Exo-Stereoselective 1,3-Dipolar Cycloadditions of Nitrile Oxides to *Endo*-7-(R^1,R^2-methylene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylates

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1,3-Dipolar cycloaddition of arylnitrile oxides to *endo-N*-(3,5-dichlorophenyl)imide 7-(R^1,R^2-methylene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylates (R^1, R^2 = phenyl, methyl, 2-thienyl, 2-furyl) led exclusively to *endo-exo* cycloadducts. Semiempirical quantum-mechanical methods AM1 showed that the exclusive *exo*-1,3-dipolar cycloaddition can be rationalized through the secondary orbital interaction between 1,3-dipole and π orbital of the *exo*-cyclic C=C double bond in the methylene bridge. Both *endo-syn-exo* and *endo-anti-exo* cycloadducts were formed in the ratio 50 50 in the case of $R^1 \neq R^2$.

The high synthetic versatility of 2-isoxazolines (4,5-dihydroisoxazoles) is based on their potential to serve as flexible synthetic equivalents of β-hydroxy ketones [1] and other related functions [2], γ-amino alcohols [3], and enaminoaldehydes [4]. Recently we have found that the selectivity of the photorearrangement of the condensed isoxazolines possessing a methylene bridge to enaminoaldehydes [5] is due to a stabilization of the biradical by the overlap of the radical electron with π-electrons of the bridge C=C double bond. With our effort to investigate the influence of substituent in methylene bridge on the photorearrangement we have paid our attention to the preparation of *N*-(3,5-dichlorophenyl)imide 10-R^1,R^2-methylene-5-phenyl-3-oxa-4-azatricyclo-[5,2,1,$0^{2,6}$]dec-4-ene-8,9-dicarboxylates *III* and *IV*. In this paper, we describe in detail the stereoselectivity of the 1,3-dipolar cycloaddition of arylnitrile oxides *I* to *endo-N*-(3,5-dichlorophenyl)imide 7-(R^1,R^2-methylene)bicyclo[2.2.1]hept-2-ene-5,6-dicarboxylates *II* (R^1, R^2 = phenyl, methyl, 2-thienyl, 2-furyl), together with AM1 calculations.

Compounds *II* were prepared by the treatment of R^1,R^2-substituted fulvenes with *N*-(3,5-dichlorophenyl)maleimide [6]. When X-substituted benzonitrile oxides *I* (where X = H, 4-CH_3, 4-Cl) were generated from the corresponding benzohydroximoyl chlorides and triethylamine in diethyl ether in the presence of symmetrically substituted derivatives *II* ($R^1 = R^2$), the *endo-exo* cycloadducts *III* were formed together with the recovered starting material *II* and 3,4-diarylfuroxan, the nitrile oxide dimer. The first prefix *endo* in *III* showed a relationship between imide moiety and methylene bridge; the second prefix *exo* a relationship of isoxazoline moiety to methylene bridge. The second possible *endo-endo* products *V* have not been detected in the crude reaction mixture by NMR spectroscopy.

There are two possible stereoisomeric adducts of *I* and *endo II*; namely *endo-exo III* and *endo-endo V*. In addition, two further stereoisomers *exo-exo VI* and *exo-endo VII* can be formed from *exo II*, which could be theoretically formed by *endo-exo* isomerization of *endo II*. It is noteworthy to mention that the attempt to isomerize *endo II* to *exo II* failed even by heating at 180 °C.

The exclusive *exo*-stereoselective 1,3-dipolar cycloaddition to *endo II* was observed also in the case of unsymmetrically substituted methylene derivatives of *II* ($R^1 \neq R^2$). Both, *endo-syn-exo III* and *endo-anti-exo IV* cycloadducts were formed in the ratio 50 50. The prefixes *syn* and *anti* showed a relationship between isoxazoline oxygen atom and R^1 substituent bonded to the methylene bridge. The distinction between these possibilities was made on the basis of spectroscopic data, in particular using NOE experiments. For example, NMR spectrum of *IIIa* showed the presence of doublets at δ = 3.40, 3.82, 3.87, and 4.94 for H-7, H-1, H-6, and H-2 atoms. The ^{1}H NMR spectrum of cycloadducts *IV* possesses significant doublets for these hydrogen atoms, too. This excludes the possibility that this is a stereoisomer *V* and proves that both isolated adducts *III* and *IV* result from the same approach be-

