

Photoredox Ketone Catalysis for Direct C-H Imidation and Acyloxylation of Arenes

Chandra Bhushan Tripathi,[†] Tsuyoshi Ohtani,[‡] Michael T. Corbett[†] and Takashi Ooi^{*,†,‡,‡}

[†]*Institute of Transformative Bio-Molecules (WPI-ITbM), ‡ Department of Molecular and Macromolecular Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8601, Japan*

[‡]*CREST, Japan Science and Technology Agency (JST), Nagoya University, Nagoya 464-8601, Japan*

tooi@chembio.nagoya-u.ac.jp

SUPPORTING INFORMATION

A. General Information	S-2
B. Synthesis of Ketone Catalysts	S-2
C. Synthesis and Characterization of Substituted <i>N</i> -Acyloxyphthalimides	S-2
D. Reaction Conditions Optimization for the Ketone-Catalyzed C-H Imidation	S-3
E. Photoexcited Ketone-Catalyzed C-H Imidation of Arenes	S-6
F. Calculation of ΔG_{et} by Rehm-Weller Equation	S-13
G. UV-Visible Absorption Spectroscopy	S-14
H. Phosphorescence Spectroscopy	S-15
I. Electrochemical Studies	S-16
J. Determination of Excited State Potentials	S-18
K. Quantum Yield Measurement	S-19
L. Crystallographic Structure Determination of 31	S-22
M. Computational Studies	S-23
N. Synthesis and Characterization of Aryl-Acylperoxide	S-36
O. Reaction Conditions Optimization for the Ketone-Catalyzed C-H Acyloxylation	S-36
P. Photoexcited Ketone-Catalyzed C-H Acyloxylation of Arenes	S-38
Q. Copies of NMR Spectra	S-40

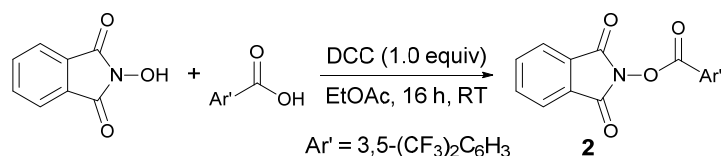
A. General Information:

Infrared (FT-IR) spectra were recorded on a Shimadzu IRAffinity-1 spectrometer (ν_{\max} in cm^{-1}). $^1\text{H-NMR}$ spectra were recorded on a JEOL JNM-ECS600 (600 MHz), JNM-ECA500II (500 MHz) and JNM-ECS400 (400 MHz) spectrometers. Chemical shifts are reported in ppm from the solvent resonance as the internal standard (CDCl_3 : δ 7.26 and DMSO-d_6 : δ 2.50). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. $^{13}\text{C-NMR}$ spectra were recorded on JEOL JNM-ECS600 (150 MHz), JNM-ECA500II (125 MHz) and JNM-ECS400 (100 MHz) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 : δ 77.16 and DMSO-d_6 : δ 39.52). Mass spectra were measured with a Thermo Fisher Scientific Exactive (ESI). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF254, 0.25 mm). Flash column chromatography was performed on silica gel 60 (spherical, 40-50 μm ; Kanto Chemical Co., Inc.), silica gel 60 (Merck 1.09385.9929, 230-400 mesh). Unless otherwise noted all reactions were carried out with distilled and dried solvents under an atmosphere of argon. All work up and purifications were carried out with reagent grade solvents in air.

B. Synthesis of Ketone Catalysts:

The commercially available ketone derivatives were used as such without any purification. Catalysts **VII-XI** were prepared by following the literature procedure.^{1,2} The spectral data are in agreement with those reported in the literature.

C. Synthesis and Characterization of Substituted *N*-Acyloxyphthalimides:



In a 200 mL round bottom flask equipped with magnetic stir bar, *N*-hydroxyphthalimide (10.0 mmol, 1.63 g, 1.0 equiv) and dicyclohexylcarbodiimide (10.0 mmol, 2.06 g 1.0 equiv) were placed. Ethyl acetate (50 mL) and 3,5-bis(trifluoromethyl)benzoic acid (10 mmol, 2.58 g, 1.0 equiv) were successively added. The resulting mixture was stirred for 16 h and the formation of a white precipitate was observed. The solid was removed by vacuum filtration and dried in vacuo to afford the crude product. Purification by column chromatography over silica gel using (Hexane/EtOAc = 3:1 as eluent) gave **2** as a white solid. Recrystallization from hot Hexane/EtOAc yielded **2** as colorless crystals (2.50

1. T. Stopka, L. Marzo, M. Zurro, S. Janich, E.-U. Würthwein, C. G. Daniliuc, J. Alemán and O. G. Mancheño, *Angew. Chem. Int. Ed.* 2015, **54**, 5049.

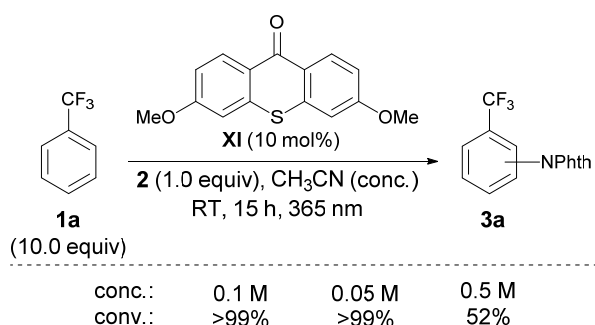
2. S. Khan, P. L. Bernad, V. A. Korshun, E. M. Southern and M. S. Shchepinov, *Synlett* 2005, 2453.

g, 6.2 mmol, 62% yield). **FT-IR (thin film)**: 3068, 1782, 1745. **¹H-NMR (CDCl₃, 500 MHz)**: δ 8.65 (s, 2H), 8.21 (s, 1H), 7.97 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.86 (dd, *J* = 5.5, 3.0 Hz, 2H). **¹³C-NMR (CDCl₃, 125 MHz)**: δ 161.6, 160.8, 135.2, 133.0 (q, *J* = 29 Hz), 128.9, 128.3 (m), 127.9, 124.5, 122.7 (q, *J* = 228 Hz). **¹⁹F-NMR (471 MHz, CDCl₃)**: δ -62.934. **HRMS (ESI+)**: Calcd. for C₁₈H₁₁O₅NF₆Na ([M + Na + MeOH]⁺): 458.0424, Found: 458.0429.

The spectral data of remaining imidation reagents are in agreement with those reported in the literature.³

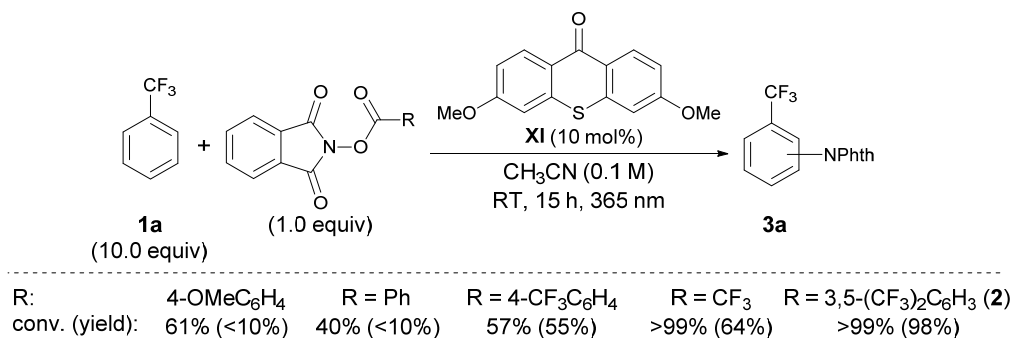
D. Reaction Conditions Optimization for the Ketone-Catalyzed C-H Imidation:

Effect of Concentration



The optimization of substrate concentration revealed that 0.1 M and 0.05 M were equally efficient.

Effect of Imidating Agent

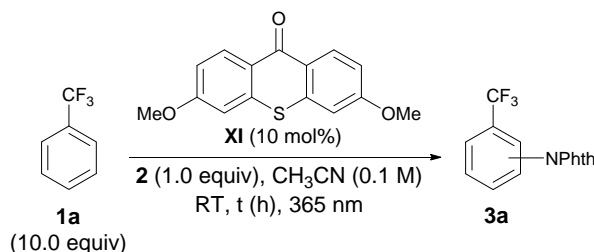


We envisioned that the imidating agents with electron-withdrawing groups might be appropriate for this direct C-H imidation of arenes. With this premise in mind, several imidating agents with different leaving ability of carboxylate anion were synthesized and screened. As shown above, the results were obtained on the expected lines. The reactions of **1a** with imidating agents possessing 4-(trifluoromethyl)phenyl and trifluoromethyl groups, which were utilized by Sanford and co-workers,³ afforded the product **3a** in good yields. At this point, we prepared 3,5-bis(trifluoromethyl)phenyl-substituted **2** and its use for the imidation of **1a** led to the production of **3a**

3. L. J. Allen, P. J. Cabrera, M. Lee and M. S. Sanford, *J. Am. Chem. Soc.* 2014, **136**, 5607.

in 98% yield. It is important to note that unlike other imidating agents, **2** can be stored at room temperature for months without any deterioration.

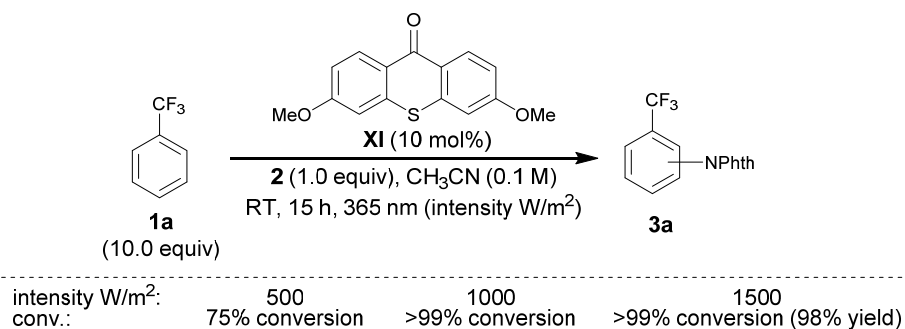
ON/OFF Experiment



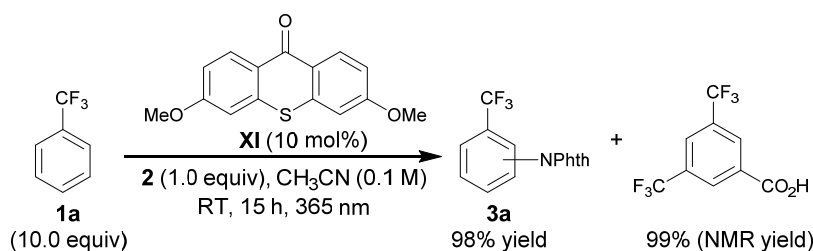
Conditions	Yield (%)
ON, 2 h	61
ON, 2 h OFF, 2 h	61
ON, 2 h OFF, 2 h ON, 2 h	83

The reaction mixture was irradiated at fixed intervals. As evident from the data listed in the above Table, the reaction proceeded only in the presence of light. This result showed that light is essential for the reaction and it also provided a preliminary support for the absence of a radical chain process, which was later confirmed by a low quantum yield of 0.036 (see page S-19).

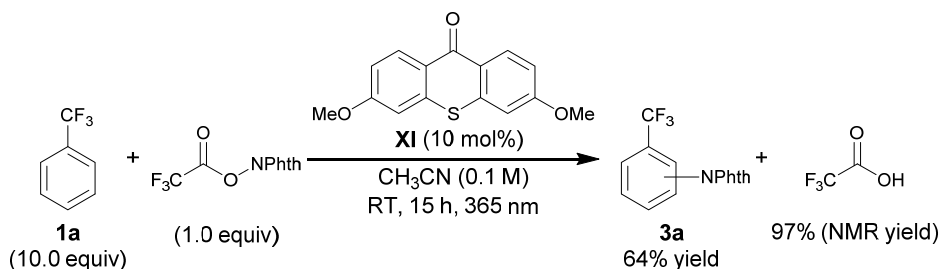
Effect of Light Intensity



The reaction relied upon the intensity of the 365 nm LED. As summarized in the above scheme, when the reaction mixture was irradiated at 500W/m^2 , low conversion (75%) was observed, whereas the imidation proceeded smoothly with the intensity of 1000W/m^2 and 1500W/m^2 . Unless otherwise stated, all reactions in this study are carried out with the intensity of 1500W/m^2 .

Recovery of the Acid

In the C-H imidation of **1a** using **2**, 3,5-bis(trifluoromethyl)benzoic acid was recovered in 99% NMR yield. This experiment corroborates the generation of a 3,5-bis(trifluoromethyl)benzoate anion in the catalytic cycle rather than the corresponding radical that would be susceptible towards decarboxylation to eventually form 1,3-bis(trifluoromethyl)benzene.



The point described above was further confirmed by carrying out the C-H imidation of **1a** with the imidating agent introduced by Sanford,³ which furnished **3a** in 64% yield and trifluoroacetic acid (TFA) in 97% NMR yield. The generation of TFA in an amount larger than that of **3a** can be accounted for by the hydrolysis of the moisture sensitive imidating agent. This outcome supports the generation of trifluoroacetate anion in the catalytic cycle rather than trifluoroacetate radical that is known to undergo rapid decarboxylation to generate the trifluoromethyl radical.⁴

Triplet Lifetime of Ketones (τ) and Catalytic Activity

Triplet lifetime (μs):	6.9	47	28	0.09	95
Triplet energy (kJ/mol):	287	293	275	310	265
Conversion (%):	9	22	70	<5	25

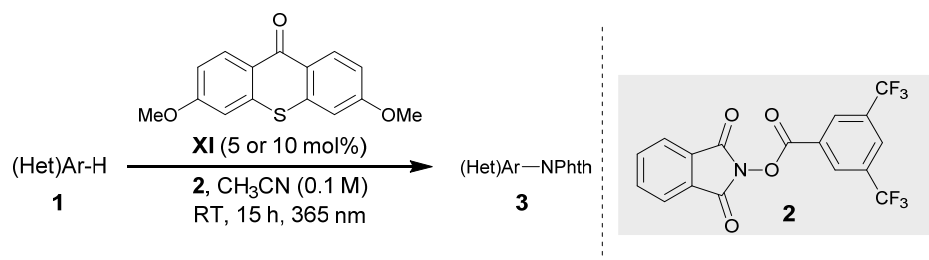
The screening of ketones with different τ values in the imidation of **1a** with **2** (triplet energy: 310.7 kJ/mol) under the conditions described for Table 1 (main text) showed no direct correlation between τ and catalytic activity. As seen in the above scheme, 4,4'-dimethoxybenzophenone was significantly less active than more electron-rich Michler's ketone that has shorter triplet lifetime and lower triplet

4. J. W. Beatty, J. J. Douglas, K. P. Cole and C. R. J. Stephenson, *Nat. Commun.*, 2015, **6**, 7919

energy.⁵ Because of the difficulty associated with further modifications of Michler's ketone and presumed instability of the resulting even more electron-rich ketones under the reaction conditions, we decided to proceed toward structural tuning of thioxanthone framework for reactivity enhancement.

E. Photoexcited Ketone-Catalyzed C-H Imidation of Arenes:

General procedure for the ketone-catalyzed C-H imidation of arenes:



In a flame and vacuum dried reaction tube, **2** (40.3 mg, 0.1 mmol, 1.0 equiv) and **XI** were taken. The reaction flask was degassed in *vacuo* and backfilled with argon. To the mixture CH_3CN (1.0 mL) and arene (1.0 mmol, 10.0 equiv) were added. The resulting solution was stirred at 25 °C under 365 nm irradiation (1500 W/m^2) for 15 h. The reaction was quenched by adding a saturated aqueous solution of NaHCO_3 (5 mL). The aqueous phase was extracted with CH_2Cl_2 ($3 \times 10 \text{ mL}$) and the combined organic phase was dried over anhydrous Na_2SO_4 , concentrated under reduced pressure. Purification of the residue by column chromatography over silica gel afforded **3**.

