Supporting Information

Light and oxygen-enabled sodium trifluoromethanesulfinate-mediated selective oxidation of C-H bonds

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1. General Information

A. Materials and general procedures

Sodium trifluoromethanesulfinate was purchased from Xiya Reagent (purity \geq 99%). All reagents and solvents were purchased from commercial suppliers Adamas, Bide, TCI, J&K Chemical, Energy Chemical, and Meryer and used directly without further purification. All reactions were conducted in oven-dried reaction vessel under O₂ atmosphere (purity \geq 99.99%) unless otherwise mentioned. The reaction solutions were concentrated under reduced pressure on Shanghai YaRong rotary evaporator.

B. Analytical methods

Gas chromatographic (GC) analysis was acquired on a JEOL JMS-Q1050GC system equipped with a flame-ionization detector. ¹H NMR, ¹³C NMR and ¹⁹F NMR spectra were recorded on a Bruker Avance 400 spectrometer or JEOL ECS-400 or JNM-ECA 600 spectrometers at ambient temperature. Proton (¹H NMR) and carbon (¹³C NMR) nuclear magnetic resonance spectra were recorded on a JEOL ECS-400 or JNM-ECA 600 spectrometers. Chemical shifts were reported in parts per million (ppm), ¹H NMR chemical shifts were internally referenced to tetramethylsilane (TMS) (¹H NMR: TMS references at 0.00 ppm) and residual proton signals of solvents (¹H NMR: CDCl₃ at 7.26 ppm, and DMSO- d_6 at 2.50 ppm), and ¹³C NMR chemical shifts were internally referenced to carbon signals of solvents (¹³C NMR: CDCl₃ at 77.16 ppm, DMSO-d₆ at 39.52 ppm, and CD₃OD at 49.00 ppm). Coupling constants (J) were reported in Hz with the following splitting abbreviations: s = singlet, d = doublet, t = doublettriplet, q = quartet, m = multiplet, dd = doublet of doublets, and br = broad. UV-Vis spectrum was measured by DRS, Hitachi U-3010. High resolution mass spectroscopy data of the product were collected on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS (ESI). Chromatographic purification of products was accomplished by column chromatography on silica gel (Qingdao Haiyang, 200-300 mesh).

2. Investigations of the Reaction Conditions

F 10	CF ₃ SO ₂ Na (50 mol%) O ₂ (1 atm) CH ₃ CN (1.0 mL) light source, r.t., 12 h	F 11
entry	light source	yield (%)
1	blue LED (400-405 nm)	100
2	dark	n.r.
3	CFL (34 W)	3
4	green LED (530-535 nm)	6
5	blue LED (450-455 nm)	64
6	blue LED (420-425 nm)	88
7	blue LED (380-385 nm)	100
8	blue LED (360-365 nm)	75

Table S1. Different light sources affecting the selective oxidation of C-H bond^a

^{*a*}Reaction conditions: **10** (0.1 mmol), CF₃SO₂Na (**1**, 50 mol%), CH₃CN (1.0 mL) under O₂ atmosphere and light irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard.

F	CF ₃ SO ₂ Na (50 mol%) O ₂ (1 atm) slovent (1.0 mL)	F
10	blue LED (400-405 nm), r.t., 12 h	11
entry	solvent	yield (%)
1	CH ₃ CN	100
2	DCM	15
3	DCE	93
4	THF	16
5	DMF	20
6	DMSO	n.r.

Table S2. Different solvents affecting the selective oxidation of C-H bond^{*a*}

7	dioxane	8
8	MeOH	n.r.
9	EtOH	n.r.
10	EtOAc	100
11	acetone	100

^{*a*}Reaction conditions: **10** (0.1 mmol), CF_3SO_2Na (**1**, 50 mol%), solvent (1.0 mL) under O_2 atmosphere and blue LED (400-405 nm) irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard.

F 10	RSO _n X (50 mol%) O ₂ (1 atm) CH ₃ CN (1.0 mL) blue LED (400-405 nm), r.t., 12 h	F 11
entry	RSO _n X	yield (%)
1	CF ₃ SO ₂ Na	100
2	CF ₃ SO ₃ Na	n.r.
3	CH ₃ SO ₂ Na	n.r.
4	CH ₃ CH ₂ SO ₂ Na	trace
5	^t BuSOCl	28
6	CF ₃ SOC1	12
7	TfOH	n.r.
8	(TfO) ₂ O	8
9	PhSO ₂ Na	n.r.
10		n.r.

Table S3. Different RSO_nNa affecting the selective oxidation of C-H bond^a

^{*a*}Reaction conditions: **10** (0.1 mmol), RSO_nX (50 mol%), CH₃CN (1.0 mL) under O₂ atmosphere and blue LED (400-405 nm) irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard.

F 10	CF ₃ SO ₂ Na (50 mol%) <u>atmosphere</u> (1 atm) CH ₃ CN(1.0 mL) blue LED (400-405 nm), r.t., 12 h	F 11
entry	atmosphere	yield (%)
1	O ₂	100
2	air	100
3	Ar	n.r.

Table S4. Different atmospheres affecting the selective oxidation of C-H bond^a

^{*a*}Reaction conditions: **10** (0.1 mmol), CF₃SO₂Na (**1**, 50 mol%), CH₃CN (1.0 mL) under different atmosphere and blue LED (400-405 nm) irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard.

Table S5. Different CF₃SO₂Na loadings affecting the selective oxidation of C-H bond^{*a*}

F 10	CF ₃ SO ₂ Na (3, X mol%) O ₂ (1 atm) CH ₃ CN(1.0 mL) blue LED (400-405 nm), r.t., 12 h	F 11
entry	Х	yield (%)
1	100	98
2	75	100
3	50	100
4	25	100
5	10	75
6	0	n.r.

^{*a*}Reaction conditions: **10** (0.1 mmol), CF_3SO_2Na (X mol%), CH_3CN (1.0 mL) under O_2 atmosphere and blue LED (400-405 nm) irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard.

Table S6. Different reaction	time and solvents affec	ting the selective oxidation of
C-H bond ^a		
	CE SO No (25 mol $\%$)	ö

I	F 10 CF ₃ SO ₂ Na (2 O ₂ (1 a) solvent (1 blue LED (400-405	25 mol%) tm) .0 mL) 5 nm), r.t., time	11
entry	solvent	time (h)	yield (%)
1	CH ₃ CN	4	62
2	CH ₃ CN	8	100
3	CH ₃ CN	12	100
4	EtOAc	4	6
5	EtOAc	8	46
6	EtOAc	12	100
7	acetone	4	9
8	acetone	8	91
9	acetone	12	100

^aReaction conditions: 10 (0.1 mmol), CF₃SO₂Na (1, 25 mol%), solvent (1.0 mL) under O₂ atmosphere and blue LED (400-405 nm) irradiation at room temperature. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard.

Table S7. Different CF₃SO₂Na loading and solvents affecting the selective oxidation of C-H bond^a

	F 10 CF ₃ SO ₂ Na (X O ₂ (1 at solvent (1. blue LED (400-405	(mol%) m) 0 mL) nm), r.t., 12 h	11
entry	solvent	Х	yield (%)
1	CH ₃ CN	50	100
2	CH ₃ CN	25	100
3	CH ₃ CN	10	75
4	EtOAc	50	100
5	EtOAc	25	100

6	EtOAc	10	35
7	acetone	50	100
8	acetone	25	100
9	acetone	10	66

^{*a*}Reaction conditions: **10** (0.1 mmol), CF_3SO_2Na (**1**, X mol%), solvent (1.0 mL) under O_2 atmosphere and blue LED (400-405 nm) irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard.

Table S8. Different amounts of MeCN affecting the selective oxidation of C-H bond^a

F 10	CF ₃ SO ₂ Na (25 mol%) O ₂ (1 atm) CH ₃ CN (X mL) blue LED (400-405 nm), r.t., 12 h	F 11
entry	Х	yield (%)
1	1.5	100
2	1.0	100
3	0.5	100

^{*a*}Reaction conditions: **10** (0.1 mmol), CF₃SO₂Na (**1**, 25 mol%), CH₃CN (X mL) under O₂ atmosphere and blue LED (400-405 nm) irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard.

3. General Experimental Procedures

3.1 Experimental procedures

General procedure A

$$\begin{array}{c} CF_{3}SO_{2}Na~(1,~25~mol\%)\\ \hline O_{2}~(1~atm)\\ \hline CH_{3}CN~(1.0~mL)\\ \hline blue~LED~(400-405~nm),~r.t.,~12~h \end{array} \\ F 11 \end{array}$$

1-Ethyl-4-fluorobenzene (10, 1.0 equiv, 0.2 mmol), sodium trifluoromethanesulfinate (1, 25 mol%)) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W

blue LED (400-405 nm) for 12 h under O_2 atmosphere. After the reaction was completed, the mixture was analyzed by GC-MS and the yield was determined using dodecane as the internal standard. The reaction solution was concentrated under reduced pressure to yield crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give the desired product (**11**) for characterization.

General procedure B

1-Fluoro-4-methylbenzene (1.0 equiv, 0.2 mmol), sodium trifluoromethanesulfinate (1, 50 mol%) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 12 h under O₂ atmosphere. After the reaction was completed, the reaction solution was concentrated under reduced pressure to yield crude product. After this, the pH value of the reaction mixture was adjusted to 12.0 with 0.1 M NaOH. The reaction mixture was then washed with methylene chloride (DCM) three times with a total DCM volume of 20 mL and the pH value of the aqueous phase was adjusted to 2.0 with 0.1 M HCl. The aqueous was then extracted with ethyl ether 3 times with a total ether volume of 20 mL and the combined organic phase was dried over anhydrous sodium sulfate and evaporated to obtain the carboxylic acid product (47).

