9)	16.0(8)	-1.4(7)	-2.3(6)	-2.7(6)
C4	22.5(8)	36.9(9)	19.4(8)	-1.9(7)	-2.5(6)	5.4(7)
C5	26.9(8)	32.1(8)	18.9(8)	-2.6(7)	-2.7(6)	2.3(6)
C6	15.7(7)	37.4(9)	13.8(7)	-0.4(6)	1.8(5)	2.3(6)
C7	17.5(7)	38.0(9)	17.4(8)	1.1(7)	1.1(5)	-2.0(6)
C8	20.5(7)	39.1(9)	19.4(8)	2.8(7)	2.0(6)	-1.8(7)
C9	19.4(7)	46.7(10)	15.5(8)	3.2(7)	0.1(6)	2.8(7)
C10	17.2(7)	43.7(10)	17.6(8)	0.3(7)	-0.5(5)	-1.1(6)
C11	17.0(7)	38.1(9)	17.1(8)	-0.2(6)	1.3(5)	-1.0(6)
C12	17.7(7)	31.6(8)	18.4(8)	2.0(6)	-2.9(6)	2.1(6)
C13	16.4(7)	43.7(10)	23.2(9)	2.5(7)	-0.4(6)	-2.0(6)
C14	15.1(7)	31.2(8)	17.5(8)	0.2(6)	-1.0(5)	-1.3(6)
C15	16.3(7)	35.7(9)	16.1(7)	1.0(7)	-0.7(5)	-1.3(6)
C16	16.1(7)	35.7(9)	21.9(9)	-1.7(7)	-2.3(6)	1.6(6)
C17	20.9(8)	34.5(9)	19.3(8)	2.8(7)	-6.4(6)	-1.9(6)
C18	24.9(8)	43.2(10)	14.6(8)	0.8(7)	0.4(6)	-1.3(7)
C19	17.8(7)	39.6(9)	18.7(8)	0.3(7)	0.8(6)	2.9(6)

Table 4 Bond Lengths for Gandelman240R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C9	1.355(2)	C6	C7	1.406(2)
O1	C12	1.232(2)	C6	C11	1.405(2)
N1	C1	1.447(2)	C7	C8	1.384(2)
N1	C3	1.468(2)	C8	C9	1.385(2)
N1	C6	1.407(2)	C9	C10	1.376(3)
C1	N2	1.476(2)	C10	C11	1.393(2)
F2	C17	1.3613(19)	C12	C13	1.511(2)
N2	N3	1.4147(19)	C14	C15	1.405(2)
N2	C12	1.370(2)	C14	C19	1.396(2)
C2	N3	1.503(2)	C15	C16	1.390(2)
C2	C3	1.544(2)	C16	C17	1.377(2)
C2	C4	1.535(2)	C17	C18	1.377(3)
C2	C5	1.523(2)	C18	C19	1.394(2)
N3	C14	1.446(2)			

Table 5 Bond Angles for Gandelman240R.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	N1	C3	111.17(13)	C8	C7	C6	121.13(15)
C6	N1	C1	121.39(14)	C7	C8	C9	119.14(17)
C6	N1	C3	119.41(14)	F1	C9	C8	118.35(17)
N1	C1	N2	113.05(14)	F1	C9	C10	120.02(15)
N3	N2	C1	118.48(13)	C10	C9	C8	121.63(17)
C12	N2	C1	121.18(13)	C9	C10	C11	119.19(16)
C12	N2	N3	117.99(13)	C10	C11	C6	120.90(16)
N3	C2	C3	109.33(13)	O1	C12	N2	120.92(15)
N3	C2	C4	107.16(13)	O1	C12	C13	121.84(15)
N3	C2	C5	110.38(13)	N2	C12	C13	117.21(14)

Table 5 Bond Angles for Gandelman240R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	C2	C3	111.04(13)	C15	C14	N3	124.71(15)
C5	C2	C3	109.37(13)	C19	C14	N3	116.72(14)
C5	C2	C4	109.53(14)	C19	C14	C15	118.55(15)
N2	N3	C2	110.41(13)	C16	C15	C14	120.45(15)
N2	N3	C14	114.46(13)	C17	C16	C15	118.99(15)
C14	N3	C2	118.64(12)	F2	C17	C16	118.79(15)
N1	C3	C2	111.68(13)	F2	C17	C18	118.70(15)
C7	C6	N1	118.84(14)	C16	C17	C18	122.51(16)
C11	C6	N1	123.13(16)	C17	C18	C19	118.15(15)
C11	C6	C7	117.97(15)	C18	C19	C14	121.32(15)

Table 6 Torsion Angles for Gandelman240R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F1	C9	C10	C11	177.96(15)	C3	C2	N3	C14	-82.84(16)
N1	C1	N2	N3	47.67(19)	C4	C2	N3	N2	-68.33(16)
N1	C1	N2	C12	-114.57(17)	C4	C2	N3	C14	156.72(13)
N1	C6	C7	C8	-178.79(15)	C4	C2	C3	N1	60.54(19)
N1	C6	C11	C10	177.23(15)	C5	C2	N3	N2	172.46(12)
C1	N1	C3	C2	55.77(18)	C5	C2	N3	C14	37.51(18)
C1	N1	C6	C7	167.94(15)	C5	C2	C3	N1	-178.47(13)
C1	N1	C6	C11	-9.2(2)	C6	N1	C1	N2	99.78(17)
C1	N2	N3	C2	-49.18(18)	C6	N1	C3	C2	-93.47(17)
C1	N2	N3	C14	87.79(17)	C6	C7	C8	C9	1.3(3)
C1	N2	C12	O1	-6.3(2)	C7	C6	C11	C10	0.1(2)
C1	N2	C12	C13	175.46(15)	C7	C8	C9	F1	-179.37(15)
F2	C17	C18	C19	179.38(16)	C7	C8	C9	C10	0.3(3)
N2	N3	C14	C15	-45.6(2)	C8	C9	C10	C11	-1.7(3)

Table 6 Torsion Angles for Gandelman240R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N2	N3	C14	C19	132.81(16)	C9	C10	C11	C6	1.5(3)
C2	N3	C14	C15	87.6(2)	C11	C6	C7	C8	-1.5(2)
C2	N3	C14	C19	-93.97(18)	C12	N2	N3	C2	113.64(15)
N3	N2	C12	O1	-168.65(15)	C12	N2	N3	C14	-109.39(16)
N3	N2	C12	C13	13.1(2)	C14	C15	C16	C17	1.6(3)
N3	C2	C3	N1	-57.50(17)	C15	C14	C19	C18	-1.2(3)
N3	C14	C15	C16	178.11(15)	C15	C16	C17	F2	179.11(15)
N3	C14	C19	C18	-179.78(16)	C15	C16	C17	C18	-1.5(3)
C3	N1	C1	N2	-48.75(17)	C16	C17	C18	C19	0.0(3)
C3	N1	C6	C7	-46.0(2)	C17	C18	C19	C14	1.4(3)
C3	N1	C6	C11	136.83(16)	C19	C14	C15	C16	-0.3(3)
C3	C2	N3	N2	52.11(15)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman240R.

Atom	*x*	*y*	*z*	U(eq)
H1A	7598.94	7984.14	7913.38	26
H1B	6539.67	7994.66	7447.3	26
H3A	5940.24	6254.35	7002.79	28
H3B	6527.66	5264.83	7303	28
H4A	9239.35	5544.16	6551.17	39
H4B	8566.57	4874.07	7056.71	39
H4C	8987.03	6001.88	7233.55	39
H5A	6437.41	5660.99	5950.48	39
H5B	7086.97	4674.81	6211.64	39
H5C	7721.39	5454.69	5752.08	39
H7	6468.12	4876.36	8256.29	29

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman240R.

Atom	*x*	*y*	*z*	U(eq)
H8	7322.15	4034.11	9096.76	32
H10	9585.94	6340.8	9265.25	31
H11	8783.82	7160.92	8395.18	29
H13A	10475.29	8549.08	6557.85	42
H13B	9413.54	8260.94	6127.73	42
H13C	10145.93	7374.52	6448.86	42
H15	5797.28	8121.9	6600.36	27
H16	4723.04	8917.11	5815.53	30
H18	6943.06	7950.14	4495.18	33
H19	8064.21	7215.9	5284.69	30

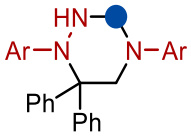
Experimental

Single crystals of $C_{19}H_{21}F_2N_3O$ **[Gandelman240R]** were obtained by slow evaporation of Et_2O/EtOAc/Hexane solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman240R]

Crystal Data for $C_{19}H_{21}F_2N_3O$ (M =345.39 g/mol): orthorhombic, space group Pbca (no. 61), a = 11.83637(14) Å, b = 13.06576(19) Å, c = 21.3083(3) Å, V = 3295.35(8) Å^3, Z = 8, T = 100.15 K, μ(CuKα) = 0.860 mm^{-1}, *Dcalc* = 1.392 g/cm^3, 15259 reflections measured (8.298° ≤ 2Θ ≤ 160.538°), 3541 unique (R_{int} = 0.0749, R_{sigma} = 0.0520) which were used in all calculations. The final R_1 was 0.0647 (I > 2σ(I)) and wR_2 was 0.1911 (all data).

3.1.8 1,4-bis(4-chlorophenyl)-6,6-diphenyl-1,2,4-triazinane (4.25)



4.25

(Ar = 4-ClC_6H_4)

Sample name: Gandelman239R

CCDC number: 2505620

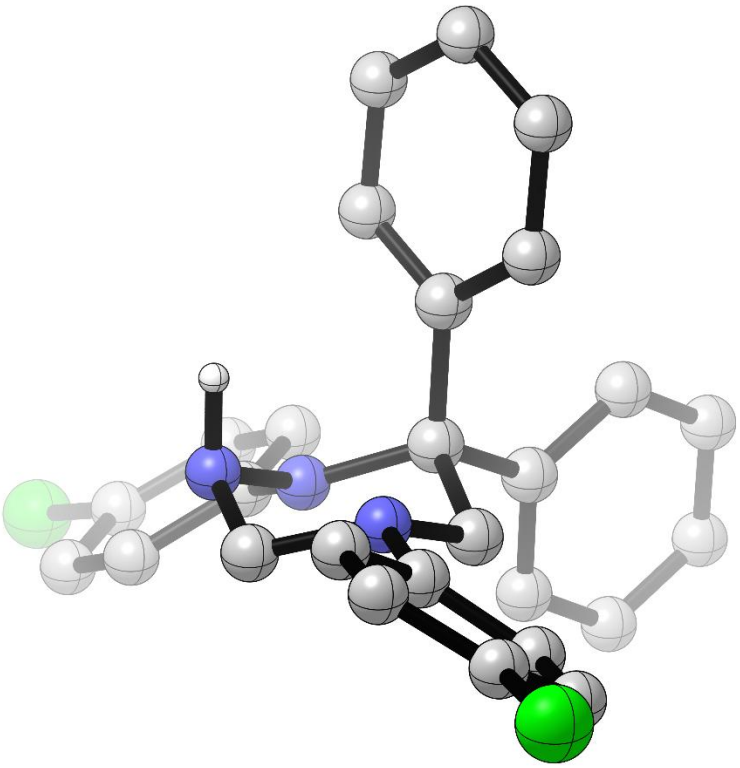


Table 1 Crystal data and structure refinement for Gandelman239R.

Identification code	Gandelman239R
Empirical formula	$C_{27}H_{23}Cl_2N_3$
Formula weight	460.38
Temperature/K	100.15
Crystal system	monoclinic
Space group	C2/c
a/Å	17.6177(5)
b/Å	8.2709(2)
c/Å	31.3118(8)
α/°	90
β/°	100.866(3)
γ/°	90
Volume/Å^3	4480.8(2)
Z	8
ρ_{calc}g/cm^3	1.365
μ/mm^{-1}	2.757
F(000)	1920.0
Crystal size/mm^3	0.21 × 0.09 × 0.06
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.748 to 159.728
Index ranges	-22 ≤ h ≤ 22, -10 ≤ k ≤ 10, -39 ≤ l ≤ 39
Reflections collected	15984
Independent reflections	4671 [R_{int} = 0.0874, R_{sigma} = 0.0652]
Data/restraints/parameters	4671/0/297
Goodness-of-fit on F^2	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0631, wR_2 = 0.1755
Final R indexes [all data]	R_1 = 0.0737, wR_2 = 0.1857
Largest diff. peak/hole / e Å^{-3}	0.61/-0.46

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman239R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	1015(4)	-1784(15)	2637.8(14)	52.0(11)
Cl1A	1068(5)	-2030(20)	2655(4)	40(2)
N1	2786.6(12)	3434(2)	3665.6(6)	18.8(4)
C1	2474.0(15)	4131(3)	4024.8(7)	22.7(5)
Cl2	3756.7(4)	12290.2(7)	5138.7(2)	24.67(19)
N2	3047.6(13)	5010(3)	4319.8(6)	22.0(4)
C2	3787.6(13)	5581(3)	3758.0(7)	17.6(4)
N3	3398.4(11)	6218(2)	4102.4(6)	18.9(4)
C3	3134.6(13)	4676(3)	3439.4(7)	16.8(4)
C4	2322.1(13)	2256(3)	3414.5(7)	17.7(4)
C5	2117.6(14)	2348(3)	2961.1(7)	20.1(5)
C6	1710.1(14)	1096(3)	2723.3(7)	24.9(5)
C7	1500.1(15)	-233(3)	2938.3(8)	26.8(5)
C8	1668.6(15)	-333(3)	3389.6(8)	24.4(5)
C9	2078.0(14)	904(3)	3624.6(7)	21.4(5)
C10	3514.1(14)	7698(3)	4332.5(7)	17.7(5)
C11	2938.2(13)	8171(3)	4558.2(7)	19.3(5)
C12	2998.8(13)	9589(3)	4799.5(7)	19.5(5)
C13	3649.9(14)	10553(3)	4812.5(7)	18.8(4)
C14	4218.2(14)	10144(3)	4585.3(7)	21.1(5)
C15	4159.1(13)	8705(3)	4345.2(7)	19.8(5)
C16	4058.1(13)	6934(3)	3488.1(6)	16.7(4)
C17	3554.1(14)	8206(3)	3338.2(7)	21.0(5)
C18	3771.1(15)	9420(3)	3078.5(7)	21.4(5)
C19	4493.5(15)	9377(3)	2963.1(8)	23.7(5)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman239R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C20	4998.2(15)	8116(3)	3106.0(8)	25.1(5)
C21	4783.7(14)	6902(3)	3369.6(7)	20.3(5)
C22	4454.0(13)	4426(3)	3944.2(7)	17.1(4)
C23	4920.4(14)	4747(3)	4349.6(7)	21.9(4)
C24	5554.1(14)	3775(3)	4510.2(7)	21.9(4)
C25	5733.5(14)	2460(3)	4277.0(8)	24.2(5)
C26	5271.2(15)	2111(3)	3875.6(8)	23.4(5)
C27	4641.5(15)	3082(3)	3713.9(7)	21.3(5)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for Gandelman239R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	74(3)	53.1(19)	29.6(14)	-23.2(10)	11.1(10)	-38.7(14)
Cl1A	22(6)	41(4)	57(6)	-32(3)	7(2)	-17(3)
N1	18.5(9)	27.0(10)	8.1(8)	-1.5(7)	-4.9(7)	-5.3(8)
C1	25.6(12)	29.1(12)	12.2(10)	-3.6(8)	0.8(9)	-6.8(9)
Cl2	31.2(3)	25.2(3)	14.9(3)	-4.26(19)	-2.7(2)	-4.1(2)
N2	25.2(10)	28.1(10)	10.5(8)	-0.5(7)	-2.0(8)	-8.3(8)
C2	15.6(10)	26.5(11)	7.7(9)	-1.1(8)	-5.2(8)	0.1(8)
N3	20.5(9)	24.6(9)	10.2(8)	-2.3(7)	-1.1(7)	-6.2(8)
C3	14.6(10)	25.4(11)	6.9(9)	0.4(8)	-6.7(8)	-2.4(8)
C4	14.3(10)	25.0(11)	10.6(10)	-2.9(8)	-6.0(8)	0.1(8)
C5	15.5(10)	27.6(11)	12.9(10)	-1.5(8)	-8.2(8)	0.4(8)
C6	18.7(11)	40.5(14)	11.9(10)	-7.7(9)	-6.0(9)	-2.0(10)
C7	21.3(12)	35.3(13)	21.1(12)	-11.8(10)	-3.0(10)	-6.5(10)
C8	23.0(12)	28.0(12)	21.1(12)	-2.6(9)	1.3(10)	-2.4(9)
C9	20.5(11)	27.2(11)	13.8(10)	-1.3(9)	-3.3(9)	-0.3(9)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman239R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C10	18.1(10)	24.6(11)	6.3(9)	0.1(8)	-8.4(8)	-0.3(8)
C11	16.4(10)	26.1(11)	11.2(9)	1.1(8)	-8.4(8)	-2.8(8)
C12	17.5(10)	27.5(11)	10.2(9)	0.8(8)	-5.7(8)	1.6(9)
C13	22.3(11)	23.7(10)	7.3(9)	-0.7(8)	-5.6(8)	-0.2(9)
C14	21.0(11)	26.3(11)	12.3(10)	1.1(8)	-6.1(9)	-5.0(9)
C15	16.8(10)	29.4(11)	10.8(9)	-0.8(8)	-3.9(8)	-3.8(9)
C16	16.5(10)	25.2(11)	5.3(9)	-1.6(8)	-6.0(8)	-1.7(8)
C17	21.2(11)	25.7(11)	12.7(10)	-0.7(8)	-5.7(9)	1.4(9)
C18	24.7(12)	24.4(11)	12.5(10)	2.1(8)	-2.6(9)	4.9(9)
C19	27.4(12)	27.8(12)	14.5(10)	3.0(8)	0.3(9)	-1.0(9)
C20	23.8(12)	32.3(12)	18.8(11)	1.7(9)	3.5(10)	0.3(10)
C21	19.9(11)	26.0(11)	12.3(10)	2.6(8)	-3.6(8)	3.0(9)
C22	17.1(10)	23.2(10)	7.9(9)	0.7(8)	-5.8(8)	-2.5(8)
C23	21.9(8)	29.6(8)	9.6(7)	1.6(6)	-8.8(6)	-3.5(7)
C24	21.9(8)	29.6(8)	9.6(7)	1.6(6)	-8.8(6)	-3.5(7)
C25	17.1(11)	30.6(12)	20.5(12)	9.7(9)	-7.9(9)	0.3(9)
C26	22.3(12)	27.2(11)	17.7(11)	1.2(9)	-3.9(9)	0.6(9)
C27	22.4(11)	27.4(11)	10.0(10)	-0.9(8)	-7.3(9)	-2.0(9)

Table 4 Bond Lengths for Gandelman239R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C7	1.720(7)	C10	C11	1.397(3)
Cl1A	C7	1.822(13)	C10	C15	1.403(3)
N1	C1	1.461(3)	C11	C12	1.389(3)
N1	C3	1.448(3)	C12	C13	1.391(3)
N1	C4	1.412(3)	C13	C14	1.375(4)

Table 4 Bond Lengths for Gandelman239R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	N2	1.432(3)	C14	C15	1.402(3)
Cl2	C13	1.752(2)	C16	C17	1.400(3)
N2	N3	1.415(3)	C16	C21	1.397(3)
C2	N3	1.480(3)	C17	C18	1.390(3)
C2	C3	1.564(3)	C18	C19	1.387(4)
C2	C16	1.531(3)	C19	C20	1.389(4)
C2	C22	1.541(3)	C20	C21	1.397(3)
N3	C10	1.415(3)	C22	C23	1.401(3)
C4	C5	1.399(3)	C22	C27	1.398(3)
C4	C9	1.406(3)	C23	C24	1.390(4)
C5	C6	1.393(3)	C24	C25	1.380(4)
C6	C7	1.376(4)	C25	C26	1.393(3)
C7	C8	1.391(4)	C26	C27	1.386(4)
C8	C9	1.381(4)			

Table 5 Bond Angles for Gandelman239R.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C3	N1	C1	110.63(18)	C11	C10	N3	116.8(2)
C4	N1	C1	115.98(19)	C11	C10	C15	118.7(2)
C4	N1	C3	118.12(18)	C15	C10	N3	124.5(2)
N2	C1	N1	112.0(2)	C12	C11	C10	121.5(2)
N3	N2	C1	111.54(18)	C11	C12	C13	118.6(2)
N3	C2	C3	104.43(17)	C12	C13	Cl2	118.95(18)
N3	C2	C16	112.16(18)	C14	C13	Cl2	119.62(19)
N3	C2	C22	111.70(17)	C14	C13	C12	121.4(2)
C16	C2	C3	105.41(16)	C13	C14	C15	119.9(2)
C16	C2	C22	111.58(19)	C14	C15	C10	119.8(2)

Table 5 Bond Angles for Gandelman239R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C22	C2	C3	111.17(18)	C17	C16	C2	119.4(2)
N2	N3	C2	113.80(18)	C21	C16	C2	121.9(2)
N2	N3	C10	113.56(18)	C21	C16	C17	118.7(2)
C10	N3	C2	129.56(19)	C18	C17	C16	120.8(2)
N1	C3	C2	110.85(17)	C19	C18	C17	120.1(2)
C5	C4	N1	122.6(2)	C18	C19	C20	119.9(2)
C5	C4	C9	118.4(2)	C19	C20	C21	120.2(2)
C9	C4	N1	119.0(2)	C20	C21	C16	120.4(2)
C6	C5	C4	120.7(2)	C23	C22	C2	120.0(2)
C7	C6	C5	119.4(2)	C27	C22	C2	122.35(18)
C6	C7	Cl1	118.7(3)	C27	C22	C23	117.6(2)
C6	C7	Cl1A	122.6(5)	C24	C23	C22	120.8(2)
C6	C7	C8	121.3(2)	C25	C24	C23	120.8(2)
C8	C7	Cl1	120.0(3)	C24	C25	C26	119.2(2)
C8	C7	Cl1A	115.9(6)	C27	C26	C25	120.1(2)
C9	C8	C7	119.2(2)	C26	C27	C22	121.5(2)
C8	C9	C4	121.0(2)				

Table 6 Torsion Angles for Gandelman239R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C7	C8	C9	178.2(5)	C4	C5	C6	C7	0.8(4)
Cl1A	C7	C8	C9	172.5(4)	C5	C4	C9	C8	2.2(4)
N1	C1	N2	N3	55.3(3)	C5	C6	C7	Cl1	-178.7(5)
N1	C4	C5	C6	174.9(2)	C5	C6	C7	Cl1A	-172.7(5)
N1	C4	C9	C8	-175.5(2)	C5	C6	C7	C8	1.7(4)
C1	N1	C3	C2	57.8(2)	C6	C7	C8	C9	-2.3(4)
C1	N1	C4	C5	127.5(2)	C7	C8	C9	C4	0.3(4)

Table 6 Torsion Angles for Gandelman239R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	N1	C4	C9	-55.0(3)	C9	C4	C5	C6	-2.7(4)
C1	N2	N3	C2	-59.5(3)	C10	C11	C12	C13	0.3(3)
C1	N2	N3	C10	138.3(2)	C11	C10	C15	C14	0.7(3)
Cl2	C13	C14	C15	176.08(17)	C11	C12	C13	Cl2	-176.70(16)
N2	N3	C10	C11	-37.3(3)	C11	C12	C13	C14	1.4(3)
N2	N3	C10	C15	143.1(2)	C12	C13	C14	C15	-2.0(3)
C2	N3	C10	C11	164.0(2)	C13	C14	C15	C10	0.9(3)
C2	N3	C10	C15	-15.6(3)	C15	C10	C11	C12	-1.3(3)
C2	C16	C17	C18	-177.50(19)	C16	C2	N3	N2	171.83(17)
C2	C16	C21	C20	177.0(2)	C16	C2	N3	C10	-29.6(3)
C2	C22	C23	C24	-175.9(2)	C16	C2	C3	N1	-175.60(18)
C2	C22	C27	C26	176.1(2)	C16	C2	C22	C23	89.1(3)
N3	C2	C3	N1	-57.2(2)	C16	C2	C22	C27	-87.9(3)
N3	C2	C16	C17	-46.0(3)	C16	C17	C18	C19	0.3(3)
N3	C2	C16	C21	136.9(2)	C17	C16	C21	C20	-0.1(3)
N3	C2	C22	C23	-37.4(3)	C17	C18	C19	C20	0.3(4)
N3	C2	C22	C27	145.7(2)	C18	C19	C20	C21	-0.7(4)
N3	C10	C11	C12	179.07(19)	C19	C20	C21	C16	0.7(4)
N3	C10	C15	C14	-179.7(2)	C21	C16	C17	C18	-0.3(3)
C3	N1	C1	N2	-55.7(3)	C22	C2	N3	N2	-62.1(2)
C3	N1	C4	C5	-7.3(3)	C22	C2	N3	C10	96.6(3)
C3	N1	C4	C9	170.2(2)	C22	C2	C3	N1	63.3(2)
C3	C2	N3	N2	58.2(2)	C22	C2	C16	C17	-172.22(19)
C3	C2	N3	C10	-143.2(2)	C22	C2	C16	C21	10.7(3)
C3	C2	C16	C17	67.0(2)	C22	C23	C24	C25	-0.8(4)
C3	C2	C16	C21	-110.1(2)	C23	C22	C27	C26	-0.9(4)
C3	C2	C22	C23	-153.6(2)	C23	C24	C25	C26	0.1(4)

Table 6 Torsion Angles for Gandelman239R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C3	C2	C22	C27	29.5(3)	C24	C25	C26	C27	0.3(4)
C4	N1	C1	N2	166.25(19)	C25	C26	C27	C22	0.2(4)
C4	N1	C3	C2	-165.21(19)	C27	C22	C23	C24	1.2(4)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman239R.

Atom	*x*	*y*	*z*	U(eq)
H1A	2041.8	4865.88	3906.46	27
H1B	2266.11	3253.82	4184.66	27
H2	3470(30)	4230(50)	4452(13)	42(10)
H3A	2733.46	5460.38	3307.91	20
H3B	3354.3	4177.99	3202.09	20
H5	2257.88	3274.13	2814.01	24
H6	1578.49	1159.24	2415.29	30
H8	1504.1	-1239.76	3534.54	29
H9	2196.45	839.71	3932.97	26
H11	2494.73	7506.67	4546.26	23
H12	2604.16	9894.82	4952.55	23
H14	4650.2	10837.07	4591.11	25
H15	4554.6	8411.26	4191.42	24
H17	3057.74	8240.88	3414.9	25
H18	3424.49	10279.37	2979.85	26
H19	4642.63	10209.05	2786.66	28
H20	5490.48	8079.65	3024.2	30
H21	5133.56	6048.59	3468.93	24
H23	4802.21	5638.5	4516.73	26
H24	5867.54	4020.02	4784.02	26

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman239R.

Atom	*x*	*y*	*z*	U(eq)
H25	6166.94	1800.01	4388.85	29
H26	5387.57	1205.6	3712.54	28
H27	4330.03	2829.48	3440.1	26

Table 8 Atomic Occupancy for Gandelman239R.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
Cl1	0.73(6)	Cl1A	0.27(6)		

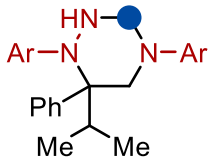
Experimental

Single crystals of $C_{27}H_{23}Cl_2N_3$ **[Gandelman239R]** were obtained by slow evaporation of C_6H_6 solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman239R]

Crystal Data for $C_{27}H_{23}Cl_2N_3$ (*M* =460.38 g/mol): monoclinic, space group C2/c (no. 15), *a* = 17.6177(5) Å, *b* = 8.2709(2) Å, *c* = 31.3118(8) Å, *β* = 100.866(3)°, *V* = 4480.8(2) Å^3, *Z* = 8, *T* = 100.15 K, μ(CuKα) = 2.757 mm^{-1}, *Dcalc* = 1.365 g/cm^3, 15984 reflections measured (5.748° ≤ 2Θ ≤ 159.728°), 4671 unique (R_{int} = 0.0874, R_{sigma} = 0.0652) which were used in all calculations. The final R_1 was 0.0631 (I > 2σ(I)) and wR_2 was 0.1857 (all data).

3.1.9 *1,4-bis(4-fluorophenyl)-6-isopropyl-6-phenyl-1,2,4-triazinane (4.26)*



4.26

(Ar = 4-FC_6H_4)

Sample name: Gandelman269R

CCDC number: 2505621

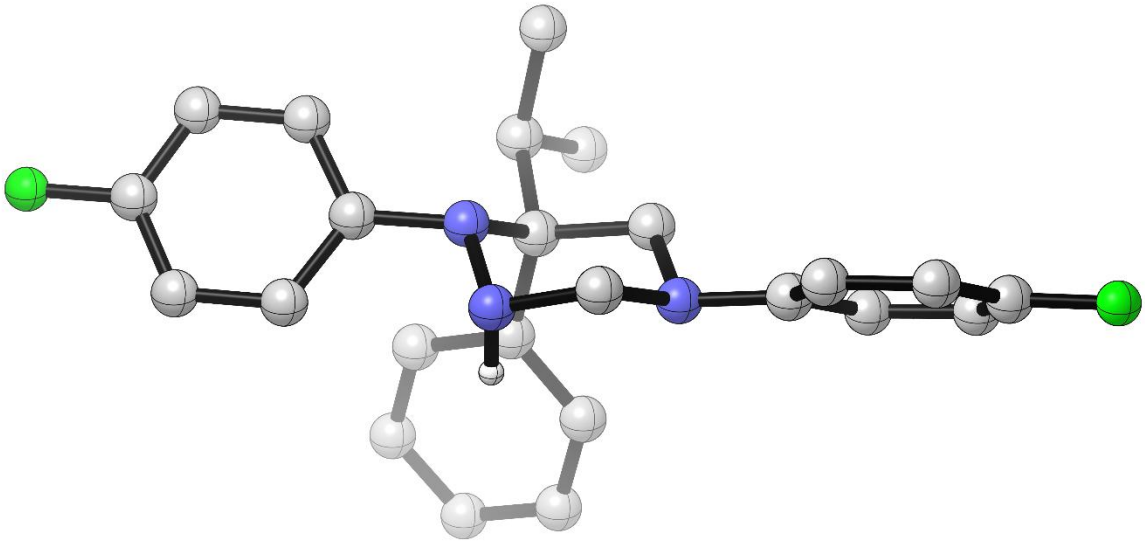


Table 1 Crystal data and structure refinement for Gandelman269R.

Identification code	Gandelman269R
Empirical formula	$C_{24}H_{25}F_2N_3$
Formula weight	393.47
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	12.9636(5)
b/Å	13.1764(4)
c/Å	13.4984(4)
α/°	75.025(3)
β/°	68.108(3)
γ/°	75.239(3)
Volume/Å^3	2034.24(13)
Z	4
ρ_{calc}g/cm^3	1.285
μ/mm^{-1}	0.089
F(000)	832.0
Crystal size/mm^3	0.24 × 0.18 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.042 to 59.998
Index ranges	-16 ≤ h ≤ 13, -16 ≤ k ≤ 17, -18 ≤ l ≤ 17
Reflections collected	25518
Independent reflections	9222 [R_{int} = 0.0520, R_{sigma} = 0.0638]
Data/restraints/parameters	9222/0/535
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0433, wR_2 = 0.1047
Final R indexes [all data]	R_1 = 0.0704, wR_2 = 0.1129
Largest diff. peak/hole / e Å^{-3}	0.28/-0.24

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman269R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	9505.5(7)	5966.6(8)	2276.6(8)	43.1(2)
N1	8763.4(8)	7995.0(8)	5662.6(9)	22.1(2)
C1	8906.9(10)	9113.2(10)	5383.8(11)	23.6(3)
F2	6918.3(7)	12150.2(7)	9989.7(8)	43.6(2)
N2	8858.7(8)	9473.9(9)	6316.6(9)	22.6(2)
C2	7539.9(10)	8328.7(10)	7555.4(11)	21.5(3)
N3	7746.9(8)	9462.2(8)	7111.4(9)	21.7(2)
C3	7701.5(10)	7865.0(11)	6565.2(11)	23.2(3)
C4	8911.9(9)	7500.3(10)	4796.3(11)	22.5(3)
C5	8843.8(10)	6418.7(11)	4991.2(12)	26.9(3)
C6	9021.3(11)	5904.6(12)	4156.1(12)	31.4(3)
C7	9288.3(11)	6472.5(12)	3115.5(12)	30.0(3)
C8	9358.9(11)	7529.0(12)	2881.5(12)	32.7(3)
C9	9165.7(11)	8047.7(11)	3722.0(11)	28.5(3)
C10	7547.0(10)	10151.6(10)	7848.3(11)	22.7(3)
C11	8426.5(11)	10406.4(11)	8041.9(12)	28.6(3)
C12	8218.1(12)	11076.9(12)	8751.9(12)	33.2(3)
C13	7121.7(12)	11502.9(11)	9276.0(12)	31.1(3)
C14	6237.7(12)	11297.7(11)	9085.4(13)	33.2(3)
C15	6451.3(11)	10631.7(11)	8365.7(12)	28.3(3)
C16	8332.5(10)	7701.8(10)	8204.2(11)	22.1(3)
C17	9194.6(10)	6855.1(10)	7858.8(11)	24.9(3)
C18	9882.3(11)	6297.3(11)	8474.0(12)	29.1(3)
C19	9733.1(11)	6564.6(11)	9445.2(12)	29.4(3)
C20	8888.9(11)	7401.8(11)	9800.6(12)	28.6(3)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman269R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C21	8200.6(10)	7962.8(10)	9187.7(11)	24.4(3)
C22	6287.9(10)	8308.2(11)	8305.5(11)	24.4(3)
C23	6079.9(11)	7163.7(11)	8804.0(12)	33.0(3)
C24	5406.5(11)	8897.8(12)	7751.1(13)	32.9(3)
F1A	6504.9(8)	4704.9(7)	9248.3(7)	42.3(2)
N1A	7213.8(8)	3213.7(9)	5520.5(9)	23.0(2)
C1A	8132.1(11)	2291.9(11)	5290.7(12)	26.3(3)
F2A	8601.6(7)	-476.4(7)	852.6(7)	40.7(2)
N2A	8370.2(8)	2077.7(9)	4226.0(9)	23.6(2)
C2A	6426.7(9)	2745.6(10)	4284.5(11)	20.7(3)
N3A	7387.4(8)	1795.7(8)	4179.7(9)	20.5(2)
C3A	6213.0(10)	3038.2(10)	5380.1(11)	22.9(3)
C4A	7014.3(10)	3571.9(10)	6489.8(11)	22.9(3)
C5A	5934.6(11)	3785.2(11)	7237.3(12)	28.1(3)
C6A	5758.7(12)	4176.4(11)	8161.5(12)	31.1(3)
C7A	6669.1(12)	4343.1(11)	8334.0(12)	30.7(3)
C8A	7747.4(12)	4151.0(12)	7621.9(13)	34.3(3)
C9A	7916.7(11)	3767.8(12)	6704.0(12)	30.5(3)
C10A	7705.0(10)	1242.8(10)	3298.6(11)	21.5(3)
C11A	8665.7(10)	1371.9(11)	2386.4(11)	25.1(3)
C12A	8963.2(11)	801.1(11)	1563.7(12)	28.8(3)
C13A	8300.1(11)	103.6(11)	1652.1(12)	28.1(3)
C14A	7351.8(11)	-54.0(11)	2533.0(12)	29.6(3)
C15A	7067.0(11)	508.5(10)	3360.9(12)	26.7(3)
C16A	6732.8(9)	3659.2(10)	3319.7(11)	22.1(3)
C17A	6885.1(10)	4626.8(11)	3432.1(13)	28.5(3)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman269R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C18A	7142.7(11)	5446.3(12)	2539.4(15)	39.8(4)
C19A	7271.8(12)	5305.2(13)	1524.0(15)	44.8(5)
C20A	7133.7(11)	4349.3(14)	1396.4(13)	40.6(4)
C21A	6854.1(11)	3536.8(12)	2282.3(12)	30.2(3)
C22A	5324.4(10)	2422.2(11)	4340.2(12)	25.6(3)
C23A	4371.4(11)	3388.0(12)	4316.4(14)	35.3(4)
C24A	4887.3(12)	1560.3(13)	5312.9(13)	37.7(4)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for Gandelman269R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	44.7(5)	54.6(6)	39.6(5)	-27.6(5)	-11.3(4)	-10.0(4)
N1	22.4(5)	22.2(5)	21.6(6)	-5.6(5)	-4.9(4)	-5.6(4)
C1	24.8(6)	21.3(6)	23.7(7)	-3.8(5)	-5.9(5)	-6.1(5)
F2	55.4(5)	40.0(5)	37.8(5)	-20.4(4)	-7.9(4)	-10.2(4)
N2	19.7(5)	23.2(6)	22.2(6)	-3.8(5)	-4.3(4)	-3.5(4)
C2	20.3(6)	20.6(6)	22.7(7)	-3.6(5)	-5.6(5)	-4.8(5)
N3	19.6(5)	19.8(5)	23.1(6)	-4.5(5)	-3.6(4)	-3.9(4)
C3	21.1(6)	26.0(7)	23.1(7)	-4.5(6)	-6.1(5)	-6.9(5)
C4	17.7(6)	25.9(7)	25.2(7)	-6.5(6)	-8.1(5)	-2.7(5)
C5	24.5(6)	27.0(7)	28.6(8)	-6.8(6)	-7.2(5)	-4.1(5)
C6	30.0(7)	28.5(7)	39.7(9)	-13.2(7)	-10.7(6)	-6.0(6)
C7	24.6(7)	40.5(8)	30.7(8)	-19.1(7)	-9.2(6)	-2.9(6)
C8	35.1(7)	39.1(8)	25.1(8)	-6.8(7)	-10.7(6)	-6.0(6)
C9	32.9(7)	27.3(7)	25.4(8)	-4.9(6)	-9.6(6)	-5.1(5)
C10	27.7(6)	16.7(6)	21.2(7)	-0.7(5)	-7.2(5)	-3.9(5)
C11	27.1(7)	28.8(7)	29.1(8)	-8.1(6)	-6.2(5)	-5.3(5)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman269R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C12	35.3(7)	35.3(8)	32.7(8)	-8.9(7)	-9.1(6)	-12.6(6)
C13	43.4(8)	23.0(7)	25.3(8)	-7.7(6)	-6.4(6)	-7.5(6)
C14	31.7(7)	28.4(7)	33.5(8)	-10.4(7)	-4.6(6)	0.7(6)
C15	26.3(7)	24.3(7)	33.5(8)	-7.9(6)	-9.7(6)	-0.9(5)
C16	20.7(6)	19.3(6)	26.1(7)	-2.6(5)	-6.5(5)	-6.6(5)
C17	25.2(6)	23.8(7)	26.0(7)	-6.4(6)	-6.8(5)	-5.1(5)
C18	26.0(7)	23.3(7)	36.7(8)	-5.3(6)	-10.4(6)	-2.3(5)
C19	31.1(7)	26.5(7)	33.0(8)	0.1(6)	-16.6(6)	-5.6(5)
C20	35.3(7)	27.4(7)	26.3(8)	-2.4(6)	-12.7(6)	-9.6(6)
C21	28.2(6)	19.8(6)	25.0(7)	-4.7(6)	-7.8(5)	-4.7(5)
C22	21.2(6)	25.2(7)	25.3(7)	-6.0(6)	-4.0(5)	-5.6(5)
C23	29.1(7)	31.6(8)	34.2(9)	-6.4(7)	-0.9(6)	-12.5(6)
C24	22.8(6)	40.6(8)	36.7(9)	-11.9(7)	-9.0(6)	-4.5(6)
F1A	58.2(5)	41.6(5)	34.5(5)	-18.1(4)	-24.0(4)	3.3(4)
N1A	20.7(5)	26.7(6)	24.1(6)	-8.7(5)	-10.6(4)	0.6(4)
C1A	26.0(6)	27.7(7)	29.1(8)	-9.1(6)	-15.2(6)	2.0(5)
F2A	55.4(5)	38.8(5)	33.1(5)	-17.8(4)	-13.5(4)	-7.4(4)
N2A	20.5(5)	27.0(6)	26.0(6)	-5.3(5)	-10.3(4)	-4.3(4)
C2A	18.7(6)	20.0(6)	24.2(7)	-4.1(5)	-7.4(5)	-4.2(5)
N3A	20.1(5)	19.3(5)	23.2(6)	-4.4(5)	-8.1(4)	-3.2(4)
C3A	19.9(6)	24.7(6)	24.8(7)	-5.3(6)	-8.2(5)	-2.7(5)
C4A	26.8(6)	21.3(6)	21.8(7)	-3.3(5)	-11.8(5)	-1.2(5)
C5A	26.5(7)	31.1(7)	28.1(8)	-8.0(6)	-11.8(6)	-0.4(5)
C6A	32.3(7)	31.7(8)	25.8(8)	-8.2(6)	-9.7(6)	3.3(6)
C7A	46.1(8)	24.1(7)	25.3(8)	-9.1(6)	-18.6(6)	3.0(6)
C8A	35.8(8)	37.1(8)	38.7(9)	-12.6(7)	-19.6(7)	-4.2(6)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman269R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C9A	29.1(7)	34.8(8)	30.9(8)	-10.4(7)	-11.4(6)	-4.3(6)
C10A	22.5(6)	18.6(6)	23.7(7)	-3.9(5)	-9.9(5)	-0.7(5)
C11A	25.7(6)	25.5(7)	25.7(7)	-5.2(6)	-8.3(5)	-6.7(5)
C12A	27.9(7)	32.2(8)	24.4(8)	-6.0(6)	-7.2(5)	-3.6(5)
C13A	36.2(7)	24.9(7)	25.5(8)	-10.2(6)	-13.6(6)	1.4(5)
C14A	31.7(7)	24.0(7)	38.0(9)	-8.6(6)	-14.0(6)	-6.3(5)
C15A	25.6(6)	23.3(7)	30.5(8)	-5.3(6)	-7.0(5)	-5.7(5)
C16A	15.4(5)	23.6(6)	26.6(7)	-1.4(6)	-8.8(5)	-2.4(5)
C17A	22.5(6)	25.2(7)	38.5(9)	-0.5(6)	-14.3(6)	-4.0(5)
C18A	28.1(7)	29.8(8)	60.1(12)	9.8(8)	-21.6(7)	-10.0(6)
C19A	26.3(7)	45.0(10)	50.2(11)	20.9(8)	-15.5(7)	-9.8(6)
C20A	27.5(7)	55.7(10)	28.2(8)	6.4(8)	-11.2(6)	-0.7(7)
C21A	26.5(7)	33.0(8)	29.6(8)	-2.5(6)	-13.4(6)	0.3(5)
C22A	20.7(6)	27.8(7)	30.7(8)	-7.7(6)	-7.7(5)	-6.9(5)
C23A	22.5(7)	38.1(8)	51.1(10)	-16.0(7)	-14.7(6)	-3.4(6)
C24A	34.1(8)	36.7(8)	40.7(9)	-7.1(7)	-2.4(6)	-18.6(6)

Table 4 Bond Lengths for Gandelman269R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C7	1.3649(16)	F1A	C7A	1.3610(16)
N1	C1	1.4656(16)	N1A	C1A	1.4735(16)
N1	C3	1.4732(15)	N1A	C3A	1.4599(15)
N1	C4	1.4112(17)	N1A	C4A	1.4164(17)
C1	N2	1.4320(17)	C1A	N2A	1.4404(17)
F2	C13	1.3586(17)	F2A	C13A	1.3642(16)
N2	N3	1.4416(14)	N2A	N3A	1.4415(14)

