Supporting Information

Metal-free photocatalytic peroxy-pyridylation of alkenes

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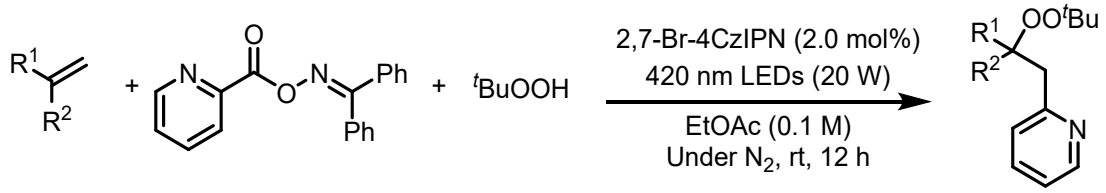
Contents

1. General experimental information 2
2. General procedure for peroxyl-functionalization of alkenes 2
3. Preparation of Starting Materials 2
   General procedure for the preparation of oxime 2
   General procedure for the preparation of oxime esters 3
   1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN) 3
   2,4,5,6-Tetrakis(2,7-dibromo-9H-carbazol-9-yl)isophthalonitrile (2,7-Br-4CzIPN) 4
4. Optimization of reaction conditions 4
   Table S1. Screening of photocatalysts[a] 4
   Table S2. Screening of solvent[a] 5
   Table S3. Screening of light[a] 5
   Table S4. Screening of substrate ratio[a] 6
   Table S5. Control experiments[a] 6
5. Mechanistic studies 8
6. Analytical data for compounds 9
7. References 15
8. NMR spectra 16

1. General experimental information

Unless otherwise noted, all the reagents were purchased from commercial suppliers and used without further purification. Oxime esters, cyanoarene-based photocatalyst were prepared based on literature procedures. The light source used for illuminating the reaction vessel consists of blue LEDs (λ_{max} = 420 nm) purchased from Taobao (https://shop35740806.taobao.com/). A clip fan was placed over the reaction vials to cool down the reaction system during the whole process of the reaction. The ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) spectra were recorded on a Bruker AV-400 spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for Chloroform-d. For ^{1}H NMR, Chloroform-d (δ = 7.26 ppm) or tetramethylsilane (TMS, δ = 0 ppm) serves as the internal standard; for ^{13}C NMR, Chloroform-d (δ = 77.16 ppm) serves as the internal standard. The peak patterns are indicated as follows: s, singlet, d, doublet, t, triplet, q, quartet, dd, doublet of doublet, m, multiplet. The coupling constants *J* were given in Hz. High resolution mass spectra (HRMS) were obtained via ESI mode by using a MicrOTOF mass spectrometer. The conversion of starting materials was monitored by thin layer chromatography (TLC) using silica gel plates (silica gel 400 mesh), and components were visualized by observation under UV light (254 and 365 nm).

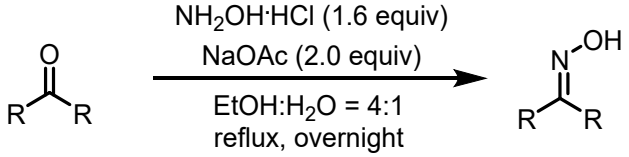
2. General procedure for peroxyl-functionalization of alkenes



In a 15 ml Schlenk tube equipped with a magnetic stir bar, oxime esters (2a, 0.6 mmol), alkene (0.4 mmol, 1.0 equiv., if solid) and 2, 7-Br-4CzIPN (11.8 mg, 2.0 mol%) were charged under air, then Schlenk tube was evacuated and re-filled with N_2 for three times. *Tert*-butyl hydroperoxide (1.2 mmol, 3.0 equiv.), EtOAc (4.0 mL, 0.1 M) and appropriate alkene (0.4 mmol, 1.0 equiv., if liquid) were added under N_2 counter flow. The Schlenk tube was tightly sealed and stirred under irradiation with 20 W blue LEDs (λ_{max} = 420 nm) using the described set-up at room temperature for 12 hours. After irradiation, the resulting homogenous solution was transferred to a 25 mL round bottom flask with aid of EtOAc. The crude product was purified by column chromatography isolation on silica gel (petroleum ether: ethyl acetate = 10:1 , v:v, as eluent) to give the pure desired product.

3. Preparation of Starting Materials

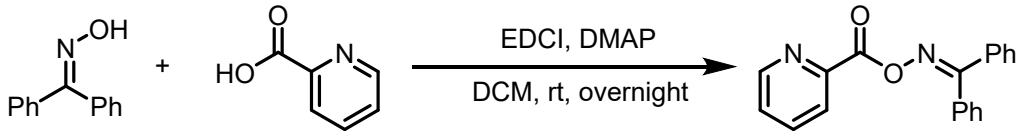
General procedure for the preparation of oxime



All oximes were prepared following reported literature procedure.[1] In a 250 mL round-bottom flask equipped with a condenser, aromatic ketones (50 mmol, 1.0 equiv.) were dissolved in the EtOH/H_2O mixture (v:v = 4:1, 125 mL). Then, hydroxylamine hydrochloride (80 mmol, 1.6 equiv.) and NaOAc (100 mmol, 2.0 equiv.) were added in one portion. The reaction mixture was refluxed (oil bath) overnight and the consumption of the starting material was monitored by TLC. After the transformation completed, the reaction was cooled to room temperature and concentrated under reduced pressure to remove ethanol as much as possible. Then the obtained white solid was diluted with brine, extracted with ethyl acetate (80 mL × 3) and dried over anhydrous $MgSO_4$. Evaporation of the solvent afforded the product in quantitative yield. This product was sufficiently pure as determined by NMR and was used without further purification for the preparation of oxime ether or ester.

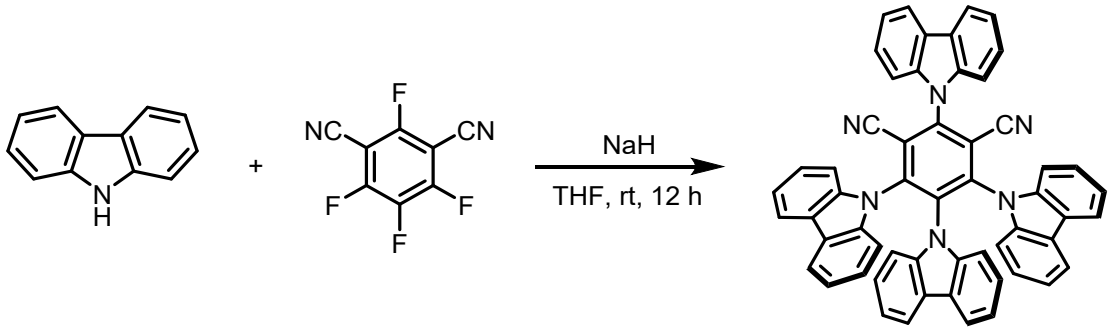
Note: The oximes did not show appreciable decomposition when stored in the fridge at -20 °C.

General procedure for the preparation of oxime esters



According to a related literature,[2] to a solution of ketoxime (10 mmol, 1.0 equiv.) and 2-picolinic acid (5.0 mmol) in CH_2Cl_2 (50 mL), DMAP (20 mol%, 1 mmol) and EDCI (12.5 mmol) was added. The mixture was stirred at room temperature under N_2 atmosphere until the reaction was complete as observed from TLC monitoring. The mixture was diluted with distilled water (50 mL) and the organic layer was separated, dried over anhydrous Na_2SO_4. The resulting mixture was then concentrated under reduced pressure. The solvent was removed and the residue was purified by silica gel column chromatography (petroleum ether: ethyl acetate = 10:1, v:v, as eluent) to give the corresponding compound (3.68 g, 61%).

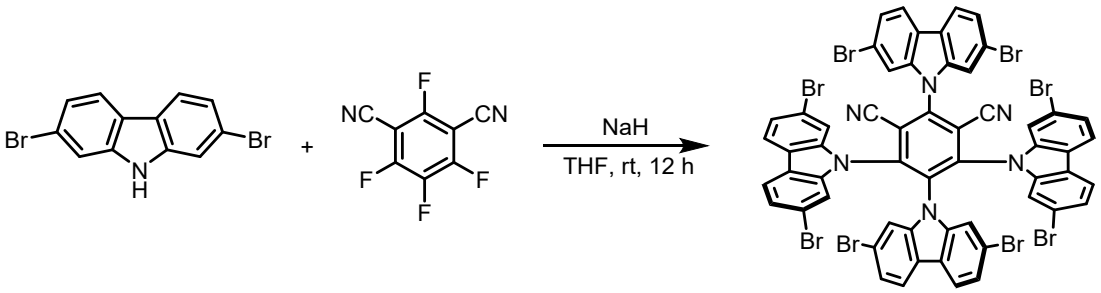
1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN)



According to a related literature,[3] sodium hydride (60% suspension in mineral oil, 7.5 equiv.) was added slowly to a stirred solution of carbazole (5.0 equiv.) in dry THF (0.05 M) under a N_2 atmosphere at room temperature. After 30 min, 2,4,5,6- tetrafluoroisophthalonitrile (1.0 mmol, 1.0 equiv.) was added. After stirring at room temperature for 12 h, 2 mL water was added to the reaction mixture to quench the excess of NaH. The resulting mixture was then concentrated under reduced pressure. The crude product was purified by recrystallization from PE/DCM then filtered. The brown liquid filtrate was concentrated and recrystallized as before. The combined solids were then

purified by column chromatography on silica gel with PE/DCM as eluent to give 4CzIPN as bright yellow powder (584 mg, 74%).

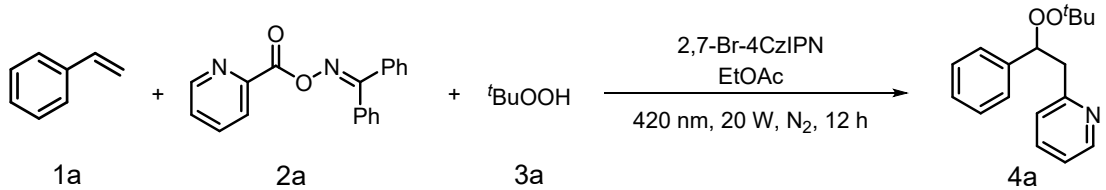
2,4,5,6-Tetrakis(2,7-dibromo-9H-carbazol-9-yl)isophthalonitrile (2,7-Br-4CzIPN)



Following our previously reported procedure.[4] Sodium hydride (60% suspension in mineral oil, 7.5 equiv.) was added slowly to a stirred solution of 2,7-Dibromo-9H-carbazole (5.0 equiv.) in dry THF (0.05 M) under a N_2 atmosphere at room temperature. After 2 hours, 2,4,5,6-tetrafluoroisophthalonitrile (1.0 mmol, 1.0 equiv.) was added. After stirring at room temperature for 12 hours, 2 mL water was added to the reaction mixture to quench the excess of NaH. The resulting mixture was then concentrated under reduced pressure. The solid residue was washed with H_2O, EtOH and acetone to yield 2,4,5,6-tetrakis (2,7-dibromo-9H-carbazol-9-yl) isophthalonitrile (2,7-Br-4CzIPN) as a greenish yellow solid (1.31 g, 93%).

4. Optimization of reaction conditions

Table S1. Screening of photocatalysts[a]

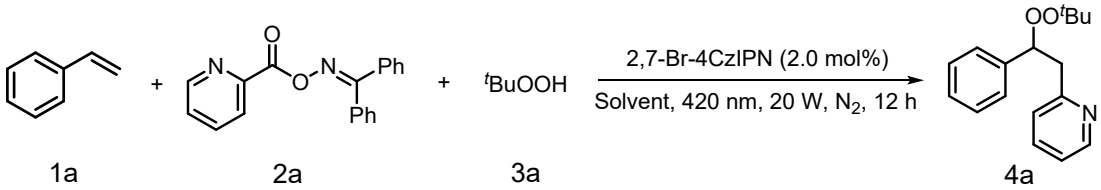


1a 2a 3a 4a

Entry	Photocatalyst	Yield (%)[b]
1	2,7-Br-4CzIPN /0.5%	39
2	2,7-Br-4CzIPN /1%	48
3	2,7-Br-4CzIPN /2%	77
4	2,7-Br-4CzIPN /3%	70
5	2,7-Br-4CzIPN /4%	67
6	2,7-Br-4CzIPN /5%	52
7	4CzIPN /2%	44
8	2-iPrTX /2%	36
9	3,6-Br-4CzIPN /2%	68
10	$[Ru(bpy)_3](PF_6)_2$ /2%	trace

[a] Reaction conditions: **1a** (0.4 mmol, 1.0 equiv.), **2a** (0.8 mmol, 2.0 equiv.), ^{t}BuOOH (5-6 M in decane, 2.0 mmol, 5.0 equiv.) in 4.0 mL dry EtOAc under an N_2 atmosphere at room temperature. [b] Yields were determined by ^{1}H NMR with 1,3,5-trimethoxy-benzene as an internal standard.

Table S2. Screening of solvent[a]

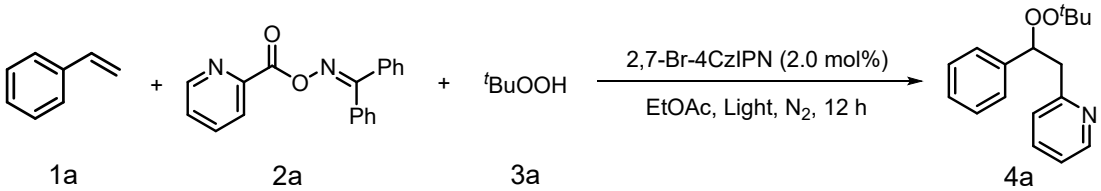


1a 2a 3a 4a

Entry	Solvent	Molarity	Yield (%)[b]
1	EtOAc	0.1 M	77
2	EtOAc	0.05 M	65
3	EtOAc	0.2 M	74
4	EtOAc	0.3 M	70
5	THF	0.1 M	9
6	DCE	0.1 M	21
7	MeCN	0.1 M	16
8	DMSO	0.1 M	Trace
9	DME	0.1 M	17
10	DCM	0.1 M	21
11	Dioxane	0.1 M	28
12	EtOH	0.1 M	18
13	Acetone	0.1 M	46
14	Toluene	0.1 M	53
15	DMF	0.1 M	32
16	DMC	0.1 M	62

[a] Reaction conditions: **1a** (0.4 mmol, 1.0 equiv.), **2a** (0.8 mmol, 2.0 equiv.), ^{t}BuOOH (5-6 M in decane, 2.0 mmol, 5.0 equiv.) in dry solvent under an N_2 atmosphere at room temperature. [b] Yields were determined by ^{1}H NMR with 1,3,5-trimethoxy-benzene as an internal standard.

Table S3. Screening of light[a]



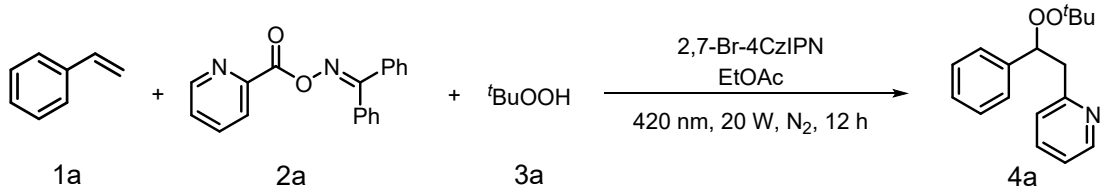
1a 2a 3a 4a

Entry	Light	Yield (%)[b]
1	36 W/450 nm	51
2	20 W/450 nm	49
3	10 W/450 nm	46

4	5 W/450 nm	24
5	20 W/495 nm	10
6	20 W/470 nm	49
7	20 W/450 nm	62
8	20 W/420 nm	76
9	20 W/400 nm	71
10	20 W/White LED	43

[a] Reaction conditions: **1a** (0.4 mmol, 1.0 equiv.), **2a** (0.8 mmol, 2.0 equiv.), ^{t}BuOOH (5-6 M in decane, 2.0 mmol, 5.0 equiv.) in 4mL dry EtOAc under an N_2 atmosphere at room temperature. [b] Yields were determined by ^{1}H NMR with 1,3,5-trimethoxy-benzene as an internal standard.

Table S4. Screening of substrate ratio[a]

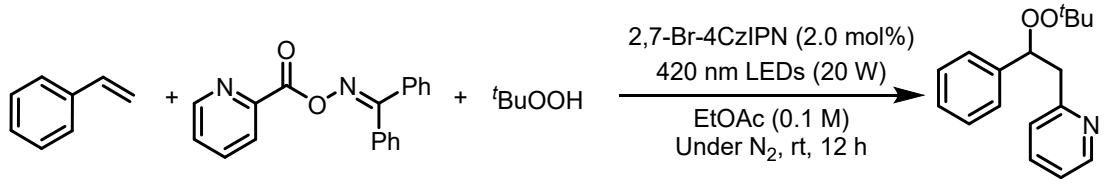


1a 2a 3a 4a

Entry	Equiv.	Yield (%)[b]
1	1:2:5	77
2	2:1:5	27
3	1:1.5:5	32
4	1:2.5:5	62
5	1:1.5:3	77

[a] Reaction conditions: **1a**, **2a**, ^{t}BuOOH in 4 mL dry EtOAc under an N_2 atmosphere at room temperature. [b] Yields were determined by ^{1}H NMR with 1,3,5-trimethoxy-benzene as an internal standard.

