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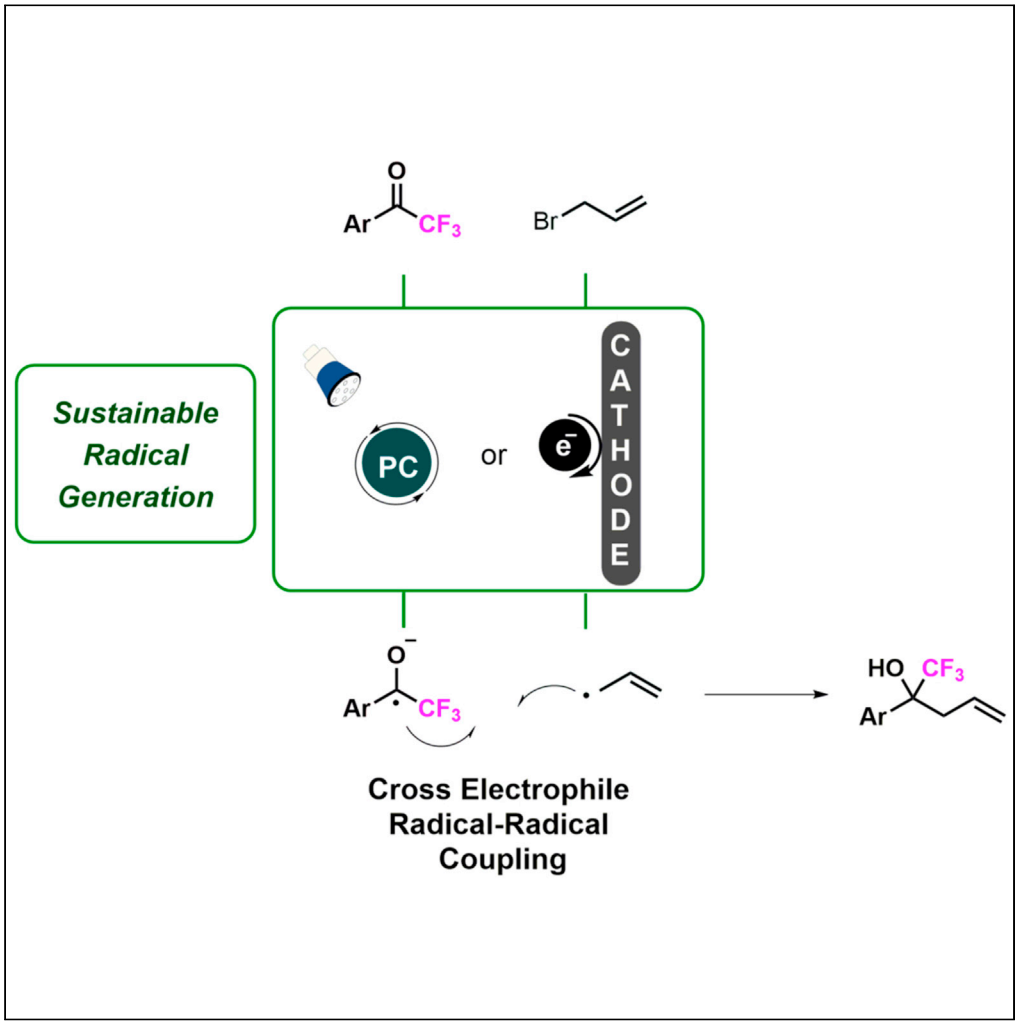
Sustainable radical approaches for cross electrophile coupling to synthesize trifluoromethyl- and allyl-substituted *tert*-alcohols



Muhammad Awais Ashraf, Yunjeong Lee, Naila Iqbal, Naeem Iqbal, Eun Jin Cho

naeem_384@yahoo.com (N.I.)
ejcho@cau.ac.kr (E.J.C.)

Highlights

Sustainable radical approaches; photoredox catalysis and electrochemistry

Cross-electrophile coupling through ketyl and allyl radical intermediates

Allylation of trifluoromethylated ketones and imines

Medicinally important trifluoromethyl- and allyl-substituted tert-alcohols

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Sustainable radical approaches for cross electrophile coupling to synthesize trifluoromethyl- and allyl-substituted *tert*-alcohols

Muhammad Awais Ashraf,[1] Yunjeong Lee,[1] Naila Iqbal,[1] Naeem Iqbal,[1,*] and Eun Jin Cho[1,2,*]

SUMMARY

Trifluoromethylated molecules have gained privileged recognition among the medicinal and pharmaceutical chemists. Sustainable photoredox- and electrochemical processes were employed to facilitate the relatively less explored radical cross-electrophile coupling to access trifluoromethyl- and allyl-substituted *tert*-alcohols. Reactions proceed through trifluoromethyl ketyl radical and allyl radical intermediates, which undergo challenging radical-radical cross-coupling. The developed transformations are mild and chemo-selective to give cross-coupled products and deliver a wide range of valuable trifluoromethyl- and allyl-containing tertiary alcohols. Both processes can also be applied for the synthesis of amine variant containing trifluoromethyl and allyl moiety, which is considered as amide bioisostere.

INTRODUCTION

The tertiary alcohol motif is a valuable unit that features in various natural products and bioactive compounds (Hjerrild et al., 2020; Lücke and Kalesse, 2019; Riant and Hannedouche, 2007; Shibasaki and Kanai, 2008; Vu et al., 2019). Considering the enormous synthetic potential of the alkene synthon, the synthesis of homoallylic tertiary alcohols has attracted considerable research interest (Brauns et al., 2017; Chen et al., 2021; Feng et al., 2019; Lee et al., 2016). Fluorinated organic compounds have found wide-ranging applications in various fields of science and technology, in part due to the dramatic variations in the characteristics of a compound upon introduction of a C–F bond (Menaa et al., 2013; Müller et al., 2007; Ni and Hu, 2016; Tsui and Hu, 2019; Zeng and Hu, 2015). Among fluoroalkyl groups, the trifluoromethyl (CF_3) moiety is considered as one of the privileged functional groups by medicinal chemists for modulating the pharmacokinetic and pharmacodynamic properties of a drug molecule, such as metabolic stability, lipophilicity, bioavailability, binding selectivity, and cell-membrane permeability (Chatterjee et al., 2016; Koike and Akita, 2014; Qing and Zheng, 2011; Shao et al., 2015; Smart, 2001; Xu et al., 2015; Zafrani et al., 2017). Therefore, the preparation of trifluoromethyl- and allyl-substituted *tert*-alcohols holds enormous importance, not only because of their established roles as functional components but also for their ability to serve as important building blocks for the synthesis of complex structures. Barbier-type allylation has been the traditional approach to the synthesis of trifluoromethyl- and allyl-substituted *tert*-alcohols (Guo et al., 2017; Nie et al., 2011; Tordeux et al., 1990). The Barbier process involves the introduction of metal complexes, such as indium (Araki et al., 1988; Loh et al., 1999; Roy and Roy, 2010; Shen et al., 2013), zinc (Grellepois et al., 2017; Metzger et al., 2010; Yin et al., 2020), ruthenium (Cicco et al., 2017; Wang et al., 2017, 2021), titanium (Li et al., 2020), or mercury (Cao et al., 2016; Gong et al., 2019), into the carbon-halide/carbon-silyl bond for generating the reactive nucleophilic allylmetal intermediates, which react with the trifluoromethyl ketone to furnish the trifluoromethyl- and allyl-substituted *tert*-alcohol (Figure 1a). Despite these advantages, the Barbier reaction requires stoichiometric amounts of metals, and catalytic approaches are limited to the use of allylboron/allylsilane reagents that are difficult to prepare. Alternative catalytic method for the synthesis of trifluoromethyl- and allyl-substituted *tert*-alcohols with inexpensive and easily available allyl halides will be complementary and useful approaches in the arsenal of the synthetic chemist.

Cross-electrophile coupling through radical intermediates has been less explored (Everson and Weix, 2014; Kerackian et al., 2020; Yi et al., 2017) because (1) the conditions must be suitable for the generation of two different radical intermediates from two different substrates and (2) their cross-coupling should be more favorable over the homocoupling process. A visible-light-photocatalyzed umpolung coupling or polarity inversion strategy has been adopted to generate ketyl radicals, which have been extensively explored to develop several addition reactions (Nakajima et al., 2015; Qi and Chen, 2016). Recently, the König group went one step ahead to present an

[1]Department of Chemistry, Chung-Ang University, 84 Heukseok-ro, Dongjak-gu, Seoul 06974, Republic of Korea

[2]Lead contact

*Correspondence: naeem_384@yahoo.com (N.I.), ejcho@cau.ac.kr (E.J.C.)

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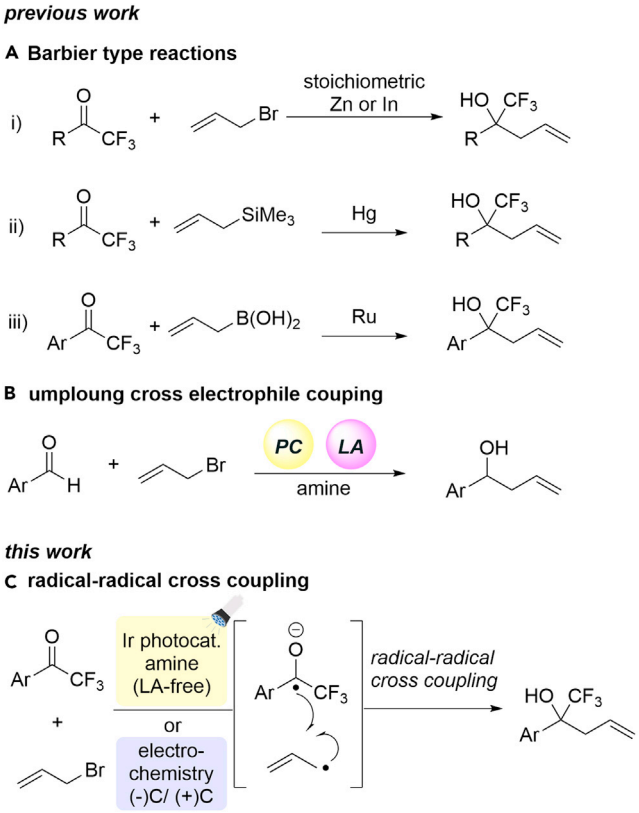


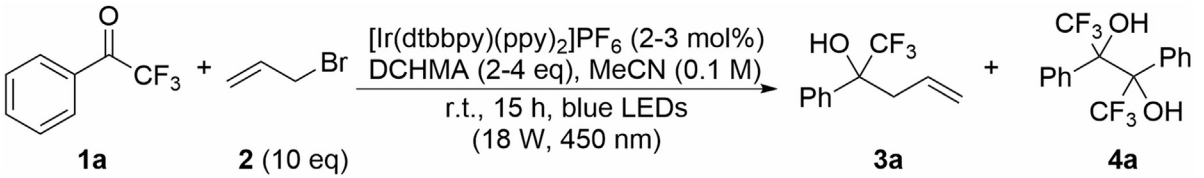
Figure 1. Synthesis of trifluoromethyl- and allyl-substituted *tert*-alcohols.

outstanding example of cross-electrophile coupling through the generation of two different radical intermediates for the allylation of the carbonyl system where a Lewis acid was used as an activating reagent (Berger et al., 2018). We envisioned that the presence of an electron-withdrawing CF_3 group could increase the reducing power of the carbonyl system, and thereby, the reactivity of the trifluoromethyl ketones might be higher even in the absence of a Lewis acid activator (Figure 1b). In this study, we developed a photocatalytic practical method for generating trifluoromethyl- and allyl-substituted *tert*-alcohols from trifluoromethyl ketones and allyl halides by selective radical-radical cross-coupling in the absence of activators (Figure 1c). In addition, the transformation also successfully proceeds electrochemically despite different mechanism for the radical generations, validating it as a radical-radical cross-coupling reaction (Bohn et al., 2012; Lennox et al., 2018; Monroe and Heien, 2013; Núñez-Vergara et al., 1997; Xiong and Xu, 2019).