Table 4 Bond Lengths for Gandelman269R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C2	N3	1.5112(16)	C2A	N3A	1.5177(15)
C2	C3	1.5336(19)	C2A	C3A	1.5319(19)
C2	C16	1.5393(17)	C2A	C16A	1.5331(17)
C2	C22	1.5630(16)	C2A	C22A	1.5631(16)
N3	C10	1.4270(17)	N3A	C10A	1.4299(17)
C4	C5	1.4003(19)	C4A	C5A	1.3961(18)
C4	C9	1.3985(19)	C4A	C9A	1.4012(18)
C5	C6	1.380(2)	C5A	C6A	1.391(2)
C6	C7	1.371(2)	C6A	C7A	1.363(2)
C7	C8	1.365(2)	C7A	C8A	1.373(2)
C8	C9	1.385(2)	C8A	C9A	1.379(2)
C10	C11	1.3941(19)	C10A	C11A	1.3972(18)
C10	C15	1.3915(18)	C10A	C15A	1.3933(18)
C11	C12	1.377(2)	C11A	C12A	1.3827(19)
C12	C13	1.373(2)	C12A	C13A	1.367(2)
C13	C14	1.366(2)	C13A	C14A	1.371(2)
C14	C15	1.381(2)	C14A	C15A	1.384(2)
C16	C17	1.3985(18)	C16A	C17A	1.3922(19)
C16	C21	1.3952(19)	C16A	C21A	1.397(2)
C17	C18	1.3883(18)	C17A	C18A	1.3931(19)
C18	C19	1.377(2)	C18A	C19A	1.373(2)
C19	C20	1.383(2)	C19A	C20A	1.378(3)
C20	C21	1.3877(18)	C20A	C21A	1.386(2)
C22	C23	1.5320(18)	C22A	C23A	1.5343(19)
C22	C24	1.5343(18)	C22A	C24A	1.5288(19)

Table 5 Bond Angles for Gandelman269R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C3	109.86(10)	C3A	N1A	C1A	109.82(10)
C4	N1	C1	116.82(11)	C4A	N1A	C1A	115.59(10)
C4	N1	C3	113.34(10)	C4A	N1A	C3A	115.13(10)
N2	C1	N1	110.74(10)	N2A	C1A	N1A	111.42(10)
C1	N2	N3	109.36(10)	C1A	N2A	N3A	109.17(10)
N3	C2	C3	105.49(10)	N3A	C2A	C3A	105.39(10)
N3	C2	C16	110.76(10)	N3A	C2A	C16A	110.67(9)
N3	C2	C22	110.91(10)	N3A	C2A	C22A	110.60(10)
C3	C2	C16	113.77(10)	C3A	C2A	C16A	113.44(11)
C3	C2	C22	106.68(10)	C3A	C2A	C22A	107.47(10)
C16	C2	C22	109.13(10)	C16A	C2A	C22A	109.18(10)
N2	N3	C2	110.32(9)	N2A	N3A	C2A	110.12(10)
C10	N3	N2	110.01(10)	C10A	N3A	N2A	109.83(9)
C10	N3	C2	119.29(10)	C10A	N3A	C2A	119.48(10)
N1	C3	C2	115.12(10)	N1A	C3A	C2A	114.40(10)
C5	C4	N1	120.15(12)	C5A	C4A	N1A	122.62(11)
C9	C4	N1	122.08(12)	C5A	C4A	C9A	117.51(13)
C9	C4	C5	117.73(13)	C9A	C4A	N1A	119.81(11)
C6	C5	C4	121.47(14)	C6A	C5A	C4A	121.37(13)
C7	C6	C5	118.48(13)	C7A	C6A	C5A	118.61(13)
F1	C7	C6	119.22(13)	F1A	C7A	C6A	118.86(13)
C8	C7	F1	118.37(14)	F1A	C7A	C8A	118.81(13)
C8	C7	C6	122.40(14)	C6A	C7A	C8A	122.33(14)
C7	C8	C9	119.05(14)	C7A	C8A	C9A	118.84(13)
C8	C9	C4	120.85(13)	C8A	C9A	C4A	121.34(13)
C11	C10	N3	122.07(11)	C11A	C10A	N3A	122.67(11)
C15	C10	N3	120.21(12)	C15A	C10A	N3A	119.38(11)

Table 5 Bond Angles for Gandelman269R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C15	C10	C11	117.66(13)	C15A	C10A	C11A	117.90(13)
C12	C11	C10	121.28(13)	C12A	C11A	C10A	121.02(12)
C13	C12	C11	119.16(13)	C13A	C12A	C11A	118.97(13)
F2	C13	C12	118.99(13)	F2A	C13A	C12A	119.20(13)
F2	C13	C14	119.63(13)	F2A	C13A	C14A	118.59(13)
C14	C13	C12	121.38(14)	C12A	C13A	C14A	122.19(14)
C13	C14	C15	119.25(13)	C13A	C14A	C15A	118.58(13)
C14	C15	C10	121.20(13)	C14A	C15A	C10A	121.32(13)
C17	C16	C2	122.85(12)	C17A	C16A	C2A	122.59(13)
C21	C16	C2	120.07(11)	C17A	C16A	C21A	117.76(12)
C21	C16	C17	117.08(12)	C21A	C16A	C2A	119.65(12)
C18	C17	C16	121.23(13)	C16A	C17A	C18A	120.98(15)
C19	C18	C17	120.71(13)	C19A	C18A	C17A	120.35(15)
C18	C19	C20	119.06(13)	C18A	C19A	C20A	119.45(14)
C19	C20	C21	120.43(14)	C19A	C20A	C21A	120.69(16)
C20	C21	C16	121.48(12)	C20A	C21A	C16A	120.76(15)
C23	C22	C2	111.48(10)	C23A	C22A	C2A	112.10(11)
C23	C22	C24	109.02(11)	C24A	C22A	C2A	114.35(11)
C24	C22	C2	114.45(11)	C24A	C22A	C23A	109.18(11)

Table 6 Torsion Angles for Gandelman269R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F1	C7	C8	C9	-178.57(11)	F1A	C7A	C8A	C9A	178.95(13)
N1	C1	N2	N3	-64.66(12)	N1A	C1A	N2A	N3A	-62.92(13)
N1	C4	C5	C6	-177.88(11)	N1A	C4A	C5A	C6A	-177.42(12)
N1	C4	C9	C8	176.96(11)	N1A	C4A	C9A	C8A	177.81(12)
C1	N1	C3	C2	-51.00(14)	C1A	N1A	C3A	C2A	-52.52(14)

Table 6 Torsion Angles for Gandelman269R.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C1	N1	C4	C5	176.84(11)	C1A	N1A	C4A	C5A	-132.35(13)
C1	N1	C4	C9	-1.01(16)	C1A	N1A	C4A	C9A	50.36(17)
C1	N2	N3	C2	66.99(12)	C1A	N2A	N3A	C2A	65.90(12)
C1	N2	N3	C10	-159.38(10)	C1A	N2A	N3A	C10A	-160.54(10)
F2	C13	C14	C15	-179.45(12)	F2A	C13A	C14A	C15A	177.89(11)
N2	N3	C10	C11	-24.75(16)	N2A	N3A	C10A	C11A	-25.18(15)
N2	N3	C10	C15	152.42(11)	N2A	N3A	C10A	C15A	151.96(11)
C2	N3	C10	C11	104.14(14)	C2A	N3A	C10A	C11A	103.41(13)
C2	N3	C10	C15	-78.68(14)	C2A	N3A	C10A	C15A	-79.45(14)
C2	C16	C17	C18	-179.00(12)	C2A	C16A	C17A	C18A	-178.82(11)
C2	C16	C21	C20	178.92(12)	C2A	C16A	C21A	C20A	-179.80(11)
N3	C2	C3	N1	51.20(13)	N3A	C2A	C3A	N1A	53.70(13)
N3	C2	C16	C17	-112.49(13)	N3A	C2A	C16A	C17A	-113.49(12)
N3	C2	C16	C21	68.15(14)	N3A	C2A	C16A	C21A	67.31(13)
N3	C2	C22	C23	-177.34(11)	N3A	C2A	C22A	C23A	-173.52(11)
N3	C2	C22	C24	58.35(15)	N3A	C2A	C22A	C24A	61.52(15)
N3	C10	C11	C12	179.70(12)	N3A	C10A	C11A	C12A	178.19(11)
N3	C10	C15	C14	179.71(12)	N3A	C10A	C15A	C14A	-179.20(11)
C3	N1	C1	N2	55.62(13)	C3A	N1A	C1A	N2A	55.40(14)
C3	N1	C4	C5	-53.91(15)	C3A	N1A	C4A	C5A	-2.55(17)
C3	N1	C4	C9	128.24(12)	C3A	N1A	C4A	C9A	-179.85(12)
C3	C2	N3	N2	-57.62(12)	C3A	C2A	N3A	N2A	-59.07(12)
C3	C2	N3	C10	173.63(9)	C3A	C2A	N3A	C10A	172.47(10)
C3	C2	C16	C17	6.13(16)	C3A	C2A	C16A	C17A	4.73(15)
C3	C2	C16	C21	-173.23(10)	C3A	C2A	C16A	C21A	-174.47(10)
C3	C2	C22	C23	68.26(13)	C3A	C2A	C22A	C23A	71.92(14)
C3	C2	C22	C24	-56.05(14)	C3A	C2A	C22A	C24A	-53.03(15)

Table 6 Torsion Angles for Gandelman269R.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C4	N1	C1	N2	-173.49(9)	C4A	N1A	C1A	N2A	-172.28(10)
C4	N1	C3	C2	176.28(10)	C4A	N1A	C3A	C2A	174.93(10)
C4	C5	C6	C7	1.13(19)	C4A	C5A	C6A	C7A	-0.5(2)
C5	C4	C9	C8	-0.94(18)	C5A	C4A	C9A	C8A	0.4(2)
C5	C6	C7	F1	177.71(11)	C5A	C6A	C7A	F1A	-178.66(12)
C5	C6	C7	C8	-1.5(2)	C5A	C6A	C7A	C8A	0.8(2)
C6	C7	C8	C9	0.7(2)	C6A	C7A	C8A	C9A	-0.5(2)
C7	C8	C9	C4	0.6(2)	C7A	C8A	C9A	C4A	-0.1(2)
C9	C4	C5	C6	0.06(18)	C9A	C4A	C5A	C6A	-0.07(19)
C10	C11	C12	C13	-0.1(2)	C10A	C11A	C12A	C13A	0.11(19)
C11	C10	C15	C14	-3.0(2)	C11A	C10A	C15A	C14A	-1.92(19)
C11	C12	C13	F2	178.92(13)	C11A	C12A	C13A	F2A	-178.77(11)
C11	C12	C13	C14	-1.8(2)	C11A	C12A	C13A	C14A	-0.4(2)
C12	C13	C14	C15	1.2(2)	C12A	C13A	C14A	C15A	-0.5(2)
C13	C14	C15	C10	1.2(2)	C13A	C14A	C15A	C10A	1.7(2)
C15	C10	C11	C12	2.5(2)	C15A	C10A	C11A	C12A	1.01(19)
C16	C2	N3	N2	65.90(13)	C16A	C2A	N3A	N2A	63.94(13)
C16	C2	N3	C10	-62.85(13)	C16A	C2A	N3A	C10A	-64.51(13)
C16	C2	C3	N1	-70.39(13)	C16A	C2A	C3A	N1A	-67.53(13)
C16	C2	C22	C23	-55.05(15)	C16A	C2A	C22A	C23A	-51.52(16)
C16	C2	C22	C24	-179.36(11)	C16A	C2A	C22A	C24A	-176.47(12)
C16	C17	C18	C19	0.0(2)	C16A	C17A	C18A	C19A	-1.20(19)
C17	C16	C21	C20	-0.47(18)	C17A	C16A	C21A	C20A	0.96(17)
C17	C18	C19	C20	-0.2(2)	C17A	C18A	C19A	C20A	0.6(2)
C18	C19	C20	C21	0.1(2)	C18A	C19A	C20A	C21A	0.7(2)
C19	C20	C21	C16	0.2(2)	C19A	C20A	C21A	C16A	-1.55(19)
C21	C16	C17	C18	0.37(18)	C21A	C16A	C17A	C18A	0.40(17)

Table 6 Torsion Angles for Gandelman269R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C22	C2	N3	N2	-172.76(10)	C22A	C2A	N3A	N2A	-174.93(10)
C22	C2	N3	C10	58.48(14)	C22A	C2A	N3A	C10A	56.61(14)
C22	C2	C3	N1	169.22(10)	C22A	C2A	C3A	N1A	171.68(10)
C22	C2	C16	C17	125.12(13)	C22A	C2A	C16A	C17A	124.55(12)
C22	C2	C16	C21	-54.23(15)	C22A	C2A	C16A	C21A	-54.66(14)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman269R.

Atom	*x*	*y*	*z*	U(eq)
H1A	9643.9	9187.35	4808.89	28
H1B	8304.55	9561.83	5097.69	28
H2	9376(11)	9018(11)	6599(11)	22(3)
H3A	7669.54	7093.83	6802.86	28
H3B	7061.94	8209.83	6291.51	28
H5	8671.71	6030.2	5714.47	32
H6	8959.72	5173.74	4299.09	38
H8	9537.99	7903.45	2152.65	39
H9	9206.23	8784.77	3566.77	34
H11	9184.39	10111.58	7676.67	34
H12	8825.23	11242.64	8877.71	40
H14	5484.46	11609.73	9443.96	40
H15	5839.11	10498.85	8221.15	34
H17	9311.83	6658.02	7190.73	30
H18	10462.16	5724.98	8221.99	35
H19	10203.44	6179.22	9865.33	35
H20	8779.45	7594.35	10468.85	34
H21	7626.64	8537.39	9443.46	29

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman269R.

Atom	*x*	*y*	*z*	U(eq)
H22	6154.54	8672.4	8918.05	29
H23A	6221.05	6775.72	8223.87	49
H23B	5295.33	7178.92	9285.16	49
H23C	6590.18	6804.49	9221.76	49
H24A	5672.13	9526.81	7233.5	49
H24B	4689.91	9122.71	8300.61	49
H24C	5294.42	8420.56	7365.1	49
H1AA	8822.06	2436.68	5341.19	32
H1AB	7915.28	1654.63	5842.62	32
H2A	8537(11)	2693(12)	3729(12)	25(4)
H3AA	5633.96	3694.38	5461.57	28
H3AB	5901.6	2458.26	5966.79	28
H5A	5307	3660.56	7112.14	34
H6A	5019.77	4324.41	8662.1	37
H8A	8366.04	4279.82	7759.06	41
H9A	8660.12	3633.93	6206.95	37
H11A	9121.55	1859.34	2330.49	30
H12A	9618.45	892.46	946.63	35
H14A	6900.07	-538.97	2574.05	36
H15A	6423.49	391.6	3984.14	32
H17A	6812.22	4729.79	4127.81	34
H18A	7229.45	6106.2	2633.54	48
H19A	7454.85	5862.04	914.7	54
H20A	7231.2	4246.08	693.77	49
H21A	6743.67	2889.17	2182.9	36
H22A	5508.55	2123.05	3672.44	31

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman269R.

Atom	*x*	*y*	*z*	U(eq)
H23D	4186.47	3722.9	4945.11	53
H23E	3701.83	3152.62	4341.75	53
H23F	4617.34	3905.4	3646.99	53
H24D	5527.67	1033.86	5451.28	57
H24E	4401.03	1205.97	5156.41	57
H24F	4453.12	1888.72	5954.67	57

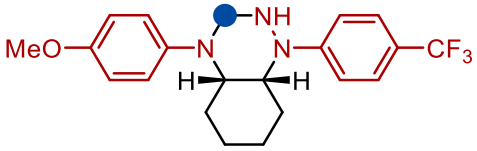
Experimental

Single crystals of $C_{24}H_{25}F_2N_3$ **[Gandelman269R]** were obtained by slow evaporation of Et_2O/Hexane solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman269R]

Crystal Data for $C_{24}H_{25}F_2N_3$ (*M* =393.47 g/mol): triclinic, space group P-1 (no. 2), *a* = 12.9636(5) Å, *b* = 13.1764(4) Å, *c* = 13.4984(4) Å, *α* = 75.025(3)°, *β* = 68.108(3)°, *γ* = 75.239(3)°, *V* = 2034.24(13) Å^3, *Z* = 4, *T* = 100.15 K, μ(MoKα) = 0.089 mm^{-1}, *Dcalc* = 1.285 g/cm^3, 25518 reflections measured (5.042° ≤ 2Θ ≤ 59.998°), 9222 unique (R_{int} = 0.0520, R_{sigma} = 0.0638) which were used in all calculations. The final R_1 was 0.0433 (I > 2σ(I)) and wR_2 was 0.1129 (all data).

3.1.10 (4aSR,8aRS)-4-(4-methoxyphenyl)-1-(4-(trifluoromethyl)phenyl)decahydrobenzo[e][1,2,4]triazine (4.31)



4.31

Sample name: Gandelman268R

CCDC number: 2505622

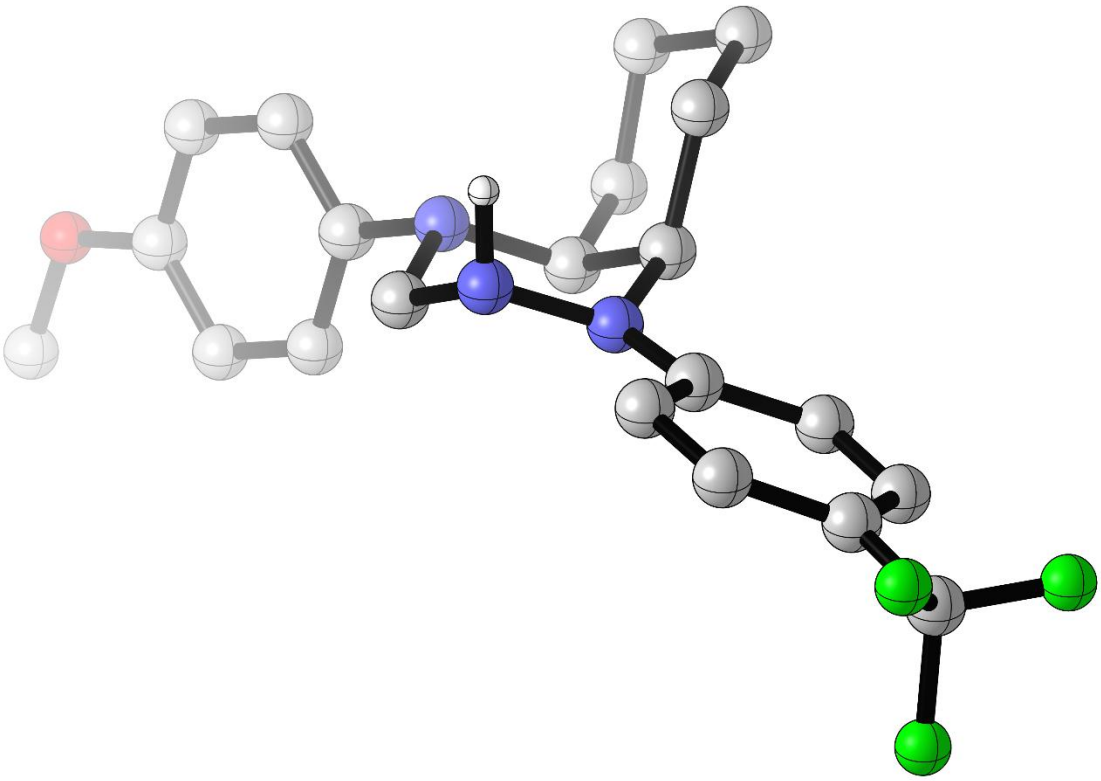


Table 1 Crystal data and structure refinement for Gandelman268R.

Identification code	Gandelman268R
Empirical formula	$C_{21}H_{24}F_3N_3O$
Formula weight	391.43
Temperature/K	100.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.4618(6)
b/Å	17.9646(6)
c/Å	6.3445(3)
α/°	90
β/°	94.807(3)
γ/°	90
Volume/Å^3	1869.67(12)
Z	4
ρ_{calc}g/cm^3	1.391
μ/mm^{-1}	0.107
F(000)	824.0
Crystal size/mm^3	0.24 × 0.18 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.966 to 60.002
Index ranges	-21 ≤ h ≤ 21, -21 ≤ k ≤ 25, -7 ≤ l ≤ 8
Reflections collected	13182
Independent reflections	4284 [R_{int} = 0.0324, R_{sigma} = 0.0336]
Data/restraints/parameters	4284/319/286
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.0963
Final R indexes [all data]	R_1 = 0.0531, wR_2 = 0.1023
Largest diff. peak/hole / e Å^{-3}	0.27/-0.22

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman268R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	-698(6)	6110(4)	-1026(17)	45.6(16)
F1A	-770(7)	6046(7)	-730(20)	74(3)
O1	7316.7(5)	6701.3(5)	7411.7(15)	24.1(2)
N1	2300.5(6)	6350.2(6)	5695.4(18)	20.1(2)
C1	3528.6(7)	6997.8(7)	5895(2)	19.6(3)
F2	-1233(6)	6907(6)	1135(18)	44.4(16)
F2A	-1168(8)	6944(6)	790(30)	67(2)
N2	2666.1(6)	7065.7(6)	6016(2)	23.5(3)
C2	3550.9(7)	5723.4(7)	7063.1(19)	17.2(2)
F3	-1305(8)	5748(7)	1670(20)	54(2)
F3A	-1366(7)	5844(8)	1957(19)	47.1(18)
N3	3916.8(6)	6469.9(6)	7429.1(17)	18.5(2)
C3	2622.2(7)	5777.0(6)	7188.2(19)	17.4(3)
C4	2374.6(7)	5901.7(7)	9438(2)	20.8(3)
C5	2769.7(8)	5329.2(7)	10987(2)	22.0(3)
C6	3695.7(7)	5331.6(7)	10915(2)	20.2(3)
C7	3915.8(7)	5161.6(7)	8680(2)	18.9(3)
C8	1512.4(7)	6340.2(7)	4711(2)	18.3(3)
C9	1094.2(8)	5664.2(7)	4311(2)	23.8(3)
C10	344.9(8)	5652.0(7)	3162(2)	24.3(3)
C11	-24.2(8)	6309.0(7)	2420(2)	22.1(3)
C12	369.8(8)	6980.9(7)	2854(2)	22.1(3)
C13	1127.1(7)	6998.9(7)	3979(2)	20.6(3)
C14A	-814.6(8)	6281.4(8)	1104(2)	27.5(3)
C15	4797.2(7)	6484.3(6)	7372(2)	17.4(2)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman268R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C16	5175.6(8)	6301.2(7)	5563(2)	20.6(3)
C17	6018.5(8)	6363.8(7)	5507(2)	20.2(3)
C18	6488.9(7)	6602.8(7)	7296(2)	19.0(3)
C19	6119.1(8)	6770.4(7)	9133(2)	20.2(3)
C20	5278.7(7)	6714.9(7)	9158(2)	19.3(3)
C21	7718.8(8)	6536.2(8)	5559(2)	27.0(3)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for Gandelman268R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	40(3)	74(4)	20(2)	-8.8(15)	-10.5(18)	7.5(17)
F1A	28(2)	171(8)	22(3)	-18(3)	-4.0(18)	19(3)
O1	15.7(4)	29.3(5)	27.1(5)	-2.7(4)	0.7(4)	-2.3(4)
N1	16.6(5)	15.7(5)	27.2(6)	4.3(4)	-4.0(4)	-1.7(4)
C1	18.1(6)	16.5(6)	23.5(7)	2.2(5)	-1.8(5)	0.0(4)
F2	23.4(18)	42(3)	65(3)	-12(2)	-13(2)	14.2(18)
F2A	44(4)	34(2)	115(6)	11(3)	-51(4)	0(2)
N2	17.4(5)	16.4(5)	35.9(7)	4.1(5)	-2.5(5)	-2.0(4)
C2	17.4(6)	16.5(5)	17.7(6)	0.1(5)	0.8(5)	0.8(4)
F3	33(3)	49(2)	74(5)	25(3)	-27(3)	-22(2)
F3A	20.3(18)	77(5)	44(2)	8(2)	0.8(19)	-13(2)
N3	15.3(5)	16.6(5)	23.2(6)	2.9(4)	-0.5(4)	0.7(4)
C3	16.9(6)	13.8(5)	20.9(6)	1.6(5)	-2.3(5)	-0.6(4)
C4	16.9(6)	20.7(6)	24.6(7)	-1.2(5)	1.7(5)	-0.6(5)
C5	22.4(6)	24.1(6)	19.5(6)	0.2(5)	1.3(5)	-3.5(5)
C6	22.2(6)	20.2(6)	17.3(6)	1.3(5)	-2.5(5)	-0.8(5)
C7	18.0(6)	16.9(6)	21.3(6)	0.6(5)	-1.0(5)	1.8(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman268R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C8	15.3(6)	20.3(6)	19.0(6)	1.2(5)	1.0(5)	0.5(4)
C9	19.9(6)	19.8(6)	30.9(7)	4.8(5)	-1.8(5)	0.1(5)
C10	19.3(6)	22.7(6)	30.1(7)	1.6(5)	-1.5(5)	-3.8(5)
C11	17.1(6)	27.3(7)	21.7(6)	1.3(5)	-0.4(5)	-0.3(5)
C12	19.4(6)	23.2(6)	23.4(7)	4.3(5)	-0.9(5)	3.4(5)
C13	18.6(6)	19.1(6)	23.6(7)	2.0(5)	-0.2(5)	-0.3(5)
C14A	20.3(6)	30.8(7)	30.4(8)	1.4(6)	-3.9(5)	0.4(5)
C15	15.6(6)	15.0(5)	21.5(6)	2.3(5)	0.0(5)	1.6(4)
C16	20.1(6)	20.2(6)	20.6(6)	-0.7(5)	-2.5(5)	-0.6(5)
C17	20.6(6)	20.0(6)	20.2(6)	-1.2(5)	2.5(5)	0.6(5)
C18	16.1(6)	15.4(5)	25.4(7)	2.7(5)	0.0(5)	0.4(4)
C19	21.2(6)	18.0(6)	20.6(6)	-2.0(5)	-2.6(5)	-0.4(5)
C20	21.2(6)	16.3(6)	20.4(6)	0.4(5)	1.7(5)	1.7(5)
C21	18.5(6)	31.8(7)	31.1(7)	-0.2(6)	4.2(5)	0.7(5)

Table 4 Bond Lengths for Gandelman268R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C14A	1.415(11)	C3	C4	1.5334(17)
F1A	C14A	1.245(11)	C4	C5	1.5296(18)
O1	C18	1.3699(14)	C5	C6	1.5289(17)
O1	C21	1.4275(16)	C6	C7	1.5233(17)
N1	N2	1.4265(14)	C8	C9	1.4084(17)
N1	C3	1.4676(15)	C8	C13	1.4033(17)
N1	C8	1.3919(16)	C9	C10	1.3792(19)
C1	N2	1.4335(16)	C10	C11	1.3915(18)
C1	N3	1.4663(16)	C11	C12	1.3869(18)

Table 4 Bond Lengths for Gandelman268R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F2	C14A	1.318(8)	C11	C14A	1.4865(19)
F2A	C14A	1.332(11)	C12	C13	1.3839(18)
C2	N3	1.4804(15)	C15	C16	1.3906(18)
C2	C3	1.5406(16)	C15	C20	1.3905(18)
C2	C7	1.5260(16)	C16	C17	1.3955(17)
F3	C14A	1.321(10)	C17	C18	1.3874(18)
F3A	C14A	1.348(10)	C18	C19	1.3921(18)
N3	C15	1.4531(15)	C19	C20	1.3885(17)

Table 5 Bond Angles for Gandelman268R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C18	O1	C21	117.19(10)	C12	C11	C14A	120.88(12)
N2	N1	C3	114.52(10)	C13	C12	C11	120.59(12)
C8	N1	N2	116.23(10)	C12	C13	C8	120.91(12)
C8	N1	C3	123.55(10)	F1	C14A	C11	111.1(4)
N2	C1	N3	113.46(10)	F1A	C14A	F2A	102.9(7)
N1	N2	C1	108.88(10)	F1A	C14A	F3A	105.8(8)
N3	C2	C3	109.13(9)	F1A	C14A	C11	114.7(5)
N3	C2	C7	111.20(10)	F2	C14A	F1	108.2(6)
C7	C2	C3	110.07(10)	F2	C14A	F3	106.4(7)
C1	N3	C2	109.44(10)	F2	C14A	C11	113.4(5)
C15	N3	C1	110.61(9)	F2A	C14A	F3A	106.3(8)
C15	N3	C2	113.93(9)	F2A	C14A	C11	113.8(5)
N1	C3	C2	108.46(9)	F3	C14A	F1	103.6(7)
N1	C3	C4	112.87(10)	F3	C14A	C11	113.5(5)
C4	C3	C2	113.54(10)	F3A	C14A	C11	112.4(6)
C5	C4	C3	111.59(10)	C16	C15	N3	122.22(11)

Table 5 Bond Angles for Gandelman268R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	C5	C4	110.49(10)	C20	C15	N3	119.11(11)
C7	C6	C5	110.05(10)	C20	C15	C16	118.63(11)
C6	C7	C2	112.47(10)	C15	C16	C17	121.11(12)
N1	C8	C9	121.01(11)	C18	C17	C16	119.50(12)
N1	C8	C13	121.06(11)	O1	C18	C17	124.63(11)
C13	C8	C9	117.82(11)	O1	C18	C19	115.47(11)
C10	C9	C8	120.74(12)	C17	C18	C19	119.90(11)
C9	C10	C11	120.74(12)	C20	C19	C18	120.01(12)
C10	C11	C14A	119.91(12)	C19	C20	C15	120.83(12)
C12	C11	C10	119.16(12)				

Table 6 Torsion Angles for Gandelman268R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C18	C19	C20	177.69(11)	C7	C2	C3	C4	50.66(13)
N1	C3	C4	C5	-175.83(10)	C8	N1	N2	C1	-148.28(11)
N1	C8	C9	C10	-173.93(12)	C8	N1	C3	C2	151.21(11)
N1	C8	C13	C12	174.85(12)	C8	N1	C3	C4	-82.09(14)
C1	N3	C15	C16	-61.15(14)	C8	C9	C10	C11	-1.6(2)
C1	N3	C15	C20	116.41(12)	C9	C8	C13	C12	-1.58(19)
N2	N1	C3	C2	-56.50(13)	C9	C10	C11	C12	-0.2(2)
N2	N1	C3	C4	70.21(13)	C9	C10	C11	C14A	177.30(13)
N2	N1	C8	C9	179.82(12)	C10	C11	C12	C13	1.1(2)
N2	N1	C8	C13	3.50(18)	C10	C11	C14A	F1	-80.6(4)
N2	C1	N3	C2	59.52(13)	C10	C11	C14A	F1A	-72.4(8)
N2	C1	N3	C15	-174.15(10)	C10	C11	C14A	F2	157.2(6)
C2	N3	C15	C16	62.63(15)	C10	C11	C14A	F2A	169.4(9)
C2	N3	C15	C20	-119.81(12)	C10	C11	C14A	F3	35.6(9)

Table 6 Torsion Angles for Gandelman268R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	C3	C4	C5	-51.88(13)	C10	C11	C14A	F3A	48.5(7)
N3	C1	N2	N1	-57.87(14)	C11	C12	C13	C8	-0.2(2)
N3	C2	C3	N1	54.68(13)	C12	C11	C14A	F1	96.8(4)
N3	C2	C3	C4	-71.64(12)	C12	C11	C14A	F1A	105.1(8)
N3	C2	C7	C6	66.73(12)	C12	C11	C14A	F2	-25.3(6)
N3	C15	C16	C17	175.96(11)	C12	C11	C14A	F2A	-13.1(9)
N3	C15	C20	C19	-176.89(11)	C12	C11	C14A	F3	-146.9(9)
C3	N1	N2	C1	57.31(14)	C12	C11	C14A	F3A	-134.0(6)
C3	N1	C8	C9	-28.32(19)	C13	C8	C9	C10	2.5(2)
C3	N1	C8	C13	155.37(12)	C14A	C11	C12	C13	-176.35(12)
C3	C2	N3	C1	-56.29(12)	C15	C16	C17	C18	0.91(19)
C3	C2	N3	C15	179.31(10)	C16	C15	C20	C19	0.76(18)
C3	C2	C7	C6	-54.34(13)	C16	C17	C18	O1	-178.45(11)
C3	C4	C5	C6	54.98(14)	C16	C17	C18	C19	0.66(18)
C4	C5	C6	C7	-58.35(13)	C17	C18	C19	C20	-1.50(18)
C5	C6	C7	C2	59.06(13)	C18	C19	C20	C15	0.78(18)
C7	C2	N3	C1	-177.90(9)	C20	C15	C16	C17	-1.61(18)
C7	C2	N3	C15	57.69(13)	C21	O1	C18	C17	-0.79(17)
C7	C2	C3	N1	176.97(10)	C21	O1	C18	C19	-179.93(11)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman268R.

Atom	*x*	*y*	*z*	U(eq)
H1A	3783.14	7493.12	6136.47	23
H1B	3632.69	6835.14	4451.69	23
H2	2568(10)	7265(10)	7440(30)	37(5)
H2A	3660.09	5551.22	5614.86	21

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman268R.

Atom	*x*	*y*	*z*	U(eq)
H3	2382.34	5290.61	6685.6	21
H4A	2540.34	6408.32	9914.39	25
H4B	1774.26	5867.1	9432.51	25
H5A	2631.58	5447.63	12438.56	26
H5B	2553.66	4827.46	10616.49	26
H6A	3916.14	5824.79	11362.12	24
H6B	3942.62	4952.99	11905.53	24
H7A	3717.46	4657.22	8273.14	23
H7B	4516.49	5162.7	8660.08	23
H9	1330.89	5211.71	4837.19	29
H10	77.74	5189.8	2875.05	29
H12	117.69	7432.74	2374.67	27
H13	1389.69	7463.59	4258.66	25
H16	4854.85	6130.6	4343.43	25
H17	6268.35	6243.75	4254.28	24
H19	6441.85	6922.68	10369.2	24
H20	5029.53	6836.03	10411.3	23
H21A	7513.53	6867.11	4407.36	40
H21B	7611.69	6017.61	5144.37	40
H21C	8307.06	6610.43	5854.55	40

Table 8 Atomic Occupancy for Gandelman268R.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
F1	0.52(4)	F1A	0.48(4)	F2	0.52(4)
F2A	0.48(4)	F3	0.52(4)	F3A	0.48(4)

Experimental

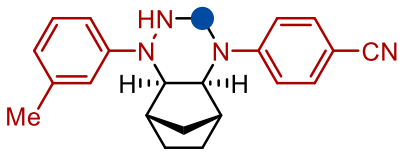
Single crystals of $C_{21}H_{24}F_3N_3O$ **[Gandelman268R]** were obtained by slow evaporation of Et_2O/Hexane solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at

100.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman268R]

Crystal Data for $C_{21}H_{24}F_3N_3O$ (M =391.43 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 16.4618(6) Å, b = 17.9646(6) Å, c = 6.3445(3) Å, β = 94.807(3)°, V = 1869.67(12) Å^3, Z = 4, T = 100.15 K, μ(MoKα) = 0.107 mm^{-1}, *Dcalc* = 1.391 g/cm^3, 13182 reflections measured (4.966° ≤ 2Θ ≤ 60.002°), 4284 unique (R_{int} = 0.0324, R_{sigma} = 0.0336) which were used in all calculations. The final R_1 was 0.0396 (I > 2σ(I)) and wR_2 was 0.1023 (all data).

3.1.11 4-((4aSR,5RS,8SR,8aRS)-1-(m-tolyl)octahydro-5,8-methanobenzo[e][1,2,4]triazin-4(1H)-yl)benzonitrile (4.34)



4.34

Sample name: Gandelman264R

CCDC number: 2505623

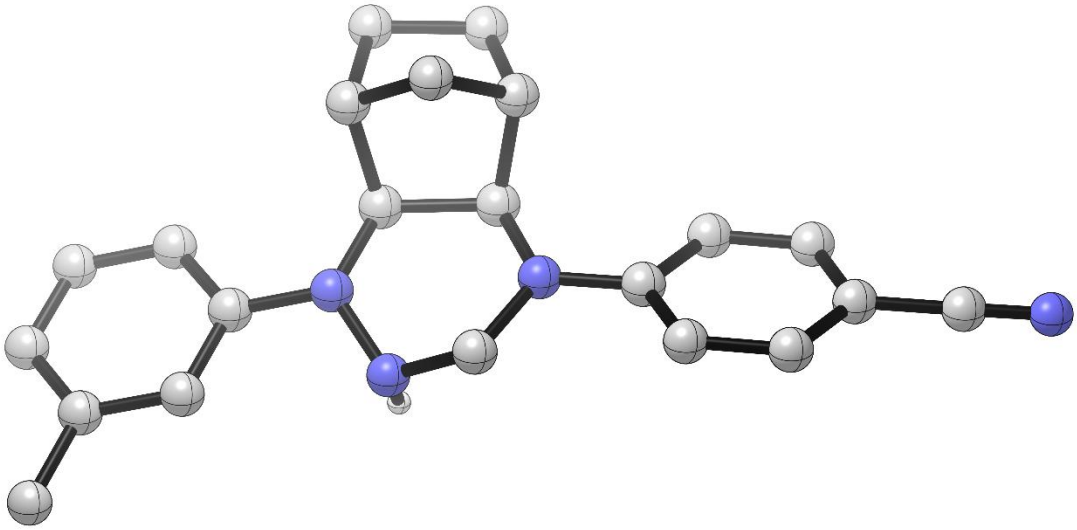


Table 1 Crystal data and structure refinement for Gandelman264R.

