Diversity-Oriented Synthesis of Novel Trihalomethyl-Containing Spirochromeno[3,4-*a*](thia)pyrrolizidines and Spirochromeno[3,4-*a*]indolizidines by One-Pot, Three-Component [3+2]-Cycloaddition Reaction

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Received: 13.11.2020

Accepted after revision: 05.12.2020

Published online: 04.01.2021

DOI: 10.1055/s-0040-1706005; Art ID: so-2020-d0043-op

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Abstract Regio- and stereoselective methods for the synthesis of 6'-trifluoro(trichloro)methyl substituted spiro[acenaphthylene-1,11'-chromeno[3,4-*a*](thia)pyrrolizidin]-2-ones and spiro[acenaphthylene-1,12'-chromeno[3,4-*a*]indolizidin]-2-ones have been developed based on the three-component reaction of 3-nitro-2-trifluoro(trichloro)methyl-2H-chromenes with azomethine ylides generated in situ from acenaphthenequinone and cyclic α -amino acids. The cycloaddition proceeds under mild conditions in ethanol or DMSO, and only *endo*-isomers of the products with *cis*-arrangement of nitro and trifluoromethyl groups are formed. The relative configuration of cycloadducts is reliably confirmed by X-ray diffraction analysis and by 2D NOESY spectroscopy.

Key words 3-nitro-2-trifluoro(trichloro)methyl-2H-chromenes, 1,3-dipolar cycloaddition, azomethine ylides, acenaphthenequinone, cyclic α -amino acids

Diversity-oriented synthesis (DOS) of small molecules followed by screening of these molecules for their ability to modulate a biological pathway in cells or organisms is one of the most effective and dynamically developing approaches to modern drug discovery. In the last decade, special attention has been paid to increasing the structural and functional diversity in the construction of collections of small molecules.¹

One DOS approach involves the creation of compound libraries based on privileged molecular scaffolds, ubiqui-

tous in clinically significant bioactive natural products, followed by an increase in the scaffold diversity about the privileged skeleton. From this point of view, 3-nitro-2-trifluoro(trichloro)methyl-2H-chromenes² are suitable starting compounds for privileged-substructure-based DOS. The molecular cores of chromenes and chromanes are present in the skeleta of numerous natural and synthetic bioactive compounds.^{2,3} For example, 3-nitro-2-trifluoromethyl-2H-chromene (TIM-38) has been shown to be a P2Y6 receptor inhibitor and a promising anti-inflammatory agent (Figure 1).^{4a} 6-Bromo-8-ethoxy-3-nitro-2H-chromene (BENC-511) exhibits antitumor activity against various cancer cell lines due to the inhibition of phosphoinositide 3-kinase.^{4b} It was recently found that 6-CF₃-spiro[chromenopyrrolidine-1,3'-oxindoles] (**A**) have a pronounced cytotoxic activity against HeLa human cervical cancer cells.^{4c} Glabridin, an isoflavane, isolated from the roots of *Glycyrrhiza glabra*, is a drug candidate for memory improvement.^{4d}

Figure 1 Representatives of synthetic and natural bioactive chromene and chromane derivatives

Due to the presence of the β -nitrostyrene fragment, 3-nitro-2*H*-chromenes actively react with nucleophiles and 1,3-dipoles. The replacement of the hydrogen atom in the 2-position with a more bulky trifluoro(trichloro)methyl group with a pronounced negative inductive effect leads to an increase in the stereoselectivity of nucleophilic addition and cycloaddition at the C=C bond.² It should be noted that nitrochromenes **1** (see Scheme 1) are readily available and can be obtained from 1-nitro-3,3,3-trifluoro(trichloro)-1-nitroprop-1-enes and the corresponding salicylaldehydes in good yield.⁵

On the other hand, the trifluoromethyl group is a pharmacophore fragment that is present in a wide variety of drugs due to its increased lipophilicity and greater strength of the C–F bond compared to the C–H bond.⁶ Among CCl_3 -containing organic molecules, compounds with GII1-inhibitory, anthelmintic, antiparasmodial and 5-HT-inhibitory effects are known.⁷

1,3-Dipolar cycloaddition (1,3-DC) of stabilized azomethine ylides to activated alkenes is the shortest and the most efficient route to construction of the spiropyrrolizidine and spiroindolizidine ring systems in a single reaction step.⁸ This procedural-, atom-, and stage-economic (PASE)⁹ strategy allows the creation of large libraries of such spiro-heterocycles from available reagents using a simple methodology based on intermolecular three-component reactions.¹⁰ Intensive developments in this direction have led to the production of new representatives of spiropyrrolizidines with anticancer^{11a} (**B**), antimicrobial^{11b} (**C**), and AChE-inhibitory^{11c} (**D**) activities, as depicted in Figure 2. Pyrrolizidine and indolizidine scaffolds are ubiquitous in natural compounds. In particular, pteropodine is an alkaloid isolated from *Uncaria tomentosa* that acts as a positive modulator of muscarinic M_1 and 5-HT₂ receptors and may be involved in the improvement of impaired higher cognitive processes.^{11d} Moreover, pteropodine has shown a pronounced enhancement effect on phagocytosis,^{11e} as well as cytostatic^{11f} and antimutagenic^{11g} properties and is used in traditional medicine to cure a number of diseases (Figure 2).

The cycloaddition of stabilized azomethine ylides based on acenaphthenequinone and α -amino acids to activated alkenes is being intensively studied.^{8d,e,12} This is largely due to the fact that the spiroacenaphthyleneone fragment is present in a number of synthetic compounds that have biological properties, including antimycobacterial^{13a,b} (**D**, **E**) and antimalarial (**F**) activities.^{13c} As was recently found, the spiroindolizidine derivative **G** is capable of enhancing osteoblast differentiation of human stem cells (Figure 3).^{13d}

Continuing our research aimed at studying the regio- and stereoselectivity of reaction of 1,3-DC of azomethine ylides with 3-nitro-2-trifluoro(trichloro)methyl-2*H*-chromenes,¹⁴ in this work we report the regioselective and diastereoselective synthesis of chromene-spiro(thia)pyrrolizidine and chromene-spiroindolizidine hybrids **4**, **6** and

Figure 2 Representatives of synthetic and natural bioactive spiro(thia)pyrrolizidines and spiroindolizidines

Figure 3 Representatives of bioactive spiroacenaphthylene-2-ones

7 from nitrochromenes **1**, acenaphthenequinone **2** and cyclic α -amino acids **3** and **5** by a one-pot, three-component [3+2]-cycloaddition approach (Scheme 1).

Diversity of substrates and reagents was provided by varying the substituents R^1 and R^2 in the benzene ring of the starting nitrochromenes, as well as the use of four cyclic α -amino acids (L-proline, L-thiaproline, L-pipecolic acid, (S)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid) in the 1,3-DC reaction. Diversity of pharmacophores was ensured by the presence of chromane, spiro(thia)pyrrolizidine, spiroindolizidine and spiroacenaphthyleneone scaffolds in the target products along with the trifluoro(trichloro)methyl group at the 6' position.

First, the three-component reaction between nitrochromenes **1**, acenaphthenequinone **2** and (thia)proline **3** was studied. To obtain spirochromeno[3,4-*a*](thia)pyrrolizidines **4**, conditions optimization for a model reaction of nitrochromene **1a** with azomethine ylide generated in situ from acenaphthenequinone **2** and L-proline **3a** was performed (Table 1). When the reaction was carried out in methanol or ethanol at reflux, the target product **4a** was obtained as a single *endo* isomer in moderate yield after 2 h,

Scheme 1 Strategy for the diversity-oriented synthesis of spiro(thia)pyrrolizidines and spiroindolizidines based on 3-nitro-2-trifluoro(trichloro)methyl-2H-chromenes

but a notable darkening of the reaction mixture was observed (entries 1 and 3). Lowering the temperature to 55 °C led to an increase in product yield (entries 2 and 4). At the same temperature in isopropanol the product yield was lower (entry 5). In acetonitrile and DMSO, the target product was obtained even at room temperature within 24 h in 46% and 68% yield, respectively (entries 6 and 7). When THF was used as a solvent at room temperature over 2.5 h, a complex mixture of products was observed (entry 9). When benzene or toluene were used as solvents, the yields of the target product were noticeably lower (entries 10 and 11).

The best results were achieved when the reaction was carried out in ethanol or DMSO at 55 °C (Table 1, entries 4 and 8). In both cases, the reaction was complete after 3 h and product **4a** was obtained in 77 and 75% yields, respectively. Considering the ease of removal of the solvent and its cost, we chose ethanol as the preferred solvent for the synthesis of compounds **4**. No other regio- or stereoisomers were detected in the crude products by ^1H NMR spectroscopic analysis.

Under the optimized conditions, the spirochromeno[3,4-*a*]pyrrolizidines **4a–q** and spirochromeno[3,4-*a*]thiapyrrolizidines **4r–y** were obtained in 36–89% yields in ethanol at 55 °C for 1–3.5 h using acenaphthenequinone **2**, L-proline **3a** or L-thiaproline **3b** and 2-CX₃ substituted (X = F, Cl) 3-nitro-2H-nitrochromenes **1** containing electron-donating or electron-withdrawing groups in the benzene ring (Table 2). Note that due to their low solubility, the target products were isolated from the reaction mixture by filtration and purified by washing with ethanol and water.

In general, the nature of halogen and substituents R^1 , R^2 in the starting chromene **1** has little effect on the yield of products **4**. However, introduction of electron-deficient substituents such as Cl, Br or NO₂ into the benzene ring of the chromene reduced the reaction time to 1–2 h, while reactions with chromenes containing electron-donating

Table 1 Conditions Optimization^a

Entry	Solvent	Temp (°C)	Time (h)	Yield (%) ^b
1	MeOH	reflux	2	55 ^c
2	MeOH	55	2.5	67
3	EtOH	reflux	2	54 ^c
4	EtOH	55	3	77
5	<i>i</i> -PrOH	55	3	43
6	MeCN	25	24	46
7	DMSO	25	24	68
8	DMSO	55	3	75
9	THF	25	2.5	— ^d
10	PhH	55	3	57
11	PhMe	55	3	57

^a Reaction conditions: **1a** (0.1 mmol), **2** (0.1 mmol), **3a** (0.13 mmol), solvent (2 mL).

^b Isolated yield.

^c Noticeable resinification.

^d A complex mixture of products was formed.

groups (R^1 , R^2 = Me, OMe, OEt) under the same conditions were complete after 3–3.5 h. 1,3-DC involving the ylide from thiaproline was accompanied by lower yields (36–72%). In this case, the lowest yields (39 and 36%, respectively) were obtained for adducts **4v** and **4w** from 2-trichloromethyl substituted chromenes **1j** and **1l**.

Table 2 Synthesis of Spirochromeno[3,4-*a*](thia)pyrrolizidines **4**

Entry	Chromene	X	R ¹	R ²	Product	Y	Time (h)	Yield (%) ^a	Entry	Chromene	X	R ¹	R ²	Product	Y	Time (h)	Yield (%) ^a
1	1a	F	H	H	4a	CH ₂	3	77	14	1n	Cl	Cl	H	4n	CH ₂	2	82
2	1b	F	Me	H	4b	CH ₂	3	78	15	1o	Cl	Cl	Cl	4o	CH ₂	2	78
3	1c	F	OMe	H	4c	CH ₂	3.5	78	16	1p	Cl	NO ₂	H	4p	CH ₂	1	79
4	1d	F	H	OEt	4d	CH ₂	3.5	80	17	1q	Cl	NO ₂	NO ₂	4q	CH ₂	1	82
5	1e	F	Cl	H	4e	CH ₂	2	81	18	1a	F	H	H	4r	S	3	56
6	1f	F	Cl	Cl	4f	CH ₂	2	67	19	1c	F	OMe	H	4s	S	3	61
7	1g	F	Br	OEt	4g	CH ₂	2	81	20	1f	F	Cl	Cl	4t	S	2	72
8	1h	F	NO ₂	H	4h	CH ₂	1	89	21	1h	F	NO ₂	H	4u	S	1	66
9	1i	F	NO ₂	NO ₂	4i	CH ₂	1	81	22	1j	Cl	H	H	4v	S	3	39
10	1j	Cl	H	H	4j	CH ₂	3	76	23	1l	Cl	OMe	H	4w	S	3	36
11	1k	Cl	Me	H	4k	CH ₂	3	71	24	1o	Cl	Cl	Cl	4x	S	2	65
12	1l	Cl	OMe	H	4l	CH ₂	3.5	75	25	1q	Cl	NO ₂	NO ₂	4y	S	1	69
13	1m	Cl	H	OEt	4m	CH ₂	3.5	63									

^a Isolated yield.

In contrast to α,β -unsaturated ketones and carboxylic acid derivatives, the reactions of strongly polar nitrostyrenes and 3-nitro-2*H*-chromenes with stabilized azomethine ylides based on cyclic carbonyl compounds and amino acids were accompanied by the binding of a more electrophilic β -C atom of the dipolarophile with the more substituted atom of the 1,3-dipole,⁸ apparently due to the charge-controlled cycloaddition. A possible reaction mechanism involves the *endo*-addition of the S-shaped azomethine ylide to nitrochromene **1** through **TS-1** (see Table 2). In addition, the ylide attacks the C=C bond from the side of the small H-2 atom, rather than from the side of the trifluoromethyl group. In the *exo*-transition state **TS-2** the pyran

ring of the chromene and the (thia)proline moiety of ylide are located one under the other, making it less favorable due to unfavorable steric interactions (Table 2).

Next, to obtain spirochromeno[3,4-*a*]indolizidines **6** and **7**, reactions of chromenes **1** with azomethine ylides based on acenaphthenequinone **2** and L-pipecolic acid **5a** or (S)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid **5b** were studied. Due to the low solubility of both amino acids in ethanol, DMSO was used as a solvent and a little water was added when L-pipecolic acid was used as reagent. It was found that these three-component reactions proceeded at 60–70 °C within 7 or 12 h and led to the corresponding products **6** or **7** as single isomers in 42–71% yields (Table 3).

Table 3 Synthesis of Spirochromeno[3,4-*a*]indolizidines **6** and **7**

Entry	Chromene	X	R ¹	R ²	Product	Yield (%) ^a	Entry	Chromene	X	R ¹	R ²	Product	Yield (%) ^a
1	1a	F	H	H	6a	58	12	1m	Cl	H	OEt	6l	49
2	1b	F	Me	H	6b	62	13	1n	Cl	Cl	H	6m	50
3	1c	F	OMe	H	6c	58	14	1o	Cl	Cl	Cl	6n	55
4	1d	F	H	OEt	6d	56	15	1a	F	H	H	7a	52
5	1e	F	Cl	H	6e	62	16	1b	F	Me	H	7b	71
6	1f	F	Cl	Cl	6f	64	17	1c	F	OMe	H	7c	63
7	1g	F	Br	OEt	6g	60	18	1d	F	H	OEt	7d	64
8	1h	F	NO ₂	H	6h	67	19	1e	F	H	Cl	7e	62
9	1j	Cl	H	H	6i	43	20	1f	F	Cl	Cl	7f	68
10	1k	Cl	Me	H	6j	44	21	1g	F	Br	OEt	7g	58
11	1l	Cl	OMe	H	6k	42	22	1h	F	NO ₂	H	7h	48

^a Isolated yield.

