

Zincation of 4,4-Dimethyloxazoline Using $\text{TMPZnCl}\cdot\text{LiCl}$.

A new Preparation of 2-Aryloxazolines

Diana Haas, Maximilian S. Hofmayer, Tomke Bresser and Paul Knochel*

Department of Chemistry, Ludwig-Maximilians-University, Butenandtstrasse 5-13, 81377Munich, Germany.

Paul.Knochel@cup.uni-muenchen.de

Supporting Information

Table of contents

- 1) General considerations (1–2)
- 2) Preparation of Organometallic Reagents (2-3)
- 3) Experimental Procedures and Analytical Data (3–16)
- 3) NMR Spectra (17–32)

1) General information

All reactions were carried out with magnetic stirring and in flame-dried glassware under argon atmosphere. Syringes used to transfer reagents and solvents were purged with argon prior to use. THF was continuously refluxed and distilled from sodium benzophenone ketyl under nitrogen and kept over 4 Å molecular sieves.

Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC). TLC were performed with aluminium plates covered with SiO_2 (Merck 60, F-254) and visualized either by UV detection or submerging in KMnO_4 solution (1.5 g KMnO_4 , 10 g K_2CO_3 , and 1.25 mL 10% NaOH solution in 200 mL H_2O). Purification *via* column chromatography was performed using Merck silica gel 60 (40 – 63 μm 230-400 mesh ASTM from Merck). Melting points were measured using a Büchi B-540 apparatus and are uncorrected. NMR spectra were recorded in CDCl_3 or DMOS-d_6 and chemical shifts (δ) are reported in parts per million (ppm). Mass spectra and high resolution mass spectra (HR-MS) were recorded using electron ionization (EI). GCs were recorded on machines of the

types *Hewlett-Packard* 6890 or 5890 Series II (5% phenylmethylpolysiloxane; column length: 10 m, diameter: 0.25 mm; film thickness: 0.25 μm).

i-PrMgCl·LiCl solution is obtained from Rockwood Lithium (Frankfurt, Germany) as 14% solution in THF and is titrated with iodine prior to use. CuCN·2LiCl (1 M) solution is prepared by heating CuCN (1.0 equiv) and LiCl (2.0 equiv) under vacuum at 130 °C for 6 h. THF is added slowly and the solution is stirred overnight. Commercially available starting materials were purchased from commercial sources and used without further purification.

2) Preparation of Organometallic Reagents

Preparation of TMPZnCl·LiCl (3):¹

A dry and argon flushed 250 mL *Schlenk*-flask is charged with freshly distilled 2,2,6,6-tetramethylpiperidine (10.2 mL, 60 mmol) dissolved in THF (60 mL). The solution is cooled to -40 °C and *n*-BuLi (2.4 M in hexane, 25 mL, 60 mmol) is added dropwise. After the addition is complete, the reaction mixture is allowed to warm slowly to -10 °C for 1 h. ZnCl₂ (1.0 M in THF, 66 mL, 66 mmol) is added dropwise and the resulting solution is stirred for 0.5 h at -10 °C and then for 0.5 h at 25 °C. The solvents are removed under vacuum affording a yellowish solid. Freshly distilled THF is then slowly added under vigorous stirring until the salts were completely dissolved. The freshly prepared TMPZnCl·LiCl (3) solution was titrated prior to use at 25 °C with benzoic acid using 4-(phenylazo)diphenylamine as indicator.²

Preparation of TMPMgCl·LiCl (6):³

A dry and argon flushed 250 mL *Schlenk*-flask is charged with *i*-PrMgCl·LiCl (100 mL, 1.2 M in THF, 120 mmol). Freshly distilled 2,2,6,6-tetramethylpiperidine (17.8 g, 126 mmol) is added dropwise at 25 °C. The reaction mixture is stirred at room temperature until gas evolution ceased (ca. 48 h). The fresh TMPMgCl·LiCl (6) solution is titrated at 25 °C with benzoic acid using 4-(phenylazo)diphenylamine as indicator.²

Preparation of TMP₂Mg·2LiCl (8):⁴

A dry and argon-flushed 500 mL *Schlenk*-flask is charged with 2,2,6,6-tetramethylpiperidine (7.1 g, 50 mmol) dissolved in THF (50 mL). The solution is cooled to -40 °C and *n*-BuLi (2.4 M in hexane,

¹M. Mosrin, P. Knochel, *Org. Lett.*, 2009, **11**, 1837.

