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Note

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Photoinduced Non–stabilized Azomethine Ylide Formation for the Preparation of Fluorine Containing Pyrrolidines

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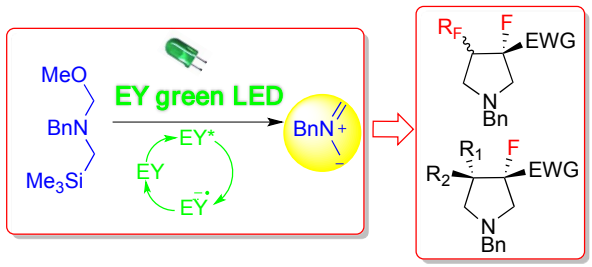
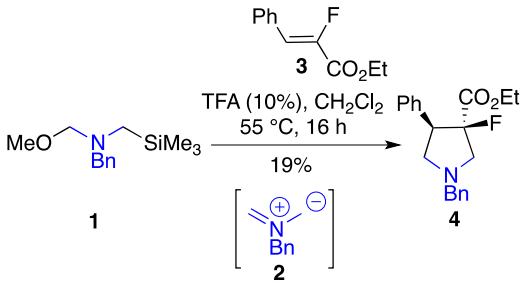
Supporting Information Placeholder



ABSTRACT: A mild and reproducible method for the formation of a non–stabilized azomethine ylide was developed by photoinduced reaction catalyzed with eosin Y under green light irradiation. Resulting 1,3-dipole was trapped with fluoroalkenes, fluoroalkylated alkenes and representative dipolarophiles to access pyrrolidine scaffolds, including spirocyclic compounds. The mechanism involved in this transformation was investigated, showing clearly a catalytic redox cycle with eosin Y.

Pyrrolidines and in particular 3-fluoro- and 3-fluoroalkylpyrrolidines play an important role in drug discovery,[1] as illustrated by the development of new important classes of antibiotics, modified amino-acids or nucleoside phosphorylase inhibitors.[2] The preparation of these derivatives was achieved by 1,3-dipolar cycloaddition reaction from alkenes and non-stabilized azomethine ylide precursor **1** (Scheme 1). While the cycloaddition reaction with non-stabilized azomethine ylides **2** was widely explored from trifluoromethylalkenes,[3] studies from mono- and di-fluoroalkenes were scarcely described. Recent works have been realized in this field,[4] and in some reports this reaction appeared capricious when the

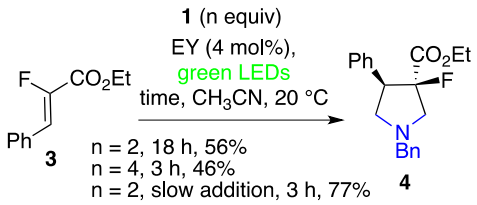
formation of the dipole **2** was performed from amine **1** in the presence of a catalytic amount of trifluoroacetic acid (TFA) at 0 °C.[5] Some modifications were introduced to improve the yield or to reach completion, including the reaction temperature (55°C up to 160 °C), the solvent nature (CH_3CN or neat), and the use of LiF instead of TFA. For trisubstituted alkenes,[4c] such as ethyl 2-fluoro-3-phenyl acrylate **3**, a longer reaction time and highest reaction temperature were necessary (55 °C instead of 0 °C) to form and trap the azomethine ylide **2** (Scheme 1). The corresponding pyrrolidine **4** was obtained in a modest 19% yield (Scheme 1), illustrating the limitations of these reaction conditions.



Scheme 1. Typical limits of 1,3-dipolar cycloaddition with non-stabilized ylides[4c]

The recent growing interest for photoredox reactions has stimulated mainly groups to develop photocatalytic cycloaddition reactions involving azomethine ylides. These works were exclusively focused on stabilized azomethine ylide formation in the presence of ruthenium complexes, Rose Bengal, or eosin Y (EY) under visible irradiation using LED light.[6]

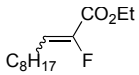
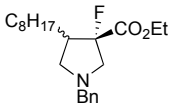
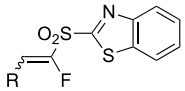
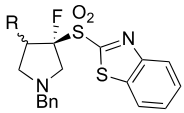
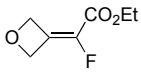
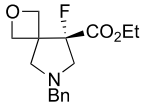
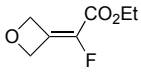
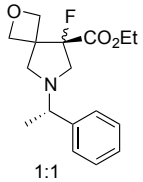
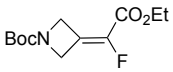
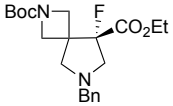
Inspired by these previous works, we developed a mild photoinitiated 1,3-dipolar cycloaddition reaction from the commercially available Achiwa's reagent **1**. Our initial investigations focused on examining the feasibility of the reaction with the poorly reactive dipolarophile **3** in the presence of eosin Y disodium salt, as photoactivator (Scheme 2). The reaction occurred in the presence of EY (4 mol%) and **1** under irradiation with a house green LED (5W) over 18 h at 20 °C. In this case, the corresponding pyrrolidine **4** was obtained in 56% yield, although the reaction reached up to 70–85% completion (determined by ^{19}F NMR analysis of the crude).



Scheme 2. Photoinduced 1,3-dipolar cycloaddition

While excess of dipole precursor **1** had a modest effect on the yield, slow addition of a solution of **1** (2 equiv) over 2 h followed by additional 1 h of stirring allowed to reach completion and afforded **4** in 77% yield (Scheme 2). Indeed, a short reaction time is preferred given the low stability of **2** in the medium. This result contrasts sharply with the reaction carried out with catalytic TFA (Scheme 1), the yield rising from 19% to 77%. The reaction was then applied to access representative fluorinated pyrrolidine derivatives from readily available fluoroalkenes (Table 1).[7] For these experiments, the corresponding pyrrolidines **10-14** were obtained in 50-95% yield depending on the alkene nature. In some cases, when applied, the product *cis*/*trans* ratio reflected the *Z*/*E* ratio of the alkene involved in the reaction, confirming the concerted mechanism expected for such cycloaddition reaction. From conjugated ester **5** substituted by an alkyl chain the pyrrolidine **10** was obtained in 50% yield (Table 1, Entry 1). In contrast, with terminal alkene **6** or trisubtituted vinylsulfones **7**, corresponding adducts **11**, **12** were isolated in 75% and 78% yield respectively (Table 1, Entry 2). The oxetanyl and *N*-Boc azetidinyl fluoroalkenes **8** and **9** gave the corresponding spirocyclic oxetanyl and azetidinyl pyrrolidine derivatives **13a** and **14** in 70-95% yield. These spirocyclic compounds are of interest for new drugs discovery.[8] Fluoropyrrolidines **13a** and **14** were recently synthesized through a 1,3-dipolar cycloaddition reaction from **1**.[4a] In this case, authors relied on the original method (TFA or LiF) to form and trap the dipole **2** but longer reaction time up to 18 h at 20 °C or high temperature up to 60 °C were required. The reaction carried on with alkene **8** and dipole precursor bearing a *N*–phenylethylamine group instead of a benzyl group afforded a mixture of adducts **13b** in 1:1 ratio.

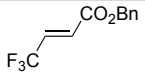
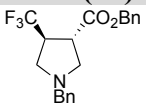
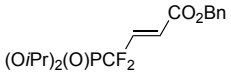
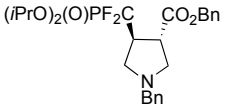
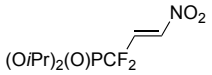
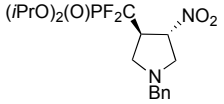
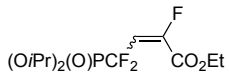
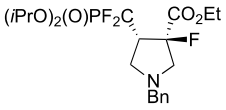
Table 1. Photoinduced 1,3-dipolar cycloaddition with fluoroalkenes

Entry	Alkene[a]	Product[b] Yield (%)[c]
1	 (*Z*:*E* = 7:3) **5**	 (*cis*:*trans* = 7:3) **10** (50)
2	 **6**: R = H **7**: R = C_6H_{13} (*Z*:*E* = 3:7)	 **11**: R = H (75) **12**: R = C_6H_{13} (78) (*cis*:*trans* = 3:7)
3	 **8**	 **13a** (95)
4	 **8**	 1:1 **13b** (65)
5	 **9**	 **14** (70)

[a] *Z*:*E* ratio determined by 19F NMR. [b] cis:trans geometry determined by HOESY experiments.[c] Isolated yield in parenthesis.

Other photosensitizers were tested, and experiments were realized in the presence of Rose Bengal (RB, green LED) in THF and acridinium derivative (Mes-Acr-Me+, blue LED) in CH_3CN (4 mol%). After 3 h of reaction performed with **8** and **1**, spirocyclic adduct **13a** was isolated in non–optimized yields of 66% and 74% respectively.

Table 2. Photoinduced 1,3-dipolar cycloaddition with tri- and di-fluoromethyl–alkenes

Entry	Alkene[a]	Product[b] Yield (%)[c]
1	 **15**	 **19** (81)
2	 **16**	 **20** (87)
3	 **17**	 **21** (85)
4	 (*E*:*Z* = 9:1) **18**	 (*trans*:*cis* = 9:1) **22** (70)

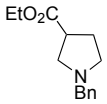
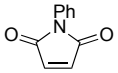
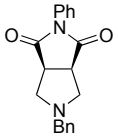
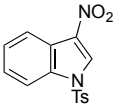
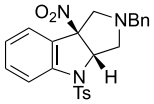
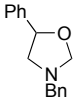
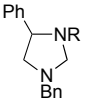
[a] *Z*:*E* ratio determined by ^{19}F NMR. [b] *cis*:*trans* ratio determined by NOESY experiments. [c] Isolated yield in parenthesis.

