Supplementary Information

An explanation about the use of (*S*)-citronelal as chiral derivatizing agent (CDA) in ^{1}H and ^{13}C NMR for *sec*-butylamine, methylbenzylamine, and amphetamine: a theoretical-experimental study

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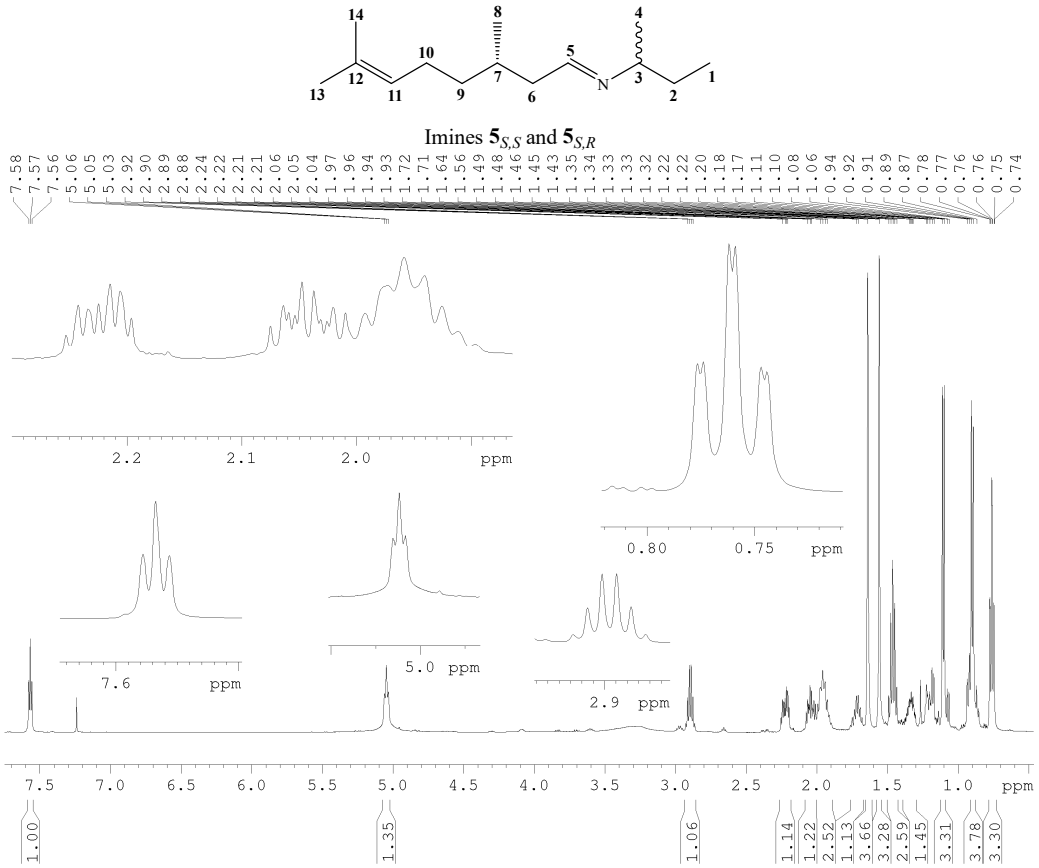


Figure S1. ^{1}H NMR spectrum of the *S,S* and *S,R* diastereoisomers derived from the reaction between (*S*)-citronellal and the racemic mixture of *sec*-butylamine (imines $\mathbf{5}_{S,S}$ and $\mathbf{5}_{S,R}$, $CDCl_3$, 500 MHz).

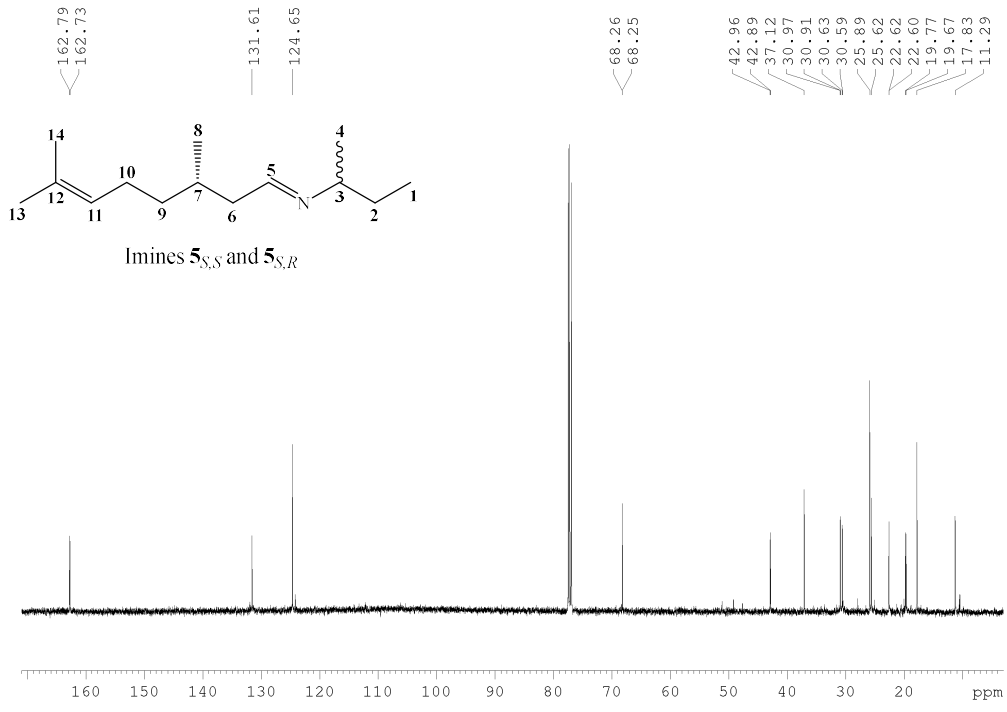


Figure S2. ^{13}C NMR spectrum of the *S,S* and *S,R* diastereoisomers derived from the reaction between (*S*)-citronellal and the racemic mixture of *sec*-butylamine (imines $\mathbf{5}_{S,S}$ and $\mathbf{5}_{S,R}$, $CDCl_3$, 500 MHz).

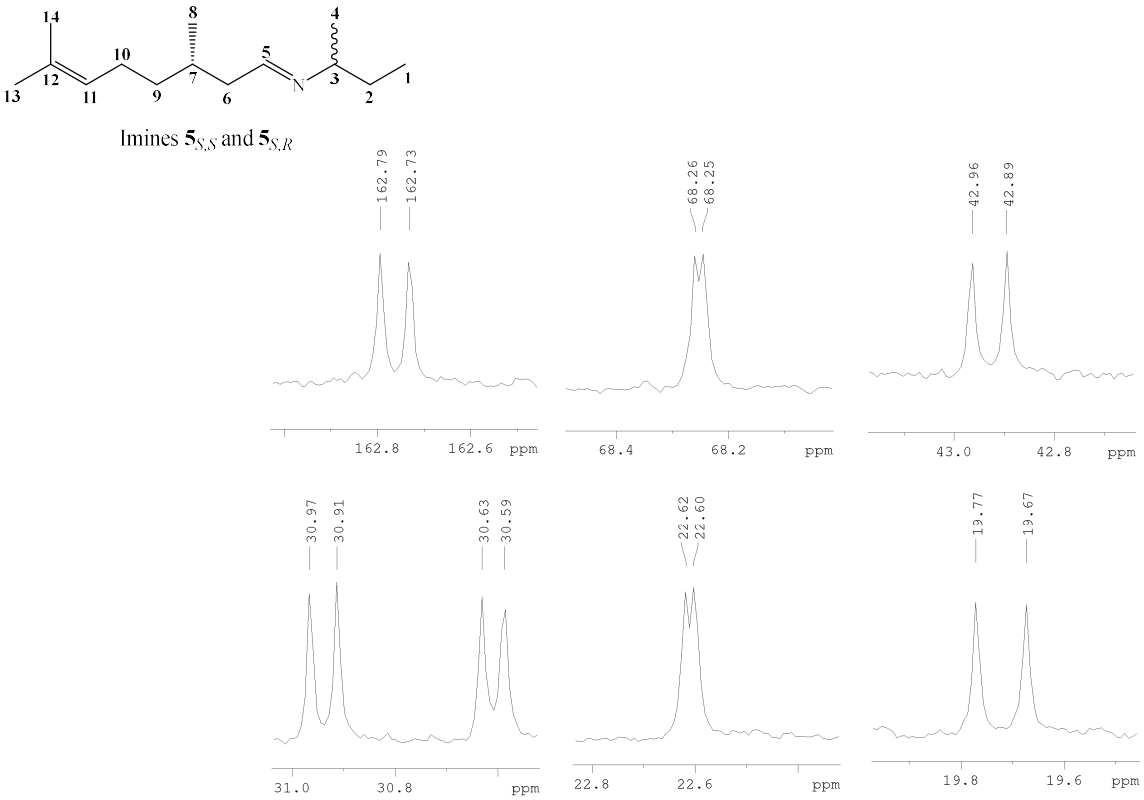
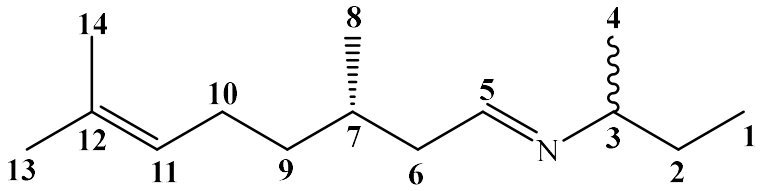


Figure S3. Expansion of ^{13}C NMR spectrum of the *S,S* and *S,R* diastereoisomers derived from the reaction between (*S*)-citronellal and the racemic mixture of *sec*-butylamine (imines $\mathbf{5}_{S,S}$ and $\mathbf{5}_{S,R}$, $CDCl_3$, 500 MHz).

