Boron chelates in the synthesis of α,β-unsaturated ketones of the coumarin series

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Condensation of aromatic aldehydes with 3(8)-acetyl-4(7)-difluoroboryloxycoumarin intramolecular complexes gave boron complexes of α,β-unsaturated ketones, whose hydrolysis afforded the corresponding hydroxy cinnamoylcoumarins. The boron complexes and their hydrolysis products intensely absorb and fluoresce in the visible region of the spectrum.

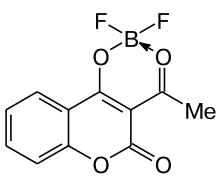
Key words: coumarins, α,β-enones, boron complexes, aldol condensation, electronic absorption spectra, fluorescence.

The syntheses and reactivities of acryloylcoumarin compounds have not been investigated systematically. For instance, discrepant data have been published on the Friedel—Crafts synthesis of crotonoyl- and cinnamoylcoumarins.[1,2] Such reactions catalyzed by strong Lewis acids impose serious limitations on the types of reagents and substrates.

Alternatively, acryloylcoumarins could be synthesized by aldol condensation involving acetylcoumarins as methylene components. Unfortunately, such reactions with 3-acetyl-4-hydroxycoumarins are hindered by strong intramolecular hydrogen bonding between the oxo and hydroxy groups, which appreciably lowers the acidity of the α-C—H bonds in the acyl group.[3—5]

Previously,[6] we have found that complexation between hydroxy acetylcoumarins and boron compounds substantially increases the acidity of the H_α atoms. For instance, reactions of 3-acetyl-4-difluoroboryloxycoumarin (**1**) with triethyl orthoformate, Fischer aldehyde, or DMF give various symmetrical and unsymmetrical polymethine dyes in high yields,[6] which show intense absorption in the visible region and fluorescence.

Here we describe condensation of compound **1** and 8-acetyl-7-difluoroboryloxy-4-methylcoumarin (**2**) with aromatic and heterocyclic aldehydes, which affords α,β-unsaturated ketones of the coumarin series. The electronic absorption spectra and fluorescence spectra of the compounds obtained were recorded.



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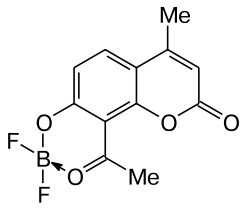

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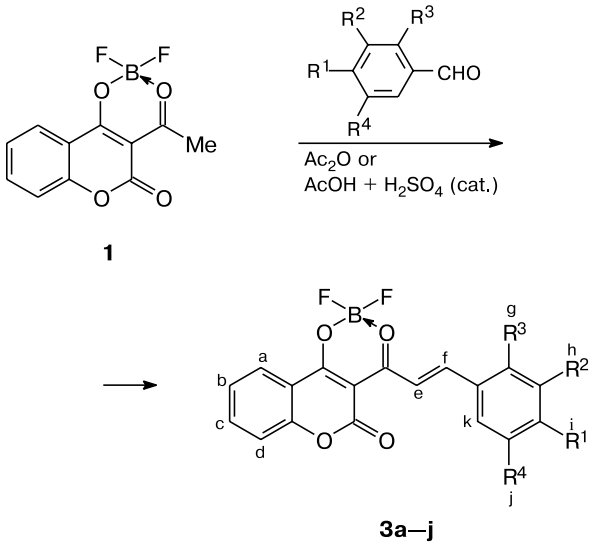
Results and Discussion

Reactions of intramolecular complex **1** with aromatic aldehydes smoothly yielded condensation products **3a—j** (Scheme 1, Table 1). The reactions were completed at 90 °C in 30 min: in acetic anhydride (procedure *A*) and in acetic acid in the presence of catalytic amounts of conc. H_2SO_4 (procedure *B*).

Scheme 1*



* The protons identified from the ^1H NMR spectra are designated with Latin letters in Schemes 1—7.

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Table 1. Yields of compounds **3a—j** and **7a—j**

3, 7	R^1	R^2	R^3	R^4	Yield* (%)	
					3	**7**
a	NMe_2	H	H	H	90 (—)	71
b	OMe	H	H	H	42 (74)	75
c	OC_5H_{11}	H	H	H	56 (78)	80
d	OEt	H	H	H	53 (81)	82
e	Me	H	Me	H	— (77)	78
f	H	H	OH	H	— (75)	65
g	H	H	OAc	H	65 (—)	61
h	OMe	H	OMe	H	— (72)	79
i	OEt	OMe	H	H	— (84)	80
j	OMe	OMe	H	OMe	— (76)	83

* The yields of compounds **3** obtained according to procedures *A* and, in parentheses, *B*.

It should be noted that in a reaction of boron complex **1** with salicylaldehyde, the condensation is accompanied by acylation of the phenolic hydroxy group.

The structures of the compounds obtained were proven by ^{1}H NMR spectroscopy (except for poorly soluble compound **3a**). The low-field region (δ 7.30—9.00) of the spectra shows, apart from the signals for aromatic protons, signals for olefinic protons as doublets with J = 12—15 Hz. These coupling constants suggest that the protons are *trans* to each other. The mass spectra of compounds **3a—j** contain molecular ion peaks (I_{rel} = 15—90%).

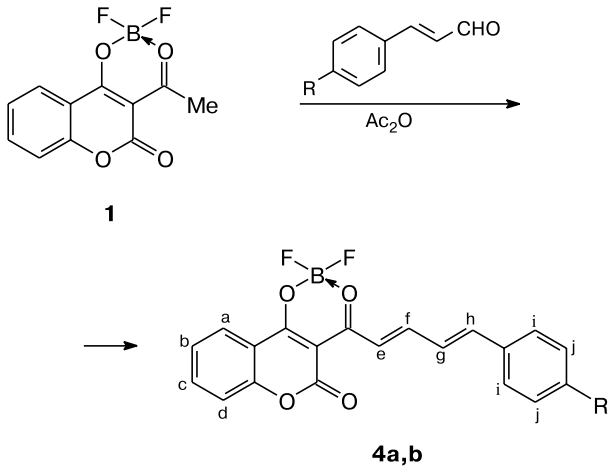
The electronic absorption spectra of compounds **3a—j** show an intense narrow band at 429—600 nm (Table 2). These compounds fluoresce as well. For instance, compound **3a** fluoresces in chloroform at 620 nm.