The reaction was extended to trifluoromethylalkene **15** and *gem*–difluoromethylalkenes **16**–**18** (Table 2). The reaction carried out with disubstituted alkenes such as benzyl trifluorocrotonate **15**, and difluoromethylphosphonates **16**, **17** afforded the corresponding pyrrolidines **19**–**21** in 81–87% yield (Table 2, Entries 1–3). From a trisubstituted fluoroalkene such as **18** bearing a phosphonodifluoromethyl group, the corresponding adduct **22** was isolated in good yield (Table 2, Entry 4). This last reaction tested following the original Achiwa's experimental conditions in the presence of catalytic amount of TFA (10 mol%) in dichloromethane was unsuccessful, and no adduct **22** was detected even after 18 h at 20 °C, showing again the photoinduced reaction is most efficient.

This method was not limited to fluorinated alkenes since good results were observed with other representative dipolarophiles (Table 3). The photoinduced reaction performed with **1** and ethylacrylate, or maleimide afforded the corresponding pyrrolidines **28** and **29** in 62% and 70% yield, respectively (Entries 1, 2).[9a,5] The dearomatization reaction of nitroindole was then tested, and was successful

leading to the corresponding dihydro–pyrroloindole **30** in 92% yield (Entry 3).[9b] Finally, the reaction was realized with two heterodipolarophiles, such as benzaldehyde and corresponding imines (Entries 4, 5). In these cases, adducts were obtained in moderate to good yields. These additional examples illustrated the scope of the photoinduced reaction.

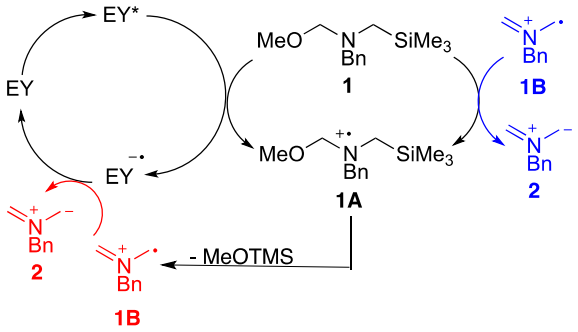
Table 3. Photoinduced 1,3-dipolar cycloaddition with representative dipolarophiles

Entry	dipolarophile	Product[a] Yield (%)[b]
1	 **23**	 **28**[9a] (62)
2	 **24**	 **29**[5] (70)
3	 **25**	 **30**[9b] (92)
4	 **26**	 **31**[9c] (78)
5	 **27a** (R = Ts) **27b** (R = S(O)*t*Bu	 **32a**[9d] (60) **32b**[9e] (65)

[a] Reaction performed with **1** (2 equiv), eosin Y (4 mol%), 3 h, 20 °C, CH_3CN.

[b] Isolated yield in parenthesis.

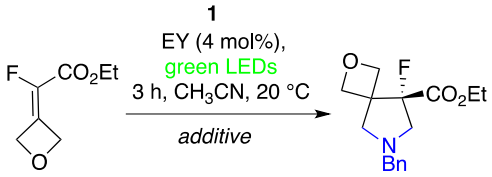
The mechanism of formation of the 1,3-dipole **2** under visible light irradiation was examined. Early studies reported the formation of α-amino radicals by irradiation of silylalkylamines.[10] It has been clearly established that the first step of the reaction is a photoinduced electron transfer (PET) occurring from the nitrogen centre to the excited photosensitizer to afford the corresponding α-silyl amino radical cation. The latter undergoes a selective desilylation reaction induced by a protic solvent (methanol) to give the α-amino radical. This method was applied to the formation of azomethine ylide but from the bis-silylated amine $(Me_3SiCH_2)_2NBn$ only.[11] To our knowledge no precedent work has been reported with Achiwa's reagent **1**.



Scheme 3. Formation of 1,3-dipole 2 from amine 1

The formation of the 1,3-dipole **2** from the silylated alkoxymethylamine **1** will follow a similar mechanism where EY* is reduced by a PET from amine **1** to lead to the radical cation **1A** (Scheme 3). This radical cation then gives the unstable and highly reactive intermediate iminium radial **1B**,[12] and next the dipole **2** after its reduction. The formation of intermediate radical in our experiment was evaluated by performing the reaction in the presence of radical scavengers (MeHQ) 4-methoxyphenol, and (BHT) dibutylhydroxytoluene (15 and 30 mol%). For these latter, the formation of the 1,3-dipole **2** was partially (15 mol%) or totally (30 mol%) inhibited (Scheme 4), suggesting a probable formation of intermediate radicals. The reaction was performed in the presence of tetramethylpiperidine *N*–oxide (TEMPO, 2 equiv), however no trapping product was detected, TEMPO seems to react with eosin Y.[13]

Contrasting with the previous works performed with silylalkylamines,[10, 11] the absence of methanol as co-solvent is essential for the TMS transfer to occur. Indeed, the formation of 1,3-dipole **2** from amine **1** was inhibited when realized in methanol/acetonitrile (1:1). In addition, the absence of oxygen in the medium is important and was confirmed by experiments realized in nitrogen saturated CH_3CN and air saturated CH_3CN. While the reaction reached completion for the former, a completion of 40% was reached for the latter.



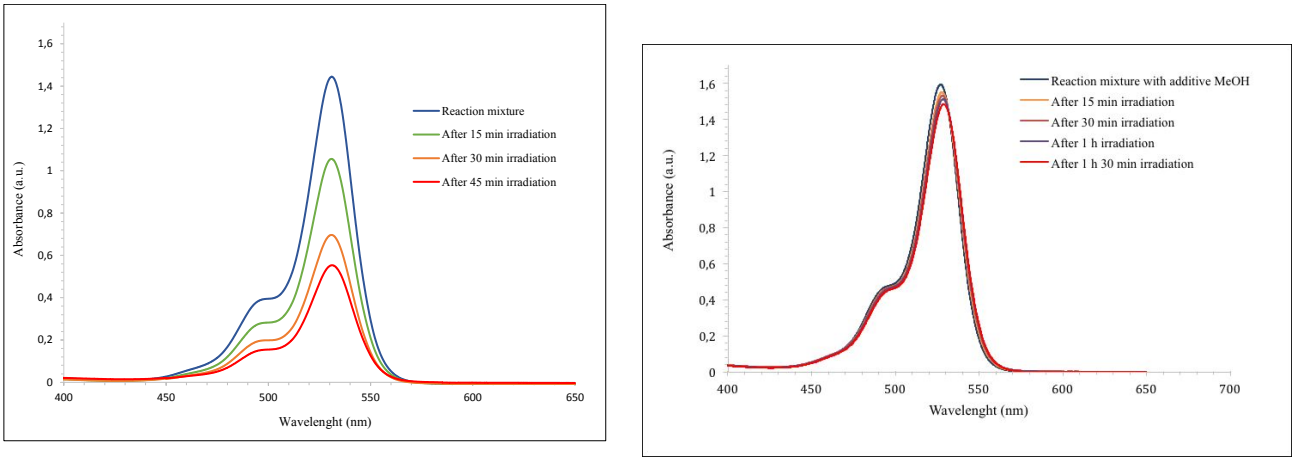
additive	conversion (%)
none	100
BHT (15 mol%)	33
BHT (30 mol%)	0
MeHQ (15 mol%)	28
MeHQ (30 mol%)	0
CH_3OH	0
air (buble)	40

Scheme 4. Effect of additives and experiment control

This mechanism is supported considering the redox potential of EY, RB, and Mes-Acr-Me+ under their excited state (E_{red}^{T1}) of +0.83, +0.81 and +1.45 V *vs* SCE, respectively.[14] These photosensitizers are able to oxidize tertiary amines ($E_{1/2}^{ox}$ = +0.78 V *vs* SCE)[15] to initiate the formation of radical cation **1A** and corresponding reduced form of the photosensitizer ($PS^{\bullet -}$). With eosin Y, the radical **1B** obtained after TMSOMe ejection, can be easily reduced into dipole **2**, $EY^{\bullet -}$ acting as strong reductant in its ground state ($E_{1/2}^{red}$ = -1.08 V *vs* SCE).

The reaction was monitored by UV-Vis analysis. The UV-Vis absorption spectrum of eosin Y (4 mol%) were recorded over time in the presence of alkene **8** (1 equiv) and amine **1** (1 equiv) in CH_3CN solution (Figure 1A). While unchanged UV-Vis spectra profile of eosin Y was observed after addition of alkene **8**, the intensity absorption was affected upon addition of amine **1** to the mixture eosin Y/alkene **8**. Again, the inhibitory effect of methanol was confirmed as the absorption profile of eosin Y

was found unaffected when the spectra of the mixture (eosin Y; alkene **8**; amine **1)** were recorded over time in CH_3CN/CH_3OH solution (Figure 1B).



(A) (B)

Figure 1. (A) UV-Vis absorption spectra of EY after addition of reagents 1 and 8. (B) Spectra after addition of methanol

The quenching rate for alkene **8** and amine **1** was directly evaluated using standard Stern–Volmer analyses. Fluorescence quenching was realized by following the emission intensity of eosin Y disodium salt with the gradual increase of the amount of each reagent (alkene **8** and amine **1**). Addition of alkene **8** has no influence of the emission intensity (*see* Figure S8), while amine **1** induced a gradual decrease (*see* Figure S7), confirming an interaction between the excited EY* and amine **1**. A possible electron transfer would be definitively confirmed by transient spectroscopy.

