Supporting information for

One-pot modular synthesis of 3-oxazolines from 2*H*-azirines, diazo compounds, and *m*-CPBA enabled by 2-azadiene–oxene (4 + 1) cycloaddition

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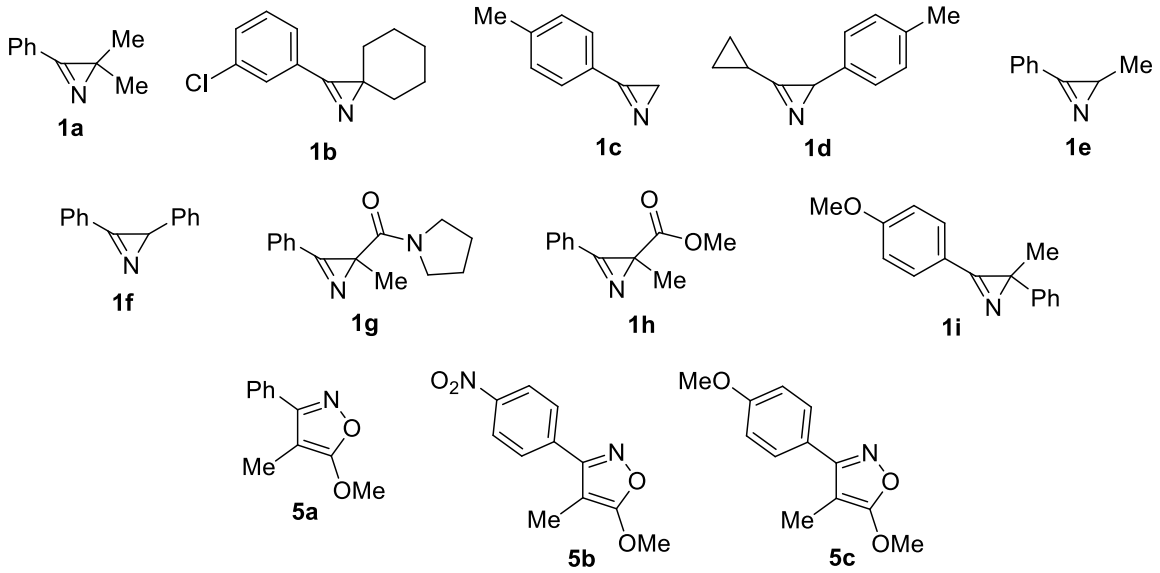
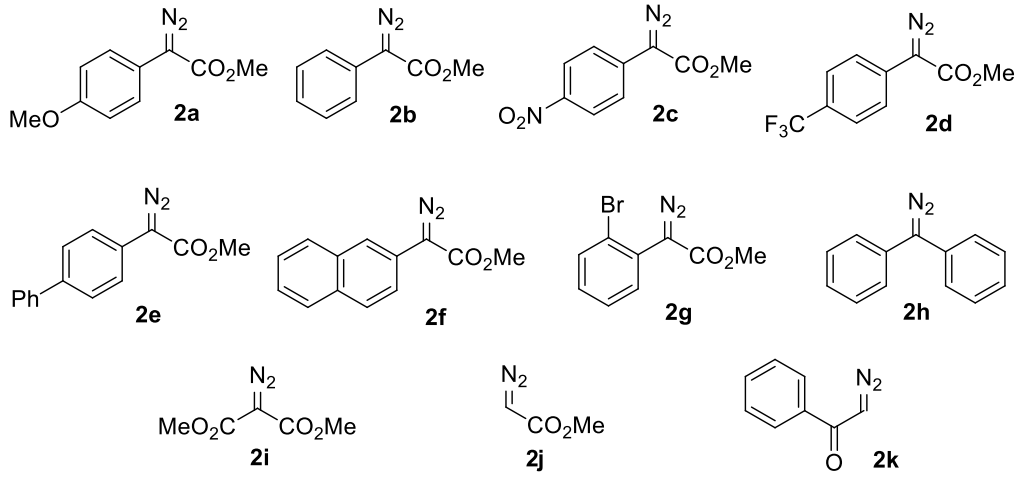
I. General Experimental Details

Melting points were determined on a melting point apparatus and are uncorrected. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were recorded in $CDCl_3$. Chemical shifts (δ) are reported in parts per million downfield from tetramethylsilane. Structural assignments were made with additional information from HSQC, HMBC, and NOESY experiments. High-resolution mass spectra were recorded on an HRMS-ESI-QTOF instrument, electrospray ionization. Thin-layer chromatography (TLC) was conducted on aluminum sheets precoated with SiO_2 ALUGRAM SIL G/UV254. Column chromatography was performed on silica gel 60 M (0.04−0.063 mm). All solvents were distilled and dried prior to use. Dichloromethane (DCM) was distilled over CaH_2 and stored over MS 4Å. Toluene was distilled and stored over sodium metal. Commercially available *m*-chloroperoxybenzoic acid and Oxone were used.

Structures of Azirines 1a−i and Isoxazoles 5a−d



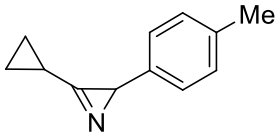
Structures of Diazo Compounds 2a−k



II. Synthesis and Characterization of Starting Compounds

Azirines **1a**,**e**,**g–i**,[1] **1b**,[2] **1c**,[3] **1f**,[4] diazo compounds **2a**–**d**,**f**,[5] **2e**,[6] **2g**,[7] **2h**,[8] **2i**,[9] **2j**,[10] **2k**[11] and isoxazole **5a**[1] are known compounds, which were prepared by the reported procedures. Isoxazole **5c** is a known compound, but in this work it was obtained using a method different from that described in the literature.[12]

3-Cyclopropyl-2-(4-methylphenyl)-2*H*-azirine (1d)



Azirine **1d** (127 mg, 11%) was obtained by thermolysis of (2-azido-2-cyclopropylvinyl)benzene (1.89 g) according to the reported procedure.[1]

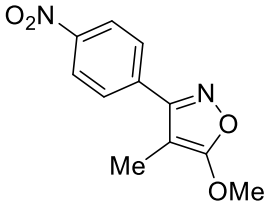
Pale-yellow solid, mp 35–37 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 2.84 (s, 1H), 2.34 (s, 3H), 2.21 (tt, *J* = 7.8, 4.6 Hz, 1H), 1.27 – 1.14 (m, 3H), 0.92 – 0.87 (m, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.8, 138.3, 136.3, 128.9, 125.5, 32.7, 21.0, 8.2, 7.5, 7.2.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{14}N^+$ 172.1121; Found 172.1121.

5-Methoxy-4-methyl-3-(4-nitrophenyl)isoxazole (5b)



Isoxazole **5b** (1.65 g, 77%) was obtained by methylation of 4-methyl-3-(4-nitrophenyl)isoxazol-5(4*H*)-one (2.0 g) with diazomethane according to the reported procedure.[1]

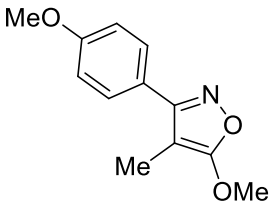
Pale-yellow solid, mp 125–126 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.9 Hz, 2H), 7.87 (d, *J* = 8.9 Hz, 2H), 4.18 (s, 3H), 2.01 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.2, 162.6, 148.4, 136.6, 128.5, 123.9, 86.7, 58.0, 6.4.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{11}N_2O_4^+$ 235.0713; Found 235.0716.

5-Methoxy-3-(4-methoxyphenyl)-4-methylisoxazole (5c)



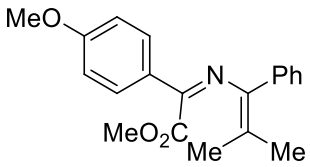
Isoxazole **5c** (0.47 g, 63%) was obtained by methylation of 3-(4-methoxyphenyl)-4-methylisoxazol-5(4*H*)-one (0.70 g) with diazomethane according to the reported procedure.[1] Analytical data are in agreement with published data.[10]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 4.13 (s, 3H), 3.87 (s, 3H), 1.97 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ 169.4, 164.3, 160.5, 129.0, 122.7, 114.1, 86.3, 57.7, 55.3, 6.6.

III. Synthesis and Characterization of 2-Azabuta-1,3-dienes 3

Methyl 2-(4-methoxyphenyl)-2-((2-methyl-1-phenylprop-1-en-1-yl)imino)acetate (3a)



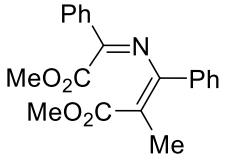
Azirine **1a** (174 mg, 1.2 mmol), diazo compound **2a** (297 mg, 1.4 mmol), $Rh_2(OAc)_4$ (2.5 mol %, 13.3 mg), and anhydrous toluene (0.8 mL) were placed in a screw cap glass tube under an ambient atmosphere. The cap was screwed, and the resulting mixture was stirred at 130 °C (oil bath temperature) for 1 min until complete consumption of the azirine (controlled by TLC). The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel (eluent EtOAc – hexane, 1:10) to give 2-azabuta-1,3-diene **3a** (349 mg, 90%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 8.9 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.28 – 7.23 (m, 1H), 6.93 (d, J = 8.9 Hz, 2H), 3.86 (s, 3H), 3.58 (s, 3H), 1.88 (s, 3H), 1.79 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 166.3, 162.1, 156.8, 141.9, 138.2, 129.8, 129.3, 127.7, 127.3, 127.0, 121.0, 113.9, 55.4, 51.4, 21.2, 20.1.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{22}NO_3^+$ 324.1594; Found 324.1590.

Methyl (*Z*)-3-((2-methoxy-2-oxo-1-phenylethylidene)amino)-2-methyl-3-phenylacrylate (3v)



Azirine **1h** (56.7 mg, 0.3 mmol), diazo compound **2b** (64 mg, 0.36 mmol), $Cu(tfacac)_2$ (5 mol %, 5.6 mg), and anhydrous toluene (0.2 mL) were placed in a screw cap glass tube under an ambient atmosphere. The cap was screwed, and the resulting mixture was stirred at 110 °C (oil bath temperature) for 1 min until complete consumption of the azirine (controlled by TLC). The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel (eluent EtOAc – hexane, 1:6) to give 2-azabuta-1,3-diene **3v** (83 mg, 82%).

Yellow solid, mp 76–77 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (br.s, 2H), 7.51 – 7.33 (m, 8H), 3.85 (s, 3H), 3.69 (s, 3H), 1.93 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 168.4, 164.0, 156.6, 155.7, 137.0, 133.7, 131.4, 128.7, 128.6, 128.5, 128.2, 128.1, 107.8, 52.1, 51.6, 16.1.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{20}NO_4^+$ 338.1387; Found 338.1395.

IV. Synthesis and Characterization of 3-Oxazolines 4

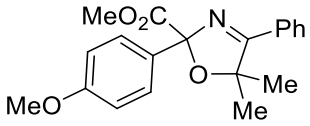
General procedure A for synthesis of oxazolines 4a–p

Azirine **1** (0.18–0.4 mmol), diazo compound **2** (0.24–0.54 mmol), catalyst [$Cu(tfacac)_2$ for diazo compounds **2a–h** (5 mol %) or $Rh_2(OAc)_4$ for diazo compound **2i** (2.5 mol %)], and anhydrous toluene (0.2 mL) were placed in a screw cap glass tube under an ambient atmosphere. The cap was screwed, and the resulting mixture was stirred at 110–130 °C (oil bath temperature) for 1 min until complete consumption of the azirine (controlled by TLC). After that, the reaction mixture containing 2-azabuta-1,3-diene **3** was diluted with 2 mL of anhydrous DCM, and *m*-CPBA (1.2–3.5 equiv calcd on azirine **1**) was added at 0 °C or room temperature. Stirring was continued for 10 min – 4.5 h until complete consumption of the 2-azabuta-1,3-diene (controlled by TLC). Then, to the reaction mixture containing oxazoline **4**, anhydrous Na_2SO_4 (2 equiv calcd on *m*-CPBA) was added and stirring was continued for 30 min. Finally, anhydrous K_2CO_3 (3 equiv calcd on *m*-CPBA) was added and stirring was continued for 2 h. Resulting mixture was passed through the Celite plug, the solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel to give oxazoline **4**. The details for each synthesis are indicated below.

General procedure B for synthesis of oxazolines 4'r–t

Isoxazole **5** (0.3 mmol), $Cu(tfacac)_2$ (5.6 mg, 5 mol %), and anhydrous toluene (0.2 mL) were placed in a screw cap glass tube under an ambient atmosphere. The cap was screwed, and the resulting mixture was stirred at 120 °C (oil bath temperature) for 3–12 h until complete consumption of the isoxazole (controlled by TLC). After that, diazo compound **2** (0.36–0.42 mmol) was added to the resulting mixture containing 2*H*-azirine **1**, and heating at 110 °C was continued under stirring for 1 min until complete consumption of the azirine (controlled by TLC). After that, the reaction mixture containing 2-azabuta-1,3-diene **3** was diluted with 2 mL of anhydrous DCM, cooled to 0 °C, and *m*-CPBA (3.0–3.6 equiv calcd on isoxazole **5**) was added. Stirring was continued for 50 min until complete consumption of the 2-azabuta-1,3-diene (controlled by TLC). Then, to the reaction mixture containing oxazoline **4'**, anhydrous Na_2SO_4 (2 equiv calcd on *m*-CPBA) was added and stirring was continued for 30 min. Finally, anhydrous K_2CO_3 (3 equiv calcd on *m*-CPBA) was added and stirring was continued for 2 h. Resulting mixture was passed through the Celite plug, the solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel to give oxazoline **4'**. The details for each synthesis are indicated below.

Methyl 2-(4-methoxyphenyl)-5,5-dimethyl-4-phenyl-2,5-dihydrooxazole-2-carboxylate (4a)



Compound **4a** (83 mg, 82%) was obtained from azirine **1a** (43.5 mg, 0.3 mmol) and diazo compound **2a** (74.2 mg, 0.36 mmol) according to the general procedure A [1st step: 130 °C; 2nd step: *m*-CPBA (1.2 equiv), 0 °C, 10 min; eluent for chromatography EtOAc – hexane, 1:4].

Synthesis on 1 mmol scale. Compound **4a** (210 mg, 62%) was obtained from azirine **1a** (143.5 mg, 1 mmol) and diazo compound **2a** (274 mg, 1.2 mmol) according to the general procedure A [1st step: toluene (0.6 mL), 130 °C; 2nd step: *m*-CPBA (1.3 equiv), 0 °C, 15 min; eluent for chromatography EtOAc – hexane, 1:4].

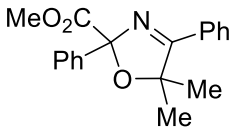
*Synthesis from azabutadiene **3a** using Oxone*. A solution of azadiene **3a** (40 mg, 0.12 mmol) and Oxone (92 mg, 0.16 mmol) in DMF (0.5 mL) was stirred at room temperature for 12 h until complete consumption of the azadiene (controlled by TLC). Oxazoline **4a** (14 mg, 33%) was isolated by column chromatography on silica gel (eluent for chromatography EtOAc–hexane, 1:5). Colorless solid, mp 84–86 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 6.9 Hz, 2H), 7.66 (d, *J* = 8.8 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.46 (t, *J* = 7.2 Hz, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.78 (s, 3H), 1.79 (s, 3H), 1.57 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.0, 170.9, 159.6, 132.7, 131.2, 130.4, 128.6, 128.5, 127.4, 113.5, 106.5, 90.8, 55.2, 52.9, 27.2, 27.1.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{22}NO_4^+$ 340.1543; Found 340.1541.

Methyl 5,5-dimethyl-2,4-diphenyl-2,5-dihydrooxazole-2-carboxylate (4b)



Compound **4b** (76 mg, 82%) was obtained from azirine **1a** (43.5 mg, 0.3 mmol) and diazo compound **2b** (63.4 mg, 0.36 mmol) according to the general procedure A [1st step: 130 °C; 2nd step: *m*-CPBA (1.2 equiv), 0 °C, 10 min; eluent for chromatography EtOAc – hexane, 1:5].

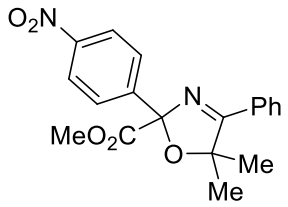
Colorless solid, mp 78–80 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 6.9 Hz, 2H), 7.75 (d, *J* = 6.7 Hz, 2H), 7.54 – 7.43 (m, 3H), 7.43 – 7.33 (m, 3H), 3.78 (s, 3H), 1.80 (s, 3H), 1.58 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 174.2, 170.7, 140.3, 131.2, 130.3, 128.6, 128.5, 128.4, 128.1, 126.0, 106.6, 90.9, 53.0, 27.2, 27.1.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{20}NO_3^+$ 310.1438; Found 310.1437.

Methyl 5,5-dimethyl-2-(4-nitrophenyl)-4-phenyl-2,5-dihydrooxazole-2-carboxylate (4c)



Compound **4c** (83 mg, 59%) was obtained from azirine **1a** (43.5 mg, 0.3 mmol) and diazo compound **2c** (80.0 mg, 0.36 mmol) according to the general procedure A [1st step: 130 °C; 2nd step: *m*-CPBA (1.2 equiv), 0 °C, 15 min; eluent for chromatography EtOAc – benzene, 1:100].

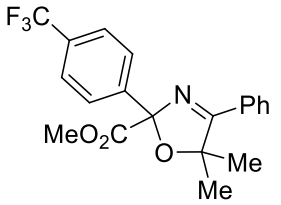
Colorless solid, mp 104–106 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.9 Hz, 2H), 7.98 – 7.94 (m, 4H), 7.50 – 7.46 (m, 1H), 7.48 (dd, *J* = 8.3, 6.5 Hz, 2H), 3.79 (s, 3H), 1.84 (s, 3H), 1.58 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.1, 169.7, 147.9, 147.2, 131.7, 129.8, 128.7, 128.6, 127.5, 123.3, 106.1, 91.8, 53.3, 27.4, 27.1.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{19}H_{18}N_2NaO_5^+$ 377.1108; Found 377.1101.

Methyl 5,5-dimethyl-4-phenyl-2-(4-(trifluoromethyl)phenyl)-2,5-dihydrooxazole-2-carboxylate (4d)



Compound **4d** (69 mg, 61%) was obtained from azirine **1a** (43.5 mg, 0.3 mmol) and diazo compound **2d** (87.8 mg, 0.36 mmol) according to the general procedure A [1st step: 130 °C; 2nd step: *m*-CPBA (1.4 equiv), 0 °C, 20 min; eluent for chromatography EtOAc – hexane, 1:4].

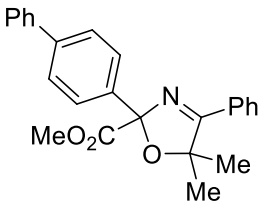
Colorless solid, mp 75–78 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.0 Hz, 2H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.56 – 7.50 (m, 1H), 7.49 – 7.45 (m, 2H), 3.79 (s, 3H), 1.83 (s, 3H), 1.58 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.7, 170.1, 144.2, 131.5, 130.5 (q, *J* = 32.4 Hz), 130.0, 128.7, 128.6, 126.7, 124.1 (q, *J* = 271.4 Hz), 125.1 (q, *J* = 3.8 Hz), 106.3, 91.5, 53.2, 27.3, 27.1.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{20}H_{19}F_3NO_3^+$ 378.1312; Found 378.1309.

Methyl 2-([1,1'-biphenyl]-4-yl)-5,5-dimethyl-4-phenyl-2,5-dihydrooxazole-2-carboxylate (4e)



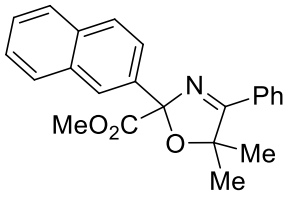
Compound **4e** (92 mg, 80%) was obtained from azirine **1a** (43.5 mg, 0.3 mmol) and diazo compound **2e** (90.7 mg, 0.36 mmol) according to the general procedure A [1st step: 130 °C; 2nd step: *m*-CPBA (1.5 equiv), 0 °C, 20 min; eluent for chromatography EtOAc – hexane, 1:5] as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 6.8 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.64 – 7.61 (m, 4H), 7.55 – 7.42 (m, 5H), 7.40 – 7.33 (m, 1H), 3.81 (s, 3H), 1.83 (s, 3H), 1.62 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.3, 170.7, 141.3, 140.7, 140.0, 131.3, 130.4, 128.7, 128.60, 128.57, 127.3, 127.1, 126.9, 126.5, 106.6, 91.0, 53.0, 27.3, 27.2.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{25}H_{24}NO_3^+$ 386.1751; Found 386.1746.

Methyl 5,5-dimethyl-2-(naphthalen-2-yl)-4-phenyl-2,5-dihydrooxazole-2-carboxylate (4f)



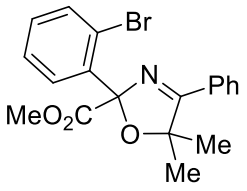
Compound **4f** (80 mg, 74%) was obtained from azirine **1a** (43.5 mg, 0.3 mmol) and diazo compound **2f** (82.0 mg, 0.36 mmol) according to the general procedure A [1st step: 130 °C; 2nd step: *m*-CPBA (1.5 equiv), 0 °C, 20 min; eluent for chromatography EtOAc – hexane, 1:6] as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 8.00 (d, *J* = 6.7 Hz, 2H), 7.93 – 7.85 (m, 4H), 7.55 – 7.45 (m, 5H), 3.79 (s, 3H), 1.84 (s, 3H), 1.60 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.5, 170.7, 137.9, 133.2, 132.9, 131.3, 130.4, 128.61, 128.57, 128.5, 127.9, 127.6, 126.3, 126.1, 125.1, 124.2, 106.8, 91.0, 53.0, 27.3, 27.2.

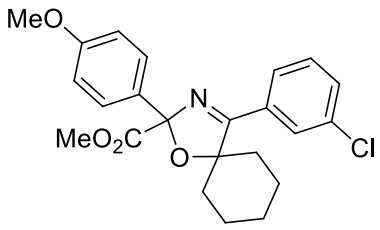
HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{22}NO_3^+$ 360.1594; Found 360.1587.

Methyl 2-(2-bromophenyl)-5,5-dimethyl-4-phenyl-2,5-dihydrooxazole-2-carboxylate (4g)



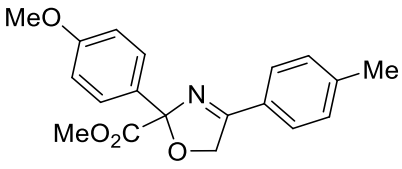
Compound **4g** (40 mg, 34%) was obtained from azirine **1a** (43.5 mg, 0.3 mmol) and diazo compound **2g** (91.8 mg, 0.36 mmol) according to the general procedure A [1st step: 130 °C; 2nd step: *m*-CPBA (2.8 equiv), 20 °C, 60 min; eluent for chromatography EtOAc – hexane, 1:4].
Colorless solid, mp 110–112 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.9 Hz, 2H), 7.69 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.64 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.49 – 7.45 (m, 2H), 7.34 (td, *J* = 7.8, 1.3 Hz, 1H), 7.23 (td, *J* = 7.7, 1.8 Hz, 1H), 3.82 (s, 3H), 1.87 (s, 3H), 1.60 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 175.7, 170.0, 140.4, 133.7, 131.5, 130.2, 129.8, 128.72, 128.65, 127.9, 127.1, 122.0, 106.8, 91.6, 53.2, 27.7, 27.2.
HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{19}{}^{79}BrNO_3{}^+$ 388.0543; Found 388.0544.

Methyl 4-(3-chlorophenyl)-2-(4-methoxyphenyl)-1-oxa-3-azaspiro[4.5]dec-3-ene-2-carboxylate (4h)



Compound **4h** (57.1 mg, 69%) was obtained from azirine **1b** (44 mg, 0.2 mmol) and diazo compound **2a** (49.5 mg, 0.24 mmol) according to the general procedure A [1st step: 130 °C; 2nd step: *m*-CPBA (1.5 equiv), 0 °C, 15 min; eluent for chromatography EtOAc – hexane, 1:6] as a pale-yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (t, *J* = 2.0 Hz, 1H), 7.75 (dt, *J* = 7.8, 1.2 Hz, 1H), 7.68 (d, *J* = 8.9 Hz, 2H), 7.46 (ddd, *J* = 7.8, 2.0, 1.2 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 2.03 – 1.66 (m, 8H), 1.59 (d, *J* = 14.6 Hz, 1H), 1.42 – 1.19 (m, 1H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.1, 170.9, 159.6, 134.7, 133.1, 132.8, 130.9, 129.7, 128.7, 127.3 (2C), 126.5, 106.5, 93.1, 55.2, 52.9, 34.6 (2C), 25.0, 21.99, 21.97.
HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{23}H_{25}{}^{35}ClNO_4{}^+$ 414.1467; Found 414.1471.

Methyl 2-(4-methoxyphenyl)-4-(4-methylphenyl)-2,5-dihydrooxazole-2-carboxylate (4i)



Compound **4i** (40.0 mg, 41%) was obtained from azirine **1c** (39.3 mg, 0.3 mmol) and diazo compound **2a** (105.0 mg, 0.51 mmol) according to the general procedure A [1st step: 110 °C; 2nd step: *m*-CPBA (1.6 equiv), 0 °C, 20 min; eluent for chromatography EtOAc – hexane, 1:4].

Colorless solid, mp 82–84 °C.

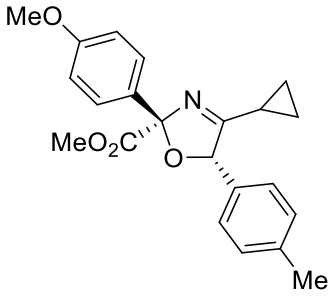
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.31 (d, *J* = 13.6 Hz, 1H), 5.15 (d, *J* = 13.6 Hz, 1H), 3.83 (s, 3H), 3.78 (s, 3H), 2.43 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.4, 169.7, 159.8, 142.6, 131.5, 129.5, 128.2, 127.52, 127.45, 113.6, 111.3, 75.2, 55.2, 52.9, 21.6.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{20}NO_4^+$ 326.1387; Found 326.1388.

Methyl 4-cyclopropyl-2-(4-methoxyphenyl)-5-(4-methylphenyl)-2,5-dihydrooxazole-2-carboxylate (4j)

Compounds **(2*RS*,5*SR*)-4j** (24.1 mg, 22%) and **(2*RS*,5*RS*)-4j** (41.6 mg, 38%) were obtained from azirine **1d** (51.3 mg, 0.3 mmol) and diazo compound **2a** (74.2 mg, 0.36 mmol) according to the general procedure A [1st step: 110 °C; 2nd step: *m*-CPBA (2.4 equiv), 0 °C, 20 min; eluent for chromatography EtOAc – hexane, 1:8].

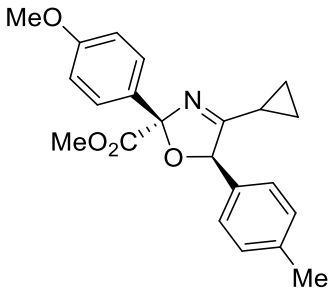


(2*RS*,5*SR*)-4j. Pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.9 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.60 (s, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.39 (s, 3H), 1.38 (tt, *J* = 8.1, 4.8 Hz, 1H), 1.20 – 1.15 (m, 1H), 1.00 – 0.83 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 177.9, 170.5, 159.7, 138.7, 133.8, 132.0, 129.5, 127.9, 127.4, 113.5, 109.1, 90.2, 55.2, 52.9, 21.2, 11.00, 10.00 (2C).

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{24}NO_4^+$ 366.1700; Found 366.1701.



(2*RS*,5*RS*)-4j. Pale-yellow oil.

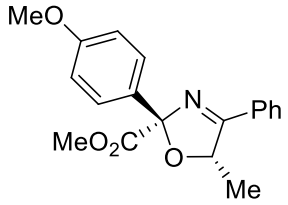
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.89 (s, 1H), 3.85 (s, 3H), 3.76 (s, 3H), 2.34 (s, 3H), 1.38 (tt, *J* = 8.1, 4.8 Hz, 1H), 1.12 (ddd, *J* = 11.7, 6.3, 3.5 Hz, 1H), 1.04 – 0.81 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 178.7, 170.9, 159.6, 138.5, 134.2, 132.2, 129.3, 127.8, 127.6, 113.4, 109.5, 91.1, 55.2, 52.9, 21.2, 11.0, 10.1, 10.0.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{22}H_{24}NO_4^+$ 366.1700; Found 366.1704.

Methyl 2-(4-methoxyphenyl)-5-methyl-4-phenyl-2,5-dihydrooxazole-2-carboxylate (4k)

Compounds **(2*RS*,5*SR*)-4k** (22.1 mg, 17%) and **(2*RS*,5*RS*)-4k** (26.0 mg, 20%) were obtained from azirine **1e** (52.4 mg, 0.4 mmol) and diazo compound **2a** (99.0 mg, 0.48 mmol) according to the general procedure A [1st step: 110 °C; 2nd step: *m*-CPBA (1.5 equiv), 0 °C, 15 min; eluent for chromatography EtOAc – hexane, 1:15].

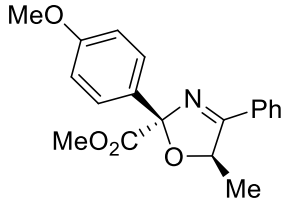


(2*RS*,5*SR*)-4k. Pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 6.7 Hz, 2H), 7.63 (d, *J* = 8.8 Hz, 2H), 7.54 – 7.45 (m, 3H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.56 (q, *J* = 6.7 Hz, 1H), 3.82 (s, 3H), 3.80 (s, 3H), 1.63 (d, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 172.6, 170.9, 159.7, 132.0, 131.6, 130.3, 128.7, 128.6, 127.3, 113.5, 109.3, 82.7, 55.2, 53.0, 20.2.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{20}NO_4^+$ 326.1387; Found 326.1390.



(2*RS*,5*RS*)-4k. Pale-yellow oil.

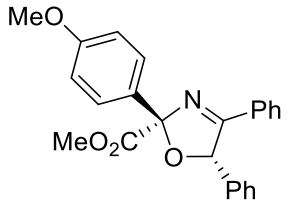
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.8 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.54 – 7.45 (m, 3H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.72 (q, *J* = 6.7 Hz, 1H), 3.84 (s, 3H), 3.77 (s, 3H), 1.43 (d, *J* = 6.7 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 173.0, 170.5, 159.7, 132.5, 131.7, 130.4, 128.7, 128.5, 127.4, 113.5, 109.4, 82.9, 55.2, 53.0, 20.2.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{19}H_{20}NO_4^+$ 326.1387; Found 326.1392.

Methyl 2-(4-methoxyphenyl)-4,5-diphenyl-2,5-dihydrooxazole-2-carboxylate (4l)

Compounds **(2*RS*,5*SR*)-4l** (12 mg, 10%) and **(2*RS*,5*RS*)-4l** (31 mg, 26%) were obtained from azirine **1f** (57.9 mg, 0.3 mmol) and diazo compound **2a** (74.2 mg, 0.36 mmol) according to the general procedure A [1st step: 110 °C; 2nd step: *m*-CPBA (2.2 equiv), 0 °C, 20 min; eluent for chromatography EtOAc – hexane, 1:7].

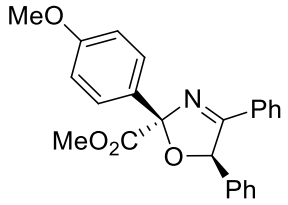


(2*RS*,5*SR*)-4l. Colorless solid, mp 125–126 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 4H), 7.44 – 7.36 (m, 6H), 7.33 – 7.29 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.17 (s, 1H), 3.84 (s, 3H), 3.80 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 170.3, 169.5, 159.9, 137.3, 131.8, 131.5, 130.2, 129.1, 129.03, 129.01, 128.6, 128.4, 127.5, 113.6, 109.7, 89.1, 55.3, 53.0.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{22}NO_4^+$ 388.1543; Found 388.1539.



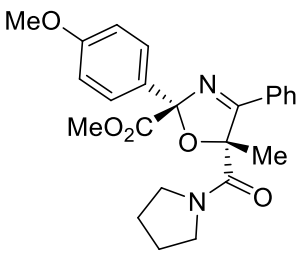
(2*RS*,5*RS*)-4l. Pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.0 Hz, 2H), 7.69 (d, *J* = 8.8 Hz, 2H), 7.43 – 7.36 (m, 1H), 7.33 – 7.29 (m, 2H), 7.26 – 7.24 (m, 3H), 7.15 – 7.13 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.44 (s, 1H), 3.85 (s, 3H), 3.80 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 170.5, 170.3, 159.7, 137.6, 131.9, 131.4, 130.3, 128.9, 128.80, 128.75, 128.5, 128.4, 127.8, 113.5, 110.2, 89.8, 55.2, 53.1.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{22}NO_4^+$ 388.1543; Found 388.1545.

(2*RS*,5*SR*)-Methyl 2-(4-methoxyphenyl)-5-methyl-4-phenyl-5-(pyrrolidine-1-carbonyl)-2,5-dihydrooxazole-2-carboxylate (4m)



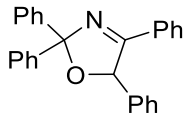
Compound **4m** (21.0 mg, 27%) was obtained from azirine **1g** (50.0 mg, 0.18 mmol) and diazo compound **2a** (52.0 mg, 0.25 mmol) according to the general procedure A [1st step: 110 °C; 2nd step: *m*-CPBA (5.0 equiv), 0 °C, 60 min; eluent for chromatography EtOAc – benzene, from 1:50 to 1:10] as a pale-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.0 Hz, 2H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.54 – 7.50 (m, 1H), 7.47 – 7.44 (m, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 3.53 – 3.43 (m, 1H), 3.40 – 3.30 (m, 1H), 2.98 – 2.91 (m, 1H), 2.83 – 2.73 (m, 1H), 1.83 (s, 3H), 1.61 – 1.57 (m, 1H), 1.55 – 1.37 (m, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 171.4, 170.6, 166.7, 159.9, 132.0 (2C), 130.3, 129.7, 129.0, 128.7, 127.6, 108.4, 92.6, 55.2, 53.0, 47.8, 46.3, 26.4, 23.3, 22.9.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{24}H_{27}N_2O_5^+$ 423.1914; Found 423.1918.

2,2,4,5-Tetraphenyl-2,5-dihydrooxazole (4n)



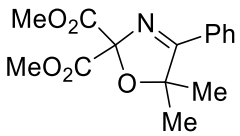
Compound **4n** (56.0 mg, 50%, calcd on azirine) was obtained from azirine **1f** (57.9 mg, 0.3 mmol) and diazo compound **2h** (105.0 mg, 0.54 mmol) according to the general procedure A with isolation of the intermediate crude azabutadiene **3l** (85.0 mg, 79%) [1st step: 110 °C eluent for chromatography EtOAc – hexane, 1:15; 2nd step: *m*-CPBA (1.5 equiv), 0 °C, 15 min; eluent for chromatography EtOAc – hexane, 1:10] as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.1 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.65 (d, *J* = 7.3 Hz, 2H), 7.39 – 7.28 (m, 12H), 7.23 – 7.21 (m, 2H), 6.24 (s, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 167.1, 144.7, 144.6, 138.2, 131.0, 130.9, 128.78, 128.76, 128.7, 128.6, 128.4, 128.2, 128.0, 127.6, 127.5, 126.5, 126.2, 112.3, 88.5.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{27}H_{22}NO^+$ 376.1696; Found 376.1699.

Dimethyl 5,5-dimethyl-4-phenyloxazole-2,2(5*H*)-dicarboxylate (4o)



<u>*Synthesis from azirine.*</u> Compound **4o** (42.8 mg, 49%) was obtained from azirine **1a** (43.5 mg, 0.3 mmol) and diazo compound **2i** (57.0 mg, 0.36 mmol) according to the general procedure A [1st step: 110 °C; 2nd step: *m*-CPBA (1.6 equiv), 20 °C, 4.5 h; eluent for chromatography EtOAc – hexane, 1:5] as a colorless oil.

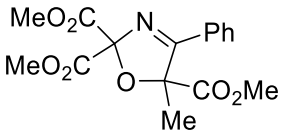
*Synthesis from oxirane **6o***. To a solution of oxirane **6o** (20 mg) in $CDCl_3$ (0.5 mL), benzoic acid (2 mg) or *p*-toluenesulfonic acid (2 mg) was added and the resulting reaction mixture was stirred at room temperature for 24 h (for $PhCO_2H$) or 10 min (for TsOH). According to ^1H NMR spectroscopy, the yields of compound **4o** were quantitative in both reactions.

^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 7.0 Hz, 2H), 7.57 – 7.52 (m, 1H), 7.49 – 7.45 (m, 2H), 3.88 (s, 6H), 1.75 (s, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 177.5, 167.2, 131.9, 129.5, 128.8, 128.7, 104.7, 92.6, 53.2, 27.2.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{18}NO_5^+$ 292.1179; Found 292.1181.

Trimethyl 5-methyl-4-phenyloxazole-2,2,5(5*H*)-tricarboxylate (4p)



Compound **4p** (13.0 mg, 13%) was obtained from azirine **1h** (56.7 mg, 0.3 mmol) and diazo compound **2i** (57.0 mg, 0.36 mmol) according to the general procedure A [1st step: 110 °C; 2nd step: *m*-CPBA (3.6 equiv), 20 °C, 40 min; eluent for chromatography EtOAc – hexane, 1:4] as a colorless oil.

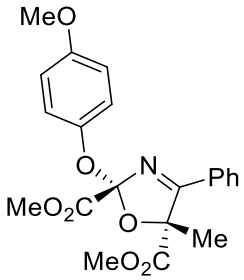
^1H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 2H), 7.57 – 7.53 (m, 1H), 7.48 – 7.44 (m, 2H), 3.91 (s, 3H), 3.90 (s, 3H), 3.76 (s, 3H), 1.90 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.2, 169.9, 166.4, 166.1, 132.5, 129.0, 128.9, 128.6, 107.6, 92.9, 53.6, 53.3 (2C), 22.0.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{16}H_{18}NO_7^+$ 336.1078; Found 336.1083.

Dimethyl 2-(4-methoxyphenoxy)-5-methyl-4-phenyl-2,5-dihydrooxazole-2,5-dicarboxylate (4'r)

Compounds **(2*RS*,5*RS*)-4'r** (37.9 mg, 33%) and **(2*RS*,5*SR*)-4'r** (31.0 mg, 27%) were obtained from isoxazole **5a** (56.7 mg, 0.3 mmol) and diazo compound **2a** (74.2 mg, 0.36 mmol) according to the general procedure B [1st step: 3 h; 3rd step: *m*-CPBA (3.0 equiv); eluent for chromatography EtOAc – hexane, 1:6].

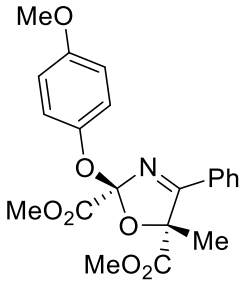


(2*RS*,5*RS*)-4'r. Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.1 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.48 – 7.44 (m, 2H), 7.14 (d, *J* = 9.0 Hz, 2H), 6.78 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H), 3.76 (s, 3H), 3.46 (s, 3H), 1.88 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 174.6, 169.1, 166.6, 156.3, 146.0, 132.6, 129.3, 128.8, 128.6, 123.7, 121.4, 113.8, 92.0, 55.4, 53.3, 53.1, 22.5.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{21}NNaO_7^+$ 422.1210; Found 422.1217.



(2*RS*,5*SR*)-4'r. Colorless solid, mp 97–99 °C.

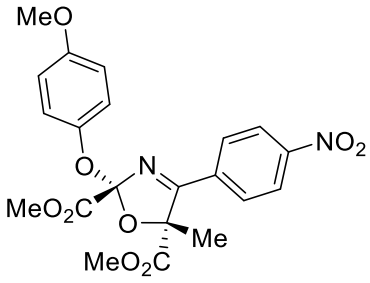
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.7 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 8.5 Hz, 2H), 3.93 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 1.29 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 173.9, 169.5, 165.7, 157.0, 144.4, 132.6, 129.0, 128.9, 128.0, 125.5, 122.1, 113.7, 92.1, 55.4, 53.20, 53.15, 21.3.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{21}NNaO_7^+$ 422.1210; Found 422.1219.

Dimethyl 2-(4-methoxyphenoxy)-5-methyl-4-(4-nitrophenyl)-2,5-dihydrooxazole-2,5-dicarboxylate (4's)

Compounds **(2*RS*,5*RS*)-4's** (20.5 mg, 16%) and **(2*RS*,5*SR*)-4's** (20.5 mg, 16%) were obtained from isoxazole **5b** (70.2 mg, 0.3 mmol) and diazo compound **2a** (86.5 mg, 0.42 mmol) according to the general procedure B [1st step: 12 h; 3rd step: *m*-CPBA (3.6 equiv); eluent for chromatography EtOAc – hexane, 1:6].

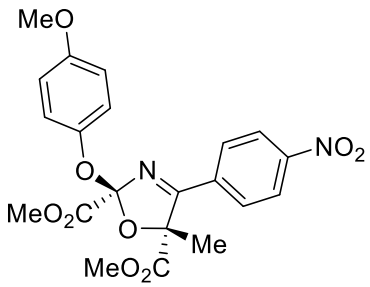


(2*RS*,5*RS*)-4's. Colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.8 Hz, 2H), 8.11 (d, *J* = 8.8 Hz, 2H), 7.11 (d, *J* = 9.1 Hz, 2H), 6.78 (d, *J* = 9.1 Hz, 2H), 3.89 (s, 3H), 3.76 (s, 3H), 3.50 (s, 3H), 1.89 (s, 3H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 173.1, 168.5, 166.0, 156.6, 149.9, 145.4, 134.2, 130.4, 123.8 (2C), 121.0, 113.8, 92.2, 55.4, 53.6, 53.3, 22.5.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{20}N_2NaO_9^+$ 467.1061; Found 467.1065.



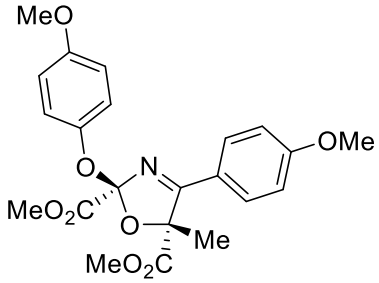
(2*RS*,5*SR*)-4's. Colorless oil.

^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.9 Hz, 2H), 8.08 (d, *J* = 8.9 Hz, 2H), 7.14 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 3.94 (s, 3H), 3.79 (s, 3H), 3.75 (s, 3H), 1.32 (s, 3H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 172.3, 169.1, 165.2, 157.2, 150.0, 144.2, 134.0, 130.2, 125.4, 123.9, 121.8, 113.8, 92.3, 55.4, 53.5, 53.3, 21.3.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{21}H_{20}N_2NaO_9^+$ 467.1061; Found 467.1064.

(2*RS*,5*SR*)-Dimethyl 2-(4-methoxyphenoxy)-4-(4-methoxyphenyl)-5-methyl-2,5-dihydrooxazole-2,5-dicarboxylate (4't)



Compound **4't** (19.8 mg, 16%) was obtained from isoxazole **5c** (65.7 mg, 0.3 mmol) and diazo compound **2a** (86.5 mg, 0.42 mmol) according to the general procedure B [1st step: 3 h; 3rd step: *m*-CPBA (3.6 equiv); eluent for chromatography EtOAc – hexane, 1:6] as a colorless oil.

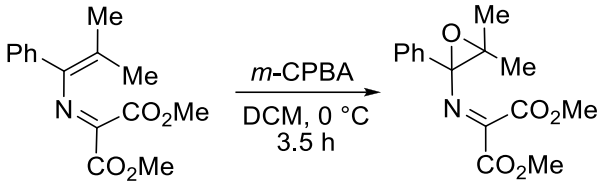
^1H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.9 Hz, 2H), 7.15 (d, *J* = 9.0 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.77 (d, *J* = 9.0 Hz, 2H), 3.92 (s, 3H), 3.87 (s, 3H), 3.74 (m, 6H), 1.29 (s, 3H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 173.1, 169.8, 165.9, 163.1, 157.0, 144.6, 131.1, 125.4, 122.2, 120.9, 114.2, 113.7, 91.9, 55.44, 55.40, 53.2, 53.1, 21.5.

HRMS (ESI/Q-TOF) *m/z*: $[M+Na]^+$ Calcd for $C_{22}H_{23}NNaO_8^+$ 452.1316; Found 452.1326.

V. Control Experiments

Synthesis of dimethyl 2-((3,3-dimethyl-2-phenyloxiran-2-yl)imino)malonate (6o)



To a solution of azabutadiene **3o**[1] (100 mg, 0.36 mmol) in anhydrous DCM (2 mL), *m*-CPBA (106 mg) was added and the resulting reaction mixture was stirred at 0 °C for 4.5 h. Then, to the reaction mixture containing oxirane **6o**, anhydrous Na_2SO_4 (2 equiv calcd on *m*-CPBA) was added and stirring was continued for 30 min. Finally, anhydrous K_2CO_3 (3 equiv calcd on *m*-CPBA) was added and stirring was continued for 2 h. The resulting mixture was passed through the Celite plug, the solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel (eluent EtOAc – hexane, 1:8) to give oxirane **6o** (39 mg, 38%).

Colorless solid, mp 63–66 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.58 (m, 2H), 7.42 – 7.34 (m, 3H), 3.96 (s, 3H), 3.91 (s, 3H), 1.35 (s, 3H), 1.16 (s, 3H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.6, 161.5, 151.0, 134.7, 128.4, 128.2, 127.4, 83.1, 67.5, 53.4, 52.7, 20.4, 18.8.

HRMS (ESI/Q-TOF) *m/z*: $[M+H]^+$ Calcd for $C_{15}H_{18}NO_5^+$ 292.1179; Found 292.1178.