Table S5. Control experiments[a]



1a **2a** **3** **4a**

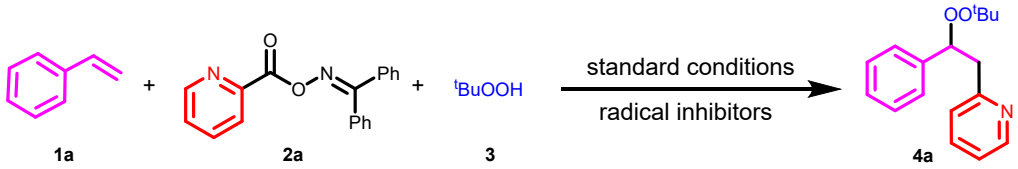
Entry	Variation from the standard conditions	Yield (%)
1	None	77
2	EA (add 0.2 mL H_2O)	75
3	use 70% aq **3**	76

4	air instead of N_2	27
5	Without photocatalyst	N.R.
6	Without light	N.R.
7	8 h	45
8	24 h	72

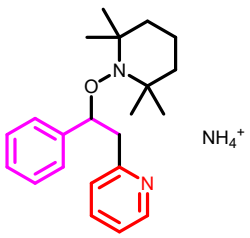
[a]Reaction condition: **1a** (0.4 mmol, 1.0 equiv.), **2a** (0.6 mmol, 1.5 equiv.), [t]BuOOH (5-6 M in decane, 1.2 mmol, 3.0 equiv.), 2,7-Br-4CzIPN (0.008 mmol), EtOAc (4.0 mL), 20 W/420 nm LEDs, 12 h, N_2 atmosphere, room temperature. [b]Yield was determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard.

5. Mechanistic studies

Radical inhibition experiment

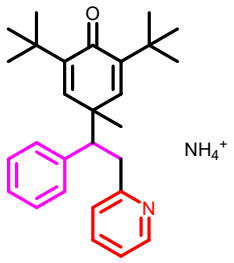


radical inhibitors	Yield of **4a**
no scavenger	72%
TEMPO (3.0 equiv.)	N.D.
BHT (3.0 equiv.)	N.D.



5

Chemical Formula: $C_{22}H_{34}N_3O^+$
Exact Mass: 356.2697
detected by HRMS
$[M+NH_4^+]$: 356.2696



6

Chemical Formula: $C_{28}H_{39}N_2O^+$
Exact Mass: 419.3057
detected by HRMS
$[M+NH_4^+]$: 419.3047

In a 15 ml Schlenk tube equipped with a stirring bar, oxime esters **2a** (0.6 mmol, 1.5 equiv.), TEMPO/BHT (1.2 mmol, 3 equiv.), and 2,7-Br-4CzIPN (2.0 mol%) were charged under air, then the vessel was evacuated and refilled with N_2 for three times. *Tert*-butyl hydroperoxide (1.2 mmol, 3.0 equiv.), EtOAc (4.0 mL, 0.1 M) and styrene **1a** (0.4 mmol, 1.0 equiv.) were added under N_2 counter flow. The vessel was sealed with the screw cap, then irradiated at 20 W/420 nm LEDs. After 12h, the reaction mixtures were analyzed by High-Resolution Mass Spectrometry (HRMS).

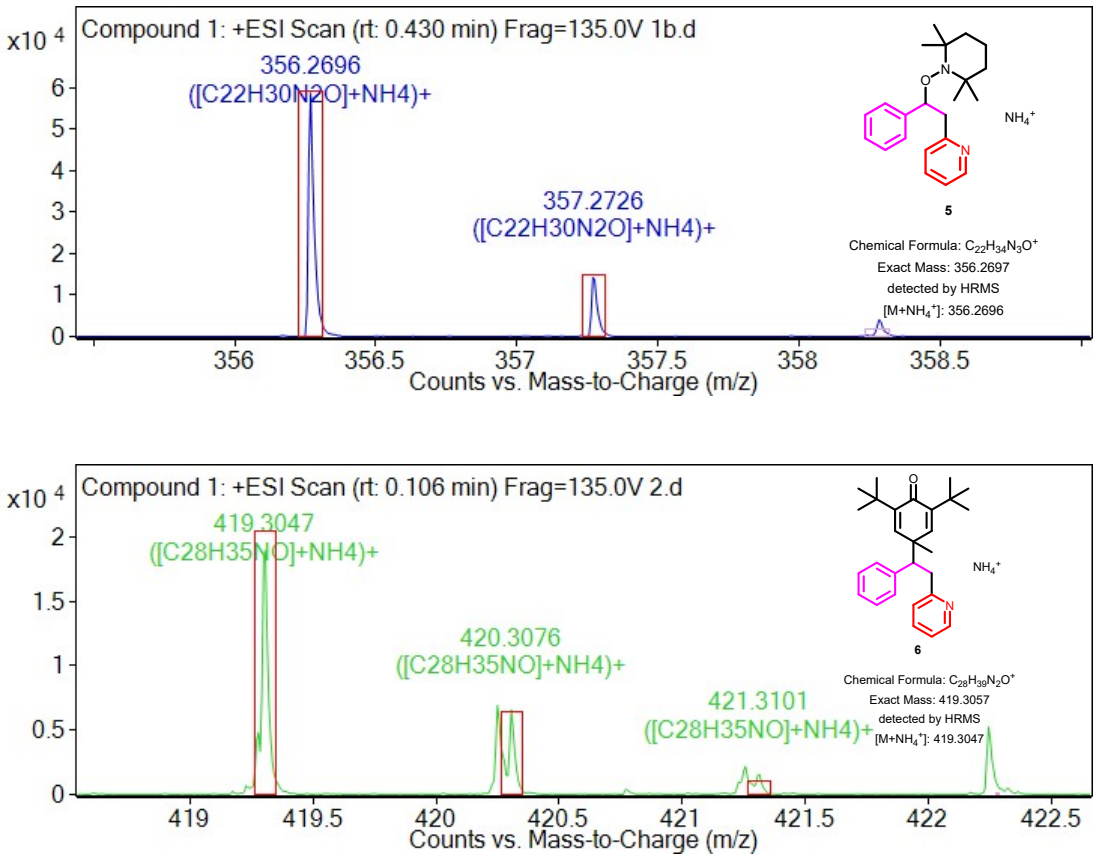


Figure S1. HRMS data for radical trapping experiment.

on/off visible light irradiation experiment

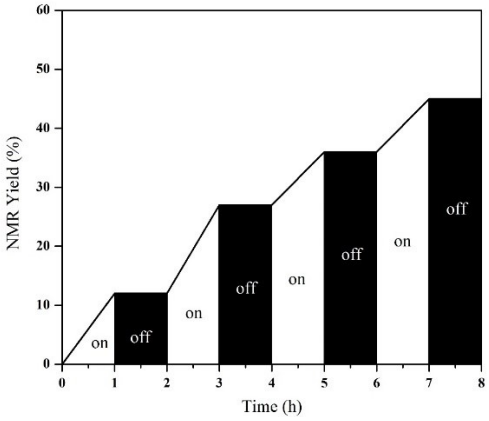


Figure S2. Time profile of the NMR yields with the light on/off over time.

The result indicates that continuous irradiation with visible light should be required in the reaction, and radical-chain propagation is not a key pathway in the present transformation.

Cyclic voltammetry experiments

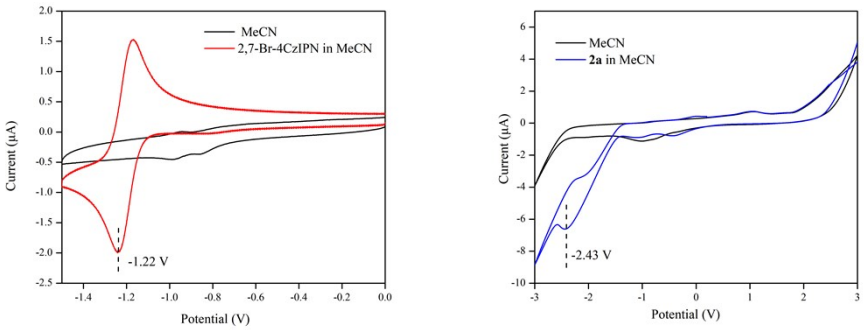


Figure S3. Cyclic voltammograms of **2,7-Br-4CzIPN** (5 mM) and **2a** (5 mM) in MeCN (50 mM $^{n}Bu_4NPF_6$).

Cyclic voltammetry experiments were performed on a CHI660B electrochemical workstation using a three-electrode cell set-up: 3 mm glassy carbon disk electrode as working electrode, Ag/AgCl (sat. KCl) as reference electrode, and a platinum wire as counter electrode.

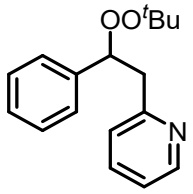
The following parameters were set:

scan rate: 0.1 V s^{-1}, sweep segments: 20, sensitivity: 10^{-4}, V_{min}: -3 V, V_{max}: 3 V. All the measurements were taken at room temperature.

All samples were prepared in degassed MeCN (5 mM) along with tetrabutylammonium-hexafluorophosphate ($^{n}Bu_4NPF_6$) as electrolyte. Prior to the CV measurement, nitrogen was bubbled through the solution (approximately 2 min) to ensure the full extrusion of air throughout the measurement. First, a blank run of 50 mM $^{n}Bu_4NPF_6$ in MeCN was performed. Next, the linear scan voltammogram for the samples with $^{n}Bu_4NPF_6$ (both 50 mM) in MeCN were measured under the above-mentioned conditions. No obvious oxidation peak of **2a** was observed, indicating that substrate **2a** could not be oxidized by the photocatalyst. The linear scan voltammogram measurement of **2,7-Br-4CzIPN** shows one distinct reduction event. The reduction takes place at approximately -1.22 V vs Ag/AgCl (sat. KCl). The linear scan voltammogram measurement of **2a** shows one distinct reduction event. The reduction takes place at approximately -2.43 V vs Ag/AgCl (sat. KCl), which means that **2a** could not be reduced by the **2,7-Br-4CzIPN**.

6. Analytical data for compounds

2-(2-(tert-butylperoxy)-2-phenylethyl)pyridine (4a)



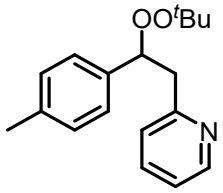
Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (78.0 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.2 Hz, 1H), 7.54 (t, *J* = 8.0 Hz, 1H), 7.38-7.30 (m, 5H), 7.12-7.08 (m, 2H), 5.33 (t, *J* = 7.8 Hz, 1H), 3.33 (dd, *J* = 12.8, 7.8 Hz, 1H), 3.11 (dd, *J* = 12.8, 7.8 Hz, 1H), 1.05 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 149.3, 141.1, 136.2, 128.3, 127.8, 127.0, 124.6, 121.6, 85.8, 80.6, 44.6, 26.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{22}NO_2$: 272.1651, found: 272.1659.

2-(2-(tert-butylperoxy)-2-(p-tolyl)ethyl)pyridine (4b)



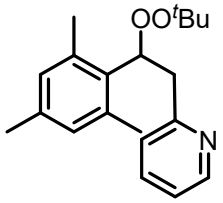
Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (79.8 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.0 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 4.0 Hz, 2H), 7.14-7.09 (m, 4H), 5.30 (dd, *J* = 8.8, 5.2 Hz, 1H), 3.34 (dd, *J* = 13.6, 8.8 Hz, 1H), 3.11 (dd, *J* = 13.6, 5.2 Hz, 1H), 2.33 (s, 3H), 1.06 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.5, 149.2, 138.0, 137.5, 136.1, 129.0, 126.9, 124.5, 121.5, 85.6, 80.5, 44.5, 26.4, 21.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{22}NO_2$: 286.1807, found: 286.1804.

2-(2-(tert-butylperoxy)-2-mesitylethyl)pyridine (4c)

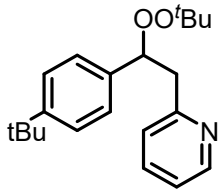


Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (81.4 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.8 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.12 (dd, *J* = 7.5, 4.8 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.77 (s, 2H), 5.71 (t, *J* = 7.1 Hz, 1H), 3.53 (dd, *J* = 13.1, 7.1 Hz, 1H), 3.18 (dd, *J* = 13.1, 7.1 Hz, 1H), 2.23 (s, 6H), 1.26 (s, 3H), 1.09 (s, 9H).

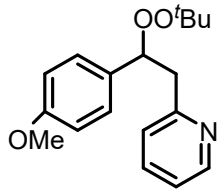
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 149.2, 136.8, 136.1, 125.9, 133.4, 124.4, 121.4, 118.0, 83.1, 80.1, 42.1, 26.5, 21.0, 20.8.
HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{20}H_{28}NO_2$: 314.2120, found: 314.2122.

2-(2-(4-(tert-butyl)phenyl)-2-(tert-butylperoxy)ethyl)pyridine (4d)



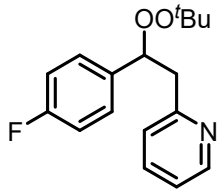
Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (105.9 mg, 81%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.4 Hz, 1H), 7.55 (dd, *J* = 8.3, 7.9 Hz, 1H), 7.36-7.29 (m, 4H), 7.14-7.09 (m, 2H), 5.33 (t, *J* = 8.0 Hz, 1H), 3.30 (dd, *J* = 16.0, 8.0 Hz, 1H), 3.12 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.31 (s, 9H), 1.04 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 150.5, 149.3, 138.1, 136.1, 126.5, 125.3, 124.6, 121.5, 85.6, 80.6, 44.7, 34.6, 31.5, 26.4.
HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{30}NO_2$: 328.2277, found: 328.2274.

2-(2-(tert-butylperoxy)-2-(4-methoxyphenyl)ethyl)pyridine (4e)



Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (95.1 mg, 79%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.3 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.3 Hz, 2H), 7.10-7.06 (m, 2H), 6.84 (d, *J* = 7.3 Hz, 2H), 5.27 (t, *J* = 8.3 Hz, 1H), 3.78 (s, 3H), 3.36 (dd, *J* = 13.5, 8.3 Hz, 1H), 3.09 (dd, *J* = 13.5, 8.3 Hz, 1H), 1.06 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 158.5, 149.3, 136.1, 133.0, 128.3, 124.5, 121.4, 113.7, 85.4, 80.5, 55.3, 44.3, 26.4.
HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{24}NO_3$: 302.1756, found: 302.1754.

2-(2-(tert-butylperoxy)-2-(4-fluorophenyl)ethyl)pyridine (4f)



Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (85.5 mg, 74%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.5 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 1H), 7.32 (dd, *J* = 8.6, 5.5 Hz, 2H), 7.10 (dd, *J* = 8.6, 8.0 Hz, 2H), 6.99 (m, 2H), 5.31 (dd, *J* = 8.5, 5.8 Hz, 1H), 3.31 (dd, *J*

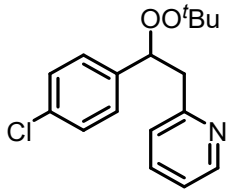
= 13.7, 8.5 Hz, 1H), 3.07 (dd, *J* = 13.7, 5.8 Hz, 1H), 1.06 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -114.94

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, $^{1}J_{C\text{-}F}$ = 244.0 Hz), 158.1, 149.3, 136.9 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 136.2, 128.6 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 124.5, 121.6, 115.2 (d, $^{2}J_{C\text{-}F}$ = 21.0 Hz), 85.0, 80.7, 44.5, 26.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{21}FNO_2$: 290.1556, found: 290.1547.

2-(2-(tert-butylperoxy)-2-(4-chlorophenyl)ethyl)pyridine (4g)



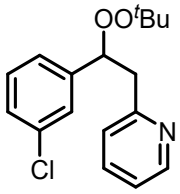
Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (85.4 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.0 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.30-7.27 (m, 4H), 7.13-7.07 (m, 2H), 5.30 (t, *J* = 6.7 Hz, 1H), 3.27 (dd, *J* = 13.8, 6.7 Hz, 1H), 3.05 (dd, *J* = 13.8, 6.7 Hz, 1H), 1.05 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 149.3, 139.8, 136.3, 133.5, 128.5, 128.3, 124.5, 121.7, 85.0, 80.7, 44.4, 26.4.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{21}ClNO_2$: 306.1261, found: 306.1269.

2-(2-(tert-butylperoxy)-2-(3-chlorophenyl)ethyl)pyridine (4h)



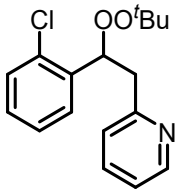
Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (91.5 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.0 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.37 (s, 1H), 7.25-7.21 (m, 3H), 7.16-7.11 (m, 2H), 5.31 (dd, *J* = 8.6, 5.5 Hz, 1H), 3.25 (dd, *J* = 13.9, 8.6 Hz, 1H), 3.06 (dd, *J* = 13.9, 5.5 Hz, 1H), 1.04 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 149.2, 143.5, 136.4, 134.3, 129.6, 127.9, 127.0, 125.1, 124.6, 121.8, 85.0, 80.8, 44.5, 26.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{21}ClNO_2$: 306.1261, found: 306.1255.

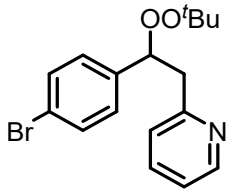
2-(2-(tert-butylperoxy)-2-(2-chlorophenyl)ethyl)pyridine (4i)



Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (82.9 mg, 68%).