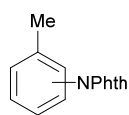
3a: Following the general procedure described above with **XI** (2.7 mg, 0.01 mmol, 0.1 equiv) and benzotrifluoride (0.122 mL, 1.0 mmol, 10.0 equiv) as the arene source, **3a** was obtained as a white solid (28.5 mg, 0.098 mmol, 98% yield, *o/m/p* = >0.1:2.6:1.0). The isomer ratios were determined through $^{19}\text{F-NMR}$. The isolated product was an inseparable mixture of isomers. All peaks observed in the $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and $^{19}\text{F-NMR}$ were assigned. **$^1\text{H-NMR}$ (500 MHz, CDCl_3)**: δ 7.99-7.98 (m, 2.1H), 7.84-7.82 (m, 2.1H), 7.78-7.77 (m, 1.25H), 7.70-7.64 (m, 3H). **$^{13}\text{C-NMR}$ (125 MHz, CDCl_3)**: δ 167.0, 134.9, 132.5, 131.7, 129.8, 126.6, 126.4, 124.8, 124.1, 123.5. **$^{19}\text{F-NMR}$ (471 MHz, CDCl_3)**: δ -61.3, -62.5, -62.6. The spectral data are consistent with those reported in the literature.³

3b: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv) and benzene (0.093 mL, 1.0 mmol, 10.0 equiv) as the arene source, **3b** was obtained as a white solid (20.2 mg, 0.091 mmol, 91% yield). **$^1\text{H-NMR}$ (600 MHz, CDCl_3)**: δ 7.97 (dd, J = 5.4, 3.6 Hz, 2H), 7.80 (dd, J = 5.4, 3.6 Hz, 2H), 7.51 (t, J = 7.8 Hz, 2H), 7.44 (d, J = 7.8 Hz, 2H),

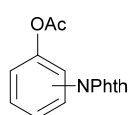
5. a) M. W. Wolf, R. E. Brown and L. A. Singer, *J. Am. Chem. Soc.*, 1977, **99**, 526; b) A. Garner and F. Wilkinson, *J. Chem. Soc., Faraday Trans. 2*, 1976, **72**, 1010; c) "Handbook of Photochemistry": Third Edition, Taylor and Francis, 2005, pp.86-156.

7.42 (t, $J = 7.8$ Hz, 1H). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 167.4, 134.6, 131.9, 131.8, 129.3, 128.3, 126.7, 123.9. The spectral data are consistent with those reported in the literature.³

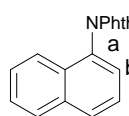
3c: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv) and toluene (0.10 mL, 1.0 mmol, 10.0 equiv) as the arene source, **3c** was obtained as a white solid (22.0 mg, 0.093 mmol, 93% yield, $o/m/p = 1.9:1:1$). The isomer ratios were determined through $^1\text{H-NMR}$. The isolated product was an inseparable mixture of isomers. All peaks observed in the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were assigned. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 7.97-7.90 (m, 8H), 7.78-7.86 (m, 8H), 7.39-7.33 (m, 5H), 7.32-7.27 (m, 7H), 7.22-7.16 (m, 5H), 2.40 (s, 3H), 2.39 (s, 3H), 2.19 (s, 5.9H). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 167.51, 167.45, 167.43, 138.3, 136.6, 134.4, 132.1, 131.91, 131.88, 131.2, 130.6, 129.8, 129.5, 129.1, 129.04, 129.01, 128.8, 127.3, 126.9, 126.5, 123.8, 123.78, 123.75, 21.47, 21.3, 18.1. The spectral data are in agreement with those reported in the literature.³



3d: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv) and phenyl acetate (0.13 mL, 1.0 mmol, 10.0 equiv) as the arene source, **3d** was obtained as a white solid (21.0 mg, 0.075 mmol, 75% yield, $o/m/p = 1.2:1:1.4$). The isomer ratios were determined through $^1\text{H-NMR}$. The isolated product was an inseparable mixture of isomers. All peaks observed in the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were assigned. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 8.01-7.92 (m, 7H), 7.85-7.76 (m, 7H), 7.52-7.45 (m, 5H), 7.41-7.35 (m, 4H), 7.32-7.29 (m, 1H), 7.25 (t, $J = 6$ Hz, 4H), 7.16 (d, $J = 8.4$ Hz, 1H), 2.32 (s, 4.4H), 2.31 (s, 3H), 2.13 (s, 3.6H). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 169.2, 169.1, 168.2, 167.2, 166.9, 166.6, 150.9, 150.0, 146.5, 134.63, 134.56, 132.7, 131.9, 131.8, 131.7, 129.9, 129.7, 129.5, 129.3, 127.5, 126.3, 124.01, 123.97, 123.94, 123.89, 123.76, 123.54, 122.34, 121.18, 119.7, 21.2, 21.0. The spectral data are in agreement with those reported in the literature.⁶

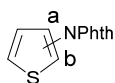


3e: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv) and naphthalene (129.0 mg, 1.0 mmol, 10.0 equiv) as the arene source, **3e** was obtained as a white solid. The crude product was obtained as a mixture of two isomers ($a/b = 7:1$). The isomer ratios were determined through $^1\text{H-NMR}$. During purification by column chromatography, only major product was isolated (19.0 mg, 0.069 mmol, 69% yield). $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 8.01 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.99 (d, $J = 8.4$ Hz, 1H), 7.94 (d, $J = 7.8$ Hz, 1H), 7.84 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.64-7.58 (m, 2H), 7.55-7.44 (m, 3H). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 167.9, 134.6, 132.1, 130.4, 130.0, 128.7, 128.3, 127.2, 127.1, 126.6, 125.5, 124.0, 122.5. The spectral data are in agreement with those reported in the literature.³

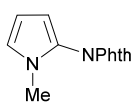


6. H. J. Kim, J. Kim, S. H. Cho and S. Chang, *J. Am. Chem. Soc.* 2011, **133**, 16382.

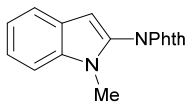
3f: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv) and thiophene (0.08 mL, 1.0 mmol, 10.0 equiv) as the arene source, **3f** was obtained as a yellow solid (14.2 mg, 0.061 mmol, 61% yield). The crude product was obtained as a mixture of $a/b = 4.2:1$. The isolated product was an inseparable mixture of isomers; however, only the peaks for major isomer are reported. ¹H-NMR (600 MHz, CDCl₃): δ 7.95-7.93 (m, 2H), 7.80-7.77 (m, 2H), 7.53 (d, $J = 3.6$ Hz, 1H), 7.22 (dd, $J = 5.4, 1.8$ Hz, 1H), 7.06 (dd, $J = 5.4, 3.6$ Hz, 1H). ¹³C-NMR (150 MHz, CDCl₃): δ 166.1, 134.8, 132.4, 131.6, 125.4, 124.1, 122.1, 120.6. The spectral data are consistent with those reported in the literature.³



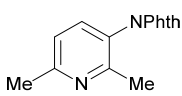
3g: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv), K₂CO₃ (27.6 mg, 0.2 mmol, 2.0 equiv) and *N*-methylpyrrole (0.09 mL, 1.0 mmol, 10.0 equiv) as the arene source, **3g** was obtained as a white solid (15.2 mg, 0.069 mmol, 69% yield). ¹H-NMR (600 MHz, CDCl₃): δ 7.97 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.81 (dd, $J = 5.4, 3.0$ Hz, 2H), 6.72 (m, 1H), 6.24 (t, $J = 3.6$ Hz, 1H), 6.19 (m, 1H), 3.48 (s, 3H). ¹³C-NMR (150 MHz, CDCl₃): δ 167.8, 134.7, 131.9, 124.1, 122.3, 118.7, 107.7, 107.7, 33.3. The spectral data are consistent with those reported in the literature.³



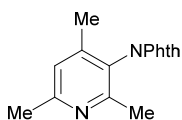
3h: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv), K₂CO₃ (27.6 mg, 0.2 mmol, 2.0 equiv) and 1-methylindole (131 mg, 1.0 mmol, 10.0 equiv) as the arene source, **3h** was obtained as a yellow solid (19.6 mg, 0.072 mmol, 72% yield). ¹H-NMR (600 MHz, CDCl₃): δ 8.01 (dd, $J = 5.4, 3.3$ Hz, 2H), 7.85 (dd, $J = 5.4, 3.3$ Hz, 2H), 7.66 (d, $J = 7.8$ Hz, 1H), 7.36 (d, $J = 8.4$ Hz, 1H), 7.30 (t, $J = 8.4$ Hz, 1H), 7.16 (t, $J = 7.8$ Hz, 1H), 6.60 (s, 1H), 3.61 (s, 3H). ¹³C-NMR (150 MHz, CDCl₃): δ 167.3, 136.2, 135.0, 132.0, 126.6, 124.3, 122.8, 121.5, 120.3, 109.8, 100.8, 29.7. The spectral data are consistent with those reported in the literature.³



3i: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv) and 2,6-lutidine (0.115 mL, 1.0 mmol, 10.0 equiv) as the arene source, **3i** was obtained as a white solid (17.1 mg, 0.068 mmol, 68% yield). ¹H-NMR (600 MHz, CDCl₃): δ 7.97 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.82 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.41 (d, $J = 7.8$ Hz, 1H), 7.15 (d, $J = 7.8$ Hz, 1H), 2.60 (s, 1H), 2.42 (s, 3H). ¹³C-NMR (150 MHz, CDCl₃): δ 167.1, 159.2, 156.1, 136.8, 134.7, 132.1, 124.4, 124.1, 121.6, 24.5, 21.3. The spectral data are consistent with those reported in the literature.³



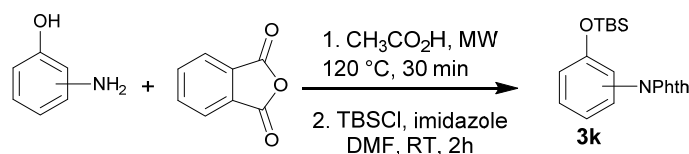
3j: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv) and 2,4,6-colidine (0.133 mL, 1.0 mmol, 10.0 equiv) as the arene source, **3j** was obtained as a white solid (19.9 mg, 0.075 mmol, 75% yield). ¹H-NMR (600 MHz, CDCl₃): δ 7.97 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.83 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.01 (s, 1H), 2.55 (s,



3H), 2.36 (s, 3H), 2.14 (s, 3H). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 167.1, 158.8, 156.4, 146.5, 134.7, 132.1, 124.1, 124.0, 123.4, 24.4, 21.1, 17.8. The spectral data are consistent with those reported in the literature.³

3k: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv) and *tert*-butyldimethyl(phenoxy)silane (208 mg, 1.0 mmol, 10.0 equiv) as the arene source, **3k** was obtained as a white solid (25.1 mg, 0.071 mmol, 71% yield, $a/b = 1:2$). The isomer ratios were determined through $^1\text{H-NMR}$. The isolated product was an inseparable mixture of isomers. All peaks observed in the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were assigned. **FT-IR (thin film)**: 2929, 1735, 1714, 1558, 1508, 1381. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 7.95-7.93 (m, 6.4H), 7.79-7.76 (m, 6.5H), 7.33 (m, 1H), 7.28 (d, $J = 8.1$ Hz, 4H), 7.23 (m, 1H), 7.08 (t, $J = 6.9$ Hz, 1H), 7.00 (d, $J = 8.4$ Hz, 1H), 6.94 (d, $J = 7.8$ Hz, 2H), 1.00 (s, 18H), 0.75 (s, 9H), 0.24 (s, 6H), 0.23 (s, 12H), 0.14 (s, 6H). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 167.7, 167.5, 134.4, 134.3, 132.4, 132.0, 130.6, 130.3, 129.8, 127.9, 124.9, 123.8, 123.7, 121.7, 120.8, 120.6, 120.0, 115.4, 25.8, 25.5, 18.3, 17.9, -4.2, -4.3. **HRMS (ESI+)**: Calcd. for $\text{C}_{20}\text{H}_{23}\text{O}_3\text{NNaSi}$ ($[\text{M} + \text{Na}]^+$): 376.1339, Found: 376.1336.

General procedure for the synthesis of authentic 3k:

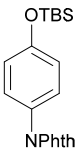


In a microwave reaction tube equipped with a magnetic stir bar, phthalic anhydride (740 mg, 5 mmol, 1.0 equiv), acetic acid (10.0 mL) and aniline derivative (5.0 mmol, 1.0 equiv) were taken. The mixture was heated at 120 °C for 30 min under microwave irradiation. The reaction mixture was cooled to rt and treated with water. A white precipitate was observed, which was filtered, washed with water and dried *in vacuo*. To the crude solid, TBSCl (900 mg, 6 mmol), imidazole (816 mg, 12 mmol) and DMF (10 mL) were added. The resulting mixture was stirred at rt for 2 h. The reaction mixture was cooled to 0 °C and a solution of 1N HCl (20 mL) was slowly added. The aqueous phase was extracted with diethyl ether (3 × 10 mL), washed with brine (1 × 30 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the residue by flash column chromatography over silica gel afforded the desired product.

3k (ortho): The general procedure described above was followed with 2-amino phenol (5.0 mmol, 1.29 g) to obtain a white solid (882 mg, 51% yield). **FT-IR (thin film)**: 2927, 1735, 1716, 1504, 1382. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 7.94 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.77 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.33 (dt, $J = 7.8, 1.2$ Hz, 1H), 7.26 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.08 (dd, J

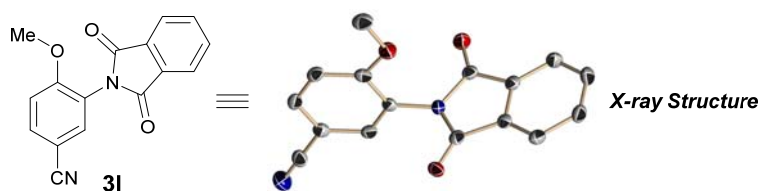
= 7.8, 1.2 Hz, 1H), 7.00 (dt, $J = 7.8, 1.2$ Hz, 1H), 0.75 (s, 9H), 0.14 (s, 6H). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 167.5, 152.1, 134.3, 132.4, 130.6, 130.3, 123.7, 123.0, 121.7, 119.8, 25.5, 17.9, -4.3. **HRMS (ESI+)**: Calcd. for $\text{C}_{20}\text{H}_{23}\text{O}_3\text{NNaSi}$ ($[\text{M} + \text{Na}]^+$): 376.1339, Found: 376.1328.

3k (para): The general procedure described above was followed with 4-amino phenol (5.0 mmol, 1.29 g) to obtain a white solid (1.412 g, 80% yield). **FT-IR (thin film)**: 2929, 1742, 1510, 1384.

 **$^1\text{H-NMR}$ (600 MHz, CDCl_3)**: δ 7.93 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.77 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.27 (dd, $J = 6.6, 2.1$ Hz, 2H), 6.93 (dd, $J = 6.6, 2.1$ Hz, 2H), 0.99 (s, 9H), 0.23 (s, 6H). **$^{13}\text{C-NMR}$ (150 MHz, CDCl_3)**: δ 167.7, 155.6, 134.4, 132.0, 127.9, 124.9, 123.8, 120.6, 25.8, 18.3, -4.2. **HRMS (ESI+)**: Calcd. for $\text{C}_{20}\text{H}_{23}\text{O}_3\text{NNaSi}$ ($[\text{M} + \text{Na}]^+$): 376.1339, Found: 376.1328.

3l: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv) and anisonitrile (0.133 mg, 1.0 mmol, 10.0 equiv) as the arene source, **3l** was obtained as a white solid (21.6 mg, 0.078 mmol, 78% yield). **FT-IR (thin film)**: 2846, 2225, 1778, 1608, 1506, 1373. **$^1\text{H-NMR}$ (600 MHz, CDCl_3)**: δ 7.96 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.82 (dd, $J = 5.4, 3.0$ Hz, 2H), 7.76 (dd, $J = 9.0, 2.4$ Hz, 1H), 7.58 (d, $J = 2.4$ Hz, 1H), 7.11 (d, $J = 9.0$ Hz, 1H), 3.87 (s, 3H). **$^{13}\text{C-NMR}$ (150 MHz, CDCl_3)**: δ 166.8, 159.1, 135.2, 134.7, 134.2, 132.1, 124.1, 121.6, 118.2, 112.9, 104.7, 56.5. **HRMS (ESI+)**: Calcd. for $\text{C}_{16}\text{H}_{10}\text{O}_3\text{N}_2\text{Na}$ ($[\text{M} + \text{Na}]^+$): 301.0584, Found: 301.0579.