RESULT AND DISCUSSION

We started our investigation using trifluoroacetophenone **1a** as the model substrate with allyl halides (iodide, bromide, and chloride) in the presence of $[Ir(dtbbpy)(ppy)_2]PF_6$ photocatalyst and *N*,*N*-dicyclohexylmethylamine (DCHMA) at 0.1 M concentration in MeCN under visible-light irradiation using 18 W blue LEDs (Table 1, entries 1–3). Gratifyingly, the reaction with allyl bromide proceeded to give cross-coupled trifluoromethyl- and allyl-substituted *tert*-alcohol **3a** in 81% yield, along with the homocoupled byproduct **4a** (entry 1). Allyl iodide and chloride did not participate in the cross-coupling process (entries 2 and 3). Control experiments showed that the reaction requires the photocatalyst, the amine as an electron-donor, and visible-light irradiation (entries 4–6). The choice of the photocatalyst and amine was critical for achieving selective cross-coupling. The use of other photocatalysts or bases instead of the $[Ir(dtbbpy)(ppy)_2]PF_6$/DCHMA catalytic system showed detrimental effects, resulting in lower yields (entries 7–12). MeCN was also the best choice as solvent because no improvement of reactivity was observed in other tested solvents (entries 13–17). The amount of allyl bromide (**2**) could be lowered to 7 equivalents without any observable decrease in overall yield (entries 18–20). However, the yield decreased under aerobic conditions, indicating that the reaction requires inert conditions (entry 21).

Table 1. Optimization of reaction conditions[a]



Entry	Variation from standard conditions	3a yield %[b]	4a yield %[b]
1	–	81	5
2	Allyl iodide instead of **2**	0	0
3	Allyl chloride instead of **2**	0	0
4	No $[Ir(dtbbpy)(ppy)_2]PF_6$	0	0
5	No DCHMA	15	17
6	No Light	0	0
7	*fac*-$Ir(ppy)_3$ instead of $[Ir(dtbbpy)(ppy)_2]PF_6$	58	0
8	$[Ru(bpy)_3Cl_2]PF_6$ instead of $[Ir(dtbbpy)(ppy)_2]PF_6$	65	0
9	$Ru(phen)_3Cl_2$ instead of $[Ir(dtbbpy)(ppy)_2]PF_6$	67	0
10	DIPEA instead of DCHMA	48	4
11	TMEDA instead of DCHMA	9	21
12	K_2CO_3 instead of DCHMA	1	0
13	DCM instead of MeCN	21	7
14	DMF instead of MeCN	6	18
15	THF instead of MeCN	66	16
16	dioxane instead of MeCN	29	6
17	DMSO instead of MeCN	12	0
18	**2** (7 eq)	81	3
19	**2** (5 eq)	60	20
20	**2** (12 eq)	81	3
21	Open air	20	35

[a]Reactions were carried out using 0.1 mmol of **1a** under an inert atmosphere.
[b]Yields were determined by ^{19}F-NMR using 4-fluorotoluene as an internal standard.

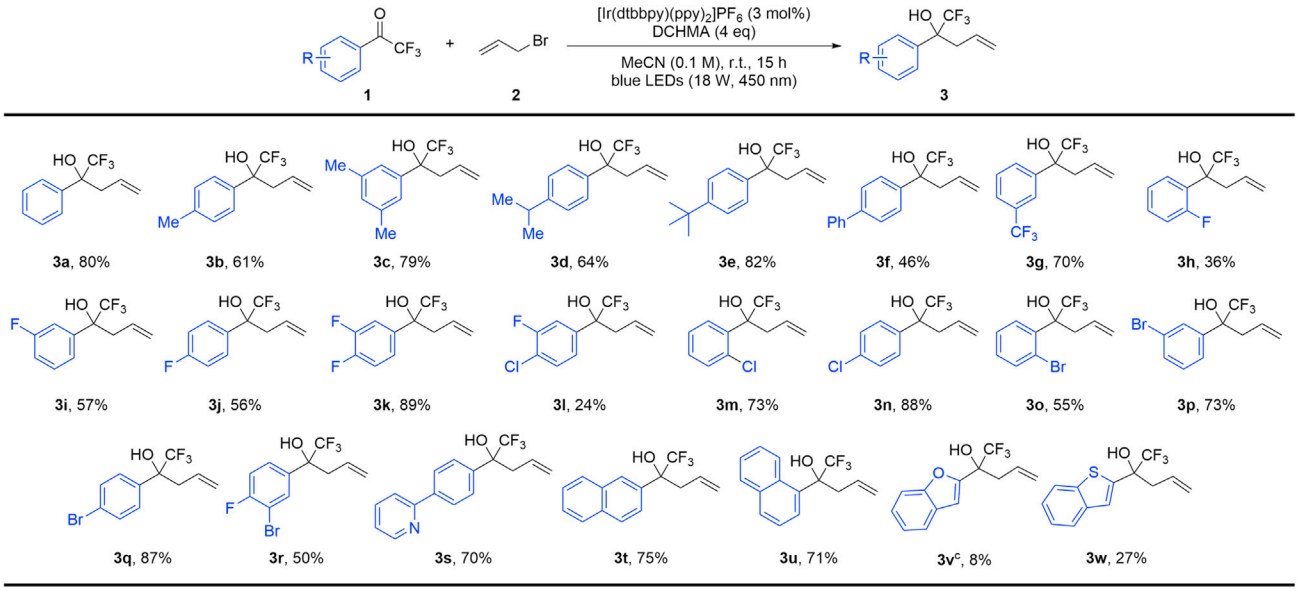


Figure 2. Substrate scope for trifluoromethyl- and allyl-substituted *tert*-alcohol synthesis

Reactions were carried out using 0.5 mmol of **1** and 7 eq of **2** under inert conditions. Isolated yields are reported. [c]The yield was determined by ^{19}F NMR spectroscopy using (trifluoromethyl)benzene as the internal standard.

With the optimized conditions in hand, we turned our attention to exploring the substrate scope of this methodology with several trifluoromethyl acetophenone derivatives (Figure 2). The substituent position on the aryl ring or its electron-density did not significantly affect the reactivity. Substrates with both electron-donating (**3b**-**3e**) and electron-withdrawing (**3g**-**3r**) substituents efficiently afforded the radical-radical cross-coupling products. Reactions of ortho- (**3h**, **3m**, and **3o**), meta- (**3c**, **3g**, **3i**, **3k**, **3l**, **3p**, and **3r**), and para (**3b**, **3d**, **3e**, **3f**, **3j**, **3k**, **3l**, **3n**, **3q**, **3r**, and **3s**)-substituted substrates proceeded well regardless of the position of the substituent. The presence of an additional CF_3 group (**3 g**) or fluorines (**3h**, **3i**, **3j**, **3k**, **3l**, and **3r**) in the product may improve the bioactivity of the compounds. The heteroaryl pyridine substituent (**3s**) on the aryl ring was tolerated in this transformation. The reactions of naphthyl (**3t**, **3u**) substrates also afforded the corresponding homoallylic alcohols in good yields. Reactions of heteroaryl substrates such as benzofuran (**3v**) and benzothiophene (**3w**) showed low reactivities under the conditions. Unfortunately, substituted allyl bromides did not undergo the transformation well under the conditions.

Recently, electrochemistry has emerged as a sustainable approach for efficient generation of radical intermediates by utilizing eco-friendly electric energy (Bohn et al., 2012; Lennox et al., 2018; Monroe and Heien, 2013; Núñez-Vergara et al., 1997; Xiong and Xu, 2019), without the use of stoichiometric amounts of external oxidizing and reducing agents (Bohn et al., 2012; Xiong and Xu, 2019). We developed a sustainable electrochemical approach for the generation of ketyl and allyl radical to synthesize trifluoromethyl- and allyl-substituted *tert*-alcohols (Figure 3). A series of optimizations showed that the reactions of **1** and **2** proceeded best under constant-current electrolysis (6 mA) in an undivided cell using tetra-*n*-butylammonium salt ($TBAPF_6$) as the electrolyte, CH_3CN as the solvent, and graphite ((−)C/(+)C) as the working and counter electrodes, at room temperature (23°C). In general, substrates with electron-withdrawing (**3l**-**3r**) substituents showed better reactivity than those with electron-donating (**3c**-**3e**) ones. Further, ortho-substituted substrates (**3m**, **3o**) were less efficient than meta- (**3c**, **3l**, **3p**, and **3r**) or para- (**3d**, **3e**, **3f**, **3l**, **3n**, **3q**, **3r**, and **3s**) substituted substrates for the transformation. The reactions of the pyridyl derivative (**3s**) and naphthyl (**3t**, **3u**) substrates also proceeded well to afford the corresponding homoallylic alcohols in good yields.

