

Supporting Information

1,3-Difunctionalization of β -Alkyl Nitroalkenes via Combination of Lewis Base Catalysis and Radical Oxidation

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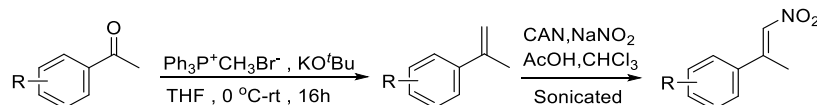
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I. General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AV400 spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (TMS) (0.00 ppm) or CDCl_3 (7.26 ppm) for ^1H , CDCl_3 (77.0 ppm) for ^{13}C . Flash column chromatography was performed on 200-300 mesh silica gel. HRMS (ESI-TOF) were measured on a Bruker Apex IV FTMS spectrometer. Melting points were measured on a melting point tester RY-1G apparatus and uncorrected.

II. General experimental procedure

2.1 General procedures for (E)- β -aryl- β -methyl nitroalkenes¹⁻³

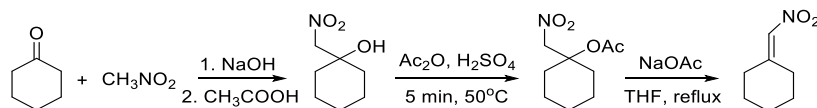


(E)- β -aryl- β -methyl nitroalkenes were prepared according to literature as known compounds.

Methyl triphenylphosphonium bromide (1.2 equiv) was taken in an oven dried flask. Dry THF (1.6 mL/mmol) was added. The suspension was cooled to 0 °C and stirred evenly, then KOtBu (1.2 equiv) was added and the resulting yellow suspension was stirred at 0 °C for 45 min. A solution of ketone (2 mmol, 1.0 equiv) in THF (0.7 mL/mmol) was added dropwise and the resulting mixture was warmed gradually to r.t. and stirred until reacted completely by TLC (around 16 h). Reaction mixture was filtered and filtrate was concentrated under reduced pressure to yield yellow oil, then purified by column chromatography over silica gel using petroleum ether as eluent.

Acetic acid (12 mmol) was added to a suspension of α -methylstyrene 4 (1 mmol), NaNO₂ (10 mmol), and CAN (1 mmol) in CHCl₃ (10 mL) and the mixture was sonicated in a sealed flask (35 KHz frequency) connected to a bubbler until the reaction reached completion determined by TLC (5-100 min). The solvent was evaporated under vacuum, the residue was dissolved in EtOAc/H₂O, extracted by ethyl acetate. The organic solution was washed with saturated NaHCO₃ and water and then dried on Na₂SO₄. Solvent was evaporated and the product was purified by flash chromatography.

2.2 General procedures for (nitromethylene)cyclohexane⁴⁻⁶



1-(Nitromethylene)cyclohexanes were prepared according to literature as known compounds.

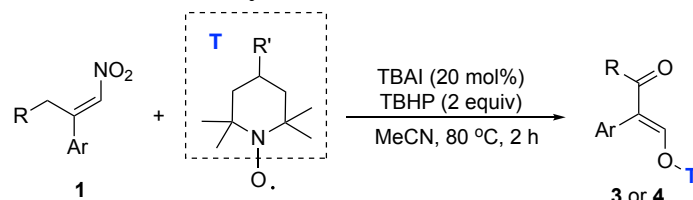
Cyclohexanone (0.1 mol), nitromethane (0.1 mol) was added into 30 mL of methanol, stirred and cooled to 5 °C. A solution of sodium hydroxide (0.125 mol) in 10 mL of water was added to the mixture below 10 °C by the use of an ice-bath. The colorless sodium derivative of the condensation product began after about one-third of the alkali had been added. After complete addition of the alkali (about one-half hour was required), the thick suspension was stirred and cooled for one-half hour. The sodium derivative was then filtered, suspended in 50 mL of water, stirred and 10 mL of acetic acid added. The mixture was poured into water, and extracted by ethyl acetate, washed with NaHCO₃ (aq) and NaCl (aq), dried with anhydrous Na₂SO₄. Then, the solvent was evaporated. Upon distillation, 1-(nitromethyl)cyclohexan-1-ol was obtained.

1-(nitromethyl)cyclohexan-1-ol (60 mmol), acetic anhydride (60 mmol) and concentrated H₂SO₄ (2 drop) were mixed and reacted at 50 °C and for 5min. Ethyl acetate and water were added. The organic layer was separated, washed with NaHCO₃ (aq), NaCl (aq), and dried over Na₂SO₄. Removal of solvent gave 1-

(nitromethyl)cyclohexyl acetate as yellow oil.

A mixture of 1-(nitromethyl)cyclohexyl acetate (62 mmol), anhydrous NaOAc (72 mmol), and 70 mL of THF was stirred and refluxed for 6.5 h. The cooled suspension was filtered, and the filtrate was evaporated and distilled to give light yellow-green liquid.

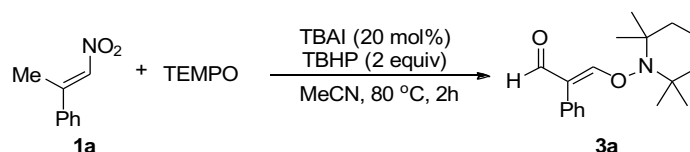
2.3 General procedures for the synthesis of 3 and 4



Under air atmosphere, β -aryl nitroalkenes (**1**, 0.3 mmol), TEMPO (0.6 mmol, 2 equiv.), TBAI (0.06 mmol, 20 mol%), and TBHP (2 equiv.) were dissolved in MeCN (3.0 mL). The mixture was stirred in an unsealed tube at 80 °C (oil bath) for 2 h. After cooling to room temperature, the mixture was washed with brine and extracted with ethyl acetate. Then the organic layer was separated and dried over anhydrous Na₂SO₄, which was then evaporated under reduced pressure. The residue was separated by column chromatography on silica gel with Petroleum/Ethyl acetate mixtures (v/v = 20/1) to get the desired product **3** or **4**.

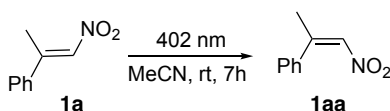
Stability of 3: The product **3** is stable in the reaction system for at least 3 hours without decomposition after reaction completion. We did not observe per esters in our reaction system. When we separated the product **3** and charged them into the reaction system, the products start to decompose, giving a messy reaction mixture after 2 hrs. This is plausible due to the per ester formation.⁷

2.4 General procedures for the synthesis of 3a in gram scale



Under air atmosphere, β -aryl nitroalkenes (**1a**, 5.0 mmol), TEMPO (10.0 mmol, 2 equiv.), TBAI (1.0 mmol, 20 mol%), and TBHP (10.0 mmol, 2 equiv.) were dissolved in MeCN (15 mL). The mixture was stirred in an unsealed round bottom flask at 80 °C (oil bath) for 2 h. After cooling to room temperature, the mixture was washed with brine and extracted with ethyl acetate. Then the organic layer was separated and dried over anhydrous Na₂SO₄, which was then evaporated under reduced pressure. The residue was separated by column chromatography on silica gel with Petroleum/Ethyl acetate mixtures (v/v = 20/1) to get the desired product **3a** (1.25 g, 87% yield)

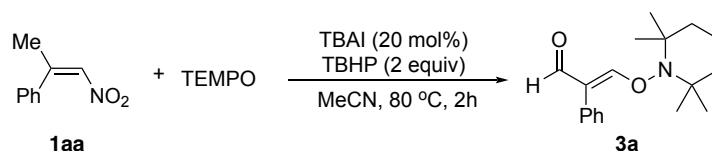
2.5 General procedures for the synthesis of Z-nitroalkenes 1aa⁸



(Z)-(1-nitroprop-1-en-2-yl)benzene **1aa** was prepared according to literature as known compound.

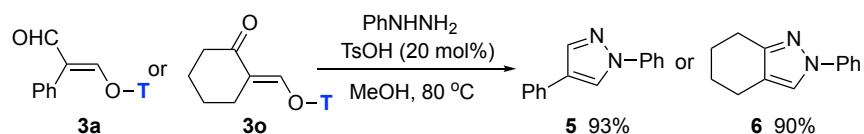
In a flame dried 10 mL round bottom flask, the (E)-nitrostyrene **1a** (0.5 mmol, 1 eq.) was dissolved in dry MeCN (0.5 mL, 1 M). The flask was sealed with a rubber septum and the mixture was degassed by bubbling argon through it with a needle for ca. 2 min. The flask was connected to a balloon filled with argon and placed in the irradiation set up. After irradiation at 402 nm for 7 h, the solvent was removed under reduced pressure and the residue was filtered over a plug of SiO₂. Subsequent elution of the products purified by column chromatography (SiO₂, Et₂O:n-pentane = 1:9) yielded the pure (Z)-nitrostyrene (58.7 mg, 72%).

2.6 General procedures for the synthesis of **3a** using Z-nitroalkenes **1aa**



Under air atmosphere, β -aryl nitroalkenes (**1aa**, 0.3 mmol), TEMPO (0.6 mmol, 2 equiv.), TBAI (0.06 mmol, 20 mol%), and TBHP (2 equiv.) were dissolved in MeCN (3.0 mL). The mixture was stirred in an unsealed tube at 80 °C (oil bath) for 2 h. After cooling to room temperature, the mixture was washed with brine and extracted with ethyl acetate. Then the organic layer was separated and dried over anhydrous Na₂SO₄, which was then evaporated under reduced pressure. The residue was separated by column chromatography on silica gel with Petroleum/Ethyl acetate mixtures (v/v = 20/1) to get the desired product **3a** (95% yield, 81.8 mg).

2.7 General procedures for the synthesis of **5** and **6**

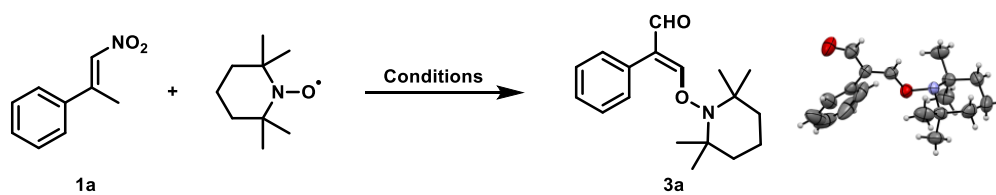


Under air atmosphere, **3a** or **3o** (0.3 mmol), PhNHNH₂ (0.6 mmol, 2 equiv.), TsOH (0.06 mmol, 20 mol%) were dissolved in MeOH (3.0 mL). The mixture was stirred in a 10mL vial at 80 °C (oil bath) for 2 h. After cooling to room temperature, the mixture was washed with brine and extracted with ethyl acetate. Then the organic layer was separated and dried over anhydrous Na₂SO₄, which was then evaporated under reduced pressure. The residue was separated by column chromatography on silica gel with Petroleum/Ethyl acetate mixtures (v/v = 10/1) to get the desired product **5** (61.4 mg, 93%) or **6** (53.5 mg, 90%).

Reference:

- (1) Tripathi, C. B.; Mukherjee, S., Catalytic Enantioselective Iodoetherification of Oximes. *Angew. Chem., Int. Ed.* **2013**, *52*, 8450-8453.
- (2) Hwu, R. J.; Chen, K.-L.; Anathan, S., A new method for nitration of alkenes to α,β -unsaturated nitroalkenes. *J. Chem. Soc. Chem. Commun.* **1994**, 1425-1426.
- (3) Fryszkowska, A.; Fisher, K.; Gardiner, J. M.; Stephens, G. M., Highly Enantioselective Reduction of β,β -Disubstituted Aromatic Nitroalkenes Catalyzed by *Clostridium sporogenes*. *J. Org. Chem.* **2008**, *73*, 4295-4298.
- (4) Wei, M.-H.; Zhou, Y.-R.; Gu, L.-H.; Luo, F.; Zhang, F.-L., Asymmetric organocatalytic Michael–hemiacetalization reaction: access to chiral spiro cis- δ -lactones by in situ oxidation of spiro δ -lactols. *Tetrahedron Lett.* **2013**, *54*, 2546-2548.
- (5) Ferrand, J. C.; Schneider, R.; Gerardin, P.; Loubinoux, B., A Convenient Two-Step Procedure for the Synthesis of DI- and Trisubstituted α -Nitroalkenes from Tertiary β -Nitro Alcohols. *Synthetic Commun.* **1996**, *26*, 4329-4336.
- (6) Cunico, R. F., Diazotative deaminosilylation of β -amino silanes. *J. Org. Chem.* **1990**, *55*, 4474-4478.
- (7) Singha, R.; Shit, P., Sunlight assisted solvent free synthesis of *tert*-butylperesters, *Synthetic Commun.* **2020**, *50*, 2698-2703.
- (8) Hostmann, T.; Molloy, J. J.; Busmann, K.; Gilmour, R., Light-Enabled Enantiodivergence: Stereospecific Reduction of Activated Alkenes Using a Single Organocatalyst Enantiomer. *Org. Lett.* **2019**, *21*, 10164–10168.

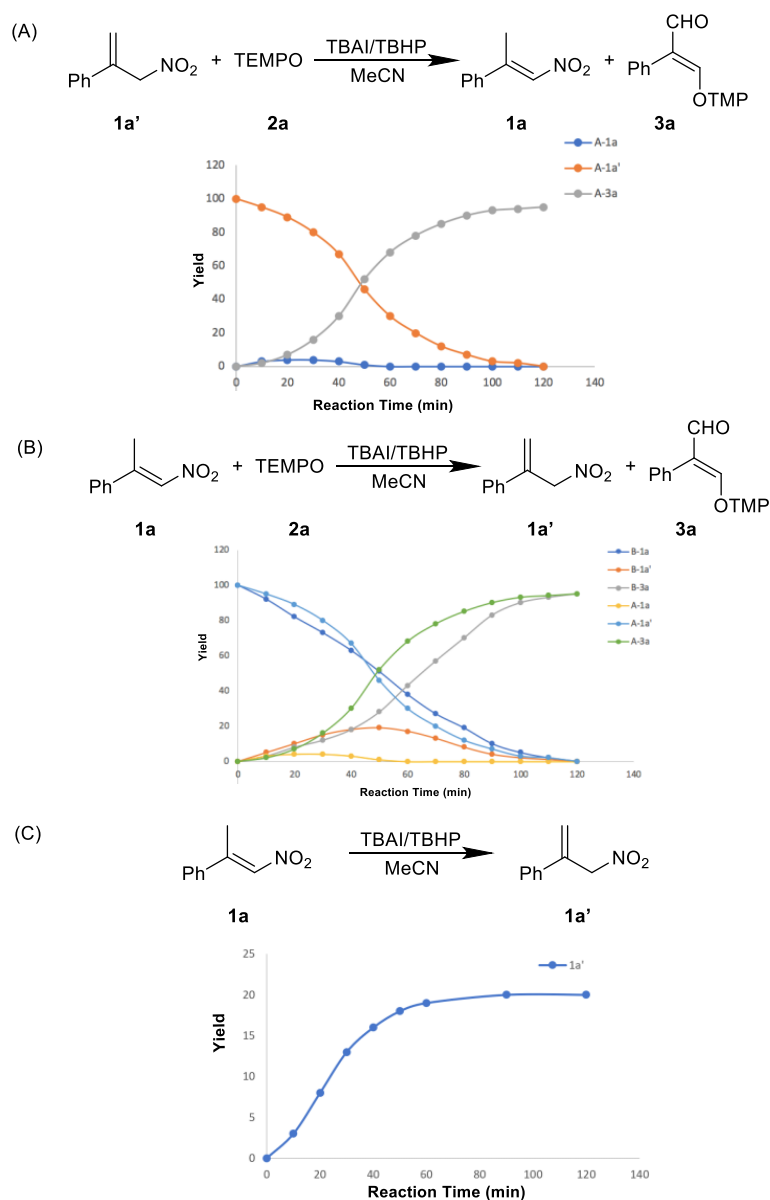
III. Reactions conditions screening^{a,b}



entry	catalyst (mol %)	oxidant (equiv.)	additive	time	yield ^b
1	TBAI (20)	TBHP in decane(2)	-	2 h	95%
2	TBAI (20)	TBHP in decane (2)	H ₂ O	2 h	95%

^aGeneral reaction conditions: **1a** (0.3 mmol, 1 equiv.), TEMPO (0.6 mmol, 2 equiv.), LB (0.06 mmol, 20 mol%), and oxidant (2 equiv.) in anhydrous MeCN (3.0 mL), N₂, reacted in oil bath at 80 °C. ^bIsolated yield..

IV. Reaction profile



Procedure for (A): Under air atmosphere, **1a'** (0.3 mmol), TEMPO (0.6 mmol, 2 equiv.), TBAI (0.06 mmol, 20 mol%), and TBHP (2 equiv.) were dissolved in MeCN (3.0 mL). The mixture was stirred in an unsealed tube at 80 °C (oil bath) for 2 h. The time-dependent reaction profile of the reaction obtained using ^1H NMR.

Procedure for (B): Under air atmosphere, **1a** (0.3 mmol), TEMPO (0.6 mmol, 2 equiv.), TBAI (0.06 mmol, 20 mol%), and TBHP (2 equiv.) were dissolved in MeCN (3.0 mL). The mixture was stirred in an unsealed tube at 80 °C (oil bath) for 2 h. The time-dependent reaction profile of the reaction obtained using ^1H NMR.

Procedure for (C): Under air atmosphere, β -aryl nitroalkenes (**1a**, 0.3 mmol), TBAI (0.06 mmol, 20 mol%), and TBHP (2 equiv.) were dissolved in MeCN (3.0 mL). The mixture was stirred in an unsealed tube at 80 °C (oil bath) for 2 h. The time-dependent reaction profile of the reaction obtained using ^1H NMR.

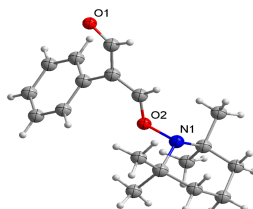
V. X-ray diffraction analysis of compounds **3a** and **3o**

5.1 X-ray diffraction analysis of compounds **3a**

Single crystals of **3a** were obtained by slow evaporation of PE/EA (20/1) at 25 °C.

The crystallographic data for the single crystal of the complexes **3a** was collected on a CrysAlis PRO 1.171.39.7a (Rigaku OD, 2015) employing graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by least-squares. Program used to solve structure is SHELXS (Sheldrick, 2008); program used to refine structure is SHELXH (Sheldrick, 2015). Hydrogen atoms of -CH, -CH₂, -CH₃, groups were placed in geometrically calculated positions and were included in the refinement process using riding model with isotropic thermal parameters.

Crystallography data and structure refinement for **3a**. (CCDC 1984460) Thermal ellipsoids are shown at 30% probability level.



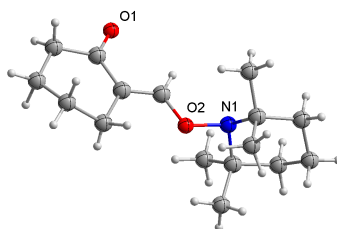
Empirical formula	C ₁₈ H ₂₅ NO ₂
Formula weight	287.39
Temperature/K	296(2) K
Wavelength/Å	0.71073 Å
Crystal system	Orthorhombic
a/Å	11.4452(11)
b/Å	19.239(2)
c/Å	7.7230(9)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	1700.6(3)
Z	4
μ /mm ⁻¹	0.072
F(000)	624
Crystal size/mm ³	0.15 x 0.12 x 0.1
2 θ range for data collection/°	2.070 to 24.997°
Reflections collected	7361
Independent reflections	2667 [R(int) = 0.0282]
Data/restraints/parameters	2667/1/183
Goodness-of-fit on F ²	1.023

Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0431$, $wR_2 = 0.0905$
Final R indexes [all data]	$R_1 = 0.0771$, $wR_2 = 0.1036$

5.2 X-ray diffraction analysis of compounds **3o**

Single crystals of **3o** were obtained by slow evaporation of PE/EA (20/1) at 25 °C. The crystallographic data for the single crystal of the complexes **3o** was collected on a CrysAlis PRO 1.171.39.7a (Rigaku OD, 2015) employing graphite-monochromated MoK α radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods and refined by least-squares. Program used to solve structure is SHELXS (Sheldrick, 2008); program used to refine structure is SHELXH (Sheldrick, 2015). Hydrogen atoms of -CH, -CH₂, -CH₃, groups were placed in geometrically calculated positions and were included in the refinement process using riding model with isotropic thermal parameters.

Crystallography data and structure refinement for **3o**. (CCDC 1984461) Thermal ellipsoids are shown at 30% probability level.

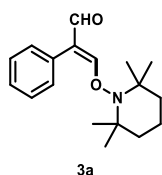


Empirical formula	$C_{16}H_{27}NO_2$
Formula weight	265.38
Temperature/K	296(2)
Wavelength/Å	0.71073
Crystal system	orthorhombic
a/Å	14.2216(14)
b/Å	9.8015(10)
c/Å	11.6005(11)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
Volume/Å ³	1617.0(3)
Z	4
μ/mm^{-1}	0.071
F(000)	584
Crystal size/mm ³	0.12 × 0.1 × 0.1
2 θ range for data collection/ $^\circ$	4.532 to 49.998
Reflections collected	4319
Independent reflections	1516 [$R_{\text{int}} = 0.0183$, $R_{\text{sigma}} = 0.0192$]

Data/restraints/parameters	1516/65/142
Goodness-of-fit on F^2	1.030
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0379$, $wR_2 = 0.0911$
Final R indexes [all data]	$R_1 = 0.0551$, $wR_2 = 0.1029$

VI. Compounds characterization

(E)-2-phenyl-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**3a**)



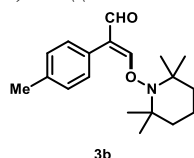
Brown solid (81.9 mg, 95%), m. p: 77-79 °C; purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.20);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.32 (s, 1H), 7.58 – 7.53 (m, 2H), 7.50 (s, 1H), 7.39 (dd, J = 8.4, 6.8 Hz, 2H), 7.31 – 7.26 (m, 1H), 1.58 (s, 5H), 1.45 – 1.36 (m, 1H), 1.17 (d, J = 15.6 Hz, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 190.3, 174.8, 130.3, 128.9, 127.8, 127.2, 117.9, 60.8, 39.4, 32.0, 29.6, 20.5, 16.6.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{26}\text{NO}_2$ 288.1958; Found 288.1949.

(E)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2-(*p*-tolyl)acrylaldehyde (**3b**)



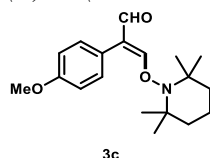
Brown solid (85.8 mg, 95%), m. p: 78-80 °C; purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.21);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.31 (s, 1H), 7.49 – 7.43 (m, 3H), 7.20 (d, J = 8.0 Hz, 2H), 2.36 (s, 3H), 1.57 – 1.35 (m, 6H), 1.18 (s, 6H), 1.16 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 190.4, 174.5, 136.8, 128.8, 128.5, 127.4, 117.9, 60.8, 39.4, 32.0, 21.2, 20.5, 16.6.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{K}]^+$ Calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_2\text{K}$ 340.1673; Found 340.1667.

(E)-2-(4-methoxyphenyl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**3c**)



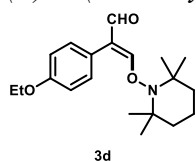
Yellow solid (88.5 mg, 93%), m. p: 72-74 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.18);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.29 (s, 1H), 7.55 – 7.50 (m, 2H), 7.44 (s, 1H), 6.95 – 6.91 (m, 2H), 3.83 (s, 3H), 1.66 – 1.51 (m, 5H), 1.42 – 1.37 (m, 1H), 1.18 (d, J = 6.3 Hz, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 190.5, 174.3, 158.4, 130.1, 122.7, 117.5, 113.2, 60.7, 55.0, 39.4, 32.0, 20.5, 16.6.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_3\text{Na}$ 340.1883; Found 340.1874.

(*E*)-2-(4-ethoxyphenyl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**3d**)



3d

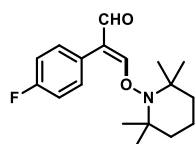
Yellow solid (91.4 mg, 92%), m. p: 69-71 °C; purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.15);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.30 (d, J = 1.6 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.44 (d, J = 1.6 Hz, 1H), 6.95 – 6.89 (m, 2H), 4.05 (q, J = 6.8 Hz, 2H), 1.65 – 1.56 (m, 5H), 1.49 – 1.42 (m, 4H), 1.20 – 1.15 (d, J = 6.0 Hz, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 190.7, 174.5, 158.0, 130.2, 122.7, 117.7, 113.9, 63.3, 60.9, 39.5, 32.1, 20.6, 16.7, 14.9.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{30}\text{NO}_3$ 332.2220; Found 332.2199.

