N-(Diazoacetyl)oxazolidin-2-thiones as Sulfur Donor Reagents: Asymmetric Synthesis of Thiiranes from Aldehydes.

*Israel Cano, Enrique Gómez-Bengoa, Aitor Landa, Miguel Maestro,[†] Antonia Mielgo, Iurre Olaizola, Mikel Oiarbide, Claudio Palomo**

((Dedication----optional))

Sulfur-containing compounds are widespread among natural products and bioactive substances, and also useful ligands in asymmetric catalysis.[1] Therefore considerable efforts have been devoted to develop stereocontrolled *C*─*S* bond forming procedures.[2] Two common approaches consist of the electrophilic sulfenylation of enolates or equivalents[3] and the conjugate addition of *S*-nucleophiles to Michael acceptors,[4] routes that afford *S*-functionalized carbonyls at either α- *or* β-position. Methods to access α,β−thioepoxy carbonyls[5] would not only provide versatile *S*-functionalized adducts at both α- *and* β-position, but also imply generation of two contiguous stereocenters (Figure 1). However, as far as we are aware there is virtually no method for achieving such a goal in a direct and stereocontrolled fashion.[6] Here we describe *N*-(diazoacetyl)oxazolidin-2-thiones as new sulfur donor reagents that in combination with aldehydes and a Rh(II) catalyst are capable of producing α,β-thioepoxy carbonyls in highly stereoselective manner.

Inspired by the dual ability demonstrated by the oxazolidin-2-thione group to act as an intramolecular sulfur-donor reagent and a stereodirecting group (Figure 2a),[7] we envisaged that *N*-(diazoacetyl)oxazolidin-2-thiones might serve as both *C*─*C* and *C*─*S* bond forming reagents while controlling reaction stereochemistry. The assumption was that thiocarbonyl ylide **I** (Figure 2b), generated from *N*-(diazoacetyl)oxazolidin-2-thione upon teatment with a metal catalyst,[8] would react with an aldehyde to afford the zwiterionic intermediate **II**, which may follow diverting paths A or B to provide either epoxide or thioepoxide product. While path A (epoxide formation) seemed to be the prefered route for both sulfide ylides[9] and carbonyl ylides,[10] and implies no sulfur-transfer, we speculated that path B might also be possible, likely through rearrangement of intermediate **III**.

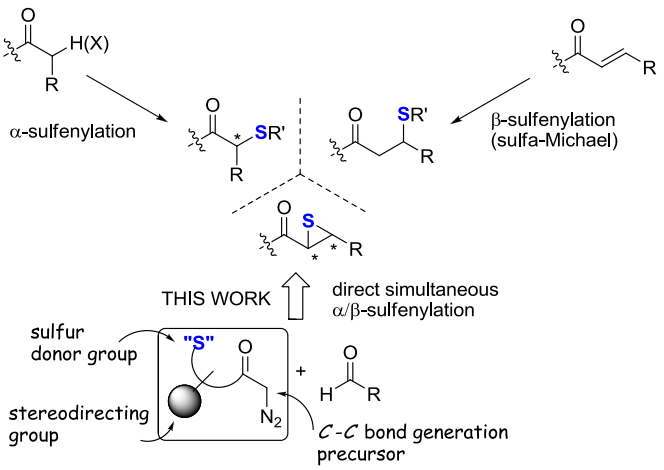

Figure 1. Common strategies for stereoselective sulfenylation of carbonyls at α or β position, and our proposal for the direct simultaneous α/β sulfenylation.

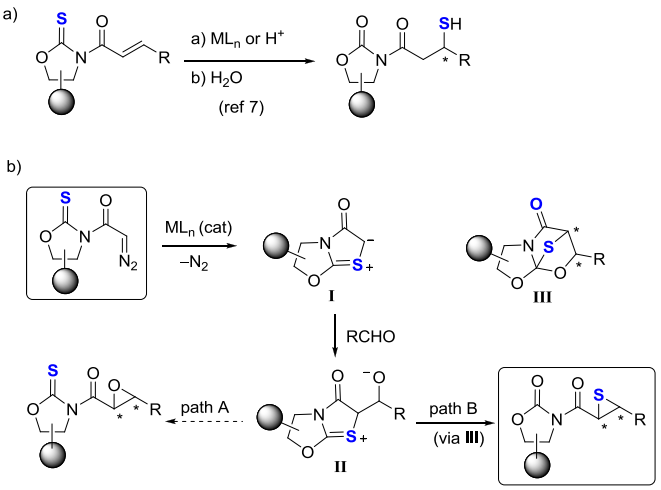

Figure 2. Working hypothesis for stereoselective thiirane synthesis via sulfur transfer with concomitant *C*─*C* bond formation.

Starting thione-diazo compounds were readily prepared by reaction of oxazolidin 2-thiones with 2-(2-tosylhydrazono)acetyl chloride in yields of 47-67%. Initial screening of catalysts and conditions

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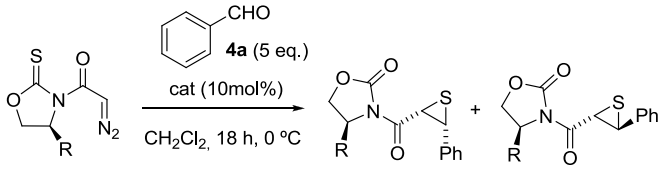
revealed that both Rh(II) or Cu(II) salts catalyzed the reaction of **1** with benzaldehyde in CH_2Cl_2 at 0 ºC to afford thiirane **5a** in isolated yields from 53% to 62% and *cis*/*trans* ratios from 85:15 to 88:12 (entries 1, 2, and 7). Remarkably, in both cases no oxirane formation was detected from the corresponding reaction crudes.[10] This process is thus particularly significant in that the new *C*─*S* σ-bond formation occurs in detriment of the *C*─*O* σ-bond and with concomitant generation of two contiguous stereocenters. The nature of the counterion of the transition metal salt used has an influence on the catalytic activity: while both $Rh_2(OAc)_4$•$2H_2O$ and $Cu(acac)_2$ demonstrated to be active and induced good reaction yields, no reaction at all was observed with either $Rh_2(OCOCF_3)_4$ or $Cu(OTf)_2$ salts (entries 1/2/7 vs. 5/8). Other divalent metal salts such as $CoCl_2$, $FeCl_2$•H_2O, or $Pd(OAc)_2$, (potentially capable of inducing ylide formation) resulted inactive and led to sluggish or no reaction at all (entries 6, 10, 13).

Table 1. Screening of catalysts for the reaction of *N*-(diazoacetyl) 2-oxazolidinethiones **1**−**3** and benzaldehyde.[a]



1 R: ^{i}Pr
2 R: ^{t}Bu
3 R: Ph

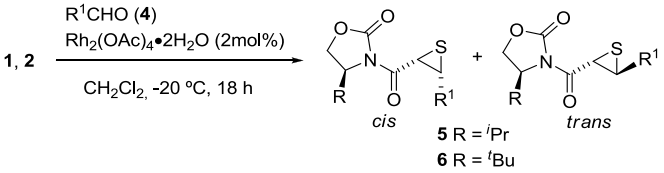
5a R: ^{i}Pr
6a R: ^{t}Bu
7a R: Ph

Entry	Substrate	Catalyst	T (ºC)	Prod.	*cis*:*trans*[b]	Yield (%)[c]
1	**1**	$Rh_2(OAc)_4$	0	**5a**	86:14	50
2	**1**	$Rh_2(OAc)_4$•$2H_2O$	0	**5a**	88:12	62
3	**1**		−10	**5a**	94:6	64[d]
4	**1**		−20	**5a**	97:3	62[d]
5	**1**	$Rh_2(OCOCF_3)_4$	0	**5a**	--	0[e]
6	**1**	$CoCl_2$	0	**5a**	--	0
7	**1**	$Cu(acac)_2$	0	**5a**	85:15	53
8	**1**	$Cu(OTf)_2$	0	**5a**	--	0[e]
9	**1**	CuCl	0	**5a**	91:9	40
10	**1**	$FeCl_2.4H_2O$	0	**5a**	--	0[e]
11	**1**	AuCl	0	**5a**	99:1	18
12	**1**	AgOTf	0	**5a**	--	0[e]
13	**1**	$Pd(OAc)_2$	0	**5a**	--	17
14	**2**	$Rh_2(OAc)_4$•$2H_2O$	−20	**6a**	94:6	60[d]
15	**3**	$Rh_2(OAc)_4$•$2H_2O$	−20	**7a**	92:8	45[d]

[a] The reactions were performed on a 0.30 mmol scale. [b] Determined by ^{1}H NMR. [c] Yield of isolated major isomer after chromatography. [d] Using 2 mol% catalyst. [e] Extensive decomposition was observed.

On the other hand, some metals in the oxidation state +1 were also effective. For instance, while no reaction was observed with AgOTf, both CuCl and AuCl promoted the reaction to give rise product **5a** with *cis/trans* ratios of 91:9 and 99:1, respectively, although yields were in these cases low or very low (40%, 18%). Further optimization of the reaction conditions using as catalyst $Rh_2(OAc)_4$•$2H_2O$ indicated that lower (2 mol%) catalyst loading suffices and the *cis/trans* ratio could be improved by lowering the temperature (up to 97:3 *cis/trans* ratio, entries 3 and 4). Finally, diazo-oxazolidinethiones **2** and **3**, bearing respectively a ^{t}Bu and a Ph substituent group, were also tolerated, although in the case of the Ph analog **3** slight erosion of both yield and selectivity was observed (entries 14 and 15).

Table 2. Scope of the reaction.[a]

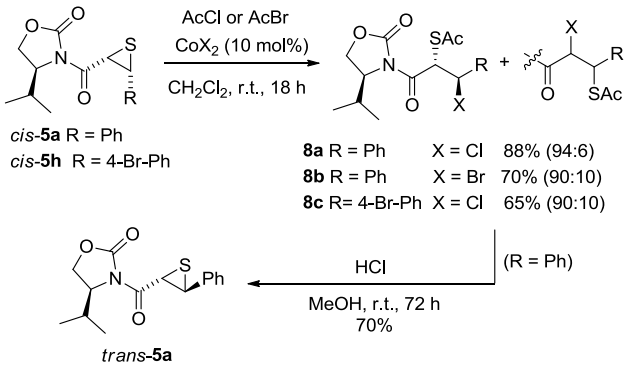


5 R = ^{i}Pr
6 R = ^{t}Bu

entry	R^1	product	cis:trans[b]	yield (%)[c]
1	Ph	**5a**	93:7	65[d]
2	4-Me-C_6H_4	**5b**	82:18	60
3	3,5-diMe-C_6H_3	**5c**	83:17	61
4	4-MeO-C_6H_4	**5d**	1:99	61
5	4-TBSO-C_6H_4	**5e**	1:99	31[e]
6[e]	4-Cl-C_6H_4	**5f**	88:12	63
7	3-Cl-C_6H_4	**5g**	86:14	57
8	4-Br-C_6H_4	**5h**	91:9	56
9	4-NO_2-C_6H_4	**5i**	92:8	61
10	4-CN-C_6H_4	**5j**	91:9	56
11	PhC≡C	**5k**	72:28	65
12[f]	PhC≡C	**6k**	83:17	75
13[g]	PhC≡C	**6k**	86:14	69
14[f]	3-Cl-PhC≡C	**6l**	85:15	60
15	3-furyl	**5m**	62:38	ND[h]
16[g]	3-furyl	**6m**	83:17	70
17	3-Pyridyl	**5n**	--	0[i]

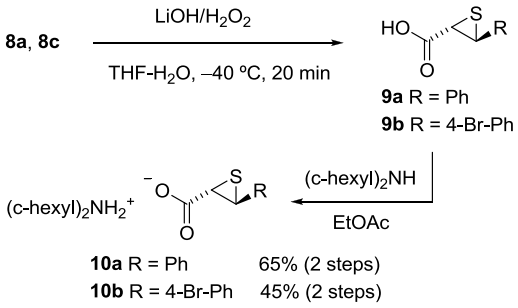
[a] Reaction conditions: **1** (0.5 mmol), **4** (3 equiv, 1.5 mmol), $Rh_2(OAc)_4$•$2H_2O$ (2 mol%), −20 ºC, 18 h in CH_2Cl_2 (1 mL). [b] Determined by ^{1}H NMR. [c] Yields of isolated compounds **5**/**6** after column chromatography. [d] Reaction carried out at 2 mmol scale. [e] Yield not optimized; partial desilylation occurred during chromatography (SiO_2). [e] 91:9 diastereoselectivity in the presence of 2,2'-bipyridyl as additive. [f] Reaction run at −60 ºC. [g] Reaction run at −78 ºC. [h] ND: Not determined [i] Unchanged SM recovered.

We next investigated the scope of the reaction with respect to the aldehyde component. As the results in Table 2 show, a range of aromatic aldehydes bearing either electron-releasing, neutral, or electron-withdrawing substituents all produced the corresponding thiirane product smoothly within 18 hours at −20 ºC. In each case a mixture of *cis/trans* isomers was formed from which the major isomer was obtained in 57%−75% isolated yield. Interestingly, while in most cases *cis*-thiirane was obtained as the major isomer (*cis/trans* ratio from 97:3 to 82:18, entries 1−3, 6−10), in case of *p*-anisidine, and *p*-*tert*-butyldimethylsilyloxybenzaldehyde (products **5d**-**e**), the *trans*-configured thiirane was the exclusive reaction product (entries 4−5). This unusual reversal of the reaction stereochemistry observed for benzaldehydes bearing electron releasing substituents could be explained on the basis of the proposed reaction mechanism (*vide infra*). The catalytic generation of thiiranes **5**/**6** did also work with other non enolizable aldehydes explored, such as alkynyl and heteroaryl aldehydes (entries 11-16). Pyridylcarbaldehyde was an exception (entry 17). Assignment of the *cis*/*trans* relative configuration of the formed thiirane ring was primarily made by correlation of the coupling constants between the two *vec* H nucleus in NMR: from 7.4 Hz to 7.7 Hz for the *cis*-thiirane systems; from 4.80 Hz to 4.90 Hz for the *trans* isomer. In addition, an X-ray single-crystal structure analysis of compound *cis*-**5a** served to confirm the proposed structure.[11]



Scheme 1. Thiirane ring opening on adducts **5**.

Next conditions for the selective opening of the thiirane ring and the release of the oxazolidinone auxiliary were explored. For example, Scheme 1, treatment of thiiranes *cis*-**5a** and *cis*-**5h** with acetyl chloride in CH_2Cl_2 at room temperature in the presence of $CoCl_2$ (10 mol%), according to the procedure of Iranpoor and Firouzabadi,[12] gave rise to the β-chloro-α-thio imide derivatives **8a** and **8c** in 88% and 65% isolated yields, respectively, after chromatography. Similarly, treatment of *cis*-**5a** with acetyl bromide in the presence of $CoBr_2$ as a catalyst afforded the corresponding bromo-derivative **8b** in 70% isolated yield. In all these three cases a minor amount (6%−10%) of the corresponding regioisomeric ring opening product was also observed in the respective reaction crude. Interestingly, acid-promoted cyclisization of compounds **8** to restore the thiirane ring took place very efficiently, with inversion of the configuration of β-carbon. For instance, the treatment of **8a** with methanolic HCl afforded *trans*-**5a** in 70% yield. Accordingly, a two-step thiirane ring isomerization from *cis* to the more stable *trans* isomer is feasible.



Scheme 2. Recovery of the auxiliary.

On the other hand, the removal of the oxazolidinone moiety from thiirane adducts **5** through imide hydrolysis or alcoholysis under usual conditions led to extensive desulfurilation. This problem could be circumvent by performing imide hydrolysis on the open adducts **8** instead (Scheme 2). Thus, saponification with $LiOH/H_2O_2$ of adducts **8a** and **8c** proceeded with restoration of the thiirane ring, affording the corresponding acids **9**, which were isolated as crystalline bench stable dicyclohexylamine salts **10**. In this transformation oxazolidinone was also formed which could be recovered and transformed into the thione auxiliary and recycled.[7] Unambiguous determination of the structure of salt **10b** and compound **8a** by X-ray analysis[11] served for further confirmation of the products identity as well as the stereochemical outcome of the reactions involved.

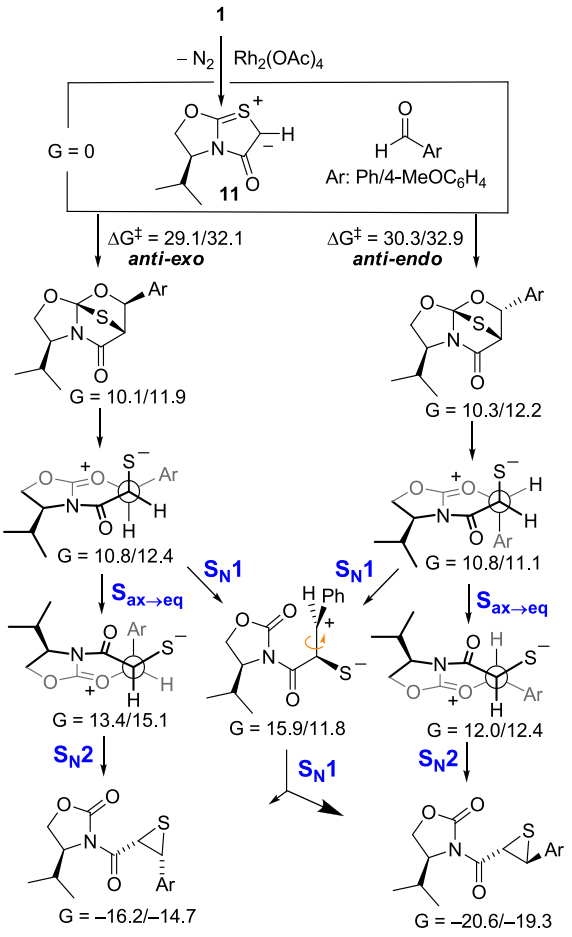


Figure 3. Principal pathways found (DFT-B3LYP) for the Rh-catalyzed reaction between diazocompound **1** and either benzaldehyde or *p*-anisaldehyde. Values of Gibbs energy in kcal/mol.

A DFT investigation was carried out at the B3LYP level of theory, which provided a plausible pathway for this intriguing thiirane forming reaction. Calculations predict that the corresponding Rh-carbenoid species[9] formed upon treatment of diazo-thione compound **1** with $Rh_2(OAc)_4$, evolves into bicyclic ylide **11** (Figure 3)[13] with no activation barrier, probably because of the high charge delocalization exhibited by this particular ylide.[14] According to calculations subsequent reaction of **11** with either benzaldehyde or *p*-anisaldehyde would generate a unique tricyclic adduct,[15] and among the four possible relative orientations of the ylide and aldehyde component during the cycloaddition, those leading to *anti-exo* and *anti-endo* isomers are preferred. The complementary *syn* transition states lie considerably higher in energy because unfavorable interactions between the ylide isopropyl substituent and the incoming aldehyde. The energy differences between *anti-exo* and *anti-endo* approaches for benzaldehyde and *p*-anisaldehyde, (1.2 and 0.8 kcal/mol, respectively) would justify preferential formation of *anti-exo* adduct with expected diastereoselectivities near 90:10. Transformation of these tricyclic high energy intermediates into the final thiirane products would follow a more or less downhill energy profile, involving *S*-ring opening, $S_{ax\rightarrow eq}$ conformational switch, and internal S_N2 displacement. Accordingly, from tricyclic *anti-exo* intermediate the *cis*-configured thiirane would be formed; reversely, from the less favorable *anti-endo* precursor, the *trans*-thiirane would be formed, a prediction that agrees with the experimentally observed trend for most of the aldehydes tested. Interestingly, calculations also offer a plausible explanation of the reversal of the reaction

stereochemistry observed experimentally for *p*-anisaldehyde and other related electron-rich aromatic aldehydes. Indeed, thiirane generation could occur through an alternatively S_N1-type pathway, which is about 2.5 kcal/mol less favorable than the S_N2 pathway for benzaldehyde, but conversely about 3.3 kcal/mol more favorable than the S_N2 pathway for *p*-anisaldehyde. As expected, S_N1-type cyclisation would preferentially lead to the most stable *trans*-thiirane product.

In conclusion, we have reported the first Rh-catalyzed reaction of a diazoacetyl compound with aldehydes that affords thiiranes, instead of oxiranes as known before. This unusual reactivity relies on the development of *N*-(diazoacetyl)oxazolidin-2-thiones as new chiral sulfur donor reagents and enables the direct production of optically active thiiranes with very high stereoselectivity. Work towards expanding the scope of this sulfur transfer technology is currently underway in our laboratory.

Experimental Section

General catalytic procedure for the synthesis of Thiiranes 5-7
To a solution of the corresponding diazocompound **1**-**3** (0.50 mmol) and aldehyde **4a**-**p** (3 eq, 1.5 mmol) in dry CH_2Cl_2 (1.5 mL) at a given temperature, was added rhodium (II) acetate dihydrate (4.8 mg, 0.01 mmol, 2 mol %) under argon atmosphere. The reaction mixture was stirred overnight at the same temperature and afterwards quenched with saturated $NaHCO_3$, the organic layer was separated, dried with $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: AcOEt/Hexane 1:4) to afford the desired product.

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[15] An alternative pathway to this tricyclic adduct would involve attack of the thione group into the epoxide initially generated from the reaction between the aldehyde and the diazocarbonyl moiety (see ref 11). However, the fact that no even traces of epoxide product was detected in the reaction mixtures and a 14.4 kcal/mol energy barrier is calculated for such epoxide formation, work against the epoxide pathway and favors the sulfur ylide mediated pathway.

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Layout 2:

Asymmetric Synthesis

Israel Cano, Enrique Gomez-Bengoa, Aitor Landa, Miguel Maestro, Antonia Mielgo, Mikel Oiarbide, Iurre Olaizola, Claudio Palomo,*

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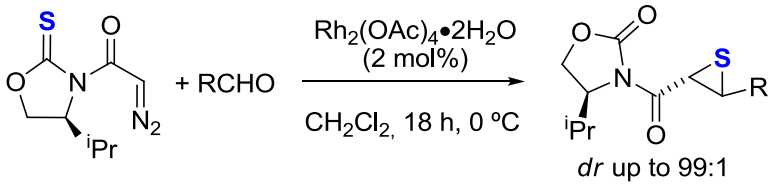

Sulphur tyranny: thiiranes, instead of oxiranes, can be obtained in highly stereoselective manner through cycloaddition reaction of *N*-acyl oxazolidine tethered diazo-thione compounds with aldehydes catalyzed by Rh(II).

N-(Diazoacetyl)oxazolidin-2-thiones as Sulfur Donor Reagents: Asymmetric Synthesis of Thiiranes from Aldehydes

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Supporting Information

Contents

1. General information.

The ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz respectively. The chemical shifts are reported in ppm relative to $CDCl_3$ ($\delta = 7.26$) for ^{1}H NMR and relative to the central resonances of $CDCl_3$ ($\delta = 77.0$) for ^{13}C NMR. Purification of reaction products was carried out by flash column chromatography using ROCC silica gel 60 (0.040-0.063mm, 230-400 mesh). Visualization was accomplished with a solution of potassium permanganate (1 g) in 100 ml of water (limited lifetime), followed by heating. Optical rotations were recorded on a Jasco P-2000 polarimeter. MS spectra were recorded on an ESI-ion trap Mass spectrometer (Agilent 1100 series LC/MSD, SL model).

2. Materials.

All solvents were of p.a. quality and were dried by standard procedures prior to use if necessary. Unless otherwise specified, materials were obtained from commercial sources and used without purification. *N*,*N*-dimetylaniline, triethylamine, acetyl chloride and acetyl bromide were purified by distillation. Aldehydes **4e**[1] and **4l**[2] were prepared following the procedure described in the literature. Liquid aldehydes were purified by distillation before usage and stored in the fridge at -30ºC under nitrogen. Dirhodium tetraacetate dihydrate ($Rh_2(OAc)_4{\cdot}2H_2O$) was purchased from Alfa Aesar. Unless otherwise stated, all reactions were carried out in an inert atmosphere of Ar and in oven dried glassware.

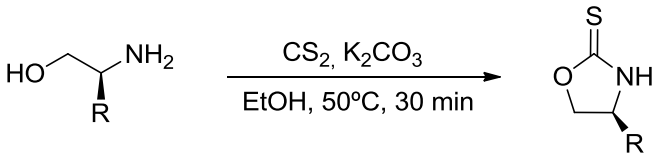
Thiiranes **5**, **6** and **7** should be stored in a refrigerator and under Ar atmosphere (at -30ºC they are stable for at least 1 month). They will decompose over time giving off the corresponding olefins and elemental sulphur.

[1] Kwong, C. K.-W.; Huang, R.; Zhang, M.; Shi, M.; Toy, P. H. *Chem. Eur. J.* **2007**, *13*, 2369-2376.
[2] L.Brandsma, *Preparative Aceyilenic Chemistry (Studies in Organic Chemistry 34)* Ed. Elsevier, Amsterdam, **1988**, 97-112.

3. Experimental procedures, analytical and spectroscopic data

3.1. General procedure for synthesis of diazocompunds.

3.1.1. General procedure for synthesis of oxazolidone-2-thiones.[3]



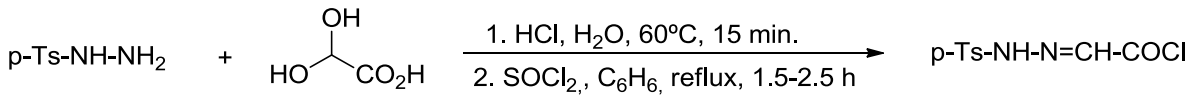
		Yield
R: ^{i}Pr	R: ^{i}Pr	78%
R: ^{t}Bu	R: ^{t}Bu	69%
R: Ph	R: Ph	72%

To a suspension of the corresponding (S)-aminoalcohol[4] (128.0 mmol) and potassium carbonate (0.5 eq, 8.83 g, 64.0 mmol) in ethanol (130 mL), was added carbon disulfide (2 eq, 15.42 mL, 256 mmol), at 0 ºC under nitrogen atmosphere. The reaction mixture was stirred at 50 ºC for 30 min and then was cooled to 0 ºC and quenched carefully with a solution of 30% H_2O_2 (1.5 eq, 32 mL, 128.0 mmol) (Note, very exotermic reaction). The resulting mixture was filtered, diluted with ethyl acetate and washed with water and brine. The organic layer was dried with $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: AcOEt/Hexane 1:4) to afford the desired product.

Following the general procedure (S)-4-isopropyloxazolidine-2-thione was obtained in 78% yield from (S)-valinol, (S)-4-phenyloxazolidine-2-thione in 69% from (S)-phenylglycinol and (S)-4-(*tert*-butyl)oxazolidine-2-thione in 72% from (S)-*tert*-leucinol. All spectroscopic data are consisted with those previously reported.[5]

[3] Li, G.; Ohtani, T. *Heterocycles* **1997**, *45*, 2471-2474.
[4] McKennon, M. J.; Meyers, A. I.; Drauz, K.; Schwarm, M. *J. Org. Chem.* **1993**, *58*, 3568-3571.
[5] a) Delaunay, D.; Toupet, L.; Le Corre, M. *J. Org. Chem.* **1995**, *60*, 6604-6607. b) Wu, Y.; Yang, Y.-Q.; Hu, Q. *J. Org. Chem.* **2004**, *69*, 3990-3992. c) Baiget, J.; Cosp, A.; Gálvez, E.; Gómez-Pinal, L.; Romea, P.; Urpí, F. *Tetrahedron*, **2008**, *64*, 5637-5644.

3.1.2. Procedure for the synthesis of 2-(2-tosylhydrazono)acetyl chloride.[6]



A) Glyoxylic acid p-toluenesulfonylhydrazone:

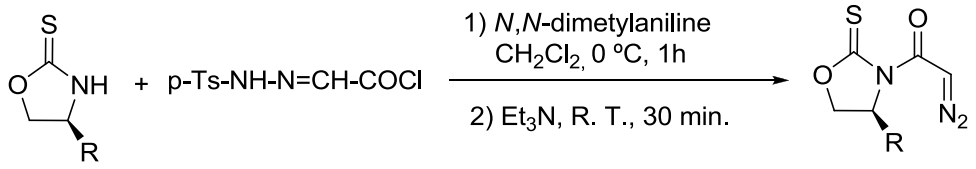
To a solution of glyoxylic acid (23.48 g, 255.1 mmol) in water (500 mL) at 60 ºC was added a solution of *p*-toluenesulfonylhydrazide (46.55 g, 250.0 mmol) in 2.5 M HCl (125 mL) at 60 ºC. The resulting mixture was stirred at the same temperature until all the hydrazone, which initially separates as an oil, solidified (about 15 min). The temperature was allowed cool to room temperature and then the reaction mixture was stored in the fridge at 0ºC overnight. The crude was filtered, washed with cool water and allowed to dry for 2 days. The crude product was dissolved in boiling ethyl acetate (200 mL), filtered to remove any insoluble material and diluted with CCl_4 (400 mL). The solution was stored in the fridge overnight and then the precipitate was filtered off and dried (for two days at 50ºC) to give the glyoxylic acid p-toluenesulfonylhydrazone as white crystals.

B) 2-(2-tosylhydrazono)acetyl chloride:

To a suspension of glyoxylic acid p-toluenesulfonylhydrazone (10.0 g, 41.24 mmol) in benzene (50 mL) was added thionyl chloride (2 eq, 6 mL, 82.42 mmol). The reaction mixture was heated under reflux until vigorous gas evolution ceased and most of suspended solid was dissolved (1.5-2.5 h). The mixture was cooled to room temperature, filtered through celite and the solvent was evaporated under reduce pressure, affording 2-(2-tosylhydrazono)acetyl chloride.

[6] a) House, H. O.; Blankley, C. J. *J. Org. Chem.* **1968**, *33*, 53-60. b) *Organic Synthesis*; John Wiley & Sons, Inc.; U. S. A., 1973; Vol. 5, p 258-263.

3.1.3. Procedure for the synthesis of thionediazocompunds 1-3.

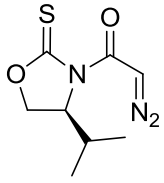


R: ^{i}Pr
R: ^{t}Bu
R: Ph

	Yield
1 R: ^{i}Pr	67%
2 R: ^{t}Bu	49%
3 R: Ph	47%

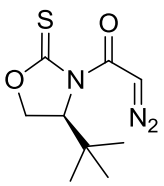
To a mixture of the corresponding *NH*-oxazolidine-2-thione (10.0 mmol) and 2-(2-tosylhydrazono)acetyl chloride (1.8 eq, 4.693 g, 18.0 mmol) in dry CH_2Cl_2 (60 mL) at 0 ºC, was added *N*,*N*-dimetylaniline (1.8 eq, 2.3 mL, 18.0 mmol) under argon atmosphere. The resulting mixture was stirred at 0 ºC for 1 h and then triethylamine (5 eq, 7.0 mL, 50.0 mmol) was added. The reaction was stirred at the same temperature for 30 min. Next, the temperature was allowed to rise to room temperature and the mixture was stirred for another 10 min. The reaction mixture was then quenched with water (50 mL) and the aqueous layer was extracted with CH_2Cl_2 (5 x 30 mL). The combined organic layers were dried with $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: AcOEt/Hexane 1:9) to afford the desired product.

(S)-2-diazo-1-(4-isopropyl-2-thioxooxazolidin-3-yl)ethanone (1)



The title compound **1** was prepared from (S)-4-isopropyloxazolidine-2-thione (1.452 g, 10 mmol) according to the general procedure. Yellow solid, yield: 1.44 g, 6.70 mmol, 67%. $[\alpha]_D^{25}$ = +132.5 (c = 1.00, CH_2Cl_2); m. p. 53-54 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.97 (s, 1H), 4.81 (dd, *J* = 9.9, 5.4 Hz, 1H), 4.39 (d, *J* = 5.4 Hz, 2H), 2.40 (m, 1H), 0.91 (dd, *J* = 17.3, 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 185.3, 164.4, 67.4, 63.2, 51.1, 29.2, 18.0, 14.8. HRMS: $C_8H_{11}N_3O_2S$ $[M+H-2N]^+$ calcd.: 186.0584, found: 186.0586.

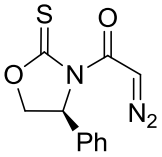
(S)-1-(4-(tert-butyl)-2-thioxooxazolidin-3-yl)-2-diazoethanone (2)



The title compound **2** was prepared from (S)-4-(*tert*-butyl)oxazolidine-2-thione (1.592 g, 10 mmol) according to the general procedure. Brown solid, yield: 1.10 g, 4.90 mmol, 49%. $[\alpha]_D^{25}$ = +194.0 (c = 1.00, CH_2Cl_2); m. p. 63-

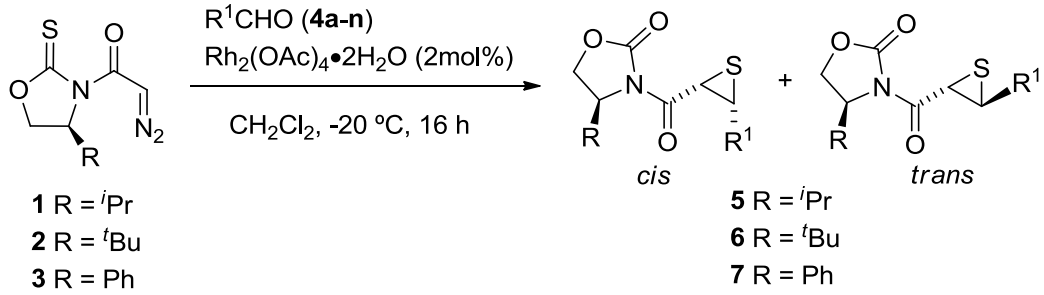
64 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.85 (s, 1H), 4.88 (dd, *J* = 7.8, 1.8 Hz, 1H), 4.47 (dd, *J* = 9.5, 1.8 Hz, 1H), 4.36 (dd, *J* = 9.5, 7.8 Hz, 1H), 0.95 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 186.2, 164.9, 69.2, 65.1, 51.2, 36.2, 25.6. UPLC-DAD-QTOF: $C_9H_{13}N_3O_2S$ $[M+Na]^+$ calcd.: 250.0626, found: 250.0620.

(S)-2-diazo-1-(4-phenyl-2-thioxooxazolidin-3-yl)ethanone (3)



The title compound **3** was prepared from (S)-4-phenyloxazolidine-2-thione (1.792 g, 10 mmol) according to the general procedure. Pale yellow solid, yield: 1.12 g, 4.70 mmol, 47%. $[\alpha]_D^{25}$ = +211.6 (c = 1.00, CH_2Cl_2); m. p. 103-105 ºC (decomposition). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.91 (s, 1H), 7.49-7.16 (m, 5H), 5.80 (dd, *J* = 8.8, 3.5 Hz, 1H), 4.80 (t, *J* = 8.9 Hz, 1H), 4.45 (dd, *J* = 9.1, 3.6 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 184.9, 163.9, 138.5, 129.3, 129.0, 126.0, 73.9, 62.1, 51.5. HRMS: $C_{11}H_9N_3O_2S$ $[M+H-2N]^+$ calcd.: 220,0427, found: 220.0444.

3.2. General procedure for the catalytic synthesis of thiiranes 5-7.

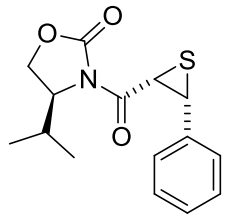


1 R = ^{i}Pr
2 R = ^{t}Bu
3 R = Ph

5 R = ^{i}Pr
6 R = ^{t}Bu
7 R = Ph

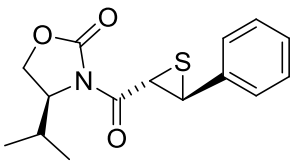
To a solution of the corresponding diazocompound **1**-**3** (0.50 mmol) and aldehyde **4a**-**p** (3 eq, 1.5 mmol) in dry CH_2Cl_2 (1.5 mL) at a given temperature, was added rhodium (II) acetate dihydrate (4.8 mg, 0.01 mmol, 2 mol %) under argon atmosphere. The reaction mixture was stirred overnight at the same temperature and afterwards quenched with saturated $NaHCO_3$. The organic layer was separated, dried with $MgSO_4$, filtered, and the solvent evaporated under reduced pressure. The residue was analyzed by NMR spectroscopy in order to determine the *cis/trans* isomeric ratio produced in each case. Subsequent purification of the crude product by flash chromatography on silica gel (eluent: AcOEt/Hexane 1:4) allowed isolation of pure major isomer (in some specific cases, minor diastereomer could also been isolated and fully characterized).