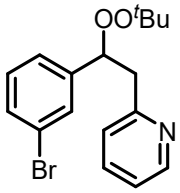
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 4.3 Hz, 1H), 7.65-7.59 (m, 2H), 7.33-7.29 (m, 2H), 7.26-7.14 (m, 3H), 5.76 (dd, *J* = 9.4, 4.4 Hz, 1H), 3.28 (dd, *J* = 14.0, 4.4 Hz, 1H), 3.12 (dd, *J* = 14.0, 9.4 Hz, 1H), 1.03 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 148.9, 138.8, 136.7, 132.6, 129.5, 128.8, 128.0, 127.1, 124.5, 121.8, 82.1, 80.9, 43.0, 26.3.
HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{21}ClNO_2$: 306.1261, found: 306.1253.

2-(2-(4-bromophenyl)-2-(tert-butylperoxy)ethyl)pyridine (4j)



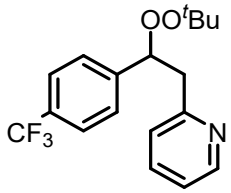
Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (103 mg, 74%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.7 Hz, 1H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.13-7.07 (m, 2H), 5.29 (t, *J* = 8.7 Hz, 1H), 3.27 (dd, *J* = 13.8, 8.7 Hz, 1H), 3.05 (dd, *J* = 13.8, 8.7 Hz, 1H), 1.04 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 149.4, 140.3, 136.3, 131.5, 128.6, 124.5, 121.7, 121.6, 85.0, 80.7, 44.4, 26.4.
HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{21}BrNO_2$: 350.0756, found: 350.0770.

2-(2-(2-bromophenyl)-2-(tert-butylperoxy)ethyl)pyridine (4k)



Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (100.5 mg, 72%).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 4.8 Hz, 1H), 7.57 (t, *J* = 7.7 Hz, 1H), 7.53 (s, 1H), 7.39 (dd, *J* = 7.9, 6.0 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.20-7.10 (m, 3H), 5.30 (dd, *J* = 8.9, 5.3 Hz, 1H), 3.24 (dd, *J* = 13.8, 8.9 Hz, 1H), 3.07 (dd, *J* = 13.8, 5.3 Hz, 1H), 1.04 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 149.4, 143.8, 136.3, 130.8, 130.0, 129.9, 125.5, 124.6, 122.5, 121.7, 85.0, 80.8, 44.6, 26.3.
HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{21}BrNO_2$: 350.0756, found: 350.0747.

2-(2-(tert-butylperoxy)-2-(4-(trifluoromethyl)phenyl)ethyl)pyridine (4l)



Prepared following the general procedure, purified by column chromatography (10/1 petroleum

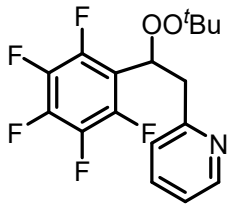
ether/ethyl acetate), and isolated as a colorless oil (100.3 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.7 Hz, 1H), 7.59-7.54 (m, 3H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.15-7.10 (m, 2H), 5.41 (dd, *J* = 8.9, 5.3 Hz, 1H), 3.24 (dd, *J* = 13.7, 8.9 Hz, 1H), 3.08 (dd, *J* = 13.7, 5.3 Hz, 1H), 1.04 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 149.4, 145.5, 136.3, 129.9 (q, $^2J_{C\text{-}F}$ = 32.3 Hz), 127.1, 125.4 (q, $^3J_{C\text{-}F}$ = 3.6 Hz), 124.6, 124.4 (q, $^1J_{C\text{-}F}$ = 276.8 Hz),121.8, 85.0, 80.9, 44.6, 26.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{21}F_3NO_2$: 340.1524, found: 340.1513.

2-(2-(tert-butylperoxy)-2-(perfluorophenyl)ethyl)pyridine (4m)



Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (90.9 mg, 63%).

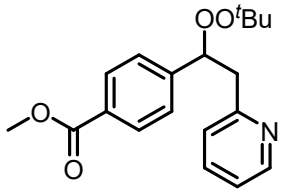
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 4.4 Hz, 1H), 7.60 (t, *J* = 7.7 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.14 (dd, *J* = 7.7, 4.4 Hz, 1H), 5.77 (t, *J* = 7.0 Hz, 1H), 3.58 (dd, *J* = 13.9, 7.0 Hz, 1H), 3.26 (dd, *J* = 13.9, 7.0 Hz, 1H), 1.08 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -142.08, -154.64, -162.45.

^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 149.6, 136.6, 124.2, 122.1, 81.2, 76.5, 40.3, 26.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{17}F_5NO_2$: 362.1179, found: 362.1185.

methyl 4-(1-(tert-butylperoxy)-2-(pyridin-2-yl)ethyl)benzoate (4n)



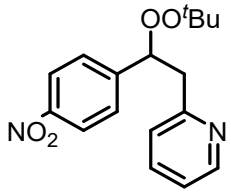
Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (105.3 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 5.3 Hz, 1H), 7.99 (d, *J* = 6.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 6.2 Hz, 2H), 7.14-7.07 (m, 2H), 5.39 (t, *J* = 8.2 Hz, 1H), 3.90 (s, 3H), 3.28 (dd, *J* = 13.8, 8.2 Hz, 1H), 3.08 (dd, *J* = 13.8, 8.2 Hz, 1H), 1.05 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 157.8, 149.4, 146.6, 136.3, 129.7, 129.6, 126.8, 124.5, 121.7, 85.2, 80.8, 52.2, 44.4, 26.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{24}NO_2$: 330.1705, found: 330.1717.

2-(2-(tert-butylperoxy)-2-(4-nitrophenyl)ethyl)pyridine (4o)



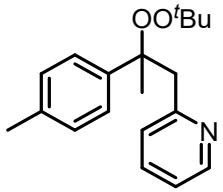
Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (74.6 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 7.4 Hz, 1H), 8.18 (d, *J* = 6.5 Hz, 2H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.53 (d, *J* = 6.5 Hz, 2H), 7.18-7.10 (m, 2H), 5.46 (t, *J* = 7.3 Hz, 1H), 3.24 (dd, *J* = 14.8, 7.3 Hz, 1H), 3.09 (dd, *J* = 14.8, 7.3 Hz, 1H), 1.05 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 149.4, 149.1, 147.6, 136.5, 127.6, 124.6, 123.7, 122.0, 84.6, 81.1, 44.3, 26.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{17}H_{21}N_2O_4$: 317.1501, found: 317.1514.

2-(2-(tert-butylperoxy)-2-(p-tolyl)propyl)pyridine (4p)



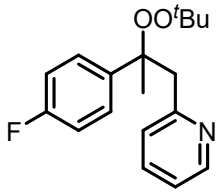
Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (93.3 mg, 78%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 4.0 Hz, 2H), 7.11-7.03 (m, 4H), 3.37 (d, *J* = 13.3 Hz, 1H), 3.23 (d, *J* = 13.3 Hz, 1H), 2.32 (s, 3H), 1.61 (s, 3H), 1.22 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1, 148.6, 142.0, 136.5, 135.5, 128.6, 126.1, 125.6, 121.4, 83.8, 79.2, 49.5, 26.9, 23.2, 21.2.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{19}H_{26}NO_2$:300.1964, found: 300.1951.

2-(2-(tert-butylperoxy)-2-(4-fluorophenyl)propyl)pyridine (4q)



Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (83.6 mg, 69%).

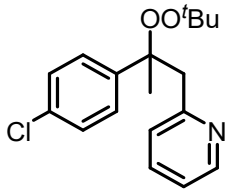
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 5.8 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.32 (dd, *J* = 8.2, 5.6 Hz, 2H), 7.07 (dd, *J* = 8.0, 5.8 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 1H), 6.95 (t, *J* = 8.2 Hz, 2H), 3.33 (d, *J* = 13.3 Hz, 1H), 3.21 (d, *J* = 13.3 Hz, 1H), 1.63 (s, 3H), 1.22 (s, 9H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.4.

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, $^1J_{C\text{-}F}$ = 244.0 Hz), 157.6, 148.7, 140.6 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 135.5, 127.8 (d, $^3J_{C\text{-}F}$ = 8.0 Hz), 125.5, 121.4, 114.6 (d, $^2J_{C\text{-}F}$ = 21.0 Hz), 83.5, 79.4, 49.6, 26.8, 23.3.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{23}FNO_2$: 304.1713, found: 304.1705.

2-(2-(tert-butylperoxy)-2-(4-chlorophenyl)propyl)pyridine (4r)



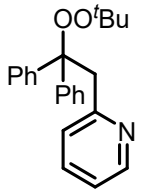
Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (93.1 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 6.8 Hz, 1H), 7.49 (t, *J* = 6.8 Hz, 1H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.5 Hz, 2H), 7.08 (t, *J* = 6.8 Hz, 1H), 7.03 (d, *J* = 6.8 Hz, 1H), 3.31 (d, *J* = 13.3 Hz, 1H), 3.20 (d, *J* = 13.3 Hz, 1H), 1.63 (s, 3H), 1.21 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 148.7, 143.6, 135.6, 132.7, 128.0, 127.7, 125.6, 121.5, 83.6, 79.5, 49.5, 26.8, 23.2.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{18}H_{23}ClNO_2$: 320.1417, found: 320.1408.

2-(2-(tert-butylperoxy)-2,2-diphenylethyl)pyridine (4s)



Prepared following the general procedure, purified by column chromatography (10/1 petroleum ether/ethyl acetate), and isolated as a colorless oil (104.1 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 5.8 Hz, 1H), 7.57 (t, *J* = 5.8 Hz, 1H), 7.47 (d, *J* = 5.8 Hz, 1H), 7.37-7.28 (m, 10H), 6.96 (t, *J* = 5.8 Hz, 1H), 4.12 (s, 2H), 1.21 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 157.8, 148.2, 144.0, 135.2, 127.8, 127.4, 127.0, 125.7, 121.1, 87.0, 79.7, 44.7, 26.8.

HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{23}H_{26}NO_2$: 348.1964, found: 348.1956.

7. References

[1] Y. Gao, J. Liu, Z. Li, T. Guo, S. Xu, H. Zhu, F. Wei, S. Chen, H. Gebru and K. Guo, *J. Org. Chem*., 2018, **83**, 2040–2049.

[2] S. C. S. Kumar, N. V. Kumar, P. Srinivas and B. K. Bettadaiah, *Synthesis*., 2014, **46**, 1847–1852.

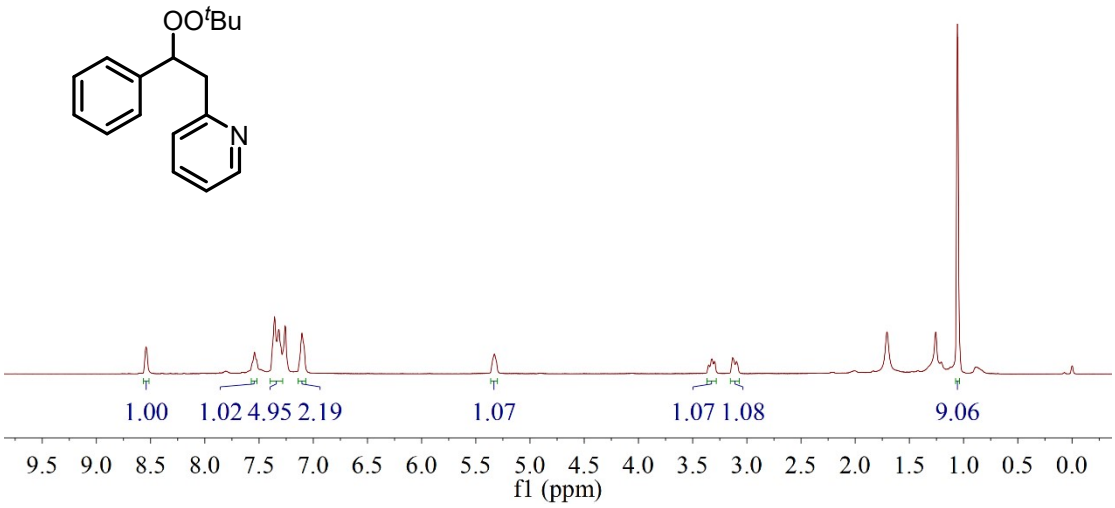
[3] J. Luo and J. Zhang, *ACS Catal*., 2020, **10**, 14302–14303.

[4] C. Gao, J. Zeng, X. Zhang, Y. Liu and Z.-P. Zhan, *Org. Lett*., 2023, **25**, 3146–3151.

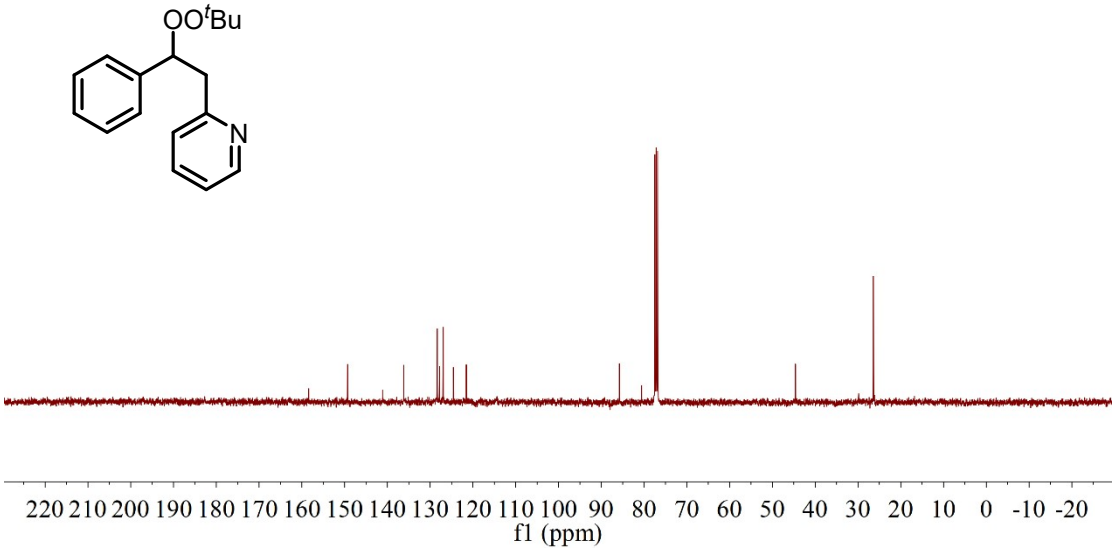
8. NMR spectra

2-(2-(tert-butylperoxy)-2-phenylethyl)pyridine (4a)

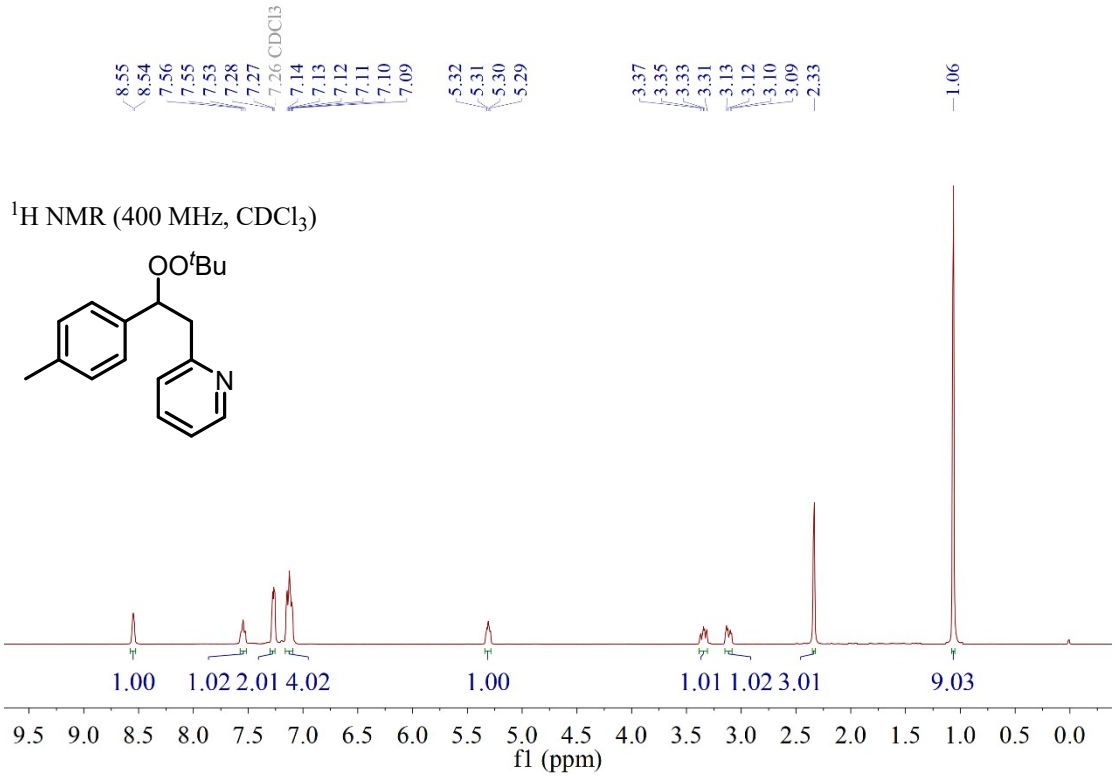
^{1}H NMR (400 MHz, $CDCl_3$)