Identification code	Gandelman264R
Empirical formula	$C_{22}H_{24}N_4$
Formula weight	344.45
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	8.8893(5)
b/Å	9.3688(5)
c/Å	11.6440(5)
α/°	69.406(5)
β/°	85.304(4)
γ/°	75.410(5)
Volume/Å^3	878.47(9)
Z	2
ρ_{calc}g/cm^3	1.302
μ/mm^{-1}	0.079
F(000)	368.0
Crystal size/mm^3	0.21 × 0.21 × 0.18
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.784 to 60.054
Index ranges	-12 ≤ h ≤ 11, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	10270
Independent reflections	4002 [R_{int} = 0.0522, R_{sigma} = 0.0587]
Data/restraints/parameters	4002/0/253
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0706, wR_2 = 0.1944
Final R indexes [all data]	R_1 = 0.0867, wR_2 = 0.2098
Largest diff. peak/hole / e Å^{-3}	0.50/-0.38

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman264R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
N1	7723.6(16)	-376.2(16)	4886.5(13)	25.1(4)
C1	5790(4)	1878(3)	4749(3)	33.2(7)
C1A	6348(19)	2092(16)	4764(13)	33.2(7)
N2	6262.5(17)	2720.5(15)	3514.9(14)	26.2(4)
C2	7594.2(18)	1976.0(17)	2906.9(15)	22.4(4)
N3	6989(3)	699(2)	5457.1(18)	30.2(7)
N3A	6242(13)	212(12)	5127(11)	49(4)
C3	8308.2(18)	190.6(17)	3642.2(15)	21.2(4)
N4	2817.6(16)	10470.7(15)	885.0(14)	28.7(4)
C4	7929.7(19)	-654.3(18)	2806.1(16)	24.4(4)
C5	6426.5(19)	451.7(19)	2156.3(17)	27.2(4)
C6	7106.7(18)	1905.9(18)	1693.4(15)	23.6(4)
C7	8602.6(19)	1354.0(19)	1034.7(16)	26.3(4)
C8	9082(2)	-446.0(19)	1746.4(16)	27.6(4)
C9	8498.6(18)	-1860.7(18)	5693.3(16)	22.1(4)
C10	9732.4(19)	-2847.7(19)	5304.1(16)	25.1(4)
C11	10413.2(19)	-4327.3(19)	6114.2(17)	27.0(4)
C12	9894(2)	-4855.9(18)	7311.5(17)	27.5(4)
C13	8682.7(19)	-3881.0(18)	7718.4(17)	26.0(4)
C14	8005.3(18)	-2389.2(18)	6912.1(16)	23.5(4)
C15	8063(2)	-4425(2)	9002.9(18)	36.0(5)
C16	5557.3(18)	4299.5(17)	2974.6(15)	22.2(4)
C17	4131.8(18)	4964.1(18)	3419.6(16)	25.2(4)
C18	3426.5(19)	6545.1(19)	2891.2(17)	25.9(4)
C19	4108.8(18)	7513.4(17)	1906.4(16)	22.9(4)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman264R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C20	5514.9(19)	6861.9(19)	1442.8(16)	26.6(4)
C21	6218.6(19)	5287.9(19)	1961.3(17)	26.7(4)
C22	3384.3(18)	9156.2(18)	1345.7(16)	23.6(4)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for Gandelman264R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N1	35.2(8)	21.1(6)	10.9(7)	-1.7(5)	2.7(6)	0.8(6)
C1	43.1(18)	21.3(11)	19.6(11)	2.4(8)	13.1(12)	1.8(11)
C1A	43.1(18)	21.3(11)	19.6(11)	2.4(8)	13.1(12)	1.8(11)
N2	36.5(8)	20.1(7)	12.9(8)	-0.6(5)	6.0(6)	-0.1(6)
C2	29.2(8)	19.6(7)	13.4(8)	-1.8(6)	2.2(6)	-3.5(6)
N3	43.0(14)	24.2(10)	14.9(10)	-4.1(7)	1.6(8)	2.6(9)
N3A	39(5)	39(5)	43(7)	7(5)	19(5)	-1(4)
C3	26.5(7)	19.4(7)	13.0(8)	-2.0(6)	1.7(6)	-2.8(6)
N4	33.2(7)	24.6(7)	23.6(8)	-3.9(6)	1.5(6)	-5.5(6)
C4	33.3(8)	22.2(8)	15.3(8)	-4.8(6)	2.4(6)	-5.7(6)
C5	28.0(8)	32.4(8)	19.9(9)	-7.2(7)	0.4(6)	-7.6(7)
C6	29.0(8)	24.8(8)	11.3(8)	-2.0(6)	0.8(6)	-2.9(6)
C7	33.6(8)	27.8(8)	11.8(8)	-2.6(6)	4.1(6)	-4.9(7)
C8	33.9(9)	26.3(8)	16.2(9)	-5.0(7)	2.8(7)	-0.5(7)
C9	28.9(8)	19.0(7)	15.1(8)	-2.8(6)	-2.5(6)	-4.0(6)
C10	30.3(8)	24.9(8)	17.0(9)	-5.6(7)	0.3(6)	-3.3(6)
C11	30.8(8)	23.1(8)	24.0(10)	-7.4(7)	-1.8(7)	-1.1(6)
C12	38.1(9)	20.2(8)	20.9(9)	-2.5(7)	-6.5(7)	-5.5(7)
C13	33.6(8)	22.8(8)	17.8(9)	-0.7(6)	-1.1(6)	-8.4(6)
C14	29.0(8)	23.2(8)	14.9(8)	-3.6(6)	0.0(6)	-4.6(6)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman264R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C15	49.5(11)	29.0(8)	18.8(10)	2.2(7)	2.8(8)	-6.6(8)
C16	29.4(8)	20.9(8)	13.8(8)	-3.9(6)	-0.2(6)	-4.6(6)
C17	31.3(8)	23.3(8)	17.5(9)	-3.1(6)	4.3(6)	-7.2(7)
C18	27.8(8)	25.2(8)	20.0(9)	-5.0(7)	4.2(6)	-3.3(6)
C19	28.9(8)	19.7(7)	17.0(9)	-3.3(6)	-1.7(6)	-4.2(6)
C20	30.1(8)	24.9(8)	19.1(9)	-1.5(7)	3.3(7)	-6.7(7)
C21	29.2(8)	25.0(8)	19.7(9)	-3.4(7)	5.4(6)	-3.4(6)
C22	26.8(8)	25.0(8)	17.1(9)	-5.7(7)	1.3(6)	-5.5(6)

Table 4 Bond Lengths for Gandelman264R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	N3	1.397(2)	C6	C7	1.546(2)
N1	N3A	1.341(9)	C7	C8	1.557(2)
N1	C3	1.458(2)	C9	C10	1.402(2)
N1	C9	1.413(2)	C9	C14	1.402(2)
C1	N2	1.461(3)	C10	C11	1.389(2)
C1	N3	1.395(4)	C11	C12	1.388(3)
C1A	N2	1.364(14)	C12	C13	1.394(2)
C1A	N3A	1.69(2)	C13	C14	1.394(2)
N2	C2	1.478(2)	C13	C15	1.507(2)
N2	C16	1.386(2)	C16	C17	1.409(2)
C2	C3	1.575(2)	C16	C21	1.410(2)
C2	C6	1.539(2)	C17	C18	1.386(2)
C3	C4	1.555(2)	C18	C19	1.392(2)
N4	C22	1.151(2)	C19	C20	1.401(2)
C4	C5	1.532(2)	C19	C22	1.440(2)

Table 4 Bond Lengths for Gandelman264R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C4	C8	1.528(2)	C20	C21	1.379(2)
C5	C6	1.535(2)			

Table 5 Bond Angles for Gandelman264R.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N3	N1	C3	119.61(14)	C5	C6	C2	101.33(13)
N3	N1	C9	114.82(14)	C5	C6	C7	102.76(13)
N3A	N1	C3	119.5(5)	C6	C7	C8	103.21(12)
N3A	N1	C9	118.1(4)	C4	C8	C7	102.49(12)
C9	N1	C3	118.70(13)	C10	C9	N1	121.89(15)
N3	C1	N2	113.9(3)	C14	C9	N1	119.53(14)
N2	C1A	N3A	105.9(12)	C14	C9	C10	118.57(14)
C1	N2	C2	121.19(15)	C11	C10	C9	119.90(16)
C1A	N2	C2	113.1(6)	C12	C11	C10	121.16(16)
C1A	N2	C16	118.6(6)	C11	C12	C13	119.68(15)
C16	N2	C1	118.64(15)	C12	C13	C15	121.26(15)
C16	N2	C2	119.75(13)	C14	C13	C12	119.38(16)
N2	C2	C3	114.21(12)	C14	C13	C15	119.35(15)
N2	C2	C6	111.71(13)	C13	C14	C9	121.29(15)
C6	C2	C3	101.79(12)	N2	C16	C17	120.46(14)
C1	N3	N1	113.0(2)	N2	C16	C21	121.76(14)
N1	N3A	C1A	97.5(10)	C17	C16	C21	117.77(14)
N1	C3	C2	114.70(12)	C18	C17	C16	120.80(15)
N1	C3	C4	113.03(13)	C17	C18	C19	120.77(14)
C4	C3	C2	103.04(13)	C18	C19	C20	119.00(14)
C5	C4	C3	102.80(13)	C18	C19	C22	121.31(14)
C8	C4	C3	107.41(13)	C20	C19	C22	119.68(14)

Table 5 Bond Angles for Gandelman264R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	C4	C5	101.35(14)	C21	C20	C19	120.49(15)
C4	C5	C6	94.22(13)	C20	C21	C16	121.15(15)
C2	C6	C7	107.72(13)	N4	C22	C19	179.14(18)

Table 6 Torsion Angles for Gandelman264R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C3	C4	C5	94.93(15)	C3	N1	N3A	C1A	-62.1(12)
N1	C3	C4	C8	-158.64(13)	C3	N1	C9	C10	-4.9(2)
N1	C9	C10	C11	-177.03(15)	C3	N1	C9	C14	176.60(15)
N1	C9	C14	C13	176.43(15)	C3	C2	C6	C5	41.11(14)
C1	N2	C2	C3	6.0(3)	C3	C2	C6	C7	-66.38(14)
C1	N2	C2	C6	120.8(2)	C3	C4	C5	C6	53.46(14)
C1	N2	C16	C17	-18.6(3)	C3	C4	C8	C7	-66.77(16)
C1	N2	C16	C21	162.2(2)	C4	C5	C6	C2	-58.43(14)
C1A	N2	C2	C3	30.9(8)	C4	C5	C6	C7	52.89(15)
C1A	N2	C2	C6	145.7(8)	C5	C4	C8	C7	40.67(17)
C1A	N2	C16	C17	-45.5(9)	C5	C6	C7	C8	-29.33(17)
C1A	N2	C16	C21	135.3(9)	C6	C2	C3	N1	-130.27(14)
N2	C1	N3	N1	-54.2(4)	C6	C2	C3	C4	-7.01(14)
N2	C1A	N3A	N1	79.3(13)	C6	C7	C8	C4	-6.75(17)
N2	C2	C3	N1	-9.7(2)	C8	C4	C5	C6	-57.54(15)
N2	C2	C3	C4	113.52(15)	C9	N1	N3	C1	-157.2(3)
N2	C2	C6	C5	-81.16(15)	C9	N1	N3A	C1A	139.8(6)
N2	C2	C6	C7	171.35(12)	C9	N1	C3	C2	-168.03(14)
N2	C16	C17	C18	179.42(16)	C9	N1	C3	C4	74.24(18)
N2	C16	C21	C20	-179.12(17)	C9	C10	C11	C12	0.0(3)
C2	N2	C16	C17	168.81(15)	C10	C9	C14	C13	-2.1(2)

Table 6 Torsion Angles for Gandelman264R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	N2	C16	C21	-10.4(3)	C10	C11	C12	C13	-0.9(3)
C2	C3	C4	C5	-29.43(15)	C11	C12	C13	C14	0.3(3)
C2	C3	C4	C8	77.00(14)	C11	C12	C13	C15	178.66(17)
C2	C6	C7	C8	77.16(16)	C12	C13	C14	C9	1.2(3)
N3	N1	C3	C2	-18.5(2)	C14	C9	C10	C11	1.4(2)
N3	N1	C3	C4	-136.28(18)	C15	C13	C14	C9	-177.16(16)
N3	N1	C9	C10	-155.84(19)	C16	N2	C2	C3	178.37(14)
N3	N1	C9	C14	25.7(2)	C16	N2	C2	C6	-66.79(19)
N3	C1	N2	C2	25.6(4)	C16	C17	C18	C19	0.1(3)
N3	C1	N2	C16	-146.8(2)	C17	C16	C21	C20	1.7(3)
N3A	N1	C3	C2	34.0(8)	C17	C18	C19	C20	0.8(3)
N3A	N1	C3	C4	-83.8(8)	C17	C18	C19	C22	179.71(17)
N3A	N1	C9	C10	153.3(9)	C18	C19	C20	C21	-0.5(3)
N3A	N1	C9	C14	-25.1(9)	C19	C20	C21	C16	-0.7(3)
N3A	C1A	N2	C2	-64.3(11)	C21	C16	C17	C18	-1.4(3)
N3A	C1A	N2	C16	147.9(6)	C22	C19	C20	C21	-179.43(16)
C3	N1	N3	C1	52.2(3)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman264R.

Atom	*x*	*y*	*z*	U(eq)
H1A	5375.74	2640.41	5175.62	40
H1B	4938.38	1403.9	4682.18	40
H1AA	5476.99	2670.59	5135.77	40
H1AB	7339.96	2138.41	5062.51	40
H2	8421.6	2573.02	2746.49	27
H3	7960(60)	1030(50)	5600(50)	108(16)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman264R.

Atom	*x*	*y*	*z*	U(eq)
H3A	5463.31	-239.67	5390.91	59
H3B	9462.3	17.85	3683.66	25
H4	7860.06	-1763.91	3247.64	29
H5A	5550.83	547.73	2728.58	33
H5B	6118.74	168.33	1482	33
H6	6379.4	2885.05	1174.25	28
H7A	9422.25	1871.45	1093.68	32
H7B	8393.51	1575.31	159.07	32
H8A	8969.74	-1051.25	1225.26	33
H8B	10166.72	-775.07	2050.66	33
H10	10102.21	-2504.72	4487.53	30
H11	11249.15	-4989.2	5844.07	32
H12	10361.13	-5877.25	7851.09	33
H14	7193.49	-1717.47	7194.23	28
H15A	7831.47	-3558.33	9325.19	54
H15B	8843.17	-5303.9	9528.17	54
H15C	7111.31	-4767.3	8990.62	54
H17	3648.01	4320.65	4090.17	30
H18	2466.06	6973.23	3204.68	31
H20	5986.89	7509.4	766.29	32
H21	7165.47	4862.18	1629.85	32

Table 8 Atomic Occupancy for Gandelman264R.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
C1	0.809(7)	H1A	0.809(7)	H1B	0.809(7)
C1A	0.191(7)	H1AA	0.191(7)	H1AB	0.191(7)

Table 8 Atomic Occupancy for Gandelman264R.

Atom	*Occupancy*	Atom	*Occupancy*	Atom	*Occupancy*
N3	0.809(7)	H3	0.809(7)	N3A	0.191(7)
H3A	0.191(7)				

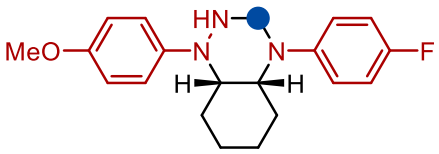
Experimental

Single crystals of $C_{22}H_{24}N_4$ **[Gandelman264R]** were obtained by slow evaporation of Et_2O/Hexane solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman264R]

Crystal Data for $C_{22}H_{24}N_4$ (M =344.45 g/mol): triclinic, space group P-1 (no. 2), a = 8.8893(5) Å, b = 9.3688(5) Å, c = 11.6440(5) Å, α = 69.406(5)°, β = 85.304(4)°, γ = 75.410(5)°, V = 878.47(9) Å^3, Z = 2, T = 100.15 K, μ(MoKα) = 0.079 mm^{-1}, *Dcalc* = 1.302 g/cm^3, 10270 reflections measured (4.784° ≤ 2Θ ≤ 60.054°), 4002 unique (R_{int} = 0.0522, R_{sigma} = 0.0587) which were used in all calculations. The final R_1 was 0.0706 (I > 2σ(I)) and wR_2 was 0.2098 (all data).

3.1.12 (4aRS,8aSR)-4-(4-fluorophenyl)-1-(4-methoxyphenyl)decahydrobenzo[e][1,2,4]triazine (4.36)



4.36

Sample name: Gandelman267R

CCDC number: 2505624

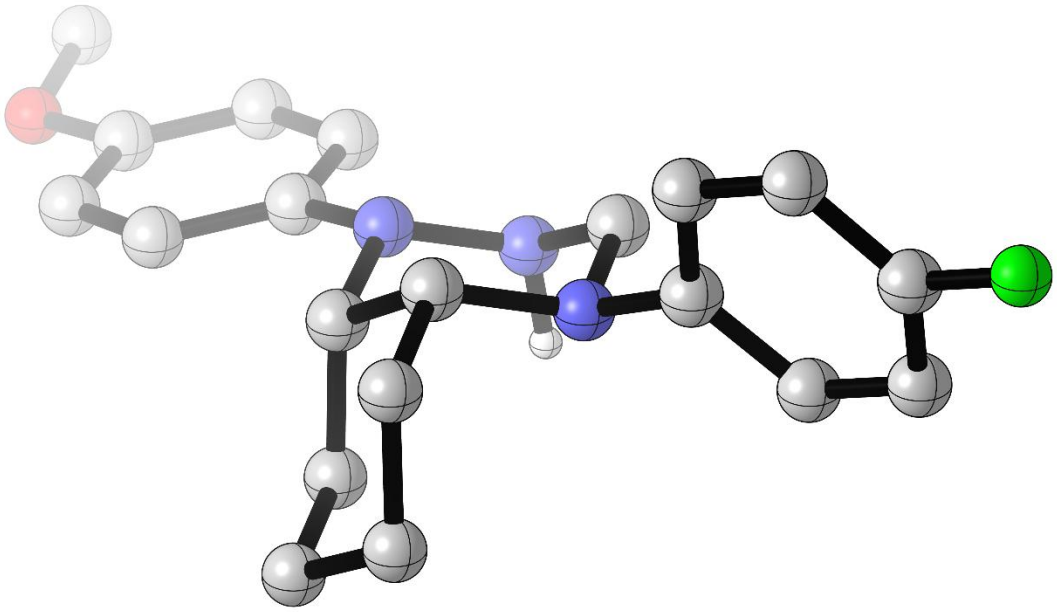


Table 1 Crystal data and structure refinement for Gandelman267R.

Identification code	Gandelman267R
Empirical formula	$C_{20}H_{24}FN_3O$
Formula weight	341.42
Temperature/K	100.15
Crystal system	monoclinic
Space group	C2/c
a/Å	22.7307(9)
b/Å	9.1912(3)
c/Å	17.8373(7)
α/°	90
β/°	111.967(5)
γ/°	90
Volume/Å^3	3456.1(3)
Z	8
ρ_{calc}g/cm^3	1.312
μ/mm^{-1}	0.726
F(000)	1456.0
Crystal size/mm^3	0.24 × 0.15 × 0.15
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.388 to 160.42
Index ranges	-28 ≤ h ≤ 24, -10 ≤ k ≤ 11, -22 ≤ l ≤ 22
Reflections collected	13045
Independent reflections	3545 [R_{int} = 0.0666, R_{sigma} = 0.0354]
Data/restraints/parameters	3545/0/231
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0730, wR_2 = 0.1935
Final R indexes [all data]	R_1 = 0.0833, wR_2 = 0.2027
Largest diff. peak/hole / e Å^{-3}	0.47/-0.29

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman267R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	9336.0(8)	3791.9(17)	4326.5(10)	50.9(4)
O1	5975.4(8)	3443.6(17)	9349.6(11)	39.7(4)
N1	8293.4(9)	2932(2)	6648.7(12)	39.8(5)
C1	7606.2(12)	2869(3)	6311.2(16)	44.2(6)
N2	7537.3(10)	3334(2)	7559.9(13)	38.3(5)
C2	8230.6(11)	3313(2)	7972.7(15)	35.1(5)
N3	7315.1(10)	2445(3)	6848.0(14)	47.8(6)
C3	8522.2(11)	3853(3)	7377.3(15)	37.7(5)
C4	9249.0(11)	3811(3)	7774.4(16)	42.2(6)
C5	9499.4(12)	2320(3)	8108.8(17)	48.7(7)
C6	9219.1(14)	1853(3)	8727.2(18)	51.8(7)
C7	8493.1(13)	1838(3)	8344.6(17)	43.1(6)
C8	8552.6(11)	3219(2)	6046.5(14)	34.9(5)
C9	8686.2(12)	2034(2)	5650.3(15)	37.7(5)
C10	8940.1(11)	2213(3)	5069.6(15)	39.0(6)
C11	9070.3(11)	3598(3)	4891.6(15)	37.8(5)
C12	8948.2(13)	4805(3)	5262.6(16)	43.2(6)
C13	8680.6(13)	4608(2)	5839.6(15)	41.5(6)
C14	7145.2(11)	3285(2)	8011.0(15)	35.5(5)
C15	6492.4(11)	3035(3)	7622.7(16)	38.7(5)
C16	6093.6(11)	3084(2)	8051.1(16)	37.9(5)
C17	6329.2(11)	3374(2)	8870.1(15)	34.8(5)
C18	6977.5(11)	3604(2)	9263.0(16)	36.8(5)
C19	7377.0(11)	3563(2)	8842.4(15)	36.9(5)
C20	5303.2(13)	3416(3)	8941.7(18)	48.0(7)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Gandelman267R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	54.9(9)	48.6(9)	58.0(9)	2.6(7)	31.4(8)	-1.4(7)
O1	37.2(9)	29.4(8)	56.1(10)	1.3(7)	21.6(8)	1.3(7)
N1	36.0(11)	40.6(11)	43.4(11)	-2.4(9)	15.5(9)	-5.0(9)
C1	36.8(13)	45.5(14)	49.0(14)	-6.7(11)	14.5(11)	0.3(11)
N2	32.8(10)	37.1(10)	44.5(11)	-4.5(8)	14.0(9)	0.5(8)
C2	33.7(12)	28.6(11)	42.4(12)	-5.0(9)	13.8(10)	2.7(9)
N3	37.7(11)	59.6(15)	46.8(12)	-11.4(11)	16.8(10)	-12.6(11)
C3	35.1(12)	28.9(11)	48.1(13)	-0.9(10)	14.3(11)	0.6(9)
C4	33.0(12)	46.8(14)	46.4(13)	-7.4(11)	14.5(11)	-2.7(11)
C5	36.8(13)	59.7(17)	51.8(15)	5.3(12)	19.3(12)	14.5(12)
C6	48.6(15)	57.8(17)	54.2(15)	12.2(13)	25.1(13)	24.8(13)
C7	49.0(15)	33.5(12)	53.1(14)	2.2(10)	26.4(12)	9.0(11)
C8	33.2(11)	28.7(11)	41.0(12)	1.8(9)	12.0(10)	1.5(9)
C9	40.7(12)	21.2(10)	48.5(13)	1.6(9)	13.6(11)	-2.7(9)
C10	39.9(12)	28.2(11)	49.0(13)	-2.4(10)	16.7(11)	2.9(10)
C11	33.5(12)	36.8(12)	43.7(12)	2.5(10)	15.0(10)	-1.2(9)
C12	55.9(15)	24.6(11)	51.5(14)	5.6(10)	22.8(12)	-3.4(10)
C13	54.8(15)	23.6(11)	49.2(13)	0.2(9)	23.0(12)	5.1(10)
C14	34.9(12)	24.4(10)	48.9(13)	-0.2(9)	17.5(11)	3.1(9)
C15	36.4(12)	31.8(11)	46.7(13)	0.3(10)	14.1(11)	0.7(10)
C16	31.7(11)	28.1(11)	54.6(14)	2.7(10)	16.8(11)	-1.9(9)
C17	38.0(12)	18.6(9)	53.0(14)	3.8(9)	22.8(11)	3.6(9)
C18	38.3(12)	23.8(10)	48.0(13)	-1.3(9)	15.7(11)	5.9(9)
C19	29.5(11)	31.2(11)	50.3(13)	-2.3(10)	15.3(10)	3.2(9)
C20	40.2(14)	46.7(15)	60.5(16)	4.3(12)	22.9(13)	4.9(11)

Table 4 Bond Lengths for Gandelman267R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C11	1.367(3)	C5	C6	1.527(4)
O1	C17	1.377(3)	C6	C7	1.532(4)
O1	C20	1.426(3)	C8	C9	1.393(3)
N1	C1	1.450(3)	C8	C13	1.389(3)
N1	C3	1.473(3)	C9	C10	1.371(4)
N1	C8	1.430(3)	C10	C11	1.370(3)
C1	N3	1.407(4)	C11	C12	1.372(4)
N2	C2	1.469(3)	C12	C13	1.389(4)
N2	N3	1.434(3)	C14	C15	1.402(3)
N2	C14	1.407(3)	C14	C19	1.399(4)
C2	C3	1.530(3)	C15	C16	1.388(4)
C2	C7	1.529(3)	C16	C17	1.381(4)
C3	C4	1.535(3)	C17	C18	1.391(3)
C4	C5	1.517(4)	C18	C19	1.378(3)

Table 5 Bond Angles for Gandelman267R.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C17	O1	C20	116.5(2)	C13	C8	N1	123.8(2)
C1	N1	C3	111.05(19)	C13	C8	C9	118.5(2)
C8	N1	C1	112.22(19)	C10	C9	C8	121.5(2)
C8	N1	C3	116.61(19)	C11	C10	C9	118.4(2)
N3	C1	N1	115.9(2)	F1	C11	C10	119.0(2)
N3	N2	C2	113.12(19)	F1	C11	C12	118.4(2)
C14	N2	C2	120.2(2)	C10	C11	C12	122.6(2)
C14	N2	N3	113.55(19)	C11	C12	C13	118.4(2)
N2	C2	C3	108.05(19)	C8	C13	C12	120.7(2)
N2	C2	C7	113.6(2)	C15	C14	N2	120.2(2)

Table 5 Bond Angles for Gandelman267R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	C2	C3	112.88(19)	C19	C14	N2	122.2(2)
C1	N3	N2	110.2(2)	C19	C14	C15	117.6(2)
N1	C3	C2	108.92(19)	C16	C15	C14	120.7(2)
N1	C3	C4	110.87(19)	C17	C16	C15	120.9(2)
C2	C3	C4	110.0(2)	O1	C17	C16	125.5(2)
C5	C4	C3	112.6(2)	O1	C17	C18	115.8(2)
C4	C5	C6	109.9(2)	C16	C17	C18	118.8(2)
C5	C6	C7	110.6(2)	C19	C18	C17	120.7(2)
C2	C7	C6	111.4(2)	C18	C19	C14	121.2(2)
C9	C8	N1	117.8(2)				

Table 6 Torsion Angles for Gandelman267R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F1	C11	C12	C13	-179.7(2)	C3	C4	C5	C6	-58.1(3)
O1	C17	C18	C19	-179.86(19)	C4	C5	C6	C7	57.7(3)
N1	C1	N3	N2	52.9(3)	C5	C6	C7	C2	-55.7(3)
N1	C3	C4	C5	-65.9(3)	C7	C2	C3	N1	69.8(2)
N1	C8	C9	C10	-179.5(2)	C7	C2	C3	C4	-51.9(3)
N1	C8	C13	C12	178.3(2)	C8	N1	C1	N3	173.8(2)
C1	N1	C3	C2	53.9(3)	C8	N1	C3	C2	-175.89(19)
C1	N1	C3	C4	175.1(2)	C8	N1	C3	C4	-54.7(3)
C1	N1	C8	C9	-89.1(3)	C8	C9	C10	C11	0.9(4)
C1	N1	C8	C13	91.2(3)	C9	C8	C13	C12	-1.3(4)
N2	C2	C3	N1	-56.7(2)	C9	C10	C11	F1	178.6(2)
N2	C2	C3	C4	-178.45(18)	C9	C10	C11	C12	-1.0(4)
N2	C2	C7	C6	177.0(2)	C10	C11	C12	C13	-0.1(4)
N2	C14	C15	C16	-175.5(2)	C11	C12	C13	C8	1.3(4)

Table 6 Torsion Angles for Gandelman267R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N2	C14	C19	C18	175.6(2)	C13	C8	C9	C10	0.2(4)
C2	N2	N3	C1	-56.2(3)	C14	N2	C2	C3	-162.34(19)
C2	N2	C14	C15	-168.2(2)	C14	N2	C2	C7	71.6(3)
C2	N2	C14	C19	15.6(3)	C14	N2	N3	C1	162.3(2)
C2	C3	C4	C5	54.7(3)	C14	C15	C16	C17	-0.3(3)
N3	N2	C2	C3	59.0(3)	C15	C14	C19	C18	-0.7(3)
N3	N2	C2	C7	-67.1(3)	C15	C16	C17	O1	-179.8(2)
N3	N2	C14	C15	-29.7(3)	C15	C16	C17	C18	-0.5(3)
N3	N2	C14	C19	154.1(2)	C16	C17	C18	C19	0.8(3)
C3	N1	C1	N3	-53.7(3)	C17	C18	C19	C14	-0.2(3)
C3	N1	C8	C9	141.2(2)	C19	C14	C15	C16	0.9(3)
C3	N1	C8	C13	-38.5(3)	C20	O1	C17	C16	-9.3(3)
C3	C2	C7	C6	53.5(3)	C20	O1	C17	C18	171.4(2)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman267R.

Atom	*x*	*y*	*z*	U(eq)
H1A	7443.02	3841.73	6093.47	53
H1B	7474.63	2180.59	5850.87	53
H2	8342.91	4033.96	8424.36	42
H3	7440(20)	1430(60)	6980(30)	115(17)
H3A	8383.33	4878.44	7221.29	45
H4A	9430.3	4093.9	7370.1	51
H4B	9391.91	4531.13	8218.88	51
H5A	9967.82	2352.22	8368.43	58
H5B	9383.6	1603.55	7662.48	58
H6A	9359.2	2535.34	9190.47	62

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman267R.

Atom	*x*	*y*	*z*	U(eq)
H6B	9375.62	870.04	8932.46	62
H7A	8353.45	1079.18	7920.22	52
H7B	8320.46	1588.82	8762.26	52
H9	8599.59	1079.3	5785.48	45
H10	9023.66	1398.08	4797.39	47
H12	9044.21	5751.87	5128.13	52
H13	8584.35	5430.49	6095.13	50
H15	6321.03	2829.54	7059.96	46
H16	5652.19	2916.69	7777	46
H18	7146.73	3792.57	9827.7	44
H19	7818.12	3725.39	9122.25	44
H20A	5172.87	4199.39	8540	72
H20B	5100.61	3554.36	9334.51	72
H20C	5174.08	2476.53	8670.28	72

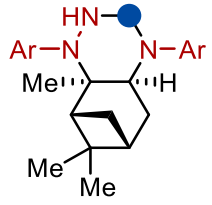
Experimental

Single crystals of $C_{20}H_{24}FN_3O$ **[Gandelman267R]** were obtained by slow evaporation of Et_2O/Hexane solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman267R]

Crystal Data for $C_{20}H_{24}FN_3O$ (*M* =341.42 g/mol): monoclinic, space group C2/c (no. 15), *a* = 22.7307(9) Å, *b* = 9.1912(3) Å, *c* = 17.8373(7) Å, *β* = 111.967(5)°, *V* = 3456.1(3) Å^3, *Z* = 8, *T* = 100.15 K, μ(CuKα) = 0.726 mm^{-1}, *Dcalc* = 1.312 g/cm^3, 13045 reflections measured (8.388° ≤ 2Θ ≤ 160.42°), 3545 unique (R_{int} = 0.0666, R_{sigma} = 0.0354) which were used in all calculations. The final R_1 was 0.0730 (I > 2σ(I)) and wR_2 was 0.2027 (all data).

3.1.13 *(4aS,6R,8R,8aR)-1,4-bis(4-fluorophenyl)-7,7,8a-trimethyldecahydro-6,8-methanobenzo[e][1,2,4]triazine (4.41)*



4.41 (Ar = 4-FC_6H_4)

Sample name: Gandelman255R

CCDC number: 2505625

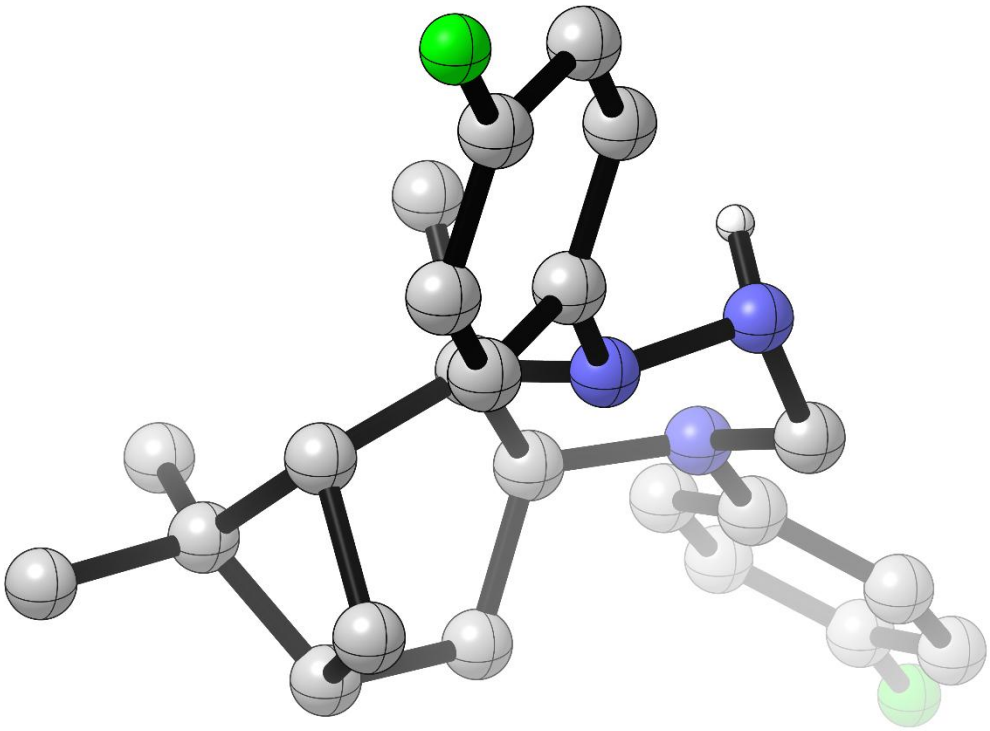


Table 1 Crystal data and structure refinement for Gandelman255R.

Identification code	Gandelman255R
Empirical formula	$C_{73}H_{91}F_6N_9O$
Formula weight	1224.54
Temperature/K	100.15
Crystal system	triclinic
Space group	P1
a/Å	11.3657(3)
b/Å	11.8109(3)
c/Å	13.9331(4)
α/°	85.375(2)
β/°	67.686(3)
γ/°	68.065(4)
Volume/Å^3	1600.96(9)
Z	1
ρ_{calc}g/cm^3	1.270
μ/mm^{-1}	0.717
F(000)	654.0
Crystal size/mm^3	0.15 × 0.15 × 0.12
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.876 to 160.484
Index ranges	-14 ≤ h ≤ 13, -14 ≤ k ≤ 15, -17 ≤ l ≤ 17
Reflections collected	21369
Independent reflections	9206 [R_{int} = 0.0653, R_{sigma} = 0.0669]
Data/restraints/parameters	9206/4/825
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0661, wR_2 = 0.1735
Final R indexes [all data]	R_1 = 0.0688, wR_2 = 0.1772
Largest diff. peak/hole / e Å^{-3}	0.55/-0.32

Flack parameter -0.04(2)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman255R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F1	7240(3)	12954(2)	-274(2)	44.4(6)
N1	5757(3)	9445(3)	2239(2)	30.8(6)
C1	6251(4)	9022(3)	3069(3)	30.3(7)
F2	1820(2)	5923(2)	6969.0(18)	37.4(5)
N2	5225(3)	8731(3)	3921(2)	28.1(6)
C2	4549(3)	7961(3)	2699(2)	25.0(6)
N3	5026(3)	7709(3)	3597(2)	25.7(5)
C3	5444(3)	8540(3)	1818(3)	28.7(6)
C4	6703(4)	7614(4)	975(3)	33.8(7)
C5	6500(4)	6425(4)	855(3)	35.6(7)
C6	6276(4)	5858(3)	1924(3)	33.3(7)
C7	4748(3)	6725(3)	2247(3)	27.8(6)
C8	4987(4)	6651(3)	1056(3)	32.5(7)
C9	4248(4)	7661(4)	502(3)	38.8(8)
C10	4793(5)	5499(4)	818(3)	43.1(9)
C11	3043(3)	8836(3)	3051(3)	29.4(6)
C12	6169(3)	10302(3)	1581(3)	27.5(6)
C13	5555(4)	10830(4)	861(3)	37.9(8)
C14	5920(4)	11719(4)	237(3)	39.5(8)
C15	6881(4)	12085(3)	341(3)	34.2(7)
C16	7508(4)	11602(3)	1031(3)	31.6(7)
C17	7158(4)	10698(3)	1644(3)	28.9(6)
C18	4192(3)	7270(3)	4483(2)	25.1(6)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman255R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C19	3145(4)	8044(3)	5323(3)	30.1(6)
C20	2338(4)	7605(3)	6166(3)	30.5(7)
C21	2603(4)	6361(3)	6150(3)	28.2(6)
C22	3645(3)	5560(3)	5341(3)	28.6(6)
C23	4450(3)	6018(3)	4506(3)	26.5(6)
F1A	7451(3)	3486(2)	3486.4(18)	37.7(5)
N1A	4461(3)	1228(3)	6538(2)	26.5(5)
C1A	4066(4)	374(3)	6158(3)	31.5(7)
F2A	99(3)	-2949(3)	10062(2)	49.6(6)
N2A	3767(3)	-468(3)	6929(2)	30.3(6)
C2A	2774(3)	1130(3)	8342(2)	26.0(6)
N3A	2566(3)	210(3)	7785(2)	28.5(6)
C3A	3489(4)	1920(3)	7534(2)	27.7(6)
C4A	2491(4)	3186(3)	7391(3)	33.9(7)
C5A	1103(4)	3639(3)	8291(3)	34.4(7)
C6A	490(4)	2647(3)	8393(3)	31.9(7)
C7A	1347(3)	1995(3)	9062(3)	27.2(6)
C8A	1238(4)	3304(3)	9358(3)	30.3(7)
C9A	-138(4)	3918(3)	10278(3)	36.5(7)
C10A	2326(4)	3521(4)	9615(3)	36.2(7)
C11A	3659(3)	470(3)	8973(3)	28.4(6)
C12A	5137(3)	1873(3)	5779(3)	26.8(6)
C13A	5885(3)	2461(3)	6001(3)	27.1(6)
C14A	6647(4)	3016(3)	5240(3)	30.1(6)
C15A	6671(4)	2976(3)	4242(3)	30.4(7)
C16A	5915(4)	2457(3)	3997(3)	32.3(7)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman255R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C17A	5142(4)	1910(3)	4763(3)	29.7(6)
C18A	1942(4)	-593(3)	8415(3)	27.7(6)
C19A	2733(4)	-1779(3)	8550(3)	30.5(7)
C20A	2109(4)	-2581(3)	9102(3)	35.3(7)
C21A	707(4)	-2177(4)	9515(3)	35.4(7)
C22A	-110(4)	-1018(4)	9400(3)	34.2(7)
C23A	518(4)	-224(3)	8841(3)	31.2(7)
F1B	10909(3)	11363(2)	1577(2)	44.0(5)
N1B	8824(3)	8107(3)	4048(2)	28.2(5)
C1B	8011(4)	8486(3)	5152(3)	30.7(7)
F2B	5368(3)	3833(2)	8374.8(18)	40.4(5)
N2B	7176(3)	7767(3)	5600(2)	32.3(6)
C2B	8936(4)	5950(3)	4480(3)	27.5(6)
N3B	8084(3)	6527(3)	5578(2)	26.6(5)
C3B	9673(3)	6799(3)	3811(3)	27.5(6)
C4B	11157(4)	6481(3)	3748(3)	31.4(7)
C5B	11835(4)	5139(4)	3948(3)	32.2(7)
C6B	10934(4)	4966(4)	5053(3)	32.6(7)
C7B	10042(4)	4724(3)	4533(3)	30.3(6)
C8B	11397(4)	4257(3)	3513(3)	32.8(7)
C9B	11423(4)	4338(4)	2409(3)	37.6(8)
C10B	12226(4)	2906(4)	3597(4)	41.6(8)
C11B	8033(4)	5743(3)	3980(3)	31.3(7)
C12B	9378(3)	8917(3)	3432(3)	27.2(6)
C13B	10009(4)	8696(3)	2341(3)	29.6(6)
C14B	10510(4)	9518(4)	1720(3)	32.6(7)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman255R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C15B	10382(4)	10574(3)	2181(3)	32.9(7)
C16B	9780(4)	10829(3)	3243(3)	33.7(7)
C17B	9273(4)	10000(3)	3871(3)	31.3(7)
C18B	7354(4)	5849(3)	6288(3)	27.6(6)
C19B	5972(4)	6075(3)	6509(3)	30.5(7)
C20B	5303(4)	5404(3)	7212(3)	30.6(7)
C21B	6020(4)	4506(3)	7700(3)	30.6(7)
C22B	7379(4)	4255(4)	7517(3)	34.2(7)
C23B	8033(4)	4950(4)	6819(3)	31.5(7)
O1	-1030(3)	9362(4)	7143(3)	54.2(9)
C24	-73(7)	10840(5)	6295(5)	62.5(14)
C25	-1341(6)	10634(6)	6981(5)	68.3(17)
C26	-2187(5)	9075(7)	7784(4)	70.0(19)
C27	-1739(7)	7716(8)	7896(4)	74(2)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for Gandelman255R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	43.3(13)	47.4(13)	42.8(12)	22.0(10)	-12.7(10)	-24.6(11)
N1	38.0(15)	35.1(14)	29.3(14)	12.0(11)	-18.2(12)	-20.7(12)
C1	31.7(16)	38.3(17)	28.7(16)	9.3(13)	-15.3(14)	-18.6(14)
F2	37.6(11)	32.0(10)	33.9(10)	11.7(8)	-5.7(9)	-13.7(9)
N2	30.2(14)	32.3(14)	26.1(13)	5.2(10)	-11.6(11)	-15.9(12)
C2	22.4(14)	27.3(14)	25.2(14)	2.6(11)	-8.6(11)	-9.7(12)
N3	25.2(12)	29.5(13)	24.8(12)	5.2(10)	-10.6(10)	-12.2(10)
C3	29.0(16)	32.3(16)	29.0(15)	7.4(12)	-14.5(13)	-13.2(13)
C4	27.9(16)	41.5(19)	29.4(16)	4.1(14)	-10.0(13)	-11.4(14)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman255R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C5	34.3(18)	38.0(18)	25.6(15)	-0.7(13)	-9.3(14)	-5.5(15)
C6	32.7(17)	28.7(15)	29.9(16)	-0.6(13)	-10.2(14)	-3.6(13)
C7	25.4(15)	28.1(15)	27.3(15)	1.6(12)	-9.2(12)	-7.7(12)
C8	35.9(18)	31.9(16)	27.3(15)	-0.9(13)	-13.1(14)	-8.3(14)
C9	43(2)	43.2(19)	34.7(18)	1.1(15)	-22.2(16)	-12.5(16)
C10	52(2)	43(2)	38.0(19)	-4.9(16)	-18.7(18)	-17.0(18)
C11	24.8(15)	32.4(15)	31.9(16)	4.3(12)	-13.0(13)	-9.4(13)
C12	28.2(15)	28.1(14)	24.1(14)	6.0(12)	-9.7(12)	-9.1(12)
C13	41(2)	42.4(19)	42.1(19)	20.3(16)	-24.5(17)	-23.0(17)
C14	40(2)	45(2)	38.2(19)	19.3(16)	-21.2(17)	-18.5(17)
C15	30.0(17)	33.7(17)	31.2(16)	9.9(13)	-5.9(14)	-10.8(14)
C16	29.4(16)	30.3(16)	32.9(17)	5.5(13)	-8.6(13)	-12.8(13)
C17	31.3(16)	27.7(14)	27.6(15)	5.6(12)	-13.2(13)	-9.6(13)
C18	23.7(14)	28.2(15)	25.4(15)	4.8(12)	-12.4(12)	-9.5(12)
C19	30.8(17)	29.0(15)	30.6(16)	6.1(12)	-10.3(13)	-13.5(13)
C20	31.6(16)	29.0(15)	27.0(15)	2.2(12)	-7.6(13)	-10.6(13)
C21	26.9(15)	30.3(16)	28.5(15)	10.5(12)	-12.7(13)	-11.2(13)
C22	26.4(15)	24.4(14)	33.9(16)	5.5(12)	-13.1(13)	-7.3(12)
C23	24.8(15)	25.6(14)	28.8(15)	5.7(11)	-13.5(13)	-6.4(12)
F1A	40.7(11)	31.6(10)	33.3(11)	7.1(8)	-5.4(9)	-15.1(9)
N1A	28.7(13)	24.8(12)	25.7(13)	0.8(10)	-9.8(11)	-10.0(11)
C1A	36.4(18)	33.4(16)	25.0(15)	0.5(12)	-6.4(13)	-18.3(14)
F2A	41.8(13)	44.7(13)	59.0(16)	9.4(11)	-6.5(12)	-26.5(11)
N2A	34.0(16)	27.9(13)	27.4(13)	0.4(11)	-6.3(12)	-14.8(12)
C2A	24.5(14)	27.3(14)	24.8(14)	1.5(11)	-8.0(12)	-9.3(12)
N3A	25.2(13)	30.7(13)	28.5(13)	3.8(11)	-9.0(11)	-10.7(11)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for Gandelman255R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C3A	28.8(15)	26.9(14)	22.6(14)	1.9(11)	-6.3(12)	-8.9(12)
C4A	34.2(18)	29.5(16)	29.5(16)	9.8(12)	-9.7(14)	-6.7(14)
C5A	30.6(17)	26.6(15)	38.2(18)	7.7(13)	-11.9(15)	-4.6(13)
C6A	26.5(16)	33.2(16)	33.9(17)	5.2(13)	-12.2(13)	-8.6(13)
C7A	26.3(15)	28.0(14)	27.7(15)	6.0(12)	-11.0(12)	-10.5(12)
C8A	31.8(16)	25.7(15)	30.7(16)	2.0(12)	-10.7(13)	-8.8(13)
C9A	34.0(18)	29.7(16)	37.0(18)	-1.3(14)	-7.6(15)	-7.7(14)
C10A	35.0(18)	36.7(17)	36.2(18)	-3.9(14)	-10.0(15)	-14.9(15)
C11A	25.2(15)	33.9(15)	25.5(14)	6.3(12)	-8.7(12)	-12.3(13)
C12A	26.1(15)	25.1(14)	25.0(15)	0.4(11)	-7.7(12)	-6.7(12)
C13A	25.3(15)	26.1(14)	27.9(15)	3.8(11)	-12.0(12)	-6.0(12)
C14A	26.3(15)	25.9(14)	33.9(17)	3.0(12)	-10.4(13)	-6.5(12)
C15A	27.5(16)	25.1(14)	28.6(16)	3.2(12)	-3.1(13)	-7.1(12)
C16A	36.6(17)	29.0(15)	25.0(15)	1.2(12)	-8.8(13)	-8.1(14)
C17A	32.0(16)	29.1(15)	27.7(15)	2.8(12)	-11.4(13)	-11.0(13)
C18A	29.4(16)	31.2(15)	25.4(14)	3.6(12)	-11.7(13)	-13.3(13)
C19A	26.0(16)	34.0(16)	30.3(15)	4.5(13)	-8.0(13)	-13.0(13)
C20A	33.9(18)	32.7(16)	38.4(18)	5.2(14)	-12.0(15)	-13.7(14)
C21A	35.9(18)	38.7(18)	33.6(17)	1.3(14)	-6.9(14)	-22.4(15)
C22A	27.4(16)	40.0(18)	35.5(17)	-3.3(14)	-7.4(14)	-16.1(14)
C23A	29.3(17)	35.4(17)	30.2(16)	-0.6(13)	-11.0(13)	-12.9(14)
F1B	49.1(14)	40.3(12)	42.6(13)	19.6(10)	-15.0(11)	-22.2(11)
N1B	25.0(13)	33.1(14)	25.2(13)	6.5(10)	-9.0(11)	-10.9(11)
C1B	30.1(16)	28.9(15)	28.7(16)	2.2(12)	-6.1(13)	-11.6(13)
F2B	42.0(12)	52.9(13)	34.5(11)	18.9(10)	-15.4(9)	-28.7(11)
N2B	30.1(14)	29.1(14)	30.6(14)	5.8(11)	-5.7(12)	-10.0(12)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman255R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C2B	28.6(16)	27.0(14)	28.7(15)	4.1(12)	-12.5(13)	-11.1(12)
N3B	27.2(13)	28.7(13)	25.3(13)	5.6(10)	-11.2(11)	-11.4(11)
C3B	24.5(15)	31.1(16)	26.7(15)	2.2(12)	-9.8(12)	-10.1(13)
C4B	26.2(16)	35.9(17)	33.0(16)	6.0(13)	-11.3(13)	-13.2(13)
C5B	24.9(15)	37.9(17)	35.1(17)	4.3(13)	-13.1(13)	-11.5(13)
C6B	30.4(16)	41.8(18)	31.3(16)	9.1(14)	-17.4(14)	-14.9(14)
C7B	28.3(15)	30.9(15)	33.1(16)	6.3(12)	-15.0(13)	-10.0(13)
C8B	27.5(16)	29.5(16)	38.3(18)	-0.6(13)	-12.4(14)	-6.9(13)
C9B	38.3(19)	37.6(18)	35.8(18)	-1.5(14)	-12.2(15)	-14.0(15)
C10B	35(2)	34.1(18)	53(2)	-0.7(16)	-16.0(17)	-9.0(15)
C11B	31.5(16)	36.2(16)	32.8(16)	5.7(13)	-16.5(14)	-15.8(14)
C12B	22.1(14)	31.9(15)	28.8(15)	6.0(12)	-12.5(12)	-9.2(12)
C13B	27.0(16)	35.2(16)	28.5(15)	6.1(13)	-12.1(13)	-12.6(13)
C14B	28.0(16)	43.1(19)	28.7(16)	13.8(14)	-14.0(13)	-14.3(14)
C15B	28.6(17)	34.1(17)	36.2(17)	14.4(14)	-13.8(14)	-12.6(14)
C16B	30.4(17)	29.3(16)	37.7(18)	5.9(13)	-11.8(14)	-8.8(13)
C17B	27.1(16)	32.9(16)	31.2(16)	4.8(13)	-10.7(13)	-9.0(13)
C18B	26.7(16)	31.7(15)	24.4(14)	3.8(12)	-10.3(12)	-10.6(13)
C19B	29.8(17)	32.4(16)	29.8(15)	5.0(12)	-13.7(13)	-10.0(13)
C20B	26.7(15)	35.6(17)	29.6(15)	5.7(13)	-10.5(13)	-12.4(13)
C21B	35.0(18)	35.7(16)	24.7(15)	7.7(13)	-10.6(13)	-19.0(14)
C22B	34.0(18)	38.9(18)	30.8(17)	11.6(14)	-16.6(14)	-12.0(15)
C23B	28.6(16)	39.9(17)	29.4(16)	12.1(13)	-14.1(13)	-15.0(14)
O1	36.9(16)	64(2)	52.4(18)	-16.3(16)	-21.0(14)	-0.9(14)
C24	75(4)	52(3)	55(3)	1(2)	-34(3)	-6(3)
C25	58(3)	65(3)	61(3)	-11(3)	-37(3)	18(3)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman255R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C26	38(2)	114(5)	42(2)	-27(3)	-13(2)	-7(3)
C27	66(3)	125(6)	39(2)	-20(3)	-6(2)	-52(4)

