Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Visible Light-mediated Syntheses of Unsymmetrical Methylene-bridged *bis*-Heterocycles *via* an Alkoxy Radical Relay Reaction

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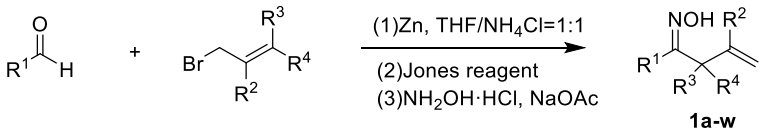
I. General Methods and Materials.

Unless otherwise specified, proton (^{1}H) and proton-decoupled carbon [^{13}C{^{1}H}] NMR spectra were recorded at room temperature in base-filtered $CDCl_3$ on a spectrometer operating at 500 MHz or 300 MHz for proton and 126 MHz or 75 MHz for carbon nuclei. For ^{1}H NMR spectra, signals arising from the residual protio-forms of the solvent were used as the internal standards. ^{1}H NMR data are recorded as follows: chemical shift (δ) [multiplicity, coupling constant(s) *J* (Hz), relative integral] where multiplicity is defined as: s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet or combinations of the above. The signal due to residual $CHCl_3$ appearing at δ_H 7.26 and the central resonance of the $CDCl_3$ "triplet" appearing at δ_C 77.0 were used to reference ^{1}H and ^{13}C{^{1}H} NMR spectra, respectively. Infrared spectra were recorded, as thin films or solids, on a Nicolet iS50 FT-IR spectrometer fitted with a Smart iTX sampling module and only major absorptions are reported (in cm^{-1}). High-resolution ESI mass spectra were recorded on a time-of-flight instrument. Melting points were measured on an automated melting point system and are uncorrected. Analytical thin layer chromatography (TLC) was performed with silica gel GF_{254} plates. Eluted plates were visualized using a 254 nm UV lamp and/or by treatment with a suitable dip followed by heating. These dips included phosphomolybdic acid: ceric sulfate: sulfuric acid (conc.): water (37.5 g : 7.5 g : 37.5 g : 720 mL) or potassium permanganate : potassium carbonate : 5% sodium hydroxide aqueous solution : water (3 g : 20 g: 5 mL : 300 mL). For column chromatography, 200-300 mesh silica gel was employed. Reagents and inorganic salts as well as dried solvents were generally available from commercial sources and used as supplied. Unless indicated otherwise, reactions were performed under a nitrogen atmosphere.

II. Procedures for the Synthesis of Substrates 1a-1w and 2a-2r

General procedure for the synthesis of *β,γ*-unsaturated oximes 1a-w



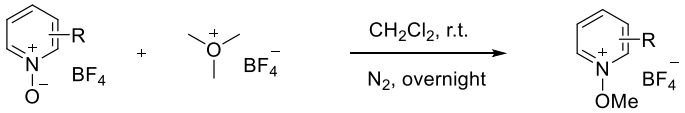
(1) In a slight modification of a literature procedure,[1] the relevant allyl bromide (20 mmol, 2.0 equiv.) was added to a magnetically stirred solution of the relevant aldehyde (10 mmol, 1.0 equiv.) in anhydrous THF (40 mL) followed by addition of saturated aqueous NH_4Cl (40 mL). Portions of activated zinc dust (20 mmol, 2.0 equiv.) were then added slowly while the reaction mixture was maintained at 0 °C. The ensuing mixture was warmed to room temperature and stirred overnight. Thereafter, the THF layer was separated from the aqueous one which was extracted with diethyl ether (3 × 50 mL). The combined organic phases were washed with water (1 × 50 mL) and brine (1 × 50 mL) before being dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue thus obtained was used without purification in the next step.

(2) Jones reagent (2.0-4.0 equiv.) was added dropwise to a magnetically stirred solution of the relevant crude homoallylic alcohol (1.0 equiv.) in diethyl ether (0.1 M) maintained at 0 °C. The ensuing mixture was warmed to room temperature and then stirred for 1 h before being quenched with NH_4Cl (30 mL of a saturated aqueous solution) and the ensuing mixture extracted with diethyl ether (3 × 50 mL). The combined organic phases were then washed with water (1 × 50 mL) and brine (1 × 50 mL) before being dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue thus obtained was used without purification in the next step.

(3) Sodium acetate (7.0 equiv.) was added to a magnetically stirred solution of the relevant hydroxylamine hydrochloride (5.0 equiv.) in ethanol (0.1 M) maintained at room temperature. An ethanolic solution of the relevant *β,γ*-unsaturated ketone (1.0 equiv.), obtained as described above, was then added to the reaction mixture which was stirred overnight before being concentrated under reduced pressure. The resulting mixture was extracted with ethyl acetate (3 × 50 mL) and the combined organic phases washed with water (1 × 50 mL) and brine (1 × 50 mL) before being dried (Na_2SO_4), filtered and

concentrated under reduced pressure. The residue thus obtained was purified by column chromatography (10:1 v/v petroleum ether/ethyl acetate elution) to afford the relevant *β*,*γ*-unsaturated oxime **1a**,[1] **1b**,[1] **1c**,[1] **1e**,[1] **1f**,[1] **1g**,[2] **1h**,[3] **1i**,[1] **1l**,[1] **1m**,[1] **1n**,[1] **1p**,[1] **1q**,[1] **1r**,[1] **1s**,[1] **1t**,[1] **1u**,[1] and **1w**.[1] The spectral data obtained on these *β*,*γ*-unsaturated oximes were in accord with the assigned structures and matched those reported in the literature.

General procedure for the synthesis of *N*-heteroarenium salts 2a-r

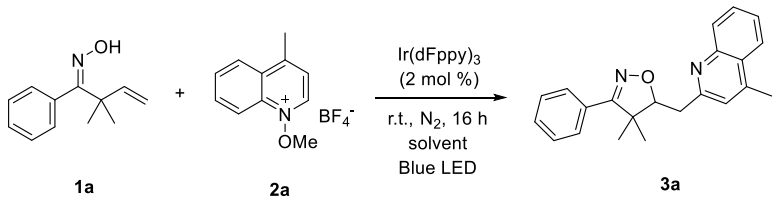


2a-r

Following a protocol reported by Hong,[4] a solution of the relevant pyridine *N*-oxide (5 mmol) and trimethyloxonium tetrafluoroborate (6 mmol, 1.2 equiv.) in CH_2Cl_2 (25 mL) was stirred for 16 h while being maintained at room temperature under a nitrogen atmosphere. The resulting mixture was concentrated under reduced pressure and the solid thus obtained was recrystallized (twice) from a mixture of CH_2Cl_2 (6 mL) and diethyl ether (60 mL) stored at –20 ºC. Compounds **2a**,[5] **2c**,[6] **2d**,[6] **2e**,[7] **2f**,[5] **2g**,[5] **2h**,[5] **2i**,[8] **2j**,[8] **2k**,[5] **2l**,[9] **2m**,[8] **2n**,[8] **2o**,[8] **2p**,[8] **2q**[10] and **2r**[9] were thus obtained and the spectral data obtained on each of them were in accord with the assigned structure and matched those reported in the literature.

III. Optimization of the Reaction Conditions

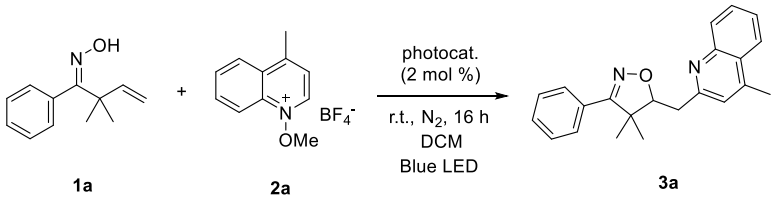
Table S1. Screening of solvents.[a]



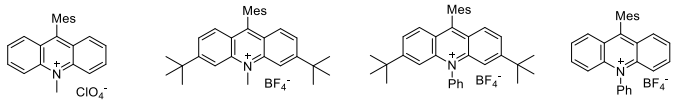
Entry	Solvent	Yield (%)[b]
1	MeCN	40
2	MeOH	0
3	DMSO	trace
4	DMF	0
5	Toluene	0
6	THF	trace
7	HFIP	0
8	1,2-DCE	48
9	DCM	49

[a] Reactions were performed using a mixture of **1a** (0.1 mmol), **2a** (0.2 mmol), in solvent (1.0 mL) at room temperature under irradiation with 40W Kessil blue LED (25% intensity, 456nm) for 16 h. [b] Yields of isolated products are given. HFIP = 1,1,1,3,3,3-Hexafluoro-2-propanol

Table S2. Screening of photocatalysts.[a]

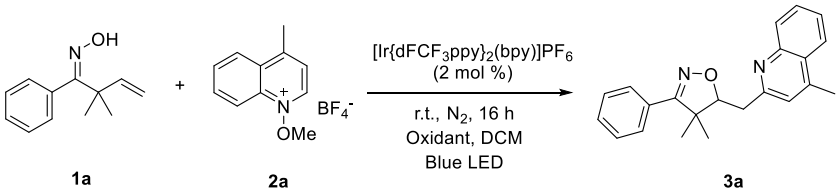


Entry	Photocatalyst	Yield (%)[b]
1	$Ir(dFppy)_3$	49
2	fac-$Ir(ppy)_3$	46
3	Eosin Y	48
4	P1	24
5	P2	52
6	P3	37
7	P4	36
8	DPA	50
9	1,4-Dicyanobenzene	49
10	$Ru(bpy)_3Cl_2.6H_2O$	50
11	$[Ru(bpz)_3][PF_6]_2$	52
12	$[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$	55
13[c]	$[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$	0
14[d]	—	0



[a] Reactions were performed using a mixture of **1a** (0.1 mmol), **2a** (0.2 mmol), in DCM (1.0 mL) at room temperature under irradiation with 40W Kessil blue LED (25% intensity, 456nm) for 16 h. [b] Yields of isolated products are given. [c] The reaction was carried out in the dark. [d] Without photocatalyst.

Table S3. Screening of oxidants.[a]

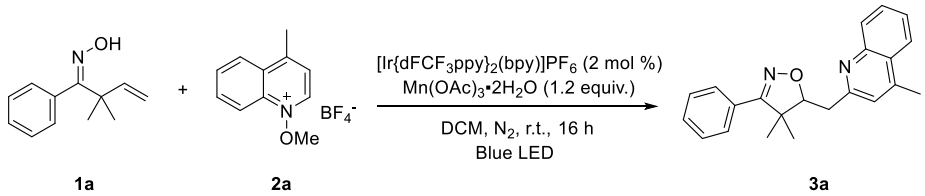


1a 2a 3a

Entry	Oxidant	Yield (%)[b]
1	—	55
2	$Cu(OTf)_2$	39
3	$Cu(OAc)_2$	64
4	$Cu(EH)_2$	65
5	$Cu(TMHD)_2$	63
6	Ag_2CO_3	68
7	$K_2S_2O_8$	51
8	$(NH_4)_2S_2O_8$	70
9	$PhI(OAc)_2$	47
10	TBHP	trace
11	BI-OH	73
12	$Mn(OAc)_3{\cdot}2H_2O$	83
13[c]	$Mn(OAc)_3{\cdot}2H_2O$	89

[a] Reactions were performed using a mixture of **1a** (0.1 mmol), **2a** (0.2 mmol), oxidant (0.12 mmol), in DCM (1.0 mL) at room temperature under irradiation with 40W Kessil blue LED (25% intensity, 456nm) for 16 h. [b] Yields of isolated products are given. [c] **2a** (0.25 mmol) was used.

Table S4. Screening of bases.[a]

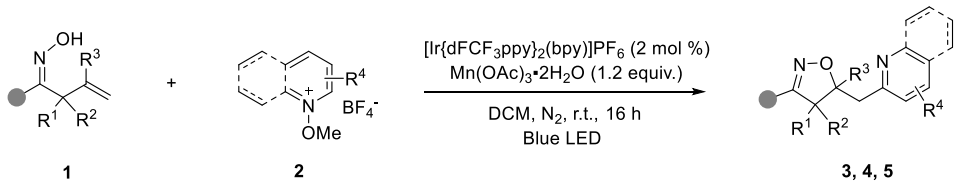


1a 2a 3a

Entry	Base	Yield (%)[b]
1	—	89
2	$NaHCO_3$	54
3	NaOAc	59
4	K_2CO_3	61
5	Cs_2CO_3	58
6	K_3PO_4	53
7	NEt_3	39

[a] Reactions were performed using a mixture of **1a** (0.1 mmol), **2a** (0.25 mmol), oxidant (0.12 mmol), in DCM (1.0 mL) at room temperature under irradiation with 40W Kessil blue LED (25% intensity, 456nm) for 16 h. [b] Yields of isolated products are given.

IV. General Procedure for the Synthesis of Compounds 3a-w, 4a-g and 5a-k

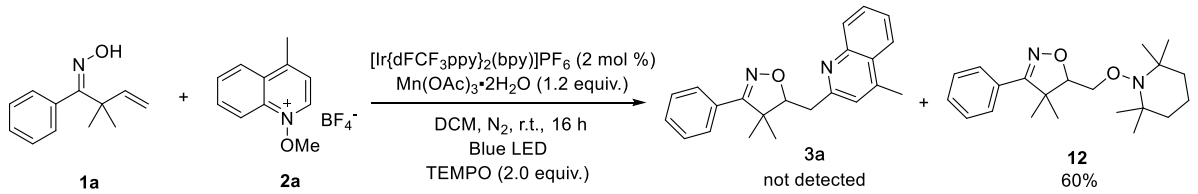


1 2 3, 4, 5

An oven-dried reaction tube equipped with a magnetic stirring bar was charged with the relevant *β,γ*-unsaturated oxime **1** (0.1 mmol), the relevant *N*-methoxyheteroarenium salt **2** (0.25 mmol), $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ (2.0 mg, 2 mol %), and $Mn(OAc)_3•2H_2O$ (32.2 mg, 0.12 mmol). The tube was evacuated and backfilled with nitrogen three times. DCM (1.0 mL) was then added to the reaction mixture *via* syringe and the resulting solution stirred at room temperature for 16 h while being irradiated, throughout this time, with two Kessil blue LED lamps (456 nm, 40 W, 25% intensity). The reaction mixture was then extracted with ethyl acetate (3 × 25 mL) and the combined organic phases washed with water (1 × 30 mL) and brine (1 × 30 mL) before being dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue thus obtained was purified by column chromatography (petroleum

ether/ethyl acetate elution) to afford the relevant product **3a-w**, **4a-g** and **5a-k.**

V. Radical Trapping Experiment Using TEMPO



An oven-dried reaction tube equipped with a magnetic stirring bar was charged with *β*,*γ*-unsaturated oxime **1a** (18.9 mg, 0.1 mmol), *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol), TEMPO (31.2 mg, 0.2 mmol), [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ (2 mg, 2 mol %) and Mn(OAc)$_3$•2H$_2$O (32.2 mg, 0.12 mmol). The tube was evacuated and backfilled with nitrogen three times. DCM (1.0 mL) was then added to the reaction mixture *via* syringe and the resulting solution stirred at room temperature for 16 h while being irradiated with two Kessil blue LED lamps (456 nm, 40 W, 25% intensity). The ensuing mixture was then extracted with ethyl acetate (3 × 25 mL) and the combined organic phases washed with water (1 × 30 mL) and brine (1 × 30 mL) before being dried (Na$_2$SO$_4$), filtered and concentrated under reduced pressure. The residue thus obtained was purified by column chromatography (6:1 v/v petroleum ether/ethyl acetate elution) to afford the TEMPO trapping product **12** (20.7 mg, 60%). No evidence for the formation of pyridine **3a** was obtained.

VI. Stern–Volmer Quenching Experiments

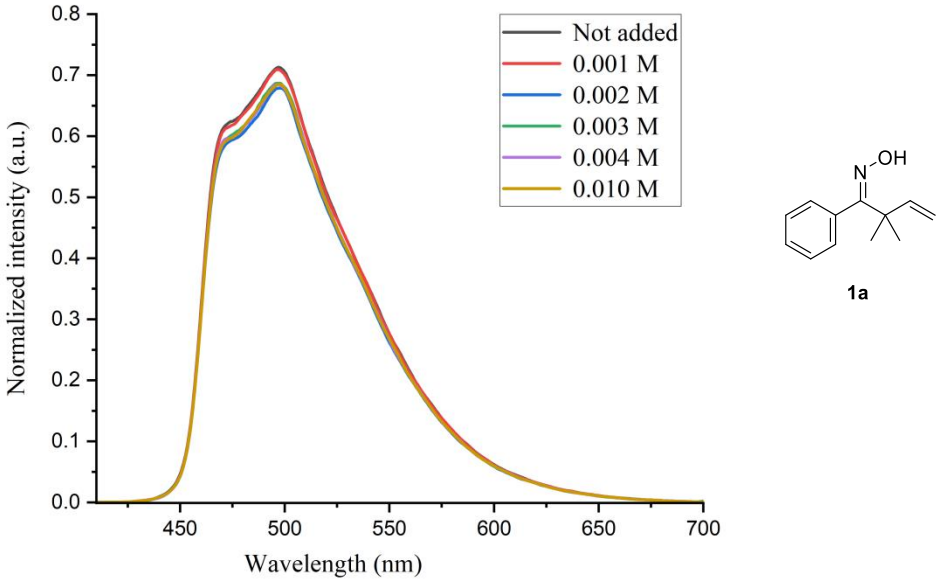


Figure S1. Quenching of the $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ emission (0.015 mM in DCM) in the presence of increasin g amounts of oxime (**1a**). Excitation wavelength : 380 nm, Bandwidth : Ex 3.0 nm, Em 3.0 nm.

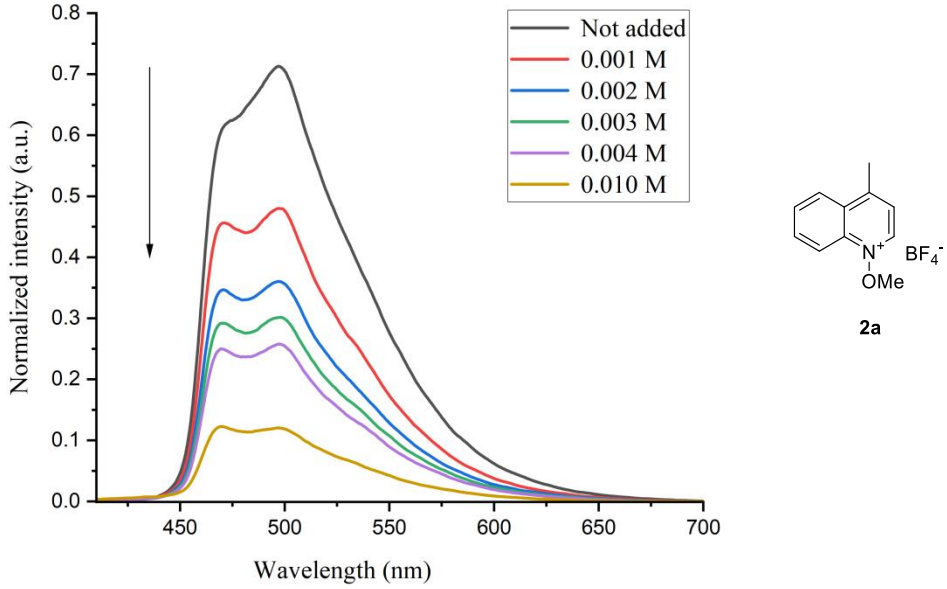


Figure S2. Quenching of the $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ emission (0.015 mM in DCM) in the presence of increasing amounts of N-methoxyquinolinium salt (**2a**). Excitation wavelength : 380 nm, Bandwidth : Ex 3.0 nm, Em 3.0 nm

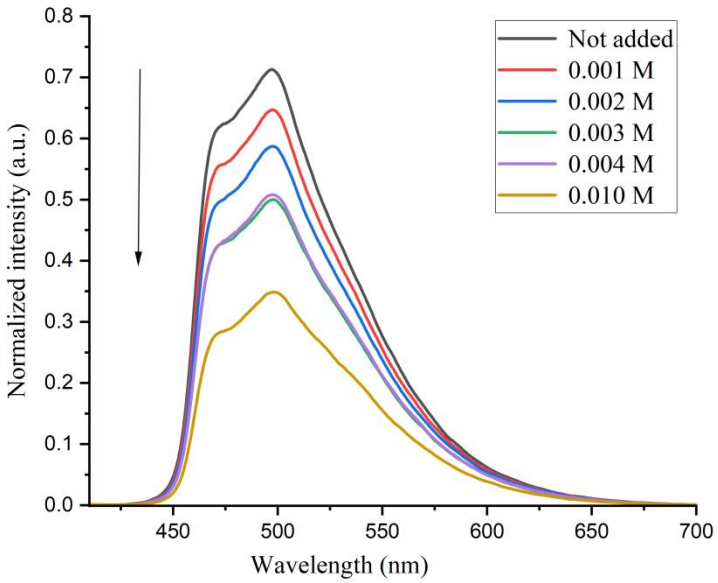


Figure S3. Quenching of the $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ emission (0.015 mM in DCM) in the presence of increasing amounts of $Mn(OAc)_3 \cdot 2H_2O$. Excitation wavelength : 380 nm, Bandwidth : Ex 3.0 nm, Em 3.0 nm

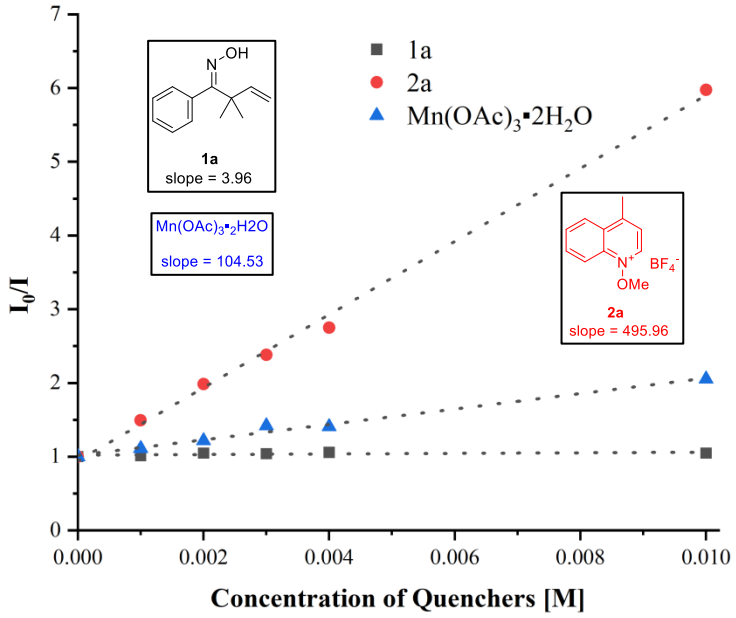


Figure S4. Stern–Volmer quenching plot of $[Ir(dF(CF_3)ppy)_2(bpy)]PF_6$ with **1a**, **2a**, and $Mn(OAc)_3 \cdot 2H_2O$

VII. Quantum Yield Measurements

Determination of the light intensity at 456 nm.

A Kessil LED lamp (λ_{max} = 456 nm) was used at 25% intensity for the measurement of quantum yield. So, following the procedure of Yoon,[11] the photon flux of the LED (λ_{max} = 456 nm) was determined by standard ferrioxalate actinometry. Specifically, a 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.737 g) in H_2SO_4 (10 mL of a 0.05 M solution) while a buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (5.0 mg) and sodium acetate (1.13 g) in H_2SO_4 (5.0 mL of a 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the LED, the ferrioxalate solution (2.0 mL) was placed in a cuvette and irradiated for 90 seconds at λ_{max} = 456 nm. After irradiation, the phenanthroline solution (0.35 mL) was added to the cuvette and the resulting mixture was allowed to stir in the dark for 1 h so as to permit the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the resulting solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq 1

	Non-irrad	Irrad 01	Irrad 02	Irrad 03
A_{510nm}	0.516	1.442	1.435	1.427
		Average $A_{510\,nm}$ of irradiation samples		1.435

$$\text{mol of } Fe^{2+} = \frac{V \cdot \Delta A_{510\,nm}}{l \cdot \epsilon} = \frac{(0.00235\ L) \cdot (0.919)}{(1.00\ cm) \cdot (11{,}100 \frac{L}{mol} \cdot cm)} = 1.95 \times 10^{-7}\ mol \quad (1)$$

V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.00 cm), and ε is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11,100 $Lmol^{-1}$ cm^{-1}).[12] The photon flux was calculated using eq 2:

$$Photon\ flux = \frac{mol\ of\ Fe^{2+}}{\emptyset \cdot t \cdot f} = \frac{1.95 \times 10^{-7} mol}{(0.84) \cdot (90\ s) \cdot (0.989)} = 2.61 \times 10^{-9}\ einstein/s \qquad (2)$$

where Φ is the quantum yield for the ferrioxalate actinometer (0.84 at λ = 456 nm)[13], t is the irradiation time (90 s), and f is the fraction of light absorbed at 456 nm by the ferrioxalate actinometer. This value is calculated using eq 3 where $A_{456\ nm}$ is the absorbance of the ferrioxalate solution at 456 nm. An absorption spectrum gave an $A_{456\ nm}$ value of 1.959, indicating that the fraction of absorbed light (f) is 0.989.

$$f = 1 - 10^{-A_{456\,nm}} \qquad (3)$$

The photon flux was thus calculated to be 2.61 × 10^{-9} Einsteins s^{-1} (average of three experiments).

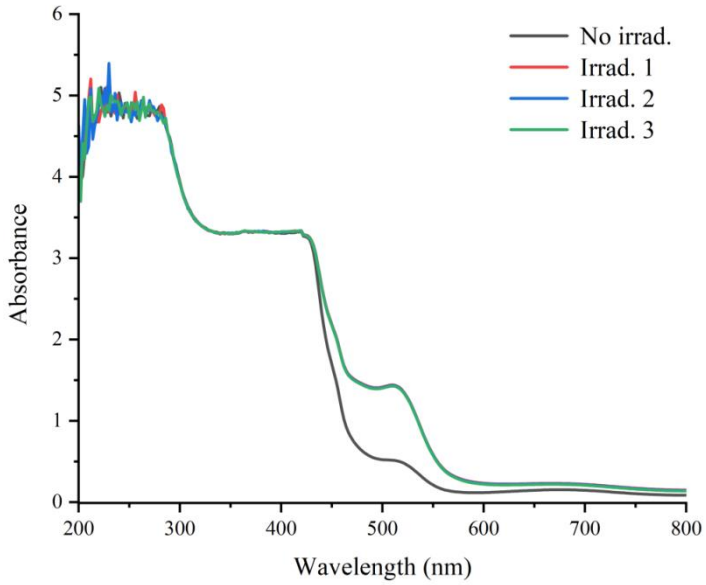


Figure S5. Absorption spectra of three irradiation experiments and non-irradiation experiment.

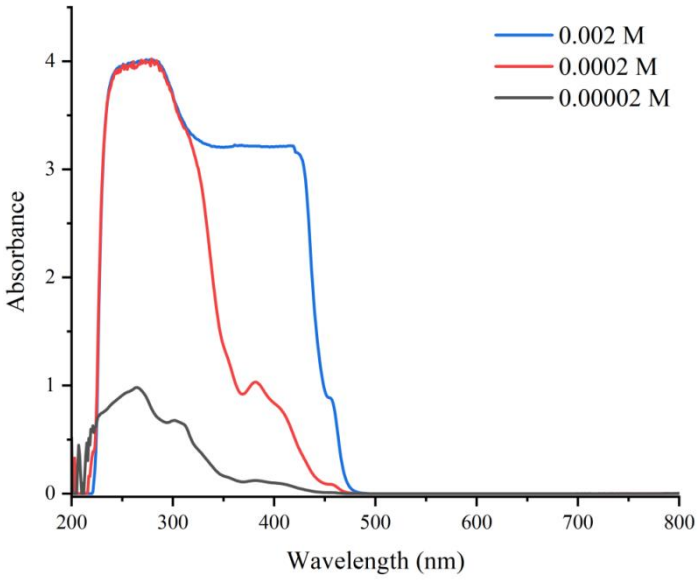
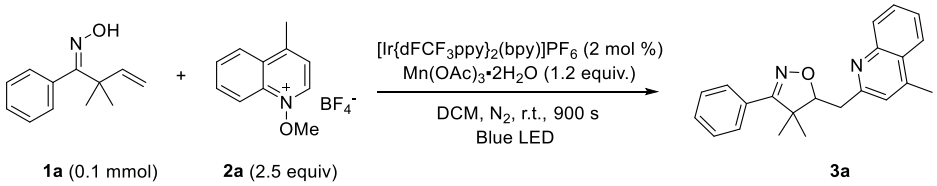


Figure S6. Absorption spectra of 0.002 M solution of [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ in DCM.

Determination of the reaction quantum yield.



The reaction mixture was stirred and irradiated by Kessil LED (λmax = 456 nm) for 900 s. The yield of product **3a** was determined, by ^{1}H NMR spectroscopic analysis using dibromomethane as an internal standard, to be 18% (0.036×10^{-3} mol of **3a**). The reaction quantum yield (Φ) was determined using eq 4 where the photon flux is 2.61×10^{-9} Einsteins s^{-1} (determined by actinometry as described above), t is the reaction time (900 s) and f is the fraction of incident light absorbed by the catalyst, determined using eq 3. An absorption spectrum of the catalyst (0.002 M) gave an absorbance value of 0.881 at 456 nm (Figure S6), indicating that the fraction of light absorbed by the photocatalyst (f) is 0.8685.

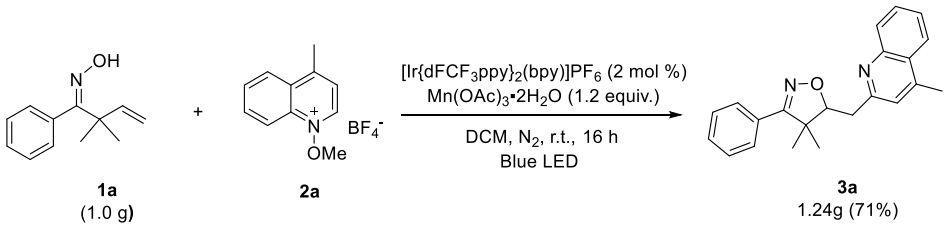
$$\Phi = \frac{mol\ of\ product}{flux \cdot t \cdot f} \qquad (4)$$

$$\Phi = \frac{0.036 \times 10^{-3}\ mol}{2.61 \times 10^{-9}\ einstein\ s^{-1} \cdot 900\ s \cdot 0.8685} = 17.7$$

The reaction quantum yield (Φ) was calculated to be 17.7

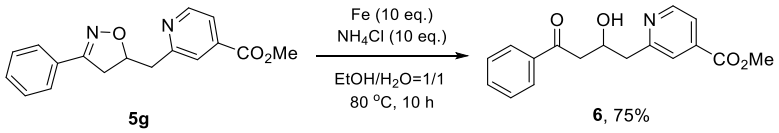
VIII. Synthetic Applications

Gram-scale reaction



An oven-dried reaction tube equipped with a magnetic stirring bar was charged with the *β*,*γ*-unsaturated oxime **1a** (1.00 g), *N*-methoxyquinolinium salt **2a** (3.45 g), $[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$ (106 mg, 2 mol %) and $Mn(OAc)_3•2H_2O$ (1.70 g, 1.2 equiv.). The tube was evacuated and backfilled with nitrogen three times. DCM (50 mL) was then added to the reaction mixture via syringe and the resulting solution stirred at room temperature for 16 h while being irradiated by two Kessil blue LEDs (456 nm, 40 W, 25% intensity). The resulting mixture was then extracted with ethyl acetate (3 × 50 mL) and the combined organic phases washed with water (1 × 50 mL) and brine (1 × 50 mL) before being dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue thus obtained was purified by column chromatography (3:1 v/v petroleum ether/ethyl acetate elution) to afford product **3a** (1.24 g, 71%) as a yellow solid.

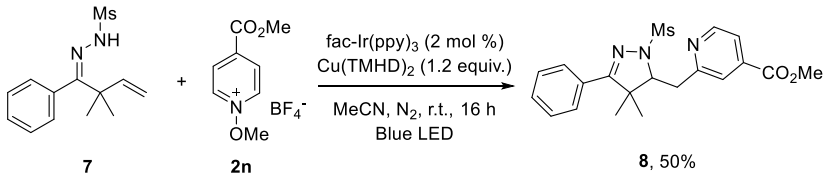
Reductive cleavage of dihydroisoxazole 5g[14]



A reaction flask equipped with a magnetic stirring bar was charged with methyl 2-((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)isonicotinate (**5g**) (88.8 mg, 0.3 mmol), NH_4Cl (161 mg, 3 mmol, 10 equiv.) and Fe powder (168 mg, 3 mmol). Ethanol/water (1:1 v/v 15 mL) was then added into the reaction and the resulting mixture stirred at 80 °C for 10 h. The cooled reaction mixture was then diluted with ethyl acetate and filtered through a silica pad. The filtrate was extracted with ethyl acetate (3 × 25 mL) and the combined organic phases were washed with water (1 × 30 mL) and brine (1 × 30 mL) before being dried (Na_2SO_4),

filtered and concentrated under reduced pressure. The residue thus obtained was purified by column chromatography (2:1 v/v petroleum ether/ethyl acetate elution) to afford *β*-hydroxyketone **6** (67 mg, 75%) as a clear, light-yellow oil.

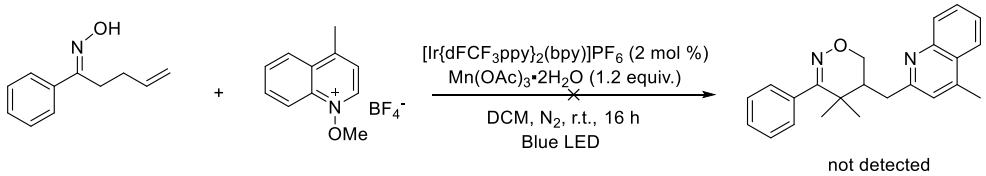
Synthesis of pyridylated 4,5-dihydropyrazole 8



7 **2n** **8**, 50%

An oven-dried reaction tube equipped with a magnetic stirring bar was charged with *β*,*γ*-unsaturated hydrazine **7**[15] (26.6 mg, 0.1 mmol), *N*-methoxyheteroarenium salt **2n** (63.8 mg, 0.25 mmol), *fac*-Ir(ppy)$_3$ (1.3 mg, 2 mol %), and Cu(TMHD)$_2$ (51.6 mg, 0.12 mmol). The tube was evacuated and backfilled with nitrogen three times. Thereafter, MeCN (1.0 mL) was added to the reaction mixture via syringe and the resulting solution stirred at room temperature for 16 h whilst being irradiated with two Kessil blue LEDs (456 nm, 40 W, 25% intensity). The reaction mixture was then extracted with ethyl acetate (3 × 25 mL) and the combined organic phases washed with water (1 × 30 mL) and brine (1 × 30 mL) before being dried (Na_2SO_4), filtered and concentrated under reduced pressure. The residue thus obtained was purified by column chromatography (3:1 v/v petroleum ether/ethyl acetate elution) to afford the pyridylated 4,5-dihydropyrazole **8** (20.1 mg, 50%) as a clear, light-yellow oil.

Attempted synthesis of a 6-exo-trig cyclisation product



not detected

An oven-dried reaction tube equipped with a magnetic stirring bar was charged with the relevant *γ*,*δ*-unsaturated oxime (17.5 mg, 0.1 mmol), the relevant *N*-methoxyheteroarenium salt **2** (65.3 mg, 0.25 mmol), [Ir{dFCF$_3$ppy}$_2$(bpy)]PF$_6$ (2.0 mg, 2 mol %) and Mn(OAc)$_3$•2H$_2$O (32.2 mg, 0.12 mmol). The tube was evacuated and backfilled with nitrogen three times. DCM (1.0 mL) was then added to the reaction mixture *via* syringe and the

resulting solution stirred at room temperature for 16 h whilst being irradiated by two Kessil blue LEDs (456 nm, 40 W, 25% intensity). Spectroscopic and chromatographic analysis of the reaction mixture obtained after work-up yielded no evidence for the formation of a 6-*exo*-trig-derived cyclisation product.

IX. Computational Studies

Theoretical Procedures

Geometries of all reactants and transition states were identified and located using density functional theory (wB97XD/6-31G(d,p))[16,17] implemented in Gaussian 16.[18] SMD[19] was used to treat effects of solvents during the mechanistic study. Electronic energies of all species were then improved by increasing the basis set size to a triple zeta basis set (def2TZVPD).[20] The global minima of reactants were identified using a systematic search. All transition states were confirmed through IRC calculations using the Hessian-based Predictor-Corrector (HPC) algorithm. Gibbs free energies of all species in dichloromethane were determined at 298.15 K using the direct method[21] in which ideal gas partition functions are applied directly to solution-phase geometries and frequencies; the resulting Gibbs free energies were then corrected to a standard state of 1M. To investigate the excited states of the [Ir^{III}] complex, TDDFT calculations (10 roots) for singlet and triplet excitations separately were performed at the same functional (wB97XD) used for investigation of the reaction mechanism above. Note that the def2SVPD[5] basis set was used for Ir during the geometrical optimizations and subsequently def2TZVPD[5] was employed for single point energy and TDDFT calculations. The orbital character of the calculated photochemical transitions was manually assigned by projecting canonical orbitals into Natural Transition Orbitals[22] (NTOs).

The Gibbs free energy barrier for the Outer Single Electron Transfer (OSET) reaction was calculated using Marcus theory as formulated in the following equation:[23-26]

$$\Delta G^{\ddagger}_{OSET} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{o}_{OSET}}{\lambda}\right)^{2} \qquad \text{(eq. 1)}$$

where ΔG^{o}_{OSET} is the Gibbs free energy of the OSET reaction, λ is the total reorganization energy. The reorganization energy (λ) is approximately determined by averaging the self-exchange reorganization energy of individual reactants in the OSET reactions[27,28] as

given in Scheme S1 below.

$$A + B \xrightarrow{\lambda} A^{\bullet+} + B^{\bullet-} \qquad (r.1)$$

$$A + A^{\bullet+} \xrightarrow{\lambda_{11}} A^{\bullet+} + A \qquad (r.2)$$

$$B^{\bullet-} + B \xrightarrow{\lambda_{22}} B + B^{\bullet-} \qquad (r.3)$$

Scheme S1. Self-exchange reactions of individual reactants in a general OSET reaction.

The total reorganization energy (λ) is approximated as follows:

$$\lambda = \frac{\lambda_{11}+\lambda_{22}}{2} \qquad \text{(eq. 2)}$$

In DFT calculations, individual reorganization energies (λ_{11} and λ_{22}) were calculated by subtracting the structurally optimized energy of the reactant (product) from unrelaxed energy of itself at the relaxed coordinate of the corresponding product (reactant) (Refer to Figure S7 for more details). In the general **Scheme S1**, unrelaxed energy of the product $A^{\bullet+}$ is the energy on the potential surface of $A^{\bullet+}$ calculated by using the optimized geometry of A; unrelaxed energy of the product $B^{\bullet-}$ is the energy on the potential surface of $B^{\bullet-}$ calculated using the optimized geometry of B. Similarly, the same procedure is applied for all other species involved in an OSET reaction. The reader is referred to refs 26-28 for further details. Note that to take into account of the effects of solvent on the reorganization energy, non-equilibrium parts of the implicit solvent (the slow/inertial charges) obtained from the optimized energy calculations were used in the corresponding unrelaxed energy calculations followed by an external iteration procedure.

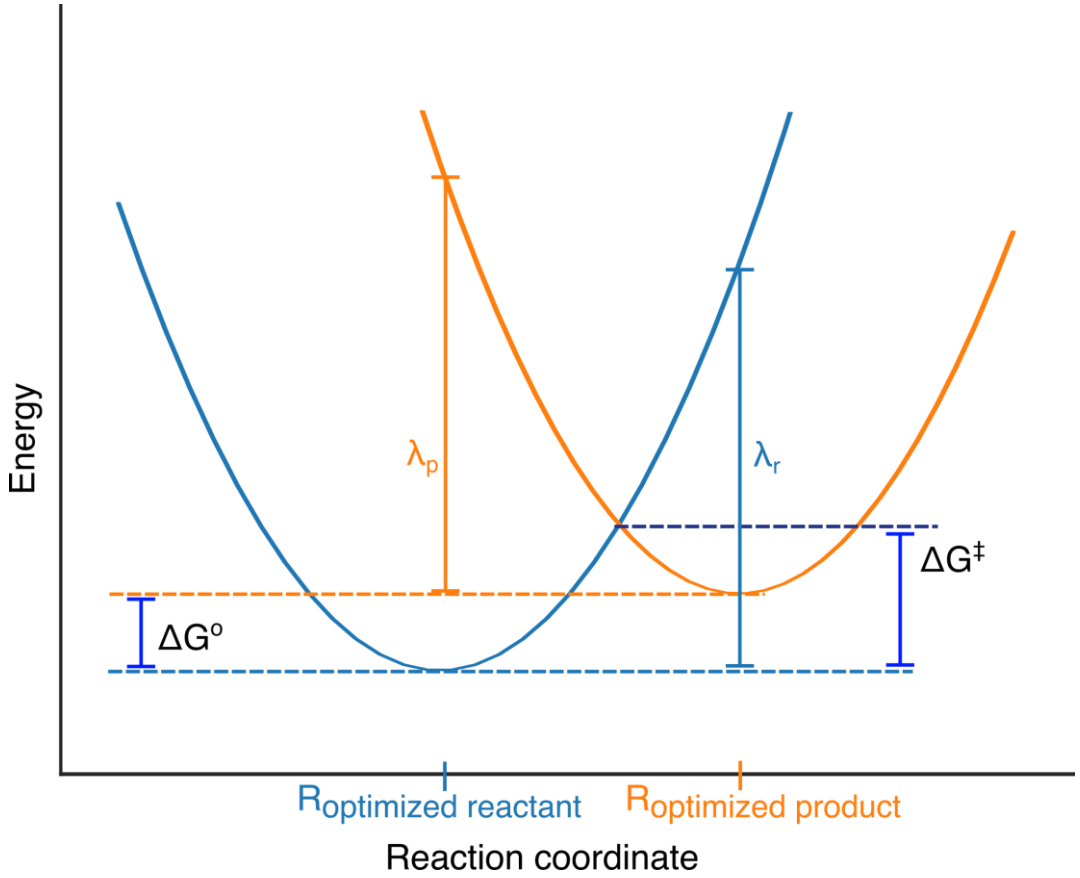


Figure S7. Energy potential curves of the reactant and product of a self-exchange reaction described in Marcus theory. OSET activation barrier ($\Delta G^{\ddagger}$) is determined as the distance from the crossing point between two potential curves to the geometrically optimized energy of the reactant. Coordinates of geometrically optimized structures of the reactant and product are noted as $R_{optimised\ reactant}$ and $R_{optimised}$ product. λ_r (λ_p) is reorganization energy of the reactant (product).

In this work, three OSET reactions were studied: **(i)** the reaction between the T_1 excited state of the photoredox catalyst **[Ir^{III}]*** and substrate **2**; **(ii)** the reaction between the ground state of **[Ir^{IV}]** and the substrate **IV**; **(iii)** the reaction between the T_1 excited state of the photoredox catalyst **[Ir^{III}]*** and substrate **VI**. As an example, the self-exchange reactions of individual reactants of the first OSET reaction (i) were given as follows.

$$[Ir^{III}]^* + \mathbf{2}^+ \xrightarrow{\lambda} [Ir^{IV}] + \mathbf{2}^{\cdot} \qquad (i)$$

$$[Ir^{III}]^* + [Ir^{IV}] \xrightarrow{\lambda_{11}} [Ir^{IV}] + [Ir^{III}]^* \qquad (i.1)$$

$$\mathbf{2}^{\cdot} + \mathbf{2}^+ \xrightarrow{\lambda_{22}} \mathbf{2}^+ + \mathbf{2}^{\cdot} \qquad (i.2)$$

Scheme S2. Individual self-exchange reactions of the reactant **Ir$^{[III]*}$** and the substrate **2** illustrated as the initial SET reaction in **Scheme 4** of main text.

Table S5 Electronic energies and Gibbs free energies of the structurally optimized species, and their corresponding unrelaxed electronic energies in three OSET reactions (i, ii, and iii) mentioned above. Note that X_Y denotes the geometry of the species X taken from the optimized geometry of the species Y.[a]

Reaction	Optimized species	$\mathbf{2^+}$	$\mathbf{2^\bullet}$	$\mathbf{[Ir^{III}]^*}$	$\mathbf{[Ir^{IV}]}$
i	E_{elec} (kJ/mol)	-953634.5	-953933.9	-6901049.6	-6900716.4
	G (kJ/mol)	-953353.2	-953667.7	-6900033.4	-6899686.4
	Unrelaxed species	$\mathbf{2^+_{2^\bullet}}$	$\mathbf{2^\bullet_2}$	$\mathbf{[Ir^{III}]^*_{[Ir^{IV}]}}$	$\mathbf{[Ir^{IV}]_{[Ir^{III}]^*}}$
	E_{elec} (kJ/mol)	-953470.9	-953904.0	-6901038.1	-6900553.6
ii	Optimized species	$\mathbf{IV^{+\bullet}}$	$\mathbf{VII^{2+}}$	$\mathbf{[Ir^{IV}]}$	$\mathbf{[Ir^{III}]}$
	E_{elec} (kJ/mol)	-2517491.7	-2516954.2	-6900716.4	-6901322.3
	G (kJ/mol)	-2516630.2	-2516073.5	-6899686.4	-6900295.8
	Unrelaxed species	$\mathbf{IV^{+\bullet}_V}$	$\mathbf{VII^{2+}_{IV}}$	$\mathbf{[Ir^{IV}]_{[Ir^{III}]}}$	$\mathbf{[Ir^{III}]_{[Ir^{IV}]}}$
	E_{elec} (kJ/mol)	-2517395.8	-2516685.6	-6900573.9	-6901324.4
iii	Unrelaxed species	$\mathbf{VI^+}$	$\mathbf{V^\bullet}$	$\mathbf{[Ir^{III}]^*}$	$\mathbf{[Ir^{IV}]}$
	E_{elec} (kJ/mol)	-2516034.6	-2516326.6	-6901049.6	-6900716.4
	G (kJ/mol)	-2515197.4	-2515504.0	-6900033.4	-6899686.4
	Unrelaxed species	$\mathbf{VI^+_V}$	$\mathbf{V^\bullet_{VI}}$	$\mathbf{[Ir^{III}]^*_{[Ir^{IV}]}}$	$\mathbf{[Ir^{IV}]_{[Ir^{III}]^*}}$
	E_{elec} (kJ/mol)	-2515867.6	-2516108.3	-6901038.1	-6900553.6

[a] **VII** is the species formed immediately after **IV** donated one electron to $\mathbf{[Ir^{IV}]}$ via a SET; afterward the deprotonation will happen to form **VI** in **Scheme 4** of main text. **V** is the species formed after the deprotonation of **IV** right before the formation of **Product** in **Scheme 4** of main text; this species is also formed after **VI** receives one electron from $\mathbf{[Ir^{III}]^*}$ via a SET in **Scheme 4** of main text, and subsequently the product is formed.

Table S6 Reaction barriers $\Delta G^{\ddagger}_{OSET}$ of the three OSET reactions (i), (ii), and (iii) calculated using Eq. 1

Reaction	$\Delta G^{\ddagger}_{OSET}$ (kJ/mol)	λ (kJ/mol)	ΔG^{o}_{OSET} (kJ/mol)
i	63.6	183.7	32.4
ii	39.5	252.5	-52.7
iii	91.6	178.4	40.4

Table S7 Energy components (Hartree, 298.15K) used to calculate Gibbs free energies of all species in **Scheme 4** of main text.

Species	E[b]	E	ZPE	TC	TS	H	G
I	-115.06569	-115.01719	0.03692	0.00206	0.02687	-115.02482	-115.04866
1	-596.24806	-596.05176	0.24629	0.01287	0.05558	-595.98701	-596.03956
MeOH	-115.74183	-115.69133	0.05178	0.00236	0.02697	-115.68581	-115.70975

II	-595.60803	-595.41351	0.23446	0.01235	0.05464	-595.35934	-595.41094
rotated II	-595.60615	-595.41155	0.23442	0.01236	0.05496	-595.35749	-595.40941
III	-595.60391	-595.41173	0.23370	0.01195	0.05340	-595.35637	-595.40674
H^+	-0.19525	-0.195249	0.00000	0.00047	0.01236	-0.19289	-0.20222
Product	-843.38024	-843.11060	0.31928	0.01603	0.06443	-843.04305	-843.10444
$IV^{+\bullet}$	-958.86287	-958.55590	0.37566	0.01893	0.07017	-958.46639	-958.53353
$VII^{\bullet}$	-958.41791	-958.10443	0.36120	0.01898	0.07121	-958.03585	-958.10402
HAT TS	-711.30091	-711.06209	0.28084	0.01616	0.06362	-711.00202	-711.06261
II to rotated-II TS	-595.59086	-595.39504	0.23318	0.01215	0.05451	-595.34364	-595.39512
Cyclization TS	-595.58320	-595.39007	0.23230	0.01181	0.05378	-595.33720	-595.38794
III to IV TS	-958.82337	-958.51552	0.37200	0.01924	0.07118	-958.43024	-958.49839
MeO Cleavage TS	-958.41269	-958.09951	0.35929	0.01903	0.07255	-958.03249	-958.10201
$[Ir^{III}]$*	-2628.47040	-2627.50130	0.46151	0.03901	0.11840	-2627.96800	-2628.08336
$[Ir^{III}]$	-2628.57427	-2627.60992	0.46450	0.03859	0.11703	-2627.10494	-2627.21894
$[Ir^{IV}]$	-2628.34352	-2627.38223	0.46533	0.03853	0.11646	-2627.83777	-2627.95120
2^+	-363.22011	-363.09995	0.13551	0.00596	0.03925	-363.07675	-363.11297
$2^{\bullet}$	-363.33415	-363.20733	0.13105	0.00651	0.04111	-363.19471	-363.23278
V^{2+}	-958.65704	-958.35727	0.37926	0.01795	0.06667	-958.25794	-958.32158
$MeO^{\bullet}$	-115.06569	-115.01719	0.03692	0.00206	0.02687	-115.02482	-115.04866

[a] Unless stated otherwise, calculations performed at the wB97XD/6-31G(d,p) level of theory using SMD to model the acetonitrile solvent environment. E is the total DFT energy, ZPE is the zero-point vibrational energy, TC is the thermal correction to the enthalpy, H is the total enthalpy, TS is the temperature times the total entropy, and G is the total Gibbs free energy in solution and includes a correction for change of state from 1atm to 1M. [b] Calculated with wB97XD/def2TZVPD//wB97XD/6-31G(d,p) using SMD to model the dichloromethane solvent environment.

Time dependent DFT Calculations on the Photoredox Catalyst

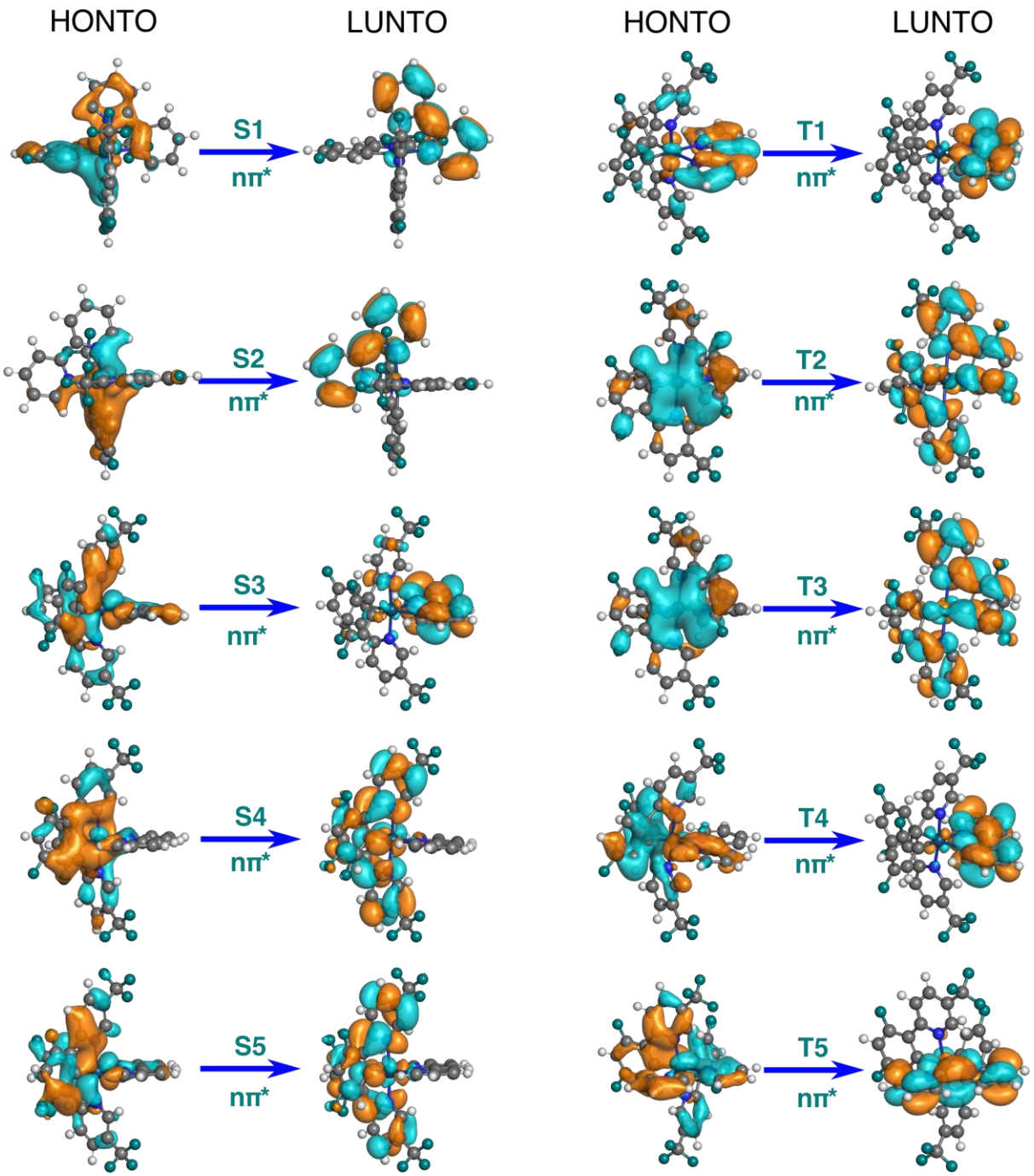


Figure S8. Highest occupied natural transition orbitals (HUNTOs) and lowest unoccupied ones (LUNTOs) describing characters of electronic transitions (S_0 to S_n, to T_n). The [Ir^{III}] complex ground state was determined to have a singlet state (S_0).