(S)-4-isopropyl-3-((2S,3R)-3-phenylthiirane-2-carbonyl)oxazolidin-2-one (*cis*-5a)



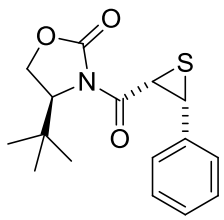
The title compound *cis*-**5a** was prepared from **1** (426 mg, 2.0 mmol) and benzaldehyde (610 μL, 6.0 mmol) according to the general procedure (1st fraction of the chromatographic column). White solid, yield: 379 mg, 1.30 mmol, 65%. $[\alpha]_D^{25}$ = +105.5 (c = 1.00, CH_2Cl_2); m. p. 96-98 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.41-7.38 (m, 2H), 7.25-7.23 (m, 3H), 4.54 (d, *J* = 7.7 Hz, 1H), 4.40 (d, *J* = 7.7 Hz, 1H), 4.24-4.19 (m, 2H), 4.07 (d, *J* = 6.5 Hz, 1H), 1.81-1.70 (m, 1H), 0.66 (d, *J* = 7.1 Hz, 3H), 0.06 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.9, 153.5, 133.8, 128.5, 128.1, 128.0, 63.6, 58.8, 43.5, 41.4, 28.0, 17.6, 13.3. HRMS: $C_{15}H_{17}NO_3S$ $[M+H]^+$ calcd.: 292.1007, found: 292.1012.

(S)-4-isopropyl-3-((2S,3S)-3-phenylthiirane-2-carbonyl)oxazolidin-2-one (*trans*-5a)



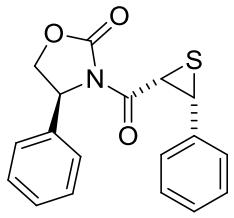
The title compound *trans*-**5a** was prepared from **1** (426 mg, 2.0 mmol) and benzaldehyde (610 μL, 6.0 mmol) according to the general procedure. Colorless oil, yield: 29 mg, 0.10 mmol, 5% (2nd fraction of the chromatographic column). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39-7.28 (m, 5H), 4.95 (d, *J* = 4.8 Hz, 1H), 4.54 (d, *J* = 4.8 Hz, 1H), 4.51-4.45 (m, 1H), 4.39-4.31 (m, 1H), 4.26 (dd, *J* = 9.1, 3.1 Hz, 1H), 2.44-2.31 (m, 1H), 0.93 (dd, *J* = 9.2, 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 168.8, 153.8, 136.7, 128.7, 128.2, 127.3, 63.7, 59.0, 41.3, 36.4, 28.6, 17.9, 14.8. HRMS: $C_{15}H_{17}NO_3S$ $[M+H]^+$ calcd.:292.1007, found: 292.15.

(S)-4-(tert-butyl)-3-((2S,3R)-3-phenylthiirane-2-carbonyl)oxazolidin-2-one (*cis*-6a)



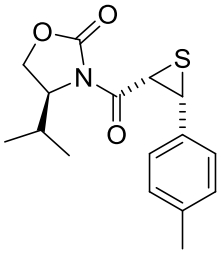
The title compound *cis*-**6a** was prepared from **2** (68 mg, 0.3 mmol) and benzaldehyde (91 μL, 0.9 mmol) according to the general procedure. White solid, yield: 55 mg, 0.181 mmol, 60%. $[\alpha]_D^{25}$ = +97.4 (c = 1.00, CH_2Cl_2); m. p. 112-115 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.49-7.44 (m, 2H), 7.29-7.20 (m, 3H), 4.51 (d, *J* = 7.7 Hz, 1H), 4.44 (d, *J* = 7.7 Hz, 1H), 4.23-4.18 (m, 2H), 4.13 (dd, *J* = 5.9, 3.0 Hz, 1H), 0.42 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.1, 154.7, 133.7, 128.9, 128.2, 128.0, 65.9, 62.1, 43.5, 41.8, 35.2, 25.1. HRMS: $C_{16}H_{19}NO_3S$ $[M+H]^+$ calcd.: 306.1164, found: 306.1171.

(S)-4-phenyl-3-((2S,3R)-3-phenylthiirane-2-carbonyl)oxazolidin-2-one (*cis*-7a)



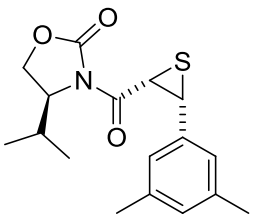
The title compound *cis*-**7a** was prepared from **3** (74 mg, 0.3 mmol) and benzaldehyde (91 μL, 0.9 mmol) according to the general procedure. White solid, yield: 45 mg, 0.14 mmol, 45%. $[\alpha]_D^{25}$ = +111.8 (c = 1.00, CH_2Cl_2); m. p. 108-110 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.49-7.05 (m, 9H), 6.57-6.48 (m, 1H), 5.29 (dd, *J* = 8.6, 3.4 Hz, 1H), 4.68 (t, *J* = 8.7 Hz, 1H), 4.60 (d, *J* = 7.6 Hz, 1H), 4.46 (d, *J* = 7.6 Hz, 1H), 4.13 (dd, *J* = 8.8, 3.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.8, 153.6, 138.0, 133.5, 129.0, 128.5, 128.3, 128.0, 125.1, 70.7, 57.8, 43.0, 41.3. HRMS: $C_{18}H_{15}NO_3S$ $[M+H]^+$ calcd.: 326.0851, found: 326.0858.

(S)-4-isopropyl-3-((2S,3R)-3-(p-tolyl)thiirane-2-carbonyl)oxazolidin-2-one (*cis*-5b)



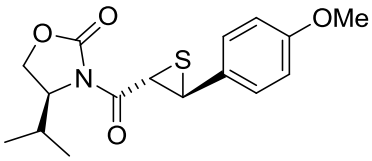
The title compound *cis*-**5b** was prepared from **1** (107 mg, 0.5 mmol) and 4-methylbenzaldehyde (177 μL, 1.5 mmol) according to the general procedure. White solid, yield: 92 mg, 0.30 mmol, 60%. $[\alpha]_D^{25}$ = +103.2 (c = 1.00, CH_2Cl_2); m. p. 101-103 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.27 (d, *J* = 7.9 Hz, 2H), 7.05 (d, *J* = 7.9 Hz, 2H), 4.51 (d, *J* = 7.6 Hz, 1H), 4.36 (d, *J* = 7.6 Hz, 1H), 4.26-4.18 (m, 2H), 4.07 (d, *J* = 6.6 Hz, 1H), 2.29 (s, 3H), 1.81-1.74 (m, 1H), 0.67 (d, *J* = 7.1 Hz, 3H), 0.05 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.2, 153.8, 137.8, 130.8, 128.8, 128.4, 63.6, 58.8, 43.6, 41.4, 28.0, 20.9, 17.7, 13.1. HRMS: $C_{16}H_{19}NO_3S$ $[M+H]^+$ calcd.: 306.1164, found: 306.1164.

(S)-3-((2S,3R)-3-(3,5-dimethylphenyl)thiirane-2-carbonyl)-4-isopropyloxazolidin-2-one (*cis*-5c)



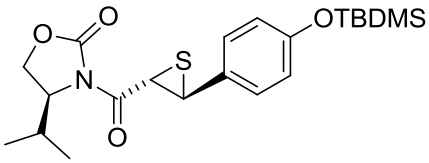
The title compound *cis*-**5c** was prepared from **1** (107 mg, 0.5 mmol) and 3,5-dimethylbenzaldehyde (202 μL, 1.5 mmol) according to the general procedure. Colorless oil, yield: 98 mg, 0.31 mmol, 61%. $[\alpha]_D^{25}$ = +66.1 (c = 1.00, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 6.98 (s, 2H), 6.85 (s, 1H), 4.52 (d, *J* = 7.7 Hz, 1H), 4.35-4.24 (m, 2H), 4.21 (d, *J* = 8.3 Hz, 1H), 4.08 (dd, *J* = 8.1, 1.5 Hz, 1H), 2.24 (s, 6H), 1.83-1.73 (m, 1H), 0.68 (d, *J* = 7.1 Hz, 3H), 0.11 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.1, 153.8, 137.7, 133.8, 129.7, 126.2, 63.8, 58.8, 43.5, 41.5, 28.2, 21.1, 17.6, 13.3. HRMS: $C_{17}H_{21}NO_3S$ $[M+H]^+$ calcd.: 320.1320, found: 320.1333.

(S)-4-isopropyl-3-((2S,3S)-3-(4-methoxyphenyl)thiirane-2-carbonyl)oxazolidin-2-one (*trans*-5d)



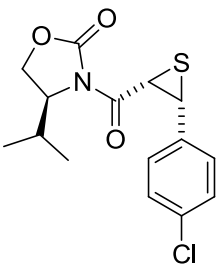
The title compound *trans*-**5d** was prepared from **1** (107 mg, 0.5 mmol) and 4-methoxybenzaldehyde (183 μL, 1.5 mmol) according to the general procedure. Colorless oil, yield: 98 mg, 0.30 mmol, 61%. $[\alpha]_D^{25}$ = -41.6 (c = 1.00, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.29 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.93 (d, *J* = 4.9 Hz, 1H), 4.52 (d, *J* = 4.9 Hz, 1H), 4.51-4.44 (m, 1H), 4.38-4.30 (m, 1H), 4.26 (dd, *J* = 9.1, 3.1 Hz, 1H), 3.80 (s, 3H), 2.43-2.32 (m, 1H), 0.92 (dd, *J* = 8.8, 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.0, 159.6, 146.0, 130.4, 128.4, 114.1, 63.6, 59.0, 55.3, 41.4, 36.1, 28.5, 17.9, 14.7. HRMS: $C_{16}H_{19}NO_4S$ $[M+H-S]^+$ calcd.: 290.1387, found: 290.1392.

(S)-3-((2S,3S)-3-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)thiirane-2-carbonyl)-4-isopropyloxazolidin-2-one (*trans*-5e)



The title compound *trans*-**5e** was prepared from **1** (107 mg, 0.5 mmol) and 4-((*tert*-butyldimethylsilyl)oxy)benzaldehyde (371 μL, 1.5 mmol) according to the general procedure. Colorless oil, yield: 64 mg, 0.15 mmol, 31%. $[\alpha]_D^{25}$ = -69.1 (c = 1.00, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.22 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.6 Hz, 2H), 4.92 (d, *J* = 4.9 Hz, 1H), 4.51 (d, *J* = 4.9 Hz, 1H), 4.49-4.43 (m, 1H), 4.34 (t, *J* = 8.6 Hz, 1H), 4.25 (dd, *J* = 9.0, 3.1 Hz, 1H), 2.43-2.31 (m, 1H), 0.98 (s, 9H), 0.92 (dd, *J* = 7.9, 7.1 Hz, 6H), 0.19 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 169.0, 155.8, 153.8, 129.2, 128.4, 120.3, 63.7, 59.0, 41.5, 36.2, 28.6, 25.6, 18.2, 17.9, 14.8, -4.4. HRMS: $C_{21}H_{31}NO_4SSi$ $[M+H-S]^+$ calcd.: 390.2101, found: 390.2117.

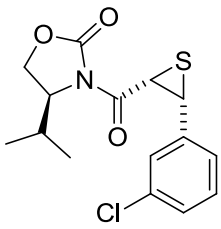
(S)-3-((2S,3R)-3-(4-chlorophenyl)thiirane-2-carbonyl)-4-isopropyloxazolidin-2-one (*cis*-5f)



The title compound *cis*-**5f** was prepared from **1** (107 mg, 0.5 mmol) and 4-chlorobenzaldehyde (211 mg, 1.5 mmol) according to the general procedure. White solid, yield: 102 mg, 0.31 mmol, 63%. $[\alpha]_D^{25}$ = +94.4 (c = 1.00, CH_2Cl_2); m. p. 106-108 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.31 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 4.49 (d, *J* = 7.6 Hz, 1H), 4.32 (d, *J* = 7.6 Hz, 1H), 4.27-4.18 (m, 2H), 4.12-4.03 (m, 1H), 1.84-1.70

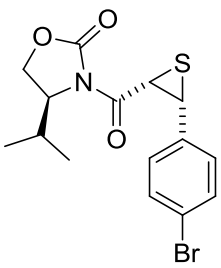
(m, 1H), 0.67 (d, *J* = 7.1 Hz, 3H), 0.09 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.8, 153.8, 134.0, 132.6, 129.9, 128.2, 63.7, 58.8, 43.5, 40.6, 28.0, 17.6, 13.1. HRMS: $C_{15}H_{16}ClNO_3S$ $[M+H]^+$ calcd.: 326.0618, found: 326.0631.

(S)-3-((2S,3R)-3-(3-chlorophenyl)thiirane-2-carbonyl)-4-isopropyloxazolidin-2-one (*cis*-5g)



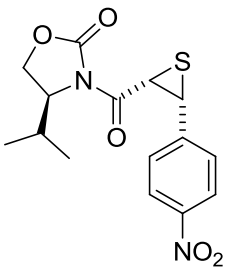
The title compound *cis*-**5g** was prepared from **1** (107 mg, 0.5 mmol) and 3-chlorobenzaldehyde (211 mg, 1.5 mmol) according to the general procedure. White solid, yield: 93 mg, 0.28 mmol, 57%. $[\alpha]_D^{25}$ = +121.7 (c = 1.00, CH_2Cl_2); m. p. 83-88 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.38-7.35 (m, 1H), 7.32-7.28 (m, 1H), 7.24-7.18 (m, 2H), 4.54 (d, *J* = 7.6 Hz, 1H), 4.32 (d, *J* = 7.6 Hz, 1H), 4.28-4.20 (m, 2H), 4.10 (d, *J* = 6.5 Hz, 1H), 1.87-1.75 (m, 1H), 0.69 (d, *J* = 7.0 Hz, 3H), 0.15 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.7, 153.8, 136.3, 134.3, 129.4, 128.3, 127.2, 63.8, 58.9, 43.4, 40.5, 28.2, 17.7, 13.4. HRMS: $C_{15}H_{16}ClNO_3S$ $[M+H-S]^+$ calcd.: 294.0897, found: 294.0888.

(S)-3-((2S,3R)-3-(4-bromophenyl)thiirane-2-carbonyl)-4-isopropyloxazolidin-2-one (*cis*-5h)



The title compound *cis*-**5h** was prepared from **1** (107 mg, 0.5 mmol) and 4-bromobenzaldehyde (278 mg, 1.5 mmol) according to the general procedure. White solid, yield: 102 mg, 0.28 mmol, 56%. $[\alpha]_D^{25}$ = +85.9 (c = 1.00, CH_2Cl_2); m. p. 82-85 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.5 Hz, 2H), 4.51 (d, *J* = 7.6 Hz, 1H), 4.33 (d, *J* = 7.6 Hz, 1H), 4.28-4.19 (m, 2H), 4.10 (d, *J* = 4.2 Hz, 1H), 1.85-1.72 (m, 1H), 0.70 (d, *J* = 7.1 Hz, 3H), 0.11 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.7, 153.7, 133.1, 131.1, 130.2, 122.1, 63.6, 58.8, 43.5, 40.6, 28.0, 17.6, 13.0. HRMS: $C_{15}H_{16}BrNO_3S$ $[M+H]^+$ calcd.: 340.0371, found: 340.0385.

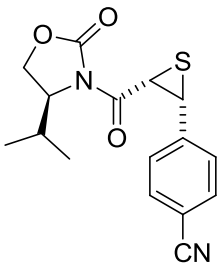
(S)-4-isopropyl-3-((2S,3R)-3-(4-nitrophenyl)thiirane-2-carbonyl)oxazolidin-2-one (*cis*-5i)



The title compound *cis*-**5i** was prepared from **1** (107 mg, 0.5 mmol) and 4-nitrobenzaldehyde (227 mg, 1.5 mmol) according to the general procedure. Yellow solid, yield: 103 mg, 0.30 mmol, 61%. $[\alpha]_D^{25}$ = +80.2 (c = 1.00, CH_2Cl_2); m. p. 104-105 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ:

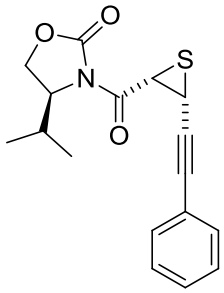
8.11 (d, *J* = 8.9 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 4.59 (d, *J* = 7.6 Hz, 1H), 4.42 (d, *J* = 7.6 Hz, 1H), 4.27-4.20 (m, 2H), 4.11-4.06 (m, 1H), 1.83-1.71 (m, 1H), 0.66 (d, *J* = 7.0 Hz, 3H), 0.05 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.4, 153.8, 147.8, 141.8, 129.7, 123.2, 63.8, 58.9, 43.5, 40.3, 28.0, 17.6, 13.3. HRMS: $C_{15}H_{16}N_2O_5S$ $[M+H-S]^+$ calcd.: 305.1137, found: 305.1139.

4-((2R,3S)-3-((S)-4-isopropyl-2-oxooxazolidine-3-carbonyl)thiiran-2-yl)benzonitrile (*cis*-5j)



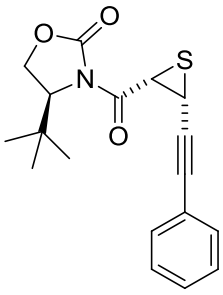
The title compound *cis*-**5j** was prepared from **1** (107 mg, 0.5 mmol) and 4-cyanobenzaldehyde (197 mg, 1.5 mmol) according to the general procedure. Yellow solid, yield: 88 mg, 0.28 mmol, 56%. $[\alpha]_D^{25}$ = +73.0 (c = 1.00, CH_2Cl_2); m. p. 102-106 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.60-7.49 (m, 4H), 4.57 (d, *J* = 7.6 Hz, 1H), 4.39 (d, *J* = 7.6 Hz, 1H), 4.28-4.21 (m, 2H), 4.14-4.06 (m, 1H), 1.83-1.70 (m, 1H), 0.69 (d, *J* = 7.1 Hz, 3H), 0.09 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 164.4, 153.8, 139.7, 131.8, 129.5, 118.3, 111.9, 63.8, 58.8, 43.5, 40.5, 28.0, 17.5, 13.2. HRMS: $C_{16}H_{16}N_2O_3S$ $[M+H-S]^+$ calcd.: 285.1239, found: 285.1244.

(S)-4-isopropyl-3-((2S,3R)-3-(phenylethynyl)thiirane-2-carbonyl)oxazolidin-2-one (*cis*-5k)



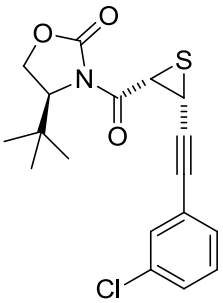
The title compound *cis*-**5k** was prepared from **1** (107 mg, 0.5 mmol) and phenylpropargyl aldehyde (183 μL, 1.5 mmol) according to the general procedure. Yellow solid, yield: 102 mg, 0.32 mmol, 65%. $[\alpha]_D^{25}$ = +93.3 (c = 1.00, CH_2Cl_2); m. p. 93-95 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.40-7.34 (m, 2H), 7.32-7.25 (m, 3H), 4.71 (d, *J* = 6.9 Hz, 1H), 4.53-4.46 (m, 1H), 4.40-4.32 (m, 1H), 4.26 (dd, *J* = 9.1, 2.8 Hz, 1H), 3.98 (d, *J* = 6.9 Hz, 1H), 2.46-2.33 (m, 1H), 0.87 (d, *J* = 7.1 Hz, 3H), 0.76 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.3, 154.1, 132.1, 131.7, 128.6, 128.1, 84.4, 83.6, 64.0, 59.2, 40.0, 28.3, 26.4, 17.8, 14.3. HRMS: $C_{17}H_{17}NO_3S$ $[M+H-S]^+$ calcd.: 284.1287, found: 284.1287.

(S)-4-(tert-butyl)-3-((2S,3R)-3-(phenylethynyl)thiirane-2-carbonyl)oxazolidin-2-one (*cis*-6k)



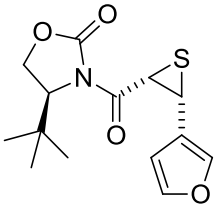
The title compound *cis*-**6k** was prepared from **2** (114 mg, 0.5 mmol) and phenylpropargyl aldehyde (183 μL, 1.5 mmol) according to the general procedure. Orange solid, yield: 123 mg, 0.38 mmol, 75%. $[\alpha]_D^{25}$ = +59.8 (c = 1.00, CH_2Cl_2); m. p. 92-94 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.39-7.33 (m, 2H), 7.30-7.22 (m, 3H), 4.70 (d, *J* = 6.9 Hz, 1H), 4.45 (dd, *J* = 5.5, 3.6 Hz, 1H), 4.38-4.32 (m, 2H), 4.01 (d, *J* = 6.9 Hz, 1H), 0.90 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.6, 154.7, 132.1, 131.9, 128.6, 128.1, 84.6, 84.2, 66.0, 62.2, 39.7, 35.8, 27.0, 25.6. HRMS: $C_{18}H_{19}NO_3S$ $[M+H-S]^+$ calcd.: 298.1438, found: 298.1456.

(S)-4-(tert-butyl)-3-((2S,3R)-3-((3-chlorophenyl)ethynyl)thiirane-2-carbonyl)oxazolidin-2-one (*cis*-6l)



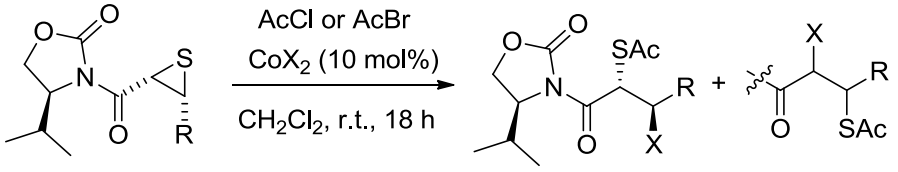
The title compound *cis*-**6l** was prepared from **2** (114 mg, 0.5 mmol) and 3-chlorophenylpropargyl aldehyde (247 mg, 1.5 mmol) according to the general procedure. Yellow oil, yield: 110 mg, 0.30 mmol, 60%. $[\alpha]_D^{25}$ = +139.6 (c = 1.00, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.37-7.34 (m, 1H), 7.30-7.16 (m, 3H), 4.72 (d, *J* = 6.9 Hz, 1H), 4.48-4.43 (m, 1H), 4.39-4.34 (m, 2H), 3.98 (d, *J* = 6.9 Hz, 1H), 0.92 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.5, 154.7, 134.0, 131.8, 130.0, 129.4, 128.9, 123.8, 86.0, 82.6, 66.0, 62.2, 39.4, 35.8, 26.6, 25.6. HRMS: $C_{18}H_{18}ClNO_3S$ $[M+H-S]^+$ calcd.: 332.1048, found: 332.1068.

(S)-4-(tert-butyl)-3-((2S,3R)-3-(furan-3-yl)thiirane-2-carbonyl)oxazolidin-2-one (*cis*-6m)



The title compound *cis*-**6m** was prepared from **2** (114 mg, 0.5 mmol) and 3-furaldehyde (130 μL, 1.5 mmol) according to the general procedure. Colorless oil, yield: 103 mg, 0.35 mmol, 70%. $[\alpha]_D^{25}$ = +101.2 (c = 1.00, CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.40-7.37 (m, 1H), 7.29 (t, *J* = 1.7 Hz, 1H), 6.45 (dd, *J* = 1.7, 0.6 Hz, 1H), 4.41 (d, *J* = 7.4 Hz, 1H), 4.29-4.21 (m, 3H), 4.18 (d, *J* = 7.3 Hz, 1H), 0.64 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 165.4, 154.8, 143.0, 142.0, 120.7, 111.6, 66.0, 62.2, 43.1, 35.4, 33.1, 25.4. HRMS: $C_{14}H_{17}NO_4S$ $[M+H-S]^+$ calcd.: 264.1230, found: 264.1243.

3.3. General procedure for ring opening of adducts *cis*-**5a** and cis-**5h.**[7]

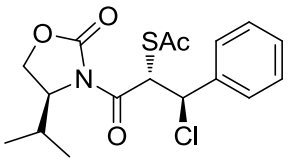


cis-**5a** R = Ph
cis-**5h** R = 4-Br-Ph

8a R = Ph X = Cl 88% (95:5)
8b R = Ph X = Br 70% (90:10)
8c R= 4-Br-Ph X = Cl 65% (90:10)

To a mixture of the corresponding Thiirane (1.0 mmol) and anhydrous $CoCl_2$ or $CoBr_2$ (0.10 mmol, 10 mol %) in dry CH_2Cl_2 (7 mL) at 0 ºC, was added acetyl chloride or acetyl bromide (2.0 mmol) under argon atmosphere. The reaction was stirred overnight at room temperature and afterwards diluted with CH_2Cl_2 (10 mL) and quenched with saturated $NaHCO_3$. The reaction mixture was washed with water and brine and the organic layer was dried with $MgSO_4$ and filtered. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (eluent: AcOEt/Hexane 1:4) to afford the desired product.

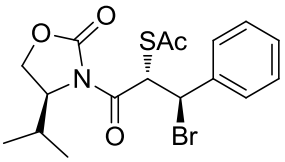
S-((1R,2S)-1-chloro-3-((S)-4-isopropyl-2-oxooxazolidin-3-yl)-3-oxo-1-phenylpropan-2-yl) ethanethioate (8a)



The title compound **8a** was prepared from the compound **5a** (291 mg, 1.0 mmol), $CoCl_2$ (13 mg, 0.10 mmol) and acetyl chloride (142 μL, 2.0 mmol) according to the general procedure. White solid, yield: 327 mg, 0.88 mmol, 88%. $[\alpha]_D^{25}$ = +37.5 (c = 1.00, CH_2Cl_2); m. p. 141-142 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.52- 7.46 (m, 2H), 7.39-7.31 (m, 3H), 6.47 (d, *J* = 11.1 Hz, 1H), 5.23 (d, *J* = 11.2 Hz, 1H), 4.55-4.48 (m, 1H), 4.35 (t, *J* = 8.5 Hz, 1H), 4.27 (dd, *J* = 9.0, 2.9 Hz, 1H), 2.52-2.40 (m, 1H), 2.08 (s, 3H), 0.97 (d, *J* = 7.0 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.6, 169.7, 153.6, 137.0, 129.3, 128.4, 128.4, 63.5, 61.6, 59.3, 49.4, 29.6, 28.6, 18.0, 15.0. HRMS: $C_{17}H_{20}ClNO_4S$ $[M+H]^+$ calcd.: 370.0874, found: 370.0869.

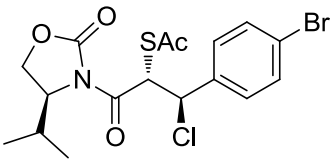
S-((1R,2S)-1-bromo-3-((S)-4-isopropyl-2-oxooxazolidin-3-yl)-3-oxo-1-phenylpropan-2-yl) ethanethioate (8b)

[7] a) Iranpoor, N.; Firouzabadi, H.; Jafari, A. A. *Synth. Commun.* **2003**, *33*, 2321-2327. b) Amer, H.; Mereiter, K.; Stanetty, C.; Hofinger, A.; Czollner, L.; Beseda, I.; Jordis, U.; Kueenburg, B.; Claßen-Houben, D.; Kosma, P. *Tetrahedron* **2010**, *66*, 4390-4402.



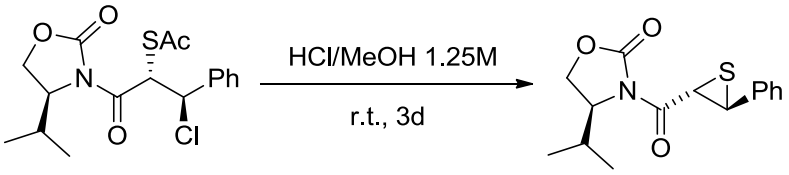
The title compound **8b** was prepared from the compound **5a** (291 mg, 1.0 mmol), $CoBr_2$ (22 mg, 0.10 mmol) and acetyl bromide (148 μL, 2.0 mmol) according to the general procedure. White solid, yield: 289 mg, 0.70 mmol, 70%. $[\alpha]_D^{25}$ = +17.9 (c = 1.00, CH_2Cl_2); m. p. 143-148 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.52- 7.46 (m, 2H), 7.37-7.28 (m, 3H), 6.63 (d, *J* = 11.7 Hz, 1H), 5.30 (d, *J* = 11.6 Hz, 1H), 4.55-4.48 (m, 1H), 4.35 (t, *J* = 8.5 Hz, 1H), 4.28 (dd, *J* = 9.0, 2.9 Hz, 1H), 2.54-2.43 (m, 1H), 2.08 (s, 3H), 0.99 (dd, *J* = 6.9, 5.4 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.2, 169.6, 153.4, 137.4, 129.1, 128.5, 128.4, 63.4, 59.3, 51.4, 48.8, 29.4, 28.5, 17.9, 15.0. HRMS: $C_{17}H_{20}BrNO_4S$ $[M+H]^+$ calcd.: 414.0369, found: 414.0379.

S-((1R,2S)-1-(4-bromophenyl)-1-chloro-3-((S)-4-isopropyl-2-oxooxazolidin-3-yl)-3-oxopropan-2-yl) ethanethioate (8c)



The title compound **8c** was prepared from the compound **5i** (370 mg, 1.0 mmol), $CoCl_2$ (13 mg, 0.10 mmol) and acetyl chloride (142 μL, 2.0 mmol) according to the general procedure. White solid, yield: 292 mg, 0.65 mmol, 65%. $[\alpha]_D^{25}$ = +21.9 (c = 1.00, CH_2Cl_2); m. p. 63-64 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.46 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 6.41 (d, *J* = 10.3 Hz, 1H), 5.19 (d, *J* = 11.1 Hz, 1H), 4.52-4.45 (m, 1H), 4.33 (t, *J* = 8.5 Hz, 1H), 4.25 (dd, *J* = 9.0, 2.9 Hz, 1H), 2.50-2.35 (m, 1H), 2.09 (s, 3H), 0.94 (dd, *J* = 7.0, 2.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.0, 169.2, 153.4, 136.1, 131.5, 130.1, 123.3, 63.5, 60.9, 59.3, 49.1, 29.6, 28.5, 17.9, 14.9. HRMS: $C_{17}H_{19}BrClNO_4S$ $[M+H]^+$ calcd.: 447.9979, found: 447.9969.

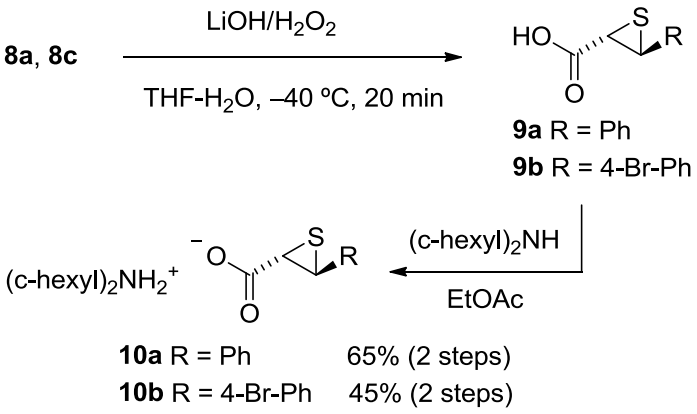
3.4. Acid-promoted cyclisization of 8a to *trans*-5a.



8a *trans*-**5a**

To an ice cold solution of **8a** (111 mg, 0.3 mmol) in methanol (1 mL) was added a solution of HCl in methanol (1.25M, 1 mL). The mixture was stirred at room temperature for 3 days and then concentrated under reduced pressure. Purification by column chromatography (eluent: AcOEt/Hexane 1:4) gave pure *trans*-**5a** compound as an oil in 70% yield (61 mg, 0.21 mmol).

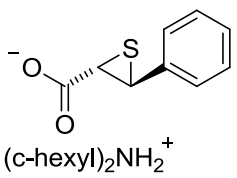
3.5. Removal of the oxazolidinone auxiliary.[8]



To a solution of LiOH (4 eq, 12 mg, 0.5 mmol) in THF (2 mL) and water (0.5 mL) at 0ºC was added a solution of 30% H_2O_2 (12 eq, 0.17 mL, 1.5 mmol) and the resulting mixture was stirred at the same temperature for 15 min. Then was cooled to -40 ºC and a solution of the corresponding adduct **8** (1 eq, 0.125 mmol) in 1.5 ml of THF was added. The reaction mixture was stirred at the same temperature for 20 min and afterwards 10 mL of water was added. The resulting mixture was extracted with CH_2Cl_2 (3 x 30 mL) and the combined organic layers were dried with $MgSO_4$ and filtered. The solvent was removed under reduced pressure to give the corresponding (S)-4-isopropyloxazolidin-2-one.

The aqueous layer was slowly acidified by dropwise addition of 6N HCl and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried with $MgSO_4$, filtered and the solvent was removed under reduced pressure to give the corresponding carboxylic acid **9** as an oil. The product was dissolved in EtOAc (1 mL) and dicyclohexylamine (40 μL, 0.2 mmol) was added dropwise via syringe. The derived dicyclohexylamine salt **10** was obtained as a solid by slow precipitation (14 h standing) from this solution.

Dicyclohexylammonium (2S,3S)-3-phenylthiirane-2-carboxylate (10a)

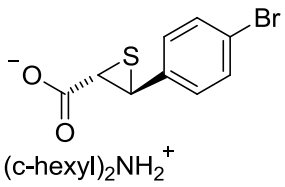


The title compound **10a** was prepared from the product **8a** (46 mg, 0.125 mmol) according to the general procedure. White solid, yield: 29 mg, 0.081 mmol, 65%. $[\alpha]_D^{25}$ = -28.4 (c = 1.00, CH_2Cl_2); m. p. 163-165 ºC.

[8] Adapted from: (a) Palomo, C.; Oiarbide, M.; Sharma, A. K.; González-Rego, M. C.; Linden, A.; García, J. M.; González, A. *J. Org. Chem.* **2000**, *65*, 9007-9012. (b) Palomo, C.; Oiarbide, M.; Dias, F.; Ortiz, A.; Linden, A. *J. Am. Chem. Soc.* **2001**, *123*, 5602-5603.

^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.32-7.20 (m, 5H), 4.11 (d, *J* = 5.0 Hz, 1H), 3.50-3.46 (m, 1H), 3.03-2.91 (m, 2H), 2.08-1.96 (m, 4H), 1.86-1.74 (m, 4H), 1.67-1.58 (m, 2H), 1.55-1.38 (m, 4H), 1.31-1.13 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.9, 138.8, 128.4, 127.5, 127.2, 52.9, 42.3, 42.0, 29.4, 29.4, 25.2, 24.8. HRMS: $C_{21}H_{31}NO_2S$ $[M+2H-C_{12}H_{22}NH_2]^+$ calcd.: 181.0318, found: 181.0364.