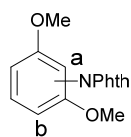
Recrystallization of **3l** from CH_2Cl_2 /hexane (1:9) mixture afforded diffraction quality crystals. The thermal ellipsoids of non-hydrogen atoms are shown at the 50% probability level. Calculated hydrogen atoms are omitted for clarity. The atoms are shown through following colour sequence: blue = nitrogen, red = oxygen, grey = carbon.



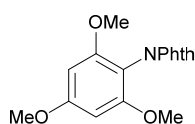
3m: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv) and anisole (0.10 mL, 1.0 mmol, 10.0 equiv) as the arene source, **3m** was obtained as a white solid (22.0 mg, 0.083 mmol, 83% yield, $o/m/p = 1.0:0:1.2$). The isomer ratios were determined through $^1\text{H-NMR}$. The isolated product was an inseparable mixture of isomers.

All peaks observed in the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were assigned. **$^1\text{H-NMR}$ (600 MHz, CDCl_3)**: δ 7.97-7.91 (m, 4H), 7.79-7.74 (m, 4H), 7.43 (t, $J = 7.8$ Hz, 1H), 7.34 (d, $J = 9.0$ Hz, 1H), 7.27-7.24 (m, 1H), 7.09-7.00 (m, 4H), 3.85 (s, 3H), 3.79 (s, 3.56H). **$^{13}\text{C-NMR}$ (150 MHz, CDCl_3)**: δ 167.7, 167.5, 159.4, 155.5, 134.4, 134.2, 132.4, 131.9, 130.8, 130.1, 128.0, 124.4, 123.8, 120.9, 120.4, 114.6, 112.2, 55.9, 55.6. The spectral data are in agreement with those reported in the literature.³

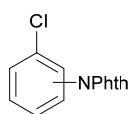
3n: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv) and 1,3-dimethoxybenzene (0.13 mL, 1.0 mmol, 10.0 equiv) as the arene source, **3n** was obtained as a white solid (24.0 mg, 0.085 mmol, 85% yield, *a/b* = 1:9). The isomer ratios were determined through ¹H-NMR. The isolated product was an inseparable mixture of isomers, however, only the peaks for major isomer are reported. ¹H-NMR (400 MHz, DMSO-d₆): δ 7.91 (dd, *J* = 5.4, 2.4 Hz, 2H), 7.74 (dd, *J* = 5.4, 2.4 Hz, 2H), 7.26 (d, *J* = 8.8 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 6.64 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.83 (s, 3H), 3.72 (s, 3H). ¹³C-NMR (100 MHz, DMSO-d₆): δ 167.2, 161.2, 156.2, 134.8, 131.6, 130.9, 123.4, 112.8, 105.2, 99.2, 55.9, 55.6. The spectral data are in agreement with those reported in the literature.⁷



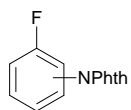
3o: Following the general procedure described above with **XI** (1.35 mg, 0.005 mmol, 0.05 equiv) and 1,3,5-trimethoxybenzene (168.0 mg, 1.0 mmol, 10.0 equiv) as the arene source, **3o** was obtained as a white solid (25.0 mg, 0.080 mmol, 80% yield). ¹H-NMR (600 MHz, CDCl₃): δ 7.90 (dd, *J* = 5.4, 3.6 Hz, 2H), 7.73 (dd, *J* = 5.4, 3.6 Hz, 2H), 6.20 (s, 2H), 3.83 (s, 3H), 3.74 (s, 6H). ¹³C-NMR (150 MHz, CDCl₃): δ 167.8, 162.2, 157.7, 133.9, 132.7, 123.6, 101.8, 91.2, 56.1, 55.6. The spectral data are in agreement with those reported in the literature.³



3p: Following the general procedure described above with **XI** (2.7 mg, 0.01 mmol, 0.1 equiv) and chlorobenzene (0.10 mL, 1.0 mmol, 10.0 equiv) as the arene source, **3p** was obtained as a white solid (20.9 mg, 0.081 mmol, 81% yield, *o/m/p* = 1.6:1:2). The isomer ratios were determined through ¹H-NMR. The isolated product was an inseparable mixture of isomers. All peaks observed in the ¹H-NMR and ¹³C-NMR were assigned. ¹H-NMR (600 MHz, CDCl₃): δ 7.99-7.94 (m, 10H), 7.83-7.79 (m, 10H), 7.58 (m, 1.69H), 7.50 (m, 1H), 7.48 (m, 3.73H), 7.45-7.35 (m, 13H). ¹³C-NMR (150 MHz, CDCl₃): δ 167.1, 167.0, 166.8, 134.8, 134.7, 133.9, 133.4, 132.9, 132.1, 131.7, 130.8, 130.6, 130.3, 130.2, 129.8, 129.4, 139.3, 128.3, 127.9, 127.8, 127.6, 126.8, 124.7, 124.1, 124.0, 124.0. The spectral data are consistent with those reported in the literature.⁸



3q: Following the general procedure described above with **XI** (2.7 mg, 0.01 mmol, 0.1 equiv) and fluorobenzene (0.094 mL, 1.0 mmol, 10.0 equiv) as the arene source, **3q** was obtained as a white solid (13.3 mg, 0.058 mmol, 58% yield, *o/m/p* = 3:1:1). The isomer ratios were determined through ¹⁹F-NMR. The isolated product was an inseparable mixture of isomers. All peaks observed in the ¹H-NMR, ¹³C-NMR and ¹⁹F-NMR were assigned. ¹H-NMR (500 MHz, CDCl₃): δ 7.99-7.94 (m, 9H), 7.83-7.79 (m, 9H), 7.50-7.40 (m, 6H), 7.37 (dt, *J* = 7.5, 1.5 Hz, 0.88H), 7.31-7.27 (m, 3H), 7.24-7.18 (m, 4H), 7.12 (dt, *J* = 8.5, 1.5 Hz, 1H). ¹³C-NMR (125 MHz, CDCl₃): δ 167.4, 167.0, 166.7, 163.9, 163.8, 163.1, 161.1, 134.8, 134.7, 134.6, 132.1, 131.8, 131.7, 131.08, 131.0, 130.4, 130.3, 130.0, 128.6, 128.5, 127.7, 124.8, 124.13, 124.06, 124.02, 122.2, 122.1, 117.0.

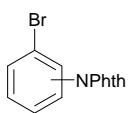


7. J. Vamecq, P. Bac, C. Herrenknecht, P. Maurois, P. Delcourt and J. P. Stables, *J. Med. Chem.* 2000, **43**, 1311.

8. H. Kim, T. Kim, D. G. Lee, A. W. Roh and C. Lee, *Chem. Commun.* 2014, **50**, 9273.

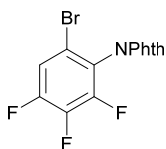
116.9, 116.4, 116.2, 115.2, 115.1, 114.2, 114.0. $^{19}\text{F-NMR}$ (471 MHz, CDCl_3): δ -111.1, -112.9, -118.6. The spectral data are consistent with those reported in the literature.⁸

3r: Following the general procedure described above with **XI** (2.7 mg, 0.01 mmol, 0.1 equiv) and bromobenzene (0.104 mL, 1.0 mmol, 10.0 equiv) as the arene source, **3r** was obtained as a white solid (21.4 mg, 0.071 mmol, 71% yield, *o/m/p* = 1.4:1.0:1.7). The isomer ratios were determined through $^1\text{H-NMR}$. The isolated product was an inseparable mixture of isomers.



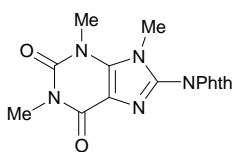
All peaks observed in the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were assigned. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 7.99-7.95 (m, 9H), 7.82-7.80 (m, 9H), 7.75 (dd, J = 7.8, 1.2 Hz, 1.38H), 7.66 (m, 1.01H), 7.64 (dd, J = 6.5, 1.8 Hz, 3.36H), 7.54 (dd, J = 6.3, 1.5 Hz, 1.00H), 7.47 (dt, J = 7.8, 1.2 Hz, 1.40H), 7.43 (dd, J = 8.4, 1.2 Hz, 0.91H), 7.39-7.34 (m, 8H). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 167.1, 167.0, 166.8, 134.8, 134.7, 134.6, 133.7, 133.1, 132.4, 132.1, 131.8, 131.7, 131.6, 131.3, 131.1, 130.9, 130.4, 129.7, 128.6, 128.1, 125.2, 124.1, 124.1, 124.0, 123.5, 122.6, 122.0. The spectral data are consistent with those reported in the literature.⁸

3s: Following the general procedure described above with **XI** (2.7 mg, 0.01 mmol, 0.1 equiv) and 1-bromo-3,4,5-trifluorobenzene (0.12 mL, 1.0 mmol, 10.0 equiv) as the arene source,



3s was obtained as a white solid (18.0 mg, 0.05 mmol, 50% yield). **FT-IR (thin film)**: 1753, 1508, 1481, 1379, 1103, 1076. $^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 7.99 (dd, J = 5.4, 3.0 Hz, 2H), 7.84 (dd, J = 5.4, 3.0 Hz, 2H), 7.45-7.39 (m, 1H). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 165.4, 152.5 (dd, J = 10.5, 4.2 Hz), 150.8 (dd, J = 11.2, 3.5 Hz), 150.1 (dd, J = 10.5, 4.2 Hz), 148.4 (dd, J = 11.2, 4.4 Hz), 139.0 (m), 134.9, 131.8, 124.4, 118.2-117.9 (m), 116.6 (dd, J = 21.6, 4.2 Hz). **HRMS (APCI-MS)**: Calcd for $\text{C}_{14}\text{H}_5\text{NO}_2\text{BrF}_3$ ($[\text{M}]^+$): 354.9450, Found: 354.9452.

3t: Following the general procedure described above with caffeine (19.4 mg, 0.1 mmol, 1.0 equiv) as the arene source, **2** (52.4 mg, 0.13 mmol, 1.3 equiv) and **XI** (2.7 mg, 0.01 mmol, 0.1 equiv), **3t** was obtained as a white solid (20.0 mg, 0.059 mmol, 59% yield).



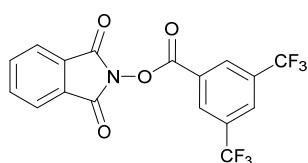
$^1\text{H-NMR}$ (600 MHz, CDCl_3): δ 8.00 (dd, J = 5.4, 3.0 Hz, 2H), 7.88 (dd, J = 5.4, 3.0 Hz, 2H), 3.88 (s, 3H), 3.57 (s, 3H), 3.42 (s, 3H). $^{13}\text{C-NMR}$ (150 MHz, CDCl_3): δ 166.5, 155.3, 151.5, 146.9, 137.0, 135.5, 131.5, 124.8, 108.3, 32.4, 30.0, 28.1. The spectral data are in agreement with those reported in the literature.³

F. Calculation of ΔG_{et} by Rehm-Weller Equation:

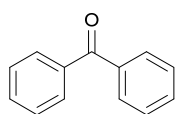
The ΔG_{et} (et: electron transfer) was calculated by the following equation:

$$\Delta G_{\text{et}} = E_{\text{ox}}(\text{D}) - E_{\text{red}}(\text{A}) - \Delta E_{\text{triplet}} + \Delta E_{\text{coulombic}}$$

$E_{\text{ox}}(\text{D})$ is the oxidation potential of the donor, $E_{\text{red}}(\text{A})$ is the reduction potential of the acceptor, $\Delta E_{\text{triplet}}$ is the triplet energy of the ketone and $\Delta E_{\text{coulombic}}$ is the term for coulombic interaction in a particular solvent. The value of $\Delta E_{\text{coulombic}}$ is usually very small in polar solvents (~ 0.03 eV for CH_3CN) and thus this parameter is not incorporated in the calculations. The calculated values are listed below:



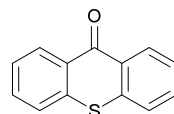
$$E_{\text{red}} = -1.1 \text{ V vs. SCE}$$



$$E_{\text{ox}} = +2.4 \text{ V vs. SCE}$$

$$E_{\text{triplet}} = +3.0 \text{ eV}$$

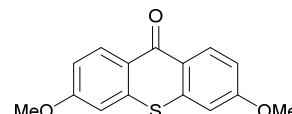
$$\Delta G_{\text{et}} = +11.5 \text{ kcal/mol}$$



$$E_{\text{ox}} = +1.7 \text{ V vs. SCE}$$

$$E_{\text{triplet}} = +2.8 \text{ eV}$$

$$\Delta G_{\text{et}} = +0 \text{ kcal/mol}$$



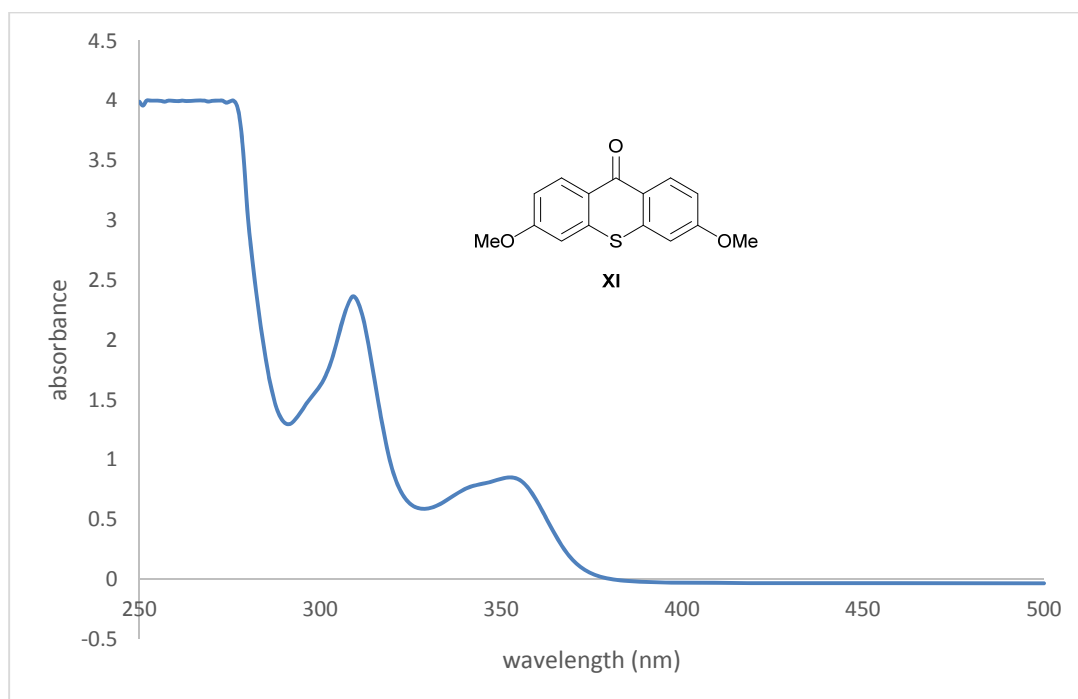
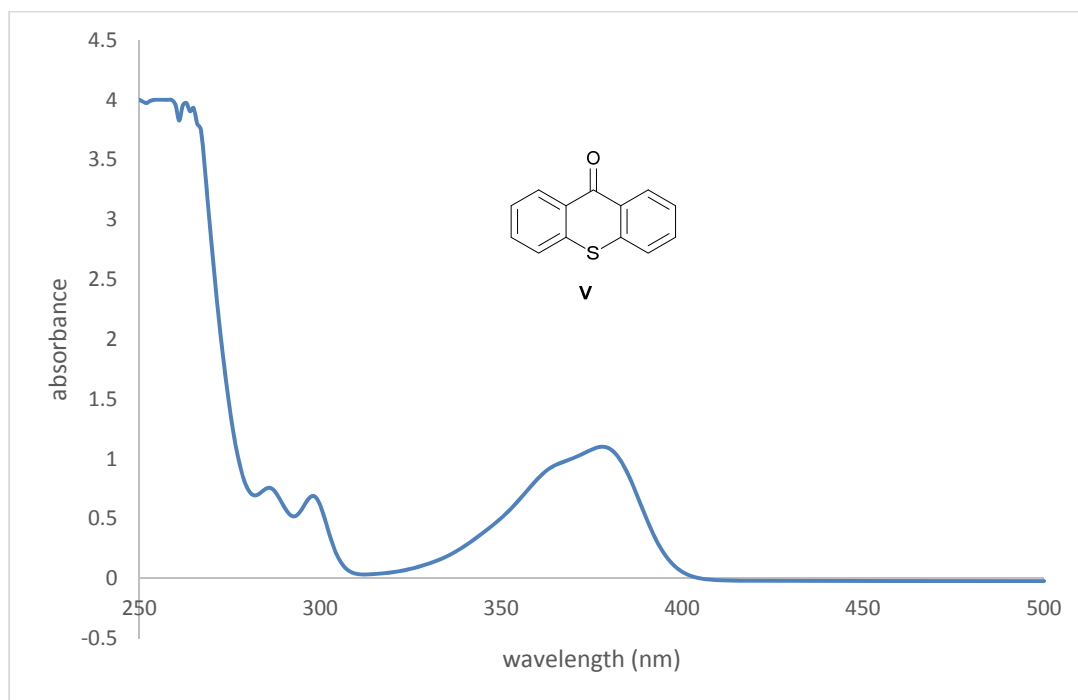
$$E_{\text{ox}} = +1.7 \text{ V vs. SCE}$$