²A. Krasovskiy, P. Knochel, *Synlett*, 2006, **5**, 890.

³A. Krasovskiy, V. Krasovskaya, and P. Knochel, *Angew. Chem., Int. Ed.*, 2006, **45**, 2958.

⁴G. C. Clososki, C. J. Rohbogner, P. Knochel, *Angew. Chem., Int. Ed.*, 2007, **46**, 7681.

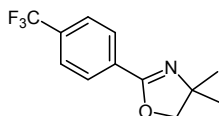
50 mmol) is added at once. The resulting mixture is stirred for 15 min at $-40\text{ }^{\circ}\text{C}$ and stirred at $0\text{ }^{\circ}\text{C}$ for further 0.5 h. $\text{TMPMgCl}\cdot\text{LiCl}$ (6, 43.5 mL, 1.15 M in THF, 50 mmol) is added and the mixture is stirred at $0\text{ }^{\circ}\text{C}$ for 0.5 h and at $25\text{ }^{\circ}\text{C}$ for 1 h. The solvents are removed *in vacuo*. The resulting pale-brown solid is redissolved in dry THF (40-50 mL) and stirred for 10 min at $25\text{ }^{\circ}\text{C}$. The freshly prepared $\text{TMP}_2\text{Mg}\cdot 2\text{LiCl}$ (**8**) is titrated prior to use at $25\text{ }^{\circ}\text{C}$ with benzoic acid using (phenylazo)diphenylamine as indicator.²

3) Experimental Procedures and Analytical Data

Typical procedure for the metalation of 4,4-dimethyloxazoline (TP 1) using $\text{TMPZnCl}\cdot\text{LiCl}$:

A dry and argon flushed *Schlenk* flask is charged with a solution of 4,4-dimethyloxazoline (**1**, 1.2 equiv, 1.2 mmol) in dry THF (1.0 mL). The solution is cooled to $0\text{ }^{\circ}\text{C}$ and $\text{TMPZnCl}\cdot\text{LiCl}$ (**3**, 1.4 equiv) is added dropwise. The reaction is stirred for 1 h at $0\text{ }^{\circ}\text{C}$ to yield the corresponding 4,4-dimethyloxazolinylzinc reagent (**4**).

Synthesis of 4,4-dimethyl-2-(4-(trifluoromethyl)phenyl)oxazoline (**5a**):



Preparation from 1-iodo-4-(trifluoromethyl)benzene:

4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with $\text{TMPZnCl}\cdot\text{LiCl}$ (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1** and is then subjected to a Pd-catalyzed cross-coupling reaction by addition of 1-iodo-4-(trifluoromethyl)benzene (272 mg, 1.0 mmol), $\text{Pd}(\text{OAc})_2$ (7 mg, 3 mol%) and SPhos (25 mg, 6 mol%). The reaction is stirred for 4 h at $50\text{ }^{\circ}\text{C}$ and is then quenched with sat. aq. NH_4Cl solution, extracted with CH_2Cl_2 and dried over Na_2SO_4 . The crude product is purified by column chromatography on silica (*i*-hexane:ethyl acetate 5:1) to afford **5a** (192 mg, 0.79 mmol, 79%) as colorless crystals.

Preparation from 1-bromo-4-(trifluoromethyl)benzene:

4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with $\text{TMPZnCl}\cdot\text{LiCl}$ (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1** and is then subjected to a Pd-catalyzed cross-coupling reaction by

addition of 1-bromo-4-(trifluoromethyl)benzene (225 mg, 1.0 mmol), Pd(dba)₂ (17 mg, 3 mol%) and SPhos (25 mg, 6 mol%). The reaction is stirred for 3 h at 50 °C and is then quenched with sat. aq. NH₄Cl solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (*i*-hexane:ethyl acetate 5:1) to afford **5a** (187 mg, 0.77 mmol, 77%) as colorless crystals.

m.p.: 34 – 36 °C

¹H-NMR (400 MHz, CDCl₃, ppm): δ = 7.97 - 8.16 (d, *J* = 8.2 Hz, 2 H), 7.58 - 7.74 (d, *J* = 8.2 Hz, 2 H), 4.16 (s, 2 H), 1.41 (s, 6 H).