General procedure C



4-Fluorobenzaldehyde (1.0 equiv, 0.2 mmol), sodium trifluoromethanesulfinate (1, 25 mol%)) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped

with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 12 h under O₂ atmosphere. After the reaction was completed, the reaction solution was concentrated under reduced pressure to yield a crude product. After this, the pH of the reaction mixture was adjusted to 12.0 with 0.1 M NaOH. The reaction mixture was then washed with methylene chloride (DCM) three times with a total DCM volume of 50 mL and the pH of the aqueous phase was adjusted to 2.0 with 0.1 M HCl. The aqueous was then extracted with ethyl ether 3 times with a total ether volume of 50 mL and the combined organic phase was dried over anhydrous sodium sulfate and evaporated to obtain the carboxylic acid product (**47**).

4. Gram-Scale Reactions

4.1 Gram-scale reaction for the oxidation of ethylbenzene



Ethylbenzene (**6**, 1.0 equiv, 10 mmol, 1.06 g), sodium trifluoromethanesulfinate (**1**, 25 mol%) and CH₃CN (50 mL) were added to an oven-dried reaction vessel (100 mL) equipped with magnetic stirring bar, and the reaction vessel was irradiated with 30 W blue LED (400-405 nm) for 12 h under O₂ atmosphere. After the reaction was completed, the yield was determined by GC-MS using dodecane as the internal standard to give the desired product acetophenone (**9**) in 95% yield. And the reaction solution was concentrated under reduced pressure to yield crude product, which was purified by flash chromatography (silica gel, petroleum ether/ethyl acetate = 30:1) to give the desired product **9** in 89% isolated yield (1.07 g).

4.2 Gram-scale reaction for the oxidation of benzaldehyde



Benzaldehyde (82, 1.0 equiv, 10 mmol, 1.06 g), sodium trifluoromethanesulfinate (1, 25 mol%) and CH₃CN (50 mL) were added to an oven-dried reaction vessel (100 mL) equipped with magnetic stirring bar, and the reaction vessel was irradiated with 30 W blue LED (400-405 nm) for 12 h under O₂ atmosphere. After the reaction was completed, the reaction solution was concentrated under reduced pressure to yield crude product. After this, the pH of the reaction mixture was adjusted to 12.0 with 0.1 M NaOH. The reaction mixture was then washed with methylene chloride (DCM) three times with a total DCM volume of 50 mL and the pH of the aqueous phase was adjusted to 2.0 with 0.1 M HCl. The aqueous was then extracted with ethyl ether 3 times with a total ether volume of 50 mL and the combined organic phase was dried over anhydrous sodium sulfate and evaporated to obtain the desired product benzoic acid (45) in 94% yield (1.15g).

5. Applications of the Synthesized Products

5.1 Synthesis of 2,6-diphenylpyrylium fluoroborate (37)



In a 10 mL two-neck round bottom flask, 1,5-diphenyl-1,5-pentadione (**37**, 0.25 mmol, 1 equiv) was dissolved in distilled toluene (2.0 mL) under N₂, and then BF₃.Et₂O (0.75 mmol, 3 equiv) was added drop by drop to the solution. The slightly red solution was refluxed at 130 °C for 12 h. After cooling down to room temperature, the reaction solution was concentrated under reduced pressure to yield a crude product. The crude product was added to 0.5 mL of acetone, and then 2 mL of diethyl ether was poured to the solution. A yellow precipitate appeared and was filtered, dried overnight under vacuum to get **38** in 55% yield (44 mg). m.p. 206.5 – 208.1 °C. ¹H of **38** is identical with the spectra of the known compound.¹ ¹H NMR (600 MHz, CDCl₃) δ 9.24 (t, *J* = 8.1 Hz, 1H), 8.67 (d, *J* = 8.2 Hz, 2H), 8.28 (d, *J* = 7.8 Hz, 4H), 7.82 (t, *J* = 7.3 Hz, 2H), 7.74 (t, *J* = 7.7 Hz, 4H).

5.2 Synthesis of antipsychotic drug Melperone (41)

5.2.1 Synthesis of 1-(4-bromobutyl)-4-fluorobenzene



1-(4-Bromobutyl)-4-fluorobenzene (39, 1.0 equiv, 0.4 mmol), sodium trifluoromethanesulfinate (1, 25 mol%)) and CH_3CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 12 h under O₂ atmosphere. After the reaction was completed, the resulting solution was concentrated under reduced pressure to get crude product, which was purified by flash chromatography (silica gel, 30:1) give petroleum ether/ethyl acetate = to the desired product 4-bromo-1-(4-fluorophenyl)butan-1-one (40) as a colorless oil in 93% yield (91.1 mg). ¹H and ¹³C NMR of 40 is identical with the spectra of the known compound.² ¹H NMR (400 MHz, CDCl₃) δ 8.00 (dd, J = 8.9, 5.4 Hz, 2H), 7.13 (t, J = 8.7 Hz, 2H), 3.54 (t, J = 6.3 Hz, 2H), 3.15 (t, J = 6.9 Hz, 2H), 2.36 – 2.24 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 197.14 (s), 165.75 (d, J = 254.9 Hz), 133.08 (d, J = 3.0 Hz), 130.60 (d, J = 9.3 Hz), 115.70 (d, J = 21.9 Hz), 36.40 (s), 33.55 (s), 26.72 (s). EI-MS: M⁺ m/z 227.

5.2.2 Synthesis of antipsychotic drug Melperone



To a stirred solution of 4-bromo-1-(4-fluorophenyl)butan-1-one (**40**, 0.25 mmol, 1 equiv), K_2CO_3 (0.5 mmol, 2.0 equiv), and KI (0.1 equiv) in dry toluene (2.0 mL) was added 4-methylpiperidine **41** (0.5 mmol, 2.0 equiv). The reaction mixture was refluxed at 125 °C for 24 h. After completion of the reaction, the reaction solution

was concentrated under reduced pressure to get crude product, which was purified by flash chromatography (silica gel, CH₂Cl₂/CH₃OH = 10:1) to give Melperone (**42**) as a colorless liquid in 87% yield (57.3 mg). ¹H and ¹³C NMR of **42** is identical with the spectra of the known compound.³ ¹H NMR (600 MHz, CDCl₃) δ 7.98 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.10 (t, *J* = 8.6 Hz, 2H), 2.95 (t, *J* = 7.2 Hz, 2H), 2.88 (d, *J* = 11.5 Hz, 2H), 2.41 – 2.37 (m, 2H), 1.96 – 1.91 (m, 4H), 1.58 (d, *J* = 13.1 Hz, 2H), 1.36-1.29 (m, 1H), 1.23 – 1.15 (m, 2H), 0.88 (d, *J* = 6.5 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 198.42 (s), 165.55 (d, *J* = 254.3 Hz), 133.46 (s), 130.63 (d, *J* = 9.2 Hz), 115.51 (d, *J* = 21.9 Hz), 57.93 (s), 53.77 (s), 36.27 (s), 33.95 (s), 30.64 (s), 21.77 (s), 21.56 (s).

5.3 Synthesis of antipsychotic drug Lenperone (44)



To a stirred solution of 4-bromo-1-(4-fluorophenyl)butan-1-one (**40**, 0.25 mmol, 1 equiv), K₂CO₃ (0.5 mmol, 2.0 equiv), and KI (0.1 equiv) in dry toluene (2.0 mL) was added (4-fluorophenyl)(piperidin-4-yl)methanone **43** (0.5 mmol, 2.0 equiv). The reaction mixture was refluxed at 125 °C for 24 h. After completion of the reaction, the reaction solution was concentrated under reduced pressure to get crude product, which was purified by flash chromatography (silica gel, CH₂Cl₂/CH₃OH = 10:1) to give Lenperone (**44**) as a pale yellow solid in 82% yield (76.1 mg). ¹H and ¹³C NMR of **44** is identical with the spectra of the known compound.⁴ ¹H NMR (600 MHz, CDCl₃) δ 8.02 – 7.97 (m, 2H), 7.97 – 7.93 (m, 2H), 7.18 – 7.07 (m, 4H), 3.20 – 3.15 (m, 1H), 3.00 – 2.96 (m, 4H), 2.43 (t, *J* = 7.0 Hz, 2H), 2.10 (t, *J* = 10.6 Hz, 2H), 1.97 – 1.92 (m, 2H), 1.84 – 1.74 (m, 4H). ¹³C NMR (150 MHz, CDCl₃) δ 201.02 (s), 198.54 (s), 165.60 (d, *J* = 251.0 Hz), 165.59 (d, *J* = 253.5 Hz), 133.56 (d, *J* = 2.0 Hz), 132.41 (s), 130.81 (d, *J* = 9.1 Hz), 130.64 (d, *J* = 8.9 Hz), 115.64 (d, *J* = 43.4 Hz). (t, *J* = 21.7 Hz), 115.64 (s), 57.69 (s), 53.05 (s), 43.62 (s), 36.08 (s), 28.60 (s), 21.57 (s).

6. Characteriation Data of the Synthesized Compounds



Acetophenone (9): Following the general procedure A. Yield was determined using dodecane as the internal standard (100% GC-MS yield). Colorless liquid. ¹H and ¹³C NMR of **9** is identical with the spectra of the known compound.⁵ ¹H NMR (600 MHz, CDCl₃) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 2.61 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 198.14, 137.09, 133.08, 128.54, 128.28, 26.60.



1-(4-Fluorophenyl)ethan-1-one (11): Following the general procedure A. Yield was determined using dodecane as the internal standard (100% GC-MS yield and ¹⁹F NMR yield). Colorless liquid. ¹H and ¹³C NMR of **11** is identical with the spectra of the known compound.⁵ ¹H NMR (600 MHz, CDCl₃) δ 7.99 – 7.97 (m, 2H), 7.14 – 7.11 (m, 2H), 2.59 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 196.46, 165.74 (d, *J* = 254.7 Hz). 133.56, 130.91 (d, *J* = 9.6 Hz), 115.63 (d, *J* = 22.1 Hz), 26.52.