An alternative mechanism, involving the formation of amino radical cation **1A** by oxidation of amine **1** with iminium radical **1B** is not excluded (Scheme 4, blue).[16] Our model reaction performed from **1** (1 equiv), and **8** realized in an NMR tube (CD_3CN) was followed by ^{19}F NMR (*see* Figure S11). The reaction run in the absence of light was slower and needed 24 h at 20 °C to reach completion to afford the expected adduct **13a**. In this experiment, no trace of intermediate fluorinated compounds was observed. This reaction carried on larger scale in the dark afforded **13a** in 74% yield after 24 h at 20 °C. In this case, it is presumed that EY initiated the formation of amino radical cation **1A** during the sample

preparation, and the subsequent generation of amino radical cation **1A** results from oxidation of amine **1** by iminium radical **1B**. Both mechanisms could work in parallel.

To conclude, the formation of a non–stabilized azomethine ylide **2** under mild experimental conditions was achieved based on a photoinduced electron transfer catalyzed with organic photosensitizers using LED light. This method was exemplified by the synthesis of useful fluorinated pyrrolidine scaffolds, and representative pyrrolidines, including spirocyclic compounds, in reproducible high yields. The mechanistic information collected will be of interest to investigate other cycloaddition reactions involving silylated azomethine ylide precursors.

EXPERIMENTAL SECTION

General Information.

All commercially available reagents were bought and used as received. For anhydrous conditions, the glassware was flame dried under a continuous nitrogen flow and cooled to 20 °C before running the experiment. Anhydrous solvents (THF, CH_3CN) were dried in a solvent generator, which uses an activated alumina column to remove water. Et_3N was distilled under CaH_2 or molecular sieves (4 Å). Products were detected by thin layer chromatography, on which the spots were visualized by a 254 nm UV lamp and/or $KMnO_4$ solution. NMR spectra were recorded with a 500 MHz or 600 MHz apparatus in deuterated solvent at 25 °C. All ^{13}C NMR spectra are decoupled from the ^1H ($^{13}C\{^1H\}$). The chemical shifts (δ) and coupling constants (*J*) are expressed in ppm and Hz respectively. The following abbreviations are used: s: singlet; d: doublet; t triplet; q: quadruplet; quint: quintet; sext: sextet; sept: septet; m: multiplet; br: broad signal. High-resolution mass spectroscopic data were recorded with a Micromass Q-TOF instrument with an electrospray source in the EI or ESI mode.

Preparation of alkene compounds 5 to 9 and 15 to 18. *Ethyl 2-fluoro-undec-2-enoate (**5**).* Compound **5** was synthesized according to literature procedure.[15] Dibromoethane (0.128 mL, 1.48 mmol, 1.5 equiv)was added dropwise to a suspension of Mg^0(34 mg, 1.38 mmol, 1.4 equiv) in THF (5 mL) at 20°C under N_2. After disappearance of all magnesium (1 h of stirring), a solution containing nonaldehyde

(305 mg, 1.18 mmol, 1.2 equiv) and 2-(1-Ethylfluoroacetate)sulfonyl-1,3-benzothiazole (300 mg, 0.989 mmol, 1 equiv) in THF (1 mL) was added. After 10 min, DBU (0.21 mL, 1.38 mmol, 1.4 equiv) was added dropwise, and the solution was stirred for 2h at 20°C. The reaction was quenched with a saturated solution of NH_4Cl (1 mL) and brine (2 mL), then extracted with CH_2Cl_2/Et_2O (1:1, 20 mL). The organiclayer was washed with brine, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The crude product was purified by chromatography (silica, pentane/AcOEt 92:8) to afford **5** (198 mg, 0.860 mmol, 87%) (Z:E = 7:3) (*E*)-isomer ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.93 (dt, $^3J_{HF}$ = 21.8 Hz, $^3J_{HH}$ = 7.9 Hz, 1H), 4.25–4.33 (m, 2H), 2.20–2.55 (m, 2H), 1.22–1.48 (m, 15H), 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$): δ –122.8 (d, $^3J_{FH}$ = 21.8 Hz). (*Z*)-isomer ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.00 (dt, $^3J_{HF}$ = 33.5 Hz, $^3J_{HH}$ = 7.9 Hz, 1H); 4.25–4.33 (m, 2H), 2.20–2.55 (m, 2H), 1.22–1.48 (m, 15H), 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 3H). ^{19}F NMR (470 MHz, $CDCl_3$): δ –131.2 (d, $^3J_{FH}$ = 33.5 Hz). NMR data are in agreement with literature data.[15]

*2-[(1-Fluorovinyl)sulfonyl]-1,3-benzothiazole (**6**).* Compound **6** was synthesized according to literature procedure.[16] To a solution of 2-benzothiazolylsulfonyl-2-fluoroethanol (300 mg, 1.14 mmol, 1 equiv) and MsCl (110 µL, 1.38 mmol, 1.2 equiv) in CH_2Cl_2 (4 mL) cooled to 0 °C was added dropwise NEt_3 (400 µL, 2.85 mmol, 2.5 equiv). The mixture was stirred for 30 min at 0 °C and then quenched with a saturated solution of NH_4Cl (1 mL). The aqueous layer was extracted with CH_2Cl_2 (20 mL). Combined organic layers were washed with a saturated solution of $NaHCO_3$ (2 mL), dried over $MgSO_4$, filtered, and evaporated under reduced pressure to furnish **6** (259 mg, 92%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.19–8.22 (m, 1H), 7.96–7.99 (m, 1H), 7.54–7.64 (m, 2H), 6.06 (dd, $^2J_{HH}$ = 5.0 Hz, $^3J_{HF}$ = 40.7 Hz, 1H), 5.65 (dd, $^2J_{HH}$ = 5.0 Hz, $^3J_{HF}$ = 11.7 Hz, 1H). NMR data are in agreement with literature data.[16]

*2-(1-Fluorooct-1-ene-1-sulfonyl)-1,3-benzothiazole (**7**).* In a 50 mL oven dried flask was added LiCl (69 mg, 1.63 mmol, 1.2 eq.), the flask was flame dried under argon flush and cooled to room temperature.

THF (30 mL) and diethyl ((benzothiazol-2-ylsulfonyl)fluoromethyl)phosphonate (500 mg, 1.36 mmol, 1.0 eq.) were added. After cooling at 0 °C, Et_3N (0.21 mL, 1.50 mmol, 1.1 eq.) was added dropwise, followed after 10 min of stirring by the addition of heptanal (155 mg, 1.36 mmol). After 18 h of stirring, the reaction mixture was quenched with 2 mL of 3N hydrochloric aqueous solution. After extraction with Et_2O, the organic layer was washed with brine, dried over magnesium sulfate, filtrated and evaporated under reduced pressure. The crude residue was purified by flash chromatography using Pentane/AcOEt (95:5) as eluent. A 3:7 ratio (*Z*:*E*) of compound **7** was obtained as a colorless oil (416 mg, 89%). (*Z*)-isomer ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.28–8.26 (m, 1H), 8.04–8.03 (m, 1H), 7.67–7.61 (m, 2H), 6.15 (dt, $^3J_{HF}$ = 21.2 Hz, $^3J_{HH}$ = 8.6 Hz, 1H), 2.70 (m, 2H), 1.54–1.47 (m, 2H), 1.40–1.25 (m, 6H), 0.88 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 164.3, 152.8, 150.3 ($^1J_{CF}$ = 286.9 Hz), 137.4, 128.4 (2C), 127.8 (2C), 125.9, 125.0 (d, $^2J_{CF}$ = 10.8 Hz), 122.3, 31.5, 29.1 (dd, $^4J_{CF}$ = 2.2 Hz), 28.7, 24.9 (d, $^3J_{CF}$ = 3.0 Hz), 22.6, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ –116.4 (d, $^3J_{FH}$ = 21.2 Hz). (*E*)-isomer ^{1}H NMR (500 MHz $CDCl_3$): δ 8.26–8.24 (m, 1H), 8.03–8.01 (m, 1H), 7.67–7.59 (m, 2H), 6.51 (dt, $^3J_{HF}$ = 32.0 Hz, $^3J_{HH}$ = 8.1 Hz, 1H), 2.30 (m, 2H), 1.51–1.47 (m, 2H), 1.40–1.25 (m, 6H), 0.87 (m, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 163.8, 152.8, 152.0 ($^1J_{CF}$ = 293.7 Hz), 137.5, 128.4 (2C), 127.8 (2C), 125.9, 123.4 (d, $^2J_{CF}$ = 7.4 Hz), 122.3, 31.4, 28.7, 27.9 (dd, $^4J_{CF}$ = 1.8 Hz), 24.8 (d, $^3J_{CF}$ = 1.8 Hz), 22.5, 14.0. ^{19}F NMR (470 MHz, $CDCl_3$): δ –128.3 (dt, $^3J_{FH}$ = 32.0 Hz, $^4J_{FH}$ = 2.5 Hz). HRMS-ESI *(m/z)* $[M+H]^+$: calculated for $C_{15}H_{19}NO_2FS_2^+$ 328.0841 found 328.0848.

