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PII: S0040-4020(15)00165-9

DOI: 10.1016/j.tet.2015.02.030

Reference: TET 26419

To appear in: *Tetrahedron* 

Received Date: 15 December 2014

Revised Date: 26 January 2015

Accepted Date: 6 February 2015

Please cite this article as: Galenko AV, . Khlebnikov AF, Novikov MS, Avdontceva MS, Synthesis of 3-(1,2-dioxoethyl)- and 2,3-dicarbonyl-containing pyrroles, *Tetrahedron* (2015), doi: 10.1016/ j.tet.2015.02.030.

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Graphical abstract

R<sup>1</sup> XH R Cu/Co(OAc)<sub>2</sub> R<sup>2</sup>  $R^1 = Ar$ , Me;  $R^2 = H$ , Ar,  $CO_2Et$ 

 $R^3 = Ar$ , Me, *t*-Bu;  $R^4 = OMe$ , OEt, Ph, X = O, NR

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# Synthesis of 3-(1,2-dioxoethyl)- and 2,3-dicarbonyl-containing pyrroles

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#### **ABSTRACT:**

The transition metal-catalyzed reaction of 2*H*-azirines with 1,2,4-tricarbonyl compounds leads to 3-(1,2-dioxoethyl)- and 2,3-dicarbonyl-pyrrole derivatives, useful building blocks for the preparation of 3-heterocyclyl pyrroles and pyrroles fused with heterocycles. The influence of catalysts and the reaction conditions on the yields of pyrroles and the regioselectivity of the reaction were studied. Experimental and theoretical results suggest that the reaction proceeds via the formation of an intermediate azirine-metal complex and subsequent nucleophilic N-C3 bond cleavage.

Keywords: pyrrole, azirine, cyclocondensation, metal catalysis

#### 1. Introduction

Pyrroles and their fused derivatives are widely present in natural compounds, medicine and materials.<sup>1,2</sup> Consequently, the development of methods for the synthesis of such compounds is a very active area of research. Although a lot of preparative methods for the synthesis of pyrroles have been developed<sup>2</sup> it is still a great challenge to find simple ways to functionalized pyrroles from cheap and available starting materials. An attractive goal would be pyrroles **1,2** containing carbonyl functions which allow them to be used as synthetic blocks for the preparation a variety of 3-heterocyclyl pyrroles **3** and pyrroles fused with heterocycles **4** by reactions with bis-nucleophiles (Scheme 1). The approach to compounds **1,2**, which seems straightforward enough, consists of using the reaction of 2*H*-azirines **5**, readily available by numerous reliable syntheses,<sup>3</sup> with C-nucleophiles **6** (Scheme 1).<sup>3,4</sup> According to this scheme cyclocondensation of azirines across the C2-C3 or C3-C4 bond of a 1,2,4-tricarbonylcompound would produce 2,3-dicarbonylpyrrole or 3-(1,2-dioxoethyl)pyrrole derivatives, respectively.

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Scheme 1. Retrosynthetic scheme for compounds 3,4.

#### 2. Results and discussion

Reaction of tricarbonyl compounds with azirines has so far not been studied to the best of our knowledge. Therefore, before starting an experimental search for the reaction conditions for the preparation of 1,2 by reaction of azirines with compounds 6, the literature on the reactions of azirines with mono- and dicarbonyl compounds, leading to pyrroles, was analyzed. This revealed that there is no general procedure for the formation of the pyrrole ring by this route. Additionally, quantum-chemical calculations for the model reaction of 3-phenyl-2*H*-azirine **7a** with acetylacetone **8**, which is often used for the preparation of pyrroles, were performed to reveal possible ways to control the reaction.

Enolates, generated from alkyl ketones<sup>4a,d,e,j</sup> and nitriles<sup>4a,d</sup> by treatment with NaH in DMSO or from aldehydes<sup>4f</sup> by treatment with KH in THF, react with non-activated azirines (e.g. 3-phenyl-, 2-alkyl-3-phenyl- and 2,2-dialkyl-3-phenyl-2*H*-azirines) to give 1*H*- and 2*H*-pyrrole derivatives. Na-enolates of acetylacetates react in boiling THF with 1-alkyl-2*H*-azirinylphosphine oxides and - phosphonates to give 1*H*-pyrrole-2-phosphine oxides and -phosphonates, whereas Na-enolates of alkyl malonates react with the same azirines already at room temperature.<sup>40</sup> Tri- or tetra-substituted pyrroles were synthesized by the reaction of vinyl azides with 1,3-dicarbonyl compounds in toluene at 100 °C. The author assumed this proceeds via the reaction of transient 2*H*-azirine with enols of 1,3-dicarbonyl compounds.<sup>41,n</sup> However, in many cases 1,3-dicarbonyl substrates do not react with non-activated azirines without a catalyst or the reaction proceeds only at high temperatures giving

low yields of the targeted pyrroles. In order to force the mentioned reaction, catalysis by  $Ni(acac)_2$ , <sup>4c</sup>  $Cu(acac)_2$  <sup>4m,q</sup> or  $VO(OSiPh_3)_3$  <sup>4k</sup> was therefore used.

The plausible mechanism that has been proposed for reactions of intermediate azirines derived from corresponding azides with enolizable ketones, involves the attack of the nucleophilic carbon of the enol on the C=N double bond of azirine (Scheme 2).<sup>4l,n</sup>



Scheme 2. Plausible mechanism for the reaction of 3-phenyl-2*H*-azirine **7a** with acetylacetone **8**.<sup>41,n</sup> Calculations of the energy profile for the reaction of 3-phenyl-2*H*-azirine **7a** with the enol of acetylacetone **9** were performed at the DFT B3LYP/6-31G(d) level to evaluate the possibility of this mechanism (Figure 1).



**Fig. 1**. Energy profiles of the reaction of 3-phenyl-2*H*-azirine **7a** with the enol of acetylacetone **9**. Relative free energies [kcal·mol<sup>-1</sup>, 298K, toluene (PCM)] computed at the DFT B3LYP/6-31G(d) level.

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According to the calculations there is indeed a transition state **A** involving simultaneous transfer of the enol hydrogen to the azirine nitrogen and formation of C-C bond between C3 of **9** and C3 of **7a**, leading to intermediate **B**. The latter can undergo inversion of nitrogen to give invertomer **C** that further can transform to conformer **D**. This in turn can form aminoketone **E** via simultaneous transfer of the hydrogen from C-3 to the nitrogen and aziridine ring opening. Cyclization of the aminoketone **E** and consecutive dehydration will give pyrrole **11**. The calculated barrier for formation of **B** (transition state **A**, 41.5 kcal·mol<sup>-1</sup>) is, however, too high for the reaction to proceed, even at 100 °C. Bearing in mind that the reaction of acetylacetone **8** with 1-phenylvinylazide **10**, which according to the authors' assumption proceeds via intermediate azirine **7a**, gave 85% of pyrrole **11** (toluene, 100 °C, 24 h),<sup>41</sup> we decided to carry out the reaction of azirine **7a** with acetylacetone **8** under the same conditions. Unexpectedly it was found that only ca. 3% of pyrrole **11** was formed after heating an equimolar solution of azirine **7a** with acetylacetone **8** in toluene at 100 °C for 12 h. This means that the reaction of acetylacetone **8** with 1-phenylvinylazide **10** most probably does not proceed via intermediate formation of azirine **7a**, since the latter is in fact unreactive under the conditions used.

Taking into account the lower nucleophilicity of the enols of tricarbonyl compounds **6** compared to the enol of acetylacetone **9** it was not surprising that enol **12a** did not react with azirine **7a** under reflux in toluene (Table 1, entry 1). There are some possibilities to force the reaction to proceed: enhance the nucleophilicity of the 1,3-dicarbonyl compound or the electrophilicity of the azirine. To fit the first possibility we reacted azirine **7a** with the anion generated from ethyl 2,4-dioxo-4-phenylbutanoate **12a** and NaH in DMSO or THF at room temperature under the conditions used for reactions of azirines with enolizable ketones and aldehydes.<sup>4a,d,e,f,j</sup> It was revealed, however, that the reaction of **7a** did not proceed at all and the starting compounds remained unchanged, whereas when heated the azirine decomposed completely without formation of any pyrrole derivatives (Table 1, entries 2-3).

To evaluate the second possibility of forcing the reaction to proceed, acid catalysis was theoretically tested at first. According to calculations the reaction of protonated azirine  $7a-H^+$  with the enol of acetylacetone **9** should proceed much easier than non-protonated azirine (Figure 2). In this case the formation of the C-C bond between C-3 of **9** and C-3 of **7a-H**<sup>+</sup>, leading to intermediate **G**, proceeds via the relatively low free energy barrier (transition state **F**). Intermediate **G** can undergo the low barrier cyclization by attack of the aziridine nitrogen on the carbon of the protonated carbonyl group, giving the bicyclic intermediate **H**. Ring opening of the aziridine will then lead to protonated

pyrrole **I**, which then will give the final product **11** by losing  $H_3O^+$ . Therefore, the reaction of azirine **7a** and acetylacetone **8** proceeds much easier under acid catalysis.



**Fig. 2**. Energy profiles of the reaction of protonated 3-phenyl-2*H*-azirine **7a-H**<sup>+</sup> with the enol of acetylacetone **9**. Relative free energies [kcal·mol<sup>-1</sup>, 298K, toluene (PCM)] computed at the DFT B3LYP/6-31G(d) level.

Unfortunately, it is known that  $\operatorname{organic}^5$  and  $\operatorname{inorganic}^6$  acids react irreversibly with azirines due to the ring opening. It is therefore not surprisingly that the addition of a catalytic amount of TsOH\*H<sub>2</sub>O or maleic acid to the reaction of azirine **7a** and acetylacetone **8** did not lead to an improved yield of the pyrrole **11** and only tarring of the reaction mixture occurred.

Faced with the inability to perform the reaction under acidic or basic conditions we turned to transition metal catalysis, since the formation of a coordination bond between the azirine nitrogen and metal should increase the electrophilicity of the azirine. Unlike the reaction of azirines with acids, however, it may be reversible, as some transition metals are complexed to azirines with retention of the azirine ring.<sup>7-9</sup>

Optimization of the reaction conditions for the condensation of azirine 7a with compound 12a (1:1)



En	Reaction conditions	Catalyst <sup>a</sup> or	Yield of	products, <sup>d</sup> %	Conversion	
try		additive	13a	14a	of <b>7a</b> , %	
1	MePh, reflux, 6 h	NaH <sup>b</sup>	0	0	0	
2	DMSO, 25 °C, 8 h	NaH <sup>b</sup>	0	0	0	
3	THF, reflux, 8 h	NaH <sup>b</sup>	0	0	100	
4	THF, reflux, 8 h	NaH, <sup>b</sup> Cu(acac) <sub>2</sub>	0	0	100	
5	MePh, reflux, 1 h	$Cu(acac)_2$	32 <sup>e</sup>	47 <sup>e, f</sup>	100	
6	MePh, reflux, 0.5 h	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	35	49	100	
7	MePh, 50 °C, 10 h	$Cu(OAc)_2 \cdot H_2O^c$	33	28	100	
8	THF, 50 °C, 48 h	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	50	28	100	
9	EtOH, 50 °C, 48 h	$Cu(OAc)_2 \cdot H_2O$	25	25	100	
10	TEA, 50 °C, 2.5 h	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	0	0	100	
11	MeCN, 50 °C, 24 h	$Cu(OAc)_2 \cdot H_2O$	58	32	100	
12	MeCN, 60 °C, 18 h	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	60	38	100	
13	MeCN, 70 °C, 7 h	$Cu(OAc)_2 \cdot H_2O$	45 <sup>e</sup>	$28^{\rm e}$	88	
14	DMF, 50 °C, 16 h	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	34	16	100	
15	CHCl <sub>3</sub> , 50 °C, 10 h	$Cu(OAc)_2 \cdot H_2O$	38	39	100	
16	CCl <sub>4</sub> , 50 °C, 24 h	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	37	32	100	
17	PhH, 50 °C, 15 h	$Cu(OAc)_2 \cdot H_2O$	28	21	100	
18	DMSO, 50 °C, 48 h	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	12	15	100	
19	MeNO <sub>2</sub> , 60 °C, 4 h	$Cu(OAc)_2 \cdot H_2O$	46	37	100	
20	DCE, 50 °C, 9 h	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	40	44	100	
21	DCE, 60 °C, 6 h	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	36	52	100	
22	DCE, 50 °C, 6 h	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O	35 <sup>e</sup>	36 <sup>e</sup>	90	
23	DCE, 70 °C, 48 h	CuI	19	28	70	
24	DCE, 50 °C, 20 h	$Co(OAc)_2 \cdot 4H_2O$	35	62	100	
25	DCE, 70 °C, 6 h	$Co(OAc)_2 \cdot 4H_2O$	31 <sup>e</sup>	63 <sup>e</sup>	98	
26	DCE, 70 °C, 65 h	NiCl <sub>2</sub> ·6H <sub>2</sub> O	29	53	100	
27	DCE, 70 °C, 65 h	FeCl <sub>3</sub> ·6H <sub>2</sub> O	0	0	0	
28	DCE, 70 °C, 65 h	$KMnO_4$	0	0	0	
29	DCE, 70 °C, 65 h	(VO)SO <sub>4</sub> ·nH <sub>2</sub> O	0	0	0	
30	DCE, 60 °C, 1 h	$Tb(NO_2)_3 \cdot 5H_2O$	0	0	100	
31	DCE, 60 °C, 26 h	YCl <sub>3</sub>	0	0	100	
32	DCE, 60 °C, 26 h	$(ZrO)Cl_2 \cdot 8H_2O$	0	0	0	

<sup>a</sup> 5 mol %.

Table 1

<sup>b</sup> 1 equivalent. <sup>c</sup> 10 mol %.

<sup>d</sup> Yield according to <sup>1</sup>H NMR analysis of reaction mixture with 2-methylnaphthalene as internal standard. <sup>e</sup> Preparative yield after column chromatography. <sup>f</sup> Additionally 1-(2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone **15** (4%) was isolated.

Unexpectedly the reaction of azirine **7a** with compound **12a** for 20 h, under conditions found for the reaction of azirines with 1,3-dicarbonyl compounds  $(1.2 \text{ mol } \% \text{ Ni}(\text{acac})_2$ , acetone, rt, 2-3 h),<sup>4c</sup> gave only traces of compounds **13a**,**14a**. When Cu(acac)<sub>2</sub> was tried as a catalyst in boiling toluene,<sup>4m,q</sup> the target products **13a**,**14a** were isolated in 79% overall yield (Table 1, entry 5). Additionally, 1-(2-methyl-4-phenyl-1*H*-pyrrol-3-yl)ethanone **15** (4%), derived from the reaction of azirine **7a** with Cu(acac)<sub>2</sub>, was isolated as byproduct. It is worth mentioning here that the addition of Cu(acac)<sub>2</sub> to a mixture of azirine **7a** with enolate generated from ethyl 2,4-dioxo-4phenylbutanoate **12a** and NaH gave no pyrroles **13a**, **14a** and led only to rapid decomposition of the azirine (Table 1, entry 4).

The structures of compounds **13a**, **14a** were verified by <sup>1</sup>H and <sup>13</sup>C NMR, IR spectroscopy, and mass-spectrometry and were confirmed by X-ray analysis (Fig. 3).



Fig. 3. Molecular structures of compounds 13a, 14a.

Encouraged with the preliminary results we tested different catalysts and reaction conditions to improve the yields of the pyrroles and to find out the possibilities of controlling the regioselectivity of the reaction (Table 1). First of all, copper(II) salts instead of Cu(acac)<sub>2</sub>, to avoid the formation of byproduct **15**, were tested on the assumption that trione **12a** can promote dissolution of the salts in organic solvents by forming complexes similar to Cu(acac)<sub>2</sub>. Surprisingly, it was found that Cu(OAc)<sub>2</sub> dissolved in 1,2-dichloroethane (DCE) in the presence of only azirine **7a** to give a turquoise colored solution. It means that most probably just the formation of the azirine copper complex facilitates the reaction with trione **12a**. It was found the Cu(II) but not Cu(I) salts are more preferable for the preparation of pyrroles **13a**, **14a** (Table 1, entries 20–23). Longer heating in toluene at a lower temperature with a higher percentage of the catalyst gave more tarry reaction mixture with reversed regioselectivity and lower yield of the products (Table 1, entries 6,7). Use of MeCN as solvent at 60 °C gave increasing relative yields of pyrrole **13a** (**13a** 60%, **14a** 38%; Table 1, entry 12) comparing with DCE (**13a** 36%, **14a** 52%; Table 1, entry 21). In other polar solvents (THF, EtOH, DMF, DMSO, MeNO<sub>2</sub>) overall yields were lower than in MeCN. In order to increase the percentage of pyrrole **14a** Co(OAc)<sub>2</sub> can be used as catalyst (**13a** 31%, **14a** 

63%; Table 1, entry 25). Use of NiCl<sub>2</sub> also provides preferably pyrrole **14a**, but its overall yield becomes slightly lower (Table 1, entry 26). Other tested salts showed poor results. Thus, we found catalysts and reaction conditions to give pyrroles **13a**, **14a** in high overall yield. Although we could not achieve complete regioselectivity of the reaction, we have found a reasonable preparation of pyrroles **13a**, **14a**, since they can be easily isolated by chromatographic separation.

Further, the scope of the reaction for the preparation of pyrroles **13**, **14** and reaction regioselectivity, depending on the substituents both in azirine **7** and carbonyl component **12**, were explored. For this study heating at 60 °C in 1,2-dichloroethane with copper(II) acetate as a catalyst was used due to the high overall yield of the products and short reaction time, found in the preliminary tests (Table 1, entry 21). The results are listed in Table 2. The structures of compounds **13**, **14** were verified by <sup>1</sup>H and <sup>13</sup>C NMR, IR spectroscopy, and mass-spectrometry and for compounds **13d**, **14f** were also confirmed by X-ray analysis (Fig. 4).



Fig. 4. Molecular structures of compounds 13d, 14f.

Electron-donor and weak electron-withdrawing substituents in the 4-aryl ring of 4-aryl-2,4dioxobutanoates only slightly influence the product yield and distribution of pyrroles (Table 2, entries 1-3). Introduction of a strong electron-withdrawing NO<sub>2</sub>-substituent at this position could increase the percentage of the corresponding pyrrole **14**, but in these cases the reaction became much slower, probably due to a lowering of the nucleophilicity of enol **12** (Table 2, entries 4,5). This resulted in the complete decomposition of the azirine in the reaction of compound **12d**, and tarring of the reaction of compound **12e**, which led to the necessity of 3 recrystallizations of pyrrole **13d** to obtain the pure compound in low yield. A 4-*tert*-butyl-group in the 2,4-dioxobutanoate **12f**, unexpectedly, had a little influence on the regioselectivity (Table 2, entry 6). Yields of analytically pure pyrroles 13 and 14 prepared by the condensation of azirines 7 with compounds 12 at 60  $^{\circ}$ C in 1,2-dichloroethane with copper(II) acetate (5 mol %.) as a catalyst



Entry	Az	irine 7		Cor	npound 12			Time, h	Yield, %	
		$\mathbf{R}^1$	$\mathbb{R}^2$		$\mathbf{R}^3$	$\mathbb{R}^4$	Х		13	14
1	a	Ph	Н	a	Ph	EtO	0	6	( <b>a</b> ) 35	( <b>a</b> ) 36
2	a	Ph	Н	b	4-MeOC <sub>6</sub> H <sub>4</sub>	EtO	0	7	( <b>b</b> ) 24	( <b>b</b> ) 39
3	a	Ph	Н	c	$4-BrC_6H_4$	MeO	0	10	( <b>c</b> ) 30	( <b>c</b> ) 46
4	a	Ph	Н	d	$4-NO_2C_6H_4$	EtO	0	42	$0^{a}$	$0^{\mathrm{a}}$
5	a	Ph	Н	e	$3-NO_2C_6H_4$	EtO	0	11	( <b>d</b> ) 11	( <b>d</b> ) 33
6	a	Ph	Н	f	<i>t</i> -Bu	EtO	0	12	( <b>e</b> ) 20 <sup>b</sup>	( <b>e</b> ) 30 <sup>b</sup>
7	a	Ph	Н	g	Ph	Ph	0	8	$({\bf f}) 0^{a}$	( <b>f</b> ) 42 <sup>c</sup>
8	a	Ph	Н	g	Ph	Ph	0	5	$({\bf f}) 0^{a}$	( <b>f</b> ) 69 <sup>d,e</sup>
9	a	Ph	Н	h	Ph	EtO	HN	7	$(a) 0^{a, c}$	( <b>a</b> ) 25 <sup>c</sup>
10	a	Ph	Н	h	Ph	EtO	HN	9	( <b>a</b> ) 0 <sup>a</sup>	( <b>a</b> ) 89 <sup>d,e</sup>
11	a	Ph	Н	i	Ph	Ph	4-ClC <sub>6</sub> H <sub>4</sub> N	7	$(f) 0^{a, c}$	( <b>f</b> ) 29 <sup>c</sup>
12	a	Ph	Н	j	Ph	EtO	4-MeOC <sub>6</sub> H <sub>4</sub> N	7	$(a) 0^{a, c}$	( <b>a</b> ) 26 <sup>c</sup>
13	a	Ph	Н	k	Ph	Ph	MeS	40	$0^{a}$	$0^{\mathrm{a}}$
14	b	Ph	Ph	a	Ph	EtO	0	24	( <b>g</b> ) 18	( <b>g</b> ) 15
15	b	Ph	Ph	b	$4-MeOC_6H_4$	EtO	0	20	( <b>h</b> ) 22	( <b>h</b> ) 19
16	b	Ph	Ph	f	<i>t</i> -Bu	EtO	0	24	( <b>i</b> ) 10	( <b>i</b> ) 10
17	b	Ph	Ph	1	Me	MeO	0	35	( <b>j</b> ) 40	( <b>j</b> ) 26
18	b	Ph	Ph	g	Ph	Ph	0	24	$(k) 0^{a}$	( <b>k</b> ) 42
19	с	Ph	EtO <sub>2</sub> C	a	Ph	EtO	0	70 <sup>e</sup>	<b>(l)</b> 28	( <b>l</b> ) 68
20	с	Ph	EtO <sub>2</sub> C	b	4-MeOC <sub>6</sub> H <sub>4</sub>	EtO	0	70 <sup>e</sup>	( <b>m</b> ) 26	( <b>m</b> ) 65
21	с	Ph	EtO <sub>2</sub> C	m	$3-BrC_6H_4$	MeO	0	100 <sup>e</sup>	( <b>n</b> ) 27	( <b>n</b> ) 56
22	d	Me	EtO <sub>2</sub> C	a	Ph	EtO	0	55	( <b>o</b> ) 28	( <b>o</b> ) 26
23	d	Me	EtO <sub>2</sub> C	b	$4-MeOC_6H_4$	EtO	0	55	( <b>p</b> ) 27	( <b>p</b> ) 33
24	d	Me	EtO <sub>2</sub> C	c	$3-BrC_6H_4$	MeO	0	60 <sup>e</sup>	( <b>q</b> ) 28	( <b>q</b> ) 22
25	e	2-BrC <sub>6</sub> H <sub>4</sub>	Н	m	$3-BrC_6H_4$	MeO	0	7.5	( <b>r</b> ) 19	( <b>r</b> ) 49
26	e	2-BrC <sub>6</sub> H <sub>4</sub>	Н	l	Me	MeO	0	2.5	( <b>s</b> ) 21	( <b>s</b> ) 49
27	e	2-BrC <sub>6</sub> H <sub>4</sub>	Н	f	<i>t</i> -Bu	EtO	0	6	$(t) 0^{a}$	( <b>t</b> ) 7 <sup>b</sup>

<sup>a</sup> No the pyrrole product according to <sup>1</sup>H NMR analysis of the reaction mixture.

