Supporting information for

Visible-Light-Induced α-Oxyamination of 1,3-Dicarbonyls with TEMPO via a Photo(electro)catalytic Process Applying DSSC Anode or in DSSC System

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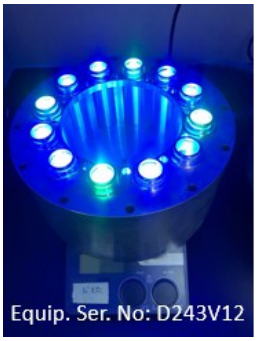
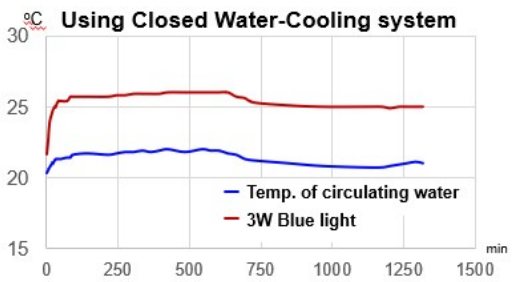
Contents:

1. General information

All reactions were performed using quartz tube. Solvents were dried and degassed by standard methods before they were used. 1,3-Dicarbonyls (**1a, 1r-1u**) were purchased from commercial suppliers and used without further purification, 1,3-Dicarbonyls (**1b-1q, 1v-1w, 1z**) were synthesized according to the method in the literature.[1] Contaminants of the fluorine-doped SnO_2 (FTO) conducting glass (7 ohm/sq, Xiang Science & Technology, or 7 ohm/sq, GOLUO glass) were removed by washing with deionized water, acetone and ethanol tree times, for 15 minutes each wash. Drying with Ar. TiO_2 film (9.45 μm to 9.6 μm) was deposited on fluorine doped tin oxide (FTO) glass (1mm * 7mm, thickness, ~ 9.5 μm, particle size, ~ 20 nm) by the doctor-blade method.[2] Nanocrystalline TiO_2 electrodes were sensitized with 0.32 mM N719 [(isothiocyanato)-bis(2,2'-bipyridyl-4,4'-dicarboxylato)ruthenium(II)bistetrabutyl-ammonium] in a mixture of isopropyl alcohol and acetonitrile (1 : 1, v / v) under dark for 12 hours.[3] Silica gel was purchased from Qing Dao Hai Yang Chemical Industry Co. ^{1}H NMR spectra was recorded on a Bruker DPX-400 (400 MHz) spectrometer with deuteraterated chloroform as solution, the chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. ^{13}C NMR spectra was recorded at 100 MHz on Bruker DPX-400. The chemical shifts δ are reported relative to residual $CHCl_3$ (δc = 77.00 ppm). The multiplicity of signals is designated by the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd = doublet of doublet. Coupling constants *J* are reported in Hertz (Hz). High resolution mass spectra (HRMS) were obtained on an Agilent LC-MSD-Trap-XCT spectrometer with micromass MS software using electrospray ionisation (ESI). The UV/VIS Absorption spectra was recorded using a Perkin Elmer Lambda 35 Spectrometer and a Cary 5000 UV-VIS-NIR spectrometer. The Cyclic voltammetry (CV) was recorded in CH_3CN by CHI660E. The Luminescence Quenching Experiments were recorded using a F-4500 FL Spectrophotometer in CH_3CN. Thickness of film measured by Bruker Dektak XT. X-Ray powder diffraction (XRD) patterns were recorded using an X-ray Diffractometer (X' Pert PRO) at a scan rate of 3 ^{o} min^{-1} by using $Cu_{K\alpha}$ radiation. Imaging of the samples was carried out by using a FEI Quanta 250 FEG scanning electron microscope. The SEM samples were platinum coated prior to examination. The LCD Digital Hotplate Magnetic Stirrer MS-H-Pro+ was purchased from Dragon Laboratory Instruments Limited. All reactions were carried out with photoreactor (Serial No: D243V12) which was purchased from LUOYANG JINFENG ELECTROMECHANICAL EQUIPMENT CO., LTD.





2. General procedure for the synthesis of product 3

1) General procedure for α-oxyaminated carbonyl compounds

1,3-Dicarbonyls (0.05 mmol), TEMPO (0.1 mmol), N719-sensitized TiO_2/FTO (N719/TiO_2 = 1.12×10^{-2} : 5×10^{-1} equiv.) or TiO_2/FTO (0.5 equiv.) and CH_3CN (1 mL) was kept at room temperature under blue LED lamp (3 W) for 48 or 36 hours. The reaction mixture was purified by chromatography on silica gel (elute: EtOAc / Petroleum ether 1 / 5-1 / 10, v / v) to give the desired product.

2) Reuse of photoanode

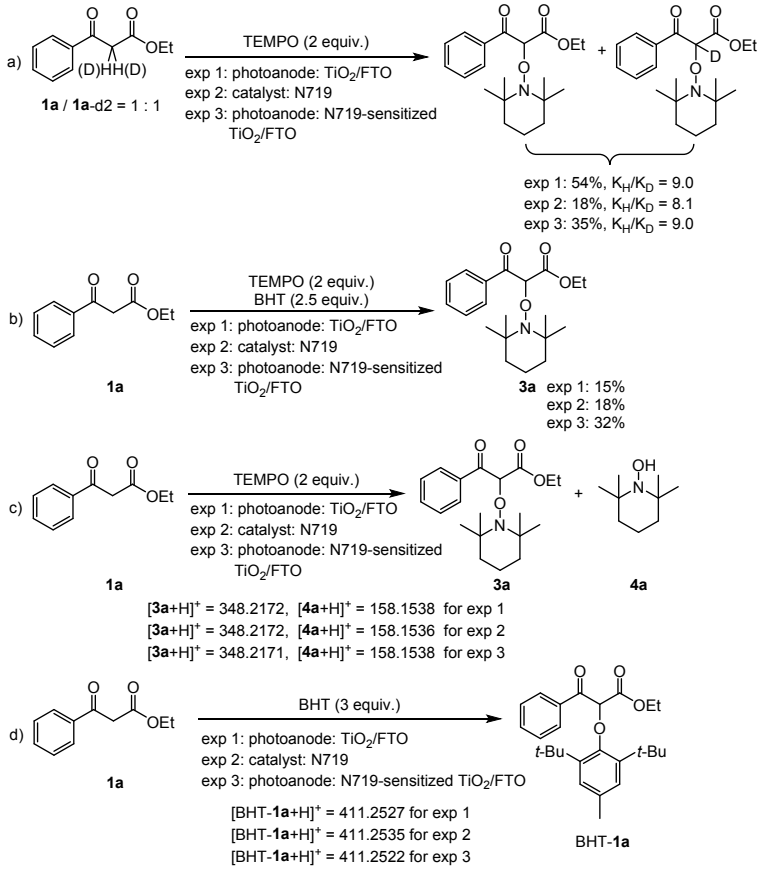
The reaction procedure is as mentioned above for synthesis α-oxyaminated carbonyls. After the completion of the reaction, the N719-sensitized TiO_2/FTO or TiO_2/FTO was separated from the reaction mixture, and was applied to the next run after cleaning with CH_2Cl_2 (3 x 0.5 mL). The product was quantitatively analyzed by NMR using mesitylene as the internal standard.

3) Photoelectrocatalytic procedure

N719-sensitized TiO_2/FTO (N719/TiO_2 = 5.6×10^{-3} : 2.5×10^{-1} equiv.) or TiO_2/FTO (0.25 equiv.) photoanode, benzoylacetate (0.05 mmol), TEMPO (0.1 mmol), Pt/$TBAPF_6$ (0.1 M or not) and CH_3CN (1.5 mL) was kept at room temperature under blue LED lamp (3 W) for 22 hours. The product was quantitatively analyzed by NMR using mesitylene as the internal standard.

3. Control Experiments

Scheme S1. Control experiments.



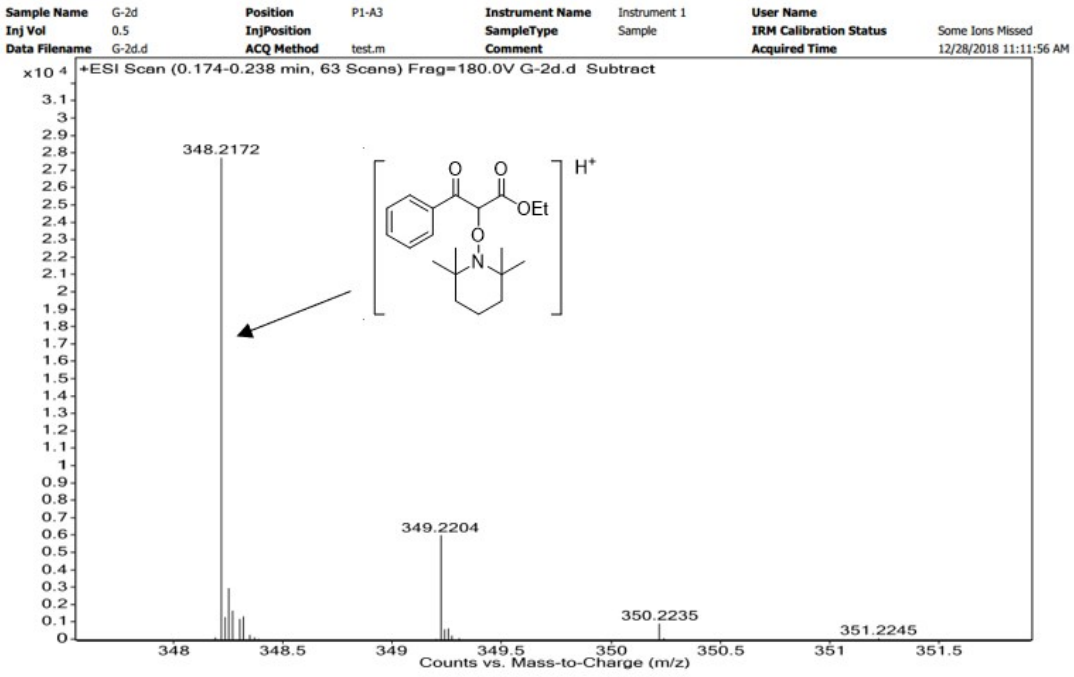


Figure S1 HRMS spectrum of compound [**3a**+H]$^+$ for exp 1

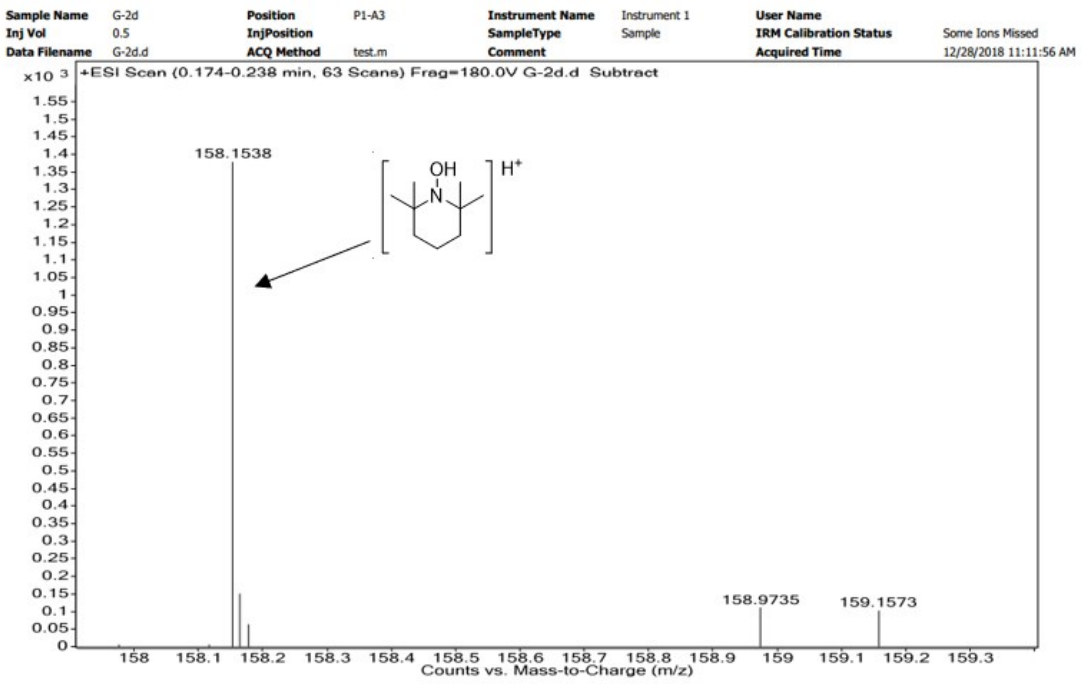


Figure S2 HRMS spectrum of compound [**4a**+H]$^+$ for exp 1

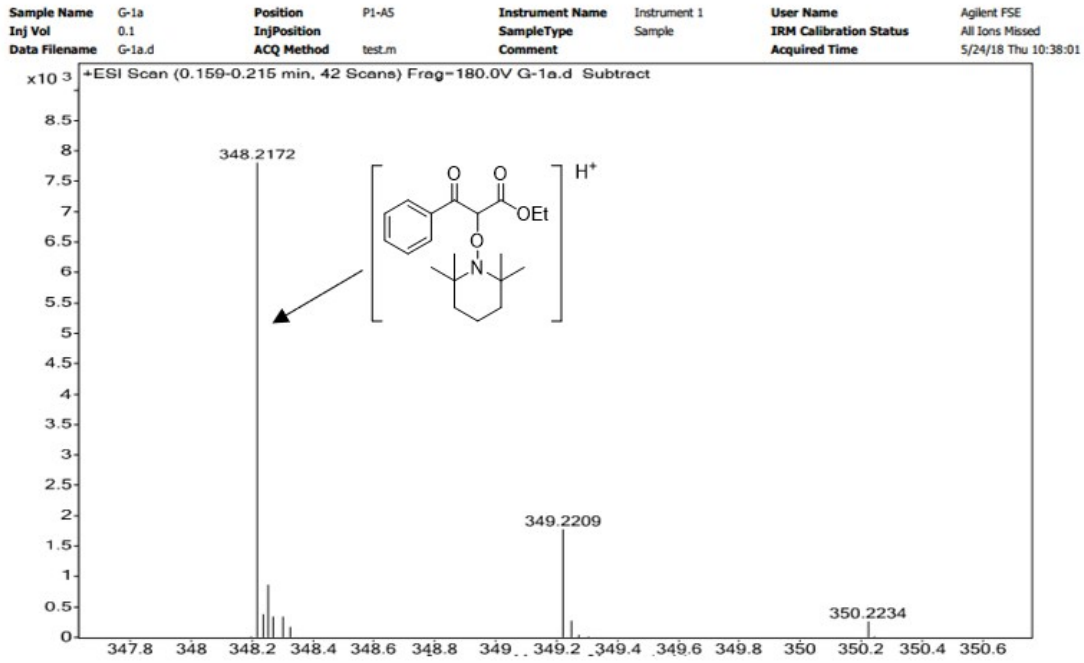


Figure S3 HRMS spectrum of compound [**3a**+H]$^+$ for exp 2

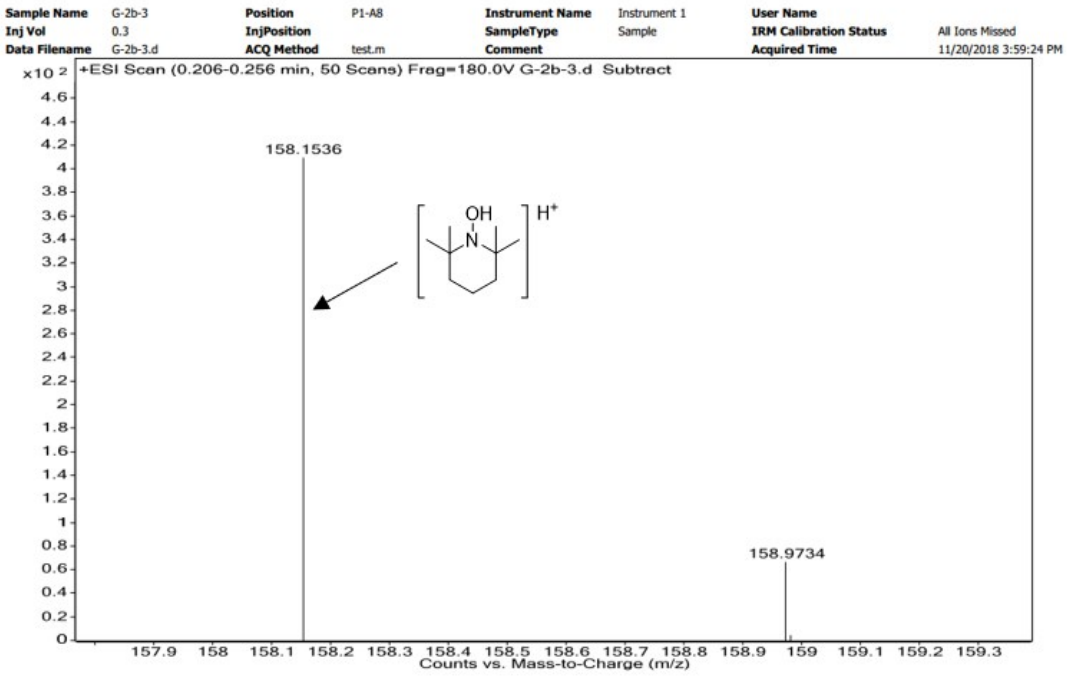


Figure S4 HRMS spectrum of compound [**4a**+H]$^+$ for exp 2

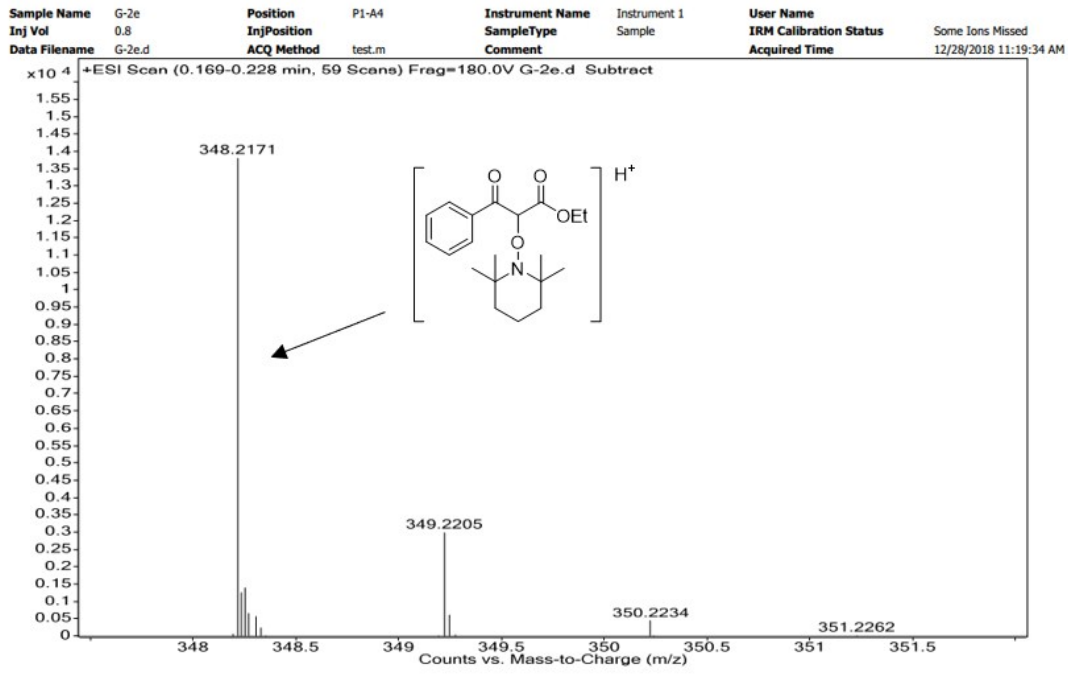


Figure S5 HRMS spectrum of compound [**3a**+H]$^+$ for exp 3

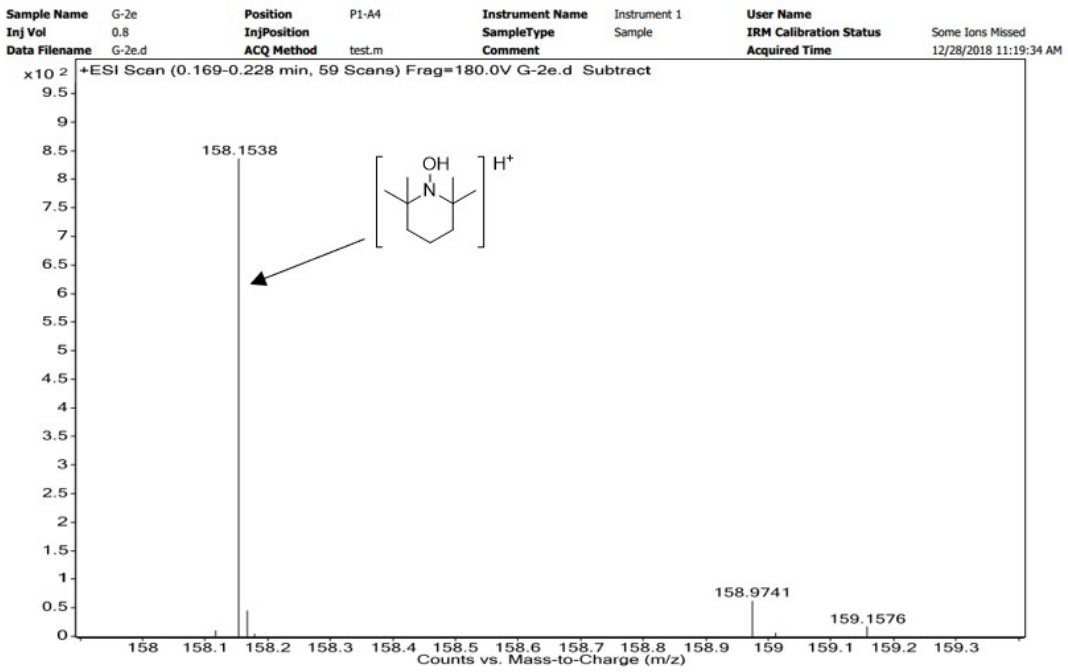


Figure S6 HRMS spectrum of compound [**4a**+H]$^+$ for exp 3

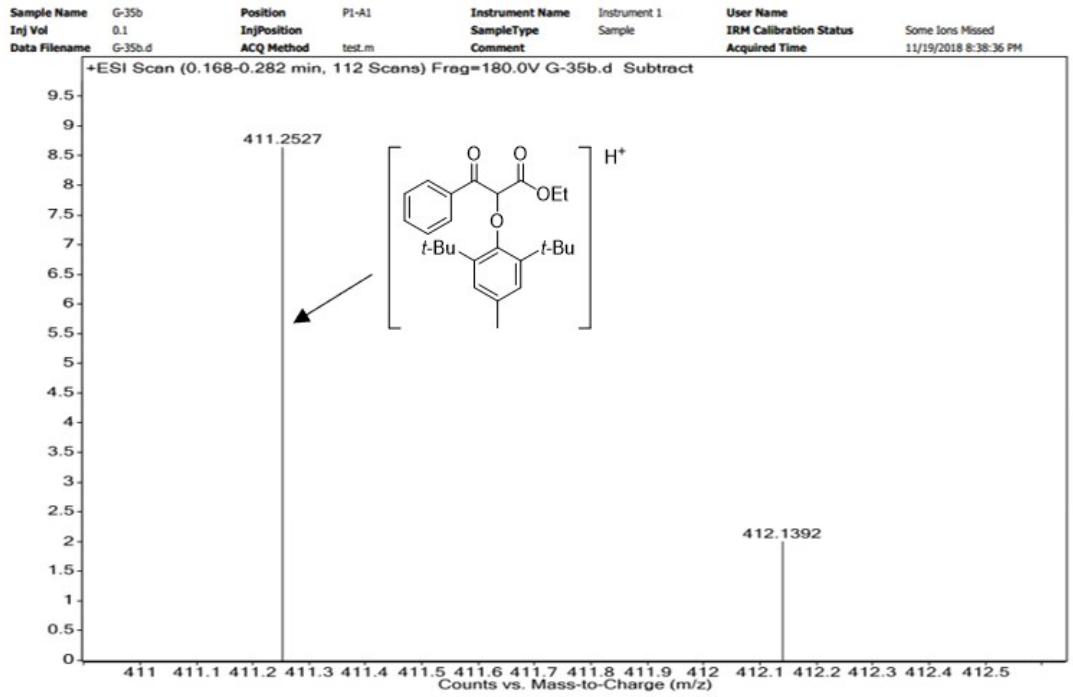


Figure S7 HRMS spectrum of compound [BHT-**1a**+H]$^+$ for exp 1

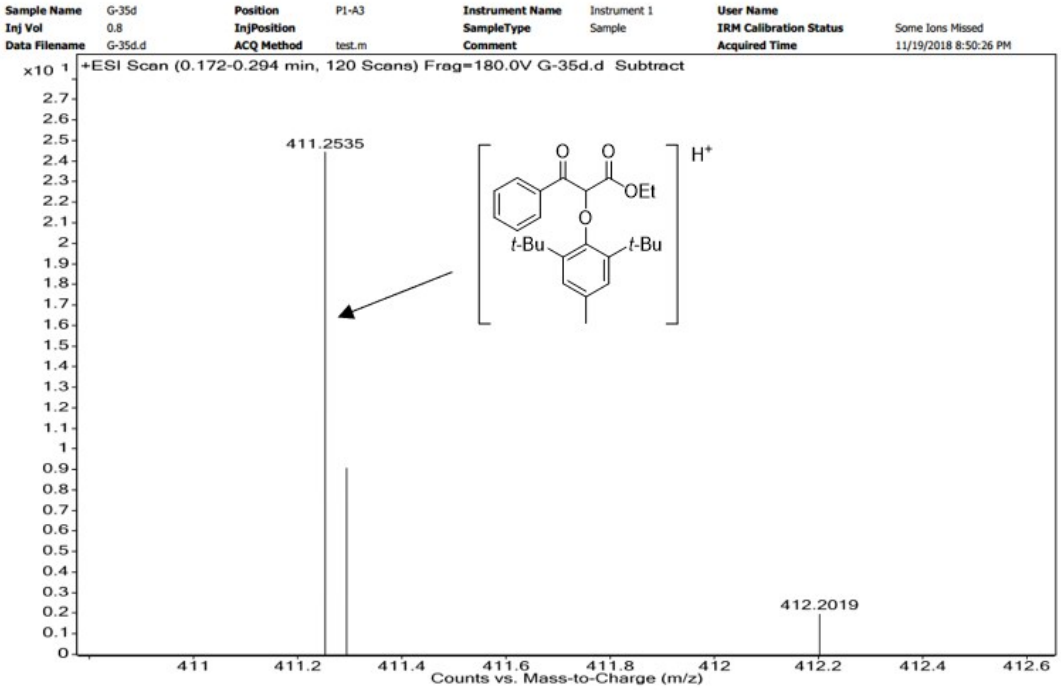


Figure S8 HRMS spectrum of compound [BHT-**1a**+H]$^+$ for exp 2

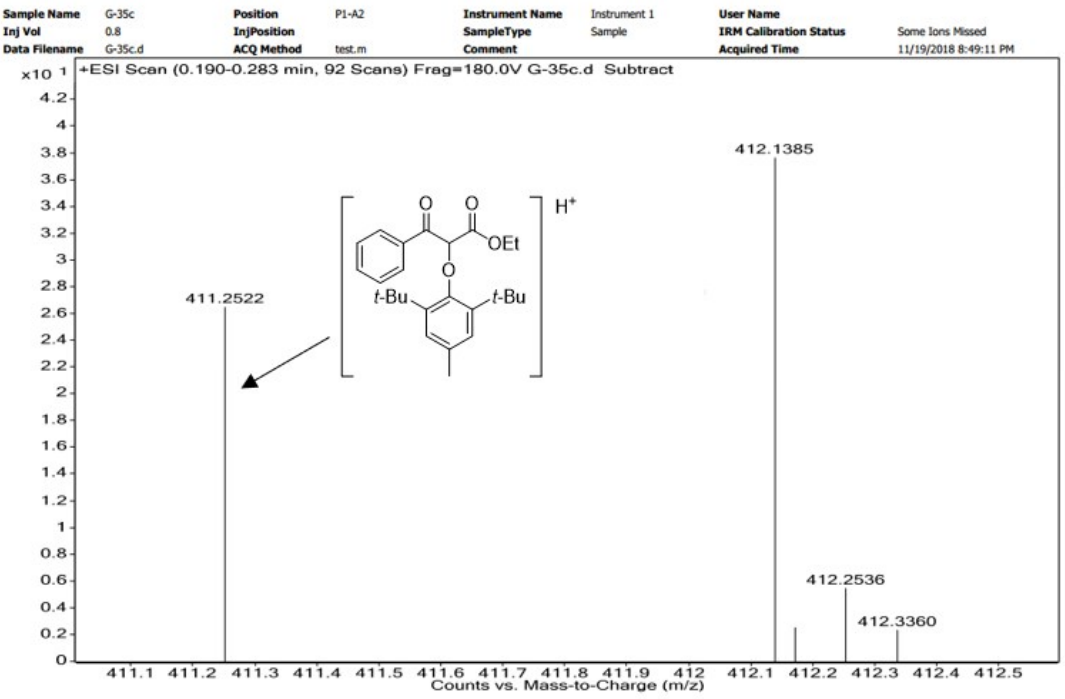
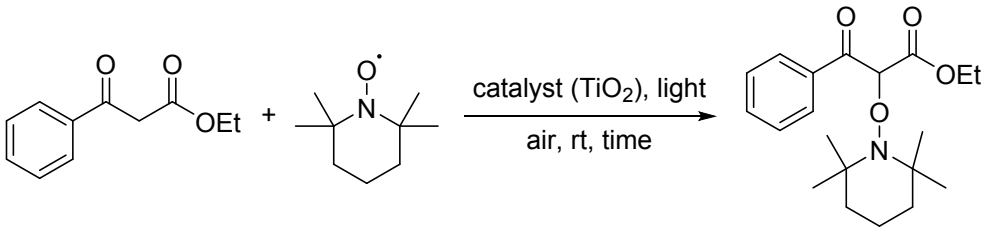


Figure S9 HRMS spectrum of compound [BHT-**1a**+H]$^+$ for exp 3

Scheme S2. Optimization of the reaction conditions[a].