1-(4-Methoxyphenyl)ethan-1-one (12): Following the general procedure A. Yield was determined using dodecane as the internal standard (100% GC-MS yield). White solid, m.p. $36.6 - 37.1 \, ^{\circ}C. ^{1}H$ and ^{13}C NMR of 12 is identical with the spectra of the known compound.⁵ ¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.80, 163.44, 130.57, 130.29, 113.64, 55.46, 26.36.



1-(4-Chlorophenyl)ethan-1-one (13): Following the general procedure A. Yield was determined using dodecane as the internal standard (98% GC-MS yield). White solid, m.p. 72.8 – 74.1 °C. ¹H and ¹³C NMR of 13 is identical with the spectra of the known compound.⁶ ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 2.59 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.83, 139.54, 135.37, 129.70, 128.86, 26.56.



1-(4-Bromophenyl)ethan-1-one (14): Following the general procedure A. Yield was determined using dodecane as the internal standard (95% GC-MS yield). Pale solid, m.p. 107.2 - 108.5 °C. ¹H and ¹³C NMR of 14 is identical with the spectra of the known compound.⁵ ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 2.58 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 197.02, 135.76, 131.87, 129.82, 128.29, 26.55.



1-(3-Bromophenyl)ethan-1-one (15): Following the general procedure A. Yield was determined using dodecane as the internal standard (96% GC-MS yield). Pale liquid. ¹H and ¹³C NMR of **15** is identical with the spectra of the known compound.⁷ ¹H NMR (600 MHz, CDCl₃) δ 8.08 (s, 1H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.68 (d, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.9 Hz, 1H), 2.59 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 196.59, 138.75, 135.92, 131.33, 130.16, 126.81, 122.91, 26.59.



1-(2-Bromophenyl)ethan-1-one (16): Following the general procedure A. Yield was determined using dodecane as the internal standard (98% GC-MS yield). Pale liquid. ¹H and ¹³C NMR of **16** is identical with the spectra of the known compound.⁸ ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.47 – 7.45 (m, 1H), 7.38 – 7.35 (m, 1H), 7.31 – 7.27 (m, 1H), 2.63 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 201.38, 141.40, 133.81, 131.77, 128.89, 127.41, 118.87, 30.31.



1-(4-Iodophenyl)ethan-1-one (17): Following the general procedure A. Yield was determined using dodecane as the internal standard (96% GC-MS yield). Pale solid, m.p. 80.3 - 81.5 °C. ¹H and ¹³C NMR of 17 is identical with the spectra of the known compound.⁹ ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, J = 8.5 Hz, 2H), 7.66 (d, J = 8.6 Hz, 2H), 2.58 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 197.35, 137.88, 136.29, 129.70, 101.11, 26.49.



1-(4-(Trifluoromethyl)phenyl)ethan-1-one (18): Following the general procedure A. Yield was determined using dodecane as the internal standard (99% GC-MS yield). Pale liquid. ¹H and ¹³C NMR of **18** is identical with the spectra of the known compound.⁵ ¹H NMR (600 MHz, CDCl₃) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 2.64 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 196.96, 139.65, 134.41 (q, *J* = 32.7 Hz), 128.60, 125.66 (q, *J* = 3.3 Hz), 123.57 (q, *J* = 273.3 Hz), 26.76.



1,1'-(1,4-Phenylene)bis(ethan-1-one) (19): Following the general procedure A. Yield was determined using dodecane as the internal standard (95% GC-MS yield). Pale solid, m.p. 109.8 – 110.6 °C. ¹H and ¹³C NMR of **19** is identical with the spectra of the known compound.⁵ ¹H NMR (400 MHz, CDCl₃) δ 8.04 (s, 4H), 2.65 (s, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 197.49, 140.13, 128.49, 26.92.



1,1'-(1,4-Phenylene)bis(ethan-1-one) (19): Following the general procedure A and irradiated under 3 W purple light emitting diode (LED) bulb (380-385 nm), Yield was determined using dodecane as the internal standard (97% GC-MS yield). ¹H and ¹³C NMR of **19** is identical with the spectra of the known compound.⁵



Methyl 4-acetylbenzoate (20): Following the general procedure A. Yield was determined using dodecane as the internal standard (99% GC-MS yield). Pale solid, m.p. 96.2 – 97.0 °C. ¹H and ¹³C NMR of **20** is identical with the spectra of the known compound.⁵ ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.5 Hz, 2H), 8.01 (d, *J* = 8.5 Hz, 2H), 3.95 (s, 3H), 2.65 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 197.54, 166.21, 140.19, 133.87, 129.81, 128.19, 52.47, 26.89.



4-Acetylbenzonitrile (21): Following the general procedure A. Yield was determined using dodecane as the internal standard (99% GC-MS yield). Pale solid, m.p. 60.5 – 61.7 °C. ¹H and ¹³C NMR of **21** is identical with the spectra of the known compound.⁵ ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.2 Hz, 2H), 2.65 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.52, 139.86, 132.50, 128.67, 117.91, 116.38, 26.77.



1-(4-Nitrophenyl)ethan-1-one (22): Following the general procedure A. Yield was determined using dodecane as the internal standard (97% GC-MS yield). Yellow solid, m.p. 77.9 - 79.1 °C. ¹H and ¹³C NMR of **22** is identical with the spectra of the known compound.⁶ ¹H NMR (600 MHz, CDCl₃) δ 8.30 (d, J = 8.8 Hz, 2H), 8.10 (d, J = 8.8 Hz, 2H), 2.68 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 196.27, 150.32, 141.34, 129.27, 123.82, 26.95.



1-([1,1'-Biphenyl]-4-yl)ethan-1-one (23): Following the general procedure A. Yield was determined using dodecane as the internal standard (95% GC-MS yield). White solid, m.p. 154.7 – 155.9 °C. ¹H and ¹³C NMR of **23** is identical with the spectra of the known compound.¹⁰ ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.3 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 2.64 (s, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 197.73, 145.75, 139.84, 135.82, 128.92, 128.88, 128.20, 127.24, 127.19, 26.64.



1-(Naphthalen-1-yl)ethan-1-one (24): Following the general procedure A. Yield was determined using dodecane as the internal standard (92% GC-MS yield). Colorless liquid. ¹H and ¹³C NMR of **24** is identical with the spectra of the known compound.⁶ ¹H NMR (400 MHz, CDCl₃) δ 8.76 (d, *J* = 8.6 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.95 (dd, *J* = 7.3, 0.8 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.63 – 7.59 (m, 1H), 7.56 – 7.48 (m, 2H), 2.76 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 201.85, 135.38, 133.92, 133.02, 130.08, 128.67, 128.37, 128.03, 126.41, 125.96, 124.29, 29.97.



1-(Naphthalen-2-yl)ethan-1-one (25): Following the general procedure A. Yield was determined using dodecane as the internal standard (92% GC-MS yield). White solid, m.p. 54.7 – 55.2 °C. ¹H and ¹³C NMR of **25** is identical with the spectra of the known compound.⁶ ¹H NMR (400 MHz, CDCl₃) δ 8.47 (s, 1H), 8.04 (dd, J = 8.6, 1.7 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.91 – 7.87 (m, 2H), 7.63 – 7.54 (m, 2H), 2.74 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 198.11, 135.55, 134.44, 132.47, 130.18, 129.52, 128.45, 128.40, 127.76, 126.75, 123.86, 26.70.



1-(Furan-2-yl)ethan-1-one (26): Following the general procedure A. Yield was determined using dodecane as the internal standard (51% GC-MS yield). Yellow liquid. ¹H and ¹³C NMR of **26** is identical with the spectra of the known compound.⁶ ¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 1.8 Hz, 1H), 7.18 (d, *J* = 3.7 Hz, 1H), 6.56 – 6.50 (m, 1H), 2.48 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 186.80 (s), 152.87 (s), 146.38 (s), 117.18 (s), 112.22 (s), 26.02 (s).



Propiophenone (27): Following the general procedure A. Yield was determined using dodecane as the internal standard (99% GC-MS yield). Colorless liquid. ¹H and ¹³C NMR of 27 is identical with the spectra of the known compound.¹⁰ ¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 3.01 (q, *J* = 7.2 Hz, 2H), 1.23 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 200.82, 136.86, 132.85, 128.52, 127.94, 31.75, 8.21.



1-Phenylbutan-1-one (**28**): Following the general procedure A. Yield was determined using dodecane as the internal standard (98% GC-MS yield). Colorless liquid. ¹H and ¹³C NMR of **28** is identical with the spectra of the known compound.⁵ ¹H NMR (600 MHz, CDCl₃) δ 7.96 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 2.95 (t, *J* = 7.3 Hz, 2H), 1.80 – 1.74 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 200.41, 137.08, 132.83, 128.51, 128.00, 40.49, 17.74, 13.86.



Cyclohexyl(phenyl)methanone (29): Following the general procedure A. Yield was determined using dodecane as the internal standard (96% GC-MS yield). White solid, m.p. 58.3 - 59.1 °C. ¹H and ¹³C NMR of **29** is identical with the spectra of the known compound.¹⁰ ¹H NMR (600 MHz, CDCl₃) δ 7.94 (d, J = 7.4 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 3.29 – 3.24 (m, 1H), 1.90 – 1.83 (m, 4H), 1.75 – 1.72 (m, 1H), 1.53 – 1.46 (m, 2H), 1.42 – 1.35 (m, 2H), 1.31 – 1.23 (m, 1H). ¹³C NMR (150 MHz, CDCl₃) δ 203.89, 136.31, 132.69, 128.55, 128.22, 45.60, 29.39, 25.94, 25.83.



2-Bromo-1-phenylethan-1-one (30): Following the general procedure A. Yield was determined using dodecane as the internal standard (98% GC-MS yield). Colorless liquid. ¹H and ¹³C NMR of **30** is identical with the spectra of the known compound.¹¹ ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 7.5 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 4.46 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 191.25, 133.95, 133.93, 128.91, 128.85, 30.88.