Table 4 Bond Lengths for Gandelman255R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C15	1.365(4)	C8A	C9A	1.547(5)
N1	C1	1.447(4)	C8A	C10A	1.520(5)
N1	C3	1.468(4)	C12A	C13A	1.406(5)
N1	C12	1.401(4)	C12A	C17A	1.411(5)
C1	N2	1.438(4)	C13A	C14A	1.385(5)
F2	C21	1.356(4)	C14A	C15A	1.385(5)
N2	N3	1.442(4)	C15A	C16A	1.372(5)
C2	N3	1.510(4)	C16A	C17A	1.389(5)
C2	C3	1.563(4)	C18A	C19A	1.397(5)
C2	C7	1.540(4)	C18A	C23A	1.395(5)
C2	C11	1.537(5)	C19A	C20A	1.400(5)
N3	C18	1.438(4)	C20A	C21A	1.371(6)
C3	C4	1.545(5)	C21A	C22A	1.375(6)
C4	C5	1.537(6)	C22A	C23A	1.397(5)
C5	C6	1.552(5)	F1B	C15B	1.357(4)
C5	C8	1.553(5)	N1B	C1B	1.464(5)
C6	C7	1.555(5)	N1B	C3B	1.467(4)
C7	C8	1.581(5)	N1B	C12B	1.399(4)
C8	C9	1.523(5)	C1B	N2B	1.442(4)
C8	C10	1.538(5)	F2B	C21B	1.362(4)
C12	C13	1.409(5)	N2B	N3B	1.437(4)

Table 4 Bond Lengths for Gandelman255R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C12	C17	1.402(5)	C2B	N3B	1.514(4)
C13	C14	1.391(5)	C2B	C3B	1.568(5)
C14	C15	1.372(6)	C2B	C7B	1.541(5)
C15	C16	1.373(5)	C2B	C11B	1.536(4)
C16	C17	1.393(5)	N3B	C18B	1.433(4)
C18	C19	1.387(5)	C3B	C4B	1.553(4)
C18	C23	1.396(4)	C4B	C5B	1.537(5)
C19	C20	1.389(5)	C5B	C6B	1.540(5)
C20	C21	1.385(5)	C5B	C8B	1.554(5)
C21	C22	1.375(5)	C6B	C7B	1.562(5)
C22	C23	1.394(5)	C7B	C8B	1.589(5)
F1A	C15A	1.358(4)	C8B	C9B	1.524(5)
N1A	C1A	1.452(4)	C8B	C10B	1.542(5)
N1A	C3A	1.469(4)	C12B	C13B	1.410(5)
N1A	C12A	1.407(4)	C12B	C17B	1.408(5)
C1A	N2A	1.436(4)	C13B	C14B	1.384(5)
F2A	C21A	1.359(4)	C14B	C15B	1.383(6)
N2A	N3A	1.424(4)	C15B	C16B	1.378(6)
C2A	N3A	1.518(4)	C16B	C17B	1.399(5)
C2A	C3A	1.581(4)	C18B	C19B	1.402(5)
C2A	C7A	1.540(5)	C18B	C23B	1.402(5)
C2A	C11A	1.538(5)	C19B	C20B	1.387(5)
N3A	C18A	1.439(4)	C20B	C21B	1.382(5)
C3A	C4A	1.555(5)	C21B	C22B	1.382(5)
C4A	C5A	1.525(5)	C22B	C23B	1.396(5)
C5A	C6A	1.543(5)	O1	C25	1.430(8)
C5A	C8A	1.558(5)	O1	C26	1.426(8)

Table 4 Bond Lengths for Gandelman255R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C6A	C7A	1.557(5)	C24	C25	1.492(11)
C7A	C8A	1.580(4)	C26	C27	1.506(12)

Table 5 Bond Angles for Gandelman255R.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C1	N1	C3	113.8(3)	C9A	C8A	C7A	108.7(3)
C12	N1	C1	120.8(3)	C10A	C8A	C5A	120.3(3)
C12	N1	C3	118.5(3)	C10A	C8A	C7A	123.4(3)
N2	C1	N1	109.5(3)	C10A	C8A	C9A	106.5(3)
C1	N2	N3	109.5(3)	N1A	C12A	C17A	121.7(3)
N3	C2	C3	110.6(2)	C13A	C12A	N1A	120.6(3)
N3	C2	C7	107.7(3)	C13A	C12A	C17A	117.7(3)
N3	C2	C11	111.2(3)	C14A	C13A	C12A	121.4(3)
C7	C2	C3	107.7(3)	C13A	C14A	C15A	118.7(3)
C11	C2	C3	108.7(3)	F1A	C15A	C14A	118.9(3)
C11	C2	C7	110.9(3)	F1A	C15A	C16A	119.0(3)
N2	N3	C2	113.3(3)	C16A	C15A	C14A	122.1(3)
C18	N3	N2	110.0(2)	C15A	C16A	C17A	119.1(3)
C18	N3	C2	114.7(2)	C16A	C17A	C12A	121.0(3)
N1	C3	C2	112.0(3)	C19A	C18A	N3A	121.3(3)
N1	C3	C4	113.8(3)	C23A	C18A	N3A	119.9(3)
C4	C3	C2	115.0(3)	C23A	C18A	C19A	118.6(3)
C5	C4	C3	112.4(3)	C18A	C19A	C20A	120.6(3)
C4	C5	C6	106.2(3)	C21A	C20A	C19A	118.8(4)
C4	C5	C8	112.2(3)	F2A	C21A	C20A	118.9(4)
C6	C5	C8	87.7(3)	F2A	C21A	C22A	118.7(3)
C5	C6	C7	86.1(3)	C20A	C21A	C22A	122.4(3)

Table 5 Bond Angles for Gandelman255R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C7	C6	109.2(3)	C21A	C22A	C23A	118.6(3)
C2	C7	C8	116.0(3)	C18A	C23A	C22A	120.9(3)
C6	C7	C8	86.6(3)	C1B	N1B	C3B	115.4(3)
C5	C8	C7	85.3(3)	C12B	N1B	C1B	117.4(3)
C9	C8	C5	118.4(3)	C12B	N1B	C3B	116.5(3)
C9	C8	C7	125.3(3)	N2B	C1B	N1B	110.4(3)
C9	C8	C10	105.6(3)	N3B	N2B	C1B	107.4(3)
C10	C8	C5	112.9(3)	N3B	C2B	C3B	109.7(3)
C10	C8	C7	108.4(3)	N3B	C2B	C7B	108.0(3)
N1	C12	C13	120.6(3)	N3B	C2B	C11B	110.6(3)
N1	C12	C17	121.4(3)	C7B	C2B	C3B	108.2(3)
C17	C12	C13	117.9(3)	C11B	C2B	C3B	109.7(3)
C14	C13	C12	120.8(3)	C11B	C2B	C7B	110.5(3)
C15	C14	C13	118.8(3)	N2B	N3B	C2B	112.3(3)
F1	C15	C14	118.7(3)	C18B	N3B	N2B	110.3(3)
F1	C15	C16	118.6(3)	C18B	N3B	C2B	116.2(2)
C14	C15	C16	122.7(3)	N1B	C3B	C2B	113.3(3)
C15	C16	C17	118.4(3)	N1B	C3B	C4B	113.4(3)
C16	C17	C12	121.3(3)	C4B	C3B	C2B	115.0(3)
C19	C18	N3	122.4(3)	C5B	C4B	C3B	112.6(3)
C19	C18	C23	118.6(3)	C4B	C5B	C6B	106.0(3)
C23	C18	N3	119.0(3)	C4B	C5B	C8B	112.6(3)
C18	C19	C20	121.6(3)	C6B	C5B	C8B	88.7(3)
C21	C20	C19	118.2(3)	C5B	C6B	C7B	86.0(3)
F2	C21	C20	118.7(3)	C2B	C7B	C6B	109.2(3)
F2	C21	C22	119.2(3)	C2B	C7B	C8B	115.8(3)
C22	C21	C20	122.1(3)	C6B	C7B	C8B	86.7(3)

Table 5 Bond Angles for Gandelman255R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C21	C22	C23	118.8(3)	C5B	C8B	C7B	84.6(3)
C22	C23	C18	120.7(3)	C9B	C8B	C5B	120.3(3)
C1A	N1A	C3A	116.4(3)	C9B	C8B	C7B	124.5(3)
C12A	N1A	C1A	115.9(3)	C9B	C8B	C10B	105.8(3)
C12A	N1A	C3A	116.1(3)	C10B	C8B	C5B	111.6(3)
N2A	C1A	N1A	110.2(3)	C10B	C8B	C7B	108.8(3)
N3A	N2A	C1A	107.6(3)	N1B	C12B	C13B	120.7(3)
N3A	C2A	C3A	110.6(2)	N1B	C12B	C17B	121.4(3)
N3A	C2A	C7A	107.4(3)	C17B	C12B	C13B	117.9(3)
N3A	C2A	C11A	110.4(3)	C14B	C13B	C12B	121.2(3)
C7A	C2A	C3A	108.3(3)	C15B	C14B	C13B	119.2(3)
C11A	C2A	C3A	109.4(3)	F1B	C15B	C14B	119.3(3)
C11A	C2A	C7A	110.7(3)	F1B	C15B	C16B	118.7(3)
N2A	N3A	C2A	113.1(3)	C16B	C15B	C14B	121.9(3)
N2A	N3A	C18A	110.5(3)	C15B	C16B	C17B	119.0(3)
C18A	N3A	C2A	117.3(3)	C16B	C17B	C12B	120.9(3)
N1A	C3A	C2A	112.9(3)	C19B	C18B	N3B	123.1(3)
N1A	C3A	C4A	112.5(3)	C19B	C18B	C23B	118.2(3)
C4A	C3A	C2A	114.7(3)	C23B	C18B	N3B	118.7(3)
C5A	C4A	C3A	113.7(3)	C20B	C19B	C18B	121.0(3)
C4A	C5A	C6A	106.6(3)	C21B	C20B	C19B	118.9(3)
C4A	C5A	C8A	111.8(3)	F2B	C21B	C20B	118.7(3)
C6A	C5A	C8A	88.3(3)	F2B	C21B	C22B	118.8(3)
C5A	C6A	C7A	86.2(3)	C20B	C21B	C22B	122.4(3)
C2A	C7A	C6A	109.0(3)	C21B	C22B	C23B	118.0(3)
C2A	C7A	C8A	116.0(3)	C22B	C23B	C18B	121.4(3)
C6A	C7A	C8A	87.0(2)	C26	O1	C25	114.1(5)

Table 5 Bond Angles for Gandelman255R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C5A	C8A	C7A	84.9(2)	O1	C25	C24	110.1(4)
C9A	C8A	C5A	111.7(3)	O1	C26	C27	109.4(5)

Table 6 Torsion Angles for Gandelman255R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
F1	C15	C16	C17	-178.8(3)	C5A	C6A	C7A	C2A	-89.2(3)
N1	C1	N2	N3	65.1(4)	C5A	C6A	C7A	C8A	27.4(3)
N1	C3	C4	C5	157.8(3)	C6A	C5A	C8A	C7A	27.4(2)
N1	C12	C13	C14	177.3(4)	C6A	C5A	C8A	C9A	-80.8(3)
N1	C12	C17	C16	-176.2(3)	C6A	C5A	C8A	C10A	153.4(3)
C1	N1	C3	C2	48.2(4)	C6A	C7A	C8A	C5A	-27.1(2)
C1	N1	C3	C4	-84.4(4)	C6A	C7A	C8A	C9A	84.0(3)
C1	N1	C12	C13	-171.8(4)	C6A	C7A	C8A	C10A	-150.3(3)
C1	N1	C12	C17	5.6(5)	C7A	C2A	N3A	N2A	166.7(3)
C1	N2	N3	C2	-60.4(4)	C7A	C2A	N3A	C18A	-62.9(3)
C1	N2	N3	C18	169.7(3)	C7A	C2A	C3A	N1A	-151.0(3)
F2	C21	C22	C23	-179.5(3)	C7A	C2A	C3A	C4A	-20.3(4)
N2	N3	C18	C19	34.2(4)	C8A	C5A	C6A	C7A	-27.8(2)
N2	N3	C18	C23	-145.2(3)	C11A	C2A	N3A	N2A	-72.4(3)
C2	N3	C18	C19	-94.8(4)	C11A	C2A	N3A	C18A	58.0(4)
C2	N3	C18	C23	85.7(4)	C11A	C2A	C3A	N1A	88.3(3)
C2	C3	C4	C5	26.7(4)	C11A	C2A	C3A	C4A	-141.1(3)
C2	C7	C8	C5	81.8(3)	C11A	C2A	C7A	C6A	179.7(3)
C2	C7	C8	C9	-40.0(5)	C11A	C2A	C7A	C8A	83.6(3)
C2	C7	C8	C10	-165.6(3)	C12A	N1A	C1A	N2A	163.0(3)
N3	C2	C3	N1	-40.6(4)	C12A	N1A	C3A	C2A	179.9(3)
N3	C2	C3	C4	91.3(3)	C12A	N1A	C3A	C4A	48.2(4)

Table 6 Torsion Angles for Gandelman255R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N3	C2	C7	C6	-56.9(3)	C12A	C13A	C14A	C15A	-0.4(5)
N3	C2	C7	C8	-152.6(3)	C13A	C12A	C17A	C16A	3.1(5)
N3	C18	C19	C20	179.1(3)	C13A	C14A	C15A	F1A	-178.0(3)
N3	C18	C23	C22	-178.5(3)	C13A	C14A	C15A	C16A	3.1(5)
C3	N1	C1	N2	-60.5(4)	C14A	C15A	C16A	C17A	-2.6(5)
C3	N1	C12	C13	39.0(5)	C15A	C16A	C17A	C12A	-0.6(5)
C3	N1	C12	C17	-143.6(3)	C17A	C12A	C13A	C14A	-2.6(5)
C3	C2	N3	N2	47.6(4)	C18A	C19A	C20A	C21A	-0.5(5)
C3	C2	N3	C18	175.0(3)	C19A	C18A	C23A	C22A	0.6(5)
C3	C2	C7	C6	62.5(3)	C19A	C20A	C21A	F2A	-179.2(3)
C3	C2	C7	C8	-33.2(4)	C19A	C20A	C21A	C22A	0.6(6)
C3	C4	C5	C6	-60.9(4)	C20A	C21A	C22A	C23A	-0.1(5)
C3	C4	C5	C8	33.3(4)	C21A	C22A	C23A	C18A	-0.5(5)
C4	C5	C6	C7	84.0(3)	C23A	C18A	C19A	C20A	-0.1(5)
C4	C5	C8	C7	-78.6(3)	F1B	C15B	C16B	C17B	-178.0(3)
C4	C5	C8	C9	49.3(4)	N1B	C1B	N2B	N3B	65.9(4)
C4	C5	C8	C10	173.4(3)	N1B	C3B	C4B	C5B	156.5(3)
C5	C6	C7	C2	-88.5(3)	N1B	C12B	C13B	C14B	177.3(3)
C5	C6	C7	C8	27.9(3)	N1B	C12B	C17B	C16B	-177.3(3)
C6	C5	C8	C7	28.0(3)	C1B	N1B	C3B	C2B	40.5(4)
C6	C5	C8	C9	155.9(3)	C1B	N1B	C3B	C4B	-93.0(4)
C6	C5	C8	C10	-80.0(3)	C1B	N1B	C12B	C13B	-171.2(3)
C6	C7	C8	C5	-28.0(3)	C1B	N1B	C12B	C17B	6.1(4)
C6	C7	C8	C9	-149.7(4)	C1B	N2B	N3B	C2B	-66.8(3)
C6	C7	C8	C10	84.7(3)	C1B	N2B	N3B	C18B	161.8(3)
C7	C2	N3	N2	165.1(3)	F2B	C21B	C22B	C23B	179.7(3)
C7	C2	N3	C18	-67.5(3)	N2B	N3B	C18B	C19B	32.4(4)

Table 6 Torsion Angles for Gandelman255R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C7	C2	C3	N1	-158.1(3)	N2B	N3B	C18B	C23B	-145.0(3)
C7	C2	C3	C4	-26.1(3)	C2B	N3B	C18B	C19B	-96.9(4)
C8	C5	C6	C7	-28.5(3)	C2B	N3B	C18B	C23B	85.8(4)
C11	C2	N3	N2	-73.2(3)	C2B	C3B	C4B	C5B	23.8(4)
C11	C2	N3	C18	54.1(4)	C2B	C7B	C8B	C5B	82.5(3)
C11	C2	C3	N1	81.8(3)	C2B	C7B	C8B	C9B	-40.9(5)
C11	C2	C3	C4	-146.3(3)	C2B	C7B	C8B	C10B	-166.5(3)
C11	C2	C7	C6	-178.7(3)	N3B	C2B	C3B	N1B	-38.1(3)
C11	C2	C7	C8	85.6(4)	N3B	C2B	C3B	C4B	94.7(3)
C12	N1	C1	N2	149.0(3)	N3B	C2B	C7B	C6B	-58.4(3)
C12	N1	C3	C2	-160.6(3)	N3B	C2B	C7B	C8B	-154.2(3)
C12	N1	C3	C4	66.8(4)	N3B	C18B	C19B	C20B	-179.2(3)
C12	C13	C14	C15	-0.6(7)	N3B	C18B	C23B	C22B	-179.7(3)
C13	C12	C17	C16	1.3(5)	C3B	N1B	C1B	N2B	-54.5(4)
C13	C14	C15	F1	179.8(4)	C3B	N1B	C12B	C13B	45.8(4)
C13	C14	C15	C16	0.5(6)	C3B	N1B	C12B	C17B	-137.0(3)
C14	C15	C16	C17	0.5(6)	C3B	C2B	N3B	N2B	52.2(3)
C15	C16	C17	C12	-1.4(5)	C3B	C2B	N3B	C18B	-179.5(3)
C17	C12	C13	C14	-0.2(6)	C3B	C2B	C7B	C6B	60.3(3)
C18	C19	C20	C21	-0.1(5)	C3B	C2B	C7B	C8B	-35.5(4)
C19	C18	C23	C22	2.0(5)	C3B	C4B	C5B	C6B	-60.3(4)
C19	C20	C21	F2	-180.0(3)	C3B	C4B	C5B	C8B	35.1(4)
C19	C20	C21	C22	1.1(5)	C4B	C5B	C6B	C7B	85.0(3)
C20	C21	C22	C23	-0.6(5)	C4B	C5B	C8B	C7B	-79.2(3)
C21	C22	C23	C18	-1.0(5)	C4B	C5B	C8B	C9B	47.9(4)
C23	C18	C19	C20	-1.5(5)	C4B	C5B	C8B	C10B	172.7(3)
F1A	C15A	C16A	C17A	178.5(3)	C5B	C6B	C7B	C2B	-88.7(3)

Table 6 Torsion Angles for Gandelman255R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1A	C1A	N2A	N3A	67.0(4)	C5B	C6B	C7B	C8B	27.5(3)
N1A	C3A	C4A	C5A	151.1(3)	C6B	C5B	C8B	C7B	27.7(3)
N1A	C12A	C13A	C14A	174.7(3)	C6B	C5B	C8B	C9B	154.8(3)
N1A	C12A	C17A	C16A	-174.2(3)	C6B	C5B	C8B	C10B	-80.4(4)
C1A	N1A	C3A	C2A	38.2(4)	C6B	C7B	C8B	C5B	-27.3(3)
C1A	N1A	C3A	C4A	-93.6(4)	C6B	C7B	C8B	C9B	-150.7(4)
C1A	N1A	C12A	C13A	-162.7(3)	C6B	C7B	C8B	C10B	83.7(3)
C1A	N1A	C12A	C17A	14.5(4)	C7B	C2B	N3B	N2B	170.0(3)
C1A	N2A	N3A	C2A	-65.9(4)	C7B	C2B	N3B	C18B	-61.7(3)
C1A	N2A	N3A	C18A	160.4(3)	C7B	C2B	C3B	N1B	-155.6(3)
F2A	C21A	C22A	C23A	179.7(3)	C7B	C2B	C3B	C4B	-22.9(4)
N2A	N3A	C18A	C19A	34.2(4)	C8B	C5B	C6B	C7B	-28.1(3)
N2A	N3A	C18A	C23A	-140.9(3)	C11B	C2B	N3B	N2B	-69.0(3)
C2A	N3A	C18A	C19A	-97.4(4)	C11B	C2B	N3B	C18B	59.3(4)
C2A	N3A	C18A	C23A	87.5(4)	C11B	C2B	C3B	N1B	83.7(3)
C2A	C3A	C4A	C5A	20.3(4)	C11B	C2B	C3B	C4B	-143.6(3)
C2A	C7A	C8A	C5A	82.6(3)	C11B	C2B	C7B	C6B	-179.5(3)
C2A	C7A	C8A	C9A	-166.2(3)	C11B	C2B	C7B	C8B	84.6(4)
C2A	C7A	C8A	C10A	-40.6(4)	C12B	N1B	C1B	N2B	162.0(3)
N3A	C2A	C3A	N1A	-33.5(4)	C12B	N1B	C3B	C2B	-175.7(3)
N3A	C2A	C3A	C4A	97.1(3)	C12B	N1B	C3B	C4B	50.8(4)
N3A	C2A	C7A	C6A	-59.6(3)	C12B	C13B	C14B	C15B	-0.3(5)
N3A	C2A	C7A	C8A	-155.8(3)	C13B	C12B	C17B	C16B	0.0(5)
N3A	C18A	C19A	C20A	-175.2(3)	C13B	C14B	C15B	F1B	178.0(3)
N3A	C18A	C23A	C22A	175.8(3)	C13B	C14B	C15B	C16B	0.6(5)
C3A	N1A	C1A	N2A	-55.1(4)	C14B	C15B	C16B	C17B	-0.6(5)
C3A	N1A	C12A	C13A	55.3(4)	C15B	C16B	C17B	C12B	0.3(5)

Table 6 Torsion Angles for Gandelman255R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C3A	N1A	C12A	C17A	-127.5(3)	C17B	C12B	C13B	C14B	0.0(5)
C3A	C2A	N3A	N2A	48.7(3)	C18B	C19B	C20B	C21B	0.3(5)
C3A	C2A	N3A	C18A	179.1(3)	C19B	C18B	C23B	C22B	2.8(5)
C3A	C2A	C7A	C6A	59.8(3)	C19B	C20B	C21B	F2B	-178.7(3)
C3A	C2A	C7A	C8A	-36.3(4)	C19B	C20B	C21B	C22B	0.3(5)
C3A	C4A	C5A	C6A	-57.6(4)	C20B	C21B	C22B	C23B	0.6(6)
C3A	C4A	C5A	C8A	37.3(4)	C21B	C22B	C23B	C18B	-2.2(5)
C4A	C5A	C6A	C7A	84.5(3)	C23B	C18B	C19B	C20B	-1.8(5)
C4A	C5A	C8A	C7A	-79.9(3)	C25	O1	C26	C27	179.8(4)
C4A	C5A	C8A	C9A	172.0(3)	C26	O1	C25	C24	-179.4(4)
C4A	C5A	C8A	C10A	46.2(4)					

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman255R.

Atom	*x*	*y*	*z*	U(eq)
H1A	7104.31	8286.94	2812.46	36
H1B	6458.31	9666.38	3308.21	36
H2	4430(50)	9470(50)	4140(40)	29(11)
H3	4837.44	9024.35	1446.21	34
H4A	6884.96	7994.09	301.37	41
H4B	7515.19	7416.12	1159.25	41
H5	7205.41	5858.39	236.83	43
H6A	6759.58	6035.89	2317.85	40
H6B	6432.49	4976.61	1897.85	40
H7	4084.55	6354.58	2701.46	33
H9A	4621.54	8307.7	382.04	58
H9B	3267.37	8002.66	934.46	58

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman255R.

Atom	*x*	*y*	*z*	U(eq)
H9C	4377.51	7321.87	-165.94	58
H10A	5235.91	5278.35	67.35	65
H10B	3812.34	5662.25	1046.92	65
H10C	5206.52	4822.8	1186.59	65
H11A	2737.18	8924.05	2470.2	44
H11B	2953.64	9637.41	3279.63	44
H11C	2477.1	8503.4	3629.51	44
H13	4883.63	10575.08	801.74	45
H14	5510.64	12066.98	-251.81	47
H16	8164.44	11878.9	1088.78	38
H17	7598.85	10343.22	2113.6	35
H19	2975.55	8894.74	5321.78	36
H20	1623.44	8142.85	6737.5	37
H22	3813.09	4709.02	5350.25	34
H23	5182.37	5472.67	3947.13	32
H1AA	3247.19	828.87	5990.14	38
H1AB	4818.8	-84.44	5513.36	38
H2A	4540(50)	-780(40)	7090(30)	20(9)
H3A	4062.18	2110.53	7844.42	33
H4AA	2922.52	3795.17	7310.32	41
H4AB	2347.36	3128.09	6741.31	41
H5A	482.65	4494.49	8266.43	41
H6AA	770.78	2186.54	7729.52	38
H6AB	-513.63	2937.95	8778.67	38
H7A	870.19	1596.26	9663.38	33
H9AA	-884.26	3855.08	10123.9	55

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman255R.

Atom	*x*	*y*	*z*	U(eq)
H9AB	-298.95	4782.39	10382.07	55
H9AC	-100.66	3505.68	10911.19	55
H10D	2400.88	3105.36	10239.43	54
H10E	2068.47	4400.97	9741.77	54
H10F	3209.12	3196.06	9030.76	54
H11D	3210.73	-10.3	9480.52	43
H11E	3769.17	1076.34	9337.64	43
H11F	4560.85	-74.89	8501.49	43
H13A	5867.17	2479.06	6686.76	32
H14A	7144.24	3415.38	5400.03	36
H16A	5919.08	2471.6	3313.01	39
H17A	4609.19	1555.1	4600.58	36
H19A	3703.94	-2044.79	8264.43	37
H20A	2647.61	-3389.53	9188.36	42
H22A	-1079.76	-761.59	9693.22	41
H23A	-33.03	577.35	8749.94	37
H1BA	8628.88	8381.19	5525.04	37
H1BB	7416.87	9363.14	5230.61	37
H2B	6740(40)	7740(40)	5180(30)	16(8)
H3B	9783.02	6626.2	3085.01	33
H4BA	11716.58	6645.21	3049.92	38
H4BB	11138.2	7020.06	4266.85	38
H5B	12836.24	4856.3	3803.38	39
H6BA	10456.88	5712.5	5531.97	39
H6BB	11399.04	4250.69	5375.54	39
H7B	9676.96	4074.2	4848.21	36

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman255R.

Atom	*x*	*y*	*z*	U(eq)
H9BA	11012.66	3791.37	2293.53	56
H9BB	12373.26	4094.63	1911.55	56
H9BC	10900.94	5181.55	2311.18	56
H10G	12216.26	2791.42	4304.44	62
H10H	13173.93	2684.55	3100.08	62
H10I	11815.51	2383.92	3440.65	62
H11G	7537.6	5247.99	4418.61	47
H11H	8610.49	5315.03	3290.29	47
H11I	7375.1	6534.59	3910.24	47
H13B	10092.54	7971.46	2026.36	36
H14B	10937.03	9357.48	986.17	39
H16B	9709.56	11556.67	3544.18	40
H17B	8851.68	10170.52	4603.71	38
H19B	5485.99	6696.54	6172.29	37
H20B	4367.38	5559.37	7355.98	37
H22B	7855.05	3627.59	7856.22	41
H23B	8957.12	4810.65	6701.82	38
H24A	317.23	10367.01	5627.04	94
H24B	596.12	10574.59	6629.53	94
H24C	-298.9	11711.69	6178.89	94
H25A	-1734.54	11107.17	7658.37	82
H25B	-2029.17	10924.25	6655.1	82
H26A	-2884.2	9336.24	7466.36	84
H26B	-2602.34	9517.85	8477	84
H27A	-1284.77	7281.49	7205.59	111
H27B	-2541.23	7511.14	8299.73	111

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman255R.

Atom	*x*	*y*	*z*	U(eq)
H27C	-1099.16	7472.52	8256.09	111

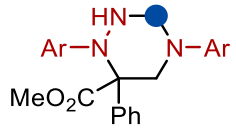
Experimental

Single crystals of $C_{73}H_{91}F_6N_9O$ **[Gandelman255R]** were obtained by slow evaporation of Et_2O solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S.The crystal was kept at 100.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman255R]

Crystal Data for $C_{73}H_{91}F_6N_9O$ (*M* =1224.54 g/mol): triclinic, space group P1 (no. 1), *a* = 11.3657(3) Å, *b* = 11.8109(3) Å, *c* = 13.9331(4) Å, *α* = 85.375(2)°, *β* = 67.686(3)°, *γ* = 68.065(4)°, *V* = 1600.96(9) Å^3, *Z* = 1, *T* = 100.15 K, μ(CuKα) = 0.717 mm^{-1}, *Dcalc* = 1.270 g/cm^3, 21369 reflections measured (6.876° ≤ 2Θ ≤ 160.484°), 9206 unique (R_{int} = 0.0653, R_{sigma} = 0.0669) which were used in all calculations. The final R_1 was 0.0661 (I > 2σ(I)) and wR_2 was 0.1772 (all data).

3.1.14 methyl 1,4-bis(4-chlorophenyl)-6-phenyl-1,2,4-triazinane-6-carboxylate (4.43)



4.43 (Ar = 4-ClC_6H_4)

Sample name: Gandelman245R

CCDC number: 2505626

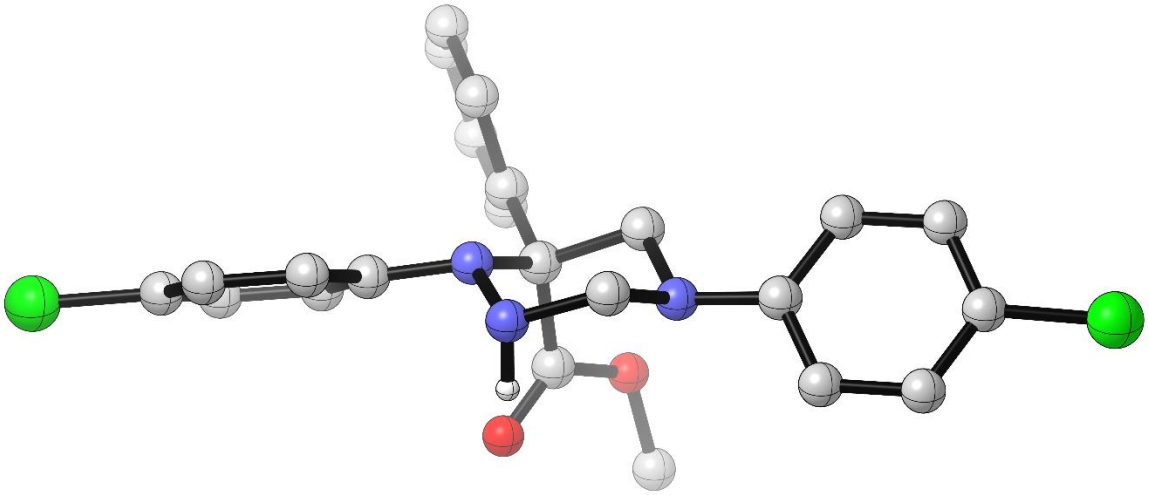


Table 1 Crystal data and structure refinement for Gandelman245R.

Identification code	Gandelman245R
Empirical formula	$C_{23}H_{21}Cl_2N_3O_2$
Formula weight	442.33
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	9.8995(5)
b/Å	10.3949(3)
c/Å	11.3626(5)
α/°	83.642(3)
β/°	83.225(4)
γ/°	66.276(4)
Volume/Å^3	1060.40(8)
Z	2
ρ_{calc}g/cm^3	1.385
μ/mm^{-1}	2.959
F(000)	460.0
Crystal size/mm^3	0.24 × 0.18 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.854 to 160.522
Index ranges	-12 ≤ h ≤ 12, -11 ≤ k ≤ 13, -14 ≤ l ≤ 14
Reflections collected	14594
Independent reflections	4518 [R_{int} = 0.0541, R_{sigma} = 0.0479]
Data/restraints/parameters	4518/0/276
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0495, wR_2 = 0.1365
Final R indexes [all data]	R_1 = 0.0524, wR_2 = 0.1392
Largest diff. peak/hole / e Å^{-3}	0.35/-0.53

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman245R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	6158.0(5)	1701.2(5)	-1488.9(4)	40.77(16)
O1	5648.4(11)	1371.3(10)	5359.7(10)	22.6(2)
N1	3763.4(14)	3471.8(12)	3369.1(12)	20.3(3)
C1	2772.6(17)	4969.9(15)	3459.0(14)	22.7(3)
Cl2	27.5(5)	7426.9(5)	10016.0(4)	39.04(16)
O2	5105.7(12)	3486.8(11)	6046.3(10)	23.2(2)
N2	2638.5(15)	5396.7(12)	4643.4(12)	21.8(3)
C2	3124.6(16)	2628.6(14)	4158.2(13)	19.5(3)
N3	2185.8(14)	4503.8(12)	5520.9(11)	19.8(3)
C3	3106.0(15)	2977.4(14)	5454.8(13)	18.3(3)
C4	4239.9(16)	3079.1(14)	2186.8(14)	20.4(3)
C5	3757.8(17)	2223.4(16)	1640.7(14)	24.2(3)
C6	4325.4(18)	1813.7(18)	501.4(15)	27.7(3)
C7	5369.3(18)	2276.1(18)	-87.3(14)	27.1(3)
C8	5832.7(18)	3166.4(16)	420.3(15)	25.8(3)
C9	5268.3(17)	3565.8(15)	1558.0(15)	24.3(3)
C10	1757.7(16)	5138.8(15)	6624.2(14)	21.1(3)
C11	873.7(17)	6593.3(16)	6593.6(16)	24.3(3)
C12	340.8(18)	7282.2(16)	7631.2(17)	28.4(4)
C13	696.4(19)	6542.6(18)	8716.2(16)	29.2(4)
C14	1583(2)	5118.9(18)	8775.1(16)	29.0(4)
C15	2122.7(18)	4425.8(16)	7730.7(15)	25.4(3)
C16	2393.6(16)	2110.2(14)	6261.6(13)	18.3(3)
C17	868.4(17)	2509.9(15)	6250.2(13)	20.8(3)
C18	146.5(17)	1763.6(16)	6954.7(14)	23.4(3)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman245R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C19	943.5(18)	599.6(15)	7686.8(14)	23.9(3)
C20	2460.2(18)	187.1(15)	7694.7(14)	23.8(3)
C21	3187.3(17)	931.9(15)	6985.0(14)	21.7(3)
C22	4721.7(16)	2653.3(15)	5674.4(13)	20.2(3)
C23	7213.1(17)	1052.1(17)	5380.2(16)	26.7(3)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for Gandelman245R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	43.8(3)	61.8(3)	17.9(2)	-9.53(19)	7.91(18)	-23.1(2)
O1	18.9(5)	19.0(5)	27.9(6)	-7.1(4)	2.9(4)	-5.3(4)
N1	23.1(6)	15.3(5)	20.2(6)	-2.2(4)	3.6(5)	-6.3(5)
C1	25.0(7)	16.3(6)	22.5(8)	-1.7(5)	3.4(6)	-5.0(6)
Cl2	47.0(3)	39.9(3)	34.6(3)	-24.13(19)	17.5(2)	-21.8(2)
O2	25.8(5)	22.0(5)	23.9(6)	-4.8(4)	2.0(4)	-11.9(4)
N2	25.4(6)	16.6(5)	22.2(7)	-2.0(5)	4.8(5)	-8.8(5)
C2	21.1(7)	16.6(6)	19.6(7)	-3.2(5)	3.0(5)	-7.0(5)
N3	23.1(6)	15.0(5)	20.3(6)	-3.2(5)	4.6(5)	-7.6(5)
C3	19.3(7)	14.2(6)	19.2(7)	-3.4(5)	2.3(5)	-4.9(5)
C4	19.5(7)	16.4(6)	19.9(7)	-0.6(5)	2.2(6)	-2.5(5)
C5	20.7(7)	28.4(7)	21.9(8)	-2.8(6)	1.8(6)	-8.6(6)
C6	26.0(8)	34.3(8)	23.1(8)	-4.9(6)	-0.5(6)	-12.1(6)
C7	26.6(7)	32.1(8)	16.6(7)	-0.2(6)	1.3(6)	-6.6(6)
C8	25.1(7)	24.3(7)	23.3(8)	3.1(6)	2.9(6)	-7.4(6)
C9	25.5(7)	19.9(7)	24.5(8)	-0.1(6)	2.0(6)	-7.2(6)
C10	20.1(7)	19.1(7)	24.9(8)	-7.5(6)	5.9(6)	-9.0(5)
C11	23.1(7)	20.3(7)	29.6(8)	-7.1(6)	2.1(6)	-8.3(6)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman245R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C12	24.9(7)	22.8(7)	38.7(10)	-13.9(7)	5.2(7)	-9.7(6)
C13	31.7(8)	30.5(8)	30.3(9)	-17.5(7)	11.9(7)	-17.4(7)
C14	36.3(9)	29.4(8)	24.5(8)	-7.9(6)	7.2(7)	-17.3(7)
C15	31.0(8)	20.5(7)	24.9(8)	-6.8(6)	5.3(6)	-11.1(6)
C16	21.7(7)	15.3(6)	17.7(7)	-5.9(5)	4.2(5)	-7.4(5)
C17	22.7(7)	17.5(6)	20.2(7)	-4.5(5)	2.3(6)	-6.2(5)
C18	23.2(7)	22.2(7)	25.2(8)	-7.6(6)	4.1(6)	-9.5(6)
C19	30.4(8)	20.6(7)	22.5(8)	-5.6(6)	6.7(6)	-13.3(6)
C20	29.6(8)	18.3(6)	21.4(7)	-1.8(5)	1.3(6)	-8.1(6)
C21	22.9(7)	19.0(6)	21.2(7)	-4.3(5)	2.8(6)	-6.7(5)
C22	24.4(7)	16.9(6)	17.7(7)	-1.9(5)	3.3(5)	-7.8(5)
C23	19.5(7)	26.2(7)	32.3(9)	-8.1(6)	3.1(6)	-6.8(6)

Table 4 Bond Lengths for Gandelman245R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C7	1.7450(17)	C5	C6	1.390(2)
O1	C22	1.3378(17)	C6	C7	1.383(2)
O1	C23	1.4502(18)	C7	C8	1.386(2)
N1	C1	1.4764(17)	C8	C9	1.385(2)
N1	C2	1.4527(18)	C10	C11	1.408(2)
N1	C4	1.4181(19)	C10	C15	1.395(2)
C1	N2	1.438(2)	C11	C12	1.385(2)
Cl2	C13	1.7450(17)	C12	C13	1.382(3)
O2	C22	1.2073(19)	C13	C14	1.383(2)
N2	N3	1.4424(17)	C14	C15	1.394(2)
C2	C3	1.552(2)	C16	C17	1.397(2)

Table 4 Bond Lengths for Gandelman245R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N3	C3	1.4833(17)	C16	C21	1.396(2)
N3	C10	1.4212(19)	C17	C18	1.388(2)
C3	C16	1.525(2)	C18	C19	1.394(2)
C3	C22	1.541(2)	C19	C20	1.387(2)
C4	C5	1.392(2)	C20	C21	1.393(2)
C4	C9	1.402(2)			

Table 5 Bond Angles for Gandelman245R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C22	O1	C23	115.95(12)	C9	C8	C7	119.08(15)
C2	N1	C1	108.21(11)	C8	C9	C4	120.46(15)
C4	N1	C1	114.08(12)	C11	C10	N3	117.19(14)
C4	N1	C2	118.01(12)	C15	C10	N3	124.95(13)
N2	C1	N1	111.55(12)	C15	C10	C11	117.85(14)
C1	N2	N3	112.18(12)	C12	C11	C10	121.03(16)
N1	C2	C3	108.36(12)	C13	C12	C11	119.82(15)
N2	N3	C3	114.26(11)	C12	C13	Cl2	119.32(13)
C10	N3	N2	109.80(11)	C12	C13	C14	120.54(15)
C10	N3	C3	121.53(12)	C14	C13	Cl2	120.14(14)
N3	C3	C2	106.70(11)	C13	C14	C15	119.66(16)
N3	C3	C16	110.44(11)	C14	C15	C10	121.06(14)
N3	C3	C22	110.48(12)	C17	C16	C3	117.67(13)
C16	C3	C2	107.34(11)	C21	C16	C3	123.54(13)
C16	C3	C22	114.82(12)	C21	C16	C17	118.77(13)
C22	C3	C2	106.62(11)	C18	C17	C16	120.86(14)
C5	C4	N1	123.26(14)	C17	C18	C19	120.03(14)
C5	C4	C9	119.22(15)	C20	C19	C18	119.49(14)

Table 5 Bond Angles for Gandelman245R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	C4	N1	117.51(14)	C19	C20	C21	120.56(14)
C6	C5	C4	120.55(15)	C20	C21	C16	120.28(14)
C7	C6	C5	119.08(16)	O1	C22	C3	112.26(12)
C6	C7	Cl1	119.58(14)	O2	C22	O1	124.20(14)
C6	C7	C8	121.54(15)	O2	C22	C3	123.48(13)
C8	C7	Cl1	118.86(13)				

Table 6 Torsion Angles for Gandelman245R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C7	C8	C9	-176.61(12)	C3	C16	C17	C18	179.53(13)
N1	C1	N2	N3	-54.20(16)	C3	C16	C21	C20	-179.67(13)
N1	C2	C3	N3	60.10(14)	C4	N1	C1	N2	-164.77(13)
N1	C2	C3	C16	178.50(11)	C4	N1	C2	C3	164.16(12)
N1	C2	C3	C22	-57.99(13)	C4	C5	C6	C7	-0.5(2)
N1	C4	C5	C6	-176.54(13)	C5	C4	C9	C8	-1.9(2)
N1	C4	C9	C8	176.92(13)	C5	C6	C7	Cl1	176.90(12)
C1	N1	C2	C3	-64.44(15)	C5	C6	C7	C8	-1.7(2)
C1	N1	C4	C5	-109.34(16)	C6	C7	C8	C9	2.0(2)
C1	N1	C4	C9	71.86(17)	C7	C8	C9	C4	-0.1(2)
C1	N2	N3	C3	52.21(16)	C9	C4	C5	C6	2.2(2)
C1	N2	N3	C10	-167.28(12)	C10	N3	C3	C2	170.78(12)
Cl2	C13	C14	C15	-179.40(13)	C10	N3	C3	C16	54.43(18)
N2	N3	C3	C2	-53.79(15)	C10	N3	C3	C22	-73.69(16)
N2	N3	C3	C16	-170.14(12)	C10	C11	C12	C13	1.0(2)
N2	N3	C3	C22	61.73(16)	C11	C10	C15	C14	2.4(2)
N2	N3	C10	C11	43.34(18)	C11	C12	C13	Cl2	179.56(12)
N2	N3	C10	C15	-137.97(15)	C11	C12	C13	C14	0.1(3)

Table 6 Torsion Angles for Gandelman245R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C2	N1	C1	N2	61.72(16)	C12	C13	C14	C15	0.0(3)
C2	N1	C4	C5	19.4(2)	C13	C14	C15	C10	-1.4(3)
C2	N1	C4	C9	-159.44(13)	C15	C10	C11	C12	-2.3(2)
C2	C3	C16	C17	-72.23(15)	C16	C3	C22	O1	68.58(16)
C2	C3	C16	C21	106.42(15)	C16	C3	C22	O2	-114.01(15)
C2	C3	C22	O1	-50.15(15)	C16	C17	C18	C19	0.1(2)
C2	C3	C22	O2	127.26(15)	C17	C16	C21	C20	-1.0(2)
N3	C3	C16	C17	43.72(17)	C17	C18	C19	C20	-0.7(2)
N3	C3	C16	C21	-137.63(14)	C18	C19	C20	C21	0.5(2)
N3	C3	C22	O1	-165.72(12)	C19	C20	C21	C16	0.4(2)
N3	C3	C22	O2	11.7(2)	C21	C16	C17	C18	0.8(2)
N3	C10	C11	C12	176.52(14)	C22	C3	C16	C17	169.43(13)
N3	C10	C15	C14	-176.26(15)	C22	C3	C16	C21	-11.9(2)
C3	N3	C10	C11	-179.51(12)	C23	O1	C22	O2	-5.6(2)
C3	N3	C10	C15	-0.8(2)	C23	O1	C22	C3	171.75(12)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman245R.