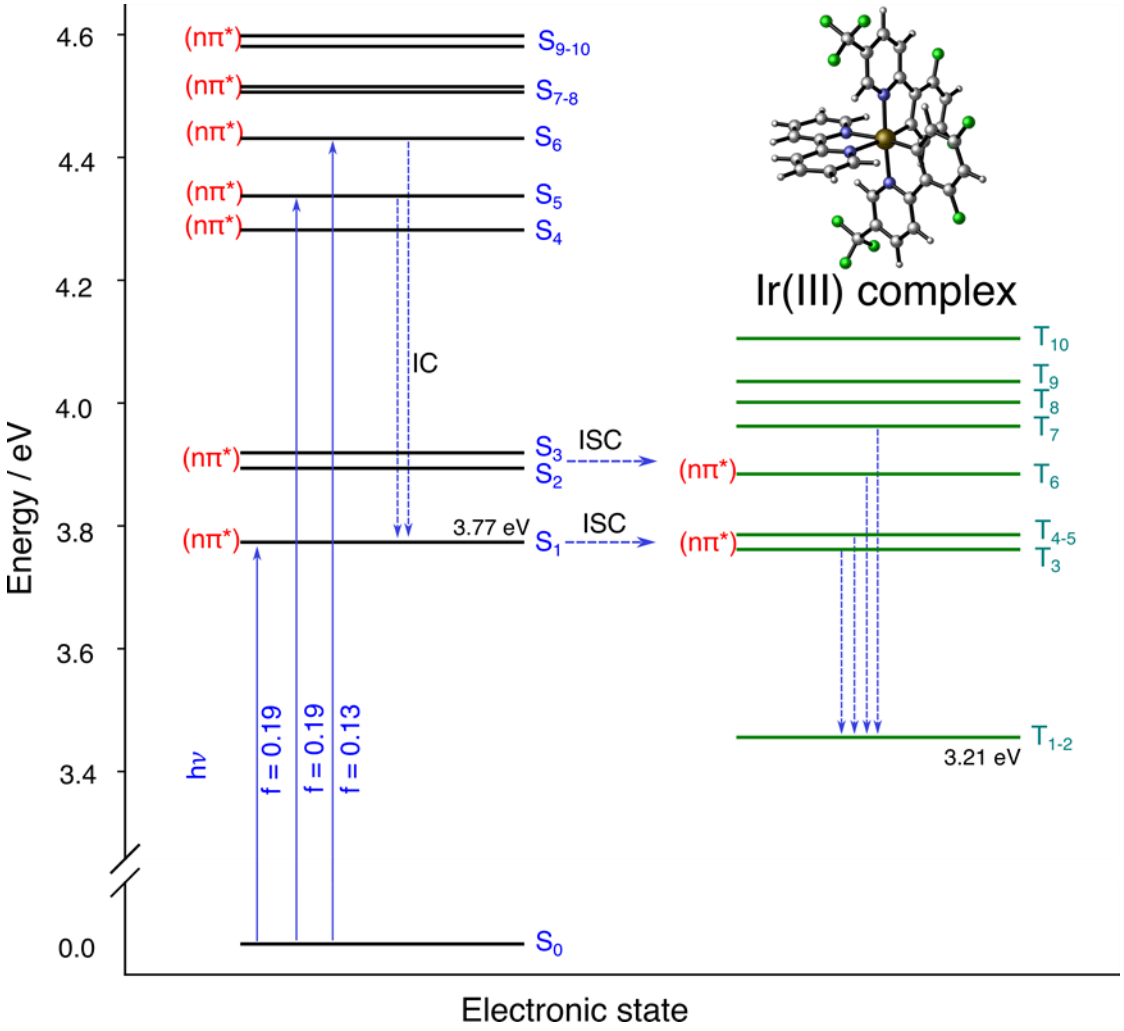


Figure S9. Jablonski energy diagram of the [Ir^{III}] complex. Singlet and triplet excited states up S_{10} and T_{10} were considered. Characters of the singlet-singlet (S_0 to S_n) and singlet-triplet (S_0 to T_n) transitions are noted in red, where n denotes electronic features of n orbitals (from nitrogen atoms of the ligands) and 6d orbitals (from the Ir metal), and π^* denotes unoccupied π orbitals of ligands.

X. The Cytotoxic Effects of Methylene-bridged *bis*-Heterocycles on Certain Cancer Cell Lines

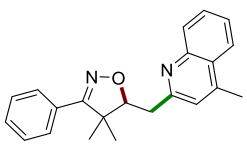
The MCF7, HepG2 and Caco-2 cells are human adherent cancer cell lines and these were obtained from Procell (Wuhan, China). The culturing conditions for cells used in the reported assays are shown in Table S10. The cytotoxicities of test compounds was investigated using a Cell Counting Kit-8 (CCK-8) assay. Cells were cultured in 96-well plates overnight and then incubated with the test compounds at various concentrations (0, 1, 5, 10 ,50 and 200 μM) for 48 h. Thereafter, each well was treated with 20 μL of CCK-8 solution (Beyotime, Shanghai, China) and incubated for 4 h. The absorbance of each sample at 450 nm was then measured using a microplate reader (Tecan infinite M1000 Pro). The relative cell viability of each sample was normalized against a DMSO control.

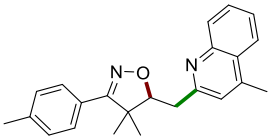
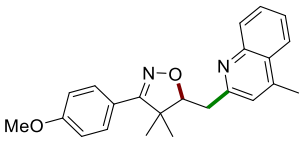
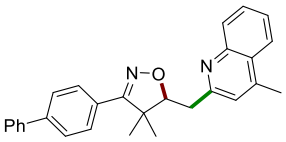
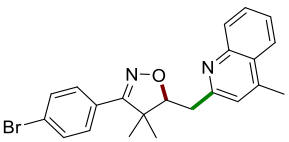
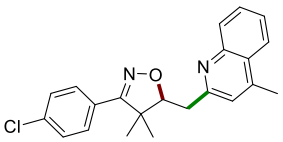
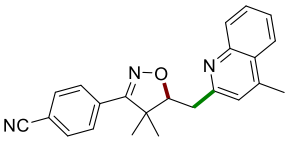
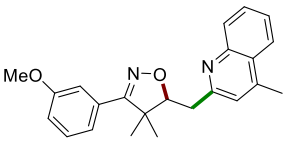
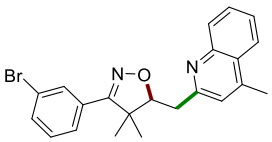
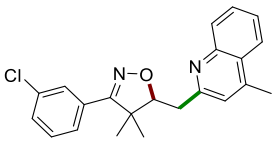
Table S10. The culturing conditions used to prepare the cells used in the reported cytotoxicity studies.

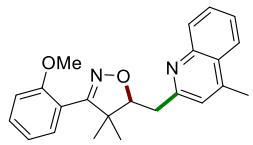
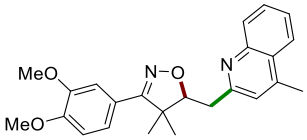
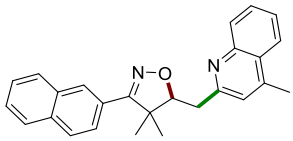
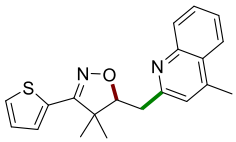
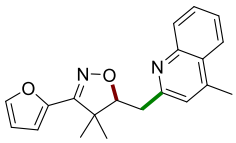
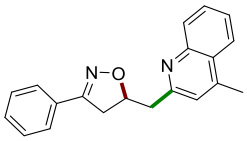
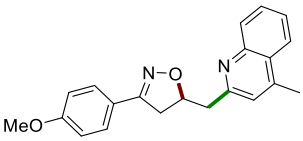
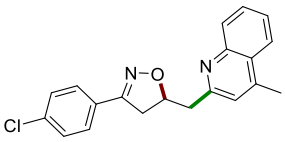
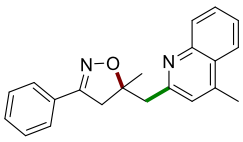
Cell line	MCF7	HepG2	Caco-2
Culture medium	DMEM+10% FBS	MEM+10% FBS	MEM+10% FBS
Culture condition	37 ℃ in 5% CO_2	37 ℃ in 5% CO_2	37 ℃ in 5% CO_2
Seeding number	3000 cell /well	3000 cell /well	5000 cell /well

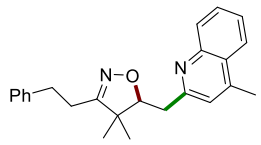
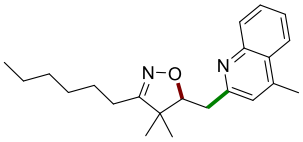
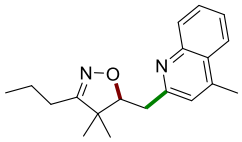
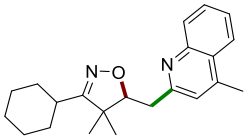
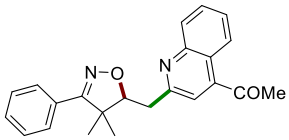
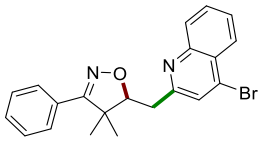
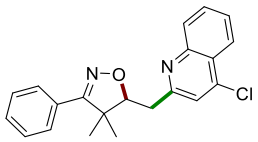
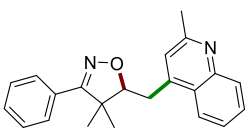
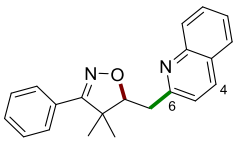
The derived cytotoxic effects of the methylene-bridged *bis*-heterocycles against HepG2 (a typical liver cancer cell line), MCF7 (breast cancer cell line) and Caco2 (colon cancer cell line) are presented in Table S11.

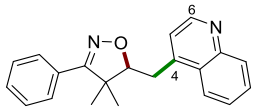
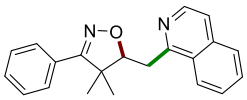
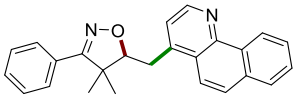
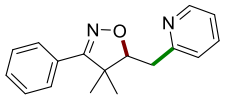
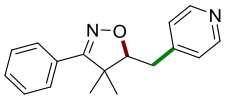
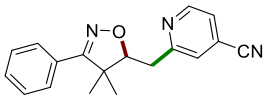
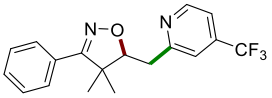
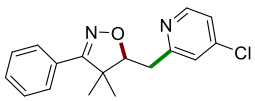
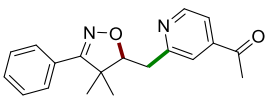
Table S11. The inhibitory effect of compounds on cancer cell viability.

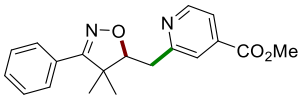
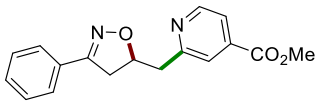
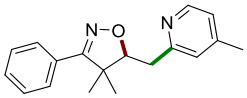
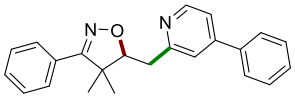
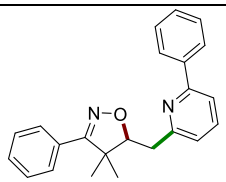
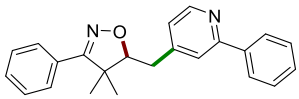
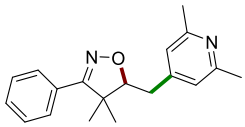
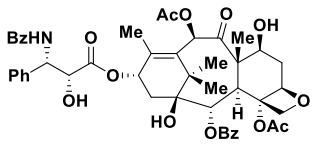
Compound	IC_{50} ± SD (μM)			
	Structure	HepG2	MCF7	Caco2
3a		38.71±0.75	78.32±3.15	39.5±3.31

3b		87.25±2.26	22.52±2.15	>200
3c		11.2±1.15	8.23±1.85	>200
3d		>200	66.77±3.15	132.9±2.21
3e		>200	16.81±1.69	68.2±3.05
3f		>200	>200	>200
3g		>200	6.53±1.66	>200
3h		>200	>200	74.26±3.15
3i		50.23±1.52	>200	>200
3j		70.37±2.14	40.91±3.58	114.7±2.66

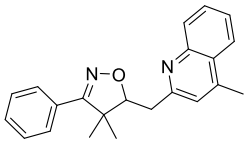
3k		6.24±0.85	63.06±3.17	>200
3l		88.62±13.22	13.22±3.15	10.66±2.61
3m		>200	>200	>200
3n		14.37±1.52	35.64±2.26	>200
3o		43.7±2.15	32.34±2.14	>200
3p		>200	13.22±2.05	140.2±3.86
3q		>200	>200	>200
3r		118.5±26.85	167.23±15.26	135.7±12.3
3s		>200	82.73±3.13	>200

3t		24.78±2.12	6.89±1.33	109.6±4.02
3u		19.6±1.22	22.16±1.84	>200
3v		8.72±0.51	142.9±4.56	>200
3w		>200	48.12±2.14	>200
4a		36.73±2.69	56.39±3.07	>200
4b		9.73±0.67	12.37±1.06	78.95±1.56
4c		6.25±1.05	46.01±2.73	96.86±3.33
4d		12.5±1.23	21.17±2.25	152.2±5.23
4e		8.75±0.74	54.21±3.05	62.18±4.26

4e'		>200	>200	>200
4f		8.53±1.02	11.29±1.34	>200
4g		57.65±1.56	8.95±1.55	>200
5a		56.13±1.74	53.26±9.56	>200
5a'		69.26±12.24	28.96±1.99	>200
5b		>200	>200	>200
5c		>200	110.4±5.02	>200
5d		50.23±2.15	76.28±2.28	>200
5e		>200	>200	>200

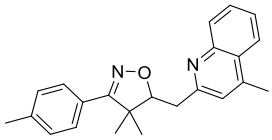
5f		>200	>200	>200
5g		>200	>200	>200
5h		18.51±1.48	6.38±1.83	100.4±3.65
5i		71.12±2.58	25.12±2.15	132.9±4.22
5j		>200	58.59±3.11	>200
5j'		>200	50.52±2.84	>200
5k		14.82±1.14	27.59±2.53	>200
Taxol (paclitaxel)		6.26±1.61	7.35±0.89	9.28±1.22

XI. Compound Characterization and Related Data



3a

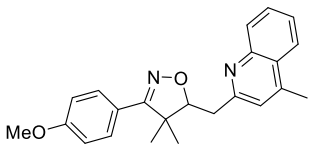
4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-3-phenyl-4,5-dihydroisoxazole (3a). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3a** (29.4 mg, 89%) as a yellow solid, m.p. = 110.5-111.0 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.99 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.72 – 7.65 (m, 3H), 7.54 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.42 (dd, *J* = 5.2, 1.8 Hz, 4H), 4.71 (dd, *J* = 9.6, 3.8 Hz, 1H), 3.29 (ddd, *J* = 17.9, 14.1, 6.7 Hz, 2H), 2.72 (s, 3H), 1.42 (d, *J* = 3.9 Hz, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 165.2, 158.4, 147.7, 144.6, 129.6, 129.5, 129.3, 129.1, 128.6, 127.4, 127.1, 125.8, 123.7, 123.0, 90.0, 51.5, 37.9, 24.1, 19.8, 18.7; IR (ATR) ν_{max} 3061, 2965, 2927, 1603, 1562, 1509, 1464, 1445, 761 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{23}N_2O$: $[M+H]^+$ = 331.1805. Found: 331.1797.



3b

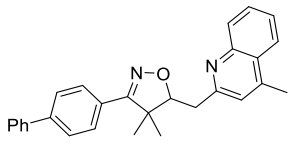
4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-3-(p-tolyl)-4,5-dihydroisoxazole (3b). Reaction of 2,2-dimethyl-1-(p-tolyl)but-3-en-1-one oxime **1b** (20.3 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3b** (21.3 mg, 62%) as a white solid, m.p. = 116.1-116.9 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.99 (dd, *J* = 14.1, 6.8 Hz, 1H), 7.85 – 7.82 (m, 1H), 7.79 (d, *J* = 6.2 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.73 (d, *J* = 10.7 Hz, 1H), 4.29 (d, *J* = 13.3 Hz, 1H), 3.27 (t, *J* = 11.9 Hz, 1H), 2.95 (s, 3H), 2.39 (s, 3H), 1.61 (s, 3H), 1.47 (s, 3H);

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 165.7, 156.5, 156.0, 140.5, 138.1, 134.1, 129.6, 129.5, 127.5, 127.3, 125.9, 124.7, 124.5, 122.4, 89.1, 52.8, 33.5, 24.7, 21.5, 20.2, 19.9; IR (ATR) ν_{max} 2922, 2853, 2588, 1644, 1606, 1466, 765 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{25}N_2O$: $[M+H]^+$ = 345.1961. Found: 345.1946.



3c

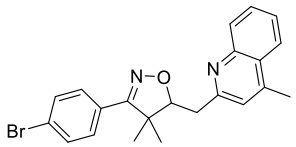
3-(4-Methoxyphenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3c). Reaction of 1-(4-methoxyphenyl)-2,2-dimethylbut-3-en-1-one oxime **1c** (21.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3c** (30.6 mg, 85%) as a yellow solid, m.p. = 127.3-127.8 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 1H), 7.73 – 7.68 (m, 1H), 7.64 – 7.59 (m, 2H), 7.57 – 7.52 (m, 1H), 7.42 (s, 1H), 6.94 – 6.89 (m, 2H), 4.65 (dd, *J* = 7.4, 5.8 Hz, 1H), 3.82 (s, 3H), 3.31 (d, *J* = 7.4 Hz, 2H), 2.72 (s, 3H), 1.41 (d, *J* = 9.0 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 165.0, 160.9, 158.5, 129.8, 128.9, 128.7, 127.2, 126.3, 123.9, 123.3, 121.8, 114.2, 89.9, 55.5, 51.7, 37.6, 24.4, 20.0, 19.0; IR (ATR) ν_{max} 2966, 2923, 1606, 1513, 1464, 1254, 761 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{25}N_2O_2$: $[M+H]^+$ = 361.1911. Found: 361.1897.



3d

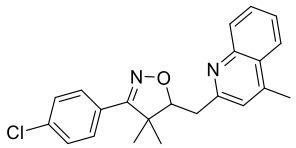
3-([1,1'-Biphenyl]-4-yl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3d). Reaction of 1-([1,1'-biphenyl]-4-yl)-2,2-dimethylbut-3-en-1-one oxime **1d** (26.5 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3d** (28.4 mg, 70%) as a white solid, m.p. = 115.2-115.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ

8.15 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.74 (dd, *J* = 18.4, 8.1 Hz, 3H), 7.63 (dd, *J* = 10.1, 8.3 Hz, 4H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.46 (dd, *J* = 9.6, 5.5 Hz, 3H), 7.37 (t, *J* = 7.2 Hz, 1H), 4.73 (dd, *J* = 8.0, 5.2 Hz, 1H), 3.36 (dd, *J* = 11.3, 7.0 Hz, 2H), 2.74 (s, 3H), 1.49 (s, 3H), 1.46 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 165.1, 158.3, 142.6, 140.3, 129.8, 129.0, 128.4, 127.9, 127.4, 127.2, 127.2, 126.3, 123.9, 123.3, 90.2, 51.7, 37.6, 24.4, 20.0, 19.0; IR (ATR) ν_{max} 3060, 2966, 2925, 1602, 1465, 885, 764 cm^{-1}; HRMS (ESI) Calcd for $C_{28}H_{27}N_2O$: $[M+H]^+$ = 407.2118. Found: 407.2101.



3e

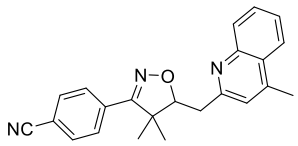
3-(4-Bromophenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3e). Reaction of 1-(4-bromophenyl)-2,2-dimethylbut-3-en-1-one oxime **1e** (26.7 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.7 in 2:1 v/v petroleum ether/ethyl acetate) gave compound **3e** (29.0 mg, 71%) as a white solid, m.p. = 106.6-107.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.7 Hz, 1H), 7.87 (d, *J* = 6.7 Hz, 1H), 7.67 (t, *J* = 6.1 Hz, 1H), 7.54 (t, *J* = 6.1 Hz, 1H), 7.48 (s, 4H), 7.43 (s, 1H), 5.23 (dd, *J* = 8.1, 2.3 Hz, 1H), 4.27 (d, *J* = 10.9 Hz, 1H), 4.09 (dd, *J* = 11.1, 8.2 Hz, 1H), 3.67 (s, 3H), 2.62 (s, 3H), 2.57 (s, 3H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 147.1, 141.6, 121.0, 120.0, 118.6, 118.1, 117.2, 117.0, 114.9, 114.7, 114.2, 87.5, 56.8, 44.7, 34.9, 31.4, 30.8; IR (ATR) ν_{max} 3063, 2966, 2924, 2853, 1643, 1603, 1465, 885, 760 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{22}BrN_2O$: $[M+H]^+$ = 409.0910. Found: 409.0901.



3f

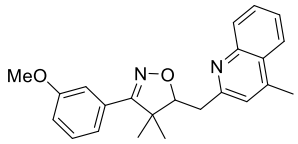
3-(4-Chlorophenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3f). Reaction of 1-(4-chlorophenyl)-2,2-dimethylbut-3-en-1-one oxime **1f** (22.3 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard

work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.3 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3f** (31.7 mg, 87%) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 6.7 Hz, 1H), 7.82 (d, *J* = 6.7 Hz, 1H), 7.60 (t, *J* = 6.1 Hz, 1H), 7.52 (d, *J* = 6.8 Hz, 2H), 7.47 (t, *J* = 6.1 Hz, 1H), 7.36 – 7.33 (m, 3H), 5.21 (t, *J* = 5.3 Hz, 1H), 4.09 (d, *J* = 5.3 Hz, 2H), 3.61 (s, 3H), 2.57 (s, 3H), 2.55 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.9, 141.9, 132.9, 132.0, 124.1, 119.2, 118.6, 118.4, 118.4, 117.8, 117.2, 116.4, 114.5, 114.0, 87.6, 56.6, 45.4, 34.8, 31.3, 30.6; IR (ATR) ν_{max} 3062, 2968, 2927, 1601, 1493, 1465, 1092, 759cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{22}ClN_2O$: $[M+H]^+$ = 365.1415. Found: 365.1404.



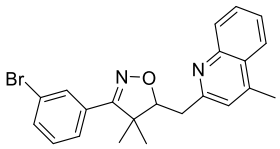
3g

4-(4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazol-3-yl)benzonitrile (3g). Reaction of 4-(1-(hydroxyimino)-2,2-dimethylbut-3-en-1-yl)benzonitrile **1g** (21.4 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.3 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3g** (27.3 mg, 77%) as a yellow solid, m.p. = 144.7-145.2 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.10 (d, *J* = 8.3 Hz, 1H), 7.87 (t, *J* = 7.6 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.71 (dd, *J* = 14.1, 8.1 Hz, 3H), 7.58 (s, 1H), 4.82 (dd, *J* = 10.5, 2.3 Hz, 1H), 3.88 (s, 1H), 3.29 (dd, *J* = 13.8, 10.6 Hz, 1H), 2.86 (s, 3H), 1.56 (s, 3H), 1.45 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.1, 156.7, 133.7, 132.6, 132.3, 129.5, 128.2, 128.0, 127.3, 124.3, 123.9, 118.4, 113.6, 90.3, 51.8, 35.1, 24.4, 19.9, 19.7; IR (ATR) ν_{max} 3066, 2968, 2924, 2228, 1644, 1604, 1467, 764 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{22}N_3O$: $[M+H]^+$ = 356.1757. Found: 356.1742.



3h

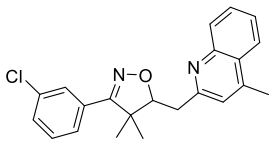
3-(3-Methoxyphenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3h). Reaction of 1-(3-methoxyphenyl)-2,2-dimethylbut-3-en-1-one oxime **1h** (21.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3h** (31.3 mg, 87%) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 7.97 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.70 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.54 (ddd, *J* = 8.2, 6.9, 1.1 Hz, 1H), 7.41 (s, 1H), 7.31 (t, *J* = 8.1 Hz, 1H), 7.22 – 7.21 (m, 2H), 6.95 (ddd, *J* = 8.3, 2.5, 0.9 Hz, 1H), 4.70 – 4.67 (m, 1H), 3.80 (s, 3H), 3.31 (d, *J* = 7.2 Hz, 2H), 2.71 (s, 3H), 1.43 (s, 3H), 1.40 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.2, 159.6, 158.2, 130.6, 129.7, 129.7, 128.6, 127.1, 126.2, 123.8, 123.2, 119.7, 115.7, 112.8, 90.1, 55.4, 51.6, 37.5, 24.3, 19.9, 19.0; IR (ATR) ν_{max} 2965, 2922, 1602, 1465, 1239, 1023, 760 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{25}N_2O_2$: $[M+H]^+$ = 361.1911. Found: 361.1898.



3i

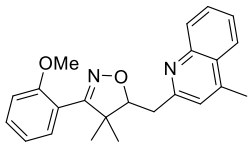
3-(3-Bromophenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3i). Reaction of 1-(3-bromophenyl)-2,2-dimethylbut-3-en-1-one oxime **1i** (26.7 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3i** (34.3 mg, 84%) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.3 Hz, 1H), 7.83 (s, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.57 (dd, *J* = 16.2, 8.2 Hz, 3H), 7.40 (s, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 4.74 (dd, *J* = 7.8, 5.5 Hz, 1H), 3.33 – 3.29 (m, 2H), 2.73 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.1, 158.1, 132.8, 131.6, 130.4, 130.2, 129.6, 128.9, 127.2, 126.2, 125.9, 123.8, 123.2, 122.8, 90.4, 51.5, 37.6, 24.3,

19.9, 18.9; IR (ATR) ν_{max} 3063, 2965, 2927, 1602, 1561, 1465, 917, 758 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{22}BrN_2O$: $[M+H]^+$ = 409.0910. Found: 409.0896.



3j

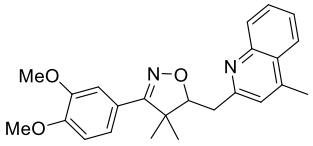
3-(3-Chlorophenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3j). Reaction of 1-(3-chlorophenyl)-2,2-dimethylbut-3-en-1-one oxime **1j** (22.3 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3j** (26.2 mg, 72%) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 6.7 Hz, 1H), 7.84 (d, *J* = 6.6 Hz, 1H), 7.62 (t, *J* = 6.0 Hz, 1H), 7.57 (s, 1H), 7.50 – 7.46 (m, 2H), 7.37 – 7.29 (m, 3H), 5.23 (dd, *J* = 7.2, 3.3 Hz, 1H), 4.15 – 4.06 (m, 2H), 3.62 (s, 3H), 2.59 (s, 3H), 2.56 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 146.8, 141.8, 132.7, 132.3, 123.2, 120.4, 119.4, 119.3, 118.3, 117.4, 117.2, 116.5, 115.8, 114.5, 114.0, 87.7, 56.6, 45.3, 34.8, 31.3, 30.6; IR (ATR) ν_{max} 3065, 2969, 2927, 1602, 1465, 887, 760 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{22}ClN_2O$: $[M+H]^+$ = 365.1415. Found: 365.1399.



3k

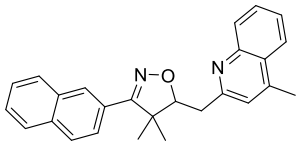
3-(2-Methoxyphenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3k). Reaction of 1-(2-methoxyphenyl)-2,2-dimethylbut-3-en-1-one oxime **1k** (21.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.3 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3k** (33.5 mg, 93%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.88 (s, 1H), 7.69 (s, 1H), 7.56 (s, 1H), 7.51 (s, 1H), 7.37 (s, 1H), 7.20 (s, 1H), 7.03 (dd, *J* = 10.2, 4.6 Hz, 2H), 5.26 (d, *J* = 7.9 Hz, 1H), 4.50 (d, *J* = 2.4 Hz, 3H), 4.35 (d, *J* = 9.8 Hz, 1H), 4.16 – 4.10

(m, 1H), 3.69 (s, 3H), 2.46 (dd, J = 15.4, 2.1 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ 148.0, 141.8, 141.8, 120.3, 120.2, 117.2, 117.2, 116.7, 114.7, 114.5, 111.8, 110.0, 104.4, 86.4, 59.9, 58.7, 44.7, 34.6, 30.9, 30.6; IR (ATR) ν_{max} 3063, 2963, 2924, 1602, 1462, 1247, 1023, 758 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{25}N_2O_2$: $[M+H]^+$ = 361.1911. Found: 361.1894.



3l

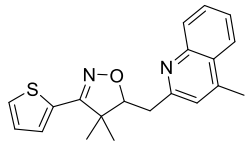
3-(3,4-Dimethoxyphenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3l). Reaction of 1-(3,4-dimethoxyphenyl)-2,2-dimethylbut-3-en-1-one oxime **1l** (24.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.3 in 2:1 v/v petroleum ether/ethyl acetate) gave compound **3l** (26.1 mg, 67%) as a light-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.5 Hz, 1H), 7.81 (d, J = 8.3 Hz, 1H), 7.55 – 7.52 (m, 1H), 7.39 – 7.36 (m, 1H), 7.15 (t, J = 2.8 Hz, 1H), 7.06 (dd, J = 8.4, 0.7 Hz, 1H), 6.71 (dd, J = 8.4, 0.9 Hz, 1H), 4.52 (dd, J = 8.8, 4.4 Hz, 1H), 3.74 (s, 6H), 3.20 – 3.12 (m, 2H), 2.55 (s, 3H), 1.29 (s, 3H), 1.26 (s, 3H); $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) δ 164.7, 158.4, 150.5, 149.0, 147.0, 145.3, 129.4, 128.8, 127.1, 126.0, 123.7, 123.1, 122.0, 119.8, 110.6, 110.5, 90.0, 55.9, 55.9, 51.4, 37.6, 24.4, 20.0, 18.8; IR (ATR) ν_{max} 2932, 1602, 1513, 1463, 1254, 1022, 759 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{27}N_2O_3$: $[M+H]^+$ = 391.2016. Found: 391.2000.



3m

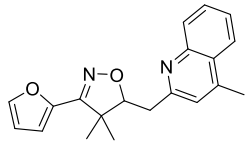
4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-3-(naphthalen-2-yl)-4,5-dihydroisoxazole (3m). Reaction of 2,2-dimethyl-1-(naphthalen-2-yl)but-3-en-1-one oxime **1m** (23.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.3 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3m** (26.6

mg, 70%) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 6.6 Hz, 1H), 7.94 (s, 1H), 7.87 (d, *J* = 6.7 Hz, 1H), 7.76 – 7.70 (m, 4H), 7.67 (t, *J* = 6.1 Hz, 1H), 7.54 (t, *J* = 6.1 Hz, 1H), 7.48 – 7.46 (m, 3H), 5.27 (dd, *J* = 8.1, 2.2 Hz, 1H), 4.29 (d, *J* = 10.9 Hz, 1H), 4.13 (dd, *J* = 11.1, 8.2 Hz, 1H), 3.67 (s, 3H), 2.71 (s, 3H), 2.66 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 147.7, 141.8, 122.5, 121.8, 119.9, 118.3, 118.3, 117.7, 117.4, 117.2, 117.2, 117.0, 116.9, 116.9, 116.8, 115.3, 114.6, 114.3, 87.5, 57.0, 44.9, 35.1, 31.5, 30.8; IR (ATR) ν_{max} 3058, 2966, 2925, 1643, 1603, 1464, 821, 756 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{25}N_2O$: $[M+H]^+$ = 381.1961. Found: 381.1950.



3n

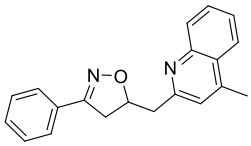
4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-3-(thiophen-2-yl)-4,5-dihydroisoxazole (3n). Reaction of 2,2-dimethyl-1-(thiophen-2-yl)but-3-en-1-one oxime **1n** (19.5 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 2:1 v/v petroleum ether/ethyl acetate) gave compound **3n** (25.2 mg, 75%) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.39 (dd, *J* = 15.6, 5.4 Hz, 3H), 7.08 – 7.06 (m, 1H), 4.72 (t, *J* = 6.7 Hz, 1H), 3.32 (d, *J* = 6.8 Hz, 2H), 2.71 (s, 3H), 1.49 (s, 3H), 1.43 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.9, 158.2, 131.2, 129.7, 128.8, 127.8, 127.5, 127.2, 127.0, 126.2, 123.9, 123.3, 90.3, 51.7, 37.7, 24.6, 20.0, 18.9; IR (ATR) ν_{max} 3066, 2969, 2926, 1602, 1463, 882, 760, 710 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{21}N_2OS$: $[M+H]^+$ = 337.1369. Found: 337.1358.



3o

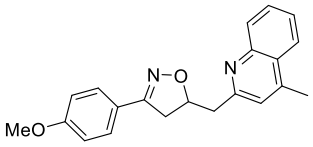
3-(Furan-2-yl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3o). Reaction of 1-(furan-2-yl)-2,2-dimethylbut-3-en-1-one oxime **1o** (17.9 mg, 0.1 mmol) with

the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (2:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 2:1 v/v petroleum ether/ethyl acetate) gave compound **3o** (23.1 mg, 72%) as a light-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 – 7.96 (m, 2H), 7.69 (ddd, *J* = 8.4, 6.9, 1.5 Hz, 1H), 7.56 – 7.50 (m, 2H), 7.37 (s, 1H), 6.84 (dd, *J* = 3.5, 0.7 Hz, 1H), 6.49 (dd, *J* = 3.5, 1.8 Hz, 1H), 4.70 (dd, *J* = 9.2, 4.1 Hz, 1H), 3.35 – 3.19 (m, 2H), 2.70 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 158.5, 157.7, 147.7, 144.9, 144.9, 144.0, 129.4, 129.4, 127.3, 126.0, 123.9, 123.2, 111.6, 111.4, 89.9, 51.4, 38.1, 24.5, 19.9, 18.9; IR (ATR) ν_{max} 2961, 2924, 1603, 1562, 1464, 1005, 879, 756 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{21}N_2O_2$: $[M+H]^+$ = 321.1598. Found: 321.1593.



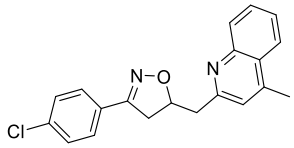
3p

5-((4-Methylquinolin-2-yl)methyl)-3-phenyl-4,5-dihydroisoxazole (3p). Reaction of 1-phenylbut-3-en-1-one oxime **1p** (16.1 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3p** (23.3 mg, 77%) as a yellow solid, m.p. = 96.0-96.7 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.86 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.60 – 7.55 (m, 3H), 7.43 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 1H), 7.29 – 7.26 (m, 3H), 7.17 (d, *J* = 2.6 Hz, 1H), 5.20 (dq, *J* = 10.3, 6.6 Hz, 1H), 3.39 – 3.31 (m, 2H), 3.17 (ddd, *J* = 12.9, 7.5, 6.4 Hz, 2H), 2.59 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 157.6, 156.7, 147.6, 144.6, 129.9, 129.6, 129.3, 129.1, 128.6, 127.0, 126.6, 125.8, 123.6, 123.0, 80.7, 43.8, 39.8, 18.6; IR (ATR) ν_{max} 3060, 2921, 1600, 1446, 1356, 910, 758, 692 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{19}N_2O$: $[M+H]^+$ = 303.1492. Found: 303.1479.



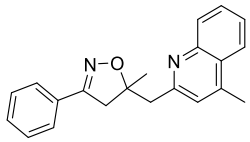
3q

3-(4-Methoxyphenyl)-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3q). Reaction of 1-(4-methoxyphenyl)but-3-en-1-one oxime **1q** (19.1 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.2 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3q** (23.3 mg, 70%) as a yellow solid, m.p. = 109.8-110.4 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 1H), 7.98 (dd, *J* = 8.4, 0.9 Hz,1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.59 – 7.54 (m, 3H), 7.34 (s, 1H), 6.90 – 6.87 (m, 2H), 5.26 (dq, *J* = 13.5, 6.9 Hz, 1H), 3.81 (s, 3H), 3.49 – 3.41 (m, 2H), 3.36 (dd, *J* = 13.9, 5.7 Hz, 1H), 3.26 (dd, *J* = 16.6, 7.3 Hz,1H), 2.71 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.1, 157.5, 156.6, 130.0, 128.3, 127.2, 126.5, 123.9, 123.5, 122.2, 114.2, 80.4, 55.4, 43.2, 40.4, 19.0; IR (ATR) ν_{max} 2926, 2840, 1605, 1515, 1357, 1253, 1178, 762 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{21}N_2O_2$: $[M+H]^+$ = 333.1598. Found: 333.1587.



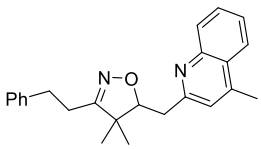
3r

3-(4-Chlorophenyl)-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3r). Reaction of 1-(4-chlorophenyl)but-3-en-1-one oxime **1r** (19.5 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3r** (25.5 mg, 76%) as yellow crystals, m.p. = 125.3-125.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 6.7 Hz, 1H), 7.83 (d, *J* = 6.6 Hz, 1H), 7.62 (t, *J* = 6.1 Hz, 1H), 7.50 – 7.49 (m, 3H), 7.32 – 7.30 (m, 3H), 5.70 (td, *J* = 11.0, 5.3 Hz, 1H), 4.24 – 4.04 (m, 4H), 3.61 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.2, 140.3, 132.5, 124.3, 119.4, 118.6, 118.2, 117.8, 117.1, 116.6, 114.6, 114.1, 80.2, 50.0, 47.3, 30.6; IR (ATR) ν_{max} 3062, 2923, 2852, 1600, 1494, 1351, 1092, 829, 761 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{18}ClN_2O$: $[M+H]^+$ = 337.1102. Found: 337.1086.



3s

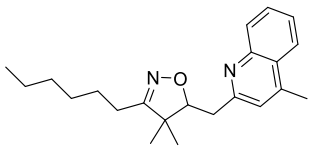
5-Methyl-5-((4-methylquinolin-2-yl)methyl)-3-phenyl-4,5-dihydroisoxazole (3s). Reaction of 3-methyl-1-phenylbut-3-en-1-one oxime **1s** (17.5 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3s** (23.4 mg, 74%) as colorless crystals, m.p. = 174.7-175.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.7 Hz, 1H), 7.83 (d, *J* = 6.7 Hz, 1H), 7.62 (t, *J* = 6.1 Hz, 1H), 7.51– 7.50 (m, 3H), 7.42 (s, 1H), 7.32 – 7.31 (m, 3H), 4.38 (d, *J* = 13.5 Hz, 1H), 4.23 (q, *J* = 10.8 Hz, 2H), 3.94 (d, *J* = 13.5 Hz, 1H), 3.63 (s, 3H), 2.71 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.2, 141.2, 119.5, 119.4, 119.3, 118.4, 117.8, 117.2, 116.8, 116.7, 114.9, 114.6, 85.3, 53.1, 51.3, 36.6, 30.7; IR (ATR) ν_{max} 3061, 2924, 2852, 1602, 1446, 1359, 922, 760, 692 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{21}N_2O$: $[M+H]^+$ = 317.1648. Found: 317.1642.



3t

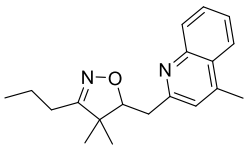
4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-3-phenethyl-4,5-dihydroisoxazole (3t). Reaction of 4,4-dimethyl-1-phenylhex-5-en-3-one oxime **1t** (21.7 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.7 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3t** (21.5 mg, 60%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.4 Hz, 1H), 7.85 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.57 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.42 (ddd, *J* = 8.1, 7.0, 1.1 Hz, 1H), 7.16 (dd, *J* = 10.2, 4.6 Hz, 2H), 7.12 – 7.07 (m, 4H), 4.38 (dd, *J* = 9.5, 3.9 Hz, 1H), 3.10 (ddd, *J* = 23.5, 14.1, 6.5 Hz, 2H), 2.89 – 2.86 (m, 2H), 2.58 (s, 3H), 2.40 – 2.37 (m, 2H), 1.04 (s, 3H), 1.01 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.5, 158.5, 141.4, 129.8, 128.6, 128.5, 127.2, 126.3, 123.9, 123.3, 88.2, 52.1, 37.9, 32.3, 27.0, 23.6, 19.0; IR (ATR) ν_{max} 3027, 2964, 2927, 1603,

1453, 886, 759, 700 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{27}N_2O$: $[M+H]^+$ = 359.2118. Found: 359.2102.



3u

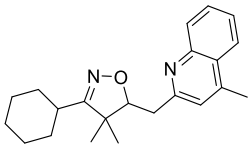
3-Hexyl-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3u). Reaction of 3,3-dimethyldec-1-en-4-one oxime **1u** (19.7 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.8 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **3u** (22.7 mg, 67%) as a light-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.3 Hz, 1H), 8.03 – 8.00 (m, 1H), 7.79 – 7.73 (m, 1H), 7.61 (dd, *J* = 11.2, 4.1 Hz, 1H), 7.47 (s, 1H), 4.48 (dd, *J* = 10.1, 3.1 Hz, 1H), 3.45 (d, *J* = 13.7 Hz, 1H), 3.19 (dd, *J* = 13.9, 10.1 Hz, 1H), 2.75 (s, 3H), 2.25 – 2.20 (m, 2H), 1.69 – 1.63 (m, 2H), 1.38 – 1.27 (m, 6H), 1.23 (s, 3H), 1.18 (s, 3H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 167.3, 158.1, 130.9, 127.2, 127.1, 126.8, 124.1, 123.7, 87.9, 52.4, 36.7, 31.7, 29.3, 26.2, 25.0, 23.8, 22.7, 19.3, 19.0, 14.2; IR (ATR) ν_{max} 2925, 2855, 1604, 1466, 1261, 1021, 799, 761 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{31}N_2O$: $[M+H]^+$ = 339.2431. Found: 339.2423.



3v

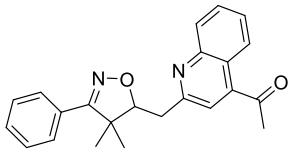
4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-3-propyl-4,5-dihydroisoxazole (3v). Reaction of 3,3-dimethylhept-1-en-4-one oxime **1v** (15.5 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.8 in 2:1 v/v petroleum ether/ethyl acetate) gave compound **3v** (18.7 mg, 63%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (ddd, *J* = 8.4, 1.3, 0.6 Hz, 1H), 7.94 (dd, *J* = 8.7, 1.2 Hz, 1H), 7.65 (ddd, *J* = 8.4, 6.8, 1.5 Hz, 1H), 7.49 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.34 (s, 1H), 4.45 (dd, *J* = 9.3, 4.1 Hz, 1H), 3.25 – 3.09 (m, 2H), 2.66 (s, 3H), 2.21 – 2.16 (m, 2H), 1.75 –

1.62 (m, 2H), 1.15 (d, J = 4.7 Hz, 6H), 0.98 (t, J = 7.4 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 166.8, 158.8, 147.6, 144.7, 129.2, 129.2, 127.1, 125.8, 123.8, 123.1, 88.1, 51.9, 38.4, 27.0, 23.6, 19.6, 19.0, 18.8, 14.1; IR (ATR) ν_{max} 2963, 2930, 2872, 1603, 1562, 1509, 1466, 885, 759 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{25}N_2O$: $[M+H]^+$ = 297.1961. Found: 297.1986.



3w

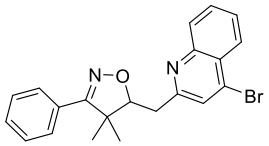
3-Cyclohexyl-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3w). Reaction of 1-cyclohexyl-2,2-dimethylbut-3-en-1-one oxime **1w** (19.5 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2a** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 4:1 v/v petroleum ether/ethyl acetate) gave compound **3w** (20.5 mg, 61%) as a yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (dd, J = 8.0, 1.1 Hz, 1H), 7.94 (dd, J = 8.3, 1.4 Hz, 1H), 7.66 (ddd, J = 8.4, 6.8, 1.5 Hz, 1H), 7.49 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.35 (s, 1H), 4.40 (dd, J = 9.2, 4.1 Hz, 1H), 3.24 – 3.08 (m, 2H), 2.66 (s, 3H), 2.15 (tt, J = 11.7, 3.3 Hz, 1H), 1.87 – 1.77 (m, 4H), 1.68 – 1.41 (m, 3H), 1.30 – 1.24 (m, 3H), 1.18 (s, 3H), 1.15 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 170.8, 158.9, 147.5, 144.7, 129.2, 127.1, 125.8, 123.8, 123.2, 88.1, 52.4, 38.3, 35.7, 32.4, 32.2, 26.5, 25.8, 23.7, 19.2, 18.8; IR (ATR) ν_{max} 2926, 2852, 1602, 1561, 1509, 1447, 892, 757 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{29}N_2O$: $[M+H]^+$ = 337.2274. Found: 337.2433.



4a

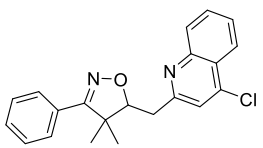
1-(2-((4,4-Dimethyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)quinolin-4-yl)ethan-1-one (4a). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2b** (72.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 2.5:1 v/v petroleum ether/ethyl acetate) gave compound **4a** (21.5 mg, 60%) as a

light-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (dd, *J* = 8.5, 0.9 Hz, 1H), 8.09 (dd, *J* = 8.4, 0.5 Hz, 1H), 7.77 (s, 1H), 7.75 – 7.72 (m, 1H), 7.67 – 7.65 (m, 2H), 7.61 – 7.58 (m, 1H), 7.43 – 7.39 (m, 3H), 4.70 (dd, *J* = 10.0, 3.3 Hz, 1H), 3.41 (dd, *J* = 14.2, 10.0 Hz, 1H), 3.32 (dd, *J* = 14.2, 3.3 Hz, 1H), 2.78 (s, 3H), 1.46 (s, 3H), 1.42 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 210.9, 201.5, 165.3, 158.5, 148.8, 143.0, 129.9, 129.8, 129.3, 129.3, 128.6, 127.7, 127.4, 125.4, 122.5, 121.3, 111.5, 89.8, 51.6, 38.1, 30.1, 24.2, 19.8; IR (ATR) ν_{max} 3062, 2967, 2921, 1692, 1592, 1463, 891, 766, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{23}N_2O_2$: $[M+H]^+$ = 359.1754. Found: 359.1738.



4b

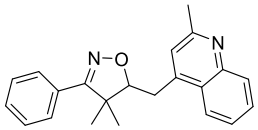
5-((4-Bromoquinolin-2-yl)methyl)-4,4-dimethyl-3-phenyl-4,5-dihydroisoxazole (4b). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2c** (81.2 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.7 in 2:1 v/v petroleum ether/ethyl acetate) gave compound **4b** (24.0 mg, 61%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 8.3, 0.8 Hz, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.87 (s, 1H), 7.75 – 7.72 (m, 1H), 7.66 – 7.64 (m, 2H), 7.61 – 7.58 (m, 1H), 7.42 – 7.38 (m, 3H), 4.70 (dd, *J* = 9.3, 4.0 Hz, 1H), 3.30 (qd, *J* = 14.2, 6.7 Hz, 2H), 1.43 (s, 3H), 1.39 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.1, 158.6, 147.9, 134.7, 130.5, 129.7, 129.2, 128.9, 128.6, 127.4, 127.3, 126.6, 126.6, 126.2, 89.6, 51.5, 37.4, 24.2, 19.7; IR (ATR) ν_{max} 3061, 2968, 1584, 1553, 1492, 908, 762, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{20}BrN_2O$: $[M+H]^+$ = 395.0754. Found: 395.0740.



4c

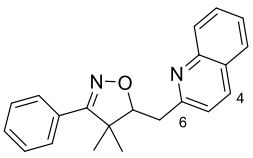
5-((4-Chloroquinolin-2-yl)methyl)-4,4-dimethyl-3-phenyl-4,5-dihydroisoxazole (4c). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2d** (70.3 mg, 0.25 mmol) followed by standard work-up and flash

column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **4c** (22.4 mg, 64%) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (dd, *J* = 8.4, 0.9 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.70 (s, 1H), 7.67 – 7.62 (m, 3H), 7.44 – 7.40 (m, 3H), 4.70 (dd, *J* = 8.6, 4.7 Hz, 1H), 3.38 – 3.29 (m, 2H), 1.46 (s, 3H), 1.41 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.4, 158.7, 147.7, 144.0, 131.1, 129.9, 129.8, 129.3, 128.8, 128.5, 127.5, 125.5, 124.3, 122.7, 89.7, 51.8, 37.5, 24.4, 19.9; IR (ATR) ν_{max} 3062, 2966, 2926, 1588, 1494, 917, 763, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{20}ClN_2O$: $[M+H]^+$ = 351.1259. Found: 351.1244.



4d

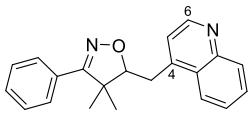
4,4-Dimethyl-5-((2-methylquinolin-4-yl)methyl)-3-phenyl-4,5-dihydroisoxazole (4d). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2e** (65.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **4d** (26.4 mg, 80%) as a yellow solid, m.p. = 117.9-118.6 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 7.73 – 7.66 (m, 3H), 7.57 – 7.51 (m, 1H), 7.45 – 7.41 (m, 4H), 4.52 (dd, *J* = 9.2, 3.7 Hz, 1H), 3.45 – 3.31 (m, 2H), 2.77 (s, 3H), 1.47 (d, *J* = 2.8 Hz, 6H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 165.3, 158.7, 147.9, 143.8, 129.9, 129.5, 129.2, 129.2, 128.7, 127.3, 125.8, 125.7, 123.0, 122.8, 89.4, 51.6, 30.4, 25.2, 24.0, 19.7; IR (ATR) νmax 3061, 2920, 2850, 1648, 1603, 1467, 902, 766, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{23}N_2O$: $[M+H]^+$ = 331.1805. Found: 331.1798.



4e-C6

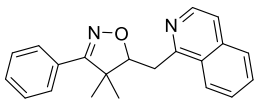
4,4-Dimethyl-3-phenyl-5-(quinolin-2-ylmethyl)-4,5-dihydroisoxazole (4e-C6) (C6:C4 = 1.2:1). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2f** (61.8 mg, 0.25 mmol) followed by standard work-up and

flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **4e-C6** (13.0 mg, 41%) as a light-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.71 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H), 7.67 – 7.64 (m, 2H), 7.53 (ddd, *J* = 10.0, 8.0, 4.7 Hz, 2H), 7.42 – 7.38 (m, 3H), 4.72 (dd, *J* = 9.4, 4.0 Hz, 1H), 3.36 (ddd, *J* = 18.0, 14.1, 6.7 Hz, 2H), 1.41 (d, *J* = 4.1 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.2, 158.7, 136.8, 129.6, 129.4, 128.5, 128.5, 127.6, 127.4, 127.0, 126.2, 122.4, 89.9, 51.5, 37.8, 24.2, 19.8; IR (ATR) ν_{max} 3058, 2968, 2927, 1619, 1599, 1504, 1464, 901, 767, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{21}N_2O$: $[M+H]^+$ = 317.1648. Found: 317.1643.



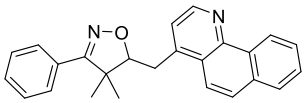
4e-C4

4,4-Dimethyl-3-phenyl-5-(quinolin-4-ylmethyl)-4,5-dihydroisoxazole (4e-C4) (C6:C4 = 1.2:1). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2f** (61.8 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.2 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **4e-C4** (10.7 mg, 34%) as yellow crystals, m.p. = 167.8-168.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.86 (d, *J* = 4.3 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 8.04 (d, *J* = 8.4 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.65 – 7.63 (m, 2H), δ 7.59 (t, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 4.4 Hz, 1H), 7.42 – 7.38 (m, 3H), 4.48 (dd, *J* = 6.8, 6.1 Hz, 1H), 3.39 (d, *J* = 6.7 Hz, 2H), 1.43 (d, *J* = 10.3 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.2, 149.7, 147.8, 144.3, 130.0, 129.8, 129.3, 129.1, 128.6, 128.5, 127.4, 127.4, 127.3, 126.7, 123.1, 122.0, 89.4, 51.5, 30.4, 23.9, 19.6; IR (ATR) ν_{max} 3061, 2967, 2926, 1592, 1509, 1464, 901, 766, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{21}N_2O$: $[M+H]^+$ = 317.1648. Found: 317.1635.



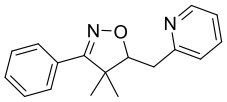
4f

5-(Isoquinolin-1-ylmethyl)-4,4-dimethyl-3-phenyl-4,5-dihydroisoxazole (4f). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2g** (61.8 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (2:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 2:1 v/v petroleum ether/ethyl acetate) gave compound **4f** (19.3 mg, 61%) as a light-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.49 (d, *J* = 5.7, 1H), 8.28 – 8.25 (m, 1H), 7.84 (d, *J* = 7.3, 1H), 7.73 – 7.64 (m, 4H), 7.58 (d, *J* = 5.7, 1H), 7.42 – 7.40 (m, 3H), 4.84 (dd, *J* = 8.9, 4.2, 1H), 3.89 (dd, *J* = 14.4, 8.9, 1H), 3.44 (dd, *J* = 14.4, 4.2, 1H), 1.47 (s, 3H), 1.41 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 165.6, 158.3, 136.8, 131.0, 129.9, 129.6, 128.8, 128.0, 127.6, 127.5, 126.1, 120.7, 90.3, 51.8, 33.5, 24.3, 20.0; IR (ATR) ν_{max} 2923, 2852, 1624, 1587, 1464, 1390, 899, 767, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{21}N_2O$: $[M+H]^+$ = 317.1648. Found: 317.1670.