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

entry	light	TiO_2[b]	time	Yield[c] %
1	Blue	0.25 equiv.	48	69
2	Blue	0.5 equiv.	48	99
3	Blue	0.5 equiv.	36	99
4	Green	0.5 equiv.	36	17
5	Orange	0.5 equiv.	36	NR[d]
6	Red	0.5 equiv.	36	NR[d]
7	White	0.5 equiv.	36	29
8	Blue	--	48	NR[d]
9	--	0.5 equiv.	48	NR[d,e]

[a]Reaction condition: **1a** (0.05 mmol), TEMPO (2 equiv.), TiO_2/FTO, CH_3CN (1 mL) in a quartz-tube under air in room temperature. [b]The thickness of TiO_2 which loaded on FTO is between 9.6 μm to 9.45 μm. [c]NMR yield (internal standard: mesitylene). [d]No reaction. [e]No light.

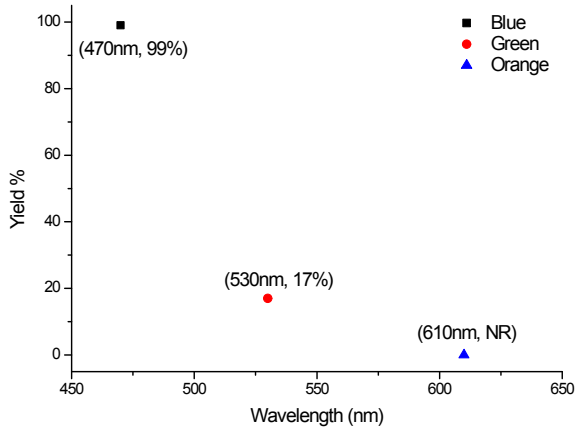


Figure S10. The yield of α-oxyamination reaction with TiO_2/FTO under visible-light irradiation of different wavelengths

4. UV/VIS Absorption spectra, Cyclic Voltammetry Luminescence Quenching Experiments and Data processing

1) UV/VIS Absorption spectra

The UV/VIS Absorption spectra was recorded in CH_3CN of a 0.1 mM solution in 10 mm path length quartz cuvette on a Perkin Elmer Lambda 35 Spectrometer.

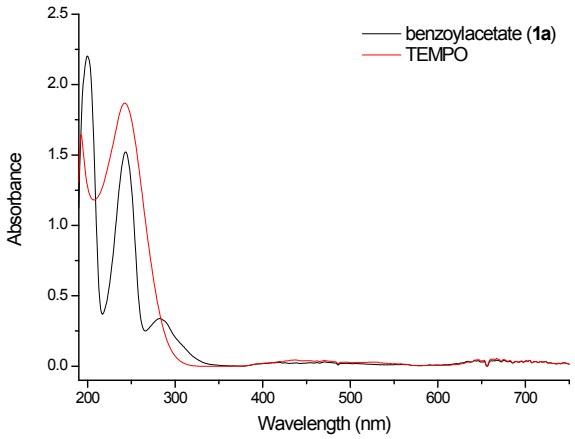


Figure S11. Absorption spectra of benzoylacetate (**1a**) (λ_{max} = 338 nm), TEMPO (λ_{max} = 320 nm) in CH_3CN (0.1 mM).

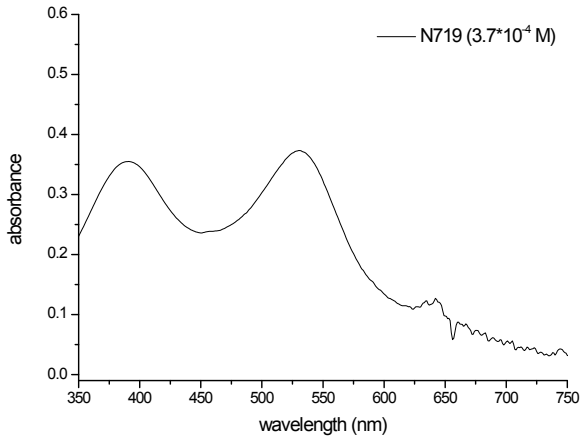


Figure S12. Absorption spectra of N719 (λ_{max} = 722 nm) in CH_3CN.

2) Cyclic Voltammetry

Cyclic voltammetry was measured under Ar balloon protection with conventional three-electrode system (Reference electrode: Ag/AgCl, working electrode: Glassy carbon, counter electrode: Pt wire, Supporting electrolyte: 0.1 M $TBAPF_6$ in CH_3CN)

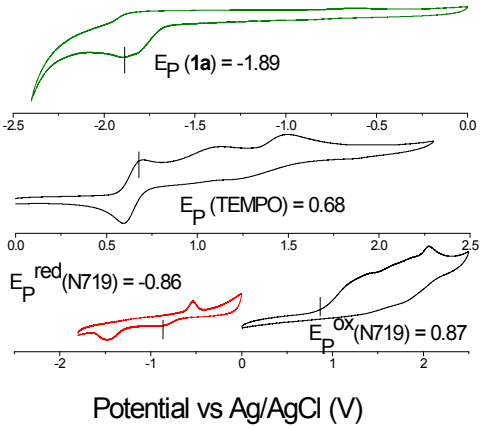


Figure S13. CV of Reaction reagents (1 mM in CH_3CN).

3) Luminescence Quenching Experiments

Emission intensities were recorded using a F-4500 FL Spectrophotometer. First, N719 solutions were excited at 530 nm and the emission intensity at 530 nm was observed. In a typical experiment, the emission spectrum of a 5×10^{-5} M solution of N719 and different concentration of (1 mM-10 mM) TEMPO or (1mM-5mM) **1a** in CH_3CN in 10 mm path length quartz cuvette was collected.

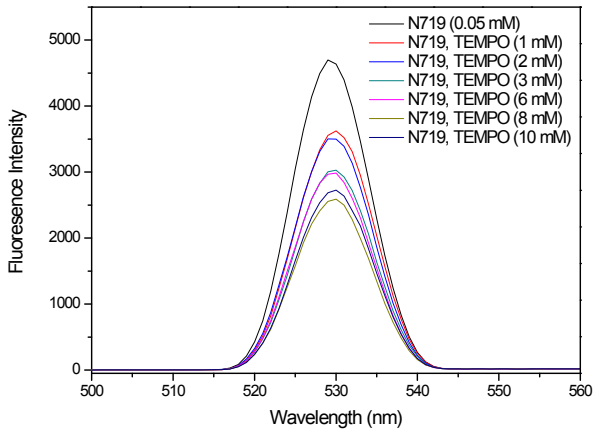


Figure S14. Luminescence quenching experiments of N719 with TEMPO.

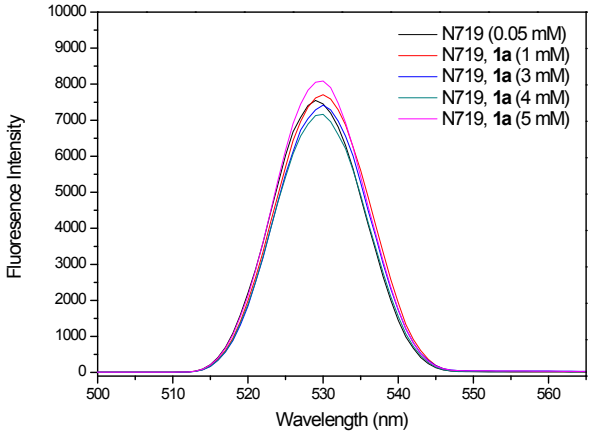


Figure S15. Luminescence quenching experiments of N719 with **1a**.

4) Data processing

With the reversible waves of all the reagents in hand, we calculated the excited redox potential, Eg of different reagents.

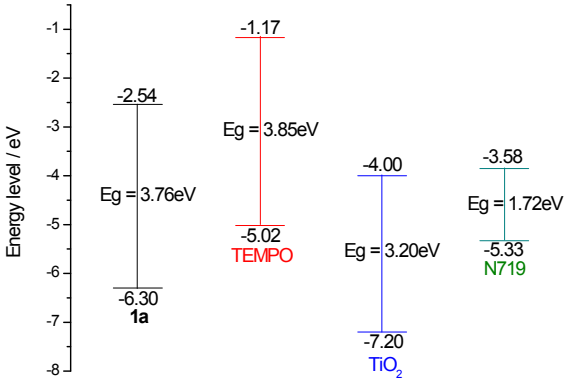


Figure S16. The E_{HOMO}, E_{LUMO} and E_g of different reagents.

5. XRD and SEM spectrum

1) XRD of TiO_2/FTO: The spectra was recorded using a X-ray Diffractometer (X' Pert PRO) at a scan rate of 3 ^{o} min^{-1} by using $Cu_{K\alpha}$ radiation. The XRD pattern showed strong XRD peaks for titanium dioxide, which suggests that the TiO_2 is anatase crystalline in nature.

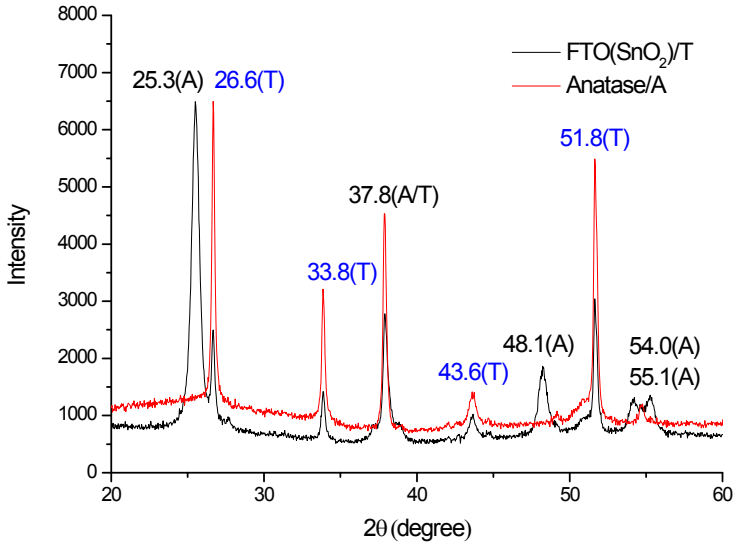


Figure S17. The XRD of TiO_2/FTO (red line) and FTO (black line).

2) SEM of TiO_2/FTO and N719-sensitized TiO_2/FTO:

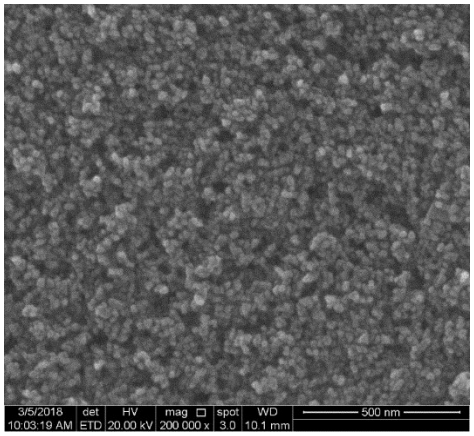


Figure S18. SEM image of TiO_2/FTO.

SEM images of the TiO_2 clearly indicate that the particles are agglomerated and homogeneously distributed having spherical shaped like morphology with particle size about 20 nm

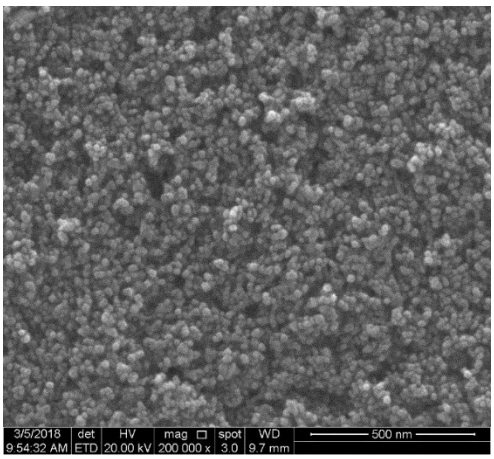
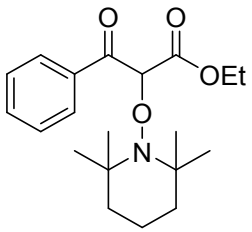
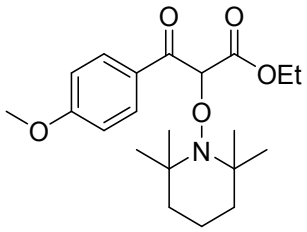


Figure S19. SEM image of N719-sensitized TiO_2/FTO.

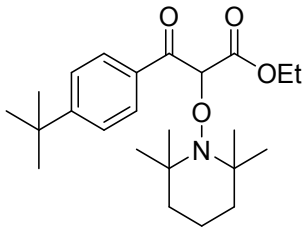
6. Characterization data



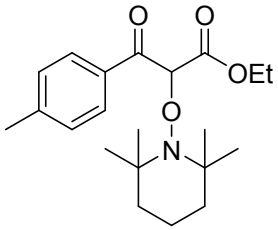
Ethyl 3-oxo-3-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3a)[4,5,6,7,8]: Colorless oil; 99% yield (17.2 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18-8.12 (m, 2H), 7.62-7.55 (m, 1H), 7.51-7.44 (m, 2H), 5.42 (s, 1H), 4.17 (dq, J = 7.1 Hz, J = 2.3 Hz, 2H), 1.60-1.35 (m, 6H), 1.29 (s, 3H), 1.21-1.12 (m, 6H), 0.99 (s, 3H), 0.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.7, 168.2, 134.5, 133.6, 129.8, 128.5, 92.9, 61.7, 60.5, 60.0, 40.2, 40.0, 33.2, 32.5, 20.2, 17.0, 14.0; HRMS (ESI) calcd. for $C_{20}H_{30}NO_4$ $(M+H)^+$: 348.2169, found: 348.2172.



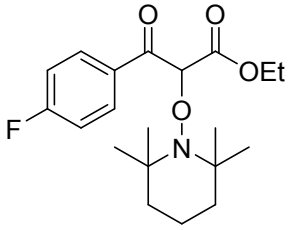
Ethyl 3-(4-methoxyphenyl)-3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3b)[6]: Colorless oil; 93% yield (17.6 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15 (d, J = 8.9, 2H), 6.95 (d, J = 8.9 Hz, 2H), 5.36 (s, 1H), 4.22-4.12 (m, 2H), 3.88 (s, 3H), 1.64-1.34 (m, 6H), 1.29 (s, 3H), 1.21-1.13 (m, 6H), 1.00 (s, 3H), 0.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.2, 168.5, 163.9, 132.3, 127.5, 113.7, 93.2, 61.6, 60.4, 59.9, 55.5, 40.2, 40.0, 33.1, 32.5, 20.3, 20.2, 17.0, 14.0; HRMS (ESI) calcd. for $C_{20}H_{29}BrNO_4$ $(M+H)^+$: 378.2275, found: 378.2279.



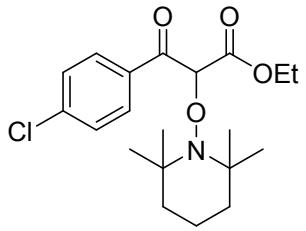
Ethyl 3-(4-(tert-butyl)phenyl)-3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3c): Colorless oil; 55% yield (11.1 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.08 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 5.42 (s, 1H), 4.22-4.11 (m, 2H), 1.52-1.37 (m, 6H), 1.34 (s, 9H), 1.29 (s, 3H), 1.22-1.12 (m, 6H), 1.02 (s, 3H), 0.85 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.3, 168.4, 157.4, 131.9, 129.8, 125.5, 92.9, 61.6, 60.4, 60.0, 40.2, 40.0, 35.2, 33.2, 32.5, 31.1, 20.2, 17.0, 14.0; HRMS (ESI) calcd. for $C_{24}H_{38}NO_4$ $(M+H)^+$: 404.2795 found: 404.2800.



Ethyl 3-(4-methylphenyl)-3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3d): Colorless oil; 94% yield (17.0 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05 (d, J = 8.2 Hz, 2H), 7.30-7.21 (m, 2H), 5.40 (s, 1H), 4.23-4.09 (m, 2H), 2.41 (s, 3H), 1.75-1.35 (m, 6H), 1.29 (s, 3H), 1.21-1.12 (m, 6H), 1.00 (s, 3H), 0.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.3, 168.3, 144.6, 132.0, 130.0, 129.2, 92.9, 61.6, 60.4, 60.0, 40.2, 40.0, 33.2, 32.5, 21.8, 20.2, 17.0, 14.0; HRMS (ESI) calcd. for $C_{21}H_{32}NO_4$ $(M+H)^+$: 362.2326 found: 362.2328.

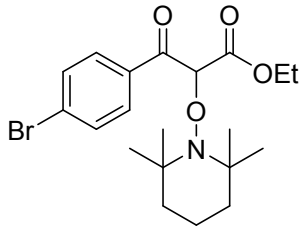


Ethyl 3-(4-fluorophenyl)-3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3e)[6]: yellow solid; mp. 66.5-67.5 °C. 95% yield (17.4 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.25-8.18 (m, 2H), 7.15 (t, J = 8.7 Hz, 2H), 5.35 (s, 1H), 4.23-4.13 (m, 2H), 1.64-1.35 (m, 6H), 1.28 (s, 3H), 1.24-1.14 (m, 6H), 0.97 (s, 3H), 0.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.2, 168.2, 166.0 (d, ^1J = 256 Hz), 132.8 (d, ^3J = 10 Hz), 130.8 (d, ^4J = 4 Hz), 115.7 (d, ^2J = 22 Hz), 93.3, 61.8, 60.5, 60.0, 40.2, 40.0, 33.2, 32.5, 20.2, 17.0, 14.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -103.7; HRMS (ESI) calcd. for $C_{20}H_{28}FNO_4$ $(M+H)^+$: 366.2075, found: 366.2078.

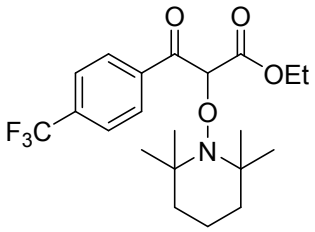


Ethyl 3-(4-chlorophenyl)-3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate

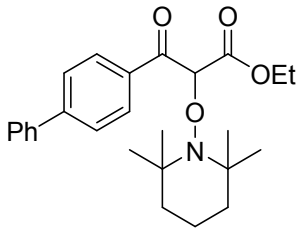
(3f)[6]: yellow solid; mp 69.5-71.0 °C. 87% yield (16.6 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12 (d, *J* = 8.8, 2H), 7.45 (d, *J* = 8.7 Hz, 2H), 5.35 (s, 1H), 4.25-4.12 (m, 2H), 1.62-1.35 (m, 6H), 1.28 (s, 3H), 1.21-1.14 (m, 6H), 0.97 (s, 3H), 0.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.6, 168.1, 140.2, 132.7, 131.4, 128.9, 93.2, 61.8, 60.5, 60.0, 40.1, 40.0, 33.2, 32.4, 20.2, 17.0, 14.0; HRMS (ESI) calcd. for $C_{20}H_{29}ClNO_4$ $(M+H)^+$: 382.1780, found: 382.1782.



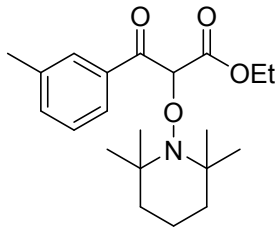
Ethyl 3-(4-bromophenyl)-3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3g): yellow solid; mp 70.5-72.4 °C. 83% yield (17.7 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04 (d, *J* = 8.7, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 5.34 (s, 1H), 4.25-4.11 (m, 2H), 1.61-1.35 (m, 6H), 1.28 (s, 3H), 1.21-1.14 (m, 6H), 0.97 (s, 3H), 0.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.8, 168.1, 133.1, 131.9, 131.4, 129.1, 93.2, 61.9, 60.5, 60.0, 40.2, 40.0, 33.2, 32.5, 20.2, 17.0, 14.0; HRMS (ESI) calcd. for $C_{20}H_{29}BrNO_4$ $(M+H)^+$: 426.1274, found: 426.1276.



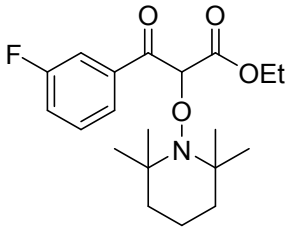
Ethyl 3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3-(4-(trifluoromethyl)phenyl)propanoate (3h): Colorless oil; 90% yield (18.7 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.29 (d, *J* = 8.2 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 1H), 5.39 (s, 1H), 4.27-4.11 (m, 2H), 1.64-1.35 (m, 6H), 1.29 (s, 3H), 1.23-1.14 (m, 6H), 0.96 (s, 3H), 0.80 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.8, 167.9, 137.0, 134.7 (d, *J* = 33.0 Hz), 130.2, 125.5 (q, *J* = 3.7 Hz), 123.5 (d, *J* = 272.9 Hz), 93.2, 62.0, 60.6, 60.0, 40.1, 39.9, 33.2, 32.4, 20.2, 16.9, 14.0; ^{19}F NMR ($CDCl_3$, 376 MHz) *δ* -63.2; HRMS (ESI) calcd. for $C_{21}H_{29}F_3NO_4$ $(M+H)^+$: 416.2043, found: 416.2048.



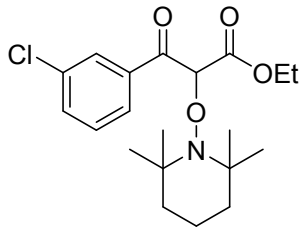
Ethyl 3-([1,1'-biphenyl]-4-yl)-3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3i): Colorless oil; 77% yield (16.3 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.24 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.67-7.61 (m, 2H), 7.48 (t, *J* = 7.1 Hz, 2H), 7.40 (d, *J* = 7.2 Hz, 1H), 5.44 (s, 1H), 4.25-4.13 (m, 2H), 1.65-1.36 (m, 6H), 1.31 (s, 3H), 1.22-1.16 (m, 6H), 1.02 (s, 3H), 0.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.3, 168.3, 146.2, 139.8, 133.1, 130.5, 129.0, 128.3, 127.3, 127.1, 93.0, 61.7, 60.5, 60.0, 40.2, 40.0, 33.2, 32.5, 20.2, 17.0, 14.0; HRMS (ESI) calcd. for $C_{26}H_{34}NO_4$ $(M+H)^+$: 424.2482 found: 424.2484.



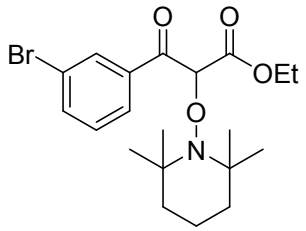
Ethyl 3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3-(m-tolyl)propanoate (3j)[6]: White solid; mp 65.2-66.5 °C. 73% yield (13.2 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00-7.91 (m, 2H), 7.42-7.32 (m, 2H), 5.43 (s, 1H), 4.22-4.12 (m, 2H), 2.41 (s, 3H), 1.65-1.35 (m, 6H), 1.29 (s, 3H), 1.20-1.13 (m, 6H), 1.01 (s, 3H), 0.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.9, 168.2, 138.3, 134.5, 130.1, 128.3, 127.2, 92.7, 61.6, 60.4, 60.0, 40.2, 40.0, 33.2, 32.5, 21.4, 20.2, 17.0, 14.0; HRMS (ESI) calcd. for $C_{21}H_{32}NO_4$ $(M+H)^+$: 362.2326 found: 362.2332.



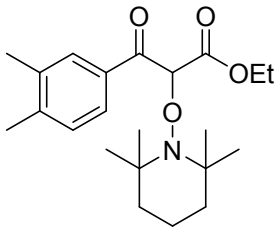
Ethyl 3-(3-fluorophenyl)-3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3k): white solid; mp. 68.6-70.4 °C. 94% yield (17.2 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.00-7.94 (m, 1H), 7.88-7.81 (m, 1H), 7.50-7.42 (m, 1H), 7.32-7.25 (m, 1H), 5.37 (s, 1H), 4.25-4.14 (m, 2H), 1.66-1.35 (m, 6H), 1.29 (s, 3H), 1.21-1.14 (m, 6H), 0.99 (s, 3H), 0.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.6, 167.9, 162.6 (d, ^1J = 247 Hz), 136.4 (d, ^3J = 7 Hz), 130.2 (d, ^3J = 7 Hz), 125.7 (d, ^4J = 3 Hz), 120.8 (d, ^2J = 21 Hz), 116.4 (d, ^2J = 23 Hz), 92.9, 61.9, 60.5, 60.0, 40.1, 40.0, 33.2, 32.4, 20.2, 16.9, 14.0; ^{19}F NMR ($CDCl_3$, 376 MHz) δ -111.6; HRMS (ESI) calcd. for $C_{20}H_{29}FNO_4$ $(M+H)^+$: 366.2075 found: 366.2072.



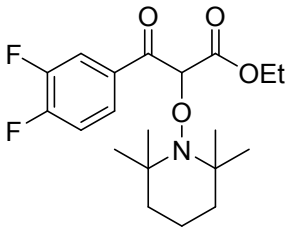
Ethyl 3-(3-chlorophenyl)-3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3l): Yellow solid; mp 78.5-80.0 °C. 87% yield (16.6 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.14-8.11 (m, 1H), 8.10-8.05 (m, 1H), 7.58-7.52 (m, 1H), 7.42 (t, J =7.8 Hz, 1H), 5.38 (s, 1H), 4.25-4.13 (m, 2H), 1.63-1.35 (m, 6H), 1.28 (s, 3H), 1.22-1.15 (m, 6H), 0.99 (s, 3H), 0.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.5, 167.9, 135.9, 134.8, 133.6, 129.8, 129.7, 128.1, 92.9, 61.9, 60.5, 60.0, 40.1, 39.9, 33.2, 32.5, 20.2, 16.9, 14.0; HRMS (ESI) calcd. for $C_{20}H_{29}ClNO_4$ $(M+H)^+$: 382.1780 found: 382.1784.



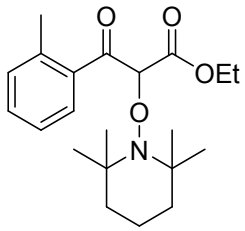
Ethyl 3-(3-bromophenyl)-3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3m): Yellow solid; mp 80.2-82.0 °C. 95% yield (20.3 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.30-8.25 (m, 1H), 8.15-8.09 (m, 1H), 7.74-7.67 (m, 1H), 7.36 (t, *J* =8.0 Hz, 1H), 5.37 (s, 1H), 4.26-4.12 (m, 2H), 1.61-1.35 (m, 6H), 1.28 (s, 3H), 1.22-1.14 (m, 6H), 0.99 (s, 3H), 0.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 192.4, 167.9, 136.5, 136.0, 132.6, 130.1, 128.6, 122.8, 92.9, 61.9, 60.5, 60.1, 40.1, 39.9, 33.2, 32.5, 20.2, 16.9, 14.0; HRMS (ESI) calcd. for $C_{20}H_{29}BrNO_4$ $(M+H)^+$: 426.1274 found: 426.1278.



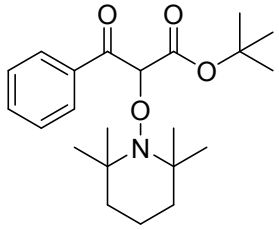
Ethyl 3-(3,4-dimethylphenyl)-3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3n): Colorless oil; 87% yield (16.4 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.95-7.86 (m, 2H), 7.22 (d, *J* = 7.8 Hz, 1H), 5.42 (s, 1H), 4.21-4.11 (m, 2H), 2.31 (s, 6H), 1.71-1.35 (m, 6H), 1.29 (s, 3H), 1.20-1.13 (m, 3H), 1.03 (s, 3H), 0.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.4, 168.3, 143.4, 136.9, 132.4, 130.6, 129.7, 127.8, 92.7, 61.6, 60.4, 60.0, 40.2, 40.0, 33.2, 32.5, 20.2, 20.2, 19.8, 17.0, 14.0; HRMS (ESI) calcd. for $C_{22}H_{34}NO_4$ $(M+H)^+$: 376.2482 found: 376.2483.



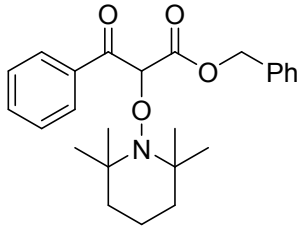
Ethyl 3-(3,4-difluorophenyl)-3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3o): Colorless oil; 93% yield (17.8 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.05-7.97 (m, 2H), 7.31-7.21 (m, 1H), 5.32 (s, 1H), 4.25-4.13 (m, 2H), 1.60-1.35 (m, 6H), 1.28 (s, 3H), 1.22-1.14 (m, 6H), 0.97 (s, 3H), 0.81 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 191.3, 168.0, 154.0 (dd, *J* = 13.2 Hz, *J* = 259.0 Hz), 150.3 (dd, *J* = 12.5 Hz, *J* = 250.2 Hz), 131.3 (t, *J* = 3.7 Hz), 127.3 (q, *J* = 3.7 Hz), 119.2 (dd, *J* = 1.5 Hz, *J* = 18.3 Hz), 117.5 (d, *J* = 17.6 Hz), 93.3, 62.0, 60.6, 60.0, 40.1, 40.0, 33.2, 32.4, 20.3, 20.2, 16.9, 14.0; ^{19}F NMR ($CDCl_3$, 376 MHz) *δ* -128.4 (d, *J* = 20.4 Hz), -135.9 (d, *J* = 20.4 Hz); HRMS (ESI) calcd. for $C_{20}H_{28}F_2NO_4$ $(M+H)^+$: 384.1981, found: 384.1980.



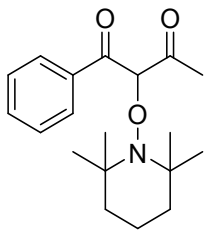
Ethyl 3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3-(o-tolyl)propanoate (3p): Colorless oil; 39% yield (7.0 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.04-7.96 (m, 1H), 7.43-7.36 (m, 1H), 7.32-7.22 (m, 2H), 5.44 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.50 (s, 3H), 1.65-1.35 (m, 6H), 1.25 (s, 3H), 1.18-1.12 (m, 6H), 0.99 (s, 3H), 0.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 196.6, 168.2, 140.0, 134.5, 132.1, 131.9, 130.6, 125.4, 93.2, 61.6, 60.2, 40.2, 40.1, 32.8, 32.7, 21.3, 20.3, 20.1, 17.0, 14.0; HRMS (ESI) calcd. for $C_{21}H_{32}NO_4$ $(M+H)^+$: 362.2326 found: 362.2330.