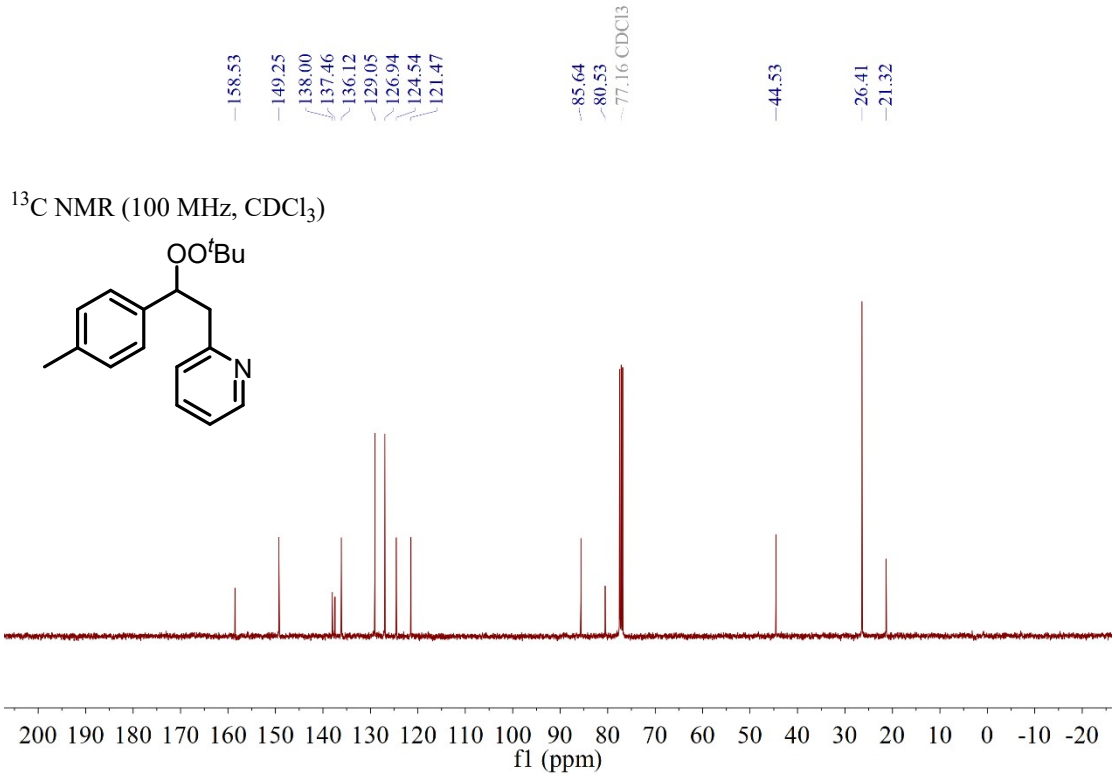


^{13}C NMR (100 MHz, $CDCl_3$)



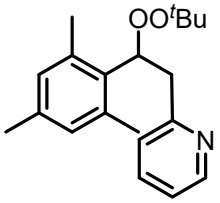
2-(2-(tert-butylperoxy)-2-(p-tolyl)ethyl)pyridine (4b)

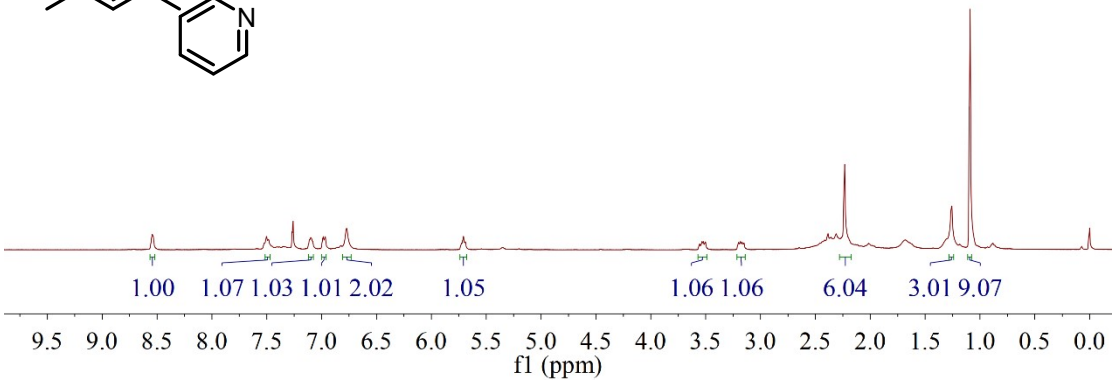




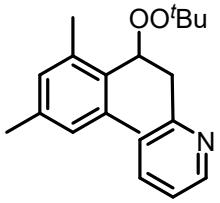
2-(2-(tert-butylperoxy)-2-mesitylethyl)pyridine (4c)

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



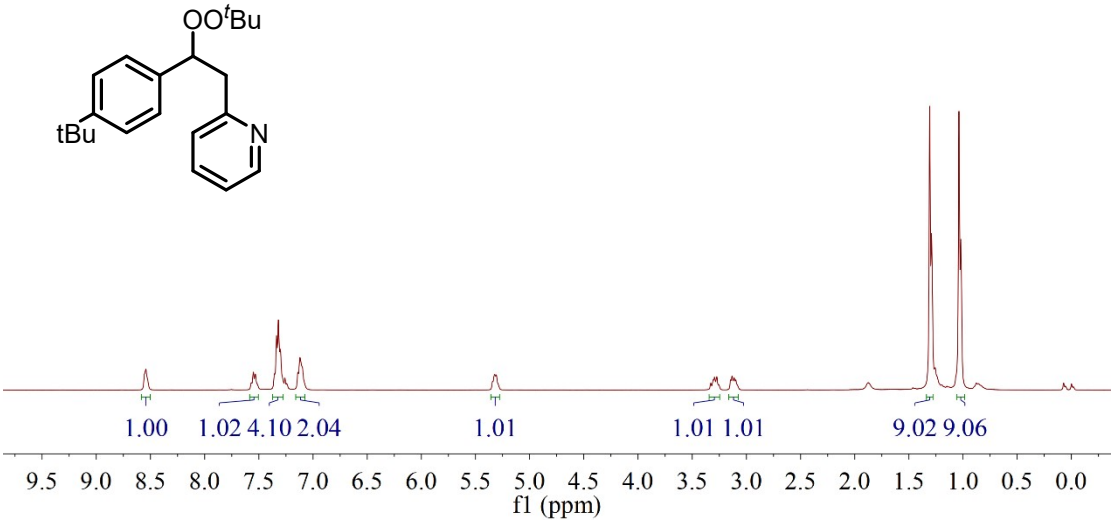


^{13}C NMR (100 MHz, $CDCl_3$)

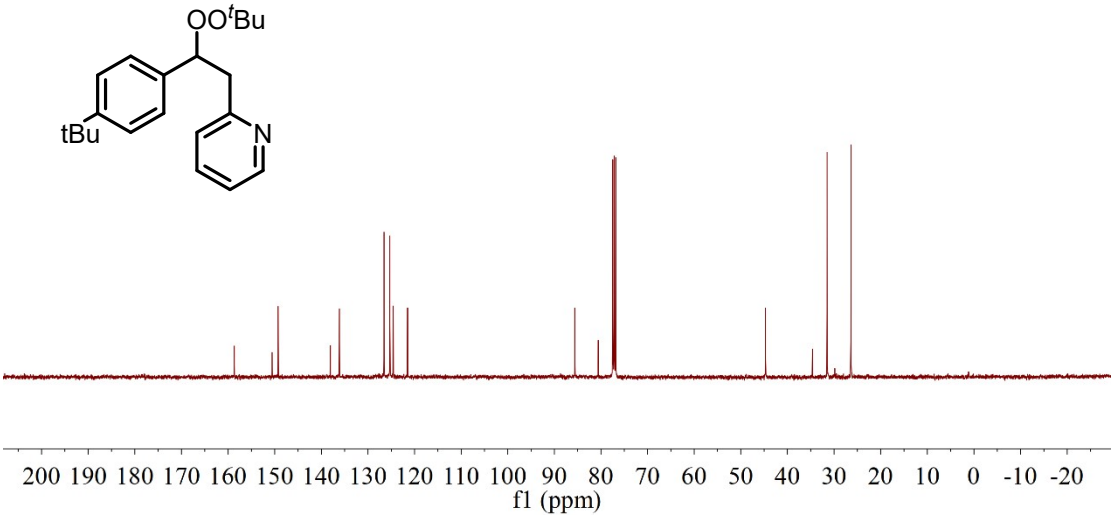


2-(2-(4-(tert-butyl)phenyl)-2-(tert-butylperoxy)ethyl)pyridine (4d)

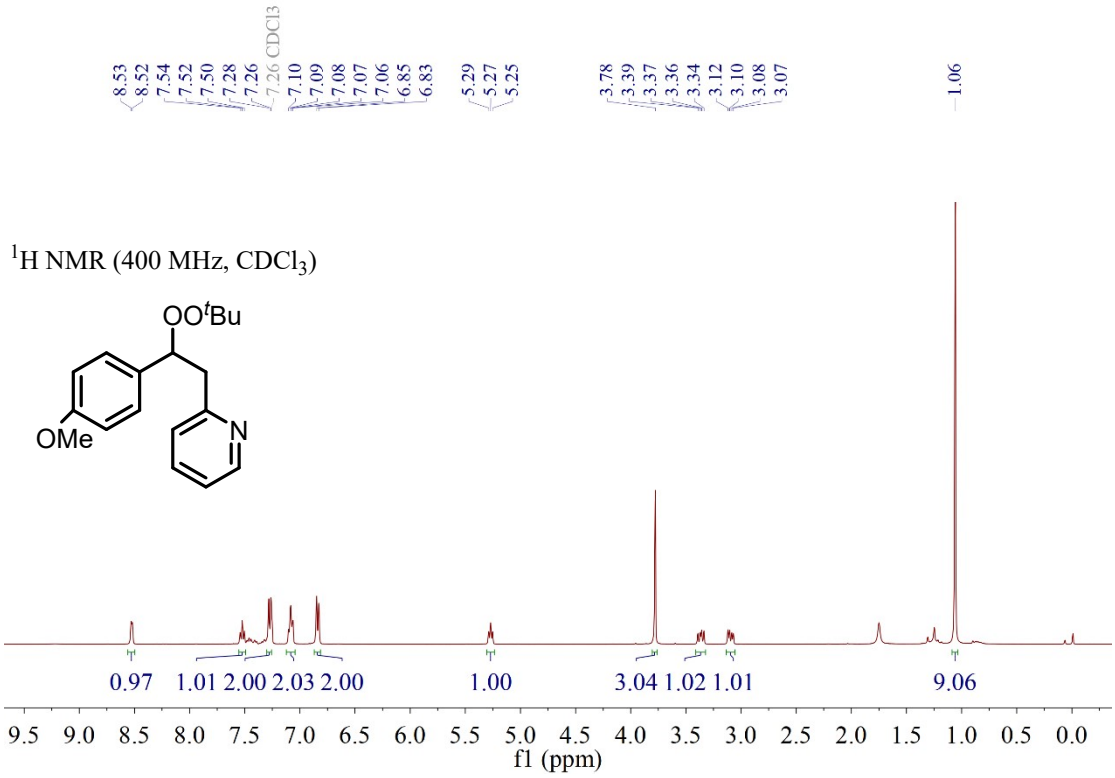
^{1}H NMR (400 MHz, $CDCl_3$)



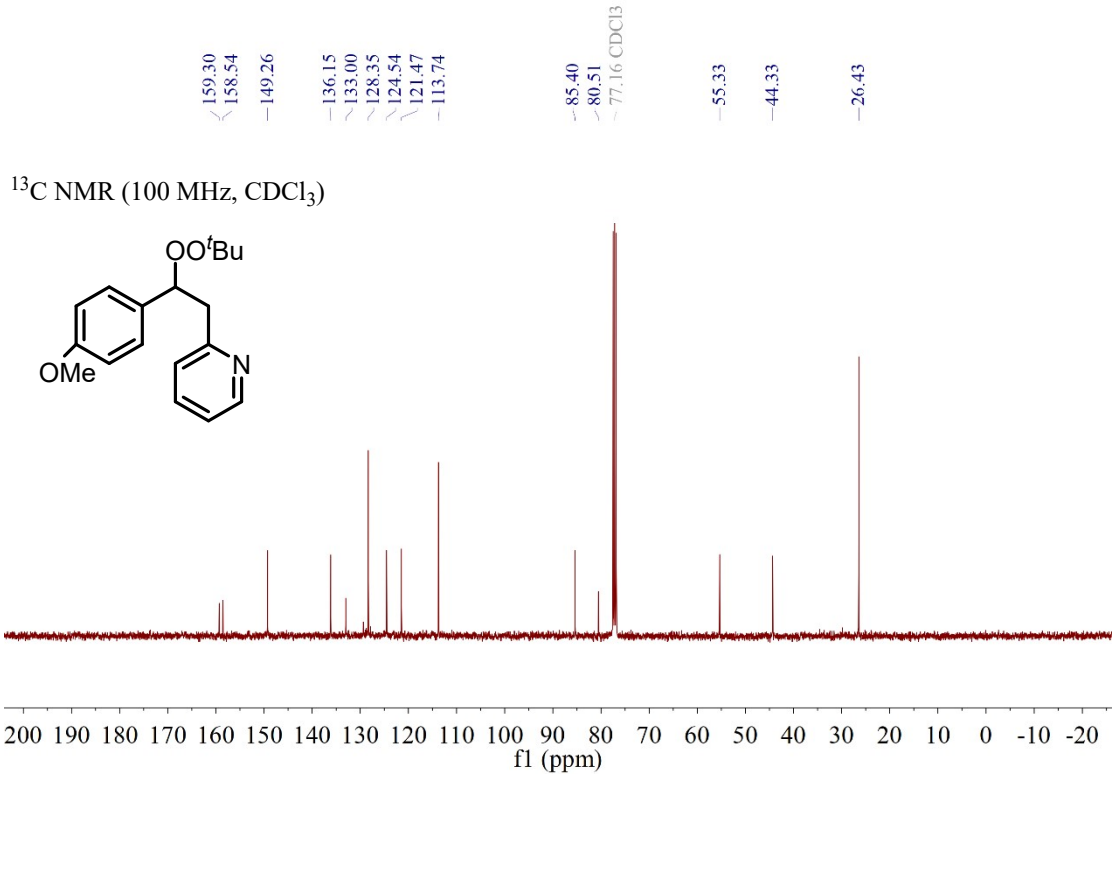
^{13}C NMR (100 MHz, $CDCl_3$)



2-(2-(tert-butylperoxy)-2-(4-methoxyphenyl)ethyl)pyridine (4e)



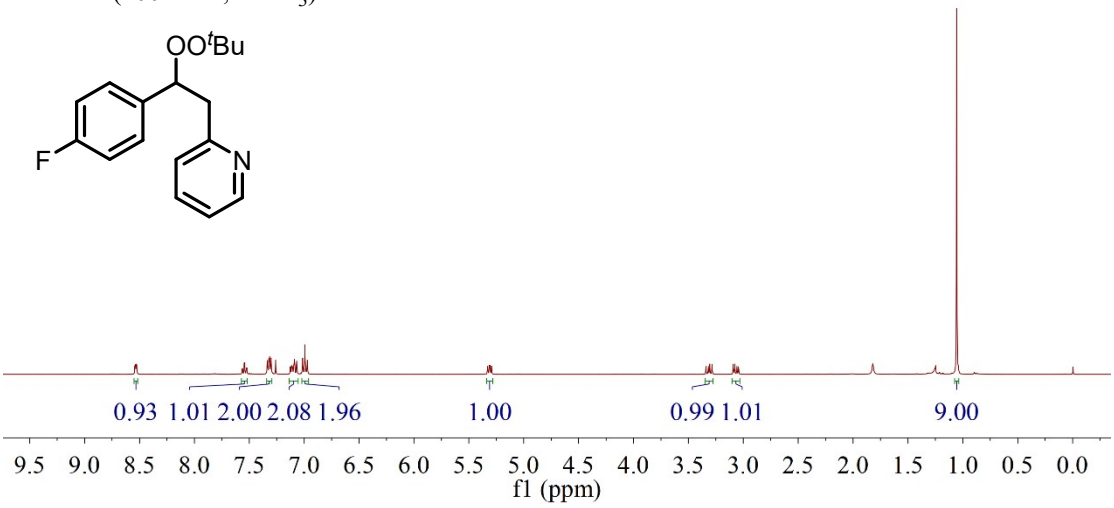
^{1}H NMR (400 MHz, $CDCl_3$)



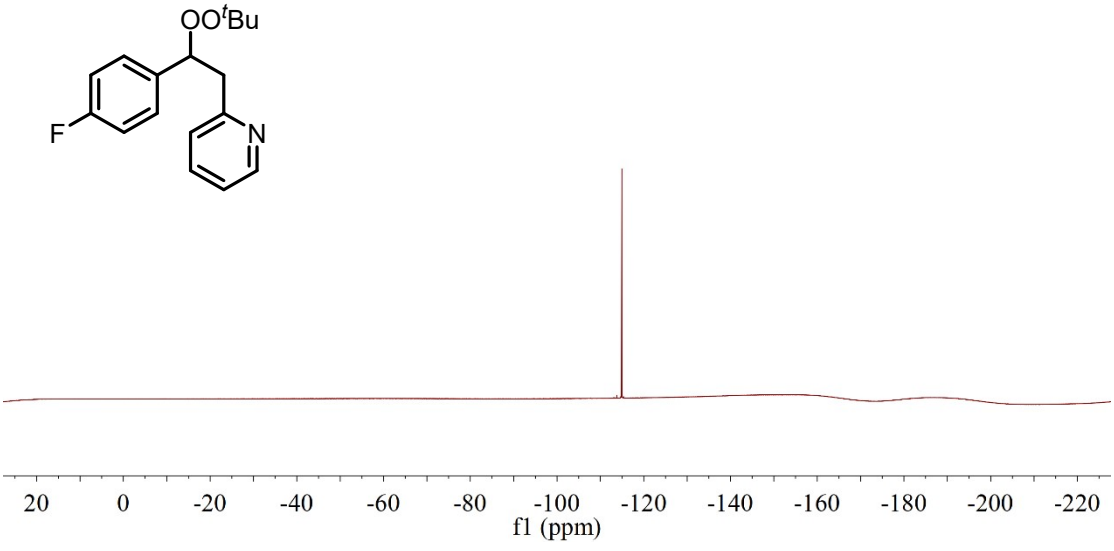
^{13}C NMR (100 MHz, $CDCl_3$)