Table S1. Spectroscopic data of the *S,S* and *S,R* diastereoisomers derived from the reaction between (*S*)-citronellal and the racemic mixture of *sec*-butylamine (imines **5***S,S* and **5***S,R*, $CDCl_3$, 500 MHz).



Imines $\mathbf{5}_{S,S}$ and $\mathbf{5}_{S,R}$

Number	δ_H (ppm)	Multiplicity	*J* (Hz)	δ_C (ppm)
1	0.76	2 triplets	7.4	(*S,R*) 11.29 and 11.25 (*S,S*)
2	1.46	Overlapping signals		(*S,R*) 30.63 and 30.59 (*S,S*)
3	2.90	Overlapping signals		(*S,R*) 68.26 and 68.25 (*S,S*)
4	1.10	Overlapping signals		(*S,S*) 22.62 and 22.60 (*S,R*)
5	7.57	Overlapping signals		(*S,R*) 162.79 and 162.73 (*S,S*)
6a	2.23	Overlapping signals		(*S,R*) 42.96 e 42.89 (*S,S*)
6b	2.05	Overlapping signals		
7	1.72	Overlapping signals		(*S,S*) 30.97 e 30.91 (*S,R*)
8	0.90	Overlapping signals		(*S,R*) 19.77 e 19.67 (*S,S*)
9a	1.33	Overlapping signals		37.12
9b	1.19	Overlapping signals		
10a	1.96	Overlapping signals		25.62
10b				
11	5.05	Overlapping signals		124.65
12	-	-	-	131.61
13	1.56	Overlapping signals		25.89
14	1.64	Overlapping signals		17.83

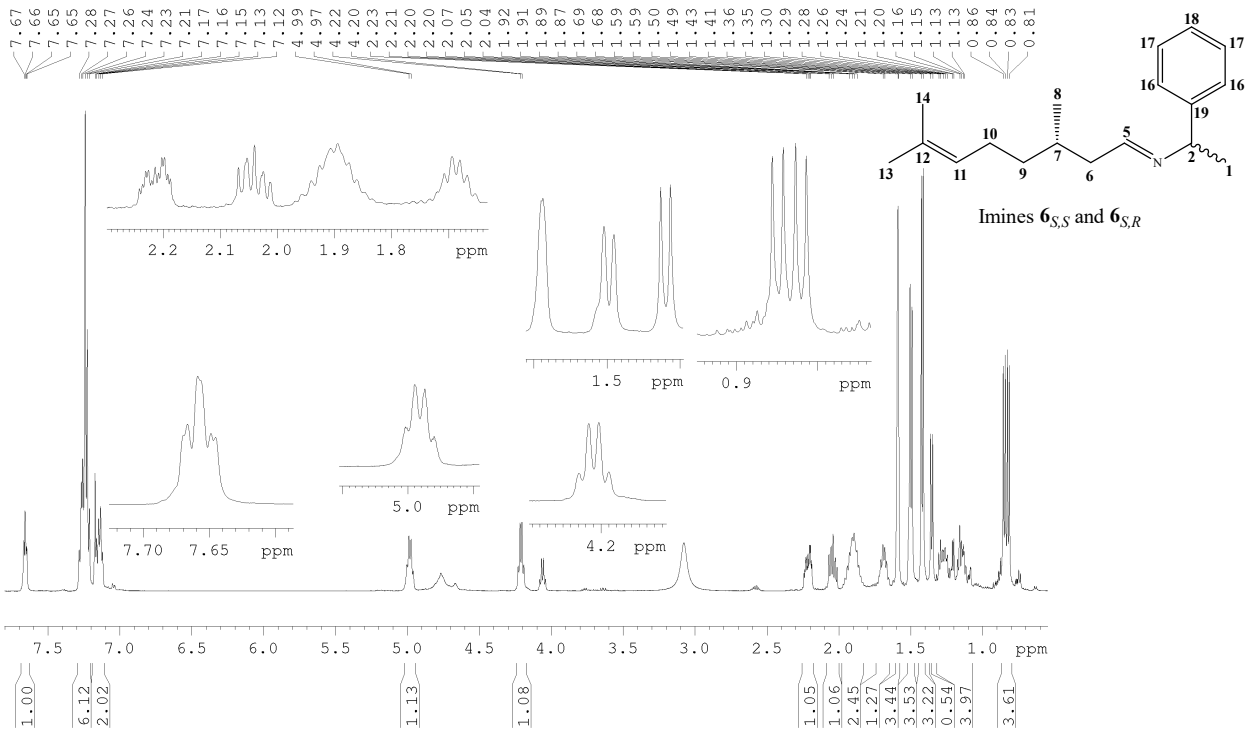


Figure S4. ^{1}H NMR spectrum of the S,S and S,R diastereoisomers derived from the reaction between (*S*)-citronellal and the racemic mixture of methylbenzylamine (imines $\mathbf{6}_{S,S}$ and $\mathbf{6}_{S,R}$, $CDCl_3$, 500 MHz).

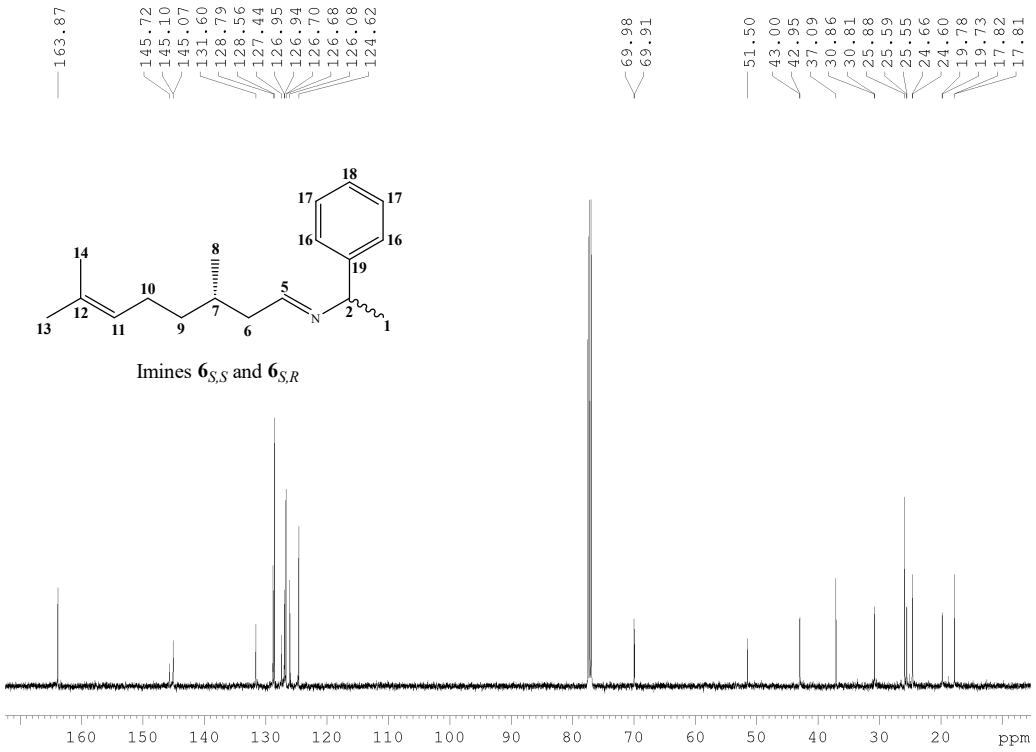


Figura S5. ^{13}C NMR spectrum of the *S,S* and *S,R* diastereoisomers derived from the reaction between (*S*)-citronellal and the racemic mixture of methylbenzylamine (imines **6*S,S*** and **6*S,R***, $CDCl_3$, 500 MHz).