$$E_{\text{triplet}} = +3.0 \text{ eV}$$

$$\Delta G_{\text{et}} = -4.61 \text{ kcal/mol}$$

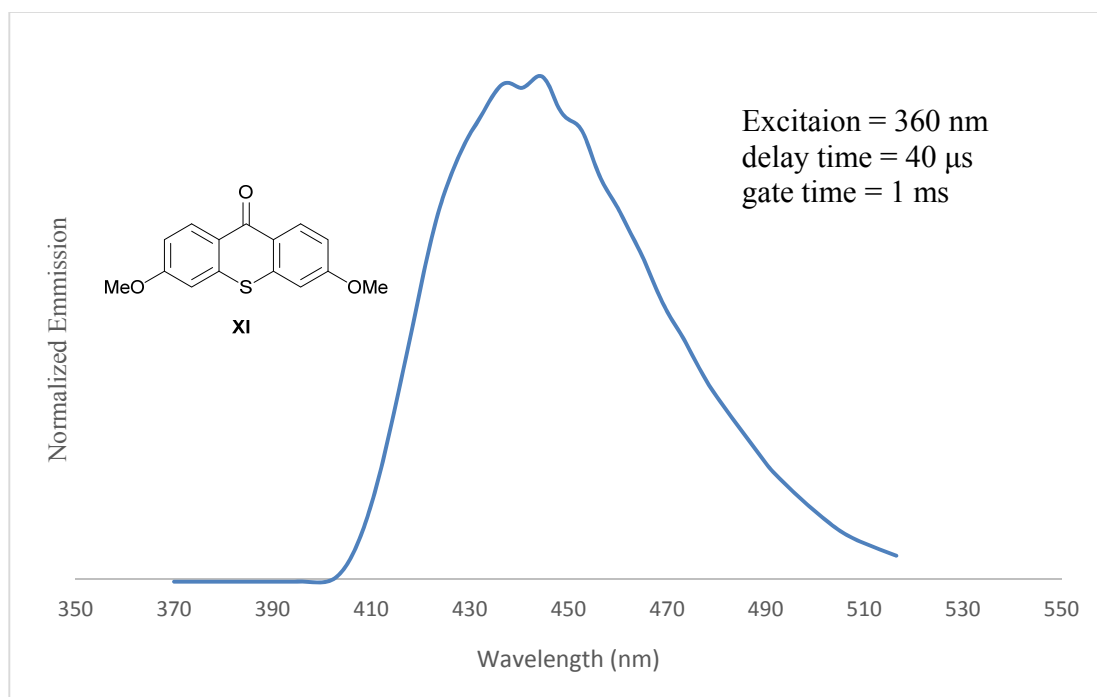
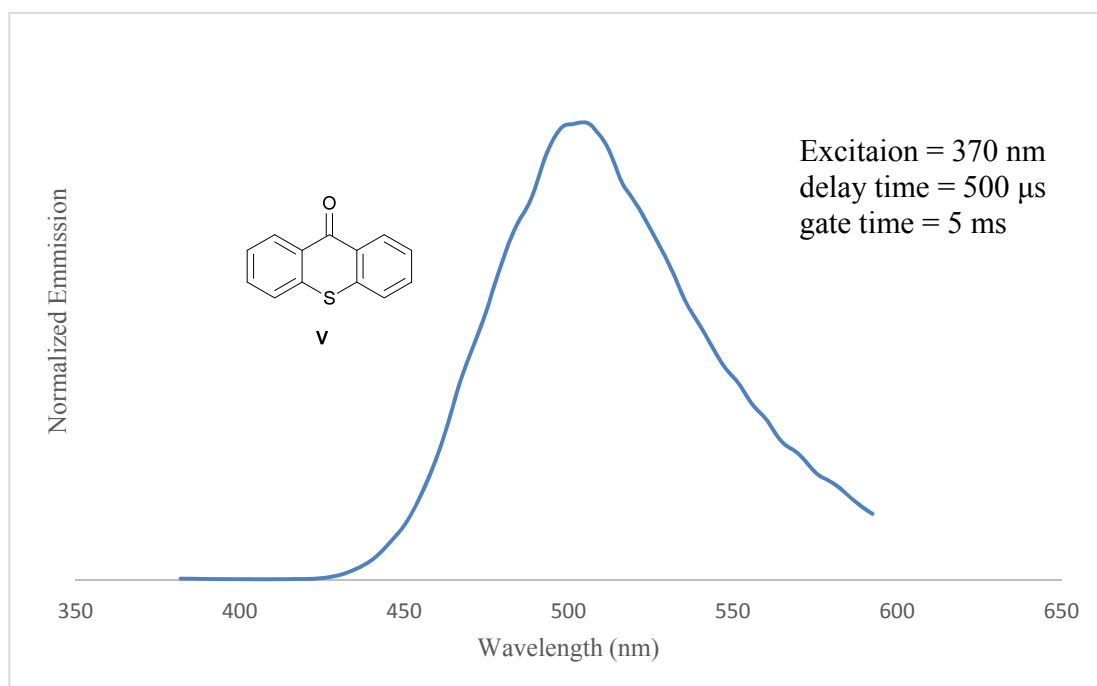
G. UV-Visible Absorption Spectroscopy:

UV-Visible absorption spectra of ketone catalysts were measured in CH₃CN (for Spectrochemical Analysis) on a Shimadzu UV-3510 spectrometer.

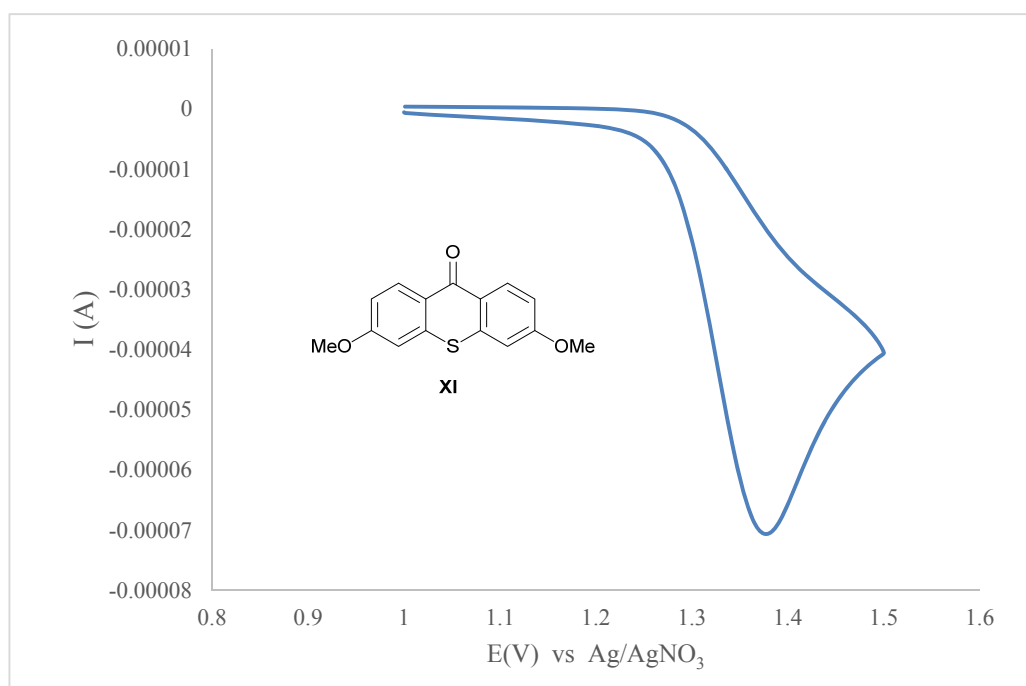
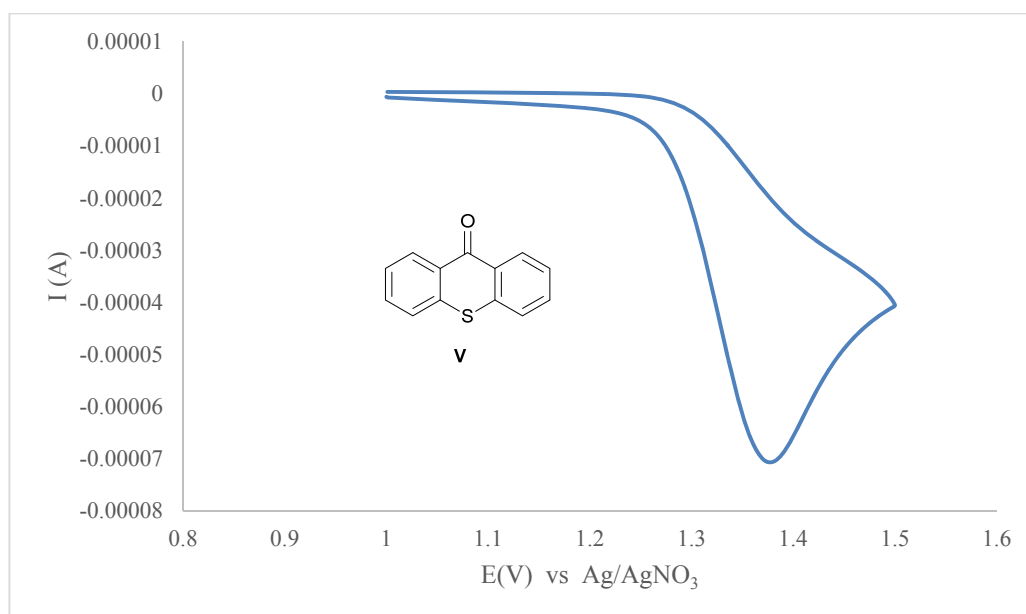


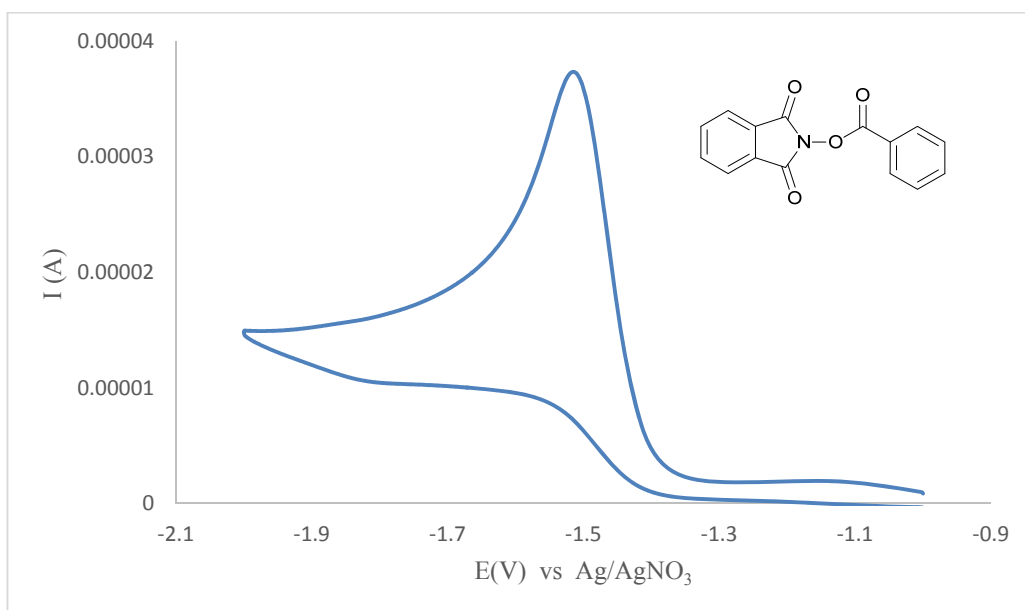
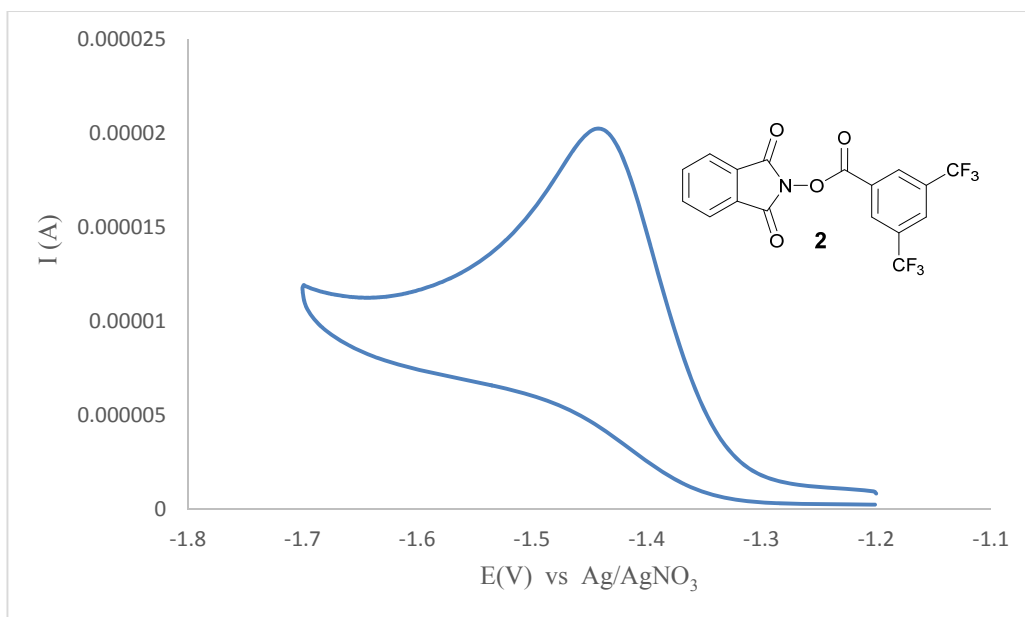
H. Phosphorescence Spectroscopy:

Phosphorescence spectra of ketone catalysts were measured at 77 K in MeOH (for Spectrochemical Analysis) with an appropriate wave length, delay time, and gate time. Experiments were performed on a LS-55 luminescence spectrometer (Perkin-Elmer Ltd, Beaconsfield, UK) equipped with low temperature phosphorescence measurement unit using a quartz tube (5 mm OD) as a sample cell.



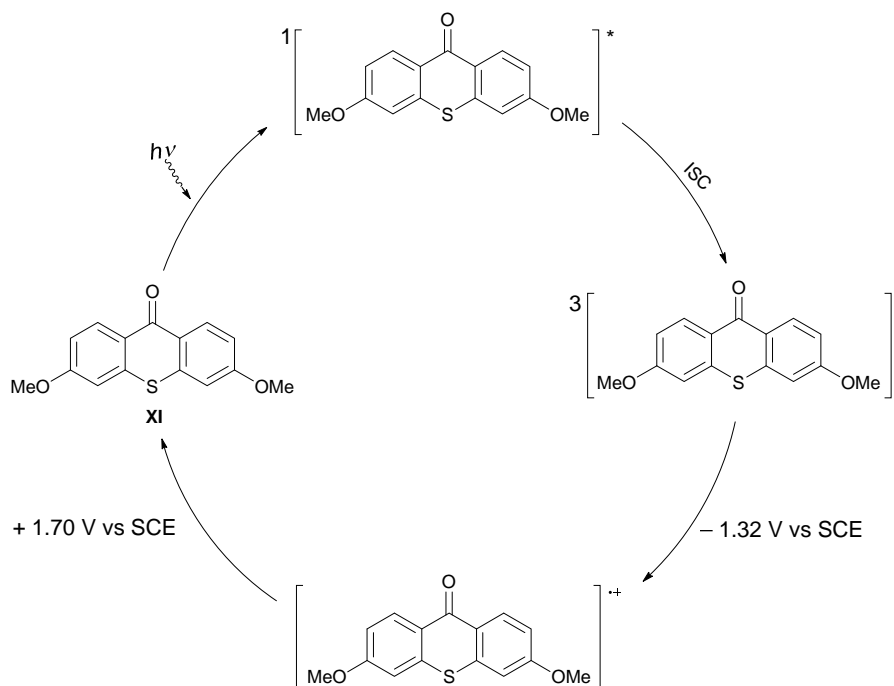
I. Electrochemical Studies: Cyclic voltammetry was performed on an ALS/chi-617A electrochemical analyser. The voltammetric cell consisted of a glassy carbon electrode, a Pt wire counter electrode and an Ag/AgNO₃ reference electrode. The measurements were carried out under N₂ using a solution of sample with a concentration of 1.0 mM in CH₃CN containing Bu₄NClO₄ as a supporting electrolyte (0.10 M). The scan rate was 100 mV/s. Nitrogen was passed through the sample between measurements to avoid the deleterious influence of oxygen. The redox potentials were calibrated to the SCE scale with a ferrocene/ferrocenium ion couple.