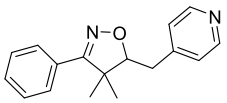
4g

5-(Benzo[h]quinolin-4-ylmethyl)-4,4-dimethyl-3-phenyl-4,5-dihydroisoxazole (4g). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxyquinolinium salt **2h** (74.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (5:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 5:1 v/v petroleum ether/ethyl acetate) gave compound **4g** (19.0 mg, 52%) as a light-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.36 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.95 (d, *J* = 4.6 Hz, 1H), 7.92 – 7.82 (m, 3H), 7.72 (ddd, *J* = 9.1, 7.5, 1.5 Hz, 2H), 7.68 – 7.65 (m, 2H), 7.56 (d, *J* = 4.6 Hz, 1H), 7.42 (dd, *J* = 5.2, 1.9 Hz, 3H), 4.51 (dd, *J* = 8.2, 4.7 Hz, 1H), 3.44 – 3.39 (m, 2H), 1.45 (s, 3H), 1.41 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 165.4, 148.4, 146.6, 143.8, 133.2, 131.9, 129.9, 129.3, 128.7, 128.3, 127.9, 127.8, 127.4, 127.3, 125.3, 124.9, 123.1, 120.6, 89.8, 51.6, 30.8, 24.1, 19.8; IR (ATR) ν_{max} 3053, 2925, 1621, 1586, 1443, 905, 830, 727, 693 cm^{-1}; HRMS (ESI) Calcd for $C_{25}H_{23}N_2O$: $[M+H]^+$ = 367.1805. Found: 367.1806.



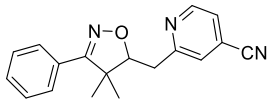
5a-C2

4,4-Dimethyl-3-phenyl-5-(pyridin-2-ylmethyl)-4,5-dihydroisoxazole (5a-C2) (C2:C4 = 3.2:1). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxypyridinium salt **2i** (49.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (2:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 2:1 v/v petroleum ether/ethyl acetate) gave compound **5a-C2** (17.8 mg, 67%) as a light-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.0 Hz, 1H), 7.69 (td, *J* = 7.7, 1.8 Hz, 1H), 7.64 (dd, *J* = 7.5, 2.2 Hz, 2H), 7.42 – 7.38 (m, 4H), 7.21 (dd, *J* = 7.6, 5.0 Hz, 1H), 4.60 (dd, J = 8.4, 4.9 Hz, 1H), 3.18 – 3.16 (m, 2H), 1.39 (s, 3H), 1.36 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.4, 157.9, 148.8, 137.3, 129.8, 129.5, 128.7, 127.5, 124.7, 122.1, 90.0, 51.5, 37.0, 24.2, 19.9; IR (ATR) ν_{max} 2968, 2927, 1590, 1467, 1438, 902, 766, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{19}N_2O$: $[M+H]^+$ = 267.1492. Found: 267.1488.



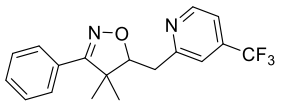
5a-C4

4,4-Dimethyl-3-phenyl-5-(pyridin-4-ylmethyl)-4,5-dihydroisoxazole (5a-C4) (C2:C4 = 3.2:1). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxypyridinium salt **2i** (49.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (2:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.2 in 2:1 v/v petroleum ether/ethyl acetate) gave compound **5a-C4** (5.6 mg, 21%) as a light-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, *J* = 5.3 Hz, 2H), 7.65 – 7.61 (m, 2H), 7.40 (dd, *J* = 5.3, 2.0 Hz, 3H), 7.32 (d, *J* = 6.1 Hz, 2H), 4.32 (dd, *J* = 10.0, 3.2 Hz, 1H), 3.05 (dd, *J* = 14.5, 10.0 Hz, 1H), 2.86 (dd, *J* = 14.5, 3.2 Hz, 1H), 1.37 (s, 3H), 1.33 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 165.3, 149.3, 147.9, 130.0, 129.2, 128.8, 127.5, 124.9, 90.0, 51.6, 34.1, 24.1, 19.8; IR (ATR) ν_{max} 2925, 2855, 1603, 1558, 1463, 904, 775, 702 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{19}N_2O$: $[M+H]^+$ = 267.1492. Found: 267.1486.



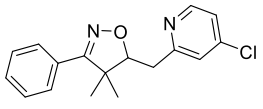
5b

2-((4,4-Dimethyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)isonicotinonitrile (5b). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxypyridinium salt **2j** (55.5 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.2 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **5b** (22.4 mg, 77%) as a yellow solid, m.p. = 96.1-96.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 3.8 Hz, 1H), 7.69 (s, 1H), 7.64 (dd, *J* = 7.5, 1.6 Hz, 2H), 7.47 (d, *J* = 2.6 Hz, 1H), 7.41 (q, *J* = 5.4 Hz, 3H), 4.58 (dd, *J* = 8.4, 4.1 Hz, 1H), 3.21 – 3.17 (m, 2H), 1.44 (s, 3H), 1.37 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.3, 159.8, 149.6, 130.0, 129.2, 128.8, 127.5, 126.5, 123.7, 121.8, 116.4, 89.4, 51.7, 36.9, 24.4, 19.9; IR (ATR) ν_{max} 3060, 2969, 2931, 2238, 1719, 1595, 1550, 1467, 1402, 891, 767, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{18}N_3O$: $[M+H]^+$ = 292.1444. Found: 292.1433.



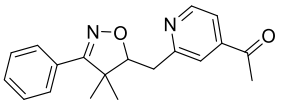
5c

4,4-Dimethyl-3-phenyl-5-((4-(trifluoromethyl)pyridin-2-yl)methyl)-4,5-dihydroisoxazole (5c). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxypyridinium salt **2k** (66.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (4:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 4:1 v/v petroleum ether/ethyl acetate) gave compound **5c** (24.4 mg, 73%) as a light-yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (d, *J* = 5.2 Hz, 1H), 7.64 (dd, *J* = 7.3, 2.1 Hz, 2H), 7.60 (s, 1H), 7.40 – 7.39 (m, 4H), 4.61 (dd, *J* = 10.1, 3.2 Hz, 1H), 3.23 (dd, *J* = 14.2, 10.1 Hz, 1H), 3.16 (dd, *J* = 14.2, 3.2 Hz, 1H), 1.41 (s, 3H), 1.36 (s, 3H); ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 165.3, 159.9, 150.3, 138.9 (q, *J* = 33.9 Hz), 129.9, 129.3, 128.7, 127.5, 122.9 (q, *J* = 273.3 Hz), 119.9 (q, *J* = 3.6 Hz), 117.5 (q, *J* = 3.7 Hz), 89.6, 51.5, 37.3, 24.2, 19.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -64.7; IR (ATR) ν_{max} 2969, 1613, 1411, 1331, 1132, 897, 765, 693 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{18}F_3N_2O$: $[M+H]^+$ = 335.1366. Found: 335.1361.



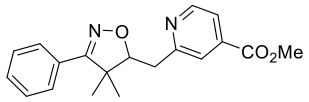
5d

5-((4-Chloropyridin-2-yl)methyl)-4,4-dimethyl-3-phenyl-4,5-dihydroisoxazole (5d). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxypyridinium salt **2l** (57.8 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.3 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **5d** (17.1 mg, 57%) as a yellow solid, m.p. = 75.9-76.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, *J* = 5.4 Hz, 1H), 7.64 – 7.62 (m, 2H), 7.42 (d, *J* = 1.7 Hz, 1H), 7.41 – 7.37 (m, 3H), 7.19 (dd, *J* = 5.4, 1.8 Hz, 1H), 4.57 (dd, *J* = 9.0, 4.2 Hz, 1H), 3.14 – 3.06 (m, 2H), 1.39 (s, 3H), 1.34 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.1, 159.6, 149.7, 144.7, 129.7, 129.2, 128.5, 127.3, 124.6, 122.2, 89.4, 51.3, 36.8, 24.1, 19.7; IR (ATR) ν_{max} 3056, 2968, 2930, 1575, 1555, 1466, 896, 766, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{18}ClN_2O$: $[M+H]^+$ = 301.1102. Found: 301.1091



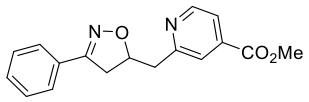
5e

1-(2-((4,4-Dimethyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)pyridin-4-yl)ethan-1-one (5e). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxypyridinium salt **2m** (59.8 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.2 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **5e** (20.0 mg, 65%) as needle crystals, m.p. = 69.1-69.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 5.1 Hz, 1H), 7.86 (s, 1H), 7.68 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.65 – 7.63 (m, 2H), 7.43 – 7.39 (m, 3H), 4.62 (dd, *J* = 9.1, 4.1 Hz, 1H), 3.29 – 3.20 (m, 2H), 2.66 (s, 3H), 1.43 (s, 3H), 1.38 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 197.2, 165.4, 159.5, 149.5, 144.2, 130.0, 129.3, 128.8, 127.5, 122.7, 119.9, 89.7, 51.6, 36.8, 27.0, 24.3, 19.9; IR (ATR) ν_{max} 2968, 2922, 1695, 1556, 1409, 1271, 768, 697 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{21}N_2O_2$: $[M+H]^+$ = 309.1598. Found: 309.1591.



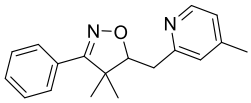
5f

Methyl 2-((4,4-dimethyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)isonicotinate (5f). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxypyridinium salt **2n** (63.8 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **5f** (25.3 mg, 78%) as a light-yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 5.2, 0.6 Hz, 1H), 8.01 (s, 1H), 7.83 (dd, *J* = 5.2, 1.4 Hz, 1H), 7.65 – 7.63 (m, 2H), 7.43 – 7.39 (m, 3H), 4.63 (dd, *J* = 9.8, 3.5 Hz, 1H), 3.97 (s, 3H), 3.33 – 3.21 (m, 2H), 1.43 (s, 3H), 1.38 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.2, 165.1, 158.8, 150.1, 148.7, 139.0, 129.8, 129.2, 128.6, 127.4, 124.3, 123.1, 121.6, 89.5, 52.9, 51.5, 36.5, 24.2, 19.8; IR (ATR) ν_{max} 2965, 2923, 1731, 1438, 1299, 1216, 764, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{21}N_2O_3$: $[M+H]^+$ = 325.1547. Found: 325.1534.



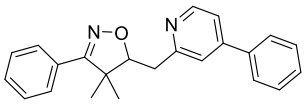
5g

Methyl 2-((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)isonicotinate (5g). Reaction of 1-phenylbut-3-en-1-one oxime **1p** (16.1 mg, 0.1 mmol) with the *N*-methoxypyridinium salt **2n** (63.8 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.3 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **5g** (21.3 mg, 72%) as a light-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 5.1, 0.9 Hz, 1H), 7.83 (s, 1H), 7.71 (dd, *J* = 5.1, 1.6 Hz, 1H), 7.66 – 7.63 (m, 2H), 7.40 – 7.36 (m, 3H), 5.22 (ddd, *J* = 13.9, 10.3, 6.4 Hz, 1H), 3.95 (s, 3H), 3.50 – 3.15 (m, 4H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 165.8, 158.7, 156.8, 150.3, 138.0, 130.2, 129.7, 128.8, 126.8, 123.5, 121.2, 80.5, 52.8, 43.4, 39.9; IR (ATR) ν_{max} 2954, 2923, 1723, 1437, 1293, 761, 692 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{17}N_2O_3$: $[M+H]^+$ = 297.1234. Found: 297.1227.



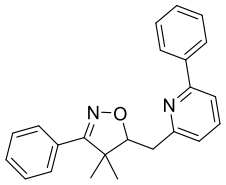
5h

4,4-Dimethyl-5-((4-methylpyridin-2-yl)methyl)-3-phenyl-4,5-dihydroisoxazole (5h). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxypyridinium salt **2o** (52.8 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (3:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.4 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **5h** (18.8 mg, 67%) as a light-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (d, *J* = 5.0 Hz, 1H), 7.65 – 7.63 (m, 2H), 7.41 – 7.38 (m, 3H), 7.20 (s, 1H), 6.98 (d, *J* = 4.8 Hz, 1H), 4.58 (dd, *J* = 9.7, 3.5 Hz, 1H), 3.08 (ddd, *J* = 17.6, 14.1, 6.6 Hz, 2H), 2.34 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.2, 157.7, 149.0, 147.6, 129.6, 129.5, 128.5, 127.3, 125.0, 122.7, 90.0, 51.2, 37.0, 24.0, 21.0, 19.7; IR (ATR) ν_{max} 3057, 2968, 2926, 1606, 1463, 906, 767, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{21}N_2O$: $[M+H]^+$ = 281.1648. Found: 281.1643.



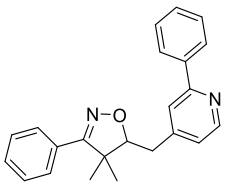
5i

4,4-Dimethyl-3-phenyl-5-((4-phenylpyridin-2-yl)methyl)-4,5-dihydroisoxazole (5i). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxypyridinium salt **2p** (68.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (2:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.3 in 2:1 v/v petroleum ether/ethyl acetate) gave compound **5i** (22.2 mg, 65%) as a light-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (d, *J* = 5.2 Hz, 1H), 7.67 – 7.65 (m, 4H), 7.60 (d, *J* = 0.6 Hz, 1H), 7.46 (td, *J* = 7.2, 1.3 Hz, 2H), 7.42 – 7.37 (m, 5H), 4.66 (dd, *J* = 9.8, 3.4 Hz, 1H), 3.19 (ddd, *J* = 17.5, 14.1, 6.6 Hz, 2H), 1.40 (s, 3H), 1.37 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.1, 158.4, 149.5, 148.8, 138.0, 129.5, 129.3, 128.9, 128.8, 128.4, 127.2, 127.0, 122.0, 119.6, 89.8, 51.1, 37.1, 23.9, 19.6; IR (ATR) ν_{max} 3057, 2967, 2928, 1597, 1545, 1464, 894, 761, 693 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{23}N_2O$: $[M+H]^+$ = 343.1805. Found: 343.1789.



5j-C2

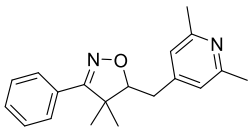
4,4-Dimethyl-3-phenyl-5-((6-phenylpyridin-2-yl)methyl)-4,5-dihydroisoxazole (5j-C2) (C2:C4 = 1.2:1). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxypyridinium salt **2q** (68.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (2:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.8 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **5j-C2** (11.6 mg, 34%) as a light-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 2H), 7.75 – 7.69 (m, 1H), 7.68 – 7.64 (m, 2H), 7.60 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.43 – 7.40 (m, 4H), 7.32 (dd, *J* = 7.6, 1.0 Hz, 1H), 4.76 (dd, *J* = 8.7, 4.6 Hz, 1H), 3.32 – 3.17 (m, 2H), 1.40 (s, 3H), 1.38 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 165.5, 158.0, 157.1, 139.7, 137.3, 129.8, 129.7, 129.0, 128.8, 128.7, 127.6, 127.1, 122.5, 118.7, 90.2, 51.4, 37.4, 24.2, 20.0; IR (ATR) ν_{max} 2925, 1572, 1448, 899, 759, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{23}N_2O$: $[M+H]^+$ = 343.1805. Found: 343.1815.



5j-C4

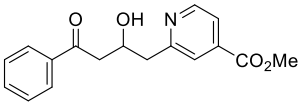
4,4-Dimethyl-3-phenyl-5-((2-phenylpyridin-4-yl)methyl)-4,5-dihydroisoxazole (5j-C4) (C2:C4 = 1.2:1). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with the *N*-methoxypyridinium salt **2q** (68.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (2:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.6 in 3:1 v/v petroleum ether/ethyl acetate) gave compound **5j-C4** (9.9 mg, 29%) as a light-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 5.0, 0.8 Hz, 1H), 8.02 – 7.99 (m, 2H), 7.73 (s, 1H), 7.67 – 7.64 (m, 2H), 7.48 – 7.45 (m, 2H), 7.44 – 7.39 (m, 4H), 7.24 (dd, *J* = 5.2, 1.8 Hz, 1H), 4.39 (dd, *J* = 9.9, 3.2 Hz, 1H), 3.13 (dd, *J* = 14.4, 9.9 Hz, 1H), 2.92 (dd, *J* = 14.5, 3.2 Hz, 1H), 1.40 (s, 3H), 1.37 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 165.4, 157.9, 149.9, 147.9, 139.5, 130.0, 129.3, 129.1, 128.8, 128.8, 127.5, 127.2,

123.1, 121.7, 90.3, 51.6, 34.3, 24.2, 19.9; IR (ATR) ν_{max} 2924, 1602, 1445, 894, 767, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{23}H_{23}N_2O$: $[M+H]^+$ = 343.1805. Found: 343.1810.



5k

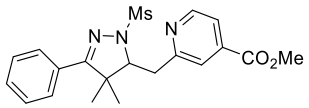
5-((2,6-Dimethylpyridin-4-yl)methyl)-4,4-dimethyl-3-phenyl-4,5-dihydroisoxazole (5k). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with t he *N*-methoxypyridinium salt **2r** (56.3 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (2:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.2 in 2:1 v/v petroleum ether/ethyl acetate) gave compound **5k** (14.7 m g, 50%) as a light-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 2H), 7. 44 – 7.39 (m, 3H), 6.98 (s, 2H), 4.31 (dd, *J* = 10.0, 3.1 Hz, 1H), 2.97 (dd, *J* = 14. 4, 10.0 Hz, 1H), 2.77 (dd, *J* = 14.4, 3.2 Hz, 1H), 2.54 (s, 6H), 1.37 (s, 3H), 1.33 (s, 3H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 165.4, 157.8, 148.1, 130.0, 129.4, 128.8, 127. 5, 121.4, 90.3, 51.5, 33.9, 29.8, 24.3, 24.1, 19.8; IR (ATR) ν_{max} 2929, 1613, 1569, 146 3, 906, 767, 695 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{23}N_2O$: $[M+H]^+$ = 295.1805. Found: 29 5.1800.



6

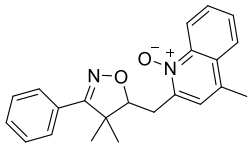
Methyl 2-(2-hydroxy-4-oxo-4-phenylbutyl)isonicotinate (6). Purified by flash column chromatography on silica gel (2:1 v/v petroleum ether/ethyl acetate elution). From methyl 2-((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)isonicotinate **5g** (88.8 mg, 0.3mmol), compound **6** (67 mg, 75%) was obtained as a light-yellow oil, R_f = 0.3 in 2:1 v/v petroleum ether/ethyl acetate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.66 (d, *J* = 5.1 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.78 (s, 1H), 7.71 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 4.70 (ddd, *J* = 12.1, 7.4, 4.8 Hz, 1H), 3.93 (s, 3H), 3.33 – 3.18 (m, 2H), 3.16 – 3.05 (m, 2H); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 199.6, 165.6, 160.5, 149.7, 137.9, 136.8, 133.4, 128.6, 128.1, 123.3, 120.9, 52.7, 44.8, 43.5; IR (ATR) ν_{max} 3435, 2954, 2923, 1719, 1681, 1438,

1293, 1214, 762, 690 cm^{-1}; HRMS (ESI) Calcd for $C_{17}H_{18}NO_4$: $[M+H]^+$ = 300.1230. Found: 300.1227.



8

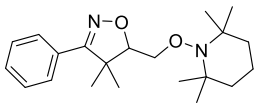
Methyl 2-((4,4-dimethyl-1-(methylsulfonyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)methyl)isonicotinate (8). Reaction of N'-(2,2-dimethyl-1-phenylbut-3-en-1-ylidene)methanesulfonohydrazide **7** (26.6 mg, 0.1 mmol) with the *N*-methoxypyridinium salt **2n** (63.8 mg, 0.25 mmol) followed by the above procedure and flash column chromatography on silica gel (2:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.5 in 2:1 v/v petroleum ether/ethyl acetate) gave compound **8** (20.1 mg, 50%) as a light-yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (dd, *J* = 5.0, 0.9 Hz, 1H), 7.82 (s, 1H), 7.70 (dd, *J* = 5.1, 1.6 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.42 – 7.38 (m, 3H), 4.47 (dd, *J* = 8.2, 5.1 Hz, 1H), 3.95 (s, 3H), 3.81 (dd, *J* = 14.9, 5.1 Hz, 1H), 3.32 (dd, *J* = 14.9, 8.2 Hz, 1H), 3.09 (s, 3H), 1.39 (s, 3H), 1.19 (s, 3H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.0, 165.8, 159.4, 150.0, 137.9, 130.7, 130.2, 128.6, 128.0, 123.3, 121.0, 70.4, 52.8, 52.2, 37.7, 36.3, 25.7, 20.2; IR (ATR) ν_{max} 2929, 1728, 1349, 1309, 1165, 958, 760, 695, 542 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{24}N_3O_4S$: $[M+H]^+$ = 402.1482. Found: 402.1470.



11

2-((4,4-Dimethyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)-4-methylquinoline 1-oxide (11). Reaction of 2,2-dimethyl-1-phenylbut-3-en-1-one oxime **1a** (18.9 mg, 0.1 mmol) with quinoline *N*-oxide **10** (39.8 mg, 0.25 mmol) followed by standard work-up and flash column chromatography on silica gel (1:1 v/v petroleum ether/ethyl acetate elution, R_f = 0.2 in 2:1 v/v petroleum ether/ethyl acetate) gave compound **11** (5.2 mg, 15%) as a light-yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.7 Hz, 1H), 7.98 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.81 – 7.75 (m, 1H), 7.69 – 7.63 (m, 3H), 7.42 (dd, *J* = 5.1, 1.9 Hz, 4H), 4.79 (dd, *J* = 10.8, 1.5 Hz, 1H), 3.88 (d, *J* = 14.5 Hz, 1H), 2.99 (dd, *J* = 14.2, 10.7 Hz, 1H), 2.68 (s, 3H), 1.53 (s, 3H),

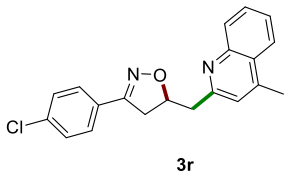
1.44 (s, 3H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 165.3, 145.1, 141.1, 134.2, 130.3, 130.0, 129.4, 129.2, 128.8, 128.0, 127.5, 124.9, 124.1, 120.1, 86.6, 51.9, 31.3, 24.3, 19.6, 18.5; IR (ATR) ν_{max} 3395, 2925, 1666, 1565, 1464, 1237, 896, 768, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{22}H_{23}N_2O_2$: $[M+H]^+$ = 347.1754. Found: 347.1748.



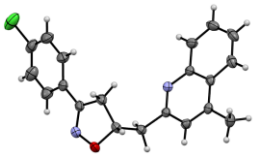
12

4,4-Dimethyl-3-phenyl-5-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-4,5-dihydrois oxazole (12). Formed (20.7 mg, 60%) according to the above procedure and obtained as colorless needles, m.p. = 93.6-94.0 °C, R_f = 0.8 in 5:1 v/v petroleum ether/ethyl acetate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 6.5, 3.0 Hz, 2H), 7.46 – 7.42 (m, 3H), 4.38 (t, *J* = 5.6 Hz, 1H), 4.14 (qd, *J* = 10.2, 5.7 Hz, 2H), 1.57 – 1.49 (m, 8H), 1.36 (s, 4H), 1.27 (d, *J* = 4.6 Hz, 6H), 1.17 (d, *J* = 2.0 Hz, 6H); $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 164.6, 129.7, 129.4, 128.6, 127.5, 88.5, 74.8, 60.1, 51.0, 39.7, 33.2, 32.9, 24.8, 20.2, 20.1, 19.7, 17.1; IR (ATR) ν_{max} 2928, 1467, 1360, 1133, 1045, 903, 765, 694 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{33}N_2O_2$: $[M+H]^+$ = 345.2537. Found: 345.2524.

XII. X-ray Crystallographic Data for Compounds 3r, 3s, 4e' and 5e



3r



Datablock: ytt-203 (CCDC : 2209584)

Bond precision: C-C = 0.0028 A Wavelength=1.54184

Cell: a=14.3458(4) b=11.8545(3) c=10.1259(3)

alpha=90 beta=106.391(3) gamma=90

Temperature: 170 K

	Calculated	Reported
Volume	1652.05(8)	1652.05(8)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C20 H17 Cl N2 O	C20 H17 Cl N2 O
Sum formula	C20 H17 Cl N2 O	C20 H17 Cl N2 O
Mr	336.81	336.80
Dx,g cm-3	1.354	1.354
Z	4	4
Mu (mm-1)	2.106	2.106
F000	704.0	704.0
F000'	707.25	
h,k,lmax	17,14,12	17,14,12
Nref	3342	3241
Tmin,Tmax	0.766,0.760	0.238,1.000
Tmin'	0.694	

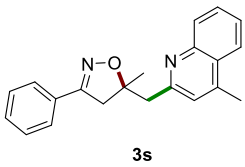
Correction method= # Reported T Limits: Tmin=0.238 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 0.970 Theta(max)= 73.657

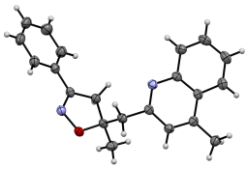
R(reflections)= 0.0566(2877) wR2(reflections)= 0.1554(3241)

S = 1.047 Npar= 219

Crystallographic Data for 3s (CCDC : 2209585)



3s



Datablock: ytt-214

Bond precision: C-C = 0.0016 A Wavelength=1.54184

Cell: a=11.5609(2) b=11.2342(2) c=25.6255(4)

alpha=90 beta=90 gamma=90

Temperature: 170 K

	Calculated	Reported
Volume	3328.18(10)	3328.18(10)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C21 H20 N2 O	C21 H20 N2 O
Sum formula	C21 H20 N2 O	C21 H20 N2 O
Mr	316.39	316.39
Dx,g cm-3	1.263	1.263
Z	8	8
Mu (mm-1)	0.613	0.613
F000	1344.0	1344.0
F000'	1347.70	
h,k,lmax	14,14,31	13,13,31
Nref	3364	3310
Tmin,Tmax	0.916,0.941	0.677,1.000
Tmin'	0.912	

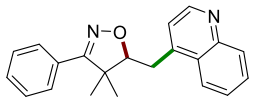
Correction method= # Reported T Limits: Tmin=0.677 Tmax=1.000 AbsCo
rr = MULTI-SCAN

Data completeness= 0.984 Theta(max)= 73.903

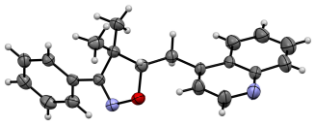
R(reflections)= 0.0350(3014) wR2(reflections)= 0.0936(3310)

S = 1.019 Npar= 220

Crystallographic Data for 4e' (CCDC : 2209586)



4e'



Datablock: 228-2_2

Bond precision: C-C = 0.0019 A Wavelength=1.54184

Cell: a=8.4599(5) b=9.7370(6) c=11.2374(6)

alpha=66.551(5) beta=78.251(5) gamma=79.553(5)

Temperature: 170 K

	Calculated	Reported
Volume	826.23(9)	826.23(9)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C21 H20 N2 O	C21 H20 N2 O
Sum formula	C21 H20 N2 O	C21 H20 N2 O
Mr	316.39	316.39
Dx,g cm-3	1.272	1.272
Z	2	2
Mu (mm-1)	0.618	0.618
F000	336.0	336.0
F000'	336.92	
h,k,lmax	10,12,13	10,12,13
Nref	3337	3214
Tmin,Tmax	0.911,0.929	0.750,1.000
Tmin'	0.911	

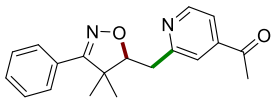
Correction method= # Reported T Limits: Tmin=0.750 Tmax=1.000 AbsC
orr = MULTI-SCAN

Data completeness= 0.963 Theta(max)= 73.586

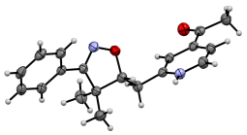
R(reflections)= 0.0426(2929) wR2(reflections)= 0.1153(3214)

S = 1.013 Npar= 331

Crystallographic Data for 5e (CCDC : 2209721)



5e



Datablock: ytt-229

Bond precision: C-C = 0.0030 A Wavelength=1.54184

Cell: a=8.3746(2) b=10.1900(3) c=20.3391(6)

alpha=90 beta=91.588(3) gamma=90

Temperature: 170 K

	Calculated	Reported
Volume	1735.02(8)	1735.01(8)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C19 H21 N2 O2, Cl	Cl, C19 H21 N2 O2
Sum formula	C19 H21 Cl N2 O2	C19 H21 Cl N2 O2
Mr	344.83	344.83
Dx,g cm-3	1.320	1.320
Z	4	4
Mu (mm-1)	2.056	2.056
F000	728.0	728.0
F000'	731.37	
h,k,lmax	10,12,25	10,12,25
Nref	3538	3446
Tmin,Tmax	0.771,0.781	0.462,1.000
Tmin'	0.700	

Correction method= # Reported T Limits: Tmin=0.462 Tmax=1.000 AbsCorr = MULTI-SCAN

Data completeness= 0.974 Theta(max)= 74.121

R(reflections)= 0.0481(3091) wR2(reflections)= 0.1394(3446)

S = 1.061 Npar= 224

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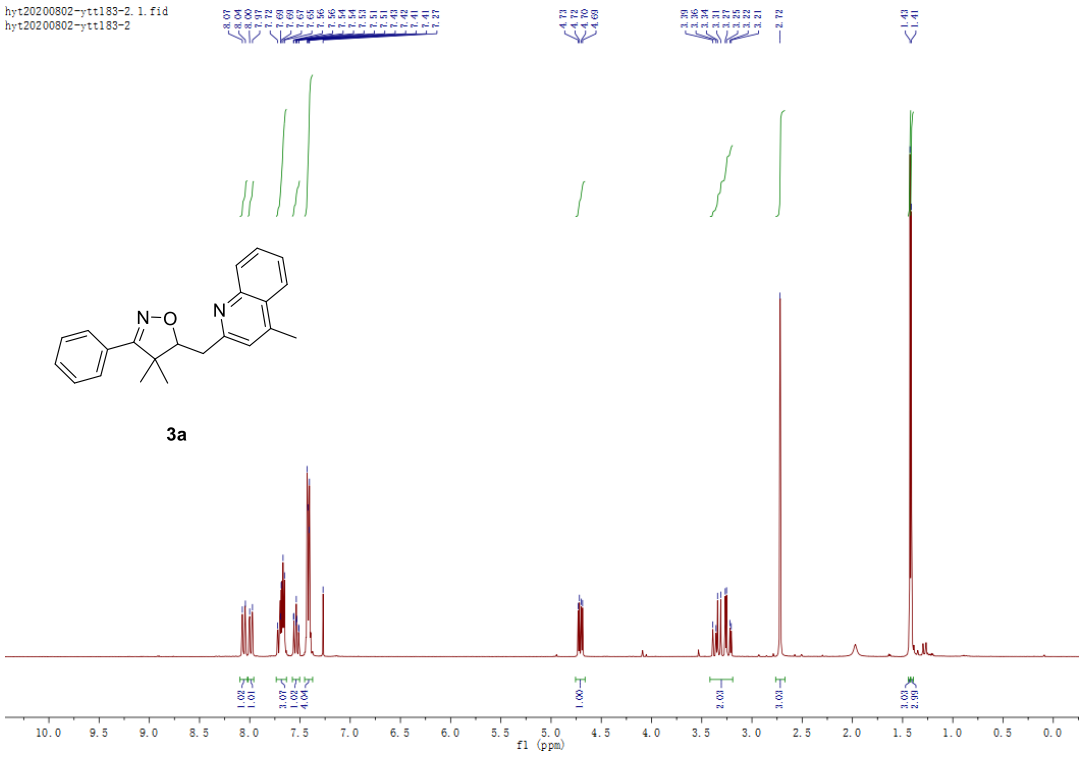
Appendix I

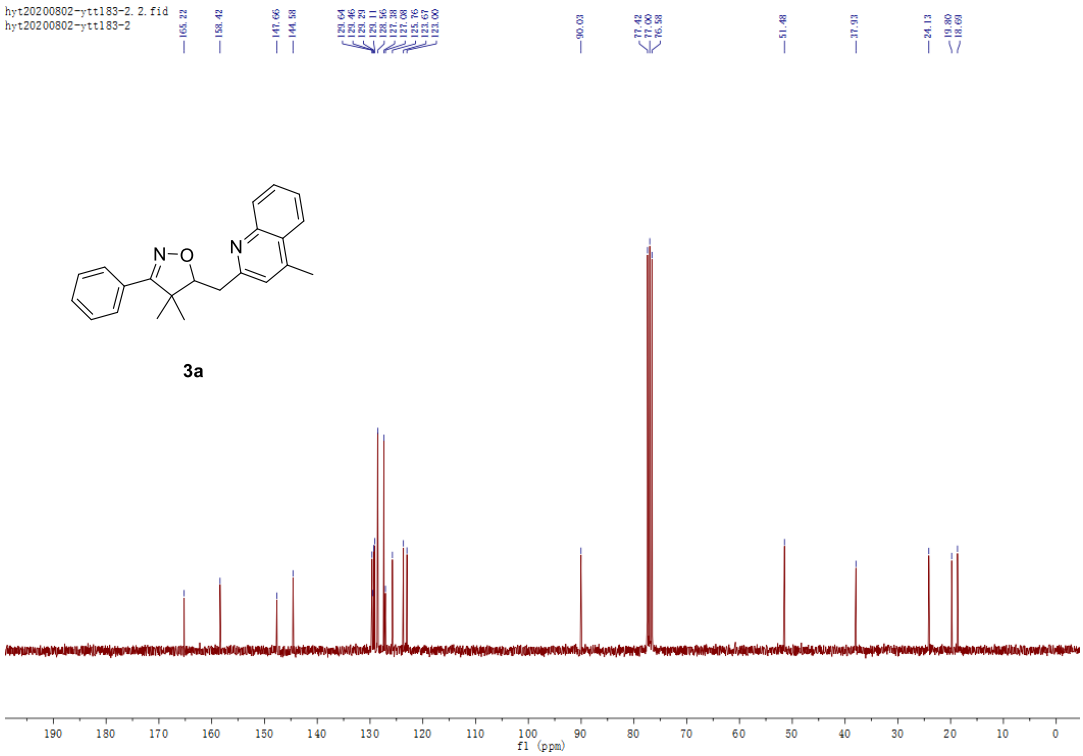
Copies of Relevant ^{1}H-, $^{13}C\{^{1}H\}$- and ^{19}F-NMR Spectra

4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-3-phenyl-4,5-dihydroisoxazole (3a).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

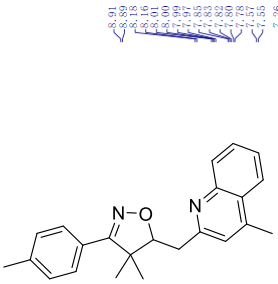


75 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

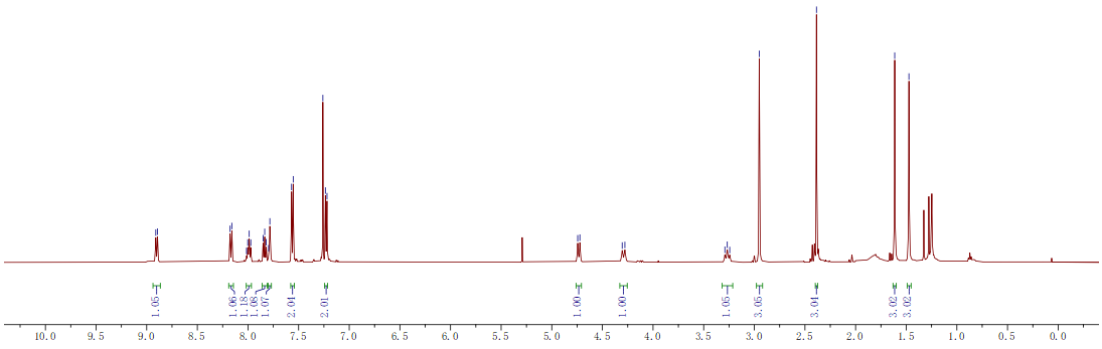


4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-3-(p-tolyl)-4,5-dihydroisoxazole (3b).

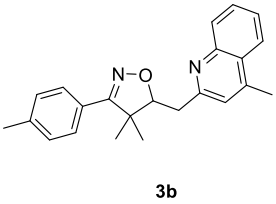
500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)



3b



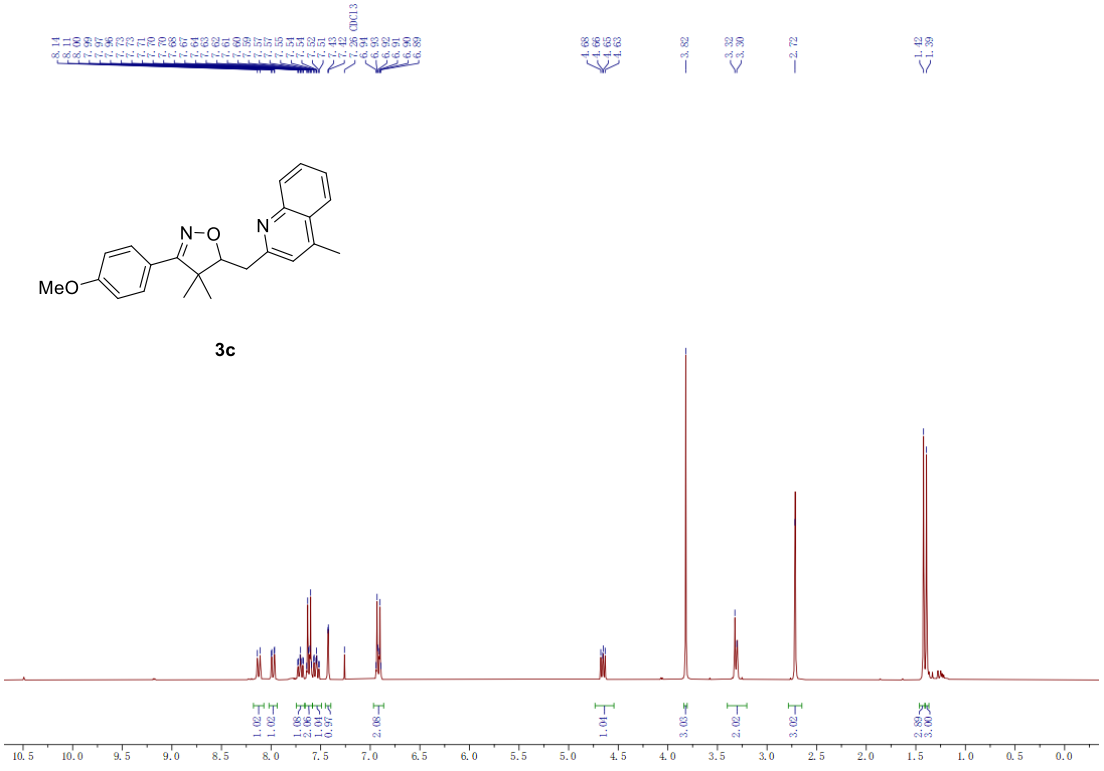
126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)



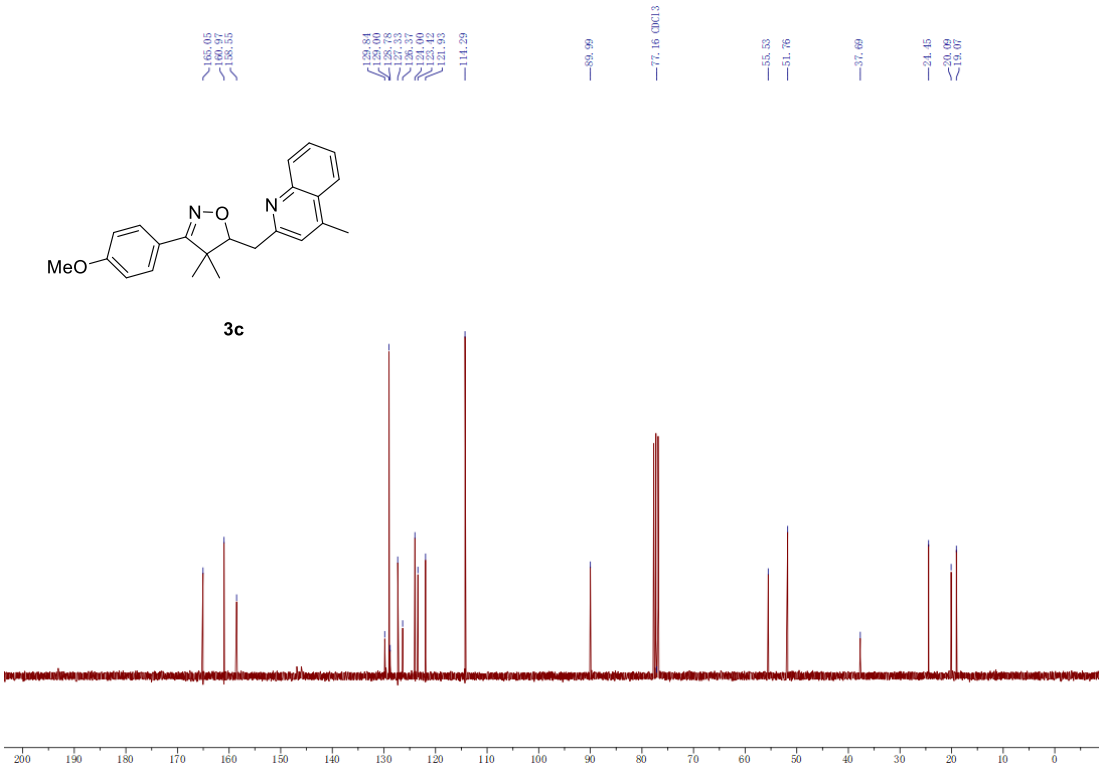
3b

3-(4-Methoxyphenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3c).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

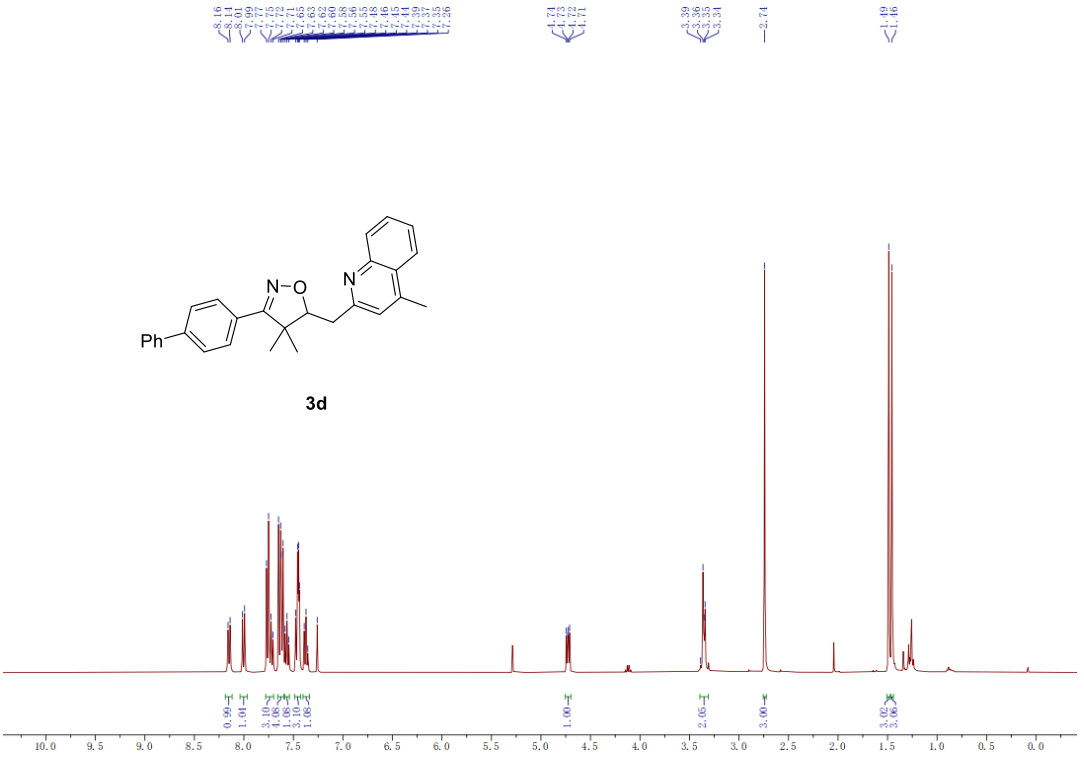


75 MHz $^{13}C\{^{1}H\}$ NMR Spectrum (recorded in $CDCl_3$)

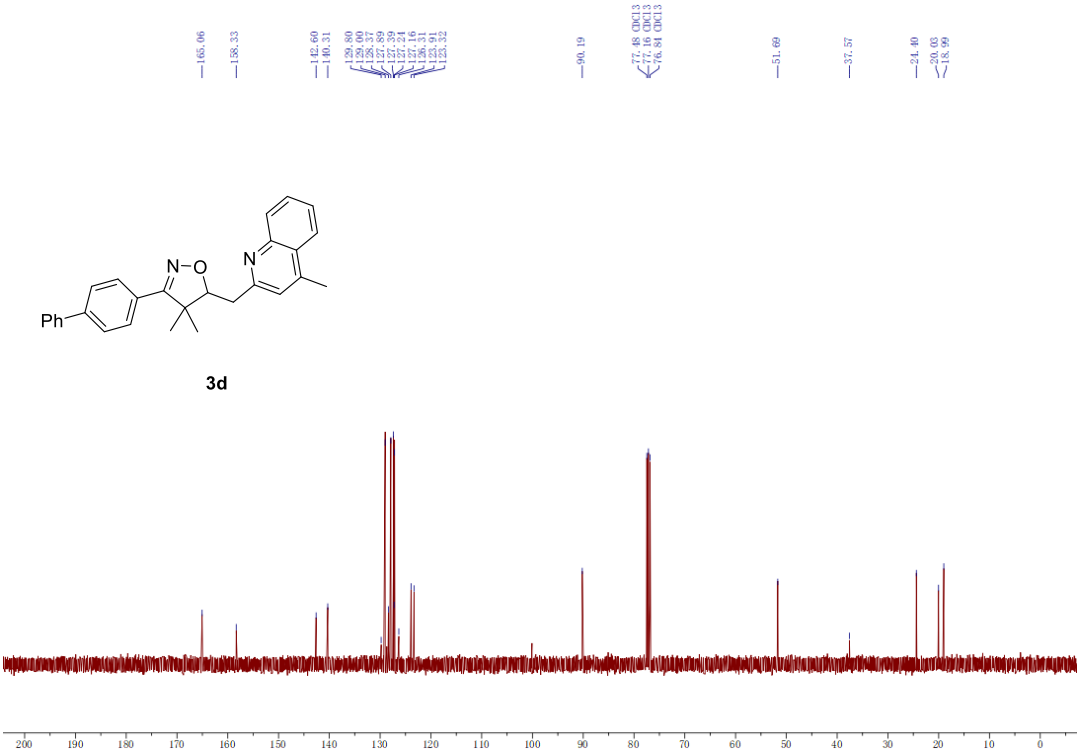


3-([1,1'-Biphenyl]-4-yl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3 d).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

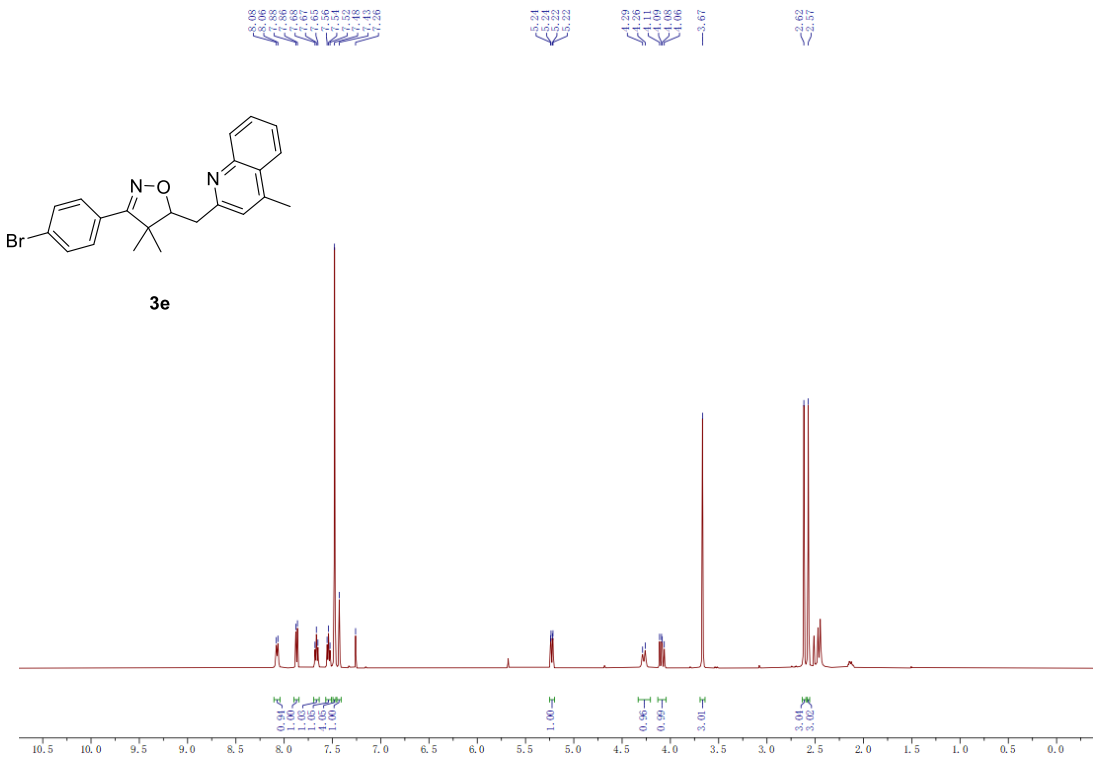


101 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

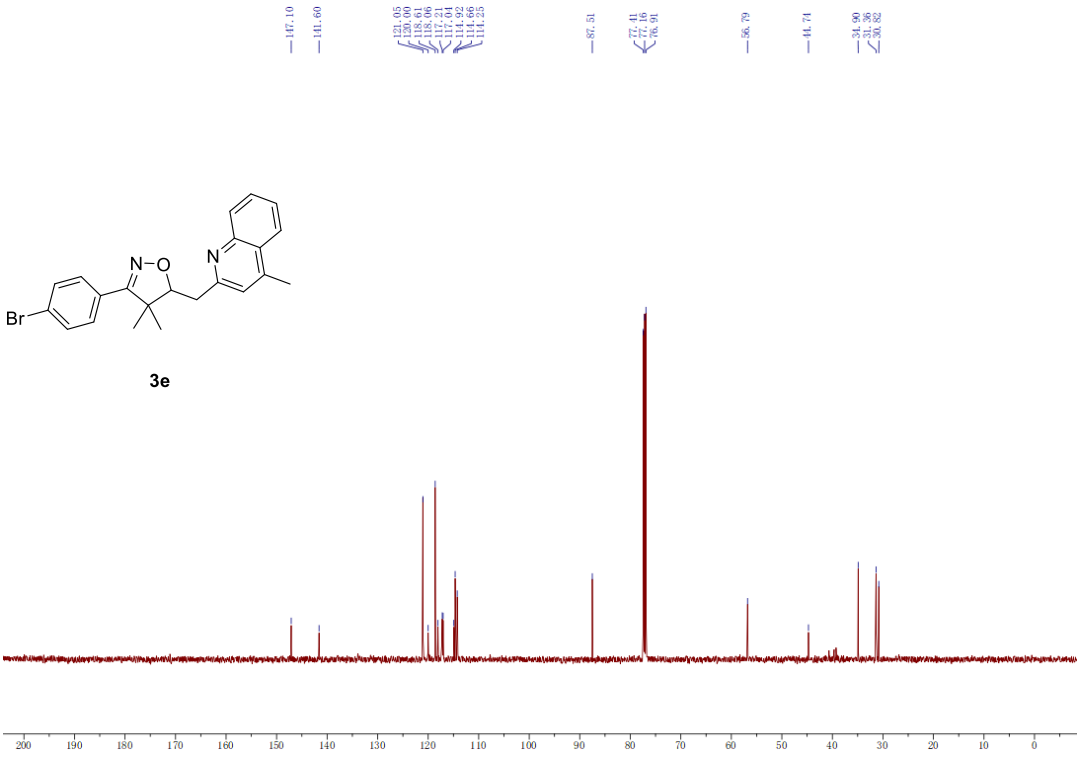


3-(4-Bromophenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3e).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

