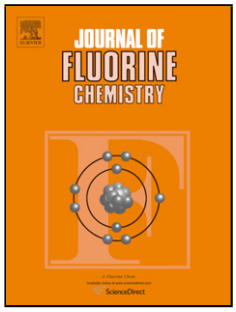

Title: Visible-Light-Induced Photocatalytic Trifluoromethylation/1,2-Carbon Migration Sequences for the Synthesis of CF_3-Substituted Cyclic Ketones

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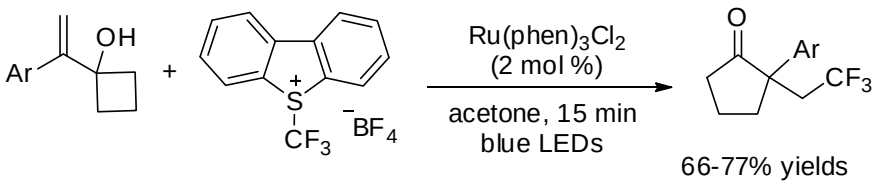
Graphical Abstract

Visible-Light-Induced Photocatalytic Trifluoromethylation/1,2-Carbon Migration Sequences for the Synthesis of CF_3-Substituted Cyclic Ketones

Saet Byeol Woo and Dae Young Kim



Communications

Visible-Light-Induced Photocatalytic Trifluoromethylation/1,2-Carbon Migration Sequences for the Synthesis of CF_3-Substituted Cyclic Ketones

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Abstract:

A visible-light-induced photoredox trifluoromethylation/1,2-carbon migration sequences of alkenols is described. This approach provides a mild and operationally simple access to the synthesis of CF_3-substituted cyclic ketones via trifluoromethylation and 1,2-carbon migration of 1-(1-arylvinyl)cyclobutanol derivatives.

Highlight

1. We have developed the photocatalyzed trifluoromethylation and 1,2-carbon migration of 1-(1-arylvinyl)cyclobutanol derivatives.
2. Moderate to high yields (3a-3f, 66-77%) observed under mild reaction conditions.
3. This reaction requires short reaction time and has broad substrate scope including 6 and 7.

Keywords: Trifluoromethylation, Photocatalysis, Radical reaction, 1,2-Carbon migration

1. Introduction

The chemistry of fluorinated molecules is a rapidly developing research area because of their their utility as medicines, agrochemicals, and functional materials [1]. Especially, the trifluoromethyl group is an important structural motif found in pharmaceuticals, agrochemicals, and biologically active compounds [2]. The introductionof a trifluoromethyl group into organic compounds usually leads to improvement of their biological and physiological characteristics due to unique physical and chemical properties [3]. For example, the incorporated trifluoromethyl group could improve their chemical and metabolic stability and increase their bioavailability [4]. Consequently, considerable effort has been contributed toward the development of expedient methods for C-CF_3 bond formation [5]. Among the most direct approaches for the construction of C-CF_3 bonds is the trifluoromethylation of alkenes by using the trifluoromethyl radical source in the presence of transition metal complexes or organic oxidants as external initiators through radical intermediate [6].