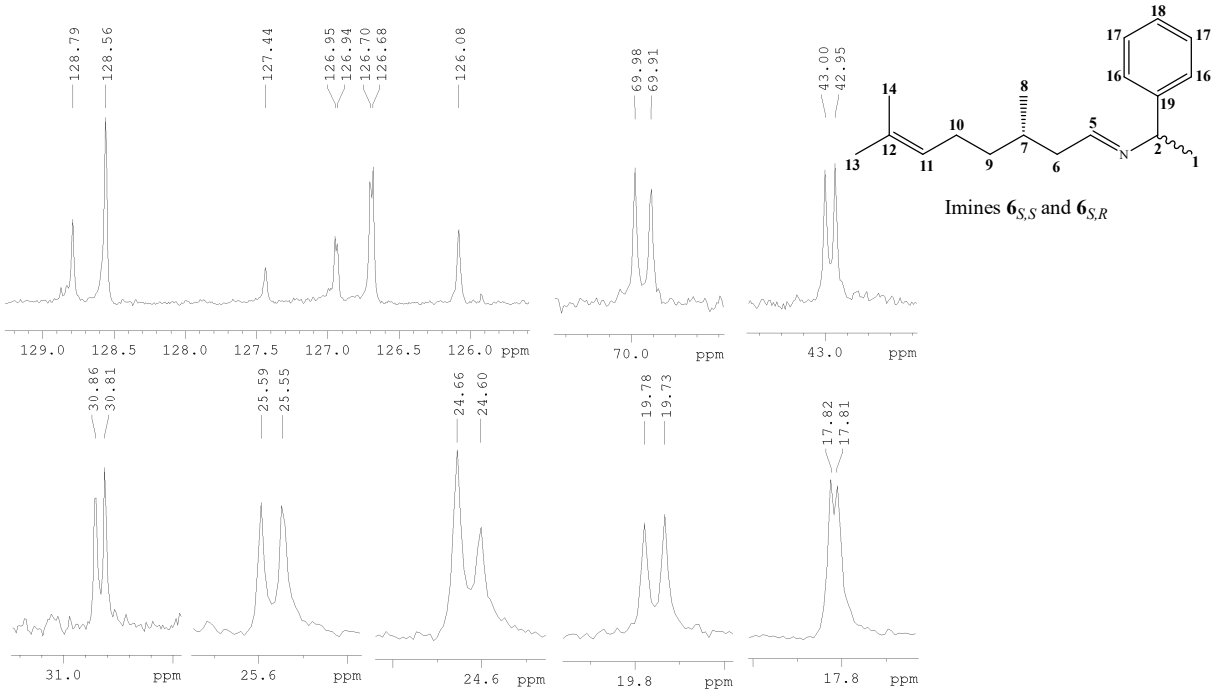
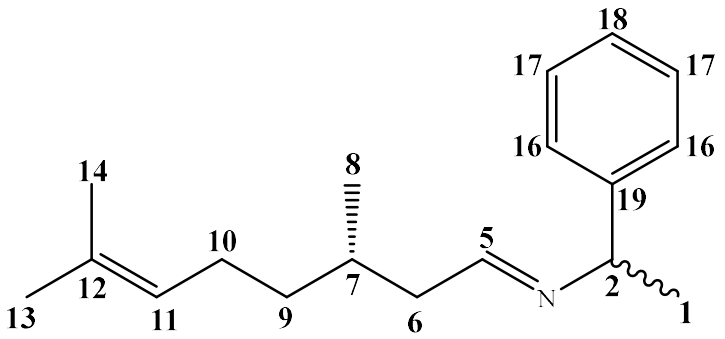


Figura S6. Expansions of ^{13}C NMR spectrum of the *S,S* and *S,R* diastereoisomers derived from the reaction between (*S*)-citronellal and the racemic mixture of methylbenzylamine (imines **6*S,S*** and **6*S,R***, $CDCl_3$, 500 MHz).

Table S2. Spectroscopic data of the S,S and S,R diastereoisomers derived from the reaction between (*S*)-citronellal and the racemic mixture of methylbenzylamine (imines **6*S,S*** and **6*S,R***, $CDCl_3$, 500 MHz).



Imines $\mathbf{6}_{S,S}$ and $\mathbf{6}_{S,R}$

Number	δ_H (ppm)	Multiplicity	*J* (Hz)	δ_C (ppm)
1	1.42	2 dublets	6.3	(*S,R*) 24.66 and 24.60 (*S,S*)
2	4.21	Overlapping signals		(*S,R*) 69.98 and 69.91 (*S,S*)
5	7.66	Overlapping signals		163,87
6a	2.21	Overlapping signals		(*S,S*) 43.00 and 42.95 (*S,R*)
6b	2.04	Overlapping signals		
7	1.69	Overlapping signals		(*S,S*) 30.86 and 30.81 (*S,R*)
8	0.84	2 dublets	6.7	(*S,S*) 19.78 and 19.73 (*S,R*)
9a	1.23	Overlapping signals		37.09
9b	1.13	Overlapping signals		
10a 10b	1.90	Overlapping signals		(*S,S*) 25.59 and 25.55 (*S,R*)
11	4.98	Overlapping signals		124.62
12	-	-	-	131.60
13	1.50	2 singlets	-	25.88
14	1.59	2 singlets	-	17.82 and 17.81
16				126.95 and 126.94
17	Overlapping signals 7.10 to 7.30 ppm			128.56
18				126.70 and 126.68
19	-	-	-	(*S,S*) 145.10 and 145.07 (*S,R*)

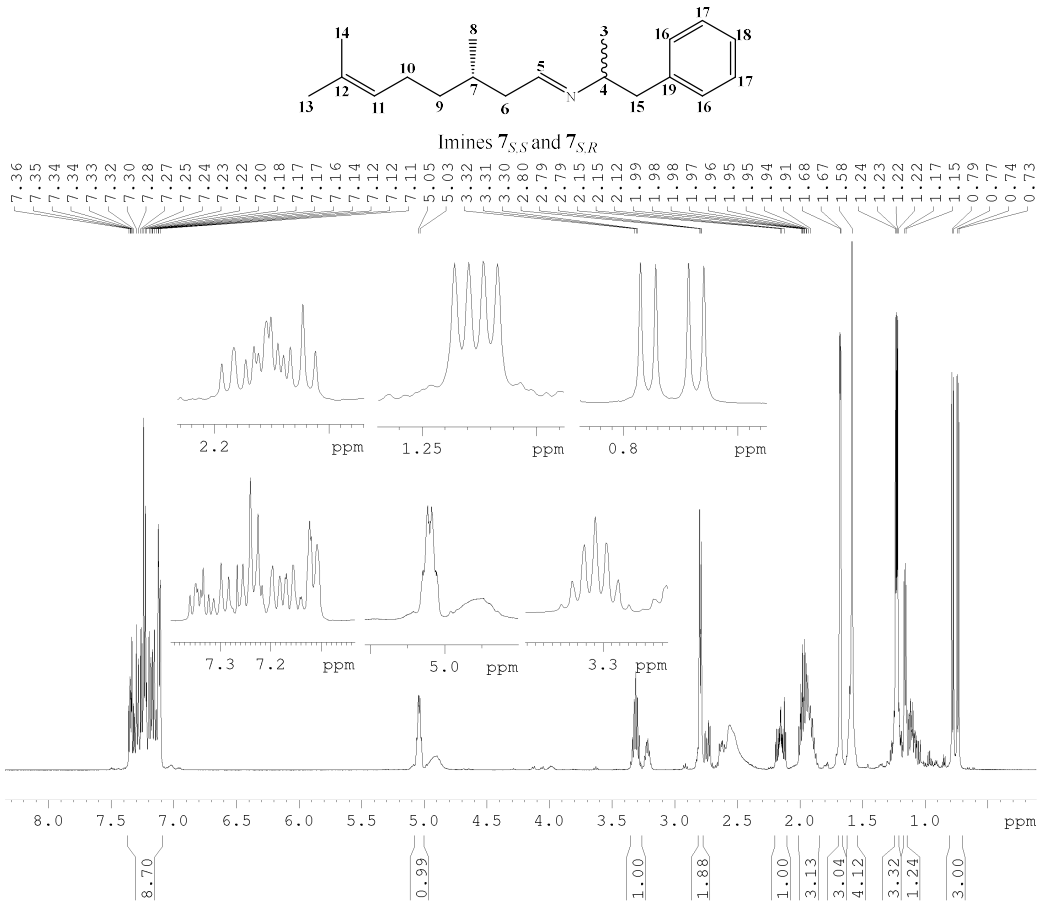


Figure S7. ^{1}H NMR spectrum of the S,S and S,R diastereoisomers derived from the reaction between (*S*)-citronellal and the racemic mixture of amphetamine (imines **7*S,S*** and **7*S,R***, $CDCl_3$, 500 MHz).

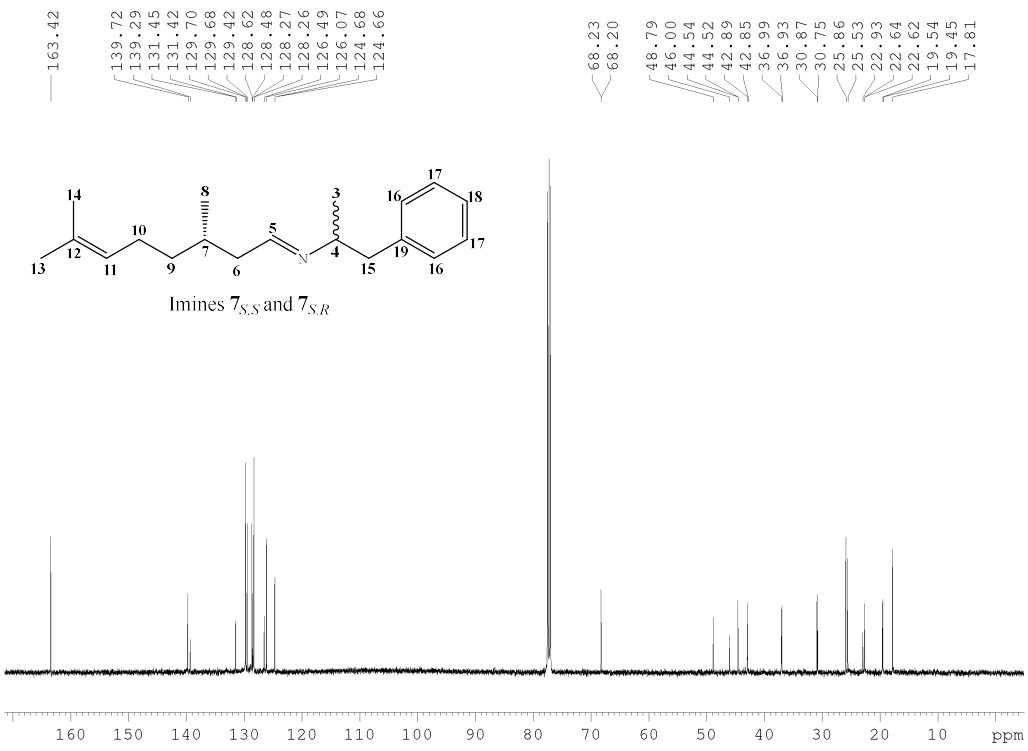


Figure S8. ^{13}C NMR spectrum of the *S,S* and *S,R* diastereoisomers derived from the reaction between (*S*)-citronellal and the racemic mixture of amphetamine (imines **7*S,S*** and **7*S,R***, $CDCl_3$, 500 MHz).