Based on the above observations and literature precedent (Bohn et al., 2012; Liu et al., 2018; Péter et al., 2021; Sharma et al., 2016; Tang et al., 2020; Zeng et al., 2019), plausible mechanisms for the photoredox (a) and electrochemical (b) reaction between **1a** and **2** are proposed in Figure 4. Upon visible-light irradiation, the excited photocatalyst $[Ir^{(III)}]^*$ ($E(Ir^{(IV)}/Ir^{(III)*}) = -0.96$ V, $E(Ir^{(III)*}/Ir^{(II)}) = +0.66$ V) (Prier et al., 2013) is formed and is reductively quenched by single-electron transfer from DCHMA ($E_{1/2} = +0.67$) (Figure S2), producing the $[Ir^{(II)}]$ complex and radical cation **A**. Compound **1a** ($E_{1/2} = -1.49$ V)* (Figure S1) is then reduced by the

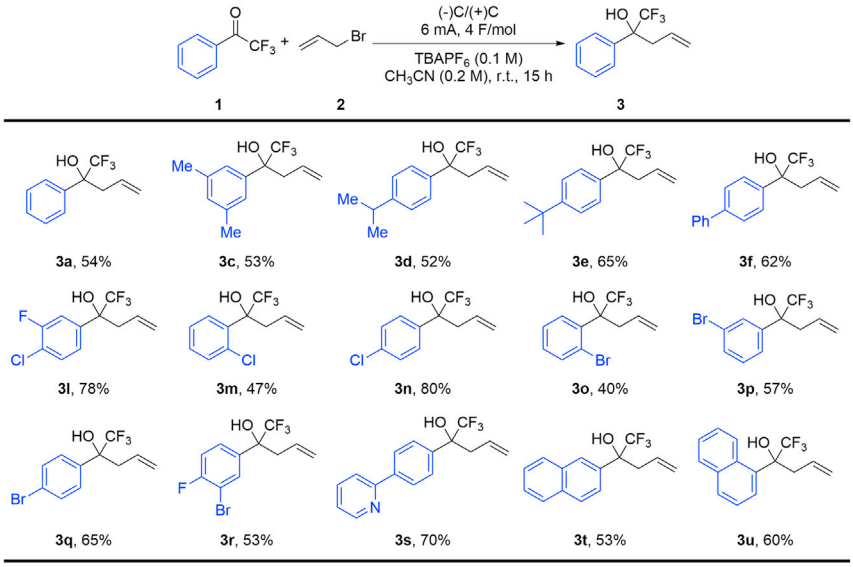


Figure 3. Substrate scope for electrochemical synthesis of trifluoromethyl- and allyl-substituted *tert*-alcohols

Reactions were carried out using 0.6 mmol of **1** and 5 equiv of **2** under inert conditions. The yields were determined by ^{19}F NMR spectroscopy with 4-fluorotoluene as an internal standard.

highly reducing [$Ir^{(II)}$] (E ($Ir^{(III)}/Ir^{(II)}$) = −1.51 V) (Prier et al., 2013) species to provide the ketyl radical intermediate **B** without any need for a Lewis acid. Considering its reduction potential (E_{red} = −2.18 V) (Figure S3), the allyl bromide (**2**) cannot be reduced by the [$Ir^{(II)}$] ($E_{1/2}$ = −1.51 V) species. However, efficient formation of an electron donor-acceptor complex between **2** and DCHMA provides the allyl radical intermediate (**C**) under visible light irradiation (Berger et al., 2018). Then, radical-radical cross-coupling occurs between the more persistent ketyl radical **B** and the transient allyl radical **C** to give **3a** after protonation. In electrochemical conditions, both reactants **1a** and **2** undergo one electron reduction on the graphite cathode to give the ketyl radical intermediate **B** and allyl radical intermediate **C**, respectively. Then radical-radical cross-coupling between persistent ketyl radical **B** and transient allyl radical **C** affords **3a** as the final product. Simultaneously, on the graphite anode, molecular bromine is produced by oxidation of bromide ions (Tang et al., 2020).

Having assessed the use of trifluoromethyl ketones as substrates, we focused on the evaluation of trifluoromethyl imines. Notably, both photoredox and electrochemical synthetic methods could be expanded to

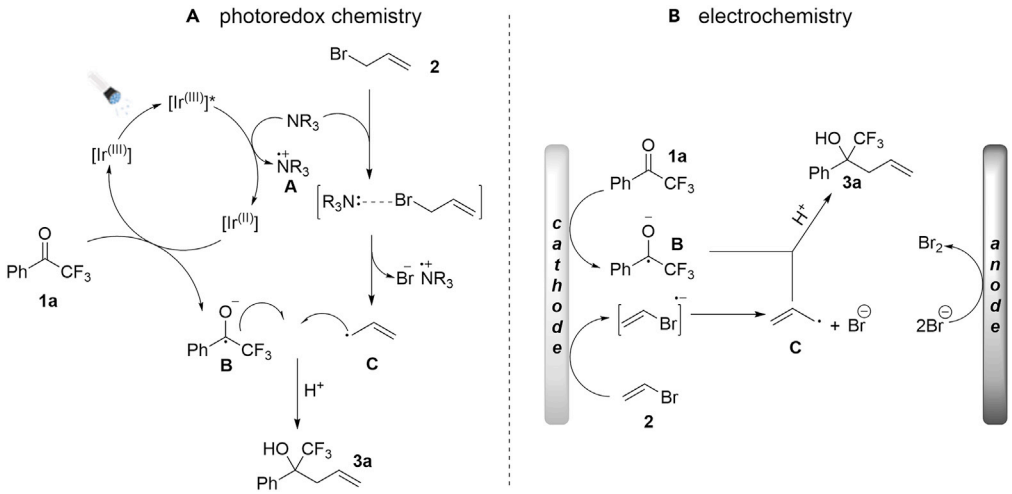
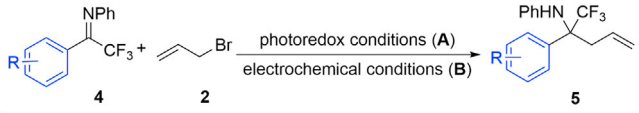


Figure 4. Proposed mechanism for the photo- and electrochemical cross-electrophile coupling.



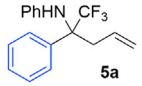
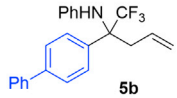
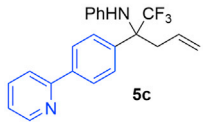
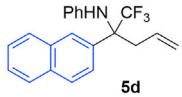
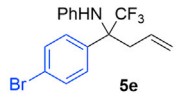
entry	product	yield under A[b]	yield under B[c]
1	 5a	30%	57%
2	 5b	31%	30%
3	 5c	10%	49%
4	 5d	32%	18%
5	 5e	52%	20%

Figure 5. Substrate scope for α-trifluoromethyl- and homoallyl-substituted amine synthesis

Reaction Conditions; (A) **4** (0.5 mmol), **2** (7 eq), $[Ir(dtbbpy)(ppy)_2]PF_6$ (3 mol%), DCHMA (4 eq), MeCN (0.1 M), r.t., 15 h, blue LEDs. (B) **4** (0.6 mmol), **2** (5 eq), $TBAPF_6$ (0.1 M), CH_3CN (0.2 M), graphite electrodes, 6 mA, 4 F/mol, r.t., 15 h. [b]Isolated yields are reported. [c]The yields were determined by ^{19}F NMR spectroscopy with 4-fluorotoluene as an internal standard.

the synthesis of α-trifluoromethyl- and homoallyl-substituted amine (Figure 5) (Enders et al., 2010; Levin et al., 2008; Rodríguez et al., 2014; Winter et al., 2019). (*Z*)-2,2,2-trifluoro-*N*,1-diphenylethan-1-imine and its derivatives (**4**) reacted with allyl bromide successfully to give the corresponding α-trifluoromethyl- and homoallyl-substituted amines **5**, indicating the generality of the developed protocols. Interestingly, the two different radical transformations showed different reactivities dependent on substrates. Substrates **4a** and **4c** (pyridyl substituent) showed better reactivities under electrochemical conditions, whereas reactions of **4d** (naphthyl) and **4e** (bromo) afforded the corresponding amines **5d** and **5e** in higher yields under photoredox conditions. It is noteworthy to mention that α-trifluoromethyl amines are considered as bioisostere of amides (Kumari et al., 2020; Qiu and Qing, 2011).

Conclusion

In conclusion, we developed highly sustainable and facile radical-radical cross-coupling processes for the synthesis of trifluoromethyl- and allyl-substituted *tert*-alcohol derivatives. Photoredox and electrochemical transformations of trifluoromethyl acetophenone derivatives and allyl bromide proceeded well through the formation of the ketyl radical and allyl radical intermediates. The developed transformations are mild, chemoselective, and provide a wide range of valuable trifluoromethyl- and allyl-substituted *tert*-alcohols by cross-coupling. In addition, the developed sustainable radical approaches could be expanded to the allylation of trifluoromethyl imines.

Limitations of the study

Despite advantages of developed methods, the substrate scope was mainly limited to allyl bromide, as substituted allyl bromides did not work under both photoredox and electrochemical conditions. Nonfluorinated ketones and aldehydes were not suitable substrates for the transformations. Reactions of heteroaryl

containing trifluoromethylated ketone substrates did not proceed well, resulting in low yields of the corresponding allylated products.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

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  - General electrochemical procedure for the preparation of the trifluoromethyl- and allyl-substituted *tert*-alcohol
  - Cyclic voltammetry measurements
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SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.isci.2021.103388.

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AUTHOR CONTRIBUTIONS

M. A. A., N. I., and E. J. C. envisioned and designed the project. M. A. A., Y. L., and N. I. conducted the methodology development, synthesis, and characterization of compounds. N. I. and E. J. C. supervised the project. All authors contributed to the discussion of experimental results. The manuscript was written by all contributing authors.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
$[Ir(dtbbpy)(ppy)_2]PF_6$	Sigma-Aldrich	CAS: 676525-77-2
N,N-Dicyclohexylmethylamine	TCI	CAS: 7560-83-0
Allyl bromide	Sigma-Aldrich	CAS: 106-95-6
2,2,2-trifluoro-1-phenylethan-1-one, **1a**	TCI	CAS: 434-45-7
1-(3,5-dimethylphenyl)-2,2,2-trifluoroethan-1-one, **1c**	Oakwood chemical	CAS: 132719-10-9
2,2,2-trifluoro-1-(4-isopropylphenyl)ethan-1-one, **1d**	Ambeed	CAS: 124211-72-9
1-(4-(tert-butyl)phenyl)-2,2,2-trifluoroethan-1-one, **1e**	Ambeed	CAS: 73471-97-3
1-([1,1′-biphenyl]-4-yl)-2,2,2-trifluoroethan-1-one, **1f**	Ambeed	CAS: 2369-31-5
2,2,2-trifluoro-1-(3-(trifluoromethyl)phenyl)ethan-1-one, **1g**	Sigma-Aldrich	CAS: 721-37-9
2,2,2-trifluoro-1-(4-fluorophenyl)ethan-1-one, **1j**	Sigma-Aldrich	CAS: 655-32-3
1-(2-chlorophenyl)-2,2,2-trifluoroethan-1-one, **1m**	Lookchem	CAS: 5860-95-7
1-(4-chlorophenyl)-2,2,2-trifluoroethan-1-one, **1n**	Sigma-Aldrich	CAS: 321-37-9
1-(2-bromophenyl)-2,2,2-trifluoroethan-1-one, **1o**	Sigma-Aldrich	CAS: 244229-34-3
1-(3-bromophenyl)-2,2,2-trifluoroethan-1-one, **1p**	Sigma-Aldrich	CAS: 655-26-5
1-(4-bromophenyl)-2,2,2-trifluoroethan-1-one, **1q**	Sigma-Aldrich	CAS: 16184-89-7
1-(3-bromo-4-fluorophenyl)-2,2,2-trifluoroethan-1-one, **1r**	Emer et al. (2014)	CAS: 150698-74-1
2,2,2-trifluoro-1-(naphthalen-2-yl)ethan-1-one, **1t**	Ambeed	CAS: 1800-42-6
2,2,2-trifluoro-1-(naphthalen-1-yl)ethan-1-one, **1u**	Ambeed	CAS: 6500-37-4
1-(benzo[*b*]thiophen-2-yl)-2,2,2-trifluoroethan-1-one, **1w**	Benassi et al. (1984)	CAS: 75277-97-3
(*Z*)-2,2,2-trifluoro-*N*,1-diphenylethan-1-imine, **4a**	Wu et al., (2015)	CAS: 37772-00-2
(*E*)-2,2,2-trifluoro-*N*-phenyl-1-(4-(pyridin-2-yl)phenyl)ethan-1-imine, **4c**	this paper	N/A
(*Z*)-2,2,2-trifluoro-1-(naphthalen-2-yl)-*N*-phenylethan-1-imine, **4d**	Zhang et al. (2020)	CAS: 2565945-63-1
(*Z*)-1-(4-bromophenyl)-2,2,2-trifluoro-*N*-phenylethan-1-imine, **4e**	Zhang et al. (2020)	CAS: 2649235-28-7

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources and reagents should be directed to and will be fulfilled by the lead contact, Eun Jin Cho (ejcho@cau.ac.kr).