J. Determination of Excited State Potentials:

Excited state potentials are estimated by using the Rehm-Weller equations as shown below.⁹



$$E^{O*}_{Red} = E^{O'}_{Red} - E^{0-0}$$

Where E^{O*} represents the excited state potential, $E^{O'}$ stands for the ground state potential and E^{0-0} refers to the energy gap between the zeroeth vibrational levels of the ground and excited state. E_{Red} refers to the ketone/ketone(radical cation) couples. E^{0-0} is approximated as the high energy onset of phosphorescence, where the emission intensity is 10% of that obtained at the maximum emission wavelength, using the “10% rule”.¹⁰

$$E^{O*}_{Red} = E^{O'}_{Red} - E^{0-0} = 1.70 - 3.02 = -1.32 \text{ V vs SCE}$$

9. J. L. Brennan, T. E. Keyes and R. J. Forster, *Langmuir* 2006, **22**, 10754.

10. A. Dossing, C. K. Ryu, S. Kudo and P. C. Ford, *J. Am. Chem. Soc.* 1993, **115**, 5132.

K. Quantum Yield Measurement:

The quantum yield was measured by standard ferrioxalate actinometry.¹¹ A 300W Xenon lamp (5% of light intensity, 365 ± 5 nm band pass filter high transmittance) was used as the light source. The measurements were carried out by following the modified literature procedure.¹² The solutions were prepared and stored in dark room. Potassium ferrioxalate solution (0.15 M): 2.21 g of potassium ferrioxalate hydrate was dissolved in 30 mL of 0.05 M H₂SO₄. Buffered solution of phenanthroline: 50 mg of 1,10-phenanthroline and 11.25 g of sodium acetate were dissolved in 50 mL of 0.5 M H₂SO₄.

a) Measurement of light intensity at 365 nm

To determine the photon flux of the spectrophotometer, 2.0 mL of ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at 365 nm with an emission slit width at 10.0 nm. After irradiation, 0.35 mL of phenanthroline solution was added to the cuvette. To ensure complete coordination of ferrous ions with phenanthroline, the solution was kept for 1 h. The absorbance of the solution was measured at 510 nm. A non-irradiated (in dark) sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using equation 1.

$$\text{mol } Fe^{2+} = \frac{V \times \Delta A (510nm)}{L \times \epsilon (510nm)} \quad (1)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ϵ is the molar absorptivity at 510 nm (11,100 L mol⁻¹ cm⁻¹). The photon flux can be calculated using equation 2.

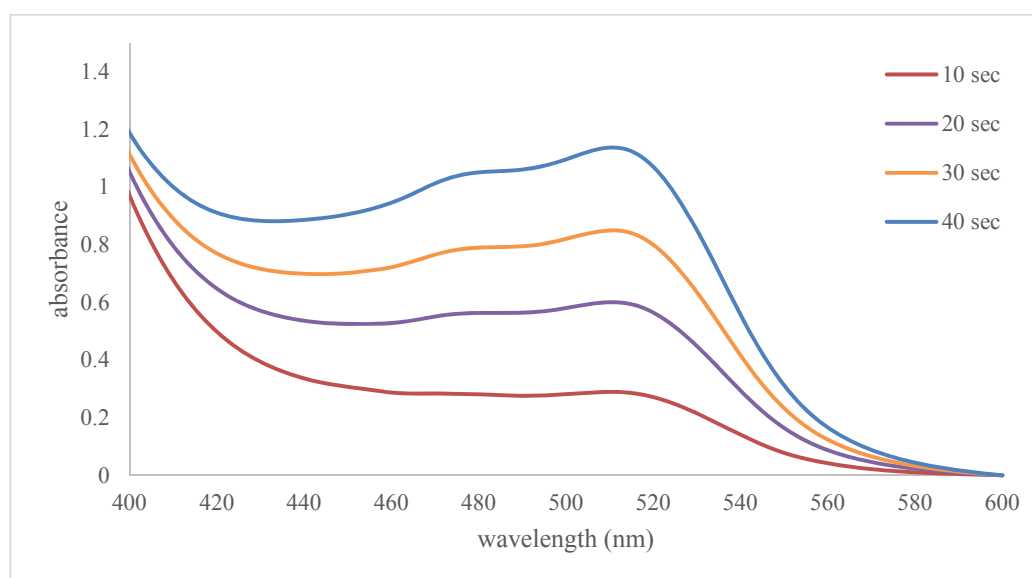
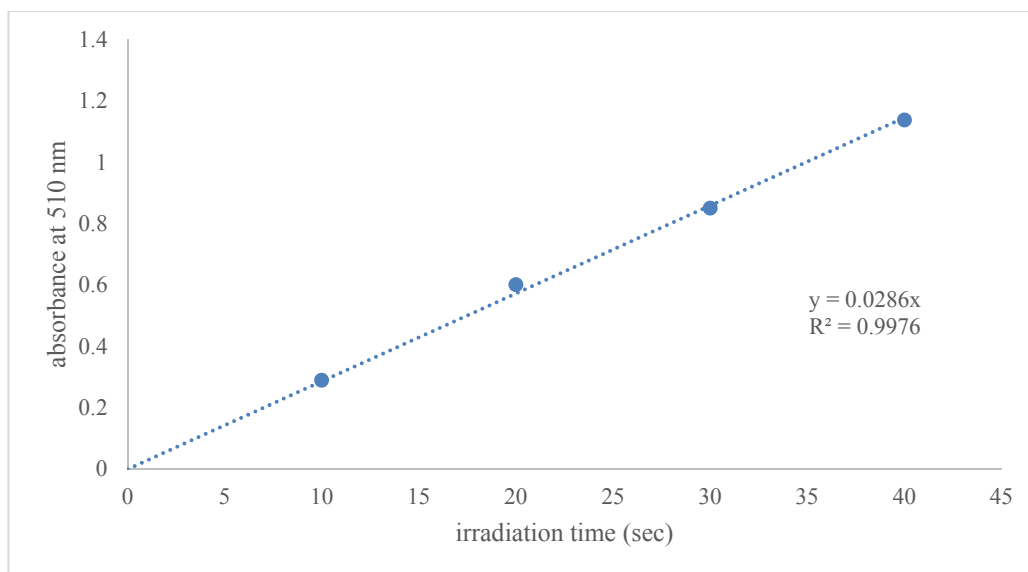
$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \times t \times f} \quad (2)$$

$$f = 1 - 10^{-A} \quad (3)$$

Where Φ is the quantum yield for ferrioxalate actinometer (1.21 for a 0.15 M solution at $\lambda = 366$ nm),¹⁰ t is the time (10 s, 20 s, 30 s, 40 s), and f is the fraction of light absorbed at 365 nm. The photon flux was calculated to be 5.00×10^{-9} einstein/sec.

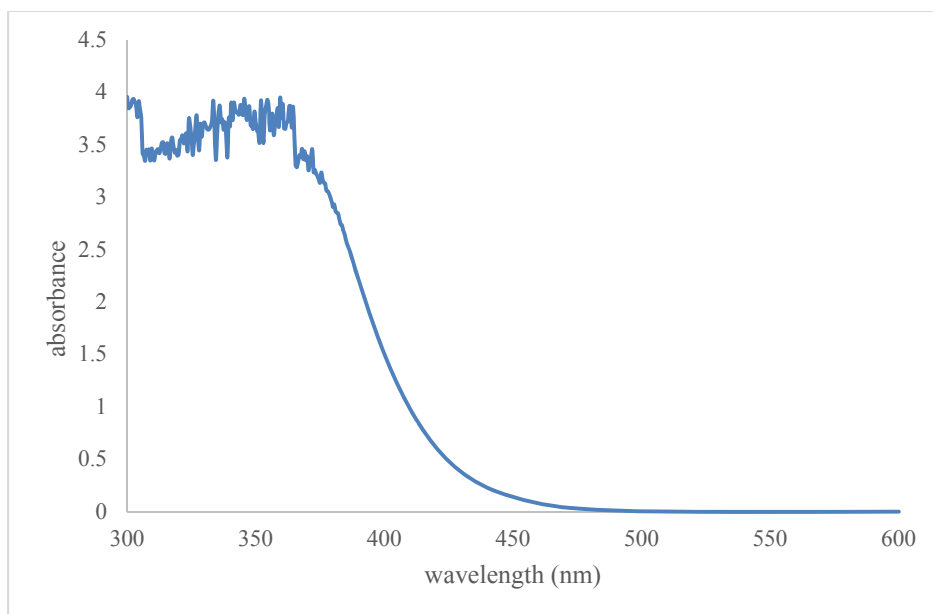
11. M. Montalti, A. Credi, L. Prodi and M. T. Gandolf, Handbook of photochemistry (3rd Ed.), New York, 2006.

12. M. A. Cismesia and T. P. Yoon, *Chem. Sci.*, 2015, **6**, 5426.

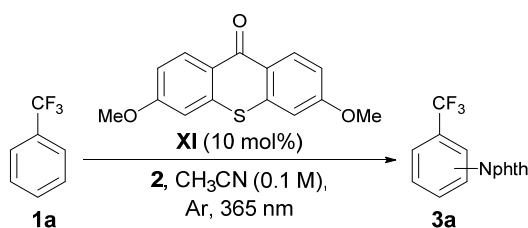


Determination of fraction of light absorbed at 365 nm for the ferrioxalate solution:

The absorbance of above ferrioxalate solution at 365 nm was measured to be > 3 . The fraction of light absorbed (f) by this solution was calculated using equation 3.



b) Measurement of quantum yield



A screw-top cuvette was charged with the catalyst **XI** (10 mol%), **1a** (0.24 mL, 2.0 mmol, 10.0 equiv), **2** (0.2 mmol, 80 mg, 1.0 equiv), CH₃CN (2 mL, 0.1 M), and a small magnetic stir bar was also introduced. The cuvette was degassed with a nitrogen stream for 10 min. After degassing, the reaction mixture was stirred and irradiated with 150 W Xenon lamp (5% of light intensity, 365 nm \pm 5 nm band pass filter) for 86400 s (24 h). After irradiation, the reaction mixture was evaporated. The reaction yield was determined through ¹H-NMR by using 1,3,5-trimethoxybenzene as internal standard. Essentially all the incident light ($f > 0.999$, vide infra) is absorbed by the catalyst under the conditions described above. The quantum yield is calculated as shown below:

$$\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f}$$

$$\Phi = \frac{1.54 \times 10^{-5} \text{ mol}}{5.004 \times 10^{-9} \times 86400 \times 1} = 0.036$$

L. Crystallographic Structure Determination of 3l: The single crystal obtained by recrystallisation in CH₂Cl₂/hexane (1:9) at room temperature was mounted on MicroMesh. X-ray diffraction data was collected at 123 K on a Rigaku VariMax with a Pilatus diffractometer and a fine-focus sealed tube Mo/K α radiation ($\lambda = 0.71075 \text{ \AA}$). An absorption correction was made using Crystal Clear. The structure was solved by direct methods and Fourier syntheses. The data was refined by full-matrix least squares on F^2 by using SHELXL-2014.¹³ All non-hydrogen atoms were refined with anisotropic displacement parameters. The other hydrogen atoms were placed in a calculated positions and isotropic thermal parameters were refined. The crystallographic data are summarized in the table below and the ORTEP diagram is shown on page S-10.

Crystal data and structure refinement for **3l**.

Identification code	3l	
Empirical formula	C ₁₆ H ₁₀ N ₂ O ₃	
Formula weight	278.26	
Temperature	123 (2) K	
Wavelength	71.073 pm	
Crystal system	Orthorhombic	
Space group	F d d 2	
Unit cell dimensions	a = 23.536(12) \AA	$\alpha = 90^\circ$.
	b = 42.75(2) \AA	$\beta = 90^\circ$.
	c = 5.126(3) \AA	$\gamma = 90^\circ$.
Volume	5158(5) \AA^3	
Z	16	
Density (calculated)	1.433 mg/m ³	
Absorption coefficient	0.101 mm ⁻¹	
F(000)	2304	
Crystal size	0.350 \times 0.050 \times 0.030 mm ³	
Theta range for data collection	3.343 to 25.493 $^\circ$.	
Index ranges	$-28 \leq h \leq 28$, $-51 \leq k \leq 51$, $-6 \leq l \leq 6$	
Reflections collected	11161	
Independent reflections	2364 [$R_{\text{int}} = 0.0934$]	
Completeness to $\theta = 25.242^\circ$	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.000 and 0.799	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2364 / 1 / 191	

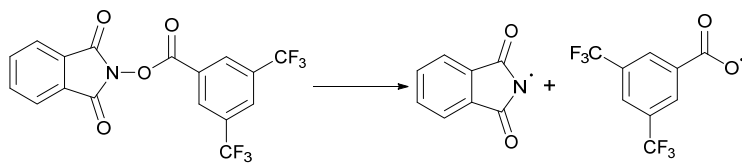
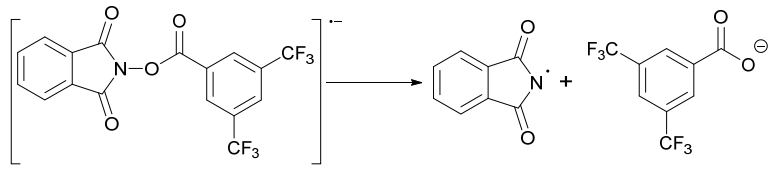
13. G. Sheldrick, *Acta Cryst. C* 2015, **71**, 3.