<sup>b</sup> Yield of crude product (*ca.* 90% purity).

<sup>c</sup> Recovery of compound **12** after chromatographic purification was 62-68%.

<sup>d</sup> 3 equivalents of azirine **7** was used.

<sup>e</sup> Reaction temperature was 75 °C.

Table 2

No pyrrole **13f** was detected in the case of the reaction of 1,4-diphenylbutane-1,2,4-trione **12g** and this is most probably due to the higher reactivity of the 2-keto group in 1,2-diketones relatively to 2-ketoesters (Table 2, entry 7). Enamines **13h-j** reacted slower than enoles, giving regioselectively pyrroles **14a,f**, but a lot of the azirine was wasted on side reactions (Table 2, entries 9–12). To

improve the yields of pyrroles **14a**,**f** an excess of azirine can be used (Table 2, entries 8, 10). Methylsulfanyl-substituted compound **12k** did not react with azirine **7a** (Table 2, entry 13).

2,3-Diphenyl-2*H*-azirine **7b** reacted much slower than azirine **7a** (Table 2, entries 14–18), and pyrroles **13** were formed in a slightly larger amount than isomers **14** (Table 2, entries 14,15). At the same time an exchange of the *tert*-butyl-group in position 4 of 2,4-dioxobutanoate with a methyl-group led to a considerable increase in the **13:14** ratio (Table 2, entries 16,17). 1,4-Diphenylbutane-1,2,4-trione **12g** again reacted regioselectively to give only pyrrole **14k** (Table 2, entry 18).

3-Substituted-2*H*-azirine-2-carboxylates **7c,d** were much less reactive than azirines **7a,b** and a higher temperature was needed for reaction completion. The reactions of ethyl 3-phenyl-2*H*azirine-2-carboxylate **7c** gave excellent overall yields of the pyrroles in a ratio of more than 2:1 in favor of isomer **14**. (Table 2, entries 19–21). The overall yields of pyrroles from azirine **7d** were less than from azirine **7c**, apparently due to less thermal stability of the former. It is noteworthy that the increase of steric bulk of the substituent in the 3-position of the azirine led to a higher regioselectivity of the condensation in favor of pyrroles **14**. This occured both on the exchange of the 3-Me-group with 3-Ph (azirines **7d**  $\rightarrow$  **7e**) and on the exchange of the 3-Ph-group with 3-(2-BrC<sub>6</sub>H<sub>4</sub>) (azirines **7a**  $\rightarrow$  **7c**).

Further, the influence on the reaction outcome of some additives that can coordinate with copper was tested. It was found that addition of 10 mol. % of L-proline practically has no effect on the pyrrole ratio, but decreases their overall yields and time of conversion of azirine, as well led to formation of a lot of by-products. Probably, L-proline acts like triethylamine (Table 1, entry 10) and acids (*vide supra*) by transforming the azirine to by-products. Addition of 10 mol. % of 1,10-phenanthroline diminished the rate of reaction by *ca*. 10 times, but practically had no influence on the regioselectivity and overall yields of the pyrroles, most probably due to the deactivation of the catalyst.

According to the structures of products **13**, **14**, the pyrrole ring is formed via cleavage of the N-C<sup>3</sup> bond of the azirine ring. Albeit azirine reactions catalyzed by transition metals often proceed via cleavage of the N-C<sup>2</sup> bond,<sup>4q, 3d,e, 10</sup> there are also examples of N-C<sup>3</sup> bond cleavage.<sup>3d,e, 4c, 11</sup> The probable pathway for the formation of pyrroles **13**, **14**, based on the results of the study, is outlined in Scheme 3. Complexes of azirines with Cu(II) are unknown, but structures of complexes of azirines with Pd,<sup>7</sup> Rh <sup>8</sup> and Re <sup>9</sup> were determined by X-ray analysis. We assume that the copper complex of type **16**, which has a higher electrophilicity than the starting azirine, reacts with the enol-form (or enamine or metal-enolate) of butane-1,2,4-trione **12**, giving intermediate **17/18**, that under further attack of the aziridine nitrogen on C-4 or C-2 of **17/18** is transformed into intermediate **19** or **20**. Intermediates **19** or **20** give pyrroles **13**, **14** via aziridine ring opening and

elimination of  $H_2X$ . The attack of the aziridine nitrogen proceeds easily on the quasi protonated C=OH<sup>+</sup> group (*cf.* Fig.2), and therefore the position of the equilibrium  $17 \Rightarrow 18$ , which depends on different factors, such as electronic character and steric bulk of substituents and metal, solvent polarity etc., determines the selectivity of the reaction. The scheme is in accord with the selectivity of the reaction of azirines with enamines 12 (Table 2, entries 9–12). In this case the equilibrium  $17 \Rightarrow 18$  has to be completely shifted to the 17 side, providing the selective formation of pyrroles 14.



**Scheme 3.** Plausible mechanism for the metal-catalyzed reaction of 2*H*-azirines with butane-1,2,4-trione derivatives.

At the end of our study we prepared 3-heterylpyrrole **23** and fused pyrrole **24** from the synthesized compounds **13a**, **14a** (Scheme 4) using the published procedure for the analogous compound.<sup>12</sup> 3,4-Substituted maleimides of type **23** are of particular interest due to their biological activity.<sup>13</sup>



Scheme 4. Synthesis of 3-heterylpyrrole 23 and fused pyrrole 24.

#### ACCEPTED MANUSCRIPT

#### **3.** Conclusions

metal-catalyzed reaction of azirines with butane-1,2,4-triones leads to 3-(1,2-The dioxoethyl)pyrroles 13 and 2,3-dicarbonylpyrroles 14, which are useful building blocks for the preparation of 3-heterocyclyl pyrroles and pyrroles fused with heterocycles. Carrying out the Cu(II)-catalyzed reaction of 3-phenyl-2H-azirine with ethyl 2,4-dioxo-4-phenylbutanoate in MeCN increases the relative yield of 3-(1,2-dioxoethyl)pyrrole derivative 13 in comparing with non-polar toluene or DCE. To increase the relative yield of the 2,3-dicarbonylpyrrole derivative 14 the Co(II)catalyzed reaction can be used. The Cu(II)-catalyzed reactions of azirines with enamines of butane-1,2,4-triones are completely regioselective and give only 2,3-dicarbonylpyrrole derivatives 14. The increase of steric bulk of the substituent in 3-position of azirine leads to higher regioselectivity of the condensation with butane-1,2,4-triones in favor of pyrroles 14. 3-Substituted-2H-azirine-2carboxylates are much less reactive than azirines without an alkoxycabonyl-group in position 2, and higher temperatures are needed for the reaction to complete. Overall yields of reactions of butane-1,2,4-triones with ethyl 3-phenyl-2*H*-azirine-2-carboxylate 7c are excellent, with yields of pyrroles 14 more than two times higher than isomers 13. Experimental and theoretical results implied that the reactions proceed via the formation of an intermediate azirine-metal complex.

#### 4. Experimental section

#### 4.1. General methods

Melting points were determined on a capillary melting point apparatus Stuart® SMP30. <sup>1</sup>H (300 MHz, 400 MHz) and <sup>13</sup>C (75 MHz, 100 MHz) NMR spectra were determined in CDCl<sub>3</sub> with Bruker DPX 300 and Bruker AVANCE III 400. Chemical shifts ( $\delta$ ) are reported in parts per million downfield from tetramethylsilane (TMS  $\delta$  = 0.00); <sup>1</sup>H NMR spectra were calibrated according to the residual peak of CDCl<sub>3</sub> (7.26 ppm) or DMSO-d<sub>6</sub> (2.50 ppm). Mass spectra were recorded on a Bruker maXis HRMS-ESI-QTOF, electrospray ionization, positive mode. IR-spectra were recorded on a Bruker FT-IR spectrometer Tensor 27 for tablets in KBr, only characteristic absorption is indicated. Single crystal X-ray data were collected using an Agilent Technologies Supernova Atlas and an Agilent Technologies Excalibur Eos diffractometers. The crystals were kept at 100 K during data collection. The structures have been solved by the direct methods and refined by means of the SHELXL–97 program<sup>14</sup> incorporated in the OLEX2 program package.<sup>15</sup> The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the 'riding' model approximation, with U<sub>*iso*</sub>(H) set to 1.2U<sub>*eq*</sub>(C) and C–H 0.97 Å for the CH<sub>2</sub> groups and U<sub>*iso*</sub>(H) set to 1.5U<sub>*eq*</sub>(N) and C–H 0.96 Å for the CH<sub>3</sub> groups. Empirical absorption correction was applied in CrysAlisPro program complex<sup>16</sup> using spherical harmonics, implemented in SCALE3 ABSPACK

scaling algorithm. The crystallographic data for all samples and refinement parameters are given in Table 1 of The Supporting Information. Supplementary crystallographic data for this paper have been deposited at Cambridge Crystallographic Data Centre (CCDC 1033500–1033503) and can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif.

Acetonitrile, 1,2-dichloroethane, carbon tetrachloride and chloroform were distilled successively over phosphorous pentoxide and calcined potassium carbonate under argon atmosphere. Tetrahydrofuran and toluene were distilled from sodium benzophenone-ketyl. Methanol and ethanol were dried with magnesium/CCl<sub>4</sub>. Triethylamine was distilled from potassium hydroxide. *N*,*N*-Dimethylformamide was purchased from Fluka, nitromethane and dimethylsulphoxide were purchased from "VEKTON" and were used without purification. Thinlayer chromatography (TLC) was conducted on aluminium sheets with 0.2 mm silica gel (fluorescent indicator, Macherey-Nagel).

The azirines were synthesized by known literature procedures: **7a**,**e**,<sup>17</sup> **7b**,<sup>18</sup> **7c**,<sup>19</sup> **7d**.<sup>20</sup> Ethyl 5,5-dimethyl-2,4-dioxohexanoate **12f**,<sup>21</sup> enamines **12h**,**j**,<sup>22</sup> 2-(methylsulfanyl)-1,4-diphenylbut-2ene-1,4-dione **12k**<sup>23</sup> and butanetriones **12g**,**i**<sup>24</sup> were prepared by the reported methods. The other compounds **12** were obtained using modified procedure A.<sup>25</sup>

4.1.1. General procedure A. A solution of the ketone (20.0 mmol) and diethyloxalate (20.0 mmol) in ethyl or methyl alcohol (in amount enough to provide clear solution) was added dropwise to a 4M solution of sodium alcoholate in alcohol (5 ml, 20.0 mmol) under vigorous stirring and cooling with ice bath. The reaction mixture was stirred overnight at room temperature. The solid formed was filtered off, thoroughly washed with alcohol (5 mL), Et<sub>2</sub>O (2×20 mL), and dried *in vacuo*. Sodium enolate of **12** obtained was then suspended in an ice-cold mixture of water (25 mL) and alcohol (5 mL), and acidified with H<sub>2</sub>SO<sub>4</sub> to give the corresponding 2,4-dioxobutanoic acid ether, that was filtered off, washed with water, dried and recrystallized from an appropriate solvent.

#### 4.2. Synthesis of pyrroles 13a-d,g-j,l-s and 14 a-d, f-s

4.2.1. General procedure B for the reaction conditions screening. Compound **12a** (0.25 mmol) was dissolved in an appropriate solvent (1 mL) in a thick-wall tube (5 mL) with screw cap, an appropriate catalyst (5-10% mol) or additives (see Table 1 for details) as well as 2-methylnaphthalene as internal standard were added and the suspension obtained was stirred at room temperature under an argon atmosphere for 30 minutes. A solution of 2*H*-azirine **7a** (0.25 mmol) in 1 mL of the same solvent was then added in one portion and stirring was continued at a temperature of 50–115 °C for the period indicated (Table 1). The solvent was removed on a rotary evaporator and the crude reaction mixture obtained was passed through silica (5.0 g) eluting with a

benzene/ethyl acetate mixture (50 mL, 4/1). Solvents were evaporated and the mixture obtained was analyzed by <sup>1</sup>H NMR. In some particular cases the products were isolated by column chromatography (silica, eluent benzene/ethyl acetate  $50/1 \rightarrow 4/1$ ).

4.2.2. General procedure C for the preparation of pyrroles 13a-d,g-j,l-s and 14a-d, f-s. Compound 12a-m (1.0 mmol) was dissolved in DCE (5 mL) in a thick-wall tube (15 mL) with screw cap, copper(II) acetate monohydrate (10.0 mg, 0.05 mmol, 5% mol) was added, and the suspension obtained was stirred at 50 °C under argon atmosphere for 15 minutes. A solution of 2*H*-azirine 7a-e (1.0 mmol) in DCE (1 mL) was then added in one portion and stirring was continued at 60–75 °C for 6–100 h (Table 2). The solvent was removed on a rotary evaporator and the reaction mixture was separated by column chromatography on silica using benzene/ethyl acetate or hexane/acetone mixtures as eluents. Isolated pyrroles were then recrystallized from an appropriate solvent.

4.2.3. Ethyl 2-(2,4-diphenyl-1H-pyrrol-3-yl)-2-oxoacetate (13a). Compound 13a (36.0 mg, 45%) was obtained from 3-phenyl-2H-azirine 7a (30.0 mg, 0.25 mmol) and ethyl 2,4-dioxo-4-phenylbutanoate 12a (55 mg, 0.25 mmol) according to procedure *B*, using MeCN as a solvent and copper(II) acetate monohydrate (2.5 mg, 12.5 µmol, 5% mol) as catalyst at 70 °C for 7 h. A benzene/ethyl acetate mixture (12/1  $\rightarrow$  4/1) was used as eluent for column chromatography. Pale yellow solid, mp 134.5–136.0 °C (hexane/chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.67 (br. s., 1 H), 7.57–7.53 (m, 2 H), 7.46–7.40 (m, 5 H), 7.36 (t, *J* = 7.3 Hz, 2 H), 7.32–7.27 (m, 1 H), 6.86 (d, *J* = 2.5 Hz, 1 H), 3.64 (q, *J* = 7.2 Hz, 2H), 1.00 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  183.5, 164.2, 140.4, 134.4, 131.2, 129.10, 129.08, 129.0, 128.6, 128.5, 128.1, 127.0, 118.1, 115.7, 61.7, 13.5. ESI/HRMS (m/z): 320.1281 calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>3</sub> [M+H]<sup>+</sup>, found 320.1282. IR (KBr, cm<sup>-1</sup>): v 3252, 1705, 1649. CCDC 1033501.

4.2.4. Ethyl 3-benzoyl-4-phenylpyrrole-2-carboxylate (14a). Compound 14a (36.0 mg, 63%) was obtained from 3-phenyl-2*H*-azirine **7a** (30.0 mg, 0.25 mmol) and ethyl 2,4-dioxo-4-phenylbutanoate 12a (55 mg, 0.25 mmol) according to procedure *B*, using DCE as a solvent and cobalt(II) acetate tetrahydrate (3.1 mg, 12.5 µmol, 5% mol) as catalyst at 70 °C for 6 h. A benzene/ethyl acetate mixture ( $12/1 \rightarrow 4/1$ ) was used as eluent for column chromatography. Light beige crystals, mp 115.5–118.0 °C (hexane/chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.63 (br. s, 1H), 7.92–7.87 (m, 2H), 7.52 (tt, *J* = 7.4, 1.3 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.33–7.29 (m, 2H), 7.25–7.21 (m, 2H), 7.19–7.14 (m, 2H), 4.06 (q, *J* = 7.2 Hz, 2H), 0.89 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  194.9, 160.5, 138.5, 133.4, 133.1, 129.5, 128.6, 128.3, 127.5, 126.9, 126.7, 126.5, 121.6, 120.5, 60.8, 13.5. ESI/HRMS (m/z): 320.1281 calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>3</sub> [M+H]<sup>+</sup>, found 320.1289. IR (KBr, cm<sup>-1</sup>): v 3283, 1691, 1641. CCDC 1033500.

Compound **14a** was also obtained in higher preparative yield (142 mg, 89%) from 3-phenyl-2*H*-azirine **7a** (176.0 mg, 1.50 mmol) and ethyl 2-imino-4-oxo-4-phenylbutanoate **12h** (110 mg, 0.5 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (5.0 mg, 25.0  $\mu$ mol, 5% mol) as catalyst at 75 °C for 9 h.

4.2.5. Ethyl 2-(2-(4-methoxyphenyl)-4-phenyl-1H-pyrrol-3-yl)-2-oxoacetate (13b) and ethyl 3-(4methoxybenzoyl)-4-phenyl-1H-pyrrole-2-carboxylate (14b).Compounds 13b (84.0 mg, 24%) and 14b (135.0 mg, 39%) were obtained from 3-phenyl-2H-azirine 7a (117.0 mg, 1.0 mmol) and ethyl 4-(4-methoxyphenyl)-2,4-dioxobutanoate 12b (250.0 mg, 1.0 mmol) according to the procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (10.0 mg, 50.0 µmol, 5% mol) as catalyst at 60 °C for 7 h. A benzene/ethyl acetate mixture (12/1  $\rightarrow$  4/1) was used as eluent for column chromatography.

Compound **13b**. Yellow crystals, mp 150.0–152.0 °C (hexane/chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.76 (br. s, 1H), 7.49 (d, J = 8.8 Hz, 2H), 7.42–7.38 (m, 2H), 7.37–7.32 (m, 2H), 7.27–7.31 (m, 1H), 6.93 (d, J = 8.8 Hz, 2H), 6.78 (d, J = 2.5 Hz, 1H), 3.83 (s, 3H), 3.64 (q, J = 7.2 Hz, 2H), 1.00 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  183.4, 164.4, 160.3, 140.6, 134.5, 130.5, 129.1, 128.5, 128.1, 126.9, 123.6, 117.7, 115.4, 113.9, 61.6, 55.3, 13.5. ESI/HRMS (m/z): 350.1387 calcd for C<sub>21</sub>H<sub>19</sub>NO<sub>4</sub> [M+H]<sup>+</sup>, found 350.1383. IR (KBr, cm<sup>-1</sup>): v 3292, 1722, 1646.

Compound **14b**. Colorless crystals, mp 122.6–124.7 °C (hexane/chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.53 (br. s, 1H), 7.86 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 7.3 Hz, 2H), 7.22 (t, J = 7.3 Hz, 2H), 7.19 -7.09 (m, 2H), 6.86 (d, J = 8.6 Hz, 2H), 4.09 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 0.96 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  193.5, 163.6, 160.5, 133.5, 131.9, 131.7, 128.6, 127.4, 126.8, 126.7, 126.6, 121.3, 120.4, 113.6, 60.8, 55.4, 13.7. ESI/HRMS (m/z): 350.1387 calcd for C<sub>21</sub>H<sub>19</sub>NO<sub>4</sub> [M+H]<sup>+</sup>, found 350.1389. IR (KBr, cm<sup>-1</sup>): v 3249, 1707, 1640.

4.2.6. Methyl 2-(2-(4-bromophenyl)-4-phenyl-1H-pyrrol-3-yl)-2-oxoacetate (**13c**) and methyl 3-(4bromobenzoyl)-4-phenyl-1H-pyrrole-2-carboxylate (**14c**). Compounds **13c** (116.0 mg, 30%) and **14c** (175.0 mg, 46%) were obtained from 3-phenyl-2H-azirine **7a** (117.0 mg, 1.0 mmol) and methyl 4-(4-bromophenyl)-2,4-dioxobutanoate **12c** (285.0 mg, 1.0 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (10.0 mg, 50.0 µmol, 5% mol) as catalyst at 60 °C for 10 h. A benzene/ethyl acetate mixture (25/1  $\rightarrow$  10/1) was used as eluent for column chromatography.

Compound **13c**. Bright yellow solid, mp 164.5–166.2 °C (hexane/chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.78 (br. s, 1H), 7.55 (d, J = 8.5 Hz, 2H), 7.44 (d, J = 8.5 Hz, 2H), 7.40–7.34 (m, 4H), 7.34–7.28 (m, 1H), 6.85 (d, J = 2.5 Hz, 1H), 3.24 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  183.0, 164.4, 138.9, 134.0,

131.7, 130.6, 130.0, 129.1, 128.9, 128.3, 127.2, 123.4, 118.1, 116.0, 52.1. ESI/HRMS (m/z): 384.0230 calcd for  $C_{19}H_{14}BrNO_3$  [M+H]<sup>+</sup>, found 384.0227. IR (KBr, cm<sup>-1</sup>): v 3238, 1736, 1629. Compound **14c**. Colorless solid, mp 165.4–166.3 °C (hexane/chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.46 (br. s, 1H), 7.72 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.29–7.14 (m, 6H), 3.63 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  193.8, 160.6, 137.0, 133.1, 131.7, 130.9, 128.7, 128.5, 127.4, 127.0, 126.9, 126.2, 121.3, 120.6, 51.8. ESI/HRMS (m/z): 384.0230 calcd for  $C_{19}H_{14}BrNO_3$  [M+H]<sup>+</sup>, found 384.0234. IR (KBr, cm<sup>-1</sup>): v 3231, 1726, 1642.