As shown in Table 3, the donor-acceptor properties of substituents on the chromene have little effect on the target product yield. At the same time, the yields of 6'-trichloromethyl substituted spirochromeno[3,4-*a*]indolizidines **6** were always 7–18% lower than the yields of the corresponding CF₃-substituted products.

Due to the low solubility of adducts **6** in the DMSO/H₂O mixture, most of them were isolated from the reaction mixture by filtration and purified by recrystallization. Spiroadducts **7**, soluble in DMSO, were precipitated from the reaction mixture by adding water and purified by column chromatography.

The IR spectra of products **4**, **6** and **7** show the stretching vibrations of the carbonyl group ($\nu = 1697\text{--}1728\text{ cm}^{-1}$) and the NO₂ group ($\nu = 1547\text{--}1566\text{ cm}^{-1}$, $1327\text{--}1345\text{ cm}^{-1}$). In the ¹H NMR spectra of spirochromeno[3,4-*a*](thia)pyrrolizidines **4** and spirochromeno[3,4-*a*]indolizidines **6** and **7** in CDCl₃, the characteristic singlet of the benzylic H-11a' proton (H-12a' proton and H-14a' proton in compounds **6** and **7**, respectively) at $\delta = 4.58\text{--}5.39\text{ ppm}$ was observed. The signal of the H-6' proton was manifest as quartet at $\delta = 5.43\text{--}6.56\text{ ppm}$ with coupling constants $^3J_{\text{HF}} = 5.5\text{--}6.8\text{ Hz}$ in the 6'-CF₃ substituted compounds **4**, **6**, and **7** or as a singlet at $\delta = 5.67\text{--}6.93\text{ ppm}$ in the 6'-CCl₃ substituted compounds **4** and **6**. The H-1' aromatic proton was shielded in all adducts by the benzene ring of acenaphthene moiety, such that its signal is shifted upfield relative to other aromatic protons of the chromene ring and resonates at $\delta = 5.04\text{--}$

6.88 ppm. The ¹⁹F NMR spectra of 6'-CF₃ substituted compounds **4**, **6**, and **7** contain a doublet or broad singlet due to the trifluoromethyl group at $\delta = 90.4\text{--}95.9\text{ ppm}$. The ¹³C NMR spectra of products **4**, **6**, and **7** exhibit a carbonyl carbon signal at $\delta = 202.9\text{--}208.9\text{ ppm}$ and quartets due the CF₃ group and the C-6' atom are observed in the range of 121.1–123.4 and 76.8–77.7 ppm, respectively, with coupling constants $^1J_{\text{CF}} = 280.9\text{--}284.4\text{ Hz}$ and $^2J_{\text{CF}} = 32.2\text{--}34.8\text{ Hz}$.

The reaction of 3,6-dinitro-2-trichloromethyl-2H-chromene **1p** with the azomethine ylide based on **2** and pipelicolic acid **5a** was accompanied by the elimination of HCl and led to a mixture of the target product **6o** and 2-dichloromethylidene derivative **8** in a 76:24 ratio (Scheme 2). It was not possible to isolate compounds **6o** and **8** in their pure form.

In the ¹H NMR spectrum of compound **8** there was no signal for the H-6 proton, while in its ¹³C NMR spectrum, 21 signals of sp²-carbon atoms were observed. Moreover, the mass spectrum of the crude product obtained in the positive ion mode ESI-HRMS showed a peak at m/z 552.0727 that corresponded to the molecular ion [**8**+H]⁺ along with the molecular ion [**6o**+H]⁺ at m/z 588.0494. A similar outcome has been previously observed in reactions of 2-trichloromethyl substituted nitrochromenes **1** with sodium azide^{15a} and in the interaction of (*E*)-3,3,3-trichloro-1-nitroprop-1-ene with diaryldiazomethanes.^{15b} The elimination of HCl is probably the main reason for the lower yields of 6'-CCl₃ products **6** compared to their 6'-CF₃ analogues.

It was not possible to obtain spirocycloadducts **7** in the reaction of 2-CCl₃ substituted nitrochromenes **1** with azomethine ylide from **2** and tetrahydroisoquinoline-3-carboxylic acid **5b**. The reaction did not proceed at 60 °C and extensive decomposition was observed at higher temperatures. This may be due to the formation of unstable 2-(di-chloromethylidene)nitrochromenes at 70 °C.^{15a}

The structures and relative configurations of compounds **4**, **6**, and **7** were unambiguously confirmed by X-ray diffraction studies of products **4a** and **6g** (Figures 4 and 5) and by a 2D ¹H-¹H NOESY experiment for product **7g** (Figure 6).

As seen in Figure 4 and Figure 5, in both molecules the carbonyl group of the acenaphthyleneone moiety and the nitro group are located on opposite sides of the plane of the condensed heterocycle, while the nitro group, CF₃ group,

and hydrogen atoms H-12a' (H-14a' in compound **6g**) and H-6b' are on the same side of this plane.

The 2D ¹H-¹H NOESY spectrum of compound **7g** shows a NOE cross-peak H-6'↔H-6b' and no cross-peak H-6'↔H-14a', indicating the *cis*-arrangement of the H-6' and H-6b' protons and a *trans*-arrangement of the H-6' and H-14a' protons relative to the plane of the heterocyclic system (Figure 6). Along with this, the cross-peaks H-14a'↔H-1' and H-8↔H-1' indicate the *endo*-configuration of adduct **7g**.

In summary, a simple and effective method for the synthesis of novel 6'-trifluoro(trichloro)methyl substituted spiro[acenaphthylene-1,11'-chromeno[3,4-*a*](thia)pyrrolizidin]-2-ones and spiro[acenaphthylene-1,12'-chromeno[3,4-*a*]indolizidin]-2-ones has been developed based on a multicomponent regio- and stereoselective PASE-strategy. Diversity of pharmacophores in the target products was ensured by the hybridization of biologically active scaffolds. This approach allows libraries of hybrid heterocycles to be obtained rapidly based on readily available 3-nitro-2-tri-

lomethyl-2*H*-chromenes in quantities sufficient for primary bioscreening. Further studies of the biological properties of the obtained spirocycloadducts are planned.

IR spectra were recorded with a Shimadzu IRSpirit-T spectrometer equipped with an ATR accessory. NMR spectra were recorded with Bruker DRX-400 (¹H, 400 MHz; ¹⁹F, 376 MHz) and Bruker Avance III-500 (¹H, 500 MHz; ¹⁹F, 471 MHz; ¹³C, 126 MHz) spectrometers in CDCl₃. The 2D ¹H-¹H NOESY spectrum of compound **7g** was acquired on a Bruker Avance NEO (600 MHz) spectrometer with 0.3 s mixing time. Chemical shifts (δ) are reported in ppm relative to the internal standard TMS (¹H NMR), C₆F₆ (¹⁹F NMR) and to residual signals of the solvents (δ = 77.16 ppm, ¹³C NMR). HRMS spectra were obtained with a Bruker maXis Impact HD (qTOF MS) instrument. Elemental analyses were performed with a Perkin Elmer PE 2400 automatic analyser. Melting points were determined with an SMP40 apparatus. The starting 3-nitro-2-trifluoro(trichloro)methyl-2*H*-chromenes **1a–q** were prepared according to described procedures.⁵

Synthesis of Spirochromeno[3,4-*a*](thia)pyrrolizidines **4**; General Procedure

A suspension of the corresponding nitrochromene **1** (0.25 mmol), acenaphthenequinone (46 mg, 0.25 mmol) and L-proline (38 mg, 0.33 mmol) or L-thiaproline (44 mg, 0.33 mmol) in EtOH (2 mL) was stirred at 55 °C for the time indicated in the Table 2. Then the mixture was cooled to r.t., the precipitate was filtered off, washed successively with EtOH (5 × 1 mL), H₂O (5 × 1 mL) and dried at 60 °C. In some cases, additional recrystallization from CH₂Cl₂–hexane (1:3) was necessary.

(1*S**,6*S**,6*a*'*S**,6*b*'*S**,11*a*'*R**)-6*a*'-Nitro-6'-(trifluoromethyl)-6*a*',6*b*',7',8',9',11*a*'-hexahydro-2*H*,6'*H*-spiro[acenaphthylene-1,11'-chromeno[3,4-*a*]pyrrolizin]-2-one (**4a**)

Obtained according to the general procedure from **1a** (61 mg) and L-proline.

Yield: 92 mg (77%); cream powder; mp 177–178 °C (decomp.).

IR (ATR): 1714, 1581, 1553, 1497, 1340 cm⁻¹.

¹H NMR (400 MHz): δ = 8.19 (d, *J* = 8.1 Hz, 1 H), 8.06 (d, *J* = 8.0 Hz, 1 H), 7.90 (d, *J* = 6.8 Hz, 1 H), 7.84 (t, *J* = 7.5 Hz, 1 H), 7.79 (d, *J* = 6.8 Hz, 1 H), 7.74 (t, *J* = 7.5 Hz, 1 H), 7.03–6.97 (m, 2 H), 6.42–6.34 (m, 1 H), 5.90 (q, *J* = 6.7 Hz, 1 H), 5.83 (d, *J* = 7.7 Hz, 1 H), 5.28 (s, 1 H), 4.61 (t, *J* = 6.9 Hz, 1 H), 3.17–1.67 (m, 6 H).

¹⁹F NMR (376 MHz): δ = 94.4 (d, *J* = 6.7 Hz, CF₃).

¹³C NMR (126 MHz): δ = 203.2, 152.6, 142.8, 137.4, 132.2, 131.9, 131.0, 128.9, 128.8, 128.7, 126.6, 126.0, 123.2 (q, *J* = 281.8 Hz, CF₃), 123.0, 122.7, 122.1, 118.7, 117.6, 96.3, 77.2, 77.1 (q, *J* = 33.5 Hz, C-6'), 69.6 (q, *J* = 2.3 Hz, C-6b'), 51.8, 49.3, 28.4, 25.1.

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₆H₂₀F₃N₂O₄: 481.1370; found: 481.1368.

(1*S**,6*S**,6*a*'*S**,6*b*'*S**,11*a*'*R**)-2'-Methyl-6*a*'-nitro-6'-(trifluoromethyl)-6*a*',6*b*',7',8',9',11*a*'-hexahydro-2*H*,6'*H*-spiro[acenaphthylene-1,11'-chromeno[3,4-*a*]pyrrolizin]-2-one (**4b**)

Obtained according to the general procedure from **1b** (65 mg) and L-proline.

Yield 97 mg (78%); grey powder; mp 172–173 °C (decomp.).

IR (ATR): 1726, 1605, 1554, 1497, 1497, 1338 cm⁻¹.

¹H NMR (400 MHz): δ = 8.19 (d, *J* = 8.0 Hz, 1 H), 8.06 (d, *J* = 8.0 Hz, 1 H), 7.89 (d, *J* = 6.9 Hz, 1 H), 7.85 (t, *J* = 7.5 Hz, 1 H), 7.78 (d, *J* = 6.9 Hz, 1 H), 7.73 (t, *J* = 7.5 Hz, 1 H), 6.86 (d, *J* = 8.0 Hz, 1 H), 6.78 (br d, *J* = 8.0 Hz, 1 H), 5.83 (q, *J* = 6.6 Hz, 1 H), 5.52 (s, 1 H), 5.21 (s, 1 H), 4.62 (t, *J* = 6.8 Hz, 1 H), 3.19–1.64 (m, 6 H), 1.59 (s, 3 H).

¹⁹F NMR (376 MHz): δ = 94.4 (d, *J* = 6.6 Hz, CF₃).

¹³C NMR (126 MHz): δ = 203.5 (C=O), 150.4, 142.8, 137.7, 132.2, 132.0 (2C), 130.9, 129.4, 128.9, 128.8, 126.5, 126.3, 123.3 (q, *J* = 281.8 Hz, CF₃), 122.5, 122.1, 118.3, 117.3, 96.0, 69.7 (q, *J* = 2.0 Hz, C-6b'), 52.2, 49.1, 28.4, 25.1, 20.4 (the signals of two carbon atoms overlap with the signal of CDCl₃).

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₇H₂₂F₃N₂O₄: 495.1526; found: 495.1522.

(1*S**,6*S**,6*a*'*S**,6*b*'*S**,11*a*'*R**)-2'-Methoxy-6*a*'-nitro-6'-(trifluoromethyl)-6*a*',6*b*',7',8',9',11*a*'-hexahydro-2*H*,6'*H*-spiro[acenaphthylene-1,11'-chromeno[3,4-*a*]pyrrolizin]-2-one (**4c**)

Obtained according to the general procedure from **1c** (69 mg) and L-proline.

Yield: 100 mg (78%); pale-yellow powder; mp 158–159 °C (decomp.).

IR (ATR): 1717, 1606, 1557, 1498, 1338 cm⁻¹.

¹H NMR (400 MHz): δ = 8.19 (d, *J* = 8.0 Hz, 1 H), 8.05 (d, *J* = 8.1 Hz, 1 H), 7.93 (d, *J* = 7.0 Hz, 1 H), 7.85 (t, *J* = 7.5 Hz, 1 H), 7.81 (d, *J* = 7.0 Hz, 1 H), 7.75 (t, *J* = 7.5 Hz, 1 H), 6.90 (d, *J* = 8.8 Hz, 1 H), 6.54 (br d, *J* = 8.8 Hz, 1 H), 5.74 (q, *J* = 6.2 Hz, 1 H), 5.27 (s, 1 H), 5.24 (s, 1 H), 4.65 (t, *J* = 6.2 Hz, 1 H), 3.24–1.65 (m, 9 H).

¹⁹F NMR (376 MHz): δ = 94.5 (d, *J* = 6.2 Hz, CF₃).

¹³C NMR (126 MHz): δ = 203.3 (C=O), 154.8, 146.6, 142.8, 137.6, 132.1, 132.0, 130.9, 129.0 (2C), 128.8, 126.5, 123.2 (q, *J* = 280.9 Hz, CF₃), 122.7, 122.3, 118.6, 115.8, 109.2, 96.6, 69.8 (q, *J* = 2.0 Hz, C-6b'), 54.7, 52.7, 49.2, 28.2, 25.1 (the signals of two carbon atoms overlap with the signal of CDCl₃).

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₇H₂₂F₃N₂O₅: 511.1475; found: 511.1471.

(1*S**,6*S**,6*a*'*S**,6*b*'*S**,11*a*'*R**)-4'-Ethoxy-6*a*'-nitro-6'-(trifluoromethyl)-6*a*',6*b*',7',8',9',11*a*'-hexahydro-2*H*,6'*H*-spiro[acenaphthylene-1,11'-chromeno[3,4-*a*]pyrrolizin]-2-one (**4d**)

Obtained according to the general procedure from **1d** (72 mg) and L-proline.

Yield: 105 mg (80%); cream powder; mp 189–190 °C (decomp.).

IR (ATR): 1720, 1589, 1549, 1489, 1475, 1332 cm⁻¹.