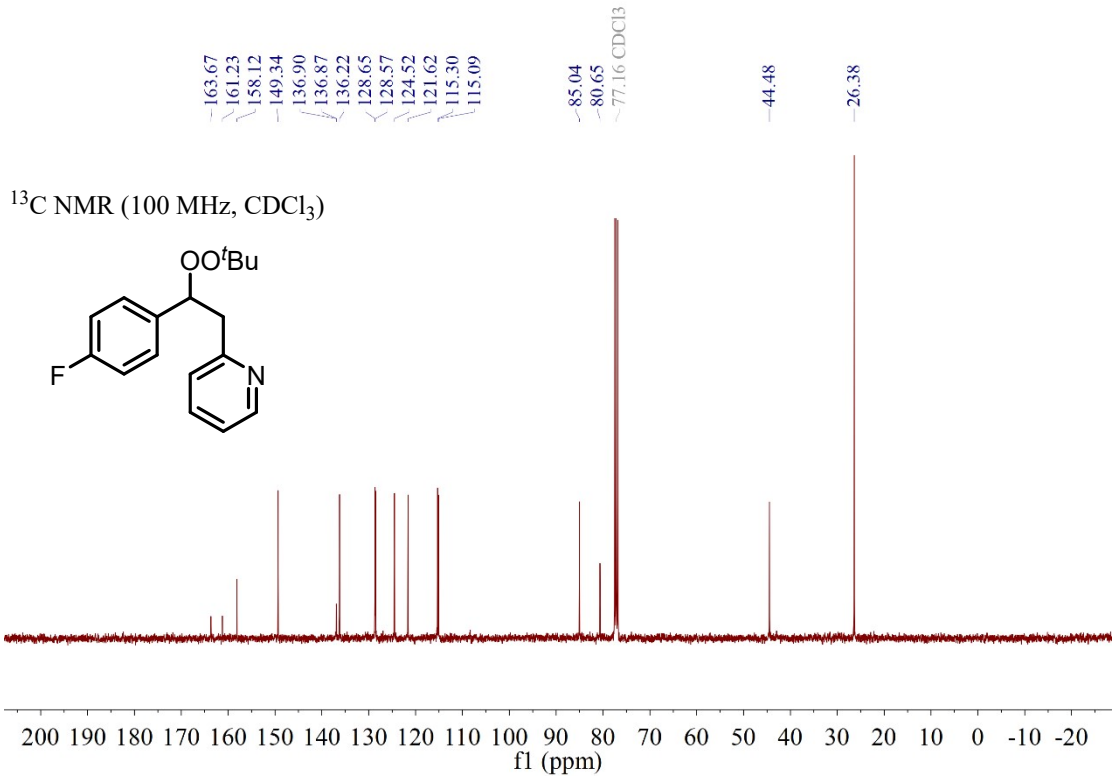
2-(2-(tert-butylperoxy)-2-(4-fluorophenyl)ethyl)pyridine (4f)

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



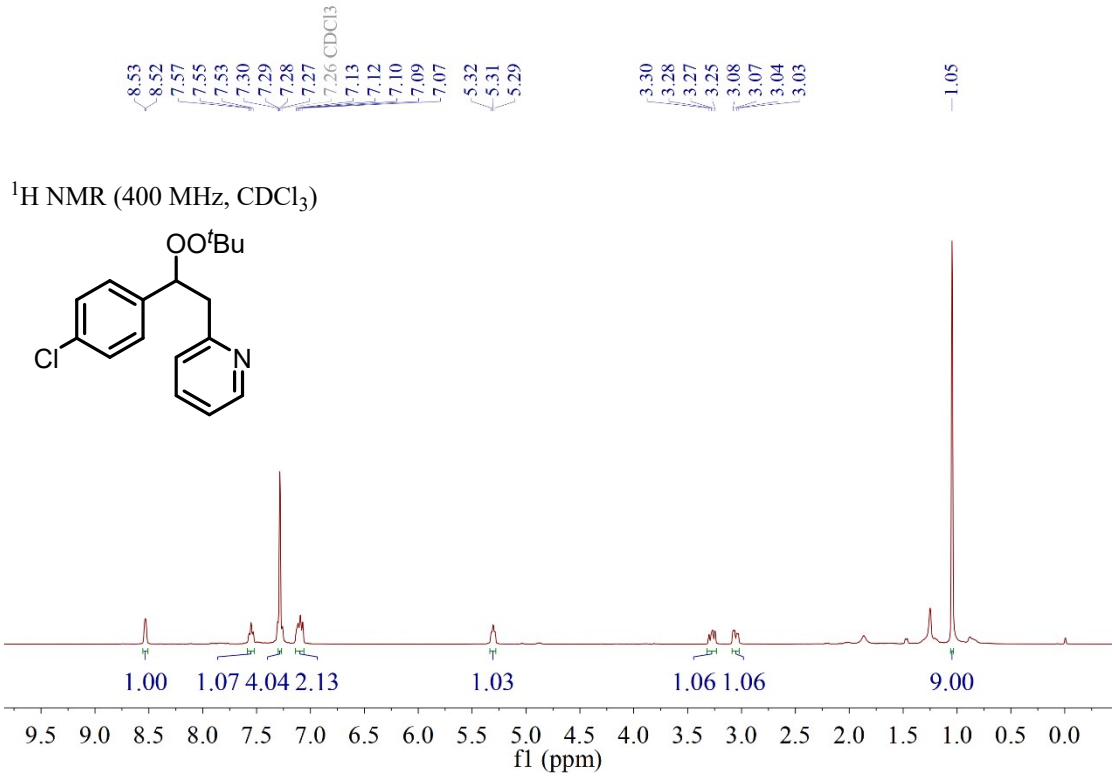
^{19}F NMR (376 MHz, $CDCl_3$)





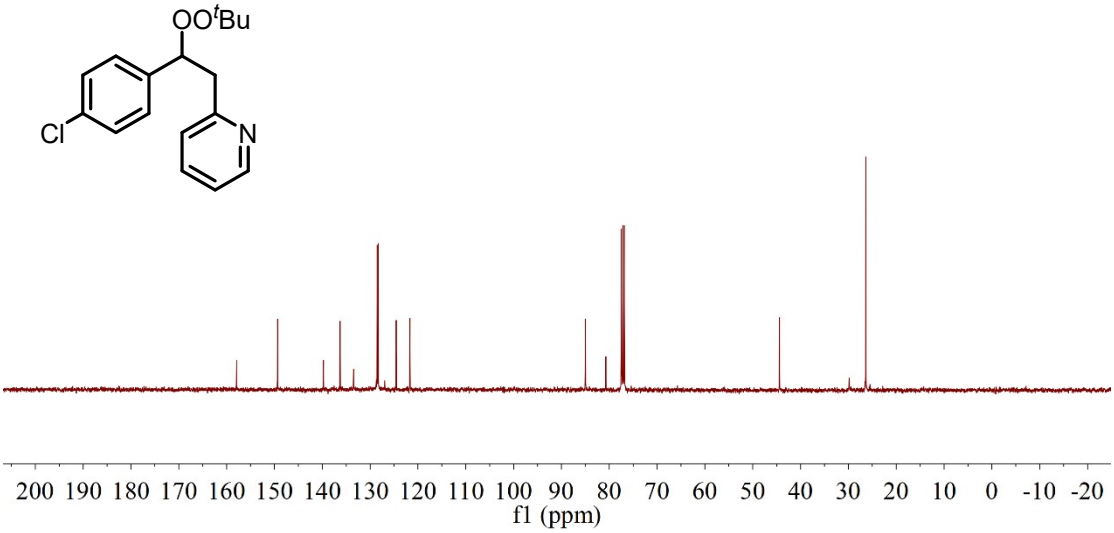
^{13}C NMR (100 MHz, $CDCl_3$)

2-(2-(tert-butylperoxy)-2-(4-chlorophenyl)ethyl)pyridine (4g)



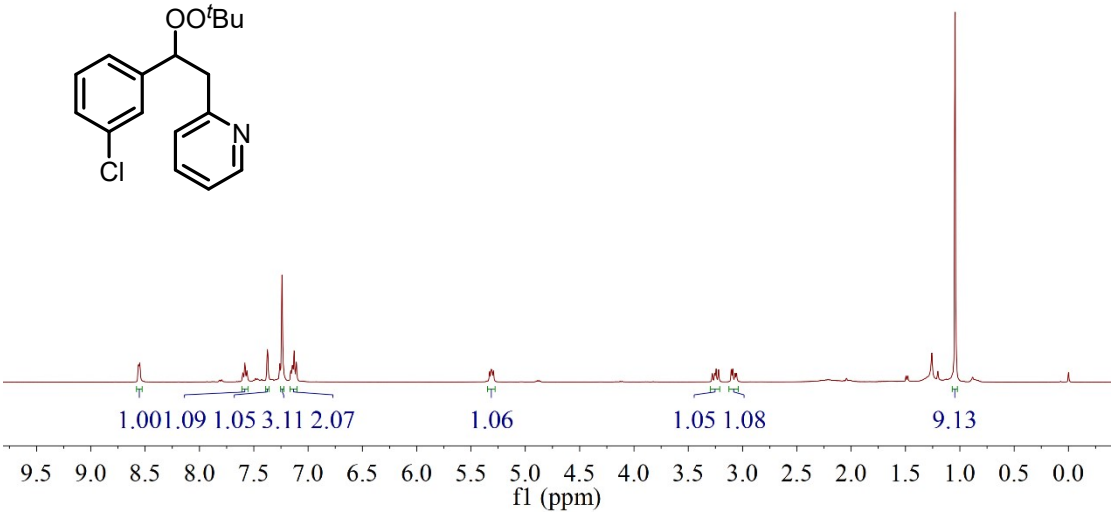
^{1}H NMR (400 MHz, $CDCl_3$)

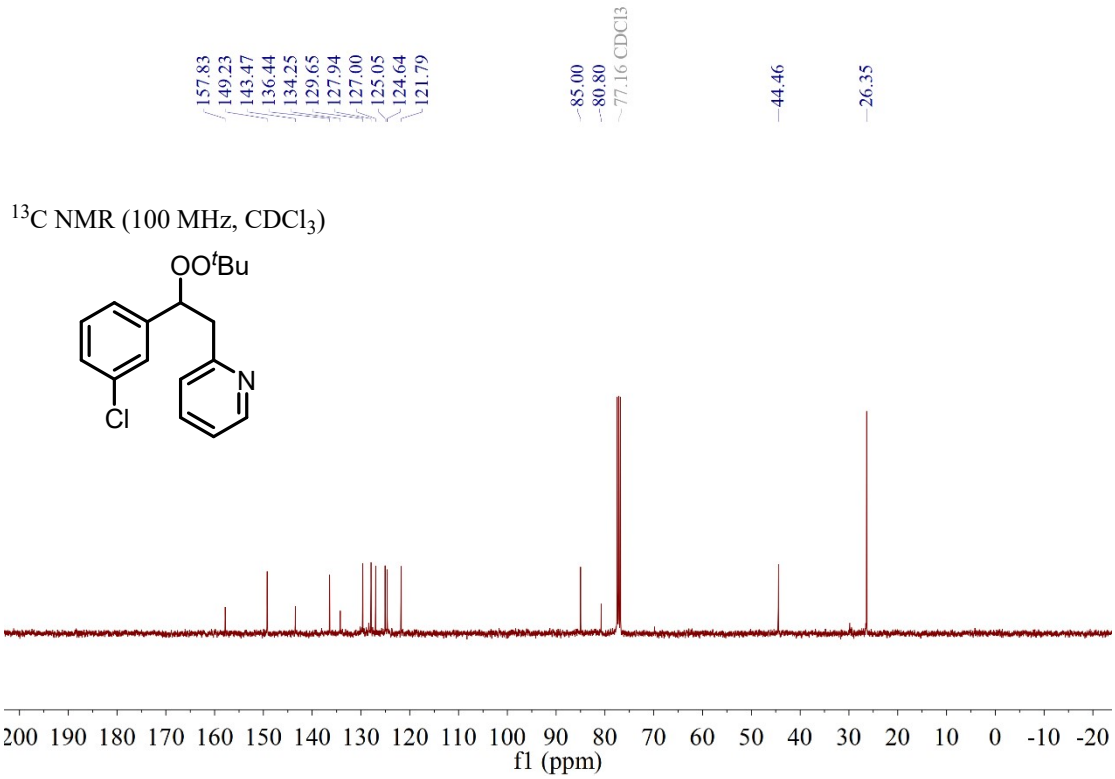
^{13}C NMR (100 MHz, $CDCl_3$)



2-(2-(tert-butylperoxy)-2-(3-chlorophenyl)ethyl)pyridine (4h)

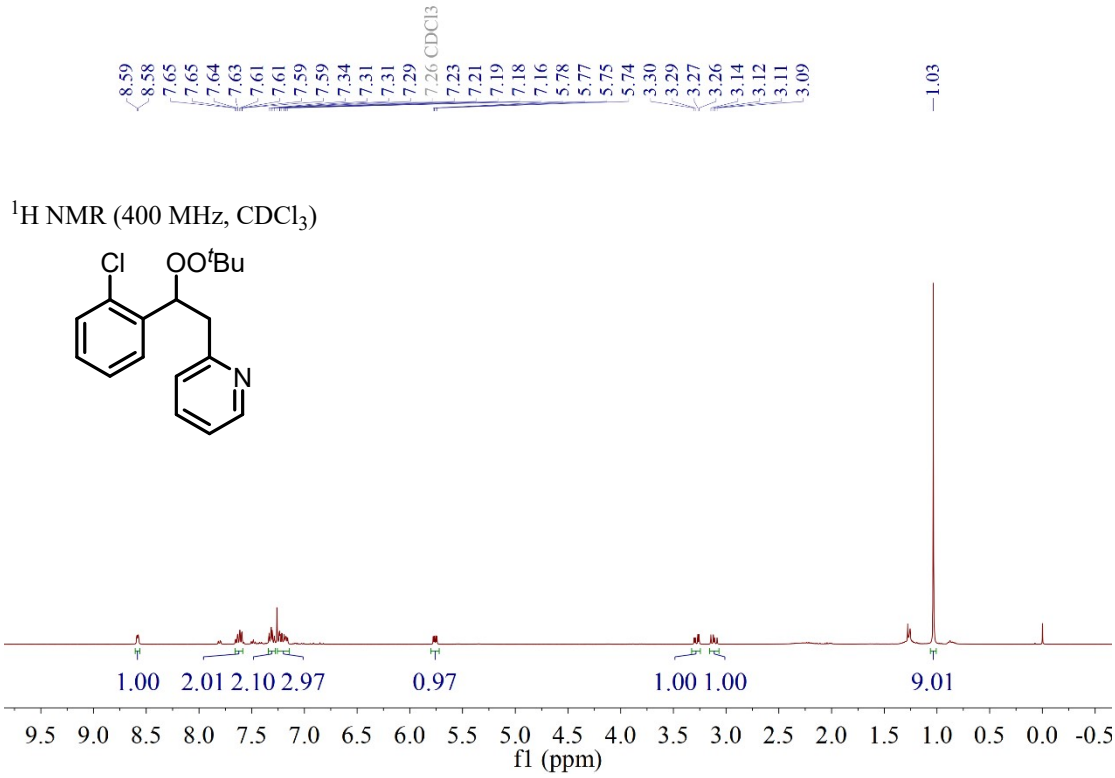
^1H NMR (400 MHz, $CDCl_3$)



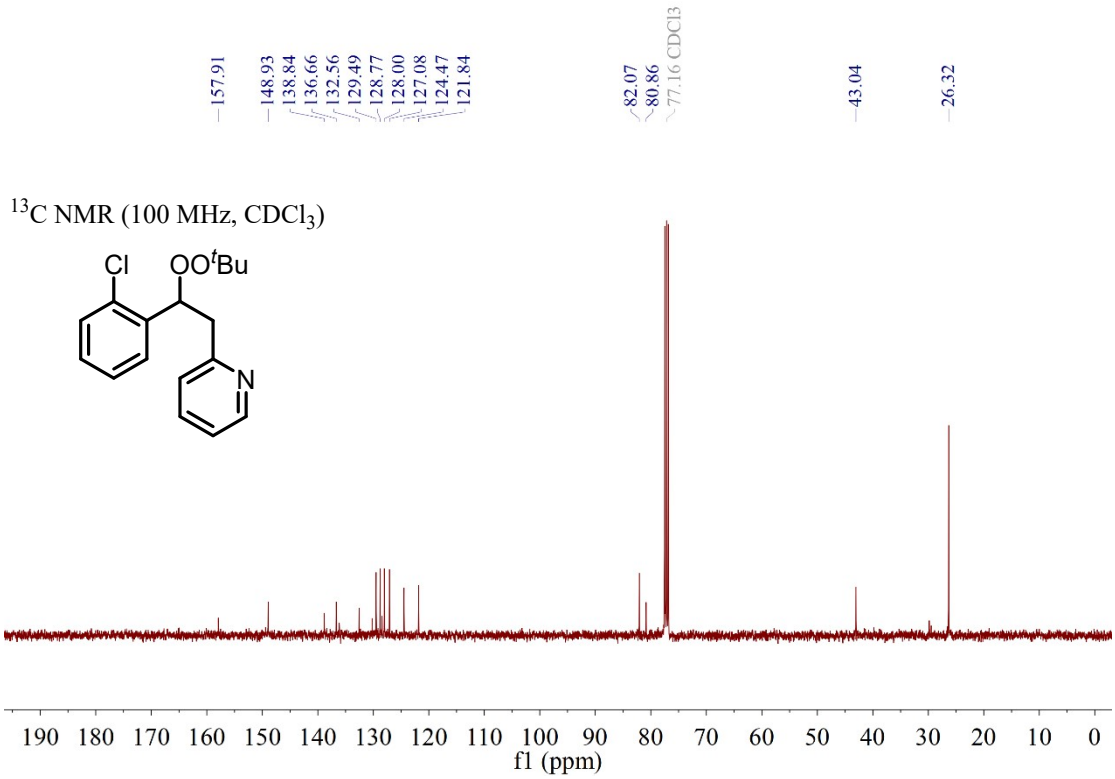


^{13}C NMR (100 MHz, $CDCl_3$)

