Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Strongly Reducing Helical Phenothiazines as Recyclable Organophotoredox Catalysts

Haru Ando,[a] Hiroyoshi Takamura,[a] Isao Kadota,[a]* and Kenta Tanaka[b]*

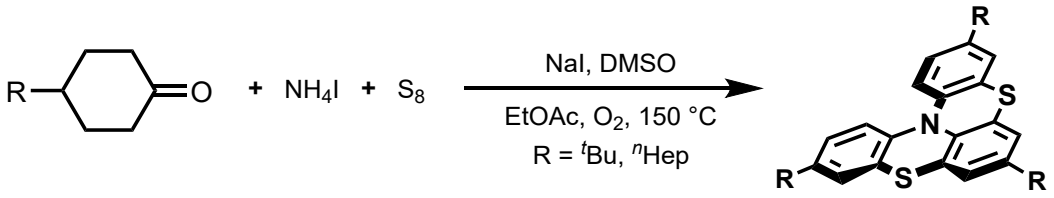
[a] *Department of Chemistry, Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-Naka, Kitaku, Okayama 700-8530, Japan*
[b] *Department of Chemistry, Research Institute for Interdisciplinary Science, Okayama University, 3-1-1 Tsushima-Naka, Kitaku, Okayama 700-8530, Japan*

1. General information

Reagents were used as received from commercial suppliers unless otherwise indicated. Heating reactions were conducted in an oil bath. The analytical thin layer chromatography (TLC) was performed with aluminum TLC plates (Merck TLC silica gel 60 F_{254}). Column chromatography was performed with Kanto Chemical silica gel 60N (40-100 mesh, spherical, neutral). The FT-IR spectra were recorded on IRSpirit-T. ^{1}H and ^{13}C NMR spectra were recorded on a Varian NMR System PS600 or a Varian 400MR ASW. Chemical shifts in the NMR spectra are reported in ppm with reference to the internal residual solvent (^{1}H NMR, $CDCl_3$ 7.26 ppm, C_6D_6 7.16 ppm; ^{13}C NMR, $CDCl_3$ 77.0 ppm). The following abbreviations are used to designate the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. The high-resolution mass spectra were recorded on Bruker micrOTOF II (ESI–TOF–MS). The UV-Vis absorption spectra were measured with a JASCO V-770 spectrometer. The fluorescence spectra were obtained on a RF-6000. The cyclic voltammetry measurements were carried out with a ECstat-101. The photochemical reaction was carried out with a photoreactor (EvoluChem™ PhotoRedOx Box) and blue LED (HCK1012-01-012, λ_{max} = 425 nm, 18 W).

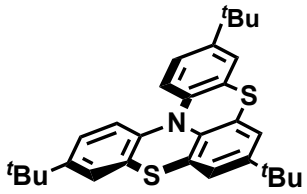
2. Experimental section

General procedure for synthesis of phenothiazine catalyst (Method A)[1]



Ammonium iodide (365.0 mg, 2.5 mmol), sodium iodide (45.0 mg, 0.3 mmol), elemental sulfur (255.0 mg, 1.0 mmol), cyclohexanone derivatives (3.0 mmol), dimethyl sulfoxide (0.14 mL, 2.0 mmol), and ethyl acetate (3.0 mL) were added into a sealed tube. After bubbled with oxygen for 5 min, the resulting solution was stirred at 150 ºC for 24 h. The reaction mixture was transferred to the recovery flask with ethyl acetate at room temperature and the volatiles were removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane) to yield the phenothiazine catalyst.

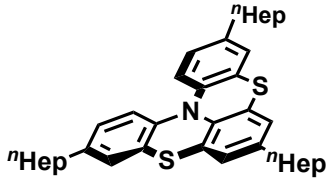
Procedure for the synthesis of 3,7,11-tri-*tert*-butylbenzo[5,6][1,4]thiazino[2,3,4-kl]phenothiazine (PTHS 1)[1]



The reaction was conducted with ammonium iodide (362.3 mg, 2.5 mmol), sodium iodide (44.7 mg, 0.3 mmol), elemental sulfur (255.0 mg, 1.0 mmol), 4-*tert*-butyl cyclohexanone (462.5 mg, 3.0 mmol), dimethyl sulfoxide (0.14 mL, 2.0 mmol), and ethyl acetate (3.0 mL). The residue was purified by column chromatography on silica gel (hexane) to yield the desired product as yellow solid (225.6 mg, 48%).

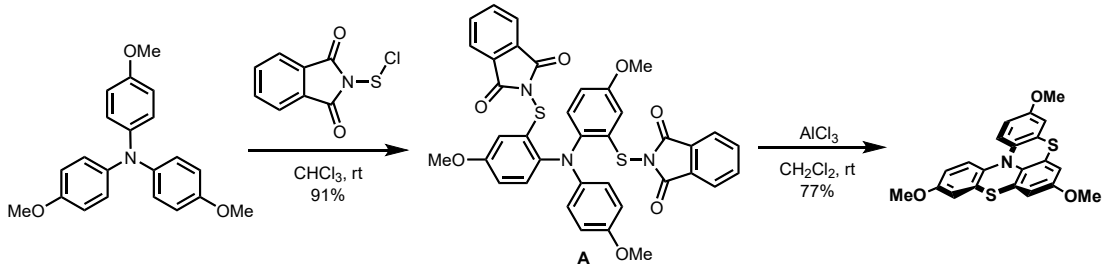
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.20 (s, 2H), 7.13-7.12 (m, 4H), 6.97 (s, 2H), 1.29 (s, 18H), 1.24 (s, 9H).

Procedure for the synthesis of 3,7,11-tri-heptylbenzo[5,6][1,4]thiazino[2,3,4-kl]phenothiazine (PTHS 2)



The reaction was conducted with ammonium iodide (362.4 mg, 2.5 mmol), sodium iodide (44.5 mg, 0.3 mmol), elemental sulfur (255.2 mg, 1.0 mmol), 4-heptyl cyclohexanone (0.67 mL, 3.0 mmol), dimethyl sulfoxide (0.14 mL, 2.0 mmol), and ethyl acetate (3.0 mL). The residue was purified by column chromatography on silica gel (hexane) to yield the desired product as yellow oil (185.3 mg, 31%). R_f = 0.58 (hexane); IR (neat) 2955, 2925, 2854, 1490, 1451, 1323, 1313, 1130 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.07 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 2.4 Hz, 2H), 6.90 (dd, J = 8.4, 1.8 Hz, 2H), 6.78 (s, 2H), 2.52 (t, J = 7.2 Hz, 4H), 2.45 (q, J = 6.6 Hz, 2H), 1.59-1.51 (m, 6H), 1.32-1.27 (m, 24H), 0.90-0.86 (m, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.4, 139.5, 139.2, 137.4, 127.4, 127.4, 126.4, 125.4, 125.3, 120.1, 35.1, 34.9, 31.8, 31.8, 31.4, 31.3, 29.2, 29.2, 29.1, 29.1, 22.7, 22.6, 14.1, 14.1; HRMS (ESI TOF) calcd for $C_{39}H_{53}NS_2$ $[M]^+$ 599.3619, found 599.3618.

Procedure for the synthesis of 3,7,11-tri-methoxy[5,6][1,4]thiazino[2,3,4-kl]phenothiazine (PTHS 3, Method B)[2]

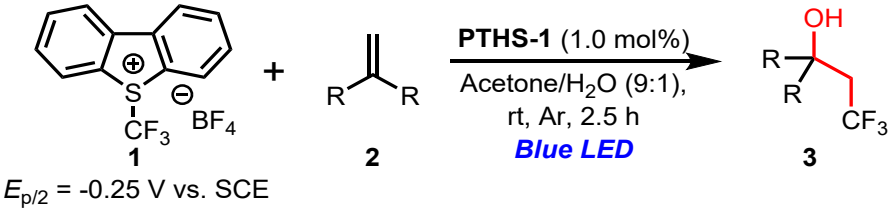


To a solution of tris(4-methoxyphenyl)amine (346 mg, 1.03 mmol) in dry $CHCl_3$ (8.24 mL) was added phthalimidesulfenyl chloride (550 mg, 2.57 mmol) under Ar atmosphere.[2,3] After stirring for 3.5 h at room temperature, the reaction mixture was diluted with CH_2Cl_2, and washed with a saturated $NaHCO_3$ aq. and water. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/EtOAc = 3:1) to provide the thiophthalimide **A** as a yellow solid (647.5 mg, 91% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (dd, J = 5.4, 3.0 Hz, 4H), 7.79 (dd, J = 5.4, 3.0 Hz, 4H), 7.56 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 9.0 Hz, 2H), 6.79 (dd, J = 9.0, 3.0 Hz, 2H), 6.76-6.75 (m, 2H), 6.56 (d, J = 3.0 Hz, 2H), 3.76 (s, 3H), 3.68 (s, 6H).

To a solution of thiophthalimide **A** (97.4 mg, 0.14 mmol) in dry CH_2Cl_2 (5.6 mL) was added $AlCl_3$ (74.7 mg, 0.56 mmol) under Ar atmosphere. After stirring for 3 h at room temperature, the mixture was diluted with CH_2Cl_2 and washed with a saturated Na_2CO_3 aq. and water. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/EtOAc = 30:1 to 10:1) to provide the desired phenothiazine catalyst as a dark yellow glassy solid (42.8 mg, 77% yield).
^{1}H NMR (600 MHz, C_6D_6) δ 6.94 (d, J = 9.0 Hz, 2H), 6.74 (d, J = 2.4 Hz, 2H), 6.53 (s, 2H), 6.49 (dd, J = 9.0, 3.0 Hz, 2H), 3.20 (s, 6H), 3.09 (s, 3H).

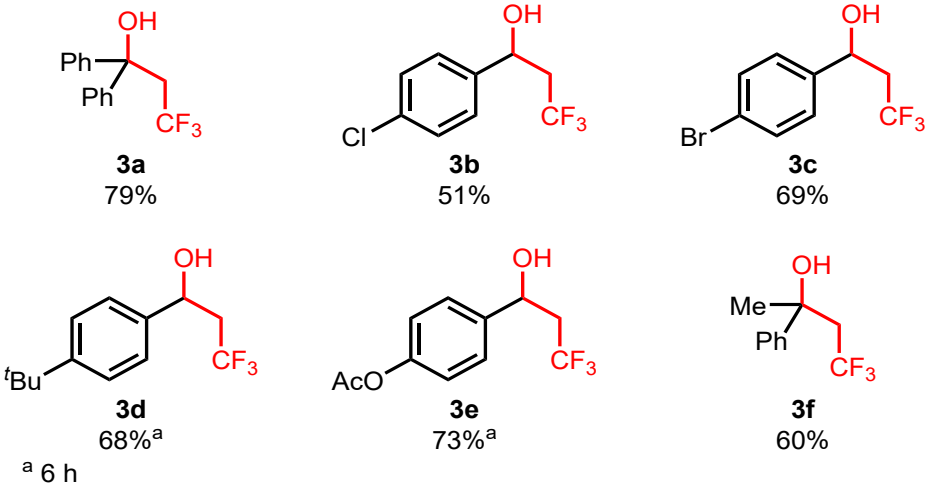
Scope and limitation of three-component oxytrifluoromethylation of 1,1-diphenylethylene



1 $E_{p/2}$ = -0.25 V vs. SCE

2

3



3a 79%

3b 51%

3c 69%

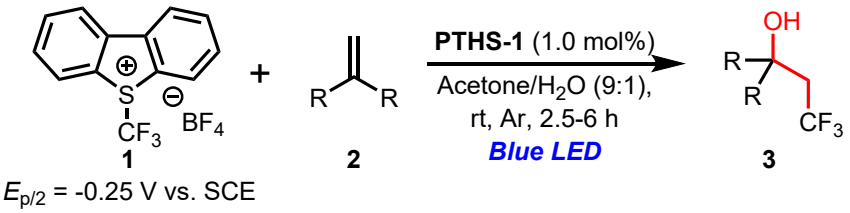
3d 68%[a]

3e 73%[a]

3f 60%

[a] 6 h

General procedure for three-component oxytrifluoromethylation of alkenes[4]

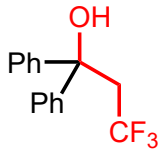


1 $E_{p/2}$ = -0.25 V vs. SCE

2

3

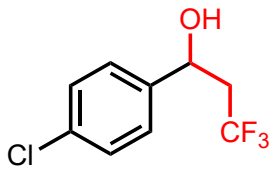
Umemoto reagent **1** (35.8 mg, 0.105 mmol), alkene **2** (0.1 mmol), phenothiazine catalyst (1.0 μmmol)), Acetone (1.8 mL), and H_2O (0.2 mL) were added into a 4 mL borosilicate vial. After bubbled with Ar for 5 min, the resulting solution was stirred at room temperature under blue LED irradiation for 2.5-6 h. The reaction mixture was added saturated Na_2SO_3 aq. and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography to give the desired product **3**.



3a

3,3,3-Trifluoro-1,1-diphenylpropan-1-ol (3a): Umemoto reagent **1** (35.8 mg, 0.105 mmol), 1,1-diphenylethelene **2a** (17.5 µL 0.1 mmol), **PTHS-1** (0.5 mg, 1.0 µmmol), Acetone (1.8 mL), and H_2O (0.2 mL) was used under irradiation with blue LED for 2.5 h. The residue was purified by column chromatography on silica gel (hexane to hexane/EtOAc = 10:1) to give the desired product **3a** (21.0 mg, 79%) as a light-yellow oil.