Reaction of azadiene 3a with *m*-CPBA in dark

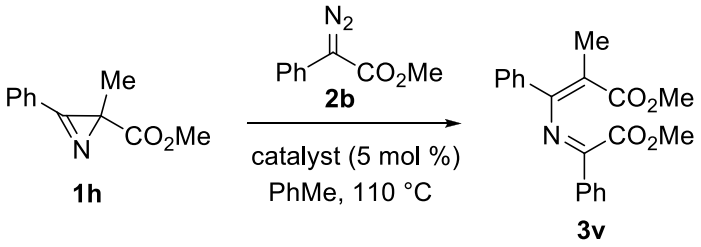
5-mL Flack containing solution of azadiene **3a** (40 mg, 0.12 mmol) in DCM (0.5 mL) was covered with foil and *m*-CPBA (24 mg, 0.14 mmol) was added at 0 °C. The reaction mixture was stirred at room temperature for 10 min until complete consumption of the azadiene (controlled by TLC). Yield of oxazoline **4a** (87%) was determined by ^{1}H NMR spectroscopy using 2-methylnaphthalene as an internal standard.

Reaction of azadiene 3a with *m*-CPBA in presence of TEMPO

To a solution of azadiene **3a** (40 mg, 0.12 mmol) and TEMPO ((2,2,6,6-tetramethylpiperidin-1-yl)oxyl) (18.7 mg, 0.12 mmol) in DCM (0.5 mL), *m*-CPBA (24 mg, 0.14 mmol) was added at 0 °C. The reaction mixture was stirred at room temperature for 10 min until complete consumption of the azadiene (controlled by TLC). Yield of oxazoline **4a** (88%) was determined by ^{1}H NMR spectroscopy using 2-methylnaphthalene as an internal standard.

VI. Optimization of Reaction Conditions for Cu-Catalyzed Synthesis of 2-Azabutadienes

Table S-1. Testing of Catalysts for the Synthesis of 2-Azabutadiene 3v



entry	catalyst	time[a]	equiv of **2b**	yield of **3v**, %[b]
1	$Rh_2(OAc)_4$	30 sec	1.2	78
2[c]	$Cu(tfacac)_2$	30 sec	1.2	82
3[d]	$Cu(hfacac)_2 \cdot H_2O$	30 sec	1.2	82
4	$Cu(OAc)_2 \cdot H_2O$	1 h	2	68
5	CuOAc	1.5 h	2.5	37
6	CuI	1 h	1.3	50
7	$Cu(PhC(O)CHC(O)CF_3)_2$	1 min	1.2	80

[a] Time until full consumption of **2b**, [b] Yields were determined by ^{1}H NMR spectroscopy using 2-methylnaphthalene as an internal standard, [c] tfacac = trifluoroacetylacetonato, [d] hfacac = hexafluoroacetylacetonato

VII. X-ray Data

Compound 4a (CCDC 2433569)

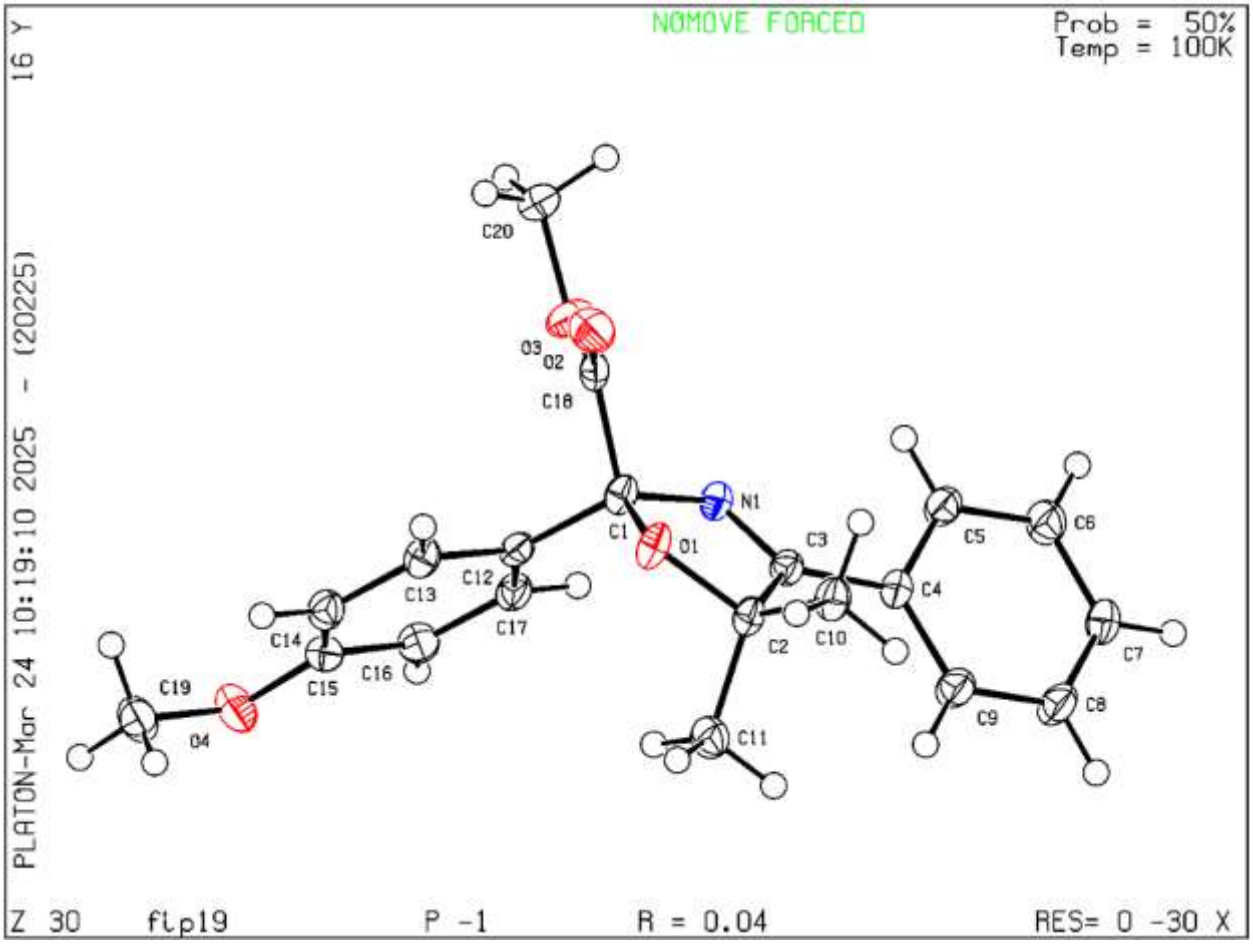
Single crystals of **4a** were grown by slow evaporation of its solution in diethyl ether–hexane mixture. A suitable crystal was selected and intensity data were collected on a XtaLAB Synergy, Single source at home/near, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2,[13] the structure was solved with the SHELXS[14] structure solution program using Direct Methods and refined with the SHELXL[15] refinement package using Least Squares minimization.

Table S-2. Crystal data and structure refinement for 4a.

Empirical formula	$C_{20}H_{21}NO_4$
Formula weight	339.38
Temperature/K	100.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.6872(2)
b/Å	9.13598(19)
c/Å	11.7463(2)
α/°	108.4856(18)
β/°	96.9997(19)
γ/°	101.3012(19)
Volume/Å^3	849.87(3)
Z	2
ρ_{calc}g/cm^3	1.326
μ/mm^{-1}	0.753
F(000)	360.0
Crystal size/mm^3	0.18 × 0.14 × 0.06
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.096 to 159.792
Index ranges	$-10 \le h \le 10$, $-11 \le k \le 11$, $-14 \le l \le 14$
Reflections collected	9847
Independent reflections	3492 [R_{int} = 0.0274, R_{sigma} = 0.0323]

Data/restraints/parameters	3492/0/230
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	$R_1 = 0.0369$, $wR_2 = 0.0990$
Final R indexes [all data]	$R_1 = 0.0410$, $wR_2 = 0.1017$
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.22

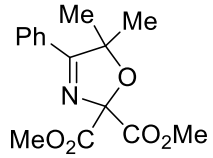
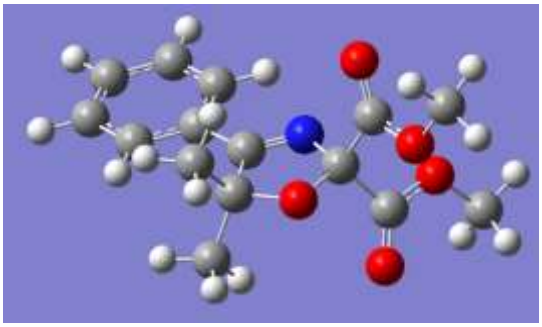
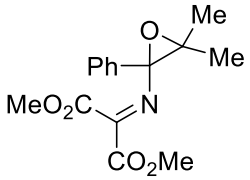
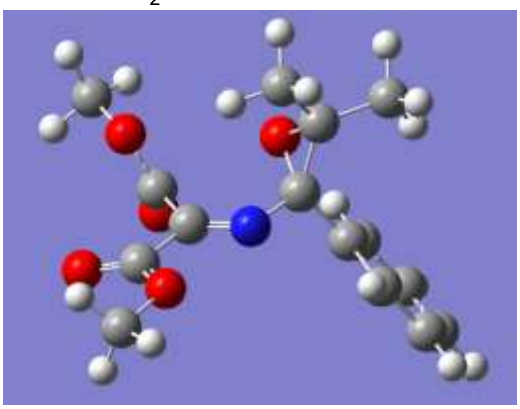
Figure S-1. X-ray crystal structure of compound **4a** with 50% ellipsoid probability

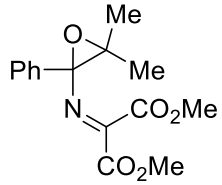
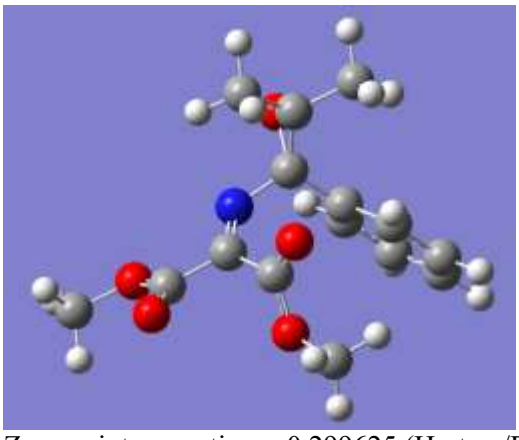
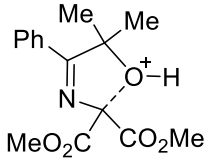
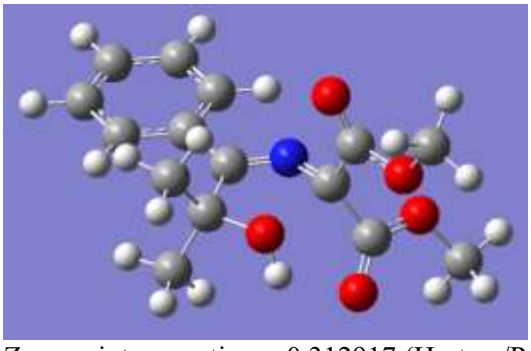


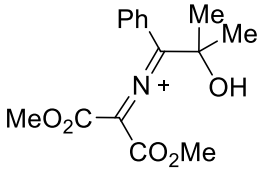
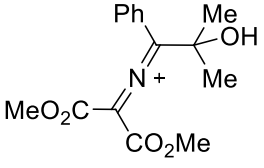
VIII. Calculation Details

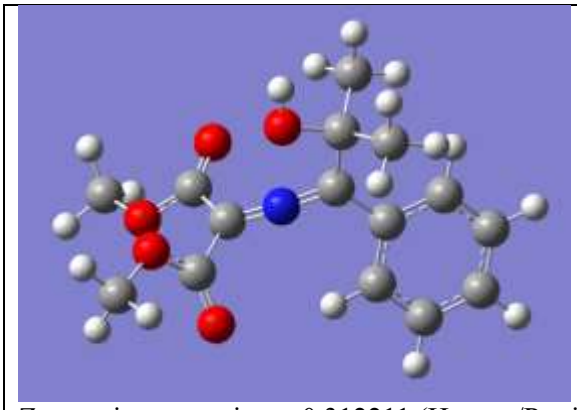
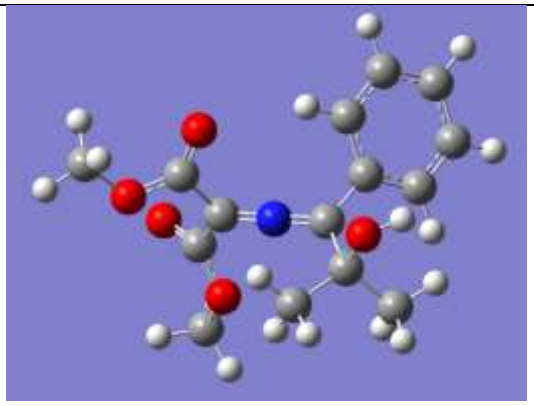
All calculations were performed by using the Gaussian 09 suite of quantum chemical programs.[16] Calculations for compounds **4o, 6o, 8o, 4o-H, 4o-H'** and transition state **TS** were performed at the DFT B3LYP/6-31+G(d,p) level using PCM model for dichloromethane (273 K). Careful verification of the unique imaginary frequency for transition state was carried out to check whether the frequency indeed pertains to the desired reaction coordinate.

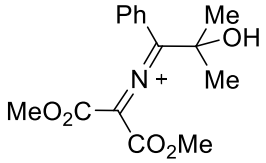
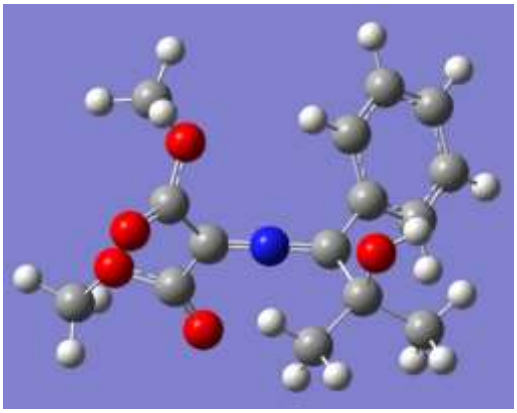
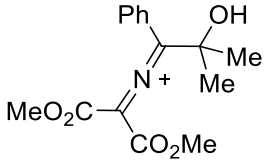
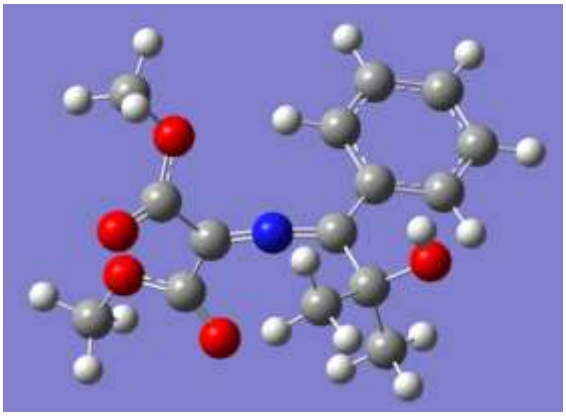
Table S-3. Energies (au) and cartesian coordinates of stationary points for compounds **4o, 6o, 8o, 4o-H, 4o-H'** and transition state **TS**.

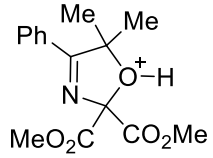
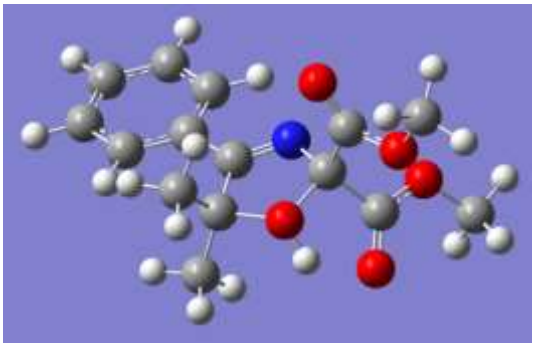
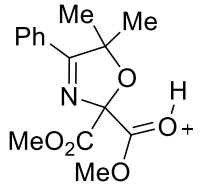
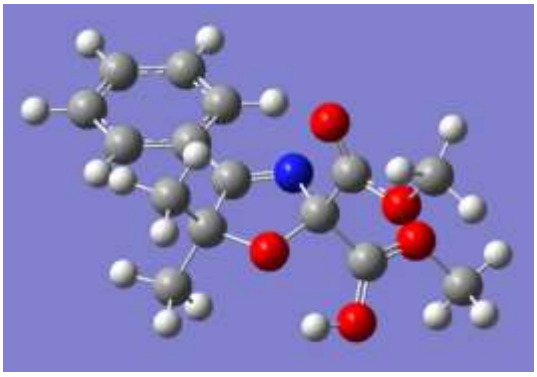
Oxazoline **4o**   Zero-point correction = 0.301734 (Hartree/Particle) Thermal correction to Energy = 0.319795 Thermal correction to Enthalpy = 0.320660 Thermal correction to Gibbs Free Energy = 0.256231 Sum of electronic and zero-point Energies = -1012.474759 Sum of electronic and thermal Energies = -1012.456697 Sum of electronic and thermal Enthalpies = -1012.455832 Sum of electronic and thermal Free Energies = -1012.520261 Imaginary frequency = 0 O -0.90734000 -1.22438600 0.83818600 O -2.45959200 1.94193600 0.15439700 C -1.20540800 -0.06984400 0.07265700 N 0.03477000 0.52307800 -0.36797600 C 1.00949400 -0.17733900 0.09619900 C 0.53810500 -1.38596700 0.92055000 C 0.92210300 -1.32120200 2.40546000 C 0.88642900 -2.73726800 0.28075100 C 2.41336300 0.19622800 -0.18693100 C 2.66676700 1.32684500 -0.99063500 C 3.97112500 1.71342400 -1.28516300	Oxirane **6o** (conformation 1)   Zero-point correction = 0.299755 (Hartree/Particle) Thermal correction to Energy = 0.318424 Thermal correction to Enthalpy = 0.319289 Thermal correction to Gibbs Free Energy = 0.253273 Sum of electronic and zero-point Energies = -1012.437681 Sum of electronic and thermal Energies = -1012.419012 Sum of electronic and thermal Enthalpies = -1012.418148 Sum of electronic and thermal Free Energies = -1012.484163 Imaginary frequency = 0 C 1.34575900 -0.33998400 0.10844000 C -0.89034800 1.47309500 -1.53606300 C -0.82572700 0.39792400 -0.49977700 N 0.26223500 -0.53048700 -0.52734000 C 1.66153500 0.82485700 1.04369600 C 2.44300400 -1.38235400 0.06621500 O 3.40403500 -1.32195300 0.81473800 O 2.23936500 -2.33090400 -0.84322500 C 3.24441000 -3.37223000 -0.91732000

C 5.05364200 0.97966100 -0.78408000 C 4.81745100 -0.14240100 0.01249800 C 3.50902700 -0.53203700 0.30891600 C -2.06630100 -0.53805500 -1.13070600 O -1.65241600 -0.67837500 -2.26189100 O -3.30226100 -0.83831900 -0.72107200 C -4.20322700 -1.38962200 -1.71256600 C -1.96684000 0.97557200 0.93348700 O -2.06112400 0.93165400 2.14068100 C -3.15872100 3.02362300 0.81794900 H 0.66366200 -0.34829000 2.83048500 H 0.36478700 -2.09303000 2.94430000 H 1.98804400 -1.50198500 2.55903400 H 0.34163100 -3.52712000 0.80624900 H 0.59471300 -2.75338900 -0.77286600 H 1.95413100 -2.95639600 0.34879800 H 1.82719300 1.89124900 -1.37995600 H 4.14582400 2.58634600 -1.90689900 H 6.07115900 1.28108800 -1.01438300 H 5.64908300 -0.71882500 0.40583700 H 3.35934300 -1.40675600 0.92824000 H -3.79757400 -2.32360500 -2.10575800 H -4.34743100 -0.67399000 -2.52402300 H -5.13733700 -1.56692900 -1.18304500 H -2.48444600 3.53551400 1.50694400 H -3.47499900 3.69222400 0.01962600 H -4.02136600 2.63255100 1.36053400	C -2.05829500 -0.25142600 0.08154800 C -2.71734800 0.33340000 1.16887900 C -3.85306000 -0.27564100 1.71145800 C -4.33781600 -1.46945100 1.16995900 C -3.67921300 -2.05613700 0.08367700 C -2.54062400 -1.45387700 -0.45602300 C 0.24567600 1.68708900 -2.51236200 C -2.23010000 1.99667100 -2.00477300 O 1.21492500 0.89829700 2.17034700 O 2.51541400 1.68053200 0.48418000 C 2.92068600 2.81471300 1.29247700 H 2.90427900 -4.03918600 -1.70704500 H 3.30622900 -3.89961200 0.03630600 H 4.21443900 -2.93815800 -1.16670600 H -2.34091000 1.26239800 1.58337700 H -4.35686900 0.18409200 2.55669000 H -5.22122400 -1.94065300 1.59076700 H -4.04996100 -2.98377800 -0.34249500 H -2.02541200 -1.91578500 -1.29237200 H 0.03276000 1.16511800 -3.45110500 H 0.33751600 2.75556600 -2.73499600 H 1.20197900 1.33467300 -2.12585700 H -2.51754800 1.50522900 -2.94028800 H -2.15380700 3.07210800 -2.19893100 H -3.01597000 1.83022200 -1.26711100 H 3.61160100 3.37738800 0.66783800 H 3.41481200 2.46601500 2.20092800 H 2.04774600 3.41816300 1.54743300 O -0.57330700 1.76149200 -0.13419600
Oxirane **6o** (conformation 2)   Zero-point correction = 0.299625 (Hartree/Particle) Thermal correction to Energy = 0.318309 Thermal correction to Enthalpy = 0.319174 Thermal correction to Gibbs Free Energy = 0.253228 Sum of electronic and zero-point Energies = -1012.430800 Sum of electronic and thermal Energies =	Transition state **TS**   Zero-point correction = 0.312917 (Hartree/Particle) Thermal correction to Energy = 0.331055 Thermal correction to Enthalpy = 0.331920 Thermal correction to Gibbs Free Energy = 0.267811 Sum of electronic and zero-point Energies = -1012.844477 Sum of electronic and thermal Energies = -1012.826339 Sum of electronic and thermal Enthalpies = -1012.825474

-1012.412116 Sum of electronic and thermal Enthalpies = -1012.411252 Sum of electronic and thermal Free Energies = -1012.477197 Imaginary frequency = 0 C -1.33294600 0.04693500 0.04007700 C 1.08708400 2.33214000 0.59018900 C 0.75215800 1.18501100 -0.30541900 N -0.63467400 0.89971200 -0.59136900 C -0.89097900 -0.77962500 1.24343700 C -2.79465200 -0.13113100 -0.31571600 O -3.59383500 -0.56019400 0.49950300 O -3.08781700 0.24167600 -1.55679000 C -4.48116800 0.14325900 -1.94414400 C 1.68107100 0.03711200 -0.61533300 C 1.95259900 -0.25796800 -1.96046100 C 2.78181600 -1.33028000 -2.29376300 C 3.34941400 -2.11841800 -1.28643500 C 3.08451100 -1.82682200 0.05418400 C 2.25080900 -0.75531400 0.39014300 C -0.02299700 3.11798100 1.25799200 C 2.43085600 2.42760000 1.28181800 O -0.49526100 -0.28823100 2.28194300 O -0.99402000 -2.08210100 0.98907300 C -0.63443700 -2.99084200 2.06250700 H -4.51167300 0.47586700 -2.97972500 H -5.09025300 0.79030400 -1.31034900 H -4.82034200 -0.89060100 -1.85769500 H 1.52140300 0.35986600 -2.74241500 H 2.98710200 -1.54848200 -3.33763400 H 3.99716600 -2.95069600 -1.54548000 H 3.52873100 -2.42863000 0.84159200 H 2.05504300 -0.53070900 1.43312900 H -0.23338500 2.70320500 2.24884900 H 0.29205100 4.15941000 1.38377200 H -0.94096800 3.10116100 0.66883600 H 2.36440500 2.04154700 2.30432100 H 2.72698300 3.48108100 1.33968700 H 3.20635000 1.87890600 0.74628600 H -0.80527600 -3.98701900 1.66008700 H -1.27066400 -2.80639400 2.92965900 H 0.41484600 -2.85463300 2.32894900 O 1.13872900 2.45260000 -0.85957100	Sum of electronic and thermal Free Energies = -1012.889583 Imaginary frequency = 1 O -0.83537900 -1.36506700 1.10655500 O -2.48998300 2.12840700 0.15563000 C -1.24813900 0.16571100 -0.15782700 N 0.01276900 0.44203400 -0.33283800 C 1.02814800 -0.17971500 0.14576500 C 0.61254600 -1.38035900 1.07974600 C 1.13213900 -1.19619400 2.51215900 C 0.99159700 -2.72109700 0.43375100 C 2.39366500 0.23048800 -0.18289700 C 2.56488800 1.37570700 -0.99410800 C 3.83664900 1.80946600 -1.34615800 C 4.96435700 1.10917400 -0.89946300 C 4.81022300 -0.02534800 -0.09863300 C 3.53723900 -0.46398600 0.26026600 C -1.98077600 -0.66385700 -1.22431600 O -1.39689800 -1.21736300 -2.12564200 O -3.27763500 -0.67642100 -0.96439400 C -4.12052600 -1.46450000 -1.85501300 C -2.07851500 1.05335700 0.78637900 O -2.27027600 0.74860800 1.94719000 C -3.29158000 3.08509300 0.91948100 H 0.82512000 -0.23066100 2.92518900 H 0.73272900 -1.99855600 3.13813400 H 2.21937400 -1.24778000 2.55404700 H 0.63153400 -3.52987700 1.07383700 H 0.52735800 -2.81459500 -0.55072200 H 2.07031100 -2.82272000 0.31755200 H 1.69173300 1.91809500 -1.34009000 H 3.95189700 2.69101100 -1.96810700 H 5.95814100 1.44743900 -1.17565600 H 5.68061300 -0.57246300 0.24767500 H 3.45476000 -1.34914400 0.87535100 H -4.03820700 -1.07311200 -2.86963500 H -5.12863500 -1.34325300 -1.46677400 H -3.80696900 -2.50853100 -1.82038900 H -4.20349100 2.59554600 1.26146000 H -2.70788600 3.45100000 1.76423000 H -3.51162100 3.88342200 0.21565000 H -1.18627100 -0.93900600 1.91860800
Azaallenium cation **8o** (conformation 1)  	Azaallenium cation **8o** (conformation 2) 

	
Zero-point correction = 0.312211 (Hartree/Particle) Thermal correction to Energy = 0.331766 Thermal correction to Enthalpy = 0.332630 Thermal correction to Gibbs Free Energy = 0.264106 Sum of electronic and zero-point Energies = -1012.852262 Sum of electronic and thermal Energies = -1012.832707 Sum of electronic and thermal Enthalpies= -1012.831843 Sum of electronic and thermal Free Energies = -1012.900367 Imaginary frequency = 0	Zero-point correction = 0.312406 (Hartree/Particle) Thermal correction to Energy = 0.331733 Thermal correction to Enthalpy = 0.332597 Thermal correction to Gibbs Free Energy = 0.264524 Sum of electronic and zero-point Energies = -1012.847747 Sum of electronic and thermal Energies = -1012.828420 Sum of electronic and thermal Enthalpies = -1012.827556 Sum of electronic and thermal Free Energies = -1012.895629 Imaginary frequency = 0
O -0.02020700 2.60653300 0.52622600 O -3.14145400 -0.80466100 -1.37837300 C -1.33099700 -0.13686600 -0.05995300 N -0.13186900 0.18902400 0.02898200 C 1.07683400 0.58470100 0.04940100 C 1.26983100 2.12063400 0.15043000 C 1.64151400 2.68397400 -1.23709300 C 2.28753400 2.46915100 1.24800000 C 2.14391300 -0.42669900 0.02162400 C 1.84056500 -1.73714900 0.45588300 C 2.81755100 -2.72577400 0.43555200 C 4.10504900 -2.42930500 -0.02554600 C 4.41421900 -1.13616000 -0.45851300 C 3.44694500 -0.13520800 -0.43094800 C -2.08850500 -0.58805300 1.19197600 O -1.75975400 -1.58402200 1.79663900 O -3.07181700 0.24602100 1.46224200 C -3.89027100 -0.05625000 2.63339600 C -1.99414500 -0.15183000 -1.44416600 O -1.48186100 0.36148900 -2.41089800 C -3.89925100 -0.93065200 -2.61744100 H 0.86370800 2.43970800 -1.96413700 H 1.71335900 3.77304900 -1.15002000 H 2.60027400 2.32008900 -1.60759900 H 2.31128800 3.55807100 1.35069200 H 1.97974200 2.03923500 2.20442900 H 3.29704100 2.12925200 1.01398600 H 0.85296500 -1.96837000 0.84061100 H 2.57809500 -3.72399000 0.78632200 H 4.86671300 -3.20234700 -0.04182800	C 1.41639200 -0.15501900 -0.17768600 C -1.18979600 1.51851600 1.56949100 C -0.94565300 0.46892900 0.42053700 N 0.24605000 0.17600300 0.11713100 C 2.06726800 -1.32432700 0.57105700 C 2.14571400 0.50655900 -1.34493200 O 2.84352600 -0.15133200 -2.08189900 O 1.86931900 1.79610600 -1.41805600 C 2.48249400 2.53118000 -2.52025800 C -2.02061700 -0.32691600 -0.22303700 C -1.91451200 -1.73123500 -0.17399600 C -2.90629300 -2.51924400 -0.75441000 C -3.98485800 -1.91893200 -1.41076500 C -4.07406700 -0.52510900 -1.48549400 C -3.10265700 0.27736900 -0.88874200 C 0.13315500 2.02681300 2.13994600 C -2.06738800 2.68325100 1.09508700 O 1.42083300 -2.26664100 0.96878500 O 3.35936700 -1.10396400 0.71210200 C 4.12749900 -2.12328500 1.41930200 H 2.14250900 3.55599700 -2.39443400 H 2.14030600 2.11445600 -3.46810700 H 3.56808800 2.46374200 -2.44138900 H -1.07611500 -2.19265500 0.33754500 H -2.83309100 -3.60019600 -0.69601900 H -4.75196500 -2.53520700 -1.86876300 H -4.89959900 -0.05828100 -2.01248600 H -3.16917900 1.35305300 -0.98408700 H 0.70619600 2.57540400 1.38856100 H -0.09216400 2.70528600 2.96487700

H 5.41072600 -0.90442500 -0.81893200 H 3.71008700 0.85199400 -0.78387700 H -3.25992600 -0.07109900 3.52290500 H -4.37915400 -1.02066100 2.49222400 H -4.61723600 0.75062700 2.67946400 H -3.30072200 -1.46588700 -3.35538800 H -4.78721800 -1.49567800 -2.34562300 H -4.15963000 0.06319000 -2.98339500 H -0.00099700 3.57412200 0.51499200	H 0.73799700 1.20643500 2.53336400 H -1.64347000 3.17312300 0.21371000 H -2.11569500 3.41486400 1.90594300 H -3.08712300 2.36615100 0.87049500 H 5.14626900 -1.74452800 1.43214200 H 4.06288600 -3.06474400 0.87289900 H 3.73459000 -2.23758300 2.43002600 O -1.81051100 0.76365100 2.60237400 H -2.75314400 0.63881900 2.41276900
Azaallenium cation **8o** (conformation 3)   Zero-point correction = 0.312321 (Hartree/Particle) Thermal correction to Energy = 0.331639 Thermal correction to Enthalpy = 0.332504 Thermal correction to Gibbs Free Energy = 0.264724 Sum of electronic and zero-point Energies = -1012.847566 Sum of electronic and thermal Energies = -1012.828248 Sum of electronic and thermal Enthalpies = -1012.827384 Sum of electronic and thermal Free Energies = -1012.895163 Imaginary frequency = 0 C 1.44072400 0.07293900 -0.07481400 C -1.36268400 1.96215400 0.97127600 C -0.99290000 0.66097100 0.16041200 N 0.22988400 0.35648000 0.05849000 C 2.16272300 0.52429800 -1.35052800 C 2.20481200 -0.61383000 1.05670600 O 3.15810200 -0.06948400 1.56326700 O 1.66334000 -1.77663700 1.36749900 C 2.29581500 -2.52305200 2.45297800 C -1.97919600 -0.34307800 -0.31144600 C -1.85093900 -1.67049400 0.14081500 C -2.75717800 -2.63779400 -0.28903200 C -3.76789600 -2.29858100 -1.19366900 C -3.87544300 -0.98720400 -1.66763200	Azaallenium cation **8o** (conformation 4)   Zero-point correction = 0.312866 (Hartree/Particle) Thermal correction to Energy = 0.332034 Thermal correction to Enthalpy = 0.332898 Thermal correction to Gibbs Free Energy = 0.265628 Sum of electronic and zero-point Energies = -1012.852991 Sum of electronic and thermal Energies = -1012.833823 Sum of electronic and thermal Enthalpies = -1012.832959 Sum of electronic and thermal Free Energies = -1012.900229 Imaginary frequency = 0 C 1.44328500 0.04509800 -0.00287300 C -1.34214200 1.96907800 0.84972900 C -1.01037500 0.54080000 0.27763700 N 0.22555900 0.23744000 0.20321000 C 2.06856000 0.56664600 -1.30365900 C 2.31941600 -0.60911500 1.06336200 O 3.32878600 -0.06504000 1.44838200 O 1.80071700 -1.75344600 1.47321900 C 2.53455800 -2.46932400 2.51302500 C -2.00652200 -0.44025300 -0.16526200 C -1.61455400 -1.78784900 -0.34347700 C -2.52857200 -2.72979300 -0.79730600 C -3.84261100 -2.34430800 -1.09170500 C -4.24029000 -1.01532300 -0.91802300

C -2.99271100 -0.00275800 -1.22552600 C -0.15232000 2.87489600 1.14677100 C -2.54571100 2.72047400 0.37124600 O 1.67828900 1.33061400 -2.11019500 O 3.31207600 -0.11468200 -1.46323400 C 4.12122100 0.19064400 -2.63730700 H 1.73117900 -3.44954200 2.51850900 H 2.22177900 -1.94835600 3.37656700 H 3.33934600 -2.71398200 2.20148500 H -1.06461300 -1.93242700 0.84084500 H -2.67011100 -3.65479000 0.07897300 H -4.46715000 -3.05570100 -1.53393400 H -4.64660200 -0.72728700 -2.38516900 H -3.06964200 1.00122400 -1.62236700 H 0.21361100 3.23277900 0.18091500 H -0.45754700 3.73695700 1.74326800 H 0.65765400 2.37069100 1.67790200 H -2.32388800 3.07637100 -0.63834400 H -2.73381600 3.59092400 1.00531300 H -3.45471800 2.11622800 0.34686400 H 4.99246800 -0.45352400 -2.55052900 H 4.40534800 1.24348600 -2.61382300 H 3.55110900 -0.03274000 -3.53972100 O -1.67758000 1.43066400 2.25834200 H -2.59731400 1.12301000 2.27689200	C -3.33795700 -0.06439900 -0.44863400 C -0.24427100 2.45303700 1.80533500 C -1.48510400 2.92003900 -0.35237400 O 1.56212800 1.45970400 -1.94335500 O 3.16144600 -0.11849900 -1.58392600 C 3.86510700 0.23590600 -2.81126800 H 1.97088100 -3.38540400 2.67076600 H 2.56298300 -1.86228900 3.41839000 H 3.54490300 -2.68294000 2.16311100 H -0.60504700 -2.10002300 -0.09877200 H -2.22167100 -3.76337400 -0.91700600 H -4.55557000 -3.08083200 -1.44872600 H -5.25877600 -0.71705500 -1.14290600 H -3.66565300 0.95417600 -0.30300800 H 0.70265800 2.62360900 1.28929100 H -0.57012100 3.40532100 2.22978600 H -0.07959900 1.74427800 2.62304200 H -0.55767100 2.95571300 -0.92786200 H -1.70402200 3.91812800 0.03676500 H -2.29961400 2.61868300 -1.01320900 H 4.71042500 -0.44610300 -2.85458800 H 4.19772800 1.27267600 -2.74968400 H 3.20009400 0.09679200 -3.66435700 O -2.59421900 1.92763400 1.50812500 H -2.49288600 1.56229900 2.39991500
Oxazoline **4o-H**   Zero-point correction = 0.313758 (Hartree/Particle) Thermal correction to Energy = 0.331925 Thermal correction to Enthalpy = 0.332789 Thermal correction to Gibbs Free Energy = 0.268743 Sum of electronic and zero-point Energies = -1012.851505 Sum of electronic and thermal Energies = -1012.833338 Sum of electronic and thermal Enthalpies = -1012.832473 Sum of electronic and thermal Free Energies = -1012.896519 Imaginary frequency = 0	Oxazoline **4o-H'**   Zero-point correction = 0.315115 (Hartree/Particle) Thermal correction to Energy = 0.332985 Thermal correction to Enthalpy = 0.333849 Thermal correction to Gibbs Free Energy = 0.270809 Sum of electronic and zero-point Energies = -1012.858206 Sum of electronic and thermal Energies = -1012.840337 Sum of electronic and thermal Enthalpies = -1012.839472 Sum of electronic and thermal Free Energies = -1012.902513 Imaginary frequency = 0

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C -1.21097500 -0.00924000 -0.03315100	O -2.37421400 2.02266800 0.06435200
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C 1.02197200 -0.16089800 0.09284600	N 0.04780600 0.48653200 -0.44858900
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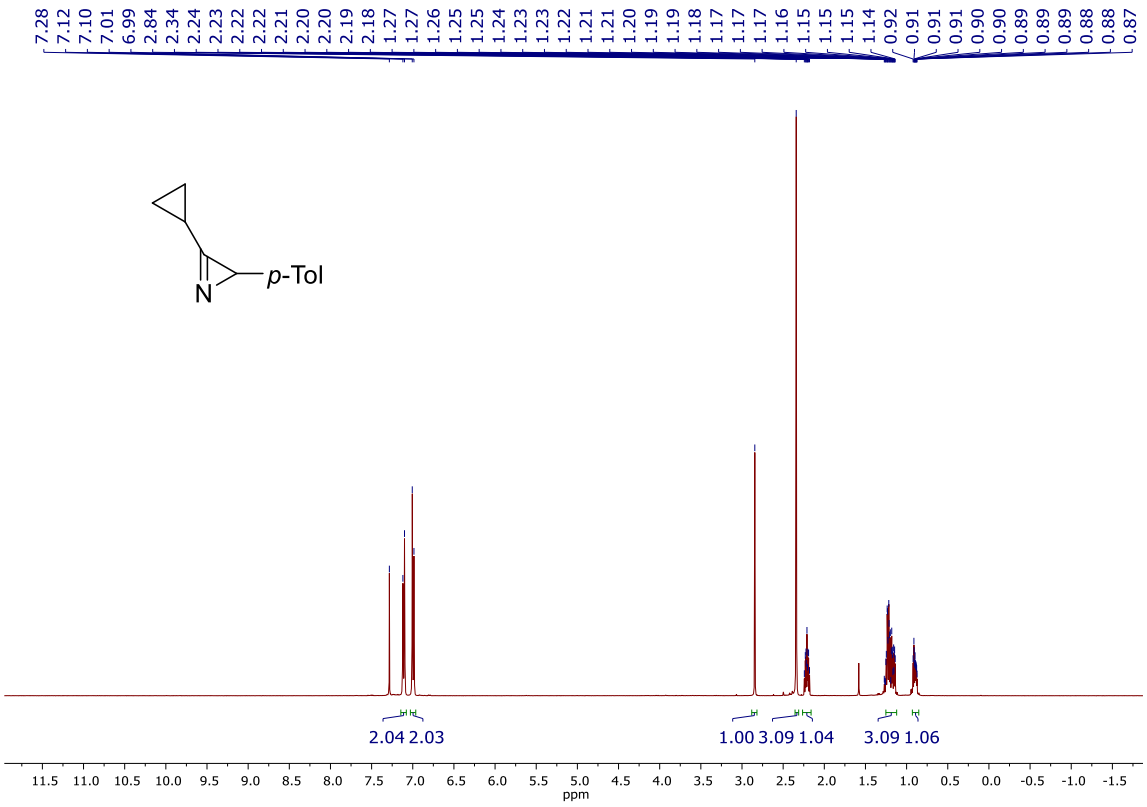
X. ^{1}H, ^{13}C and 2D NMR Spectra

^{1}H NMR spectrum of azirine **1d** (400 MHz, $CDCl_3$)



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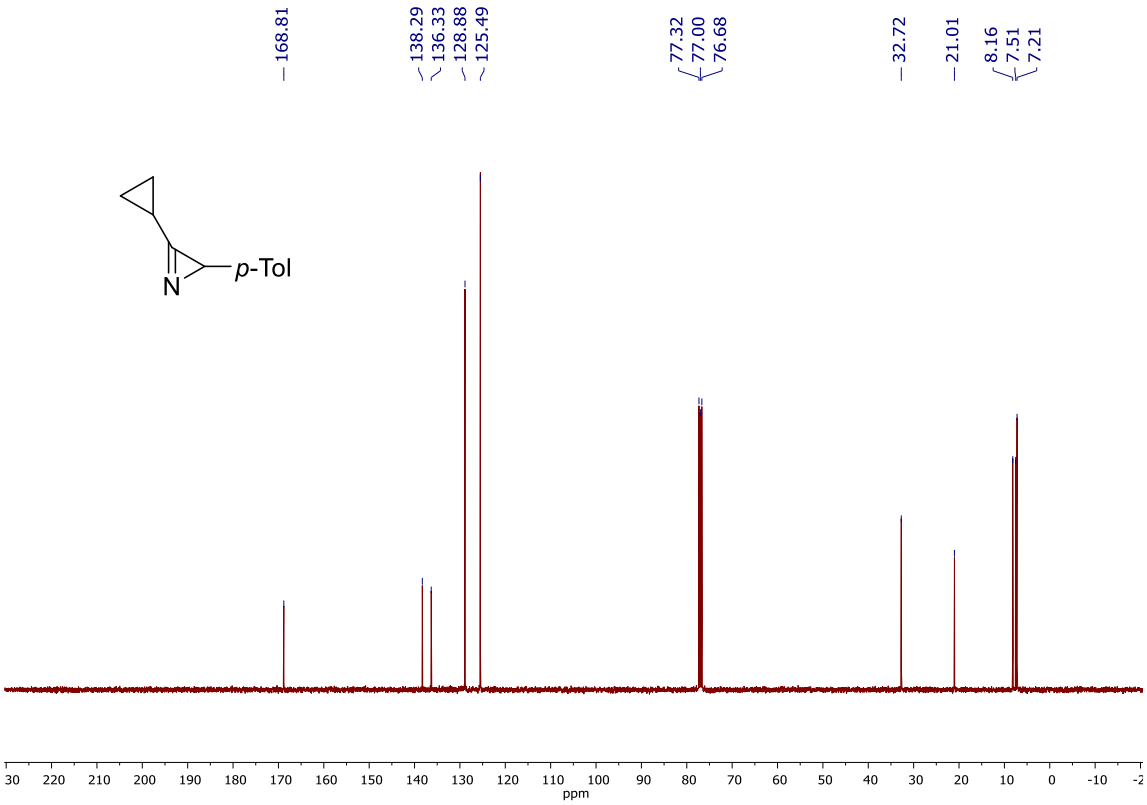
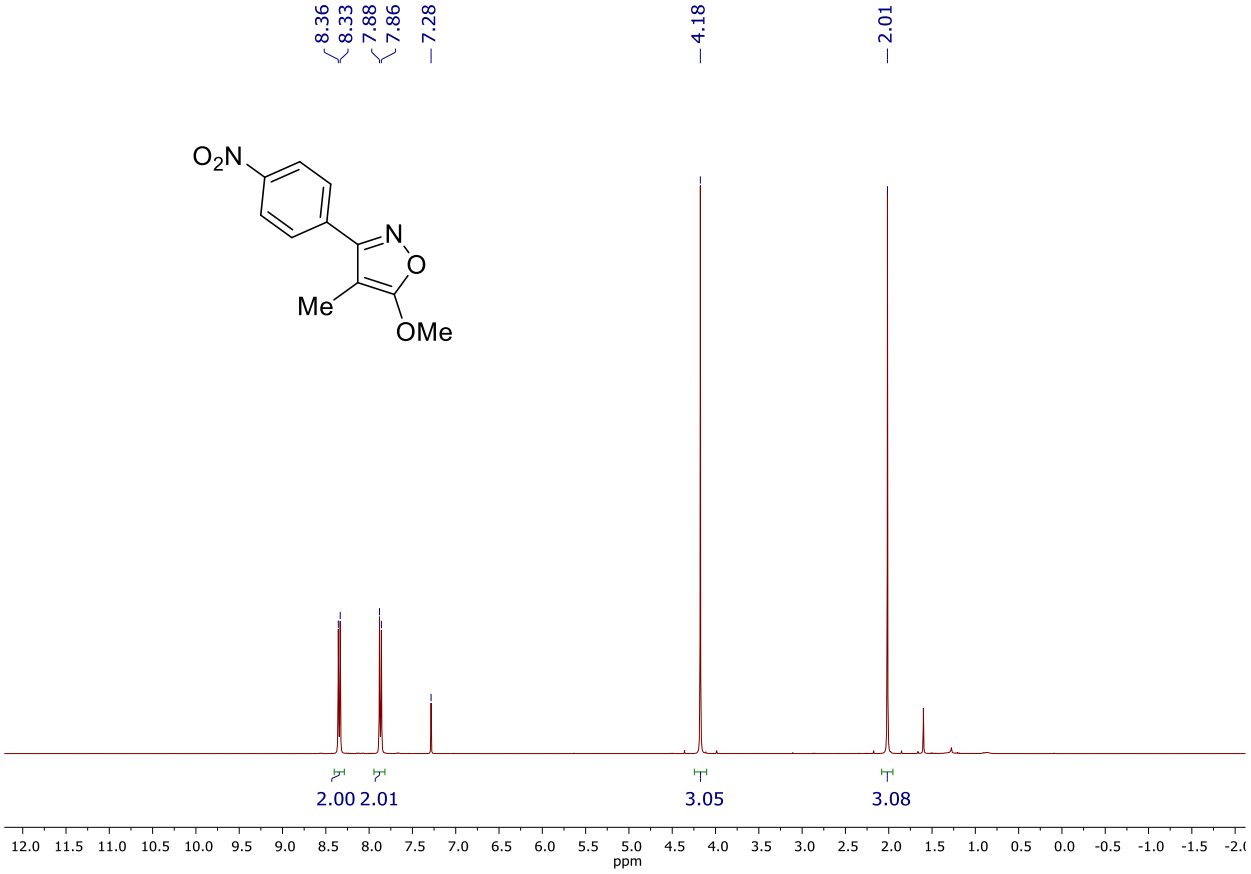
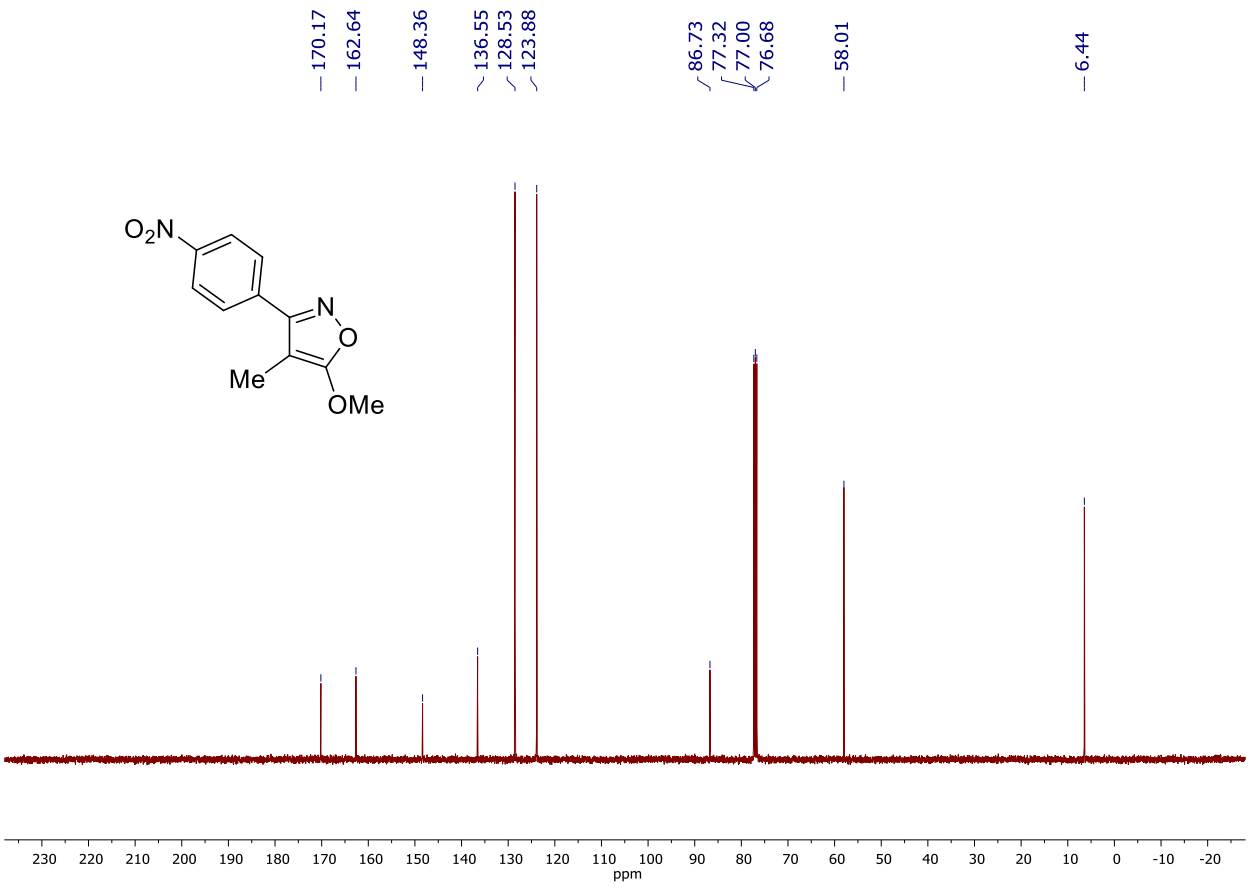