4.2.7. Ethyl 2-((3-nitrophenyl)-4-phenyl-1H-pyrrol-3-yl)-2-oxoacetate (13d) and ethyl 3-(3nitrobenzoyl)-4-phenyl-1H-pyrrole-2-carboxylate (14d). Compounds 13d (40.0 mg, 11%) 14d (120.0 mg, 33%) were obtained from 3-phenyl-2H-azirine 7a (120.0 mg, 1.03 mmol) and ethyl 4-(3-nitrophenyl)-2,4-dioxobutanoate 12e (265.0 mg, 1.0 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (10.0 mg, 50.0 µmol, 5% mol) as catalyst at 60 °C for 11 h. A benzene/ethyl acetate mixture (50/1  $\rightarrow$  12/1) was used as eluent for column chromatography. Further, compound 13d was recrystallized twice from hexane/ethyl acetate and subsequently from light petroleum/dichloromethane.

Compound **13d**. Bright yellow crystals, mp 193.0–194.3 °C (light petroleum/dichloromethane). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.92 (br. s, 1H), 8.45 (t, J = 1.7 Hz, 1H), 8.24 (dd, J = 8.2, 1.2 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.60 (t, J = 8.0 Hz, 1H), 7.43–7.28 (m, 5H), 6.93 (d, J = 2.5 Hz, 1H), 3.67 (q, J = 7.2 Hz, 3H), 1.02 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  183.5, 163.7, 148.1, 136.5, 135.5, 133.8, 132.7, 129.4, 129.3, 129.1, 128.39, 128.37, 123.6, 123.5, 118.4, 117.0, 61.9, 13.5. ESI/HRMS (m/z): 365.1132 calcd for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup>, found 365.1135. IR (KBr, cm<sup>-1</sup>): v 3258, 1723, 1657. CCDC 1033502.

Compound **14d**. Yellow crystals, mp 143.9–145.8 °C (petrol ether/dichloroethane). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.55 (br. s, 1H), 8.64 (t, J = 1.8 Hz, 1H), 8.35 (ddd, J = 8.0, 2.3, 1.1 Hz, 1H), 8.22 (dt, J = 8.0, 1.4 Hz, 1H), 7.59 (t, J = 7.9 Hz, 1H), 7.32–7.13 (m, 6H), 4.12 (d, J = 7.1 Hz, 2H), 1.00 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  192.3, 159.9, 148.3, 139.7, 134.8, 133.0, 129.6, 128.7, 127.7, 127.30, 127.27, 127.1, 125.1, 124.3, 121.8, 120.8, 61.1, 13.8. ESI/HRMS (m/z): 365.1132 calcd for C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub> [M+H]<sup>+</sup>, found 365.1137. IR (KBr, cm<sup>-1</sup>): v 3256, 1696, 1672, 1350.

4.2.8. (4-Phenyl-1H-pyrrole-2,3-diyl)bis(phenylmethanone) (14f). Compound 14f (149.0 mg, 42%) was obtained as the single identified product from ethyl 3-phenyl-2H-azirine 7a (117.0 mg, 1.0 mmol) and 1,4-diphenylbutane-1,2,4-trione 12g (252.0 mg, 1.0 mmol) according to procedure C, using DCE as a solvent and copper(II) acetate monohydrate (10.0 mg, 50.0  $\mu$ mol, 5% mol) as catalyst at 60 °C for 8 h. A benzene/ethyl acetate mixture (50/1  $\rightarrow$  12/1) was used as eluent for

column chromatography. Brown crystals, mp 143.5–145.5 °C (petrol ether/dichloromethane). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.72 (br. s, 1H), 7.45–7.38 (m, 4H), 7.37–7.31 (m, 4H), 7.29–7.19 (m, 4H), 7.18–7.12 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  194.1, 186.8, 139.2, 138.6, 133.3, 132.6, 131.9, 131.0, 129.1, 128.6, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 126.9, 122.4. ESI/HRMS (m/z): 352.1332 calcd for C<sub>24</sub>H<sub>17</sub>NO<sub>2</sub> [M+H]<sup>+</sup>, found 352.1335. IR (KBr, cm<sup>-1</sup>): v 3273, 1657, 1628. CCDC 1033503. Compound **14f** was also obtained in higher preparative yield (121 mg, 69%) from 3-phenyl-2*H*-azirine **7a** (176.0 mg, 1.50 mmol) and ethyl 1,4-diphenylbutane-1,2,4-trione **12g** (126 mg, 0.5 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (5.0 mg, 25.0 µmol, 5% mol) as catalyst at 75 °C for 5 h.

4.2.9. Ethyl 2-oxo-2-(2,4,5-triphenyl-1H-pyrrol-3-yl)acetate (**13g**) and ethyl 3-benzoyl-4,5diphenyl-1H-pyrrole-2-carboxylate (**14g**). Compounds **13g** (52.0 mg, 18%) and **14g** (44.0 mg, 15%) were obtained from 2,3-diphenyl-2H-azirine **7b** (145.0 mg, 0.75 mmol) and ethyl 2,4-dioxo-4-phenylbutanoate **12a** (165.0 mg, 0.75 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (8.0 mg, 40.2 µmol, 5% mol) as catalyst at 60 °C for 24 h. A benzene/ethyl acetate mixture (50/1  $\rightarrow$  12/1) was used as eluent for column chromatography.

Compound **13g**. Yellow solid, mp 166.7–167.6 °C (petrol ether/dichloroethane). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.62 (br. s, 1H), 7.93–7.85 (m, 2H), 7.52–7.47 (m, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.34–7.27 (m, 5H), 7.20–7.13 (m, 5H), 4.01 (q, J = 7.1 Hz, 2H), 0.85 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  183.5, 164.2, 139.5, 133.9, 131.3, 131.1, 130.9, 129.9, 129.09, 129.06, 128.7, 128.6, 128.1, 127.4, 127.3, 127.2, 124.4, 118.1, 61.5, 13.6. ESI/HRMS (m/z): 396.1594 calcd for C<sub>26</sub>H<sub>21</sub>NO<sub>3</sub> [M+H]<sup>+</sup>, found 396.1595. IR (KBr, cm<sup>-1</sup>): v 3346, 1718, 1657.

Compound **14g**. Colorless crystals, mp 202.2–204.1 °C (petrol ether/dichloroethane). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.62 (br. s, 1H), 7.93–7.85 (m, 2H), 7.52–7.47 (m, 1H), 7.38 (t, J = 7.6 Hz, 2H), 7.34–7.27 (m, 5H), 7.20–7.13 (m, 5H), 4.01 (q, J = 7.1 Hz, 2H), 0.85 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  194.2, 160.7, 138.6, 133.6, 133.3, 132.9, 131.0, 130.0, 129.5, 129.3, 128.7, 128.3, 128.2, 128.1, 127.9, 126.9, 123.8, 120.2, 60.9, 13.5. ESI/HRMS (m/z): 396.1594 calcd for C<sub>26</sub>H<sub>21</sub>NO<sub>3</sub> [M+H]<sup>+</sup>, found 396.1603. IR (KBr, cm<sup>-1</sup>): v 3297, 1677.

4.2.10. Ethyl 2-(2-(4-methoxyphenyl)-2-oxo-4,5-diphenyl-1H-pyrrol-3-yl)acetate (**13h**) and. ethyl 3-(4-methoxybenzoyl)-4,5-diphenyl-1H-pyrrole-2-carboxylate (**14h**). Compounds **13h** (71.0 mg, 22%) and **14h** (60.0 mg, 19%) were obtained from 2,3-diphenyl-2H-azirine **7b** (145.0 mg, 0.75 mmol) and ethyl 4-(4-methoxyphenyl)-2,4-dioxobutanoate **12b** (188.0 mg, 0.75 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (8.0 mg, 40.2 µmol, 5% mol) as catalyst at 60 °C for 20 h. A benzene/ethyl acetate mixture (25/1) was used as eluent for column chromatography.

Compound **13h**. Bright yellow crystals, > 128.0 °C (dec., petrol ether/diethyl ether). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.69 (br. s, 1H), 7.58 (d, J = 8.8 Hz, 2H), 7.33–7.27 (m, 5H), 7.26–7.17 (m, 5H), 6.96 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H), 3.59 (q, J = 7.2 Hz, 2H), 1.02 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  183.5, 164.4, 160.4, 139.7, 134.0, 131.4, 131.0, 130.5, 129.5, 128.6, 128.0, 127.3, 127.2, 127.1, 124.2, 123.5, 117.7, 114.0, 61.5, 55.4, 13.6. ESI/HRMS (m/z): 426.1700 calcd for C<sub>27</sub>H<sub>23</sub>NO<sub>4</sub> [M+H]<sup>+</sup>, found 426.1705. IR (KBr, cm<sup>-1</sup>): v 3444, 1733, 1630.

Compound **14h**. Pale yellow solid, mp 179.4–180.4 °C (petrol ether/diethyl ether). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.52 (br. s, 1H), 7.85 (d, J = 8.7 Hz, 2H), 7.33–7.27 (m, 5H), 7.19–7.12 (m, 5H), 6.85 (d, J = 8.7 Hz, 2H), 4.05 (q, J = 7.1 Hz, 2H), 3.83 (s, 3H), 0.93 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  192.8, 163.5, 160.7, 133.5, 131.83, 131.81, 131.1, 130.0, 129.7, 128.7, 128.3, 128.1, 127.9, 126.9, 123.6, 119.9, 113.5, 60.8, 55.4, 13.7. ESI/HRMS (m/z): 426.1700 calcd for C<sub>27</sub>H<sub>23</sub>NO<sub>4</sub> [M+H]<sup>+</sup>, found 426.1710. IR (KBr, cm<sup>-1</sup>): v 3262, 1678, 1648, 1600.

4.2.11. Ethyl 2-(2-(tert-butyl)-2-oxo-4,5-diphenyl-1H-pyrrol-3-yl)acetate (13i) and ethyl 4,5diphenyl-3-pivaloyl-1H-pyrrole-2-carboxylate (14i). Compound 13i (79.0 mg, 14%) and 14i (63.0 mg, 11%) were obtained from 2,3-diphenyl-2H-azirine 7b (300.0 mg, 1.55 mmol) and ethyl 5,5dimethyl-2,4-dioxohexanoate 12f (300.0 mg, 1.50 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (10.0 mg, 50.0 µmol, 3.3% mol) as catalyst at 60 °C for 30 h. A benzene/ethyl acetate mixture (50/1  $\rightarrow$  10/1) was used as eluent for column chromatography.

Compound **13i**. Bright yellow crystals, mp 195.0–197.0 °C (petrol ether/diethyl ether).<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.53 (br. s, 1H), 7.31–7.17 (m, 8H), 7.11 (d, J = 6.7 Hz, 2H), 3.51 (q, J = 7.1 Hz, 2H), 1.54 (s, 9H), 1.05 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  184.9, 164.9, 148.6, 134.1, 131.6, 131.2, 128.7, 128.0, 127.13, 127.12, 127.0, 126.0, 124.9, 116.9, 61.4, 33.5, 28.5, 13.6. ESI/HRMS (m/z): 376.1907 calcd for C<sub>24</sub>H<sub>25</sub>NO<sub>3</sub> [M+H]<sup>+</sup>, found 376.1909. IR (KBr, cm<sup>-1</sup>): v 3296, 2964, 1728, 1641.

Compound **14i**. Colorless crystals, mp 206.6–207.8 °C (petrol ether/dichloromethane).<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.18 (br. s, 1H), 7.30–7.23 (m, 8H), 7.22–7.18 (m, 2H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H), 0.90 (s, 9H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  121.0, 160.5, 134.4, 133.0, 131.0, 130.9, 130.4, 128.7, 128.5, 128.1, 127.8, 127.2, 121.7, 118.3, 61.0, 45.1, 27.0, 14.4. ESI/HRMS (m/z): 376.1907 calcd for C<sub>24</sub>H<sub>25</sub>NO<sub>3</sub> [M+H]<sup>+</sup>, found 376.1906. IR (KBr, cm<sup>-1</sup>): v 3300, 2976, 1678.

4.2.12. Methyl 2-(4,5-diphenyl-2-methyl-1H-pyrrol-3-yl)-2-oxoacetate (13j) and methyl 3-acetyl-4,5-diphenyl-1H-pyrrole-2-carboxylate (14j). Compounds 13j (123.0 mg, 40%) 14j (82.0 mg, 26%) and were obtained from 2,3-diphenyl-2H-azirine 7b (193.0 mg, 1.0 mmol) and methyl 2,4dioxopentanoate 12l (143.0 mg, 1.0 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (10.0 mg, 50.0 µmol, 5% mol) as catalyst at 60 °C for 35 h. A benzene/ethyl acetate mixture (10/1  $\rightarrow$  5/1) was used as eluent for column chromatography.

Compound **13j**. Yellow crystals, mp 187.1–189.0 °C (hexane-dichloromethane).<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.40 (br. s, 1H), 7.32–7.23 (m, 8H), 7.23–7.18 (m, 2H), 3.86 (s, 3H), 2.30 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  201.2, 160.9, 133.4. 133.2, 132.4, 130.8, 130.1, 128.7, 128.5, 128.2, 127.8, 127.3, 122.4, 118.2, 52.0, 32.5. ESI/HRMS (m/z): 320.1281 calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>3</sub> [M+H]<sup>+</sup>, found 320.1287. IR (KBr, cm<sup>-1</sup>): v 3231, 1740, 1624, 1602.

Compound **14j**. Colorless crystals, mp 161.8–163.5 °C (hexane-dichloromethane).<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.78 (br. s, 1H), 7.33–7.16 (m, 3H), 7.25–7.15 (m, 5H), 7.14–7.09 (m, 2H), 3.18 (s, 3H), 2.64 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  184.0, 165.3, 139.5, 134.0, 131.4, 130.9, 128.6, 128.2, 127.9, 127.2, 127.1, 126.9, 123.0, 117.6, 51.7, 14.1. ESI/HRMS (m/z): 320.1281 calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>3</sub> [M+H]<sup>+</sup>, found 320.1285. IR (KBr, cm<sup>-1</sup>): v 3287, 1707, 1687.

4.2.13. (4,5-Diphenyl-1H-pyrrole-2,3-diyl)bis(phenylmethanone) (14k). Compound 14k (133.0 mg, 42%) was obtained from 2,3-diphenyl-2H-azirine **7b** (145.0 mg, 0.75 mmol) and 1,4-diphenylbutane-1,2,4-trione **12g** (189.0 mg, 0.75 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (8.0 mg, 40.2 µmol, 5% mol) as catalyst at 60 °C for 24 h A benzene/ethyl acetate mixture (50/1  $\rightarrow$  25/1) was used as eluent for column chromatography. Pale yeillow solid, mp 227.0–229.5 °C (petrol ether/chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.94 (br. s, 1H), 7.45–7.28 (m, 11H), 7.24–7.16 (m, 5H), 7.16–7.08 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  193.5, 186.7, 139.3, 138.9, 135.1, 133.2, 132.4, 131.9, 131.0, 130.6, 130.5, 129.8, 129.0, 128.7, 128.4, 128.2, 128.0, 128.0, 127.8, 127.2, 125.5. ESI/HRMS (m/z): 428.1645 calcd for C<sub>30</sub>H<sub>21</sub>NO<sub>2</sub> [M+H]<sup>+</sup>, found 428.1653. IR (KBr, cm<sup>-1</sup>): v 3305, 1660, 1607.

4.2.14. Ethyl 2-(2-ethoxycarbonyl-3,5-diphenyl-1H-pyrrol-4-yl)-2-oxoacetate (13l) and diethyl 3benzoyl-4-phenyl-1H-pyrrole-2,5-dicarboxylate (14l). Compound 13l (111.0 mg, 28%) and 14l (265.0 mg, 68%) were obtained from ethyl 3-phenyl-2H-azirine-2-carboxylate 7c (190.0 mg, 1.0 mmol) and ethyl 4-phenyl-2,4-dioxobutanoate 12a (220.0 mg, 1.0 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (10.0 mg, 50.0 µmol, 5% mol) as catalyst at 75 °C for 70 h. A benzene/ethyl acetate mixture (50/1  $\rightarrow$  20/1) was used as eluent for column chromatography. Compound **131**. Colorless crystals, mp 138.4–139.7 °C (hexane/benzene). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.76 (br. s, 1H), 7.62 (dd, J = 6.3, 2.8 Hz, 2H), 7.49–7.42 (m, 3H), 7.40–7.33 (m, 5H), 4.09 (q, J = 7.2 Hz, 2H), 3.59 (q, J = 7.2 Hz, 2H), 1.06 (t, J = 7.2 Hz, 3H), 1.02 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  183.4, 163.6, 161.0, 141.3, 133.6, 132.6, 130.7, 130.2, 129.6, 129.2, 128.5, 127.8, 127.3, 120.1, 119.0, 61.7, 60.9, 13.8, 13.6. ESI/HRMS (m/z): 392.1492 calcd for C<sub>23</sub>H<sub>21</sub>NO<sub>5</sub> [M+H]<sup>+</sup>, found 392.1498. IR (KBr, cm<sup>-1</sup>): v 3267, 1730, 1656.

Compound **141**. Colorless crystals, mp 150.1–152.1 °C (hexane/benzene). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 10.02 (br. s, 1H), 7.78 (d, J = 7.3 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.7 Hz, 2H), 7.31–7.26 (m, 2H), 7.25–7.19 (m, 3H), 4.25 (q, J = 7.1 Hz, 2H), 4.09 (q, J = 7.1 Hz, 2H), 1.19 (t, J = 7.1 Hz, 3H), 0.92 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  192.7, 160.1, 159.6, 138.2, 133.1, 132.0, 131.2, 130.1, 129.4, 128.8, 128.3, 127.7, 127.5, 122.7, 122.1, 61.4, 61.2, 14.0, 13.5. ESI/HRMS (m/z): 392.1492 calcd for C<sub>23</sub>H<sub>21</sub>NO<sub>5</sub> [M+H]<sup>+</sup>, found 392.1494. IR (KBr, cm<sup>-1</sup>): v 3278, 1712, 1673.

4.2.15. Ethyl 2-(2-ethoxycarbonyl-5-(4-methoxyphenyl)-3-phenyl-1H-pyrrol-4-yl)-2-oxoacetate (13m) and diethyl 3-(4-methoxybenzoyl)-4-phenyl-1H-pyrrole-2,5-dicarboxylate (14m). Compounds 13m (109.0 mg, 26%) and 14m (280.0 mg, 65%) were obtained from ethyl 3-phenyl-2H-azirine-2-carboxylate 7c (190.0 mg, 1.0 mmol) and ethyl 4-(4-methoxyphenyl)-2,4-dioxobutanoate 12b (250.0 mg, 1.0 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (10.0 mg, 50.0  $\mu$ mol, 5% mol) as catalyst at 75 °C for 70 h. A benzene/ethyl acetate mixture (25/1  $\rightarrow$  10/1) was used as eluent for column chromatography.

Compound **13m**. Pale yellow crystals, mp 138.3–140.7 °C (hexane/benzene). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.53 (br. s, 1H), 7.59 (d, J = 8.7 Hz, 2H), 7.39–7.33 (m, 5H), 6.97 (d, J = 8.7 Hz, 2H), 4.11 (q, J =7.1 Hz, 2H), 3.85 (s, 3H), 3.59 (q, J = 7.2 Hz, 2H), 1.08 (t, J = 7.1 Hz, 3H), 1.03 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  183.4, 163.7, 161.0, 160.8, 141.4, 133.6, 132.7, 130.7, 130.6, 127.7, 127.3, 122.5, 119.7, 118.6, 114.0, 61.7, 60.8, 55.4, 13.8, 13.6. ESI/HRMS (m/z): 422.1598 calcd for C<sub>24</sub>H<sub>23</sub>NO<sub>6</sub> [M+H]<sup>+</sup>, found 422.1604. IR (KBr, cm<sup>-1</sup>): v 3283, 1724, 1666.

Compound **14m**. Colorless crystals, mp 144.1–145.6 °C (hexane/benzene). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.92 (br. s, 1H), 7.75 (d, J = 8.9 Hz, 2H), 7.31–7.27 (m, 2H), 7.25–7.19 (m, 3H), 6.83 (d, J = 8.9 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 4.13 (q, J = 7.10 Hz, 2H), 3.83 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 0.99 (t, J = 7.10 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  191.3, 163.6, 160.1, 159.6, 132.1, 131.7, 131.4, 131.0, 130.1, 129.2, 127.6, 127.5, 122.4, 121.9, 113.5, 61.4, 61.2, 55.4, 14.0, 13.7. ESI/HRMS (m/z): 422.1598 calcd for C<sub>24</sub>H<sub>23</sub>NO<sub>6</sub> [M+H]<sup>+</sup>, found 422.1604. IR (KBr, cm<sup>-1</sup>): v 3278, 1714, 1596.

4.2.16. *Methyl* 2-(5-(3-bromophenyl)-2-ethoxycarbonyl-3-phenyl-1H-pyrrol-4-yl)-2-oxoacetate (13n). Compound 13n (123.0 mg, 27%) and 14n (255.0 mg, 56%) were obtained from ethyl 3-

phenyl-2*H*-azirine-2-carboxylate **7c** (190.0 mg, 1.0 mmol) and methyl 4-(3-bromophenyl)-2,4dioxobutanoate **12m** (285.0 mg, 1.0 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (10.0 mg, 50.0  $\mu$ mol, 5% mol) as catalyst at 75 °C for 100 h. A benzene/ethyl acetate mixture (20/1  $\rightarrow$  10/1) was used as eluent for column chromatography.

Compound **13n**. Colorless solid, mp 124.5–126.3 °C (hexane/dichloromethane). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.82 (br. s, 1H), 7.79 (t, J = 1.9 Hz, 1H), 7.58 (dt, J = 8.0, 1.9 Hz, 2H), 7.40–7.30 (m, 6H), 4.10 (q, J = 7.1 Hz, 2H), 3.23 (s, 3H), 1.07 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  182.9, 163.8, 161.0, 139.5, 133.6, 132.6, 132.3, 132.1, 132.0, 130.7, 130.0, 128.1, 127.9, 127.4, 122.5, 120.4, 119.2, 61.1, 52.1, 13.8. ESI/HRMS (m/z): 456.0441 calcd for C<sub>22</sub>H<sub>18</sub>BrNO<sub>5</sub> [M+H]<sup>+</sup>, found 456.0446. IR (KBr, cm<sup>-1</sup>): v 3265, 1750, 1660.