3-Hydroxy-1-phenylpropan-1-one (31): Following the general procedure A. Yield was determined using dodecane as the internal standard (95% GC-MS yield). Colorless liquid. ¹H and ¹³C NMR of **31** is identical with the spectra of the known compound.¹² ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (dd, *J* = 10.7, 4.6 Hz, 2H), 4.03 (t, *J* = 5.3 Hz, 2H), 3.23 (t, *J* = 5.3 Hz, 2H), 2.79 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 200.47, 136.58, 133.49, 128.65, 128.01, 58.01, 40.34.



1-(3,5-Diethylphenyl)ethan-1-one (32): Following the general procedure A. Yield was determined using dodecane as the internal standard (61% GC-MS yield). Pale liquid. ¹H and ¹³C NMR of **32** is identical with the spectra of the known compound.⁴ ¹H NMR (600 MHz, CDCl₃) δ 7.61 (s, 1H), 7.24 (s, 1H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.59 (s, 2H), 1.26 (t, *J* = 7.6 Hz, 4H). ¹³C NMR (150 MHz, CDCl₃) δ 198.61, 144.61, 137.36, 132.42, 125.18, 28.68, 26.69, 15.51.



1,1',1''-(Benzene-1,3,5-triyl)tris(ethan-1-one) (33): Following the general procedure A and irradiated under 3 W purple light emitting diode (LED) bulb (380-385 nm). Yield was determined using dodecane as the internal standard (96% GC-MS yield). Yellow solid, m.p. 160.5 – 161.7 °C. ¹H and ¹³C NMR of **33** is identical with the spectra of the known compound.⁴ ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.60 (s, 3H), 2.71 (s, 9H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 197.10, 137.53, 131.28, 27.01.



Benzophenone (34): Following the general procedure A. Yield was determined using dodecane as the internal standard (98% GC-MS yield). White solid, m.p. 49.3 – 50.1 °C. ¹H and ¹³C NMR of **34** is identical with the spectra of the known compound.¹¹ ¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 7.3 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 196.77, 137.56, 132.41, 130.05, 128.26.



1,2-Diphenylethan-1-one (**35**): Following the general procedure A. Yield was determined using dodecane as the internal standard (97% GC-MS yield). Yellow solid, m.p. 55.1 - 56.4 °C. ¹H and ¹³C NMR of **35** is identical with the spectra of the known compound.⁵ ¹H NMR (600 MHz, CDCl₃) δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.24 (m, 3H), 4.28 (s, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 197.60, 136.57, 134.50, 133.13, 129.44, 128.64, 128.61, 128.58, 126.86, 45.47.



1,4-Diphenylbutane-1,4-dione (36): Following the general procedure A. Column chromatography afforded **36** as a colorless solid (42.4 mg, 89%). m.p. 144.1 – 145.1 °C. ¹H and ¹³C NMR of **36** is identical with the spectra of the known compound.^{13 1}H NMR (600 MHz, CDCl₃) δ 8.05 (d, *J* = 7.2 Hz, 4H), 7.58 (t, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.7 Hz, 4H), 3.47 (s, 4H). ¹³C NMR (150 MHz, CDCl₃) δ 198.68, 136.76, 133.15, 128.59, 128.11, 32.58.



1,5-Diphenylpentane-1,5-dione (37): Following the general procedure A. Column chromatography afforded **37** as a colorless solid (43.3 mg, 86%). m.p. 61.0 - 62.1 °C. ¹H and ¹³C NMR of **37** is identical with the spectra of the known compound.¹³ ¹H NMR (600 MHz, CDCl₃) δ 7.98 (d, *J* = 7.5 Hz, 4H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.7 Hz, 4H), 3.13 (t, *J* = 6.9 Hz, 4H), 2.21 (p, *J* = 7.0 Hz, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 199.85, 136.83, 133.06, 128.59, 128.05, 37.59, 18.70.



4-Bromo-1-(4-fluorophenyl)butan-1-one (40): Following the general procedure A. Column chromatography afforded **37** as a colorless oil 93% yield (91.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.00 (dd, J = 8.9, 5.4 Hz, 2H), 7.13 (t, J = 8.7 Hz, 2H), 3.54 (t, J = 6.3 Hz, 2H), 3.15 (t, J = 6.9 Hz, 2H), 2.36 – 2.24 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 197.14 (s), 165.75 (d, J = 254.9 Hz), 133.08 (d, J = 3.0 Hz), 130.60 (d, J = 9.3 Hz), 115.70 (d, J = 21.9 Hz), 36.40 (s), 33.55 (s), 26.72 (s).



Benzoic acid (45): Following the general procedure B. **45** was obtained as a colorless solid (22.7 mg, 93%); Following the general procedure C. **45** was obtained as a colorless solid (23.2 mg, 95%). White solid, m.p. 124.6 - 125.7 °C. ¹H and ¹³C NMR of **45** is identical with the spectra of the known compound.¹⁴ ¹H NMR (400 MHz, CDCl₃) δ 8.14 (d, *J* = 7.0 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 172.42, 133.81, 130.21, 129.30, 128.48.



4-Methoxybenzoic acid (46): Following the general procedure B. **46** was obtained as a colorless solid (26.5 mg, 87%); Following the general procedure C. **46** was obtained as a colorless solid (27.7 mg, 91%). White solid, m.p. 185.2 – 185.8 °C. ¹H and ¹³C NMR of **46** is identical with the spectra of the known compound.¹⁴ ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.63 (s, 1H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 8.9 Hz, 2H), 3.82 (s, 3H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.05, 162.88, 131.39, 122.99, 113.85, 55.47.



4-Fluorobenzoic acid (47): Following the general procedure B. **47** was obtained as a colorless solid (26.9 mg, 96%); Following the general procedure C. **47** was obtained as a colorless solid (27.2 mg, 97%)and is identical with the spectra of the known compound.¹⁴ m.p. 182.4 – 183.1 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.06 (s, 1H), 8.04 – 7.96 (m, 2H), 7.36 – 7.29 (m, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.69, 165.15 (d, *J* = 250.5 Hz), 132.35 (d, *J* = 9.5 Hz), 127.52 (d, *J* = 2.8 Hz), 115.86 (d, *J* = 22.0 Hz).



4-Chlorobenzoic acid (48): Following the general procedure B. **48** was obtained as a pale solid (29.7 mg, 95%); Following the general procedure C. **48** was obtained as a pale solid (28.8 mg, 92%). m.p. 233.6 – 234.3 °C. ¹H and ¹³C NMR of **48** is identical with the spectra of the known compound. ^{15 1}H NMR (400 MHz, DMSO-*d*₆) δ 13.16 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.78, 138.08, 131.38, 129.79, 128.97.



3-Chlorobenzoic acid (49): Following the general procedure B. **49** was obtained as a pale solid (28.8 mg, 92%); Following the general procedure C. **49** was obtained as a pale solid (29.1 mg, 93%). m.p. 155.7 – 156.4 °C. ¹H and ¹³C NMR of **49** is identical with the spectra of the known compound.¹⁴ ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.32 (s, 1H), 7.90 – 7.88 (m, 2H), 7.71 – 7.68 (m, 1H), 7.54 (t, *J* = 8.1 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.08, 133.35, 132.90, 132.73, 130.66, 128.84, 127.93.



2-Chlorobenzoic acid (50): Following the general procedure B. **50** was obtained as a pale solid (28.5 mg, 91%); Following the general procedure C. **50** was obtained as a pale solid (29.4 mg, 94%). m.p. 140.1 – 140.8 °C. ¹H and ¹³C NMR of **50** is identical with the spectra of the known compound.¹⁴ ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.40 (s, 1H), 7.78 (d, *J* = 7.4 Hz, 1H), 7.58 – 7.50 (m, 2H), 7.46 – 7.40 (m, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.76, 132.62, 131.59, 131.49, 130.83, 130.65, 127.27.



4-Bromobenzoic acid (51): Following the general procedure B. 51 was obtained as a

pale solid (39.0 mg, 97%); Following the general procedure C. **51** was obtained as a pale solid (38.6 mg, 96%). m.p. 252.4 – 253.2 °C. ¹H and ¹³C NMR of **51** is identical with the spectra of the known compound.¹⁵ ¹H NMR (400 MHz, DMSO- d_6) δ 13.21 (s, 1H), 7.86 (d, J = 8.5 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H). ¹³C NMR (100 MHz, DMSO- d_6) δ 166.96, 131.97, 131.56, 130.18, 127.18.



3-Bromobenzoic acid (52): Following the general procedure B. **52** was obtained as a white solid (37.4 mg, 93%); Following the general procedure C. **52** was obtained as a white solid (37.8 mg, 94%). m.p. 156.5 – 157.3 °C. ¹H and ¹³C NMR of **52** is identical with the spectra of the known compound.¹⁶ ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.30 (s, 1H), 8.03 (s, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.9 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 165.79, 135.43, 132.88, 131.56, 130.74, 128.10, 121.54.



2-Bromobenzoic acid (53): Following the general procedure B. **53** was obtained as a white solid (35.8 mg, 89%); Following the general procedure C. **53** was obtained as a white solid (38.2 mg, 95%). m.p. 148.7 – 150.0 °C. ¹H and ¹³C NMR of **53** is identical with the spectra of the known compound.¹⁷ ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.96 (br, 1H), 7.76 – 7.65 (m, 2H), 7.49 – 7.37 (m, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.52, 134.28, 133.67, 132.30, 130.48, 127.67, 119.85.



4-(Trifluoromethyl)benzoic acid (54): Following the general procedure B. **54** was obtained as a pale solid (33.1 mg, 87%); Following the general procedure C. **54** was obtained as a pale solid (25.4 mg, 93%). m.p. 220.7 – 221.9 °C. ¹H and ¹³C NMR of **54** is identical with the spectra of the known compound.¹⁴ ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.44 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 2H), 7.85 (d, *J* = 7.5 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.18, 134.59, 132.49 (q, *J* = 31.9 Hz), 130.07, 125.55 (q, *J* = 7.2 Hz), 123.79 (q, *J* = 272.7 Hz).