Atom	*x*	*y*	*z*	U(eq)
H1A	3166.14	5558.4	2897.17	27
H1B	1781.07	5124.39	3231.3	27
H2	3570(20)	5340(20)	4813(19)	27(5)
H2A	3721.54	1614.33	4066.43	23
H2B	2104.34	2845.84	3960.88	23
H5	3034.75	1917.01	2050.36	29
H6	4000.64	1224.07	132.12	33
H8	6527.8	3497.84	-6.43	31

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman245R.

Atom	*x*	*y*	*z*	U(eq)
H9	5580.05	4173.84	1914.89	29
H11	639.44	7109.75	5849.41	29
H12	-267.54	8260.62	7597.31	34
H14	1823.19	4615.72	9523.59	35
H15	2749.17	3452.13	7773.12	30
H17	317.91	3302.73	5753.77	25
H18	-891.18	2046.43	6937.87	28
H19	451.43	92.6	8176.59	29
H20	3008.08	-610.01	8188.23	29
H21	4227.78	636.5	6993.5	26
H23A	7433.58	1839.62	4982.63	40
H23B	7793.49	196.3	4966.18	40
H23C	7469.61	904.69	6205.46	40

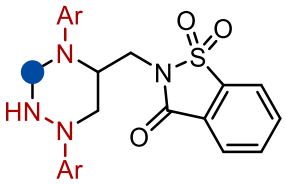
Experimental

Single crystals of $C_{23}H_{21}Cl_2N_3O_2$ **[Gandelman245R]** were obtained by slow evaporation of C_6H_6 solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman245R]

Crystal Data for $C_{23}H_{21}Cl_2N_3O_2$ (*M* =442.33 g/mol): triclinic, space group P-1 (no. 2), *a* = 9.8995(5) Å, *b* = 10.3949(3) Å, *c* = 11.3626(5) Å, *α* = 83.642(3)°, *β* = 83.225(4)°, *γ* = 66.276(4)°, *V* = 1060.40(8) Å^3, *Z* = 2, *T* = 100.15 K, μ(CuKα) = 2.959 mm^{-1}, *Dcalc* = 1.385 g/cm^3, 14594 reflections measured (7.854° ≤ 2Θ ≤ 160.522°), 4518 unique (R_{int} = 0.0541, R_{sigma} = 0.0479) which were used in all calculations. The final R_1 was 0.0495 (I > 2σ(I)) and wR_2 was 0.1392 (all data).

3.1.15 *2-((1,4-bis(4-chlorophenyl)-1,2,4-triazinan-5-yl)methyl)benzo[d]isothiazol-3(2H)-one 1,1-dioxide (4.44)*



4.44 (Ar = 4-ClC_6H_4)

Sample name: Gandelman271R

CCDC number: 2505627

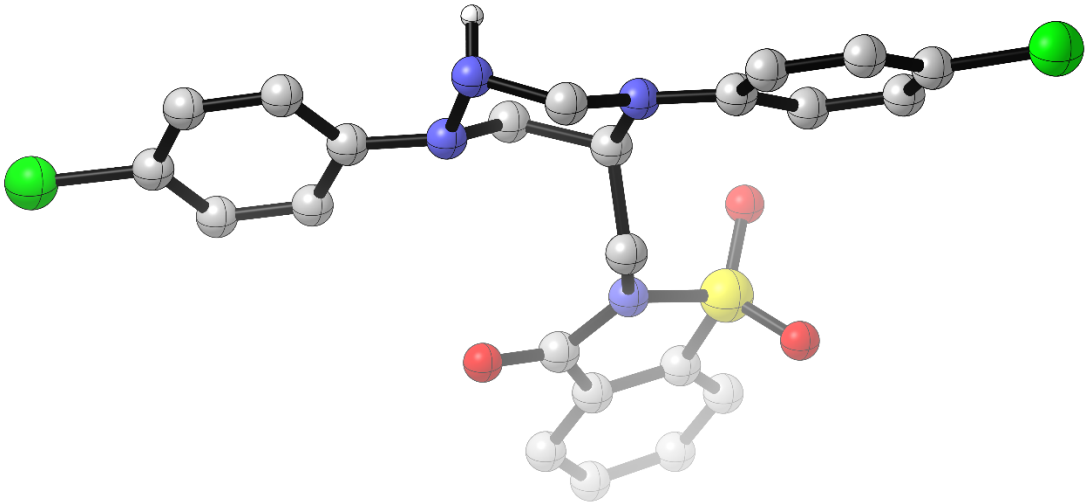


Table 1 Crystal data and structure refinement for Gandelman271R.

Identification code	Gandelman271R
Empirical formula	$C_{23}H_{20}Cl_2N_4O_3S$
Formula weight	503.39
Temperature/K	293.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.7924(2)
b/Å	15.8202(3)
c/Å	16.5795(4)
α/°	90
β/°	103.388(2)
γ/°	90
Volume/Å^3	2243.50(9)
Z	4
ρ_{calc}g/cm^3	1.490
μ/mm^{-1}	3.768
F(000)	1040.0
Crystal size/mm^3	0.21 × 0.12 × 0.09
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.828 to 159.852
Index ranges	-10 ≤ h ≤ 8, -20 ≤ k ≤ 19, -21 ≤ l ≤ 21
Reflections collected	20514
Independent reflections	4765 [R_{int} = 0.1069, R_{sigma} = 0.0690]
Data/restraints/parameters	4765/0/302
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0537, wR_2 = 0.1473
Final R indexes [all data]	R_1 = 0.0716, wR_2 = 0.1609
Largest diff. peak/hole / e Å^{-3}	0.23/-0.54

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman271R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	478.1(11)	8178.1(5)	5812.3(7)	85.1(3)
S1	10072.7(7)	4328.3(4)	7476.6(4)	49.00(19)
O1	7794(2)	6207.9(11)	6508.5(12)	54.4(4)
N1	3966(2)	4944.7(12)	6036.3(13)	44.2(4)
C1	4049(3)	3644.4(16)	5397.9(16)	50.4(6)
Cl2	8171.7(10)	-22.1(5)	5825.8(6)	75.6(3)
O2	9522(2)	3844.8(12)	8075.4(13)	65.4(5)
N2	3039(2)	4251.6(13)	5647.6(14)	49.7(5)
C2	6132(3)	3996.4(14)	6633.3(14)	41.9(5)
O3	10925(2)	3878.9(12)	6974.7(14)	64.1(5)
N3	5270(2)	3332.0(12)	6095.5(12)	44.6(4)
C3	5001(3)	4666.4(16)	6813.7(14)	45.7(5)
N4	8595(2)	4853.9(12)	6873.1(13)	46.3(5)
C4	3110(3)	5699.7(15)	6025.1(14)	41.9(5)
C5	3867(3)	6448.3(16)	6337.0(16)	50.8(6)
C6	3064(3)	7200.4(16)	6270.8(18)	57.5(6)
C7	1498(3)	7223.1(16)	5881.2(17)	53.9(6)
C8	730(3)	6502.1(18)	5570.2(17)	55.1(6)
C9	1526(3)	5744.2(16)	5645.5(16)	50.0(6)
C10	6024(3)	2570.5(15)	5998.6(14)	43.4(5)
C11	5400(3)	2007.7(16)	5356.8(16)	53.1(6)
C12	6052(3)	1220.0(17)	5304.4(18)	58.5(7)
C13	7362(3)	980.0(16)	5884.6(17)	51.7(6)
C14	8041(3)	1528.1(16)	6505.3(17)	51.8(6)
C15	7386(3)	2313.8(15)	6562.8(16)	49.1(6)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman271R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C16	7405(3)	4392.1(15)	6255.9(14)	44.0(5)
C17	8740(3)	5726.1(15)	6911.1(15)	44.7(5)
C18	10214(3)	5952.7(16)	7517.7(14)	45.9(5)
C19	11025(3)	5251.8(17)	7887.0(16)	49.6(6)
C20	12416(3)	5311(2)	8482.3(18)	61.2(7)
C21	12992(3)	6119(2)	8679.5(19)	67.0(8)
C22	12220(3)	6821(2)	8300.6(19)	63.2(7)
C23	10797(3)	6751.6(17)	7718.6(17)	54.7(6)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for Gandelman271R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	80.5(6)	60.6(4)	109.0(7)	7.5(4)	11.1(5)	25.3(4)
S1	34.3(3)	53.5(4)	56.4(4)	6.0(3)	4.9(2)	4.3(2)
O1	43.3(10)	55.1(10)	60.6(11)	6.3(8)	3.7(8)	6.8(8)
N1	33.9(10)	48.7(10)	46.3(10)	-7.5(8)	1.9(8)	2.2(8)
C1	42.6(13)	50.5(12)	52.4(14)	-8.3(11)	-0.6(10)	4.2(11)
Cl2	72.8(5)	56.7(4)	92.1(6)	-11.1(3)	8.6(4)	17.4(3)
O2	52.0(11)	70.2(12)	70.2(12)	21.9(10)	6.5(9)	-0.7(9)
N2	35.3(11)	53.2(12)	57.8(12)	-9.9(9)	4.8(9)	-2.3(9)
C2	37.0(12)	48.1(11)	39.1(11)	-1.7(9)	5.9(9)	0.3(10)
O3	46.9(11)	63.3(11)	82.3(14)	-6.1(10)	15.3(10)	11.9(9)
N3	37.7(10)	43.9(9)	47.8(10)	-1.6(8)	1.1(8)	0.7(8)
C3	38.1(12)	53.0(12)	44.9(12)	-5.4(10)	7.5(9)	2.4(11)
N4	33.1(10)	49.3(10)	53.0(11)	1.9(9)	3.0(8)	0.2(8)
C4	35.1(11)	50.1(12)	41.0(11)	-3.5(9)	10.0(9)	1.3(10)
C5	37.5(13)	53.7(13)	58.2(14)	-5.4(11)	5.1(10)	-1.3(11)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman271R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C6	54.1(16)	49.7(13)	67.1(17)	-3.9(12)	10.8(13)	-2.5(12)
C7	51.6(15)	52.6(14)	57.5(15)	5.9(11)	12.6(12)	11.9(12)
C8	38.5(13)	65.9(15)	58.4(15)	0.4(12)	6.3(11)	7.4(12)
C9	35.5(12)	56.5(13)	55.9(14)	-7.3(11)	6.3(10)	0.1(11)
C10	38.6(12)	45.9(11)	46.9(12)	1.2(9)	12.4(10)	1.0(10)
C11	48.9(14)	56.1(14)	49.5(13)	-4.0(11)	1.8(11)	4.6(12)
C12	55.6(16)	57.8(14)	58.7(15)	-12.9(12)	6.1(12)	2.0(12)
C13	46.9(14)	49.3(13)	60.1(15)	0.7(11)	14.8(11)	6.6(11)
C14	44.5(14)	55.0(13)	55.1(14)	2.1(11)	10.0(11)	5.8(12)
C15	42.6(13)	50.6(13)	51.2(13)	-3.9(11)	5.3(10)	0.4(11)
C16	38.2(12)	50.5(12)	41.9(11)	-0.5(9)	6.6(9)	1.3(10)
C17	33.9(12)	51.7(12)	48.5(12)	-0.2(10)	10.0(9)	1.7(10)
C18	37.5(12)	54.6(13)	46.9(12)	-2.9(10)	12.7(10)	-0.3(11)
C19	34.5(12)	62.1(14)	51.2(13)	-1.2(11)	8.3(10)	-0.9(11)
C20	39.9(14)	78.8(18)	59.7(16)	0.6(14)	1.1(11)	3.2(14)
C21	40.9(15)	94(2)	61.7(17)	-15.0(16)	3.7(12)	-6.4(15)
C22	48.1(15)	74.4(18)	67.2(17)	-18.1(14)	13.9(13)	-11.6(14)
C23	47.5(15)	59.8(14)	59.6(15)	-6.5(12)	18.2(12)	-0.5(12)

Table 4 Bond Lengths for Gandelman271R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C7	1.747(3)	C4	C9	1.391(3)
S1	O2	1.424(2)	C5	C6	1.375(4)
S1	O3	1.431(2)	C6	C7	1.380(4)
S1	N4	1.667(2)	C7	C8	1.364(4)
S1	C19	1.742(3)	C8	C9	1.380(4)

Table 4 Bond Lengths for Gandelman271R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C17	1.209(3)	C10	C11	1.398(4)
N1	N2	1.428(3)	C10	C15	1.398(3)
N1	C3	1.463(3)	C11	C12	1.383(4)
N1	C4	1.409(3)	C12	C13	1.373(4)
C1	N2	1.432(3)	C13	C14	1.372(4)
C1	N3	1.470(3)	C14	C15	1.383(4)
Cl2	C13	1.750(3)	C17	C18	1.489(3)
C2	N3	1.470(3)	C18	C19	1.382(4)
C2	C3	1.530(3)	C18	C23	1.376(4)
C2	C16	1.537(3)	C19	C20	1.385(4)
N3	C10	1.402(3)	C20	C21	1.386(4)
N4	C16	1.476(3)	C21	C22	1.375(5)
N4	C17	1.386(3)	C22	C23	1.396(4)
C4	C5	1.397(3)			

Table 5 Bond Angles for Gandelman271R.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
O2	S1	O3	116.55(13)	C8	C7	C6	120.5(2)
O2	S1	N4	110.04(11)	C7	C8	C9	119.7(2)
O2	S1	C19	112.87(13)	C8	C9	C4	121.3(2)
O3	S1	N4	109.82(12)	C11	C10	N3	121.4(2)
O3	S1	C19	112.00(12)	C15	C10	N3	121.8(2)
N4	S1	C19	93.07(11)	C15	C10	C11	116.7(2)
N2	N1	C3	109.89(19)	C12	C11	C10	121.8(2)
C4	N1	N2	113.45(18)	C13	C12	C11	119.9(3)
C4	N1	C3	119.19(18)	C12	C13	Cl2	119.9(2)
N2	C1	N3	112.8(2)	C14	C13	Cl2	120.2(2)

Table 5 Bond Angles for Gandelman271R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N1	N2	C1	108.57(19)	C14	C13	C12	120.0(2)
N3	C2	C3	110.32(19)	C13	C14	C15	120.3(2)
N3	C2	C16	111.47(18)	C14	C15	C10	121.4(2)
C3	C2	C16	111.42(19)	N4	C16	C2	112.68(18)
C1	N3	C2	114.63(18)	O1	C17	N4	123.9(2)
C10	N3	C1	118.53(19)	O1	C17	C18	127.0(2)
C10	N3	C2	119.54(19)	N4	C17	C18	109.1(2)
N1	C3	C2	109.64(18)	C19	C18	C17	112.7(2)
C16	N4	S1	119.86(16)	C23	C18	C17	127.0(2)
C17	N4	S1	114.74(17)	C23	C18	C19	120.3(2)
C17	N4	C16	124.6(2)	C18	C19	S1	110.34(19)
C5	C4	N1	120.4(2)	C18	C19	C20	122.8(3)
C9	C4	N1	121.6(2)	C20	C19	S1	126.9(2)
C9	C4	C5	117.7(2)	C19	C20	C21	116.4(3)
C6	C5	C4	120.8(2)	C22	C21	C20	121.5(3)
C5	C6	C7	119.9(2)	C21	C22	C23	121.4(3)
C6	C7	Cl1	119.6(2)	C18	C23	C22	117.6(3)
C8	C7	Cl1	119.8(2)				

Table 6 Torsion Angles for Gandelman271R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Cl1	C7	C8	C9	-178.2(2)	N4	S1	C19	C18	-2.87(18)
S1	N4	C16	C2	82.9(2)	N4	S1	C19	C20	178.7(2)
S1	N4	C17	O1	178.93(19)	N4	C17	C18	C19	-0.9(3)
S1	N4	C17	C18	-1.3(2)	N4	C17	C18	C23	178.4(2)
S1	C19	C20	C21	176.6(2)	C4	N1	N2	C1	157.3(2)
O1	C17	C18	C19	178.8(2)	C4	N1	C3	C2	-163.90(19)

Table 6 Torsion Angles for Gandelman271R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C17	C18	C23	-1.8(4)	C4	C5	C6	C7	-1.0(4)
N1	C4	C5	C6	174.9(2)	C5	C4	C9	C8	0.7(4)
N1	C4	C9	C8	-174.0(2)	C5	C6	C7	Cl1	179.1(2)
C1	N3	C10	C11	-16.1(3)	C5	C6	C7	C8	0.9(4)
C1	N3	C10	C15	167.5(2)	C6	C7	C8	C9	0.0(4)
Cl2	C13	C14	C15	-178.73(19)	C7	C8	C9	C4	-0.8(4)
O2	S1	N4	C16	-71.8(2)	C9	C4	C5	C6	0.2(4)
O2	S1	N4	C17	118.13(18)	C10	C11	C12	C13	-1.2(4)
O2	S1	C19	C18	-116.14(18)	C11	C10	C15	C14	-2.5(4)
O2	S1	C19	C20	65.4(3)	C11	C12	C13	Cl2	179.2(2)
N2	N1	C3	C2	62.7(2)	C11	C12	C13	C14	-1.3(4)
N2	N1	C4	C5	-176.2(2)	C12	C13	C14	C15	1.8(4)
N2	N1	C4	C9	-1.6(3)	C13	C14	C15	C10	0.2(4)
N2	C1	N3	C2	-49.0(3)	C15	C10	C11	C12	3.0(4)
N2	C1	N3	C10	160.9(2)	C16	C2	N3	C1	-80.4(2)
C2	N3	C10	C11	-164.7(2)	C16	C2	N3	C10	69.3(3)
C2	N3	C10	C15	19.0(3)	C16	C2	C3	N1	74.1(2)
O3	S1	N4	C16	57.8(2)	C16	N4	C17	O1	9.4(4)
O3	S1	N4	C17	-112.30(18)	C16	N4	C17	C18	-170.81(19)
O3	S1	C19	C18	109.95(19)	C17	N4	C16	C2	-108.1(2)
O3	S1	C19	C20	-68.5(3)	C17	C18	C19	S1	2.6(2)
N3	C1	N2	N1	58.5(3)	C17	C18	C19	C20	-178.8(2)
N3	C2	C3	N1	-50.3(2)	C17	C18	C23	C22	-179.2(2)
N3	C2	C16	N4	-161.88(18)	C18	C19	C20	C21	-1.7(4)
N3	C10	C11	C12	-173.5(2)	C19	S1	N4	C16	172.47(18)
N3	C10	C15	C14	174.0(2)	C19	S1	N4	C17	2.42(18)
C3	N1	N2	C1	-66.5(3)	C19	C18	C23	C22	0.1(4)

Table 6 Torsion Angles for Gandelman271R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C3	N1	C4	C5	52.0(3)	C19	C20	C21	C22	-0.2(4)
C3	N1	C4	C9	-133.5(2)	C20	C21	C22	C23	2.0(4)
C3	C2	N3	C1	44.0(3)	C21	C22	C23	C18	-1.9(4)
C3	C2	N3	C10	-166.31(19)	C23	C18	C19	S1	-176.78(18)
C3	C2	C16	N4	74.4(2)	C23	C18	C19	C20	1.8(4)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman271R.

Atom	*x*	*y*	*z*	U(eq)
H1A	4539.64	3900.62	4990.85	60
H1B	3427.38	3170.21	5135.2	60
H2	2540(30)	4027(17)	6004(18)	48(7)
H2A	6647.53	3734.09	7161.29	50
H3A	4385.37	4432.53	7175.91	55
H3B	5585.11	5145.06	7092.57	55
H5	4926.53	6437.45	6592.52	61
H6	3576.59	7693.05	6488.1	69
H8	-326.4	6521.41	5308.47	66
H9	994.07	5253.58	5438.46	60
H11	4523.76	2167.65	4954.47	64
H12	5602.6	853.55	4876.78	70
H14	8945.11	1370.4	6888.96	62
H15	7860.48	2679.32	6985.73	59
H16A	7914.2	3949.1	6010.78	53
H16B	6919.93	4778.15	5816.96	53
H20	12934.93	4833.97	8735.89	73
H21	13921.34	6187.95	9077.13	80

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman271R.

Atom	*x*	*y*	*z*	U(eq)
H22	12655.34	7353.02	8434.81	76
H23	10263.1	7228.53	7475.31	66

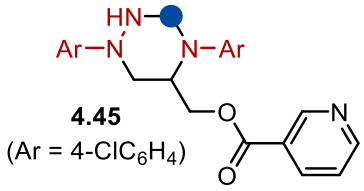
Experimental

Single crystals of $C_{23}H_{20}Cl_2N_4O_3S$ **[Gandelman271R]** were obtained by slow evaporation of Et_2O solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at 293.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman271R]

Crystal Data for $C_{23}H_{20}Cl_2N_4O_3S$ (*M* =503.39 g/mol): monoclinic, space group $P2_1/n$ (no. 14), *a* = 8.7924(2) Å, *b* = 15.8202(3) Å, *c* = 16.5795(4) Å, *β* = 103.388(2)°, *V* = 2243.50(9) Å^3, *Z* = 4, *T* = 293.15 K, μ(CuKα) = 3.768 mm^{-1}, *Dcalc* = 1.490 g/cm^3, 20514 reflections measured (7.828° ≤ 2Θ ≤ 159.852°), 4765 unique (R_{int} = 0.1069, R_{sigma} = 0.0690) which were used in all calculations. The final R_1 was 0.0537 (I > 2σ(I)) and wR_2 was 0.1609 (all data).

3.1.16 (1,4-bis(4-chlorophenyl)-1,2,4-triazinan-5-yl)methyl nicotinate (4.45)



4.45
(Ar = 4-ClC_6H_4)

Sample name: Gandelman258R

CCDC number: 2505628

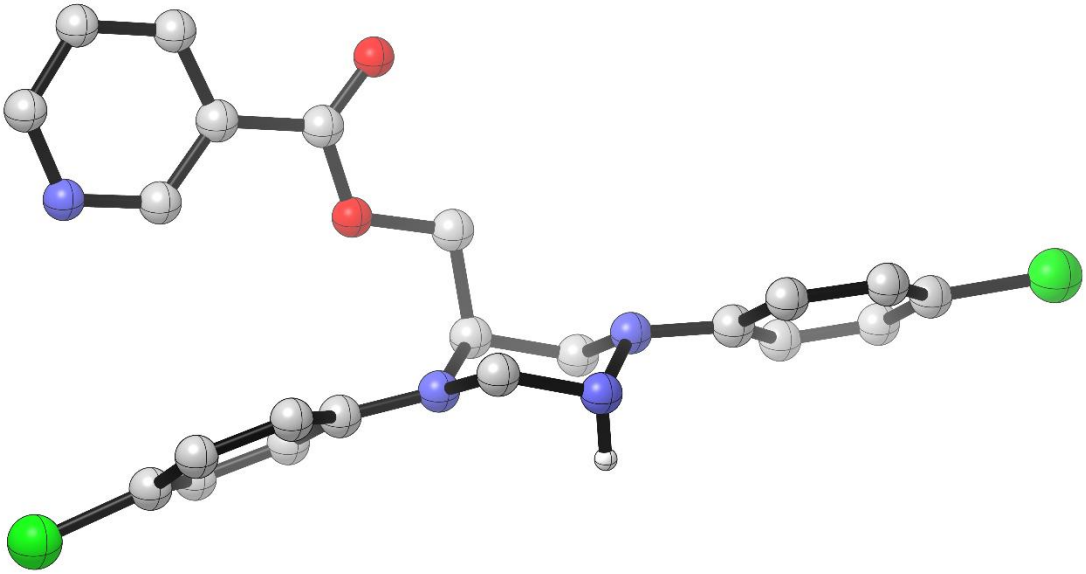


Table 1 Crystal data and structure refinement for Gandelman258R.

Identification code	Gandelman258R
Empirical formula	$C_{22}H_{20}Cl_2N_4O_2$
Formula weight	443.32
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	11.9428(3)
b/Å	12.6772(4)
c/Å	14.5756(4)
α/°	102.636(2)
β/°	95.393(3)
γ/°	105.544(4)
Volume/Å^3	2047.05(11)
Z	4
ρ_{calc}g/cm^3	1.438
μ/mm^{-1}	0.345
F(000)	920.0
Crystal size/mm^3	0.21 × 0.15 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.912 to 60.084
Index ranges	-16 ≤ h ≤ 16, -16 ≤ k ≤ 16, -18 ≤ l ≤ 20
Reflections collected	34444
Independent reflections	9542 [R_{int} = 0.0577, R_{sigma} = 0.0559]
Data/restraints/parameters	9542/0/549
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0428, wR_2 = 0.0965
Final R indexes [all data]	R_1 = 0.0738, wR_2 = 0.1045
Largest diff. peak/hole / e Å^{-3}	0.57/-0.24

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman258R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Cl1	8019.4(5)	3838.2(5)	9975.8(4)	39.90(14)
O1	6078.2(12)	7553.8(12)	9332.2(9)	33.1(3)
N1	5214.3(12)	5697.8(12)	7507.4(10)	20.2(3)
C1	5624.0(15)	6022.9(16)	6664.8(12)	22.6(4)
Cl2	1052.3(4)	8208.1(4)	3735.2(3)	30.63(12)
O2	7740.6(14)	7994.6(13)	8703.2(10)	43.4(4)
N2	4659.2(13)	6043.8(14)	5985.4(10)	22.7(3)
C2	3592.0(16)	6483.1(18)	7259.8(12)	27.5(4)
N3	4068.9(12)	6819.6(13)	6446.9(10)	22.5(3)
C3	4570.9(16)	6436.1(17)	7984.5(12)	26.3(4)
N4	7669.2(16)	7030.7(16)	11694.0(12)	39.8(4)
C4	5899.4(15)	5243.9(14)	8067.8(12)	20.3(4)
C5	5410.8(16)	4746.9(15)	8762.3(12)	22.4(4)
C6	6055.4(17)	4309.6(15)	9340.2(12)	25.5(4)
C7	7203.4(17)	4357.6(16)	9218.1(13)	26.7(4)
C8	7688.6(16)	4793.3(17)	8513.6(14)	29.5(4)
C9	7045.9(16)	5244.0(16)	7936.6(13)	25.5(4)
C10	3307.1(15)	7087.6(15)	5786.7(12)	21.5(4)
C11	3565.2(15)	7114.0(16)	4873.6(13)	25.6(4)
C12	2871.8(16)	7448.9(16)	4245.4(13)	26.6(4)
C13	1905.0(15)	7756.2(15)	4521.4(13)	24.0(4)
C14	1618.0(15)	7723.8(15)	5410.5(13)	24.8(4)
C15	2309.9(15)	7384.9(16)	6039.2(13)	24.0(4)
C16	5358.0(19)	7627.9(18)	8494.4(14)	36.2(5)
C17	7224.7(19)	7711.0(16)	9321.3(14)	31.2(4)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman258R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C18	8766.7(19)	6975.3(18)	11713.4(15)	38.4(5)
C19	9431.3(19)	7166(2)	11023.1(17)	45.5(6)
C20	8943.7(19)	7417(2)	10230.5(16)	43.2(5)
C21	7787.5(16)	7472.6(15)	10184.4(13)	25.9(4)
C22	7212.2(17)	7282.6(17)	10934.5(14)	30.5(4)
Cl1A	7199.5(4)	129.8(4)	7895.8(3)	33.76(13)
O1A	2014.9(11)	352.6(11)	6702.9(9)	29.0(3)
N1A	3666.8(12)	1719.3(12)	5878.3(10)	20.7(3)
C1A	3643.9(16)	2886.3(15)	6197.5(12)	22.8(4)
Cl2A	-444.8(4)	4729.7(5)	2561.9(4)	34.96(13)
O2A	294.9(12)	225.9(12)	7246.1(11)	36.6(3)
N2A	3280.8(13)	3311.6(13)	5403.3(11)	23.0(3)
C2A	2174.3(16)	1429.6(15)	4505.2(12)	22.9(4)
N3A	2140.2(13)	2573.4(12)	4905.9(10)	21.4(3)
C3A	2556.0(15)	944.6(15)	5318.2(12)	23.7(4)
N4A	3481(2)	-606(2)	8906.2(14)	59.1(6)
C4A	4412.1(15)	1304.4(15)	6419.4(12)	19.9(4)
C5A	4548.2(15)	233.8(15)	6054.7(12)	23.0(4)
C6A	5382.3(16)	-133.4(15)	6522.1(12)	24.5(4)
C7A	6089.1(16)	562.6(16)	7357.5(12)	25.0(4)
C8A	5920.0(17)	1584.3(16)	7761.1(12)	26.7(4)
C9A	5081.6(16)	1953.4(16)	7299.1(12)	25.4(4)
C10A	1583.1(14)	3096.1(15)	4310.0(12)	20.5(4)
C11A	1489.9(15)	4170.0(15)	4698.2(13)	23.6(4)
C12A	881.5(15)	4685.4(16)	4161.2(13)	25.1(4)
C13A	358.5(15)	4105.2(16)	3233.4(13)	25.2(4)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Gandelman258R. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C14A	452.0(15)	3053.4(16)	2829.7(13)	25.1(4)
C15A	1079.9(15)	2547.5(16)	3365.4(12)	23.5(4)
C16A	1577.8(16)	724.7(17)	5909.5(14)	28.9(4)
C17A	1283.0(17)	149.1(16)	7324.6(14)	28.6(4)
C18A	2837(3)	-797(2)	9596.4(16)	53.4(7)
C19A	1719(2)	-710(2)	9602.4(15)	46.8(6)
C20A	1209(2)	-406.6(18)	8859.3(15)	38.5(5)
C21A	1835.4(18)	-194.9(16)	8131.5(14)	29.3(4)
C22A	2965(2)	-295(2)	8184.3(15)	41.1(5)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for Gandelman258R. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	47.6(3)	41.2(3)	35.6(3)	12.4(2)	-6.3(2)	23.2(3)
O1	39.7(8)	32.1(8)	27.4(7)	2.8(6)	-4.4(6)	17.6(7)
N1	20.8(7)	23.9(8)	18.9(7)	7.5(6)	5.4(6)	9.5(6)
C1	22.2(9)	29.1(10)	22.6(9)	11.8(8)	7.8(7)	11.9(8)
Cl2	28.1(2)	31.3(3)	32.7(2)	10.5(2)	-5.97(19)	10.8(2)
O2	62.5(10)	41.2(9)	33.7(8)	16.8(7)	16.9(8)	18.2(8)
N2	24.2(8)	25.0(9)	22.6(7)	6.4(7)	5.6(6)	12.4(7)
C2	26.6(9)	42.5(12)	20.7(9)	10.7(8)	5.9(7)	19.2(9)
N3	22.2(7)	27.0(8)	21.4(7)	5.9(6)	4.2(6)	12.7(7)
C3	28.7(9)	36.6(11)	19.8(8)	8.1(8)	5.2(7)	19.0(9)
N4	42.3(10)	45.5(11)	30.6(9)	12.6(8)	0.1(8)	11.1(9)
C4	22.7(8)	17.8(9)	19.5(8)	3.3(7)	2.1(7)	5.8(7)
C5	26.4(9)	22.6(9)	19.1(8)	3.2(7)	5.6(7)	9.8(8)
C6	35.9(10)	22.8(9)	17.4(8)	3.6(7)	4.1(8)	9.4(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman258R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C7	34.4(10)	23.5(10)	22.6(9)	3.8(7)	-3.4(8)	13.5(8)
C8	24.4(9)	31.5(11)	35.1(10)	8.6(9)	3.7(8)	12.6(9)
C9	24.8(9)	26.6(10)	27.7(9)	9.7(8)	6.5(8)	8.9(8)
C10	20.2(8)	20.0(9)	23.7(9)	5.2(7)	0.2(7)	6.7(7)
C11	21.1(9)	32.0(11)	26.7(9)	10.2(8)	4.4(7)	10.4(8)
C12	25.8(9)	30.2(10)	25.1(9)	9.8(8)	2.6(8)	8.9(8)
C13	21.4(9)	20.6(9)	27.9(9)	7.6(7)	-4.6(7)	4.8(8)
C14	19.1(8)	24.2(10)	29.8(10)	3.9(8)	1.8(7)	7.4(8)
C15	21.7(9)	27.5(10)	23.0(9)	5.7(8)	3.2(7)	8.3(8)
C16	50.6(12)	35.5(12)	25.6(10)	2.6(8)	-5.1(9)	26.1(11)
C17	45.4(12)	20.7(10)	28.6(10)	4.6(8)	8.3(9)	12.3(9)
C18	43.5(12)	33.3(12)	32.8(11)	2.3(9)	-10.9(10)	12.7(10)
C19	32.6(11)	52.8(15)	49.0(13)	2.0(11)	-4.0(10)	21.8(11)
C20	39.7(12)	50.8(15)	40.5(12)	9.7(11)	13.4(10)	15.0(11)
C21	31.8(10)	17.9(9)	24.9(9)	2.3(7)	-0.8(8)	6.7(8)
C22	27.0(10)	30.8(11)	32.1(10)	9.5(9)	1.4(8)	5.6(9)
Cl1A	42.2(3)	34.6(3)	27.1(2)	8.2(2)	-5.6(2)	19.3(2)
O1A	29.0(7)	31.9(7)	32.4(7)	16.0(6)	8.0(6)	12.0(6)
N1A	24.4(7)	16.7(7)	20.5(7)	3.3(6)	0.1(6)	7.5(6)
C1A	27.2(9)	20.0(9)	20.9(8)	3.5(7)	2.5(7)	8.2(8)
Cl2A	30.2(2)	43.8(3)	41.7(3)	25.7(2)	6.1(2)	16.9(2)
O2A	29.2(7)	36.3(8)	46.3(9)	14.1(7)	10.2(6)	8.8(7)
N2A	24.6(8)	21.9(8)	22.0(7)	4.6(6)	0.6(6)	8.0(7)
C2A	25.8(9)	19.1(9)	22.9(9)	4.3(7)	1.4(7)	7.1(8)
N3A	23.2(7)	18.5(8)	21.1(7)	2.5(6)	-0.3(6)	7.1(6)
C3A	25.5(9)	21.3(9)	24.5(9)	5.4(7)	0.5(7)	8.9(8)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Gandelman258R. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N4A	80.4(16)	78.4(16)	42.4(11)	31.3(11)	17.5(11)	47.5(14)
C4A	22.2(8)	19.9(9)	19.5(8)	7.5(7)	6.0(7)	6.4(7)
C5A	24.4(9)	23.3(9)	19.7(8)	1.7(7)	1.1(7)	8.2(8)
C6A	29.4(9)	20.9(9)	25.3(9)	5.4(7)	4.3(8)	11.5(8)
C7A	30.1(9)	27.1(10)	21.4(9)	10.1(8)	2.2(7)	12.0(8)
C8A	36.8(10)	23.6(10)	17.4(8)	4.4(7)	-1.9(8)	8.4(9)
C9A	35.6(10)	21.9(9)	20.0(9)	4.6(7)	3.1(8)	11.6(8)
C10A	17.9(8)	21.3(9)	24.3(9)	8.8(7)	7.0(7)	5.6(7)
C11A	20.9(9)	23.3(9)	26.2(9)	5.9(7)	3.0(7)	6.4(8)
C12A	23.6(9)	23.0(9)	32.6(10)	9.0(8)	8.5(8)	10.2(8)
C13A	20.6(9)	31.5(10)	30.8(10)	19.0(8)	7.8(7)	9.6(8)
C14A	24.3(9)	29.1(10)	22.3(9)	9.1(8)	3.6(7)	6.4(8)
C15A	26.2(9)	24.1(9)	22.2(9)	7.5(7)	7.0(7)	8.1(8)
C16A	24.9(9)	26.9(10)	36.3(11)	14.8(8)	0.3(8)	6.1(8)
C17A	32.8(10)	18.4(9)	31.3(10)	3.9(8)	7.1(8)	3.4(8)
C18A	93(2)	51.7(15)	26.8(11)	16.5(11)	11.5(12)	34.4(15)
C19A	72.6(17)	42.1(14)	30.0(11)	12.1(10)	22.0(11)	17.2(13)
C20A	44.9(12)	31.9(12)	35.3(11)	4.6(9)	11.9(10)	7.2(10)
C21A	39.3(11)	17.5(9)	29.1(10)	3.7(8)	7.9(8)	6.0(9)
C22A	53.5(14)	48.7(14)	32.2(11)	17.7(10)	12.9(10)	25.6(12)

Table 4 Bond Lengths for Gandelman258R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C7	1.7501(16)	Cl1A	C7A	1.7487(17)
O1	C16	1.462(2)	O1A	C16A	1.446(2)
O1	C17	1.332(2)	O1A	C17A	1.335(2)

Table 4 Bond Lengths for Gandelman258R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
N1	C1	1.464(2)	N1A	C1A	1.459(2)
N1	C3	1.467(2)	N1A	C3A	1.462(2)
N1	C4	1.414(2)	N1A	C4A	1.411(2)
C1	N2	1.457(2)	C1A	N2A	1.457(2)
Cl2	C13	1.7491(16)	Cl2A	C13A	1.7536(16)
O2	C17	1.203(2)	O2A	C17A	1.207(2)
N2	N3	1.445(2)	N2A	N3A	1.446(2)
C2	N3	1.459(2)	C2A	N3A	1.453(2)
C2	C3	1.523(2)	C2A	C3A	1.535(2)
N3	C10	1.419(2)	N3A	C10A	1.420(2)
C3	C16	1.528(3)	C3A	C16A	1.518(3)
N4	C18	1.329(3)	N4A	C18A	1.347(3)
N4	C22	1.327(2)	N4A	C22A	1.354(3)
C4	C5	1.398(2)	C4A	C5A	1.404(2)
C4	C9	1.400(2)	C4A	C9A	1.398(2)
C5	C6	1.386(2)	C5A	C6A	1.390(2)
C6	C7	1.386(3)	C6A	C7A	1.382(2)
C7	C8	1.373(3)	C7A	C8A	1.376(3)
C8	C9	1.395(2)	C8A	C9A	1.392(2)
C10	C11	1.399(3)	C10A	C11A	1.394(2)
C10	C15	1.399(2)	C10A	C15A	1.394(2)
C11	C12	1.386(2)	C11A	C12A	1.392(2)
C12	C13	1.381(3)	C12A	C13A	1.386(3)
C13	C14	1.378(3)	C13A	C14A	1.373(3)
C14	C15	1.388(2)	C14A	C15A	1.397(2)
C17	C21	1.497(2)	C17A	C21A	1.497(3)
C18	C19	1.362(3)	C18A	C19A	1.369(4)

Table 4 Bond Lengths for Gandelman258R.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C19	C20	1.382(3)	C19A	C20A	1.370(3)
C20	C21	1.397(3)	C20A	C21A	1.387(3)
C21	C22	1.376(3)	C21A	C22A	1.385(3)

Table 5 Bond Angles for Gandelman258R.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C17	O1	C16	118.16(16)	C17A	O1A	C16A	116.07(14)
C1	N1	C3	112.27(13)	C1A	N1A	C3A	113.70(13)
C4	N1	C1	119.71(14)	C4A	N1A	C1A	120.04(14)
C4	N1	C3	118.73(13)	C4A	N1A	C3A	119.58(14)
N2	C1	N1	111.91(14)	N2A	C1A	N1A	111.60(14)
N3	N2	C1	109.34(13)	N3A	N2A	C1A	108.95(14)
N3	C2	C3	110.44(15)	N3A	C2A	C3A	108.82(14)
N2	N3	C2	111.45(13)	N2A	N3A	C2A	111.92(13)
C10	N3	N2	112.45(13)	C10A	N3A	N2A	111.77(14)
C10	N3	C2	117.23(14)	C10A	N3A	C2A	118.06(14)
N1	C3	C2	109.14(14)	N1A	C3A	C2A	109.23(14)
N1	C3	C16	113.52(15)	N1A	C3A	C16A	112.97(15)
C2	C3	C16	110.67(15)	C16A	C3A	C2A	109.63(14)
C22	N4	C18	115.98(19)	C18A	N4A	C22A	116.0(2)
C5	C4	N1	119.28(15)	C5A	C4A	N1A	120.04(15)
C5	C4	C9	118.31(15)	C9A	C4A	N1A	122.02(15)
C9	C4	N1	122.39(16)	C9A	C4A	C5A	117.85(15)
C6	C5	C4	121.34(17)	C6A	C5A	C4A	120.89(16)
C5	C6	C7	119.11(17)	C7A	C6A	C5A	119.75(17)
C6	C7	Cl1	118.55(15)	C6A	C7A	Cl1A	119.27(14)
C8	C7	Cl1	120.59(15)	C8A	C7A	Cl1A	120.38(14)

Table 5 Bond Angles for Gandelman258R.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C8	C7	C6	120.85(16)	C8A	C7A	C6A	120.35(15)
C7	C8	C9	120.12(17)	C7A	C8A	C9A	120.02(16)
C8	C9	C4	120.16(17)	C8A	C9A	C4A	120.84(17)
C11	C10	N3	120.63(15)	C11A	C10A	N3A	118.70(15)
C15	C10	N3	121.37(16)	C15A	C10A	N3A	122.05(16)
C15	C10	C11	117.93(15)	C15A	C10A	C11A	119.18(15)
C12	C11	C10	121.15(17)	C12A	C11A	C10A	120.84(17)
C13	C12	C11	119.54(17)	C13A	C12A	C11A	118.71(17)
C12	C13	Cl2	119.32(14)	C12A	C13A	Cl2A	119.09(14)
C14	C13	Cl2	119.97(14)	C14A	C13A	Cl2A	119.34(14)
C14	C13	C12	120.70(15)	C14A	C13A	C12A	121.58(16)
C13	C14	C15	119.80(17)	C13A	C14A	C15A	119.52(17)
C14	C15	C10	120.86(17)	C10A	C15A	C14A	120.12(17)
O1	C16	C3	108.08(15)	O1A	C16A	C3A	107.33(13)
O1	C17	C21	110.50(17)	O1A	C17A	C21A	111.68(16)
O2	C17	O1	125.13(18)	O2A	C17A	O1A	124.37(18)
O2	C17	C21	124.4(2)	O2A	C17A	C21A	123.95(19)
N4	C18	C19	124.67(19)	N4A	C18A	C19A	124.6(2)
C18	C19	C20	118.9(2)	C18A	C19A	C20A	118.4(2)
C19	C20	C21	117.8(2)	C19A	C20A	C21A	119.3(2)
C20	C21	C17	119.01(19)	C20A	C21A	C17A	119.35(19)
C22	C21	C17	123.09(18)	C22A	C21A	C17A	122.09(19)
C22	C21	C20	117.89(18)	C22A	C21A	C20A	118.55(19)
N4	C22	C21	124.69(18)	N4A	C22A	C21A	123.1(2)

Table 6 Torsion Angles for Gandelman258R.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
Cl1	C7	C8	C9	-177.59(15)	Cl1A	C7A	C8A	C9A	176.17(15)
O1	C17	C21	C20	170.08(18)	O1A	C17A	C21A	C20A	178.11(17)
O1	C17	C21	C22	-8.7(3)	O1A	C17A	C21A	C22A	-1.0(3)
N1	C1	N2	N3	57.79(19)	N1A	C1A	N2A	N3A	56.80(18)
N1	C3	C16	O1	-71.1(2)	N1A	C3A	C16A	O1A	-53.65(19)
N1	C4	C5	C6	-178.81(16)	N1A	C4A	C5A	C6A	172.18(16)
N1	C4	C9	C8	179.51(17)	N1A	C4A	C9A	C8A	-171.74(17)
C1	N1	C3	C2	53.0(2)	C1A	N1A	C3A	C2A	52.07(19)
C1	N1	C3	C16	-70.95(18)	C1A	N1A	C3A	C16A	-70.22(18)
C1	N1	C4	C5	-168.43(16)	C1A	N1A	C4A	C5A	-171.86(16)
C1	N1	C4	C9	9.8(3)	C1A	N1A	C4A	C9A	4.6(3)
C1	N2	N3	C2	-59.85(18)	C1A	N2A	N3A	C2A	-62.00(18)
C1	N2	N3	C10	166.18(15)	C1A	N2A	N3A	C10A	163.02(14)
Cl2	C13	C14	C15	-178.79(14)	Cl2A	C13A	C14A	C15A	-179.30(14)
O2	C17	C21	C20	-9.3(3)	O2A	C17A	C21A	C20A	-2.3(3)
O2	C17	C21	C22	171.94(19)	O2A	C17A	C21A	C22A	178.7(2)
N2	N3	C10	C11	-31.3(2)	N2A	N3A	C10A	C11A	-51.3(2)
N2	N3	C10	C15	151.79(17)	N2A	N3A	C10A	C15A	131.78(17)
C2	N3	C10	C11	-162.41(17)	C2A	N3A	C10A	C11A	176.73(16)
C2	N3	C10	C15	20.7(2)	C2A	N3A	C10A	C15A	-0.2(3)
C2	C3	C16	O1	165.75(15)	C2A	C3A	C16A	O1A	-175.72(14)
N3	C2	C3	N1	-54.2(2)	N3A	C2A	C3A	N1A	-54.09(19)
N3	C2	C3	C16	71.4(2)	N3A	C2A	C3A	C16A	70.20(19)
N3	C10	C11	C12	-175.57(17)	N3A	C10A	C11A	C12A	-175.61(16)
N3	C10	C15	C14	175.35(16)	N3A	C10A	C15A	C14A	174.42(16)
C3	N1	C1	N2	-56.19(19)	C3A	N1A	C1A	N2A	-54.5(2)
C3	N1	C4	C5	47.4(2)	C3A	N1A	C4A	C5A	38.6(2)

Table 6 Torsion Angles for Gandelman258R.

