JOC The Journal of Organic Chemistry

Note

Metal-free Visible Light Promoted Trifluoromethylation of Vinylcyclopropanes Using Pyrylium Salt as Photoredox Catalyst

Palasetty Chandu, Krishna Gopal Ghosh, and Devarajulu Sureshkumar

J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.9b01033 • Publication Date (Web): 03 Jun 2019

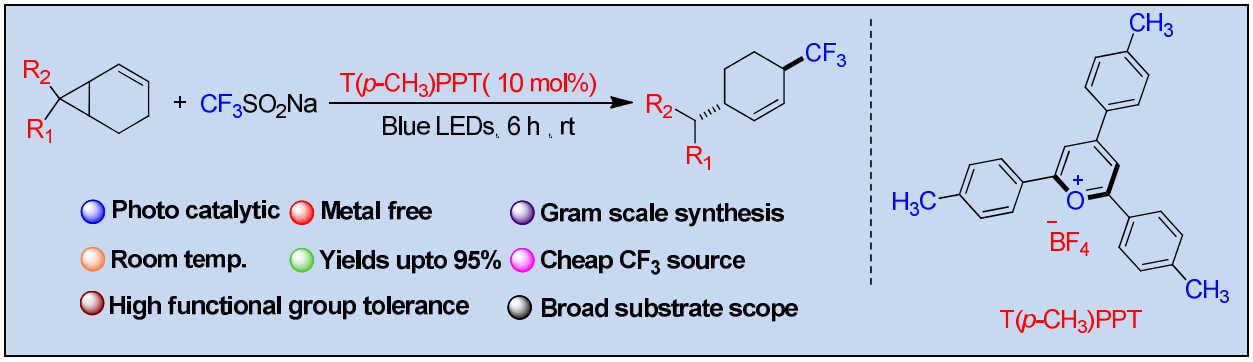
Just Accepted

is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Metal-Free Visible Light Promoted Trifluoromethylation of Vinylcyclopropanes Using Pyrylium Salt as Photoredox Catalyst

Palasetty Chandu, Krishna Gopal Ghosh and Devarajulu Sureshkumar*

Department of chemical sciences, Indian Institute of Science Education and Research Kolkata Mohanpur-741246, West Bengal, India

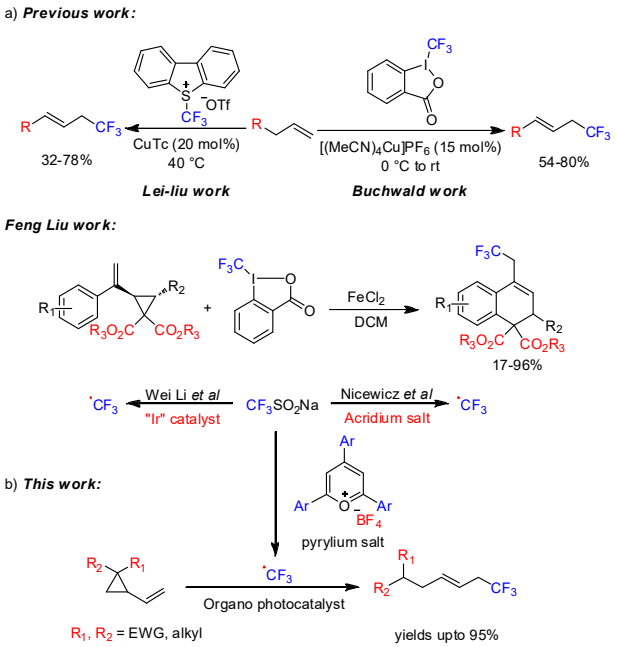


Abstract: Visible light induced metal-free trifluoromethylation of activated, carbocyclic and unactivated vinylcyclopropanes *via* ring opening reaction using Langlois reagent (CF_3SO_2Na) is reported to synthesize allylic trifluoromethylated derivatives. Allylic trifluoromethylation was achieved by photo-oxidative single electron transfer (SET) process at ambient temperature and metal-free condition under visible-light irradiation using pyrylium salt as photoredox catalyst. The reported methodology has operational simplicity, broad substrate scope, high functional group tolerance and scalability.

Trifluoromethyl group is a valuable moiety in pharmaceutical and agrochemical fields.[1] Introduction of a trifluoromethyl moiety into biologically important molecule will affect different properties like bioactivity, electrostatic interactions with targets, metabolic stability, lipophilicity, and increase oxidative metabolism.[2] Hence, the incorporation of fluorine moieties into organic compounds is one of the essential topics in the field of organic synthesis. Csp^2–CF_3 formation is well studied,[3] but Csp^3–CF_3 formation especially terminal allylic trifluoromethylation is limited due to challenges associated with regio and stereoselective installation of CF_3 group.[4] Allylic trifluoromethylated compounds are the essential building blocks to synthesize many pharmaceutical drugs.[5] Buchwald[6a] and Liu *et al.*[6b] showed allylic trifluoromethylation of terminal alkenes using electrophilic fluorinating reagents, Togni and

Umemoto respectively, by copper catalysis (Scheme 1a). Recently, Feng Liu group reported Fe-catalyzed trifluoromethylation of activated vinylcyclopropanes using Togni reagent[6c] to synthesis dihydronapthalene derivatives (Scheme 1a). Here, we report cheaper and atom economical approach to synthesize allylic trifluoromethylated compounds using photoredox catalysis.

Polypyridyl complexes of ruthenium and iridium metals are widely used as photocatalysts due to their unique photophysical properties like longer excited state lifetime, different oxidative and reductive potentials that can engage with organic molecules making them reactive intermediate species.[7] For instance, $[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbpy)](PF_6)$ is used in water splitting for



Scheme 1. a) Known allylic trifluoromethylation of alkenes. b) Generation of CF_3 radicals by photocatalytic pathway and trifluoromethylation of VCPs.

the production of hydrogen,[8a-b] OLED application[8c-d] and also in photoredox catalysis.[8e-f] The major drawbacks of using Ru (0.0001 ppm) and Ir (0.01 ppm) are toxic and their low abundance making them expensive.[9] Organo-based photocatalysts are one of the best alternatives that are sustainable and cost effective. Recently, Nicewicz *et al.*[10] have developed the acridinium based organo photocatalysts. Acridinium[10] and pyrylium[11] photocatalysts have high oxidative potentials that can promote a new chemical reaction under visible light irradiation. However, the preparation of acridinium salts requires tedious multistep processes.[12] In contrast, pyrylium photocatalysts can be prepared in a single step from corresponding aromatic aldehyde and

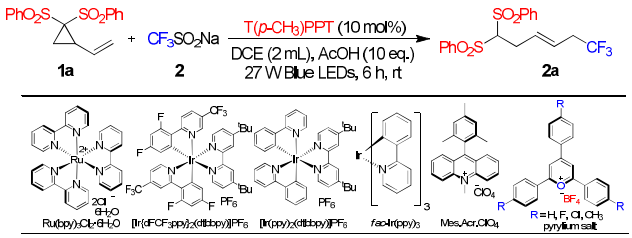
acetophenone derivatives, which is very cost-effective.[13] Pyrylium salts absorb in the visible region and act as powerful oxidizing agents in their excited states.[11,13,14] They can enhance the formation of free radicals because of no net charge separation in electron transfer step.[14]

Among the many trifluoromethylating reagents (Togni, Umemoto, $TMSCF_3$, CF_3SO_2Na, CF_3I, CF_3SO_2Cl, *etc.*), Langlois (CF_3SO_2Na) reagent has received special attention due to its easy handling, stability and cost-effectiveness. However, this reagent has high oxidation potential (E_{oxd} = +1.05 V *vs* SCE)[15] making the generation of the CF_3 radical difficult. Few methods are known for trifluoromethylation from CF_3SO_2Na using transition metal catalysts at high temperatures[16a-c] and excess of explosive peroxides as strong oxidant.[16d-f] In the case of photocatalysis, generation of CF_3 radical directly from CF_3SO_2Na using $Mes.Acr.ClO_4$[17a] and $[Ir(dF\text{-}CF_3\text{-}ppy)_2(dtbpy)](PF_6)$[17b] is known (Scheme 1b). However, till date, no other photocatalysts have been explored. Here, we report for the first time, pyrylium organic salt as a photocatalyst for the generation of CF_3 radical using visible light and subsequent trifluoromethylation of vinylcyclopropanes (VCPs) using Langlois' reagent (Scheme 1b).

Though vinylcyclopropanes (VCP) are well known for radical clock experiments,[4c,18] there is no detailed study of ring opening of VCPs using photoredox catalysis. Here, we are reporting trifluoromethylation of VCPs using Langlois reagent by organic photoredox catalysis. We hypothesized generation of CF_3 radical that could react with the vinyl moiety of VCPs and undergo ring opening to form long alkyl chained allylic trifluoromethylated products. First, we tried trifluoromethylation on activated VCP **1a** as a model substrate using Macmillan[19a] and Stephenson *et al.*[19b] conditions (Entry 1 and 2). However, these conditions failed to yield the expected product. Next, we screened different photocatalysts as shown in Table 1.

Initially, we screened different Ru and Ir-metal photocatalysts for the trifluoromethylation of VCP. Catalysts like $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (bpy = bipyridyl) $\{E_{1/2}^{red} = [^*Ru^{II}/Ru^{I}] = +0.77$ V *vs* SCE in MeCN$\}$,[20a] $Ir(ppy)_2(dtbbpy)PF_6$ (dtbbpy = 4,4′-di-*tert*-butyl-2,2′-dipyridyl) $\{E_{1/2}^{red}[^*Ir^{III}/Ir^{II}] = +0.66$ V *vs* SCE in MeCN$\}$[20b] and *fac*-$Ir(ppy)_3$(ppy = 2-phenylpyridine) $\{E_{1/2}^{red}[^*Ir^{III}/Ir^{II}] = +0.31$ V *vs* SCE in MeCN$\}$[20c] and Eosin Y $\{E_{1/2}^{red} = [^3EY^*/EY^{\bullet-}] = +0.83$ V *vs* SCE in MeCN$\}$[20d] have insufficient potentials to generate the CF_3 radical, hence the reaction failed to provide expected product (Entry 3-5 and 7).

Table 1. Optimization of the Allylic Trifluoromethylation[a]



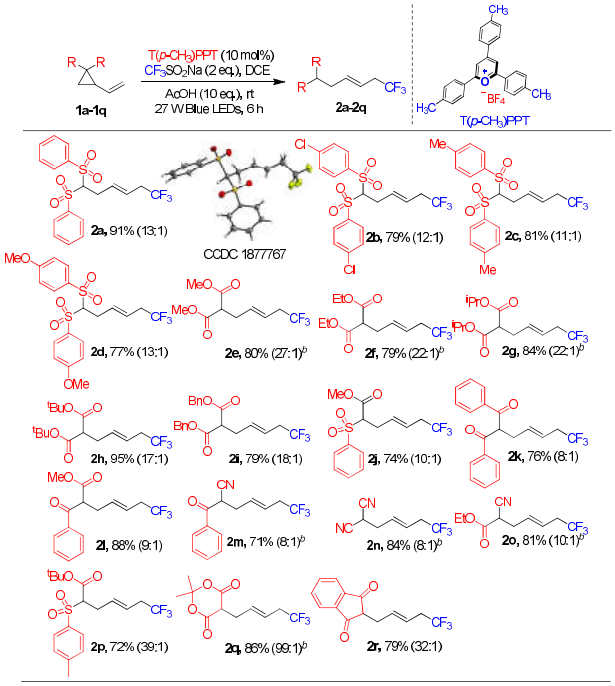
Entry	Photocatalyst	Solvent	Additive	Yield (*E:Z*)[g]
1[b]	2 mol% $Ru(Phen)_3Cl_2$	CH_3CN	K_2HPO_4	13 (6:1)
2[c]	2 mol% $Ru(bpy)_3Cl_2·6H_2O$	CH_3CN	-	6 (7:1)
3	2 mol% $Ru(bpy)_3Cl_2·6H_2O$	MeOH	-	NR
4	2 mol% $[Ir(ppy)_2(dtbbpy)]PF_6$	MeOH	-	NR
5	2 mol% *fac*-$Ir(ppy)_3$	MeOH	-	NR
6	2 mol% $Ir[(dFCF_3ppy)_2(dtbbpy)]PF_6$	DCE	-	39 (10:1)
7	5 mol% Eosin Y	DCE	-	NR
8	5 mol% Mes.Acr.ClO_4	DCE	-	42 (9:1)
9	5 mol% Rhodamine B	DCE	-	10 (7:1)
10	10 mol% TPPT	DCE	-	52 (12:1)
11	10 mol% T(*p*-F)PPT	DCE	-	40 (11:1)
12	10 mol% T(*p*-Cl)PPT	DCE	-	38 (9:1)
13	10 mol% T(*p*-CH_3)PPT	DCE	-	69 (13:1)
14	10 mol% T(*p*-CH_3)PPT	DMSO	-	29 (10:1)
15	10 mol% T(*p*-CH_3)PPT	CH_3CN	-	49 (8:1)
16	10 mol% T(*p*-CH_3)PPT	Toluene	-	38 (9:1)
17	10 mol% T(*p*-CH_3)PPT	DCE	Open air	trace
18	10 mol% T(*p*-CH_3)PPT	DCE	10 eq. HCO_2H	63 (12:1)
19	10 mol% T(*p*-CH_3)PPT	DCE	10 eq. H_2O	79 (13:1)
20	**10 mol% T(*p*-CH_3)PPT**	**DCE**	**10 eq. AcOH**	**95 (13:1)**
21[d]	10 mol% T(*p*-CH_3)PPT	DCE	10 eq. AcOH	81 (12:1)
21[e]	-	DCE	10eq. AcOH	NR
22[f]	10 mol% T(*p*-CH_3)PPT	DCE	10 eq. AcOH	trace

[a]All reactions were performed in 0.15 mmol scale, 2 eq. of CF_3SO_2Na, 2 mL solvent, irradiated with 27 W Blue LEDs under Ar atm. [b]CF_3SO_2Cl as CF_3 source, [c]Pyridine *N*-Oxide and TFAA as CF_3 source (details in ESI). [d]27 W household CFL as light source for 18 h, [e]No photocatalyst, [f]no light, [g]yields measured using $C_6H_5CF_3$ as internal standard. *E:Z* ratio based on ^{19}F NMR.