Compound **14n**. Colorless crystals, mp 112.6–114.6 °C (hexane/dichloromethane). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 10.01 (br. s, 1H), 7.86 (t, J = 1.8 Hz, 1H), 7.65 (d, J = 7.8 Hz, 1H), 7.60–7.56 (m, 1H), 7.27–7.18 (m, 6H), 4.26 (q, J = 7.1 Hz, 2H), 3.70 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  191.2, 159.9, 159.7, 139.5, 136.0, 132.2, 131.7, 131.1, 130.0, 129.9, 128.4, 127.9, 127.8, 127.6, 122.6, 122.5, 122.1, 61.3, 52.3, 14.0. ESI/HRMS (m/z): 456.0441 calcd for C<sub>22</sub>H<sub>18</sub>BrNO<sub>5</sub> [M+H]<sup>+</sup>, found 456.0447. IR (KBr, cm<sup>-1</sup>): v 3268, 1722, 1676.

4.2.17. Ethyl 2-(2-ethoxycarbonyl-3-methyl-5-phenyl-1H-pyrrol-4-yl)-2-oxoacetate (**130**) and Diethyl 3-benzoyl-4-methyl-1H-pyrrole-2,5-dicarboxylate (**140**). Compounds **130** (92.0 mg, 28%) and **140** (86.0 mg, 26%) were obtained from ethyl 3-methyl-2H-azirine-2-carboxylate **7d** (130.0 mg, 1.02 mmol) and ethyl 4-phenyl-2,4-dioxobutanoate **12a** (220.0 mg, 1.0 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (10.0 mg, 50.0 µmol, 5% mol) as catalyst at 60 °C for 55 h. A hexane/acetone mixture (10/1) was used as eluent for column chromatography.

Compound **130**. Colorless crystals, mp 153.0–155.1 °C (hexane/dichloromethane). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.42 (br. s, 1H), 7.47–7.39 (m, 5H), 4.31 (q, J = 7.1 Hz, 2H), 3.67 (q, J = 7.2 Hz, 2H), 2.61 (s, 3H), 1.36 (t, J = 7.10 Hz, 3H), 1.02 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  183.7, 164.0, 161.7, 142.5, 131.6, 130.6, 129.6, 129.1, 128.7, 120.8, 118.7, 61.7, 60.9, 14.4, 13.5, 11.7. ESI/HRMS (m/z): 330.1336 calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>5</sub> [M+H]<sup>+</sup>, found 330.1343. IR (KBr, cm<sup>-1</sup>): v 3241, 1741, 1677, 1648.

Compound **140**. Light beige crystals, mp 146.6–148.5 °C (petrol ether/diethyl ether). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.76 (br. s, 1H), 7.82 (d, J = 7.3 Hz, 2H), 7.56 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 4.39 (q, J = 7.2 Hz, 2H), 4.02 (q, J = 7.2 Hz, 2H), 2.28 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H), 0.87 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  193.3, 160.6, 159.6, 138.5, 133.2, 129.4, 128.5, 128.4, 127.6,

122.8, 122.7, 61.3, 61.1, 14.4, 13.4, 10.7. ESI/HRMS (m/z): 330.1336 calcd for  $C_{18}H_{19}NO_5$  [M+H]<sup>+</sup>, found 330.1344. IR (KBr, cm<sup>-1</sup>): v 3284, 1713, 1656.

4.2.18. Ethyl 2-(5-(4-methoxyphenyl)-2-ethoxycarbonyl-3-methyl-1H-pyrrol-4-yl)-2-oxoacetate (13p) and diethyl 3-(4-methoxybenzoyl)-4-methyl-1H-pyrrole-2,5-dicarboxylate (14p). Compounds 13p (97.0 mg, 27%) and 14p (119.0 mg, 33%) were obtained from ethyl 3-methyl-2H-azirine-2-carboxylate 7d (130.0 mg, 1.02 mmol) and ethyl 4-(4-methoxyphenyl)-2,4-dioxobutanoate 12b (250.0 mg, 1.0 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (10.0 mg, 50.0  $\mu$ mol, 5% mol) as catalyst at 60°C for 55 h. A hexane/acetone mixture (10/1) was used as eluent for column chromatography.

Compound **13p**. Colorless crystals, mp 159.7–161.2 °C (petrol ether/diethyl ether). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.24 (br. s, 1H), 7.34 (d, J = 8.6 Hz, 2H), 6.95 (d, J = 8.6 Hz, 2H), 4.32 (q, J = 7.1 Hz, 2H), 3.84 (s, 3H), 3.75 (q, J = 7.2 Hz, 2H), 2.60 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H), 1.06 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  183.8, 164.2, 161.7, 160.8, 142.5, 131.6, 130.5, 122.9, 120.5, 118.5, 114.1, 61.7, 60.8, 55.4, 14.4, 13.6, 11.7. ESI/HRMS (m/z): 360.1442 calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>6</sub> [M+H]<sup>+</sup>, found 360.1448. IR (KBr, cm<sup>-1</sup>): v 3272, 1736, 1680, 1649.

Compound **14p**. Colorless crystals, mp 133.1–134.8 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.72 (br. s, 1H), 7.80 (d, J = 8.7 Hz, 2H), 6.91 (d, J = 8.7 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 4.07 (q, J = 7.2 Hz, 2H), 3.86 (s, 3H), 2.25 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  191.9, 163.8, 160.7, 159.7, 131.8, 131.5, 129.1, 127.3, 122.6, 122.4, 113.7, 61.2, 61.0, 55.5, 14.4, 13.6, 10.7. ESI/HRMS (m/z): 360.1442 calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>6</sub> [M+H]<sup>+</sup>, found 360.1449. IR (KBr, cm<sup>-1</sup>): v 3270, 1704, 1649, 1599.

4.2.19. Methyl 2-(5-(4-bromophenyl)-2-ethoxycarbonyl-3-methyl-1H-pyrrol-4-yl)-2-oxoacetate (13q) 5-ethyl 2-methyl 3-(4-bromobenzoyl)-4-methyl-1H-pyrrole-2,5-dicarboxylate (14q). Compound 13q (110.0 mg, 28%) and 14q (87.0 mg, 22%) were obtained from ethyl 3-methyl-2Hazirine-2-carboxylate 7d (130.0 mg, 1.02 mmol) and methyl 4-(4-bromophenyl)-2,4-dioxobutanoate 12c (285.0 mg, 1.0 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (10.0 mg, 50.0 µmol, 5% mol) as catalyst at 75 °C for 60 h. A benzene/ethyl acetate mixture (20/1  $\rightarrow$  10/1) was used as eluent for column chromatography.

Compound **13q**. Colorless crystals, mp 149.9–151.7 °C (hexane/ethyl acetate). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.64 (br. s, 1H), 7.58 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 4.25 (q, J = 7.1 Hz, 2H), 3.38 (s, 3H), 2.58 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  183.1, 164.2, 161.7, 141.2, 131.8, 131.5, 130.7, 129.4, 124.1, 121.1, 118.9, 61.1, 52.2, 14.4, 11.6. ESI/HRMS (m/z): 394.0285 calcd for C<sub>17</sub>H<sub>16</sub>BrNO<sub>5</sub> [M+H]<sup>+</sup>, found 394.0289. IR (KBr, cm<sup>-1</sup>): v 3263, 1745, 1677, 1657. Compound **14q**. Light yellow crystals, mp 139.6–140.1 °C (hexane/ethyl acetate). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.77 (br. s, 1H), 7.68 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H), 3.60 (s, 3H), 2.24 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  192.2, 160.5, 159.8, 137.1, 131.8, 130.8, 128.5, 128.4, 127.4, 122.9, 122.4, 61.2, 52.1, 14.4, 10.8. ESI/HRMS (m/z): 394.0285 calcd for C<sub>17</sub>H<sub>16</sub>BrNO<sub>5</sub> [M+H]<sup>+</sup>, found 394.0291. IR (KBr, cm<sup>-1</sup>): v 3251, 1729, 1702, 1666.

4.2.20. Methyl 2-(2-(3-bromophenyl)-4-(2-bromophenyl)-1H-pyrrol-3-yl)-2-oxoacetate (13r) and methyl 3-(3-bromobenzoyl)-4-(2-bromophenyl)-1H-pyrrole-2-carboxylate (14r). Compounds 13r (66.0 mg, 19%) and 14r (175.0 mg, 49%) were obtained from 3-(2-bromophenyl)-2H-azirine 7e (147.0 mg, 0.75 mmol) and methyl 4-(3-bromophenyl)-2,4-dioxobutanoate 12m (214.0 mg, 0.75 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (7.5 mg, 37.5 µmol, 5% mol) as catalyst at 60 °C for 7.5 h. A benzene/ethyl acetate mixture (100/1  $\rightarrow$  10/1) was used as eluent for column chromatography.

Compound **13r.** Light yellow crystals, mp 168.2–170.1 °C (hexane/chloroform).<sup>1</sup>H NMR (CDCl<sub>3</sub>): 8.74 (br. s, 1H), 7.72 (s, 1H), 7.64 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.51 (d, J = 7.8 Hz, 1H), 7.28–7.34 (m, 3H), 7.15–7.23 (m, 1H), 6.86 (d, J = 2.4 Hz, 1H), 3.30 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  182.2, 164.2, 137.7, 135.0, 133.1, 132.6, 132.3, 132.1, 131.8, 130.1, 129.0, 127.8, 127.0, 126.9, 124.8, 122.5, 119.2, 116.9, 52.0. ESI/HRMS (m/z): 463.9314 calcd for C<sub>19</sub>H<sub>13</sub>Br<sub>2</sub>NO<sub>3</sub> [M+H]<sup>+</sup>, found 463.9318. IR (KBr, cm<sup>-1</sup>): v 3294, 1726, 1654.

Compound **14r.** Light brown glassy solid, mp 65.0–75.0 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>): 9.55 (br. s, 1H), 7.93 (t, J = 1.7 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.56 (dd, J = 7.8, 0.9 Hz, 1H), 7.51 (dd, J = 7.8, 0.9 Hz, 1H), 7.25–7.14 (m, 4H), 7.04 (td, J = 7.6, 1.8 Hz, 1H), 3.64 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  191.8, 160.6, 139.9, 135.7, 133.9, 132.8, 132.3, 132.2, 129.7, 129.0, 128.1, 127.2, 127.0, 125.8, 123.8, 122.6, 122.4, 121.1, 51.9. ESI/HRMS (m/z): 463.9314 calcd for C<sub>19</sub>H<sub>13</sub>Br<sub>2</sub>NO<sub>3</sub> [M+H]<sup>+</sup>, found 463.9323. IR (KBr, cm<sup>-1</sup>): v 3285, 1709, 1659.

4.2.21. Methyl 2-(4-(2-bromophenyl)-2-methyl-1H-pyrrol-3-yl)-2-oxoacetate (**13s**) and methyl 3acetyl-4-(2-bromophenyl)-1H-pyrrole-2-carboxylate (**14s**). Compounds **13s** (67.0 mg, 21%) and **14s** (156.0 mg, 49%) were obtained from 3-(2-bromophenyl)-2H-azirine **7e** (196.0 mg, 1.0 mmol) and methyl 2,4-dioxopentanoate **12l** (143.0 mg, 1.0 mmol) according to procedure *C*, using DCE as a solvent and copper(II) acetate monohydrate (10.0 mg, 50.0  $\mu$ mol, 5% mol) as catalyst at 60 °C for 6 h. A hexane/acetone mixture (5/1) was used as eluent for column chromatography.

Compound **13s**. Light beige crystals, mp 131.0–132.7 °C (hexane/dichloromethane).<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.72 (br. s, 1H), 7.64–7.59 (m, 1H), 7.32–7.24 (m, 2H), 7.16 (ddd, J = 2.2, 6.9, 7.9 Hz,

1H), 6.62 (d, J = 2.3 Hz, 1H), 3.28 (s, 3H), 2.60 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  182.9, 165.1, 139.3, 135.4, 132.5, 128.7, 126.8, 125.4, 124.9, 117.1, 115.8, 52.8, 14.1. ESI/HRMS (m/z): 322.0073 calcd for C<sub>14</sub>H<sub>12</sub>BrNO<sub>3</sub> [M+H]<sup>+</sup>, found 322.0074. IR (KBr, cm<sup>-1</sup>): v 3282, 1745, 1720, 1646. Compound **14s**. Colorless solid, mp 159.6–161.2 °C (hexane/chloroform). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.41 (br. s, 1H), 7.64–7.59 (m, 1H), 7.33–7.27 (m, 2H), 7.21–7.13 (m, 1H), 6.94 (d, J = 3.0 Hz, 1H), 3.89 (s, 3H), 2.41 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  199.4, 160.6, 134.7, 132.7, 132.1, 130.2, 129.0, 127.2, 125.2, 124.1, 121.8, 119.8, 52.0, 31.6. ESI/HRMS (m/z): 322.0073 calcd for C<sub>14</sub>H<sub>12</sub>BrNO<sub>3</sub> [M+H]<sup>+</sup>, found 322.0077. IR (KBr, cm<sup>-1</sup>): v 3188, 1714, 1671.

#### 4.3. Synthesis of 3-heterylpyrrole 23 and fused pyrrole 24

4.3.1. 4-(Naphthalen-1-yl)-2',4'-diphenyl-1H,1'H-[3,3'-bipyrrole]-2,5-dione (23). Compound 23 was synthesized according to published procedure.<sup>12a</sup> A solution of potassium *tert*-butoxide (115 mg, 0.90 mmol) in THF (5 mL) was added dropwise to a solution of ethyl 2-oxo-2-(2,4-diphenyl-1H-pyrrol-3-yl)acetate (13a) (144 mg, 0.45 mmol) and 2-(naphthalene-1-yl)acetamide (56 mg, 0.3 mmol) in THF (10 mL) at 0 ~ -5 °C The reaction was stirred at 0 °C for 0.5 h and then at room temperature overnight. The mixture was cooled down to 0°C and quenched with saturated aqueous NH<sub>4</sub>Cl (8 ml). Water was added to provide full dissolution of the precipitate formed and the mixture was extracted with dichloromethane  $(2 \times 10 \text{ ml})$ . The combined organic extracts were washed with water (10 ml), brine and dried over Na<sub>2</sub>SO<sub>4</sub>. Volatiles were removed *in vacuo* and the residue was subjected to column chromatography on silica with 0.2% methyl alcohol in dichloromethane as eluent to provide the maleimide 23 (34 mg, 26%) that was recrystallized from chloroform/hexane to give deep red crystals, mp 298.8–299.2 °C.<sup>1</sup>H NMR (DMSO-d<sub>6</sub>): 11.55 (br. s, 1H), 11.21 (br. s, 1H), 7.84–7.68 (m, 2H), 7.44–6.90 (m, 15H), 6.68 (s, 1H).  $^{13}$ C NMR (DMSO-d<sub>6</sub>):  $\delta$  171.8, 171.5, 139.4, 139.1, 135.4, 132.7, 132.4, 130.0, 128.9, 128.5, 128.2, 127.8, 127.6, 127.1, 126.7, 126.5, 126.3, 125.6, 125.33, 125.26, 124.6, 117.9, 106.7. ESI/HRMS (m/z): 441.1598 calcd for  $C_{30}H_{20}N_2O_2$  [M+H]<sup>+</sup>, found 441.1610.

4.3.2. 3,4-Diphenyl-1H-pyrrolo[2,3-d]pyridazin-7(6H)-one (24). Compound 24 was obtained analogously to the published procedure.<sup>12c</sup> A solution of the ethyl 3-benzoyl-4-phenylpyrrole-2-carboxylate (14a) (96 mg, 0.30 mmol), hydrazine hydrate (50 mg, 1.0 mmol) and a drop of hydrochloric acid in EtOH (2 mL) was refluxed for 48 h. The precipitate formed after cooling the reaction mixture was filtered off, washed with cold EtOH and dried *in vacuo* to give the title compound 24 (69 mg, 80%) as colourless crystals, dec.  $\geq$  363 °C.<sup>1</sup>H NMR (DMSO-d<sub>6</sub>): 12.97 (br. s, 1H), 12.64 (s, 1H), 7.57 (s, 1H), 7.23–7.16 (m, 1H), 7.16–7.10 (m, 2H), 7.10–7.02 (m, 3H), 6.99 (t, J = 7.5 Hz, 2H), 6.87 (d, J = 7.3 Hz, 2H).<sup>13</sup>C NMR (DMSO-d<sub>6</sub>):  $\delta$  154.6, 144.0, 136.1, 133.6,

129.3, 128.6, 127.8, 127.6, 127.4, 127.3, 126.8, 125.9, 120.3, 119.6. ESI/HRMS (m/z): 288.1131 calcd for  $C_{18}H_{13}N_3O [M+H]^+$ , found 288.1137.

#### 4.4. Calculation details

All calculations were carried out at the DFT B3LYP/6-31G(d) level<sup>26-28</sup> by using the Gaussian 09 suite of quantum chemical programs<sup>29</sup> at Resource center 'Computer center of Saint Petersburg State University'. Geometry optimizations of intermediates, transition states, reactants, and products in toluene were performed using PCM model. Intrinsic reaction coordinates were calculated to authenticate all transition states.

#### Acknowledgments

We gratefully acknowledge the financial support of the Russian Foundation for Basic Research (Grant No. 14-03-00187) and Saint Petersburg State University (Grant No. 12.50.1565.2013, 12.38.239.2014, 12.38.217.2015). This research used resources of the resource center 'Computer Center', 'Research resource center for Magnetic Resonance', 'Center for Chemical Analysis and Material Research', and 'Research resource Center for X-ray Diffraction Studies' of Saint Petersburg State University.

#### Supplementary data

Crystallographic data, <sup>1</sup>H and <sup>13</sup>C NMR spectra for all new compounds. Computational details: energies of molecules, transition states and their Cartesian coordinates of atoms. Supplementary data related to this article can be found online at http://dx.doi.org/.....

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#### ACCEPTED MANUSCRIPT Supporting Information for Tetrahedron

### Simple approach to pyrrole-based 1,2- and 1,4-dicarbonyl building blocks

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#### **X-Ray diffraction experiments**

For the single crystal X-Ray diffraction studies the crystals of the samples **13a** and **14a** were placed on the Agilent Technologies Supernova Atlas diffractometer and measured using micro focused monochromated Cu*Ka* radiation. The **13d** and **14f** samples were fixed on a micro mount and placed on the Agilent Technologies Excalibur Eos diffractometer and measured using monochromated Mo*Ka* radiation. All measurements were performed at 100 K. The structures have been solved by the direct methods by means of the SHELXL–97 program<sup>2</sup> incorporated in the *OLEX2* program package.<sup>3</sup> The carbon-bound H atoms were placed in calculated positions and were included in the refinement in the 'riding' model approximation, with  $U_{iso}(H)$  set to  $1.2U_{eq}(C)$  and C–H 0.97 Å for the CH<sub>2</sub> groups and  $U_{iso}(H)$  set to  $1.5U_{eq}(N)$  and C–H 0.96 Å for the CH<sub>3</sub> groups. Empirical absorption correction was applied in CrysAlisPro<sup>4</sup> program complex using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The crystallographic data for all samples and refinement parameters are given in **Table 1**. Supplementary crystallographic data for this paper have been deposited at Cambridge Crystallographic Data Centre (CCDC 1033500 - 1033503) and can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif.

<b>Tuble I</b> . Crystanographic	auta una remientente	purumeters for the	Jumpies.						
Identification code	<b>14a</b> (1033500)	<b>13a</b> (1033501)	<b>13d</b> (1033502)	<b>14f</b> (1033503)					
Empirical formula	$C_{20}H_{17}NO_3$	$C_{20}H_{17}NO_3$	$C_{20}H_{16}N_2O_5$	$C_{24}H_{17}NO_2$					
Formula weight	319.35	319.35	364.35	351.39					
T(K)	100(2)	100(2)	100(2)	100(2)					
Crystal system	monoclinic	monoclinic	triclinic	monoclinic					
Space group	$P2_1/n$	$P2_1$	<i>P-1</i>	$P2_1/c$					
a(Å)	7.3630(2)	9.911(2)	8.5223(10)	7.9324(3)					
b(Å)	14.2554(5)	7.1103(15)	8.7710(14)	14.2196(5)					
c(Å)	15.3787(5)	11.404(3)	12.1780(15)	15.8241(6)					
α(°)	90.00	90.00	95.236(12)	90.00					
β(°)	95.808(3)	102.57(2)	95.048(10)	102.013(3)					
γ(°)	90.00	90.00	101.813(12)	90.00					
$V(Å^3)$	1605.89(8)	784.4(3)	882.0(2)	1745.81(11)					
Ζ	4	2	2	4					
$D_{calc}(g/cm^3)$	1.321	1.352	1.372	1.337					
$\mu(\text{mm}^{-1})$	0.721	0.738	0.100	0.085					
F(000)	672.0	336.0	380.0	736.0					
Crystal size (mm <sup>3</sup> )	$0.16 \times 0.12 \times 0.08$	0.20  imes 0.16  imes 0.10	$0.27 \times 0.18 \times 0.13$	$0.20 \times 0.15 \times 0.09$					
Radiation	CuKα	CuKα	ΜοΚα	ΜοΚα					
20 range, °	8.48 - 139.94°	9.14 - 144.86°	5.66 - 53.98°	5.26 - 53°					
Index renges	$-8 \le h \le 6, -15 \le k$	$-12 \le h \le 12, -8 \le k$	$-9 \le h \le 10, -11 \le k$	$-9 \le h \le 9, -15 \le k$					
Index ranges	$\leq 17, -18 \leq 1 \leq 16$	$\leq 8, -14 \leq l \leq 14$	$\leq 11, -13 \leq l \leq 15$	$\leq 17, -19 \leq l \leq 19$					
Reflections collected	7379	11125	6890	10338					
Independent reflections	2896	3041	3758	3604					
R <sub>int</sub>	0.0166	0.1497	0.0536	0.0318					
$R_{\sigma}$	0.0166	0.0745	0.0941	0.0457					
Data/restraints/parameters	2896/0/218	3041/1/219	3758/0/245	3604/0/244					
GOOF	1.059	1.129	1.033	0.899					
Final R indexes $[ F_0  \ge$	$R_1 = 0.0329, wR_2 =$	$R_1 = 0.0566, wR_2 =$	$R_1 = 0.0583, wR_2 =$	$R_1 = 0.0435, wR_2$					
$4\sigma_F$	0.0832	0.1385	0.1223	= 0.1211					
	$R_1 = 0.0355, wR_2 =$	$R_1 = 0.0636, wR_2 =$	$R_1 = 0.0922, wR_2 =$	$R_1 = 0.0653, WR_2$					
Final R indexes [all data]	0.0849	0.1607	0.1560	= 0.1387					
$\rho_{\rm min}, \rho_{\rm max} e/{\rm \AA}^{-3}$	0.29, -0.22	0.32, -0.48	0.29, -0.33	0.23, -0.21					
$R_1 = \Sigma   F_0  -  F_c   / \Sigma  F_0 ; wH$	$R_2 = \{ \sum [w(F_0^2 - F_c^2)^2 \}$	$\frac{1}{\Sigma}[w(F_0^2)^2]^{1/2}; w = 1$	$1/[\Sigma^2(F_0^2) + (aP)^2 + bP$	<u>'</u> ],					
where $P = (F_0^2 + 2F_c^2)/3$ :									
$s = \{\Sigma[w(F_0^2 - F_c^2)]/(n-p)\}^{1/2}$ where <i>n</i> is the number of reflections and <i>p</i> is the number of refinement									
$s = \{\Sigma_{l}   n(r_0 - r_c) \} / (n - p) \}$ where <i>n</i> is the number of reflections and <i>p</i> is the number of reflection narrows									
r									

Table 1. Crystallographic data and refinement parameters for the samples.