Material availability

All data supporting the newly synthesized compounds can be found within the manuscript and the supplemental information or can be received from the lead contact upon request.

Data and code availability

Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

METHOD DETAILS

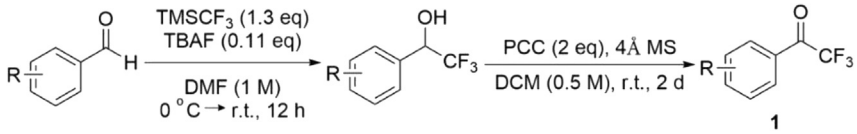
General reagent information

$[Ir(dtbbpy)(ppy)_2]PF_6$ and commercially available reagents were purchased from Sigma-Aldrich, Alfa Aesar, TCI, or Acros chemical companies. Flash column chromatography was performed using Zeochem silica gel 60 (60–200 mesh).

General analytical information

The synthesized trifluoromethyl ketones **1a**-**1u** and trifluoromethyl- and allyl-substituted *tert*-alcohols **3a**-**3u** were characterized using ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and FT-IR spectroscopies. NMR spectra were recorded on a Varian 600 MHz instrument (600 MHz for ^{1}H NMR, 151 MHz for ^{13}C NMR, and 564 MHz for ^{19}F NMR). Copies of ^{1}H, ^{13}C, and ^{19}F NMR spectra are included. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to residual chloroform (7.26 ppm) in the deuterated solvent. ^{13}C NMR spectra are reported in ppm relative to deuterated chloroform (77.23 ppm). ^{19}F NMR spectra are reported in ppm and all were obtained in composite pulse decoupling (CPD) mode. Coupling constants were reported in Hz. FT-IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer (ThermoFisher). Melting points for solid compounds were recorded on a Stuart SMP30 apparatus. The reactions were monitored by thin layer chromatography and GC-MS spectroscopy (Agilent GC 7890B/5977A inert MSD with Triple-Axis Detector) analysis of the crude reaction mixture.

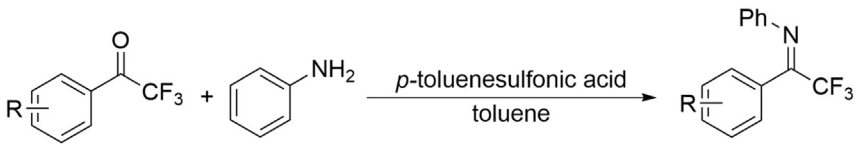
General procedure for the synthesis of trifluoromethyl ketone substrates 1a-1u



Step 1: To a solution of aldehyde (10 mmol) in DMF (1 M, 10 mL) in a 50 mL round-bottom flask equipped with a stirring bar, under argon atmosphere, $TMSCF_3$ (13 mmol) was added, and the mixture was stirred in an ice bath. After approximately 15 min, TBAF (1 M in THF, 0.1 mmol, 0.1 mL, 0.01 eq) was added dropwise. After 10 min, the ice bath was removed, and the solution was stirred for approximately 6 h at room temperature. After consumption of the aldehyde, the reaction mixture was cooled down to 0°C in an ice bath, and additional TBAF (1 M in THF, 1 mL, 1 mmol, 0.1 eq), and water (10 mL) were added to cleave the silyl ether intermediate. After 10 min, the ice bath was removed, and the reaction mixture was stirred for 5 h at room temperature. Then the mixture was washed with brine, extracted with ethyl acetate (30 mL × 3), and dried over anhydrous $MgSO_4$. The mixture was concentrated under reduced pressure and purified using silica gel flash column chromatography using (hexane-EtOAc) as eluents to give trifluoromethyl alcohols (Kelly et al., 2012).

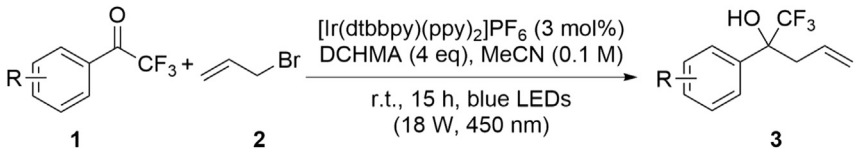
Step 2: To a solution of the alcohol (8 mmol) in DCM (0.5 M, 16 mL) in 50 mL round-bottom flask quipped with stirring bar, pyridinium chlorochromate (16 mmol), and 4Å molecular sieves were added. Reaction mixture was stirred at room temperature for 2 days. Reaction progress was monitored with help of the thin layer chromatography and GC-MS spectroscopy. After completion, reaction mixture was filtered through the celite pad. Filtrate was concentrated under reduced pressure and purified by silica gel flash column chromatography by using (hexane-EtOAc) as eluent to give the desired trifluoromethyl ketone **1**.

General procedure for the synthesis of trifluoromethyl imine substrates 4a-4e



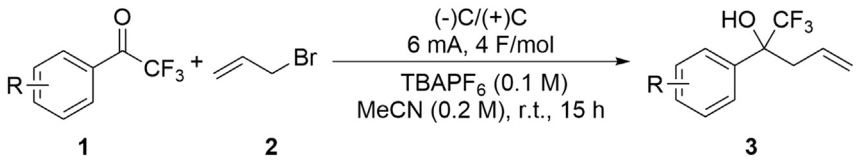
To a solution of 2,2,2-trifluoroacetephenone derivatives (5 mmol) in toluene (10 mL) was added aniline (7 mmol) followed by *p*-toluenesulfonic acid monohydrate (0.25 mmol). The solution was allowed to reflux in toluene for 24 h with removal of water via Dean-Stark trap. After cooling to room temperature, the reaction mixture was diluted with pentane (15 mL) and filtered. The crude residue was subjected to Kugelrohr distillation (0.5 mmHg, bath temp 150-200°C) to give ketamine (Elliott et al., 2019).

General photochemical procedure for the preparation of the trifluoromethyl- and allyl-substituted *tert*-alcohol 3a-3u



An oven-dried 20 mL reaction tube, equipped with a magnetic stirring bar, was charged with trifluoromethyl ketone derivative **1** (0.5 mmol), allyl bromide **2** (3.5 mmol), $[Ir(dtbbpy)(ppy)_2]PF_6$ (3 mol%), and DCHMA (2 mmol). The reaction mixture was purged with argon for 10 minutes before the addition of degassed acetonitrile (0.1 M, 5 mL), and allowed to stir at room temperature for 15 hours under the blue LEDs (18 W, 450 nm). The reaction progress was monitored using thin layer chromatography and GC-MS spectroscopy. After completion, the reaction mixture was diluted with water, extracted with dichloromethane, washed with brine, and dried over $MgSO_4$. The crude product was obtained by removing the solvent under reduced pressure and purified by silica gel flash column chromatography using a (hexane-EtOAc) mixture as the eluent to give the trifluoromethyl- and allyl-substituted *tert*-alcohol **3**.

General electrochemical procedure for the preparation of the trifluoromethyl- and allyl-substituted *tert*-alcohol



An oven dried IKA Electrochemistry kit 10 mL vial, equipped with a magnetic stirring bar, was charged with trifluoromethyl ketone derivative **1** (0.6 mmol), allyl bromide **2** (3 mmol) in acetonitrile (0.2 M, 3 mL) using $TBAPF_6$ (0.1 M) as electrolyte. The vial cap equipped with graphite ((-)C/(+)C) as working and counter electrodes was inserted into the mixture. The reaction mixture was purged with argon for 10 minutes and electrolyzed under the constant current of 6 mA for 15 h (4 F/mol) with stirring at room temperature. The reaction progress was monitored using thin layer chromatography and GC-MS spectroscopy. After completion, the reaction mixture was diluted with water, extracted with dichloromethane, washed with brine, and dried over $MgSO_4$. The crude product was obtained by removing the solvent under reduced pressure and purified by silica gel flash column chromatography using a (hexane-EtOAc) mixture as the eluent to give the trifluoromethyl- and allyl-substituted *tert*-alcohol **3**.

Cyclic voltammetry measurements

The electrochemical properties were characterized by standard cyclic voltammetry (CV) techniques. The samples were dissolved in Ar-saturated CH_3CN (6 mL) to a concentration of 5.0 mM. The solution contained 0.10 M $TBAPF_6$ supporting electrolyte. A three-elecrode cell assembly consisting of a glassy carbon (GC) working electrode, a Pt wire counter electrode, and Ag/AgCl pseudo reference electrode was employed for the voltametric measurements. Voltammograms were acquired at scan rates of 0.10 V s^{-1}.

Spectroscopic details

2,2,2-trifluoro-1-phenylethan-1-one, **1a**: (Laliberté et al., 2008) colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.08 (d, *J* = 8.1 Hz, 2H), 7.71 (t, *J* = 7.7 Hz, 1H), 7.55 (dd, *J* = 8.1, 7.7 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 180.73 (q, *J* = 35.0 Hz), 135.72, 130.31 (q, *J* = 2.2 Hz), 130.17, 129.30, 116.91 (q, *J* = 291.3 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -71.49; **IR (neat)**: ν_{max} = 1717, 1598, 1452, 1176, 1139, 938, 714, 669, 526 cm^{-1}; R_f = 0.71 (hex/EtOAc 9/1).

1-(3,5-dimethylphenyl)-2,2,2-trifluoroethan-1-one, **1c**: (Nie et al., 2009) colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.67 (s, 2H), 7.34 (s, 1H), 2.40 (s, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 181.01 (q, *J* = 34.7 Hz), 139.11, 137.50, 130.23, 128.00 (q, *J* = 2.0 Hz), 116.97 (d, *J* = 291.6 Hz), 21.38; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -71.24; **IR (neat)**: ν_{max} = 1714, 1606, 1268, 1141, 1042, 973, 865, 765, 718, 677 cm^{-1}; R_f = 0.84 (hex/EtOAc 9/1).

2,2,2-trifluoro-1-(4-isopropylphenyl)ethan-1-one, **1d**: (Hall et al., 2010) colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 3.01 (hept, *J* = 6.9 Hz, 1H), 1.30 (s, 3H), 1.29 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 180.31 (q, *J* = 34.8 Hz), 157.82, 130.67 (q, *J* = 2.2 Hz), 128.00, 127.48, 117.02 (q, *J* = 291.3 Hz), 34.72, 23.63; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -70.55; **IR (neat)**: ν_{max} = 1713, 1605, 1204, 1176, 1140, 940, 850, 770, 726, 615, 544 cm^{-1}; R_f = 0.88 (hex/EtOAc 9/1).