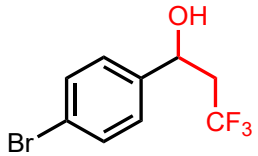
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43-7.42 (m, 4H), 7.35-7.33 (m, 4H), 7.28-7.25 (m, 2H), 3.21 (q, J = 10.2 Hz, 2H), 2.64 (d, J = 1.2 Hz, 1H).



3b

1-(4-Chlorophenyl)-3,3,3-trifluoropropan-1-ol (3b): Umemoto reagent **1** (35.8 mg, 0.105 mmol), 4-chlorostyrene **2b** (12.7 µL, 0.1 mmol), **PTHS-1** (0.5 mg, 1.0 µmmol)), Acetone (1.8 mL), and H_2O (0.2 mL) was used under irradiation with blue LED for 2.5 h. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1 to hexane/EtOAc = 10:1) to give the desired product **3b** (11.5 mg, 51%) as a color less oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.32 (m, 4H), 5.08 (d, J = 6.0 Hz, 1H), 2.66-2.56 (m, 1H), 2.47-2.39 (m, 1H), 2.15 (d, J = 2.0 Hz, 1H).

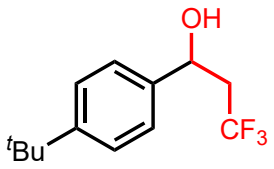


3c

1-(4-Bromophenyl)-3,3,3-trifluoropropan-1-ol (3c): Umemoto reagent **1** (35.8 mg, 0.105 mmol), 4-bromostyrene **2c** (13.5 µL, 0.1 mmol), **PTHS-1** (0.5 mg, 1.0 µmmol)), Acetone (1.8 mL), and H_2O (0.2 mL) was used under irradiation with blue LED for 2.5

h. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1 to hexane/EtOAc = 10:1) to give the desired product **3c** (18.5 mg, 69%) as a color less oil.

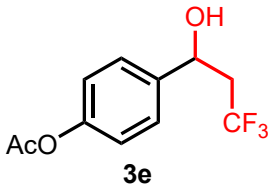
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 5.06 (d, J = 7.8 Hz, 1H), 2.65-2.56 (m, 1H), 2.46-2.38 (m, 1H), 2.19 (s, 1H).



3d

1-(4-(*tert*-Butyl)phenyl)-3,3,3-trifluoropropan-1-ol (3d): Umemoto reagent **1** (35.8 mg, 0.105 mmol), 4-*tert*-butylstyrene **2d** (17.8 µL, 0.1 mmol), **PTHS-1** (0.5 mg, 1.0 µmmol)), Acetone (1.8 mL), and H_2O (0.2 mL) was used under irradiation with blue LED for 6 h. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1 to hexane/EtOAc = 10:1) to give the desired product **3d** (16.7 mg, 68%) as a color less oil.

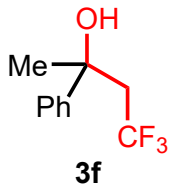
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 5.07 (dd, J = 9.6, 3.6 Hz, 1H), 2.69-2.60 (m, 1H), 2.49-2.41 (m, 1H), 2.07 (s, 1H), 1.32 (s, 9H).



3e

4-(3,3,3-Trifluoro-1-hydroxypropyl)phenyl acetate (3e): Umemoto reagent **1** (35.8 mg, 0.105 mmol), 4-vinylphenyl acetate **2e** (15.2 µL, 0.1 mmol), **PTHS-1** (0.5 mg, 1.0 µmmol)), Acetone (1.8 mL), and H_2O (0.2 mL) was used under irradiation with blue LED for 6 h. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1 to hexane/EtOAc = 4:1) to give the desired product **3e** (18.0 mg, 73%) as a color less oil.

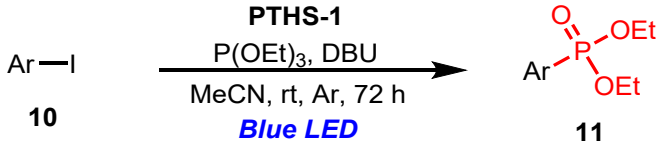
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 5.09 (dd, J = 9.0, 3.0 Hz, 1H), 2.66-2.57 (m, 1H), 2.48-2.40 (m, 1H), 2.31 (s, 3H), 2.20 (s, 1H).

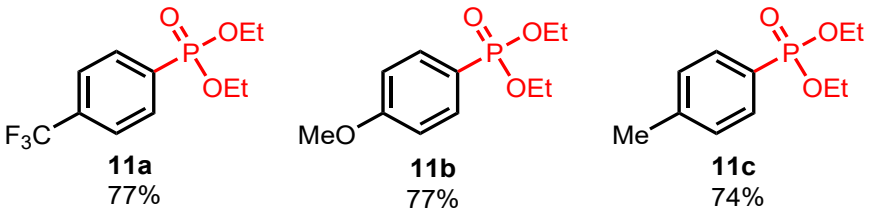


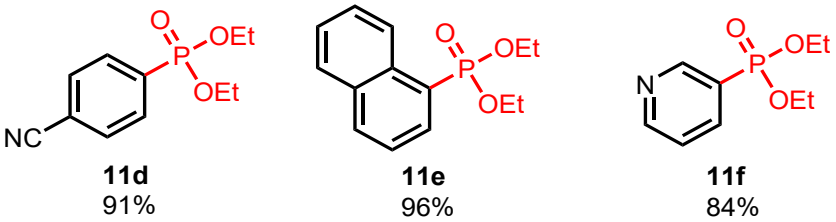
3f

4,4,4-Trifluoro-2-phenylbutan-2-ol (3d): Umemoto reagent **1** (35.8 mg, 0.105 mmol), α-methylstyrene **2f** (13.0 µL, 0.1 mmol), **PTHS-1** (0.5 mg, 1.0 µmmol)), Acetone (1.8 mL), and H_2O (0.2 mL) was used under irradiation with blue LED for 2.5 h. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1 to hexane/EtOAc = 10:1) to give the desired product **3f** (12.2 mg, 60%) as a color less oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47 (dd, J = 7.8, 1.2 Hz, 2H), 7.37 (t, J = 7.8 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 2.72-2.59 (m, 2H), 2.16 (s, 1H), 1.72 (s, 3H).

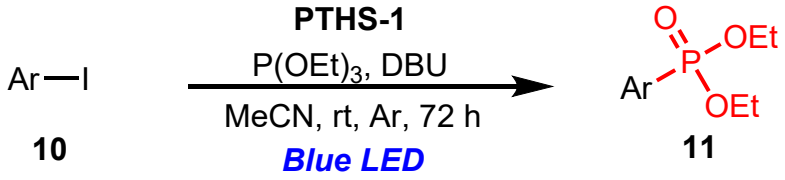
Scope and limitation of photoredox cross-coupling reaction of aryl iodides with triethylphophite



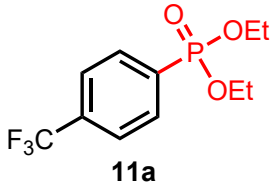




General procedure for photoredox cross-coupling reaction of aryl iodides with triethylphophite[9]



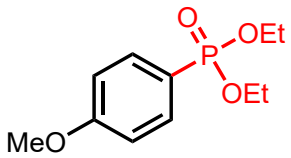
Aryl iodide **10** (0.1 mmol), **t**riethyl phosphite (50 µL, 0.3 mmol), DBU (30 µL, 0.2 mmol), **PTHS-1** (1.0 µmol), and MeCN (1.0 mL) were added into a 4 mL borosilicate vial. After bubbled with Ar for 5 min at 0 ºC, the resulting solution was stirred at room temperature under blue LED irradiation for 72 h. The reaction mixture was added H_2O and extracted with EtOAc. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography to give the product **11**.



11a

Diethyl (4-(trifluoromethyl)phenyl)phosphonate (11a): 4-Iodobenzotrifluoride **10a** (14.5 μL, 0.1 mmol), **t**riethyl phosphite (50 μL, 0.3 mmol), DBU (30 μL, 0.2 mmol), **PTHS-1** (4.7 mg, 10 μmol), and MeCN (1.0 mL) was used under irradiation with Blue LED for 72 h. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 10:1 to hexane/EtOAc = 1:1) to give the desired product **11a** (21.8 mg, 77%) as a light-yellow oil.

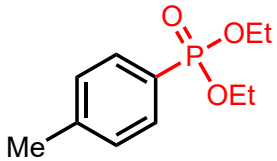
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (dd, J = 12.6, 7.8 Hz, 2H), 7.73 (dd, J = 7.8, 3.6 Hz, 2H), 4.21-4.07 (m, 4H), 1.33 (t, J = 7.2 Hz, 6H).



11b

Diethyl (4-methoxyphenyl)phosphonate (11b): 4-Iodoanisole **10b** (23.4 mg, 0.1 mmol), **t**riethyl phosphite (50 μL, 0.3 mmol), DBU (30 μL, 0.2 mmol), **PTHS-1** (4.7 mg, 10 μmol), and MeCN (1.0 mL) was used under irradiation with blue LED for 72 h. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 10:1 to EtOAc) to give the desired product **11b** (18.9 mg, 77%) as a color less oil.

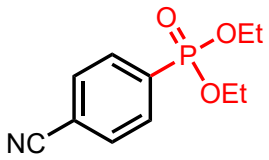
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 12.4, 8.8 Hz, 2H), 6.96 (dd, J = 8.8, 4.8 Hz, 2H), 4.16-3.99 (m, 4H), 3.84 (s, 3H), 1.30 (t, J = 7.2 Hz, 6H).



11c

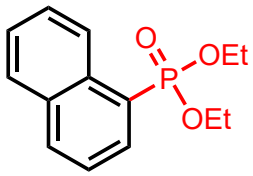
Diethyl *p*-tolylphosphonate (11c): 4-Iodotoluene **10c** (21.8 mg, 0.1 mmol), **t**riethyl phosphite (50 μL, 0.3 mmol), DBU (30 μL, 0.2 mmol), **PTHS-1** (4.7 mg, 10 μmol), and MeCN (1.0 mL) was used under irradiation with blue LED for 72 h. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1 to hexane/EtOAc = 1:2) to give the desired product **11c** (16.9 mg, 74%) as a color less oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (dd, J = 13.2, 8.4 Hz, 2H), 7.27 (dd, J = 8.4, 4.2 Hz, 2H), 4.16-4.02 (m, 4H), 2.40 (s, 3H), 1.31 (t, J = 7.2 Hz, 6H).



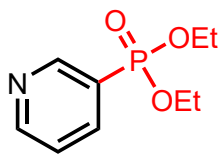
11d

Diethyl (4-cyanophenyl)phosphonate (11d): 4-Iodobenzonitrile **10d** (22.9 mg, 0.1 mmol), **t**riethyl phosphite (50 µL, 0.3 mmol), DBU (30 µL, 0.2 mmol), **PTHS-1** (4.7 mg, 10 µmol), and MeCN (1.0 mL) was used under irradiation with blue LEDs for 72 h. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1 to hexane/EtOAc = 1:2) to give the desired product **11d** (21.7 mg, 91%) as a color less oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, J = 13.2, 8.4 Hz, 2H), 7.77-7.73 (m, 2H), 4.23-4.06 (m, 4H), 1.33 (t, J = 7.0 Hz, 6H).



11e

Diethyl naphthalen-1-ylphosphonate (11e): 1-Iodonaphthalene **10e** (14.6 µL, 0.1 mmol), **t**riethyl phosphite (50 µL, 0.3 mmol), DBU (30 µL, 0.2 mmol), **PTHS-1** (4.7 mg, 10 µmol), and MeCN (1.0 mL) was used under irradiation with blue LED for 72 h. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1 to hexane/EtOAc = 1:1) to give the desired product **11e** (25.3 mg, 96%) as a color less oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.52 (d, J = 8.4 Hz, 1H), 8.25 (ddd, J = 16.8, 7.2, 1.2 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.62-7.60 (m, 1H), 7.57-7.52 (m, 2H), 4.24-4.18 (m, 2H), 4.13-4.04 (m, 2H), 1.31 (t, J = 7.2 Hz, 6H).

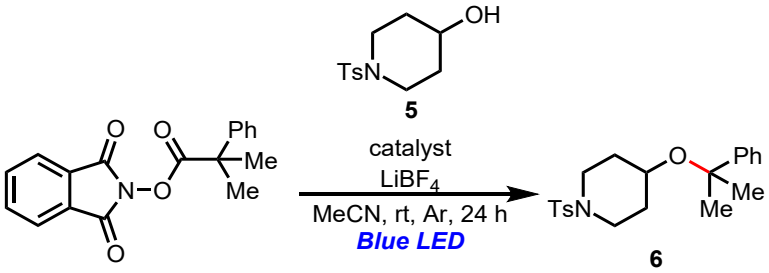


11f

Diethyl pyridin-3-ylphosphonate (11f): 3-Iodopyridine **10f** (20.5 mg, 0.1 mmol), **t**riethyl phosphite (50 µL, 0.3 mmol), DBU (30 µL, 0.2 mmol), **PTHS-1** (4.7 mg, 10 µmol), and MeCN (1.0 mL) was used under irradiation with blue LED for 72 h. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1 to

EtOAc) to give the desired product **11f** (18.1 mg, 84%) as a light-yellow oil.
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.97 (dd, J = 6.0, 1.2 Hz, 1H), 8.78-8.76 (m, 1H), 8.10 (ddt, J = 13.2, 7.8, 1.8 Hz, 1H), 7.42-7.39 (m, 1H), 4.22-4.09 (m, 4H), 1.34 (t, J = 6.9 Hz, 6H).