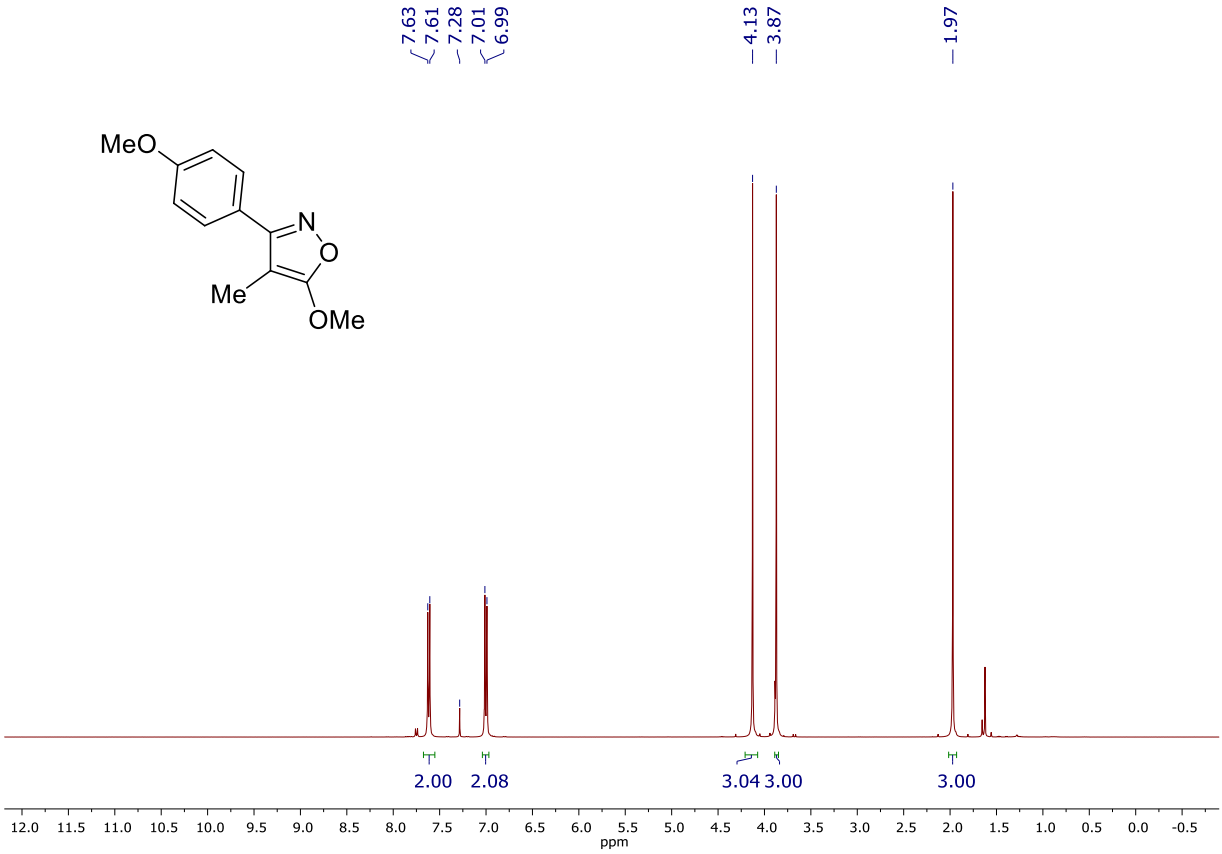
^{1}H NMR spectrum of isoxazole **5b** (400 MHz, $CDCl_3$)



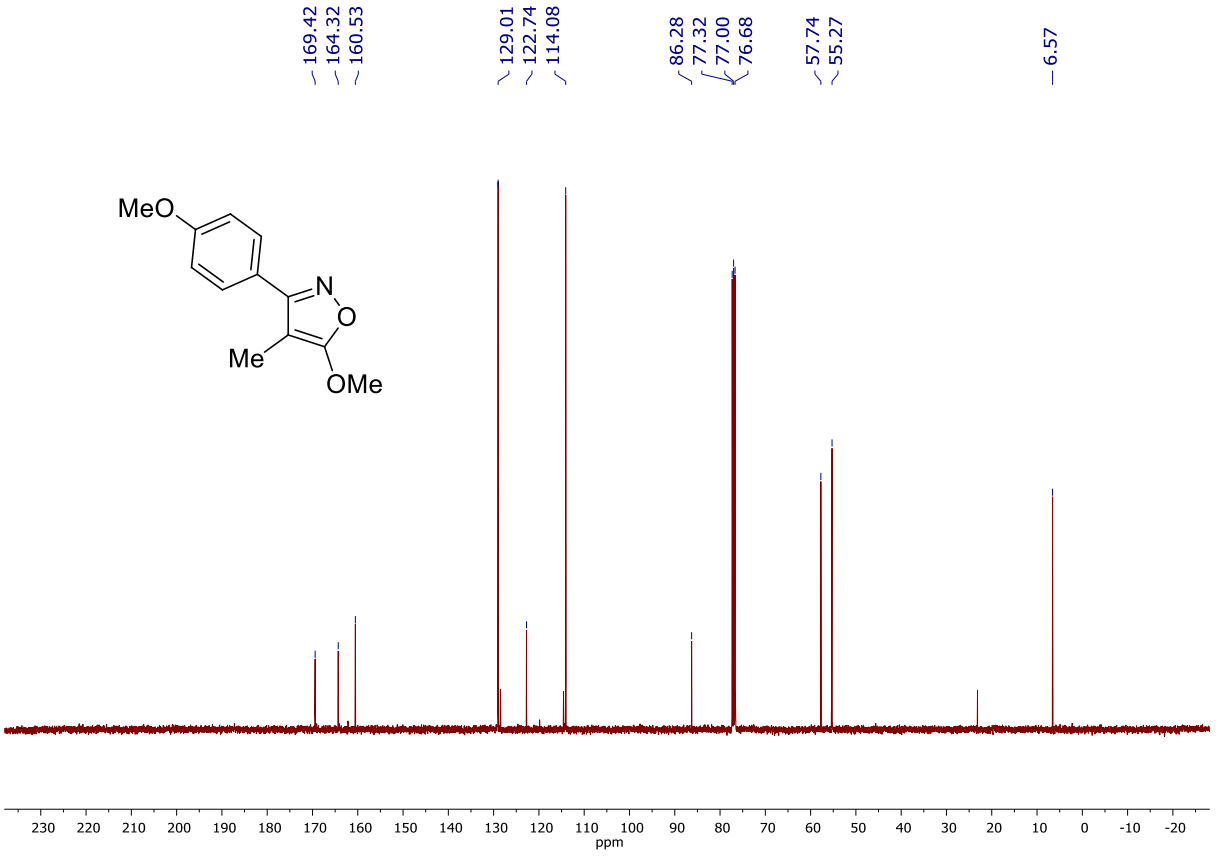
^{13}C{^{1}H} NMR spectrum of isoxazole **5b** (100 MHz, $CDCl_3$)



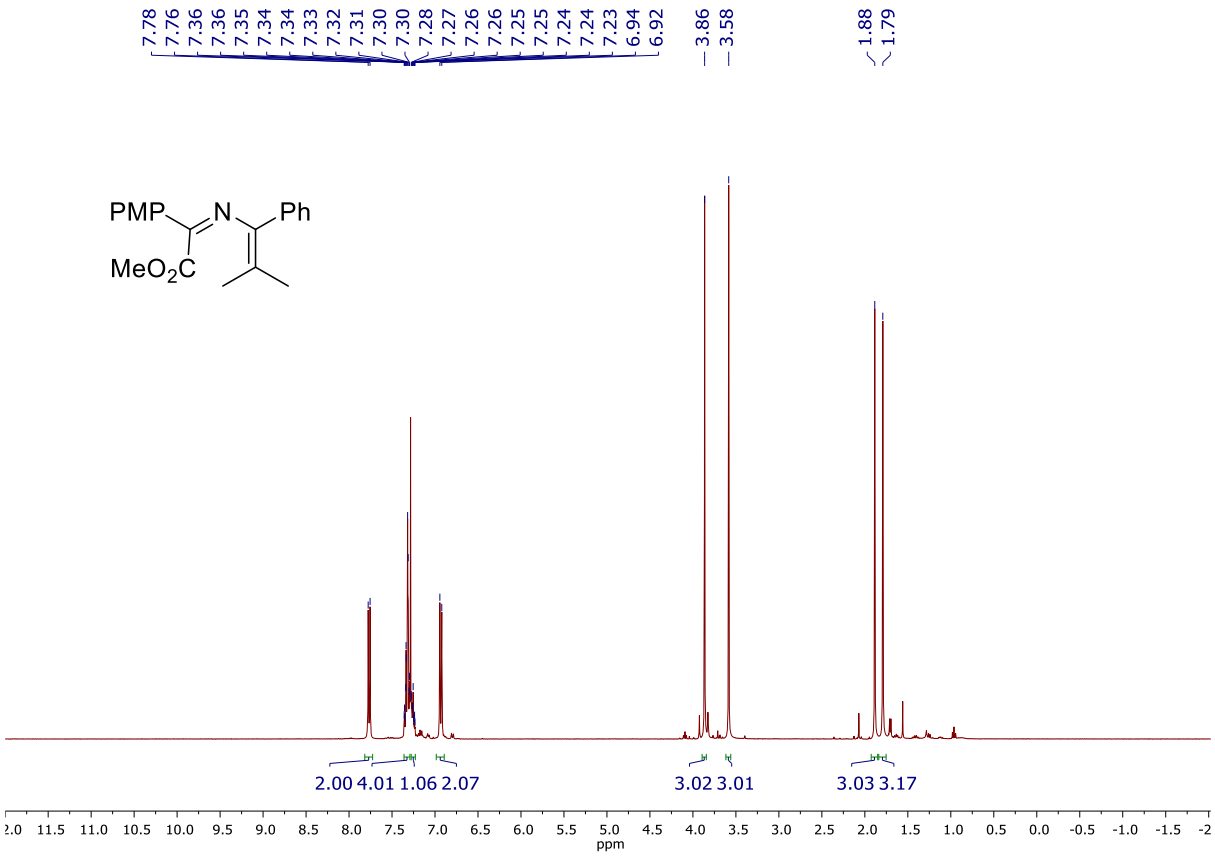
^{1}H NMR spectrum of isoxazole **5c** (400 MHz, $CDCl_3$)



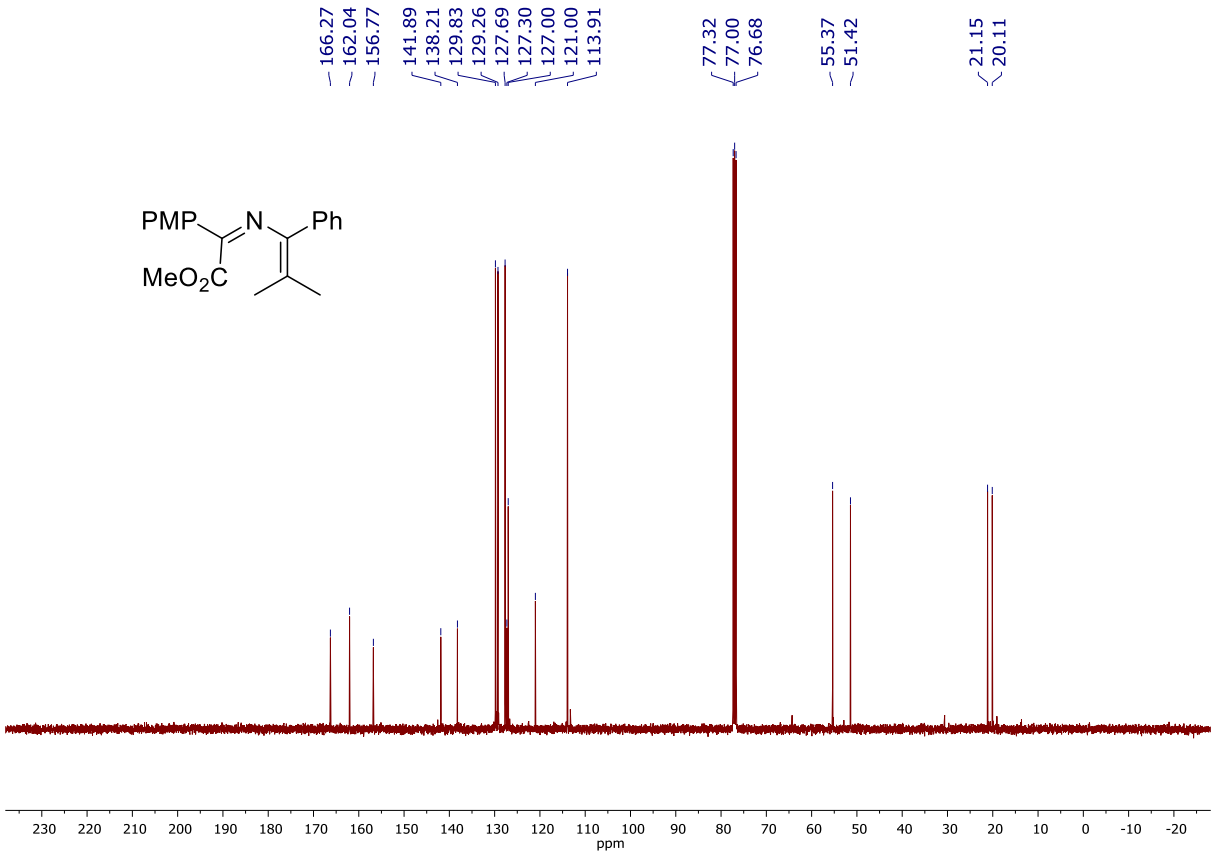
^{13}C{^{1}H} NMR spectrum of isoxazole **5c** (100 MHz, $CDCl_3$)



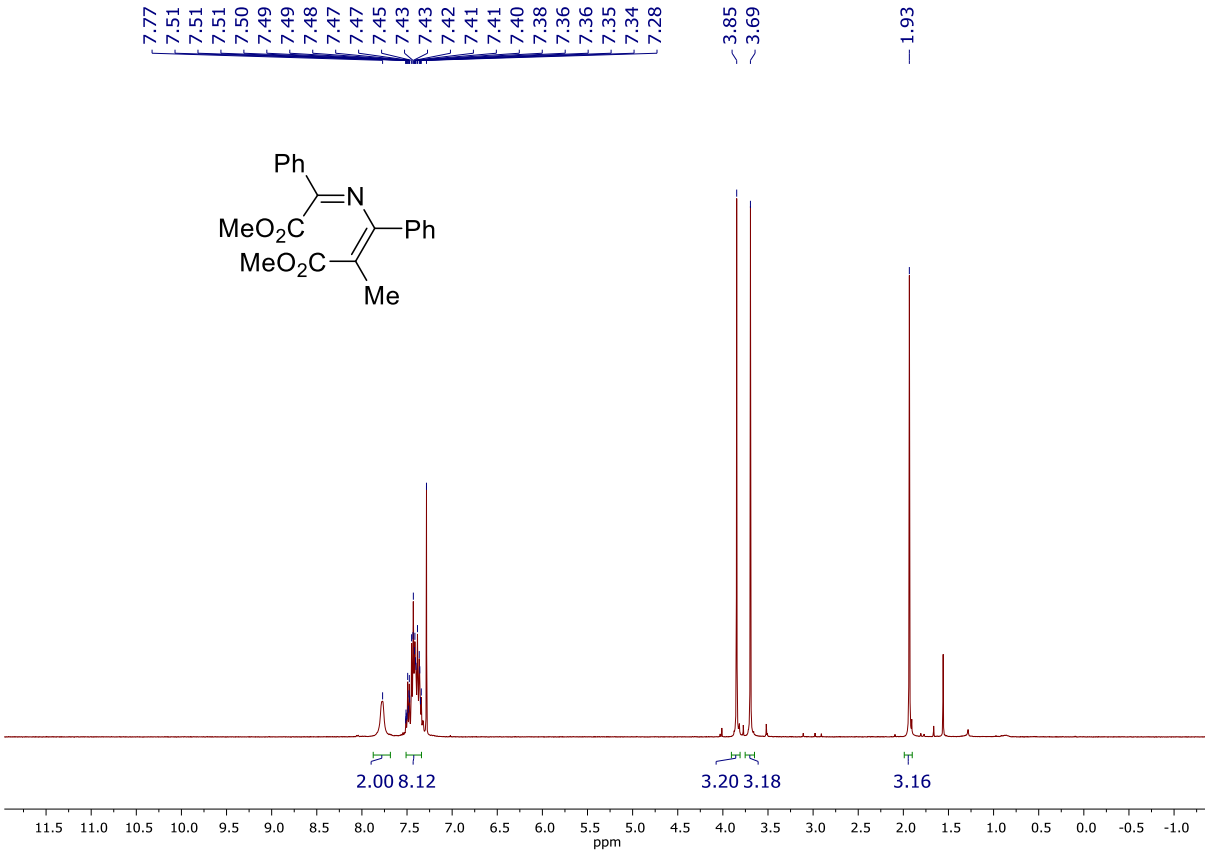
^{1}H NMR spectrum of azabutadiene **3a** (400 MHz, $CDCl_3$)



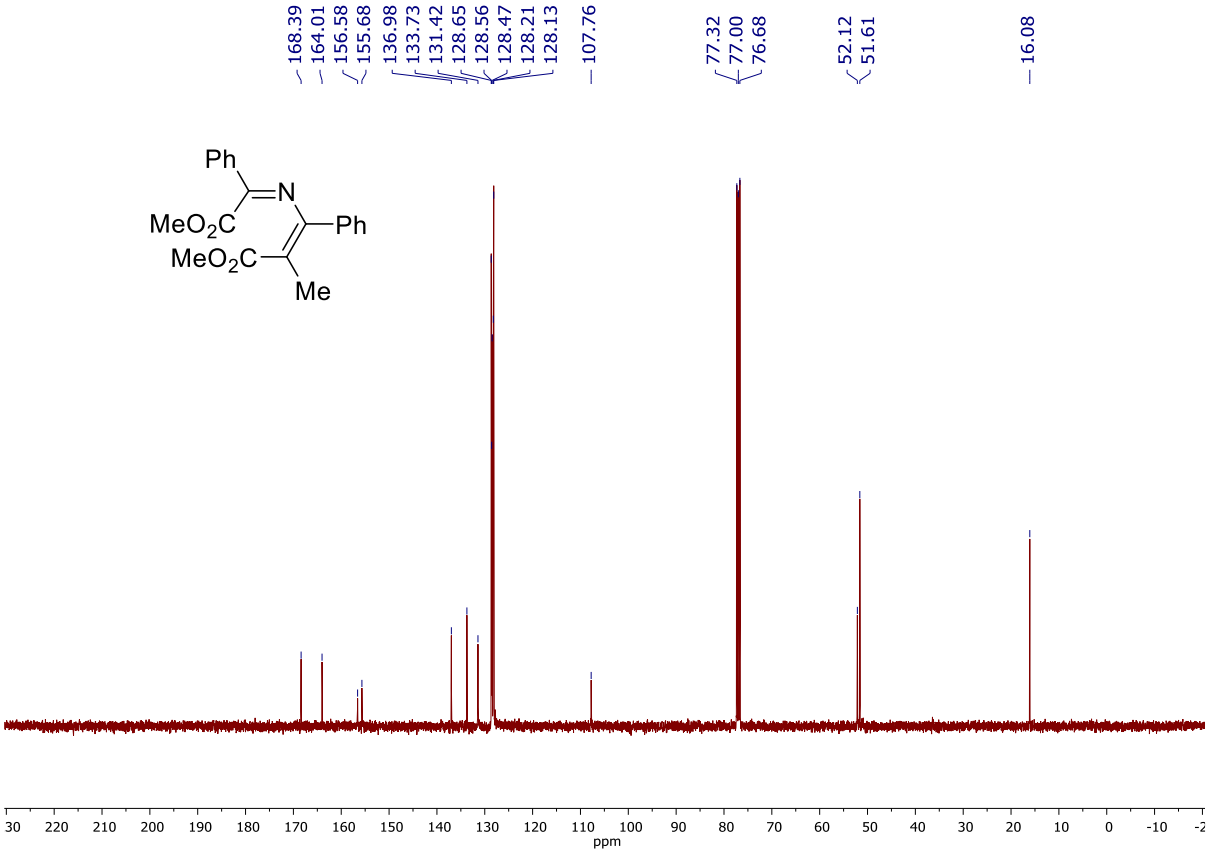
$^{13}C\{^{1}H\}$ NMR spectrum of azabutadiene **3a** (100 MHz, $CDCl_3$)



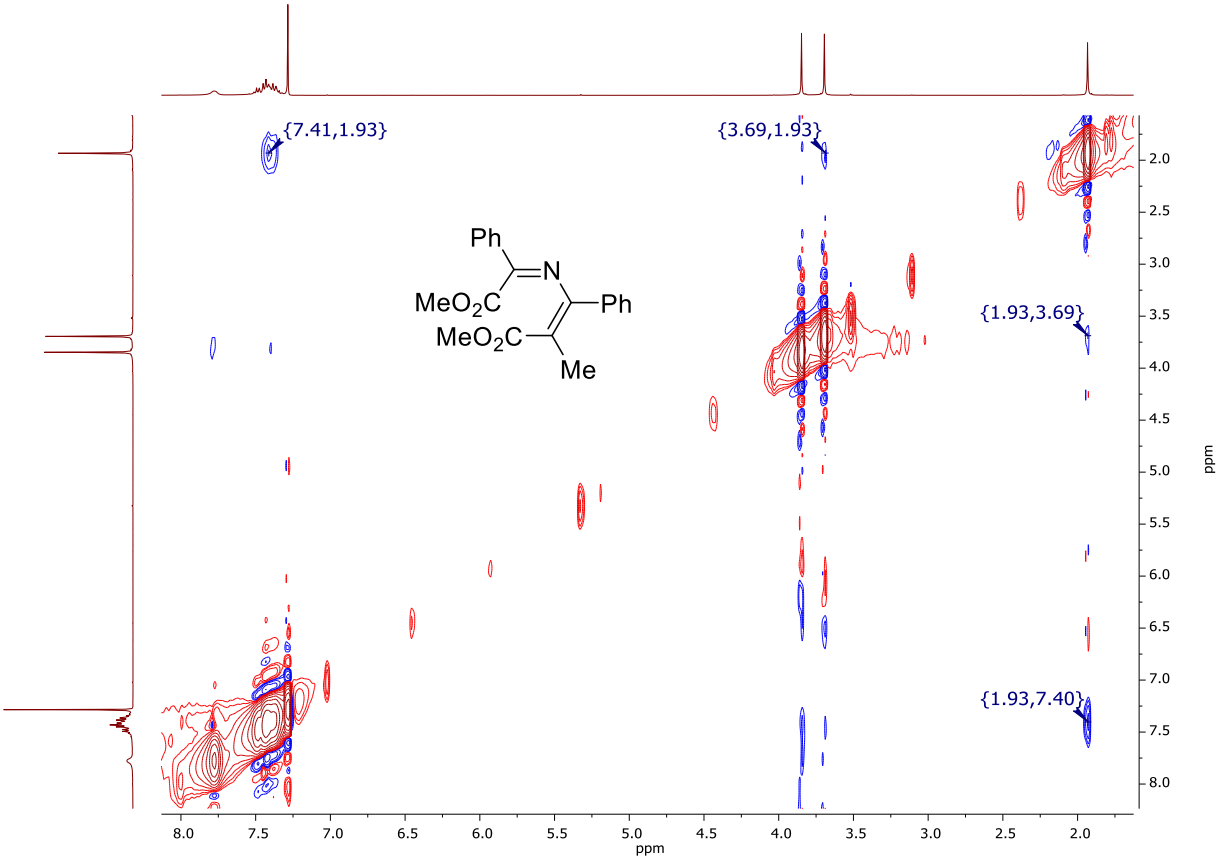
^{1}H NMR spectrum of azabutadiene **3v** (400 MHz, $CDCl_3$)



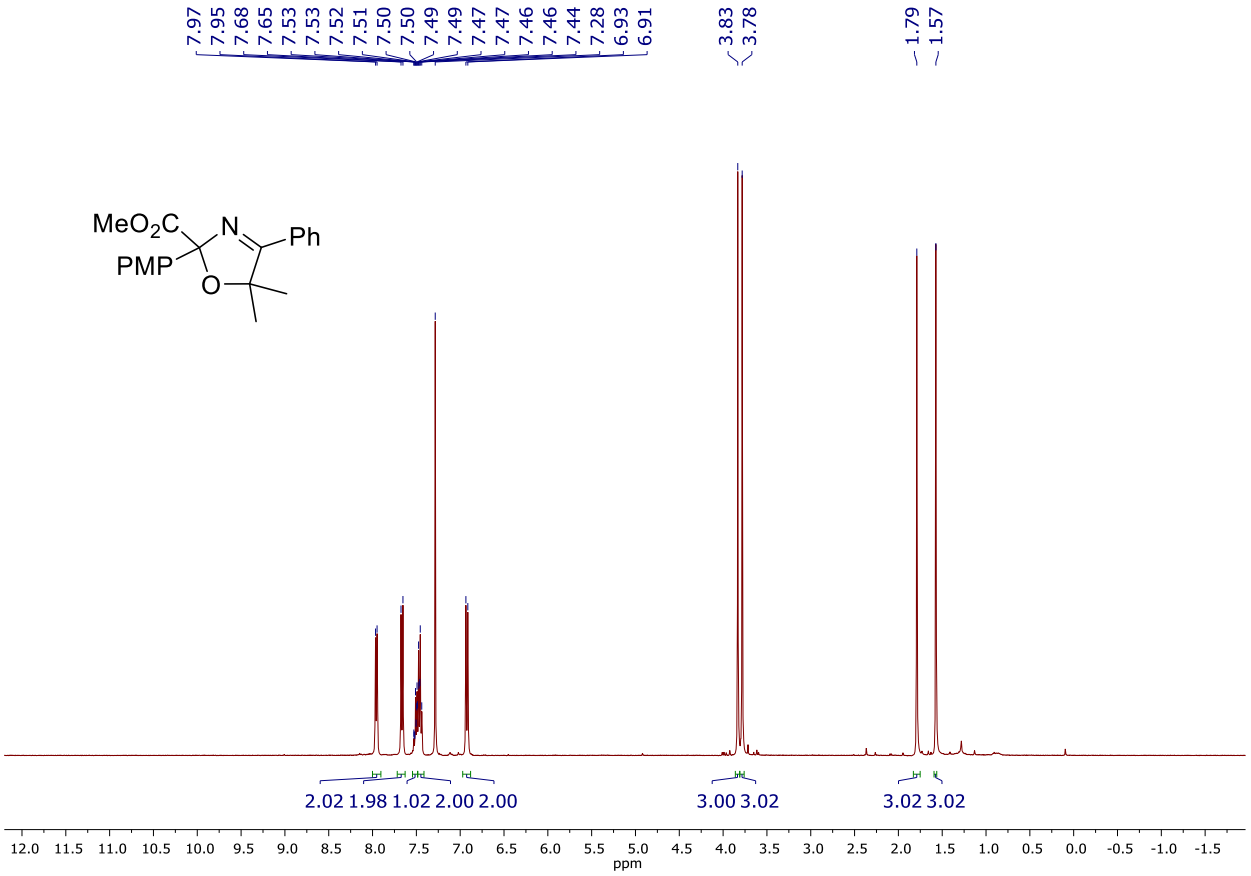
$^{13}C\{^{1}H\}$ NMR spectrum of azabutadiene **3v** (100 MHz, $CDCl_3$)



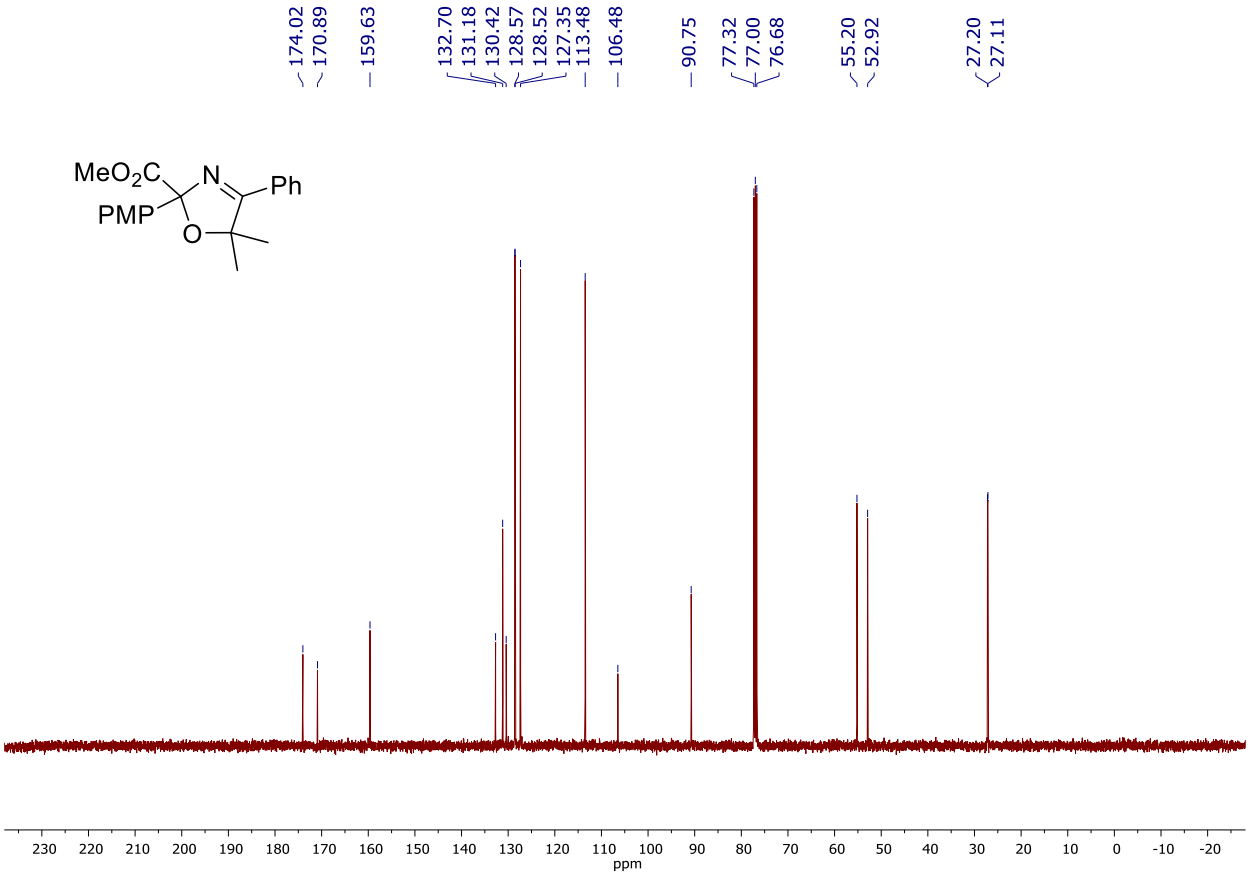
^{1}H-^{1}H NOESY spectrum of azabutadiene **3v** (400 MHz, $CDCl_3$)



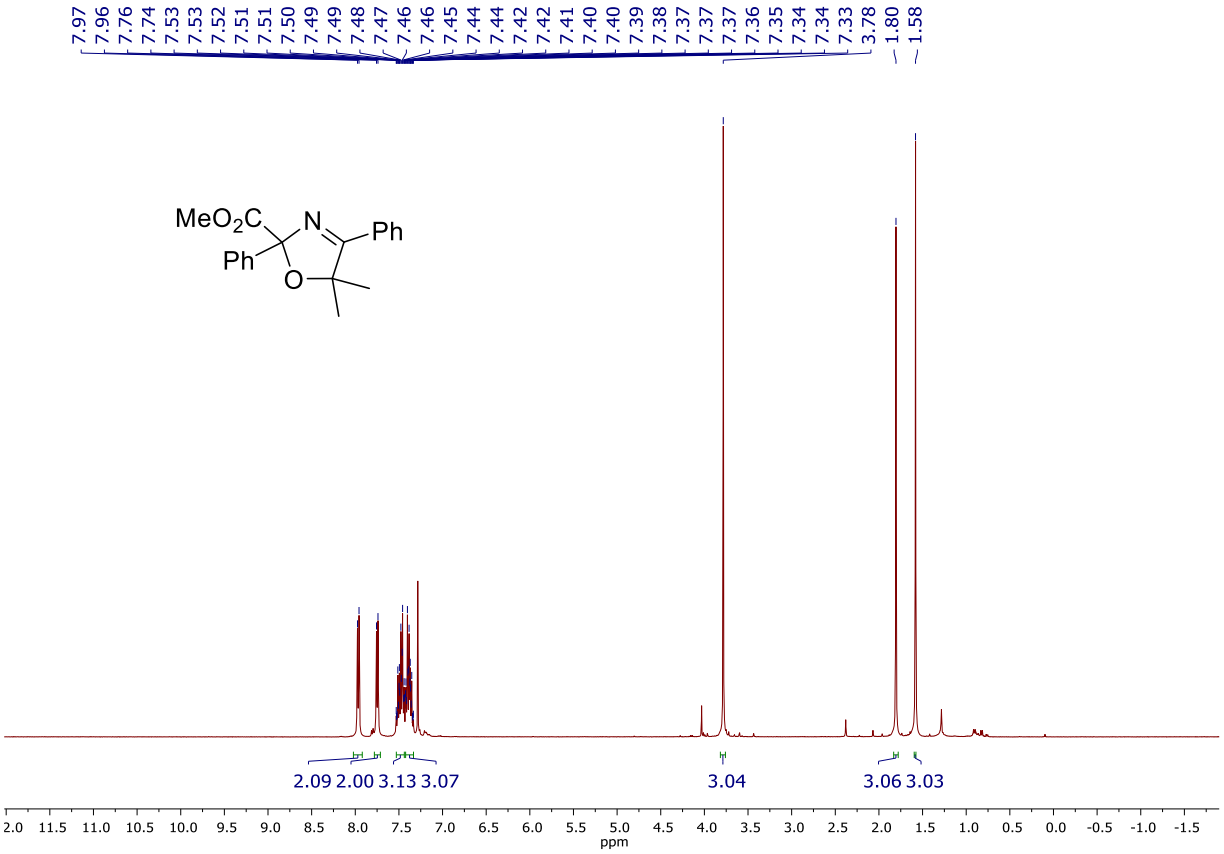
^{1}H NMR spectrum of oxazoline **4a** (400 MHz, $CDCl_3$)



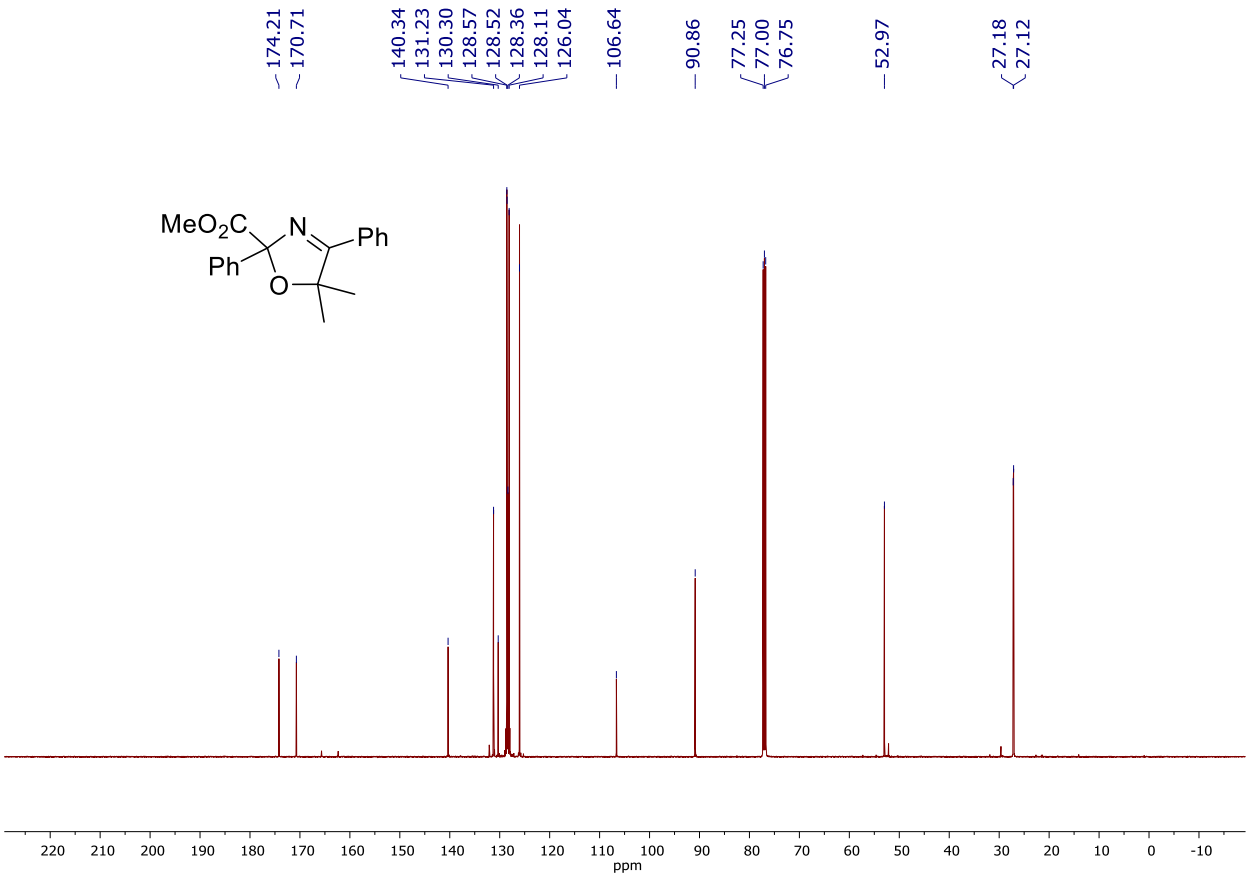
^{13}C{^{1}H} NMR spectrum of oxazoline **4a** (100 MHz, $CDCl_3$)



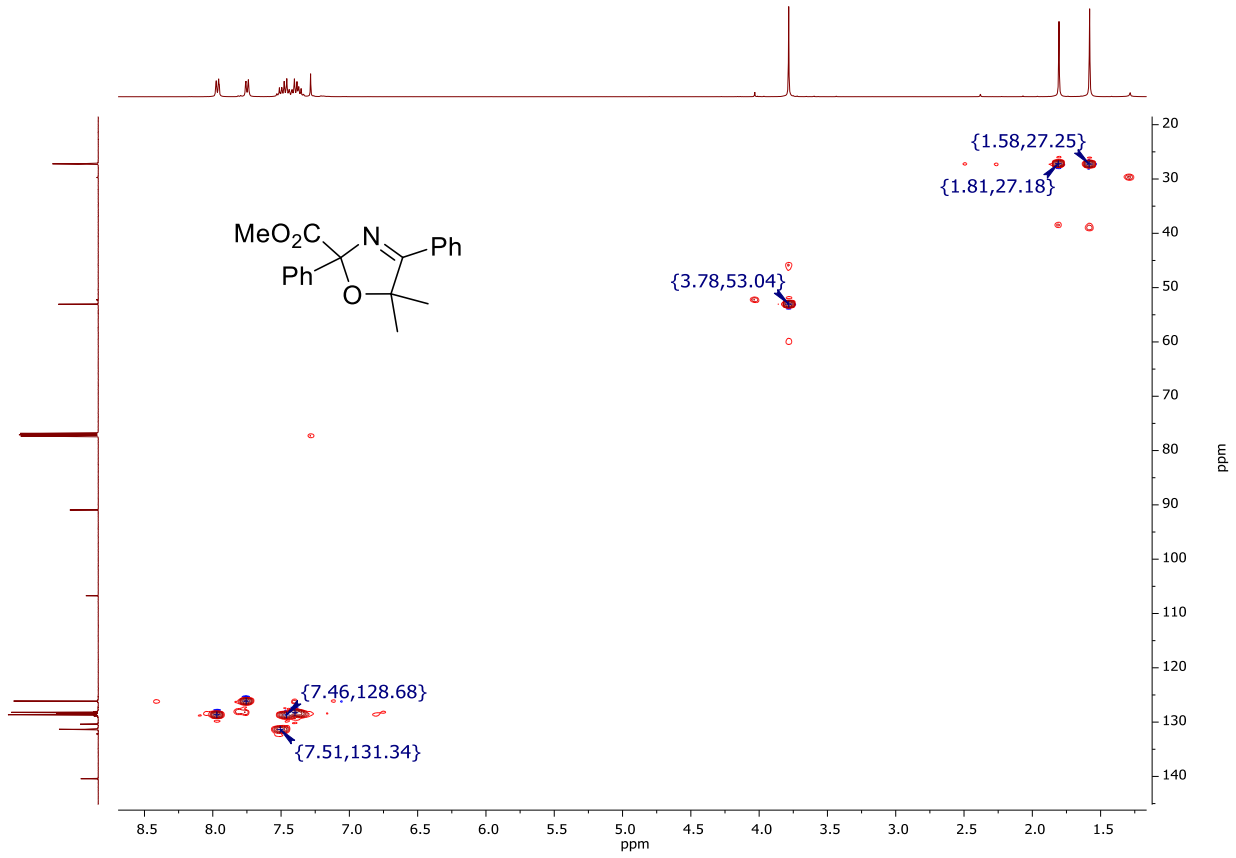
^{1}H NMR spectrum of oxazoline **4b** (400 MHz, $CDCl_3$)