A	B	C	D	Angle/˚	A	B	C	D	Angle/˚
C3	N1	C4	C9	-134.39(18)	C3A	N1A	C4A	C9A	-144.97(18)
C3	C2	N3	N2	58.76(19)	C3A	C2A	N3A	N2A	60.70(18)
C3	C2	N3	C10	-169.66(15)	C3A	C2A	N3A	C10A	-167.42(15)
N4	C18	C19	C20	-1.2(4)	N4A	C18A	C19A	C20A	-0.1(4)
C4	N1	C1	N2	157.52(15)	C4A	N1A	C1A	N2A	154.25(15)
C4	N1	C3	C2	-160.35(16)	C4A	N1A	C3A	C2A	-156.52(15)
C4	N1	C3	C16	75.7(2)	C4A	N1A	C3A	C16A	81.18(19)
C4	C5	C6	C7	-0.6(3)	C4A	C5A	C6A	C7A	0.0(3)
C5	C4	C9	C8	-2.3(3)	C5A	C4A	C9A	C8A	4.8(3)
C5	C6	C7	Cl1	178.21(14)	C5A	C6A	C7A	Cl1A	-175.81(15)
C5	C6	C7	C8	-2.4(3)	C5A	C6A	C7A	C8A	4.2(3)
C6	C7	C8	C9	3.0(3)	C6A	C7A	C8A	C9A	-3.9(3)
C7	C8	C9	C4	-0.6(3)	C7A	C8A	C9A	C4A	-0.7(3)
C9	C4	C5	C6	2.9(3)	C9A	C4A	C5A	C6A	-4.4(3)
C10	C11	C12	C13	-0.4(3)	C10A	C11A	C12A	C13A	0.6(3)
C11	C10	C15	C14	-1.7(3)	C11A	C10A	C15A	C14A	-2.5(3)
C11	C12	C13	Cl2	178.59(14)	C11A	C12A	C13A	Cl2A	178.22(14)
C11	C12	C13	C14	-0.6(3)	C11A	C12A	C13A	C14A	-1.6(3)
C12	C13	C14	C15	0.3(3)	C12A	C13A	C14A	C15A	0.5(3)
C13	C14	C15	C10	0.8(3)	C13A	C14A	C15A	C10A	1.5(3)
C15	C10	C11	C12	1.5(3)	C15A	C10A	C11A	C12A	1.4(3)
C16	O1	C17	O2	5.9(3)	C16A	O1A	C17A	O2A	2.2(3)
C16	O1	C17	C21	-173.48(15)	C16A	O1A	C17A	C21A	-178.21(15)
C17	O1	C16	C3	108.89(19)	C17A	O1A	C16A	C3A	178.03(15)
C17	C21	C22	N4	177.56(19)	C17A	C21A	C22A	N4A	-179.9(2)
C18	N4	C22	C21	0.7(3)	C18A	N4A	C22A	C21A	-1.3(4)
C18	C19	C20	C21	0.6(3)	C18A	C19A	C20A	C21A	-0.2(3)

Table 6 Torsion Angles for Gandelman258R.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C19	C20	C21	C17	-178.31(19)	C19A	C20A	C21A	C17A	-179.34(19)
C19	C20	C21	C22	0.5(3)	C19A	C20A	C21A	C22A	-0.2(3)
C20	C21	C22	N4	-1.2(3)	C20A	C21A	C22A	N4A	1.0(3)
C22	N4	C18	C19	0.6(3)	C22A	N4A	C18A	C19A	0.8(4)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman258R.

Atom	*x*	*y*	*z*	U(eq)
H1A	6210.79	6782.29	6864.99	27
H1B	6017.37	5479.69	6351.09	27
H2	4133(18)	5322(19)	5797(15)	33(6)
H2A	2996.18	5729.82	7038.87	33
H2B	3199.62	7032.74	7563.51	33
H3	4194.6	6084.75	8473.37	32
H5	4620.98	4708.31	8839.65	27
H6	5714.93	3981.24	9813.66	31
H8	8463.44	4787.99	8418.64	35
H9	7386.94	5551.55	7453.61	31
H11	4227.32	6898.52	4681.12	31
H12	3060.4	7466.97	3629.05	32
H14	948.62	7932.77	5592.84	30
H15	2103.71	7354.5	6648.73	29
H16A	5869.06	7944.17	8062.91	43
H16B	4868.83	8130.79	8689.68	43
H18	9112.03	6789.08	12246.79	46
H19	10217.3	7127.68	11085.65	55
H20	9380.31	7548.07	9732.97	52

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Gandelman258R.

Atom	*x*	*y*	*z*	U(eq)
H22	6431.77	7335.56	10906.52	37
H1AA	3091.52	2927.16	6660.58	27
H1AB	4438.07	3371.52	6525.67	27
H2AA	3830(19)	3262(19)	4981(16)	40(6)
H2AB	2738.56	1439.2	4048.92	27
H2AC	1385.7	950.55	4159.48	27
H3A	2691.35	206.01	5031.66	28
H5A	4063.89	-246.44	5480.83	28
H6A	5466.31	-859.86	6268.36	29
H8A	6375.57	2037.76	8355.29	32
H9A	4962.86	2655.42	7585.36	30
H11A	1845.91	4555.32	5337.44	28
H12A	826.13	5420.7	4425.82	30
H14A	91.97	2672.54	2190.55	30
H15A	1164.24	1828.11	3085.39	28
H16C	1360.23	1425.14	6143.39	35
H16D	871.36	134.06	5520.04	35
H18A	3182.79	-1006.72	10115.82	64
H19A	1307.51	-856.84	10109.68	56
H20A	433.04	-341.84	8842.65	46
H22A	3398.59	-137.18	7690.75	49

Experimental

Single crystals of $C_{22}H_{20}Cl_2N_4O_2$ **[Gandelman258R]** were obtained by slow evaporation of C_6H_6 solution. A suitable crystal was selected and measured on diffractometer Rigaku XtaLAB Synergy-S. The crystal was kept at 100.15 K during data collection. Using Olex2,[19] the structure was solved with the olex2.solve[22] structure solution program using Charge Flipping and refined with the SHELXL[21] refinement package using Least Squares minimisation.

Crystal structure determination of [Gandelman258R]

Crystal Data for $C_{22}H_{20}Cl_2N_4O_2$ (*M* =443.32 g/mol): triclinic, space group P-1 (no. 2), *a* = 11.9428(3) Å, *b* = 12.6772(4) Å, *c* = 14.5756(4) Å, *α* = 102.636(2)°, *β* = 95.393(3)°, *γ* = 105.544(4)°, *V* = 2047.05(11) Å^3, *Z* = 4, *T* = 100.15 K, μ(MoKα) = 0.345 mm^{-1}, *Dcalc* = 1.438 g/cm^3, 34444 reflections measured (4.912° ≤ 2Θ ≤ 60.084°), 9542

unique (R_{int} = 0.0577, R_{sigma} = 0.0559) which were used in all calculations. The final R_1 was 0.0428 (I > 2σ(I)) and wR_2 was 0.1045 (all data).

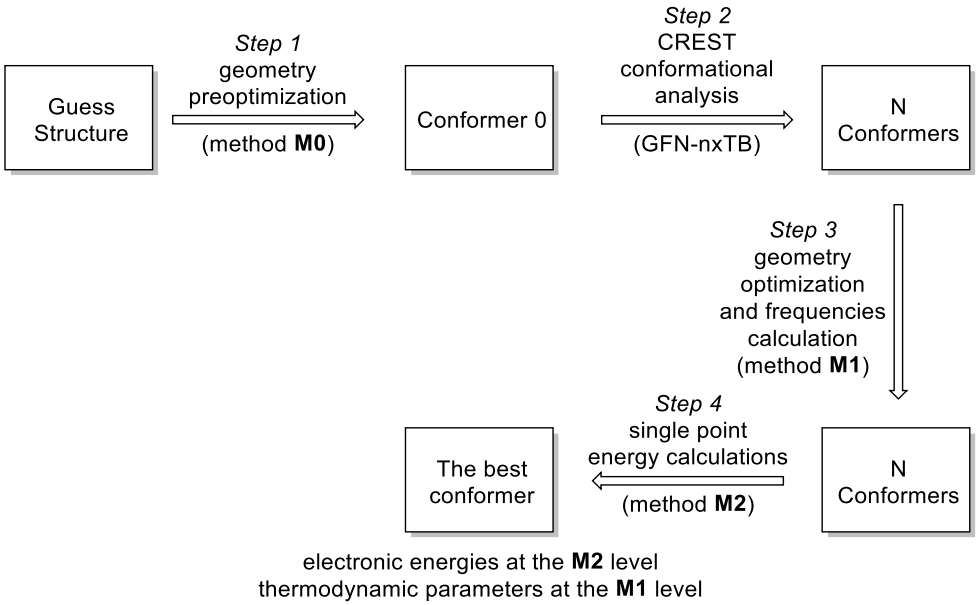
4 Calculations

4.1 General Information

Orca 5.0.4 was used for the computations.[23] The geometries were optimized and the frequencies calculations were performed by BP86 functional[24,25] with Becke-Johnson damped dispersion correction D3(BJ)[26,27] using 6-31+G(d,p) basis set[28–31] (methods **M0** and **M1**) treated with RI-J approximation with def2/J auxiliary basis set. The frequency calculations were performed to validate each structure as a minimum and to evaluate its zero-point energy and the thermal corrections at 298 K. The single point energy calculations were performed by M062x functional[32] with D3zero dispersion correction[26] using 6-311++G(2d,2p)[28,33,34] basis set (method **M2**) treated with RIJCOSX[35] approximation and def2/J auxiliary basis set. Solvation effects were dealt with C-PCM model in THF for both optimizations and single point energy calculations.[36,37] Optimized geometries are presented in the separately attached supplementary files: see "SI_calculations_compounds_table.xlsx" for the structures, its file names and parameters; see folder "_xyz_files" for corresponding coordinates.

The lowest energy conformers of intermediates and transition states were found by the conformational search and analysis using CREST program[38] followed by a set of DFT calculations (see the general workflow for the calculations at scheme sC1; for the parameters used in CREST program see scheme sC2). The transition-state structures were confirmed to connect corresponding reactants and products by intrinsic reaction coordinate (IRC) calculations (see the general workflow for the calculations at scheme sC3). The quoted energies include zero-point, enthalpy, and entropic corrections determined from vibrational frequencies. The pictures of TS and intermediates presented were made with CYLview20 software.[39] The graphs presented were made with EveRplot.[40]

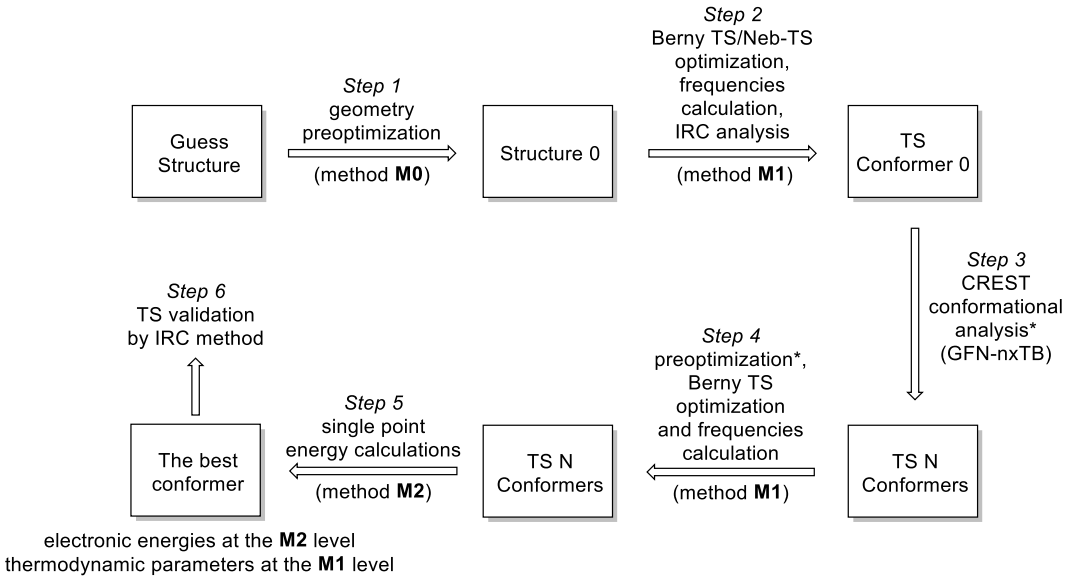
Scheme sC1. Calculations workflow for the reaction intermediates.



Scheme sC2. Parameters utilized within CREST program package.

--rthr	--ethr	--bthr	--ewin
0.125	0.1	0.02	45[24]

Scheme sC3. Calculations workflow for the transition states.



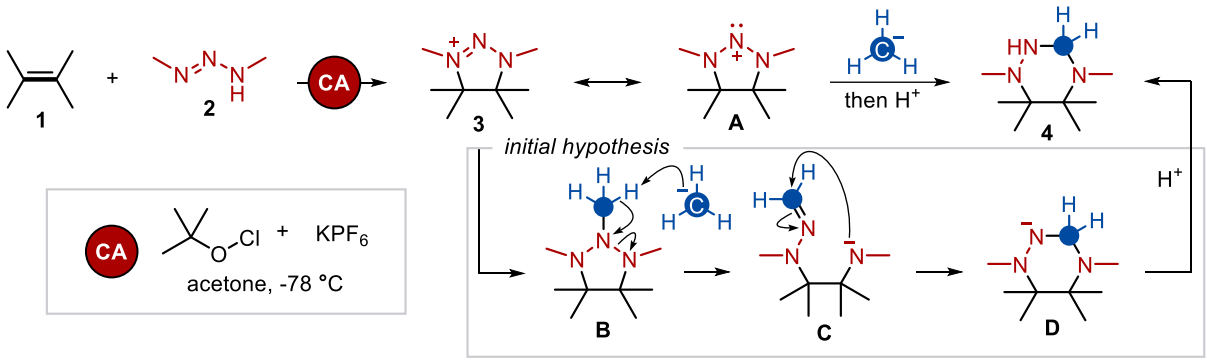
* The coordinates which underwent the most changes in the transformation were frozen.

[24] 45 kcal/mol energy cut-off was used for the calculations of conformational ensembles. For some of the structures which possess many degrees of freedom 30 kcal/mol cut-off was used.

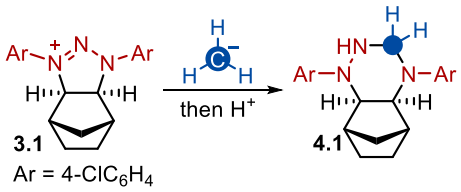
4.2 Discussion of the Reaction Mechanism

4.2.1 Mechanistic hypothesis

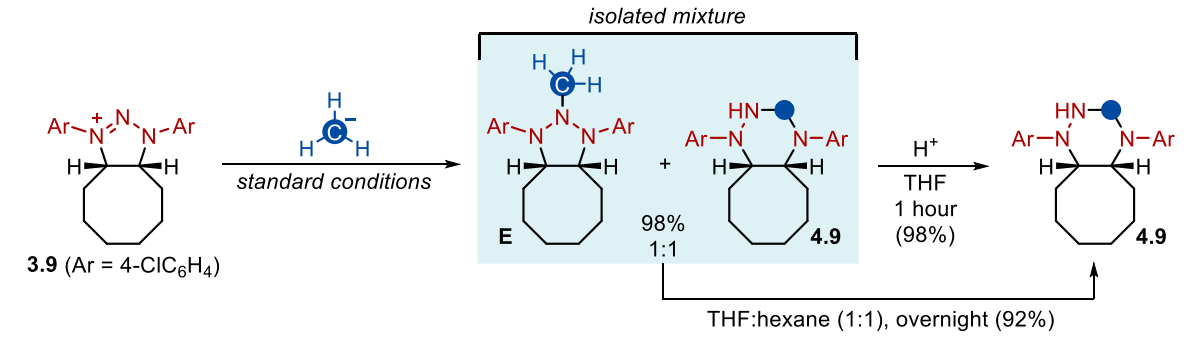
Our initial mechanistic hypothesis was the one described in the main text which is shown additionally below.



However, when we performed optimization study, 4 equivalents of MeMgBr provided inferior results to 1 or 2 equivalents. Additionally, we were able to isolate the intermediate triazanes and show that they undergo acid mediated rearrangement (for more information see section "2.3.7 Step 2: optimization of acidic quench for compound 4 synthesis").

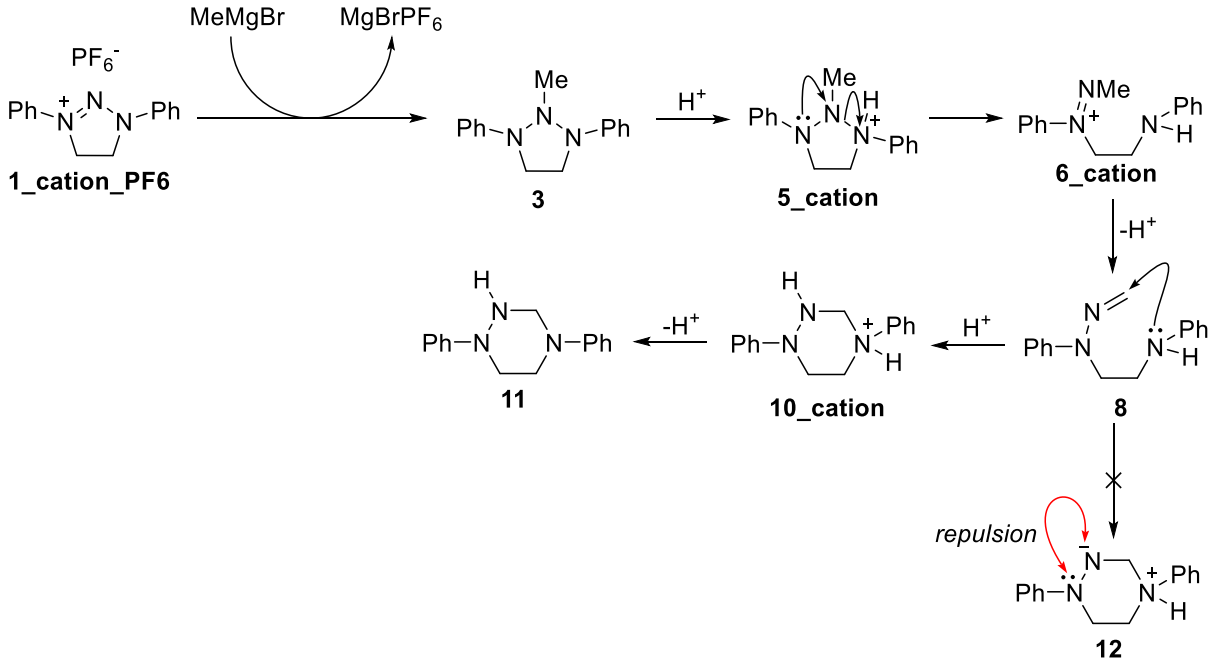


Entry	H_3C^- source	Solvent	Temperature	Yield
1	MeMgBr (4 eq)	THF	0 °C to RT	82%
7	MeMgBr (2 eq)	THF	0 °C to RT	94%
8	**MeMgBr (1 eq)**	**THF**	**0 °C to RT**	**98%**



Therefore, we refined the mechanistic hypothesis and envisioned that the reaction under investigation should proceed via the following general mechanistic scheme shown below.

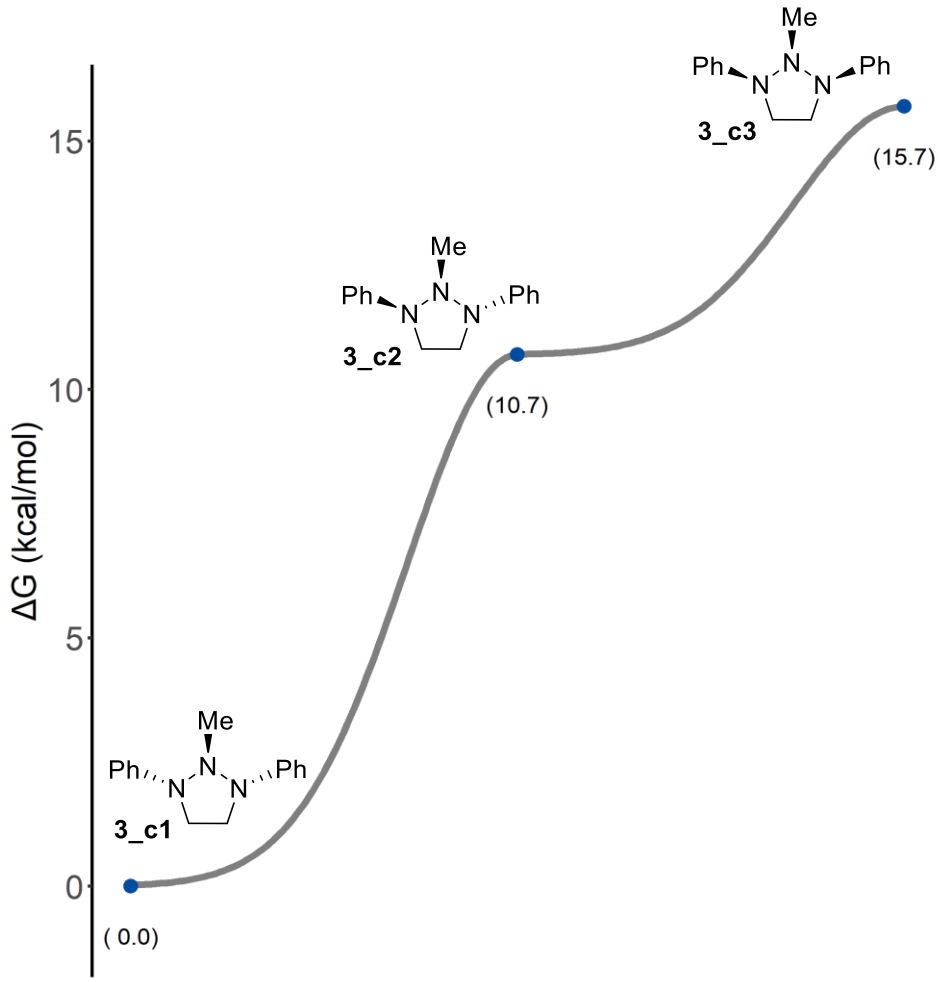
Nitrenium salt reacts with MeMgBr to produce triazane **3**. The protonation should yield cation **5** or its isomer where the middle nitrogen is protonated (see discussion on this below). N-N bond may be cleaved to produce intermediate **6** which upon deprotonation gives intermediate **8**. Cyclization from **8** to **12** is not favorable since there is a presence of negative change in it next to proximate nitrogen lone pair. This cyclization should be better coupled with protonation allowing cation **10** which upon deprotonation gives final product **11**.



Later, all the relevant parts of this mechanistic hypothesis are discussed in more detail.

4.2.2 *Discussion of stereochemistry of compound 3*

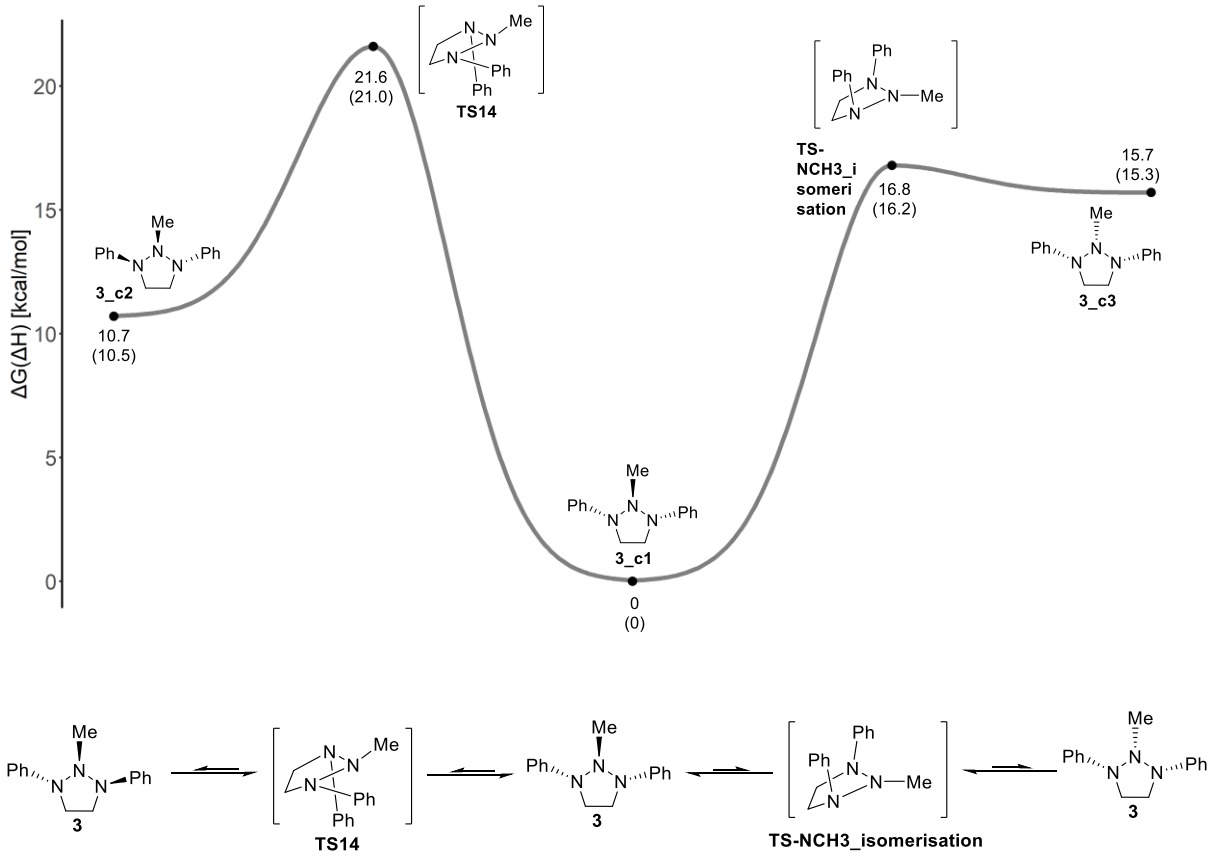
There were found three possible conformers for compound 3 presented below with their relative energies.[25]



[25] This diagram does not contain reaction pathway for interconversion between those conformers (see below).

Triazane **3** has three saturated nitrogen atoms in a row, which in principle may block the flip for the middle nitrogen in conformers presented above. However, we demonstrated that the energy barrier for this conformational change is surmountable.

The interconversion for the side nitrogen is also possible according to the energies calculated.



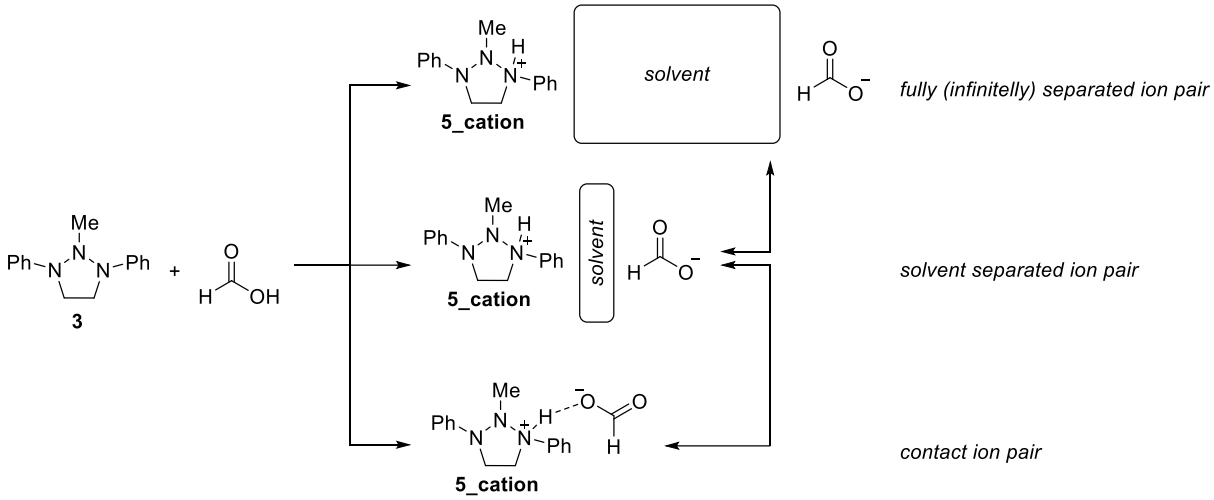
4.2.3 Discussion of the protonation step

Protonation step of compound 3 depends on several factors:

- Solvent used,
- Acid used,
- Conditions used.

In this part we will consider the reaction that is mediated by formic acid because such a possibility was shown during optimization of the rearrangement step.

In principle, there are three major mechanistic scenarios for the protonation step as presented in the scheme below.



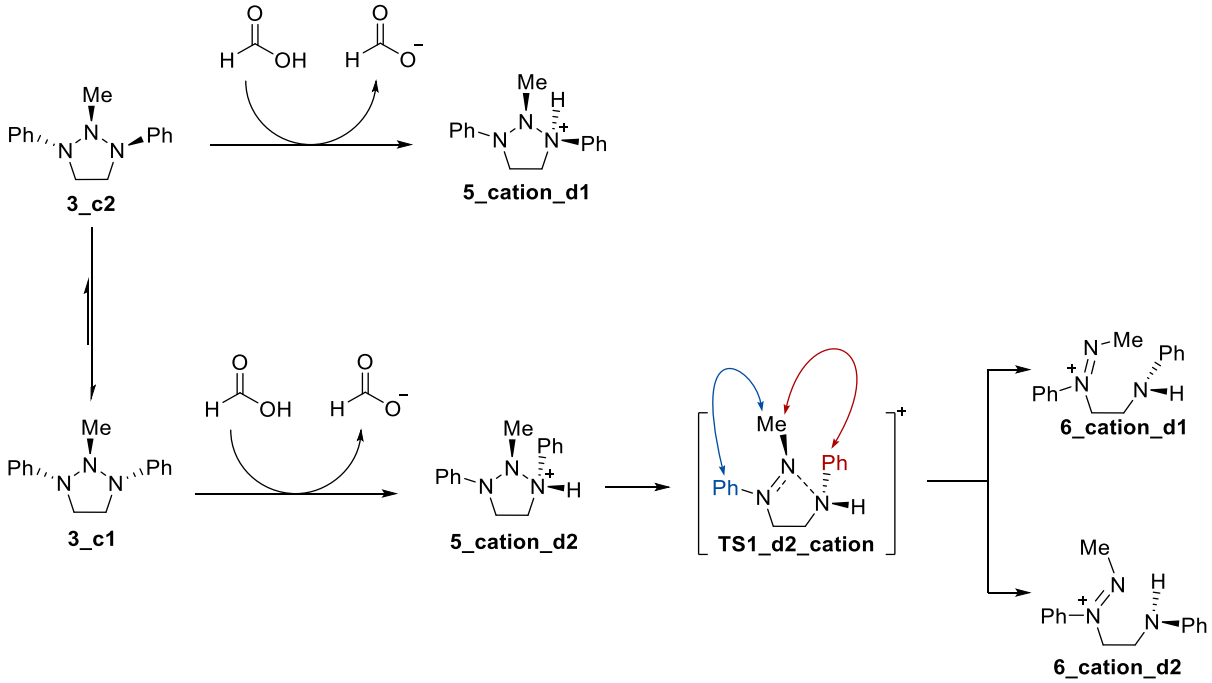
We used an implicit solvent model for our calculations; however, it is inferior to explicit solvation model. Implicit solvation can lead to the underestimation of more polar transition state stabilization relative to the preceding less polar reactant. Regrettably, a model with explicit solvation (including even just the first shell of the solvent) is not rather feasible at reasonable calculations cost. Since solvent separated ion pair model should involve explicit solvation for correct description of the system (e.g., hydrogen bonding stabilization of protonated species), we did not investigate this option.

In this study, we focused on the fully separated ion pair model as well as contact ion pair model as described below.

4.2.4 *Discussion of the protonation step: infinitely separated ion pair model*

In this part, we will consider the fully separated ion pair model.

Protonation of different conformers of 3 will give different diastereomers of cation 5 (d1 and d2).

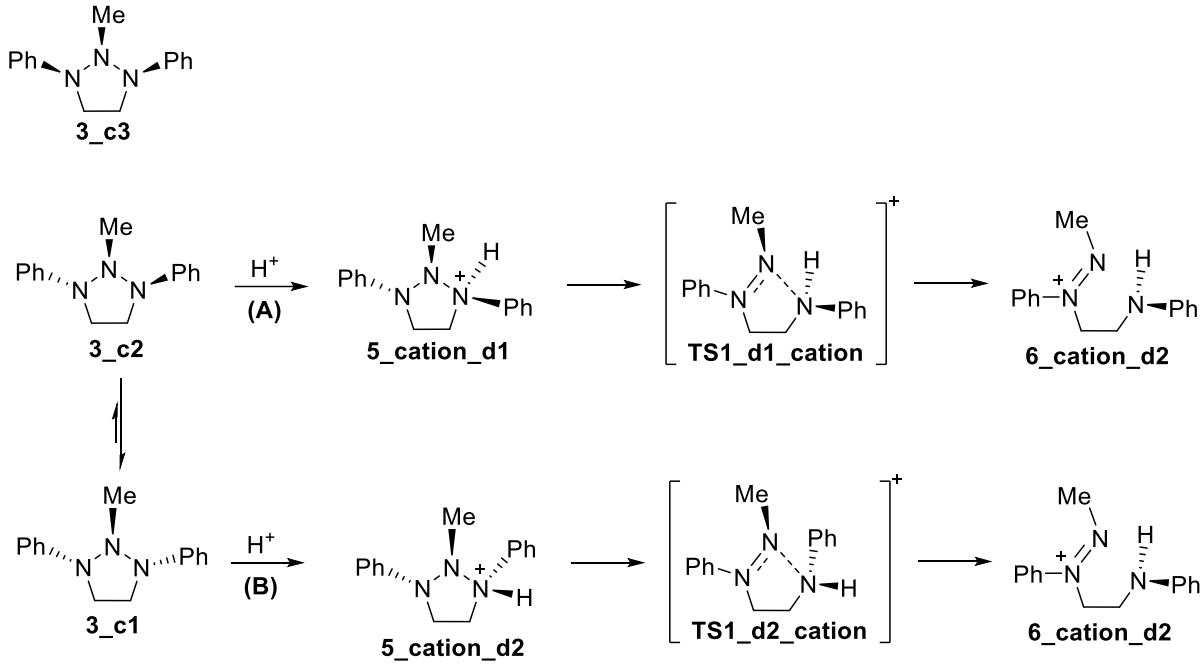


Configuration of N=N in 6 depends on the relative position of Me and blue Ph, rather than on configuration of red phenyl in the cation 5.

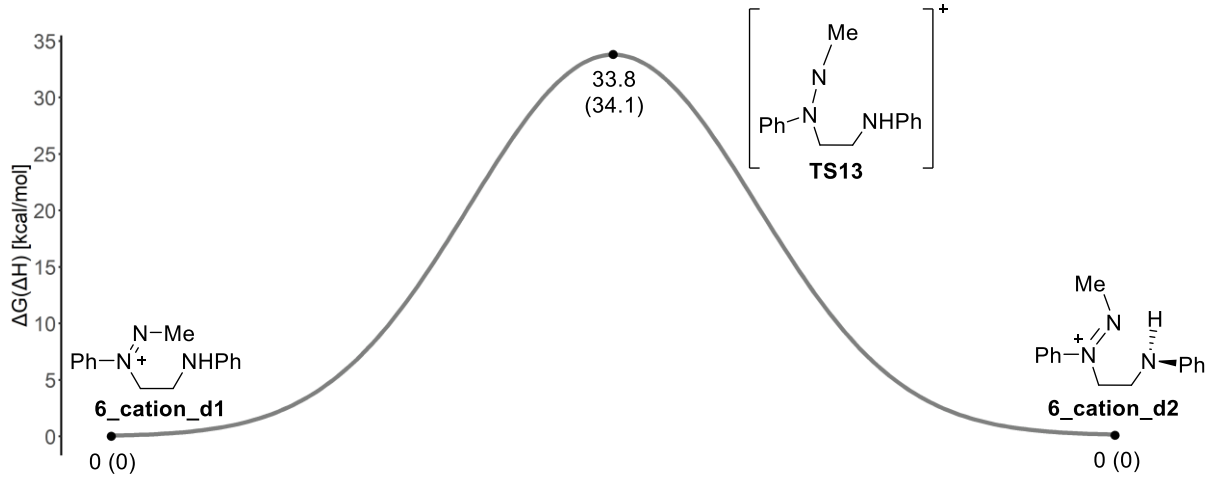
We did not consider possible protonation of the least stable conformer 3_c3 because it is too high in energy. Additionally, CREST program package did not predict the existence of this protonated form within 60 kcal energy window used for conformational search, while the other protonated forms discussed further existed within the chosen range of the search.

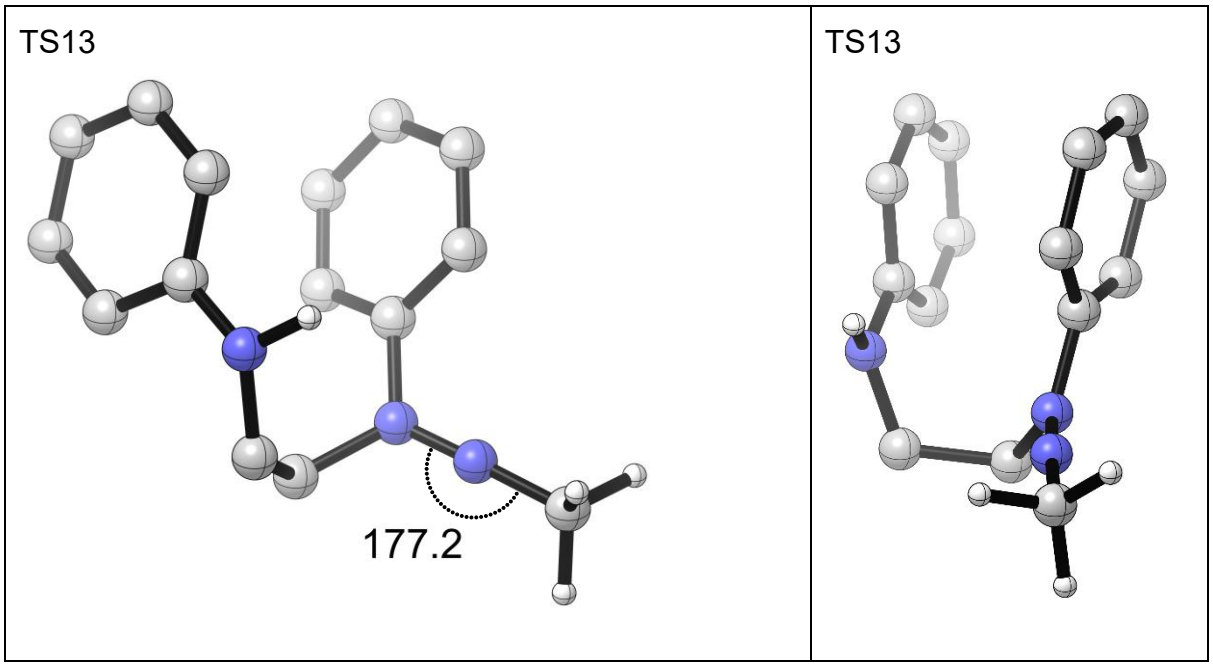
Protonation of 3_c2 generates cation 5_d1 (A) which upon N-N cleavage yields 6_d2. Interestingly, such a substitution pattern can provide 2nd diastereomer of cation 6.