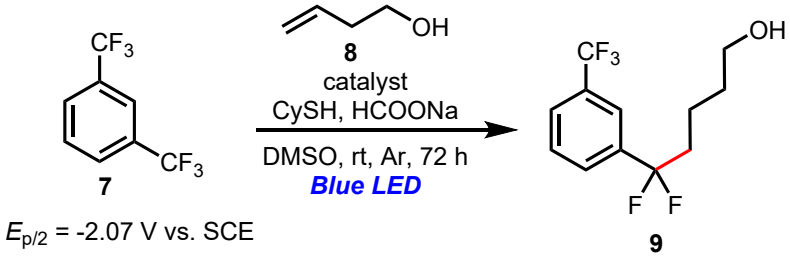
General procedure for decarboxylative C(sp^3)−O bond formation[5]



$E_{p/2}$ = -1.06 V vs. SCE

Ester **4** (61.9 mg, 0.2 mmol), alcohol **5** (153.2 mg, 0.6 mmol), phenothiazine catalyst (10 mol%), $LiBF_4$ (1.9 mg, 10 mol%), and MeCN (1.0 mL) were added into a 4 mL borosilicate vial. After bubbled with Ar for 5 min, the resulting solution was stirred at room temperature under blue LED irradiation for 24 h.[6,7] The reaction mixture was filtered through with a short plug of silica gel using diethyl ether and the residue was concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/EtOAc = 20:1 to 10:1) to give the desired product **6** as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 7.2 Hz, 2H), 7.31-7.21 (m, 5H), 3.40- 3.34 (m, 2H), 3.20-3.14 (m, 1H), 2.56 (td, J = 10.4, 3.2 Hz, 2H), 2.43 (s, 3H), 1.72-1.58 (m, 4H), 1.49 (s, 6H).

General procedure for defluoroalkylation of 1,3-bis(trifluoromethyl)benzene[8]



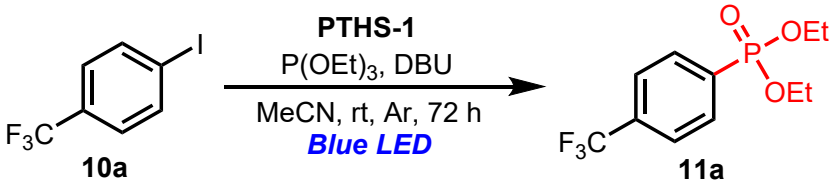
$E_{p/2}$ = -2.07 V vs. SCE

1,3-Bis(trifluoromethyl)benzene **7** (15.3 µL, 0.1 mmol), 3-butene-1-ol **8** (25.5 µL, 0.3 mmol), phenothiazine catalyst (10 mol%), sodium formate (20.4 mg, 0.3 mmol), and DMSO (1.0 mL) were added into a 4 mL borosilicate vial followed by cyclohexane thiol (1.2 µL, 0.01 mmol). The solution was bubbled with Ar for 5 min and stirred at room temperature under blue LED irradiation for 72 h. The reaction mixture was diluted with

saturated Na_2SO_3 aq. and extracted with EtOAc. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/EtOAc = 6:1 to 4:1) to give the product **9** as a colorless oil.

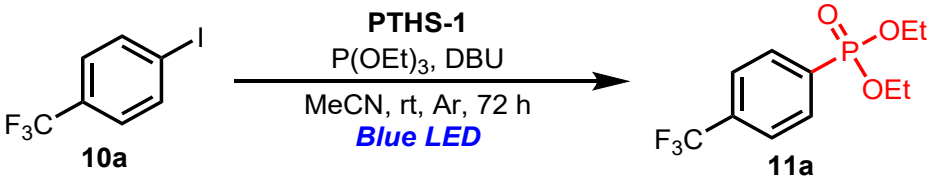
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (s, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.56 (t, J = 7.8 Hz, 1H), 3.65 (t, J = 6.3 Hz, 2H), 2.21-2.13 (m, 2H), 1.63-1.59 (m, 2H), 1.56-1.51 (m, 2H), 1.25 (s, 1H).

Procedure for recycling performance of PTHS-1[9]



(Run 1) According to the general procedure for photoredox cross-coupling of 4-trifluoroiodobenzene with triethylphosphite, 4-iodotrifluromethylbenzene **10a** (14.5 μL, 0.1 mmol), triethyl phosphite (50 μL, 0.3 mmol), DBU (30 μL, 0.2 mmol), **PTHS-1** (4.7 mg, 0.01 mmol), and MeCN (1.0 mL) was used under irradiation with blue LED for 72 h. The reaction mixture was added H_2O and extracted with EtOAc. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1 to EtOAc) to give the desired product **11a** (21.8 mg, 77%) as a light-yellow oil. Run 2-4 were carried out with the same procedure with recovered catalyst. The reactions with **PTH-1** were also carried out the same procedure.

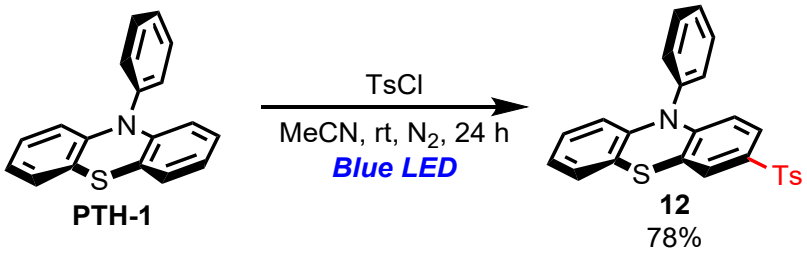
Gram scale condition of photoredox cross-coupling reaction of 4-trifluoromethylbenzene with triethylphophite[9]



4-Iodotrifluromethylbenzene **10** (0.72 mL, 5.0 mmol), triethyl phosphite (2.57 mL, 15.0 mmol), DBU (1.49 mL, 10.0 mmol), **PTHS-1** (236.9 mg, 10 mol%), and MeCN (50.0 mL) were added into a 200 mL 3 neck flask. After bubbled with Ar for 5 min at 0 ºC, the resulting solution was stirred at room temperature under blue LED irradiation for 72 h. The reaction mixture was added H_2O and extracted with EtOAc. The organic layer was

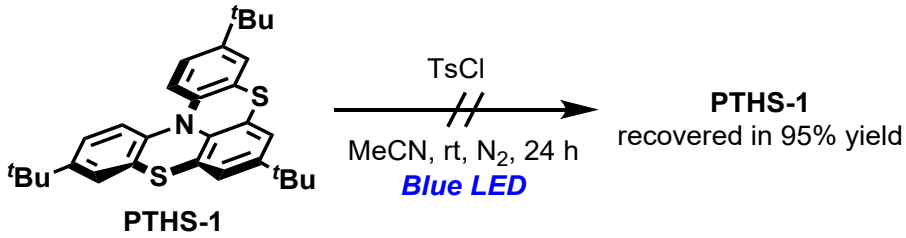
dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/EtOAc = 100:1 to 1:1) to give the product **11** (1.194 g, 85%) as a light-yellow oil and recover **PTHS-1** (228.4 mg, 96%) as a yellow solid.

Photochemical sulfonylation of phenothiazines[10]



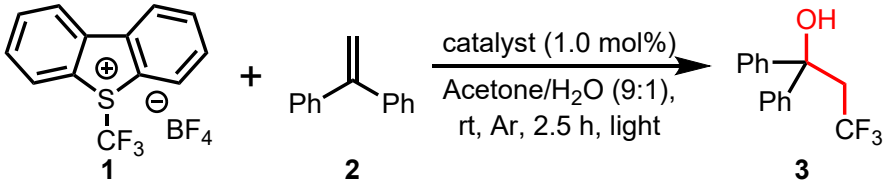
PTH-1 (55.1 mg, 0.2 mmol) and tosyl chloride (38.1 mg, 0.2 mmol) were added into a 4 mL borosilicate vial. After bubbled with N_2 for 5 min, MeCN (1.0 mL) was added to the mixture via syringe. The resulting solution was irradiated with blue LED and stirred at room temperature for 24 h. The mixture was concentrated in vacuo and purified by flash column chromatography (hexane/EtOAc = 100:1 to 4:1) to give the product **12** (67.3 mg, 78%) as a yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 8.4 Hz, 2H), 7.62 (t, J = 7.8 Hz, 2H), 7.52 (t, J = 7.8 Hz, 1H), 7.47 (d, J = 1.8 Hz, 1H), 7.33-7.31 (m, 3H), 7.27-7.26 (m, 2H), 6.96-6.94 (m, 1H), 6.84-6.80 (m, 2H), 6.12-6.09 (m, 2H), 2.38 (s, 3H)



PTHS-1 (94.7 mg, 0.2 mmol) and tosyl chloride (38.1 mg, 0.2 mmol) were added into a 4 mL borosilicate vial. After bubbled with N_2 for 5 min, MeCN (1.0 mL) was added to the mixture via a syringe. The resulting solution was irradiated with blue LED and stirred at room temperature for 24 h. The mixture was concentrated in vacuo and purified by flash column chromatography (hexane/EtOAc = 100:1) to recover **PTHS-1** (89.5 mg, 95%) as a yellow solid.

Blank experiments of three-component oxytrifluoromethylation of 1,1-diphenylethylene[a]



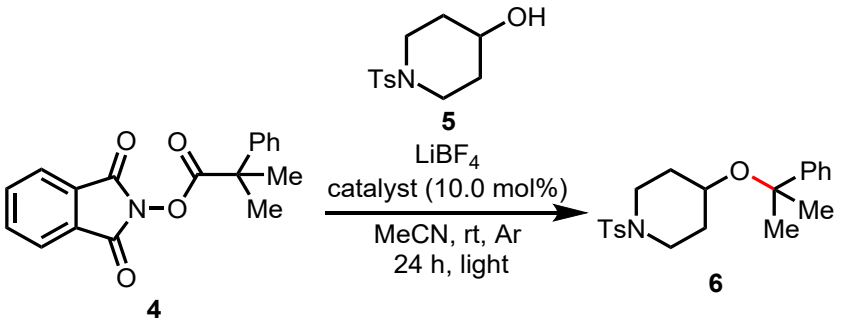
1 2 3

$E_{p/2}$ = -0.25 V vs. SCE

entry	catalyst	light	yield (%)
1	PTHS-1	Blue LED	79
2	/	Blue LED	trace
3	PTHS-1	/	trace

[a] All reactions were carried out with **1** (0.105 mmol), **2** (0.1 mmol) in acetone/H_2O (9:1) at room temperature under Ar atmosphere.

Blank experiments of decarboxylative C(sp^3)−O bond formation[a]

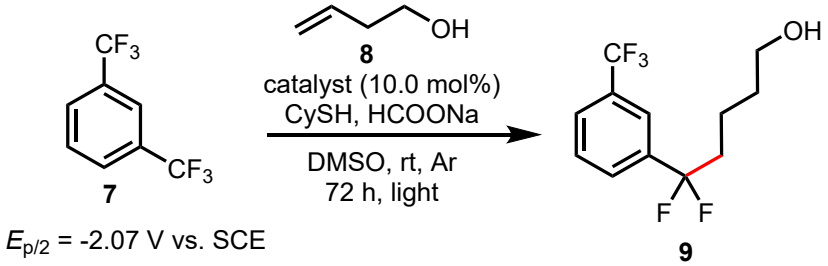


$E_{p/2}$ = -1.06 V vs. SCE

entry	catalyst	light	yield (%)
1	PTHS-1	Blue LED	60
2	/	Blue LED	0
3	PTHS-1	/	0

[a] All reactions were carried out with **4** (0.2 mmol), **5** (0.6 mmol), $LiBF_4$ (10 mol%) in MeCN at room temperature under Ar atmosphere.

Blank experiments of defluoroalkylation of 1,3-bis(trifluoromethyl)benzene[a]



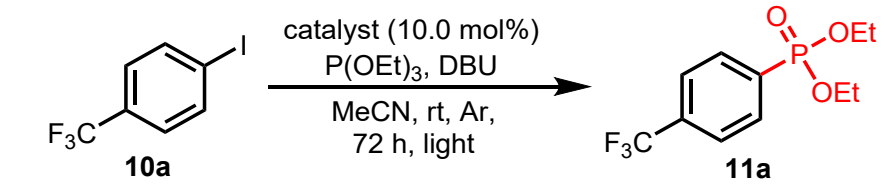
7 9

$E_{p/2}$ = -2.07 V vs. SCE

entry	catalyst	light	yield (%)
1	PTHS-1	Blue LED	83
2	/	Blue LED	0
3	PTHS-1	/	0

[a] All reactions were carried out with **7** (0.1 mmol), **8** (0.3 mmol), cyclohexane thiol (10 mol%), sodium formate (0.3 mmol) in DMSO at room temperature under Ar atmosphere.

Blank experiments of photoredox cross-coupling reaction of 4-trifluoromethyliodobenzene with triethylphophite[a]

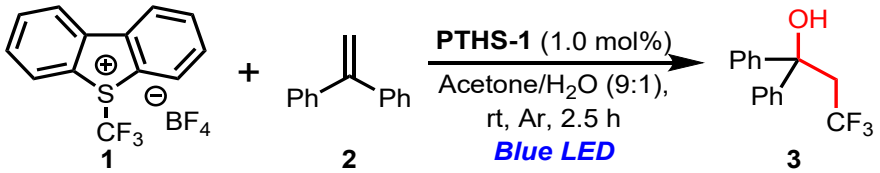


$E_{p/2}$ = -2.16 V vs. SCE

entry	catalyst	light	yield (%)
1	PTHS-1	Blue LED	77
2	/	Blue LED	trace
3	PTHS-1	/	0

[a] All reactions were carried out with **10a** (0.1 mmol), triethylphosphite (0.3 mmol), DBU (0.2 mmol) in MeCN at room temperature under Ar atmosphere.