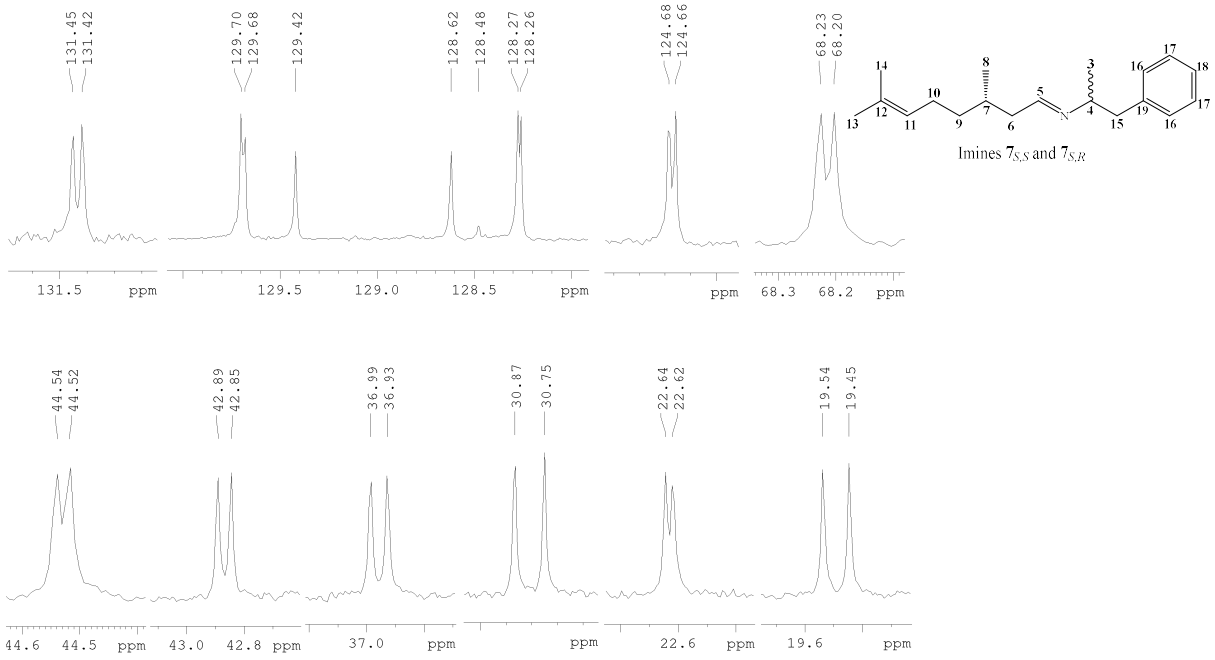
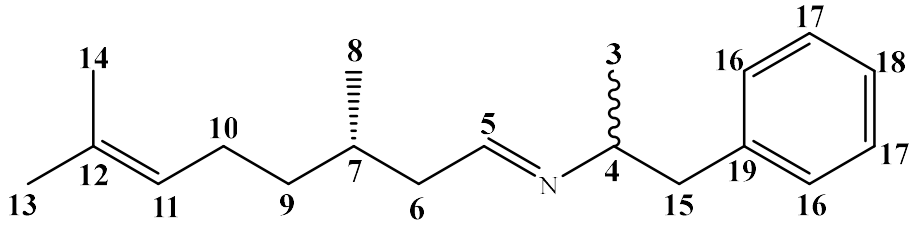


Figure S9. Expansions of ^{13}C NMR spectrum of the *S,S* and *S,R* diastereoisomers derived from the reaction between (*S*)-citronellal and the racemic mixture of amphetamine (imines **7*S,S*** and **7*S,R***, $CDCl_3$, 500 MHz).

Table S3. Spectroscopic data of the S,S and S,R diastereoisomers derived from the reaction between (*S*)-citronellal and the racemic mixture of amphetamine (imines **7*S,S*** and **7*S,R***, $CDCl_3$, 500 MHz).



Imines $7_{S,S}$ and $7_{S,R}$

Number	δ_H (ppm)	Multiplicity	*J* (Hz)	δ_C (ppm)
3	1.22	2 doublets	6.3	22.64 and 22.62
4	3.28	Overlapping signals		68.23 and 68.20
5	Overlapping with H16, H17 and H18			163.42
6a	2.15	Overlapping signals		42.89 and 42.85
6b	1.98	Overlapping signals		
7	1.60	Overlapping signals		30.87 and 30.75
8	0.75	2 doublets	6.6	19.54 and 19.45
9a	1.11	Overlapping signals		36.99 and 36.93
9b	1.25	Overlapping signals		
10a 10b	1.93	Overlapping signals		25.53
11	5.04	Overlapping signals		124.68 and 124.66
12	-	-	-	131.45 and 131.42
13	1.58	Overlapping signals		25.86
14	1.67	2 singlets	-	17.81
15a 15b	2.79	Overlapping signals		44.54 and 44.52
16				128.27 and 128.26
17	Overlapping with H5 7.1 to 7.4 ppm			129.70 and 129.68
18				126.07
19	-	-	-	139.72

Table S4. ΔEnergy (kcal/mol) and most stable conformers distribution of the diastereoisomer **5** (*S,S* and *S,R*) using B3LYP-D3(BJ)/def2-TZVP(-f) level

Conformer	ΔEnergy (kcal/mol)	Conformer	ΔEnergy (kcal/mol)
$5_{S,S}$.1	0.00	$5_{S,R}$.1	0.00
$5_{S,S}$.2	0.20	$5_{S,R}$.2	0.14
$5_{S,S}$.3	0.27	$5_{S,R}$.3	0.16
$5_{S,S}$.4	0.38	$5_{S,R}$.4	0.87
$5_{S,S}$.5	0.43	$5_{S,R}$.5	0.88
$5_{S,S}$.6	0.63	$5_{S,R}$.6	0.92
$5_{S,S}$.7	0.88	$5_{S,R}$.7	0.97
$5_{S,S}$.8	0.89	$5_{S,R}$.8	1.11
$5_{S,S}$.9	1.06		
$5_{S,S}$.10	1.13		
$5_{S,S}$.11	1.15		
$5_{S,S}$.12	1.16		
$5_{S,S}$.13	1.20		
$5_{S,S}$.14	1.25		
$5_{S,S}$.15	1.27		
$5_{S,S}$.16	1.38		
$5_{S,S}$.17	1.39		
$5_{S,S}$.18	1.47		
$5_{S,S}$.19	1.50		
$5_{S,S}$.20	1.61		
$5_{S,S}$.21	1.61		
$5_{S,S}$.22	1.64		
$5_{S,S}$.23	1.64		
$5_{S,S}$.24	1.65		
$5_{S,S}$.25	1.70		
$5_{S,S}$.26	1.71		
$5_{S,S}$.27	1.77		
$5_{S,S}$.28	1.81		

Table S5. ΔEnergy (kcal/mol) and most stable conformers distribution of the diastereoisomer **6** (*S,S* and *S,R*) using B3LYP-D3(BJ)/def2-TZVP(-f) level

Conformer	ΔEnergy kcal/mol)	Conformer	ΔEnergy (kcal/mol)
$6_{S,R}$.1	0.00	$6_{S,S}$.1	0.00
$6_{S,R}$.2	0.06	$6_{S,S}$.2	0.68
$6_{S,R}$.3	0.12	$6_{S,S}$.3	0.87
$6_{S,R}$.4	0.26	$6_{S,S}$.4	1.08
$6_{S,R}$.5	0.26	$6_{S,S}$.5	1.10
$6_{S,R}$.6	0.59	$6_{S,S}$.6	1.33
$6_{S,R}$.7	0.84	$6_{S,S}$.7	1.43
$6_{S,R}$.8	0.93		
$6_{S,R}$.9	0.95		
$6_{S,R}$.10	0.99		
$6_{S,R}$.11	1.12		
$6_{S,R}$.12	1.15		
$6_{S,R}$.13	1.15		
$6_{S,R}$.14	1.26		
$6_{S,R}$.15	1.29		
$6_{S,R}$.16	1.34		
$6_{S,R}$.17	1.40		
$6_{S,R}$.18	1.41		
$6_{S,R}$.19	1.41		
$6_{S,R}$.20	1.50		