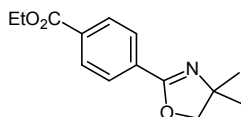
¹³C-NMR (100 MHz, CDCl₃, ppm): δ = 160.9, 132.8 (q, *J* = 33.0 Hz), 131.4, 128.6, 125.2 (q, *J* = 4.2 Hz), 123.8 (q, *J* = 272.1 Hz), 79.3, 67.9, 28.4.

FT-IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2970, 2930, 1651, 1620, 1581, 1521, 1463, 1412, 1386, 1367, 1355, 1323, 1298, 1249, 1216, 1166, 1128, 1107, 1069, 1016, 989, 963, 921, 870, 852, 818, 774, 754, 687, 664.

MS (EI, 70 eV): *m/z* (%) = 243 (3), 242 (2), 230 (4), 229 (12), 228 (100), 224 (6), 214 (3), 200 (22), 173 (19), 172 (62), 171 (4), 121 (3), 95 (3), 57 (3), 57 (7), 42 (5), 41 (6).

HR-MS (EI, 70 eV): [C₁₂H₁₂F₃NO], calc.: 243.0871; found: 243.0868.

Synthesis of ethyl 4-(4,4-dimethyloxazoliny)benzoate (**5b**):



Preparation from ethyl 4-iodobenzoate:

4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl·LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1** and is then subjected to a Pd-catalyzed cross-coupling reaction by addition of ethyl 4-iodobenzoate (276 mg, 1.0 mmol), Pd(OAc)₂ (7 mg, 3 mol%) and SPhos (25 mg, 6 mol%). The reaction is stirred for 3 h at 50 °C and is then quenched with sat. aq. NH₄Cl solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (*i*-hexane:diethyl ether 2:1) to afford **5b** (195 mg, 0.79 mmol, 79%) as a yellow oil.

Preparation from ethyl 4-bromobenzoate:

4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl-LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1** and is then subjected to a Pd-catalyzed cross-coupling reaction by addition of ethyl 4-bromobenzoate (229 mg, 1.0 mmol), Pd(dba)₂ (17 mg, 3 mol%) and SPhos (25 mg, 6 mol%). The reaction is stirred for 5 h at 50 °C and is then quenched with sat. aq. NH₄Cl solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (*i*-hexane:diethyl ether 2:1) to afford **5b** (228 mg, 0.92 mmol, 92%) as a yellow oil.

¹H-NMR (300 MHz, CDCl₃, ppm): δ = 8.04 - 8.13 (m, 2 H), 7.97 - 8.04 (m, 2 H), 4.40 (q, *J* = 7.2 Hz, 2 H), 4.14 (s, 2 H), 1.32 - 1.50 (m, 9 H).

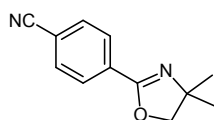
¹³C-NMR (75 MHz, CDCl₃, ppm): δ = 166.0, 161.4, 132.7, 131.9, 129.4, 128.2, 79.3, 67.8, 61.2, 28.3, 14.3.

FT-IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2970, 2930, 2361, 2340, 1716, 1648, 1613, 1463, 1409, 1365, 1354, 1310, 1299, 1269, 1215, 1190, 1173, 1102, 1064, 1018, 990, 965, 922, 867, 849, 780, 710, 678.

MS (EI, 70 eV): *m/z* (%) = 247 (3), 246 (1), 233 (14), 232 (100), 217 (13), 204 (11), 202 (9), 176 (21), 159 (4), 148 (14), 130 (5), 103 (5), 102 (4), 76 (4).

HR-MS (EI, 70 eV): [C₁₄H₁₇NO₃], calc.: 247.1208; found: 247.1203

Synthesis of 4-(4,4-dimethyloxazoliny)benzonitrile (**5c**):



Preparation from 4-iodobenzonitrile:

4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl-LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1** and is then subjected to a Pd-catalyzed cross-coupling reaction by addition of 4-iodobenzonitrile (229 mg, 1.0 mmol), Pd(OAc)₂ (7 mg, 3 mol%) and SPhos (25 mg, 6 mol%). The reaction is stirred for 5 h at 50 °C and is then quenched with sat. aq. NH₄Cl solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (CH₂Cl₂:diethyl ether 5:1) to afford **5c** (160 mg, 0.80 mmol, 80%) as a white solid.