*Ethyl 2-fluoro-2-(oxetan-3-ylidene)acetate (**8**)*. DBU (5.55 mL, 37.2 mmol, 1.5 equiv.) was added dropwise to a THF (50 mL) solution of triethyl 2-fluoro-2-phosphonoacetate (6.0 g, 24.78 mmol) and 3-oxetanone (1.97 g, 27.25 mmol, 1.2 equiv.). The resulting mixture was stirred 2 h at 20 °C. The reaction was monitored by TLC and quenched with a saturated NH_4Cl solution. The aqueous layer was extracted twice with CH_2Cl_2. The organic layers were combined, washed with brine, dried with $MgSO_4$, filtered and evaporated under reduced pressure. The crude product was purified by flash SiO_2 column chromatography with DCM as eluent to give compound **8** (3.97 g, 84 %).^{1}H NMR (500 MHz, $CDCl_3$): δ

5.44–5.31 (m, 4H), 4.28 (q, $^{3}J_{HH}$ = 7.2 Hz, 2H), 1.32 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H). ^{19}F NMR (472 Hz, $CDCl_3$): δ –136.4, (quint, $^{4}J_{HF}$ = 3.8 Hz). NMR data are in good agreement with literature data.[17]

*Tert-butyl 3-(2-ethoxy-1-fluoro-2-oxoethylidene)azetidine-1-carboxylate (**9**)*. DBU (0.46 mL, 3.1 mmol, 1.5 equiv.) was added dropwise to a THF (5 mL) solution of triethyl 2-fluoro-2-phosphonoacetate (0.5 g, 2.07 mmol) and tert-butyl 3-oxoazetidine-1-carboxylate (0.389 g, 2.27 mmol, 1.2 equiv.). The resulting mixture was stirred 4 h 30 at 20 °C. The reaction was monitored by TLC and quenched with a saturated NH_4Cl solution. The aqueous layer was extracted twice with CH_2Cl_2. The organic layers were combined, washed with brine, dried with $MgSO_4$, filtered and evaporated under reduced pressure. The crude product was purified by flash SiO_2 column chromatography with pentane/AcOEt (80/20) as eluent to give compound **8** (0.44 g, 82 %). ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.74–4.73 (m, 2H), 4.31–4.27 (m, 2H), 4.31 (q, $^{3}J_{HH}$ = 7.2 Hz, 2H), 1.47 (s, 9H), 1.33 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$): δ –133.9 (quint, $^{4}J_{HF}$ = 3.8 Hz). NMR data are in good agreement with literature data.[17]

*(E)-Benzyl 4,4,4-trifluoro-3-(trifluoromethyl)but-2-enoate (**15**)*. In a 50 mL oven dried flask was added LiCl (88 mg, 2.07 mmol, 1.2 eq.), the flask was flame dried under Argon flush and cooled to room temperature. THF (4 mL) and benzyl 2-(diethoxyphosphoryl)acetate (494 mg, 1.72 mmol) was added. After cooling at 0 °C, Et_3N (0.3 mL, 1.9 mmol, 1.1 eq.) was added dropwise followed after 10 min of stirring by the addition of 1-methoxy-2,2,2-trifluoroethanol (225 mg, 1.72 mmol). After 18 h of stirring, the reaction mixture was quenched with 2 mL of 3N hydrochloric aqueous solution. After extraction with Et_2O, the organic layer was washed with brine, dried over magnesium sulfate, filtrated and evaporated under reduced pressure. The crude residue was purified by flash chromatography using Pentane/EtOAc (90 :10) as eluent to obtain compound **15** as a colorless oil (320 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.37 (m, 5H), 6.82 (dq, $^{3}J_{HH}$ = 15.8 Hz, $^{3}J_{HF}$ = 6.5 Hz, 1H), 6.55 (dq, $^{3}J_{HH}$ = 15.8 Hz, $^{4}J_{HF}$ = 2.0 Hz, 1H), 5.26 (s, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 163.9, 135.1, 131.9 (q, $^{2}J_{CF}$ = 35.6 Hz), 128.9 (2C), 128.8, 128.8 (q, $^{3}J_{CF}$ = 6.2 Hz), 128.6 (2C), 122.0 (q, $^{1}J_{CF}$ = 269.7 Hz), 67.6

^{19}F NMR (470 MHz, $CDCl_3$): δ –65.60 (d.br, $^{3}J_{FH}$ = 6.5 Hz, $^{4}J_{FH}$ not resolved). HRMS-ESI *(m/z)* [M+H]$^{+}$: calculated for $C_{11}H_{10}F_3O_2^{+}$ $[M + H]^{+}$ 231.0634, found 231.0632.

*(E)-Benzyl (2)-4-(diisopropoxyphosphoryl)-4,4 difluorobut-2-enoate (**16**)*. In a 50 mL oven dried flask was added LiCl (39 mg, 0.91 mmol, 1.2 eq.), the flask was flame dried under argon flush and cooled to room temperature. THF (4 mL) and benzyl 2-(diethoxyphosphoryl)acetate (218 mg, 0.76 mmol, 1.0 eq.) was added. After cooling at 0 °C, Et_3N (0.12 mL, 0.84 mmol, 1.1 eq.) was added dropwise, followed after 10 min of stirring by the addition of diisopropyl 1,1-difluoro-2,2-dihydroxyethylphosphonate (200 mg, 0.76 mmol) in THF solution (1 mL). After 18 h of stirring, the reaction mixture was quenched with 2 mL of 3N hydrochloric aqueous solution. After extraction with Et_2O, the organic layer was washed with brine, dried over magnesium sulfate, filtrated and evaporated under reduced pressure. The crude residue was purified by flash chromatography using Pentane/EtOAc (80 :20) as eluent. Compound **16** was obtained as a colorless oil (251 mg, 87%). ^{1}H NMR (500 MHz $CDCl_3$): δ 7.39–7.36 (m, 5H), 6.98–6.89 (m, 1H), 6.47–6.43 (m, 1H), 5.23 (s, 2H), 4.86 (dsept, $^{3}J_{HP}$ = $^{3}J_{HH}$ = 6.2 Hz, 2H), 1.39 (d, $^{3}J_{HH}$ = 6.2 Hz, 2H), 1.36 (d, $^{3}J_{HH}$ = 6.2 Hz, 2H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 164.3, 136.2 (dt, $^{2}J_{CF}$ = 22.1 Hz, $^{2}J_{CP}$ = 13.1 Hz), 135.3, 128.7 (2C), 128.5, 128.4 (2C), 127.4 (dt, $^{3}J_{CF}$ = 9.5 Hz, $^{3}J_{CP}$ = 5.5 Hz), 115.8 (dt, $^{1}J_{CF}$ = 260.1 Hz, $^{1}J_{CP}$ = 218.6 Hz), 74.3 (d, $^{2}J_{CP}$ = 7.0 Hz, 2C), 67.1, 24.1 (d, $^{3}J_{CP}$ = 3.6 Hz, 2C), 23.7 (d, $^{3}J_{CP}$ = 4.9 Hz, 2C). ^{19}F NMR (470 MHz, $CDCl_3$): δ–112.51 (ddd, $^{2}J_{FP}$ = 107.8 Hz, $^{3}J_{FH}$ = 12.7, $^{4}J_{FH}$ = 1.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 3.12 (tt, $^{2}J_{PF}$ = 107.8 Hz, $^{3}J_{PH}$ = 6.2 Hz). HRMS-ESI *(m/z)* $[M+Na]^{+}$: calculated for $C_{17}H_{23}F_2O_5PNa^{+}$ 399.1149 found 399.1150.

*(E)-diisopropyl-1,1-difluoro-3-nitroprop-2-en-1-ylphosphonate (**17**)*. In a 50 mL oven dried flask was added KF (44 mg, 0.76 mmol, 1.0 eq), the flask was flame dried under argon flush and cooled to room temperature. Isopropanol (4 mL) and diisopropyl 1,1-difluoro-2,2-dihydroxyethylphosphonate (200 mg, 0.76 mmol, 1.0 eq.) was added. After 10 min of stirring at room temperature, nitromethane (0.12 mL,

2.29 mmol, 3.0 eq.) was added. After 18 h of stirring at room temperature, the reaction mixture was diluted with Et_2O, the organic layer was washed twice with brine, dried over magnesium sulfate, filtrated and evaporated under reduced pressure. The crude residue was diluted in CH_2Cl_2 then cooled to 0 °C. Mesyl chloride (0.16 mL, 2.11 mmol, 3.0 eq.) was added and the reaction mixture was stirred 30 min at 0 °C under argon. Et_3N (0.28 mL, 2.11 mmol, 3.0 eq.) was added dropwise. After 1 h 30 min at room temperature the reaction mixture was quenched with water and extracted with Et_2O. Organic layer was washed with brine, dried over magnesium sulfate, filtrated and evaporated under reduced pressure. The crude yellow residue was purified by flash chromatography using Pentane/EtOAc 80/20 as eluent. Compound **17** was obtained as a slight yellow oil (124 mg, 61%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37–7.34 (m, 1H), 7.22–7.14 (m, 1H), 4.90 (dsept, $^3J_{HP}$ = $^3J_{HH}$ = 6.3 Hz, 2H), 1.41 (d, $^3J_{HH}$ = 6.3 Hz, 6H), 1.39 (d, $^3J_{HH}$ = 6.3 Hz, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 144.1 (m), 130.6 (td, $^2J_{CF}$ = 23.0 Hz, $^2J_{CP}$ = 13.6 Hz), 115.0 (td, $^1J_{CF}$ = 263.0 Hz, $^1J_{CP}$ = 218.5 Hz), 75.1 (d, $^2J_{CP}$ = 7.1 Hz, 2C), 24.1 (d, $^3J_{CP}$ = 3.7 Hz, 2C), 23.7 (d, $^3J_{CP}$ = 4.9 Hz, 2C). ^{19}F NMR (470 MHz, $CDCl_3$): δ –112.43 (dd, $^3J_{FP}$ = 102.9 Hz, $^3J_{FH}$ = 11.9 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 1.86 (tt, $^3J_{PF}$ = 102.9 Hz, $^3J_{HP}$ = 6.3 Hz). HRMS-ESI *(m/z)* $[M+Na]^+$: calculated for $C_9H_{16}F_2NO_5PNa^+$ 310.0632 found 310.0640.