The application of visible-light photoredox catalysis has emerged as a novel and

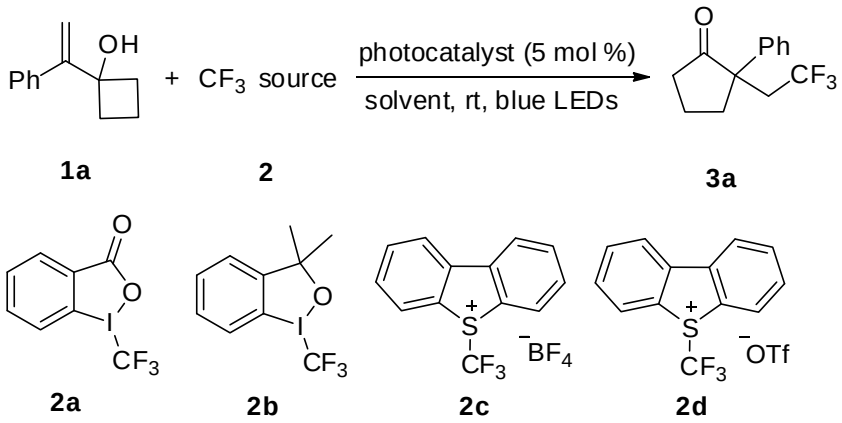
powerful tool for chemical transformations in organic chemistry, because of its attractive features such as environmental compatibility, mild and green conditions, excellent functional group tolerance, and versatility in promoting various reactions [7]. The visible-light-induced photocatalytic difunctionalization of alkenes provides a useful approach to obtain various diversely functionalized molecules [8]. The photocatalytic difunctionalization of alkenes with suitable trifluoromethyl sources also enable the facile incorporation of the trifluoromethyl moiety into valuable organic compounds [9]. The application of such a visible-light-induced photocatalytic strategy to achieve functionalized trifluoromethyl-containing compounds is highly desirable. Recently, several groups independently reported the preparation of β-trifluoromethyl ketones from allylic alcohols via 1,2-aryl migration using Togni's reagent in the presence of transition metal complexes [10] and Langlois' reagent under metal-free condition [11]. After completion of this work and during the preparation of this manuscript, a paper by Glorius group on visible-light photoredox catalyzed semipinacol-type rearrangement via trifluomethylation/ring expansion was published [12]. This reported protocol requires 1.2 eq. of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and long reaction time (8 h).

In the framework of our research program on the internal redox reaction and cyclization sequences, we recently reported the C-H bond functionalization via 1,5-hydride transfer and cyclization cascade [13]. In this communication, we wish to describe visible-light-induced photoredox trifluoromethylation/1,2-carbon migration [14] sequences of 1-(1-arylvinyl)cyclobutanol derivatives for the synthesis of trifluoromethyl-substituted cyclic ketones.

2. Results and discussion

To determine suitable reaction conditions for the visible-light-induced photocatalytic trifluoromethylation/1,2-carbon migration of 1-(1-arylvinyl)cyclobutanols, we examined the visible-light-induced photocatalytic reaction of 1-(1-phenylvinyl)cyclobutanol (**1a**) with electrophilic trifluromethylation reagents (**2**) in the presence of 5 mol% of $Ru(phen)_3Cl_2$ under visible-light irradiation from blue LEDs (5 W, λ_{max} = 455 nm) in dichloromethane at room temperature (Table 1). By screening trifluromethylation reagents **2a-2d**, we found that Umemoto's reagent **2c** was the best trifluromethylation reagent for this trifluoromethylation/1,2-carbon migration, affording the corresponding product **3a** in 70% yield (Table 1, entry 3). Next, we examined the effect of photocatalysts in dichloromethane (entries 3 and 5-9). A. survey of the different photocatalysts indicate that $Ru(bpy)_3(PF_6)_2$, $Ru(bpy)_3Cl_2{\cdot}6H_2O$, and fluorescein gave moderate to low yields (68-22%), while eosin Y and eosin $Y{\cdot}Na_2$ gave trace amount of product **3a**. In addition, the solvent was found to have an effect on reactivity. Among the solvents probed (entries 3 and 10-14), the best result was achieved when the reaction was conducted in acetone (77% yield, entry 12). The present catalytic system tolerates photocatalyst loading down to 2 mol % without compromising the yield (entries 12 and 15).The control experiment showed that the reaction could not proceed in the absence of a photocatalyst and visible-light (entries 16-17).

Table 1. Optimization of the reaction conditions [a]