Preparation from 4-bromobenzonitrile:

4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl·LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1** and is then subjected to a Pd-catalyzed cross-coupling reaction by addition of 4-bromobenzonitrile (182 mg, 1.0 mmol), Pd(dba)₂ (17 mg, 3 mol%) and SPhos (25 mg, 6 mol%). The reaction is stirred for 2 h at 50 °C and is then quenched with sat. aq. NH₄Cl solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (CH₂Cl₂:diethyl ether 5:1) to afford **5c** (174 mg, 0.87 mmol, 87%) as a white solid.

m.p.: 107 – 108 °C

¹H-NMR (300 MHz, CDCl₃, ppm): δ = 7.96 - 8.14 (d, *J* = 8.3 Hz, 2 H), 7.60 - 7.81 (d, *J* = 8.3 Hz, 2 H), 4.15 (s, 2 H), 1.39 (s, 6 H).

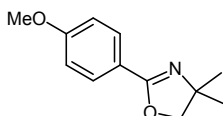
¹³C-NMR (75 MHz, CDCl₃, ppm): δ = 160.5, 132.2, 132.0, 128.8, 118.2, 114.6, 79.5, 68.0, 28.3.

FT-IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2972, 2906, 2229, 1930, 1641, 1610, 1564, 1502, 1462, 1408, 1383, 1357, 1320, 1310, 1292, 1250, 1218, 1186, 1111, 1071, 1017, 952, 924, 872, 845, 831, 820, 741, 676.

MS (EI, 70 eV): *m/z* (%) = 204 (3), 200 (3), 199 (2), 186 (14), 185 (100), 170 (28), 157 (21), 130 (7), 129 (59), 128 (5), 102 (21), 75 (6), 74 (9), 59 (13), 57 (9), 45 (9), 44 (14), 43 (5), 42 (11), 41 (15).

HR-MS (EI, 70 eV): [C₁₂H₁₂N₂O], calc.: 200.0950; found: 200.0942.

Synthesis of 2-(4-methoxyphenyl)-4,4-dimethyloxazoline (**5d**):



4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl·LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1** and is then subjected to a Pd-catalyzed cross-coupling reaction by addition of 4-bromoanisole (187 mg, 1.0 mmol), Pd(OAc)₂ (7 mg, 3 mol%) and SPhos (25 mg, 6 mol%). The reaction is stirred for 3 h at 50 °C and is then quenched with sat. aq. NH₄Cl solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (CH₂Cl₂:diethyl ether 4:1) to afford **5d** (168 mg, 0.82 mmol, 82%) as a colorless liquid.

¹H-NMR (300 MHz, CDCl₃, ppm): δ = 7.84 - 7.91 (m, 2 H), 6.86 - 6.94 (m, 2 H), 4.08 (s, 2 H), 3.84 (s, 3 H), 1.37 (s, 6 H).

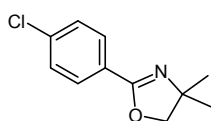
¹³C-NMR (75 MHz, CDCl₃, ppm): δ = 161.9, 161.8, 129.8, 120.5, 113.5, 79.0, 67.4, 55.3, 28.4.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2975, 1733, 1701, 1684, 1602, 1575, 1468, 1458, 1447, 1402, 1380, 1366, 1307, 1296, 1276, 1256, 1216, 1189, 1154, 1059, 1034, 1029, 992, 968, 927, 914, 901, 806, 794, 778, 742, 715, 691, 662.

MS (EI, 70 eV): m/z (%) = 205 (13), 191 (13), 190 (100), 175 (11), 162 (29), 135 (9), 134 (36), 133 (13), 119 (5), 103 (6), 97 (6), 92 (6), 91 (8), 90 (7), 77 (5), 69 (5), 57 (5), 40 (5).

HR-MS (EI, 70 eV): $[\text{C}_{12}\text{H}_{15}\text{NO}_2]$, calc.: 205.1103; found: 205.1102.