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tween nitrile oxide *I* and dipolarophile *II*, namely that which binds the 1,3-dipole with the C=C double bond of *II* from the *exo*-side to the methylene bridge. The NMR spectrum of the *endo-endo* stereoisomer *V* would have doublet of doublets for the aforementioned H-1, H-2, H-6, and H-7 protons. In *III* and *IV* the zero coupling constants between H-1 and H-2 as well as between H-6 and H-7 are consistent only with *exo* stereochemistry, since in the *endo-endo* isomer *V* the above-mentioned hydrogens would be nearly eclipsed, and would give rise to a much larger coupling constant.

The relative configuration of the R^1 and R^2 substituents related to H-1 and H-7 in the case of *III* and *IV* was confirmed by NOE difference spectroscopy. For example, the irradiation of the methyl group in *IIIℓ* caused NOE's for H-1 (δ = 4.52), which suggested that these groups were on the same side. Moreover, the presence of NOE between H-1 and H-2 (δ = 4.89, proton in the neighbourhood to the isoxazoline oxygen atom) as well as the absence of NOE between H-1 and H-6 confirmed the suggested structure *IIIℓ*. Similarly, the irradiation of the methyl group in *IVℓ* caused NOE's for H-7. Irradiation of H-7 results in signal enhancement of H-6 proton (δ = 3.86), consistent with the *endo-anti-exo* configuration of *IVℓ*.

In order to rationalize the above cycloadditions, we have carried out quantum-mechanical calculations. The relative stabilities of all possible cycloadducts *III, V—VII* (Ar = Ar^1 = R^1 = R^2 = Ph) have been assessed by the semiempirical AM1 method [7]. Geometries of starting compounds and cycloadducts were totally optimized. The calculated relative energies are expressed as energy differences, the energy of the most stable structure being the reference.

$$\Delta E \text{ (endo-exo } III) = 34.3 \text{ kJ mol}^{-1}$$
$$\Delta E \text{ (endo-endo } V) = 0.0 \text{ kJ mol}^{-1}$$
$$\Delta E \text{ (exo-exo } VI) = 17.5 \text{ kJ mol}^{-1}$$
$$\Delta E \text{ (exo-endo } VII) = 16.5 \text{ kJ mol}^{-1}$$

AM1 calculations of compounds *III* and *V* reveal that the *endo-endo V* is by 34.3 kJ mol^{-1} more stable than the *endo-exo III*. Thus, thermodynamics will favour the formation of *V via endo*-stereoselective 1,3-dipolar cycloaddition, which is in contrast to the obtained results. The *endo-exo* stereoselectivity of the cycloaddition reactions is due to secondary orbital interactions or steric effects [8]. The steric hindrance favours the *endo-endo V* adduct formation through the *endo* transition state. Since the 1,3-dipolar cycloadditions are kinetically controlled reactions, we have paid our attention to the secondary orbital interactions. Optimized geometries (AM1) of reactants *I* and *II* are shown in Formulae 1. The most notable feature of AM1 calculations of the transition states for the 1,3-dipolar cycloaddition of benzonitrile oxide to *II* is that the HOMO in *II* is localized also at methylene bridge (Formulae 1) , since the *exo*-cyclic double bond of methylene bridge mixes its π orbitals with unsubstituted double bond in *II*. In addition, this overlap in *II* can support the exclusive *exo* attack of the dipole related to the methylene bridge through the secondary orbital interactions between LUMO of nitrogen in 1,3-dipole *I* and the HOMO, *i.e.* π orbital of the double bond in methylene bridge in *II*. This qualitative argument rationalizes the experimental observation.

EXPERIMENTAL

The melting points are uncorrected (Boetius), the ^{1}H and ^{13}C NMR spectra of deuterochloroform solutions were measured with Varian VXR 300 instrument, tetramethylsilane being the internal reference. All reagents were purified and dried if necessary prior to use. TLC analyses were carried out with Lachema UV_{254} silica gel plates.