¹H NMR (400 MHz): δ = 8.18 (d, *J* = 8.0 Hz, 1 H), 8.04 (d, *J* = 8.1 Hz, 1 H), 7.91 (d, *J* = 6.9 Hz, 1 H), 7.83 (t, *J* = 7.5 Hz, 1 H), 7.78 (d, *J* = 7.0 Hz, 1 H), 7.73 (t, *J* = 7.5 Hz, 1 H), 6.59 (d, *J* = 8.0 Hz, 1 H), 6.29 (t, *J* = 8.0 Hz, 1 H), 5.83 (q, *J* = 6.3 Hz, 1 H), 5.42 (d, *J* = 8.0 Hz, 1 H), 5.32 (s, 1 H), 4.64 (t, *J* = 7.5 Hz, 1 H), 4.01 (q, *J* = 6.8 Hz, 2 H), 3.15–1.64 (m, 6 H), 1.39 (t, *J* = 6.8 Hz, 3 H).

¹⁹F NMR (376 MHz): δ = 94.8 (br s, CF₃).

¹³C NMR (126 MHz): δ = 203.1 (C=O), 148.3, 143.1, 142.8, 137.6, 132.0 (2C), 131.0, 128.9, 128.8, 126.5, 123.3 (q, *J* = 282.0 Hz, CF₃), 122.8, 122.6, 122.1, 120.1, 117.6, 113.5, 96.4, 69.7 (q, *J* = 2.0 Hz, C-6b'), 65.3, 52.1, 48.9, 28.0, 25.1, 14.9 (the signals of two carbon atoms overlap with the signal of CDCl₃).

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₈H₂₄F₃N₂O₅: 525.1632; found: 525.1636.

(1S*,6S*,6a'S*,6b'S*,11a'R*)-2'-Chloro-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',8',9',11a'-hexahydro-2H,6'H-spiro[acenaphthylene-1,11'-chromeno[3,4-a]pyrrolizin]-2-one (4e)

Obtained according to the general procedure from **1e** (70 mg) and L-proline.

Yield: 104 mg (81%); beige powder; mp 183–184 °C (decomp.).

IR (ATR): 1722, 1605, 1557, 1481, 1468, 1336 cm⁻¹.

¹H NMR (400 MHz): δ = 8.22 (d, *J* = 8.0 Hz, 1 H), 8.12–8.05 (m, 1 H), 7.89–7.84 (m, 2 H), 7.82 (d, *J* = 7.0 Hz, 1 H), 7.76 (t, *J* = 7.5 Hz, 1 H), 6.54 (dd, *J* = 8.8, 2.0 Hz, 1 H), 6.93 (d, *J* = 8.8 Hz, 1 H), 5.91 (q, *J* = 6.6 Hz, 1 H), 5.73 (d, *J* = 2.0 Hz, 1 H), 5.17 (s, 1 H), 4.60 (t, *J* = 7.1 Hz, 1 H), 3.11–1.66 (m, 6 H).

¹⁹F NMR (376 MHz): δ = 94.2 (d, *J* = 6.6 Hz, CF₃).

¹³C NMR (126 MHz): δ = 203.2 (C=O), 151.0, 142.8, 136.8, 132.4, 131.6, 130.9, 129.1, 128.9 (2C), 127.9, 126.9, 125.9, 123.0 (q, *J* = 281.6 Hz, CF₃), 122.9, 122.0, 120.2, 119.0, 96.3, 77.1, 76.9 (q, *J* = 33.6 Hz, C-6'), 69.5 (q, *J* = 2.4 Hz, C-6b'), 51.5, 49.3, 28.5, 25.1.

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₆H₁₉ClF₃N₂O₄: 515.0980; found: 515.0977.

(1S*,6S*,6a'S*,6b'S*,11a'R*)-2',4'-Dichloro-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',8',9',11a'-hexahydro-2H,6'H-spiro[acenaphthylene-1,11'-chromeno[3,4-a]pyrrolizin]-2-one (4f)

Obtained according to the general procedure from **1f** (79 mg) and L-proline.

Yield 90 mg (67%); cream powder; mp 179–180 °C (decomp.).

IR (ATR): 1719, 1605, 1557, 1461, 1432, 1411, 1338 cm⁻¹.

¹H NMR (400 MHz): δ = 8.22 (d, *J* = 7.9 Hz, 1 H), 8.14–8.05 (m, 1 H), 7.91–7.81 (m, 3 H), 7.78 (t, *J* = 7.5 Hz, 1 H), 7.09 (s, 1 H), 5.95 (q, *J* = 5.8 Hz, 1 H), 5.66 (s, 1 H), 5.18 (s, 1 H), 4.60 (t, *J* = 6.7 Hz, 1 H), 3.10–1.66 (m, 6 H).

¹⁹F NMR (376 MHz): δ = 94.2 (d, *J* = 5.8 Hz, CF₃).

¹³C NMR (126 MHz): δ = 203.0 (C=O), 147.2, 142.7, 136.6, 132.5, 131.5, 131.0, 129.4, 129.1, 129.0, 127.7, 127.0, 124.3, 124.0, 123.1, 122.8 (q, *J* = 281.7 Hz, CF₃), 122.0, 121.7, 95.0, 77.3 (q, *J* = 33.9 Hz, C-6'), 77.0, 69.5 (q, *J* = 2.0 Hz, C-6b'), 51.7, 49.1, 28.5, 25.1.

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₆H₁₈Cl₂F₃N₂O₄: 549.0590; found: 549.0582.

(1S*,6S*,6a'S*,6b'S*,11a'R*)-2'-Bromo-4'-ethoxy-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',8',9',11a'-hexahydro-2H,6'H-spiro[acenaphthylene-1,11'-chromeno[3,4-a]pyrrolizin]-2-one (4g)

Obtained according to the general procedure from **1g** (92 mg) and L-proline.

Yield: 123 mg (81%); cream powder; mp 205–206 °C (decomp.).

IR (ATR): 1709, 1603, 1557, 1484, 1469, 1339 cm⁻¹.

¹H NMR (400 MHz): δ = 8.21 (d, *J* = 8.0 Hz, 1 H), 8.07 (d, *J* = 8.0 Hz, 1 H), 7.88 (d, *J* = 6.9 Hz, 1 H), 7.84 (t, *J* = 7.5 Hz, 1 H), 7.81 (d, *J* = 6.9 Hz, 1 H), 7.76 (t, *J* = 7.5 Hz, 1 H), 6.69 (s, 1 H), 5.82 (q, *J* = 6.5 Hz, 1 H), 5.46 (s, 1 H), 5.19 (s, 1 H), 4.63 (t, *J* = 7.1 Hz, 1 H), 3.98 (q, *J* = 6.9 Hz, 2 H), 3.08–1.65 (m, 6 H), 1.40 (t, *J* = 6.9 Hz, 3 H).

¹⁹F NMR (376 MHz): δ = 94.6 (br s, CF₃).

¹³C NMR (126 MHz): δ = 203.3 (C=O), 149.0, 142.7, 141.8, 137.1, 132.3, 131.8, 130.9, 129.0, 128.9, 126.7, 123.0 (q, *J* = 282.1 Hz, CF₃), 122.7, 122.0, 121.4, 120.2, 116.3, 115.0, 95.4, 77.0 (q, *J* = 34.4 Hz, C-6'), 69.7 (q, *J* = 1.8 Hz, C-6b'), 65.4, 51.9, 48.8, 28.1, 25.1, 14.7 (the signal of one carbon atom overlaps with the signal of CDCl₃).

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₈H₂₃BrF₃N₂O₅: 603.0737; found: 603.0726.

(1S*,6S*,6a'S*,6b'S*,11a'R*)-2',6a'-Dinitro-6'-(trifluoromethyl)-6a',6b',7',8',9',11a'-hexahydro-2H,6'H-spiro[acenaphthylene-1,11'-chromeno[3,4-a]pyrrolizin]-2-one (4h)

Obtained according to the general procedure from **1h** (73 mg) and L-proline.

Yield: 117 mg (89%); beige powder; mp 190–191 °C (decomp.).

IR (ATR): 1706, 1582, 1562, 1524, 1482, 1339, 1329 cm⁻¹.

¹H NMR (400 MHz): δ = 8.24 (d, *J* = 7.8 Hz, 1 H), 8.14 (d, *J* = 8.0 Hz, 1 H), 7.94–7.85 (m, 4 H), 7.74 (t, *J* = 7.5 Hz, 1 H), 7.12 (d, *J* = 9.0 Hz, 1 H), 6.67 (d, *J* = 2.1 Hz, 1 H), 6.12 (q, *J* = 6.2 Hz, 1 H), 5.14 (s, 1 H), 4.61 (t, *J* = 7.4 Hz, 1 H), 3.09–1.70 (m, 6 H).

¹⁹F NMR (376 MHz): δ = 93.6 (d, *J* = 6.2 Hz, CF₃).

¹³C NMR (126 MHz): δ = 203.5 (C=O), 156.8, 142.9, 142.7, 136.3, 132.9, 131.3, 131.1, 129.2, 129.1, 127.3, 124.6, 123.1, 122.7 (q, *J* = 281.5 Hz, CF₃), 122.4, 122.1, 119.2, 118.4, 93.7, 76.8 (q, *J* = 33.8 Hz, C-6'), 69.5 (q, *J* = 2.0 Hz, C-6b'), 51.4, 49.4, 29.0, 25.1 (the signal of one carbon atom overlaps with the signal of CDCl₃).

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₆H₁₉F₃N₃O₆: 526.1220; found: 526.1212.

(1S*,6S*,6a'S*,6b'S*,11a'R*)-2',4',6a'-Trinitro-6'-(trifluoromethyl)-6a',6b',7',8',9',11a'-hexahydro-2H,6'H-spiro[acenaphthylene-1,11'-chromeno[3,4-a]pyrrolizin]-2-one (4i)

Obtained according to the general procedure from **1i** (84 mg) and L-proline.

Yield: 115 mg (81%); cream powder; mp 178–179 °C (decomp.).

IR (ATR): 1709, 1599, 1557, 1548, 1467, 1363, 1339 cm⁻¹.

¹H NMR (400 MHz): δ = 8.55 (d, *J* = 2.4 Hz, 1 H), 8.27 (dd, *J* = 7.8, 1.0 Hz, 1 H), 8.17 (d, *J* = 8.2 Hz, 1 H), 7.93 (dd, *J* = 8.2, 7.2 Hz, 1 H), 7.86 (d, *J* = 7.0 Hz, 1 H), 7.82–7.74 (m, 2 H), 6.88 (d, *J* = 2.4 Hz, 1 H), 6.31 (q, *J* = 5.9 Hz, 1 H), 5.13 (s, 1 H), 4.59 (t, *J* = 7.5 Hz, 1 H), 3.00–1.71 (m, 6 H).

¹⁹F NMR (376 MHz): δ = 93.3 (d, *J* = 5.9 Hz, CF₃).

¹³C NMR (126 MHz): δ = 203.2 (C=O), 150.2, 142.9, 141.1, 138.6, 135.7, 133.2, 131.2, 131.0, 129.4, 129.2, 127.6, 125.5, 123.5, 123.3, 122.1 (q, *J* = 282.1 Hz, CF₃), 122.0, 121.0, 92.1, 77.5, 77.2 (q, *J* = 34.8 Hz, C-6'), 69.4 (q, *J* = 2.5 Hz, C-6b'), 51.1, 49.2, 29.1, 25.1.

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₆H₁₈F₃N₄O₈: 571.1071; found: 571.1068.

(1S*,6S*,6a'S*,6b'S*,11a'R*)-6a'-Nitro-6'-(trichloromethyl)-6a',6b',7',8',9',11a'-hexahydro-2H,6'H-spiro[acenaphthylene-1,11'-chromeno[3,4-a]pyrrolizin]-2-one (4j)

Obtained according to the general procedure from **1j** (74 mg) and L-proline.

Yield: 100 mg (76%); beige powder; mp 169–170 °C (decomp.).

IR (ATR): 1713, 1602, 1587, 1549, 1492, 1457, 1436, 1344, 1331 cm⁻¹.

¹H NMR (400 MHz): δ = 8.12 (d, *J* = 7.9 Hz, 1 H), 8.05 (d, *J* = 8.0 Hz, 1 H), 7.84 (t, *J* = 7.5 Hz, 1 H), 7.81–7.69 (m, 3 H), 7.06–6.97 (m, 2 H), 6.40–6.33 (m, 1 H), 6.16 (s, 1 H), 5.81 (d, *J* = 7.0 Hz, 1 H), 5.17 (s, 1 H), 5.10 (t, *J* = 6.6 Hz, 1 H), 2.81–1.76 (m, 6 H).

¹³C NMR (126 MHz): δ = 204.3 (C=O), 152.5, 142.8, 137.7, 132.2, 131.8, 130.9, 129.0, 128.9, 128.7, 126.5, 125.6, 122.7, 122.4, 121.6, 118.7, 117.3, 96.8, 95.1, 84.9, 76.4, 70.0, 52.9, 47.8, 29.7, 24.7.

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₆H₂₀Cl₃N₂O₄: 529.0483; found: 529.0474.

(1S*,6'S*,6a'S*,6b'S*,11a'R*)-2'-Methyl-6a'-nitro-6'-(trichloromethyl)-6a',6b',7',8',9',11a'-hexahydro-2H,6'H-spiro[acenaphthylene-1,11'-chromeno[3,4-a]pyrrolizin]-2-one (4k)

Obtained according to the general procedure from **1k** (77 mg) and L-proline.

Yield: 97 mg (71%); cream powder; mp 165–166 °C (decomp.).

IR (ATR): 1720, 1605, 1549, 1502, 1496, 1467, 1340, 1329 cm⁻¹.

¹H NMR (400 MHz): δ = 8.18 (d, *J* = 7.8 Hz, 1 H), 8.05 (d, *J* = 8.2 Hz, 1 H), 7.84 (t, *J* = 7.5 Hz, 1 H), 7.81–7.69 (m, 3 H), 6.91 (d, *J* = 8.3 Hz, 1 H), 6.79 (br d, *J* = 8.3 Hz, 1 H), 6.07 (s, 1 H), 5.50 (s, 1 H), 5.17–5.06 (m, 2 H), 2.83–1.81 (m, 6 H), 1.58 (s, 1 H).

¹³C NMR (126 MHz): δ = 204.5, 150.3, 142.8, 138.0, 132.03, 131.97, 130.9, 130.7, 129.4, 129.0, 128.8, 126.3, 126.0, 122.2, 121.6, 117.0, 116.2, 96.9, 95.0, 85.0, 76.3, 70.1, 53.4, 47.6, 29.6, 24.8, 20.4.

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₇H₂₂Cl₃N₂O₄: 545.0610; found: 545.0615.

(1S*,6'S*,6a'S*,6b'S*,11a'R*)-2'-Methoxy-6a'-nitro-6'-(trichloromethyl)-6a',6b',7',8',9',11a'-hexahydro-2H,6'H-spiro[acenaphthylene-1,11'-chromeno[3,4-a]pyrrolizin]-2-one (4l)

Obtained according to the general procedure from **1l** (81 mg) and L-proline.

Yield: 105 mg (75%); pale-yellow powder; mp 170–171 °C (decomp.).