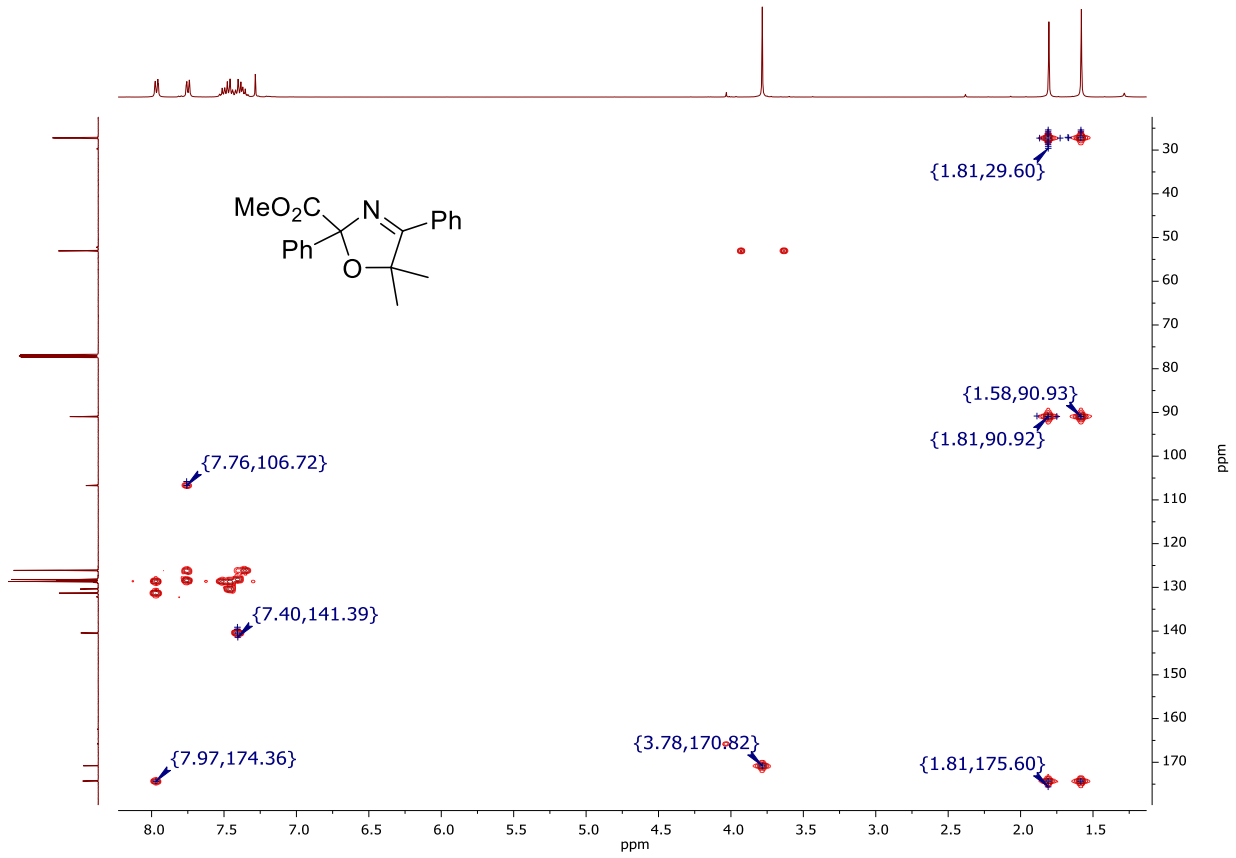
^{13}C{^{1}H} NMR spectrum of oxazoline **4b** (125 MHz, $CDCl_3$)



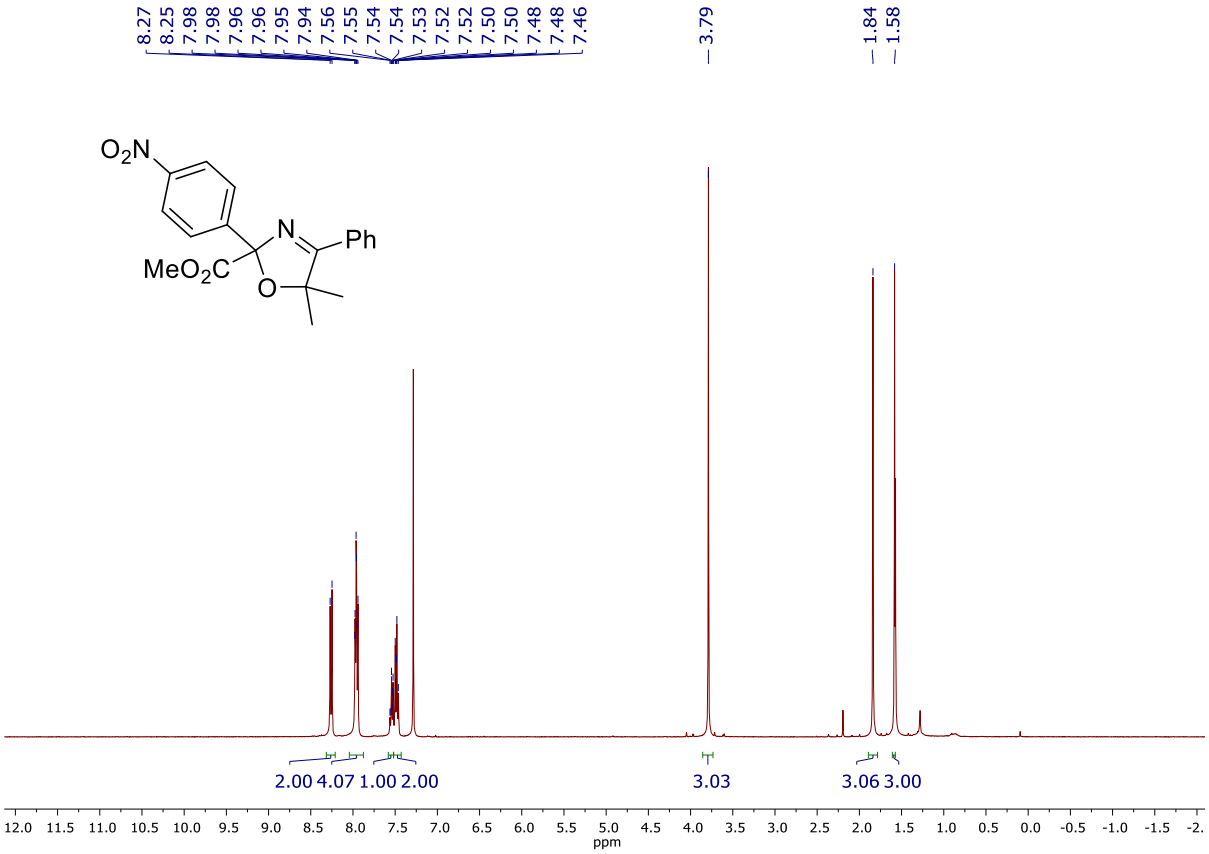
^{1}H-^{13}C HSQC NMR spectrum of oxazoline **4b** (400 MHz, $CDCl_3$)



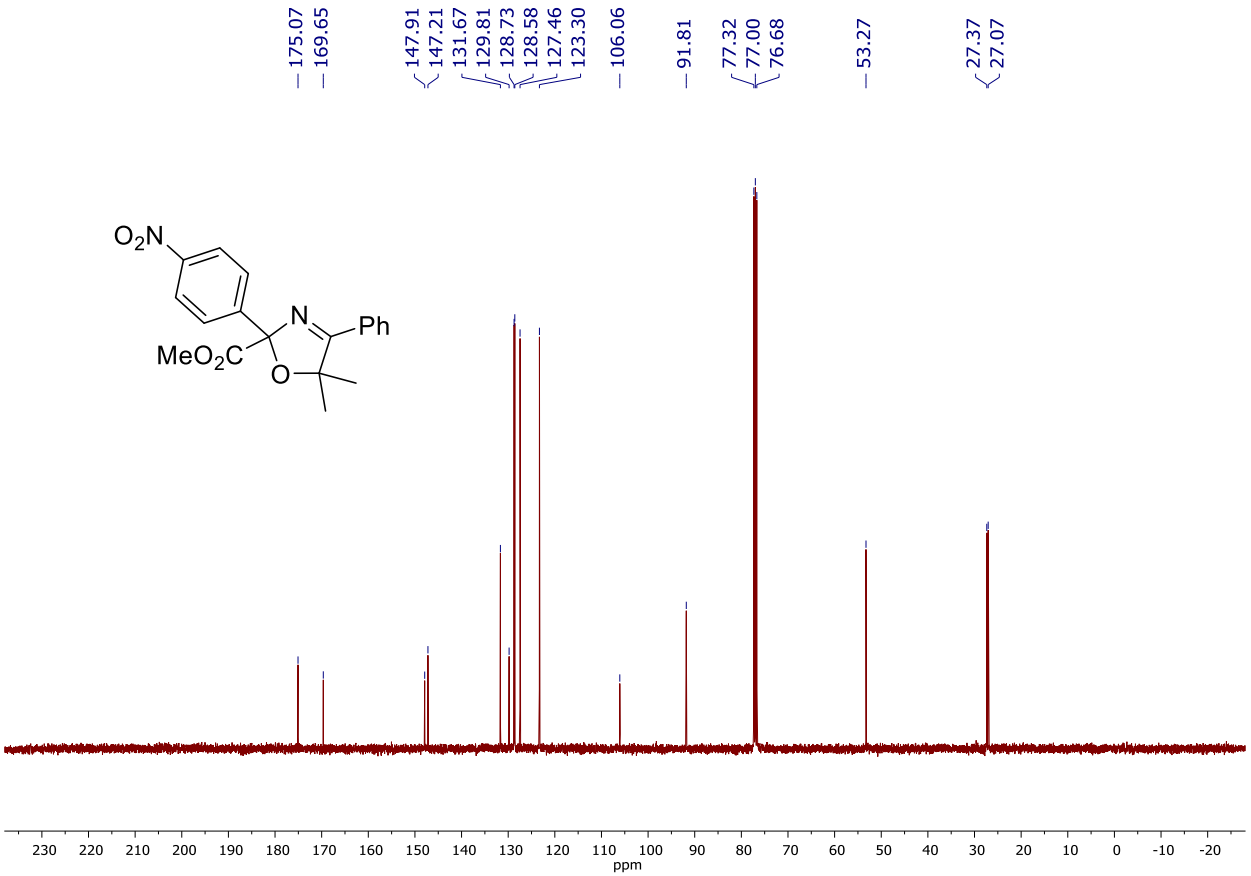
^{1}H-^{13}C HMBC NMR spectrum of oxazoline **4b** (400 MHz, $CDCl_3$)



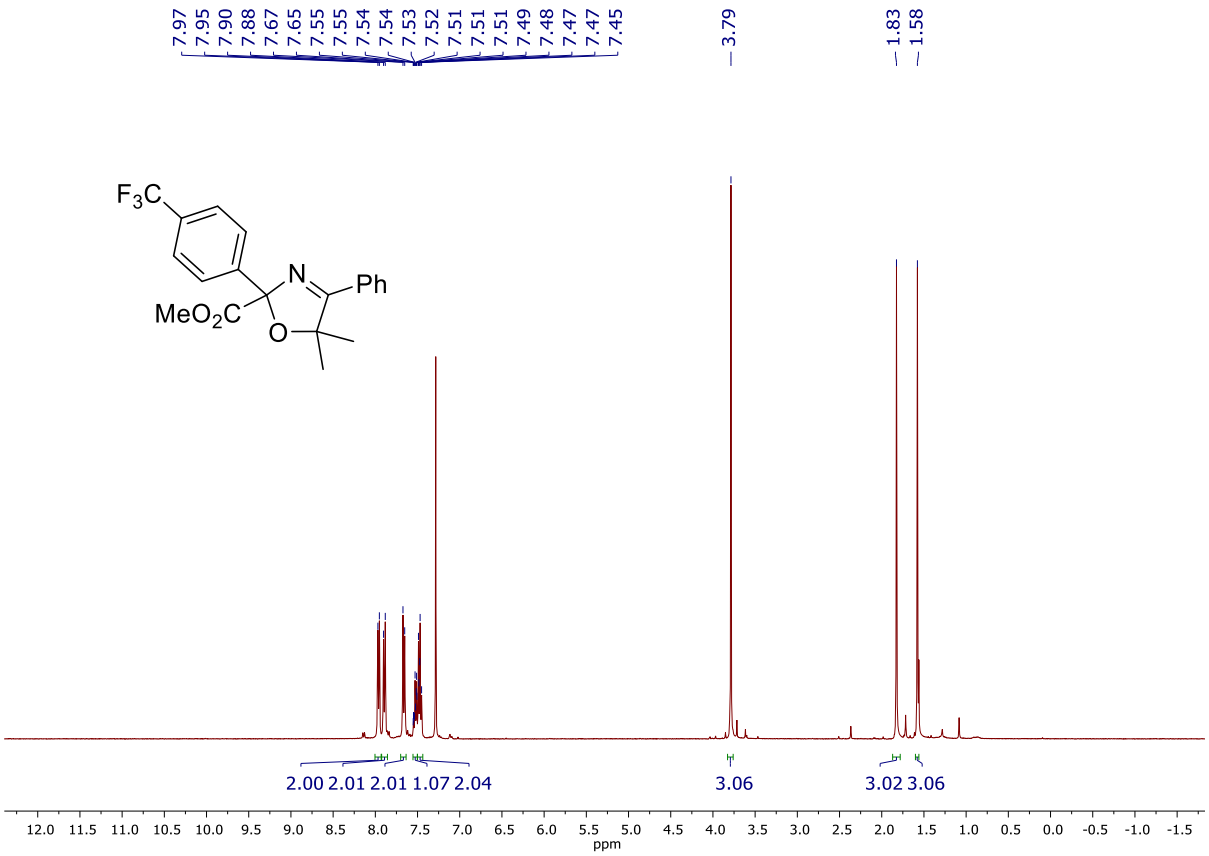
^{1}H NMR spectrum of oxazoline **4c** (400 MHz, $CDCl_3$)



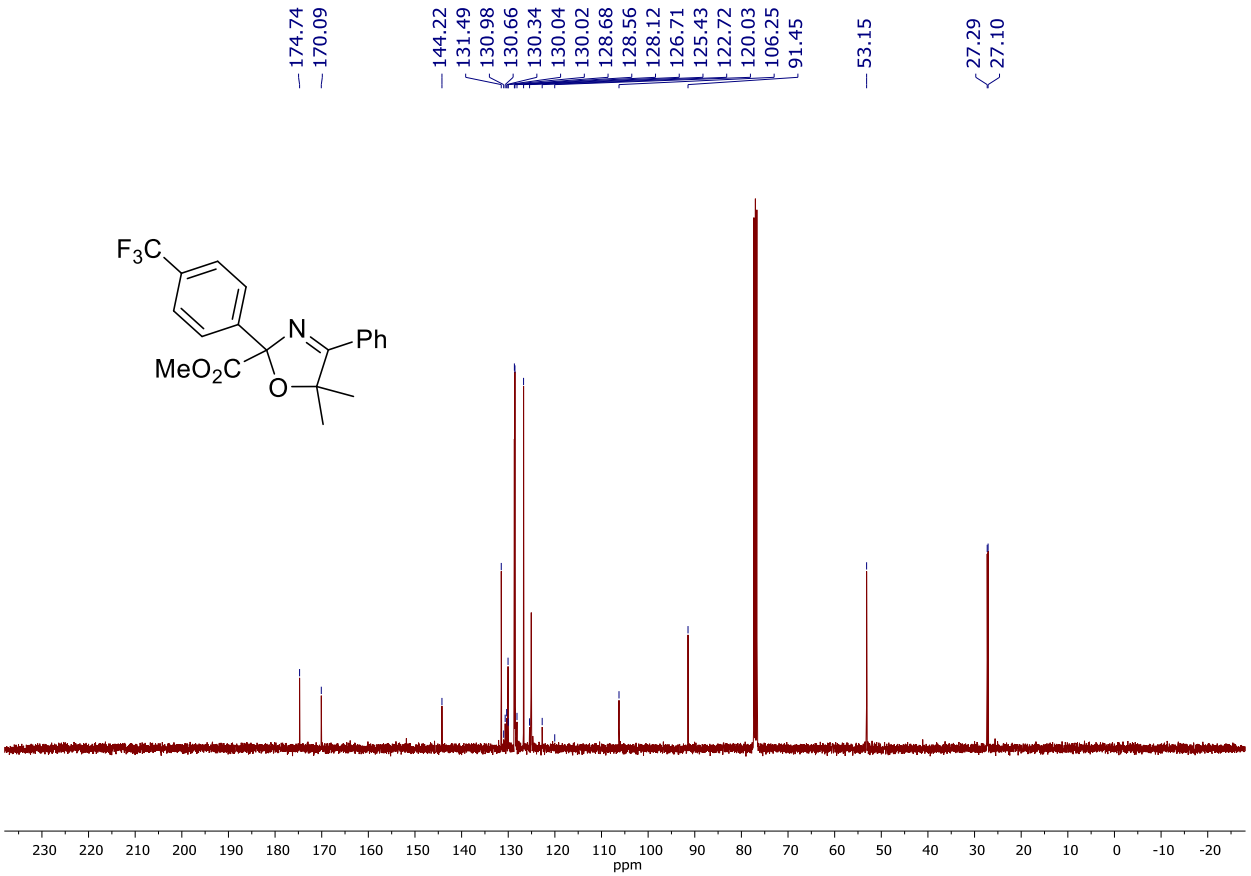
$^{13}C\{^{1}H\}$ NMR spectrum of oxazoline **4c** (100 MHz, $CDCl_3$)



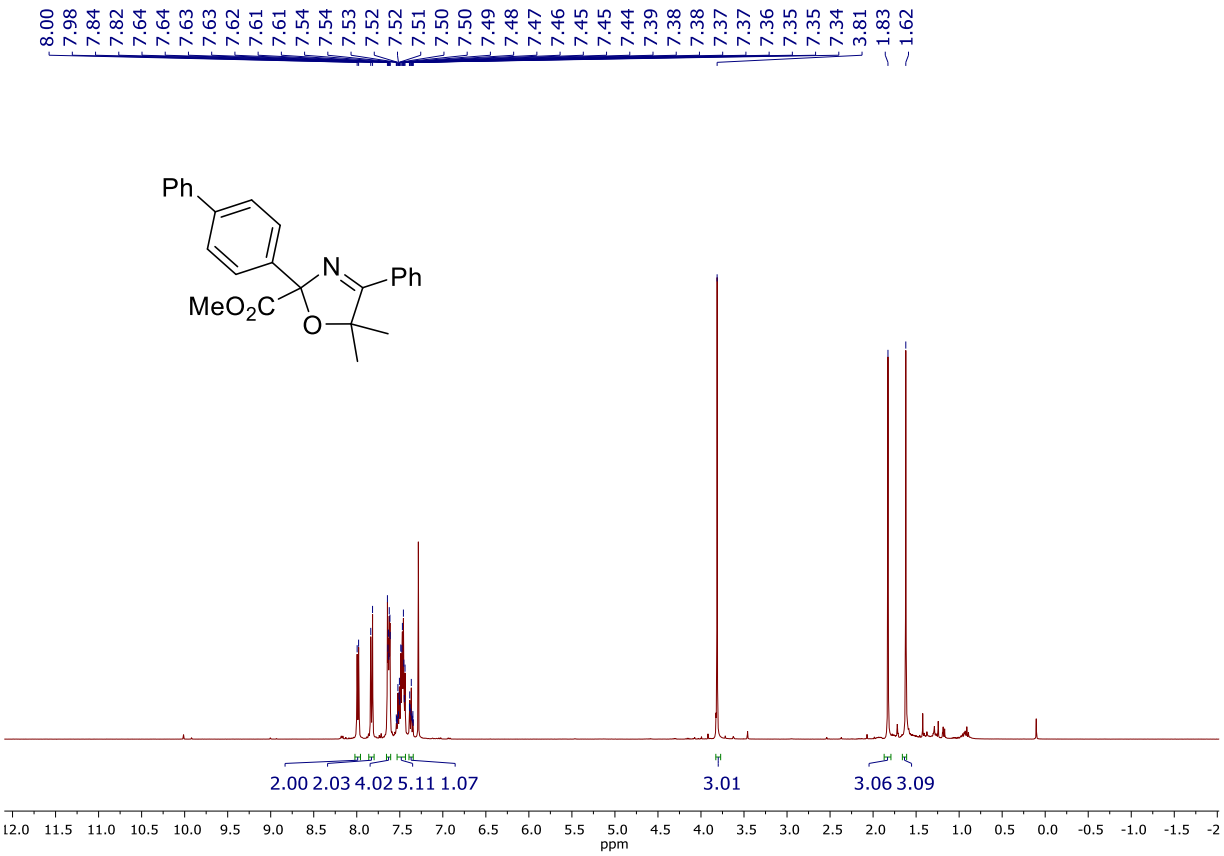
^{1}H NMR spectrum of oxazoline **4d** (400 MHz, $CDCl_3$)



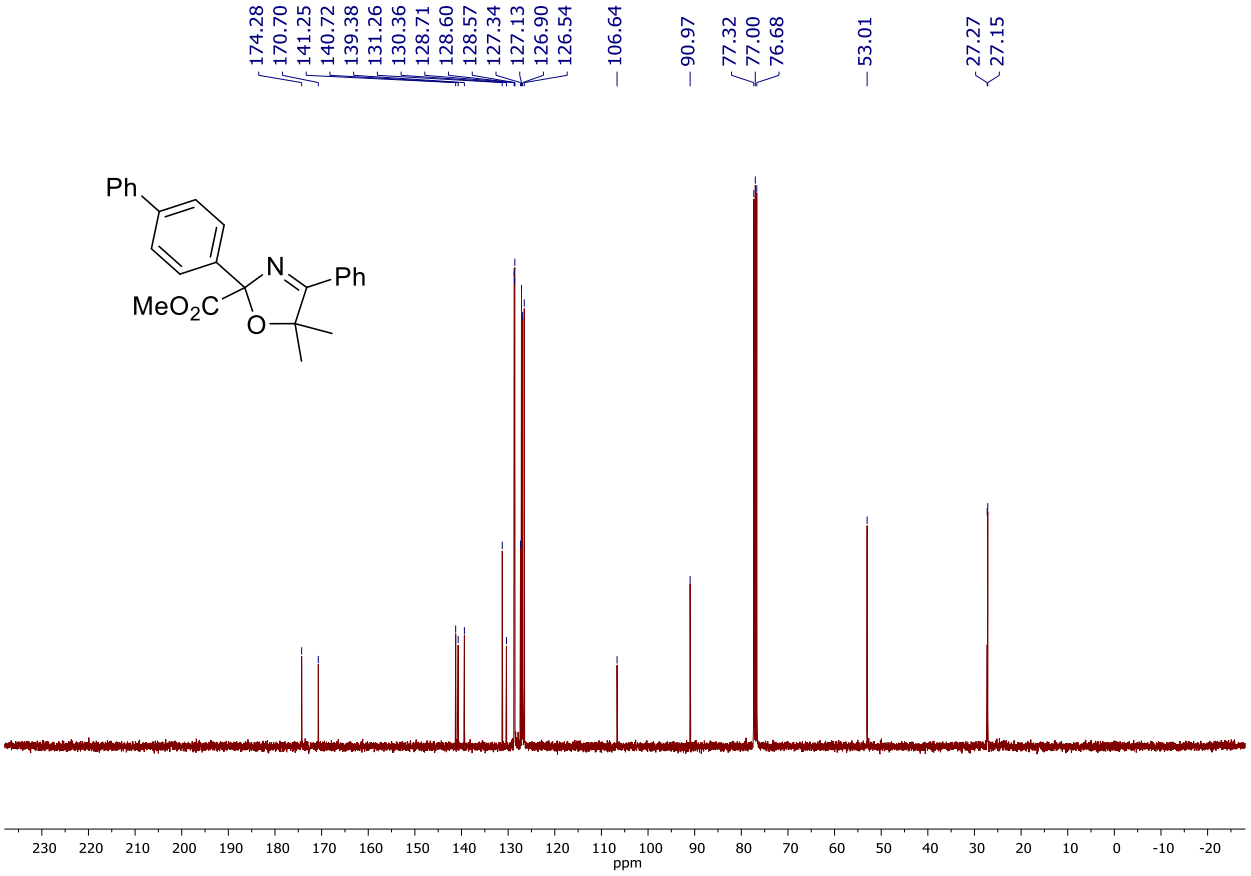
$^{13}C\{^{1}H\}$ NMR spectrum of oxazoline **4d** (100 MHz, $CDCl_3$)



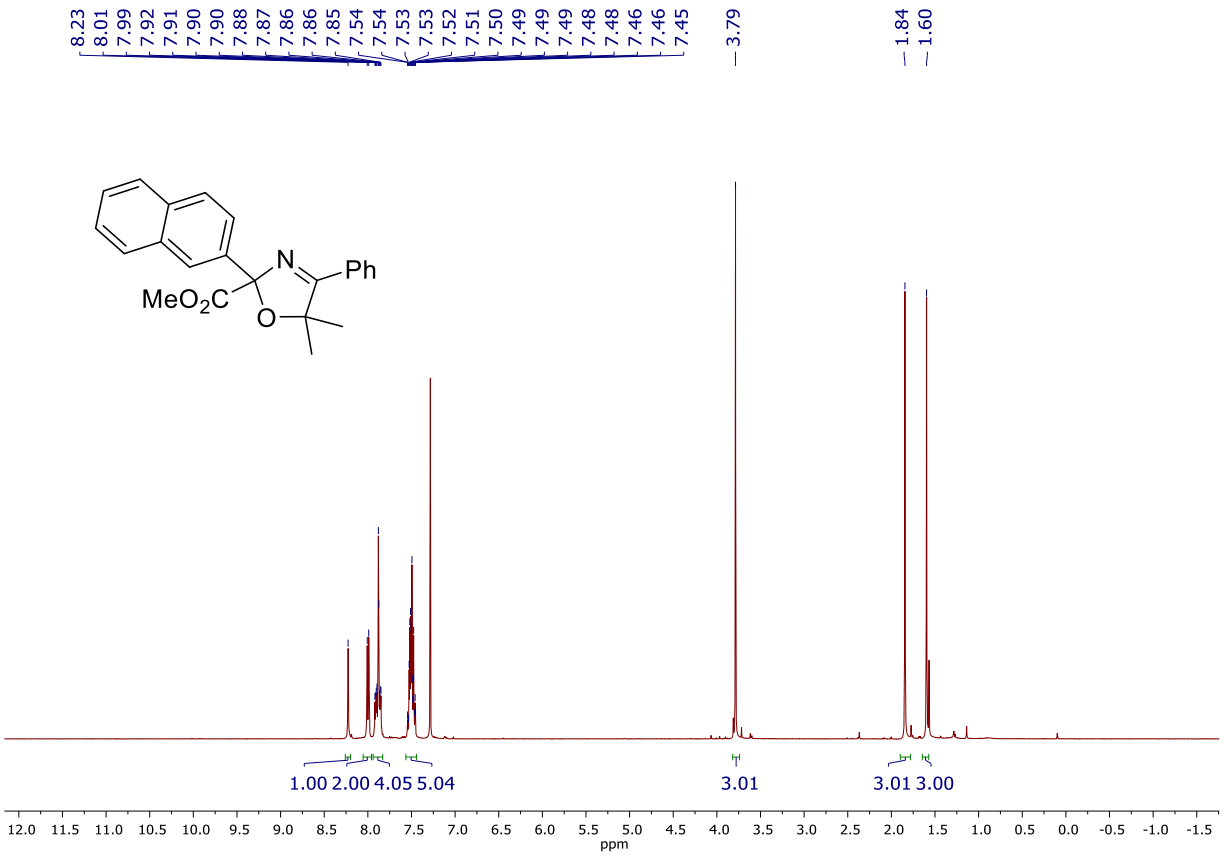
^{1}H NMR spectrum of oxazoline **4e** (400 MHz, $CDCl_3$)



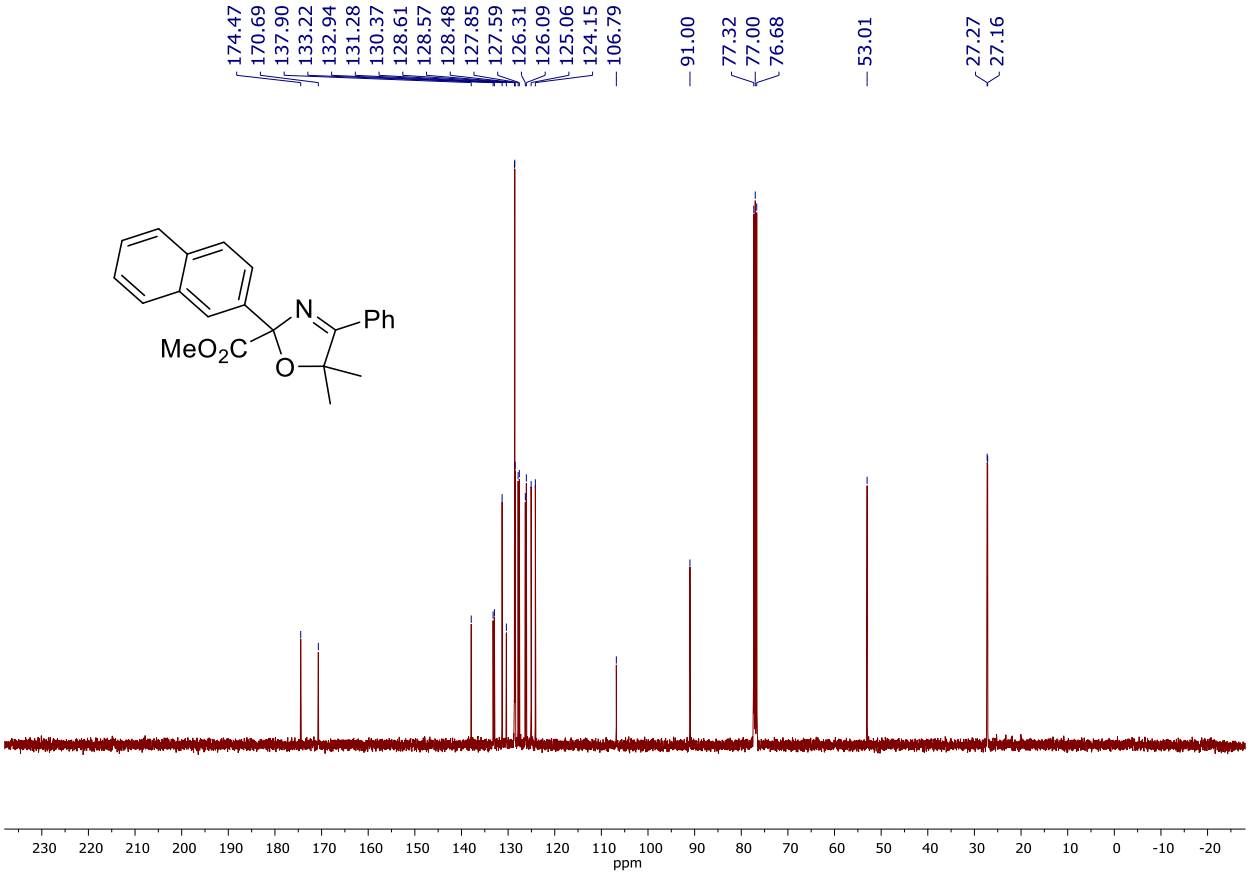
$^{13}C\{^{1}H\}$ NMR spectrum of oxazoline **4e** (100 MHz, $CDCl_3$)



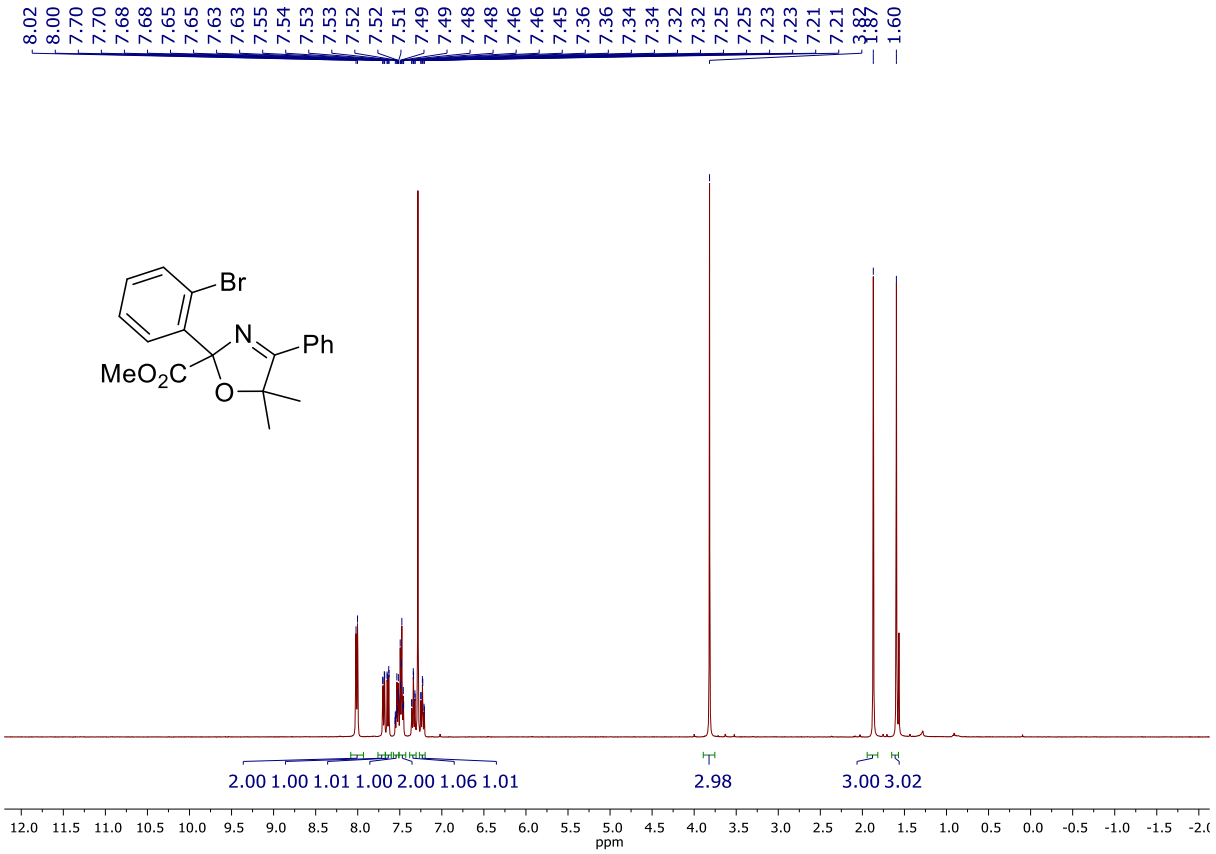
^{1}H NMR spectrum of oxazoline **4f** (400 MHz, $CDCl_3$)



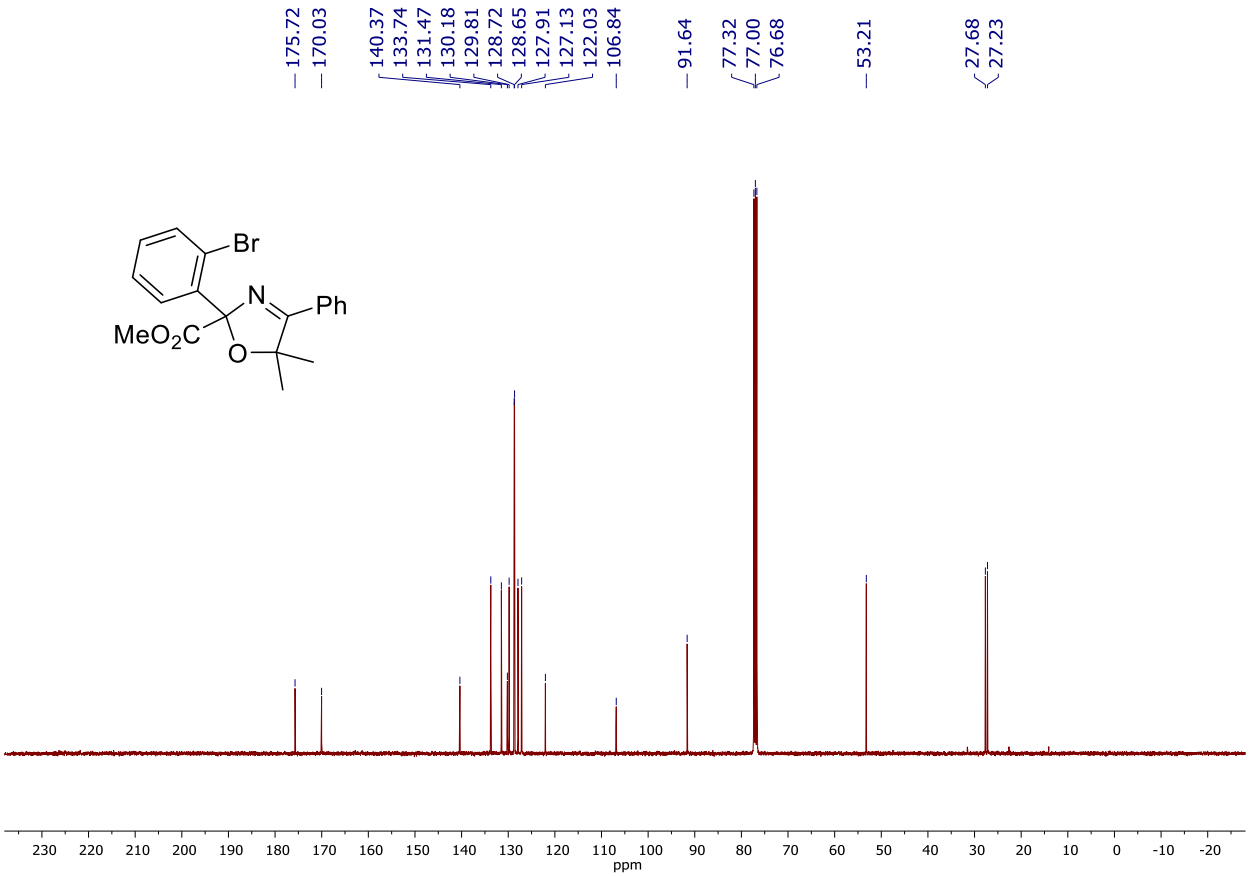
$^{13}C\{^{1}H\}$ NMR spectrum of oxazoline **4f** (100 MHz, $CDCl_3$)



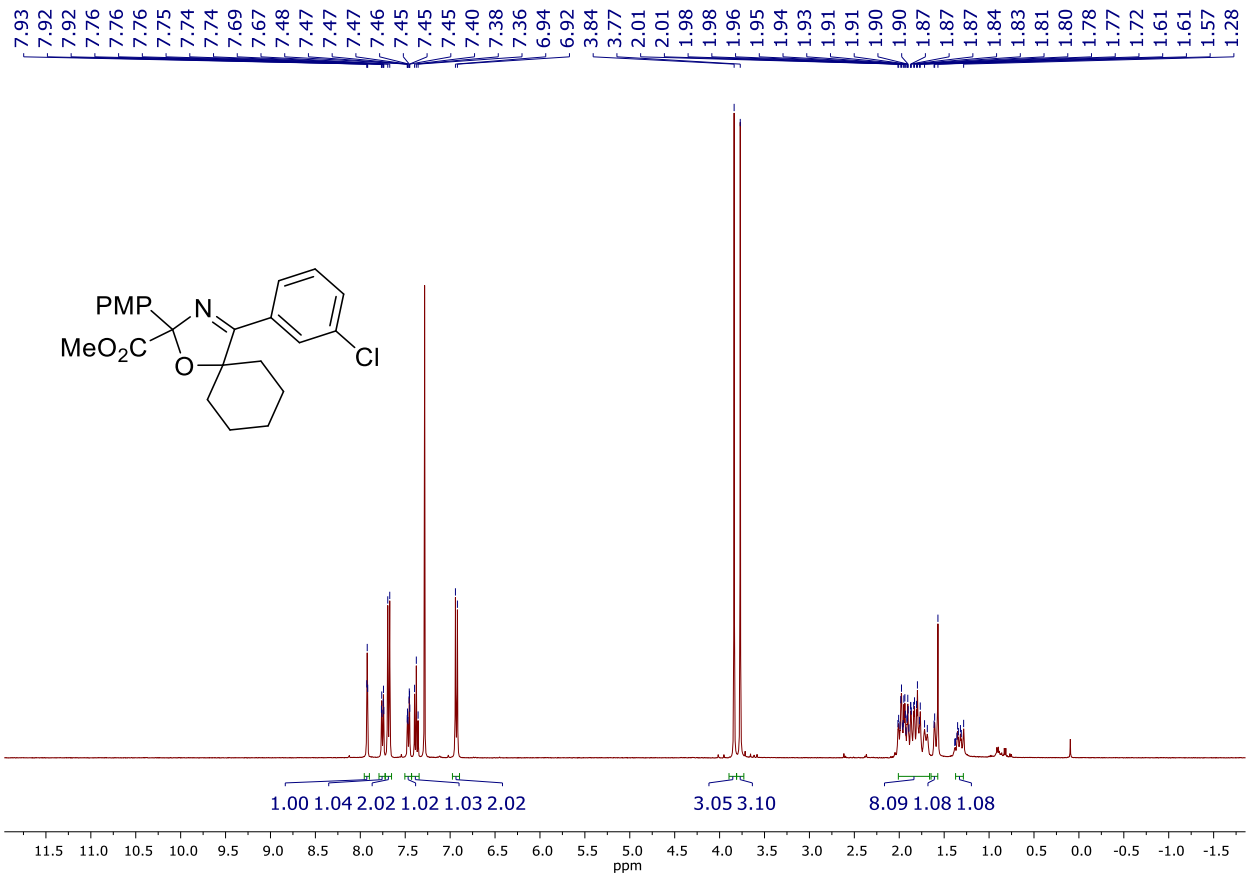
^{1}H NMR spectrum of oxazoline **4g** (400 MHz, $CDCl_3$)



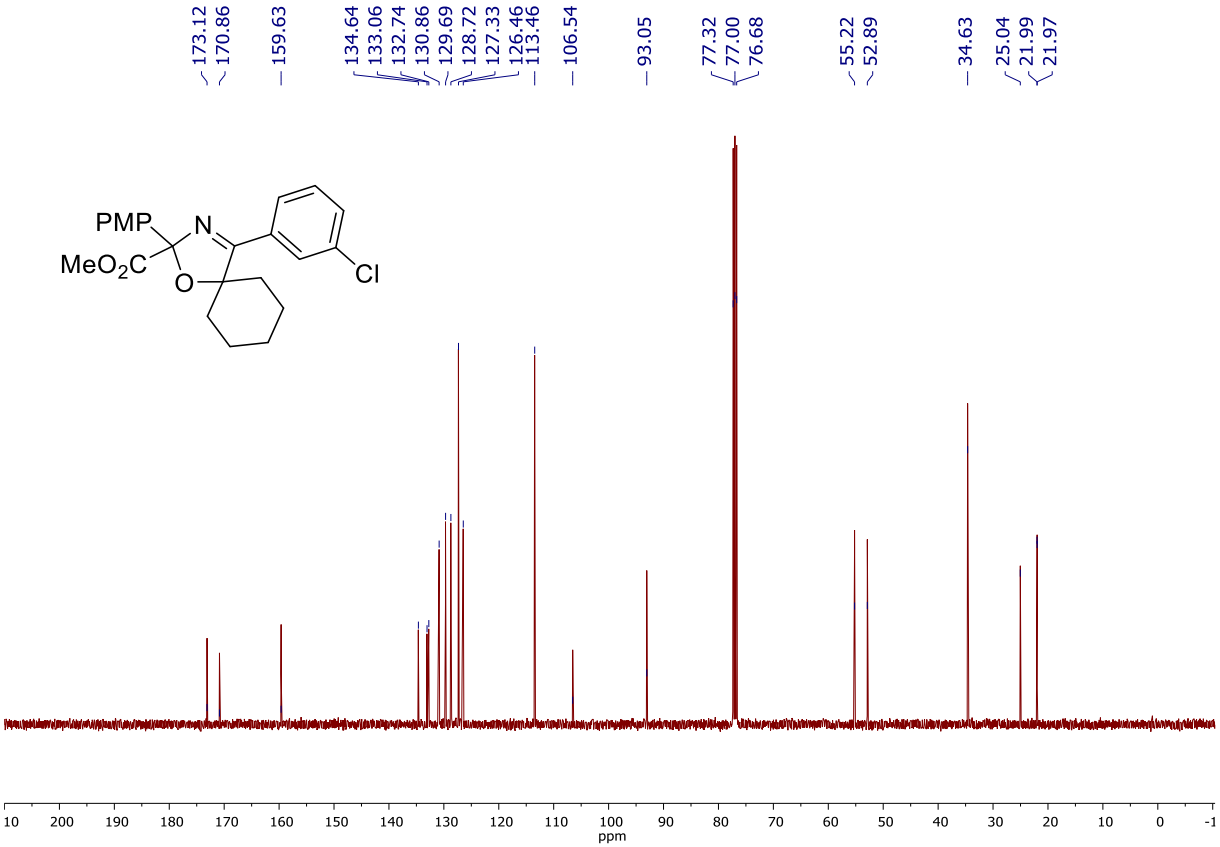
$^{13}C\{^{1}H\}$ NMR spectrum of oxazoline **4g** (100 MHz, $CDCl_3$)