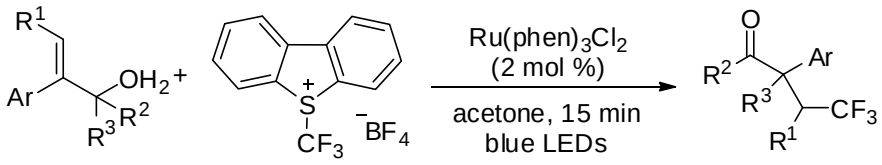


entry	**2**	photocatalyst	solvent	time	yield (%)[b]
1	**2a**	$Ru(phen)_3Cl_2$	CH_2Cl_2	14 h	trace
2	**2b**	$Ru(phen)_3Cl_2$	CH_2Cl_2	10 h	trace
3	**2c**	$Ru(phen)_3Cl_2$	CH_2Cl_2	15 min	70
4	**2d**	$Ru(phen)_3Cl_2$	CH_2Cl_2	15 min	60
5	**2c**	$Ru(bpy)_3(PF_6)_2$	CH_2Cl_2	15 min	24
6	**2c**	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	CH_2Cl_2	15 min	68
7[c]	**2c**	Fluorescein	CH_2Cl_2	1 h	22
8[c]	**2c**	Eosin Y	CH_2Cl_2	6 h	trace
9[c]	**2c**	Eosin Y·Na_2	CH_2Cl_2	6 h	trace
10	**2c**	$Ru(phen)_3Cl_2$	CH_3Cl	1 h	7
11	**2c**	$Ru(phen)_3Cl_2$	$CH_2CH_2Cl_2$	1 h	27
12	**2c**	$Ru(phen)_3Cl_2$	acetone	15 min	77
13	**2c**	$Ru(phen)_3Cl_2$	CH_3CN	30 min	36
14	**2c**	$Ru(phen)_3Cl_2$	DMF	30 min	26
15[d]	**2c**	$Ru(phen)_3Cl_2$	acetone	15 min	77
16	**2c**	-	acetone	1 h	0
17[e]	**2c**	$Ru(phen)_3Cl_2$	acetone	1 h	0

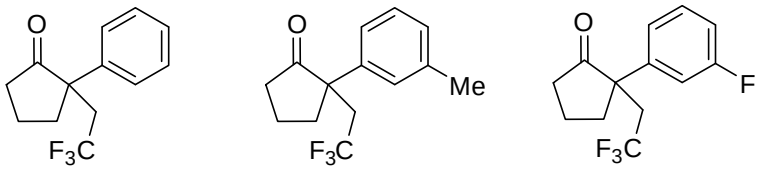
[a] Reaction conditions: 1-(1-phenylvinyl)cyclobutanol (**1a**, 0.3 mmol), CF_3 reagent (**2**, 0.6 mmol), photocatalyst (0.015 mmol), solvent (3.0 mL) at room temperature under visible-light irradiation. [b] Isolated yield. [c] 10 mol% photocatalyst loading. [d] 2 mol% photocatalyst loading. [e] The reaction was performed in the dark.

With optimal reaction conditions in hand, we investigated the scope of this visible-light-induced photocatalytic reaction of 1-(1-phenylvinyl)cyclobutanolderivatives **1** with electrophilic trifluromethylation reagent (**2c**) in the presence of 2 mol% of $Ru(phen)_3Cl_2$ under light irradiation from blue LEDs (5 W, λ_{max} = 455 nm) in acetone at room temperature. As it can be seen by the results summarized in Table 2, various 1-(1-phenylvinyl)cyclobutanols **1** with electron-withdrawing or electron-donating aryl groups furnished the corresponding migration products with moderate to good yields (**3a**–**3f**). 3-(1-Phenylvinyl)oxetan-3-ol (**1g**) afforded the corresponding product **3g** in low yield. Also, 1-(1*H*-inden-3-yl)cyclobutanol (**1h**) and 1-(3,4-dihydronaphthalen-1-yl)cyclobutanol (**1i**) gave the desired products **3h-3i** in moderate to low yields with 2:1 dr.

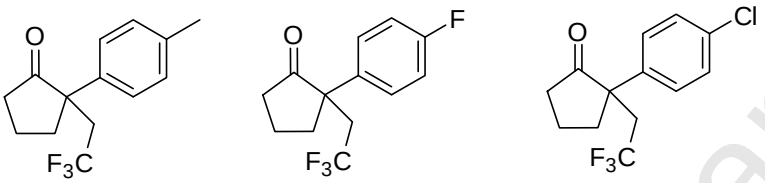
Table 2. Variation of substrates **1**[a,b]