*4-(diisopropoxyphosphoryl)-2,4,4-trifluorobut-2-enoate (**18**).* In a 50 mL oven dried flask was added LiCl (57 mg, 1.34 mmol, 1.2 eq.), the flask was flame dried under argon flush and cooled to room temperature. THF (10 mL) and ethyl 2-(diethoxyphosphoryl)-2-fluoroacetate (270 mg, 1.12 mmol, 1.0 eq.) was added. After cooling at 0 °C, Et_3N (0.2 mL, 1.23 mmol, 1.1 eq.) was added dropwise, followed after 10 min of stirring by the addition of diisopropyl 1,1-difluoro-2,2-dihydroxyethylphosphonate (291 mg, 0.37 mmol) in THF solution (1 mL). After 18 h of stirring, the reaction mixture was quenched with 2 mL of 3N hydrochloric aqueous solution. After extraction with Et_2O, the organic layer was washed with brine, dried over magnesium sulfate, filtrated and evaporated under reduced pressure. The crude residue was purified by chromatography using DCM/MeOH (95:5) as eluent. A (90:10) mixture of (*E*:*Z*)

compound **18** was obtained as a colorless oil (90 mg, 24%). (*E*) isomer: ^{1}H NMR (500 MHz $CDCl_3$): δ 5.93 (dtd, $^{3}J_{HF}$ = 18.5 Hz, $^{3}J_{HF}$ = 15.0 Hz, $^{3}J_{HP}$ = 3.5 Hz, 1H), 4.92–4.85 (dsept, $^{3}J_{HP}$ = $^{3}J_{HH}$ = 6.3 Hz, 2H), 4.38–4.34 (q, $^{3}J_{HH}$ = 7.1 Hz 2H), 1.40–1.36 (m, 15H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) : δ 158.8 (dd, $^{2}J_{CF}$ = 34.0, $^{4}J_{CF}$ = 1.4 Hz), 153.7 (d, $^{1}J_{CF}$ = 271.7, $^{3}J_{CF}$ = 9.9 Hz), 114.5 (ddt, $^{1}J_{CF}$ = 260.9, $^{1}J_{CP}$ = 224.8, $^{3}J_{CF}$ = 15.1 Hz), 108.4 (dtd, $^{2}J_{CF}$ = 26.1, $^{2}J_{CF}$ = 23.4, $^{2}J_{CP}$ = 15.4 Hz), 74.4 (d, $^{2}J_{CP}$ = 6.7 Hz, 2C), 62.7, 24.1 (d, $^{3}J_{CP}$ = 3.5 Hz, 2C), 23.7 (d, $^{3}J_{CP}$ = 5.2 Hz, 2C), 13.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ –103.59 (ddt, $^{3}J_{FH}$ = 18.5 Hz, $^{4}J_{FP}$ = 9.5 Hz, $^{4}J_{FF}$ = 4.4 Hz, 1F), –105.96 (ddd, $^{2}J_{FP}$ = 106.8 Hz, $^{3}J_{FH}$ = 15.0 Hz, $^{4}J_{FF}$ = 4.4 Hz, 2F). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 3.64 (td, $^{2}J_{PF}$ = 106.8 Hz, $^{3}J_{PH}$ = 9.5 Hz). HRMS-ESI *(m/z)* $[M + Na]^+$: calculated for $C_{12}H_8F_6O_2Na^+$ 355.0895 found 355.0890. (*Z*) isomer visible on ^{1}H, ^{19}F and ^{31}P spectra: ^{1}H NMR (500 MHz $CDCl_3$): δ 6.24 (dtd, $^{3}J_{HF}$ = 29.5 Hz, $^{3}J_{HF}$ = 14.3 Hz, $^{3}J_{HP}$ = 3.5 Hz, 1H), ^{19}F NMR (376 MHz, $CDCl_3$): δ –109.4 (ddd, $^{2}J_{FP}$ = 107.6 Hz, $^{4}J_{FF}$ = 23.1 Hz, $^{3}J_{FH}$ = 14.3 Hz, 2F), –113.5 (dtd, $^{3}J_{FH}$ = 29.5 Hz, $^{4}J_{FF}$ = 23.1 Hz, $^{4}J_{FP}$ = 7.2 Hz, 1F). ^{31}P NMR ($CDCl_3$, 202 MHz): δ 2.8 (td, $^{2}J_{PF}$ = 107.6 Hz, $^{3}J_{PH}$ = 7.2 Hz).

General procedure for the 1,3-dipolar cycloadditions. A CH_3CN (1.0 mL) solution of *N*-methoxymethyl-*N*-(trimethylsilylmethyl)benzylamine 1 (2.2 eq.) was added during 2 h (with syringe pump) to an irradiated CH_3CN (2.0 mL) solution of dipolarophile (1.0 eq.) and eosin Y disodium salt (4 mol%) with a 5W green LED. After 3 h of irriadiation, the solvent was removed under reduced pressure. Residue was purified via SiO_2 column chromatography to give corresponding cycloadducts.

(cis)-Ethyl-1-Benzyl-3-fluoro-4-phenylpyrrolidine-3-carboxylate (4). Compound **4** was obtained, in accordance with general procedure, from (*Z*)-2-fluoro-3-phenyl acrylate **3** (0.10 g, 0.52 mmol), **1** (0.3 mL, 1.03 mmol) and Eosin Y (0.01 g, 0.02 mmol). The crude product was purified by chromatography: eluent (80:20) pentane/AcOEt to give a colorless oil (0.13 g, 77%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22−7.40 (m, 10H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.78−3.92 (m, 3H), 3.49−3.58 (dd, $^{3}J_{HF}$ = 29.0, $^{2}J_{HH}$ = 11.9, 1H), 3.25−3.29 (m, 1H), 3.14 (m, 1H), 3.08 (dd, $^{3}J_{HF}$ = 30.5, $^{2}J_{HH}$ = 11.9, 1H), 1.28 (t, *J* = 7.1 Hz,

3H). ^{19}F NMR (471 MHz, $CDCl_3$): δ –161.5 (ddd, $^3J_{HF}$ = $^3J_{HF}$ = 30.5, $^3J_{HF}$ = 29.0). NMR data are in agreement with those reported in the literature.[4c]

*Ethyl-1-benzyl-3-fluoro-4octylpyrrolidine-3-carboxylate (**10**).* A 3:7 (*trans*/*cis*) diastereoisomeric mixture of compound **10** was obtained, in accordance with general procedure, from a 3:7 (*E*/*Z*) mixture of ethyl-2-fluoroundec-2-enoate **5** (0.10 g, 0.43 mmol), **1** (0.2 mL, 0.87 mmol) and Eosin Y (0.01 g, 0.02 mmol). The crude residue was purified by chromatography: eluent (80:20) pentane/Et_2O to give a not separable mixture of isomers as colorless oil (0.08 g, 50%). (*cis*) isomer : ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.25 (m, 5H), 4.32–4.24 (m, 2H), 3.70 (d, $^2J_{HH}$ = 13.0 Hz, 1H), 3.62 (d, $^2J_{HH}$ = 13.0 Hz, 1H), 3.28–3.21 (m, 2H), 2.93 (dd, $^3J_{HF}$ = 26.0 Hz, $^2J_{HH}$ = 11.8 Hz, 1H), 2.70–2.50 (m, 1H), 2.14–2.11 (m, 1H), 1.49–1.39 (m, 1H), 1.34–1.17 (m, 16H), 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) : δ 169.8 (d, $^2J_{CF}$ = 28,0 Hz), 138.1, 128.4 (2C), 128.0 (2C), 126.6, 102.0 (d, $^1J_{CF}$ = 196.3 Hz), 62.8 (d, $^2J_{CF}$ = 24.8 Hz), 61.3, 59.2, 49.7 (d, $^2J_{CF}$ = 24.1 Hz), 31.5, 29.3, 29.0, 28.9, 28.5, 28.1, 22.7, 14.3, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ –166.72 (ddd, $^3J_{FH}$ = $^3J_{FH}$ = 30.0 Hz, $^3J_{FH}$ = 26.0 Hz). (*trans*) isomer : ^{1}H NMR (500 MHz, $CDCl_3$) : δ 7.36–7.25 (m, 5H), 4.32–4.24 (m, 2H), 3.76 (d, $^2J_{HH}$ = 13.0 Hz, 1H), 3.69 (d, $^2J_{HH}$ = 13.0 Hz, 1H), 3.41 (dd, $^3J_{HF}$ = 27.1 Hz, $^2J_{HH}$ = 11.8 Hz, 1H), 3.10–3.06 (dd, $^2J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 7.2 Hz, 1H), 2.85 (dd, $^3J_{HF}$ = 19.8 Hz, $^2J_{HH}$ = 11.0 Hz, 1H), 2.70–2.50 (m, 1H), 2.48–2.45 (m, 1H), 1.59–1.51 (m, 1H), 1.49–1.39 (m, 1H), 1.34–1.17 (m, 15H) 0.88 (t, $^3J_{HH}$ = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) 170.9 (d, $^2J_{CF}$ = 28.0 Hz) , 138.4, 128.7 (2C), 128.4 (2C), 127.1, 100.1 (d, $^1J_{CF}$ = 197.1 Hz), 64.0 (d, $^2J_{CF}$ = 24.8 Hz), 61.9, 60.3, 58.3, 47.5 (d, $^2J_{CF}$ = 20.2 Hz), 31.9, 29.7, 29.4, 29.2, 28.0, 26.3, 22.7, 14.2, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$)*:* δ –144.35 (ddd, $^3J_{FH}$ = 30.0 Hz, $^3J_{FH}$ = 27.1 Hz $^3J_{FH}$ = 19.8 Hz). HRMS-ESI *(m/z)* $[M+H]^+$ calculated for $C_{22}H_{35}NO_2F^+$ 364.2652, found 364.2654.

