Radical α -Trifluoromethoxylation of Ketones by Means of Organic Photoredox Catalysis

Thibaut Duhail,^{[a]†} Tommaso Bortolato,^{[b]†} Javier Mateos,^[b] Elsa Anselmi,^[a,c] Benson Jelier,^[d] Antonio Togni,^[d] Emmanuel Magnier,^{[a]*} Guillaume Dagousset^{[a]*} and Luca Dell'Amico^{[b]*}

Abstract: The first light-driven method for the α -trifluoromethoxylation of ketones is reported. Enol carbonates, in particular Boc derivatives, react with *N*-trifluoromethoxy-4-cyano-pyridinium triflimide (**2a**) using the photoredox-catalyst **4-CzIPN** (5 mol-%) under irradiation at 456 nm affording the corresponding α -trifluoromethoxy ketones in up to 50% isolated yield and virtually complete chemoselectivity. As shown by 35 examples, representing a great variety of substrates, the reaction is general and proceeds rapidly under batch (1h) and flow conditions (2 min). Mechanistic investigations reveal that a radical-chain propagation is operative, as efficiently orchestrated by the activity of the organic photoredox catalyst. Diverse products manipulations, including ketone reduction and reductive amination, demonstrate the synthetic potential of the disclosed method to accessing elusive trifluoromethoxylated potentially bioactive ingredients.

Among the rapidly emerging perfluorinated groups whose introduction into organic structures is of great interest, the OCF₃ moiety occupies a very special place.^[1] Electronic and steric properties are among the main reasons for the popularity of this group. It brings indeed a high lipophilicity (Hansch parameter: $\pi = +1.04$)^[2] to the molecules and possesses a high electronegativity (Pauling's electronegativity scale: $\chi = 3.7$) which earned it the nickname of super-halogen.^[3] These remarkable physico-chemical properties associated to good metabolic stability and unique conformational properties make this group particularly attractive for the life sciences.^[4]

Figure 1. The four drugs containing a OCF₃ moiety in their skeleton.

[a] T. Duhail, Dr. E. Anselmi, Dr. E. Magnier, Dr. G. Dagousset
 Université Paris-Saclay, UVSQ, CNRS, UMR 8180
 Institut Lavoisier de Versailles, 78035 Versailles Cedex (France)
 E-mail: emmanuel.magnier@uvsq.fr, guillaume.dagousset@uvsq.fr
 [b] T. Bortolato, J. Mateos, Dr. L. Dell'Amico. Department of Chemical
 Sciences, University of Padova, Via Marzolo 1, 35131, Padova (Italy)
 E-mail: luca.dellamico@unipd.it

[c] Dr. E. Anselmi. Université de Tours, Faculté des Sciences et Techniques,
 37200 Tours (France)

[d] Dr. B. Jelier, Prof. Dr. A. Togni
 Department of Chemistry and Applied Biosciences, Swiss Federal Institute of
 Technology, ETH Zurich, Vladimir-Prelog-Weg 2, 8093 Zurich (Switzerland)

† These authors contributed equally.

Despite this, the number of marketed pharmaceutical and agrochemical products containing OCF₃ remains low. To date, only 4 of the 340 identified drugs containing at least one fluorine atom bear a OCF₃ group (Figure 1).^[5] Among the 424 fluoro-agrochemicals, 10 with OCF₃ are listed.^[6] It should also be pointed out that for these 14 commercial molecules the OCF₃ is always attached to an aromatic ring. This contrasting situation is mainly due to the small number of existing methods and/or the lack of reagents capable of delivering this functional target under selective conditions at intermediate or late stage of a synthetic route. Pioneering works have focused on the construction of the O–CF₃ bond from already installed OH group, *via* i) multistep processes, requiring harsh conditions/toxic reagents (e.g. HF, SF₄),^[7] or ii) direct electrophilic trifluoromethylation of alcohols, either with hypervalent iodine reagents which require large excesses of alcohol (5–75 equiv) to achieve reasonable yields, or with an unstable oxonium salt.^[8] Despite recent improvements,^[9] such approaches are still limited in practicality and scope. An elegant alternative to access trifluoromethoxylated compounds is the direct introduction of the OCF₃ functionality (Scheme 1). To this end, nucleophilic routes have been proposed, with recent leading advances involving the description of new sources of the trifluoromethoxide anion or new methods for its *in-situ* formation (Scheme 1a).^[10] However, the use of this approach is hampered by several issues: 1) decomposition of the OCF₃ entity to fluorophosgene, 2) reagent synthesis from gaseous or expensive chemicals, 3) the requirement of several additives and inert-atmosphere techniques, and 4) the need for pre-functionalized starting materials. Previously unknown, the radical approach emerged in 2018 and has seen rapid and dramatic developments,^[11] in particular with the invention of three new reagents (Scheme 1b).

Scheme 1. Direct trifluoromethoxylation processes.

One of us designed a pyridine *N*-oxide reagent^[12] and the group of Ngai reported the use of azole-based compounds.^[13] Under

photoredox conditions, these three reagents proved efficient for the catalytic C-H trifluoromethoxylation of arenes and heteroarenes.^[14] To date, their scope has not been extended beyond (hetero)aromatic substrates. This represents an unprecedented challenge, the success of which would give access to new or hitherto poorly described molecules due to their cumbersome synthesis.

We herein report a mild metal-free visible-light-driven strategy to tackle this unsolved synthetic issue. We identified enol carbonates as substrates for their peculiar stereoelectronic properties, their ease of preparation and for the molecular diversity they offer in view of the trifluoromethoxylation of structurally diverse ketones (Scheme 1c).^[15]

Table 1. Selected optimisation results for the light-driven α -trifluoromethoxylation of ketones.

Reaction scheme showing the conversion of enol carbonate **1** and N-trifluoromethoxypyridinium salt **2a** to products **3** and **4** under irradiation at 456 nm with a photocatalyst (PC, 5 mol%) in MeCN at room temperature for 1 hour.

PC		NTC1		Mes-Acr ⁺		Ru(bpy) ₃ ²⁺		4-CzIPN	

^[a] Unless otherwise stated reaction conditions: 1.5 mL of MeCN, [2a]₀ = 0.033 M, at rt for 1 h irradiation time (see SI for details). ^[b] ¹⁹F-NMR yield using CF₃-Ph as the internal standard. ^[c] The reaction was performed at [2a]₀ = 0.01 M. ^[d] The reaction was conducted at 50 °C.

Our optimization began by studying the reaction between enol acetate **1a** (10 equiv.) and the *N*-trifluoromethoxypyridinium **2a**, commercially available as NTF₂⁻ salt (Table 1, entry 1). We initially evaluated the possibility of exploiting an electron-donor-acceptor (EDA) complex between the two reagents.^[16] Indeed, by mixing **1a** and **2a** a clear charge-transfer (CT) band was observed in the absorption spectra. Irradiation of the CT band at 400 nm delivered the trifluoromethoxylated target **3** in 17% yield. Quite unexpectedly, product **3** was accompanied by the undesired side-product **4**, where the OCF₃ group was introduced onto the aromatic ring.^[12] We reasoned that the low chemoselectivity of the process could be overcome by channeling the process towards a purely photoredox manifold, possibly resulting in a chain-propagation process (*vide infra*). We thus screened various

photocatalysts (PCs) characterized by diverse redox and photochemical properties.^[17] Naphthochromenone (NTC1, Table 1, entry 2) resulted in only slight improvements (20% yield and 12:1 ratio).^[18] This fact was attributed to the EDA-based pathway being concomitantly operating at 420 nm. We thus selected a more red-shifted light source (456 nm) and evaluated the performance of Mes-Acr⁺, Ru(bpy)₃²⁺ and 4-CzIPN. The low yield (7%) and chemoselectivity (9:1) obtained with the highly oxidizing Mes-Acr⁺ is attributed to a possibly operating unproductive reductive quenching cycle involving the initial oxidation of **1a**.^[19] On the other hand, PCs, characterized by a balanced distribution of the reductive and oxidative power (entry 4 and 5), delivered the product **3** in promising yield and selectivity, up to 37% and >20:1, respectively. Remarkably, when using the 4-CzIPN PC, **4** was not detected. Interestingly, we observed additional improvements by increasing the temperature in a more diluted medium (entry 6 and 7). Finally, replacing the acetyl (Ac) for a *tert*-butyloxycarbonyl group (Boc) led to 52% yield in only 1 h reaction time (entry 8). Under these conditions we were able to halve the substrate loading with minimal yield erosion (entry 9). Longer reaction times (3 h) resulted in the appearance of the side-product **4**. Furthermore, the reaction did not proceed in the dark, confirming the light-driven nature of the process (entry 10). Before exploring the generality of the optimised conditions, we decided to decipher the operative mechanism to understand the impact of alternative reaction manifolds on the reaction outcome. As mentioned, the EDA-based pathway resulted inefficient and poorly chemoselective. The poor chemoselectivity was ascribed to the rapid *in-situ* deprotection of **1a**, promoted by its single-electron oxidation and the following trifluoromethoxylation of the resulting acetophenone.^[12] This observation was supported by the fact that more diluted conditions disfavour the EDA complex formation supporting a chain-propagation mechanism (Table 1 entry 5 vs entry 6).

Figure 2 a) UV absorption spectra of **1a**, **2a** and their mixture. b) Stern-Volmer quenching experiment of 4-CzIPN with **1a** versus **2b**. c) Proposed reaction manifold under the optimised reaction conditions.

The reaction catalysed by Mes-Acr⁺ further corroborated this hypothesis, indicating that the initial oxidation of **1a** is detrimental to the reaction outcome. Hence, the available concentration of **1a** in the reaction mixture is a key parameter to channel the reactivity towards the intended α -trifluoromethoxylation. Interestingly, the identification of enol carbonate **1b** was key to increase the overall reactivity of the system. Specifically, we speculated that the use of the Boc group facilitates the formation of the final product by exploiting the driving force for CO₂ and isobutylene formation. The higher reactivity observed under the optimised reaction conditions, together with the Stern-Volmer analysis (Figure 2b) led us to depict the mechanistic scenario shown in Figure 2c. Upon excitation, the PC (4-CzIPN) reaches an electronically excited state that reduces **2** by SET, with the generation of the OCF₃ radical, and the formation of the PC^{•+} radical cation. The OCF₃ radical is readily intercepted by **1**, with the formation of the O-C bond within the radical intermediate **5**. At this juncture, **5** can reduce a second molecule of **2**, in a radical-chain process which delivers carbocation **6**. This rapidly evolves to the final product **3** with the formation of CO₂ and isobutylene. Finally, the chain process is terminated by the oxidation of **5** by PC^{•+}. This mechanistic hypothesis was also supported by quantum yield measurements in the presence of different trifluoromethoxylating agents **2a** and **2b**. When using the easily reducible **2a** ($E_{\text{red}} = -0.03$ V) we measured a quantum yield of 1.47, indicating that a

chain propagation is operating.^[20] On the contrary, when using the more electron-rich **2b** ($E_{\text{red}} = -0.90$ V) the quantum yield dropped drastically to less than 0.01, indicating that intermediate **5** is not able to reduce this pyridinium reagent and the mechanism switches to a classic photoredox cycle. Additionally, the reaction appeared much slower affording in 1 h product **3** in 12% yield instead of 50%.

Having deciphered the operative reaction manifold, we moved to test the generality of the developed trifluoromethoxylation method. We first focused our attention on acetophenone derivatives. We were pleased to see that substitutions on all the positions of the aromatic ring were tolerated. Alkyl substituents (**7-9**) gave comparable results with yields up to 46%. Remarkably, the reaction was easily transferred into a flow photoreactor without any significant erosion of the yield (48%), while allowing a shorter reaction time of only 2 min. On the other hand, electron-donating groups led to a considerable yield decrease (**10-11**). As investigated, this was due to a competing undesired reductive quenching mechanism hampering the chain-propagation process (Figure 2c). Interestingly, electron-withdrawing functionalities such as cyano and mono- and disubstituted trifluoromethyl enol carbonates are competent substrates under the developed trifluoromethoxylation method (**12-14**), affording the products in up to 42% yield in 1 h.

* Volatile substrate. Batch reactions were performed in 10 mL of MeCN at 0.1 mmol scale. Yields determined using the triflimide peak or PhCF₃ as the internal standard. Isolated yields are reported in parentheses. ** Isolated yield of the reaction performed with 6 equiv. of starting material. >20:1 chemoselectivity was observed in all the cases.

The OCF₃ group was readily installed also onto mono- and dihalogenated derivatives (**15-18**) in yields up to 46%, as well as on the diketo derivative (**19**), in 44% yield. It is worth noting that this mild photoredox-catalyzed protocol is not limited to terminal enol carbonates, and that trifluoromethoxylated ketones (**20-21**) bearing a methyl, or benzyl group at the α position can also be prepared.

We then turned our attention to cyclic ketones (**22-26**). 1-Indanone- and benzosuberone-derived enol carbonates (**22, 26**) were found to react more efficiently than the corresponding tetralone (**25**). Regarding the substitution pattern on the indanone scaffold, we observed a trend similar to that of acyclic derivatives. Electron-withdrawing groups such as a fluorine atom led a better yield (29%) than the electron-donating OMe group (9%). The developed method was amenable to diverse aromatic systems. Thiophene and 2-naphtyl derivatives delivered the corresponding products **27** and **28** in 12% and 14% yield, respectively. Synthetically appealing difluorinated enol carbonates were also investigated. Remarkably, the unprecedented perfluoroalkylated ketones **29** and **30** were easily obtained. We then attempted the trifluoromethoxylation of challenging enol carbonates derived from aliphatic ketones and enones. We were pleased to see that the intended trifluoromethoxylated ketones (**31-33**) were still successfully produced, in spite of a less important stabilization of the corresponding radical intermediate. Noteworthy, **32** and **33** were formed as single regioisomers despite the presence of two conjugated double bonds in the starting materials. We next tested the versatility of the developed method for the mild late-stage trifluoromethoxylation of biorelevant targets. To our delight, α -OCF₃ ketones **34-36** derived from Fixolide, Musk ketone and Celestolide were readily obtained. Remarkably, even the structurally complex bioactive natural products α -ionone, and pregnenolone participated in the developed trifluoromethoxylation process although with inferior results (**37-39**). Despite the presence of several double bonds, full chemoselectivity was observed in all these reactions, while preserving the fragile nature of these complex natural scaffolds. Encouraged by these results, we attempted the installation of the OCF₃ fragment into the testosterone scaffold. In this case however, two conjugated double bonds are present in the starting material, possibly leading to the formation of two diverse regioisomers (α - vs γ -OCF₃). We were pleased to see that under the developed method the trifluoromethoxylation occurred selectively at the vinylogous γ -position, furnishing **39** exclusively, in 11% isolated yield and 1:1 dr.

To further demonstrate the synthetic potential of the developed visible-light-driven method, we performed a large-scale flow-synthesis of the trifluoromethoxylated ketones **12** and **17**.^[21] By applying a flow rate of 5 mL · min⁻¹ and a residence time of 2 min, we were able to perform a 20-fold scale up of the process, without yield erosion. A routine reduction with NaBH₄ furnished the synthetically appealing mono-trifluoromethylated vicinal diol **40**. This molecule was subsequently subjected to a Buchwald-Hartwig amination with morpholine, resulting in the formation of derivative **41**. Simple treatment with ammonium acetate under reductive conditions of **17** delivered the trifluoromethylated amino alcohol **42**, which is an essential ingredient for the synthesis of allosteric modulators of muscarinic receptors.^[22] Additionally, ketone **12** was reacted with dimethylformamide-dimethylacetal exploiting its pronucleophilic nature giving the

trifluoromethoxylated enaminone **43**. These experiments demonstrate the synthetic potential of the developed method and the versatility of the products as synthetic building blocks.

Scheme 2. a) In-flow implementation and products manipulations. b) One-pot two-steps sequence to access biorelevant synthetic target **45**.

Finally, to test the robustness of the described process we set up a one-pot two-step sequence starting from acetophenone **44**. The crude enol carbonate was directly subjected to the optimized reaction conditions without any purification step. Noteworthy, also under these conditions the reaction proceeded with the formation of the biorelevant target **45** in 23% yield within an overall reaction time of 2 h, while previous approaches required longer times (up to 92 h) and prefunctionalised substrates.^[23]

In conclusion, a mild and selective visible-light method for the α -trifluoromethoxylation of ketones has been developed. The process uses a commercially available trifluoromethoxylating reagent, an organic photocatalyst and a wide range of structurally diverse enol carbonates. Mechanistic investigations revealed that a radical chain mechanism is essential to access the desired trifluoromethoxylated products in useful synthetic yields. The easy in-flow upscaling and the straightforward manipulations of the products make of this methodology an unprecedented general tool for the incorporation of the OCF₃ fragment into synthetically relevant targets, including bioactive ones.

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Supporting Information

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A. General Information

All reactions were carried out in anhydrous solvents purchased from commercial suppliers over molecular sieves in a sealed bottle which were used without further purification. Chemicals were purchased from commercial sources (Sigma–Aldrich, Alfa Aesar, Fluorochem, TCI or ABCR) and used without further purification. Organic solvents were purchased from Sigma–Aldrich and Carlo Erba companies. Reactions were monitored by thin-layer chromatography on silica gel 60F254, and/or by ^{19}F NMR spectroscopy.

NMR spectra were collected on a Bruker AC-300 spectrometer fitted with a Bruker PABBO BB/19F-1H/D probe head, Bruker 200 equipped with a QNP probehead, Bruker 400 Avance III HD spectrometer equipped with a BBI-z grad probehead, Bruker 500 Avance III equipped with a BBI-ATM-z grad probehead and Bruker Neo 600 equipped with a Prodigy probehead operating at the denoted spectrometer frequency given in MHz for the specified nucleus. Reported coupling constants and chemical shifts were based on a first order analysis. The internal reference for ^1H NMR was the residual peak of CDCl_3 (7.26 ppm), central peak of CDCl_3 (77.16 ppm) for ^{13}C NMR spectra, CFCl_3 (0.0 ppm) as internal reference for ^{19}F NMR spectra. All coupling constants (J) are reported in Hz with the following abbreviations: s = singlet, d = doublet, dd = double doublet, t = triplet, dt = double triplet, q = quadruplet, m = multiplet, br = broad. High resolution mass spectrometry (HRMS) was recorded on a Mass Spectrometer XEVO-QTOF in the Institute Lavoisier of Versailles – University of Versailles Saint Quentin or on a Xevo G2-XS QToF in the Department of Pharmaceutical Sciences – University of Padua.