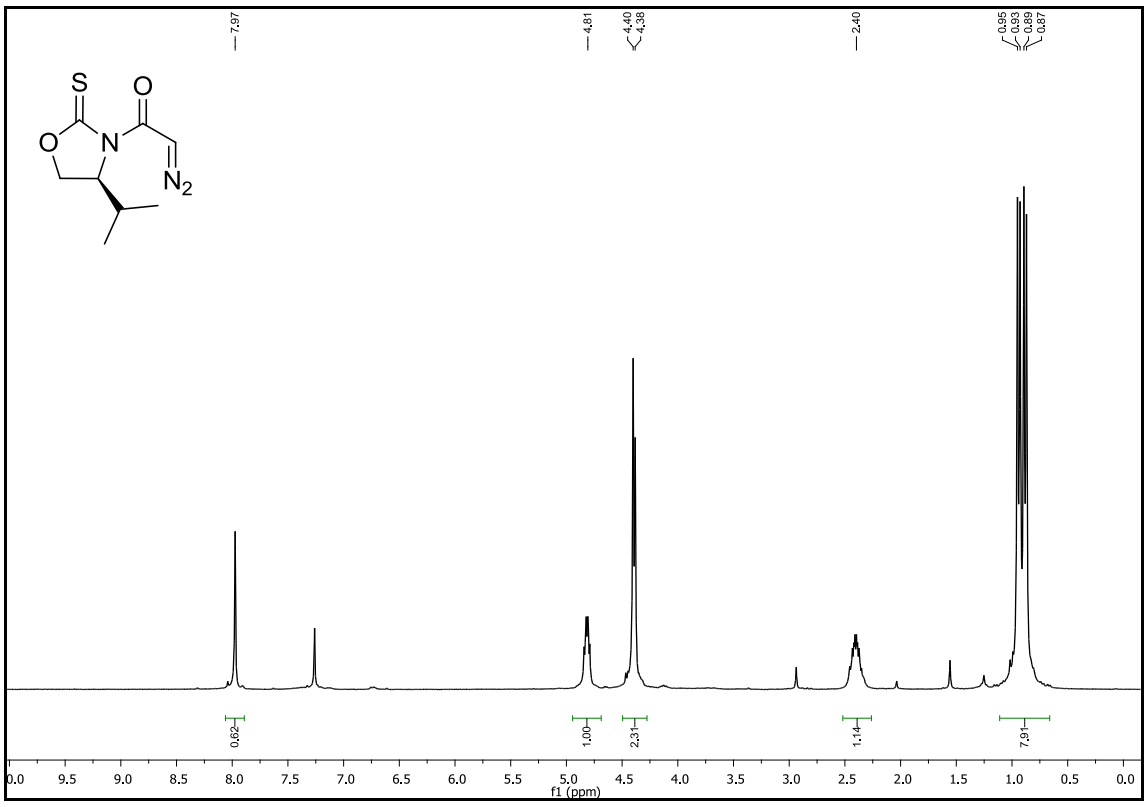
Dicyclohexylammonium (2S,3S)-3-(4-bromophenyl)thiirane-2-carboxylate (10b)

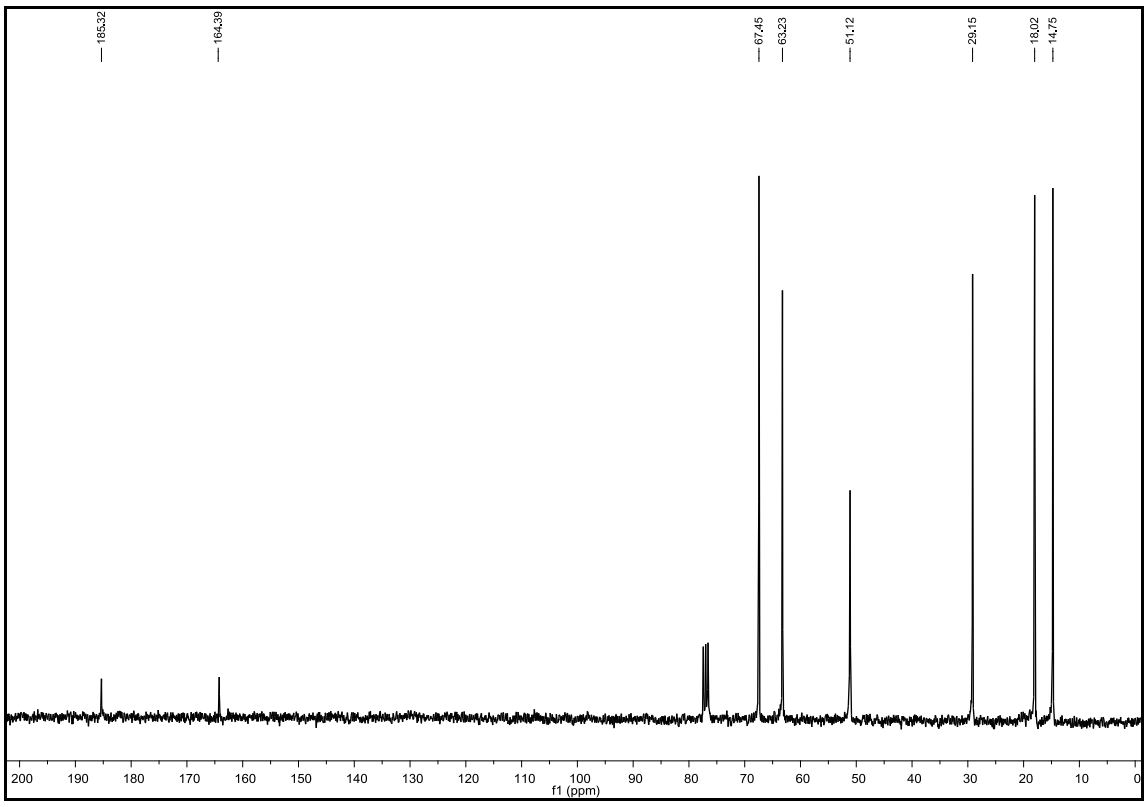


The title compound **10b** was prepared from the product **8c** (56 mg, 0.125 mmol) according to the general procedure. White solid, yield: 25 mg, 0.056 mmol, 45%. $[\alpha]_D^{25}$ = -31.7 (c = 1.00, CH_2Cl_2); m. p. 184-186 ºC. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.40 (d, *J* = 8.5 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 4.04 (d, *J* = 5.0 Hz, 1H), 3.39 (d, *J* = 5.0 Hz, 1H), 3.02-2.88 (m, 2H), 2.08-1.94 (m, 4H), 1.87-1.73 (m, 4H), 1.67-1.58 (m, 2H), 1.53-1.36 (m, 4H), 1.33-1.13 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.7, 138.0, 131.5, 128.8, 121.3, 53.0, 42.3, 41.2, 29.5, 29.4, 25.1, 24.8. HRMS: $C_{21}H_{30}BrNO_2S$ $[M+2H-S-C_{12}H_{22}NH_2]^+$ calcd.: 226.9702, found: 226.9715.

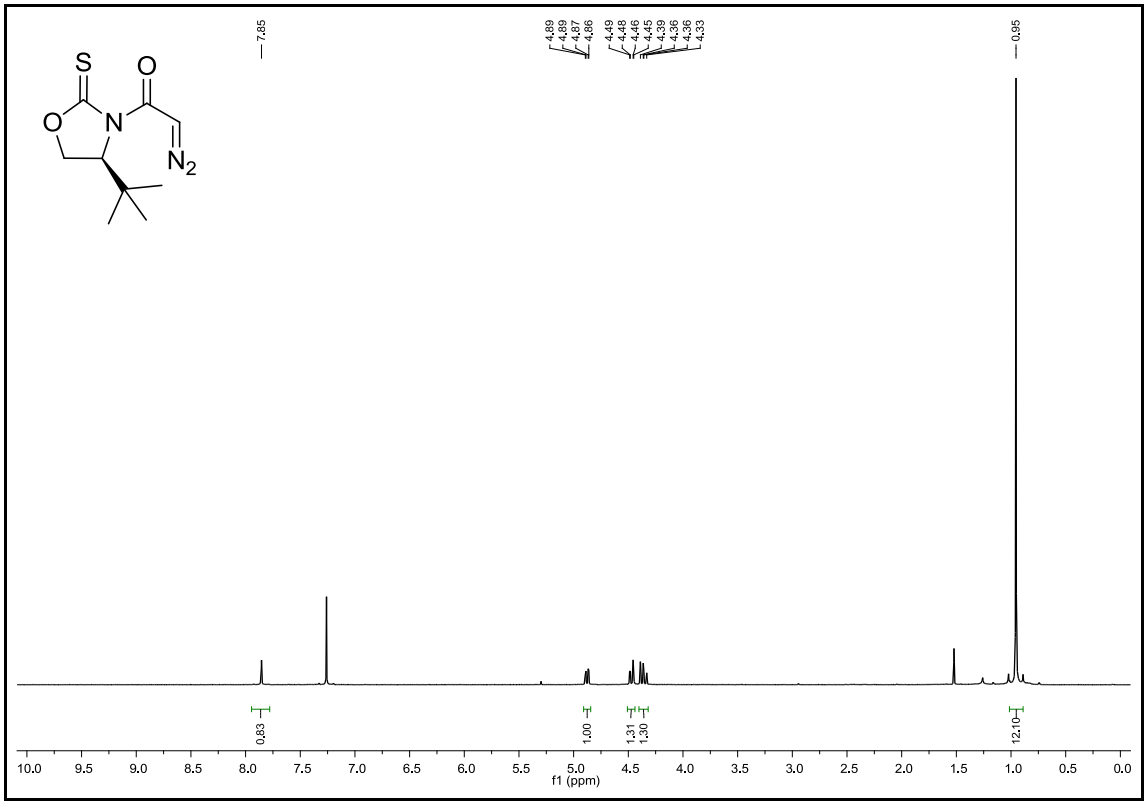
4. ^{1}H and ^{13}C NMR Spectra.

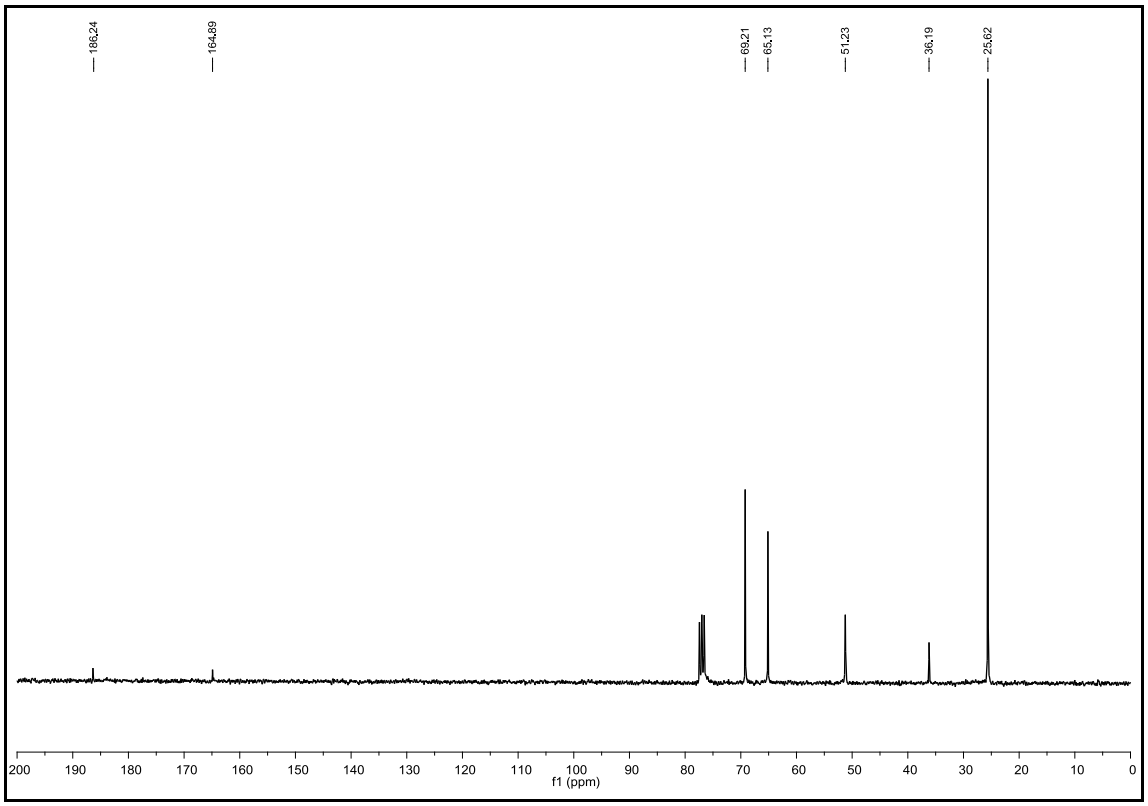
(S)-2-diazo-1-(4-isopropyl-2-thioxooxazolidin-3-yl)ethanone



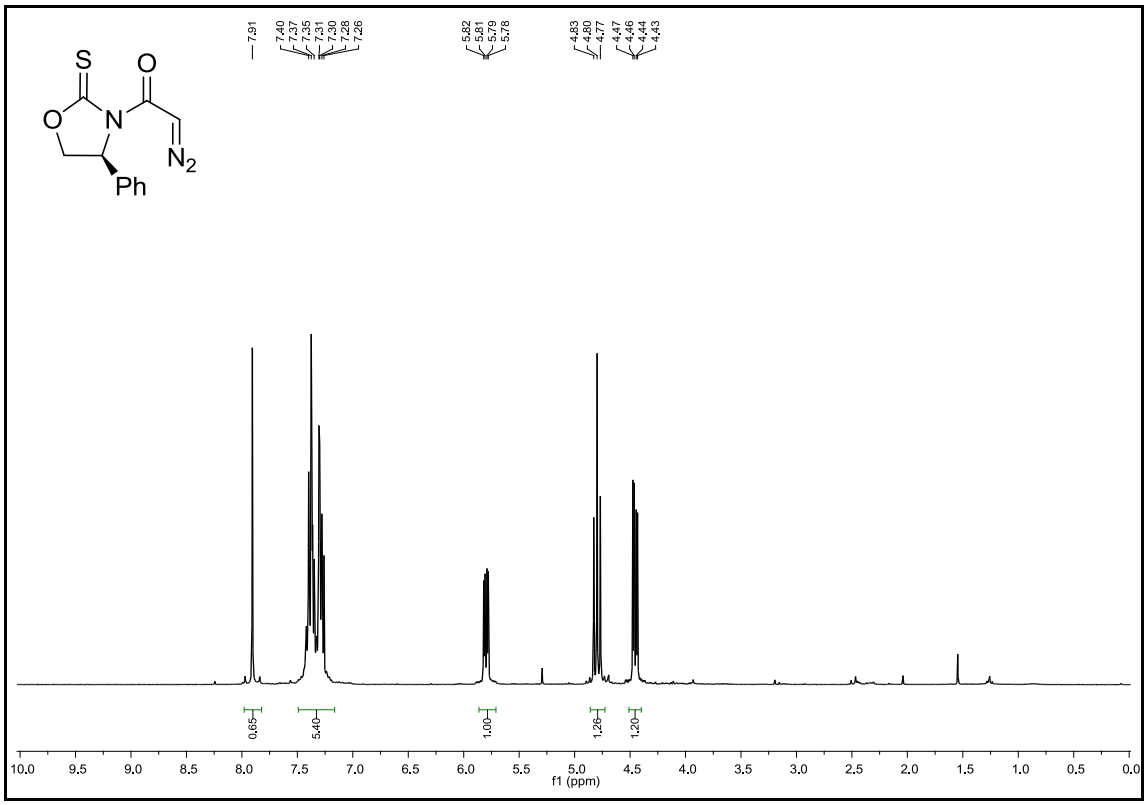


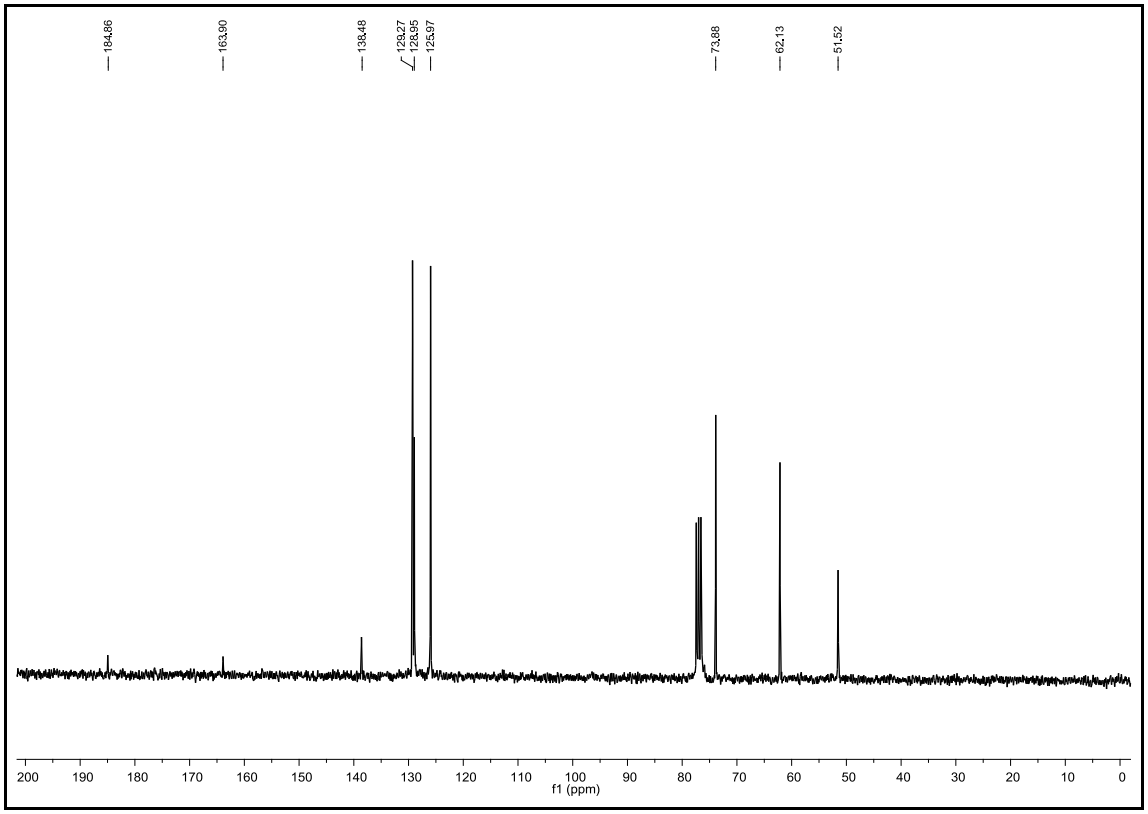
(S)-1-(4-(tert-butyl)-2-thioxooxazolidin-3-yl)-2-diazoethanone



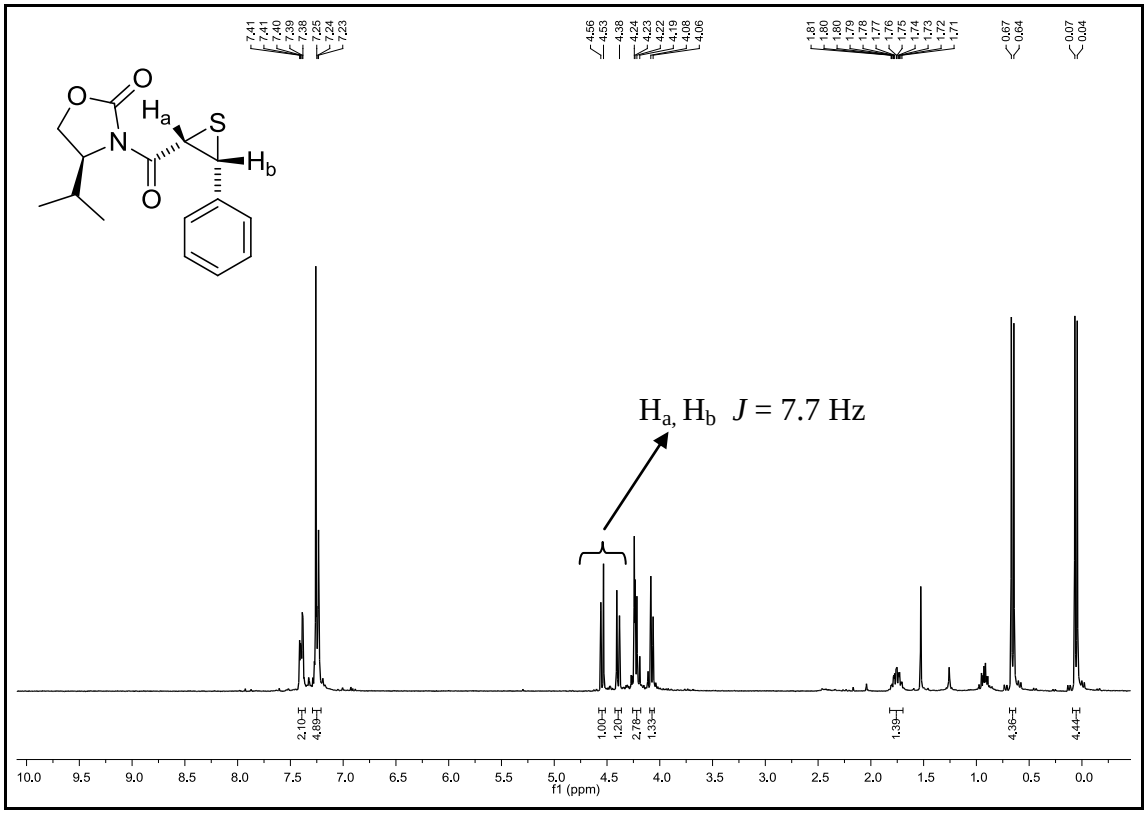


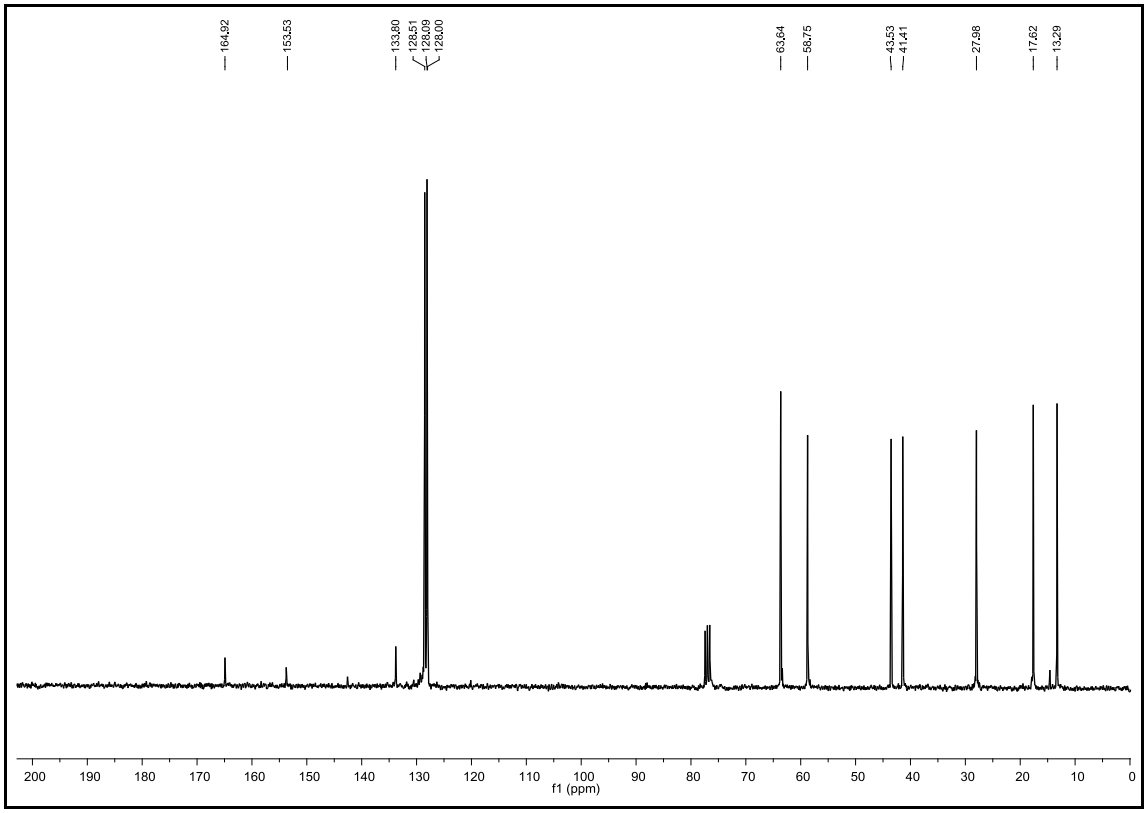
(S)-2-diazo-1-(4-phenyl-2-thioxooxazolidin-3-yl)ethanone





(S)-4-isopropyl-3-((2S,3R)-3-phenylthiirane-2-carbonyl)oxazolidin-2-one





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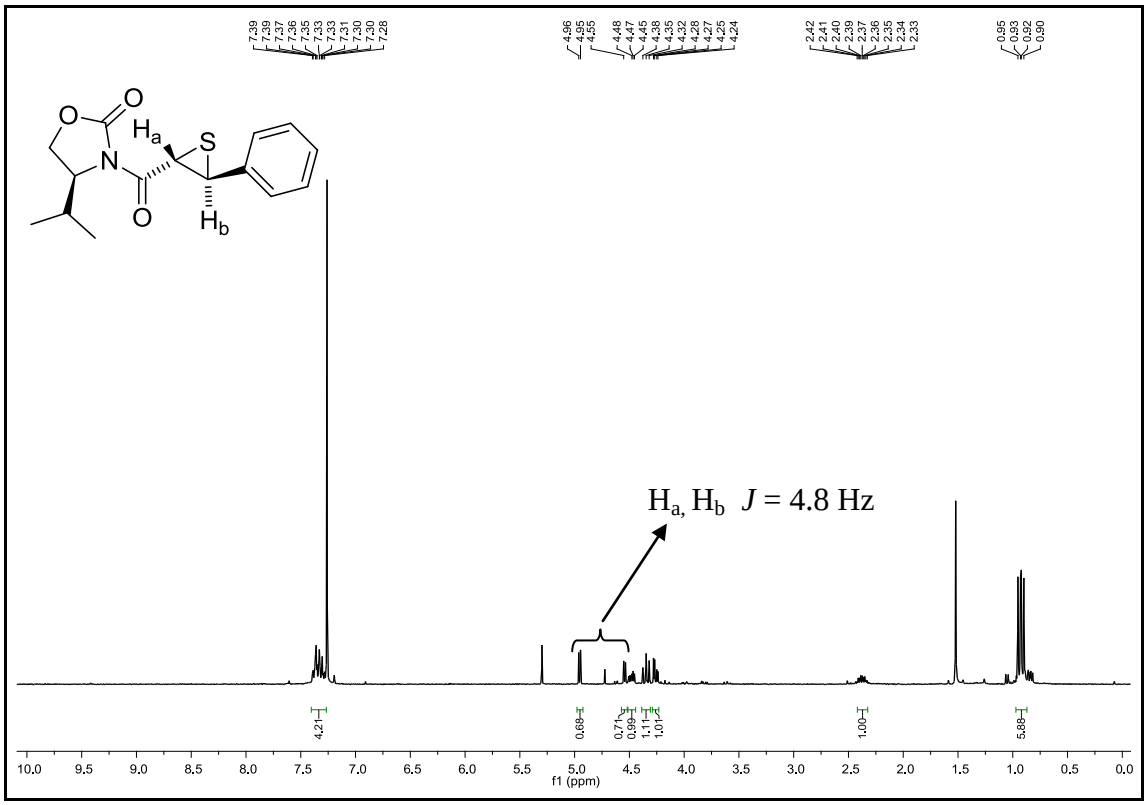
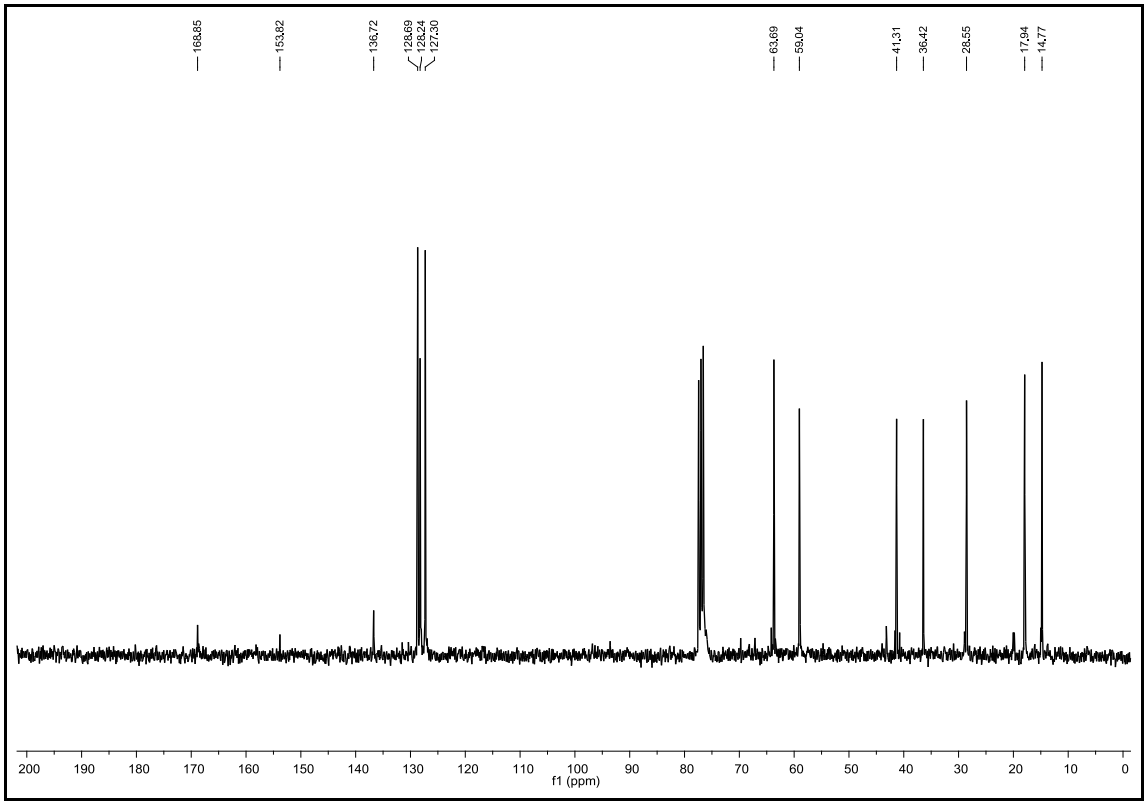
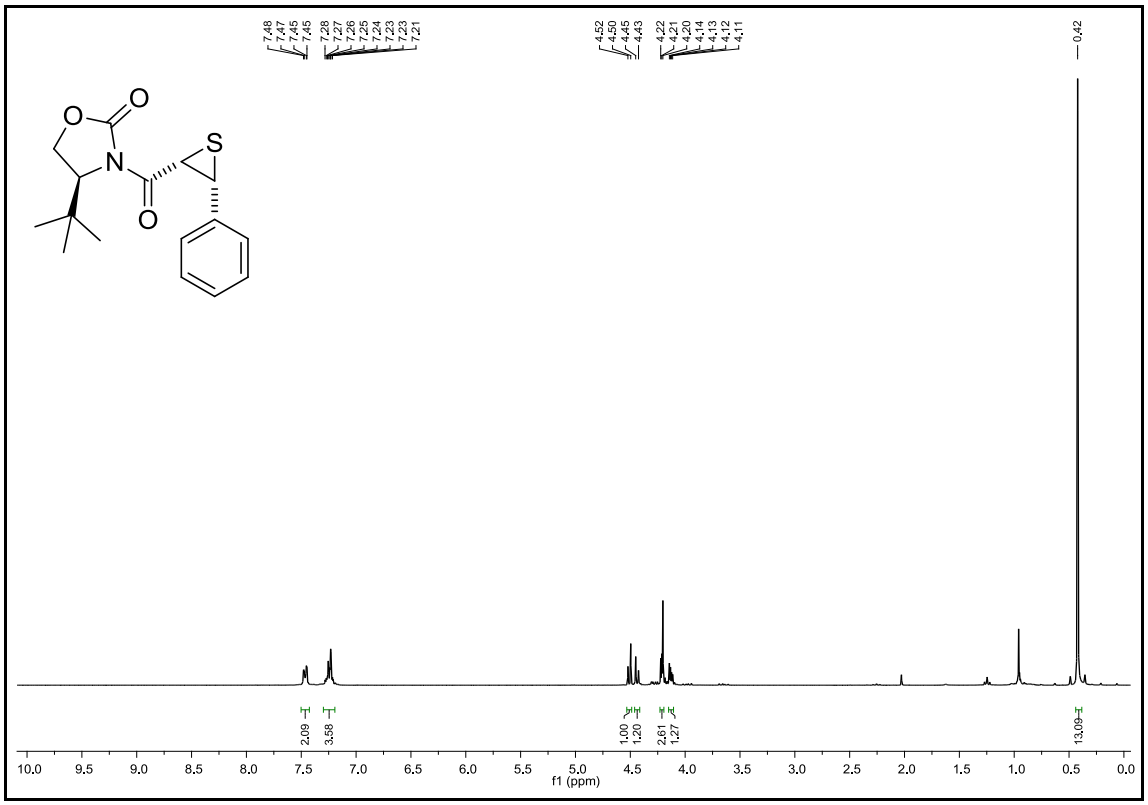
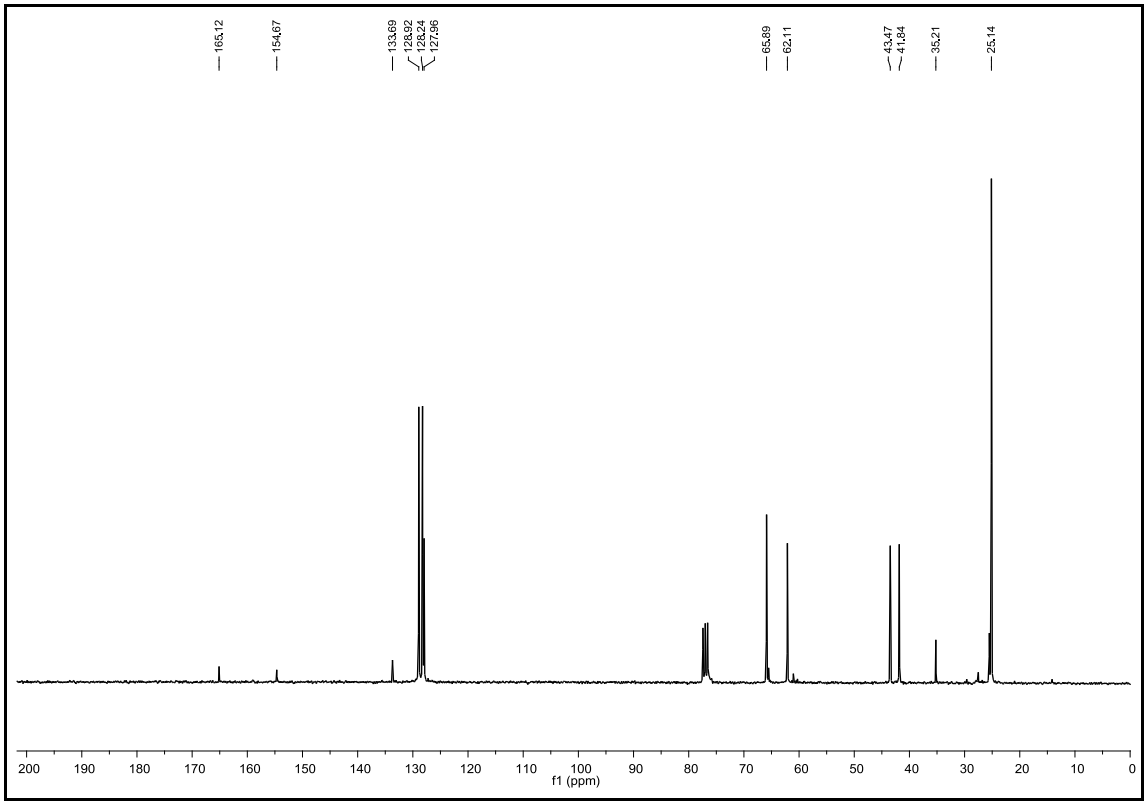