Rhodamine-B $\{E_{1/2}^{red} = [RhB^*/RhB^{\bullet-}] = +1.62$ V *vs* SCE$\}$[20e] furnished yield of 10% (entry 9). $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (dF(CF_3)ppy = 3, 5-difluoro-2-[5-(trifluoromethyl)-2-pyridinyl] phenyl) $\{E_{1/2}^{red}$ $[^*Ir^{III/II}] = +1.21$ V and $E_{1/2}^{red}$ $[Ir^{III/II}] = -1.37$ V *vs* SCE in MeCN$\}$[20f] and Acridinium catalyst $\{E_{1/2}^{red}$ $[*Acr/Acr^{\bullet-}] = +2.06$ V and $E_{1/2}^{red}$ $[Acr/Acr^-] = -0.57$ V *vs* SCE in MeCN$\}$[17a] are well known catalysts for trifluoromethylation[17a,b] but they resulted in poor yields 39% and 42% respectively in this case (entry 6 and 8). Pyrylium salts have higher oxidation potentials (1.8 V to 2.3 V *vs* SCE in MeCN)[11] and large absorption in the visible region. When the reaction was carried out using 2,4,6-triphenylpyrylium tetrafluoroborate (TPPT) as a photocatalyst, interestingly, the expected product was obtained with 52% yield (Entry 10).Further, we examined different substituted TPPT. Pyrylium salts with electron withdrawing groups (*p*-F, *p*-Cl) decreased the catalytic activity of the reaction (Entry 11 and 12), while electron donating group (Me) showed high catalytic reactivity with a yield of 69% (Entry 13) in DCE as the solvent. Different proton sources were screened to improve catalyst efficiency. We tried AcOH as proton source additive and the best yield of 95% was observed using 10 eq. of AcOH (Entry 20). Addition of AcOH after the reaction did not improve the yield of the reaction. Probably AcOH is involved in protonation of anionic species (**7**) during reaction and increases

catalytic efficiency. We also tried H_2O as additive its giving 79% of product. Blue LEDs gives better yields and less time compared to house hold light (entry 21). Further, we also performed background reactions in the absence of photocatalyst and light (Entry 22 and 23) that showed a trace amount of the product. The yield of the reaction was profoundly affected by atmospheric conditions, for example, when the reaction was carried out in the open air, only trace amounts of the product was observed (Entry 17).

Table 2. Substrate Scope for Allylic Trifluoromethylation[a]

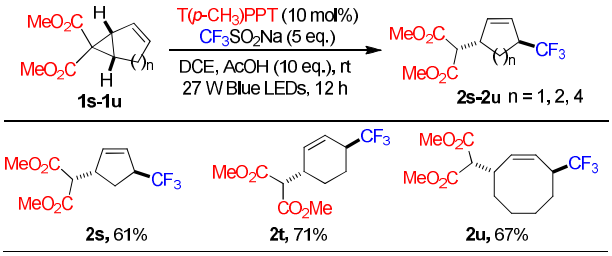


[a]All reactions were performed with 0.15 mmol scale, 2 eq. CF_3SO_2Na, 10 mol% T(p-CH_3)PPT, 10 eq. AcOH, irradiated with 27 W blue LEDs under Ar atm., parenthesis *E*:*Z* ratio based on ^{19}F NMR, [b]reaction scale 0.3 mmol.

With optimized conditions, we envisage the substrate scope and limitation of this trifluoromethylation reaction. This protocol was suitable for a broad range of VCPs (Table 2). Synthetically interesting functional groups such as esters, cyano, keto, spiro, and sulphonates are tolerable in this protocol. In all the cases allylic trifluoromethylated products were obtained **2a-2d** in good yields and selectivity. The substrates with di-esters **2e-2i** showed yields in the range of 79% to 95% with *E:Z* ratio up to 24:1. This protocol is highly chemoselective, for instance, selective installation of trifluoromethyl group at vinyl center in the presence of C=O and C≡N, trifluoromethyl group is selectively incorporated at vinyl center. Substrates like di-cyano **2n** and di-keto **2k** VCPs show good yields with moderate selectivity. We examined the two different

substituted VCPs, which also gave good yields and regio-selectivity (**2j, 2l, 2m, 2o** and **2p**). Next, we tried spiro-VCPs as substrates. Interestingly, these spiro-VCPs showed high selectivity up to 99:1 (**2q** and **2r**) than the normal VCPs.

Table 3. Allylic Trifluoromethylation of Carbocyclic Vinylcyclopropanes[a]

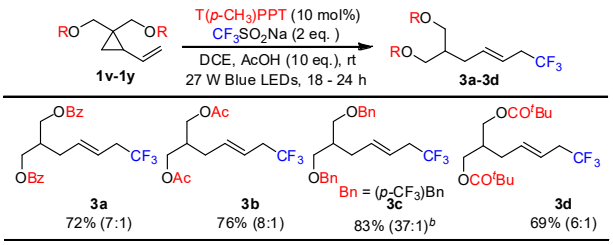


[a]All reaction were performed with 0.3 mmol scale, 10 mol% photocatalyst, 5 eq. CF_3SO_2Na, 4 mL DCE, 10 eq. AcOH, irradiated with 27 W blue LEDs, under Ar atm. Yields are based on ^{19}F NMR using $PhCF_3$ as an internal standard.

Next, we tested our protocol with few carbocyclic VCPs. Carbocyclic motifs are essential skeleton found in many natural products.[21] This methodology was successfully tested with 5, 6, and 8 membered carbocyclic VCPs (Table 3). In these cases, 4-(trifluoromethyl)cyclo-2-ene derivatives (**2s, 2u** and **2v**) were obtained in good yields[22] as a single *trans* isomer.

Trifluoromethylation of unactivated VCPs is challenging compared to activated VCPs due to their low reactivity. Here, we synthesized unactivated VCPs **1v-1y** by reduction followed by protection of **1f** using benzoyl, acetyl, benzyl and *tert*-butyl groups. Trifluoromethylation of unactivated VCPs was achieved by enhancing the reaction time, trifluoromethylated products **3a-3d** were obtained with good yields and selectivity (Table 4).

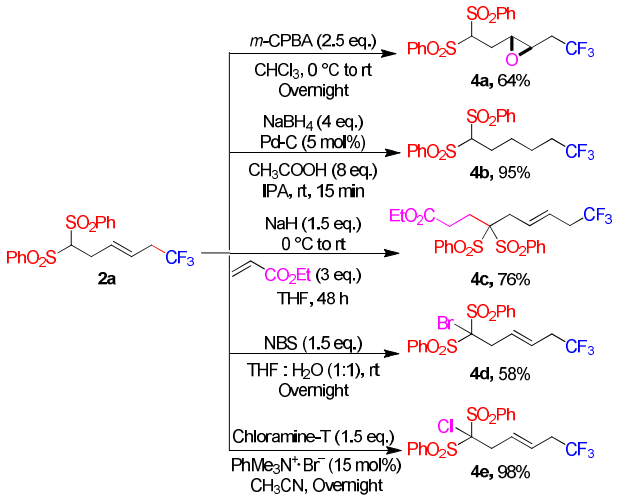
Table 4. Allylic Trifluoromethylation of Unactivated Cyclopropanes[a]



[a]All reaction were performed with 0.3 mmol scale, 10 mol% photocatalyst, 2 eq. CF_3SO_2Na, 4 mL DCE, 10 eq. AcOH, irradiated with 27 W blue LEDs under Ar atm. [b]5 eq. CF_3SO_2Na, *E:Z* ratios based on ^{19}F NMR.

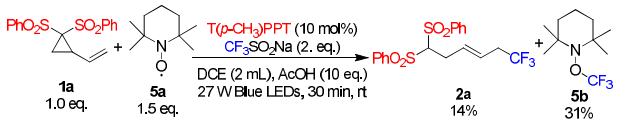
To demonstrate the scalability of this methodology with readily available organic pyrylium (T(*p*-CH_3)PPT) photocatalyst and starting materials, we performed a gram-scale reaction of **1e** with Langlois reagent to get product **2e** in 71% yield. The solid-state structure confirmed the *trans*-geometry across the double bond in the trifluoromethylated product **2a**.

To demonstrate the synthetic utility of the allylic trifluoromethylated product, we performed different synthetic transformations (Scheme 2). Allylic trifluoromethylated product **2a** was converted into trifluoromethylated epoxide **4a**, trifluoromethylated alkane **4b**, 1,4-addition product **4c**, bromo, and chlorinated derivatives **4d**, **4e** respectively in good chemical yields and selectivity.[23a-d]



Scheme 2. Transformation of product **2a** into different functional groups

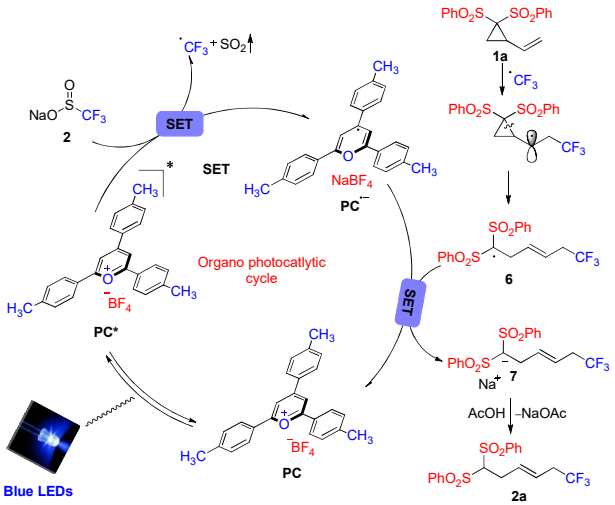
To gain mechanistic insights, we performed a control experiment in the presence of a radical quencher (Scheme 3). In the presence of TEMPO **5a** (1.5 eq.), formation of TEMPO-CF_3 adduct **5b** was observed by ^{19}F NMR (376 MHz, $CDCl_3$) as singlet (s, 3F) at δ –55.86 ppm. This experiment suggests that the reaction follows a radical pathway.



Scheme 3. Control experiment with TEMPO

In line with this, we propose a mechanism for allylic trifluoromethylation photoredox cycle as shown in Scheme 4. Irradiation of photocatalyst **PC** with visible light generates the excited-state photocatalyst **PC*** species, which acts as a strong oxidant to generate the CF_3 radical from the Langlois reagent {$CF_3SO_2Na/CF_3^{\bullet}$, $E_{1/2}^{oxi}$ = +1.05 V *vs* SCE}.[17a] This CF_3 radical reacts with

the terminal alkene of **1a** and further undergoes cyclopropane ring opening due to ring strain and generates stable tertiary radical **6**. Finally, the photocatalytic cycle could be accomplished by reduction of tertiary radical **6** to give stable carbanion **7** and regeneration of photocatalyst **PC**.[17b] Further, protonation of **7** forms the long alkyl chain product **2a**.



Scheme 4. Proposed mechanism for allylic trifluoromethylation of VCPs

In summary, we have developed a new methodology for the synthesis of allylic trifluoromethylated derivatives from activated, carbocyclic and unactivated VCPs that is scalable to gram scale. To our knowledge, this is the first report to use the cheap pyrylium photocatalyst for trifluoromethylation of VCPs. The reported protocol is an excellent alternative for expensive and harsh metal catalyst conditions. Trifluoromethylation demonstrated here has good functional group tolerance and the final product can be further functionalized into useful synthetic intermediates.

EXPERIMENTAL SECTION:

General Information:

All solvents were dried and commercial reagents were purified following guidelines of L. L Chai and Armarego purification of laboratory chemicals. Langlois reagent (CF_3SO_2Na) was purchased from Tokyo Chemical Industries Chemicals (TCI) and all metal catalysts were either prepared as per literature procedures or purchased (Sigma-Aldrich) and used without purification, unless specified. Other reagents were obtained from commercial suppliers (Alfa Aesar and Spectrochem). All reactions were conducted in dried glassware with magnetic stirring under

Argon atmosphere, unless otherwise stated. Ethanolic solution of potassium permanganate or *p*-anisaldehyde was used as TLC staining agent. Flash column chromatography was performed using silica gel (230-400 μm, Merck) using the eluent system described for each experiment. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Blue LEDs (9 x 3 = 27 W) were used as a visible light source. The light source was placed at a distance of ~5 cm from the reaction tube with cooling fan. The yields were calculated based on isolation after column purification, and the purity was determined by ^{19}F NMR spectra. All NMR spectra were recorded on 400 MHz Jeol and 500 MHz Bruker spectrometers. ^{1}H, ^{13}C and ^{19}F NMR spectral data are reported as chemical shifts (δ) in parts per million (ppm) and coupling constants (J) are measured in Hertz (Hz). The following abbreviations are used to describe multiplicities s=singlet, d=doublet, t=triplet, q=quartet, pent=pentet, br=broad, m=multiplet. NMR spectra were processed in Mestrenova keeping $CDCl_3$ residual peak at 7.26 ppm. High resolution mass spectra (HRMS, m/z) were recorded on a Bruker Micro-TOF spectrometry. IR spectra were recorded on Perkin Elmer Frontier FT-IR spectrometer. Melting points of solids were measured on a Griffin apparatus and are uncorrected. IUPAC names were obtained using the ChemDraw software.

General procedure for the synthesis of the pyrylium salts:

Pyrylium salts were prepared according to the literature procedure.[24] $BF_3{\cdot}OEt_2$ was slowly added to a mixture of the carbonyl compounds (if starting materials are solids, they were dissolved in a small amount of toluene). After heating for 2 h at 100 ºC or until no fumes observed then cooled to the room temperature, add THF slowly and stirred for 5 min. Solid was filtered and washed several times with ether and purification was performed by multiple time recrystallization from acetone.

