Supplementary Information (SI) for ChemComm.

Umpolung Reactivity of *N*-Sulfonylhydrazones and Imino Esters to Access Functionalized Oxazoles

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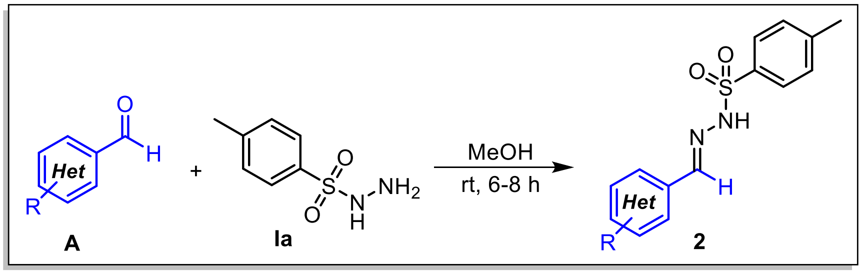
1.0 General information

All chemicals were purchased from Aldrich, TCI, GLR Innovations and Avra chemicals in analytical grade and were used as supplied. All reaction were carried out under nitrogen atmosphere using oven dried reaction vials. Dry solvents were prepared by distilling over sodium metal with benzophenone, Calcium hydride and stored over molecular sieves 4 Å under N_2 atmosphere. All compounds were purified by column chromatography using silica gel (100-200 mesh). Thin layer chromatography was performed on 0.25 mm thick aluminium-baked silica gel plates purchased from Merck and visualized with ultraviolet (λ = 254 nm). ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra were recorded on JEOL ECZ500R/S1 (500, 126, and 471 MHz respectively) instrument. ^1H signals are referenced to residual $CDCl_3$ at 7.26 ppm. ^{13}C signals are referenced to $CDCl_3$ at 77.16 ppm. IR spectra were recorded on Bruker Alpha II compact FT-IR spectrophotometer. Only characteristic peak was reported. High resolution mass spectra quadrupole time-of-flight (HRMS-QTOF) was obtained in ESI mode. The UV-Vis spectrum of compounds was recorded using a UV-Vis spectrophotometer (Shimadzu-2600). The reaction vials were purchased from Aldrich. The small Air Circulator fan Vornado 133 were purchased from amazon.com. The 40W Blue LED lamps were used Kessil LED photoreaction lighting PR160L (https://www.kessil.com).

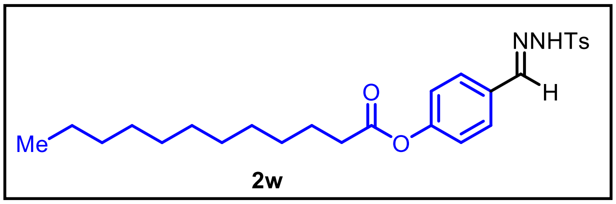
2.0 Synthesis of starting materials

General procedure 2.1: Synthesis of *N*-sulfonylhydrazone**s** **2** derived from corresponding aldehydes **A**



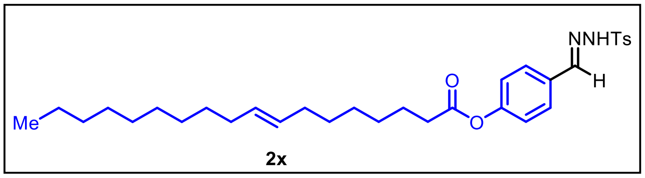
Starting material **2** is prepared according to the reported literature.[] To a stirred solution of *p*-toluenesulfonylhydrazide **Ia** (1.0 equiv.) in MeOH (1.0 M, 2.0 mL), corresponding aldehydes **A** (1.0 equiv.) in MeOH (0.5 M, 4.0 mL) solution were added dropwise. The reaction mixture was stirred at room temperature until complete conversion was observed by TLC. Solvent was removed under reduced pressure by rotary evaporator. Crude compound was purified by column chromatography on silica gel using (10% -15% EtOAc:Hexane) as an eluent to furnish the title product **2**.

4-(Tosylhydrazineylidene) methyl-phenyl dodecanoate **(2w)**



2w was prepared according to the general procedure **2.1** 64% (550 mg) white solid compound. Purification done by washing with diethyl ether and recrystallized with hot methanol. **TLC** (5% Methanol in DCM): ***R*$_f$** = 0.30; **MP:** 120-122 °C; **IR neat (cm^{-1}):** 3230, 2858, 1690, 1595, 1385, 1185, 850 cm^{-1}; **^{1}H NMR** (500 MHz CDCl$_3$): δ 7.86 (d, J = 8.3 Hz, 2H), 7.69 (s, 1H), 7.57 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 7.9 Hz, 2H), 7.05 (d, J = 8.5 Hz, 2H), 2.56 (t, J = 7.4 Hz, 2H), 2.40 (s, 3H), 1.77-1.65 (m, 2H), 1.65 (br s, 1H), 1.41-1.37 (m, 3H), 1.29-1.26 (m, 12H), 0.87 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (126 MHz, CDCl$_3$): δ 172.3, 152.4, 146.8, 145.5, 135.3, 130.8, 129.8, 128.6, 128.0, 122.1, 34.5, 32.0, 29.7, 29.5, 29.4, 29.3, 29.2, 25.0, 22.8, 21.7, 14.2; **HRMS** (ESI/Q-TOF) m/z: $[M+H]^+$ Calcd for $[C_{26}H_{37}N_2O_4S]^+$ 473.2469, Found 473.2469.

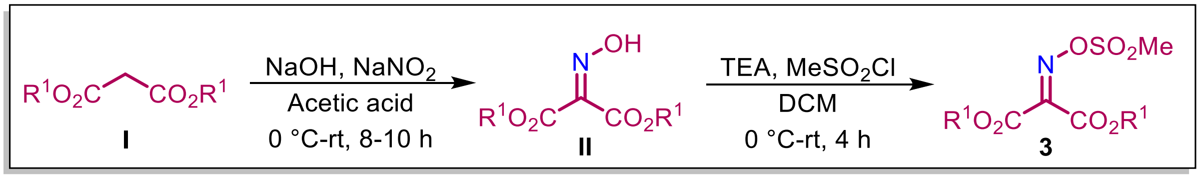
4-(Tosylhydrazineylidene) methyl-phenyl-octadec-9-enoate **2x**



2x

2x was prepared according to the general procedure **2.1** in 69% (500 mg) white solid compound. Purification done by washing with diethyl ether and recrystallized with hot methanol. **TLC** (5% Methanol in DCM): ***R*$_f$** = 0.25; **MP:** 102-104 °C; **IR neat (cm^{-1}):** 3134, 2956, 1692, 1596, 1330, 1153, 789 cm^{-1}; **^{1}H NMR** (500 MHz CDCl$_3$): δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.70 (s, 1H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 5.36-5.33 (m, 2H), 2.56 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 3H), 2.02-1.99 (m, 4H), 1.75-1.72 (m, 2H), 1.59 (br s, 1H), 1.36-1.33 (m, 7H), 1.29-1.26 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (126 MHz, CDCl$_3$): δ 172.3, 152.4, 146.7, 144.5, 135.3, 130.9, 130.2, 129.8(6), 129.8(3), 128.6, 128.0, 122.0, 34.5, 32.0, 29.9, 29.8, 29.6, 29.4, 29.2(8). 29.2(2), 29.1, 27.3, 27.2, 24.9, 22.8, 21.7, 14.2; **HRMS** (ESI/Q-TOF) m/z: $[M-H]^-$ Calcd for $[C_{32}H_{47}N_2O_4S]^+$ 555.3251, Found 555.3245.

General procedure 2.2.1: Synthesis of dialkyl-2-(methylsulfonyl-oxy) imino malonate **3** derived fromdialkyl-2-(hydroxyimino)malonate**II**

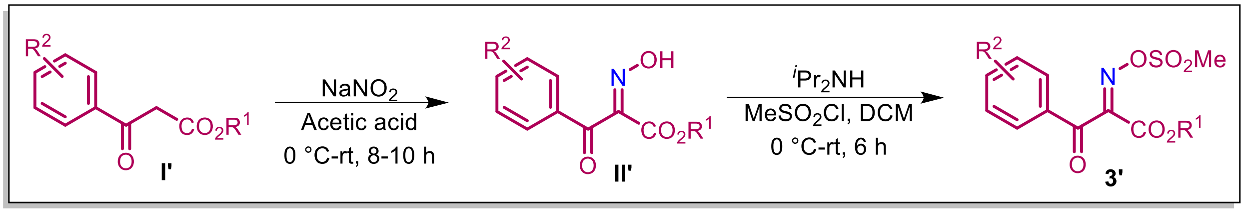


Step 1: Starting material **II** is prepared according to the reported literature.[2] To a stirred solution of NaOH (0.6 equiv.) in glacial acetic acid (formation of white thick slurry was observed), corresponding dialkyl malonate **I** (1.0 equiv.) solution were added dropwise to the reaction mixture. Temperature of reaction were maintained at 0 °C and then saturated solution of $NaNO_2$ (1.2 equiv.) was added dropwise in reaction mixture and reaction was stirred continuously at room temperature for 8-10 h. After completion of the reaction which was monitored by TLC analysis, the reaction mixture was extracted with EtOAc and brine solution followed by organic layer was washed with saturated solution of $NaHCO_3$ until the aqueous layer reached at 8-9 pH. Organic solvent was removed under reduced pressure using rotary evaporator and crude compound was

purified by column chromatography on silica gel using (12-15% EtOAc:Hexanes) as an eluent to furnish the title product **II**.

Step 2: To a stirred solution of dialkyl-2-(hydroxyimino) malonate **II** (1.0 equiv.) and TEA (1.2 equiv.) in DCM (5.0 M, 5 mL), solution of $MeSO_2Cl$ (1.2 equiv.) in DCM were added in dropwise at 0 °C. The reaction was stirred at ambient temperature for 4 hours. After completion of the reaction, reaction mixture was extracted with DCM, the solvent was removed under reduced pressure using rotary evaporator. The crude compound was purified by column chromatography on silica gel using (3-5% EtOAc:Hexanes) as an eluent to furnish the title product **3**.

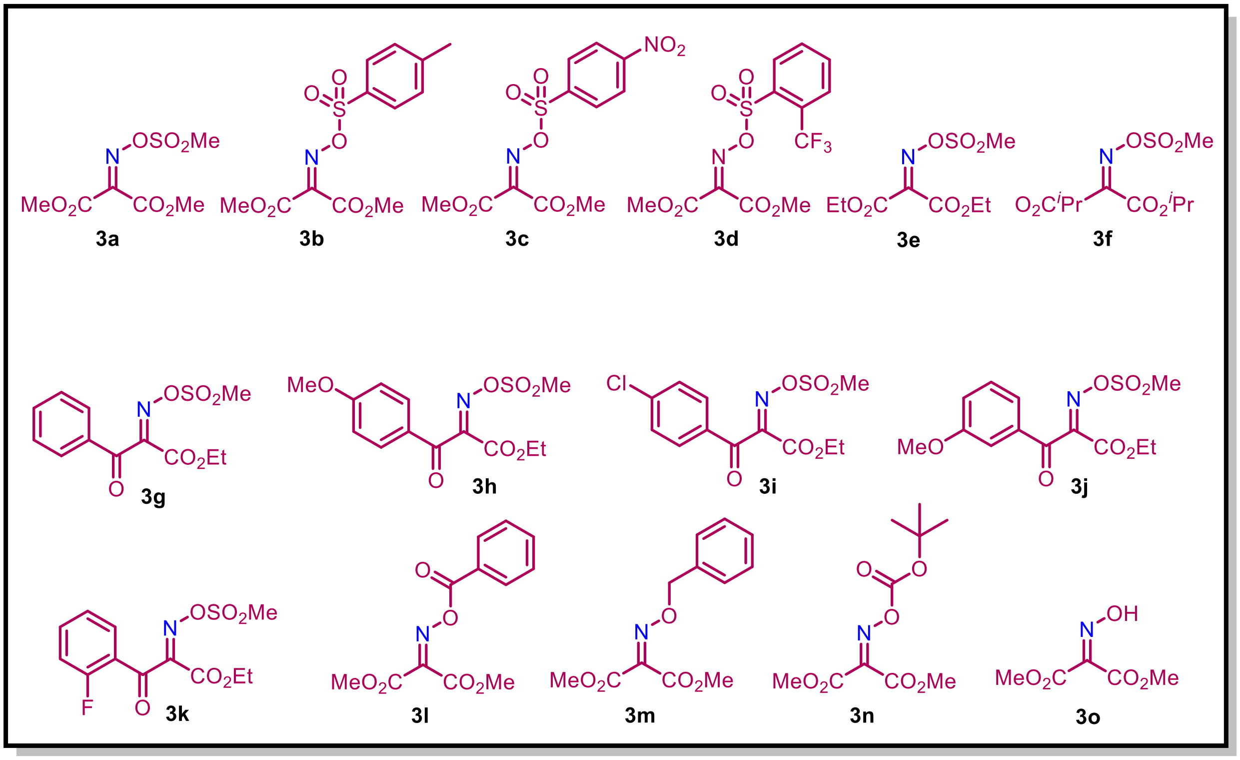
General procedure 2.2.2: Synthesis of alkyl-2-(methylsulfonyl-oxy)imino-3-oxo-3-arylpropanoate **3'** derived from alkyl-2-(hydroxyimino)-3-oxo-3-arylpropanoate **II'**



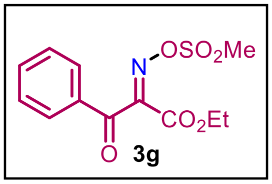
Step 1: Starting material **II'** is prepared according to the reported literature. [2] To a stirred solution of substituted 3-oxo-3-arylpropanoate **I'** (1.0 equiv.) in glacial acetic acid (1.0 M, 3.0 mL), saturated solution of $NaNO_2$ (1.2 equiv.) was added dropwise at 0 °C in reaction mixture and reaction was stirred continuously at room temperature for 8-10 h. After completion of reaction monitored by TLC analysis, crude reaction mixture was extracted with EtOAc and organic layer was washed with saturated solution of $NaHCO_3$, solvent was removed under reduced pressure using rotary evaporator and crude compound was purified by column chromatography on silica gel using (15-18% EtOAc:Hexanes) as an eluent to furnish the title product **II'**.

Step 2: To a stirred solution of alkyl-2-(hydroxyimino)-3-oxo-3-arylpropanoate **II'** (1.0 equiv.) and di-isopropyl amine ($^{i}Pr_2NH$) (1.2 equiv.) in DCM (5.0 M, 5 mL), a solution of $MeSO_2Cl$ (1.2 equiv.) were added dropwise at 0 °C. The reaction was stirred at room temperature for 4 hours. After completion of the reaction monitored by TLC analysis, reaction mixture was extracted with DCM, the solvent was removed under reduced pressure using rotary evaporator. The crude compound was purified by column chromatography on silica gel using (15-20% EtOAc:Hexanes) as an eluent to furnish the title product **3'**.

List of 2-(sulfonyloxy imino) malonate esters

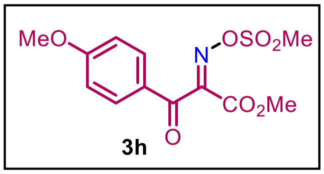


Ethyl-2-(methylsulfonyl-oxy)imino-3-oxo-3-phenylpropanoate **(3g)**



3g was prepared according to the general procedure **2.2.2** in 66% (450 mg) white solid compound. Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane): $\boldsymbol{R_f} = 0.35$; **MP:** 110-112 °C; **IR neat (cm^{-1})**: 2990, 1748, 1654, 1495, 1325, 1163; **^{1}H NMR** (500 MHz CDCl$_3$): δ 7.86 (d, J = 8.3 Hz, 2H), 7.70 (t, J = 7.4 Hz, 1H), 7.55 (t, J = 8.1 Hz, 2H), 4.38 (q, J = 7.1 Hz, 2H), 3.22 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H) **^{13}C NMR** (126 MHz, CDCl$_3$): δ 186.1, 158.7, 156.3, 135.7, 133.0, 129.5, 129.4, 63.9, 37.1, 14.0; **HRMS** (ESI/Q-TOF) *m/z*: [M+Na]$^+$ Calcd for [$C_{12}H_{13}NNaO_6S$]$^+$ 322.0356, Found 322.0356.

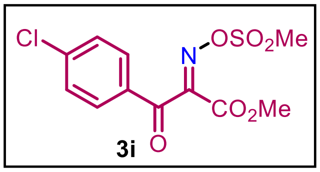
Methyl-4-methoxyphenyl-2-(methylsulfonyl-oxy)imino-3-oxopropanoate **(3h)**



3h

3h was prepared according to the general procedure **2.2.2** in 72% (544 mg) white solid compound. Purification done by column chromatography on silica gel using (hexane: EtOAc = 85:15) as an eluent, **TLC** (30% ethyl acetate in hexane): $\boldsymbol{R_f}$ = 0.30; **MP:** 123-125 °C; **IR neat (cm^{-1})**: 2964, 1726, 1666, 1438, 1320, 1158 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): δ 7.81 (d, J = 9.1 Hz, 2H), 6.99 (d, J = 9.1 Hz, 2H), 3.88 (s, 3H), 3.87 (s, 3H), 3.21 (s, 3H); **^{13}C NMR** (126 MHz, CDCl$_3$): δ 184.0, 165.7, 159.4, 156.2, 132.0, 126.0, 114.9, 56.8, 54.0, 37.1; **HRMS** (ESI/Q-TOF) *m/z*: [M+H]$^+$ Calcd for $[C_{12}H_{14}NO_6S]^+$ 316.0485, Found 316.0484.

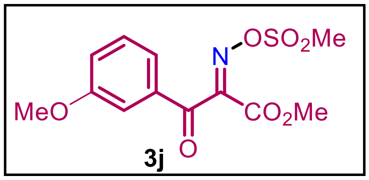
Methyl-4-chlorophenyl-2-(methylsulfonyl-oxy)imino-3-oxopropanoate **(3i)**



3i

3i was prepared according to the general procedure **2.2.2** in 59% (442 mg) green solid compound. Purification done by column chromatography on silica gel using (hexane: EtOAc = 85:15) as an eluent, **TLC** (30% ethyl acetate in hexane): $\boldsymbol{R_f}$ = 0.35; **MP:** 122-124 °C; **IR neat (cm^{-1})**: 2957, 1745, 1682, 1371, 1284, 1130 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): δ 7.81 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 8.8 Hz, 2H), 3.93 (s, 3H), 3.24 (s, 3H) **^{13}C NMR** (126 MHz, CDCl$_3$): δ 184.9, 159.1, 155.5, 142.7, 131.1, 130.7, 130.0, 54.2, 37.2; **HRMS** (ESI/Q-TOF) *m/z*: [M+Na]$^+$ Calcd for $[C_{11}H_{10}ClNNaO_6S]^+$ 341.9810, Found 341.9803.

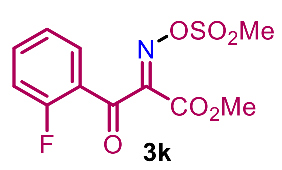
Methyl-3-methoxyphenyl-2-(methylsulfonyl-oxy)imino-3-oxopropanoate **(3j)**



3j

3j was prepared according to the general procedure **2.2.2** in 57% (431 mg) green solid compound. Purification done by column chromatography on silica gel using (hexane: EtOAc = 85:15) as an eluent, **TLC** (30% ethyl acetate in hexane): $\boldsymbol{R_f}$ = 0.30; **MP:** 133-135 °C; **IR neat (cm^{-1})**: 2948, 1752, 1676, 1435, 1323, 1125 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): δ 7.45-7.43 (m, 1H), 7.41-7.40 (m, 1H), 7.37-7.36 (m, 1H), 7.24-7.21 (m, 1H), 3.91 (s, 3H), 3.86 (s, 3H), 3.00 (s, 3H)**; ^{13}C NMR** (126 MHz, CDCl$_3$): δ 186.8, 160.4, 159.2, 156.0, 134.1, 130.9, 122.9, 122.6, 112.4, 55.6, 54.1, 37.1; **HRMS** (ESI/Q-TOF) *m/z*: [M+H]$^+$ Calcd for $[C_{12}H_{14}NO_6S]^+$ 316.0485, Found 316.0484.

Methyl-2-fluorophenyl-2-(methylsulfonyl-oxy)imino-3-oxopropanoate **(3k)**



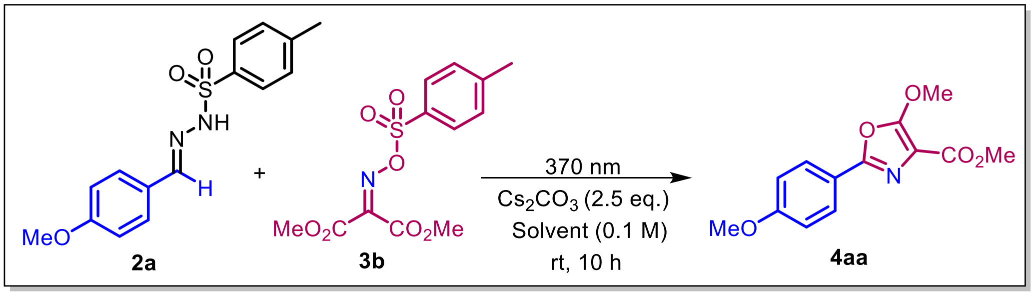
3k

3k was prepared according to the general procedure **2.2.2** in 68% (533 mg) yellow solid compound. Purification done by column chromatography on silica gel using (hexane: EtOAc = 80:20) as an eluent, **TLC** (20% ethyl acetate in hexane): ***R*$_f$** = 0.35; **MP:** 110-112 °C; **IR neat (cm^{-1})**: 2916, 1730, 1588, 1475, 1325, 1177 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): δ 8.08-8.00 (m, 1H), 7.71-7.66 (m, 1H), 7.37-7.33 (m, 1H), 7.20-7.16 (m, 1H), 3.94 (s, 3H), 3.22 (s, 3H); **^{13}C NMR** (126 MHz, CDCl$_3$): δ 181.9, 164.0 (d, $^1J_{CF}$ = 258 Hz), 159.1(9), 159.1(6), 156.2, 137.9 (d, $^3J_{CF}$ = 9.8 Hz), 130.6, 125.5 (d, $^4J_{CF}$ = 3.7 Hz), 122.1 (d, $^3J_{CF}$ = 8.3 Hz), 117.0 (d, $^2J_{CF}$ = 22.1 Hz), 54.0, 37.1; **^{19}F NMR** (471 MHz, CDCl$_3$): δ -111.3; **HRMS** (ESI/Q-TOF) *m/z*: [M+Na]$^+$ Calcd for [$C_{11}H_{10}FNNaO_6S$]$^+$ 326.0105, Found 326.0106.

3.0 Reaction optimization

3.1 Synthesis of Methyl-5-methoxy-2-(4-methoxyphenyl) oxazole-4-carboxylate **4aa**

3.11: Solvent optimization

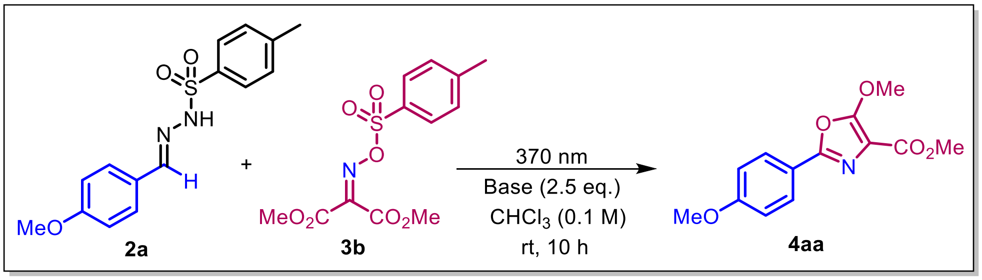


To an oven dried 5 mL glass vial was charged with magnetic stir bar, 4-(methoxybenzylidene)-4-methylbenzenesulfonohydrazide **2a** (60.8 mg, 0.2 mmol, 1.0 equiv.) was added, then Cs$_2$CO$_3$ (163 mg, 0.25 mmol, 0.5 equiv.) and dimethyl 2-(tosyloxy-imino) malonate **3b** (94.5 mg, 0.3 mmol, 1.5 equiv.) were added followed by solvent (0.1 M, 2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 40 W 370 nm LEDs (the reaction vial distance from light source ~ 2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35 ˚C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (15%-18% EtOAc:Hexane) as an eluent to furnish the title product **4aa**.

Entry	Solvent	Isolated yield (**4aa**)[a]
1	DCM	42%
2	DCE	14%
3	Toluene	38%
4	Mesitylene	10%
5	Benzene	22%
6	2-MeTHF	44%
7	THF	30%
8	Benzotrifluoride	34%
9	DMSO	ND
10	Acetonitrile	ND
11	$CHCl_3$	58%

Reaction conditions: **2a** (0.2 mmol), **3b** (0.3 mmol), solvent (0.1 M, 2 mL), Cs_2CO_3 (0.5 mmol), 370 nm LEDs (40 W), rt, 30-35 °C, 10 h. [a]All are isolated yield for 0.2 mmol scale reaction. ND = not detected. NR = no reaction.

3.12: Base optimization

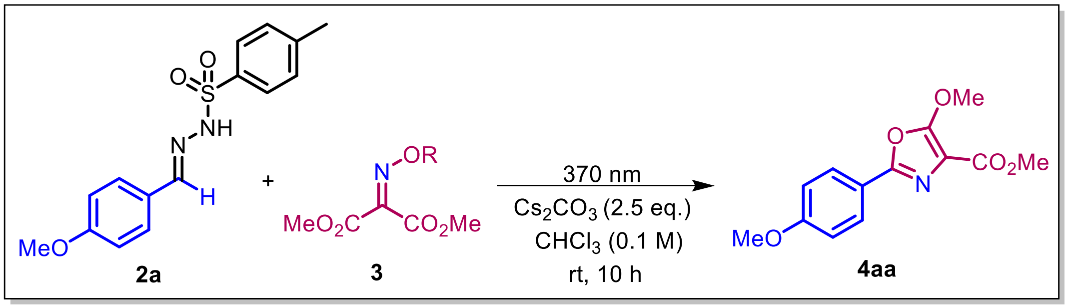


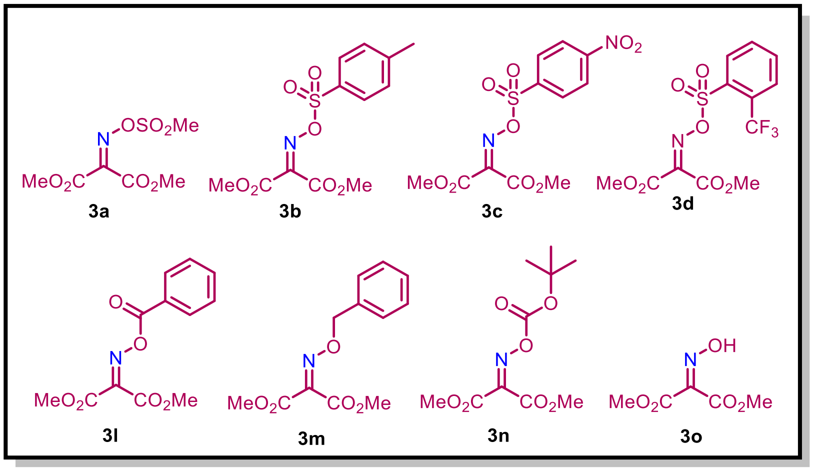
To an oven dried 5 mL glass vial was charged with magnetic stir bar, 4-(methoxybenzylidene)-4-methylbenzenesulfonohydrazide **2a** (60.8 mg, 0.2 mmol, 1.0 equiv.) was added, then various base (0.5 mmol, 2.5 equiv.) and dimethyl 2-(tosyloxy-imino) malonate **3b** (94.5 mg, 0.3 mmol, 1.5 equiv.) were added followed by addition of $CHCl_3$ (0.1 M, 2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 40 W 370 nm LEDs (the reaction vial distance from light source ~ 2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35˚C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (15-18% EtOAc:Hexane) as an eluent to furnish the title product **4aa**.

Entry	Base	Isolated yield (**4aa**)[a]
1	No base	ND
2	Cs_2CO_3	58%
3	K_2CO_3	34%
4	LiO^{t}Bu	25%
5	NaOMe	23%
6	K_3PO_4	30%
7	KOH	10%
8	NaH	35%
9	$NaNH_2$	13%
10	KOAc	19%
11	TEA	NR
12	DBU	NR

Reaction conditions: **2a** (0.2 mmol), **3b** (0.3 mmol), $CHCl_3$ (0.1 M, 2 mL), base (0.5 mmol), 370 nm LEDs (40 W), rt, 30-35 °C, 10 h. [a]All are isolated yield for 0.2 mmol scale reaction. ND = not detected. NR = no reaction.

3.13 Optimization of for *N*-protected malonate ester **3**



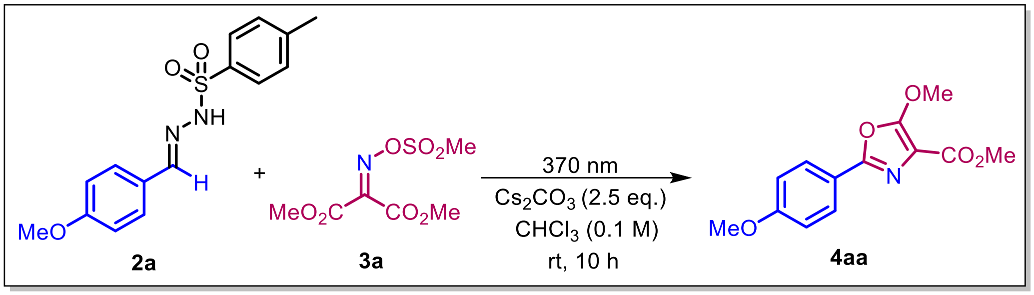


Entry	**Imino-esters (3)**	Isolated yield (**4aa**)[a]
1	Mesyl (**3a**)	62%
2	Tosyl (**3b**)	58%
3	*p*-Nosyl (**3c**)	23%
4	*o*-Triftosyl (**3d**)	15%
5	Benzoyl (**3l**)	30%
6	Benzyl (**3m**)	ND
7	Boc (**3n**)	35%
8	2-(Hydroxy)-imino-malonate (**3o**)	ND

Reaction conditions: **2a** (0.2 mmol), **3** (0.3 mmol), $CHCl_3$ (0.1 M, 2 mL), base (0.5 mmol), 370 nm LEDs (40 W), rt, 30-35 °C, 10 h. [a]All are isolated yield for 0.2 mmol scale reaction. ND = not detected.

To an oven dried 5 mL glass vial was charged with magnetic stir bar, 4-(methoxybenzylidene)-4-methylbenzenesulfonohydrazide **2a** (60.8 mg, 0.2 mmol, 1.0 equiv.) was added, then Cs_2CO_3 (163 mg, 0.25 mmol, 0.5 equiv.) and various dimethyl 2-(sulfonyloxy-imino)malonate **3** (0.3 mmol, 1.5 equiv.) were added followed by addition of $CHCl_3$ (0.1 M, 2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 370 nm 40 W LEDs (the reaction vial distance from light source ~ 2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35 ˚C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (15-18% EtOAc:Hexane) as an eluent to furnish the title product **4aa**.

3.14: Optimization of equivalent of dimethyl 2-(mesyl-oxy) imino malonate **3a**

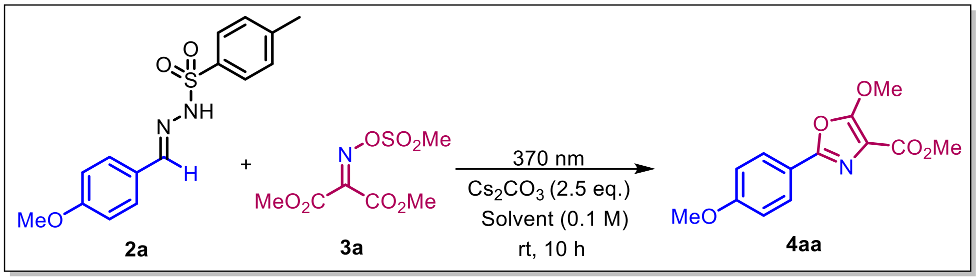


To an oven dried 5 mL glass vial was charged with magnetic stir bar, 4-(methoxybenzylidene)-4-methylbenzenesulfonohydrazide **2a** (60.8 mg, 0.2 mmol, 1.0 equiv.) was added, then Cs_2CO_3 (163 mg, 0.5 mmol, 2.5 equiv.) and dimethyl 2-(mesyloxy-imino) malonate **3a** (xx equiv.) were added followed by addition of $CHCl_3$ (0.1 M, 2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 370 nm 40 W LEDs (the reaction vial distance from light source ~2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35 ° C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (15-18% EtOAc:Hexane) as an eluent to furnish the title product **4aa**.

Entry	**3a** (equiv.)	Isolated yield (**4aa**)[a]
1	1.0	42%
2	1.5	62%
3	2.0	74%
4	2.5	58%

Reaction conditions: 2a (0.2 mmol), **3a** (x mmol), $CHCl_3$ (0.1 M, 2 mL), Cs_2CO_3 (0.5 mmol), 370 nm LEDs (40 W), rt, 30-35 °C, 10 h. [a]All are isolated yield for 0.2 mmol scale reaction.

3.15: Solvent optimization with our optimized substrates **2a** and **3a.**

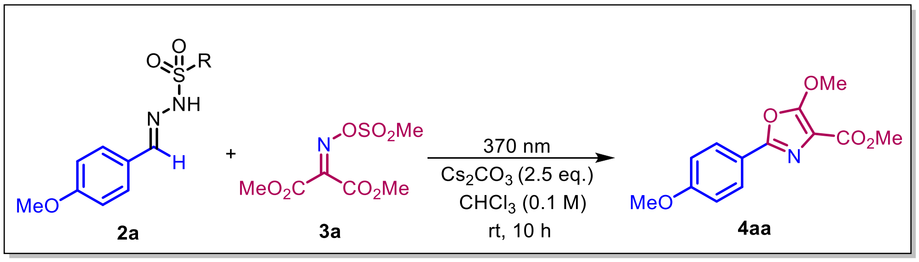


To an oven dried 5 mL glass vial was charged with magnetic stir bar, 4-(methoxybenzylidene)-4-methylbenzenesulfonohydrazide **2a** (60.8 mg, 0.2 mmol, 1.0 equiv.) was added, then Cs_2CO_3 (163 mg, 0.5 mmol, 2.5 equiv.) and dimethyl 2-(mesyloxy-imino) malonate **3a** (95.6 mg, 0.4 mmol, 2.0 equiv.) were added followed by solvents (0.1 M, 2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 40 W 370 nm LEDs (the reaction vial distance from light source ~ 2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35 ˚C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (15-18% EtOAc:Hexane) as an eluent to furnish the title product **4aa**.

Entry	Solvent	Isolated yield (**4aa**)[a]
1	DCM	48%
2	Toluene	38%
3	2-MeTHF	49%
4	$CHCl_3$	74%
5	2-MeTHF:DCM	52%
6	2-MeTHF:$CHCl_3$	64%
7	Benzotrifluoride	38%

Reaction conditions: **2a** (0.2 mmol), **3a** (0.4 mmol), solvent (0.1 M, 2 mL), Cs_2CO_3 (0.5 mmol), 370 nm LEDs (40 W), rt, 30-35 °C, 10 h. [a]All are isolated yield for 0.2 mmol scale reaction.

3.16: Optimization of *N*-sulfonylhydrazones **2**

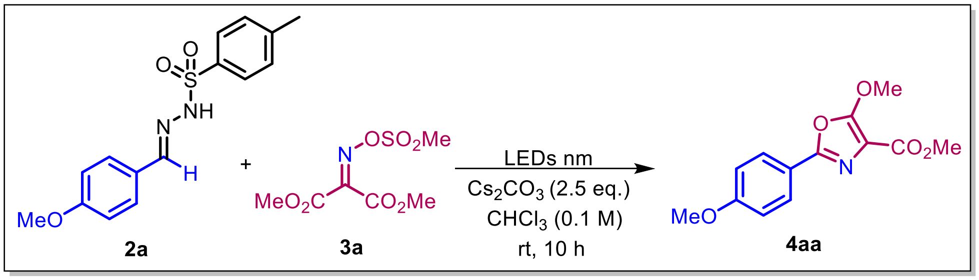


To an oven dried 5 mL glass vial was charged with magnetic stir bar, various *N*-sulfonylhydrazones **2** (0.2 mmol, 1.0 equiv.) was added, then Cs_2CO_3 (163 mg, 0.5 mmol, 2.5 equiv.) and dimethyl 2-(mesyloxy-imino) malonate **3a** (95.6 mg, 0.4 mmol, 2.0 equiv.) were added followed by addition of $CHCl_3$ (0.1 M, 2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 370 nm 40 W LEDs (the reaction vial distance from light source ~ 2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35 ° C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (15-18% EtOAc:Hexane) as an eluent to furnish the title product **4aa**.

Entry	*N*-sulfonylhydrazones (**2**)	Isolated yield (**4aa**)[a]
1	R = Tolyl	74%
2	R= Mesityl	48%
3	R = *p*-Nosyl	32%
4	R = *o*-Trifloro-tolyl	38%
5	R = Methyl	42%

Reaction conditions: 2 (0.2 mmol), **3a** (0.4 mmol), $CHCl_3$ (0.1 M, 2 mL), Cs_2CO_3 (0.5 mmol), 370 nm LEDs (40 W), rt, 30-35 °C, 10 h. [a]All are isolated yield for 0.2 mmol scale reaction.

3.17: Optimization of light source (LEDs nm)

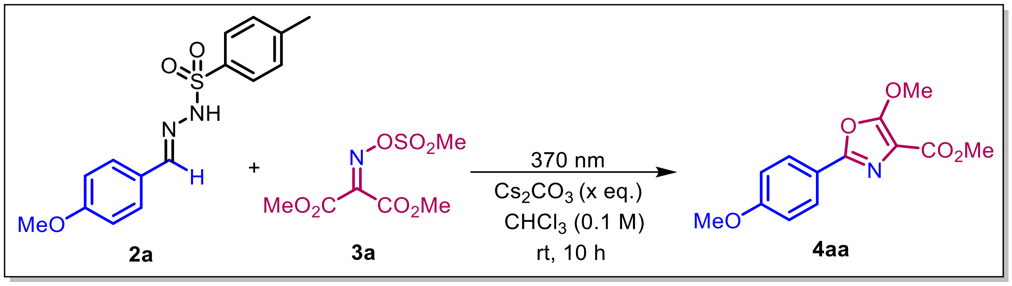


To an oven dried 5 mL glass vial was charged with magnetic stir bar, 4-(methoxybenzylidene)-4-methylbenzenesulfonohydrazide **2a** (60.8 mg, 0.2 mmol, 1.0 equiv.) was added, then Cs_2CO_3 (163 mg, 0.5 mmol, 2.5 equiv.) and dimethyl 2-(mesyloxy-imino)malonate **3a** (95.6 mg, 0.4 mmol, 2.0 equiv.) were added followed by addition of $CHCl_3$ (0.1 M, 2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of various 40 W LEDs (the reaction vial distance from light source ~2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35 ˚C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (15-18% EtOAc:Hexane) as an eluent to furnish the title product **4aa**.

Entry	LEDs (nm)	Isolated yield (**4aa**)[a]
1	365	48%
2	370	74%
3	390	42%
4	427	32%
5	440	15%
6	Dark condition	ND
7	40 °C & 60 °C	ND

Reaction conditions: **2a** (0.2 mmol), **3a** (0.4 mmol), $CHCl_3$ (0.1 M, 2 mL), Cs_2CO_3 (0.5 mmol), LEDs (40 W), rt, 30-35 °C, 10 h. [a]All are isolated yield for 0.2 mmol scale reaction. ND = not detected.

3.16: Optimization of equivalent of Cs_2CO_3



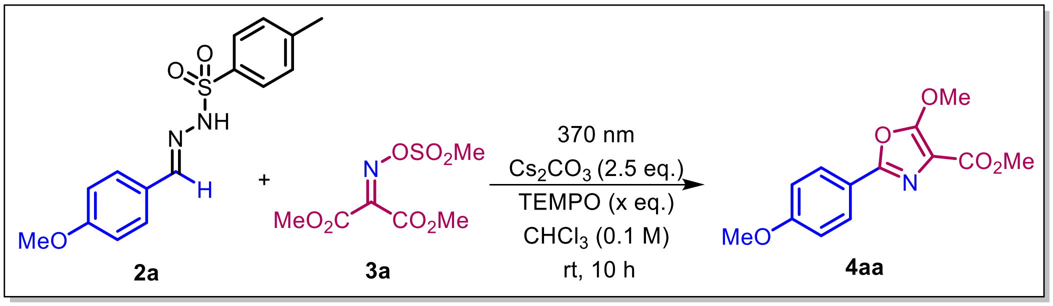
To an oven dried 5 mL glass vial was charged with magnetic stir bar, various *N*-sulfonylhydrazones **2** (0.2 mmol, 1.0 equiv.) was added, then Cs_2CO_3 (xx equiv.) and dimethyl 2-(mesyloxy-imino) malonate **3a** (95.6 mg, 0.4 mmol, 2.0 equiv.) were added followed by addition of $CHCl_3$ (0.1 M, 2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 370 nm 40 W LEDs (the reaction vial distance from light source ~ 2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35 ° C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (15-18% EtOAc:Hexane) as an eluent to furnish the title product **4aa**.