4-Acetylbenzoic acid (**55**): Following the general procedure B. **55** was obtained as a pale solid (30.2 mg, 92%), m.p. 208.7 – 209.9 °C. ¹H and ¹³C NMR of **55** is identical with the spectra of the known compound.¹⁴ ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.19 (s, 1H), 8.05 (s, 4H), 2.62 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 197.75 (s), 166.65 (s), 139.85 (s), 134.50 (s), 129.56 (s), 128.34 (s), 27.03 (s).



4-Benzoylbenzoic acid (**56**): Following the general procedure B. **56** was obtained as a white solid (40.7 mg, 90%). m.p. 199.2 – 200.1 °C. ¹H and ¹³C NMR of **56** is identical with the spectra of the known compound.¹⁸ ¹H NMR (600 MHz, DMSO-D6) δ 13.25 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.70 (t, *J* = 7.3 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 2H). ¹³C NMR (150 MHz, DMSO-D6) δ 195.41, 166.66, 140.56, 136.50, 133.98, 133.12, 129.74, 129.63, 129.42, 128.70.



4-(Methoxycarbonyl)benzoic acid (57): Following the general procedure B. 57 was obtained as a pale solid (34.2 mg, 95%); Following the general procedure C. 57 was obtained as a pale solid (33.8 mg, 94%). m.p. 216.9 – 218.2 °C. ¹H and ¹³C NMR of 57 is identical with the spectra of the known compound.¹⁵ ¹H NMR (400 MHz, DMSO- d_6) δ 8.05 (s, 4H), 3.88 (s, 3H). ¹³C NMR (150 MHz, DMSO- d_6) δ 166.63, 165.64, 135.08, 133.07, 129.58, 129.32, 52.45.



4-Carbamoylbenzoic acid (58): Following the general procedure B. **58** was obtained as a pale solid (30.1 mg, 91%); Following the general procedure C. **58** was obtained as a pale solid (31.7 mg, 96%). m.p. 247.7 – 249.2 °C. ¹H and ¹³C NMR of **58** is identical with the spectra of the known compound.¹⁵ ¹H NMR (600 MHz, DMSO-*d*₆) δ 13.15 (s, 1H), 8.12 (s, 1H), 7.98 (dd, J = 22.2, 8.2 Hz, 4H), 7.53 (s, 1H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 167.27, 166.84, 138.10, 133.06, 129.21, 127.70.



4-Cyanobenzoic acid (59): Following the general procedure B. **59** was obtained as a white solid (27.1 mg, 92%); Following the general procedure C. **59** was obtained as a white solid (26.8 mg, 91%). m.p. 218.8 – 219.3 °C. ¹H and ¹³C NMR of **59** is identical with the spectra of the known compound.¹⁵ ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.40 (s, 1H), 8.08 (d, J = 7.8 Hz, 2H), 7.99 (d, J = 7.5 Hz, 2H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 166.07, 134.88, 132.67, 129.94, 118.20, 115.08.



3-Bromo-4-cyanobenzoic acid (60): Following the general procedure B. 60 was obtained as a white solid (26.8 mg, 91%). m.p. 200.6 – 201.5 °C. ¹H NMR (400 MHz, DMSO- d_6) δ 8.25 (d, J = 14.2 Hz, 1H), 8.18 – 7.93 (m, 2H). ¹³C NMR (151 MHz, DMSO- d_6) δ 164.92 (s), 136.41 (s), 135.35 (s), 133.12 (s), 128.74 (s), 124.76 (s), 118.04 (s), 116.76 (s). HRMS (ESI) ([M+H⁺]) Calcd. For C₈H₅BrNO₂⁺: 227.0365, Found: 227.0359.



[1,1'-Biphenyl]-4-carboxylic acid (61): Following the general procedure B. 61 was obtained as a white solid (36.5 mg, 92%); Following the general procedure B. 61 was obtained as a white solid (27.7 mg, 95%). m.p. 222.9 – 224.0 °C. ¹H and ¹³C NMR of 61 is identical with the spectra of the known compound.¹⁵ ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.00 (s, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.73 (d, *J* = 7.4 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 167.16, 144.29, 139.03, 129.96, 129.67, 129.08, 128.28, 126.96, 126.80.



Furan-2-carboxylic acid (62): Following the general procedure B. **62** was obtained as a pale solid (11.7 mg, 52%). m.p. 132.9 – 134.0 °C. ¹H and ¹³C NMR of **62** is identical with the spectra of the known compound.^{15 1}H NMR (400 MHz, DMSO- d_6) δ 13.07 (s, 1H), 7.91 (dd, J = 1.7, 0.8 Hz, 1H), 7.21 (d, J = 3.9 Hz, 1H), 6.65 (dd, J =3.5, 1.7 Hz, 1H). ¹³C NMR (101 MHz, DMSO- d_6) δ 159.35 (s), 147.09 (s), 144.92 (s), 117.75 (s), 112.13 (s).



Thiophene-2-carboxylic acid (63): Following the general procedure B. **63** was obtained as a white solid (17.4 mg, 68%). m.p. 125.3 - 136.0 °C. ¹H and ¹³C NMR of **63** is identical with the spectra of the known compound.¹⁵ ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.05 (s, 1H), 7.88 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.73 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.18 (dd, *J* = 4.8, 3.8 Hz, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 162.92 (s), 134.65 (s), 133.28, 133.21, 128.23 (s).



3-Methoxybenzoic acid (64): Following the general procedure C. **64** was obtained as a pale solid (28.3 mg, 93%). m.p. 107.1 – 108.0 °C. ¹H and ¹³C NMR of **64** is identical with the spectra of the known compound.^{15 1}H NMR (600 MHz, DMSO-*d*₆) δ 13.69 (s, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.44 (s, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 167.25, 159.21, 132.54, 129.66, 121.55, 118.74, 113.91, 55.24.



2-Methoxybenzoic acid (65): Following the general procedure C. **65** was obtained as a pale solid (28.6 mg, 94%). m.p. 101.5 – 102.1 °C. ¹H and ¹³C NMR of **65** is identical with the spectra of the known compound.¹⁴ ¹H NMR (400 MHz, DMSO- d_6) δ 12.59 (s, 1H), 7.63 (dd, J = 7.6, 1.7 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.11 (d, J = 8.4Hz, 1H), 6.99 (t, J = 7.4 Hz, 1H), 3.81 (s, 3H). ¹³C NMR (100 MHz, DMSO- d_6) δ 167.38, 158.08, 133.07, 130.66, 121.29, 120.03, 112.42, 55.70.



4-Hydroxybenzoic acid (66): Following the general procedure C. 66 was obtained as a white solid (24.6 mg, 89%). m.p. 217.6 – 218.2 °C. ¹H and ¹³C NMR of 66 is identical with the spectra of the known compound.^{19 1}H NMR (400 MHz, DMSO- d_6)

δ 12.41 (s, 1H), 10.22 (s, 1H), 7.79 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H). ¹³C NMR (100 MHz, DMSO- d_6) δ 167.23, 161.65, 131.59, 121.40, 115.17.



3-Fluorobenzoic acid (67): Following the general procedure C. **67** was obtained as a white solid (26.6 mg, 95%). m.p. 124.1 – 125.6 °C. ¹H and ¹³C NMR of **67** is identical with the spectra of the known compound.^{20 1}H NMR (600 MHz, DMSO-*d*₆) δ 13.08 (s, 1H), 7.86 (dd, *J* = 10.5, 4.5 Hz, 1H), 7.63 (dd, *J* = 12.8, 7.3 Hz, 1H), 7.30 (dd, *J* = 12.9, 5.5 Hz, 2H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 165.05, 161.10 (d, *J* = 256.8 Hz), 134.69 (d, *J* = 8.8 Hz), 131.89, 124.45 (d, *J* = 3.3 Hz), 119.34 (d, *J* = 10.5 Hz), 116.91 (d, *J* = 22.0 Hz).



3,4-Dichlorobenzoic acid (68): Following the general procedure C. **68** was obtained as a white solid (36.3 mg, 95%). m.p. 204.9 – 206.3 °C. ¹H and ¹³C NMR of **68** is identical with the spectra of the known compound.¹⁴ ¹H NMR (400 MHz, DMSO- d_6) δ 8.05 (s, 1H), 7.87 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H). ¹³C NMR (100 MHz, DMSO- d_6) δ 165.93, 136.31, 132.04, 131.91, 131.58, 131.48, 129.84.



2-Bromo-4-fluorobenzoic acid (69): Following the general procedure C. **69** was obtained as a pale solid (40.3 mg, 92%). m.p.176.3 – 177.5 °C. ¹H and ¹³C NMR of **69** is identical with the spectra of the known compound.²¹ ¹H NMR (600 MHz, DMSO-*d*₆) δ 13.46 (s, 1H), 7.86 (dd, *J* = 8.5, 6.3 Hz, 1H), 7.69 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.35 (td, *J* = 8.4, 2.2 Hz, 1H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 166.39, 162.85

(d, *J* = 253.1 Hz), 132.95 (d, *J* = 9.6 Hz), 129.95, 121.45 (d, *J* = 10.1 Hz), 121.12 (d, *J* = 24.9 Hz), 114.95 (d, *J* = 21.2 Hz).