Thin-layer chromatography (TLC) analysis was performed on pre-coated Merck TLC plates (silica gel 60G F254, 0.25 mm). Visualization of the developed purification was performed by checking UV absorbance (254 nm) as well as with aqueous ceric ammonium molybdate and potassium permanganate solutions. Chromatographic purification of the products was accomplished using flash chromatography on silica gel (SiO_2 , 0.04-0.0063 mm) purchased from Sigma-Aldrich, with the indicated solvent system according to the standard techniques, or with pre-coated Merck preparative TLC plates (silica gel 60G F254, 20x20 cm). Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator.

Steady-state absorption spectroscopy studies were performed at room temperature on a Varian Cary 50 UV-vis; 10 mm path length Hellma Analytics 100 QS quartz cuvettes were used.

The electrochemical characterizations were carried out in acetonitrile (MeCN)/0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) at room temperature, on an BASi EC Epsilon potentiostat-galvanostat in a glass cell. All the cyclic voltammograms were recorded with a scan rate of 0.1 V/s. A typical three-electrode cell was employed, which was composed of a glassy carbon (GC) working electrode (3 mm diameter), a platinum wire as counter electrode and a saturated aqueous calomel electrode (SCE) as reference electrode. The glass electrochemical cell was kept closed with a stopper annexed to the potentiostat. Oxygen was removed by purging the solvent with high-purity Nitrogen (N_2), introduced from a line into the cell by means of a glass pipe. The potential of ferrocenium/ferrocene (Fc^+/Fc) couple was used as internal reference system to calibrate the potentiostat. All the results are subsequently converted in V vs SCE, in agreement with the value reported in literature [$E_{1/2}(\text{Fc}^+/\text{Fc}) = +0.395 \text{ V vs SCE}$].^[1] The IR compensation implemented within the potentiostat was used, and every effort was made throughout the experiments to minimize the resistance of the solution. The full electrochemical reversibility of the voltammetric wave of ferrocene was taken as an indicator of the absence of uncompensated resistance effects. The GC electrode was polished before any measurement with diamond paste, carefully rinsed with de-ionized water, ethanol, acetone and ultrasonically rinsed with a methanol/ethanol/acetone 1:1:1 (v/v) mixture for 5 minutes. After each series of CV experiments, the electrochemical cell was carefully rinsed with

ethanol, acetone and de-ionized water; afterwards, the cell and the magnetic stirrer were sonicated for 5-10 min with acetone.

456 nm LEDs were purchased on Amazon (<https://www.amazon.it/Striscia-Decorazioni-Connettori-Connessione-Alimentatore/dp/B00HSF64E6>), as well as the waterproof silicone tubing used for submerging the LEDs under water (https://www.amazon.it/Silicone-Guaine-Flessibile-Bobina-Striscia/dp/B00TOM6NWO/ref=sr_1_4?mk_it_IT=%C3%85M%C3%85%C5%BD%C3%95%C3%91&dchild=1&keywords=tubo+silicone+led&qid=1622812658&s=lighting&sr=1-4).

Flow reactions were performed on a Vapourtec apparatus equipped with a UV-150 10 mL photochemical reactor.

B. Light sources emission spectra

The following spectrum was recorded by an AvaSpec ULS3648 high-resolution fiber-optic spectrometer which was placed at a fixed distance of 0.5 cm from the light source.

(more info at: <https://www.avantes.com/products/spectrometers/starline/item/209-avaspec-uls3648-high-resolution-spectrometer>).

Figure S1 Emission spectrum of the 456 nm LEDs used in this work

C. Experimental setup

456 nm reaction setup – room temperature

Figure S2 shows the general setup of a batch reaction under 456 nm irradiation. The reaction mixture was placed in the middle of the photoreactor (at about 1.5 cm distance from the light source). To maintain a stable reaction temperature one fan was placed close to the vials (25 ± 2 °C) and the temperature was controlled by a thermometer.

Figure S2 Left: top view of the photoreactor used in this work. Right: Front view of the photoreactor used in this work.

456 nm reaction setup – 50°C

Figure S3 shows the general setup of a batch reaction under 456 nm irradiation at 50°C. The reaction mixture was wrapped by 456 nm LEDs inserted in the silicone tubing to avoid contact with water and placed in a water bath at a stable temperature of 50°C.

Figure S3 Front view of the reaction setup under 456 nm irradiation at 50°C

D. Reaction optimization

For the trifluoromethoxylation reaction between enol derivatives **1** and the pyridinium reagent **2a** investigated in the present work, different reaction conditions were tested in function of the used enol derivative, reagents ratio, concentration, solvent, photocatalyst, additives, temperature and reaction time (Table S1). Photocatalysts NTC1, 4CzIPN and 3DPAFIPN were synthesised according to reported procedures.^[2,3]

Table S1 Exploratory studies of the reaction between enol derivative **1** and pyridinium **2a**

Entry	PG	Ratio (1a/2a)	Concentration	PC (mol%)	Additive	Yield of 3a (%) ^{a)}
1	TIPS	1:3	0.1 M	Ru(bpy) ₃ (PF ₆) ₂ (1)	-	0
2	Ac	1:3	0.1 M	Ru(bpy) ₃ (PF ₆) ₂ (1)	-	8
3	Ac	1:1.5	0.1 M	Ru(bpy) ₃ (PF ₆) ₂ (1)	-	5
4	Ac	3:1	0.1 M	Ru(bpy) ₃ (PF ₆) ₂ (1)	-	6
7	Ac	1:3	0.1 M	Ru(bpy) ₃ (PF ₆) ₂ (1)	K ₃ PO ₄ (2 eq)	0
8	Ac	1:3	0.1 M	Ru(bpy) ₃ (PF ₆) ₂ (1)	K ₂ CO ₃ (2 eq)	0
9	Ac	1:3	0.1 M	Ru(bpy) ₃ (PF ₆) ₂ (1)	K ₂ HPO ₄ (2 eq)	17
10	Ac	10:1	0.1 M	Ru(bpy) ₃ (PF ₆) ₂ (5)	K ₂ HPO ₄ (2 eq)	23
11	Ac	10:1	0.1 M	Ru(bpy) ₃ (PF ₆) ₂ (5)	-	30
12	Ac	10:1	0.033 M	Ru(bpy) ₃ (PF ₆) ₂ (5)	-	33
13^{b)}	Ac	10:1	0.033 M	Ru(bpy) ₃ (PF ₆) ₂ (5)	-	28
14^{c)}	Ac	10:1	0.033 M	Ru(bpy) ₃ (PF ₆) ₂ (5)	-	30
15^{d)}	Ac	10:1	0.033 M	Ru(bpy) ₃ (PF ₆) ₂ (5)	-	26

Entry	PG	Ratio (1a/2a)	Concentration	PC (mol%)	Additive	Yield of 3a (%) ^{a)}
16 ^{e)}	Ac	10:1	0.033 M	Ru(bpy) ₃ (PF ₆) ₂ (5)	-	25
17 ^{f)}	Ac	10:1	0.033 M	-	-	17
18	Ac	10:1	0.033 M	Ir(ppy) ₃ (5)	-	0
19	Ac	10:1	0.033 M	Ir(Fppy) ₃ (5)	-	15
20	Ac	10:1	0.033 M	Ir(ppy) ₂ (dtbbpy)PF ₆ (5)	-	3
21	Ac	10:1	0.033 M	Eosin Y (5)	-	14
22	Ac	10:1	0.033 M	Mes-Acr-BF ₄ (5)	-	7
23	Ac	10:1	0.033 M	3-DPAFIPN (5)	-	27
24 ^{g)}	Ac	10:1	0.033 M	NTC1 (5)	-	20
25	Ac	10:1	0.033 M	4CzIPN (5)	-	37
26	Ac	10:1	0.033 M	4CzIPN (10)	-	30
27	Ac	1:3	0.033 M	4CzIPN (5)	-	2
28	Ac	10:1	0.01 M	4CzIPN (5)	-	41
29	Ac	10:1	0.01 M	4CzIPN (2)	-	33
30 ^{h)}	Ac	10:1	0.01 M	4CzIPN (5)	-	44
31 ^{h)}	Boc	10:1	0.01 M	4CzIPN (5)	-	52
32 ^{h)}	Boc	5:1	0.01 M	4CzIPN (5)	-	50
33 ^{h)}	Boc	1.5:1	0.01 M	4CzIPN (5)	-	30
34 ^{h)}	Boc	5:1	0.01 M	4CzIPN (5)	BF ₃ OEt ₂ (1 eq)	8
35 ^{h)}	Boc	5:1	0.01 M	4CzIPN (5)	Bu ₄ NOAc (1 eq)	0
36 ^{h,i)}	Boc	5:1	0.01 M	4CzIPN (5)	-	0

a) ¹⁹F-NMR yield using PhCF₃ or the peak of triflimide as the internal standard b) The reaction was performed with a total reaction time of 6h c) The reaction was performed in acetone as solvent d) The reaction was performed in ethyl acetate as solvent e) **2a** was added with a driver syringe at a flow of 0.2 mL per hour in 0.6 mL of acetonitrile f) The reaction was performed under 400 nm light irradiation g) The reaction was performed under 420 nm light irradiation h) The reaction was performed at 50°C i) The reaction was performed in the dark

E. Synthetic procedures and characterization

General procedures for the synthesis of starting materials

General procedure A, for enol carbonates synthesis

A round-bottomed flask was charged with the required ketone (3.2 mmol, 1.2 equiv.) and suspended in THF (5 mL, 0.6M) at 0°C under argon atmosphere. LiHMDS (1.06 M in THF, 3.0 mL, 1.2 equiv.) was added at once to this suspension, which was then stirred for 5 mins at 0°C. Boc₂O (600 μ L, 2.6 mmol, 1 equiv.) was then added and the reaction medium was stirred for 1h at room temperature. The resulting mixture was then quenched with water (20 mL) and extracted with CH₂Cl₂ (3x20mL). The organic phases were then dried over MgSO₄ and concentrated under vacuum. Corresponding enol carbonates were isolated by column chromatography on silica gel (Pentane/EtOAc 95/5).

General procedure B, for enol carbonates synthesis

This procedure is the modification of a literature one.^[4] A round-bottomed flask was charged with the required ketone (5 mmol, 1 equiv.) and dissolved in dry THF (5 mL, 1M) at 0°C under nitrogen atmosphere. NaH (60% dispersion in mineral oil, 400 mg, 10 mmol, 2 equiv.) was added portionwise to the reaction mixture, which was then stirred for 15 mins at 0°C. Boc₂O (1.38 mL, 6 mmol, 1.2 equiv.) was then added dropwise and the reaction mixture was stirred for 16h at room temperature. The resulting mixture was then quenched with water (20 mL) and DMAP (61 mg, 0.5 mmol, 0.1 equiv.) was added and the reaction mixture stirred for 2 hours. The crude was then diluted with CH₂Cl₂ (50 mL) and washed with brine (3x20 mL). The organic phase was then dried over MgSO₄ and concentrated under vacuum. Corresponding enol carbonates were isolated by column chromatography on silica gel with the indicated eluent system.

General procedure C, for enol carbonates synthesis

A flame-dried, nitrogen flushed round-bottomed flask was charged with the required ketone (5 mmol, 1 equiv.) and dissolved in dry THF (5 mL, 1M) under nitrogen atmosphere. A freshly prepared solution of LDA (0.5 M in THF, 11 mL, 5.5 mmol, 1.1 equiv.) was dropwise at -78°C to the reaction mixture, which was then stirred for 90 minutes at -78°C. Boc₂O (1.21 mL, 5.25 mmol, 1.05 equiv.) was then added dropwise and the reaction medium was stirred for 30 minutes at -78°C and at room temperature for 16 hours. The resulting mixture was then quenched with water (20 mL), DMAP (61 mg, 0.5 mmol, 0.1 equiv.) was added and the resulting mixture stirred for 2 hours. The crude was then diluted with CH₂Cl₂ (50mL) and washed with brine (3x20 mL). The organic phase was then dried over MgSO₄ and

concentrated under vacuum. Corresponding enol carbonates were isolated by column chromatography on silica gel with the indicated eluent system.

1-(4-fluorophenyl)ethenyl acetate **1a**

1-(4-fluorophenyl)ethenyl acetate **1a** was synthesized according to a procedure reported in the literature.^[5] The spectral data matched with those reported in the literature.

tert-butyl (1-(4-fluorophenyl)vinyl) carbonate **1b**

According to general procedure B, 1-(4-fluorophenyl)vinyl tert-butyl carbonate **1b** was obtained from 1-(4-fluorophenyl)ethan-1-one as a yellow oil in 41% yield (494 mg, 2.07 mmol) after purification by column chromatography on silica gel (hexane/EtOAc 95/5). ¹H NMR (500 MHz, CDCl₃) δ 7.50 – 7.44 (m, 2H), 7.06 – 7.00 (m, 2H), 5.32 (d, *J* = 2.4 Hz, 1H), 5.07 (d, *J* = 2.4 Hz, 1H), 1.49 (s, 9H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 163.2 (d, *J* = 248.7 Hz, C-F), 152.5, 151.4, 130.8 (d, *J* = 3.4 Hz), 126.9 (d, *J* = 8.2 Hz), 115.6 (d, *J* = 21.9 Hz), 101.4 (d, *J* = 1.7 Hz, C=CH₂), 83.4 (O-C-(CH₃)₃), 27.6 (C-(CH₃)₃) ppm. ¹⁹F NMR (188 MHz, ¹H decoupled, CDCl₃) δ -112.84 ppm. HRMS (ESI+) Calcd. for C₈H₆F⁺ [M - OBoc]⁺: 121.0448. Found: 121.0409.

tert-butyl (1-phenylvinyl) carbonate **1c**

According to general procedure B, tert-butyl (1-phenylvinyl) carbonate **1c** was obtained from acetophenone as a yellow oil in 21% yield (233 mg, 1.06 mmol) after purification by column chromatography on silica gel (hexane/DCM 75/25). The spectral data matched with those reported in the literature.^[4]

tert-butyl (1-(o-tolyl)vinyl) carbonate **1d**

According to general procedure A, tert-butyl (1-(o-tolyl)vinyl) carbonate **1d** was obtained from 2'-methylacetophenone as a yellow oil in 96% yield (600 mg, 2.5 mmol). ¹H NMR (300 MHz, CDCl₃) δ 7.40 (d, *J* = 7.0 Hz, 1H), 7.29 – 7.14 (m, 3H), 5.25 (s, 1H), 4.97 (s, 1H), 2.44 (s, 3H), 1.44 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 154.1, 151.1, 136.0, 135.2, 130.6, 129.0, 128.8, 125.7, 104.9 (s, C=CH₂), 83.1 (s, 1C, O-C-(CH₃)₃), 27.7 (s, 3C, C-(CH₃)₃), 20.5 ppm. HRMS (ASAP +) Calcd for C₁₄H₁₈O₃Na⁺ [M + Na]⁺: 257.1148. Found: 257.1156.

tert-butyl (1-(m-tolyl)vinyl) carbonate **1e**

According to general procedure A, tert-butyl (1-(m-tolyl)vinyl) carbonate **1e** was obtained from 3'-methylacetophenone as a yellow oil in 90% yield (550 mg, 2.3 mmol). **¹H NMR (300 MHz, CDCl₃)** δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 5.43 (d, *J* = 2.2 Hz, 1H), 5.12 (d, *J* = 2.3 Hz, 1H), 2.40 (s, 3H), 1.55 (s, 9H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 153.6, 151.5, 138.2, 134.4, 129.8, 128.5, 125.6, 122.0, 101.4 (s, C=CH₂), 83.2 (s, 1C, O-C-(CH₃)₃), 27.7 (s, 3C, C-(CH₃)₃), 21.5 ppm. **HRMS (ASAP +)** Calcd for C₁₄H₁₈O₃Na⁺ [M + Na]⁺: 257.1148. Found: 257.1154.

tert-butyl (1-(p-tolyl)vinyl) carbonate **1f**

According to general procedure A, tert-butyl (1-(p-tolyl)vinyl) carbonate **1f** was obtained from 4'-methylacetophenone as a yellow oil in 90% yield (550 mg, 2.3 mmol). **¹H NMR (300 MHz, CDCl₃)** δ 7.40 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 5.36 (d, *J* = 2.4 Hz, 1H), 5.04 (d, *J* = 2.5 Hz, 1H), 2.35 (s, 3H), 1.50 (s, 9H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 153.5, 151.6, 139.1, 131.7, 129.4, 124.9, 100.9 (s, C=CH₂), 83.3 (s, 1C, O-C-(CH₃)₃), 27.8 (s, 3C, C-(CH₃)₃), 21.4 ppm. **HRMS (ASAP +)** Calcd for C₁₄H₁₈O₃Na⁺ [M + Na]⁺: 257.1148. Found: 257.1153.

tert-butyl 1-(3-methoxyphenyl)vinyl carbonate **1g**

According to general procedure B, tert-butyl 1-(3-methoxyphenyl)vinyl tert-butyl carbonate **1g** was obtained from 1-(3-methoxyphenyl)ethan-1-one as a yellow solid in 38% yield (472 mg, 1.90 mmol) after purification by column chromatography on silica gel (hexane/EtOAc 9/1). **¹H NMR (500 MHz, CDCl₃)** δ 7.27 (t, *J* = 8.0 Hz, 1H), 7.10 (ddd, *J* = 7.7, 1.7, 0.9 Hz, 1H), 7.03 (dd, *J* = 2.6, 1.7 Hz, 1H), 6.88 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 5.40 (d, *J* = 2.2 Hz, 1H), 5.10 (d, *J* = 2.2 Hz, 1H), 3.81 (s, 3H), 1.50 (s, 9H) ppm. **¹³C NMR (126 MHz, CDCl₃)** δ 159.8, 153.3, 151.5, 136.0, 129.7, 117.5, 114.8, 110.6, 102.1 (C=CH₂), 83.4 (O-C-(CH₃)₃), 55.4, 27.8 (C-(CH₃)₃) ppm. **HRMS (ESI+)** Calcd. for C₁₄H₁₈O₄Na⁺ [M + Na]⁺: 273.1097. Found: 273.1083.