2-(2-(tert-butylperoxy)-2-(2-chlorophenyl)ethyl)pyridine (4i)

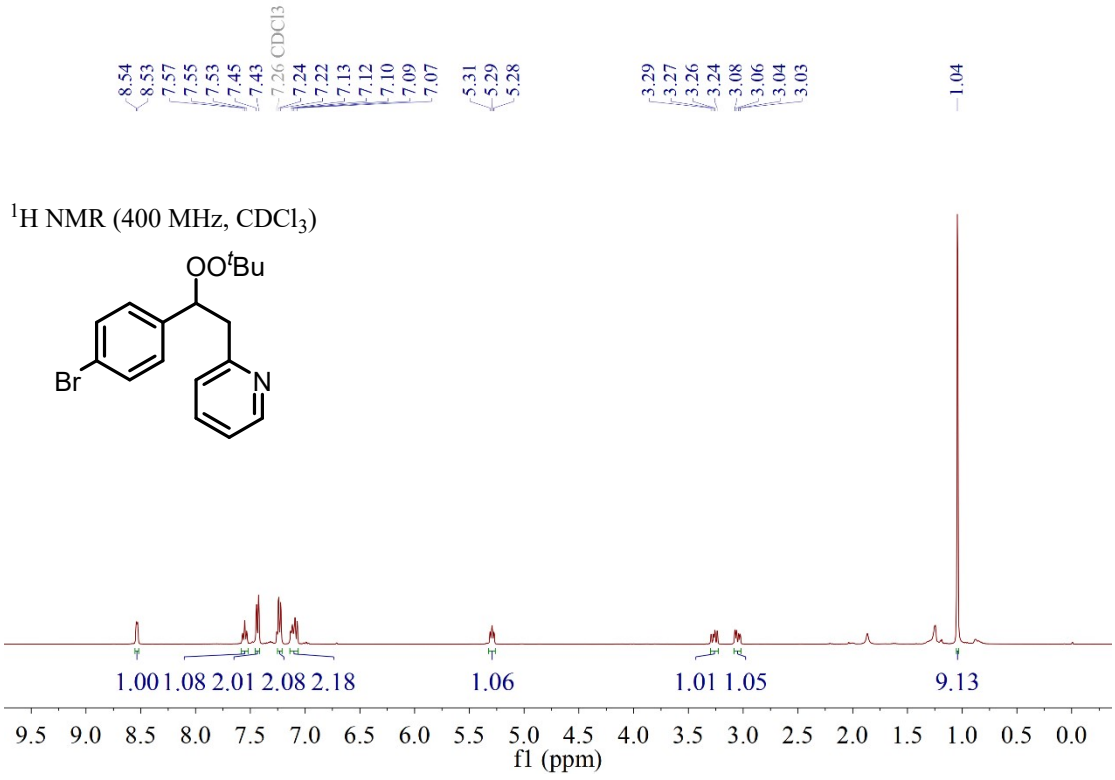


^{1}H NMR (400 MHz, $CDCl_3$)

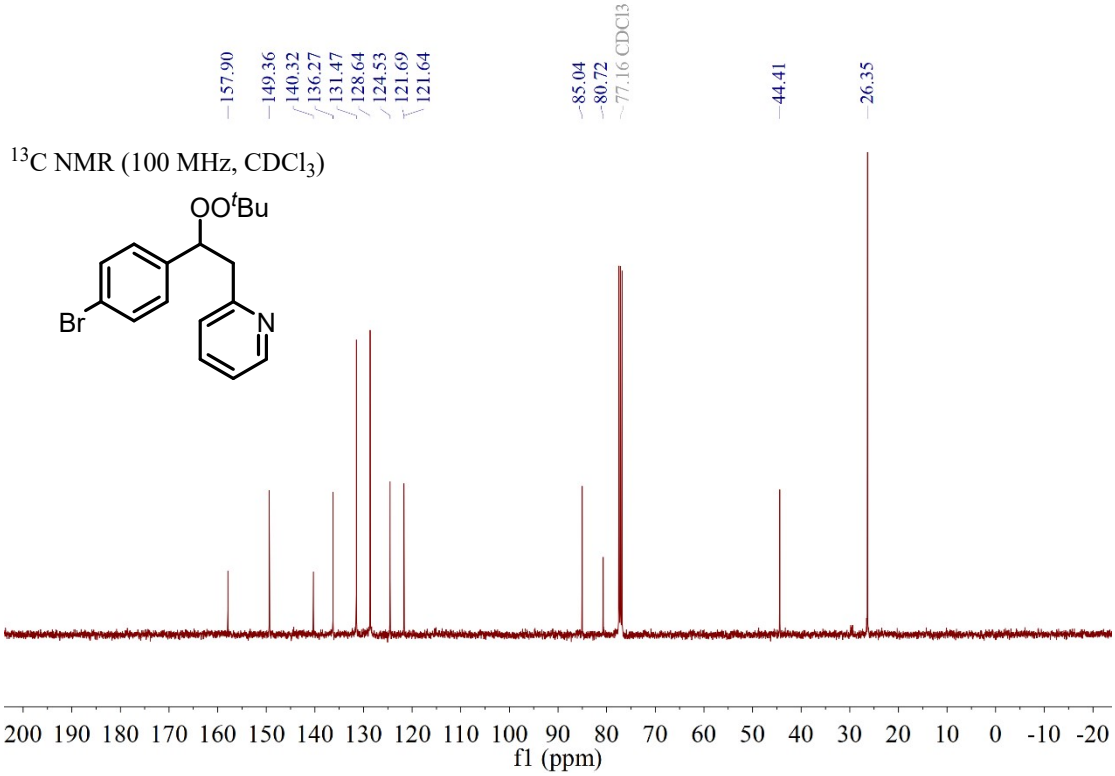


^{13}C NMR (100 MHz, $CDCl_3$)

2-(2-(4-bromophenyl)-2-(tert-butylperoxy)ethyl)pyridine (4j)

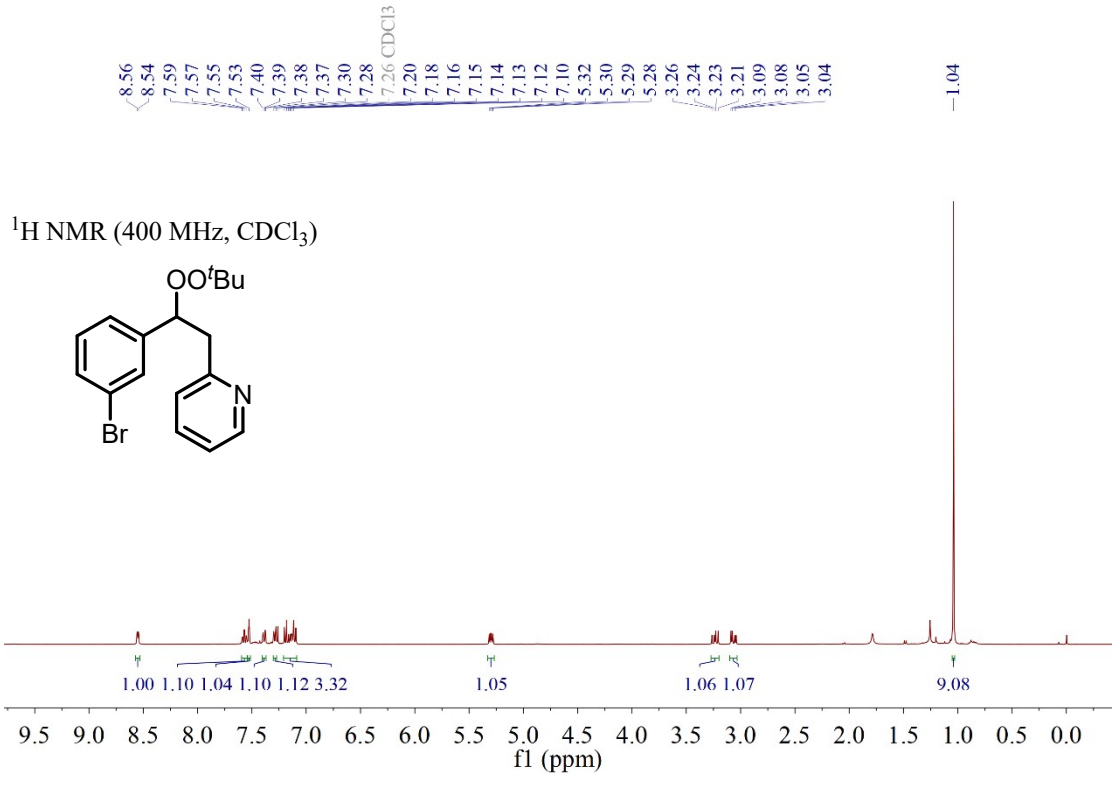


^{1}H NMR (400 MHz, $CDCl_3$)

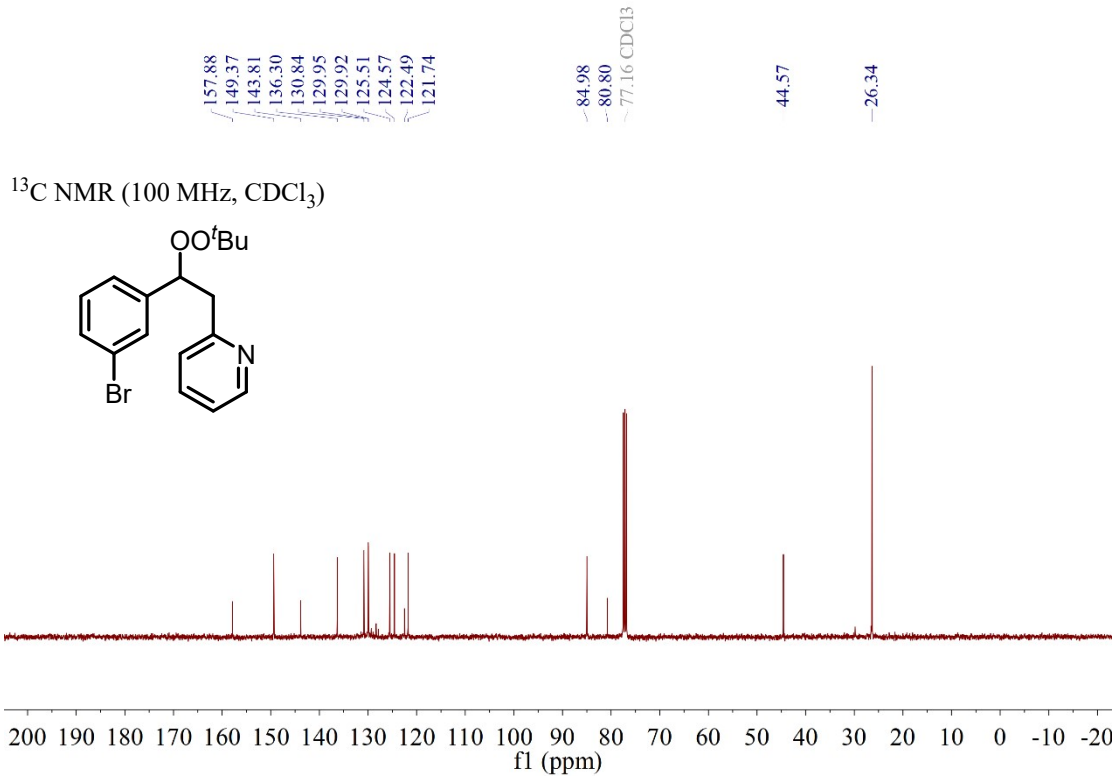


^{13}C NMR (100 MHz, $CDCl_3$)

2-(2-(2-bromophenyl)-2-(tert-butylperoxy)ethyl)pyridine (4k)

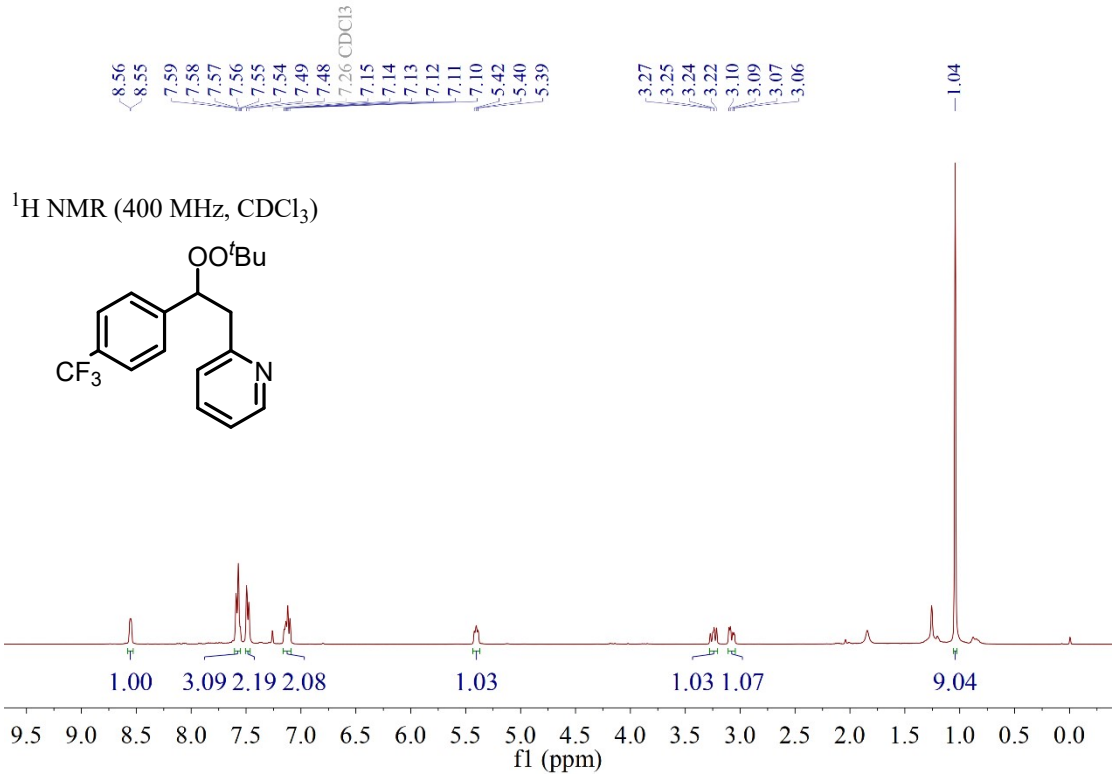


^{1}H NMR (400 MHz, $CDCl_3$)



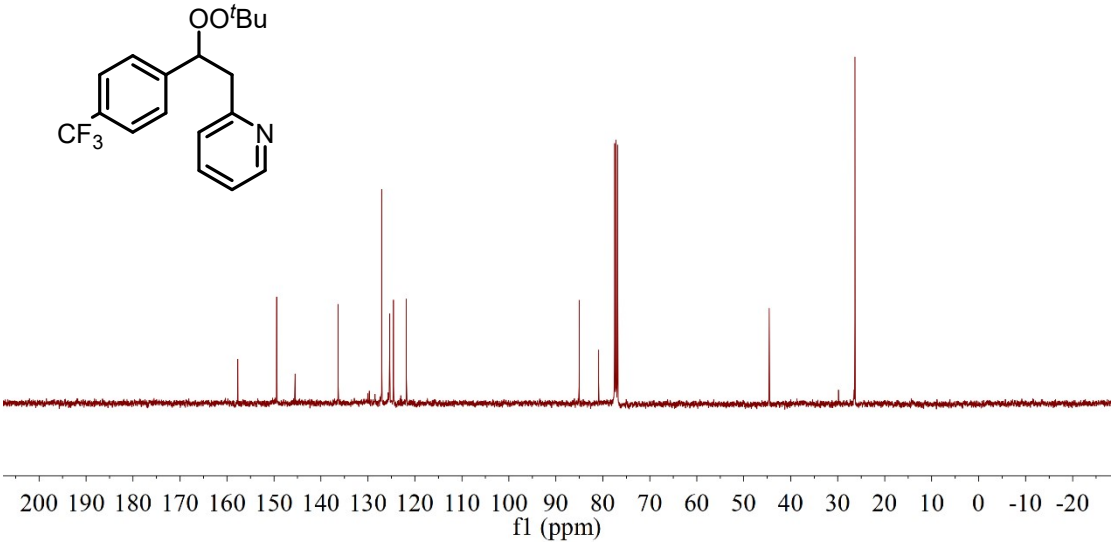
^{13}C NMR (100 MHz, $CDCl_3$)