Synthesis of 2-(4-chlorophenyl)-4,4-dimethyloxazoline (5e):



4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl·LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1** and is then subjected to a Pd-catalyzed cross-coupling reaction by addition of 4-bromo-1-chlorobenzene (191 mg, 1.0 mmol), Pd(OAc)₂ (7 mg, 3 mol%) and SPhos (25 mg, 6 mol%). The reaction is stirred for 2 h at 50 °C and is then quenched with sat. aq. NH₄Cl solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (CH₂Cl₂:diethyl ether 9:1) to afford **5e** (149 mg, 0.71 mmol, 71%) as a white solid.

m.p.: 79 – 81 °C

¹H-NMR (400 MHz, CDCl₃, ppm): δ = 7.83 - 7.97 (m, 2 H), 7.31 - 7.53 (m, 2 H), 4.11 (s, 2 H), 1.38 (s, 6 H).

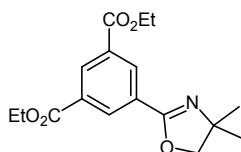
¹³C-NMR (100 MHz, CDCl₃, ppm): δ = 161.2, 137.3, 129.5, 128.5, 126.5, 79.2, 67.7, 28.4.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2968, 2929, 1650, 1599, 1492, 1463, 1404, 1352, 1312, 1297, 1246, 1214, 1186, 1173, 1090, 1062, 1015, 989, 963, 920, 870, 839, 820, 731, 678.

MS (EI, 70 eV): m/z (%) = 211 (2), 209 (7), 196 (30), 195 (10), 194 (100), 181 (5), 179 (16), 168 (6), 166 (18), 142 (14), 140 (15), 139 (11), 138 (50), 111 (12), 102 (9), 75 (12), 71 (9), 57 (5), 50 (5), 42 (6), 41 (12).

HR-MS (EI, 70 eV): $[\text{C}_{11}\text{H}_{12}\text{ClNO}]$, calc.: 209.0607; found: 209.0596.

Synthesis of diethyl 5-(4,4-dimethyloxazoliny)isophthalate (5f):



4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl·LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1** and is then subjected to a Pd-catalyzed cross-coupling reaction by addition of diethyl 5-bromoisophthalate (301 mg, 1.0 mmol), Pd(OAc)₂ (7 mg, 3 mol%) and SPhos (25 mg, 6 mol%). The reaction is stirred for 8 h at 50 °C and is then quenched with sat. aq. NH₄Cl solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (CH₂Cl₂:diethyl ether 2:1) to afford **5f** (217 mg, 0.68 mmol, 68%) as a yellowish solid.

m.p.: 83 – 85 °C

¹H-NMR (300 MHz, CDCl₃, ppm): δ = 8.69 - 8.85 (m, 3 H), 4.43 (q, *J* = 7.0 Hz, 4 H), 4.18 (s, 2 H), 1.30 - 1.50 (m, 12 H).

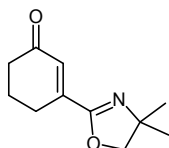
¹³C-NMR (75 MHz, CDCl₃, ppm): δ = 165.1, 133.1, 131.4, 79.5, 67.9, 61.5, 28.3, 14.3.

FT-IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2969, 2932, 1716, 1674, 1651, 1598, 1468, 1440, 1397, 1374, 1365, 1354, 1331, 1267, 1231, 1207, 1137, 1104, 1086, 1027, 999, 978, 939, 923, 901, 864, 817, 782, 764, 732, 721, 710, 663.

MS (EI, 70 eV): m/z (%) = 319 (2), 318 (3), 306 (3), 305 (19), 304 (100), 289 (17), 276 (13), 274 (15), 249 (4), 248 (17), 246 (4), 220 (7), 202 (6), 192 (9), 174 (4), 43 (4), 41 (4).

HR-MS (EI, 70 eV): [C₁₇H₂₀NO], calc.: 318.1341; found: 318.1330 [M-H⁺].