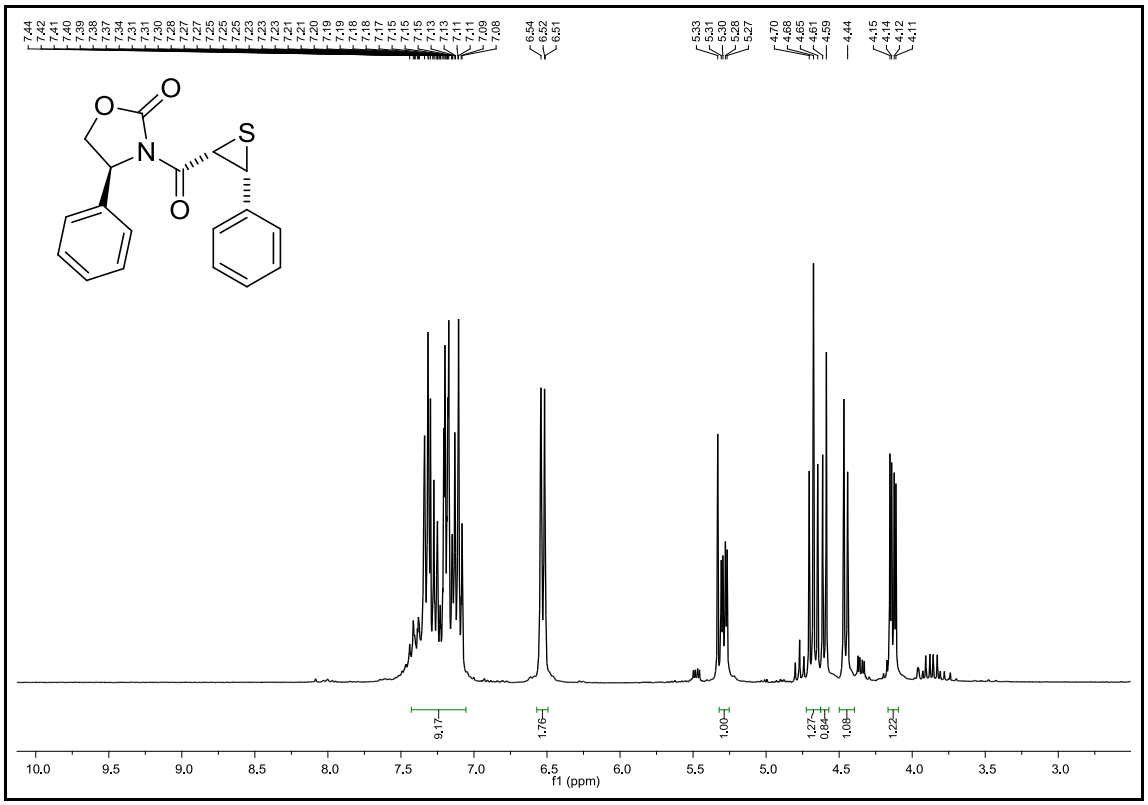


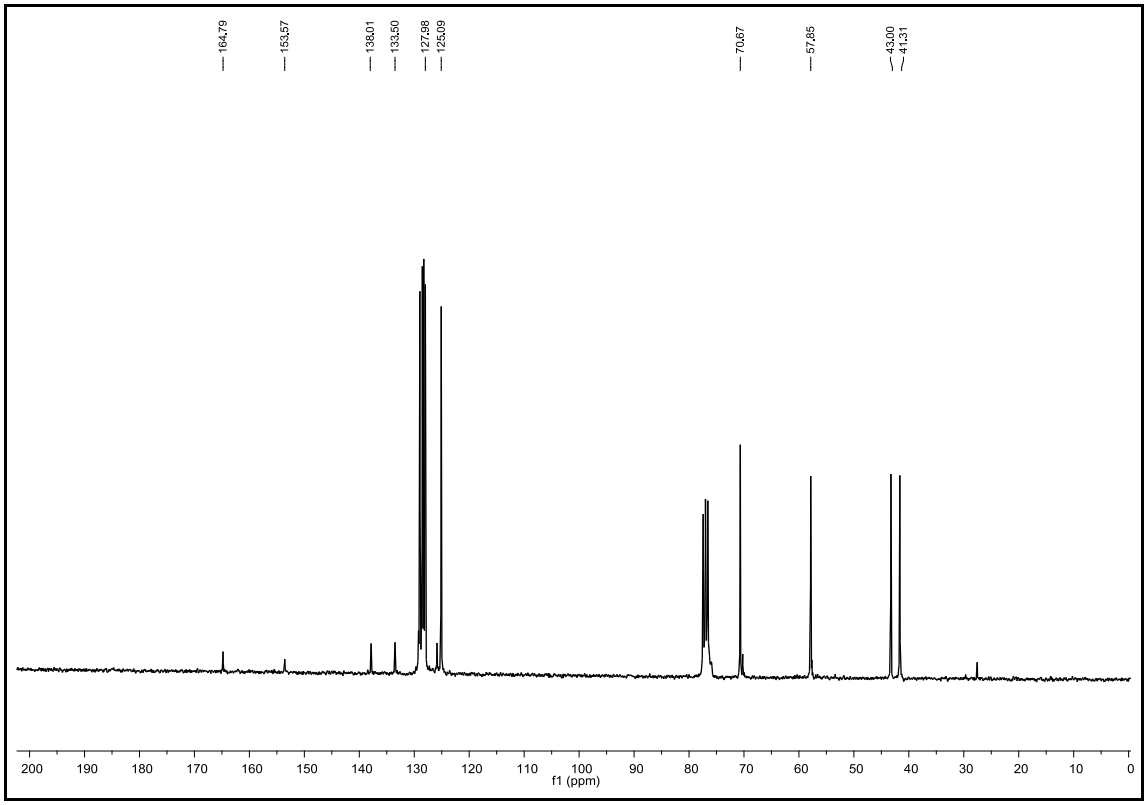
(S)-4-(tert-butyl)-3-((2S,3R)-3-phenylthiirane-2-carbonyl)oxazolidin-2-one



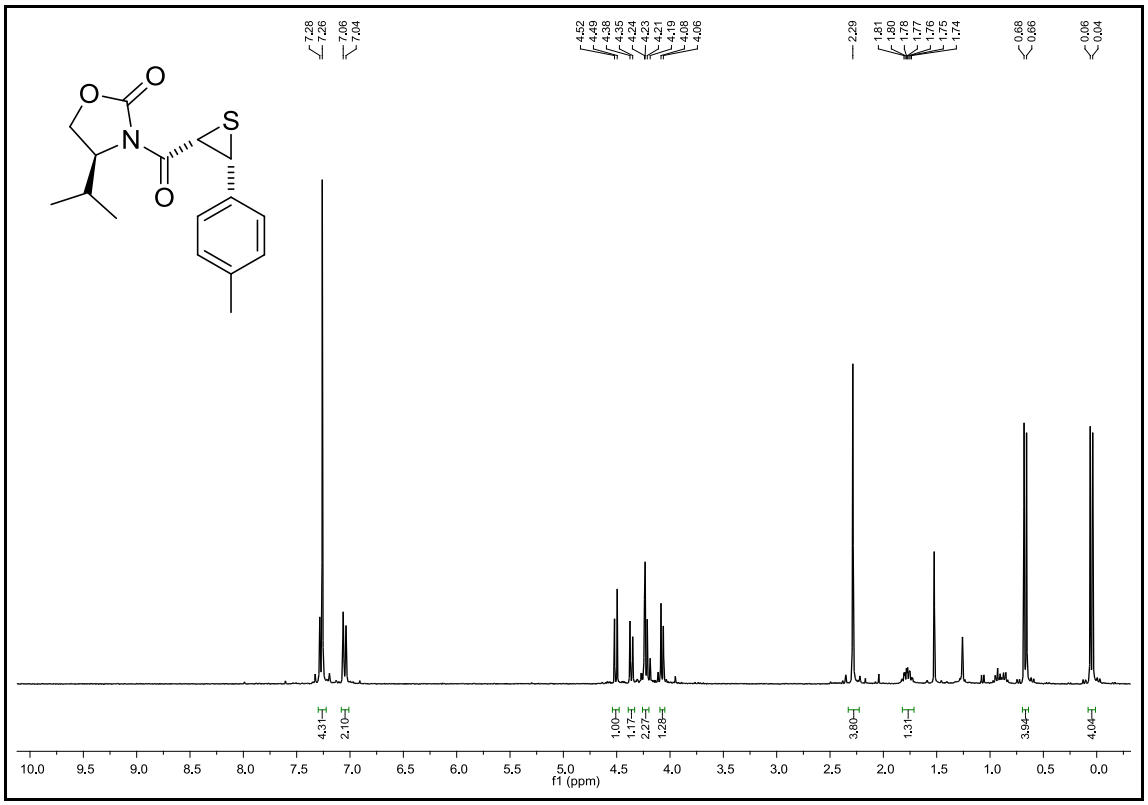


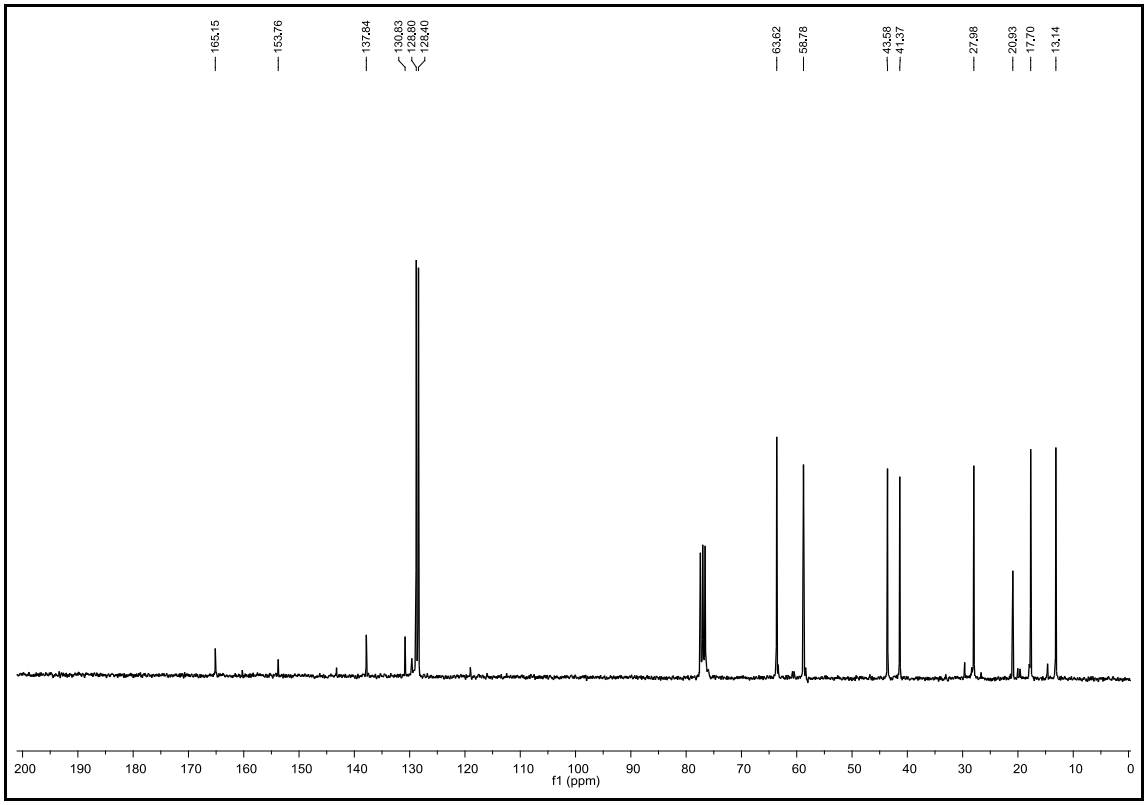
(S)-4-phenyl-3-((2S,3R)-3-phenylthiirane-2-carbonyl)oxazolidin-2-one



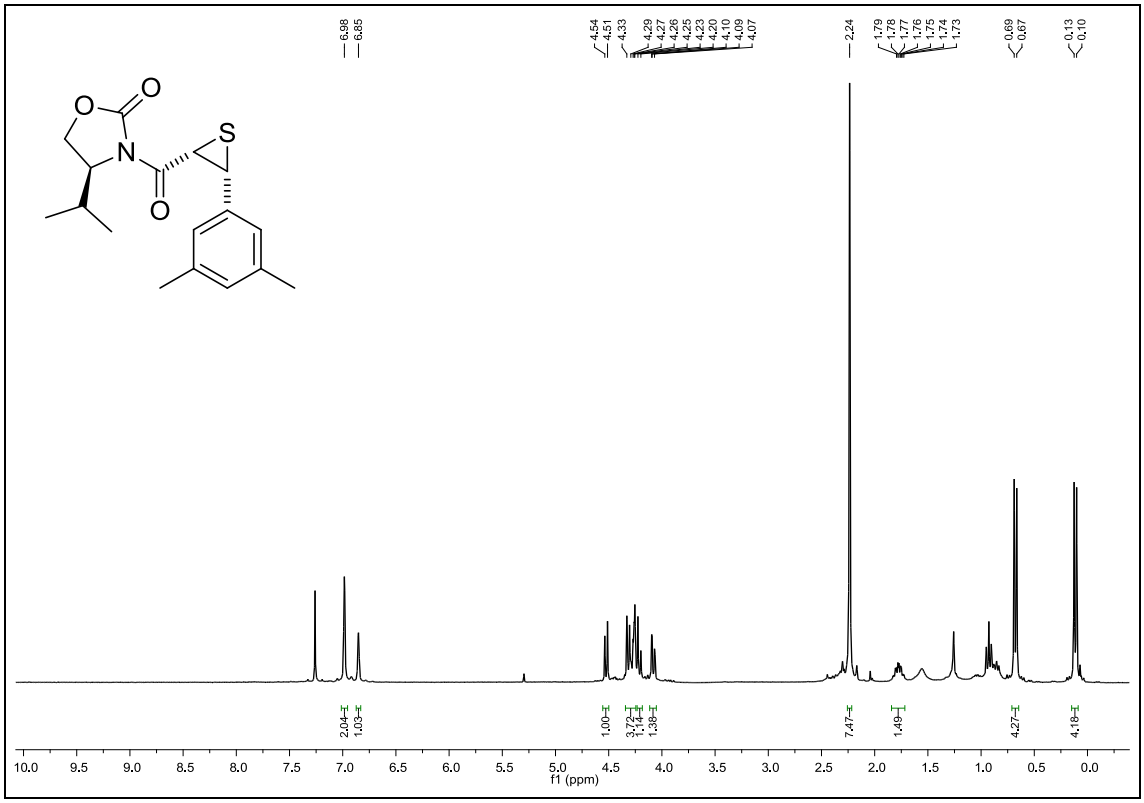


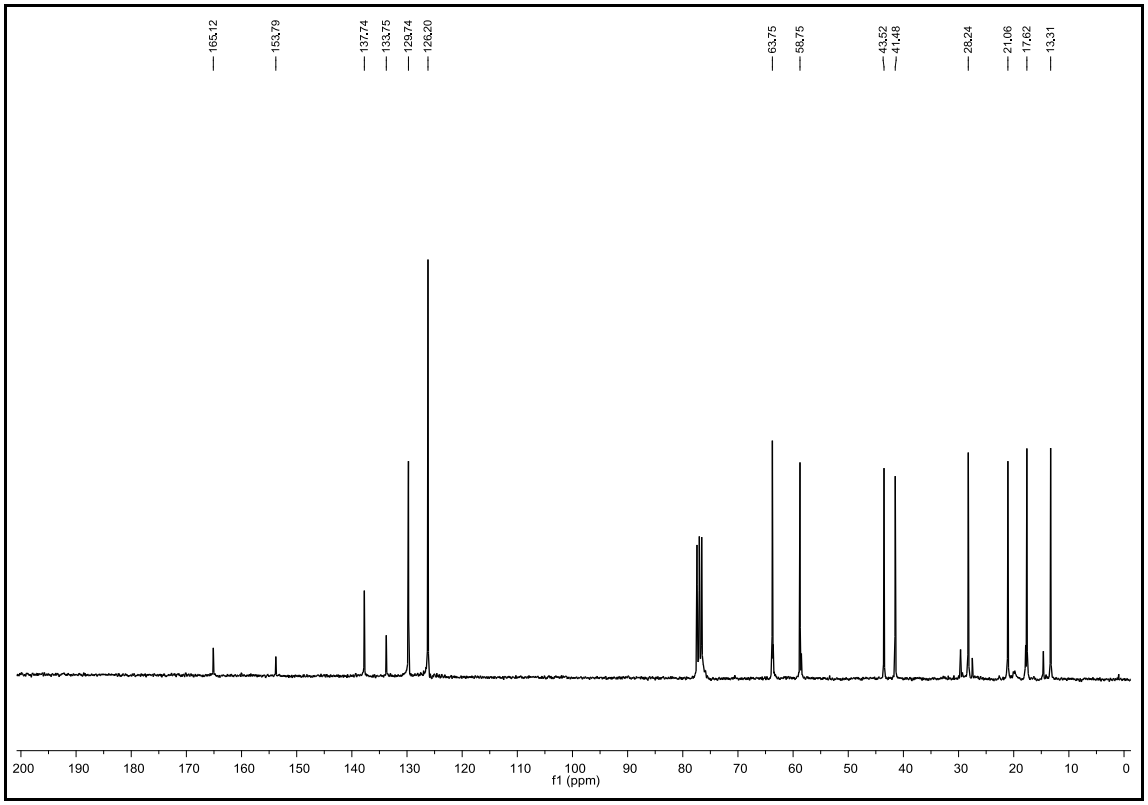
(S)-4-isopropyl-3-((2S,3R)-3-(p-tolyl)thiirane-2-carbonyl)oxazolidin-2-one



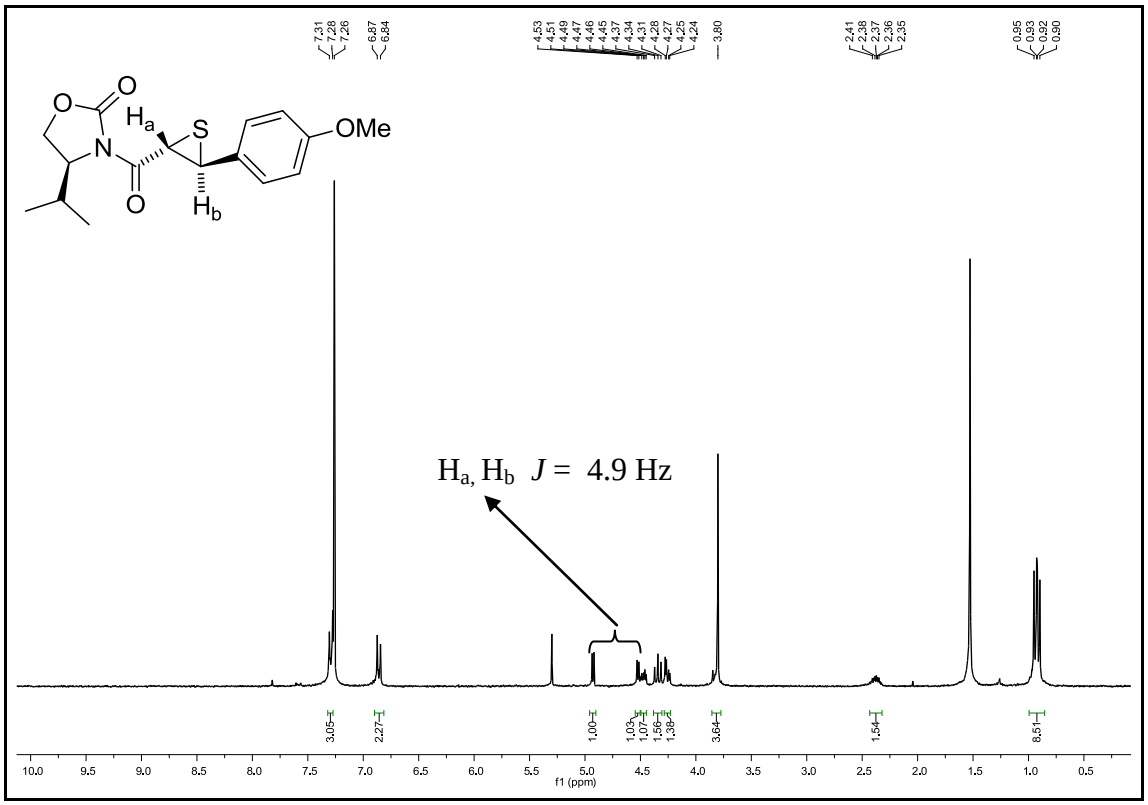


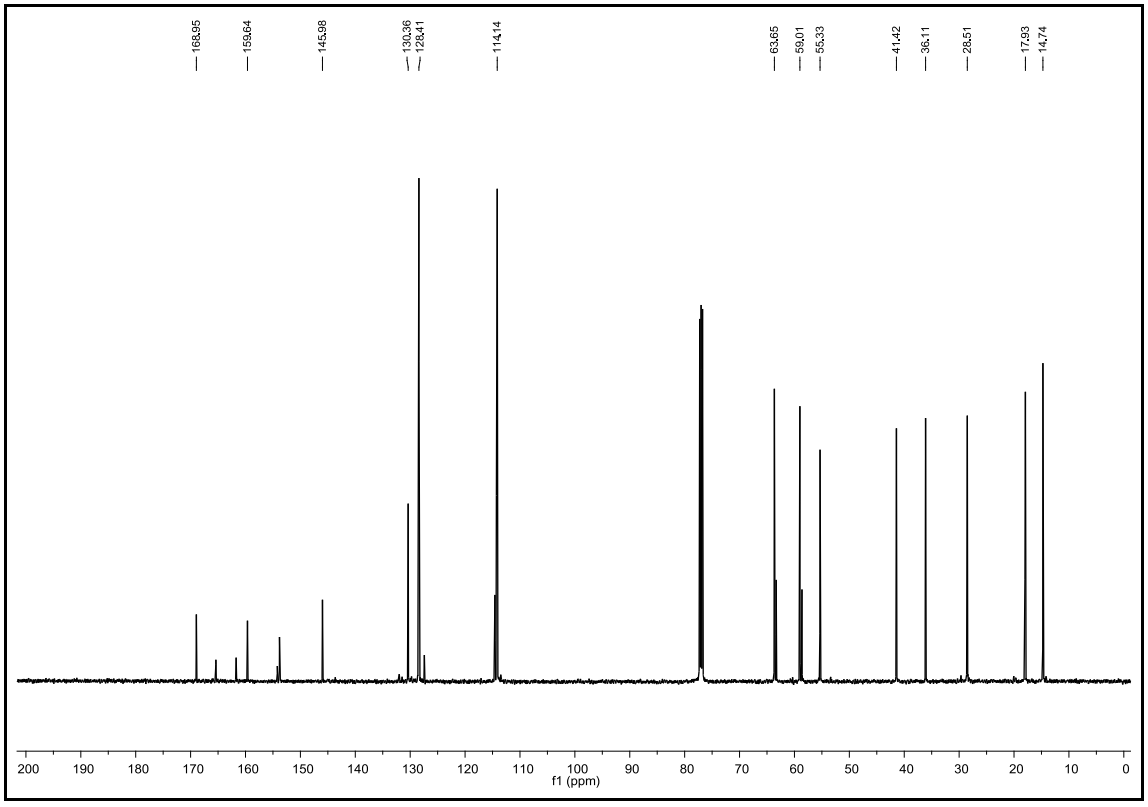
(S)-3-((2S,3R)-3-(3,5-dimethylphenyl)thiirane-2-carbonyl)-4-isopropyloxazolidin-2-one



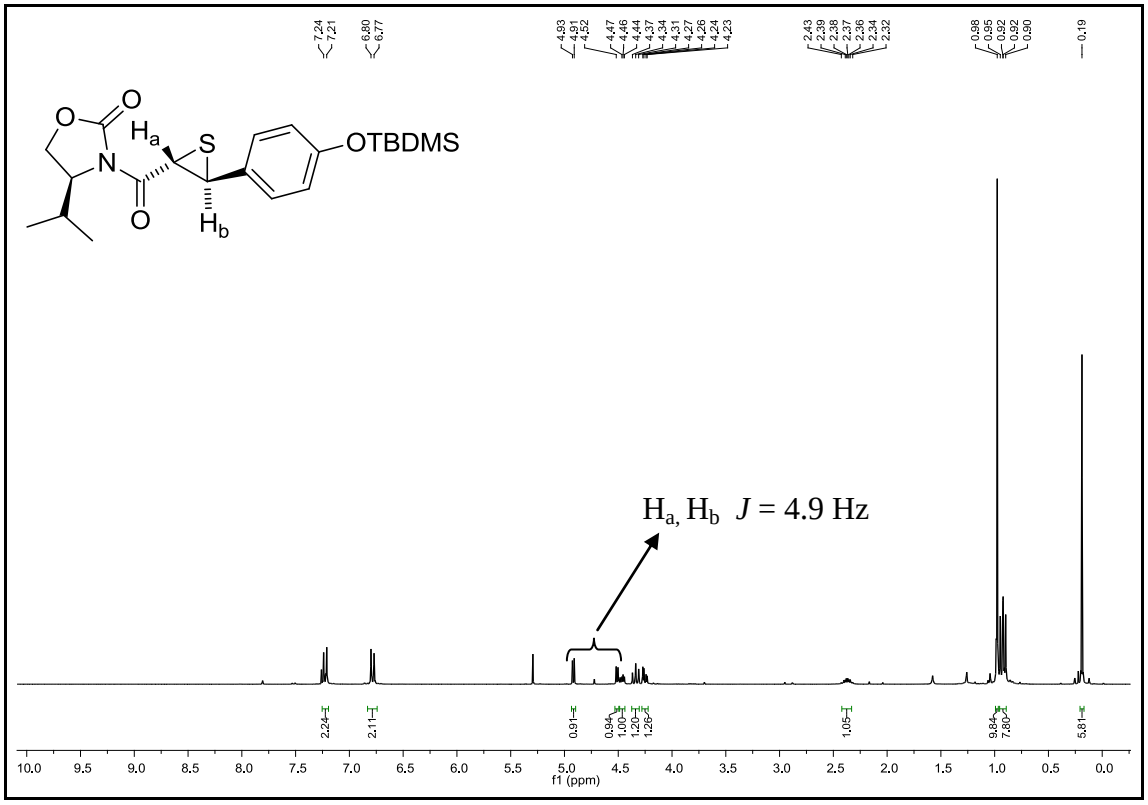


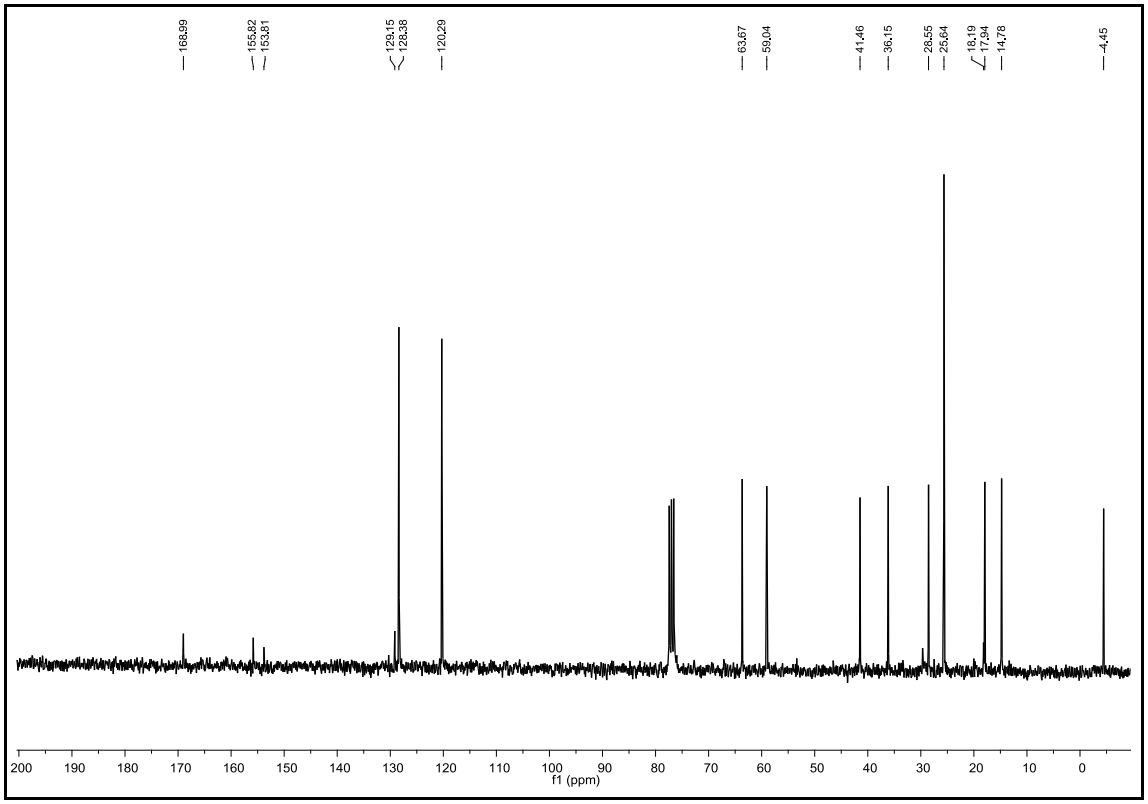
(S)-4-isopropyl-3-((2S,3S)-3-(4-methoxyphenyl)thiirane-2-carbonyl)oxazolidin-2-one



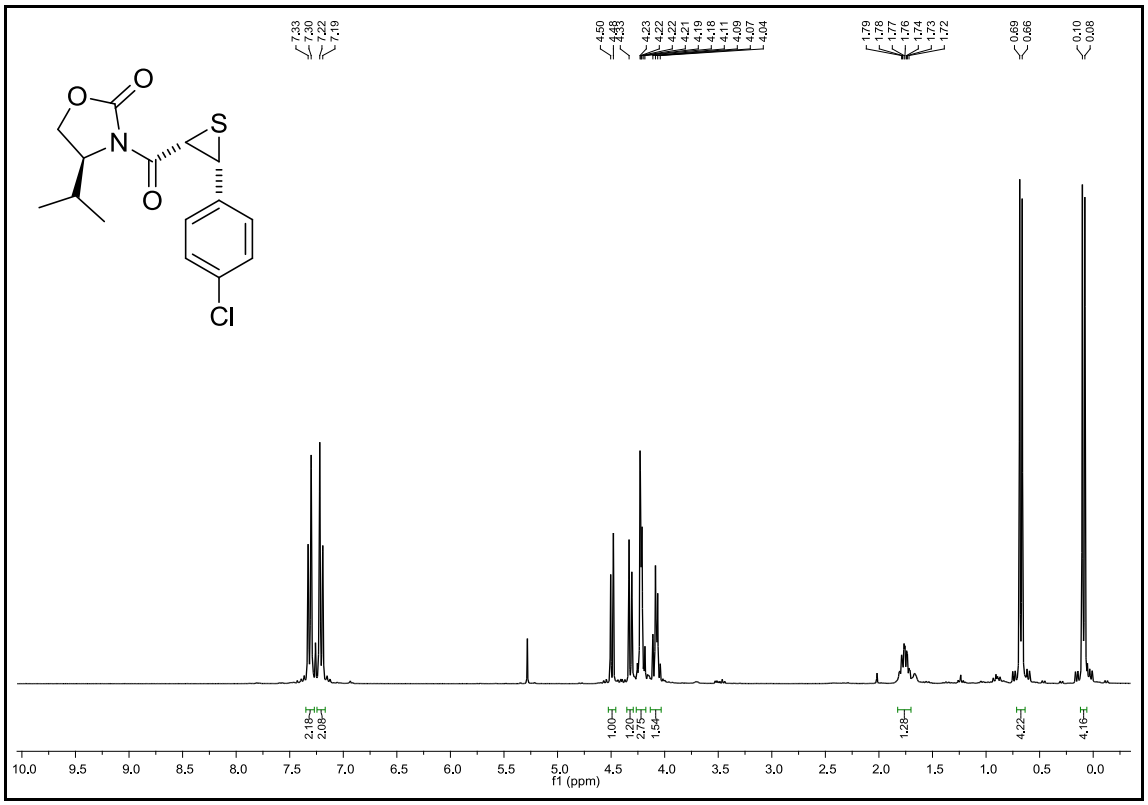


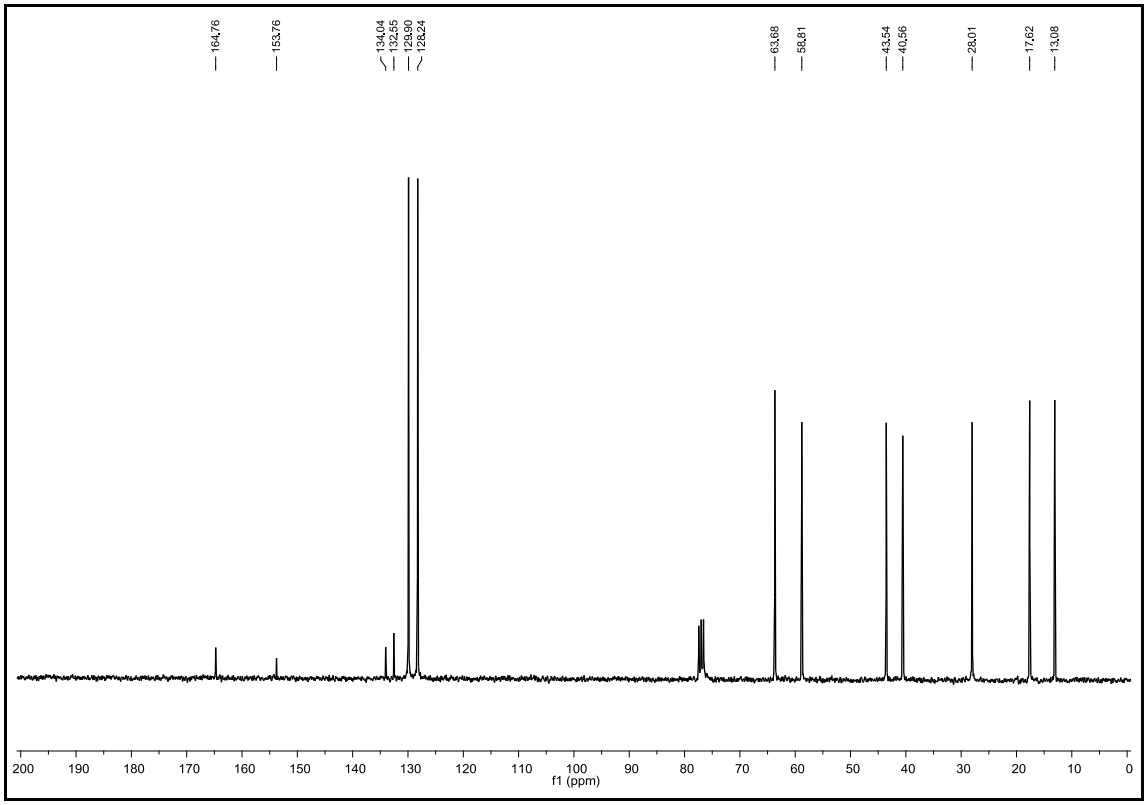
(S)-3-((2S,3S)-3-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)thiirane-2-carbonyl)-4-isopropyloxazolidin-2-one





(S)-3-((2S,3R)-3-(4-chlorophenyl)thiirane-2-carbonyl)-4-isopropyloxazolidin-2-one