Examination of catalyst amount



entry	PTHS-1	yield (%)
1	0.1 mol%	48%
2	1.0 mol%	79%

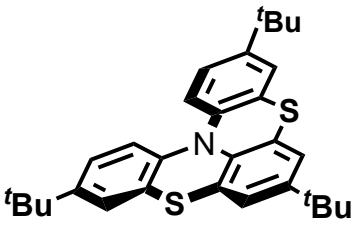
[a] All reactions were carried out with **1** (0.105 mmol), **2** (0.1 mmol), and PTHS-1 catalyst in acetone/H_2O (9:1, v/v) at room temperature under an Ar atmosphere and blue-light irradiation (λ_{max} = 425 nm, 18 W).

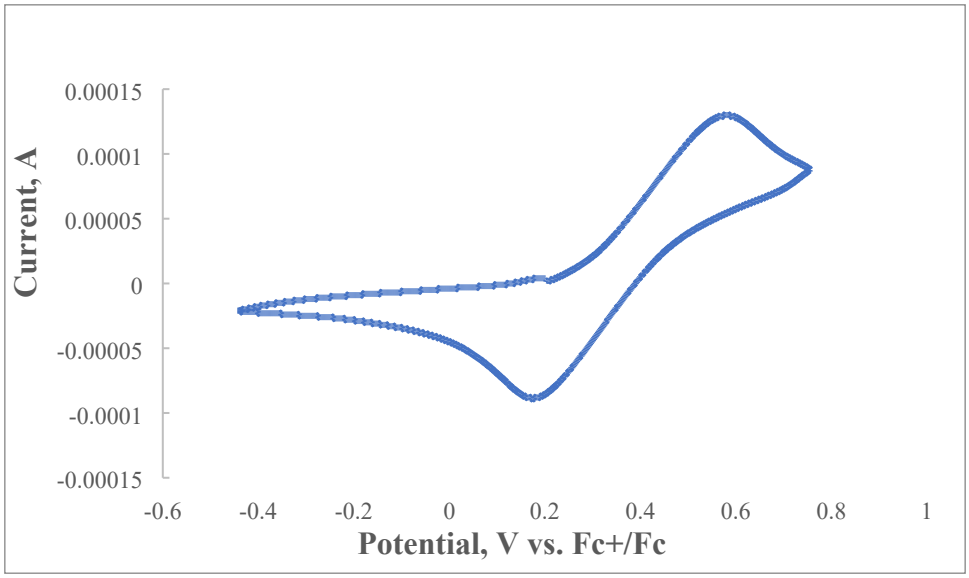
3. Photophysical and redox properties of phenothiazine catalysts and ester

The samples for the electrochemical measurements were prepared with 10 mL of a 0.1 M tetrabutylammonium perchlorate solution in dry CH_2Cl_2 or dry MeCN and 0.1 mmol of substrates. Cyclic voltammetry measurements were carried out with a computer-controlled potentiostat (ECstat-101, EC FRONTIER CO., LTD). Cyclic voltammetry was recorded using an undivided cell equipped with a working electrode (Pt disk electrode, φ 3mm), a counter electrode (Pt wire), and a reference electrode (Ag wire). The ferrocene/ ferrocenium couple (Fc/Fc^+) was also measured in the same electrochemical system, and the electrode potential was reported as values referred to the apparent standard potential of the system. The referenced value was converted to SCE by adding 0.48 V (in CH_2Cl_2) or 0.38 V (in MeCN).[11] A scan rate was used 0.1 V/s.

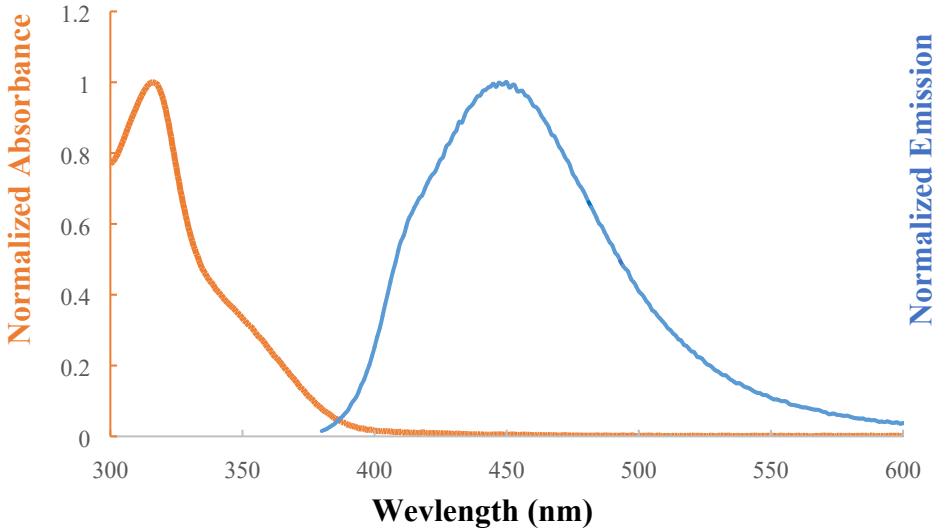
Samples for photophysical measurements were prepared using high purity chloroform. Solutions of the catalysts were diluted to a concentration of 10 μM and a total volume of 10.0 mL before being transferred to a 3.5 mL quartz cell.

Excited-state oxidation potentials ($E_{1/2}$ ($C^{\bullet+}/C^*$)) were calculated by subtracting the ground-state oxidation potential ($E_{1/2}$ ($C^{\bullet+}/C$)), obtained by cyclic voltammetry, from the excitation energy ($E_{0,0}$); $E_{0,0}$ is determined by calculating the energy of the wavelength at which the substrate's UV-Vis absorption and emission spectra overlap.





$E_{1/2}$ ($C^{\bullet+}$/C) = +0.38 V vs. Fc/Fc^{+} (+0.86 V vs. SCE) in CH_2Cl_2

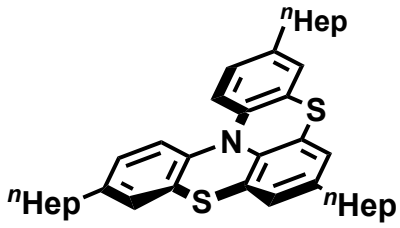


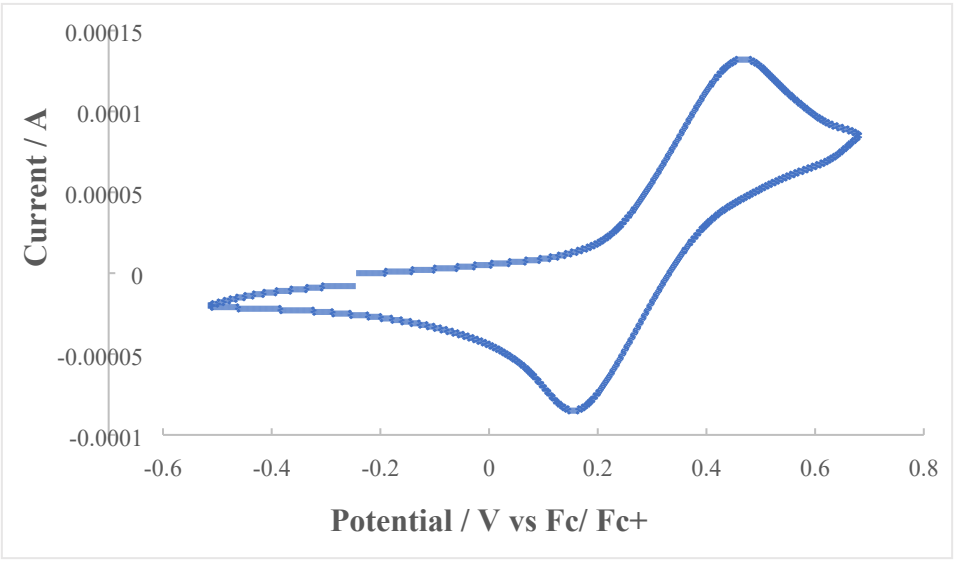
$$E_{0,0} = \frac{1240\ nm \cdot eV}{387\ nm} = 3.20\ \text{eV}$$

$$E_{1/2}(C^{\bullet+}/C^{*}) = E_{1/2}(C^{\bullet+}/C) - E_{0,0}$$

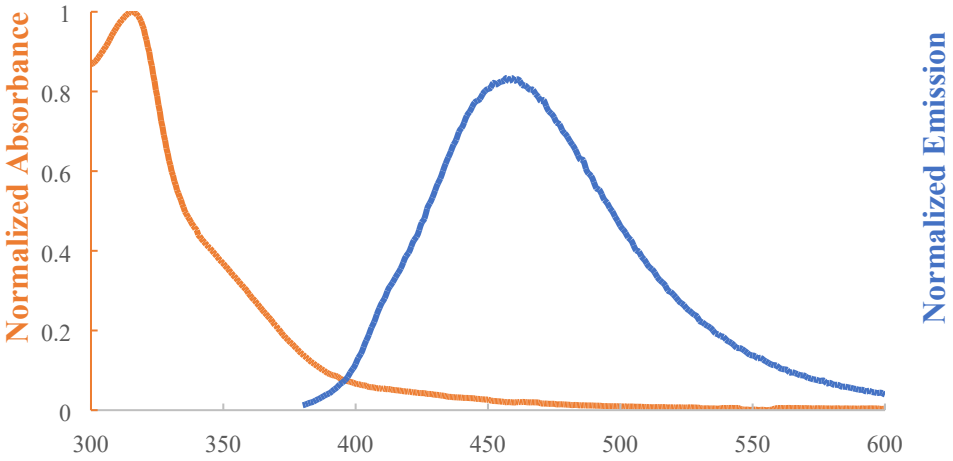
$$= +0.86\ \text{V} - 3.20\ \text{V}$$

$$= -2.34\ \text{V vs. SCE in } CH_2Cl_2$$





$E_{1/2}$ ($C^{\bullet+}$/C) = +0.32 V vs. Fc/Fc^{+} (+0.80 V vs. SCE) in CH_2Cl_2

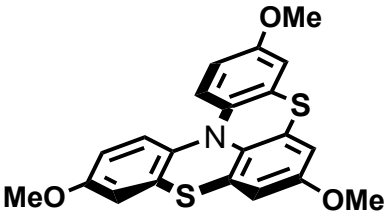


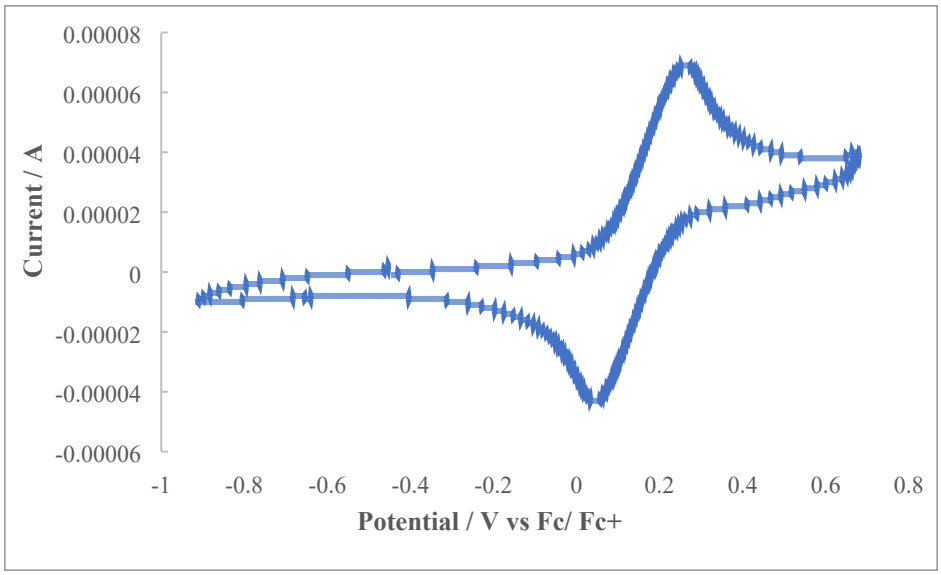
$$E_{0,0} = \frac{1240\ nm \cdot eV}{394\ nm} = 3.15\ \text{eV}$$