IR (ATR): 1714, 1607, 1547, 1494, 1429, 1351, 1338 cm⁻¹.

¹H NMR (400 MHz): δ = 8.18 (d, *J* = 8.0 Hz, 1 H), 8.06–8.01 (m, 1 H), 7.86–7.81 (m, 2 H), 7.78 (d, *J* = 6.9 Hz, 1 H), 7.74 (t, *J* = 7.5 Hz, 1 H), 6.94 (d, *J* = 8.9 Hz, 1 H), 6.79 (dd, *J* = 8.9, 2.6 Hz, 1 H), 5.96 (s, 1 H), 5.25 (d, *J* = 2.6 Hz, 1 H), 5.20 (s, 1 H), 5.09 (t, *J* = 6.8 Hz, 1 H), 2.86–1.80 (m, 9 H).

¹³C NMR (126 MHz): δ = 204.4 (C=O), 154.8, 146.6, 142.8, 137.9, 132.1, 132.0, 130.9, 129.1, 128.9, 126.4, 122.4, 121.8, 119.4, 118.3, 115.8, 109.0, 96.8, 95.6, 85.6, 76.1, 70.2, 54.7, 53.9, 47.4, 29.4, 24.7.

Anal. Calcd for C₂₇H₂₁Cl₃N₂O₅: C, 57.93; H, 3.78; N, 5.00. Found: C, 57.79; H, 3.83; N, 4.87.

(1S*,6'S*,6a'S*,6b'S*,11a'R*)-4'-Ethoxy-6a'-nitro-6'-(trichloromethyl)-6a',6b',7',8',9',11a'-hexahydro-2H,6'H-spiro[acenaphthylene-1,11'-chromeno[3,4-a]pyrrolizin]-2-one (4m)

Obtained according to the general procedure from **1m** (85 mg) and L-proline.

Yield: 90 mg (62%); cream powder; mp 143–144 °C (decomp.).

IR (ATR): 1715, 1602, 1586, 1548, 1478, 1334 cm⁻¹.

¹H NMR (400 MHz): δ = 8.17 (d, *J* = 7.8 Hz, 1 H), 8.05–7.99 (m, 1 H), 7.85–7.79 (m, 2 H), 7.75 (d, *J* = 6.8 Hz, 1 H), 7.72 (t, *J* = 7.5 Hz, 1 H), 6.61 (d, *J* = 8.0 Hz, 1 H), 6.28 (t, *J* = 7.9 Hz, 1 H), 6.06 (s, 1 H), 5.42 (d, *J* = 7.8 Hz, 1 H), 5.26 (s, 1 H), 5.09 (t, *J* = 6.9 Hz, 1 H), 4.09–3.98 (m, 2 H), 2.78–1.77 (m, 6 H), 1.39 (t, *J* = 6.9 Hz, 3 H).

¹³C NMR (126 MHz): δ = 204.1 (C=O), 148.2, 142.9, 142.8, 137.9, 132.1, 132.0, 130.9, 129.0, 128.8, 126.3, 122.6, 122.2, 121.6, 120.0, 117.5, 114.1, 96.9, 95.6, 85.5, 76.0, 70.2, 65.6, 53.3, 47.3, 29.1, 24.7, 15.1.

Anal. Calcd for C₂₈H₂₃Cl₃N₂O₅: C, 58.61; H, 4.04; N, 4.88. Found: C, 58.45; H, 3.93; N, 5.08.

(1S*,6'S*,6a'S*,6b'S*,11a'R*)-2'-Chloro-6a'-nitro-6'-(trichloromethyl)-6a',6b',7',8',9',11a'-hexahydro-2H,6'H-spiro[acenaphthylene-1,11'-chromeno[3,4-a]pyrrolizin]-2-one (4n)

Obtained according to the general procedure from **1n** (82 mg) and L-proline.

Yield: 116 mg (82%); white powder; mp 175–176 °C (decomp.).

IR (ATR): 1715, 1600, 1551, 1481, 1467, 1435, 1339 cm⁻¹.

¹H NMR (400 MHz): δ = 8.21 (d, *J* = 7.9 Hz, 1 H), 8.07 (d, *J* = 7.9 Hz, 1 H), 7.85 (t, *J* = 7.5 Hz, 1 H), 7.81–7.73 (m, 3 H), 7.01–6.94 (m, 2 H), 6.16 (s, 1 H), 5.71 (s, 1 H), 5.10 (t, *J* = 6.6 Hz, 1 H), 5.06 (s, 1 H), 2.78–1.80 (m, 6 H).

¹³C NMR (126 MHz): δ = 204.2 (C=O), 150.9, 142.8, 137.2, 132.4, 131.6, 130.9, 129.1, 129.0, 128.9, 127.6, 126.7, 125.5, 122.6, 121.6, 120.3, 118.7, 96.6, 94.2, 84.7, 76.3, 70.0, 52.8, 47.8, 29.7, 24.8.

Anal. Calcd for C₂₆H₁₈Cl₄N₂O₄: C, 55.35; H, 3.22; N, 4.96. Found: C, 55.39; H, 3.15; N, 4.78.

(1S*,6'S*,6a'S*,6b'S*,11a'R*)-2',4'-Dichloro-6a'-nitro-6'-(trichloromethyl)-6a',6b',7',8',9',11a'-hexahydro-2H,6'H-spiro[acenaphthylene-1,11'-chromeno[3,4-a]pyrrolizin]-2-one (4o)

Obtained according to the general procedure from **1o** (91 mg) and L-proline.

Yield: 117 mg (82%); cream powder; mp 165–166 °C (decomp.).

IR (ATR): 1722, 1599, 1546, 1464, 1339 cm⁻¹.

¹H NMR (400 MHz): δ = 8.22 (d, *J* = 7.8 Hz, 1 H), 8.08 (d, *J* = 8.3 Hz, 1 H), 7.85 (dd, *J* = 8.3, 7.2 Hz, 1 H), 7.82–6.74 (m, 3 H), 7.10 (d, *J* = 2.3 Hz, 1 H), 6.20 (s, 1 H), 5.63 (d, *J* = 2.3 Hz, 1 H), 5.08 (dd, *J* = 7.8, 6.7 Hz, 1 H), 5.07 (s, 1 H), 2.75–1.81 (m, 6 H).

¹³C NMR (126 MHz): δ = 204.0 (C=O), 147.1, 142.8, 136.9, 132.6, 131.5, 130.9, 129.3, 129.1, 129.0, 127.3, 126.9, 123.9, 123.7, 122.8, 121.6, 121.5, 96.1, 94.1, 85.0, 76.2, 69.9, 52.9, 47.7, 29.7, 24.7.

Anal. Calcd for C₂₆H₁₇Cl₅N₂O₄: C, 52.16; H, 2.86; N, 4.68. Found: C, 52.35; H, 2.84; N, 4.59.

(1S*,6'S*,6a'S*,6b'S*,11a'R*)-2',6a'-Dinitro-6'-(trichloromethyl)-6a',6b',7',8',9',11a'-hexahydro-2H,6'H-spiro[acenaphthylene-1,11'-chromeno[3,4-a]pyrrolizin]-2-one (4p)

Obtained according to the general procedure from **1p** (85 mg) and L-proline.

Yield: 114 mg (79%); beige powder; mp 163–164 °C (decomp.).

IR (ATR): 1720, 1591, 1546, 1524, 1492, 1343, 1329 cm⁻¹.

¹H NMR (400 MHz): δ = 8.25–8.20 (m, 1 H), 8.12 (d, *J* = 8.4 Hz, 1 H), 7.95–7.87 (m, 2 H), 7.76 (d, *J* = 7.0 Hz, 1 H), 7.74–7.71 (m, 2 H), 7.15 (d, *J* = 9.0 Hz, 1 H), 6.66 (d, *J* = 2.2 Hz, 1 H), 6.41 (s, 1 H), 5.15 (dd, *J* = 8.0, 6.8 Hz, 1 H), 4.99 (s, 1 H), 2.79–1.82 (m, 6 H).

¹³C NMR (126 MHz): δ = 204.4 (C=O), 156.9, 142.9, 142.3, 136.5, 132.9, 131.1, 131.0, 129.2, 129.1, 127.2, 124.7, 122.8, 122.1, 121.6, 119.0, 117.9, 96.0, 92.5, 84.3, 76.7, 70.0, 52.4, 48.2, 30.2, 24.8.

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₆H₁₉Cl₃N₃O₆: 574.0334; found: 574.0328.

(1S*,6'S*,6a'S*,6b'S*,11a'R*)-2',4',6a'-Trinitro-6'-(trichloromethyl)-6a',6b',7',8',9',11a'-hexahydro-2H,6'H-spiro[acenaphthylene-1,11'-chromeno[3,4-a]pyrrolizin]-2-one (4q)

Obtained according to the general procedure from **1q** (96 mg) and L-proline.

Yield: 127 mg (82%); pale-yellow powder; mp 162–163 °C (decomp.).

IR (ATR): 1713, 1606, 1553, 1544, 1474, 1345 cm⁻¹.

¹H NMR (400 MHz): δ = 8.56 (d, *J* = 2.7 Hz, 1 H), 8.26 (dd, *J* = 7.3, 1.6 Hz, 1 H), 8.15 (d, *J* = 8.3 Hz, 1 H), 7.78–7.74 (m, 3 H), 6.87 (dd, *J* = 2.7, 0.6 Hz, 1 H), 6.62 (s, 1 H), 5.16 (dd, *J* = 8.8, 6.1 Hz, 1 H), 4.97 (s, 1 H), 2.79–1.85 (m, 6 H).

¹³C NMR (126 MHz): δ = 203.9 (C=O), 150.2, 142.9, 140.5, 138.0, 135.8, 133.2, 131.1, 130.7, 129.4, 129.2, 127.5, 125.1, 123.3, 122.6, 121.6, 121.1, 95.0, 91.0, 84.7, 76.9, 69.9, 51.8, 48.3, 30.3, 24.8.

Anal. Calcd for C₂₆H₁₇Cl₃N₄O₈: C, 50.39; H, 2.76; N, 9.04. Found: C, 50.45; H, 2.66; N, 8.86.

(1S*,6'S*,6a'S*,6b'R*,11a'R*)-6a'-Nitro-6'-(trifluoromethyl)-6a',6b',7',11a'-tetrahydro-2H,6'H,9'H-spiro[acenaphthylene-1,11'-chromeno[3',4':3,4]pyrrolo[1,2-c]thiazol]-2-one (4r)

Obtained according to the general procedure from **1a** (61 mg) and L-thiaproline.

Yield: 70 mg (56%); cream powder; mp 248–249 °C (decomp.).

IR (ATR): 1728, 1603, 1590, 1549, 1492, 1459, 1447, 1404, 1366, 1337 cm⁻¹.

¹H NMR (400 MHz): δ = 8.20 (dd, *J* = 7.2, 1.5 Hz, 1 H), 8.07 (d, *J* = 8.1 Hz, 1 H), 7.89 (d, *J* = 7.2 Hz, 1 H), 7.84 (t, *J* = 6.8 Hz, 1 H), 7.75–7.67 (m, 2 H), 6.96–7.08 (m, 2 H), 6.44 (q, *J* = 5.7 Hz, 1 H), 6.36 (t, *J* = 7.8 Hz, 1 H), 5.64 (d, *J* = 7.8 Hz, 1 H), 4.68 (s, 1 H), 4.65 (dd, *J* = 10.3, 5.8 Hz, 1 H), 4.14 (d, *J* = 9.9 Hz, 1 H), 3.64 (dd, *J* = 10.3, 5.8 Hz, 1 H), 3.34 (d, *J* = 9.9 Hz, 1 H), 2.83 (t, *J* = 10.3 Hz, 1 H).

¹⁹F NMR (376 MHz): δ = 90.7 (d, *J* = 5.7 Hz, CF₃).

¹³C NMR (126 MHz): δ = 203.3 (C=O), 151.3, 143.1, 135.0, 132.5, 130.62, 130.60, 129.4, 129.3, 128.9, 127.0, 126.3, 122.8, 122.7 (q, *J* = 282.1 Hz, CF₃), 122.6, 122.4, 117.3, 116.6, 88.6, 77.5, 74.2 (q, *J* = 32.6 Hz, C-6'), 70.7 (q, *J* = 3.8 Hz, C-6b'), 54.9, 49.6, 36.8.

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₅H₁₈F₃N₄O₄S: 499.0934; found: 499.0940.

(1S*,6'S*,6a'S*,6b'R*,11a'R*)-2'-Methoxy-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',11a'-tetrahydro-2H,6'H,9'H-spiro[acenaphthylene-1,11'-chromeno[3',4':3,4]pyrrolo[1,2-c]thiazol]-2-one (4s)

Obtained according to the general procedure from **1c** (69 mg) and L-thiaproline.

Yield: 80 mg (92%); cream powder; mp 224–225 °C (decomp.).

IR (ATR): 1723, 1617, 1603, 1555, 1496, 1467, 1442, 1427, 1365, 1334 cm⁻¹.

¹H NMR (400 MHz): δ = 8.24–8.17 (m, 1 H), 8.06 (d, *J* = 7.9 Hz, 1 H), 7.92–7.83 (m, 2 H), 7.77–7.70 (m, 2 H), 6.91 (d, *J* = 9.0 Hz, 1 H), 6.60 (dd, *J* = 9.0, 2.3 Hz, 1 H), 6.32 (q, *J* = 5.5 Hz, 1 H), 5.05 (d, *J* = 2.3 Hz, 1 H), 4.66 (dd, *J* = 10.4, 5.8 Hz, 1 H), 4.64 (s, 1 H), 4.15 (d, *J* = 9.8 Hz, 1 H), 3.63 (dd, *J* = 10.4, 5.8 Hz, 1 H), 3.39 (d, *J* = 9.8 Hz, 1 H), 2.86 (s, 3 H), 2.81 (t, *J* = 10.4 Hz, 1 H).

¹⁹F NMR (376 MHz): δ = 90.8 (d, *J* = 5.5 Hz, CF₃).

¹³C NMR (126 MHz): δ = 203.2 (C=O), 154.5, 145.4, 142.9, 135.2, 132.4, 130.9, 130.6, 129.4, 128.9, 126.9, 122.8 (2C), 122.7 (q, *J* = 281.8 Hz, CF₃), 118.3, 117.1, 116.4, 109.9, 88.9, 77.6, 74.4 (q, *J* = 32.8 Hz, C-6'), 70.6 (q, *J* = 3.8 Hz, C-6b'), 54.9, 54.8, 50.3, 36.8.

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₆H₂₀F₃N₄O₅S: 529.1040; found: 529.1045.

(1S*,6'S*,6a'S*,6b'R*,11a'R*)-2',4'-Dichloro-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',11a'-tetrahydro-2H,6'H,9'H-spiro[acenaphthylene-1,11'-chromeno[3',4':3,4]pyrrolo[1,2-c]thiazol]-2-one (4t)

Obtained according to the general procedure from **1f** (79 mg) and L-thiaproline.

Yield: 102 mg (72%); grey powder; mp 229–230 °C (decomp.).

IR (ATR): 1721, 1600, 1557, 1467, 1390, 1364, 1345, 1329 cm⁻¹.