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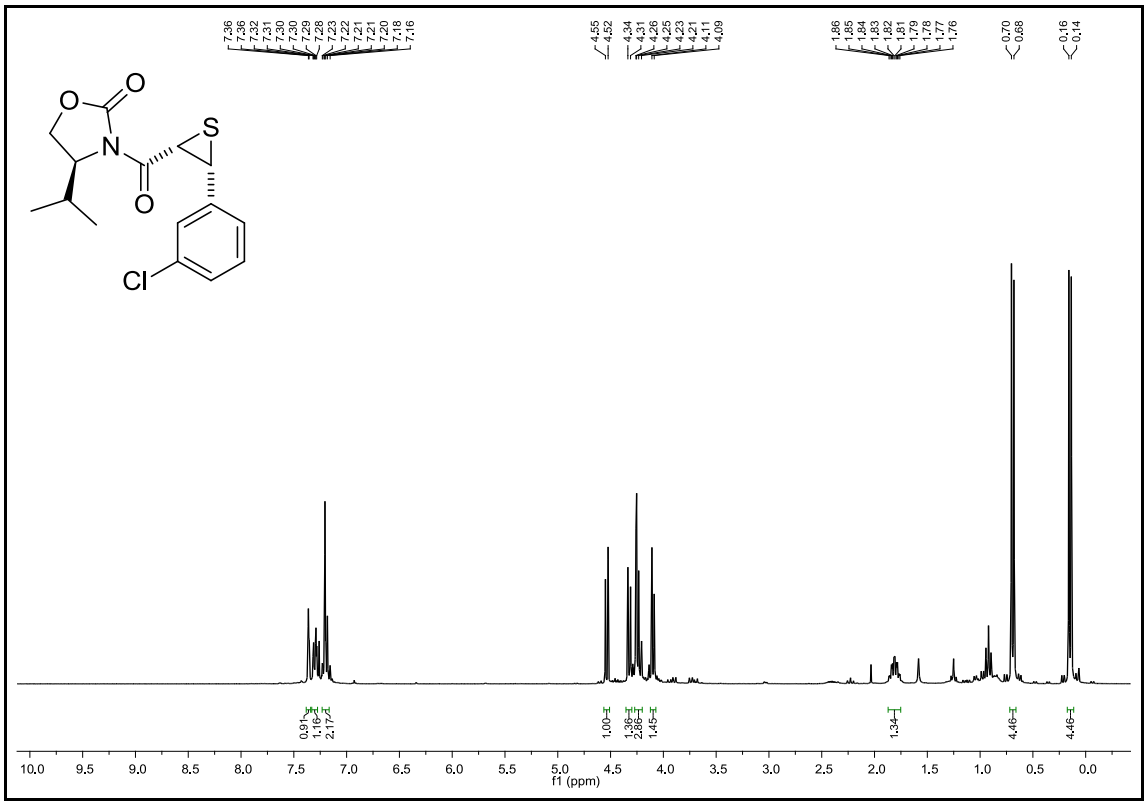
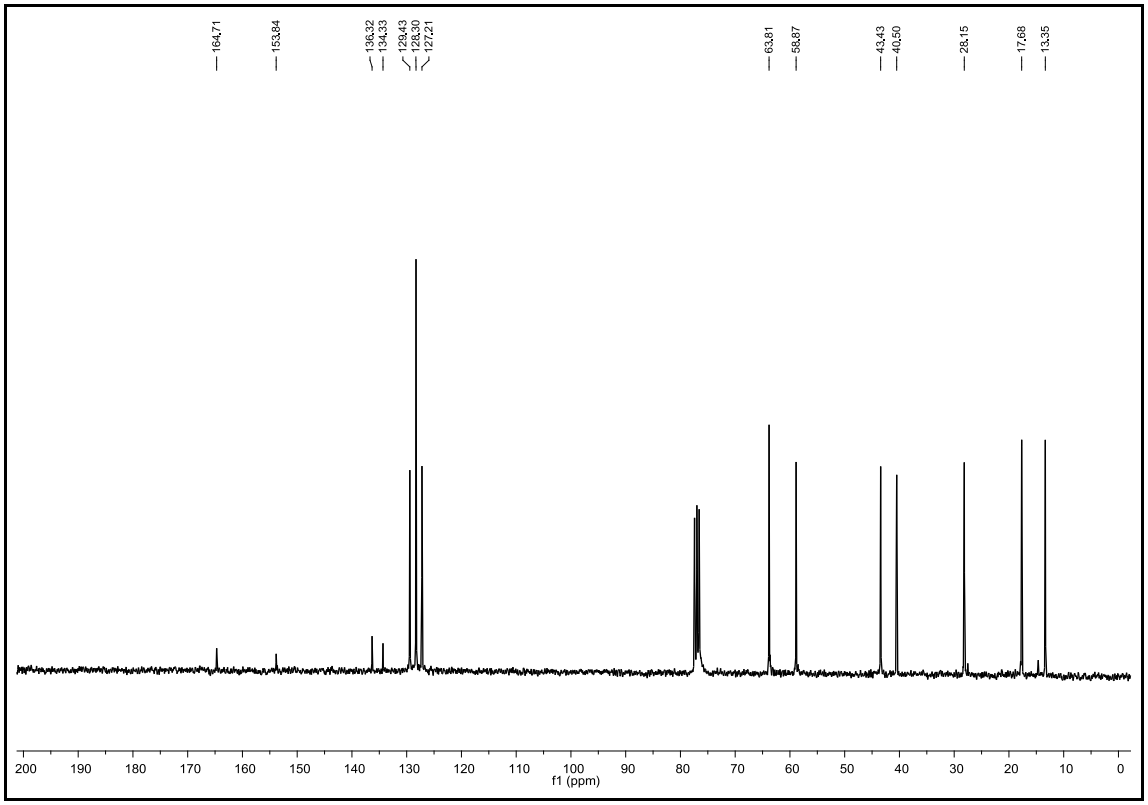
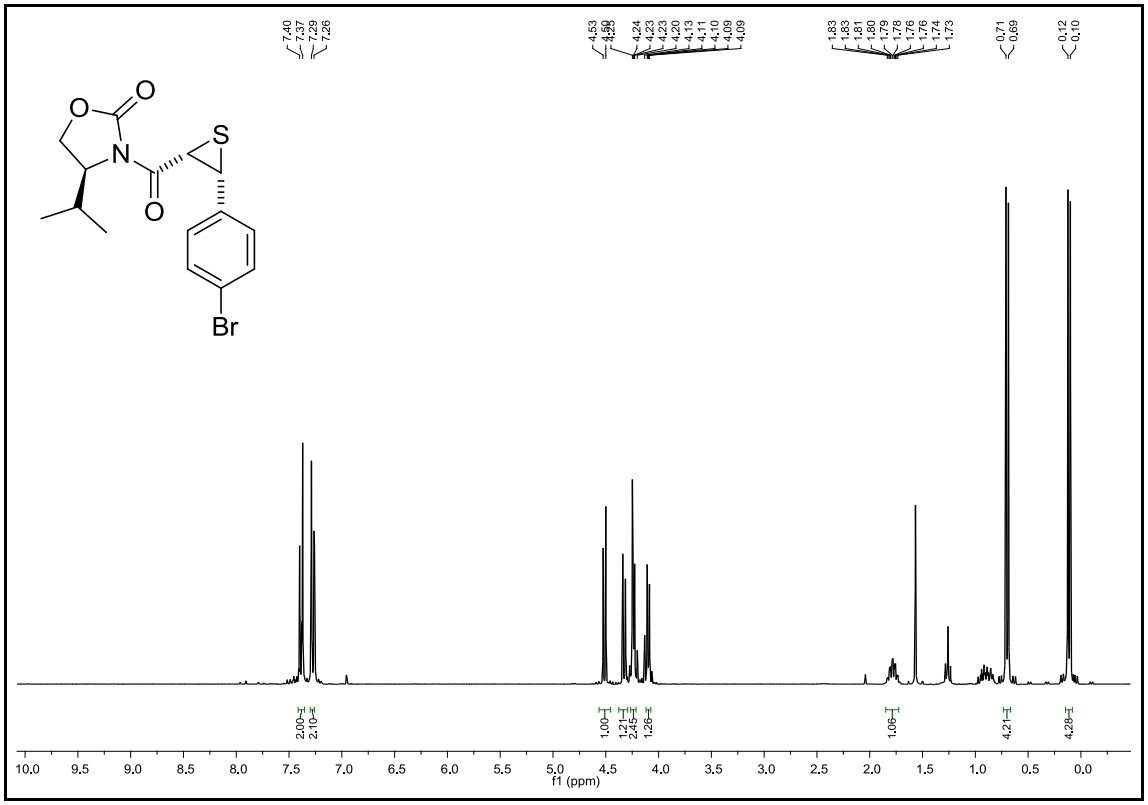
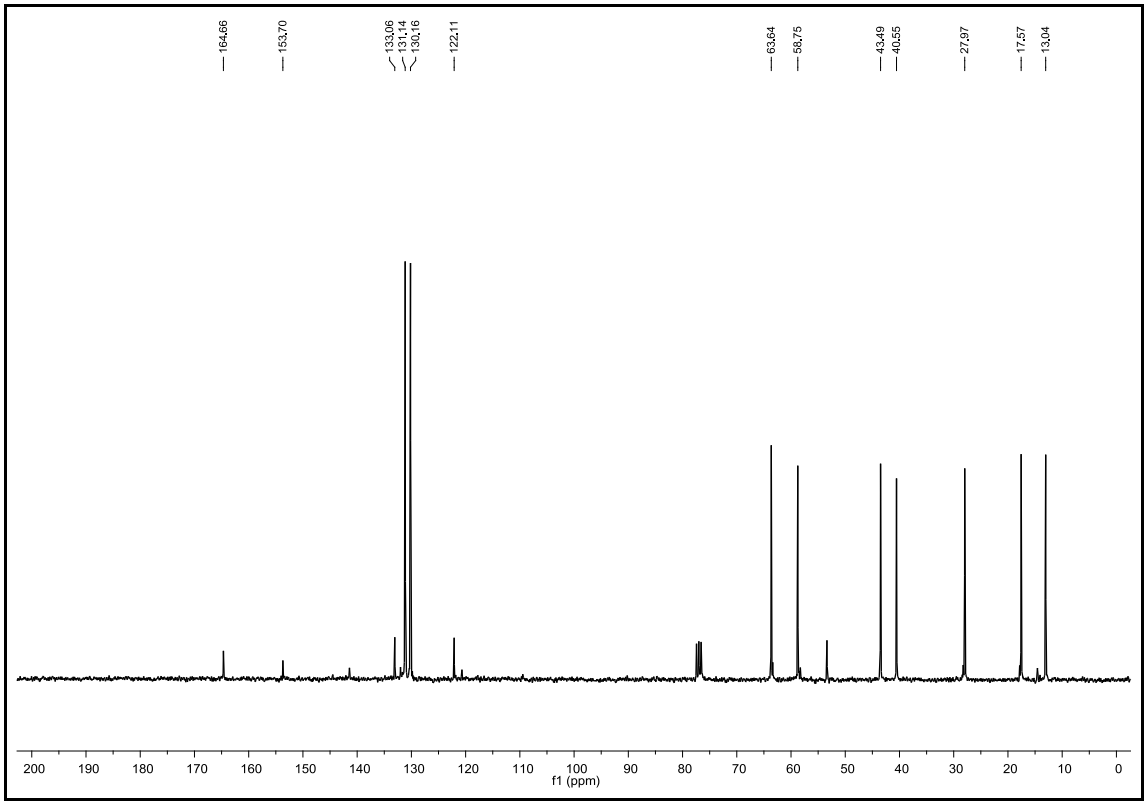


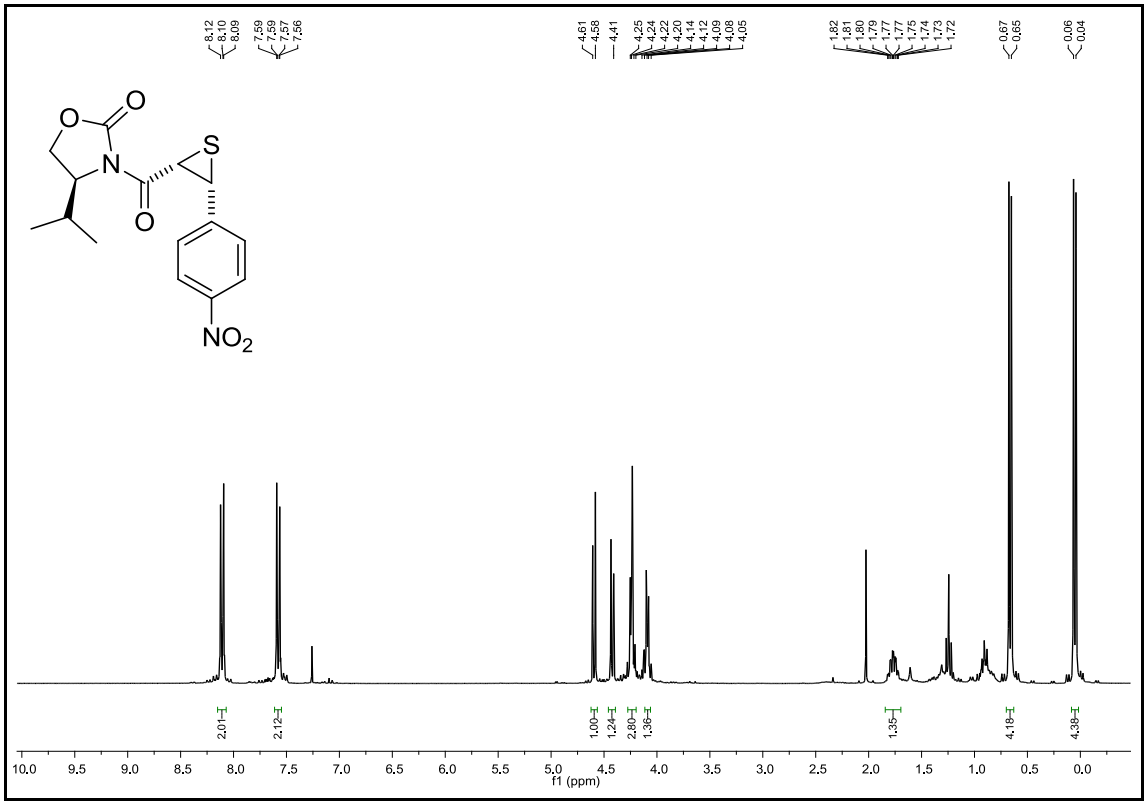


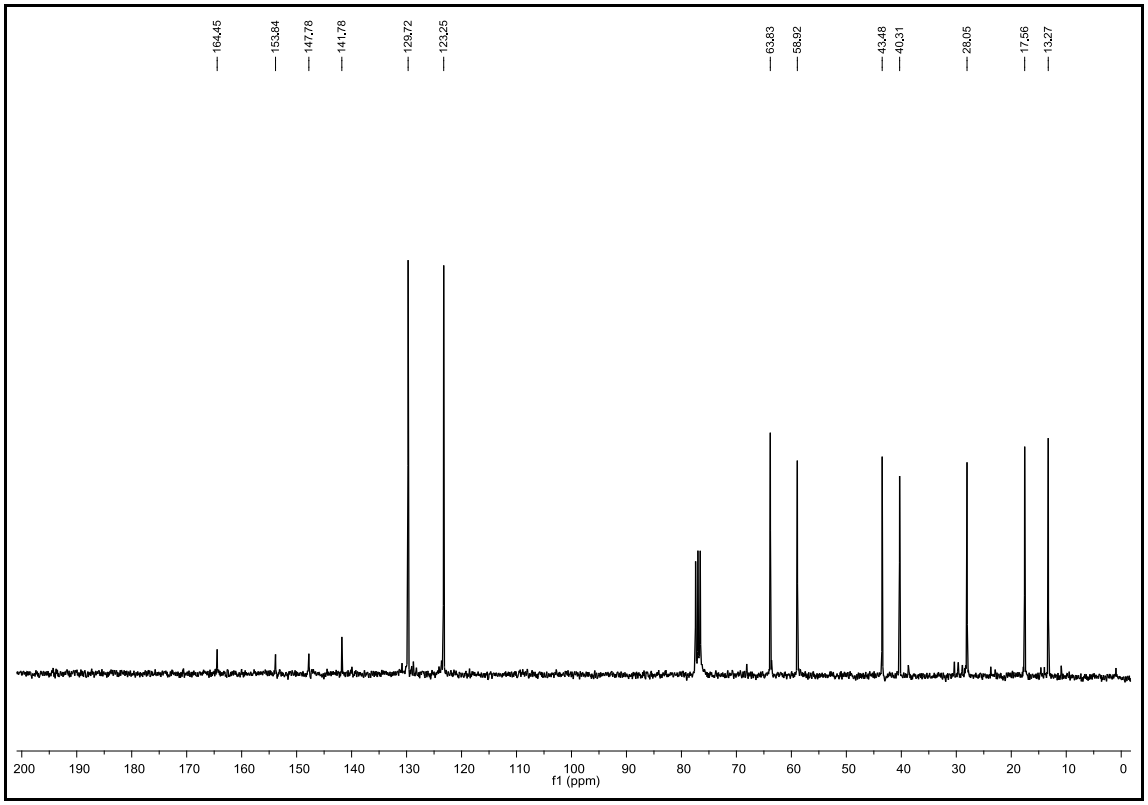
(S)-3-((2S,3R)-3-(4-bromophenyl)thiirane-2-carbonyl)-4-isopropyloxazolidin-2-one



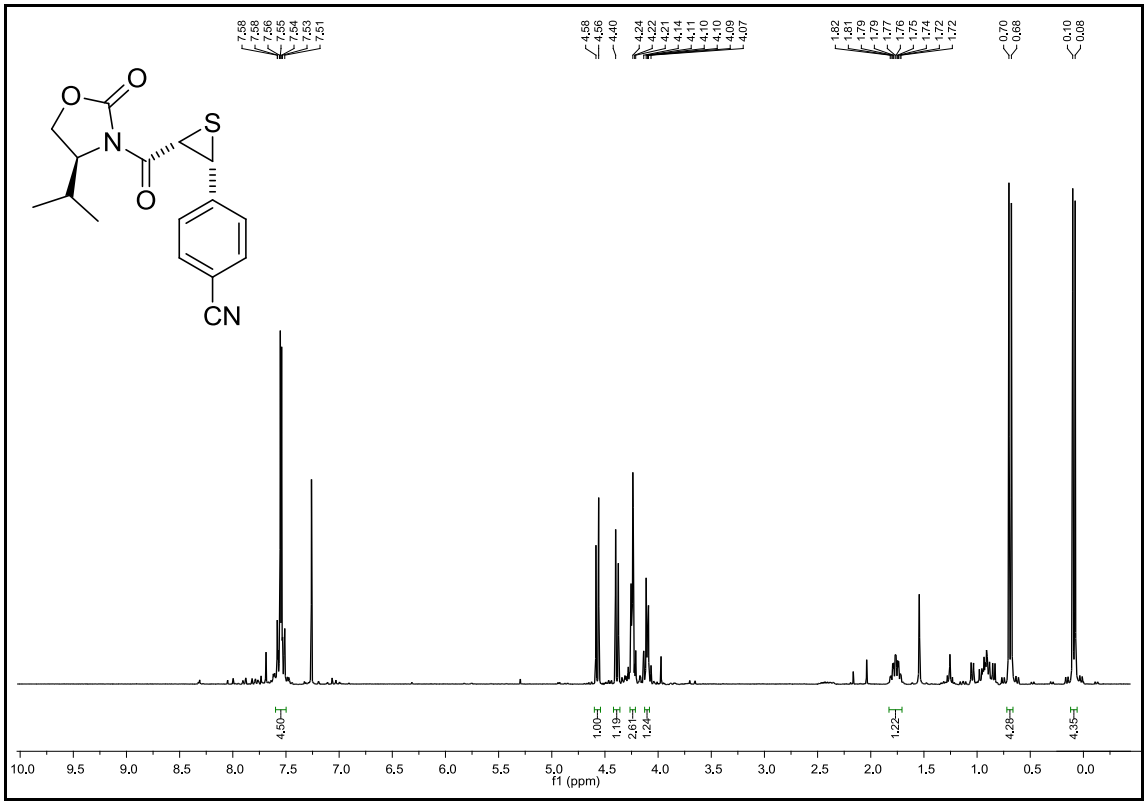


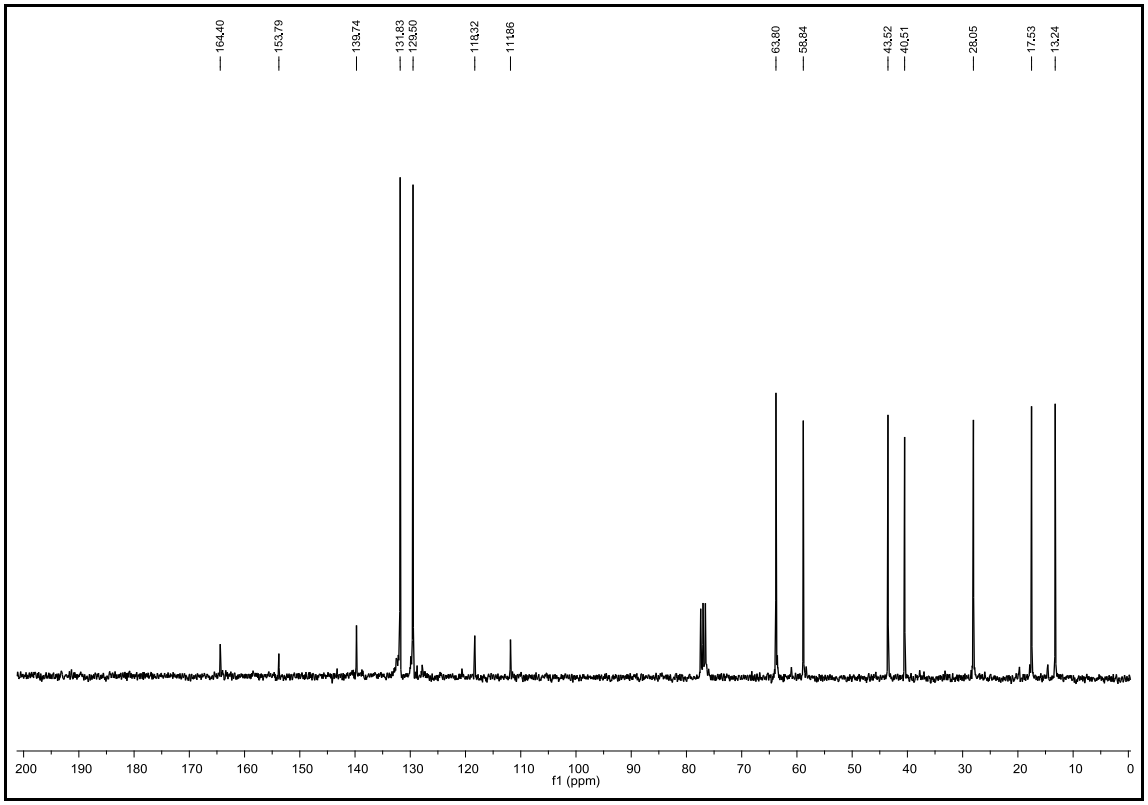
(S)-4-isopropyl-3-((2S,3R)-3-(4-nitrophenyl)thiirane-2-carbonyl)oxazolidin-2-one



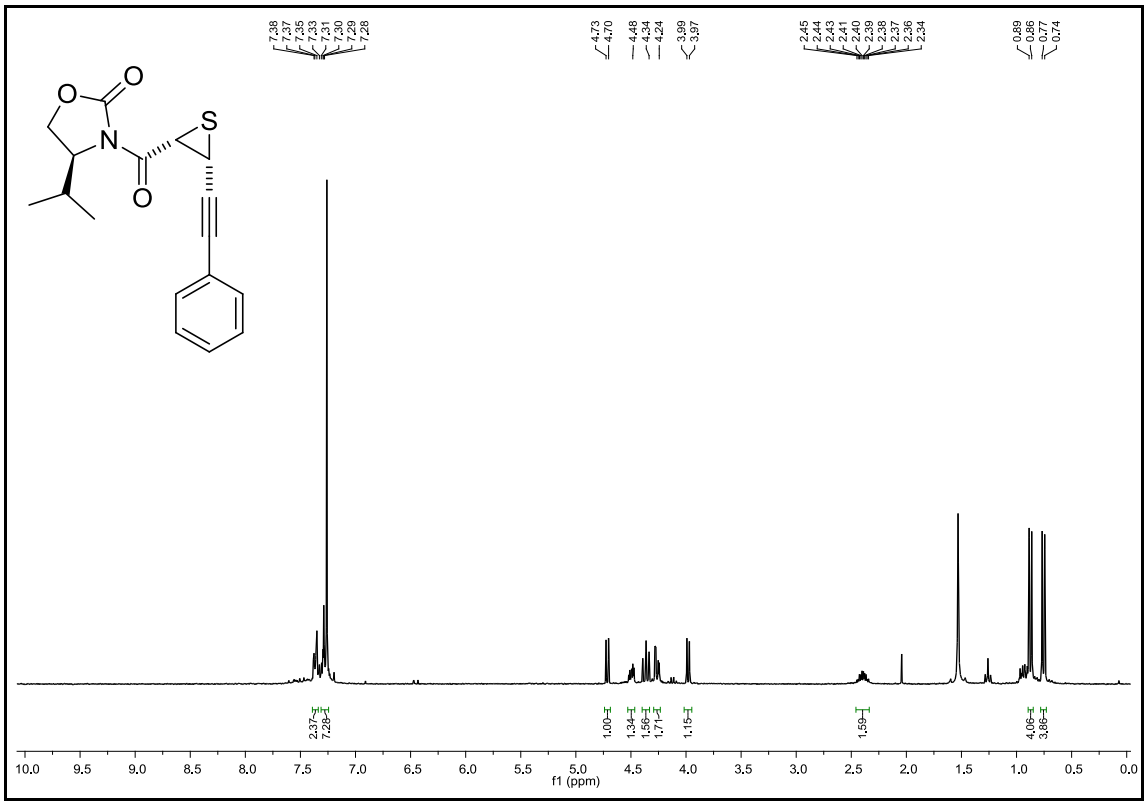


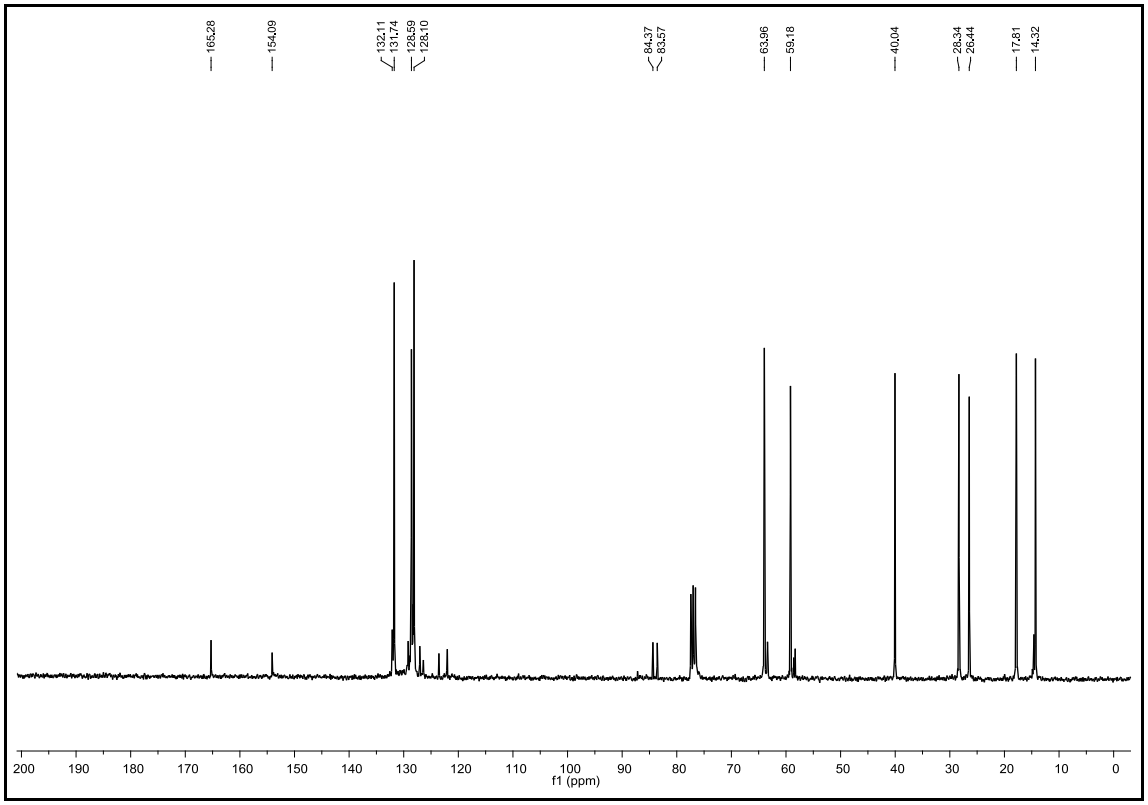
4-((2R,3S)-3-((S)-4-isopropyl-2-oxooxazolidine-3-carbonyl)thiiran-2-yl)benzonitrile



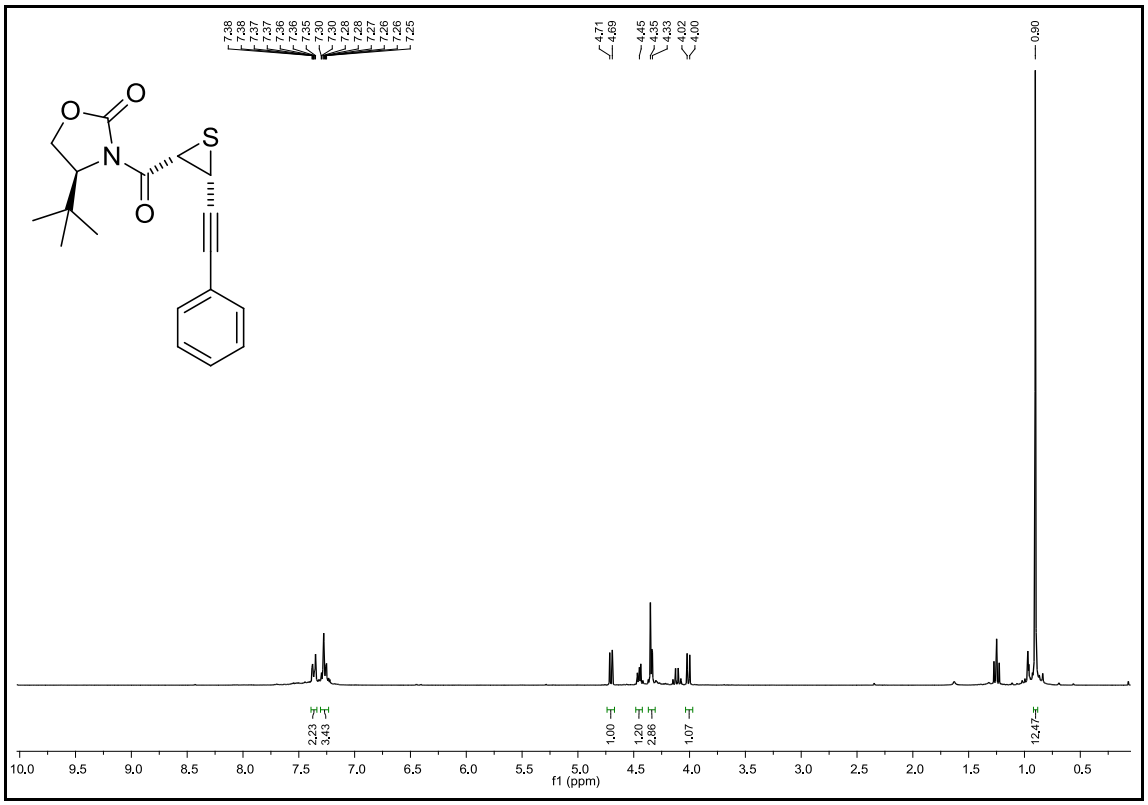


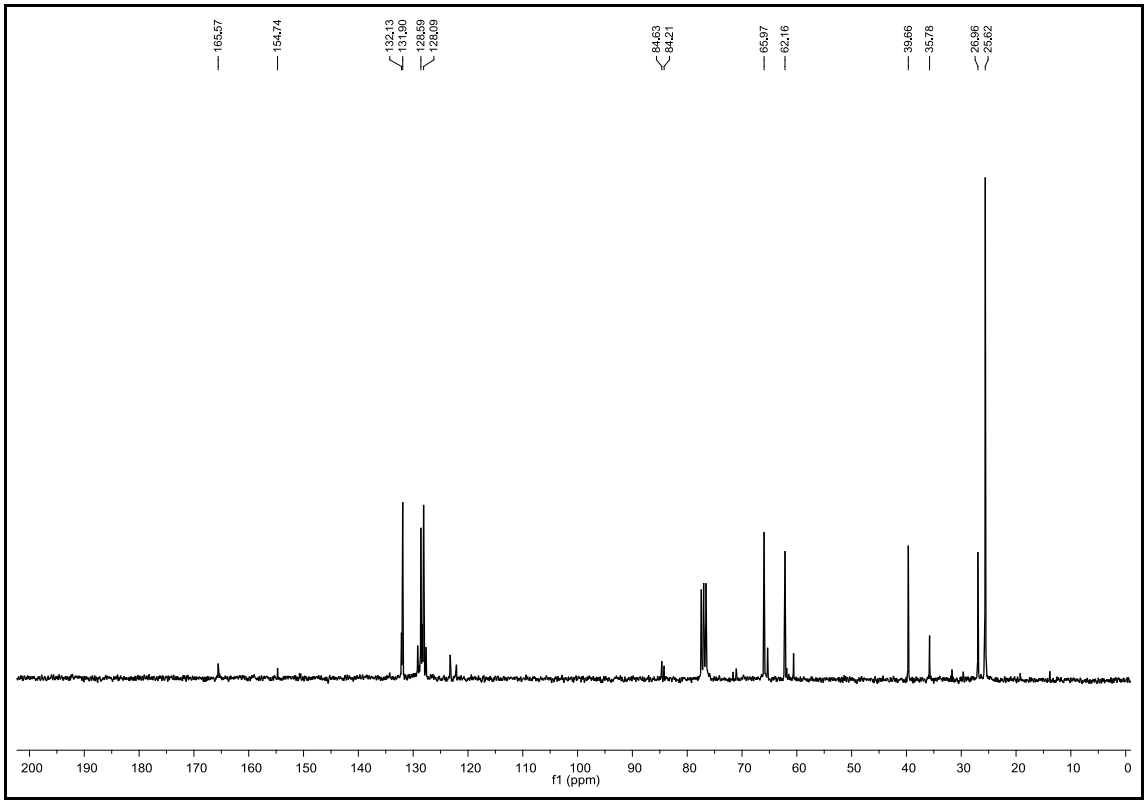
(S)-4-isopropyl-3-((2S,3R)-3-(phenylethynyl)thiirane-2-carbonyl)oxazolidin-2-one