Reactivity of vinylcyclopropane under MacMillan's reaction conditions[25a]

In a glovebox, substrate **1a** (17.4 mg, 0.05 mmol, 1 eq.), $Ru(phen)_3Cl_2$ (0.36 mg, 0.0005 mmol, 0.01 eq.), and K_2HPO_4 (26.1 mg, 0.15 mmol, 3 eq.) were weighed into a 10 mL reaction tube. The vial was fitted with rubber septum and removed from the glove box, and the vial was sealed with parafilm. The CF_3SO_2Cl (10.64 μL, 2 eq.) in MeCN (2 mL) was added by syringe and reaction tube placed in the above-mentioned photo reactor setup with cooling fan. The reaction mixture was allowed to stir for 24 h. The reaction was quenched with water (5 mL) and extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. Trifluoromethyltoulene (0.1 mmol, 2 eq.) was added as internal standard, and the reaction was analyzed by ^{1}H and ^{19}F NMR spectroscopy. The starting material **1a** was recovered in 80% yield, and trifluoromethylated product **2a** was formed in less than 13% yield.

Reactivity of vinylcyclopropane under Stephenson's reaction conditions[25b]

To a 5 mL reaction tube equipped with a stir bar was added pyridine *N*-oxide (38 mg, 0.40 mmol, 1.0 eq.), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (3.0 mg, 1.0 mol%) and substrate **1a** (139.2 mg, 0.40 mmol). The combined materials were then dissolved in MeCN (2.0 mL) and stirred to form a homogeneous solution. Trifluoroacetic anhydride (60 µL, 90 mg, 0.44 mmol, 1.1 eq.) was then added to the resulting solution. The reaction tube was equipped with a rubber septum, and syringe needle was placed through the septum for the duration of the reaction. 9 x 3 W Blue LED lights (positioned 5 cm away) were turned on and the reaction was allowed to run for 12–15 h before the light source was removed. Workup was done by diluting the reaction with CH_2Cl_2 and washing with 1 N HCl, followed by saturated $NaHCO_3$ and then brine. The organic layer was dried over Na_2SO_4 and concentrate under reduced pressure. Trifluoromethyltoulene (0.4 mmol, 1 eq.) was added as internal standard, and the reaction was analyzed by ^1H and ^{19}F NMR spectroscopy, and trifluoromethylated product **2a** was formed in less than 6% yield.

General Procedure for synthesis of vinylcyclopropanes:

Vinylcyclopropanes (**1a**, **1e-1i**, **1k**, **1l**, **1n**, **1q** and **1r**) were prepared from the reported literature procedure[26] and other vinylcyclopropanes (**1b-1d**, **1j**, **1m**, **1o** and **1p**) were synthesized by following protocol. The corresponding active methylene compound (2 mmol, 1 eq.) and 1,4-dibromobut-2-ene (1 eq.) were added to a round bottom flask with a stir bar under nitrogen atmosphere. To this was added tetrahydrofuran (0.2 M) and Cesium carbonate (2.5 eq.). After fitting the condenser, reaction mixture was stirred for overnight at 60 °C. After cooling down to room temperature, the reaction mixture was filtered over Celite and washed with diethyl ether. The organic phase was washed with saturated aqueous $NaHCO_3$, followed by water and brine. After filtration over Na_2SO_4, the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography using hexane and ethyl acetate as the eluent. Corresponding vinylcyclopropanes obtained as solid/liquid with good yields.

Spectral data of activated vinylcyclopropanes:

*4,4'-(2-Vinylcyclopropanedisulfonyl)bis(chlorobenzene) (**1b**):* White solid (mp: 152-156 °C), (650 mg, Yield 79%); ^1H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.7 Hz, 2H), 7.90 (d, *J* = 8.5 Hz, 2H), 7.53 (dd, *J* = 17.2, 8.7 Hz, 4H), 6.11 – 5.86 (m, 1H), 5.43 (d, *J* = 17.1 Hz, 1H), 5.34 (d, *J* = 10.3 Hz, 1H), 3.24 (dd, *J* = 18.6, 9.2 Hz, 1H), 2.33 (dd, *J* = 8.5, 6.6 Hz, 1H), 2.05 (dd, *J* = 10.1, 6.3 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 141.3, 141.2, 137.6, 136.9, 131.1, 131.0, 130.5, 129.3, 128.9, 122.7, 64.0, 32.8, 20.4. FT-IR data (KBr, in cm^{-1}): 3092, 2906, 1578, 1477, 1429, 1396, 1336, 1319, 1296, 1280, 1262, 1248, 1214, 1197, 1177, 1151, 1139, 1088, 1059, 1011, 970, 942. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{15}Cl_2O_4S_2$ 416.9783; Found: 416.9781.

*4,4'-(2-Vinylcyclopropanedisulfonyl)bis(methylbenzene) (**1c**):* White solid (mp: 110-114 °C), (544

mg, yield 72%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 7.32 (dd, *J* = 11.2, 8.4 Hz, 4H), 6.06 (dt, *J* = 17.4, 9.7 Hz, 1H), 5.40 (d, *J* = 17.1 Hz, 1H), 5.31 (d, *J* = 10.2 Hz, 1H), 3.21 (dd, *J* = 18.4, 9.2 Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 2.30 (dd, *J* = 8.3, 6.3 Hz, 1H), 2.09 (dd, *J* = 10.0, 6.2 Hz, 1H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 145.2, 145.1, 136.3, 135.6, 131.1, 129.5, 129.4, 129.3, 129.0, 121.7, 64.0, 32.6, 21.6, 20.0. FT-IR data (KBr, in cm^{-1}): 3056, 3034, 3001, 2981, 2956, 2923, 1923, 1869, 1801, 1631, 1596, 1405, 1382, 1330, 1198, 1164, 1136. HRMS (ES-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{21}O_4S_2$ 377.0876; Found: 377.0872.

*4,4'-(2-Vinylcyclopropanedisulfonyl)bis(methoxybenzene) (**1d**):* White solid (mp: 48-51 °C), (550 mg, yield 68%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 9.0 Hz, 2H), 7.86 (d, *J* = 9.0 Hz, 2H), 6.97 (dd, *J* = 12.2, 9.0 Hz, 4H), 6.05 (dt, *J* = 17.0, 9.7 Hz, 1H), 5.39 (d, *J* = 17.1 Hz, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 3.87 (s, 4H), 3.86 (s, 2H), 3.19 (dd, *J* = 18.4, 9.1 Hz, 1H), 2.26 (dd, *J* = 8.3, 6.2 Hz, 1H), 2.03 (dd, *J* = 10.0, 6.1 Hz, 1H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 164.0, 164.0, 131.8, 131.2, 130.7, 130.0, 121.6, 113.9, 113.6, 64.3, 55.6, 32.6, 20.1. FT-IR data (KBr, in cm^{-1}): 3901, 3866, 3852, 3817, 3671, 3648, 3628, 3116, 3090, 3016, 2954, 2843, 1594, 1499, 1441, 1416, 1322, 1299, 1269, 1156, 1116, 1080, 1020. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{19}H_{21}O_6S_2$ 409.0774; Found: 409.0769.

*Methyl-1-(phenylsulfonyl)-2-vinylcyclopropanecarboxylate (**1j**):* White solid, (mp: 66-69 °C), (400 mg, yield 74%, single isomer); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.4 Hz, 2H), 7.63 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 5.60 – 5.47 (m, 1H), 5.36 (d, *J* = 16.9 Hz, 1H), 5.18 (d, *J* = 10.2 Hz, 1H), 3.61 (s, 3H), 2.89 (dd, *J* = 18.0, 8.5 Hz, 1H), 2.25 (dd, *J* = 9.9, 5.5 Hz, 1H), 1.97 (dd, *J* = 8.3, 5.5 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.0, 139.8, 133.6, 130.9, 128.8, 120.5, 52.7, 51.0, 32.0, 19.7. FT-IR data (KBr, in cm^{-1}): 3447, 3097, 3064, 3037, 3015, 3005, 2959, 1978, 1873, 1834, 1733, 1635, 1442, 1309, 1207, 1164, 1143, 1085, 1062, 1032. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{15}O_4S$ 267.0686; Found: 267.0683.

*1-Benzoyl-2-vinylcyclopropanecarbonitrile (**1m**):* Colorless oil, (183 mg, yield 46%, single Isomer); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 5.84 – 5.73 (m, 1H), 5.50 (d, *J* = 16.2 Hz, 1H), 5.45 (d, *J* = 10.3 Hz, 1H), 2.57 (dd, *J* = 16.6, 8.6 Hz, 1H), 2.33 (dd, *J* = 8.8, 4.9 Hz, 1H), 1.74 (dd, *J* = 7.8, 4.9 Hz, 1H).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 191.4, 135.5, 133.6, 132.5, 128.6, 128.6, 121.2, 118.9, 99.9, 35.9, 26.3, 23.9. FT-IR data (KBr, in cm^{-1}): 2264, 1728, 1437, 1269, 1166. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{13}H_{11}NO$ 198.0913; Found: 198.0910.

*Ethyl-1-cyano-2-vinylcyclopropanecarboxylate (**1o**):* Colorless oil, (mixture of diastereomers 1:1) (285 mg, yield 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.70 – 5.51 (m, 1H), 5.39 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.32 (d, *J* = 10.3 Hz, 0.6H), 5.22 (d, *J* = 10.1 Hz, 0.4H), 4.26 – 4.14 (m, 2H), 2.52 (dt, *J* = 16.8, 8.6 Hz, 1H), 1.95 – 1.81 (m, 1.5H), 1.60 (dd, *J* = 7.9, 5.1 Hz, 0.5H), 1.28 (q, *J* = 7.0 Hz, 3H).^{13}C{^{1}H} NMR (101

MHz, $CDCl_3$): δ 166.9, 164.9, 132.0, 130.4, 121.1, 120.5, 118.4, 116.5, 62.7, 62.5, 35.4, 33.4, 23.6, 22.3, 20.9, 20.1, 13.9, 13.8. FT-IR data (KBr, in cm^{-1}): 2985, 2959, 2934, 2850, 1736, 1438, 1370, 1343, 1252, 1138, 1053, 973, 913, 858, 646. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_9H_{12}NO_2$ 166.0863; Found: 166.0862.

*tert-Butyl-1-tosyl-2-vinylcyclopropanecarboxylate (**1p**):* White solid (mp: 60-64 °C) (457 mg, yield 71%, single isomer); ^1H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.55 (ddd, *J* = 17.4, 10.1, 8.3 Hz, 1H), 5.37 (d, *J* = 16.8 Hz, 1H), 5.19 (d, *J* = 10.6 Hz, 1H), 2.82 (dd, *J* = 18.0, 8.3 Hz, 1H), 2.44 (s, 3H), 2.17 (dd, *J* = 9.9, 5.4 Hz, 1H), 1.89 (dd, *J* = 7.8, 5.4 Hz, 1H), 1.29 (s, 9H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 163.3, 144.3, 137.3, 131.2, 129.4, 128.5, 120.0, 83.7, 51.4, 31.2, 27.8, 21.6, 18.9. FT-IR data (KBr, in cm^{-1}): 3100, 2982, 2932, 1722, 1645, 1598, 1497, 1480, 1461, 1432, 1398, 1369, 1321, 1256, 1213, 1157, 1136, 1083. HRMS (ESI-TOF) m/z: $[M + Na]^+$ for calcd for $C_{17}H_{22}O_4SNa$ 345.1131; Found: 345.1128.

Synthesis of the carbocyclic vinylcyclopropanes:

*Dimethyl-bicyclo[3.1.0]hex-2-ene-6,6-dicarboxylate (**1s**):*[27a] In an oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar and cooled under argon, was added $Rh_2(OAc)_4$ (13 mg, 0.03 mmol) and freshly cracked cyclopentadiene (2.8 mL, 32.5 mmol). Dimethyl 2-diazomalonate (0.86 mL, 6.5 mmol) was added neat over 10 h by means of a gas-tight syringe (using syringe pump) at room temperature. The solution was run through a pipette plug of silica and eluted with hexane. The collected organic layer was concentrated and purified by medium pressure liquid chromatography using 5% EtOAc and hexane as eluent to obtain the compound **1s** in 61% yield (779 mg) as a colorless oil. 1H NMR (400 MHz, $CDCl_3$): δ 5.76 (dd, *J* = 3.8, 1.2 Hz, 1H), 5.58 (d, *J* = 5.3 Hz, 1H), 3.68 (s, 3H), 3.60 (s, 3H), 2.82 – 2.59 (m, 3H), 2.40 (t, *J* = 6.1 Hz, 1H).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 170.3, 166.5, 132.1, 129.4, 52.6, 52.2, 39.3, 38.6, 34.3, 31.6.

*Dimethyl-bicyclo[4.1.0]hept-2-ene-7,7-dicarboxylate (**1t**):*[27b] In an oven-dried 10 mL Sealed tube equipped with a magnetic stir bar under argon, was added $Rh_2(OAc)_4$ (13 mg, 0.03 mmol). Dimethyl 2-diazomalonate (0.86 mL, 6.5 mmol) was added and excess of cyclohexadiene (5-10 eq.) added. The reaction mixture was heated to 120 °C for 1 h, until no dimethyl 2-diazomalonate remains. Reaction mixture was concentrated and purified by silica column using 5% EtOAc and hexane. The compound **1t** was isolated as gummy solid in 93% yield (1.3 g) which became solid at 20 °C; ^1H NMR (400 MHz, $CDCl_3$): δ 5.92 – 5.76 (m, 1H), 5.72 – 5.57 (m, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 2.17 – 1.56 (m, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 170.0, 167.6, 127.8, 121.7, 52.6, 52.4, 40.7, 26.6, 24.4, 20.4, 15.9.