Entry	Cs_2CO_3 (equiv.)	Isolated yield (**4aa**)[a]
1	1.0	57%
2	2.0	70%
3	3.0	65%
4	4.0	67%
5	5.0	61%

Reaction conditions: **2** (0.2 mmol), **3a** (0.4 mmol), $CHCl_3$ (0.1 M, 2 mL), Cs_2CO_3 (x mmol), 370 nm LEDs (40 W), rt, 30-35 °C, 10 h. [a]All are isolated yield for 0.2 mmol scale reaction.

4.0 Control experiments

4.1 Reaction in presence of TEMPO

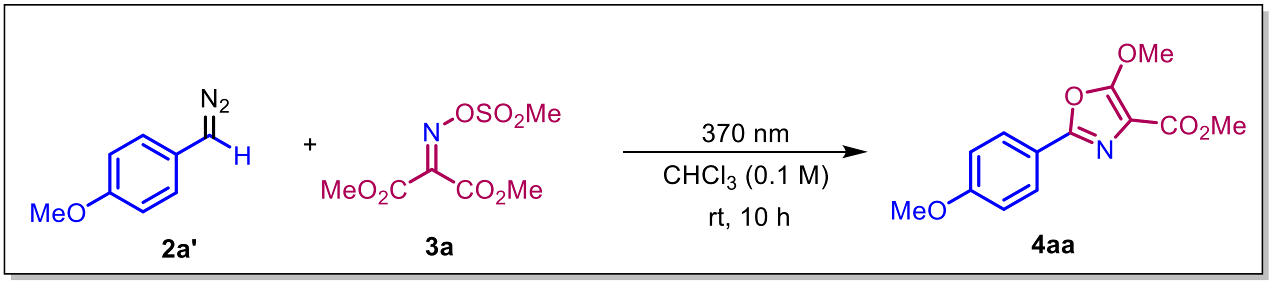


To an oven dried 5 mL glass vial was charged with magnetic stir bar, 4-(methoxybenzylidene)-4-methylbenzenesulfonohydrazide **2a** (60.8 mg, 0.2 mmol, 1.0 equiv.) was added, then Cs_2CO_3 (163 mg, 0.5 mmol, 2.5 equiv.), TEMPO (x equiv.) and dimethyl 2-(mesyloxy-imino)malonate **3a** (95.6 mg, 0.4 mmol, 2.0 equiv.) were added followed by addition of $CHCl_3$ (0.1 M, 2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 370 nm 40 W LEDs (the reaction vial distance from light source ~ 2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35 ° C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (15-18% EtOAc:Hexane) as an eluent to furnish the title product **4aa**.

Entry	TEMPO (x equiv.)	Isolated yield (**4aa**)[a]
1	1.0	51%
2	2.0	48%
3	3.0	48%

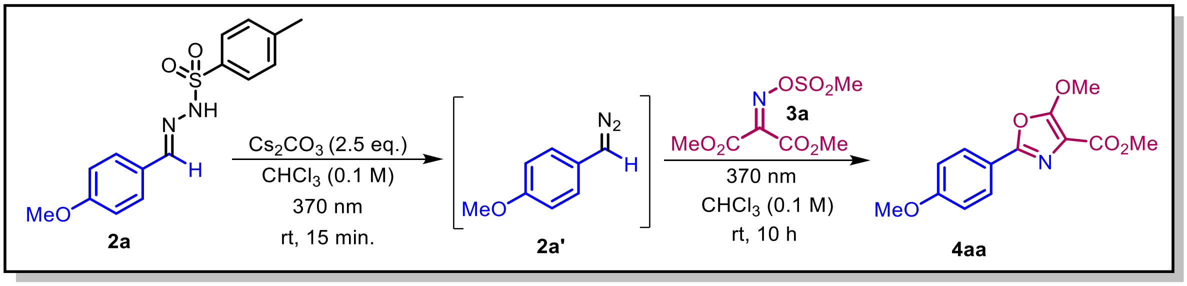
Reaction conditions: **2a** (0.2 mmol), **3a** (0.4 mmol), $CHCl_3$ (0.1 M, 2 mL), Cs_2CO_3 (0.5 mmol), TEMPO (xx equiv.), 370 nm LEDs (40 W), rt, 30-35 °C, 10 h. [a]All are isolated yield for 0.2 mmol scale reaction.

4.2 Reaction with diazo intermediate under 370 nm LEDs.



To an oven dried 5 mL glass vial was charged with magnetic stir bar, diazomethyl-4-methoxybenzene **2a'** (29.6 mg, 0.2 mmol, 1.0 equiv.) was added, then dimethyl 2-(mesyloxy-imino) malonate **3a** (95.6 mg, 0.4 mmol, 2.0 equiv.) were added followed by addition of $CHCl_3$ (0.1 M, 2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 370 nm 40 W LEDs (the reaction vial distance from light source ~ 2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35 ˚C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (15-18% EtOAc:Hexane) as an eluent to furnish the title product **4aa** with 42% yield.

4.3 Reaction with in-situ generated diazo intermediate under 370 nm LEDs.

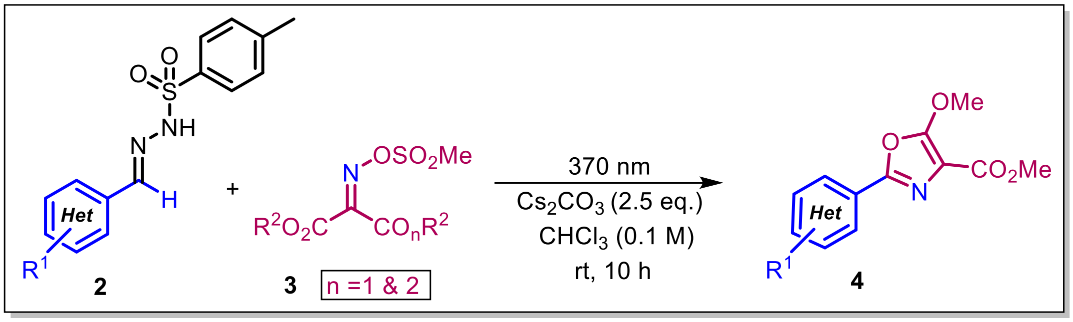


To an oven dried 5 mL glass vial was charged with magnetic stir bar, 4-(methoxybenzylidene)-4-methylbenzenesulfonohydrazide **2a** (60.8 mg, 0.2 mmol, 1.0 equiv.) was added, then Cs_2CO_3 (163 mg, 0.5 mmol, 2.5 equiv.) were added followed by addition of $CHCl_3$ (0.1 M, 2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 370 nm LEDs (the reaction vial distance from light source ~2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35 ˚C) for 15 min. Upon the complete consumption of **2a**, monitored by the TLC. After this, dimethyl 2-(mesyloxy-imino) malonate **3a**

(95.6 mg, 0.4 mmol, 2.0 equiv.) was added in reaction mixture and reaction was allowed to stir under irradiation of 370 nm LEDs at room temperature till diazo is consumed, monitored by the TLC analysis. After complete consumption of diazo, reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (15-18% EtOAc:Hexane) as an eluent to furnish the title product **4aa** with 44% yield.

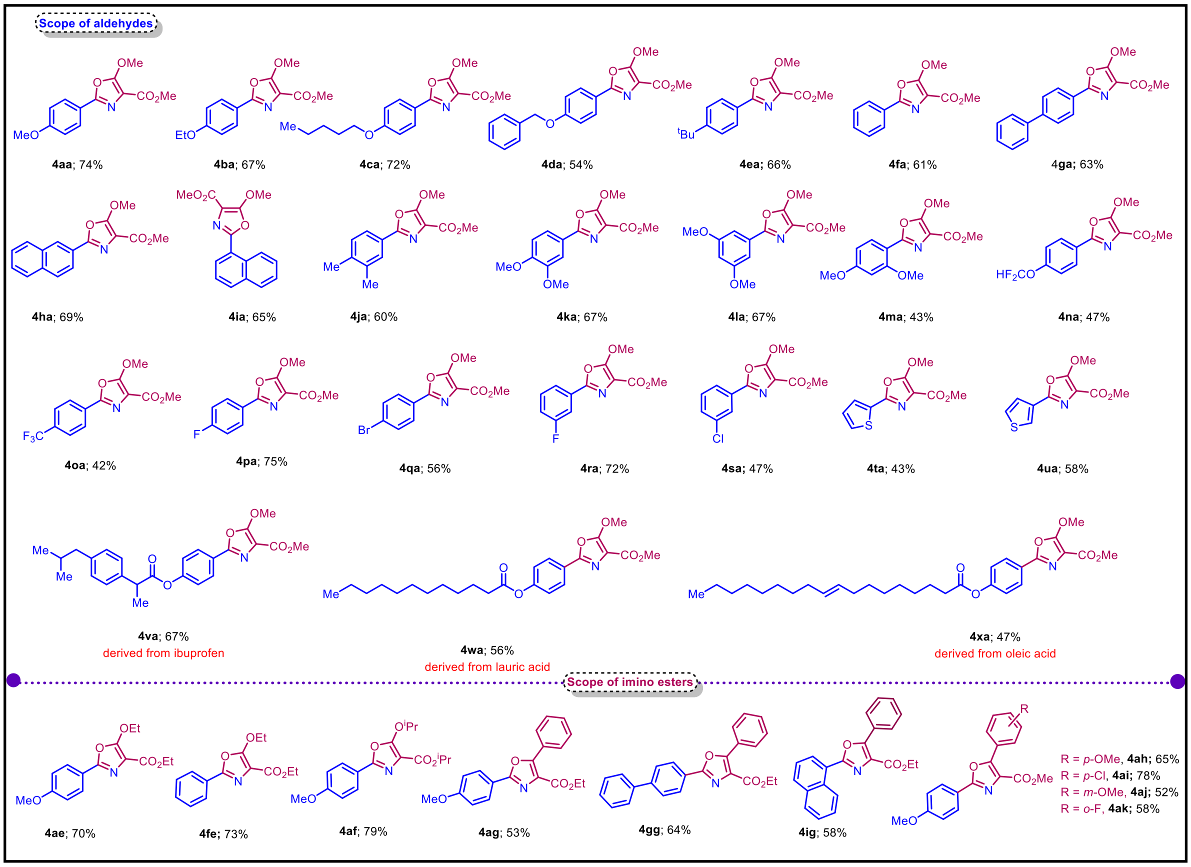
5.0 General procedure for light driven synthesis of substituted oxazoles

5.1 General procedure for light-driven synthesis of substituted oxazoles **4**

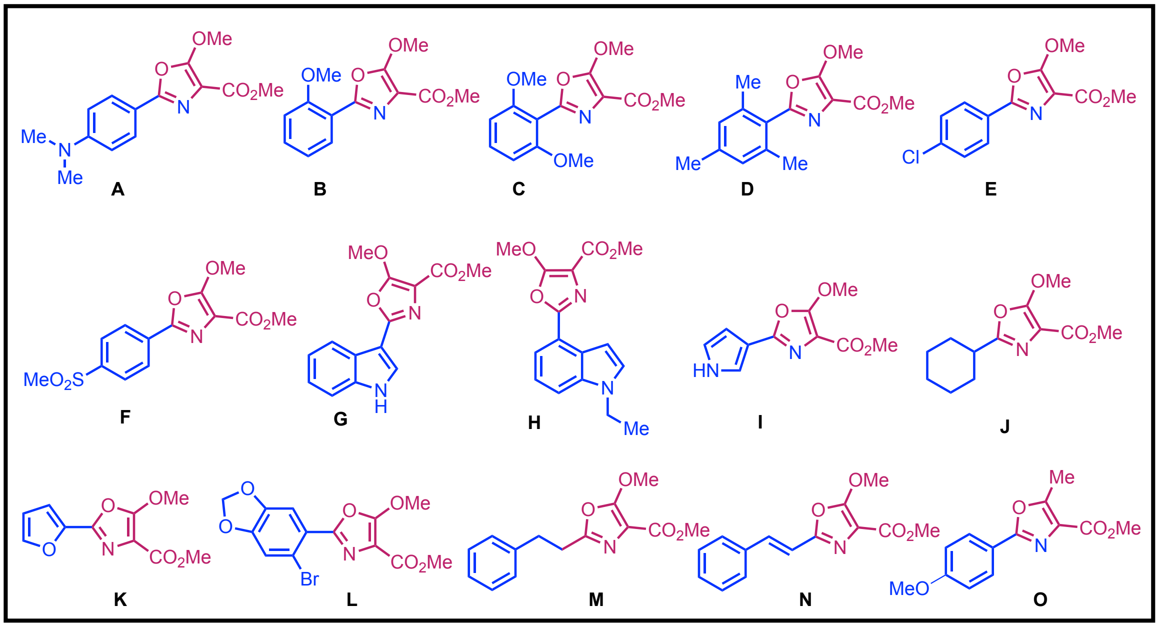


General procedure 4.1: To an oven dried 5 mL glass vial was charged with magnetic stir bar, *N*-sulfonylhydrazones **2** (0.2 mmol, 1.0 equiv.) was added, then Cs_2CO_3 (163 mg, 0.5 mmol, 2.5 equiv.) and substituted-2-(mesyloxy-imino)malonate **3** (0.4 mmol, 2.0 equiv.) were added followed by addition of $CHCl_3$ (0.1 M, 2.0 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 370 nm 40 W LEDs (the reaction vial distance from light source ~ 2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35 ° C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. The crude compound was purified by column chromatography on silica gel using (8-25% EtOAc:Hexane) as an eluent to furnish the product **4.**

Substrate scope:

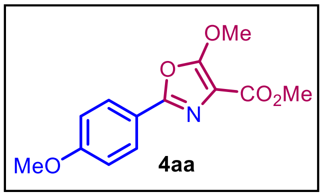


Failed substrates



Spectral data of isolated compounds:

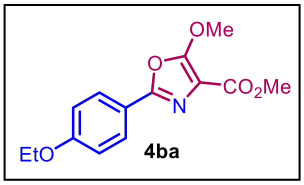
Methyl 5-methoxy-2-(4-methoxyphenyl)-oxazole-4-carboxylate (**4aa**)


4aa

4aa was prepared according to the general procedure **4.1** in 74% (39.0 mg) isolated yield. Pale yellow oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 85:15) as an eluent, **TLC** (30% ethyl acetate in hexane); ***R***$_\mathbf{f}$ = 0.25; **IR** (KBr): 2956, 1730, 1573, 1395, 1150, 1084, 830, 549 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.90 (d, *J* = 9.1 Hz, 2H), 6.93 (d, *J* = 9.1 Hz, 2H), 4.25 (s, 3H), 3.91 (s, 3H), 3.85 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* 162.2, 161.7, 161.5, 151.2, 127.7, 119.1, 114.3, 107.3, 59.9, 55.5, 52.0; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{13}H_{14}O_5]^+$ 264.0866, Found 264.0866.

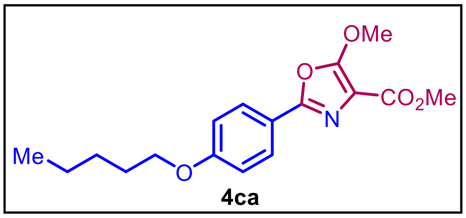
Spectral data matched with the reported literature. [3]

Methyl 2-(4-ethoxyphenyl)-5-methoxyoxazole-4-carboxylate (**4ba**)


4ba

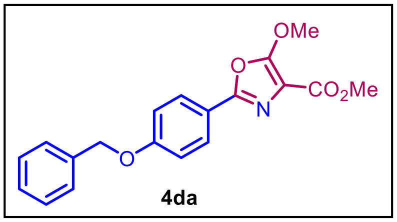
4ba was prepared according to the general procedure **4.1** in 67% (37.0 mg) isolated yield. Yellow oil; Purification done by column chromatography on silica gel using (hexane: EtOAc =85:15) as an eluent, **TLC** (30% ethyl acetate in hexane); $\boldsymbol{R}_\mathbf{f}$ = 0.25; **IR** (KBr): 2859, 1742, 1490, 1370, 1180, 1075, 889, 585 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.90 (d, *J* = 8.7 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 4.24 (s, 3H), 4.08 (q, *J* = 6.9 Hz, 2H), 3.91 (s, 3H), 1.43 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* 162.2, 161.7, 161.0, 151.3, 127.7, 118.9, 114.7, 107.3, 63.7, 59.9, 51.9, 14.8; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{14}H_{16}O_5]^+$ 278.1023, Found 278.1019.

Methyl 5-methoxy-2-(4-(pentyloxy)phenyl)-oxazole-4-carboxylate (**4ca**)


4ca

4ca was prepared according to the general procedure **4.1** in 72% (46.0 mg) isolated yield. White solid; Purification done by column chromatography on silica gel using (hexanes: EtOAc = 90:10) as the eluent, **TLC** (20% ethyl acetate in hexanes): $\boldsymbol{R}_\mathbf{f}$ = 0.30; ; **MP:** 92-94 °C; **IR** (KBr): 2956, 2859, 1704, 1503, 1395, 1252, 1022, 837, 631 cm^{-1}; **1H NMR (**500 MHz, $CDCl_3$): *δ* 7.90 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 4.24 (s, 3H), 3.99 (t, *J* = 6.9 Hz, 2H), 3.91 (s, 3H), 1.82-1.77 (m, 2H), 1.40-1.38 (m, 4H), 0.93 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* 162.2, 161.7, 161.2, 151.3, 132.1, 127.7, 118.9, 114.8, 68.3, 59.9, 51.9, 28.9, 28.2, 22.5, 14.1; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{17}H_{22}NO_5]^+$ 320.1492, Found 320.1492.

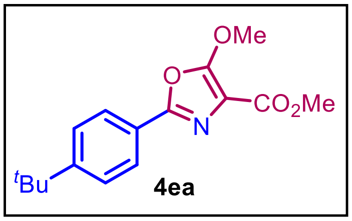
Methyl 2-(4-(benzyloxy)-phenyl)-5-methoxyoxazole-4-carboxylate (**4da**)



4da

4da was prepared according to the general procedure **4.1** in 54% (36.6 mg) in isolated yield. White solid; Purification done by column chromatography on silica gel using (hexanes: EtOAc = 85:15) as the eluent, **TLC** (30% ethyl acetate in hexanes): ***R*$_f$** = 0.30; **MP:** 108-110 °C; **IR** (KBr): 2954, 1712, 1503, 1399, 1240, 1046, 813, 661 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.93 (d, *J* = 9.1 Hz, 2H), 7.44-7.38 (m, 4H), 7.3 (d, *J* = 7.2 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 2H), 5.11 (s, 2H), 4.25 (s, 3H), 3.91 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* 162.2, 161.7, 160.7, 136.4, 128.9, 128.8, 128.5, 128.3, 127.8, 127.6, 119.4, 115.2, 70.2, 59.9, 52.0; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{19}H_{18}NO_5]^+$ 340.1179, Found 340.1184.

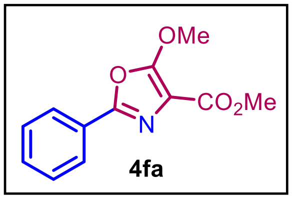
Methyl 2-(4-(*tert*-butyl-phenyl)-5-methoxyoxazole-4-carboxylate (**4ea**)



4ea

4ea was prepared according to the general procedure **4.1** in 66% (38.0 mg) isolated yield. Yellow oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*$_f$** = 0.35; **IR** (KBr): 2955, 1721, 1509, 1392, 1245, 1096, 829, 698 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.91 (d, *J* = 8.8 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 4.26 (s, 3H), 3.91 (s, 3H), 1.33 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* 162.1, 161.8, 154.0, 151.2, 150.6, 125.8, 123.6, 107.4, 59.8, 51.9, 35.0, 31.2; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{16}H_{20}NO_4]^+$ 290.1387, Found 290.1382.

Methyl 5-methoxy-2-phenyloxazole-4-carboxylate (**4fa**)



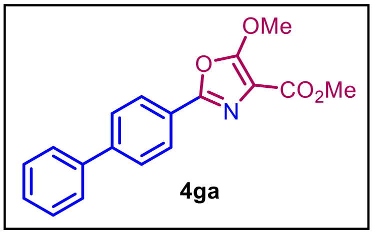
4fa

4fa was prepared according to the general procedure **4.1** in 61% (28.5 mg) in isolated yield. Colourless oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 92:8) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*$_f$** = 0.40; **IR** (KBr): 2885, 1735, 1490, 1380, 1195, 1045, 875, 589 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.99-7.97 (m, 2H), 7.45-

7.43 (m, 3H), 4.27 (s, 3H), 3.92 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 162.1, 161.9, 151.0, 130.6, 128.9, 126.4, 126.0, 107.6, 59.9, 52.0; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{12}H_{12}NO_4]^+$ 234.0761, Found 234.0760.

Spectral data matched with the reported literature. [3]

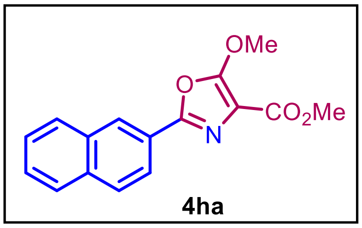
Methyl 2-([1,1'-biphenyl]-4-yl)-5-methoxyoxazole-4-carboxylate (**4ga**)



4ga

4ga was prepared according to the general procedure **4.1** in 63% (39.0 mg) in isolated yield. White solid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*$_f$** = 0.40; ; **MP:** 118-120 °C; **IR** (KBr): 3062, 1721, 1598, 1449, 1217, 1098, 846, 664 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 7.4 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 4.29 (s, 3H), 3.93 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 162.1, 161.9, 150.9, 143.3, 140.1, 129.0, 128.8, 128.1, 127.5, 127.2, 126.5, 125.2, 60.0, 52.0; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{18}H_{16}NO_4]^+$ 310.1074, Found 310.1069.

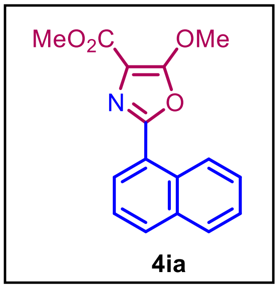
Methyl 5-methoxy-2-(naphthalen-2-yl)-oxazole-4-carboxylate (**4ha**)



4ha

4ha was prepared according to the general procedure **4.1** in 69% (39.0 mg) in isolated yield. Yellow oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*$_f$** = 0.40; **IR** (KBr): 2919, 1709, 1593, 1454, 1152, 1030, 803, 675 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.43 (s, 1H), 8.09 (dd, *J* = 2.2 Hz, 8.8 Hz, 1H), 7.91 (d, *J* = 9.1 Hz, 2H), 7.86-7.84 (m, 1H), 7.55-7.53 (m. 2H), 4.33 (s, 3H), 3.94 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 162.1, 162.0, 151.2, 134.2, 133.0, 129.6, 128.8, 128.7, 128.0, 127.5, 127.0, 126.0, 123.7, 122.8, 60.0, 52.0; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{16}H_{14}NO_4]^+$ 284.0917, Found 284.0916.

Methyl 5-methoxy-2-(naphthalen-1-yl)-oxazole-4-carboxylate (**4ia**)

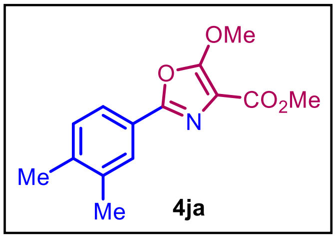


4ia

4ia was prepared according to the general procedure **4.1** in 65% (37.0 mg) in isolated yield. Yellow oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*$_f$** = 0.40; **IR** (KBr): 3065, 1820, 1580, 1510, 1180, 1045, 835, 690 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): *δ* 9.19 (d, *J* = 9.2 Hz, 1H) 8.09 (d, *J* = 7.8 Hz, 1H) 7.96 (d, *J* = 8.5 Hz, 1H) 7.90 (d, *J* = 8.5 Hz, 1H), 7.67 (t, *J* = 7.3 Hz, 1H), 7.54-7.51 (m, 2H), 4.31 (s, 3H), 3.95 (s, 3H); **^{13}C NMR** (126 MHz, CDCl$_3$): *δ* 162.1, 161.8, 150.8, 133.9, 131.4, 129.9, 128.6, 127.9, 127.5, 126.5, 126.0, 124.8, 122.8, 107.5, 59.9, 51.9; **HRMS** (ESI/Q-TOF) *m/z*: [M+H]$^+$ Calcd for [$C_{16}H_{14}NO_4$]$^+$ 284.0917, Found 284.0914.

Spectral data matched with the reported literature.[5]

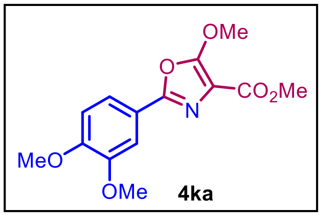
Methyl 2-(3,4-dimethylphenyl)-5-methoxyoxazole-4-carboxylate (**4ja**)



4ja

4ja was prepared according to the general procedure **4.1** in 60% (31.5 mg) in isolated yield. Yellow solid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*$_f$** = 0.40; ; **MP:** 140-142 °C; **IR** (KBr): 2952, 1709, 1485, 1380, 1233, 1048, 840, 608 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): *δ* 7.78 (s, 1H) 7.68 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 4.26 (s, 3H), 3.91 (s, 3H), 2.30 (s, 6H); **^{13}C NMR** (126 MHz, CDCl$_3$): *δ* 162.2, 161.8, 151.4, 139.7, 137.3, 130.1, 127.1, 124.0, 123.5, 107.3, 59.9, 52.0, 19.9, 19.7; **HRMS** (ESI/Q-TOF) *m/z*: [M+H]$^+$ Calcd for [$C_{14}H_{16}NO_4$]$^+$ 262.1074, Found 262.1074.

Methyl 2-(3,4-dimethoxyphenyl)-5-methoxyoxazole-4-carboxylate **(4ka)**

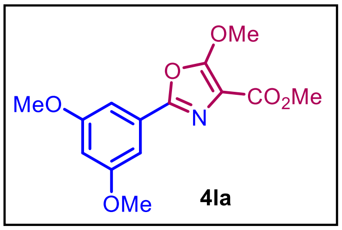


4ka

4ka was prepared acco rding to the general procedure **4.1** in 67% (39.5 mg) in isolated yield. Yellow solid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 80:20) as an eluent, **TLC** (30% ethyl acetate in hexane); ***R*$_f$** = 0.25; ; **MP:** 120-122 °C; **IR** (KBr): 3034, 1741, 1494, 1390, 1188, 1055, 802, 665 cm^{-1}; **^{1}H**

NMR (500 MHz, CDCl$_3$): δ 7.43 (s, 1H), 6.98-6.96 (m, 1H), 6.94-6.92 (m, 1H), 4.24 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.81 (s, 3H); ^{13}**C NMR** (126 MHz, CDCl$_3$): δ 162.2, 161.8, 153.5, 152.0, 149.6, 129.3, 118.2, 116.0, 114.3, 113.6, 59.8, 56.7, 56.1, 51.8; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{14}H_{16}NO_6]^+$ 294.0972, Found 294.0972.

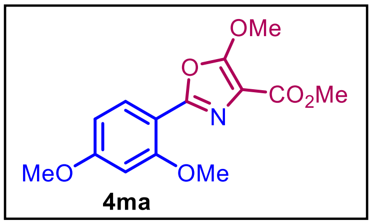
Methyl 2-(3,5-dimethoxyphenyl)-5-methoxyoxazole-4-carboxylate **(4la)**



4la

4la was prepared according to the general procedure **4.1** in 67% (39.5 mg) isolated yield. Yellow solid; Purification done by column chromatography on silica gel using (hexanes: EtOAc = 80:20) as an eluent, **TLC** (30% ethyl acetate in hexanes): **R_f** = 0.25; ; **MP:** 138-140 °C; **IR** (KBr): 2985, 1745, 1525, 1380, 1210, 1110, 845, 610 cm^{-1}; ^{1}**H NMR** (500 MHz, CDCl$_3$): δ 7.12 (s, 1H), 7.11(s, 1H), 6.54 (s, 1H), 4.26 (s, 3H), 3.92 (s, 3H), 3.84 (s, 6H); ^{13}**C NMR** (126 MHz, CDCl$_3$): δ 162.0, 161.8, 161.1, 128.0, 103.9, 103.3, 102.3, 59.9, 55.8, 52.1; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{16}H_{16}NO_6]^+$ 294.0972, Found 294.0976.

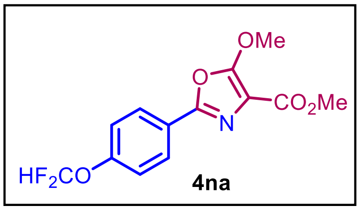
Methyl 2-(2,4-dimethoxyphenyl)-5-methoxyoxazole-4-carboxylate (**4ma**)



4ma

4ma was prepared according to the general procedure **4.1** in 43% (25.1 mg) isolated yield. Yellow solid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 80:20) as an eluent, **TLC** (30% ethyl acetate in hexane); **R_f** = 0.25; ; **MP:** 133-135 °C; **IR** (KBr): 3085, 1789, 1525, 1410, 1167, 1086, 817, 687 cm^{-1}; ^{1}**H NMR** (500 MHz, CDCl$_3$): δ 7.51 (s, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 1H), 4.26 (s, 3H), 3.95 (s, 3H), 3.92 (s, 3H), 3.91 (s, 3H); ^{13}**C NMR** (126 MHz, CDCl$_3$): δ 162.1, 161.8(2), 161.8 151.2, 149.3, 119.3, 110.9, 108.8, 108.6, 107.5, 60.0, 56.3, 56.1, 52.0; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{14}H_{10}Cl_2NO]^+$ $[C_{16}H_{16}NO_6]^+$ 294.0972, Found 294.0970.

Methyl 2-(4-(difluoromethoxy-phenyl)-5-methoxyoxazole-4-carboxylate (**4na**)

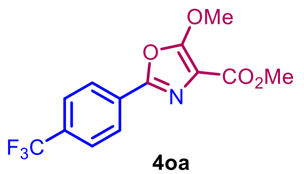


4na

4na was prepared according to the general procedure **4.1** in 47% (28.0 mg) isolated yield. Colorless oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); **R_f** = 0.35; **IR** (KBr): 3085, 1789, 1525, 1410, 1167, 1086, 817, 687 cm^{-1}; ^{1}**H NMR** (500 MHz, CDCl$_3$): δ 7.99 (d, *J* =

9.1 Hz, 2H), 7.19 (d, *J* = 9.1 Hz, 2H), 6.71 (t, *J* = 73.5 Hz, 1H), 4.27 (s, 3H), 3.92 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* 162.0, 161.9, 152.8, 150.1, 127.8, 123.6, 119.6, 117.6 (t, $^1J_{CF}$ = 261.3 Hz), 107.6, 60.0, 52.1; **^{19}F NMR** (471 MHz, $CDCl_3$): *δ* -81.3 (d, *J* = 77.9 Hz, 2F); **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{13}H_{12}F_2NO_5]^+$ 300.0678, Found 300.0677.

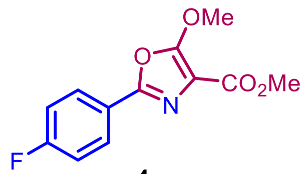
Methyl 5-methoxy-2-(4-trifluoromethyl)-phenyl-oxazole-4-carboxylate **(4oa)**



4oa

4oa was prepared according to the general procedure **4.1** in 42% (25.0 mg) isolated yield. Colorless oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*f** = 0.30; **IR** (KBr): 3050, 1734, 1512, 1225, 1135, 930, 638 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 8.10 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 4.30 (s, 3H), 3.93 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* 162.1, 161.8, 149.5, 132.3 (q, $^1J_{CF}$ = 313.0 Hz), 128.7 (q, $^2J_{CF}$ = 24.0 Hz), 128.5, 126.2, 126.0 (q, $^3J_{CF}$ = 3.9 H z), 108.1, 60.1, 52.1; **^{19}F NMR** (471 MHz, $CDCl_3$): δ -62.8; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{13}H_{11}F_3NO_4]^+$ 302.0635, Found 302.0637.

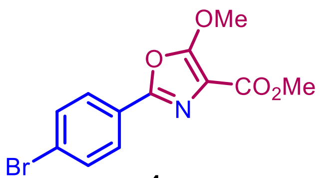
Methyl 2-(4-fluorophenyl)-5-methoxyoxazole-4-carboxylate **(4pa)**



4pa

4pa was prepared according to the general procedure **4.1** in 75% (38.0 mg) isolated yield. Colorless oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*f** = 0.35; **IR** (KBr): 2985, 1709, 1528, 1380, 1240, 1033, 852, 667 cm^{-1}; ^{1}**H NMR** (500 MHz, $CDCl_3$): *δ* 7.99-7.96 (m, 2H), 7.15 (t, *J* = 8.5 Hz, 2H), 4.26 (s, 3H), 3.92 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* 165.2 (d, $^1J_{CF}$ = 252.1 Hz), 162.0, 161.9, 150.3, 128.2 (d, $^3J_{CF}$ = 8.7 Hz), 122.8 (d, $^4J_{CF}$ = 3.5 Hz), 116.2 (d, $^2J_{CF}$ = 22.4 Hz), 107.6, 60.0, 52.0; **^{19}F NMR** (471 MHz, $CDCl_3$): *δ* -108.7; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{12}H_{11}FNO_4]^+$ 252.0667, Found 252.0667.

Methyl 2-(4-bromophenyl)-5-methoxyoxazole-4-carboxylate (**4qa**)

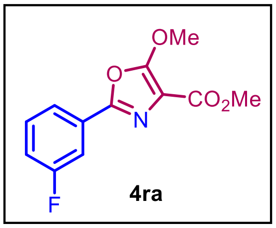


4qa

4qa was prepared according to the general procedure **4.1** in 56% (35.0 mg) isolated yield. Yellow oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*f** = 0.35; **IR** (KBr): 3090, 1720, 1545, 1289, 1059, 839, 585 cm^{-1}; **^{1}H NMR** (500 MHz,

$CDCl_3$): δ 7.92 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 8.9 Hz, 2H), 4.27 (s, 3H), 3.9 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 162.0, 161.9, 150.1, 136.7, 129.2, 127.3, 124.9, 107.7, 60.0, 52.1; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{12}H_{11}BrNO_4]^+$ 311.9866, Found 311.9869.

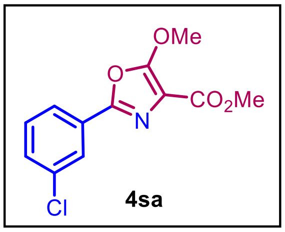
Methyl 2-(3-fluorophenyl)-5-methoxyoxazole-4-carboxylate **(4ra)**



4ra

4ra was prepared according to the general procedure **4.1** in 72% (36.1 mg) isolated yield. Colorless oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*$_f$** = 0.35; **IR** (KBr): 3025, 1729, 1520, 1380, 1298, 1025, 838, 656 cm^{-1};**^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.78-7.76 (m, 1H), 7.68-7.66 (m, 1H), 7.44-7.39 (m, 1H), 7.16-7.12 (m, 1H), 4.28 (s, 3H), 3.92 (s, 3H); **^{13}C NMR** (176 MHz, $CDCl_3$): δ 163.9 (d, $^1J_{CF}$ = 252.7 Hz), 163.8, 161.9, 130.7 (d, $^3J_{CF}$ = 11.8 Hz), 128.4 (d, $^3J_{CF}$ = 11.9 Hz), 121.7 (d, $^4J_{CF}$ = 5.2 Hz), 117.3 (d, $^2J_{CF}$ = 30.0 Hz), 113.1, 112.9, 107.8, 60.0, 52.1; **^{19}F NMR** (471 MHz, $CDCl_3$): δ -108.7; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{12}H_{11}FNO_4]^+$ 252.0667, Found 252.0670.

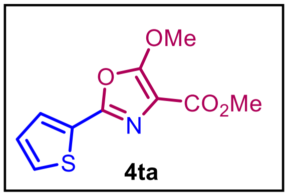
Methyl 2-(3-chlorophenyl)-5-methoxyoxazole-4-carboxylate **(4sa)**



4sa

4sa was prepared according to the general procedure **4.1** in 47% (25.0 mg) isolated yield. Colorless oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*$_f$** = 0.35; **IR** (KBr): 2923, 1708, 1465, 1212, 1101, 986, 748, 585 cm^{-1}; **H NMR** (500 MHz, $CDCl_3$): δ 7.88-7.85 (m, 1H), 7.41-7.38 (m, 1H), 4.28 (s, 3H), 3.92 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 161.9, 161.4, 150.1, 136.7, 132.2, 129.7, 129.2, 127.2, 124.9, 107.7, 60.0, 52.0; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{12}H_{11}ClNO_4]^+$ 268.0371, Found 268.0370.

Methyl 5-methoxy-2-(thiophen-2-yl)-oxazole-4-carboxylate (**4ta**)

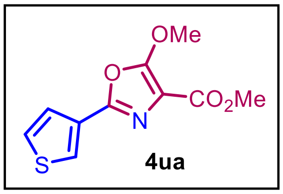


4ta

4ta was prepared according to the general procedure **4.1** in 43% (20.5 mg) isolated yield. Yellow oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*$_f$** = 0.35; **IR** (KBr): 3063, 1706, 1593, 1397, 1205, 1089, 835, 702 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): 7.63-7.62 (m, 1H), 7.42-7.40 (m, 1H), 7.09

(dd, $J = 3.7, 5.0$ Hz, 1H), 4.24 (s, 3H), 3.90 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 161.9, 161.4, 147.5, 128.2, 128.6, 127.9(8), 127.9(6), 107.4, 60.1, 52.0; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{10}H_{10}NO_4S]^+$ 240.0325, Found 240.0325.

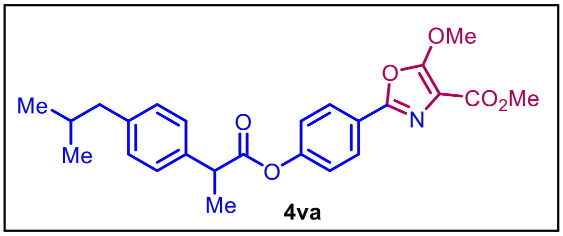
Methyl 5-methoxy-2-(thiophen-3-yl)-oxazole-4-carboxylate (**4ua**)



4ua

4ua was prepared according to the general procedure **4.1** in 58% (27.5 mg) isolated yield. Yellow oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*$_f$** = 0.35; **IR** (KBr): 3018, 1750, 1526, 1393, 1201, 1052, 858, 637 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): 7.89-7.88 (m, 1H), 7.61 (d, $J = 6.3$ Hz, 1H), 7.38 (dd, $J = 3.2$ Hz, 5.1 Hz, 1H), 4.24 (s, 3H), 3.91 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 161.9, 161.4, 147.5, 129.7, 128.8, 128.6, 127.9, 107.4, 60.1, 52.0; **HRMS (**ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{10}H_{10}NO_4S]^+$ 240.0325, Found 240.0324.

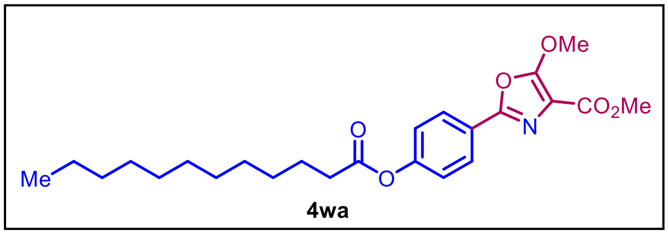
Methyl 2-(4-isobutylphenyl-propanoyl)-oxy-phenyl)-5-methoxyoxazole-4-carboxylate (**4va**)



4va

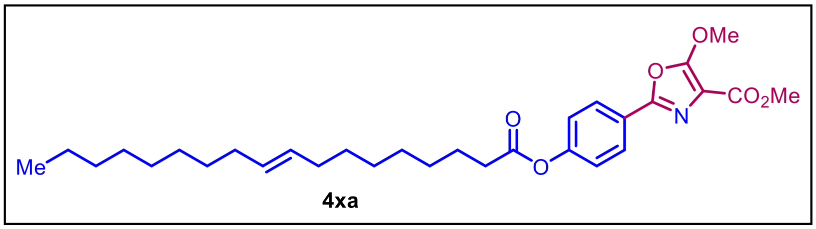
4va was prepared according to the general procedure **4.1** in 67% (58.5 mg) isolated yield. Yellow oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 85:15) as an eluent, **TLC** (30% ethyl acetate in hexane); ***R*$_f$** = 0.30; **IR** (KBr): 2945, 1745, 1548, 1474, 1237, 1090, 829, 685 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): 7.96 (d, $J = 7.9$ Hz, 2H), 7.30 (d, $J = 7.3$ Hz, 2H), 7.16 (d, $J = 8.3$ Hz, 2H), 7.08 (d, $J = 8.9$ Hz, 2H), 4.25 (s, 3H), 3.91 (s, 3H), 3.87-3.84 (m, 1H), 2.48 (d, $J = 8.9$ Hz, 3H), 1.88-.83 (m, 1H), 1.60 (d, $J = 3.3$ Hz, 2H), 0.91 (d, $J = 7.1$ Hz, 6H); **^{13}C NMR HRMS** (126 MHz, $CDCl_3$): δ 172.9, 162.0, 161.9, 152.6, 150.4, 141.1, 137.0, 129.7, 127.3, 127.2, 124.0, 122.1, 107.7, 60.0, 52.0 45.4, 45.1, 30.3, 22.5, 18.5; (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{25}H_{28}NO_6]^+$ 438.1911, Found 438.1915

Methyl 2-(4-dodecanoyloxy-phenyl)-5-methoxyoxazole-4-carboxylate (**4wa**)


4wa

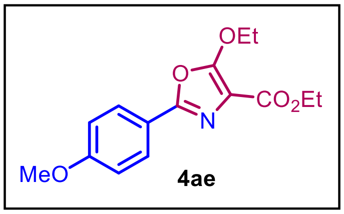
4wa was prepared according to the general procedure **4.1** in 56% (48.0 mg) isolated yield. Colorless oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 85:15) as an eluent, **TLC** (30% ethyl acetate in hexane); $\boldsymbol{R_f}$ = 0.30; **IR** (KBr): 2956, 1752, 1510, 1400, 1203, 1050, 850, 695 cm^{-1}; ^{1}**H NMR** (500 MHz, $CDCl_3$): 7.99 (d, J = 8.7 Hz, 2H), 7.18 (d, J = 8.7 Hz, 2H), 4.26 (s, 3H), 3.91 (s, 3H), 2.57 (t, J = 7.5 Hz, 2H), 1.77-1.71 (m, 3H), 1.42-1.36 (m, 3H), 1.30-1.26 (m, 10 H), 0.8 (t, J = 6.6 Hz, 5H); ^{13}**C NMR** (126 MHz, $CDCl_3$): δ 172.0, 162.0, 161.9, 152.5, 150.4, 127.3, 123.9, 122.2, 107.7, 60.0, 52.0, 34.5, 32.0, 29.7, 29.5, 29.4, 29.3, 29.2, 24.9, 22.8, 14.2; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{24}H_{34}NO_6]^+$ 432.2381, Found 432.2385.