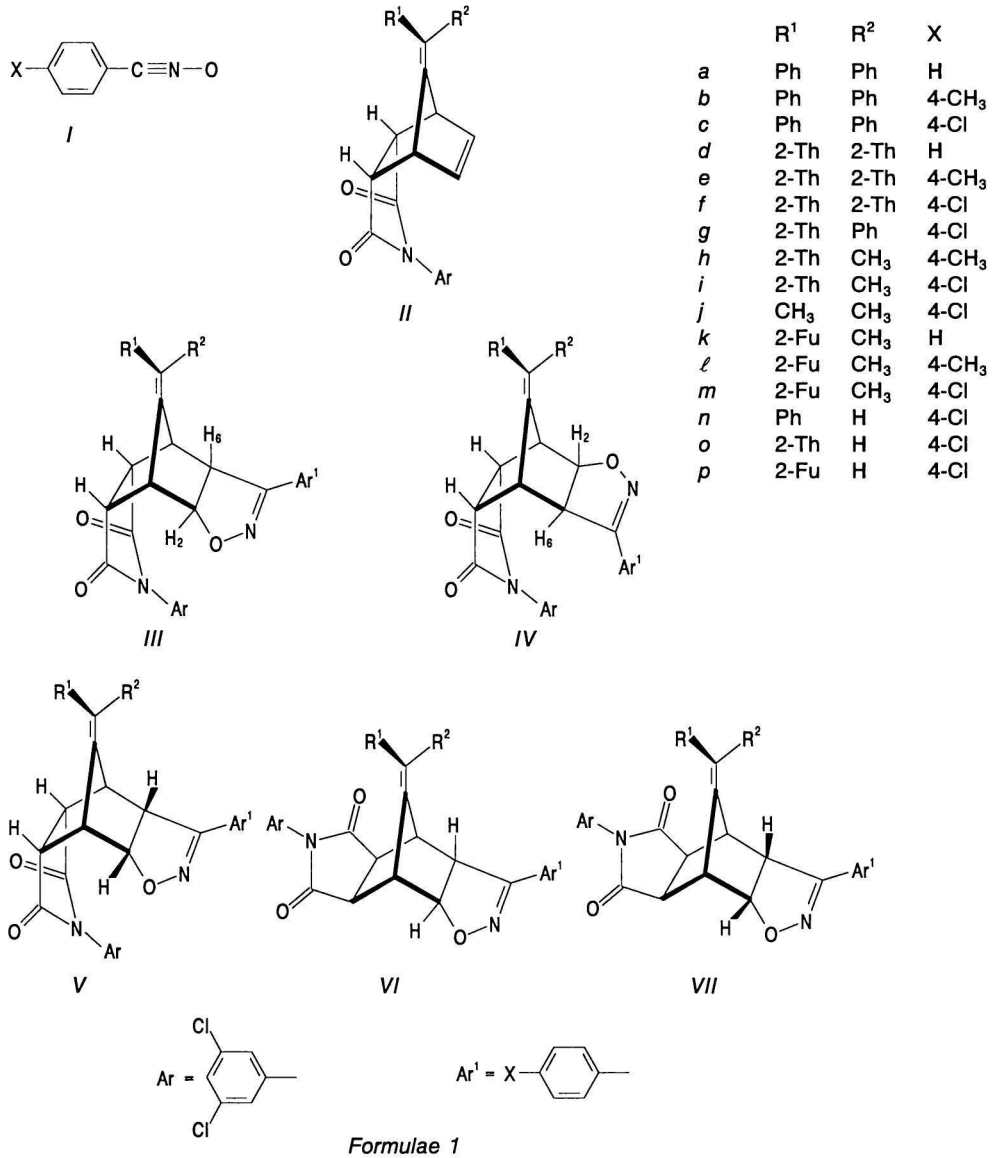
The *endo* derivatives *II* were prepared by the treatment of R^1,R^2-substituted fulvenes with *N*-(3,5-dichlorophenyl)maleimide [6].