¹H NMR (400 MHz): δ = 8.27–8.21 (m, 1 H), 8.10 (d, *J* = 8.3 Hz, 1 H), 7.89 (t, *J* = 7.7 Hz, 1 H), 7.82 (d, *J* = 7.0 Hz, 1 H), 7.80–7.74 (m, 2 H), 7.14 (d, *J* = 2.2 Hz, 1 H), 6.45 (q, *J* = 5.5 Hz, 1 H), 5.49 (d, *J* = 2.2 Hz, 1 H), 4.64 (dd, *J* = 10.4, 5.8 Hz, 1 H), 4.59 (s, 1 H), 4.15 (d, *J* = 9.9 Hz, 1 H), 3.65 (dd, *J* = 10.4, 5.8 Hz, 1 H), 3.34 (d, *J* = 9.9 Hz, 1 H), 2.79 (t, *J* = 10.4 Hz, 1 H).

¹⁹F NMR (376 MHz): δ = 90.7 (d, *J* = 5.5 Hz, CF₃).

¹³C NMR (126 MHz): δ = 202.9 (C=O), 146.2, 143.0, 134.2, 133.0, 130.6, 130.2, 130.0, 129.3, 129.1, 127.4, 127.2, 124.5, 123.6, 123.2, 122.7, 122.3 (q, *J* = 282.0 Hz, CF₃), 119.7, 88.1, 77.3, 74.7 (q, *J* = 33.3 Hz, C-6'), 70.4 (q, *J* = 3.6 Hz, C-6b'), 54.8, 49.5, 36.8.

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₅H₁₆Cl₂F₃N₄O₄S: 567.0154; found: 567.0162.

(1S*,6'S*,6a'S*,6b'R*,11a'R*)-2',6a'-Dinitro-6'-(trifluoromethyl)-6a',6b',7',11a'-tetrahydro-2H,6'H,9'H-spiro[acenaphthylene-1,11'-chromeno[3',4':3,4]pyrrolo[1,2-c]thiazol]-2-one (4u)

Obtained according to the general procedure from **1h** (73 mg) and L-thiaproline.

Yield: 90 mg (66%); beige powder; mp 244–245 °C (decomp.).

IR (ATR): 1718, 1590, 1557, 1519, 1488, 1362, 1340, 1330 cm⁻¹.

¹H NMR (400 MHz): δ = 8.25 (d, *J* = 7.9 Hz, 1 H, Ar), 8.14 (d, *J* = 7.9 Hz, 1 H), 7.97 (dd, *J* = 9.0, 2.0 Hz, 1 H), 7.96–7.84 (m, 2 H), 7.75–7.65 (m, 2 H), 7.13 (d, *J* = 9.0 Hz, 1 H), 6.56 (q, *J* = 5.6 Hz, 1 H), 6.54 (d, *J* = 2.0 Hz, 1 H), 4.70–4.59 (m, 2 H), 4.18 (d, *J* = 10.0 Hz, 1 H), 3.70 (dd, *J* = 10.4, 5.7 Hz, 1 H), 3.40 (d, *J* = 10.0 Hz, 1 H), 2.84 (t, *J* = 10.4 Hz, 1 H).

¹⁹F NMR (376 MHz): δ = 90.4 (d, *J* = 5.6 Hz, CF₃).

¹³C{¹H} NMR (126 MHz): δ = 203.2 (C=O), 155.9, 143.1, 142.3, 133.9, 133.3, 130.8, 130.0, 129.5, 129.1, 127.6, 125.3, 123.4, 122.8, 122.6, 122.3 (q, *J* = 282.0 Hz, CF₃), 118.1, 117.7, 87.5, 77.5, 74.8 (q, *J* = 33.3 Hz, C-6'), 70.6 (q, *J* = 3.8 Hz, C-6b'), 54.8, 49.4, 36.8.

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₅H₁₇F₃N₄O₆S: 544.0785; found: 544.0782.

(1S*,6'S*,6a'S*,6b'R*,11a'R*)-6a'-Nitro-6'-(trichloromethyl)-6a',6b',7',11a'-tetrahydro-2H,6'H,9'H-spiro[acenaphthylene-1,11'-chromeno[3',4':3,4]pyrrolo[1,2-c]thiazol]-2-one (4v)

Obtained according to the general procedure from **1j** (74 mg) and L-thiaproline.

Yield: 53 mg (39%); beige powder; mp 204–205 °C (decomp.).

IR (ATR): 1723, 1596, 1547, 1493, 1456, 1436, 1364, 1345, 1327 cm⁻¹.

¹H NMR (400 MHz): δ = 8.22–8.16 (m, 1 H), 8.07 (d, *J* = 7.8 Hz, 1 H), 7.92–7.81 (m, 2 H), 7.74–7.64 (m, 2 H), 7.09–6.97 (m, 2 H), 6.67 (s, 1 H), 6.33 (t, *J* = 7.3 Hz, 1 H), 5.62 (d, *J* = 7.3 Hz, 1 H), 5.48 (dd, *J* = 10.4, 5.7 Hz, 1 H), 4.66 (s, 1 H), 4.17 (d, *J* = 9.9 Hz, 1 H), 3.72 (dd, *J* = 10.4, 5.7 Hz, 1 H), 3.36 (d, *J* = 9.9 Hz, 1 H), 2.84 (t, *J* = 10.4 Hz, 1 H).

¹³C{¹H} NMR (126 MHz): δ = 203.4 (C=O), 151.8, 143.2, 134.9, 132.5, 130.63, 130.57, 129.4, 129.2, 128.9, 126.9, 125.8, 122.8, 122.7, 122.1, 116.9, 116.4, 96.5, 90.2, 81.8, 77.5, 71.8, 55.1, 51.0, 37.4.

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₅H₁₈Cl₃N₂O₄S: 547.0047; found: 547.0052.

(1S*,6'S*,6a'S*,6b'R*,11a'R*)-2'-Methoxy-6a'-nitro-6'-(trichloromethyl)-6a',6b',7',11a'-tetrahydro-2H,6'H,9'H-spiro[acenaphthylene-1,11'-chromeno[3',4':3,4]pyrrolo[1,2-c]thiazol]-2-one (4w)

Obtained according to the general procedure from **11** (81 mg) and L-thiaproline.

Yield: 52 mg (36%); brown powder; mp 192–193 °C (decomp.).

IR (ATR): 1716, 1602, 1545, 1502, 1462, 1434, 1344 cm⁻¹.

¹H NMR (400 MHz): δ = 8.24–8.15 (m, 1 H), 8.06 (d, J = 7.5 Hz, 1 H), 7.92–7.83 (m, 2 H), 7.76–7.68 (m, 2 H), 6.95 (d, J = 8.9 Hz, 1 H), 6.60 (dd, J = 8.9, 2.2 Hz, 1 H), 6.55 (s, 1 H), 5.49 (dd, J = 10.4, 5.8 Hz, 1 H), 5.04 (d, J = 2.2 Hz, 1 H), 4.62 (s, 1 H), 4.18 (d, J = 9.8 Hz, 1 H), 3.72 (dd, J = 10.4, 5.7 Hz, 1 H), 3.41 (d, J = 9.8 Hz, 1 H), 2.85 (s, 3 H), 2.83 (t, J = 10.4 Hz, 1 H).

¹³C NMR (126 MHz): δ = 203.3 (C=O), 154.3, 145.9, 143.1, 135.1, 132.3, 130.9, 130.5, 129.4, 128.9, 126.9, 122.9, 122.7, 118.0, 116.9, 116.4, 109.4, 96.5, 90.5, 82.0, 77.5, 71.7, 55.0, 54.9, 51.7, 37.4.

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₆H₂₀Cl₃N₂O₅S: 577.0153; found: 577.0149.

(1S*,6'S*,6a'S*,6b'R*,11a'R*)-2',4'-Dichloro-6a'-nitro-6'-(trichloromethyl)-6a',6b',7',11a'-tetrahydro-2H,6'H,9'H-spiro[acenaphthylene-1,11'-chromeno[3',4':3,4]pyrrolo[1,2-c]thiazol]-2-one (4x)

Obtained according to the general procedure from **10** (91 mg) and L-thiaproline.

Yield: 95 mg (65%); beige powder; mp 224–255 °C (decomp.).

IR (ATR): 1716, 1599, 1553, 1453, 1432, 1364, 1327 cm⁻¹.

¹H NMR (400 MHz): δ = 8.27–8.20 (m, 1 H), 8.10 (d, J = 8.1 Hz, 1 H), 7.94–7.70 (m, 4 H), 7.13 (d, J = 2.2 Hz, 1 H), 6.67 (s, 1 H), 5.52–5.40 (m, 2 H), 4.58 (s, 1 H), 4.17 (d, J = 9.9 Hz, 1 H), 3.72 (dd, J = 10.3, 5.8 Hz, 1 H), 3.36 (d, J = 9.9 Hz, 1 H), 2.81 (t, J = 10.3 Hz, 1 H).

¹³C NMR (126 MHz): δ = 203.0 (C=O), 146.7, 143.1, 134.1, 132.9, 130.6, 130.3, 129.8, 129.3, 129.1, 127.4, 126.8, 124.0, 123.3, 123.2, 122.8, 119.3, 95.9, 89.7, 82.2, 77.3, 71.6, 55.0, 50.9, 37.4.

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₅H₁₆Cl₅N₂O₄S: 614.9268; found: 614.9270.

(1S*,6'S*,6a'S*,6b'R*,11a'R*)-2',4',6a'-Trinitro-6'-(trichloromethyl)-6a',6b',7',11a'-tetrahydro-2H,6'H,9'H-spiro[acenaphthylene-1,11'-chromeno[3',4':3,4]pyrrolo[1,2-c]thiazol]-2-one (4y)

Obtained according to the general procedure from **1q** (96 mg) and L-thiaproline.

Yield: 110 mg (69%); beige powder; mp 214–215 °C (decomp.).

IR (ATR): 1708, 1602, 1557, 1547, 1535, 1479, 1340 cm⁻¹.

¹H NMR (400 MHz): δ = 8.62 (d, J = 1.8 Hz, 1 H), 8.30–8.24 (m, 1 H), 8.17 (d, J = 8.0 Hz, 1 H), 7.95 (t, J = 7.6 Hz, 1 H), 7.91 (d, J = 6.9 Hz, 1 H), 7.78–7.70 (m, 2 H), 6.93 (s, 1 H), 6.75 (d, J = 1.8 Hz, 1 H), 5.47 (dd, J = 10.4, 5.8 Hz, 1 H), 4.69 (s, 1 H), 4.21 (d, J = 10.2 Hz, 1 H), 3.79 (dd, J = 10.4, 5.8 Hz, 1 H), 3.39 (d, J = 10.2 Hz, 1 H), 2.85 (t, J = 10.4 Hz, 1 H).

¹³C NMR (126 MHz): δ = 202.9 (C=O), 149.9, 143.3, 140.2, 137.6, 133.6, 133.0, 130.7, 129.6, 129.5, 129.3, 128.0, 125.2, 123.7, 123.1, 121.7, 121.1, 94.7, 88.0, 83.2, 77.3, 71.8, 54.9, 50.2, 37.2.

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₅H₁₇Cl₃N₃O₆S: 636.9749; found: 636.9744.

Synthesis of Spirochromeno[3,4-a]indolizidines 6 and 7; General Procedure

A suspension of the requisite nitrochromene **1** (0.25 mmol), acenaphthenequinone (46 mg, 0.25 mmol) and L-pipecolic acid (43 mg, 0.33 mmol) or (S)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid (58 mg, 0.33 mmol) in DMSO (2 mL, 100 μL of H₂O was added to the reaction mixture in order to dissolve the pipecolic acid) was stirred at 60 °C for 7 h (compounds **6**) or at 70 °C for 12 h (compounds **7**). Then the mixture was cooled to r.t., water (4 mL) was added, the precipitate was filtered off, washed with H₂O (5 × 1 mL) and dried at 60 °C. After drying, compounds **7** were purified by column chromatography on silica gel, elution with chloroform.

(1S*,6'S*,6a'S*,6b'S*,12a'R*)-6a'-Nitro-6'-(trifluoromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6a)

Obtained according to the general procedure from **1a** (61 mg) and L-pipecolic acid.

Yield: 72 mg (58%); pale-yellow powder; mp 231–232 °C (decomp.).

IR (ATR): 1703, 1605, 1585, 1562, 1487, 1457, 1409, 1354, 1342, 1338 cm⁻¹.

¹H NMR (500 MHz): δ = 8.18 (d, J = 8.0 Hz, 1 H), 8.03 (d, J = 8.2 Hz, 1 H), 7.98 (d, J = 6.9 Hz, 1 H), 7.87 (t, J = 7.6 Hz, 1 H), 7.71 (t, J = 7.5 Hz, 1 H), 7.66 (d, J = 6.9 Hz, 1 H), 7.04–6.90 (m, 1 H), 6.36 (t, J = 7.6 Hz, 1 H), 5.80 (d, J = 7.6 Hz, 1 H), 5.55 (q, J = 6.3 Hz, 1 H), 5.23 (s, 1 H), 4.02 (d, J = 10.2 Hz, 1 H), 2.43–1.10 (m, 8 H).

¹⁹F NMR (471 MHz): δ = 95.0 (br s, CF₃).

¹³C NMR (126 MHz): δ = 207.6 (C=O), 153.0, 143.2, 138.6, 132.4, 132.3, 130.6, 129.6, 128.8, 128.7, 126.6, 126.1, 123.3 (q, J = 282.1 Hz, CF₃), 123.2, 121.3, 121.1, 118.7, 117.7, 96.1, 78.4, 77.4 (q, J = 33.8 Hz, C-6'), 65.0, 50.8, 46.3, 28.9, 25.1, 24.3.

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₇H₂₂F₃N₂O₄: 495.1526; found: 495.1529.

(1S*,6'S*,6a'S*,6b'S*,12a'R*)-2'-Methyl-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6b)

Obtained according to the general procedure from **1b** (65 mg) and L-pipecolic acid.

Yield: 79 mg (62%); yellow powder; mp 221–222 °C (decomp.).

IR (ATR): 1706, 1606, 1557, 1502, 1464, 1439, 1403, 1336 cm⁻¹.

¹H NMR (400 MHz): δ = 8.18 (d, J = 8.0 Hz, 1 H), 8.03 (d, J = 8.3 Hz, 1 H), 7.98 (d, J = 6.9 Hz, 1 H), 7.87 (dd, J = 8.3, 6.9 Hz, 1 H), 7.70 (t, J = 7.5 Hz, 1 H), 7.65 (d, J = 6.9 Hz, 1 H), 6.84 (d, J = 8.4 Hz, 1 H), 6.77 (dd, J = 8.4, 1.4 Hz, 1 H), 5.49 (d, J = 1.4 Hz, 1 H), 5.46 (q, J = 6.8 Hz, 1 H), 5.14 (s, 1 H), 4.05 (d, J = 10.5 Hz, 1 H), 2.42–1.11 (m, 11 H).

¹⁹F NMR (376 MHz): δ = 95.3 (br s, CF₃).