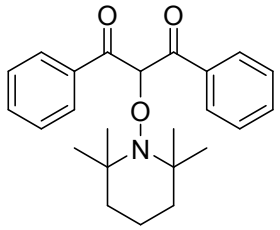
Tert-butyl 3-oxo-3-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3r): Colorless oil; 57% yield (10.7 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.17-8.10 (m, 2H), 7.60-7.53 (m, 1H), 7.49-7.43 (m, 2H), 5.29 (s, 1H), 1.56-1.36 (m, 6H), 1.33 (s, 9H), 1.30 (s, 3H), 1.22 (s, 3H), 0.99 (s, 3H), 0.82 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 194.1, 167.2, 134.8, 133.4, 129.7, 128.4, 93.1, 82.8, 60.5, 59.9, 40.2, 40.0, 33.3, 32.4, 27.8, 20.2, 17.0; HRMS (ESI) calcd. for $C_{22}H_{34}NO_4$ $(M+H)^+$: 376.2482 found: 376.2484.



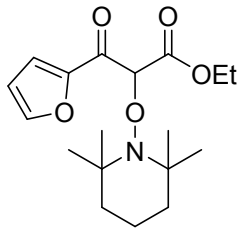
Benzyl 3-oxo-3-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3s): Colorless oil; 96% yield (19.7 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.16-8.04 (m, 2H), 7.60-7.51 (m, 1H), 7.48-7.38 (m, 2H), 7.26-7.20 (m, 3H), 7.19-7.13 (m,2H), 5.47 (s, 1H), 5.13 (s, 2H), 1.72-1.35 (m, 6H), 1.26 (s, 3H), 1.11 (s, 3H), 0.99 (s, 3H), 0.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.4, 168.0, 135.0, 134.4, 133.6, 129.8, 128.5, 128.4, 128.2, 128.1, 92.8, 67.2, 60.5, 60.0, 40.1, 40.0, 33.2, 32.4, 20.2, 17.0; HRMS (ESI) calcd. for $C_{25}H_{32}NO_4$ $(M+H)^+$: 410.2326 found: 410.2328.



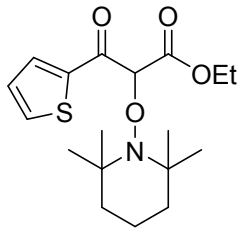
1-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butane-1,3-dione (3t)[5]: White solid; mp 66.2-68.0 °C. 50% yield (8.0 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12-8.06 (m, 2H), 7.61-7.54 (m, 1H), 7.50-7.43 (m, 2H), 5.60 (s, 1H), 2.24 (s, 3H), 1.61-1.34 (m, 6H), 1.26 (s, 3H), 1.09-1.02 (m, 6H), 0.83 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.7, 195.3, 134.8, 133.9, 129.9, 128.6, 100.2, 60.2, 60.0, 40.1, 40.1, 33.0, 32.9, 26.8, 20.3, 20.2, 17.0; HRMS (ESI) calcd. for $C_{19}H_{28}NO_3$ $(M+H)^+$: 318.2064 found: 318.2067.



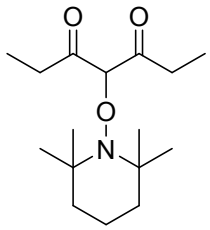
1,3-diphenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propane-1,3-dione (3u)[4,5]: White solid; mp 106.3-108.1 °C. 74% yield (14.0 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22-8.15 (m, 4H), 7.58-7.51 (m, 2H), 7.49-7.41 (m, 4H), 6.29 (s, 1H), 1.50-1.23 (m, 6H), 1.13 (s, 6H), 0.95 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.0, 134.7, 133.7, 130.2, 128.4, 99.2, 60.2, 40.1, 33.0, 20.2, 17.0; HRMS (ESI) calcd. for $C_{24}H_{30}NO_3$ $(M+H)^+$: 380.2220 found: 380.2223.



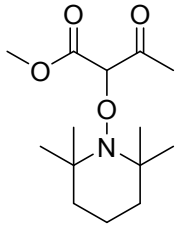
Ethyl 3-(furan-2-yl)-3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanoate (3v): White solid; mp 98.5-99.5 °C. 92% yield (15.5 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.68 (d, J = 1.0 Hz, 1H), 7.54 (d, J = 3.6 Hz, 1H), 6.60-6.55 (m, 1H), 5.28 (s, 1H), 4.24-4.14 (m, 2H), 1.64-1.37 (m, 6H), 1.27 (s, 3H), 1.24-1.18 (m, 3H), 1.15 (s, 3H), 1.06 (s, 3H), 0.90 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 182.1, 167.7, 150.1, 147.7, 121.6, 112.4, 91.6, 61.8, 60.5, 60.0, 40.2, 40.0, 33.1, 32.5, 20.2, 17.0, 14.0; HRMS (ESI) calcd. for $C_{18}H_{28}NO_5$ $(M+H)^+$: 338.1962 found: 338.1960.



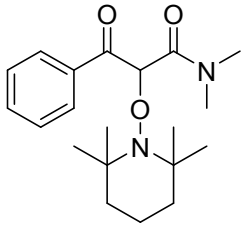
Ethyl 3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3-(thiophen-2-yl)propanoate (3w): Colorless oil; 85% yield (15.0 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.12 (dd, J = 3.9 Hz, J = 1.1 Hz, 1H), 7.71 (dd, J = 4.9 Hz, J = 1.1 Hz, 1H), 7.19-7.13 (m, 1H), 5.27 (s, 1H), 4.26-4.14 (m, 2H), 1.62-1.37 (m, 6H), 1.28 (s, 3H), 1.23-1.12 (m, 6H), 1.04 (s, 3H), 0.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 186.8, 168.0, 141.0, 135.4, 135.0, 128.4, 93.1, 61.8, 60.5, 60.0, 40.1, 40.0, 33.1, 32.5, 20.2, 17.0, 14.0; HRMS (ESI) calcd. for $C_{18}H_{28}NO_4S$ $(M+H)^+$: 354.1734 found: 354.1731.



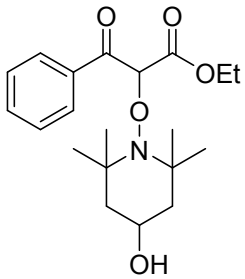
4-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)heptane-3,5-dione (3x): Colorless oil; 34% yield (4.8 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.49 (s, 1H), 2.84-2.71 (m, 2H), 2.52-2.39 (m, 2H), 1.53-1.37 (m, 6H), 1.19 (s, 6H), 1.02 (t, *J* = 7.2 Hz, 6H), 0.95 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 206.8, 100.7, 60.0, 40.2, 33.0, 20.2, 16.9, 7.0; HRMS (ESI) calcd. for $C_{16}H_{30}NO_3$ $(M+H)^+$: 284.2220 found: 284.2219.



Methyl 3-oxo-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)butanoate (3y)[5]: Colorless oil; 56% yield (7.6 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.83 (s, 1H), 3.75 (s, 3H), 2.31 (s, 3H), 1.61-1.37 (m, 6H), 1.20 (s, 6H), 1.09-0.94 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 203.0, 168.4, 93.5, 60.3, 60.1, 52.5, 40.1, 33.1, 32.5, 26.6, 20.2, 16.9; HRMS (ESI) calcd. for $C_{14}H_{26}NO_4$ $(M+H)^+$: 272.1856 found: 272.1855.

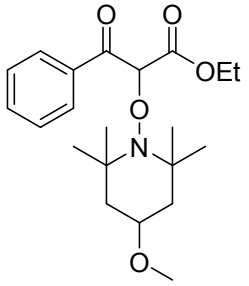


***N,N*-dimethyl-3-oxo-3-phenyl-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)propanamide (3z)**[7]: Yellow oil; 32% yield (5.5 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32-8.20 (m, 2H), 7.60-7.52 (m, 1H), 7.49-7.41 (m, 2H), 5.89 (s, 1H), 3.22 (s, 3H), 2.89 (s, 3H), 1.54-1.26 (m, 6H), 1.22 (s, 3H), 1.13-1.02 (m, 6H), 0.88 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 195.8, 167.0, 134.8, 133.6, 130.1, 128.4, 94.0, 60.2, 59.9, 40.0, 40.0, 37.3, 36.2, 32.7, 20.9, 20.1, 17.0; HRMS (ESI) calcd. for $C_{20}H_{31}N_2O_3$ $(M+H)^+$: 347.2329 found: 347.2328.

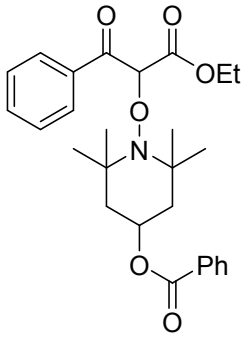


Ethyl 2-((4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3-oxo-3-phenylpropanoate (3ab): Colorless oil; 52% yield (9.5 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.16-8.09 (m, 2H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 5.41 (s, 1H), 4.23-4.12 (m, 2H), 4.00-3.90 (m,

1H), 1.89-1.80 (m, 1H), 1.78-1.68 (m, 1H), 1.59 (s, 1H), 1.52-1.32 (m, 5H), 1.22 (s, 3H), 1.19-1.12 (m, 3H), 1.05 (s, 3H), 0.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.4, 168.0, 134.4, 133.8, 129.8, 128.6, 92.7, 62.9, 61.8, 60.8, 60.4, 48.6, 48.4, 33.2, 32.5, 21.2, 21.2, 14.0; HRMS (ESI) calcd. for $C_{20}H_{30}NO_5$ $(M+H)^+$: 364.2118, found: 364.2121.



Ethyl 2-((4-methoxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)-3-oxo-3-phenylpropanoate (3ac): Colorless oil; 50% yield (9.5 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18-8.06 (m, 2H), 7.63-7.54 (m, 1H), 7.52-7.43 (m, 2H), 5.42 (s, 1H), 4.22-4.12 (m, 2H), 3.48-3.37 (m, 1H), 3.30 (s, 3H), 1.95-1.74 (m, 2H), 1.44-1.27 (m, 5H), 1.23 (s, 3H), 1.19-1.13 (m, 3H), 1.05 (s, 3H), 0.87 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.4, 168.0, 134.4, 133.7, 129.8, 128.6, 92.7, 71.4, 61.8, 60.7, 60.3, 55.8, 45.0, 44.7, 33.3, 32.7, 21.3, 21.2, 14.0; HRMS (ESI) calcd. for $C_{21}H_{32}NO_5$ $(M+H)^+$: 378.2275, found: 378.2273.



1-((1-ethoxy-1,3-dioxo-3-phenylpropan-2-yl)oxy)-2,2,6,6-tetramethylpiperidin-4-yl benzoate (3ad): Colorless oil; 52% yield (12.2 mg), ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.18-8.10 (m, 2H), 8.03-7.96 (m, 2H), 7.63-7.51 (m, 2H), 7.51-7.38 (m, 4H), 5.41 (s, 1H), 5.31-5.18 (m, 1H), 4.24-4.14 (m, 2H), 2.08-1.98 (m, 1H), 1.97-1.87 (m, 1H), 1.76-1.60 (m, 2H), 1.46 (s, 3H), 1.27 (s, 3H), 1.21-1.10 (m, 6H), 0.91 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 193.4, 168.0, 166.1, 134.3, 133.8, 132.9, 130.4, 129.8, 129.5, 128.6, 128.3, 93.0, 66.9, 61.9, 60.9, 60.5, 44.5, 44.3, 33.2, 32.5, 21.1, 21.1, 14.0; HRMS (ESI) calcd. for $C_{27}H_{33}NO_6$ $(M+H)^+$: 468.2381, found: 468.2380.

7. References

1. (*a*) J. L. Howard, W. Nicholson, Y. Sagatov and D. L. Browne, *Beilstein J. Org. Chem.*, 2017, **13**, 1950; (*b*) N. S. Y. Loy, S. Choi, S. Kim and C.-M. Park, *Chem. Commun.*, 2016, **52**, 7336; (*c*) R. Chen, A. A. Ogunlana, S. Fang, W. Long, H. Sun, X. Bao and X. Wan, *Org. Biomol. Chem.*, 2018, **16**, 4683; (*d*) M. Yoshida, A. Kubara and S. Hara, *Chem. Lett.*, 2013, **42**, 180; (*e*) L.-S. Ge, Z.-L. Wang, X.-L. An, X. Luo and W.-P. Deng, *Org. Biomol. Chem.*, 2014,

12, 8473.
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8. Z.-L. Wang, X.-L. An, L.-S. Ge, J.-H. Jin, X.-Y. Luo and W.-P. Deng, *Tetrahedron*, 2014, **70**, 3788.