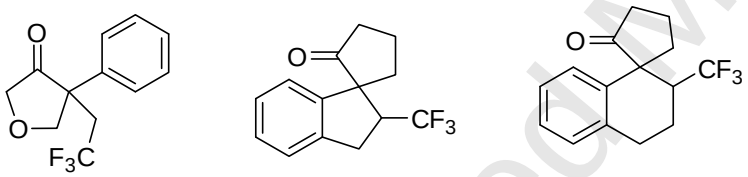
1 **2c** **3**



3a, 77% **3b**, 73% **3c**, 66%



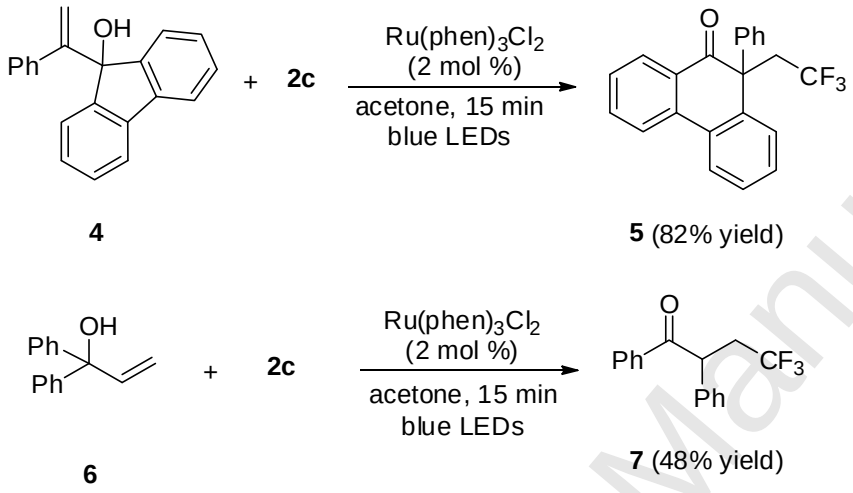
3d, 73% **3e**, 70% **3f**, 70%



3g, 25% **3h**, 42% (2:1 dr) **3i**, 37% (2:1 dr)

[a] Reaction conditions: cyclobutanols (**1**, 0.3 mmol), CF_3 reagent (**2a**, 0.6 mmol), $Ru(phen)_3Cl_2$ (0.006 mmol), acetone (3.0 mL) at room temperature under visible-light irradiation. [b] Isolated yields.

Furthermore, 9-(1-phenylvinyl)-9*H*-fluoren-9-ol **4** derived from fluoreone and allyl alcohol **6** were also used as a substrate in this visible-light-induced photocatalytic reaction under the optimal conditions. It was found that the corresponding products **5** and **7** were obtained in 82% and 48% yields (Scheme 1).



Scheme 1. Visible-light-induced photocatalytic trifluoromethylation/1,2-carbon migration of **4** and **6**.

To get an insight of the mechanism of this transformation, a radical-trapping experiment was carried out. It was found that no product was detected in the presence of a radical inhibitor TEMPO. Based on this result, we propose a plausible mechanism for the reaction in Figure 1. A photocatalyst $Ru(phen)_3^{2+}$ undergoes a metal to ligand charge transfer process by visible-light to produce the excited state $Ru^*(phen)_3^{2+}$A single electron transfer process then occurs to trifluormethylation reagent **2c** would generate $Ru(phen)_3^{3+}$ and an CF_3 radical. Subsequently, CF_3 radical will react with substrate **1** to generate intermediate **I**, which undergoes single electron transfer from $Ru(phen)_3^{3+}$ and intermediate **I** generate to cation **II**. A 1,2-carbon migration of cation **II** afford the product **3**.