(*E*)-2-(4-fluorophenyl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**3e**)



3e

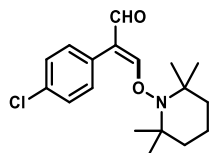
Brown oil (82.4 mg, 90%); purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.18);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.30 (s, 1H), 7.54 (dd, J = 8.8, 5.6 Hz, 2H), 7.49 (s, 1H), 7.07 (t, J = 8.8 Hz, 2H), 1.67 – 1.36 (m, 6H), 1.18 (s, 6H), 1.15 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 190.0, 174.7, 162.8 ($C-F$, $1\text{JC}-F$ = 246.6 Hz), 160.4 ($C-F$, $1\text{JC}-F$ = 246.6 Hz), 130.6 ($C-F$, $3\text{JC}-F$ = 8.0 Hz), 130.6 ($C-F$, $3\text{JC}-F$ = 8.0 Hz), 126.2 ($C-F$, $4\text{JC}-F$ = 3.3 Hz), 126.2 ($C-F$, $4\text{JC}-F$ = 3.3 Hz), 117.0, 114.8 ($C-F$, $2\text{JC}-F$ = 21.3 Hz), 114.6 ($C-F$, $2\text{JC}-F$ = 21.3 Hz), 60.8, 39.3, 31.9, 20.4, 16.5.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{24}\text{FNO}_2\text{Na}$ 328.1683; Found 328.1675.

(*E*)-2-(4-chlorophenyl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**3f**)



3f

Yellow solid (87.7 mg, 91%), m. p: 80-82 °C; purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.17);

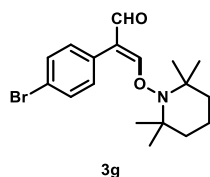
$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.30 (s, 1H), 7.51 (d, J = 8.0 Hz, 3H), 7.35 (d, J = 8.8 Hz, 2H), 1.67 - 1.32 (m, 6H), 1.18 (s, 6H), 1.15 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 189.8, 174.8, 132.8, 130.2, 128.7, 127.9, 116.8, 60.8, 39.3, 31.9, 20.5, 16.5.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{24}\text{ClNO}_2\text{Na}$ 344.1388; Found

344.1378.

(*E*)-2-(4-bromophenyl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**3g**)



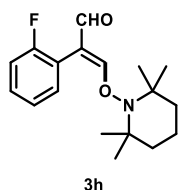
Brown solid (100.8 mg, 92%), m. p: 85-87 °C; purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.21);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.29 (s, 1H), 7.54 – 7.48 (m, 3H), 7.44 (d, J = 8.8 Hz, 2H), 1.57 – 1.36 (m, 6H), 1.17 (s, 6H), 1.15 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 189.8, 174.9, 131.0, 130.6, 129.3, 121.2, 116.9, 60.9, 39.4, 32.0, 20.6, 16.6.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{24}\text{BrNO}_2\text{Na}$ 388.0883; Found 388.0875.

(*E*)-2-(2-fluorophenyl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**3h**)



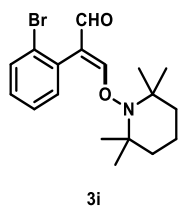
Yellow oil (83.3 mg, 91%); purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.19);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.36 (s, 1H), 7.62 (s, 1H), 7.33 – 7.24 (m, 2H), 7.19 – 7.13 (m, 1H), 7.10 (t, J = 9.1 Hz, 1H), 1.55 (s, 5H), 1.43 – 1.27 (m, 1H), 1.12 (d, J = 44.4 Hz, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 189.0, 174.6, 161.1 ($C-F$, $1J_{C-F}$ = 248.4 Hz), 158.6 ($C-F$, $1J_{C-F}$ = 248.4 Hz), 131.54 ($C-F$, $4J_{C-F}$ = 3.9 Hz), 131.50 ($C-F$, $4J_{C-F}$ = 3.9 Hz), 129.45 ($C-F$, $3J_{C-F}$ = 8.3 Hz), 129.37 ($C-F$, $3J_{C-F}$ = 8.3 Hz), 123.58 ($C-F$, $4J_{C-F}$ = 3.5 Hz), 123.55 ($C-F$, $4J_{C-F}$ = 3.5 Hz), 118.1, 115.5 ($C-F$, $2J_{C-F}$ = 22.1 Hz), 115.3 ($C-F$, $2J_{C-F}$ = 22.1 Hz), 113.6, 60.9, 39.4, 31.9, 20.2, 16.6.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{24}\text{FNO}_2\text{Na}$ 328.1683; Found 328.1675.

(*E*)-2-(2-bromophenyl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**3i**)



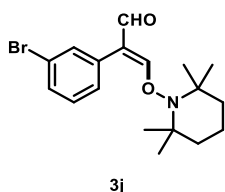
Yellow solid (100.8 mg, 92%), m. p: 95-97 °C; purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.22);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.36 (s, 1H), 7.65 – 7.59 (m, 2H), 7.33 – 7.30 (m, 1H), 7.22 – 7.11 (m, 2H), 1.54 – 1.51 (m, 6H), 1.20 (s, 6H), 1.01 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 188.7, 173.6, 132.6, 132.4, 131.5, 129.3, 127.1, 124.2, 119.9, 60.9, 39.5, 32.1, 20.2, 16.7.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{24}\text{BrNO}_2\text{Na}$ 388.0883; Found 388.0874.

(E)-2-(3-bromophenyl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**3j**)



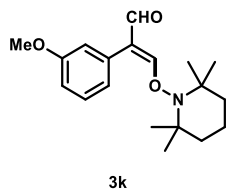
Yellow solid (101.9 mg, 93%), m. p: 83-85 °C; purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.23);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.29 (s, 1H), 7.75 (t, J = 1.6 Hz, 1H), 7.51 (s, 2H), 7.27 – 7.26 (m, 1H), 7.26 – 7.24 (m, 1H), 1.65 – 1.37 (m, 5H), 1.45 – 1.35 (m, 1H), 1.17 (d, J = 3.6 Hz, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 189.1, 174.6, 131.9, 131.4, 129.6, 128.8, 127.0, 121.3, 116.0, 60.4, 38.9, 31.5, 20.0, 16.1.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{K}]^+$ Calcd for $\text{C}_{18}\text{H}_{24}\text{BrNO}_2\text{K}$ 404.0622; Found 404.0612.

(E)-2-(3-methoxyphenyl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**3k**)



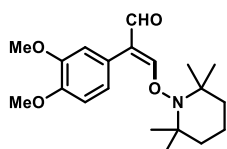
Yellow solid (87.6 mg, 92%), m. p: 64-66 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.17);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.33 (s, 1H), 7.51 (s, 1H), 7.31 (t, J = 8.0 Hz, 1H), 7.17 (dd, J = 8.8, 1.6 Hz, 2H), 6.86 (ddd, J = 8.4, 2.4, 1.6 Hz, 1H), 3.83 (s, 3H), 1.66 – 1.37 (m, 6H), 1.20 (s, 6H), 1.18 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 189.9, 174.5, 158.8, 131.4, 128.4, 121.2, 117.5, 114.0, 113.0, 60.6, 54.8, 39.2, 31.8, 20.3, 16.4.

HRMS (ESI-TOF) m/z: $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_3\text{Na}$ 340.1883; Found 340.1880.

(E)-2-(3,4-dimethoxyphenyl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**3l**)



3l

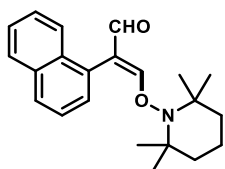
Brown solid (92.7 mg, 89%), m. p: 56-58 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.13);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.30 (s, 1H), 7.45 (s, 1H), 7.25 – 7.20 (m, 2H), 6.92 (d, J = 8.8 Hz, 1H), 3.91 (d, J = 1.2 Hz, 6H), 1.65 – 1.39 (m, 6H), 1.20 (d, J = 2.0 Hz, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 190.1, 174.1, 147.6, 147.5, 122.6, 121.2, 116.9, 111.7, 110.1, 60.3, 55.2, 55.2, 38.9, 31.6, 20.1, 16.1.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_4\text{Na}$ 370.1989; Found 370.1978.

(E)-2-(naphthalen-1-yl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**3m**)



3m

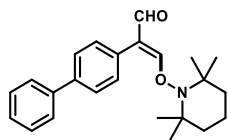
Brown solid (88.0 mg, 87%), m. p: 96-98 °C; purification by silica gel chromatography (eluent: PE/EA = 25:1, R_f = 0.15);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.42 (s, 1H), 8.09 (d, J = 1.6 Hz, 1H), 7.91 – 7.80 (m, 3H), 7.70 (dd, J = 8.8, 1.6 Hz, 1H), 7.59 (s, 1H), 7.48 (dd, J = 6.4, 3.6 Hz, 2H), 1.67– 1.37 (m, 6H), 1.23 (s, 6H), 1.17 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 190.3, 175.1, 133.1, 132.5, 128.3, 128.2, 127.9, 127.4, 127.2, 126.9, 125.9, 125.7, 118.0, 60.9, 39.4, 32.1, 20.6, 16.6.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{28}\text{NO}_2$ 338.2115; Found 338.2122.

(E)-2-([1,1'-biphenyl]-4-yl)-3-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**3n**)



3n

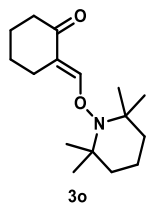
Yellow solid (97.0 mg, 89%), m. p: 88-90°C; purification by silica gel chromatography (eluent: PE/EA = 25:1, R_f = 0.17);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.35 (s, 1H), 7.70 – 7.60 (m, 6H), 7.53 (s, 1H), 7.44 (dd, J = 8.4, 6.8 Hz, 2H), 7.38 – 7.31 (m, 1H), 1.67 – 1.38 (m, 6H), 1.22 (s, 6H), 1.20 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 190.4, 175.0, 140.9, 139.9, 129.5, 129.4, 128.7, 127.2, 127.0, 126.6, 117.6, 61.0, 39.5, 32.1, 20.7, 16.7.

HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{24}H_{30}NO_2$ 364.2271; Found 364.2282.

(*E*)-2-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methylene)cyclohexan-1-one (**3o**)

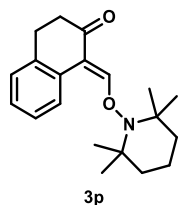


Yellow solid (55.7 mg, 70%), m. p: 64-66 °C; purification by silica gel chromatography (eluent: PE/EA = 25:1, R_f = 0.20);

1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.66 (t, J = 2.0 Hz, 1H), 2.42 – 2.46 (m, 2H), 2.34 (t, J = 6.5 Hz, 2H), 1.91 – 1.75 (m, 2H), 1.75 – 1.62 (m, 3H), 1.52 (s, 5H), 1.11 (s, 12H).
 ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 200.3, 162.6, 110.3, 60.2, 39.6, 39.5, 29.7, 23.2, 23.1, 22.7, 20.2, 16.8.

HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{16}H_{28}NO_2$ 266.2115; Found 266.2118.

(*E*)-1-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methylene)-3,4-dihydronaphthalen-2(1H)-one (**3p**)

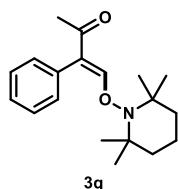


Brown oil (78.0 mg, 83%); purification by silica gel chromatography (eluent: PE/EA = 20:1, R_f = 0.13);

1H NMR (400 MHz, $CDCl_3$, ppm) δ 8.09 (s, 1H), 7.88 (dd, J = 7.6, 1.2 Hz, 1H), 7.28 (d, J = 1.6 Hz, 1H), 7.20 (d, J = 1.6 Hz, 1H), 7.18 – 7.13 (m, 1H), 3.02 – 2.93 (m, 2H), 2.63 – 2.57 (m, 2H), 1.58-1.42 (m, 6H), 1.23 (s, 6H), 1.16 (s, 6H).
 ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ 200.5, 163.8, 135.1, 132.2, 127.7, 127.6, 126.4, 125.8, 108.7, 60.5, 39.5, 38.3, 32.0, 28.3, 20.9, 16.8.

HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{20}H_{28}NO_2$ 314.2120; Found 314.2128.

(*E*)-3-phenyl-4-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methylene)but-3-en-2-one (**3q**)



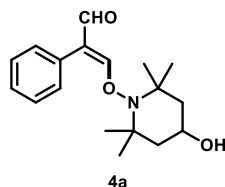
Yellow solid (81.3 mg, 90%), m. p: 80-82 °C; purification by silica gel chromatography (eluent: PE/EA = 22:1, R_f = 0.20);

1H NMR (400 MHz, $CDCl_3$, ppm) δ 7.87 (s, 1H), 7.35 (d, J = 7.6 Hz, 2H), 7.28 – 7.24 (m, 3H), 2.25 (s, 3H), 1.53 – 1.25 (m, 6H), 1.16 (s, 6H), 1.00 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 196.6, 165.5, 133.3, 129.9, 127.7, 126.8, 117.4, 60.4, 39.3, 32.0, 29.6, 26.6, 20.2, 16.6.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{28}\text{NO}_2$ 302.2115; Found 302.2107.

(*E*)-3-((4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2-phenylacrylaldehyde (**4a**)



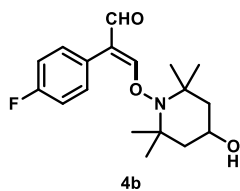
Yellow solid (86.4 mg, 95%), m. p: 124-126 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.19);

^1H NMR (400 MHz, CDCl_3 , ppm) δ 9.37 (s, 1H), 7.60 – 7.49 (m, 3H), 7.43 (m, 2H), 7.33 (m, 1H), 4.12 (s, 1H), 2.03 – 1.53 (m, 5H), 1.25 (m, J = 14.8 Hz, 12H).

^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 189.4, 173.4, 129.2, 128.0, 126.9, 126.4, 117.6, 61.3, 60.1, 46.9, 31.2, 20.4.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{26}\text{NO}_3$ 304.1907; Found 304.1898.

(*E*)-2-(4-fluorophenyl)-3-((4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**4b**)



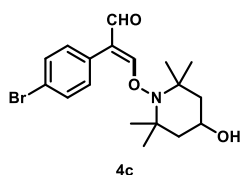
Yellow solid (87.7 mg, 91%), m. p: 121-123 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.14);

^1H NMR (400 MHz, CDCl_3 , ppm) δ 9.33 (s, 1H), 7.59 – 7.45 (m, 3H), 7.12 (d, J = 8.4 Hz, 2H), 4.12 (d, J = 10.0 Hz, 1H), 2.03 – 1.53 (d, J = 11.6 Hz, 5H), 1.25 (s, 6H), 1.22 (s, 6H).

^{13}C NMR (100 MHz, CDCl_3 , ppm) δ 189.4, 173.6, 162.3 ($C-F$, $1J_{C-F}$ = 247.0 Hz), 160.0 ($C-F$, $1J_{C-F}$ = 247.0 Hz), 130.05 ($C-F$, $3J_{C-F}$ = 7.9 Hz), 129.97 ($C-F$, $3J_{C-F}$ = 7.9 Hz), 125.3, 117.0, 114.3 ($C-F$, $2J_{C-F}$ = 21.3 Hz), 114.0 ($C-F$, $2J_{C-F}$ = 21.3 Hz), 61.5, 60.38, 47.1, 31.5, 20.7.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{18}\text{H}_{25}\text{FNO}_3$ 322.1813; Found 322.1818.

(*E*)-2-(4-bromophenyl)-3-((4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**4c**)



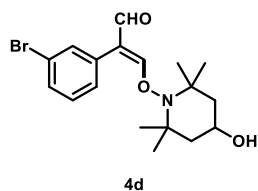
Yellow solid (106.3 mg, 93%), m. p: 146-148 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.15);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.31 (s, 1H), 7.55 – 7.47 (m, 3H), 7.44 – 7.38 (m, 2H), 4.05 (s, 1H), 2.02 – 1.84 (m, 2H), 1.57 (s, 3H), 1.21 (d, J = 9.2 Hz, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 189.6, 174.2, 130.9, 130.4, 128.9, 121.2, 117.3, 62.1, 61.0, 47.6, 32.0, 21.3.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{24}\text{BrNO}_3\text{Na}$ 404.0832; Found 404.0823.

(E)-2-(3-bromophenyl)-3-((4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**4d**)



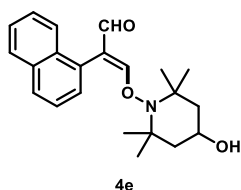
Yellow solid (105.2 mg, 92%), m. p: 138-140 °C; purification by silica gel chromatography (eluent: PE/EA = 15:1, R_f = 0.16);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.32 (s, 1H), 7.72 (d, J = 1.6 Hz, 1H), 7.50 (t, J = 4.0 Hz, 2H), 7.43 (dd, J = 7.6, 1.6 Hz, 1H), 7.30 – 7.26 (m, 1H), 4.07 (s, 1H), 2.01 – 1.86 (m, 2H), 1.58 (t, J = 11.6 Hz, 3H), 1.24 (s, 6H), 1.23 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 189.4, 174.4, 132.0, 131.8, 130.2, 129.3, 127.4, 121.7, 117.0, 62.2, 61.1, 47.7, 32.1, 21.3.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{24}\text{BrNO}_3\text{Na}$ 404.0832; Found 404.0823.

(E)-3-((4-hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2-(naphthalen-1-yl)acrylaldehyde (**4e**)



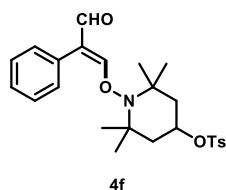
Brown solid (93.2 mg, 88%), m. p: 146-148 °C; purification by silica gel chromatography (eluent: PE/EA = 18:1, R_f = 0.15);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.41 (s, 1H), 8.05 – 8.02 (m, 1H), 7.84 (td, J = 7.6, 6.8, 4.4 Hz, 3H), 7.64 (dd, J = 8.4, 1.6 Hz, 1H), 7.55 (s, 1H), 7.50 – 7.44 (m, 2H), 4.09 – 3.98 (m, 1H), 1.93 (dd, J = 12.8, 4.0 Hz, 2H), 1.58 (t, J = 12.0 Hz, 3H), 1.26 (s, 6H), 1.20 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 190.3, 174.5, 133.1, 132.6, 128.4, 128.2, 127.8, 127.5, 127.3, 126.9, 126.0, 125.8, 118.6, 62.5, 61.2, 47.8, 32.3, 21.5.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{27}\text{NO}_3\text{Na}$ 376.1883; Found 376.1874.

(*E*)-2,2,6,6-tetramethyl-1-((3-oxo-2-phenylprop-1-en-1-yl)oxy)piperidin-4-yl 4-methylbenzenesulfonate (**4f**)



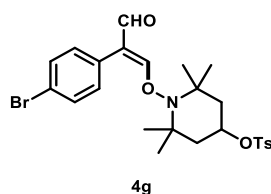
Brown solid (113.8 mg, 83%), m. p: 145-147 °C; purification by silica gel chromatography (eluent: PE/EA = 22:1, R_f = 0.15);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.32 (s, 1H), 7.79 (d, J = 8.4 Hz, 2H), 7.50 – 7.43 (m, 2H), 7.42 – 7.33 (m, 5H), 7.29 (d, J = 7.2 Hz, 1H), 4.83 – 4.69 (m, 1H), 2.46 (s, 3H), 1.99 – 1.87 (m, 2H), 1.76 (t, J = 12.0 Hz, 2H), 1.17 (d, J = 23.6 Hz, 12H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 190.1, 173.5, 144.9, 134.0, 130.0, 129.8, 129.0, 127.9, 127.5, 127.5, 119.0, 73.6, 61.1, 44.5, 32.0, 21.6, 21.2.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{25}\text{H}_{31}\text{NO}_5\text{SNa}$ 480.1815; Found 480.1808.

(*E*)-1-((2-(4-bromophenyl)-3-oxoprop-1-en-1-yl)oxy)-2,2,6,6-tetramethylpiperidin-4-yl 4-methylbenzenesulfonate (**4g**)



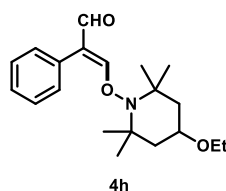
Yellow solid (130.0 mg, 81%), m. p: 149-151 °C; purification by silica gel chromatography (eluent: PE/EA = 21:1, R_f = 0.16);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 9.29 (s, 1H), 7.80 (s, 2H), 7.52 – 7.49 (m, 2H), 7.41 (s, 1H), 7.37 – 7.33 (m, 4H), 4.80 – 4.71 (m, 1H), 2.46 (s, 3H), 1.95 – 1.72 (m, 4H), 1.19 (s, 6H), 1.14 (s, 6H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 189.6, 173.7, 144.9, 133.8, 131.1, 130.6, 129.8, 128.8, 127.5, 121.5, 117.8, 73.4, 61.1, 44.4, 31.9, 21.6, 21.2.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{K}]^+$ Calcd for $\text{C}_{25}\text{H}_{30}\text{BrNO}_5\text{SK}$ 574.0660; Found 574.0640.

(*E*)-3-((4-ethoxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)-2-phenylacrylaldehyde (**4h**)



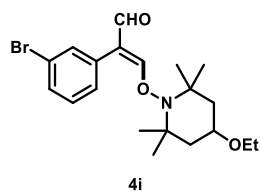
Yellow solid (89.4 mg, 90%), m. p: 90-92 °C; purification by silica gel chromatography (eluent: PE/EA = 18:1, R_f = 0.18);

¹H NMR (400 MHz, CDCl₃, ppm) δ 9.33 (s, 1H), 7.53 – 7.46 (m, 3H), 7.40 – 7.36 (m, 2H), 7.31 – 7.26 (m, 1H), 3.64 – 3.55 (m, 1H), 3.50 (q, *J* = 6.8 Hz, 2H), 1.97 (ddd, *J* = 11.6, 4.4, 2.0 Hz, 2H), 1.52 (t, *J* = 12.0 Hz, 2H), 1.24 – 1.15 (m, 15H).

¹³C NMR (100 MHz, CDCl₃, ppm) δ 190.2, 174.3, 130.2, 129.0, 127.9, 127.3, 118.6, 69.3, 63.6, 61.0, 44.8, 32.3, 21.5, 15.6.

HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₀H₂₉NO₃Na 354.2049; Found 354.2029.

(E)-2-(3-bromophenyl)-3-((4-ethoxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)acrylaldehyde (**4i**)



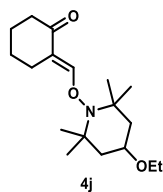
Yellow solid (109.2 mg, 89%), m. p: 120-122 °C; purification by silica gel chromatography (eluent: PE/EA = 18:1, *R_f* = 0.19);

¹H NMR (400 MHz, CDCl₃, ppm) δ 9.30 (s, 1H), 7.71 (t, *J* = 1.6 Hz, 1H), 7.48 (d, *J* = 6.4 Hz, 2H), 7.41 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.26 – 7.22 (m, 1H), 3.65 – 3.56 (m, 1H), 3.50 (q, *J* = 7.2 Hz, 2H), 2.02 – 1.93 (m, 2H), 1.51 (t, *J* = 12.0 Hz, 2H), 1.20 (t, *J* = 4.4 Hz, 15H).

¹³C NMR (100 MHz, CDCl₃, ppm) δ 189.5, 174.6, 132.2, 131.9, 130.2, 129.4, 127.5, 121.8, 117.0, 69.2, 63.6, 61.1, 44.8, 32.2, 21.4, 15.5.

HRMS (ESI-TOF) *m/z*: [M + Na]⁺ Calcd for C₂₀H₂₈BrNO₃Na 432.1145; Found 432.1132.

(E)-2-(((4-ethoxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy)methylene)cyclohexan-1-one (**4j**)



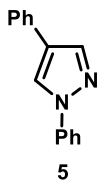
Yellow solid (63.1 mg, 68%), m. p: 68-70 °C; purification by silica gel chromatography (eluent: PE/EA = 19:1, *R_f* = 0.18);

¹H NMR (400 MHz, CDCl₃, ppm) δ 7.63 (s, 1H), 3.62 – 3.52 (m, 1H), 3.47 (t, *J* = 6.8 Hz, 2H), 2.43 (t, *J* = 7.6 Hz, 2H), 2.34 (t, *J* = 6.4 Hz, 2H), 1.91 (d, *J* = 10.8 Hz, 2H), 1.84 – 1.74 (m, 2H), 1.72 – 1.64 (m, 2H), 1.52 – 1.44 (m, 2H), 1.25 – 1.12 (m, 15H).

¹³C NMR (100 MHz, CDCl₃, ppm) δ 200.2, 162.2, 110.6, 69.5, 63.4, 60.4, 44.7, 39.5, 32.3, 23.2, 23.0, 22.6, 21.2, 15.6.

HRMS (ESI-TOF) *m/z*: [M + K]⁺ Calcd for C₁₈H₃₁NO₃K 348.1936; Found 348.1928.