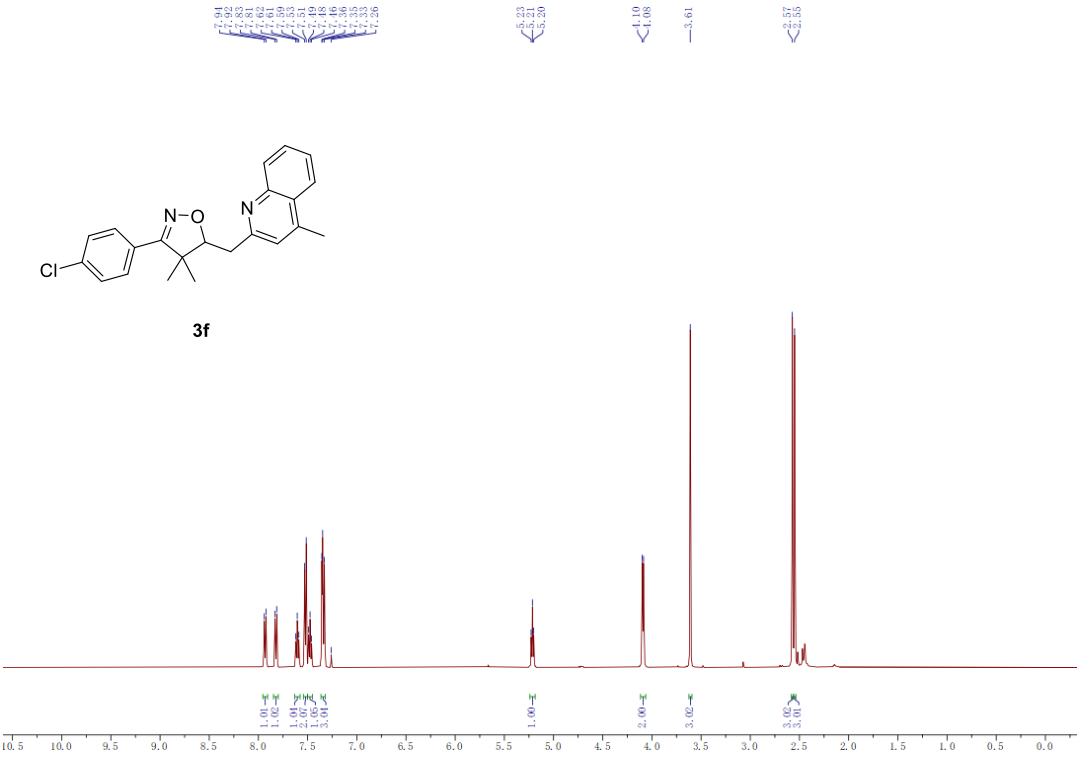


101 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

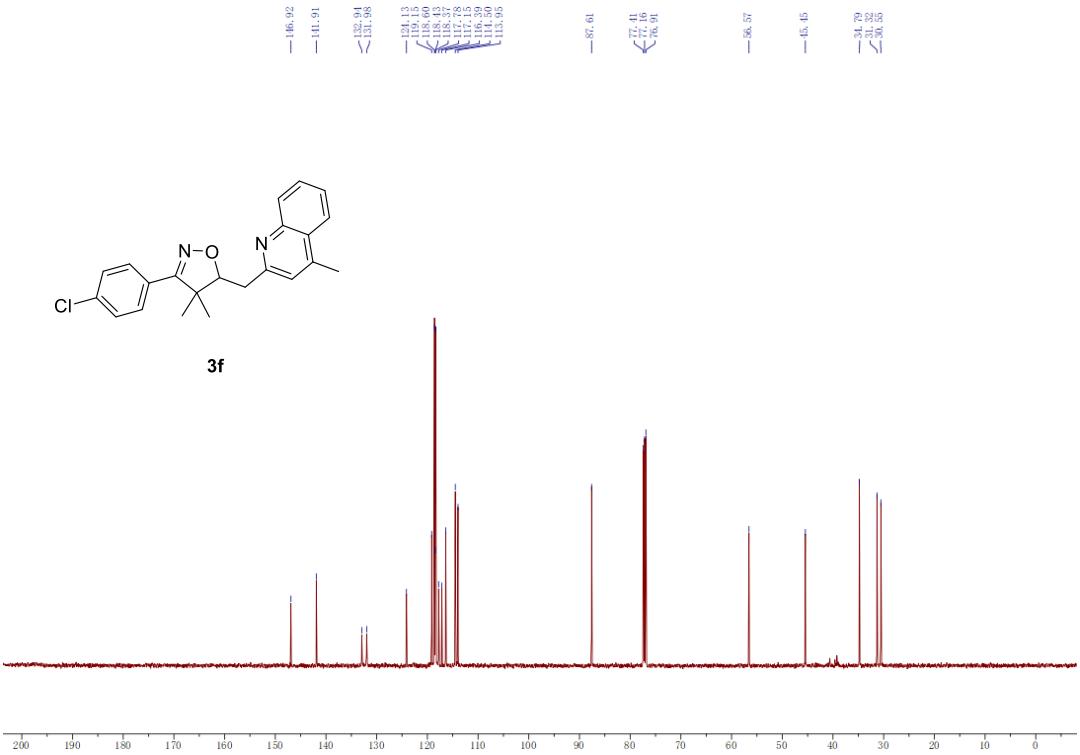


3-(4-Chlorophenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3f).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

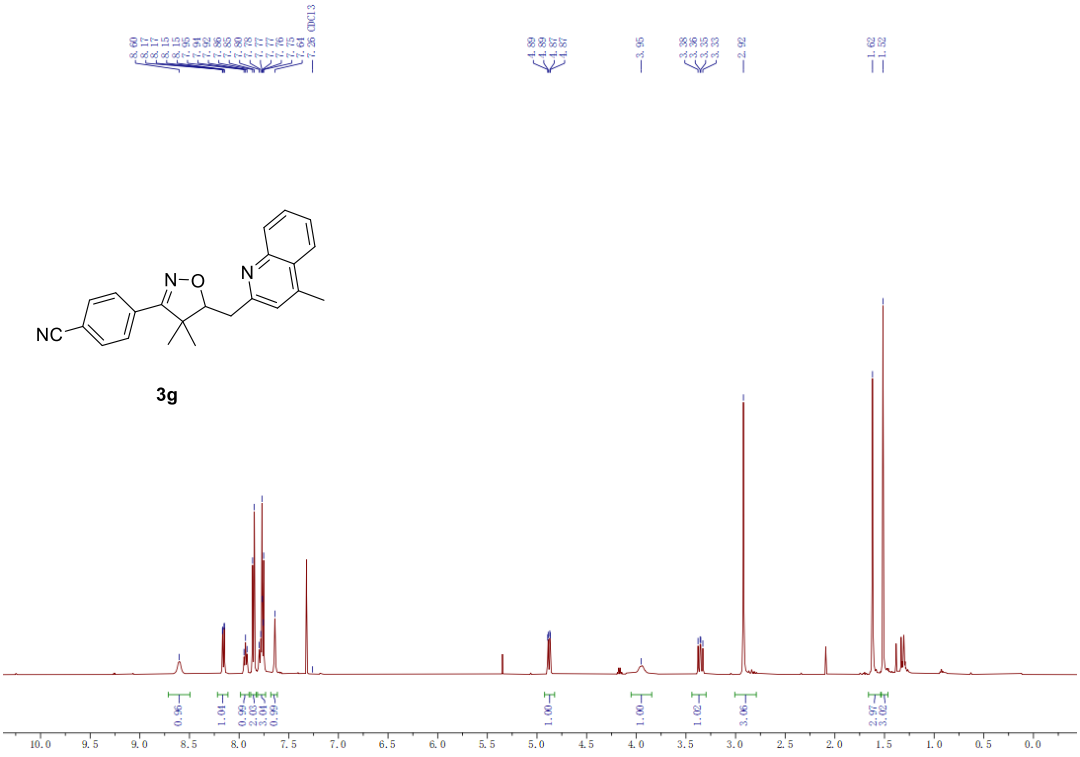


101 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

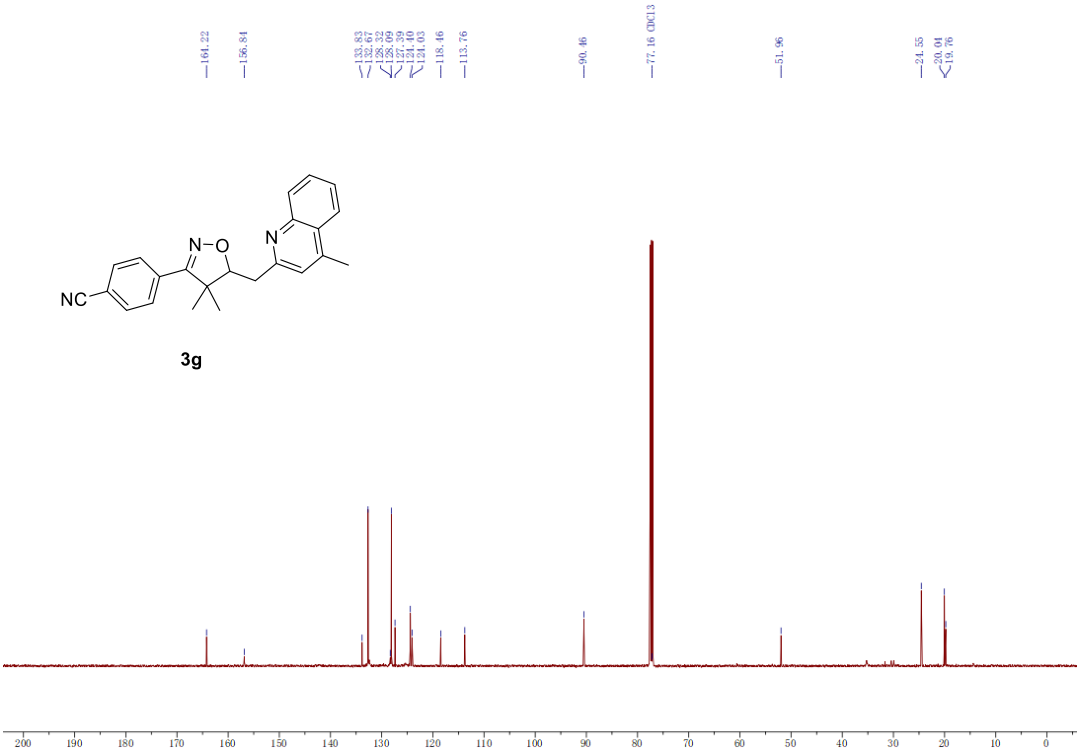


4-(4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazol-3-yl)benzonitrile (3g)

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

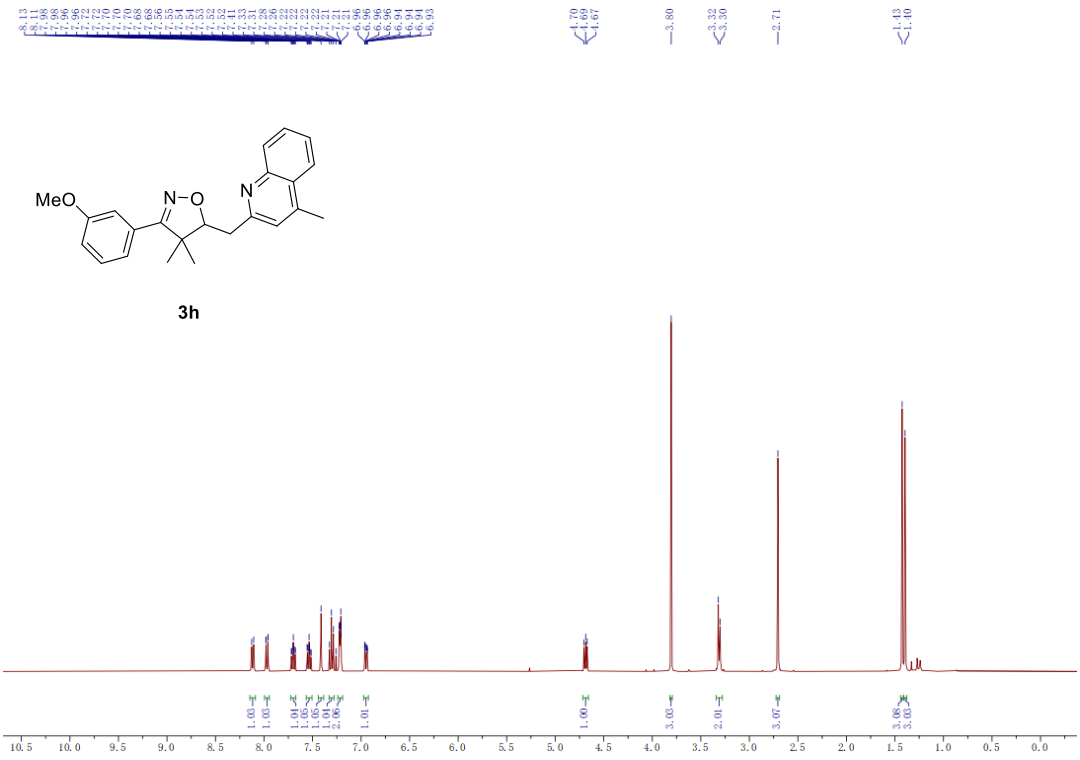


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

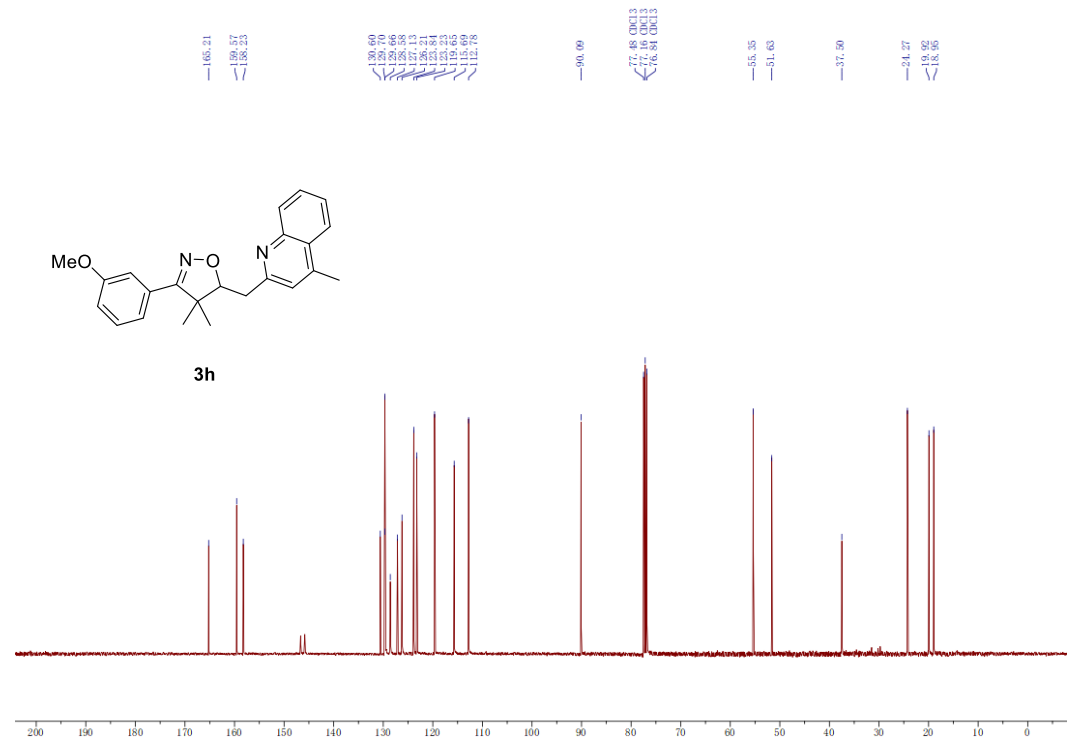


3-(3-Methoxyphenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3h).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

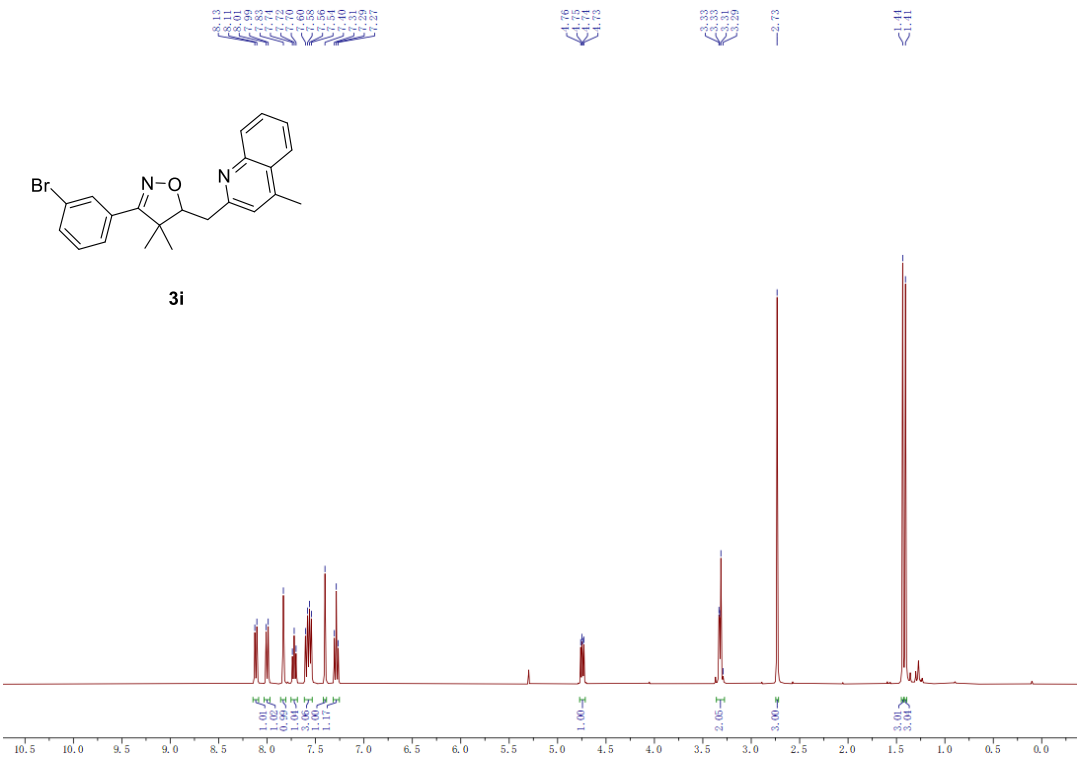


101 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

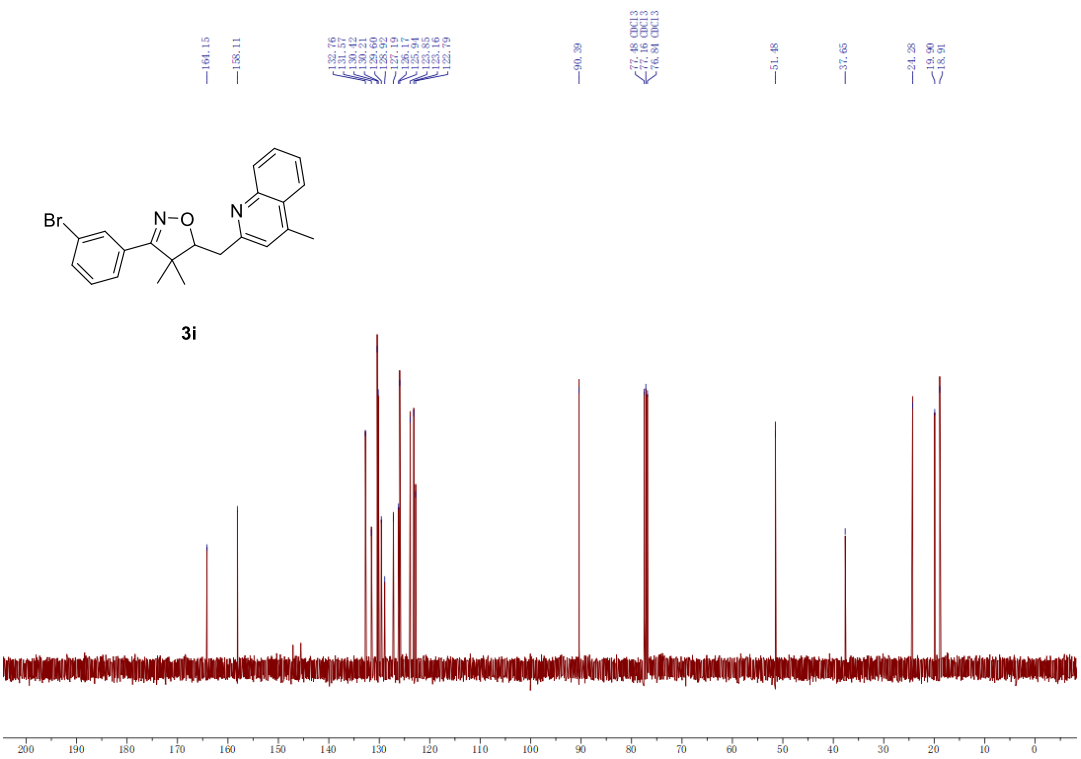


3-(3-Bromophenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3i).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

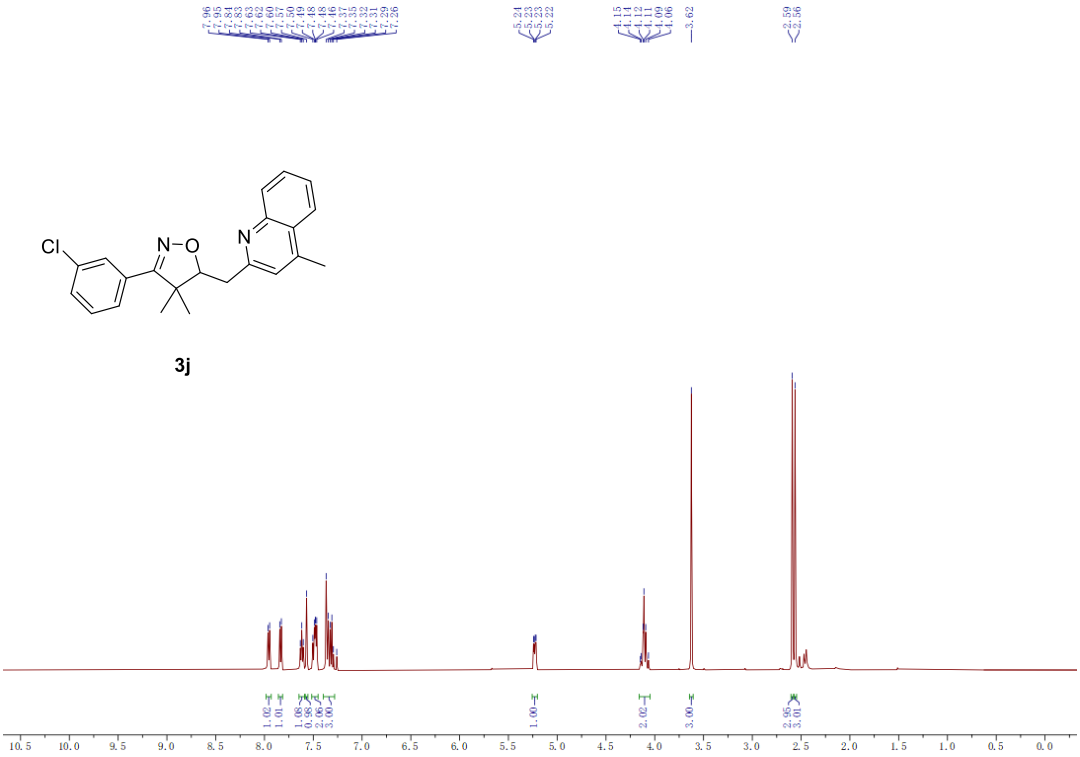


101 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)



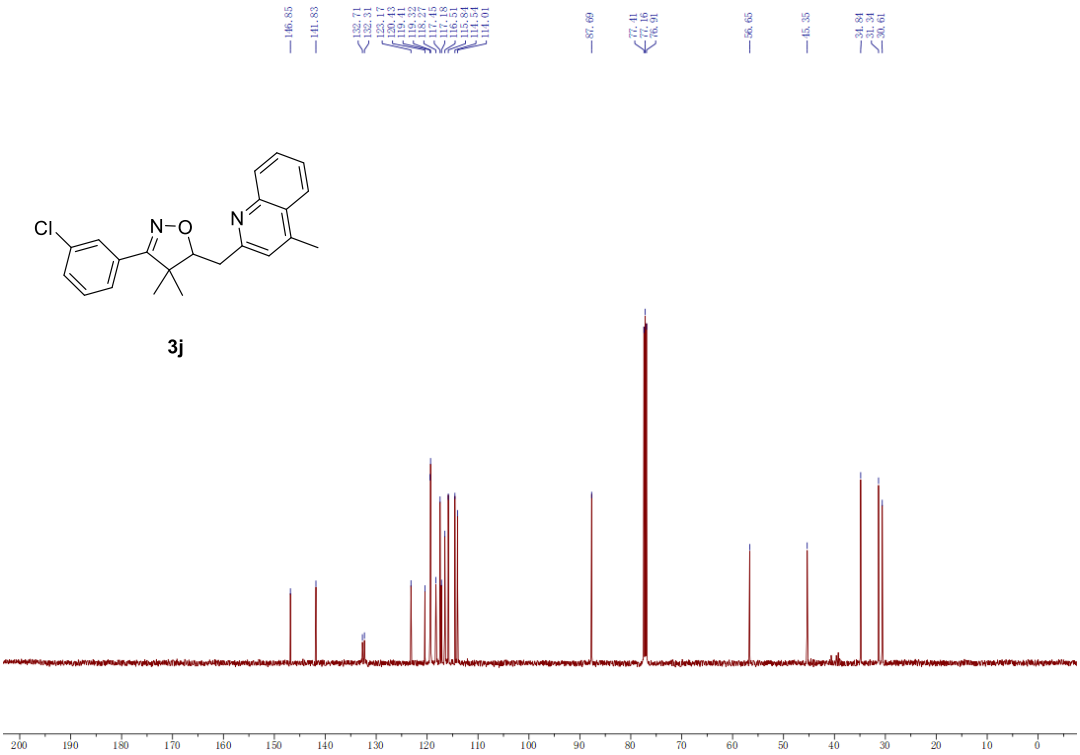
3-(3-Chlorophenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3j).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)



3j

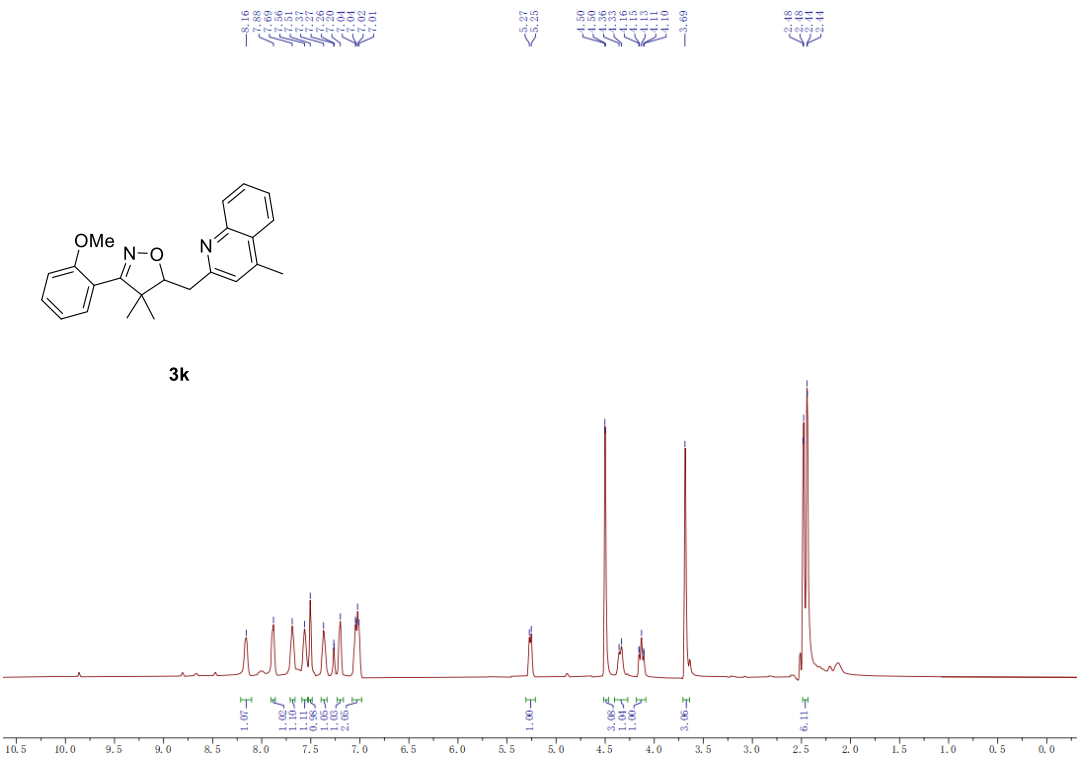
101 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)



3j

3-(2-Methoxyphenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3k).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)



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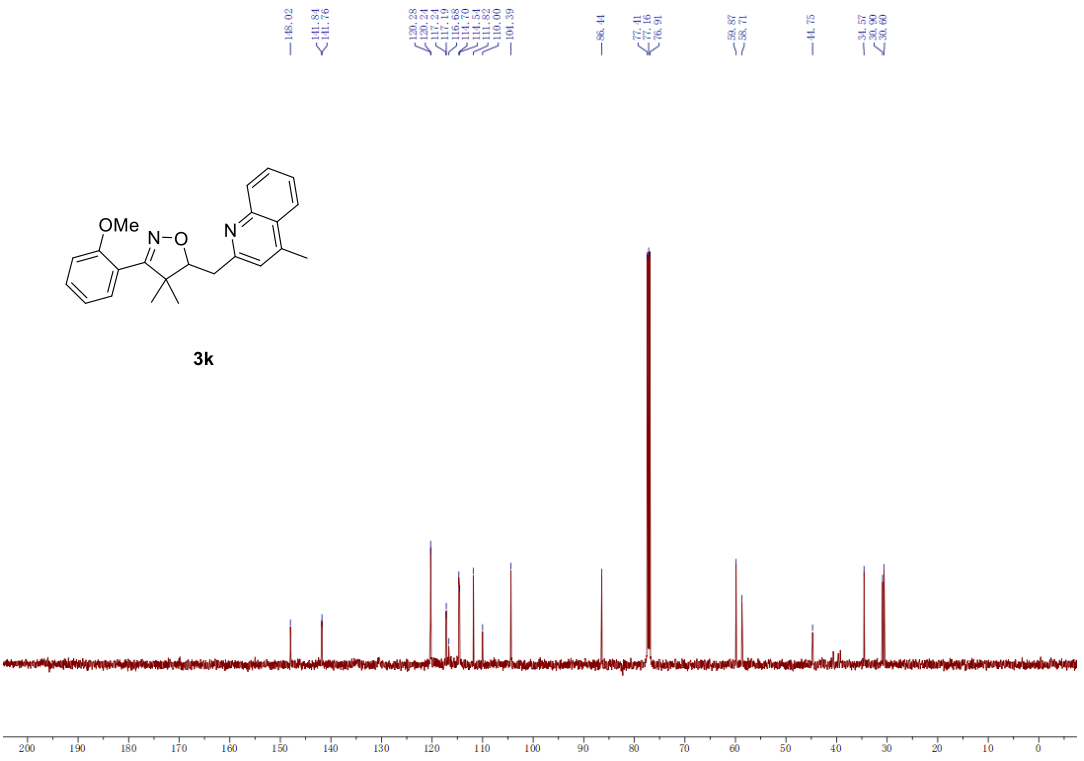
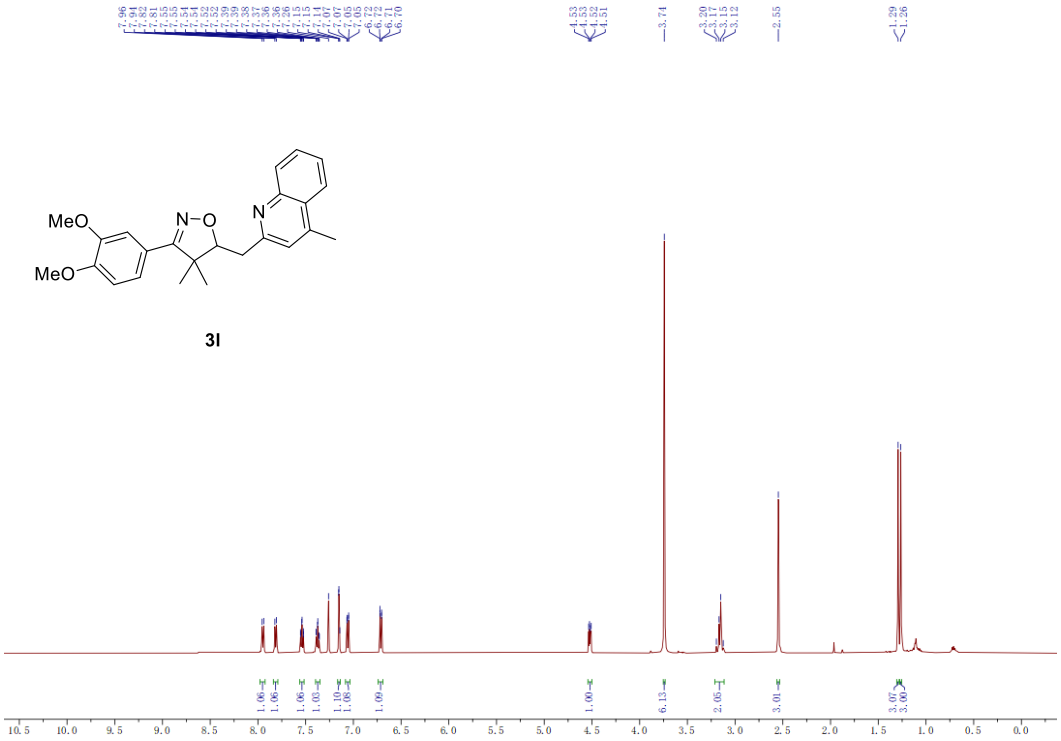
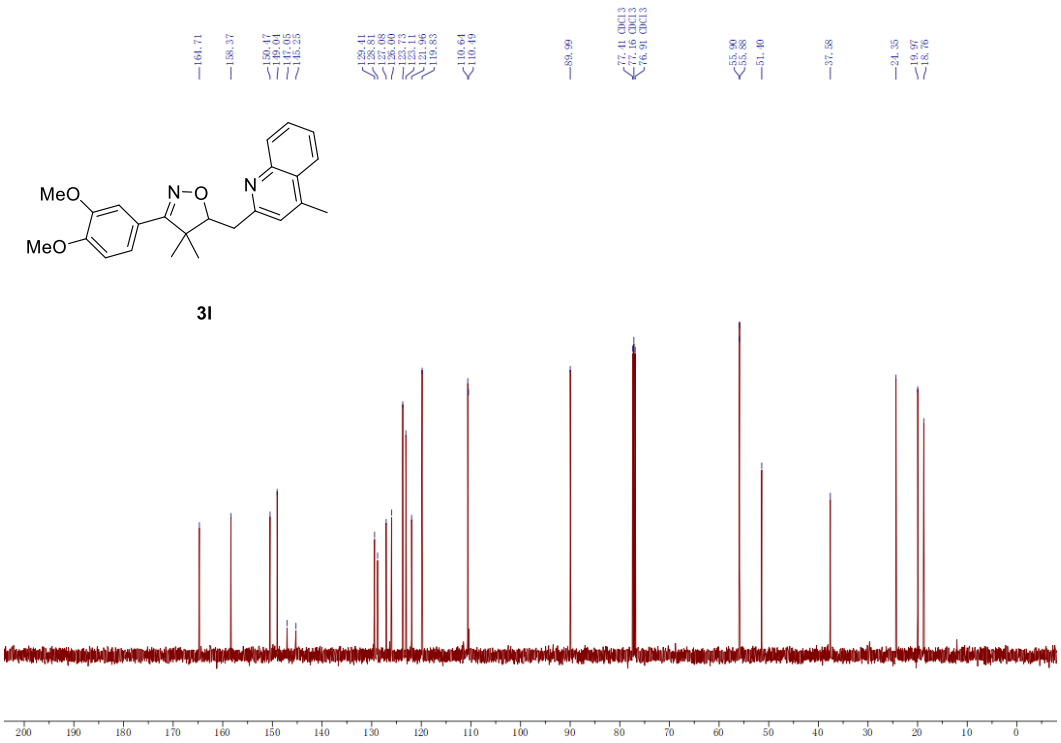


3-(3,4-Dimethoxyphenyl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3l).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

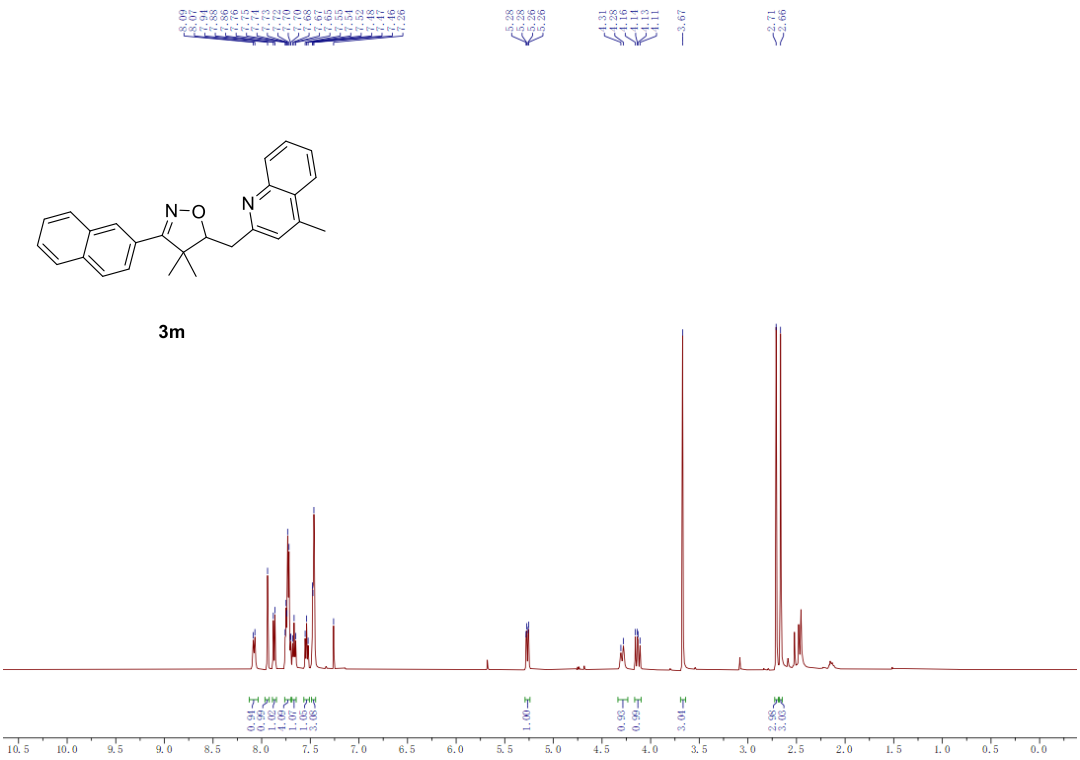


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

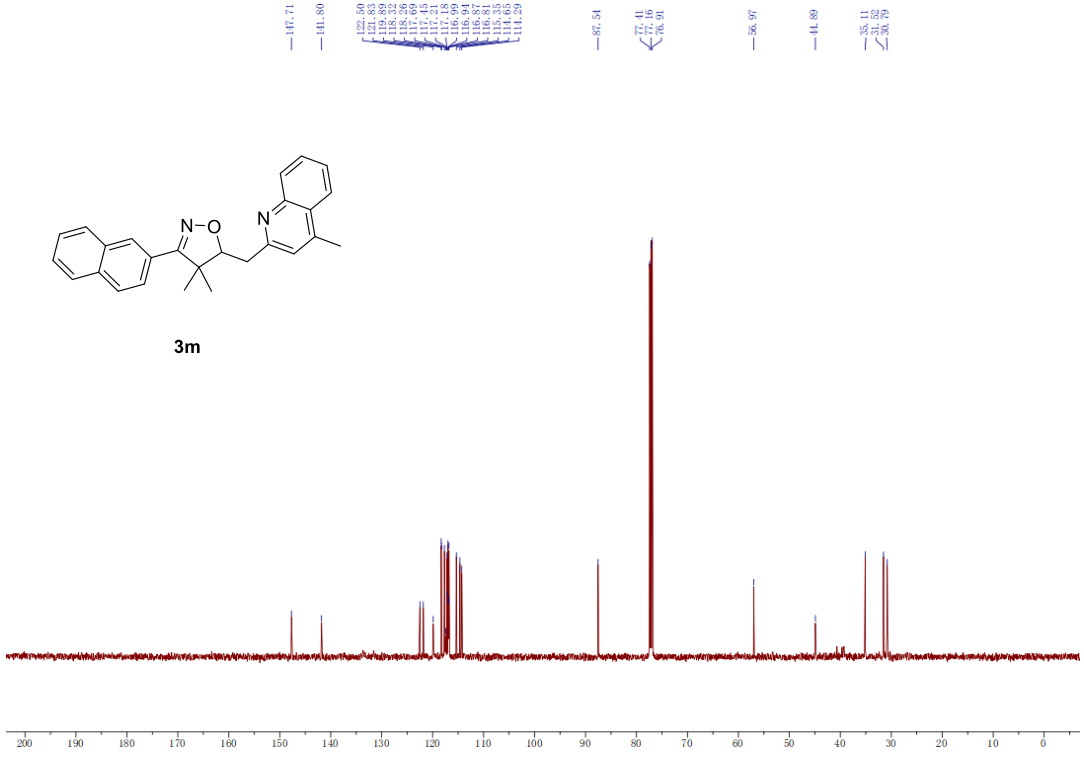


4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-3-(naphthalen-2-yl)-4,5-dihydroisoxazole (3m).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

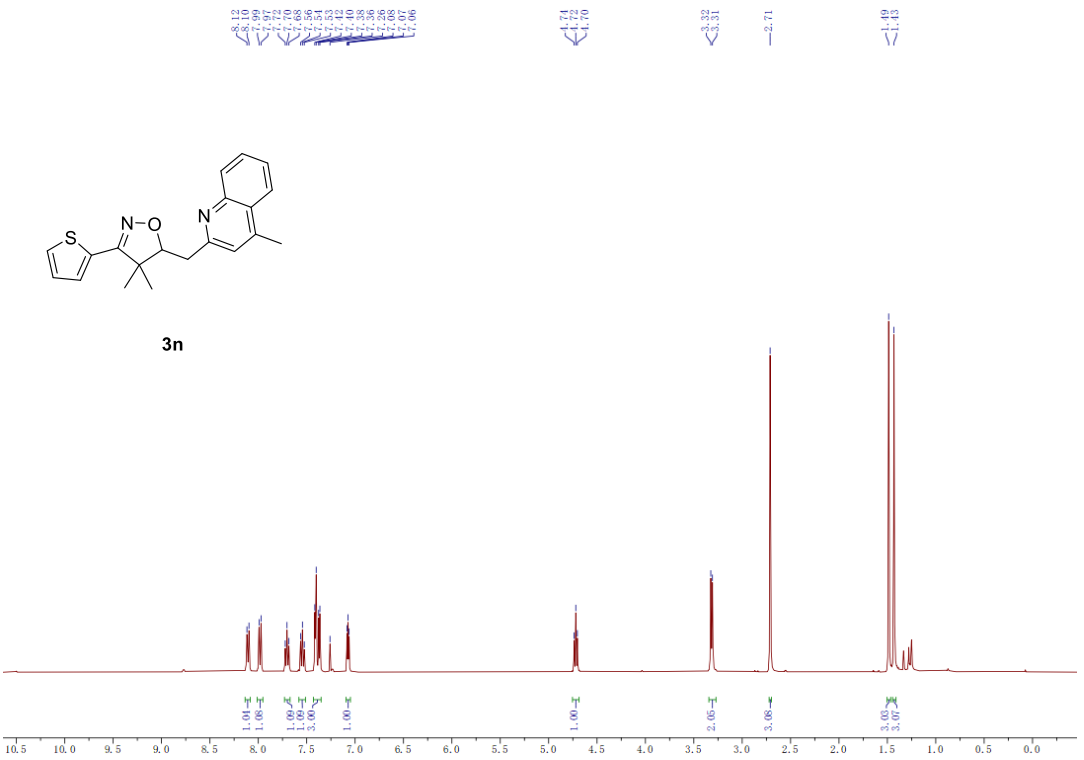


101 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)



4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-3-(thiophen-2-yl)-4,5-dihydroisoxazole (3n).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)



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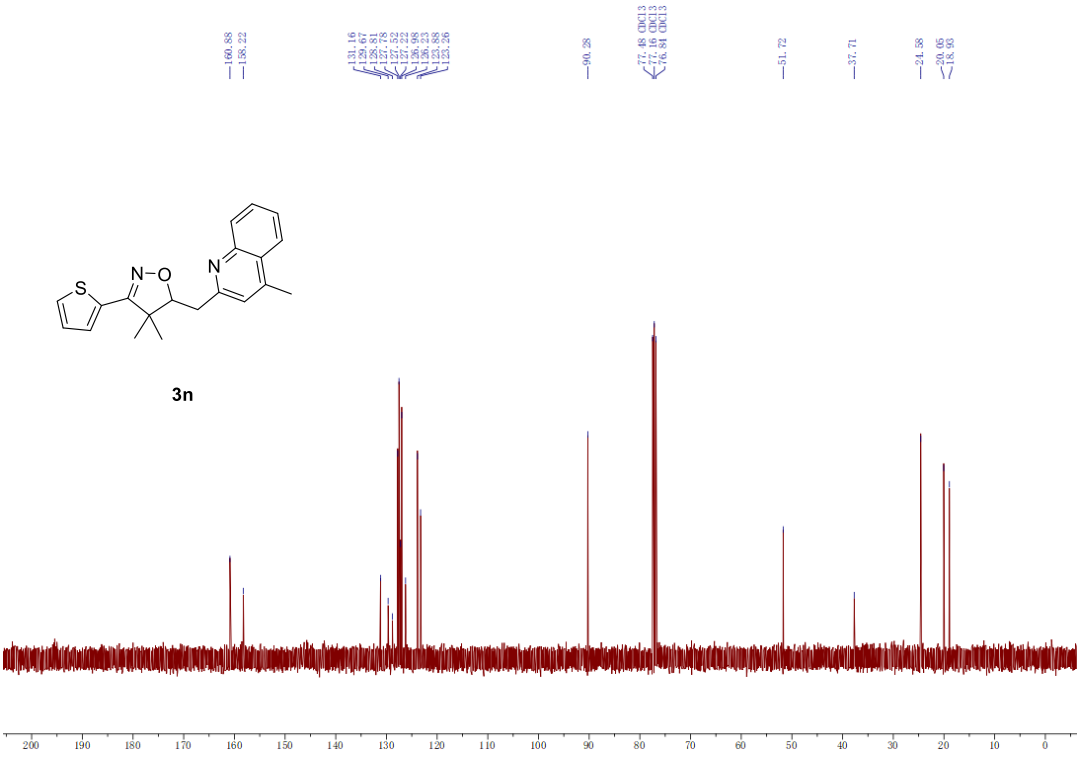
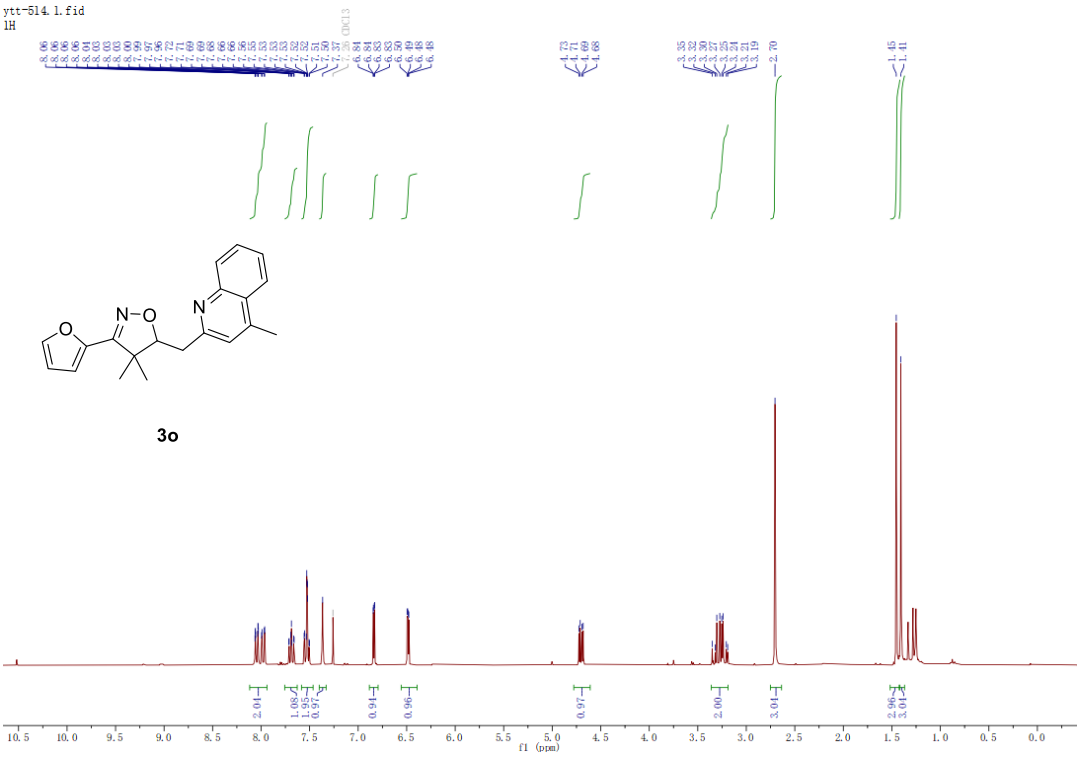
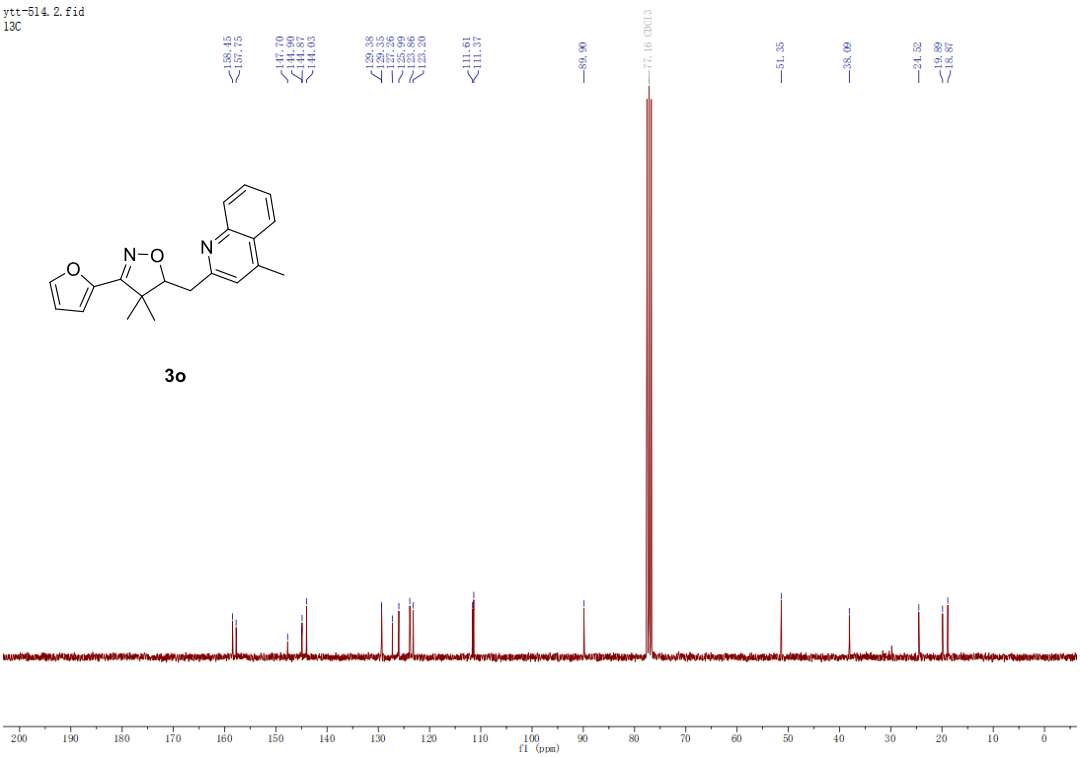


3-(Furan-2-yl)-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3o).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

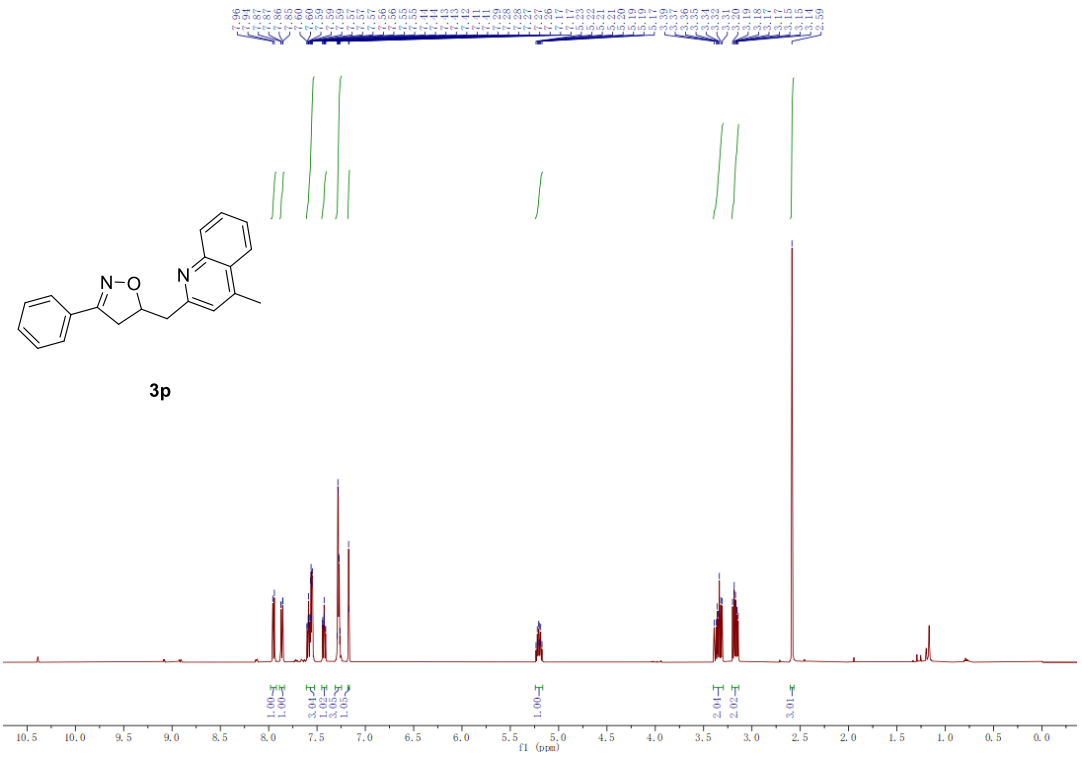


75 MHz $^{13}C\{^{1}H\}$ NMR Spectrum (recorded in $CDCl_3$)

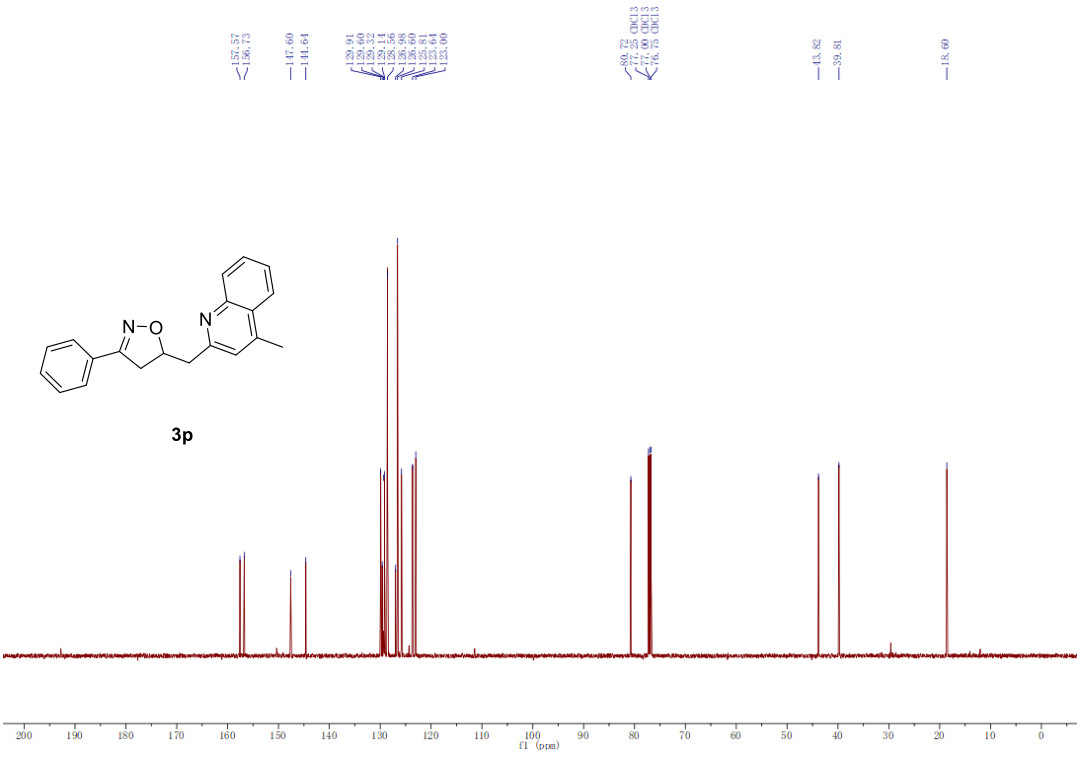


5-((4-Methylquinolin-2-yl)methyl)-3-phenyl-4,5-dihydroisoxazole (3p).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