Table S6. ΔEnergy (kcal/mol) and most stable conformers distribution of the diastereoisomer **7** (*S,S* and *S,R*) using B3LYP-D3(BJ)/def2-TZVP(-f) level

Conformer	ΔEnergy (kcal/mol)	Conformer	ΔEnergy (kcal/mol)
$7_{S,S}$.1	0.00	$7_{S,R}$.1	0.00
$7_{S,S}$.2	0.00	$7_{S,R}$.2	0.77
$7_{S,S}$.3	0.59		
$7_{S,S}$.4	0.80		
$7_{S,S}$.5	0.91		
$7_{S,S}$.6	0.92		
$7_{S,S}$.7	1.02		
$7_{S,S}$.8	1.10		

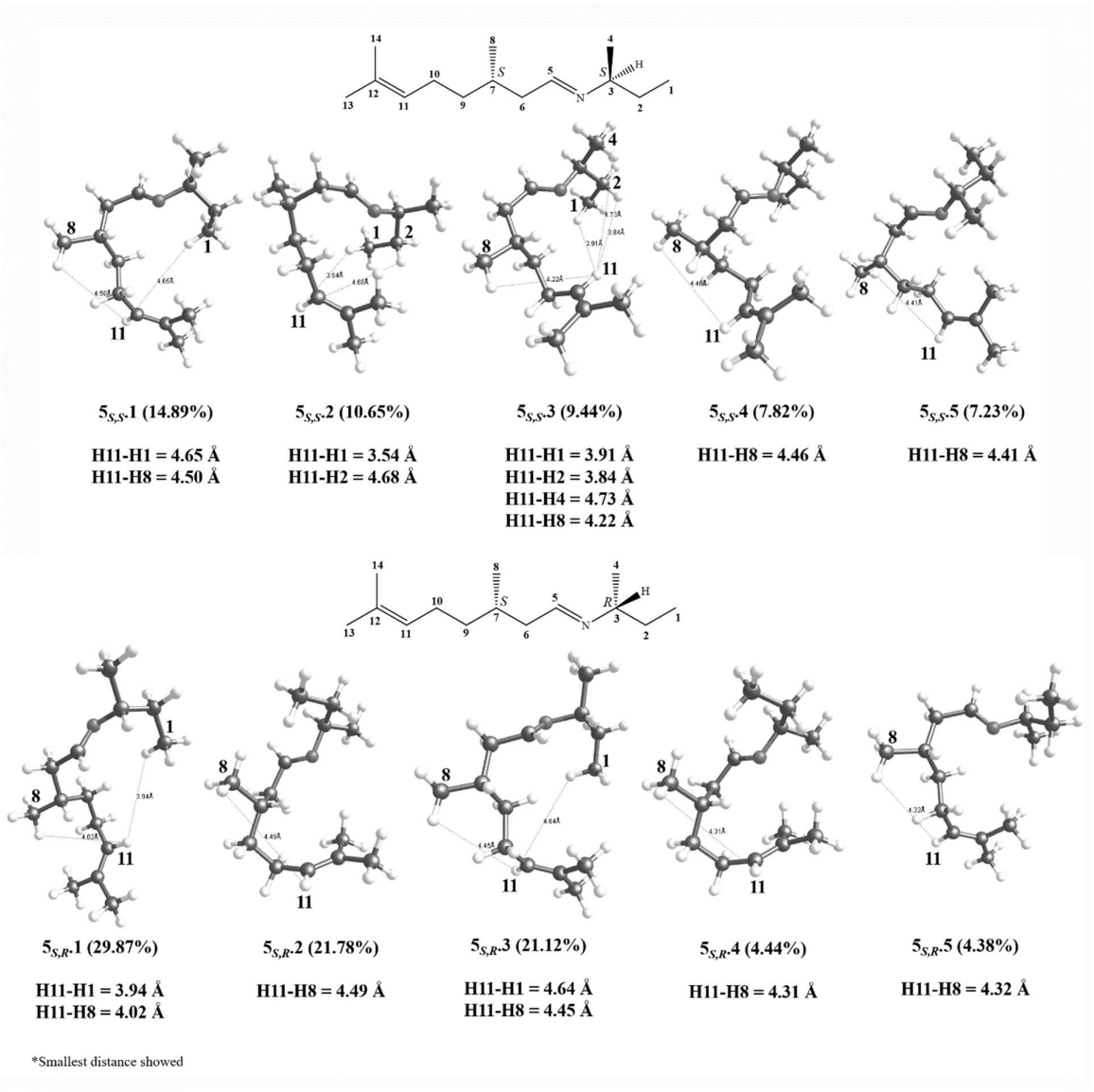


Figure S10. Five most stable conformers distribution of the diastereoisomer **5** (*S,S* and *S,R*) using B3LYP-D3(BJ)/def2-TZVP(-f) level. In parentheses is the percentage of Boltzmann's population. Just below each conformer, there is the distance, less than 5 Å, between the hydrogens.

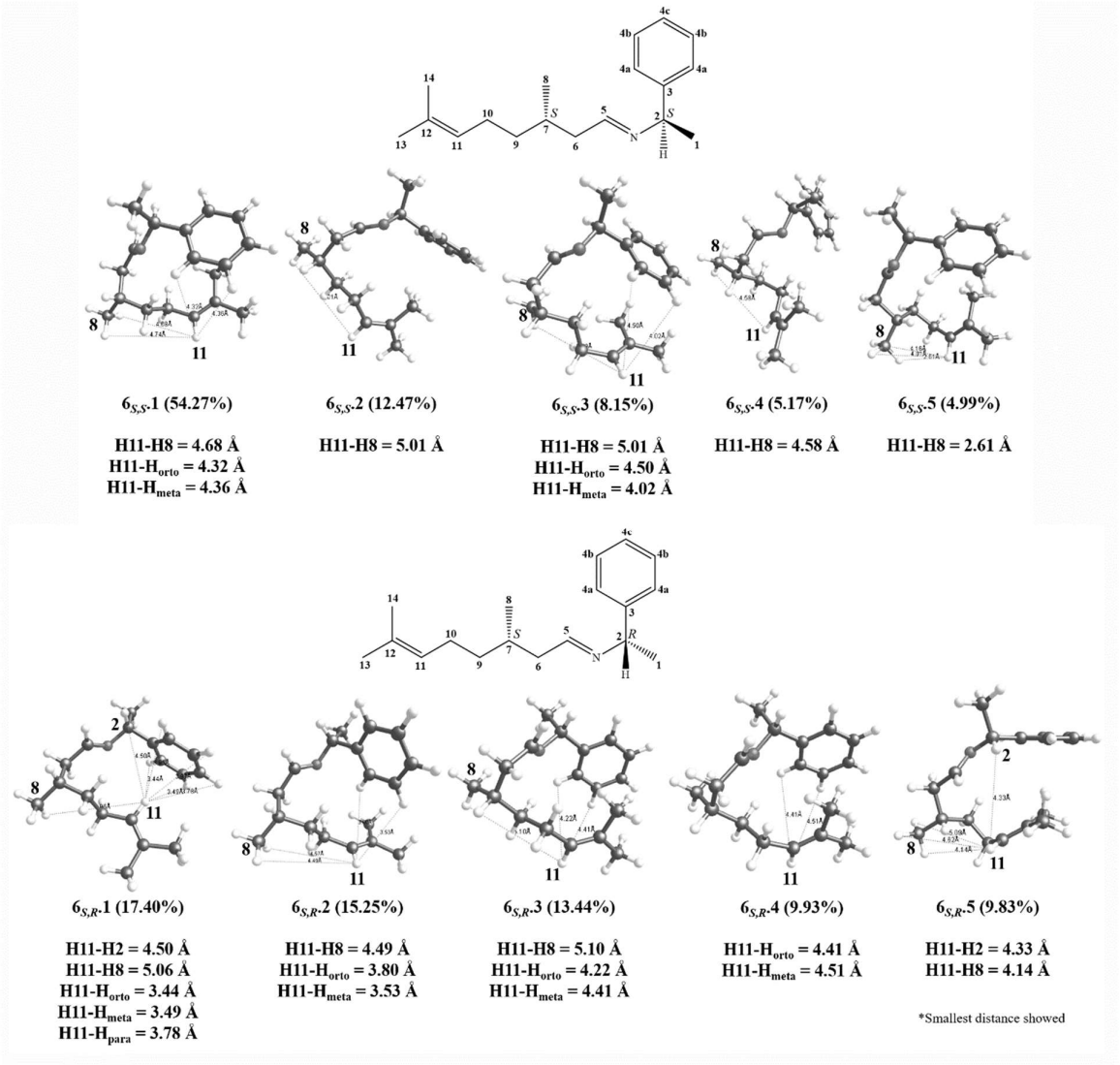


Figure S11. Five most stable conformers distribution of the diastereoisomer **6** (*S,S* and *S,R*) using B3LYP-D3(BJ)/def2-TZVP(-f) level. In parentheses is the percentage of Boltzmann's population. Just below each conformer, there is the distance, less than 5 Å, between the hydrogens.