$$E_{1/2}(C^{\bullet+}/C^{*}) = E_{1/2}(C^{\bullet+}/C) - E_{0,0}$$

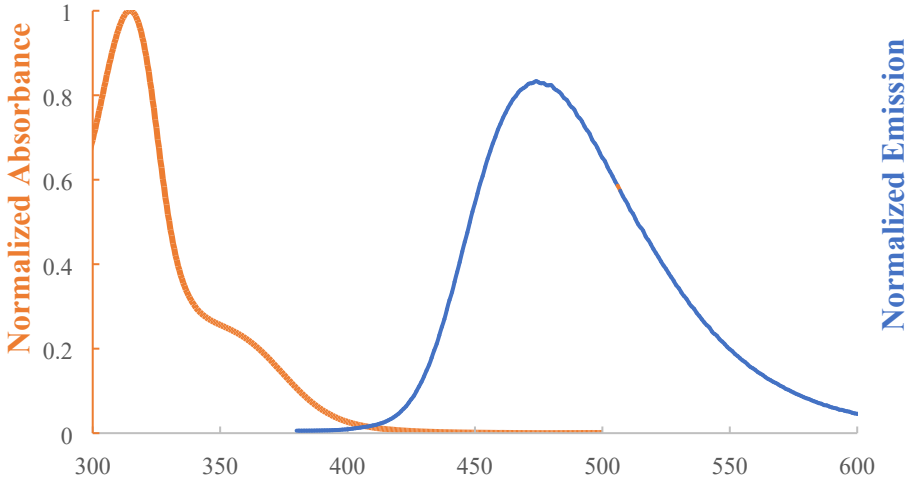
$$= +0.80\ \text{V} - 3.15\ \text{V}$$

$$= -2.35\ \text{V vs. SCE in } CH_2Cl_2$$





$E_{1/2}$ ($C^{\bullet+}$/C) = +0.16 V vs. Fc/Fc^+ (+0.64 V vs. SCE) in CH_2Cl_2

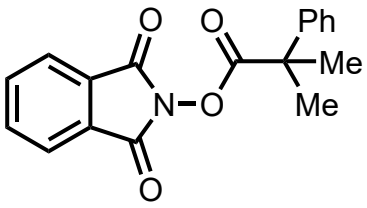


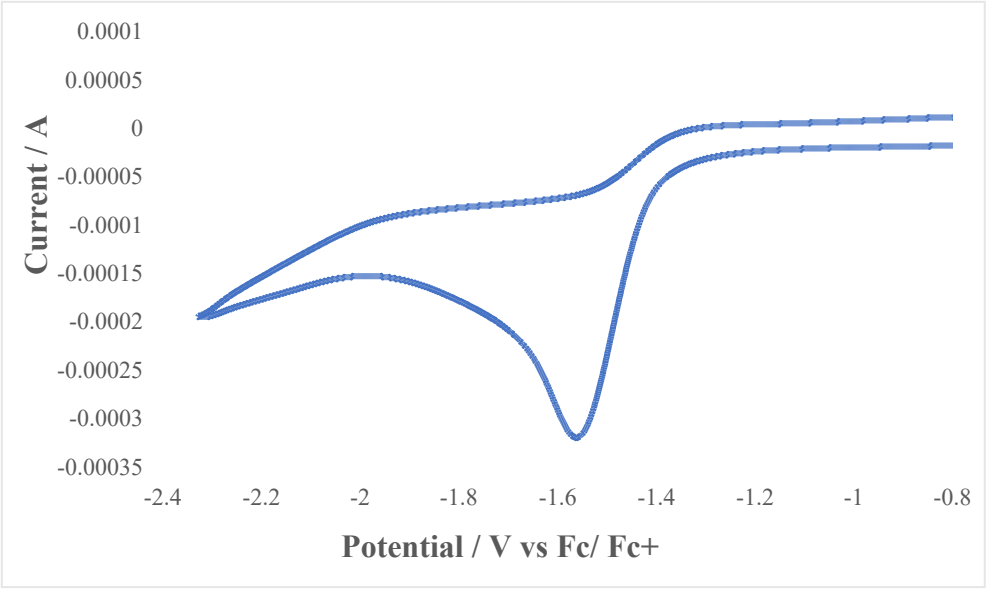
$$E_{0,0} = \frac{1240\ nm \cdot eV}{407\ nm} = 3.04\ \text{eV}$$

$$E_{1/2}(C^{\bullet+}/C^*) = E_{1/2}(C^{\bullet+}/C) - E_{0,0}$$

$$= +0.64\ \text{V} - 3.04\ \text{V}$$

$$= -2.40\ \text{V vs. SCE in } CH_2Cl_2$$



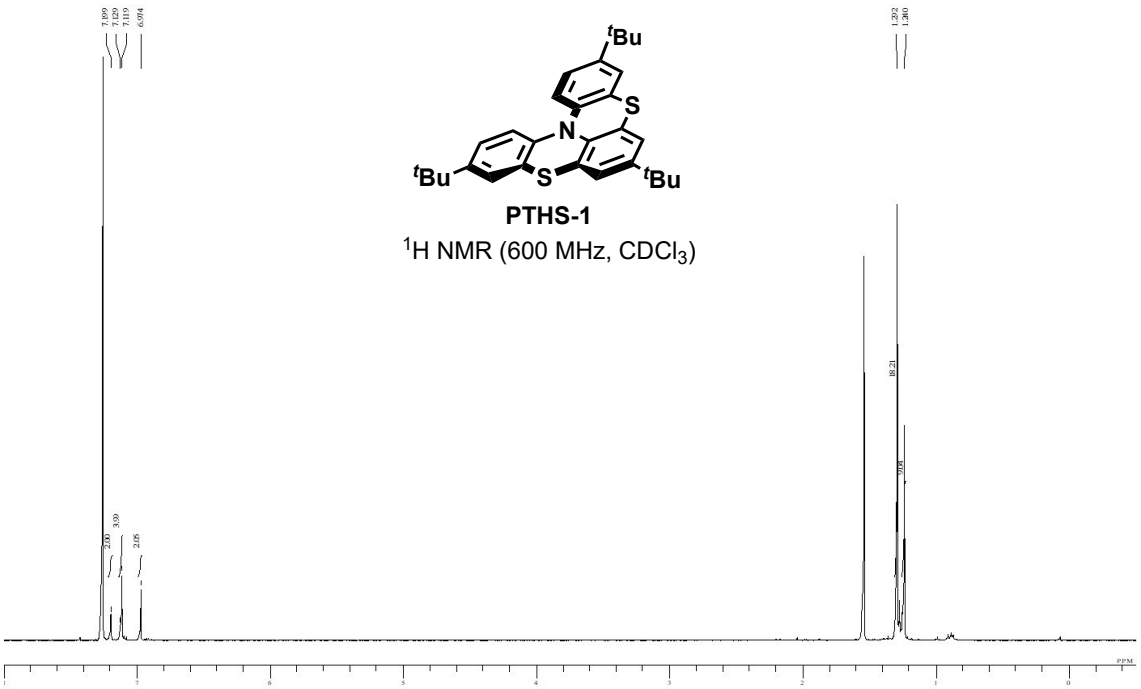


$E_{p/2}$ = -1.46 V vs Fc/Fc^+ (-1.08 V vs. SCE) in MeCN

4. Reference

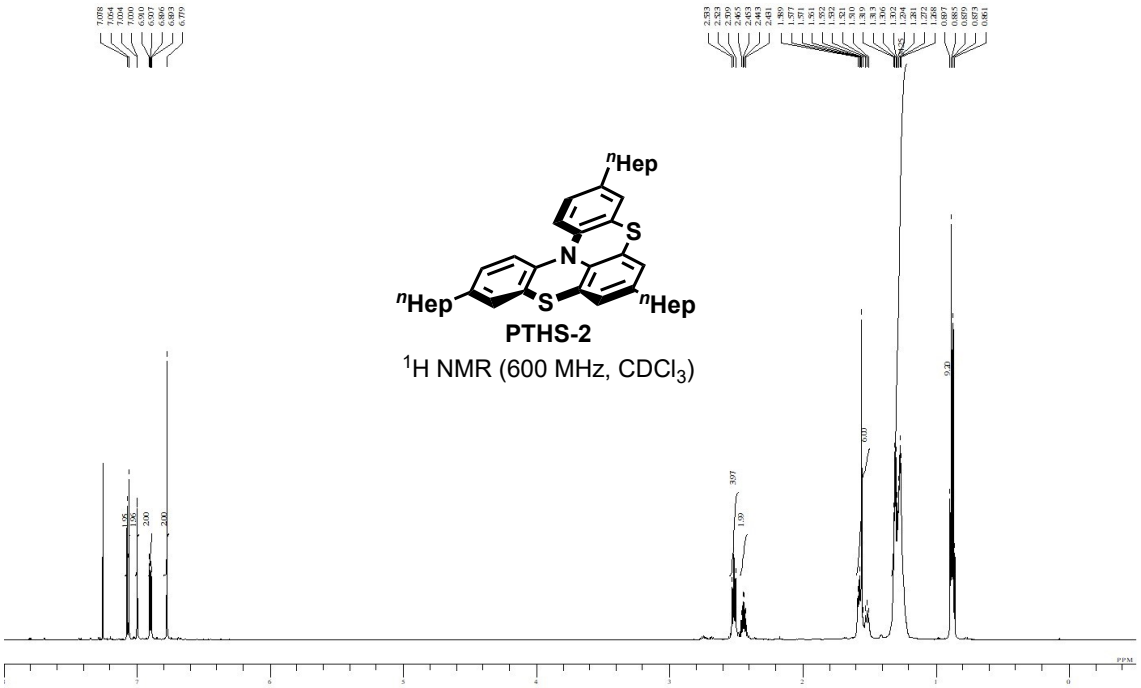
1. S. Chen, Z. Li, K. Hu, W. Feng, G. Mao, F. Xiao and G. Deng, *Org. Biomol. Chem*., 2023, **21**, 1920-1926.
2. G. Lamanna, C. Faggi, F. Gasparrini, A. Ciogli, C. Villani, P. J. Stephens, F. J. Devlin and S. Menichetti, *Chem. Eur. J*., 2008, **14**, 5747-5750.
3. Y. Liu, Y. Xu, Y, Zhang, W. Gao and X. Shao, *Org. Chem. Front.* 2022, **9**, 6490-6497.
4. Y. Yasu, T. Koike and M. Akita, *Angew. Chem. Int. Ed*., 2012, **51**, 9567-9571.
5. S. Shibutani, T. Kodo, M. Takeda, K. Nagao, N. Tokunaga, Y. Sasaki and H. Ohmiya, *J. Am. Chem. Soc*., 2020, **142**, 1211-1216.
6. C. Zheng, Y. Wang, Y. Xu, Z. Chen, G. Chen and S. H. Liang, *Org. Lett*., 2018, **20**, 4824-4827.
7. V. Soulard, G. Villa, D. P. Vollmar and P. Renaud, *J. Am. Chem. Soc*., 2018, **140**, 155-158.
8. H. Wang and N. T. Jui, *J. Am. Chem. Soc*., 2018, **140**, 163-166.
9. L. Pan, A. S. Kelley, M. V. Cooke, M. M. Deckert and S. Laulhe, *ACS Sustainable Chem. Eng*., 2022, **10**, 691-695.
10. J. Liu, H. Liu, X. Guo, Z. Wang, X. Wu, J. Li and C. Zhu, *Green Chem.,* 2023, **25**, 3847-3851.
11. G. C. Neil and E. G. William. *Chem. Rev.,* 1996, **96**, 877-910.

5. ^{1}H and ^{13}C NMR spectra data



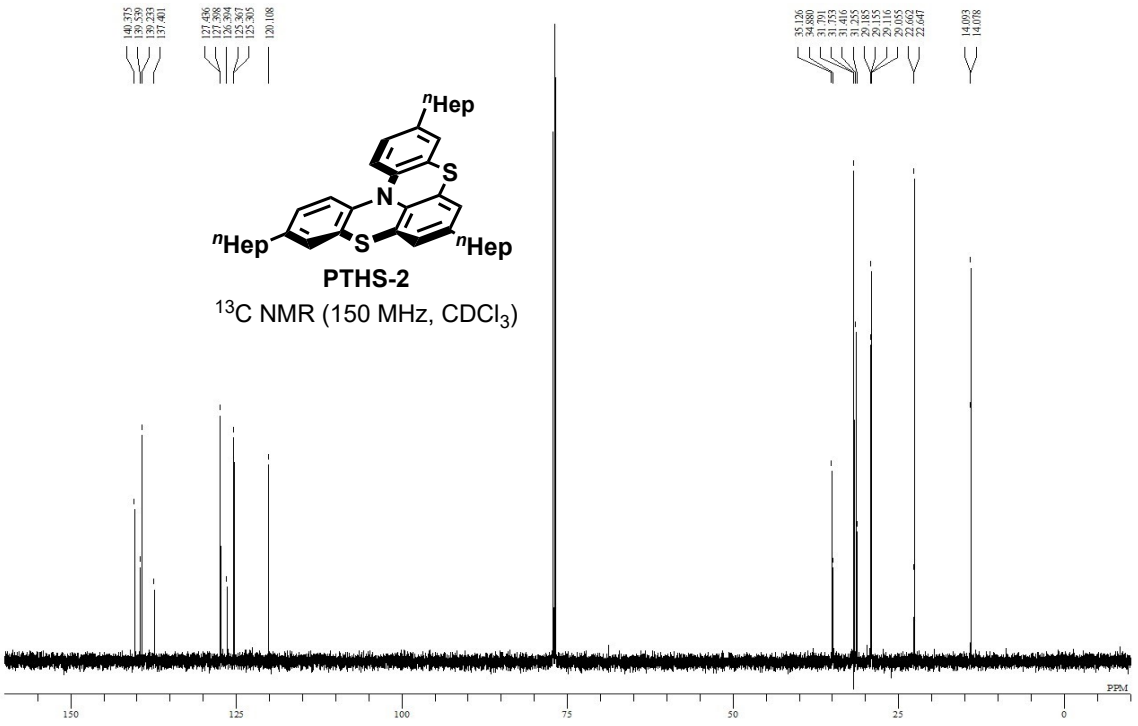
PTHS-1

^{1}H NMR (600 MHz, $CDCl_3$)