<sup>&</sup>lt;sup>2</sup> Sheldrick, G. M. Acta Cryst. 2008, A64, 112-122;

<sup>&</sup>lt;sup>3</sup> Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. Appl. Cryst. **2009**, 42, 339-341;

<sup>&</sup>lt;sup>4</sup> CrysAlisPro, Agilent Technologies, Version 1.171.36.20 (release 27-06-2012).

#### ACCEPTED MANUSCRIPT

CCDC 1033500-1033503

Summary of Data CCDC 1033500 Compound Name: ethyl 3-benzoyl-4-phenyl-1H-pyrrole-2-carboxylate (14a) Formula: C<sub>20</sub>H<sub>17</sub>NO<sub>3</sub> Unit Cell Parameters: a 7.36298(19) b 14.2554(5) c 15.3787(5) P2<sub>1/n</sub> Summary of Data CCDC 1033501 Compound Name: ethyl 2-(2,4-diphenyl-1H-pyrrol-3-yl)-2-oxo-acetate (13a) Formula: C<sub>20</sub>H<sub>17</sub>NO<sub>3</sub> Unit Cell Parameters: a 9.911(2) b 7.1103(15) c 11.404(3) P2<sub>1</sub> Summary of Data CCDC 1033502 Compound Name: ethyl 2-((3-nitrophenyl)-4-phenyl-1H-pyrrol-3-yl)-2-oxoacetate (13d) Formula: C<sub>20</sub>H<sub>16</sub>N<sub>2</sub>O<sub>5</sub> Unit Cell Parameters: a 8.5223(10) b 8.7710(14) c 12.1780(15) P-1 Summary of Data CCDC 1033503 Compound Name: (4-phenyl-1H-pyrrole-2,3-diyl)bis(phenylmethanone) (14f) Formula: C<sub>24</sub>H<sub>17</sub>NO<sub>2</sub> Unit Cell Parameters: a 7.9324(3) b 14.2196(5) c 15.8241(6) P2<sub>1/c</sub>

All XRD studies were carried out in the Research center for X-Ray diffraction studies of St.Petersburg State University.

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#### **Computational Details**

All calculations were performed with the B3LYP density functional method<sup>5</sup> by using the Gaussian 09 suite of quantum chemical programs<sup>6</sup> at Resource center "Computer center of Saint Petersburg State University". Geometry optimizations of molecules were performed at the B3LYP/6-31G(d) with PCM solvent model for toluene. **Table 2.** B3LYP/6-31G(d) Absolute Energies (au). Cartesian Coordinates of stationary points

Compound 9					Compound 7a				
$\mathbf{E} = -345\ 80243524\ \mathbf{H}(\mathbf{0K}) = -345\ 679108$				$\mathbf{E} = -36375345506$ <b>H</b> ( <b>0K</b> ) = -363625896					
H = -345.00243524, $H = -345.079100$ , H = -345.670253, $G = -345.712268$ au.					H = -303.73343300, H (0K) = -303.023890, H (298K) = -363.617694 G (298K) = -363.657989.20				
Imaginary frequency = $0$ .					Imaginary frequency = $0.$				
C	-0.0089330	-0.7343310	-0.0000280	C	2.9074780	-0.6246710	-0.0002200		
Č	-1.2473200	0.0077370	-0.0000220	Ň	2.6015440	0.8898250	0.0003860		
Č	1.2000250	-0.0842630	0.0000010	C	1.6347080	0.0725640	-0.0000120		
Ō	1.2890440	1.2428410	0.0000360	Č	0.1866960	0.0284540	-0.0000170		
С	2.5269790	-0.7769900	-0.0000010	С	-0.4743420	-1.2090220	0.0000370		
0	-1.2669060	1.2600420	-0.0000320	С	-1.8673330	-1.2543440	0.0000810		
Н	-0.0304310	-1.8176480	-0.0000510	С	-2.6035380	-0.0668860	0.0000260		
Н	0.3373850	1.5784080	0.0000480	С	-1.9479670	1.1697340	-0.0000690		
Н	2.4130060	-1.8629280	-0.0000330	С	-0.5576200	1.2211660	-0.0001140		
Н	3.1045160	-0.4756080	0.8816940	Η	3.3184700	-1.0371340	-0.9218360		
Н	3.1045400	-0.4755580	-0.8816640	Η	3.3185810	-1.0379370	0.9209730		
С	-2.5516970	-0.7601160	0.0000160	Η	0.1112670	-2.1239820	0.0000670		
Н	-3.3927650	-0.0641570	-0.0005420	Η	-2.3785980	-2.2126690	0.0001330		
Η	-2.6136170	-1.4093820	-0.8816880	Н	-3.6894580	-0.1031510	0.0000300		
Η	-2.6140530	-1.4084100	0.8824120	Н	-2.5241150	2.0906100	-0.0001410		
				Н	-0.0354450	2.1735250	-0.0002010		
TS A					Intermediate <b>B</b>				
<b>E</b> = -	709.51016711, <b>H</b>	( <b>0K</b> ) = -709.2605	94,	E =	-709.57229418. <b>H</b>	(0K) = -709.317	189		
H(298K) = -709.243949, G(298K) = -709.304065 au.						(011) / / / / / / / / / / / / / / / / / /	10,		
	<b>/8K) = -</b> 709.24394	49, <b>G</b> (298K) = -7	09.304065 au.	H (2	<b>298K</b> ) = -709.30065	55, G (298K) = -7	09.361312 au.		
Imagi	<b>/8K)</b> = -709.24394 inary frequency =	49, <b>G</b> ( <b>298K</b> ) = -7 1.	09.304065 au.	H (2 Imag	<b>298K</b> ) = -709.30065 ginary frequency = 0	$55, \mathbf{G} (298\mathbf{K}) = -7$	09.361312 au.		
Imagi C	<b>98K)</b> = -709.24394 inary frequency = -1.4394090	49, <b>G</b> ( <b>298K</b> ) = -7 1. 0.7141320	09.304065 au. 0.7391040	H (2 Imag C	<b>298K</b> ) = -709.30065 ginary frequency = -1.1380000	55, <b>G</b> ( <b>298K</b> ) = -7 0. 0.2437770	09.361312 au. 0.3757130		
Imagi C C	<b>98K)</b> = -709.24394 inary frequency = -1.4394090 -0.6866530	49, <b>G</b> ( <b>298K</b> ) = -7 1. 0.7141320 1.6660690	09.304065 au. 0.7391040 -0.0762470	H (2 Imag C C	<b>298K</b> ) = -709.30065 ginary frequency = -1.1380000 -1.0182080	$\begin{array}{c} \textbf{(5.1)} \\ \textbf{(5.5)}, \textbf{G} (\textbf{298K}) = -7 \\ \textbf{(0.1)} \\ \textbf{(0.2437770)} \\ \textbf{(1.4741260)} \end{array}$	09.361312 au. 0.3757130 -0.5644250		
Imagi C C C	<b>28K)</b> = -709.24394 inary frequency = -1.4394090 -0.6866530 -2.6673130	49, <b>G</b> ( <b>298K</b> ) = -7 1. 0.7141320 1.6660690 0.1446430	09.304065 au. 0.7391040 -0.0762470 0.3228500	H (2 Imag C C C	<b>298K</b> ) = -709.30065 ginary frequency = - -1.1380000 -1.0182080 -2.6082560	$\begin{array}{l} \textbf{(27)} \textbf{(298K)} = -7 \\ \textbf{(298K)} = -7 \\ \textbf{(27)} \textbf{(27)} \{(27)} \textbf{(27)} \\ \textbf{(27)} \textbf{(27)} \{(27)} \textbf{(27)} \\ \textbf{(27)} \textbf{(27)} \{(27)} \textbf{(27)} \\ \textbf{(27)} \textbf{(27)} \textbf{(27)} \\textbf{(27)} \textbf{(27)} \\textbf{(27)} \textbf{(27)} \\textbf{(27)} \textbf{(27)} (2$	09.361312 au. 0.3757130 -0.5644250 0.4244940		
Imagi C C C O	<b>28K)</b> = -709.24394 inary frequency = -1.4394090 -0.6866530 -2.6673130 -2.9629060	49, <b>G</b> ( <b>298K</b> ) = -7 1. 0.7141320 1.6660690 0.1446430 -0.0666910	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990	H (2 Imag C C C O	(298K) = -709.30065 ginary frequency = $(-1.1380000)$ -1.0182080 -2.6082560 -3.1574460	$\begin{array}{l} \textbf{(55, G (298K) = -7)} \\ (55, G (298K$	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780		
Imagi C C C O C	<b>28K)</b> = -709.24394 inary frequency = -1.4394090 -0.6866530 -2.6673130 -2.9629060 -3.6880430	49, <b>G</b> ( <b>298K</b> ) = -7 1. 0.7141320 1.6660690 0.1446430 -0.0666910 -0.2706760	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990 1.3710110	H (2 Imag C C C C O C	<b>298K</b> ) = -709.30065 ginary frequency = - -1.1380000 -1.0182080 -2.6082560 -3.1574460 -3.3363750	$\begin{array}{l} \textbf{(27)}  \textbf{(298K)} = -7 \\ \textbf{(27)} \\ $	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780 1.7340210		
Imagi C C C O C O O	(28K) = -709.24394 inary frequency = -1.4394090 -0.6866530 -2.6673130 -2.9629060 -3.6880430 -0.7484480	49, <b>G</b> ( <b>298K</b> ) = -7 1. 0.7141320 1.6660690 0.1446430 -0.0666910 -0.2706760 1.7395880	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990 1.3710110 -1.3055530	H (2 Imag C C C C O C O C	<b>298K</b> ) = -709.30065 ginary frequency = 1 -1.1380000 -1.0182080 -2.6082560 -3.1574460 -3.3363750 -1.2899570	$\begin{array}{l} \textbf{(21)} & \textbf{(298K)} = -7 \\ \textbf{(20)} & \textbf{(298K)} = -7 \\ \textbf{(20)} & \textbf{(20)} & \textbf{(20)} \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} \\ \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} \\ \textbf{(20)} & (20$	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780 1.7340210 -1.7431030		
Imagi C C C O C O H	(28K) = -709.24394 inary frequency = -1.4394090 -0.6866530 -2.6673130 -2.9629060 -3.6880430 -0.7484480 -1.2689260	49, <b>G</b> ( <b>298K</b> ) = -7 1. 0.7141320 1.6660690 0.1446430 -0.0666910 -0.2706760 1.7395880 0.7711460	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990 1.3710110 -1.3055530 1.8115610	H (2 Imag C C C C O C O C O H	<b>298K</b> ) = -709.30065 ginary frequency = 0 -1.1380000 -1.0182080 -2.6082560 -3.1574460 -3.3363750 -1.2899570 -0.8300620	$\begin{array}{l} \textbf{(27)}  \textbf{(298K)} = -7 \\ \textbf{(27)} \\ $	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780 1.7340210 -1.7431030 1.3820140		
Imagi C C C O C O H H	(1, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2,	49, <b>G</b> ( <b>298K</b> ) = -7 1. 0.7141320 1.6660690 0.1446430 -0.0666910 -0.2706760 1.7395880 0.7711460 -0.7038900	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990 1.3710110 -1.3055530 1.8115610 -1.5013600	H (2 Imag C C C C O C O H H H	<b>298K</b> ) = -709.30065 ginary frequency = 1 -1.1380000 -1.0182080 -2.6082560 -3.1574460 -3.3363750 -1.2899570 -0.8300620 -1.4235260	$\begin{array}{l} \textbf{(21)} & \textbf{(298K)} = -7 \\ \textbf{(20)} & \textbf{(298K)} = -7 \\ \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} \\ \textbf{(20)} & \textbf{(20)} & \textbf{(20)} \\ \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} \\ \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} \\ \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} \\ \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} \\ \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} & \textbf{(20)} \\ \textbf{(20)} & (20$	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780 1.7340210 -1.7431030 1.3820140 -1.6491750		
Imagi C C C O C O H H H H	(1, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2, 2,	49, <b>G</b> ( <b>298K</b> ) = -7 1. 0.7141320 1.6660690 0.1446430 -0.0666910 -0.2706760 1.7395880 0.7711460 -0.7038900 0.4793560	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990 1.3710110 -1.3055530 1.8115610 -1.5013600 1.4052770	H (2 Imag C C C C O C O H H H	$\begin{array}{l} \textbf{298K}) = -709.30065\\ \textbf{ginary frequency} = 1\\ -1.1380000\\ -1.0182080\\ -2.6082560\\ -3.1574460\\ -3.3363750\\ -1.2899570\\ -0.8300620\\ -1.4235260\\ -3.2917490 \end{array}$	$\begin{array}{l} \textbf{(27)} (298 \text{K}) = -7 \\ \textbf{(27)} \\ ($	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780 1.7340210 -1.7431030 1.3820140 -1.6491750 2.0324340		
Imagi C C C O C O H H H H	(28K) = -709.24394 inary frequency = -1.4394090 -0.6866530 -2.6673130 -2.9629060 -3.6880430 -0.7484480 -1.2689260 -1.7520920 -4.4884420 -3.2561750	49, <b>G</b> ( <b>298K</b> ) = -7 1. 0.7141320 1.6660690 0.1446430 -0.0666910 -0.2706760 1.7395880 0.7711460 -0.7038900 0.4793560 -0.3470240	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990 1.3710110 -1.3055530 1.8115610 -1.5013600 1.4052770 2.3732360	H (2 Imag C C C C O C O H H H H	$\begin{array}{l} \textbf{298K}) = -709.30065\\ \textbf{ginary frequency} = 0\\ -1.1380000\\ -1.0182080\\ -2.6082560\\ -3.1574460\\ -3.3363750\\ -1.2899570\\ -0.8300620\\ -1.4235260\\ -3.2917490\\ -2.8489210 \end{array}$	$\begin{array}{l} \textbf{(27)} (298 \text{K}) = -7 \\ \textbf{(27)} \\ ($	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780 1.7340210 -1.7431030 1.3820140 -1.6491750 2.0324340 2.5309710		
Imagi C C C O C O H H H H H H	P(K) = -709.24394 inary frequency = -1.4394090 -0.6866530 -2.6673130 -2.9629060 -3.6880430 -0.7484480 -1.2689260 -1.7520920 -4.4884420 -3.2561750 -4.1510640	<pre>49, G (298K) = -7 1.</pre>	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990 1.3710110 -1.3055530 1.8115610 -1.5013600 1.4052770 2.3732360 1.0918340	H (2 Imag C C C C O C O H H H H H H	$\mathbf{298K}) = -709.30065$ ginary frequency = 1.1380000 -1.0182080 -2.6082560 -3.1574460 -3.3363750 -1.2899570 -0.8300620 -1.4235260 -3.2917490 -2.8489210 -4.3780470	$\begin{array}{l} \textbf{(2)}\\ \textbf{(2)}\\$	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780 1.7340210 -1.7431030 1.3820140 -1.6491750 2.0324340 2.5309710 1.6383230		
Imagi C C C O C O H H H H H C	(120) = -709.24394 inary frequency = -1.4394090 -0.6866530 -2.6673130 -2.9629060 -3.6880430 -0.7484480 -1.2689260 -1.7520920 -4.4884420 -3.2561750 -4.1510640 0.2083720	$\begin{array}{l} \textbf{49, G (298K) = -7} \\ \textbf{1.} \\ \textbf{0.7141320} \\ \textbf{1.6660690} \\ \textbf{0.1446430} \\ \textbf{-0.0666910} \\ \textbf{-0.2706760} \\ \textbf{1.7395880} \\ \textbf{0.7711460} \\ \textbf{-0.7038900} \\ \textbf{0.4793560} \\ \textbf{-0.3470240} \\ \textbf{-1.2228050} \\ \textbf{2.6246650} \end{array}$	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990 1.3710110 -1.3055530 1.8115610 -1.5013600 1.4052770 2.3732360 1.0918340 0.7045770	H (2 Imag C C C C C O C O H H H H H H H C	$\begin{array}{l} \textbf{298K}) = -709.30065\\ \textbf{ginary frequency} = 0\\ -1.1380000\\ -1.0182080\\ -2.6082560\\ -3.1574460\\ -3.3363750\\ -1.2899570\\ -0.8300620\\ -1.4235260\\ -3.2917490\\ -2.8489210\\ -4.3780470\\ -0.5420080 \end{array}$	$\begin{array}{l} \textbf{(2)} \textbf{(2)} \textbf{(3)} \textbf{(2)} \textbf{(3)} $	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780 1.7340210 -1.7431030 1.3820140 -1.6491750 2.0324340 2.5309710 1.6383230 0.0658240		
Imagi C C C O C O H H H H H H H H H H H H	(12) (1) $(26)$ (2)	$\begin{array}{l} \textbf{49, G (298K) = -7} \\ \textbf{1.} \\ \textbf{0.7141320} \\ \textbf{1.6660690} \\ \textbf{0.1446430} \\ \textbf{-0.0666910} \\ \textbf{-0.2706760} \\ \textbf{1.7395880} \\ \textbf{0.7711460} \\ \textbf{-0.7038900} \\ \textbf{0.4793560} \\ \textbf{-0.3470240} \\ \textbf{-1.2228050} \\ \textbf{2.6246650} \\ \textbf{3.2292840} \end{array}$	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990 1.3710110 -1.3055530 1.8115610 -1.5013600 1.4052770 2.3732360 1.0918340 0.7045770 0.0083140	H (2 Imag C C C C O C O C O H H H H H H H H H H C H	$\begin{array}{l} \textbf{298K}) = -709.30065\\ \textbf{ginary frequency} = 0\\ -1.1380000\\ -1.0182080\\ -2.6082560\\ -3.1574460\\ -3.3363750\\ -1.2899570\\ -0.8300620\\ -1.4235260\\ -3.2917490\\ -2.8489210\\ -4.3780470\\ -0.5420080\\ -0.5015960 \end{array}$	$\begin{array}{l} (55, \mathbf{G} \ (\mathbf{298K}) = -7 \\ 0. \\ 0.2437770 \\ 1.4741260 \\ -0.1947880 \\ -0.6796530 \\ 0.0150240 \\ 1.3766600 \\ 0.5432490 \\ -1.3321140 \\ 1.0700230 \\ -0.5607310 \\ -0.2970760 \\ 2.7637440 \\ 3.5553860 \end{array}$	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780 1.7340210 -1.7431030 1.3820140 -1.6491750 2.0324340 2.5309710 1.6383230 0.0658240 -0.6847870		
Imagi C C C O C O H H H H H H H H H H H H	(1, 2, 3, 3, 2, 3, 3, 2, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3, 3,	$\begin{array}{l} \textbf{49, G (298K) = -7} \\ \textbf{1.} \\ \textbf{0.7141320} \\ \textbf{1.6660690} \\ \textbf{0.1446430} \\ \textbf{-0.0666910} \\ \textbf{-0.2706760} \\ \textbf{1.7395880} \\ \textbf{0.7711460} \\ \textbf{-0.7038900} \\ \textbf{0.4793560} \\ \textbf{-0.3470240} \\ \textbf{-1.2228050} \\ \textbf{2.6246650} \\ \textbf{3.2292840} \\ \textbf{3.2871100} \end{array}$	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990 1.3710110 -1.3055530 1.8115610 -1.5013600 1.4052770 2.3732360 1.0918340 0.7045770 0.0083140 1.3350900	H (2 Imag C C C C C C O C O H H H H H H H H H H H	<b>298K</b> ) = -709.30065 ginary frequency = 1 -1.1380000 -1.0182080 -2.6082560 -3.1574460 -3.3363750 -1.2899570 -0.8300620 -1.4235260 -3.2917490 -2.8489210 -4.3780470 -0.5420080 -0.5015960 -1.2114820	$\begin{array}{l} (5), \mathbf{G} \left( \mathbf{298K} \right) = -7 \\ 0, \\ 0.2437770 \\ 1.4741260 \\ -0.1947880 \\ -0.6796530 \\ 0.0150240 \\ 1.3766600 \\ 0.5432490 \\ -1.3321140 \\ 1.0700230 \\ -0.5607310 \\ -0.2970760 \\ 2.7637440 \\ 3.5553860 \\ 3.0607880 \end{array}$	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780 1.7340210 -1.7431030 1.3820140 -1.6491750 2.0324340 2.5309710 1.6383230 0.0658240 -0.6847870 0.8832140		
Imagi C C C O C O H H H H H H H H H H H	(12) (1) $(26)$ (2)	$\begin{array}{l} \textbf{49, G (298K) = -7} \\ \textbf{1.} \\ \textbf{0.7141320} \\ \textbf{1.6660690} \\ \textbf{0.1446430} \\ \textbf{-0.0666910} \\ \textbf{-0.2706760} \\ \textbf{1.7395880} \\ \textbf{0.7711460} \\ \textbf{-0.7038900} \\ \textbf{0.4793560} \\ \textbf{-0.3470240} \\ \textbf{-1.2228050} \\ \textbf{2.6246650} \\ \textbf{3.2292840} \\ \textbf{3.2871100} \\ \textbf{2.0743000} \end{array}$	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990 1.3710110 -1.3055530 1.8115610 -1.5013600 1.4052770 2.3732360 1.0918340 0.7045770 0.0083140 1.3350900 1.3711050	H (2 Imag C C C C C C C C C C C C C C C C C C C	$\begin{array}{l} \textbf{298K}) = -709.30065\\ \textbf{ginary frequency} = 1\\ -1.1380000\\ -1.0182080\\ -2.6082560\\ -3.1574460\\ -3.3363750\\ -1.2899570\\ -0.8300620\\ -1.4235260\\ -3.2917490\\ -2.8489210\\ -4.3780470\\ -0.5420080\\ -0.5015960\\ -1.2114820\\ 0.4522740\\ \end{array}$	$\begin{array}{l} (55, \mathbf{G} \ (\mathbf{298K}) = -7 \\ 0. \\ 0.2437770 \\ 1.4741260 \\ -0.1947880 \\ -0.6796530 \\ 0.0150240 \\ 1.3766600 \\ 0.5432490 \\ -1.3321140 \\ 1.0700230 \\ -0.5607310 \\ -0.2970760 \\ 2.7637440 \\ 3.5553860 \\ 3.0607880 \\ 2.6155940 \end{array}$	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780 1.7340210 -1.7431030 1.3820140 -1.6491750 2.0324340 2.5309710 1.6383230 0.0658240 -0.6847870 0.8832140 0.5048840		
Imagi C C C O C O H H H H H H H H H C H H H C	(12) (1) $(12)$ (1)	$\begin{array}{l} \textbf{49, G (298K) = -7} \\ \textbf{1.} \\ \textbf{0.7141320} \\ \textbf{1.6660690} \\ \textbf{0.1446430} \\ \textbf{-0.0666910} \\ \textbf{-0.2706760} \\ \textbf{1.7395880} \\ \textbf{0.7711460} \\ \textbf{-0.7038900} \\ \textbf{0.4793560} \\ \textbf{-0.3470240} \\ \textbf{-1.2228050} \\ \textbf{2.6246650} \\ \textbf{3.2292840} \\ \textbf{3.2871100} \\ \textbf{2.0743000} \\ \textbf{-2.3603440} \end{array}$	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990 1.3710110 -1.3055530 1.8115610 -1.5013600 1.4052770 2.3732360 1.0918340 0.7045770 0.0083140 1.3350900 1.3711050 -0.2347690	H (2 Imag C C C C C C C O C O C O C O H H H H H H	$\begin{array}{l} \textbf{298K}) = -709.30065\\ \textbf{ginary frequency} = 1\\ -1.1380000\\ -1.0182080\\ -2.6082560\\ -3.1574460\\ -3.3363750\\ -1.2899570\\ -0.8300620\\ -1.4235260\\ -3.2917490\\ -2.8489210\\ -4.3780470\\ -0.5420080\\ -0.5015960\\ -1.2114820\\ 0.4522740\\ -0.5598580 \end{array}$	$\begin{array}{l} (55, \mathbf{G} \ (\mathbf{298K}) = -7 \\ 0. \\ 0.2437770 \\ 1.4741260 \\ -0.1947880 \\ -0.6796530 \\ 0.0150240 \\ 1.3766600 \\ 0.5432490 \\ -1.3321140 \\ 1.0700230 \\ -0.5607310 \\ -0.2970760 \\ 2.7637440 \\ 3.5553860 \\ 3.0607880 \\ 2.6155940 \\ -2.2997580 \end{array}$	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780 1.7340210 -1.7431030 1.3820140 -1.6491750 2.0324340 2.5309710 1.6383230 0.0658240 -0.6847870 0.8832140 0.5048840 -0.0566400		
Imagi C C C C C C C C C C C C C C C C C C C	(10, 10, 10, 10, 10, 10, 10, 10, 10, 10,	$\begin{array}{l} \textbf{49, G (298K) = -7} \\ \textbf{1.} \\ 0.7141320 \\ 1.6660690 \\ 0.1446430 \\ -0.0666910 \\ -0.2706760 \\ 1.7395880 \\ 0.7711460 \\ -0.7038900 \\ 0.4793560 \\ -0.3470240 \\ -1.228050 \\ 2.6246650 \\ 3.2292840 \\ 3.2871100 \\ 2.0743000 \\ -2.3603440 \\ -1.2260350 \end{array}$	09.304065 au. 0.7391040 -0.0762470 0.3228500 -0.8931990 1.3710110 -1.3055530 1.8115610 -1.5013600 1.4052770 2.3732360 1.0918340 0.7045770 0.0083140 1.3350900 1.3711050 -0.2347690 -0.3692280	H (2 Imag C C C C C C C O C O C O H H H H H H H C C C C	$\begin{array}{l} \textbf{298K}) = -709.30065\\ \textbf{ginary frequency} = 1\\ -1.1380000\\ -1.0182080\\ -2.6082560\\ -3.1574460\\ -3.3363750\\ -1.2899570\\ -0.8300620\\ -1.4235260\\ -3.2917490\\ -2.8489210\\ -4.3780470\\ -0.5420080\\ -0.5015960\\ -1.2114820\\ 0.4522740\\ -0.5598580\\ -0.1660720\\ \end{array}$	$\begin{array}{l} (5), \mathbf{G} \left( \mathbf{298K} \right) = -7 \\ 0, \\ 0.2437770 \\ 1.4741260 \\ -0.1947880 \\ -0.6796530 \\ 0.0150240 \\ 1.3766600 \\ 0.5432490 \\ -1.3321140 \\ 1.0700230 \\ -0.5607310 \\ -0.2970760 \\ 2.7637440 \\ 3.5553860 \\ 3.0607880 \\ 2.6155940 \\ -2.2997580 \\ -0.8579110 \\ \end{array}$	09.361312 au. 0.3757130 -0.5644250 0.4244940 -0.5499780 1.7340210 -1.7431030 1.3820140 -1.6491750 2.0324340 2.5309710 1.6383230 0.0658240 -0.6847870 0.8832140 0.5048840 -0.0566400 -0.1197800		