Methyl (*E*)-5-methoxy-2-(4-(octadec-8-enoyloxy-phenyl)-oxazole-4-carboxylate (**4xa**)


4xa

4xa was prepared according to the general procedure **4.1** in 47% (48.0 mg) isolated yield. Brown oil; Purification done by column chromatography on silica gel using (hexane: EtOAc = 80:20) as an eluent, **TLC** (30% ethyl acetate in hexane); $\boldsymbol{R_f}$ = 0.25; **IR** (KBr): 2943, 1729, 1535, 1460, 1270, 1050, 820, 635 cm^{-1}; ^{1}**H NMR** (700 MHz, $CDCl_3$): 7.98 (d, J = 8.2 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 5.38 (s, 2H), 4.26 (s, 3H), 3.92 (s, 3H), 2.57 (t, J = 6.6 Hz, 2H), 1.97 (s, 3H), 1.76 (t, J = 7.0 Hz, 2H) 1.34-1.33 (m, 8H), 1.32-1.26 (m, 13H), 0.88 (t, J = 5.8 Hz, 3H); ^{13}**C NMR HRMS** (176 MHz, $CDCl_3$): δ 172.0, 162.0, 161.9, 152.6, 130.7, 130.3, 127.3, 124.0, 122.2, 60.0, 52.0, 32.7, 32.6, 32.0, 29.8, 29.6, 29.4, 29.3, 29.2(4), 29.2(0), 29.0, 24.9, 22.8, 14.2; (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{30}H_{44}NO_6]^+$ 514.3162, Found 514.3158.

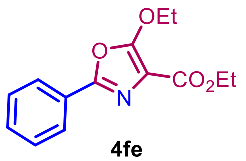
Ethyl 5-ethoxy-2-(4-methoxyphenyl)-oxazole-4-carboxylate (**4ae**)



4ae

4ae was prepared according to the general procedure **4.1** in 70% (41.0 mg) isolated yield. Yellow liquid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 85:15) as an eluent, **TLC** (30% ethyl acetate in hexane); ***R*f** = 0.25; **IR** (KBr): 3104, 1743, 1509, 1389, 1243, 1075, 845, 611 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.90 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 2H), 4.57 (q, *J* = 7.1 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 1.52 (t, *J* = 7.0 Hz, 3H), 1.39 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* 161.9, 161.4, 161.2, 151.4, 127.7, 119.2, 114.2, 108.4, 70.1, 60.7, 55.4, 15.0, 14.5; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{15}H_{18}NO_5]^+$ 292.1179, Found 292.1176.

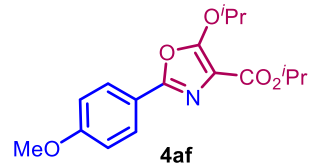
Ethyl 5-ethoxy-2-(4-ethoxyphenyl)-oxazole-4-carboxylate (**4fe**)



4fe

4fe was prepared according to the general procedure **4.1** in 73% (38.0 mg) isolated yield. Colorless liquid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 90:10) as an eluent, **TLC** (20% ethyl acetate in hexane); ***R*f** = 0.30; **IR** (KBr): 3025, 1740, 1489, 1357, 1210, 1043, 867, 565 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.98-7.96 (m, 2H), 7.44-7.42 (m, 3H), 4.61 (q, *J* = 7.5 Hz, 2H), 4.40 (q, *J* = 7.5 Hz, 2H), 1.53 (t, *J* = 7.3 Hz, 3H), 1.39 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* 161.8, 161.4, 151.2, 130.5, 128.8, 126.6, 126.0, 108.7, 70.1, 60.8, 15.1, 14.5; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{14}H_{16}NO_4]^+$ 262.1074, Found 262.1080

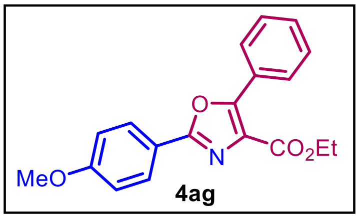
Isopropyl 5-isopropoxy-2-(4-methoxyphenyl)-oxazole-4-carboxylate (**4af**)



4af

4af was prepared according to the general procedure **4.1** in 79% (50.5 mg) isolated yield. Orange liquid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 85:15) as an eluent, **TLC** (30% ethyl acetate in hexane); ***R*f** = 0.25; **IR** (KBr): 2981, 1707, 1504, 1413, 1254, 1085, 835, 702 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 7.92 (d, *J* = 9.0 Hz, 2H), 6.94 (d, *J* = 9.0 Hz, 2H), 5.26-5.21 (m, 1H), 4.98-4.93 (m, 1H), 3.84 (s, 3H), 1.47 (d, *J* = 6.2 Hz, 6H), 1.37 (d, *J* = 6.3 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* 161.6, 161.4, 160.4, 152.1, 127.8, 119.5, 114.2, 110.7, 79.4, 68.2, 55.4, 22.4, 22,0; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{17}H_{22}NO_5]^+$ 320.1492, Found 320.1487.

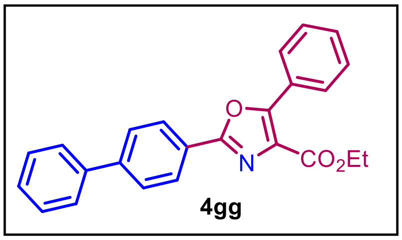
Ethyl 2-(4-methoxyphenyl)-5-phenyloxazole-4-carboxylate (**4ag**)



4ag

4ag was prepared according to the general procedure **4.1** in 53% (34.0 mg) isolated yield. Orange liquid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 85:15) as an eluent, **TLC** (30% ethyl acetate in hexane); ***R*f** = 0.25; **IR** (KBr): 3008, 1731, 1501, 1444, 1253, 1021, 833, 689 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.10 (d, *J* = 9.1 Hz, 4H), 7.48-7.45 (m, 3H), 6.99 (d, *J* = 9 Hz , 2H) ; 4.46 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 162.5, 162.0, 160.0, 154.7, 130.2, 128.7, 128.6, 128.4, 128.2, 127.4, 119.2, 114.3, 61.5, 55.5, 14.4; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{19}H_{18}NO_4]^+$ 324.1230, Found 324.1227.

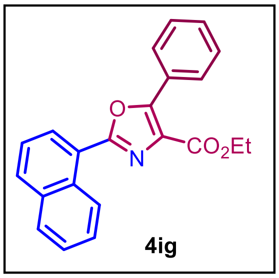
Ethyl 2-([1,1'-biphenyl]-4-yl)-5-phenyloxazole-4-carboxylate (**4gg**)



4gg

4gg was prepared according to the general procedure **4.1** in 64% (47.0 mg) isolated yield. Orange solid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 85:15) as an eluent, **TLC** (30% ethyl acetate in hexane); ***R*f** = 0.25; **MP:** 120-122 °C; **IR** (KBr): 3008, 1731, 1501, 1444, 1253, 1021, 833, 689 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.6 Hz, 2H), 8.14-8.12 (m, 2H), 7.73 (d, *J* = 8.5 Hz , 2H), 7.66 (d, *J* = 7.9 Hz, 2H), 7.51-7.46 (m, 5H), 7.41 (t, *J* = 7.3 Hz, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 162.4, 159.8, 155.2, 143.9, 143.8(8), 143.8(5), 140.1, 130.4, 129.0, 128.7, 128.5, 128.1, 127.5, 127.4, 127.2, 125.3, 61.6, 14.4; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{24}H_{20}NO_3]^+$ 370.1438, Found 370.1431.

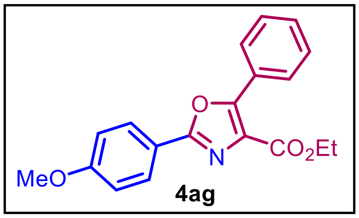
Ethyl 2-(naphthalen-1-yl)-5-phenyloxazole-4-carboxylate (**4ig**)



4ig

4ig was prepared according to the general procedure **4.1** in 58% (40.0 mg) isolated yield. Yellow liquid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 85:15) as an eluent, **TLC** (30% ethyl acetate in hexane); $\boldsymbol{R_f}$ = 0.25; **IR** (KBr): 3055, 1755, 1550, 1445, 1220, 1085, 845, 664 cm^{-1}; $^{\mathbf{1}}$**H NMR** (500 MHz, CDCl$_3$): δ 9.23 (d, J = 7.95 Hz, 1H), 8.31 (d, J = 7.2 Hz, 1H), 8.18 (d, J = 9.7 Hz, 2H), 8.01 (d, J = 8.1 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.69 (d, J = 7.1 Hz, 1H), 7.60-7.57 (m, 2H), 7.56-7.51 (m, 3H), 4.51 (q, J = 7.1 Hz, 2H), 1.47 (t, J = 7.1 Hz, 3H); $^{\mathbf{13}}$**C NMR** (126 MHz, CDCl$_3$): δ 162.6, 159.9, 155.0, 134.0, 132.0, 130.4, 130.3, 128.7, 128.6(8), 128.6(1), 128.5, 128.4, 128.0, 127.3, 126.6, 126.1, 125.0, 123.1, 61.5, 14.4; **HRMS** (ESI/Q-TOF) *m/z*: [M+H]$^+$ Calcd for [C$_{22}$H$_{18}$NO$_3$]$^+$ 344.1281, Found 344.1276.

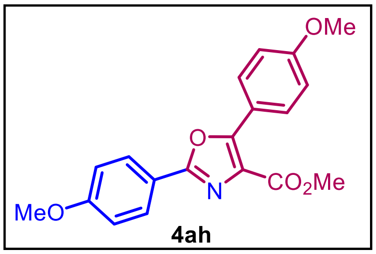
Ethyl 2-(4-methoxyphenyl)-5-phenyloxazole-4-carboxylate (**4ag**)



4ag

4ag was prepared according to the general procedure **4.1** in 53% (34.0 mg) isolated yield. Orange liquid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 85:15) as an eluent, **TLC** (30% ethyl acetate in hexane); $\boldsymbol{R_f}$ = 0.25; **IR** (KBr): 3008, 1731, 1501, 1444, 1253, 1021, 833, 689 cm^{-1}; $^{\mathbf{1}}$**H NMR** (500 MHz, CDCl$_3$): δ 8.10 (d, J = 9.1 Hz, 4H), 7.48-7.45 (m, 3H), 6.99 (d, J = 9.0 Hz , 2H) ; 4.46 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H); $^{\mathbf{13}}$**C NMR** (126 MHz, CDCl$_3$): δ 162.5, 162.0, 160.0, 154.7, 130.2, 128.7, 128.6, 128.4, 128.2, 127.4, 119.2, 114.3, 61.5, 55.5, 14.4; **HRMS** (ESI/Q-TOF) *m/z*: [M+H]$^+$ Calcd for [C$_{19}$H$_{18}$NO$_4$]$^+$ 324.1230, Found 324.1227.

Methyl 2,5-bis(4-methoxyphenyl)-oxazole-4-carboxylate (**4ah**)

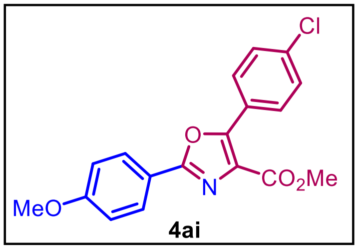


4ah

4ah was prepared according to the general procedure **4.1** in 65% (44.0 mg) isolated yield. Yellow solid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 80:20) as an eluent, **TLC** (30% ethyl acetate in hexane); $\boldsymbol{R_f}$ = 0.20; **MP:** 109-111 °C; **IR neat (cm^{-1})**: 3064, 1707, 1503, 1362, 1175, 1028, 815, 662 cm^{-1}; $^{\mathbf{1}}$**H NMR** (500 MHz, CDCl$_3$): δ 8.13 (d, J = 9.1 Hz, 2H), 8.09 (d, J = 9.1 Hz, 2H), 7.02 (d, J = 9.3 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 3.96 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H); $^{\mathbf{13}}$**C**

NMR (126 MHz, $CDCl_3$): *δ* 163.1, 161.9, 161.2, 159.4, 156.3, 130.2, 128.6, 126.6, 119.8, 119.2, 114.3, 114.0, 55.5(7), 55.5(4), 52.4; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{19}H_{18}NO_5]^+$ 340.1179, Found 340.1173

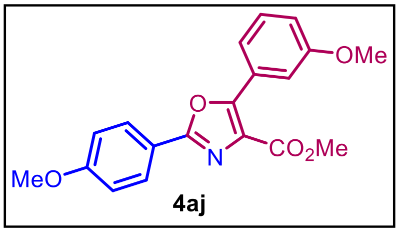
Methyl 5-(4-chlorophenyl)-2-(4-methoxyphenyl)oxazole-4-carboxylate (**4ai**)



4ai

4ai was prepared according to the general procedure **4.1** in 78% (53.0 mg) isolated yield. White solid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 85:15) as an eluent, **TLC** (30% ethyl acetate in hexane); R_f = 0.25; **MP:** 112-114 °C; **IR neat (cm^{-1})**: 2956, 1713, 1590, 1485, 1256, 1087, 834, 701 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 8.10 (d, *J* = 8.9 Hz, 2H), 8.09 (d, *J* = 9.0 Hz, 2H), 7.48 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 2H), 3.98 (s, 3H), 3.88 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* 162.9, 162.2, 160.2, 153.8, 136.4, 129.7, 128.9, 128.8, 128.2, 125.7, 118.9, 114.4, 55.6, 52.6; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{18}H_{15}ClNO_4]^+$ 344.0684, Found 344.0688.

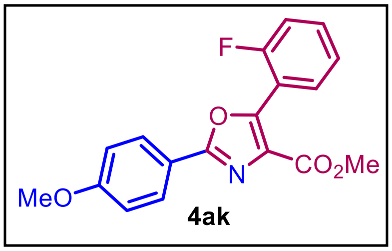
Methyl 5-(3-methoxyphenyl)-2-(4-methoxyphenyl)oxazole-4-carboxylate (**4aj**)



4aj

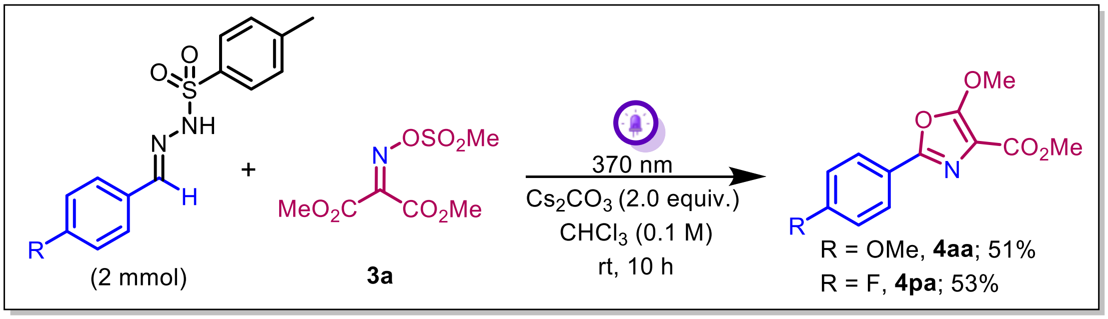
4aj was prepared according to the general procedure **4.1** in 52% (35.0 mg) isolated yield. Yellow solid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 80:20) as an eluent, **TLC** (30% ethyl acetate in hexane); R_f = 0.20; **MP:** 118-120 °C; **IR neat (cm^{-1})**: 2951, 1791, 1587, 1425, 1216, 1095, 839, 701 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): *δ* 8.10 (d, *J* = 9.1 Hz, 2H), 7.80-7.79 (m, 1H), 7.71-7.70 (m, 1H), 7.42-7.39 (m, 1H), 7.0 (d, *J* = 9 Hz , 3H); 3.97 (s, 3H), 3.90 (s, 3H), 3.87 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): *δ* 162.9, 162.1, 160.0, 159.6, 154.6, 129.6, 128.7, 128.4, 128.1, 120.8, 119.1, 116.4, 114.4, 113.8, 55.6, 55.5, 52.5; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{19}H_{18}NO_5]^+$ 340.1179, Found 340.1183.

Methyl 5-(2-fluorophenyl)-2-(4-methoxyphenyl)-oxazole-4-carboxylate (**4ak**)



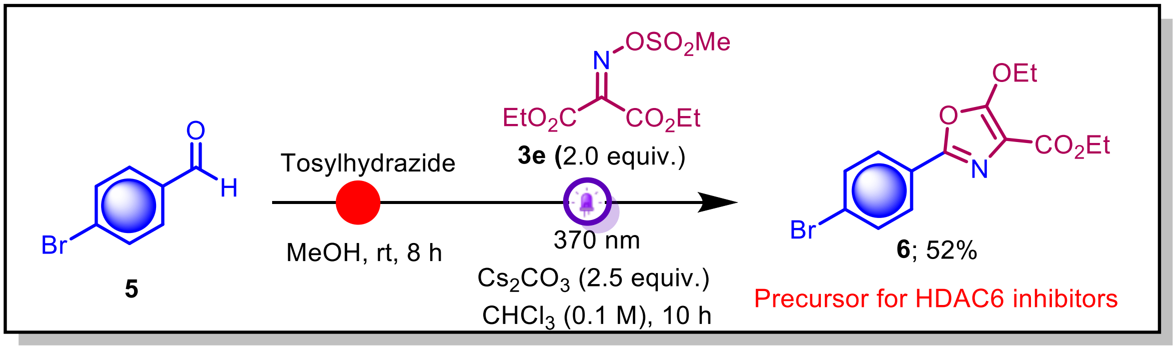
4ak was prepared according to the general procedure **4.1** in 58% (38.0 mg) isolated yield. Yellow liquid; Purification done by column chromatography on silica gel using (hexane: EtOAc = 80:20) as an eluent, **TLC** (30% ethyl acetate in hexane); ***R*$_f$** = 0.20; **IR neat (cm^{-1})**: 3025, 1695, 1485, 1352, 1213, 1004, 815, 737 cm^{-1}; **^{1}H NMR** (500 MHz, CDCl$_3$): δ 8.09 (d, J = 8.7 Hz, 2H), 7.73 (t, J = 6.1 Hz, 1H), 7.23-7.19 (m, 1H) ; 7.13 (d, J = 8.7 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 6.82 (d, J = 8.9 Hz, 1H) 3.90 (s, 3H), 3.87 (s, 3H); **^{13}C NMR** (126 MHz, CDCl$_3$): δ 162.1, 161.4 (d, $^1J_{CF}$ = 215 Hz), 159.1, 157.3 (d, $^2J_{CF}$ = 35 Hz), 154.9 (d, $^2J_{CF}$ = 44 Hz), 132.4, 131.4, 128.8, 127.9, 124.0, 119.1, 116.3 (d, $^3J_{CF}$ = 13 Hz), 114.4, 114.1, 56.9, 52.3; **^{19}F NMR** (471 MHz, CDCl$_3$): δ -110.7 **HRMS** (ESI/Q-TOF) *m/z*: [M+H]$^+$ Calcd for [C$_{18}$H$_{15}$FNO$_4$]$^+$ 328.0980, Found 328.0978

6.0 General procedure for 2 mmol scale reaction



To an oven dried 25 mL round bottom flask was charged with magnetic stir bar, *N*-sulfonyl hydrazones **2a** and **2p** (2.0 mmol, 1.0 equiv.) was added, then Cs$_2$CO$_3$ (1.63 gm, 5.0 mmol, 2.5 equiv.) and dimethyl 2-(mesyloxy-imino)malonate **3a** (957mg, 4.0 mmol, 2.0 equiv.) were added followed by addition of CHCl$_3$ (0.1 M, 20 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 370 nm 40 W LEDs (the reaction vial distance from light source ~ 2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35 ˚ C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (15-18% EtOAc:Hexane) as an eluent to furnish the corresponding product **4aa** (268 mg, 51% yield) and **4pa** (266 mg, 53% yield), respectively.

7.0 Synthesis of compound 6



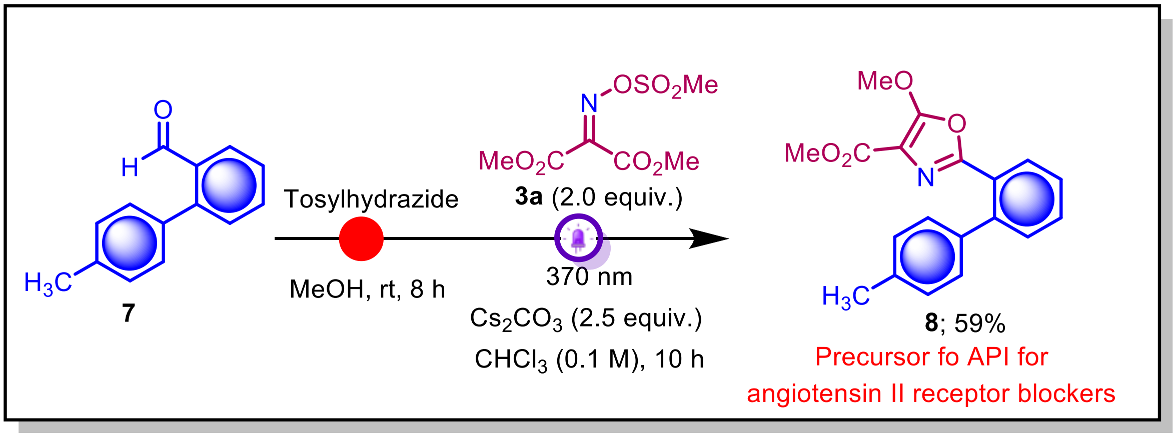
7.1 Compound **6** was prepared by three component approach via one pot manner

7.2 Synthesis of ethyl 2-(4-bromophenyl)-5-ethoxyoxazole-4-carboxylate **(6)**

To a stirred solution of *p*-toluene sulfonylhydrazide (37.2 mg, 0.2 mmol, 1.0 equiv) in MeOH (0.5 M), *p*-bromo benzaldehydes **5** (37 mg, 0.2 mmol, 1.0 equiv) in MeOH (0.25 M) solution were added dropwise. The reaction mixture was stirred at room temperature for 8 h followed by removal of MeOH under reduced pressure. In the crude reaction mixture, Cs_2CO_3 (163.0 mg, 0.5 mmol, 2.5 equiv) and diethyl 2-(methyl sulfonyloxy)imino-malonate **3e** (107 mg, 0.4 mmol, 2.0 equiv) were added followed by $CHCl_3$ solvent (0.1 M, 2 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 370 nm 40 W LEDs (the reaction vial distance from light source ~ 2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35 °C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (8%-10% EtOAc:Hexane) as an eluent to furnish the title product **6** with (35.5 mg) 52% yield. Colorless liquid; **TLC** (20% ethyl acetate in hexane); $R_f = 0.35$; **IR** (KBr): 2982, 1716, 1595, 1430, 1155, 1008, 843, 679 cm^{-1}; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.84 (d, $J = 8.7$ Hz, 2H), 7.57 (d, $J = 8.7$ Hz, 2H), 4.60 (q, $J = 7.1$ Hz, 2H), 4.39 (q, $J = 7.1$ Hz, 2H), 1.53 (t, $J = 7.1$ Hz, 3H), 1.39 (t, $J = 7.1$ Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$): δ 161.7, 161.5, 150.4, 132.2, 127.5, 125.6, 125.1, 108.9, 70.4, 61.0, 15.2, 14.6; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{14}H_{15}BrNO_4]^+$ 340.0179, Found 340.0179.

Spectral data matched with the reported literature.[4]

7.3 Synthesis of compound **8**



To a stirred solution of *p*-toluene sulfonylhydrazide (37.2 mg, 0.2 mmol, 1.0 equiv) in MeOH (0.5 M), 4'-methyl-[1,1'-biphenyl]-2-carbaldehyde **7** (39.2 mg, 0.2 mmol, 1.0 equiv) in MeOH (0.25 M) solution were added dropwise. The reaction mixture was stirred at room temperature for 8 h followed by removal of MeOH under reduced pressure. In the crude reaction mixture, Cs_2CO_3 (163.0 mg, 0.5 mmol, 2.5 equiv) and dimethyl 2-(methyl sulfonyloxy)imino-malonate **3a** (95.6 mg, 0.4 mmol, 2.0 equiv) were added followed by $CHCl_3$ solvent (0.1 M, 2 mL) under nitrogen atmosphere. The reaction mixture was stirred in presence of 370 nm 40 W LEDs (the reaction vial distance from light source ~ 2 cm) at room temperature using fan (we control the temperature by using the fan, temperature of the reaction reaching ~35˚ C) for 10 h. Upon the complete consumption of the starting materials, the reaction mixture was diluted with ethyl acetate and then passed through the celite pad, the solvent was removed under reduced pressure. Compound was purified by column chromatography on silica gel using (12-14% EtOAc:Hexane) as an eluent to furnish the title product **8** with (38 mg) 59% yield. White solid; **TLC** (20% ethyl acetate in hexane); $\boldsymbol{R_f}$ = 0.30; **MP:** 116-118 °C; **IR** (KBr): 3241, 2940, 1697, 1261, 1131, 759 cm^{-1}; ^{1}**H NMR** (500 MHz, $CDCl_3$): δ 8.02 (d, J = 7.7 Hz, 1H), 7.50-7.47 (m, 1H), 7.43-7.40 (m, 1H), 7.37-7.36 (m, 1H), 7.27 (d, J = 7.9 Hz, 1H), 7.17 (t, J = 8.1 Hz, 3H), 3.89 (s, 3H), 3.50 (s, 3H), 2.35 (s, 3H); ^{13}**C NMR** (126 MHz, $CDCl_3$): δ 162.9, 161.7, 151.3, 141.0, 138.7, 136.9, 130.7, 130.4, 129.9, 128.9, 128.7, 127.5, 125.5, 106.3, 58.6, 51.9, 21.2; **HRMS** (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $[C_{19}H_{18}NO_4]^+$ 324.1230, Found 324.1227.

Spectral data matched with the reported literature.[5]

8.0 UV-vis. spectra

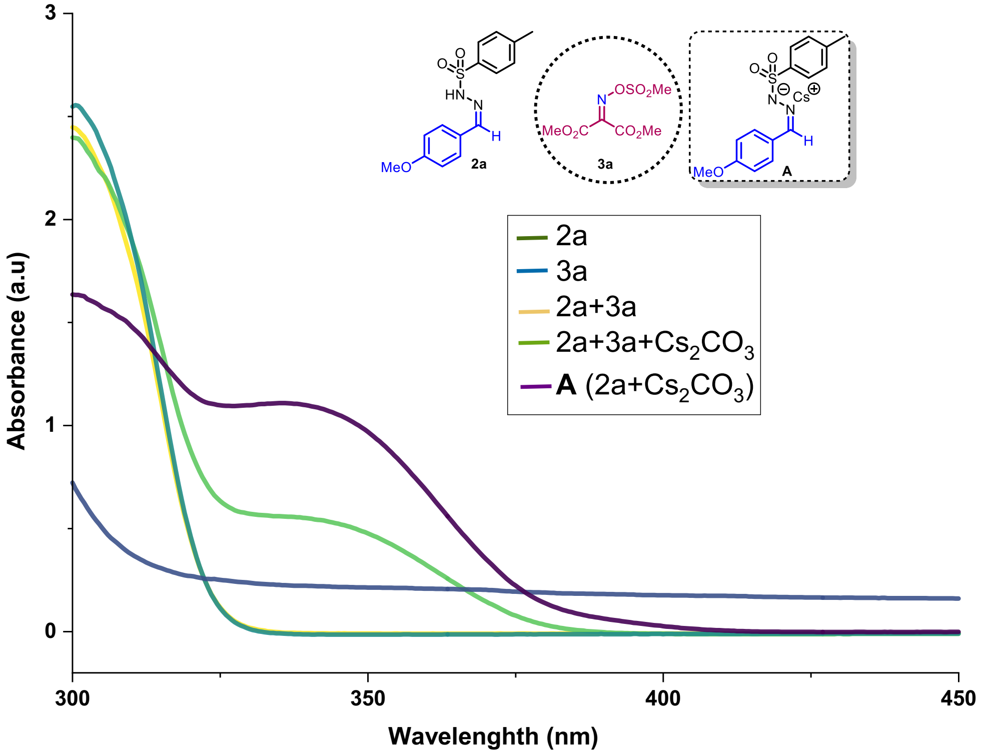
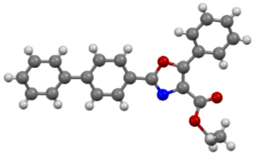


Figure S1: UV-Vis. spectrum of **2a** (0.1 M, dark green line), **3a** (0.1 M, blue line), **2a**+**3a** (0.1 M, yellow line), **2a**+**3a**+Cs_2CO_3 (0.1 M green line) and intermediate **A** (**2a** + Cs_2CO_3) (0.1 M, violet line) in MeCN.

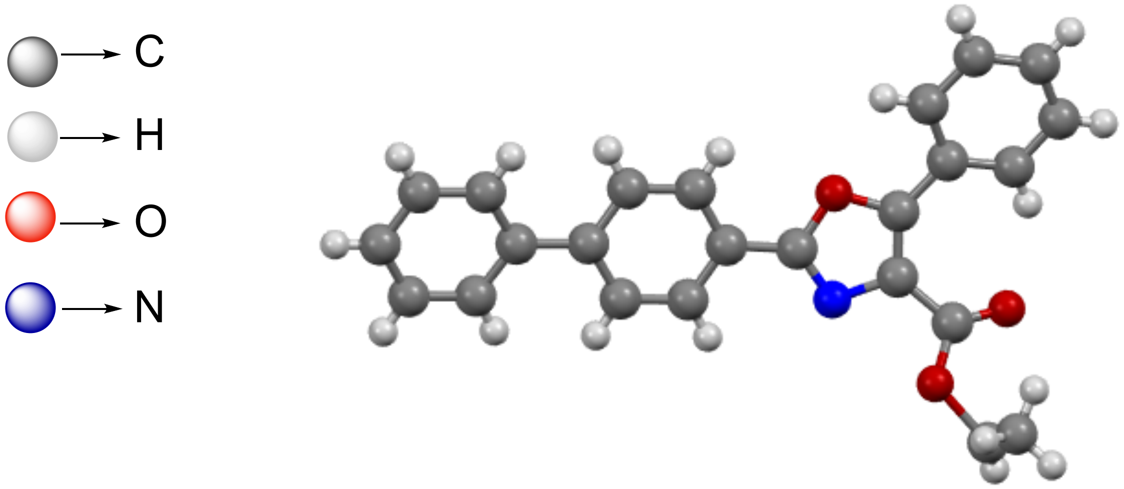
8.0 Single crystal XRD data.

Compound **4gg** was crystalized from 1: 4 mixtures of EtOAc: Hexane.

Data	**4gg**
Molecular Structure	
Formula	$C_{24}H_{19}NO_3$
Formula weight	369.42
Crystal system	Orthorhombic
Space group	$P\ 2_12_12_1$
a (Å)	4.9899(9)
b (Å)	11.217(2)
c (Å)	31.913(6)
α (°)	90.000
β (°)	90.000
γ (°)	90.000
Volume (Å^3)	1786.3(6)
Z	4
Crystal size, mm^3	0.1199× 0.1196 × 0.0814
Density (g/cm^3)	1.3735
λ (Å)	0.71073
Temp. (K)	298.00
Total reflns.	48644
Indepnt. reflns.	4632
Final R indices	$R_1 = 0.0746$,

$[I > 2\sigma(I)]$	$wR_2 = 0.1635$
R indices (all data)	$R_1 = 0.1054$, $wR_2 = 0.1828$
GOOF	1.034
CCDC	2532599

Crystal Structure of compound 4gg (Thermal Ellipsoid Contour Probability 50%)



10.0 References

1. a) Fulton, J. R.; Aggarwal, V. K.; Vicente, J. De. The Use of Tosylhydrazone Salts as a Safe Alternative for Handling Diazo Compounds and Their Applications in Organic Synthesis. *Eur. J. Org. Chem.* **2005**, *2005*, 1479–1492; b) Junaid, M.; Happy, S.; Yadagiri, D. Light-Induced Arylation (Alkylation) of *N*-Sulfonylhydrazone with Boronic Acids. *Chem. Commun.* **2024**, *60*, 2796–2799.

2. a) Kattamuri, P. V.; Yin, J.; Siriwongsup, S.; Kwon, D.-H.; Ess, D. H.; Li, Q.; Li, G.; Yousufuddin, M.; Richardson, P. F.; Sutton, S. C.; Kurti, L. Practical Singly and Doubly Electrophilic Aminating Agents: A New, More Sustainable Platform for Carbon-Nitrogen Bond-Formation. *J. Am. Chem. Soc.* **2017**, *139*, 11184–11196; b) Nicastri, M. C.; Lehnherr, D.; Lam, Y.-h.; DiRocco, D. A.; Rovis, T. Synthesis of Sterically Hindered Primary Amines by Concurrent Tandem Photoredox Catalysis. *J. Am. Chem. Soc.* **2020**, *142*, 987–998.

3. Connell, R. D.; Tebbe, M.; Gangloff, A. R.; Helquist, P.; Akermark, B. Rhodium-catalyzed heterocycloaddition route to 1,3-oxazoles as building blocks in natural products synthesis. *Tetrahedron* **1993**, *49,* 5445–5459.

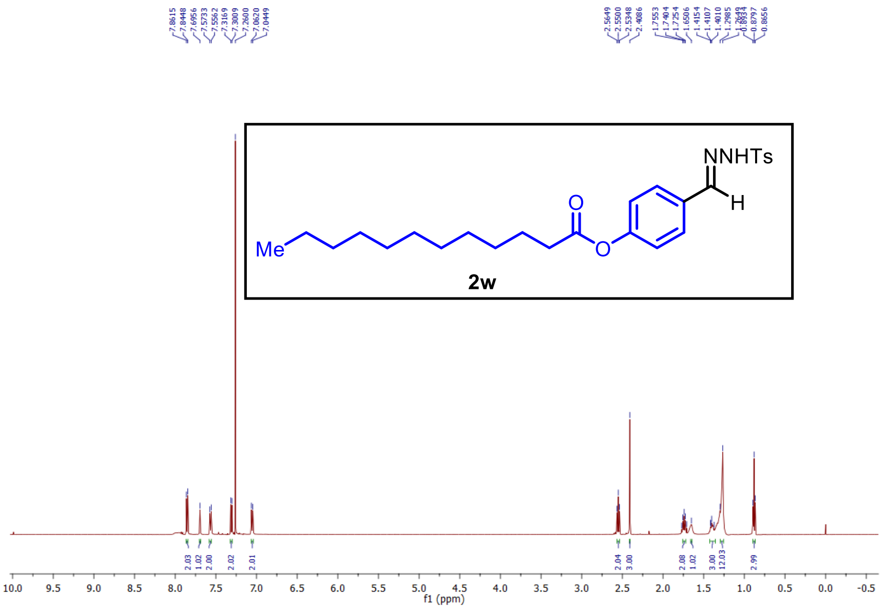
4. Saha, A.; Casali, E.; Ghosh, A.; Maiti, D. Modular Approach for Photoinduced Cycloaddition Enabling the Synthesis of Diverse Bioactive Oxazoles. *Org. Lett.* **2025**, *27*, 2811–2814.

5. Saha, A.; Bianchi, M.; Casali, E.; Maiti, D. Scalable Photoinduced Cycloaddition for the Synthesis of Biorelevant Oxazoles. *Org. Lett.* 2025, *27*, 6122–6126.