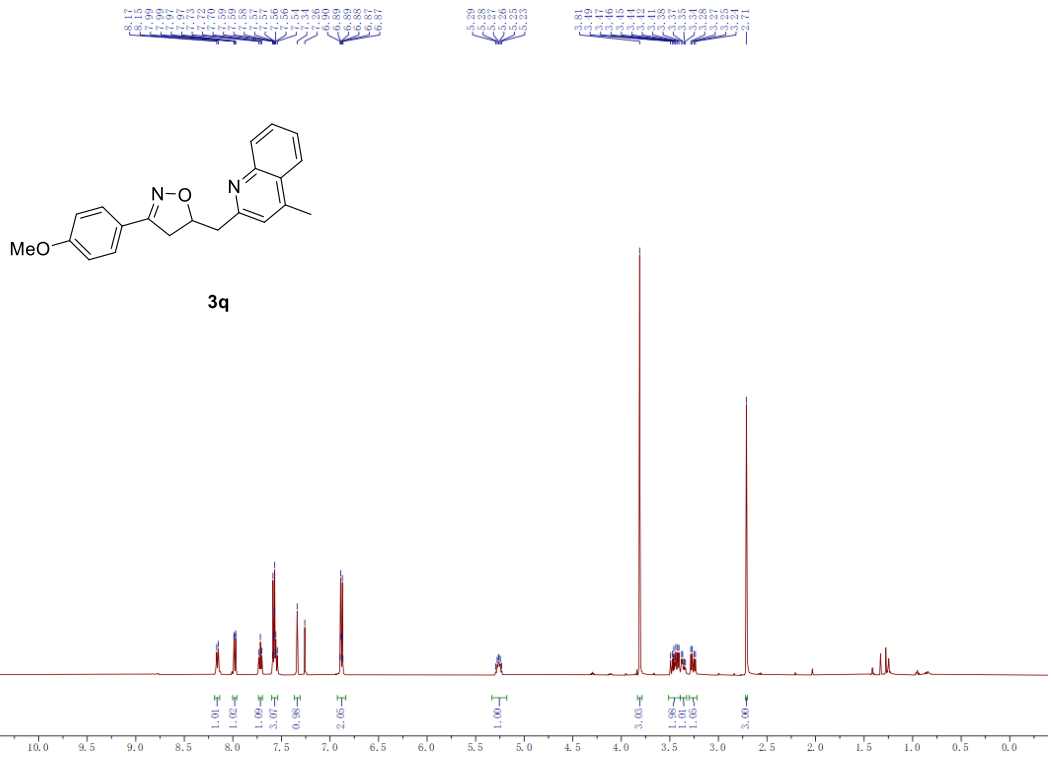


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

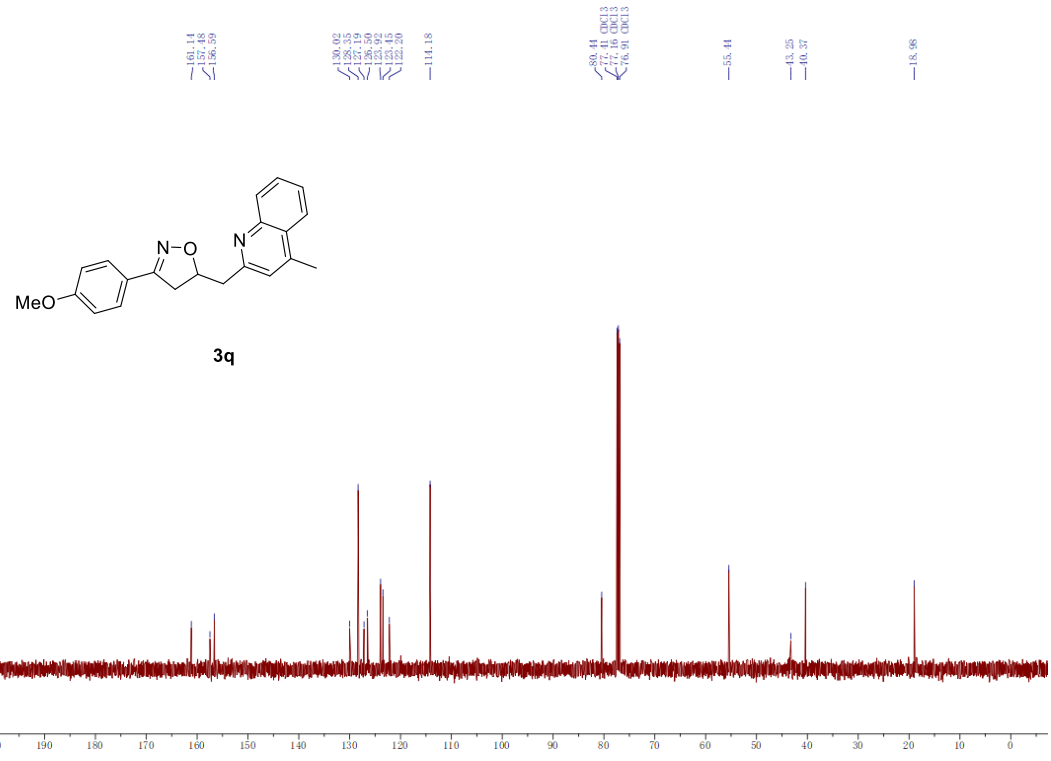


3-(4-Methoxyphenyl)-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3q).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

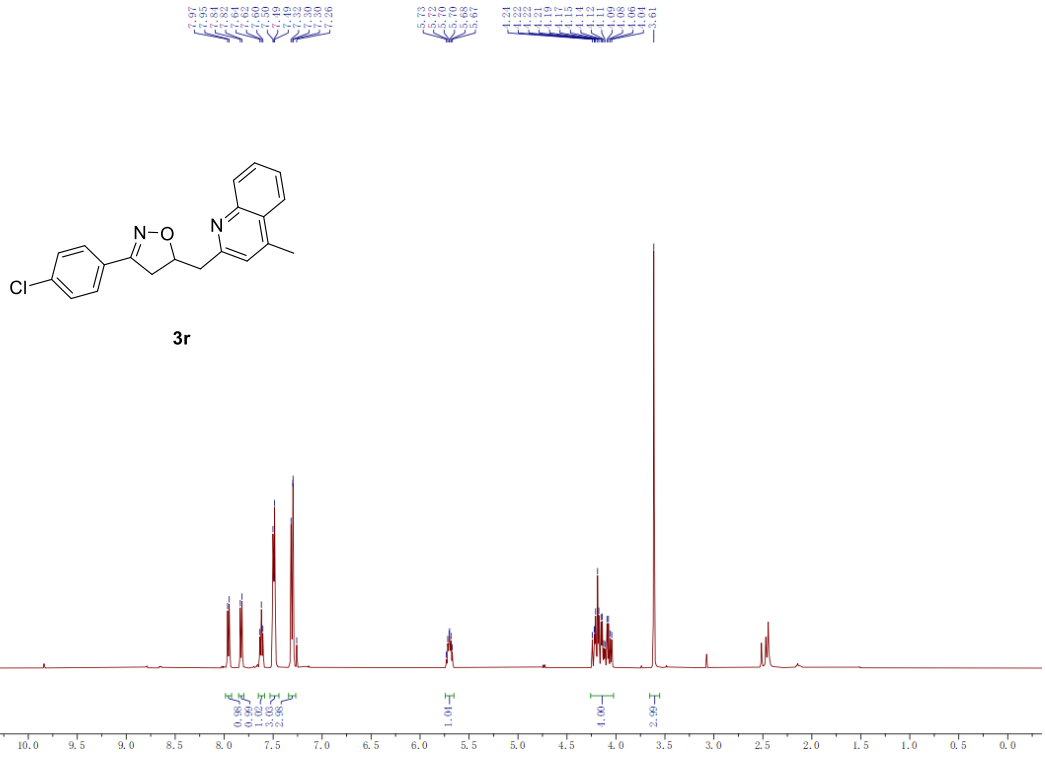


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

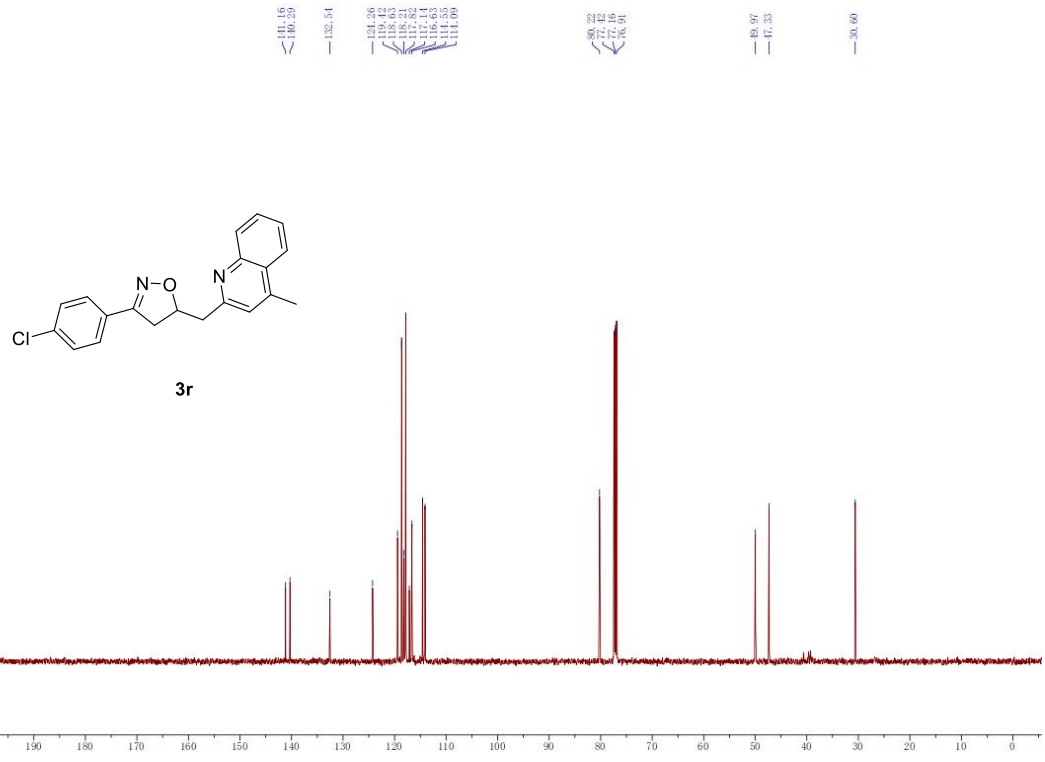


3-(4-Chlorophenyl)-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3r).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

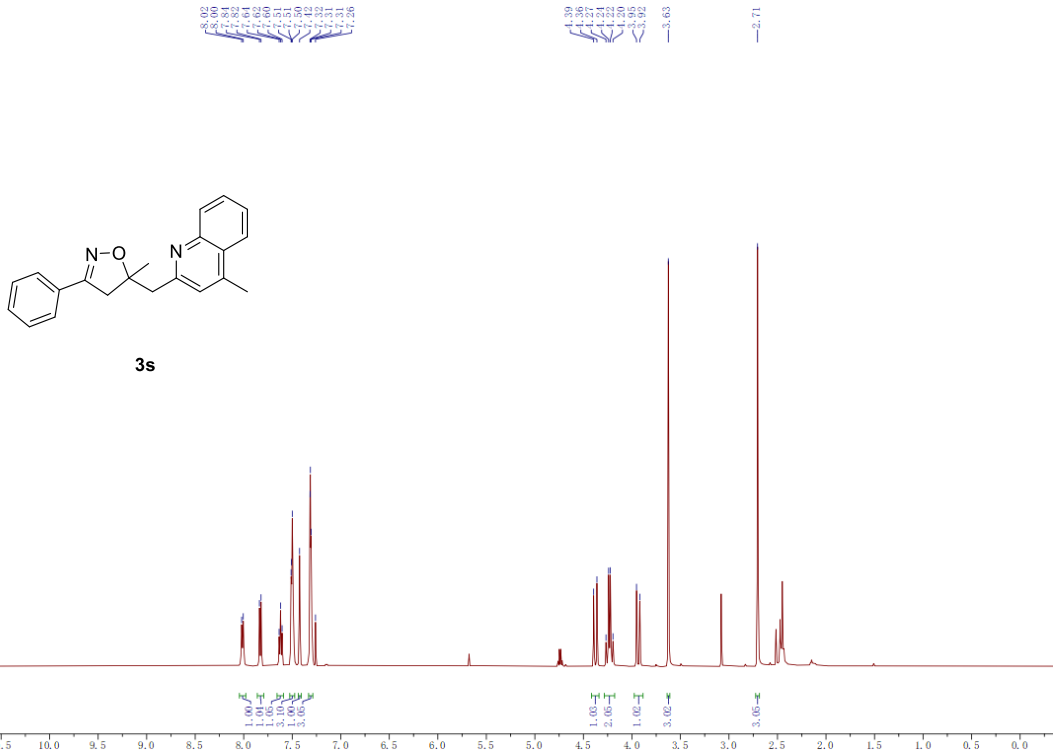


101 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

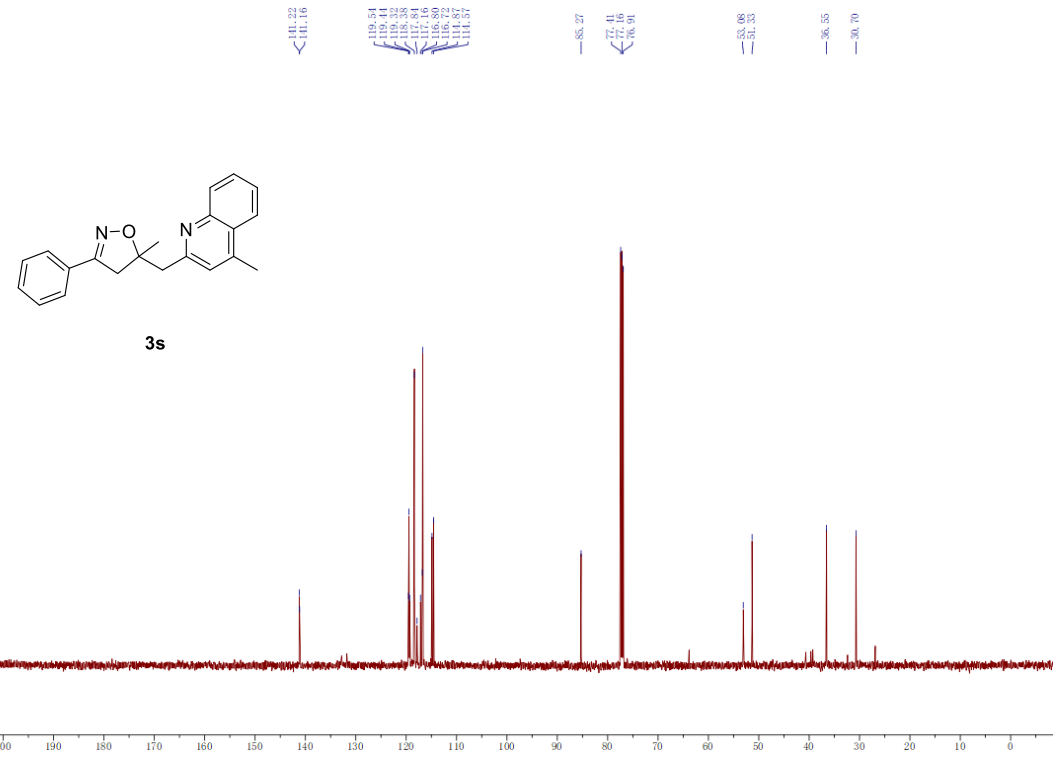


5-Methyl-5-((4-methylquinolin-2-yl)methyl)-3-phenyl-4,5-dihydroisoxazole (3s).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

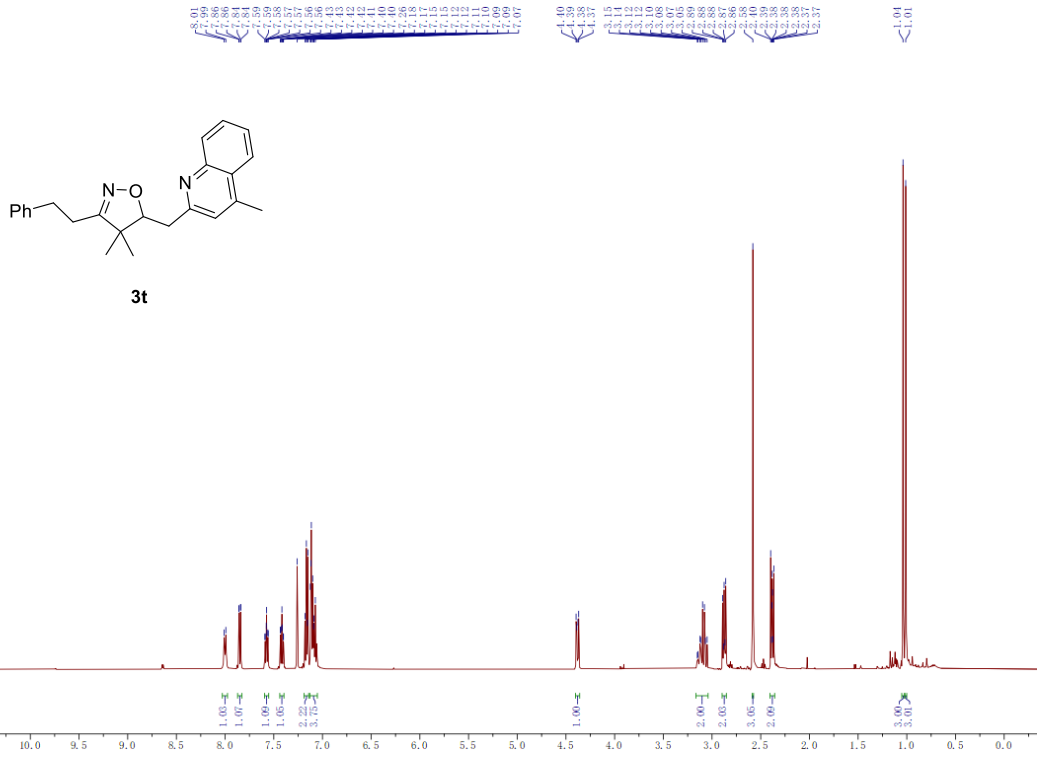


101 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

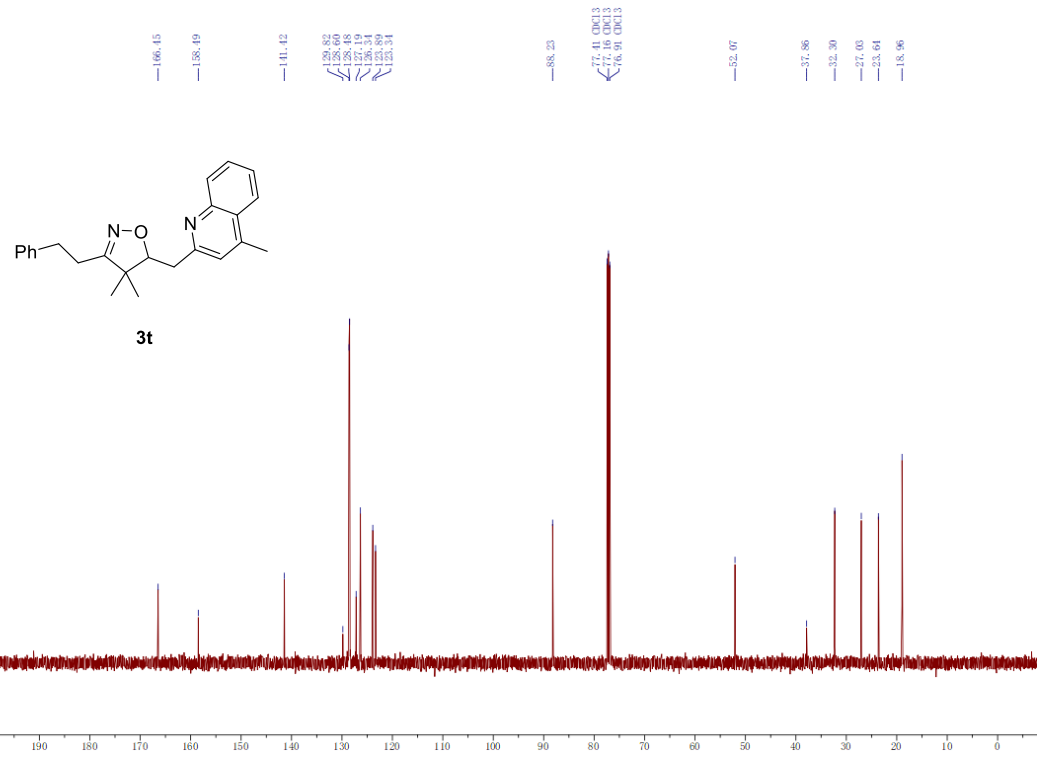


4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-3-phenethyl-4,5-dihydroisoxazole (3t).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

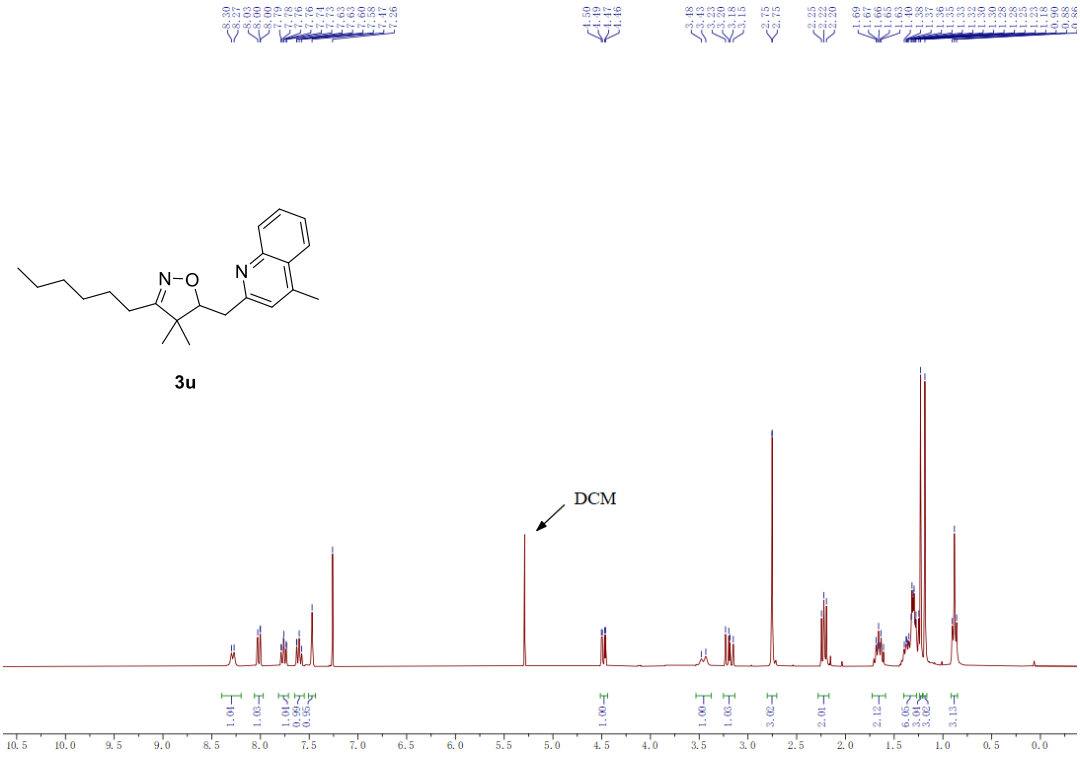


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

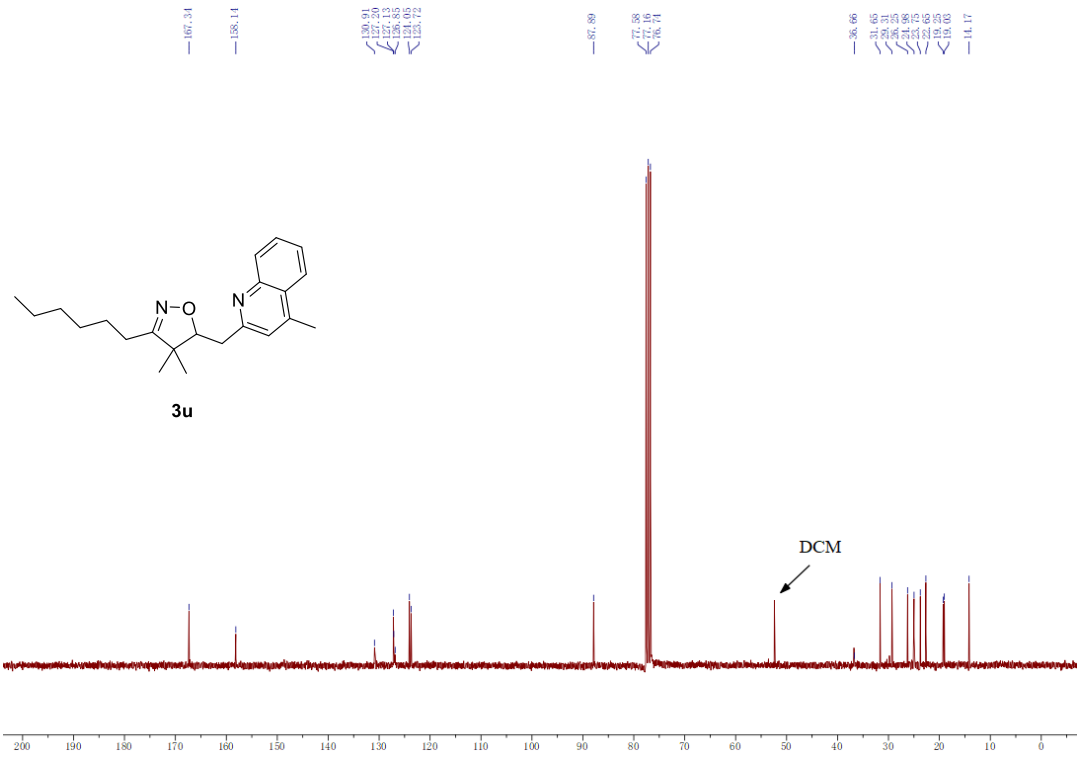


3-Hexyl-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3u).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

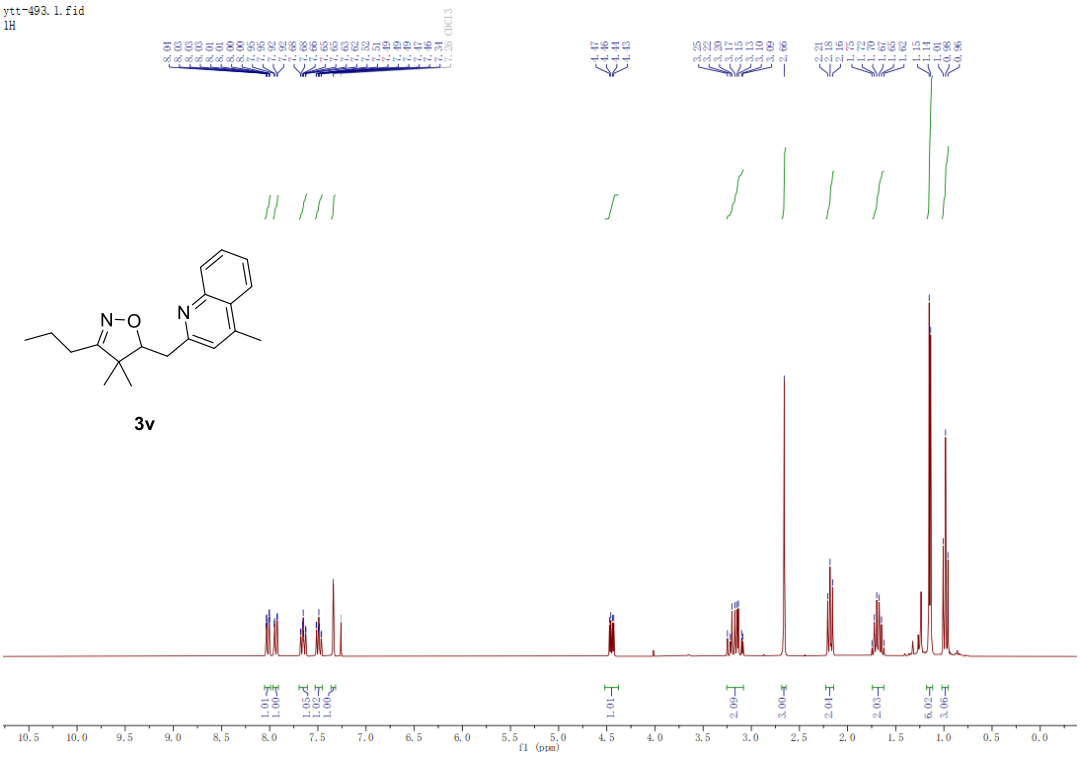


75 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

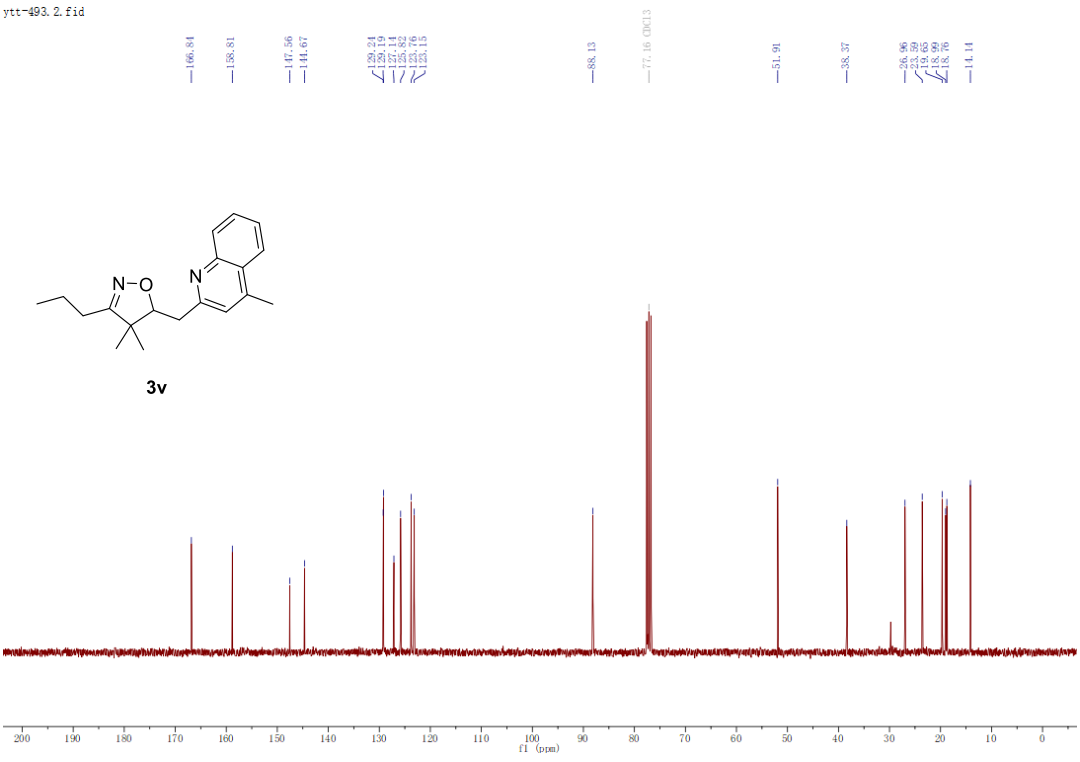


4,4-Dimethyl-5-((4-methylquinolin-2-yl)methyl)-3-propyl-4,5-dihydroisoxazole (3v).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

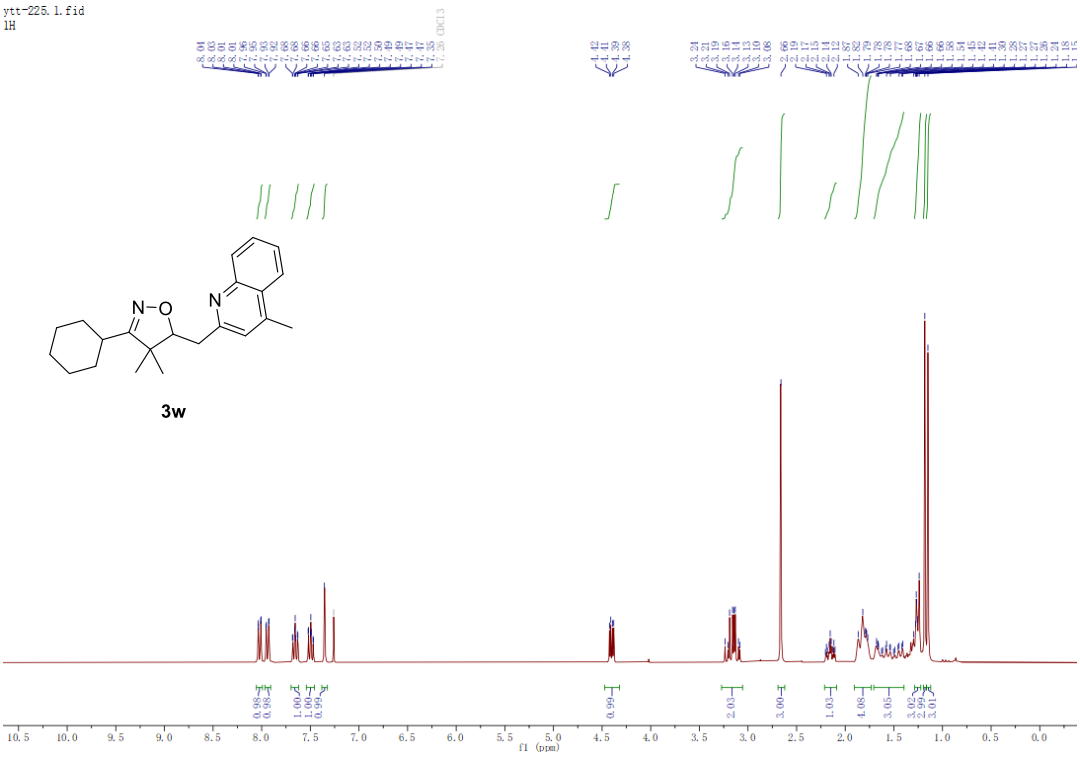


75 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

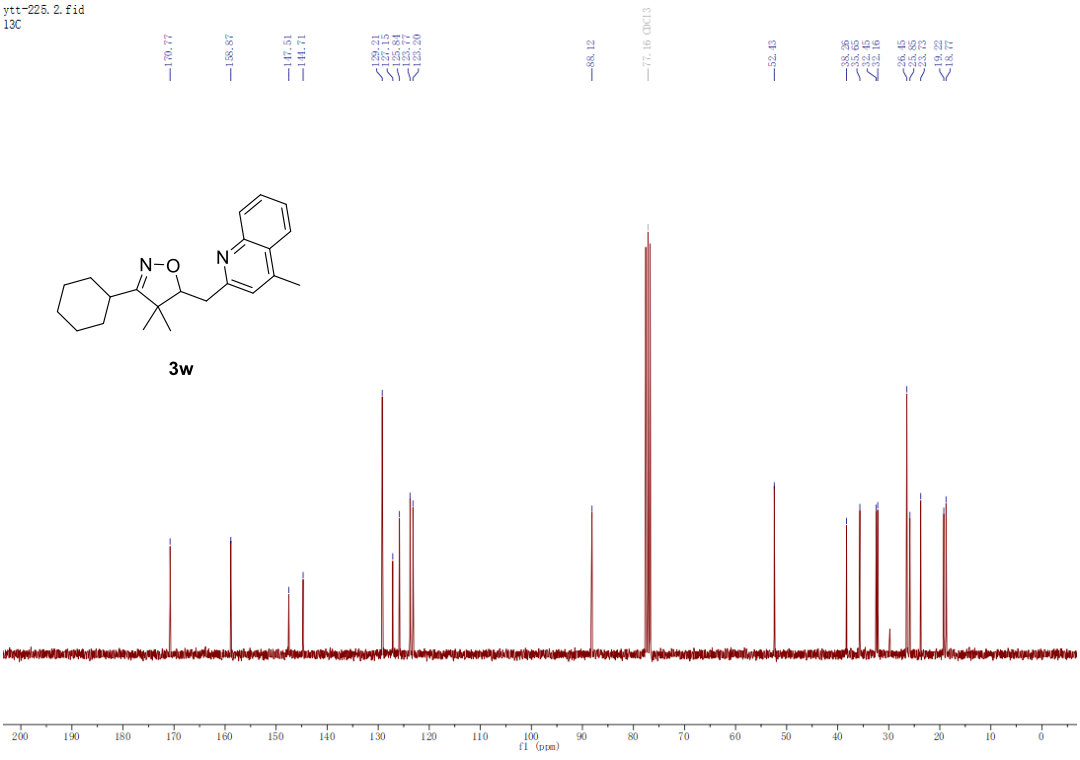


3-Cyclohexyl-4,4-dimethyl-5-((4-methylquinolin-2-yl)methyl)-4,5-dihydroisoxazole (3w).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

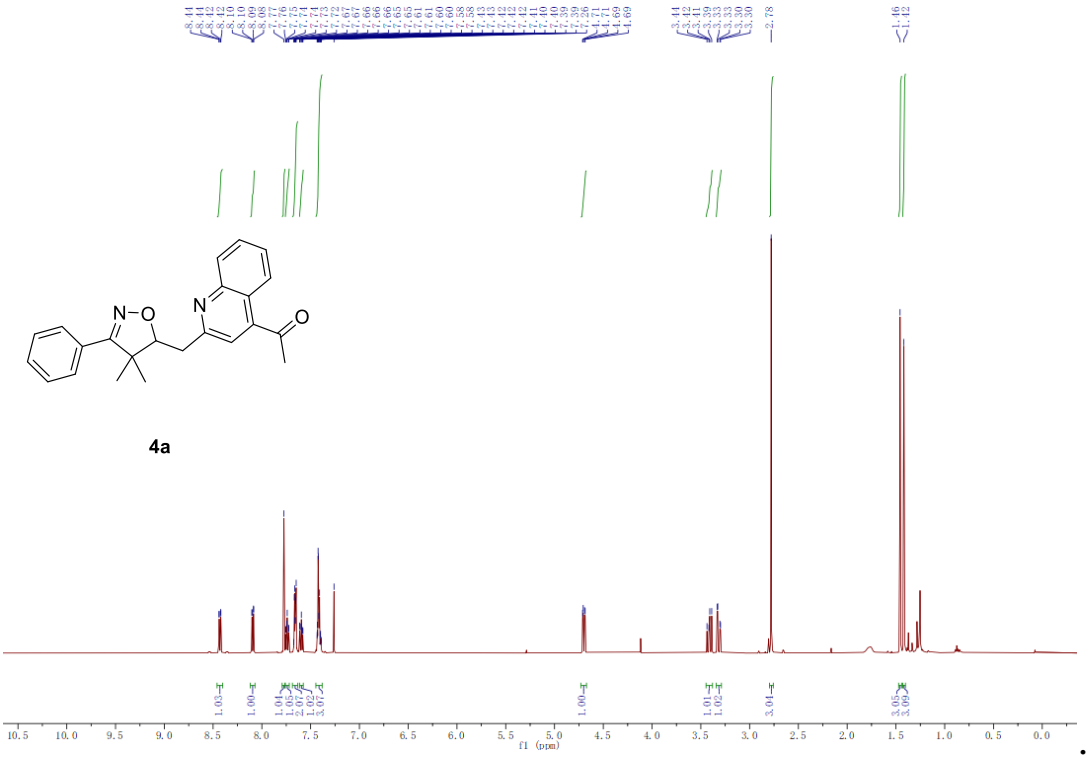


75 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

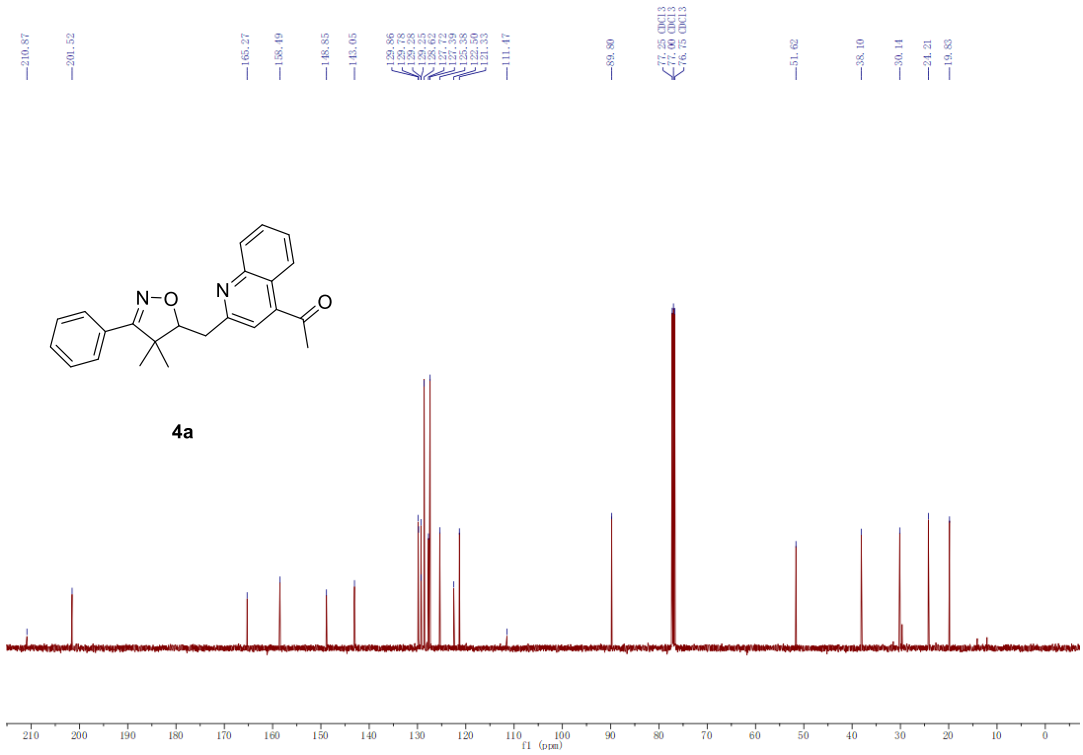


1-(2-((4,4-Dimethyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)quinolin-4-yl)ethan-1-one (4a).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

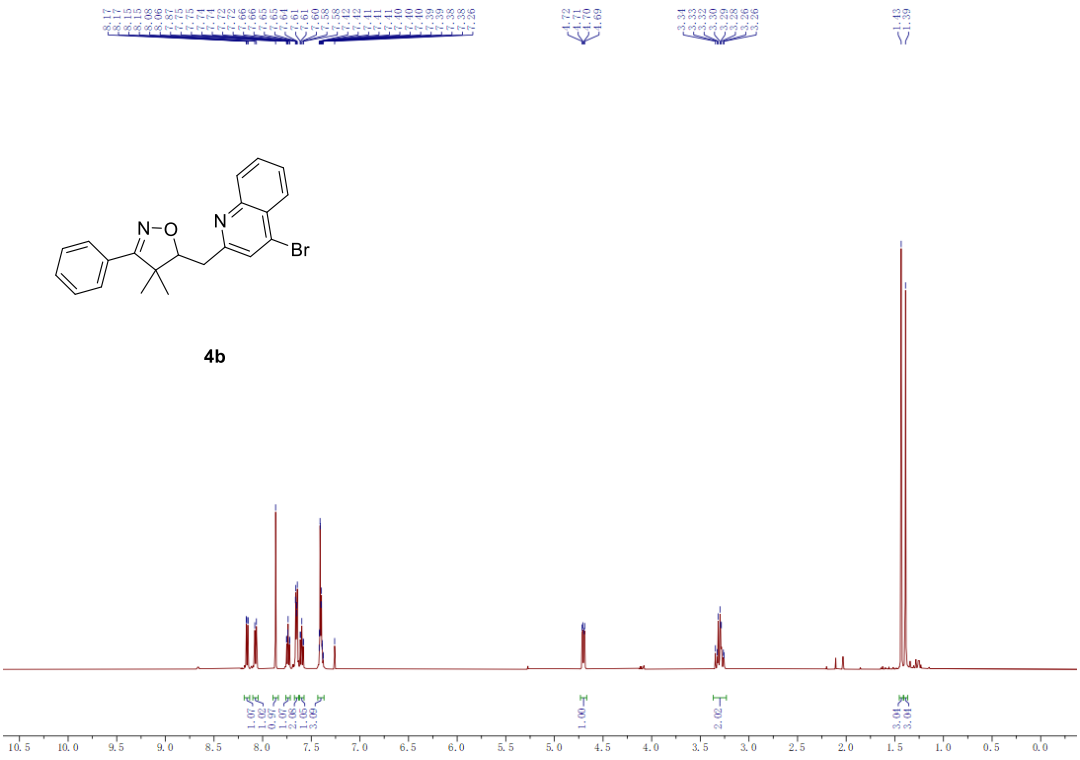


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

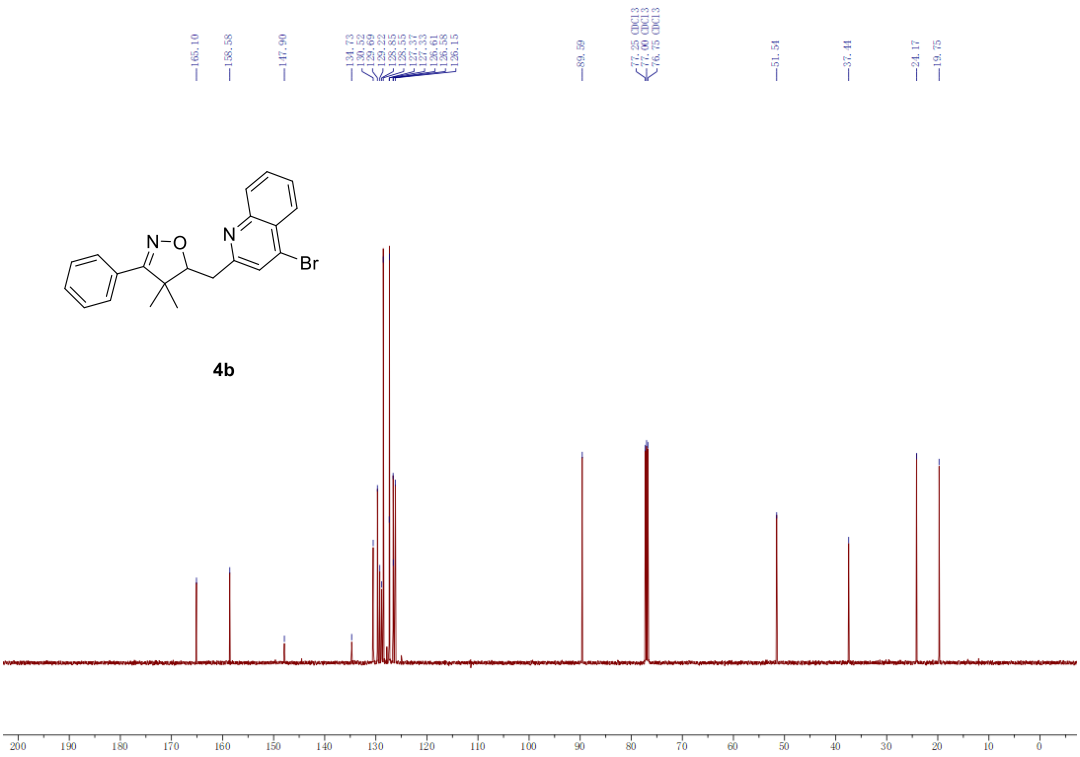


5-((4-Bromoquinolin-2-yl)methyl)-4,4-dimethyl-3-phenyl-4,5-dihydroisoxazole (4b).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

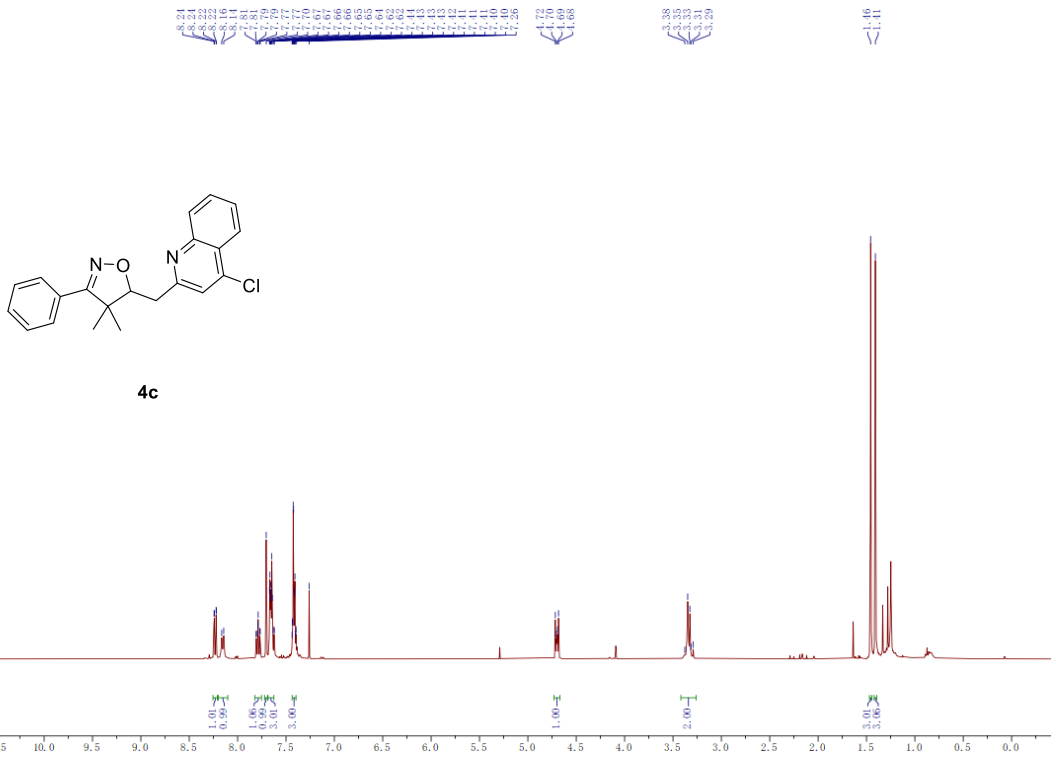


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

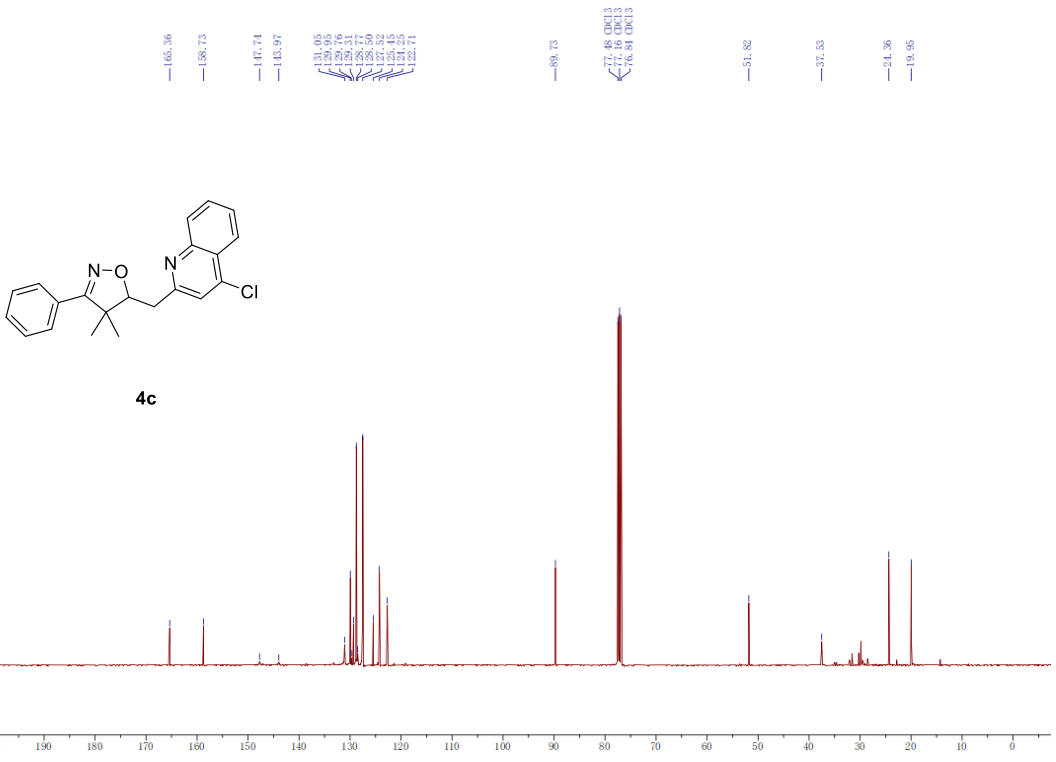


5-((4-Chloroquinolin-2-yl)methyl)-4,4-dimethyl-3-phenyl-4,5-dihydroisoxazole (4c).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