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<sup>6</sup> Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G.W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ő.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc.; Wallingford CT, **2013**.

			σάτει μαν	II ISO	<b>TDIDT</b>		
С	1.2607630	-0.7482630	-0.1214410	$\mathbf{C}$	1.2866220	-0.4819260	0.0586440
Ċ	1 9268620	1 1346760	1.0574030	Ĉ	1 8287520	0.3125200	1 3/1/150
C	2.2269760	-1.13+0700	1.0074030		1.0207520	-0.5125270	1.5414150
C	3.2368/60	-0.7250150	1.2805170	C	3.1000500	0.04/2580	1.5064080
С	3.8927150	0.0653110	0.3296880	C	3.9817560	0.2429680	0.3883970
С	3.2370080	0.4465760	-0.8454450	С	3.4506120	0.0721300	-0.8912570
С	1.9245130	0.0466000	-1.0772740	С	2.1116480	-0.2892370	-1.0554210
н	-1 8275990	-2 2739420	0 4462860	н	-1 5392130	-2 5674870	0 3334020
11	0.6590570	2.2737420	0.4402000	11	0.2145210	2.0455010	0.1092040
п	-0.0389370	-5.5752750	-0.4629570	п	0.2145510	-5.0455010	0.1085040
н	1.40/5450	-1.7521450	1./845630	н	1.2056700	-0.4778820	2.2180520
Н	3.7509850	-1.0240800	2.1891670	Н	3.5741920	0.1678220	2.5068090
Η	4.9180010	0.3797730	0.5032440	Н	5.0244490	0.5215550	0.5156260
Н	3.7524810	1.0543560	-1.5831380	н	4.0794690	0.2184910	-1.7656290
н	1 4026880	0 3372070	-1 9816370	н	1 6917840	-0.4399170	-2 0444120
11	1.4020000	TC D C	1.7010570	11	1.07170+0	0.4377170	2.0444120
		13 <b>D-C</b>			1110	ermediate C	
$\mathbf{E} = -$	709.54244908, <b>H</b>	(0K) = -709.2901	53,	$\mathbf{E} = \mathbf{E}$	-709.56651995, <b>H</b>	( <b>0K</b> ) = -709.3119	47,
H (2	98K) = -709.2734	69, G (298K) = -7	09.334856 au.	H (2	<b>98K</b> ) = -709.29526	66, G (298K) = -7	'09.356606 au.
Imag	inary frequency =	1.		Imag	pinary frequency =	0.	
C	-1 1167230	0 1067080	0.4002120	C	_1 1171800	0.0587960	0 3871040
C	1.2400020	1 5025570	0.4002120	C	1.2262000	1 5775140	0.2277510
C	-1.2499030	1.3933370	0.0099070	C	-1.3302090	1.3773140	0.2277310
C	-2.4848470	-0.5796600	0.3295490	C	-2.4471810	-0.7108790	0.2970730
0	-3.2750730	-0.3054290	-0.5563150	0	-3.3523590	-0.3326200	-0.4222660
С	-2.8015190	-1.5979880	1.4079470	С	-2.5700120	-1.9510080	1.1608250
0	-0.7158960	2.0461270	-0.9833850	0	-0.6989390	2.2430400	-0.5638950
Н	-0 7694700	0.0648080	1 4398290	н	-0.7283050	-0.0919540	1 4046800
ц	0.7094700	0.0040000	2 7388100	ц	0.11205050	0.0717340	2 5670880
11	-0.4643910	-0.2737130	-2.7366100		0.4110040	-0.1404220	-2.3070880
H	-2.9988190	-1.0/338/0	2.3527420	н	-2./123/10	-1.6435180	2.2057830
Н	-1.9556150	-2.2706160	1.5860380	Н	-1.6592270	-2.5582370	1.1278450
Н	-3.6883810	-2.1723800	1.1316630	H	-3.4321310	-2.5435720	0.8473330
С	-2.0723760	2.4620320	0.9420020	C	-2.3685890	2.2128760	1.1404050
Н	-2.0500670	3.4975420	0.5969050	H	-2.2047160	3.2917650	1.1795950
н	-3 1107020	2 1110480	0 9653800	н	-3 3678260	2.0190230	07348310
н	-1 683/11/0	2 4061110	1 9660280	н	-23345140	1 7908740	2 1513890
	0.2741040	1.0620500	1.1704720	C	0.2125420	1.7700740	1 4204220
	-0.5/41940	-1.9029300	-1.1704730	C	-0.5125450	-1./123/10	-1.4304320
C	-0.0688580	-0.591/810	-0.5136570	C	-0.0588370	-0.490/800	-0.5969290
Ν	-0.3811190	-0.7458240	-1.860/580	Ν	-0.4158330	-0.3/14430	-2.0148280
С	1.3659690	-0.3175160	-0.1000710	C	1.3732780	-0.2583030	-0.1673530
С	1.8269340	-0.6554530	1.1805050	С	1.9950280	-1.1641170	0.7045160
С	3.1502370	-0.4126120	1.5501600	С	3.3140200	-0.9695430	1.1155450
С	4.0336370	0.1780980	0.6433640	С	4.0333370	0.1356700	0.6546450
Ċ	3 5839840	0 5174110	-0.6338680	Ċ	3 4230380	1 0435450	-0 2124580
C	2 2600300	0.2605360	1 0013400	C	2 1000810	0.8510100	0.6172360
	1.2000300	2 4616070	-1.0013400		1.2522220	2 25 ( ( 400	-0.0172300
п	-1.5254990	-2.4010070	-0.930/4/0	п	-1.2322520	-2.2300490	-1.5728180
H	0.46/6310	-2.6525580	-1.2935660	Н	0.5505400	-2.3313420	-1.6680910
Н	1.1531010	-1.1276250	1.8927200	Н	1.4434970	-2.0340440	1.0543470
Н	3.4926020	-0.6890320	2.5441270	Н	3.7821840	-1.6845860	1.7869720
Н	5.0639830	0.3702600	0.9305880	Н	5.0626010	0.2867960	0.9688030
Н	4.2631440	0.9794980	-1.3457510	Н	3.9748730	1.9076970	-0.5728710
н	1 9074560	0 5305330	-1 9940210	н	1 6175680	1 5730390	-1 2683640
	11/07/10/00		100010		Int	ermediate <b>D</b>	1.20000.0
		15 <b>C-D</b>			1110		
Б	700 56262046 H	( <b>0IZ</b> ) 700 2001	50	Б	700 57010457 II	$(0\mathbf{V})$ 700 2172	20
E = -	·/09.30303940, <b>H</b>	$(\mathbf{0K}) = -709.3091$	50,	$\mathbf{E} = \mathbf{E}$	-/09.5/21045/, <b>H</b>	$(\mathbf{0K}) = -709.3173$	20,
<b>H</b> (2)	<b>98K</b> ) = -709.29320	$00, \mathbf{G} (\mathbf{298K}) = -7$	09.353416 au.	H (2	(98K) = -7/09.3007	(26, G(298K)) = -	709.361197 au.
Imag	inary frequency =	1.		Imag	ginary frequency =	0.	
С	-1.3374780	0.2537860	-0.5187090	С	1.4826140	0.0823990	0.2950750
С	-2.6399660	-0.1232310	0.2231190	С	1.8775390	-1.2753190	-0.309367
С	-0.8192640	1.6039300	0.0115660	С	1.4237290	1.2137780	-0.745631
õ	-0 5302070	1 7635340	1 1835390	Ő	1 1452990	0 9916860	-1 910293
Ċ	0.725/150	2 7220020	1 0010520		1 7120270	2 6076110	0 221047
	-0.7234130	2.1227030	-1.0019320		1./1525/0	2.0070440	-0.23190/
0	-3.6/49200	-0.2313/10	-0.4082630		1.2/40320	-2.2965200	-0.035536
Н	-1.6280850	0.3697090	-1.5651270	Н	2.2799120	0.3386300	1.0084100
Η	0.4582220	-2.1891090	-1.8972250	Η	-0.7034690	1.2604980	2.5200450
		$\Delta CCI$	έρτερ μαν	$\mathbb{N}$	<u>'RTPT'</u>		
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Η	-1.7064520	2.8972060	-1.4617050	H	2.7976390	2.7131640	-0.089181
Н	-0.0409660	2.4406650	-1.8115490	Н	1.2505260	2.7704220	0.7470480
Н	-0.3712790	3.6367850	-0.5211100	Н	1.3794760	3.3535070	-0.956576
C	-2 5995510	-0 3245450	1 7240480	C	3 0956130	-1 2988520	-1 210058
н	-2 5714880	0.6537130	2 2159410	н	3 4614080	-2 3236460	-1 301175
и П	2.00000	0.0557150	2.2137410	и П	2 8087000	-2.5250+00	2 100076
	-3.4988820	-0.8389910	2.0378970	11 11	2.8087090	-0.9277710	-2.133370
п	-1.7020110	-0.8000400	2.0449550	п	0.0716450	-0.0400100	-0.034390
	-0.0940080	-2.2973830	-0.2012940	C	0.2710430	-0.3444220	2.4884280
C	-0.2694190	-0.8899850	-0.4/61930		0.1800/80	0.0346530	1.1219590
N	-0.4540660	-1.8565420	-1.5816/40	N	0.2365060	0.9203450	2.3129960
С	1.1513670	-0.5109600	-0.1372440	С	-1.1305770	-0.0598320	0.3774230
С	1.6625070	-0.6709670	1.1566140	С	-1.6879420	-1.3013500	0.0408120
C	2.9800680	-0.3163460	1.4491300	C	-2.9082450	-1.3698800	-0.632746
C	3.8044770	0.2066130	0.4505840	C	-3.5885050	-0.2011080	-0.981398
С	3.3048160	0.3726560	-0.8425130	С	-3.0412680	1.0400000	-0.652768
С	1.9865580	0.0173080	-1.1331040	С	-1.8207910	1.1079790	0.0210390
Н	-1.7329940	-2.5272150	0.0260660	Н	1.2180780	-0.9466030	2.8421380
Н	0.0262460	-2.9604090	0.2736270	Н	-0.6099440	-1.0416680	2.8858090
Н	1.0243310	-1.0726610	1.9385080	Н	-1.1513910	-2.2069640	0.3005860
н	3.3622100	-0.4481300	2,4577350	н	-3.3289230	-2.3399500	-0.884210
н	4 8308090	0 4811700	0.6782940	н	-4 5391540	-0.2573720	-1 504928
н	3 9409520	0.7746700	-1 6264690	н	-3 5621760	1 9556860	-0.919370
н	1 6052770	0.1396510	-2 1446250	н	-1 4055720	2 0801940	0.2766210
11	1.0032770	TS D F	-2.1440230	11	-1.4033720	2.0001940	0.2700210
		15 <b>D-E</b>					
E /	700 50310030 II	(017) 700 2522	01		700 505 (0210 H	$(0\mathbf{V})$ 700 2211	25
E = -	709.50218029, <b>H</b>	$(\mathbf{0K}) = -709.2523$	91, 	$\mathbf{E} = \mathbf{E}$	-709.58568318, <b>H</b>	$(\mathbf{0K}) = -709.3311$	35,
H (29	(98K) = -709.23619	98, G (298K) = -7	09.295749 au.	H (2	<b>98K</b> ) = -709.31386	68, G(298K) = -7	09.375786 au.
Imagi	inary frequency =	1.		Imag	ginary frequency =	0.	
С	1.3791320	0.1282820	0.1818170	C	1.2908950	0.0744450	0.0391610
С	2.1881230	-1.0006530	-0.333441	C	2.7190910	-0.3753180	-0.008749
С	1.5020410	1.4694170	-0.432118	C	1.0618100	1.5725990	0.1235620
0	2.4586680	1.7965650	-1.136359	0	1.4241630	2.3074400	-0.782498
С	0.4269970	2.5148000	-0.137829	С	0.4883840	2.1299230	1.4120580
0	1.7194700	-2.1433720	-0.374020	0	3.0208320	-1.5650640	0.0129190
Н	1.4570640	0.5444600	1.6399370	Н	-0.6222240	-4.0409130	-0.204490
Н	-0.3413090	0.7147000	2.8437880	Н	-1.3259260	-2.8392560	-1.046373
Н	0.1751200	2.5762500	0.9270000	Н	-0.3795070	1.5613100	1.7549700
н	-0.4981380	2.2816660	-0.676281	н	0.2255710	3,1815860	1.2764610
Н	0 7978990	3 4846750	-0.475602	H	1 2559820	2.0540440	2 1949910
C	3 6165640	-0.7638860	-0.785822	C	3 8143940	0.6753830	-0.073854
ч	1 1153650	1 7322770	0.703022	ц	1 7806780	0.1601040	0.073034
ц	3 617/000	-0.2488020	-0.070120	ц	3 7785250	1 2650570	-0.041403
	J.01/4070 1 1615220	0.1127450	-1.751102	и П	27/200000	1.2037370	-0.2200/1
	4.1013320	-0.113/430	-0.0930/0	п	J./4J8900	1.3010/00	0.7027750
	0.2751980	-1.1803930	2.013/810		0.4202870	-2.3030390	-0.106/69
	0.0637000	-0.2754740	0.8512/30		0.23/1450	-0./936010	-0.013192
N ~	0.3589890	0.2679370	2.24/9610	N	-0.8426310	-3.0468430	-0.173329
C	-1.2918280	-0.2040750	0.2214160	C	-1.1546210	-0.2573100	-0.060362
C	-1.4648920	-0.8462910	-1.014116	C	-1.5316400	0.6438740	-1.070726
C	-2.7119370	-0.8474450	-1.636918	C	-2.8269290	1.1643110	-1.114682
С	-3.8011230	-0.2097770	-1.037172	С	-3.7599330	0.8001300	-0.144423
С	-3.6350510	0.4282910	0.1921790	С	-3.3971270	-0.0992620	0.8632350
С	-2.3867080	0.4312040	0.8185480	С	-2.1126220	-0.6375550	0.8982420
Н	1.2023820	-1.7348100	2.1288980	Н	0.9734940	-2.6520150	0.7727860
Н	-0.6116700	-1.6598000	2.4226540	Н	1.1020670	-2.4996320	-0.949684
Н	-0.6204250	-1.3572590	-1.466560	Н	-0.8093350	0.9298040	-1.828800
н	-2.8327270	-1 3501010	-2 592491	н	-3 1012220	1 8552320	-1 907023
н	-4 7716710	-0 2103100	-1 5252721	н	-4 7661150	1 200/670	_0 173001
ц	_1 /7/0220	0.2103100	-1.525200 0 6661390	н	_/ 1207060	_0 388/070	1 6205060
ц	- <del></del>	0.7502450	1 7607/20	и Ц	1 8/15220	1 2502200	1 6670000
п	-2.2701200	0.9400890	1./09/420	п	-1.0413320	-1.3302290	1.00/9900
	Cor	npound 7 <b>a-H</b>				15 F	
_			4.0	_			
<b>E</b> = -364.15193470, <b>H</b> ( <b>0K</b> ) = -364.012040,				<b>E</b> = -709.94535725, <b>H</b> ( <b>0K</b> ) = -709.679757,			