Table 2. Elemental analysis data and band positions in the electronic absorption spectra (λ_{max}/nm) and fluorescence spectra (λ^{fl}/nm) of compounds **3a—j**, **4a,b**, **5a—c**, **6a,b**, **7a—j**, **8**, **9a,b**, and **11**

Compound	Found / Calcd (%) C	H	N	Molecular formula	λ_{max} ($\varepsilon \cdot 10^{-4}$)	λ^{fl}
3a	62.58	4.15	3.70	$C_{20}H_{16}BF_2NO_4$	582	625
	62.69	4.21	3.66		(6.42)	
3b	61.54	3.52	—	$C_{19}H_{13}BF_2O_5$	471	530
	61.66	3.54			(5.80)	
3c	64.79	4.91	—	$C_{23}H_{21}BF_2O_5$	473	530
	64.81	4.97			(5.76)	
3d	62.48	3.95	—	$C_{20}H_{15}BF_2O_5$	471	—
	62.53	3.94			(5.79)	
3e	65.27	4.15	—	$C_{20}H_{15}BF_2O_4$	445	—
	65.25	4.11			(4.24)	
3f	60.69	3.12	—	$C_{18}H_{11}BF_2O_5$	464	—
	60.71	3.11			(6.08)	
3g	60.34	3.28	—	$C_{20}H_{13}BF_2O_6$	424	—
	60.34	3.29			(3.03)	
3h	60.04	3.75	—	$C_{20}H_{15}BF_2O_6$	485	—
	60.03	3.78			(4.62)	
3i	60.95	4.09	—	$C_{21}H_{17}BF_2O_6$	478	—
	60.90	4.14			(3.59)	
3j	58.57	3.98	—	$C_{21}H_{17}BF_2O_7$	480	—
	58.64	3.98			(3.94)	
4a	64.51	4.31	3.50	$C_{22}H_{18}BF_2NO_4$	638	—
	64.58	4.43	3.42		(7.81)	
4b	63.58	3.86	—	$C_{21}H_{15}BF_2O_5$	509	—
	63.67	3.82			(2.29)	
5a	62.90	3.84	2.97	$C_{25}H_{18}BF_2NO_6$	527	—
	62.92	3.80	2.93		(2.80)	
5b	63.24	3.26	3.70	$C_{20}H_{12}BF_2NO_4$	496	—
	63.36	3.19	3.69		(2.38)	
5c	58.97	3.51	2.54	$C_{27}H_{19}BBrF_2NO_4$	536	—
	58.95	3.48	2.55		(7.60)	
6a	63.54	4.59	3.57	$C_{21}H_{18}BF_2NO_4$	586	—
	63.50	4.57	3.53		(6.14)	
6b	62.53	3.98	—	$C_{20}H_{15}BF_2O_5$	450	—
	62.53	3.94			(2.30)	
7a	71.60	5.07	4.24	$C_{20}H_{17}NO_4$	500	540
	71.63	5.11	4.18		(4.46)	
7b	70.84	4.40	—	$C_{19}H_{14}O_5$	406	480
	70.80	4.38			(3.69)	
7c	73.00	5.83	—	$C_{23}H_{22}O_5$	406	485
	73.00	5.86			(3.72)	
7d	71.49	4.74	—	$C_{20}H_{16}O_5$	406	—
	71.42	4.79			(3.64)	
7e	74.95	5.06	—	$C_{20}H_{14}O_4$	381	—
	74.99	5.03			(2.21)	
7f	70.14	3.87	—	$C_{18}H_{12}O_5$	395	480
	70.13	3.92			(2.12)	
7g	68.61	3.98	—	$C_{20}H_{14}O_6$	372	420
	68.57	4.03			(1.55)	
7h	68.14	4.53	—	$C_{20}H_{16}O_6$	420	520
	68.18	4.58			(2.17)	
7i	68.90	4.98	—	$C_{21}H_{18}O_6$	410	—
	68.85	4.95			(1.86)	
7j	65.92	4.71	—	$C_{21}H_{18}O_7$	415	—
	65.97	4.74			(1.67)	
8	72.14	5.45	4.05	$C_{21}H_{19}NO_4$	484	—
	72.19	5.48	4.01		(6.34)	
9a	69.98	4.42	3.30	$C_{25}H_{19}NO_6$	475	520
	69.92	4.46	3.26		(1.8)	
9b	72.51	3.96	4.27	$C_{20}H_{13}NO_4$	453	520
	72.50	3.95	4.23		(5.84)	
11	74.36	5.40	3.57	$C_{24}H_{21}NO_4$	531	560
	74.40	5.46	3.62		(5.89)	

Under the same conditions, complex **1** reacted with 4-dimethylamino- and 4-methoxycinnamaldehydes (Scheme 2) to give diene ketones **4a,b** in high yields.

Scheme 2



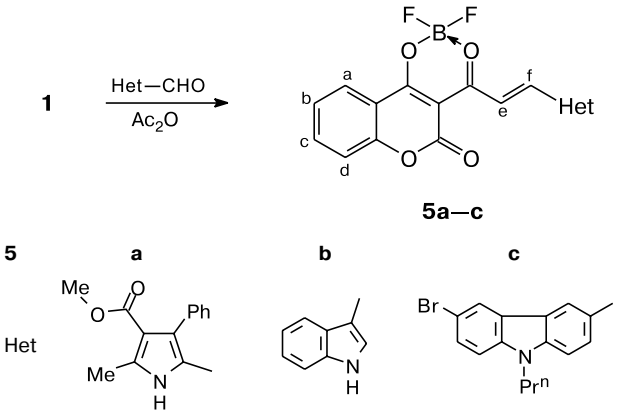
R = NMe_2 (**4a**), OMe (**4b**)

The structures of compounds **4** were proven by ^{1}H NMR spectroscopy in $CDCl_3$. The low-field region of the spectra of compounds **4a,b** show, apart from signals for the aromatic protons, signals for the protons of the conjugated diene system as two triplets and two doublets at δ 7.0—8.0. The mass spectra of compounds **4** contain low-intensity molecular ion peaks.

The electronic absorption spectra of compounds **4a,b** show the intense narrow bands. Compared to the absorption spectra of monoene compounds **3a,b**, the absorption band in the spectra of diene derivatives **4a,b** are distinguished by a considerable bathochromic shift: by 56 (**4a**, **3a**) and 40 nm (**4b**, **3b**).