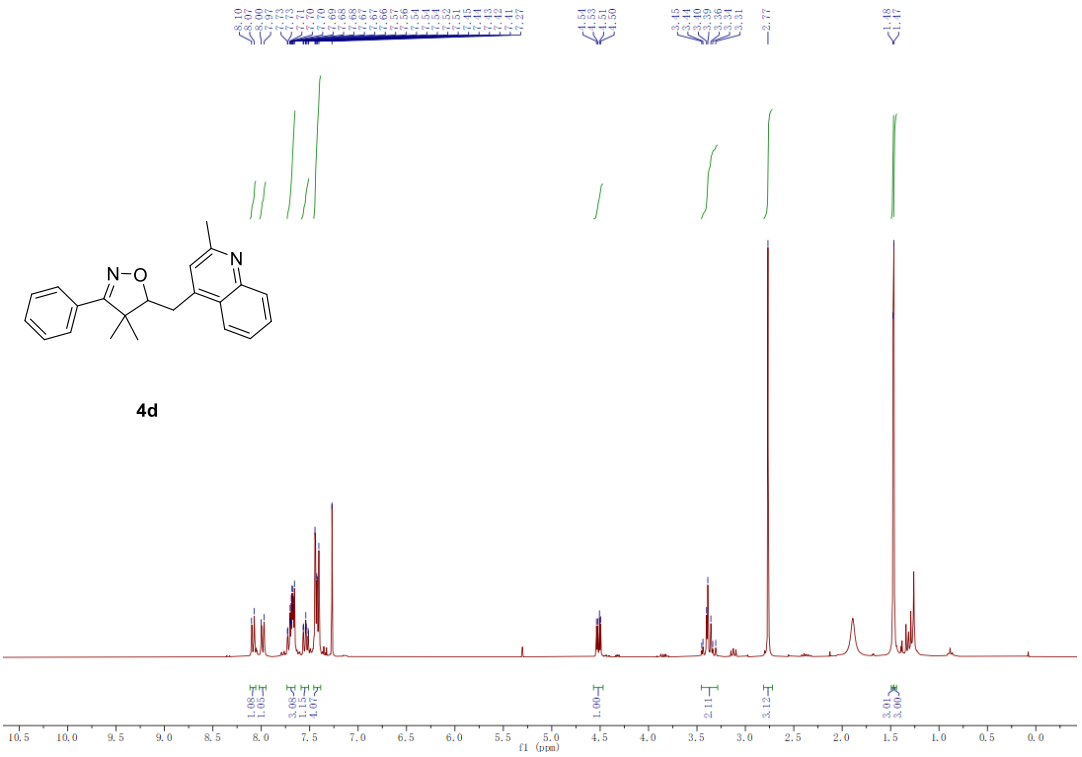


101 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

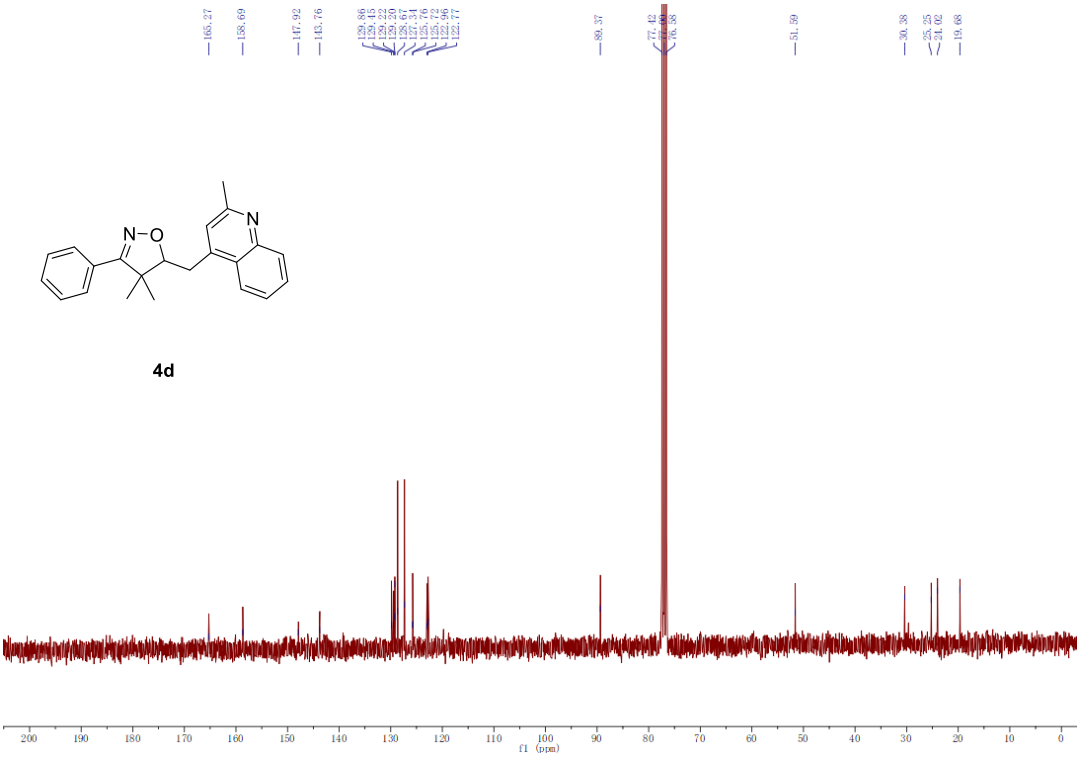


4,4-Dimethyl-5-((2-methylquinolin-4-yl)methyl)-3-phenyl-4,5-dihydroisoxazole (4d).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

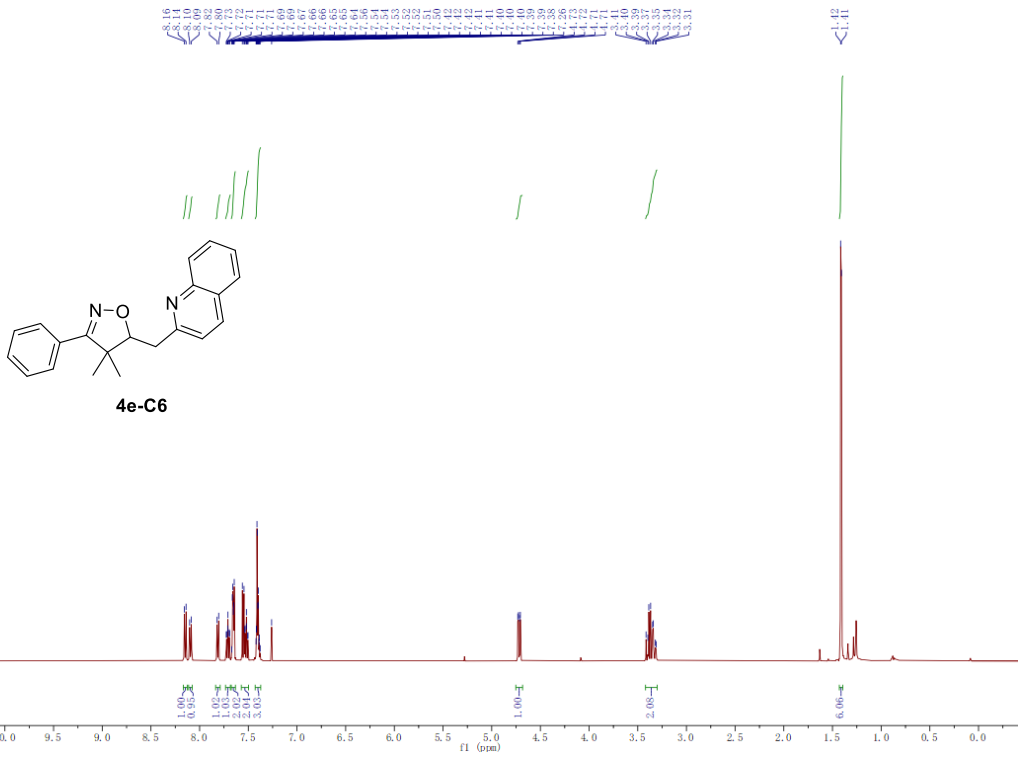


75 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

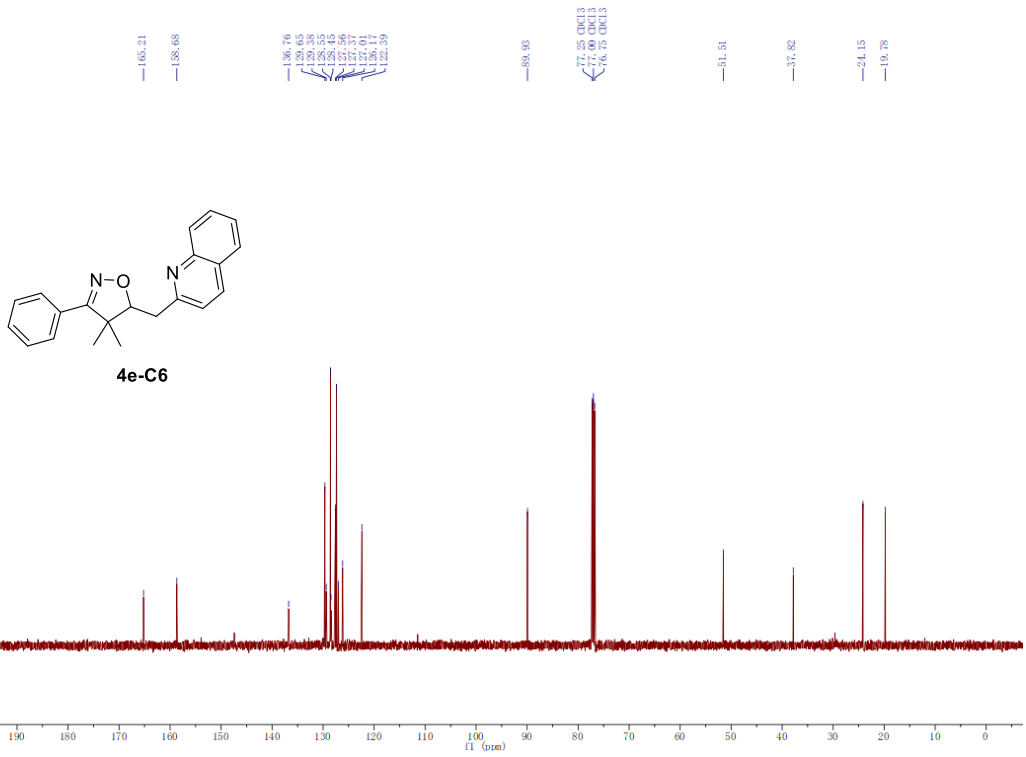


4,4-Dimethyl-3-phenyl-5-(quinolin-2-ylmethyl)-4,5-dihydroisoxazole (4e-C6).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

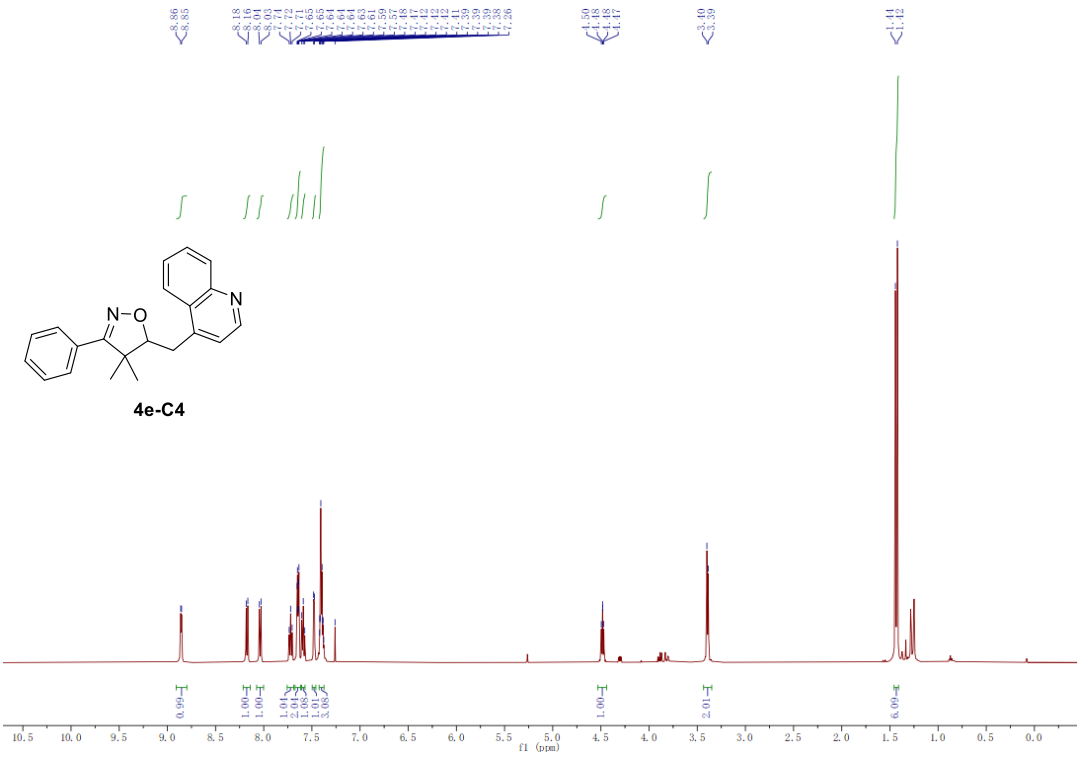


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

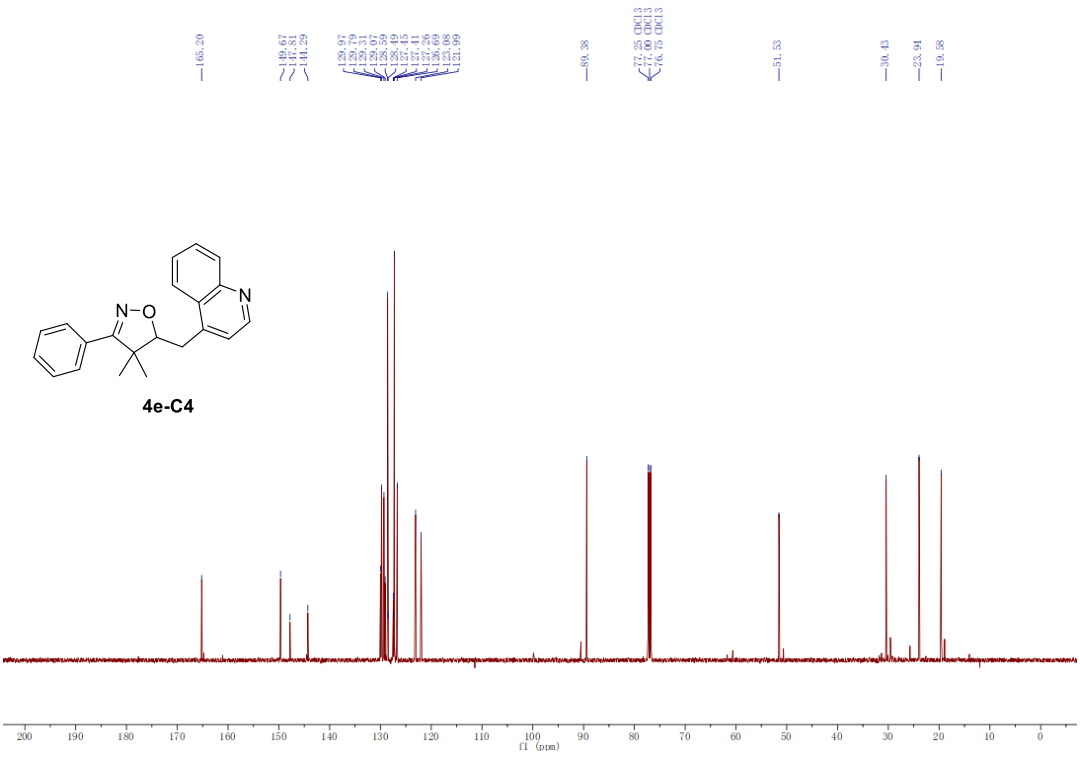


4,4-Dimethyl-3-phenyl-5-(quinolin-4-ylmethyl)-4,5-dihydroisoxazole (4e-C4).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

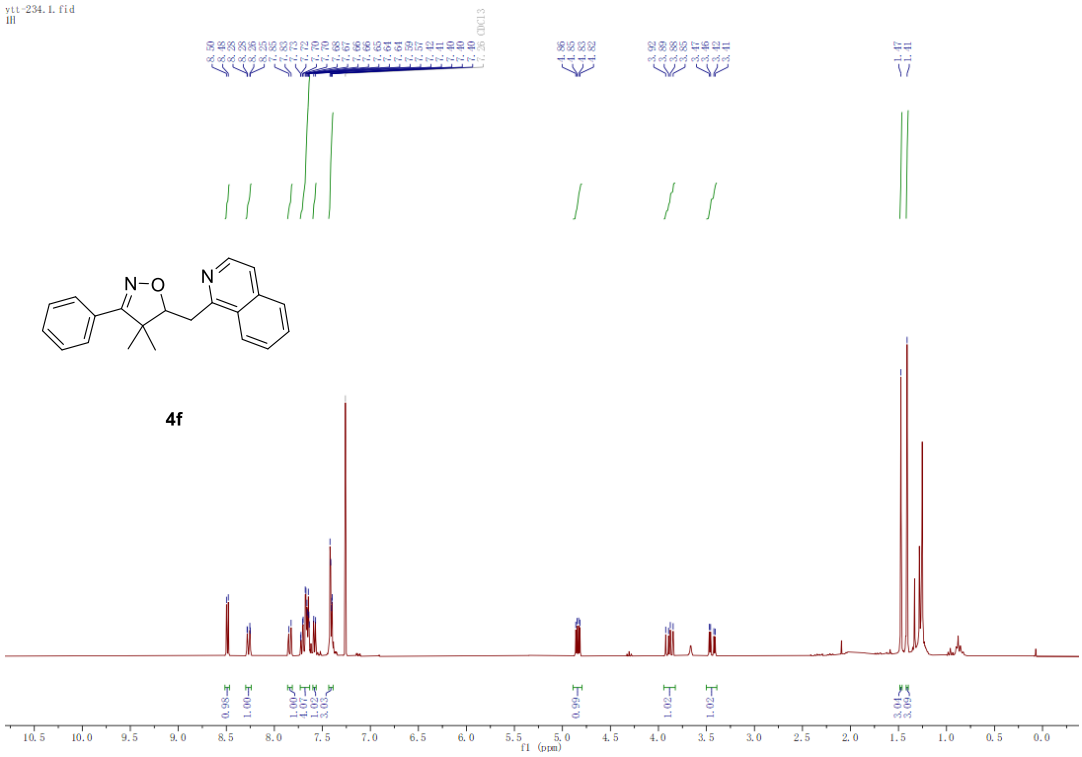


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

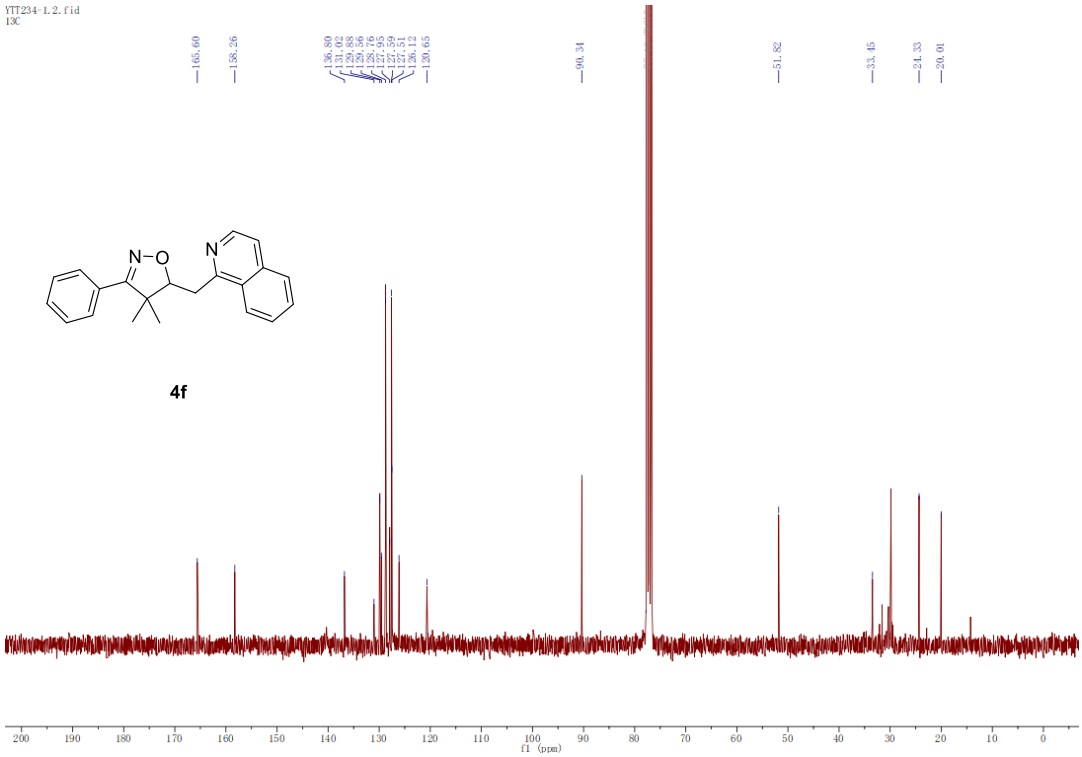


5-(Isoquinolin-1-ylmethyl)-4,4-dimethyl-3-phenyl-4,5-dihydroisoxazole (4f).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

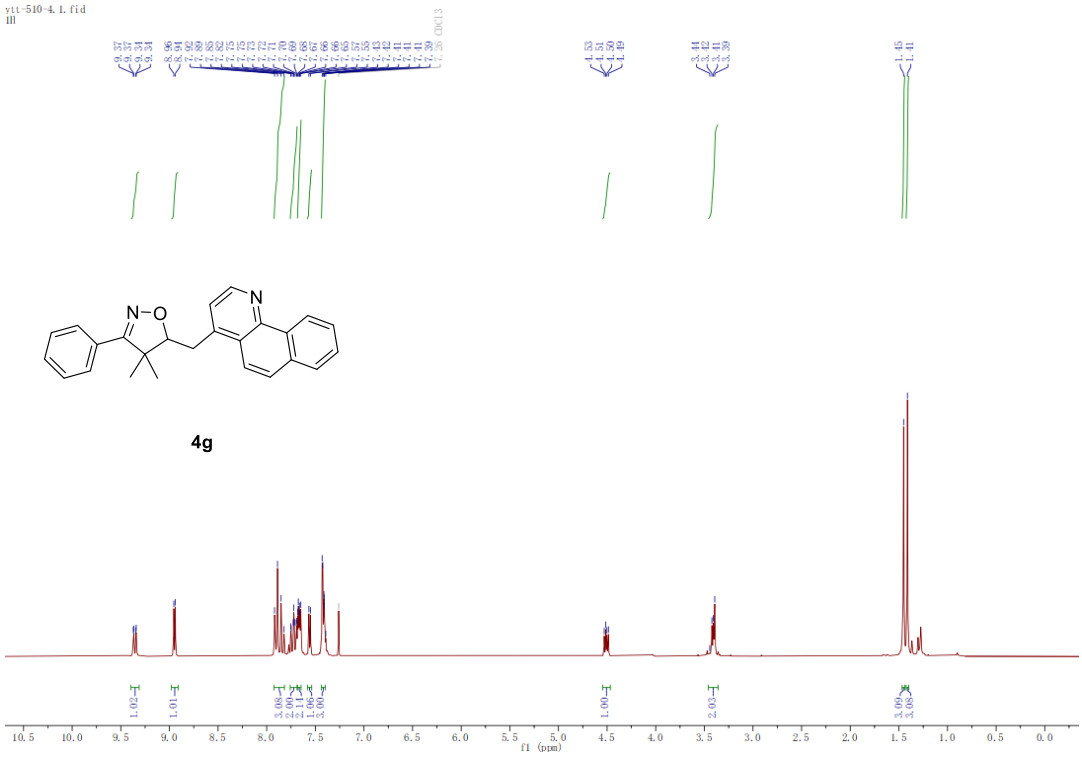


75 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

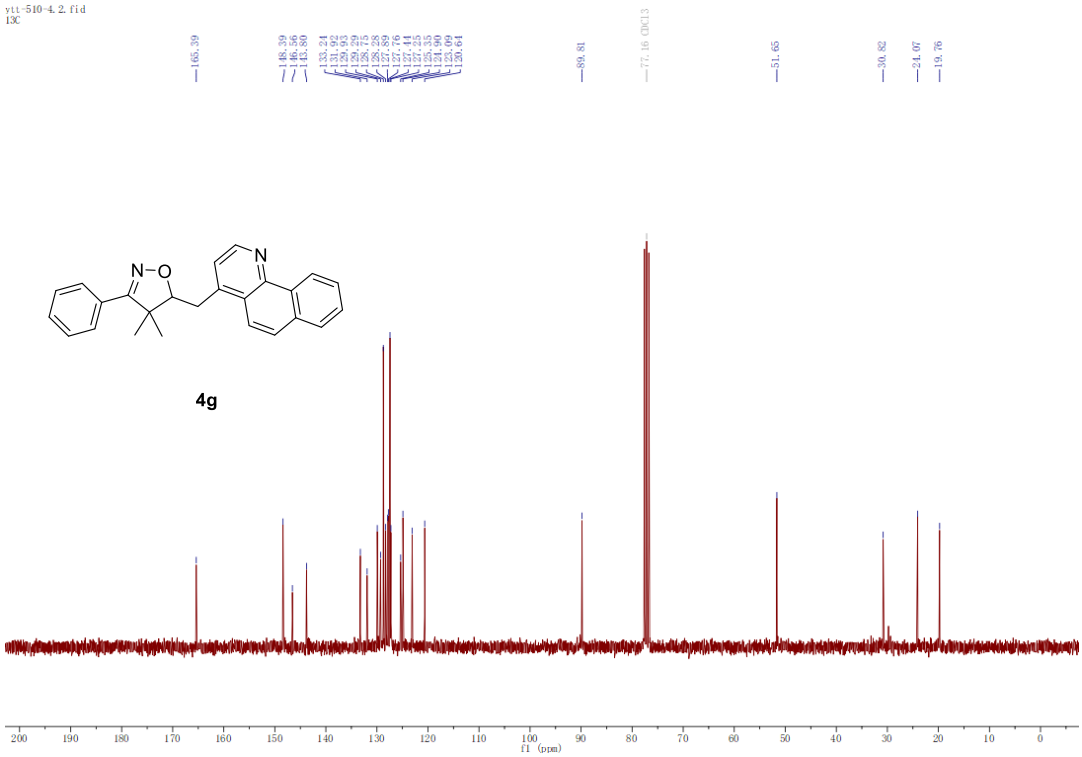


5-(Benzo[h]quinolin-4-ylmethyl)-4,4-dimethyl-3-phenyl-4,5-dihydroisoxazole (4g).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

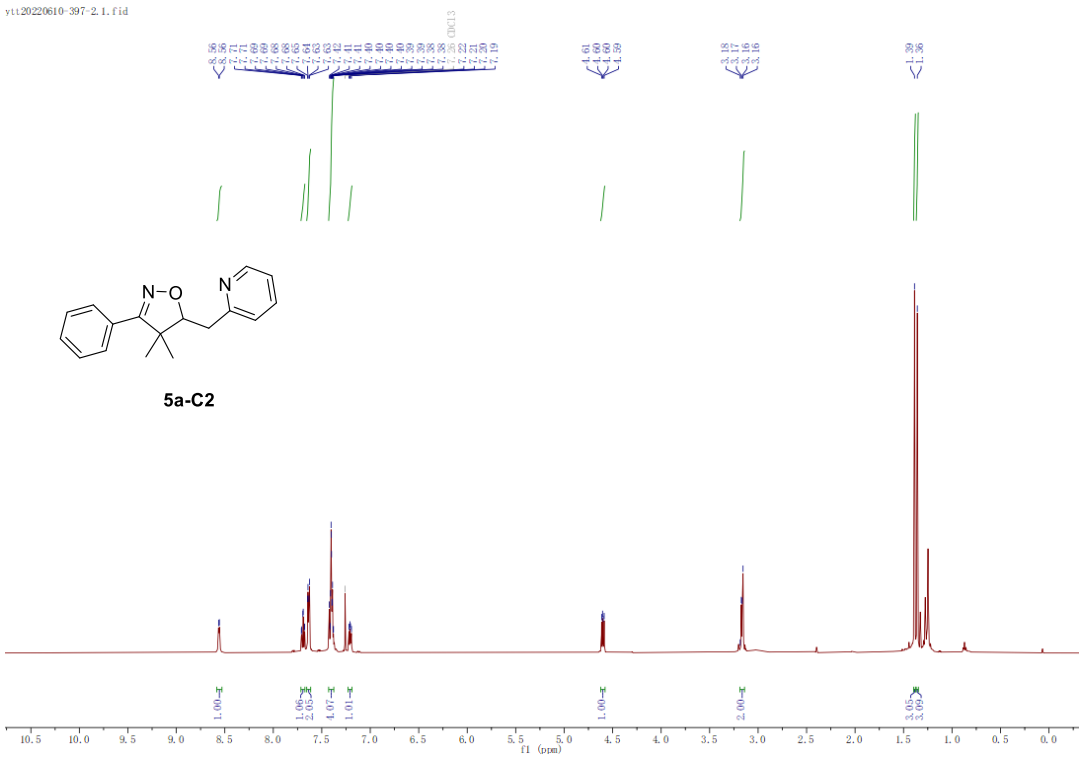


75 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

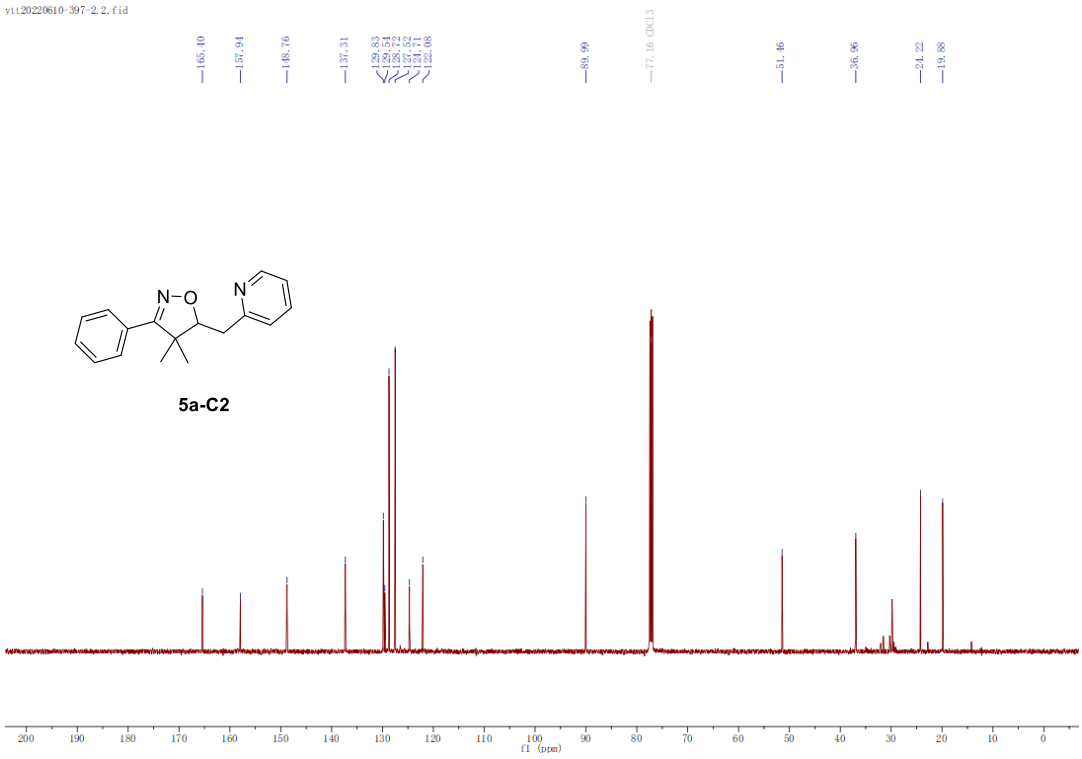


4,4-Dimethyl-3-phenyl-5-(pyridin-2-ylmethyl)-4,5-dihydroisoxazole (5a-C2).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

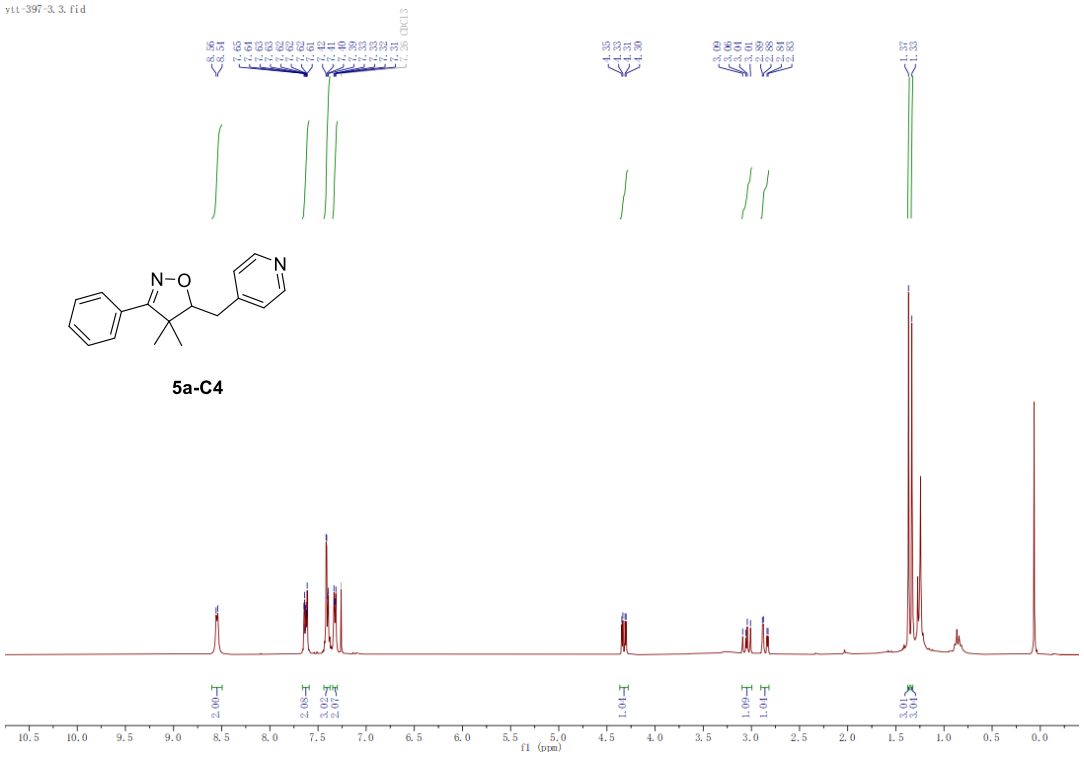


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

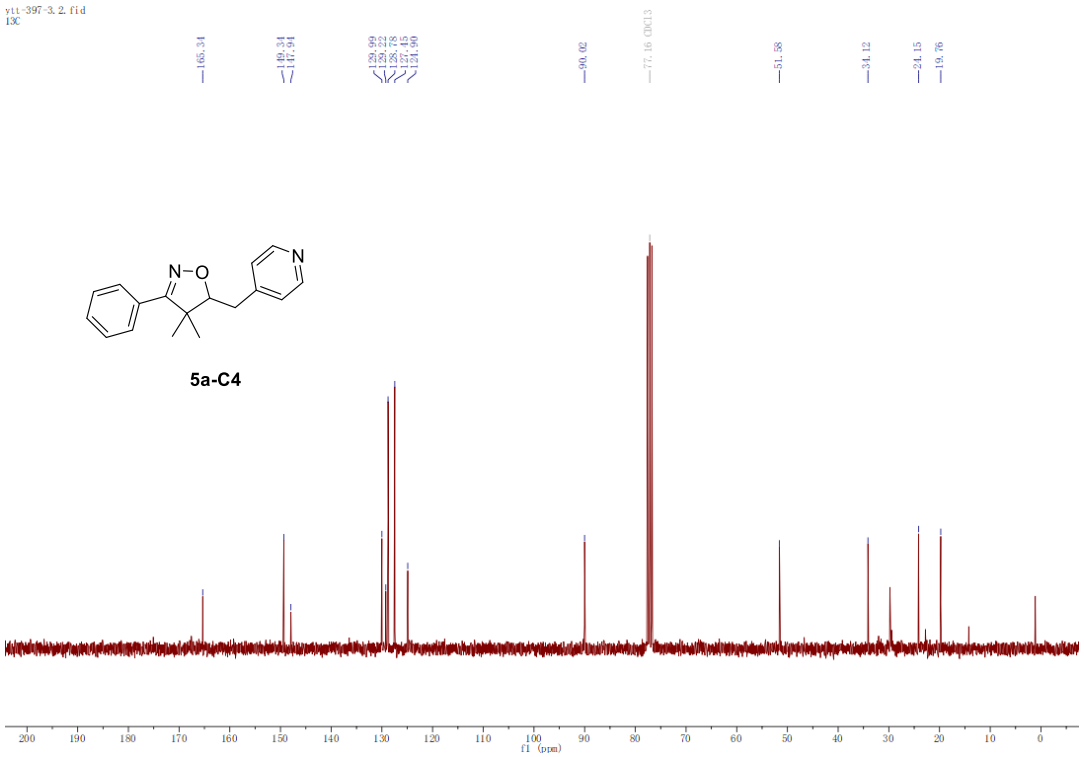


4,4-Dimethyl-3-phenyl-5-(pyridin-4-ylmethyl)-4,5-dihydroisoxazole (5a-C4).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

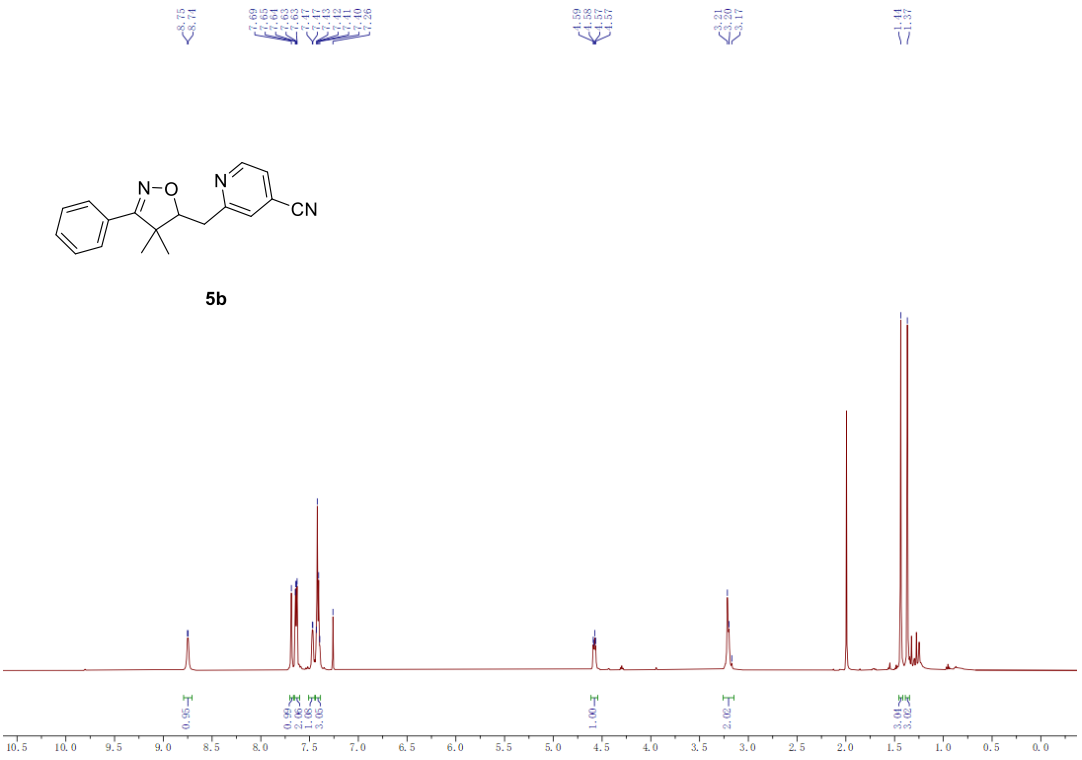


75 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

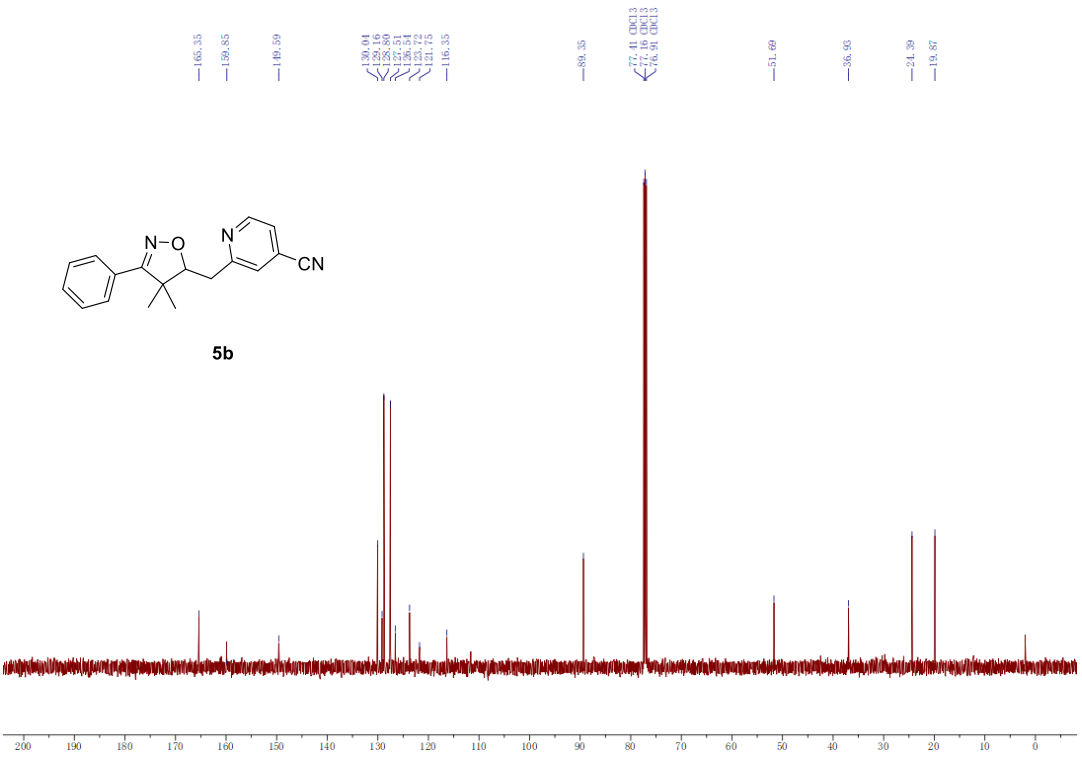


2-((4,4-Dimethyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)isonicotinonitrile (5b).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

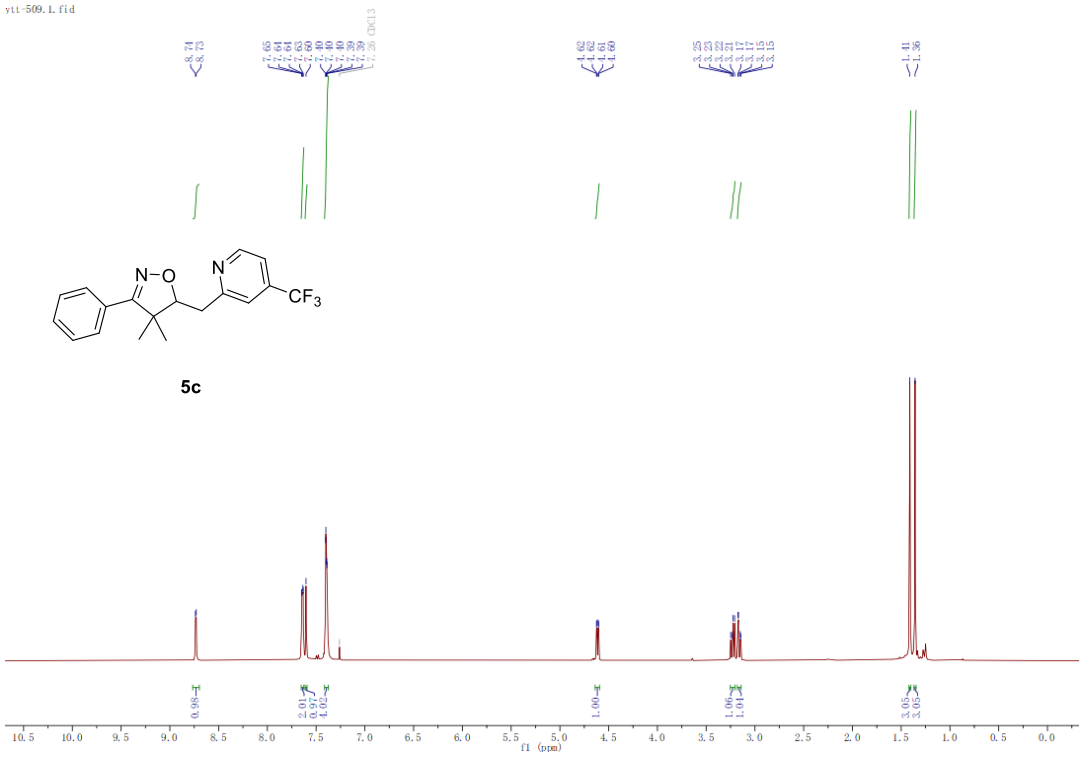


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

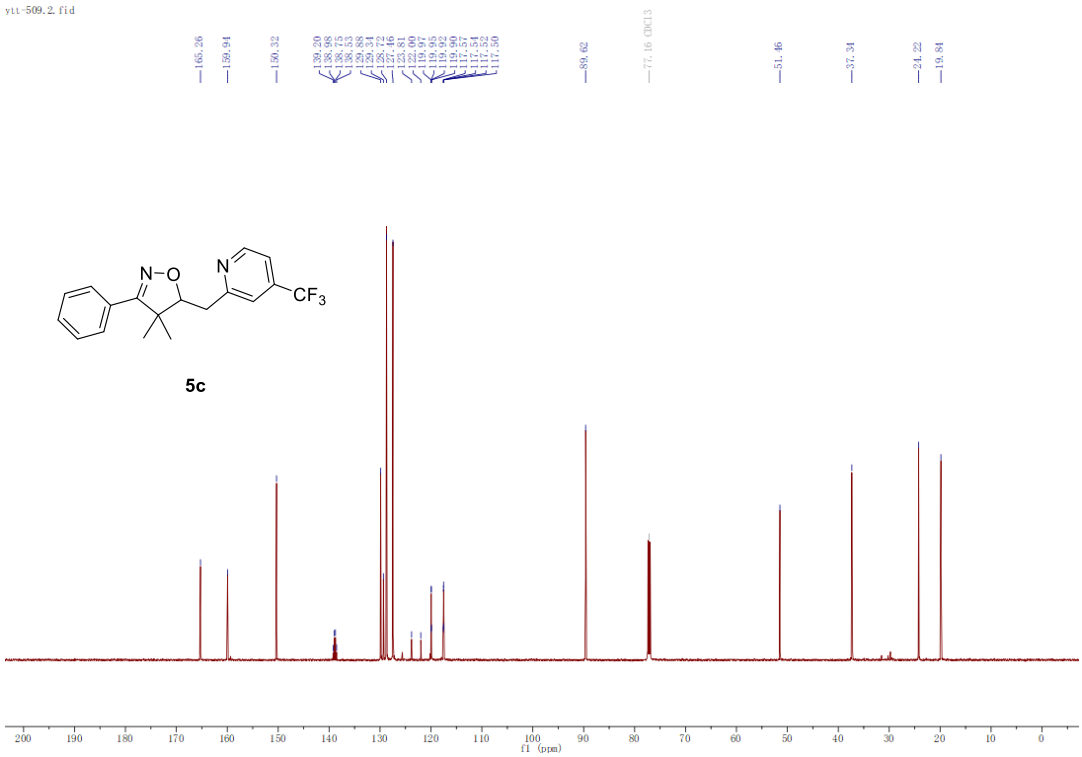


4,4-Dimethyl-3-phenyl-5-((4-(trifluoromethyl)pyridin-2-yl)methyl)-4,5-dihydroisoxazole (5c).