¹³C NMR (126 MHz): δ = 207.5 (C=O), 150.7, 143.2, 138.9, 132.5, 132.4, 132.2, 130.6, 129.7, 129.5, 128.6, 127.1, 125.9, 123.4 (q, J = 283.0 Hz, CF₃), 121.3, 120.9, 118.5, 117.3, 96.1, 78.5, 65.1, 51.0, 46.4, 28.9, 25.2, 24.2, 20.3 (the signal of the C-6' atom overlaps with the signal of CD-Cl₃).

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₈H₂₄F₃N₂O₄: 509.1683; found: 509.1682.

(1S*,6S*,6aS*,6bS*,12a'R*)-2'-Methoxy-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6c)

Obtained according to the general procedure from **1c** (69 mg) and L-pipecolic acid.

Yield: 76 mg (58%); pale-yellow powder; mp 210–211 °C (decomp.).

IR (ATR): 1705, 1604, 1566, 1499, 1466, 1423, 1409, 1357, 1335 cm⁻¹.

¹H NMR (400 MHz): δ = 8.18 (d, *J* = 8.0 Hz, 1 H), 8.05–7.95 (m, 2 H), 7.87 (t, *J* = 7.6 Hz, 1 H), 7.76–7.65 (m, 2 H), 6.86 (d, *J* = 8.9 Hz, 1 H), 6.52 (dd, *J* = 8.9, 2.0 Hz, 1 H), 5.43 (q, *J* = 6.6 Hz, 1 H), 5.20 (d, *J* = 2.0 Hz, 1 H), 5.18 (s, 1 H), 4.04 (d, *J* = 10.3 Hz, 1 H), 2.73 (s, 3 H), 2.46–1.11 (m, 8 H).

¹⁹F NMR (376 MHz): δ = 94.9 (br s, CF₃).

¹³C{¹H} NMR (126 MHz): δ = 207.5 (C=O), 154.9, 146.9, 143.2, 138.8, 132.5, 132.2, 130.6, 129.7, 128.7, 126.0, 123.3 (q, *J* = 282.4 Hz, CF₃), 121.4, 121.2, 119.0, 118.6, 116.3, 109.5, 96.0, 78.4, 77.7 (q, *J* = 33.3 Hz, C-6'), 65.1, 54.6, 51.4, 46.4, 28.9, 25.1, 24.3.

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₈H₂₃F₃N₂O₅: 525.1632; found: 525.1630.

(1S*,6S*,6aS*,6bS*,12a'R*)-4'-Ethoxy-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6d)

Obtained according to the general procedure from **1d** (72 mg) and L-pipecolic acid.

Yield: 75 mg (56%); pale-yellow powder; mp 235–236 °C (decomp.).

IR (ATR): 1703, 1607, 1586, 1557, 1487, 1475, 1452, 1444, 1438, 1377, 1345, 1334 cm⁻¹.

¹H NMR (400 MHz): δ = 8.16 (d, *J* = 8.0 Hz, 1 H), 8.01 (d, *J* = 7.0 Hz, 1 H), 8.00 (d, *J* = 8.3 Hz, 1 H), 7.85 (dd, *J* = 8.3, 7.0 Hz, 1 H), 7.69 (dd, *J* = 8.0, 7.0 Hz, 1 H), 7.63 (d, *J* = 7.0 Hz, 1 H), 6.59 (d, *J* = 8.0 Hz, 1 H), 6.29 (t, *J* = 8.0 Hz, 1 H), 5.52 (q, *J* = 6.8 Hz, 1 H), 5.41 (d, *J* = 8.0 Hz, 1 H), 5.19 (s, 1 H), 4.11 (dd, *J* = 10.7, 1.5 Hz, 1 H), 4.04 (dq, *J* = 9.5, 7.0 Hz, 1 H), 4.00 (dq, *J* = 9.5, 7.0 Hz, 1 H), 2.34–1.07 (m, 11 H).

¹⁹F NMR (376 MHz): δ = 95.9 (br s, CF₃).

¹³C NMR (126 MHz): δ = 206.9 (C=O), 148.4, 143.1, 142.9, 139.0, 132.4, 132.1, 130.6, 129.6, 128.6, 125.9, 123.4 (q, *J* = 284.0 Hz, CF₃), 123.0, 121.5, 120.9, 120.6, 118.2, 113.2, 96.2, 78.5, 77.1 (q, *J* = 32.2 Hz, C-6'), 65.1, 65.0, 50.7, 46.3, 28.8, 25.1, 24.1, 14.9.

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₉H₂₆F₃N₂O₅: 539.1788; found: 539.1784.

(1S*,6S*,6aS*,6bS*,12a'R*)-2'-Chloro-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6e)

Obtained according to the general procedure from **1e** (70 mg) and L-pipecolic acid.

Yield: 87 mg (62%); beige powder; mp 214–215 °C (decomp.).

IR (ATR): 1705, 1605, 1557, 1481, 1402, 1336 cm⁻¹.

¹H NMR (400 MHz): δ = 8.21 (d, *J* = 7.7 Hz, 1 H), 8.06 (d, *J* = 8.2 Hz, 1 H), 8.01–7.64 (m, 4 H), 6.99–6.85 (m, 2 H), 5.69 (s, 1 H), 5.52 (q, *J* = 6.4 Hz, 1 H), 5.14 (s, 1 H), 4.03 (d, *J* = 10.2 Hz, 1 H), 2.43–1.10 (m, 8 H).

¹⁹F NMR (376 MHz): δ = 95.1 (br s, CF₃).

¹³C NMR (126 MHz): δ = 207.4 (C=O), 151.4, 143.2, 138.0, 132.6, 132.1, 130.7, 129.7, 129.0, 128.8, 128.2, 126.6, 126.3, 123.1 (q, *J* = 282.7 Hz, CF₃), 121.34, 121.31, 120.5, 119.0, 95.5, 78.3, 77.3 (q, *J* = 34.0 Hz, C-6'), 65.1, 50.6, 46.4, 28.9, 25.1, 24.2.

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₇H₂₁ClF₃N₂O₄: 529.1136; found: 529.1129.

(1S*,6S*,6aS*,6bS*,12a'R*)-2',4'-Dichloro-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6f)

Obtained according to the general procedure from **1f** (79 mg) and L-pipecolic acid.

Yield: 85 mg (60%); yellow powder; mp 219–220 °C (decomp.).

IR (ATR): 1699, 1605, 1557, 1481, 1441, 1402, 1336 cm⁻¹.

¹H NMR (400 MHz): δ = 8.21 (d, *J* = 8.0 Hz, 1 H), 8.05 (d, *J* = 8.3 Hz, 1 H), 8.00 (d, *J* = 6.9 Hz, 1 H), 7.88 (dd, *J* = 8.3, 6.9 Hz, 1 H), 7.74 (t, *J* = 7.5 Hz, 1 H), 7.70 (d, *J* = 6.9 Hz, 1 H), 7.09 (d, *J* = 1.8 Hz, 1 H), 5.64 (d, *J* = 1.8 Hz, 1 H), 5.56 (q, *J* = 6.7 Hz, 1 H), 5.13 (s, 1 H), 4.08 (d, *J* = 10.2 Hz, 1 H), 2.40–1.11 (m, 8 H).

¹⁹F NMR (376 MHz): δ = 95.5 (br s, CF₃).

¹³C NMR (126 MHz): δ = 207.7 (C=O), 147.4, 143.1, 137.8, 132.7, 132.0, 130.6, 129.7, 129.4, 128.9, 128.1, 126.4, 125.0, 124.2, 122.9 (q, *J* = 283.6 Hz, CF₃), 122.3, 121.5, 121.4, 95.4, 78.3, 65.0, 50.5, 46.3, 28.8, 25.0, 24.0 (the signal of the C-6' atom overlaps with the signal of CDCl₃).

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₇H₂₀Cl₂F₃N₂O₄: 563.0747; found: 563.0745.

(1S*,6S*,6aS*,6bS*,12a'R*)-2'-Bromo-4'-ethoxy-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6g)

Obtained according to the general procedure from **1g** (92 mg) and L-pipecolic acid.

Yield: 92 mg (60%); yellow powder; mp 211–212 °C (decomp.).

IR (ATR): 1700, 1602, 1554, 1487, 1473, 1422, 1401, 1344, 1329 cm⁻¹.

¹H NMR (400 MHz): δ = 8.19 (d, *J* = 8.0 Hz, 1 H), 8.03 (d, *J* = 8.4 Hz, 1 H), 8.01 (d, *J* = 7.0 Hz, 1 H), 7.86 (dd, *J* = 8.4, 7.0 Hz, 1 H), 7.72 (dd, *J* = 8.0, 7.0 Hz, 1 H), 7.67 (d, *J* = 7.0 Hz, 1 H), 6.70 (d, *J* = 2.0 Hz, 1 H), 5.48 (q, *J* = 6.8 Hz, 1 H), 5.46 (d, *J* = 2.0 Hz, 1 H), 5.07 (s, 1 H), 4.13 (d, *J* = 10.5 Hz, 1 H), 4.01 (dq, *J* = 9.3, 6.9 Hz, 1 H), 3.99 (dq, *J* = 9.3, 6.9 Hz, 1 H), 2.38–1.07 (m, 11 H).

¹⁹F NMR (376 MHz): δ = 96.1 (br s, CF₃).

¹³C NMR (126 MHz): δ = 206.7 (C=O), 149.1, 143.0, 141.6, 138.4, 132.3, 132.2, 130.6, 129.6, 128.7, 126.1, 123.2 (q, *J* = 284.4 Hz, CF₃), 122.3, 121.5, 121.1, 120.9, 116.1, 115.4, 95.7, 78.4, 65.3, 65.1, 50.3, 46.3, 28.7, 25.1, 23.9, 14.7 (the signal of the C-6' atom overlaps with the signal of CDCl₃).

HRMS (ESI): *m/z* [M + H]⁺ calcd for C₂₉H₂₅BrF₃N₂O₅: 617.0893; found: 617.0886.

(1S*,6S*,6aS*,6bS*,12a'R*)-2',6a'-Dinitro-6'-(trifluoromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6h)

Obtained according to the general procedure from **1h** (73 mg) and L-pipecolic acid.

Yield: 90 mg (67%); yellow powder; mp 241–242 °C (decomp.).

IR (ATR): 1697, 1603, 1585, 1565, 1527, 1483, 1434, 1341 cm⁻¹.

^1H NMR (400 MHz): δ = 8.25 (d, J = 8.0 Hz, 1 H), 8.12 (d, J = 8.3 Hz, 1 H), 8.00 (d, J = 6.9 Hz, 1 H), 7.92 (dd, J = 8.3, 6.9 Hz, 1 H), 7.87 (dd, J = 9.0, 2.2 Hz, 1 H), 7.71 (t, J = 7.5 Hz, 1 H), 7.66 (d, J = 6.9 Hz, 1 H), 7.09 (d, J = 9.0 Hz, 1 H), 6.64 (d, J = 2.2 Hz, 1 H), 5.66 (q, J = 6.4 Hz, 1 H), 5.19 (s, 1 H), 4.05 (d, J = 10.7 Hz, 1 H), 2.51–1.18 (m, 8 H).

^{19}F NMR (376 MHz): δ = 94.7 (br s, CF_3).

^{13}C NMR (126 MHz): δ = 207.7 (C=O), 157.4, 143.3, 143.0, 137.2, 133.2, 131.9, 130.9, 129.8, 128.9, 126.8, 124.6, 123.0, 122.8 (q, J = 282.3 Hz, CF_3), 121.5, 121.4, 119.5, 118.6, 94.8, 78.4, 77.6 (q, J = 34.5 Hz, C-6'), 65.3, 50.7, 46.4, 29.0, 25.0, 24.3.

HRMS (ESI): m/z [$M + H$] $^+$ calcd for $\text{C}_{27}\text{H}_{21}\text{F}_3\text{N}_3\text{O}_6$: 540.1377; found: 540.1378.

(1S*,6'S*,6a'S*,6b'S*,12a'R*)-6a'-Nitro-6'-(trichloromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6i)

Obtained according to the general procedure from **1j** (74 mg) and L-pipecolic acid.

Yield: 58 mg (43%); yellow powder; mp 219–220 °C (decomp.).

IR (ATR): 1701, 1606, 1554, 1489, 1455, 1443, 1329 cm^{-1} .

^1H NMR (500 MHz): δ = 8.17 (d, J = 8.0 Hz, 1 H), 8.02 (d, J = 8.2 Hz, 1 H), 7.93 (d, J = 6.9 Hz, 1 H), 7.86 (t, J = 7.6 Hz, 1 H), 7.69 (t, J = 7.5 Hz, 1 H), 7.65 (d, J = 6.9 Hz, 1 H), 7.02–6.98 (m, 2 H), 6.38–6.34 (m, 1 H), 5.81 (d, J = 8.0 Hz, 1 H), 5.80 (s, 1 H), 5.18 (s, 1 H), 4.44 (d, J = 9.4 Hz, 1 H), 2.66–1.22 (m, 8 H).

^{13}C NMR (126 MHz): δ = 207.7 (C=O), 152.4, 143.3, 138.8, 132.34, 132.29, 130.6, 129.6, 128.7 (2C), 126.2, 126.0, 123.1, 121.3, 121.1, 119.5, 117.8, 97.6, 97.5, 85.8, 78.2, 66.0, 51.7, 46.8, 30.5, 25.2, 24.6.

HRMS (ESI): m/z [$M + H$] $^+$ calcd for $\text{C}_{27}\text{H}_{22}\text{Cl}_3\text{N}_2\text{O}_4$: 543.0640; found: 543.0637.

(1S*,6'S*,6a'S*,6b'S*,12a'R*)-2'-Methyl-6a'-nitro-6'-(trichloromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6j)

Obtained according to the general procedure from **1k** (77 mg) and L-pipecolic acid.

Yield: 62 mg (44%); yellow powder; mp 223–224 °C (decomp.).

IR (ATR): 1698, 1605, 1550, 1498, 1443, 1432, 1339, 1331 cm^{-1} .

^1H NMR (400 MHz): δ = 8.16 (d, J = 8.0 Hz, 1 H), 8.02 (d, J = 8.3 Hz, 1 H), 7.95 (d, J = 6.8 Hz, 1 H), 7.86 (t, J = 7.6 Hz, 1 H), 7.69 (t, J = 7.5 Hz, 1 H), 7.63 (d, J = 6.9 Hz, 1 H), 6.88 (d, J = 8.2 Hz, 1 H), 6.79 (dd, J = 8.2, 1.5 Hz, 1 H), 5.70 (s, 1 H), 5.51 (d, J = 1.5 Hz, 1 H), 5.11 (s, 1 H), 4.46 (d, J = 9.6 Hz, 1 H), 2.60–1.23 (m, 8 H).

^{13}C NMR (126 MHz): δ = 207.5 (C=O), 149.9, 143.2, 139.1, 132.5, 132.3, 132.0, 130.5, 129.6, 129.3, 128.5, 126.8, 125.8, 121.4, 120.8, 119.5, 117.6, 97.73, 97.65, 85.8, 78.3, 66.1, 51.7, 46.8, 30.3, 25.2, 24.5, 20.4.

HRMS (ESI): m/z [$M + H$] $^+$ calcd for $\text{C}_{28}\text{H}_{24}\text{Cl}_3\text{N}_2\text{O}_4$: 557.0796; found: 557.0798.