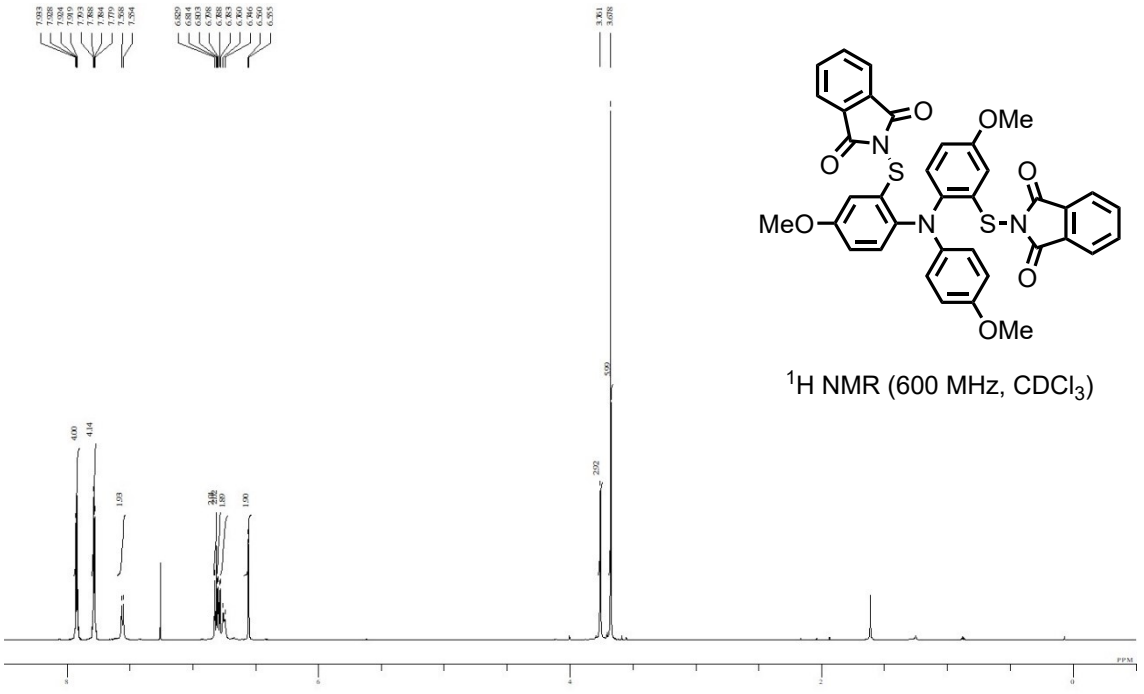
PTHS-2

^{1}H NMR (600 MHz, $CDCl_3$)

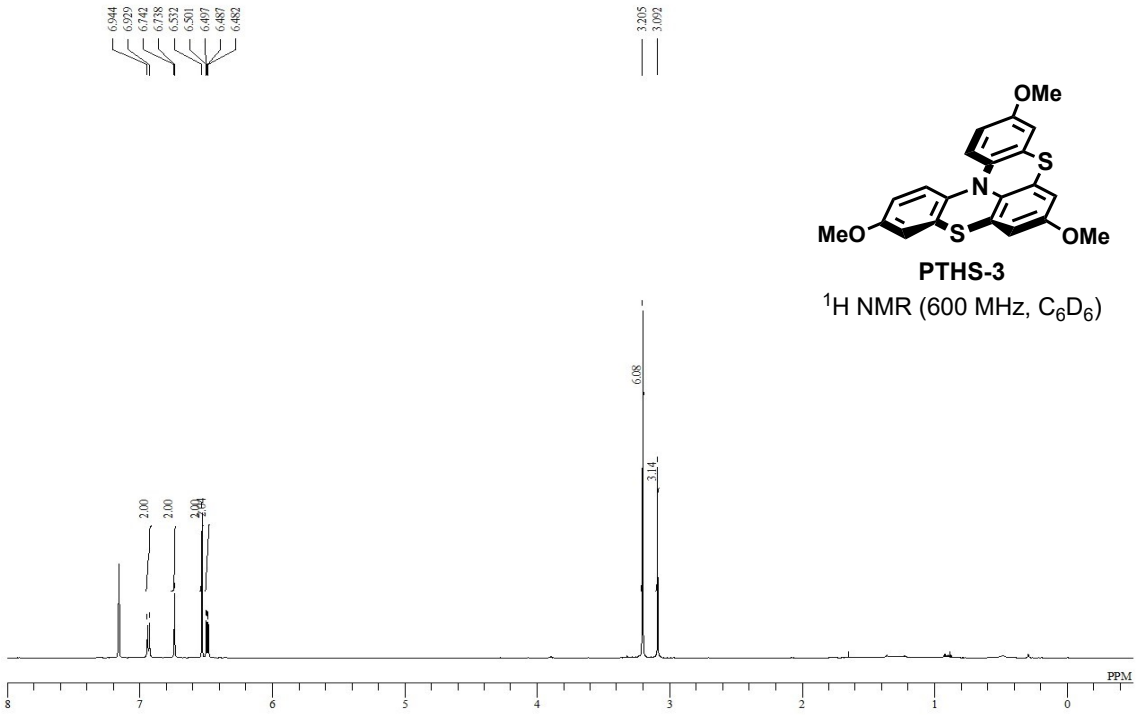


PTHS-2

^{13}C NMR (150 MHz, $CDCl_3$)

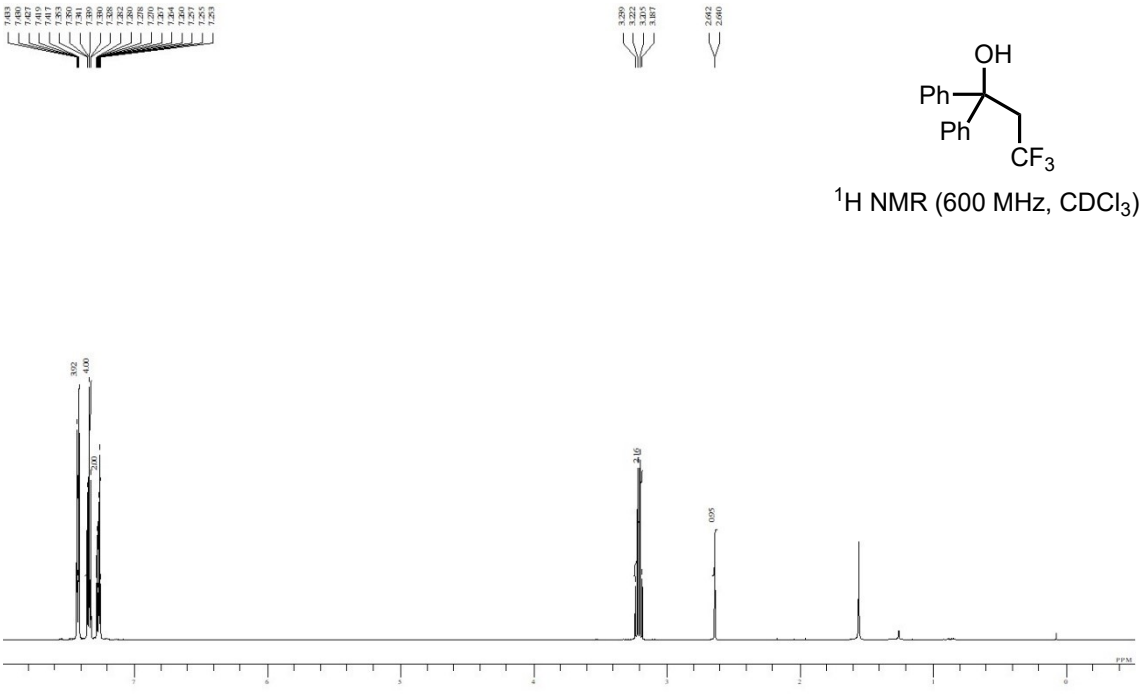


^{1}H NMR (600 MHz, $CDCl_3$)

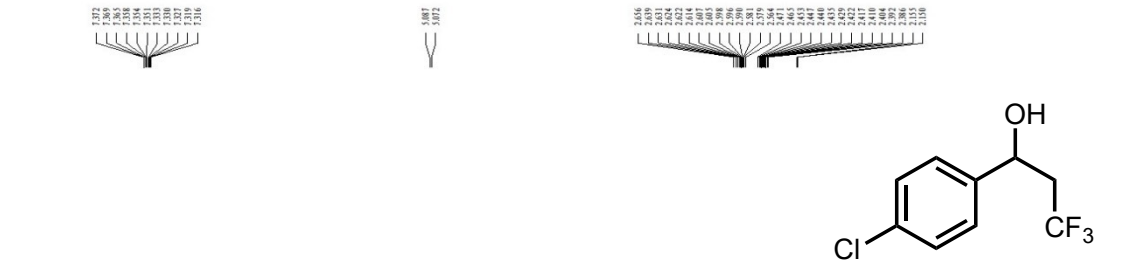


PTHS-3

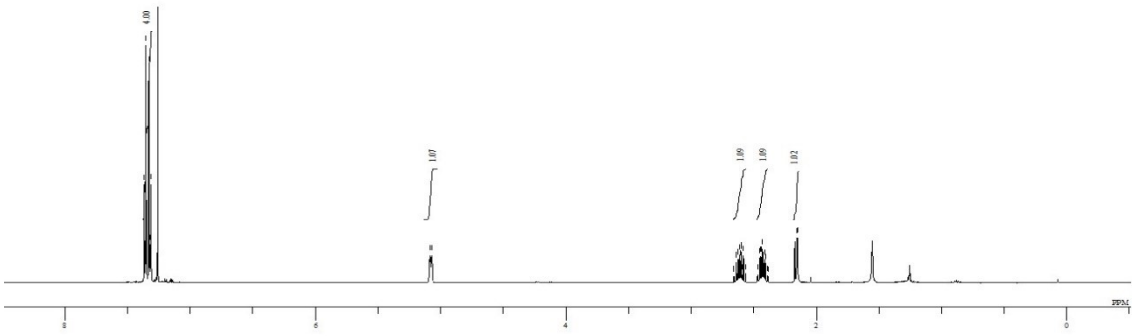
^{1}H NMR (600 MHz, C_6D_6)

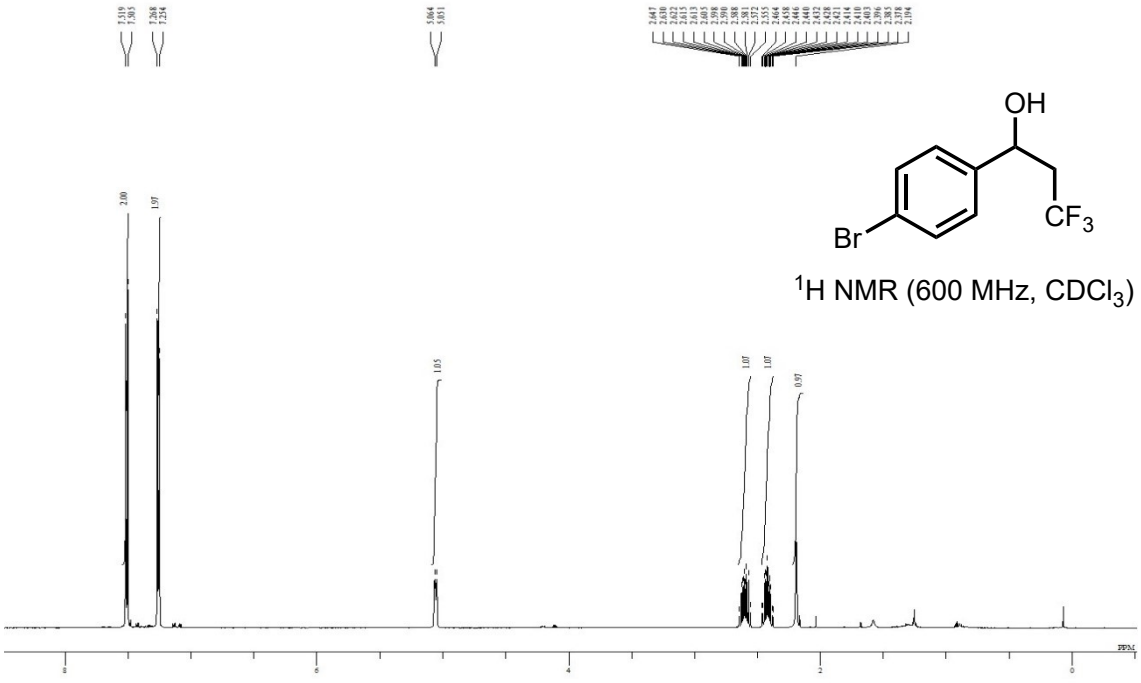


^{1}H NMR (600 MHz, $CDCl_3$)