TT (2)	0017) 26400224	$57 C (200 V) \sim 2$	CA 044521 au	1 11 73	(0017) 700 ((24)	24 C (200 V) 7	00 722091
H (2)	(30K) = -304.00333	57, G(298K) = -3	64.044521 au.	H (2	98K) = -709.0034	34, G(298K) = -7	09.722081 au.
Imag	inary frequency =	0.		Imag	inary frequency =	1.	
С	-2.8457990	-0.7076120	0.0008990	C	1.2251690	0.1797820	-0.831652
С	-1.5465450	0.0241480	-0.0002560	С	1.7247590	1.5025820	-0.428977
С	-0.1349440	0.0221710	-0.0001110	С	2.0947600	-0.9275600	-0.740252
С	0.5348480	-1.2236510	-0.0002450	0	3.1725570	-0.8719370	-0.013796
С	1.9219950	-1.2498540	-0.0002460	С	1.8233660	-2.2475670	-1.368180
С	2.6383620	-0.0467930	0.0000840	0	2,7253330	1.5966310	0.3064430
C	1 9787970	1 1918850	0.0003390	н	0.4459320	0.1333520	-1 581931
C	0.5944110	1.1710050	0.0003570	ц	3 2723050	0.1999920	0.3055810
	2 2100070	1.2303050	0.0001010		0.0521600	0.0900470	0.3033810
п	-3.2109070	-1.1380030	0.9299040	п	0.9321000	-2.2100210	-2.025817
H	-3.2116690	-1.1406320	-0.9269430	H	1.6613420	-2.9840830	-0.5/0149
Н	-0.0401530	-2.1443890	-0.0004730	Н	2.7029180	-2.5744330	-1.932868
Н	2.4488270	-2.1978790	-0.0004800	С	1.0242730	2.7314990	-0.936354
Н	3.7238840	-0.0716510	0.0002000	Η	1.3044470	3.5987990	-0.335956
Н	2.5523490	2.1125260	0.0006420	Η	1.3349580	2.9102330	-1.974508
Н	0.0722160	2.1882980	0.0003000	Η	-0.0624390	2.6022460	-0.946888
Ν	-2.5980580	0.7471910	-0.0008980	С	0.6017550	-0.0188720	2.1843480
Н	-2.9948930	1.6820940	-0.0006720	С	-0.1025570	-0.3783490	0.9462550
				C	-1 4248510	-0 2033180	0 3897300
				C	-2.0562040	1.0528750	0.4844390
				C	3 3531100	1 2120340	0.4044320
				C	-5.5551100	0.12120340	0.0070700
					-4.01/3000	0.1515050	-0.582309
				C	-3.3913590	-1.1166/60	-0.68/295
				C	-2.099/480	-1.2888410	-0.204350
				H	-0.0166210	0.2641110	3.0347240
				H	1.6103800	0.3790860	2.1726050
				Η	-1.5381890	1.8836090	0.9536700
				H	-3.8478820	2.1738730	0.0950520
				Н	-5.0278560	0.2600330	-0.958063
				н	-3.9155210	-1.9519870	-1.140376
				1 TT	1 (122240	2 2572120	0.280456
					-1 01 1 1 140	-7.7177100	-1//01411
				п	-1.0155540	-2.23/2150	-0.280430
				п N ц	-1.0135340 0.4802810 0.1010020	-2.2372130 -1.3949550 2.1168500	1.6280090
	L	torma lista C	Y	н N H	-1.6133340 0.4802810 -0.1010020	-2.2372130 -1.3949550 -2.1168590	1.6280090 2.0516590
	In	termediate G		N H	-1.6133340 0.4802810 -0.1010020	-2.2372130 -1.3949550 -2.1168590 TS G-H	1.6280090 2.0516590
	In	termediate G		N H	-1.0133340 0.4802810 -0.1010020	-2.2372130 -1.3949550 -2.1168590 TS <b>G-H</b>	-0.280430 1.6280090 2.0516590
<b>E</b> = -	In 709.96835499, <b>H</b>	termediate <b>G</b> ( <b>0K</b> ) = -709.7011	68,	н N H	-1.0133340 0.4802810 -0.1010020	-2.2372130 -1.3949550 -2.1168590 TS G-H (0K) = -709.7007	-0.280430 1.6280090 2.0516590
E = - H (29	In 709.96835499, <b>H</b> <b>98K</b> ) = -709.68490	termediate <b>G</b> ( <b>0K</b> ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7	68, 09.744094 au.	H H E = - H (2	-1.0133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854	-2.2372130 -1.3949550 -2.1168590 TS G-H (0K) = -709.7007 46, G (298K) = -7	-0.280430 1.6280090 2.0516590 70, 09.741829 au.
E = - H (29 Imag	In 709.96835499, <b>H</b> <b>98K</b> ) = -709.68490 inary frequency =	termediate <b>G</b> ( <b>0K</b> ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0.	68, 09.744094 au.	H H E = - H (2) Imag	-1.0133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854 ;inary frequency =	-2.2372130 -1.3949550 -2.1168590 TS G-H (0K) = -709.7007 46, G (298K) = -7 1.	-0.280430 1.6280090 2.0516590 70, 09.741829 au.
E = - H (29 Imag C	In 709.96835499, <b>H</b> <b>98K</b> ) = -709.68490 inary frequency = 1.0988710	termediate <b>G</b> ( <b>0K</b> ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190	68, 09.744094 au. -0.576553	н N H E = - H (2 Imag C	-1.0133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854 tinary frequency = 1.0927470	-2.2372130 -1.3949550 -2.1168590 TS G-H (0K) = -709.7007 46, G (298K) = -7 1. 0.1126580	-0.2804.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506
E = - H (29 Imag C C	In 709.96835499, <b>H</b> 98K) = -709.68490 inary frequency = 1.0988710 1.4041850	termediate <b>G</b> ( <b>0K</b> ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360	68, 09.744094 au. -0.576553 -0.453235	н Н Н Е = - Н (2) Г Птад С С	-1.0133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854 tinary frequency = 1.0927470 1.4978930	-2.2372130 -1.3949550 -2.1168590 TS G-H (0K) = -709.7007 46, G (298K) = -7 1. 0.1126580 1.5851440	-0.2804.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768
E = - H (2 <sup>t</sup> Imag C C C	In 709.96835499, <b>H</b> <b>98K</b> ) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970	termediate <b>G</b> ( <b>0K</b> ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750	68, 09.744094 au. -0.576553 -0.453235 -0.382587	H H <b>E</b> = - <b>H</b> (2) Imag C C C	-1.0133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854 ;inary frequency = 1.0927470 1.4978930 2.2349770	-2.2372130 -1.3949550 -2.1168590 TS G-H (0K) = -709.7007 46, G (298K) = -7 1. 0.1126580 1.5851440 -0.8752890	-0.2804.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061
E = - H (2) Imag C C C C O	In 709.96835499, <b>H</b> <b>98K</b> ) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020	termediate <b>G</b> ( <b>0K</b> ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390	H H E = - H (2 Imag C C C C C O	-1.0133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854 ginary frequency = 1.0927470 1.4978930 2.2349770 3.2911190	-2.2372130 -1.3949550 -2.1168590 TS G-H (0K) = -709.7007 46, G (298K) = -7 1. 0.1126580 1.5851440 -0.8752890 -0.4738130	-0.2804.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760
E = - H (22) Imag C C C C C O C	In 709.96835499, <b>H</b> <b>98K</b> ) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200	termediate <b>G</b> ( <b>0K</b> ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608	H H E = - H (2 Imag C C C C C C O C	-1.0133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854 ginary frequency = 1.0927470 1.4978930 2.2349770 3.2911190 2.3157030	-2.2372130 -1.3949550 -2.1168590 TS G-H (0K) = -709.7007 46, G (298K) = -7 1. 0.1126580 1.5851440 -0.8752890 -0.4738130 -2.1783670	-0.2804.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693
E = - H (22) Imag C C C C C O C O C	In 709.96835499, <b>H</b> <b>98K</b> ) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600	termediate <b>G</b> ( <b>0K</b> ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610	H H E = - H (2 Imag C C C C C O C O C	-1.0133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854 (inary frequency = 1.0927470 1.4978930 2.2349770 3.2911190 2.3157030 2.4847430	$-2.2372130 \\ -1.3949550 \\ -2.1168590 \\ \overline{TS \ G-H} \\ (0K) = -709.7007 \\ 46, G \ (298K) = -7 \\ 1. \\ 0.1126580 \\ 1.5851440 \\ -0.8752890 \\ -0.4738130 \\ -2.1783670 \\ 1.9025430 \\ \end{array}$	-0.2804.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260
E = - H (22) Imag C C C C C O C O C O H	In 709.96835499, <b>H</b> <b>98K</b> ) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010	termediate <b>G</b> ( <b>0K</b> ) = $-709.7011$ 08, <b>G</b> ( <b>298K</b> ) = $-7$ 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1 549530	н N H E = H (2 Imag C C C C C C C C C C C C C	-1.0133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854 (inary frequency = 1.0927470 1.4978930 2.2349770 3.2911190 2.3157030 2.4847430 0.6430810	-2.2372130 $-1.3949550$ $-2.1168590$ TS G-H $(0K) = -709.7007$ 46, G (298K) = -7 1. 0.1126580 1.5851440 -0.8752890 -0.4738130 -2.1783670 1.9025430 -0.1034550	-0.2804.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260 -1.551356
E = - H (22) Imag C C C C C O C O C O H H	In 709.96835499, <b>H</b> <b>98K</b> ) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 2.1201850	termediate <b>G</b> $(0\mathbf{K}) = -709.7011$ $0.8, \mathbf{G} (298\mathbf{K}) = -7$ 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677620	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4022700	H H E = H (2 Imag C C C C C C O C O H H	-1.6133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854 (inary frequency = 1.0927470 1.4978930 2.2349770 3.2911190 2.3157030 2.4847430 0.6439810 2.1090100	-2.2372130 $-1.3949550$ $-2.1168590$ TS G-H $(0K) = -709.7007$ 46, G (298K) = -7 1. 0.1126580 1.5851440 -0.8752890 -0.4738130 -2.1783670 1.9025430 -0.1034550 0.5205000	-0.2804,50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260 -1.551356 0.4678570
E = - H (2) Imag C C C C O C O H H H	In 709.96835499, <b>H</b> <b>98K</b> ) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.0514540	termediate <b>G</b> $(0\mathbf{K}) = -709.7011$ $08, \mathbf{G} (298\mathbf{K}) = -7$ 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 1.8405250	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 2.057296	H H E = H (2 Imag C C C C C C O C O H H H	-1.0133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854 ;inary frequency = 1.0927470 1.4978930 2.2349770 3.2911190 2.3157030 2.4847430 0.6439810 3.1989190 2.9120940	-2.2372130 $-1.3949550$ $-2.1168590$ TS G-H $(0K) = -709.7007$ 46, G (298K) = -7 1. 0.1126580 1.5851440 -0.8752890 -0.4738130 -2.1783670 1.9025430 -0.1034550 0.5305960 1.09969200	-0.2604.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260 -1.551356 0.4678570 1.001156
E = H (22) Imag C C C C C O C O H H H H	In 709.96835499, <b>H</b> 98K) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540	termediate <b>G</b> ( $0\mathbf{K}$ ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286	H H E = H (2 Imag C C C C C C C O C O H H H	$\begin{array}{r} -1.6133340\\ 0.4802810\\ -0.1010020\\ \end{array}$ $\begin{array}{r} -709.96834369, \mathbf{H}\\ \mathbf{98K}) = -709.6854\\ \text{;inary frequency} =\\ 1.0927470\\ 1.4978930\\ 2.2349770\\ 3.2911190\\ 2.3157030\\ 2.4847430\\ 0.6439810\\ 3.1989190\\ 2.8130840\\ 1.6204662\\ \end{array}$	$\begin{array}{r} -2.2372130 \\ -1.3949550 \\ -2.1168590 \\ \hline {\rm TS} \ {\rm G-H} \\ (0{\rm K}) = -709.7007 \\ 46, {\rm G} \ (298{\rm K}) = -7 \\ 1. \\ 0.1126580 \\ 1.5851440 \\ -0.8752890 \\ -0.4738130 \\ -2.1783670 \\ 1.9025430 \\ -0.1034550 \\ 0.5305960 \\ -1.9886820 \\ -1.9886820 \\ \end{array}$	-0.2804.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260 -1.551356 0.4678570 -1.991156
E = - H (2) Imag C C C C C O C O H H H H H	In 709.96835499, <b>H</b> <b>98K</b> ) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510	termediate <b>G</b> ( $0\mathbf{K}$ ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942	H H E = H (2 Imag C C C C C C C O C O H H H H H	-1.0133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854 ;inary frequency = 1.0927470 1.4978930 2.2349770 3.2911190 2.3157030 2.4847430 0.6439810 3.1989190 2.8130840 1.3304190	$\begin{array}{r} -2.2372130 \\ -1.3949550 \\ -2.1168590 \\ \hline {\rm TS} \ {\rm G-H} \\ (0{\rm K}) = -709.7007 \\ 46, \ {\rm G} \ (298{\rm K}) = -7 \\ 1. \\ 0.1126580 \\ 1.5851440 \\ -0.8752890 \\ -0.4738130 \\ -2.1783670 \\ 1.9025430 \\ -0.1034550 \\ 0.5305960 \\ -1.9886820 \\ -2.6008460 \\ \end{array}$	-0.2604,30         1.6280090         2.0516590         70,         09.741829 au.         -0.577506         -0.489768         -0.323061         0.2760760         -1.027693         0.1758260         -1.551356         0.4678570         -1.991156         -1.225194
E = - H (2 <sup>t</sup> Imag C C C C C O C O H H H H H H	In 709.96835499, <b>H</b> 98K) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510 3.1741650	termediate <b>G</b> ( $0\mathbf{K}$ ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870 -2.7175240	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942 -0.524507	н N H E = H (2 Imag C C C C C C C C C C C C C	$\begin{array}{r} -1.6133340\\ 0.4802810\\ -0.1010020\\ \end{array}$ $\begin{array}{r} -709.96834369, \mathbf{H}\\ \mathbf{98K}) = -709.6854\\ \text{;inary frequency} =\\ 1.0927470\\ 1.4978930\\ 2.2349770\\ 3.2911190\\ 2.3157030\\ 2.4847430\\ 0.6439810\\ 3.1989190\\ 2.8130840\\ 1.3304190\\ 2.9302690\\ \end{array}$	$\begin{array}{r} -2.2372130\\ -1.3949550\\ -2.1168590\\ \hline {\rm TS} \ {\rm G-H}\\ (0{\rm K}) = -709.7007\\ 46, \ {\rm G} \ (298{\rm K}) = -7\\ 1.\\ 0.1126580\\ 1.5851440\\ -0.8752890\\ -0.4738130\\ -2.1783670\\ 1.9025430\\ -0.1034550\\ 0.5305960\\ -1.9886820\\ -2.6008460\\ -2.8791100\\ \end{array}$	-0.2604.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260 -1.551356 0.4678570 -1.991156 -1.225194 -0.459397
E = H (2 <sup>t</sup> Imag C C C C C C O C O H H H H H H H C	In 709.96835499, <b>H</b> 98K) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510 3.1741650 0.5046130	termediate <b>G</b> ( $0\mathbf{K}$ ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870 -2.7175240 2.5700270	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942 -0.524507 -1.143846	H H E = H (2 Imag C C C C C C C C O C O H H H H H H C	$\begin{array}{c} -1.6133340\\ 0.4802810\\ -0.1010020\\ \end{array}$ $\begin{array}{c} -709.96834369, \mathbf{H}\\ \mathbf{98K}) = -709.6854\\ \text{;inary frequency} =\\ 1.0927470\\ 1.4978930\\ 2.2349770\\ 3.2911190\\ 2.3157030\\ 2.4847430\\ 0.6439810\\ 3.1989190\\ 2.8130840\\ 1.3304190\\ 2.9302690\\ 0.6376560\\ \end{array}$	$\begin{array}{r} -2.2372130\\ -1.3949550\\ -2.1168590\\ \hline {\rm TS} \ {\rm G-H}\\ (0{\rm K}) = -709.7007\\ 46, {\rm G} \ (298{\rm K}) = -7\\ 1.\\ 0.1126580\\ 1.5851440\\ -0.8752890\\ -0.4738130\\ -2.1783670\\ 1.9025430\\ -0.1034550\\ 0.5305960\\ -1.9886820\\ -2.6008460\\ -2.8791100\\ 2.5932200\\ \end{array}$	-0.2604.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260 -1.551356 0.4678570 -1.991156 -1.225194 -0.459397 -1.180427
E = - H (2 <sup>g</sup> C C C C C C C C O C O H H H H H H H H H	In 709.96835499, <b>H</b> 98K) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510 3.1741650 0.5046130 0.7588430	termediate <b>G</b> ( $0\mathbf{K}$ ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870 -2.7175240 2.5700270 3.5909390	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942 -0.524507 -1.143846 -0.856059	H H E = H (2 Imag C C C C C C C C O C O H H H H H H H H H	$\begin{array}{c} -1.6133340\\ 0.4802810\\ -0.1010020\\ \end{array}$ $\begin{array}{c} -709.96834369, \mathbf{H}\\ \mathbf{98K}) = -709.6854\\ \text{;inary frequency} =\\ 1.0927470\\ 1.4978930\\ 2.2349770\\ 3.2911190\\ 2.3157030\\ 2.4847430\\ 0.6439810\\ 3.1989190\\ 2.8130840\\ 1.3304190\\ 2.9302690\\ 0.6376560\\ 0.9406830\\ \end{array}$	$\begin{array}{r} -2.2372130\\ -1.3949550\\ -2.1168590\\ \hline {\rm TS} \ {\rm G-H}\\ (0{\rm K}) = -709.7007\\ 46, {\rm G} \ (298{\rm K}) = -7\\ 1.\\ 0.1126580\\ 1.5851440\\ -0.8752890\\ -0.4738130\\ -2.1783670\\ 1.9025430\\ -0.1034550\\ 0.5305960\\ -1.9886820\\ -2.6008460\\ -2.8791100\\ 2.5932200\\ 3.6032850\\ \end{array}$	-0.2604.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260 -1.551356 0.4678570 -1.991156 -1.225194 -0.459397 -1.180427 -0.901578
E = H (2 <sup>y</sup> C C C C C C C O C O H H H H H H H H H H	In 709.96835499, <b>H</b> 98K) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510 3.1741650 0.5046130 0.7588430 0.6161130	termediate <b>G</b> ( $0\mathbf{K}$ ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870 -2.7175240 2.5700270 3.5909390 2.4529260	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942 -0.524507 -1.143846 -0.856059 -2.229892	н N H E = H (2) Imag C C C C C C C C C C C C C	$\begin{array}{r} -1.6133340\\ 0.4802810\\ -0.1010020\\ \end{array}$ $\begin{array}{r} -709.96834369, \mathbf{H}\\ \mathbf{98K}) = -709.6854\\ \text{;inary frequency} =\\ 1.0927470\\ 1.4978930\\ 2.2349770\\ 3.2911190\\ 2.3157030\\ 2.4847430\\ 0.6439810\\ 3.1989190\\ 2.8130840\\ 1.3304190\\ 2.9302690\\ 0.6376560\\ 0.9406830\\ 0.7353850\\ \end{array}$	$\begin{array}{r} -2.2372130 \\ -1.3949550 \\ -2.1168590 \\ \hline {\rm TS} \ {\rm G-H} \\ (0{\rm K}) = -709.7007 \\ 46, {\rm G} \ (298{\rm K}) = -7 \\ 1. \\ 0.1126580 \\ 1.5851440 \\ -0.8752890 \\ -0.4738130 \\ -2.1783670 \\ 1.9025430 \\ -0.1034550 \\ 0.5305960 \\ -1.9886820 \\ -2.6008460 \\ -2.8791100 \\ 2.5932200 \\ 3.6032850 \\ 2.4656290 \end{array}$	-0.2604.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260 -1.551356 0.4678570 -1.991156 -1.225194 -0.459397 -1.180427 -0.901578 -2.266659
E = H (2 <sup>y</sup> C C C C C C C C O C O H H H H H H H H H	In 709.96835499, <b>H</b> 98K) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510 3.1741650 0.5046130 0.7588430 0.6161130 -0.5444310	termediate <b>G</b> ( $0\mathbf{K}$ ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870 -2.7175240 2.5700270 3.5909390 2.4529260 2.3532090	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942 -0.524507 -1.143846 -0.856059 -2.229892 -0.910595	н N H E = H (2 Imag C C C C C C C C C C C C C	$\begin{array}{r} -1.6133340\\ 0.4802810\\ -0.1010020\\ \hline \end{array}$	$\begin{array}{r} -2.2372130 \\ -1.3949550 \\ -2.1168590 \\ \hline {\rm TS} \ {\rm G-H} \\ (0{\rm K}) = -709.7007 \\ 46, {\rm G} \ (298{\rm K}) = -7 \\ 1. \\ 0.1126580 \\ 1.5851440 \\ -0.8752890 \\ -0.4738130 \\ -2.1783670 \\ 1.9025430 \\ -0.1034550 \\ 0.5305960 \\ -1.9886820 \\ -2.6008460 \\ -2.8791100 \\ 2.5932200 \\ 3.6032850 \\ 2.4656290 \\ 2.4260260 \end{array}$	-0.2604.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260 -1.551356 0.4678570 -1.991156 -1.225194 -0.459397 -1.180427 -0.901578 -2.266659 -0.937546
E = - H (2 <sup>y</sup> C C C C C C C C C C C O C O H H H H H H	In 709.96835499, <b>H</b> 98K) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510 3.1741650 0.5046130 0.7588430 0.6161130 -0.5444310 0.5669250	termediate <b>G</b> $(0\mathbf{K}) = -709.7011$ $0.8, \mathbf{G} (298\mathbf{K}) = -7$ 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870 -2.7175240 2.5700270 3.5909390 2.4529260 2.3532090 -0.2605260	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942 -0.524507 -1.143846 -0.856059 -2.229892 -0.910595 1.9595700	н N H E = H (2) Imag C C C C C C C C C C C C C	$\begin{array}{c} -1.6133340\\ 0.4802810\\ -0.1010020\\ \end{array}$ $\begin{array}{c} -709.96834369, \mathbf{H}\\ \mathbf{98K}) = -709.6854\\ \text{;inary frequency} =\\ 1.0927470\\ 1.4978930\\ 2.2349770\\ 3.2911190\\ 2.3157030\\ 2.4847430\\ 0.6439810\\ 3.1989190\\ 2.8130840\\ 1.3304190\\ 2.9302690\\ 0.6376560\\ 0.9406830\\ 0.7353850\\ -0.4185100\\ 0.5749510\\ \end{array}$	-2.2372130 $-1.3949550$ $-2.1168590$ TS G-H $(0K) = -709.7007$ 46, G (298K) = -7 1. 0.1126580 1.5851440 -0.8752890 -0.4738130 -2.1783670 1.9025430 -0.1034550 0.5305960 -1.9886820 -2.6008460 -2.8791100 2.5932200 3.6032850 2.4656290 2.4260260 -0.1486890	-0.2604.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260 -1.551356 0.4678570 -1.991156 -1.225194 -0.459397 -1.180427 -0.901578 -2.266659 -0.937546 1.9492900
E = H (2 <sup>y</sup> C C C C C C C C C C C C C C C C C C C	In 709.96835499, <b>H</b> 98K) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510 3.1741650 0.5046130 0.7588430 0.6161130 -0.5444310 0.5669250 0.0976270	termediate <b>G</b> $(0\mathbf{K}) = -709.7011$ $0.8, \mathbf{G} (298\mathbf{K}) = -7$ 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870 -2.7175240 2.5700270 3.5909390 2.4529260 2.3532090 -0.2605260 -0.3394520	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942 -0.524507 -1.143846 -0.856059 -2.229892 -0.910595 1.9595700 0.5468580	$\mathbf{E} = -\mathbf{H} (2)$ $\mathbf{H} ($	$\begin{array}{c} -1.6133340\\ 0.4802810\\ -0.1010020\\ \end{array}$ $\begin{array}{c} -709.96834369, \mathbf{H}\\ \mathbf{98K}) = -709.6854\\ \text{;inary frequency} =\\ 1.0927470\\ 1.4978930\\ 2.2349770\\ 3.2911190\\ 2.3157030\\ 2.4847430\\ 0.6439810\\ 3.1989190\\ 2.8130840\\ 1.3304190\\ 2.9302690\\ 0.6376560\\ 0.9406830\\ 0.7353850\\ -0.4185100\\ 0.5749510\\ 0.0766220\\ \end{array}$	$\begin{array}{r} -2.2372130\\ -1.3949550\\ -2.1168590\\ \hline {\rm TS} \ {\rm G-H}\\ (0{\rm K}) = -709.7007\\ 46, {\rm G} \ (298{\rm K}) = -7\\ 1.\\ 0.1126580\\ 1.5851440\\ -0.8752890\\ -0.4738130\\ -2.1783670\\ 1.9025430\\ -0.1034550\\ 0.5305960\\ -1.9886820\\ -2.6008460\\ -2.8791100\\ 2.5932200\\ 3.6032850\\ 2.4656290\\ 2.4260260\\ -0.1486890\\ -0.2559390\\ \end{array}$	-0.2604.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260 -1.551356 0.4678570 -1.991156 -1.225194 -0.459397 -1.180427 -0.901578 -2.266659 -0.937546 1.9492900 0.5470120
E = - H (2) C C C C C C C C C C C C C C C C C C C	In 709.96835499, <b>H</b> 98K) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510 3.1741650 0.5046130 0.7588430 0.6161130 -0.5444310 0.5669250 0.0976270 -13665640	termediate <b>G</b> (0K) = -709.7011 08, G (298K) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870 -2.7175240 2.5700270 3.5909390 2.4529260 2.3532090 -0.2605260 -0.3394520 -0.2548720	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942 -0.524507 -1.143846 -0.856059 -2.229892 -0.910595 1.9595700 0.5468580 0.2277500	$\mathbf{E} = -\mathbf{H} (2)$	-1.6133340 $0.4802810$ $-0.1010020$ $-709.96834369, H$ $98K) = -709.6854$ $;inary frequency =$ $1.0927470$ $1.4978930$ $2.2349770$ $3.2911190$ $2.3157030$ $2.4847430$ $0.6439810$ $3.1989190$ $2.8130840$ $1.3304190$ $2.9302690$ $0.6376560$ $0.9406830$ $0.7353850$ $-0.4185100$ $0.5749510$ $0.0796920$ $-13841210$	$\begin{array}{r} -2.2372130\\ -1.3949550\\ -2.1168590\\ \hline {\rm TS} \ {\rm G-H}\\ (0{\rm K}) = -709.7007\\ 46, \ {\rm G} \ (298{\rm K}) = -7\\ 1.\\ 0.1126580\\ 1.5851440\\ -0.8752890\\ -0.4738130\\ -2.1783670\\ 1.9025430\\ -0.1034550\\ 0.5305960\\ -1.9886820\\ -2.6008460\\ -2.8791100\\ 2.5932200\\ 3.6032850\\ 2.4656290\\ 2.4260260\\ -0.1486890\\ -0.2559390\\ -0.2029200\\ \end{array}$	-0.2604.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260 -1.551356 0.4678570 -1.991156 -1.225194 -0.459397 -1.180427 -0.901578 -2.266659 -0.937546 1.9492900 0.5470120 0.2359550
E = - H (2) C C C C C C C C C C C C C C C C C C C	In 709.96835499, <b>H</b> 98K) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510 3.1741650 0.5046130 0.7588430 0.6161130 -0.5444310 0.5669250 0.0976270 -1.3665640 2.1775480	termediate <b>G</b> ( $0$ <b>K</b> ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870 -2.7175240 2.5700270 3.5909390 2.4529260 2.3532090 -0.2605260 -0.3394520 -0.2548720 0.6644200	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942 -0.524507 -1.143846 -0.856059 -2.229892 -0.910595 1.9595700 0.5468580 0.2277500 0.8672290	$\mathbf{E} = -\mathbf{H} (2)$	-1.6133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854 ;inary frequency = 1.0927470 1.4978930 2.2349770 3.2911190 2.3157030 2.4847430 0.6439810 3.1989190 2.8130840 1.3304190 2.9302690 0.6376560 0.9406830 0.7353850 -0.4185100 0.5749510 0.0796920 -1.3841210 2.2101620	$\begin{array}{r} -2.2372130\\ -1.3949550\\ -2.1168590\\ \hline {\rm TS} \ {\rm G-H}\\ (0{\rm K}) = -709.7007\\ 46, {\rm G} \ (298{\rm K}) = -7\\ 1.\\ 0.1126580\\ 1.5851440\\ -0.8752890\\ -0.4738130\\ -2.1783670\\ 1.9025430\\ -0.1034550\\ 0.5305960\\ -1.9886820\\ -2.6008460\\ -2.8791100\\ 2.5932200\\ 3.6032850\\ 2.4656290\\ 2.4260260\\ -0.1486890\\ -0.2559390\\ -0.2029200\\ 0.7120800\\ \end{array}$	-0.2604.50 1.6280090 2.0516590 70, 09.741829 au. -0.577506 -0.489768 -0.323061 0.2760760 -1.027693 0.1758260 -1.551356 0.4678570 -1.991156 -1.225194 -0.459397 -1.180427 -0.901578 -2.266659 -0.937546 1.9492900 0.5470120 0.2359550 0.8014770
E = - H (2 <sup>y</sup> C C C C C C C C C C C C C C C C C C C	In 709.96835499, <b>H</b> 98K) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510 3.1741650 0.5046130 0.7588430 0.6161130 -0.5444310 0.5669250 0.0976270 -1.3665640 -2.1775480 2.5202020	termediate <b>G</b> ( $0$ <b>K</b> ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870 -2.7175240 2.5700270 3.5909390 2.4529260 2.3532090 -0.2605260 -0.3394520 -0.2548720 0.6944390 0.772150	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942 -0.524507 -1.143846 -0.856059 -2.229892 -0.910595 1.9595700 0.5468580 0.2277500 0.8673280	$\mathbf{E} = -\mathbf{H} (2)$	$\begin{array}{r} -1.6133340\\ 0.4802810\\ -0.1010020\\ \hline \end{array}$	$\begin{array}{r} -2.2372130\\ -1.3949550\\ -2.1168590\\ \hline {\rm TS} \ {\rm G-H}\\ (0{\rm K}) = -709.7007\\ 46, \ {\rm G}\ (298{\rm K}) = -7\\ 1.\\ 0.1126580\\ 1.5851440\\ -0.8752890\\ -0.4738130\\ -2.1783670\\ 1.9025430\\ -0.1034550\\ 0.5305960\\ -1.9886820\\ -2.6008460\\ -2.8791100\\ 2.5932200\\ 3.6032850\\ 2.4656290\\ 2.4260260\\ -0.1486890\\ -0.2559390\\ -0.2029200\\ 0.7130800\\ 0.7625900\end{array}$	-0.2604,30           1.6280090           2.0516590           70,           09.741829 au.           -0.577506           -0.489768           -0.323061           0.2760760           -1.027693           0.1758260           -1.551356           0.4678570           -1.991156           -1.225194           -0.459397           -1.180427           -0.901578           -2.266659           -0.937546           1.9492900           0.5470120           0.2359550           0.8914770
E = - H (2 <sup>y</sup> C C C C C C C C C C C C C C C C C C C	In 709.96835499, <b>H</b> 98K) = $-709.68490$ inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510 3.1741650 0.5046130 0.7588430 0.6161130 -0.5444310 0.5669250 0.0976270 -1.3665640 -2.1775480 -3.5393820 -3.5393820	termediate <b>G</b> ( $0\mathbf{K}$ ) = -709.7011 D8, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870 -2.7175240 2.5700270 3.5909390 2.4529260 2.3532090 -0.2605260 -0.3394520 -0.2548720 0.6944390 0.7762150	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942 -0.524507 -1.143846 -0.856059 -2.229892 -0.910595 1.9595700 0.5468580 0.2277500 0.8673280 0.5714200		-1.6133340 0.4802810 -0.1010020 -709.96834369, <b>H</b> <b>98K</b> ) = -709.6854 ;inary frequency = 1.0927470 1.4978930 2.2349770 3.2911190 2.3157030 2.4847430 0.6439810 3.1989190 2.8130840 1.3304190 2.9302690 0.6376560 0.9406830 0.7353850 -0.4185100 0.5749510 0.0796920 -1.3841210 -2.2191620 -3.5819350	$\begin{array}{r} -2.2372130\\ -1.3949550\\ -2.1168590\\ \hline {\rm TS} \ {\rm G-H}\\ (0{\rm K}) = -709.7007\\ 46, \ {\rm G} \ (298{\rm K}) = -7\\ 1.\\ 0.1126580\\ 1.5851440\\ -0.8752890\\ -0.4738130\\ -2.1783670\\ 1.9025430\\ -0.1034550\\ 0.5305960\\ -1.9886820\\ -2.6008460\\ -2.8791100\\ 2.5932200\\ 3.6032850\\ 2.4656290\\ 2.4260260\\ -0.1486890\\ -0.2559390\\ -0.2029200\\ 0.7130800\\ 0.7635890\\ -0.95560\\ -0.955$	-0.2604,30           1.6280090           2.0516590           70,           09.741829 au.           -0.577506           -0.489768           -0.323061           0.2760760           -1.027693           0.1758260           -1.551356           0.4678570           -1.991156           -1.225194           -0.459397           -1.180427           -0.901578           -2.266659           -0.937546           1.9492900           0.5470120           0.2359550           0.8914770           0.5926110
E = - H (2 <sup>y</sup> Imag C C C C C C C C C C C C C C C C C C C	In 709.96835499, <b>H</b> 98K) = $-709.68490$ inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510 3.1741650 0.5046130 0.7588430 0.6161130 -0.5444310 0.5669250 0.0976270 -1.3665640 -2.1775480 -3.5393820 -4.1045870	termediate <b>G</b> ( $0\mathbf{K}$ ) = -709.7011 D8, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870 -2.7175240 2.5700270 3.5909390 2.4529260 2.3532090 -0.2605260 -0.3394520 -0.2548720 0.6944390 0.7762150 -0.0910530	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942 -0.524507 -1.143846 -0.856059 -2.229892 -0.910595 1.9595700 0.5468580 0.2277500 0.8673280 0.5714200 -0.364145	$ \begin{array}{c} \mathbf{H} \\ \mathbf{N} \\ \mathbf{H} \end{array} \\ \mathbf{E} = - \mathbf{H} \left( 2 \right) \\ \mathbf{H} \\ $	$\begin{array}{r} -1.6133340\\ 0.4802810\\ -0.1010020\\ \hline \end{array}$	$\begin{array}{r} -2.2372130\\ -1.3949550\\ -2.1168590\\ \hline {\rm TS} \ {\rm G-H}\\ (0{\rm K}) = -709.7007\\ 46, \ {\rm G}\ (298{\rm K}) = -7\\ 1.\\ 0.1126580\\ 1.5851440\\ -0.8752890\\ -0.4738130\\ -2.1783670\\ 1.9025430\\ -0.1034550\\ 0.5305960\\ -1.9886820\\ -2.6008460\\ -2.8791100\\ 2.5932200\\ 3.6032850\\ 2.4656290\\ 2.4260260\\ -0.1486890\\ -0.2559390\\ -0.2029200\\ 0.7130800\\ 0.7635890\\ -0.1005120\\ \end{array}$	-0.2604,30           1.6280090           2.0516590           70,           09.741829 au.           -0.577506           -0.489768           -0.323061           0.2760760           -1.027693           0.1758260           -1.551356           0.4678570           -1.991156           -1.225194           -0.459397           -1.180427           -0.901578           -2.266659           -0.937546           1.9492900           0.5470120           0.2359550           0.8914770           0.5926110           -0.361058
E = - H (2 <sup>y</sup> Imag C C C C C C C C C C C C C C C C C C C	In 709.96835499, H 98K) = -709.68490 inary frequency = 1.0988710 1.4041850 2.3221970 3.3169020 2.4916200 2.3585600 0.6525010 3.1391850 2.9514540 1.5402510 3.1741650 0.5046130 0.7588430 0.6161130 -0.5444310 0.5669250 0.0976270 -1.3665640 -2.1775480 -3.5393820 -4.1045870 -3.3045470	termediate <b>G</b> ( $0$ <b>K</b> ) = -709.7011 08, <b>G</b> ( <b>298K</b> ) = -7 0. 0.1034190 1.5994360 -0.7803750 -0.3307750 -2.0730470 1.9619690 -0.1207780 0.6677630 -1.8495250 -2.5738870 -2.7175240 2.5700270 3.5909390 2.4529260 2.3532090 -0.2605260 -0.3394520 -0.2548720 0.6944390 0.7762150 -0.0910530 -1.0394880	68, 09.744094 au. -0.576553 -0.453235 -0.382587 0.2699390 -1.081608 0.2388610 -1.549530 0.4922700 -2.057286 -1.256942 -0.524507 -1.143846 -0.856059 -2.229892 -0.910595 1.9595700 0.5468580 0.2277500 0.8673280 0.5714200 -0.364145 -1.006971	$ \begin{array}{c} \mathbf{H} \\ \mathbf{N} \\ \mathbf{H} \end{array} \\ \mathbf{E} = - \mathbf{H} \left( 2 \right) \\ \mathbf{H} \\ $	$\begin{array}{r} -1.6133340\\ 0.4802810\\ -0.1010020\\ \end{array}$	$\begin{array}{r} -2.2372130\\ -1.3949550\\ -2.1168590\\ \hline {\rm TS} \ {\rm G-H}\\ (0{\rm K}) = -709.7007\\ 46, \ {\rm G}\ (298{\rm K}) = -7\\ 1.\\ 0.1126580\\ 1.5851440\\ -0.8752890\\ -0.4738130\\ -2.1783670\\ 1.9025430\\ -0.1034550\\ 0.5305960\\ -1.9886820\\ -2.6008460\\ -2.8791100\\ 2.5932200\\ 3.6032850\\ 2.4656290\\ 2.4260260\\ -0.1486890\\ -0.2559390\\ -0.2029200\\ 0.7130800\\ 0.7635890\\ -0.1005120\\ -1.0137710\\ \end{array}$	-0.2604,30           1.6280090           2.0516590           70,           09.741829 au.           -0.577506           -0.489768           -0.323061           0.2760760           -1.027693           0.1758260           -1.551356           0.4678570           -1.991156           -1.225194           -0.459397           -1.180427           -0.901578           -2.266659           -0.937546           1.9492900           0.5470120           0.2359550           0.8914770           0.5926110           -0.361058           -1.022096