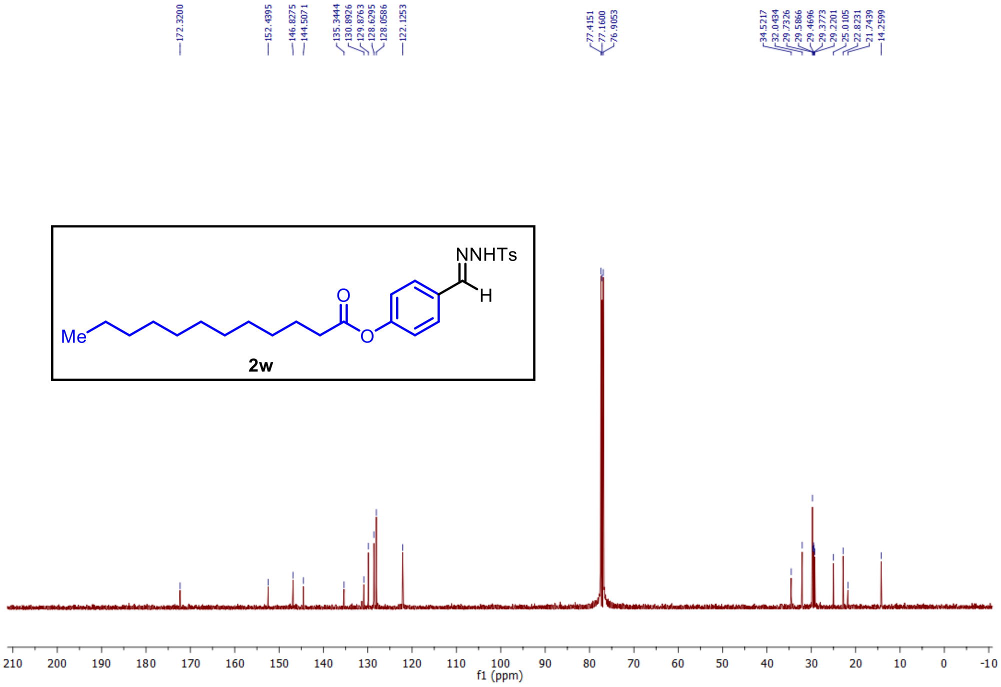
11.0 Spectral data

4-(Tosylhydrazineylidene)methyl-phenyl dodecanoate (**2w**)

^{1}H NMR (500 MHz, CDCl$_3$, 24 °C)

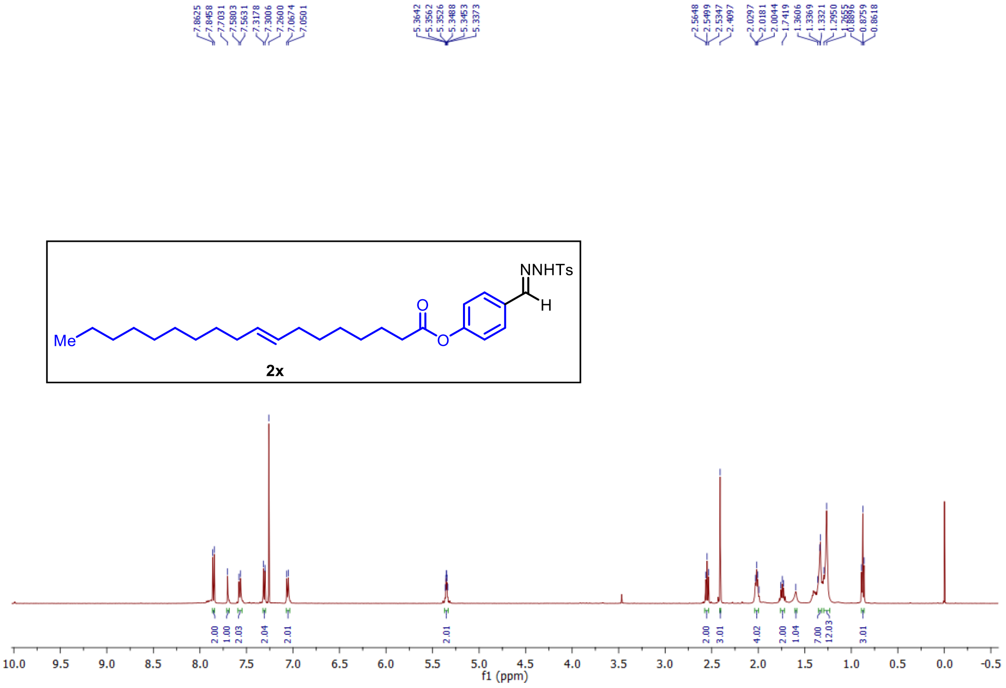


^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 24 °C)

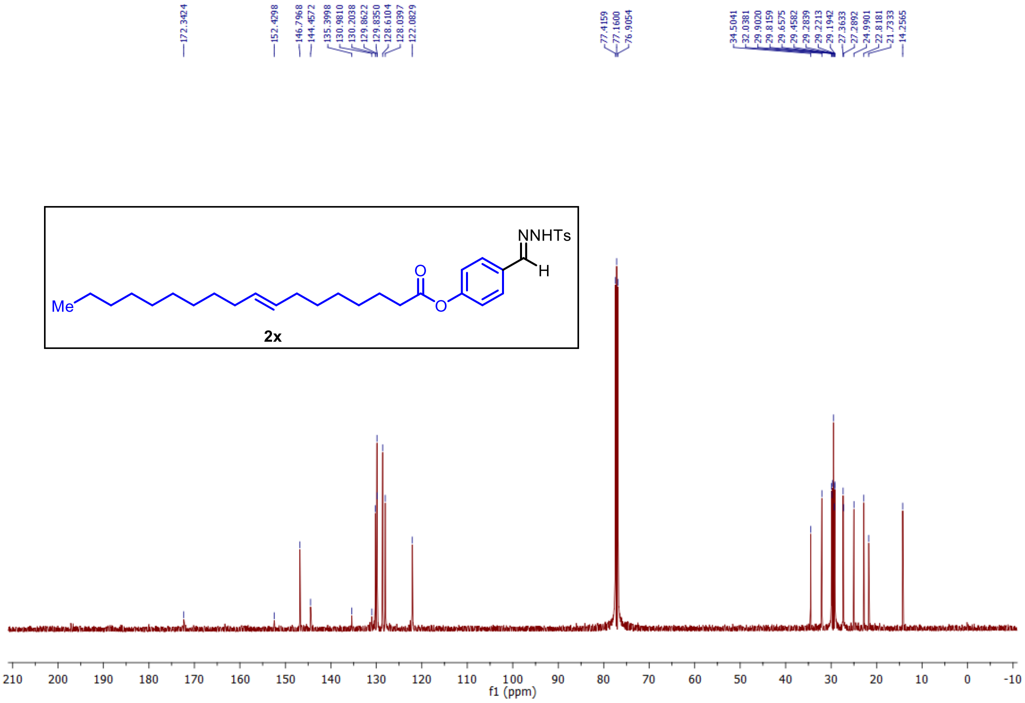


4-(Tosylhydrazineylidene) methyl-phenyl-octadec-9-enoate (**2x**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

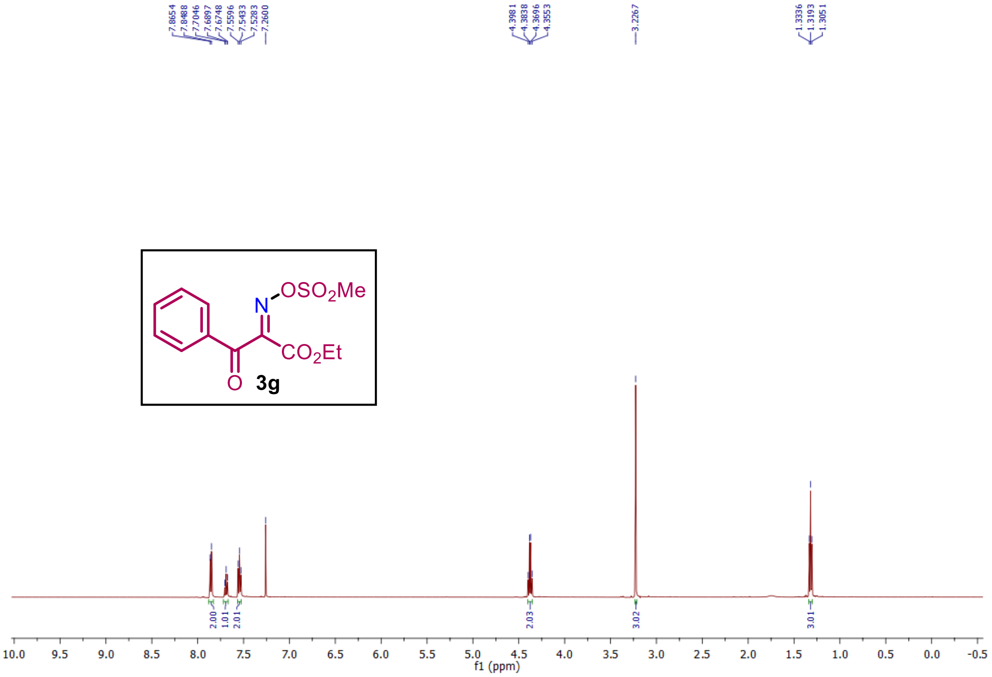


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

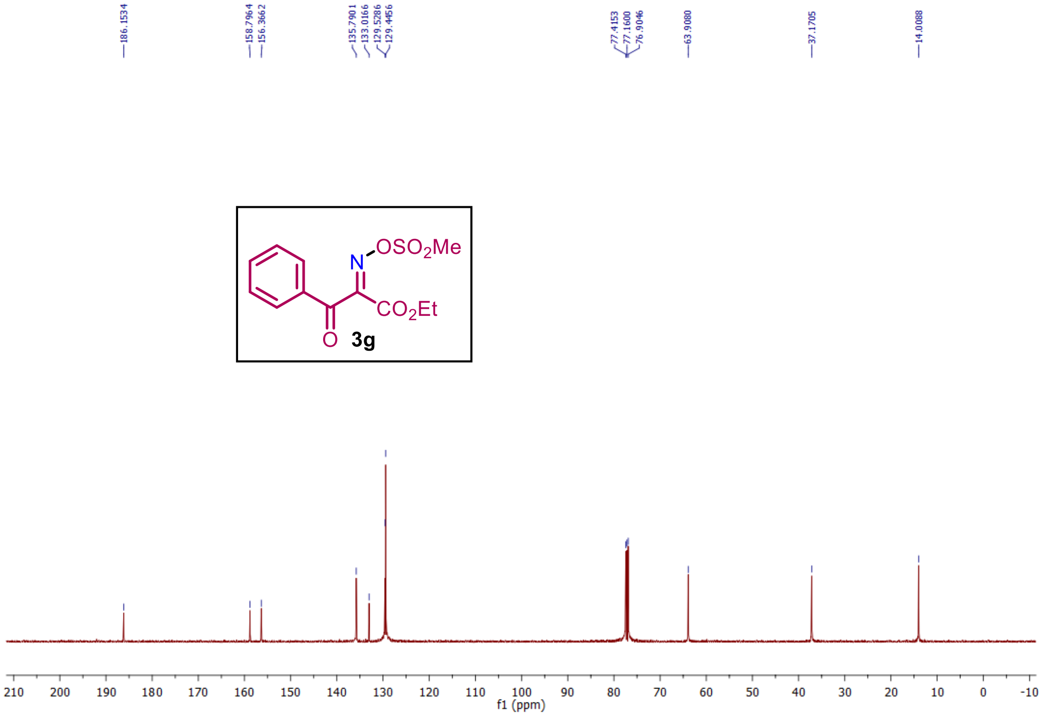


Ethyl-2-(methylsulfonyl-oxy) imino-3-oxo-3-phenylpropanoate (**3g**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

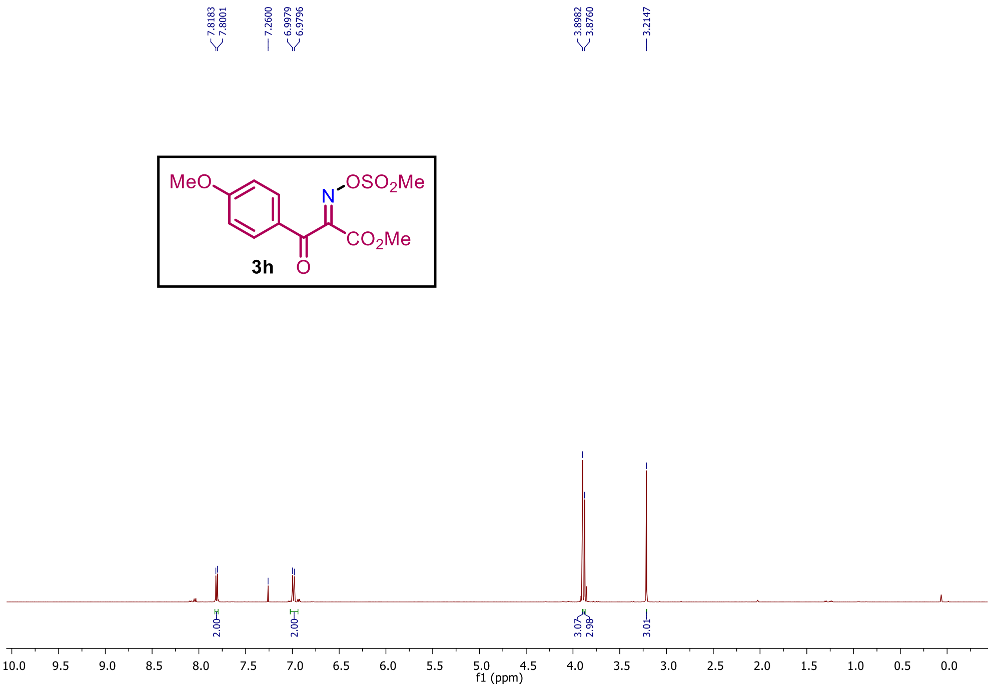


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

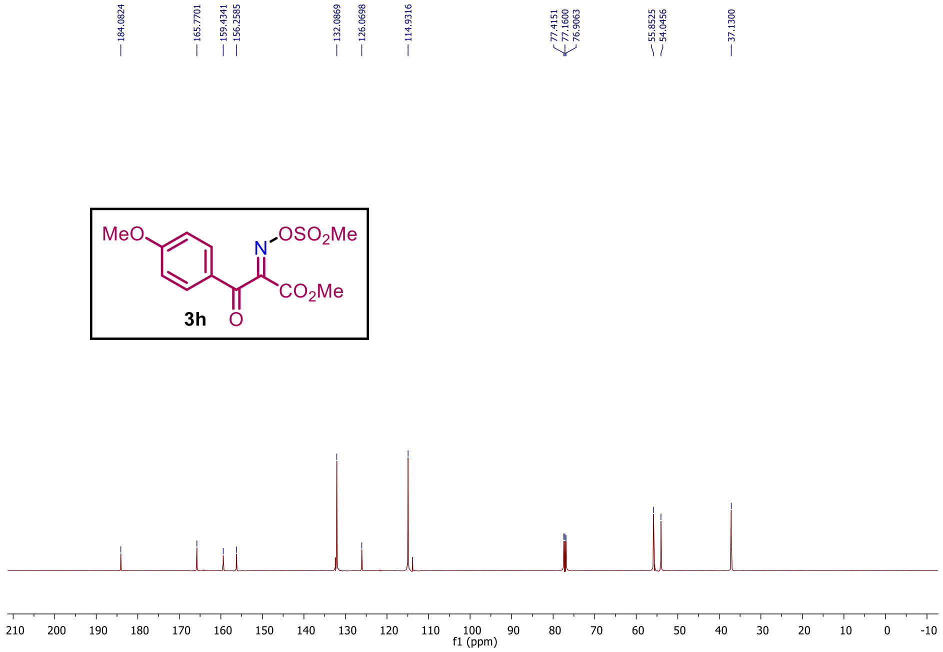


Methyl-3-(4-methoxyphenyl)-2-methylsulfonyloxy) imino-3-oxopropanoate (**3h**)

^{1}H NMR (500 MHz, CDCl$_3$, 24 °C)

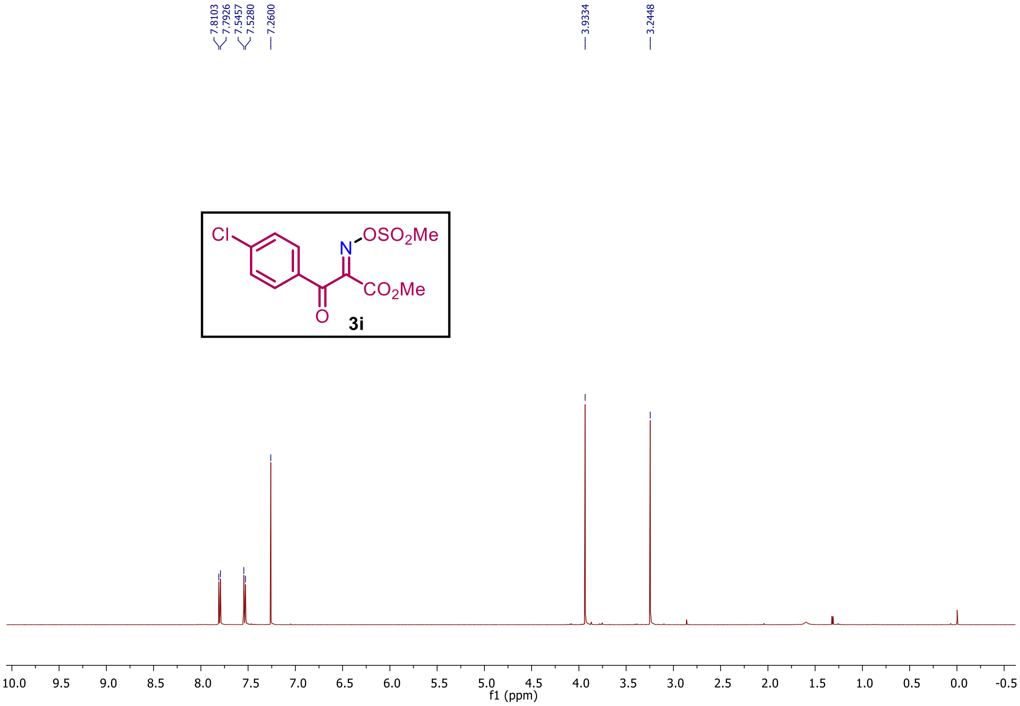


^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 24 °C)

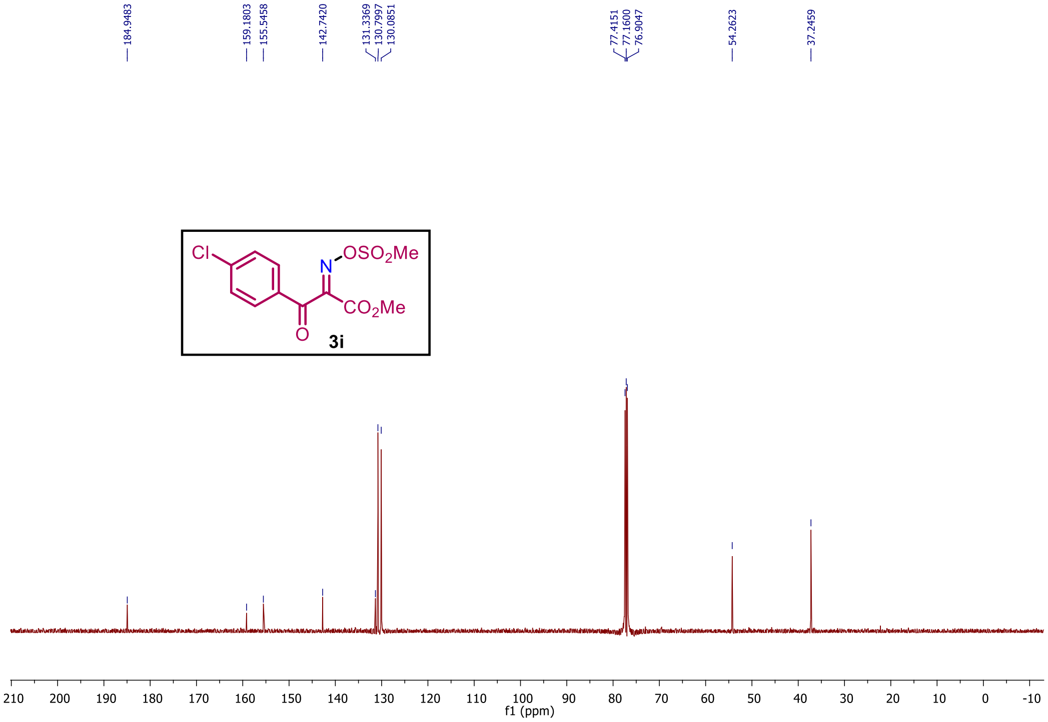


Methyl-3-(4-chlorophenyl)-2-methylsulfonyloxy) imino-3-oxopropanoate (**3i**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

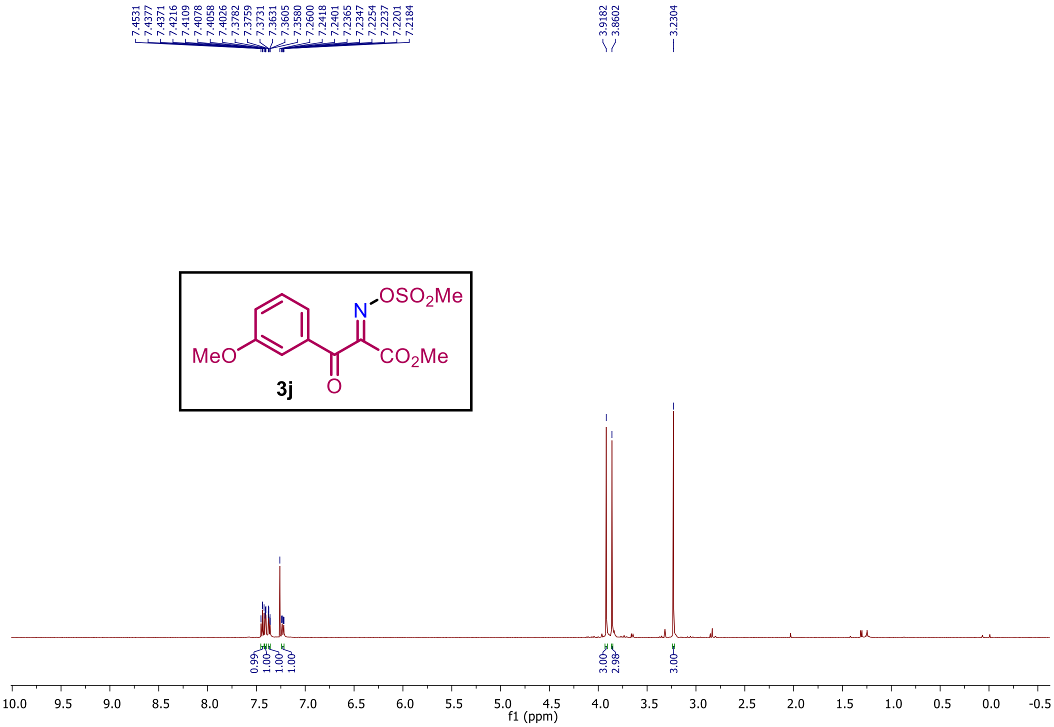


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

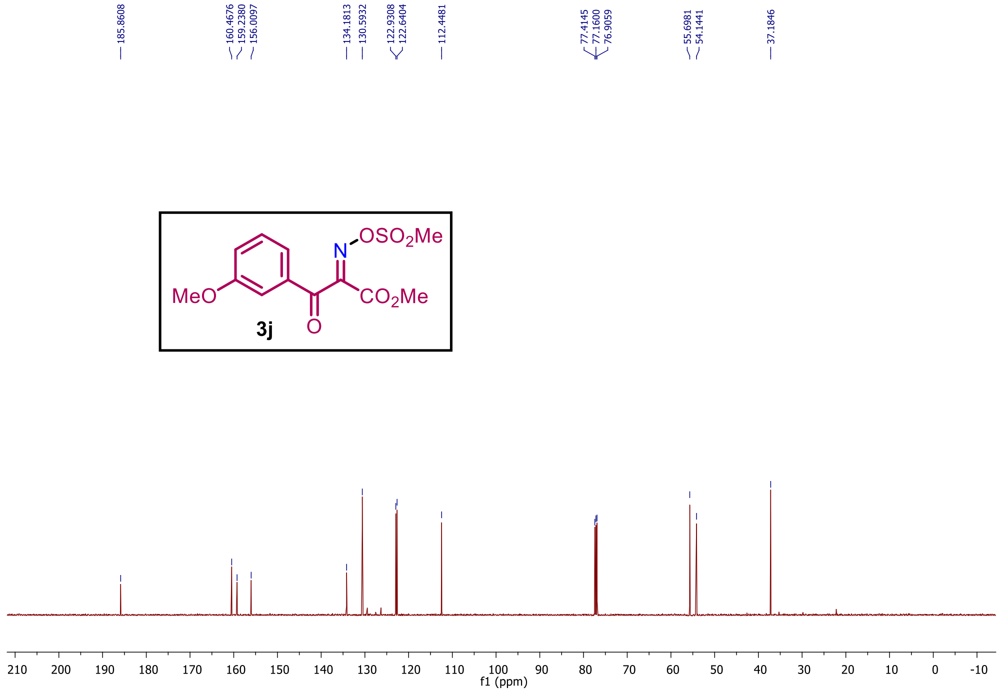


Methyl-3-(3-methoxyphenyl)-2-methylsulfonyloxy) imino-3-oxopropanoate (**3j**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

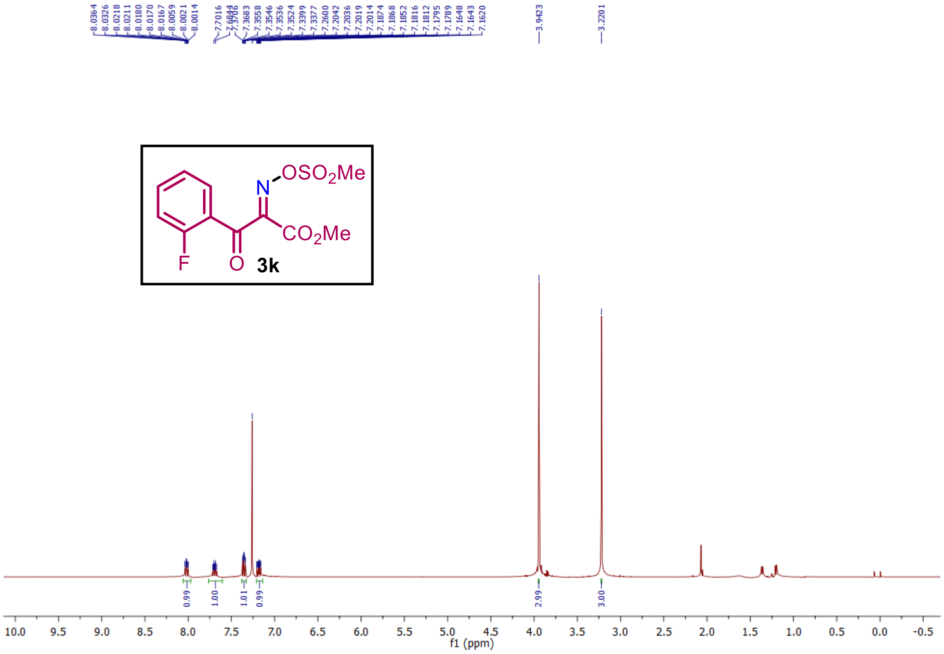


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$, 24 °C)

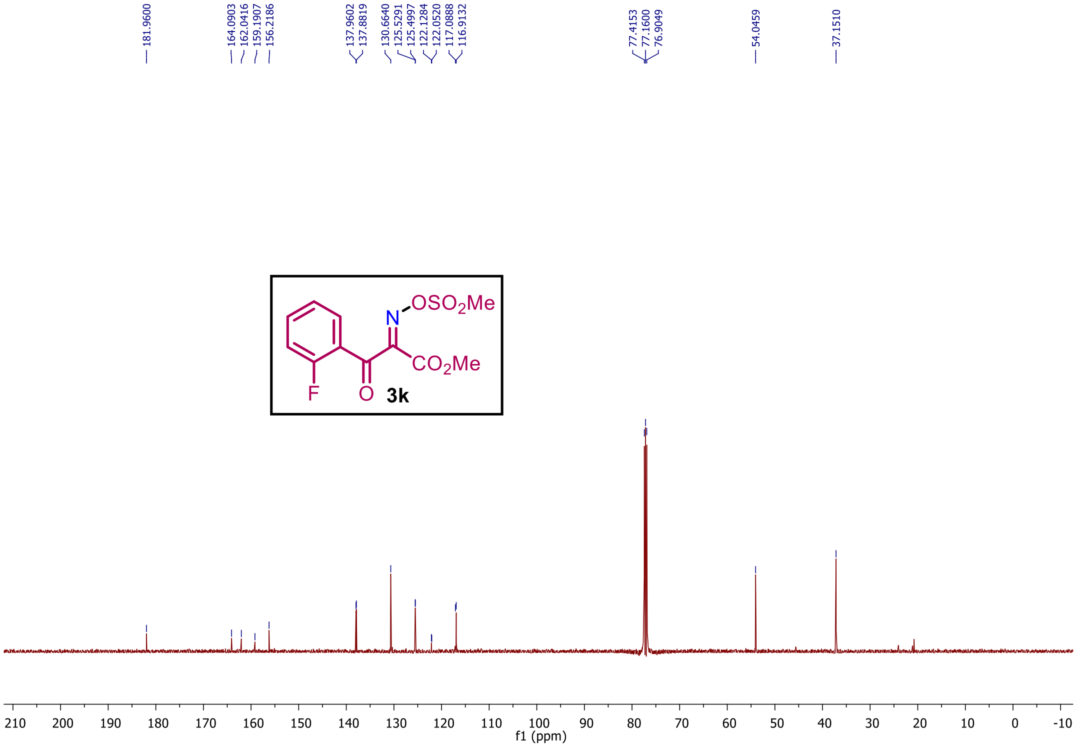


Methyl-3-(2-fluorophenyl)-2-methylsulfonyloxy) imino-3-oxopropanoate (**3k**)

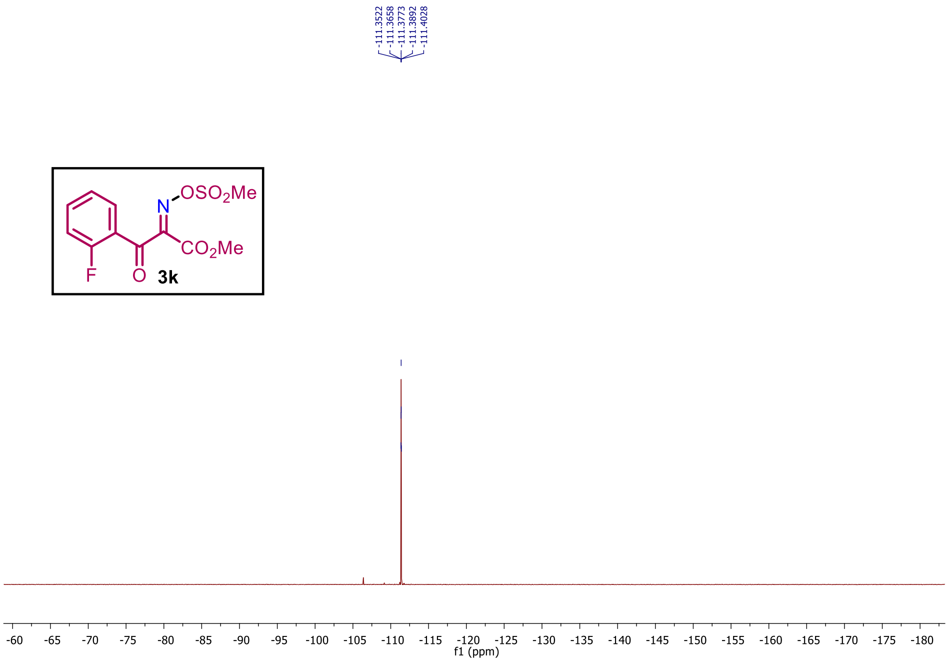
^{1}H NMR (500 MHz, CDCl$_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 24 °C)

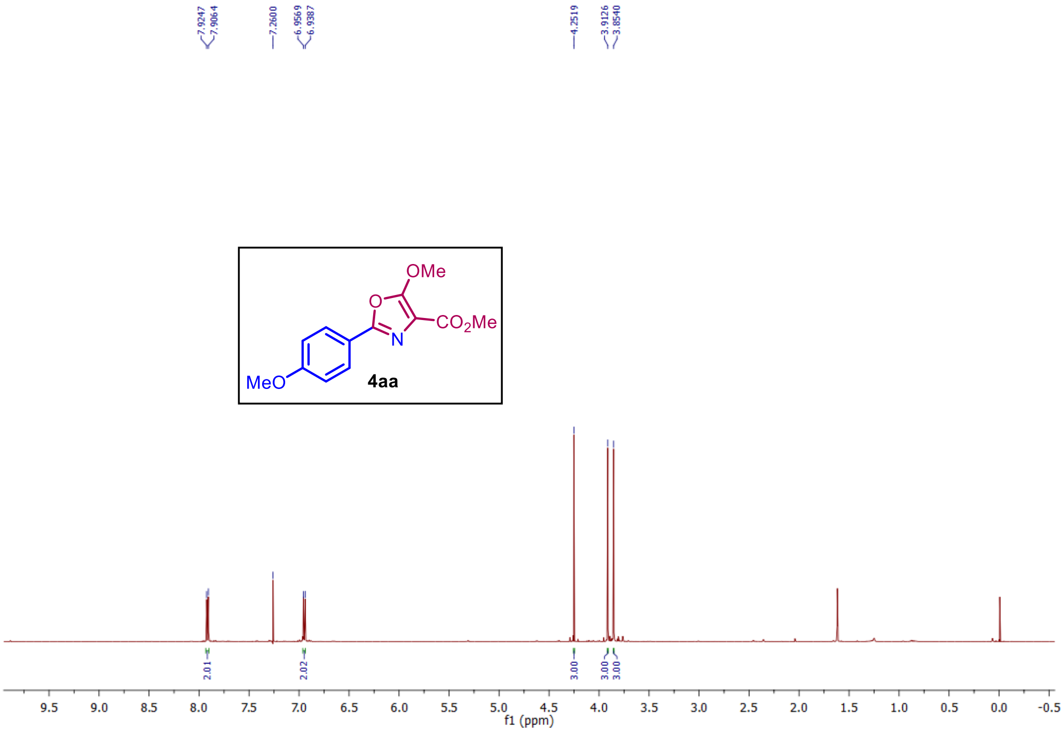


^{19}F NMR (471 MHz, CDCl$_3$, 24 °C)

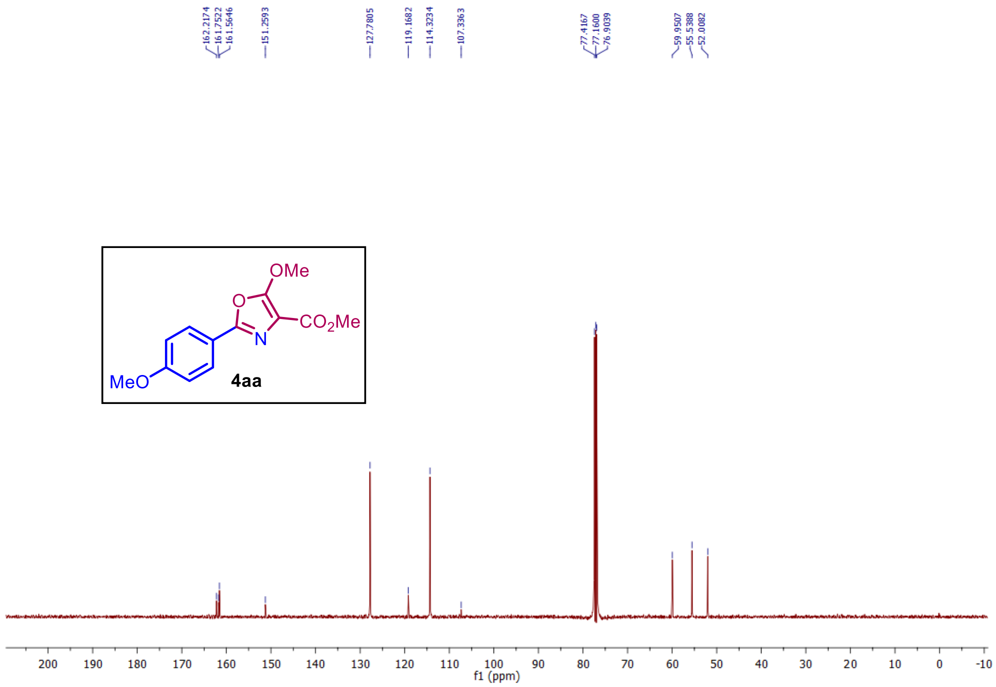


Methyl 5-methoxy-2-(4-methoxyphenyl)oxazole-4-carboxylate (**4aa**)

^{1}H NMR (500 MHz, CDCl$_3$, 24 °C)

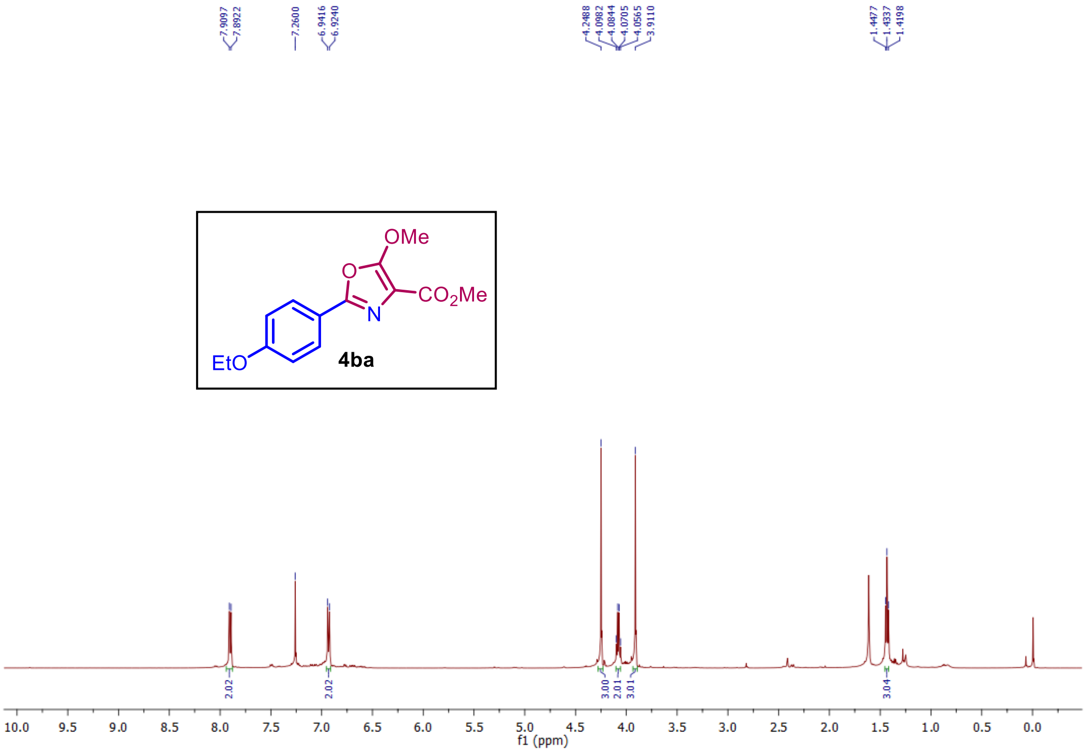


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

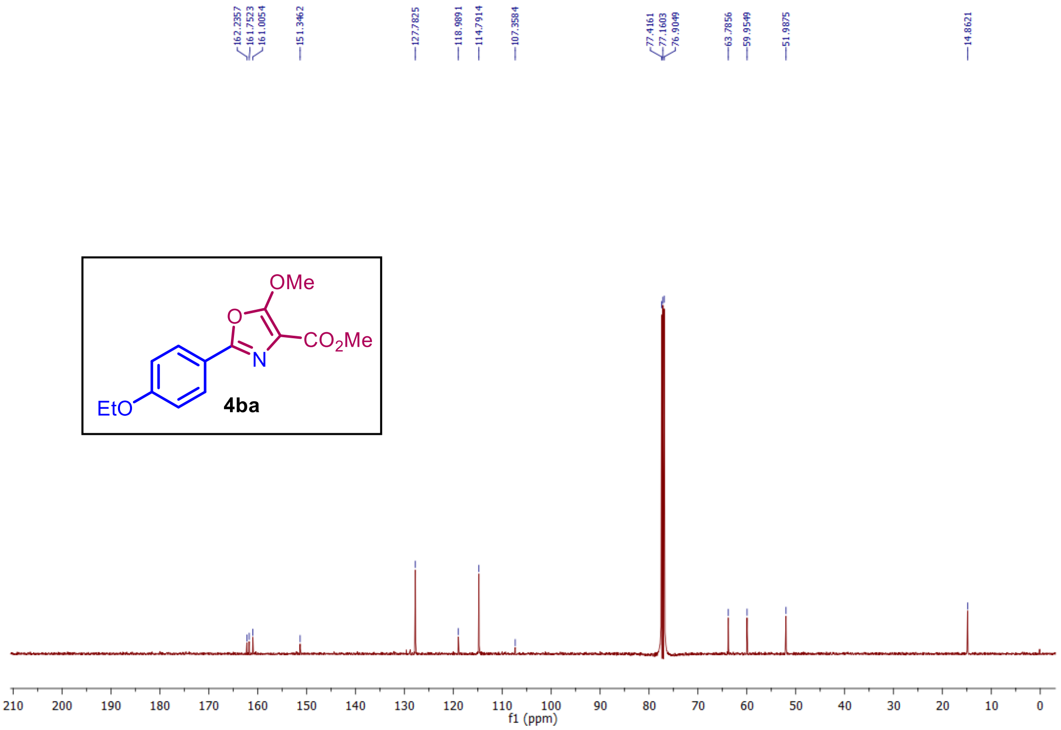


Methyl 5-methoxy-2-(4-ethoxyphenyl)oxazole-4-carboxylate (**4ba**)

^1H NMR (500 MHz, $CDCl_3$, 24 °C)

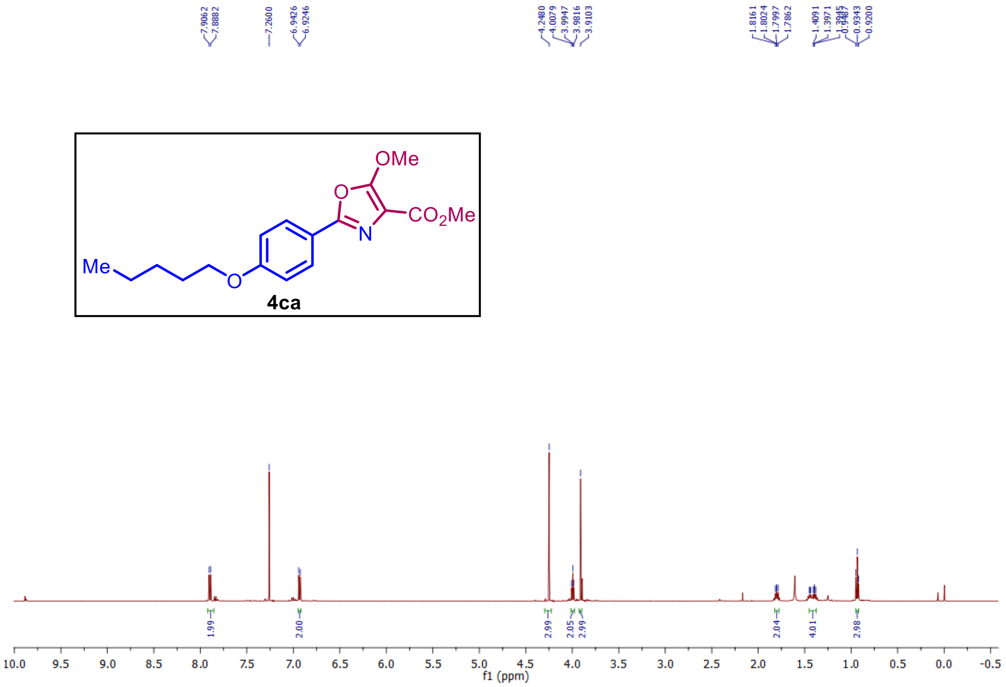


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

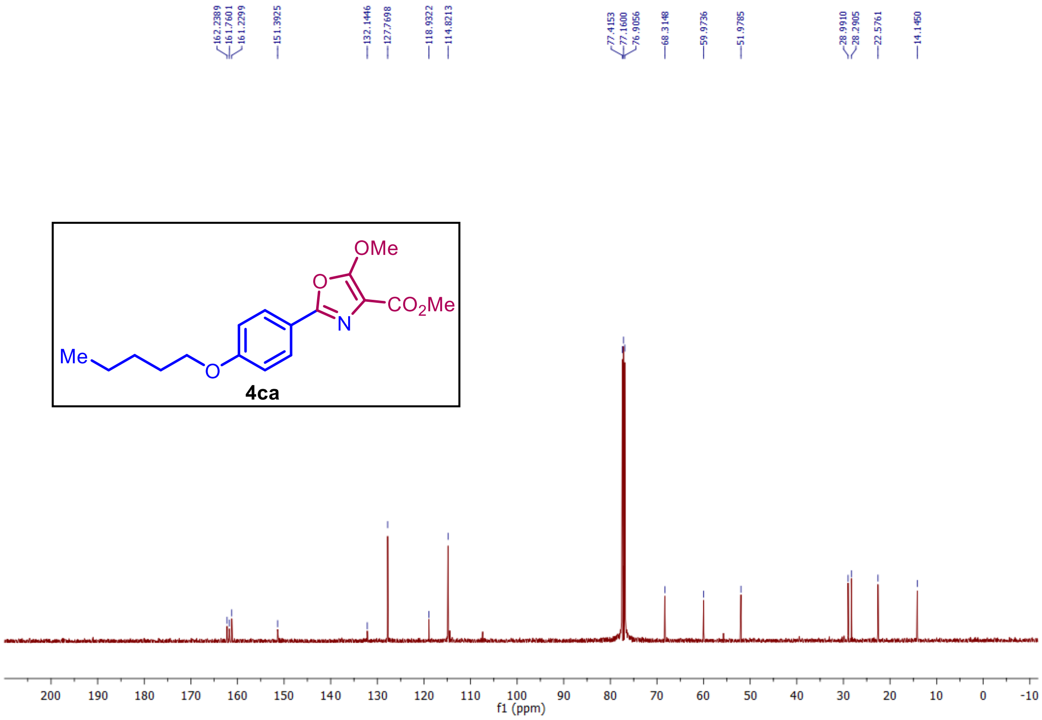


Methyl 5-methoxy-2-(4-pentyloxyphenyl)oxazole-4-carboxylate (**4ca**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