8. NMR Spectra

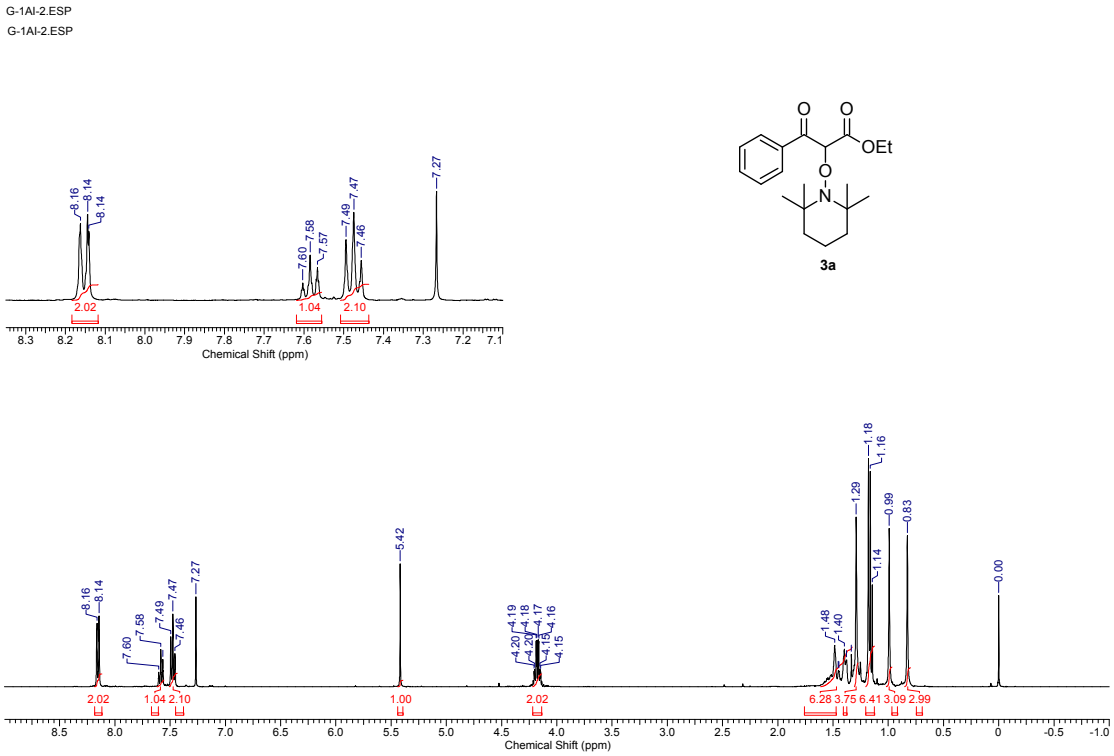


Figure S20. ^{1}H NMR spectrum of compound **3a**

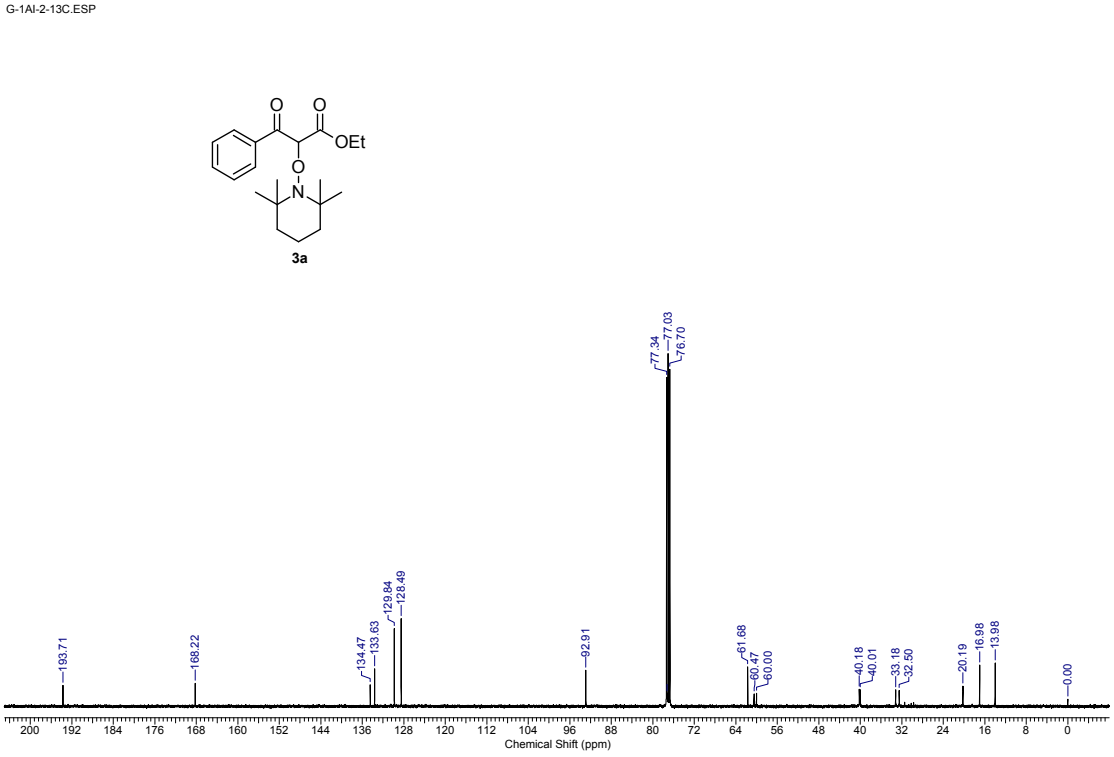


Figure S21. ^{13}C NMR spectrum of compound **3a**

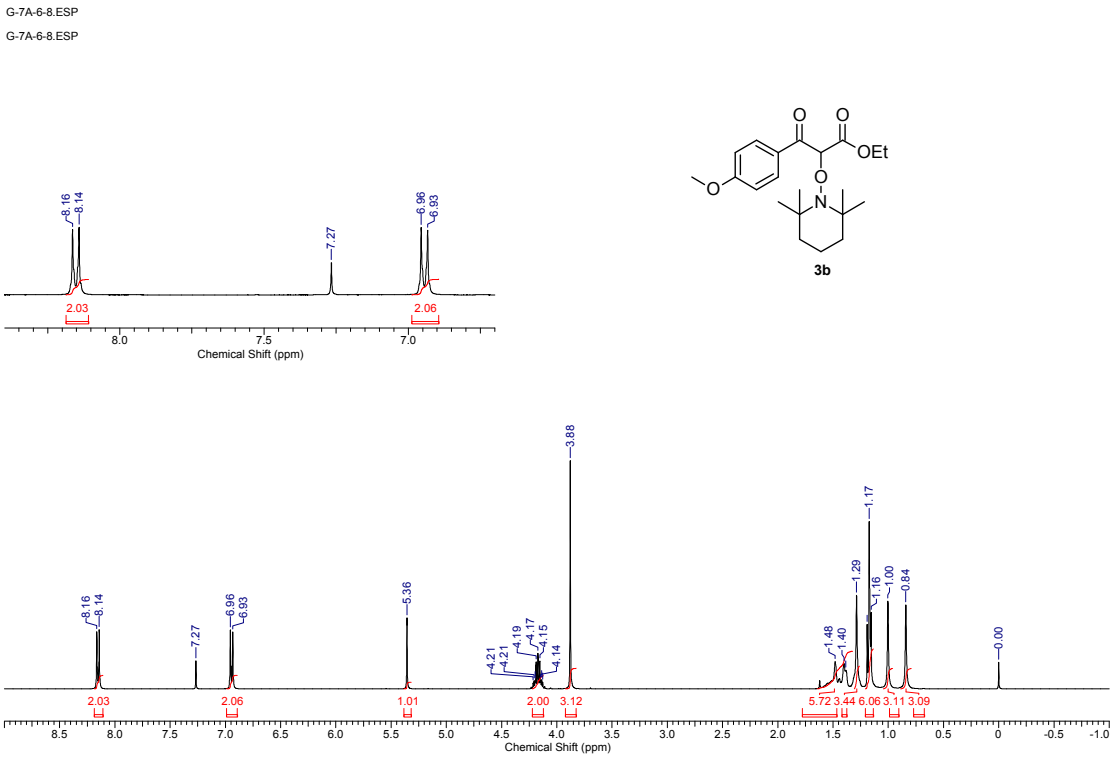


Figure S22. ^{1}H NMR spectrum of compound **3b**

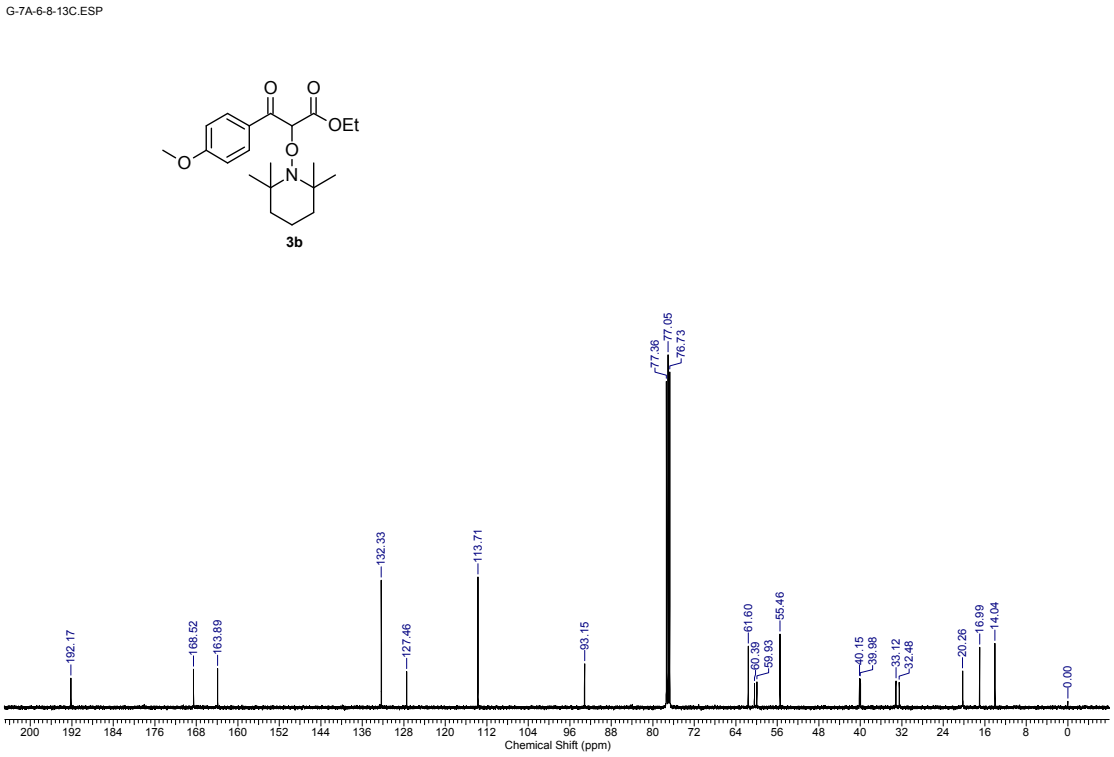


Figure S23. ^{13}C NMR spectrum of compound **3b**

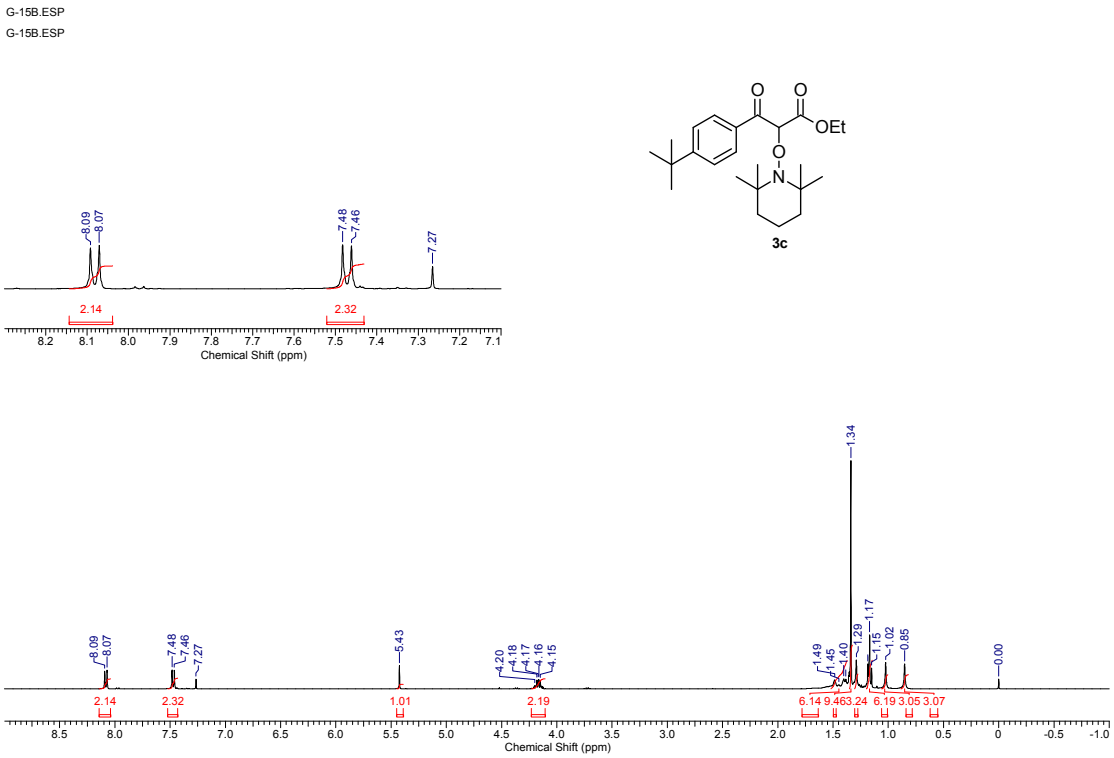


Figure S24. ^{1}H NMR spectrum of compound **3c**

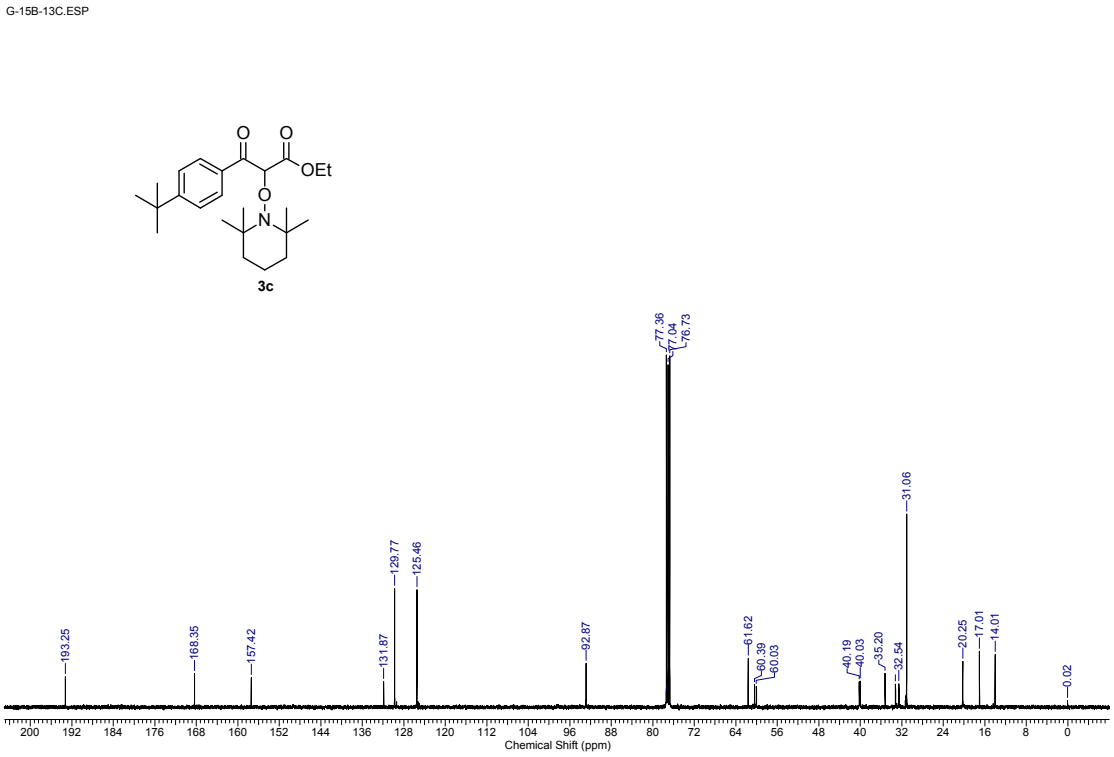


Figure S25. ^{13}C NMR spectrum of compound **3c**

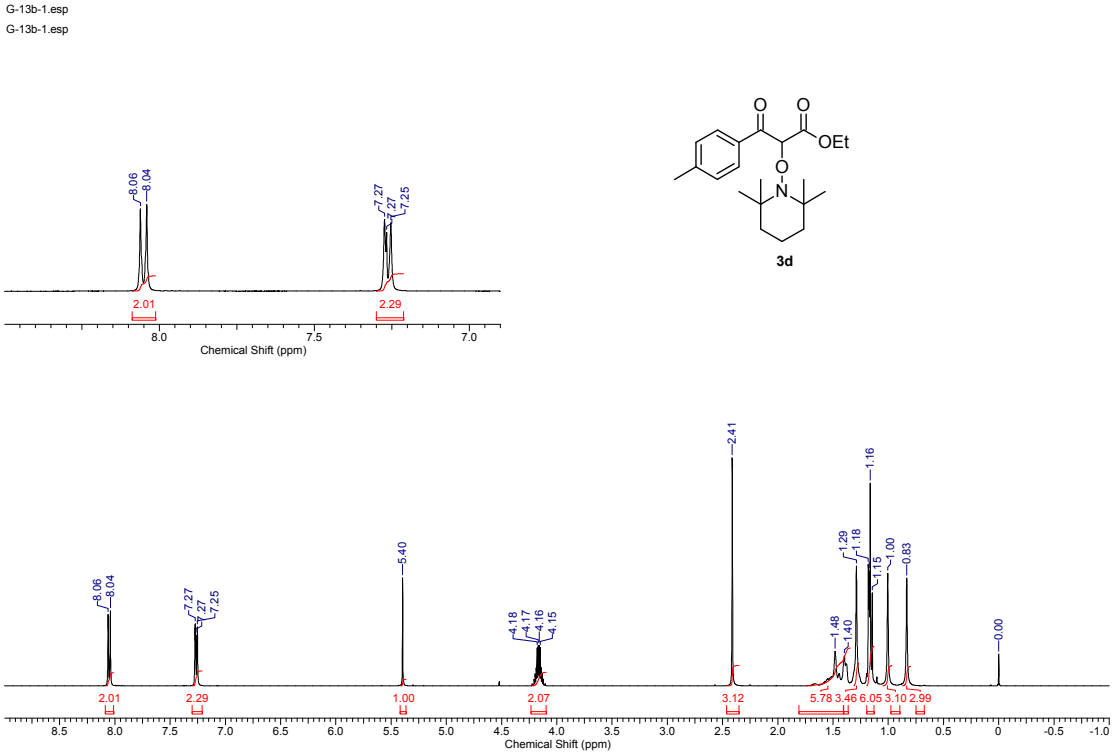


Figure S26. ^{1}H NMR spectrum of compound **3d**

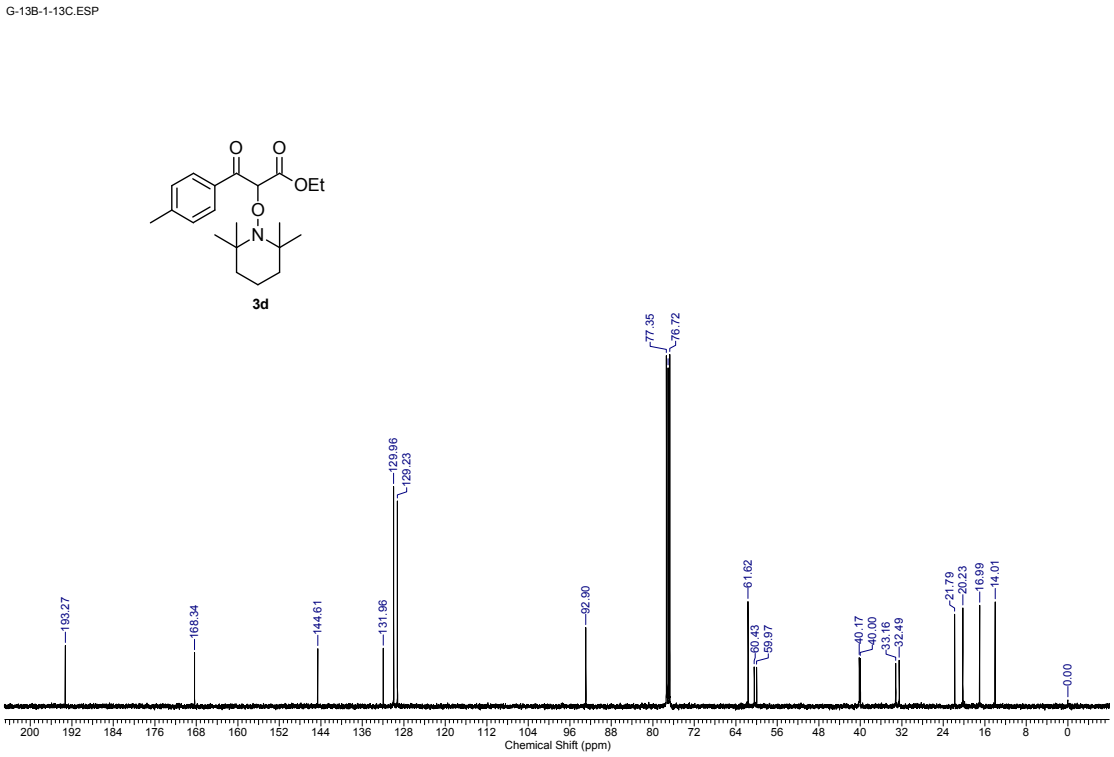


Figure S27. ^{13}C NMR spectrum of compound **3d**

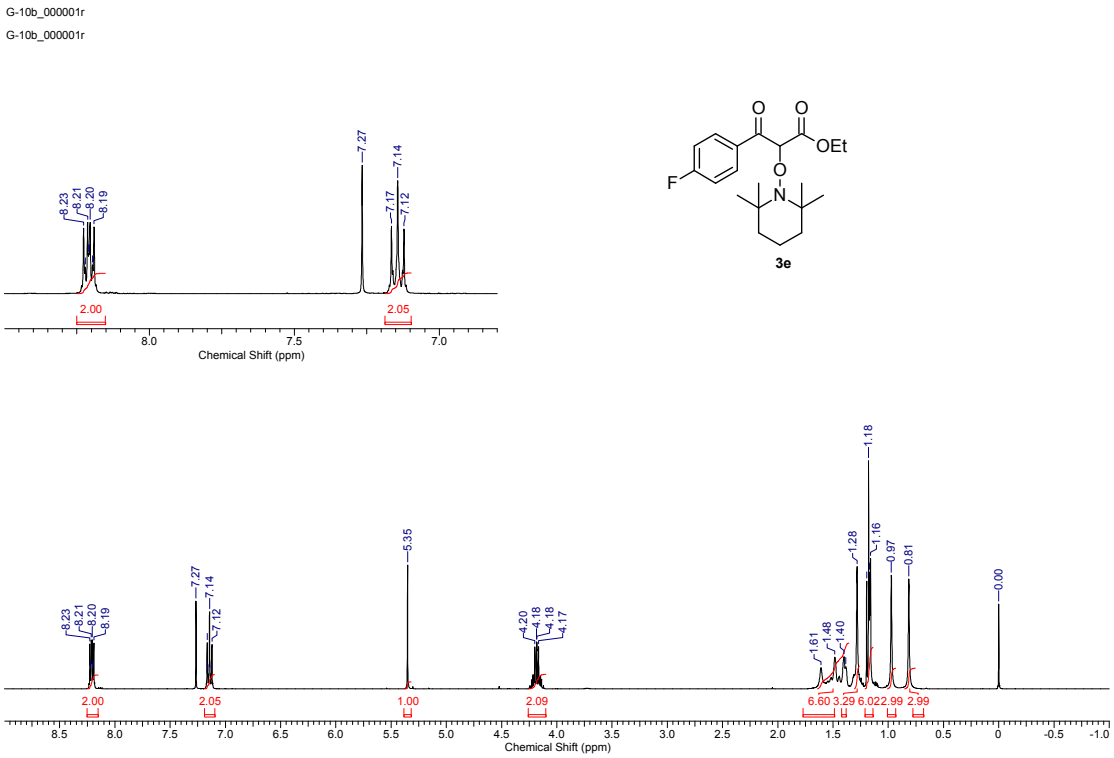


Figure S28. ^{1}H NMR spectrum of compound **3e**

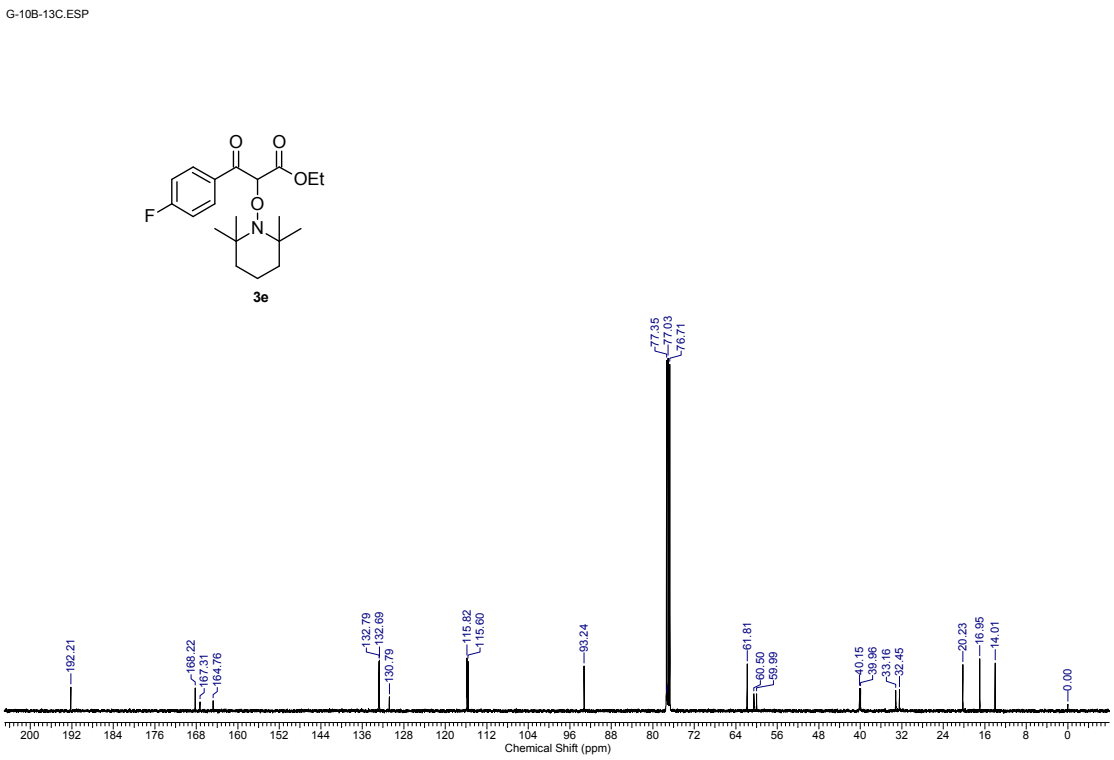
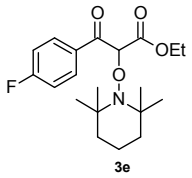


Figure S29. ^{13}C NMR spectrum of compound **3e**

G-10A-3-19F.ESP



3e

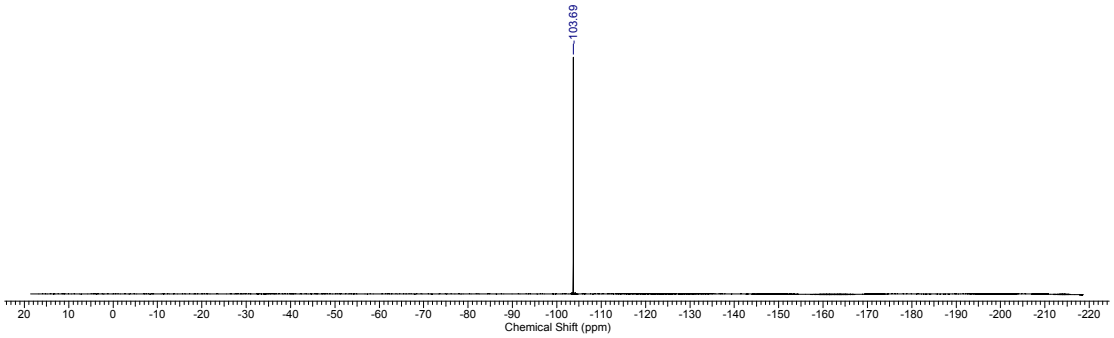
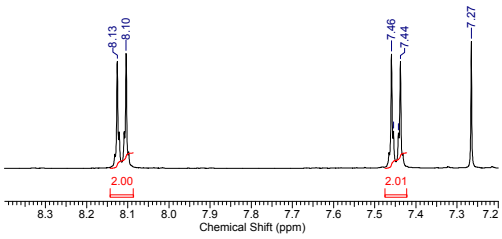
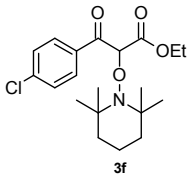