tert-butyl 1-(4-methoxyphenyl)vinyl carbonate **1h**

According to general procedure B, tert-butyl 1-(4-methoxyphenyl)vinyl tert-butyl carbonate **1h** was obtained from 1-(4-methoxyphenyl)ethan-1-one as a yellow solid in 10% yield (130 mg, 0.52 mmol) after purification by column chromatography on silica gel (hexane/EtOAc 9/1). **¹H NMR (500 MHz, CDCl₃)** δ 7.47 – 7.40 (m, 2H), 6.92 – 6.84 (m, 2H), 5.28 (d, *J* = 2.2 Hz, 1H), 4.99 (d, *J* = 2.2 Hz, 1H), 3.82 (s, 3H), 1.50 (s, 9H) ppm. **¹³C NMR (126 MHz, CDCl₃)** δ 160.3, 153.3, 151.6, 127.2, 126.4, 114.1, 100.0

(C=CH₂), 83.3 (O-C-(CH₃)₃), 55.4, 27.8 (C-(CH₃)₃) ppm. **HRMS (ESI+)** Calcd. for C₉H₁₁O₂⁺ [M - Boc + H]⁺: 151.0754. Found: 151.0729.

tert-butyl (1-(4-cyanophenyl)vinyl) carbonate **1i**

A round-bottomed flask was charged with 4-acetylbenzonitrile (23 mmol, 1.2 equiv.) and suspended in THF (50 mL, 0.5M) at 0°C under argon atmosphere. LiHMDS (1.06 M in THF, 21.7 mL, 1.2 equiv.) was added at once to this suspension, which was then stirred for 5 mins at 0°C. Boc₂O (4.4 mL, 19 mmol, 1 equiv.) was then added and the reaction medium was stirred for 1h at room temperature. The resulting mixture was then quenched with water (50 mL) and extracted with CH₂Cl₂ (3x100mL). The organic phases were then dried over MgSO₄ and concentrated under vacuum. Tert-butyl (1-(4-cyanophenyl)vinyl) carbonate **1i** was isolated by column chromatography on silica gel (Pentane/EtOAc 95/5) as a white solid in 87% yield (4.1 g, 16.7 mmol). **¹H NMR (300 MHz, CDCl₃)** δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 5.53 (s, 1H), 5.28 (s, 1H), 1.50 (s, 9H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 151.8, 151.2, 139.0, 132.6, 125.6, 118.6, 112.6, 105.0 (C=CH₂), 84.2 (O-C-(CH₃)₃), 27.8 (C-(CH₃)₃) ppm. **MP** 59-61°C. **HRMS (ASAP +)** Calcd for C₁₄H₁₆NO₃⁺ [M + H]⁺: 246.1125. Found: 246.1119.

tert-butyl (1-(3-(trifluoromethyl)phenyl)vinyl) carbonate **1j**

According to general procedure A, tert-butyl (1-(3-(trifluoromethyl)phenyl)vinyl) carbonate **1j** was obtained from 1-(3-(trifluoromethyl)phenyl)ethanone as a yellow oil in 96% yield (725 mg, 2.5 mmol). **¹H NMR (300 MHz, CDCl₃)** δ 7.74 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 5.47 (s, 1H), 5.20 (s, 1H), 1.49 (s, 9H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 152.1, 151.3, 135.5, 131.2 (q, *J* = 32.5 Hz), 129.2, 128.2, 125.6 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 272.3 Hz, CF₃), 121.7 (q, *J* = 3.9 Hz), 103.1 (s, C=CH₂), 83.8 (s, 1C, O-C-(CH₃)₃), 27.5 (s, 3C, C-(CH₃)₃) ppm. **¹⁹F NMR (188 MHz, CDCl₃)** δ -63.4 ppm. **HRMS (ASAP +)** Calcd for C₁₄H₁₆F₃O₃⁺ [M + H]⁺: 289.1046. Found: 289.1060.

1-(3,5-bis(trifluoromethyl)phenyl)vinyl tert-butyl carbonate **1k**

According to general procedure B, 1-(3,5-bis(trifluoromethyl)phenyl)vinyl tert-butyl carbonate **1k** was obtained from 1-(3,5-bis(trifluoromethyl)phenyl)ethan-1-one as a brown solid in 14% yield (241 mg, 0.68 mmol) after purification by column chromatography on silica gel (hexane/DCM 9/1). **¹H NMR (400 MHz, CDCl₃)** δ 7.92 (s, 2H), 7.84 (s, 1H), 5.58 (d, *J* = 2.9 Hz, 1H), 5.34 (d, *J* = 2.9 Hz, 1H), 1.51 (s, 9H) ppm. **¹³C NMR (101 MHz, CDCl₃)** δ 151.1, 150.8, 136.9, 132.3 (q, *J* = 33.5 Hz, C-CF₃), 125.1 (d, *J* = 2.7 Hz), 123.2 (q, *J* = 272.9 Hz, C-CF₃), 122.6 (p, *J* = 7.1, 3.7, 3.4 Hz), 104.9 (C=CH₂), 84.5 (O-C-(CH₃)₃), 27.7 (C-(CH₃)₃) ppm. **¹⁹F NMR (188 MHz, ¹H decoupled, CDCl₃)** δ -63.6 ppm. **HRMS (ASAP +)** Calcd for C₁₀H₇F₆O⁺ [M - Boc + H]⁺: 257.0396. Found: 257.0390.

1-(2-bromophenyl)vinyl tert-butyl carbonate **1l**

According to general procedure B, 1-(2-bromophenyl)vinyl tert-butyl carbonate **1l** was obtained from 1-(2-bromophenyl)ethan-1-one as a yellow oil in 34% yield (508 mg, 1.7 mmol) after purification by column chromatography on silica gel (hexane/EtOAc 95/5). **¹H NMR (500 MHz, CDCl₃)** δ 7.57 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.44 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.29 (td, *J* = 7.5, 1.2 Hz, 1H), 7.17 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 5.32 (d, *J* = 2.0 Hz, 1H), 5.16 (d, *J* = 2.0 Hz, 1H), 1.44 (s, 9H) ppm. **¹³C NMR (126 MHz, CDCl₃)** δ 152.4, 150.8, 136.4, 133.4, 130.8, 130.1, 127.3, 121.5, 106.3 (C=CH₂), 83.3 (O-C-(CH₃)₃), 27.7 (C-(CH₃)₃) ppm. **HRMS (ESI+)** Calcd. for C₈H₆Br⁺ [M - OBoc]⁺: 180.9647. Found: 180.9623.

1-(3-bromophenyl)vinyl tert-butyl carbonate **1m**

According to general procedure B, 1-(2-bromophenyl)vinyl tert-butyl carbonate **1m** was obtained from 1-(3-bromophenyl)ethan-1-one as a yellow oil in 67% yield (772 mg, 3.35 mmol) after purification by column chromatography on silica gel (hexane/EtOAc 95/5). **¹H NMR (500 MHz, CDCl₃)** δ 7.64 (t, *J* = 1.9 Hz, 1H), 7.45 (ddd, *J* = 7.9, 2.0, 1.0 Hz, 1H), 7.42 (ddd, *J* = 7.9, 1.8, 1.0 Hz, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 5.41 (d, *J* = 2.5 Hz, 1H), 5.14 (d, *J* = 2.5 Hz, 1H), 1.50 (s, 9H) ppm. **¹³C NMR (126 MHz, CDCl₃)** δ 152.0, 151.3, 136.6, 132.0, 130.1, 128.1, 123.5, 122.8, 102.9 (C=CH₂), 83.7 (O-C-(CH₃)₃), 27.7 (C-(CH₃)₃) ppm. **HRMS (ASAP +)** Calcd for C₈H₈BrO⁺ [M - Boc + H]⁺: 198.9753. Found: 198.9759.

1-(4-bromophenyl)vinyl tert-butyl carbonate **1n**

According to general procedure B, 1-(4-bromophenyl)vinyl tert-butyl carbonate **1n** was obtained from 1-(4-bromophenyl)ethan-1-one as a yellow solid in 39% yield (586 mg, 1.95 mmol) after purification by column chromatography on silica gel (hexane/EtOAc 95/5). **¹H NMR (500 MHz, CDCl₃)** δ 7.48 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 5.40 (d, *J* = 2.4 Hz, 1H), 5.12 (d, *J* = 2.4 Hz, 1H), 1.50 (s, 9H) ppm. **¹³C NMR (126 MHz, CDCl₃)** δ 152.5, 151.4, 133.6, 131.8, 126.6, 123.2, 102.4 (C=CH₂), 83.7 (O-C-(CH₃)₃), 27.8 (C-(CH₃)₃) ppm. **HRMS (ESI+)** Calcd. for C₁₃H₁₅BrO₃Na⁺ [M + Na]⁺: 321.0102. Found: 321.0110.

tert-butyl 1-(2,5-dichlorophenyl)vinyl carbonate **1o**

According to general procedure B, tert-butyl 1-(2,5-dichlorophenyl)vinyl carbonate **1o** was obtained from 1-(2,5-dichlorophenyl)ethan-1-one as a yellow oil in 10% yield (150 mg, 0.52 mmol) after purification by column chromatography on silica gel (hexane/DCM 7/3). **¹H NMR (400 MHz, CDCl₃)** δ 7.45 (d, *J* = 2.5 Hz, 1H), 7.32 (d, *J* = 8.5 Hz, 1H), 7.24 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.37 (d, *J* = 2.2 Hz, 1H), 5.24 (d, *J* = 2.2 Hz, 1H), 1.46 (s, 9H) ppm. **¹³C NMR (101 MHz, CDCl₃)** δ 150.8, 150.1, 135.8, 132.7, 131.4,

130.6, 130.1, 129.9, 107.6 (C=CH₂), 83.8 (O-C-(CH₃)₃), 27.7 (C-(CH₃)₃) ppm. **HRMS (ESI+)** Calcd. for C₁₃H₁₄Cl₂O₃Na⁺ [M + Na]⁺: 311.0212. Found: 311.0193.

1-(4-acetylphenyl)vinyl tert-butyl carbonate **1p**

According to general procedure C, 1-(4-acetylphenyl)vinyl tert-butyl carbonate **1p** was obtained from 1,4-diacetylbenzene as a colourless oil in 26% yield (344 mg, 1.3 mmol) after purification by column chromatography on silica gel (hexane/EtOAc 8/2). **¹H NMR (400 MHz, CDCl₃)** δ 7.98 – 7.90 (m, 2H), 7.61 – 7.53 (m, 2H), 5.52 (d, *J* = 2.5 Hz, 1H), 5.22 (d, *J* = 2.5 Hz, 1H), 2.59 (s, 3H), 1.49 (s, 9H) ppm. **¹³C NMR (101 MHz, CDCl₃)** δ 197.4, 152.5, 151.3, 138.9, 137.2, 128.8, 125.1, 104.1 (C=CH₂), 83.8 (O-C-(CH₃)₃), 27.7 (C-(CH₃)₃), 26.7 ppm. **HRMS (ESI+)** Calcd. for C₁₅H₁₉O₄H⁺ [M + H]⁺: 263.1278. Found: 263.1286.

tert-butyl (1-phenylprop-1-en-1-yl) carbonate **1q**

According to general procedure B, tert-butyl (1-phenylprop-1-en-1-yl) carbonate **1q** was obtained from propiophenone as a colourless oil in 24% yield (276 mg, 1.2 mmol) after purification by column chromatography on silica gel (hexane/DCM 7/3). **¹H NMR (500 MHz, CDCl₃)** δ 7.37 – 7.32 (m, 1H), 7.27 – 7.21 (m, 2H), 7.20 – 7.15 (m, 1H), 5.75 (q, *J* = 7.0 Hz, 1H), 1.69 (d, *J* = 7.0 Hz, 3H), 1.42 (s, 9H) ppm. **¹³C NMR (126 MHz, CDCl₃)** δ 151.2, 147.4, 135.4, 128.6, 128.1, 124.4, 112.7 (C=CHR), 83.1 (O-C-(CH₃)₃), 27.8 (C-(CH₃)₃), 11.4 ppm. **HRMS (ESI+)** Calcd. for C₉H₉⁺ [M - OBoc]⁺: 117.0699. Found: 117.0701.

tert-butyl (1,3-diphenylprop-1-en-1-yl) carbonate **1r**

According to general procedure C, tert-butyl (1,3-diphenylprop-1-en-1-yl) carbonate **1r** was obtained from dihydrochalcone as a white solid in 79% yield (1.23 g, 3.9 mmol) after purification by column chromatography on silica gel (hexane/DCM 7/3). **¹H NMR (500 MHz, CDCl₃)** δ 7.41 – 7.35 (m, 2H), 7.28 – 7.15 (m, 7H), 7.16 – 7.09 (m, 1H), 5.82 (t, *J* = 7.5 Hz, 1H), 3.48 (d, *J* = 7.5 Hz, 2H), 1.41 (s, 9H) ppm. **¹³C NMR (126 MHz, CDCl₃)** δ 151.3, 147.0, 139.8, 135.2, 128.7, 128.6, 128.6, 128.4, 126.4, 124.6, 116.8 (C=CHR), 83.4 (O-C-(CH₃)₃), 32.3, 27.7 (C-(CH₃)₃) ppm. **HRMS (ESI+)** Calcd. for C₁₅H₁₃⁺ [M - OBoc]⁺: 193.1012. Found: 193.1002.

tert-butyl 1H-inden-3-yl carbonate **1s**

According to general procedure A, tert-butyl 1H-inden-3-yl carbonate **1s** was obtained from 1-Indanone as a yellow oil in 99% yield (600 mg, 2.6 mmol). **¹H NMR (300 MHz, CDCl₃)** δ 7.45 (dd, *J* =

15.5, 7.3 Hz, 2H), 7.39 – 7.27 (m, 2H), 6.34 (s, 1H), 3.44 (s, 2H), 1.62 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 150.9, 149.6, 142.0, 139.0, 126.4, 125.8, 124.2, 118.3, 114.6, 83.7 (s, 1C, O-C-(CH₃)₃), 34.9, 27.8 (s, 3C, C-(CH₃)₃) ppm.

tert-butyl (5-methoxy-1H-inden-3-yl) carbonate 1t

According to general procedure A, tert-butyl (5-methoxy-1H-inden-3-yl) carbonate **1t** was obtained from 6-methoxy-2,3-dihydro-1H-inden-1-one as a yellow oil in 88% yield (600 mg, 2.3 mmol). ¹H NMR (300 MHz, CDCl₃) δ 7.30 (d, *J* = 8.2 Hz, 1H), 6.91 (s, 1H), 6.80 (d, *J* = 8.2 Hz, 1H), 6.33 (s, 1H), 3.84 (s, 3H), 3.34 (s, 2H), 1.59 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 159.0, 150.9, 149.3, 140.3, 134.0, 124.7, 115.8, 112.6, 103.4, 83.8 (s, 1C, O-C-(CH₃)₃), 55.7, 34.2, 27.8 (s, 3C, C-(CH₃)₃) ppm.

tert-butyl (6-fluoro-1H-inden-3-yl) carbonate 1u

According to general procedure A, tert-butyl (6-fluoro-1H-inden-3-yl) carbonate **1u** was obtained from 5-fluoro-2,3-dihydro-1H-inden-1-one as a yellow oil in 92% yield (600 mg, 2.4 mmol). ¹H NMR (300 MHz, CDCl₃) δ 7.34 – 7.25 (m, 3H), 7.15 (d, *J* = 8.8 Hz, 1H), 7.03 (t, *J* = 8.9 Hz, 1H), 6.28 (s, 1H), 3.39 (s, 2H), 1.59 (s, 9H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 163.8, 160.5, 150.8, 148.9, 144.0 (d, *J* = 8.8 Hz, 1C), 135.0 (d, *J* = 2.2 Hz, 1C), 119.1 (d, *J* = 8.9 Hz, 1C), 114.0 (d, *J* = 3.8 Hz, 1C), 112.70 (dd, *J* = 121.1, 23.3 Hz), 83.8 (s, 1C, O-C-(CH₃)₃), 34.9 (d, *J* = 2.4 Hz, 1C), 27.8 (s, 3C, C-(CH₃)₃) ppm. ¹⁹F NMR (188 MHz, CDCl₃) δ -117.84 (td, *J* = 9.0, 5.0 Hz, 1F) ppm.

tert-butyl 3,4-dihydronaphthalen-1-yl carbonate 1v

According to general procedure B, tert-butyl 3,4-dihydronaphthalen-1-yl carbonate **1v** was obtained from α-tetralone as a colourless oil in 20% yield (244 mg, 0.99 mmol) after purification by column chromatography on silica gel (hexane/EtOAc 9/1). ¹H NMR (500 MHz, CDCl₃) δ 7.21 – 7.12 (m, 4H), 5.78 (t, *J* = 4.7 Hz, 1H), 2.86 (ddd, *J* = 8.3, 7.6, 0.9 Hz, 2H), 2.44 (ddd, *J* = 8.9, 7.6, 4.7 Hz, 2H), 1.54 (s, 9H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 152.0, 146.2, 136.5, 130.7, 128.0, 127.7, 126.6, 120.7, 115.3 (C=CHR), 83.3 (O-C-(CH₃)₃), 27.8 (C-(CH₃)₃), 27.6, 22.1 ppm. HRMS (ESI+) Calcd. for C₁₅H₁₈O₃Na⁺ [M + Na]⁺: 269.1148. Found: 269.1136.

tert-butyl (6,7-dihydro-5H-benzo[7]annulen-9-yl) carbonate **1w**

According to general procedure A, tert-butyl (6,7-dihydro-5H-benzo[7]annulen-9-yl) carbonate **1w** was obtained from 1-Benzosuberone as a colorless oil in 92% yield (620 mg, 2.4 mmol). **¹H NMR (300 MHz, CDCl₃)** δ 7.47 – 7.34 (m, 1H), 7.27 – 7.16 (m, 3H), 5.93 (t, *J* = 6.1 Hz, 1H), 2.83 (t, *J* = 6.0 Hz, 2H), 2.18 (q, *J* = 6.5 Hz, 2H), 2.13 – 7.02 (m, 2H), 1.47 (s, 9H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 152.3, 146.2, 141.8, 134.5, 129.2, 128.2, 126.2, 125.3, 119.3, 82.9 (s, 1C, O-C-(CH₃)₃), 33.8, 31.1, 27.8 (s, 3C, C-(CH₃)₃), 25.3 ppm.