*Dimethyl-bicyclo[6.1.0]non-2-ene-9,9-dicarboxylate (**1u**):*[27c] In an oven-dried 10 mL Sealed tube equipped with a magnetic stir bar under argon, was added $Rh_2(OAc)_4$ (13 mg, 0.03 mmol). Dimethyl 2-diazomalonate (0.86 mL, 6.5 mmol) was added and excess of cyclooctadiene (2-5 eq.) added. Reaction

mixture was heated to 120 °C for 1 h, until no dimethyl 2-diazomalonate remains. Reaction mixture was concentrated and purified by silica column using 5% EtOAc and hexane. The compound **1u** was isolated as colorless oily liquid in 68% yield (1.05 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.77 (tdd, ***J*** = 7.2, 4.4, 2.4 Hz, 1H), 5.54 (d, *J* = 11.3 Hz, 1H), 3.72 (s, 3H), 3.71 (s, 3H), 2.45 – 2.31 (m, 2H), 2.07 – 1.68 (m, 6H), 1.51 – 1.36 (m, 1H), 1.11 (ddd, *J* = 15.2, 12.5, 3.1 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 171.1, 167.0, 136.2, 120.5, 52.6, 52.0, 36.0, 32.8, 30.1, 29.6, 29.5, 24.7, 23.9.

Synthesis of the unactivated vinylcyclopropanes:

(*2-Vinylcyclopropane-1,1-diyl)dimethanol (**S1**):* To a solution of diester 1f (14 mmol) in THF (50 mL) was cooled to 0 °C and $LiAlH_4$ (4 eq.) was added in several portions**.** After heating for 2 h, the mixture was cooled to rt, add 2 mL H_2O followed by 1 M solution of Rochelle's salt (10 mL) were cautiously added, the layers are separate out. The solid part filtered off. The filtrate was concentrated and extract with 3 x 50 mL DCM. Combine the organic layers and dried over Na_2SO_4. After evaporation of solvent, di-alcohol **S1** appeared as colorless liquid, which was used further without purification (1.7 g, crude yield 95%); ^{1}H NMR (400 MHz, $CDCl_3$ δ 5.67 (ddd, J = 17.02, 10.14, 8.09 Hz, 1H), 5.15 (dd, J = 17.02, 0.85 Hz, 1H), 5.04 (dd, *J* = 10.14, 0.85 Hz, 1H), 3.83 (dd, *J* = 11.71, 6.52 Hz, 1H), 3.63- 3.57 (m, 3H), 3.30 (br s, 2H), 1.63-1.51 (m, 1H), 0.83 (dd, *J* = 8.09, 5.43 Hz, 1H), 0.65 (t, *J* = 5.43 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 136.2, 115.9, 69.1, 64.4, 30.5, 25.2, 15.5.

*(2-Vinylcyclopropane-1,1-diyl)bis(methylene)dibenzoate (**1v**):* It was prepared from the following literature report.[28a] A solution of 200 mg (1.6 mmol) of (2-vinylcyclopropane-1,1-diyl)dimethanol **S1** in 5 mL of pyridine stirred at 0 °C under protection from moisture was treated with 15.2 mL (680 mg, 4.8 mmol) of benzoyl chloride (added dropwise over 15 min.). The reaction mixture was stirred at room temperature for 2 h, then treated with 2 mL of H_2O, and stirred overnight. The mixture was concentrated under reduced pressure. The residual oil was dissolved in 50 mL of EtOAc and washed successively with Sat. $CuSO_4$ solution and bicarbonate. The organic phase was dried ($MgSO_4$), filtered, concentrated and purified by column chromatography using 5-10% EtOAc and hexane to obtain compound **1v** as colorless oil in 77% yield (410 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (dd, *J* = 7.0, 1.4 Hz, 4H), 7.55 (dd, *J* = 14.8, 7.2 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 4H), 5.83 – 5.68 (m, 1H), 5.24 (d, *J* = 16.9 Hz, 1H), 5.12 (d, *J* = 10.4 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.36 (dt, *J* = 17.5, 11.8 Hz, 3H), 1.87 (dd, *J* = 14.5, 7.5 Hz, 1H), 1.16 (dd, *J* = 8.4, 5.5 Hz, 1H), 0.97 (t, *J* = 5.8 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 166.5, 134.9, 133.0, 132.9, 130.1, 130.0, 129.6, 128.3, 128.3, 116.9, 69.1, 65.3, 25.8, 25.7, 15.9.

*(2-Vinylcyclopropane-1,1-diyl)bis(methylene)diacetate (**1w**):* It was prepared from the following the literature reports.[28b] A 25 mL of two neck round bottom flask was dried by heat gun under nitrogen atmosphere. After nitrogen was filled, to the solution of (2-vinylcyclopropane-1,1-diyl)dimethanol **S1**

(150 mg, 1.2 mmol) in pyridine (0.6 mL) was added anhydrous acetic anhydride (1.5 mL) dropwise slowly. The resulting mixture was stirred at rt for 24 hours. After cooling to 0 °C, 4 mL of H_2O was added slowly. The reaction mixture was filtered and extracted with DCM (4 x 10 mL). The combined organic layer was washed successively with sat. aq. $CuSO_4$ (10 mL), 5% HCl (10 mL), sat. aq. $NaHCO_3$ (10 mL), and brine (10 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by column chromatography using 5-10% EtOAc and hexane to obtain compound **1w** in 53% yield (135 mg)**;** ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.63 (ddd, *J* = 10.6, 8.9, 5.7 Hz, 1H), 5.15 (d, *J* = 16.8 Hz, 1H), 5.07 (d, *J* = 10.6 Hz, 1H), 4.20 (d, *J* = 12.0 Hz, 1H), 4.07 (d, *J* = 12.0 Hz, 1H), 3.99 (d, *J* = 12.0 Hz, 1H), 3.93 (d, *J* = 12.0 Hz, 1H), 2.07 (s, 1H), 2.05 (s, 1H), 1.70 – 1.62 (m, 1H), 0.96 (dd, *J* = 8.5, 5.5 Hz, 1H), 0.78 (t, *J* = 5.5 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 171.1, 134.9, 116.8, 68.2, 64.2, 25.5, 25.4, 20.9, 20.8, 15.6.

*4,4'-(Vinylcyclopropane1,1diyl)bis(methylene)bis(oxy))bis(methylene)bis((trifluoro-methyl)benzene) (**1x**):* A 25 mL of two neck round bottom flask was dried using heat gun under Argon atmosphere. Added 3 equivalents of NaH (55% washed with pentane) and argon back filed for 3 times. Reaction mixture was cooled to 0 °C then 200 mg (1.56 mmol) of (2-vinylcyclopropane-1,1-diyl)dimethanol **S1** in DMF (5 mL) added slowly, stirred for 15 min. Then add 1-(bromomethyl)-4-(trifluoromethyl)benzene 1.1 g (4.5 mmol) in DMF added dropwise over 15 min. Stirred at rt for overnight. Reaction quenched by addition of water, extracted with 2 x 10 mL ethyl acetate, the organic layer washed with H_2O (4 x 10 mL) and brine respectively. Combined organic layer was dried over Na_2SO_4, evaporated the solvent and purified by column chromatography using 5% EtOAc and hexane as eluent to obtained product **1x** in 78% yield (520 mg); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.9 Hz, 4H), 7.42 (d, *J* = 7.9 Hz, 4H), 5.74 – 5.55 (m, 1H) 5.15 (d, *J* = 16.5 Hz, 1H), 5.05 (d, *J* = 10.0 Hz, 1H), 4.56 (s, 2H), 4.54 (d, *J* = 2.9 Hz, 2H), 3.68 (d, *J* = 10.1 Hz, 1H), 3.62 (d, *J* = 9.8 Hz, 1H), 3.42 (d, *J* = 10.1 Hz, 1H), 3.34 (d, *J* = 9.8 Hz, 1H), 1.59 (dd, *J* = 15.0, 8.4 Hz, 1H), 0.93 (dd, *J* = 8.4, 5.2 Hz, 1H), 0.71 (t, *J* = 5.2 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 142.6, 136.1, 127.5, 127.4, 126.9 (q, 272 Hz), 125.3, 125.2, 125.2, 115.7, 74.5, 72.1, 72.0, 70.1, 27.3, 25.0, 15.3. ^{19}F NMR (471 MHz, $CDCl_3$): δ -62.54 (s, 6F). IR data (KBr, in cm^{-1}): 1399, 1330, 1190, 1123. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{23}F_6O_2$ 445.1597; Found: 445.1597.

*(2-Vinylcyclopropane-1,1-diyl)bis(methylene)bis(2,2-dimethylpropanoate) (**1y**):* A 25 mL of round bottom two neck flask was dried by heat gun under Argon atm. Added 20 mol% of DMAP and argon back filed for 3 times. Then 1.0 mL of pyridine was added and cooled to 0 °C followed by 200 mg (1.56 mmol) of (2-vinylcyclopropane-1,1-diyl)dimethanol in DCM (5 mL) was added slowly and stirred for 15 min. Next *tert*-butyl acetyl chloride (40.7 mmol) in DCM was added drop wise over 15 min. Reaction mixture was stirred overnight at room temperature, Reaction mixture was diluted with DCM, washed with

$CuSO_4$, brine solution and dried over Na_2SO_4. Solvent was evaporated under reduced pressure and purified by flash column chromatography using 5% EtOAc and hexane as eluent. Compound **1y** was obtained as a colorless liquid in 89% yield (410 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.67 – 5.54 (m, 1H), 5.14 (d, *J* = 16.8 Hz, 1H), 5.04 (dd, *J* = 9.2, 8.1 Hz, 1H), 4.20 (d, *J* = 12 Hz, 1H), 4.11 (d, *J* = 11.5 Hz, 1H), 3.91 (dd, *J* = 11.7, 7.3 Hz, 2H), 1.65 (dd, *J* = 14.3, 7.5 Hz, 1H),1.25 (s, 9H), 1.20 (s, 9H), 1.01 – 0.93 (m, 1H), 0.77 (t, *J* = 5.7 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 178.4, 174.0, 135.1, 116.5, 67.5, 64.1, 40.2, 38.9, 38.8, 27.1, 26.5, 25.8, 25.1, 15.6. IR data (KBr, in cm^{-1}): 1813, 1729, 1483, 1403, 1281, 1141, 1001, 604. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{17}H_{29}O_4$ 297.2060; Found: 297.2059.

General procedure for the allylic trifluoromethylation of vinylcyclopropanes: To an oven dried borosilicate test tube equipped with a magnetic stir bar was added VCP (0.15 mmol, 1 eq.), CF_3SO_2Na (0.3 mmol, 2 eq.) and 10 mol% photocatalyst T(*p*-CH_3)PPT (6.6 mg, 0.1 eq.). The reaction tube was vacuumed and backfilled with argon (3 times) and put a septum over the reaction tube. Next, 90 µL AcOH (10 eq.) and 2 mL of DCE was added through the septum by a syringe, and placed approximately 5 cm from light setup. After 6 h of the reaction, 10 mL of water was added and extracted with DCM (3 x 20 mL). The combined organic layer was dried over Na_2SO_4 and solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel (mesh 230-400) using hexane and EtOAc as an eluent to afford the corresponding allylic trifluoromethylated product.

Spectral data of allylic trifluoromethyl derivatives:

*(E)-(6,6,6-Trifluorohex-3-ene-1,1-diyldisulfonyl)dibenzene (**2a**):* White solid, (mp: 98-102 °C), dr (13 : 1); (57.2 mg, yield 91%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.91 (m, 4H), 7.68 (t, *J* = 7.6 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 4H), 5.80 – 5.66 (m, 1H), 5.46 – 5.30 (m, 1H), 4.50 (t, *J* = 6.0 Hz, 1H), 2.93 (t, *J* = 6.3 Hz, 2H), 2.77 – 2.65 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 137.6, 134.7, 131.4, 129.5, 129.4, 129.2, 129.1, 125.5 (q, *J* = 276.8 Hz), 122.4 (d, *J* = 3.2 Hz), 83.0, 36.9 (q, *J* = 29.9 Hz), 28.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.04 (t, *J* = 10.7 Hz). FT-IR (KBr, in cm^{-1}): 3171, 2935, 2853, 1816, 1585, 1480, 1379, 1328, 1311, 1293, 1270, 1254, 1203, 1112, 1081, 997, 970, 940, 895, 841, 740, 688, 646. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{18}F_3O_4S_2$ 419.0593; Found: 419.0590.

*(E)-4,4'-(6,6,6-Trifluorohex-3-ene-1,1-diyldisulfonyl)bis(chlorobenzene) (**2b**):* White solid, (mp: 90-92 °C), dr (12 : 1); (57.3 mg; yield 79%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.7 Hz, 4H), 7.56 (d, *J* = 8.5 Hz, 4H), 5.83 – 5.71 (m, 1H), 5.51 – 5.35 (m, 1H), 4.45 (t, *J* = 6.1 Hz, 1H), 2.91 (t, *J* = 6.5 Hz, 2H), 2.84 – 2.68 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 141.9, 135.8, 131.1, 131.1, 129.6, 129.5, 125.5 (q, *J* = 276.8 Hz), 122.9 (d, *J* = 3.1 Hz), 83.4, 37.0 (q, *J* = 30.0 Hz), 28.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.08 (t, *J* = 10.6 Hz). FT-IR (KBr, in cm^{-1}): 3093, 2904, 1577, 1475, 1429, 1397, 1334, 1321, 1296, 1261, 1247, 1215, 1198, 1176, 1089, 1057, 1012, 762, 711, 655. HRMS (ESI-TOF) m/z: [M -

H]$^+$ calcd for $C_{18}H_{14}Cl_2F_3O_4S_2$ 484.9688; Found: 484.9677.