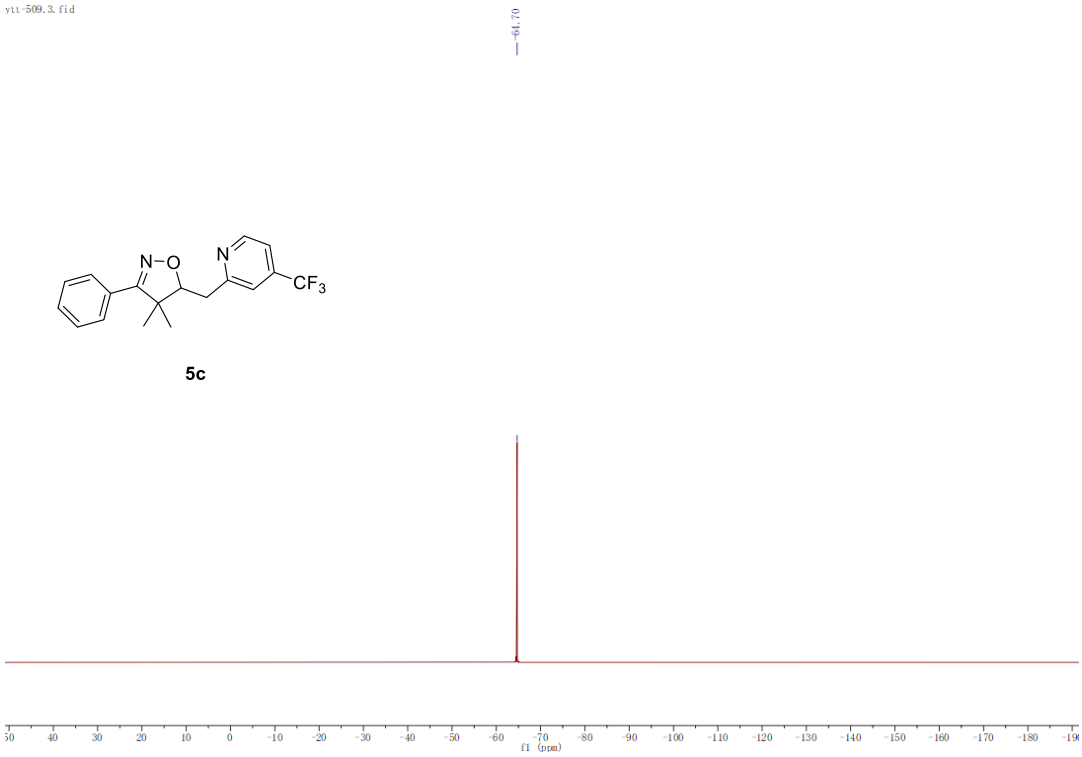
600 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)



151 MHz $^{13}C\{^{1}H\}$ NMR Spectrum (recorded in $CDCl_3$)



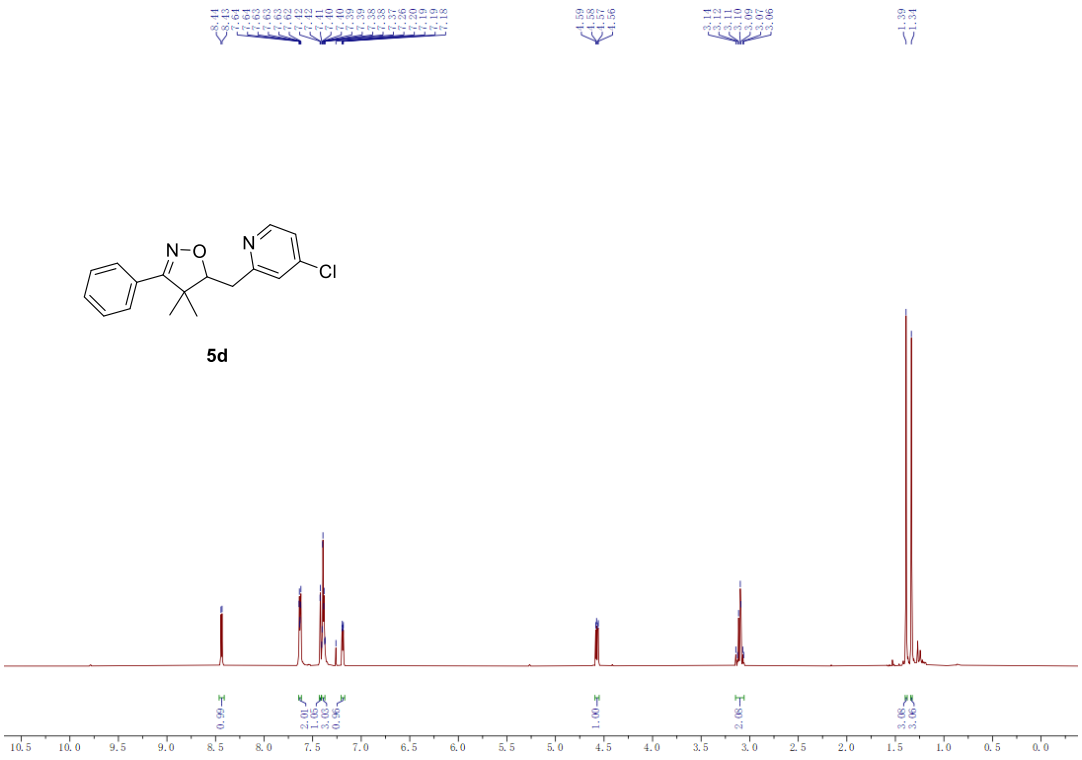
565 MHz ^{19}F NMR Spectrum (recorded in $CDCl_3$)



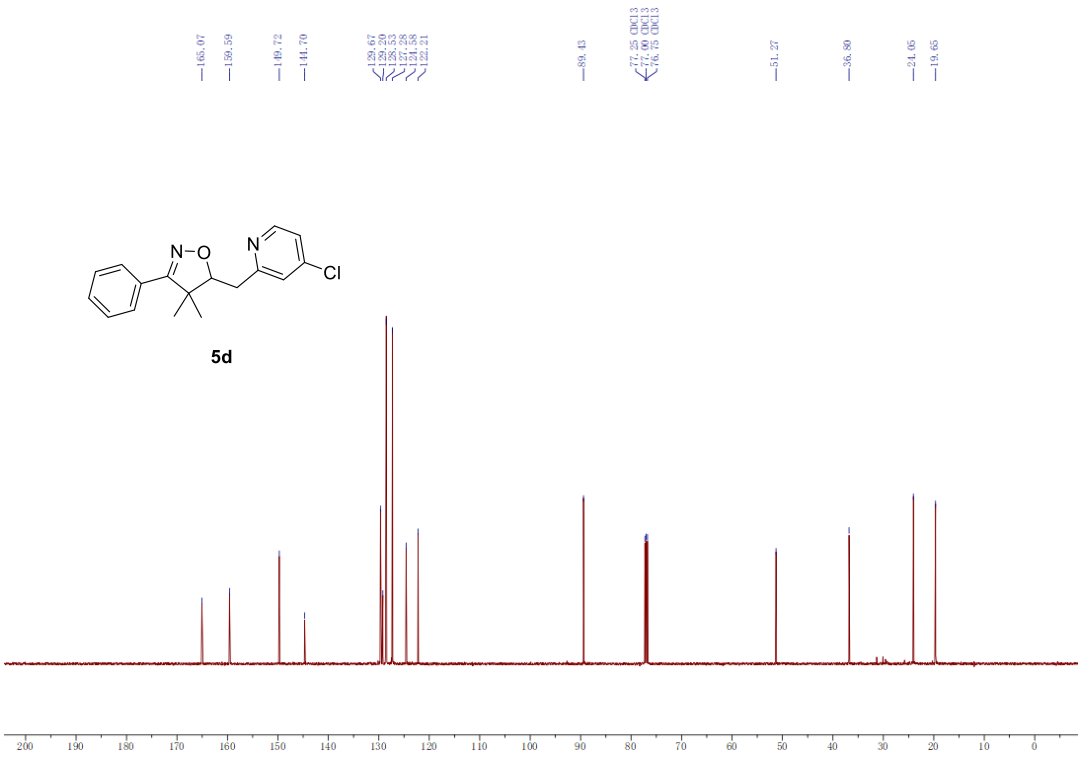
5c

5-((4-Chloropyridin-2-yl)methyl)-4,4-dimethyl-3-phenyl-4,5-dihydroisoxazole (5d).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

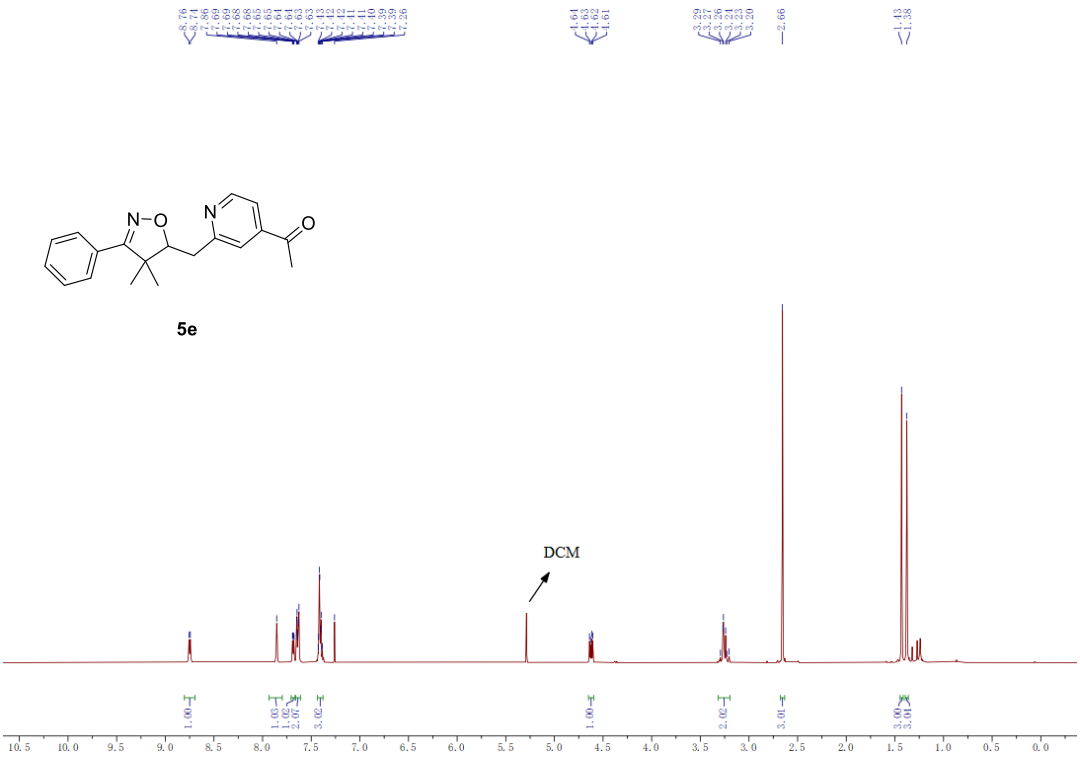


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

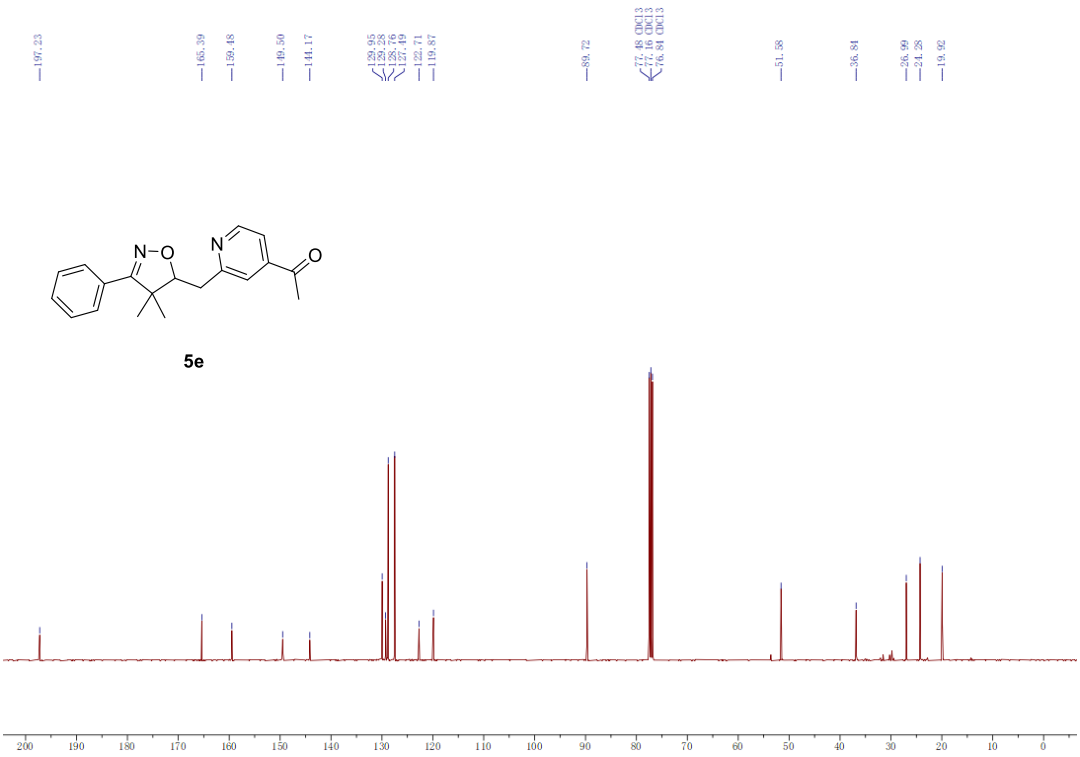


1-(2-((4,4-Dimethyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)pyridin-4-yl)ethan-1-one (5e).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

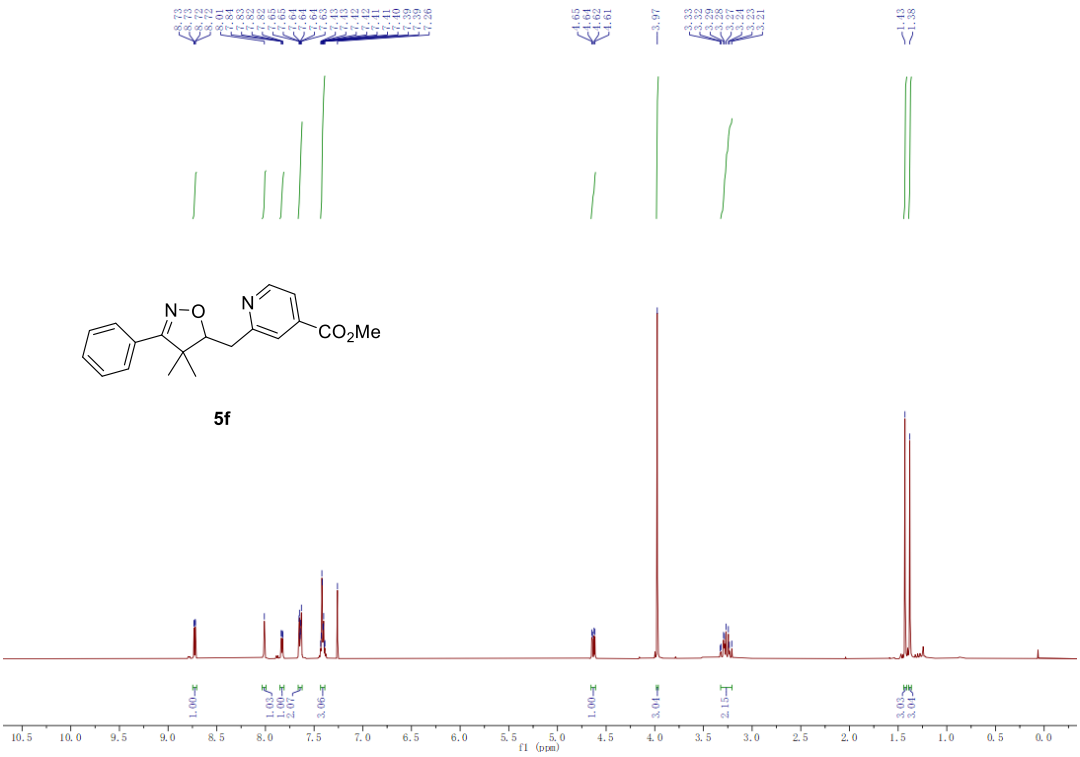


101 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

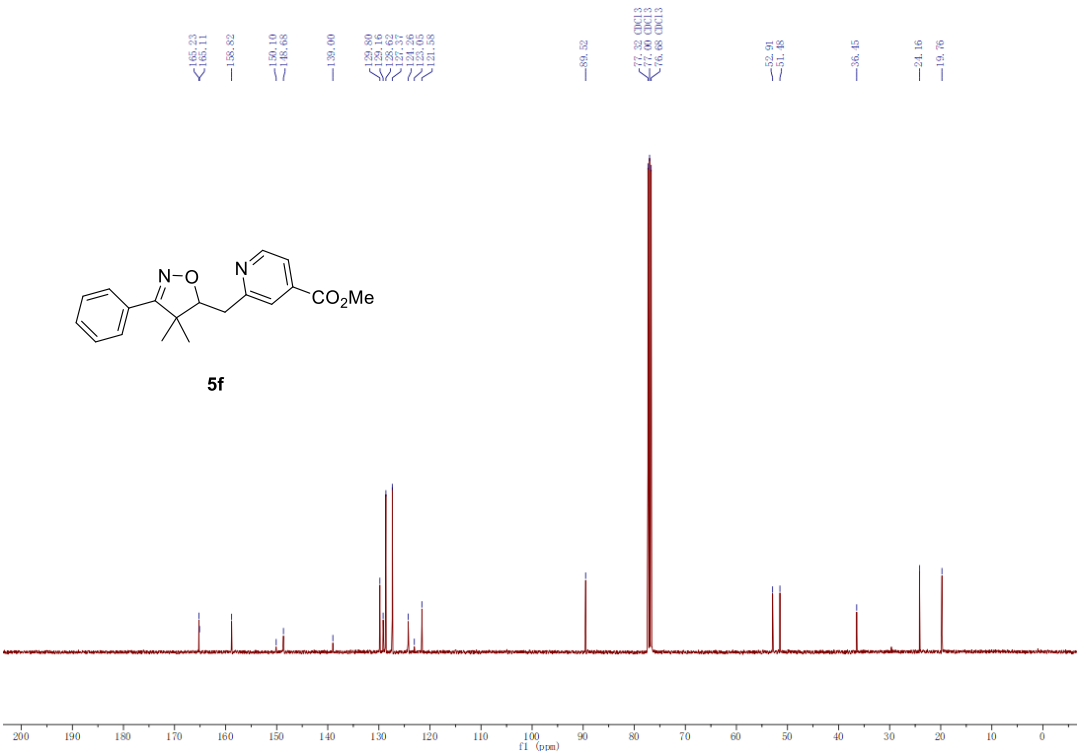


Methyl 2-((4,4-dimethyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)isonicotinate (5f).

400 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

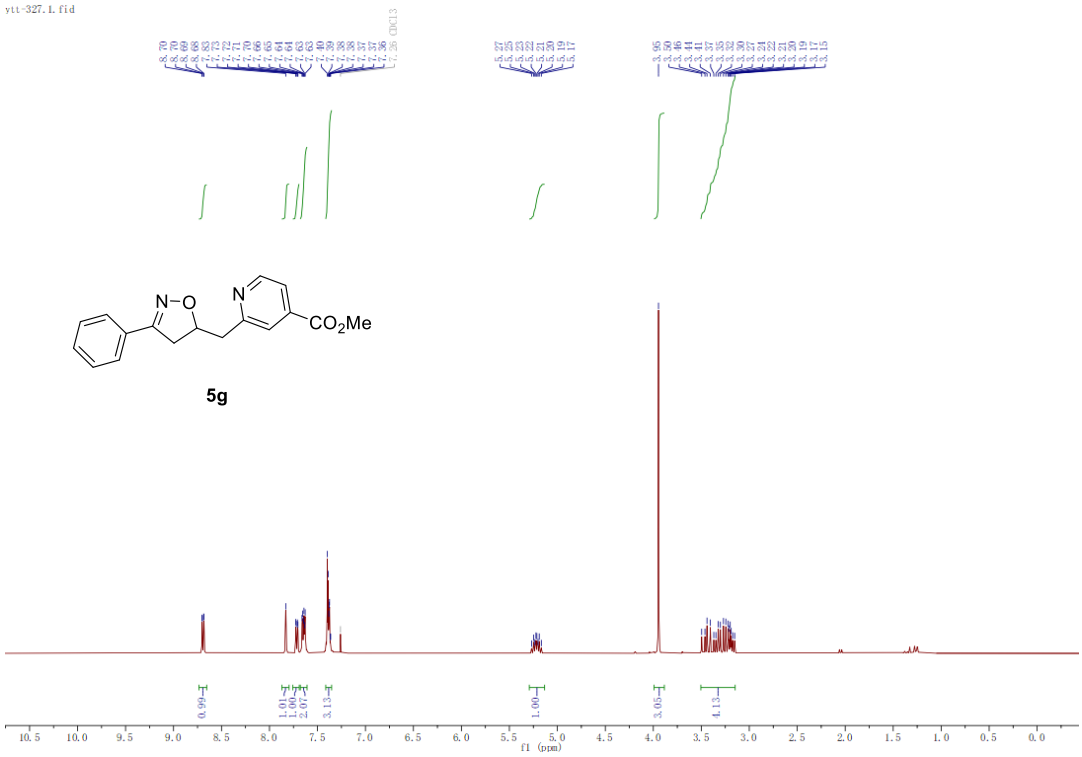


101 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

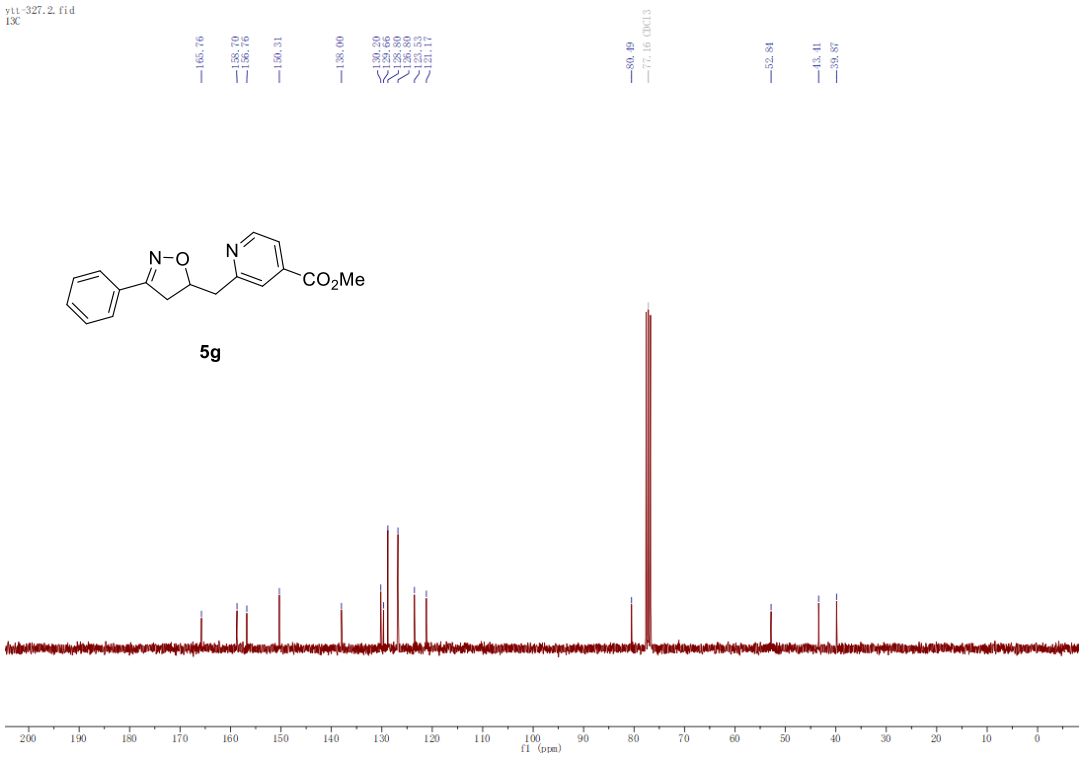


Methyl 2-((3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)isonicotinate (5g).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

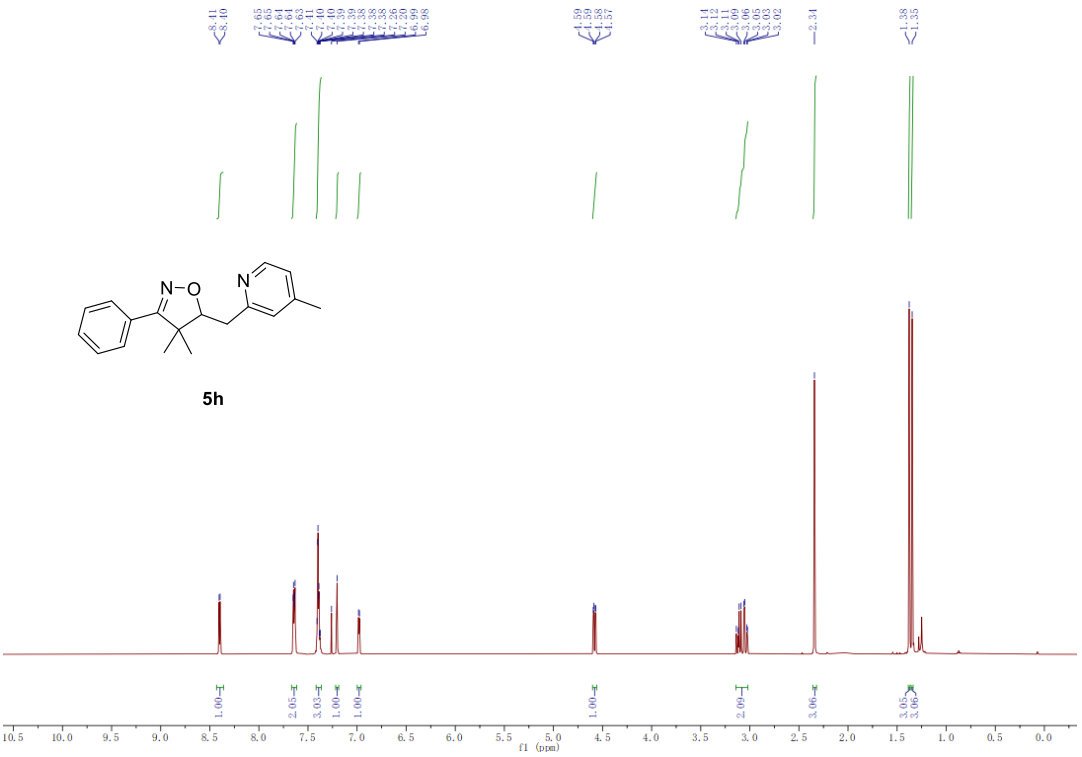


75 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

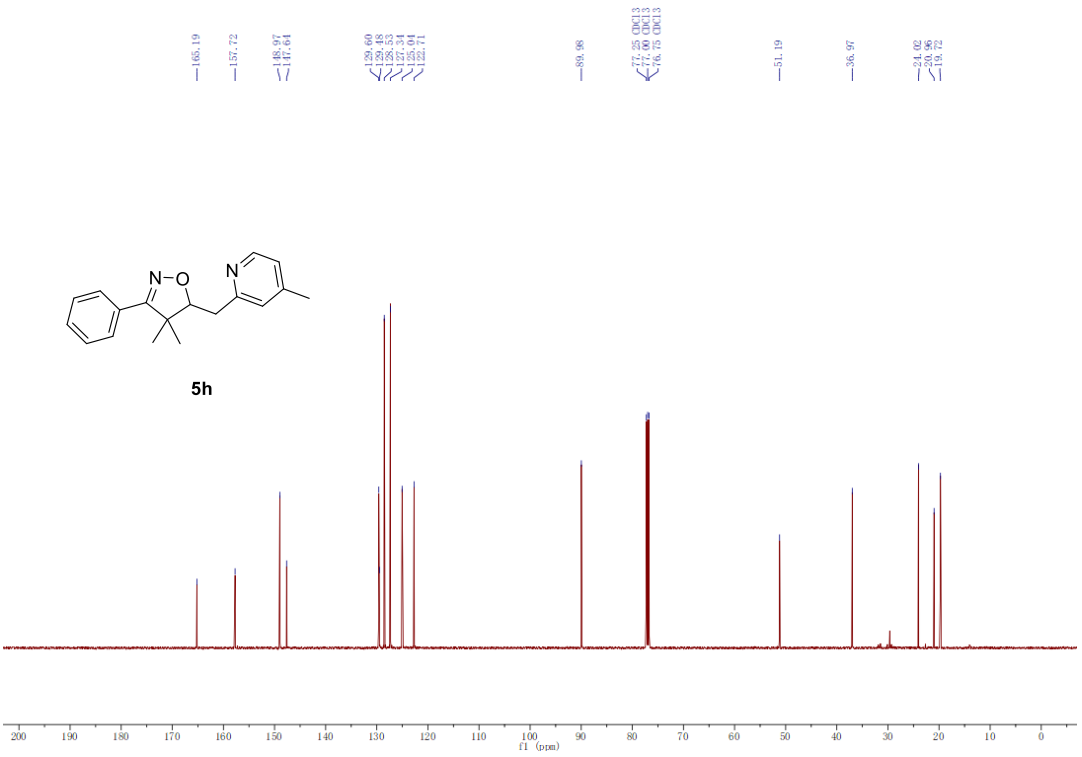


4,4-Dimethyl-5-((4-methylpyridin-2-yl)methyl)-3-phenyl-4,5-dihydroisoxazole (5h).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

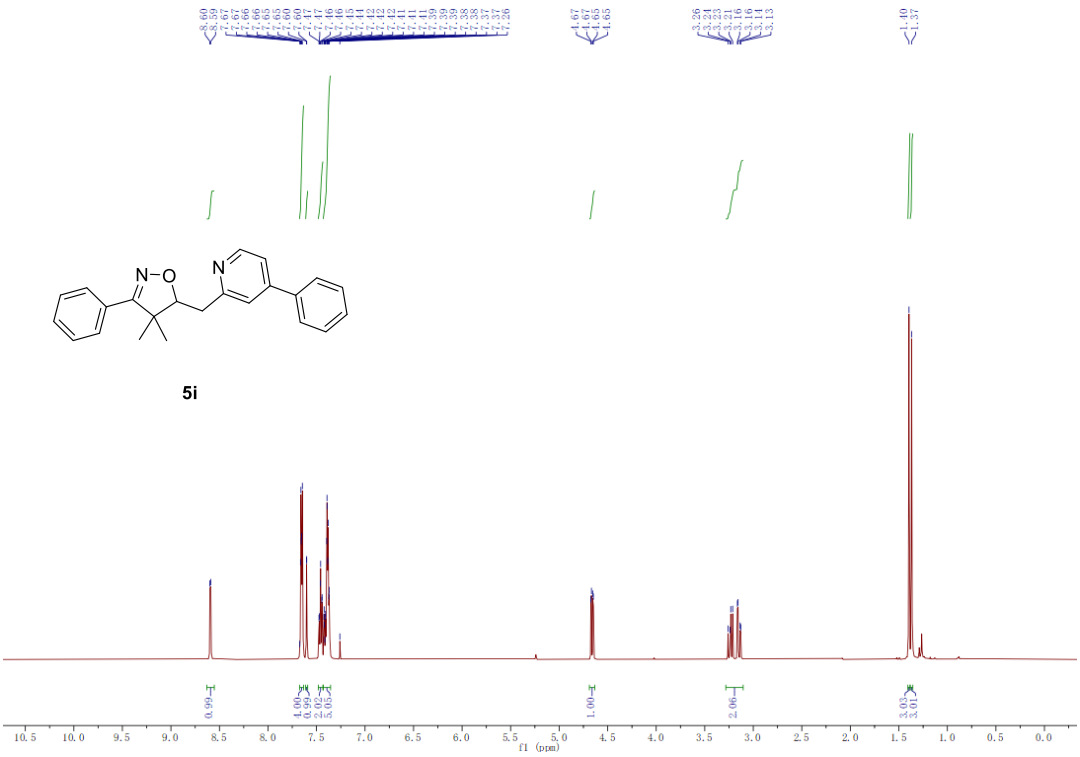


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

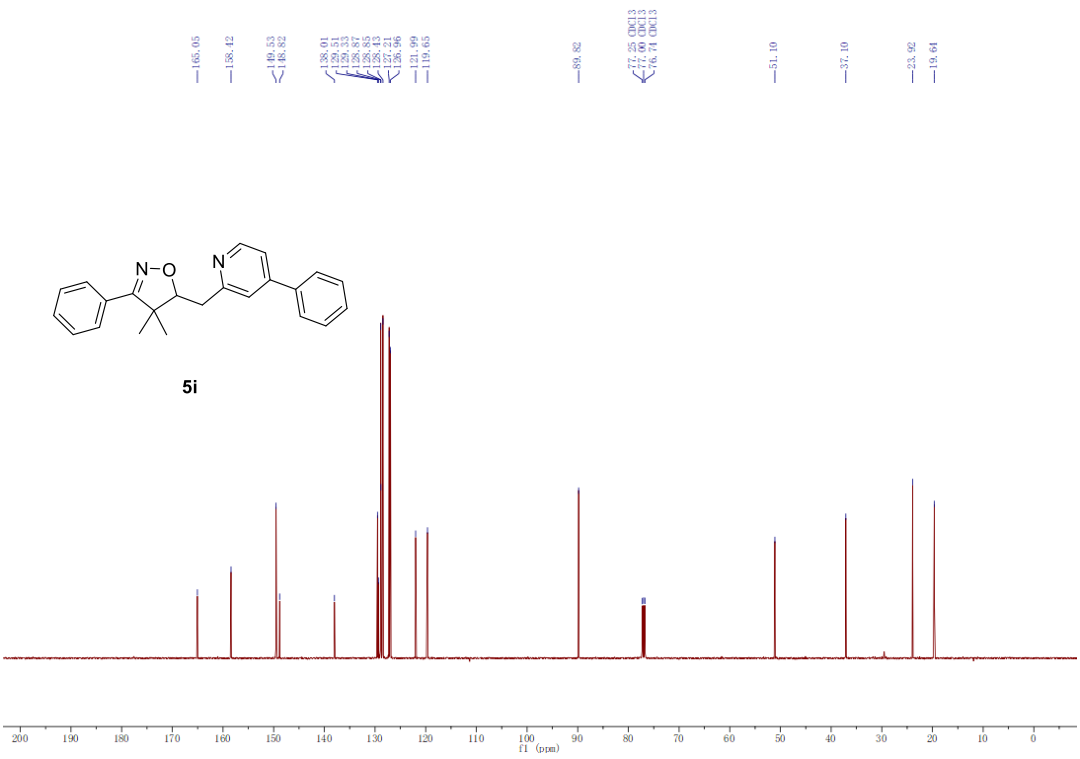


4,4-Dimethyl-3-phenyl-5-((4-phenylpyridin-2-yl)methyl)-4,5-dihydroisoxazole (5i).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

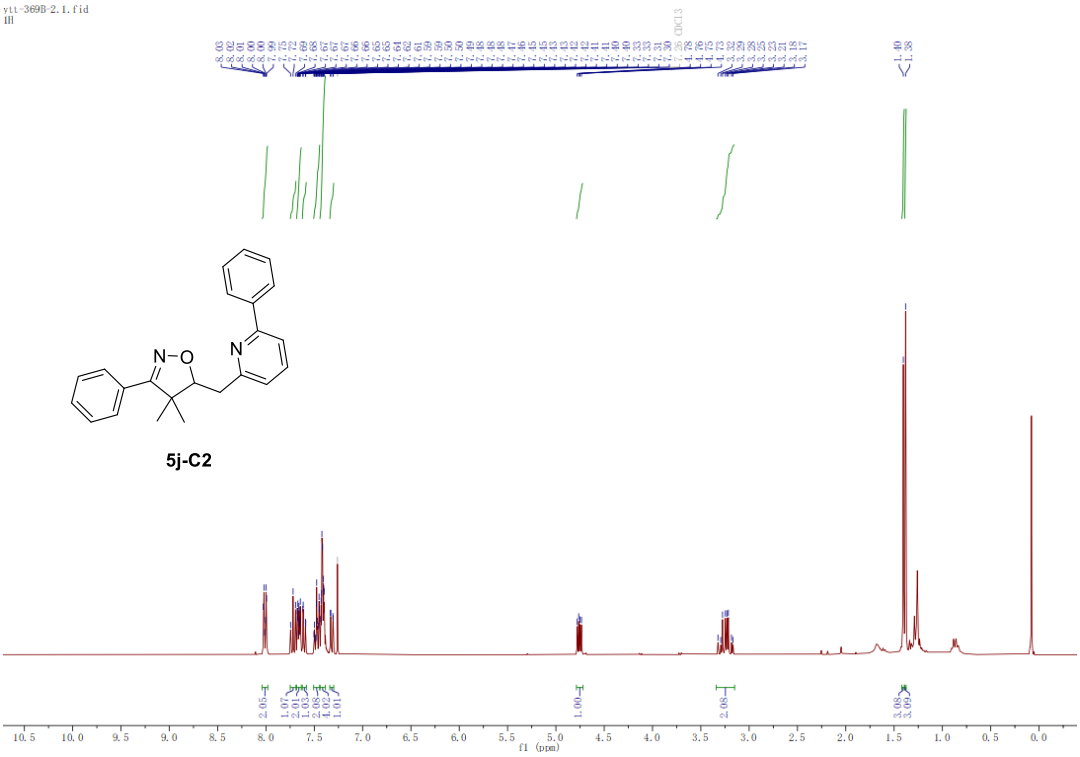


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

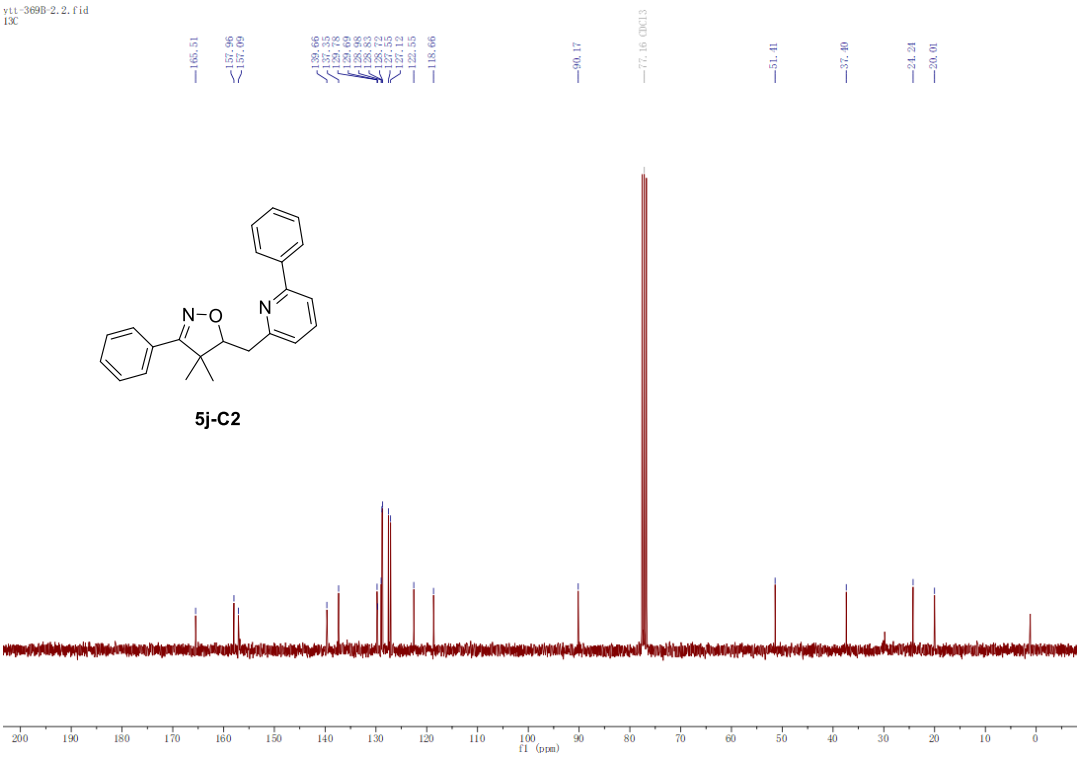


4,4-Dimethyl-3-phenyl-5-((6-phenylpyridin-2-yl)methyl)-4,5-dihydroisoxazole (5j-C2).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

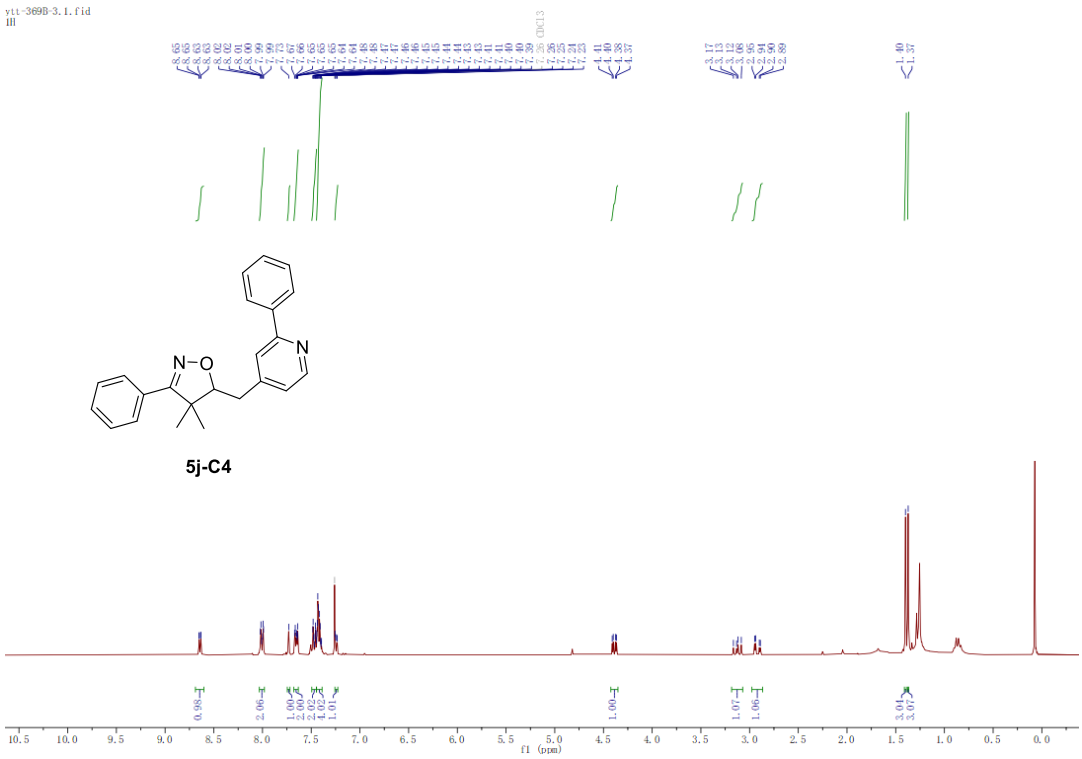


75 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

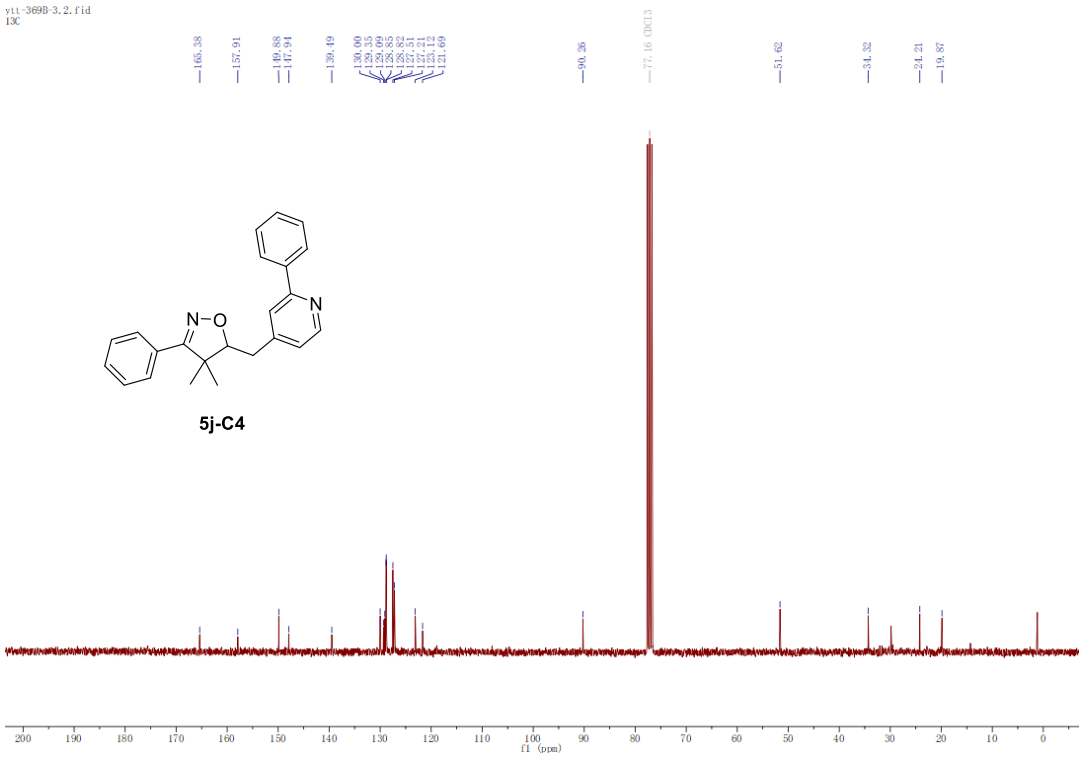


4,4-Dimethyl-3-phenyl-5-((2-phenylpyridin-4-yl)methyl)-4,5-dihydroisoxazole (5j-C4).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

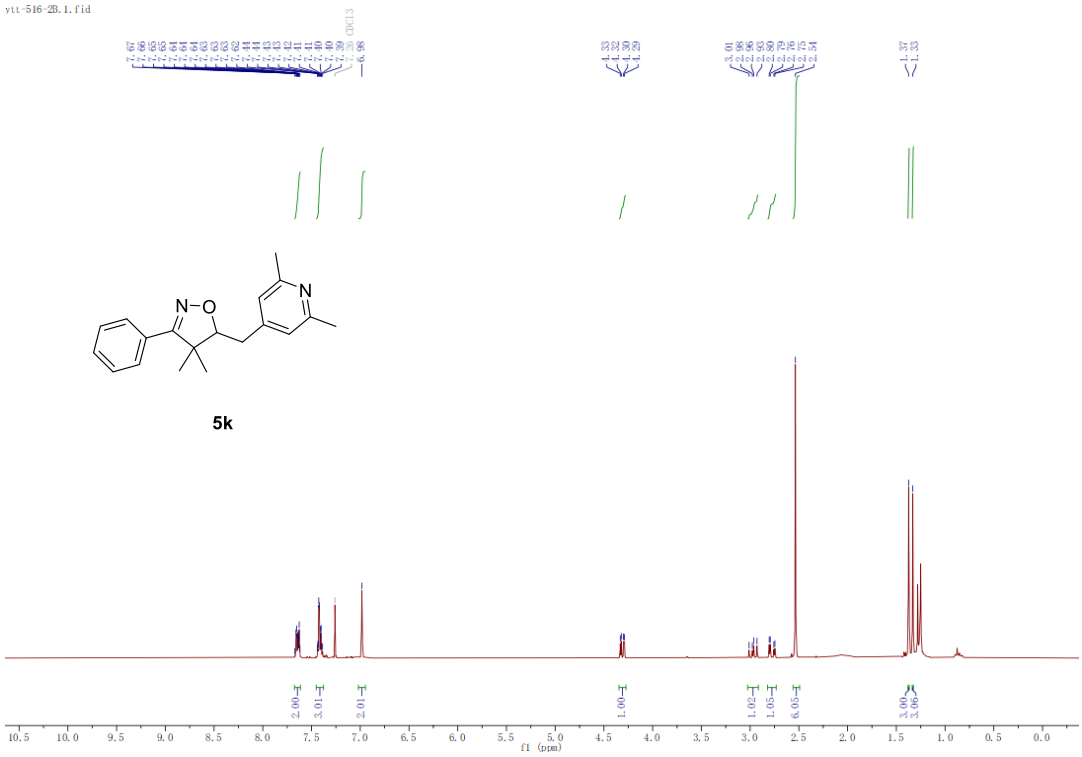


75 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

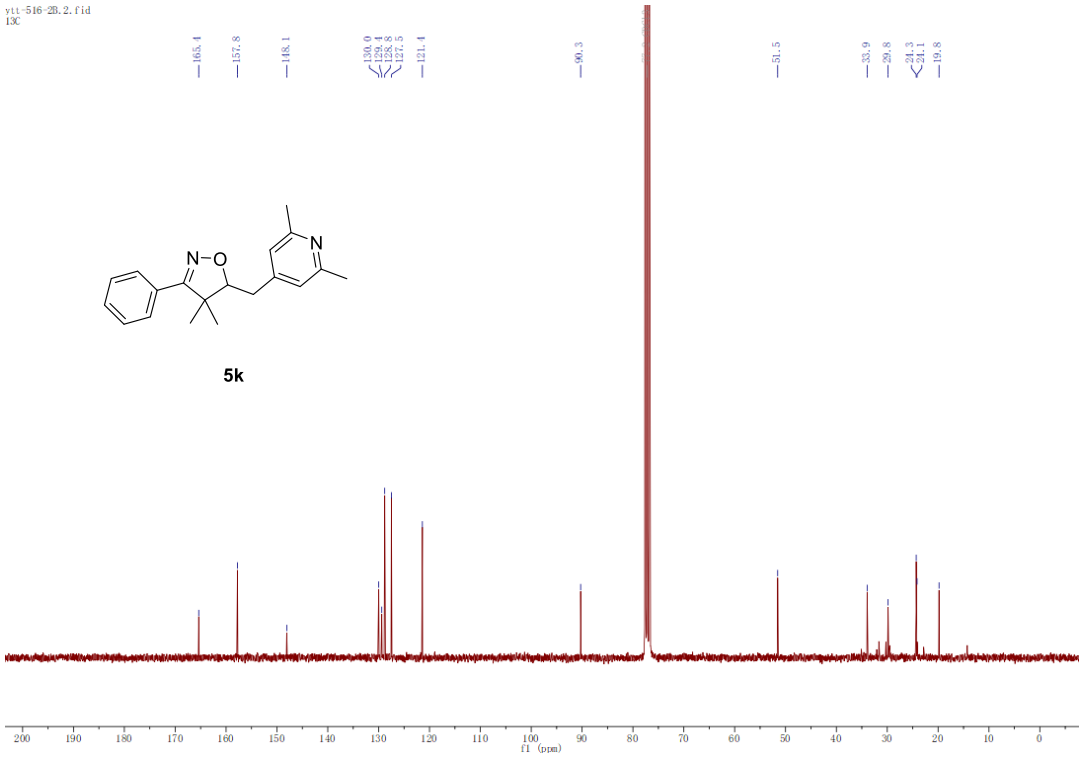


5-((2,6-Dimethylpyridin-4-yl)methyl)-4,4-dimethyl-3-phenyl-4,5-dihydroisoxazole (5k).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

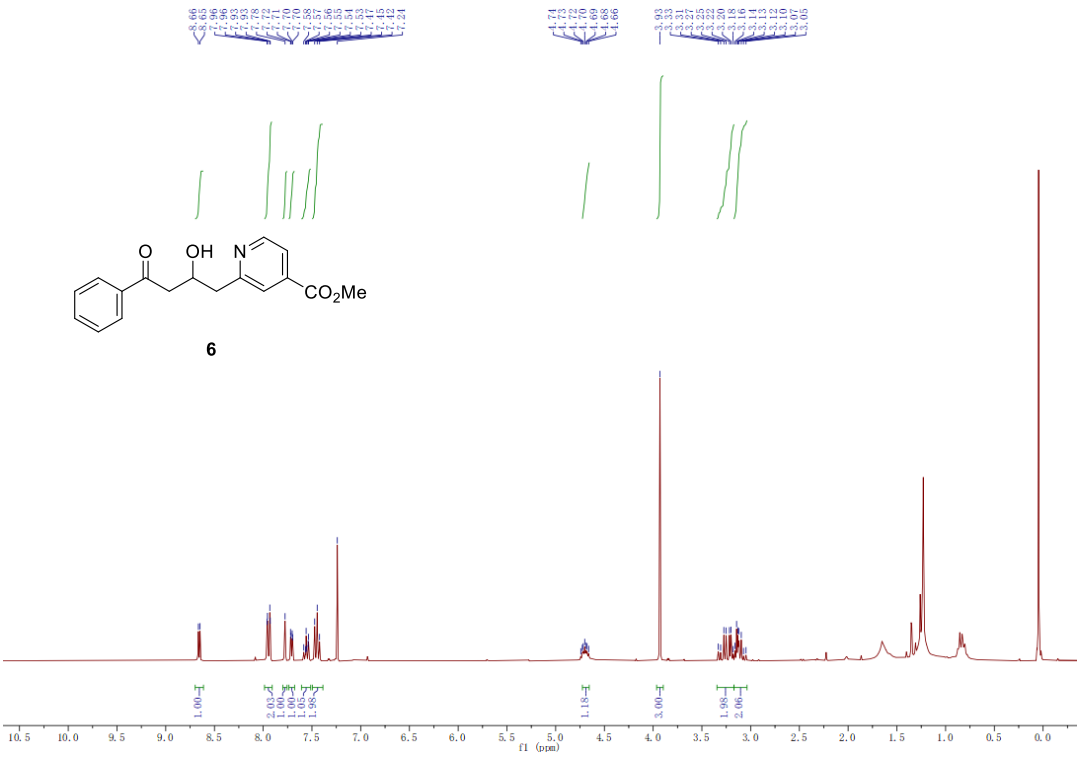


75 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

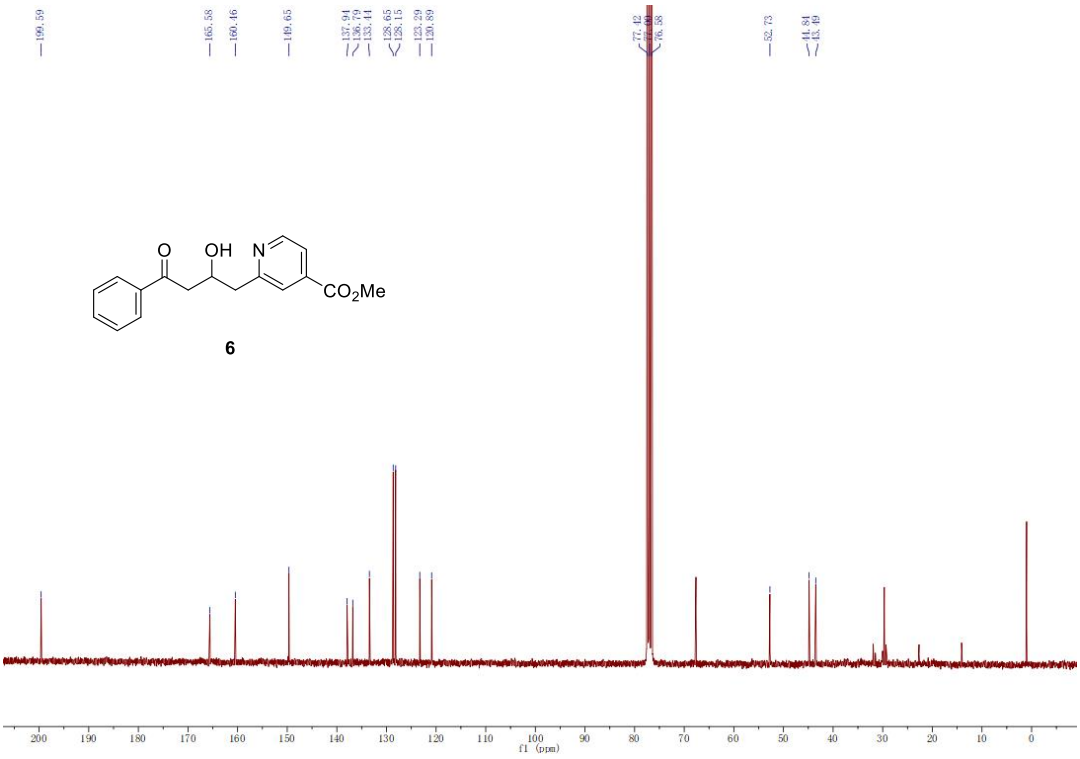


Methyl 2-(2-hydroxy-4-oxo-4-phenylbutyl)isonicotinate (6).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)



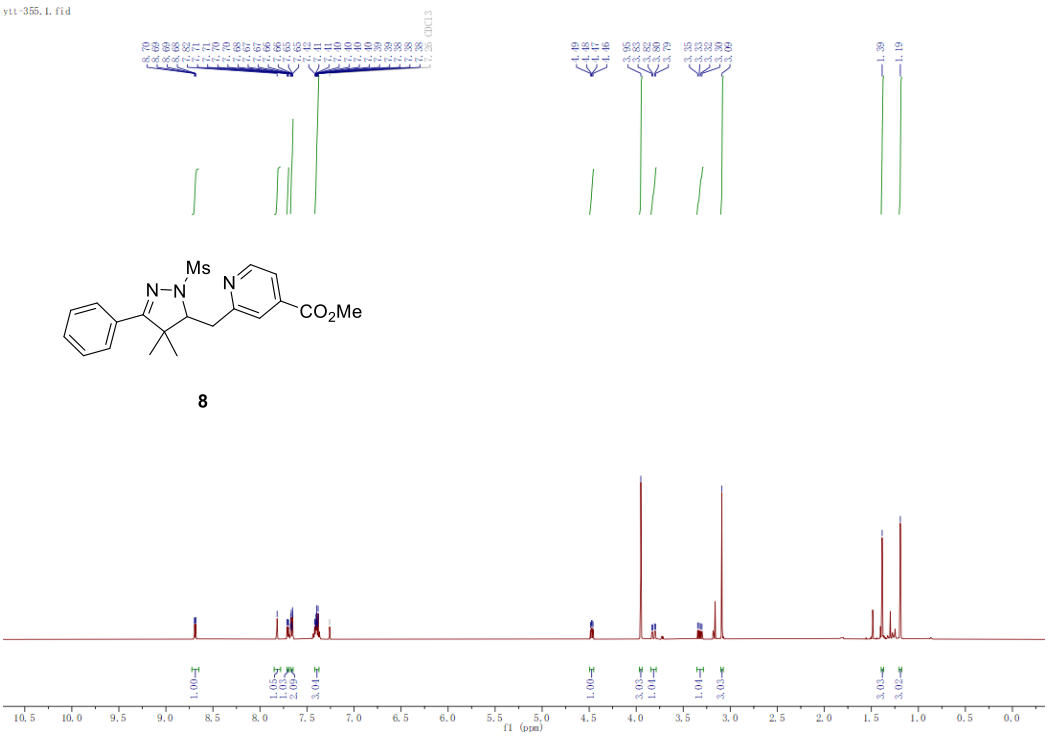
75 MHz $^{13}C\{^{1}H\}$ NMR Spectrum (recorded in $CDCl_3$)



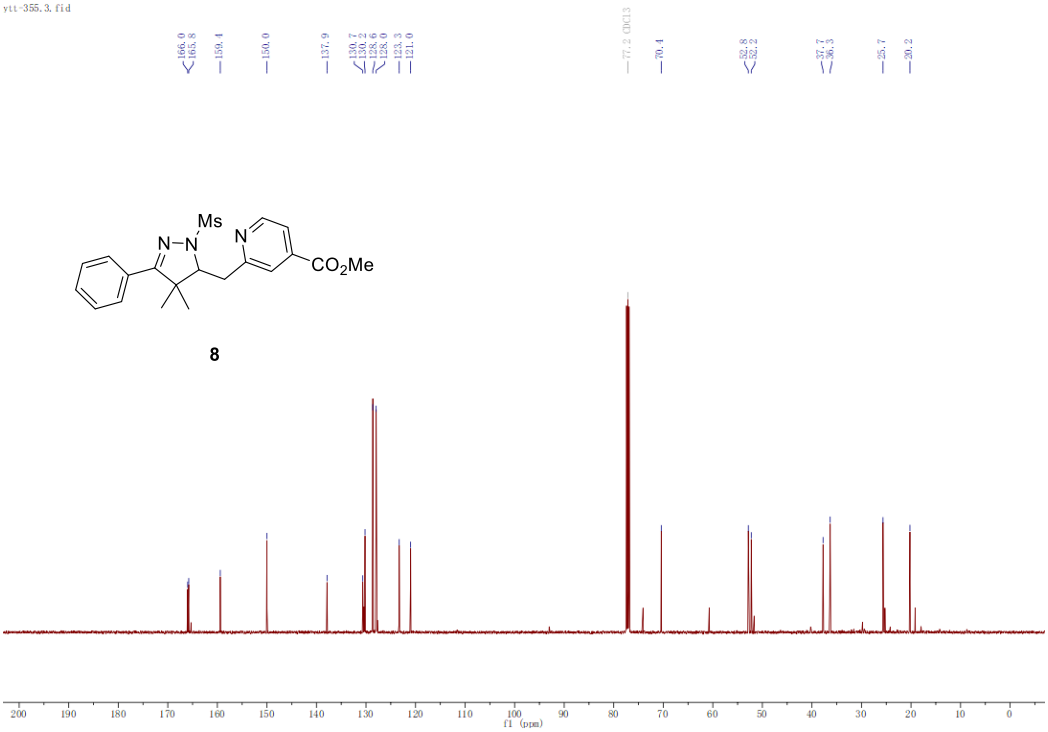
Methyl

2-((4,4-dimethyl-1-(methylsulfonyl)-3-phenyl-4,5-dihydro-1H-pyrazol-5-yl)methyl)isonicotinate (8).