1,3-Dipolar Cycloaddition

Triethylamine (13 mmol) in ether (30 cm^3) was added to a stirred solution of arylhydroximoyl chloride (10 mmol) and the dipolarophile *II* (10 mmol) in ether (30 cm^3) at 0—5 °C within 1 h. The reaction mixture was stirred overnight at room temperature, the separated triethylammonium chloride was filtered off, removed by dissolving in water and organic material was evaporated under diminished pressure, dried, and separated by chromatography on a silica gel column and purified by crystallization. Characteristic data for compounds *III* and *IV* are presented in Table 1 and ^{1}H NMR data are in Tables 2 and 3. ^{13}C NMR data (δ) are following:

IIIa: 43.50, 43.87 (d, C-8, C-9), 44.93 (d, C-7), 46.70 (d, C-1), 53.25 (d, C-6), 82.16 (d, C-2), 124.96, 125.17, 126.72, 127.35, 127.89, 128.31, 129.22, 129.29, 130.28, 132.90, 135.24, 135.59, 137.93, 138.88, 139.39, 140.14 (C_{arom}, C_{vinyl}), 156.00 (s, C=N), 174.00, 175.84 (s, C=O).

IIIb: 21.66 (q, CH_3), 43.46, 43.93 (d, C-8, C-9), 45.26 (d, C-7), 46.73 (d, C-1), 53.37 (d, C-6), 82.00 (d, C-2), 124.96, 125.05, 126.88, 127.31, 127.85, 127.89, 128.30, 128.67, 129.24, 129.31, 129.90, 132.88, 135.62, 137.85, 138.94, 139.66, 140.18, 140.56 (C_{arom}, C_{vinyl}), 155.92 (s, C=N), 174.05, 175.88 (s, C=O).



	R^1	R^2	X
a	Ph	Ph	H
b	Ph	Ph	4-CH_3
c	Ph	Ph	4-Cl
d	2-Th	2-Th	H
e	2-Th	2-Th	4-CH_3
f	2-Th	2-Th	4-Cl
g	2-Th	Ph	4-Cl
h	2-Th	CH_3	4-CH_3
i	2-Th	CH_3	4-Cl
j	CH_3	CH_3	4-Cl
k	2-Fu	CH_3	H
ℓ	2-Fu	CH_3	4-CH_3
m	2-Fu	CH_3	4-Cl
n	Ph	H	4-Cl
o	2-Th	H	4-Cl
p	2-Fu	H	4-Cl

Formulae 1

IIIc: 43.52, 43.75 (d, C-8, C-9), 45.17 (d, C-7), 46.61 (d, C-1), 53.14 (d, C-6), 82.39 (d, C-2), 124.92, 126.42, 127.53, 127.91, 127.97, 128.33, 128.53, 129.06, 129.28, 129.36, 132.79, 135.64, 136.26, 138.12, 138.60, 139.41, 140.10 (C_{arom}, C_{vinyl}), 155.17 (s, C=N), 173.89, 174.82 (s, C=O).

IIId: 43.36 (d, C-7), 44.75, 45.22 (d, C-8, C-9), 47.75 (d, C-1), 53.48 (d, C-6), 82.35 (d, C-2), 124.22, 125.31, 126.43, 126.84, 126.99, 127.14, 127.96, 128.22, 129.22, 129.70, 130.79, 133.18, 135.97, 140.81, 141.33, 141.59 (C_{arom}, $C_{thienyl}$, C_{vinyl}), 156.07 (s, C=N), 174.15, 174.97 (s, C=O).

IIIe: 21.76 (q, CH_3), 42.99 (d, C-7), 44.48, 44.90 (d, C-8, C-9), 47.43 (d, C-1), 53.26 (d, C-6), 81.83 (d, C-2), 124.94, 125.07, 126.05, 126.59, 126.73, 126.99, 127.88, 128.83, 129.35, 129.56, 132.83, 135.64, 140.54, 140.62, 141.05, 141.28 (C_{arom}, $C_{thienyl}$, C_{vinyl}), 155.61 (s, C=N), 173.82, 174.63 (s, C=O).

IIIf: 43.06 (d, C-7), 44.31, 44.85 (d, C-8, C-9), 47.39 (d, C-1), 53.02 (d, C-6), 82.76 (d, C-2), 124.93, 126.19, 126.54, 126.58, 126.71, 127.02, 127.91, 127.99, 128.87, 129.16, 129.38, 132.84, 135.66, 136.44, 140.23, 141.12 (C_{arom}, $C_{thienyl}$, C_{vinyl}), 154.89 (s, C=N), 173.65, 174.54 (s, C=O).