*(E)-4,4'-(6,6,6-Trifluorohex-3-ene-1,1-diyldisulfonyl)bis(methylbenzene) (**2c**):* Semi solid, dr (11 : 1); (54.3 mg, yield 81%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.3 Hz, 4H), 7.36 (d, *J* = 8.1 Hz, 4H), 5.85 – 5.63 (m, 1H), 5.42 – 5.29 (m, 1H), 4.40 (t, *J* = 5.8 Hz, 1H), 2.90 (t, *J* = 6.5 Hz, 2H), 2.81 – 2.64 (m, 2H), 2.46 (s, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 146.1, 146.0, 134.7, 131.8, 129.8, 129.7, 129.7, 129.6, 125.6 (q, *J* = 276.7 Hz), 122.3 (d, *J* = 3.2 Hz), 83.3, 37.0 (q, *J* = 29.9 Hz), 28.8, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.16 (t, *J* = 10.6 Hz). FT-IR (KBr, in cm^{-1}): 3103, 3072, 3011, 2944, 2843, 1597, 1579, 1497, 1464, 1443, 1416, 1332, 1301, 1266, 1151, 1080, 1050, 1022, 971, 863, 805, 764, 724, 703, 674, 625. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{20}H_{22}F_3O_4S_2$ 447.0906; Found: 447.0901.

*(E)-4,4'-(6,6,6-Trifluorohex-3-ene-1,1-diyldisulfonyl)bis(methoxybenzene (**2d**):* White solid, (mp: 97-98 °C), dr (13 : 1); (55.3 mg, yield 77%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 9.0 Hz, 4H), 7.01 (d, *J* = 9.0 Hz, 4H), 5.95 – 5.62 (m, 1H), 5.52 – 5.24 (m, 1H), 4.37 (t, *J* = 5.9 Hz, 1H), 3.90 (s, 6H), 2.89 (t, *J* = 6.3 Hz, 2H), 2.81 – 2.68 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, CDCl3): δ 164.5, 132.0, 132.0, 128.9, 125.6 (q, *J* = 276.6 Hz), 122.1 (d, *J* = 3.1 Hz), 114.4, 114.3, 83.5, 55.7, 37.0 (q, *J* = 29.9 Hz), 29.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.13 (t, *J* = 10.7 Hz). FT-IR (KBr, in cm^{-1}): 3103, 3072, 3011, 2944, 2843, 1597, 1579, 1497, 1464, 1443, 1416, 1332, 1301, 1266, 1151, 1080, 1050, 1022, 971, 863, 805, 764, 724, 703, 674, 625. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{20}H_{22}F_3O_6S_2$ 479.0804; Found: 479.0799.

*(E)-Dimethyl-2-(5,5,5-trifluoropent-2-en-1-yl)malonate (**2e**):* Colorless liquid, dr (27 : 1); (61.2 mg, yield 80%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73 – 5.60 (m, 1H), 5.49 (dt, *J* = 15.2, 7.0 Hz, 1H), 3.72 (s, 6H), 3.44 (t, *J* = 7.5 Hz, 1H), 2.75 (qd, *J* = 10.7, 7.4 Hz, 2H), 2.64 (t, *J* = 7.1 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 169.0, 133.2, 125.7 (q, *J* = 276.6 Hz), 121.3 (d, *J* = 3.5 Hz), 52.5, 51.2, 37.2 (q, *J* = 29.8 Hz), 31.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.56 (t, *J* = 10.7 Hz). FT-IR (KBr, in cm^{-1}): 1737, 1436, 1402, 1261, 1146, 605. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{10}H_{14}F_3O_4$ 255.0839; Found: 255.0839.

*(E)-Diethyl-2-(5,5,5-trifluoropent-2-en-1-yl)malonate (**2f**):* Colorless oil, dr (22 : 1); (67.1 mg, yield 79%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 – 5.57 (m, 1H), 5.59 – 5.31 (m, 1H), 4.18 (qd, *J* = 7.2, 2.3 Hz, 4H), 3.39 (t, *J* = 7.5 Hz, 1H), 2.75 (qd, *J* = 10.6, 7.3 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 6H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 168.7, 133.4, 125.7 (q, *J* = 276.4 Hz), 121.0 (d, *J* = 3.5 Hz), 61.5, 51.5, 37.2 (q, *J* = 29.8 Hz), 31.6, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.54 (t, *J* = 10.7 Hz). FT-IR (KBr, in cm^{-1}): 3099, 3034, 2983, 2932, 2874, 1722, 1643, 1597, 1496, 1479, 1459, 1437, 1397, 1370, 1325, 1082, 1015, 878, 668. HRMS (ESI-TOF) m/z: [M + H]$^+$ calcd for $C_{12}H_{18}F_3O_4$ 283.1152; Found: 283.1148.

*(E)-Diisopropyl-2-(5,5,5-trifluoropent-2-en-1-yl)malonate (**2g**):* Colorless oil, dr (22 : 1); (78.1 mg, yield 84%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.76 – 5.63 (m, 1H), 5.48 (dt, *J* = 15.3, 3.9 Hz, 1H), 5.10 – 4.98 (m, 2H), 3.33 (t, *J* = 7.6 Hz, 1H), 2.83 – 2.67 (m, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 1.23 (d, *J* = 6.4 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 168.2, 133.6, 125.8 (q, *J* = 276.5 Hz), 120.8 (d, *J* = 3.4 Hz), 69.0, 51.9, 31.4, 37.2 (q, *J* = 29.8 Hz), 21.6, 21.5. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.49 (t, *J* = 10.6 Hz). FT-IR (KBr, in cm^{-1}): 2985, 2936, 2881, 1747, 1731, 1471, 1432, 1374, 1340, 1272, 1253, 1178, 1139, 1105, 1057, 972, 911, 844, 824, 647. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{14}H_{21}F_3O_4Na$ 333.1284; Found: 333.1280.

*(E)-Di-tert-butyl-2-(5,5,5-trifluoropent-2-en-1-yl)malonate (**2h**):* Colorless oil, dr (17 : 1); (48.2 mg, yield 95%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 – 5.58 (m, 1H), 5.55 – 5.39 (m, 1H), 3.19 (t, *J* = 7.6 Hz, 1H), 2.81 – 2.67 (m, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 1.43 (s, 18H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 168.1, 133.9, 125.8 (q, *J* = 276.3 Hz), 120.4 (d, *J* = 3.3 Hz), 81.6, 53.3, 37.2 (q, *J* = 29.8 Hz), 31.5, 27.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.46 (t, *J* = 10.7 Hz). FT-IR (KBr, in cm^{-1}): 2982, 2935, 1728, 1481, 1460, 1433, 1395, 1371, 1344, 1255, 1140, 1058, 971, 848, 745, 646. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{16}H_{25}F_3O_4Na$ 361.1597; Found: 361.1591.

*(E)-Dibenzyl-2-(5,5,5-trifluoropent-2-en-1-yl)malonate (**2i**):* Colourless oil, dr (18 : 1); (48.2 mg, yield 79%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.27 (m, 10H), 5.71 – 5.58 (m, 1H), 5.52 – 5.39 (m, 1H), 5.16 (d, *J* = 2.1 Hz, 4H), 3.55 (t, *J* = 7.4 Hz, 1H), 2.76 – 2.62 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 168.3, 135.2, 133.0, 128.5, 128.4, 128.2, 125.7 (q, *J* = 276.7 Hz), 121.3 (d, *J* = 3.5 Hz), 67.2, 51.5, 37.1 (q, *J* = 29.7 Hz), 31.6. ^{19}F NMR (376 MHz, $CDCl_3$): δ -66.39 (t, *J* = 10.6 Hz). FT-IR (KBr, in cm^{-1}): 3089, 3066, 2915, 1728, 1671, 1638, 1596, 1446, 1320, 1289, 1208, 1159, 1144, 1084, 755, 724, 688, 665. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{22}H_{22}F_3O_4$ 407.1470; Found: 407.1468.

*(E)-Methyl-7,7,7-trifluoro-2-(phenylsulfonyl)hept-4-enoate (**2j**):* Colorless oil, dr (10 : 1); (37.3 mg, yield 74%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, *J* = 7.4 Hz, 2H), 7.70 (t, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 2H), 5.63 – 5.44 (m, 2H), 4.00 (dd, *J* = 11.4, 3.9 Hz, 1H), 3.63 (s, 3H), 2.88 – 2.50 (m, 4H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 165.6, 136.8, 134.5, 130.9, 129.3, 129.2, 129.1, 125.5 (q, *J* = 276.4 Hz), 122.8 (d, *J* = 3.4 Hz), 69.9, 52.9, 37.1 (q, *J* = 29.9 Hz), 29.8. 19F NMR (376 MHz, $CDCl_3$): δ –66.45 (t, *J* = 10.6 Hz). FT-IR (KBr, in cm^{-1}): 2987, 1741, 1641, 1447, 1372, 1326, 1270, 1204, 1139, 1084, 1057, 1036, 974, 916, 861, 841, 761, 741, 723, 689, 649. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{16}F_3O_4S$ 337.0716; Found: 337.0710.

*(E)-1,3-Diphenyl-2-(5,5,5-trifluoropent-2-en-1-yl)propane-1,3-dione (**2k**):* White solid, mp: 49-51 °C, dr (8 : 1); (39.5 mg, yield 76%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (dd, *J* = 9.1, 2.0 Hz, 4H), 7.57

(dt, *J* = 8.4, 1.3 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 4H), 5.78 (dt, *J* = 14.5, 7.1 Hz, 1H), 5.53 – 5.42 (m, 1H), 5.30 (t, *J* = 6.7 Hz, 1H), 2.88 (t, *J* = 7.0 Hz, 2H), 2.71 (qd, *J* = 10.7, 7.9 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 195.4, 135.8, 134.4, 133.6, 128.9, 128.5, 125.7 (q, *J* = 276.5 Hz), 120.7 (d, *J* = 3.3 Hz), 56.5, 37.1 (q, *J* = 29.8 Hz), 32.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.35 (t, *J* = 10.7 Hz). FT-IR (KBr, in cm^{-1}): 2956, 1743, 1688, 1597, 1581, 1451, 1435, 1344, 1269, 1253, 1137, 1058, 975, 847, 782, 739, 691, 646. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{20}H_{18}F_3O_2$ 347.1253; Found: 347.1248.

*(E)-Methyl-2-benzoyl-7,7,7-trifluorohept-4-enoate (**2l**):* Colorless oil, dr (9 : 1); (39.7 mg, yield 88%); ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.57 (dd, *J* = 9.1, 5.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 5.78 – 5.62 (m, 1H), 5.61 – 5.38 (m, 1H), 4.41 (t, *J* = 7.2 Hz, 1H), 3.65 (s, 3H), 2.81 – 2.62 (m, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 194.1, 169.6, 135.9, 133.7, 133.6, 128.7, 128.5, 125.7 (d, *J* = 276.5 Hz), 120.9 (d, *J* = 3.5 Hz), 53.4, 52.4, 37.0 (q, *J* = 29.8 Hz), 31.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.51 (t, *J* = 10.7 Hz). FT-IR (KBr, in cm^{-1}): 3034, 2981, 2933, 1720, 1644, 1599, 1497, 1434, 1397, 1369, 1325, 1288, 1211, 1132, 1081, 1016, 988, 949, 904, 877, 841, 818, 731, 706, 668. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{15}H_{16}F_3O_3$ 301.1046; Found: 301.1043.

(*E)-2-Benzoyl-7,7,7-trifluorohept-4-enenitrile (**2m**):* Colorless oil, dr (8 : 1); (56.8 mg, yield 71%); ^1H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 1.6 Hz, 2H), 7.67 (t, *J* = 7.9 Hz, 1H), 7.53 (t, *J* = 7.7 Hz, 2H), 5.84 – 5.72 (m, 1H), 5.70 – 5.56 (m, 1H), 4.38 (dd, *J* = 7.9, 6.1 Hz, 1H), 2.93 – 2.69 (m, 4H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 189.8, 134.9, 134.9, 134.0, 131.3, 129.3, 128.9, 125.7 (q, *J* = 276.5 Hz), 123.5 (d, *J* = 3.4 Hz), 116.7, 39.5, 37.3 (q, *J* = 30.0 Hz), 32.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.27 (t, *J* = 10.6 Hz). FT-IR (KBr, in cm^{-1}): 3433, 3094, 3023, 2933, 2864, 1743, 1720, 1589, 1432, 1372, 1334, 1269, 1242, 1126, 1056, 971, 915, 842, 801, 743, 687, 651. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{14}H_{11}F_3NO$ 266.0798; Found: 266.0802.

*(E)-2-(5,5,5-Trifluoropent-2-en-1-yl)malononitrile (**2n**):* Colorless liquid, dr (8 : 1); (47.2 mg, yield 84%); ^1H NMR (400 MHz, $CDCl_3$): δ 5.87 – 5.74 (m, 2H), 3.79 (t, *J* = 6.6 Hz, 1H), 2.99 – 2.84 (m, 2H), 2.78 (t, *J* = 6.1 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 128.2, 126.4 (d, *J* = 3.3 Hz), 125.3 (q, *J* = 276.6 Hz), 111.8, 37.1 (q, *J* = 30.3 Hz), 33.6, 22.9. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.14 (t, *J* = 10.5 Hz). FT-IR (KBr, in cm^{-1}): 2921, 2258, 1721, 1431, 1373, 1343, 1325, 1254, 1212, 1186, 1143, 1059, 976, 911, 845, 649. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_8H_6F_3N_2$ 187.0489; Found: 187.0481.

*(E)-Ethyl-2-cyano-7,7,7-trifluorohept-4-enoate (**2o**):* Colorless oil, dr (10 : 1); (57.2 mg, yield 81%); ^1H NMR (400 MHz, $CDCl_3$): δ 5.76 – 5.66 (m, 1H), 5.66 – 5.54 (m, 1H), 4.22 (q, *J* = 7.3 Hz, 2H), 3.55 (t, *J* = 6.6 Hz, 1H), 2.86 – 2.73 (m, 2H), 2.66 (t, *J* = 6.8 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 165.2, 130.6, 125.5 (q, *J* = 276.6 Hz), 123.4 (d, *J* = 3.1 Hz), 115.8, 62.8, 37.2, 36.9

(q, J = 30.1 Hz), 32.4, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.46 (t, J = 10.6 Hz). FT-IR (KBr, in cm^{-1}): 2988, 2940, 2252, 1746, 1620, 1432, 1371, 1340, 1253, 1211, 1140, 1057, 975, 911, 854, 648. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{10}H_{13}F_3NO_2$ 236.0893; Found: 236.0890.