			FPTED MAN	<b>NZLI</b>	<b>PIPT</b>		
Н	-0.1993190	-0.1956160	2.7266910	H	-0.1771260	-0.1073820	2.7316130
н	1 5036280	0 2237160	2 2263420	н	1 5011640	0 3670410	2 1924000
U II	1.5050200	1 2677700	1 6020860	ц	1.9051270	1 2860000	1 6267680
п	-1.7452000	1.5077790	1.0020800	п	-1.6031270	1.3800900	1.0307080
Н	-4.1561850	1.5139430	1.0756280	н	-4.2196460	1.4/56230	1.10/5390
Н	-5.1647260	-0.0310510	-0.591239	Н	-5.1820360	-0.0640470	-0.589930
Н	-3.7413510	-1.7200830	-1.731550	Н	-3.7116330	-1.6893380	-1.763003
Н	-1.3370740	-1.8662490	-1.222755	Н	-1.2998730	-1.7756390	-1.250094
N	0 6929570	-1 5208550	1 2224030	Ν	0 7202050	-1 4158360	1 2314890
ц	0.0021680	2 2148520	1.5000070	ц	0.0780260	2 1502000	1.5229120
11	-0.0021080	-2.2146520	1.3000970	11	0.0789200	-2.1303900	1.5556120
	In	termediate H				15 H-I	
<b>E</b> =	-709.97818532, <b>H</b>	$(\mathbf{0K}) = -709.7082$	81,	$\mathbf{E} = \mathbf{E}$	-709.97176726, <b>H</b>	( <b>0K</b> ) = -709.7029	85,
H (2	<b>298K</b> ) = -709.6928'	75, G (298K) = -7	09.749201 au.	H (2	98K) = -709.68766	55, G (298K) = -7	09.744098 au.
Imag	ginary frequency =	0.		Imag	ginary frequency =	1.	
C	1,1053530	0.2092500	-0.574858	C	-1.0455690	0.3493470	0.4380060
Ċ	1 7722700	1 5712900	-0 394412	Ĉ	-1 6734760	1 6113900	-0 1937240
	1.0122200	1.0759490	0.1/1695	C	1 0516120	0.0540520	0.1266840
	1.9122290	-1.0736460	-0.141065	C	-1.9510150	-0.9349330	0.4300840
0	3.1510/00	-0.9264630	0.3921560	0 ã	-3.2644780	-0.8133600	0.0242450
C	1.8925030	-2.2187000	-1.136365	С	-1.9608190	-1.6503830	1.7911970
0	2.6790780	1.6952570	0.4219850	0	-2.4634070	1.4902530	-1.1171430
Н	0.7154450	0.1052040	-1.589329	Η	-0.7055140	0.5803750	1.4473360
Н	3.2753940	0.0189660	0.6444440	Н	-3.2951920	-0.1613560	-0.7058140
н	2.5236620	-1.9509710	-1.987888	н	-2.5198080	-1.0451250	2.5086870
н	0.8826730	-2 /336620	-1 /197283	н	-0.9/69520	-1 8169090	2 16/2500
и П	2 2007860	2.1156220	0.660122	ц	2 4671820	2 6165440	2.1042300
П	2.3097800	-5.1150250	-0.009122	п	-2.40/1030	-2.0103440	0.2670000
C	1.2615520	2./164060	-1.218668	C	-1.2683350	2.9452950	0.3670000
Н	1.7017500	3.6535400	-0.874984	Н	-1.6875660	3.7491430	-0.2396690
Н	1.5309400	2.5529200	-2.270765	Н	-1.6384420	3.0345740	1.3969120
Н	0.1669430	2.7698230	-1.176510	H	-0.1763900	3.0341650	0.4117610
С	0.5900130	-0.2060170	1.8392710	C	-0.5601030	-0.9131260	-1.5897100
С	0.0071110	-0.1068290	0.4760680	C	0.0659400	-0.1973280	-0.4363460
Ċ	-1 4510060	-0.0832710	0.2065500	Ć	1 4703050	-0 1314420	-0 1602940
C	-2 318/350	0.5472670	1 1113390	C	2 /076980	-0.3625830	-1 2009940
	2 6972060	0.5472070	0.8404420	C	2.4070700	-0.3023030	-1.2007740
	-5.08/2900	0.3982280	0.8494450	C	5.7085710	-0.2433290	-0.9012770
C	-4.1991/10	0.0144370	-0.310212	C	4.2256010	0.0884950	0.3189590
С	-3.3403170	-0.6154110	-1.215929	С	3.3181280	0.3155140	1.3614020
C	-1.9715130	-0.6579660	-0.964924	С	1.9554320	0.2119520	1.1285930
Η	-0.0976130	-0.4317290	2.6476520	Η	0.1297210	-1.4902280	-2.2013710
Н	1.4827930	0.3403050	2.1259900	Н	-1.2827170	-0.3724020	-2.2046980
Н	-1.9254380	1.0131120	2.0103590	Н	2.0629730	-0.5999740	-2.2011810
н	-4 3507950	1 0942470	1 5508300	н	4 4760250	-0 4095350	-1 7673170
н	-5 2654840	0.051/030	-0 511288	н	5 2918690	0 17/2330	0 5051460
и П	2 7260000	1.0700570	0.011200	ц	2 6801400	0.5706270	2 2518060
п	-3.7309900	-1.0709370	-2.11/033	п	1.2659.400	0.3700370	2.3316900
H	-1.3135830	-1.1498600	-1.0/0310	H	1.2658490	0.3805460	1.947/670
N	0.8013670	-1.3546310	0.9381010	N	-1.1095350	-1.7263690	-0.5153830
Н	0.4100020	-2.2717620	1.1585200	Н	-1.1075470	-2.7420600	-0.5546160
	Ir	termediate I					
E =	-709.97636401. H	(0K) = -709.7080	39.				
н (2	(98K) = -709.6919	42 G (298K) = -7	09 750235 au				
Ima	$r_{inerv}$ frequency -	(2, 0)(2)(1) = 7	07.750255 dd.				
C	ginary frequency $=$	0.2200500	0 4052250				
C	-0.9343880	0.5290590	0.4032230				
C	-1.2855810	1.4481550	-0.0/135/0				
C	-2.2047690	-0.6581080	0.5195080				
0	-3.3948480	-0.1291550	-0.0205840				
C	-2.5176670	-0.9588350	1.9836340				
0	-1.6058900	1.1293330	-1.7929610				
Н	-0.7244160	0.8250700	1.3482700				
н	-3,2752360	-0.0049130	-0.9786430				
н	-2 8791/20	-0.0623860	2 4972280				
и П	-1 6781800	_1 228/1200	2.7772200				
	-1.0201090	-1.5504000	2.4752/00				
н	-3.2983290	-1.7233910	2.0282390	1			

		ACCI	EPTED MAN	USCRIPT
С	-1.2378820	2.8658930	-0.1726370	
Н	-1.4336950	3.5529880	-0.9970260	
Н	-2.0063840	2.9868680	0.6015980	
Н	-0.2706930	3.0927110	0.2890030	
С	-0.5054340	-1.5846020	-0.9399000	
Ċ	0 1396690	-0 5004790	-0 1365700	
C	1 5235270	-0 2879140	0.0205540	
C	2 4660040	1 1251530	0.6526700	
C	2.4000040	-1.1251550	-0.0320700	
C	3.8227100	-0.0000320	-0.3333300	
C	4.2795040	0.1081330	0.2004430	
C	3.3773040	0.9975540	0.9329300	
	2.0195870	0.7700070	0.8559950	
п	0.1038510	-2.4630330	-1.0428780	
п	-0.0363190	-1.1029910	-1.9373130	
п u	2.118/230	-1.9401850	-1.2083480	
п u	4.3331200	-1.3223140	-1.0349230	
п	2.7403960	1.9020120	1 5764690	
п u	3.7473910	1.0039130	1.3704060	
п N	1.3270930	1.4090400	0.1000200	
	-1.7230830	-1.0400400	-0.1000300	
11	-2.+377700	-2.3230200	-0.7025200	
			1	
	Y			

## <sup>1</sup>H and <sup>13</sup>C NMR data for the new compounds

## General experimental conditions

<sup>1</sup>H (300 MHz, 400 MHz) and <sup>13</sup>C (75 MHz, 100 MHz) NMR spectra were determined in CDCl<sub>3</sub> and DMSO-d<sub>6</sub> with Bruker DPX 300 and Bruker AVANCE III 400. Chemical shifts ( $\delta$ ) are reported in parts per million downfield from tetramethylsilane (TMS  $\delta$  = 0.00); <sup>1</sup>H NMR spectra were calibrated according to the residual peak of CDCl<sub>3</sub> (7.26 ppm) or DMSO-d<sub>6</sub> (2.50 ppm).


































































































































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