Figure S30. ^{19}F NMR spectrum of compound **3e**

G-8B.ESP

G-8B.ESP





3f

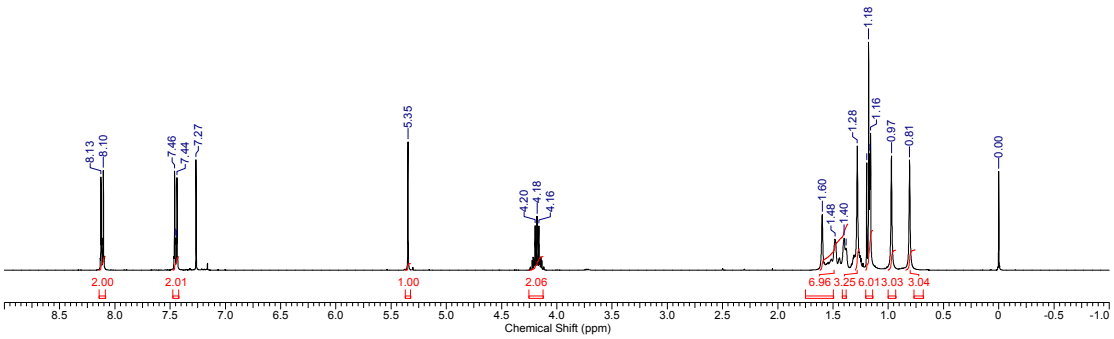


Figure S31. ^{1}H NMR spectrum of compound **3f**

G-8A-2-13C.ESP

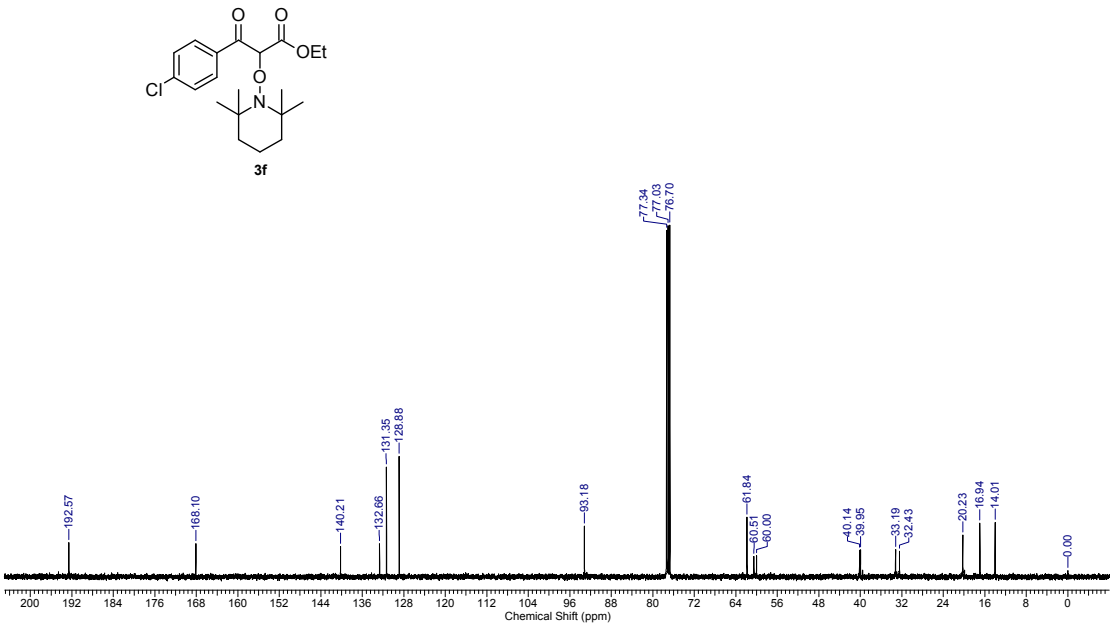


Figure S32. ^{13}C NMR spectrum of compound **3f**

G-9B.ESP

G-9B.ESP

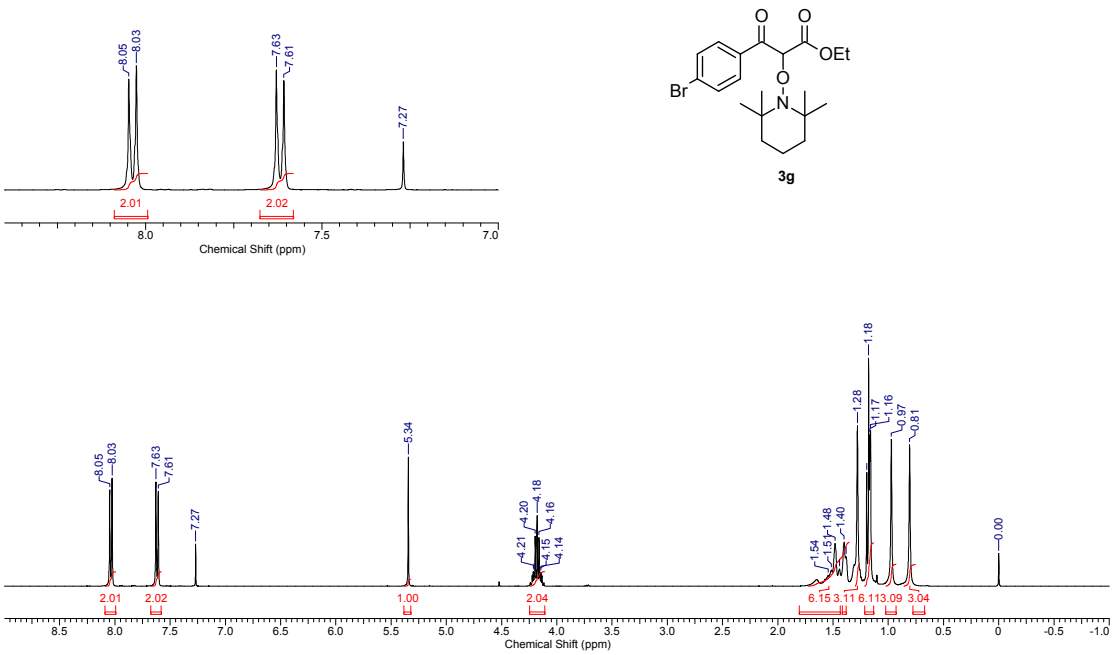


Figure S33. ^{1}H NMR spectrum of compound **3g**

G-9A-3+4-13C.ESP

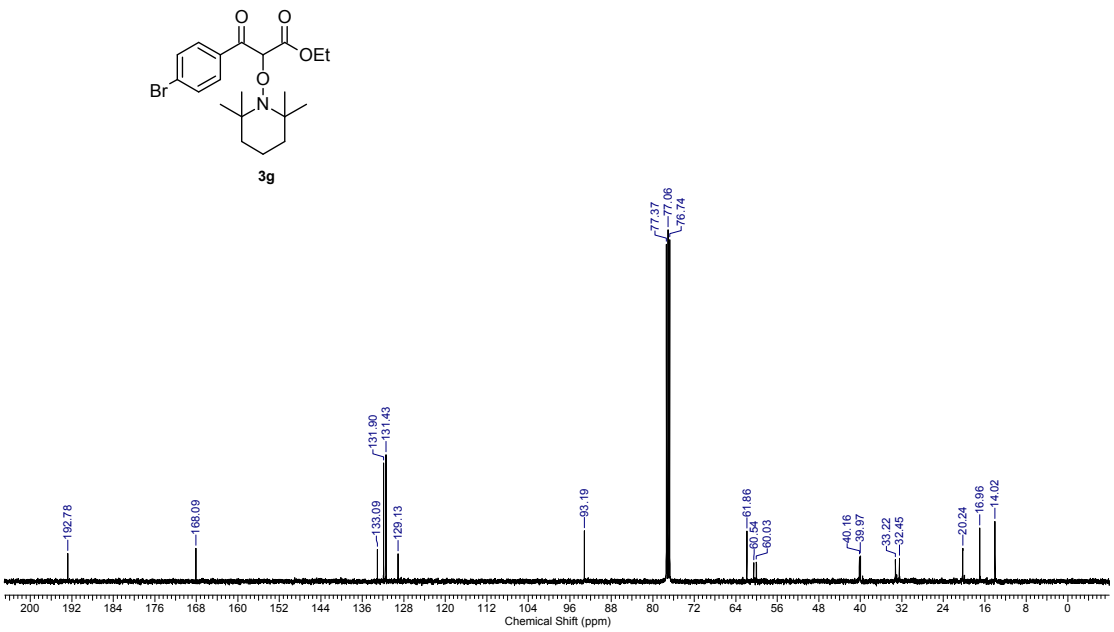


Figure S34. ^{13}C NMR spectrum of compound **3g**

G-12b-3_000001r.esp
G-12b-3_000001r.esp

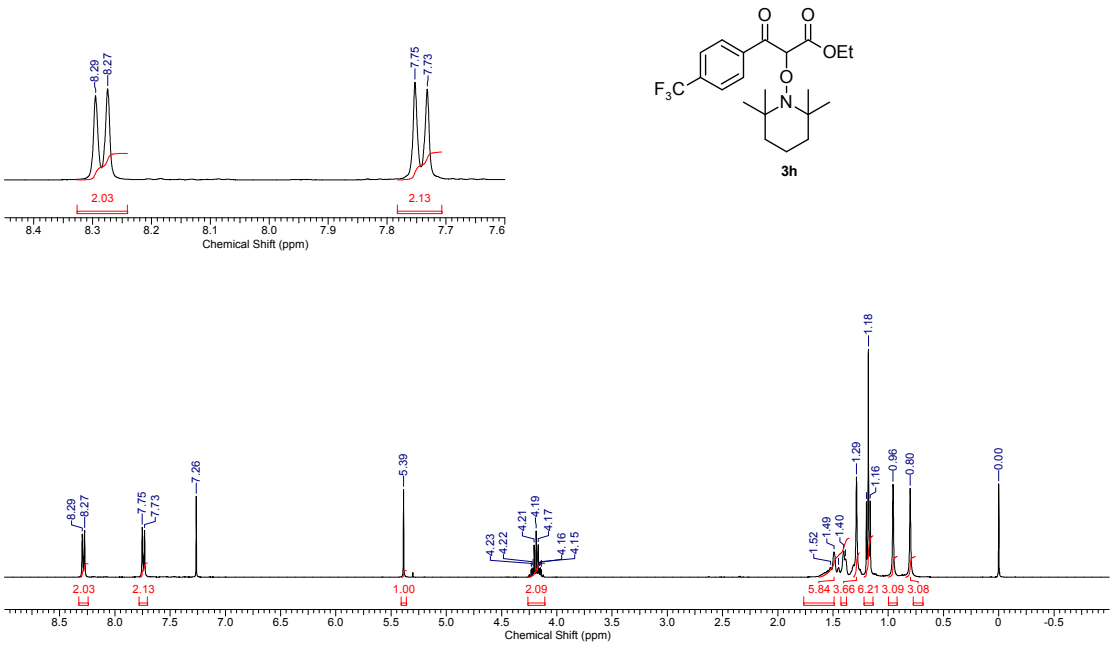


Figure S35. ^{1}H NMR spectrum of compound **3h**

G-12A-13C.ESP

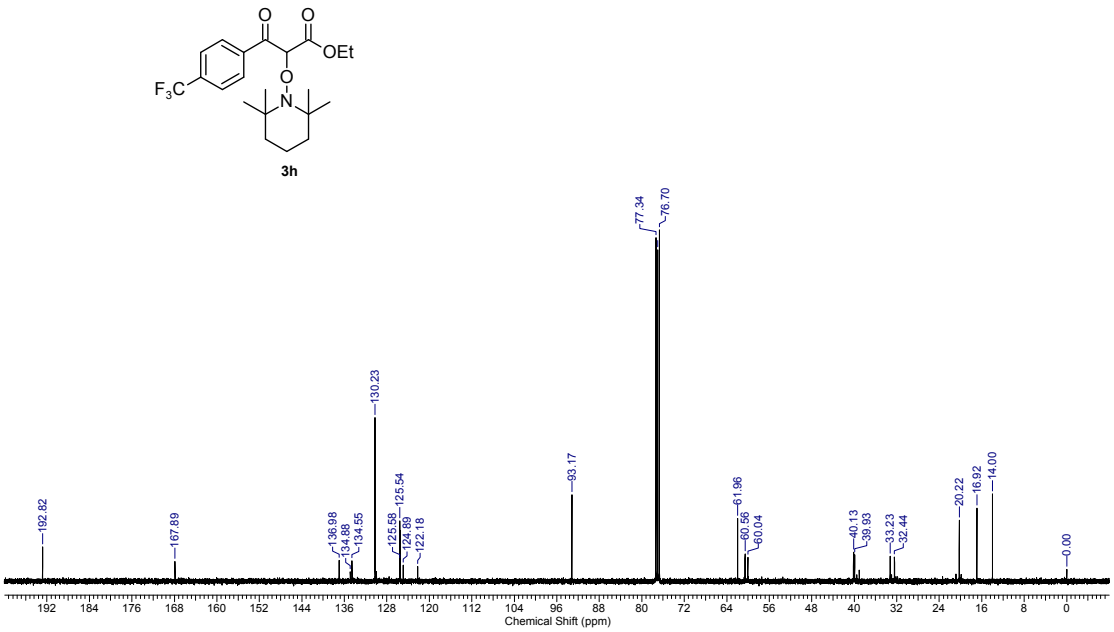


Figure S36. ^{13}C NMR spectrum of compound **3h**

G-12A-19F.ESP

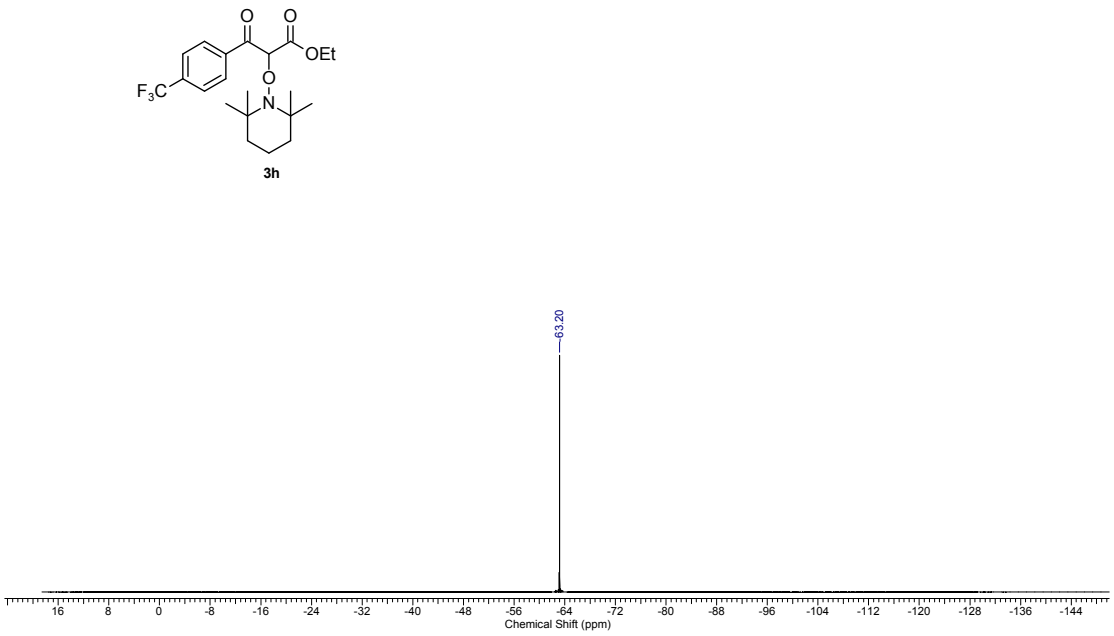


Figure S37. ^{19}F NMR spectrum of compound **3h**

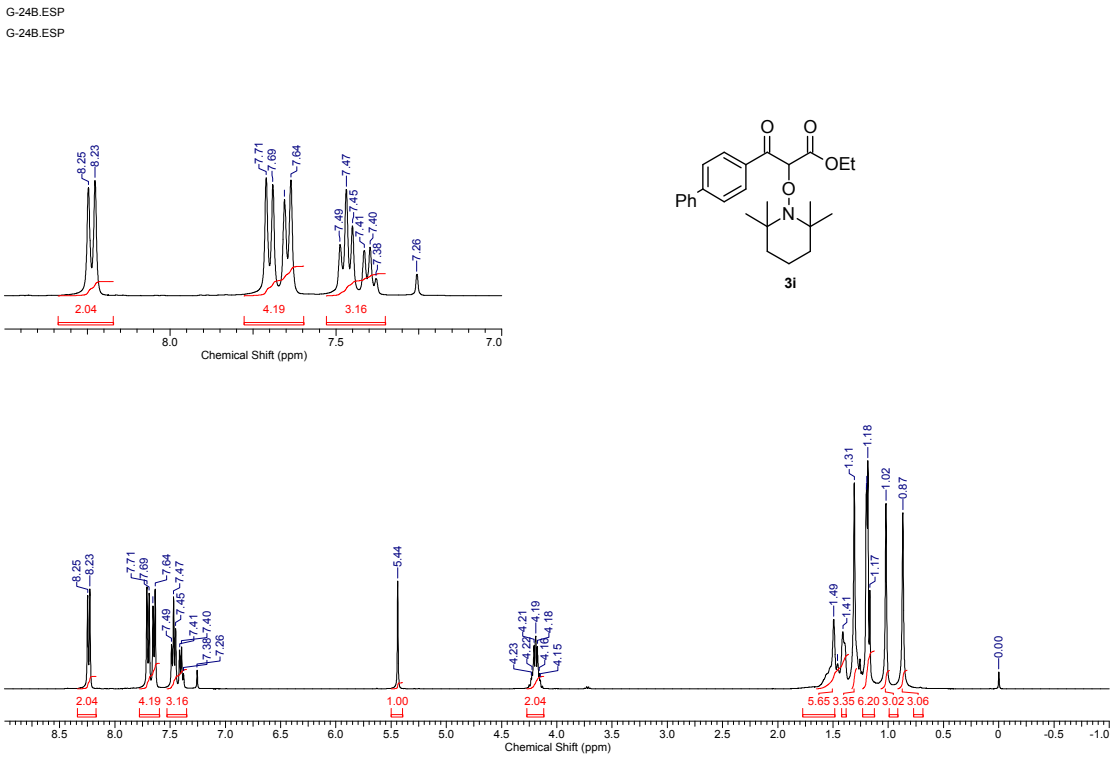


Figure S38. ^{1}H NMR spectrum of compound **3i**

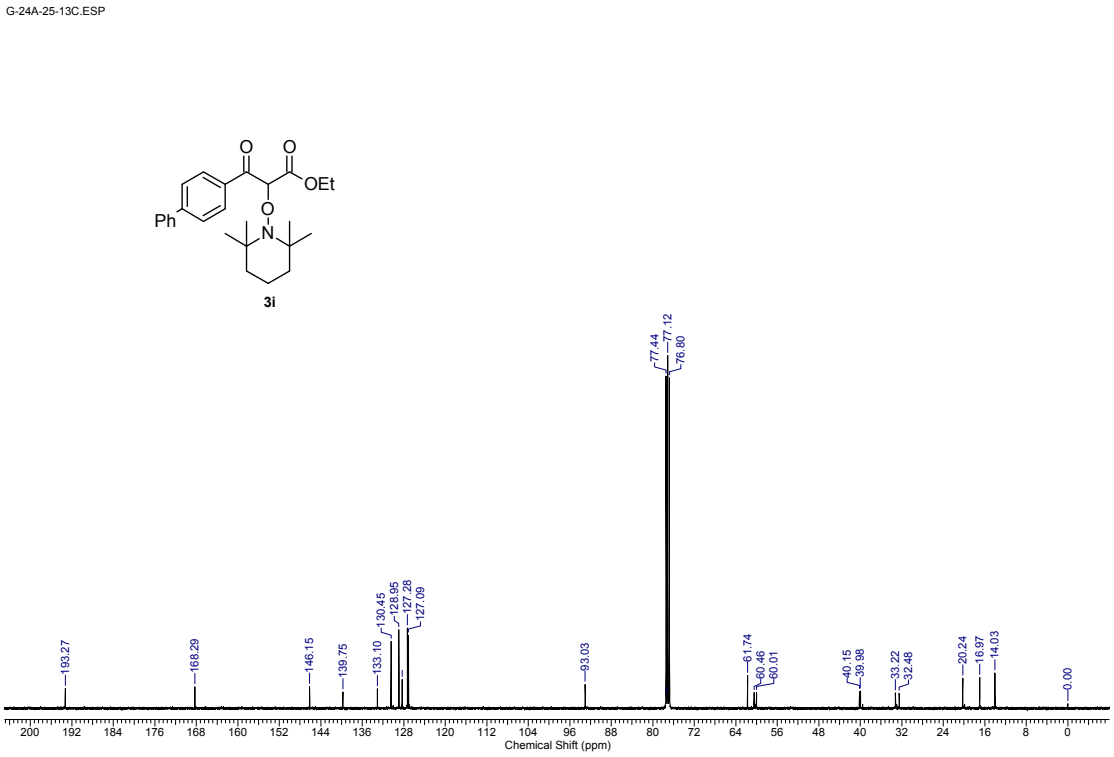


Figure S39. ^{13}C NMR spectrum of compound **3i**

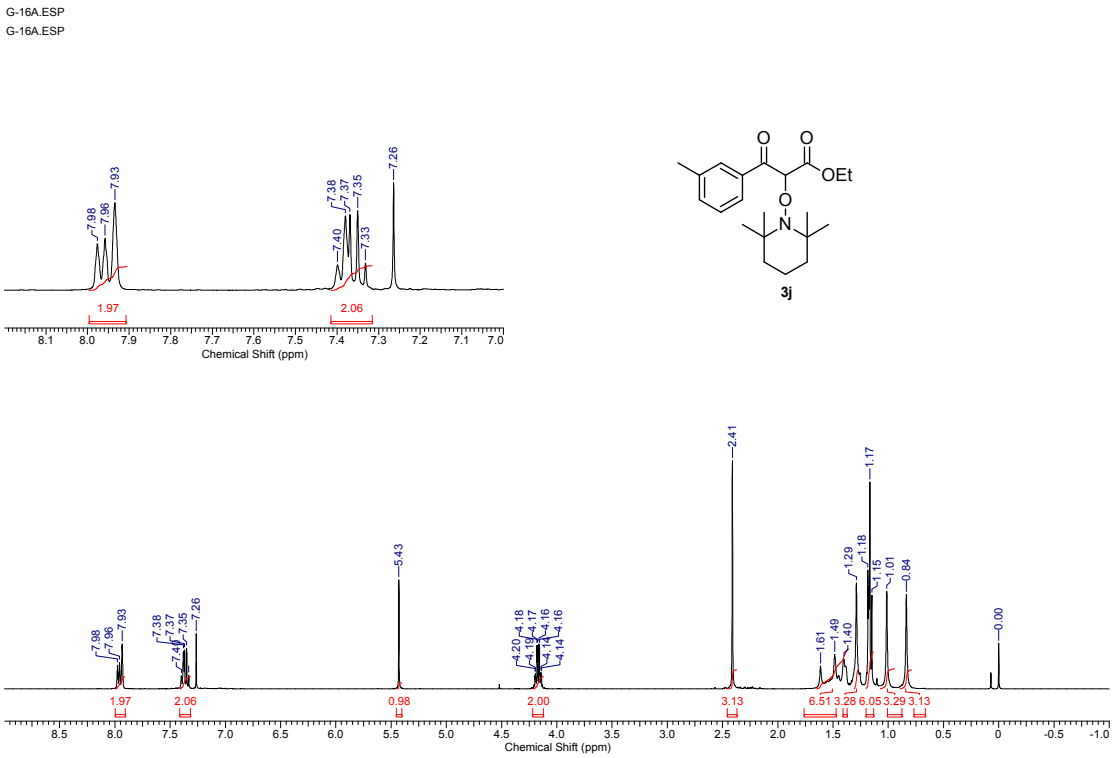


Figure S40. ^{1}H NMR spectrum of compound **3j**

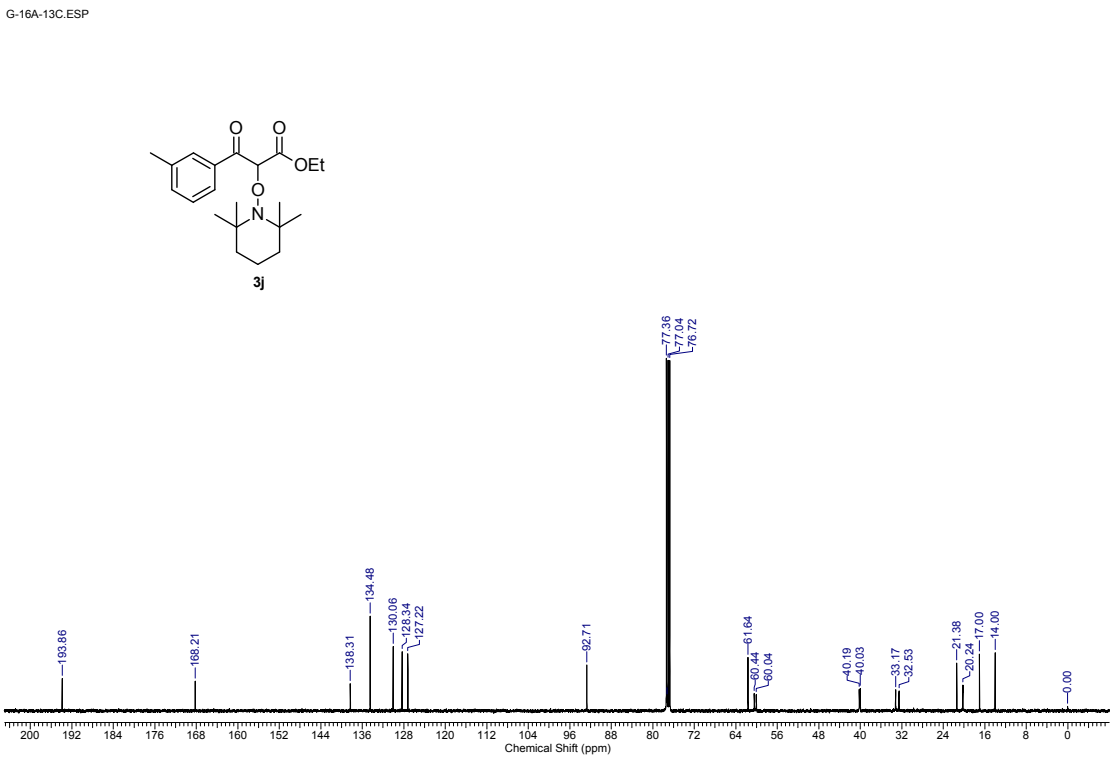


Figure S41. ^{13}C NMR spectrum of compound **3j**

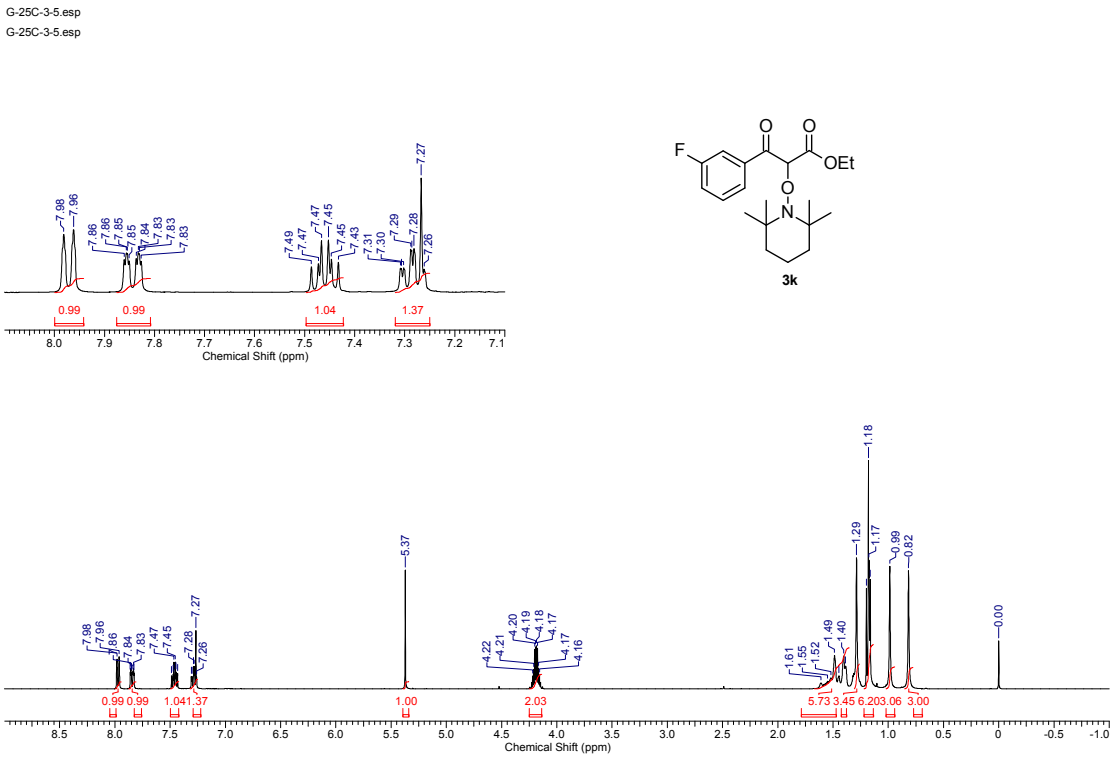


Figure S42. ^{1}H NMR spectrum of compound **3k**

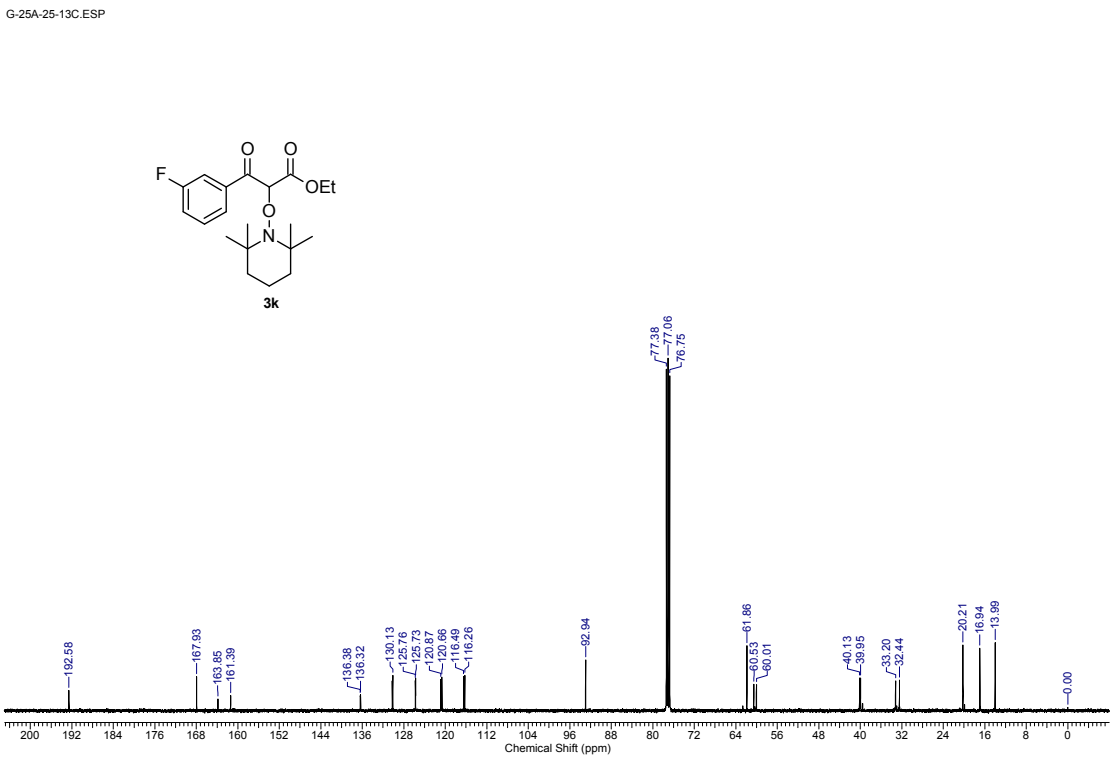


Figure S43. ^{13}C NMR spectrum of compound **3k**

G-25A-25-19F.ESP

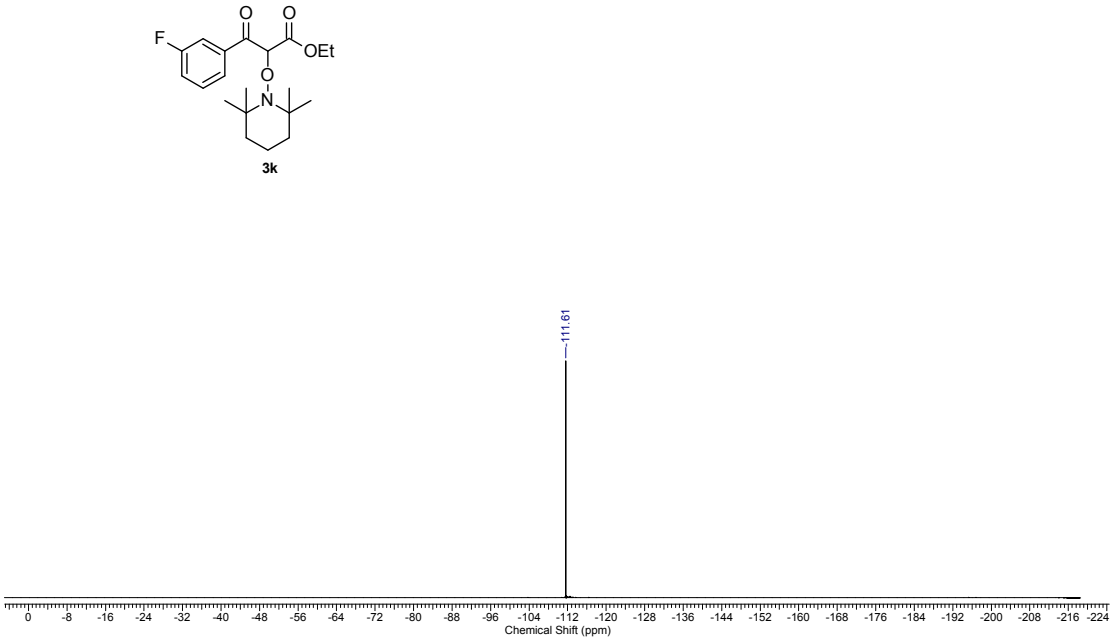


Figure S44. ^{19}F NMR spectrum of compound **3k**

G-18A-2+3.ESP

G-18A-2+3.ESP

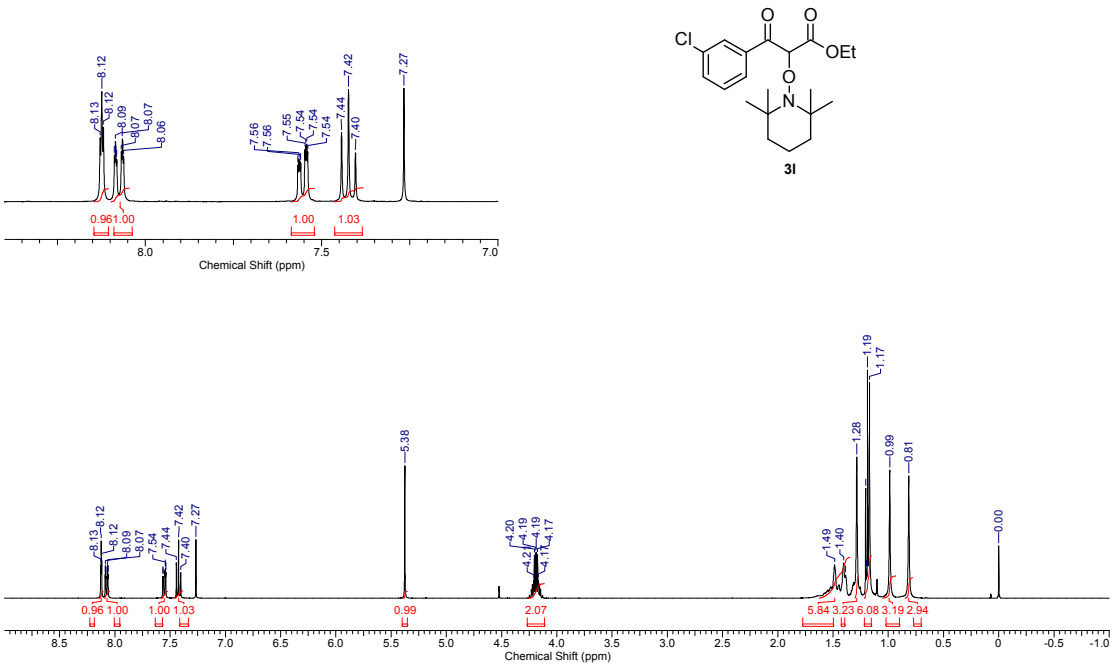