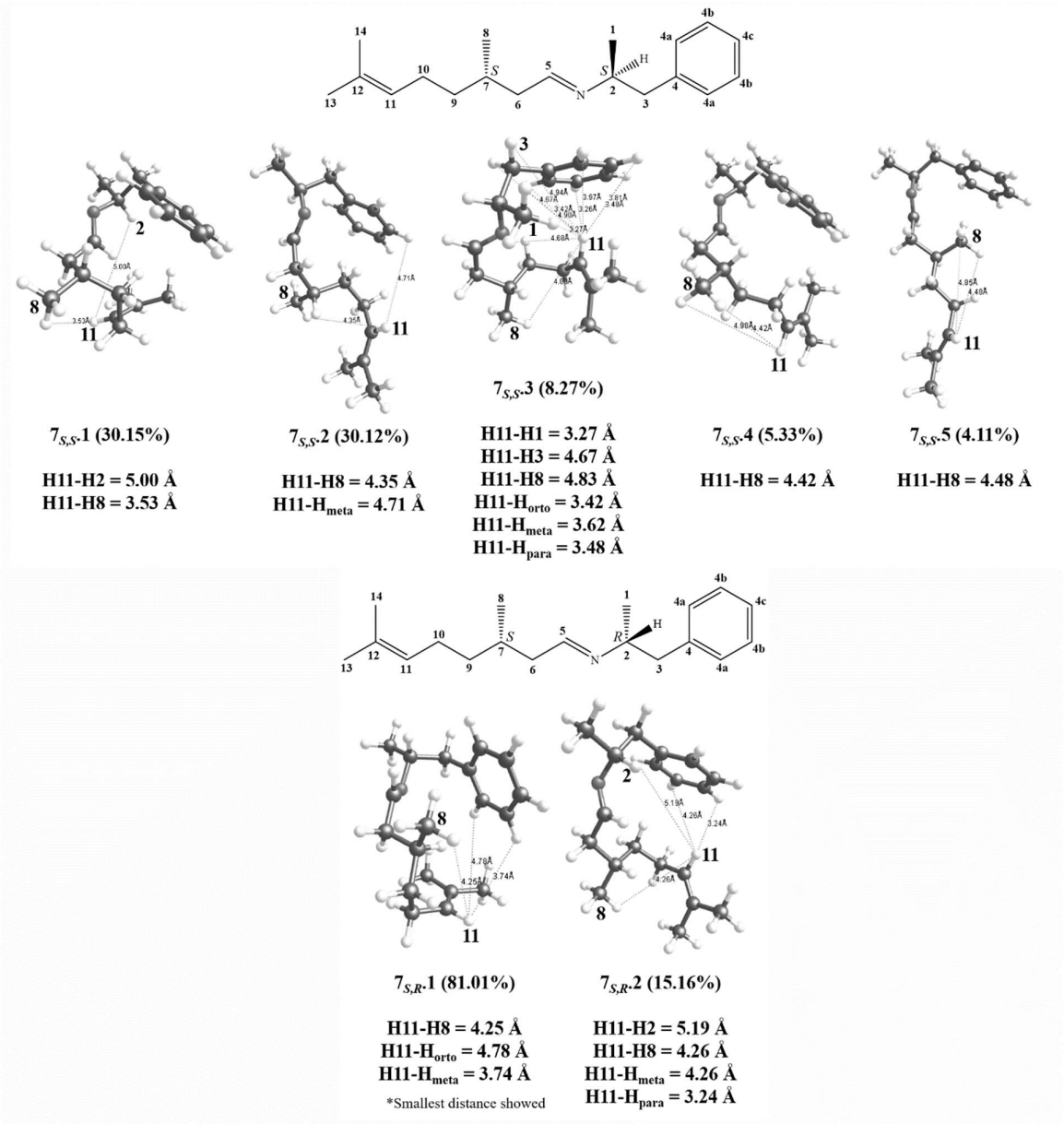


Figure S12. Five most stable conformers distribution of the diastereoisomer **7** (*S,S* and *S,R*) using B3LYP-D3(BJ)/def2-TZVP(-f) level. In parentheses is the percentage of Boltzmann's population. Just below each conformer, there is the distance, less than 5 Å, between the hydrogens.

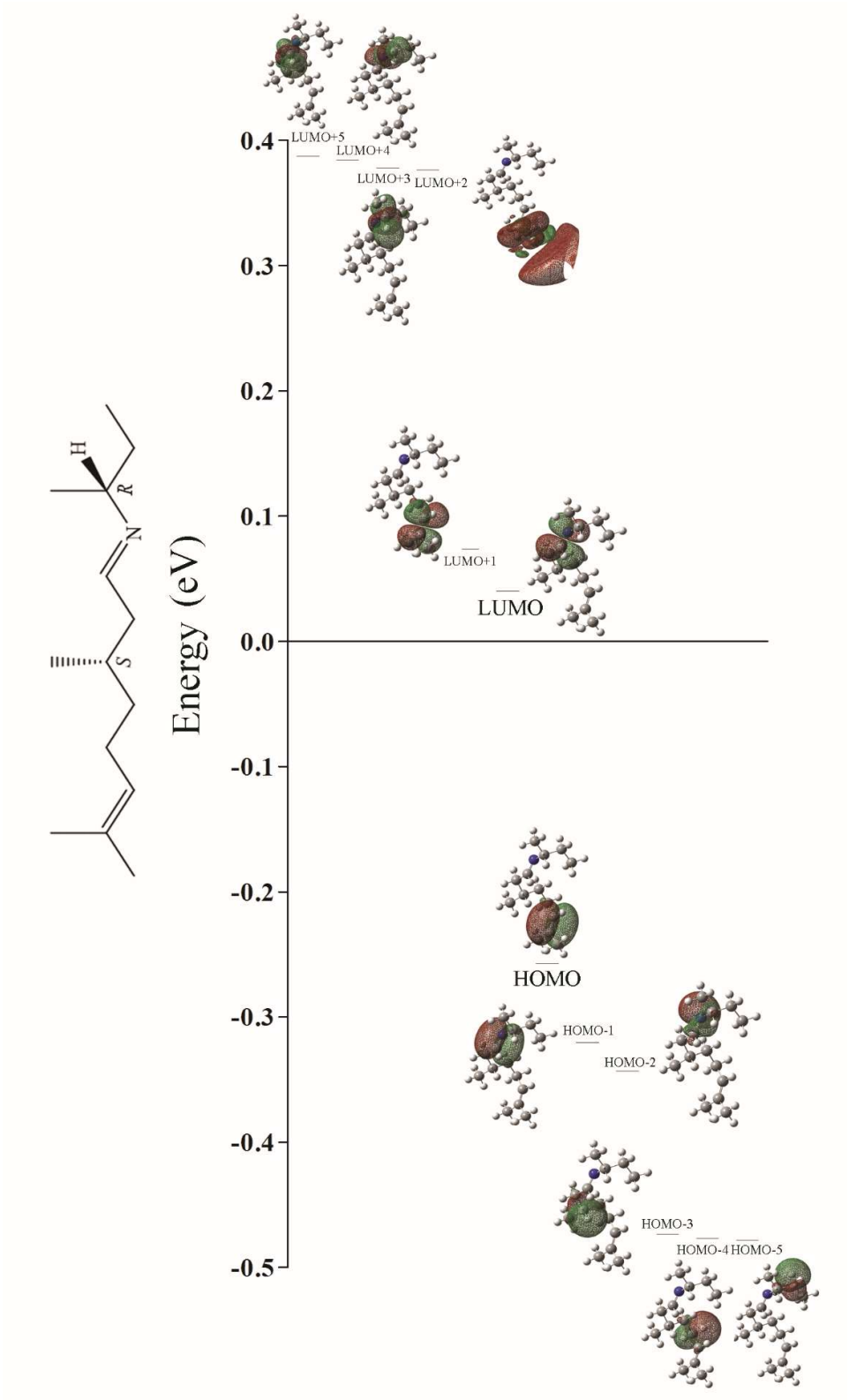


Figure S13. Energy diagram of the molecular orbitals of the diastereomeric imine $\mathbf{5}_{S,R.}$