IIIh: 21.76 (q, CH_3), 42.79 (d, C-7), 45.45, 45.54 (d, C-8, C-9), 46.67 (d, C-1), 53.13 (d, C-6), 82.05 (d, C-2), 124.70, 124.83, 124.98, 125.26, 125.57, 126.62, 126.78, 129.33, 129.66, 132.96, 135.66, 137.15, 140.64, 142.62 (C_{arom}, $C_{thienyl}$, C_{vinyl}), 155.51 (s, C=N), 174.22, 174.89 (s, C=O).

IVh: 21.50, 21.74 (q, CH_3), 46.63 (d, C-7), 43.21, 43.51 (d, C-8, C-9), 44.95 (d, C-1), 53.47 (d, C-6), 81.91 (d, C-2), 124.70, 124.77, 124.98, 125.09, 125.23, 126.58, 126.72, 129.66, 132.96, 135.59, 137.15, 140.70, 142.70 (C_{arom}, $C_{thienyl}$, C_{vinyl}), 155.68 (s, C=N), 174.09, 174.99 (s, C=O).

IIIj: 20.99 (q, CH_3), 21.13 (q, CH_3), 42.04 (d, C-7), 45.44, 45.77 (d, C-8, C-9), 43.42 (d, C-1), 52.81 (d,

Table 1. Characteristic Data for Compounds *III*, *IV*

Compound	Formula M_r	Yield/%[a] M.p./°C	w_i(calc.)/% w_i(found)/%		
			C	H	N
IIIa	$C_{35}H_{24}Cl_2N_2O_3$ 591.5	39 221—223	71.07 70.77	4.09 4.12	4.74 4.79
IIIb	$C_{36}H_{26}Cl_2N_2O_3$ 605.5	31 233—235	67.30 66.91	3.72 3.65	4.69 4.68
IIIc	$C_{35}H_{23}Cl_3N_2O_3$ 625.9	48 268—270	67.16 67.30	3.70 3.72	4.48 4.69
IIId	$C_{31}H_{20}Cl_2N_2S_2O_3$ 603.6	27 210—213	61.69 61.27	3.34 3.34	4.64 4.59
IIIe	$C_{32}H_{22}Cl_2N_2S_2O_3$ 617.6	36 231—234	62.24 61.83	3.59 3.59	4.54 4.59
IIIf	$C_{31}H_{19}Cl_3N_2S_2O_3$ 638.0	37 234—236	58.36 57.86	3.00 3.07	4.39 4.47
IIIg + *IVg*	$C_{33}H_{21}Cl_3N_2SO_3$ 632.0	54 237—240	62.72 62.66	3.35 3.45	4.43 4.56
IIIh + *IVh*	$C_{29}H_{22}Cl_2N_2SO_3$ 549.5	47 275—278	63.39 63.15	4.04 4.02	5.10 5.02
IIIi + *IVi*	$C_{28}H_{19}Cl_3N_2O_3$ 569.9	53 269—272	59.01 58.95	3.36 3.38	4.92 5.22
IIIj	$C_{25}H_{19}Cl_3N_2O_3$ 501.8	36 283—285	59.84 60.01	3.82 3.96	5.58 5.39
IIIk + *IVk*	$C_{28}H_{20}Cl_2N_2O_4$ 519.4	38 248—251	64.75 64.98	3.88 4.01	5.39 5.46
IIIℓ + *IVℓ*	$C_{29}H_{22}Cl_2N_2O_4$ 533.4	36 273—276	65.30 65.13	4.16 4.09	5.25 5.32
IIIm	$C_{28}H_{19}Cl_3N_2O_4$ 553.8	37 226—228	60.72 60.65	3.46 3.61	5.06 4.98
IIIn + *IVn*	$C_{29}H_{19}Cl_3N_2O_3$ 549.8	51 269—270	63.35 63.51	3.48 3.57	5.09 5.27
IIIo + *IVo*	$C_{27}H_{17}Cl_3N_2SO_3$ 555.9	46 227—231	58.34 58.02	3.08 3.21	5.04 4.98
IIIp + *IVp*	$C_{27}H_{17}Cl_3N_2O_4$ 539.8	52 270—273	60.08 59.78	3.17 3.30	5.19 5.16

a) Yields are calculated for compounds purified by chromatography.