1-(benzo[b]thiophen-2-yl)vinyl tert-butyl carbonate **1x**

According to general procedure A, 1-(benzo[b]thiophen-2-yl)vinyl tert-butyl carbonate **1x** was obtained from 1-(benzo[b]thiophen-2-yl)ethanone as a yellow oil in 95% yield (680 mg, 2.5 mmol). **¹H NMR (300 MHz, CDCl₃)** δ 7.82 – 7.70 (m, 2H), 7.38 (s, 1H), 7.37 – 7.28 (m, 2H), 5.47 (m, 1H), 5.20 (m, 1H), 1.57 (s, 9H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 151.2, 148.3, 139.7, 139.5, 137.9, 125.3, 124.7, 124.1, 122.2, 121.5, 103.3 (s, C=CH₂), 83.8 (s, 1C, O-C-(CH₃)₃), 27.7 (s, 3C, C-(CH₃)₃) ppm. **HRMS (ASAP +)** Calcd for C₁₅H₁₆NaO₃S⁺ [M + Na]⁺: 299,0712. Found: 299,0718.

tert-butyl 1-(naphthalen-2-yl)vinyl carbonate **1y**

According to general procedure B, tert-butyl 1-(naphthalen-2-yl)vinyl carbonate **1y** was obtained from 1-(naphthalen-2-yl)ethan-1-one as a white solid in 12% yield (165 mg, 0.61 mmol) after purification by column chromatography on silica gel (hexane/EtOAc 95/5). **¹H NMR (400 MHz, CDCl₃)** δ 7.95 (d, *J* = 0.9 Hz, 1H), 7.90 – 7.77 (m, 3H), 7.63 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.52 – 7.45 (m, 2H), 5.56 (d, *J* = 2.4 Hz, 1H), 5.21 (d, *J* = 2.4 Hz, 1H), 1.53 (s, 9H) ppm. **¹³C NMR (101 MHz, CDCl₃)** δ 153.5, 151.6, 133.6, 133.2, 131.8, 128.6, 128.5, 127.8, 126.7, 126.6, 124.2, 122.8, 102.3 (C=CH₂), 83.6 (O-C-(CH₃)₃), 27.8 (C-(CH₃)₃) ppm. **HRMS (ESI+)** Calcd. for C₁₇H₁₈O₃Na⁺ [M + Na]⁺: 293.1148. Found: 293.1138.

tert-butyl 2,2-difluoro-1-phenylvinyl carbonate **1z**

tert-butyl 2,2-difluoro-1-phenylvinyl carbonate **1z** was synthesized according to a procedure reported in the literature.^[6] The spectral data matched with those reported in the literature.

tert-butyl 2,2-difluoro-1-(naphthalen-2-yl)vinyl carbonate 1aa

2,2,2-trifluoro-1-(naphthalen-2-yl)ethan-1-one was synthesized according to a reported literature procedure.^[7] The spectral data matched with those reported in the literature.

2,2,2-trifluoro-1-(naphthalen-2-yl)ethan-1-one (433 mg, 1.93 mmol, 1 equiv.) was dissolved in MeOH (5 mL, 0.4M) at 0°C. NaBH₄ (80 mg, 2.12 mmol, 1.1 equiv.) was then added portionwise and the reaction stirred for 1h at room temperature. The reaction was then cooled to 0°C, quenched with sat. NH₄Cl until gas evolution stopped and evaporated to dryness. The crude residue was diluted with DCM (20 mL) and washed with brine (3x 10 mL). The organic phase was then dried over MgSO₄ and concentrated under reduced pressure. The crude 2,2,2-trifluoro-1-(naphthalen-2-yl)ethan-1-ol product was used in the subsequent step without further purification. The spectral data matched with those reported in the literature.^[8]

Crude 2,2,2-trifluoro-1-(naphthalen-2-yl)ethan-1-ol (340 mg) was dissolved in MeCN (7 mL) and DMAP (18.3 mg, 0.15 mmol) was added. Boc₂O (517 μL, 2.25 mmol) was then added dropwise and the reaction mixture stirred for 20h, after which time the mixture was concentrated under reduced pressure. The residue was filtered on silica using DCM as eluent and the eluted solution evaporated under reduced pressure. The crude tert-butyl (2,2,2-trifluoro-1-(naphthalen-2-yl)ethyl) carbonate product was used in the subsequent step without further purification.

To a solution of crude tert-butyl (2,2,2-trifluoro-1-(naphthalen-2-yl)ethyl) carbonate (485 mg) in dry THF (7 mL) at -78 °C was added dropwise a freshly prepared solution of LDA (0.7 M, 3.21 mL). After stirring for 1h at -78 °C, the reaction mixture was stirred for an additional 1 h at room temperature. The reaction mixture was then diluted with water (10 mL) and extracted with EtOAc (3 × 10 mL), dried over anhydrous MgSO₄, and the solvent evaporated to give a residue. Finally, the residue was purified by silica gel chromatography (hexane/EtOAc 97/3) to give tert-butyl 2,2-difluoro-1-(naphthalen-2-yl)vinyl carbonate **1aa** in 45% yield over 3 steps (266 mg, 0.87 mmol). ¹H NMR (500 MHz, CDCl₃) δ 7.92 – 7.88 (m, 1H), 7.89 – 7.79 (m, 3H), 7.56 (dt, *J* = 8.7, 1.8 Hz, 1H), 7.54 – 7.47 (m, 2H), 1.53 (s, 9H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 155.2 (dd, *J* = 292.4, 290.5 Hz, (C=CF₂)), 151.0 (dd, *J* = 3.5, 2.3 Hz), 133.2 (d, *J* = 10.5 Hz), 128.6, 128.4, 127.8, 126.9, 126.9, 126.8, 126.8, 125.1 (t, *J* = 5.3 Hz), 122.9 (dd, *J* = 7.0, 2.3 Hz), 113.4 (dd, *J* = 38.8, 19.5 Hz, C=CF₂), 84.7 (O-C-(CH₃)₃), 27.7 (C-(CH₃)₃) ppm. ¹⁹F NMR (188 MHz, CDCl₃) δ -92.4 (d, *J* = 46.6 Hz), -103.9 (d, *J* = 46.6 Hz) ppm. HRMS (ASAP +) Calcd for C₁₂H₉F₂O⁺ [M - Boc + H]⁺: 207.0616. Found: 207.0621.

tert-butyl oct-1-en-2-yl carbonate 1ab

According to general procedure C, tert-butyl oct-1-en-2-yl carbonate **1ab** was obtained from octan-2-one as a colourless oil in 33% yield (380 mg, 1.66 mmol) after purification by column chromatography on silica gel (hexane/EtOAc 98/2). ¹H NMR (400 MHz, CDCl₃) δ 4.75 – 4.67 (m, 1H), 4.62 – 4.56 (m, 1H), 2.21 – 2.10 (m, 2H), 1.43 (s, 9H), 1.41 – 1.38 (m, 4H), 1.24 – 1.21 (m, 4H), 0.83 – 0.80 (m, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 156.6, 151.46, 100.4 (C=CH₂), 82.4 (O-C-(CH₃)₃), 33.1, 31.6, 28.6, 27.6 (C-(CH₃)₃), 26.4, 22.5, 14.0 ppm. HRMS (ESI+) Calcd. for C₁₃H₂₄O₃Na⁺ [M + Na]⁺: 251.1618. Found: 251.1596.

(E)-tert-butyl (4-phenylbuta-1,3-dien-2-yl) carbonate **1ac**

According to general procedure A, (E)-tert-butyl (4-phenylbuta-1,3-dien-2-yl) carbonate **1ac** was obtained from 4- (E)-4-phenylbut-3-en-2-one as a colorless oil in 63% yield (400 mg, 1.6 mmol). This product had to be stored at -20°C, decomposition was noticed after few days in the fridge. **¹H NMR (300 MHz, CDCl₃)** δ 7.44 (d, *J* = 7.5 Hz, 2H), 7.40 – 7.27 (m, 3H), 6.70 (dd, *J* = 16.1, 11.3 Hz, 2H), 5.10 (d, *J* = 8.7 Hz, 2H), 1.58 (s, 9H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 152.3, 136.2, 130.1, 128.8, 128.4, 127.0, 122.6, 105.7 (s, C=CH₂), 83.4 (s, 1C, O-C-(CH₃)₃), 27.8 (s, 3C, C-(CH₃)₃) ppm.

(E)-tert-butyl nona-1,3-dien-2-yl carbonate **1ad**

According to general procedure A, (E)-tert-butyl nona-1,3-dien-2-yl carbonate **1ad** was obtained from (E)-non-3-en-2-one as a colorless oil in 99% yield (620 mg, 2.6 mmol). **¹H NMR (300 MHz, CDCl₃)** δ 5.99 – 5.78 (m, 2H), 4.83 (s, 2H), 2.10 (q, *J* = 7.0 Hz, 2H), 1.52 (s, 9H), 1.40 (t, *J* = 7.0 Hz, 2H), 1.29 (s, 4H), 0.92 – 0.82 (t, *J* = 6.7 Hz, 3H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 152.2, 151.4, 132.9, 124.0, 102.8 (s, C=CH₂), 82.8 (s, 1C, O-C-(CH₃)₃), 32.2, 31.3, 28.6, 27.6 (s, 3C, C-(CH₃)₃), 22.5, 14.0 ppm. **HRMS (ASAP +)** Calcd for C₁₄H₂₄NaO₃⁺ [M + Na]⁺: 263,1613. Found: 263,1618.

tert-butyl 1-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl carbonate **1ae**

According to general procedure C, tert-butyl 1-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl carbonate **1ae** was obtained from 6-Acetyl-1,1,2,4,4,7-hexamethyltetralin as a white solid in 42% yield (752 mg, 2.1 mmol) after purification by column chromatography on silica gel (hexane/DCM 7/3). **¹H NMR (500 MHz, CDCl₃)** δ 7.29 (s, 1H), 7.15 (s, 1H), 5.21 (d, *J* = 1.6 Hz, 1H), 4.96 (d, *J* = 1.6 Hz, 1H), 2.39 (s, 3H), 1.85 (dq, *J* = 13.5, 6.8, 2.6 Hz, 1H), 1.61 (t, *J* = 13.2 Hz, 1H), 1.43 (s, 9H), 1.36 (dd, *J* = 13.5, 2.6 Hz, 1H), 1.31 (s, 3H), 1.27 (s, 3H), 1.23 (s, 3H), 1.06 (s, 3H), 0.98 (d, *J* = 6.8 Hz, 3H) ppm. **¹³C NMR (126 MHz, CDCl₃)** δ 153.9, 151.2, 146.8, 142.3, 132.8, 132.4, 129.3, 126.5, 104.3 (C=CH₂), 83.0 (O-C-(CH₃)₃), 43.8, 37.7, 34.7, 34.1, 32.5, 32.1, 28.7, 27.8 (C-(CH₃)₃), 25.0, 20.5, 17.0 ppm. **HRMS (ESI+)** Calcd. for C₁₈H₂₅⁺ [M - OBoc]⁺: 241.1951. Found: 241.1967.

tert-butyl (1-(4-(tert-butyl)-2,6-dimethyl-3,5-dinitrophenyl)vinyl) carbonate **1af**

According to general procedure A, tert-butyl (1-(4-(tert-butyl)-2,6-dimethyl-3,5-dinitrophenyl)vinyl) carbonate **1af** was obtained from musk ketone as a colorless oil in 99% yield (620 mg, 2.6 mmol). **¹H NMR (300 MHz, CDCl₃)** δ 5.56 (s, 1H), 4.94 (s, 1H), 2.28 (s, 6H), 1.48 (s, 9H), 1.44 (s, 9H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 150.4, 148.6, 136.8, 131.9, 131.8, 108.2 (s, C=CH₂), 84.2 (s, 1C, O-C-(CH₃)₃), 37.5, 30.5, 27.7 (s, 3C, C-(CH₃)₃), 16.1 ppm. **HRMS (ASAP +)** Calcd for C₁₉H₂₇N₂O₇⁺ [M + H]⁺: 395.1813. Found: 395.1813.

tert-butyl (1-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)vinyl) carbonate **1ag**

According to general procedure A, tert-butyl (1-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)vinyl) carbonate **1ag** was obtained from celestolide as a white solid in 70% yield (630 mg, 1.8 mmol). **¹H NMR (300 MHz, CDCl₃)** δ 7.28 (s, 1H), 7.14 (s, 1H), 5.16 (d, *J* = 9.7 Hz, 2H), 2.96 (t, *J* = 7.1 Hz, 2H), 1.93 (t, *J* = 7.2 Hz, 2H), 1.45 (s, 9H), 1.32 (s, 9H), 1.26 (s, 6H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 153.9, 153.5, 151.4, 150.0, 137.3, 130.7, 121.5, 119.6, 103.8 (s, C=CH₂), 83.1 (s, 1C, O-C-(CH₃)₃), 43.9, 41.6, 34.8, 31.7, 30.1, 28.8, 27.8 (s, 3C, C-(CH₃)₃) ppm. **HRMS (ASAP +)** Calcd for C₃₄H₅₀O₂⁺ [2(M - Boc + H) + H]⁺: 489.3727. Found: 489.3726.

(E)-tert-butyl (4-(2,6,6-trimethylcyclohex-2-en-1-yl)buta-1,3-dien-2-yl) carbonate **1ah**

According to general procedure A, (E)-tert-butyl (4-(2,6,6-trimethylcyclohex-2-en-1-yl)buta-1,3-dien-2-yl) carbonate **1ah** was obtained from α-ionone as an orange oil in 72% yield (550 mg, 1.9 mmol). **¹H NMR (300 MHz, CDCl₃)** δ 5.91 (d, *J* = 15.6 Hz, 1H), 5.64 (dd, *J* = 15.4, 9.4 Hz, 1H), 5.34 (d, *J* = 36.8 Hz, 1H), 4.84 (s, 2H), 2.16 (d, *J* = 9.5 Hz, 1H), 1.98 (s, 2H), 1.55 (s, 3H), 1.49 (s, 9H), 1.42 – 1.32 (m, 1H), 1.23 – 1.09 (m, 1H), 0.88 (s, 3H), 0.80 (s, 3H) ppm. **¹³C NMR (75 MHz, CDCl₃)** δ 152.2, 151.4, 133.8, 133.6, 125.2, 121.5, 103.3 (s, C=CH₂), 82.9 (s, 1C, O-C-(CH₃)₃), 54.1, 32.6, 31.7, 27.7 (s, 3C, C-(CH₃)₃), 27.5, 27.1, 23.1, 23.0 ppm. **HRMS (ASAP +)** Calcd for C₁₃H₂₁O⁺ [M - Boc + H]⁺: 193.1587. Found: 193.1586.

tert-butyl (1-((3S,10R,13S,17S)-3-methoxy-10,13-dimethyl-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)vinyl) carbonate **1ai**

Pregnenolone methyl ether was synthesised according to a literature procedure.^[9] Spectral data matched with those reported in the literature.

According to general procedure C, tert-butyl (1-((3S,10R,13S,17S)-3-methoxy-10,13-dimethyl-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)vinyl) carbonate **1ai** was obtained from pregnenolone methyl ether as a white solid in 57% yield (1.23 g, 2.85 mmol) after purification by column chromatography on silica gel (hexane/EtOAc 9/1). **¹H NMR (500 MHz, CDCl₃)** δ 5.34 (dt, *J* = 5.4, 2.1 Hz, 1H), 4.85 (dd, *J* = 1.9, 1.0 Hz, 1H), 4.74 (t, *J* = 1.7 Hz, 1H), 3.34 (s, 3H), 3.04 (tt, *J* = 11.4, 4.6 Hz, 1H), 2.43 – 2.31 (m, 2H), 2.19 – 2.10 (m, 1H), 2.02 – 1.94 (m, 2H), 1.93 – 1.81 (m, 2H), 1.74 – 1.64 (m, 2H), 1.58 – 1.50 (m, 2H), 1.49 (s, 9H), 1.45 – 1.35 (m, 2H), 1.25 (ddd, *J* = 18.7, 9.0, 4.6 Hz, 2H), 1.21 – 1.14 (m, 2H), 1.14 – 1.02 (m, 2H), 0.99 (s, 3H), 0.65 (s, 3H). **¹³C NMR (126 MHz, CDCl₃)** δ 157.6, 151.8, 141.1, 121.4, 101.8 (C=CH₂), 82.6 (O-C-(CH₃)₃), 80.4, 56.1, 55.7, 53.3, 50.3, 43.1, 38.8, 38.0, 37.3, 37.1, 32.3, 31.9, 28.1, 27.9 (C-(CH₃)₃), 24.9, 24.3, 21.1, 19.5, 12.7 ppm. **HRMS (ESI+)** Calcd. for C₂₇H₄₂O₄Na⁺ [M + Na]⁺: 453.2975. Found: 453.2980.

tert-butyl ((10R,13S,17S)-17-methoxy-10,13-dimethyl-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl) carbonate **1aj**

17 β -methoxy-4-androsten-3-one was synthesised according to a literature procedure.^[10] Spectral data matched with those reported in the literature.