Figure S45. ^{1}H NMR spectrum of compound **3l**

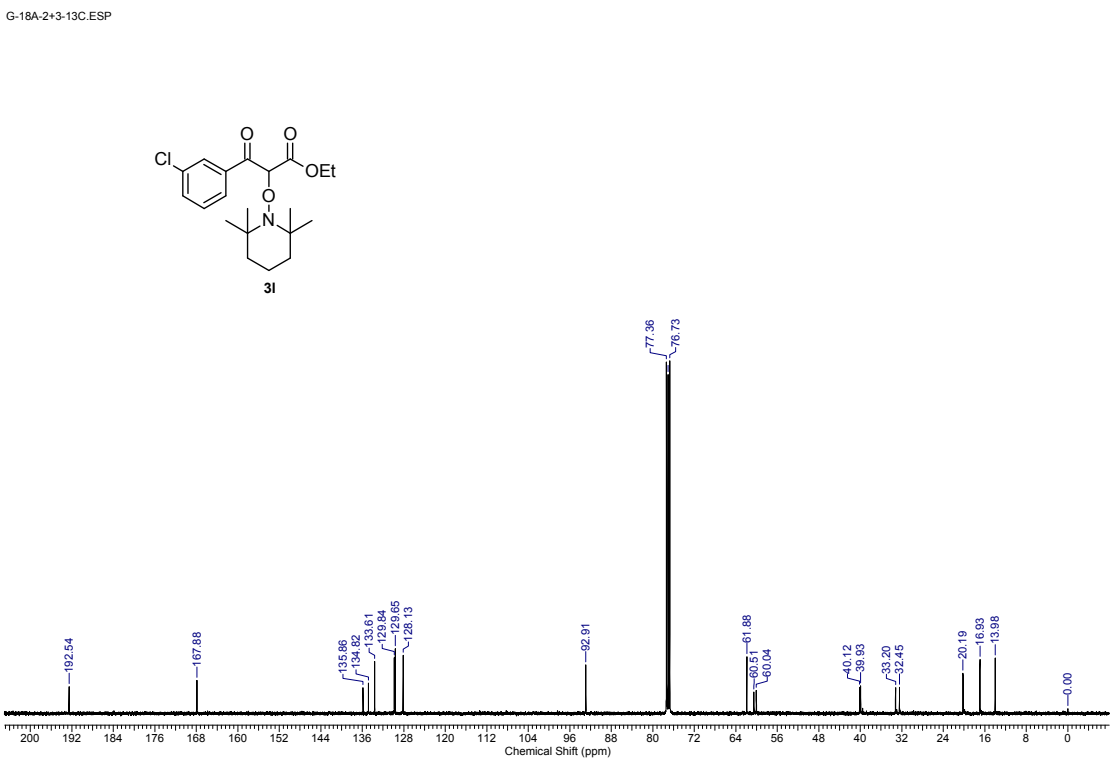


Figure S46. ^{13}C NMR spectrum of compound **3l**

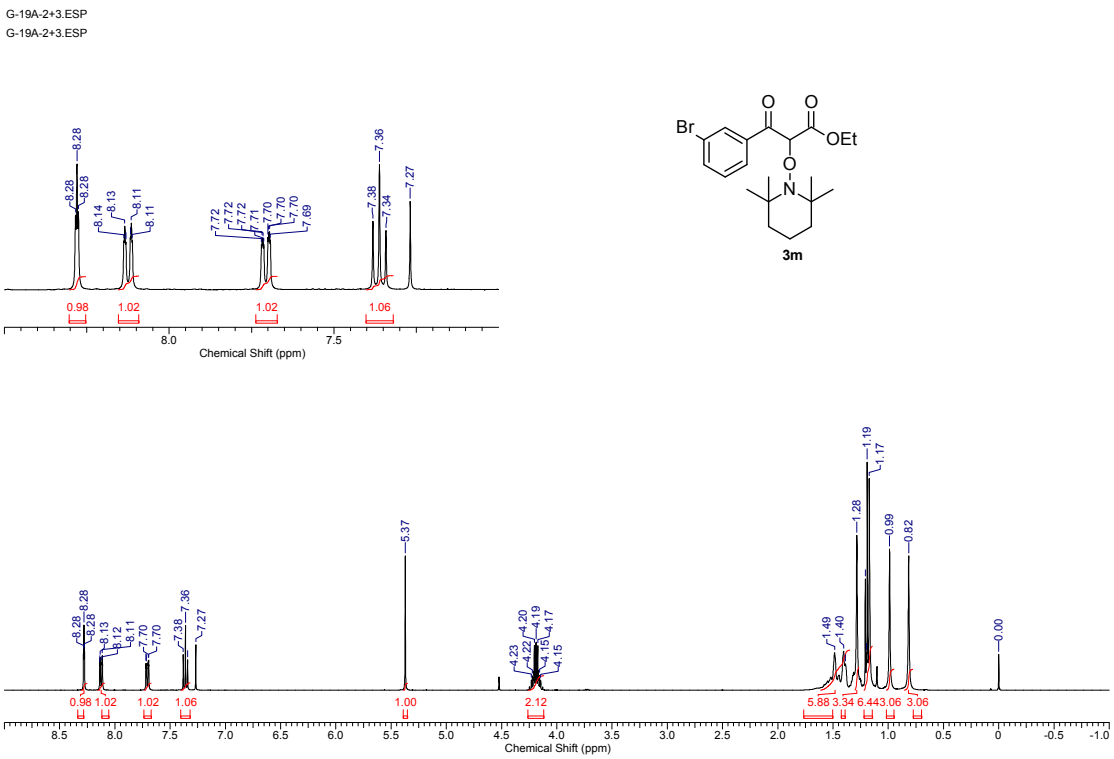


Figure S47. ^{1}H NMR spectrum of compound **3m**

G-19A-2+3-13C.ESP

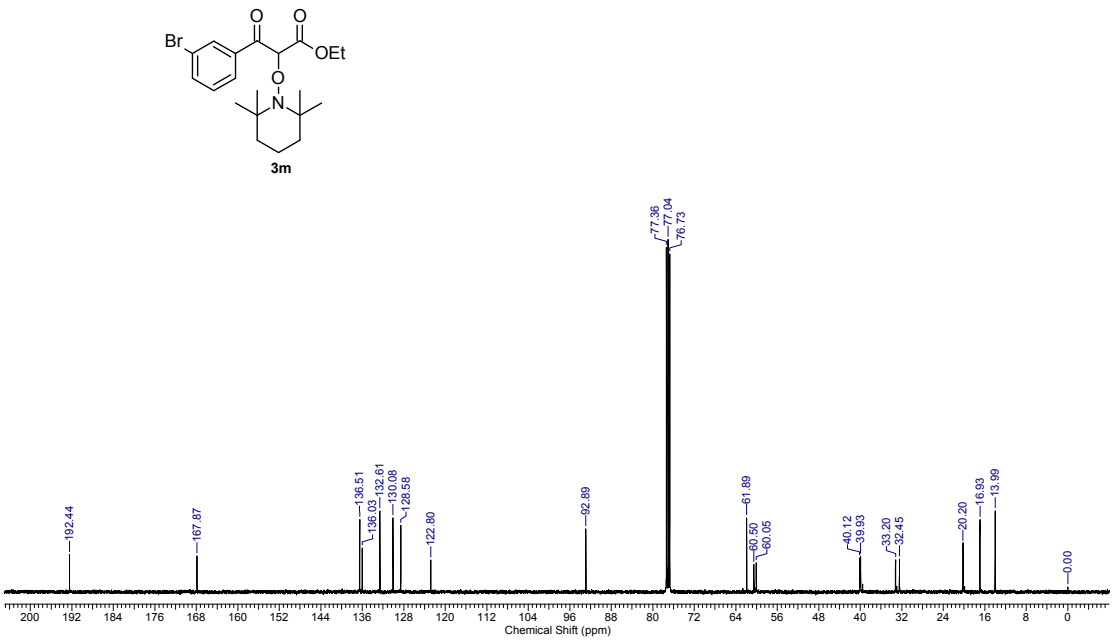


Figure S48. ^{13}C NMR spectrum of compound **3m**

G-28B.ESP

G-28B.ESP

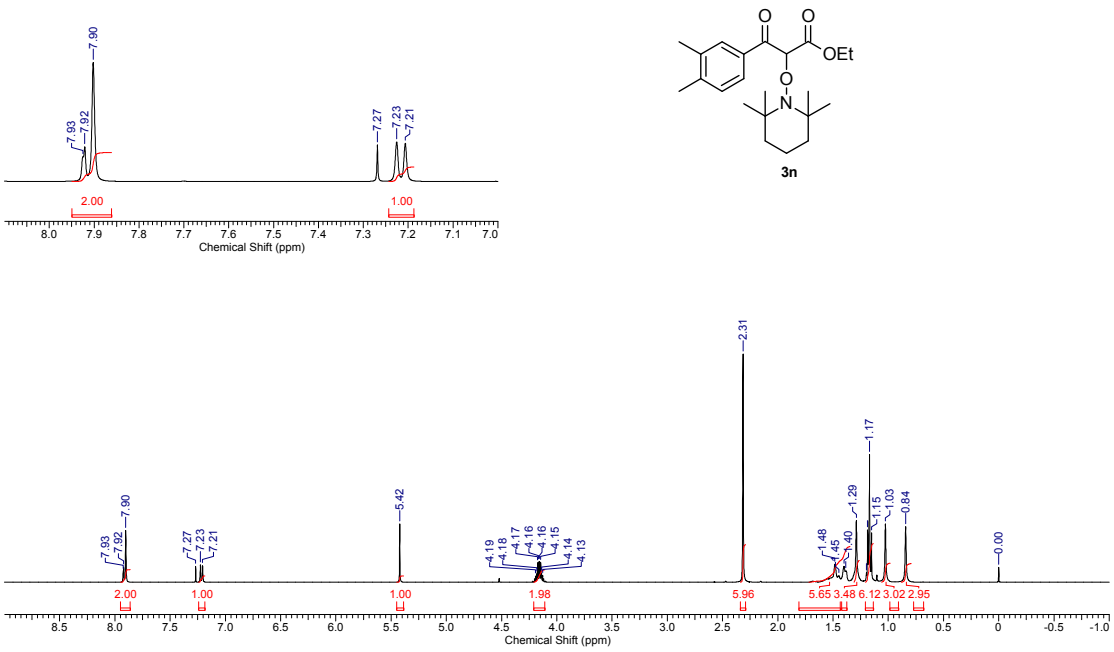


Figure S49. ^{1}H NMR spectrum of compound **3n**

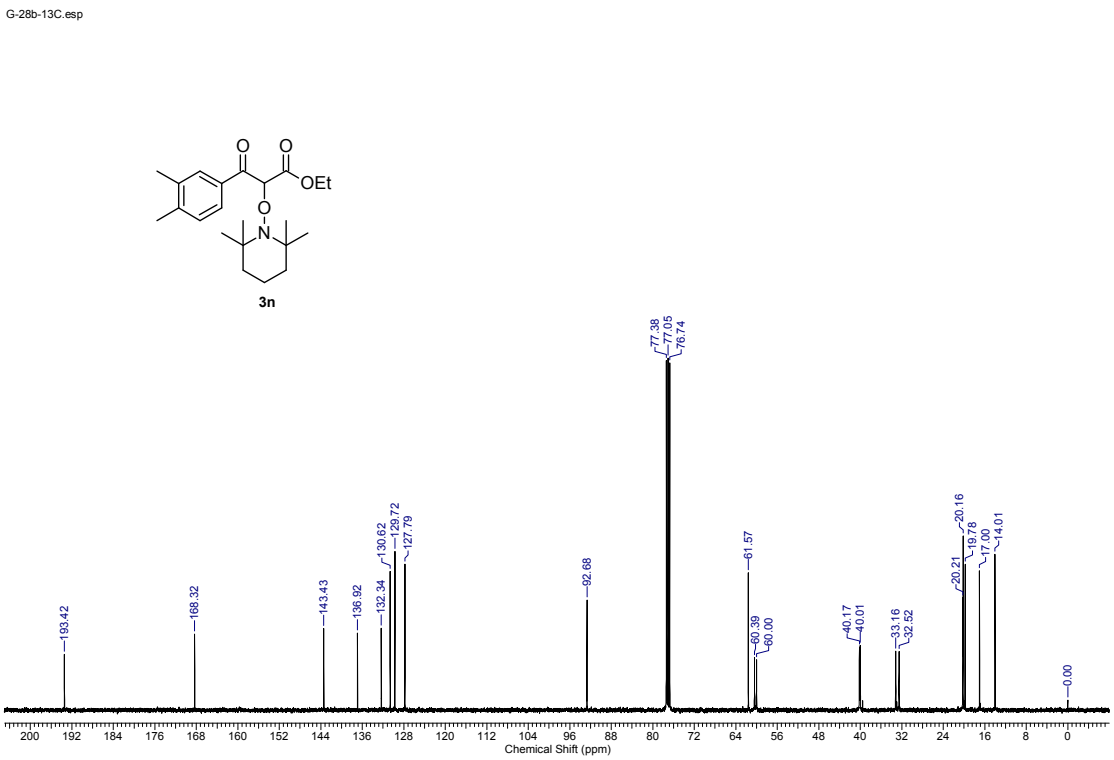


Figure S50. ^{13}C NMR spectrum of compound **3n**

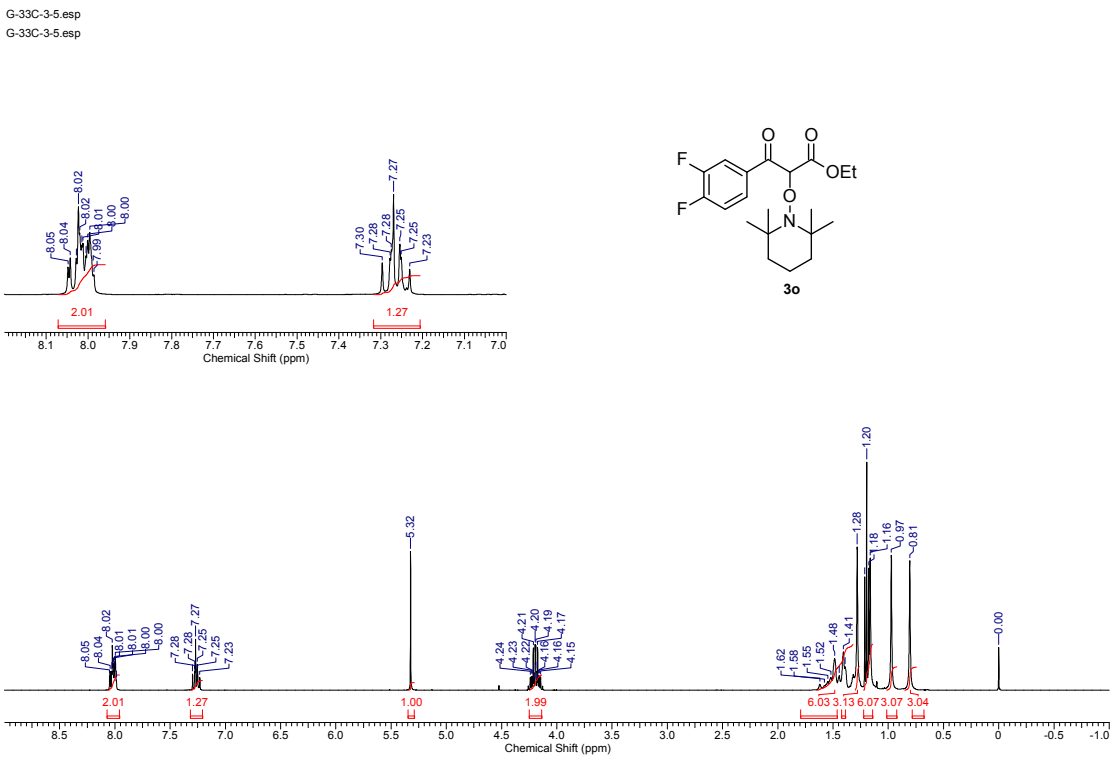


Figure S51. ^{1}H NMR spectrum of compound **3o**

G-33A-2-3-13C.ESP

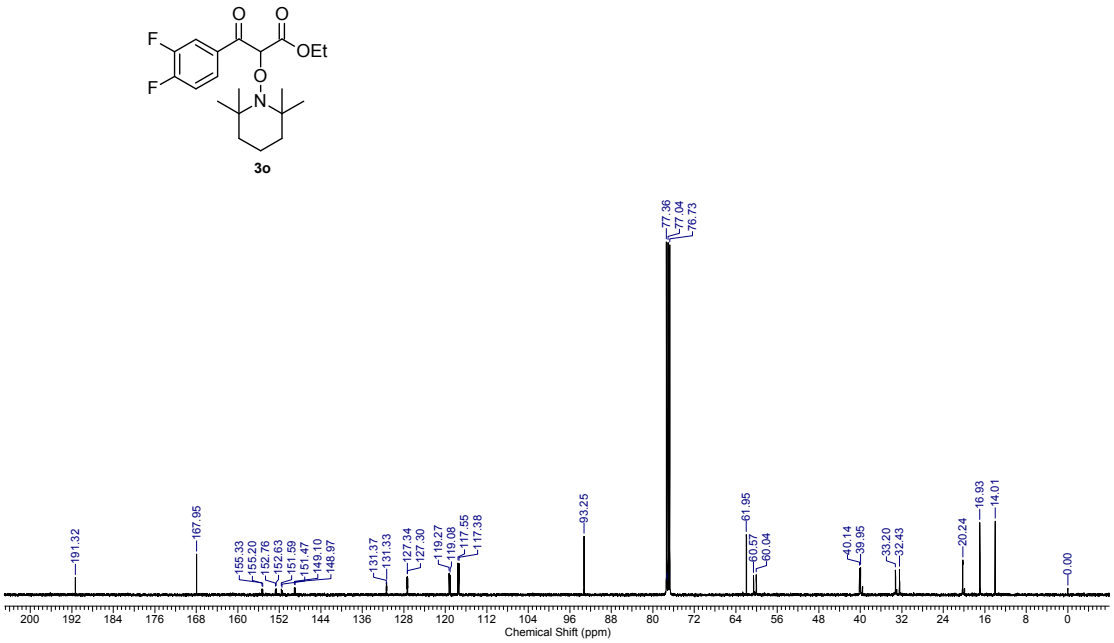


Figure S52. ^{13}C NMR spectrum of compound **3o**

G-33A-2-3-19F.ESP

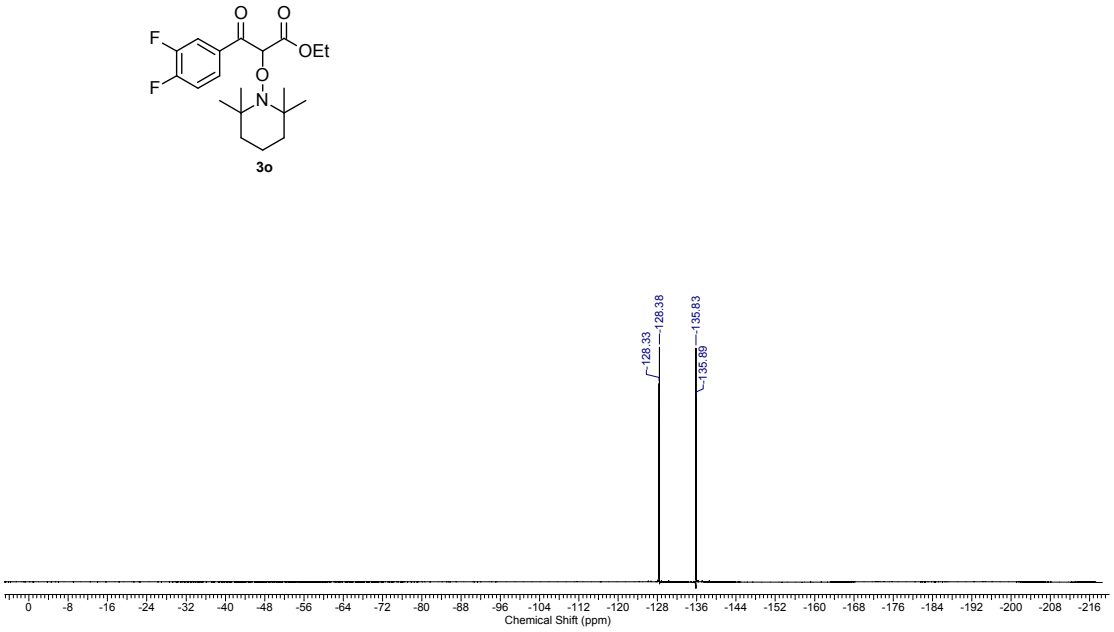


Figure S53. ^{19}F NMR spectrum of compound **3o**

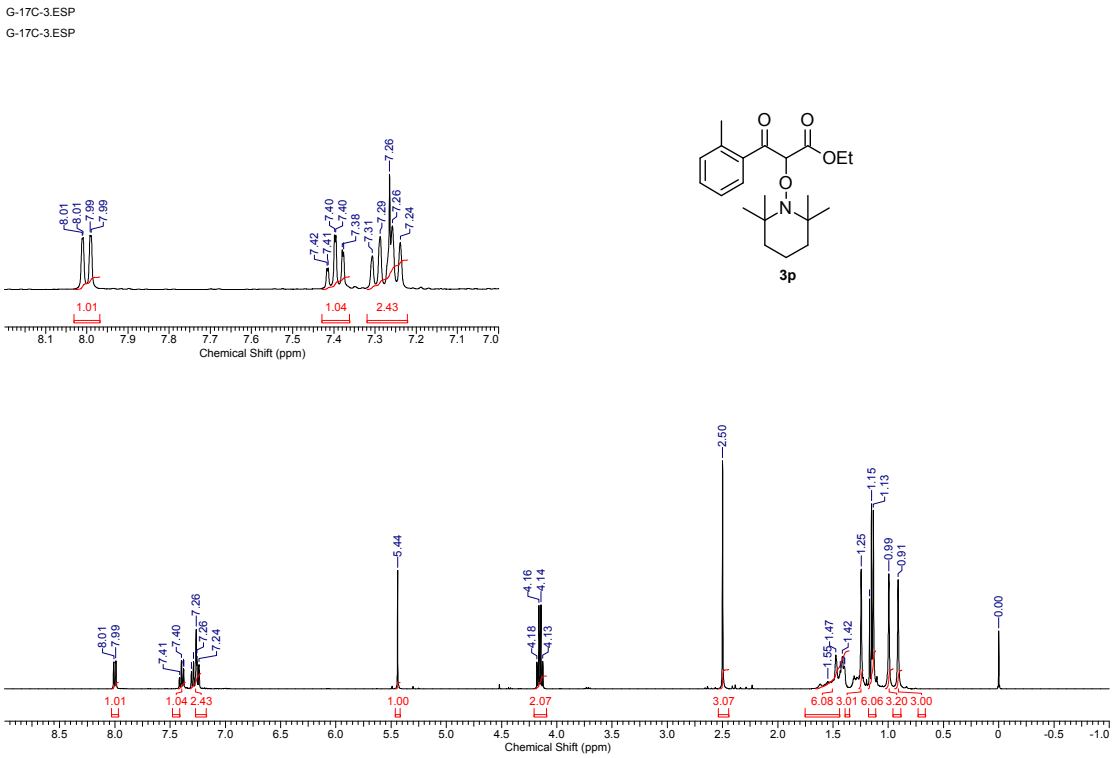


Figure S54. ^{1}H NMR spectrum of compound **3p**

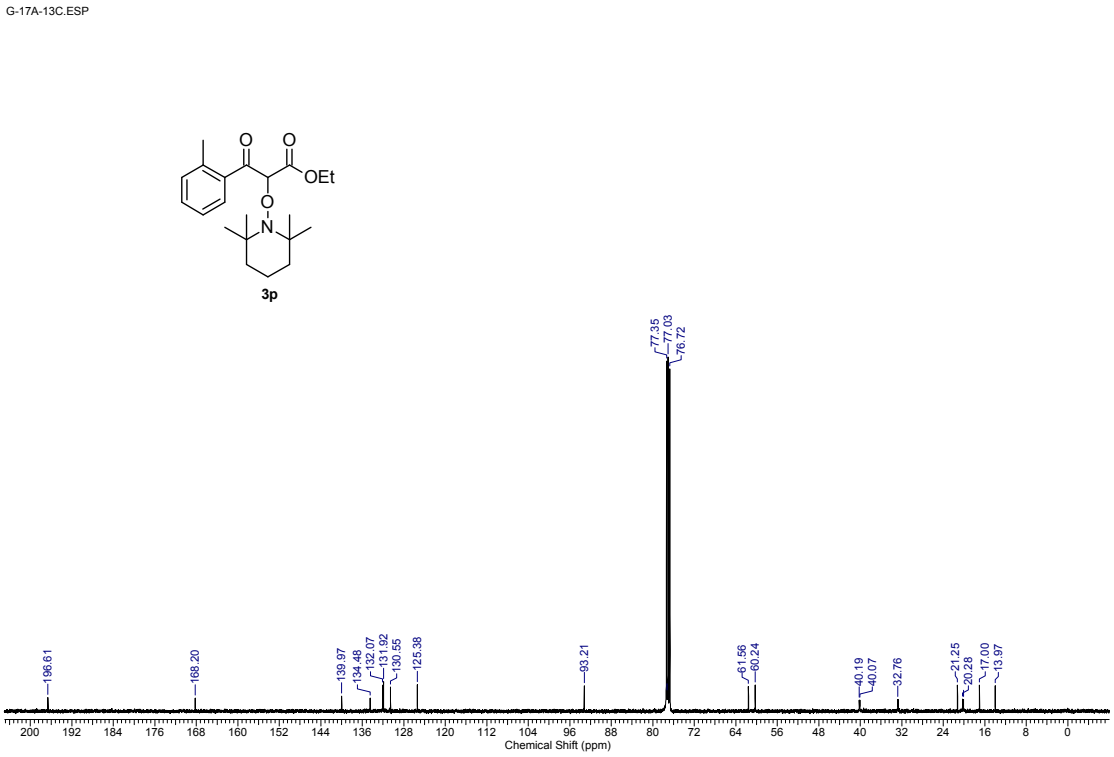


Figure S55. ^{13}C NMR spectrum of compound **3p**

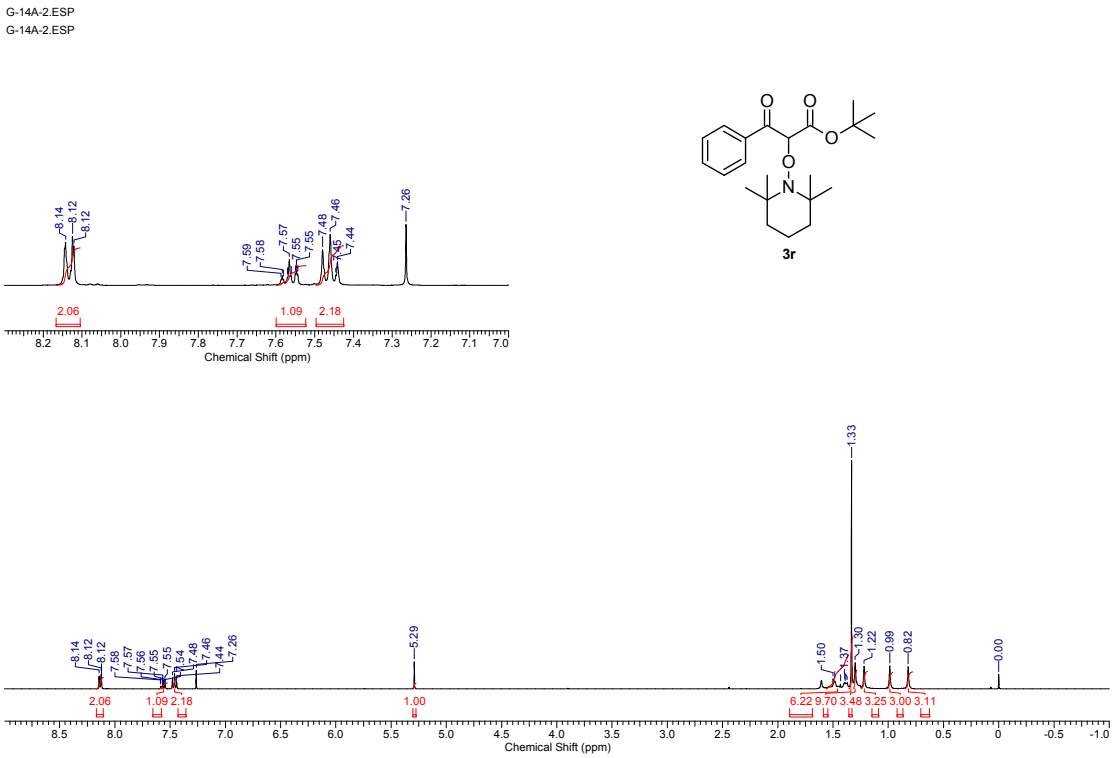


Figure S56. ^{1}H NMR spectrum of compound **3r**

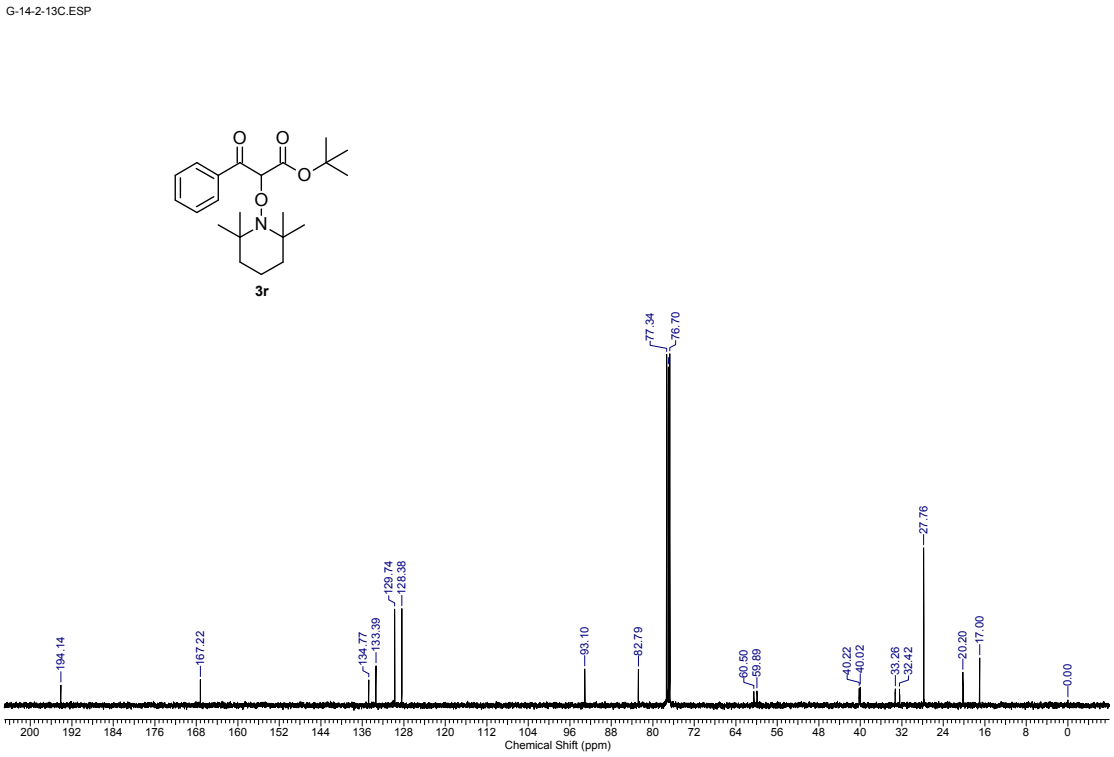


Figure S57. ^{13}C NMR spectrum of compound **3r**

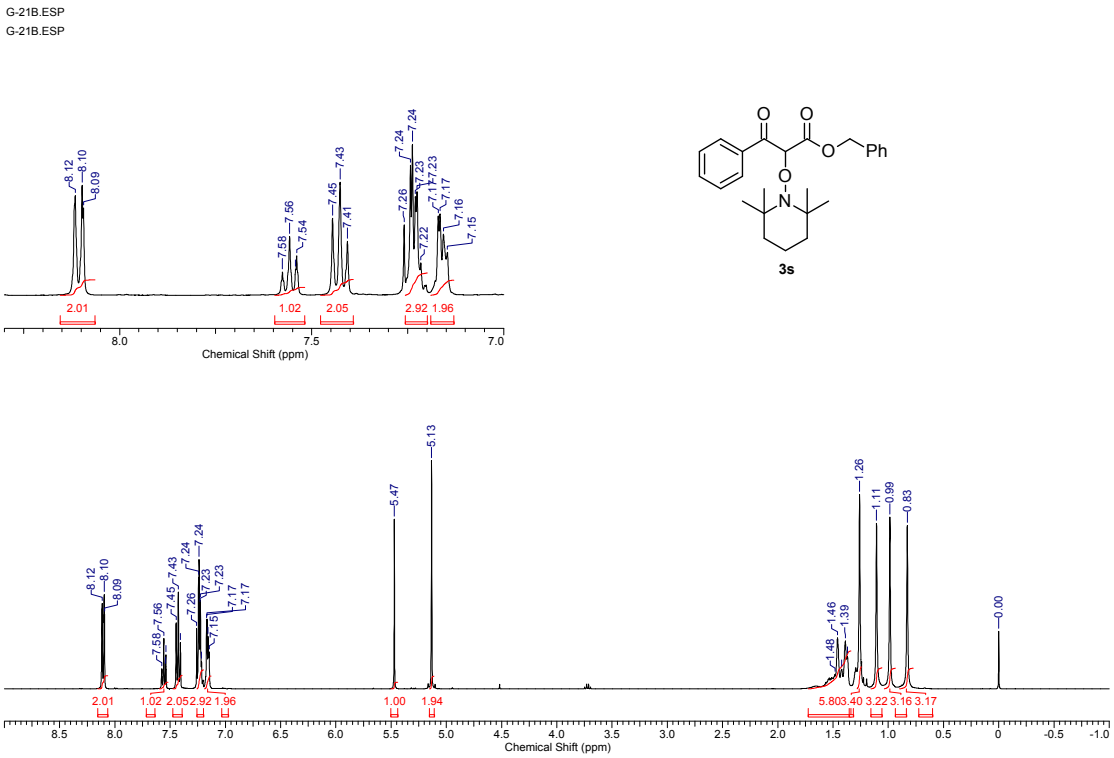


Figure S58. ^{1}H NMR spectrum of compound **3s**

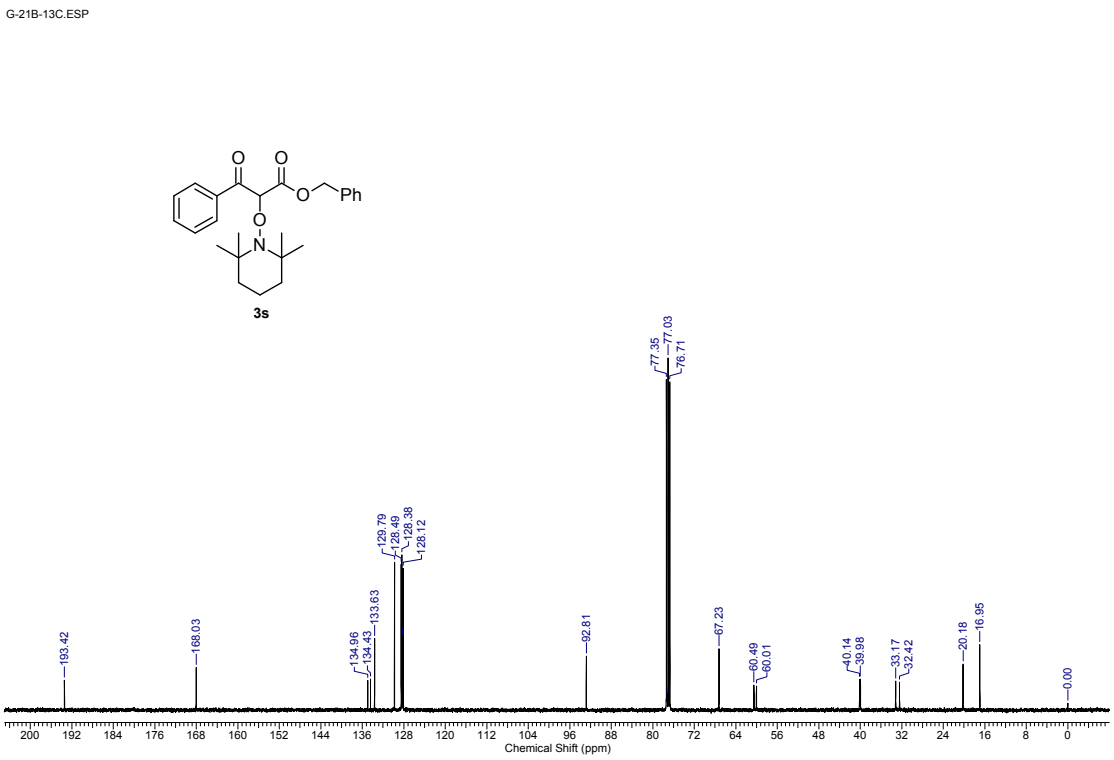


Figure S59. ^{13}C NMR spectrum of compound **3s**

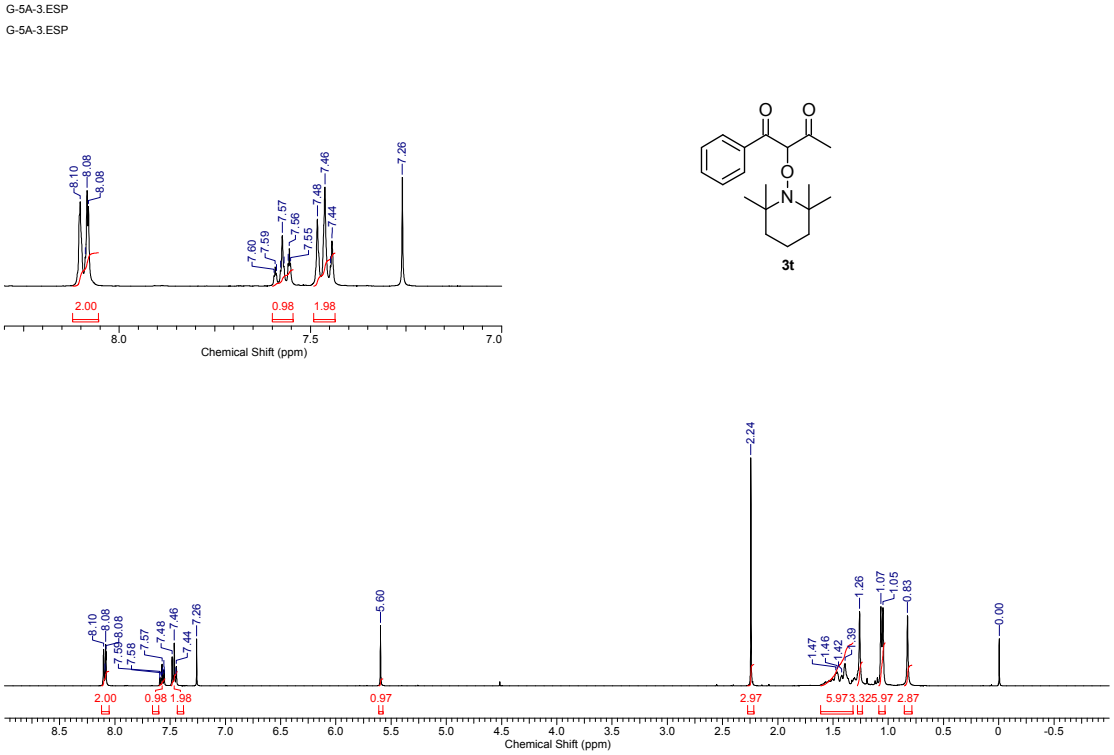


Figure S60. ^{1}H NMR spectrum of compound **3t**

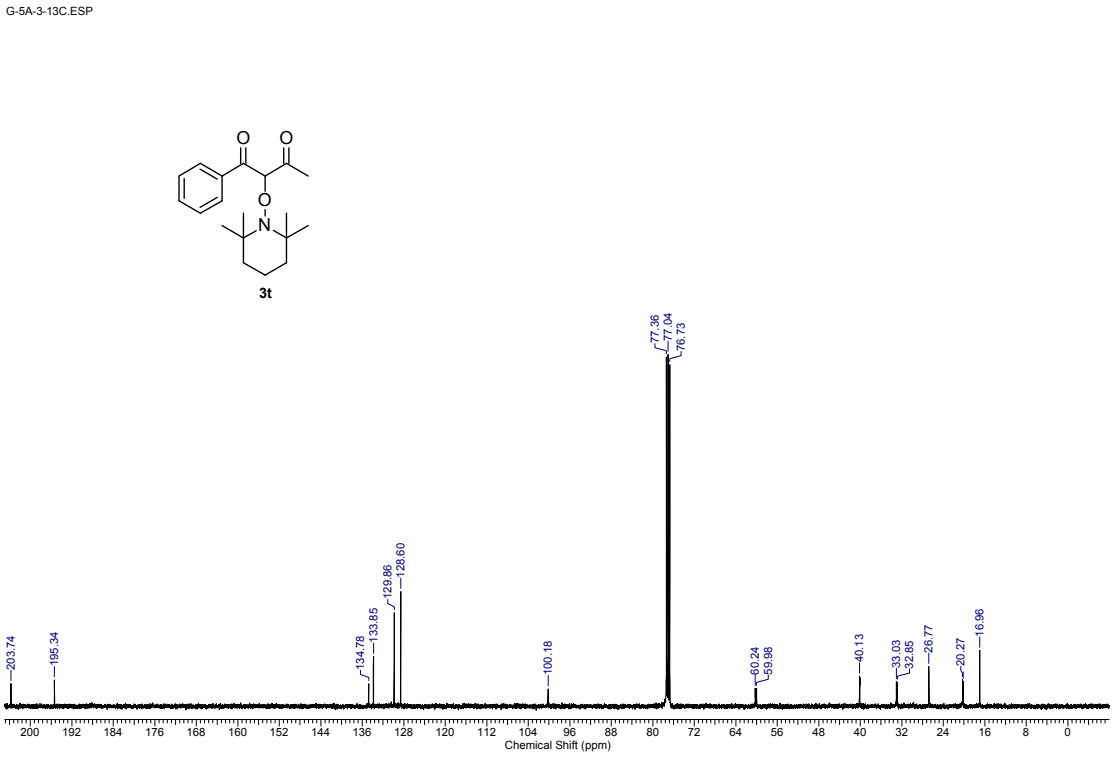


Figure S61. ^{13}C NMR spectrum of compound **3t**