1,4-diphenyl-1*H*-pyrazole (**5**)



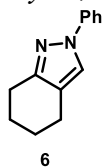
Pale yellow solid (61.4 mg, 93%), m. p: 96-97 °C; purification by silica gel chromatography (eluent: PE/EA = 10:1, R_f = 0.30);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 8.15 (d, J = 1 Hz, 1H) , 7.99 (d, J = 0.5 Hz, 1H), 7.74–7.71 (m, 2H), 7.56 – 7.54 (m, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.39 (t, J = 7.5 Hz, 2H), 7.29 – 7.24 (m, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 140.0, 138.8, 132.0, 129.4, 128.9, 126.8, 126.5, 125.7, 124.9, 123.3, 119.0.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2$ 221.1073; Found 221.1075.

2-phenyl-4,5,6,7-tetrahydro-2H-indazole (6)



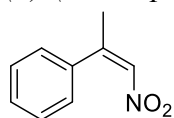
Faint orange oil (53.5 mg, 90%); purification by silica gel chromatography (eluent: PE/EA = 10:1, R_f = 0.40);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 7.65-7.61 (m, 3H) , 7.44-7.38 (t, J = 7.2 Hz, 2H), 7.25–7.20 (t, J = 7.3 Hz, 1H), 2.80 (t, J = 6.4 Hz, 2H), 2.63 (t, J = 6.4 Hz, 2H), 1.94 – 1.83 (m, 2H), 1.80 – 1.75 (m, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 151.2, 140.2, 129.3, 125.7, 123.9, 118.7, 118.3, 29.7, 23.4, 23.4, 20.6.

HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2$ 199.1230; Found 199.1235.

(Z)-(1-nitroprop-1-en-2-yl)benzene (1aa)

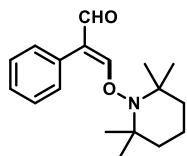
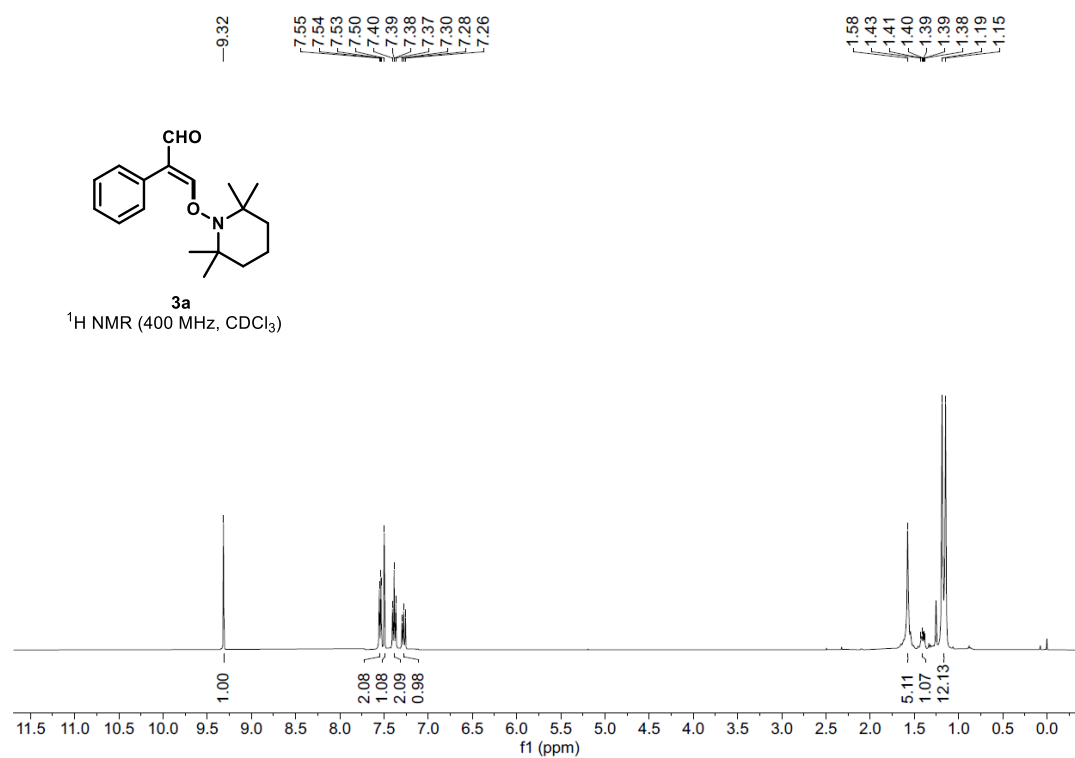


Yellow oil (58.7 mg, 72%); purification by silica gel chromatography (eluent: PE/ Et_2O = 9:1, R_f = 0.42);

$^1\text{H NMR}$ (400 MHz, CDCl_3 , ppm) δ 7.43 – 7.35 (m, 3H), 7.23 – 7.19 (m, 2H), 7.08 – 7.05 (m, 1H), 2.19 (d, J = 1.4 Hz, 3H).

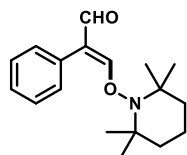
$^{13}\text{C NMR}$ (100 MHz, CDCl_3 , ppm) δ 148.4, 137.1, 134.4, 128.8, 128.5, 126.2, 24.0.

VII. ^1H NMR and ^{13}C NMR spectra



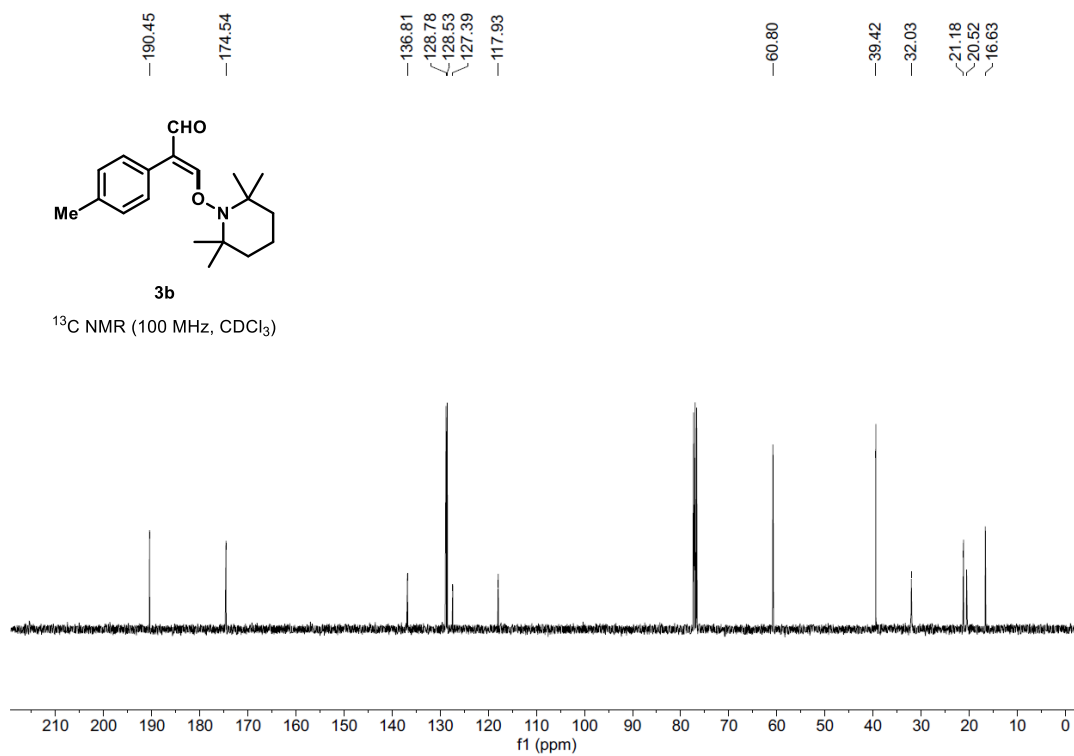
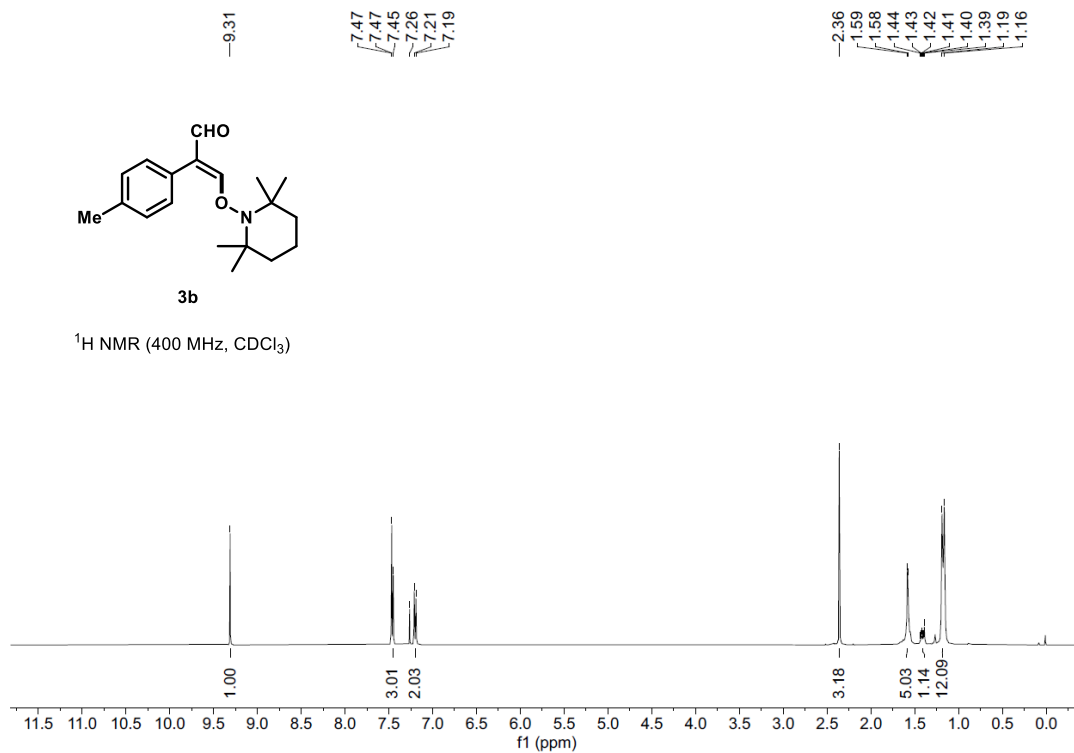
3a

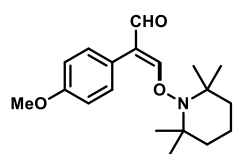
^1H NMR (400 MHz, CDCl_3)



3a

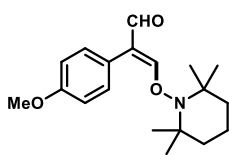
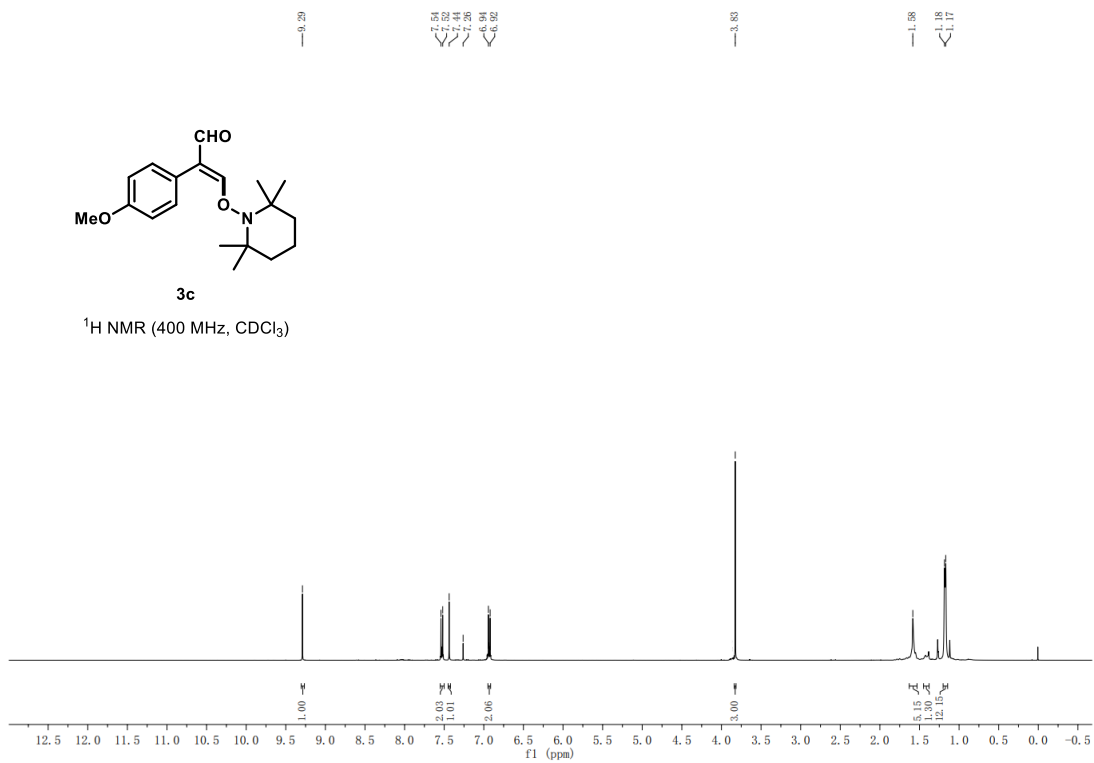
^{13}C NMR (100 MHz, CDCl_3)





3c

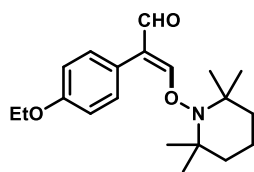
¹H NMR (400 MHz, CDCl₃)



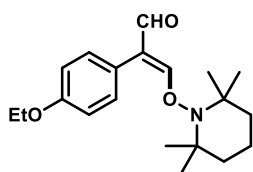
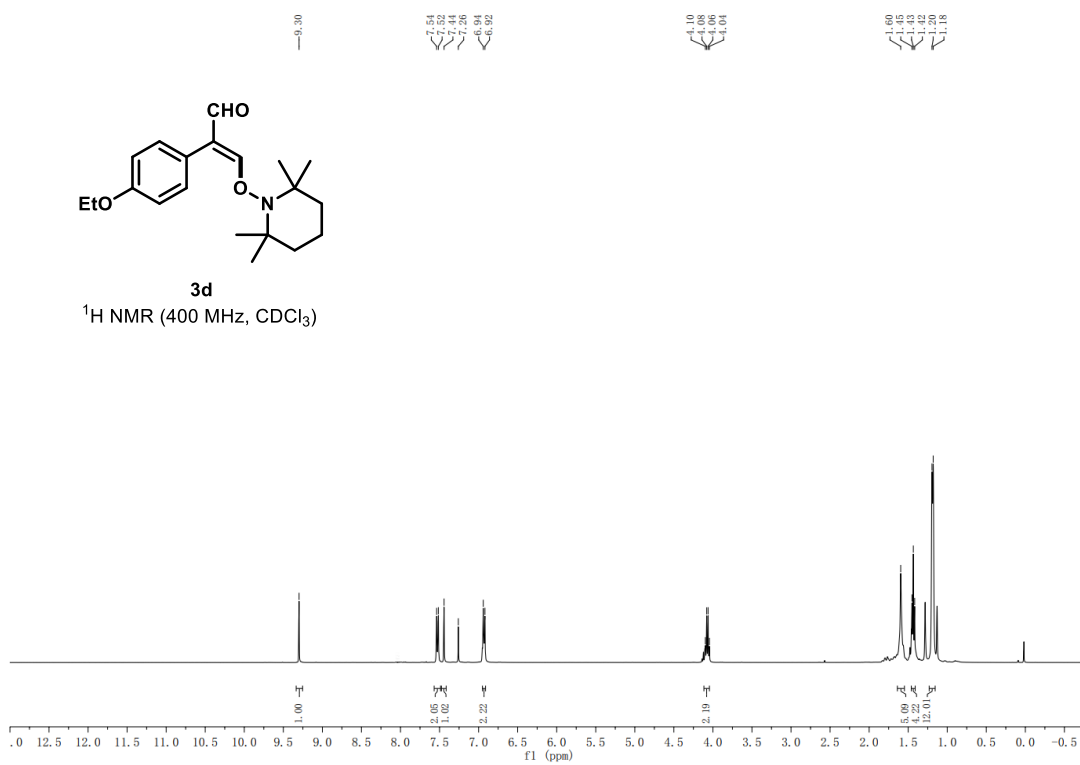
3c

¹³C NMR (100 MHz, CDCl₃)

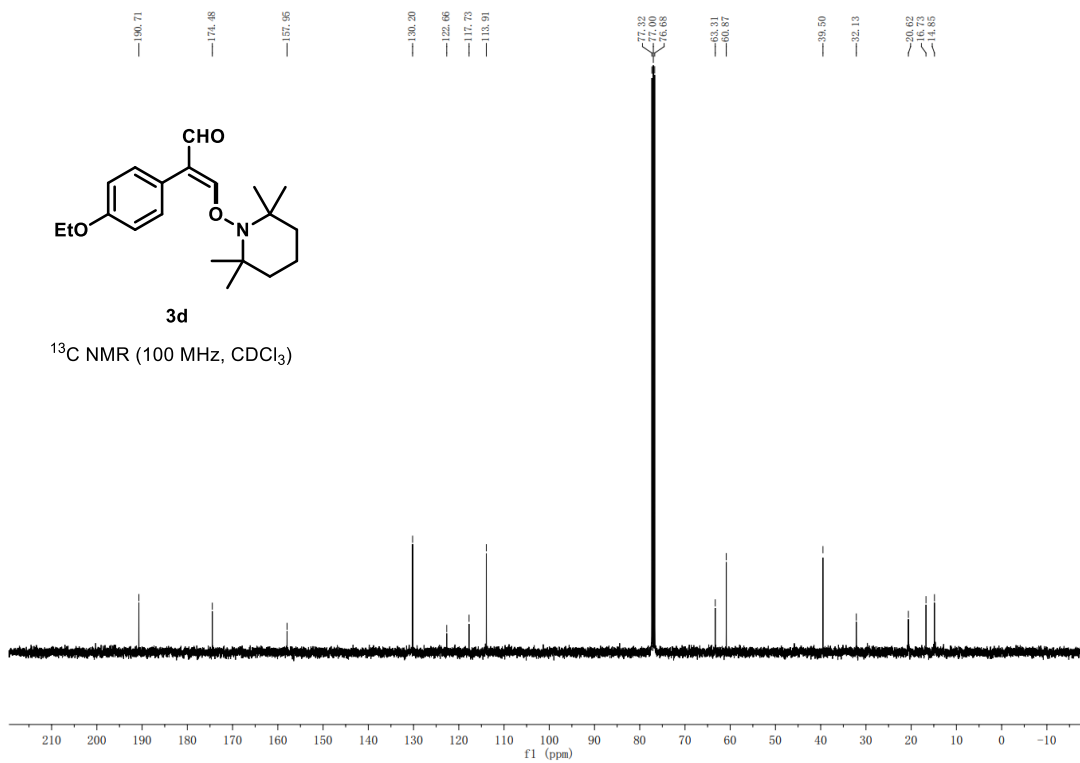


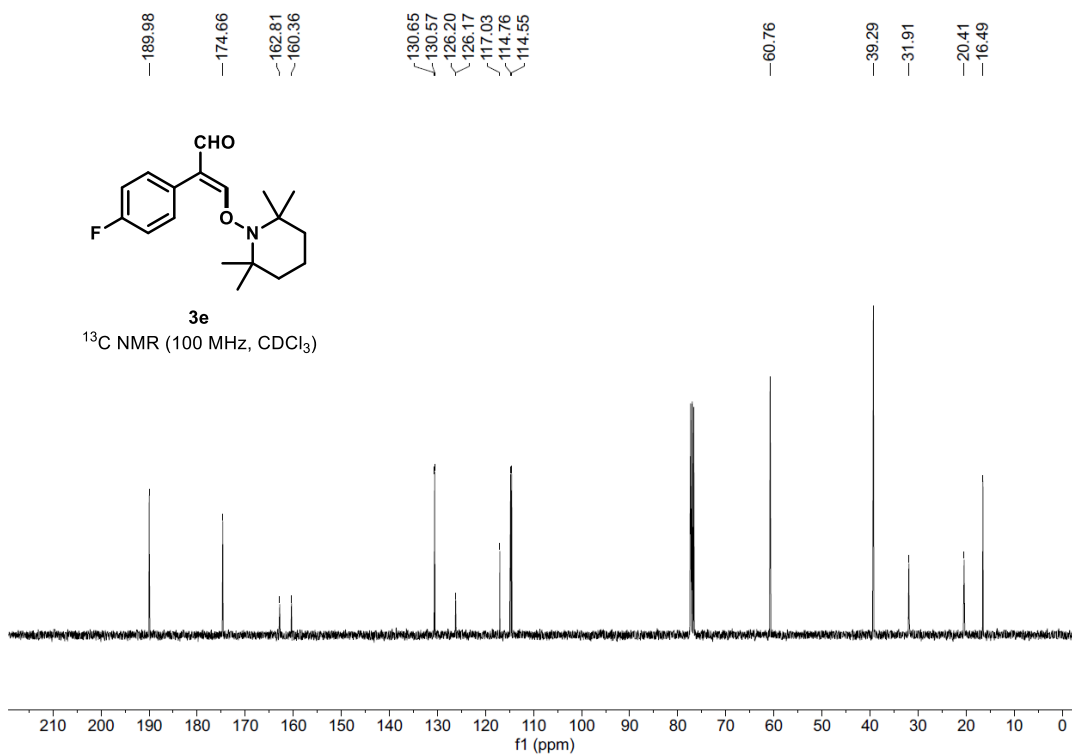
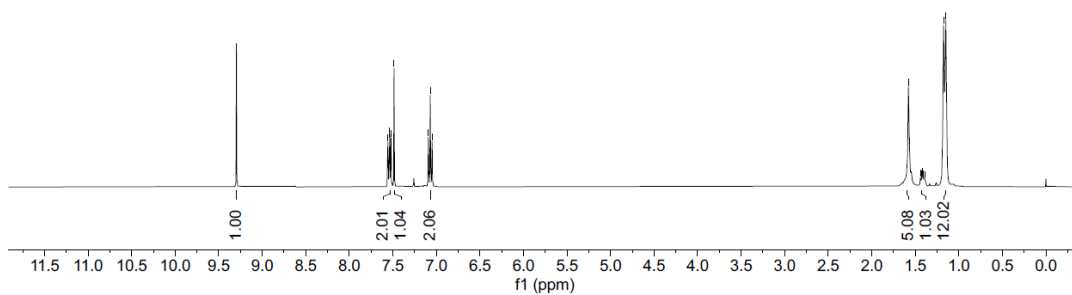
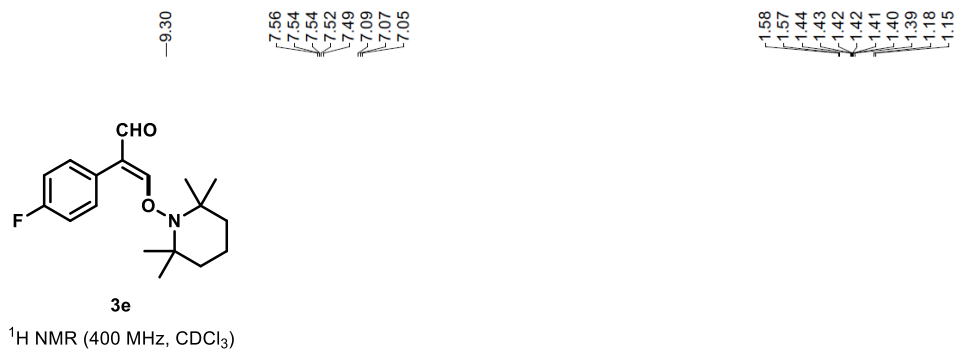