Boron complex **1** also reacted with heterocyclic aldehydes to give condensation products **5a—c** (Scheme 3).

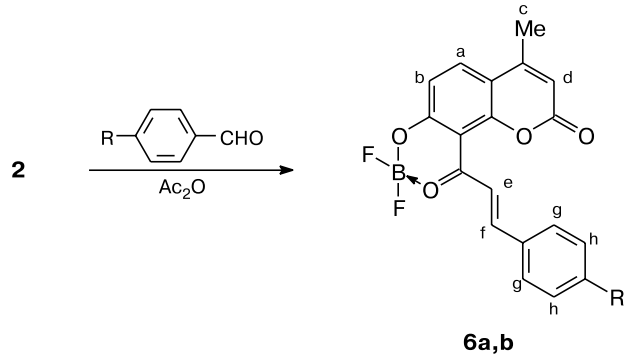
Scheme 3



The structures of compounds **5a—c** were proven by ^{1}H NMR spectroscopy in DMSO-d_6. In the spectrum of compound **5b**, the signals for the olefinic protons do not overlap the signals for the benzene protons and appear as two low-field doublets (δ 8.50 and 8.85) with J = 14.6 Hz. The proton in the α-position of the indole ring resonates as a singlet at δ 8.13. The signal for the NH proton appears as a broadened singlet at δ 12.51. Such a considerable downfield shift of the signal for the NH proton compared to 3-methylindole (δ 10.5) is probably due to electron density transfer along the —CH=CH— chain from the indole ring to the difluoroborate fragment. The mass spectrum of compound **5b** contains a molecular ion peak with m/z 379 (I_{rel} = 10%). Its electronic absorption spectrum shows an intense band at 496 nm (ε 23 800).

8-Acetyl-7-difluoroboryloxy-4-methylcoumarin (**2**) also smoothly reacted with aromatic aldehydes to give condensation products **6a,b** (Scheme 4).

Scheme 4



R = NMe_2 (**6a**), OMe (**6b**)

Compounds **6a,b** were characterized by mass spectra and ^{1}H NMR spectra (the ^{1}H NMR spectrum of compound **6a** was not recorded because of its low solubility).

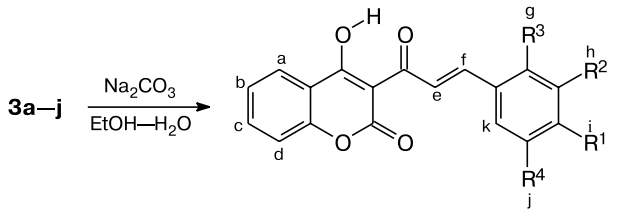
The electronic absorption spectra of compounds **6a,b** show an intense narrow band in virtually the same region as for compounds **3a,b**.

To obtain substituted hydroxy cinnamoylcoumarins, boron complexes **3** and **6** were hydrolyzed in aqueous 60% ethanol in the presence of Na_2CO_3. Substituted hydroxy cinnamoylcoumarin was precipitated by acidification of the water—ethanol solution of its sodium salt.

The hydrolysis of compounds **3a—j** gave 3-(R-cinnamoyl)-4-hydroxycoumarins **7a—j** (Scheme 5).

The structures of compounds **7a—j** were proven by ^{1}H NMR spectroscopy. In contrast to the spectra of the starting complexes **3a—j**, the ^{1}H NMR spectra of compounds **7a—j** show a signal for the OH proton at a very low field (δ 18.0—19.0), which suggests hydrogen bonding. The mass spectra of compounds **7a—j** contain molecular ion peaks. In their electronic absorption spectra,

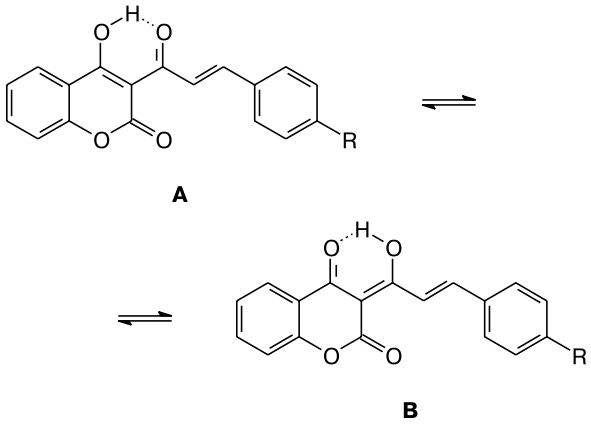
Scheme 5



the intense bands in the visible region are shifted by 40 to 80 nm to the shorter wavelengths compared to boron complexes **3a**—**j**. Compounds **7a**—**j** also fluoresce intensely in solutions. The Stokes shifts in the fluorescence spectra of chalcones **7a**—**j** are larger than in the spectra of complexes **3a**—**j** (see Table 2).

Like 3-acetyl-4-hydroxycoumarin, compounds **7a**—**j** can exist in several tautomeric forms. The most stable tautomers **A** and **B** are stabilized by intramolecular hydrogen bonding (Scheme 6). The calculated enthalpies of formation ΔH_f^0 of these tautomers are given in Table 3.

Scheme 6



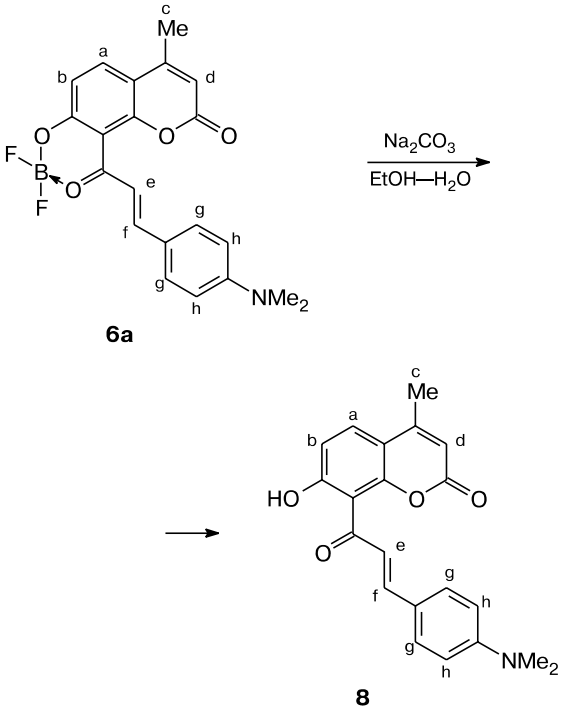
In contrast to 3-acetyl-4-hydroxycoumarin, the chromane-2,4-dione form **B** is more stable for all compounds **7**. A very small (0.18—0.70 kcal mol^{-1}) difference in the enthalpies of formation of the two tautomers allow their interconversions. This is confirmed by the isosbestic point at 370 nm in the electronic absorption spectrum.