According to general procedure A, tert-butyl ((10R,13S,17S)-17-methoxy-10,13-dimethyl-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl) carbonate **1aj** was obtained from 17 β -methoxy-4-androsten-3-one as a white solid in 76% yield (800 mg, 2.0 mmol). ¹H NMR (300 MHz, CDCl₃) δ 5.38 (s, 1H), 5.25 (s, 1H), 3.33 (s, 3H), 3.20 (t, *J* = 8.3, 1H), 2.23 (t, *J* = 7.7 Hz, 4H), 2.05 – 1.85 (m, 2H), 1.74 – 1.55 (m, 2H), 1.49 (d, 9H), 1.46 – 1.35 (m, 4H), 1.33 – 1.07 (m, 3H), 1.00 – 0.90 (m, 5H), 0.77 (s, 3H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 152.0, 149.5, 145.1, 115.6, 107.2, 90.8, 82.9 (s, 1C, O-C-(CH₃)₃), 58.0, 54.7, 50.9, 43.0, 38.1, 38.0, 37.2, 36.2, 31.2, 30.8, 27.9, 27.8 (s, 3C, C-(CH₃)₃), 23.6, 21.4, 17.5, 11.6 ppm. HRMS (ASAP +) Calcd for C₂₅H₃₈O₄Na⁺ [M + Na]⁺: 425.2662. Found: 425.2677.

General procedures for the trifluoromethoxylation of enol carbonates

General procedure D, for trifluoromethoxylation of enol carbonates

A sealable tube surrounded by blue LEDs with a watertight protection, purged with argon and equipped with a cap was charged with 4-cyano-1-(trifluoromethoxy)pyridin-1-ium bis((trifluoromethyl)sulfonyl)amide **2a** (46.9 mg, 0.1 mmol, 1 equiv.), the desired enol carbonate (0.5 mmol, 5 equiv.) and 4CzIPN (3.9 mg, 0.005 mmol, 0.05 equiv.). Dry acetonitrile (10 mL, 0.01 M) was finally added and the reaction medium purged with argon again. The resulting mixture in the sealable tube was placed in a water bath and allowed to stir vigorously for 1h at 50°C under irradiation of the blue LEDs. The crude was then concentrated under vacuum. Alpha-trifluoromethoxylated ketones were isolated by preparative thin layer chromatography (PTLC).

General procedure E, for trifluoromethoxylation of enol carbonates

Two 8-mL vials surrounded by blue LEDs with a watertight protection, equipped with a screwcap and a septum were purged with argon and each one charged with 4-cyano-1-(trifluoromethoxy)pyridin-1-ium bis((trifluoromethyl)sulfonyl)amide **2a** (23.5 mg, 0.05 mmol, 1 equiv.), the desired enol carbonate (0.25 mmol, 5 equiv.) and 4CzIPN (1.9 mg, 0.0025 mmol, 0.05 equiv.). Dry acetonitrile (5 mL, 0.01 M) was finally added and the reaction medium purged with argon again. The resulting mixtures in the vials were placed in a water bath and allowed to stir vigorously for 1h at 50°C under irradiation of the blue LEDs. The crude reaction mixture was then transferred to a round-bottom flask, 1 mL of 6M HCl was added and the reaction mixture stirred until complete hydrolysis of the unreacted starting material (controlled by TLC analysis). The crude reaction mixture was then quenched with sat. NaHCO₃ until gas evolution stopped, diluted with DCM (30 mL) and washed with brine (3x10 mL). The organic phase was

dried over MgSO_4 and concentrated under vacuum. Corresponding alpha-trifluoromethoxylated ketones were isolated by column chromatography on silica gel.

1-(4-fluorophenyl)-2-(trifluoromethoxy)ethanone **3**

According to general procedure D, 1-(4-fluorophenyl)-2-(trifluoromethoxy)ethanone **3** was obtained from the corresponding enol carbonate **1b**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 50%. The product was isolated by PTLC (Pentane/ Et_2O (85/15, 2 elutions)) in 32% yield (7.0 mg, 0.031 mmol). ^1H NMR (300 MHz, CDCl_3) δ 8.02 – 7.89 (m, 1H), 7.19 (t, J = 8.4 Hz, 1H), 5.13 (s, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 188.9 (C=O), 166.5 (d, J = 257.2 Hz, C1), 130.9 (d, J = 9.5 Hz, C2), 130.4 (d, J = 3.1 Hz, C4), 121.8 (q, J = 256.6 Hz, ROCF_3), 116.48 (d, J = 22.2 Hz, C3), 68.3 (q, J = 2.9 Hz, $\text{RCH}_2\text{-OCF}_3$) ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -61.56 (s, 3F), -102.88 (m, 1F) ppm. HRMS (ASAP +) Calcd for $\text{C}_9\text{H}_7\text{F}_4\text{O}_2^+$ [$\text{M} + \text{H}$] $^+$: 223.0377. Found: 223.0386.

1-(*o*-tolyl)-2-(trifluoromethoxy)ethanone **7**

According to general procedure D, 1-(*o*-tolyl)-2-(trifluoromethoxy)ethanone **7** was obtained from the corresponding enol carbonate **1d**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 41%. The product was isolated by PTLC (Pentane/ Et_2O (95/5, 2 elutions)) in 36% yield (8.5 mg, 0.036 mmol). ^1H NMR (300 MHz, CDCl_3) δ 7.54 (d, J = 7.7 Hz, 1H), 7.46 (t, J = 7.6 Hz, 1H), 7.31 (d, J = 8.0 Hz, 2H), 5.04 (s, 2H), 2.54 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 193.6, 139.7, 133.8, 132.8, 132.7, 128.3, 126.0, 121.8 (q, J = 256 Hz, ROCF_3), 69.3 (q, J = 2.9 Hz, $\text{RCH}_2\text{-OCF}_3$), 21.4 ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -61.40 ppm. HRMS (ASAP +) Calcd for $\text{C}_{10}\text{H}_{10}\text{F}_3\text{O}_2^+$ [$\text{M} + \text{H}$] $^+$: 219.0627. Found: 219.0634.

1-(*m*-tolyl)-2-(trifluoromethoxy)ethanone **8**

According to general procedure D, 1-(*m*-tolyl)-2-(trifluoromethoxy)ethanone **8** was obtained from the corresponding enol carbonate **1e**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 43%. The product was isolated by PTLC (Pentane/ Et_2O (95/5, 2 elutions)) in 28% yield (6.1 mg, 0.028 mmol). ^1H NMR (300 MHz, CDCl_3) δ 7.74 – 7.65 (m, 2H), 7.49 – 7.34 (m, 2H), 5.17 (s, 2H), 2.43 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 190.4, 139.2, 135.2, 133.9, 129.0, 128.5, 125.2, 121.8 (q, J = 256.5 Hz, ROCF_3), 68.4 (q, J = 2.9 Hz, $\text{RCH}_2\text{-OCF}_3$), 21.5 ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -61.41 ppm. HRMS (ASAP +) Calcd for $\text{C}_{10}\text{H}_{10}\text{F}_3\text{O}_2^+$ [$\text{M} + \text{H}$] $^+$: 219.0627. Found: 219.0625.

1-(*p*-tolyl)-2-(trifluoromethoxy)ethanone **9**

According to general procedure D, 1-(*p*-tolyl)-2-(trifluoromethoxy)ethanone **9** was obtained from the corresponding enol carbonate **1f**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 46%. The product was isolated by PTLC (Pentane/ Et_2O (95/5, 2 elutions)) in 41% yield (9.0 mg, 0.041 mmol). ^1H NMR (300 MHz, CDCl_3) δ 7.80 (d, J = 7.8 Hz, 2H), 7.30 (d, J = 7.8 Hz, 2H), 5.15 (s, 2H), 2.43 (s, 3H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 189.9, 145.6, 131.4, 129.8, 128.2, 121.8 (q, J = 257 Hz, ROCF_3), 68.4 (q, J = 2.8 Hz, $\text{RCH}_2\text{-OCF}_3$), 21.9 ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -61.46 ppm. HRMS (ASAP +) Calcd for $\text{C}_{10}\text{H}_{10}\text{F}_3\text{O}_2^+$ [$\text{M} + \text{H}$] $^+$: 219.0627. Found: 219.0627.

1-(3-methoxyphenyl)-2-(trifluoromethoxy)ethan-1-one **10**

According to general procedure E, 1-(3-methoxyphenyl)-2-(trifluoromethoxy)ethan-1-one **10** was obtained from the corresponding enol carbonate **1g**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 12%. ^{19}F NMR (188 MHz, CDCl_3) δ -61.05 ppm.

1-(4-methoxyphenyl)-2-(trifluoromethoxy)ethan-1-one **11**

According to general procedure E, 1-(4-methoxyphenyl)-2-(trifluoromethoxy)ethan-1-one **11** was obtained from the corresponding enol carbonate **1h**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 13%. ^{19}F NMR (188 MHz, CDCl_3) δ -60.98 ppm.

4-(2-(trifluoromethoxy)acetyl)benzonitrile **12**

According to general procedure E, 4-(2-(trifluoromethoxy)acetyl)benzonitrile **12** was obtained from the corresponding enol carbonate **1i**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 42%. The product was isolated by flash column chromatography on silica gel hexane/ EtOAc 8/2) in 27% yield (6.2 mg, 0.027 mmol). ^1H NMR (300 MHz, CDCl_3) δ 8.01 (d, J = 7.8 Hz, 2H), 7.82 (d, J = 8.0 Hz, 2H), 5.15 (s, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 189.6, 136.8, 133.0, 128.7, 121.7 (q, J = 257.4 Hz, ROCF_3), 117.8, 117.6, 68.5 (q, J = 3.0 Hz, $\text{RCH}_2\text{-OCF}_3$) ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -61.63 ppm. HRMS (ASAP +) Calcd for $\text{C}_{10}\text{H}_7\text{F}_3\text{NO}_2^+$ [$\text{M} + \text{H}$] $^+$: 230.0423. Found: 230.0422.

2-(trifluoromethoxy)-1-(3-(trifluoromethyl)phenyl)ethanone **13**

According to general procedure D, 2-(trifluoromethoxy)-1-(3-(trifluoromethyl)phenyl)ethanone **13** was obtained from the corresponding enol carbonate **1j**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 38%. PTLC conditions: 2 successive purifications with Pentane/Et₂O (9/1) and then 100% DCM. The product was isolated in 15% yield (4.0 mg, 0.015 mmol). ^1H NMR (300 MHz, CDCl₃) δ 8.16 (s, 1H), 8.10 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 7.7 Hz, 1H), 7.68 (t, J = 7.8 Hz, 1H), 5.18 (s, 2H) ppm. ^{13}C NMR (75 MHz, CDCl₃) δ 189.4, 134.4, 131.9 (d, J = 33 Hz), 131.3, 130.8 (q, J = 3.5 Hz), 129.9, 125.1 (q, J = 3.9 Hz), 123.6 (d, J = 272 Hz), 121.7 (q, J = 256 Hz, ROCF₃), 68.4 (q, J = 3.0 Hz, RCH₂-OCF₃) ppm. ^{19}F NMR (188 MHz, CDCl₃) δ -61.59 (OCF₃), -63.44 (CF₃) ppm. HRMS (ASAP +) Calcd for C₁₀H₇F₆O₂⁺ [M + H]⁺: 273.0345. Found: 273.0341.

1-(3,5-bis(trifluoromethyl)phenyl)-2-(trifluoromethoxy)ethan-1-one **14**

According to general procedure E, 1-(3,5-bis(trifluoromethyl)phenyl)-2-(trifluoromethoxy)ethan-1-one **14** was obtained from the corresponding enol carbonate **1k**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 13%. ^{19}F NMR (188 MHz, CDCl₃) δ -61.23 (s, 3F), -63.36 (s, 6F) ppm.

1-(2-bromophenyl)-2-(trifluoromethoxy)ethan-1-one **15**

According to general procedure E, 1-(2-bromophenyl)-2-(trifluoromethoxy)ethan-1-one **15** was obtained from the corresponding enol carbonate **1l**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 36%. The product was isolated by flash column chromatography on silica gel (hexane/EtOAc 8/2) in 18% yield (5.1 mg, 0.018 mmol). Particular care was taken during solvent evaporation steps due to the observed volatility of the product. ^1H NMR (500 MHz, CDCl₃) δ 7.66 (d, J = 7.8 Hz, 1H), 7.51 – 7.33 (m, 3H), 5.05 (s, 2H) ppm. ^{13}C NMR (126 MHz, CDCl₃) δ 194.8, 137.8, 134.0, 133.1, 129.6, 127.8, 121.6 (q, J = 256.8 Hz, ROCF₃), 119.4, 69.8 (q, J = 3.0 Hz, RCH₂-OCF₃) ppm. ^{19}F NMR (188 MHz, CDCl₃) δ -61.53 ppm. HRMS (ASAP +) Calcd for C₈H₅BrF₃O₂⁺ [M + H]⁺: 282.9576. Found: 282.9580.

1-(3-bromophenyl)-2-(trifluoromethoxy)ethan-1-one **16**

According to general procedure E, 1-(3-bromophenyl)-2-(trifluoromethoxy)ethan-1-one **16** was obtained from the corresponding enol carbonate **1m**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 38%. The product was isolated by flash column chromatography on silica gel (hexane/DCM 7/3) in 27% yield (7.6 mg, 0.027 mmol). ^1H NMR (500 MHz, CDCl_3) δ 8.04 (t, J = 1.8 Hz, 1H), 7.83 (dt, J = 7.8, 1.3 Hz, 1H), 7.77 (ddd, J = 8.0, 2.0, 1.0 Hz, 1H), 7.40 (t, J = 7.9 Hz, 1H), 5.13 (s, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 189.2, 137.4, 135.6, 131.2, 130.7, 126.6, 123.6, 121.8 (q, J = 256.8 Hz, ROCF_3), 68.3 (q, J = 3.0 Hz, $\text{RCH}_2\text{-OCF}_3$) ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -61.59 ppm. HRMS (ASAP +) Calcd for $\text{C}_8\text{H}_5\text{BrF}_3\text{O}_2^+$ [$\text{M} + \text{H}$] $^+$: 282.9576. Found: 282.9576.

1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-one **17**

According to general procedure E, 1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-one **17** was obtained from the corresponding enol carbonate **1n**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 46%. The product was isolated by flash column chromatography on silica gel (hexane/EtOAc 95/5) in 34% yield (9.6 mg, 0.034 mmol). ^1H NMR (500 MHz, CDCl_3) δ 7.78 (d, J = 8.6 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H), 5.12 (s, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 189.6, 132.6, 132.6, 129.8, 129.6, δ 121.8 (q, J = 256.8 Hz, ROCF_3), 68.3 (q, J = 3.0 Hz, $\text{RCH}_2\text{-OCF}_3$) ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -61.56 ppm. HRMS (ASAP +) Calcd for $\text{C}_8\text{H}_5\text{BrF}_3\text{O}_2^+$ [$\text{M} + \text{H}$] $^+$: 282.9576. Found: 282.9572.

1-(2,5-dichlorophenyl)-2-(trifluoromethoxy)ethan-1-one **18**

According to general procedure E, 1-(2,5-dichlorophenyl)-2-(trifluoromethoxy)ethan-1-one **18** was obtained from the corresponding enol carbonate **1o**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 13%. ^{19}F NMR (188 MHz, CDCl_3) δ -61.20 ppm.

1-(4-acetylphenyl)-2-(trifluoromethoxy)ethan-1-one **19**

According to general procedure E, 1-(4-acetylphenyl)-2-(trifluoromethoxy)ethan-1-one **19** was obtained from the corresponding enol carbonate **1p**. The yield of the desired product was determined

by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 44%. ^{19}F NMR (188 MHz, CDCl_3) δ -61.32 ppm.

1-phenyl-2-(trifluoromethoxy)propan-1-one **20**

According to general procedure E, 1-phenyl-2-(trifluoromethoxy)propan-1-one **20** was obtained from the corresponding enol carbonate **1q**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 34%. The product was isolated by flash column chromatography on silica gel (hexane/DCM 8/2) in 32% yield (7.0 mg, 0.032 mmol). ^1H NMR (500 MHz, CDCl_3) δ 7.97 (d, J = 8.0 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.51 (t, J = 7.7 Hz, 2H), 5.48 (q, J = 6.9 Hz, 1H), 1.66 (d, J = 6.9 Hz, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 195.1, 134.2, 133.7, 129.1, 128.9, 121.6 (q, J = 256.2 Hz, ROCF_3), δ 75.5 (q, J = 2.5 Hz, $\text{RCH}_2\text{-OCF}_3$), 18.8 ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -59.29 ppm. HRMS (ASAP +) Calcd for $\text{C}_{10}\text{H}_{10}\text{F}_3\text{O}_2^+$ [$\text{M} + \text{H}$] $^+$: 219.0627. Found: 219.0629.

1,3-diphenyl-2-(trifluoromethoxy)propan-1-one **21**

According to general procedure E, 1,3-diphenyl-2-(trifluoromethoxy)propan-1-one **21** was obtained from the corresponding enol carbonate **1r**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 31%. The product was isolated by flash column chromatography on silica gel (hexane/DCM 8/2) in 27% yield (7.9 mg, 0.027 mmol). ^1H NMR (500 MHz, CDCl_3) δ 7.98 – 7.83 (m, 2H), 7.69 – 7.55 (m, 1H), 7.55 – 7.42 (m, 2H), 7.32 – 7.28 (m, 2H), 7.27 – 7.24 (m, 1H), 7.24 – 7.20 (m, 2H), 5.50 (dd, J = 7.8, 5.3 Hz, 1H), 3.31 – 3.14 (m, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 194.7, 135.0, 134.2, 134.2, 129.5, 129.1, 128.9, 127.6, 121.4 (q, J = 256.8 Hz, ROCF_3), 79.5 (q, J = 2.0 Hz, $\text{RCH}_2\text{-OCF}_3$), 39.0 ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -59.46 ppm. HRMS (ASAP +) Calcd for $\text{C}_{10}\text{H}_{10}\text{F}_3\text{O}_2^+$ [$\text{M} + \text{H}$] $^+$: 295.0940. Found: 295.0941.