*2-((1-Benzyl-3-fluoropyrrolidin-3-yl)sulfonyl)benzothiazole (**11**).* Compound **11** was obtained, in accordance with general procedure, from **6** (0.10 g, 0.41 mmol), **1** (0.2 mL, 0.82 mmol) and Eosin Y

(0.01 g, 0.02 mmol). The crude residue was purified by chromatography: eluent (90:10) pentane/Et_2O to give a colorless oil (0.12 g, 77%).^{1}H NMR (500 MHz, $CDCl_3$) : δ 8.25–8.22 (m, 1H), 8.00–7.95 (m, 1H), 7.61–7.58 (m, 2H), 7.29–7.25 (m, 5H), 3.70 (d, $^2J_{HH}$ = 13.1 Hz, 1H), 3.68 (d, $^2J_{HH}$ = 13.1 Hz, 1H), 3.50 (dd, $^3J_{HF}$ = 24.5 Hz, $^2J_{HH}$ = 12.5 Hz, 1H), 3.18–2.92 (m, 3H), 2.70 (m, 1H), 2.28 (ddd, $^3J_{HF}$ = 28.8, $^2J_{HH}$ = 13.0, $^3J_{HH}$ = 7.1 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 161.9, 152.9, 137.7, 137.7, 128.6 (2C), 128.5 (2C), 128.4, 127.8, 127.4, 126.0, 122.2, 114.2 (d, $^1J_{CF}$ = 230.3 Hz), 59.5 (d, $^2J_{CF}$ = 23.2 Hz), 59.4, 52.8, 33.7 (d, $^2J_{CF}$ = 21.2 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): δ –139.0 (dddd, $^3J_{FH}$ = 28.8 Hz, $^3J_{FH}$ = $^3J_{FH}$ = 24.5 Hz, $^3J_{FH}$ = 19.1 Hz). HRMS-ESI *(m/z)* $[M+H]^+$ calculated for $C_{18}H_{18}N_2O_2S_2F^+$ 377.0794, found 377.0799.

((1-Benzyl-3-fluoro-4-hexylpyrrolidin-3-yl)sulfonyl)benzothiazole ***(12)****. A* 7:3 (*trans*/*cis*) diastereoisomeric mixture of compound **12** was obtained, in accordance with general procedure, from a 7:3 (*E*/*Z*) mixture of **7** (0.10 g, 0.31 mmol), **1** (0.2 mL, 0.61 mmol) and Eosin Y (0.01 g, 0.02 mmol). The crude residue was purified by chromatography: eluent 90:10 pentane/Et_2O to give a not separable mixture of isomers as colorless oil (0.11 g, 78%). (*trans*) isomer ^{1}H NMR (500 MHz, $CDCl_3$) : δ 8.29–8.25 (m, 1H), 8.05–7.98 (m, 1H), 7.71–7.56 (m, 2H), 7.35–7.22 (m, 5H), 3.90 (dd, $^3J_{HF}$ = 17.7 Hz, $^2J_{HH}$ = 12.5 Hz, 1H), 3.70 (d, $^2J_{HH}$ = 13.1 Hz, 1H), 3.67 (d, $^2J_{HH}$ = 13.1 Hz, 1H), 3.20–3.06 (m, 2H), 2.83 (dd, $^3J_{HF}$ = 27.5 Hz, $^2J_{HH}$ = 12.5 Hz, 1H), 2.47–2.44 (m, 1H), 1.50–1.10 (m, 10H), 0.83 (t, $^3J_{HH}$ = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) : δ 162.1, 152.9, 137.8, 137.7, 128.6 (2C), 128.5 (2C), 128.4, 127.8, 127.3, 126.0, 122.2, 114.0 (d, $^1J_{CF}$ = 233.6 Hz), 60.5 (d, $^2J_{CF}$ = 24.3 Hz), 59.1, 58.6, 43.2 (d, $^2J_{CF}$ = 18.6 Hz), 31.5, 29.2, 27.9, 27.4 (d, $^3J_{CF}$ = 10.8 Hz), 22.5, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$)*:* δ –155.6 (ddd, $^3J_{FH}$ = 27.5 Hz, $^3J_{FH}$ = $^3J_{FH}$ = 17.7 Hz). (*cis*) isomer ^{1}H NMR (500 MHz, $CDCl_3$) : δ 8.29–8.25 (m, 1H), 8.05–7.98 (m, 1H), 7.71–7.56 (m, 2H), 7.35–7.22 (m, 5H), 3.71–3.70 (m, 2H), 3.58 (dd, $^3J_{HF}$ = 28.5 Hz, $^2J_{HH}$ = 12.80 Hz, 1H), 3.24 (dd, $^2J_{HH}$ = 9.1 Hz, $^3J_{HH}$ = 7.0 Hz, 1H), 3.20–3.06 (m, 1H), 2.88–2.76 (m, 1H), 2.47–2.44 (m, 1H), 1.50–1.10 (m, 10H), 0.83 (t, $^3J_{HH}$ = 7.0 Hz, 3H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) : δ 163.4, 152.7, 137.8, 137.7, 128.6 (2C), 128.5 (2C), 128.4, 127.7, 127.4, 126.0, 122.2,

114.9 (d, $^{1}J_{CF}$ = 231.4 Hz), 61.0 (d, $^{2}J_{CF}$ = 24.3 Hz), 59.8, 59.1, 50.0 (d, $^{2}J_{CF}$ = 21.1 Hz), 31.7, 29.1, 28.7, 26.8 (d, $^{3}J_{CF}$ = 4.0 Hz), 22.6, 14.1. ^{19}F NMR (470 MHz, $CDCl_3$): δ –132.19—132.24 (m). HRMS-ESI *(m/z)* $[M+H]^+$ calculated for $C_{24}H_{29}N_2O_2FS_2^+$ 461.1729, found 461.1735.

*Ethyl-6-benzyl-8-fluoro-2-oxa-6-azaspiro[3.4]octane-8-carboxylate (**13a**)*. Compound **13a** was obtained, in accordance with general procedure, from **8** (0.10 g, 0.63 mmol), **1** (0.32 mL, 1.2 mmol) and Eosin Y (0.03 g, 0.05 mmol). The crude residue was purified by chromatography: eluent (70:30) pentane/EtOAc to give a colorless oil (0.35 g, 95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.28 (m, 5H), 5.00 (d, $^{2}J_{HH}$ = 6.5 Hz, 1H), 4.57 (d, $^{2}J_{HH}$ = 6.5 Hz, 1H), 4.39–4.28 (m, 4H), 3.68–3.66 (m, 2H), 3.28 (d, $^{2}J_{HH}$ = 9.3 Hz, 1H), 3.15 (dd, $^{3}J_{HF}$ = 26.0, $^{2}J_{HH}$ = 11.6 Hz, 1H), 3.04 (dd, $^{3}J_{HF}$ = 26.0 Hz, $^{2}J_{HH}$ = 11.6 Hz, 1H), 2.98 (d, $^{2}J_{HH}$ = 9.3 Hz, 1H), 1.36 (t, $^{3}J_{HH}$ = 7.1 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$): δ –158.95 (t, $^{3}J_{FH}$ = 26.0 Hz). NMR data are in good agreement with those reported in the literature.[4a]

Rose bengale reaction: compound **13a** was obtained, in accordance with general procedure, from **8** (0.10 g, 0.63 mmol), **1** (0.32 mL, 1.2 mmol) and rose bengale (0.008 g, 0.008 mmol) in THF (2 mL). The crude residue was purified by chromatography: eluent (90:10) pentane/acetone to give a colorless oil (0.12 g, 66%).

9-mesityl-10-methylacridinium perchlorate reaction: compound **13a** was obtained, in accordance with general procedure, from **8** (0.10 g, 0.63 mmol), **1** (0.32 mL, 1.2 mmol) and 9-mesityl-10-methylacridinium perchlorate (0.01 g, 0.024 mmol) under blue light LED irradiation (230V/5W). The crude residue was purified by chromatography: eluent (7:3) pentane/AcOEt to give a colorless oil (0.135 g, 74%).

*Ethyl 5-fluoro-7-[(1S)-1-phenylethyl]-2-oxa-7-azaspiro[3.4]octane-5-carboxylate (**13b**)*. Compound **13b** was obtained, in accordance with general procedure, from **8** (0.3 g, 1.9 mmol), (1S)-*N*-(methoxymethyl)-1-phenyl-*N*-(trimethylsilylmethyl)ethanamine (0.94 g, 3.75 mmol) and Eosin Y (0.052 g, 0.08 mmol). The crude residue was purified by chromatography: eluent (95:5) pentane/AcOEt to give

a yellow oil (0.38 g, 65%). ^{1}H NMR (500 MHz, $CDCl_3$, both diastereomers): δ 7.40–7.15 (m, 5H), 4.98 (t, J = 6.5 Hz, 1H), 4.55 (dd, J = 11.3, 7.0 Hz, 1H), 4.42–4.20 (m, 4H), 3.41–2.72 (m, 5H), 1.42–1.30 (m, 6H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, , both diastereomers): δ 169.4 (d, $^{2}J_{CF}$ = 28.0 Hz), 169.3 (d, $^{2}J_{CF}$ = 28.2 Hz), 144.5, 144.4, 128.67 (2C), 128.65 (2C), 127.4 (2C), 127.1 (4C), 99.5 (d, $^{1}J_{CF}$ = 198.8 Hz), 99.4 (d, $^{1}J_{CF}$ = 198.2 Hz), 77.1 (d, $^{3}J_{CF}$ = 7.0 Hz), 76.6 (d, $^{3}J_{CF}$ = 6.5 Hz), 76.1 (d, $^{2}J_{CF}$ = 17.5 Hz), 75.7 (d, $^{2}J_{CF}$ = 17.5 Hz), 64.7, 64.6, 62.5, 62.36, 62.34, 62.2, 62.0 (d, $^{2}J_{CF}$ = 25.1 Hz), 61.9 (d, $^{2}J_{CF}$ = 25.3 Hz), 52.0 (d, $^{2}J_{CF}$ = 22.6 Hz), 51.9 (d, $^{2}J_{CF}$ = 22.6 Hz), 23.0, 22.9, 14.4 (2C). ^{19}F NMR (471 MHz, $CDCl_3$): δ –158.54 (t, $^{3}J_{FH}$ = 26.9 Hz), –158.84 (t, $^{3}J_{FH}$ = 26.5 Hz). HRMS-ESI *(m/z)* $[M+H]^+$ calculated for $C_{17}H_{23}NO_3F^+$ 308.1662, found 308.1664.