3-Bromo-4-fluorobenzoic acid (**70**): Following the general procedure C. **70** was obtained pale solid (42.0 mg, 96%). m.p. 140.4 – 141.6 °C. ¹H and ¹³C NMR of **70** is identical with the spectra of the known compound.²² ¹H NMR (600 MHz, DMSO-*d*₆) δ 13.23 (s, 1H), 8.16 (d, *J* = 6.5 Hz, 1H), 7.97 (s, 1H), 7.48 (t, *J* = 8.5 Hz, 1H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 165.25, 161.03 (d, *J* = 251.4 Hz), 134.55, 131.19 (d, *J* = 8.9 Hz), 128.94, 117.08 (d, *J* = 22.9 Hz), 108.34 (d, *J* = 21.7 Hz).



2-Bromo-5-fluorobenzoic acid (71): Following the general procedure C. 71 was obtained as a pale solid (41.6 mg, 95%). m.p. 155.7 – 156.9 °C. ¹H and ¹³C NMR of 71 is identical with the spectra of the known compound.¹⁴ ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.54 (s, 1H), 7.74 (dd, *J* = 8.9, 5.1 Hz, 1H), 7.58 (dd, *J* = 9.0, 3.1 Hz, 1H), 7.33 (td, *J* = 8.5, 3.1 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.29, 160.93 (d, *J* = 246.3 Hz), 135.67 (d, *J* = 7.7 Hz), 135.58, 119.71 (d, *J* = 22.4 Hz), 117.47 (d, *J* = 24.6 Hz), 114.64.



2-Bromo-6-fluorobenzoic acid (72): Following the general procedure C. 72 was obtained as a pale solid (40.3 mg, 92%). m.p. 153.4 - 154.3 °C. ¹H and ¹³C NMR of 72 is identical with the spectra of the known compound.²³ ¹H NMR (600 MHz, DMSO-*d*₆) δ 7.54 (d, *J* = 7.8 Hz, 1H), 7.44 (dd, *J* = 14.5, 7.4 Hz, 1H), 7.37 (t, *J* = 8.6

Hz, 1H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 164.66, 158.26 (d, *J* = 250.0 Hz), 132.27 (d, *J* = 8.7 Hz), 128.71, 125.82 (d, *J* = 21.8 Hz), 118.66, 115.26 (d, *J* = 21.1 Hz).



3-(Trifluoromethyl)benzoic acid (73): Following the general procedure C. 73 was obtained as a white solid (34.6 mg, 91%). m.p. 103.7 - 105.2 °C. ¹H and ¹³C NMR of 73 is identical with the spectra of the known compound.¹⁵ ¹H NMR (600 MHz, DMSO-*d*₆) δ 13.41 (s, 1H), 8.31 – 8.08 (m, 2H), 7.98 (d, *J* = 6.1 Hz, 1H), 7.75 (s, 1H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 166.05, 133.22, 132.01, 130.07, 129.45 (q, *J* = 64.6 Hz), 129.34, 125.53, 123.82 (q, *J* = 272.7 Hz).



2-Fluoro-5-(trifluoromethyl)benzoic acid (74): Following the general procedure C. 74 was obtained as a pale solid (39.1 mg, 94%). m.p. 101.5 – 102.9 °C. ¹H NMR (600 MHz, DMSO- d_6) δ 13.69 (s, 1H), 8.14 (d, J = 4.9 Hz, 1H), 8.06 – 8.00 (m, 1H), 7.57 (t, J = 9.5 Hz, 1H). ¹³C NMR (150 MHz, DMSO- d_6) δ 163.80, 163.14 (d, J = 263.3 Hz), 131.76 (d, J = 7.2 Hz), 129.16, 125.40 (q, J = 65.3 Hz), 123.44 (q, J = 272.2 Hz), 120.42 (d, J = 11.7 Hz), 118.67 (d, J = 24.0 Hz). HRMS (ESI) ([M+H⁺]) Calcd. For C8H5F4O2+: 209.1191, Found: 209.1187.



2-Bromo-5-(trifluoromethyl)benzoic acid (75): Following the general procedure C. **75** was obtained as a pale solid (49.5 mg, 92%). m.p. 118.9 – 120.2 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.04 (d, *J* = 2.1 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.82 – 7.76 (m, 1H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 166.21, 135.15, 134.94, 128.83 (q, *J* = 7.2 Hz), 128.42 (q, *J* = 65.7 Hz), 127.03 (q, *J* = 7.2 Hz), 124.64, 123.50 (q, *J* = 272.6 Hz). HRMS (ESI) ([M+H⁺]) Calcd. For C₈H₅BrF₃O₂⁺: 270.0247, Found: 270.0238.



2-Naphthoic acid (**76**): Following the general procedure C. **76** was obtained as a white solid (29.6 mg, 86%). m.p. 185.8 – 187.2 °C. ¹H and ¹³C NMR of **76** is identical with the spectra of the known compound.^{15 1}H NMR (400 MHz, DMSO- d_6) δ 13.06 (s, 1H), 8.57 (s, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.99 – 7.92 (m, 3H), 7.64 – 7.54 (m, 2H). ¹³C NMR (100 MHz, DMSO- d_6) δ 167.47, 134.96, 132.18, 130.55, 129.32, 128.37, 128.21, 128.08, 127.69, 126.85, 125.19.



Isonicotinic acid (77): Following the general procedure C. 77 was obtained as a brown solid (23.6 mg, 96%). m.p. 311.6 – 312.9 °C. ¹H and ¹³C NMR of 77 is identical with the spectra of the known compound.²⁴ ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.40 (s, 1H), 8.77 (d, *J* = 5.9 Hz, 2H), 7.81 (d, *J* = 5.9 Hz, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.22, 150.63, 138.10, 122.79.



Nicotinic acid (78): Following the general procedure C. 78 was obtained as a pale solid (23.4 mg, 95%). m.p. 237.5 – 238.6°C. ¹H and ¹³C NMR of 78 is identical with the spectra of the known compound.¹⁹ ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.39 (s, 1H), 9.07 (s, 1H), 8.79 (d, *J* = 4.5 Hz, 1H), 8.27 (d, *J* = 7.9 Hz, 1H), 7.54 (dd, *J* = 7.9, 4.9 Hz, 1H). ¹³C NMR (100 MHz, DMSO-*d*₆) δ 166.31, 153.35, 150.26, 137.00, 126.59, 123.86.



Picolinic acid (79): Following the general procedure C. **79** was obtained as a white solid (23.4 mg, 95%). m.p. 136.3 - 138.4 °C. ¹H and ¹³C NMR of **79** is identical with the spectra of the known compound.^{25 1}H NMR (600 MHz, DMSO-*d*₆) δ 13.69 (s, 1H), 8.70 (d, *J* = 4.6 Hz, 1H), 8.04 (d, *J* = 7.7 Hz, 1H), 7.98 (td, *J* = 7.7, 1.5 Hz, 1H), 7.64 – 7.60 (m, 1H). ¹³C NMR (150 MHz, DMSO-*d*₆) δ 166.25, 149.48, 148.42, 137.58, 127.14, 124.72.



Benzo[b]thiophene-2-carboxylic acid (80): Following the general procedure C. **80** was obtained as a yellow solid (33.1 mg, 93%). m.p. $231.2 - 232.4^{\circ}$ C. ¹H and ¹³C NMR of **80** is identical with the spectra of the known compound.²⁶ ¹H NMR (600 MHz, DMSO-*d*₆) δ 8.07 (s, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H). ¹³C NMR (151 MHz, DMSO-*d*₆) δ 163.72, 141.26, 138.85, 135.94, 129.68, 126.81, 125.62, 124.97, 122.94.

Decanoic acid (81): Following the general procedure C. **81** was obtained as a white solid (31.4 mg, 91%). m.p. 30.1 - 32.3 °C. ¹H and ¹³C NMR of **81** is identical with the spectra of the known compound.¹⁴ ¹H NMR (600 MHz, CDCl₃) δ 11.24 (s, 1H), 2.34 (t, *J* = 7.5 Hz, 2H), 1.65 – 1.60 (m, 2H), 1.38 – 1.20 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 180.53, 34.10, 31.83, 29.36, 29.22, 29.03, 24.64, 22.63, 14.05.

7. Description of the LED Light Source

The spectrum of the blue LED light was performed on a Hitachi U-3010 spectrophotometer. As shown in **Figure S1**, the wavelength of the LED light was 400-405 nm.



Figure S1. Spectrum of the LED light

8. Studies on Reaction Mechanism

8.1. DFT calculations

8.1.1 Computational methods

The DFT calculations in this study were performed by the GAUSSIAN 09. DFT method B3LYP with a standard 6-31G basis set was used for searching the transition state, the geometry optimizations and frequencies calculations.

8.1.2 Geometries for the optimized compounds and transition state

Table S9. The cartesian coordinates for the optimized reactants ($CF_3SO_2Na + O_2$)

Reactants: $CF_3SO_2Na + O_2$			
S	-0.24381	0.96567	0.04414
0	-0.88589	1.00715	1.3654
0	-1.36146	0.49337	-1.10333
Na	-2.08177	-1.37787	-0.63088
С	1.10275	-0.19804	0.07509
F	0.6307	-1.42434	0.38471
F	2.00624	0.18377	1.00269
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F	1.69257	-0.23614	-1.13864
0	0.54	2.35528	-0.26054
0	-0.58045	2.65487	-0.3251

Table S10.	The	cartesian	coordinates	for	the	transition	state
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Transition State:			
S	1.37428	-0.48723	0
0	1.40859	0.48835	1.32464
0	1.40521	0.48703	-1.32572
Na	0.61764	2.2786	-0.0002
С	-1.59157	-0.34249	0.00048
F	-1.22356	1.08405	0.00211
F	-2.40793	-0.46527	1.11317
F	-2.40162	-0.46391	-1.11709
0	-0.54561	-1.14817	0.00315
0	2.11492	-1.90317	-0.00013

Table S11. The cartesian coordinates for product ${\bf 2}$

Product:			
S	-1.04506	0.07611	0.00002
0	-0.581	-0.76602	1.36544
0	-0.57474	-0.76861	-1.36165
Na	0.33775	-2.53254	-0.00025
С	1.49597	0.7212	-0.00001