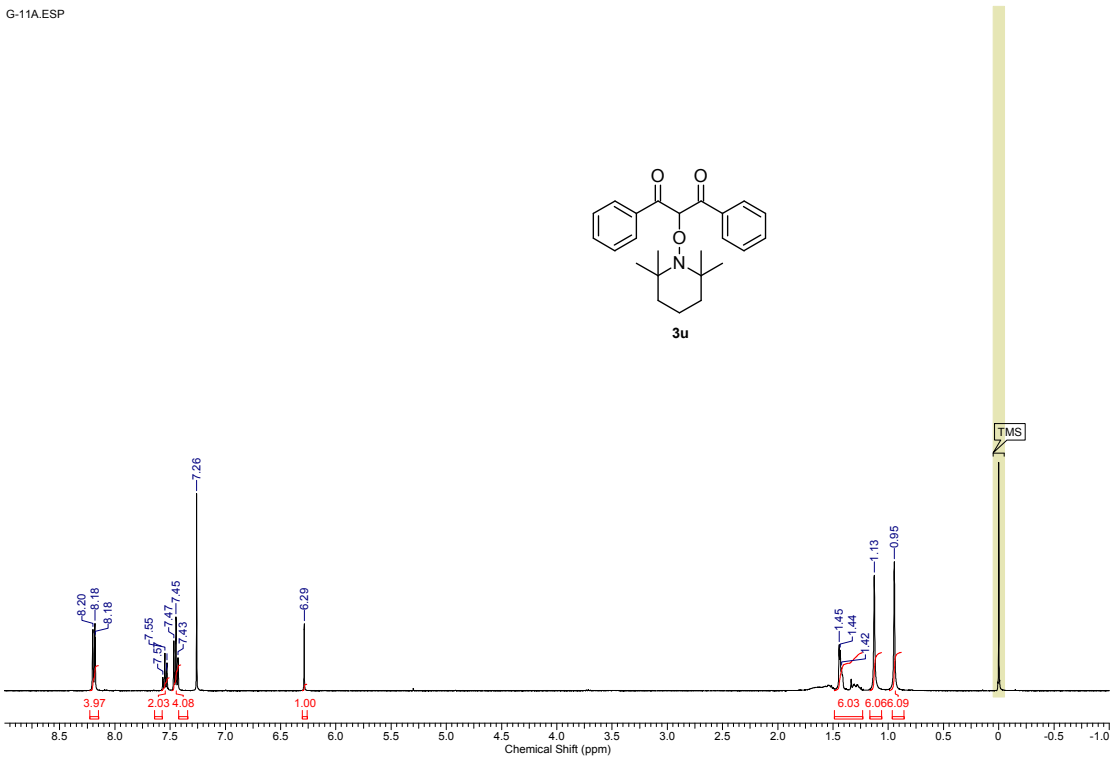


Figure S62. ^{1}H NMR spectrum of compound **3u**

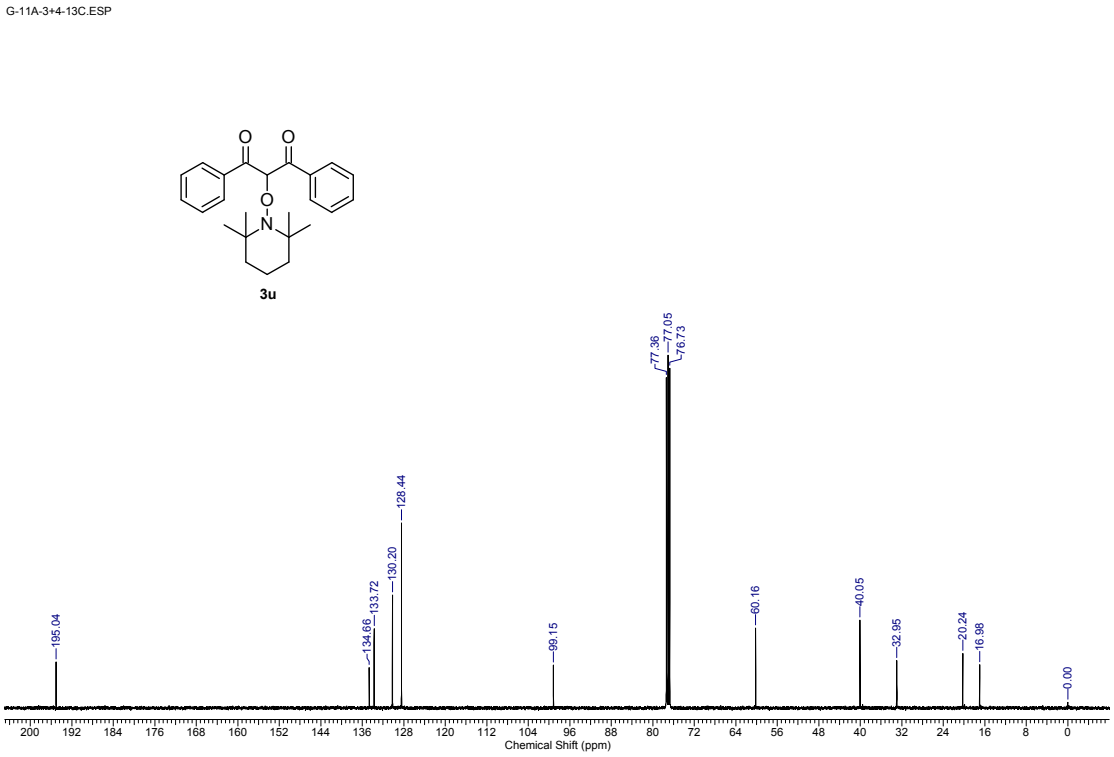


Figure S63. ^{13}C NMR spectrum of compound **3u**

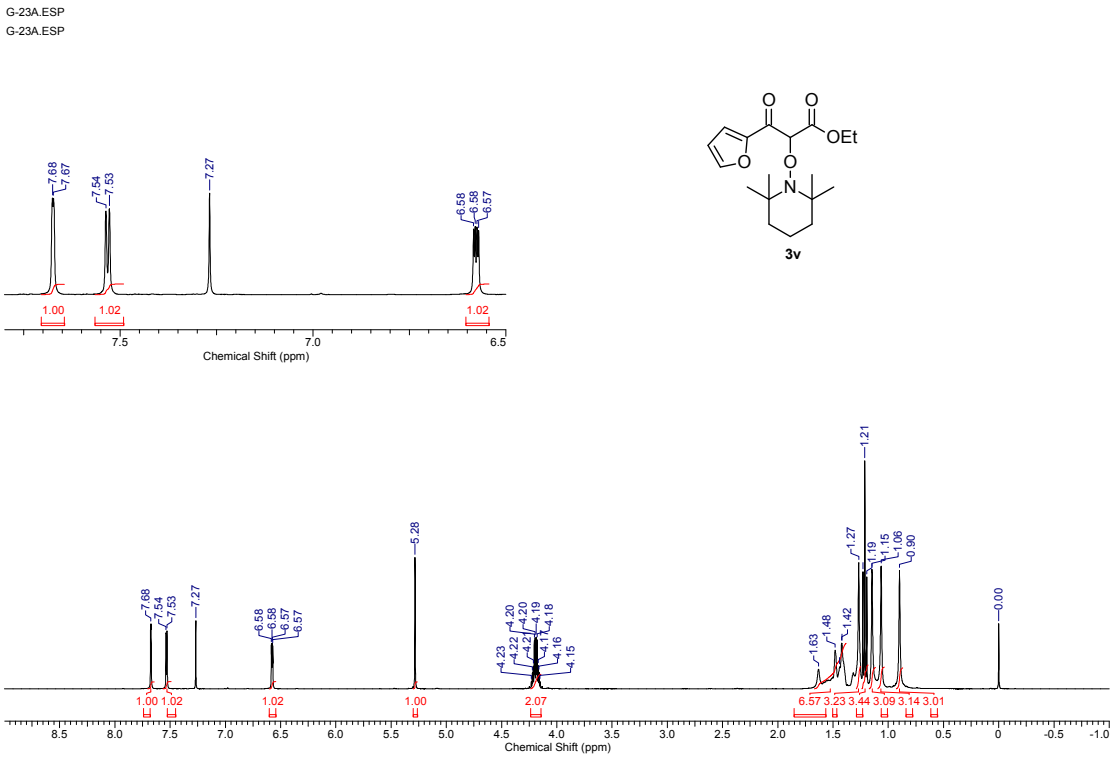


Figure S64. ^{1}H NMR spectrum of compound **3v**

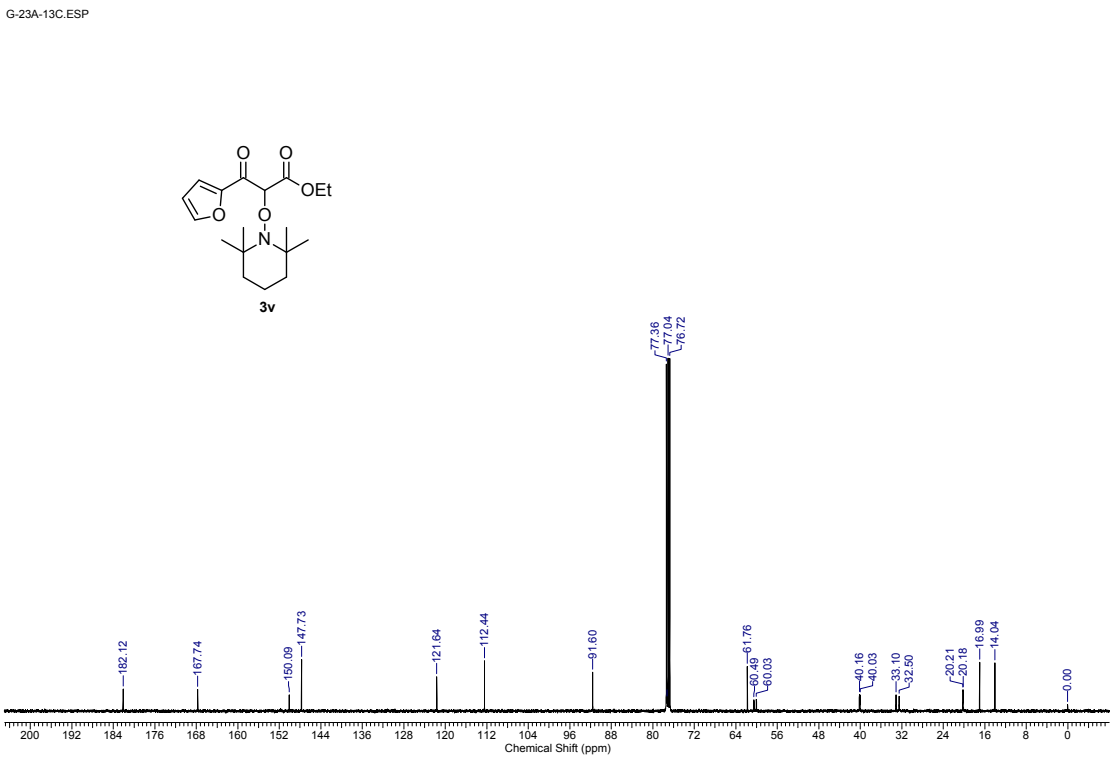


Figure S65. ^{13}C NMR spectrum of compound **3v**

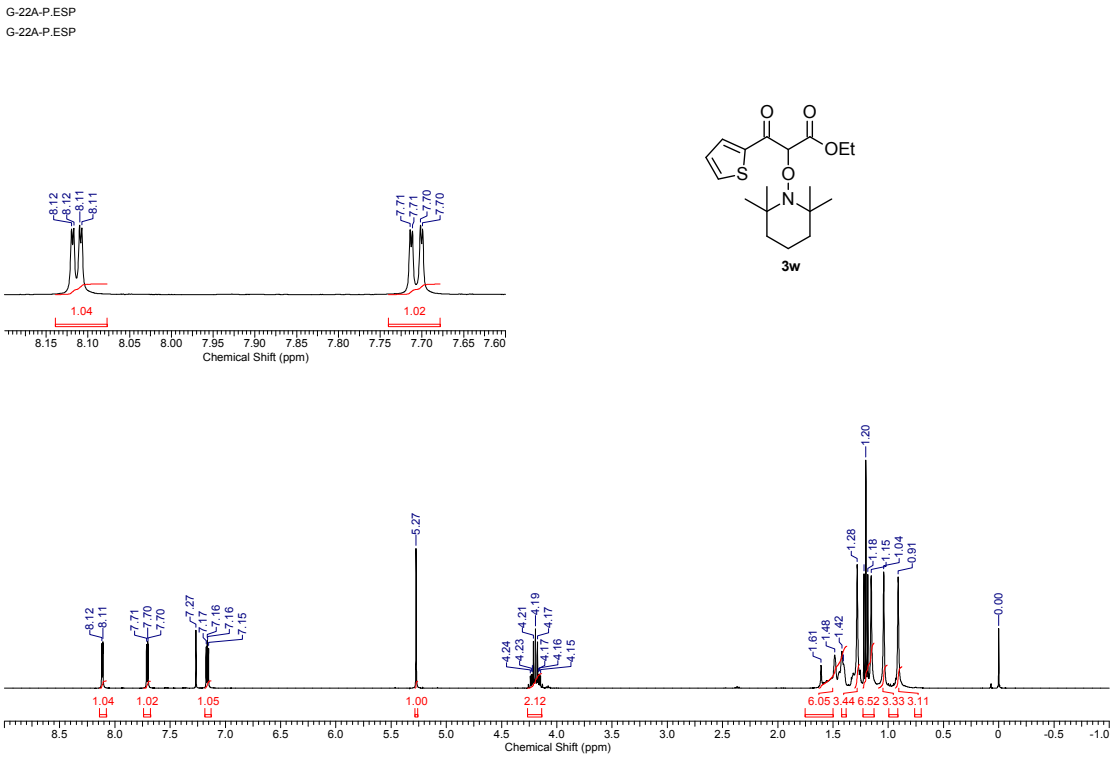


Figure S66. ^{1}H NMR spectrum of compound **3w**

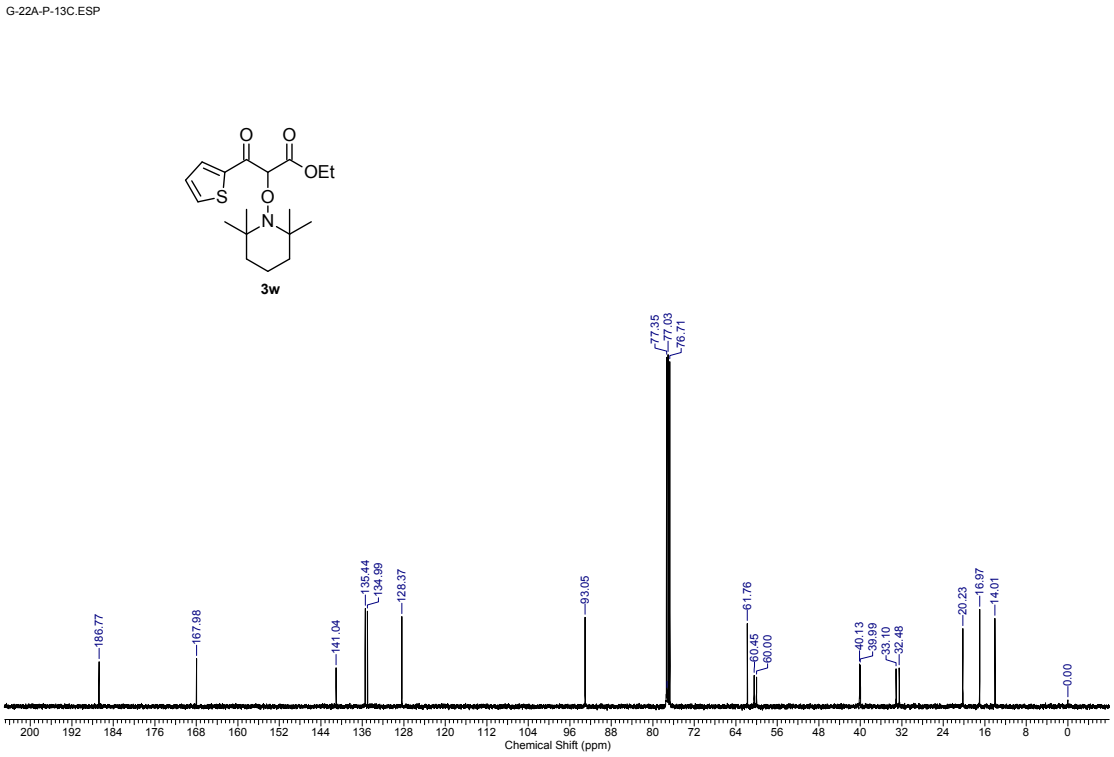


Figure S67. ^{13}C NMR spectrum of compound **3w**

GM-166-2.esp

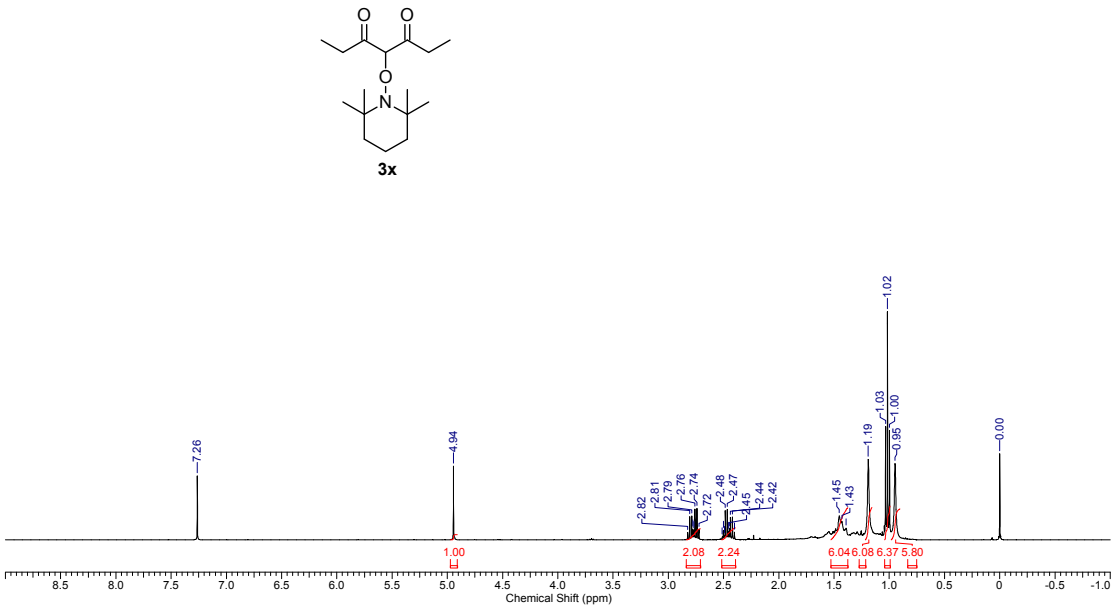


Figure S68. ^{1}H NMR spectrum of compound **3x**

GM-166-2-13C_000001r

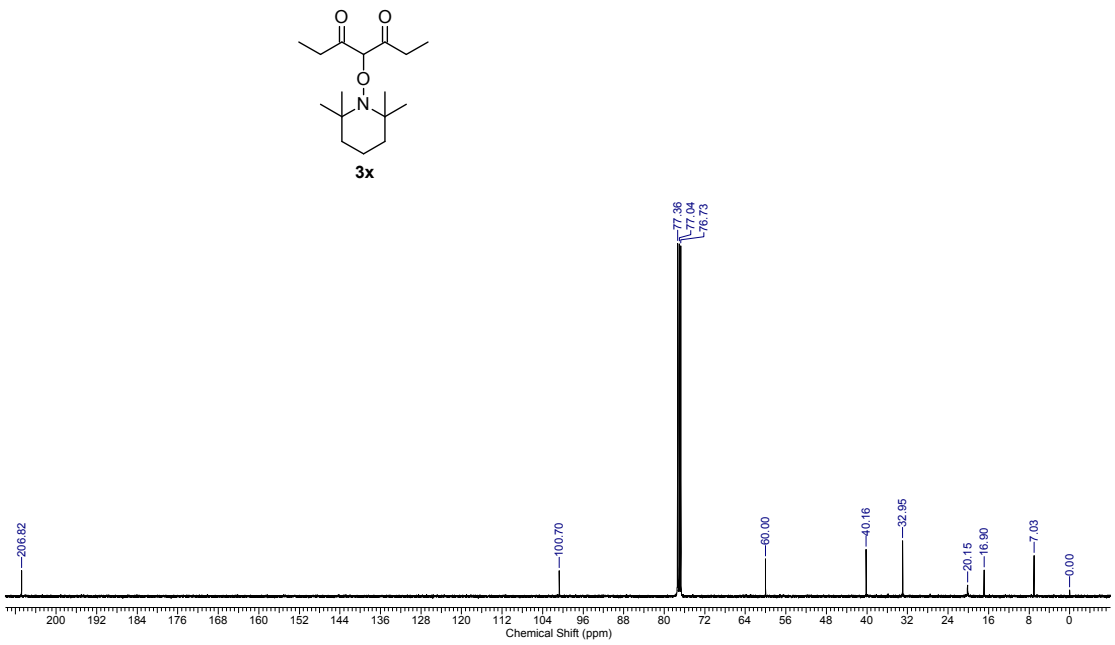


Figure S69. ^{13}C NMR spectrum of compound **3x**

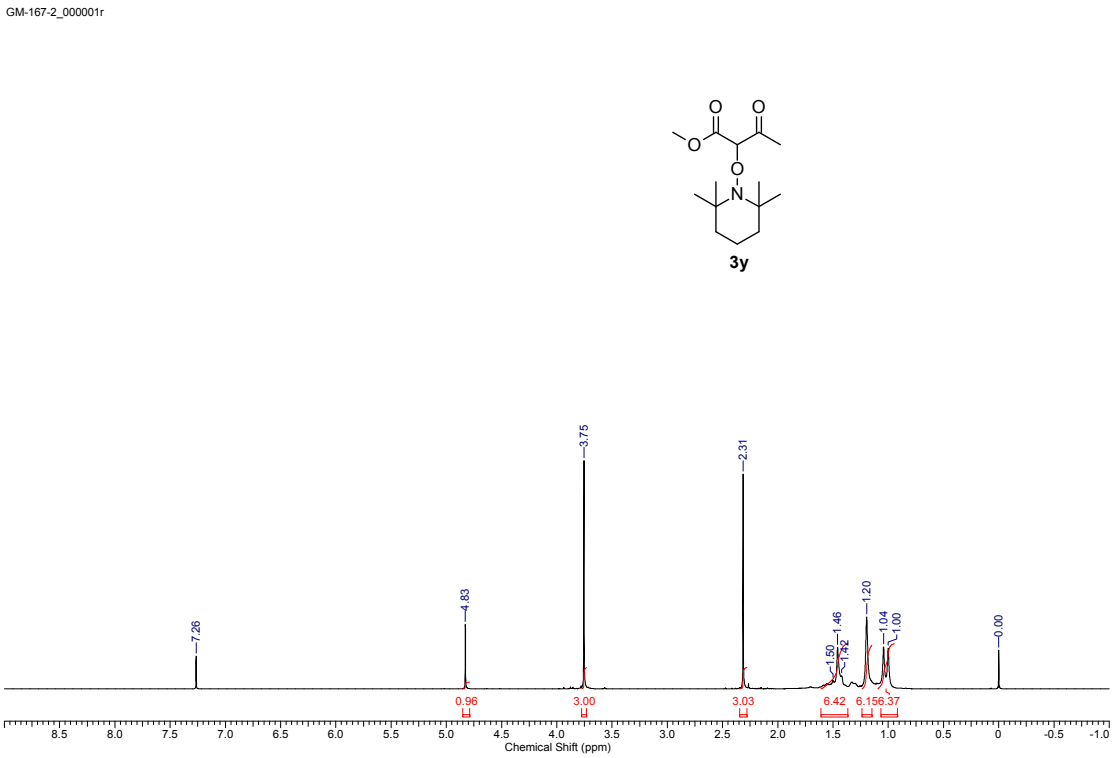


Figure S70. ^{1}H NMR spectrum of compound **3y**

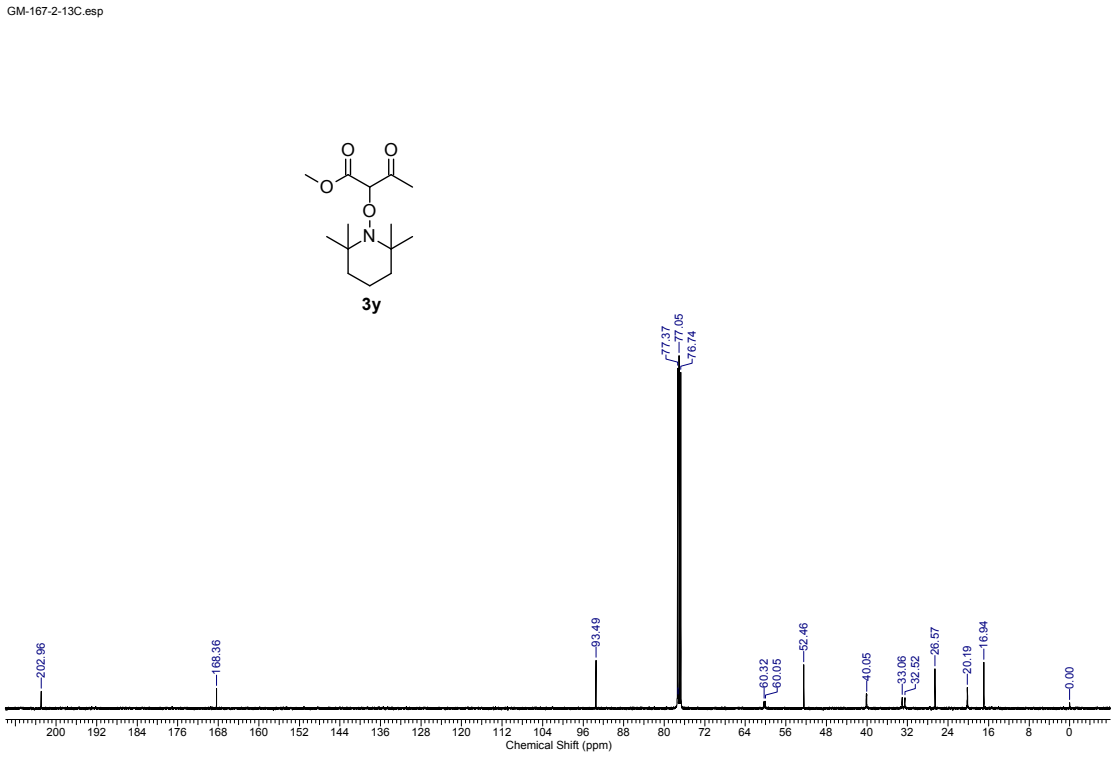


Figure S71. ^{13}C NMR spectrum of compound **3y**

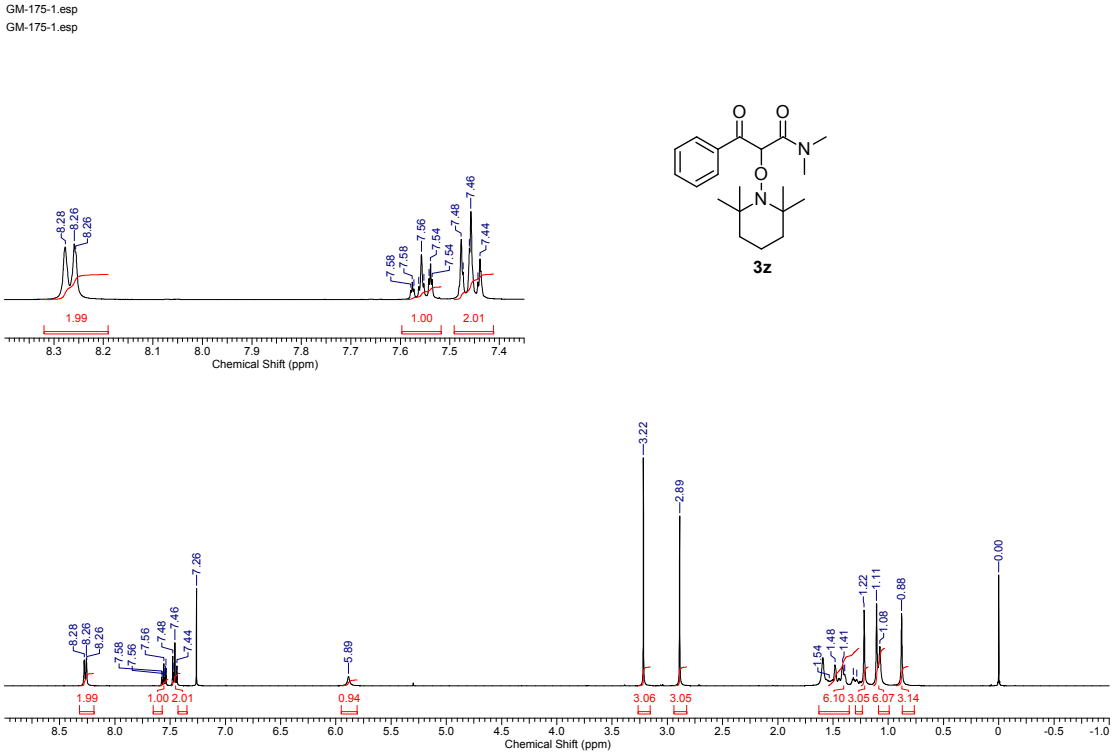


Figure S72. ^{1}H NMR spectrum of compound **3z**

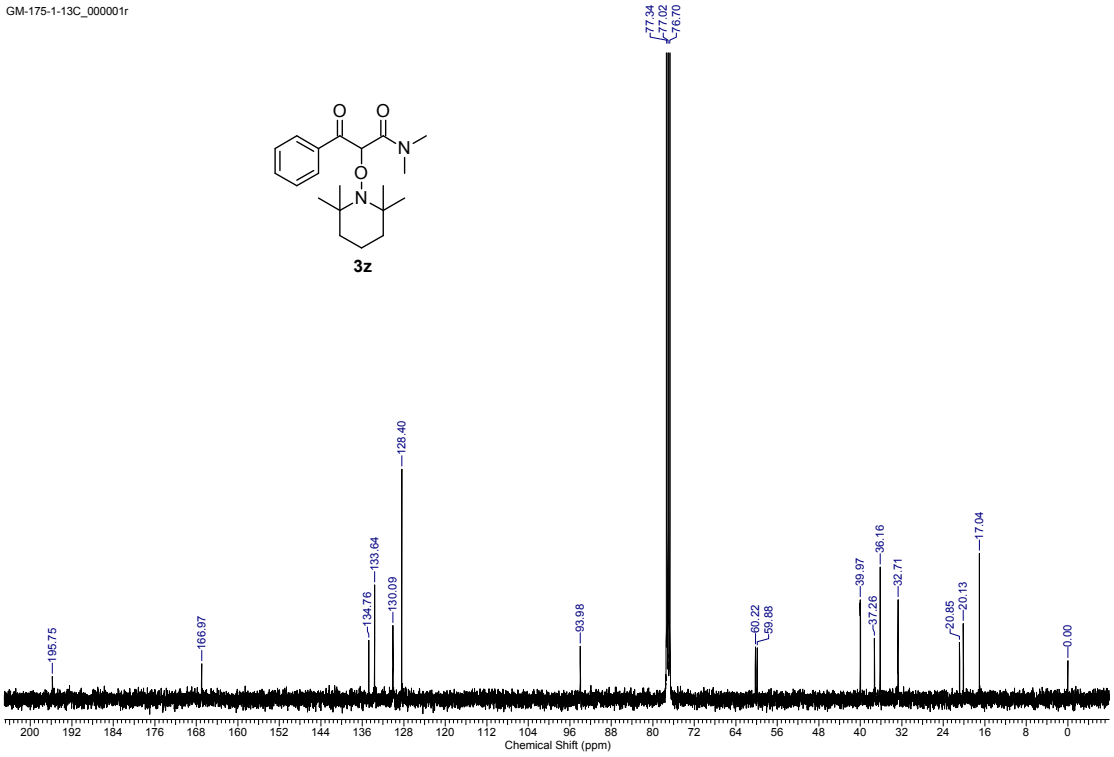


Figure S73. ^{13}C NMR spectrum of compound **3z**

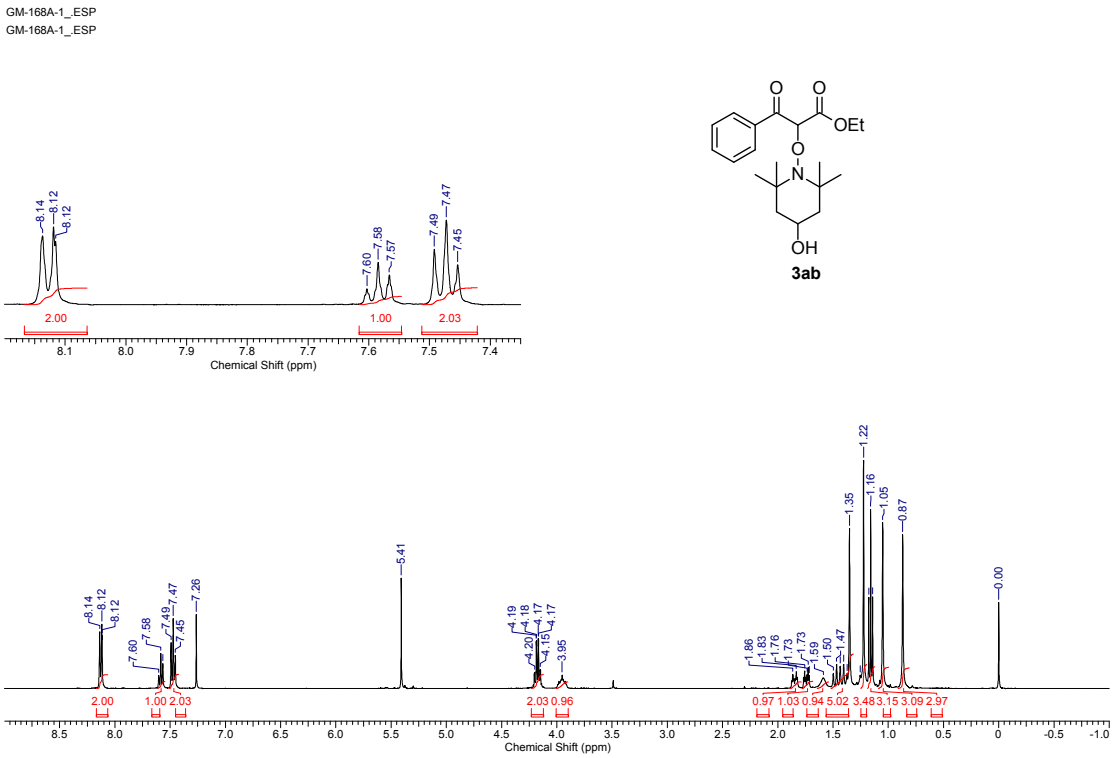


Figure S74. ^{1}H NMR spectrum of compound **3ab**

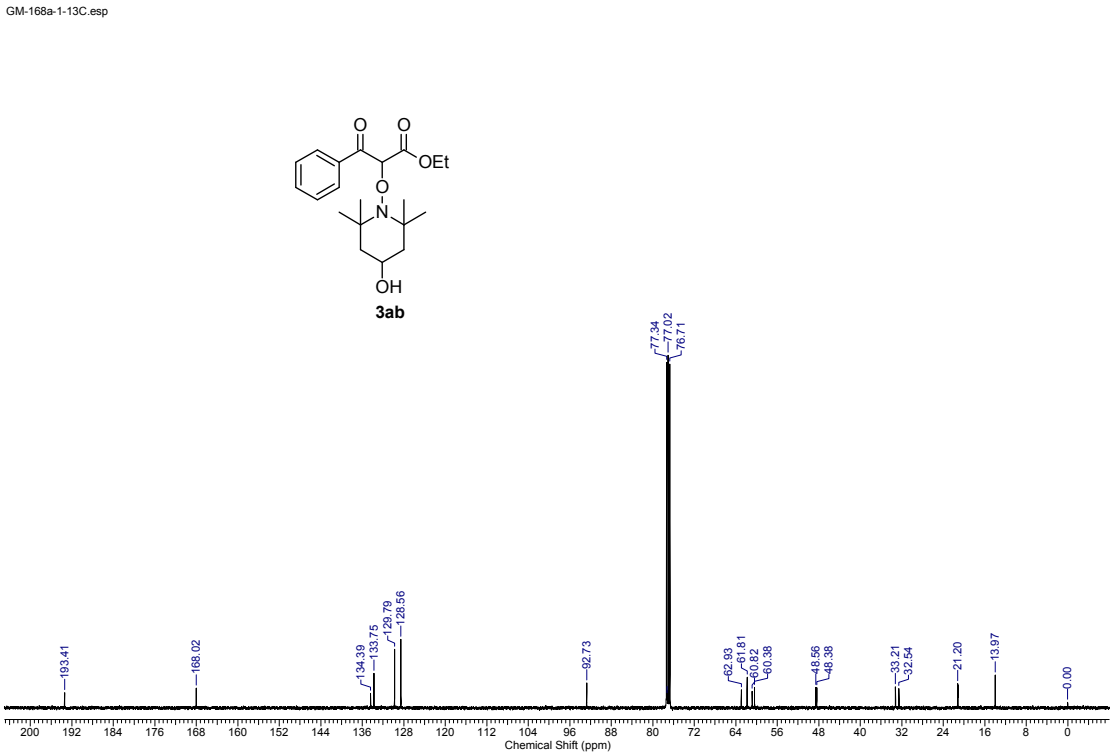


Figure S75. ^{13}C NMR spectrum of compound **3ab**

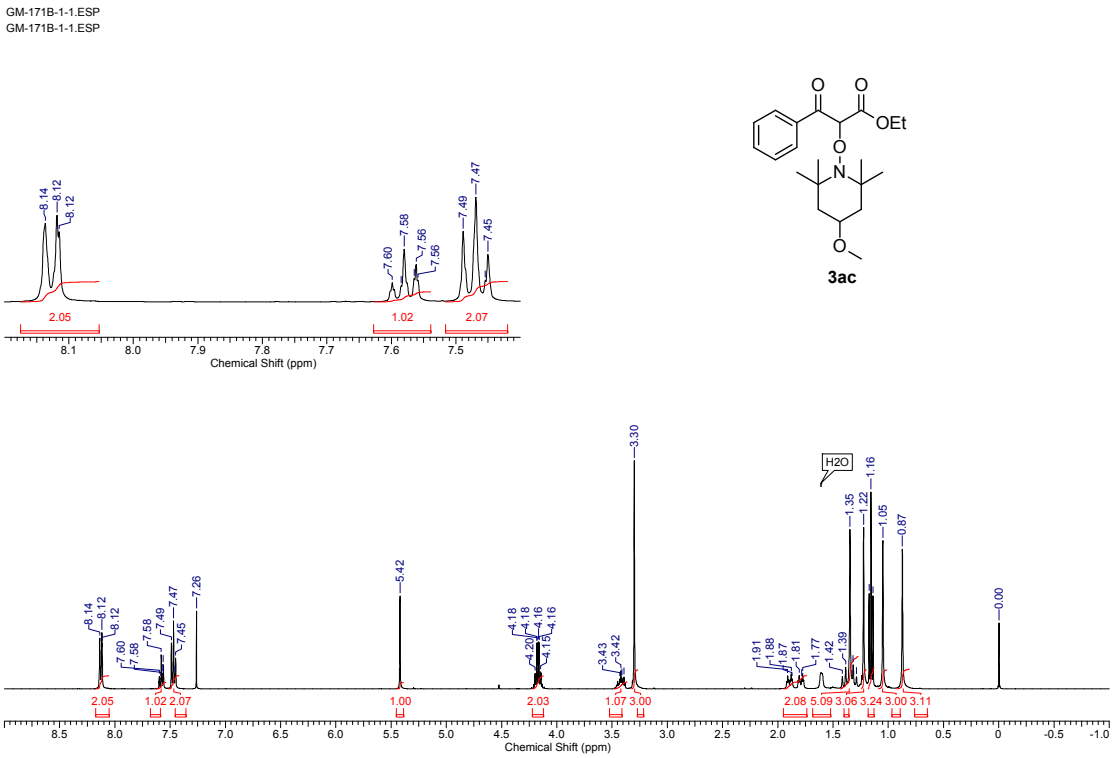


Figure S76. ^{1}H NMR spectrum of compound **3ac**

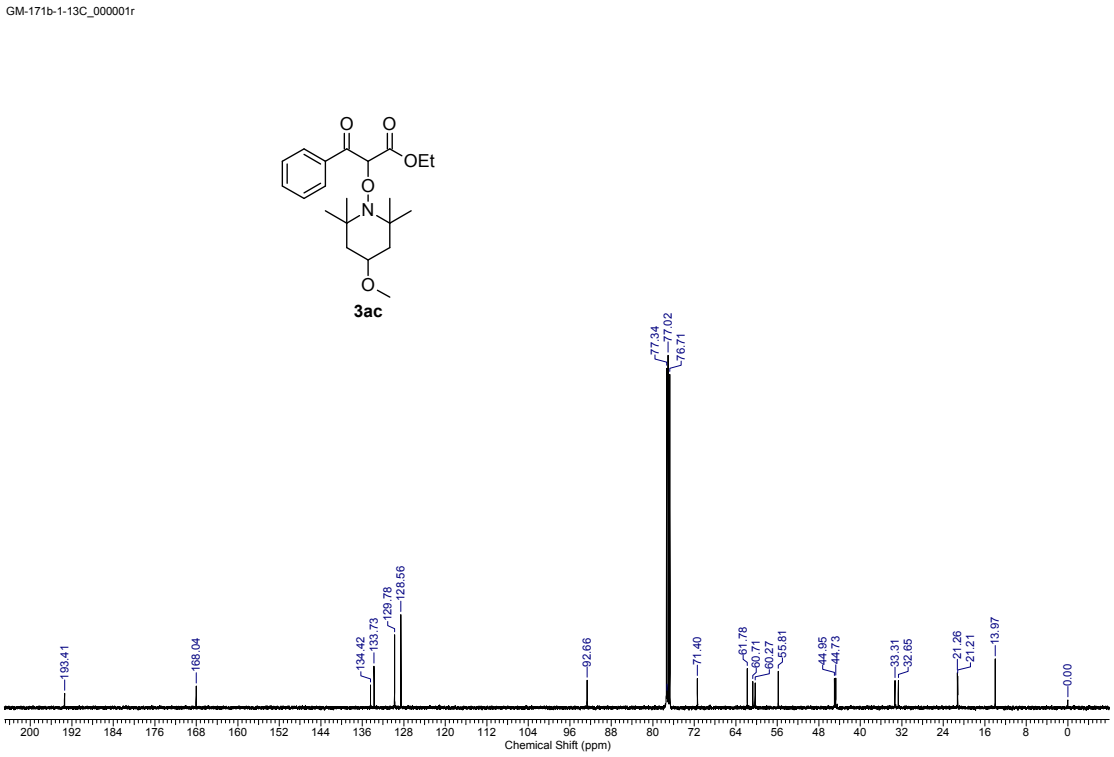


Figure S77. ^{13}C NMR spectrum of compound **3ac**

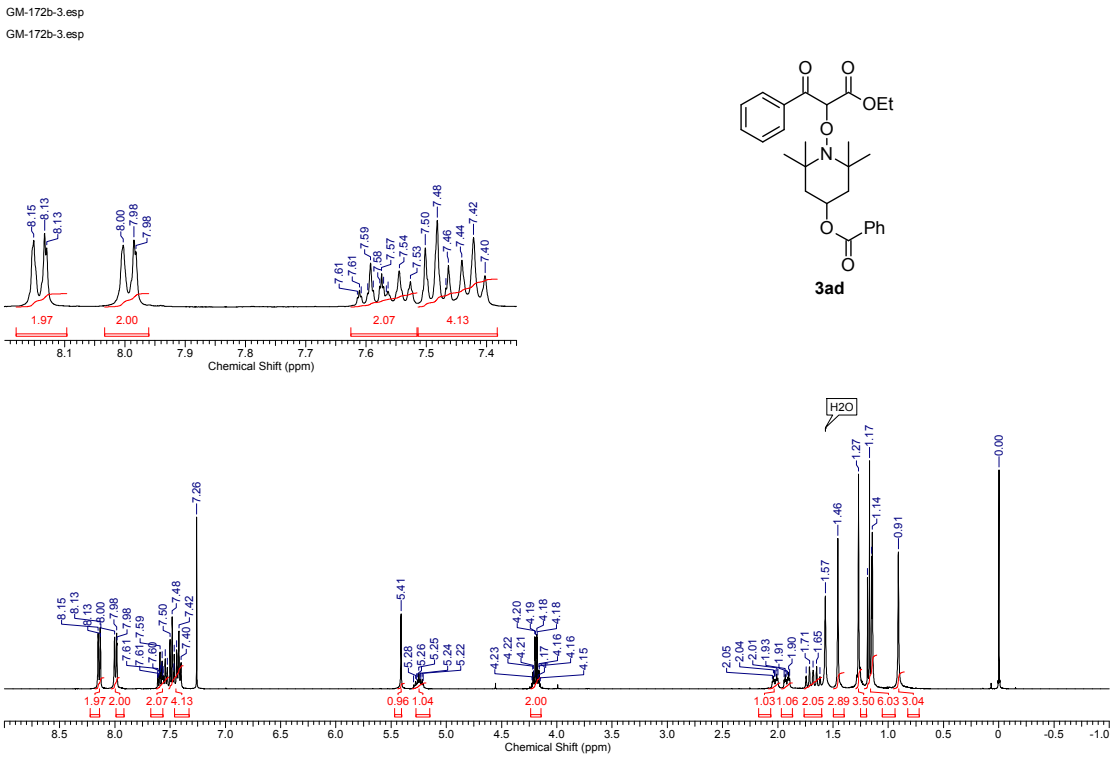


Figure S78. ^{1}H NMR spectrum of compound **3ad**