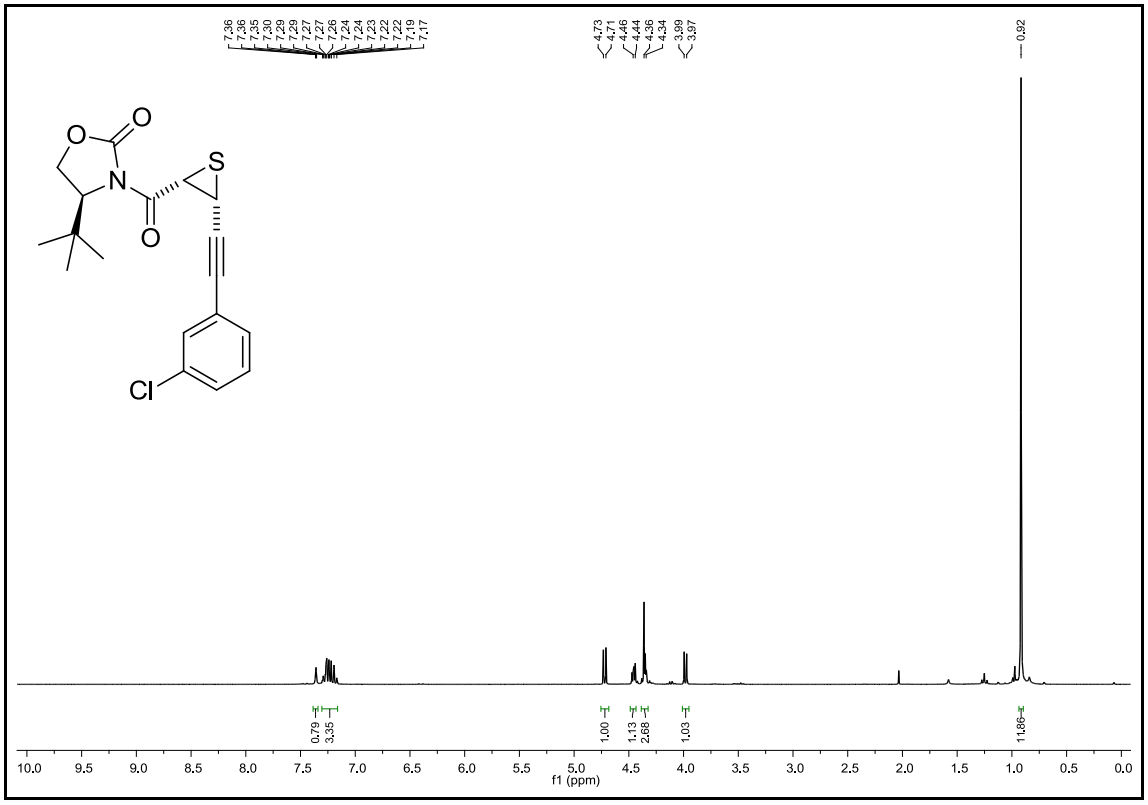


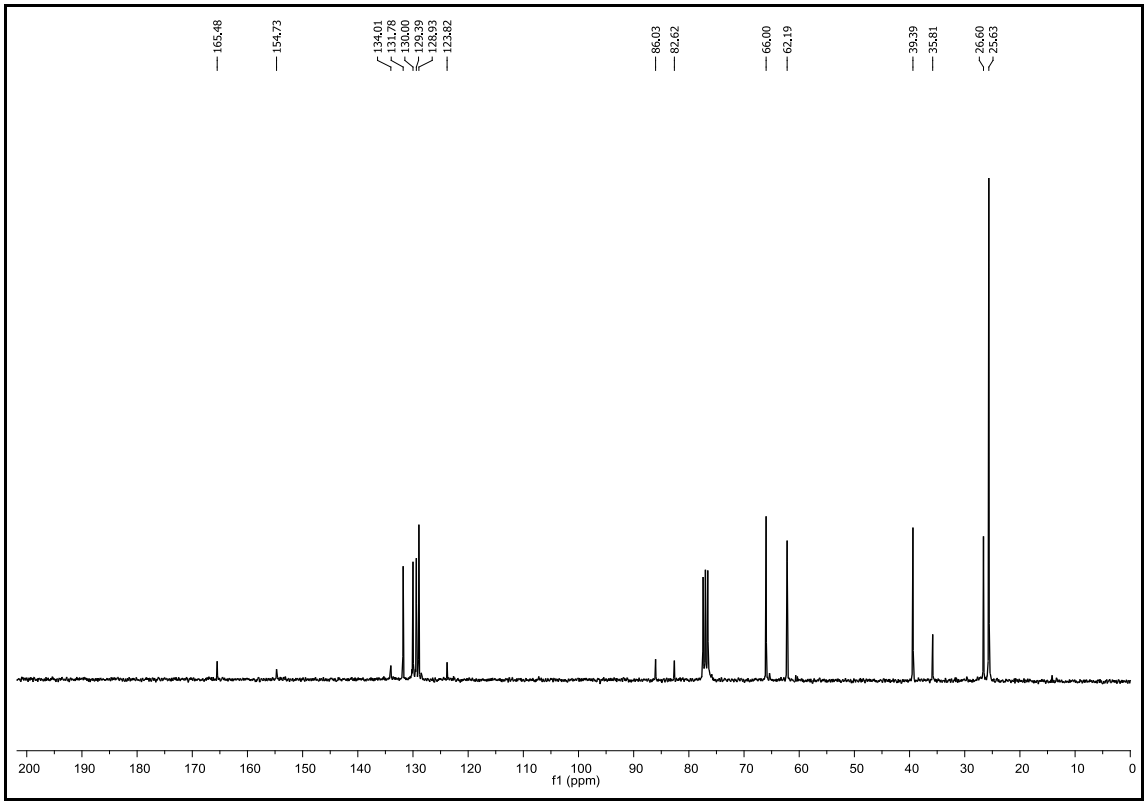
(S)-4-(tert-butyl)-3-((2S,3R)-3-(phenylethynyl)thiirane-2-carbonyl)oxazolidin-2-one



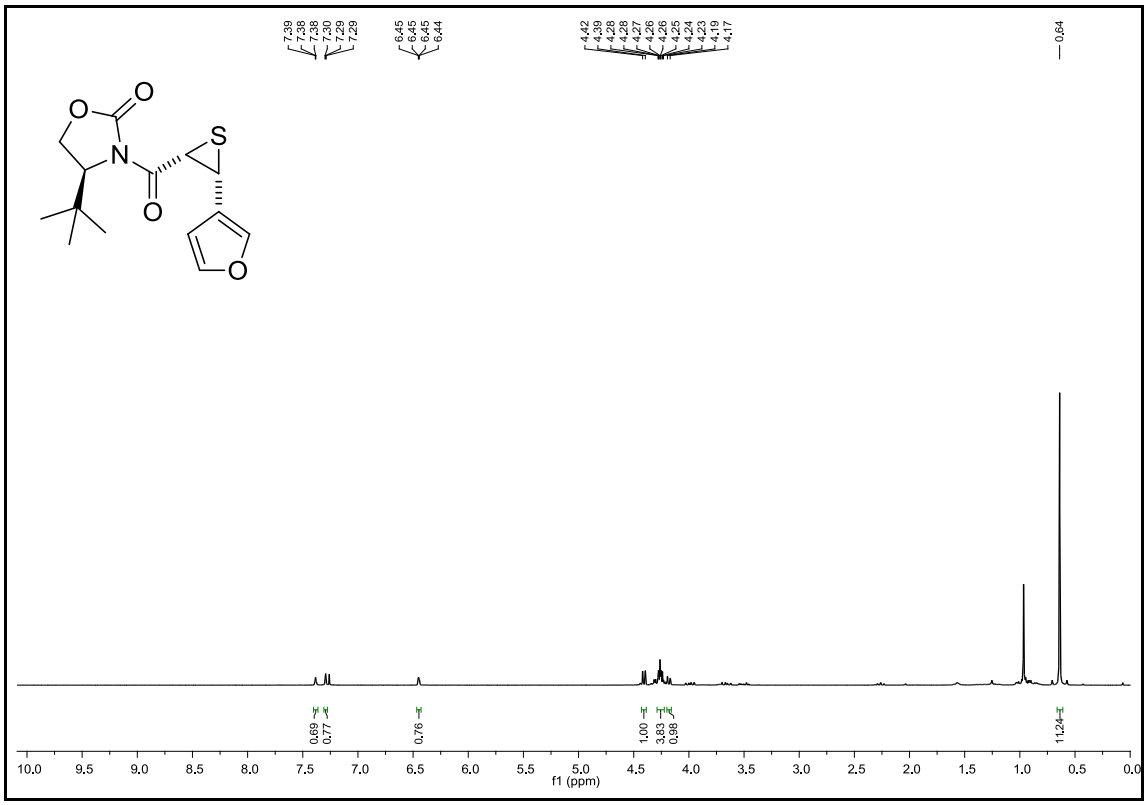


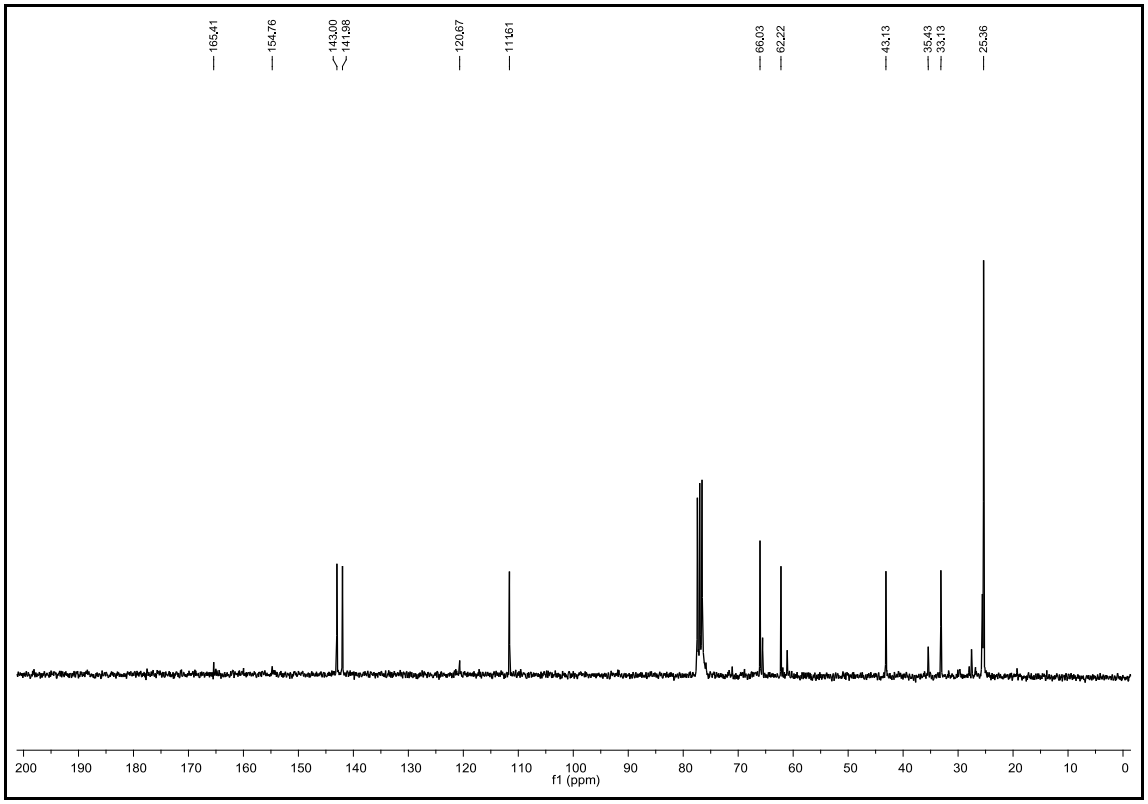
(S)-4-(tert-butyl)-3-((2S,3R)-3-((3-chlorophenyl)ethynyl)thiirane-2-carbonyl)oxazolidin-2-one



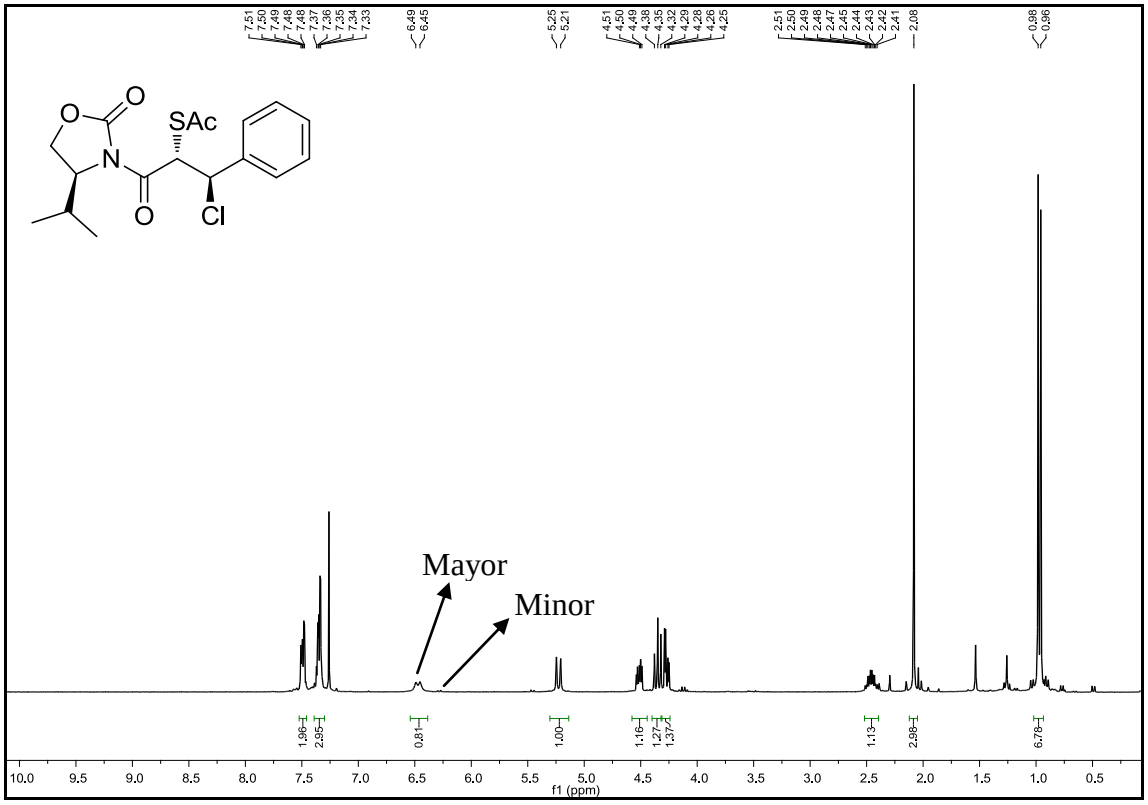


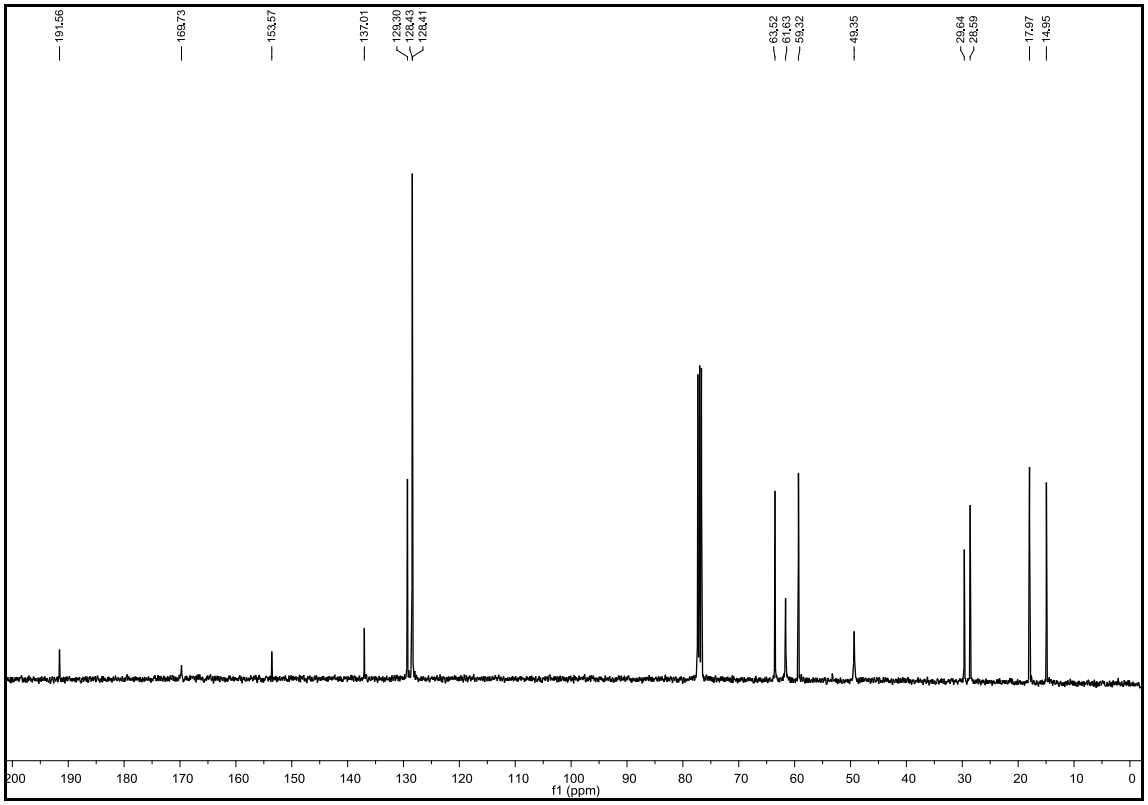
(S)-4-(tert-butyl)-3-((2S,3R)-3-(furan-3-yl)thiirane-2-carbonyl)oxazolidin-2-one



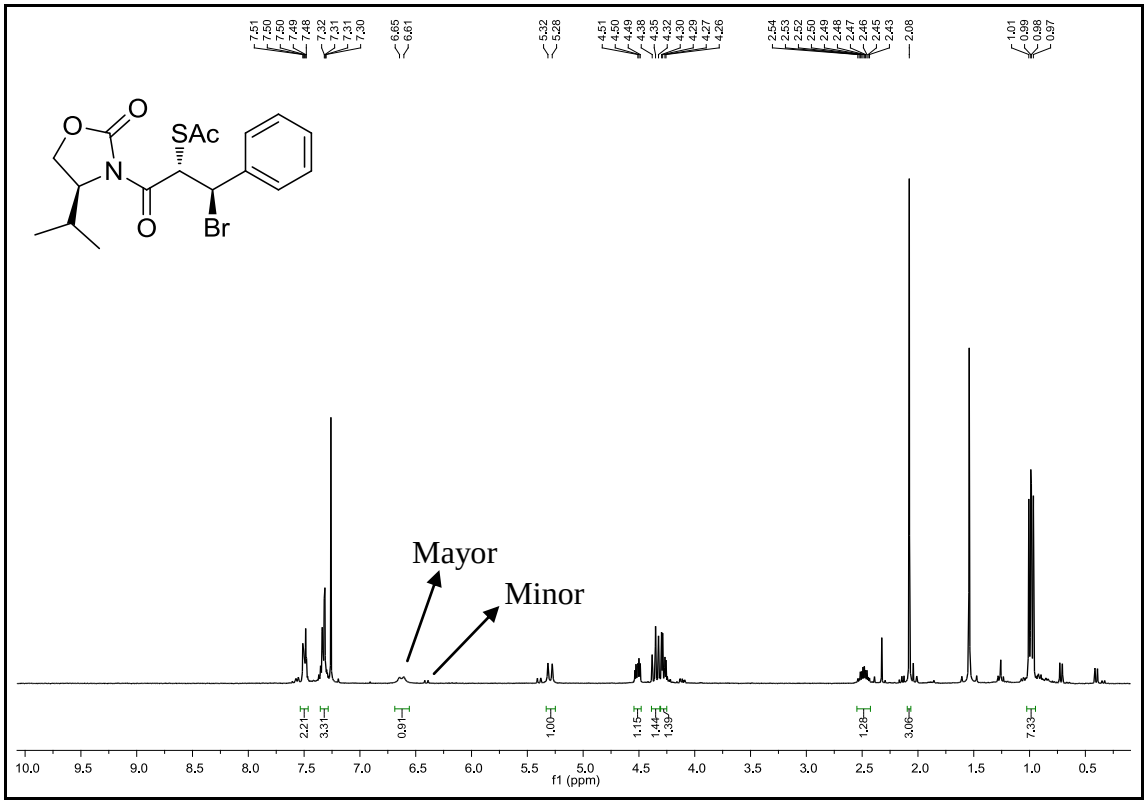


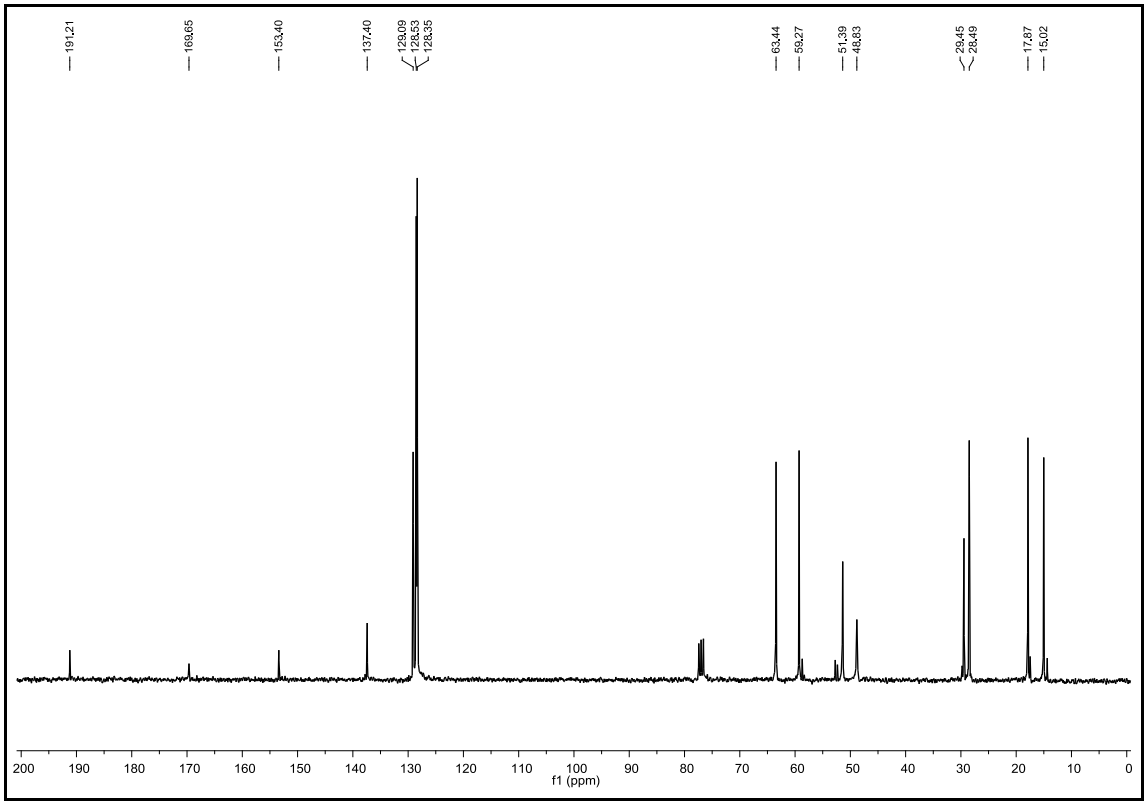
S-((1R,2S)-1-chloro-3-((S)-4-isopropyl-2-oxooxazolidin-3-yl)-3-oxo-1-phenylpropan-2-yl) ethanethioate



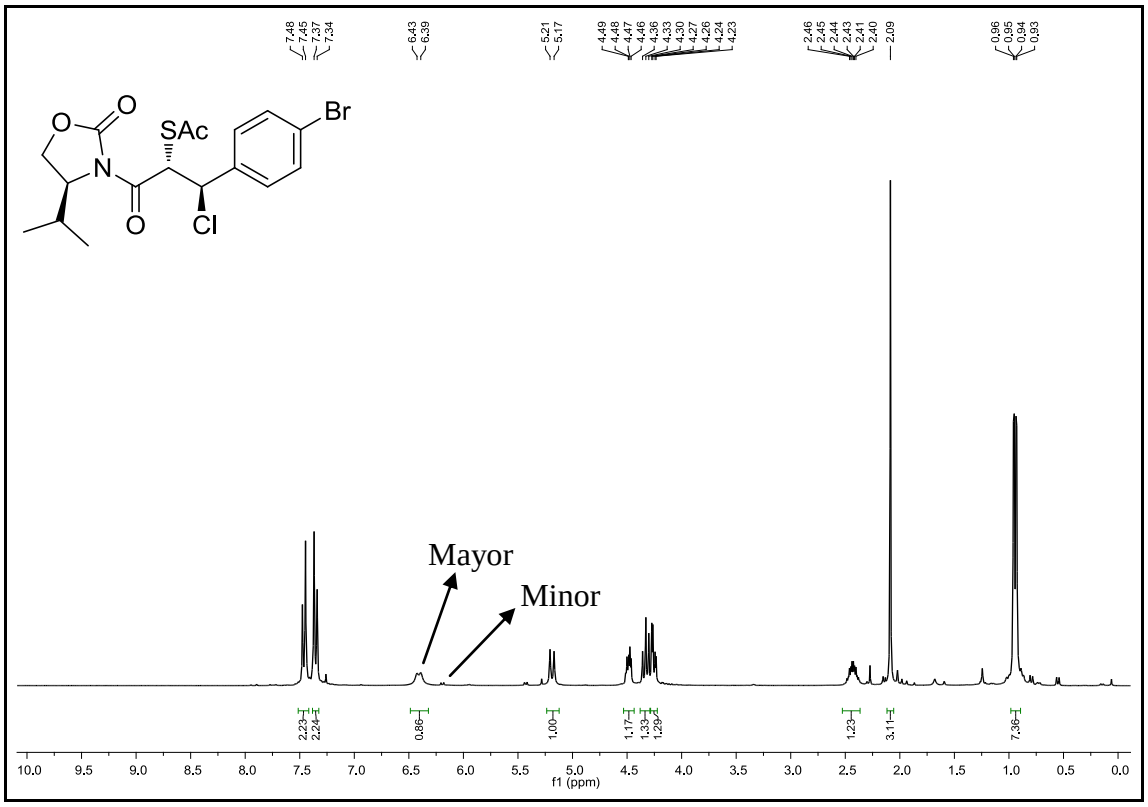


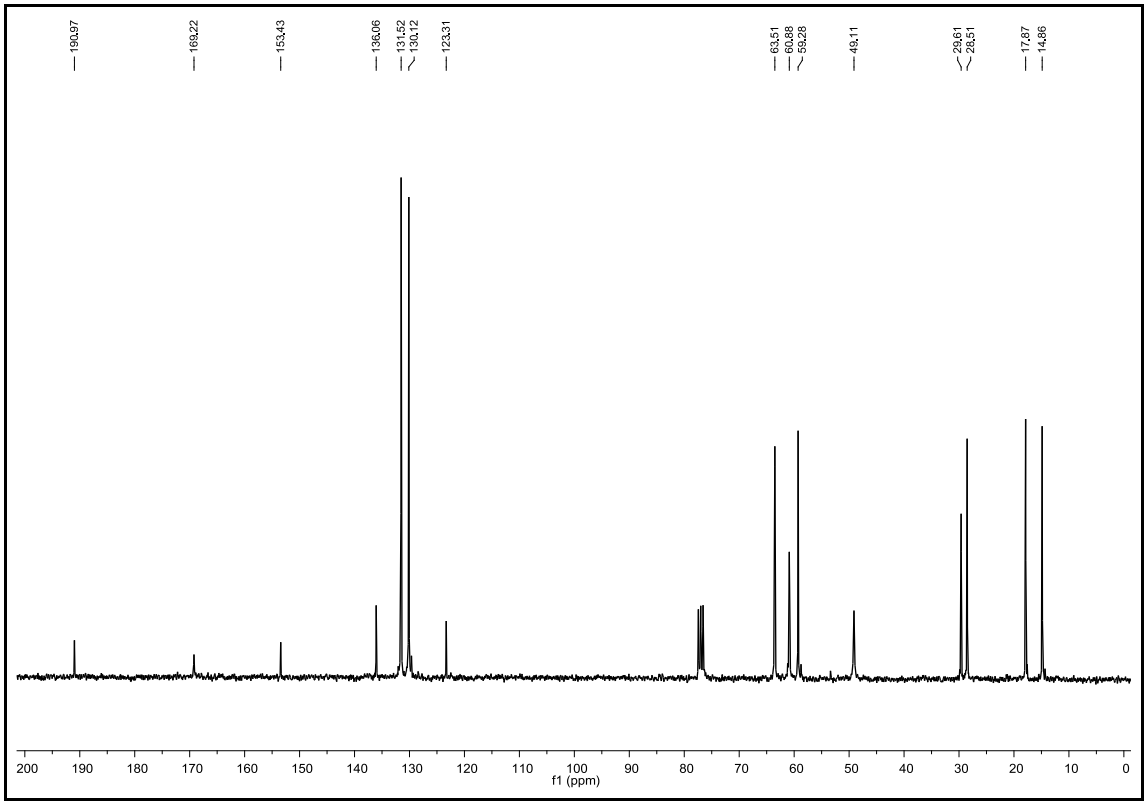
S-((1R,2S)-1-bromo-3-((S)-4-isopropyl-2-oxooxazolidin-3-yl)-3-oxo-1-phenylpropan-2-yl) ethanethioate



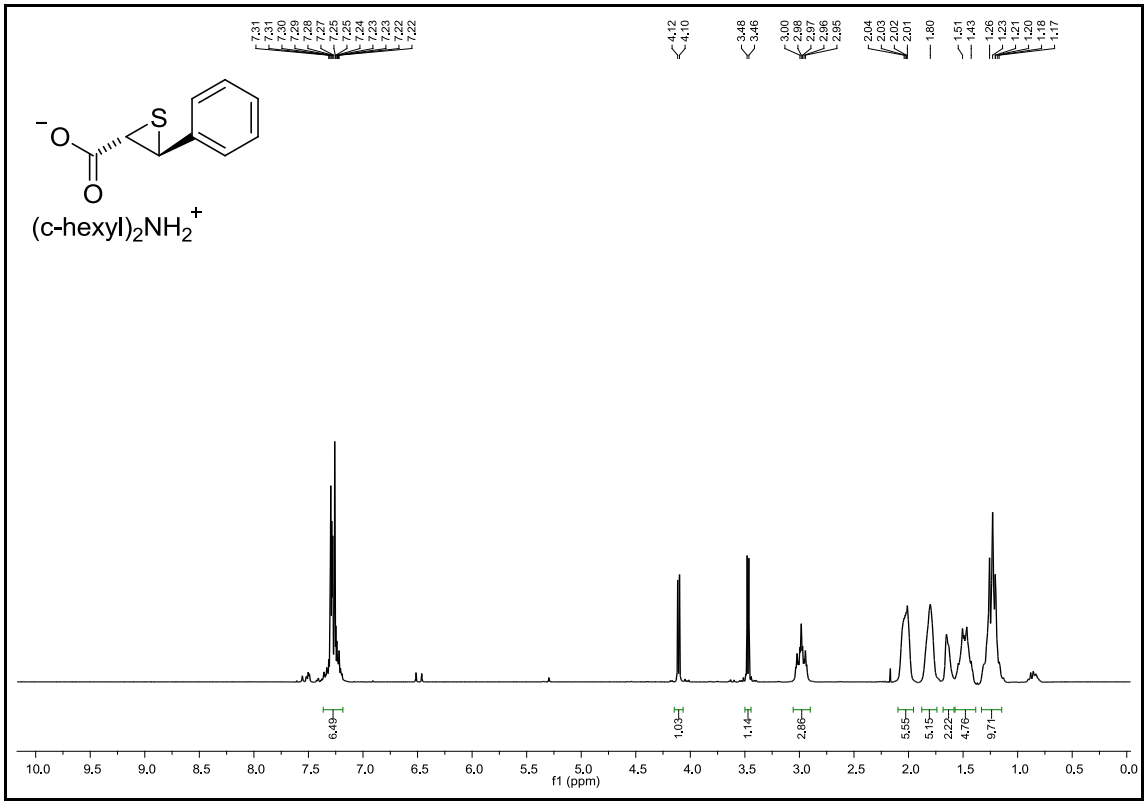


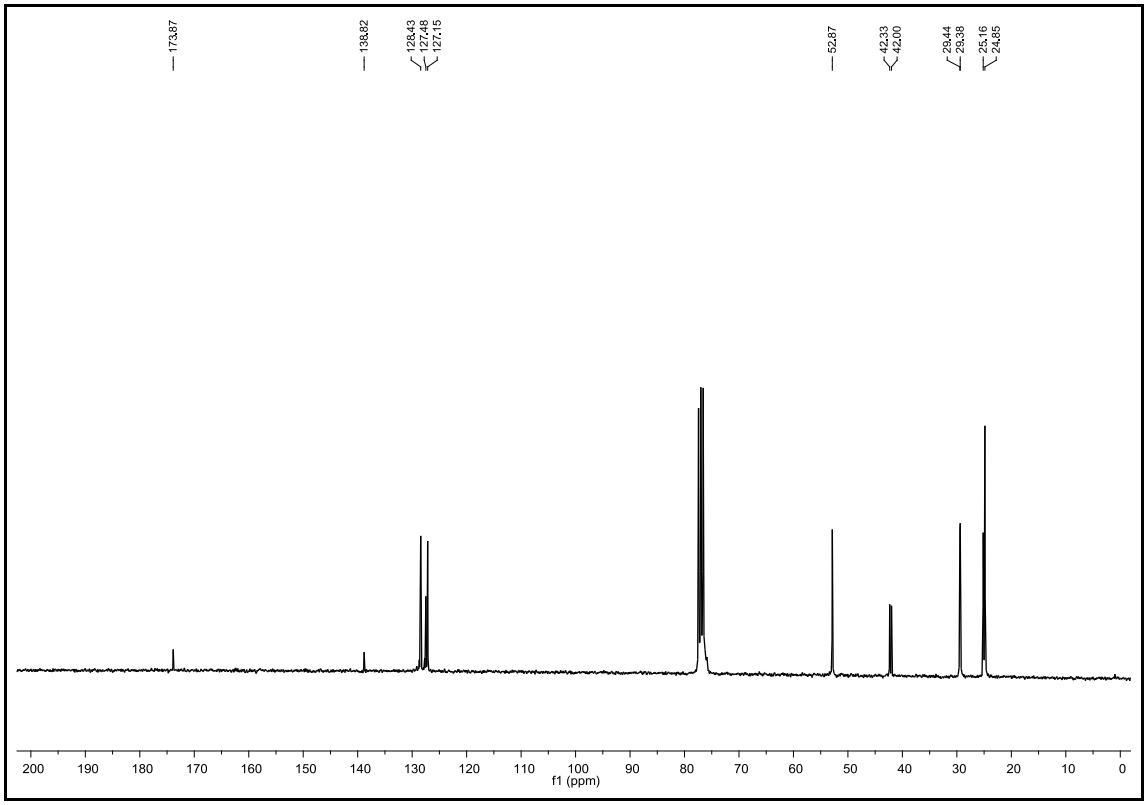
S-((1R,2S)-1-(4-bromophenyl)-1-chloro-3-((S)-4-isopropyl-2-oxooxazolidin-3-yl)-3-oxopropan-2-yl) ethanethioate