*(E)-tert-Butyl-7,7,7-trifluoro-2-tosylhept-4-enoate (**2p**):* Colorless oil, dr (39 : 1); (42.3 mg, yield-72%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8.3 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 5.65 – 5.54 (m, 1H), 5.54 – 5.44 (m, 1H), 3.87 (dd, J = 11.4, 3.8 Hz, 1H), 2.81 – 2.57 (m, 4H), 2.46 (s, 3H), 1.34 (s, 9H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 164.1, 145.4, 134.1, 131.3, 129.6, 129.4, 125.6 (q, J = 276.6 Hz), 122.3 (d, J = 3.4 Hz), 37.2 (q, J = 29.9 Hz). 83.5, 70.4, 37.2 (q, J = 29.9 Hz), 29.8, 27.6, 21.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.31 (t, J = 10.6 Hz). FT-IR (KBr, in cm^{-1}): 2975, 2932, 1727, 1599, 1573, 1493, 1456, 1395, 1369, 1319, 1260, 1140, 1111, 1083, 1015, 843, 813, 709, 665, 583. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{18}H_{22}F_3O_4S$ 391.1196; Found: 391.1204.

*(E)-2,2-Dimethyl-5-(5,5,5-trifluoropent-2-en-1-yl)-1,3-dioxane-4,6-dione (**2q**):* White solid, (m.p: 102-104 °C) dr (99 : 1); (68.6 mg, yield 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.83 – 5.69 (m, 1H), 5.67 – 5.57 (m, 1H), 3.59 (t, J = 5.1 Hz, 1H), 2.88 – 2.84 (m, 2H), 2.83 – 2.70 (m, 2H), 1.78 (s, 3H), 1.74 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 164.7, 131.8, 125.7 (d, J = 276.4 Hz), 123.1 (d, J = 3.4 Hz), 105.1, 46.1, 37.2 (q, J = 29.8 Hz), 29.0, 28.3, 26.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.36 (t, J = 10.7 Hz). FT-IR (KBr, in cm^{-1}): 3446, 3098, 3016, 3004, 2988, 1978, 1923, 1874, 1733, 1634, 1584, 1421, 1307, 1205, 1164, 1085, 1065, 1020, 989, 883, 826, 795, 689, 666. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{11}H_{12}F_3O_4$ 265.0693; Found: 265.0695.

*(E)-2-(5,5,5-Trifluoropent-2-en-1-yl)-1H-indene-1,3(2H)-dione (**2r**):* Colorless oil, dr (32 : 1); (31.6 mg, yield 79%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, J = 5.7, 3.1 Hz, 2H), 7.84 (dd, J = 5.7, 3.1 Hz, 2H), 5.70 – 5.60 (m, 1H), 5.55 – 5.45 (m, 1H), 3.10 (t, J = 5.8 Hz, 1H), 2.74 (t, J = 6.5 Hz, 2H), 2.65 (qd, J = 10.6, 7.2 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 199.9, 142.5, 135.7, 132.3, 125.6 (q, J = 276.5 Hz), 123.2, 121.9 (d, J = 3.3 Hz), 53.1, 37.1 (q, J = 29.8 Hz), 29.4. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.60 (t, J = 10.7 Hz). FT-IR (KBr, in cm^{-1}): 3101, 2978, 2930, 1723, 1646, 1460, 1433, 1396, 1369, 1323, 1260, 1210, 1016, 991, 948, 921, 669. HRMS (ESI-TOF) m/z: $[M - H]^+$ calcd for $C_{14}H_{10}F_3O_2$ 267.0638; Found: 267.0641.

*(Z)-Dimethyl-2-(4-(trifluoromethyl)cyclopent-2-en-1-yl)malonate (**2s**):* Colorless liquid, (yield 61%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.99 (d, J = 4.6 Hz, 1H), 5.75 – 5.70 (m, 1H), 3.75 (s, 3H), 3.74 (s, 3H), 3.60 – 3.51 (m, 1H), 3.47 – 3.38 (m, 1H), 3.34 (d, J = 8.5 Hz, 1H), 2.33 – 2.21 (m, 1H), 1.94 (ddd, J = 14.5, 8.5, 5.5 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 168.6, 168.5, 137.7, 127.1 (d, J = 278.5 Hz), 127.0 (d, J = 2.4 Hz), 55.9, 52.6, 49.4 (d, J = 28.6 Hz), 44.9, 29.7, 28.0. ^{19}F NMR (376 MHz,

$CDCl_3$): δ –72.82 (d, *J* = 8.7 Hz). FT-IR (KBr, in cm^{-1}): 1733, 1400, 1119, 601. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{11}H_{14}F_3O_4$ 267.0839; Found: 267.0834.

*(Z)-Dimethyl-2-4-(trifluoromethyl)cyclohex-2-en-1-yl)malonate (**2t**):* Colorless liquid**,** (yield 71%); ^1H NMR (400 MHz, $CDCl_3$): δ 5.83 (d, *J* = 10.3 Hz, 1H), 5.70 (d, *J* = 10.0 Hz, 1H), 3.74 (s, 3H), 3.74 (s, 3H), 3.30 (d, *J* = 8.2 Hz, 1H), 3.00 – 2.79 (m, 1H), 2.08 – 1.87 (m, 1H), 1.63 (dd, *J* = 10.7, 2.4 Hz, 2H), 1.40 (tdd, *J* = 13.1, 10.6, 2.6 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 168.4, 168.4, 132.5, 126.9 (q, *J* = 279.0 Hz), 122.6 (d, *J* = 2.8 Hz), 40.4 (q, *J* = 27.3 Hz), 56.0, 52.5, 35.3, 24.9, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ –72.94 (d, *J* = 8.7 Hz). FT-IR (KBr, in cm^{-1}): 1739, 1435, 1338, 1253, 1151, 605. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{16}F_3O_4$ 281.0995; Found: 281.0997.

(Z)-Dimethyl-2-(4-(trifluoromethyl)cyclooct-2-en-1-yl)malonate (**2u***):* Colorless liquid, (yield 67%); ^1H NMR (400 MHz, $CDCl_3$): δ 5.68 (dd, *J* = 12.1, 6.1 Hz, 1H), 5.50 (ddd, *J* = 12.2, 6.9, 1.2 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.42 (d, *J* = 7.1 Hz, 1H), 3.39 – 3.18 (m, 2H), 1.93 – 1.60 (m, 8H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 168.8, 168.6, 133.2, 127.4 (q, *J* = 279.3 Hz), 123.6 (d, *J* = 2.4 Hz), 57.2, 52.5, 43.0 (q, *J* = 25.8 Hz).39.5, 29.7, 29.5, 25.5, 25.5, 23.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ –72.63 (d, *J* = 8.8 Hz). FT-IR (KBr, in cm^{-1}): 1738, 1434, 1394, 1265, 1165, 606. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{14}H_{20}F_3O_4$ 309.1308; Found: 309.1300.

*(E)-2-(5,5,5-Trifluoropent-2-en-1-yl)propane-1,3-diyl-dibenzoate (**3a**):* Colorless liquid dr (7: 1); (87.7 mg, yield 72%); ^1H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 7.6 Hz, 4H), 7.56 (t, *J* = 7.5 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 4H), 5.83 – 5.73 (m, 1H), 5.60 – 5.47 (m, 1H), 4.43 (ddd, *J* = 25.4, 11.3, 5.6 Hz, 4H), 2.89 – 2.71 (m, 2H), 2.43 (ddd, *J* = 11.2, 7.8, 3.3 Hz, 1H), 2.37 (t, *J* = 7.0 Hz, 2H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 166.4, 134.3, 133.1, 129.9, 129.6, 128.4, 125.8 (q, *J* = 276.7 Hz), 121.0 (d, *J* = 3.4 Hz), 64.4, 37.6, , 37.3 (q, *J* = 29.8 Hz), 31.7. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.43 (t, *J* = 10.7 Hz). FT-IR (KBr, in cm^{-1}): 3065, 3034, 2956, 2897, 2853, 1723, 1603, 1586, 1493, 1451, 1375, 1314, 1270, 1175, 1135, 1111, 1069, 1025, 971, 842, 802, 710, 688, 651. HRMS (ESI-TOF) m/z: $[M + Na]^+$ calcd for $C_{22}H_{21}F_3O_4Na$ 429.1284; Found: 429.1279.

*(E)-2-(5,5,5-Trifluoropent-2-en-1-yl)propane-1,3-diyl-diacetate (**3b**):* Colorless liquid, dr (8 : 1); (64.5 mg, yield 76%); ^1H NMR (400 MHz, $CDCl_3$): δ 5.79 – 5.58 (m, 1H), 5.57 – 5.33 (m, 1H), 4.05 (qd, *J* = 11.2, 5.6 Hz, 4H), 3.05 – 2.41 (m, 2H),2.20 – 2.08 (m, 3H), 2.06 (s, 6H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ 170.9, 134.3, 125.8 (q, *J* = 276.7 Hz), 120.8 (d, *J* = 3.2 Hz), 63.7, 37.3 (q, *J* = 29.6 Hz), 37.1, 31.4, 20.8. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.61 (t, *J* = 10.7 Hz). FT-IR (KBr, in cm^{-1}): 1736, 1403, 1134, 603. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{12}H_{18}F_3O_4$ 283.1152; Found: 283.1149.

(E)-4,4'-(((2-(5,5,5-Trifluoropent-2-en-1-yl)propane-1,3-diyl)bis(oxy))bis(methylene))bis

((trifluoromethyl)benzene) **(3c):** Colorless liquid, dr (37 : 1); (128.mg, yield 83%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.1 Hz, 4H), 7.42 (d, *J* = 8.0 Hz, 4H), 5.77 – 5.60 (m, 1H), 5.50 – 5.32 (m, 1H), 4.54 (s, 4H), 3.56 – 3.46 (m, 4H), 2.82 – 2.67 (m, 2H), 2.23 (t, *J* = 7.0 Hz, 2H), 2.05 (dt, *J* = 12.5, 6.3 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 142.6, 135.7, 127.4, 126.0 (q, J = 277.7 Hz), 125.5 (q, J = 276 Hz), 125.3(d, J = 3.6 Hz), 119.8 (d, *J* = 3.2 Hz), 72.3, 70.4, 39.3, 37.3 (d, *J* = 29.6 Hz), 31.7. ^{19}F NMR (471 MHz, $CDCl_3$): δ –62.54 (6F, s), –66.65 (3F, t, *J* = 10.1 Hz). FT-IR (KBr, in cm^{-1}): 1406, 1329, 1253, 1134, 601. HRMS (ESI-TOF) m/z: [M + H]+ calcd for $C_{24}H_{24}F_9O_2$ 515.1627; Found: 515.1628.

*(E)-2-(5,5,5-Trifluoropent-2-en-1-yl)propane-1,3-diyl bis(2,2-dimethylpropanoate)) (**3d**):* Colorless liquid, dr (6 : 1); (75.9 mg, yield- 69%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.73 – 5.63 (m, 1H), 5.49 – 5.40 (m, 1H), 4.03 (qd, *J* = 11.1, 5.4 Hz, 4H), 2.88 – 2.69 (m, 2H), 2.25 – 2.07 (m, 3H), 1.19 (s, 18H). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$): δ 178.3, 134.3, 126.1 (q, 280.78 Hz), 120.8 (d, *J* = 3.6 Hz). 63.3, 37.3, 38.8,37.3 (q, 24.24 Hz), 31.5, 27.1. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.62 (t, *J* = 10.7 Hz). FT-IR (KBr, in cm^{-1}): 1734, 1411, 1387, 1164, 1077, 600. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{30}F_3O_4$ 367.2091; Found: 367.2082.

Procedure for the further functionalization of allylic trifluoromethylated product:

*2-(2,2-bis(Phenylsulfonyl)ethyl)-3-(2,2,2-trifluoroethyl)oxirane (**4a**):* To an oven dried two neck round bottom flask, add **2a** (0.2 mmol, 84 mg) in Argon atmosphere. Next 5 mL of $CHCl_3$ added and cooled in ice bath, then freshly recrystallized 75% *m*-CPBA (0.5 mmol, 86 mg) in $CHCl_3$ was added over 15 min. then allowed to the room temperature for overnight. The reaction mixture was concentrated on rotor vapor and purified by column chromatography. The the compound **4a** was isolated as colorless liquid in 64% yield (55.6 mg), dr (4 : 1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (dd, *J* = 14.3, 7.4 Hz, 4H), 7.70 (td, *J* = 7.6, 2.9 Hz, 2H), 7.60 – 7.51 (m, 4H), 4.61 (dd, *J* = 6.9, 4.8 Hz, 1H), 3.22 (td, *J* = 5.7, 1.8 Hz, 1H), 2.92 (ddd, *J* = 6.6, 4.9, 1.7 Hz, 1H), 2.54 – 2.25 (m, 4H). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ 137.6, 137.0, 134.8, 129.6, 129.4, 129.3, 129.3, 129.3, 125.5 (d, *J* = 274.2 Hz), 80.5, 54.3, 53.1 (d, *J* = 3.9 Hz), 36.8 (q, *J* = 29.1 Hz), 28.3. ^{19}F NMR (376 MHz, $CDCl_3$): δ –64.34 (t, *J* = 10.4 Hz). FT-IR data (KBr, in cm^{-1}): 3101, 2978, 2930, 1496, 1478, 1396, 1323, 1260, 1134, 1082, 903, 880, 841, 818, 730, 669. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd For $C_{18}H_{18}F_3O_5S_2$ 435.0542; Found: 435.0538.