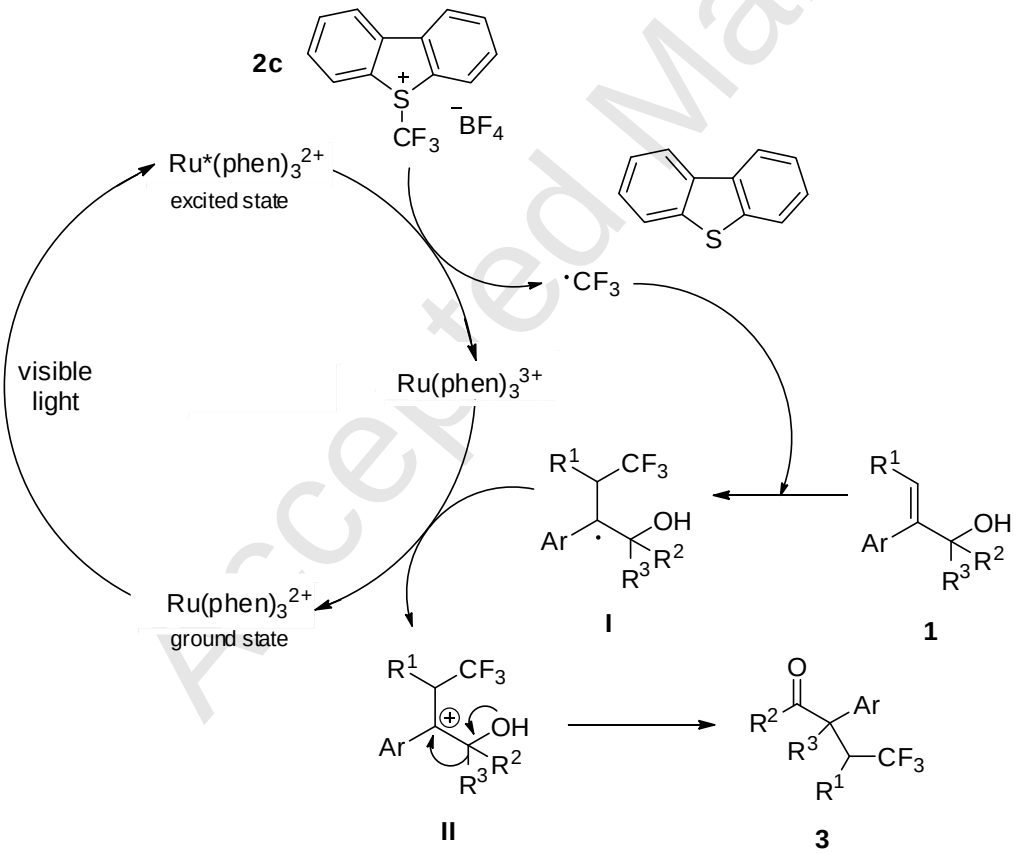


Figure 1. Proposed reaction mechanism.

3. Conclusions

In conclusion, we have developed the visible-light-induced photoredox-catalyzed trifluoromethylation and 1,2-carbon migration sequences of 1-(1-arylvinyl)cyclobutanol derivatives using $Ru(phen)_3Cl_2$ and Umemoto's reagent **2c** under mild reaction conditions. It provides an efficient method for the synthesis of CF_3-substituted cyclic ketone derivatives. The approach offers a quick and convenient way to prepare CF_3-substituted cyclic ketone derivatives as compared to the recently reported methods [12]. Further study on asymmetric version of the visible-light-induced photoredox-catalyzed trifluoromethylation and 1,2-carbon migration are currently underway in our laboratory.

4. Experimental

4.1.General information

All commercial reagents and solvents were used without purification. TLC analyses were carried out on pre-coated silica gel plates with F_{254} indicator. Visualization was accomplished by UV light (254 nm), I_2, *p*-anisaldehyde, ninhydrin, and phosphomolybdic acid solution as an indicator. Purification of reaction products was carried out by flash chromatography using E. Merck silica gel 60 (230-400 mesh). ^{1}H NMR,^{13}C NMR, and^{19}F NMRspectra were recorded at 400 MHz, 100 MHz, 376 MHzrespectively, on a Jeol ECS 400 MHz NMR spectrometer. Chemical shift values (δ) are reported in ppm relative to Me_4Si as the internal references and $PhCF_3$ as the external references. Mass spectra were measured on Jeol HX110/110A using electrospray ionization technique.