Table 3. AM1- and PM3-calculated enthalpies of formation (ΔH_f^0) and relative energies (E_{rel}) of the tautomers **A** and **B** of compounds **7a,b,g**

Compound	Tautomer	$-\Delta H_f^0$ (E_{rel})/kcal mol^{-1}	
		AM1	PM3
7a	**A**	57.72 (0.32)	83.55 (0.25)
	B	58.04 (0.00)	83.80 (0.00)
7b	**A**	132.37 (0.70)	140.45 (0.43)
	B	133.07 (0.00)	140.88 (0.00)
7g	**A**	140.19 (0.47)	161.07 (0.18)
	B	140.66 (0.00)	161.24 (0.00)

Under analogous conditions, hydrolysis of boron complex **6a** easily gave 8-(4-dimethylaminocinnamoyl)-7-hydroxy-4-methylcoumarin (**8**) (Scheme 7).

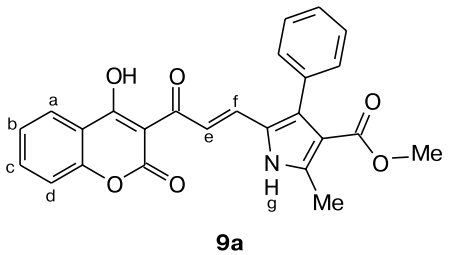
Scheme 7

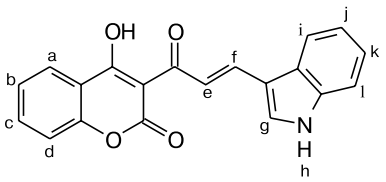


The structure of compound **8** was proven by ^{1}H NMR spectroscopy in $CDCl_3$. Apart from signals for the benzene protons, the spectrum shows signals for the olefinic protons as two doublets at δ 8.04 and 8.09 with J = 15.2 Hz. The OH proton resonates as a singlet at δ 14.38. The mass spectrum of compound **8** contains a molecular ion peak with m/z 349 (I_{rel} = 45%).

The electronic absorption spectrum of compound **8** shows an intense narrow band in the visible region, which is shifted by 102 nm to the shorter wavelengths compared to the spectrum of compound **6a**.

Analogous hydrolysis of complexes **5a,b** yielded compounds **9a,b**.



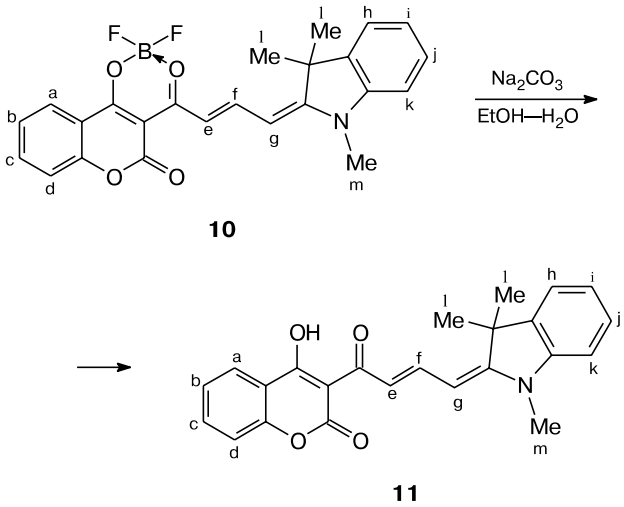


9b

Compound **9b** absorbs at shorter (by 46 nm) wavelengths than the starting boron complex **5b**.

Hydrolysis of boron complex **10** (see Ref. 6) gave (*E*,*E*)-4-hydroxy-3-[4-(1,3,3-trimethyl-2,3-dihydroindol-2-ylidene)but-2-enoyl]coumarin(**11**) (Scheme 8).

Scheme 8



10

11

The electronic absorption spectrum of compound **11** shows a hypsochromic shift of the longer-wavelength band by 38 nm and no vibrational structure characteristic of compound **9a**.

Experimental

^{1}H NMR spectra were recorded on a Bruker WP-200-SY instrument in DMSO-d_6 and $CDCl_3$ with Me_4Si as the internal standard. ^{11}B NMR spectra were recorded on a Bruker WM-250 instrument (DMSO-d_6). Electronic absorption spectra were recorded on a Specord UV—Vis spectrometer ($CHCl_3$). GC-MS spectra were recorded on a PE SCIEX API165 spectrometer with ELSD and $UV_{254\ nm}$ detectors.

Quantum-chemical semiempirical AM1 and PM3 calculations were performed with the MOPAC program package.[7] For preliminary geometry optimization, the molecular mechanics method (MM+ version) was used.

Condensation of boron complexes 1 and 2 with aldehydes. ***A.*** A solution of an aldehyde (4 mmol) in Ac_2O (2 mL) was added at 60 °C to a solution of boron complex **1**[8] or **2**[8] (4 mmol) in Ac_2O (10 mL). The mixture was heated at 90 °C for 30 min. On cooling, the precipitate that formed was filtered off, washed with AcOH, and recrystallized from AcOH.

B. A solution of an aldehyde (4 mmol) in AcOH (2 mL) and conc. H_2SO_4 (0.5 mL) were added at 60 °C to a solution of boron complex **1** or **2** (4 mmol) in AcOH (6 mL). The mixture was heated at 90 °C for 30 min. On cooling, the precipitate that formed was filtered off, washed with AcOH, and recrystallized from AcOH.

4-Difluoroboryloxy-3-[3-(4-dimethylaminophenyl)prop-2*E*-enoyl]coumarin (3a), m.p. 332—333 °C. ^{1}H NMR spectrum was not recorded because of its low solubility. MS, *m/z* (I_{rel} (%)): 383 (90).