Goodness-of-fit on F^2	0.889
Final R indices [$I > \sigma(I)$]	$R1 = 0.0372, \omega R2 = 0.0805$
R indices (all data)	$R1 = 0.0438, \omega R2 = 0.0816$
Absolute structure parameter	-1.0(10)
Extinction coefficient	0
Largest diff. peak and hole	0.157 and -0.188 $e.\text{\AA}^{-3}$

M. Computational Studies

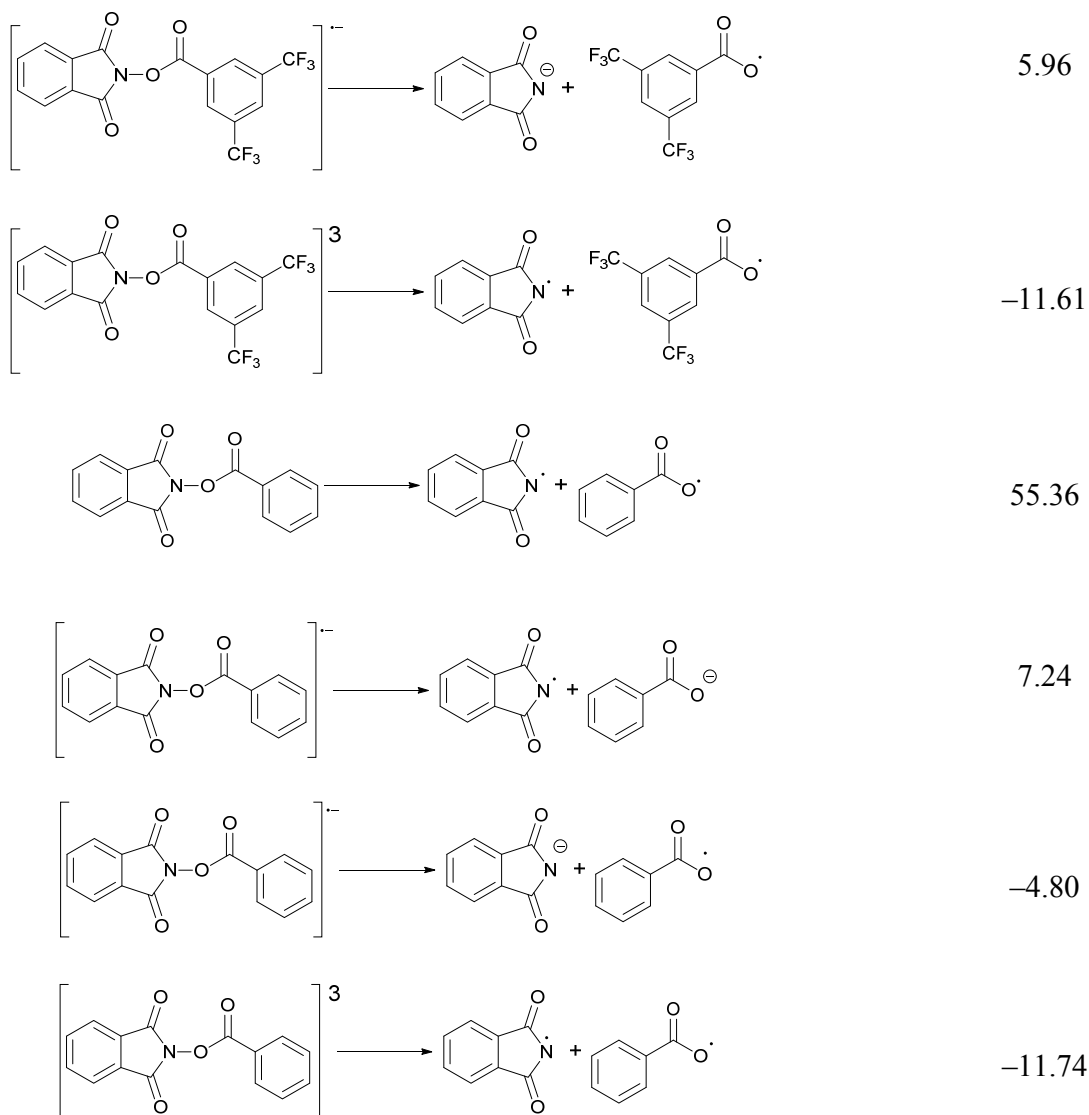
M.1 Computational Methods: Density functional theory (DFT)¹⁴ calculations was performed using the Gaussian 09 program (Revision D.01)¹⁵ and the results are produced with Gauss View 5.0.8. All calculations were performed at the B3LYP/6-311+G (d,p) level of theory, followed by frequency calculations at the same level. Homolytic bond dissociation enthalpies (BDE) were calculated using B3LYP/6-311+G (d,p). The results are summarized below.

M.2 N–O Bond BDEs–DFT Studies: The DFT studies were performed for determining the N–O bond dissociation energies of imidating agent (**2**) in the ground state, triplet excited state and the corresponding radical anion.

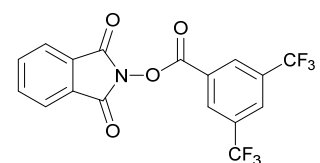
N–O bond cleavage	N–O bond dissociation energy (kcal/mol)
	55.50
	0.83

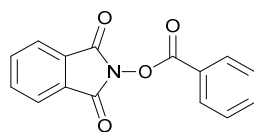
14. R. G. Parr, *Density-Functional Theory of Atoms and Molecules* 1989, Oxford University Press, Oxford, UK.

15. Gaussian 09, Revision B.01: M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.



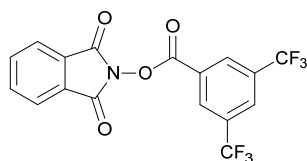
M.3 Triplet Excited Energy of 2: Energy of the imidating agents (2) in triplet excited state is determined through DFT calculations.

Imidating agent (2)	Triplet excited energy (kcal/mol)
	74.26



74.45

M.4 Optimized Structures and Cartesian Coordinates



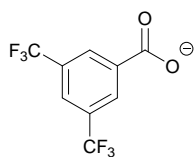
SCF Done: E(RB3LYP) = -1607.19140108 A.U.

Total Energy: E(TD-HF/TD-KS) = -1607.07298428 A.U.

Excited State 1: Triplet-A 3.2223 eV, 384.77 nm, f=0.0000 <S**2> = 2.000

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.896743	1.235918	-0.039927
2	6	0	-1.521133	1.030606	-0.029458
3	6	0	-1.021660	-0.275420	-0.016929
4	6	0	-1.896742	-1.362566	-0.012922
5	6	0	-3.270925	-1.141901	-0.021299
6	6	0	-3.777575	0.154749	-0.031947
7	1	0	-0.842779	1.872022	-0.040205
8	1	0	-1.491434	-2.366691	-0.010356
9	1	0	-4.846185	0.321404	-0.047475
10	6	0	0.434271	-0.575749	-0.010840
11	8	0	0.937180	-1.658620	0.004280
12	8	0	1.174495	0.608129	-0.024197
13	7	0	2.529140	0.402703	-0.014268
14	6	0	3.263475	0.252218	1.182257
15	8	0	2.812188	0.310297	2.294646
16	6	0	3.276418	0.216935	-1.197731
17	8	0	2.837481	0.242023	-2.316264
18	6	0	5.834389	-0.202728	-1.408400
19	6	0	4.664818	0.001084	-0.695664
20	6	0	4.657171	0.021872	0.702092

21	6	0	5.818754	-0.160353	1.433484
22	6	0	7.004865	-0.367232	0.720653
23	6	0	7.012536	-0.388102	-0.676654
24	1	0	5.830206	-0.219194	-2.491436
25	1	0	5.802545	-0.144629	2.516418
26	1	0	7.933212	-0.515531	1.259825
27	1	0	7.946745	-0.552283	-1.200894
28	6	0	-4.203281	-2.328451	0.011783
29	6	0	-3.446773	2.640819	-0.008234
30	9	0	-4.204325	-2.921178	1.228620
31	9	0	-5.477126	-1.982506	-0.262623
32	9	0	-3.838346	-3.273176	-0.881572
33	9	0	-3.641478	3.066068	1.263048
34	9	0	-4.638300	2.727358	-0.636644
35	9	0	-2.613561	-3.523564	-0.594752

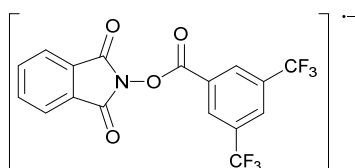


SCF Done: E(RB3LYP) = 1094.71336365 A.U.

Sum of electronic and thermal Enthalpies = -1094.590115 A.U

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.199210	-0.431810	0.000000
2	6	0	1.199857	0.964849	0.000006
3	6	0	0.000106	1.676310	0.000008
4	6	0	-1.199722	0.965145	0.000004
5	6	0	-1.199321	-0.431658	-0.000002
6	6	0	-0.000138	-1.143615	-0.000004
7	1	0	2.118325	1.541499	0.000010
8	1	0	-2.118301	1.541542	0.000005
9	1	0	-0.000060	-2.224104	-0.000009
10	6	0	0.000362	3.234663	0.000013
11	8	0	-1.135268	3.755517	-0.000009
12	8	0	1.136370	3.755178	-0.000008
13	6	0	-2.511201	-1.158240	-0.000001

14	6	0	2.510993	-1.158644	-0.000001
15	9	0	3.274241	-0.857446	-1.084323
16	9	0	3.274236	-0.857456	1.084329
17	9	0	2.370380	-2.510815	-0.000008
18	9	0	-2.370993	-2.510327	-0.000063
19	9	0	-3.274440	-0.856831	1.084358
20	9	0	-3.274496	-0.856736	-1.084293

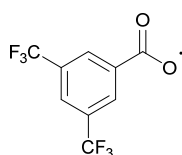


SCF Done: E(UB3LYP) = -1607.25506401 A.U.

Sum of electronic and thermal Enthalpies = -1607.017553 A.U.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.903229	1.203707	0.013116
2	6	0	-1.527029	1.052239	0.011927
3	6	0	-0.957132	-0.243010	-0.006367
4	6	0	-1.818310	-1.365386	-0.022506
5	6	0	-3.190337	-1.192799	-0.022505
6	6	0	-3.763605	0.091538	-0.004495
7	1	0	-0.881495	1.918051	0.025132
8	1	0	-1.380008	-2.353869	-0.036651
9	1	0	-4.837434	0.220389	-0.006599
10	6	0	0.477632	-0.483827	-0.008843
11	8	0	1.046151	-1.551201	-0.023716
12	8	0	1.190827	0.738632	0.009029
13	7	0	2.548934	0.566320	0.007846
14	6	0	3.271751	0.313092	1.198009
15	8	0	2.817224	0.373314	2.327937
16	6	0	3.273939	0.347235	-1.187709
17	8	0	2.821531	0.439766	-2.316307
18	6	0	5.797116	-0.207994	-1.420043
19	6	0	4.625414	0.031499	-0.705771
20	6	0	4.624111	0.011251	0.709737
21	6	0	5.794493	-0.248641	1.419038

22	6	0	6.962259	-0.497083	0.702432
23	6	0	6.963566	-0.476867	-0.708676
24	1	0	5.788821	-0.189314	-2.504153
25	1	0	5.784216	-0.260842	2.503224
26	1	0	7.884000	-0.711697	1.232781
27	1	0	7.886271	-0.676287	-1.243265
28	6	0	-4.106404	-2.379071	0.008997
29	6	0	-3.519087	2.570369	0.010575
30	9	0	-4.783781	-2.495585	1.169509
31	9	0	-5.066975	-2.300829	-0.972006
32	9	0	-3.466953	-3.553961	-0.197330
33	9	0	-4.419698	2.731420	1.020996
34	9	0	-4.213847	2.820851	-1.136376
35	9	0	-2.618042	3.567852	0.135824

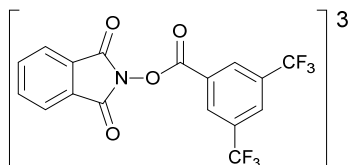


SCF Done: E(UB3LYP) = -1094.55831167 A.U.

Sum of electronic and thermal Enthalpies = -1094.435059 A.U.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.204817	-0.440453	-0.000025
2	6	0	1.212040	0.951307	0.000001
3	6	0	0.000100	1.642115	-0.000005
4	6	0	-1.211935	0.951422	-0.000030
5	6	0	-1.204891	-0.440312	-0.000067
6	6	0	-0.000068	-1.141430	-0.000063
7	1	0	2.146007	1.501237	0.000021
8	1	0	-2.145829	1.501478	-0.000041
9	1	0	-0.000166	-2.222683	-0.000091
10	6	0	0.000214	3.120800	0.000007
11	8	0	-1.041702	3.826853	-0.000021
12	8	0	1.042110	3.826781	0.000024
13	6	0	-2.525915	-1.172106	-0.000004
14	6	0	2.525777	-1.172341	0.000000

15	9	0	3.265278	-0.850992	-0.850992
16	9	0	3.265142	-0.851151	1.085324
17	9	0	2.369616	-2.509525	-0.000106
18	9	0	-2.369854	-2.509312	-0.001071
19	9	0	-3.264812	-0.851608	1.085841
20	9	0	-3.265826	-0.849980	-1.084671

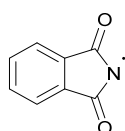


SCF Done: E(UB3LYP) = -1607.08023147 A.U.

Sum of electronic and thermal Enthalpies = -1606.842674 A.U.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.845578	1.251859	0.024785
2	6	0	-1.477799	1.008466	-0.016503
3	6	0	-1.015291	-0.312190	-0.013154
4	6	0	-1.919400	-1.373810	-0.015855
5	6	0	-3.288065	-1.114654	-0.022079
6	6	0	-3.757403	0.194681	-0.024886
7	1	0	-0.776773	1.830567	0.019526
8	1	0	-1.542550	-2.388966	-0.019272
9	1	0	-4.821681	0.390304	-0.037766
10	6	0	0.431357	-0.652229	-0.009685
11	8	0	0.908647	-1.745151	-0.005591
12	8	0	1.201257	0.517889	-0.011055
13	7	0	2.544496	0.296820	-0.005755
14	6	0	3.271907	0.191655	1.220978
15	8	0	2.782901	0.250848	2.330694
16	6	0	3.280336	0.181353	-1.226513
17	8	0	2.799085	0.231184	-2.340066
18	6	0	5.831034	-0.171238	-1.452994
19	6	0	4.633512	0.002905	-0.748939
20	6	0	4.628322	0.009237	0.754322
21	6	0	5.820882	-0.158940	1.468186
22	6	0	6.983852	-0.324418	0.757114

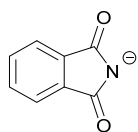
23	6	0	6.989013	-0.330724	-0.732440
24	1	0	5.829113	-0.178024	-2.536265
25	1	0	5.811351	-0.156624	2.551437
26	1	0	7.928522	-0.455991	1.269967
27	1	0	7.937219	-0.466643	-1.237581
28	6	0	-4.251966	-2.275701	0.004781
29	6	0	-3.373977	2.665054	-0.002319
30	9	0	-4.262885	-2.879869	1.215933
31	9	0	-5.517491	-1.893418	-0.259835
32	9	0	-3.916863	-3.221455	-0.899260
33	9	0	-3.888169	2.980694	1.210247
34	9	0	-4.368582	2.836423	-0.901695
35	9	0	-2.418920	3.573363	0.278051



SCF Done: E(UB3LYP) = -512.535994605 A.U.

Sum of electronic and thermal Enthalpies = -512.426115 A.U.

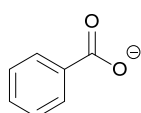
Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	7	0	-0.260611	-2.087863	0.000000
2	6	0	-0.014265	-1.279611	1.150523
3	8	0	0.141508	-1.718136	-2.264339
4	6	0	-0.014265	-1.279611	-1.150523
5	8	0	0.141508	-1.718136	-2.264339
6	6	0	-0.010030	1.327790	-1.425467
7	6	0	-0.012316	0.143196	0.698900
8	6	0	-0.012316	0.143196	0.698900
9	6	0	-0.010030	1.327790	1.425467
10	6	0	-0.000120	2.519874	0.702726
11	6	0	-0.000120	2.519874	-0.702726
12	1	0	-0.010152	1.318335	-2.508647
13	1	0	-0.010152	1.318335	2.508647
14	1	0	0.010610	3.466785	1.230114
15	1	0	0.010610	3.466785	-1.230114



SCF Done: E(RB3LYP) = -512.683427930 A.U.

Sum of electronic and thermal Enthalpies = -512.572998 A.U.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.000040	2.531187	0.699222
2	6	0	-0.000040	1.325447	1.416329
3	6	0	-0.000040	0.142907	0.694117
4	6	0	-0.000040	0.142907	-0.694117
5	6	0	-0.000040	1.325447	-1.416329
6	6	0	-0.000040	2.531187	-0.699222
7	1	0	-0.000040	3.477897	1.231998
8	1	0	-0.000039	1.311147	2.501446
9	1	0	-0.000039	1.311147	-2.501446
10	1	0	-0.000040	3.477897	-1.231998
11	6	0	-0.000040	-1.324702	-1.113330
12	8	0	0.000102	-1.679948	-2.293406
13	6	0	-0.000040	1.324702	1.113330
14	8	0	0.000102	-1.679948	2.293406
15	7	0	0.000063	-2.113857	0.000000

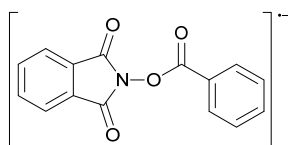


SCF Done: E(RB3LYP) = -420.396698283 A.U.

Sum of electronic and thermal Enthalpies = -420.287472 A.U.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.833028	1.205596	-0.000001
2	6	0	0.437804	1.201215	0.000009
3	6	0	-0.279020	-0.000042	0.000013
4	6	0	0.437919	-1.201237	0.000006
5	6	0	1.833153	-1.205519	-0.000004
6	6	0	2.538243	0.000053	-0.000008

7	1	0	2.374163	2.148358	-0.000004
8	1	0	-0.135447	2.121713	0.000013
9	1	0	-0.135202	-2.121801	0.000009
10	1	0	2.374306	-2.148269	-0.000009
11	1	0	3.624618	0.000157	-0.000016
12	6	0	-1.833938	-0.000014	0.000022
13	8	0	-2.369034	-1.133462	-0.000010
14	8	0	-2.369162	1.133404	-0.000016

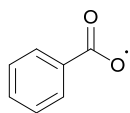


SCF Done: E(UB3LYP) = -932.947939500 A.U.