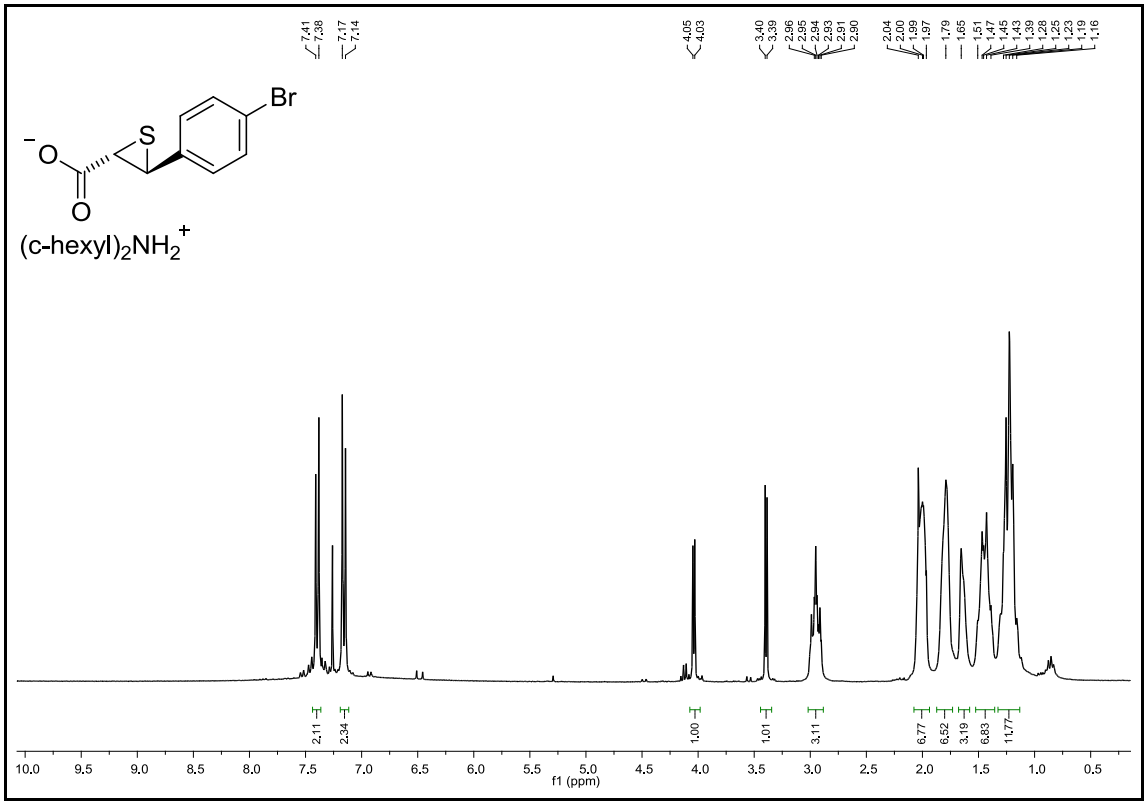


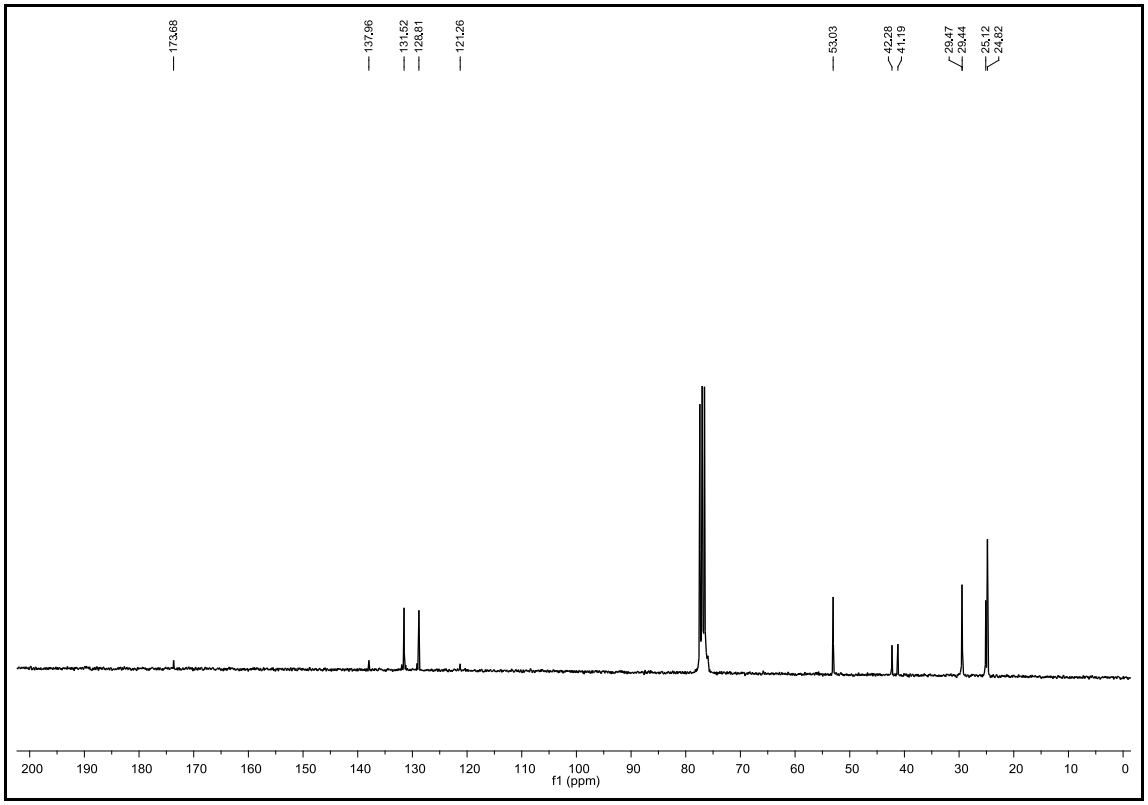
Dicyclohexylammonium (2S,3S)-3-phenylthiirane-2-carboxylate



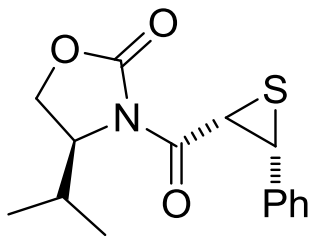


Dicyclohexylammonium (2S,3S)-3-(4-bromophenyl)thiirane-2-carboxylate

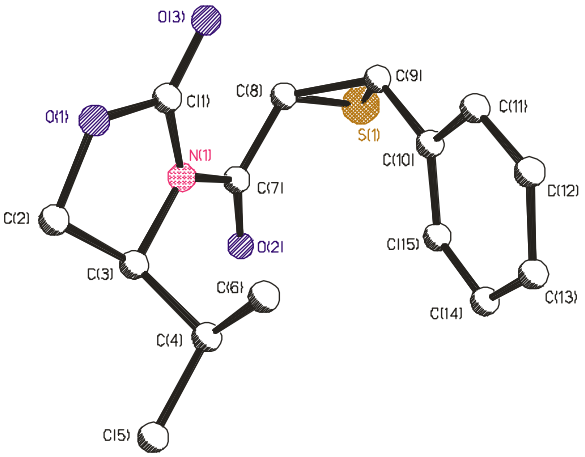


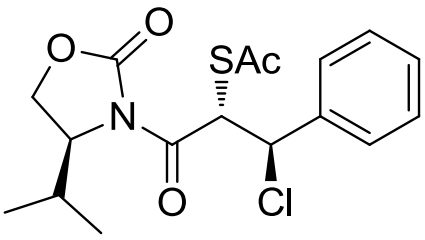


5. ORTEP diagrams of compounds *cis*-5a, 8a and 10b.

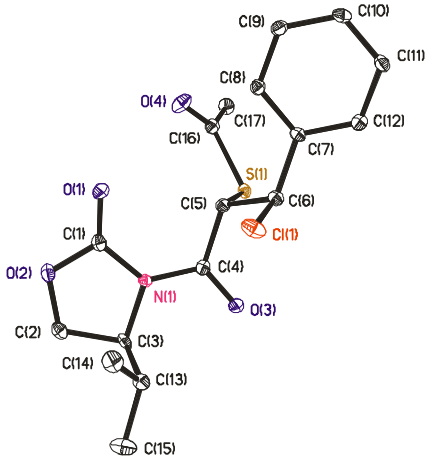


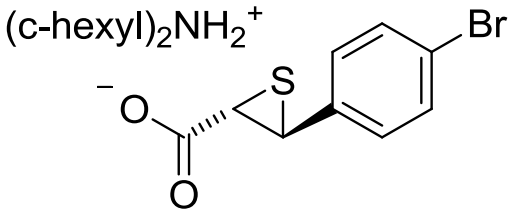
cis-**5a**



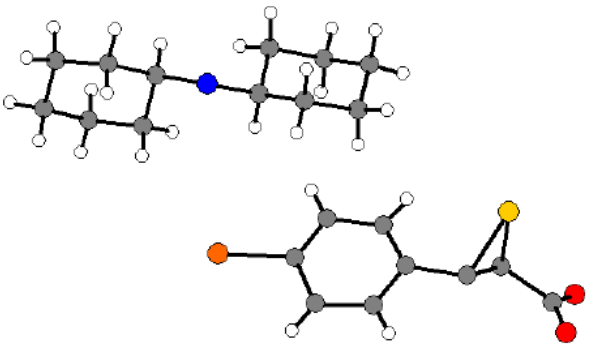


8a





10b



6. Computational Studies.

All structures were optimized using the functional B3LYP[9] and the 6-31G* basis set as implemented in Gaussian 09.[10] All energy minima and transition structures were characterized by frequency analysis. The stationary points were characterized by frequency calculations in order to verify that they have the right number of negative eigenvalues. The intrinsic reaction coordinates (IRC)[11] were followed to verify the energy profiles connecting each transition state to the correct associated local minima. The energies reported in this work include single-point calculations at B3LYP/6-311++G** level on the IEF-PCM solvation model (solvent = dichloromethane),[12] using the previously optimized gas-phase structures (B3LYP/6-31G*).

[9] Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.

[10] Gaussian 09, Revision B.01; M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[11] Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.

[12] (a) Cancès, E.; Mennucci, B.; Tomasi, J. *J. Chem. Phys.* **1997**, *107*, 3032-3047. (b) Tomasi, J.; Mennucci, B.; Cancès, E. *J. Mol. Struct. (Theochem)* **1999**, *464*, 211-226.

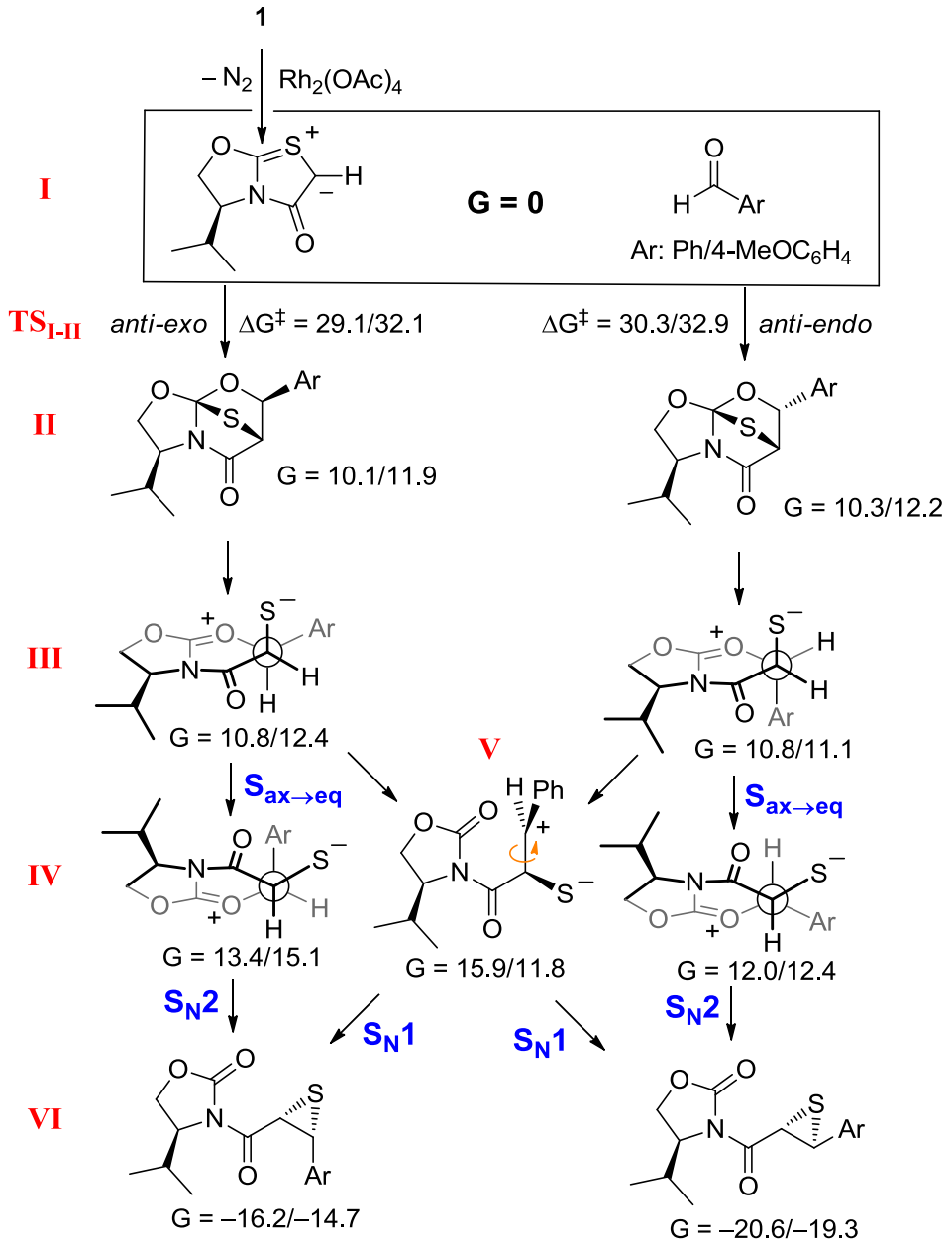


Table S1. Energies of the structures involved in the computational study.

	G (B3LYP/6-311++G**, IEF-PCM, CH_2Cl_2)	relative **G**	Frequency
I	-914.861019		
Benzaldehyde series			
Benzaldehyde	-345.595765		
I + Benzaldehyde	-1260.456784	0	
TS_{I-II} anti-exo	-1260.410323	29.15	-384.6
TS_{I-II} anti-endo	-1260.408515	30.29	-397.5
II exo	-1260.440763	10.05	
II endo	-1260.440432	10.26	
III exo	-1260.439590	10.79	
III endo	-1260.439545	10.82	
IV exo	-1260.435395	13.42	

IV endo	-1260.437630	12.02	
V	-1260.431414	15.92	
VI exo	-1260.482608	-16.20	
VI endo	-1260.489673	-20.64	
***p*-Methoxybenzaldehyde series**			
p-Methoxybenzaldehyde	-460.127569		
I + *p*-Methoxybenzaldehyde	-1374.988588	0	
TS_{I-II} anti-exo	-1374.937324	32.17	-171.0
TS_{I-II} anti-endo	-1374.936089	32.94	-187.2
II exo	-1374.969695	11.86	
II endo	-1374.969206	12.16	
III exo	-1374.968754	12.45	
III endo	-1374.970844	11.13	
IV exo	-1374.964540	15.09	
IV endo	-1374.968778	12.43	
V	-1374.966397	13.92	
VI exo	-1374.012006	-14.69	
VI endo	-1374.019274	-19.26	

We also sought for an alternative mechanistic scenario involving the initial reaction between the rhodium carbene **A** and benzaldehyde to generate an epoxide **B**, which could eventually lead to the final products. However, in contrast with the spontaneous intramolecular displacement of the rhodium fragment by the sulfur, the intermolecular formation of the epoxide shows a measurable barrier of 14.4 kcal/mol. Also, the epoxide **B** lies much higher in energy than **I**, supporting the aforementioned mechanism through **I**.

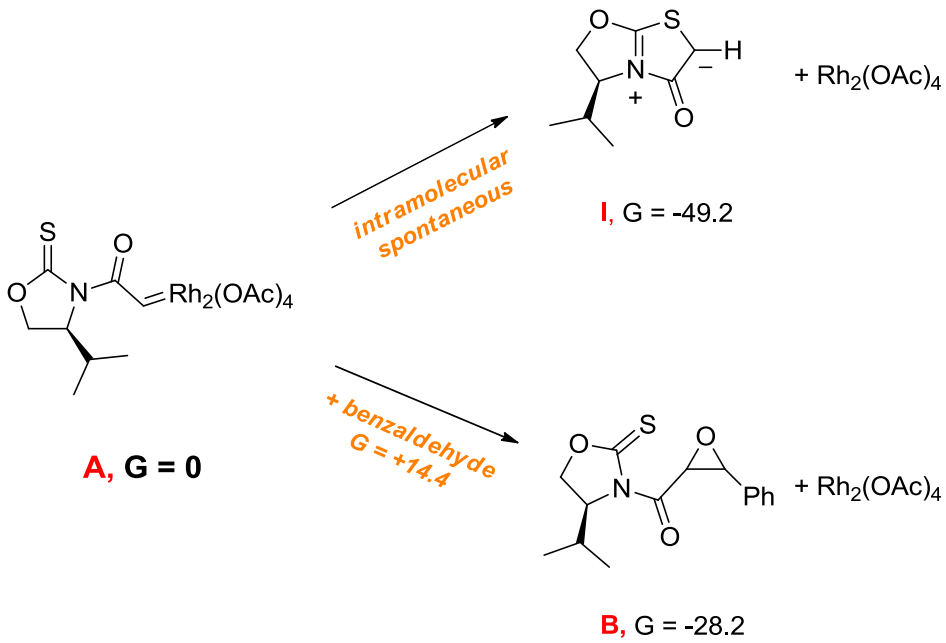


Figure S1. Comparison of the mechanisms through zwitterionic **I** and epoxide **B**

Cartesian Coordinates of the structures involved in the computational study

I

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.114984	1.438279	-0.268518
2	6	0	1.040162	-1.611995	-0.814183
3	6	0	-0.961653	-0.912932	-0.094189
4	6	0	-2.379653	1.058706	0.169604
5	6	0	1.077165	-0.057823	-0.733006
6	6	0	2.058910	0.555004	0.288317
7	6	0	3.503605	0.357616	-0.192154
8	6	0	1.856482	0.036566	1.717355
9	1	0	-3.221182	1.701799	0.361302
10	1	0	1.821733	-2.105955	-0.243467
11	1	0	1.033573	-1.977837	-1.839170
12	1	0	1.280928	0.364796	-1.718105
13	1	0	1.843857	1.627867	0.281075
14	1	0	3.785938	-0.700071	-0.213550
15	1	0	3.652011	0.767796	-1.195068
16	1	0	4.196217	0.865806	0.482714
17	1	0	2.088859	-1.029525	1.805069
18	1	0	2.521202	0.569656	2.401230
19	1	0	0.833361	0.193744	2.068000
20	7	0	-0.332958	0.204085	-0.392549
21	8	0	-0.250043	-2.020831	-0.211516
22	8	0	-0.598602	2.537027	-0.546327
23	16	0	-2.574802	-0.688548	0.386325

TS_{I-II} anti,exo – Benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.777088	-0.033638	-0.716079
2	6	0	0.757596	1.362065	0.251749
3	6	0	2.743321	-1.588874	-0.754426
4	6	0	0.952810	-0.924014	0.427855
5	6	0	-0.601465	0.889852	0.677919
6	6	0	5.244355	0.369684	-1.008488
7	6	0	4.035163	0.605383	-0.091831
8	6	0	4.307343	0.147863	1.346601
9	1	0	2.511588	-1.986443	-1.738975
10	1	0	3.633160	-2.062842	-0.350399
11	1	0	-1.151114	1.594045	1.293311
12	1	0	5.056622	0.736229	-2.021357
13	1	0	6.117773	0.896349	-0.617775
14	1	0	4.546248	-0.918745	1.403184
15	1	0	5.164895	0.691988	1.749003
16	1	0	3.457070	0.342298	2.005241
17	1	0	2.630270	0.366741	-1.720769
18	1	0	3.835011	1.681350	-0.073411
19	1	0	5.505248	-0.691486	-1.074312

20	7	0	1.551303	0.221804	0.063662
21	8	0	1.093620	2.486888	-0.049376
22	8	0	1.620453	-1.994617	0.129398
23	16	0	-0.374368	-0.742181	1.506989
24	6	0	-1.354061	0.512426	-0.781110
25	6	0	-2.832590	0.248957	-0.469607
26	6	0	-5.545808	-0.235268	0.070882
27	6	0	-3.343481	-1.049396	-0.514315
28	6	0	-3.698483	1.305017	-0.163731
29	6	0	-5.045378	1.067971	0.106561
30	6	0	-4.691089	-1.291985	-0.243118
31	1	0	-1.293803	1.499554	-1.287472
32	1	0	-2.672707	-1.858079	-0.777959
33	1	0	-3.319205	2.323236	-0.145327
34	1	0	-5.705166	1.897374	0.337704
35	1	0	-5.075602	-2.305734	-0.282873
36	1	0	-6.593863	-0.422511	0.277127
37	8	0	-0.682522	-0.464435	-1.375721

TS_{I-II} anti,endo – Benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.632044	-0.540999	-0.669317
2	6	0	2.598262	-0.346223	0.253610
3	6	0	4.759315	1.443729	0.123079
4	6	0	2.667029	0.747484	1.118503
5	6	0	3.738766	1.638615	1.053593
6	6	0	4.704120	0.346848	-0.739142
7	6	0	1.436814	-1.343711	0.343815
8	1	0	1.853943	-2.347497	0.107321
9	1	0	5.594588	2.133690	0.074954
10	1	0	3.780266	2.482985	1.733625
11	1	0	5.498750	0.180440	-1.458533
12	1	0	3.604394	-1.400053	-1.334218
13	1	0	1.877867	0.879830	1.848944
14	8	0	0.671317	-1.289621	1.416735
15	6	0	-0.203760	0.210503	-0.866128
16	6	0	-2.824115	-0.239272	1.709637
17	6	0	-1.572321	-1.309679	0.195909
18	6	0	0.480538	-1.106883	-1.048894
19	6	0	-2.188583	0.850665	0.803791
20	6	0	-3.227661	1.699122	0.037565
21	6	0	-4.039810	0.883855	-0.977180
22	6	0	-2.609783	2.948015	-0.603873
23	1	0	1.032542	-1.203389	-1.977743
24	1	0	-3.906899	-0.179787	1.772949
25	1	0	-2.380234	-0.282556	2.701339
26	1	0	-1.541810	1.499947	1.394979
27	1	0	-3.911909	2.042153	0.824463
28	1	0	-3.410604	0.533816	-1.800310
29	1	0	-4.526133	0.013755	-0.526962
30	1	0	-4.826448	1.507722	-1.407058
31	1	0	-1.913161	2.687220	-1.402386
32	1	0	-3.398604	3.575199	-1.026720
33	1	0	-2.065158	3.543754	0.133617
34	7	0	-1.330914	-0.013464	-0.044787
35	8	0	-2.509121	-1.537280	1.061729

36	8	0	0.180366	1.304107	-1.211936
37	16	0	-0.805663	-2.417690	-0.867923

II exo - Benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.739674	0.017361	-0.859952
2	6	0	0.829890	1.544279	0.083852
3	6	0	2.499794	-1.502174	-1.064479
4	6	0	0.609194	-0.768558	-0.022535
5	6	0	-1.280310	0.437725	-0.603403
6	6	0	-0.548942	1.090261	0.619583
7	6	0	-2.746928	0.142529	-0.387554
8	6	0	-5.481714	-0.304105	0.031070
9	6	0	-3.211038	-1.135325	-0.068455
10	6	0	-3.664716	1.192743	-0.508354
11	6	0	-5.023409	0.973336	-0.294498
12	6	0	-4.573414	-1.355763	0.138339
13	7	0	1.438614	0.391012	-0.303316
14	8	0	1.240635	2.686215	-0.020274
15	8	0	1.385756	-1.863693	-0.188545
16	8	0	-0.522748	-0.762820	-0.885244
17	16	0	-0.122465	-0.384723	1.668945
18	6	0	3.935544	0.406171	0.039466
19	6	0	3.914775	-0.266842	1.417463
20	6	0	5.255276	0.145061	-0.700265
21	1	0	2.214278	-1.728160	-2.092574
22	1	0	3.342488	-2.123164	-0.772205
23	1	0	2.870237	0.497174	-1.833587
24	1	0	-1.174486	1.109403	-1.461854
25	1	0	-1.105783	1.867452	1.130922
26	1	0	-2.508466	-1.954310	0.008195
27	1	0	-3.317340	2.186424	-0.773798
28	1	0	-5.723358	1.795683	-0.390073
29	1	0	-4.923456	-2.352434	0.382859
30	1	0	-6.539539	-0.478324	0.192181
31	1	0	3.847730	1.487532	0.190001
32	1	0	4.051726	-1.350242	1.343509
33	1	0	2.977780	-0.079363	1.946538
34	1	0	4.729480	0.122818	2.033267
35	1	0	5.411699	-0.922435	-0.886936
36	1	0	6.099348	0.498383	-0.103014
37	1	0	5.285601	0.664225	-1.662505

II endo – Benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.710081	0.545521	0.387930
2	6	0	2.507603	0.214030	-0.248093
3	6	0	4.549731	-1.688263	0.015363
4	6	0	2.341475	-1.075206	-0.759498

5	6	0	3.359254	-2.020535	-0.628489
6	6	0	4.723284	-0.400094	0.523292
7	6	0	1.428208	1.271003	-0.345177
8	1	0	1.883697	2.236916	-0.574341
9	1	0	5.339945	-2.423704	0.114523
10	1	0	3.220925	-3.016529	-1.033954
11	1	0	5.649488	-0.129503	1.017417
12	1	0	3.858299	1.549149	0.773859
13	1	0	1.424842	-1.333509	-1.273838
14	8	0	0.472506	0.980123	-1.396271
15	6	0	-0.146678	0.106508	1.234938
16	6	0	-2.221634	-0.590693	-1.697909
17	6	0	-0.823847	0.981689	-0.811212
18	6	0	0.562708	1.448825	0.943836
19	6	0	-1.913504	-1.110479	-0.269181
20	6	0	-3.120922	-1.223441	0.691051
21	6	0	-3.994304	-2.422064	0.293323
22	6	0	-3.944476	0.065233	0.802367
23	1	0	1.092069	1.865534	1.793835
24	1	0	-3.277541	-0.613217	-1.954377
25	1	0	-1.648192	-1.127886	-2.454336
26	1	0	-1.434059	-2.090756	-0.335195
27	1	0	-2.691794	-1.437617	1.675656
28	1	0	-4.452281	-2.280924	-0.691167
29	1	0	-3.415408	-3.349725	0.266446
30	1	0	-4.804940	-2.554641	1.013921
31	1	0	-4.444453	0.311257	-0.139668
32	1	0	-4.721831	-0.055831	1.561261
33	1	0	-3.326841	0.918524	1.090549
34	7	0	-0.923667	-0.111941	0.138322
35	8	0	-1.810666	0.812802	-1.721234
36	8	0	-0.005266	-0.607267	2.210675
37	16	0	-0.821295	2.513661	0.290034

III exo - Benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.924642	0.481389	-0.623622
2	6	0	-0.858236	-1.066080	-1.083675
3	6	0	-2.869039	1.975524	-0.219392
4	6	0	-0.763805	1.186960	-0.175863
5	6	0	1.291556	0.164975	-0.771431
6	6	0	0.565398	-1.184171	-0.626497
7	6	0	2.706733	0.238889	-0.282597
8	6	0	5.378675	0.285871	0.541815
9	6	0	3.020372	0.372580	1.074014
10	6	0	3.738029	0.136736	-1.221934
11	6	0	5.069627	0.150933	-0.811118
12	6	0	4.352997	0.403116	1.479989
13	7	0	-1.469209	0.170323	-0.652751
14	8	0	-1.513467	-1.849913	-1.728096
15	8	0	-1.465801	2.223128	0.177684
16	8	0	0.509166	1.241853	-0.061420

17	16	0	0.376236	-1.867686	1.069063
18	6	0	-3.723598	-0.437929	0.323212
19	6	0	-5.223854	-0.152479	0.156490
20	6	0	-3.280883	-0.346222	1.789136
21	1	0	1.255406	0.475931	-1.819146
22	1	0	1.076405	-1.886175	-1.287460
23	1	0	2.225484	0.454059	1.802358
24	1	0	3.501798	0.045911	-2.277110
25	1	0	5.861296	0.067852	-1.546687
26	1	0	4.589799	0.512815	2.532096
27	1	0	6.413903	0.306526	0.863110
28	1	0	-3.071914	2.652957	-1.045229
29	1	0	-3.483915	2.227048	0.638855
30	1	0	-3.309540	0.375872	-1.637880
31	1	0	-3.537500	-1.457175	-0.026891
32	1	0	-5.485314	0.858926	0.484157
33	1	0	-5.804195	-0.850934	0.763176
34	1	0	-5.542718	-0.266051	-0.883363
35	1	0	-2.220907	-0.584887	1.906912
36	1	0	-3.846759	-1.066577	2.384789
37	1	0	-3.471798	0.643504	2.216054

III endo - Benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-4.040362	-0.121258	-1.612236
2	1	0	-4.762651	1.039008	-0.505026
3	1	0	-3.061278	1.199037	-0.930131
4	1	0	-4.393683	-1.967479	1.736997
5	1	0	-5.554145	-0.833257	1.038663
6	1	0	-4.831767	-2.078864	0.024216
7	1	0	-3.358113	0.258766	1.360624
8	1	0	-2.008069	-1.778389	1.234088
9	1	0	-2.961684	-2.094596	-1.527705
10	1	0	-1.678631	-3.048786	-0.733810
11	1	0	1.113617	2.028997	1.282990
12	6	0	-3.850503	0.474844	-0.713916
13	6	0	-4.630103	-1.381880	0.844212
14	6	0	-3.502216	-0.398205	0.498021
15	16	0	-0.648642	2.939396	-0.169613
16	8	0	0.557050	0.141328	-1.517536
17	8	0	-1.033335	-1.382047	-1.766647
18	8	0	-0.850415	0.595530	2.258086
19	7	0	-0.999338	-0.288856	0.157468
20	6	0	0.475838	1.631311	0.493507
21	6	0	1.381658	1.020551	-0.577524
22	6	0	-0.456374	-0.467868	-1.041518
23	6	0	-2.055866	-2.048373	-0.931357
24	6	0	-0.479909	0.654595	1.109004
25	6	0	-2.178813	-1.175981	0.341683
26	1	0	1.694639	1.808499	-1.256829
27	6	0	2.566581	0.198911	-0.138396
28	6	0	4.819571	-1.310377	0.568535
29	6	0	3.706229	0.195402	-0.952794
30	6	0	2.571606	-0.557509	1.040175
31	6	0	3.692704	-1.307587	1.389828

32	6	0	4.825681	-0.555205	-0.603818
33	1	0	3.716265	0.786816	-1.861931
34	1	0	1.716787	-0.559309	1.705717
35	1	0	3.686880	-1.884121	2.307446
36	1	0	5.701604	-0.545638	-1.241886
37	1	0	5.691319	-1.892024	0.845271

IV exo – Benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.656793	0.255603	0.102543
2	6	0	-0.494642	1.573342	-0.465409
3	6	0	-3.025603	-0.269208	1.509328
4	6	0	-0.813394	0.185531	1.524448
5	6	0	1.481682	0.889614	0.966225
6	6	0	0.816912	1.999754	0.179917
7	1	0	-3.497689	-1.246716	1.512754
8	1	0	-3.610941	0.437792	2.092431
9	7	0	-1.238944	0.644685	0.336499
10	8	0	-0.991514	1.991122	-1.475695
11	8	0	-1.736647	-0.424084	2.213631
12	8	0	0.353218	0.293185	1.995494
13	1	0	-3.213746	1.165304	-0.121866
14	6	0	-2.833923	-0.741114	-1.061464
15	1	0	-2.400277	-0.249320	-1.936922
16	6	0	-4.332015	-0.942945	-1.334437
17	1	0	-4.468096	-1.590290	-2.203414
18	1	0	-4.841070	-1.418747	-0.490034
19	1	0	-4.833167	0.006403	-1.541639
20	6	0	-2.109532	-2.077096	-0.852943
21	1	0	-1.039064	-1.944822	-0.679252
22	1	0	-2.525686	-2.647544	-0.016961
23	1	0	-2.217522	-2.694018	-1.747876
24	1	0	0.486291	2.743999	0.917560
25	16	0	2.069176	2.784656	-0.892845
26	1	0	2.149819	1.306182	1.711016
27	6	0	2.068388	-0.316736	0.305311
28	6	0	3.159959	-2.656836	-0.779961
29	6	0	2.969843	-1.092917	1.045981
30	6	0	1.727619	-0.721203	-0.990896
31	6	0	2.270716	-1.884950	-1.528319
32	6	0	3.511267	-2.257416	0.509082
33	1	0	3.250236	-0.779855	2.045930
34	1	0	1.077520	-0.111893	-1.605079
35	1	0	2.009903	-2.181362	-2.537512
36	1	0	4.210469	-2.845842	1.091555
37	1	0	3.585440	-3.558896	-1.204546

IV endo – Benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	3.139604	0.210349	-0.469974
2	6	0	0.660190	0.140668	-0.757228
3	6	0	4.048741	-0.948929	-0.029522
4	6	0	1.927452	-1.469659	0.700121
5	6	0	-1.883107	0.119071	-0.973772
6	6	0	-0.662310	-0.469579	-0.377411
7	7	0	1.812213	-0.364151	-0.155232
8	8	0	0.752945	1.045989	-1.565782
9	8	0	3.231868	-1.755120	0.859326
10	6	0	3.389772	1.564399	0.232702
11	1	0	4.925298	-0.631852	0.529650
12	1	0	4.352780	-1.580855	-0.864081
13	1	0	2.581765	2.222735	-0.099454
14	1	0	4.848769	3.168801	0.165830
15	1	0	3.201628	0.359541	-1.547721
16	1	0	5.574995	1.568513	0.040779
17	1	0	4.727770	2.266742	-1.348506
18	1	0	4.138442	0.856681	2.170188
19	1	0	3.460818	2.481929	2.191427
20	1	0	-0.720403	-0.882602	0.618932
21	1	0	2.383226	1.091365	2.122730
22	8	0	1.050617	-2.092123	1.242466
23	6	0	4.711849	2.171510	-0.259030
24	6	0	3.338517	1.483558	1.764368
25	16	0	-1.418936	-1.556263	-1.663070
26	6	0	-3.145107	0.288715	-0.200837
27	6	0	-5.526255	0.731607	1.219002
28	6	0	-3.530561	-0.578795	0.830359
29	6	0	-3.973572	1.372526	-0.515778
30	6	0	-5.155509	1.594741	0.190269
31	6	0	-4.709297	-0.356261	1.535476
32	1	0	-2.918017	-1.438921	1.076330
33	1	0	-3.689065	2.048062	-1.315473
34	1	0	-5.783834	2.440308	-0.065539
35	1	0	-4.993807	-1.034964	2.331527
36	1	0	-6.444805	0.900467	1.769262
37	1	0	-1.693969	0.899833	-1.700688

V – Benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.938138	-0.615728	0.529289
2	6	0	-0.850819	0.645986	1.165294
3	6	0	-3.024547	-1.992608	-0.156911
4	6	0	-0.872978	-1.255531	-0.436116
5	6	0	1.537844	-0.065832	0.822480
6	6	0	0.569729	1.038539	0.777769
7	6	0	2.864342	-0.132658	0.340061
8	6	0	5.532496	-0.365473	-0.466989
9	6	0	3.422620	0.803409	-0.569975
10	6	0	3.678551	-1.197511	0.817669
11	6	0	4.996026	-1.309210	0.418602
12	6	0	4.748490	0.683959	-0.954520
13	6	0	-3.788324	0.506311	-0.107927
14	6	0	-5.276952	0.250464	0.169588

15	6	0	-3.512993	0.713290	-1.602874
16	1	0	3.254419	-1.918309	1.507331
17	1	0	5.611795	-2.120087	0.787458
18	1	0	5.175644	1.400280	-1.645760
19	1	0	6.565842	-0.454959	-0.782418
20	1	0	-3.090493	-2.812640	0.557641
21	1	0	-3.828933	-2.072092	-0.883187
22	1	0	-3.199003	-0.697220	1.584651
23	1	0	1.279472	-0.852682	1.528268
24	1	0	-3.507777	1.423953	0.417031
25	1	0	0.927448	1.625411	1.648323
26	1	0	-5.636219	-0.655313	-0.329774
27	1	0	-5.876376	1.085341	-0.200902
28	1	0	-5.473107	0.146743	1.240634
29	1	0	2.791042	1.593074	-0.954955
30	1	0	-2.458893	0.928648	-1.794080
31	1	0	-4.090788	1.565829	-1.968612
32	1	0	-3.805243	-0.155915	-2.200542
33	7	0	-1.482948	-0.363540	0.424151
34	8	0	-1.465386	1.209253	2.050518
35	8	0	-1.769048	-2.146291	-0.878094
36	8	0	0.297188	-1.288483	-0.762996
37	16	0	0.420481	2.254653	-0.576765

VI exo – Benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.524968	-0.150056	-0.568509
2	6	0	0.260842	-1.199813	-0.787933
3	6	0	3.575936	-0.471277	0.507305
4	6	0	1.541772	-1.110465	1.370349
5	6	0	-2.082708	-1.305964	0.389900
6	6	0	-0.838470	-1.983217	-0.109565
7	6	0	-2.328844	0.167746	0.301545
8	6	0	-2.776828	2.940411	0.298776
9	6	0	-2.353199	0.882173	-0.902305
10	6	0	-2.547839	0.858771	1.501359
11	6	0	-2.766047	2.235237	1.501326
12	6	0	-2.571383	2.258261	-0.900763
13	6	0	2.277422	1.352441	-0.836748
14	6	0	3.478176	1.951295	-1.583902
15	6	0	1.934728	2.157663	0.423461
16	1	0	-2.545439	0.314981	2.440088
17	1	0	-2.933094	2.752690	2.439261
18	1	0	-2.590843	2.797043	-1.841524
19	1	0	-2.952974	4.010109	0.294905
20	1	0	4.181924	-1.340598	0.250486
21	1	0	4.222491	0.365952	0.756999
22	1	0	2.777397	-0.635821	-1.511075
23	1	0	-2.457327	-1.740776	1.310418
24	1	0	1.415998	1.392927	-1.509228
25	1	0	-0.472773	-2.776977	0.529359
26	1	0	4.386138	1.944733	-0.972052
27	1	0	3.274074	2.990774	-1.851555
28	1	0	3.689034	1.403529	-2.506912