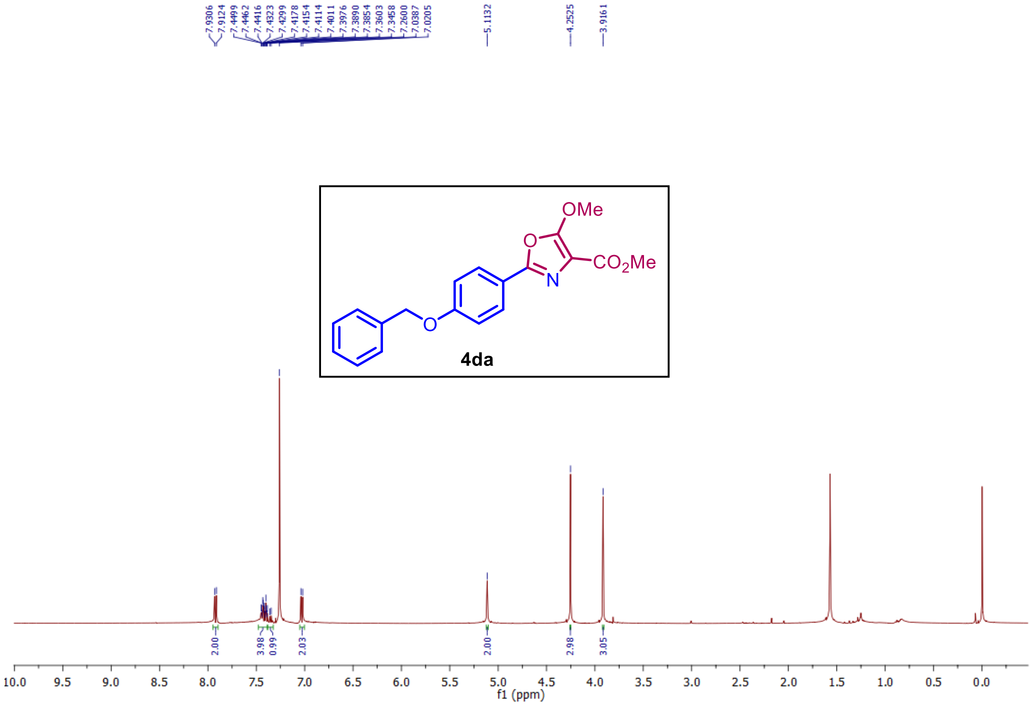


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

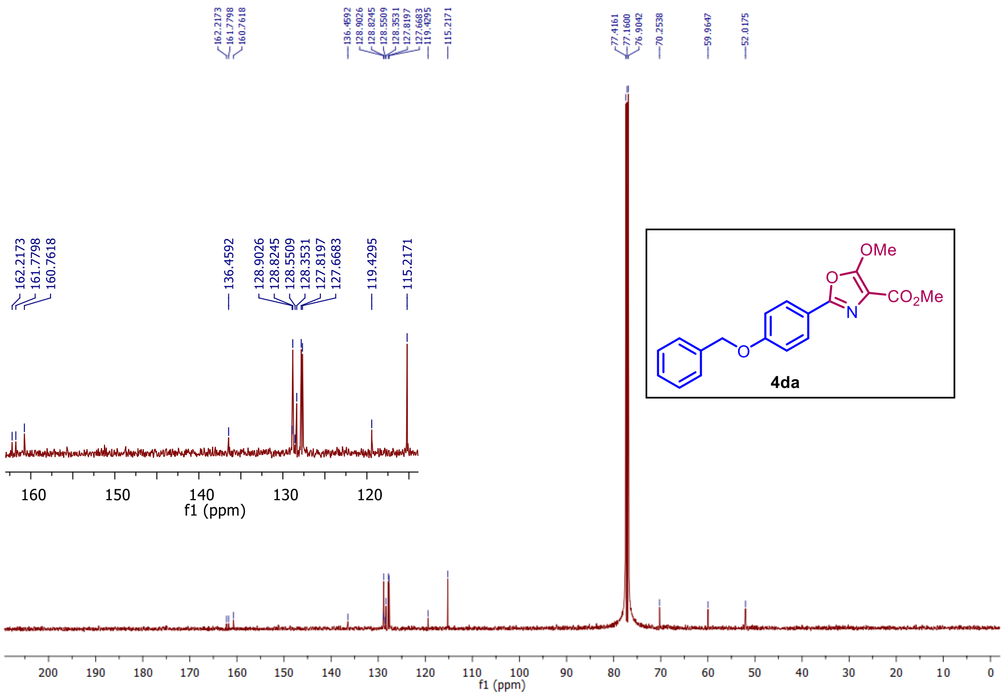


Methyl 2-(4-(benzyloxy)phenyl)-5-methoxyoxazole-4-carboxylate (**4da**)

^1H NMR (500 MHz, $CDCl_3$, 24 °C)

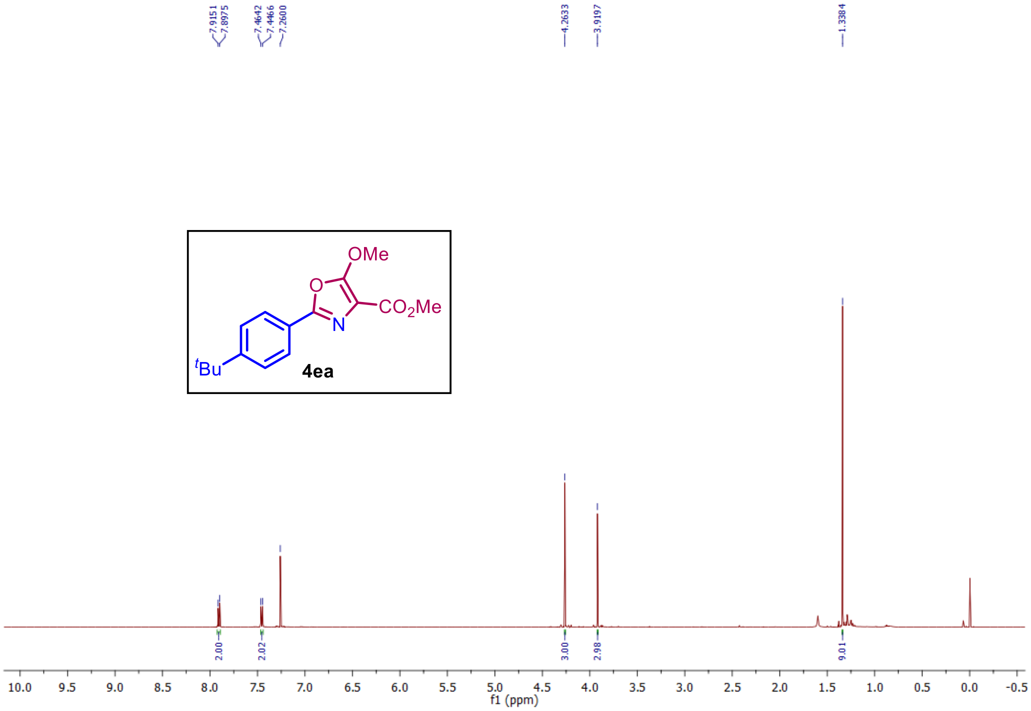


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

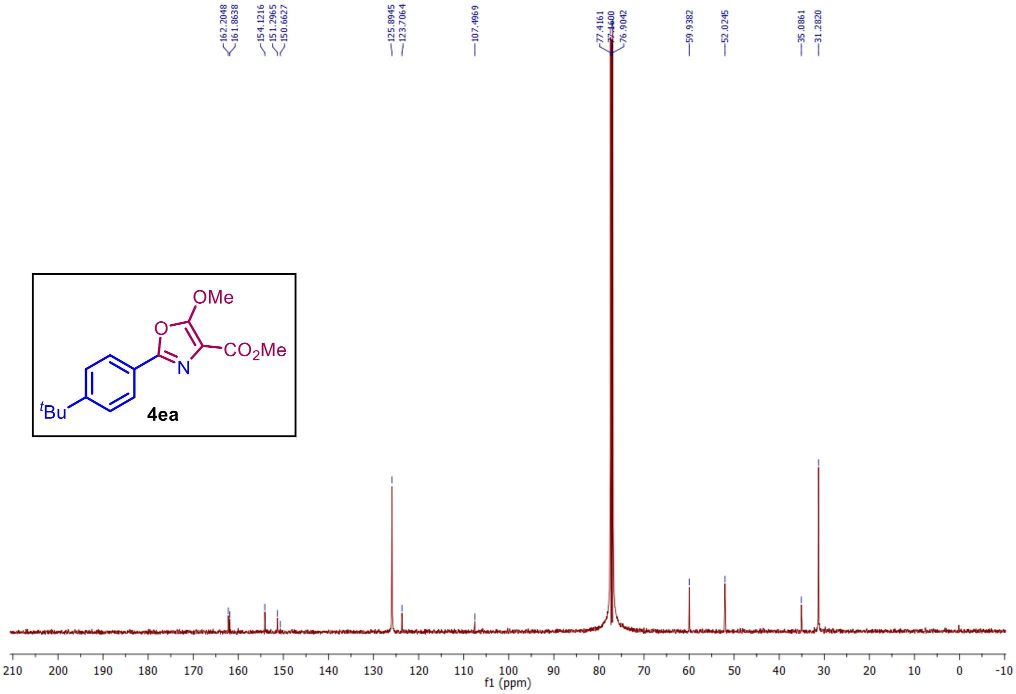


Methyl 2-(4-*tert.*butyl-phenyl)-5-methoxyoxazole-4-carboxylate (**4ea**)

^1H NMR (500 MHz, $CDCl_3$, 24 °C)

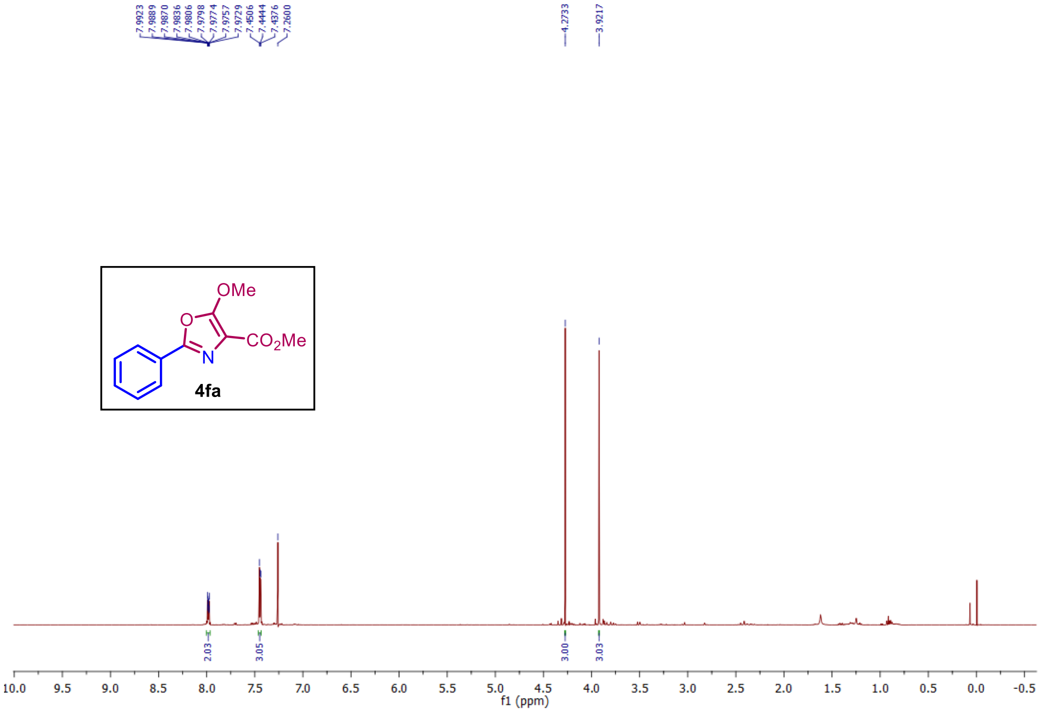


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

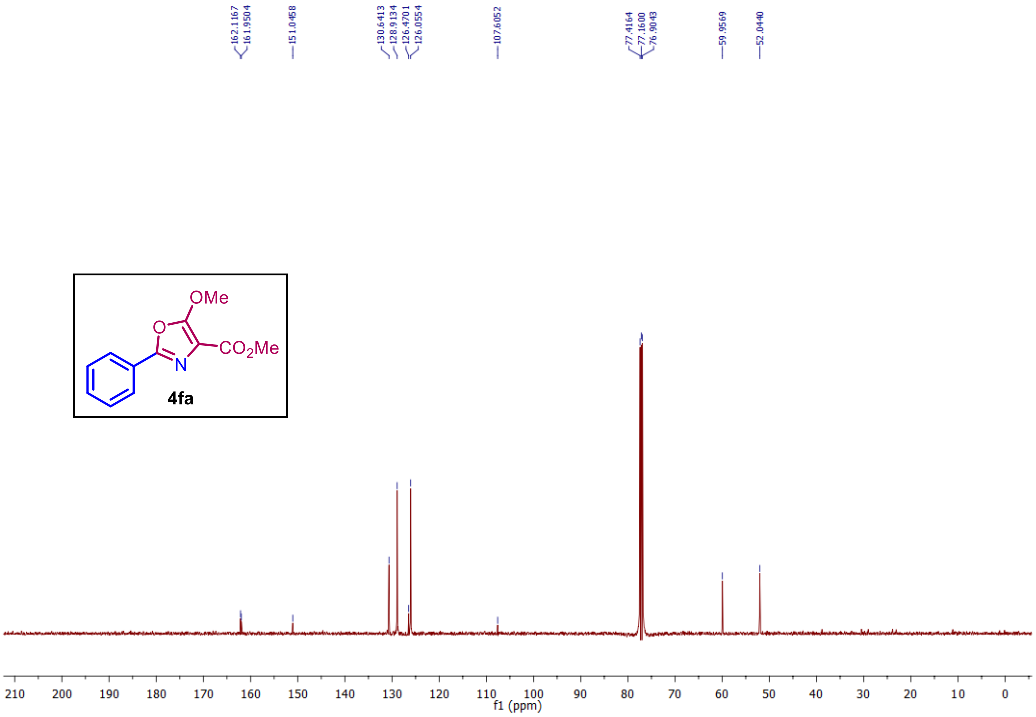


Methyl 5-methoxy-2-phenyloxazole-4-carboxylate (**4fa**)

^1H NMR (500 MHz, $CDCl_3$, 24 °C)

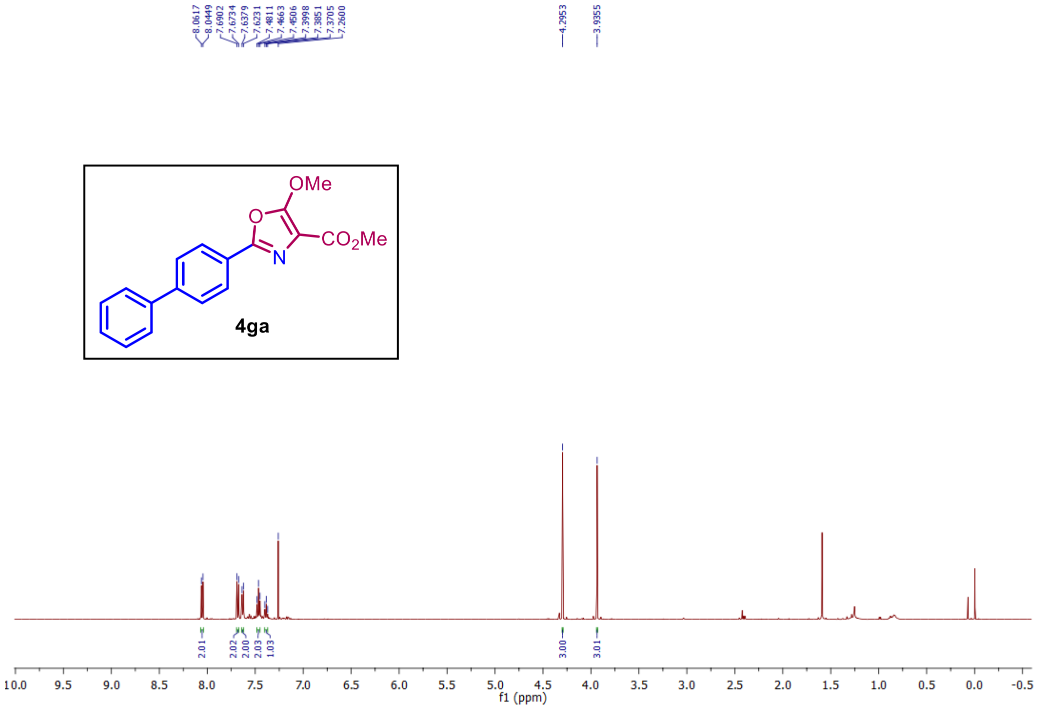


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

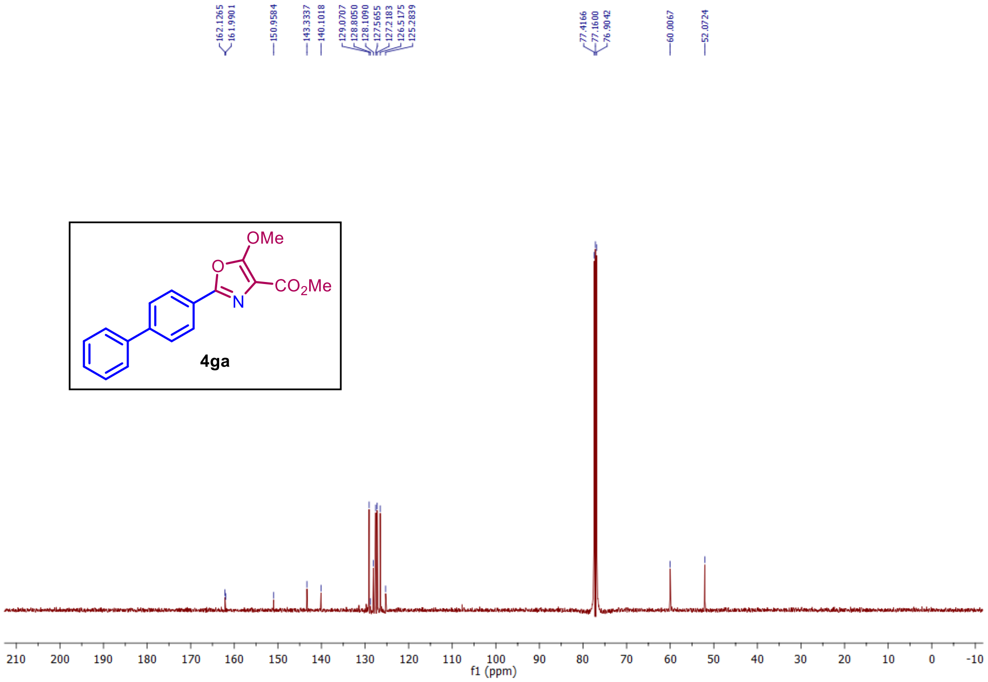


Methyl 2-([1,1'-biphenyl]-4-yl)-5-methoxyoxazole-4-carboxylate (**4ga**)

^1H NMR (500 MHz, $CDCl_3$, 24 °C)

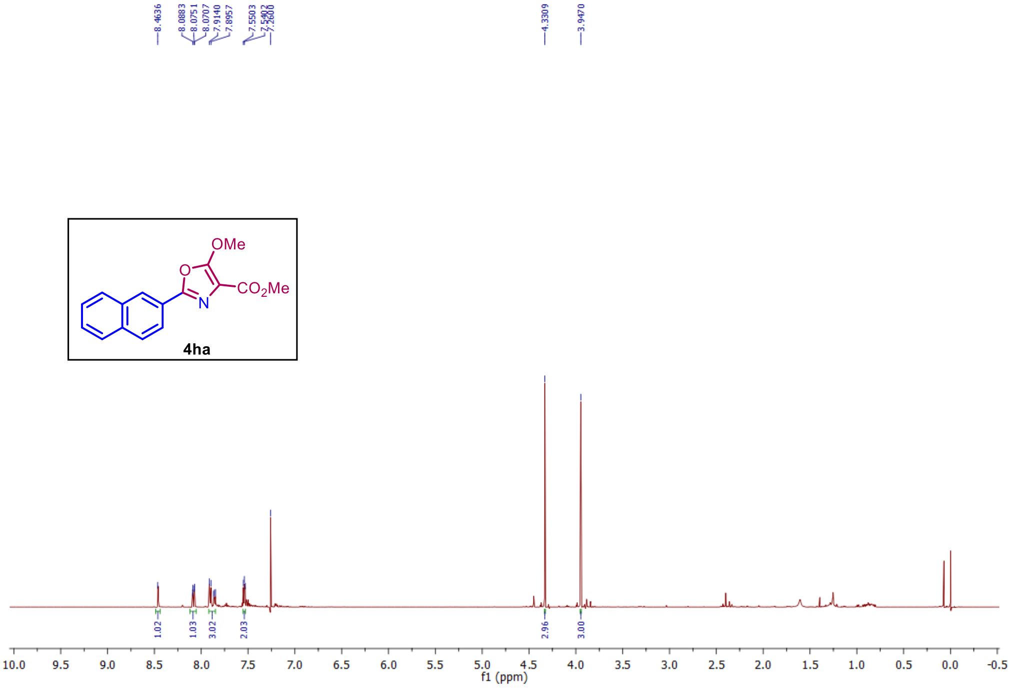


$^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$, 24 °C)

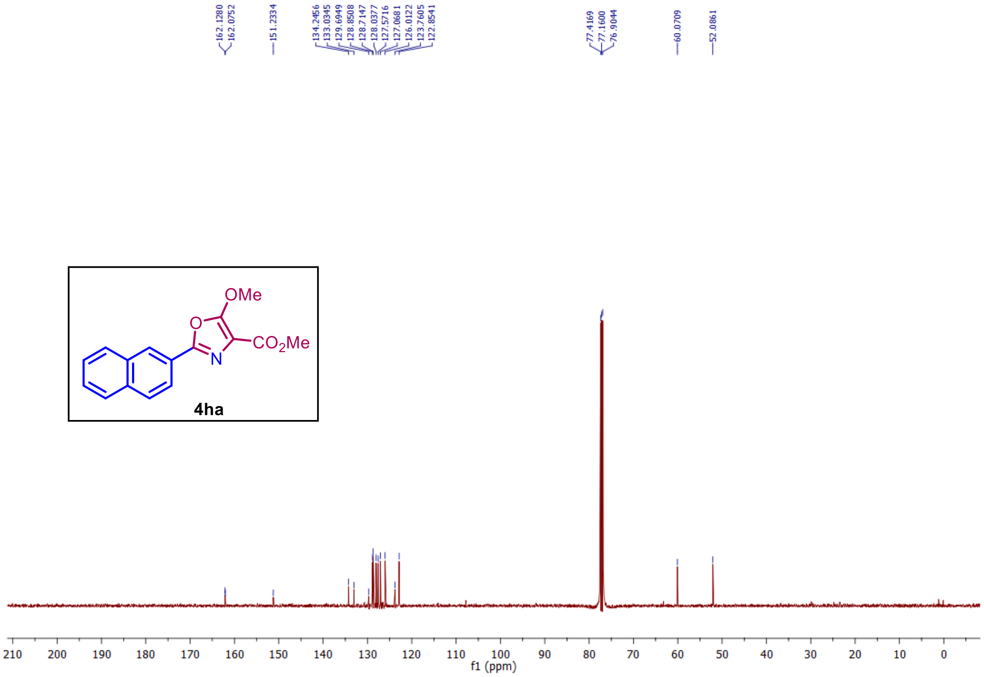


Methyl 5-methoxy-2-(naphthalen-2-yl)oxazole-4-carboxylate (**4ha**)

^1H NMR (500 MHz, CDCl$_3$, 24 °C)

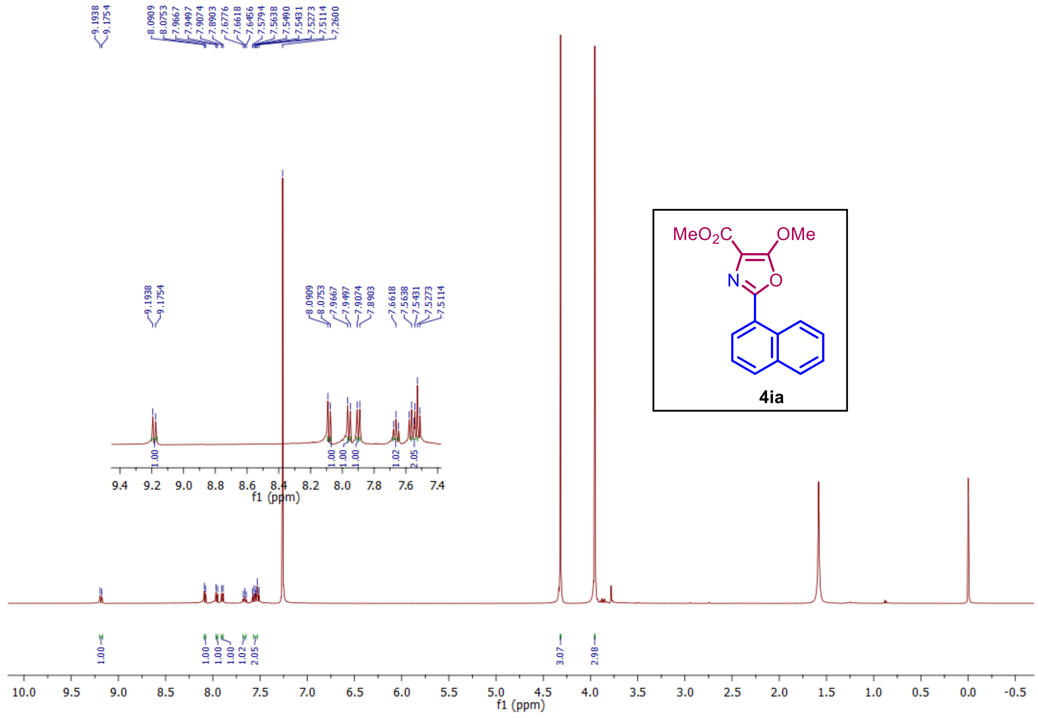


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

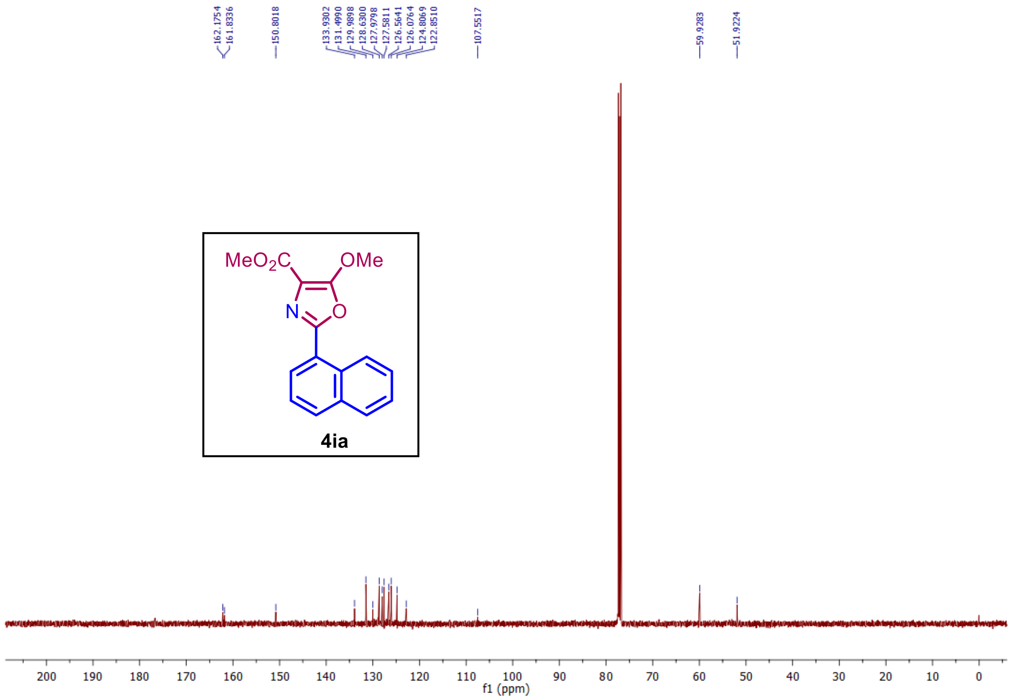


Methyl 5-methoxy-2-(naphthalen-1-yl)oxazole-4-carboxylate (**4ia**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

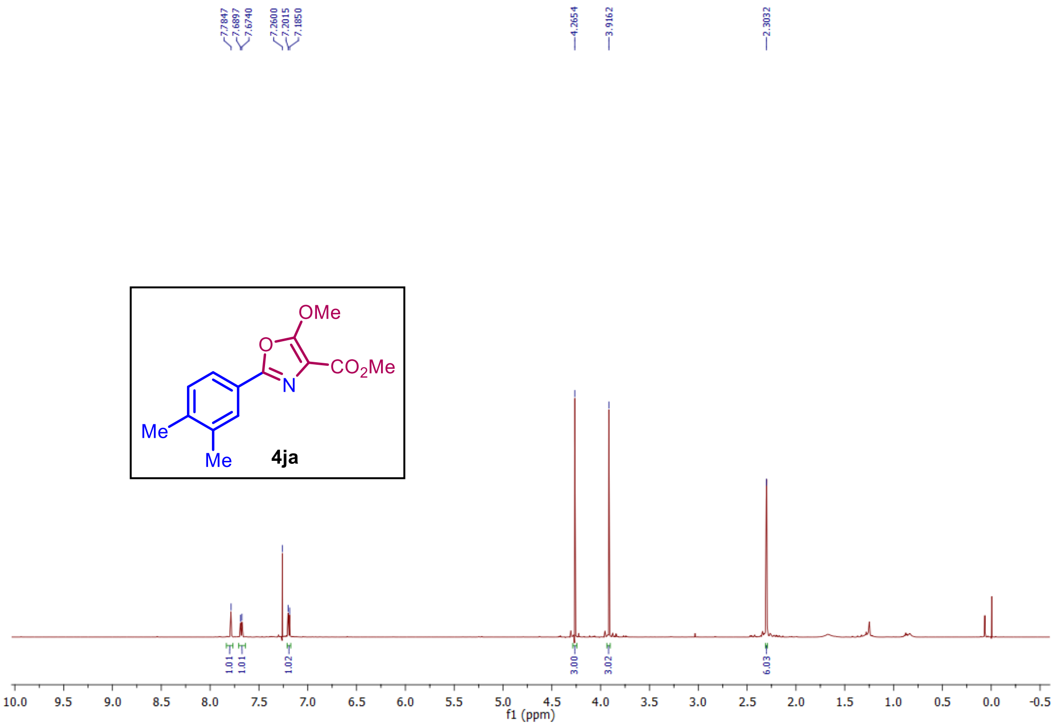


^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 24 °)

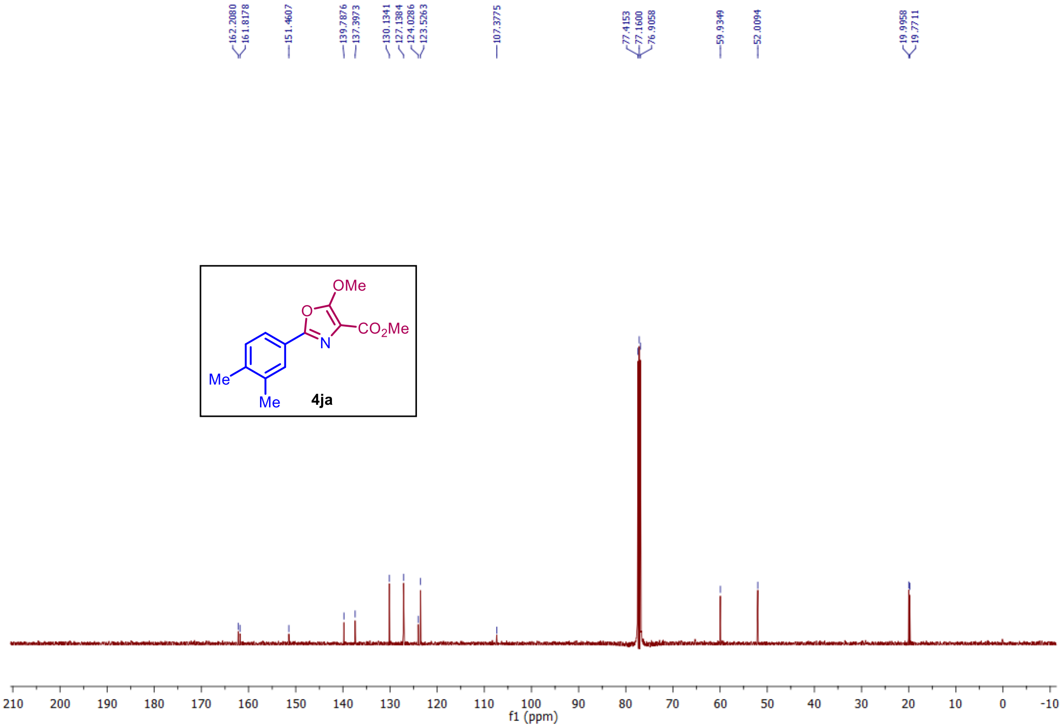


Methyl 2-(3,4-dimethylphenyl)-5-methoxyoxazole-4-carboxylate (**4ja**)

^{1}H NMR (500 MHz, CDCl$_3$, 24 °C)

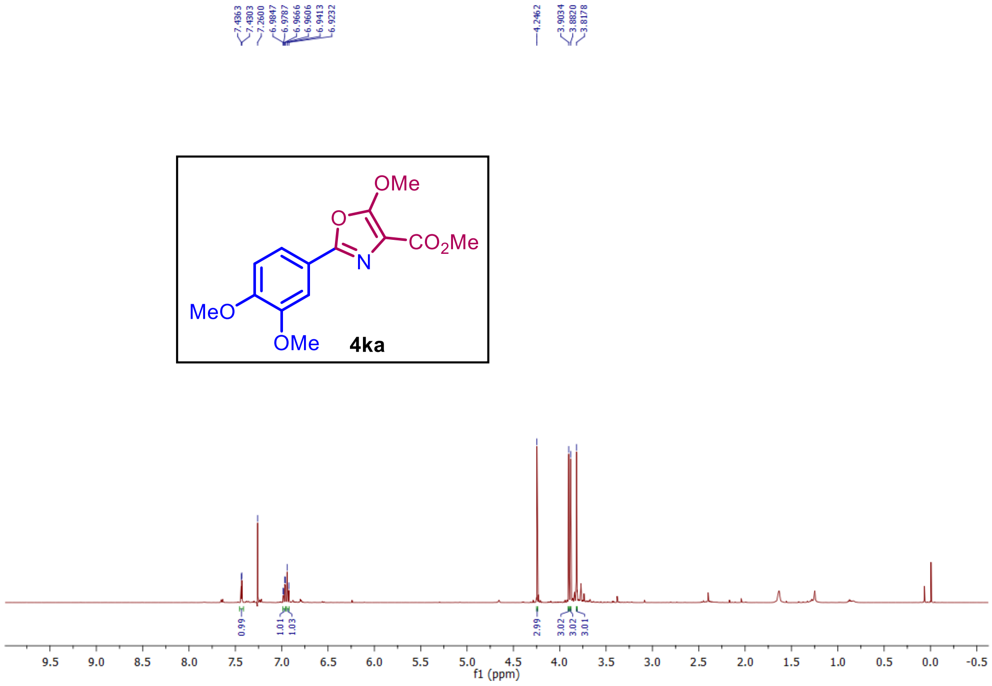


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

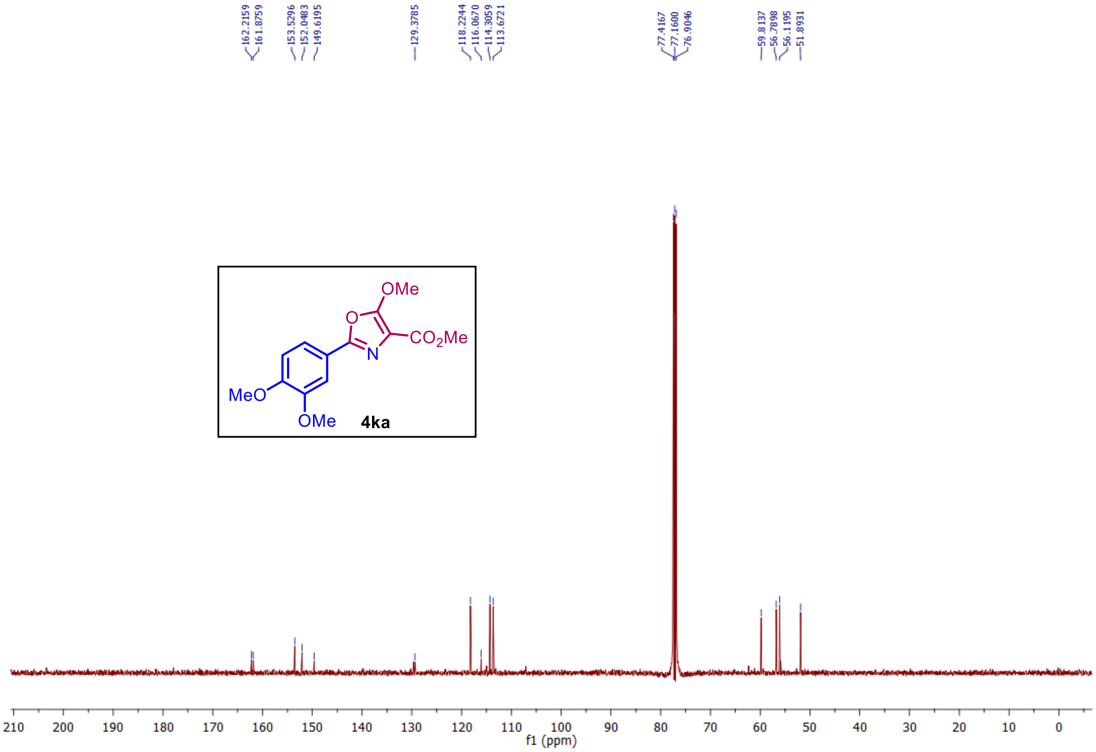


Methyl 2-(3,4-dimethoxyphenyl)-5-methoxyoxazole-4-carboxylate (**4ka**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

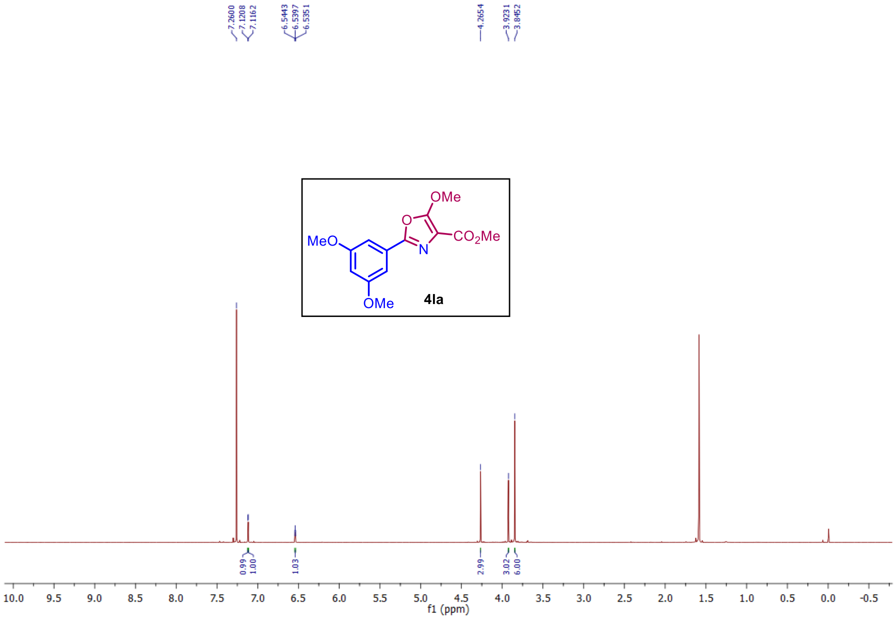


$^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$, 24 °C)