4-Difluoroboryloxy-3-[3-(4-methoxyphenyl)prop-2*E*-enoyl]coumarin (3b), m.p. 310—312 °C. ^{1}H NMR ($CDCl_3$), δ: 3.93 (s, 3 H, Me); 7.02 (d, 2 H, H_h, H_j, J = 8.8 Hz); 7.40—7.50 (m, 3 H, H_b, H_c, H_d); 7.80 (d, 1 H, H_f, J = 14.8 Hz);7.82 (d, 2 H, H_g, H_k, J = 8.8 Hz); 8.26 (d, 1 H, H_a, J = 8.1 Hz); 8.48 (d, 1 H, H_e, J = 14.8 Hz). MS, *m/z* (I_{rel} (%)): 370 (70).

4-Difluoroboryloxy-3-[3-(4-pentyloxyphenyl)prop-2*E*-enoyl]coumarin (3c), m.p. 194—196 °C. ^{1}H NMR (acetone-d_6), δ: 0.94 (t, 3 H, Me, J = 6.5 Hz); 1.45 (m, 4 H, —CH_2CH_2—); 1.82 (m, 2 H, —CH_2—); 4.10 (t, 2 H, —OCH_2—, J = 6.8 Hz); 7.07 (d, 2 H, H_h, H_j, J = 8.9 Hz); 7.35 (m, 2 H, H_c, H_d); 7.76 (d, 2 H, H_g, H_k, J = 8.9 Hz); 7.95 (m, 2 H, H_b, H_f); 8.31 (d, 1 H, H_e, J = 15.0 Hz); 8.39 (d, 1 H, H_a, J = 8.2 Hz). MS, *m/z* (I_{rel} (%)): 426 (15).

4-Difluoroboryloxy-3-[3-(4-ethoxyphenyl)prop-2*E*-enoyl]coumarin (3d), m.p. 293—294 °C. ^{1}H NMR ($CDCl_3$), δ: 1.45 (t, 3 H, Me); 4.02 (t, 2 H, —OCH_2—); 7.14 (d, 2 H, H_h, J = 8.1 Hz); 7.40 (m, 2 H, H_c, H_d); 7.71 (d, 2 H, H_g, J = 8.1 Hz); 7.78 (t, 1 H, H_b, J = 8.1 Hz); 7.96 (d, 1 H, H_f, J = 15.1 Hz); 8.12 (d, 1 H, H_a, J = 8.1 Hz); 8.24 (d, 1 H, H_e, J = 15.1 Hz). MS, *m/z* (I_{rel} (%)): 384 (55).

4-Difluoroboryloxy-3-[3-(2,4-dimethylphenyl)prop-2*E*-enoyl]coumarin (3e), m.p. 312—313 °C. ^{1}H NMR ($CDCl_3$), δ: 1.38, 1.46 (both s, 3 H each, Me); 6.65 (m, 2 H, H_g, H_h); 7.30 (m, 2 H, H_c, H_d); 7.54 (d, 1 H, H_h, J = 7.8 Hz); 7.84 (t, 1 H, H_b, J = 8.0 Hz); 8.05 (d, 1 H, H_a, J = 8.0 Hz); 8.24 (d, 1 H, H_f, J = 14.8 Hz); 8.33 (d, 1 H, H_e, J = 14.8 Hz). MS, *m/z* (I_{rel} (%)): 368 (85).

4-Difluoroboryloxy-3-[3-(2-hydroxyphenyl)prop-2*E*-enoyl]coumarin (3f), m.p. >350 °C (decomp.). ^{1}H NMR ($CDCl_3$), δ: 6.80 (t, 1 H, H_j); 7.12 (d, 1 H, H_h, J = 7.9 Hz); 7.25 (t, 1 H, H_i, J = 7.9 Hz); 7.38 (m, 2 H, H_c, H_d); 7.60 (d, 1 H, H_k, J = 7.8 Hz); 7.71 (t, 1 H, H_b, J = 8.1 Hz); 8.04 (d, 1 H, H_a, J = 8.1 Hz); 8.38 (d, 1 H, H_f, J = 15.3 Hz); 8.46 (d, 1 H, H_e, J = 15.3 Hz). MS, *m/z* (I_{rel} (%)): 356 (100).

3-[3-(2-Acetoxyphenyl)prop-2*E*-enoyl]-4-difluoroboryloxycoumarin (3g), m.p. 268—270 °C. ^{1}H NMR ($CDCl_3$), δ: 2.50 (s, 3 H, Me); 7.30 (m, 4 H, H_c, H_d, H_j, H_h); 7.49 (t, 1 H, H_i, J = 7.8 Hz); 7.71 (t, 1 H, H_b, J = 8.2 Hz); 7.86 (d, 1 H, H_k, J = 7.8 Hz); 8.16 (m, 2 H, H_a, H_f); 8.37 (d, 1 H, H_e, J = 15.8 Hz). MS, *m/z* (I_{rel} (%)): 398 (55).

4-Difluoroboryloxy-3-[3-(2,4-dimethoxyphenyl)prop-2*E*-enoyl]coumarin (3h), m.p. 273—274 °C. ^{1}H NMR ($CDCl_3$), δ: 3.85 (t, 3 H, MeO, J = 6.7 Hz); 3.98 (s, 3 H, MeO); 6.89 (m, 2 H, H_g, H_h); 7.36 (m, 2 H, H_c, H_d); 7.70 (d, 1 H, H_h, J = 7.9 Hz); 7.78 (t, 1 H, H_b, J = 8.1 Hz); 8.04 (d, 1 H, H_a, J = 8.1 Hz); 8.12 (d, 1 H, H_f, J = 15.0 Hz); 8.36 (d, 1 H, H_e, J = 15.0 Hz). MS, *m/z* (I_{rel} (%)): 400 (95).

4-Difluoroboryloxy-3-[3-(4-ethoxy-3-methoxyphenyl)prop-2*E*-enoyl]coumarin (3i), m.p. 297—298 °C. ^{1}H NMR ($CDCl_3$), δ: 1.46 (t, 3 H, Me, J = 6.7 Hz); 3.96 (s, 3 H, Me); 4.13 (t, 2 H,

—OCH_2—, J = 6.7 Hz); 6.83 (d, 1 H, H_h, J = 8.4 Hz); 7.21 (s, 1 H, H_g); 7.30 (m, 3 H, H_c, H_d, H_g); 7.81 (t, 1 H, H_b, J = 8.0 Hz); 8.00 (d, 1 H, H_f, J = 15.1 Hz); 8.06 (d, 1 H, H_a, J = 8.0 Hz); 8.18 (d, 1 H, H_e, J = 15.1 Hz). MS, m/z (I_{rel} (%)): 414 (96).