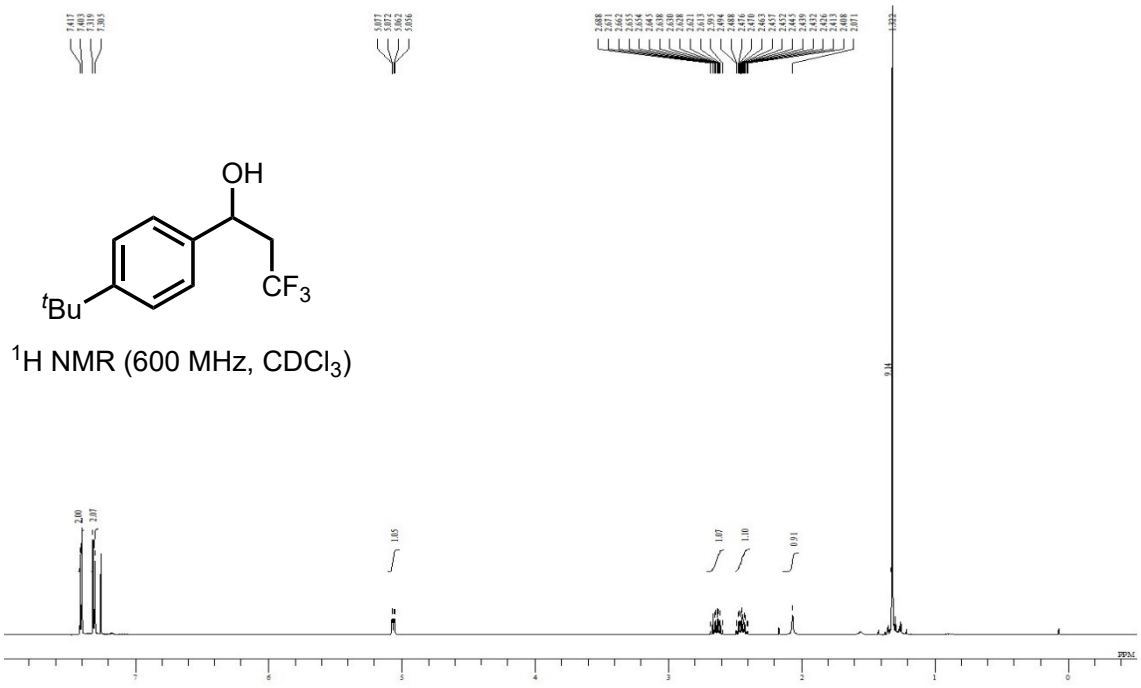


^{1}H NMR (400 MHz, $CDCl_3$)

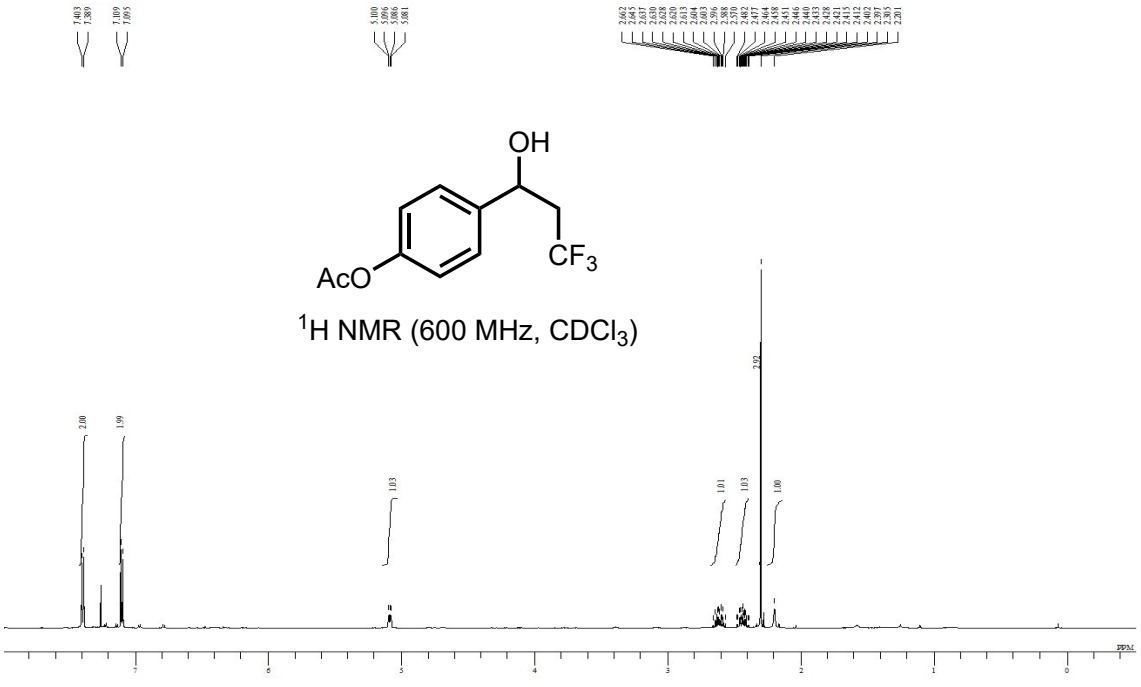




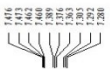
^{1}H NMR (600 MHz, $CDCl_3$)

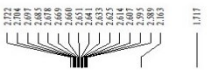


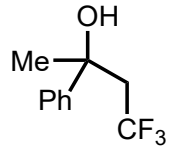
^{1}H NMR (600 MHz, $CDCl_3$)



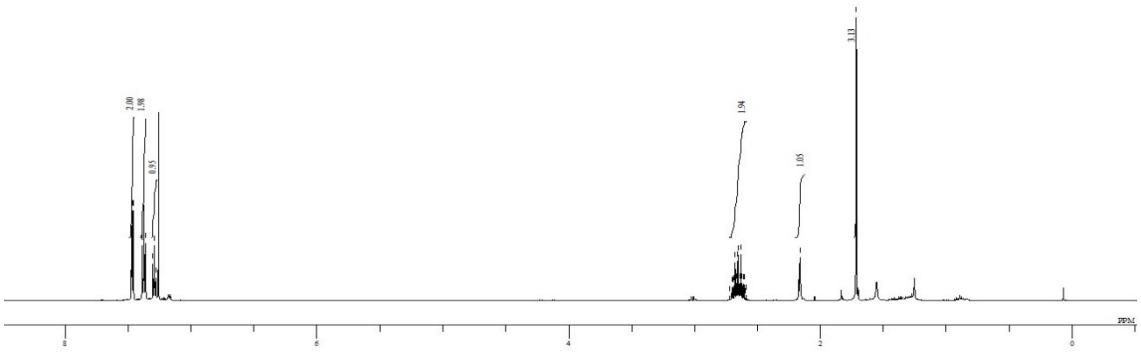
^{1}H NMR (600 MHz, $CDCl_3$)

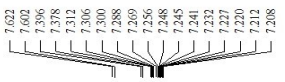


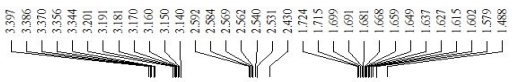


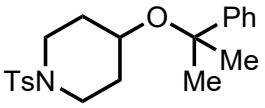


^{1}H NMR (600 MHz, $CDCl_3$)

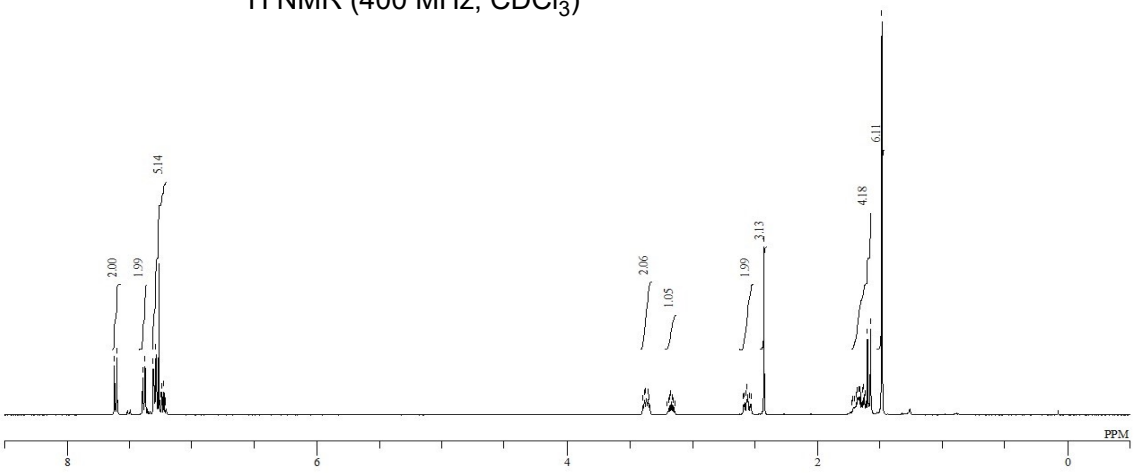


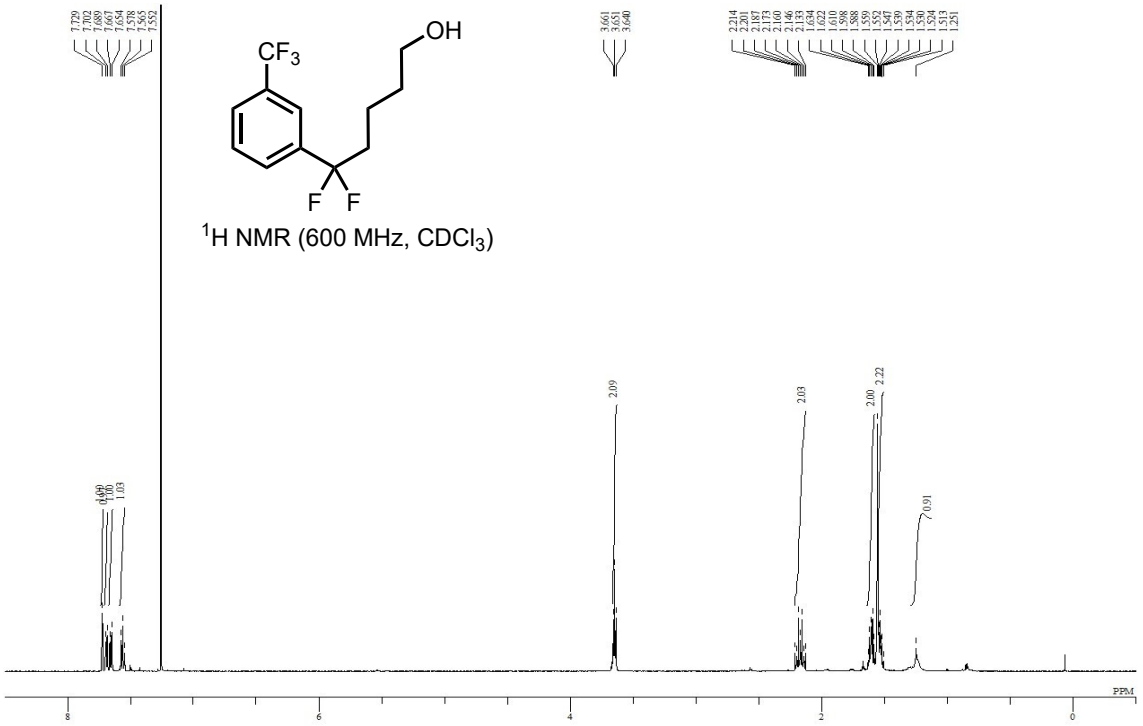




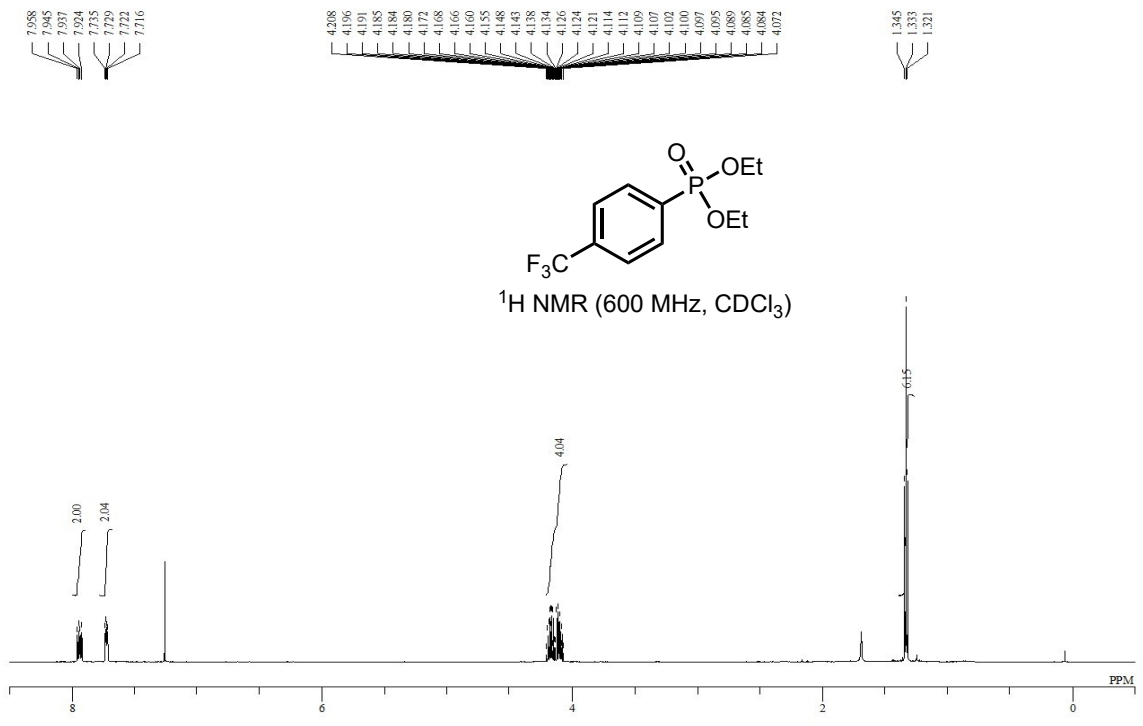


^{1}H NMR (400 MHz, $CDCl_3$)