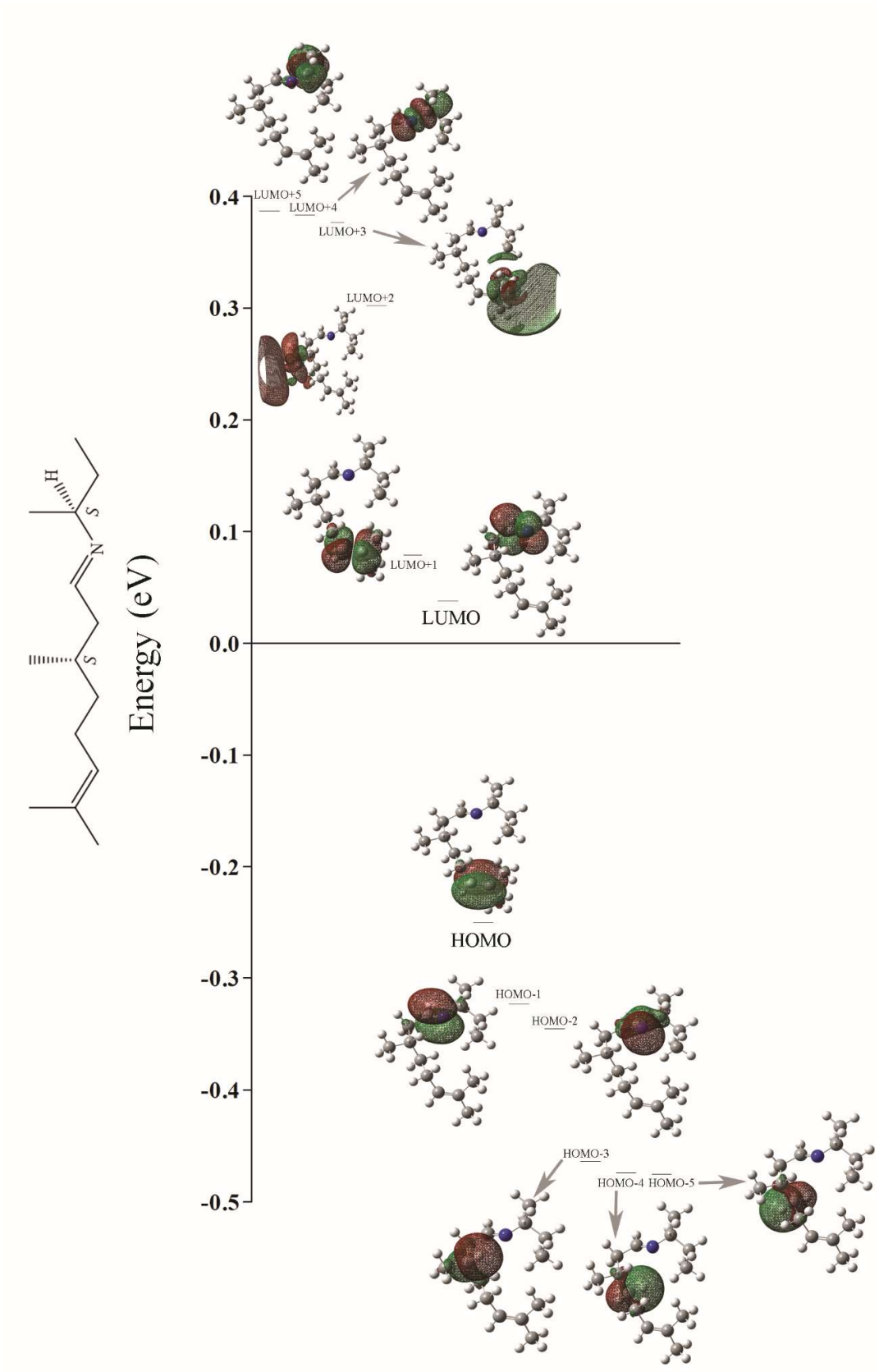


Figure S14. Energy diagram of the molecular orbitals of the diastereomeric imine **5**$_{S,S.}$

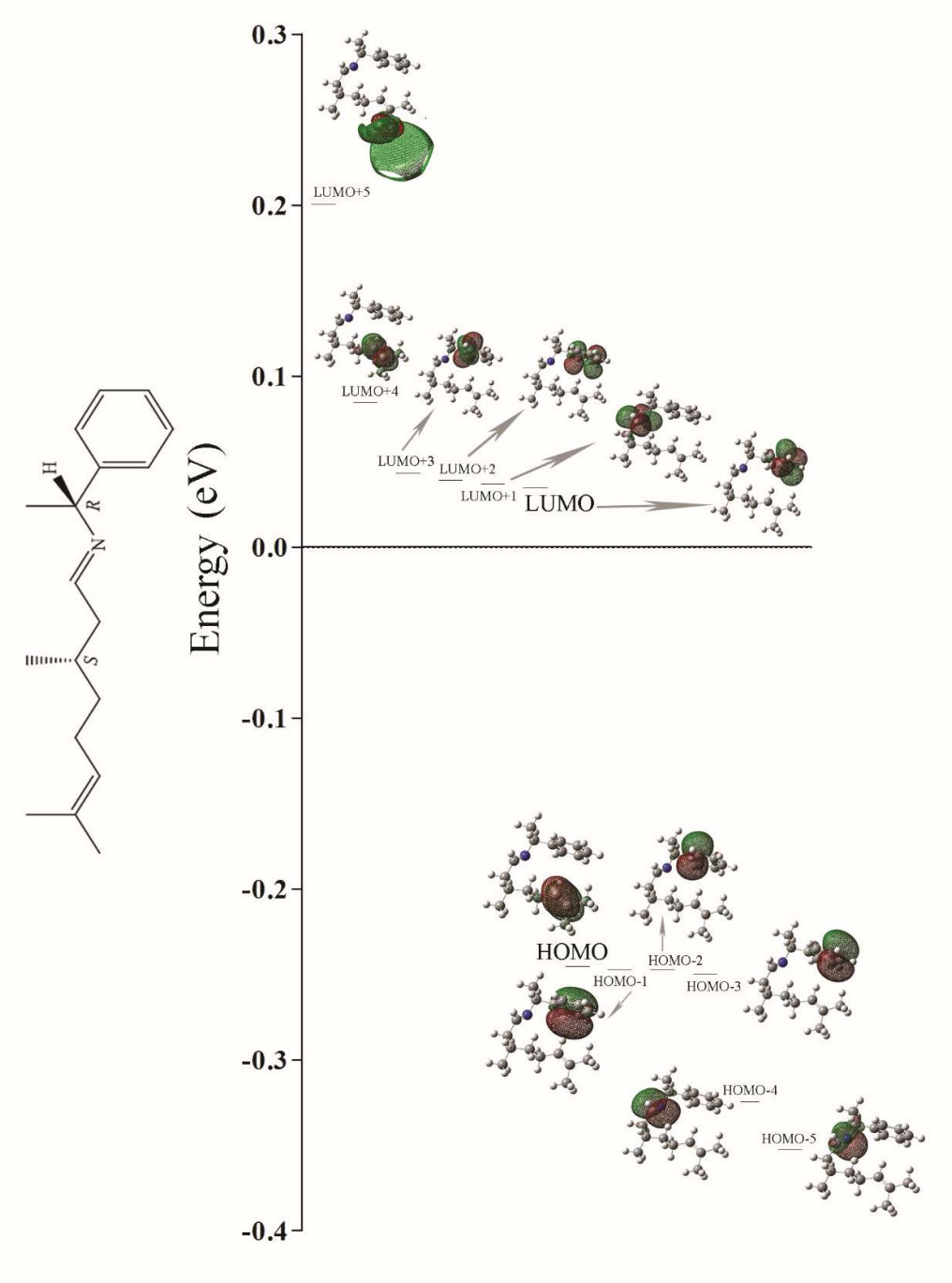


Figure S15. Energy diagram of the molecular orbitals of the diastereomeric imine $\mathbf{6}_{S,R}$.

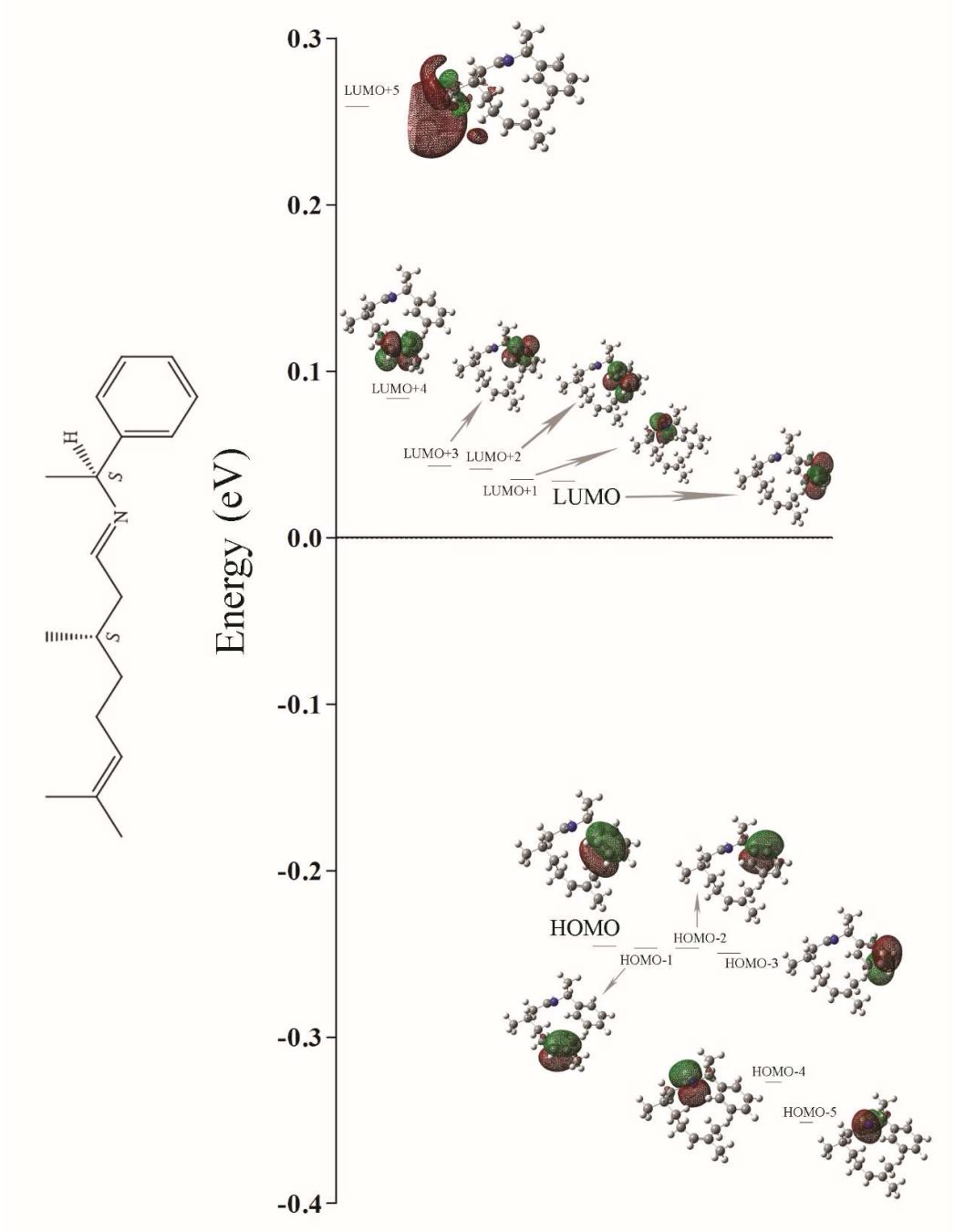


Figure S16. Energy diagram of the molecular orbitals of the diastereomeric imine **6**$_{S,S}$.