*(6,6,6-Trifluorohexane-1,1-diyldisulfonyl)dibenzene (**4b**):* To an oven dried two neck round bottom flask, added **2a** (0.2 mmol, 84 mg) in Ar atm. followed by 5 mol% Pd-C, 8 eq. AcOH and 5 mL of isopropanol. Finally added 8 eq. of $NaBH_4$ in one portion and reaction was monitored by TLC. Reaction was quenched using 2 N HCl, extract with EtOAc (2 x 10 mL), concentrated under vacuum and purified by column chromatography using 5-10% EtOAc and hexane as eluent, the compound **4b** isolated as Colorless liquid in 95% yield(79.8 mg) which can become solid in low temperatures. White solid, mp: 34-

35 °C, (yield 95%) ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 8.3, 1.3 Hz, 4H), 7.73 – 7.66 (m, 2H), 7.57 (t, *J* = 7.7 Hz, 4H), 4.38 (t, *J* = 5.6 Hz, 1H), 2.19 (dt, *J* = 7.9, 7.5 Hz, 2H), 2.08 – 1.95 (m, 2H), 1.67 (dt, *J* = 11.9, 7.7 Hz, 2H), 1.57-1.41 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 137.7, 134.676, 129.5, 129.2, 126.8 (q, *J* = 276.3 Hz), 83.2, 33.1 (q, *J* = 28.7 Hz), 27.0, 25.3, 21.5 (d, *J* = 2.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.22 (t, *J* = 10.8 Hz). FT- IR data (KBr, in cm^{-1}): 2923, 2259, 1720, 1432, 1372, 1340, 1323, 1253, 1210, 1187, 1142, 1059, 972, 910, 848, 648. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{20}F_3O_4S_2$ 421.075; Found: 421.0747.

*(E)-Ethyl-9,9,9-trifluoro-4,4-bis(phenylsulfonyl)non-6-enoate (**4c**):* To an oven dried two neck round bottom flask, added NaH (1.5 eq.) and cooled to 0 °C then **2a** (0.2 mmol, 84 mg) in THF (5 mL) was added under Ar atm. Then ethyl acrylate (3. eq.) in THF added drop wise over 10 min and allowed the reaction to stir at rt for 48 h. The reaction was quenched by addition of the 5 mL water. Organic part separated and washed with brine, dried over Na_2SO_4 and concentrated under vacuum. Product was purified by column chromatography using 10-15% EtOAc and hexane as eluent. The compound **4c** was isolated as a colorless liquid in 76% yield (78.9 mg), dr (10 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, *J* = 7.7 Hz, 4H), 7.73 (t, *J* = 7.3 Hz, 2H), 7.60 (t, *J* = 7.8 Hz, 4H), 5.97 – 5.83 (m, 1H), 5.59 – 5.50 (m, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.99 (d, *J* = 6.6 Hz, 2H), 2.87 – 2.73 (m, 4H), 2.58 – 2.51 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 172.0, 136.6, 135.0, 134.9, 131.4, 129.5, 128.9, 125.7 (q, J = 276.3 Hz), 124.4 (d, *J* = 3.6 Hz), 89.5, 60.9, 37.4 (q, *J* = 30.0 Hz), 33.2, 28.8, 25.3, 25.2, 14.2. ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.11 (t, *J* = 10.6 Hz). FT-IR data (KBr, In cm^{-1}): 3074, 2984, 2925, 2850, 1734, 1582, 1448, 1380, 1335, 1313, 1253. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{23}H_{26}F_3O_6S_2$ 519.1117; Found: 519.1102.

*(E)-(1-Bromo-6,6,6-trifluorohex-3-ene-1,1-diyldisulfonyl)dibenzene (**4d**):* To oven dried 20 mL round bottom flask charged with magnetic stirred, added **2a** (0.2 mmol) in 1:1 THF followed by water and NBS (0.3 mmol, 1.5 eq.). The reaction stirred for overnight and workup with ethyl acetate (2 x 10 mL), the combined organic layer was washed with $NaHCO_3$, brine and dried over Na_2SO_4. Organic layer was concentrated under reduced pressure and purified by column chromatography using 5-10% EtOAc and hexane as eluent. The compound **4d** was isolated as colorless oil in 58% yield (57.5 mg), dr (15 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (dd, *J* = 8.4, 1.3 Hz, 4H), 7.75 (dd, *J* = 10.8, 4.6 Hz, 2H), 7.60 (t, *J* = 7.9 Hz, 4H), 5.98 – 5.88 (m, 1H), 5.53 (m, 1H), 3.25 (d, *J* = 6.9 Hz, 2H), 2.92 – 2.78 (m, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 135.3, 135.1, 132.1, 129.7, 128.7, 125.6 (d, *J* = 276.8 Hz), 124.1 (d, *J* = 3.2 Hz), 93.5, 38.1, 37.2 (q, *J* = 30.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –66.01 (t, *J* = 10.6 Hz). FT-IR data (KBr, In cm^{-1}): 1748, 1463, 1394, 1294, 1168, 611 HRMS (ESI-TOF) m/z: [M + H]+ calcd for $C_{18}H_{17}BrF_3O_4S_2$ 496.9698; Found: 496.9694.

*(E)-(1-Chloro-6,6,6-trifluorohex-3-ene-1,1-diyldisulfonyl)dibenzene (**4e**):* To an oven dried 20 mL round bottom flask charged with magnetic stirred, added **2a** (0.2 mmol), chloramine T (0.3 mmol, 1.5 eq.) and $PhMe_3NBr$ (0.03 mmol, 0.15 eq.). Argon was back filled for 3 times over 10 min, 5 mL CH_3CN added and stirred for overnight. After finishing of the reaction, filter off the solid, the liquid part concentrated and purified by column chromatography using 5-10% EtOAc and hexane as eluent. The desired compound **4e** was isolated as colorless liquid in 98% yield (88.9 mg), dr (12 : 1). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (dd, *J* = 8.6, 1.2 Hz, 4H), 7.77 – 7.71 (m, 2H), 7.59 (t, *J* = 7.0 Hz, 4H), 5.97 – 5.84 (m, 1H), 5.57 – 5.47 (m, 1H), 3.25 (dd, *J* = 6.7, 1.2 Hz, 2H), 2.84 (td, *J* = 17.8, 10.1 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 135.3, 135.0, 132.1, 131.8, 129.6, 128.8, 128.6, 125.6 (q, *J* = 277.0 Hz), 124.0 (d, *J* = 3.6 Hz), 93.5, 38.1, 37.1 (q, *J* = 30.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$): δ –65.97 (t, *J* = 10.7 Hz). FT-IR data (KBr, In cm^{-1}) 1739, 1434, 1403, 1254, 1160, 608. HRMS (ESI-TOF) m/z: $[M + H]^+$ calcd for $C_{18}H_{17}ClF_3O_4S_2$ 453.0203; Found: 453.0206.

Typical procedure for the gram scale synthesis: To an oven dried 100 mL round bottom flask equipped with a magnetic stir bar was added VCP **1e** (1.10 g, 6 mmol), CF_3SO_2Na (1.87 g, 12 mmol) and 10 mol% photocatalyst T(*p*-CH_3)PPT (262 mg, 0.6 mmol). The reaction tube was vacuumed and backfilled with argon (3 times) and put a septum over the reaction tube. Then 1.8 mL AcOH and 80 mL of DCE was added through the septum by a syringe, and placed approximately 5 cm from light setup. After 6 h of the reaction 50 mL of water was added and extracted with DCM (3 x 50 mL). The combined organic layer was dried over Na_2SO_4 and solvent was removed under reduced pressure. The crude product was then purified by flash column chromatography on silica gel mesh 230-400 using 10% DCM and hexane as an eluent to afford the product **2e** (1.07 g, 71%)

Typical procedure for Control experiment with TEMPO:

To an oven dried borosilicate test tube equipped with a magnetic stir bar was added VCP (0.15 mmol, 1 eq.), CF_3SO_2Na (0.3 mmol, 2 eq.) TEMPO (0.23 mmol, 1.5 eq.) and 10 mol% photocatalyst T(*p*-CH_3)PPT (6.6 mg, 0.1 eq.). The reaction tube was vacuumed and backfilled with argon (3 times) and put a septum over the reaction tube. Next, 90 µL AcOH (10 eq.) and 2 mL of DCE was added through the septum by a syringe, and after 30 min reaction quenched and added $PhCF_3$ (0.15 mmol) to the reaction mixture and taken ^{19}F NMR. Formation of TEMPO-CF_3 adduct **5b** was observed by ^{19}F NMR (376 MHz, $CDCl_3$): as singlet (s, 3F) at δ –55.86 ppm with 31% yield.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the

X-ray crystallographic data of **2a**

Copies of ^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR spectra of known and all new compounds

COSY and NOESY spectra of compound **2s**

AUTHOR INFORMATION

Corresponding Author

suresh@iiserkol.ac.in

pc16rs018@iiserkol.ac.in

kgg15rs014@iiserkol.ac.in

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

Dedicated to Professor Srinivasan Chandrasekaran on the occasion of his 73rd birthday. Financial support from the IISER Kolkata for startup Grant, SERB for Early Carrier Research (ECR) Grant and DST-SERB *for Ramanujan Fellowship* are acknowledged. *PC and KGG* thank *UGC* and *DST for* their PhD fellowship.

REFERENCES

(1) (a) Shimizu, M.; Hiyama, T. Modern Synthetic Methods for Fluorine-Substituted Target Molecules. *Angew. Chem. Int. Ed.* **2005***, 44,* 214-231. (b) Muller, K.; Feah, C.; Diederich, F. Fluorine in Pharmaceuticals: Looking Beyond Intuition. *Science* **2007***, 317*, 1881-1886.

(2) (a) Hagmann, W. K. The Many Roles for Fluorine in Medicinal Chemistry. *J. Med. Chem.* **2008**, *51*, 4359-4369. (b) Muller, K. Unveiling the Mystery and Beauty of Organic Fluorine. *ChemBioChem* **2004**, *5*, 559-562. (c) Purser, S.; Moore, P. R.; Swallow. S.; Gouverneur, V. Fluorine in medicinal chemistry. *Chem. Soc. Rev.* **2008**, *37*, 320-330.

(3) (a) Cho, E. J.; Senecal, T. D.; Kinzel, T.; Zhang, Y.; Watson, D. A.; Buchwald, S. L. The Palladium-Catalyzed Trifluoromethylation of Aryl Chlorides. *Science* **2010**, *328*, 1679-1681. (b) Shimizu, R.; Egami, H.; Nagi, T.; chae, J.; Homashima, Y.; Sodeoka, M. Direct *C*2-trifluoromethylation of indole derivatives catalyzed by copper acetate. *Tetrahedron Lett.* **2010**, *51*, 5947-5949. (c) Zhang, X-G.; Dai, H-X.; Wasa, M.; Yu, J-Q. Pd(II)-Catalyzed Ortho Trifluoromethylation of Arenes and Insights into the Coordination Mode of Acidic Amide Directing Groups. *J. Am. Chem. Soc.* **2012,** *134*, 11948-11951. (d) Wang, X.; Ye, Y.; Ji, G.; Xu, Y.; Zhang, S.; Fang, J.; Zhang, Y.; Wang, J. Copper-Catalyzed Direct C–H Trifluoromethylation of Quinones. *Org. Lett.* **2013**, *15*, 3730-3733. (e) Ye, Y.; Lee, S. H.; Sanford, M. S. Silver-Mediated Trifluoromethylation of Arenes Using $TMSCF_3$. *Org. Lett.* **2011**, *13*, 5464-5467; (f) Hafner, A.; Brase, S. *Ortho*-Trifluoromethylation of Functionalized Aromatic Triazenes. *Angew. Chem. Int. Ed.* **2012,** *51*, 3713-3715.

(4) (a) Furukawa, T.; Nishimine, T.; Tokunaga, E.; Hasegawa, K.; Shiro, M.; Shibata, N. Organocatalyzed Regio- and Enantioselective Allylic Trifluoromethylation of Morita-Baylis-Hillman Adducts Using Ruppert–Prakash Reagent. *Org. Lett.* **2011**, *13*, 3972-3975. (b) Larsson, J. M.; Pathipati, S. R.; Szabó, K. J. Regio- and Stereoselective Allylic Trifluoromethylation and Fluorination using $CuCF_3$ and CuF Reagents. *J. Org. Chem.* **2013***, 78,* 7330-7336. c) Mizuta, S.; G-Lapez, O.; Engle, K. M.; Verhoog, S.; Wheelhouse, K.; Rassias, G.; Gouverneur, V. Trifluoromethylation of Allylsilanes under Copper Catalysis. *Chem. Eur. J*. **2012**, *18*, 8583-8587.

(5) (a) Miyake, Y.; Ota, S-I.; Nishibayashi, Y. Copper-Catalyzed Nucleophilic Trifluoromethylation of Allylic Halides: A Simple Approach to Allylic Trifluoromethylation. *Chem. Eur. J.* **2012**, *18*, 13255-13258; (b) Isanbor, C.; Hagan, D. O. Fluorine in medicinal chemistry: A review of anti-cancer agents. *J. Fluorine Chem*. **2006**, *127*, 303-319.

(6) (a) Parsons, A. T.; Buchwald, S. L. Copper-Catalyzed Trifluoromethylation of Unactivated Olefins. *Angew. Chem. Int. Ed.* **2011***, 50,* 9120-9123;(b) Xu, J.; Fu, Y.; Luo, D-F.; Jiang, Y-Y.; Xiao, B.; Liu, Z-J.; Gong, T-J.; Liu, L. Copper-Catalyzed Trifluoromethylation of Terminal Alkenes through Allylic C–H Bond Activation. *J. Am. Chem. Soc.* **2011**, *133*, 15300-15303. (c) Li, Z-R.; Bao, X-X.; Sun, J.; Shen, J.; Wu, D-Q.; Liu, Y-K.; Deng, Q-H.; Liu, F. Iron-catalyzed trifluoromethylation of vinylcyclopropanes: facile synthesis of CF_3-containing dihydronaphthalene derivatives. *Org. Chem. Front*. **2016**, *3*, 934-938.