4-Difluoroboryloxy-3-[3-(3,4,5-trimethoxyphenyl)prop-2*E*-enoyl]coumarin (3j), m.p. 224—225 °C. ^{1}H NMR ($CDCl_3$), δ: 3.78 (s, 3 H, MeO); 3.90 (s, 6 H, $(MeO)_2$); 6.91 (s, 2 H, H_g); 7.30 (m, 2 H, H_c, H_d); 7.76 (t, 1 H, H_b, J = 8.1 Hz); 7.98 (d, 1 H, H_f, J = 14.8 Hz); 8.08 (d, 1 H, H_a, J = 8.1 Hz); 8.32 (d, 1 H, H_e, J = 14.8 Hz). MS, m/z (I_{rel} (%)): 430 (100).

4-Difluoroboryloxy-3-[5-(4-dimethylaminophenyl)penta-2*E*,4*E*-dienoyl]coumarin (4a). The yield was 84% (*A*), m.p. 300—301 °C. ^{1}H NMR ($CDCl_3$), δ: 3.12 (s, 6 H, Me_2); 6.70 (d, 2 H, H_j, J = 9.0 Hz); 7.20 (d, 1 H, H_h, J = 13.0 Hz); 7.30—7.41 (m, 3 H, H_c, H_d, H_g); 7.53 (d, 2 H, H_i, J = 9.0 Hz); 7.74 (t, 1 H, H_b, J = 8.2 Hz); 7.88 (d, 1 H, H_e, J = 13.2 Hz); 8.19 (d, 1 H, H_a, J = 8.2 Hz); 8.33 (t, 1 H, H_f, J = 13.2 Hz). MS, m/z (I_{rel} (%)): 409 (5). UV-VIS, λ_{max}/nm (ε): 638 (78100).

4-Difluoroboryloxy-3-[5-(4-methoxyphenyl)penta-2*E*,4*E*-dienoyl]coumarin (4b). The yield was 49% (*A*), m.p. 298—290 °C. ^{1}H NMR ($CDCl_3$), δ: 3.88 (s, 3 H, Me); 6.96 (d, 2 H, H_j, J = 8.8 Hz); 7.23 (d, 1 H, H_h, J = 13.4 Hz); 7.36—7.44 (m, 3 H, H_c, H_d, H_g); 7.57 (d, 2 H, H_i, J = 8.8 Hz); 7.79 (t, 1 H, H_b, J = 8.1 Hz); 8.00 (d, 1 H, H_e, J = 13.4 Hz); 8.23 (d, 1 H, H_a, J = 8.1 Hz); 8.30 (t, 1 H, H_f, J = 13.2 Hz). MS, m/z (I_{rel} (%)): 396 (30). UV-VIS, λ_{max}/nm (ε): 509 (22900).

4-Difluoroboryloxy-3-[3-(4-methoxycarbonyl-5-methyl-3-phenylpyrrol-2-yl)prop-2*E*-enoyl]coumarin (5a). The yield was 58% (*A*), m.p. >350 °C (decomp.). ^{1}H NMR ($CDCl_3$), δ: 2.66 (s, 3 H, Me); 3.48 (s, 3 H, MeO); 7.21 (m, 2 H, H_c, H_d); 7.44 (m, 5 H, H_{Ph}); 7.65 (d, 1 H, H_f, J = 15.0 Hz); 7.71 (t, 1 H, H_b, J = 8.0 Hz); 8.26 (d, 1 H, H_a, J = 8.0 Hz); 8.48 (d, 1 H, H_e, J = 15.0 Hz); 8.61 (s, 1 H, H_h). MS, m/z (I_{rel} (%)): 477 (90).

4-Difluoroboryloxy-3-[3-(3-indolyl)prop-2*E*-enoyl]coumarin (5b). The yield was 63% (*A*), m.p. 320 °C (decomp.). ^{1}H NMR (DMSO-d_6), δ: 7.36 (m, 4 H, H_i, H_j, H_k); 7.40 (m, 2 H, H_c, H_d); 7.79 (t, 1 H, H_b, J = 8.4 Hz); 8.13 (d, 1 H, H_l, J = 8.8 Hz); 8.18 (d, 1 H, H_a, J = 8.4 Hz); 8.43 (s, 1 H, H_g); 8.50 (d, 1 H, H_f, J = 14.6 Hz); 8.85 (d, 1 H, H_e, J = 14.6 Hz); 12.51 (s, 1 H, H_h). MS, m/z (I_{rel} (%)): 379 (10).

3-[3-(6-Bromo-9-propylcarbazol-3-yl)prop-2*E*-enoyl]-4-difluoroboryloxycoumarin (5c). The yield was 21% (*A*), m.p. >350 °C (decomp.). ^{1}H NMR ($CDCl_3$), δ: 0.99 (t, 3 H, Me, J = 6.3 Hz); 1.93 (m, 2 H, CH_2); 4.28 (t, 2 H, NCH_2, J = 7.0 Hz); 7.30—7.40 (m, 4 H, H_c, H_d, H_i, H_k); 7.46 (d, 1 H, H_h, J = 9.2 Hz); 7.59 (t, 1 H, H_b, J = 8.1 Hz); 7.96 (d, 1 H, H_a, J = 8.1 Hz); 8.24 (m, 2 H, H_j, H_l); 8.50—8.70 (m, 3 H, H_e, H_f, H_g). MS, m/z (I_{rel} (%)): 550 (5).

7-Difluoroboryloxy-8-[3-(4-dimethylaminophenyl)prop-2*E*-enoyl]-4-methylcoumarin (6a). The yield was 86% (*A*), m.p. 328—330 °C. ^{1}H NMR spectrum was not recorded because of its low solubility. MS, m/z (I_{rel} (%)): 397 (90).