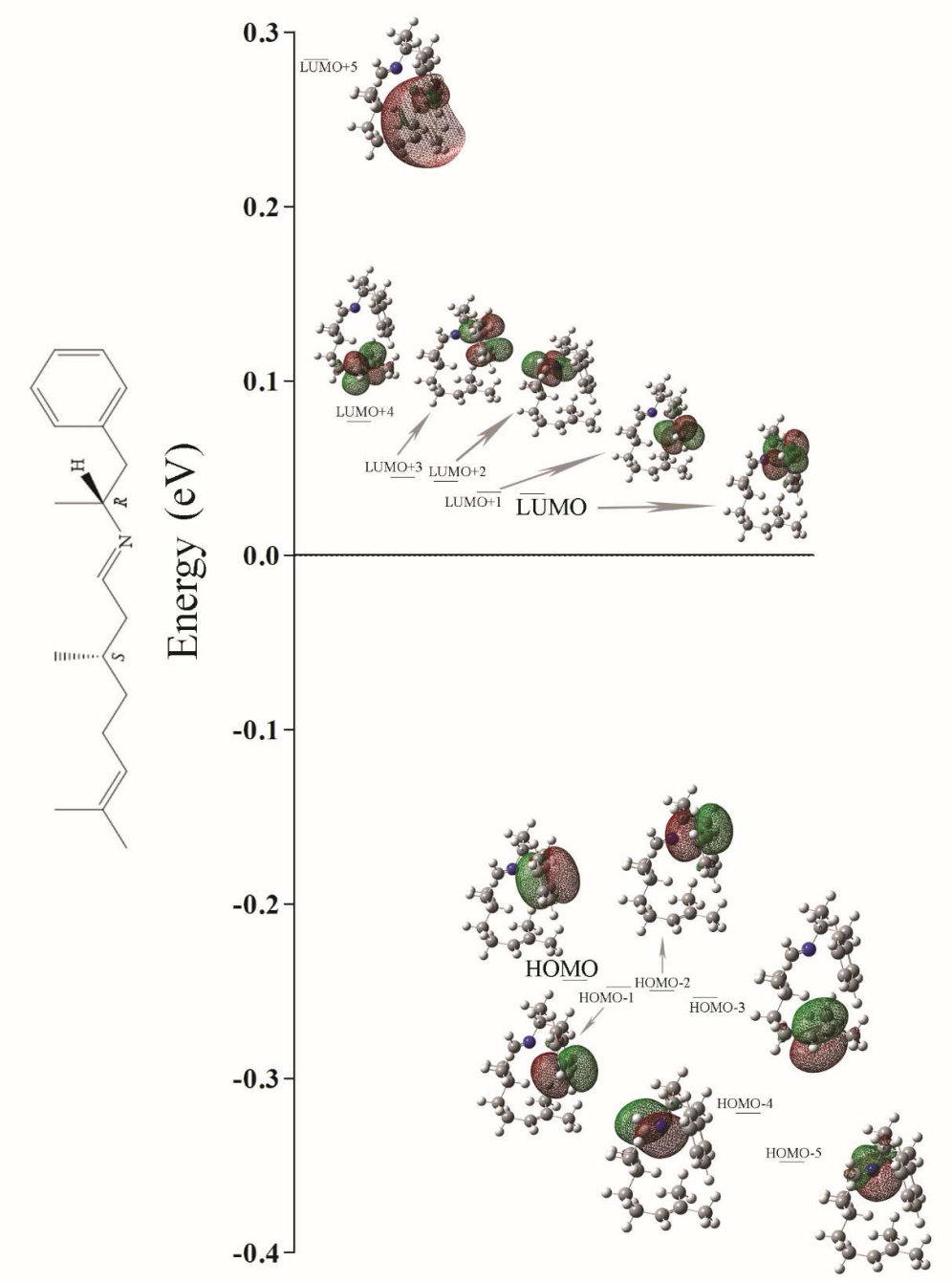


Figure S17. Energy diagram of the molecular orbitals of the diastereomeric imine $\mathbf{7}_{S,R.}$

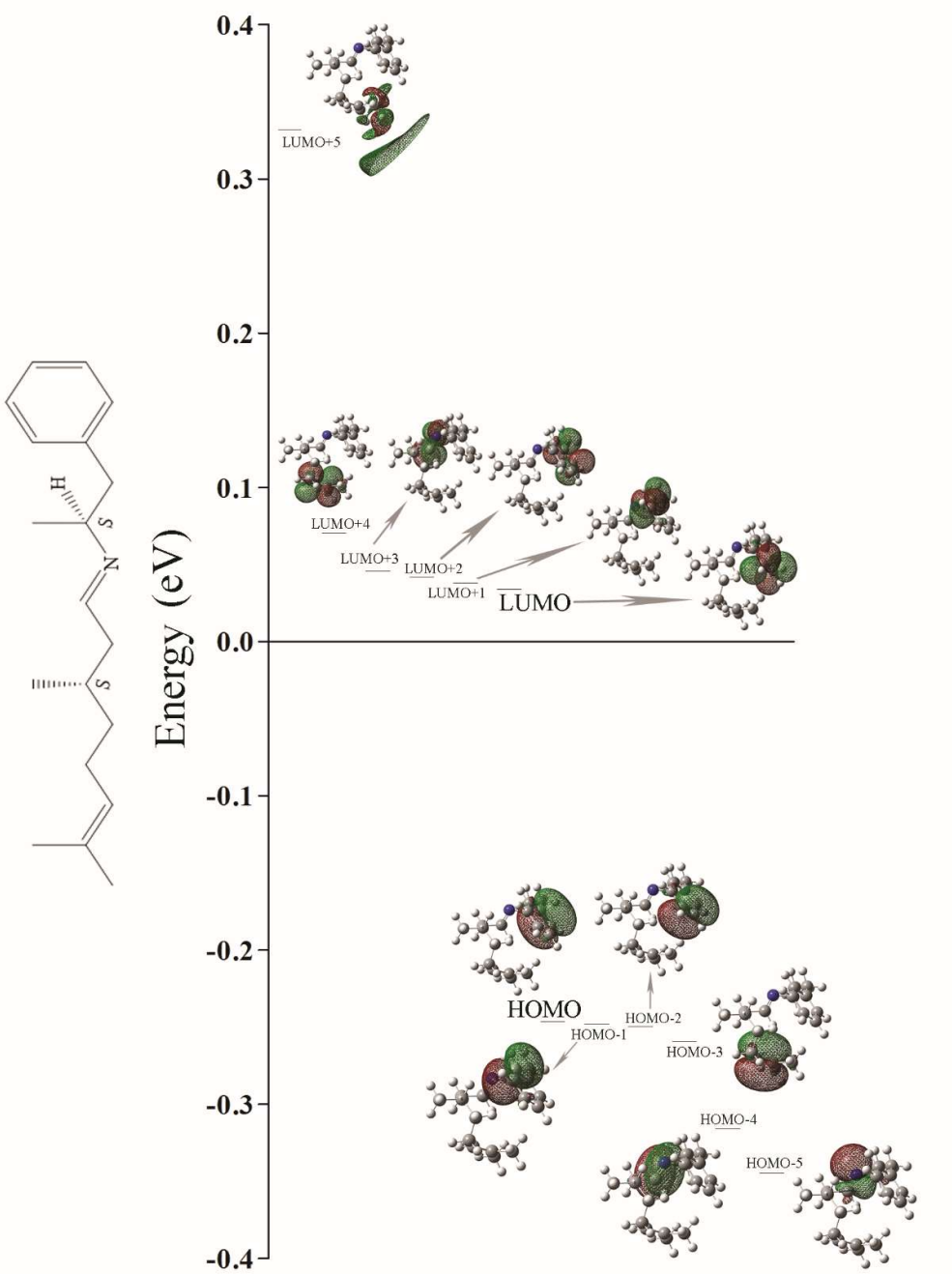


Figure S18. Energy diagram of the molecular orbitals of the diastereomeric imine $\mathbf{7}_{S,S.}$