500 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

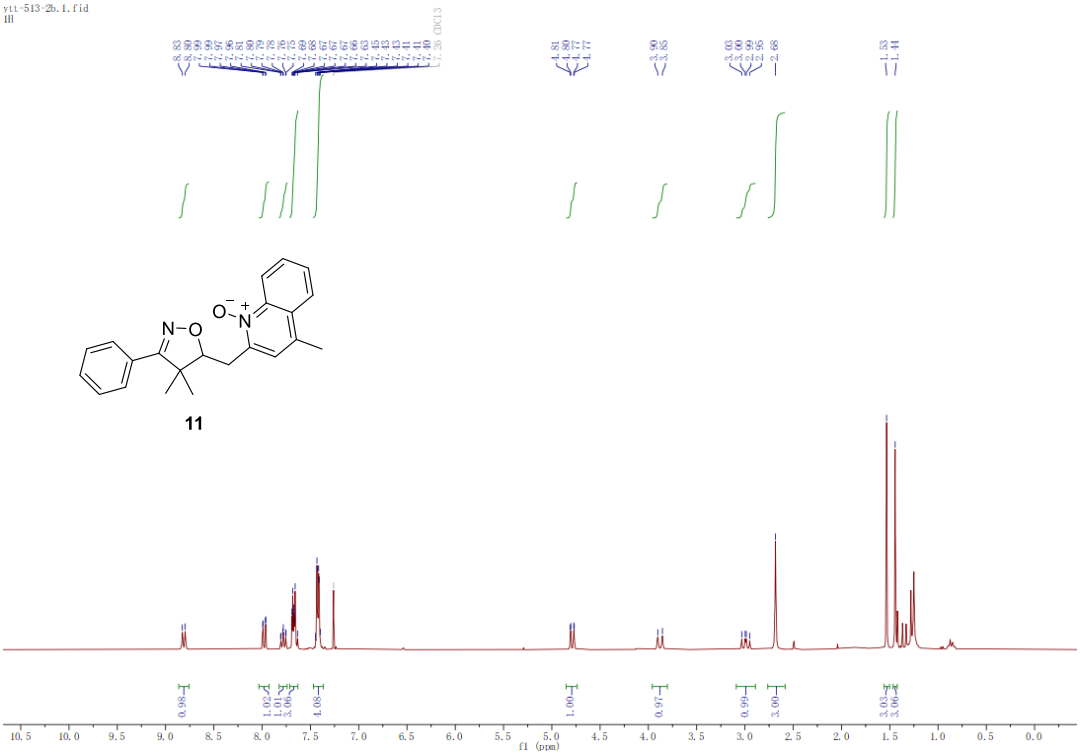


126 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

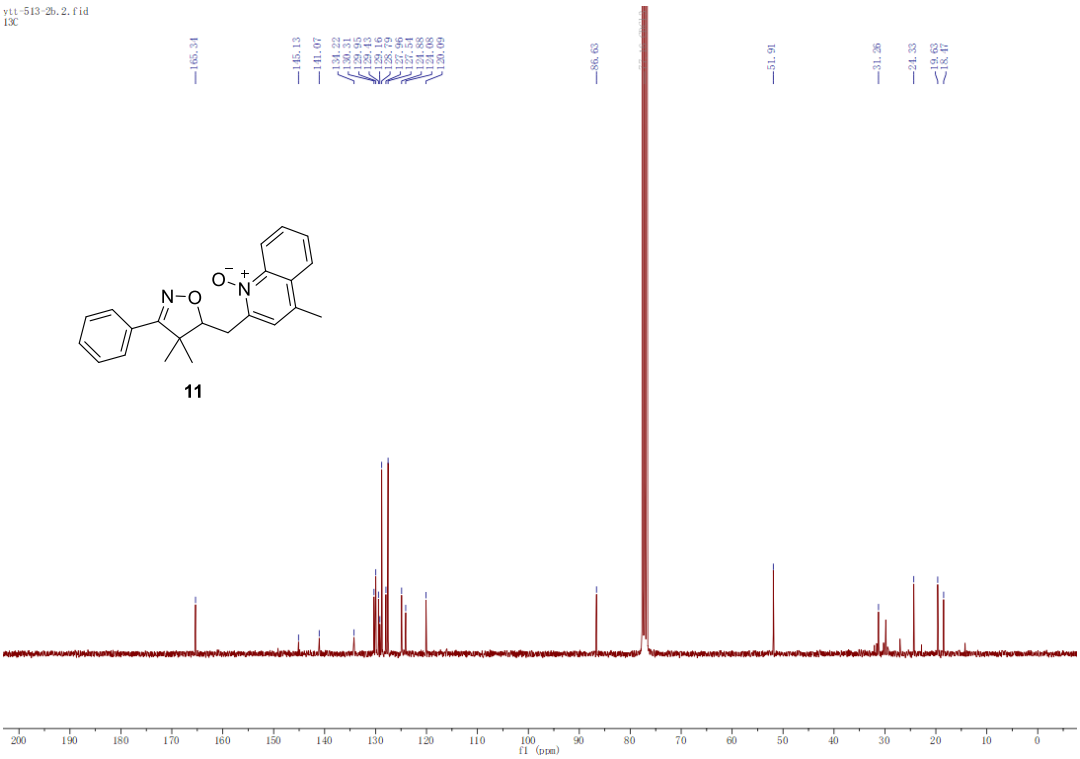


2-((4,4-Dimethyl-3-phenyl-4,5-dihydroisoxazol-5-yl)methyl)-4-methylquinoline 1-oxide (11).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)

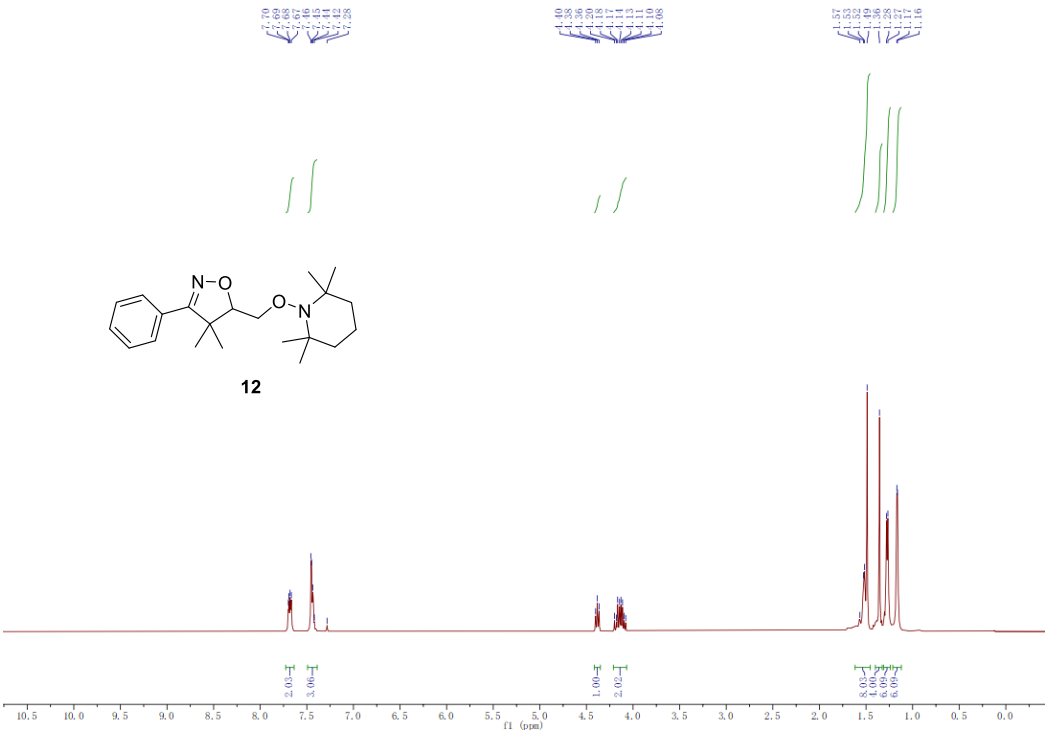


75 MHz ^{13}C{^{1}H} NMR Spectrum (recorded in $CDCl_3$)

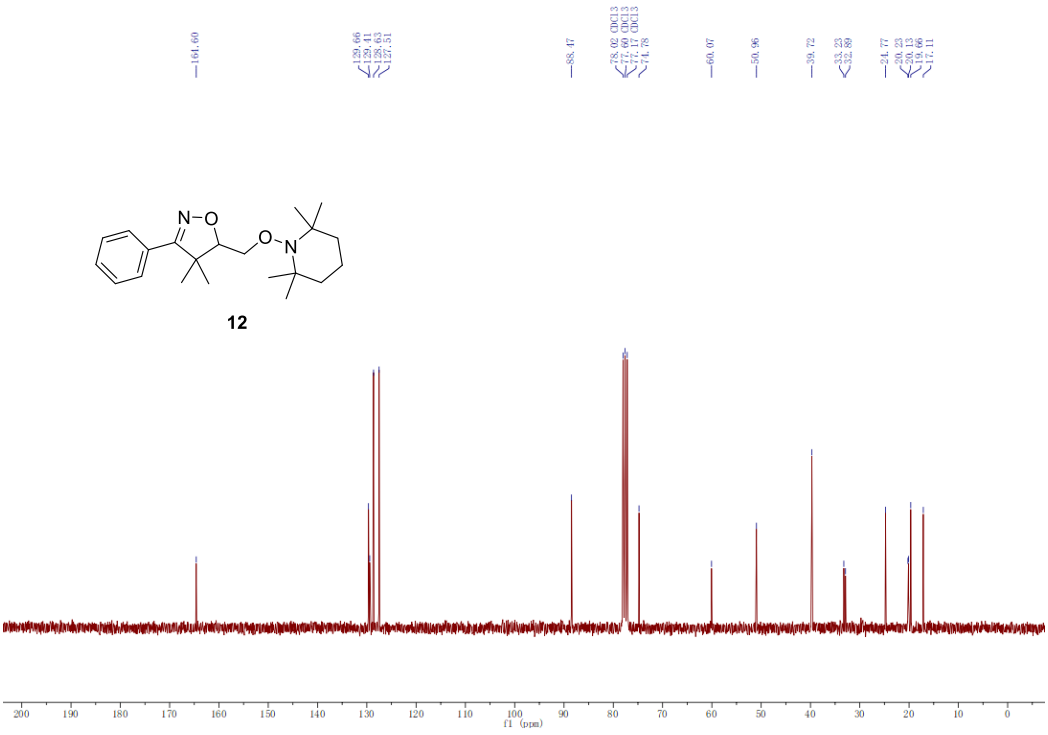


4,4-Dimethyl-3-phenyl-5-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)-4,5-dihydroisoxazole (12).

300 MHz ^{1}H NMR Spectrum (recorded in $CDCl_3$)



75 MHz $^{13}C\{^{1}H\}$ NMR Spectrum (recorded in $CDCl_3$)



Appendix II

Data from DFT Calculations

Coordinates of all species

2•.xyz

C	0.2311430000	-1.2022590000	0.0413180000
C	1.5963130000	-1.2076000000	0.0151370000
C	2.3295900000	0.0000050000	0.0177440000
C	1.5963040000	1.2076070000	0.0151350000
C	0.2311350000	1.2022550000	0.0413160000
H	-0.3829330000	-2.0938430000	0.0364420000
H	2.1056040000	-2.1657860000	-0.0063610000
H	3.4121130000	0.0000100000	-0.0124770000
H	2.1055890000	2.1657950000	-0.0063660000
H	-0.3829500000	2.0938340000	0.0364380000
N	-0.4746980000	-0.0000050000	0.1399920000
O	-1.6808010000	-0.0000090000	-0.6153600000
C	-2.7887680000	0.0000040000	0.2756860000
H	-2.7930500000	-0.8945690000	0.9090090000
H	-3.6763490000	0.0000000000	-0.3607470000
H	-2.7930440000	0.8945920000	0.9089880000

2^{+}.xyz

C	-0.1940800000	1.1869950000	-0.1637550000
C	-1.5505140000	1.2054810000	0.0873380000
C	-2.2361650000	-0.0000610000	0.2142950000
C	-1.5503060000	-1.2056020000	0.0872220000
C	-0.1939770000	-1.1870020000	-0.1638130000
H	0.4278450000	2.0639660000	-0.2891500000
H	-2.0551490000	2.1588860000	0.1749380000
H	-3.3027770000	-0.0002220000	0.4069630000
H	-2.0549850000	-2.1589990000	0.1746830000
H	0.4282610000	-2.0637630000	-0.2891690000
N	0.4255290000	0.0001150000	-0.2744620000
O	1.7574130000	0.0001740000	-0.5956330000
C	2.5797100000	-0.0000920000	0.5933150000
H	2.3957290000	0.9005310000	1.1847840000
H	3.5993780000	-0.0000330000	0.2111420000
H	2.3956830000	-0.9008800000	1.1844990000

1.xyz

N	-0.9030120000	1.9297960000	-0.5142590000
O	0.2142630000	2.6694490000	-0.8865530000
C	-1.7707500000	-0.1640930000	0.2972060000
C	-1.4760380000	-0.7408740000	1.6888720000
C	-3.0984010000	0.6099090000	0.3444210000
C	-1.9054810000	-1.2448550000	-0.7634150000
C	-1.7444220000	-2.5546240000	-0.5977690000
C	2.8980230000	0.1178890000	1.1363190000
C	1.5968350000	0.5990900000	1.0361800000
C	0.7892210000	0.2338970000	-0.0453520000
C	1.3056280000	-0.6119470000	-1.0292060000
C	2.6107430000	-1.0886940000	-0.9296120000

C	3.4077610000	-0.7282320000	0.1532910000
H	3.5150030000	0.4050210000	1.9822480000
H	1.2002470000	1.2609410000	1.8001850000
H	0.6881870000	-0.8959160000	-1.8747320000
H	3.0033890000	-1.7439280000	-1.7010890000
H	4.4235350000	-1.1035070000	0.2309990000
C	-0.6112370000	0.7476200000	-0.1240990000
H	-0.1719420000	3.5163030000	-1.1423330000
H	-0.5535690000	-1.3268710000	1.7067810000
H	-2.2987730000	-1.3877340000	2.0083220000
H	-1.3779850000	0.0688350000	2.4187010000
H	-3.8997950000	-0.0696560000	0.6501750000
H	-3.3567220000	1.0306150000	-0.6305510000
H	-3.0460940000	1.4321350000	1.0639430000
H	-2.1753300000	-0.8653800000	-1.7497450000
H	-1.4706120000	-2.9948780000	0.3568150000
H	-1.8838560000	-3.2406560000	-1.4284820000

HAT-TS.xyz

N	1.3892040000	-0.4228710000	-0.1210980000
O	1.3702860000	-1.7222290000	-0.3863060000
C	0.3356900000	1.7035450000	0.3371610000
C	-0.4590500000	1.9763270000	1.6223210000
C	1.7828180000	2.1867070000	0.5267730000
C	-0.2355870000	2.4331720000	-0.8682290000
C	-1.3023560000	3.2269770000	-0.8892190000
C	-2.5899630000	-2.0258320000	1.0645490000
C	-1.3693610000	-1.3596670000	1.0657850000
C	-1.0274280000	-0.5116080000	0.0074720000
C	-1.9174350000	-0.3471280000	-1.0560330000
C	-3.1363830000	-1.0214450000	-1.0571950000
C	-3.4765340000	-1.8572390000	0.0025550000
H	-2.8484540000	-2.6779640000	1.8929800000
H	-0.6762300000	-1.4927780000	1.8908590000
H	-1.6568100000	0.3026490000	-1.8840550000
H	-3.8203180000	-0.8917170000	-1.8901530000
H	-4.4285960000	-2.3788460000	0.0006820000
C	0.2842810000	0.2014490000	0.0429460000
H	2.4228540000	-2.0486230000	-0.3809360000
H	-1.5058940000	1.6754830000	1.5304640000
H	-0.4283190000	3.0431050000	1.8629710000
H	-0.0190010000	1.4263140000	2.4598710000
H	1.7752790000	3.2572230000	0.7516830000
H	2.3825490000	2.0325180000	-0.3743940000
H	2.2670470000	1.6617320000	1.3555510000
H	0.3289480000	2.2790720000	-1.7885290000
H	-1.9087930000	3.4168940000	-0.0082910000
H	-1.6080710000	3.7206380000	-1.8072690000
C	4.2173860000	-0.9420200000	-0.0726050000
H	5.0129430000	-0.5576770000	-0.7267230000
H	3.3895950000	-0.1713020000	-0.0815500000
H	4.5478030000	-0.9850370000	0.9782290000
O	3.6812860000	-2.1066490000	-0.5251190000

II-IIrotated-TS.xyz

N	-0.6614400000	1.8967130000	-0.3624940000
O	-0.8421800000	3.0667110000	-0.6467570000
C	-1.6977680000	-0.2018090000	0.2859710000
C	-1.4558550000	-0.8975810000	1.6319180000
C	-2.9428740000	0.6960750000	0.4092980000
C	-1.9617570000	-1.1680630000	-0.8565350000
C	-2.1448110000	-2.4822660000	-0.7600380000
C	2.5971740000	-1.5670140000	-0.2339230000
C	1.2681930000	-1.1527870000	-0.2627450000
C	0.9397750000	0.1873840000	-0.0315880000
C	1.9715780000	1.0989970000	0.2271200000
C	3.2970000000	0.6828070000	0.2532860000
C	3.6155890000	-0.6542840000	0.0241290000
H	2.8342450000	-2.6100310000	-0.4197170000
H	0.4890890000	-1.8733520000	-0.4808670000
H	1.7311310000	2.1419460000	0.4127910000
H	4.0821730000	1.4038650000	0.4582270000
H	4.6503720000	-0.9812960000	0.0468780000
C	-0.4741230000	0.6833460000	-0.0683470000
H	-1.2508210000	-0.1513200000	2.4053060000
H	-0.6147910000	-1.5938860000	1.6006800000
H	-2.3483390000	-1.4552270000	1.9313650000
H	-2.8072150000	1.4478750000	1.1934420000
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H	-3.1645360000	1.2134510000	-0.5289650000
H	-2.0516180000	-0.6898640000	-1.8323020000
H	-2.0697910000	-3.0142150000	0.1843960000
H	-2.3770920000	-3.0769300000	-1.6387200000

II.xyz

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C	-1.7473530000	-0.0490380000	0.2931990000
C	-1.5299920000	-0.7748710000	1.6283540000
C	-2.9323390000	0.9242980000	0.4531940000
C	-2.1108000000	-0.9896780000	-0.8467210000
C	-2.3842070000	-2.2880350000	-0.7516090000
C	2.4100590000	-1.7195800000	-0.2875480000
C	1.1227920000	-1.1949800000	-0.3388850000
C	0.8925090000	0.1535810000	-0.0370430000
C	1.9819380000	0.9588110000	0.3198860000
C	3.2662350000	0.4287470000	0.3758710000
C	3.4860890000	-0.9119410000	0.0705880000
H	2.5702390000	-2.7649730000	-0.5323900000
H	0.2960080000	-1.8335460000	-0.6265190000
H	1.8265620000	2.0046090000	0.5629690000
H	4.0967400000	1.0672010000	0.6603300000
H	4.4896090000	-1.3238210000	0.1103550000
C	-0.4801840000	0.7323710000	-0.0815940000

H	-1.2514400000	-0.0543430000	2.4032100000
H	-0.7443400000	-1.5318480000	1.5710380000
H	-2.4548350000	-1.2671250000	1.9429420000
H	-2.7306100000	1.6597430000	1.2382780000
H	-3.8256320000	0.3570060000	0.7289820000
H	-3.1442780000	1.4621700000	-0.4753350000
H	-2.1904960000	-0.4994470000	-1.8173630000
H	-2.3211760000	-2.8309150000	0.1874250000
H	-2.6814750000	-2.8584780000	-1.6267690000

III-IV-TS.xyz

C	3.0461820000	-0.5364050000	-1.0806330000
C	2.8187860000	-1.8512540000	-0.6387420000
C	3.1652110000	-2.2128570000	0.6462800000
C	3.7851750000	-1.2837870000	1.4968370000
C	4.0772990000	-0.0275110000	1.0189970000
H	3.0306900000	-0.2451290000	-2.1231450000
H	2.3321190000	-2.5426230000	-1.3138450000
H	2.9635200000	-3.2174950000	0.9988790000
H	4.0531760000	-1.5358670000	2.5144840000
H	4.5705350000	0.7529450000	1.5841530000
N	3.7552160000	0.2786580000	-0.2518490000
O	4.0246600000	1.5463690000	-0.6965420000
C	5.3143080000	1.5984310000	-1.3427770000
H	6.1059830000	1.3478490000	-0.6318950000
H	5.4116680000	2.6327810000	-1.6699200000
H	5.3385320000	0.9241820000	-2.2031850000
N	-1.2796280000	-1.4227970000	0.1648270000
O	0.0828140000	-1.2920630000	0.4286050000
C	-0.9013110000	0.8317660000	0.6985260000
C	-1.0884600000	2.1603610000	-0.0322950000
C	-0.9831680000	1.0238320000	2.2230350000
C	0.4315830000	0.1033020000	0.3538940000
C	0.9928460000	0.4039830000	-0.9945750000
C	-5.4647030000	0.8624290000	0.2365470000
C	-4.1089530000	0.7989630000	0.5440360000
C	-3.2919450000	-0.1703250000	-0.0491970000
C	-3.8625980000	-1.0676750000	-0.9633740000
C	-5.2168260000	-1.0031720000	-1.2658190000
C	-6.0229810000	-0.0365860000	-0.6674210000
H	-6.0853290000	1.6172000000	0.7089560000
H	-3.6992590000	1.5013480000	1.2603250000
H	-3.2319660000	-1.8105570000	-1.4403220000
H	-5.6422570000	-1.7040700000	-1.9770930000
H	-7.0801070000	0.0173640000	-0.9077330000
C	-1.8515410000	-0.2783600000	0.2585960000
H	-1.1378380000	2.0268910000	-1.1165720000
H	-0.2561940000	2.8331450000	0.1964970000
H	-2.0082500000	2.6536220000	0.2900000000
H	-1.9611330000	1.4006480000	2.5318680000
H	-0.2278010000	1.7499650000	2.5405630000
H	-0.7983420000	0.0807880000	2.7458950000

H	1.1745320000	0.2954060000	1.1346460000
H	0.5497830000	-0.1002210000	-1.8498600000
H	1.3756150000	1.4055530000	-1.1715350000

III.xyz

N	0.8244540000	-1.4934350000	-0.6435370000
O	2.2008240000	-1.5550450000	-0.4573880000
C	1.4247650000	0.4374820000	0.5439320000
C	1.3756990000	1.9452860000	0.3077630000
C	1.3190600000	0.1351830000	2.0486910000
C	2.6843320000	-0.2439830000	-0.0653710000
C	3.2838820000	0.4245780000	-1.2457740000
C	-3.0336220000	1.2284470000	-0.5434180000
C	-1.6536250000	1.0491370000	-0.5568100000
C	-1.0961490000	-0.1699060000	-0.1544810000
C	-1.9462820000	-1.2032710000	0.2588810000
C	-3.3247850000	-1.0204800000	0.2711020000
C	-3.8719050000	0.1970220000	-0.1276070000
H	-3.4540970000	2.1763050000	-0.8645110000
H	-1.0140100000	1.8528000000	-0.9033690000
H	-1.5163480000	-2.1475050000	0.5771460000
H	-3.9718280000	-1.8289650000	0.5968140000
H	-4.9477460000	0.3414020000	-0.1153640000
C	0.3656510000	-0.3987410000	-0.1615710000
H	0.4956460000	2.3828720000	0.7871720000
H	1.3564300000	2.1952670000	-0.7566880000
H	2.2604910000	2.4139550000	0.7502390000
H	0.3491040000	0.4564810000	2.4406460000
H	2.1031390000	0.6713500000	2.5934160000
H	1.4322960000	-0.9356710000	2.2438660000
H	3.4397430000	-0.4024410000	0.7112060000
H	4.0967280000	1.1319480000	-1.1244470000
H	2.8305800000	0.3020790000	-2.2242920000

IIrotated.xyz

N	0.6680260000	-1.8422700000	-0.6175680000
O	1.6317280000	-2.5710500000	-0.8547500000
C	1.6134560000	0.2305220000	0.3797050000
C	1.1563290000	0.9744740000	1.6429310000
C	2.8596120000	-0.5998190000	0.7432380000
C	1.9990790000	1.1619240000	-0.7586700000
C	2.0470430000	2.4907480000	-0.7170020000
C	-2.7245020000	1.3573830000	-0.4234460000
C	-1.3778720000	1.0101330000	-0.4629440000
C	-0.9650060000	-0.2677930000	-0.0681870000
C	-1.9280370000	-1.1863470000	0.3648940000
C	-3.2744990000	-0.8380920000	0.3979780000
C	-3.6769660000	0.4361480000	0.0061820000
H	-3.0301410000	2.3508340000	-0.7368340000
H	-0.6448590000	1.7290190000	-0.8126880000
H	-1.6147590000	-2.1758880000	0.6839650000

H	-4.0083280000	-1.5618660000	0.7387090000
H	-4.7268340000	0.7104140000	0.0363090000
C	0.4673420000	-0.6760140000	-0.1211610000
H	0.8590590000	0.2564060000	2.4129380000
H	0.3129950000	1.6429160000	1.4597020000
H	1.9835080000	1.5707190000	2.0385470000
H	2.6204070000	-1.3607030000	1.4925590000
H	3.6146770000	0.0712510000	1.1625760000
H	3.2962840000	-1.0952610000	-0.1264230000
H	2.2908290000	0.6471100000	-1.6743820000
H	1.7697500000	3.0581030000	0.1670570000
H	2.3715320000	3.0616450000	-1.5821640000

$IV^{+\bullet}$.xyz

C	-2.5332690000	0.1323170000	-1.0531500000
C	-2.3304880000	1.6035730000	-1.1953910000
C	-3.0654510000	2.5311800000	-0.5158900000
C	-4.0293090000	2.1166390000	0.4220070000
C	-4.2220000000	0.7517280000	0.6510690000
H	-2.9423660000	-0.2313440000	-2.0096460000
H	-1.5727730000	1.9014090000	-1.9108840000
H	-2.8912190000	3.5881470000	-0.6791820000
H	-4.6192180000	2.8234740000	0.9902810000
H	-4.9233840000	0.3660540000	1.3818640000
N	-3.5402670000	-0.1494210000	-0.0249400000
O	-3.7225740000	-1.4603520000	0.3169830000
C	-4.5460600000	-2.1559980000	-0.6430180000
H	-5.5040190000	-1.6427080000	-0.7588830000
H	-4.6936530000	-3.1418220000	-0.2040420000
H	-4.0367620000	-2.2518520000	-1.6055300000
N	0.9934570000	1.2895780000	0.2148350000
O	-0.3251480000	1.0536680000	0.6236640000
C	0.8124120000	-0.9900070000	0.7335570000
C	1.0147260000	-2.3321290000	0.0327680000
C	1.1265290000	-1.1376860000	2.2343040000
C	-0.5810580000	-0.3609040000	0.5404450000
C	-1.2409170000	-0.6678670000	-0.8014360000
C	5.0432240000	-0.6765510000	-1.2003280000
C	3.6770920000	-0.7275920000	-0.9409020000
C	3.0906440000	0.1972510000	-0.0696020000
C	3.8949350000	1.1713850000	0.5348430000
C	5.2599360000	1.2177360000	0.2740760000
C	5.8374390000	0.2927570000	-0.5927550000
H	5.4864010000	-1.3942430000	-1.8833460000
H	3.0674050000	-1.4747840000	-1.4359120000
H	3.4427240000	1.8848880000	1.2159790000
H	5.8735190000	1.9750510000	0.7516780000
H	6.9034060000	0.3274050000	-0.7946780000
C	1.6405640000	0.1837730000	0.2196190000
H	0.9110170000	-2.2643980000	-1.0529540000
H	0.2804150000	-3.0536970000	0.4044290000
H	2.0082260000	-2.7281740000	0.2574250000

H	2.1813380000	-1.3867170000	2.3822820000
H	0.5204400000	-1.9414080000	2.6640740000
H	0.9106720000	-0.2117430000	2.7754510000
H	-1.2523010000	-0.6097850000	1.3675390000
H	-0.5601130000	-0.4263990000	-1.6239700000
H	-1.4739910000	-1.7326100000	-0.8677180000

MeO.xyz

C	-0.5716880000	0.0002820000	-0.0139270000
H	-0.8725440000	-0.0100470000	1.0542740000
H	-1.0093750000	0.9128030000	-0.4478170000
H	-1.0084750000	-0.9052540000	-0.4632840000
O	0.7900650000	0.0001010000	-0.0074510000

MeOH.xyz

H	-1.1246170000	0.7631180000	-0.0000160000
O	-0.7472210000	-0.1226560000	0.0000010000
C	0.6592280000	0.0188370000	0.0000060000
H	1.0295140000	0.5459810000	-0.8907360000
H	1.0295120000	0.5460700000	0.8906720000
H	1.0879890000	-0.9869420000	0.0000320000

MeOdetachment-TS.xyz

C	2.5365110000	-0.4065170000	-0.4144940000
C	2.8665110000	-1.5835390000	-1.0561570000
C	4.0892090000	-2.2183160000	-0.8090150000
C	4.9600890000	-1.6386000000	0.1208950000
C	4.6034480000	-0.4666700000	0.7486310000
H	2.1436430000	-2.0205210000	-1.7380000000
H	4.3487520000	-3.1386440000	-1.3194110000
H	5.9047190000	-2.1076860000	0.3751300000
H	5.2326780000	0.0265780000	1.4807550000
N	3.4089430000	0.1533860000	0.4934310000
O	3.6462670000	1.7383400000	0.2064780000
C	4.3151550000	1.8804080000	-1.0225470000
H	5.2925530000	1.3761800000	-1.0318650000
H	4.4806700000	2.9550290000	-1.1561720000
H	3.7224460000	1.5132350000	-1.8740500000
N	-1.1912850000	-1.2962410000	0.6647390000
O	0.1004120000	-0.9893380000	1.0844010000
C	-0.9725070000	1.0342540000	0.5661790000
C	-1.0689340000	2.1281680000	-0.4958360000
C	-1.4029600000	1.6022290000	1.9320050000
C	0.4098560000	0.3626870000	0.6795600000
C	1.2343690000	0.3135910000	-0.6091000000
C	-5.0722080000	0.2716620000	-1.5209920000
C	-3.7233670000	0.3624190000	-1.1907500000
C	-3.2288760000	-0.2906150000	-0.0559540000
C	-4.1094860000	-1.0355560000	0.7382380000
C	-5.4569330000	-1.1234660000	0.4056390000

C	-5.9421550000	-0.4680540000	-0.7237270000
H	-5.4424390000	0.7771950000	-2.4073930000
H	-3.0533050000	0.9250720000	-1.8308720000
H	-3.7297100000	-1.5379040000	1.6220690000
H	-6.1291250000	-1.7014320000	1.0321280000
H	-6.9944640000	-0.5341300000	-0.9820470000
C	-1.8004610000	-0.2221180000	0.3227860000
H	-0.8774000000	1.7545910000	-1.5047950000
H	-0.3419330000	2.9171780000	-0.2787520000
H	-2.0627840000	2.5835980000	-0.4815580000
H	-2.4546620000	1.9039230000	1.9116720000
H	-0.7979430000	2.4812580000	2.1767830000
H	-1.2714000000	0.8602400000	2.7253520000
H	1.0087500000	0.8023840000	1.4814560000
H	0.6602830000	-0.1798080000	-1.3989370000
H	1.4400560000	1.3398380000	-0.9278710000

Product.xyz

C	-3.0180060000	-0.0071060000	0.5474370000
C	-3.2807860000	-1.3761920000	0.6173100000
C	-4.5532740000	-1.8366070000	0.3030300000
C	-5.5243320000	-0.9155290000	-0.0762100000
C	-5.1695950000	0.4279220000	-0.1236900000
H	-2.4936040000	-2.0621870000	0.9110490000
H	-4.7826000000	-2.8966080000	0.3512150000
H	-6.5319140000	-1.2258100000	-0.3301270000
H	-5.9014170000	1.1773370000	-0.4174090000
N	-3.9499770000	0.8835030000	0.1782260000
N	0.5680370000	-0.9832060000	-0.8426290000
O	-0.6968240000	-0.4762080000	-1.1344650000
C	0.5866640000	1.2889720000	-0.2713180000
C	0.8265170000	2.1308650000	0.9801820000
C	1.0338970000	2.0764700000	-1.5175600000
C	-0.8590510000	0.7856280000	-0.4490480000
C	-1.6475550000	0.5460080000	0.8419240000
C	4.6225900000	-0.2835700000	1.4619630000
C	3.2811840000	-0.0096280000	1.2128780000
C	2.7126650000	-0.3355420000	-0.0236630000
C	3.5099500000	-0.9409390000	-1.0024850000
C	4.8506280000	-1.2119620000	-0.7504900000
C	5.4105640000	-0.8817810000	0.4815230000
H	5.0512540000	-0.0326660000	2.4271650000
H	2.6723750000	0.4379140000	1.9905630000
H	3.0717550000	-1.1893480000	-1.9638090000
H	5.4591780000	-1.6781760000	-1.5190440000
H	6.4576460000	-1.0907410000	0.6774770000
C	1.2894670000	-0.0623670000	-0.3205830000
H	0.6168020000	1.5839140000	1.9026620000
H	0.1869880000	3.0188280000	0.9557790000
H	1.8646010000	2.4725610000	1.0131180000
H	2.1108220000	2.2682740000	-1.4882210000
H	0.5143470000	3.0394340000	-1.5552530000

H	0.8059180000	1.5243330000	-2.4343310000
H	-1.4350350000	1.4337140000	-1.1158320000
H	-1.0883130000	-0.1395090000	1.4869430000
H	-1.7597970000	1.4984620000	1.3673960000

V^{2+}.xyz

C	-2.3842200000	-0.0277760000	-0.9005070000
C	-1.6777870000	1.2730680000	-0.5154680000
C	-2.4716460000	2.2993960000	0.2183890000
C	-3.6768330000	2.0046600000	0.7167900000
C	-4.2185450000	0.6722170000	0.5799120000
H	-2.6732730000	0.0049440000	-1.9532440000
H	-1.1623370000	1.6909390000	-1.3794320000
H	-2.0248280000	3.2791450000	0.3429630000
H	-4.2742630000	2.7271840000	1.2575010000
H	-5.1355430000	0.3734530000	1.0778920000
N	-3.6249610000	-0.2293430000	-0.1234210000
O	-4.1416380000	-1.4900890000	-0.1036300000
C	-4.7285660000	-1.8611910000	-1.3759760000
H	-5.4554410000	-1.1065590000	-1.6836890000
H	-5.2243390000	-2.8074030000	-1.1656910000
H	-3.9570640000	-2.0037460000	-2.1355860000
N	0.7766840000	1.1520790000	-0.1666710000
O	-0.5742130000	0.8373380000	0.4123430000
C	0.8167650000	-0.9956590000	0.8725260000
C	1.1539340000	-2.4181470000	0.4251050000
C	1.1992600000	-0.8008420000	2.3539580000
C	-0.6542060000	-0.6480800000	0.6419130000
C	-1.3572200000	-1.1281760000	-0.6133490000
C	4.9146330000	-0.6411910000	-1.2934610000
C	3.5644430000	-0.7707700000	-0.9908250000
C	2.9294960000	0.2227480000	-0.2376870000
C	3.6468150000	1.3400530000	0.2055360000
C	4.9995350000	1.4527410000	-0.0928580000
C	5.6328260000	0.4641040000	-0.8416180000
H	5.4065300000	-1.4064700000	-1.8842420000
H	3.0094200000	-1.6251910000	-1.3590770000
H	3.1479110000	2.1017700000	0.7954500000
H	5.5576960000	2.3132830000	0.2600910000
H	6.6888180000	0.5545540000	-1.0745210000
C	1.4953770000	0.1284200000	0.0973450000
H	0.9891140000	-2.5772760000	-0.6427120000
H	0.5253750000	-3.1181010000	0.9825000000
H	2.1957530000	-2.6456480000	0.6582090000
H	2.2787630000	-0.9127120000	2.4784070000
H	0.7001590000	-1.5665150000	2.9536440000
H	0.9048920000	0.1856220000	2.7228580000
H	-1.2629820000	-0.7583950000	1.5410420000
H	-0.6695680000	-1.1732370000	-1.4613390000
H	-1.8145440000	-2.1073800000	-0.4743560000

VII^{+}.xyz

C	-2.4689450000	0.4927840000	-0.4884740000
C	-2.7048000000	1.6217320000	-1.2256940000
C	-3.8910830000	2.3747370000	-1.0843460000
C	-4.8383090000	1.9357280000	-0.1360860000
C	-4.6072310000	0.8161800000	0.6106620000
H	-1.9334300000	1.9399270000	-1.9206740000
H	-4.0658480000	3.2580680000	-1.6860700000
H	-5.7595610000	2.4855210000	0.0282510000
H	-5.2824750000	0.4324020000	1.3651930000
N	-3.4087890000	0.1094870000	0.4859460000
O	-3.5377350000	-1.2846770000	0.6857590000
C	-4.2322480000	-1.9093010000	-0.3951700000
H	-5.2582070000	-1.5333550000	-0.4779300000
H	-4.2490670000	-2.9732060000	-0.1524250000
H	-3.7106040000	-1.7564090000	-1.3473900000
N	1.2768080000	1.3123570000	0.5613700000
O	-0.0325880000	1.1258940000	0.9965840000
C	0.9379470000	-0.9969170000	0.7555570000
C	0.9893510000	-2.2247980000	-0.1519610000
C	1.3229960000	-1.4012780000	2.1914940000
C	-0.4084870000	-0.2470860000	0.7561470000
C	-1.2094990000	-0.3176960000	-0.5489330000
C	5.0939810000	-0.7168970000	-1.3411650000
C	3.7389530000	-0.6975520000	-1.0244520000
C	3.2663810000	0.1226750000	0.0062870000
C	4.1753340000	0.9225260000	0.7101510000
C	5.5287250000	0.9004950000	0.3911830000
C	5.9918990000	0.0786400000	-0.6337580000
H	5.4471520000	-1.3524420000	-2.1471950000
H	3.0480940000	-1.3055530000	-1.5973420000
H	3.8124390000	1.5552330000	1.5136930000
H	6.2227630000	1.5229840000	0.9472460000
H	7.0487600000	0.0588920000	-0.8809270000
C	1.8327520000	0.1743610000	0.3669110000
H	0.8282160000	-1.9792660000	-1.2045800000
H	0.2203600000	-2.9410690000	0.1545370000
H	1.9580530000	-2.7233860000	-0.0603260000
H	2.3579770000	-1.7546920000	2.2297260000
H	0.6708340000	-2.2095320000	2.5381310000
H	1.2207370000	-0.5558110000	2.8784780000
H	-1.0393190000	-0.5525480000	1.5949640000
H	-0.5954710000	0.0493700000	-1.3767980000
H	-1.4442700000	-1.3673540000	-0.7519090000

VI$^{\bullet}$.xyz

C	-2.4689450000	0.4927840000	-0.4884740000
C	-2.7048000000	1.6217320000	-1.2256940000
C	-3.8910830000	2.3747370000	-1.0843460000
C	-4.8383090000	1.9357280000	-0.1360860000
C	-4.6072310000	0.8161800000	0.6106620000
H	-1.9334300000	1.9399270000	-1.9206740000

H	-4.0658480000	3.2580680000	-1.6860700000
H	-5.7595610000	2.4855210000	0.0282510000
H	-5.2824750000	0.4324020000	1.3651930000
N	-3.4087890000	0.1094870000	0.4859460000
O	-3.5377350000	-1.2846770000	0.6857590000
C	-4.2322480000	-1.9093010000	-0.3951700000
H	-5.2582070000	-1.5333550000	-0.4779300000
H	-4.2490670000	-2.9732060000	-0.1524250000
H	-3.7106040000	-1.7564090000	-1.3473900000
N	1.2768080000	1.3123570000	0.5613700000
O	-0.0325880000	1.1258940000	0.9965840000
C	0.9379470000	-0.9969170000	0.7555570000
C	0.9893510000	-2.2247980000	-0.1519610000
C	1.3229960000	-1.4012780000	2.1914940000
C	-0.4084870000	-0.2470860000	0.7561470000
C	-1.2094990000	-0.3176960000	-0.5489330000
C	5.0939810000	-0.7168970000	-1.3411650000
C	3.7389530000	-0.6975520000	-1.0244520000
C	3.2663810000	0.1226750000	0.0062870000
C	4.1753340000	0.9225260000	0.7101510000
C	5.5287250000	0.9004950000	0.3911830000
C	5.9918990000	0.0786400000	-0.6337580000
H	5.4471520000	-1.3524420000	-2.1471950000
H	3.0480940000	-1.3055530000	-1.5973420000
H	3.8124390000	1.5552330000	1.5136930000
H	6.2227630000	1.5229840000	0.9472460000
H	7.0487600000	0.0588920000	-0.8809270000
C	1.8327520000	0.1743610000	0.3669110000
H	0.8282160000	-1.9792660000	-1.2045800000
H	0.2203600000	-2.9410690000	0.1545370000
H	1.9580530000	-2.7233860000	-0.0603260000
H	2.3579770000	-1.7546920000	2.2297260000
H	0.6708340000	-2.2095320000	2.5381310000
H	1.2207370000	-0.5558110000	2.8784780000
H	-1.0393190000	-0.5525480000	1.5949640000
H	-0.5954710000	0.0493700000	-1.3767980000
H	-1.4442700000	-1.3673540000	-0.7519090000

[IrIII]*.xyz

F	-2.1391720000	3.6078960000	3.4929610000
C	-1.0511400000	3.0013060000	3.0099160000
C	0.1803360000	3.3314170000	3.5575270000
C	1.3039270000	2.6959970000	3.0534120000
F	2.4829360000	3.0295690000	3.5946980000
C	1.2339480000	1.7497100000	2.0332770000
C	2.3699360000	1.0141890000	1.4685690000
N	2.0203360000	0.1694040000	0.4640660000
C	2.9341440000	-0.5935950000	-0.1449460000
C	4.2667250000	-0.5422430000	0.2160700000
C	5.2824920000	-1.4097950000	-0.4745360000
F	6.2820200000	-0.6723410000	-0.9847510000
F	5.8366830000	-2.2827010000	0.3814450000

F	4.7435310000	-2.1135580000	-1.4794050000
C	4.6567260000	0.3184770000	1.2382050000
C	3.7039520000	1.0994300000	1.8685200000
C	-0.0460070000	1.4555880000	1.4812780000
Ir	0.0076720000	0.1193640000	-0.0001150000
N	0.1235880000	-1.5990710000	-1.3121890000
C	0.0050280000	-2.8324980000	-0.6923740000
C	-0.1280450000	-2.8233310000	0.7172610000
C	-0.2393760000	-3.9905700000	1.5249650000
C	-0.3494980000	-3.8872730000	2.8827770000
C	-0.3523910000	-2.6050970000	3.4887630000
C	-0.2500530000	-1.5046140000	2.6783690000
N	-0.1490850000	-1.5806970000	1.3300730000
C	0.0305800000	-4.0101350000	-1.4921480000
C	0.1655500000	-3.9251680000	-2.8489370000
C	0.2819680000	-2.6514510000	-3.4613890000
C	0.2523670000	-1.5407170000	-2.6589890000
N	-2.0036710000	0.1928010000	-0.4671000000
C	-2.3384240000	1.0206520000	-1.4906040000
C	-1.1915490000	1.7341290000	-2.0617360000
C	-1.2468380000	2.6644310000	-3.0972350000
F	-2.4194860000	2.9990750000	-3.6514440000
C	-0.1147310000	3.2825480000	-3.6038460000
C	1.1102650000	2.9515570000	-3.0423970000
F	2.2064210000	3.5420380000	-3.5270560000
C	1.2363230000	2.0420620000	-2.0065730000
C	0.0823930000	1.4370170000	-1.4973960000
C	-3.6687300000	1.1100180000	-1.9015280000
C	-4.6333910000	0.3506780000	-1.2624580000
C	-4.2587560000	-0.4914010000	-0.2194600000
C	-5.2890860000	-1.3113410000	0.5068050000
F	-6.1155180000	-0.5302010000	1.2221780000
F	-6.0510820000	-2.0049870000	-0.3526800000
F	-4.7287250000	-2.1861910000	1.3532980000
C	-2.9292630000	-0.5466290000	0.1526620000
C	-1.1916670000	2.0770410000	1.9891630000
H	0.2683900000	4.0600970000	4.3542520000
H	2.5744720000	-1.2430660000	-0.9325850000
H	5.6961420000	0.3785970000	1.5421980000
H	3.9896820000	1.7680770000	2.6658800000
H	-0.2321510000	-4.9665990000	1.0551690000
H	-0.4321160000	-4.7813710000	3.4917970000
H	-0.4363510000	-2.4806760000	4.5611410000
H	-0.2579780000	-0.5055390000	3.0984560000
H	-0.0612500000	-4.9790580000	-1.0165080000
H	0.1831990000	-4.8269630000	-3.4519450000
H	0.3943150000	-2.5413220000	-4.5327500000
H	0.3450240000	-0.5482540000	-3.0846040000
H	-0.1914420000	3.9992960000	-4.4124830000
H	2.2213050000	1.8242710000	-1.6103690000
H	-3.9425240000	1.7637330000	-2.7153040000
H	-5.6695710000	0.4120740000	-1.5769760000
H	-2.5815640000	-1.1822120000	0.9568310000

H	-2.1812870000	1.8610870000	1.6035850000

[IrIII].xyz

F	-2.1263300000	-3.7377180000	-3.3305710000
C	-1.0338820000	-3.0972570000	-2.8873030000
C	0.1838660000	-3.4063160000	-3.4748170000
C	1.2925500000	-2.7341050000	-2.9986940000
F	2.4735900000	-3.0309310000	-3.5707010000
C	1.2222610000	-1.7821340000	-1.9767430000
C	2.3578820000	-1.0396310000	-1.4287340000
N	2.0109310000	-0.1523050000	-0.4573140000
C	2.9454050000	0.5900420000	0.1513260000
C	4.2821530000	0.4920710000	-0.1760230000
C	5.3064020000	1.3476110000	0.5114620000
F	6.2984220000	0.6041020000	1.0283140000
F	5.8749310000	2.2130210000	-0.3459130000
F	4.7763530000	2.0665090000	1.5128830000
C	4.6663350000	-0.4065060000	-1.1700110000
C	3.7022120000	-1.1720480000	-1.7956270000
C	-0.0437700000	-1.4873870000	-1.4041920000
Ir	-0.0012930000	-0.0482530000	0.0011130000
N	0.1389150000	1.6740030000	1.3311590000
C	0.0783690000	2.8883180000	0.7411830000
C	-0.0536370000	2.8888890000	-0.7386190000
C	-0.1038610000	4.0549040000	-1.4968160000
C	-0.2325720000	3.9655400000	-2.8766180000
C	-0.3087060000	2.7131450000	-3.4711050000
C	-0.2529500000	1.5916710000	-2.6592600000
N	-0.1306390000	1.6752860000	-1.3280640000
C	0.1431210000	4.0537750000	1.4991650000
C	0.2684140000	3.9630840000	2.8792190000
C	0.3266450000	2.7099970000	3.4742510000
C	0.2576200000	1.5891190000	2.6626040000
N	-2.0136570000	-0.1423780000	0.4628640000
C	-2.3626750000	-1.0260810000	1.4370030000
C	-1.2307170000	-1.7790480000	1.9783060000
C	-1.3047590000	-2.7362750000	2.9951560000
F	-2.4859610000	-3.0274420000	3.5697510000
C	-0.1998040000	-3.4202490000	3.4630360000
C	1.0181070000	-3.1179060000	2.8724040000
F	2.1069770000	-3.7699090000	3.3076410000
C	1.1604200000	-2.1793910000	1.8636350000
C	0.0353600000	-1.4917930000	1.4021350000
C	-3.7055130000	-1.1445850000	1.8140720000
C	-4.6668890000	-0.3710850000	1.1940570000
C	-4.2810480000	0.5209240000	0.1948370000
C	-5.3054000000	1.3593590000	-0.5129230000
F	-6.1492900000	0.6003520000	-1.2324800000
F	-6.0549530000	2.0539640000	0.3594250000
F	-4.7433850000	2.2413680000	-1.3538560000
C	-2.9456560000	0.6064730000	-0.1415560000
C	-1.1725480000	-2.1632510000	-1.8737600000

H	0.2690250000	-4.1390660000	-4.2672060000
H	2.5995870000	1.2678830000	0.9204550000
H	5.7096580000	-0.5080270000	-1.4492310000
H	3.9833470000	-1.8767300000	-2.5627640000
H	-0.0435880000	5.0269840000	-1.0252420000
H	-0.2720700000	4.8676030000	-3.4769010000
H	-0.4103040000	2.5968140000	-4.5431840000
H	-0.3112050000	0.5907950000	-3.0711190000
H	0.0968040000	5.0264530000	1.0272490000
H	0.3190680000	4.8647180000	3.4793050000
H	0.4246750000	2.5926360000	4.5465490000
H	0.3019810000	0.5877200000	3.0748770000
H	-0.2879290000	-4.1570160000	4.2513610000
H	2.1484180000	-2.0033400000	1.4524190000
H	-3.9875390000	-1.8433600000	2.5862600000
H	-5.7086120000	-0.4602870000	1.4831640000
H	-2.5994880000	1.2812470000	-0.9132990000
H	-2.1606930000	-1.9808930000	-1.4656150000

cyclization-TS.xyz

N	0.8428570000	-1.4663700000	-0.7758600000
O	2.1272200000	-1.6752040000	-0.7222120000
C	1.4204050000	0.4260210000	0.5688880000
C	1.2026950000	1.9419990000	0.4595910000
C	1.2812410000	-0.0001600000	2.0433390000
C	2.7865740000	0.0072040000	0.0468920000
C	3.3836930000	0.5853860000	-1.0561370000
C	-3.0330420000	1.1655300000	-0.6705510000
C	-1.6535010000	0.9866440000	-0.7118170000
C	-1.0738810000	-0.1746910000	-0.1884920000
C	-1.9040000000	-1.1532230000	0.3710410000
C	-3.2833130000	-0.9738550000	0.4092070000
C	-3.8508330000	0.1878610000	-0.1086390000
H	-3.4700690000	2.0684050000	-1.0856860000
H	-1.0276500000	1.7449430000	-1.1700050000
H	-1.4584170000	-2.0552160000	0.7790800000
H	-3.9143900000	-1.7412260000	0.8468100000
H	-4.9266040000	0.3301800000	-0.0771170000
C	0.3920840000	-0.4019580000	-0.2225560000
H	0.2407730000	2.2218870000	0.8971970000
H	1.2217300000	2.2918300000	-0.5755550000
H	1.9875010000	2.4673710000	1.0113770000
H	0.2771290000	0.2209970000	2.4170630000
H	2.0034640000	0.5424860000	2.6625750000
H	1.4644840000	-1.0730390000	2.1577300000
H	3.4386040000	-0.4853970000	0.7636870000
H	4.4142100000	0.3565530000	-1.3059840000
H	2.8227390000	1.1958980000	-1.7570590000