Sum of electronic and thermal Enthalpies = -932.725129 A.U.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.640704	0.000138	-1.506624
2	6	0	-3.294158	0.000073	-1.150556
3	6	0	-2.929455	-0.000045	0.200290
4	6	0	-3.922470	-0.000101	1.184820
5	6	0	-5.266655	-0.000036	0.825674
6	6	0	-5.628300	0.000085	-0.521943
7	1	0	-4.919032	0.000228	-2.554911
8	1	0	-2.522677	0.000110	-1.908519
9	1	0	-3.617808	-0.000194	2.224273
10	1	0	-6.031819	-0.000079	1.594478
11	1	0	-6.676184	0.000136	-0.803562
12	6	0	-1.501082	-0.000115	0.653299
13	8	0	-1.150268	-0.000274	1.800824
14	8	0	-0.667736	0.000087	-0.429111
15	7	0	0.682410	0.000049	-0.129870
16	6	0	1.438048	1.208153	-0.158492
17	8	0	0.942737	2.338966	-0.226894
18	6	0	1.438016	-1.208073	-0.158691
19	8	0	0.942663	-2.338862	-0.227175

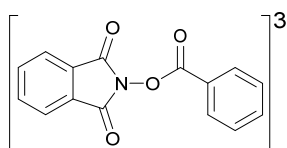
20	6	0	4.008173	-1.421226	-0.033241
21	6	0	2.794298	-0.720150	-0.088917
22	6	0	2.794320	0.720178	-0.088840
23	6	0	4.008215	1.421211	-0.033097
24	6	0	5.197571	0.712641	0.018239
25	6	0	5.197550	-0.712696	0.018168
26	1	0	4.002822	-2.506627	-0.032729
27	1	0	4.002895	2.506612	-0.032450
28	1	0	6.142803	1.245081	0.060482
29	1	0	6.142766	-1.245169	0.060349



SCF Done: E(UB3LYP) = -420.269145039 A.U.

Sum of electronic and thermal Enthalpies = -420.159778 A.U.

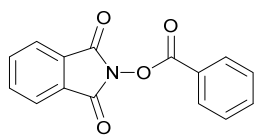
Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.837379	1.211198	-0.000131
2	6	0	0.446865	1.214539	0.000022
3	6	0	-0.247221	-0.000090	0.000191
4	6	0	0.447040	-1.214639	0.000182
5	6	0	1.837455	-1.211278	0.000037
6	6	0	2.530853	0.000022	-0.000121
7	1	0	2.380981	2.148586	-0.000267
8	1	0	-0.105829	2.146911	0.000009
9	1	0	-0.105892	-2.146897	0.000317
10	1	0	2.381133	-2.148612	0.000061
11	1	0	3.615066	0.000239	-0.000239
12	6	0	-1.719439	0.000018	0.000386
13	8	0	-2.435536	-1.039408	-0.000431
14	8	0	-2.434846	1.039569	0.000021



SCF Done: E(UB3LYP) = -932.788727182 A.U.

Sum of electronic and thermal Energies = -932.568131 A.U.

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.723575	0.000028	-1.348159
2	6	0	-3.353730	-0.000029	-1.106252
3	6	0	-2.882581	-0.000045	0.212535
4	6	0	-3.787921	-0.000002	-1.281451
5	6	0	-5.154810	0.000055	1.031663
6	6	0	-5.623384	0.000070	-0.282704
7	1	0	-5.089056	0.000041	-2.368326
8	1	0	-2.653222	-0.000062	-1.930130
9	1	0	-3.404772	-0.000014	2.294242
10	1	0	-5.854717	0.000087	1.859041
11	1	0	-6.690219	0.000114	-0.476252
12	6	0	-1.442082	-0.000108	0.545318
13	8	0	-0.940357	-1.628040	1.628040
14	8	0	-0.664293	-0.000045	-0.638832
15	7	0	0.673522	-0.000023	-0.420605
16	6	0	1.407716	1.223915	-0.305973
17	8	0	0.924562	2.336305	-0.366359
18	6	0	1.407759	-1.223935	-0.305977
19	8	0	0.924641	-2.336341	-0.366359
20	6	0	3.954381	-1.458866	0.066570
21	6	0	2.759447	-0.750445	-0.115874
22	6	0	2.759421	0.750471	-0.115873
23	6	0	3.954329	1.458933	0.066581
24	6	0	5.113195	0.743785	0.239334
25	6	0	5.113222	-0.743677	0.239327
26	1	0	3.948257	-2.542187	0.069304
27	1	0	3.948167	2.542254	0.069324
28	1	0	6.058058	1.253567	0.381665
29	1	0	6.058103	-1.253428	0.381653

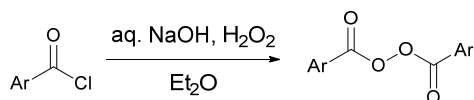


SCF Done: E(RB3LYP) = -932.899971218 A.U.

after Total Energy, E(TD-HF/TD-KS) = -932.781254851

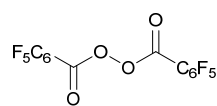
Excited State 1: Triplet-A 3.2304 eV 383.80 nm f=0.0000 <S**2> = 2.000

Center number	Atomic number	Atomic type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.781414	-0.001016	-1.301049
2	6	0	3.404735	-0.000883	-1.100992
3	6	0	2.892966	0.000159	0.202963
4	6	0	3.765837	0.001044	1.298497
5	6	0	5.139748	0.001007	1.090708
6	6	0	5.648378	-0.000032	-0.208721
7	1	0	5.177866	-0.001916	-2.309609
8	1	0	2.729890	-0.001601	-1.945999
9	1	0	3.351854	0.001776	2.299082
10	1	0	5.814158	0.001789	1.939014
11	1	0	6.720620	-0.000128	-0.369627
12	6	0	1.441721	0.000174	0.491456
13	8	0	0.913893	0.000550	1.564330
14	8	0	0.699079	-0.000546	-0.704806
15	7	0	-0.653574	-0.000336	-0.498821
16	6	0	-1.395450	-1.187868	-0.332911
17	8	0	-0.956455	-2.306339	-0.380180
18	6	0	-1.395252	1.187400	-0.333775
19	8	0	-0.956062	2.305771	-0.381781
20	6	0	-3.952927	1.420936	0.086984
21	6	0	-2.787706	0.698533	-0.107398
22	6	0	-2.787801	-0.698581	-0.106772
23	6	0	-3.953136	-1.420617	0.088344
24	6	0	-5.135137	-0.698436	0.286252
25	6	0	-5.135046	0.699124	0.285550
26	1	0	-3.942139	2.504103	0.086799
27	1	0	-3.942569	-2.503788	0.089063
28	1	0	-6.066271	-1.230106	0.444450
29	1	0	-6.066103	1.231072	0.443259

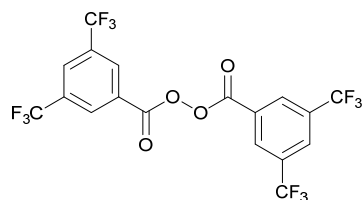
N. Synthesis and Characterization of Aryl-Acylperoxide:

The aryl-acylperoxides were prepared by following the modified literature procedure.¹⁶ In a 100 mL round bottom flask equipped with magnetic stir bar, a solution of the acid chloride (7.3 mmol) in Et₂O (3.0 mL) was cooled to 0 °C. H₂O₂ (aq. 30% by wt., 0.5 mL) was added dropwise followed by the dropwise addition of an aqueous solution of NaOH (364.0 mg in 2.0 mL H₂O) over 20 minutes. The reaction was quenched by adding a saturated aqueous solution of NaHCO₃ (15 mL). The resulting solid was filtered and the aqueous phase was extracted with Et₂O (2 × 20 mL). The filtered solid was mixed with the organic phase, dried over anhydrous Na₂SO₄ and concentrated under reduced pressure at low temperature to afford a white solid. Recrystallization from hexane yielded the aryl-acylperoxides as a white solid.

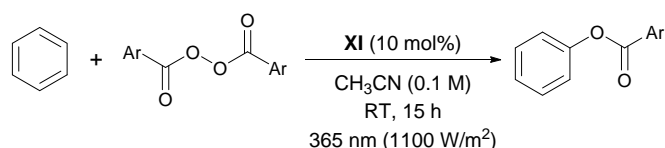
4: Following the general procedure described above with 2,3,4,5,6-pentafluorobenzoyl chloride, **4** was obtained as a white solid (502 mg, 1.18 mmol, 16% yield), which was stored at -40 °C. ¹³C-NMR (150 MHz, CDCl₃): δ 154.9, 147.0-146.6 (m), 146.0-145.6 (m), 145.3-144.9 (m), 144.2-143.8 (m), 139.1-138.5 (m), 137.4-136.8 (m), 102.58 (t, *J* = 17.2 Hz). ¹⁹F-NMR (471 MHz, CDCl₃): δ -158.104, -143.278, -133.679.



Following the general procedure described above with 3,5-bis-(trifluoromethyl)benzoyl chloride, the corresponding peroxide was obtained as a white solid (1.4 g, 2.72 mmol, 38% yield), which was stored at -40 °C. ¹H-NMR (400 MHz, CDCl₃): δ 8.53 (s, 2H), 8.21 (s, 1H). ¹³C-NMR (100 MHz, CDCl₃): δ 160.4, 133.1 (q, *J* = 69 Hz), 130.0, 128.1, 127.4, 122.5 (q, *J* = 69 Hz), 123.9, 121.2. ¹⁹F-NMR (471 MHz, CDCl₃): δ -62.97.

**O. Reaction Conditions Optimization for the Ketone-Catalyzed C-H Acyloxylation:****Effect of Oxygenating Agent**

Considering our results for C-H imidation of arenes, we thought that the aryl-acylperoxides with electron-withdrawing groups would be suitable for the C-H acyloxylation of arenes. Among the several candidates examined in the reaction of benzene, pentafluorobenzoyl peroxide led to afford the acyloxylation product in the highest yield.



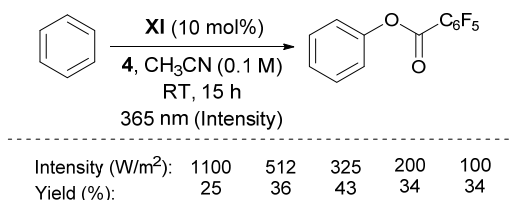
16. W.-Y. Yu, W. N. Sit, Z. Zhou and A. S. C. Chan, *Org. Lett.*, 2009, **11**, 3174.

Entry	Ar	Yield (%)
1	C ₆ H ₅	<5
2	4-CF ₃ C ₆ H ₄	6
3	3,5-(CF ₃) ₂ C ₆ H ₃	20
4	C ₆ F ₅ (4)	25

(a) Reactions were carried out on a 0.2 mmol scale with oxygenating agent (1.0 equiv) and arenes (10.0 equiv). (b) NMR yields are indicated.

Effect of Light Intensity

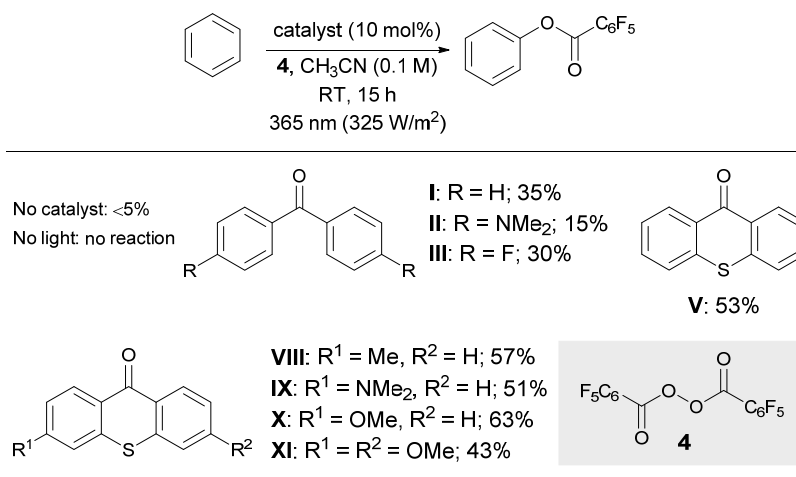
During optimization of the reaction conditions, we observed that 365 nm light with high intensity caused the decomposition of **4**. Therefore, we reasoned that decreasing the light intensity might be beneficial for improving the efficiency. After carefully conducting the C-H acyloxylation with different intensity of 365 nm light, we concluded that 325 W/m² was an optimum intensity.



(a) Reactions were carried out on a 0.2 mmol scale with **4** (1.0 equiv) and arenes (10.0 equiv). (b) NMR yields are indicated.

Catalyst Optimization

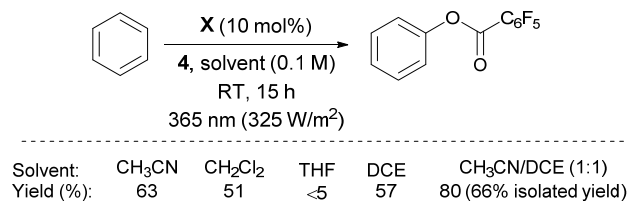
A brief catalyst screening revealed that **X** was optimal and the product was obtained in 63% yield.



(a) Reactions were carried out on a 0.2 mmol scale with **4** (1.0 equiv) and arenes (10.0 equiv). (b) NMR yields are indicated.

Effect of Solvent

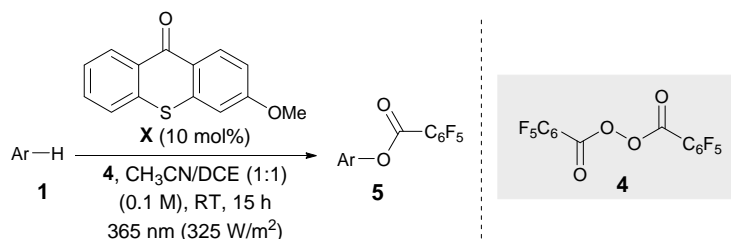
The reaction yield greatly depended upon the solvents and the best result was obtained by using a 1:1 mixture of toluene and 1,2-dichloroethane.



(a) Reactions were carried out on a 0.1 mmol scale with **4** (1.0 equiv) and arenes (10.0 equiv). (b) NMR yields are indicated.

P. Photoexcited Ketone-Catalyzed C-H Acyloxylation of Arenes:

General procedure for the ketone-catalyzed C-H acyloxylation of arenes:



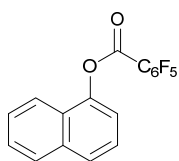
In a flame and vacuum dried reaction tube, **4** (84.4 mg, 0.2 mmol, 1.0 equiv) and **X** (5.0 mg, 0.02 mmol, 0.1 equiv) were taken. The reaction flask was degassed in *vacuo* and backfilled with argon. Then, CH₃CN/DCE (2.0 mL, v/v = 1:1) and arene (2.0 mmol, 10.0 equiv) were added. The resulting solution was stirred at 25 °C under 365 nm irradiation (325 W/m²) for 15 h. The reaction was quenched by adding a saturated aqueous solution of NaHCO₃ (5 mL). The aqueous phase was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic phase was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification of the residue by column chromatography over silica gel afforded **5**.

5a: Following the general procedure described above with benzene (0.18 mL, 2.0 mmol, 10.0 equiv) as the arene source, **5a** was obtained as a white solid (38.0 mg, 0.13 mmol, 66% yield).

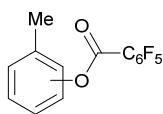
FT-IR (thin film): 1751, 1552, 1489, 1234. **¹H-NMR (600 MHz, CDCl₃)**: δ 7.47-7.41 (m, 2H), 7.79-7.76 (m, 6.5H), 7.33-7.28 (m, 1H), 7.26-7.21 (m, 2H). **¹³C-NMR (150 MHz, CDCl₃)**: δ 157.6, 150.1, 146.6, 144.8, 144.6, 142.9, 138.7, 137.0, 129.8, 126.8, 121.3, 107.8. **¹⁹F-NMR (471 MHz, CDCl₃)**: δ -159.78, -147.16, -137.13. **HRMS (APCI-MS)**: Calcd. for C₁₃H₅F₅O₂H ([M + H]⁺): 289.0282, Found: 289.0282.