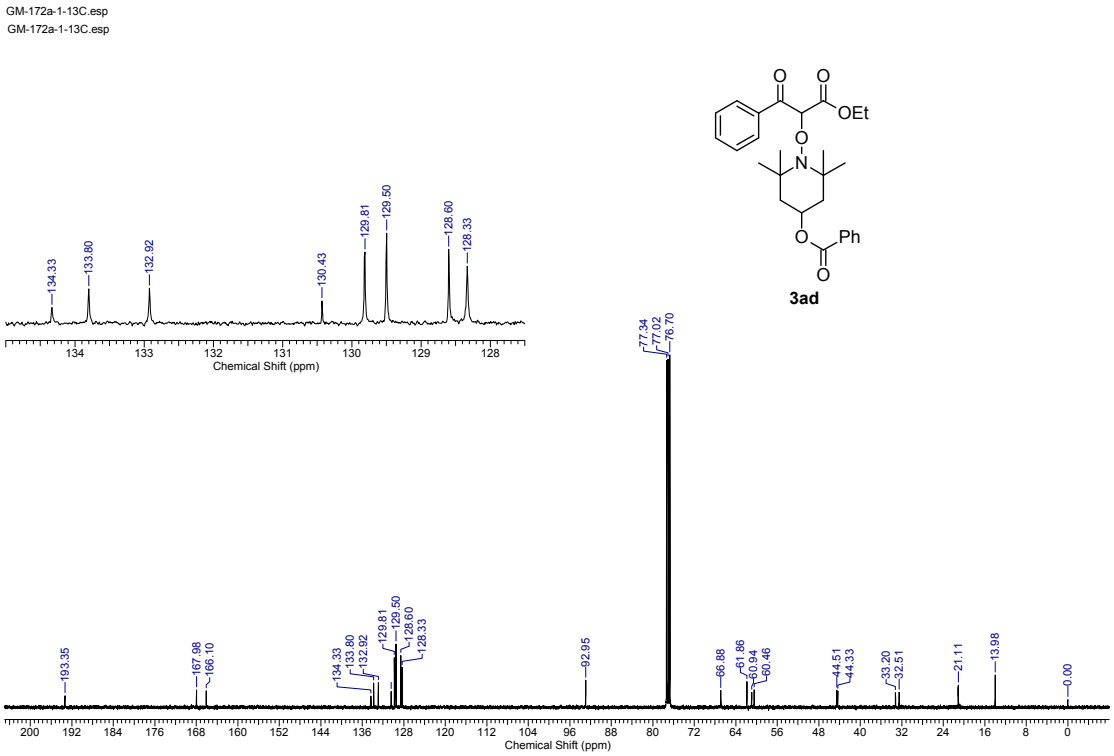


Figure S79. ^{13}C NMR spectrum of compound **3ad**

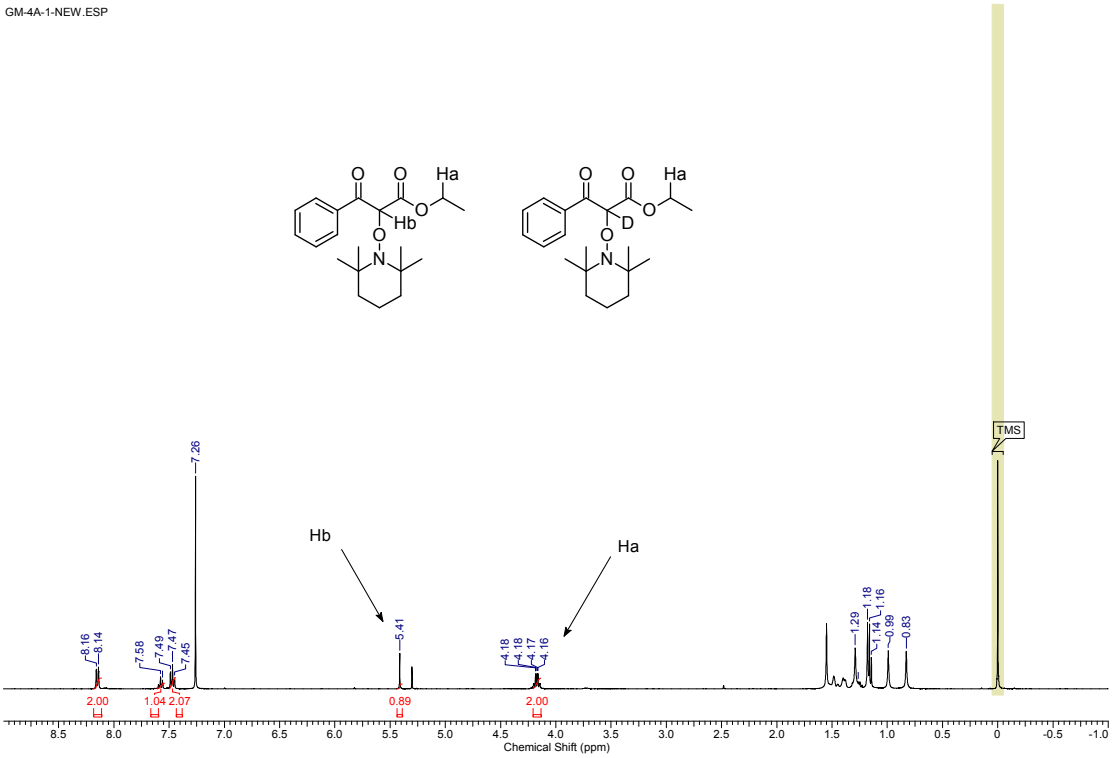


Figure S80. ^{1}H NMR spectrum of compound **3a** and **[D]3a** with N719

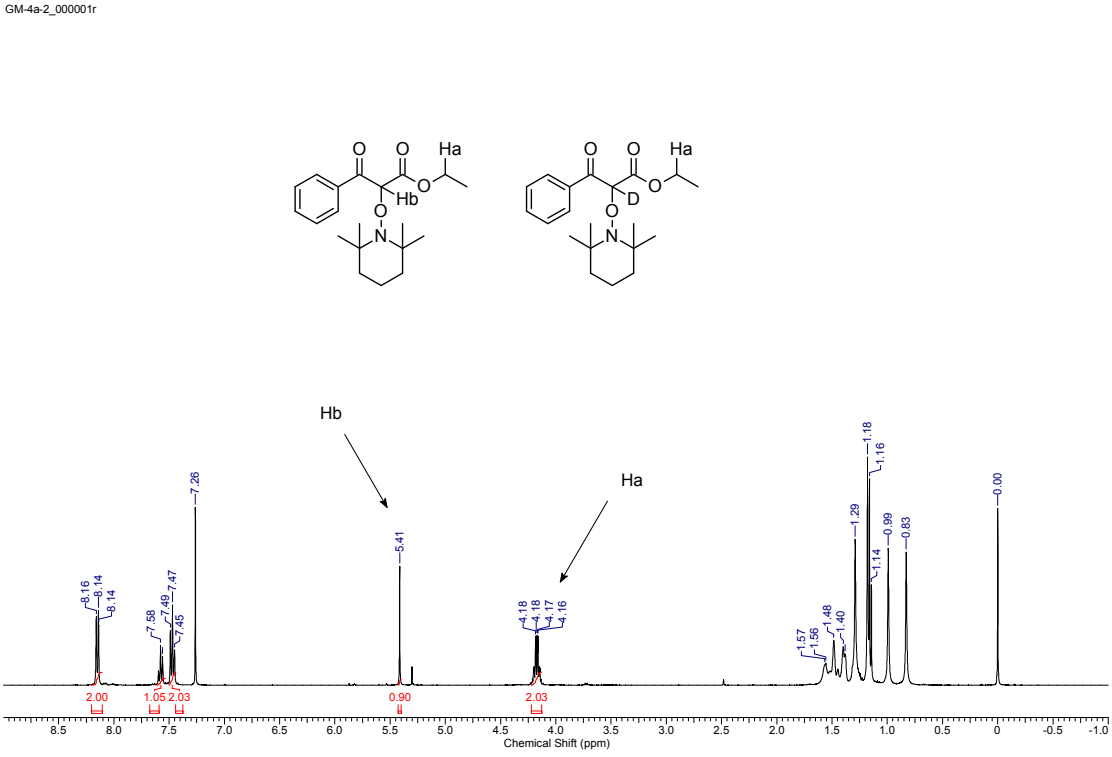


Figure S81. ^{1}H NMR spectrum of compound **3a** and **[D]3a** with N719-TiO_2/FTO

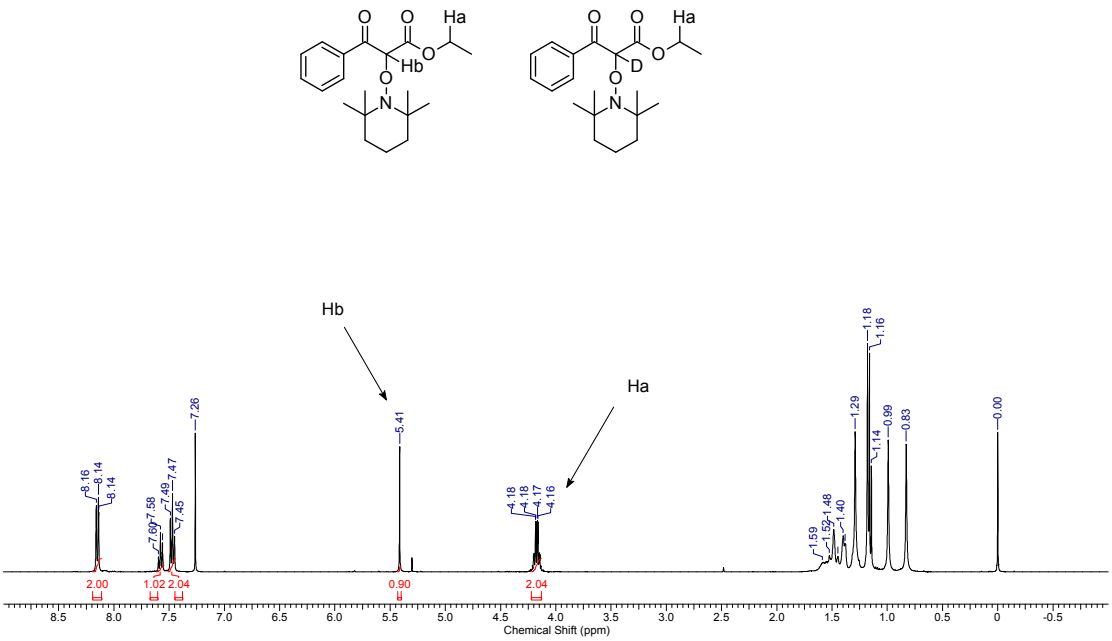


Figure S82. ^{1}H NMR spectrum of compound **3a** and **[D]3a** with TiO_2/FTO

9. Determination of Structure of 3u

The structure of **3u** was determined by the X-ray diffraction. Recrystallized from hexane/dichloromethane. Further information can be found in the CIF file. The crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC **1893275.**

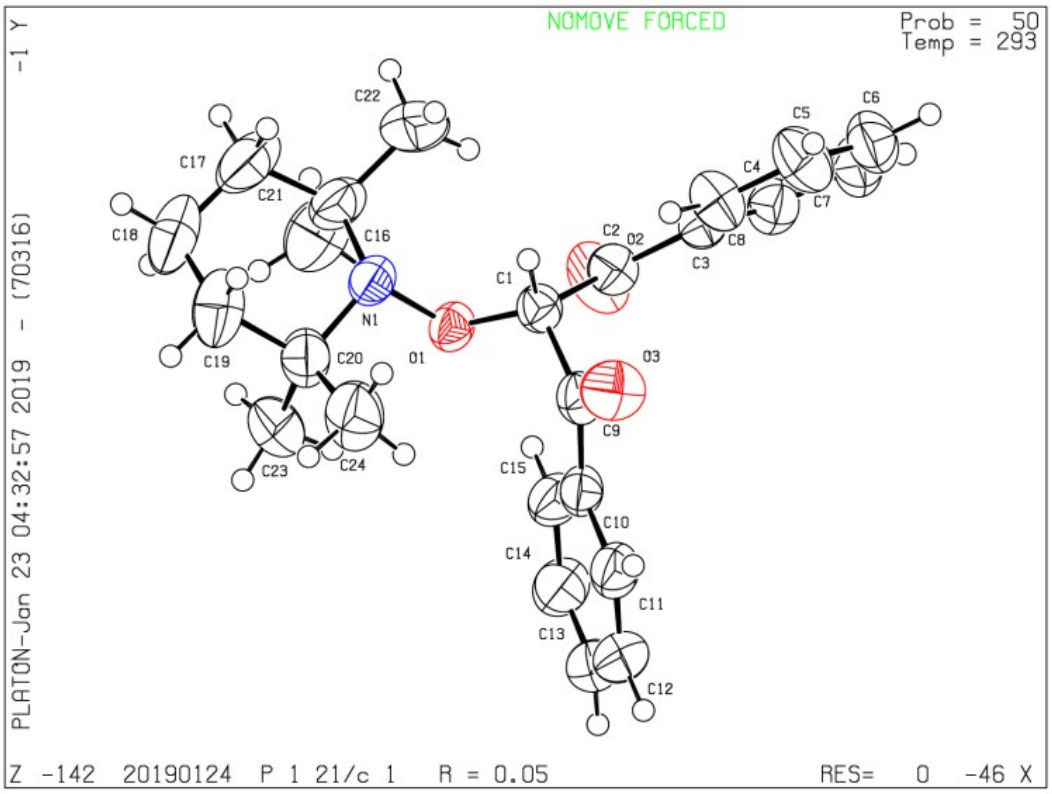


Table 1 Crystal data and structure refinement for 3u.

Identification code	20190124
Empirical formula	$C_{24}H_{29}NO_3$
Formula weight	379.48
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.3821(5)
b/Å	8.3089(4)
c/Å	21.5533(8)
α/°	90
β/°	105.353(4)
γ/°	90
Volume/Å^3	2138.31(16)
Z	4
ρ_{calc}g/cm^3	1.179
μ/mm^{-1}	0.610

F(000)	816.0
Crystal size/mm^3	0.18 × 0.13 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.404 to 134.144
Index ranges	$-9 \leq h \leq 14$, $-8 \leq k \leq 9$, $-23 \leq l \leq 25$
Reflections collected	7740
Independent reflections	3806 [R_{int} = 0.0320, R_{sigma} = 0.0406]
Data/restraints/parameters	3806/0/258
Goodness-of-fit on F^2	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0479, wR_2 = 0.1208
Final R indexes [all data]	R_1 = 0.0681, wR_2 = 0.1402
Largest diff. peak/hole / e Å^{-3}	0.15/-0.16