Table 2. ^{1}H NMR Data for Compounds *III*

Compound	δ, J/Hz							
	H-2[a]	$J_{2,6}$	H-6[a]	H-1[b]	$J_{1,9}$	H-7, H-8, H-9[c]	H_{arom}	CH_3[d]
IIIa	4.94	8.4	3.87	3.82	5.1	3.48	6.83—7.55	
IIIb	4.92	8.4	3.85	3.81	5.1	3.17	6.83—7.55	2.32
IIIc	4.90	8.4	3.75	3.73	5.0	3.48	6.84—7.50	
IIId	4.94	8.4	3.89	4.06	3.9	3.63	6.56—7.59	
IIIe	4.93	8.7	3.87	4.05	3.9	3.64	6.57—7.49	2.36
IIIf	4.95	8.4	3.84	4.05	3.9	3.63	6.61—7.51	
IIIg	4.98	8.4	3.77	4.26	5.4	3.40	6.52—7.80	
IIIh	4.88	8.7	3.61	3.92	5.1	3.42	6.58—7.51	2.37, 2.18
IIIi	4.91	8.4	3.80	3.92	3.9	3.42	6.61—7.61	2.19
IIIj	4.82	8.7	3.76	3.64	5.1	3.40	7.26—7.58	1.73, 1.44
IIIk	4.91	8.4	3.91	4.55	5.1	3.58	6.35—7.67	1.73
IIIℓ	4.89	8.4	3.88	4.52	5.1	3.57	6.37—7.56	2.36, 1.73
IIIm	4.90	8.4	3.86	4.42	5.1	3.49	6.18—7.46	2.06
IIIn	4.97	8.4	3.86	4.07	5.4	3.41	6.40—7.60	
IIIo	4.96	8.4	3.83	4.26	4.8	3.39	6.45—7.59	
IIIp	4.95	8.7	3.84	4.50	3.9	3.40	6.10—7.52	

a) Doublet; *b*) doublet of doublets; *c*) multiplet; *d*) singlet.

Table 3. ^{1}H NMR Data for Compounds *IV*

Compound	δ, *J*/Hz							
	H-2[a]	$J_{2,6}$	H-6[a]	H-7[b]	$J_{7,8}$	H-1, H-8, H-9[c]	H_{arom}	CH_3[d]
IVg	4.89	8.4	3.89	4.01	5.1	3.50	6.52—7.80	
IVh	4.88	8.7	3.90	4.02	5.7	3.52	6.55—7.55	2.37, 2.18
IVi	4.90	8.4	3.88	4.09	5.4	3.43	6.61—7.61	2.19
IVk	4.89	8.4	3.91	4.70	4.8	3.59	6.14—7.57	2.07
IVℓ	4.86	8.4	3.86	4.40	5.1	3.57	6.14—7.43	2.36, 2.07
IVn	4.84	8.4	3.86	3.66	3.9	3.56	6.59—7.59	
IVo	4.89	8.7	3.92	4.16	5.4	3.49	6.66—7.55	
IVp	4.87	8.4	3.91	4.31	5.7	3.47	6.25—7.52	

a) Doublet; *b*) doublet of doublets; *c*) multiplet; *d*) singlet.

C-6), 82.45 (d, C-2), 124.95, 126.58, 127.33, 129.24, 132.94, 135.48, 136.28 (C_{arom}, C_{vinyl}), 154.79 (s, C=N), 175.26, 174.43 (s, C=O).

IIIk: 17.27 (q, CH_3), 45.34 (d, C-7), 43.15, 43.58 (d, C-8, C-9), 46.52 (d, C-1), 52.64 (d, C-6), 82.04 (d, C-2), 109.39, 111.08, 119.41, 124.98, 126.75, 128.06, 129.04, 129.29, 130.38, 132.97, 135.26, 135.64, 142.47, 153.30 (C_{arom}, C_{furyl}, C_{vinyl}), 155.47 (s, C=N), 174.38, 175.03 (s, C=O).