F	1.7954	-0.59518	0.00107
F	1.34617	1.38032	1.16859
F	1.34635	1.37844	-1.16968
0	-0.31948	1.58025	0.00026
0	-2.70503	0.25882	-0.00396

Table S12. The absolute energies, enthalpies, and Gibbs free energies of all structures calculated at B3LYP/6-31G level by Gaussian 09

	ZPE ¹	Energy Corr ²	Enthalpy Corr ³	Gibbs Free Energy Corr ⁴
Reactant	0.026061	0.037371	0.038315	-0.011949
TS	0.023666	0.035041	0.035985	-0.014516
Product	0.027460	0.037546	0.038490	-0.008694
	Sum ⁵	Sum ⁶	Sum ⁷	Sum ⁸
Reactant	Sum ⁵ -1198.475774	Sum ⁶ -1198.464465	Sum ⁷ -1198.463521	Sum ⁸ -1198.513785
Reactant TS	Sum ⁵ -1198.475774 -1198.439731	Sum ⁶ -1198.464465 -1198.428356	Sum ⁷ -1198.463521 -1198.427411	Sum ⁸ -1198.513785 -1198.477912

¹ZPE: Zero-point correction (Hartree/Particle); ²Thermal correction to Energy; ³Thermal correction to Enthalpy; ⁴Thermal correction to Gibbs Free Energy; ⁵Sum of electronic and zero-point Energies; ⁶Sum of electronic and thermal Energies; ⁷Sum of electronic and thermal Enthalpies; ⁸Sum of electronic and thermal Free Energies.

8.1.3 Analysis of the DFT calculations on the formation of pentacoordinate sulfide 2

Intrigued by the hypothesis of formation of pentacoordinate sulfide 2 via reaction sodium trifluoromethanesulfinate (CF₃SO₂Na) (1) with oxygen, density functional theory (DFT) calculations were undertaken to gain insight into the possibility of this transformation. As shown in **Figure S2**, the desired pentacoordinate sulfide (2) is energetically favored over the reactants (CF₃SO₂Na + O₂) by 105.02 kcal/mol. Moreover, the DFT calculations on transition state indicated that only 24.12 kcal/mol activation energy was needed. Based on the above density functional theory (DFT) calculations results, it is theoretically feasible for the formation of pentacoordinate sulfide 2



Figure S2. The DFT calculations on the formation of pentacoordinate sulfide 2

8.2 Structural investigations on pentacoordinate sulfide 2

8.2.1 Preparation of pentacoordinate sulfide 2

$$F_{3}C^{-S}ONa \xrightarrow{O_{2} (1 \text{ atm}), CH_{3}CN} F_{3}C^{-S}ONa \xrightarrow{O_{1} (1 \text{ atm}), CH_{3}CN} F_{3}C^{-S}ONa \xrightarrow{O_{1} (1 \text{ atm}), r.t., 12 h} F_{3}C^{-S}ONA \xrightarrow{O_{1} (1 \text{ atm$$

Sodium trifluoromethanesulfinate (1, 0.25 mmol) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 12 h under O₂ atmosphere. After the reaction was completed, the reaction solution was concentrated under reduced pressure to yield crude product that was used for further research without further purification.

8.2.2 XPS analysis of pentacoordinate sulfide 2

X-Ray photoelectron spectroscopy (XPS) analysis was carried out using a PHI-Quanter spectrometer.

The deposition of the pentacoordinate sulfide (2) was further verified by X-ray

photoelectron spectroscopy (XPS). As shown in **Figure S3**, the XPS spectrum of the S 2p energy region could be reasonably well resolved to S^{6+} . The binding-energy (BE) peak at 169.89 eV can be assigned to S^{6+} atom of sulfate, sulfonate or other hexavalent sulfur atoms.



Figure S3. XPS spectrum of the S 2p energy region

Moreover, the XPS spectrum of the O 1s energy region could be resolved with three strong peaks (**Figure S4**), which suggested that the pentacoordinate sulfide (**2**) was distinct from the sulfates or sulfonates like Na₂SO₄ and CF₃SO₃Na with two kind of O atoms. Therefore, the results indicated that a novel bonding structure of sulfate was obtained, which is consistent with the later XRD and ¹⁹F NMR spectrum results. The lower-binding-energy (BE) peak at 525.15 can be assigned to oxygen atoms of peroxy three-membered ring. The higher-BE peak at 533.02 eV can be assigned to oxygen atom of S=O. The highest-BE peak at 537.49 eV can be assigned to oxygen anion.



Figure S4. XPS spectra of the O 1s energy region

8.2.3 Solid ¹⁹F NMR analysis of pentacoordinate sulfide 2

Solid ¹⁹F NMR of sodium trifluoromethanesulfinate (1): ¹⁹F NMR (565 MHz) δ -86.244 – -88.701 (m) (**Figure S5**).





Figure S5. Solid ¹⁹F NMR spectrum of sodium trifluoromethanesulfinate (1). The upper one is a full spectrum; the lower one is a partial spectrum between chemical shift -75 ~ -99 ppm.

Solid ¹⁹F NMR of sodium trifluoromethanesulfonate: ¹⁹F NMR (565 MHz) δ -78.875 (s) (**Figure S6**).



Figure S6. Solid ¹⁹F NMR spectrum of sodium trifluoromethanesulfonate



Solid ¹⁹F NMR of pentacoordinate sulfide **2**: ¹⁹F NMR (565 MHz) δ -77.156 (s)

(Figure S7).

Figure S7. Solid ¹⁹F NMR spectrum of the pentacoordinate sulfide (2)

Solid ¹⁹F NMR spectrum of the pentacoordinate sulfide (2) (**Fig. S7**) is distinct from spectra of CF₃SO₂Na (1) (**Fig. S5**) and CF₃SO₃Na (**Fig. S6**). Therefore, the results indicated that 2 was a novel structure of sulfate.

8.2.4 Powder X-ray diffraction (PXRD) patterns of pentacoordinate sulfide 2

The powder X-ray diffraction (PXRD) spectra were obtained on a Bruker D8 Advance X-ray diffractometer using Cu-Ka radiation ($\lambda = 1.5418$ Å). As shown in **Figure S8**, the PXRD spectrum of the pentacoordinate sulfide (**2**) is very distinct from the CF₃SO₂Na (**1**) or CF₃SO₃Na. The result is consistent with solid ¹⁹F NMR spectrum of the pentacoordinate sulfide, indicating a novel bonding structure of sulfate was obtained.



Figure S8. PXRD spectra of CF₃SO₂Na (1), CF₃SO₃Na and CF₃SO₄Na (2)

8.2.5 UV-vis absorption spectroscopic measurements

8.2.5.1 UV-vis absorption spectroscopic measurement of CF₃SO₂Na

The UV-vis absorption spectrum of CF_3SO_2Na (1) was recorded on DRS, Hitachi U-3010. The sample was prepared by mixing CF_3SO_2Na (1) (0.2 mmol, 31.2 mg) in DMF (total volume = 3.0 mL). The reaction mixture was stirred for 10 min, and the reaction mixture was filtered with a filter. The resulted solution was stored in a light path quartz fluorescence cuvette, and UV-vis absorption spectrum was recorded. As shown in **Figure S9**, the absorption peak at 400 nm was observed.



Figure S9. The UV-vis absorption spectrum of CF₃SO₂Na (1)

8.2.5.2 UV-vis absorption spectroscopic measurement of CF₃SO₃Na

The UV-vis absorption spectrum of CF_3SO_3Na was recorded on DRS, Hitachi U-3010. The sample was prepared by mixing CF_3SO_3Na (0.2 mmol, 34.4 mg) in DMF (total volume = 3.0 mL). The reaction mixture was stirred for 10 min, and the reaction mixture was filtered with a filter. The resulted solution was stored in a light path quartz fluorescence cuvette, and UV-vis absorption spectrum was recorded. As shown in **Figure S10**, no absorption peak at 400 nm was measured.



Figure S10. The UV-vis absorption spectrum of CF₃SO₃Na

8.2.5.3 UV-vis absorption spectroscopic measurement of CF₃SO₄Na (2)

The UV-vis absorption spectrum of CF_3SO_4Na (2) was recorded on DRS, Hitachi U-3010. The sample was prepared by mixing CF_3SO_2Na (0.2 mmol, 31.2 mg) in DMF (total volume = 3.0 mL) to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 12 h under O₂ (1 atm.) atmosphere. After the reaction was completed, the reaction mixture was detected by ¹⁹F NMR, which showed the CF_3SO_2Na had converted into the corresponding pentacoordinate sulfide (2). Then the reaction mixture was filtered with a filter. The resulted solution was stored in a light path quartz fluorescence cuvette, and UV-vis absorption spectrum was recorded. As shown in **Figure S11**, the absorption at 400 nm was observed.



Figure S11. The UV-vis absorption spectrum of CF₃SO₄Na (2)

On the basis of the above investigations, the UV-vis absorption spectrum of CF_3SO_4Na (2) (Figure S11) is very distinct from the spectra of CF_3SO_2Na (Figure S9) and CF_3SO_3Na (Figure S10). Moreover, the absorption intensity of CF_3SO_4Na (2) at 400 nm was bigger than that of CF_3SO_2Na (1) (Figure S9) or CF_3SO_3Na (Figure S10).

8.2.6 Fourier-transform attenuated total reflectance (FTIR-ATR) analysis of pentacoordinate sulfide 2

The Fourier-transform attenuated total reflectance (FTIR-ATR) was measured by using KBr pellets and recorded on a Perkin Elmer FT-IR spectrometer. As shown in **Figure S12**, the FTIR spectrum of the pentacoordinate sulfid (2) is very distinct from the FTIR spectra of CF_3SO_2Na (1) and CF_3SO_3Na . The result is consistent with the solid ¹⁹F NMR spectrum and PXRD spectrum results of the pentacoordinate sulfide (2), which indicated that a novel bonding structure of sulfate was obtained.