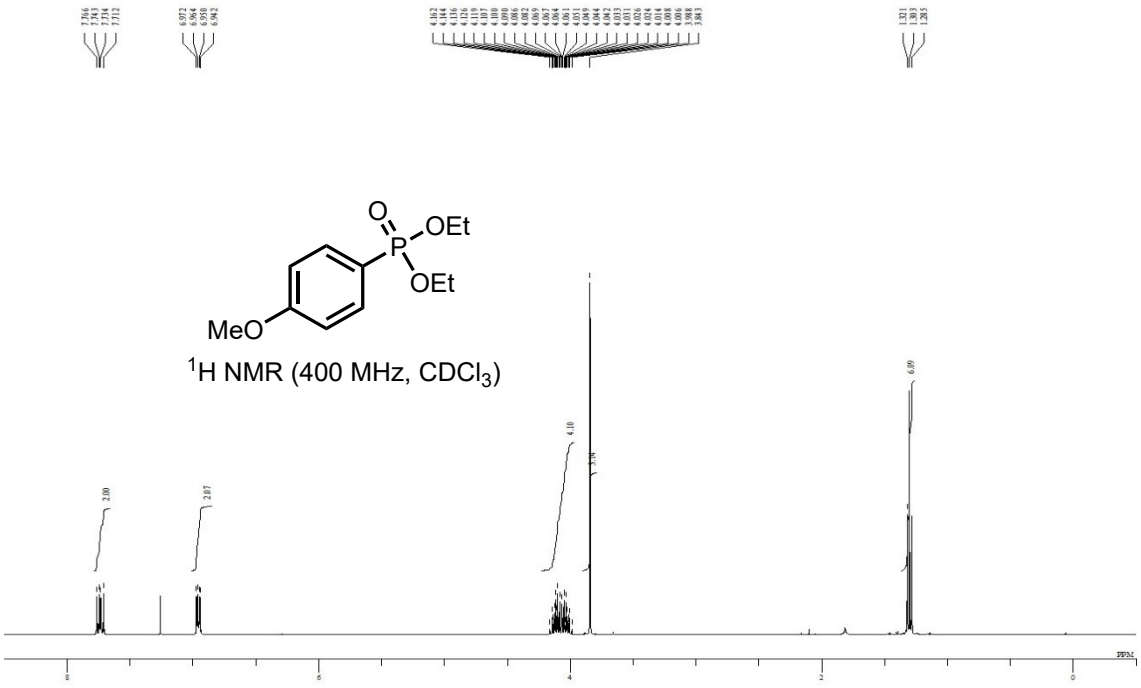




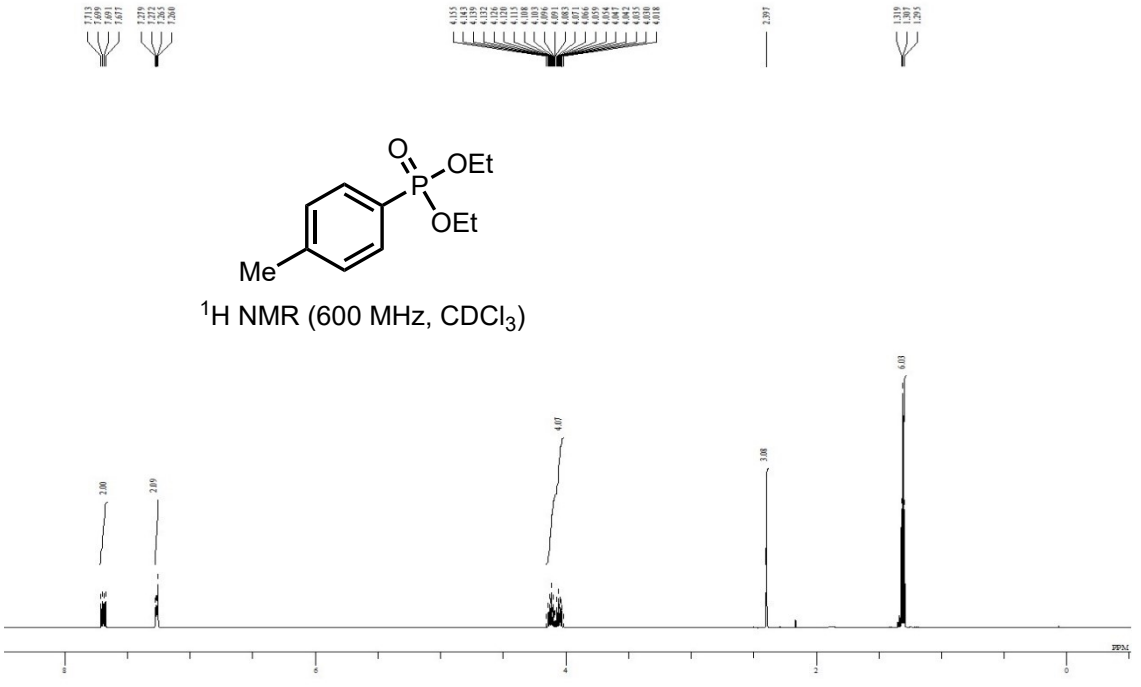
^{1}H NMR (600 MHz, $CDCl_3$)



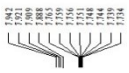
^{1}H NMR (600 MHz, $CDCl_3$)

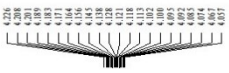


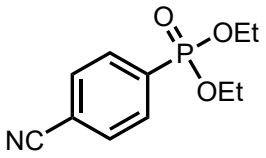
^{1}H NMR (400 MHz, $CDCl_3$)



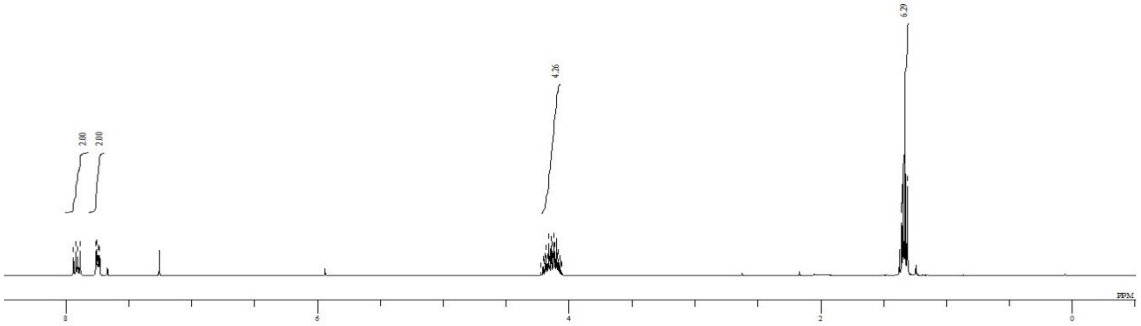
^{1}H NMR (600 MHz, $CDCl_3$)

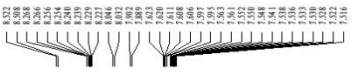


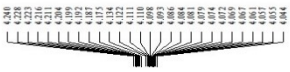


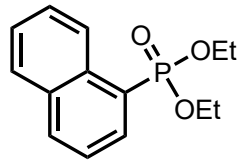


^{1}H NMR (400 MHz, $CDCl_3$)

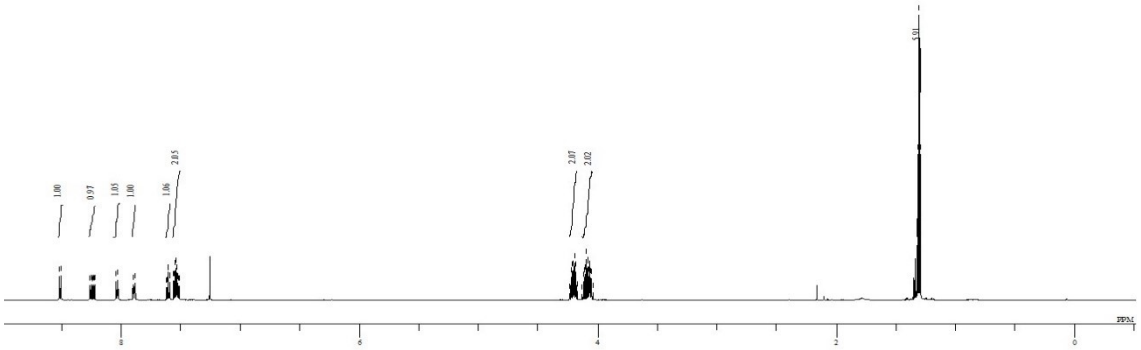


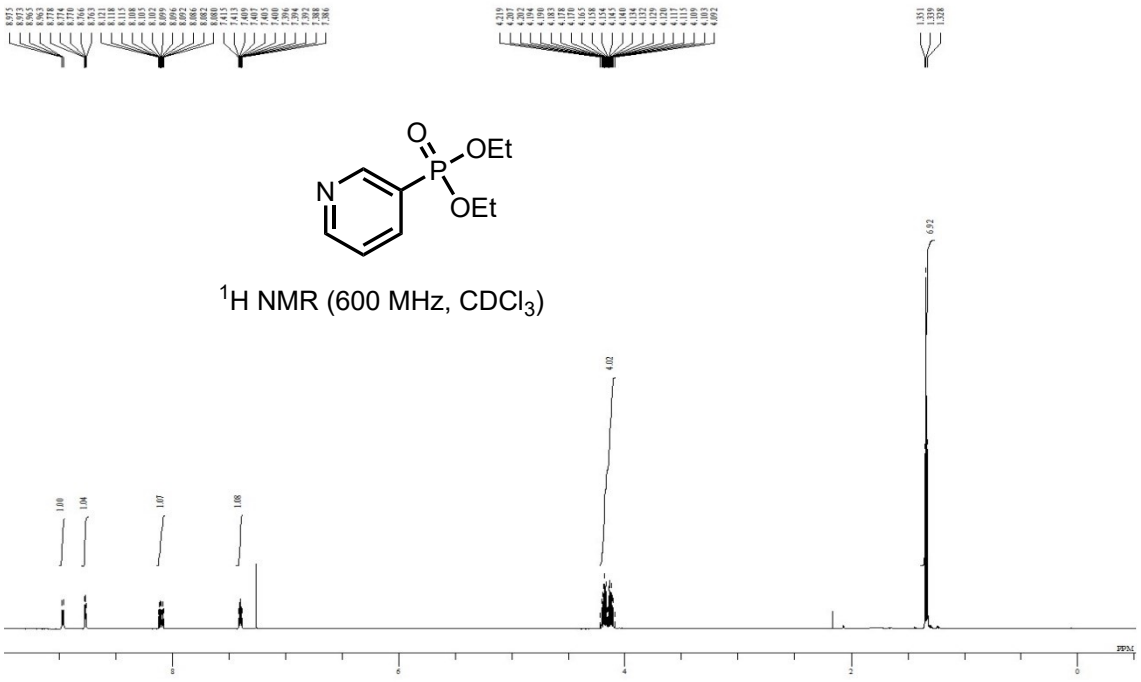




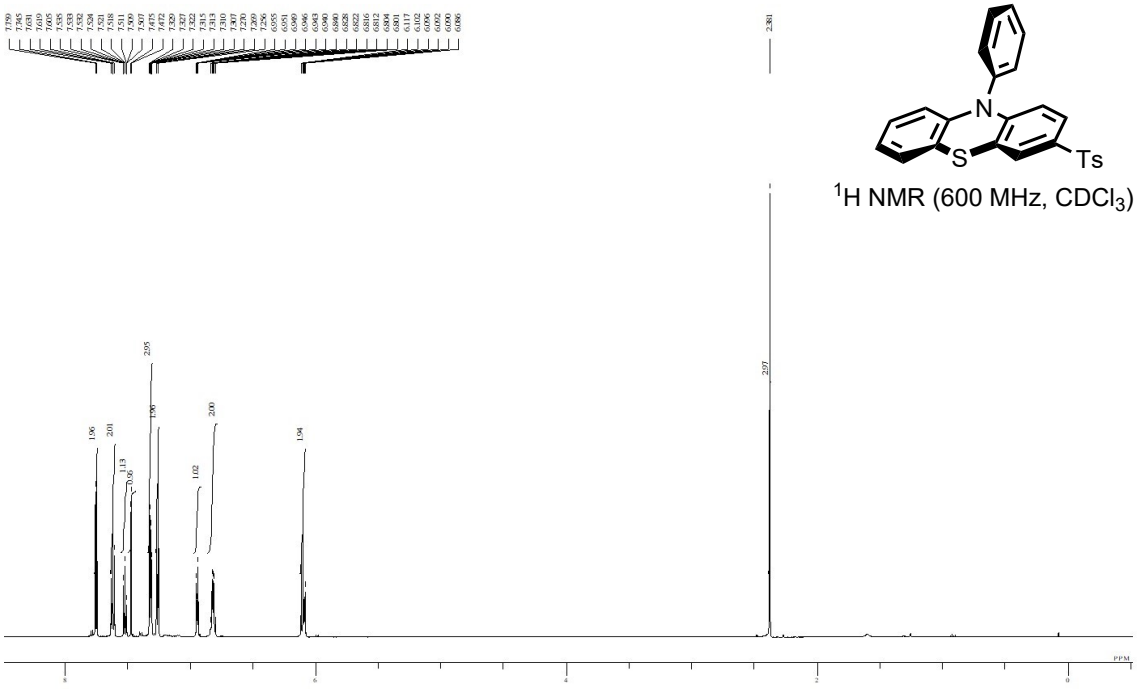


^{1}H NMR (600 MHz, $CDCl_3$)





^{1}H NMR (600 MHz, $CDCl_3$)



^{1}H NMR (600 MHz, $CDCl_3$)