7-Difluoroboryloxy-8-[3-(4-methoxyphenyl)prop-2*E*-enoyl]-4-methylcoumarin (6b). The yield was 52% (*A*), m.p. 289—291 °C (decomp.). ^{1}H NMR ($CDCl_3$), δ: 2.45 (d, 3 H, H_c, J = 1.0 Hz); 4.16 (s, 3 H, MeO); 6.27 (d, 1 H, H_d, J = 1.0 Hz); 6.85 (d, 2 H, H_h, J = 8.9 Hz); 6.94 (d, 1 H, H_b, J = 8.1 Hz); 7.64 (m, 3 H, H_a, H_g); 8.14 (d, 1 H, H_f, J = 15.2 Hz); 8.25 (d, 1 H, H_e, J = 15.2 Hz). MS, m/z (I_{rel} (%)): 384 (85).

Hydrolysis of boron complexes 3a—j, 5a,b, 6a, and 10. An appropriate boron complex **3a—j**, **5a,b**, **6a**, or **10** (3 mmol) was dissolved in aqueous 60% EtOH (10 mL) (see Ref. 6) and anhydrous Na_2CO_3 (1.59 g, 15 mmol) was added. The reaction mixture was refluxed for 1—5 h until the starting boron complex was completely consumed (monitoring by TLC). On cooling, the resulting solution was filtered and acidified to pH 6.5—7. The precipitate that formed was filtered off, washed with water, and recrystallized from propan-2-ol.

3-[3-(4-Dimethylaminophenyl)prop-2*E*-enoyl]-4-hydroxycoumarin (7a), m.p. 212—213 °C. ^{1}H NMR (DMSO-d_6+TFA), δ: 3.05 (s, 6 H, Me_2); 6.82 (d, 2 H, H_h, J = 8.0 Hz); 7.35 (m, 2 H, H_c, H_d); 7.61 (d, 2 H, H_g, J = 8.0 Hz); 7.75 (t, 1 H, H_b, J = 8.0 Hz); 8.00 (d, 1 H, H_a, J = 8.0 Hz); 8.05 (d, 1 H, H_f, J = 12.4 Hz); 8.12 (d, 1 H, H_e, J = 12.4 Hz). MS, m/z (I_{rel} (%)): 335 (100).

4-Hydroxy-3-[3-(4-methoxyphenyl)prop-2*E*-enoyl]coumarin (7b), m.p. 185—186 °C. ^{1}H NMR (DMSO-d_6), δ: 3.72 (s, 3 H, Me); 7.01 (d, 2 H, H_h, J = 8.1 Hz); 7.40 (m, 2 H, H_c, H_d); 7.71 (d, 2 H, H_g, J = 8.1 Hz); 7.74 (t, 1 H, H_b, J = 8.0 Hz); 7.98 (d, 1 H, H_f, J = 15.1 Hz); 8.13 (d, 1 H, H_a, J = 8.0 Hz); 8.31 (d, 1 H, H_e, J = 15.1 Hz). MS, m/z (I_{rel} (%)): 322 (70).

4-Hydroxy-3-[3-(4-pentyloxyphenyl)prop-2*E*-enoyl]coumarin (7c), m.p. 140—142 °C. ^{1}H NMR ($CDCl_3$), δ: 0.94 (t, 3 H, Me, J = 6.4 Hz); 1.46 (m, 4 H, CH_2CH_2); 1.79 (m, 2 H, CH_2); 4.02 (t, 2 H, OCH_2, J = 6.7 Hz); 6.94 (d, 2 H, H_h, H_j, J = 9.0 Hz); 7.30 (m, 2 H, H_c, H_d); 7.67 (m, 3 H, H_b, H_g, H_k); 8.10 (m, 2 H, H_a, H_f); 8.34 (d, 1 H, H_e, J = 15.4 Hz); 19.06 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 378 (40).

3-[3-(4-Ethoxyphenyl)prop-2*E*-enoyl]-4-hydroxycoumarin (7d), m.p. 182—183 °C. ^{1}H NMR (DMSO-d_6), δ: 1.41 (t, 3 H, Me, J = 6.9 Hz); 4.12 (t, 2 H, OCH_2, J = 6.9 Hz); 7.04 (d, 2 H, H_h, J = 8.1 Hz); 7.38 (m, 2 H, H_c, H_d); 7.71 (d, 2 H, H_g, J = 8.1 Hz); 7.78 (t, 1 H, H_b, J = 8.0 Hz); 7.96 (d, 1 H, H_f, J = 15.1 Hz); 8.10 (d, 1 H, H_a, J = 8.0 Hz); 8.34 (d, 1 H, H_e, J = 15.1 Hz). MS, m/z (I_{rel} (%)): 336 (65).

3-[3-(2,4-Dimethylphenyl)prop-2*E*-enoyl]-4-hydroxycoumarin (7e), m.p. 161—162 °C. ^{1}H NMR (DMSO-d_6), δ: 1.42, 1.47 (both s, 3 H each, Me); 6.75 (m, 2 H, H_g, H_h); 7.35 (m, 2 H, H_c, H_d); 7.69 (d, 1 H, H_h, J = 8.0 Hz); 7.76 (t, 1 H, H_b, J = 8.1 Hz); 8.03 (d, 1 H, H_a, J = 8.1 Hz); 8.22 (d, 1 H, H_f, J = 14.8 Hz); 8.30 (d, 1 H, H_e, J = 14.8 Hz). MS, m/z (I_{rel} (%)): 320 (95).

4-Hydroxy-3-[3-(2-hydroxyphenyl)prop-2*E*-enoyl]coumarin (7f), m.p. 154—155 °C. ^{1}H NMR (DMSO-d_6), δ: 6.83 (t, 1 H, H_j, J = 8.0 Hz); 6.91 (d, 1 H, H_h, J = 8.4 Hz); 7.21 (t, 1 H, H_i, J = 8.4 Hz); 7.31 (m, 2 H, H_c, H_d); 7.58 (d, 1 H, H_k, J = 8.9 Hz); 7.71 (t, 1 H, H_b, J = 7.9 Hz); 8.03 (d, 1 H, H_a, J = 7.9 Hz); 8.36 (d, 1 H, H_f, J = 15.3 Hz); 8.41 (d, 1 H, H_e, J = 15.3 Hz). MS, m/z (I_{rel} (%)): 308 (100).