1-(4-(tert-butyl)phenyl)-2,2,2-trifluoroethan-1-one, **1e**: (Tur and Saá, 2007) white solid; melting point 43-45°C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 1.36 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 180.31 (q, *J* = 34.8 Hz), 160.05, 130.38 (q, *J* = 2.2 Hz), 127.59, 126.35, 117.02 (q, *J* = 291.3 Hz), 35.67, 31.10; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -71.87; **IR (neat)**: ν_{max} = 1714, 1605, 1180, 1141, 940, 772, 710, 551 cm^{-1}; R_f = 0.82 (hex/EtOAc 9/1).

1-([1,1′-biphenyl]-4-yl)-2,2,2-trifluoroethan-1-one, **1f**: (Saunders et al., 1949) yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 7.1 Hz, 2H), 7.51 (dd, *J* = 7.1, 7.5 Hz, 2H), 7.46 (t, *J* = 7.5 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 180.30 (q, *J* = 35.0 Hz), 148.43, 139.34, 130.95 (q, *J* = 2.2 Hz), 129.34, 129.12, 128.80, 127.85, 127.57, 116.99 (q, *J* = 291.3 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -71.33; **IR (neat)**: ν_{max} = 1711, 1603, 1174, 1138, 938, 853, 745, 694, 650, 601, 521 cm^{-1}; R_f = 0.71 (hex/EtOAc 9/1).

2,2,2-trifluoro-1-(3-(trifluoromethyl)phenyl)ethan-1-one, **1g**: (Yang et al., 2004) colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.33 (s, 1H), 8.26 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.73 (dd, *J* = 7.9, 8.2 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 179.47 (q, *J* = 36.0 Hz), 133.07 (q, *J* = 2.7 Hz), 132.16, 131.84 (q, *J* = 3.5 Hz), 130.49, 129.90, 126.87 (ddt, *J* = 5.9, 3.9, 2.1 Hz), 123.17 (q, *J* = 272.7 Hz), 116.36 (q, *J* = 290.8 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -63.20, -71.75; **IR (neat)**: ν_{max} = 1727, 1613, 1328, 1127, 1026, 958, 757, 692, 681 cm^{-1}; R_f = 0.88 (hex/EtOAc 9/1).

2,2,2-trifluoro-1-(4-fluorophenyl)ethan-1-one, **1j**: (Li et al., 2006) colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.11 (dd, *J* = 8.5, 5.7 Hz, 2H), 7.25 – 7.18 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 179.23 (q, *J* = 35.4 Hz), 168.22, 166.50, 133.32 (dq, *J* = 9.8, 2.0 Hz), 126.63 (d, *J* = 2.9 Hz), 118.04 – 115.68 (m); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -71.61, -99.91; **IR (neat)**: ν_{max} = 1723, 1589, 1496, 1278, 1175, 1145, 950, 760, 678, 637; R_f = 0.66 (hex/EtOAc 9/1).

1-(2-chlorophenyl)-2,2,2-trifluoroethan-1-one, **1m**: (Tanaka et al., 2012) pale yellow liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.72 (d, *J* = 7.3 Hz, 1H), 7.58 – 7.52 (m, 2H), 7.47 – 7.38 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 181.89 (q, *J* = 36.6 Hz), 134.35, 134.29, 131.89, 130.72, 130.29 (q, *J* = 2.9 Hz), 127.06, 116.02 (q, *J* = 292.0 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -73.14; **IR (neat)**: ν_{max} = 2926, 1730, 1591, 1276, 1150, 1070, 937, 854, 746, 637 cm^{-1}; R_f = 0.62 (hex/EtOAc 9/1).

1-(4-chlorophenyl)-2,2,2-trifluoroethan-1-one, **1n**: (Motoki et al., 2007) pale yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.02 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 179.69 (q, *J* = 35.4 Hz), 142.71, 131.65 (q, *J* = 2.0 Hz), 129.81, 128.47, 116.75 (q, *J* = 291.0 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -71.57; **IR (neat)**: ν_{max} = 1719, 1589, 1176, 1141, 1094, 936, 845, 757, 712, 603, 529 cm^{-1}; R_f = 0.59 (hex/EtOAc 9/1).

1-(2-bromophenyl)-2,2,2-trifluoroethan-1-one, **1o**: (Omote et al., 1999) yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 (d, J = 6.7 Hz, 1H), 7.69 (dd, J = 6.7, 6.0 Hz, 1H), 7.50 – 7.42 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 182.48 (q, *J* = 36.6 Hz), 135.23, 134.26, 132.57, 130.26 – 130.07 (m), 127.58, 121.96, 115.87 (q, *J* = 292.2 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -73.11; **IR (neat)**: ν_{max} = 1730, 1587, 1433, 1184, 1142, 1052, 934, 742, 683 cm^{-1}; R_f = 0.59 (hex/EtOAc 9/1).

1-(3-bromophenyl)-2,2,2-trifluoroethan-1-one, **1p**: (Kogon et al., 1992) pale yellow liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.19 (s, 1H), 8.00 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.44 (dd, *J* = 9.0, 8.0 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 179.62 (q, *J* = 35.7 Hz), 138.63, 133.09 (q, *J* = 2.2 Hz), 131.80, 130.85,

128.78 (q, *J* = 2.3 Hz), 123.61, 116.60 (q, *J* = 291.2 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -71.60; **IR (neat)**: ν_{max} = 1722, 1566, 1176, 1143, 1074, 967, 952, 747, 695, 671 cm^{-1}; R_f = 0.76 (hex/EtOAc 9/1).

1-(4-bromophenyl)-2,2,2-trifluoroethan-1-one, **1q**: (Motoki et al., 2007) white solid; melting point 26-28°C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 8.8 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 179.90 (q, *J* = 35.5 Hz), 132.80, 131.65 – 131.55 (m), 131.45, 128.86, 116.72 (q, *J* = 291.3 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -71.60; **IR (neat)**: ν_{max} = 1719, 1583, 1174, 1139, 1072, 1012, 938, 842, 754, 602, 527 cm^{-1}; R_f = 0.60 (hex/EtOAc 9/1).

1-(3-bromo-4-fluorophenyl)-2,2,2-trifluoroethan-1-one, **1r**: (Emer et al., 2014) colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.30 (d, *J* = 6.6 Hz, 1H), 8.04 (s, 1H), 7.30 (td, *J* = 8.3, 2.4 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 178.38 (q, *J* = 36.1 Hz), 163.74 (d, *J* = 260.1 Hz), 136.34 (p, *J* = 2.3 Hz), 131.81 – 131.62 (m), 127.67 (d, *J* = 3.8 Hz), 117.60 (d, *J* = 23.4 Hz), 116.57 (q, *J* = 291.0 Hz), 110.91 (d, *J* = 22.0 Hz).; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -71.53, -93.92. **IR (neat)**: ν_{max} = 1722, 1590, 1494, 1279, 1176, 1140, 956, 762, 674, 631 cm^{-1}; R_f = 0.42 (hex/EtOAc 9/1).

2,2,2-trifluoro-1-(naphthalen-2-yl)ethan-1-one, **1t**: (Liu et al., 2021) white solid; melting point 36-38°C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.63 (s, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.7 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.69 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H), 7.62 (ddd, *J* = 8.5, 6.9, 1.4 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 180.69 (q, *J* = 34.8 Hz), 136.70, 133.40 (q, *J* = 2.7 Hz), 132.41, 130.41, 130.28, 129.32, 128.12, 127.65, 127.42, 124.41 (d, *J* = 1.4 Hz), 117.09 (q, *J* = 291.4 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -70.76; **IR (neat)**: ν_{max} = 1710, 1627, 1250, 1197, 1122, 924, 824, 775, 733, 471 cm^{-1}; R_f = 0.71 (hex/EtOAc 9/1).

2,2,2-trifluoro-1-(naphthalen-1-yl)ethan-1-one, **1u**: (Liu et al., 2021) white solid; melting point 28-30°C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.85 (d, *J* = 8.8 Hz, 1H), 8.21 (dt, *J* = 7.5, 1.7 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.93 (d, *J* = 7.3 Hz, 1H), 7.70 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1H), 7.61 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.59 – 7.55 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 182.32 (q, *J* = 34.1 Hz), 136.18, 133.98, 131.67 (q, *J* = 3.9 Hz), 131.20, 129.50, 129.00, 127.15, 126.36, 125.21, 124.15, 116.65 (q, *J* = 292.9 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -70.17; **IR (neat)**: ν_{max} = 1740, 1573, 1510, 1136, 1064, 916, 774, 752, 659, 495 cm^{-1}; R_f = 0.71 (hex/EtOAc 9/1).

1-(benzo[*b*]thiophen-2-yl)-2,2,2-trifluoroethan-1-one, **1w**: (Benassi et al., 1984) colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.23 (s, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.91 (dq, *J* = 8.2, 1.0 Hz, 1H), 7.57 (ddt, *J* = 8.5, 6.4, 1.6 Hz, 1H), 7.48 (ddt, *J* = 8.5, 6.4, 1.6 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.46 (q, *J* = 37.1 Hz), 143.81, 139.05, 135.83, 134.52 (q, *J* = 3.4 Hz), 129.42, 127.30, 125.96, 123.14, 116.59 (q, *J* = 285.0 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -71.84; **IR (neat)**: ν_{max} = 1690, 1595, 1509, 1226, 1148, 761, 719, 604 cm^{-1}; R_f = 0.50 (hex/EtOAc 9/1).

1,1,1-trifluoro-2-phenylpent-4-en-2-ol, **3a**: (Li and Zhang, 1998) pale yellow liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.59 (d, *J* = 7.7 Hz, 2H), 7.44 – 7.34 (m, 3H), 5.62 – 5.52 (m, 1H), 5.29 – 5.21 (m, 2H), 2.99 (dd, *J* = 14.4, 6.6 Hz, 1H), 2.86 (dd, *J* = 14.4, 8.0 Hz, 1H), 2.64 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 137.06, 130.61, 128.75, 128.55, 126.66 (q, *J* = 1.4 Hz), 125.53 (d, *J* = 289.0 Hz), 122.19, 76.00 (q, *J* = 28.3 Hz), 40.53 (q, *J* = 1.3 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -80.03; **IR (neat)**: ν_{max} = 3546, 2928, 1715, 1449, 1269, 1154, 1072, 995, 926, 766, 712, 641 cm^{-1}; R_f = 0.64 (hex/EtOAc 9/1).