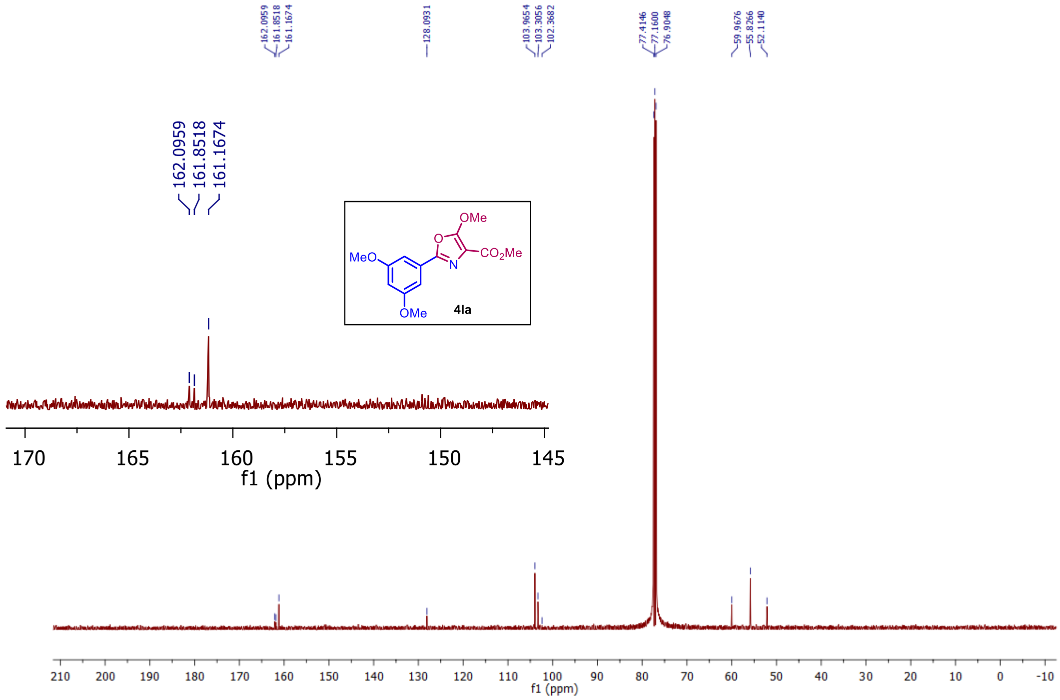


Methyl 2-(3,5-dimethoxyphenyl)-5-methoxyoxazole-4-carboxylate **(4la)**

^1H NMR (500 MHz, CDCl$_3$, 24 °C)

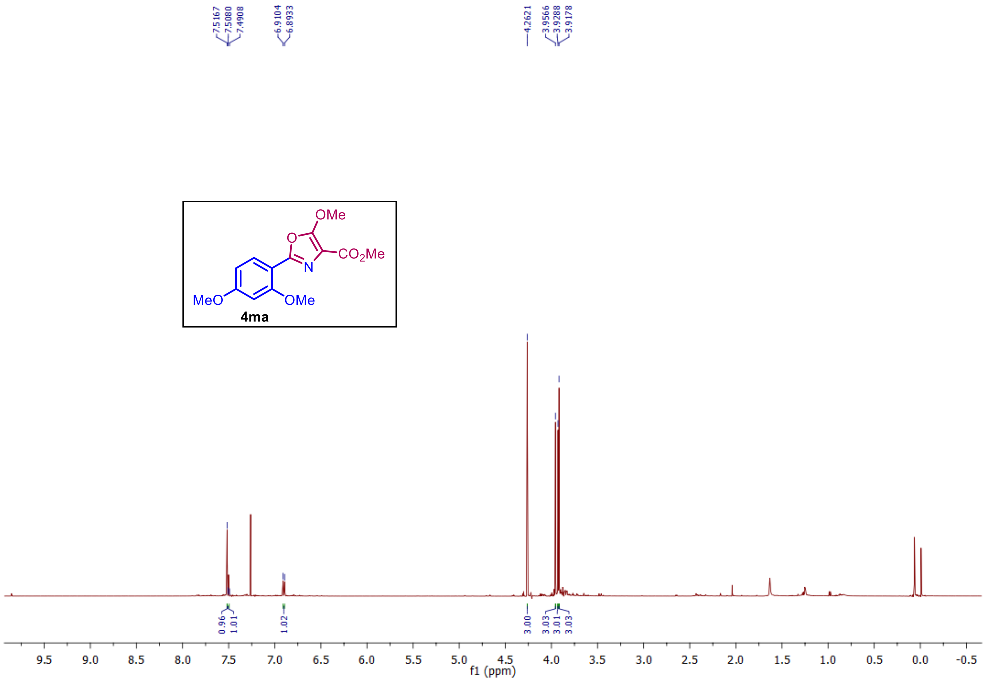


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

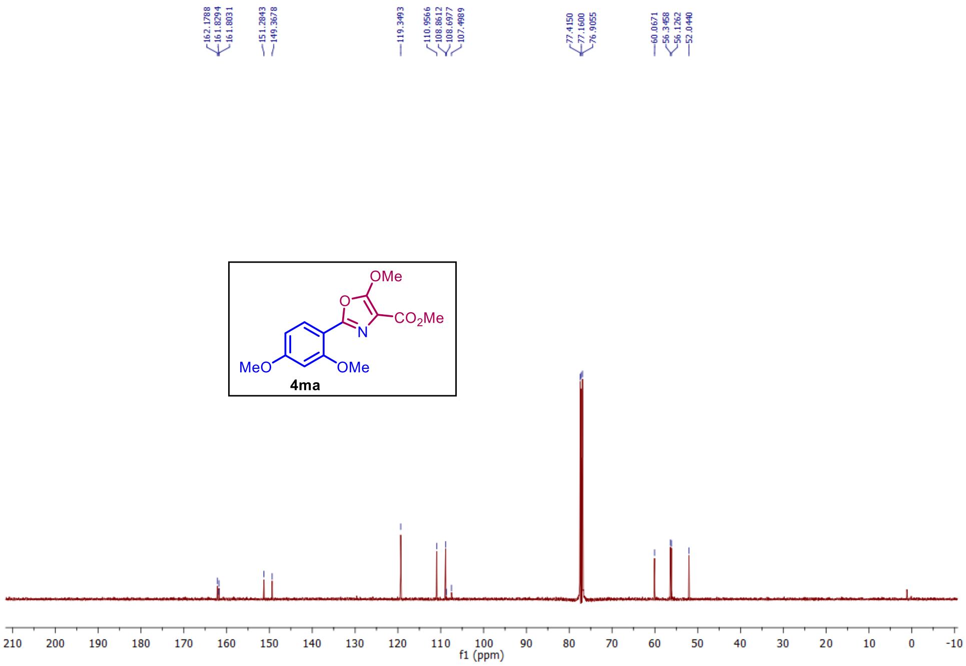


Methyl 2-(2,4-dimethoxyphenyl)-5-methoxyoxazole-4-carboxylate (**4ma**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

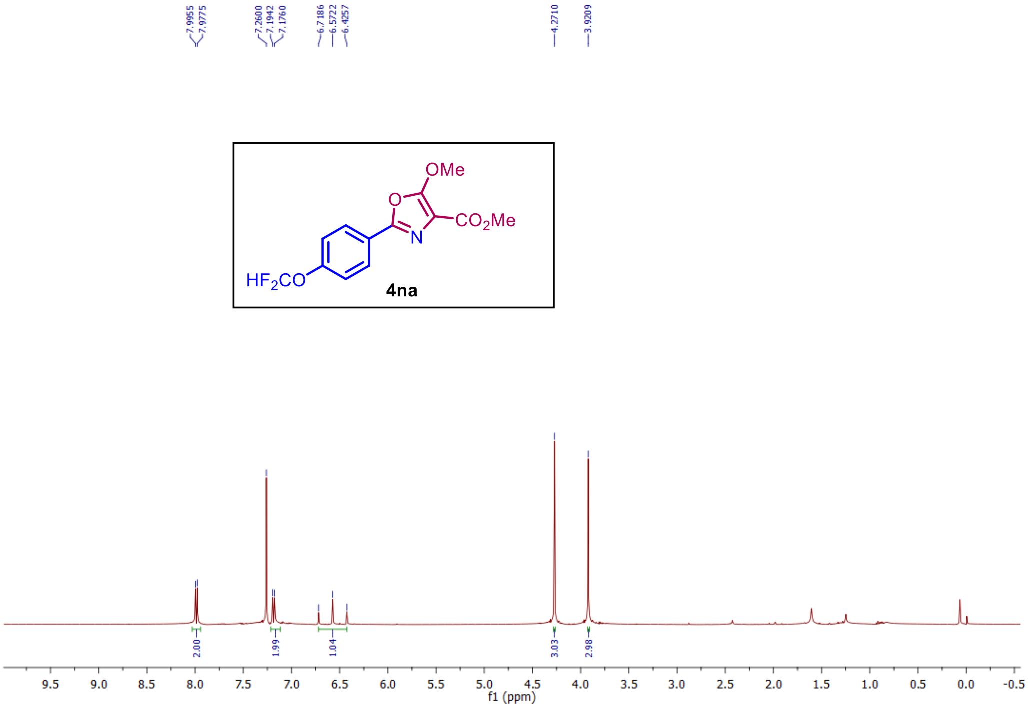


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

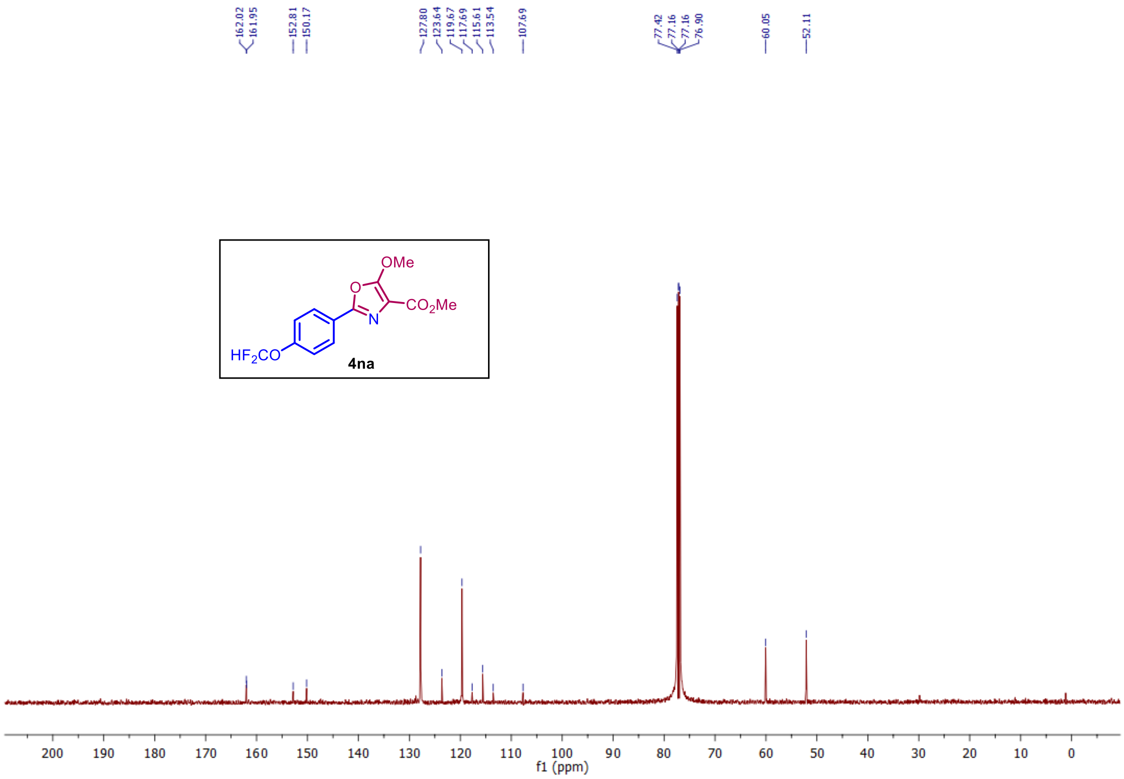


Methyl 2-(4-(difluoromethoxy)phenyl)-5-methoxyoxazole-4-carboxylate (**4na**)

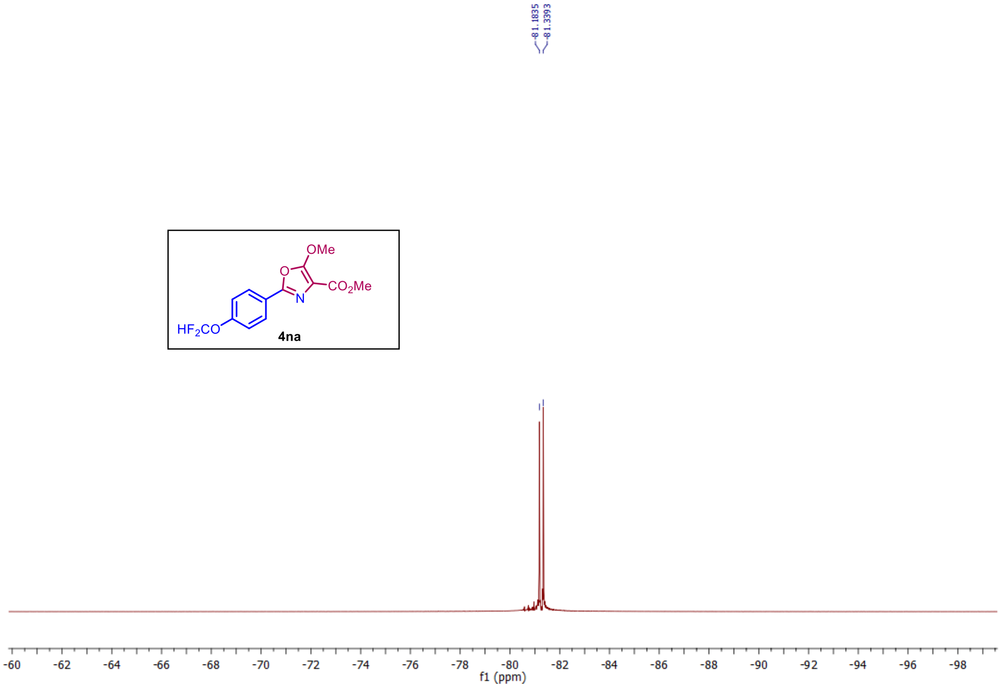
^1H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

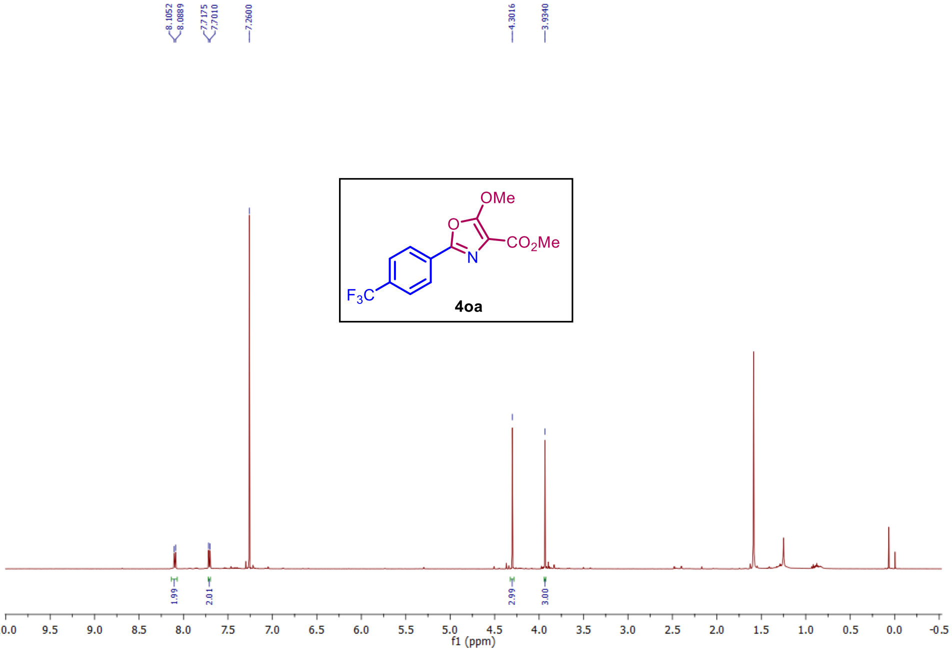


^{19}F NMR (471 MHz, $CDCl_3$, 24 °C)

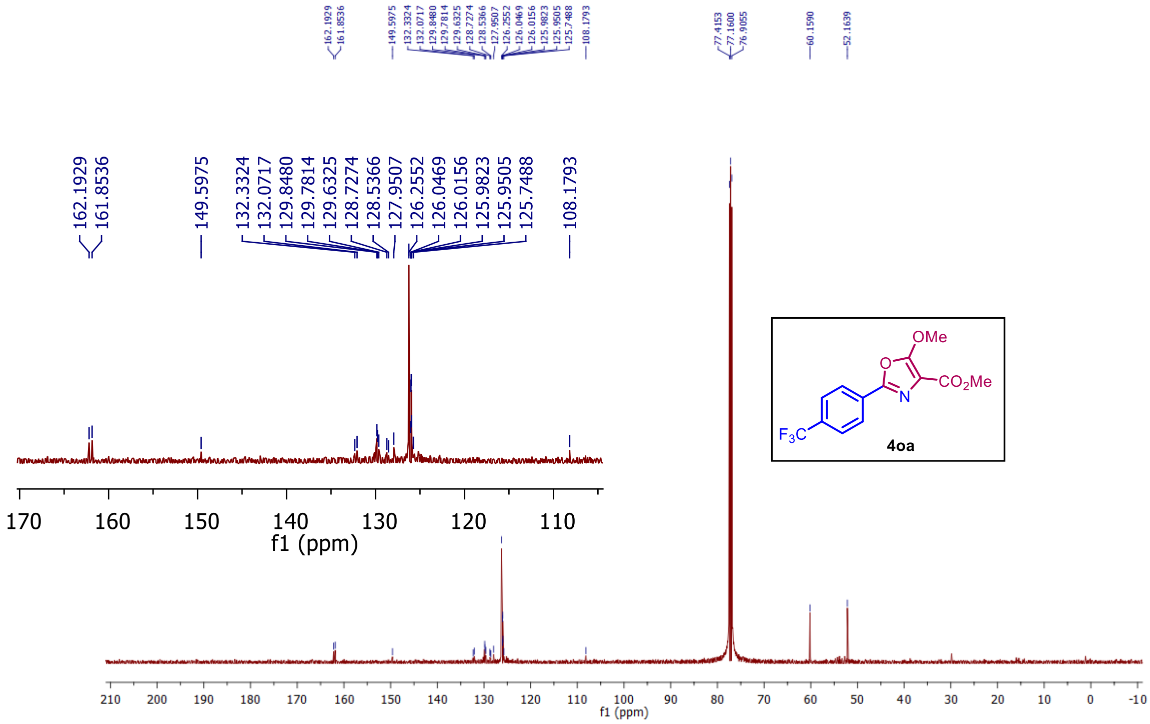


Methyl 5-methoxy-2-(4-(trifluoromethyl)phenyl)oxazole-4-carboxylate (**4oa**)

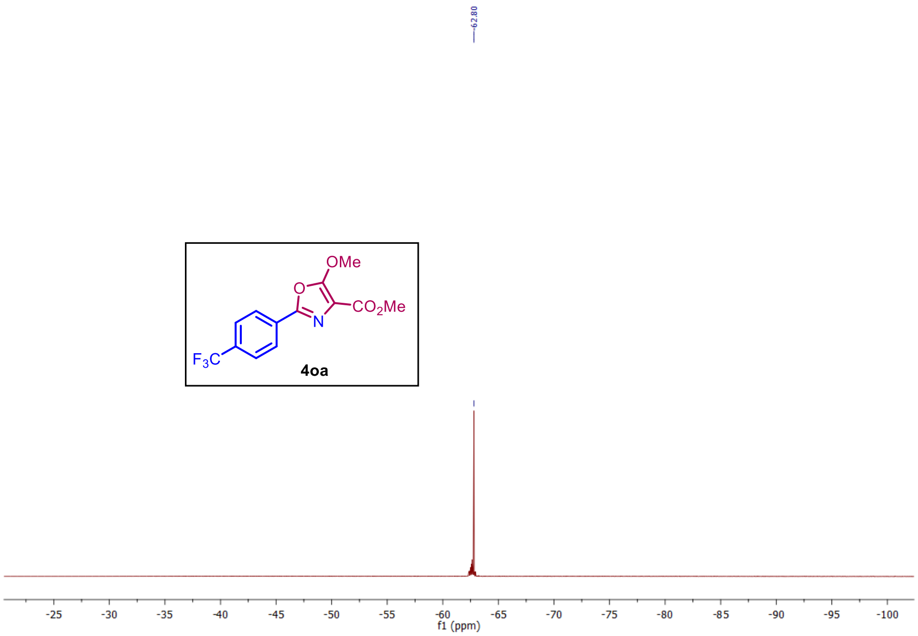
^{1}H NMR (500 MHz, CDCl$_3$, 24 °C)



^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 24 °C)



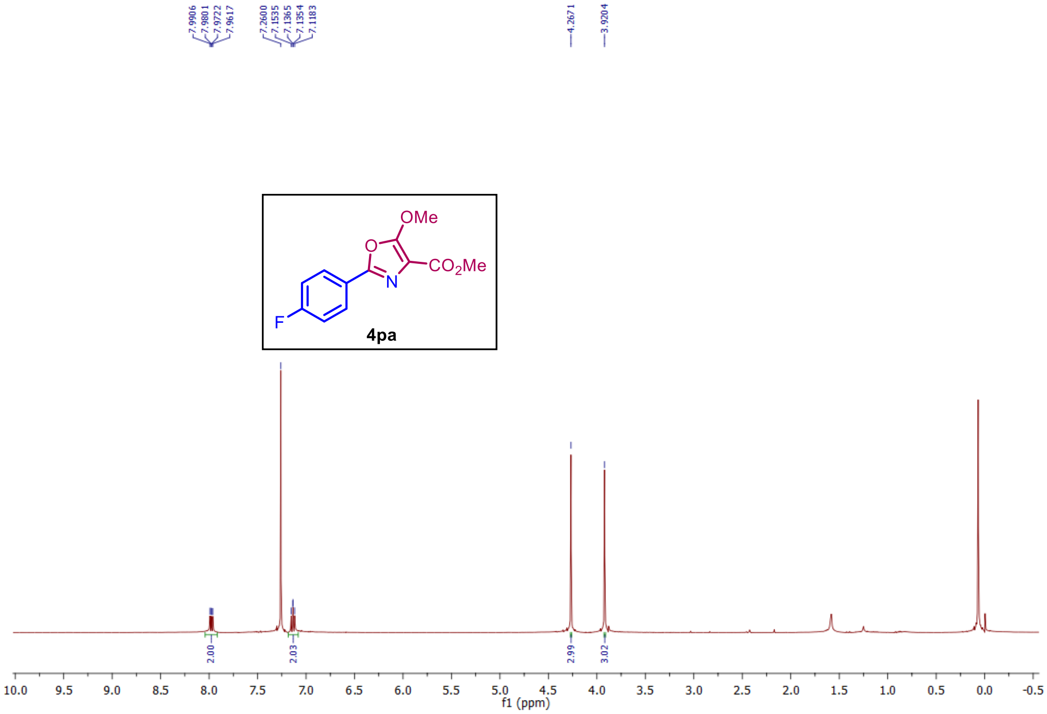
^{19}F NMR (471 MHz, $CDCl_3$, 24 °C)



4oa

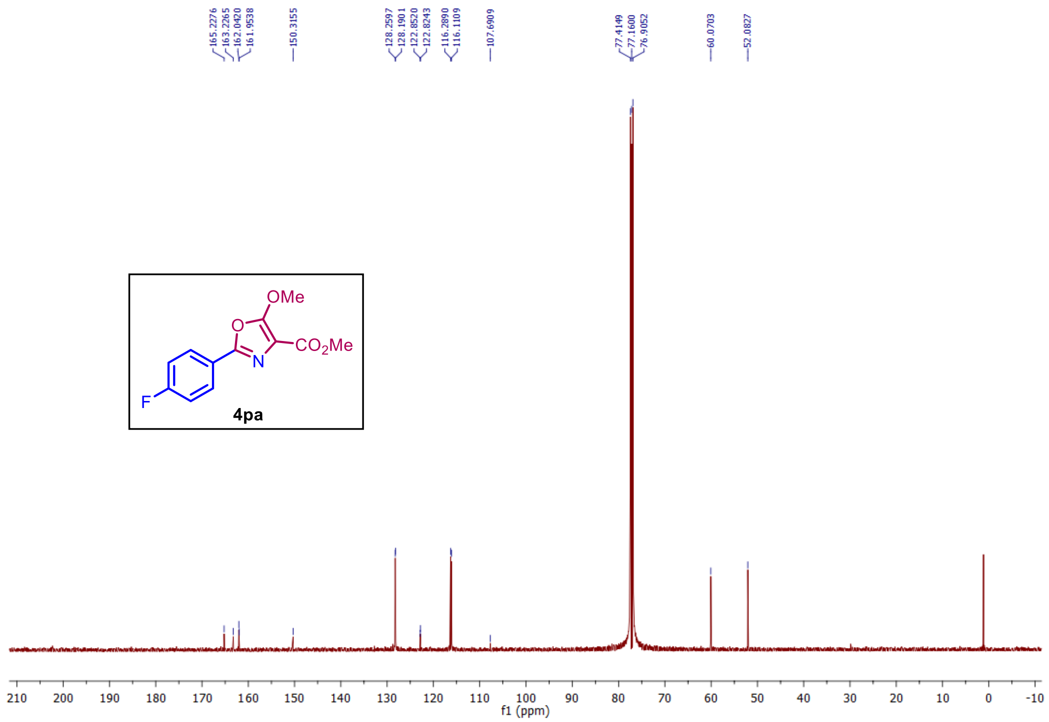
Methyl 2-(4-fluorophenyl)-5-methoxyoxazole-4-carboxylate (**4pa**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

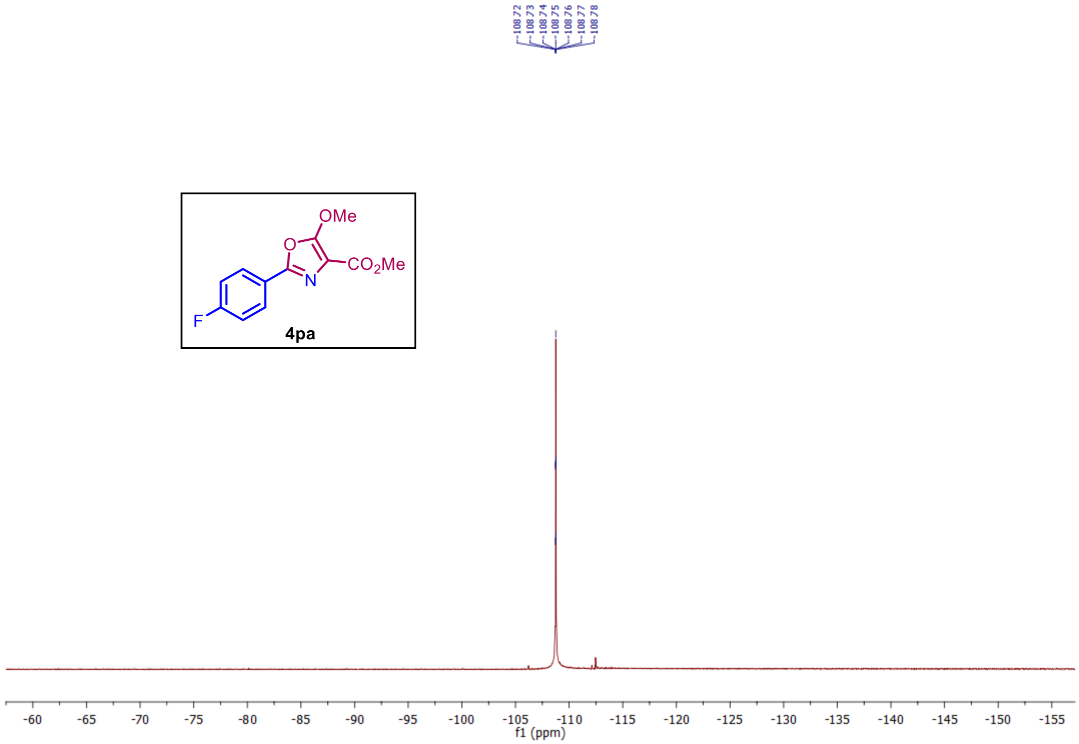


4pa

$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

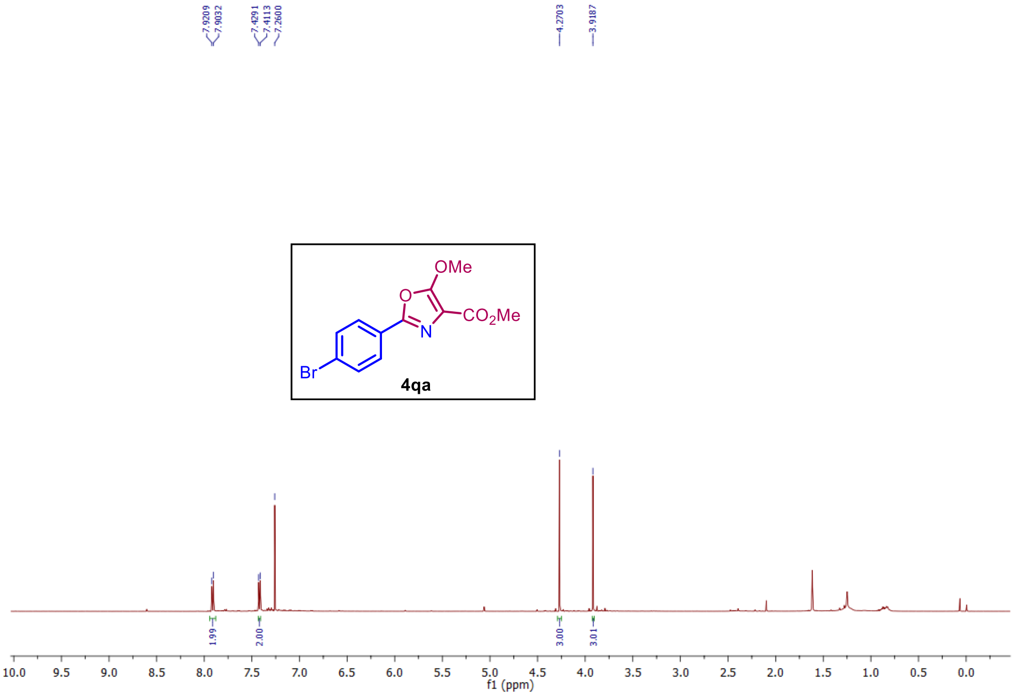


^{19}F NMR (471 MHz, $CDCl_3$, 24 °C)

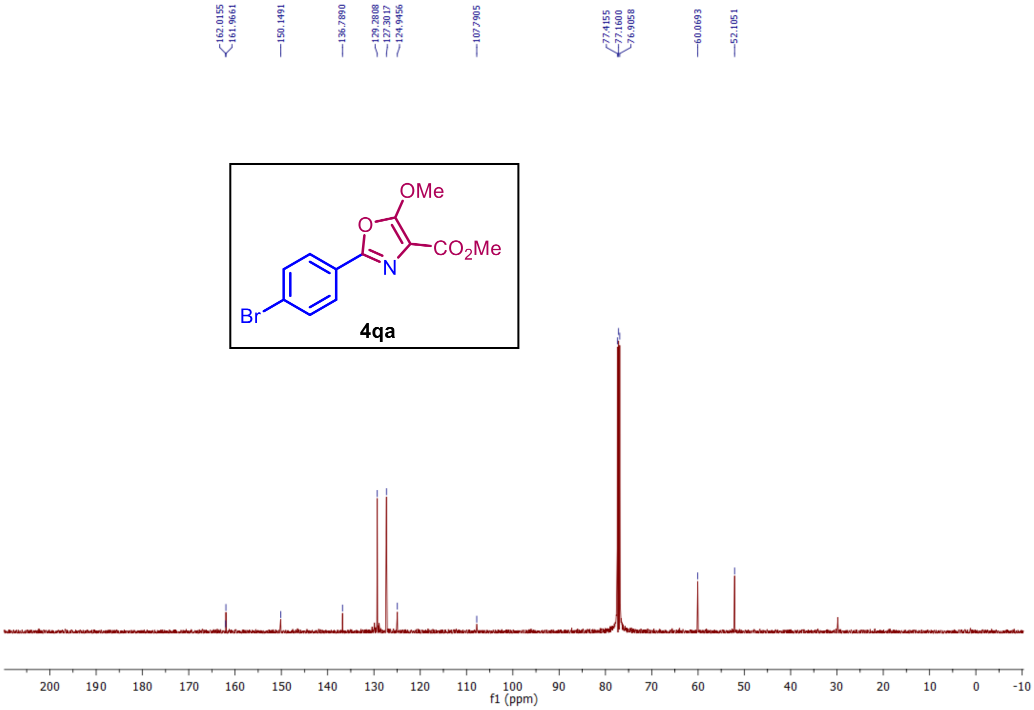


Methyl 5-methoxy-2-(4-bromo-phenyl)oxazole-4-carboxylate (**4qa**)

^{1}H NMR (500 MHz, CDCl$_3$, 24 °C)

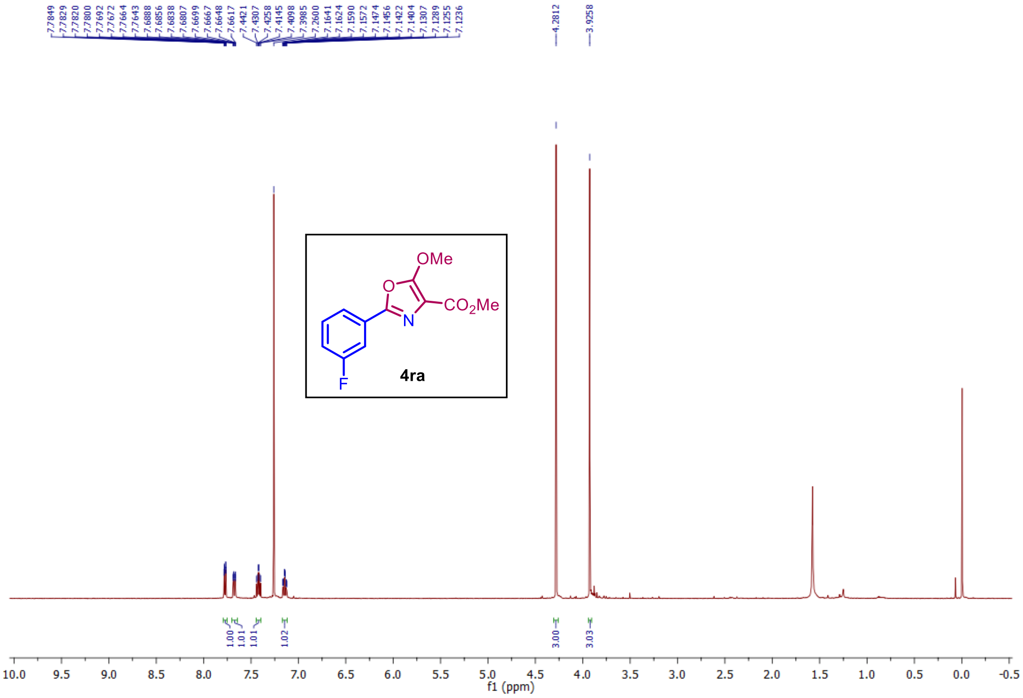


^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$, 24 °C)

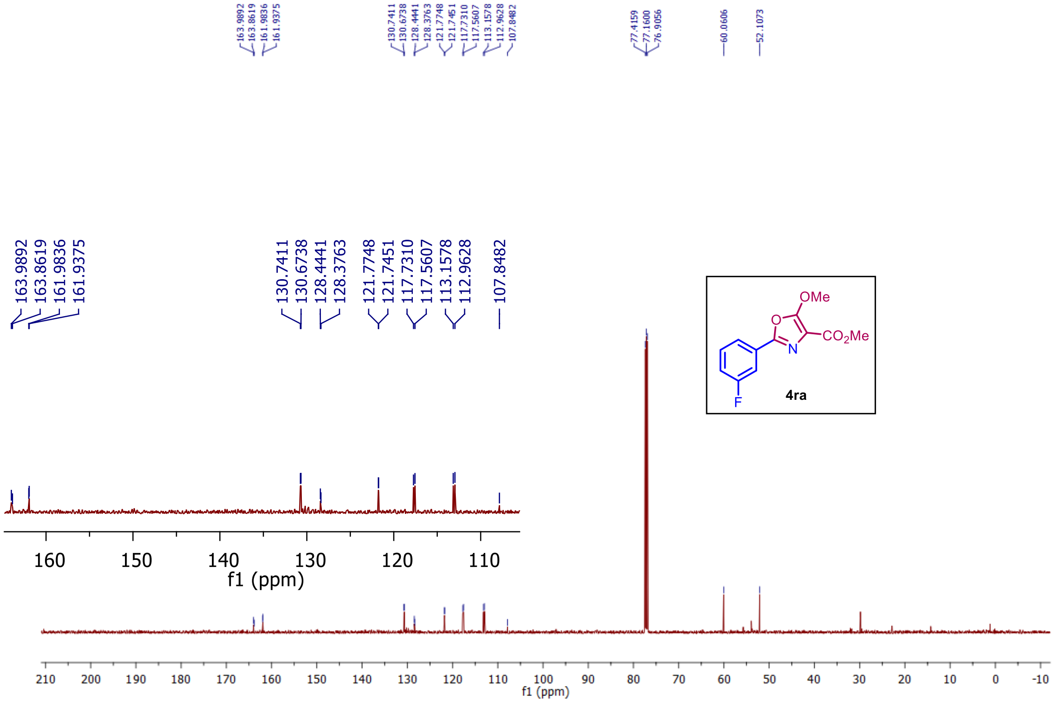


Methyl 2-(3-fluorophenyl)-5-methoxyoxazole-4-carboxylate (**4ra**)

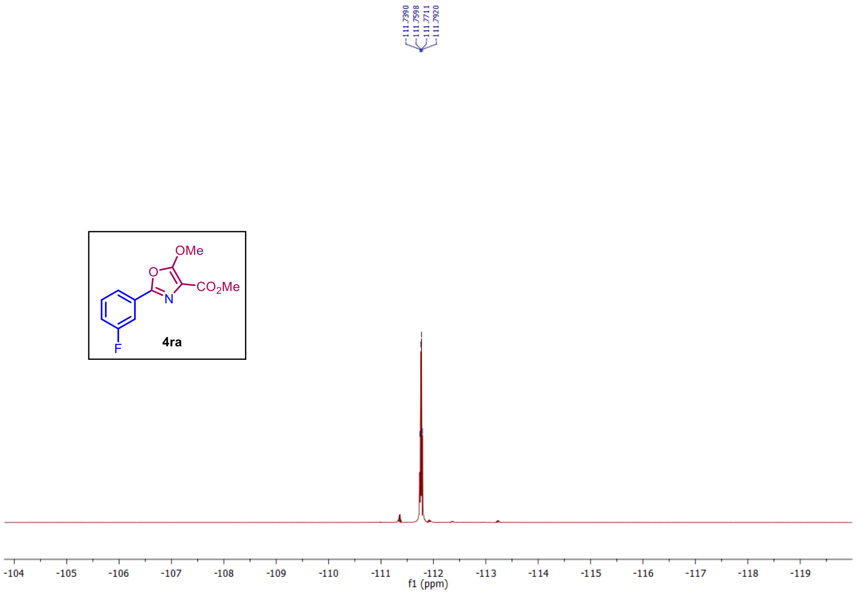
^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 24 °C)

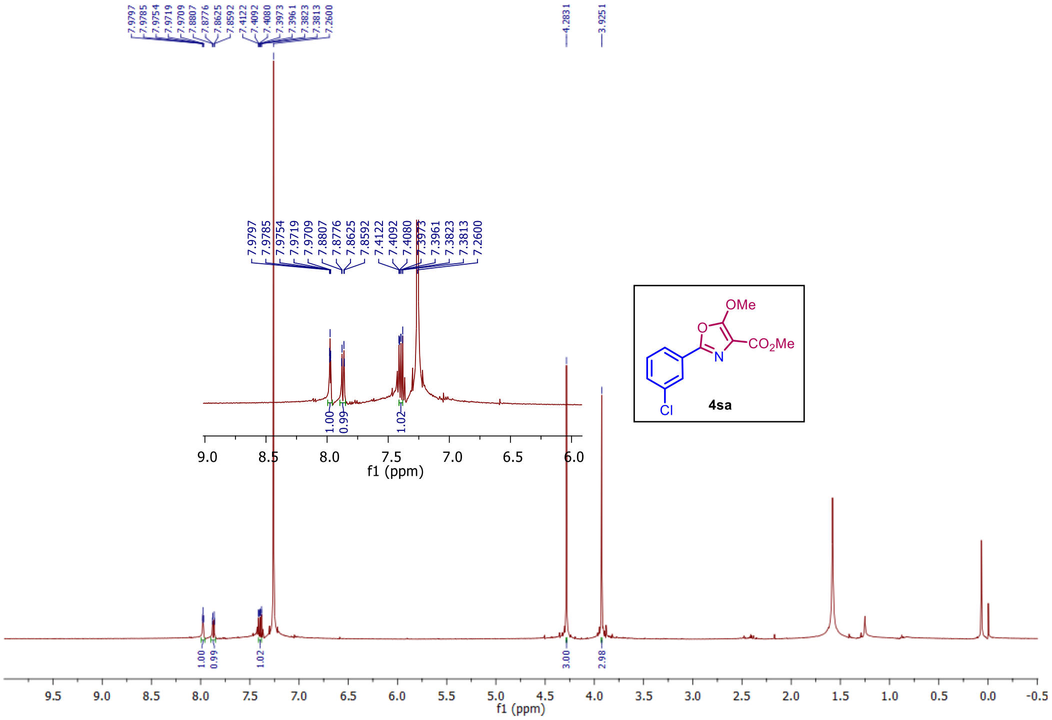


^{19}F NMR (471 MHz, $CDCl_3$, 24 °C)