(7) (a) Narayanam, J. M. R.; Stephenson, C. R. J. Visible light photoredox catalysis: applications in organic synthesis. *Chem. Soc. Rev.* **2011**, *40*, 102-113. (b) Ischay, M. A.; Du, J.; Yoon, T. P. Visible light photocatalysis as a greener approach to photochemical synthesis. *Nat. Chem.* **2010**, *2*, 527-532. (c) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.* **2013**, *113*, 5322-5363. (d) Koike, T.; Akita, M. Fine Design of Photoredox Systems for Catalytic Fluoromethylation of Carbon–Carbon Multiple Bonds. *Chem. Res.*, **2016**, *49*, 1937–1945.

(8) (a) Kalyanasundaram, K.; Kiwi, J.; Gratzel, M. Hydrogen Evolution from Water by Visible Light, a Homogeneous Three Component Test System for Redox Catalysis. *Helv. Chim. Acta* **1978**, *61*, 2720-2730. (b) Goldsmith, J. I.; Hudson, W. R.; Lowry, M. S.; Anderson, T. H.; Bernhard, S. Discovery and High-Throughput Screening of Heteroleptic Iridium Complexes for Photoinduced Hydrogen Production. *J. Am. Chem. Soc*. **2005**, *127*, 7502-7510. (c) Laskar, I. R.; Chen, T-M. Tuning of Wavelengths: Synthesis and Photophysical Studies of Iridium Complexes and Their Applications in Organic Light Emitting Devices**.** *Chem. Mater*. **2004**, *16*, 111-117. (d) Tsuboyama, A.; Iwawaki, H.; Furugori, M.; Mukaide, T.; Kamatani, J.; Igawa, S.; Moriyama, T.; Miura, S.; Takiguchi, T.; Okada, S.; Hoshino, M.; Ueno, K. Homoleptic Cyclometalated Iridium Complexes with Highly Efficient Red Phosphorescence and Application to Organic Light-Emitting Diode. *J. Am. Chem. Soc.* **2003**, *125*, 12971-12979. (e) Shaw, M. H.; Shurtleff, V. W.; Terrett, J. A.; Cuthbertson, J. D.; Macmillan, D. W. Native functionality in triple catalytic cross-coupling: sp^3 C–H bonds as latent nucleophiles. *Science* **2016**, *352*, 1304-1308. (f) Lu, Z.; Yoon, T. P. Visible Light Photocatalysis of [2+2] Styrene Cycloadditions *via* Energy Transfer. *Angew. Chem. Int. Ed.* **2012**, *51*, 10329-10332.

(9) Greenwood, N. N.; A. Earnshaw, A. *Chemistry of the Elements. 1071-1113.* ISBN: 9780080501093.

(10) (a) Nguyen, T. M.; Manohar, N.; Nicewicz, D. A. *anti*-Markovnikov hydroamination of alkenes catalyzed by a two-component organic photoredox system: direct access to phenethylamine derivatives. *Angew. Chem. Int. Ed.* **2014**, *53*, 6198-6201. (b) Hamilton, D. S.; Nicewicz, D. A. Direct Catalytic *anti*-Markovnikov Hydroetherification of Alkenols. *J. Am. Chem. Soc.* **2012**, *134*, 18577-18580.

(11) (a) Gesmundo, N. J.; Nicewicz, D. A. Cyclization-endoperoxidation cascade reactions of dienes mediated by a pyrylium photoredox catalyst. *Beilstein J. Org. Chem.* **2014**, *10*, 1272-1281. (b) Wang, K.; Meng, L-G.; Wang, L. Visible-Light-Promoted [2 + 2 + 2] Cyclization of Alkynes with Nitriles to Pyridines Using Pyrylium Salts as Photoredox Catalysts. *Org. Lett*. **2017**, *19*, 1958-1961.

(12) Tsudaka, T.; Kotani, H.; Ohkubo, K.; Nakagawa, T.; Tkachenko, N. V.; Lemmetyinen, H.; Fukuzumi, S. Photoinduced Electron Transfer in 9-Substituted 10-Methylacridinium Ions. *Chem. Eur. J.* **2017**, *23*, 1306-1317.

(13) Balaban, A. T.; Schroth, W.; Fischer, G. Pyrylium Salts Part I. Syntheses. *Adv. Heterocycl. Chem.* **1969***, 10,* 241-326.

(14) Miranda, M. A.; Garcia, H. 2,4,6-Triphenylpyrylium Tetrafluoroborate as an Electron-Transfer Photosensitizer. *Chem. Rev*. **1994**, *94*, 1063-1089.

(15) (a) Tommasino, J-B.; Brondex, A.; Médebielle, M.; Thomalla, M.; Langlois, B. R.; Billard, T. Trifluoromethylation Reactions with Potassium Trifluoromethanesulfinate under Electrochemical Oxidation. *Synlett* **2002**, *10*, 1697-1699; (b) Qin, H-T.; Wu, S-W.; Liua, J-L.; Liu, F. Photoredox-catalysed redox-neutral trifluoromethylation of vinyl azides for the synthesis of *α*-trifluoromethylated ketones. *Chem. Commun.* **2017**, *53*, 1696-1699.(c) Guyon, H.; Chachignon, H.; Cahard, D. CF_3SO_2X (X = Na, Cl) as reagents for trifluoromethylation, trifluoromethylsulfenyl-, -sulfinyl- and -sulfonylation. Part 1: Use of CF_3SO_2Na. *Beilstein J. Org. Chem.* **2017***, 13,* 2764–2799.

(16) (a) Mai, W-P.; Wang, J-T.; Yang, L-R.; Yuan, J-W.; Xiao, Y-M.; Mao. P.; Qu, L-B. Silver-Catalyzed Radical Tandem Cyclization for the Synthesis of 3,4-Disubstituted Dihydroquinolin-2(1*H*)-ones. *Org. Lett.* **2014**, *16*, 204-207. (b) Cao, X-H.; Pan, X.; Zhou, P-J.; Zou, J-P.; Asekun, O. T. Manganese(III)-mediated direct C_{sp^2}–H radical trifluoromethylation of coumarins with sodium trifluoromethanesulfinate. *Chem. Commun*. **2014**, *50*, 3359-3362. (c) Yang, F.; Klumphu, P.; Liang, Y-M.; Lipshutz, B. H. Copper-catalyzed trifluoromethylation of *N*-arylacrylamides “on water” at room temperature. *Chem. Commun*. **2014**, *50*, 936-938; (d) Jiang, H.; Huang, W.; Yu, Y.; Yi, S.; Li, J.; Wu, W. Transition-metal-free synthesis of *β*-trifluoromethylated enamines with trifluoromethanesulfinate**.** *Chem. Commun*. **2017**, *53*, 7473-7476. (e) Luo, H-Q.; Zhang, Z-P.; Dong, W.; Luo, X-Z. A Practical Method for Metal-Free Radical Trifluoromethylation of Styrenes with $NaSO_2CF_3$. *Synlett.* **2014**, *25*, 1307-1311. (f) Ji, Y.; Brueckl, T.; Baxter, R. D.; Fujiwara, Y.; Seiple, I. B.; Su, S.; Blackmond, D. G.; Baran, P. S. Innate C–H trifluoromethylation of heterocycles. *Proc. Natl. Acad. Sci. USA* **2011***, 108,* 14411-14415.

(17) (a)Wilger, D. J.; Gesmundo, N. J.; Nicewicz, D. A. Catalytic hydrotrifluoromethylation of styrenes and unactivated aliphatic alkenes *via* an organic photoredox system. *Chem. Sci.* **2013**, *4*, 3160-3165. (b) Zhu, L.; Wang, L-S.; Li, B.; Fu, B.; Zhang, C-P.; Li, W. Operationally simple hydrotrifluoromethylation of alkenes with sodium triflinate enabled by Ir photoredox catalysis. *Chem. Commun.* **2016**, *52*, 6371-6374.

(18) Miyazawa, K.; Koike, T.; Akita, M. Regiospecific Intermolecular Amino-hydroxylation of Olefins by Photoredox Catalysis. *Chem. Eur. J.* **2015**, *21*, 11677-11680.

(19) (a) Nagib, D. A.; MacMillan, D. W. C. Trifluoromethylation of arenes and heteroarenes by means of photoredox catalysis. *Nature* **2011**, *480*, 224-228. (b) Beatty, J. W.; Douglas, J. J.; Cole, K. P.; Stephenson, C. R. J. A scalable and operationally simple radical trifluoromethylation. *Nature Commun*. **2015**, *6,* 7919-7924.

(20) (a) Kalyanasundaram, K. Photophysics, photochemistry and solar energy conversion with tris(bipyridyl)ruthenium(II) and its analogues. *Coordination Chemistry Reviews.* **1982**, *46,* 159-244. (b) Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J.; Parker, S.; Rohl, R.; Bernhard, S.; Malliaras, G. G. Efficient Yellow Electroluminescence from a Single Layer of a Cyclometalated Iridium Complex**.** *J. Am. Chem. Soc.* **2004**, *126*, 2763-2767. (c) Flamigni, L.; Barbieri, A.; Sabatini, C.; Ventura, B.; Barigelletti, F. Photochemistry and Photophysics of Coordination Compounds: Iridium. *Top. Curr. Chem.* **2007**, *281*, 143-203. (d) Hari, D. P.; Konig, B. Synthetic applications of eosin-Y in photoredox catalysis. *Chem. Commun*. **2014**, *50*, 6688-6699. (e) Pitre, S. P.; McTiernan, C. D.; Scaiano, J. C. Library of Cationic Organic Dyes for Visible-Light-Driven Photoredox Transformations. *ACS Omega.* **2016**, *1*, 66-76. (f) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. Single-Layer Electroluminescent Devices and Photoinduced Hydrogen Production from an Ionic Iridium(III) Complex. *Chem. Mater.* **2005**, *17*, 5712-5719.

(21) (a) Clark, J. S.; Marlin, F.; Nay, B.; Wilson, C. Synthesis of the carbocyclic core of the cornexistins by ring-closing metathesis. *Org. Lett.* **2003**, *5*, 89-92. (b) Nguyen, T. V.; Hartmann, J. M.; Enders, D. Recent Synthetic Strategies to Access Seven-Membered Carbocycles in Natural Product Synthesis**.** *Synthesis* **2013**, *45*, 845-873. (c) Atta-Ur-Rhaman. *Studies in Natural Products Chemistry*. ISBN: 978-0-444-53836-9.

(22) ^{19}F NMR yields were used because the final products and starting materials having same R_f value and unable to separate the products in completely pure form.

(23) (a) Linker, T. The Jacobsen–Katsuki Epoxidation and Its Controversial Mechanism. *Angew. Chem. Int. Ed.* **1997**, *36*, 2060-2062. (b) Russo, A. T.; Amezcua, K. L.; Huynh, V. A.; Rousslang, Z. M.; Cordes, D. B. A simple borohydride-based method for selective 1, 4-conjugate reduction of *α,β*-unsaturated carbonyl compounds. *Tetrahrdron Lett.* **2011**, *52*, 6823-6826. (c) Ooi, T.; Ohara, D.; Fukumato, K.; Maruoka, K. Importance of Chiral Phase-Transfer Catalysts with Dual Functions in Obtaining High Enantioselectivity in the Michael Reaction of Malonates and Chalcone Derivatives. *Org. Lett.* **2005**, *7*, 3195-3197. (d) Prakash, G. K. S.; Mathew, T.; Hoole, D.; Esteves, P. M.; Wang, Q.; Rasul, G.; Olah, G. A. *N*-Halosuccinimide/BF_3-H_2O, Efficient Electrophilic Halogenating Systems for Aromatics. *J. Am. Chem. Soc.* **2004**, *126,* 15770-15776.

(24) Martiny, M.; Steckhan, E.; Esch, T. Cycloaddition Reactions Initiated by Photochemically Excited Pyrylium Salts. *Chem. Ber*. **1993**, *126*, 1671-1682.

(25) (a) Nagib, D. A.; MacMillan, D. W. C. Trifluoromethylation of arenes and heteroarenes by means of photoredox catalysis. *Nature* **2011**, *480*, 224-228. (b) Beatty, J. W.; Douglas, J. J.; Cole, K. P.;

Stephenson, C. R. J. A scalable and operationally simple radical trifluoromethylation. *Nature Comm.* **2015,** *6,* 7919-7925.

(26) Dieskau, A. P.; Holzwarth, M. S.; Plietker, B. Fe-Catalyzed Allylic C–C-Bond Activation: Vinylcyclopropanes As Versatile a1,a3,d5-Synthons in Traceless Allylic Substitutions and [3 + 2]-Cycloadditions. *J. Am. Chem. Soc.* **2012,** *134*, 5048-5051.

(27) (a) Hubert, A. J.; Noels, A. F.; Anciaux, A. J.; Teyssie, P. Rhodium(II) Carboxylates: Novel Highly Efficient Catalysts for the Cyclopropanation of Alkenes with Alkyl Diazoacetates. *Synthesis* **1976**, *7*, 600-602. (b) M. Yang, M.; Webb, T. R.; Livan, P. High-Yield Double Cyclopropanation of Benzene. *J. Org. Chem.* **2001**, *66*, 4945-4949. (c) Peace, B. W.; Carman, F.; Wulfman, D. S. The Soluble Copper(I)-Catalyzed Decomposition of Dimethyl Diazomalonate and Di-*t*-butyl Diazomalonate in the Presence of Some Cycloalkenes. *Synthesis* **1971**, *12*, 658-661.

(28) (a) Ashton, W. T. ; Meurer, L. C.; Cantone, C. L.; Field, A. K.; Hannah, J.; Karkas, J. D.; Liou, R.; Patel, G. F.; Perry, H. C.; Wagner, A. F.; Walton, E.; Tolman, R. L. *J. Med. Chem.* Synthesis and antiherpetic activity of (.+-.)-9-[[(Z)-2-(hydroxymethyl)cyclopropyl]methyl]guanine and related compounds. **1988**, *31*, 2304-2315. (b) Leki, R.; Kani, Y.; Tsunoi, S.; Shibata, I. Transition-Metal-Free Coupling Reaction of Vinylcyclopropanes with Aldehydes Catalyzed by Tin Hydride. *Chem. Eur. J.* **2015***, 21*, 6295-6300.