1,1,1-trifluoro-2-(*p*-tolyl)pent-4-en-2-ol, **3b**: (Gong et al., 2019) brown liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.3 Hz, 2H), 5.62 – 5.52 (m, 1H), 5.28 – 5.20 (m, 2H), 2.98 (dd, *J* = 14.3, 6.6 Hz, 1H), 2.83 (dd, *J* = 14.3, 8.1 Hz, 1H), 2.58 (s, 1H), 2.37 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.59, 134.07, 130.74, 129.28, 126.58 (q, *J* = 1.4 Hz), 125.56 (q, *J* = 285.4 Hz), 122.03, 75.95 (q, *J* = 28.3 Hz), 40.42 (q, *J* = 1.5 Hz), 21.26; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.43; **IR (neat)**: ν_{max} = 3542, 2927, 1720, 1469, 1270, 1157, 1075, 1014, 995, 766, 712, 641 cm^{-1}; R_f = 0.66 (hex/EtOAc 9/1).

2-(3,5-dimethylphenyl)-1,1,1-trifluoropent-4-en-2-ol, **3c**: yellow liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.18 (s, 2H), 7.00 (s, 1H), 5.63 – 5.53 (m, 1H), 5.29 – 5.20 (m, 2H), 2.96 (dd, *J* = 14.3, 6.5 Hz, 1H), 2.83 (dd, *J* = 14.3, 8.2 Hz, 1H), 2.60 (s, 1H), 2.35 (s, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.08, 136.96, 130.86, 130.40, 125.57 (q, *J* = 185.0 Hz), 124.36 (q, *J* = 1.2 Hz), 122.00, 75.95 (q, *J* = 28.5, 27.9 Hz), 40.60, 21.69; **^{19}F NMR (564**

MHz, $CDCl_3$) δ -79.10; **IR (neat)**: ν_{max} = 3481, 2923, 1607, 1450, 1263, 1153, 993, 922, 851, 731 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 244.1075, Found 244.1072; R_f = 0.55 (hex/EtOAc 9/1).

1,1,1-trifluoro-2-(4-isopropylphenyl)pent-4-en-2-ol, **3d**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 5.63 – 5.53 (m, 1H), 5.29 – 5.19 (m, 2H), 2.95 (dp, *J* = 27.7, 6.7 Hz, 2H), 2.84 (dd, *J* = 14.4, 8.1 Hz, 1H), 2.59 (s, 1H), 1.27 (s, 3H), 1.25 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 149.39, 134.39, 130.84, 126.65 – 126.59 (m), 126.47, 125.60 (q, *J* = 285.0 Hz), 122.03, 75.91 (q, *J* = 28.3 Hz), 40.48, 33.91, 24.05 (q, *J* = 1.1 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.28; **IR (neat)**: ν_{max} = 3549, 2862, 1514, 1270, 1160, 828, 715 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 258.1231, Found 258.1232; R_f = 0.62 (hex/EtOAc 9/1).

2-(4-(tert-butyl)phenyl)-1,1,1-trifluoropent-4-en-2-ol, **3e**: pale yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 8.0 Hz, 2H), 7.41 (dq, *J* = 8.0, 1.4 Hz, 2H), 5.64 – 5.54 (m, 1H), 5.33 – 5.19 (m, 2H), 2.98 (dd, *J* = 14.4, 7.5 Hz, 1H), 2.84 (dd, *J* = 14.4, 7.5 Hz, 1H), 2.56 (s, 1H), 1.33 (s, 9H).; **^{13}C NMR (151 MHz, $CDCl_3$)** δ 134.04, 130.86, 127.10, 126.34 (d, *J* = 1.4 Hz), 125.60 (q, *J* = 285.5 Hz), 125.47, 124.56, 75.87 (q, *J* = 28.2 Hz), 40.47 (q, *J* = 1.3 Hz), 34.72 (d, *J* = 5.5 Hz), 31.48; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.24; **IR (neat)**: ν_{max} = 3548, 2962, 1364, 1268, 1157, 1110, 914, 826, 711, 555 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 272.1388, Found 272.1389; R_f = 0.62 (hex/EtOAc 9/1).

2-([1,1'-biphenyl]-4-yl)-1,1,1-trifluoropent-4-en-2-ol, **3f**: white solid; melting point 80-82°C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.67 – 7.59 (m, 6H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.40 – 7.34 (m, 1H), 5.67 – 5.57 (m, 1H), 5.35 – 5.20 (m, 2H), 3.03 (dd, *J* = 14.3, 6.6 Hz, 1H), 2.89 (dd, *J* = 14.3, 8.1 Hz, 1H), 2.64 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.63, 140.56, 136.03, 130.59, 129.04, 127.79, 127.36, 127.26, 127.14 (q, *J* = 1.3 Hz), 125.54 (q, *J* = 285.4 Hz), 122.33, 75.98 (q, *J* = 28.6 Hz), 40.55 (q, *J* = 1.4 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.17; **IR (neat)**: ν_{max} = 3593, 2931, 1488, 1158, 943, 834, 763, 734, 691 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 292.1075, Found 292.1075; R_f = 0.44 (hex/EtOAc 9/1).

1,1,1-trifluoro-2-(3-(trifluoromethyl)phenyl)pent-4-en-2-ol, **3g**: colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.62 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.27 (dd, *J* = 8.0, 7.8 Hz, 1H), 5.34 – 5.24 (m, 1H), 5.04 – 4.98 (m, 2H), 2.70 (dd, *J* = 14.5, 6.9 Hz, 1H), 2.64 (dd, *J* = 14.5, 7.8 Hz, 1H), 2.52 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.29, 131.15 (q, *J* = 32.5 Hz), 130.11 (dt, *J* = 2.9, 1.2 Hz), 129.90, 129.11, 125.71 (q, *J* = 3.8 Hz), 125.25 (q, *J* = 285.5 Hz), 124.21 (q, *J* = 272.2 Hz), 123.89 – 123.70 (m), 122.87, 75.82 (q, *J* = 28.2 Hz), 40.59 (q, *J* = 1.2 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -62.70, -79.15; **IR (neat)**: ν_{max} = 3545, 2832, 1446, 1328, 1268, 1156, 1124, 1076, 996, 925, 801, 727, 702, 665 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 284.0436, Found 284.0633; R_f = 0.64 (hex/EtOAc 9/1).

1,1,1-trifluoro-2-(2-fluorophenyl)pent-4-en-2-ol, **3h**: colorless iquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.69 (td, *J* = 8.0, 1.9 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.20 (td, *J* = 7.6, 1.3 Hz, 1H), 7.08 (ddd, *J* = 12.5, 8.2, 1.3 Hz, 1H), 5.68 – 5.58 (m, 1H), 5.28 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.21 (dd, *J* = 10.2, 1.7 Hz, 1H), 3.32 (dd, *J* = 14.6, 6.8 Hz, 1H), 2.91 (s, 1H), 2.83 (dd, *J* = 14.6, 7.8 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 160.28 (d, *J* = 248.6 Hz), 131.21 (d, *J* = 9.0 Hz), 130.87, 130.38 (d, *J* = 3.4 Hz), 128.39 – 122.05 (m), 126.25 – 124.22 (m), 123.51 (d, *J* = 11.0 Hz), 121.93, 116.69 (d, *J* = 24.9 Hz), 76.19 – 75.25 (m), 38.90 (dq, *J* = 7.8, 1.5 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -80.18, -110.94; **IR (neat)**: ν_{max} = 3549, 2931, 1488, 1444, 1268, 1220, 1168, 1092, 912, 761, 701, 632 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 234.0668, Found 234.0663; R_f = 0.58 (hex/EtOAc 3/1).

1,1,1-trifluoro-2-(3-fluorophenyl)pent-4-en-2-ol, **3i**: colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.40 – 7.30 (m, 3H), 7.07 (tdd, *J* = 8.1, 2.6, 1.3 Hz, 1H), 5.60 – 5.50 (m, 1H), 5.29 – 5.22 (m, 2H), 2.93 (dd, *J* = 14.4, 6.7 Hz, 1H), 2.85 (dd, *J* = 14.4, 8.1 Hz, 1H), 2.64 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.79 (d, *J* = 245.9 Hz), 139.49 (d, *J* = 7.2 Hz), 129.87 (d, *J* = 8.1 Hz), 125.04 (q, *J* = 285.5 Hz), 124.10, 122.02 (dq, *J* = 2.9, 1.4 Hz), 115.59, 115.45, 114.03 (d, *J* = 23.7 Hz), 76.00 – 74.84 (m), 40.40; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.14, -112.38; **IR (neat)**: ν_{max} = 3546, 2930, 1592, 1444, 1230, 1169, 1147, 994, 923, 787, 728, 706 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 234.0668, Found 234.0665; R_f = 0.58 (hex/EtOAc 9/1).

1,1,1-trifluoro-2-(4-fluorophenyl)pent-4-en-2-ol, **3j**: (Xie et al., 2010) white solid; melting point 92-94°C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.56 (dd, *J* = 8.8, 5.3 Hz, 2H), 7.12 – 7.05 (m, 2H), 5.75 – 5.44 (m, 1H), 5.34 – 5.21 (m, 2H), 2.95 (dd, *J* = 14.5, 6.7 Hz, 1H), 2.84 (dd, *J* = 14.5, 8.0 Hz, 1H), 2.64 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 163.03 (d, *J* = 247.7 Hz), 132.83 (d, *J* = 3.2 Hz), 130.30, 128.68 (dq, *J* = 8.1, 1.4 Hz), 125.40 (q, *J* = 286.0 Hz),

122.45, 115.49 (d, *J* = 21.7 Hz), 75.74 (q, *J* = 28.5 Hz), 40.55 (q, *J* = 1.5 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.07, -115.86; **IR (neat)**: ν_{max} = 3549, 2933, 1512, 1235, 1160, 1093, 834, 738, 586, 524 cm^{-1}; R_f = 0.60 (hex/EtOAc 9/1).

2-(3,4-difluorophenyl)-1,1,1-trifluoropent-4-en-2-ol, **3k**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.46 – 7.38 (m, 2H), 7.28 (dd, *J* = 8.4, 2.3 Hz, 1H), 5.58 – 5.50 (m, 1H), 5.29 – 5.25 (m, 2H), 2.89 (dd, *J* = 15.0, 7.3 Hz, 1H), 2.84 (dd, *J* = 15.0, 7.3 Hz, 1H), 2.68 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 151.32 (dd, *J* = 32.9, 12.4 Hz), 149.66 (dd, *J* = 30.9, 12.6 Hz), 134.29 – 134.06 (m), 129.87, 125.18 (q, *J* = 289.0 Hz), 122.97 (ddd, *J* = 6.6, 3.7, 1.5 Hz), 122.84, 117.39 (d, *J* = 17.3 Hz), 116.56 (d, *J* = 19.1 Hz), 75.46 (q, *J* = 28.0 Hz), 40.56 (q, *J* = 1.2 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.38, -136.92, -137.91; **IR (neat)**: ν_{max} = 3672, 2987, 1612, 1522, 1426, 1282, 1175, 1118, 880, 819, 780, 732, 612 cm^{-1}; R_f = 0.64 (hex/EtOAc 9/1).