2-(trifluoromethoxy)-2,3-dihydro-1H-inden-1-one **22**

According to general procedure D, 2-(trifluoromethoxy)-2,3-dihydro-1H-inden-1-one **22** was obtained from the corresponding enol carbonate **1s**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 28%. PTLC conditions: Pentane/ Et_2O (85/15, 2 elutions). ^1H NMR (300 MHz, CDCl_3) δ 7.82 (d, J = 7.7 Hz, 1H), 7.68 (t, J = 7.1 Hz, 1H), 7.50 – 7.40 (m, 2H), 4.98 – 4.89 (m, 1H), 3.68 (dd, J = 17.1, 8.0 Hz, 1H), 3.26 (dd, J = 16.7, 4.2 Hz, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 197.6, 149.7, 136.6, 133.8, 128.7, 126.8, 125.0, 122.1 (q, J = 257 Hz, ROCF_3), 33.9 ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -59.73 ppm. HRMS (ASAP +) Calcd for $\text{C}_{20}\text{H}_{15}\text{F}_3\text{O}_4^+$ [$2\text{M} + \text{H}$] $^+$: 433.0869. Found: 433.0864.

6-methoxy-2-(trifluoromethoxy)-2,3-dihydro-1H-inden-1-one **23**

According to general procedure D, 6-methoxy-2-(trifluoromethoxy)-2,3-dihydro-1H-inden-1-one **23** was obtained from the corresponding enol carbonate **1t**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 9%. PTLC conditions: Pentane/Et₂O (8/2). ^1H NMR (300 MHz, CDCl₃) δ 7.36 (d, J = 8.3 Hz, 1H), 7.30 – 7.21 (m, 3H), 4.97 – 4.89 (m, 1H), 3.85 (s, 3H), 3.60 (dd, J = 16.6, 7.9 Hz, 1H), 3.17 (dd, J = 16.9, 4.6 Hz, 1H) ppm. ^{13}C NMR (75 MHz, CDCl₃) δ 197.7, 160.3, 142.5, 134.9, 127.6, 126.0, 122.07 (q, J = 256.8 Hz, ROCF₃), 106.0, 55.9, 33.3 ppm. ^{19}F NMR (188 MHz, CDCl₃) δ -59.72 ppm. HRMS (ASAP +) Calcd for C₁₁H₁₀F₃O₃⁺ [M + H]⁺: 247.0577. Found: 247.0572.

5-fluoro-2-(trifluoromethoxy)-2,3-dihydro-1H-inden-1-one **24**

According to general procedure D, 5-fluoro-2-(trifluoromethoxy)-2,3-dihydro-1H-inden-1-one **24** was obtained from the corresponding enol carbonate **1u**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 29%. The product was isolated by PTLC (Pentane/Et₂O (85/15, 2 elutions)) in 22% yield (5.2 mg, 0.022 mmol). ^1H NMR (300 MHz, CDCl₃) δ 7.88 – 7.80 (m, 1H), 7.20 – 7.09 (m, 2H), 4.98 – 4.89 (m, 1H), 3.67 (dd, J = 17.3, 7.9 Hz, 1H), 3.25 (dd, J = 17.1, 4.8 Hz, 1H) ppm. ^{13}C NMR (75 MHz, CDCl₃) δ 195.6, 168.19 (d, J = 259 Hz, F-C_{Ar}), 152.66 (d, J = 10.5 Hz), 130.3, 127.61 (d, J = 10.6 Hz), 122.03 (q, J = 257 Hz, ROCF₃), 117.20 (d, J = 23.8 Hz), 113.62 (d, J = 22.8 Hz), 76.38 (q, J = 2.4 Hz, RCH₂-OCF₃), 33.8 ppm. ^{19}F NMR (188 MHz, CDCl₃) δ -59.80 (s, CF₃), -99.41 (q, J = 7.7 Hz) ppm. HRMS (ASAP +) Calcd for C₁₀H₇F₄O₂⁺ [M + H]⁺: 235.0377. Found: 235.0380.

2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2H)-one **25**

According to general procedure E, 2-(trifluoromethoxy)-3,4-dihydronaphthalen-1(2H)-one **25** was obtained from the corresponding enol carbonate **1v**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 14%. ^{19}F NMR (188 MHz, CDCl₃) δ -58.76 ppm.

6-(trifluoromethoxy)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one **26**

According to general procedure D, 6-(trifluoromethoxy)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one **26** was obtained from the corresponding enol carbonate **1w**; the yield of the desired product was

determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 24%. PTLC conditions: Pentane/Et₂O (85/15). ^1H NMR (300 MHz, CDCl₃) δ 7.71 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.4 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.23 (s, 1H), 4.99 (t, J = 7.0 Hz, 1H), 3.14 – 2.91 (m, 2H), 2.40 – 2.24 (m, 1H), 2.22 – 2.0 (m, 2H), 1.99 – 1.81 (m, 1H) ppm. ^{13}C NMR (75 MHz, CDCl₃) δ 198.9, 141.7, 136.5, 132.4, 130.2, 129.4, 127.0, 121.50 (q, J = 257 Hz, ROCF₃), 81.0 (q, J = 2.6 Hz, RCH₂-OCF₃). 34.2, 30.8, 23.2 ppm. ^{19}F NMR (188 MHz, CDCl₃) δ -59.52 ppm. HRMS (ASAP +) Calcd for C₁₂H₁₂F₃O₂⁺ [M + H]⁺: 245.0784. Found: 245.0781.

1-(benzo[b]thiophen-2-yl)-2-(trifluoromethoxy)ethanone **27**

According to general procedure D, 1-(benzo[b]thiophen-2-yl)-2-(trifluoromethoxy)ethanone **27** was obtained from the corresponding enol carbonate **1x**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 12%. PTLC conditions: Pentane/Et₂O (9/1). ^1H NMR (300 MHz, CDCl₃) δ 8.05 (s, 1H), 7.92 (t, J = 8.2 Hz, 2H), 7.49 (dt, J = 22.0, 7.4 Hz, 2H), 5.13 (s, 1H) ppm. ^{13}C NMR (75 MHz, CDCl₃) δ 185.2, 142.7, 139.5, 139.0, 130.4, 128.4, 126.5, 125.6, 123.1, 121.7 (d, J = 257.2 Hz, ROCF₃), 68.5 (q, J = 3.7, 3.0 Hz, RCH₂-OCF₃) ppm. ^{19}F NMR (188 MHz, CDCl₃) δ -61.41 ppm. HRMS (ASAP +) Calcd for C₁₁H₈F₃O₂S⁺ [M + H]⁺: 261.0192. Found: 261.0204.

1-(naphthalen-2-yl)-2-(trifluoromethoxy)ethan-1-one **28**

According to general procedure E, 1-(naphthalen-2-yl)-2-(trifluoromethoxy)ethan-1-one **28** was obtained from the corresponding enol carbonate **1y**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 14%. ^{19}F NMR (188 MHz, CDCl₃) δ -60.95 ppm.

2,2-difluoro-1-phenyl-2-(trifluoromethoxy)ethan-1-one **29**

According to general procedure E, 2,2-difluoro-1-phenyl-2-(trifluoromethoxy)ethan-1-one **29** was obtained from the corresponding enol carbonate **1z**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 20%. ^{19}F NMR (188 MHz, CDCl₃) δ -54.91 (t, J = 8.7 Hz, 3F), -76.80 (q, J = 9.1 Hz, 2F) ppm.

2,2-difluoro-1-(naphthalen-2-yl)-2-(trifluoromethoxy)ethan-1-one **30**

According to general procedure E, 2,2-difluoro-1-(naphthalen-2-yl)-2-(trifluoromethoxy)ethan-1-one **30** was obtained from the corresponding enol carbonate **1aa**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 19%. ^{19}F NMR (188 MHz, CDCl_3) δ -54.92 (t, J = 8.7 Hz, 3F), -76.23 (q, J = 8.5 Hz, 2F) ppm.

1-(trifluoromethoxy)octan-2-one **31**

31

According to general procedure E, 1-(trifluoromethoxy)octan-2-one **31** was obtained from the corresponding enol carbonate **1ab**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 16%. ^{19}F NMR (188 MHz, CDCl_3) δ -61.30 ppm.

(E)-4-phenyl-1-(trifluoromethoxy)but-3-en-2-one **32**

32

According to general procedure D, (E)-4-phenyl-1-(trifluoromethoxy)but-3-en-2-one **32** was obtained from the corresponding enol carbonate **1ac**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 21%. PTLC conditions: Pentane/ Et_2O (9/1, 2 elutions). ^1H NMR (300 MHz, CDCl_3) δ 7.76 (d, J = 16.1 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.48 – 7.36 (m, 3H), 6.97 (d, J = 16.1 Hz, 1H), 4.69 (s, 2H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 191.4, 145.7, 134.0, 131.5, 129.2, 128.9, 128.6, 121.7 (q, J = 256 Hz, ROCF_3), 69.9 (q, J = 2.5 Hz, $\text{RCH}_2\text{-OCF}_3$) ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -61.63 ppm. HRMS (ASAP +) Calcd for $\text{C}_{11}\text{H}_{10}\text{F}_3\text{O}_2^+$ [M + H] $^+$: 231.0627. Found: 231.0634.

(E)-1-(trifluoromethoxy)non-3-en-2-one **33**

33

According to general procedure D, (E)-1-(trifluoromethoxy)non-3-en-2-one **33** was obtained from the corresponding enol carbonate **1ad**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 18%. ^{19}F NMR (188 MHz, CDCl_3) δ -61.67 ppm. HRMS (ASAP +) Calcd for $\text{C}_{10}\text{H}_{16}\text{F}_3\text{O}_2^+$ [M + H] $^+$: 225.1097. Found: 225.1093.

1-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-2-(trifluoromethoxy)ethan-1-one 34

34

According to general procedure E, 1-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-2-(trifluoromethoxy)ethan-1-one **34** was obtained from the corresponding enol carbonate **1ae**. The yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 33%. The product was isolated by flash column chromatography on silica gel (hexane/DCM 7/3) in 26% yield (8.9 mg, 0.026 mmol). ^1H NMR (500 MHz, CDCl_3) δ 7.48 (s, 1H), 7.26 (s, 1H), 5.02 (s, 2H), 2.50 (s, 3H), 1.88 (dq, J = 13.5, 6.8, 2.6 Hz, 1H), 1.64 (t, J = 13.3 Hz, 1H), 1.41 (dd, J = 13.6, 2.6 Hz, 1H), 1.33 (s, 3H), 1.32 (s, 3H), 1.27 (s, 3H), 1.08 (s, 3H), 1.00 (d, J = 6.8 Hz, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 193.0, 151.7, 142.7, 136.5, 131.3 (x2), 127.2, 121.8, (q, J = 256.2 Hz, ROCF_3), 69.3 (q, J = 2.9 Hz, $\text{RCH}_2\text{-OCF}_3$), 43.4, 38.2, 34.5, 34.2, 32.6, 32.0, 28.4, 24.8, 21.3, 16.9 ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -61.29 ppm. HRMS (ESI+) Calcd. for $\text{C}_{19}\text{H}_{26}\text{F}_3\text{O}_2$ $[\text{M} + \text{H}]^+$: 343.1879. Found: 343.1870.

1-(4-(tert-butyl)-2,6-dimethyl-3,5-dinitrophenyl)-2-(trifluoromethoxy)ethanone 35

35

According to general procedure D, 1-(4-(tert-butyl)-2,6-dimethyl-3,5-dinitrophenyl)-2-(trifluoromethoxy)ethanone **35** was obtained from the corresponding enol carbonate **1af**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 29%. The product was isolated by PTLC (Pentane/ Et_2O 9/1) in 21% yield (7.9 mg, 0.021 mmol) as a white solid. ^1H NMR (300 MHz, CDCl_3) δ 4.74 (s, 2H), 2.12 (s, 6H), 1.45 (s, 9H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 197.6, 150.7, 138.5, 133.8, 128.5, 121.4 (q, J = 258 Hz, ROCF_3), 70.7 (q, J = 2.9 Hz, $\text{RCH}_2\text{-OCF}_3$), 37.8, 30.4, 15.2 ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -61.74 ppm. HRMS (ASAP +) Calcd for $\text{C}_{15}\text{H}_{18}\text{F}_3\text{N}_2\text{O}_6$ $[\text{M} + \text{H}]^+$: 379.1111. Found: 379.1126.

1-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)-2-(trifluoromethoxy)ethanone 36

36

According to general procedure D, 1-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)-2-(trifluoromethoxy)ethanone **36** was obtained from the corresponding enol carbonate **1ag**; the yield of the desired product was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 20%. The product was isolated by PTLC (Pentane/ EtOAc (98/2, 2 elutions)) in 16% yield (5.2 mg, 0.016 mmol). ^1H NMR (300 MHz, CDCl_3) δ 7.52 (s, 1H), 7.40 (s, 1H), 5.12 (s, 2H), 3.17 (t, J = 7.3 Hz, 2H), 1.96 (t, J = 7.3 Hz, 2H), 1.36 (s, 9H), 1.27 (s, 6H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 191.8, 155.2, 150.5, 142.2, 130.2, 124.7, 123.2, 117.5 (q, J = 336.7 Hz, ROCF_3), 69.2 (q, J = 2.6 Hz, $\text{RCH}_2\text{-OCF}_3$), 43.7, 41.5, 34.9, 31.6, 30.9, 28.9 ppm. ^{19}F

NMR (188 MHz, CDCl₃) δ -61.24 ppm. **HRMS (ASAP +)** Calcd for C₁₈H₂₄F₃O₂⁺ [M + H]⁺: 329.1723. Found: 329.1679.

(E)-1-(trifluoromethoxy)-4-(2,6,6-trimethylcyclohex-2-en-1-yl)but-3-en-2-one 37

According to general procedure D, (E)-1-(trifluoromethoxy)-4-(2,6,6-trimethylcyclohex-2-en-1-yl)but-3-en-2-one **38** was obtained from the corresponding enol carbonate **1ah**; the yield of the desired product was determined by comparing the integration of the ¹⁹F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ¹⁹F NMR yield of 14%. The product was isolated by PTLC (Pentane/EtOAc 98/2) in 11% yield (3.2 mg, 0.011 mmol). ¹H NMR (200 MHz, CDCl₃) δ 6.87 (dd, *J* = 15.7, 9.8 Hz, 1H), 6.28 (d, *J* = 15.6 Hz, 1H), 5.53 (bs, 1H), 4.61 (s, 2H), 2.32 (d, *J* = 9.6 Hz, 1H), 1.66 (s, 1H), 2.14 – 1.98 (m, 3H), 1.52 (s, 3H), 0.93 (s, 3H), 0.85 (s, 3H) ppm. ¹³C NMR (151 MHz, CDCl₃) δ 191.04, 151.82, 131.35, 125.79, 123.39, 69.54 (q, *J* = 2.9 Hz, CH₂OCF₃), 54.77, 28.00, 27.81, 26.89, 23.14, 22.87 ppm. ¹⁹F NMR (188 MHz, CDCl₃) δ -61.62 ppm. **HRMS (ASAP +)** Calcd for C₁₄H₂₀F₃O₂⁺ [M + H]⁺: 277.1410. Found: 277.1407.

1-((3S,8S,9S,10R,13S,14S)-3-methoxy-10,13-dimethyl-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(trifluoromethoxy)ethan-1-one 38

According to general procedure E, 1-((3S,8S,9S,10R,13S,14S)-3-methoxy-10,13-dimethyl-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)-2-(trifluoromethoxy)ethan-1-one **38** was obtained from the corresponding enol carbonate **1ai**. The yield of the desired product was determined by comparing the integration of the ¹⁹F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ¹⁹F NMR yield of 10%. ¹⁹F NMR (188 MHz, CDCl₃) δ -61.10 ppm.

(8R,9S,10R,13S,14S,17S)-17-methoxy-10,13-dimethyl-6-(trifluoromethoxy)-dodecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one 39

According to general procedure D, (8R,9S,10R,13S,14S,17S)-17-methoxy-10,13-dimethyl-6-(trifluoromethoxy)-dodecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one **39** was obtained from the corresponding enol carbonate **1aj**; the yield of the desired product was determined by comparing the integration of the ¹⁹F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ¹⁹F NMR yield of 8%. PTLC conditions: Pentane/Et₂O (9/1). The compound was isolated as an

inseparable 1:1 mixture of diastereoisomers. In ^1H NMR, only characteristic peaks are listed.^[10] **^1H NMR (600 MHz, CDCl_3)** δ 5.82 (d, J = 1.0 Hz, 1H, $\text{C}=\text{CHC}=\text{O}$), 5.77 (d, J = 1.4 Hz, 1H, $\text{C}=\text{CHC}=\text{O}$), 4.72 (dd, J = 14.0, 5.3 Hz, 1H, CHOCH_3), 4.57 (dd, J = 9.2, 4.5 Hz, 1H, CHOCH_3), 3.35 (s, 3H x2, OCH_3), 3.25 – 3.20 (m, 2H x2, CHOCH_3), 2.54 – 2.45 (m, 1H, $\text{CH}_2\text{C}=\text{O}$), 2.34 (dt, J = 4.9, 2.3 Hz, 1H, $\text{CH}_2\text{C}=\text{O}$), 2.29 (dd, J = 4.2, 2.6 Hz, 1H, $\text{CH}_2\text{C}=\text{O}$), 2.27 (dt, J = 5.2, 2.7 Hz, 1H, $\text{CH}_2\text{C}=\text{O}$), 1.32 (s, 3H, C-19 CH_3), 1.27 (s, 3H, C-19 CH_3), 0.80 (s, 3H, C-18 CH_3), 0.80 (s, 3H, C-18 CH_3). **^{13}C NMR (151 MHz, CDCl_3)** δ 191.5, 191.1, 173.6, 171.3, 123.5 (d, J = 239.1 Hz, ROCF_3), 121.8, 120.8, 117.1, 90.8, 90.5, 75.2 – 75.1 (m, CHOCH_3), 74.5 – 74.4 (m, CHOCH_3), 58.0 (x2), 54.4, 54.2, 52.7, 51.0, 50.7 (x2), 43.2, 43.0, 42.9, 42.7, 40.9, 40.4, 39.6, 38.0, 37.8, 37.7, 37.6, 35.7, 35.5, 35.0, 33.7, 33.6, 33.1, 32.7, 32.5, 32.1, 31.6, 29.8, 27.8, 27.7, 27.6, 23.4 (x3), 21.9, 21.8, 21.2, 20.8, 18.3, 17.6, 11.8, 11.7 (x2). **^{19}F NMR (188 MHz, CDCl_3)** δ -59.05 (s, CF_3), -59.11 (s, CF_3) ppm. **HRMS (ASAP +)** Calcd for $\text{C}_{21}\text{H}_{30}\text{F}_3\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 387.2142. Found: 387.2152.