4.2. General procedure for the visible-light-induced photocatalytic trifluoromethylation/1,2-carbon migration sequences for the synthesis of CF_3-substituted cyclic ketones

An oven-dried Schlenk tube was equipped with a magnetic stir bar, 1-(1 arylvinyl)cyclobutanol derivatives (**1**, 0.3 mmol), $Ru(phen)_3Cl_2$ (0.006 mmol), 5-(trifluoromethyl)dibenzothiophenium tetrafluoroborate (**2c**, 0.6 mmol). The reaction tube was evacuated and backfilled with N_2 for 3 times. Dry acetone (3 mL) was added with syringe under N_2. The reaction mixture was allowed to stir for 15 min under irradiation of blue LEDs (5 W). After the reaction was finished, the mixture was concentrated under vacuum to remove solvent, and the residue was purified by chromatography on silica gel (ethyl acetate: *n*-hexane = 1:50) to afford the CF_3-substituted cyclic ketones **3**.

2-Phenyl-2-(2,2,2-trifluoroethyl)cyclopentanone (3a):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.28 (m, 5 H), 2.93 (dd, *J* = 12.0 Hz, 5.6 Hz, 1 H), 2.80 (dq, *J* = 15.5 Hz, 11.2 Hz, 1 H), 2.49 (dq, *J* = 15.5 Hz, 11.2 Hz, 1 H), 2.36-2.16 (m, 2 H), 2.14-1.97 (m, 2 H), 1.86-1.73 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.2, 136.0, 129.0, 127.8, 126.9, 126.3 (q, *J* = 276.8 Hz), 53.4, 42.1 (q, *J* = 27.0 Hz), 35.6, 32.5, 18.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ −60.3 (t, *J* = 11.0 Hz); IR (film) 1739 cm^{-1}; ESI-HRMS: m/z calcd for $C_{13}H_{13}F_3NaO$ $[M+Na]^+$: 265.0816; found 265.0821.

2-(*m*-Tolyl)-2-(2,2,2-trifluoroethyl)cyclopentanone(3b):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.21 (m, 1 H), 7.18-7.16 (m, 2 H), 7.09-7.07 (m, 1 H), 2.90 (dd, *J* = 13.4 Hz, 5.8 Hz, 1 H), 2.77 (dq, *J* = 15.4 Hz, 11.3 Hz, 1 H), 2.49 (dq, *J* = 15.4 Hz, 11.3 Hz, 1 H), 2.39-2.29 (m, 4 H), 2.25-2.15 (m, 1 H), 2.12-1.95 (m, 2 H), 1.85-1.72 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.4, 138.7, 136.1, 128.9, 128.5, 127.6, 126.3 (q, *J* =

276.8 Hz), 123.8, 53.4, 42.0 (q, *J* = 27.3 Hz), 35.6, 32.5, 21.7, 18.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –60.3 (t, *J* = 11.1 Hz); IR (film) 1741 cm^{-1}; ESI-HRMS: m/z calcd for $C_{14}H_{15}F_3NaO$ $[M+Na]^+$: 279.0973; found 279.0971.

2-(3-Fluorophenyl)-2-(2,2,2-trifluoroethyl)cyclopentanone (3c):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.30 (m, 1 H), 7.19-7.17 (m, 1 H), 7.14-7.10 (m, 1 H), 7.01-6.96 (m, 1 H), 2.88 (dd, *J* = 13.2 Hz, 5.6 Hz, 1 H), 2.80 (dq, *J* = 15.5 Hz, 10.9 Hz, 1 H), 2.45 (dq, *J* = 15.5 Hz, 10.9 Hz, 1 H), 2.37-2.18 (m, 2 H), 2.15-1.99 (m, 2 H), 1.86-1.73 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.7, 163.2 (d, *J* = 245 Hz), 138.8 (d, *J* = 6.7 Hz), 130.5 (d, *J* = 8.6 Hz), 126.2 (q, *J* = 276.8 Hz), 122.6, 114.9 (d, *J* = 21.0 Hz), 114.2 (d, *J* = 21.9 Hz), 53.2, 42.1 (q, *J* = 27.3 Hz), 35.6, 32.6, 18.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –60.4 (t, *J* = 11.0 Hz), –111.6; IR (film) 1744 cm^{-1}; ESI-HRMS: m/z calcd for $C_{13}H_{12}F_4NaO$ $[M+Na]^+$: 283.0722; found 283.0727.