(1S*,6'S*,6a'S*,6b'S*,12a'R*)-2'-Methoxy-6a'-nitro-6'-(trichloromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6k)

Obtained according to the general procedure from **1l** (81 mg) and L-pipecolic acid.

Yield: 75 mg (52%); yellow powder; mp 229–230 °C (decomp.).

IR (ATR): 1698, 1605, 1552, 1493, 1468, 1454, 1447, 1429, 1377, 1341 cm^{-1} .

^1H NMR (400 MHz): δ = 8.16 (d, J = 7.4 Hz, 1 H), 8.00 (d, J = 8.2 Hz, 1 H), 7.95 (d, J = 6.8 Hz, 1 H), 7.86 (t, J = 7.6 Hz, 1 H), 7.74–7.65 (m, 2 H), 6.91 (d, J = 8.9 Hz, 1 H), 6.54 (dd, J = 8.9, 2.1 Hz, 1 H), 5.67 (s, 1 H), 5.25 (d, J = 2.1 Hz, 1 H), 5.14 (s, 1 H), 4.46 (d, J = 8.7 Hz, 1 H), 2.75 (s, 3 H), 2.65–1.21 (m, 8 H).

^{13}C NMR (126 MHz): δ = 207.5 (C=O), 154.9, 146.3, 143.2, 139.0, 132.6, 132.1, 130.6, 129.7, 128.7, 125.9, 121.4, 121.1, 119.9, 118.8, 116.2, 109.3, 97.6, 97.5, 86.2, 78.2, 66.0, 54.6, 52.1, 46.9, 30.5, 25.2, 24.6.

HRMS (ESI): m/z [$M + H$] $^+$ calcd for $\text{C}_{28}\text{H}_{23}\text{Cl}_3\text{N}_2\text{O}_5$: 573.0745; found: 573.0747.

(1S*,6'S*,6a'S*,6b'S*,12a'R*)-4'-Ethoxy-6a'-nitro-6'-(trichloromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6l)

Obtained according to the general procedure from **1m** (85 mg) and L-pipecolic acid.

Yield: 87 mg (59%); yellow powder; mp 222–223 °C (decomp.).

IR (ATR): 1708, 1607, 1586, 1548, 1488, 1470, 1435, 1392, 1335 cm^{-1} .

^1H NMR (400 MHz): δ = 8.14 (d, J = 7.6 Hz, 1 H), 8.05–7.94 (m, 2 H), 7.84 (t, J = 7.5 Hz, 1 H), 7.67 (t, J = 7.4 Hz, 1 H), 7.60 (d, J = 6.7 Hz, 1 H), 6.61 (d, J = 8.0 Hz, 1 H), 6.32 (t, J = 8.0 Hz, 1 H), 5.77 (s, 1 H), 5.45 (d, J = 8.0 Hz, 1 H), 5.22 (s, 1 H), 4.48 (d, J = 9.1 Hz, 1 H), 4.17–3.93 (m, 2 H), 2.53–1.14 (m, 11 H).

^{13}C NMR (126 MHz): δ = 206.6 (C=O), 148.5, 143.0, 141.4, 139.3, 132.5, 131.9, 130.5, 129.6, 128.5, 125.7, 123.2, 122.0, 121.6, 120.7, 118.1, 113.2, 98.2, 97.9, 85.9, 78.3, 66.2, 65.1, 51.2, 46.6, 29.8, 25.2, 24.1, 15.1.

HRMS (ESI): m/z [$M + H$] $^+$ calcd for $\text{C}_{29}\text{H}_{26}\text{Cl}_3\text{N}_2\text{O}_5$: 587.0902; found: 587.0908.

(1S*,6'S*,6a'S*,6b'S*,12a'R*)-2'-Chloro-6a'-nitro-6'-(trichloromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6m)

Obtained according to the general procedure from **1n** (82 mg) and L-pipecolic acid.

Yield: 87 mg (60%); yellow powder; mp 222–223 °C (decomp.).

IR (ATR): 1698, 1605, 1554, 1482, 1446, 1432, 1339 cm^{-1} .

^1H NMR (400 MHz): δ = 8.20 (d, J = 8.0 Hz, 1 H), 8.05 (d, J = 8.3 Hz, 1 H), 7.93 (d, J = 6.8 Hz, 1 H), 7.87 (t, J = 7.6 Hz, 1 H), 7.73 (t, J = 7.5 Hz, 1 H), 7.69 (d, J = 6.9 Hz, 1 H), 6.97 (dd, J = 8.8, 1.8 Hz, 1 H), 6.94 (d, J = 8.8 Hz, 1 H), 5.76 (s, 1 H), 5.71 (br s, 1 H), 5.09 (s, 1 H), 4.44 (d, J = 9.4 Hz, 1 H), 2.66–1.21 (m, 8 H).

^{13}C NMR (126 MHz): δ = 207.5 (C=O), 150.7, 143.2, 138.3, 132.5, 132.2, 130.6, 129.6, 128.83, 128.78, 128.1, 126.26, 126.24, 121.4, 121.3, 121.3, 111.3, 97.3, 97.0, 85.7, 78.2, 66.1, 51.4, 46.8, 30.4, 25.1, 24.6.

HRMS (ESI): m/z [$M + H$] $^+$ calcd for $\text{C}_{27}\text{H}_{21}\text{Cl}_4\text{N}_2\text{O}_4$: 579.0220; found: 579.0229.

(1S*,6'S*,6a'S*,6b'S*,12a'R*)-2',4'-Dichloro-6a'-nitro-6'-(trichloromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6n)

Obtained according to the general procedure from **1o** (91 mg) and L-pipecolic acid.

Yield: 100 mg (65%); pale-yellow powder; mp 199–200 °C (decomp.).

IR (ATR): 1704, 1603, 1555, 1493, 1464, 1442, 1433, 1420, 1409, 1329 cm^{-1} .

¹H NMR (400 MHz): δ = 8.20 (d, J = 8.0 Hz, 1 H), 8.05 (d, J = 8.3 Hz, 1 H), 7.95 (d, J = 6.8 Hz, 1 H), 7.87 (t, J = 7.6 Hz, 1 H), 7.73 (t, J = 7.5 Hz, 1 H), 7.69 (d, J = 6.9 Hz, 1 H), 7.09 (d, J = 1.8 Hz, 1 H), 5.82 (s, 1 H), 5.65 (d, J = 1.8 Hz, 1 H), 5.10 (s, 1 H), 4.42 (d, J = 9.5 Hz, 1 H), 2.61–1.24 (m, 8 H).

¹³C NMR (126 MHz): δ = 207.1 (C=O), 146.8, 143.1, 138.0, 132.6, 132.0, 130.6, 129.7, 129.3, 128.8, 127.9, 126.3, 124.7, 124.2, 122.9, 121.5, 121.4, 97.0, 96.7, 86.0, 78.1, 66.1, 51.4, 46.8, 30.3, 25.1, 24.4.

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₇H₂₀Cl₅N₂O₄: 612.9831; found: 612.9839.

(1S*,6'S*,6a'S*,6b'S*,12a'R*)-2',6a'-Dinitro-6'-(trichloromethyl)-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (6o) and (1S*,6a'S*,6b'S*,12a'R*)-6'-(dichloromethylene)-2',6a'-dinitro-6a',6b',7',9',10',12a'-hexahydro-2H,6'H,8'H-spiro[acenaphthylene-1,12'-chromeno[3,4-a]indolizin]-2-one (8)

Obtained according to the general procedure from **1p** (85 mg) and L-pipecolic acid.

Combined yield: 39 mg; **6o/8** = 76:24; pale-brown powder; mp 168–170 °C (decomp.).

¹H NMR (400 MHz): δ (**6o**) = 8.23 (d, J = 8.0 Hz, 1 H), 8.12 (d, J = 8.3 Hz, 1 H), 7.99–7.87 (m, 3 H), 7.70 (t, J = 7.5 Hz, 1 H), 7.65 (d, J = 6.9 Hz, 1 H), 7.12 (d, J = 9.0 Hz, 1 H), 6.66 (d, J = 2.2 Hz, 1 H), 5.92 (s, 1 H), 5.08 (s, 1 H), 4.42 (d, J = 9.5 Hz, 1 H), 2.76–1.19 (m, 8 H); δ (**8**) = 8.64–7.60 (m, 7 H), 7.06 (d, J = 9.0 Hz, 1 H), 6.74 (d, J = 2.2 Hz, 1 H), 5.25 (s, 1 H), 4.50 (d, J = 10.2 Hz, 1 H), 2.76–1.19 (m, 8 H).

¹³C NMR (126 MHz): δ (**6o**) = 207.9, 157.0, 143.3, 142.8, 137.5, 133.1, 131.9, 130.9, 129.7, 128.9, 126.8, 124.5, 122.7, 121.5, 121.3, 120.1, 118.5, 96.5, 95.9, 85.8, 78.2, 66.4, 51.8, 47.0, 30.7, 25.1, 24.8; δ (**8**) = 206.1, 154.6, 143.4, 142.6, 141.9, 135.9, 132.8, 131.6, 130.8, 129.5, 128.8, 126.9, 124.9, 122.9, 121.2 (2C), 118.5, 117.6, 116.0, 95.8, 79.0, 67.5, 51.6, 47.0, 29.8, 25.1, 24.4.

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₇H₂₁Cl₃N₃O₆: 588.0490; found: 588.0494 (**6o**).

HRMS (ESI): m/z [M + H]⁺ calcd for C₂₇H₂₀Cl₂N₃O₆: 552.0724; found: 552.0727 (**8**).

(1S*,6'S*,6a'S*,6b'S*,14a'R*)-6a'-Nitro-6'-(trifluoromethyl)-6a',6b',7',14a'-tetrahydro-2H,6'H,12'H-spiro[acenaphthylene-1,14'-chromeno[3',4':3,4]pyrrolo[1,2-b]isoquinolin]-2-one (7a)

Obtained according to the general procedure from **1a** (61 mg) and (S)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid.

Yield: 71 mg (52%); pale-yellow powder; mp 239–240 °C (decomp.).

IR (ATR): 1702, 1607, 1556, 1490, 1442, 1436, 1403, 1346, 1333 cm⁻¹.

¹H NMR (400 MHz): δ = 8.26 (dd, J = 8.2, 1.0 Hz, 1 H), 8.08 (d, J = 8.2 Hz, 1 H), 7.95 (d, J = 6.8 Hz, 1 H), 7.87 (dd, J = 8.2, 7.2 Hz, 1 H), 7.97–7.72 (m, 2 H), 7.21–6.94 (m, 5 H), 6.72 (d, J = 7.6 Hz, 1 H), 6.38–6.32 (m, 1 H), 5.79 (q, J = 6.5 Hz, 1 H), 5.75 (d, J = 7.9 Hz, 1 H), 5.38 (s, 1 H), 4.42 (dd, J = 11.1, 2.9 Hz, 1 H), 3.67 (d, J = 14.5 Hz, 1 H), 3.47 (d, J = 14.5 Hz, 1 H), 3.29 (dd, J = 15.2, 2.9 Hz, 1 H), 2.81 (dd, J = 15.2, 11.1 Hz, 1 H).

¹⁹F NMR (376 MHz): δ = 94.2 (d, J = 6.5 Hz, CF₃).

¹³C NMR (126 MHz): δ = 208.3 (C=O), 153.0, 143.3, 137.9, 132.8 (2C), 132.7, 132.3, 130.8, 129.7, 129.6, 128.9, 128.87, 126.8, 126.6, 126.44, 126.41, 126.3, 123.2 (q, J = 281.3 Hz, CF₃), 123.1, 121.5 (2C), 117.7, 117.3, 95.8, 78.3, 77.4 (q, J = 34.0 Hz, C-6'), 61.7, 51.0, 48.5, 33.5.

HRMS (ESI): m/z [M + H]⁺ calcd for C₃₁H₂₂F₃N₂O₄: 543.1526; found: 543.1518.

(1S*,6'S*,6a'S*,6b'S*,14a'R*)-2'-Methyl-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',14a'-tetrahydro-2H,6'H,12'H-spiro[acenaphthylene-1,14'-chromeno[3',4':3,4]pyrrolo[1,2-b]isoquinolin]-2-one (7b)

Obtained according to the general procedure from **1b** (65 mg) and (S)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid.

Yield: 99 mg (71%); yellow powder; mp 226–227 °C (decomp.).

IR (ATR): 1700, 1603, 1587, 1559, 1488, 1438, 1421, 1403, 1336 cm⁻¹.

¹H NMR (500 MHz): δ = 8.25 (d, J = 7.8 Hz, 1 H), 8.09 (d, J = 8.3 Hz, 1 H), 7.98 (d, J = 6.9 Hz, 1 H), 7.88 (dd, J = 8.3, 7.2 Hz, 1 H), 7.78–7.71 (m, 2 H), 7.19–7.03 (m, 3 H), 6.83 (d, J = 8.3 Hz, 1 H), 6.76 (dd, J = 8.3, 1.2 Hz, 1 H), 6.73 (d, J = 7.7 Hz, 1 H), 5.70 (q, J = 6.6 Hz, 1 H), 5.44 (d, J = 1.2 Hz, 1 H), 5.31 (s, 1 H), 4.43 (dd, J = 11.2, 2.8 Hz, 1 H), 3.70 (d, J = 14.4 Hz, 1 H), 3.52 (d, J = 14.4 Hz, 1 H), 3.29 (dd, J = 15.2, 2.8 Hz, 1 H), 2.81 (dd, J = 15.2, 11.2 Hz, 1 H), 1.55 (s, 3 H, Me).

¹⁹F NMR (376 MHz): δ = 94.2 (d, J = 6.6 Hz, CF₃).

¹³C NMR (126 MHz): δ = 208.4 (C=O), 150.9, 143.3, 138.0, 132.9, 132.8, 132.6, 132.4, 132.3, 130.7, 129.7, 129.61, 129.56, 128.8, 127.0, 126.8, 126.4, 126.28, 126.26, 123.2 (q, J = 281.4 Hz, CF₃), 121.4, 121.3, 117.3, 116.9, 95.7, 78.4, 77.5 (q, J = 33.8 Hz, C-6'), 61.7, 51.2, 48.5, 33.5, 20.3.

HRMS (ESI): m/z [M + H]⁺ calcd for C₃₂H₂₄F₃N₂O₄: 557.1683; found: 557.1677.

(1S*,6'S*,6a'S*,6b'S*,14a'R*)-2'-Methoxy-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',14a'-tetrahydro-2H,6'H,12'H-spiro[acenaphthylene-1,14'-chromeno[3',4':3,4]pyrrolo[1,2-b]isoquinolin]-2-one (7c)

Obtained according to the general procedure from **1c** (69 mg) and (S)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid.

Yield: 90 mg (63%); yellow powder; mp 201–202 °C (decomp.).

IR (ATR): 1704, 1607, 1556, 1431, 1408, 1337 cm⁻¹.