Scale-up experiments

4-(2-(trifluoromethoxy)acetyl)benzonitrile **12**

A round-bottomed flask purged with argon was charged with 4-cyano-1-(trifluoromethoxy)pyridin-1-ium bis((trifluoromethyl)sulfonyl)amide **2a** (939 mg, 2.1 mmol, 1 equiv.), tert-butyl (1-(4-cyanophenyl)vinyl) carbonate **1i** (2.58 g, 10.5 mmol, 5 equiv.) and 4CzIPN (83 mg, 0.11 mmol, 0.05 equiv.). Dry acetonitrile (210 mL, 0.01 M) was finally added and the reaction medium purged with argon again. 200 mL of the resulting mixture were taken at a flow rate of 5 mL/min (2 minutes of residence time in a 10 mL coil UV-150 reactor) by the VapourTec apparatus, equipped with a blue lamp irradiating at 450 nm inside the reactor, at 50°C. The resulting mixture exiting the apparatus was concentrated under vacuum. ^{19}F NMR yield of 37%. 4-(2-(trifluoromethoxy)acetyl)benzonitrile **12** was isolated as a white solid by column chromatography on silica gel (Pentane/EtOAc 9/1) in 36% yield (165 mg, 0.72 mmol).

The scaled-up synthesis of **12** was then repeated with 4-cyano-1-(trifluoromethoxy)pyridin-1-ium bis((trifluoromethyl)sulfonyl)amide **2a** (1.06 g, 2.26 mmol, 1 equiv.) and tert-butyl (1-(4-cyanophenyl)vinyl) carbonate **1i** (3.0 g, 13.6 mmol, 6 equiv.). 4-(2-(trifluoromethoxy)acetyl)benzonitrile **12** was isolated as a white solid by column chromatography on silica gel (Pentane/EtOAc 9/1) in 50% yield (260 mg, 1.13 mmol).

1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-one **17**

A 250 mL round-bottomed flask purged with argon was charged with 4-cyano-1-(trifluoromethoxy)pyridin-1-ium bis((trifluoromethyl)sulfonyl)amide **2a** (469 mg, 1 mmol, 1 equiv.), 1-(4-bromophenyl)vinyl tert-butyl carbonate **1n** (1.50 g, 5 mmol, 5 equiv.) and 4CzIPN (39 mg, 0.05 mmol, 0.05 equiv.). Dry acetonitrile (100 mL, 0.01 M) was finally added and the reaction medium purged with argon again. The resulting mixture was taken at a flow rate of 5 mL/min (2 minutes of residence time in a 10 mL coil UV-150 reactor) by the VapourTec apparatus, equipped with a medium pressure mercury lamp set at 75% of its maximum power output and a band-pass filter N°4 irradiating at 370 nm inside the reactor, at 50°C. The resulting mixture exiting the apparatus was treated with 10 mL of

6M HCl and the reaction mixture stirred until complete hydrolysis of the unreacted starting material (controlled by TLC analysis). The crude reaction mixture was then quenched with sat. NaHCO₃ until gas evolution stopped, diluted with DCM (200 mL) and washed with brine (3x50 mL). The organic phase was dried over MgSO₄ and concentrated under vacuum. ¹⁹F NMR yield of 37%. 1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-one **17** was isolated as a yellow solid by column chromatography on silica gel (hexane/EtOAc 95/5) in 33% yield (94 mg, 0.33 mmol).

Post-modifications

1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-ol **40**

A 4 mL vial was charged with 1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-one **17** (30 mg, 0.106 mmol, 1 equiv.) and MeOH was added (300 µL). The solution was cooled to 0°C and NaBH₄ (4.8 mg, 0.127 mmol, 1.2 equiv.) was added. The reaction mixture was stirred at 0°C for 1h, after which time it was quenched with 1M HCl (1 mL), extracted with EtOAc (3x10 mL) and washed with brine (10 mL). The organic phase was dried over MgSO₄ and concentrated under vacuum. 1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-ol **40** was isolated without the need of further purification as a yellow oil, which solidified upon standing, in 88% yield (26.6 mg, 0.093 mmol). ¹H NMR (500 MHz, CDCl₃) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 4.97 (dd, *J* = 8.5, 3.4 Hz, 1H), 4.05 (dd, *J* = 10.2, 3.5 Hz, 1H), 3.98 (dd, *J* = 10.2, 8.5 Hz, 1H), 2.44 (br s, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 137.5, 132.1, 128.0, 122.8, 119.7 (q, *J* = 238.3 Hz, ROCF₃), 71.6 (q, *J* = 2.6 Hz, RCH₂-OCF₃), 71.4 ppm. ¹⁹F NMR (188 MHz, CDCl₃) δ -61.24 ppm. HRMS (ESI-) Calcd. for C₁₈H₁₄O₄Br₂F₆K [2M - 2H + K]⁻: 604.8806. Found: 604.8813.

1-(4-morpholinophenyl)-2-(trifluoromethoxy)ethan-1-ol **41**

The procedure was adapted from the literature.^[11] A 4 mL vial purged with nitrogen was charged with 1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-ol **40** (14 mg, 0.05 mmol, 1 equiv.), Pd(OAc)₂ (0.22 mg, 0.001 mmol, 0.02 equiv.), 2-(di-*tert*-butylphosphino)biphenyl (JohnPhos, 0.44 mg, 0.0015 mmol, 0.03 equiv.) and anhydrous Cs₂CO₃ (24 mg, 0.075 mmol, 1.5 equiv.). The vial was closed with a cap equipped with a septum and 400 µL of degassed anhydrous 1,4-dioxane were added. Morpholine (5 µL, 0.06 mmol, 1.2 equiv.) was added and the reaction was stirred at 80°C for 16 hours, after which time the reaction mixture was concentrated under reduced pressure. ¹⁹F NMR yield of 19%. 1-(4-morpholinophenyl)-2-(trifluoromethoxy)ethan-1-ol **41** was isolated as a yellow oil by column chromatography on silica gel (hexane/EtOAc 1/1) in 22% yield (3.2 mg, 0.011 mmol). ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.27 (m, 2H), 6.94 – 6.89 (m, 2H), 4.93 (t, *J* = 6.2 Hz, 2H), 4.07 – 3.98 (m, 2H), 3.91 – 3.78 (m, 4H), 3.20 – 3.13 (m, 4H), 2.34 (d, *J* = 2.9 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 151.71, 129.65, 127.39, 121.78 (q, *J* = 255.0 Hz, ROCF₃), 115.76, 71.90 (q, *J* = 2.3 Hz, RCH₂-OCF₃), 71.63, 66.98, 49.23 ppm. ¹⁹F NMR (188 MHz, CDCl₃) δ -61.10 ppm. HRMS (ASAP +) Calcd for C₁₃H₁₇F₃NO₃⁺ [M + H]⁺: 292.1155. Found: 292.1161.

1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-aminium acetate **42**

The procedure was adapted from the literature.^[12] A flame-dried schlenk tube purged with nitrogen was charged with 1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-one **17** (14 mg, 0.05 mmol), anhydrous NH_4OAc (77 mg, 1 mmol, 20 equiv.) and NaBH_3CN (8.5 mg, 0.135 mmol, 2.7 equiv.). Finally, 200 μL of anhydrous MeOH were added and the schlenk tube sealed with a screw cap. The reaction was stirred at 70°C for 16 hours, after which time the reaction was concentrated under reduced pressure. ^{19}F NMR yield of 34%. 1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-aminium acetate **42** was isolated as a white solid by column chromatography on silica gel (DCM/MeOH 95/5) in 31% yield (5.3 mg, 0.016 mmol). ^1H NMR (500 MHz, CDCl_3) δ 7.50 (d, $J = 8.4$ Hz, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 4.66 (s, 3H), 4.31 (dd, $J = 9.1, 4.2$ Hz, 1H), 4.05 (dd, $J = 9.7, 4.0$ Hz, 1H), 3.94 (t, $J = 9.1$ Hz, 1H), 2.09 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 175.8, 132.3, 132.1, 128.8, 122.4, 121.7 (q, $J = 255.3$ Hz, ROCF_3), 71.9, 54.1, 20.7 ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -61.24 ppm. HRMS (ESI+) Calcd. for $\text{C}_9\text{H}_7\text{OBrF}_3^+ [\text{M} + \text{H} - \text{NH}_3]^+$: 266.9627. Found: 266.9619.

4-(3-(dimethylamino)-2-(trifluoromethoxy)acryloyl)benzonitrile **43**

The procedure was adapted from the literature.^[13] A 4 mL vial was charged with 4-(2-(trifluoromethoxy)acetyl)benzonitrile **12** (20 mg, 0.09 mmol, 1 equiv.) and *N,N*-dimethylformamide dimethyl acetal (25 μL , 0.18 mmol, 2 equiv.). The vial was closed with a septum and stirred at 90°C for 3h. The resulting mixture was then diluted in CH_2Cl_2 (10 mL) and washed with water (10 mL), dried over MgSO_4 and concentrated under vacuum. The product was isolated by PTLC (Pentane/EtOAc 6/4) in 64% yield (16.5 mg, 0.06 mmol) as a yellow solid. ^1H NMR (300 MHz, CDCl_3) δ 7.69 (s, 4H), 7.11 (bs, 1H), 3.16 (s, 6H) ppm. ^{13}C NMR (75 MHz, CDCl_3) 186.5, 145.2 (bs, $\text{RC}=\text{C}-\text{N}(\text{CH}_3)_2$), 143.3, 132.1, 129.0, 122.1 (bs, $\text{RC}=\text{C}-\text{N}(\text{CH}_3)_2$), 121.2 (q, $J = 257.1$ Hz, ROCF_3), 118.5, 114.1 ppm. ^{19}F NMR (188 MHz, CDCl_3) δ -59.29 (s, 3F) ppm. HRMS (ASAP +) Calcd for $\text{C}_{13}\text{H}_{11}\text{F}_3\text{N}_2\text{NaO}_2^+ [2\text{M} + \text{Na}]^+$: 591.1438. Found: 591.1440.

One-pot procedure for the trifluoromethoxylation of acetophenone

A round-bottomed flask was charged with acetophenone (5 mmol, 1 equiv.) and dissolved in dry THF (5 mL, 1M) at 0°C under nitrogen atmosphere. NaH (60% dispersion in mineral oil, 400 mg, 10 mmol, 2 equiv.) was added portionwise to the reaction mixture, which was then stirred for 15 mins at 0°C . Boc_2O (1.38 mL, 6 mmol, 1.2 equiv.) was then added dropwise and the reaction mixture was stirred for 1h at room temperature. The resulting mixture was then quenched with water (20 mL), diluted with CH_2Cl_2 (50 mL) and washed with brine (3x20 mL). The organic phase was then dried over MgSO_4 and concentrated under vacuum. The resulting crude compound was diluted with 1 mL of CDCl_3 and trichloroethylene (450 μL , 5 mmol) was added as the internal standard to determine the yield by ^1H NMR. ^1H NMR yield: 43%. The crude was then evaporated and redissolved in 25 mL of DCM in a volumetric flask. 2.9 mL of the resulting solution (containing 0.25 mmol of enol carbonate according to the previously measured ^1H NMR yield) were placed in an 8 mL vial and the solvent evaporated. The

vial was then purged with argon and charged with 4-cyano-1-(trifluoromethoxy)pyridin-1-ium bis((trifluoromethyl)sulfonyl)amide **2a** (23.5 mg, 0.05 mmol, 1 equiv.) and 4CzIPN (1.9 mg, 0.0025 mmol, 0.05 equiv.) and subjected to the trifluoromethoxylation reaction according to General procedure E. The yield of product **45** was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 23%. The compound is reported in the literature.^[14]

F. Mechanistic studies

Alpha-trifluoromethoxylation of **1b** with Pyridinium **2b** and 4CzIPN as the photocatalyst

An 8-mL vial surrounded by blue LEDs with a watertight protection, equipped with a screwcap and a septum was purged with argon and charged with 4-methoxy-1-(trifluoromethoxy)pyridin-1-ium bis((trifluoromethyl)sulfonyl)amide **2b** (23.7 mg, 0.05 mmol, 1 equiv.), 1-(4-fluorophenyl)vinyl tert-butyl carbonate **1b** (0.25 mmol, 5 equiv.) and 4CzIPN (1.9 mg, 0.0025 mmol, 0.05 equiv.). Dry acetonitrile (5 mL, 0.01 M) was finally added and the reaction medium purged with argon again. The resulting mixture in the vial was placed in a water bath and allowed to stir vigorously for 1h at 50°C under irradiation of the blue LEDs. The yield of product **3** was determined by comparing the integration of the ^{19}F NMR resonance of the product with that of bis((trifluoromethyl)sulfonyl)amide. ^{19}F NMR yield of 12%.

Luminescence quenching experiments

Rates of quenching (k_q) were determined using Stern-Volmer kinetics:

$$I_0/I = k_q\tau_0[\text{quencher}] + 1$$

Where I_0 is the luminescence intensity without the quencher, I is the intensity with the quencher, and τ_0 is the excited state lifetime of the photocatalyst.

The following stock solutions were prepared in distilled acetonitrile and degassed by three freeze-pump-thaw cycles.

General procedure:

A stock solution of 4CzIPN was prepared by dissolving 4CzIPN (25 μmol) in 10 mL of acetonitrile. Of this solution, 0.1 mL were further diluted with acetonitrile to give a total volume of 10 mL. Concentration of [4CzIPN] = 2.5×10^{-5} M. A stock solution of 4-cyano-1-(trifluoromethoxy)pyridin-1-ium bis((trifluoromethyl)sulfonyl)amide **2a** was prepared by dissolving **2a** (30 μmol) in 10 mL of acetonitrile. Concentration of [**2a**] = 3×10^{-3} M. A stock solution of tert-butyl (1-(4-fluorophenyl)vinyl) carbonate **1b** was prepared by dissolving **1b** (30 μmol) in 10 mL of acetonitrile. Concentration of [**1b**] = 3×10^{-3} M. For each experiment, 6 samples were prepared in the dark. Quartz cuvettes (3.5 mL) were filled with photocatalyst stock solution (0.3 mL), reagent stock solution (0 mL, 0.2 mL, 0.4 mL, 0.6 mL, 0.8 mL, 1.0 mL) and acetonitrile (2.7 mL, 2.5 mL, 2.3 mL, 2.1 mL, 1.9 mL, 1.7 mL) to obtain a total volume of 3 mL. The final concentrations were [4CzIPN] = 2.5×10^{-6} M and [quencher] = 2×10^{-4} M, 4×10^{-4} M, 6×10^{-4} M, 8×10^{-4} M, 1×10^{-3} M. For each sample, emission spectra were acquired between 470 nm and 700 nm (excitation at 450 nm).

Figure S4 Stern-Volmer plots for pyridinium **2a** and enol carbonate **1b** as quenchers

$$k_2 = 5.7 \cdot 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \quad k_1 = 1.9 \cdot 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \quad (\tau_0 = 5.1 \text{ } \mu\text{s for 4CzIPN})^{[15]}$$

Quantum yield measurements

A ferrioxalate actinometry solution was prepared by following the Hammond variation of the Hatchard and Parker procedure outlined in Handbook of Photochemistry.^[16] Ferrioxalate actinometer solution measures the decomposition of ferric ions to ferrous ions, which are complexed by 1,10-phenanthroline and monitored by UV/Vis absorbance at 510 nm. The moles of iron-phenanthroline complex formed are related to moles of photons absorbed. The solutions were prepared and stored in the dark:

1. Potassium ferrioxalate solution: 589.5 mg of potassium ferrioxalate (commercially available from Sigma Aldrich) and 278 μL of sulfuric acid (96%) were added to a 100 mL volumetric flask and filled to the mark with water (MilliQ grade).
2. Phenanthroline solution: 0.2% by weight of 1,10-phenanthroline in water (200 mg in 100 mL volumetric flask).
3. Buffer solution: to a 100 mL volumetric flask 4.94 g of NaOAc and 1 mL of sulfuric acid (96%) were added and filled to the mark with water (MilliQ grade).

The actinometry measurements were done as follows:

1a. 456 nm LED: 1 mL of the actinometer solution was added to a quartz cuvette ($l = 10 \text{ mm}$). The actinometry solutions (placed 1 cm away from a 456 nm LED) were irradiated for specified time intervals (0, 15, 30, 45, 60) seconds.

1b. 400 nm LED: 1 mL of the actinometer solution was added to a quartz cuvette ($l = 10 \text{ mm}$). The actinometry solutions (placed 2 cm away from a 3W 400 nm LED) were irradiated for specified time intervals (0, 15, 20, 30, 40) seconds.

2. After irradiation all the actinometer solution was removed and placed in a 10 mL volumetric flask. 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution was added to this flask and filled to the mark with water (MilliQ grade).

3. The UV-Vis spectra of actinometry samples were recorded for each time interval (Figure S5 and Figure S6). The absorbance of the actinometry solution was monitored at 510 nm.

Figure S5 UV-Vis spectra of actinometry samples irradiated with 456 nm light for the indicated time intervals

Figure S6 UV-Vis spectra of actinometry samples irradiated with 400 nm light for the indicated time intervals

4. The moles of Fe^{2+} formed for each sample are determined using Beers' Law:

$$\text{Moles } \text{Fe}^{2+} = \frac{V_1 V_3 \Delta A_{(510 \text{ nm})}}{10^3 V_2 l \epsilon_{(510 \text{ nm})}}$$

where V_1 is the irradiated volume (1 mL), V_2 is the aliquot of the irradiated solution taken for the determination of the ferrous ions (1 mL), V_3 is the final volume after complexation with phenanthroline (10 mL), l is the optical path-length of the irradiation cell (1 cm), $\Delta A_{(510 \text{ nm})}$ the optical difference in absorbance between the irradiated solution and that taken in the dark, $\epsilon_{(510 \text{ nm})}$ is the molar extinction coefficient of the complex $\text{Fe}(\text{phen})_3^{2+}$ ($11100 \text{ L mol}^{-1} \text{ cm}^{-1}$).