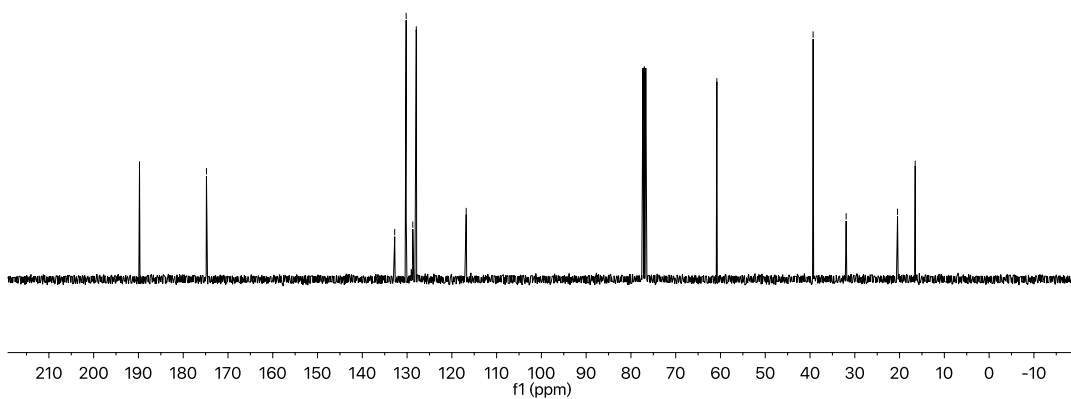
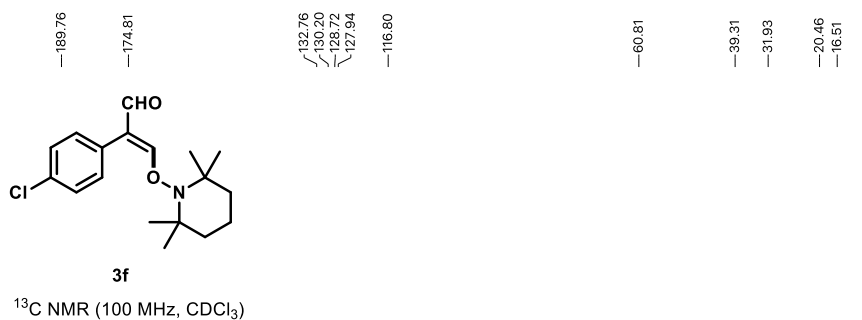
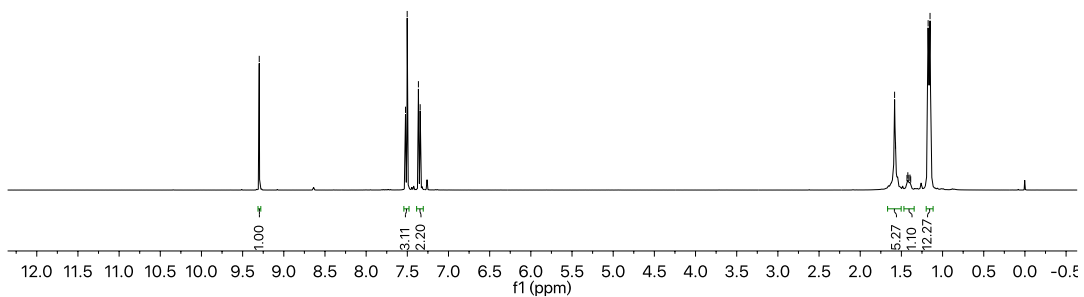
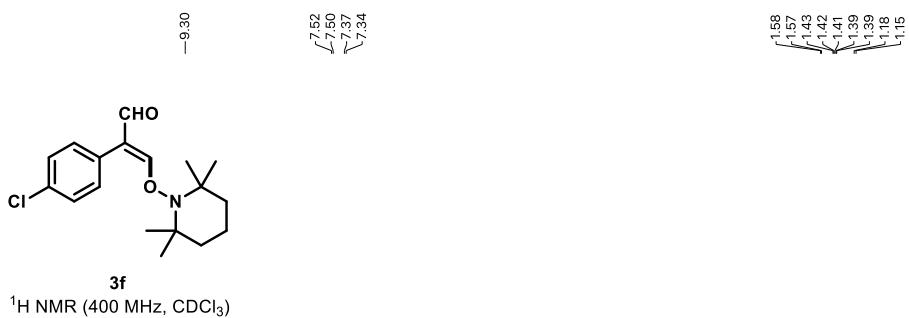
3d
¹H NMR (400 MHz, CDCl₃)

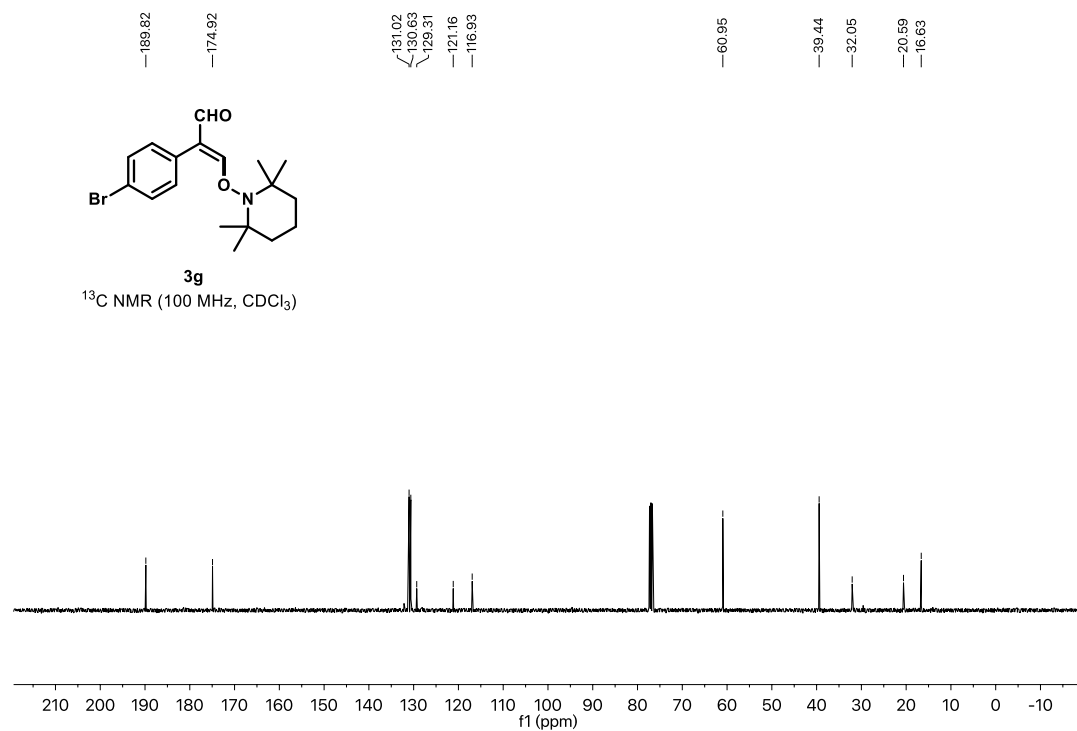
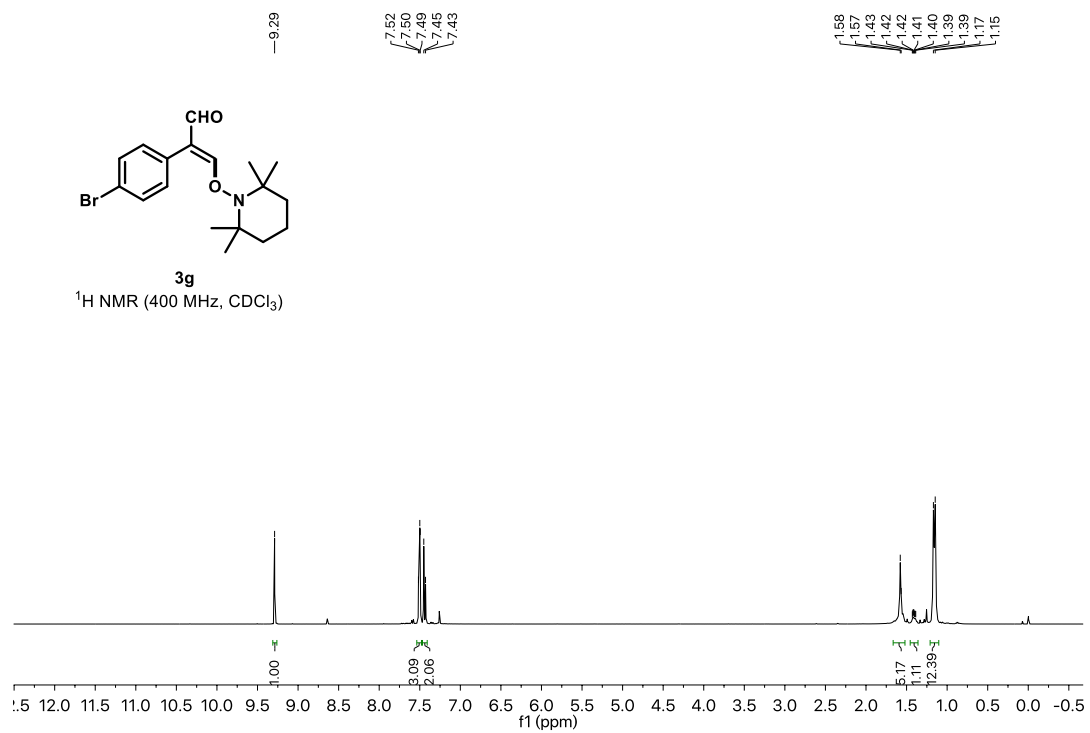


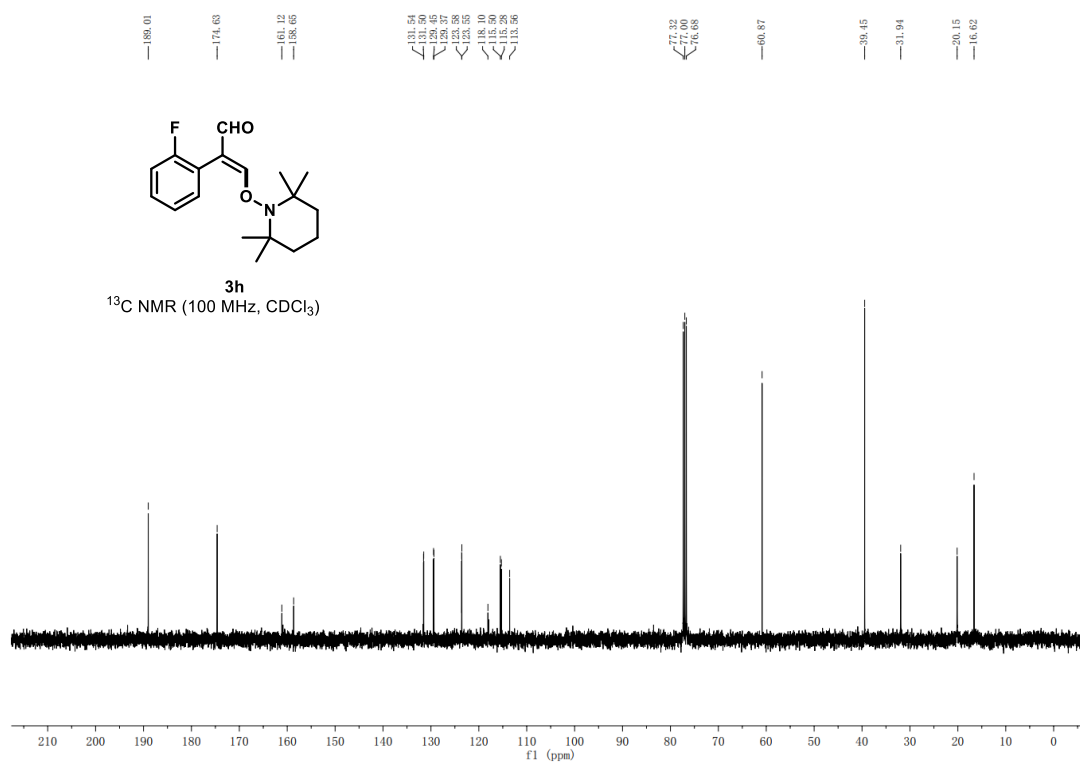
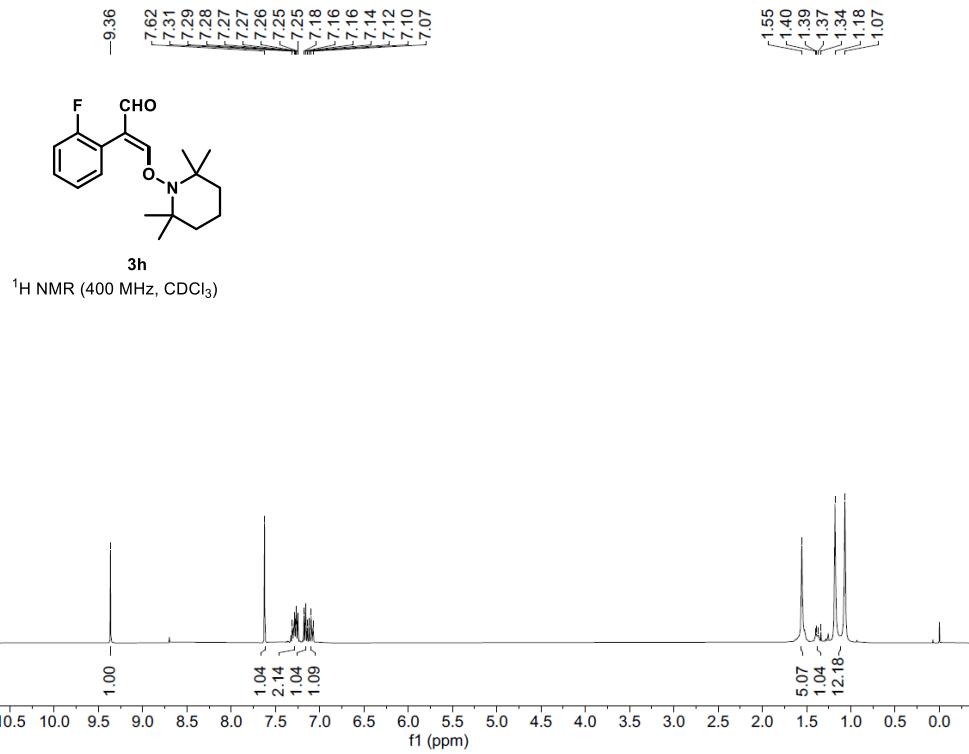
3d
¹³C NMR (100 MHz, CDCl₃)

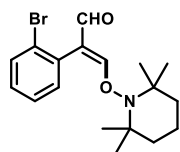




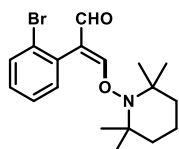
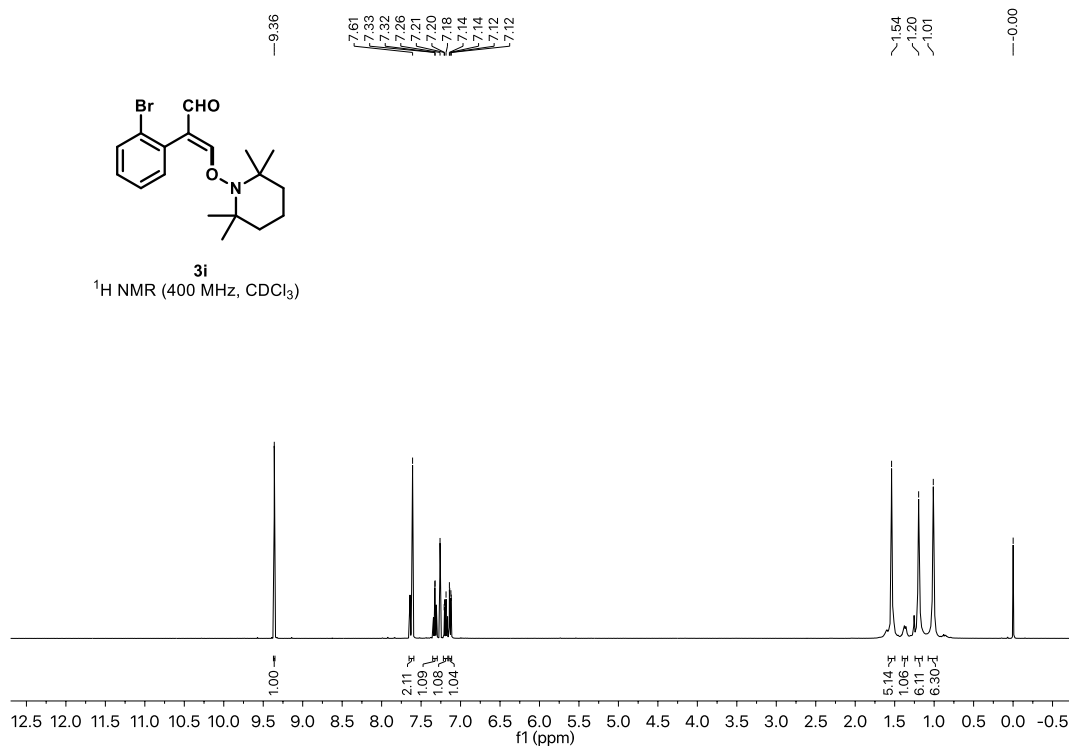




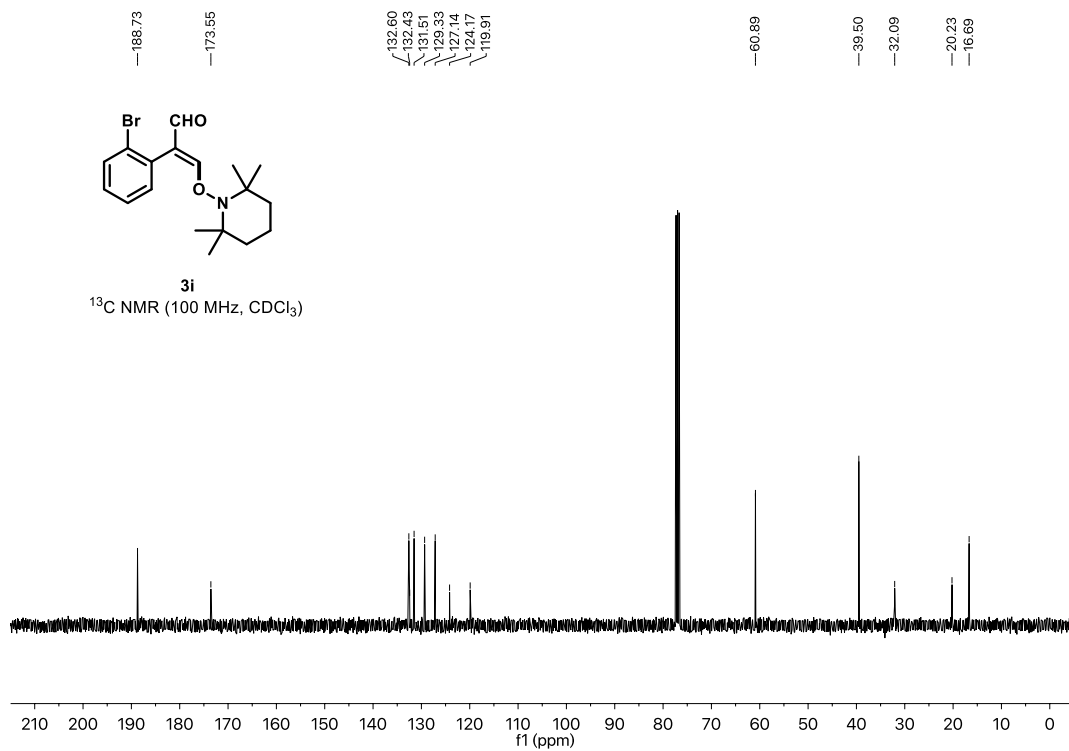


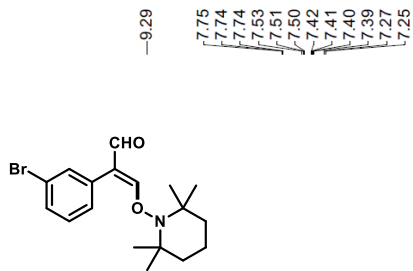


3i
 $^1\text{H NMR}$ (400 MHz, CDCl_3)

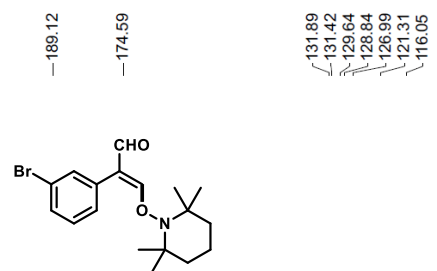
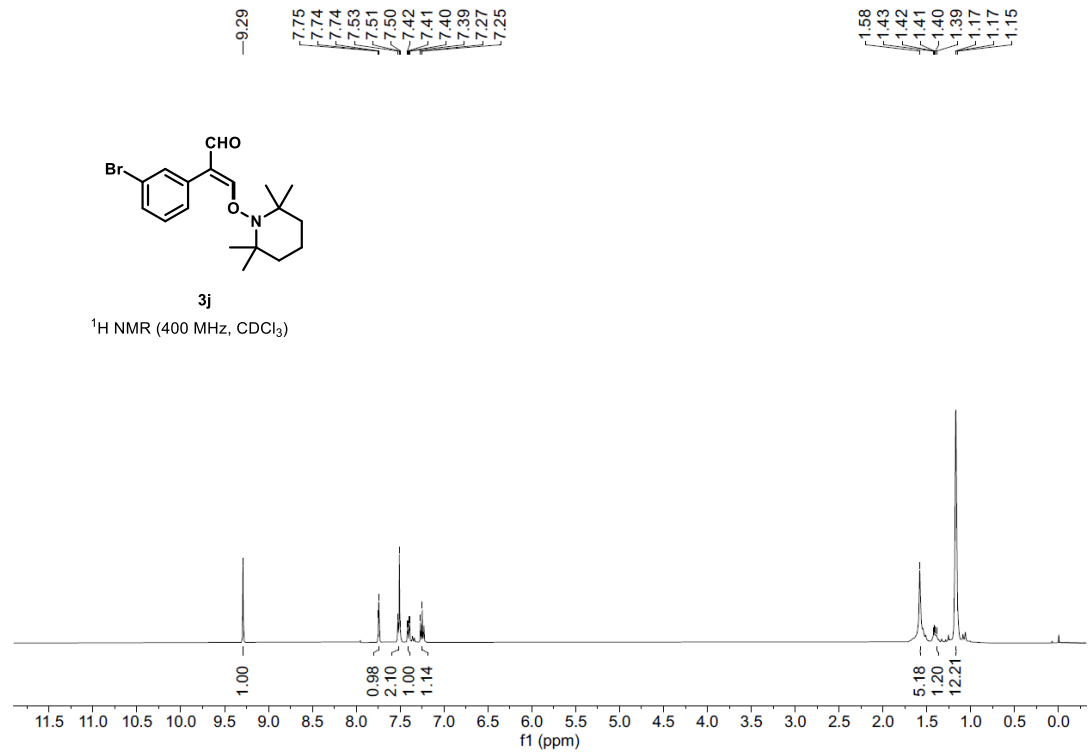


3i
 $^{13}\text{C NMR}$ (100 MHz, CDCl_3)