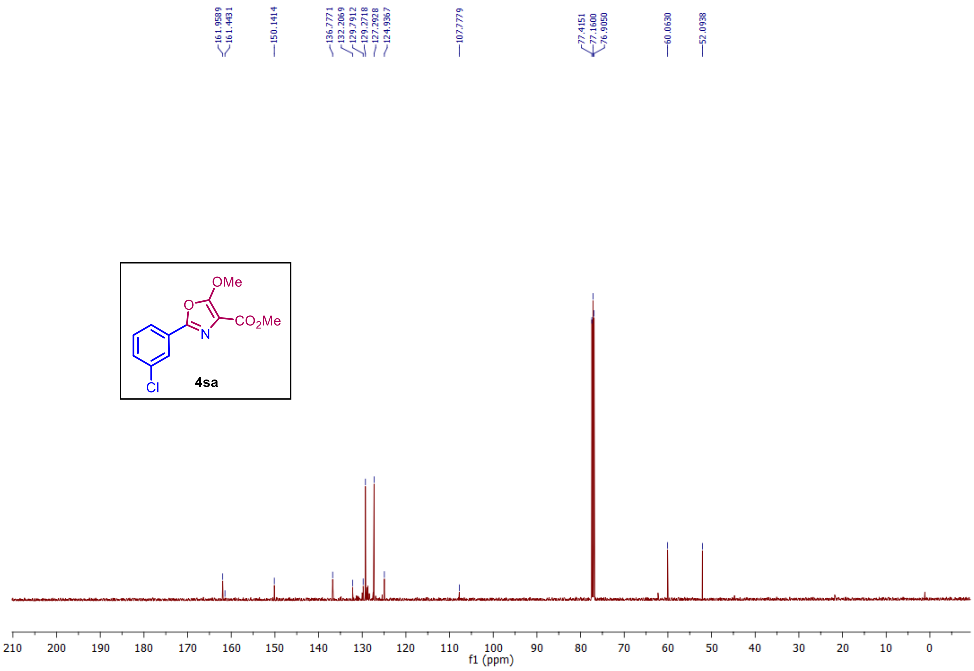


Methyl 2-(3-chlorophenyl)-5-methoxyoxazole-4-carboxylate (**4sa**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

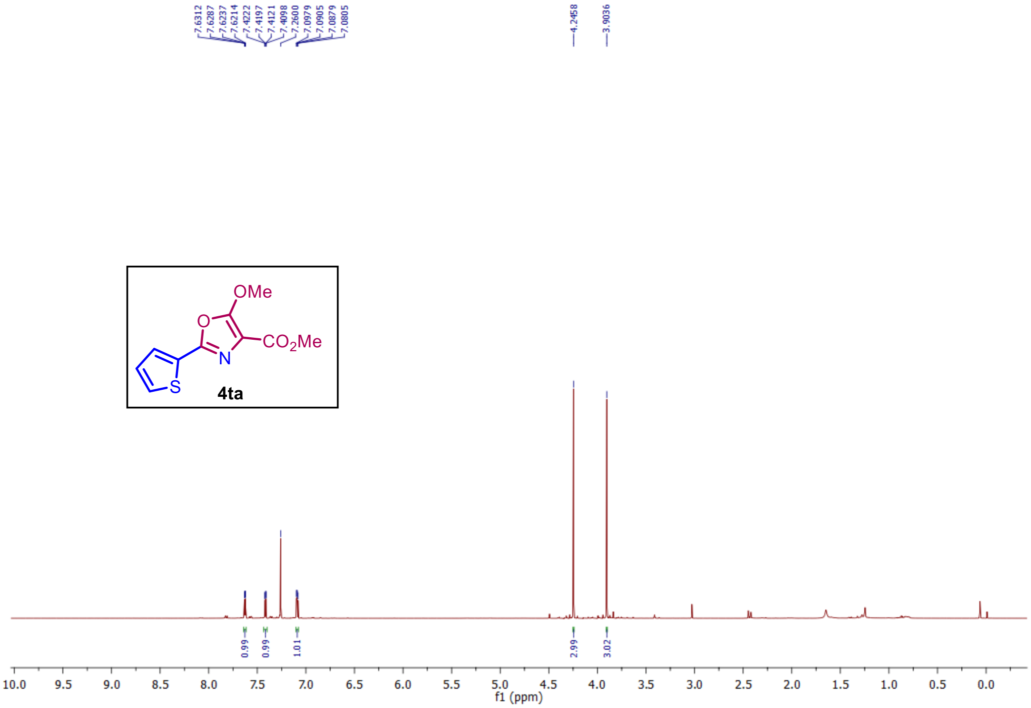


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

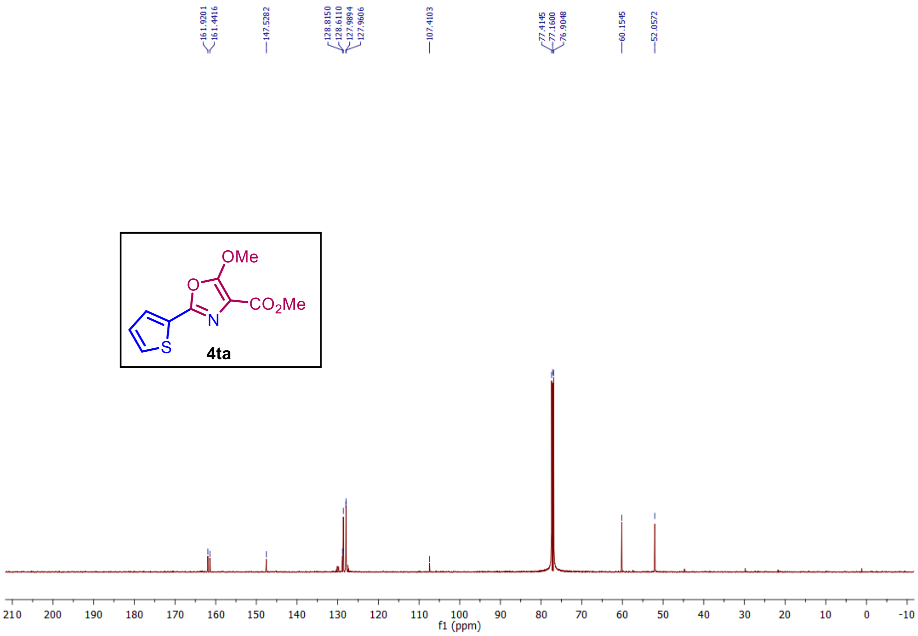


Methyl 5-methoxy-2-(thiophen-2-yl)oxazole-4-carboxylate (**4ta**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

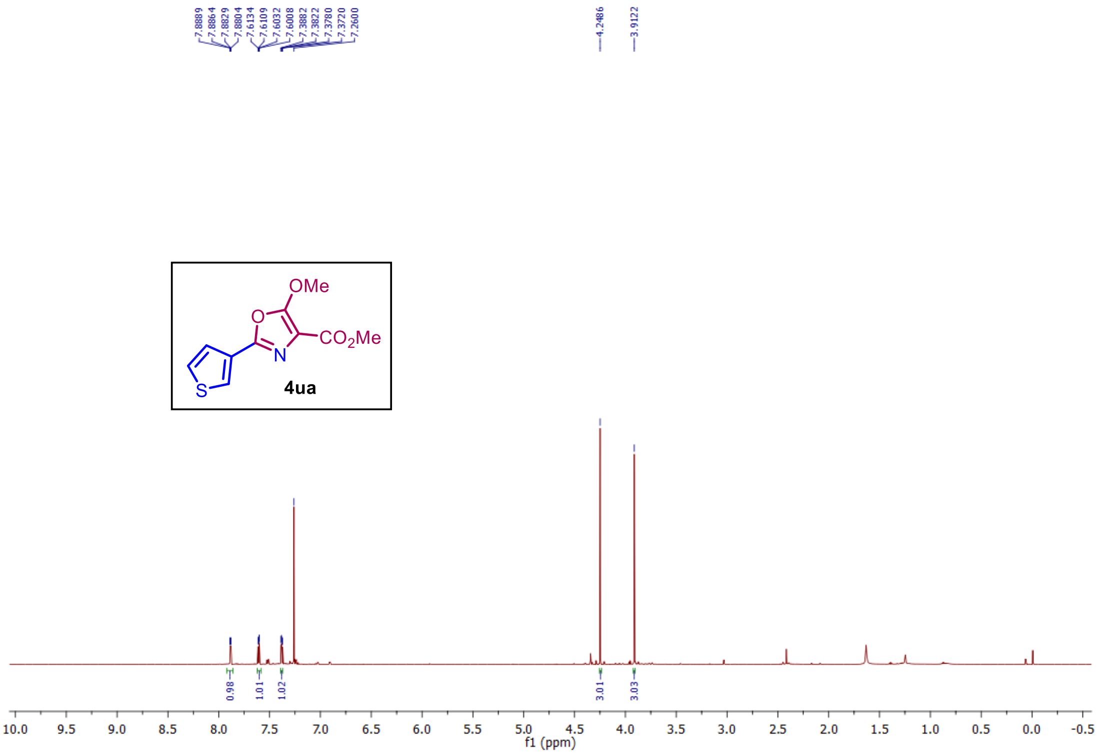


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

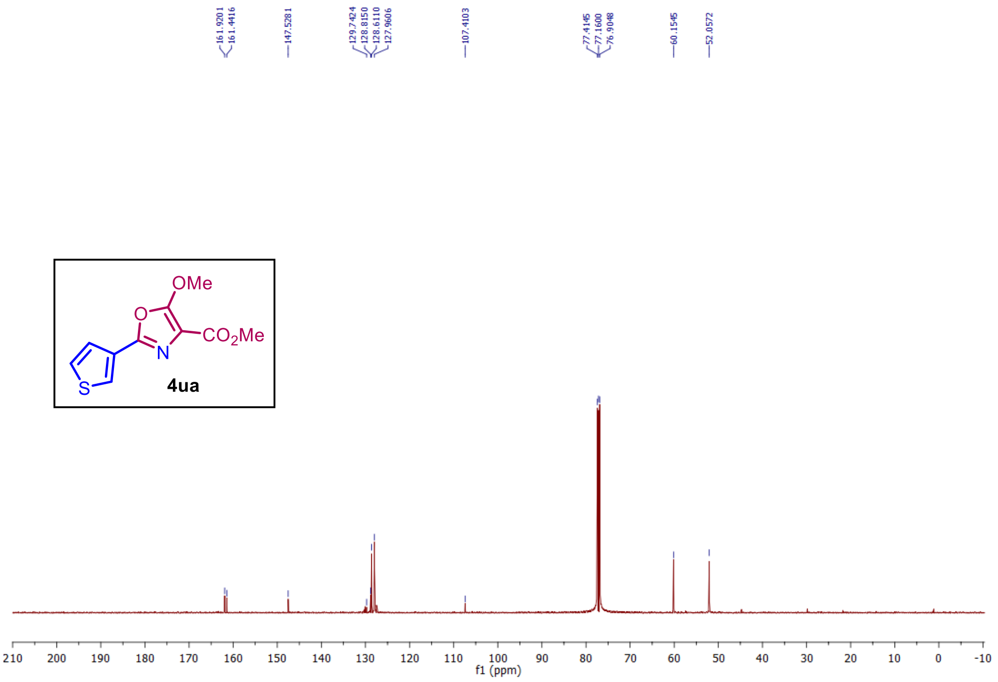


Methyl 5-methoxy-2-(thiophen-3-yl)oxazole-4-carboxylate (**4ua**)

^1H NMR (500 MHz, $CDCl_3$, 24 °C)

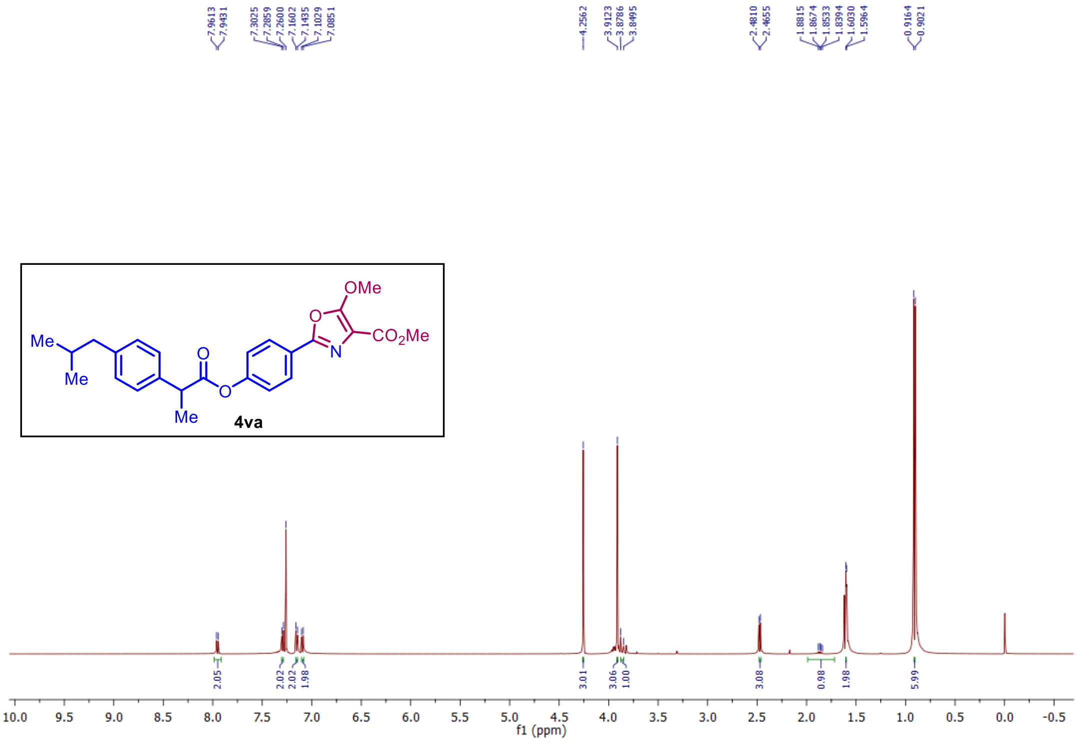


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

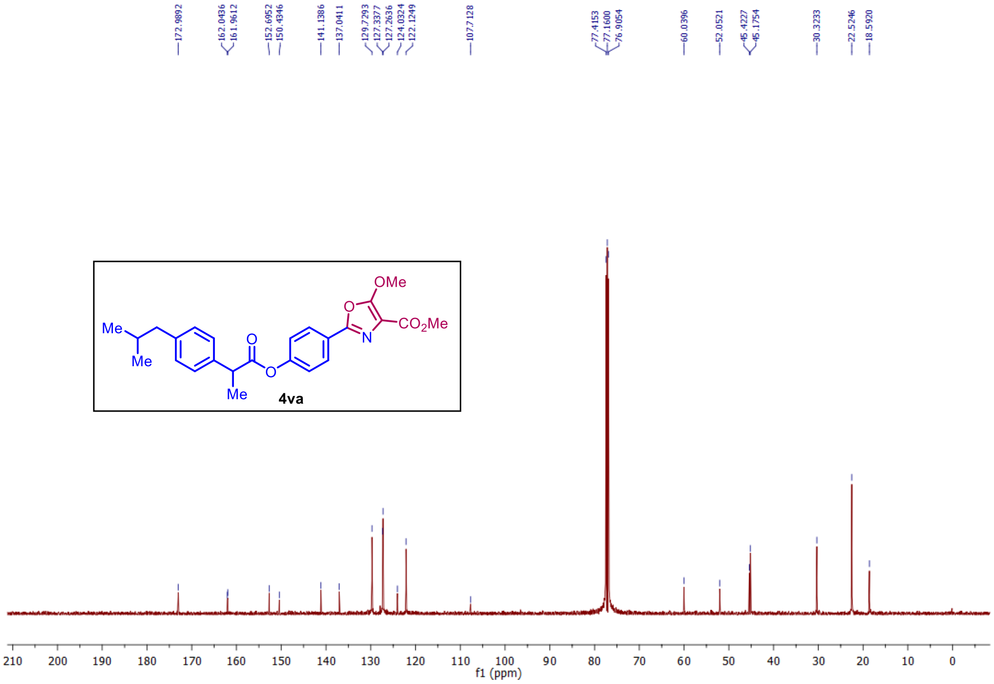


Methyl 2-(4-isobutylphenyl-propanoyl)oxy-phenyl)-5-methoxyoxazole-4-carboxylate (**4va**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

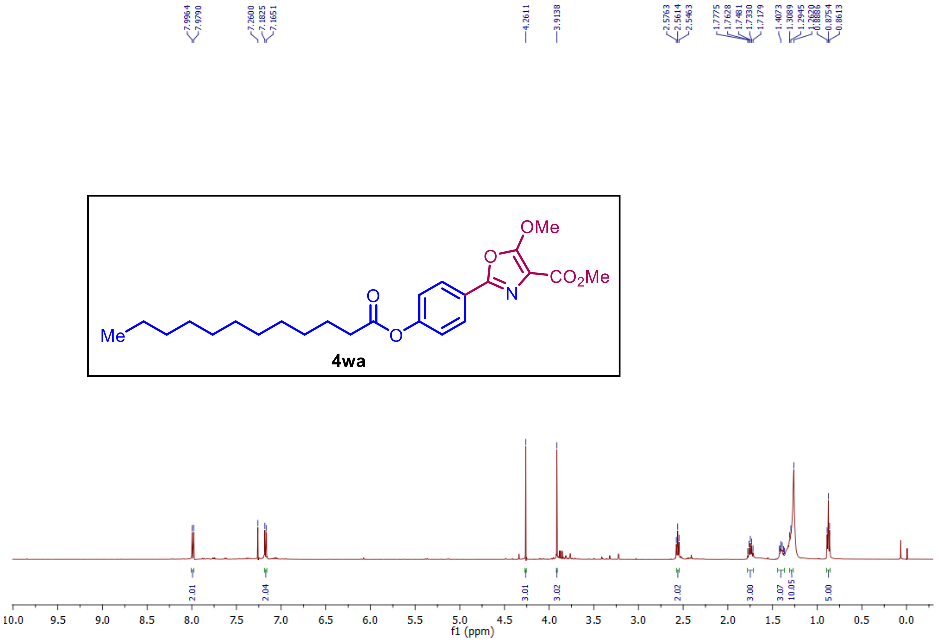


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

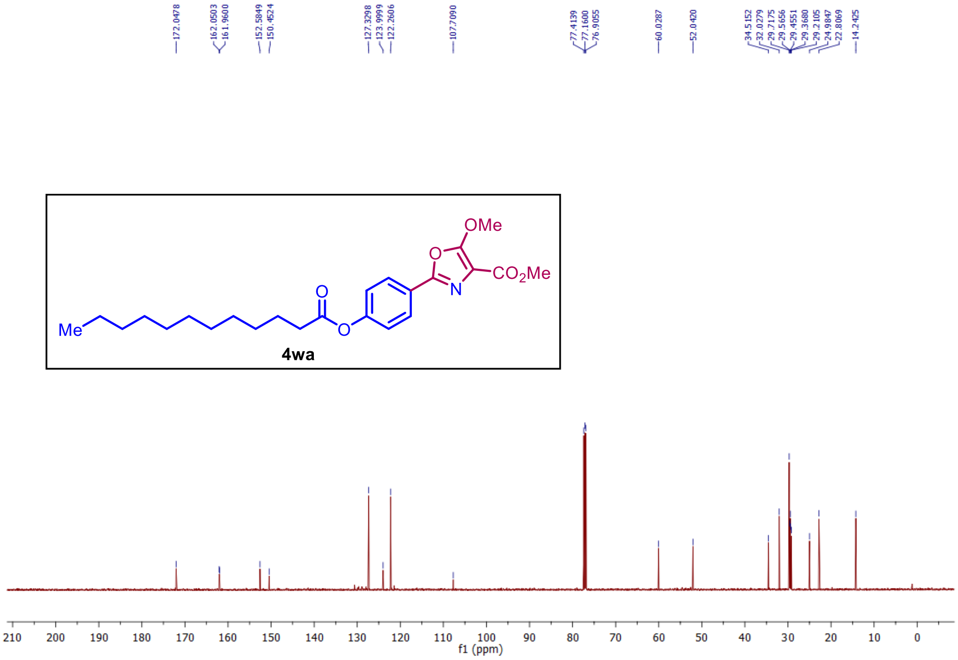


Methyl 2-(4-dodecanoyloxy-phenyl)-5-methoxyoxazole-4-carboxylate (**4wa**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

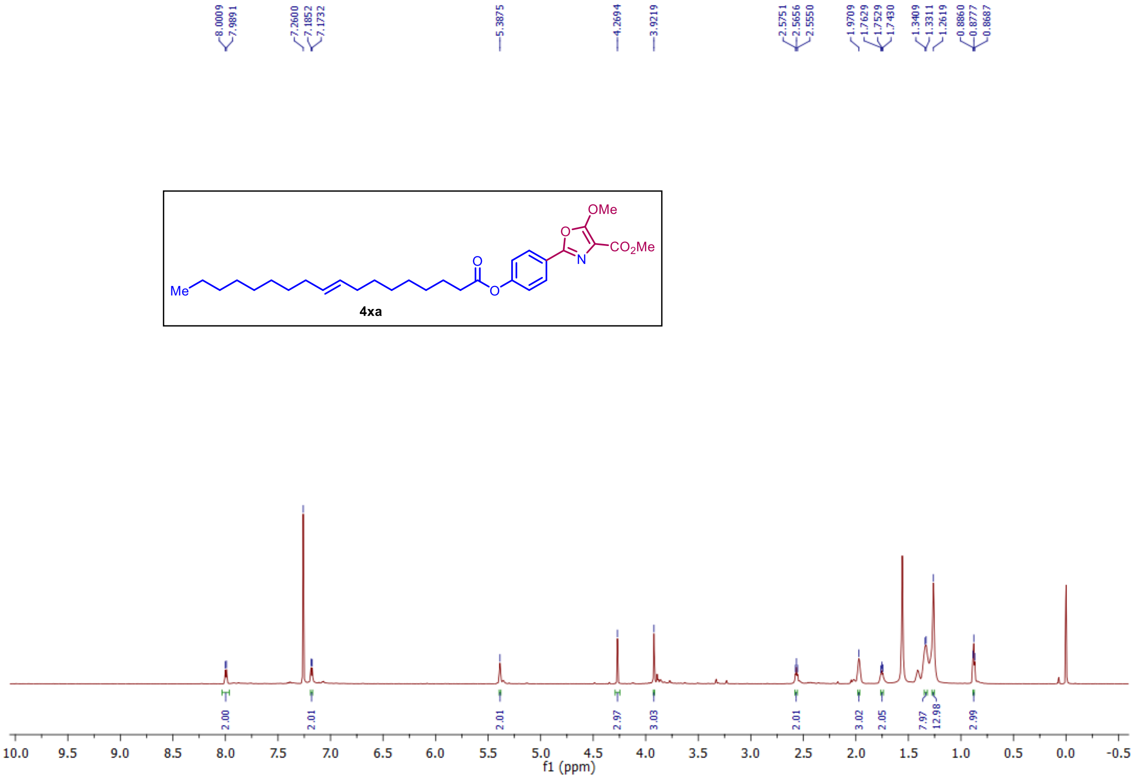


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

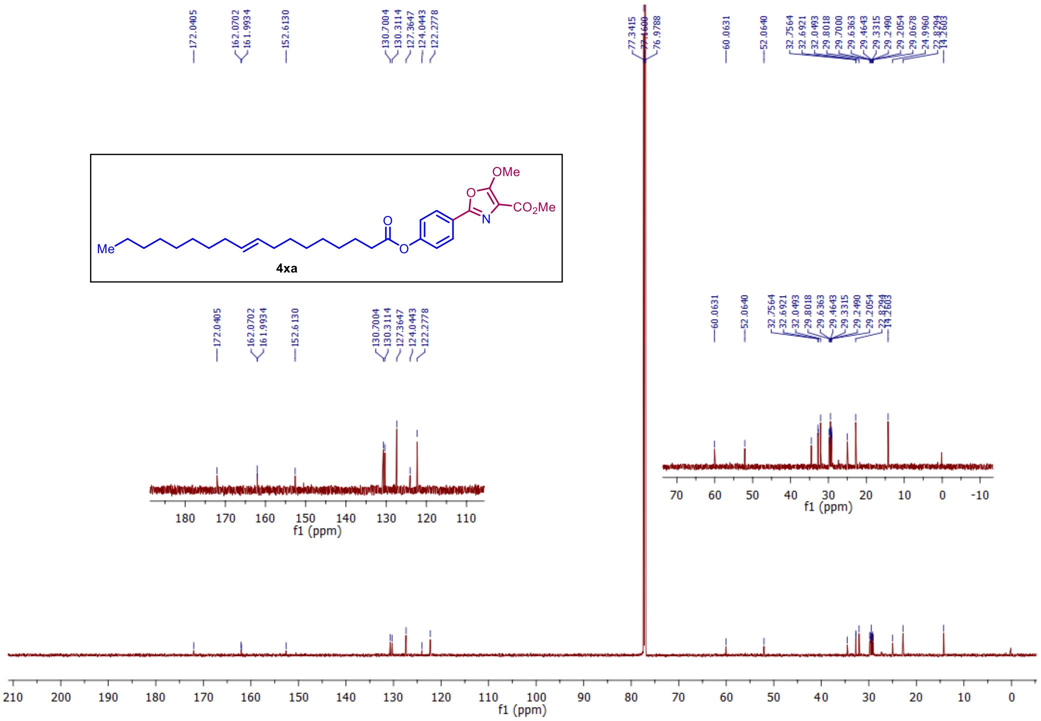


Methyl (E)-5-methoxy-2-(4-(octadec-8-enoyloxy)phenyl)oxazole-4-carboxylate (**4xa**)

^1H NMR (700 MHz, $CDCl_3$, 24 °C)

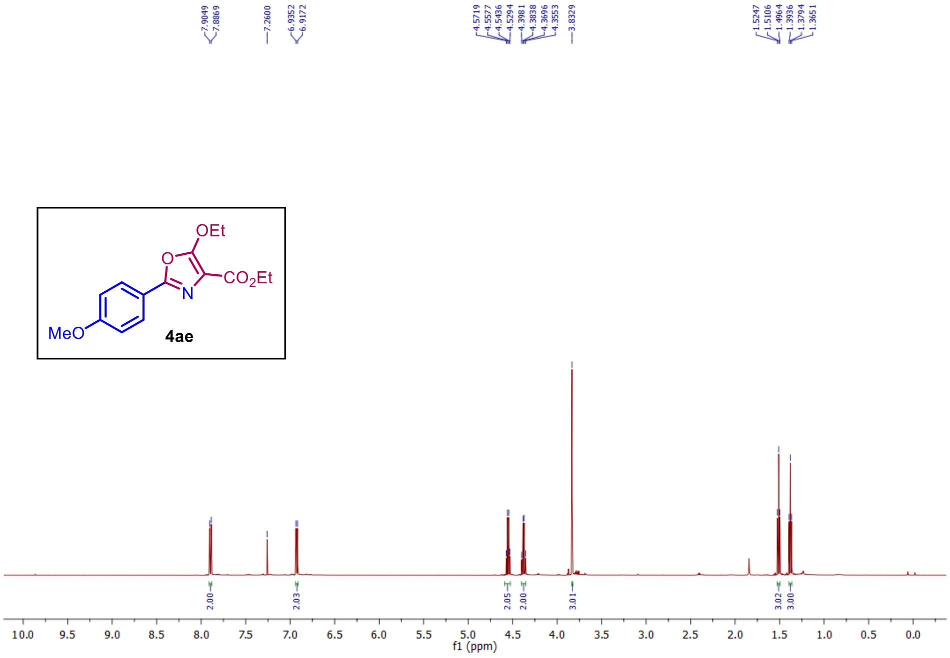


$^{13}C\{^1H\}$ NMR (176 MHz, $CDCl_3$, 24 °C)

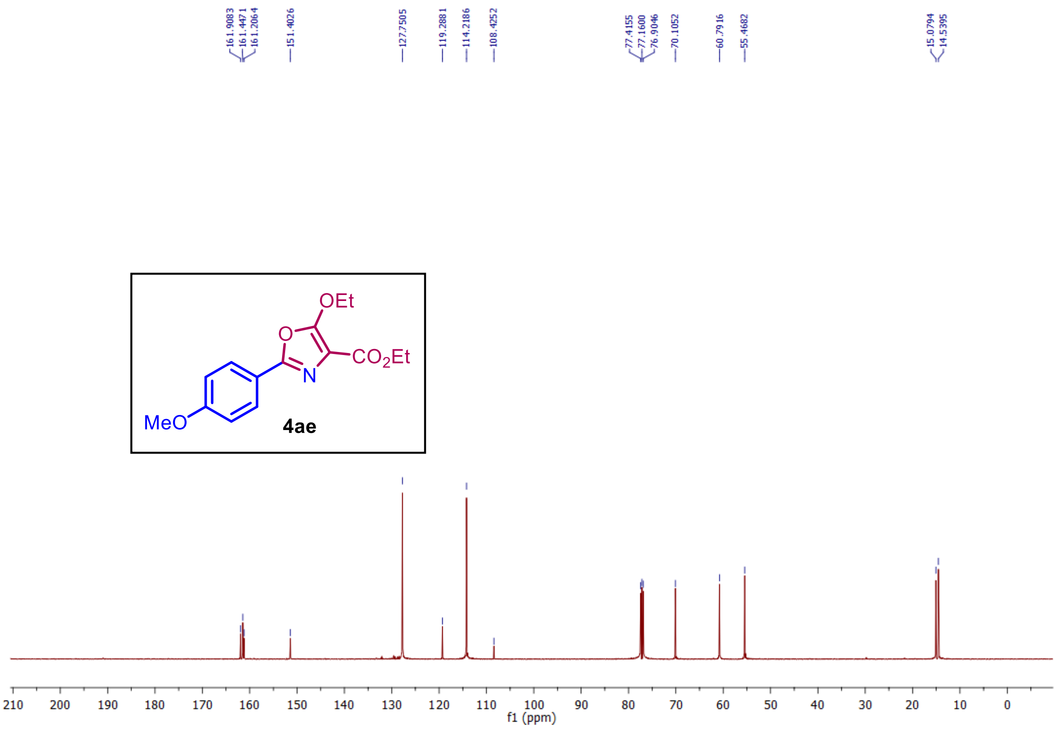


Ethyl 5-ethoxy-2-(4-methoxyphenyl)oxazole-4-carboxylate (**4ae**)

^1H NMR (500 MHz, $CDCl_3$, 24 °C)

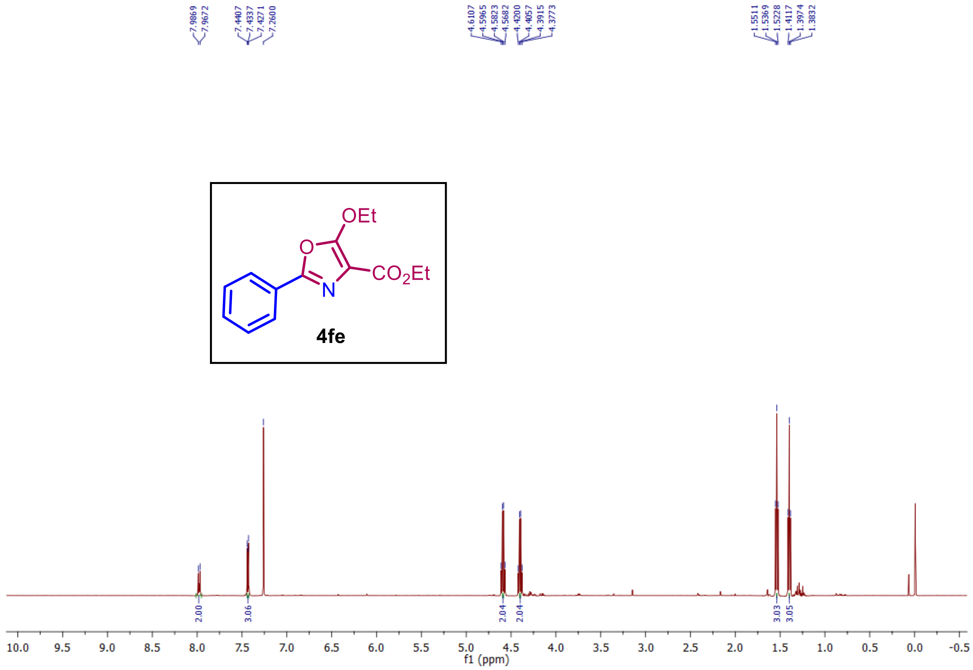


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

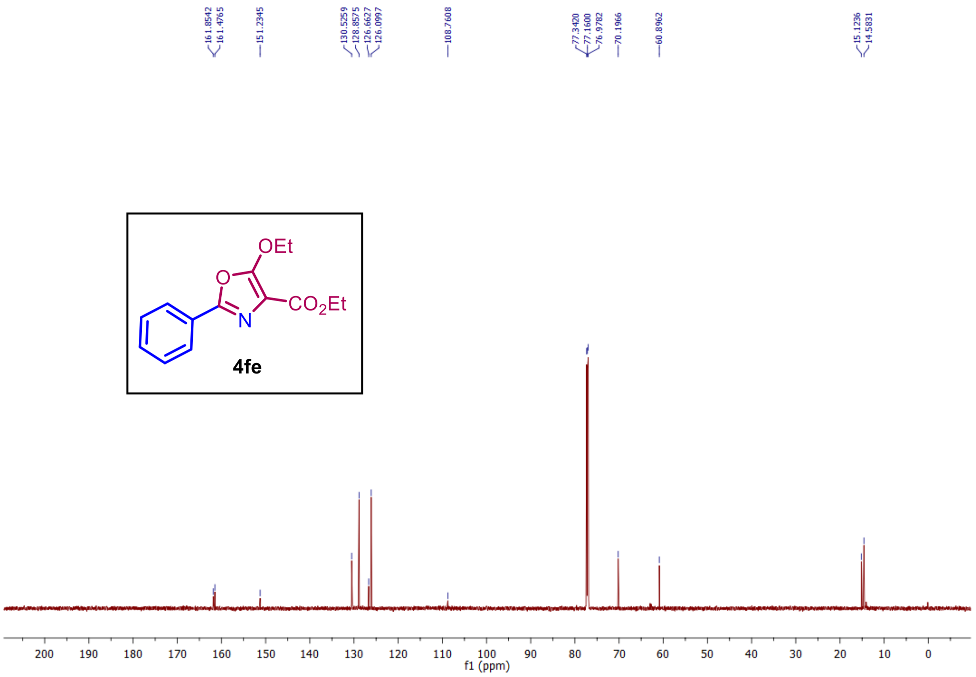


Ethyl 5-ethoxy-2-(4-ethoxyphenyl)oxazole-4-carboxylate (**4fe**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

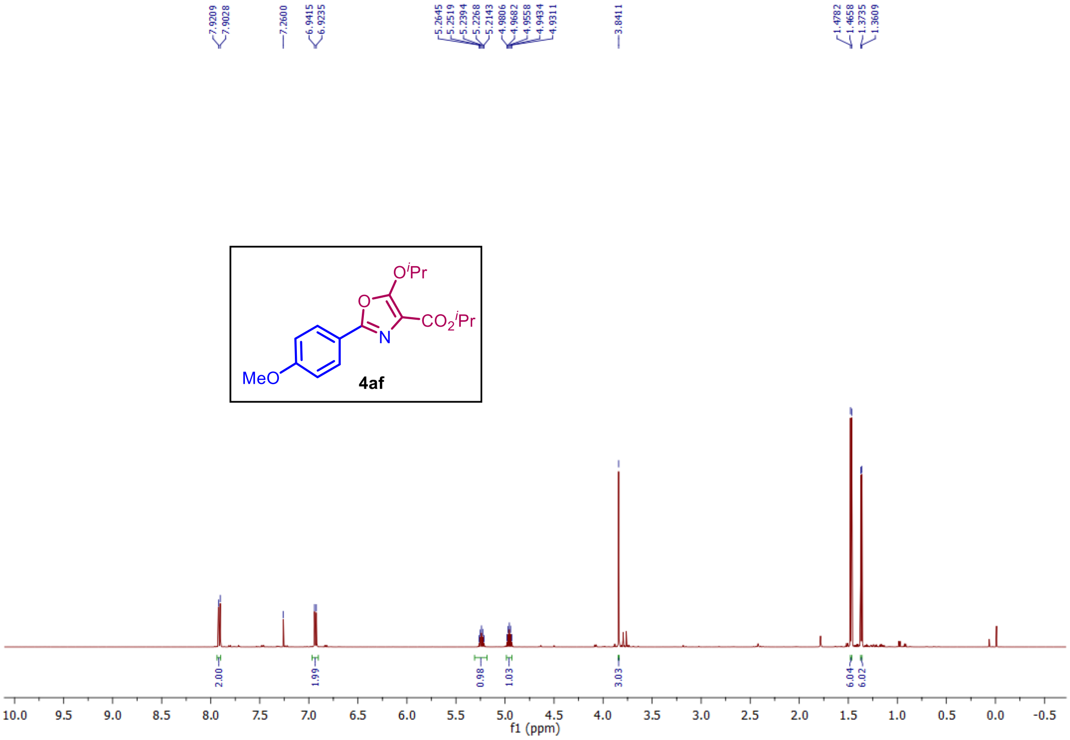


$^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$, 24 °C)

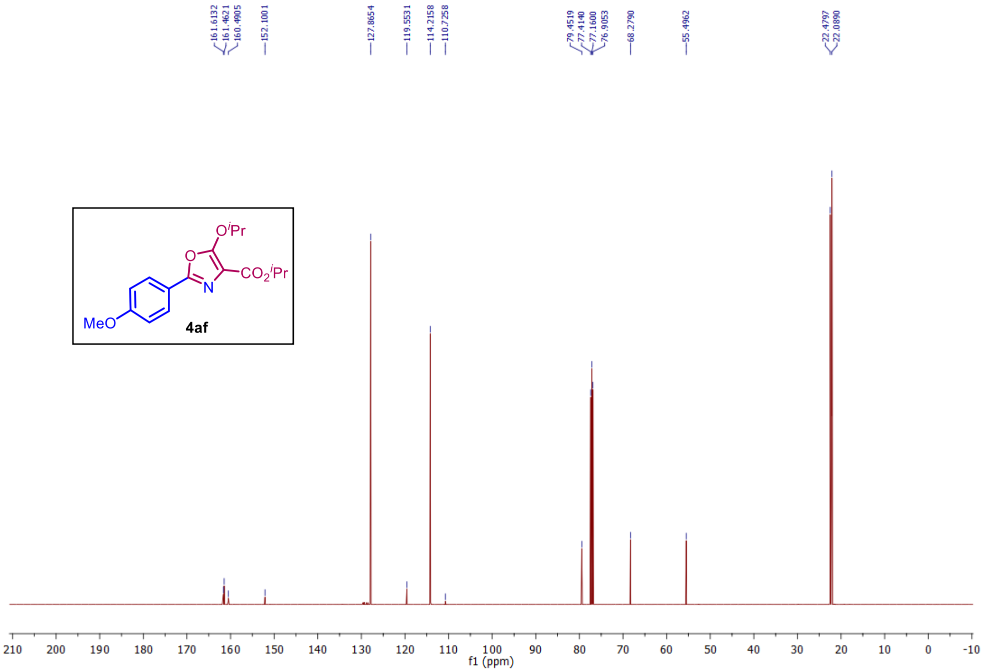


Isopropyl 5-isopropoxy-2-(4-methoxyphenyl)oxazole-4-carboxylate (**4af**)

^1H NMR (500 MHz, CDCl$_3$, 24 °C)