5. The moles of Fe^{2+} formed (N) are plotted as a function of time (t) (Figure S7 and Figure S8). The slope is a product of the photon flux (F) and the quantum yield for Fe^{2+} ($\phi(\text{Fe}^{2+}) = 1.13$), since $F = N/\phi(\text{Fe}^{2+})t$.

456 nm: The $F_{456 \text{ nm}}$ was determined to be $2.20 \cdot 10^{-8} \text{ einstein s}^{-1}$.

400 nm: The $F_{400 \text{ nm}}$ was determined to be $3.52 \cdot 10^{-8} \text{ einstein s}^{-1}$.

Figure S7 Moles of Fe²⁺ formed after irradiation with 456 nm light as a function of time

Figure S8 Moles of Fe²⁺ formed after irradiation with 400 nm light as a function of time

Since the ferrioxalate actinometer absorbance at 456 nm is 0.12 and at 400 nm is 0.47 and inferior to 2 in both cases (if is major than 2 at the wavelength used, it can be assumed that the entire incident light is absorbed), a correction factor (C) based on the fraction of light absorbed by the actinometer has to be considered to calculate the photon flux and the final quantum yield of the reaction (note that this is also needed if the absorbance of the reaction under study at the optimized concentration is inferior to 2 at the wavelength used). Thus, according to the definition of quantum yield:^[17]

$$\Phi_{Fe^{2+}} = \frac{\left(\frac{\partial \text{moles } Fe^{2+}}{\partial \text{time}}\right)}{F C_{Fe^{2+}}} \rightarrow F = \frac{\left(\frac{\partial \text{moles } Fe^{2+}}{\partial \text{time}}\right)}{\Phi_{Fe^{2+}} C_{Fe^{2+}}} \quad C = 1 - 10^{-A(\lambda)}$$

The photon flux (F) previously found must be divided by the appropriate correction factor C.

456 nm: C = 0.24, calculated with $A_{456 \text{ nm}} = 0.12$. Corrected photon flux: $5.33 \cdot 10^{-9}$ einstein s⁻¹

400 nm: C = 0.66, calculated with $A_{400 \text{ nm}} = 0.47$. Corrected photon flux: $2.33 \cdot 10^{-8}$ einstein s⁻¹

6. 1 mL of the model reaction solutions were irradiated using the same systems and the moles of product formed for the reaction of interest are described below. The moles of product formed were determined by ^{19}F NMR measurements using the peak of triflimide as the internal standard. The number of moles of product per unit of time is related to the number of photons absorbed.

Alpha-trifluoromethoxylation of **1b** with Pyridinium **2a** and 4CzIPN as the photocatalyst

Figure S9 Moles of product formed after irradiation with 456 nm light as a function of the moles of emitted photons

The absorbance of the reaction at the irradiation wavelength (456 nm) is $A_{(456\text{ nm})} > 2$, hence no correction factor must be applied since it can be assumed that the entire incident light is absorbed. The quantum yield (ϕ) corresponding to the registered slope is 0.63 (Figure S9).

According to the IUPAC definition of the quantum yield,^[17] we also calculated it considering the overall consumption of **2a**:

Figure S10 Moles of pyridinium consumed after irradiation with 456 nm light as a function of the moles of emitted photons

The quantum yield (ϕ) corresponding to the registered slope is 1.47 (Figure S10).

Alpha-trifluoromethoxylation of **1b** with pyridinium **2a** in the absence of a photocatalyst

Figure S11 Moles of product formed after irradiation with 400 nm light as a function of the moles of emitted photons

The registered slope is 0.0016. The absorbance of the reaction at the irradiation wavelength (400 nm) is $A_{(400\text{ nm})} = 0.086$ (Figure S11). The registered slope must be divided by the correction factor $C = 1 - 10^{-A(400\text{ nm})} = 0.18$ to obtain the quantum yield $\phi = 0.0089$.

Alpha-trifluoromethoxylation of **1b** with pyridinium **2b** and 4CzIPN as the photocatalyst

After 30 minutes of irradiation, no product **3** could be detected by ^{19}F NMR. Hence, the quantum yield can be estimated to be $\phi < 0.01$.

Chain length calculation

The length L of the radical chain propagation can be calculated according to the following equation:^[18]

$$L = \frac{\Phi}{Q} \quad \text{with} \quad Q = \frac{k_q[\text{quencher}]}{\tau_0^{-1} + k_q[\text{quencher}] + \text{other processes}}$$

Where τ_0 is the lifetime of the photocatalyst and k_q is the quenching rate constant obtained from Stern-Volmer analysis and "other processes" include quenching of the photocatalyst through non-productive pathways. The quenching fraction Q expresses the ratio of the rate at which the excited photocatalyst is productively quenched by **2a** to the sum of the rates of all the relaxation processes available to the excited state. Based on our mechanistic hypothesis (see main text Figure 2), assuming that i) the

quenching of 4CzIPN by **2a** is the only productive pathway for the reaction, ii) the quenching of 4CzIPN by **1b** is not productive (falling under “other processes”), and iii) considering $\tau_0=5.1 \mu\text{s}$ for 4CzIPN:^[15]

$$L = \frac{\Phi}{Q} = \frac{0.63}{0.33} = 1.9 \quad \text{with} \quad Q = \frac{5.7 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1} \cdot 0.01 \text{ M}}{(5.1 \cdot 10^{-6})^{-1} + 5.7 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1} \cdot 0.01 \text{ M} + 1.9 \cdot 10^7 \text{ M}^{-1} \text{ s}^{-1} \cdot 0.05 \text{ M}} = 0.33$$

The calculated length of the radical chain propagation $L = 1.9$, suggests that about 2 cycles of radical propagation are carried out between **2a** and intermediate **5** termination.

G. Cyclic Voltammetries

Figure S12 Cyclic Voltammogram of 1a in a supporting electrolyte 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ in MeCN referenced to SCE at 0.1 Vs^{-1} sweep rate.

Figure S13 Cyclic Voltammogram of 1b in a supporting electrolyte 0.1 M $[\text{Bu}_4\text{N}][\text{PF}_6]$ in MeCN referenced to SCE at 0.1 Vs^{-1} sweep rate.

H. UV-Vis spectra

Figure S14 shows the UV-Vis spectra of 1a and 2a and the mixture of both components. The redshift of the absorbance in the orange trace with respect to the individual components suggests the formation of an EDA complex.

Figure S14 UV-Vis traces of enol acetate 1a, pyridinium 2a and the mixture of 1a and 2a. [1a]=0.1 M (black trace); [2a]=0.1 M (blue trace); [1a]=0.1 M and [2a]=0.1 M (orange trace).

Figure S15 shows the UV-Vis traces of 1a, 2a, mixture of 1a + 2a (5:1 equiv.) and the reaction mixture in the optimized reaction conditions ([2a]=0.01 M, 5 equiv. of enol derivative and 5 mol% of 4CzIPN).

Figure S15 UV-Vis traces of enol acetate 1a, pyridinium 2a, mixture of 1a and 2a and the mixture of 1a and 2a with 5 mol% of 4CzIPN. [1a]=0.05 M (black trace); [2a]=0.01 M (blue trace); [1a]=0.05 M and [2a]=0.01 M (orange trace); [1a]=0.05 M, [2a]=0.01 M and [4CzIPN]=0.0005 M (red trace).

Figure S16 shows the UV-Vis traces of 1b, 2a, mixture of 1b + 2a (5:1 equiv.) and the reaction mixture in the optimized reaction conditions ($[2a]=0.01$ M, 5 equiv. of enol derivative and 5 mol% of 4CzIPN).

Figure S16 UV-Vis traces of enol carbonate 1b, pyridinium 2a, mixture of 1b and 2a and the mixture of 1b and 2a with 5 mol% of 4CzIPN. $[1b]=0.05$ M (black trace); $[2a]=0.01$ M (blue trace); $[1b]=0.05$ M and $[2a]=0.01$ M (orange trace); $[1b]=0.05$ M, $[2a]=0.01$ M and $[4CzIPN]=0.0005$ M (red trace).

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J. NMR spectra

tert-butyl (1-(4-fluorophenyl)vinyl) carbonate 1b

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (126 MHz, CDCl_3)

^{19}F NMR (188 MHz, ^1H decoupled, CDCl_3)

tert-butyl (1-(o-tolyl)vinyl) carbonate 1d

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

tert-butyl (1-(m-tolyl)vinyl) carbonate **1e**

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

tert-butyl (1-(p-tolyl)vinyl) carbonate **1f**

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

tert-butyl 1-(3-methoxyphenyl)vinyl carbonate **1g**

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (126 MHz, CDCl_3)

tert-butyl 1-(4-methoxyphenyl)vinyl carbonate 1h

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (126 MHz, CDCl_3)

tert-butyl (1-(4-cyanophenyl)vinyl) carbonate 1i

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

tert-butyl (1-(3-(trifluoromethyl)phenyl)vinyl) carbonate 1j

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

1-(3,5-bis(trifluoromethyl)phenyl)vinyl tert-butyl carbonate 1k

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (101 MHz, CDCl₃)

^{19}F NMR (188 MHz, ^1H decoupled, CDCl_3)

1-(2-bromophenyl)vinyl tert-butyl carbonate **1l**

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (126 MHz, CDCl_3)

1-(3-bromophenyl)vinyl tert-butyl carbonate **1m**

^1H NMR (500 MHz, CDCl_3)

¹³C NMR (126 MHz, CDCl₃)

1-(4-bromophenyl)vinyl tert-butyl carbonate 1n

¹H NMR (500 MHz, CDCl₃)

^{13}C NMR (126 MHz, CDCl_3)

tert-butyl 1-(2,5-dichlorophenyl)vinyl carbonate 1o

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (101 MHz, CDCl_3)

1-(4-acetylphenyl)vinyl tert-butyl carbonate 1p

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (101 MHz, CDCl_3)

tert-butyl (1-phenylprop-1-en-1-yl) carbonate 1q

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (126 MHz, CDCl_3)

tert-butyl (1,3-diphenylprop-1-en-1-yl) carbonate 1r

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (126 MHz, CDCl_3)

tert-butyl 1H-inden-3-yl carbonate **1s**

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

tert-butyl (5-methoxy-1H-inden-3-yl) carbonate 1t

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

tert-butyl (6-fluoro-1H-inden-3-yl) carbonate 1u

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

tert-butyl 3,4-dihydronaphthalen-1-yl carbonate 1v

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (126 MHz, CDCl_3)

tert-butyl (6,7-dihydro-5H-benzo[7]annulen-9-yl) carbonate **1w**

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

1-(benzo[b]thiophen-2-yl)vinyl tert-butyl carbonate **1x**

¹H NMR (300 MHz, CDCl₃)

¹³C NMR (75 MHz, CDCl₃)

tert-butyl 1-(naphthalen-2-yl)vinyl carbonate **1y**

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (101 MHz, CDCl_3)

tert-butyl 2,2-difluoro-1-(naphthalen-2-yl)vinyl carbonate 1aa

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (126 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

tert-butyl oct-1-en-2-yl carbonate 1ab

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (101 MHz, CDCl_3)

(E)-tert-butyl (4-phenylbuta-1,3-dien-2-yl) carbonate 1ac

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

(E)-tert-butyl nona-1,3-dien-2-yl carbonate 1ad

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

tert-butyl 1-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl carbonate 1ae

^1H NMR (500 MHz, CDCl_3)

Chemical structure of **1ae** is shown in the top left corner. The ¹³C NMR spectrum (f1 (ppm)) is displayed below the structure, showing peaks corresponding to the carbon atoms in the molecule. The x-axis ranges from 210 to 10 ppm, and the y-axis represents intensity from 0 to 7000.

Peak list (ppm):

- 153.93
- 151.24
- 146.77
- 142.29
- 132.83
- 132.41
- 129.29
- 126.49
- 104.30
- 82.98
- 43.80
- 37.70
- 34.67
- 34.12
- 32.49
- 32.14
- 28.66
- 27.77
- 25.01
- 23.85
- 16.96

¹H NMR (300 MHz, CDCl₃)

¹³C NMR (75 MHz, CDCl₃)

tert-butyl (1-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)vinyl) carbonate **1ag**

¹H NMR (300 MHz, CDCl₃)

^{13}C NMR (75 MHz, CDCl_3)

(E)-tert-butyl (4-(2,6,6-trimethylcyclohex-2-en-1-yl)buta-1,3-dien-2-yl) carbonate 1ah

^1H NMR (300 MHz, CDCl_3)

¹³C NMR (75 MHz, CDCl₃)

tert-butyl (1-((3S,10R,13S,17S)-3-methoxy-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-17-yl)vinyl) carbonate **1ai**

¹H NMR (500 MHz, CDCl₃)

^{13}C NMR (126 MHz, CDCl_3)

tert-butyl ((10R,13S,17S)-17-methoxy-10,13-dimethyl-2,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl) carbonate 1aj

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

1-(4-fluorophenyl)-2-(trifluoromethoxy)ethanone 3

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

1-(*o*-tolyl)-2-(trifluoromethoxy)ethanone **7**

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

1-(*m*-tolyl)-2-(trifluoromethoxy)ethanone 8

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

1-(*p*-tolyl)-2-(trifluoromethoxy)ethanone **9**

¹H NMR (300 MHz, CDCl₃)

¹³C NMR (75 MHz, CDCl₃)

^{19}F NMR (188 MHz, CDCl_3)

4-(2-(trifluoromethoxy)acetyl)benzonitrile 12

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

2-(trifluoromethoxy)-1-(3-(trifluoromethyl)phenyl)ethanone **13**

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

1-(2-bromophenyl)-2-(trifluoromethoxy)ethan-1-one 15

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (126 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

1-(3-bromophenyl)-2-(trifluoromethoxy)ethan-1-one 16

¹H NMR (500 MHz, CDCl₃)

¹³C NMR (126 MHz, CDCl₃)

^{19}F NMR (188 MHz, CDCl_3)

1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-one **17**

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (126 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

1-phenyl-2-(trifluoromethoxy)propan-1-one 20

¹H NMR (500 MHz, CDCl₃)

¹³C NMR (126 MHz, CDCl₃)

^{19}F NMR (188 MHz, CDCl_3)

1,3-diphenyl-2-(trifluoromethoxy)propan-1-one 21

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (126 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

2-(trifluoromethoxy)-2,3-dihydro-1H-inden-1-one 22

¹H NMR (300 MHz, CDCl₃)

¹³C NMR (75 MHz, CDCl₃)

^{19}F NMR (188 MHz, CDCl_3)

6-methoxy-2-(trifluoromethoxy)-2,3-dihydro-1H-inden-1-one 23

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

5-fluoro-2-(trifluoromethoxy)-2,3-dihydro-1H-inden-1-one 24

¹H NMR (300 MHz, CDCl₃)

¹³C NMR (75 MHz, CDCl₃)

^{19}F NMR (188 MHz, CDCl_3)

6-(trifluoromethoxy)-6,7,8,9-tetrahydro-5H-benzo[7]annulen-5-one 26

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

1-(benzo[b]thiophen-2-yl)-2-(trifluoromethoxy)ethanone 27

¹H NMR (300 MHz, CDCl₃)

¹³C NMR (75 MHz, CDCl₃)

¹⁹F NMR (188 MHz, CDCl₃)

(E)-4-phenyl-1-(trifluoromethoxy)but-3-en-2-one 32

¹H NMR (300 MHz, CDCl₃)

^{13}C NMR (75 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

(E)-1-(trifluoromethoxy)non-3-en-2-one 33

¹⁹F NMR (188 MHz, CDCl₃)

1-(3,5,5,6,8,8-hexamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)-2-(trifluoromethoxy)ethan-1-one 34

¹H NMR (500 MHz, CDCl₃)

^{13}C NMR (126 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

1-(4-(tert-butyl)-2,6-dimethyl-3,5-dinitrophenyl)-2-(trifluoromethoxy)ethanone 35

¹H NMR (300 MHz, CDCl₃)

¹³C NMR (75 MHz, CDCl₃)

^{19}F NMR (188 MHz, CDCl_3)

1-(6-(tert-butyl)-1,1-dimethyl-2,3-dihydro-1H-inden-4-yl)-2-(trifluoromethoxy)ethanone 36

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

(E)-1-(trifluoromethoxy)-4-(2,6,6-trimethylcyclohex-2-en-1-yl)but-3-en-2-one 37

¹H NMR (200 MHz, CDCl₃)

¹³C NMR (151 MHz, CDCl₃)

^{19}F NMR (188 MHz, CDCl_3)

(8R,9S,10R,13S,14S,17S)-17-methoxy-10,13-dimethyl-6-(trifluoromethoxy)-6,7,8,9,10,11,12,13,14,15,16,17-dodecahydro-1H-cyclopenta[a]phenanthren-3(2H)-one 39

^1H NMR (600 MHz, CDCl_3)

^{13}C NMR (151 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

COSY (600 MHz, CDCl₃)

HSQC (600 MHz, CDCl₃)

1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-ol 40

¹H NMR (500 MHz, CDCl₃)

¹³C NMR (126 MHz, CDCl₃)

Chemical structure of 1-(4-bromophenyl)ethan-1-ol trifluoromethanesulfonate (40) is shown. The structure consists of a benzene ring with a bromine atom (Br) at the para position and a trifluoromethanesulfonate group (OTf) at the other para position. The trifluoromethanesulfonate group is represented as OCF₃ in blue.

The ¹H NMR spectrum (400 MHz, CDCl₃) shows two main signals: a multiplet at 7.2 ppm (labeled 40) and a multiplet at 7.8 ppm (labeled 40). The x-axis is labeled f1 (ppm) and ranges from 0 to 210. The y-axis ranges from -400 to 2200.

¹H NMR (500 MHz, CDCl₃)

^{13}C NMR (126 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

1-(4-bromophenyl)-2-(trifluoromethoxy)ethan-1-aminium acetate **42**

^1H NMR (500 MHz, CDCl_3)

^{13}C NMR (126 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)

4-(3-(dimethylamino)-2-(trifluoromethoxy)acryloyl)benzonitrile 43

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^{19}F NMR (188 MHz, CDCl_3)