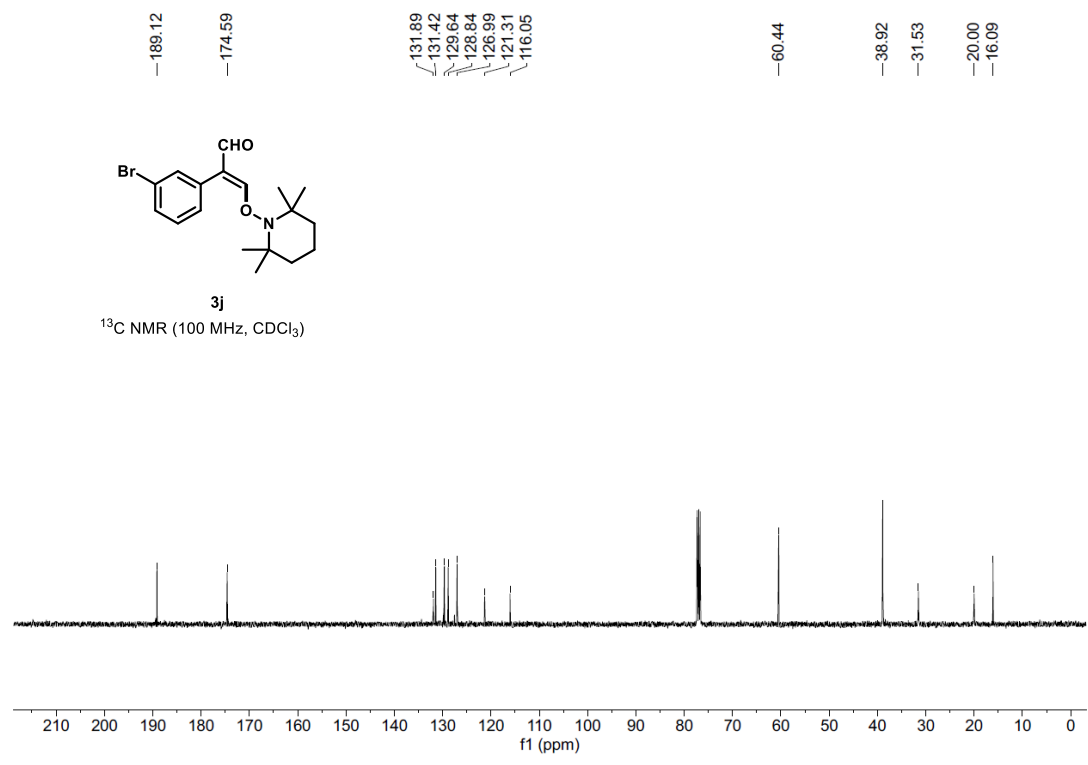


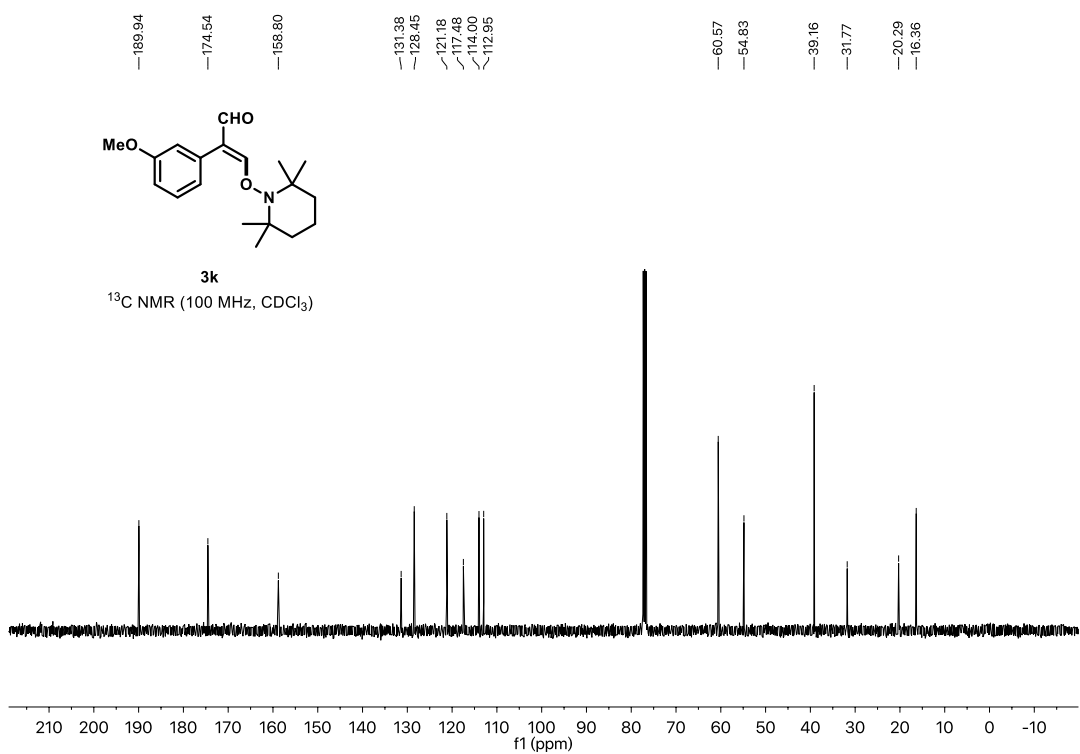
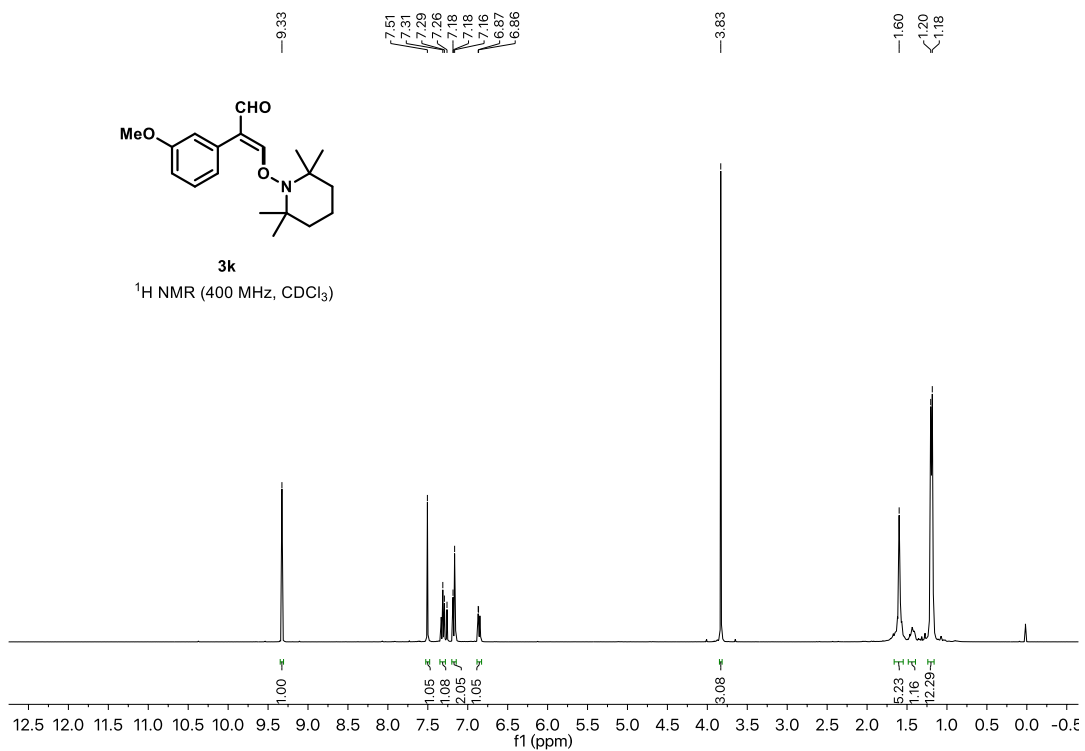


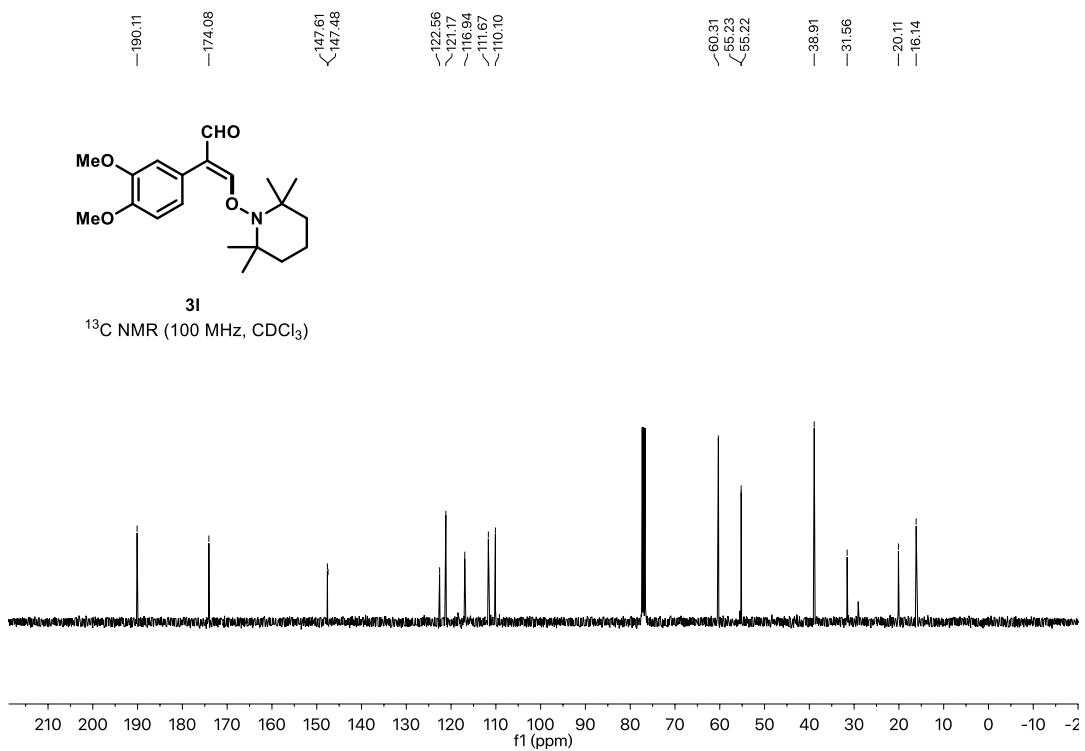
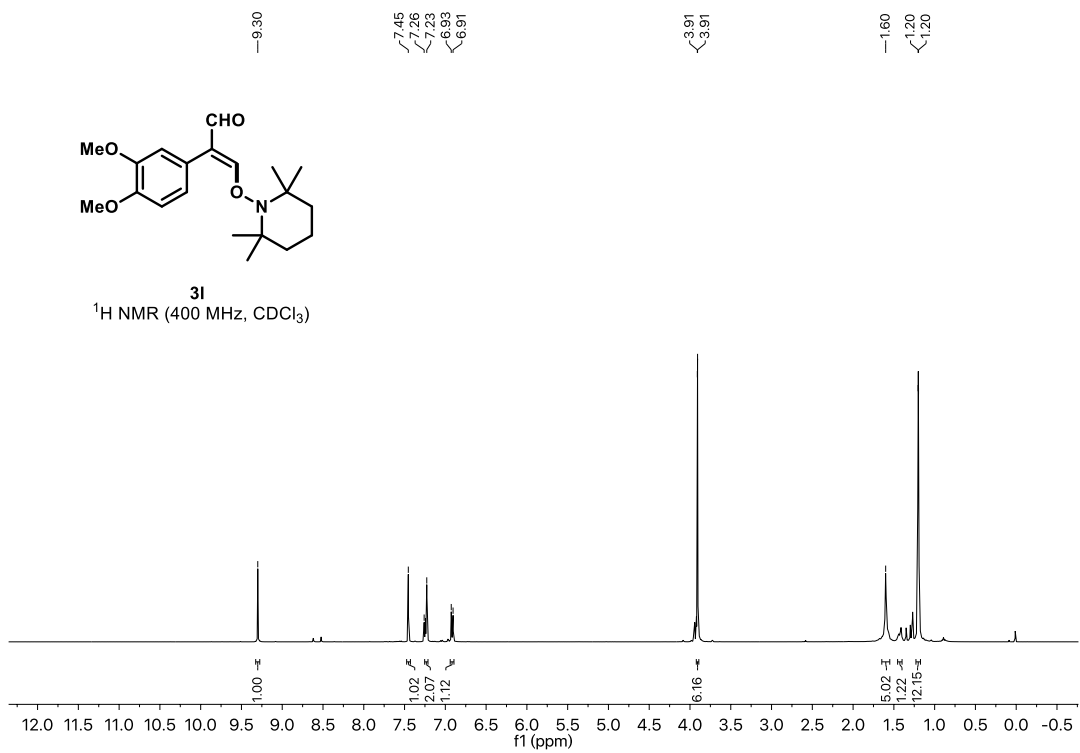
3j
¹H NMR (400 MHz, CDCl₃)

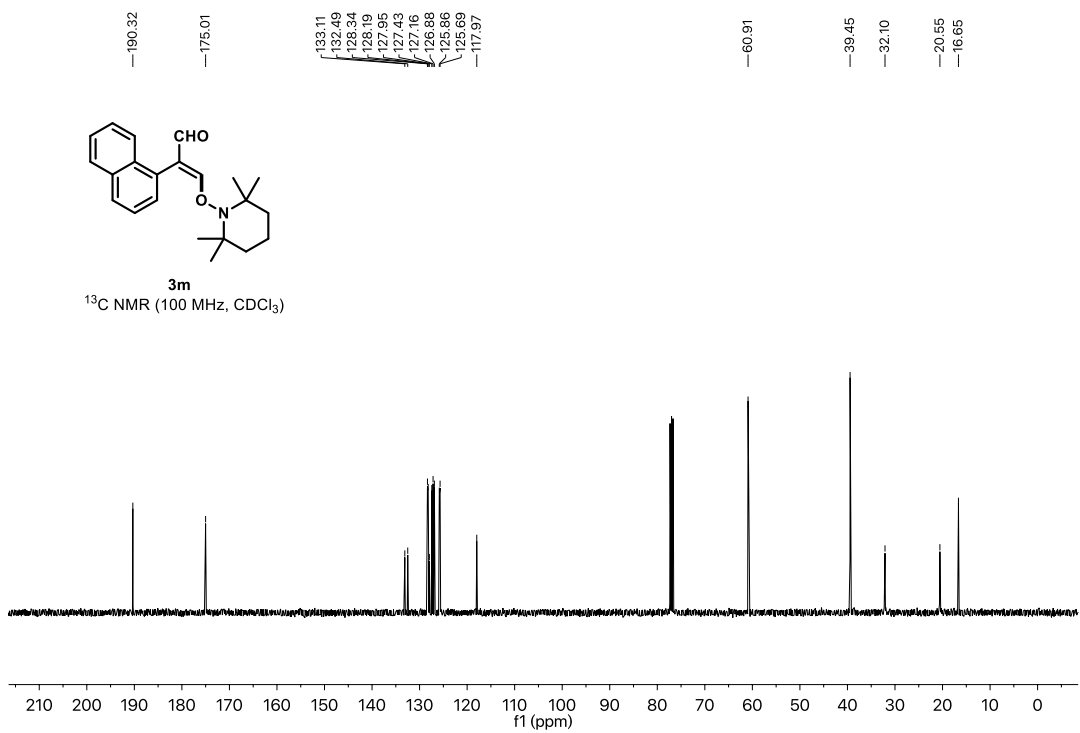
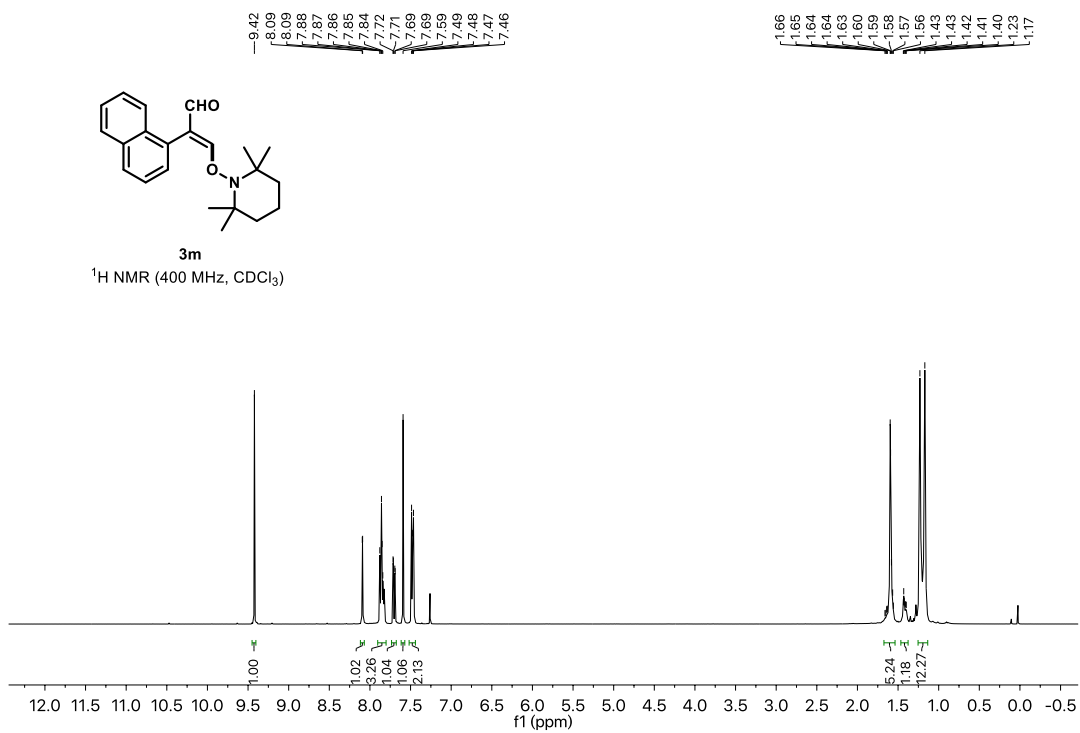


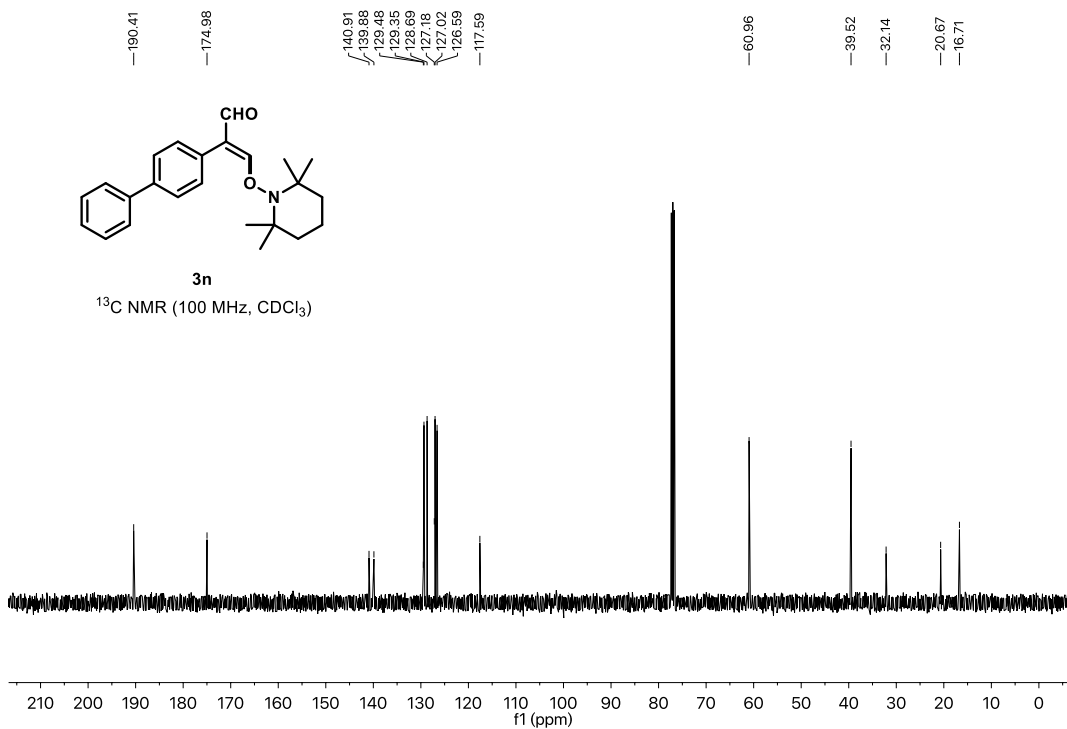
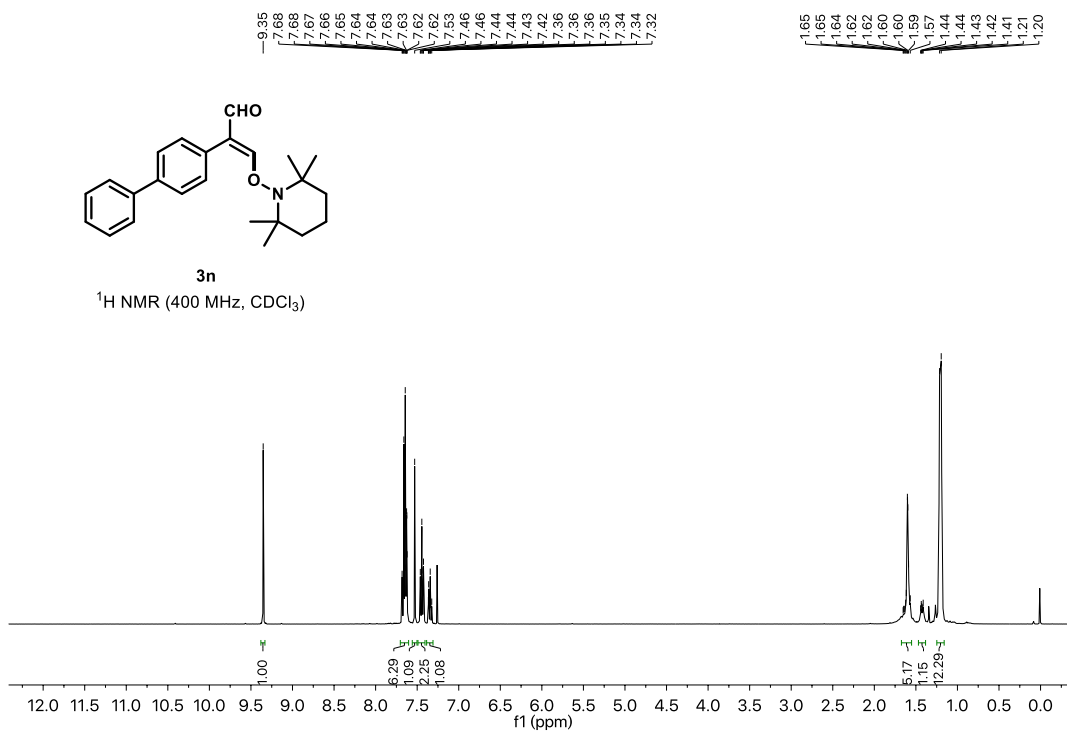
3j
¹³C NMR (100 MHz, CDCl₃)

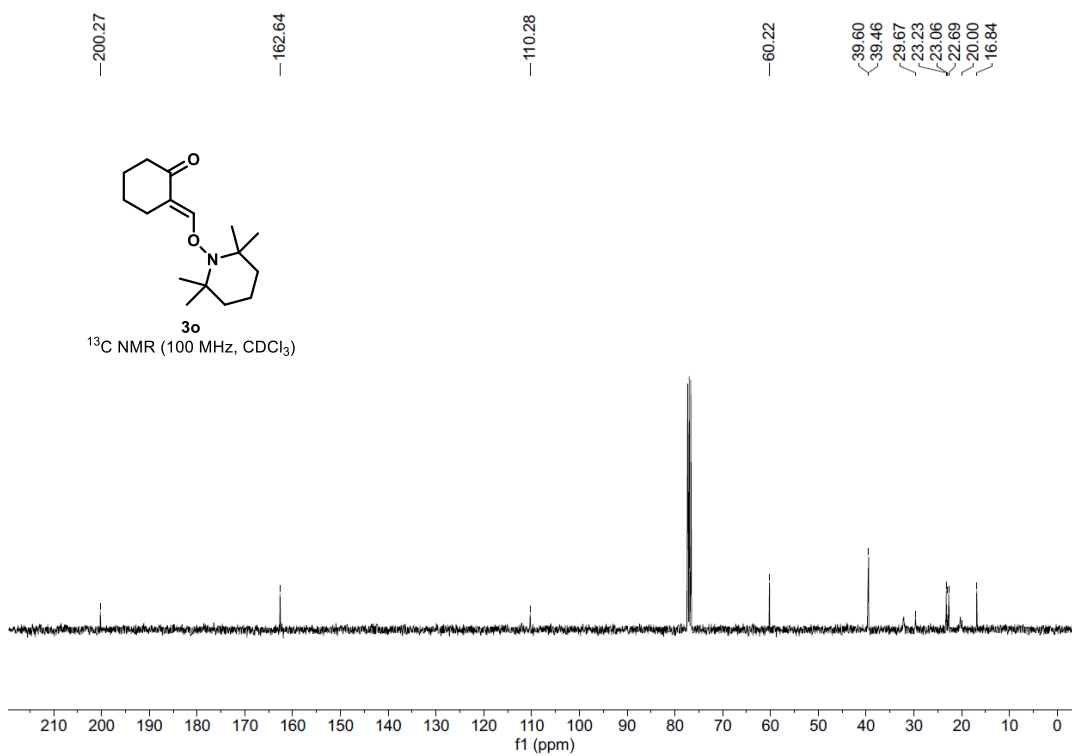
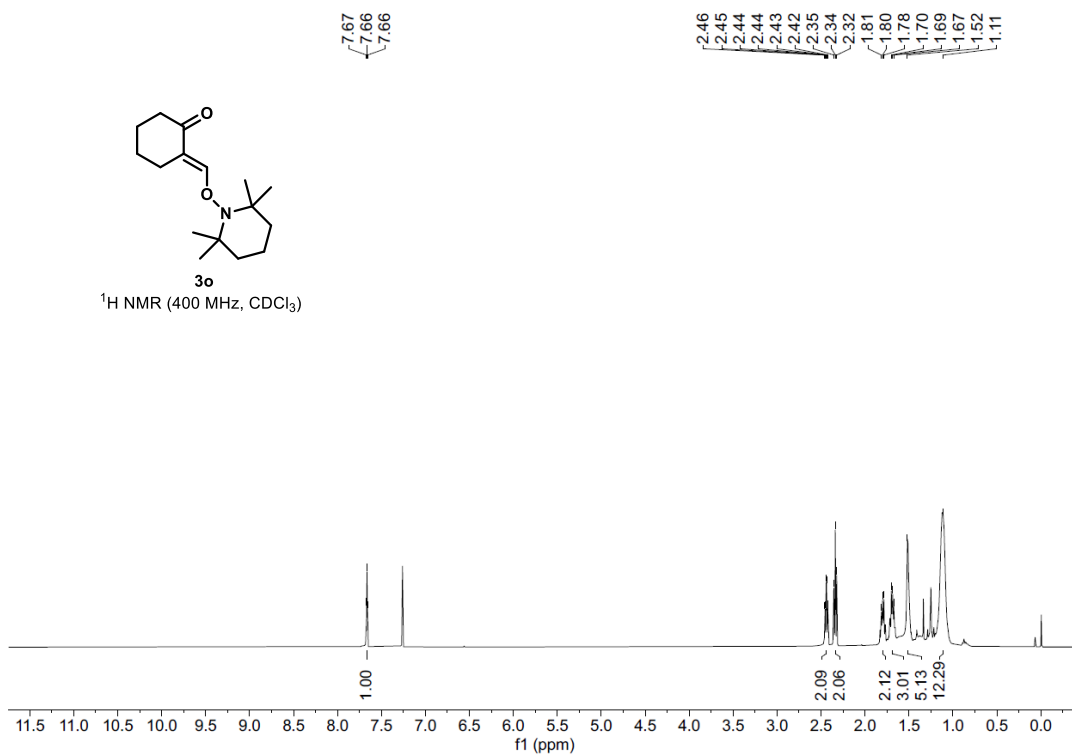