2-(2-(tert-butylperoxy)-2-(4-(trifluoromethyl)phenyl)ethyl)pyridine (4l)



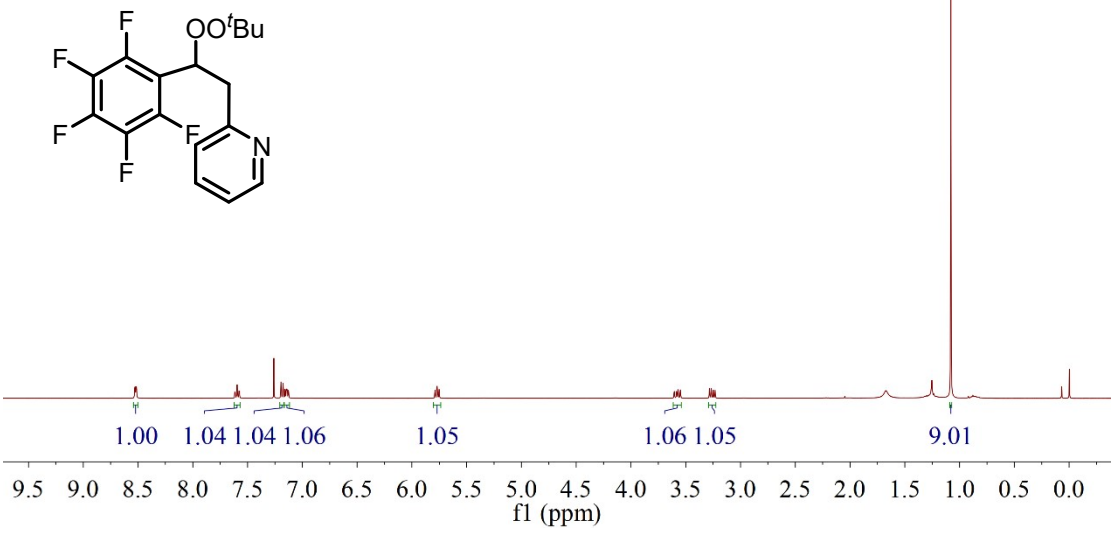
^{1}H NMR (400 MHz, $CDCl_3$)

^{13}C NMR (100 MHz, $CDCl_3$)

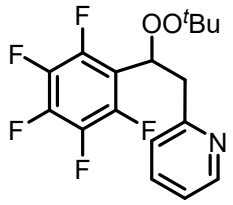


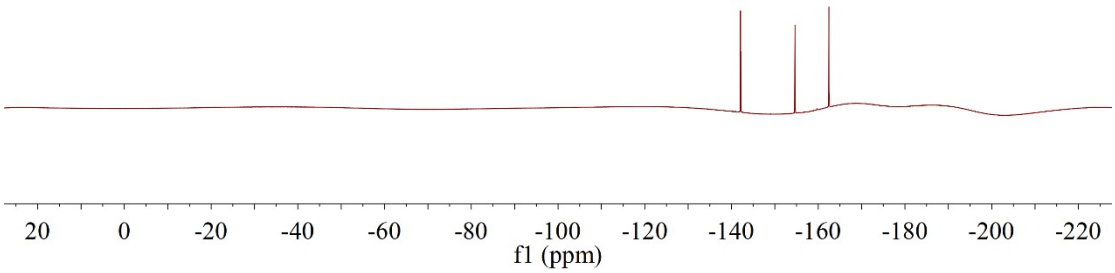
2-(2-(tert-butylperoxy)-2-(perfluorophenyl)ethyl)pyridine (4m)

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

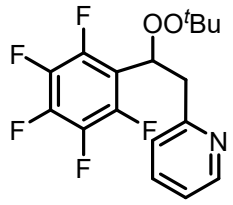


^{19}F NMR (376 MHz, $CDCl_3$)



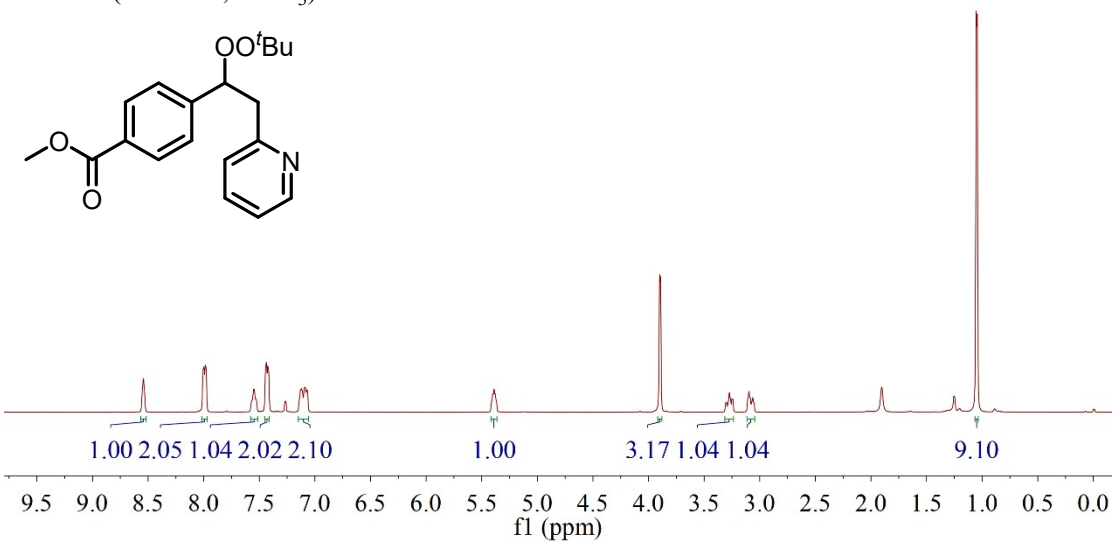


^{13}C NMR (100 MHz, $CDCl_3$)

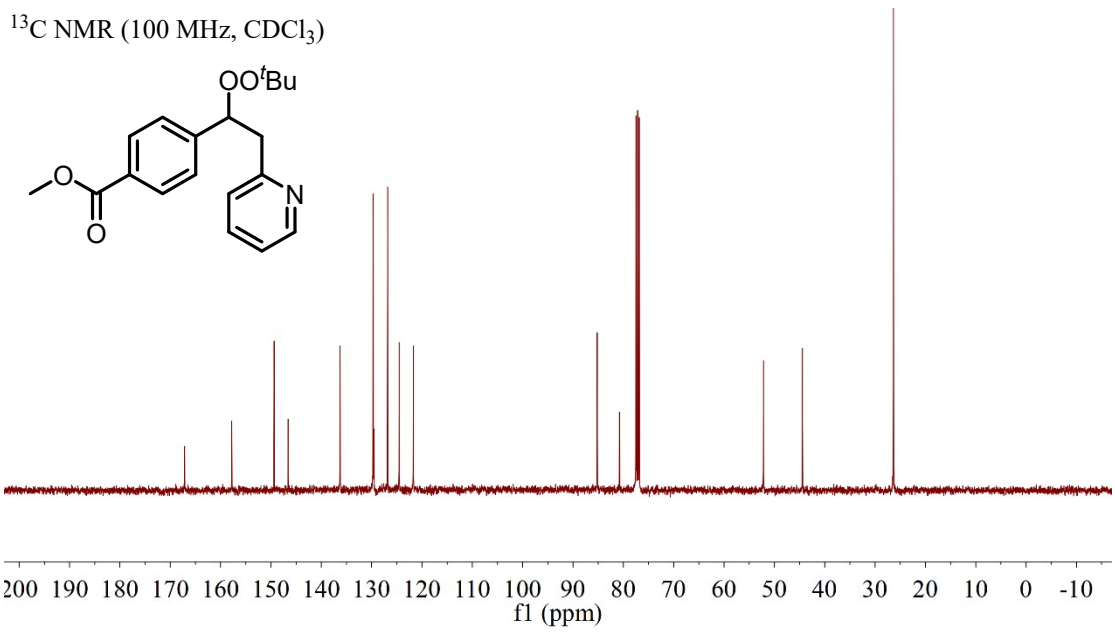


methyl 4-(1-(tert-butylperoxy)-2-(pyridin-2-yl)ethyl)benzoate (4n)

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

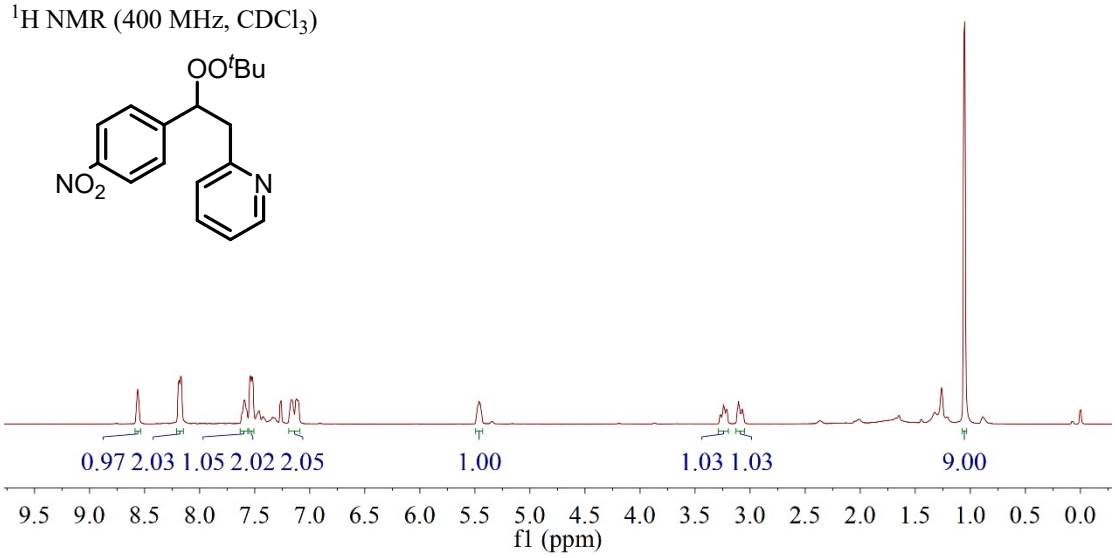


^{13}C NMR (100 MHz, $CDCl_3$)

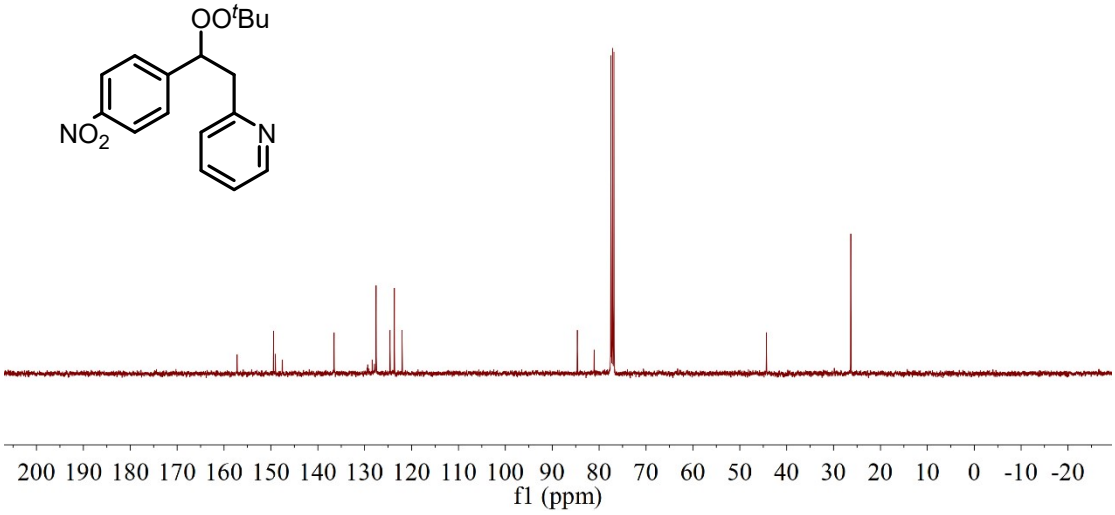


2-(2-(tert-butylperoxy)-2-(4-nitrophenyl)ethyl)pyridine (4o)

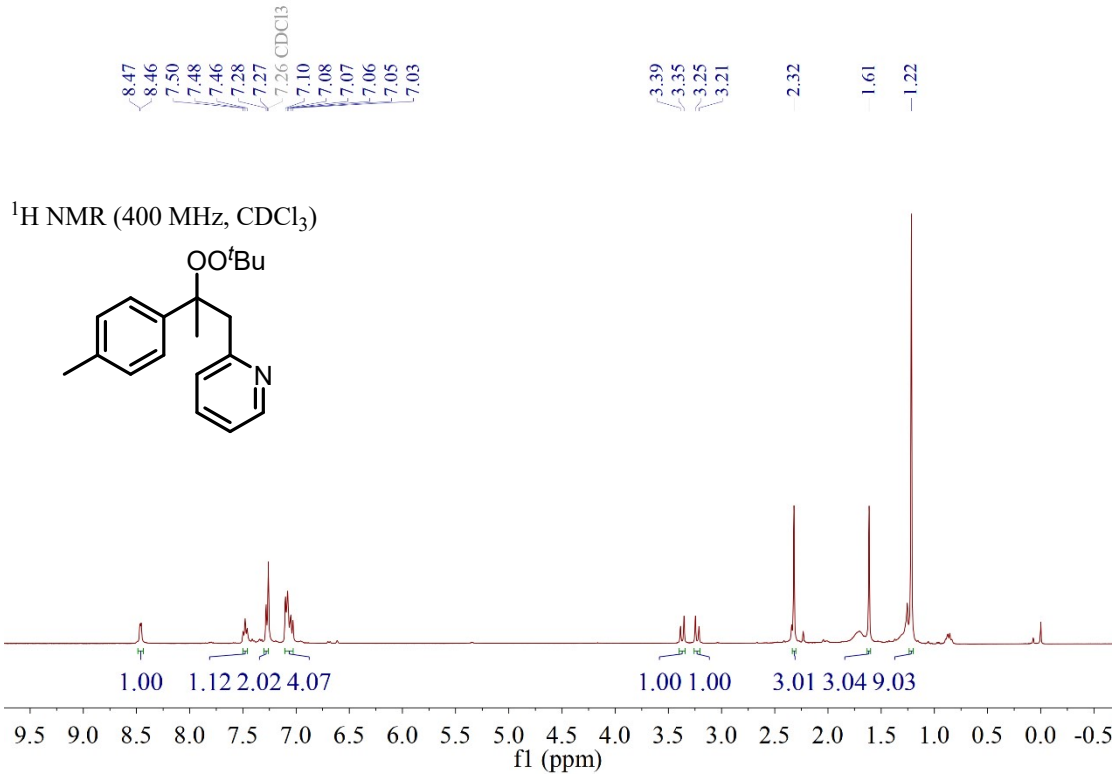
^{1}H NMR (400 MHz, $CDCl_3$)



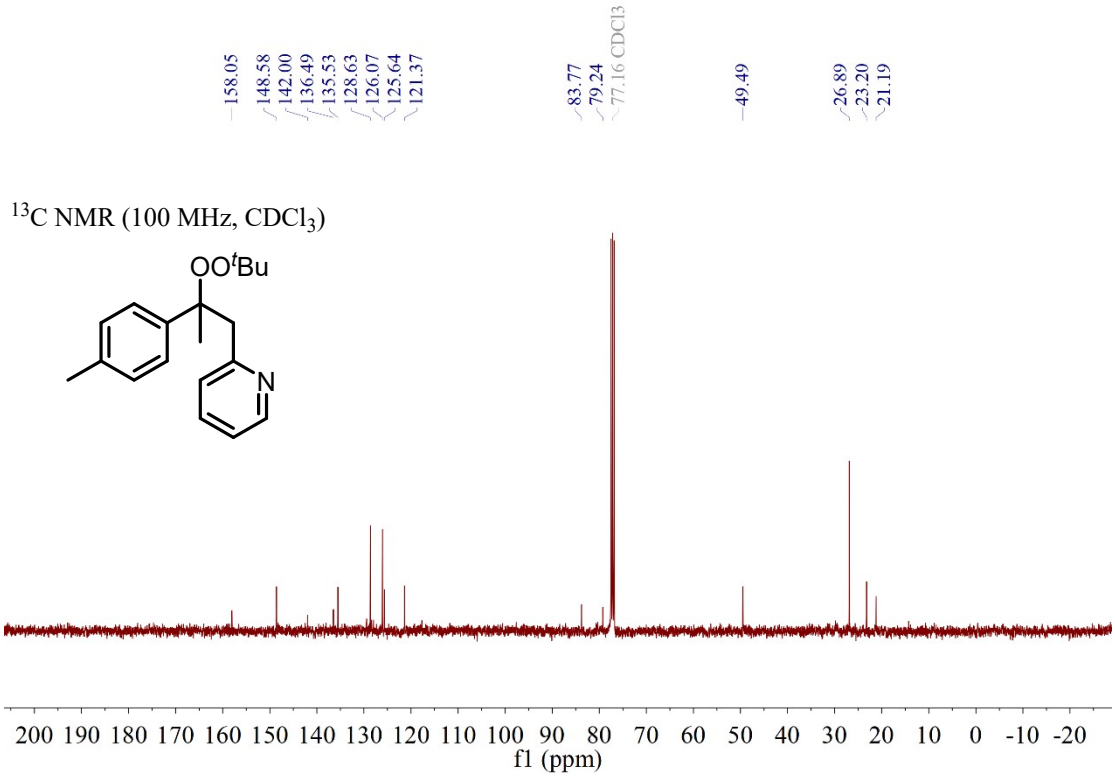
^{13}C NMR (100 MHz, $CDCl_3$)