5b: Following the general procedure described above with naphthalene (256.3 mg, 2.0 mmol, 10.0 equiv) as the arene source, **5b** was obtained as a white solid (56 mg, 0.165 mmol, 82% yield, only *ortho*). The isomer ratios were determined by hydrolysis of the product to the corresponding phenol

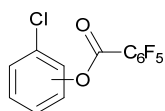
derivatives and comparing the crude $^1\text{H-NMR}$ with literature data. **FT-IR (thin film)**: 1745, 1498, 1325. **$^1\text{H-NMR}$ (400 MHz, CDCl_3)**: δ 8.02-7.96 (m, 1H), 7.95-7.90 (m, 1H), 7.83 (d, $J = 8.4$ Hz, 1H), 7.59-7.48 (m, 3H), 7.43 (dd, $J = 7.6, 1.0$ Hz, 1H). **$^{13}\text{C-NMR}$ (150 MHz, CDCl_3)**: δ 157.6, 146.7, 146.0, 145.0, 144.7, 142.8, 138.8, 137.2, 134.8, 128.2, 127.08, 127.03, 126.9, 126.2, 125.4, 120.9, 118.0, 107.8 (td, $J = 16.2, 3$ Hz). **$^{19}\text{F-NMR}$ (471 MHz, CDCl_3)**: δ -159.51 (t, $J = 29$ Hz), -146.94 (t, $J = 29$ Hz), -136.79 (d, $J = 29$ Hz). **HRMS (APCI-MS)**: Calcd. for $\text{C}_{17}\text{H}_7\text{F}_5\text{O}_2\text{H}$ ($[\text{M} + \text{H}]^+$): 339.0437, Found: 339.0439.



5c: Following the general procedure described above with toluene (0.21 mL, 2.0 mmol, 10.0 equiv) as the arene source, **5c** was obtained as a white solid (43 mg, 0.14 mmol, 71% yield, $o/m/p = 4.5:1:1.8$). The isomer ratios were determined after hydrolysis of the product to the corresponding phenol derivatives and comparing the crude $^1\text{H-NMR}$ with literature data. The isolated product was an inseparable mixture of isomers. All peaks observed in the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were assigned. **FT-IR (thin film)**: 1757, 1524, 1500, 1329. **$^1\text{H-NMR}$ (600 MHz, CDCl_3)**: δ 7.34-7.18 (m, 7.3H), 7.16-7.07 (m, 3H), 7.05-7.00 (m, 0.7H), 2.39 (s, 1H), 2.37 (s, 1.8H), 2.26 (s, 4.5H). **$^{13}\text{C-NMR}$ (150 MHz, CDCl_3)**: δ 148.8, 136.6, 131.6, 130.3, 129.9, 129.5, 127.6, 127.3, 127.0, 121.8, 121.6, 120.9, 118.2, 21.4, 21.0, 16.3. **$^{19}\text{F-NMR}$ (471 MHz, CDCl_3)**: δ -159.78, -147.37, -137.22. **HRMS (APCI-MS)**: Calcd. for $\text{C}_{14}\text{H}_7\text{F}_5\text{O}_2\text{H}$ ($[\text{M} + \text{H}]^+$): 303.0439, Found: 303.0439.

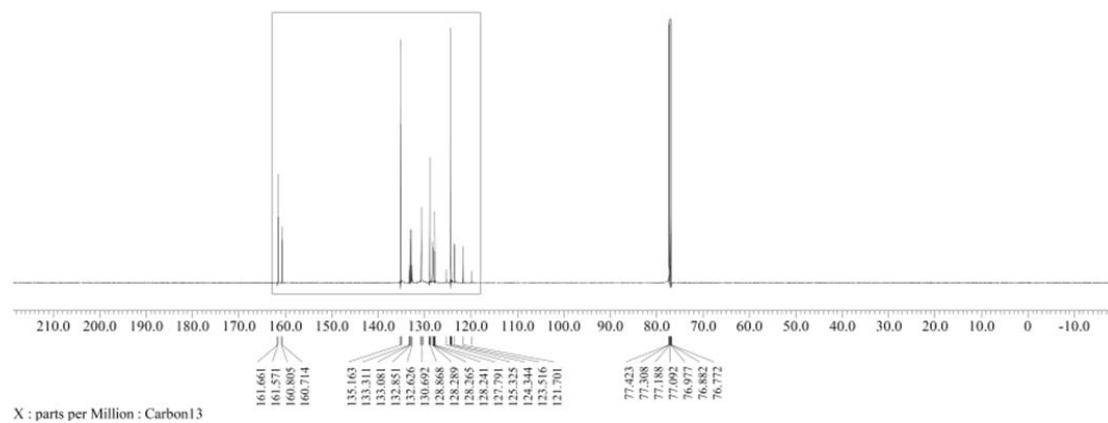
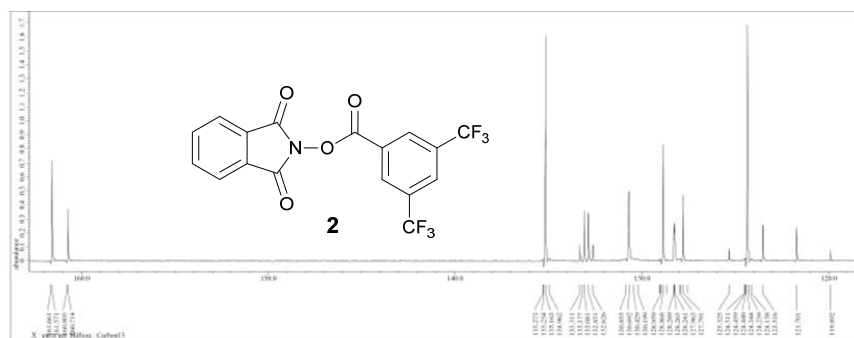
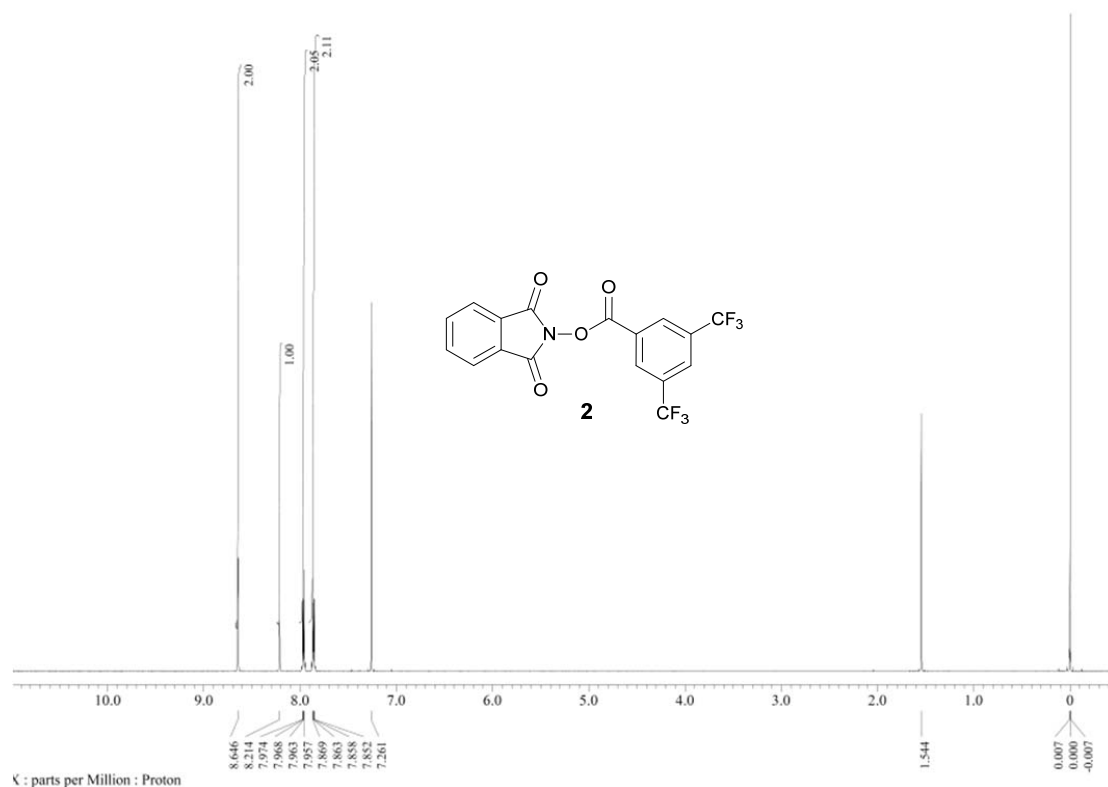


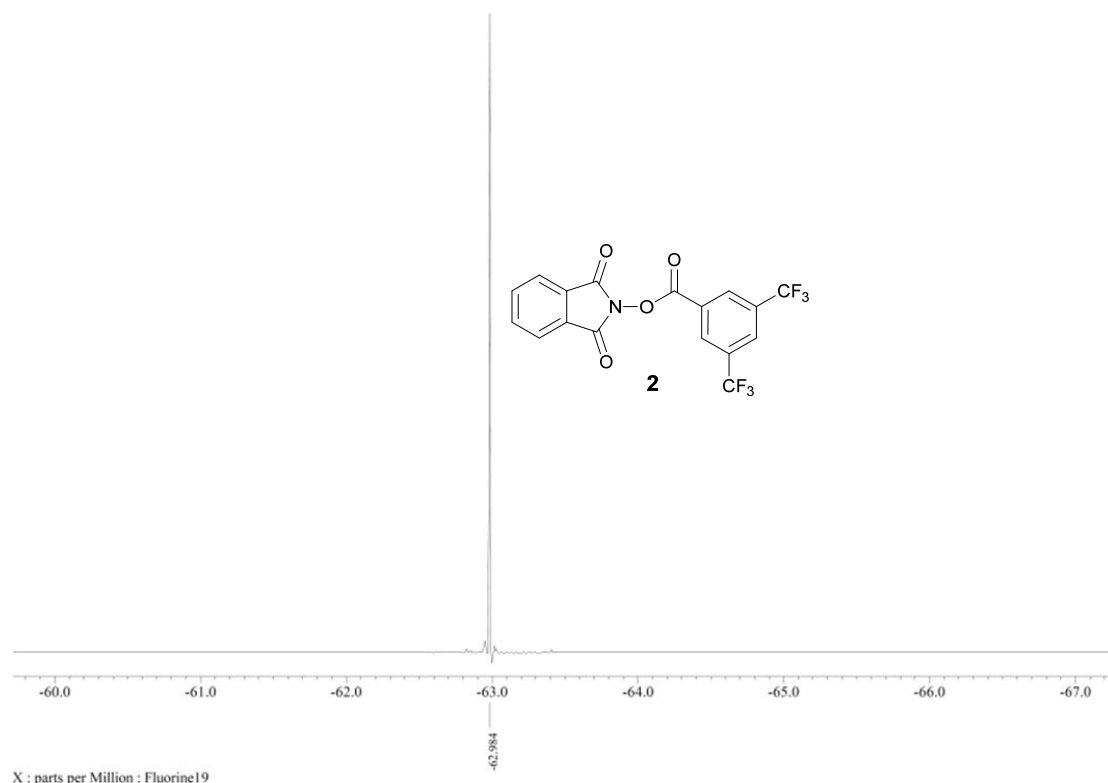
5d: Following the general procedure described above with chlorobenzene (0.20 mL, 2.0 mmol, 10.0 equiv) as the arene source, **5d** was obtained as a white solid (27 mg, 0.083 mmol, 42% yield, $o/m/p = 2.4:1:3.3$). The isomer ratios were determined after hydrolysis of the product to the corresponding phenol derivatives and comparing the crude $^1\text{H-NMR}$ with literature data. The isolated product was an inseparable mixture of isomers. All peaks observed in the $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ were assigned. **FT-IR (thin film)**: 1753, 1525, 1330. **$^1\text{H-NMR}$ (600 MHz, CDCl_3)**: δ 7.53-7.36 (m, 2H), 7.36-7.22 (m, 2H), 7.22-7.14 (m, 1H). **$^{13}\text{C-NMR}$ (150 MHz, CDCl_3)**: δ 148.5, 146.3, 132.3, 130.7, 130.5, 129.9, 129.8, 128.1, 128.0, 127.2, 126.8, 126.7, 123.5, 122.7, 122.1, 121.3, 119.7. **$^{19}\text{F-NMR}$ (471 MHz, CDCl_3)**: δ -159.66, -147.19, -146.49, -137.19, -136.88, -136.06. **HRMS (APCI-MS)**: Calcd. for $\text{C}_{13}\text{H}_4\text{ClF}_5\text{O}_2\text{H}$ ($[\text{M} + \text{H}]^+$): 322.9893, Found: 322.9893.



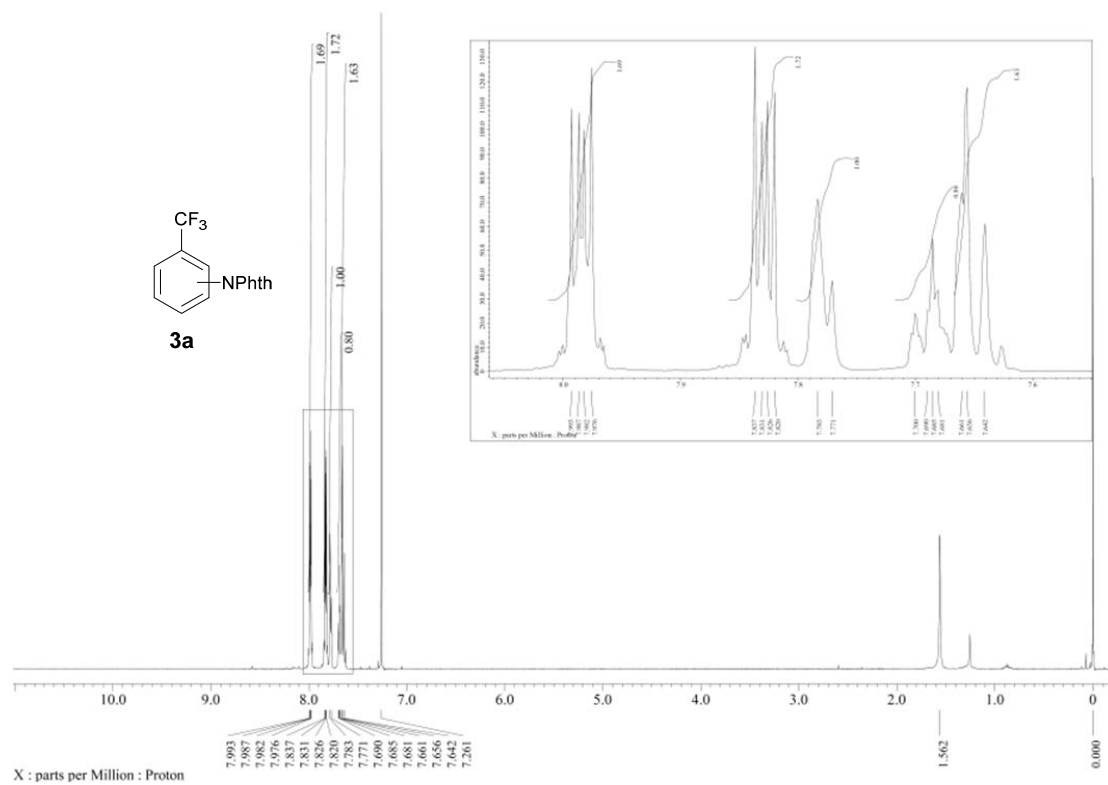
General procedure for the hydrolysis of 5: In a 10 mL round bottom flask, a solution of **5** (0.15 mmol) in EtOH (0.3 mL) was taken and a 2N aqueous solution of NaOH (0.3 mL) was added. The resulting mixture was stirred at 25 °C for 15 h. The reaction mixture was cooled to 0 °C and acidified with a 1N aqueous solution of HCl. The aqueous phase was extracted with EtOAc ($\times 2$). The organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the residue by column chromatography over silica gel afforded corresponding phenol derivatives.

Q. Copies of NMR Spectra:





X : parts per Million : Fluorine19



X : parts per Million : Proton