*2-(Tert-butyl) 8-ethyl-6-benzyl-8-fluoro-2,6-diazaspiro[3.4]octane-2,8-dicarboxylate (**14**).* Compound **14** was obtained, in accordance with general procedure, from **9** (0.10 g, 0.39 mmol), **1** (0.2 mL, 0.77 mmol) and Eosin Y (0.01 g, 0.02 mmol). The crude residue was purified by chromatography: eluent 9:1 pentane/EtOAc to give a colorless oil (0.13 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.35–7.30 (m, 5H), 4.32–4.25 (m, 3H), 3.80 (d, $^{2}J_{HH}$ = 9.5 Hz, 1H), 3.67–3.65 (m, 4H), 3.28–3.25 (m, 1H), 3.05–2.99 (m, 2H), 2.88 (d, $^{2}J_{HH}$ = 9.5 Hz, 1H), 1.41 (s, 9H), 1.33 (t, $^{3}J_{HH}$ = 7.2 Hz, 3H). ^{19}F NMR (471 MHz, $CDCl_3$): δ –157.3 (m). NMR data are in good agreement with those reported in the literature.[4a]

*(trans)-Benzyl-1-benzyl-4-(trifluoromethyl)pyrrolidine-3-carboxylate (**19**).* Compound **19** was obtained, in accordance with general procedure, from **15** (0.10 g, 0.44 mmol), **1** (0.22 mL, 0.87 mmol) and Eosin Y (0.01 g, 0.02 mmol). The crude residue was purified by chromatography: eluent 85:15 pentane/Et_2O to give a colorless oil (0.13 g, 81%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.16 (m, 10H), 5.17 (d, $^{2}J_{HH}$ = 12.3 Hz, 1H), 5.13 (d, $^{2}J_{HH}$ = 12.3 Hz, 1H), 3.62 (d, $^{2}J_{HH}$ = 13.1 Hz, 1H), 3.56 (d, $^{2}J_{HH}$ = 13.1 Hz, 1H), 3.42–3.36 (m, 1H), 3.15 (dd, $^{2}J_{HH}$ = 12.9, $^{3}J_{HH}$ = 6.3 Hz, 1H), 2.88–2.85 (m, 3H), 2.66 (dd, $^{2}J_{HH}$ = 9.7, $^{3}J_{HH}$ = 6.3 Hz, 1H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 172.8, 138.0, 135.6, 128.6 (2C), 128.5 (2C), 128.4 (2C), 128.3, 128.1 (2C), 127.3, 127.2 (q, $^{1}J_{CF}$ = 277.3 Hz), 67.2, 59.1, 56.8, 53.2 (q, $^{3}J_{CF}$ = 2.5

Hz), 44.35 (q, $^{2}J_{CF}$ = 28.2 Hz), 43.8 (q, $^{3}J_{CF}$ = 2.1 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): δ –70.56 (d, $^{3}J_{HH}$ = 9.5 Hz). HRMS-ESI *(m/z)* $[M+H]^+$ calculated for $C_{20}H_{21}NO_2F_3^+$ 364.1524, found 364.1528.

(trans)-Benzyl 1-benzyl-4-((diisopropoxyphosphoryl)difluoromethyl)pyrrolidine-3-carboxylate ***(20)***. Compound **20** was obtained, in accordance with procedure, from **16** (0.10 g, 0.27 mmol), **1** (0.1 mL, 0.53 mmol) and Eosin Y (0.01 g, 0.02 mmol). The crude residue was purified by chromatography: eluent 85:15 pentane/acetone to give a colorless oil (0.12 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.24 (m, 10H), 5.20 (d, $^{2}J_{HH}$ = 12.4 Hz, 1H), 5.11 (d, $^{2}J_{HH}$ = 12.4 Hz, 1H), 4.83–4.81 (m, 2H), 3.65 (d, $^{2}J_{HH}$ = 13.0 Hz, 1H), 3.55 (d, $^{2}J_{HH}$ = 13.0 Hz, 1H), 3.52–3.43 (m, 1H) 3.38–3.35 (m, 1H), 2.99 (dd, $^{2}J_{HH}$ = 9.5 Hz, $^{3}J_{HH}$ = 9.1 Hz, 1H), 2.92 (dd, $^{2}J_{HH}$ = 9.5 Hz, $^{3}J_{HH}$ = 4.6 Hz 1H), 2.73–2.67 (m, 2H), 1.39–1.28 (m, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) : δ 173.2, 138.4, 135.9, 128.6 (2C), 128.6 (2C), 128.3 (2C), 128.2, 128.0 (2C), 127.1, 119.9 (dt, $^{1}J_{CF}$ = 267.5 Hz, $^{1}J_{CP}$ = 215.5 Hz), 73.8 (d, $^{2}J_{CP}$ = 5.6 Hz) , 73.8 (d, $^{2}J_{CP}$ = 5.6 Hz), 66.8, 59.3, 57.1, 53.5–53.7 (m), 44.1–44.3 (m), 43.1–43.2 (m), 24.2 (d, $^{3}J_{CP}$ = 3.5 Hz), 24.1 (d, $^{3}J_{CP}$ = 3.5 Hz), 23.7 (d, $^{3}J_{CP}$ = 5.0 Hz), 23.6 (d, $^{3}J_{CP}$ = 5.0 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): δ –113.82 (ddd, $^{2}J_{FF}$ = 299.5, $^{2}J_{FP}$ = 108.8 Hz, $^{3}J_{FH}$ = 15.3 Hz), –117.50 (ddd, $^{2}J_{FF}$ = 299.5 Hz, $^{2}J_{FP}$ = 106.9 Hz, $^{3}J_{FH}$ = 20.5 Hz). ^{31}P NMR (202 MHz, $CDCl_3$): δ 4.54 (t, $^{2}J_{FP}$ = 108.0 Hz). HRMS-ESI *(m/z)* $[M+H]^+$ calculated for $C_{26}H_{34}NO_5F_2P^+$ 510.2221, found 510.2215.

(trans)-Diisopropyl ((-1-benzyl-4-nitropyrrolidin-3-yl)difluoromethyl)phosphonate ***(21)***. Compound **21** was obtained, in accordance with general procedure, **17** (0.10 g, 0.35 mmol), **1** (0.18 mL, 0.70 mmol) and Eosin Y (0.01 g, 0.02 mmol). The crude residue was purified by chromatography: eluent (70:30) pentane/acetone to give a colorless oil (0.13 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.26 (m, 5H), 5.17–5.14 (m, 1H), 4.85 (dsept, $^{3}J_{HP}$ = $^{3}J_{HH}$ = 6.2 Hz, 2H), 3.93–3.86 (m, 1H), 3.67 (d, $^{2}J_{HH}$ = 13.1 Hz, 1H), 3.60 (d, $^{2}J_{HH}$ = 13.1 Hz, 1H), 3.42 (d, $^{2}J_{HH}$ = 11.1 Hz, 1H), 3.23 (dd, $^{2}J_{HH}$ = $^{3}J_{HH}$ = 8.9 Hz, 1H), 2.79 (dd, $^{2}J_{HH}$ = 11.1 Hz, $^{3}J_{HH}$ = 7.0 Hz, 1H), 2.59 (dd, $^{2}J_{HH}$ = $^{3}J_{HH}$ = 8.9 Hz, 1H), 1.58–1.33 (m, 12H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 137.5, 128.5 (2C), 128.5 (2C), 127.5, 118.4 (dt, $^{1}J_{CF}$ = 264.3 Hz,

$^{1}J_{CP}$ = 220.5 Hz) 84.0, 74.5 (d, $^{2}J_{CP}$ = 7.1 Hz), 74.4 (d, $^{2}J_{CP}$ = 7.1 Hz), 58.9, 58.8, 52.7 (m), 46.2 (m), 24.1 (d, $^{3}J_{CP}$ = 3.5 Hz), 24.0 (d, $^{3}J_{CP}$ = 3.5 Hz), 23.7 (d, $^{3}J_{CP}$ = 3.5 Hz), 23.7 (d, $^{3}J_{CP}$ = 3.5 Hz). ^{19}F NMR (471 MHz, $CDCl_3$): δ –115.11 (ddd, $^{2}J_{FF}$ = 303.1 Hz, $^{2}J_{FP}$ = 106.2 Hz, $^{3}J_{FH}$ = 17.5 Hz), –115.73 (ddd, $^{2}J_{FF}$ = 303.1 Hz, $^{2}J_{FP}$ = 103.2 Hz, $^{3}J_{FH}$ = 17.5 Hz). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 3.63 (t, $^{2}J_{PF}$ = 104.8 Hz). HRMS-ESI *(m/z)* $[M+H]^+$ calculated for $C_{18}H_{28}N_2O_5F_2P^+$ 421.1704, found 421.1704.