Protonation of the most stable conformer 3_c1 yields cation 5_d2 (B). This later produces 2nd diastereomer of cation 6 as well.

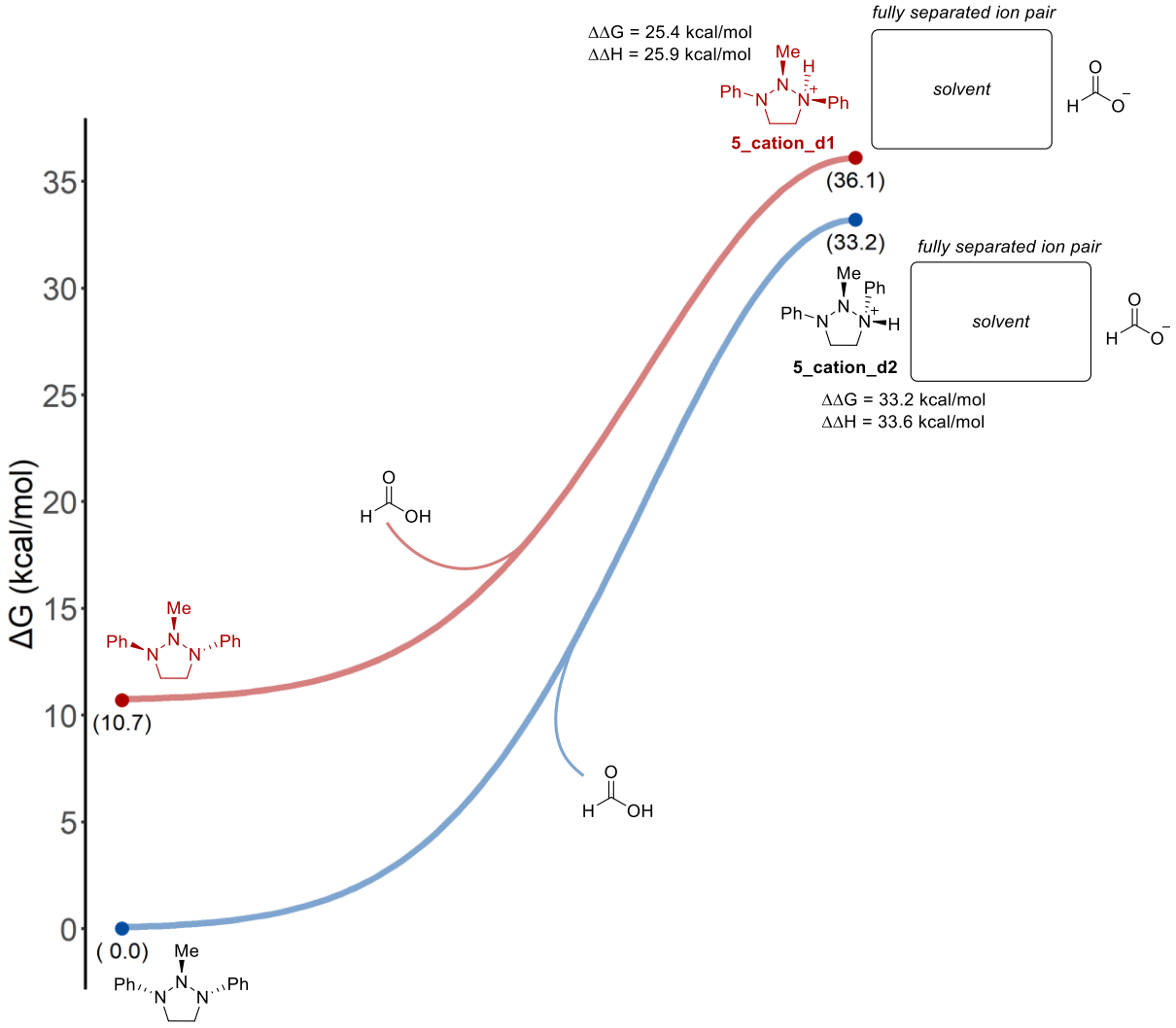


We additionally showed that interconversion between two diastereomers of cation 6 is not really feasible at the reaction conditions.

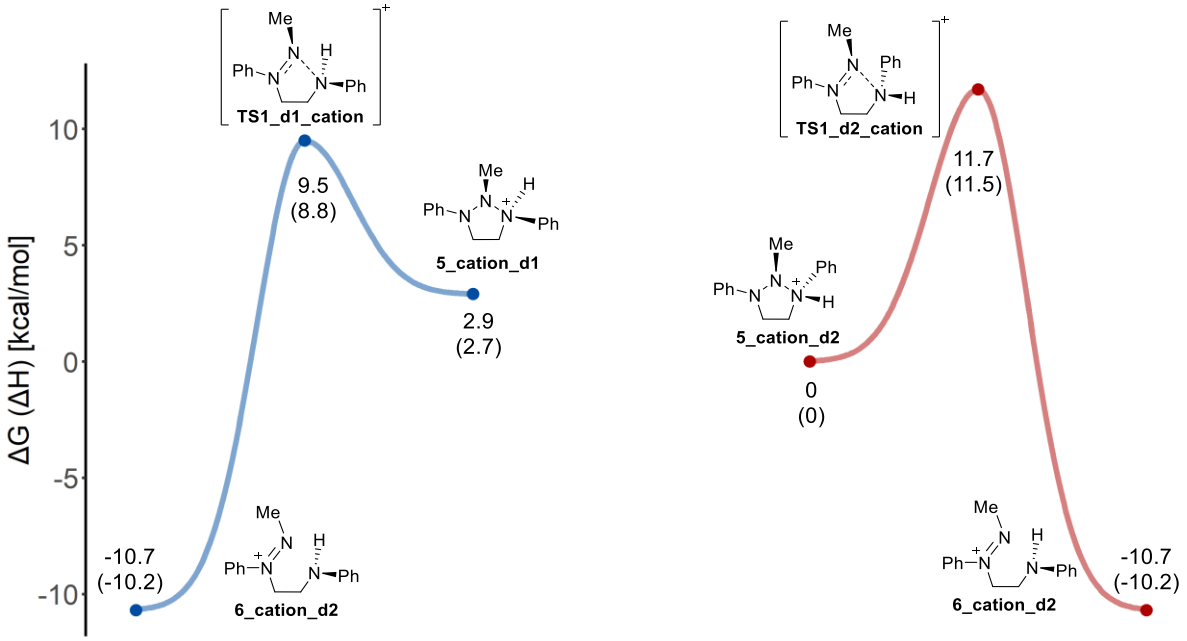


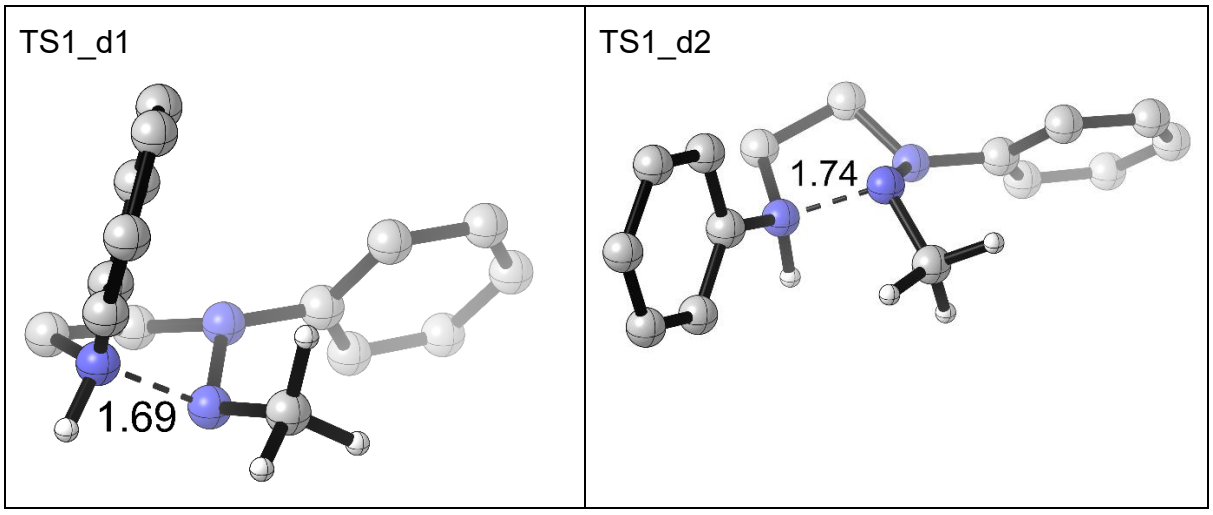


We calculated the thermodynamics of fully separated ion pair formation as presented below. Likely, implicit solvation model cannot accurately describe the formation of the fully separated ion pair as there should be other factors that can be introduced by explicit solvent (e.g., a hydrogen bonding that additionally stabilizes cations 5).



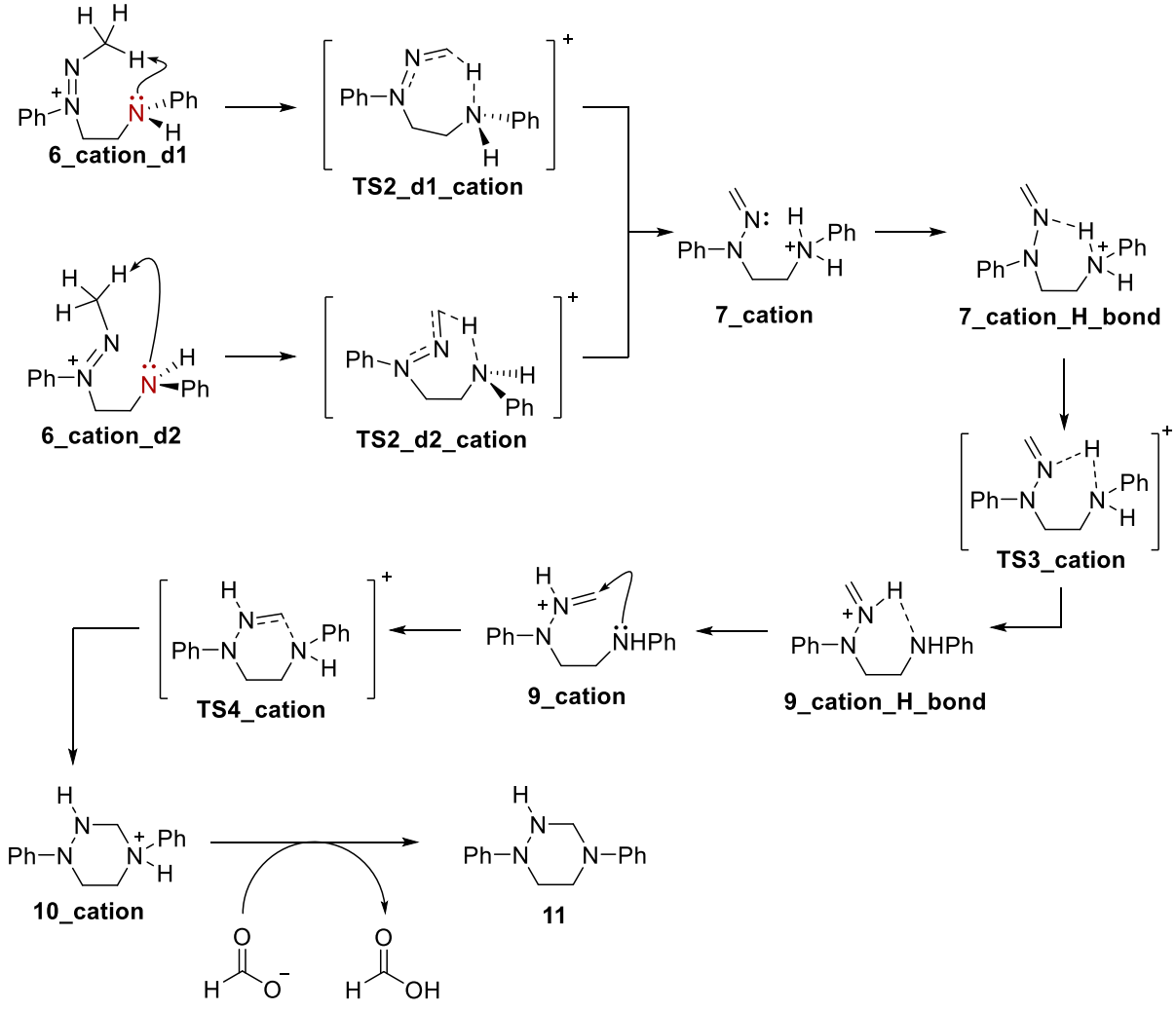
We compared two diastereomeric transition states TS1 as presented below for the ring opening step.



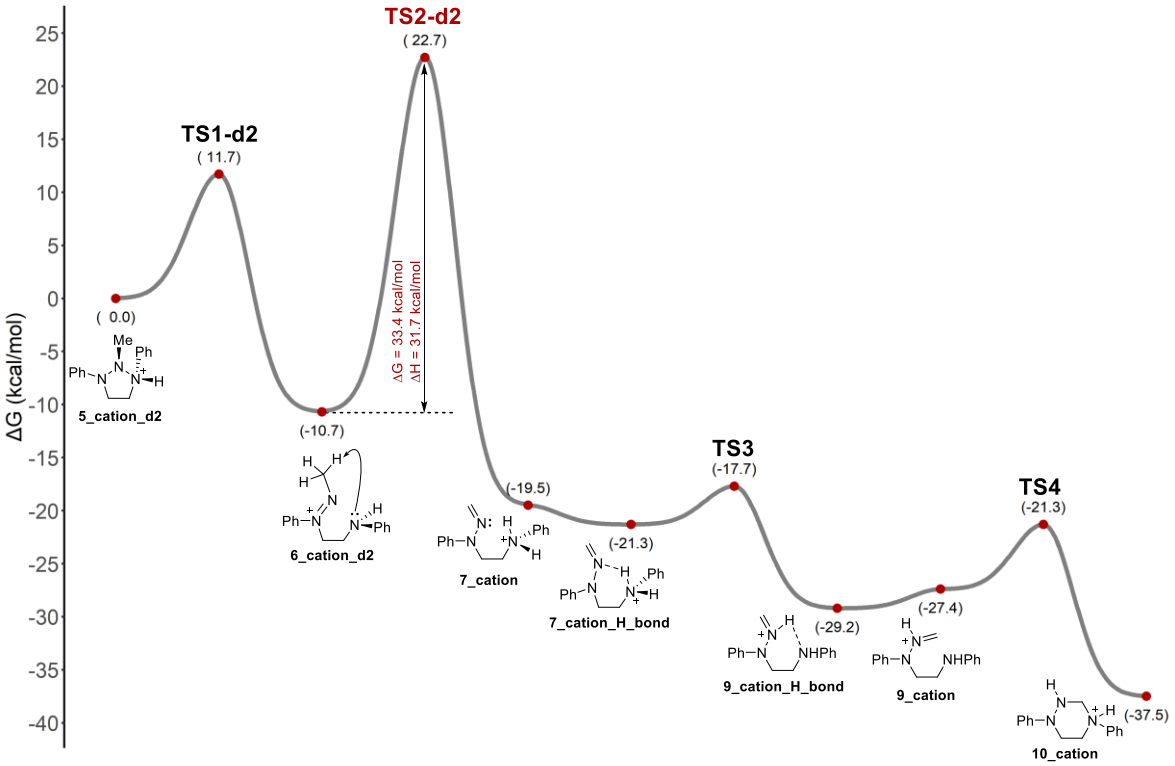


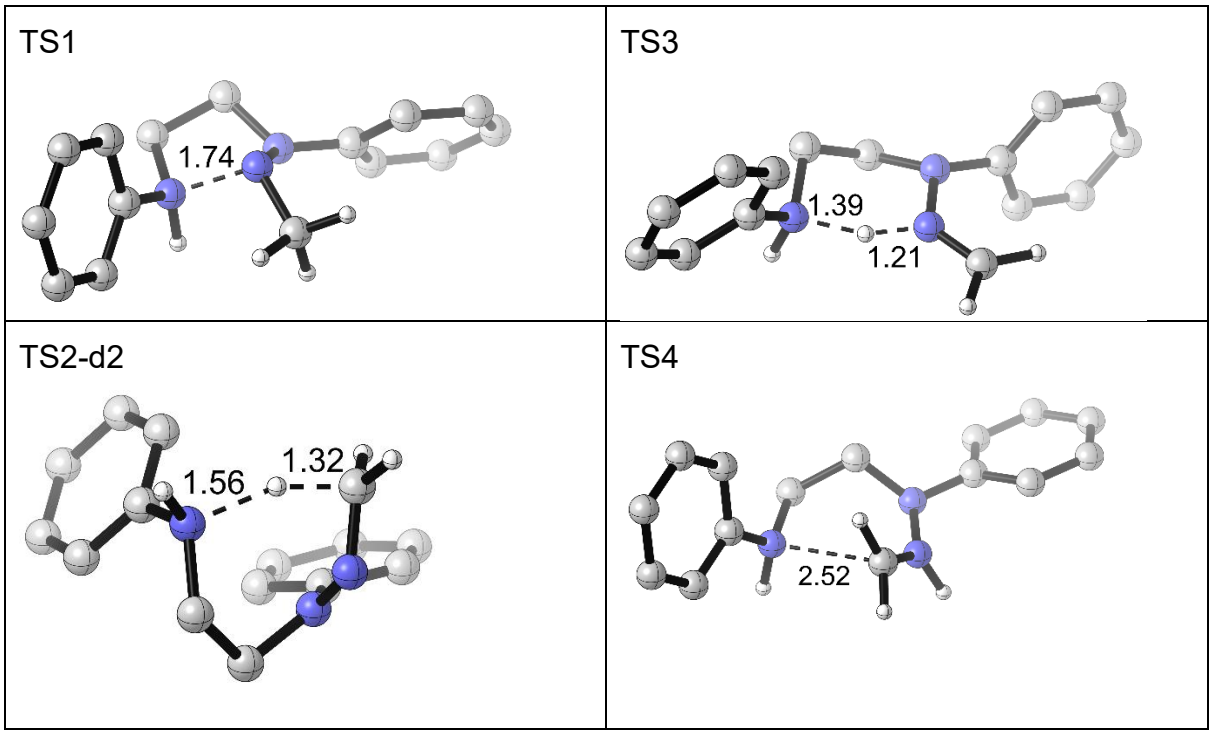
After the N-N cleavage, there should be deprotonation step. It can be either carboxylate assisted (*vide infra*) or it can happen within one molecule as red nitrogen atom has a lone pair. If we consider intramolecular reaction, two diastereomeric transition states TS2 are possible which correspond to each diastereomer of cation 6. As was described before, both TS1 should lead to 2nd diastereomer of cation 6, meaning that intramolecular reaction should go via TS2_d2. However, later we consider another diastereomer of TS2 (TS2_d1) as it can be formed in carboxylate assisted pathway.

The cation 7 formed can be stabilized by intramolecular hydrogen bonding, which facilitates proton transfer to give cation 9 (TS3). Rotation which breaks intramolecular H-bonding should enable cyclization via TS4. Final deprotonation of 10 gives product 11.

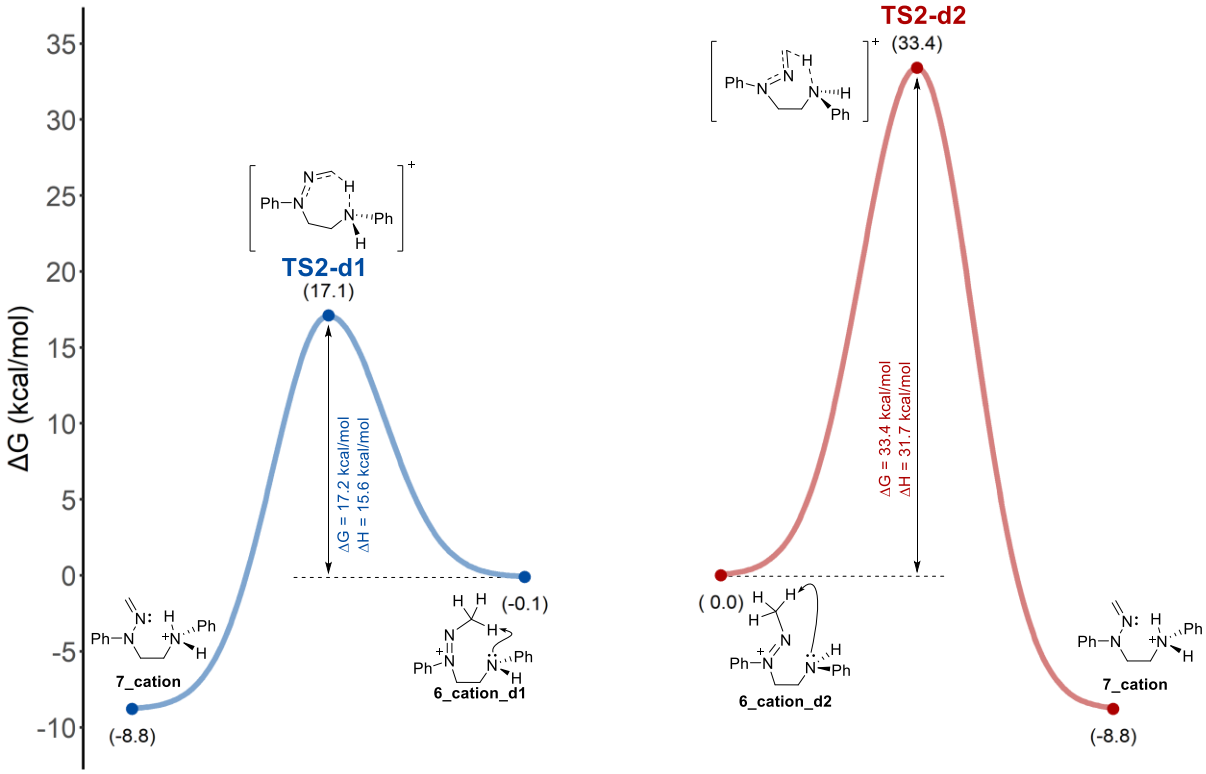


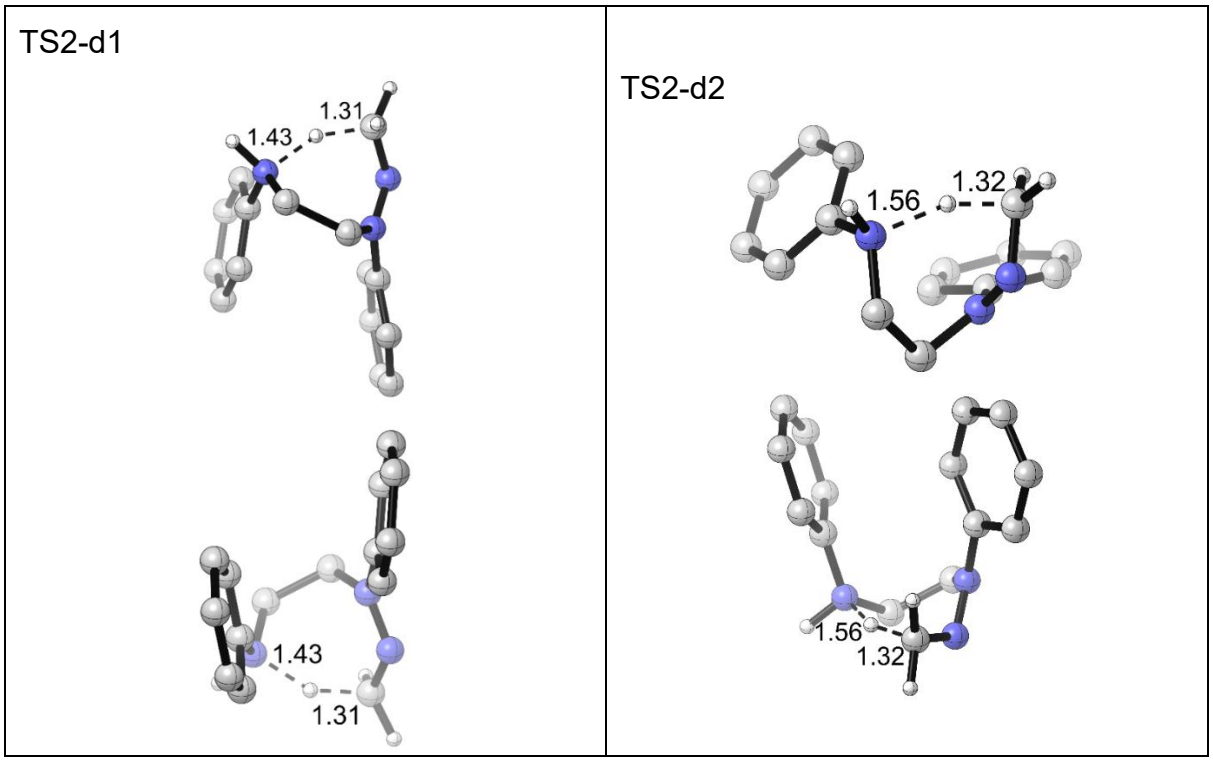
The overall calculated path is presented in the scheme below for the second diastereomer. All the energy barriers are surmountable under the reaction conditions used except TS2-d2.





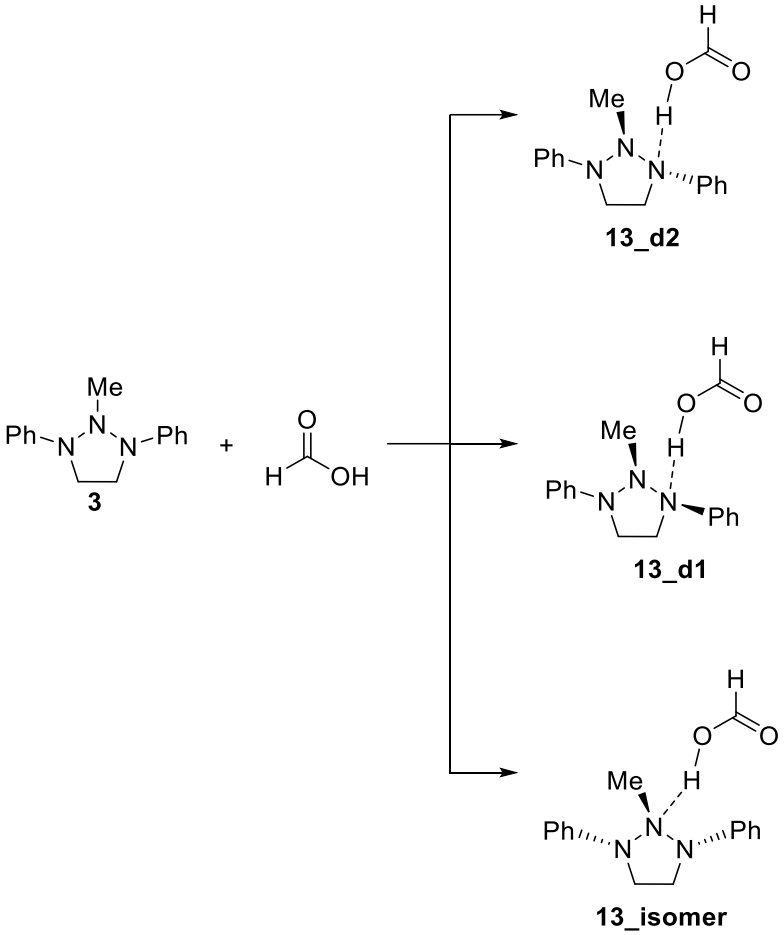
We calculated the second diastereomer of plausible TS2, which starts from 6-d1 (inaccessible in this version of the mechanism, see “contact ion pair model” section). Both diastereomers of cation 6 are similar in energy, thus, no big preference can be detected between two configurations of N=N bond in 6. Agreeably, TS2-d1 is a better option for the system due to less strain in it (compare the geometries of two TS2).





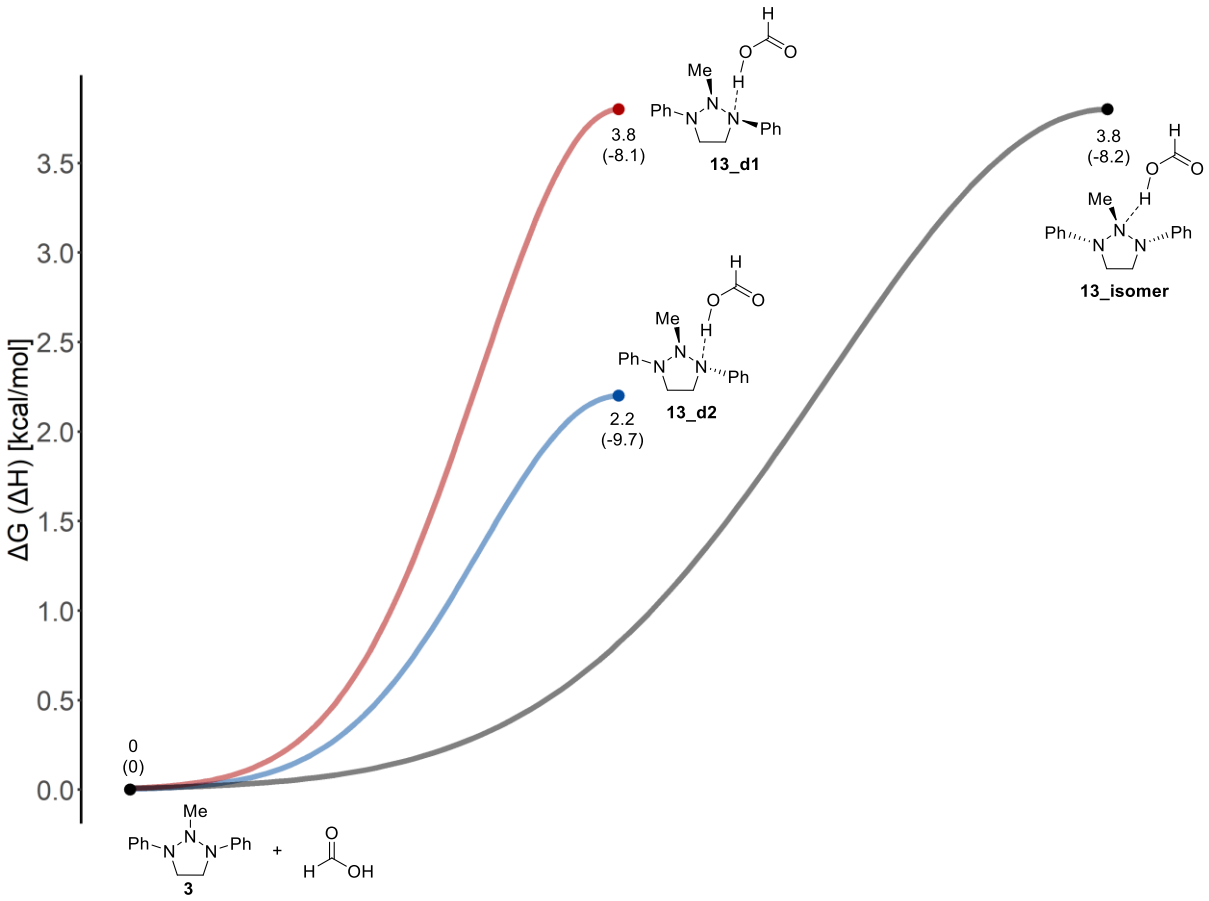
4.2.5 Discussion of the protonation step: contact ion pair

Next, we evaluated the possibility of the contact ion pair mechanism. Plausibly, coordination of formic acid can lead to three different diastereomeric ion pairs 13 as presented below.

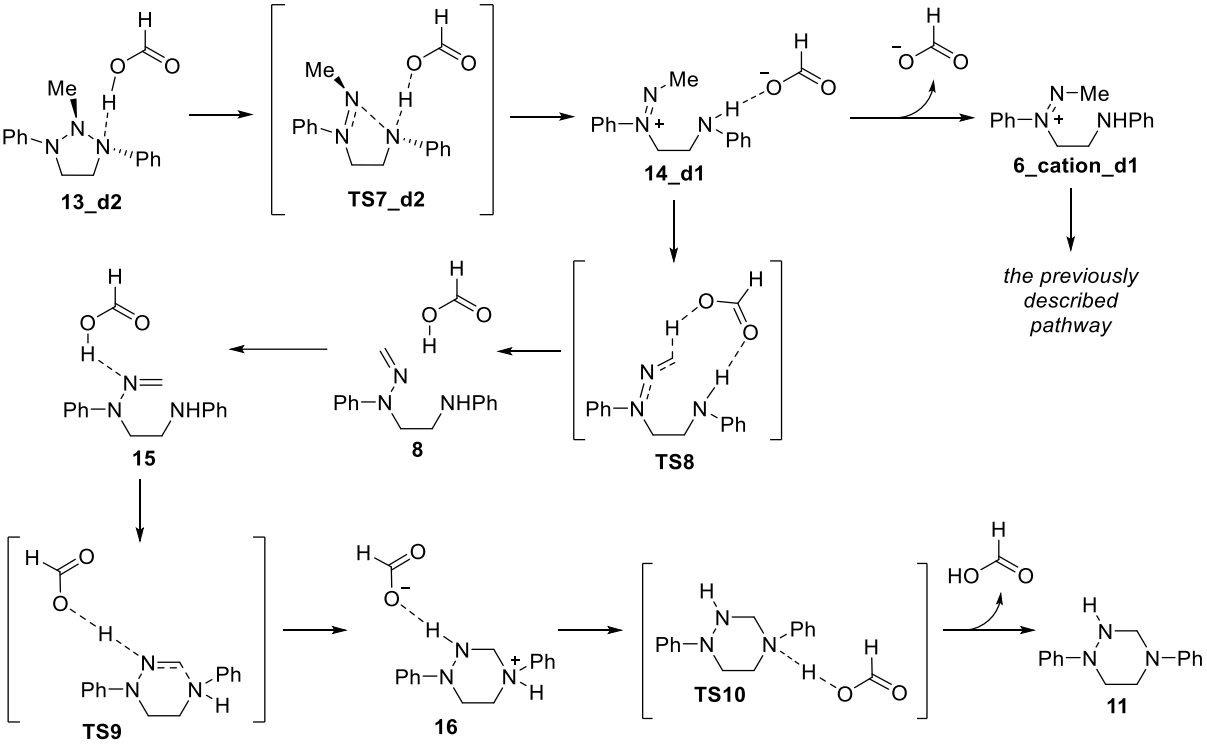


We compared thermodynamics of the three options, the results indicated that formation of H-bonding with side nitrogen is more favorable than that with the middle one. Moreover, if Ph and Me groups are trans to each other, more stable complex is formed similarly to the case with infinitely separated ion pair (see above).

Interestingly we did not observe any energetic barrier for the formation of such complexes (probably, due to implicit solvent model).

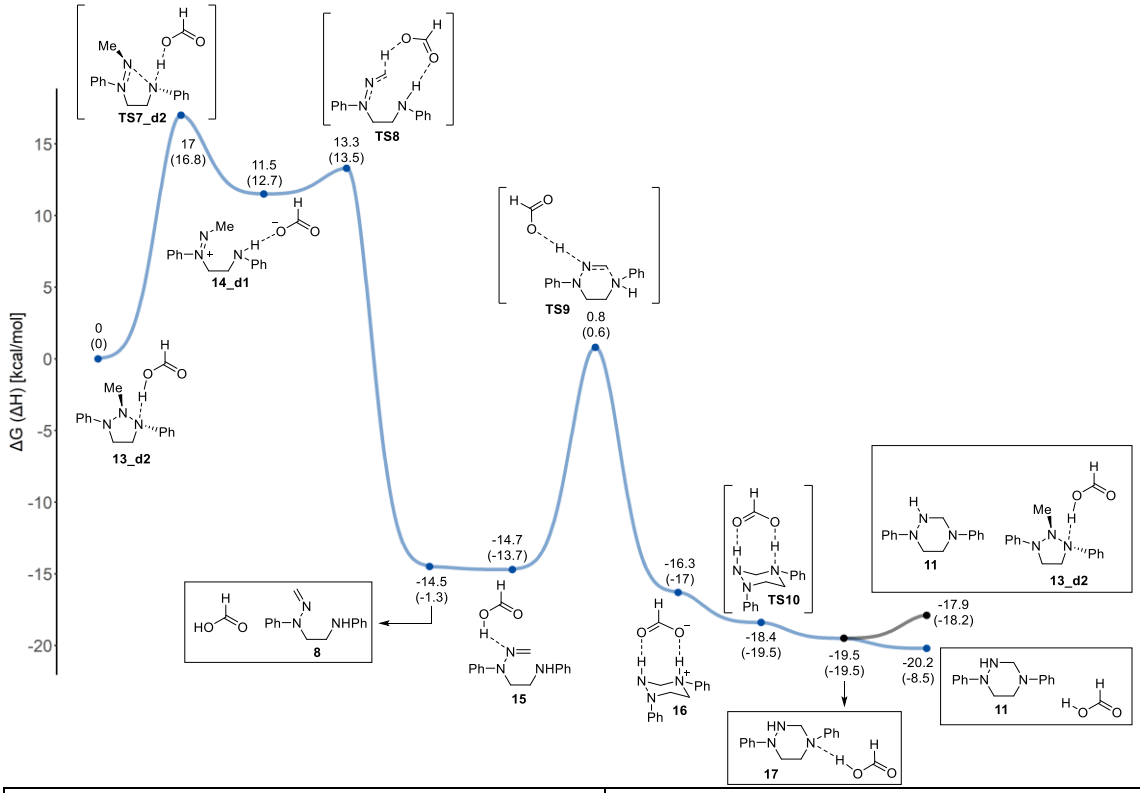


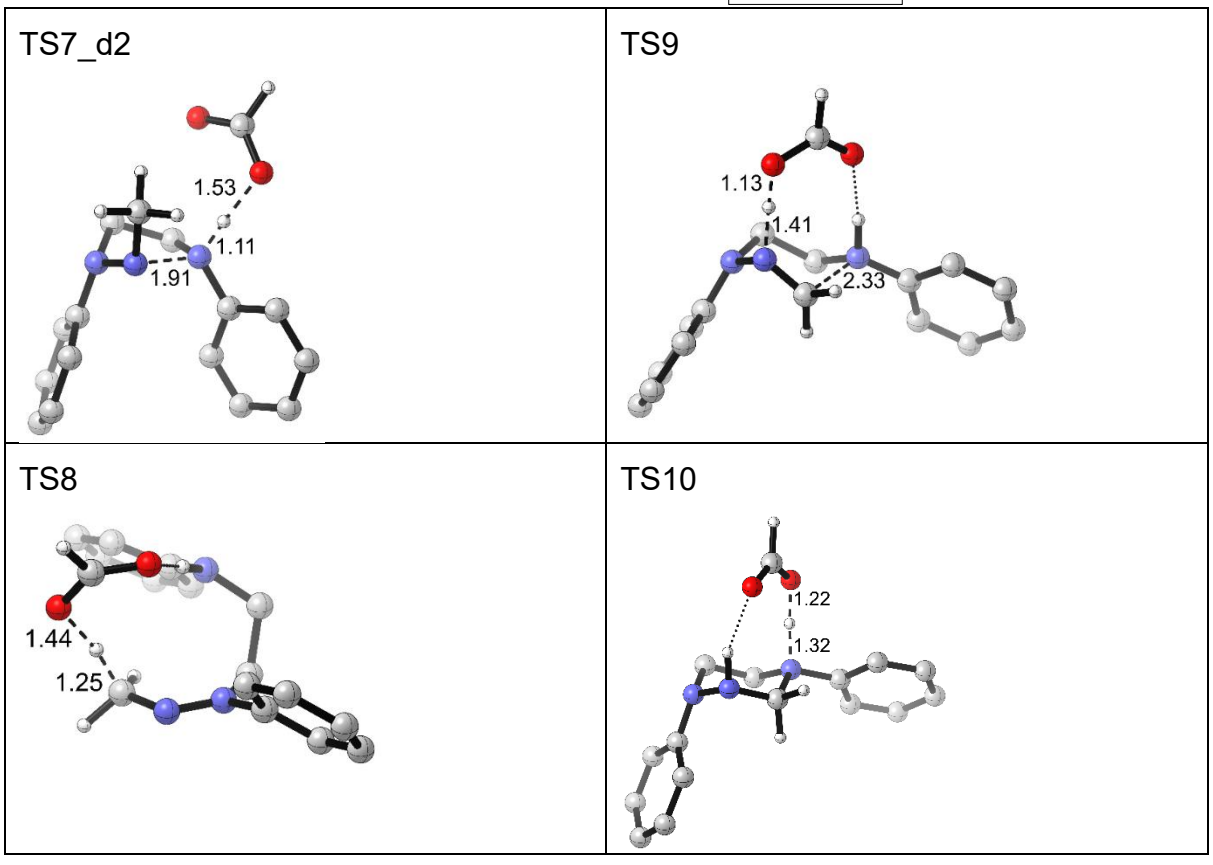
The overall mechanistic scheme should include the steps described below for the most stable diastereomer of compound 13_d2. First, N-N bond cleavage leads to compound 14_d1 via TS7_d2. Carboxylate anion can leave and liberate cation 6_d1 which can go to the final product by previously described reaction pathway (see section “fully separated ion pair”). Alternatively, carboxylate can assist in deprotonation (TS8) to generate formic acid and compound 8. Protonation of hydrazone nitrogen and cyclization via TS9 will lead to protonated product 16, which may be deprotonated and, thus, final 11 is generated.