¹H NMR (400 MHz): δ = 8.27–8.21 (m, 1 H), 8.06 (d, J = 8.2 Hz, 1 H), 7.97 (d, J = 7.1 Hz, 1 H), 7.88 (dd, J = 8.2, 7.1 Hz, 1 H), 7.80–7.74 (m, 2 H), 7.19–7.12 (m, 2 H), 7.09–7.03 (m, 1 H), 6.87 (d, J = 9.0 Hz, 1 H), 6.73 (d, J = 7.6 Hz, 1 H), 6.53 (dd, J = 9.0, 2.9 Hz, 1 H), 5.65 (q, J = 6.6 Hz, 1 H), 5.34 (s, 1 H), 5.17 (d, J = 2.9 Hz, 1 H), 4.44 (dd, J = 11.3, 3.1 Hz, 1 H), 3.71 (d, J = 14.3 Hz, 1 H), 3.54 (d, J = 14.3 Hz, 1 H), 3.29 (dd, J = 15.4, 3.1 Hz, 1 H), 2.80 (dd, J = 15.4, 11.3 Hz, 1 H), 2.72 (s, 3 H).

¹⁹F NMR (376 MHz): δ = 94.2 (d, J = 6.6 Hz, CF₃).

¹³C NMR (126 MHz): δ = 208.2 (C=O), 154.8, 147.0, 143.3, 138.0, 132.8, 132.7, 132.5, 132.4, 130.7, 129.8, 129.6, 129.0, 126.8, 126.4, 126.29, 126.25, 123.2 (q, J = 281.2 Hz, CF₃), 121.6 (2C), 118.7, 117.6, 116.7, 109.3, 95.7, 78.3, 77.5 (q, J = 33.8 Hz, C-6'), 61.7, 54.6, 51.5, 48.5, 33.5.

HRMS (ESI): m/z [M + H]⁺ calcd for C₃₂H₂₄F₃N₂O₅: 573.1632; found: 573.1621.

(1S*,6'S*,6a'S*,6b'S*,14a'R*)-4'-Ethoxy-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',14a'-tetrahydro-2H,6'H,12'H-spiro[acenaphthylene-1,14'-chromeno[3',4':3,4]pyrrolo[1,2-b]isoquinolin]-2-one (7d)

Obtained according to the general procedure from **1d** (72 mg) and (S)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid.

Yield: 94 mg (64%); pale-yellow powder; mp 226–227 °C (decomp.).

IR (ATR): 1698, 1605, 1585, 1557, 1487, 1471, 1436, 1405, 1337 cm⁻¹.

¹H NMR (400 MHz): δ = 8.27 (d, J = 7.8 Hz, 1 H), 8.07 (d, J = 8.3 Hz, 1 H), 7.95 (d, J = 6.7 Hz, 1 H), 7.86 (t, J = 7.8 Hz, 1 H), 7.79–7.70 (m, 3 H), 7.19–7.10 (m, 2 H), 7.05 (t, J = 7.2 Hz, 1 H), 6.71 (d, J = 8.0 Hz, 1 H),

6.57 (d, $J = 8.0$ Hz, 1 H), 6.25 (t, $J = 8.0$ Hz, 1 H), 5.76 (q, $J = 6.6$ Hz, 1 H), 5.39 (s, 1 H), 5.34 (d, $J = 8.0$ Hz, 1 H), 4.43 (dd, $J = 11.2$, 2.5 Hz, 1 H), 4.03–3.94 (m, 2 H), 3.66 (d, $J = 14.4$ Hz, 1 H), 3.45 (d, $J = 14.4$ Hz, 1 H), 3.29 (dd, $J = 15.3$, 2.5 Hz, 1 H), 2.79 (dd, $J = 15.3$, 11.2 Hz, 1 H), 1.39 (t, $J = 6.9$ Hz, 3 H).

^{19}F NMR (376 MHz): $\delta = 94.5$ (d, $J = 6.6$ Hz, CF_3).

^{13}C NMR (126 MHz): $\delta = 208.9$ (C=O), 148.3, 143.5, 143.3, 138.0, 132.8, 132.7, 132.3, 130.8, 129.7, 129.6, 128.8, 128.6, 126.8, 126.38, 126.35, 126.2, 123.2 (q, $J = 281.4$ Hz, CF_3), 122.8, 122.2, 121.5, 121.3, 118.1, 113.5, 95.9, 78.3, 77.6 (q, $J = 33.8$ Hz, C-6'), 65.3, 61.6, 51.0, 48.4, 33.4, 14.9.

HRMS (ESI): m/z [M + H] $^+$ calcd for $\text{C}_{33}\text{H}_{26}\text{F}_3\text{N}_2\text{O}_5$: 587.1788; found: 587.1792.

(1S*,6S*,6aS*,6bS*,14aR*)-2'-Chloro-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',14a'-tetrahydro-2H,6'H,12'H-spiro[acenaphthylene-1,14'-chromeno[3',4':3,4]pyrrolo[1,2-b]isoquinolin]-2-one (7e)

Obtained according to the general procedure from **1e** (70 mg) and (S)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid.

Yield: 89 mg (62%); pale-yellow powder; mp 240–241 °C (decomp.).

IR (ATR): 1703, 1605, 1557, 1482, 1435, 1415, 1404, 1344, 1333 cm^{-1} .

^1H NMR (500 MHz): $\delta = 8.29$ (d, $J = 7.6$ Hz, 1 H), 8.11 (d, $J = 8.2$ Hz, 1 H), 7.94 (d, $J = 6.9$ Hz, 1 H), 7.89 (t, $J = 7.7$ Hz, 1 H), 7.82–7.74 (m, 2 H), 7.19–7.12 (m, 2 H), 7.06 (t, $J = 7.8$ Hz, 1 H), 6.95 (dd, $J = 8.8$, 2.1 Hz, 1 H), 6.90 (d, $J = 8.8$ Hz, 1 H), 6.73 (d, $J = 7.7$ Hz, 1 H), 5.77 (q, $J = 6.3$ Hz, 1 H), 5.64 (d, $J = 2.1$ Hz, 1 H), 5.29 (s, 1 H), 4.43 (dd, $J = 11.2$, 2.6 Hz, 1 H), 3.69 (d, $J = 14.5$ Hz, 1 H), 3.51 (d, $J = 14.5$ Hz, 1 H), 3.29 (dd, $J = 15.2$, 2.6 Hz, 1 H), 2.81 (dd, $J = 15.2$, 11.2 Hz, 1 H).

^{19}F NMR (376 MHz): $\delta = 94.1$ (d, $J = 6.3$ Hz, CF_3).

^{13}C NMR (126 MHz): $\delta = 208.2$ (C=O), 151.5, 143.3, 137.2, 133.1, 132.7, 132.6, 132.0, 130.7, 129.7, 129.6, 129.1, 129.0, 128.1, 126.8, 126.7, 126.6, 126.5, 126.3, 122.0 (q, $J = 281.5$ Hz, CF_3), 121.7, 121.5, 119.1, 118.9, 95.1, 78.2, 77.4 (q, $J = 34.0$ Hz, C-6'), 61.7, 50.8, 48.5, 33.5.

HRMS (ESI): m/z [M + H] $^+$ calcd for $\text{C}_{31}\text{H}_{21}\text{ClF}_3\text{N}_2\text{O}_4$: 577.1136; found: 577.1135.

(1S*,6S*,6aS*,6bS*,14aR*)-2',4'-Dichloro-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',14a'-tetrahydro-2H,6'H,12'H-spiro[acenaphthylene-1,14'-chromeno[3',4':3,4]pyrrolo[1,2-b]isoquinolin]-2-one (7f)

Obtained according to the general procedure from **1f** (79 mg) and (S)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid.

Yield: 104 mg (68%); pale-yellow powder; mp 184–185 °C (decomp.).

IR (ATR): 1699, 1606, 1564, 1495, 1460, 1435, 1411, 1335 cm^{-1} .

^1H NMR (500 MHz): $\delta = 8.29$ (d, $J = 7.3$ Hz, 1 H), 8.12 (d, $J = 8.3$ Hz, 1 H), 7.94 (d, $J = 6.8$ Hz, 1 H), 7.89 (t, $J = 7.5$ Hz, 1 H), 7.84–7.75 (m, 2 H), 7.20–7.03 (m, 4 H), 6.73 (d, $J = 7.6$ Hz, 1 H), 5.81 (q, $J = 6.4$ Hz, 1 H), 5.57 (s, 1 H), 5.30 (s, 1 H), 4.44 (dd, $J = 11.4$, 2.5 Hz, 1 H), 3.69 (d, $J = 14.4$ Hz, 1 H), 3.51 (d, $J = 14.4$ Hz, 1 H), 3.30 (dd, $J = 15.2$, 2.5 Hz, 1 H), 2.81 (dd, $J = 15.2$, 11.4 Hz, 1 H).

^{19}F NMR (376 MHz): $\delta = 94.1$ (d, $J = 6.4$ Hz, CF_3).

^{13}C NMR (126 MHz): $\delta = 208.0$ (C=O), 147.7, 143.3, 136.9, 133.2, 132.50, 132.45, 131.9, 130.8, 129.8, 129.61, 129.55, 129.1, 128.0, 126.90, 126.85, 126.5, 126.3, 125.0, 124.1, 122.8 (q, $J = 281.7$ Hz, CF_3), 121.9, 121.6, 120.4, 95.0, 78.2, 77.4 (q, $J = 34.6$ Hz, C-6'), 61.7, 50.9, 48.5, 33.4.

HRMS (ESI): m/z [M + H] $^+$ calcd for $\text{C}_{31}\text{H}_{20}\text{Cl}_2\text{F}_3\text{N}_2\text{O}_4$: 611.0747; found: 611.0723.

(1S*,6S*,6aS*,6bS*,14aR*)-2'-Bromo-4'-ethoxy-6a'-nitro-6'-(trifluoromethyl)-6a',6b',7',14a'-tetrahydro-2H,6'H,12'H-spiro[acenaphthylene-1,14'-chromeno[3',4':3,4]pyrrolo[1,2-b]isoquinolin]-2-one (7f)

Obtained according to the general procedure from **1f** (92 mg) and (S)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid.

Yield: 96 mg (58%); yellow powder; mp 183–184 °C (decomp.).

IR (ATR): 1705, 1607, 1562, 1482, 1473, 1429, 1396, 1336 cm^{-1} .

^1H NMR (400 MHz): $\delta = 8.27$ (d, $J = 7.6$ Hz, 1 H), 8.10 (d, $J = 8.3$ Hz, 1 H), 7.93 (d, $J = 6.8$ Hz, 1 H), 7.87 (t, $J = 7.5$ Hz, 1 H), 7.82–7.72 (m, 2 H), 7.20–7.11 (m, 2 H), 7.06 (t, $J = 7.0$ Hz, 1 H), 6.72 (d, $J = 7.6$ Hz, 1 H), 6.67 (s, 1 H), 5.71 (q, $J = 6.0$ Hz, 1 H), 5.36 (s, 1 H), 5.28 (s, 1 H), 4.44 (dd, $J = 11.6$, 2.6 Hz, 1 H), 4.02–3.90 (m, 2 H), 3.69 (d, $J = 14.4$ Hz, 1 H), 3.51 (d, $J = 14.4$ Hz, 1 H), 3.29 (dd, $J = 14.8$, 2.6 Hz, 1 H), 2.79 (dd, $J = 14.8$, 11.6 Hz, 1 H), 1.39 (t, $J = 6.9$ Hz, 3 H).

^{19}F NMR (376 MHz): $\delta = 94.4$ (d, $J = 6.0$ Hz, CF_3).

^{13}C NMR (126 MHz): $\delta = 208.1$ (C=O), 148.9, 143.2, 142.4, 137.3, 133.0, 132.63, 132.61, 132.1, 130.7, 129.7, 129.6, 128.9, 126.8, 126.6, 126.4, 126.3, 123.0 (q, $J = 281.9$ Hz, CF_3), 121.6, 121.5, 120.8, 120.0, 116.2, 115.1, 95.3, 78.3, 65.4, 61.7, 50.7, 48.5, 33.4, 14.7 (the signal of the C-6' carbon atom overlaps with the signal of CDCl_3).

HRMS (ESI): m/z [M + H] $^+$ calcd for $\text{C}_{33}\text{H}_{25}\text{BrF}_3\text{N}_2\text{O}_5$: 667.0873; found: 667.0867.

(1S*,6S*,6aS*,6bS*,14aR*)-2',6a'-Dinitro-6'-(trifluoromethyl)-6a',6b',7',14a'-tetrahydro-2H,6'H,12'H-spiro[acenaphthylene-1,14'-chromeno[3',4':3,4]pyrrolo[1,2-b]isoquinolin]-2-one (7h)

Obtained according to the general procedure from **1h** (73 mg) and (S)-1,2,3,4-tetrahydroisoquinoline-3-carboxylic acid.

Yield: 70 mg (48%); yellow powder; mp 232–233 °C (decomp.).

IR (ATR): 1706, 1607, 1587, 1557, 1525, 1494, 1486, 1450, 1432, 1398, 1346, 1339 cm^{-1} .

^1H NMR (400 MHz): $\delta = 8.31$ (d, $J = 8.0$ Hz, 1 H), 8.18 (d, $J = 8.2$ Hz, 1 H), 8.02–7.69 (m, 5 H), 7.21–7.07 (m, 4 H), 6.76 (d, $J = 6.7$ Hz, 1 H), 6.60 (d, $J = 2.5$ Hz, 1 H), 5.90 (q, $J = 6.2$ Hz, 1 H), 5.32 (s, 1 H), 4.47 (dd, $J = 11.3$, 2.9 Hz, 1 H), 3.74 (d, $J = 14.5$ Hz, 1 H), 3.59 (d, $J = 14.5$ Hz, 1 H), 3.33 (dd, $J = 15.5$, 2.9 Hz, 1 H), 2.86 (dd, $J = 15.5$, 11.3 Hz, 1 H).

^{19}F NMR (376 MHz): $\delta = 93.9$ (d, $J = 6.2$ Hz, CF_3).

^{13}C NMR (126 MHz): $\delta = 208.3$ (C=O), 157.3, 143.4, 142.9, 136.5, 133.6, 132.50, 132.45, 131.8, 131.0, 129.8, 129.6, 129.1, 127.2, 126.9, 126.6, 126.3, 124.7, 123.1, 122.7 (q, $J = 281.9$ Hz, CF_3), 121.9, 121.6, 118.6, 118.2, 94.4, 78.2, 77.6 (q, $J = 34.4$ Hz, C-6'), 61.9, 50.9, 48.5, 33.5.

HRMS (ESI): m/z [M + H] $^+$ calcd for $\text{C}_{31}\text{H}_{21}\text{F}_3\text{N}_3\text{O}_6$: 588.1377; found: 588.1380.

Funding Information

The work was financially supported by the Russian Foundation for Basic Research (grant 20-03-00716) and by the Ministry of Science and Higher Education of the Russian Federation (project FEUZ-2020-0052).

Acknowledgment

Analytical studies were carried out using equipment at the Centre for Joint Use 'Spectroscopy and Analysis of Organic Compounds' at the Postovsky Institute of Organic Synthesis of the Russian Academy of Sciences (Ural Branch) and Centre for Joint Use 'Laboratory of Complex Investigations and Expert Evaluation of Organic Materials' at the Ural Federal University.

Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0040-1706005>.

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