IVk: 17.46 (q, CH_3), 47.03 (d, C-7), 42.85, 43.17 (d, C-8, C-9), 45.62 (d, C-1), 53.21 (d, C-6), 81.86 (d, C-2), 108.77, 110.77, 119.40, 124.99, 126.81, 128.29, 128.68, 129.27, 129.98, 133.00, 135.18, 135.62, 141.79, 153.16 (C_{arom}, C_{furyl}, C_{vinyl}), 155.95 (s, C=N), 174.33, 175.16 (s, C=O).

IIIℓ: 17.28 (q, CH_3), 21.49 (q, CH_3), 45.31 (d, C-7), 43.13, 43.59 (d, C-8, C-9), 46.50 (d, C-1), 52.74 (d, C-6), 82.19 (d, C-2), 109.32, 111.05, 119.30, 124.99, 125.12, 127.67, 129.24, 129.72, 132.99, 135.38, 135.58, 140.65, 142.41, 153.12 (C_{arom}, C_{furyl}, C_{vinyl}), 155.40 (s, C=N), 174.42, 175.07 (s, C=O).

IVℓ: 17.49 (q, CH_3), 21.48 (q, CH_3), 47.00 (d, C-7), 42.86, 43.59 (d, C-8, C-9), 45.62 (d, C-1), 53.04 (d, C-6), 81.71 (d, C-2), 108.71, 110.78, 119.32, 125.03, 125.44, 126.75, 129.25, 129.38, 135.35, 135.60, 140.18, 141.78, 153.23 (C_{arom}, C_{furyl}, C_{vinyl}), 155.87 (s, C=N), 174.39, 175.21 (s, C=O).

IIIm: 17.43 (q, CH_3), 45.56 (d, C-7), 42.79, 42.88 (d, C-8, C-9), 46.95 (d, C-1), 53.00 (d, C-6), 82.13 (d, C-2), 108.92, 110.92, 119.42, 124.99, 126.83, 127.91, 128.00, 128.92, 129.26, 129.35, 132.93, 134.91, 135.57, 135.90, 141.80, 153.12 (C_{arom}, C_{furyl}, C_{vinyl}), 155.12 (s, C=N), 174.26, 175.14 (s, C=O).

IIIn: 44.76, 44.86 (d, C-8, C-9), 43.16 (d, C-7), 46.55 (d, C-1), 52.85 (d, C-6), 82.61 (d, C-2), 124.15, 124.96, 126.38, 127.96, 128.09, 128.30, 128.63, 129.34, 132.84, 135.41, 135.62, 136.53, 141.21 (C_{arom}, C_{vinyl}), 154.91 (s, C=N), 173.76, 174.75 (s, C=O).

IVn: 41.50, 42.78 (d, C-8, C-9), 45.38 (d, C-7), 50.21 (d, C-1), 53.17 (d, C-6), 81.97 (d, C-2), 124.33, 124.93, 126.39, 127.67, 128.10, 128.37, 128.63, 129.34, 132.87, 135.42, 135.60, 136.51, 141.24 (C_{arom}, C_{vinyl}), 155.91 (s, C=N), 173.78, 174.77 (s, C=O).

IIIo: 45.26, 45.61 (d, C-8, C-9), 42.92 (d, C-7), 46.88 (d, C-1), 52.65 (d, C-6), 82.70 (d, C-2), 116.98, 124.96, 126.09, 126.37, 127.22, 128.10, 128.63, 129.35, 132.83, 135.65, 136.53, 138.23, 138.99 (C_{arom}, $C_{thienyl}$, C_{vinyl}), 154.63 (s, C=N), 173.72, 174.84 (s, C=O).

IVo: 42.33, 42.97 (d, C-8, C-9), 50.39 (d, C-7), 45.30 (d, C-1), 53.30 (d, C-6), 81.91 (d, C-2), 117.24, 124.92, 125.82, 126.50, 126.97, 128.07, 128.61, 129.24, 132.84, 135.65, 136.39, 138.12, 138.52 (C_{arom}, $C_{thienyl}$, C_{vinyl}), 154.59 (s, C=N), 173.77, 174.59 (s, C=O).

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