2-(2-(tert-butylperoxy)-2-(p-tolyl)propyl)pyridine (4p)

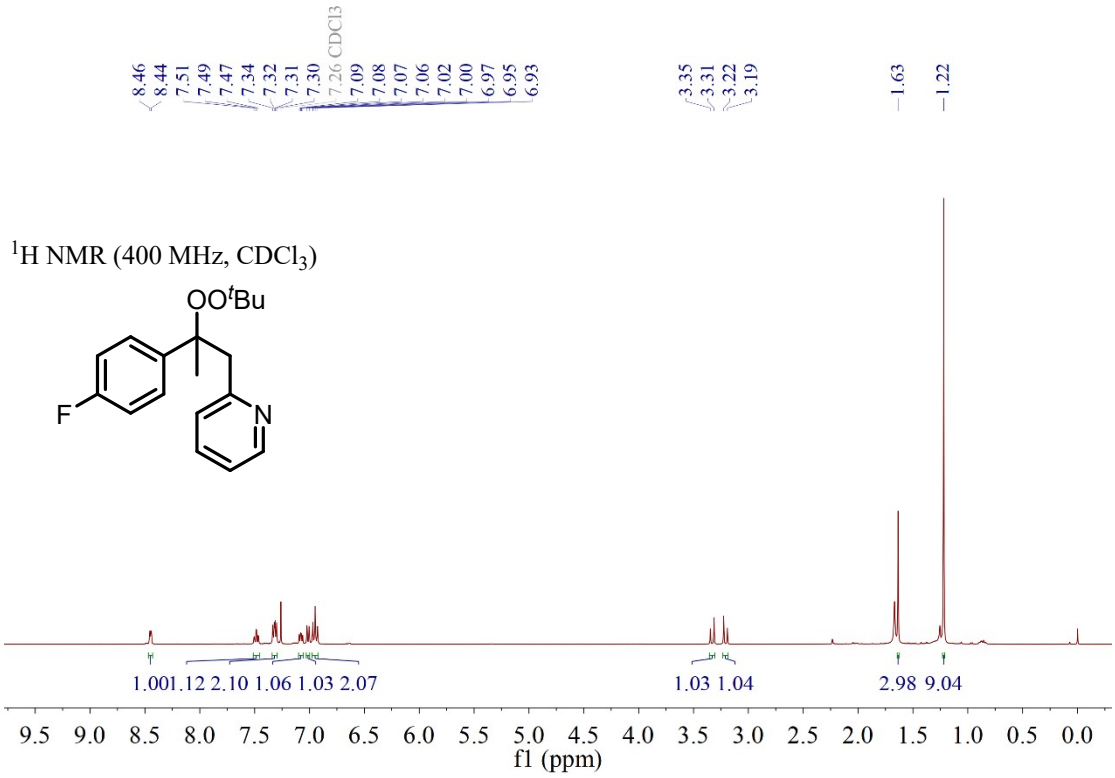


^{1}H NMR (400 MHz, $CDCl_3$)

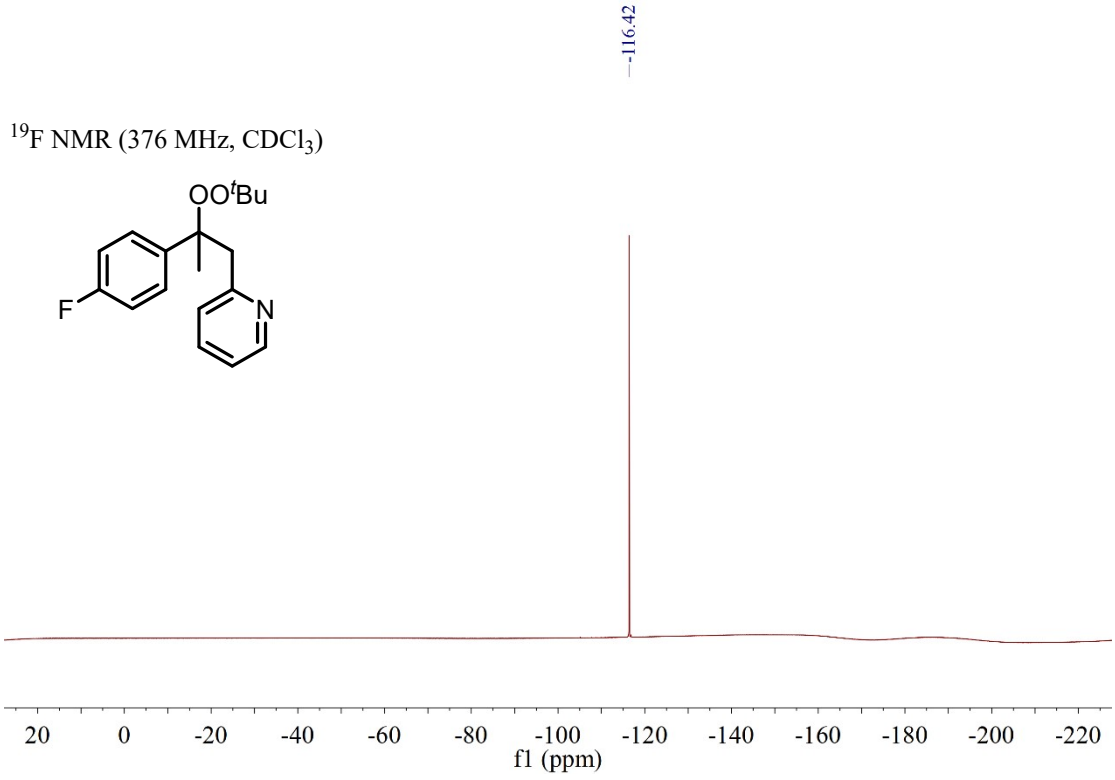


^{13}C NMR (100 MHz, $CDCl_3$)

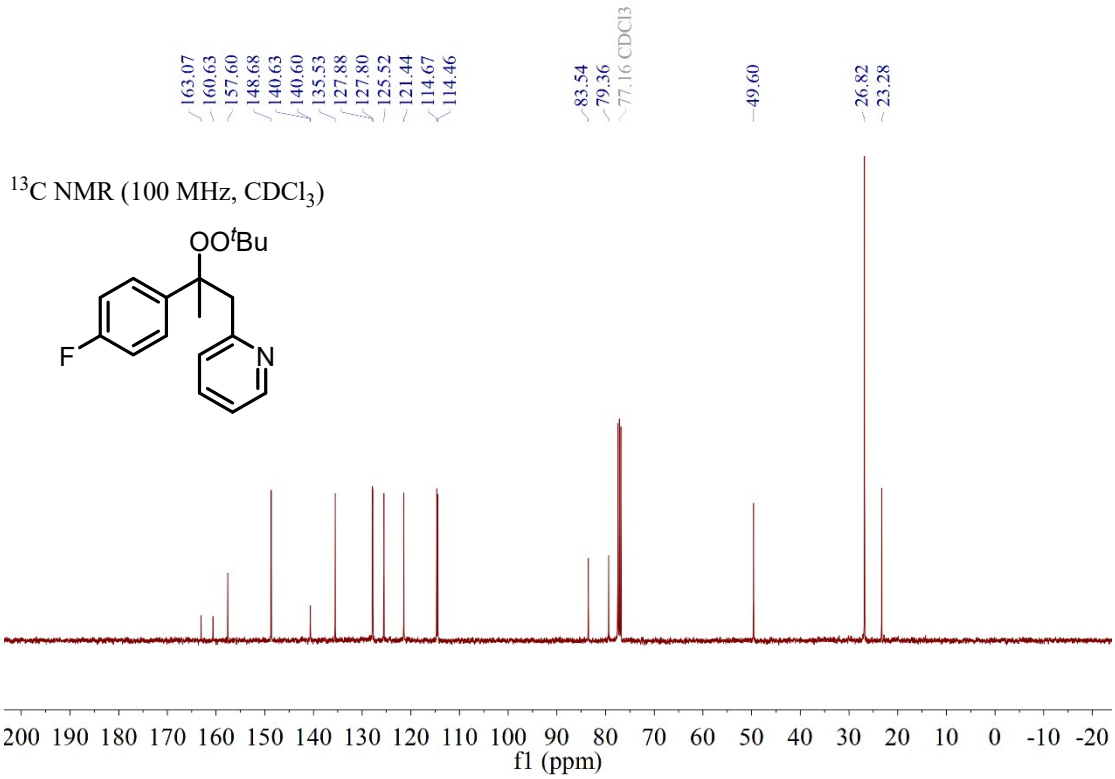
2-(2-(tert-butylperoxy)-2-(4-fluorophenyl)propyl)pyridine (4q)



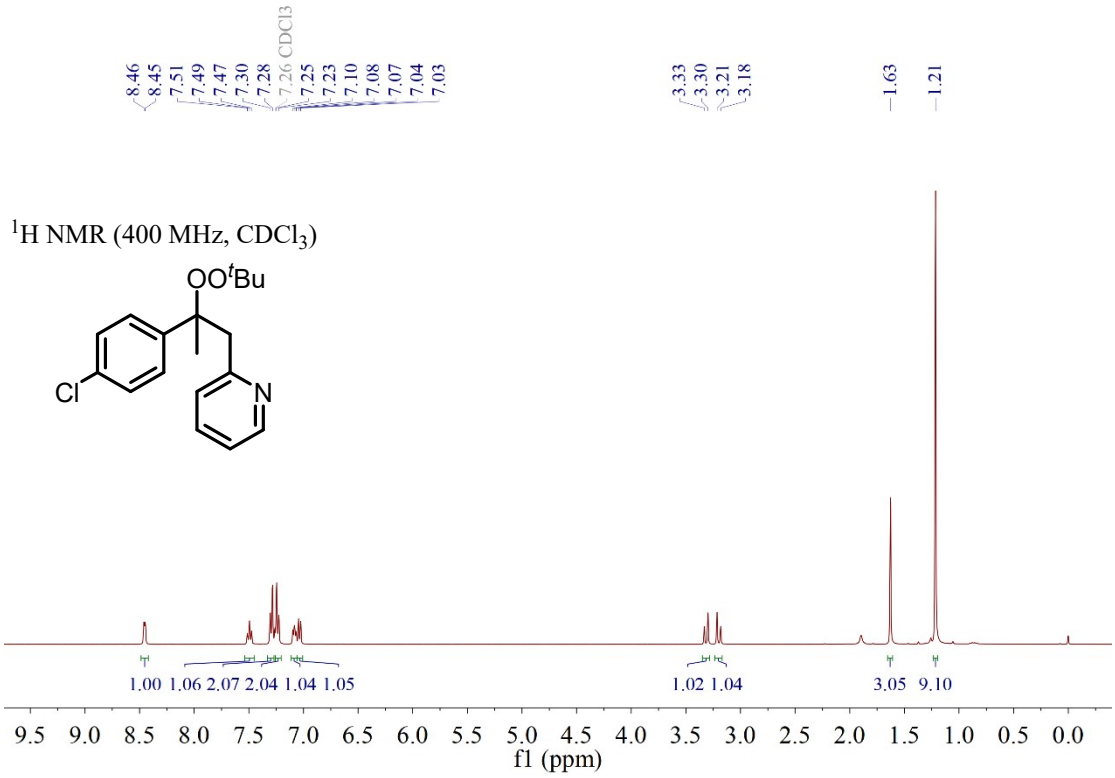
^{1}H NMR (400 MHz, $CDCl_3$)

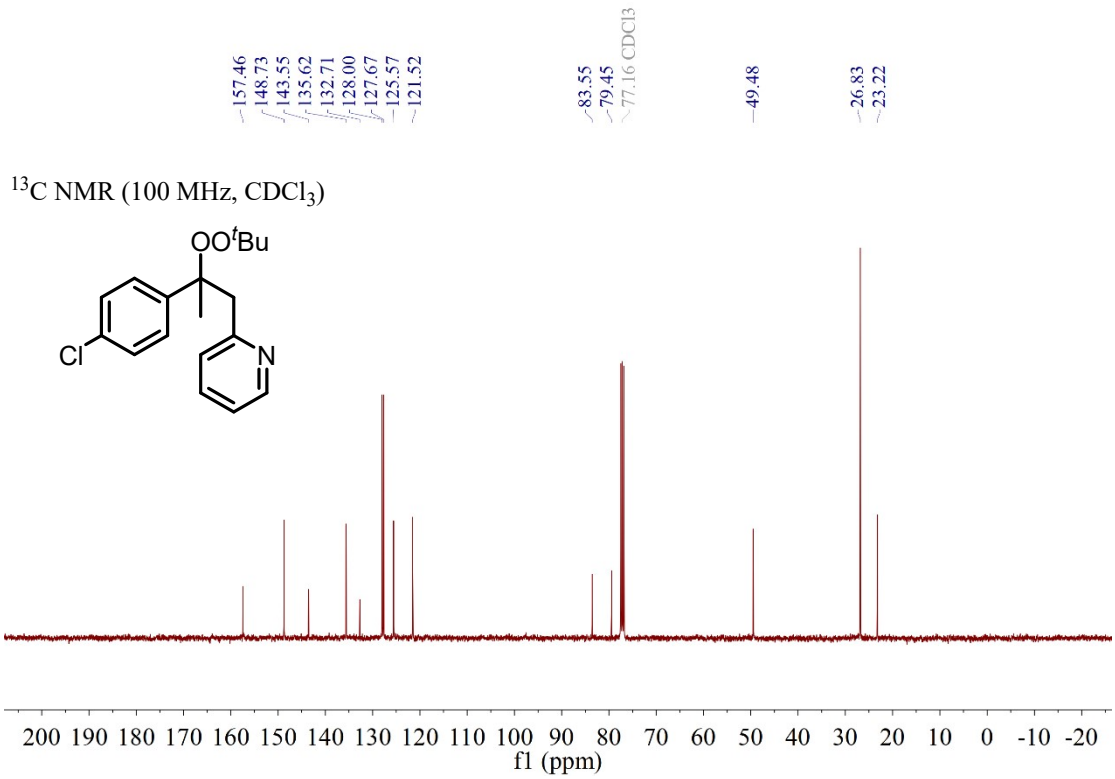


^{19}F NMR (376 MHz, $CDCl_3$)



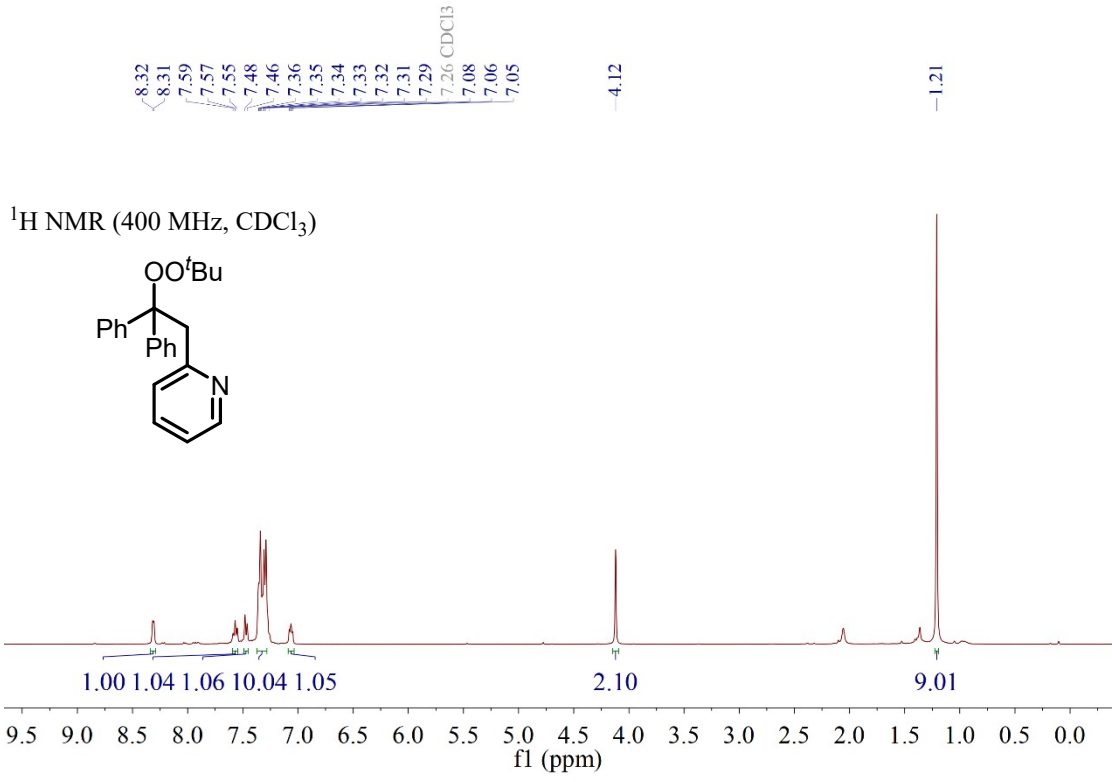
2-(2-(tert-butylperoxy)-2-(4-chlorophenyl)propyl)pyridine (4r)





^{13}C NMR (100 MHz, $CDCl_3$)

2-(2-(tert-butylperoxy)-2,2-diphenylethyl)pyridine (4s)



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

^{13}C NMR (100 MHz, $CDCl_3$)