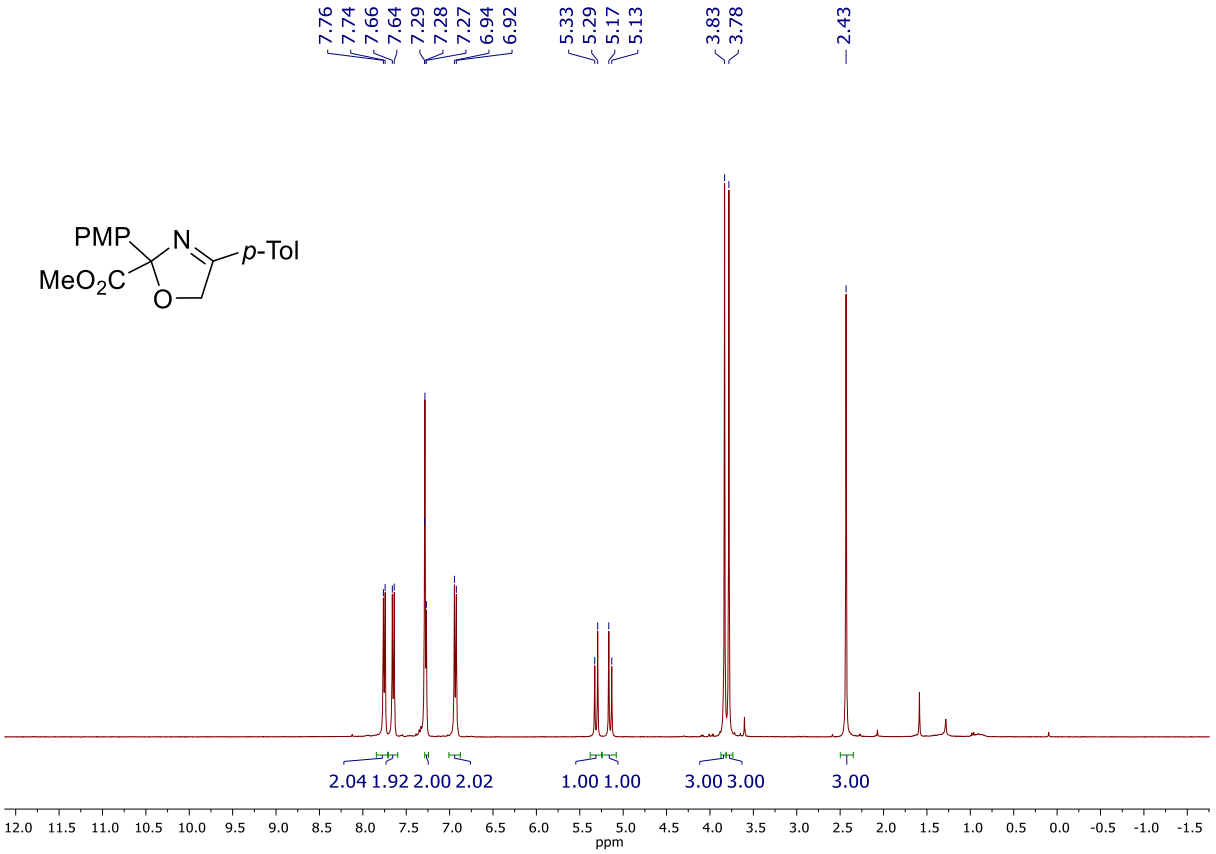
^{1}H NMR spectrum of oxazoline **4h** (400 MHz, $CDCl_3$)



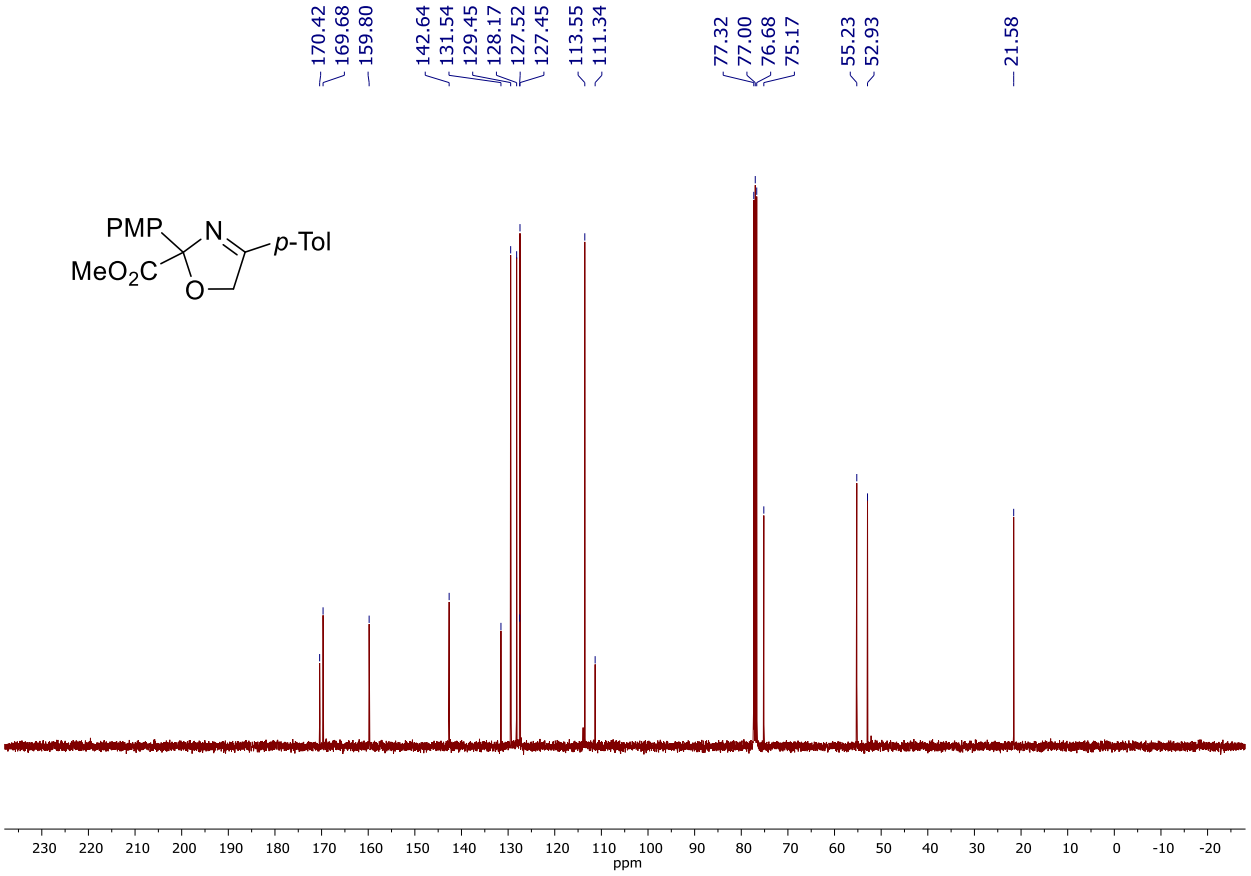
$^{13}C\{^{1}H\}$ NMR spectrum of oxazoline **4h** (100 MHz, $CDCl_3$)



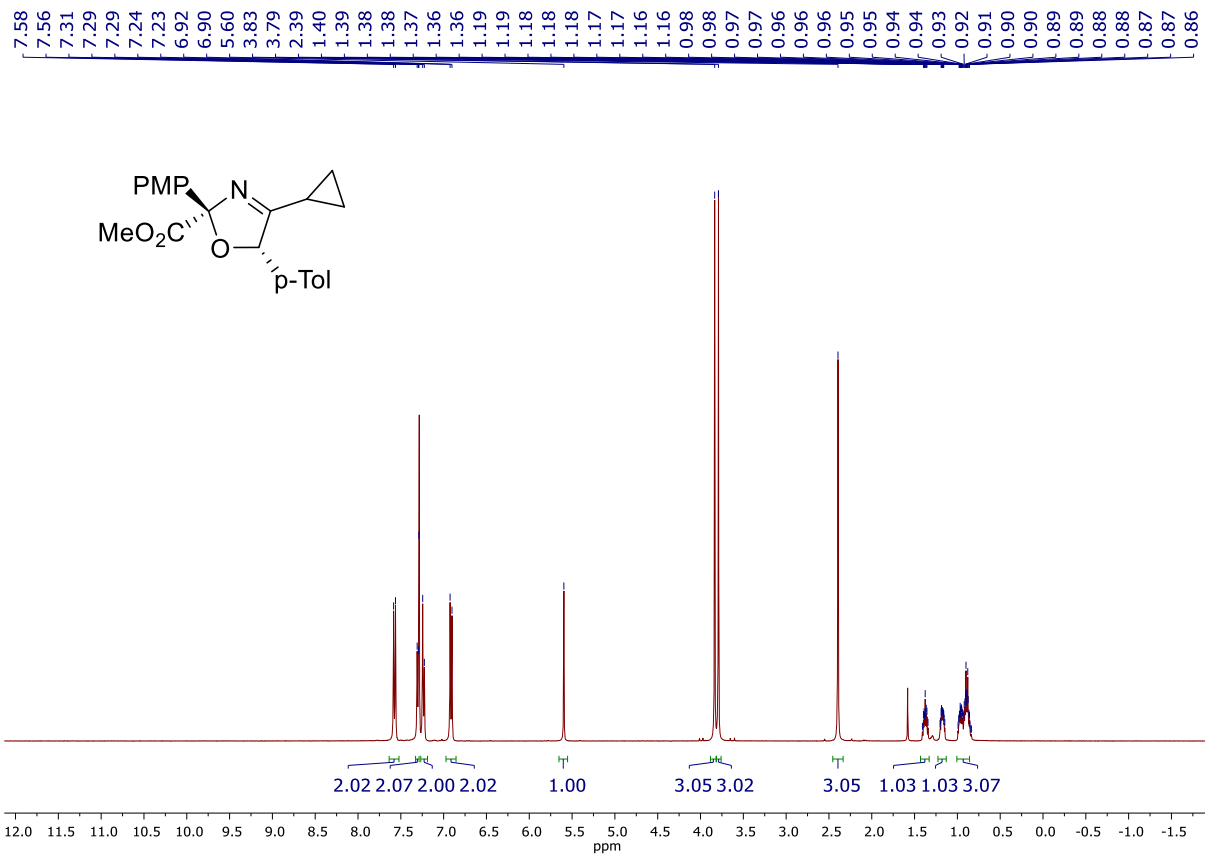
^{1}H NMR spectrum of oxazoline **4i** (400 MHz, $CDCl_3$)



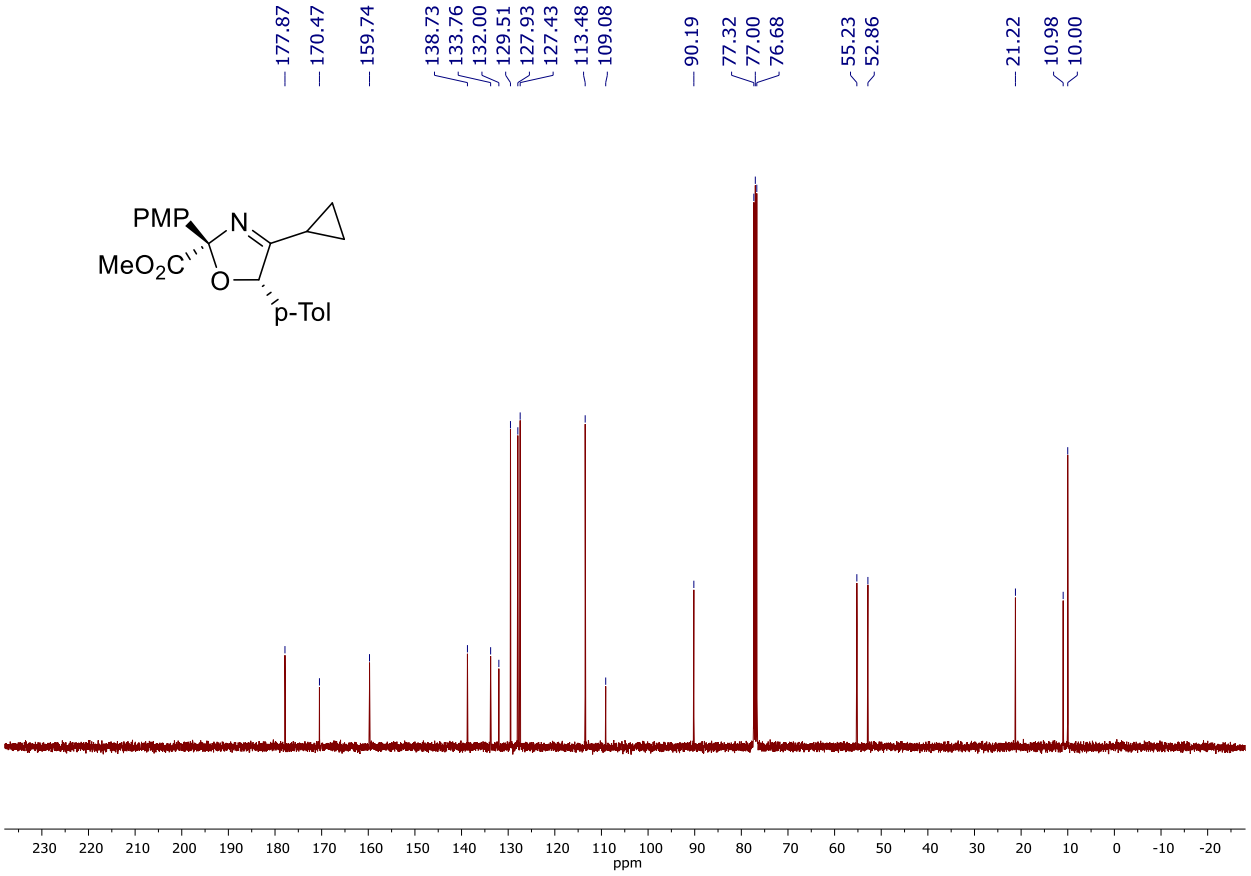
$^{13}C\{^{1}H\}$ NMR spectrum of oxazoline **4i** (100 MHz, $CDCl_3$)



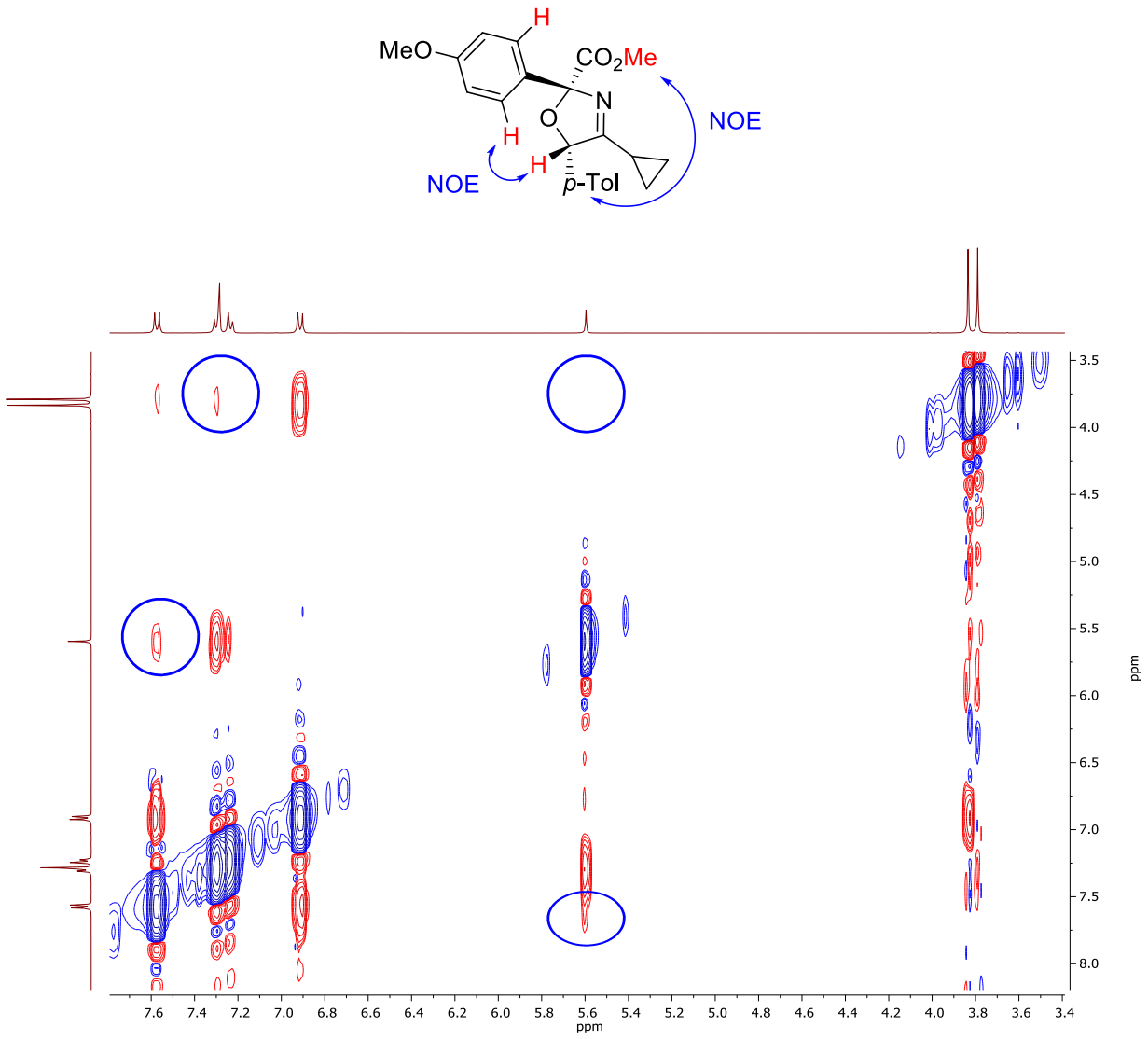
^{1}H NMR spectrum of oxazoline **(2*RS*,5*SR*)-4j** (400 MHz, $CDCl_3$)



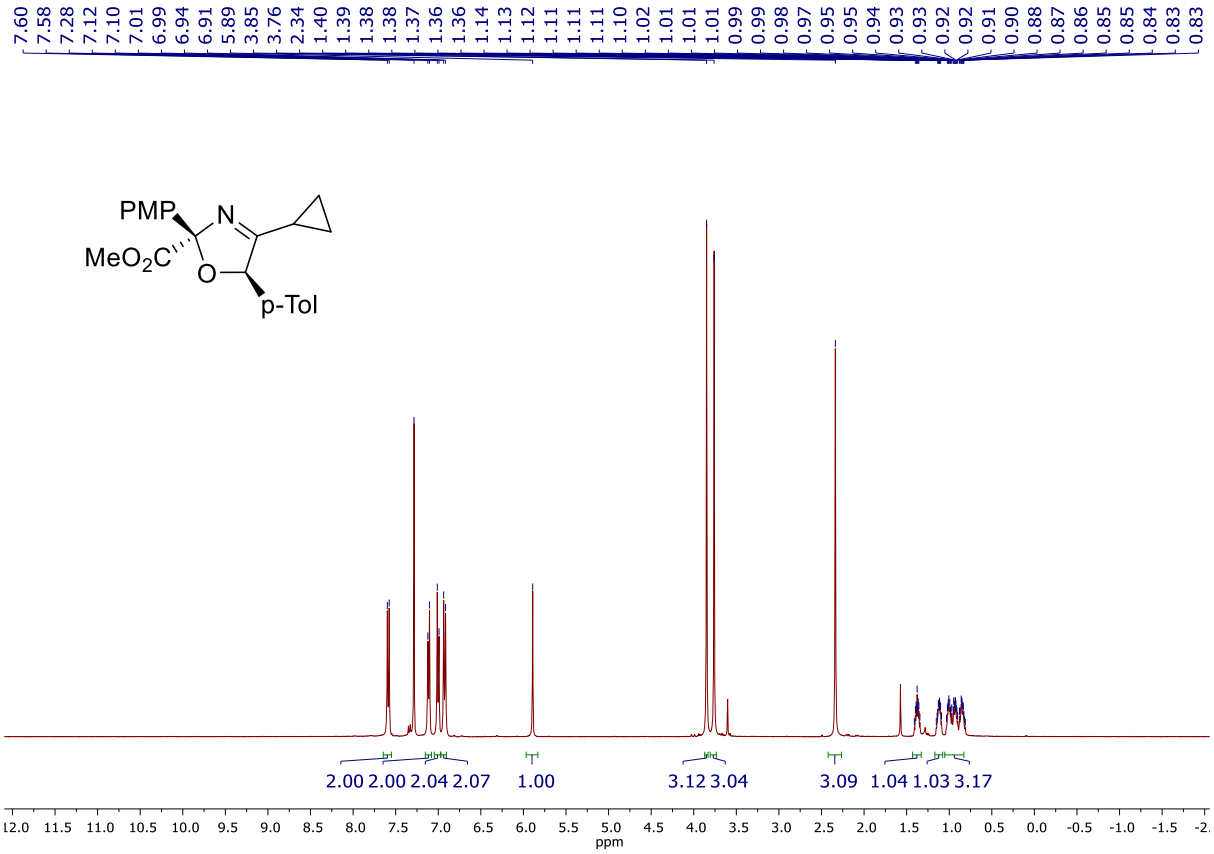
$^{13}C\{^{1}H\}$ NMR spectrum of oxazoline **(2*RS*,5*SR*)-4j** (100 MHz, $CDCl_3$)



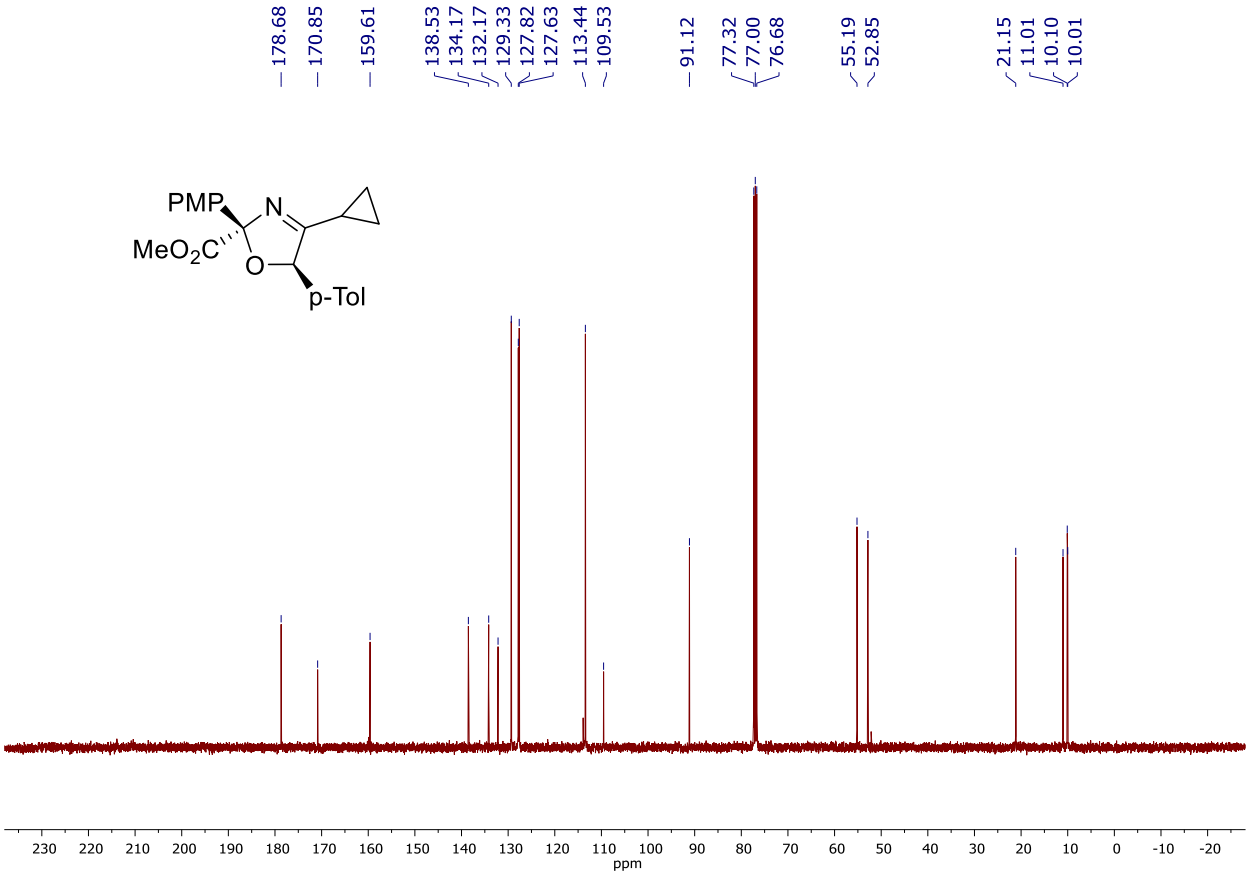
^{1}H-^{1}H NOESY NMR spectrum of oxazoline **(2*RS*,5*SR*)-4j** (400 MHz, $CDCl_3$)


MeO
H
CO2Me
N
O
H
H
p-Tol
NOE
NOE
ppm
ppm

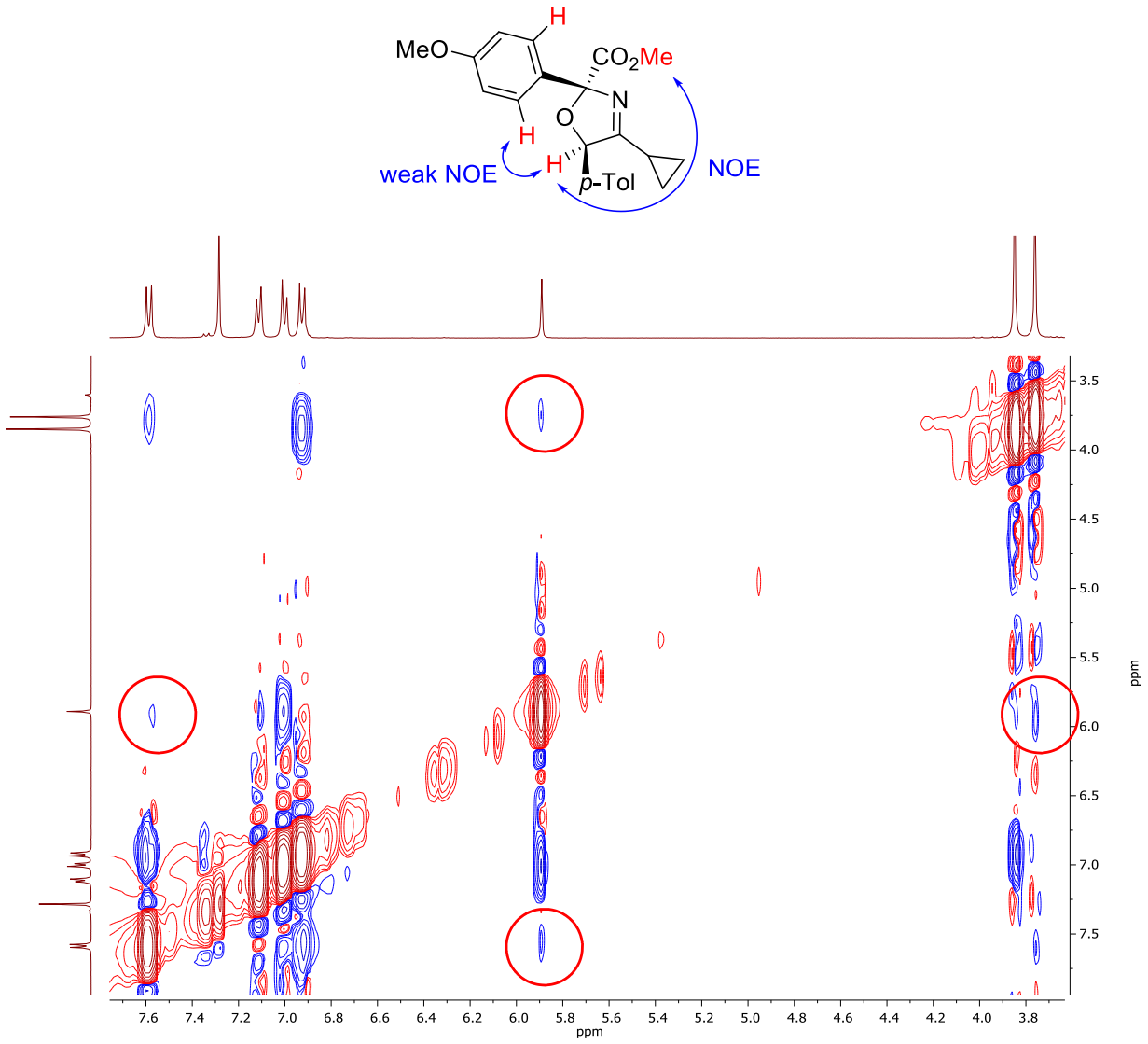
^{1}H NMR spectrum of oxazoline **(2*RS*,5*RS*)-4j** (400 MHz, $CDCl_3$)



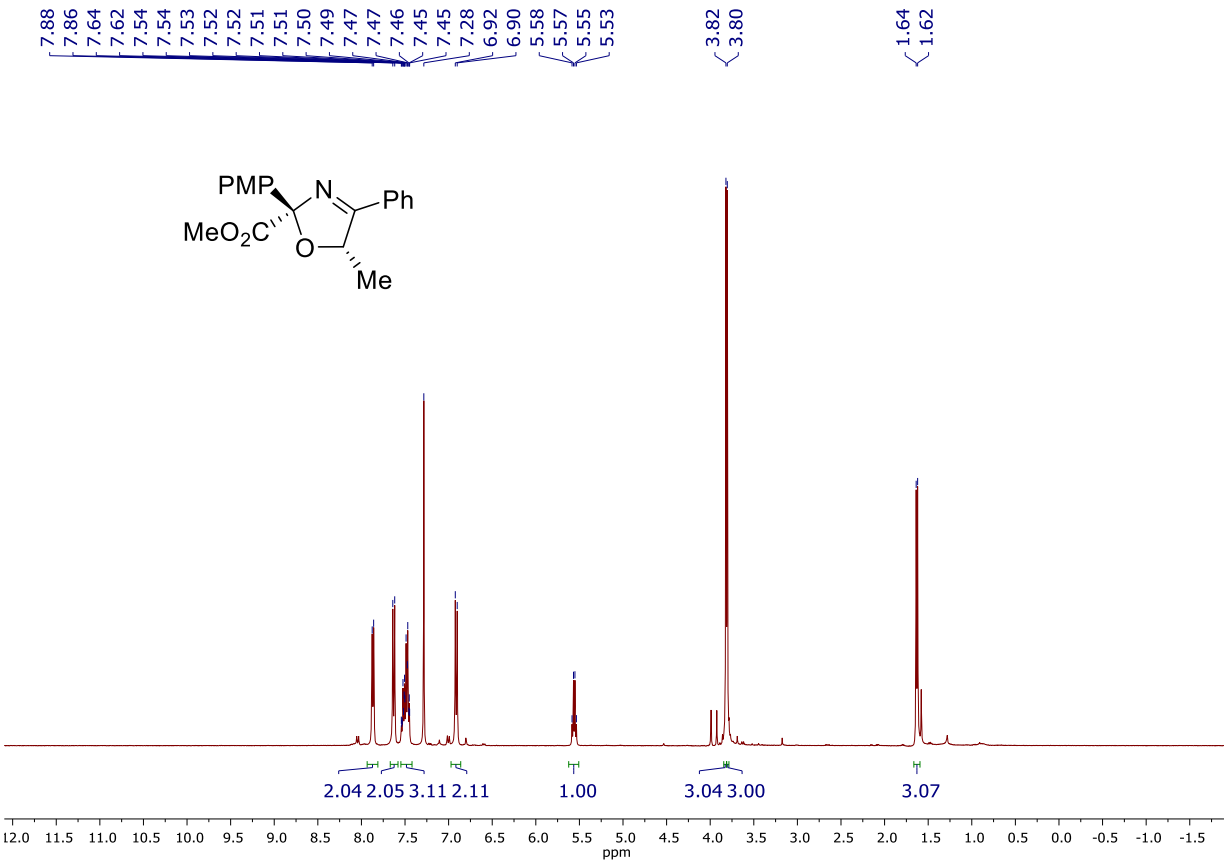
^{13}C{^{1}H} NMR spectrum of oxazoline **(2*RS*,5*RS*)-4j** (100 MHz, $CDCl_3$)



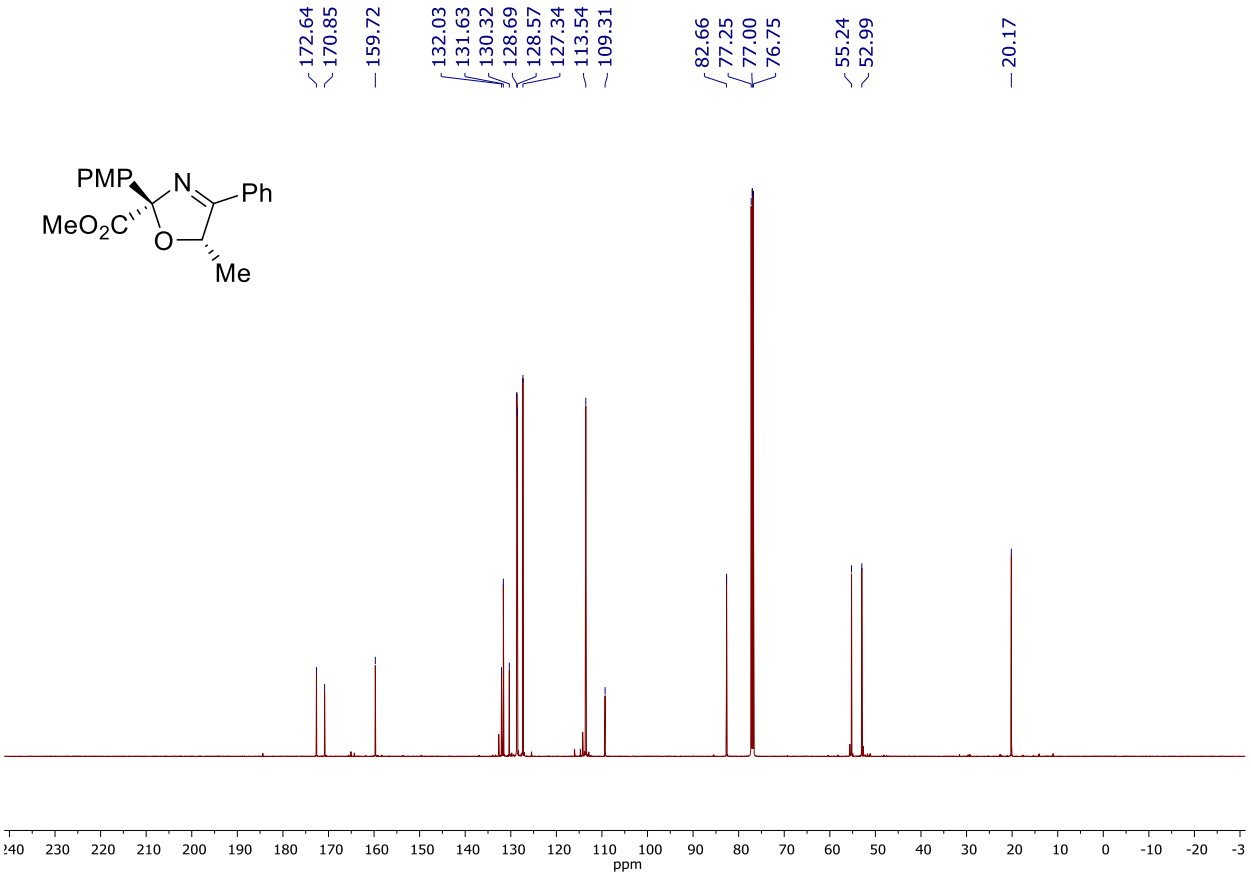
^{1}H-^{1}H NOESY NMR spectrum of oxazoline **(2*RS*,5*RS*)-4j** (400 MHz, $CDCl_3$)



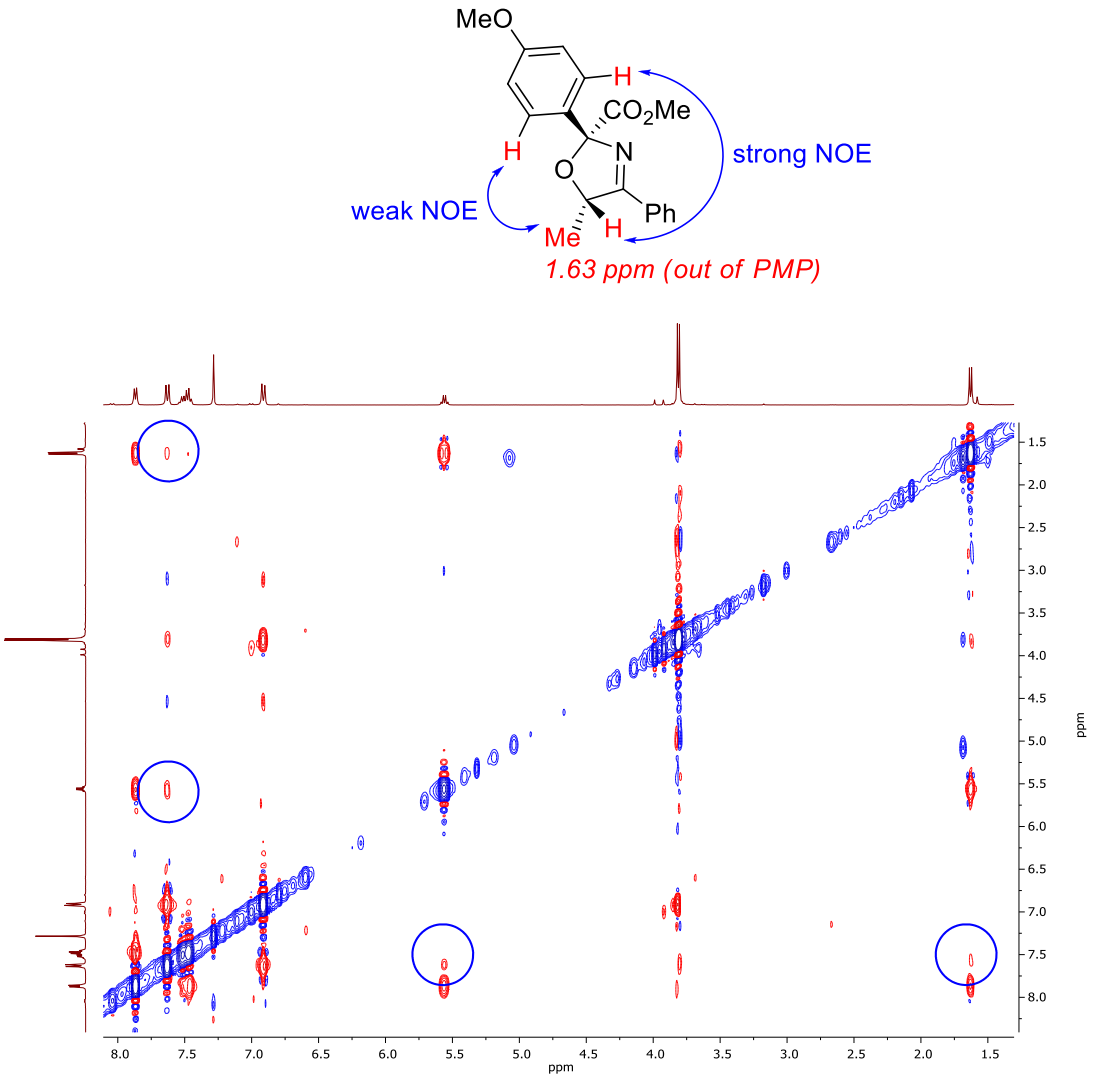
^{1}H NMR spectrum of oxazoline **(2*RS*,5*SR*)-4k** (400 MHz, $CDCl_3$)



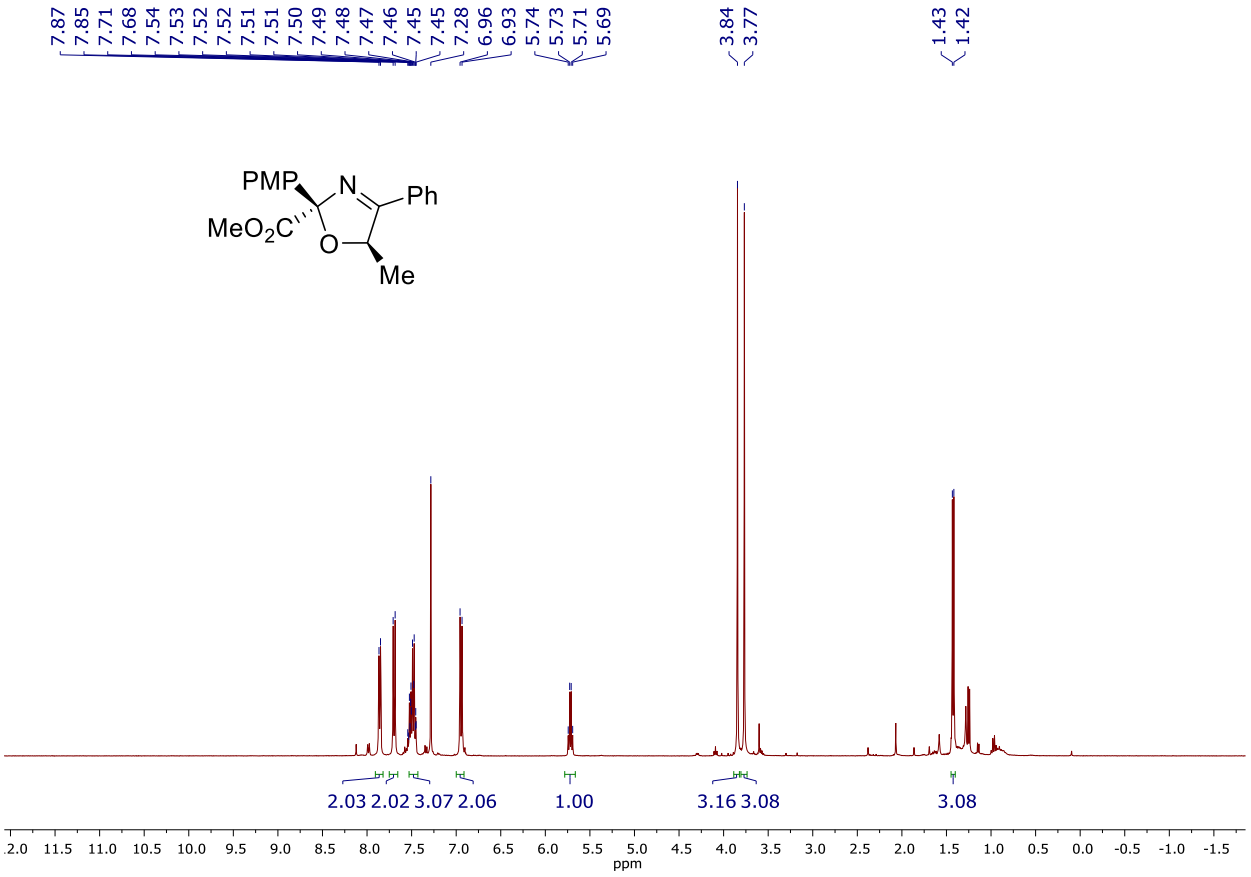
$^{13}C\{^{1}H\}$ NMR spectrum of oxazoline **(2*RS*,5*SR*)-4k** (125 MHz, $CDCl_3$)



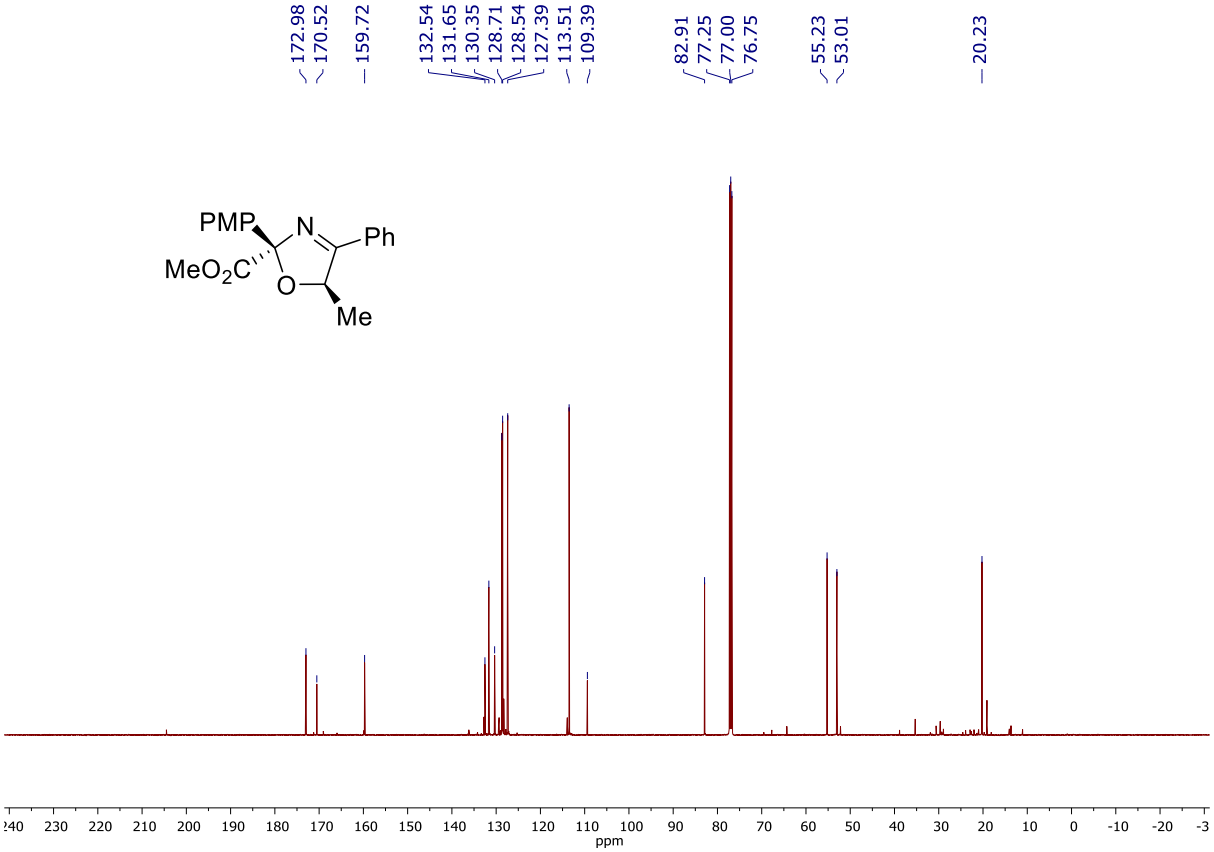
^{1}H-^{1}H NOESY NMR spectrum of oxazoline **(2*RS*,5*SR*)-4k** (400 MHz, $CDCl_3$)