2-(*p*-Tolyl)-2-(2,2,2-trifluoroethyl)cyclopentanone(3d):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.26 (m, 2 H), 7.17-7.15 (m, 2 H), 2.90 (dd, *J* = 12.0 Hz, 6.0 Hz, 1 H), 2.78 (dq, *J* = 15.4 Hz, 11.2 Hz, 1 H), 2.52-2.431 (m, 1 H), 2.35-2.26 (m, 4 H), 2.24-1.95 (m, 3 H), 1.85-1.74(m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.2, 137.5, 132.8, 129.6, 126.7, 126.5 (q, *J* = 276.8 Hz), 53.0, 42.0 (q, *J* = 27.0 Hz), 35.4, 32.4, 20.1, 18.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ –60.3 (t, *J* = 11.1 Hz); IR (film) 1738 cm^{-1}; ESI-HRMS: m/z calcd for $C_{14}H_{15}F_3NaO$ $[M+Na]^+$: 279.0973; found 279.0977.

2-(4-Fluorophenyl)-2-(2,2,2-trifluoroethyl)cyclopentanone (3e):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.35 (m, 2 H), 7.07-6.99 (m, 2 H), 2.90 (dd, *J* = 13.0 Hz,

5.8 Hz, 1 H), 2.79 (dq, *J* = 15.4 Hz, 11.1 Hz, 1 H), 2.42 (dq, *J* = 15.4 Hz, 11.1 Hz, 1 H), 2.36-2.17 (m, 2 H), 2.13-1.98 (m, 2 H), 1.85-1.72 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.0, 162.3 (d, *J* = 246.9 Hz), 131.5, 131.3 (d, *J* = 9.5 Hz), 128.8 (d, *J* = 8.5 Hz), 126.3 (q, *J* = 276.8 Hz), 116.3 (d, *J* = 21.9 Hz), 116.0 (d, *J* = 21.0 Hz), 52.8, 42.2 (q, *J* = 27.3 Hz), 35.5, 32.8, 18.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –60.3 (t, *J* = 11.2 Hz), –114.5; IR (film) 1741 cm^{-1}; ESI-HRMS: m/z calcd for $C_{13}H_{12}F_4NaO$ $[M+Na]^+$: 283.0722; found 283.0725.

2-(4-Chlorophenyl)-2-(2,2,2-trifluoroethyl)cyclopentanone (3f):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.30 (m, 4 H), 2.89 (dd, *J* = 13.0 Hz, 5.8 Hz, 1 H), 2.79 (dq, *J* = 15.6 Hz, 11.0 Hz, 1 H), 2.43 (dq, *J* = 15.6 Hz, 11.0 Hz, 1 H), 2.37-2.17 (m, 2 H), 2.13-1.99 (m, 2H), 1.85-1.71 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.8, 134.4, 133.9, 129.9, 128.4, 126.2 (q, *J* = 276.8 Hz), 52.9, 42.1 (q, *J* = 27.3 Hz), 35.5, 32.6, 18.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ –60.3 (t, *J* = 11.1 Hz); IR (film) 1742 cm^{-1}; ESI-HRMS: m/z calcd for $C_{13}H_{12}ClF_3NaO$ $[M+Na]^+$: 299.0426; found 299.0421.

4-Phenyl-4-(2,2,2-trifluoroethyl)dihydrofuran-3(2H)-one (3g):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.47 (m, 2 H), 7.44-7.32 (m, 2 H), 7.32-7.28 (m, 1 H), 5.06 (d, *J* = 10.6 Hz, 1 H), 4.22 (d, *J* = 10.6 Hz, 1 H), 4.11 (d, *J* = 17.4 Hz, 1 H), 3.92 (d, *J* = 17.4 Hz, 1 H), 3.04 (dq, *J* = 15.6 Hz, 10.8 Hz, 1 H), 2.53 (dq, *J* = 15.6 Hz, 10.8 Hz, 1 H);^{13}C NMR (100 MHz, $CDCl_3$) δ 211.7, 134.2, 129.2, 128.4, 126.7, 126.0 (q, *J*= 278.1 Hz), 74.1 (q, *J* = 2.4 Hz), 69.6, 52.1, 38.9 (q, *J* = 28.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –60.8 (t, *J* = 11.0 Hz); IR (film) 1766 cm^{-1}; ESI-HRMS: m/z calcd for $C_{12}H_{11}F_3NaO_2$ $[M+Na]^+$: 267.0609; found 267.0611.