29	1	0	-2.214993	0.357294	-1.838960
30	1	0	1.052328	1.763363	0.933401
31	1	0	1.715852	3.193060	0.151249
32	1	0	2.763773	2.177176	1.137223
33	7	0	1.350502	-0.840698	0.009923
34	8	0	0.260615	-0.903959	-1.965303
35	8	0	2.810197	-0.801902	1.696157
36	8	0	0.742380	-1.534539	2.165551
37	16	0	-2.327611	-2.416288	-1.067410

VI endo – Benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.139718	0.210258	-0.469955
2	6	0	0.660241	0.140882	-0.757273
3	6	0	4.048682	-0.949194	-0.029638
4	6	0	1.927308	-1.469700	0.699936
5	6	0	-1.883002	0.119732	-0.973499
6	6	0	-0.662271	-0.469561	-0.377782
7	6	0	3.389903	1.564140	0.233002
8	6	0	4.712074	2.171258	-0.258522
9	6	0	3.338560	1.483039	1.764651
10	1	0	4.352549	-1.581078	-0.864292
11	1	0	4.925340	-0.632288	0.529475
12	1	0	3.201875	0.359610	-1.547671
13	1	0	2.581977	2.222599	-0.099092
14	1	0	-0.720093	-0.883533	0.618180
15	1	0	5.575113	1.567984	0.041029
16	1	0	4.849170	3.168354	0.166740
17	1	0	4.727957	2.266920	-1.347957
18	1	0	2.383311	1.090667	2.122938
19	1	0	3.460686	2.481362	2.191872
20	1	0	4.138559	0.856224	2.170413
21	7	0	1.812234	-0.364280	-0.155484
22	8	0	0.753064	1.046521	-1.565437
23	8	0	3.231721	-1.755292	0.859195
24	8	0	1.050412	-2.092040	1.242325
25	16	0	-1.419104	-1.555146	-1.664312
26	1	0	-1.693866	0.901055	-1.699819
27	6	0	-3.144996	0.288886	-0.200472
28	6	0	-5.526378	0.730757	1.219308
29	6	0	-3.529983	-0.578644	0.830874
30	6	0	-3.974019	1.372237	-0.515546
31	6	0	-5.156070	1.593943	0.190460
32	6	0	-4.708845	-0.356627	1.535948
33	1	0	-2.916980	-1.438387	1.077054
34	1	0	-3.689865	2.047832	-1.315318
35	1	0	-5.784817	2.439165	-0.065458
36	1	0	-4.992987	-1.035355	2.332113
37	1	0	-6.445013	0.899217	1.769554

$TS_{I\text{-}II}$ anti,exo – *p*-Methoxy-benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.466309	-0.122641	-0.691304
2	6	0	1.527153	1.373584	0.290213
3	6	0	3.341609	-1.672373	-0.764053
4	6	0	1.570811	-0.924827	0.399222
5	6	0	0.134424	0.980118	0.678656
6	6	0	5.958452	0.131265	-0.943085
7	6	0	4.752383	0.426905	-0.039818
8	6	0	4.973717	-0.070646	1.393900
9	6	0	-0.616584	0.695020	-0.811347
10	6	0	-2.110410	0.509354	-0.532103
11	6	0	-4.861495	0.166190	-0.035390
12	6	0	-2.703245	-0.746531	-0.623896
13	6	0	-2.924889	1.600906	-0.200118
14	6	0	-4.281110	1.439628	0.047361
15	6	0	-4.067468	-0.931027	-0.377415
16	1	0	4.125694	0.163588	2.042255
17	1	0	3.354538	0.306796	-1.688586
18	1	0	4.618309	1.512701	-0.005277
19	1	0	6.157272	-0.942679	-1.017930
20	1	0	3.114654	-2.035736	-1.762751
21	1	0	4.190673	-2.206327	-0.346887
22	1	0	-0.382528	1.699587	1.304409
23	1	0	5.807287	0.519561	-1.953927
24	1	0	6.855760	0.600910	-0.534152
25	1	0	5.146577	-1.150578	1.434808
26	1	0	5.855963	0.413557	1.818880
27	1	0	-0.483808	1.693637	-1.280250
28	1	0	-2.085671	-1.590268	-0.907802
29	1	0	-2.494319	2.596904	-0.141848
30	1	0	-4.909757	2.286249	0.298869
31	1	0	-4.492317	-1.922559	-0.461220
32	7	0	2.249127	0.189124	0.081034
33	8	0	1.942208	2.481728	0.025905
34	8	0	2.173342	-2.028402	0.081059
35	8	0	0.009855	-0.300022	-1.423069
36	16	0	0.234649	-0.688018	1.455526
37	8	0	-6.203208	0.102854	0.225111
38	6	0	-6.851035	-1.166330	0.152040
39	1	0	-6.780738	-1.590845	-0.854123
40	1	0	-7.895930	-0.981088	0.394087
41	1	0	-6.429247	-1.869819	0.876561

$TS_{I\text{-}II}$ anti,endo – *p*-Methoxy-benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.988076	-1.221961	-0.377962
2	6	0	1.929553	-0.802052	0.426120
3	6	0	4.298674	0.708915	0.235146
4	6	0	2.083334	0.386828	1.147270
5	6	0	3.249041	1.136256	1.056798

6	6	0	4.168570	-0.482187	-0.485320
7	6	0	0.653998	-1.635831	0.552250
8	1	0	0.944507	-2.705259	0.462070
9	1	0	3.367981	2.055379	1.619492
10	1	0	4.967502	-0.843684	-1.118399
11	1	0	2.907198	-2.152466	-0.934040
12	1	0	1.276675	0.707388	1.796398
13	8	0	-0.157582	-1.355319	1.554098
14	6	0	-0.692127	-0.060966	-0.973104
15	6	0	-3.468756	0.257705	1.459934
16	6	0	-2.289153	-1.207191	0.235375
17	6	0	-0.199698	-1.470782	-0.930671
18	6	0	-2.589464	1.087066	0.480072
19	6	0	-3.347615	1.973805	-0.531872
20	6	0	-4.000605	3.154273	0.201098
21	6	0	-4.358824	1.199116	-1.385074
22	1	0	0.376400	-1.781910	-1.794617
23	1	0	-4.531811	0.467905	1.394033
24	1	0	-3.128327	0.316315	2.489448
25	1	0	-1.882934	1.699845	1.039830
26	1	0	-2.578675	2.377214	-1.197333
27	1	0	-4.783131	2.824966	0.891885
28	1	0	-3.264460	3.728248	0.771907
29	1	0	-4.466413	3.829727	-0.520608
30	1	0	-5.176729	0.789243	-0.782484
31	1	0	-4.805788	1.867977	-2.124055
32	1	0	-3.890080	0.375758	-1.929800
33	7	0	-1.845321	-0.011124	-0.165816
34	8	0	-3.298399	-1.161392	1.049628
35	8	0	-0.164983	0.913849	-1.460808
36	16	0	-1.669553	-2.549076	-0.643827
37	8	0	5.406479	1.512635	0.209794
38	6	0	6.509402	1.125784	-0.608597
39	1	0	7.262215	1.901977	-0.479287
40	1	0	6.222324	1.070368	-1.663098
41	1	0	6.923091	0.163236	-0.289880

II exo – *p*-Methoxy-benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.595291	-0.326169	1.975283
2	1	0	5.355590	-0.286953	2.103474
3	1	0	4.566147	-1.640395	1.296613
4	1	0	6.802068	0.146489	0.038703
5	1	0	6.047203	0.480780	-1.523626
6	1	0	6.033747	-1.160630	-0.859956
7	1	0	4.623335	1.279880	0.351243
8	1	0	3.627796	0.524540	-1.756837
9	1	0	2.834694	-1.623308	-2.213436
10	1	0	3.898247	-2.198202	-0.905565
11	1	0	-0.322081	1.912103	1.240497
12	16	0	0.498928	-0.437455	1.603240
13	8	0	2.100019	2.663027	0.205667
14	8	0	1.947444	-1.856295	-0.345532

15	7	0	2.151192	0.392097	-0.271270
16	6	0	4.523562	-0.557317	1.448113
17	6	0	5.951630	-0.099837	-0.601615
18	6	0	4.634312	0.208365	0.124248
19	6	0	3.439035	-0.022407	-0.829270
20	6	0	0.194046	1.143860	0.675496
21	6	0	1.240564	-0.728214	-0.103210
22	6	0	3.105634	-1.500811	-1.164050
23	6	0	1.611580	1.547044	0.204055
24	8	0	0.131817	-0.575048	-0.980587
25	6	0	-0.553281	0.647650	-0.610908
26	1	0	-0.381280	1.380795	-1.406274
27	6	0	-2.037812	0.430042	-0.450679
28	6	0	-4.812005	0.122696	-0.110775
29	6	0	-2.900479	1.530840	-0.554789
30	6	0	-2.588777	-0.822142	-0.189204
31	6	0	-3.966036	-0.985363	-0.021085
32	6	0	-4.268638	1.386129	-0.382489
33	1	0	-2.498473	2.514869	-0.775248
34	1	0	-1.942043	-1.686939	-0.124386
35	1	0	-4.359190	-1.973423	0.175603
36	1	0	-4.934247	2.237293	-0.463280
37	8	0	-6.166855	0.075368	0.039967
38	6	0	-6.778174	-1.184068	0.324129
39	1	0	-6.604791	-1.899423	-0.485234
40	1	0	-7.844310	-0.983347	0.408526
41	1	0	-6.409261	-1.598571	1.267031

II endo – *p*-Methoxy-benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-4.021935	-0.287287	-1.108051
2	1	0	-5.142671	0.988821	-1.589431
3	1	0	-4.970273	0.572427	0.113985
4	1	0	-4.633902	3.436206	-1.055984
5	1	0	-3.100143	3.884604	-0.302246
6	1	0	-4.366720	3.099498	0.653450
7	1	0	-2.840959	1.845224	-1.694404
8	1	0	-1.475740	2.194775	0.315848
9	1	0	-1.930737	1.350706	2.445873
10	1	0	-3.630452	1.212837	1.933506
11	1	0	0.016141	-2.281520	-1.764377
12	1	0	1.139709	0.792656	1.241950
13	1	0	2.802628	-2.626957	-0.744447
14	1	0	4.938996	-1.418717	-1.024150
15	1	0	3.255863	1.994736	0.971477
16	1	0	0.707305	-2.801189	0.606399
17	16	0	-1.988210	-2.429253	-0.245825
18	8	0	-0.458013	0.375311	-2.216173
19	8	0	-2.526728	-0.514119	1.741791
20	7	0	-1.453432	0.145694	-0.133040
21	6	0	-4.420763	0.689186	-0.825306
22	6	0	-3.882363	3.120437	-0.328320

23	6	0	-3.315583	1.745964	-0.712387
24	6	0	-2.175679	1.357155	0.257672
25	6	0	-0.391996	-1.738192	-0.919089
26	6	0	-1.613247	-0.926457	0.832342
27	6	0	-2.605281	0.945088	1.690807
28	6	0	-0.759637	-0.269634	-1.228728
29	8	0	-0.351758	-1.227391	1.413824
30	6	0	0.500564	-1.756129	0.364304
31	6	0	4.096426	-0.941216	-0.538234
32	6	0	3.168343	0.989854	0.581600
33	6	0	1.959389	0.305458	0.729697
34	6	0	4.242075	0.368881	-0.060438
35	6	0	1.800708	-0.992913	0.251087
36	6	0	2.892972	-1.609277	-0.377833
37	8	0	5.462066	0.944104	-0.259933
38	6	0	5.670804	2.280512	0.199939
39	1	0	6.695120	2.529499	-0.069900
40	1	0	5.553462	2.348164	1.285554
41	1	0	4.984772	2.978151	-0.289308

III exo – *p*-Methoxy-benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	4.011893	0.360456	-2.473068
2	1	0	4.388013	-1.356412	-2.409396
3	1	0	2.791438	-0.806297	-1.909124
4	1	0	6.270563	-0.066370	0.593132
5	1	0	6.445442	-0.861088	-0.975059
6	1	0	6.100037	0.864986	-0.904219
7	1	0	4.248452	-1.393382	0.039786
8	1	0	4.074835	0.646313	1.389794
9	1	0	4.029976	2.149226	-1.140795
10	1	0	3.744022	2.810358	0.492729
11	1	0	-4.180279	-0.165344	-2.017327
12	1	0	-5.031448	0.567640	2.132557
13	1	0	-2.606523	0.610629	2.612595
14	1	0	-1.777149	-0.160004	-1.526525
15	1	0	-0.242698	-1.745100	1.672443
16	1	0	-0.432112	0.665274	1.908348
17	6	0	3.854482	-0.554624	-1.893190
18	6	0	5.885446	-0.098314	-0.429778
19	6	0	4.385856	-0.430275	-0.459680
20	16	0	0.281367	-2.028347	-0.711571
21	8	0	0.134074	1.203925	-0.000045
22	8	0	2.056850	2.184260	-0.517826
23	8	0	2.367814	-1.590101	1.905988
24	7	0	2.181751	0.262499	0.575170
25	6	0	-3.849781	-0.003969	-1.000545
26	6	0	-4.310074	0.408170	1.340298
27	6	0	-2.948404	0.429428	1.598876
28	6	0	-2.483554	0.002824	-0.724119
29	6	0	-4.770660	0.191745	0.034682
30	6	0	-2.014961	0.217829	0.574079
31	6	0	0.193771	-1.124327	0.888073
32	6	0	-0.562112	0.213974	0.920893

33	6	0	1.411929	1.191213	0.022258
34	6	0	3.492822	2.017188	-0.207025
35	6	0	1.643073	-0.915653	1.213545
36	6	0	3.620893	0.597728	0.399963
37	8	0	-6.121776	0.199084	-0.127868
38	6	0	-6.658651	-0.019967	-1.434799
39	1	0	-6.336508	0.760968	-2.129544
40	1	0	-7.739801	0.020122	-1.319656
41	1	0	-6.368428	-1.001092	-1.820918

III endo – *p*-Methoxy-benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-4.699219	-0.506543	-1.540492
2	1	0	-5.522393	0.462634	-0.325424
3	1	0	-3.883835	0.894219	-0.805037
4	1	0	-4.611164	-2.615034	1.659975
5	1	0	-5.959938	-1.631944	1.081132
6	1	0	-5.090750	-2.671106	-0.044841
7	1	0	-3.950512	-0.230905	1.427476
8	1	0	-2.305243	-2.012691	1.110917
9	1	0	-3.298323	-2.276890	-1.642515
10	1	0	-1.857857	-3.074311	-0.953089
11	1	0	0.197932	2.211455	1.382331
12	6	0	-4.551086	0.051153	-0.610209
13	6	0	-4.969573	-2.011887	0.821066
14	6	0	-4.022947	-0.839215	0.521426
15	16	0	-1.712326	2.952947	0.024186
16	8	0	-0.164834	0.469666	-1.547663
17	8	0	-1.512114	-1.259707	-1.873162
18	8	0	-1.506660	0.443456	2.279643
19	7	0	-1.581249	-0.309514	0.124968
20	6	0	-0.392592	1.780526	0.573759
21	6	0	0.569629	1.384560	-0.546620
22	6	0	-1.056219	-0.318478	-1.096669
23	6	0	-2.389816	-2.132841	-1.066539
24	6	0	-1.179777	0.633223	1.131150
25	6	0	-2.600707	-1.383140	0.271518
26	1	0	0.754151	2.251973	-1.173593
27	6	0	1.857168	0.702939	-0.189374
28	6	0	4.313436	-0.555680	0.358569
29	6	0	2.969886	0.903294	-1.011582
30	6	0	2.000882	-0.136839	0.927387
31	6	0	3.208724	-0.757638	1.199298
32	6	0	4.190755	0.285393	-0.753032
33	1	0	2.887280	1.556366	-1.873702
34	1	0	1.176229	-0.304678	1.609577
35	1	0	3.321185	-1.399567	2.064543
36	1	0	5.027984	0.468845	-1.411847
37	8	0	5.450403	-1.208826	0.707784
38	6	0	6.616217	-1.051977	-0.107432
39	1	0	6.435364	-1.410705	-1.124421
40	1	0	7.386186	-1.660565	0.361582
41	1	0	6.940635	-0.008168	-0.133442

IV exo – *p*-Methoxy-benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	3.512958	-0.365295	2.564427
2	1	0	3.222970	-0.849942	-1.696167
3	1	0	1.588173	0.965894	-1.793732
4	1	0	1.855866	1.464628	2.458412
5	1	0	0.631989	3.052658	1.236210
6	1	0	-1.575850	2.835953	0.405189
7	1	0	-0.289032	-3.403239	0.310442
8	1	0	-1.733846	-3.040238	1.249732
9	1	0	-0.486881	-1.803051	1.015783
10	1	0	-2.852285	-3.033811	-2.421337
11	1	0	-3.194674	-3.783854	-0.854355
12	1	0	-1.684093	-4.138669	-1.688891
13	1	0	-0.937067	-1.792191	-1.442219
14	1	0	-3.148504	-0.767204	-1.540463
15	1	0	-4.765411	-0.831914	0.177729
16	1	0	-3.924110	-2.286666	0.766966
17	6	0	3.077101	-0.072725	1.616526
18	6	0	2.925420	-0.361704	-0.778163
19	6	0	1.989906	0.671383	-0.832512
20	6	0	2.147151	0.953782	1.546703
21	6	0	3.473201	-0.741183	0.451355
22	6	0	1.577614	1.339651	0.322285
23	16	0	0.224604	3.459312	-1.172615
24	6	0	-1.021964	-2.623278	0.530814
25	6	0	-2.404995	-3.346420	-1.473420
26	6	0	-1.707303	-2.174859	-0.767013
27	8	0	-1.990505	1.205600	2.097164
28	8	0	-3.357966	-0.516685	1.654389
29	8	0	-1.119047	0.755460	-1.992561
30	7	0	-2.083759	0.213277	-0.025272
31	6	0	-0.826124	2.334497	-0.193456
32	6	0	0.573389	2.445546	0.339127
33	6	0	-2.427816	0.396244	1.319566
34	6	0	-3.802857	-1.245318	0.479726
35	6	0	-1.319554	1.059301	-0.834149
36	6	0	-2.707368	-1.011801	-0.574110
37	8	0	4.396900	-1.730701	0.613713
38	6	0	4.852859	-2.437638	-0.541149
39	1	0	4.028617	-2.958051	-1.037641
40	1	0	5.574136	-3.166100	-0.176243
41	1	0	5.342676	-1.763091	-1.249525

IV endo – *p*-Methoxy-benzaldehyde

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	1	0	-0.813567	0.321681	-2.181547
2	1	0	-4.498096	-0.755503	1.832280
3	1	0	-5.159863	1.912948	-1.472340
4	1	0	-2.912469	1.367938	-2.348493
5	1	0	-2.291933	-1.301700	0.959551
6	1	0	2.783015	1.653920	1.885144
7	1	0	-0.082367	-0.823011	0.586093
8	1	0	3.819610	3.065391	1.707088
9	1	0	4.524299	1.524013	2.184733
10	1	0	5.505531	2.007993	-1.490063
11	1	0	6.191878	1.727465	0.118024
12	1	0	4.041578	0.048268	-1.357981
13	1	0	5.432146	3.271805	-0.257964
14	1	0	3.227214	2.188730	-0.519903
15	1	0	5.138823	-1.595363	-0.075641
16	1	0	5.517258	-0.301858	1.087722
17	6	0	-4.164043	-0.280326	0.920110
18	6	0	-4.518935	1.214890	-0.947127
19	6	0	-3.256946	0.902326	-1.431256
20	6	0	-2.899338	-0.583101	0.420822
21	6	0	-4.982690	0.625990	0.235356
22	6	0	-2.419461	0.003173	-0.753947
23	16	0	-0.478487	-2.043417	-1.536686
24	6	0	3.767049	1.986100	1.543995
25	6	0	5.361613	2.193935	-0.421995
26	8	0	1.612045	-1.715961	1.706895
27	6	0	3.999182	1.674249	0.059479
28	8	0	3.817211	-1.388090	1.495118
29	8	0	1.601226	0.614702	-1.815380
30	7	0	2.507204	-0.360015	0.009298
31	6	0	0.083248	-0.646339	-0.466335
32	6	0	-1.070559	-0.273018	-1.313067
33	6	0	2.536929	-1.210249	1.124082
34	6	0	4.722296	-0.790748	0.530317
35	6	0	1.427419	-0.074195	-0.826872
36	6	0	3.853771	0.175849	-0.291944
37	8	0	-6.232460	0.991098	0.635764
38	6	0	-6.764289	0.419538	1.832842
39	1	0	-6.150285	0.677458	2.700633
40	1	0	-6.846412	-0.667920	1.748605
41	1	0	-7.756641	0.850090	1.950004

V – *p*-Methoxy-benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.660594	-0.588272	0.432135
2	6	0	-1.592964	0.642212	1.149171
3	6	0	-3.732327	-1.979453	-0.220514
4	6	0	-1.582574	-1.230120	-0.507366
5	6	0	0.825233	-0.078501	0.993247
6	6	0	-0.142744	1.029058	0.882853

7	6	0	2.165660	-0.148227	0.617124
8	6	0	4.898231	-0.384442	-0.004414
9	6	0	2.814972	0.811648	-0.214098
10	6	0	2.944115	-1.247571	1.105351
11	6	0	4.273017	-1.363095	0.807498
12	6	0	4.154519	0.701643	-0.512355
13	6	0	-4.491941	0.519277	-0.254384
14	6	0	-5.983937	0.306495	0.040587
15	6	0	-4.225204	0.648978	-1.760116
16	6	0	6.933135	0.355546	-1.048674
17	1	0	4.870388	-2.186700	1.177206
18	1	0	4.623204	1.442373	-1.144760
19	1	0	-3.773913	-2.782992	0.515191
20	1	0	-4.546357	-2.091314	-0.931824
21	1	0	-3.947715	-0.641364	1.482141
22	1	0	0.491769	-0.895599	1.630595
23	1	0	-4.190021	1.455209	0.224689
24	1	0	0.126599	1.605196	1.788897
25	1	0	-6.359384	-0.622019	-0.402207
26	1	0	-6.571333	1.127253	-0.377966
27	1	0	-6.177716	0.270432	1.116439
28	1	0	2.223594	1.626298	-0.613023
29	1	0	-3.167859	0.820973	-1.974903
30	1	0	-4.780624	1.500900	-2.160281
31	1	0	-4.550339	-0.237972	-2.312914
32	1	0	2.465921	-1.992340	1.731244
33	1	0	6.523252	0.393387	-2.059347
34	1	0	7.948812	-0.029501	-1.074274
35	1	0	6.921486	1.347091	-0.592859
36	7	0	-2.202997	-0.341750	0.357712
37	8	0	6.194164	-0.580742	-0.239254
38	8	0	-2.255276	1.200423	2.005572
39	8	0	-2.485188	-2.121658	-0.953376
40	8	0	-0.418431	-1.259136	-0.835102
41	16	0	-0.160658	2.275049	-0.461563

VI exo – *p*-Methoxy-benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.707639	-1.011299	-0.574166
2	6	0	-1.319138	1.059383	-0.834080
3	6	0	-3.803257	-1.244414	0.479623
4	6	0	-2.427485	0.396479	1.319609
5	6	0	0.573857	2.445581	0.339210
6	6	0	-0.825624	2.334570	-0.193387
7	6	0	1.577936	1.339518	0.322330
8	6	0	3.473123	-0.741664	0.451391
9	6	0	1.990681	0.671711	-0.832570
10	6	0	2.146838	0.953042	1.546841
11	6	0	3.076596	-0.073653	1.616663
12	6	0	2.926022	-0.361531	-0.778230
13	6	0	-1.708019	-2.174698	-0.767088
14	6	0	-2.406014	-3.345749	-1.474077

15	6	0	-1.023335	-2.623841	0.530847
16	7	0	-2.083553	0.213518	-0.025204
17	16	0	0.225189	3.459362	-1.172513
18	1	0	1.855233	1.463550	2.458640
19	1	0	3.511967	-0.366681	2.564646
20	1	0	3.223990	-0.849370	-1.696310
21	1	0	-4.765597	-0.830514	0.177618
22	1	0	-3.925017	-2.285745	0.766727
23	1	0	-3.148645	-0.766429	-1.540509
24	1	0	0.632514	3.052607	1.236347
25	1	0	-0.937404	-1.792165	-1.441939
26	1	0	-1.575375	2.836066	0.405198
27	1	0	-3.196507	-3.782587	-0.855634
28	1	0	-1.685526	-4.138513	-1.689023
29	1	0	-2.852333	-3.032742	-2.422320
30	1	0	1.589463	0.966739	-1.793848
31	1	0	-0.488451	-1.803912	1.016538
32	1	0	-0.290360	-3.403737	0.310418
33	1	0	-1.735623	-3.041111	1.249181
34	8	0	-1.118575	0.755460	-1.992436
35	8	0	-3.358047	-0.516136	1.654376
36	8	0	-1.989798	1.205515	2.097324
37	8	0	4.396607	-1.731404	0.613742
38	6	0	4.852653	-2.438191	-0.541180
39	1	0	4.028352	-2.958084	-1.038117
40	1	0	5.573493	-3.167075	-0.176253
41	1	0	5.343007	-1.763641	-1.249186

VI endo – *p*-Methoxy-benzaldehyde

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-4.498212	-0.755328	1.832442
2	1	0	-5.160377	1.912100	-1.472934
3	1	0	-2.912908	1.367193	-2.348919
4	1	0	-2.291947	-1.301394	0.959901
5	1	0	-0.813779	0.321598	-2.181516
6	1	0	4.524879	1.523398	2.184890
7	1	0	3.820163	3.064964	1.707909
8	1	0	2.783548	1.653475	1.885668
9	1	0	5.505424	2.008546	-1.489930
10	1	0	5.432435	3.271901	-0.257332
11	1	0	6.192099	1.727345	0.117911
12	1	0	-0.082360	-0.822468	0.586320
13	1	0	3.227350	2.189096	-0.519294
14	1	0	4.041345	0.048773	-1.358170
15	1	0	5.517257	-0.302086	1.087431
16	1	0	5.139073	-1.595100	-0.076546
17	6	0	-4.164206	-0.280315	0.920165
18	6	0	-4.519335	1.214310	-0.947502
19	6	0	-3.257292	0.901808	-1.431531
20	6	0	-2.899454	-0.583028	0.420976
21	6	0	-4.982985	0.625716	0.235177
22	6	0	-2.419644	0.003023	-0.753936
23	16	0	-0.478260	-2.043324	-1.536270

24	8	0	1.612211	-1.716314	1.706454
25	8	0	3.817392	-1.388776	1.494266
26	8	0	1.601019	0.615452	-1.815076
27	7	0	2.507201	-0.359719	0.009277
28	6	0	3.767530	1.985730	1.544445
29	6	0	5.361768	2.194100	-0.421761
30	6	0	3.999382	1.674379	0.059792
31	6	0	0.083203	-0.645901	-0.466133
32	6	0	-1.070664	-0.272998	-1.312940
33	6	0	2.537052	-1.210510	1.123640
34	6	0	4.722386	-0.790841	0.529767
35	6	0	1.427325	-0.073676	-0.826693
36	6	0	3.853760	0.176085	-0.292059
37	8	0	-6.232774	0.990784	0.635506
38	6	0	-6.764202	0.420115	1.833194
39	1	0	-6.149859	0.678651	2.700564
40	1	0	-6.846429	-0.667399	1.749796
41	1	0	-7.756491	0.850804	1.950383

A

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.694329	1.119276	-0.200245
2	6	0	3.930286	-1.198690	0.104663
3	6	0	1.041647	0.242214	-1.728722
4	6	0	2.264661	-0.534516	-1.555322
5	6	0	3.789445	0.775252	1.280417
6	1	0	4.716389	1.292935	-0.569629
7	1	0	0.900768	0.715727	-2.704740
8	1	0	2.808873	0.774222	1.767559
9	1	0	4.503478	1.380905	1.837751
10	7	0	3.314949	-0.229456	-0.714415
11	8	0	2.094767	-1.594131	-2.152687
12	8	0	4.297302	-0.583252	1.253234
13	16	0	4.203916	-2.780034	-0.185329
14	8	0	-0.308059	1.965607	0.349683
15	6	0	-1.139895	2.356232	1.243776
16	6	0	-0.945092	3.765045	1.761719
17	1	0	-1.341530	4.471254	1.024474
18	1	0	0.117427	3.980719	1.892388
19	1	0	-1.481752	3.897931	2.701314
20	8	0	-2.105810	1.689777	1.706419
21	45	0	-0.499539	0.062624	-0.503739
22	45	0	-2.463503	-0.206815	0.951191
23	8	0	0.658671	-0.723123	1.032850
24	8	0	-1.163624	-1.028754	2.355613
25	6	0	0.945386	-1.797641	3.135342
26	1	0	2.001386	-1.598042	2.951007
27	1	0	0.654380	-1.470185	4.135715
28	1	0	0.782026	-2.878836	3.078288
29	6	0	0.070213	-1.125554	2.100118
30	8	0	-1.758640	0.845574	-1.945055
31	8	0	-3.575385	0.628321	-0.594424
32	8	0	-0.911742	-1.848040	-1.169686

33	8	0	-2.748341	-2.081700	0.142179
34	6	0	-1.919549	-2.494509	-0.719962
35	6	0	-3.007052	0.953479	-1.676374
36	6	0	-3.876129	1.503134	-2.786418
37	1	0	-4.825008	1.857008	-2.382459
38	1	0	-3.356407	2.306340	-3.312651
39	1	0	-4.075058	0.703693	-3.508054
40	6	0	-2.117240	-3.877972	-1.295618
41	1	0	-2.948313	-4.379237	-0.799587
42	1	0	-2.317484	-3.798039	-2.368171
43	1	0	-1.197481	-4.456636	-1.177512
44	6	0	2.843188	2.326325	-0.619095
45	6	0	3.128489	2.725813	-2.078298
46	6	0	3.140542	3.516118	0.311606
47	1	0	1.779938	2.087678	-0.494370
48	1	0	3.017347	1.893446	-2.779345
49	1	0	2.447497	3.521120	-2.396104
50	1	0	4.152852	3.102521	-2.180544
51	1	0	2.849790	3.311621	1.346486
52	1	0	4.205990	3.777076	0.298895
53	1	0	2.581993	4.395865	-0.020374

TS_{A-B}

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.181499	-3.538431	1.148026
2	6	0	1.995021	-2.365877	3.245154
3	6	0	1.719819	-2.223144	1.737083
4	6	0	-2.091796	2.386135	-3.506269
5	6	0	-3.032814	3.304520	2.208129
6	6	0	-2.730044	2.070391	1.393282
7	6	0	-2.134226	1.501757	-2.284710
8	8	0	-3.249265	1.029424	-1.916408
9	8	0	-1.011105	1.291194	-1.706571
10	8	0	-3.701390	1.399284	0.933912
11	8	0	-1.492532	1.798876	1.217666
12	45	0	-3.352411	-0.234183	-0.282067
13	45	0	-0.947507	0.229621	0.033404
14	8	0	-3.302436	-1.430579	1.392746
15	6	0	-2.301861	-2.233952	3.388526
16	6	0	-2.233925	-1.489836	2.071665
17	8	0	-1.114251	-0.954501	1.773146
18	16	0	4.482863	-1.040252	-2.609974
19	8	0	4.788208	-2.255703	-0.346889
20	8	0	1.684381	-0.130203	-2.034384
21	7	0	2.856894	-1.142658	-0.343806
22	6	0	4.068405	-2.737654	0.800736
23	6	0	1.856613	-0.247825	-0.826002
24	6	0	1.058854	0.568672	0.182590
25	6	0	3.993011	-1.469282	-1.096244
26	6	0	2.996131	-1.679860	1.048575
27	6	0	-1.573398	-2.100485	-1.632785
28	6	0	-1.228141	-3.264929	-2.533658
29	8	0	-2.800689	-1.822796	-1.492507
30	8	0	-0.591618	-1.478591	-1.100781

31	6	0	1.323448	2.243675	-0.188959
32	6	0	2.751103	2.449882	0.282877
33	6	0	5.351563	3.033126	1.145098
34	6	0	2.978529	2.901365	1.595591
35	6	0	3.837449	2.300136	-0.591519
36	6	0	5.132091	2.598136	-0.161733
37	6	0	4.269508	3.187141	2.024400
38	8	0	0.467276	3.028021	0.330484
39	1	0	0.239684	-3.795702	1.640853
40	1	0	1.860908	-4.380710	1.309640
41	1	0	0.978416	-3.452224	0.076704
42	1	0	2.737200	-3.145565	3.453983
43	1	0	1.075293	-2.641902	3.768665
44	1	0	2.358736	-1.428658	3.680195
45	1	0	0.922178	-1.487631	1.620818
46	1	0	-1.357765	1.993333	-4.214722
47	1	0	-1.763387	3.387467	-3.212847
48	1	0	-3.076581	2.438240	-3.970628
49	1	0	-2.897466	4.183988	1.569893
50	1	0	-2.329864	3.387790	3.039131
51	1	0	-4.061229	3.279752	2.569677
52	1	0	-3.197308	-2.854867	3.416794
53	1	0	-1.409978	-2.845690	3.542587
54	1	0	-2.350573	-1.503270	4.202858
55	1	0	4.763924	-2.867278	1.629904
56	1	0	3.641145	-3.704267	0.523926
57	1	0	1.404013	0.511598	1.218197
58	1	0	3.432251	-0.881103	1.665857
59	1	0	-1.325129	-2.940742	-3.574923
60	1	0	-1.934465	-4.081510	-2.369305
61	1	0	-0.203685	-3.596801	-2.365872
62	1	0	1.169750	2.037547	-1.279913
63	1	0	2.124222	3.037969	2.251472
64	1	0	3.673756	1.967521	-1.609248
65	1	0	5.963012	2.480763	-0.850553
66	1	0	4.441308	3.537645	3.038141
67	1	0	6.360198	3.254862	1.482385

B

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.662234	1.559655	-0.477378
2	16	0	-1.994632	3.055286	0.083342
3	7	0	-1.176007	0.426931	0.201954
4	6	0	-0.245607	0.487332	1.261618
5	8	0	0.143318	1.521691	1.751049
6	8	0	-1.884276	1.202500	-1.767262
7	6	0	-1.378951	-0.129328	-2.004710
8	1	0	-2.018188	-0.593703	-2.755308
9	1	0	-0.351862	-0.058555	-2.379497
10	6	0	-1.449793	-0.778940	-0.619881
11	1	0	-0.653370	-1.512820	-0.478525
12	6	0	0.253351	-0.864422	1.737589
13	1	0	-0.520468	-1.576230	2.025179

14	6	0	1.576031	-1.411848	1.305821
15	1	0	1.656947	-2.501690	1.314500
16	8	0	1.380056	-0.830705	2.595409
17	6	0	-2.838952	-1.412543	-0.344301
18	1	0	-3.585020	-0.692562	-0.708017
19	6	0	-3.126030	-1.663111	1.141311
20	1	0	-4.160222	-1.997041	1.268778
21	1	0	-2.996550	-0.758983	1.741908
22	1	0	-2.482912	-2.452047	1.548840
23	6	0	-2.989128	-2.715898	-1.145559
24	1	0	-2.839311	-2.573711	-2.220405
25	1	0	-3.990981	-3.133691	-1.010281
26	1	0	-2.268617	-3.469225	-0.804508
27	6	0	2.486712	-0.732881	0.338654
28	6	0	4.182023	0.481617	-1.530594
29	6	0	2.879137	-1.423102	-0.816605
30	6	0	2.960894	0.566899	0.560308
31	6	0	3.804236	1.167042	-0.374270
32	6	0	3.718454	-0.816909	-1.750616
33	1	0	2.534355	-2.441985	-0.979882
34	1	0	2.662020	1.092085	1.459840
35	1	0	4.168561	2.174263	-0.196095
36	1	0	4.017928	-1.360514	-2.641879
37	1	0	4.840209	0.954047	-2.253693