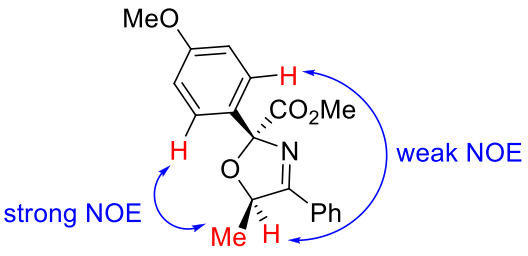
^{1}H NMR spectrum of oxazoline **(2*RS*,5*RS*)-4k** (400 MHz, $CDCl_3$)



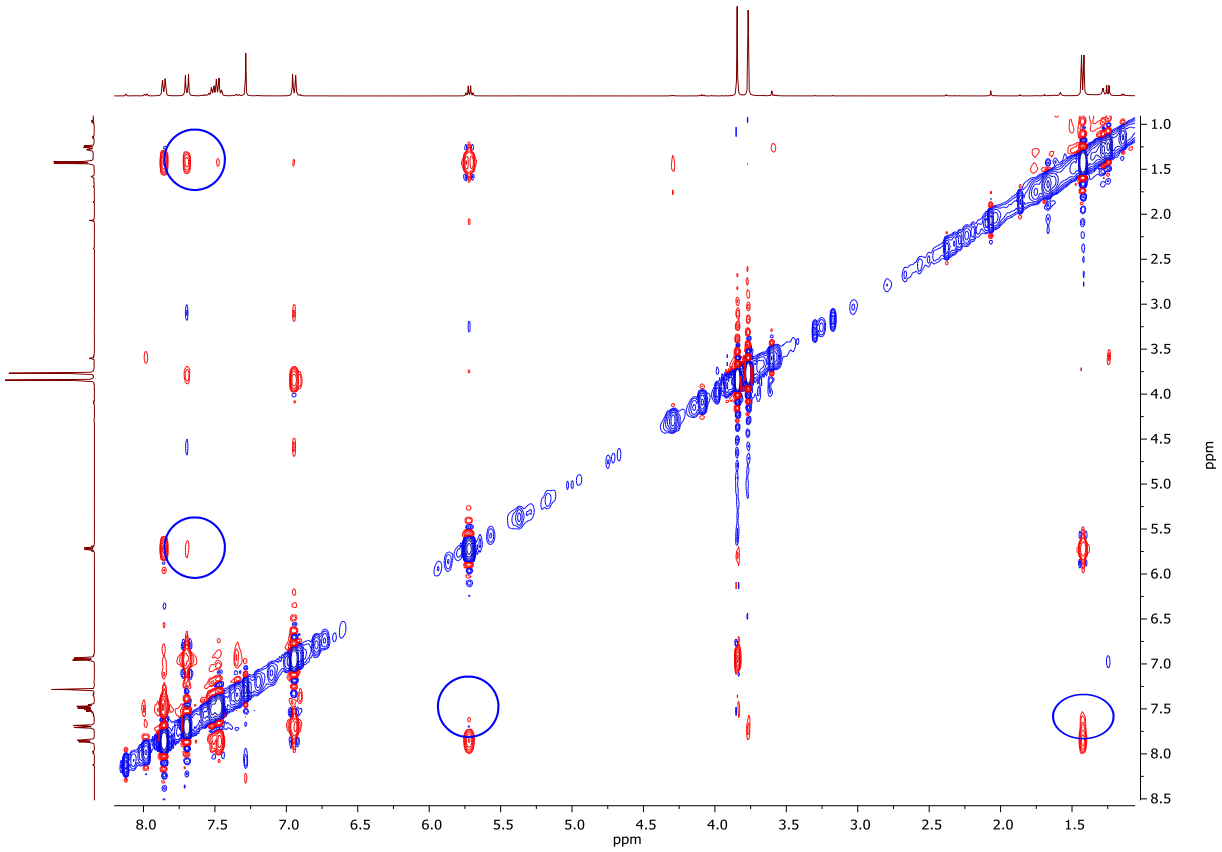
$^{13}C\{^{1}H\}$ NMR spectrum of oxazoline **(2*RS*,5*RS*)-4k** (125 MHz, $CDCl_3$)



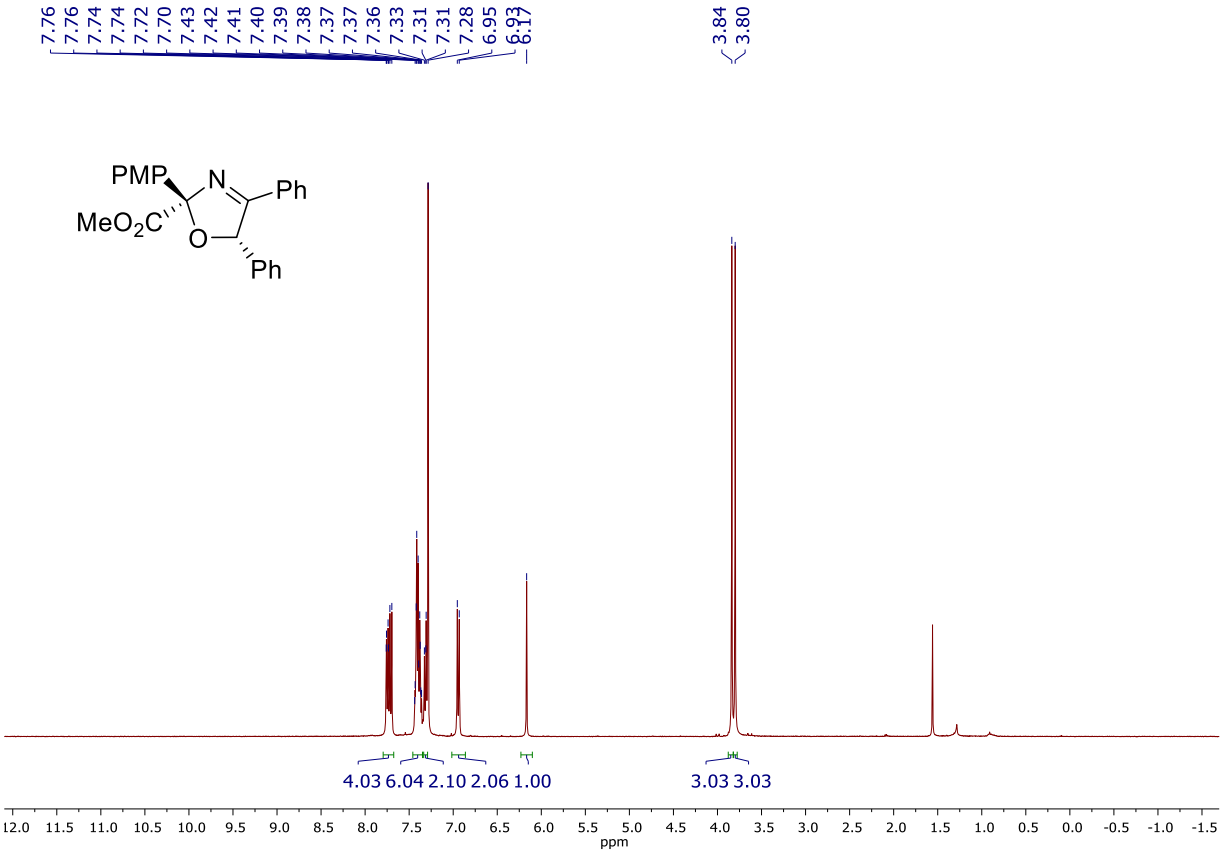
^{1}H-^{1}H NOESY NMR spectrum of oxazoline **(2*RS*,5*RS*)-4k** (400 MHz, $CDCl_3$)



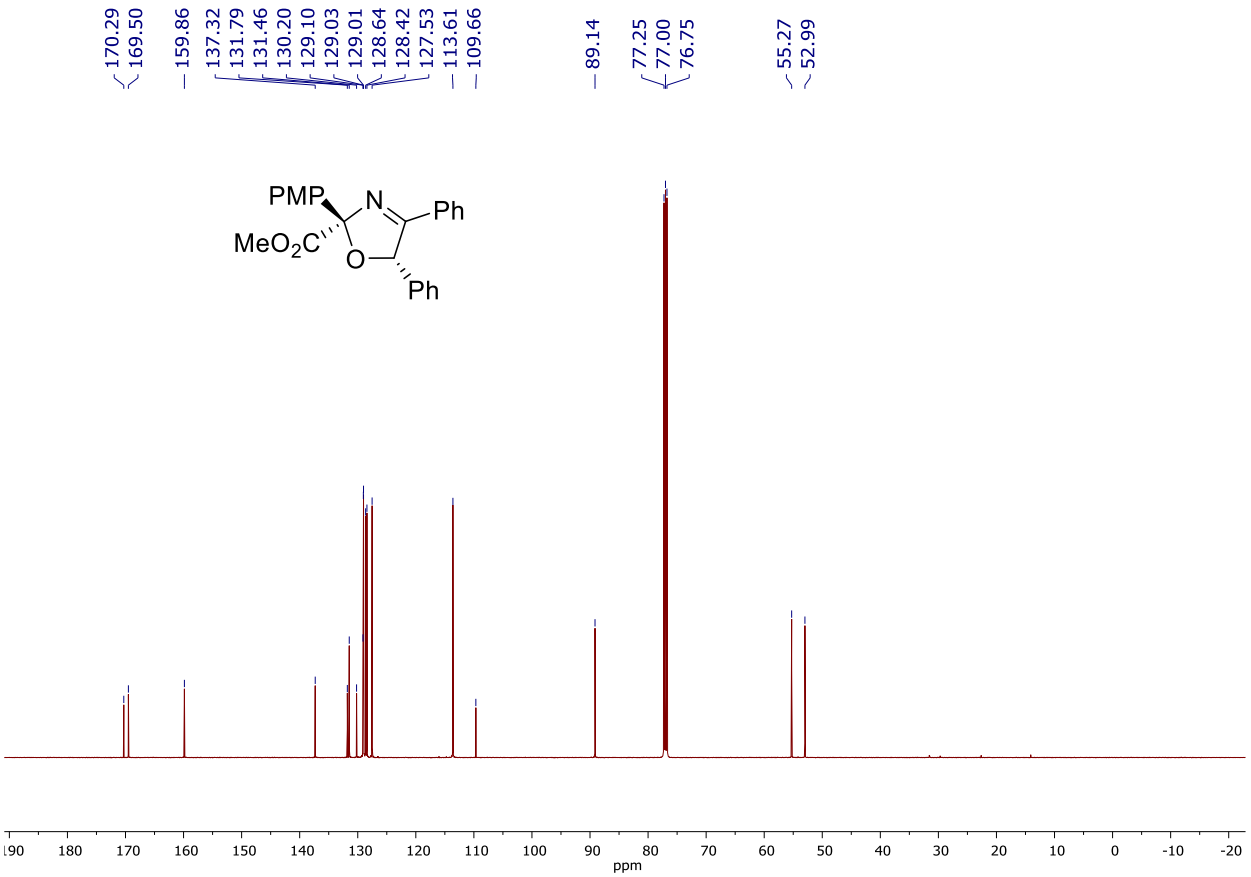
1.42 ppm (shielded by PMP)



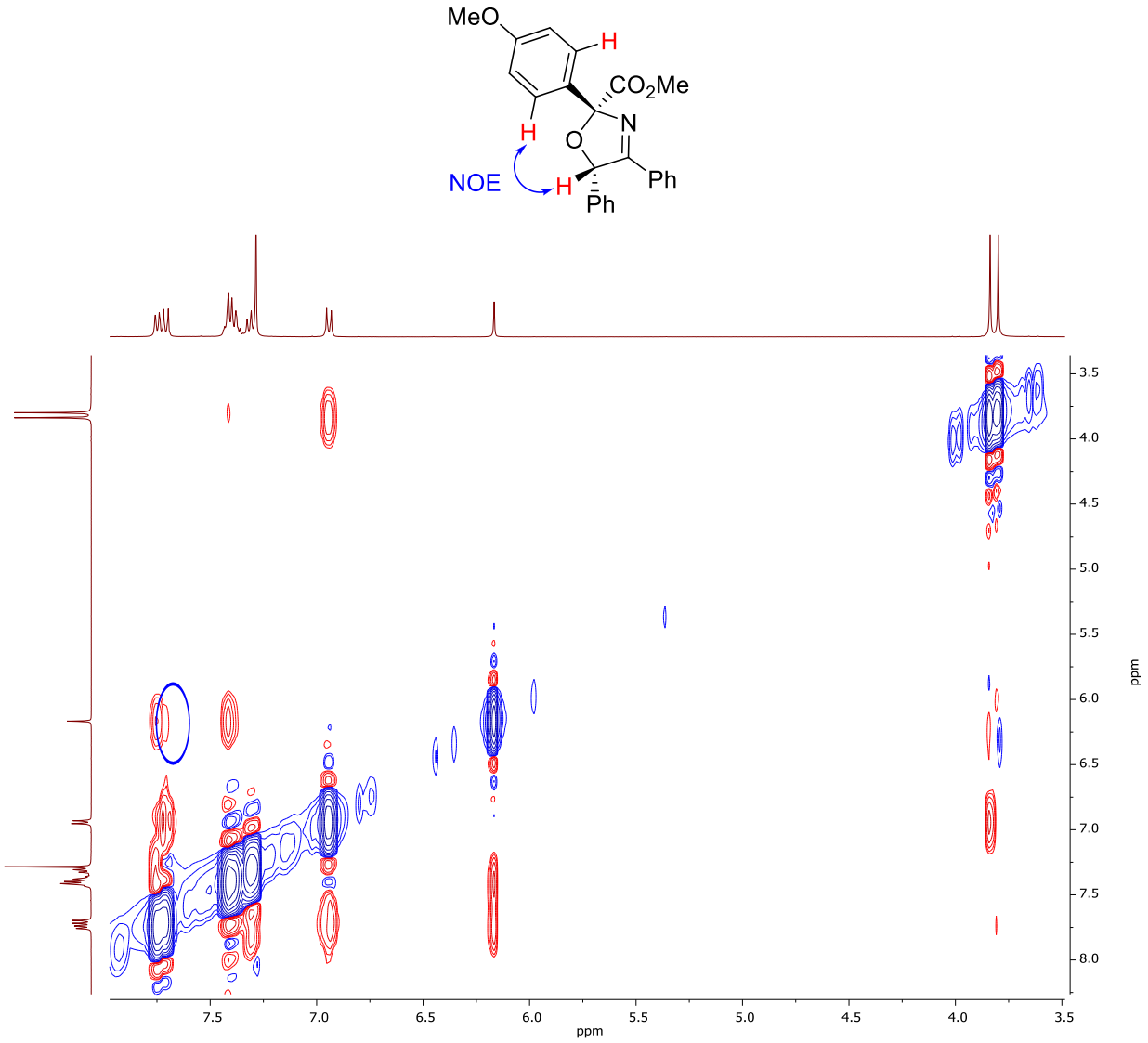
^{1}H NMR spectrum of oxazoline **(2*RS*,5*SR*)-4l** (400 MHz, $CDCl_3$)



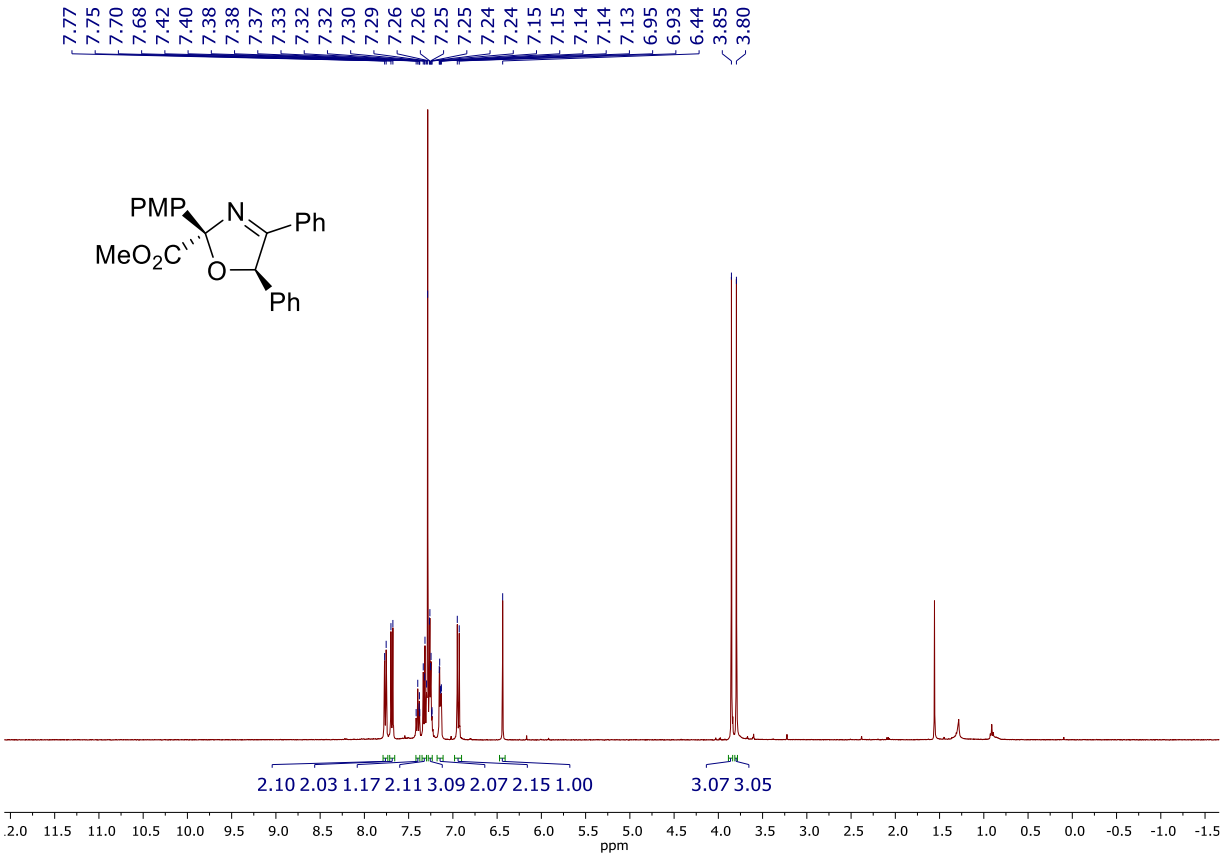
^{13}C{^{1}H} NMR spectrum of oxazoline **(2*RS*,5*SR*)-4l** (100 MHz, $CDCl_3$)



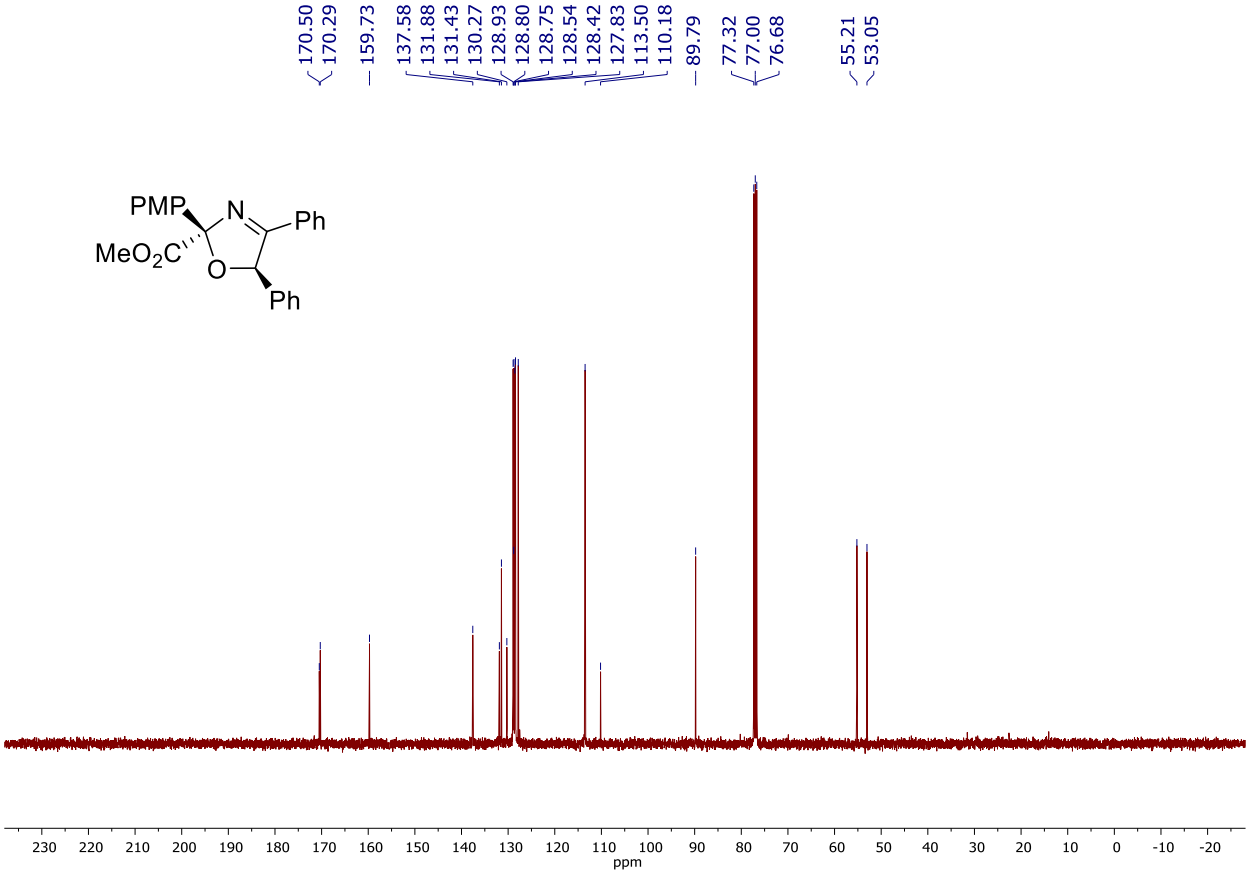
^{1}H-^{1}H NOESY NMR spectrum of oxazoline **(2*RS*,5*SR*)-4l** (400 MHz, $CDCl_3$)



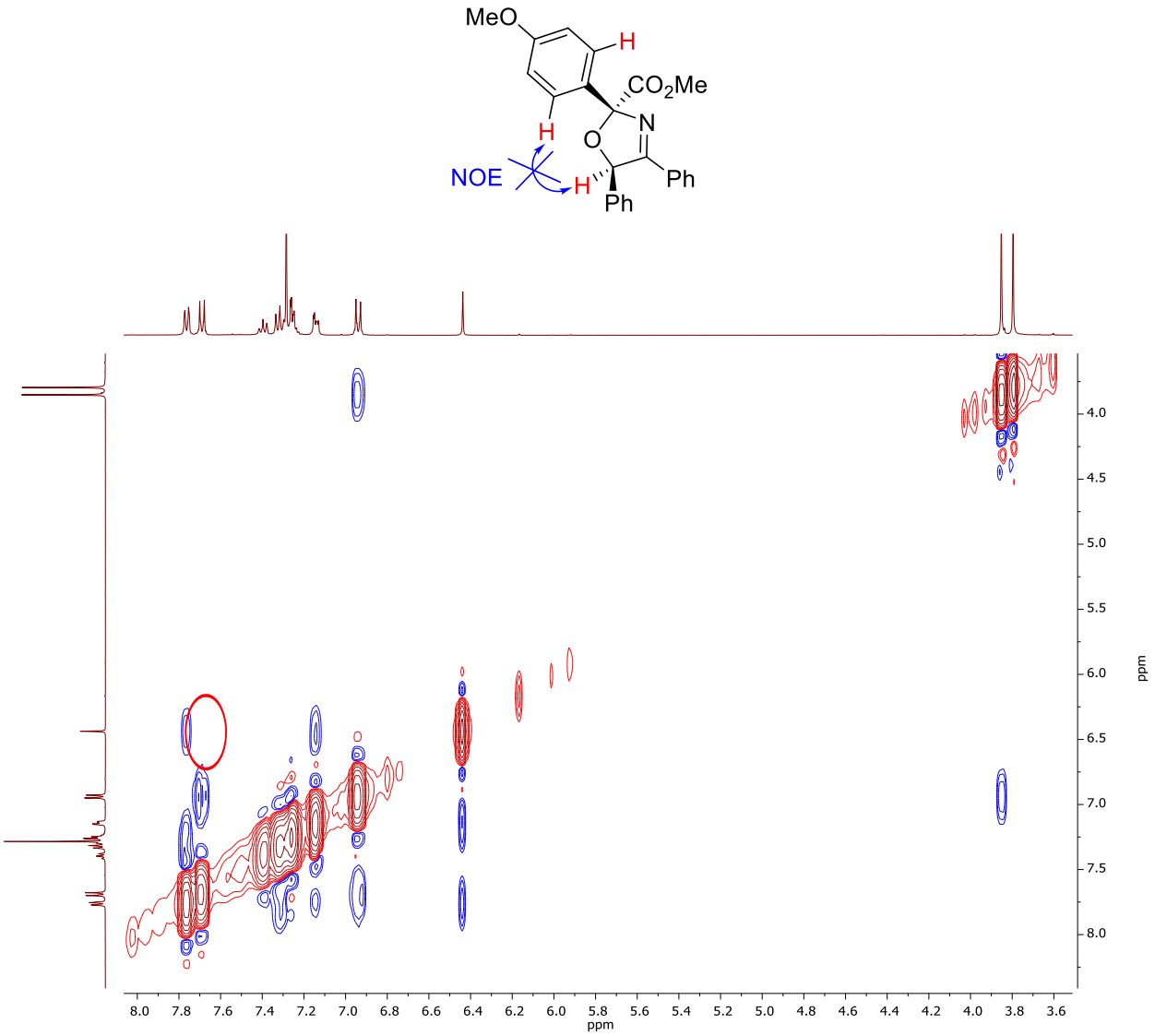
^{1}H NMR spectrum of oxazoline **(2*RS*,5*RS*)-4l** (400 MHz, $CDCl_3$)



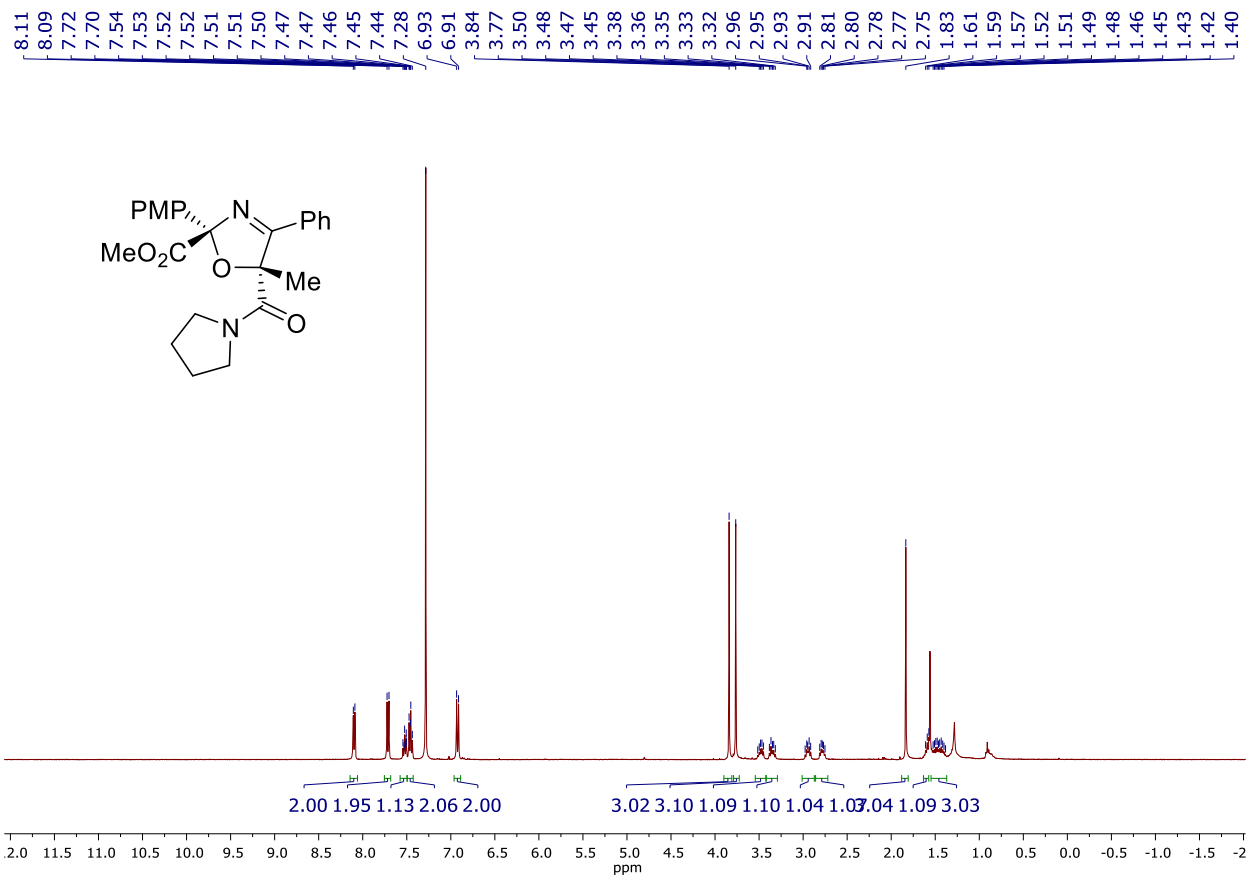
$^{13}C\{^{1}H\}$ NMR spectrum of oxazoline **(2*RS*,5*RS*)-4l** (100 MHz, $CDCl_3$)



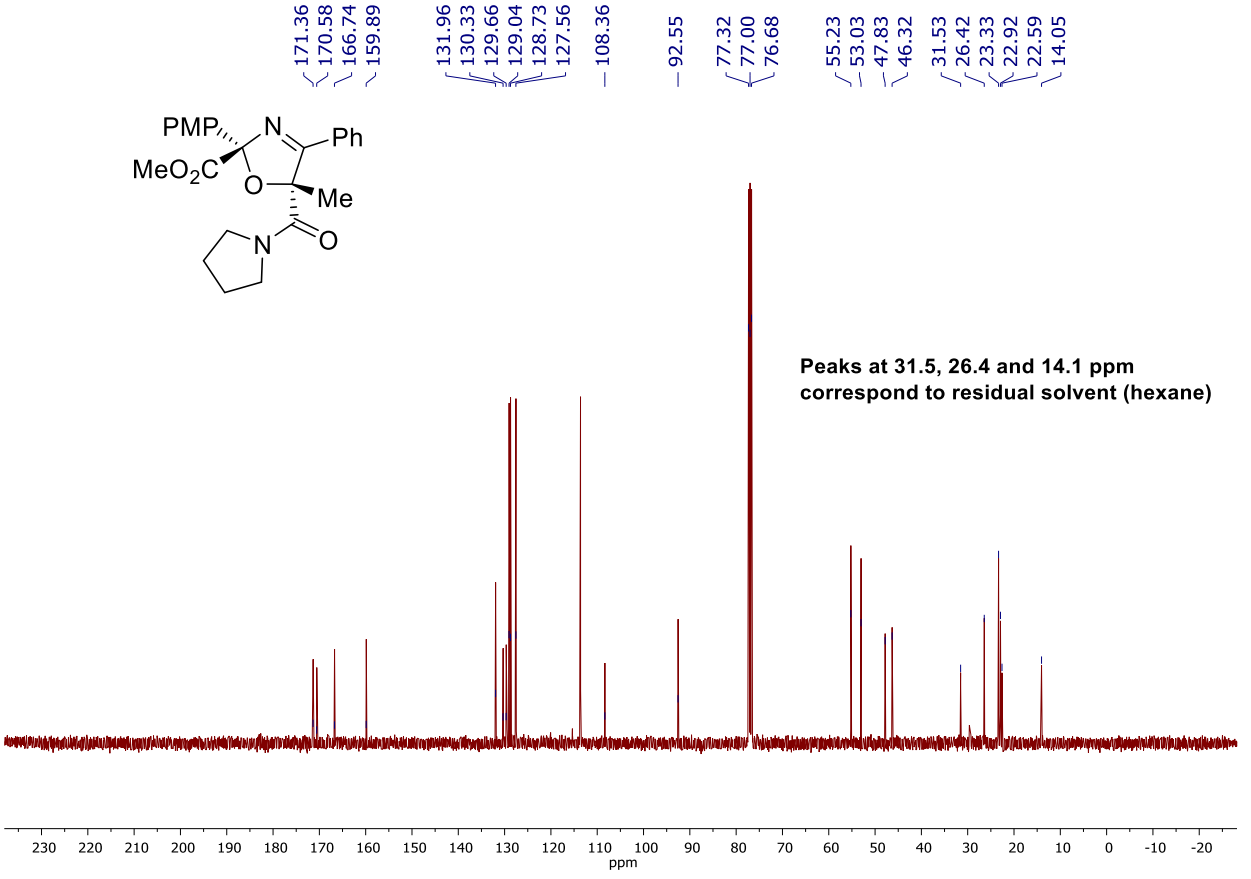
^{1}H-^{1}H NOESY NMR spectrum of oxazoline **(2*RS*,5*RS*)-4l** (400 MHz, $CDCl_3$)



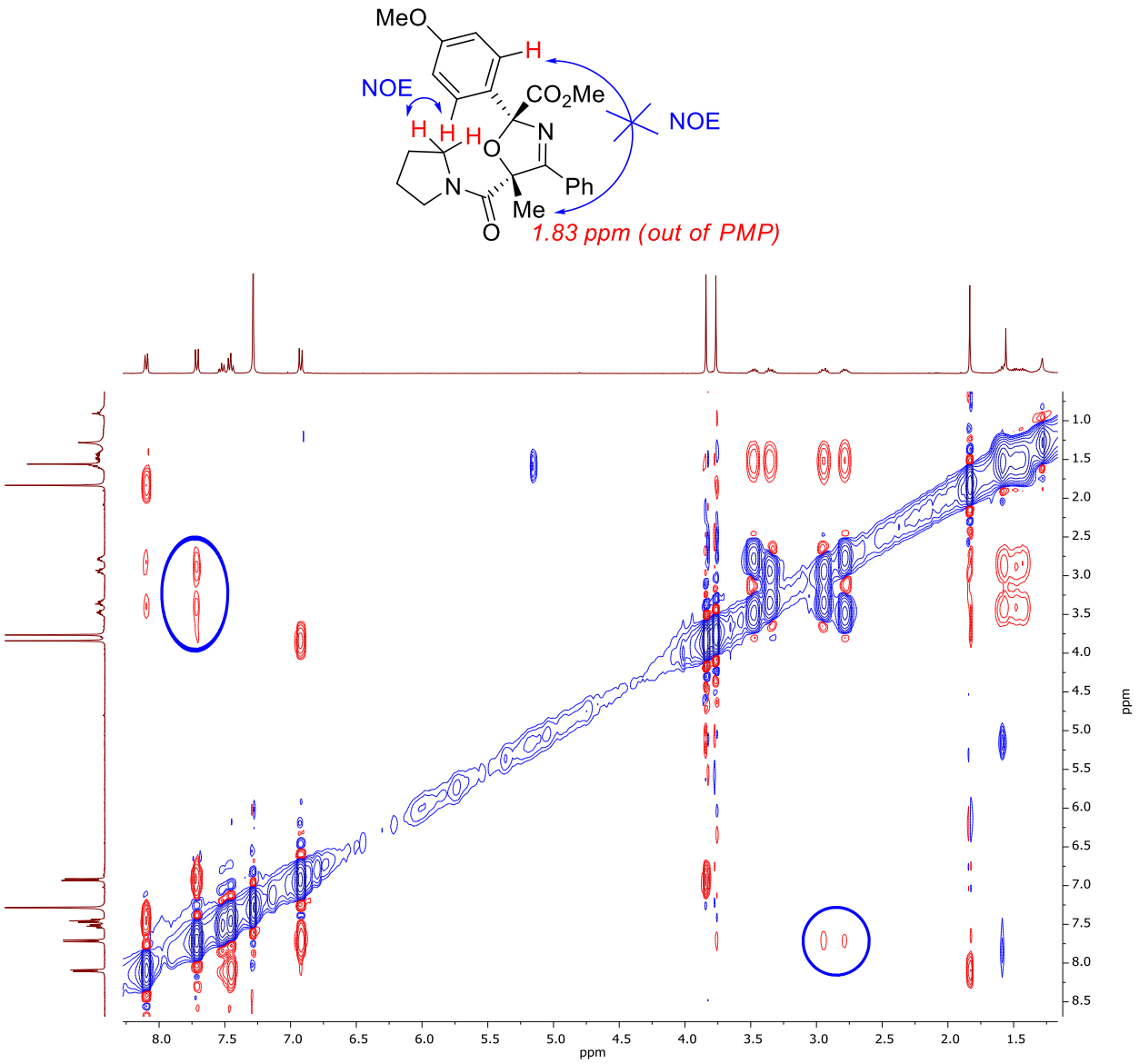
^{1}H NMR spectrum of oxazoline **4m** (400 MHz, $CDCl_3$)



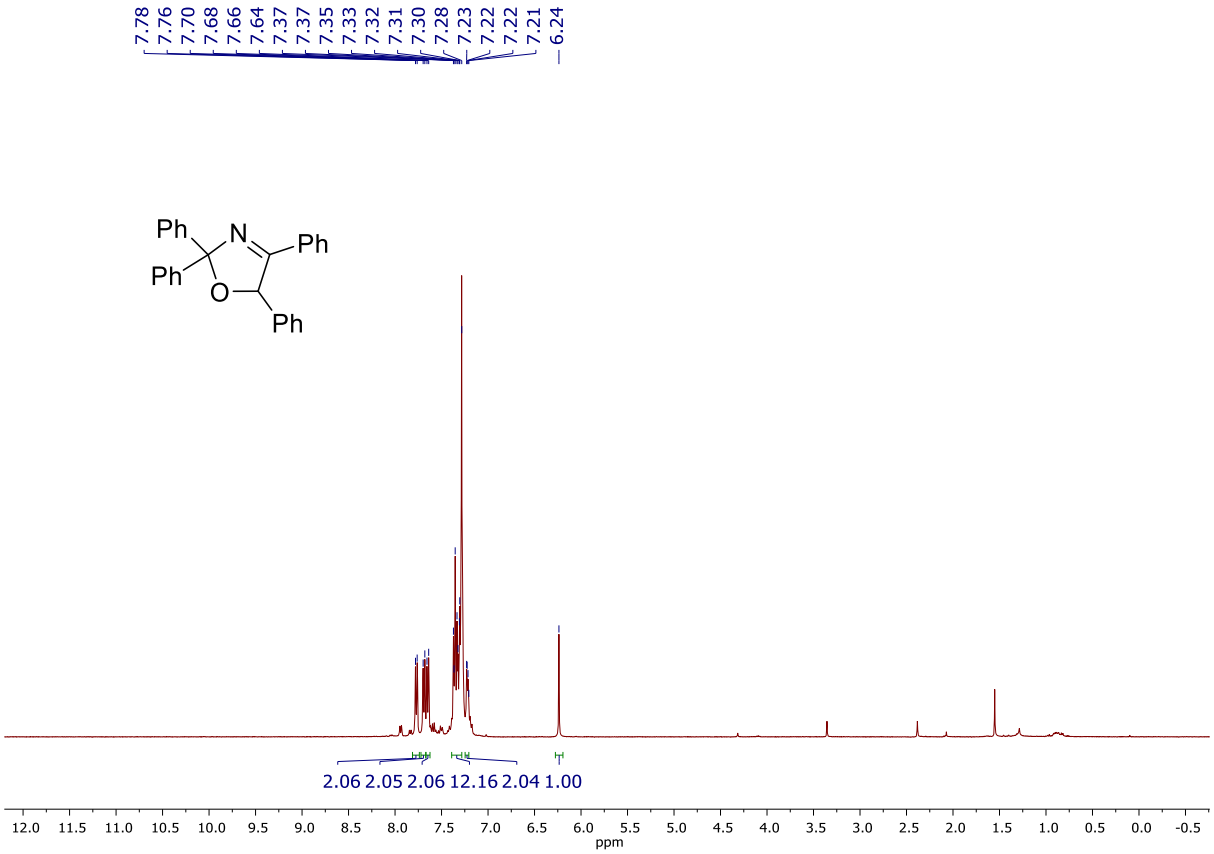
$^{13}C\{^{1}H\}$ NMR spectrum of oxazoline **4m** (100 MHz, $CDCl_3$)



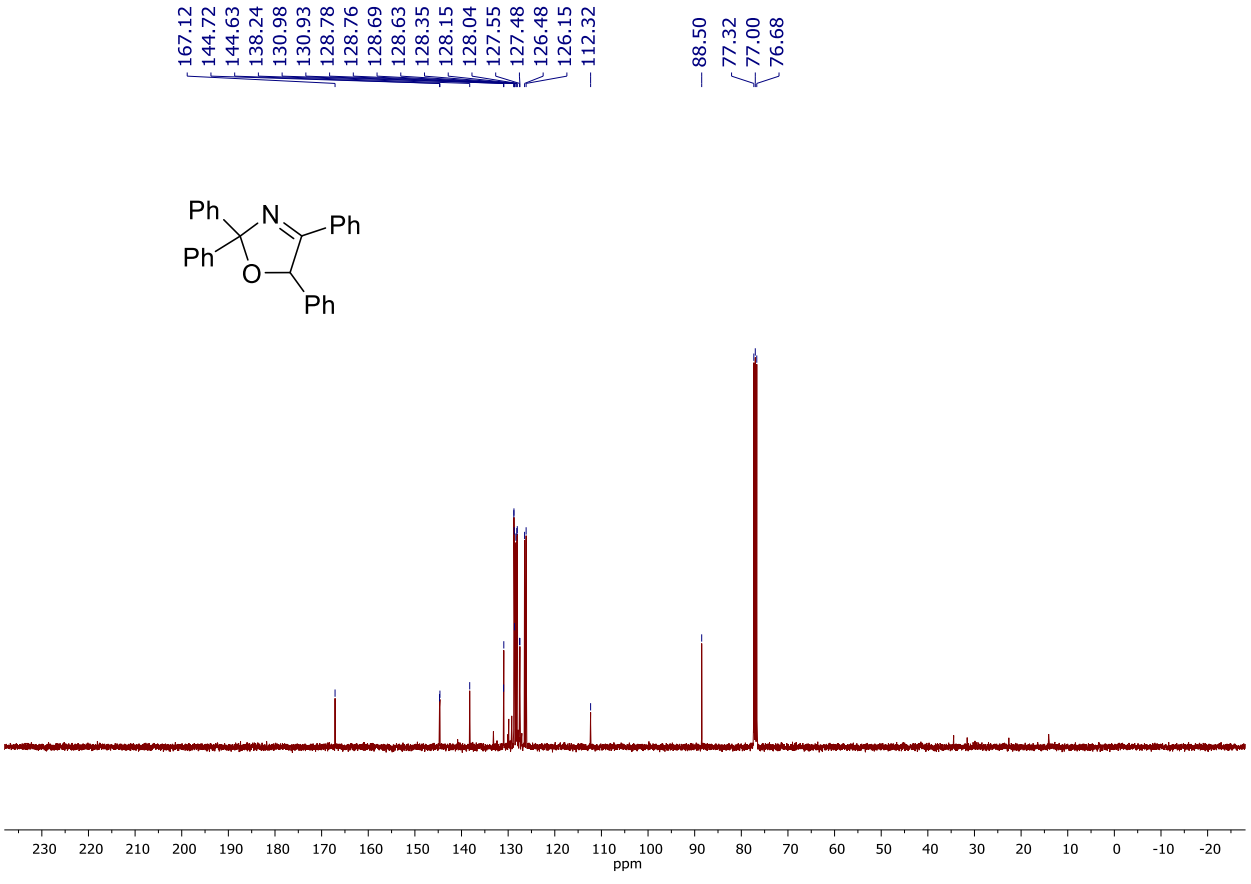
^{1}H-^{1}H NOESY NMR spectrum of oxazoline **4m** (400 MHz, $CDCl_3$)