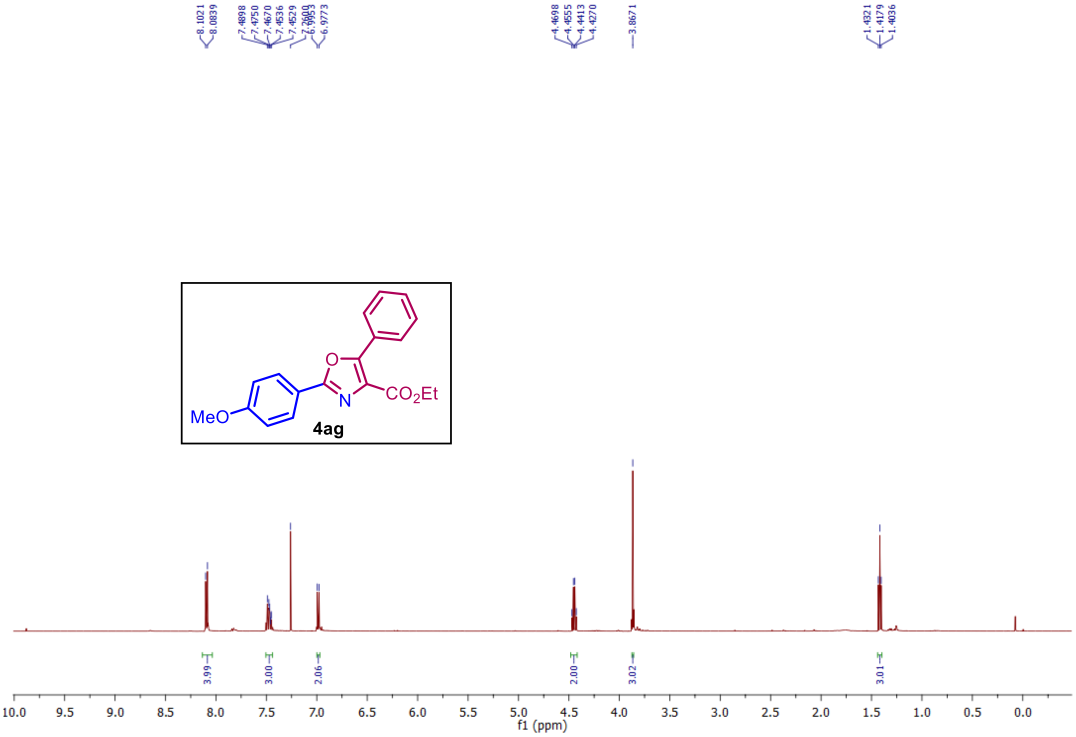


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

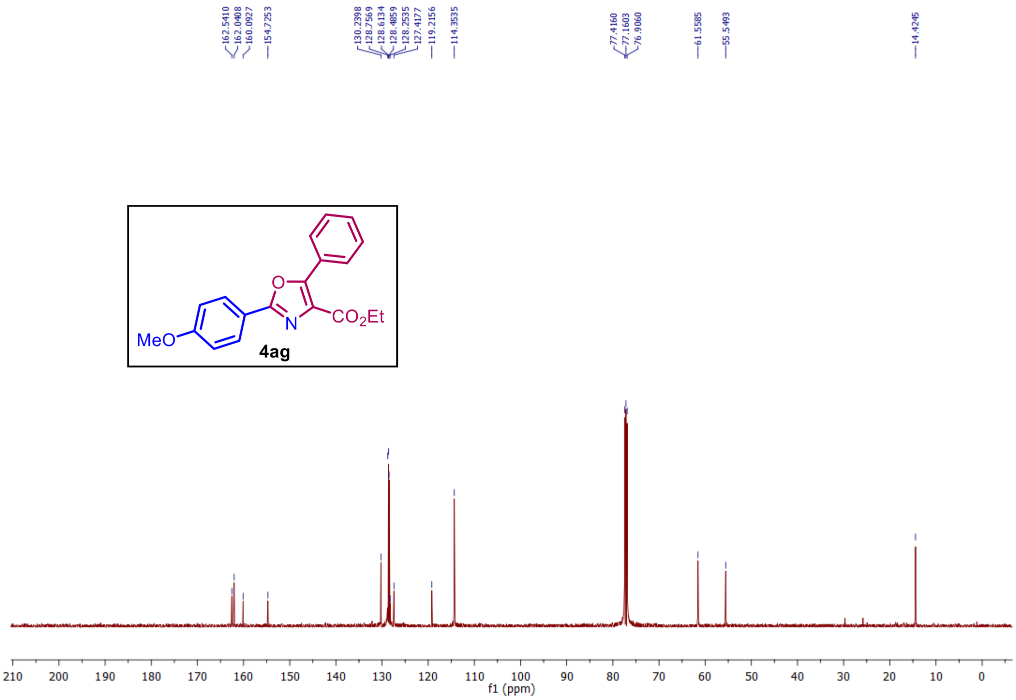


Ethyl 2-(4-methoxyphenyl)-5-phenyloxazole-4-carboxylate (**4ag**)

^1H NMR (500 MHz, $CDCl_3$, 24 °C)

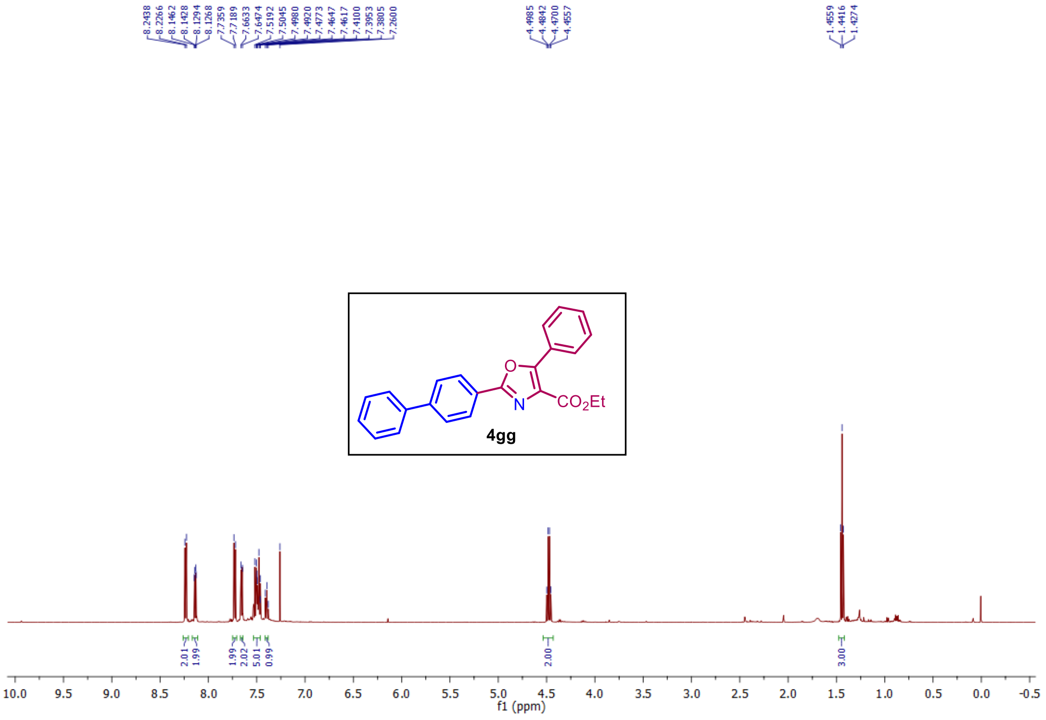


$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

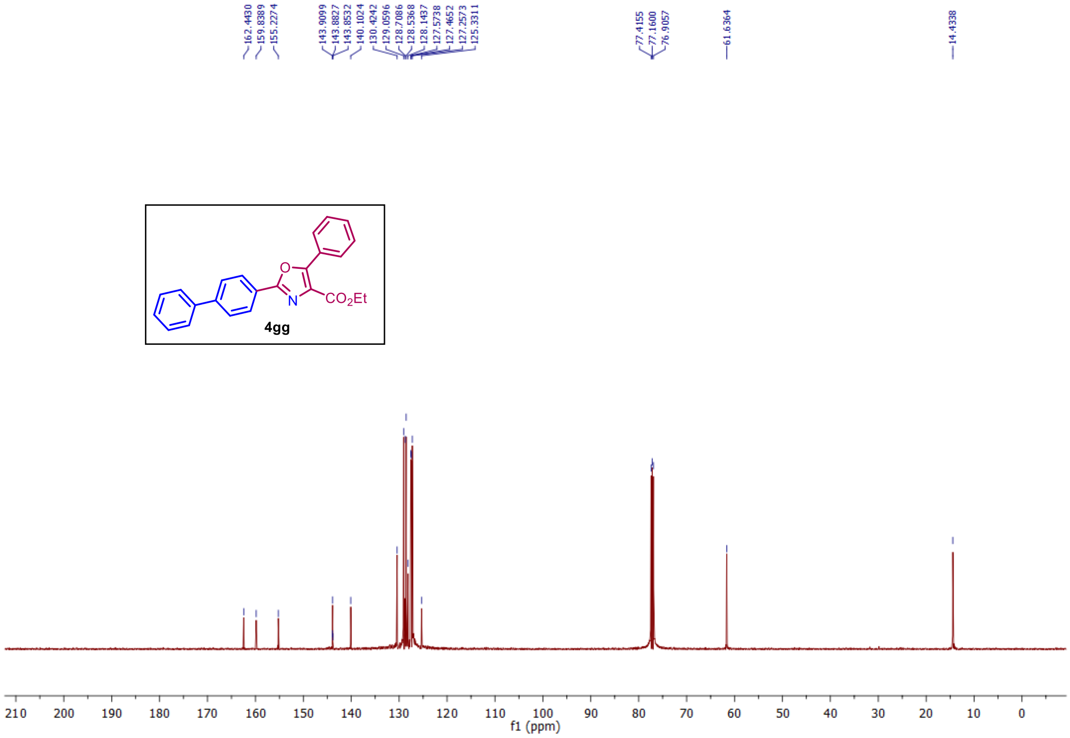


Ethyl 2-([1,1'-biphenyl]-4-yl)-5-phenyloxazole-4-carboxylate (**4gg**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

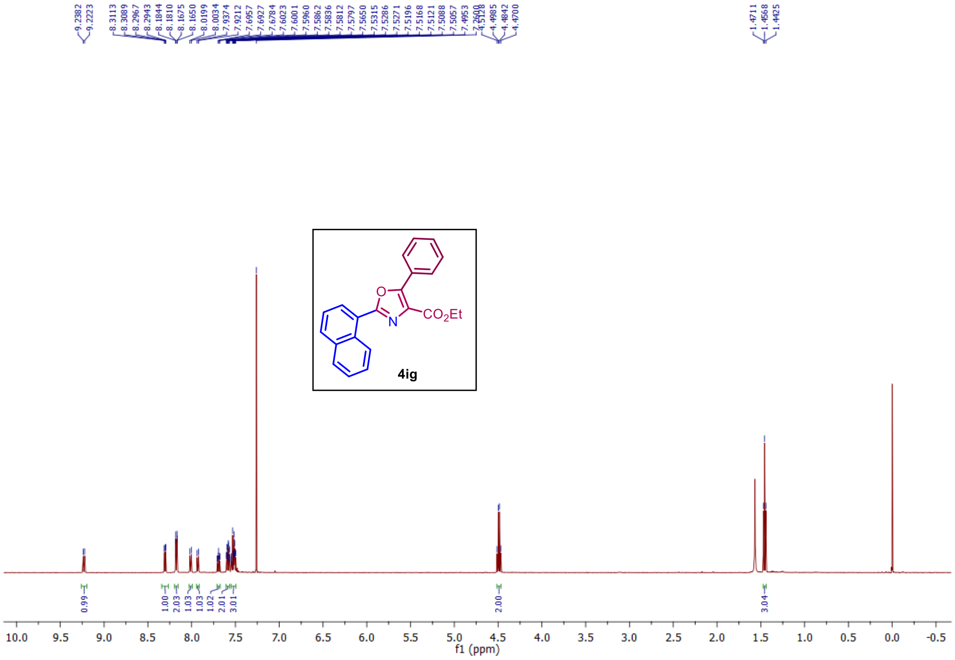


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

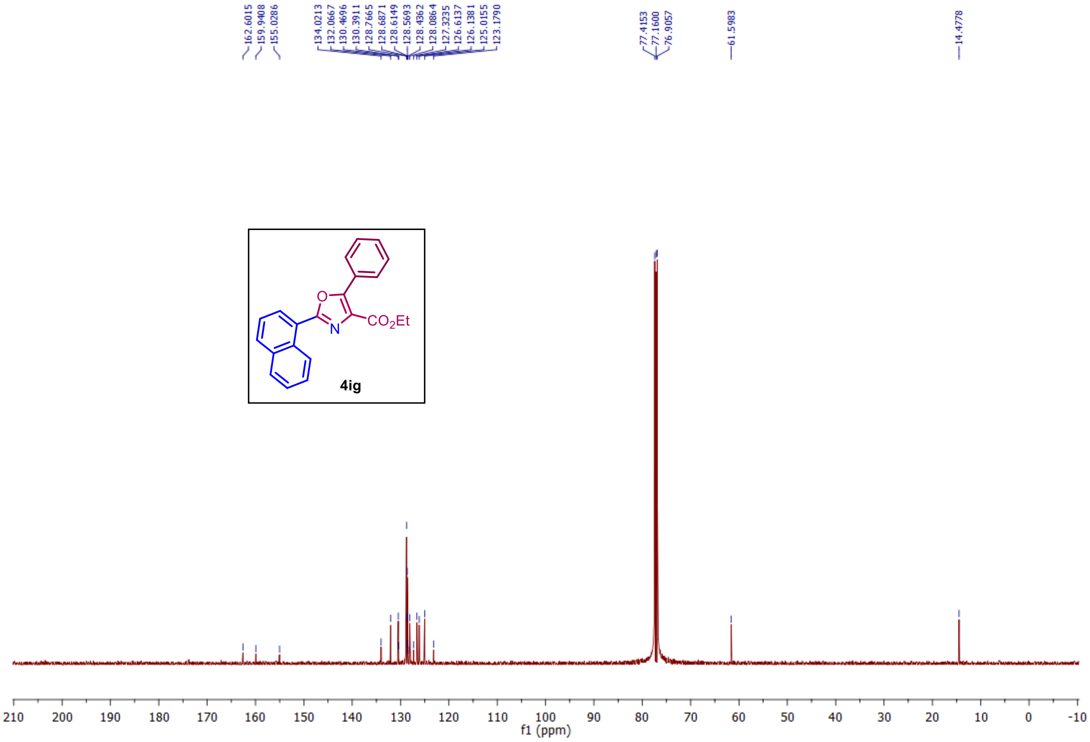


Ethyl 2-(naphthalen-1-yl)-5-phenyloxazole-4-carboxylate (**4ig**)

^1H NMR (500 MHz, $CDCl_3$, 24 °C)

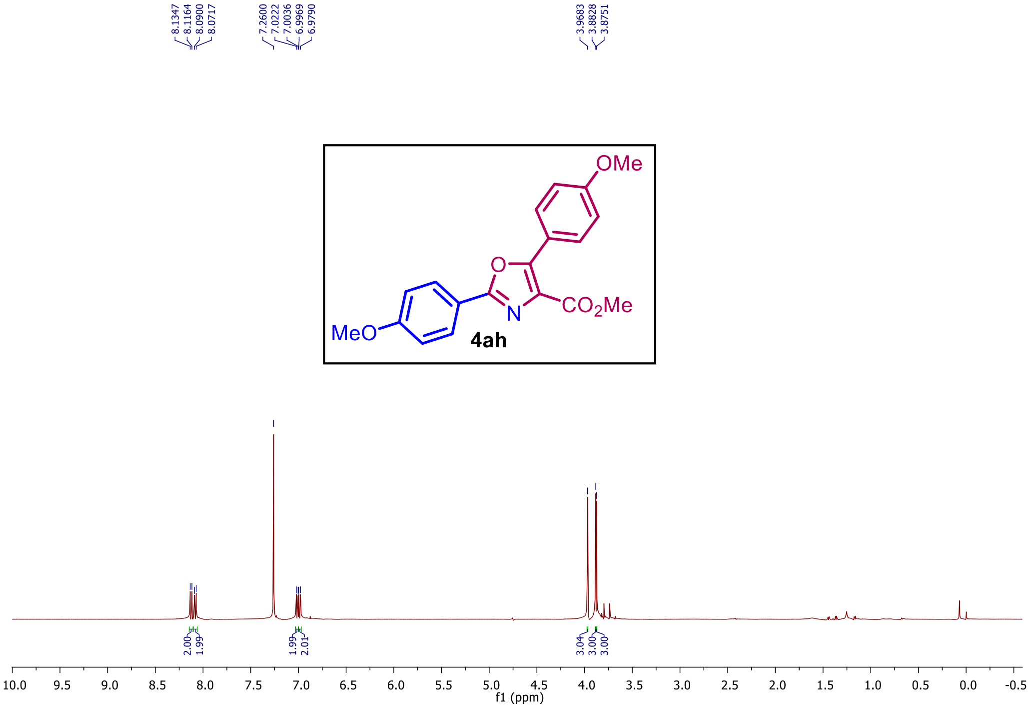


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

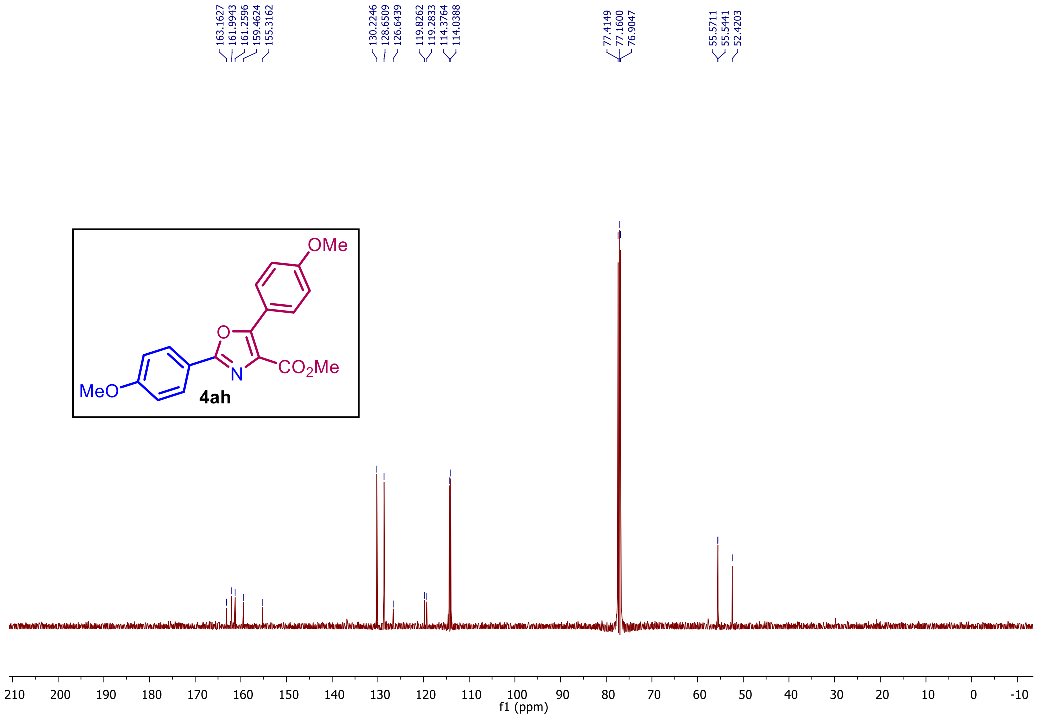


Methyl-5-(4-methoxyphenyl)-2-(4-methoxyphenyl) oxazole-4-carboxylate (**4ah**)

^1H NMR (500 MHz, $CDCl_3$, 24 °C)

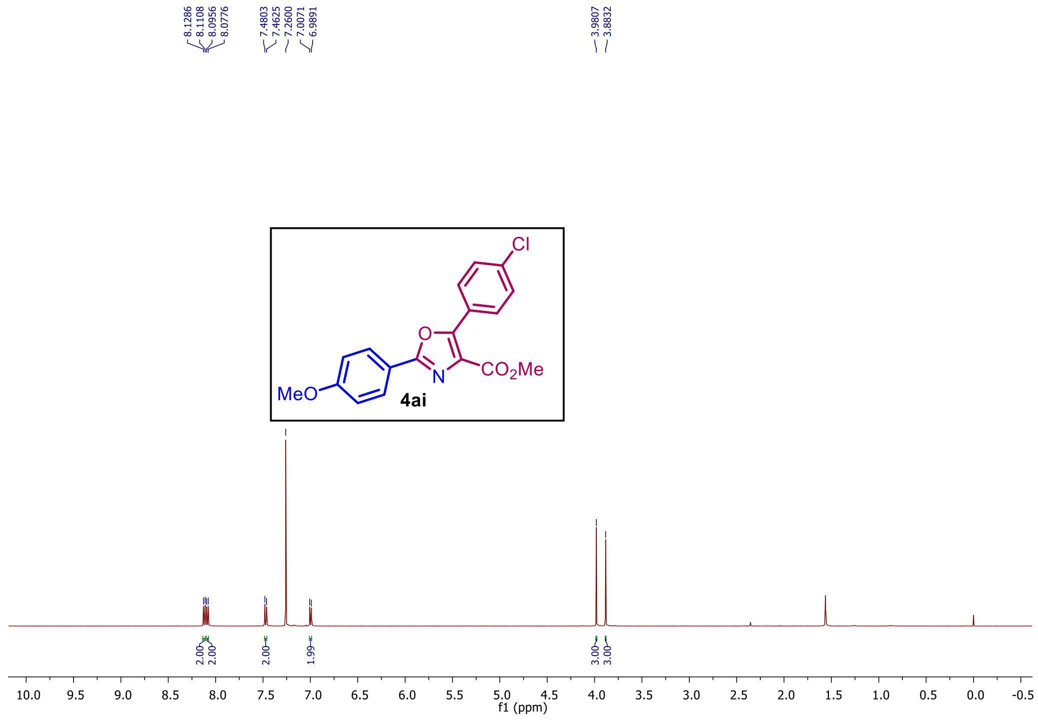


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

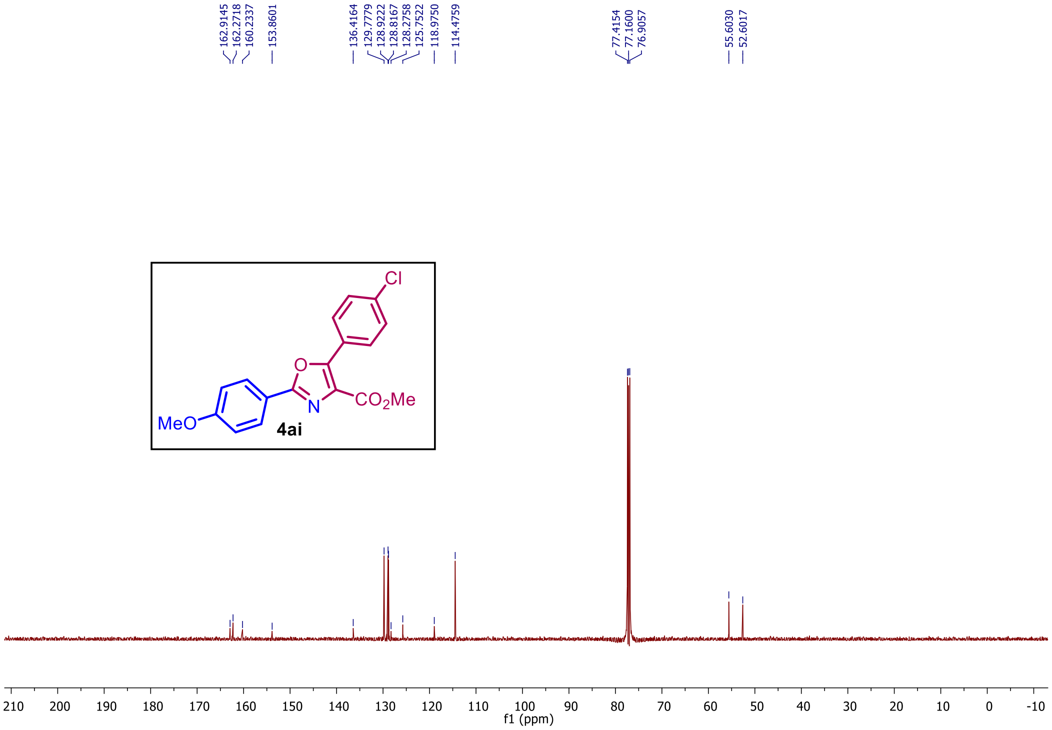


Methyl-5-(4-chlorophenyl)-2-(4-methoxyphenyl) oxazole-4-carboxylate (**4ai**)

^1H NMR (500 MHz, $CDCl_3$, 24 °C)

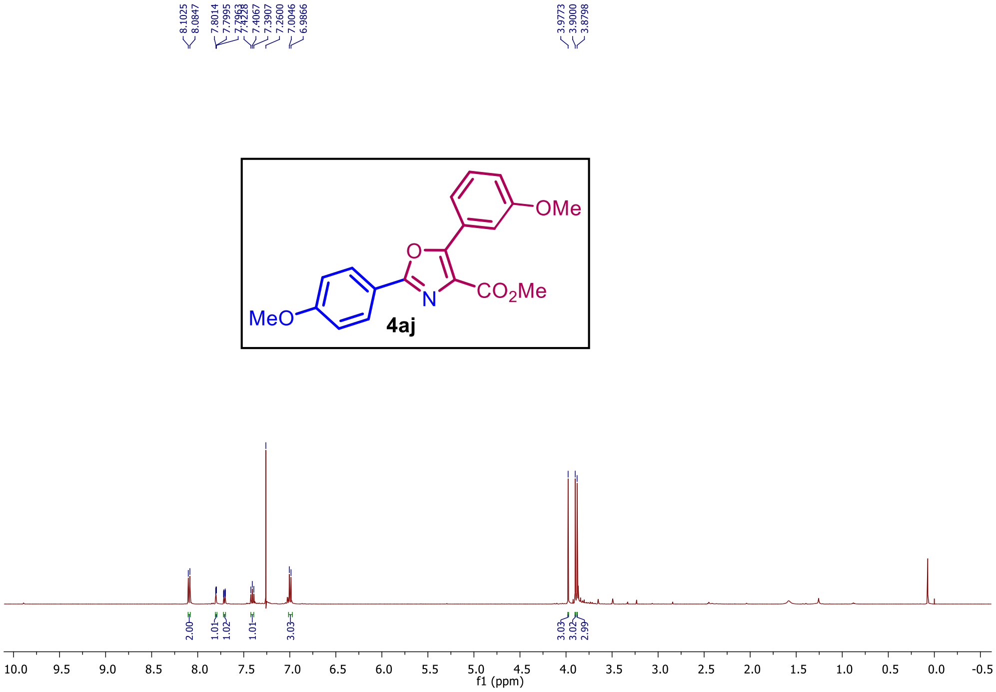


$^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$, 24 °C)

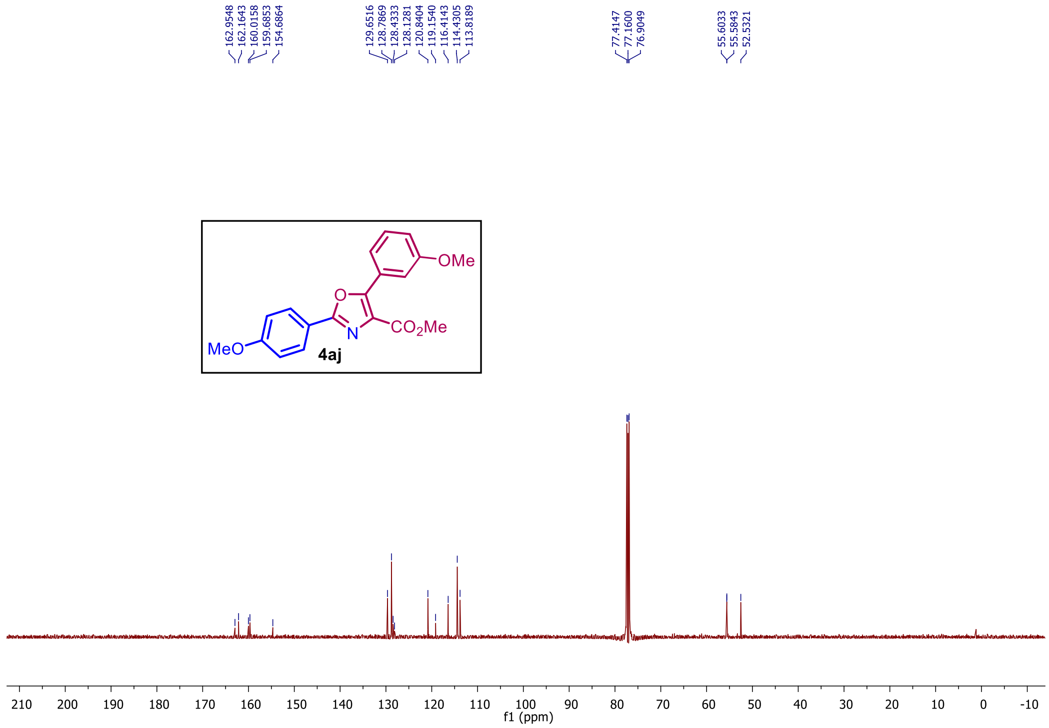


Methyl 5-(3-methoxyphenyl)-2-(4-methoxyphenyl) oxazole-4-carboxylate (**4aj**)

^1H NMR (500 MHz, CDCl$_3$, 24 °C)

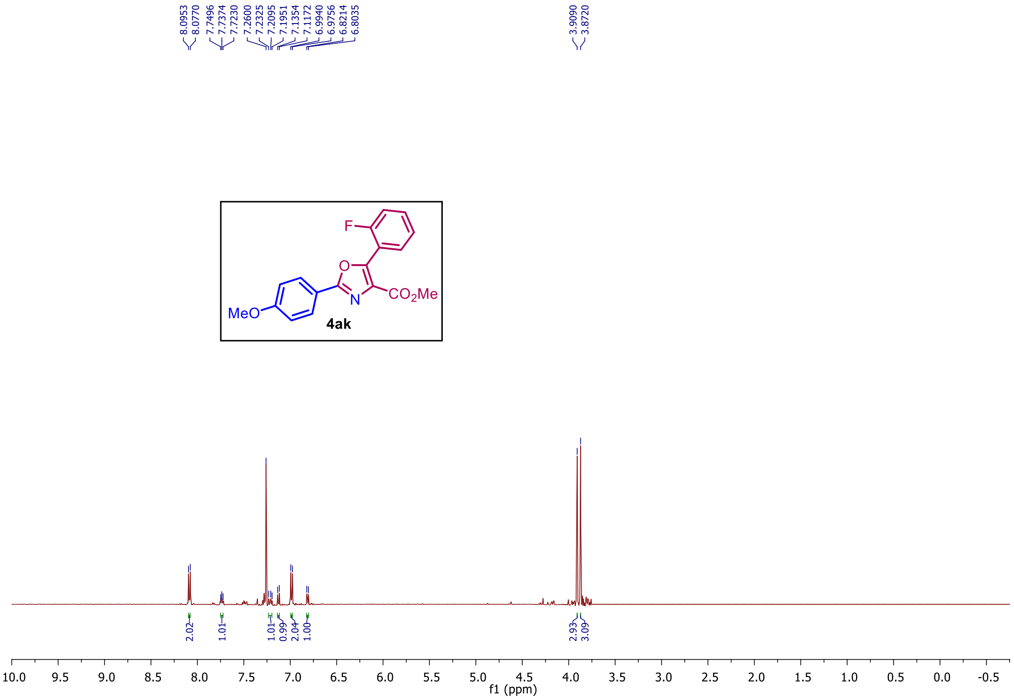


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

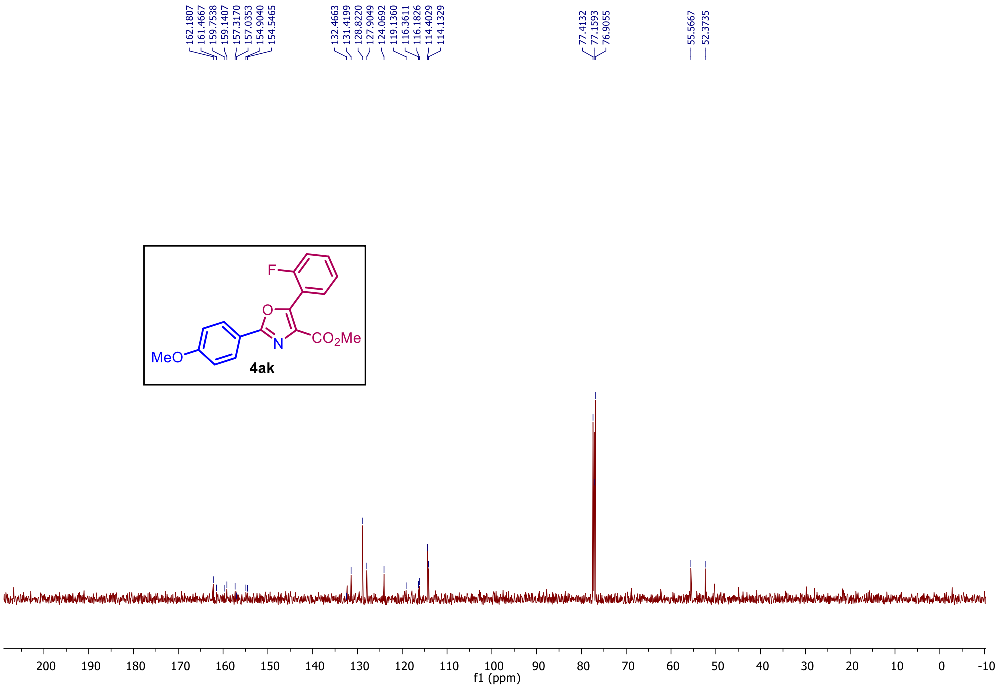


Methyl 5-(2-fluorophenyl)-2-(4-methoxyphenyl) oxazole-4-carboxylate (**4ak**)

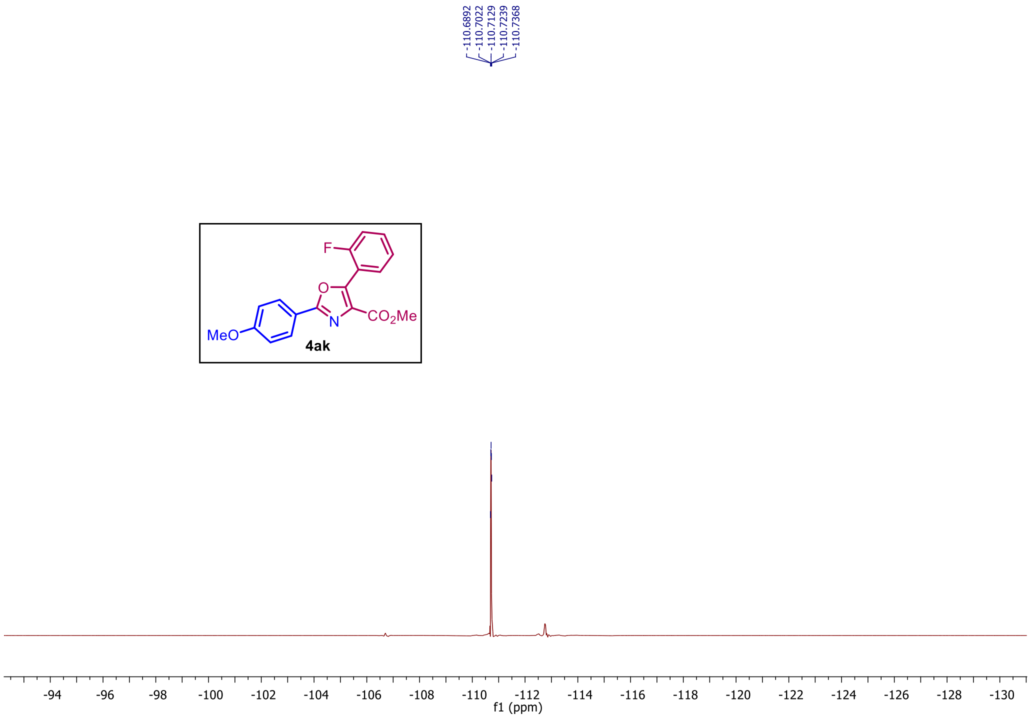
^1H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)

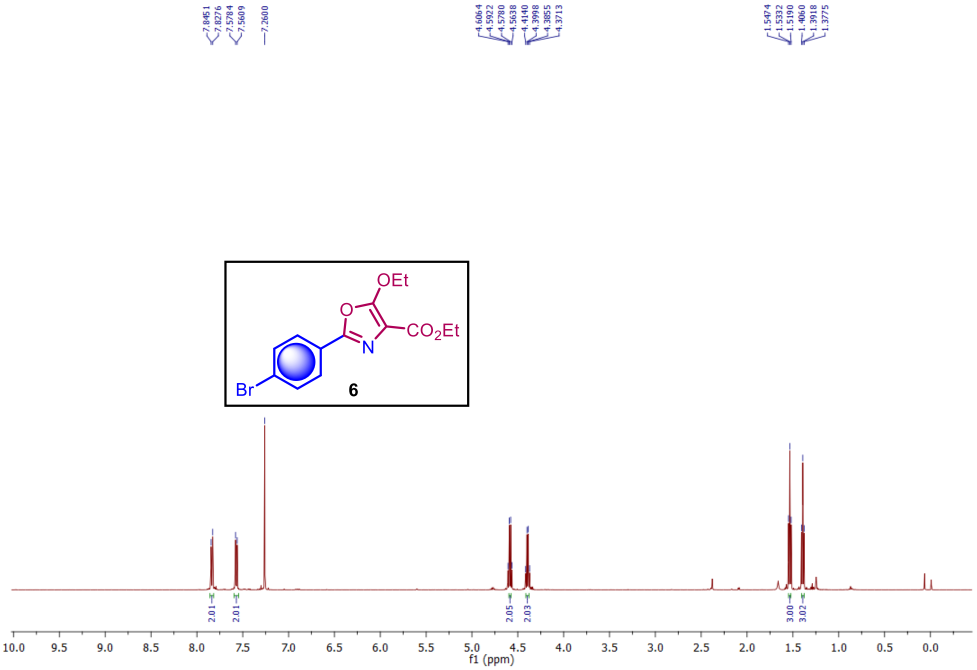


^{19}F NMR (471 MHz, $CDCl_3$, 24 °C)

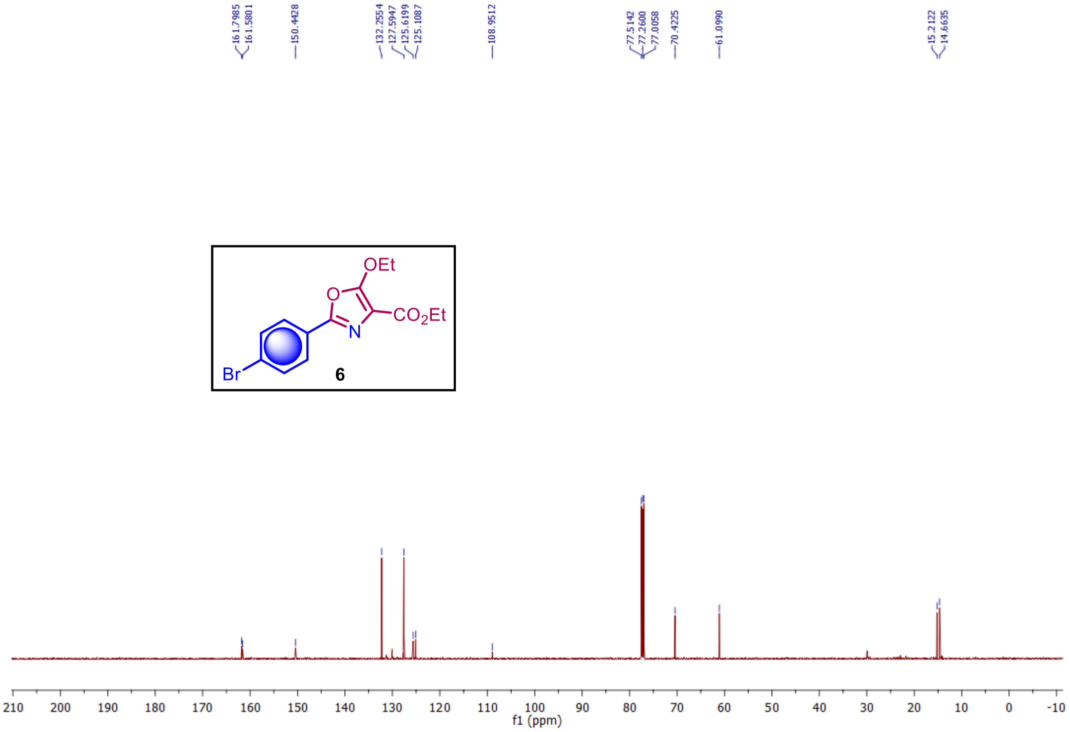


Ethyl 2-(4-bromophenyl)-5-ethoxyoxazole-4-carboxylate (**6**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)

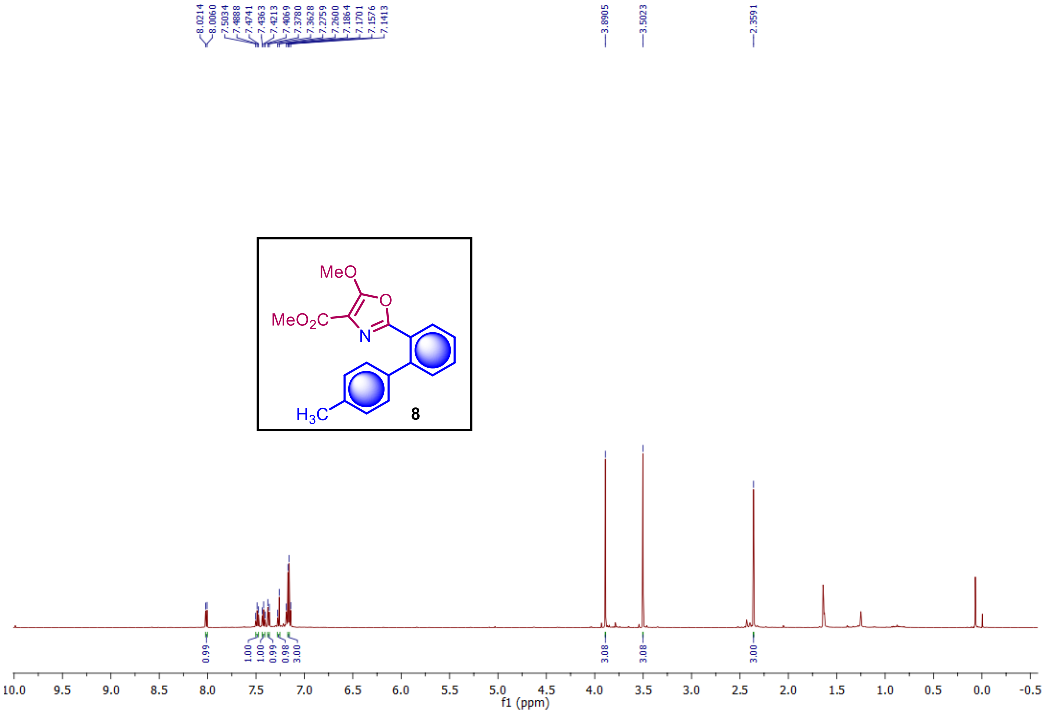


$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)



Methyl 5-methoxy-2-(4'-methyl-[1,1'-biphenyl]-2-yl)oxazole-4-carboxylate (**8**)

^{1}H NMR (500 MHz, $CDCl_3$, 24 °C)



$^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$, 24 °C)