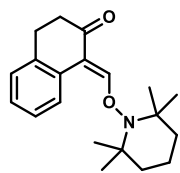






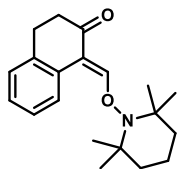
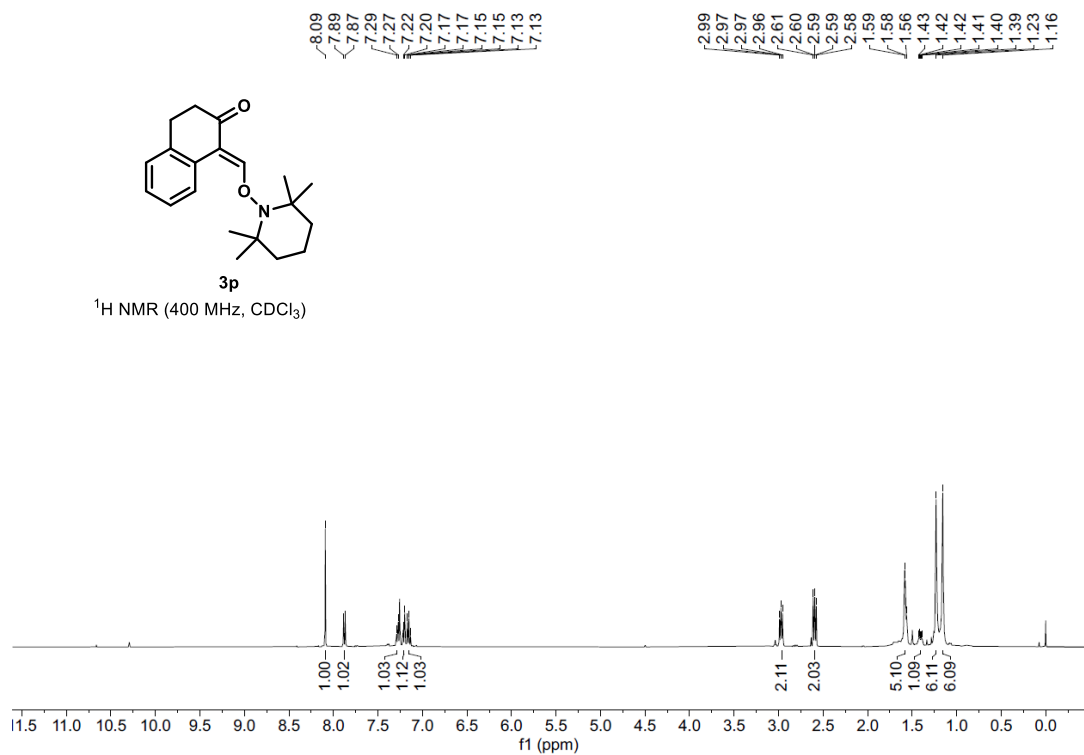






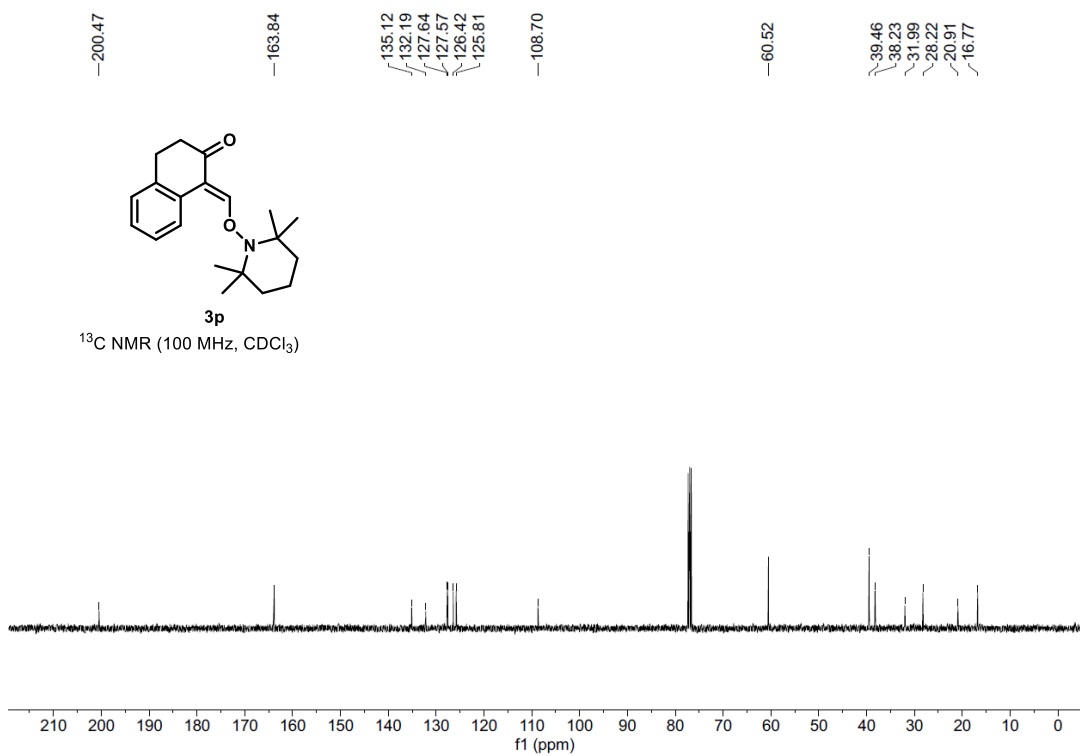
3p

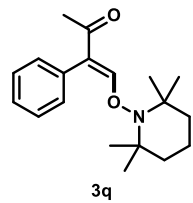
¹H NMR (400 MHz, CDCl₃)



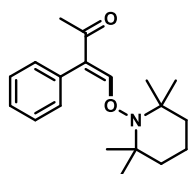
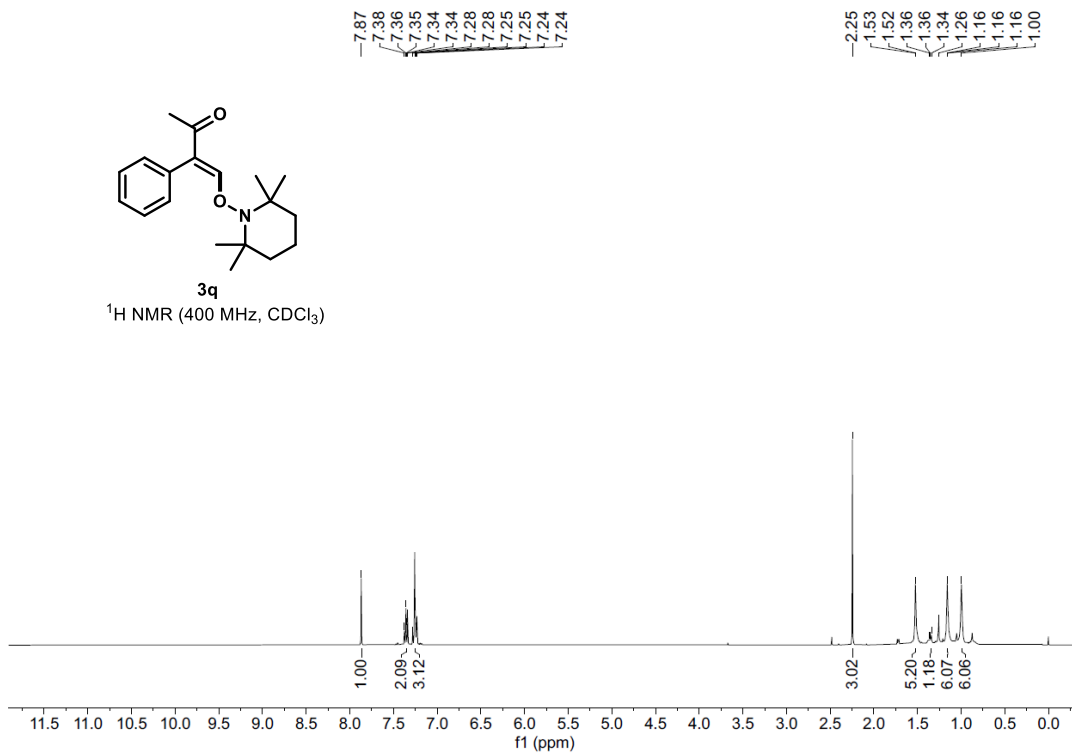
3p

¹³C NMR (100 MHz, CDCl₃)

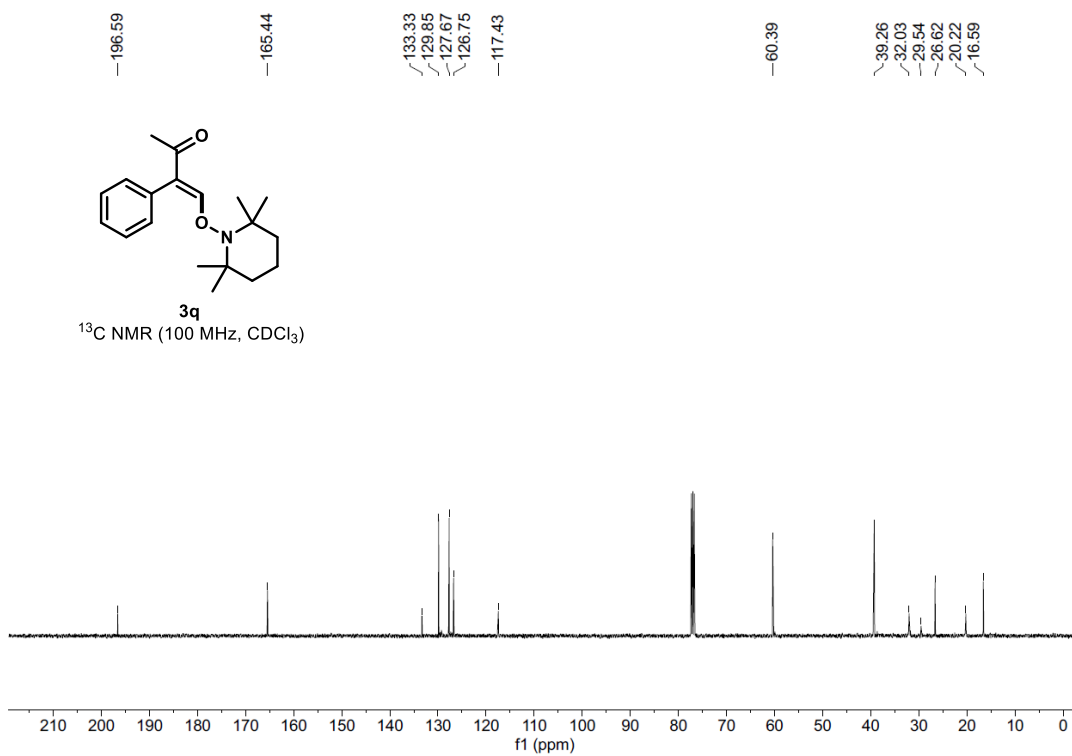


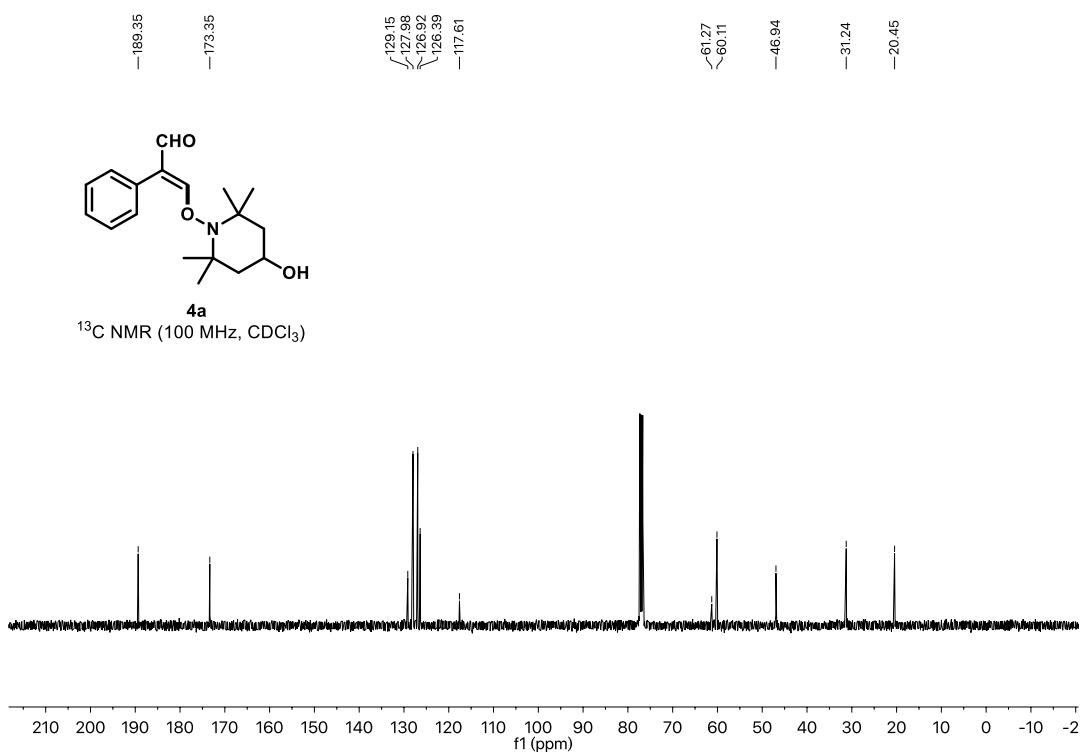
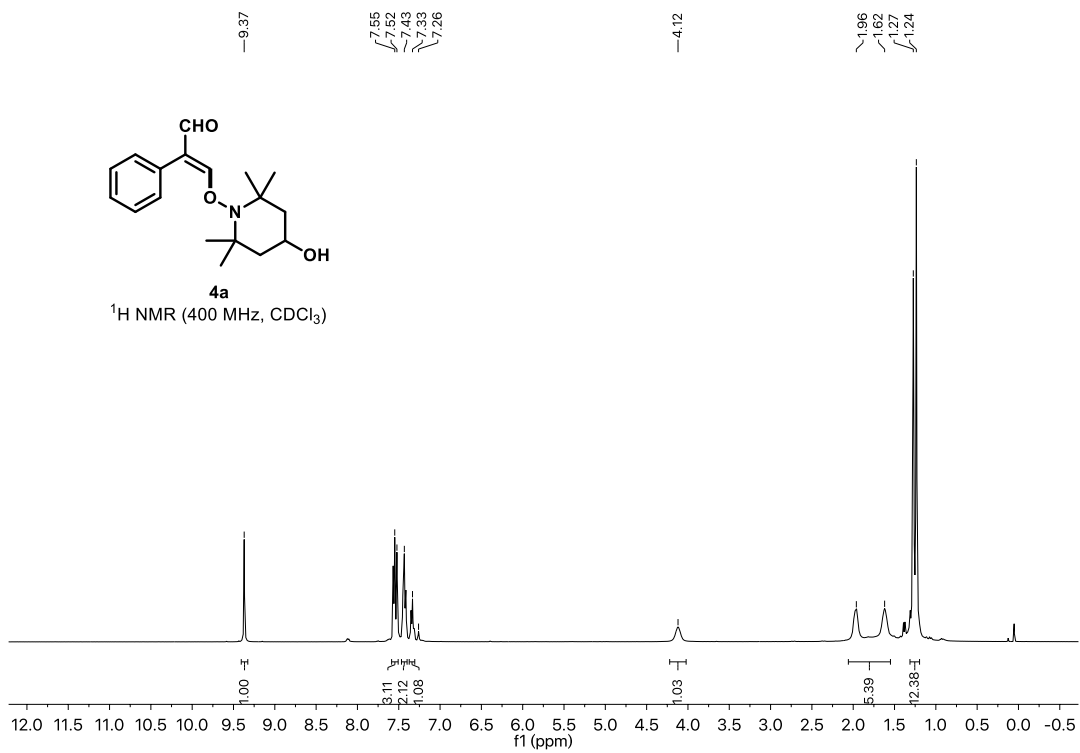


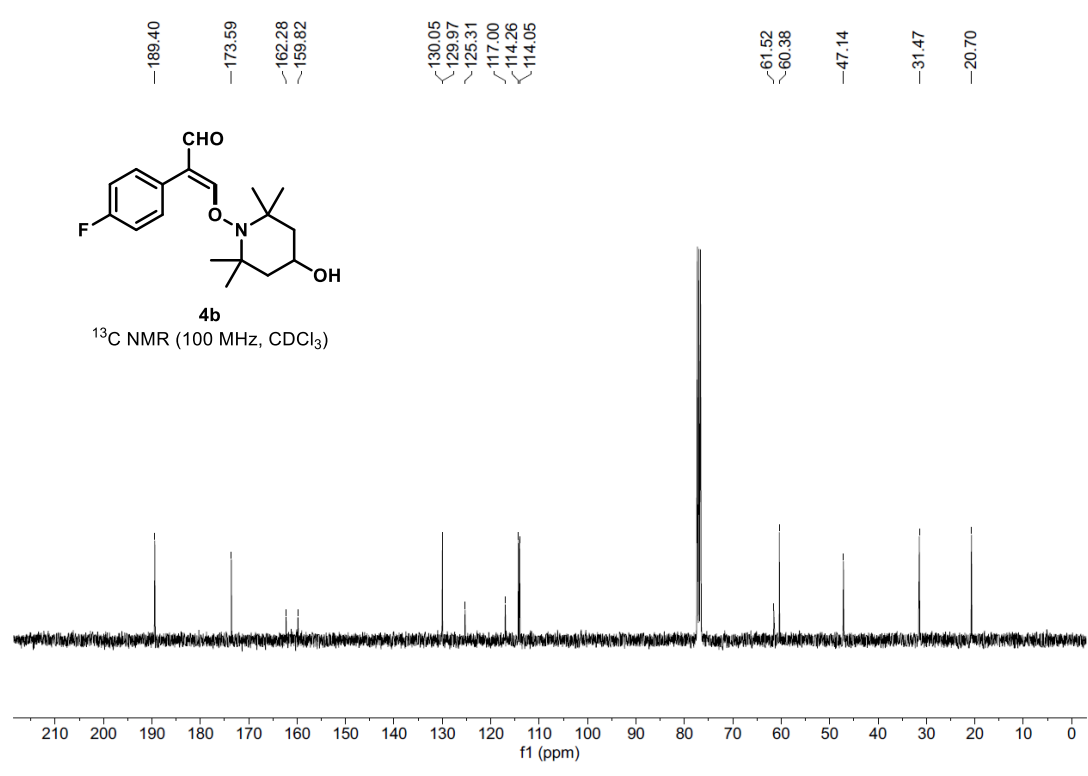
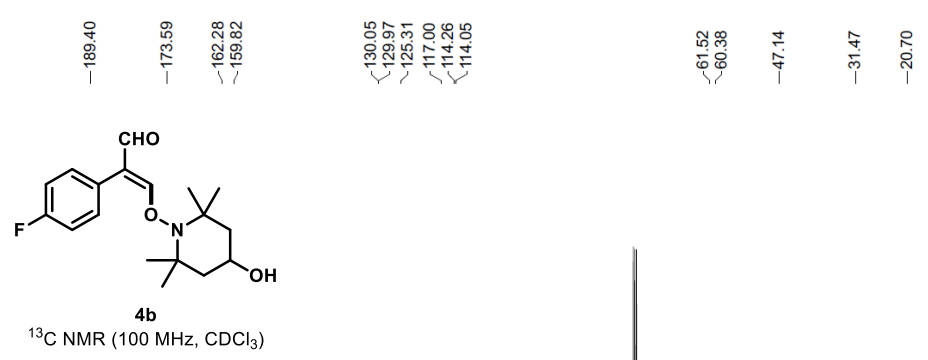
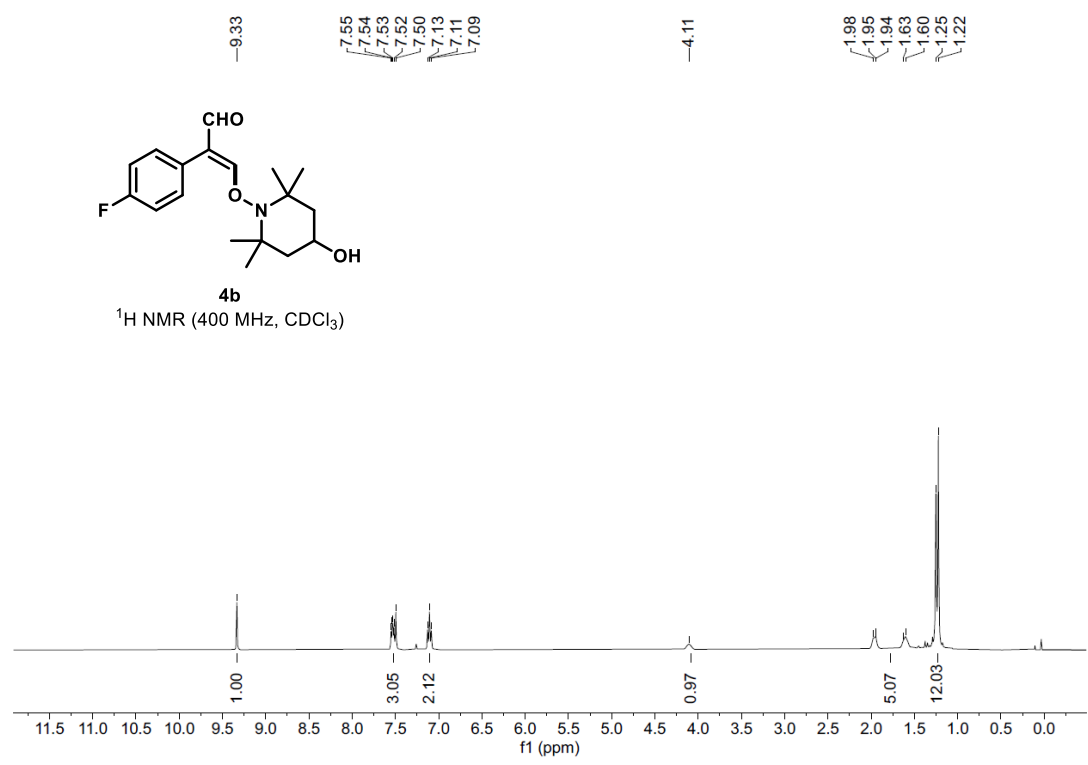
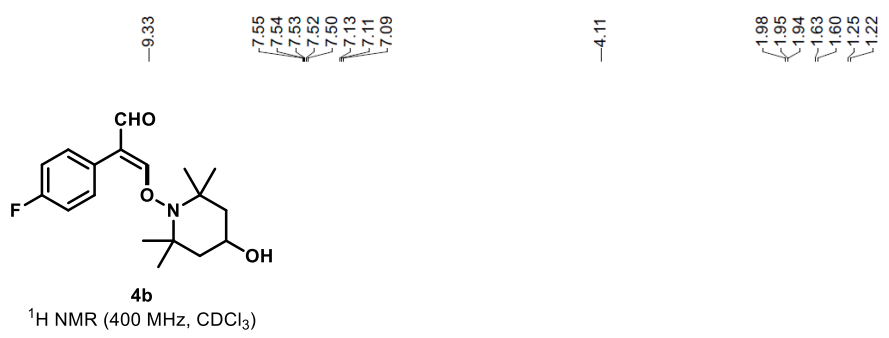
$^1\text{H NMR}$ (400 MHz, CDCl_3)