Figure S12. FTIR-ATR Spectra of CF₃SO₂Na (1), CF₃SO₃Na and CF₃SO₄Na (3)

8.3 Oxygen type investigations determined by EPR

8.3.1 Determination of singlet oxygen in the reaction



Figure S13. The X-band electron paramagnetic resonance (EPR) spectra of the singlet oxygen captured by TMPD. The g-value (g = 2.0068) is derived from the spectrum. (a) solution of TMPD, ethylbenzene (6) and CF₃SO₂Na (1) in air-saturated CH₃CN without light irradiation; (b) solution of TMPD, ethylbenzene (6) and CF₃SO₂Na (1) in air-saturated CH₃CN with light irradiation for 10 min.

In order to determine the active species of oxygen involved in the present reaction,

2,2,6,6-tetramethylpiperidin-4-one (TMPD) was employed to capture ${}^{1}O_{2}$. As shown in **Figure S13a**, no signal was detected when the acetonitrile solution of TMPD, ethylbenzene and CF₃SO₂Na (1) was not irradiated with light. However, when the same solution was irradiated with full wavelength light, a characteristic signal of ${}^{1}O_{2}$ adduct with TMPD was observed (**Figure S13b**).

8.3.2 Determination of superoxide radical anion in the reaction

Superoxide radical anion (O_2^{-}) is generated from molecular oxygen by single electron transfer (SET).²⁷ 5,5-Dimethyl-1-pyrroline-*N*-oxide (DMPO) was used as a probe to capture active species O_2^{-} . As shown in **Figure S14**, no signal was detected when the acetonitrile solution of DMPO, ethylbenzene (6) and CF₃SO₂Na (1) was not irradiated with light. However, when the same solution was irradiated full wavelength light, a characteristic signal of O_2^{-} adduct with DMPO was observed. In addition, when the irradiation time was prolonged, a series of stronger characteristic signal of O_2^{-} were collected (**Figure S14**).



Figure S14. The X-band electron paramagnetic resonance (EPR) spectra of the superoxide radical anion captured by DMPO. (a) solution of DMPO, ethylbenzene (6) and CF₃SO₂Na (1) in air-saturated CH₃CN without light irradiation; (b) solution of DMPO, ethylbenzene (6) and

 CF_3SO_2Na (1) in air-saturated CH_3CN with light irradiation for 2 min; (c) solution of DMPO, ethylbenzene (6) and CF_3SO_2Na (1) in air-saturated CH_3CN with light irradiation for 4 min. (d) solution of DMPO, ethylbenzene (6) and CF_3SO_2Na (1) in air-saturated CH_3CN with light irradiation for 6 min.

8.4 Controlled experiments

In order to explore the possible mechanism of the present transformation, various control experiments were conducted as follows.

8.4.1 Controlled experiments of atmospheres

Ethylbenzene (**6**, 1.0 equiv, 0.2 mmol), sodium trifluoromethanesulfinate (**1**, 25 mol%) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 8 h under Ar atmosphere. TLC (PE/EA = 30:1) and GCMS showed that no desired product **9** was detected. However, when the above reaction solution was further conducted with irradiation of 3 W blue LED under O₂ atmosphere, the reaction underwent smoothly to generate the desired product (**9**) in 99% yield (GC-MS determination). These results indicated that O₂ played a crucial role in this transformation.



8.4.2 Step by step experiments



Sodium trifluoromethanesulfinate (1, 0.05 mmol) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 8 h under O_2 atmosphere. After the reaction was completed, the resulting solution was detected by liquid ¹⁹F NMR spectrometer. The result showed that the CF₃SO₂Na (1) (see **Figure S15**) had converted into intermediate **2** (a possible pentacoordinate sulfide) (see **Figure S16**). When ethylbenzene (**6**, 0.1 mmol) was added to the above resulting solution with **2**, then the solution was irradiated with 3 W blue LED (400-405 nm) for another 12 h under O₂ atmosphere, and the reaction underwent smoothly to generate the desired product (**9**) in 99% yield determined by GC-MS using dodecane as the internal standard.



Figure S15. Liquid ¹⁹F NMR spectrum of sodium trifluoromethanesulfinate (1)



Figure S16. Liquid ¹⁹F NMR spectrum of intermediate 2



Intermediate 2 was previously prepared, then 6 was added to the system, and no product 9 was observed in the absence of oxygen or light after 12 h. Therefore, intermediate 2 could not directly oxidize substrate 6 in the absence of light or O_2 .

8.4.3 Radical inhibited experiment

Ethylbenzene (**6**, 1.0 equiv, 0.2 mmol), sodium trifluoromethanesulfinate (**1**, 25 mol%), 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO, 3.0 equiv) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 12 h under O_2 atmosphere. No desired product **9** was detected by TLC, as well as GC-MS, indicating that the reaction was completely inhibited and a radical progress was involved in this transformation.



8.4.4 CF₃SO₃Na instead of 1

Ethylbenzene (6, 0.2 mmol), sodium trifluoromethanesulfonate (CF₃SO₃Na) (0.1 mmol)) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 12 h under O₂ atmosphere. TLC (PE/EA =30 :1) and GC-MS showed that no desired product **9** was detected, which implied that CF₃SO₃Na was not a photocatalyst for this transformation.



These results certainly suggested that the pentacoordinate sulfide (2) (different with CF₃SO₃Na) could be a photocatalyst in this transformation.

8.4.5 Investigations on other S(VI) compounds instead of 1 for the selective oxidation of C-H bond^{*a*}

Ethylbenzene (**6**, 0.2 mmol), S(VI) compound (0.1 mmol)) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 12 h under O₂ atmosphere. As shown in Table S9, only intermediate **2** could promote this selective oxidation of C-H bond.

Table S13. Investigations on other S(VI) compounds instead of 1 for the selective oxidation of C-H bond^{*a*}

F 10	S(VI) compound (50 mol%) O ₂ (1 atm) CH ₃ CN (1.0 mL) blue LED (400-405 nm), r.t., 12 h	0 11
entry	S(VI) compound	yield (%)
1	Intermediate 2	99
2	G ⊮ F ₃ C−S−ONa O	n.r.
3	O II NaO-S-ONa II O	n.r.
4	O NaO−S−OH O	n.r.
5	0 0 NaO-S-O-O-S-ONa 0 0	n.r.

6	о КО-О-О- ["] О	n.r.
7	NaBr	n.r.

^{*a*}Reaction conditions: **10** (0.2 mmol), S(VI) compound (50 mol%), CH₃CN (1.0 mL) under O₂ atmosphere and blue LED (400-405 nm) irradiation at room temperature for 12 h. The yields were determined by ¹⁹F NMR using benzotrifluoride as the internal standard.

8.5 Isotopic labeling experiments

8.5.1 ¹⁸O-Labeling experiment for the oxidation of 1-propylbenzene

The ¹⁸O-labeling experiments were performed with ¹⁸O₂ (from Energy Chemical, ¹⁸O atom 99.7%). 1-Propylbenzene (0.2 mmol), sodium trifluoromethanesulfinate (**1**, 0.05 mmol) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 12 h under ¹⁸O₂ atmosphere. After the reaction was completed, products **27** and **27'** were confirmed by GC-MS (**Figure S17**), and they were also determined by high resolution EI-MS. **27**: m/z calcd. C₉H₁₀O (M⁺) 134.0726, found 134.0726; **27'**: m/z calcd. C₉H₁₀¹⁸O (M⁺) 136.0769, found 136.0769. The results showed that origin of oxygen element in the desired product (**27**) in text was mainly from oxygen.





Figure S17. GC-MS of products 27 and 27'

8.5.2¹⁸O-Labeling experiment for oxidation of toluene

The ¹⁸O-labeling experiments were performed with ¹⁸O₂ (from Energy Chemical, ¹⁸O 99.7%). 1-Fluoro-4-methylbenzene atom (0.2)mmol), sodium trifluoromethanesulfinate (1, 0.1 mmol) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 12 h under ¹⁸O₂ atmosphere. After the reaction was complete, products 47, 47' and 47'' were confirmed by GC-MS as shown in Figure S18. Products 47, 47' and 47'' were further confirmed by negative ion high resolution ESI-MS. 47: m/z calcd. C₇H₄FO₂ ([M-H]⁻) 139.0201, found 139.0196; **47'**: m/z calcd. C₇H₄FO¹⁸O ([M-H]⁻) 141.0243, found: 141.0251; **47''**: m/z calcd. $C_7H_4F^{18}O_2$ ([M-H]⁻) 143.0286, found: 143.0294. The results showed that origin of oxygen element in the desired products (47) in text was mainly from oxygen.





Figure S18. GC-MS of products 47, 47' and 47"

8.5.3 ¹⁸O-Labeling experiment for oxidation of benzaldehyde

4-Fluorobenzaldehyde (0.2 mmol), sodium trifluoromethanesulfinate (**1**, 0.05 mmol) and CH₃CN (2.0 mL) were added to an oven-dried reaction vessel equipped with magnetic stirring bar, and the reaction vessel was irradiated with 3 W blue LED (400-405 nm) for 12 h under ¹⁸O₂ atmosphere. After the reaction was completed, products **47** and **47'** were confirmed by GC-MS) as shown in **Figure S19**. Products **47** and **47'** were further confirmed by negative ion high resolution ESI-MS. **47**: m/z calcd. C₇H₄FO₂ ([M-H]⁻) 139.0201, found 139.0196; **47'**: m/z calcd. C₇H₄FO¹⁸O ([M-H]⁻) 141.0243, found: 141.0251. The results showed that origin of oxygen element in the desired products (**47**) in text was mainly from oxygen.





Figure S19. GC-MS of products 47 and 47'

9. References

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10. NMR Spectra





220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 f1 (ppm)













-S63 -






























20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 f1 (ppm)





---46







-S80 -

















-S86 -







-S89 -




























































-**S119** -