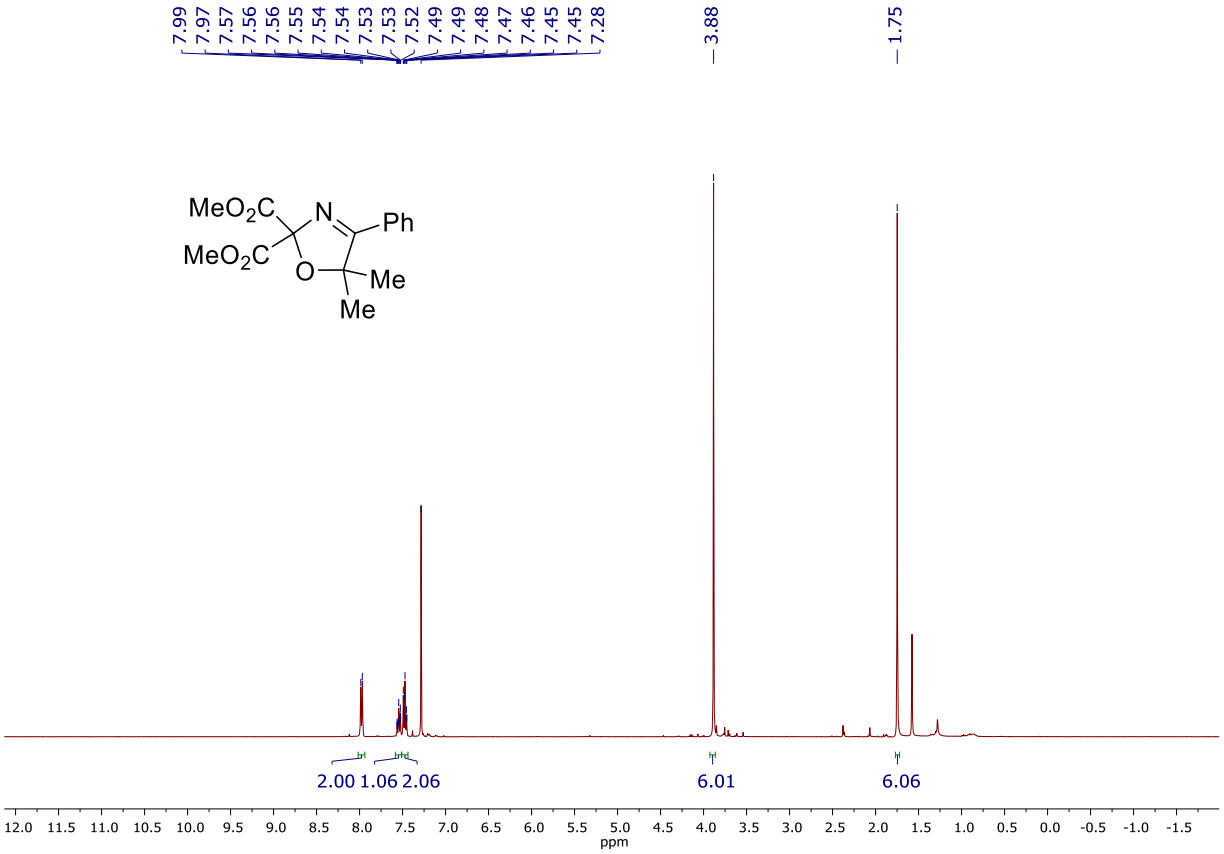
^{1}H NMR spectrum of oxazoline **4n** (400 MHz, $CDCl_3$)



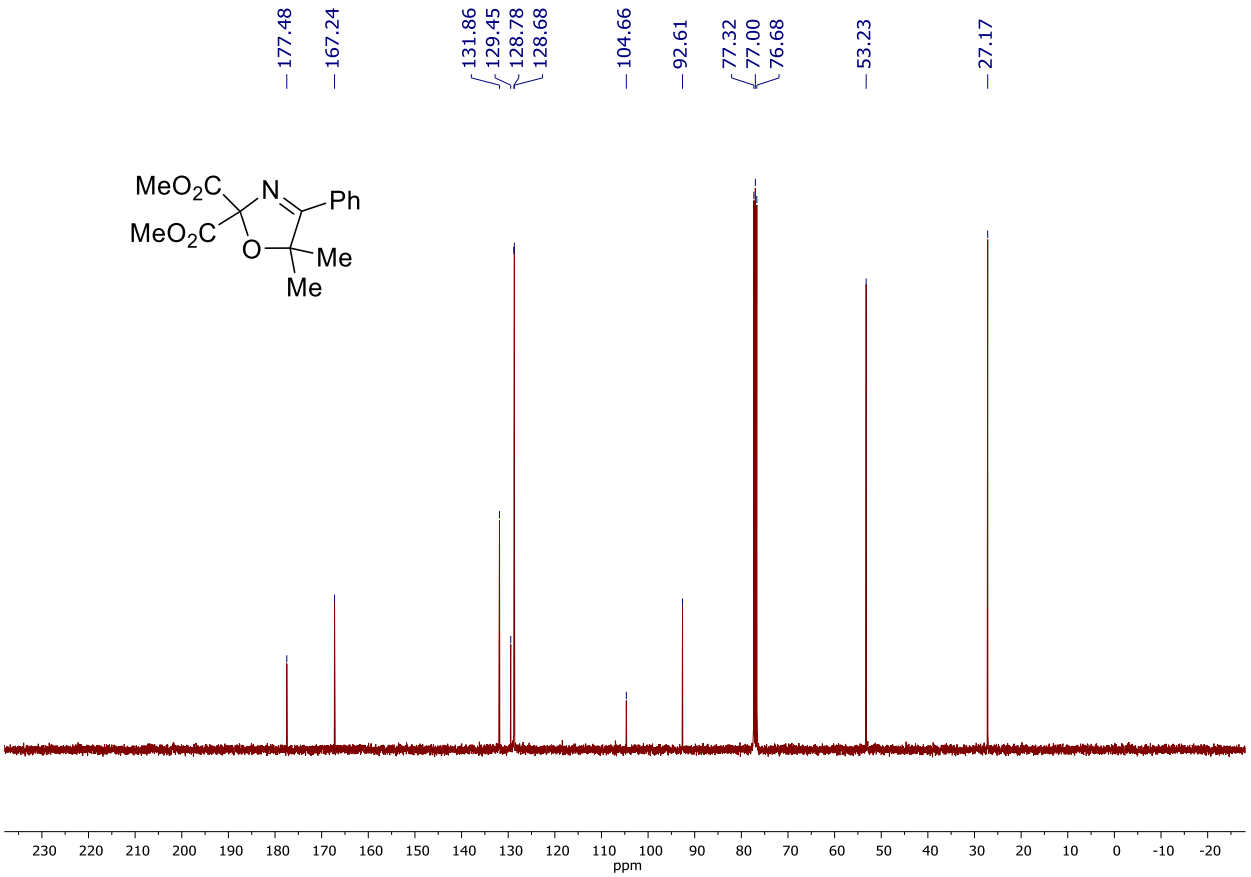
^{13}C{^{1}H} NMR spectrum of oxazoline **4n** (100 MHz, $CDCl_3$)



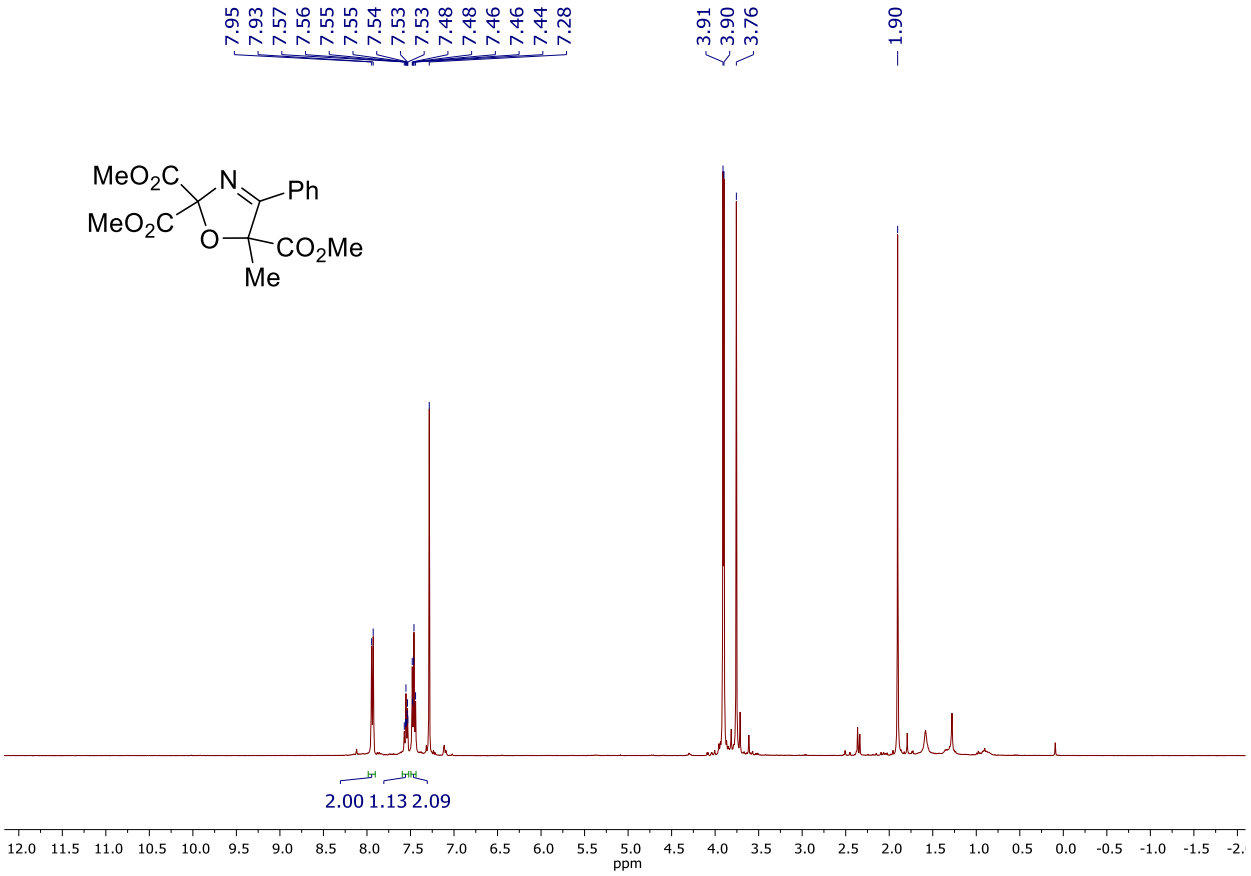
^{1}H NMR spectrum of oxazoline **4o** (400 MHz, $CDCl_3$)



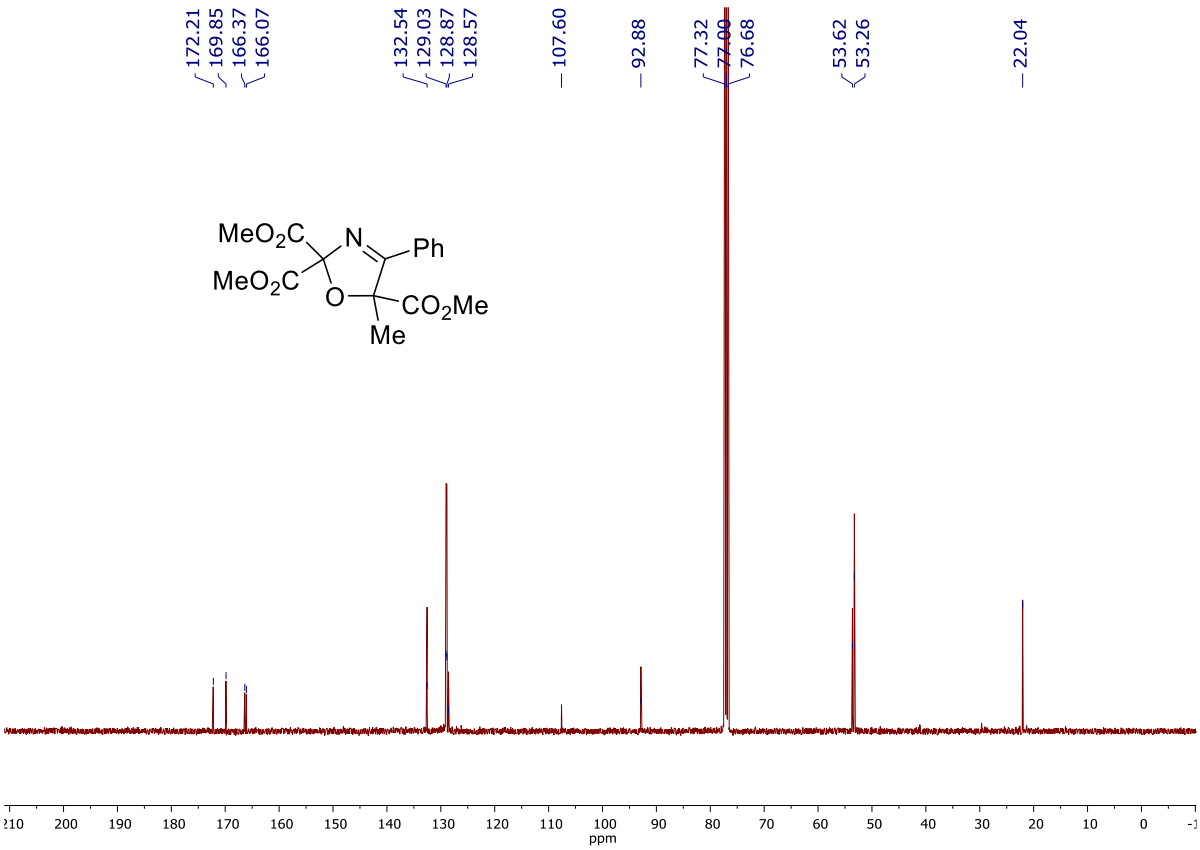
^{13}C{^{1}H} NMR spectrum of oxazoline **4o** (100 MHz, $CDCl_3$)



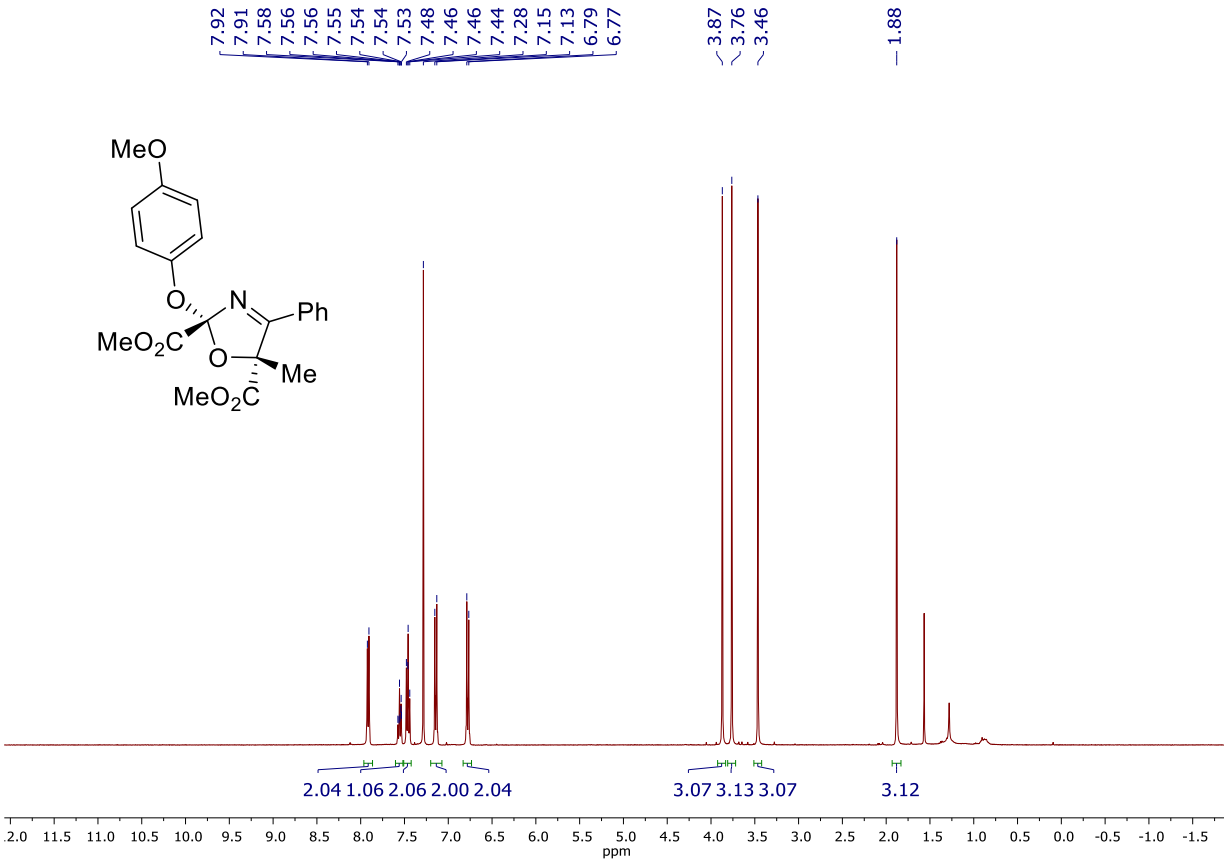
^{1}H NMR spectrum of oxazoline **4p** (400 MHz, $CDCl_3$)



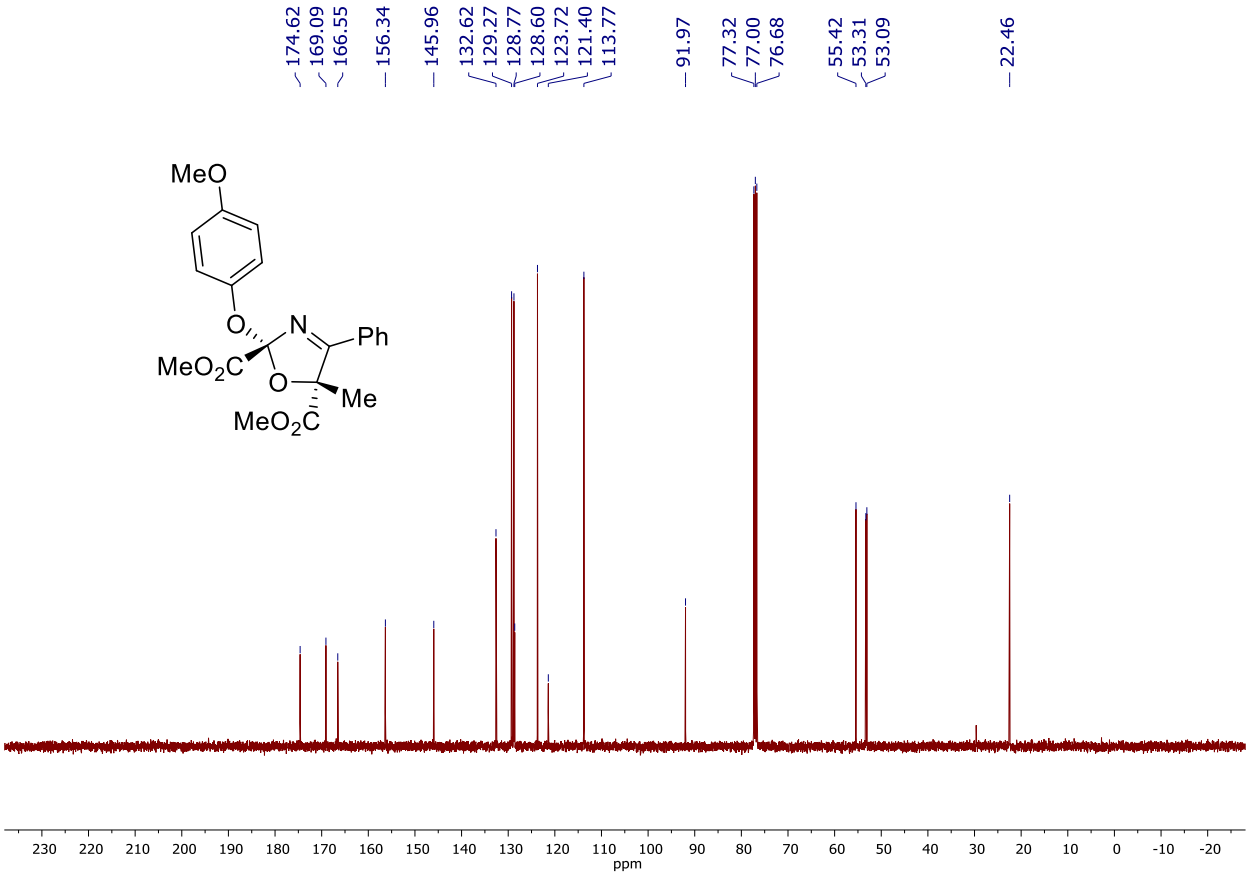
^{13}C{^{1}H} NMR spectrum of oxazoline **4p** (100 MHz, $CDCl_3$)



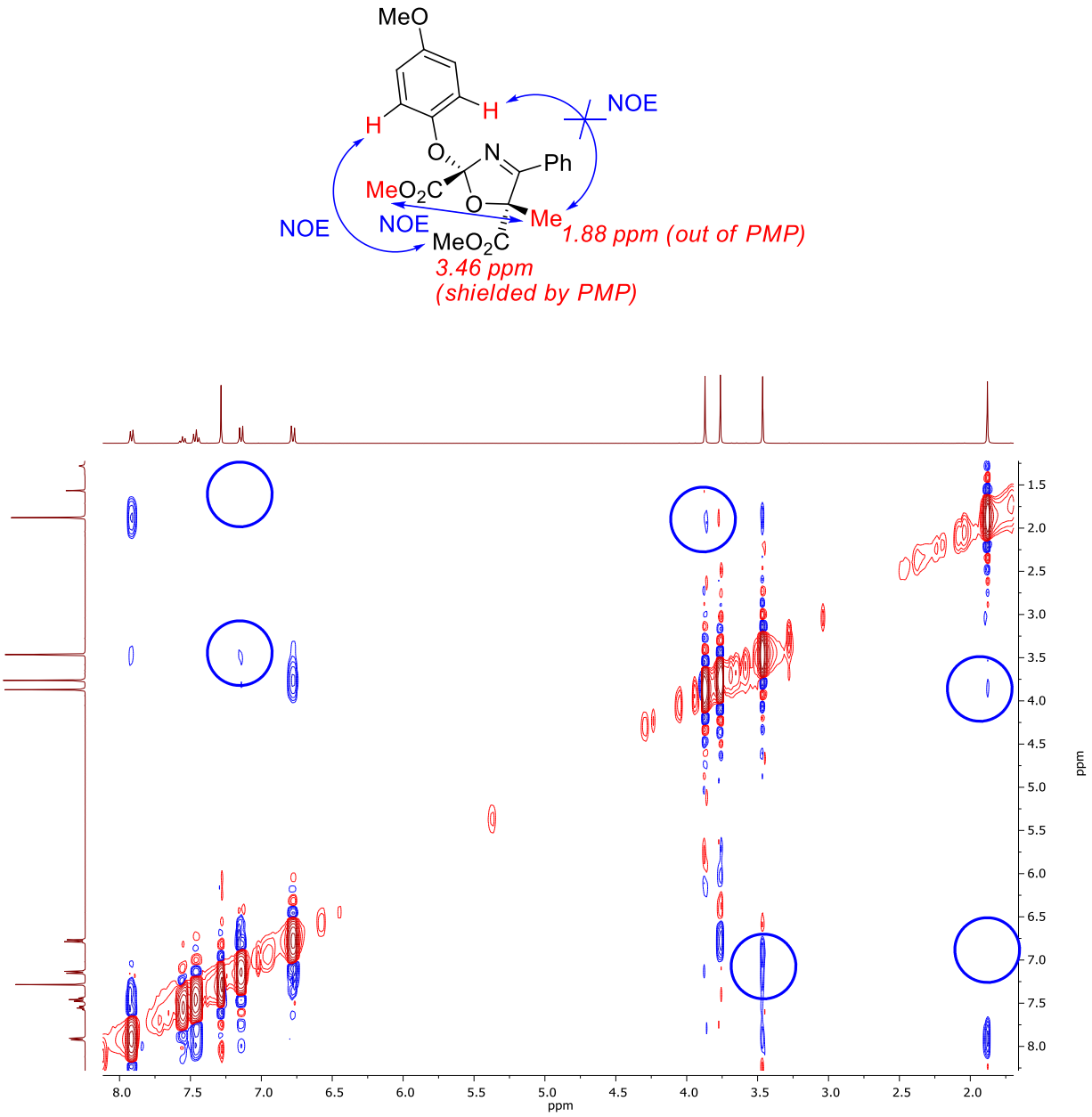
^{1}H NMR spectrum of oxazoline **(2*RS*,5*RS*)-4'r** (400 MHz, $CDCl_3$)



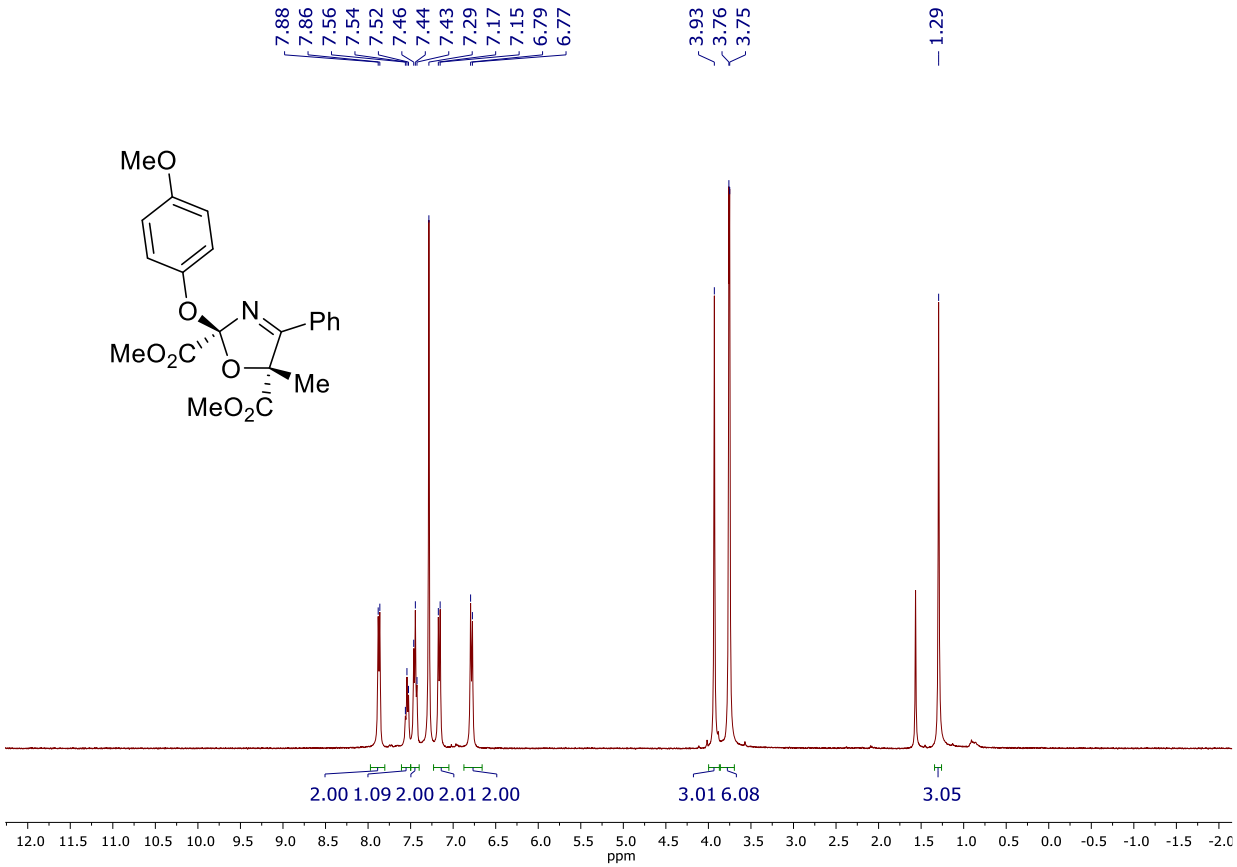
^{13}C{^{1}H} NMR spectrum of oxazoline **(2*RS*,5*RS*)-4'r** (100 MHz, $CDCl_3$)



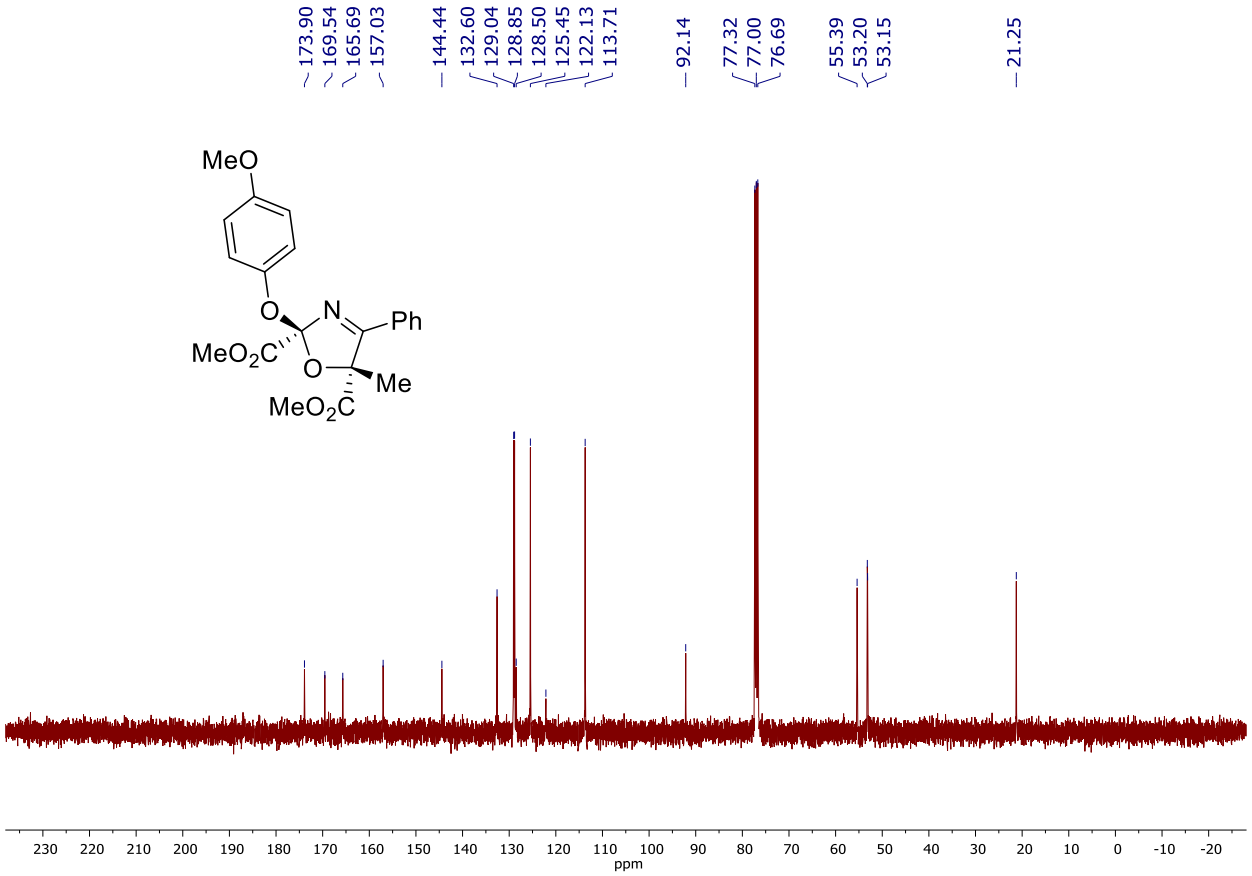
^{1}H-^{1}H NOESY NMR spectrum of oxazoline **(2*RS*,5*RS*)-4'r** (400 MHz, $CDCl_3$)



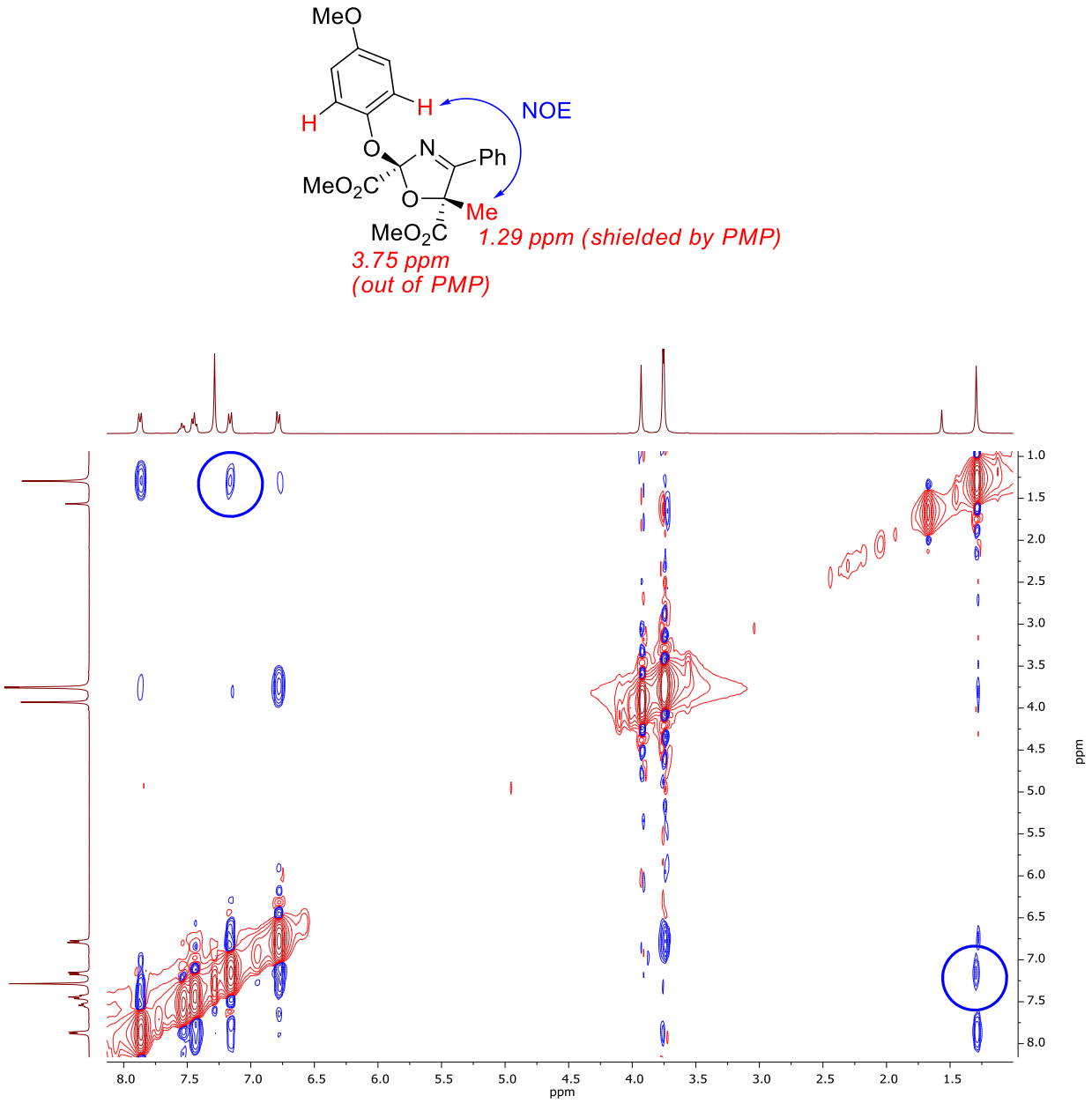
^{1}H NMR spectrum of oxazoline **(2*RS*,5*SR*)-4'r** (400 MHz, $CDCl_3$)



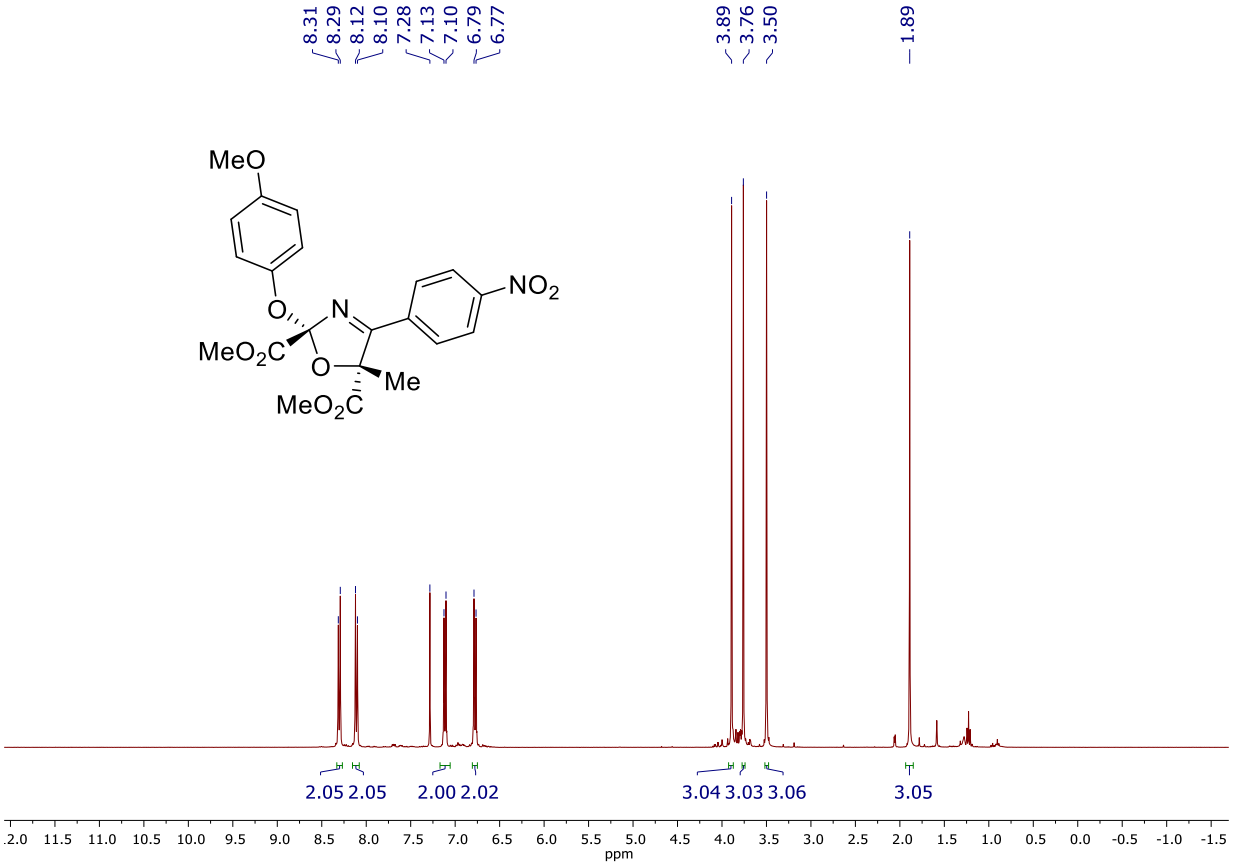
^{13}C{^{1}H} NMR spectrum of oxazoline **(2*RS*,5*SR*)-4'r** (100 MHz, $CDCl_3$)



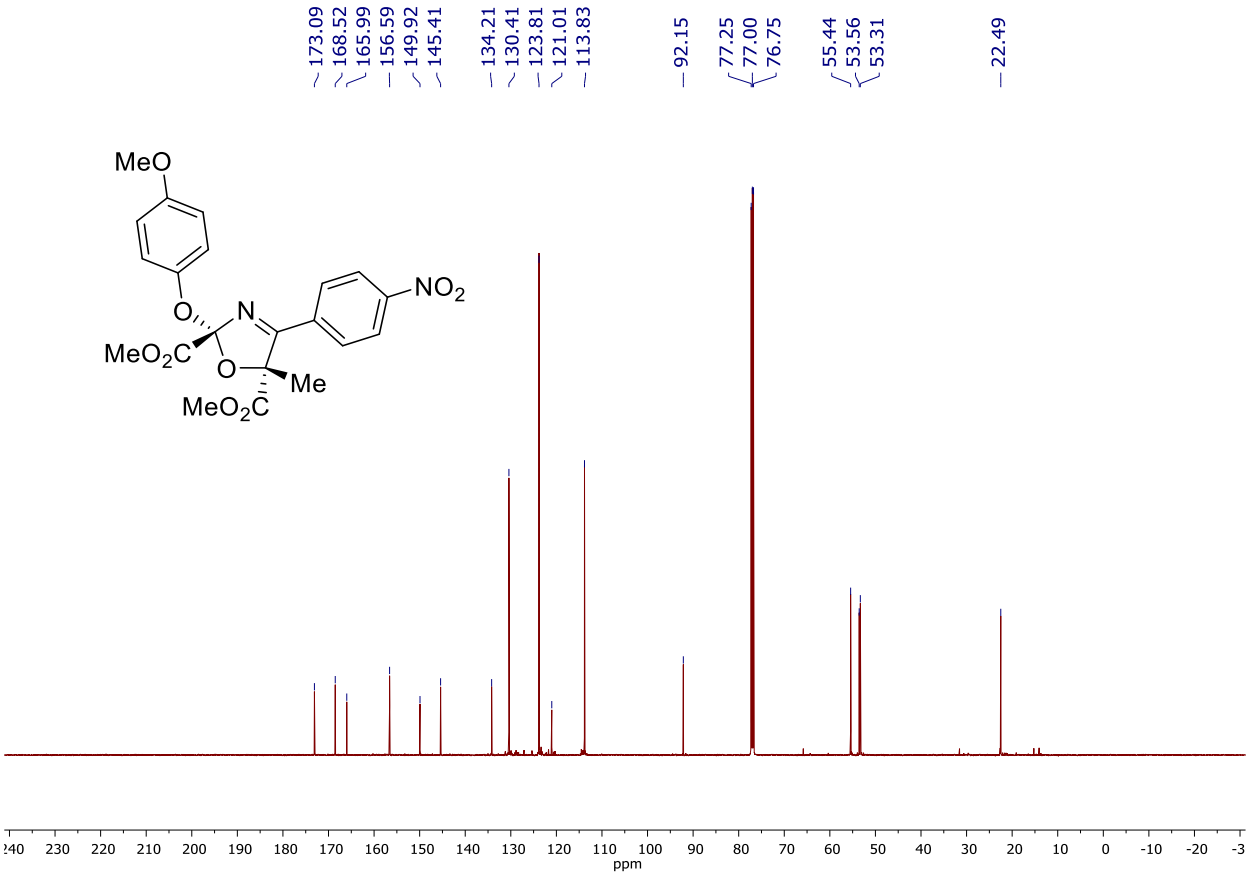
^{1}H-^{1}H NOESY NMR spectrum of oxazoline **(2*RS*,5*SR*)-4'r** (400 MHz, $CDCl_3$)



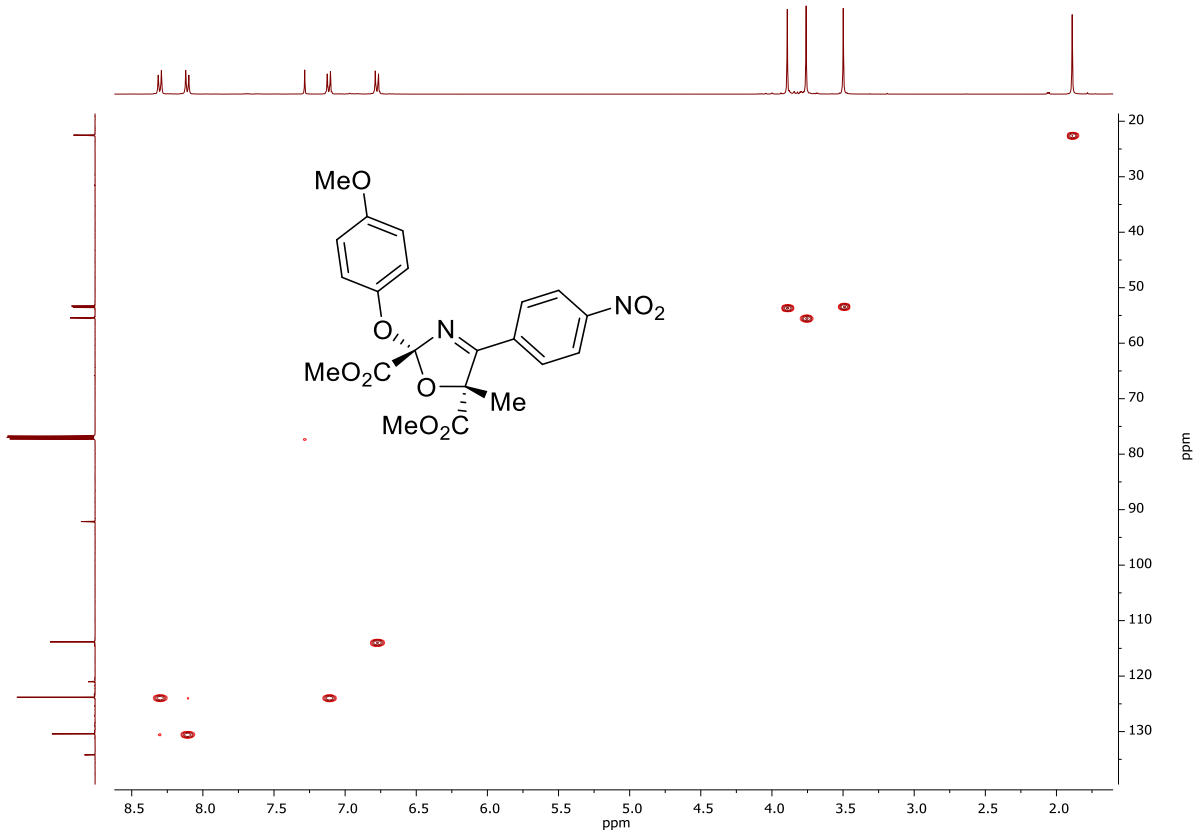
^{1}H NMR spectrum of oxazoline **(2*RS*,5*RS*)-4's** (400 MHz, $CDCl_3$)