*Ethyl -1-benzyl-4-((diisopropoxyphosphoryl)difluoromethyl)-3-fluoropyrrolidine-3-carboxylate (**22**).* A 9:1 ratio of (*trans/cis*) compound **22** was obtained, in accordance with general procedure, from **18** (0.13 g, 0.39 mmol), **1** (0.2 mL, 0.78 mmol) and Eosin Y (0.01 g, 0.02 mmol). The crude residue was purified by chromatography: eluent 80:20 pentane/acetone to give a trans **22** contaminated with *cis* isomer as colorless oil (0.13 g, 70%). (*trans*) isomer: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36–7.25 (m, 5H), 4.82 (dsept, $^{3}J_{HP}$ = $^{3}J_{HH}$ = 6.2 Hz, 2H), 4.35–4.22 (m, 2H), 3.76 (d, $^{2}J_{HH}$ = 12.8 Hz, 1H), 3.64 (d, $^{2}J_{HH}$ = 12.8 Hz, 1H), 3.45–3.25 (m, 3H), 3.00 (dd, $^{3}J_{HF}$ = 26.8 Hz, $^{2}J_{HH}$ = 11.6 Hz, 1H), 2.64–2.61 (m, 1H), 1.37–1.30 (m, 15H). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$): δ 168.6 (d, $^{2}J_{CF}$ = 28.5 Hz), 137.8, 128.7 (2C), 128.4 (2C), 127.3, 115.8 (dt, $^{1}J_{CF}$ = 228.1 Hz, $^{1}J_{CP}$ = 189.0 Hz), 98.5 (d, $^{1}J_{CF}$ = 197.1 Hz) 74.3 (d, $^{2}J_{CP}$ = 7.1 Hz) , 74.3 (d, $^{2}J_{CP}$ = 7.1 Hz), 63.4 (d, $^{2}J_{CF}$ = 23.8 Hz), 62.3, 59.7, 54.1, 29.7, 24.1 (d, $^{3}J_{CP}$ = 3.5 Hz), 24.1 (d, $^{3}J_{CP}$ = 3.5 Hz), 23.7 (d, $^{3}J_{CP}$ = 5.0 Hz), 23.6 (d, $^{3}J_{CP}$ = 5.0 Hz), 13.9. ^{19}F NMR (471 MHz, $CDCl_3$): δ –109.40 (dd, $^{2}J_{FF}$ = 303.7, $^{2}J_{FP}$ = 103.4 Hz), –118.87 (ddd, $^{2}J_{FF}$ = 303.7, $^{2}J_{FP}$ = 108.6 Hz, $^{3}J_{FH}$ = 31.0 Hz), –140.96 (ddd appears q, $^{3}J_{FH}$ = $^{3}J_{FH}$ = $^{3}J_{FH}$ = 25.8 Hz). ^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$): δ 3.53 (t, $^{2}J_{PF}$ = 106.4 Hz). HRMS-ESI *(m/z)* $[M+H]^+$ calculated for $C_{21}H_{32}NO_5F_3P^+$ 466.1970, found 466.1964. (*cis*) isomer visible on ^{19}F spectra: ^{19}F NMR (376 MHz, $CDCl_3$): δ –112.07 (ddd, $^{2}J_{FF}$ = 309.8 Hz, $^{2}J_{FP}$ =102.8, $^{4}J_{FF}$ =11.6 Hz), –116.77 (dddd appears ddt, $^{2}J_{FF}$ = 309.8 Hz, $^{2}J_{FP}$ = 106.8, $^{3}J_{FH}$ = $^{4}J_{FF}$ = 28.4 Hz), –166.27 (ddddd appears quintd, $^{3}J_{FH}$ = $^{3}J_{FH}$ = $^{4}J_{FF}$ = 28.4 Hz, $^{3}J_{FH}$ = 25,4 Hz, $^{4}J_{FF}$ =11.6 Hz Hz).

*ethyl 1-benzylpyrrolidine-3-carboxylate (**28**)*. Compound **28** was obtained, in accordance with general procedure, from ethyl acrylate **23** (0.10 g, 1.0 mmol), **1** (0.51 mL, 2.0 mmol) and Eosin Y (0.028 g, 0.04 mmol). The crude residue was purified by chromatography: eluent (80:20) pentane/AcOEt to give a colorless oil (0.145 g, 62%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.12 (m, 5H), 4.15 (q, $^3J_{HH}$ = 7.1 Hz, 2H), 3.65 (d, $^2J_{HH}$ = 12.9 Hz, 1H), 3.63 (d, $^2J_{HH}$ = 12.9 Hz, 1H), 3.07–2.99 (m, 1H), 2.92 (dd, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 8.6 Hz, 1H), 2.75–2.71 (m, 1H), 2.62 (dd, $^2J_{HH}$ = 9.3 Hz, $^3J_{HH}$ = 7.5 Hz, 1H), 2.52 (ddd appears q, $^2J_{HH}$ = $^3J_{HH}$ = $^3J_{HH}$ = 7.7 Hz, 1H), 2.15–2.05 (m, 2H), 1.27 (t, $^3J_{HH}$ = 7.1 Hz, 3H).
NMR data are in agreement with those reported in the literature.[9a]

*2-benzyl-5-phenyl-1,3,3a,6a-tetrahydropyrrolo[3,4-c]pyrrole-4,6-dione (**29**)*. Compound **29** was obtained, in accordance with general procedure, from *N*-phenylmaleimide **24** (0.1 g, 0.58 mmol), **1** (0.30 mL, 1.16 mmol) and Eosin Y (0.016 g, 0.02 mmol). The crude residue was purified by chromatography: eluent (60:40) pentane/AcOEt then recrystallized in (90:10) pentane/EtOH to give white powder (0.18 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45–7.15 (m, 10H), 3.57 (s, 1H), 3.39–3.22 (m, 4H), 2.45–2.37 (m, 2H). NMR data are in agreement with those reported in the literature.[5]

*(3aS,8bS)-2-benzyl-8b-nitro-4-(p-tolylsulfonyl)-3,3a-dihydro-1H-pyrrolo[3,4-b]indole (**30**)*. Compound **30** was obtained, in accordance with general procedure, from 3-nitro-1-(p-tolylsulfonyl)indole **25** (0.05 g, 0.16 mmol), **1** (0.08 mL, 0.32 mmol) and Eosin Y (0.004 g, 0.006 mmol). The crude residue was purified by chromatography: eluent (80:20) pentane/AcOEt to give a white solid (0.065 g, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.82–6.80 (m, 13H), 5.23 (dd, $^3J_{HH}$ = 6.5 Hz, $^3J_{HH}$ = 4.4, Hz, 1H), 3.53 (s, 2H), 3.45–3.35 (m, 1H), 3.32–3.21 (m, 1H), 2.97 (d, $^2J_{HH}$ = 10.4 Hz, 1H), 2.94–2.85 (m, 2H), 2.28 (s, 3H). NMR data are in agreement with those reported in the literature.[9b]

*3-benzyl-5-phenyl-oxazolidine (**31**).* Compound **31** was obtained, in accordance with general procedure, from benzaldehyde **26** (0.05 g, 0.47 mmol), **1** (0.24 mL, 0.94 mmol) and Eosin Y (0.013 g, 0.02 mmol). The crude residue was purified by chromatography: eluent (80:20) pentane/AcOEt to give a colorless oil

(0.09 g, 78%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40–7.27 (m, 10H), 5.08 (dd appears t, $^3J_{HH}$ = 7.3 Hz, 1H), 4.64–4.61 (m, 2H), 3.85 (s, 2H), 3.45 (dd, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 6.7 Hz, 1H), 2.85 (dd, $^2J_{HH}$ = 11.4 Hz, $^3J_{HH}$ = 7.9 Hz, 1H). NMR data are in agreement with those reported in the literature.[9c]

*1-Benzyl-4-phenyl-3-tosylimidazolidine (**32a**)*. Compound **32a** was obtained, in accordance with general procedure, from *N*-benzylidene-4-methyl-benzenesulfonamide **27a** (0.3 g, 1.16 mmol), **1** (0.591 mL, 2.31 mmol) and Eosin Y (0.032 g, 0.05 mmol). The crude residue was purified by chromatography: eluent (90:10) pentane/AcOEt to give a yellow oil (0.27 g, 60%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62–7.61 (m, 2 H), 7.36–7.22 (m, 10H), 7.15–7.13 (m, 2H), 4.75 (dd appears t, $^3J_{HH}$ = 7.5 Hz, 1H), 4.43 (d, $^2J_{HH}$ = 8.3 Hz, 1H), 4.09 (d, $^2J_{HH}$ = 8.3 Hz, 1H), 3.58 (d, $^2J_{HH}$ = 13.2 Hz, 1H), 3.41 (d, $^2J_{HH}$ = 13.2 Hz, 1 H), 3.27 (dd, $^2J_{HH}$ = 10.4 Hz, , $^3J_{HH}$ = 7.1 Hz, 1H), 2.67 (dd, $^2J_{HH}$ = 10.4 Hz, $^3J_{HH}$ = 7.8 Hz, 1H), 2.44 (s, 3 H). NMR data are in agreement with those reported in the literature.[9d]

*1-Benzyl-3-tert-butylsulfinyl-4-phenyl-imidazolidine (**32b**)*. Compound **32b** was obtained, in accordance with general procedure, from *N*-benzylidene-2-methyl-propane-2-sulfonamide **27b** (0.09 g, 0.43 mmol), **1** (0.22 mL, 0.86 mmol) and Eosin Y (0.012 g, 0.017 mmol). The crude residue was purified by chromatography: eluent (90:10) pentane/AcOEt to give a colorless oil (0.95 g, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69–6.72 (m, 10H), 5.02 (t, $^3J_{HH}$ = 7.4 Hz, 1H), 4.27 and 4.19 (AB system, $^2J_{HH}$ = 9.1 Hz, 2H), 3.73 and 3.63 (AB system, $^2J_{HH}$ = 13.0 Hz, 2H), 3.38–3.33 (m, 1H), 2.65 (dd, $^2J_{HH}$ = 10.7, $^3J_{HH}$ =7.4 Hz, 1H), 0.94 (s, 9H). NMR data are in agreement with those reported in the literature.[9e]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

NMR spectra (^{1}H, ^{13}C, and ^{19}F, or ^{31}P) for all new compounds. NMR HOESY spectra for compounds **10-12-18**. UV-Vis and fluorescence spectra (PDF).

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