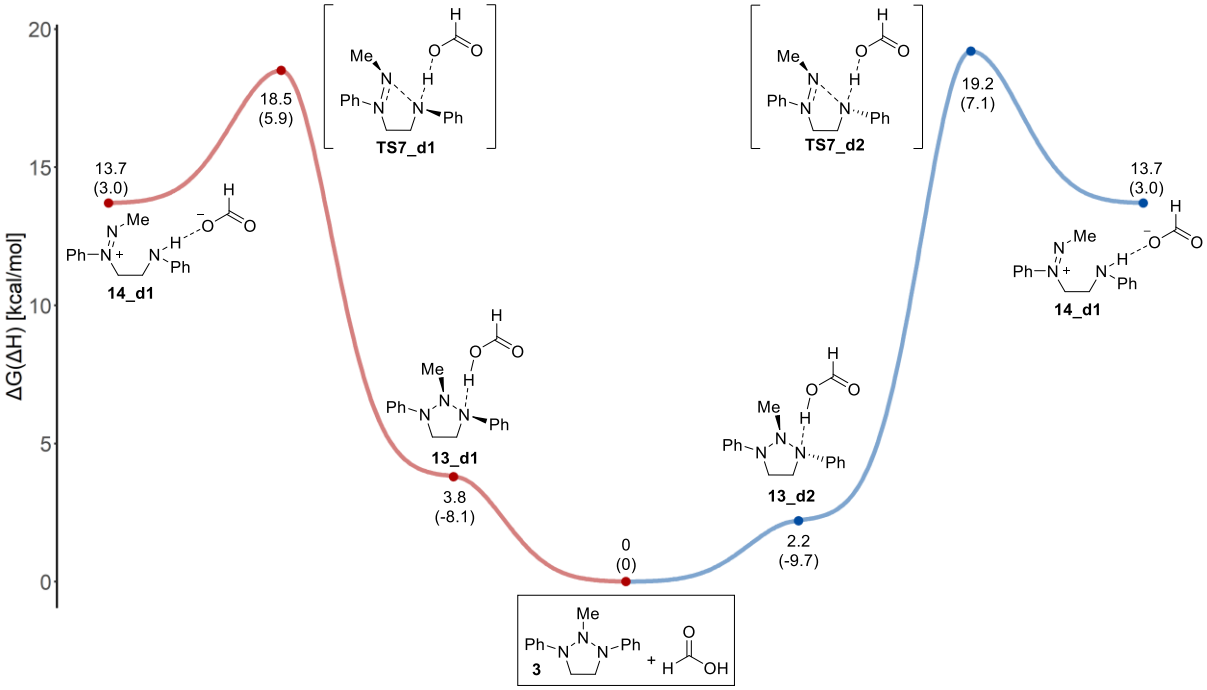
4.2.6 *Full reaction pathway*

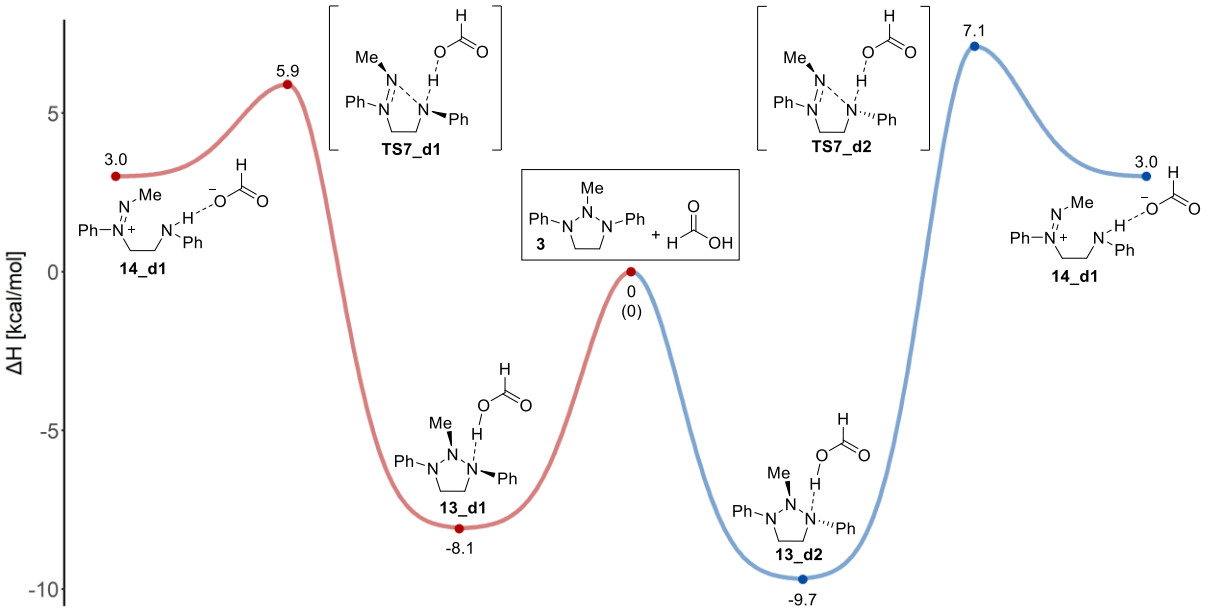
Full calculated reaction pathway is presented below.





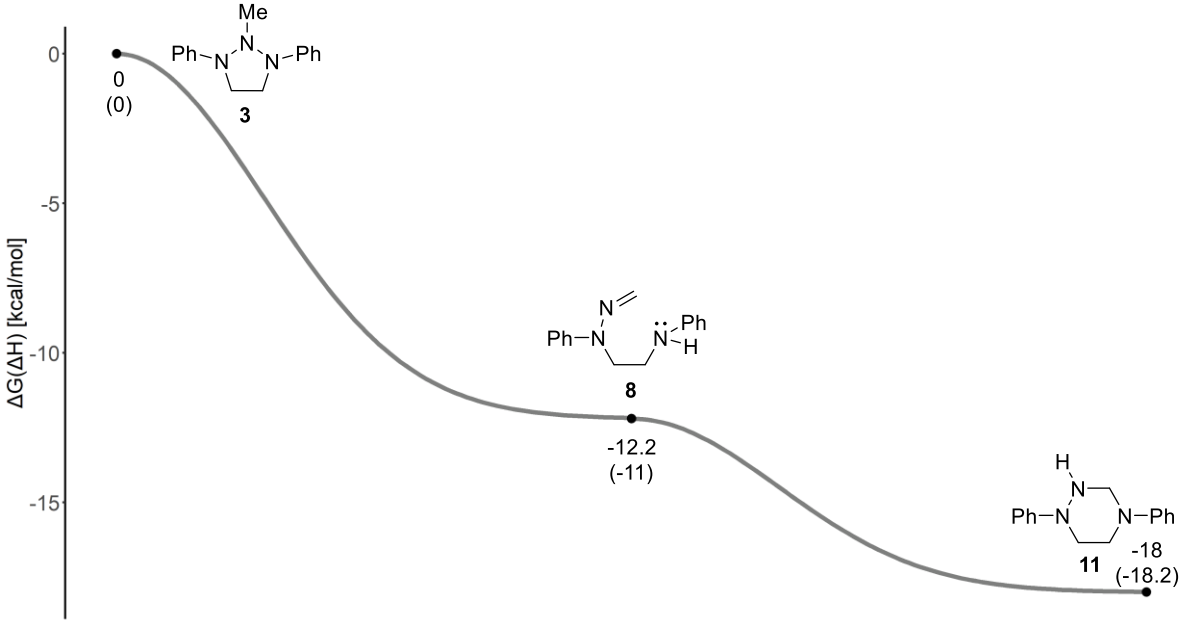
We computed the second diastereomeric TS7. Comparison of two pathways is presented below. Both seem to be feasible, and they lead to the same diastereomer of compound 14.



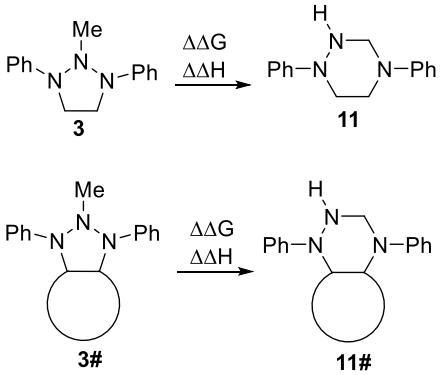


4.2.7 Calculation of reaction thermodynamics for different substrates

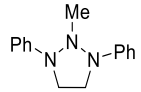
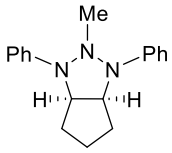
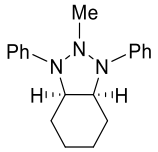
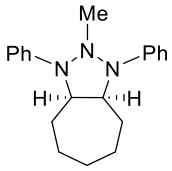
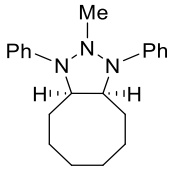
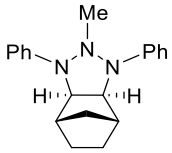
We calculated overall reaction thermodynamics for the transformation. The energy of the system should decrease if 3 converts to intermediate 8 followed by cyclization to 11.



Additionally, we evaluated the thermodynamics of the overall transformation for different ring sizes at the backbone of the molecule according to the equations below.

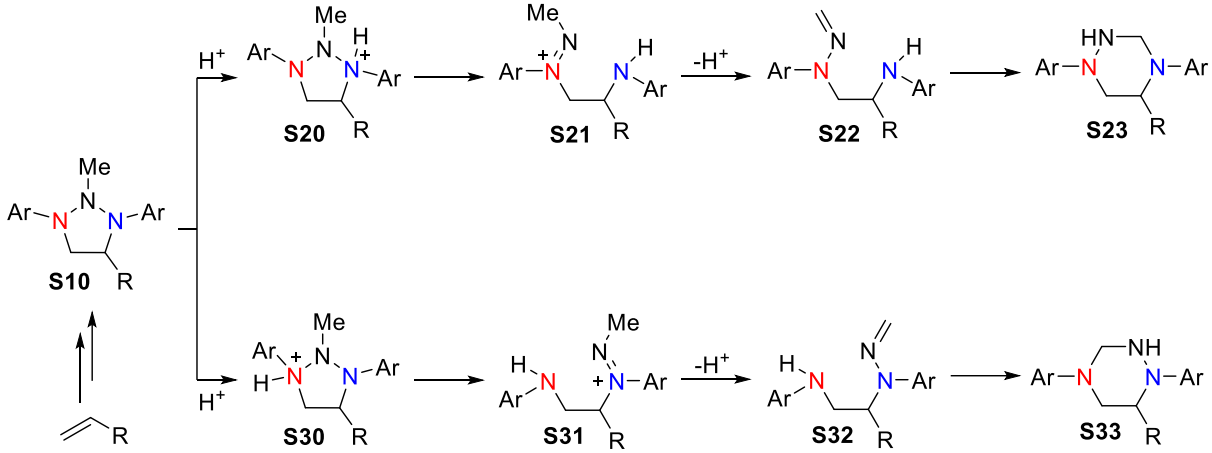


The results are presented in the table below. They indicate that the reaction is a favorable process in all cases.

Compound 3 or 3#	ΔΔG (kcal/mol)	ΔΔH (kcal/mol)
	-18.2	-18.2
	-18.2	-18.4
	-18.9	-19.1
	-18.8	-19.1
	-14.9	-15.2
	-14.5	-14.8

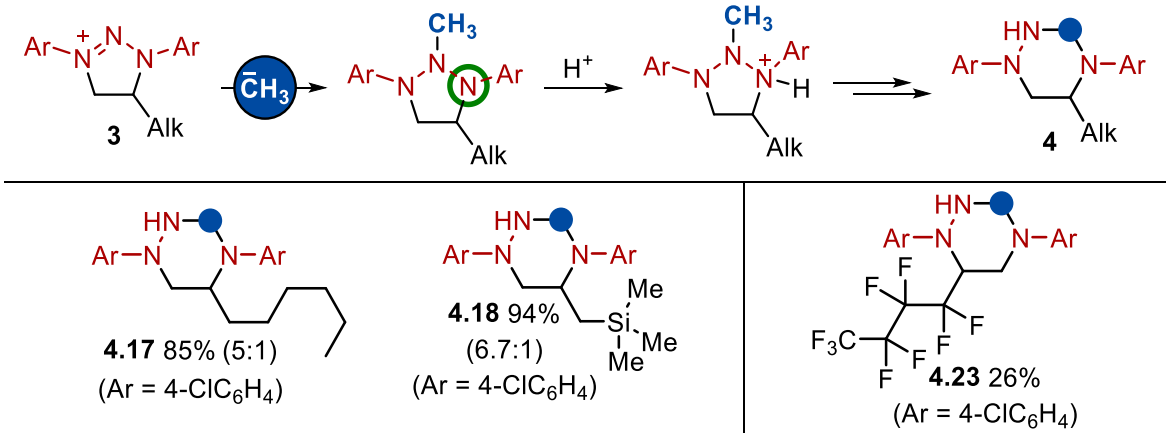
4.2.8 Discussion of protonation step with non-symmetrical substrates

In case of non-symmetrical alkenes, intermediate triazane **S10** will be non-symmetrical as well. This can possibly lead to formation of two protonated intermediates: **S20** if blue nitrogen is protonated in **S10**, or **S30** if red nitrogen is protonated in **S10** (acid is shown as H^+ for simplicity). Intermediate **S20** produces **S21** after N-N cleavage that upon deprotonation leads to **S22** which can cyclize to **S23**. The same applies to **S30** which produces **S33** via **S31** and **S32**. As can be seen from the energy profile of the full reaction pathway (see section "4.2.6 Full reaction pathway"), the selectivity determining step is likely the step from **S20** to **S21** or the step from **S30** to **S31** (since deprotonation step from **S21** to **S22** or from **S31** to **S32** should have lower energetic barrier while the reversed protonation from **S22** to **S21** or from **S32** to **S31** should have very high energetic barrier similarly to the energetic profile in section "4.2.6 Full reaction pathway").

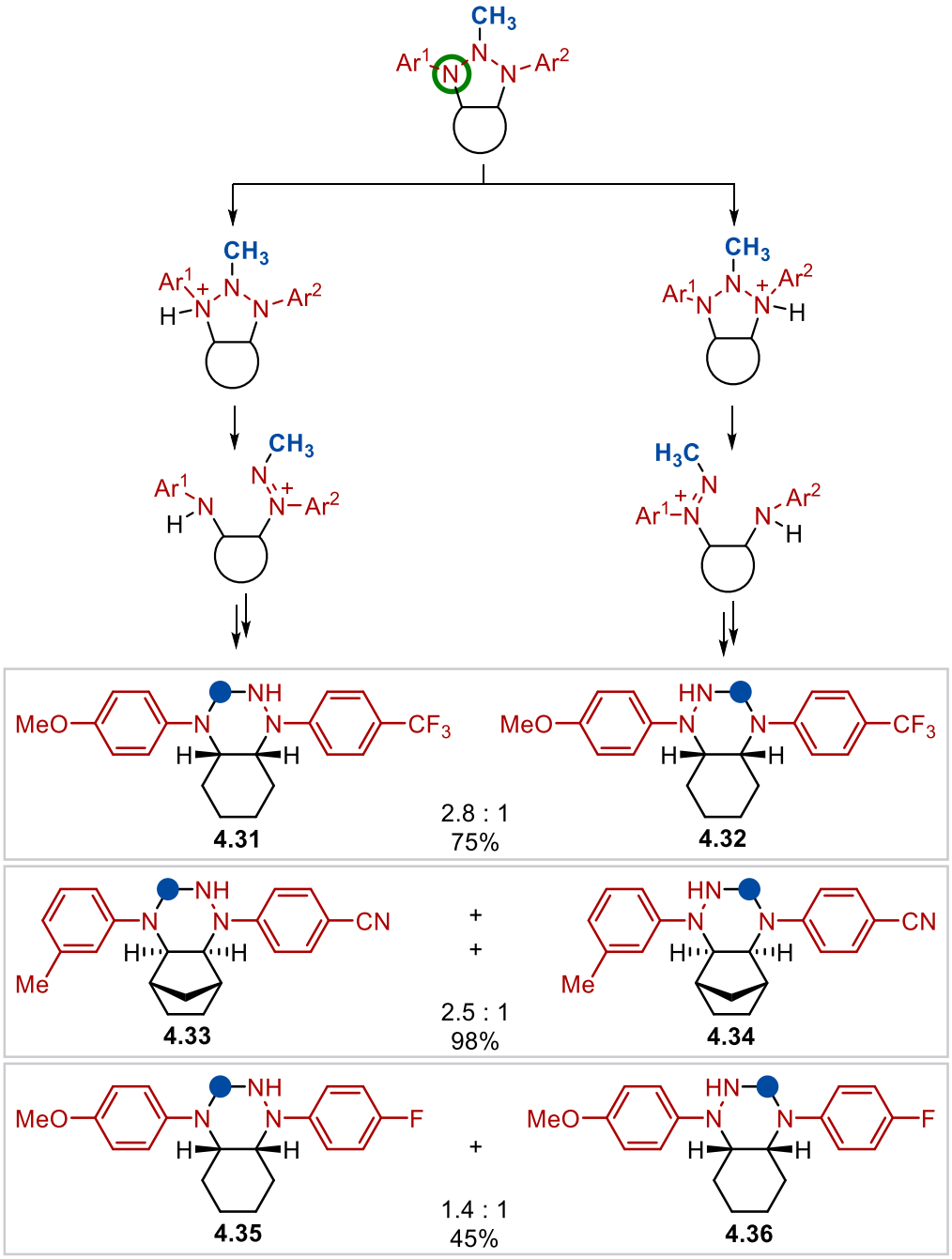


4.2.8.1 Selectivity towards **S23** above

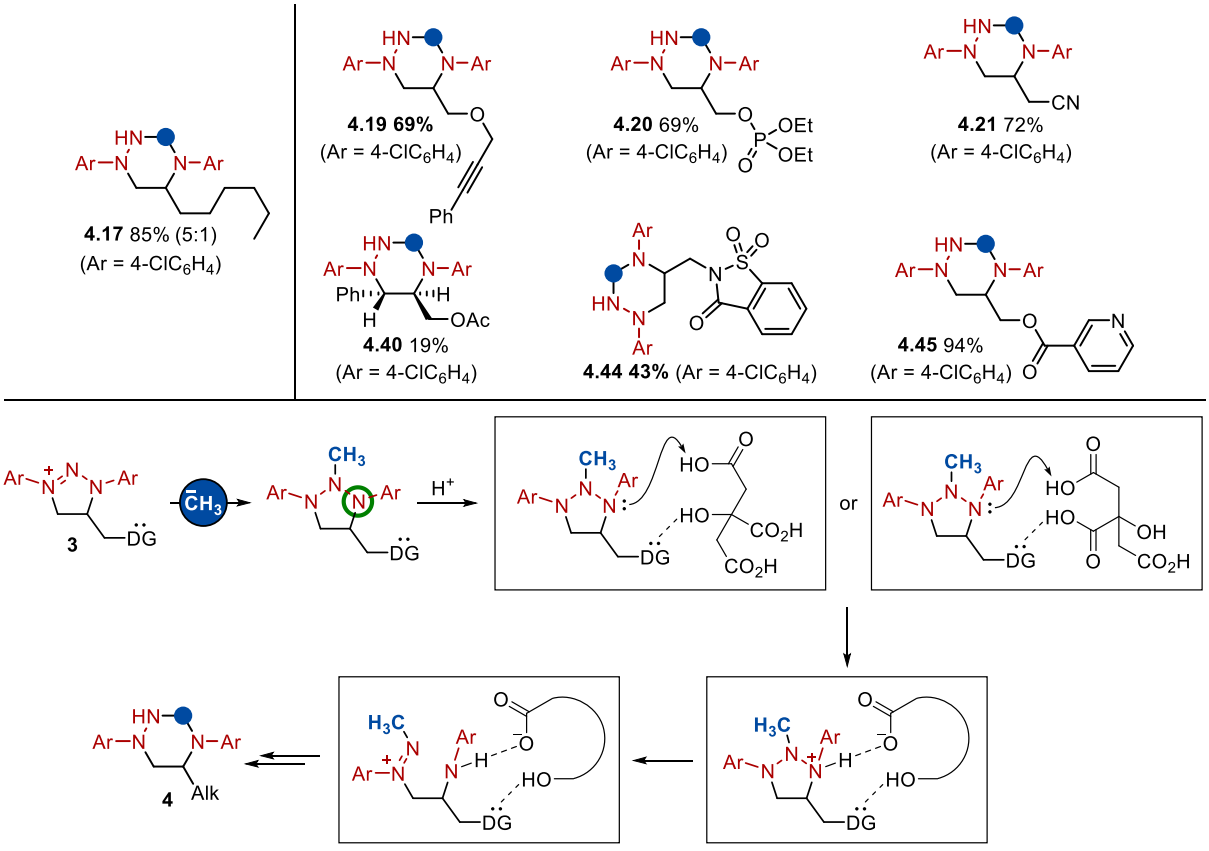
We assume that the first factor is basicity of nitrogen atoms. For instance, if the substrate **3** contains alkyl substituent, the product selectivity will be as the one shown on the picture below taking the mechanistic pathway like **S20**-**S23** sequence. The right nitrogen atom (highlighted in green) is likely to be more basic due to donation of electron density from alkyl substituent. Examples **4.17** and **4.18** provide good evidence of that, while perfluoroalkyl group gives the opposite selectivity in **4.23** supporting this hypothesis (since such an electron withdrawing group will decrease the basicity of the proximate nitrogen).



This theory is additionally confirmed by the following examples, where the "CH_2"-group inserted with a similar selectively into N-N bond. Starting triazene has two different aryl groups, while the alkene is symmetric and cyclic. Specifically, acid reacts preferably with nitrogen which has more electron donating aromatic substituent (Ar^1) highlighted in green. This produces the product **4** which has carbon inserted near this Ar^1 substituent (compare **4.31** vs **4.32** and other following examples).

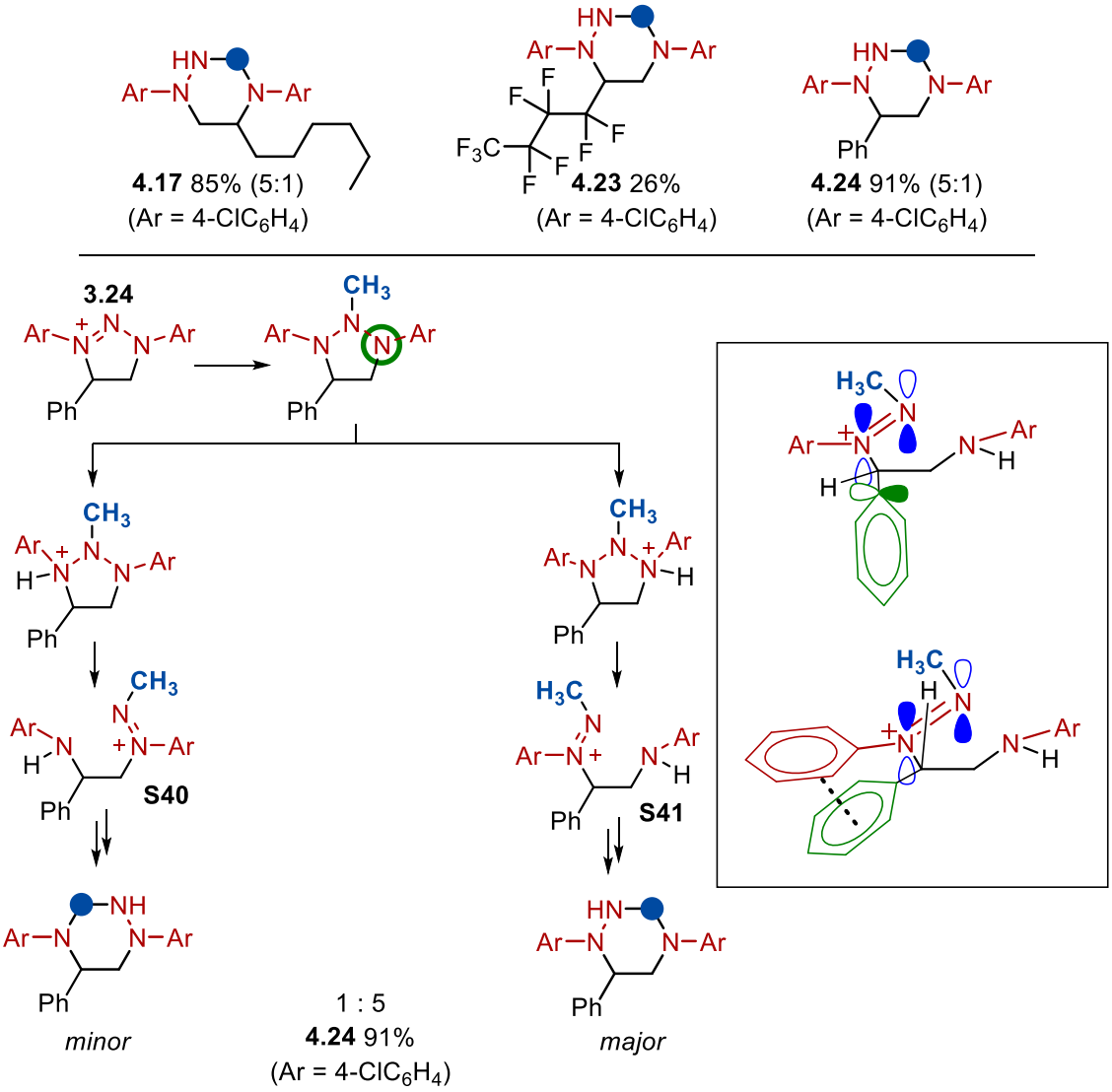


Interestingly, selectivity became exceptional when an inductive acceptor was introduced at the alkyl fragment (e.g., compare product **4.17** and **4.19-4.21**, **4.40**, **4.44**, **4.45**). We assume that in such instance hydrogen bonding may play a role during protonation step. Likely the nitrogen atom highlighted in green is protonated due to H-bonding in possible intermediate structures presented below where a lone pain in directing group DG coordinates one OH-bond of acid and the second one attacks the nitrogen. This should increase the selectivity of the reaction for the examples presented below.

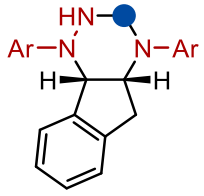


4.2.8.2 *Selectivity towards **S33***[above]

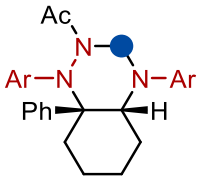
When a phenyl substituent is introduced to triazolinium cation (e.g. substrate **3.24**), selectivity changes to an opposite one like in **S33** (see scheme above and compare products **4.17** and **4.24**). Firstly, Ph-substituent should decrease the basicity of the proximate nitrogen atom (compare pKa of benzylammonium and butylammonium) and that should lead to protonation of the nitrogen highlighted in green in the scheme below (similarly to example **4.23** which gives similar selectivity). Moreover, intermediate **S41** should be stabilized by orbital overlap after N-N cleavage step comparatively to **S40**. Two examples of such stabilization is presented on the scheme: the top one highlights the possibility of orbital overlap similarly to neighboring group participation (green phenyl pi-electrons can overlap with LUMO localized on N-N), while another one suggest possible pi-pi stacking between green phenyl and red phenyl on nitrogen that is conjugated with LUMO localized on N-N. This stabilization can be similar in transition state of N-N cleavage which lowers the activation barrier of N-N cleavage step.



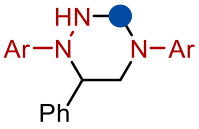
Likely, the same reasons conserve this selectivity (at least partially) throughout the following examples below as all of them have phenyl group in the same position in the final product.



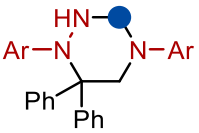
4.11 91%
(Ar = 4-ClC$_6$H$_4$)



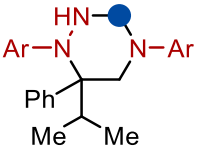
4.12 91% (5.1:1)
(Ar = 4-FC$_6$H$_4$)



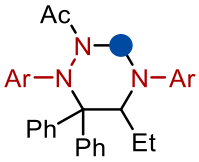
4.24 91% (5:1)
(Ar = 4-ClC$_6$H$_4$)



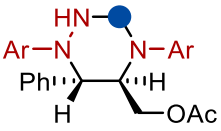
4.25 53%
(Ar = 4-ClC$_6$H$_4$)



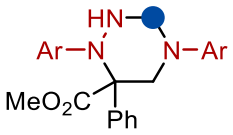
4.26 95%
(Ar = 4-FC$_6$H$_4$)



4.27 38%
(Ar = 4-FC$_6$H$_4$)

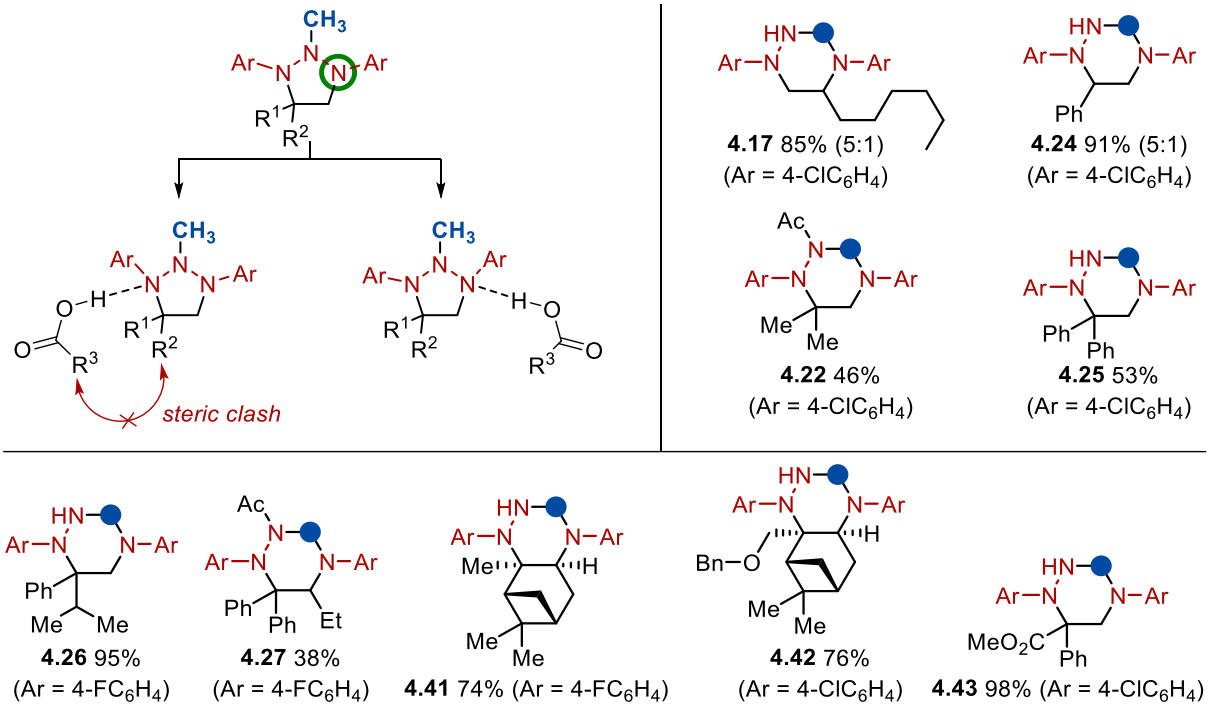


4.40 19%
(Ar = 4-ClC$_6$H$_4$)



4.43 98% (Ar = 4-ClC$_6$H$_4$)

Another reason for selectivity is likely a steric factor. As such, a contrast in reaction outcome is observed when we compare products **4.17** and **4.24**. Contrary, another pair **4.22** and **4.25** pronounces the same reaction selectivity, while **4.17** and **4.22** differ only by one extra alkyl substituent. We assume that there is a steric clash between R^1-R^2 on triazane and R^3 of the acid, which guides the acid to protonate the nitrogen highlighted in green. Likely, examples **4.26-4.27** and **4.41-4.43** have exceptional selectivity partially for this steric reason.



4.17 85% (5:1) (Ar = 4-ClC$_6$H$_4$)

4.24 91% (5:1) (Ar = 4-ClC$_6$H$_4$)

4.22 46% (Ar = 4-ClC$_6$H$_4$)

4.25 53% (Ar = 4-ClC$_6$H$_4$)

4.26 95% (Ar = 4-FC$_6$H$_4$)

4.27 38% (Ar = 4-FC$_6$H$_4$)

4.41 74% (Ar = 4-FC$_6$H$_4$)

4.42 76% (Ar = 4-ClC$_6$H$_4$)

4.43 98% (Ar = 4-ClC$_6$H$_4$)

4.2.8.3 Comparison of selectivity in miscellaneous examples

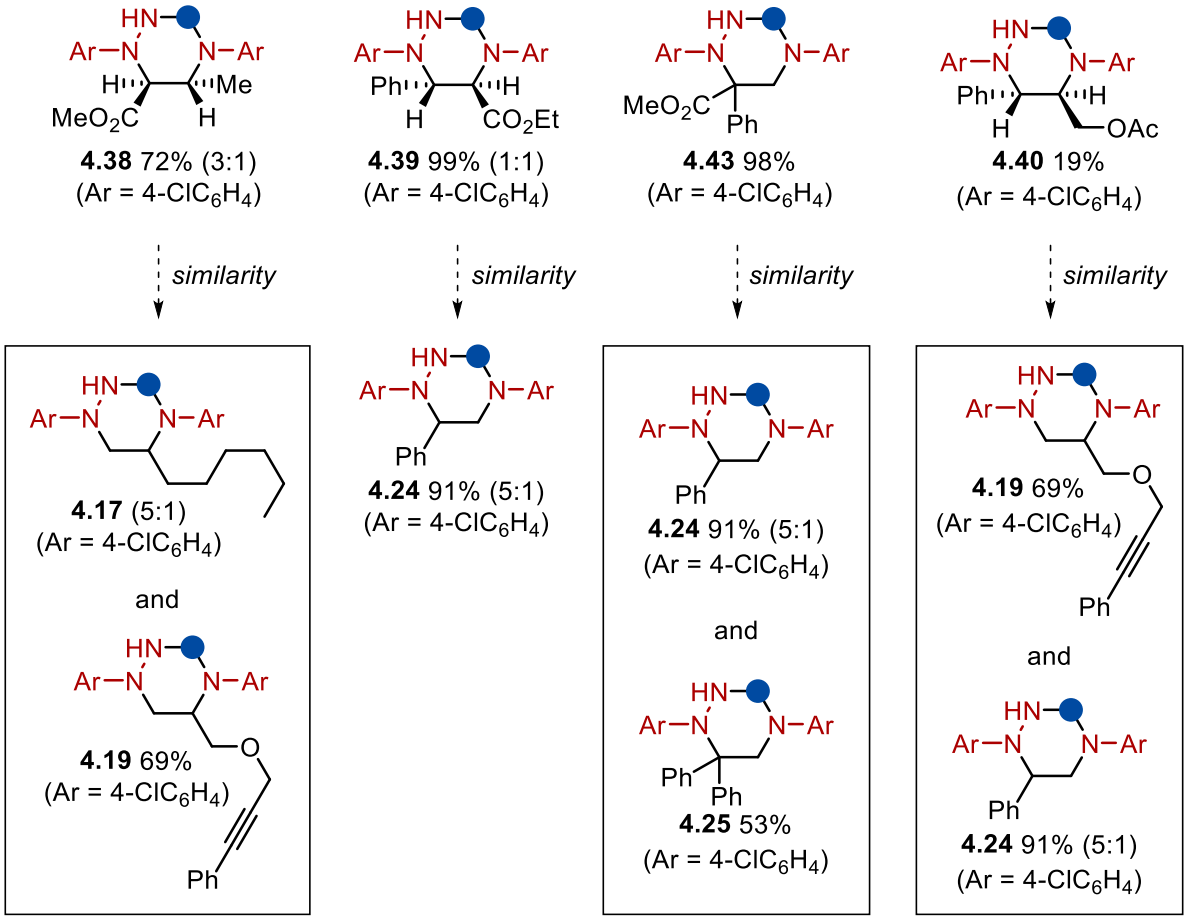
Based on the examples and conclusions made above, we aimed to rationalize more complex cases when several factors may play a role in selectivity determining step.

Product **4.38** is similar to **4.17** and the selectivity obtained can be based on basicity of the nitrogen atom. However, ratio of major/minor product is lower likely because ester group can coordinate with the acid similarly to **4.19** where a directing group may interact with the acid and thus favor the reaction in another direction.

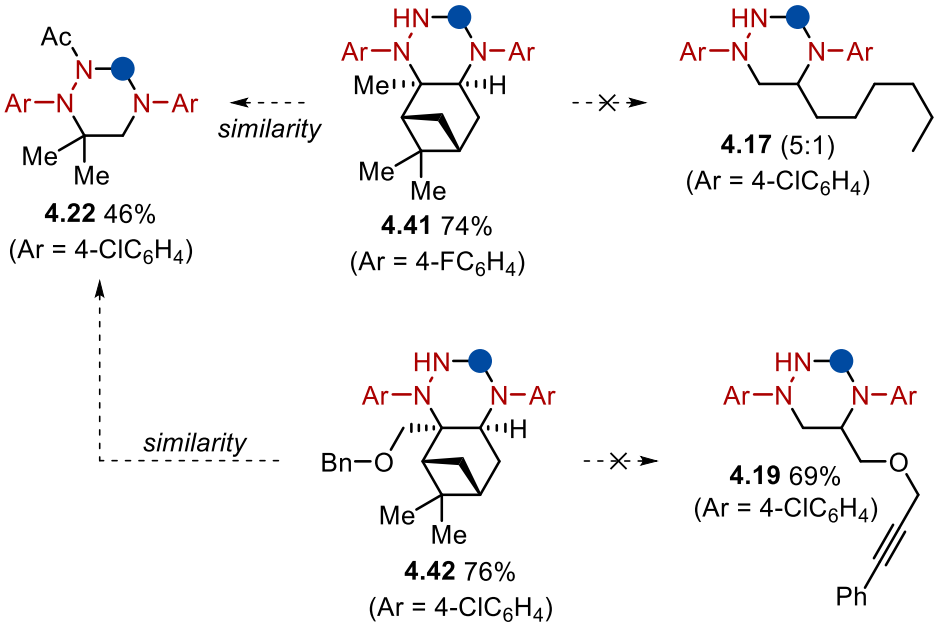
Product **4.39** has no preference in reaction selectivity. Plausibly, ester and aryl group both acts as inductive acceptors which leads to unselective reaction.

Interestingly, when both ester and aryl are present on the same carbon atom the selectivity is exceptional like in **4.43**. Probably, selectivity is governed by pi-pi stacking like in **4.24** and steric factor like in **4.25**. Both factors lead to the same reaction direction and, thus, the process is very selective.

Similar situation is observed in case of **4.40**. OAc-group aims the process similarly to **4.19**, while phenyl substituent directs the reaction to the same direction as it does in **4.24**. Both factors lead the reaction in the same direction and, thus, exceptional selectivity is observed.



When a trisubstituted alkene is utilized for the reaction (see products **4.41** and **4.42**), we observed the selectivity similar to the case of **4.22** where the steric factor likely played the major role (see 4.2.8.2above). We did not observe the similarity of reaction to **4.17**; moreover, when a benzyloxy group was introduced, reaction was not governed by the presence of this directing group like it was in **4.19**. This indicates that sterics overrides these two possibilities.



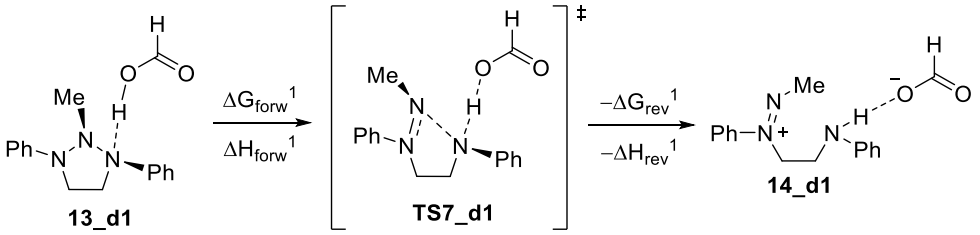
4.3 Additional Information

Computational Benchmark

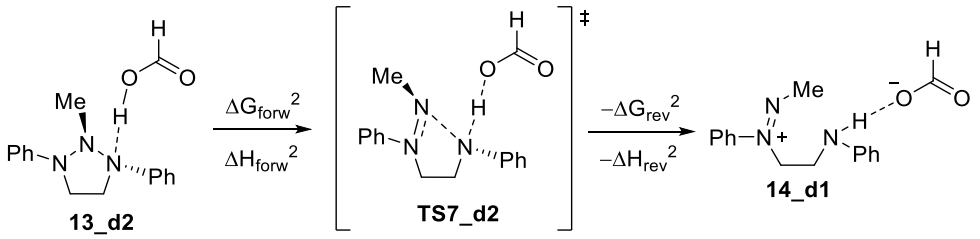
We tested various methods and basis sets for the reaction under investigation. The following four reactions were used for the method benchmarking.

Thermodynamic parameters are presented in Table sC2 for this reaction (ΔG and ΔH) as well as the energy difference between product and starting material of each reaction (ΔΔG = ΔG_{rev} - ΔG_{forw}; ΔΔH = ΔH_{rev} - ΔH_{forw}).

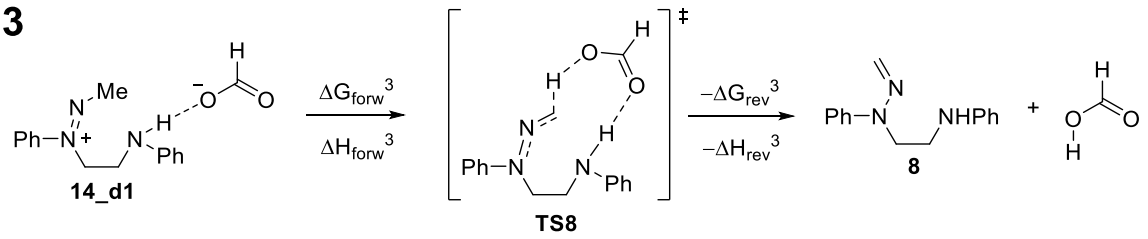
1



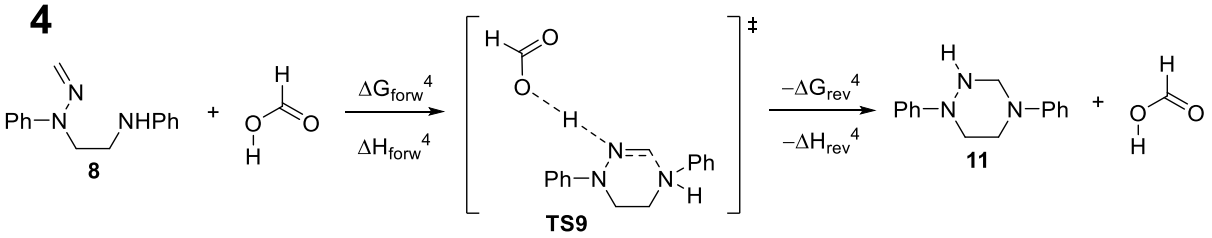
2



3

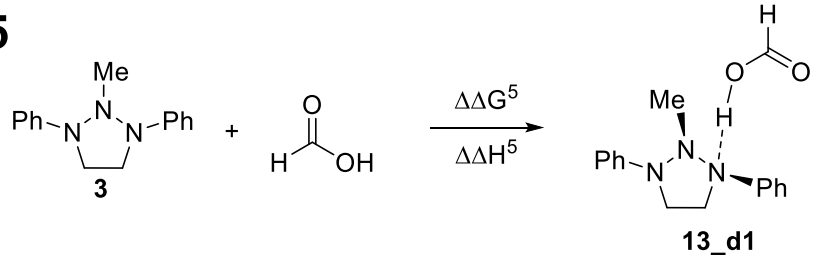


4



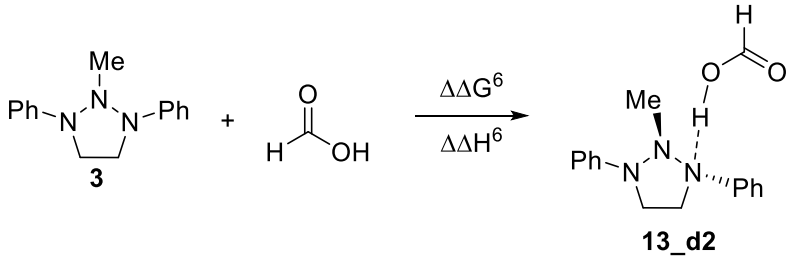
Additionally, we evaluated energy of complex 13 formation as presented on the scheme below.

5



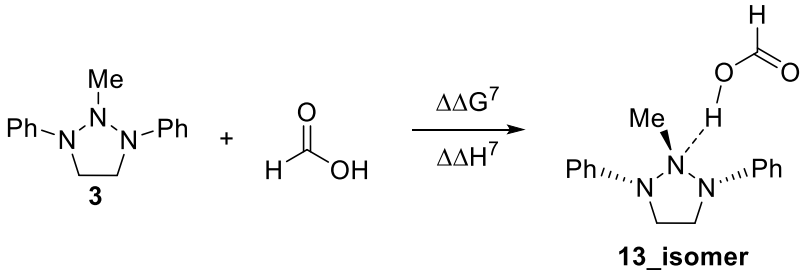
13_d1

6



13_d2

7



13_isomer

First we explored M1 method for optimization of both method (M1:m) and basis set (M1:b). Then we tested methods for single point calculation M2 for method (M2:m) and basis set (M2:b).

Results are presented for each set in the additional supplementary excel table attached (see supplementary archive, file “SI_calculations_benchmark.xlsx”).

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