3-[3-(2-Acetoxyphenyl)prop-2*E*-enoyl]-4-hydroxycoumarin (7g), m.p. 174—175 °C. ^{1}H NMR ($CDCl_3$), δ: 2.48 (s, 3 H, Me); 7.25 (d, 1 H, H_j, J = 8.4 Hz); 7.34 (m, 3 H, H_c, H_d, H_h); 7.45 (t, 1 H, H_i, J = 8.7 Hz); 7.70 (t, 1 H, H_b, J = 8.2 Hz); 7.83 (d, 1 H, H_k, J = 8.4 Hz); 8.10 (m, 2 H, H_a, H_f); 8.50 (d, 1 H, H_e, J = 15.8 Hz); 18.79 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 350 (35).

3-[3-(2,4-Dimethoxyphenyl)prop-2*E*-enoyl]-4-hydroxycoumarin (7h), m.p. 143—144 °C. ^{1}H NMR (DMSO-d_6), δ: 3.81 (t, 3 H, MeO); 3.92 (s, 3 H, MeO); 6.70 (m, 2 H, H_g, H_h); 7.35 (m, 2 H, H_c, H_d); 7.63 (d, 1 H, H_h, J = 8.5 Hz); 7.76 (t, 1 H, H_b, J = 7.8 Hz); 8.03 (d, 1 H, H_a, J = 7.8 Hz); 8.22 (d, 1 H, H_f,

J = 14.8 Hz); 8.30 (d, 1 H, H_e, J = 14.8 Hz). MS, m/z (I_{rel} (%)): 352 (95).

3-[3-(4-Ethoxy-3-methoxyphenyl)prop-2*E*-enoyl]-4-hydroxycoumarin (7i), m.p. 169—171 °C. ^{1}H NMR (DMSO-d_6), δ: 1.41 (t, 3 H, Me, J = 6.8 Hz); 3.87 (s, 3 H, Me); 4.12 (t, 2 H, OCH_2, J = 6.8 Hz); 6.77 (d, 1 H, H_h, J = 8.4 Hz); 7.20 (s, 1 H, H_g); 7.33 (m, 3 H, H_c, H_d, H_g); 7.80 (t, 1 H, H_b, J = 7.8 Hz); 7.96 (d, 1 H, H_f, J = 15.1 Hz); 8.06 (d, 1 H, H_a, J = 7.8 Hz); 8.17 (d, 1 H, H_e, J = 15.1 Hz). MS, m/z (I_{rel} (%)): 366 (85).

4-Hydroxy-3-[3-(3,4,5-trimethoxyphenyl)prop-2*E*-enoyl]coumarin (7j), m.p. 189—190 °C. ^{1}H NMR (DMSO-d_6), δ: 3.76 (s, 3 H, MeO); 3.91 (s, 6 H, $(MeO)_2$); 6.87 (s, 2 H, H_g); 7.32 (m, 2 H, H_c, H_d); 7.76 (t, 1 H, H_b, J = 8.0 Hz); 7.95 (d, 1 H, H_f, J = 15.2 Hz); 8.03 (d, 1 H, H_a, J = 8.0 Hz); 8.22 (d, 1 H, H_e, J = 15.2 Hz). MS, m/z (I_{rel} (%)): 382 (100).

8-[3-(4-Dimethylaminophenyl)prop-2*E*-enoyl]-7-hydroxy-4-methylcoumarin (8). The yield was 70%, m.p. 240—241 °C. ^{1}H NMR ($CDCl_3$), δ: 2.42 (d, 3 H, H_c, J = 1.0 Hz); 3.06 (s, 6 H, Me_2); 6.16 (d, 1 H, H_d, J = 1.0 Hz); 6.67 (d, 2 H, H_h, J = 9.0 Hz); 6.92 (d, 1 H, H_b, J = 8.1 Hz); 7.64 (m, 3 H, H_a, H_g); 8.04 (d, 1 H, H_f, J = 15.2 Hz); 8.09 (d, 1 H, H_e, J = 15.2 Hz); 14.38 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 349 (45).

Methyl 5-[3-(4-hydroxycoumarin-3-yl)-3-oxoprop-1*E*-enyl]-2-methyl-4-phenyl-1*H*-pyrrole-3-carboxylate (9a). The yield was 75%, m.p. 210—212 °C. ^{1}H NMR (DMSO-d_6+TFA), δ: 2.60 (s, 3 H, Me); 3.54 (s, 3 H, MeO); 7.25 (m, 2 H, H_c, H_d); 7.40 (m, 5 H, H_{Ph}); 7.59 (d, 1 H, H_f, J = 15.0 Hz); 7.70 (t, 1 H, H_b, J = 8.4 Hz); 8.18 (d, 1 H, H_a, J = 8.4 Hz); 8.45 (d, 1 H, H_e, J = 15.0 Hz); 8.53 (s, 1 H, H_g). MS, m/z (I_{rel} (%)): 429 (94).

4-Hydroxy-3-[3-(3-indolyl)prop-2*E*-enoyl]coumarin (9b). The yield was 80%, m.p. 250 °C (decomp.). ^{1}H NMR ($CDCl_3$), δ: 7.32—7.42 (m, 5 H, H_c, H_d, H_i, H_j, H_l); 7.45 (t, 1 H, H_k, J = 9.1 Hz); 7.70 (t, 1 H, H_b, J = 8.0 Hz); 7.76 (s, 1 H, H_g); 8.18 (d, 1 H, H_a, J = 9.1 Hz); 8.39 (d, 1 H, H_f, J = 15.0 Hz); 8.45 (d, 1 H, H_e, J = 15.0 Hz); 8.53 (s, 1 H, H_h); 19.24 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 331 (78).

(*E*,*E*)-4-Hydroxy-3-[4-(1,3,3-trimethyl-2,3-dihydroindol-2-ylidene)but-2-enoyl]coumarin (11). The yield was 58%, m.p. 229—231 °C. ^{1}H NMR ($CDCl_3$), δ: 1.69 (s, 6 H, H_l); 3.36 (s, 3 H, H_m); 5.90 (d, 1 H, H_g, J = 13.4 Hz); 6.88 (d, 1 H, H_k, J = 8.9 Hz); 7.09 (d, 1 H, H_h, J = 8.7 Hz); 7.23—7.30 (m, 4 H, H_c, H_d, H_i, H_j); 7.56 (d, 1 H, H_e, J = 13.4 Hz); 7.60 (t, 1 H, H_b, J = 8.1 Hz); 8.10 (d, 1 H, H_a, J = 8.1 Hz); 8.55 (t, 1 H, H_f, J = 13.4 Hz); 18.92 (s, 1 H, OH). MS, m/z (I_{rel} (%)): 387 (45).

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