2-(4-chloro-3-fluorophenyl)-1,1,1-trifluoropent-4-en-2-ol, **3l**: colorless oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.46 – 7.38 (m, 2H), 7.31 – 7.27 (m, 1H), 5.59 – 5.49 (m, 1H), 5.31 – 5.22 (m, 2H), 2.89 (dd, *J* = 14.5, 6.8 Hz, 1H), 2.84 (dd, *J* = 14.5, 7.8 Hz, 1H), 2.69 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.99 (d, *J* = 249.0 Hz), 137.84 (d, *J* = 6.1 Hz), 130.49, 129.53, 124.87 (q, *J* = 285.7 Hz), 122.87 (dd, *J* = 3.6, 1.6 Hz), 122.69, 121.43 (d, *J* = 17.6 Hz), 115.40 (dd, *J* = 23.4, 1.4 Hz), 75.30 (q, *J* = 289.0 Hz), 40.29 (q, *J* = 1.6 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.21, -114.44; **IR (neat)**: ν_{max} = 3549, 2929, 1582, 1490, 1420, 1273, 1175, 1016, 1019, 925, 817, 729, 680, 571 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 268.0778, Found 268.0280; R_f = 0.44 (hex/EtOAc 9/1).

2-(2-chlorophenyl)-1,1,1-trifluoropent-4-en-2-ol, **3m**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.77 (dd, *J* = 7.3, 2.4 Hz, 1H), 7.43 – 7.40 (m, 1H), 7.31 (tt, *J* = 7.3, 5.3 Hz, 2H), 5.71 – 5.61 (m, 1H), 5.29 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.20 (ddt, *J* = 10.1, 2.1, 1.2 Hz, 1H), 3.60 (dd, *J* = 14.9, 6.7 Hz, 1H), 3.46 (s, 1H), 2.89 (dd, *J* = 14.9, 7.6 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 133.27, 132.42, 132.10, 131.30 (q, *J* = 1.4 Hz), 130.77, 130.19, 126.96, 125.30 (q, *J* = 286.5 Hz), 121.38, 77.54 (q, *J* = 28.0 Hz), 38.82 (q, *J* = 1.4 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.07; **IR (neat)**: ν_{max} = 3548, 2931, 1430, 1263, 1162, 1043, 758, 736, 702, 633 cm^{-1}; R_f = 0.70 (hex/EtOAc 9/1).

2-(4-chlorophenyl)-1,1,1-trifluoropent-4-en-2-ol, **3n**: (Xie et al., 2010) yellow liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.51 (d, *J* = 8.7 Hz, 2H), 7.40 – 7.35 (m, 2H), 5.60 – 5.50 (m, 1H), 5.29 – 5.22 (m, 2H), 2.93 (dd, *J* = 14.4, 6.7 Hz, 1H), 2.84 (dd, *J* = 14.4, 7.9 Hz, 1H), 2.60 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 135.36, 134.71, 129.93, 128.54, 127.99 (q, *J* = 1.4 Hz), 125.07 (q, *J* = 285.5 Hz), 122.34, 75.53 (q, *J* = 28.3 Hz), 40.26 (q, *J* = 1.2 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.33; **IR (neat)**: ν_{max} = 3543, 2929, 1494, 1268, 1158, 1095, 1013, 822, 735, 507 cm^{-1}; R_f = 0.54 (hex/EtOAc 9/1).

2-(2-bromophenyl)-1,1,1-trifluoropent-4-en-2-ol, **3o**: pale yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.65 (dq, *J* = 8.0, 0.9 Hz, 1H), 7.35 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.20 (td, *J* = 7.6, 1.8 Hz, 1H), 5.66 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.28 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.20 (dq, *J* = 10.2, 1.2 Hz, 1H), 3.65 – 3.55 (m, 2H), 2.90 (dd, *J* = 14.9, 7.4 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 136.13, 134.89, 131.70 (q, *J* = 1.7 Hz), 130.95, 130.46, 127.62, 125.48 (q, *J* = 287.0 Hz), 121.48, 121.15, 77.90 (q, *J* = 28.6 Hz), 39.11 (q, *J* = 1.4 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -77.01; **IR (neat)**: ν_{max} = 3524, 2928, 1700, 1424, 1262, 1161, 914, 759, 733, 699, 631 cm^{-1}; R_f = 0.60 (hex/EtOAc 9/1).

2-(3-bromophenyl)-1,1,1-trifluoropent-4-en-2-ol, **3p**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.76 (s, 1H), 7.50 (ddt, *J* = 8.1, 7.0, 1.0 Hz, 2H), 7.27 (t, *J* = 7.9 Hz, 1H), 5.55 (td, *J* = 17.5, 7.3 Hz, 1H), 5.30 – 5.22 (m, 2H), 2.93 (dd, *J* = 14.4, 6.7 Hz, 1H), 2.84 (dd, *J* = 14.4, 7.9 Hz, 1H), 2.68 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 139.40, 131.95, 130.35, 130.19, 130.00 (q, *J* = 1.3 Hz), 125.33 (q, *J* = 1.4 Hz), 125.25 (q, *J* = 285.5 Hz), 122.90, 122.72, 75.65 (q, *J* = 28.5 Hz), 40.56 (q, *J* = 1.2 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.07; **IR (neat)**: ν_{max} = 3544, 2929, 1569, 1421, 1265, 1159, 1076, 996, 924, 787, 726, 675 cm^{-1}; R_f = 0.68 (hex/EtOAc 9/1).

2-(4-bromophenyl)-1,1,1-trifluoropent-4-en-2-ol, **3q**: (Xie et al., 2010) pale yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.56 – 7.51 (m, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 5.60 – 5.50 (m, 1H), 5.29 – 5.22 (m, 2H), 2.93 (dd, *J* = 14.3, 6.7 Hz, 1H), 2.84 (dd, *J* = 14.3, 7.9 Hz, 1H), 2.64 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 136.13, 131.74, 130.12, 128.53 (q, *J* = 1.4 Hz), 125.23 (q, *J* = 285.5 Hz), 123.19, 122.60, 75.82 (q, *J* = 28.8 Hz), 40.43 (q, *J* = 1.3 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.29; **IR (neat)**: ν_{max} = 3542, 2985, 1592, 1491, 1399, 1267, 1157, 1075, 1094, 941, 819, 751, 733, 670 cm^{-1}; R_f = 0.62 (hex/EtOAc 9/1).

2-(3-bromo-4-fluorophenyl)-1,1,1-trifluoropent-4-en-2-ol, **3r**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.81 (d, *J* = 6.5 Hz, 1H), 7.50 – 7.46 (m, 1H), 7.15 (td, *J* = 8.4, 2.3 Hz, 1H), 5.55 (h, *J* = 9.2 Hz, 1H), 5.30 – 5.25 (m, 2H), 2.91 (dd, *J* = 14.5, 7.2 Hz, 1H), 2.84 (dd, *J* = 14.5, 7.9 Hz, 1H), 2.64 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 160.17, 158.52, 134.53 (d, *J* = 3.8 Hz), 129.86, 127.55 (dd, *J* = 7.5, 1.4 Hz), 128.26 – 121.41 (m), 122.95, 116.52 (d, *J* = 22.3 Hz), 109.43 (d, *J* = 21.1 Hz), 75.37 (q, *J* = 29.0 Hz), 40.57 (q, *J* = 1.2 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.30, -107.47; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 311.9773, Found 311.9773; **IR (neat)**: ν_{max} = 354, 2931, 1600, 1497, 1266, 1159, 1049, 1018, 925, 821, 731, 673, 602 cm^{-1}; R_f = 0.48 (hex/EtOAc 9/1).

1,1,1-trifluoro-2-(4-(pyridin-2-yl)phenyl)pent-4-en-2-ol, **3s**: white solid; melting point 86-88°C; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.70 (dt, *J* = 4.8, 1.5 Hz, 1H), 8.04 – 7.98 (m, 2H), 7.79 – 7.72 (m, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.28 – 7.22 (m, 1H), 5.58 (td, *J* = 17.2, 7.0 Hz, 1H), 5.27 – 5.18 (m, 2H), 3.02 (dd, *J* = 14.4, 6.6 Hz, 1H), 2.97 (s, 1H), 2.87 (dd, *J* = 14.4, 7.9 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.00, 149.94, 139.78, 137.80, 137.05, 130.50, 127.18 (q, *J* = 1.3 Hz), 127.11, 125.51 (q, *J* = 285.7 Hz), 122.59, 122.12, 120.92, 76.13 (q, *J* = 28.2 Hz), 40.50 (q, *J* = 1.3 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.12; **IR (neat)**: ν_{max} = 3546, 3081, 1592, 1470, 1436, 1267, 1157, 994, 918, 844, 783, 741 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 293.1027, Found 293.1030; R_f = 0.55 (hex/EtOAc 9/1).

1,1,1-trifluoro-2-(naphthalen-2-yl)pent-4-en-2-ol, **3t**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.11 (d, *J* = 1.9 Hz, 1H), 7.93 – 7.84 (m, 3H), 7.66 (dq, *J* = 8.6, 1.1 Hz, 1H), 7.55 – 7.51 (m, 2H), 5.63 – 5.54 (m, 1H), 5.29 (dq, *J* = 13.0, 1.6 Hz, 1H), 5.23 (dq, *J* = 13.0, 1.9, 0.8 Hz, 1H), 3.13 (dd, *J* = 14.4, 7.0 Hz, 1H), 2.94 (dd, *J* = 14.4, 7.0 Hz, 1H), 2.77 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 134.43, 133.30, 133.12, 130.55, 128.69, 128.33, 127.74, 126.90, 126.61, 126.53 (q, *J* = 1.2 Hz), 125.62 (q, *J* = 285.7 Hz), 123.94 (d, *J* = 1.4 Hz), 122.29, 76.24 (q, *J* = 28.5 Hz), 40.55 (q, *J* = 1.1 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -78.92; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 266.0918, Found 266.0920; **IR (neat)**: ν_{max} = 3545, 3063, 1508, 1217, 1155, 936, 816, 749, 578, 477 cm^{-1}; R_f = 0.55 (hex/EtOAc 9/1).

1,1,1-trifluoro-2-(naphthalen-1-yl)pent-4-en-2-ol, **3u**: (Kelly et al., 2015) pale yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.91 (d, *J* = 9.1 Hz, 1H), 7.90 – 7.85 (m, 2H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.56 – 7.43 (m, 3H), 5.73 (dq, *J* = 17.0, 8.0 Hz, 1H), 5.31 (dq, *J* = 13.0, 1.5 Hz, 1H), 5.25 (dd, *J* = 13.0, 1.7 Hz, 1H), 3.43 (dd, *J* = 14.8, 7.4 Hz, 1H), 3.06 (dd, *J* = 14.7, 7.4 Hz, 1H), 2.98 (s, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 138.51, 136.65, 135.15, 132.28 (d, *J* = 4.3 Hz), 131.01, 130.79, 129.29, 127.37 (q, *J* = 3.5, 2.9 Hz), 126.27, 126.08 (q, *J* = 286.7 Hz), 125.72, 124.56, 122.48, 78.93 (q, *J* = 28.1 Hz), 41.27 (q, *J* = 1.6 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -78.41; **IR (neat)**: ν_{max} = 3537, 3052, 1265, 1159, 1047, 990, 936, 801, 776, 636 cm^{-1}; R_f = 0.71 (hex/EtOAc 9/1).