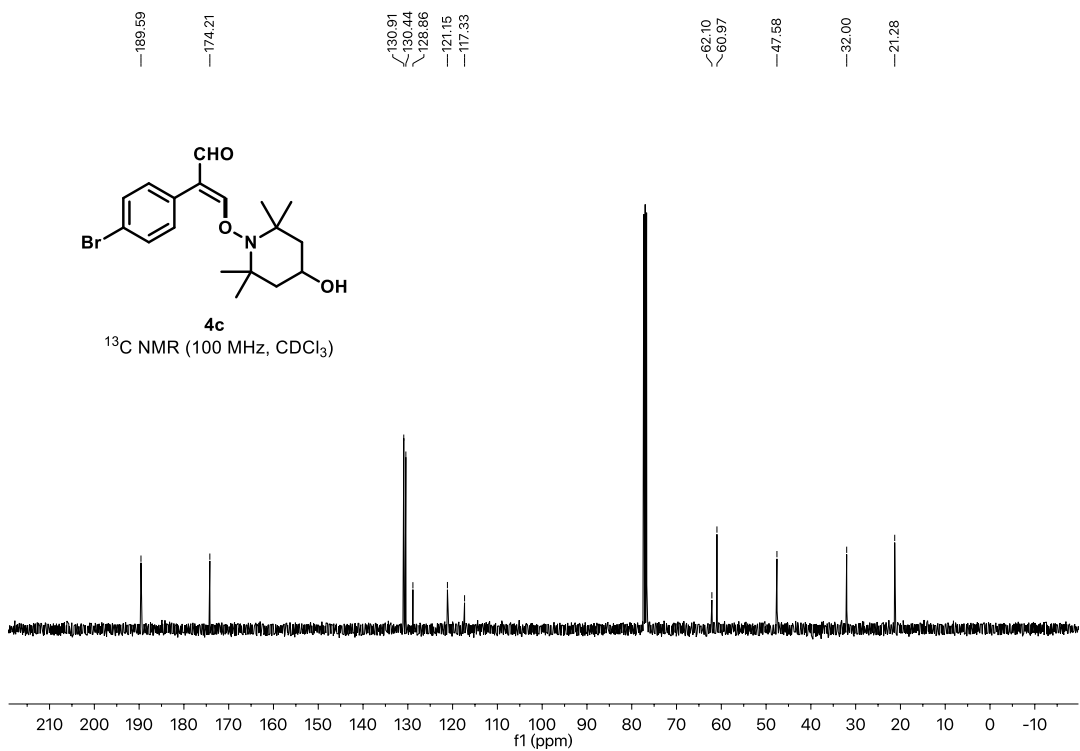
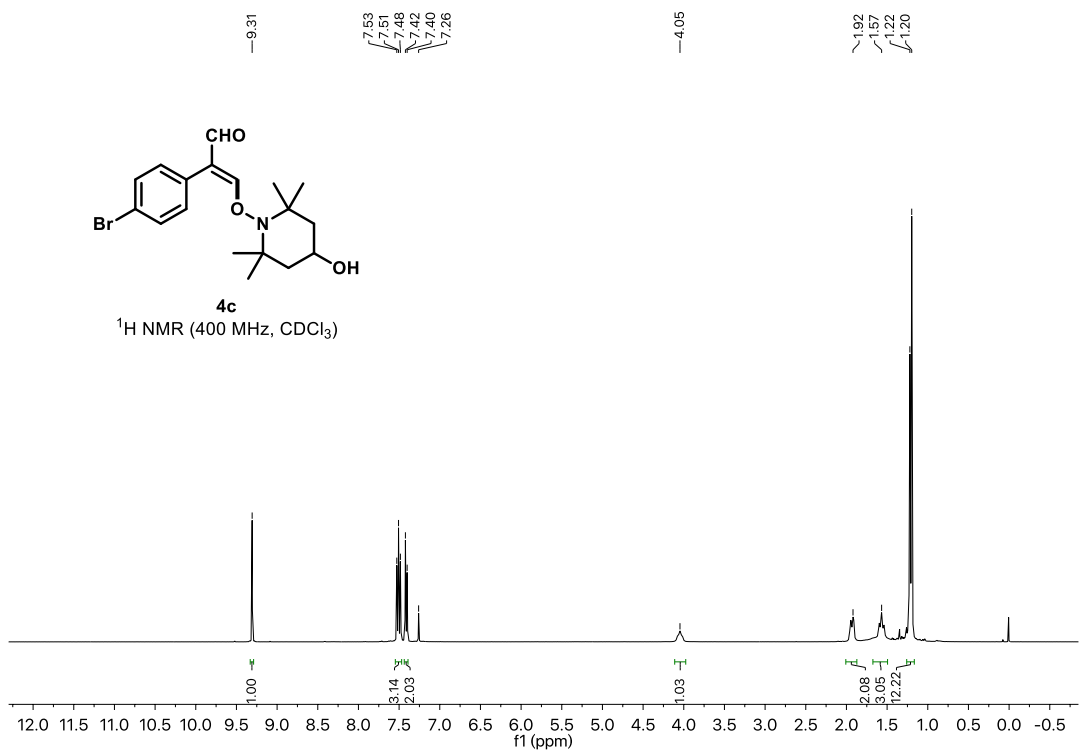


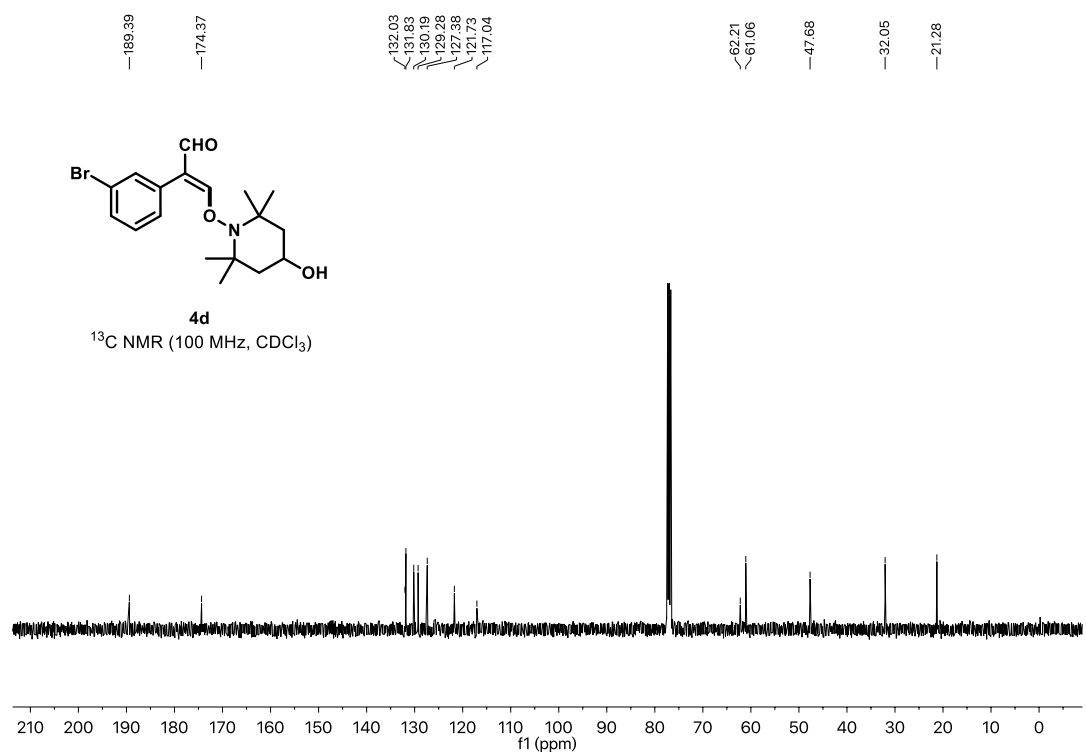
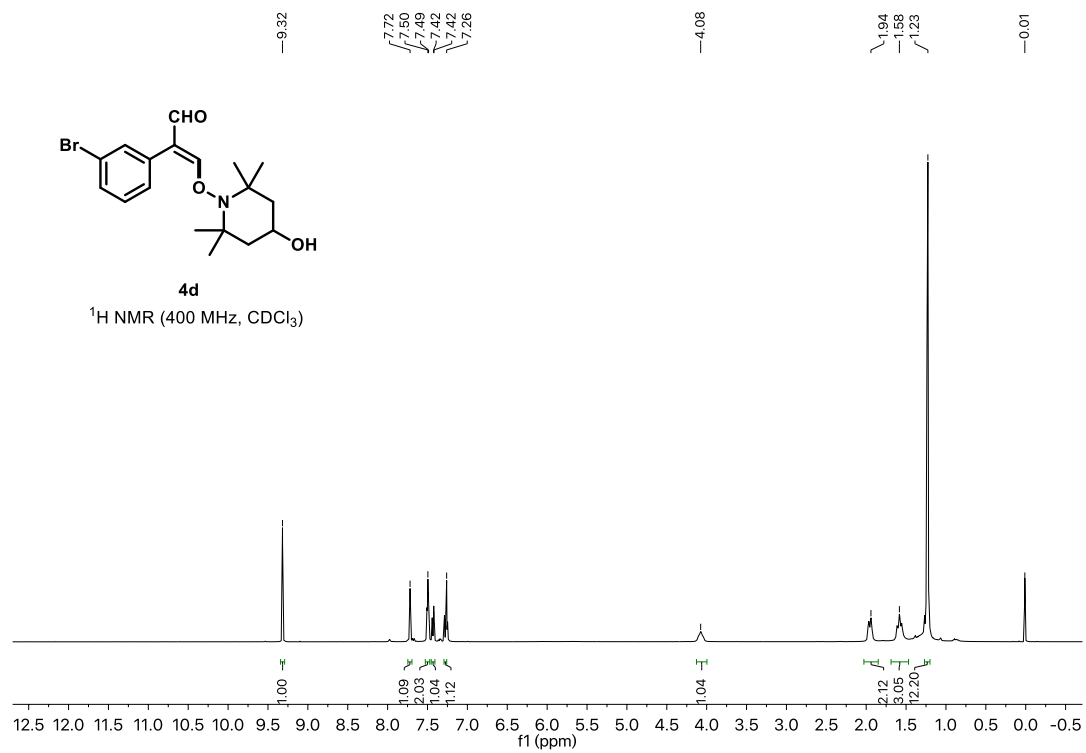
$^{13}\text{C NMR}$ (100 MHz, CDCl_3)

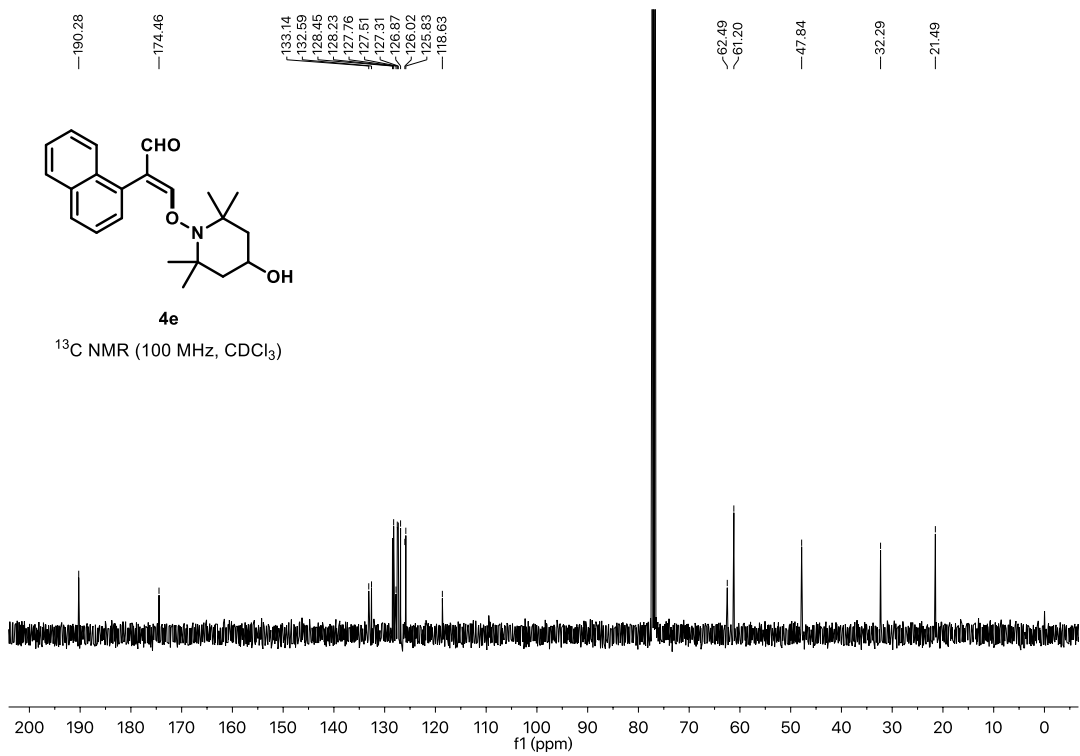
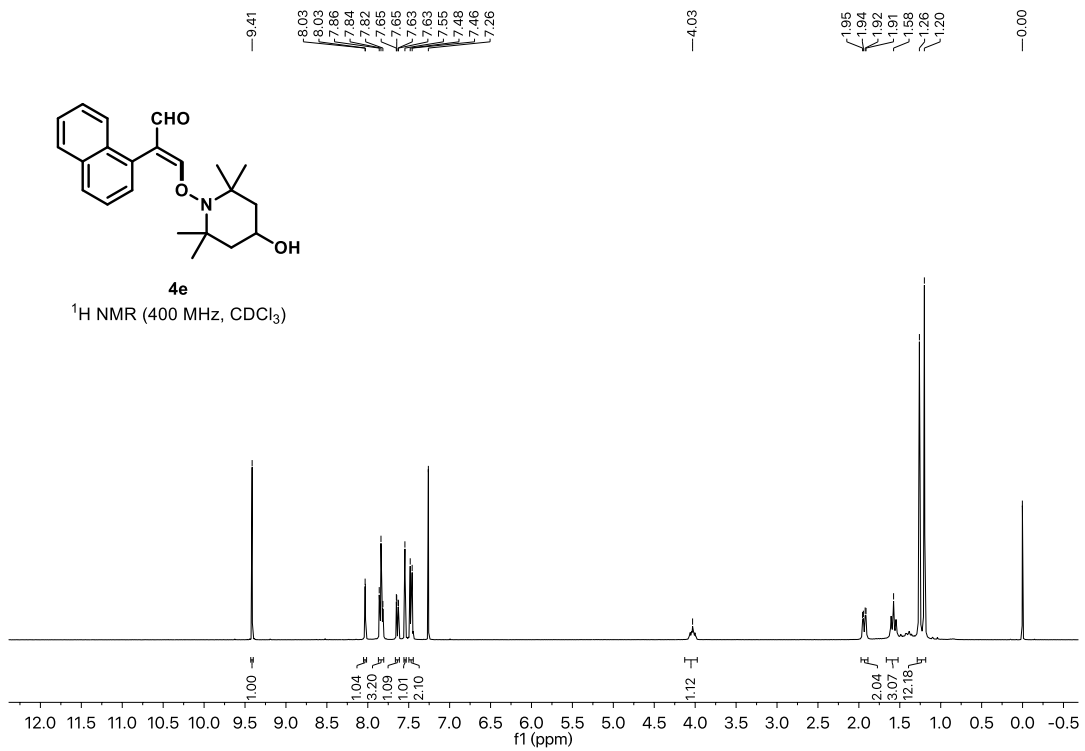


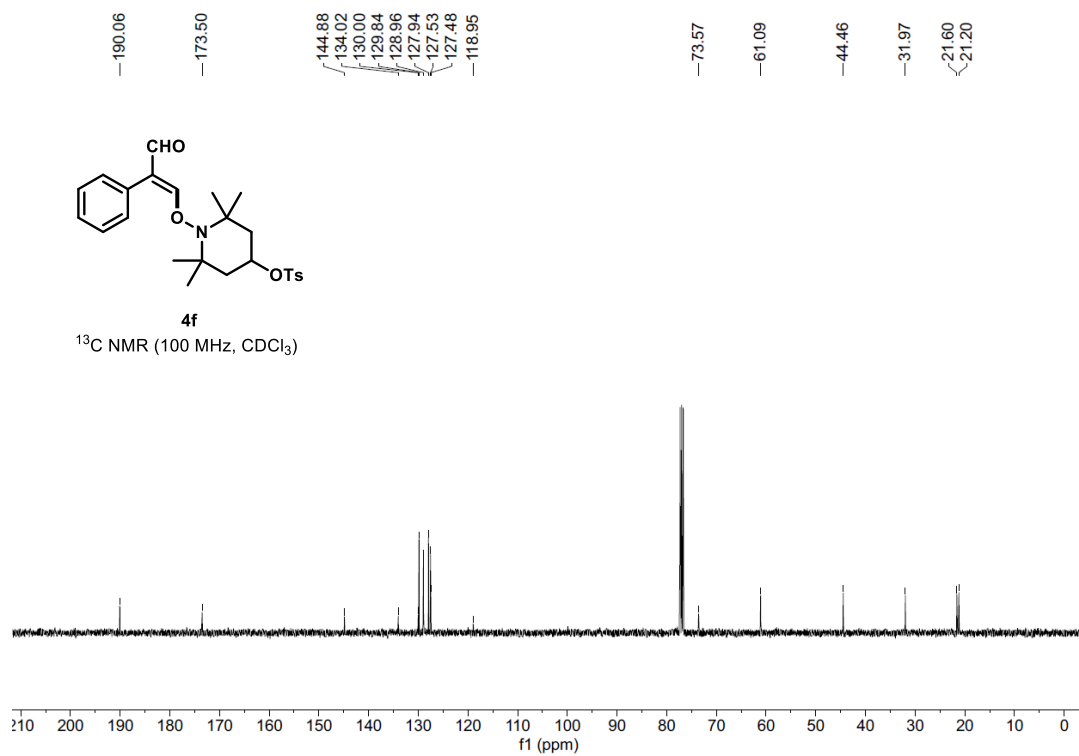
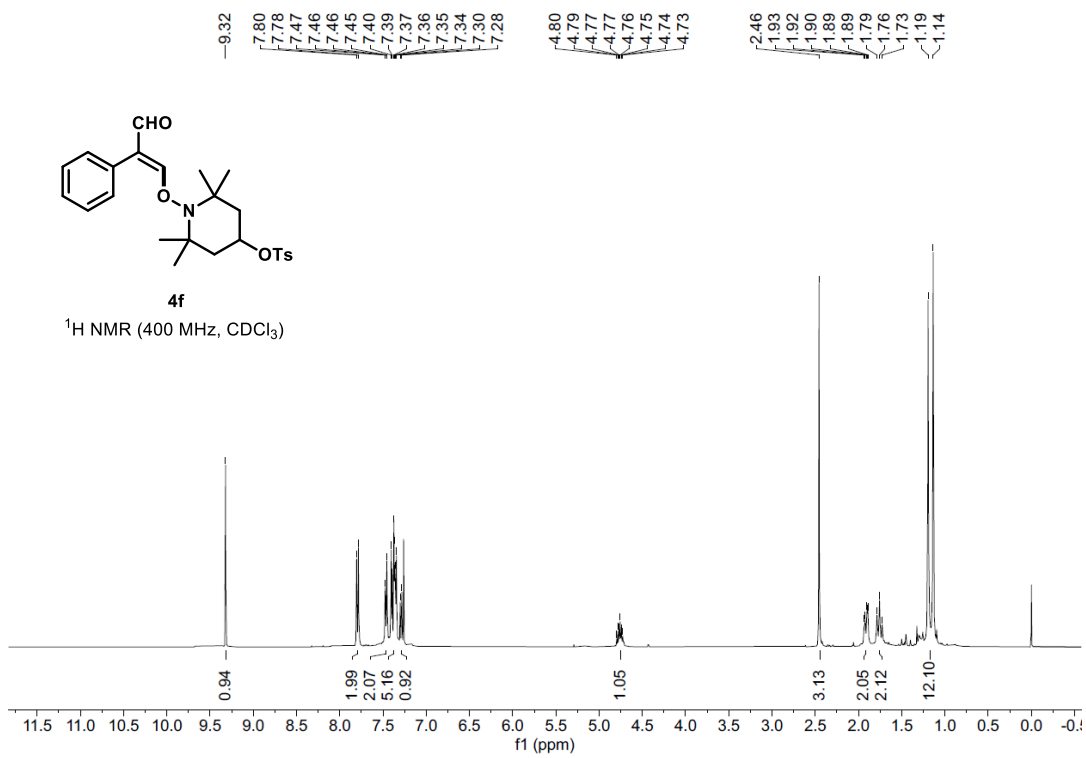


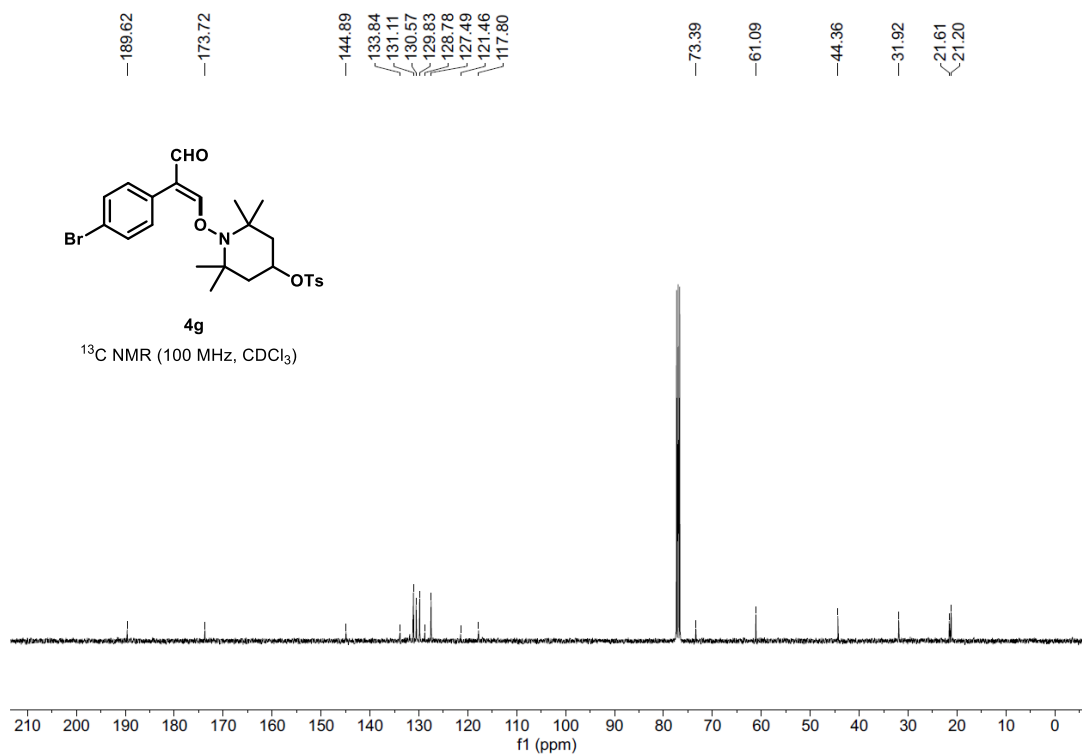
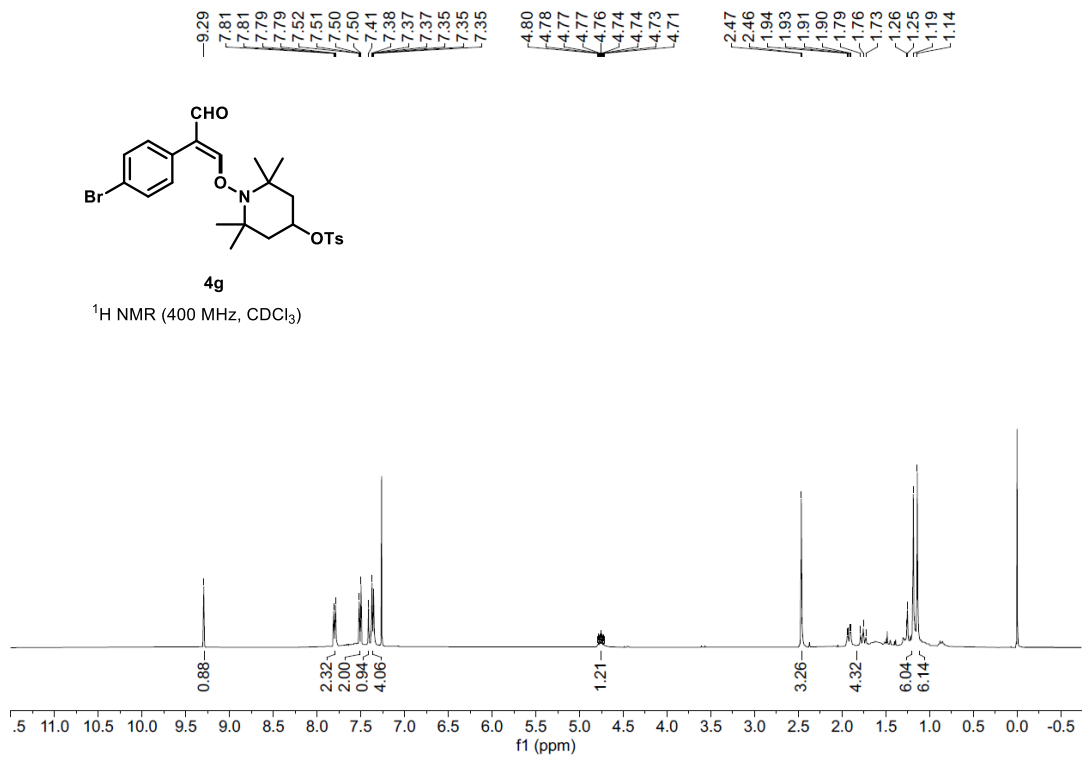