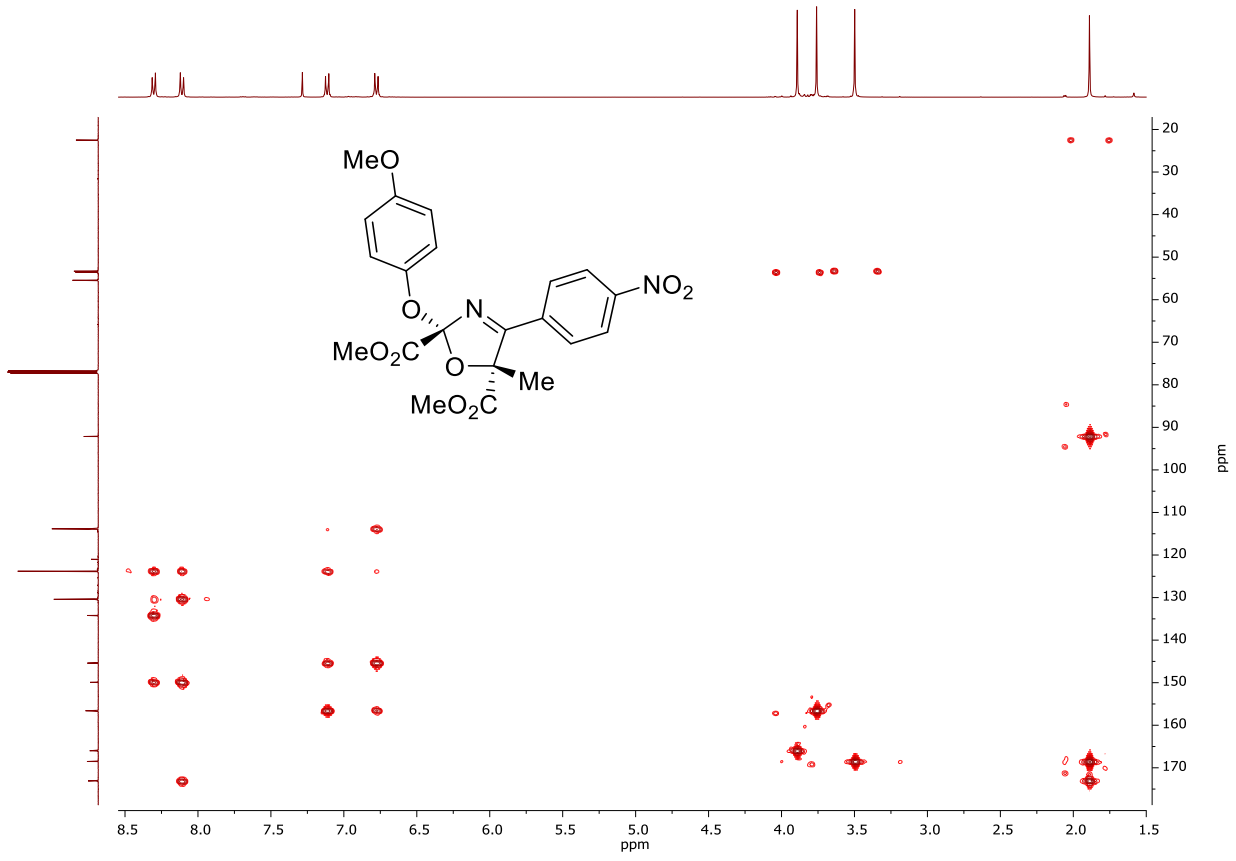
^{13}C{^{1}H} NMR spectrum of oxazoline **(2*RS*,5*RS*)-4's** (125 MHz, $CDCl_3$)



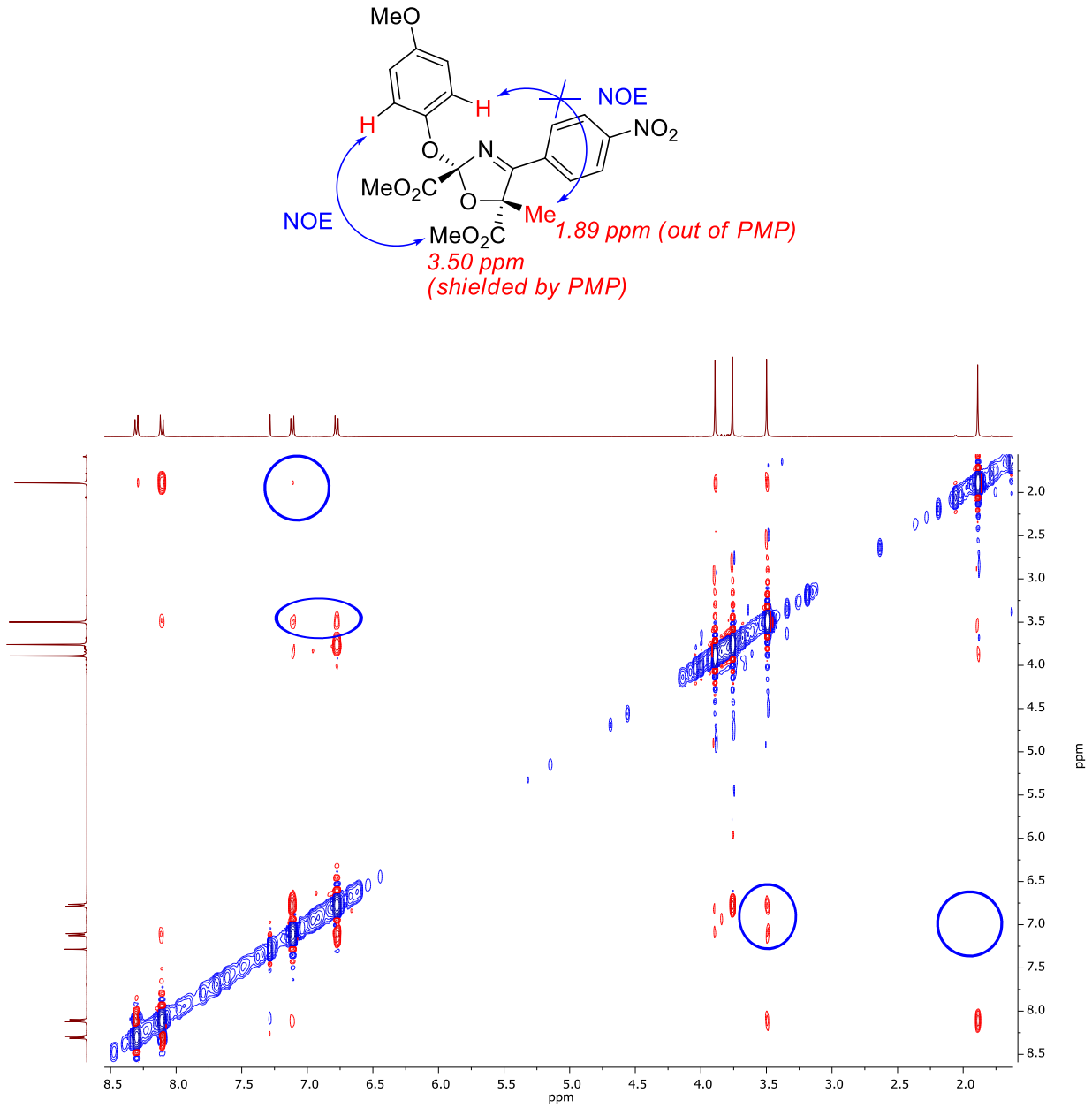
^{1}H-^{13}C HSQC NMR spectrum of oxazoline **(2*RS*,5*RS*)-4's** (400 MHz, $CDCl_3$)



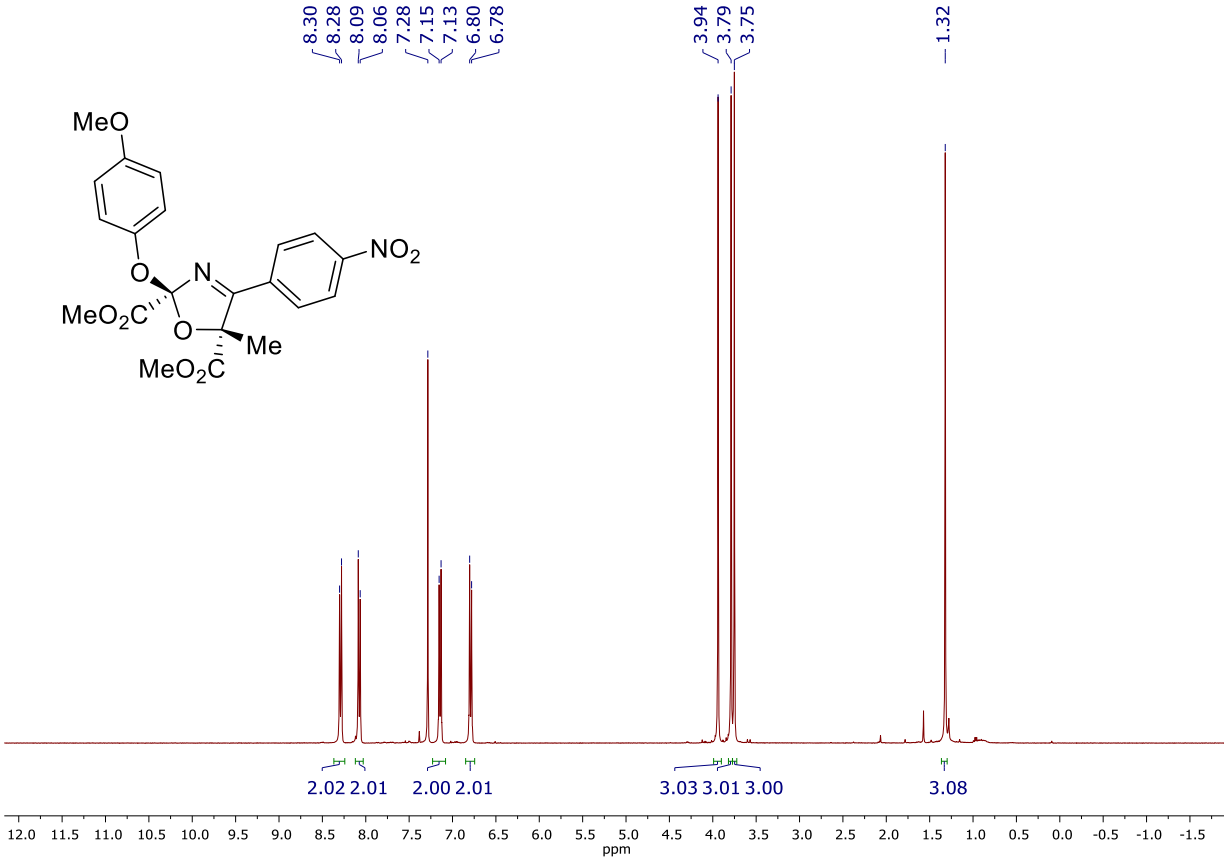
^{1}H-^{13}C HMBC NMR spectrum of oxazoline **(2*RS*,5*RS*)-4's** (400 MHz, $CDCl_3$)



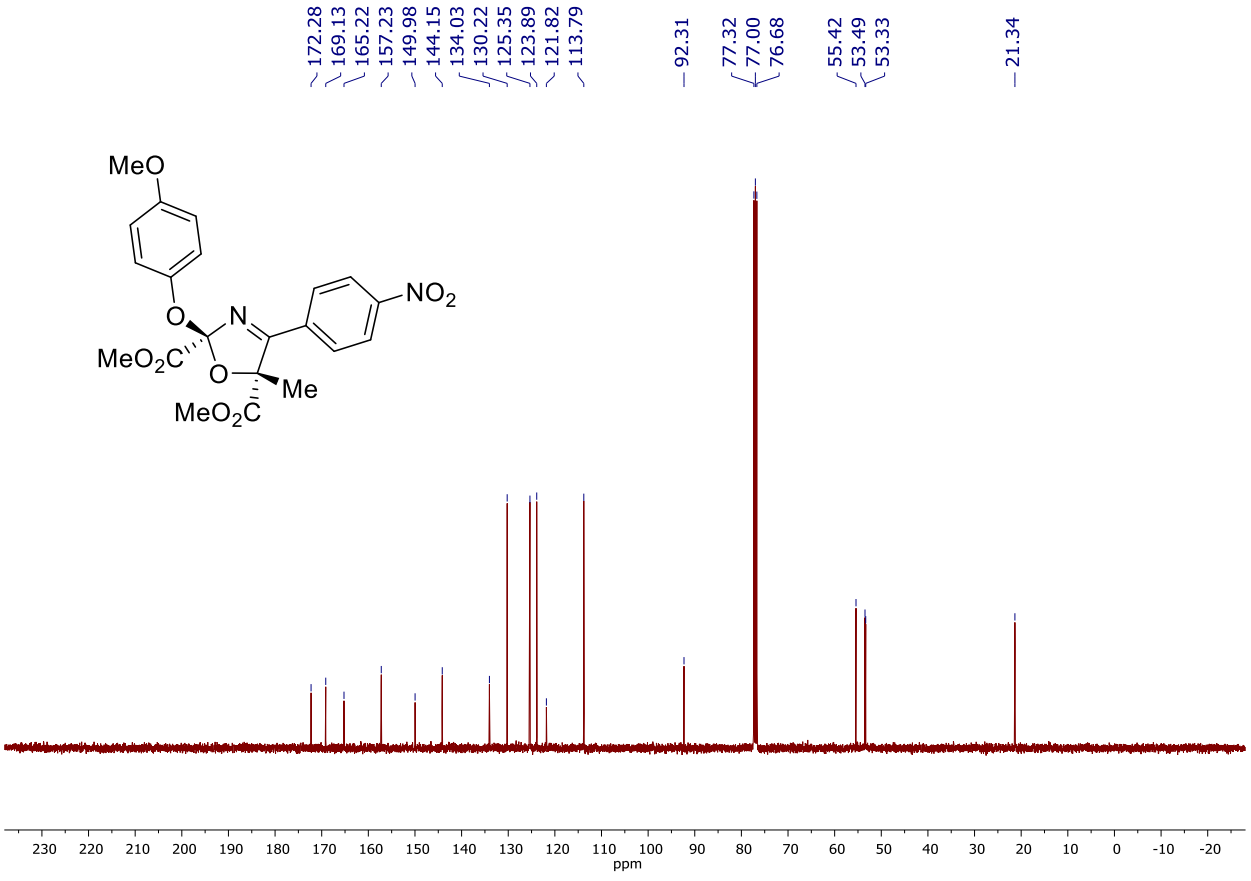
^{1}H-^{1}H NOESY NMR spectrum of oxazoline **(2*RS*,5*RS*)-4's** (400 MHz, $CDCl_3$)



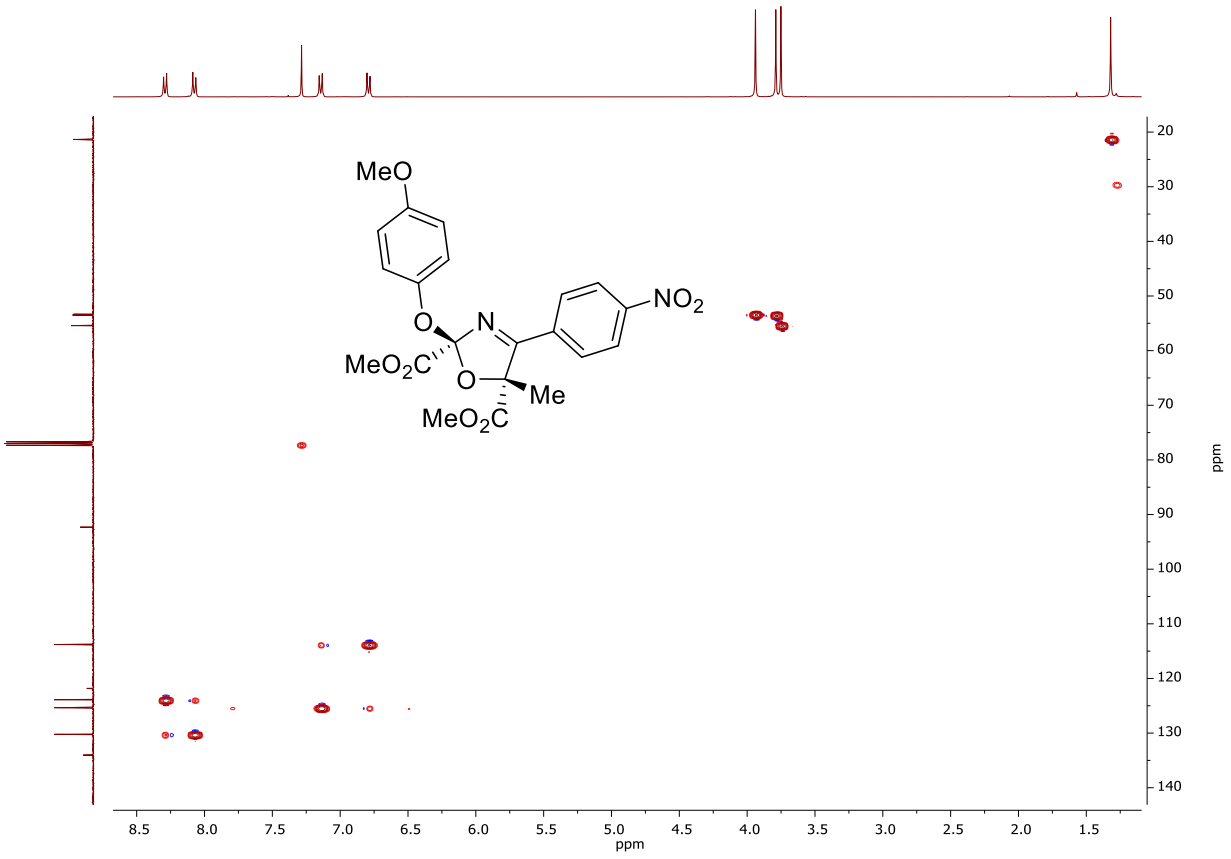
^{1}H NMR spectrum of oxazoline **(2*RS*,5*SR*)-4's** (400 MHz, $CDCl_3$)



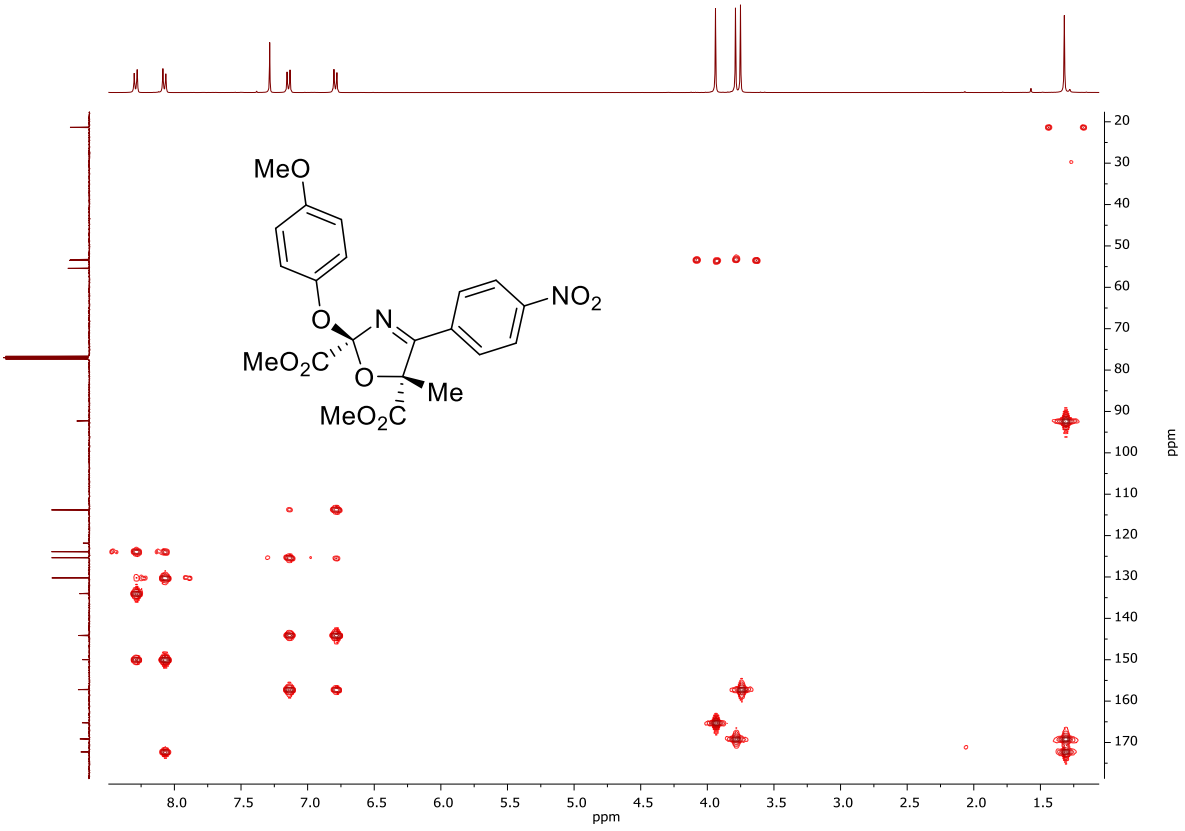
^{13}C{^{1}H} NMR spectrum of oxazoline **(2*RS*,5*SR*)-4's** (100 MHz, $CDCl_3$)



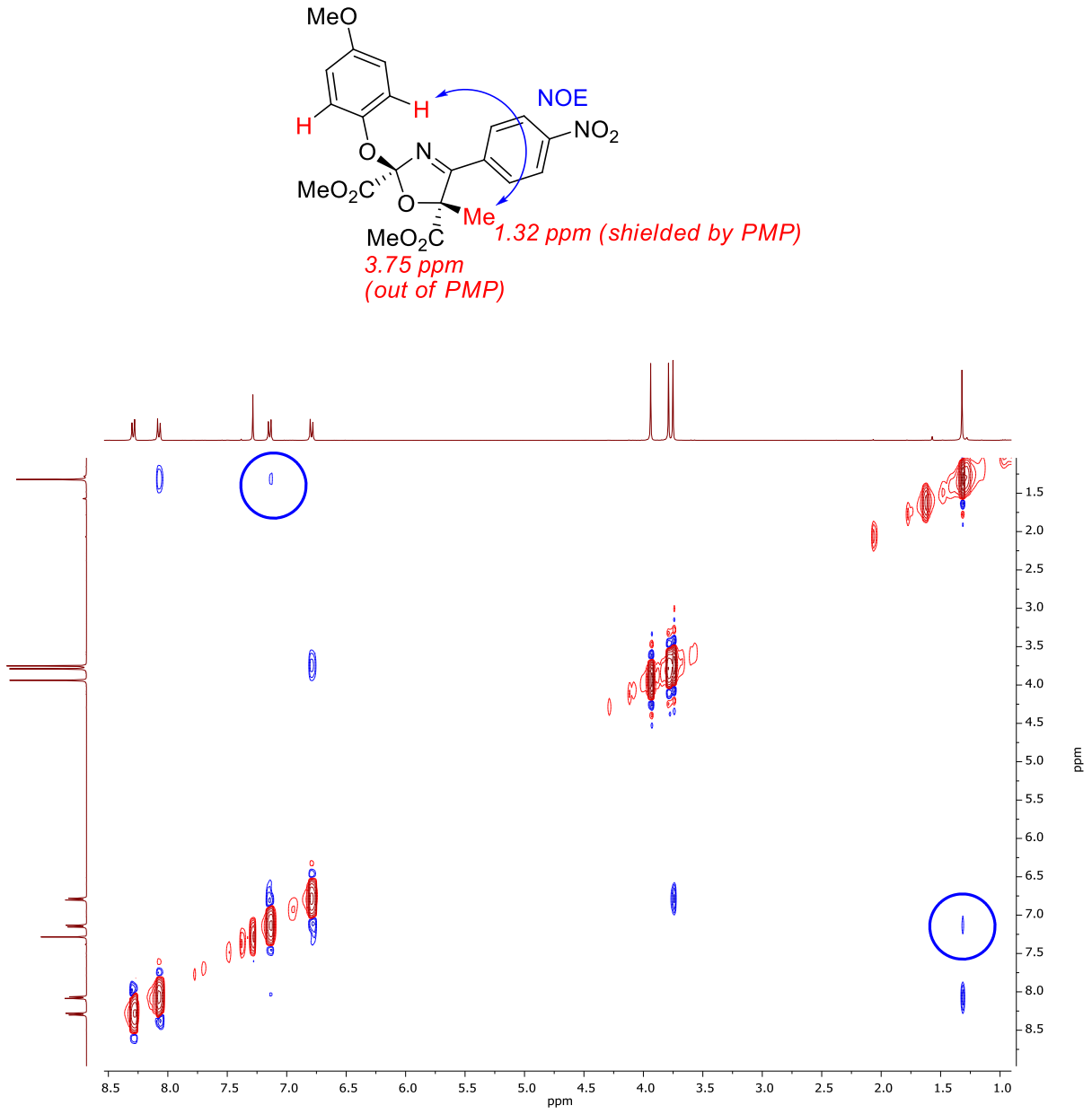
^{1}H-^{13}C HSQC NMR spectrum of oxazoline **(2*RS*,5*SR*)-4's** (400 MHz, $CDCl_3$)



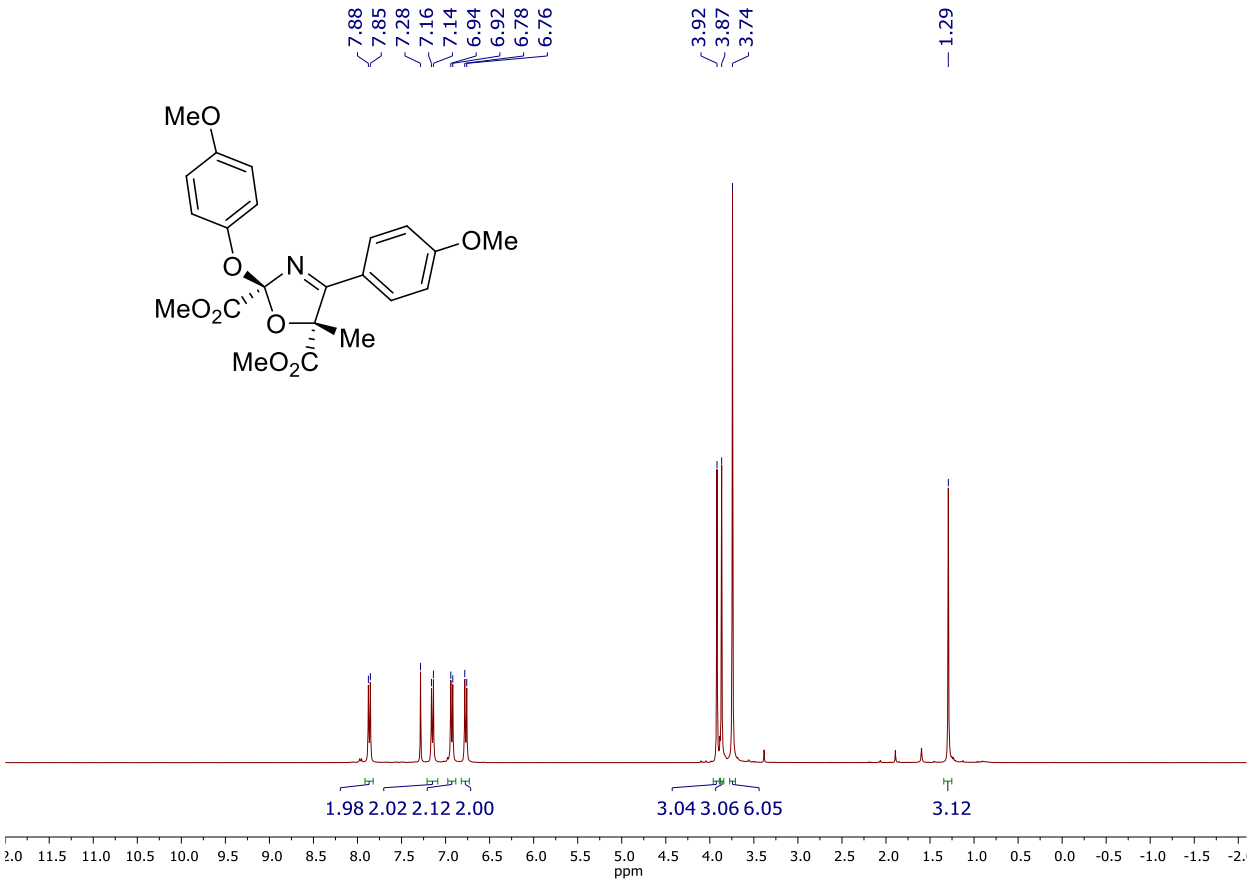
^{1}H-^{13}C HMBC NMR spectrum of oxazoline **(2*RS*,5*SR*)-4's** (400 MHz, $CDCl_3$)



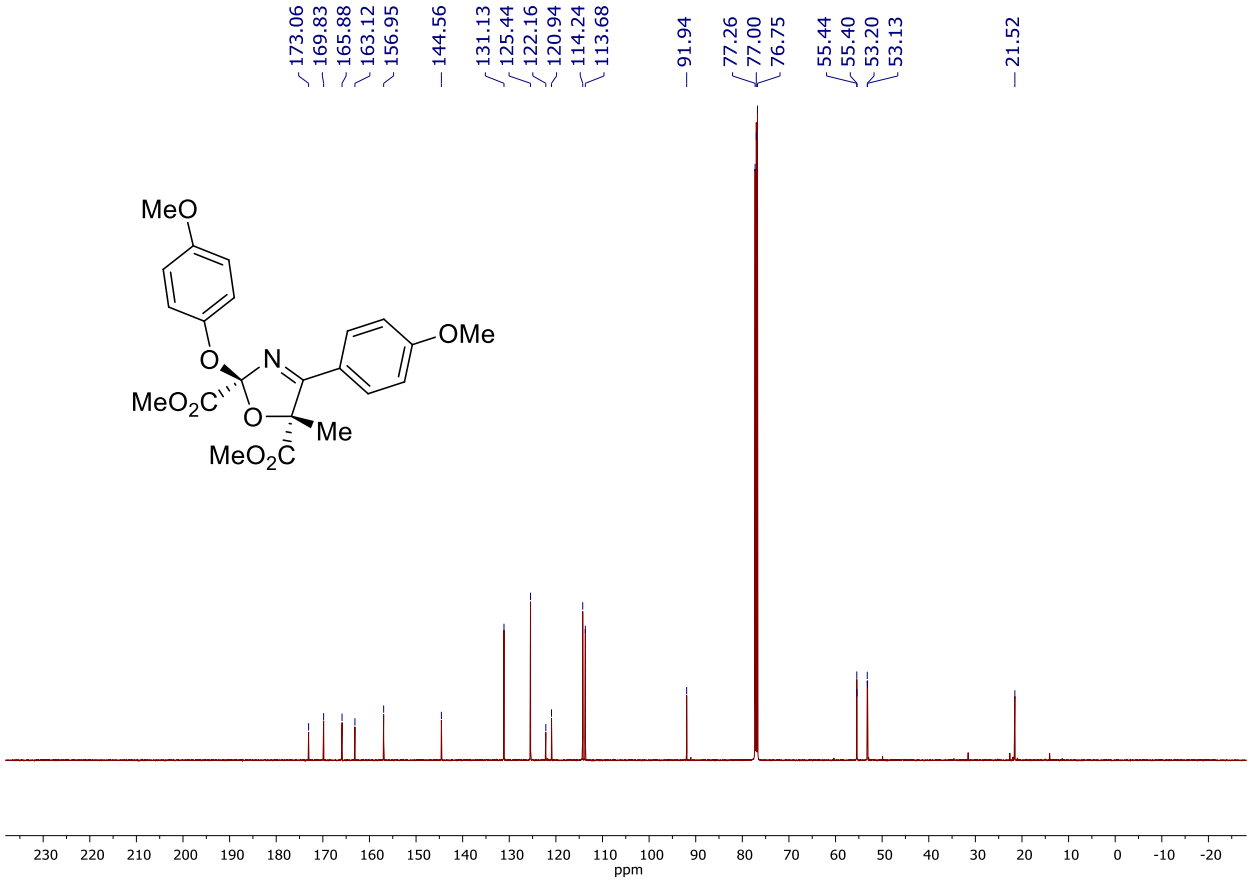
^{1}H-^{1}H NOESY NMR spectrum of oxazoline **(2*RS*,5*SR*)-4's** (400 MHz, $CDCl_3$)



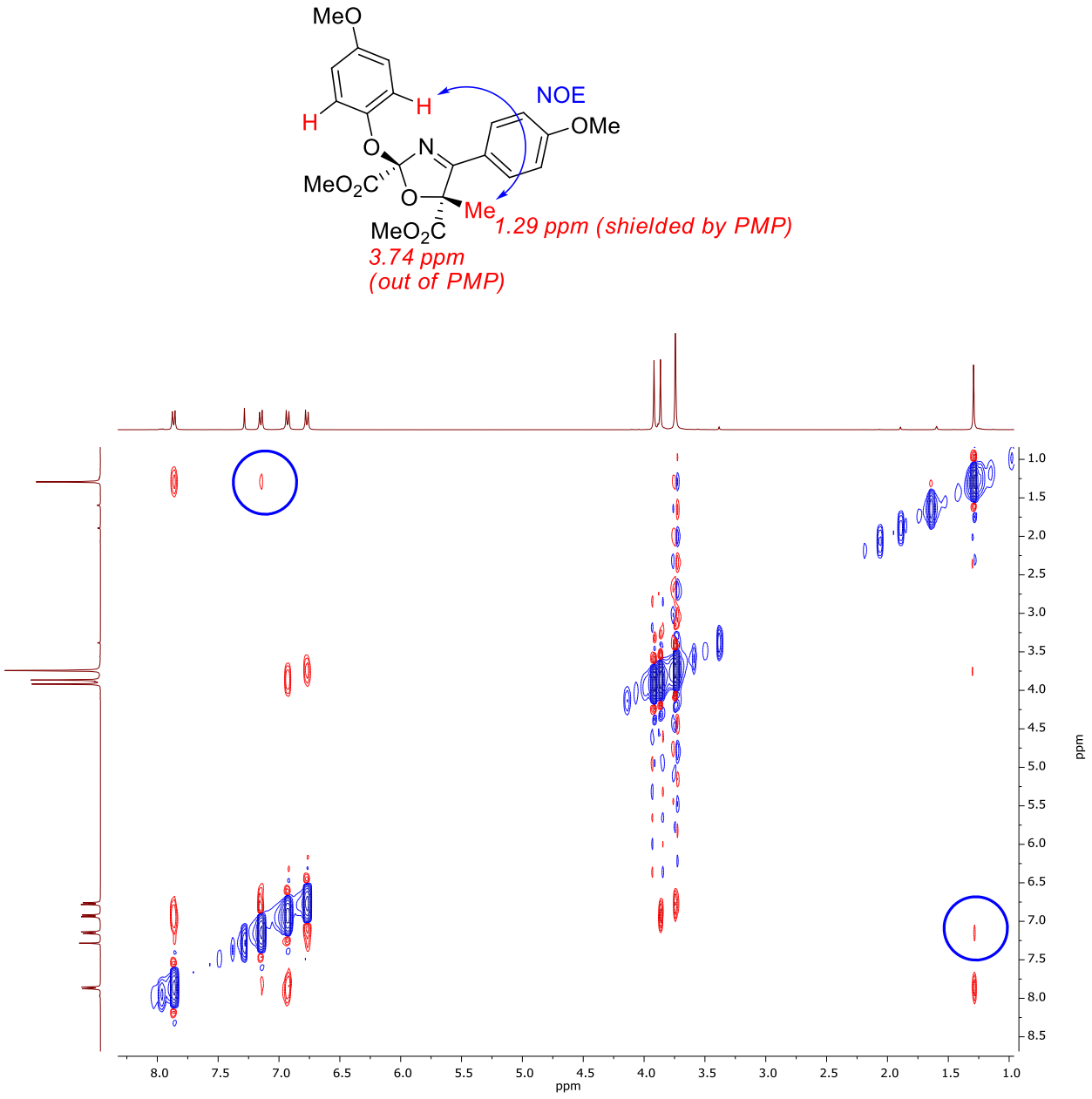
^{1}H NMR spectrum of oxazoline **4't** (400 MHz, $CDCl_3$)



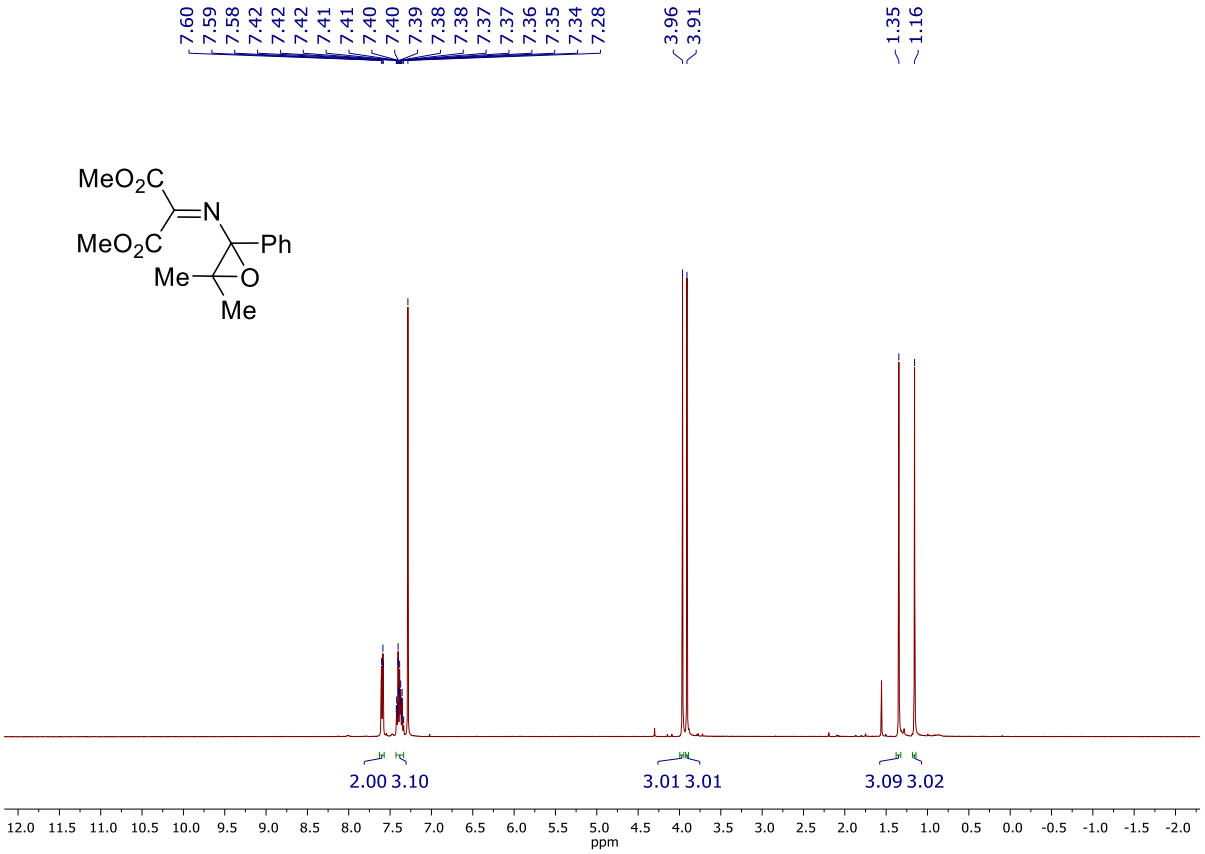
^{13}C{^{1}H} NMR spectrum of oxazoline **4't** (126 MHz, $CDCl_3$)



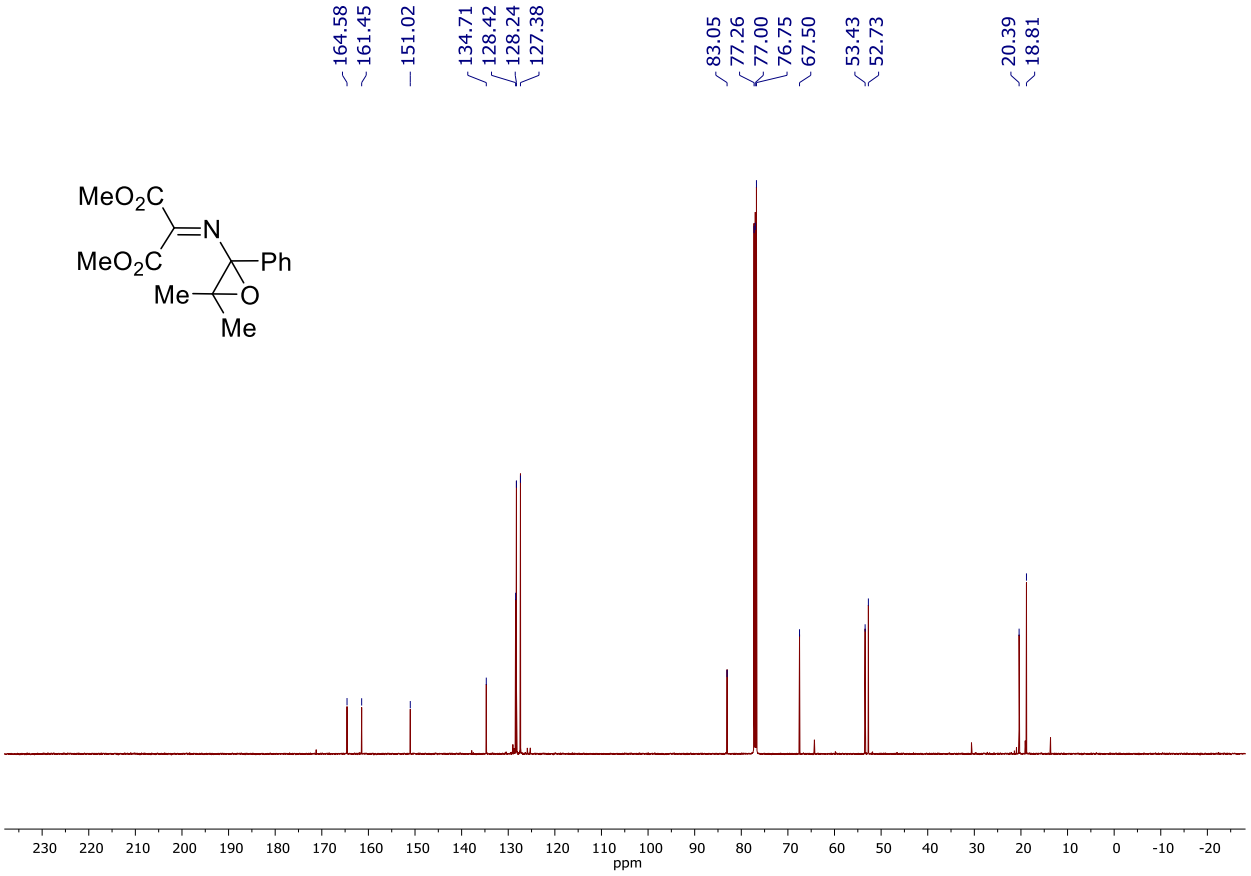
^{1}H-^{1}H NOESY NMR spectrum of oxazoline **4't** (400 MHz, $CDCl_3$)



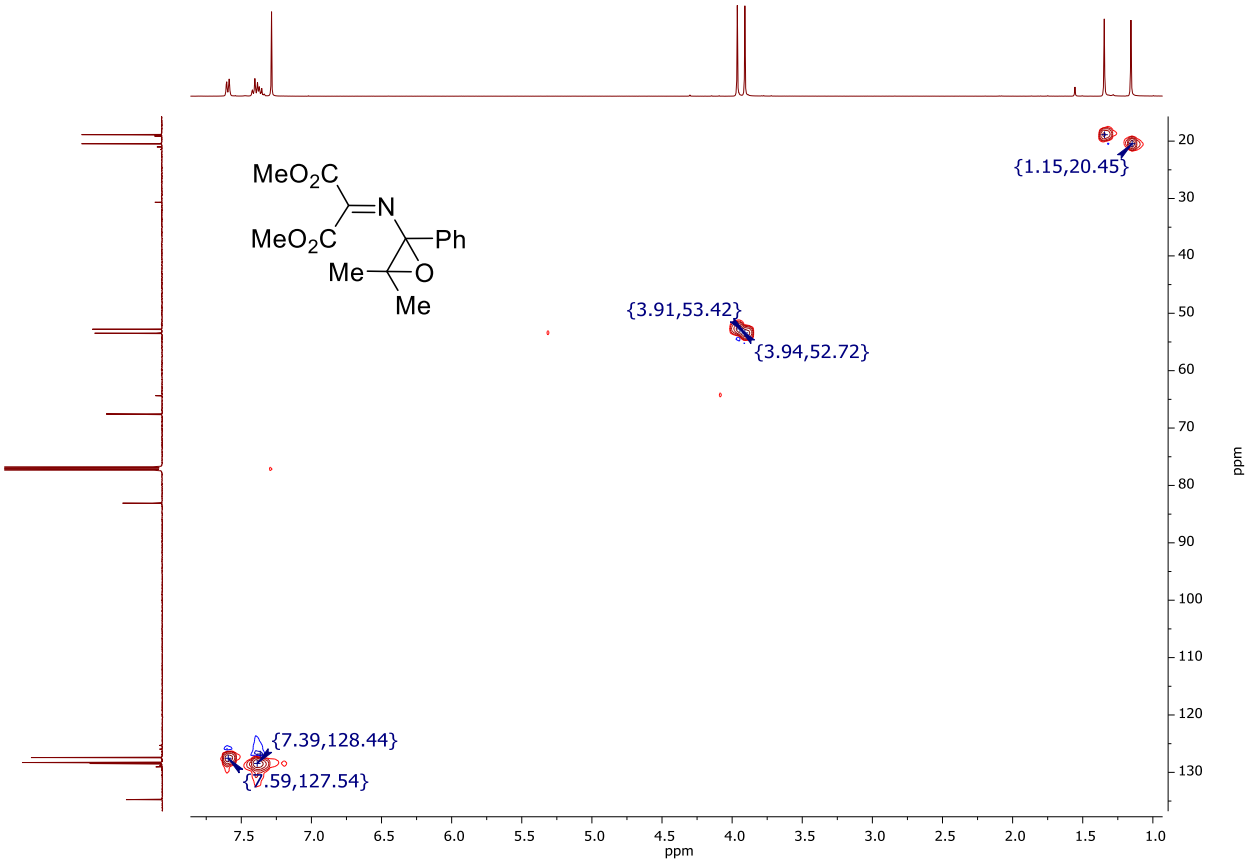
^{1}H NMR spectrum of oxirane **6o** (400 MHz, $CDCl_3$)



$^{13}C\{^{1}H\}$ NMR spectrum of oxirane **6o** (125 MHz, $CDCl_3$)



^{1}H-^{13}C HSQC NMR spectrum of oxirane **6o** (400 MHz, $CDCl_3$)



^{1}H-^{13}C HMBC NMR spectrum of oxirane **6o** (400 MHz, $CDCl_3$)