2-(benzo[*b*]thiophen-2-yl)-1,1,1-trifluoropent-4-en-2-ol, **3w**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.84 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.78 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.40 – 7.34 (m, 3H), 5.74 – 5.64 (m, 1H), 5.34 – 5.27 (m, 2H), 3.01 (dd, *J* = 14.3, 7.3 Hz, 2H), 2.89 (dd, *J* = 14.3, 7.3 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 141.92, 140.01, 139.66 (q, *J* = 1.3 Hz), 129.97, 124.97, 124.87 (q, *J* = 285.4 Hz), 124.72, 124.12, 123.01, 122.82, 122.42, 75.96 (q, *J* = 29.9 Hz), 41.44 (q, *J* = 1.4 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -79.84; **IR (neat)**: ν_{max} = 2927, 1436, 1272, 1148, 990, 928, 831, 747, 723, 432 cm^{-1}; R_f = 0.40 (hex/EtOAc 9/1).

(*Z*)-2,2,2-trifluoro-*N*,1-diphenylethan-1-imine, **4a**: (Wu et al., 2015) yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.37 – 7.34 (m, 1H), 7.31 – 7.28 (m, 2H), 7.25 – 7.17 (m, 4H), 7.08 – 7.02 (m, 1H), 6.75 (dt, *J* = 6.3, 1.3 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.06 (q, *J* = 33.8 Hz), 147.10, 130.22, 130.04, 128.79, 128.66 (q, *J* = 2.4, 1.8 Hz), 128.50, 125.33, 120.55, 119.86 (q, *J* = 279.2 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -70.01; **IR (neat)**: ν_{max} = 1666, 1594, 1330, 1229, 1193, 1127, 970, 769, 518 cm^{-1}; R_f = 0.60 (hex/EtOAc 9/1).

(*E*)-2,2,2-trifluoro-*N*-phenyl-1-(4-(pyridin-2-yl)phenyl)ethan-1-imine, **4c**: colorless liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.68 (ddd, *J* = 4.8, 1.8, 1.0 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.69 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.34 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.24 (m, 1H), 7.22 – 7.17 (m, 2H), 7.07 – 7.00 (m, 1H), 6.78 (dd, *J* = 8.6, 1.2 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.01 (q, *J* = 25.0 Hz), 156.19, 150.07, 147.30, 141.27, 137.11, 130.57, 129.45, 129.14, 127.18, 125.67, 123.02, 120.96, 120.76, 120.08 (q, *J* = 279.0 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -69.81; **IR (neat)**: ν_{max} = 1715, 1587, 1467, 1435, 1331, 1229, 1198, 1137, 972, 756, 694, cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 326.1031, Found 326.1012; R_f = 0.33 (hex/EtOAc 4/1).

(*Z*)-2,2,2-trifluoro-1-(naphthalen-2-yl)-*N*-phenylethan-1-imine, **4d**: (Zhang et al., 2020) pale yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.86 (s, 1H), 7.79 (dd, *J* = 8.3, 3.9 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.21 – 7.15 (m, 3H), 7.05 – 7.01 (m, 1H), 6.81 (dd, *J* = 8.3, 1.3 Hz, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 157.03 (q, *J* = 33.7 Hz), 147.31, 133.76, 132.72, 129.40 (q, *J* = 1.6 Hz), 129.10, 128.82, 128.49, 127.99, 127.97, 127.59, 127.07, 125.66, 125.30, 120.93, 120.23 (q, *J* = 279.3 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -69.56; **IR (neat)**: ν_{max} = 1725, 1596, 1484, 1323, 1188, 1126, 763, 694, 475 cm^{-1}; R_f = 0.51 (hex/EtOAc 9/1).

(*Z*)-1-(4-bromophenyl)-2,2,2-trifluoro-*N*-phenylethan-1-imine, **4e**: (Zhang et al., 2020) brown liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.46 – 7.43 (m, 2H), 7.25 – 7.19 (m, 2H), 7.12 – 7.05 (m, 3H), 6.77 – 6.71 (m, 2H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 155.85 (q, *J* = 34.1 Hz), 146.79, 131.91, 131.39 (q, *J* = 1.4 Hz), 130.26, 128.99, 125.62, 124.99, 120.38, 119.64 (q, *J* = 278.0 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -69.95; **IR (neat)**: ν_{max} = 1665, 1587, 1486, 1329, 1194, 1128, 1072, 968, 735, 691 cm^{-1}; R_f = 0.71 (hex/EtOAc 9/1).

N-(1,1,1-trifluoro-2-phenylpent-4-en-2-yl)aniline, **5a**: brown oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.42 – 7.34 (m, 3H), 7.05 – 6.99 (m, 2H), 6.71 (tt, *J* = 7.3, 1.2 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 2H), 5.79 (dddd, *J* = 16.8, 8.2, 4.9, 1.5 Hz, 1H), 5.18 (dd, *J* = 10.2, 1.8 Hz, 1H), 5.12 (dq, *J* = 17.0, 1.5 Hz, 1H), 4.34 (s, 1H), 3.03 (dd, *J* = 11.2, 4.5 Hz, 1H), 2.91 (dd, *J* = 11.2, 4.5 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 143.98, 136.87, 131.28, 128.61, 128.56, 128.24 (q, *J* = 1.8 Hz), 127.46 (q, *J* = 1.7 Hz), 126.56 (q, *J* = 289.6 Hz), 120.61, 118.83, 116.27, 65.25 (q, *J* = 25.4 Hz), 41.82; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -69.63; **IR (neat)**: ν_{max} = 2921, 1603, 1498, 1254, 1152, 1072, 750, 703, , 801, 776, 636 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 291.1235, Found 291.1234; R_f = 0.68 (hex/EtOAc 9/1).

N-(2-([1,1′-biphenyl]-4-yl)-1,1,1-trifluoropent-4-en-2-yl)aniline, **5b**: pale yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.68 (d, *J* = 8.5 Hz, 2H), 7.65 – 7.61 (m, 4H), 7.48 – 7.44 (m, 2H), 7.39 – 7.35 (m, 1H), 7.04 (tt, *J* = 7.4, 1.5 Hz, 2H), 6.73 (td, *J* = 7.3, 1.2 Hz, 1H), 6.45 (d, *J* = 8.7 Hz, 2H), 5.88 – 5.77 (m, 1H), 5.21 (dd, *J* = 14.0, 2.3 Hz, 1H), 5.15 (dd, *J* = 14.0, 2.3 Hz, 1H), 4.37 (s, 1H), 3.07 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.94 (dd, *J* = 14.4, 7.5 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 144.21, 141.17, 140.45, 136.11, 131.47, 129.05, 128.89, 128.16 (q, *J* = 1.7 Hz), 127.78, 127.39, 127.28, 126.79 (q, *J* = 289.0 Hz), 120.91, 119.13, 116.56, 65.39 (q, *J* = 25.3 Hz), 41.99; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -69.65; **IR (neat)**: ν_{max} = 2929, 1602, 1498, 1154, 750, 695, 667 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 367.1548, Found 367.1551; R_f = 0.64 (hex/EtOAc 9/1).

N-(1,1,1-trifluoro-2-(4-(pyridin-2-yl)phenyl)pent-4-en-2-yl)aniline, **5c**: brown liquid; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.71 (d, *J* = 4.8 Hz, 1H), 8.04 – 7.99 (m, 2H), 7.79 – 7.73 (m, 2H), 7.72 (d, *J* = 8.7 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.05 – 6.99 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.44 (d, *J* = 8.0 Hz, 2H), 5.86 – 5.76 (m, 1H), 5.19 (dd, *J* = 10.1, 1.8 Hz, 1H), 5.14 (dq, *J* = 17.0, 1.6 Hz, 1H), 4.36 (s, 1H), 3.05 (dd, *J* = 14.5, 7.5 Hz, 1H), 2.93 (dd, *J* = 14.5, 7.5 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 156.97, 149.99, 144.13, 139.53, 137.87, 137.04, 131.37, 128.89, 128.20, 127.32, 126.64 (q, *J* = 289.0 Hz), 122.58, 120.98, 120.86, 119.17, 116.57, 65.48 (q, *J* = 25.7, 25.3 Hz), 42.06; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -69.63; **IR (neat)**: ν_{max} = 2924, 1602, 1498, 1467, 1434, 1284, 1155, 781, 748, 694 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 368.1500, Found 368.1503; R_f = 0.42 (hex/EtOAc 4/1).

N-(1,1,1-trifluoro-2-(naphthalen-2-yl)pent-4-en-2-yl)aniline, **5d**: pale yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.10 (s, 1H), 7.91 – 7.84 (m, 3H), 7.76 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.53 (qd, *J* = 7.1, 3.4 Hz, 2H), 7.04 – 6.98 (m, 2H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.44 (d, *J* = 8.1 Hz, 2H), 5.90 – 5.77 (m, 1H), 5.24 – 5.13 (m, 2H), 4.44 (s, 1H), 3.15 (dd, *J* = 14.5, 6.7 Hz, 1H), 3.02 (dd, *J* = 14.5, 6.7 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 144.08, 134.70, 133.15, 132.98, 131.26, 128.70, 128.56, 128.30, 127.52, 126.74, 126.68 (q, *J* = 289.0 Hz), 126.67, 126.32, 125.29, 120.76, 118.99, 116.38, 65.49 (q, *J* = 24.9 Hz), 41.90; **^{19}F NMR (564 MHz, $CDCl_3$)** δ -69.30; **IR (neat)**: ν_{max} = 3058, 1602, 1497, 1437, 1284, 1150, 1119, 926, 818, 747, 693, 476 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 341.1391, Found 341.1389; R_f = 0.62 (hex/EtOAc 9/1).

N-(2-(4-bromophenyl)-1,1,1-trifluoropent-4-en-2-yl)aniline, **5e**: yellow oil; **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.57 – 7.48 (m, 4H), 7.06 (td, *J* = 7.5, 2.2 Hz, 2H), 6.78 – 6.74 (m, 1H), 6.41 (d, *J* = 7.5 Hz, 2H), 5.84 – 5.73 (m, 1H), 5.21 (dd, *J* = 10.1, 1.6 Hz, 1H), 5.14 (dq, *J* = 17.0, 1.5 Hz, 1H), 4.34 (s, 1H), 3.01 (dd, *J* = 14.8, 6.9 Hz, 1H), 2.89 (dd, *J* = 14.8, 6.9 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 143.82, 136.23, 131.98, 131.01, 129.54 (q, *J* = 1.8 Hz), 128.95, 126.49 (q, *J* = 289.6 Hz), 122.83, 121.19, 119.36, 116.49, 65.30 (q, *J* = 25.9 Hz), 41.79 (q, *J* = 1.7 Hz); **^{19}F NMR (564 MHz, $CDCl_3$)** δ -69.74; **IR (neat)**: ν_{max} = 2982, 1602, 1496, 1438, 1285, 1154, 1077, 1010, 749, 693, 512 cm^{-1}; HRMS m/z (EI) calc. for $C_{27}H_{23}NOS$ [M^+] = 369.0340, Found 369.0338; R_f = 0.62 (hex/EtOAc 9/1).