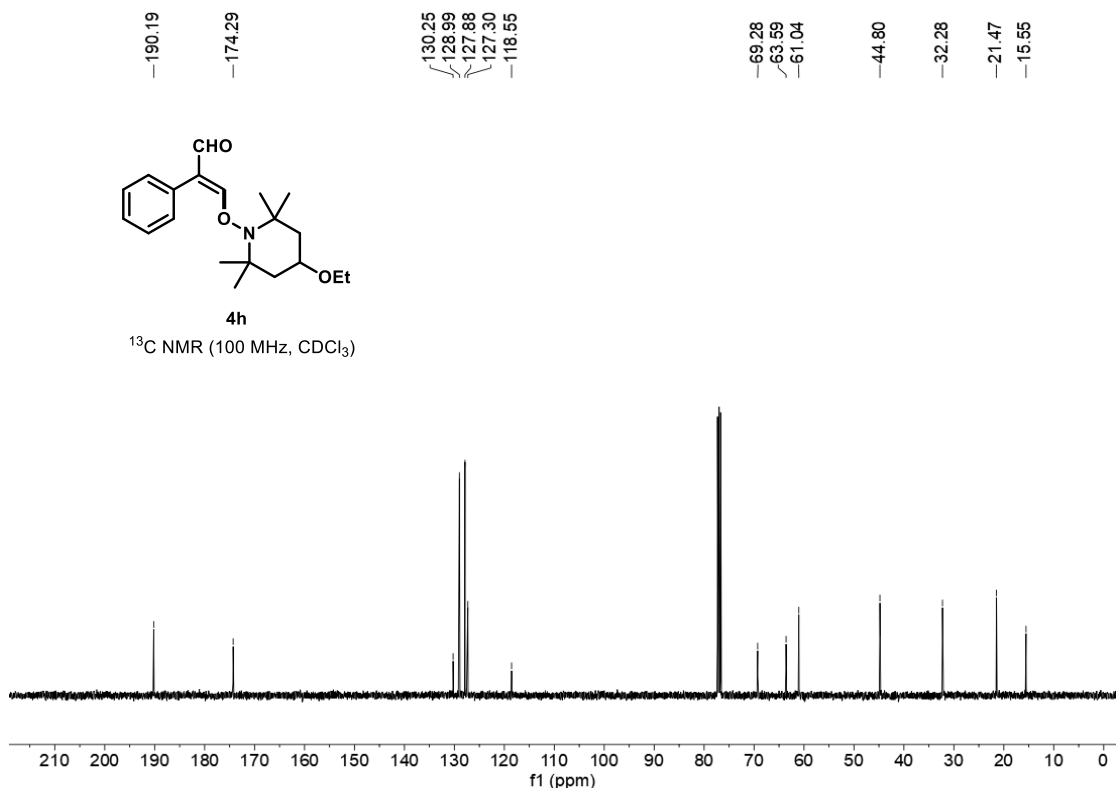
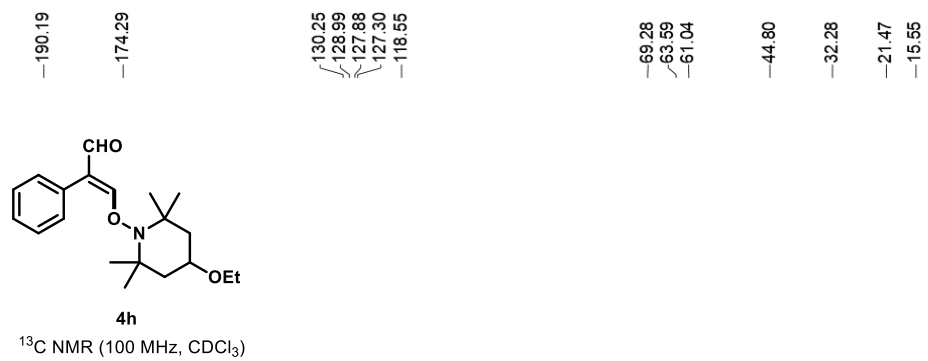
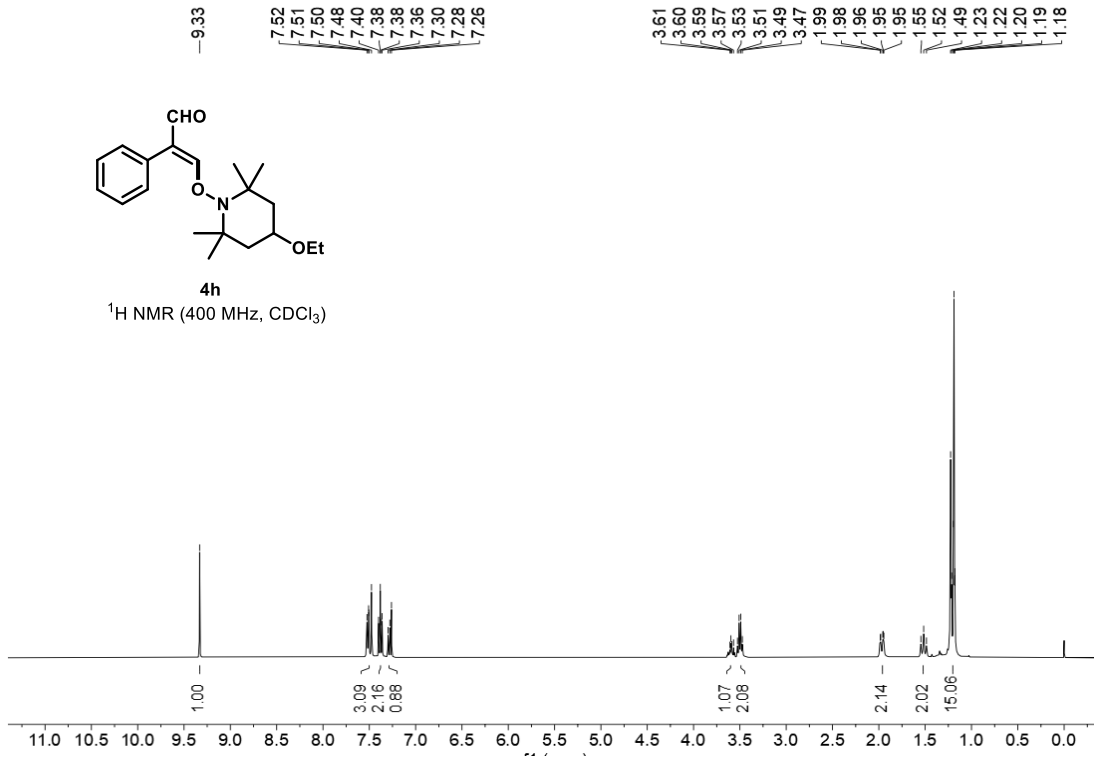
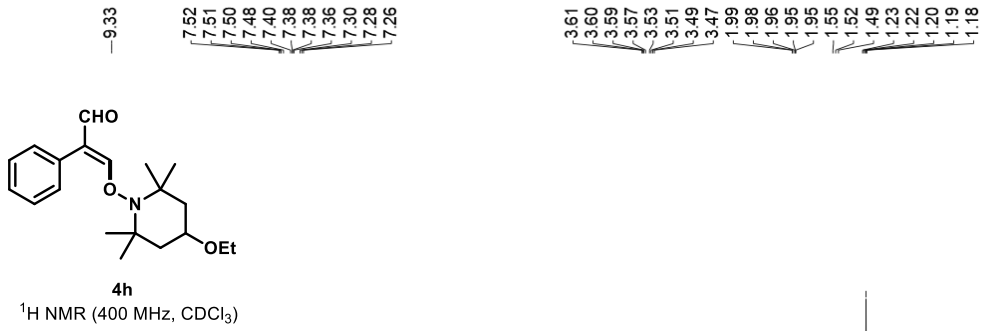


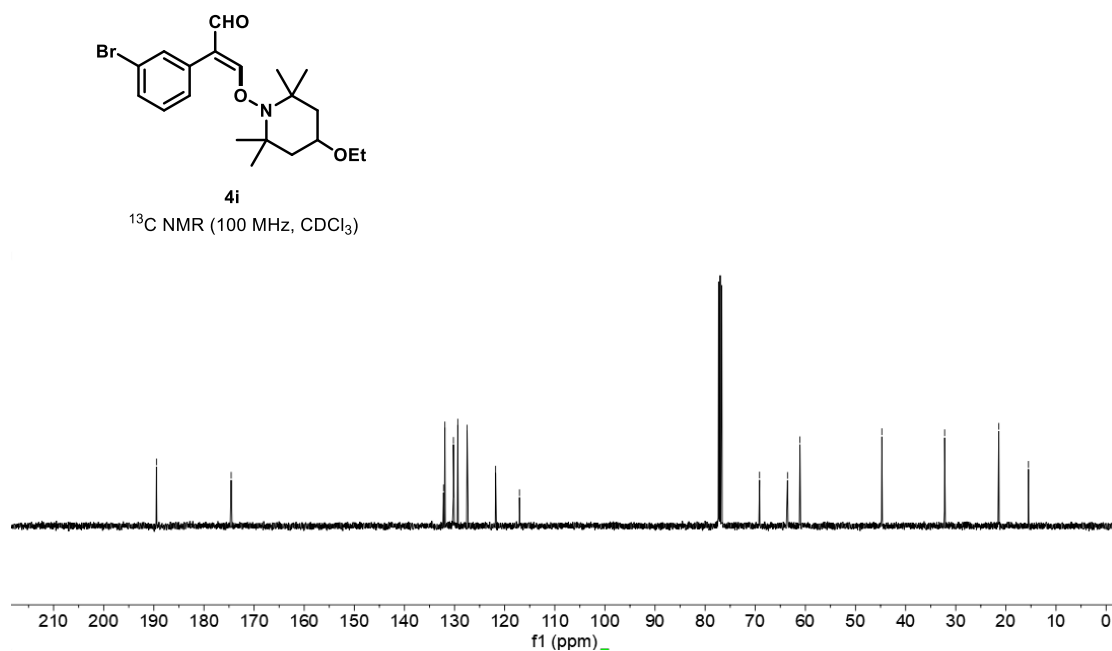
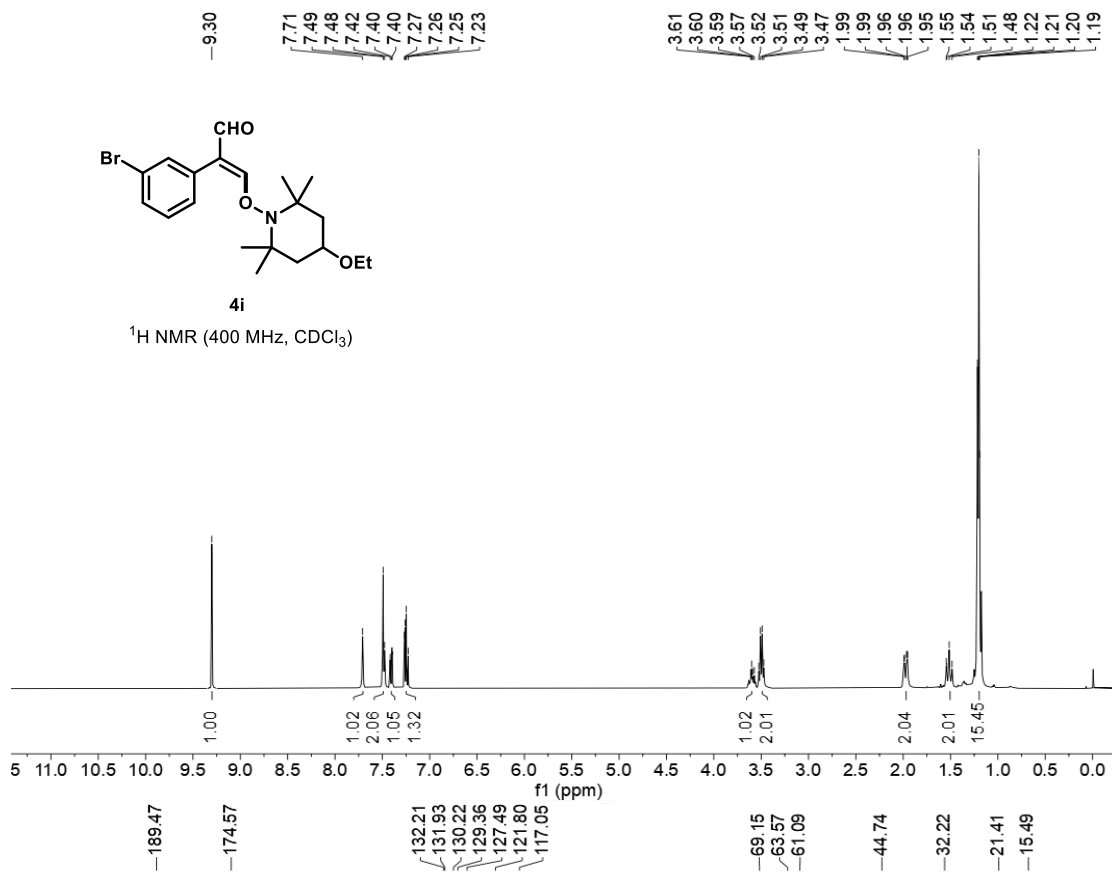


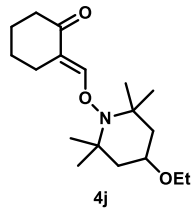




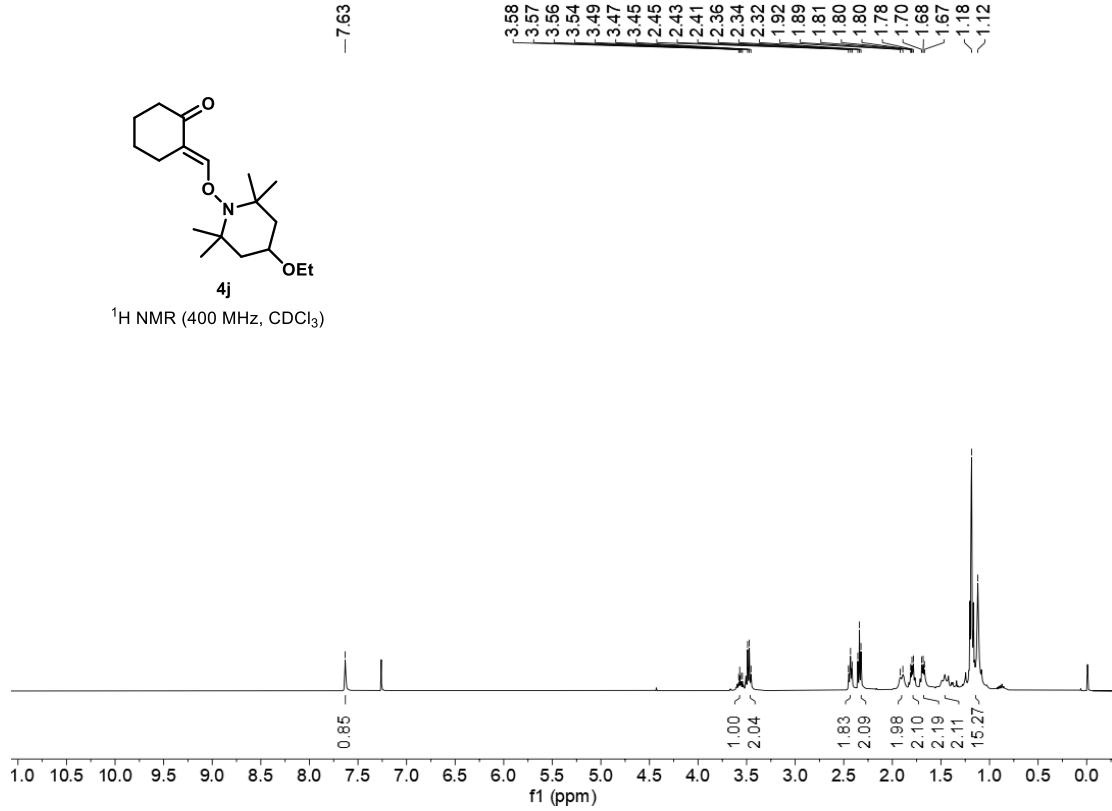




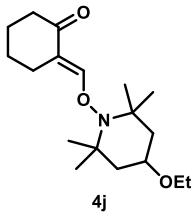




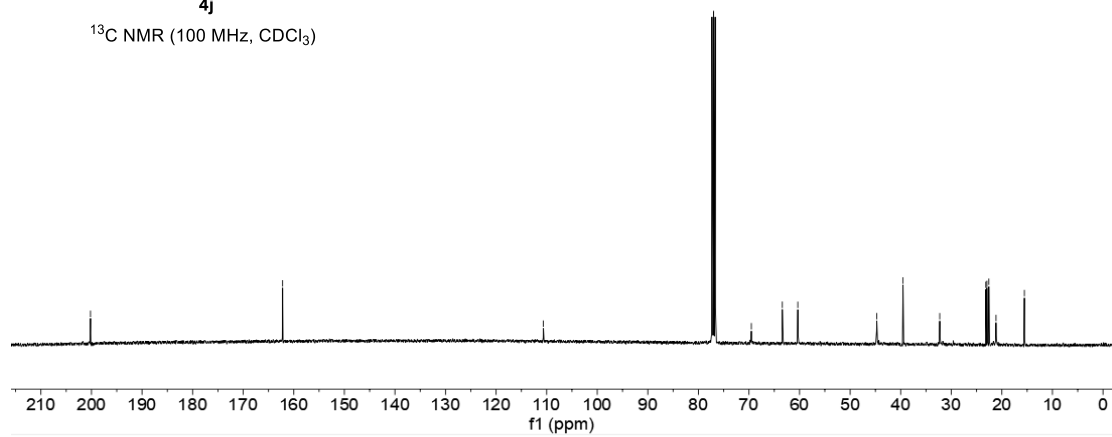
¹H NMR (400 MHz, CDCl₃)



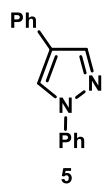
Chemical shift values (ppm): 200.20, 162.21, 110.65, 69.53, 63.41, 60.35, 44.73, 39.54, 32.28, 23.17, 22.95, 22.58, 21.16, 15.55.



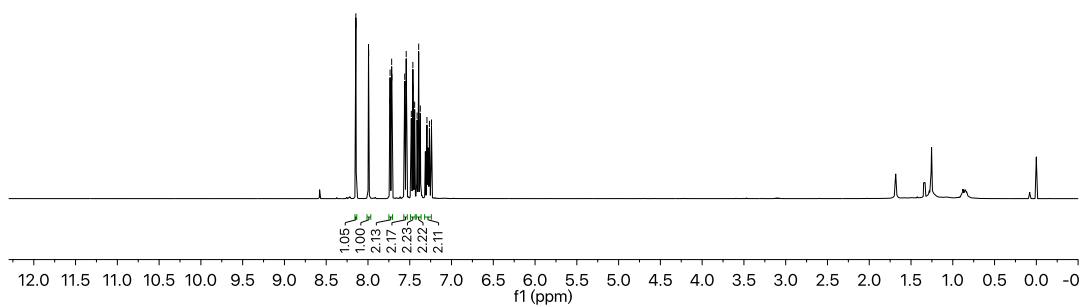
¹³C NMR (100 MHz, CDCl₃)



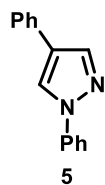
8.15
8.14
7.99
7.99
7.74
7.74
7.73
7.72
7.71
7.56
7.56
7.56
7.54
7.54
7.48
7.46
7.46
7.44
7.41
7.39
7.37
7.26
7.24



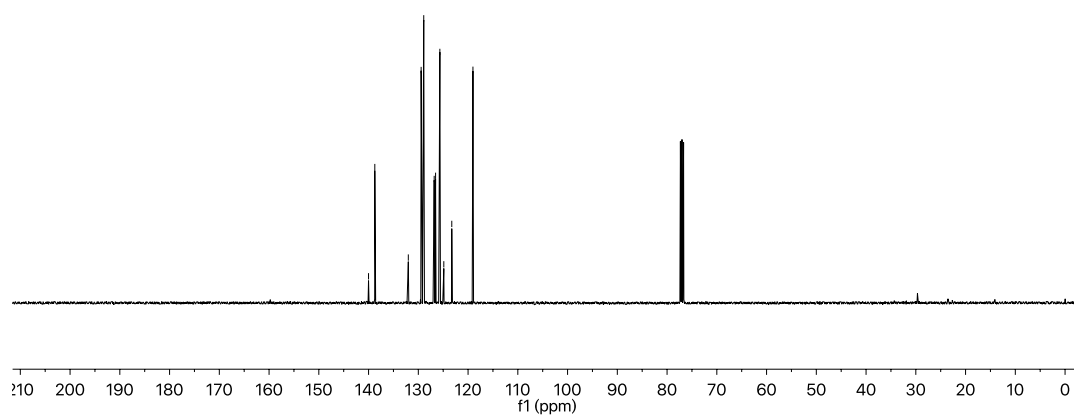
¹H NMR (400 MHz, CDCl₃)

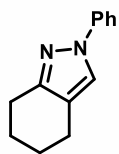


140.01
136.75
132.01
129.43
128.91
126.81
126.53
125.67
124.88
123.27
119.02



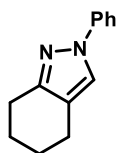
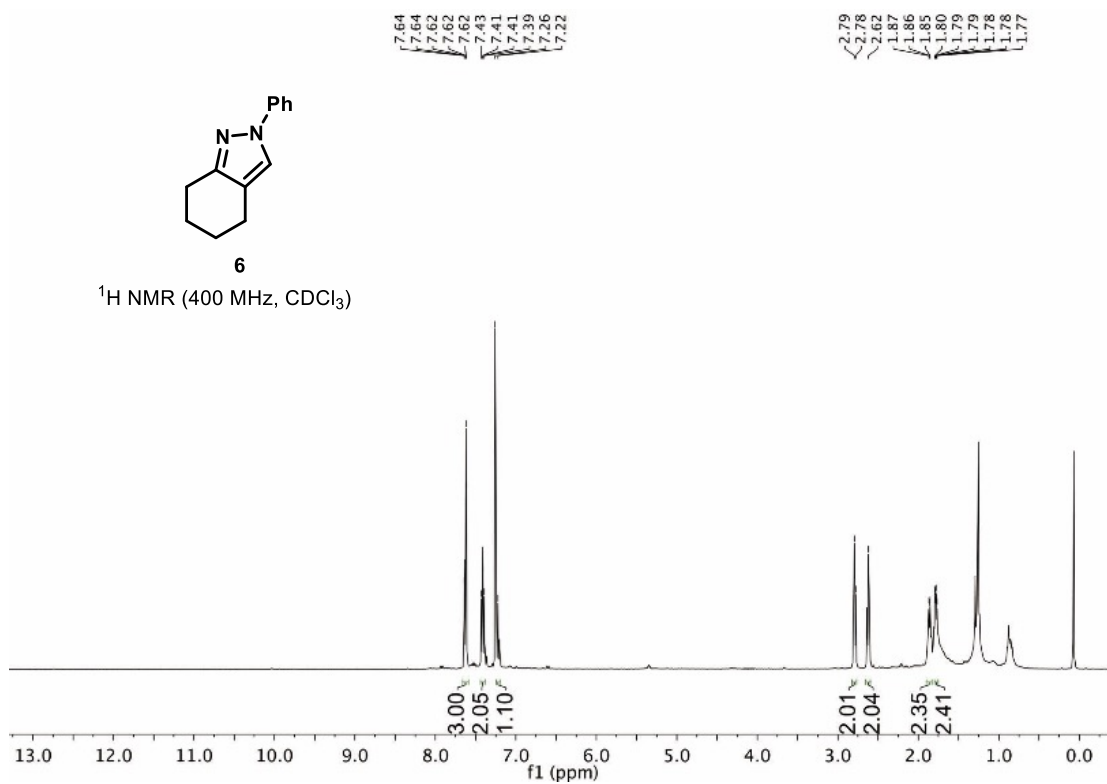
¹³C NMR (100 MHz, CDCl₃)





6

¹H NMR (400 MHz, CDCl₃)



6

¹³C NMR (100 MHz, CDCl₃)