2'-(Trifluoromethyl)-2',3'-dihydrospiro[cyclopentane-1,1'-inden]-2-one (3h):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.18 (m, 3 H), 7.07-7.05 (m, 1 H), 3.48-3.41 (m, 1 H), 3.26-3.01 (m, 2 H), 2.60-2.37 (m, 4 H), 2.27-2.09 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 216.3 145.2, 141.0, 128.0, 127.6, 126.8 (q, *J* = 277.1 Hz), 124.9, 122.5, 60.7, 54.3 (q, *J* = 26.7 Hz), 38.4, 37.2, 32.0, 19.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –64.6 (d, *J* = 9.0 Hz); IR (film) 1743 cm^{-1}; ESI-HRMS: m/z calcd for $C_{14}H_{13}F_3NaO$ $[M+Na]^+$: 277.0816; found 277.0811.

2'-(Trifluoromethyl)-3',4'-dihydro-2'H-spiro[cyclopentane-1,1'-naphthalen]-2-one (3i):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.09 (m, 3 H), 7.00-6.95 (m, 1 H), 3.03-2.93 (m, 1 H), 2.85-2.77 (m, 1 H), 2.75-2.64 (m, 2 H), 2.61-2.48 (m, 2 H), 2.46-2.34 (m, 2 H), 2.19-2.12 (m, 2 H), 2.10-2.04 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.6, 138.9, 136.3, 129.1, 128.0, 126.8, 126.7, 125.4 (q, *J* = 280.0 Hz), 52.9, 46.4 (q, *J* = 24.8 Hz), 41.4, 38.2, 29.8, 27.1, 20.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.3 (d, *J* = 9.7 Hz); IR (film) 1744 cm^{-1}; ESI-HRMS: m/z calcd for $C_{15}H_{15}F_3NaO$ $[M+Na]^+$: 291.0973; found 291.0969.

10-Phenyl-10-(2,2,2-trifluoroethyl)phenanthren-9(10H)-one (5):

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19-8.07 (m, 3 H), 7.72-7.66 (m, 1 H), 7.50-7.46 (m, 1 H), 7.43-7.37 (m, 2 H), 7.29-7.15 (m, 4 H), 7.06-7.00 (m, 2 H), 4.17 (dq, *J* = 15.0 Hz, 10.1 Hz, 1 H), 3.21 (dq, *J* = 15.0 Hz, 10.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 141.7, 138.5, 137.1, 135.1, 130.5, 130.3, 129.0, 128.9, 128.8, 128.6, 128.3, 128.1, 127.8, 127.0, 125.7 (q, *J* = 277.9 Hz), 124.0, 123.3, 55.1, 42.2 (q, *J* = 27.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –58.0 (t, *J* = 10.9 Hz); IR (film) 1680 cm^{-1}; ESI-HRMS: m/z calcd for $C_{22}H_{15}F_3NaO$ $[M+Na]^+$: 375.0973; found 375.0975.

4,4,4-Trifluoro-1,2-diphenylbutan-1-one (7):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.95 (m, 2 H), 7.53-7.49 (m, 1 H), 7.43-7.39 (m, 2 H), 7.34-7.29 (m, 4 H), 7.27-7.22 (m, 1 H), 4.91 (dd, *J* = 7.6 Hz, 5.6 Hz, 1 H), 3.38-3.24 (m, 1 H), 2.61-2.49 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 137.4, 135.7, 133.3, 129.3, 128.8, 128.7, 128.0, 127.8, 125.8 (q, *J* = 278.5 Hz), 47.1, 37.3 (q, *J* = 28.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –64.5 (t, *J* = 11.4 Hz); IR (film) 1686 cm^{-1}; ESI-HRMS: m/z calcd for $C_{16}H_{13}F_3NaO$ $[M+Na]^+$: 301.0816; found 301.0814.

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