Synthesis of 3-(4,4-dimethyloxazoliny)cyclohex-2-en-1-one (**5g**):



4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl·LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1** and is then subjected to a Pd-catalyzed cross-coupling reaction by addition of 3-iodocyclohex-2-en-1-one (222 mg, 1.0 mmol), Pd(OAc)₂ (7 mg, 3 mol%) and SPhos (25 mg, 6 mol%). The reaction is stirred for 1 h at r.t. and is then quenched with sat. aq. NH₄Cl solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column

chromatography on silica (CH₂Cl₂:diethyl ether 2:1) to afford **5g** (131 mg, 0.68 mmol, 68%) as a yellow oil.

¹H-NMR (400 MHz, CDCl₃, ppm): δ = 6.56 (t, *J* = 1.7 Hz, 1 H), 4.03 (s, 2 H), 2.68 (td, *J* = 6.0, 1.7 Hz, 2 H), 2.36 - 2.54 (m, 2 H), 1.97 - 2.14 (m, 2 H), 1.34 (s, 6 H).

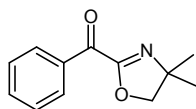
¹³C-NMR (100 MHz, CDCl₃, ppm): δ = 199.9, 161.8, 146.7, 130.5, 79.0, 68.1, 37.7, 28.2, 25.6, 22.3.

FT-IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2963, 2928, 1668, 1644, 1598, 1537, 1463, 1455, 1432, 1418, 1364, 1346, 1326, 1317, 1275, 1252, 1237, 1203, 1187, 1135, 1063, 1020, 953, 904, 890, 702.

MS (EI, 70 eV): *m/z* (%) = 195 (1), 194 (3), 193 (21), 178 (100), 165 (4), 164 (8), 163 (30), 150 (18), 134 (7), 123 (3), 122 (22), 108 (3), 107 (4), 93 (5), 67 (4), 66 (3), 65 (3), 41 (4).

HR-MS (EI, 70 eV): [C₁₁H₁₅NO₂], calc.: 193.1103; found: 193.1133.

Synthesis of (4,4-dimethyloxazoliny)(phenyl)methanone (**5h**):



4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl·LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1**. The reaction mixture is cooled to -40 °C, CuCN·2LiCl (1.4 mL, 1.4 mmol, 1 M solution in THF) is added and the reaction is stirred for 15 min at this temperature. Then, benzoyl chloride (141 mg, 1.0 mmol) is added, the reaction is allowed to warm to r.t. over 2 h and is then quenched with sat. aq. NH₄Cl/NH₃ solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (CH₂Cl₂:*i*-hexane 8:1) to afford **5h** (130 mg, 0.64 mmol, 64%) as a colorless liquid.

¹H-NMR (400 MHz, CDCl₃, ppm): δ = 8.23 - 8.31 (m, 2 H), 7.59 - 7.67 (m, 1 H), 7.46 - 7.53 (m, 2 H), 4.16 (s, 2 H), 1.45 (s, 6 H).

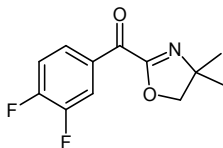
¹³C-NMR (100 MHz, CDCl₃, ppm): δ = 184.0, 157.6, 134.8, 134.2, 130.6, 128.5, 78.9, 69.2, 28.2.

FT-IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2975, 1733, 1701, 1684, 1602, 1575, 1468, 1458, 1447, 1402, 1380, 1366, 1307, 1296, 1276, 1256, 1216, 1189, 1154, 1059, 1034, 1029, 992, 968, 927, 914, 901, 806, 794, 778, 742, 715, 691, 662.

MS (EI, 70 eV): *m/z* (%) = 205 (10), 204 (33), 203 (5), 189 (6), 188 (4), 175 (10), 160 (8), 119 (9), 106 (9), 105 (100), 77 (36), 73 (11), 57 (5), 51 (8), 45 (8).

HR-MS (EI, 70 eV): [C₁₂H₁₄NO₂], calc.: 204.1019; found: 204.1018 [M+H⁺].

Synthesis of (3,4-difluorophenyl)(4,4-dimethyloxazoliny)methanone (5i):



4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl·LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1**. The reaction mixture is cooled to -40 °C, CuCN·2LiCl (1.4 mL, 1.4 mmol, 1 M solution in THF) is added and the reaction is stirred for 15 min at this temperature. Then, 3,4-difluorobenzoyl chloride (177 mg, 1.0 mmol) is added, the reaction is allowed to warm to r.t. over 2 h and is then quenched with sat. aq. NH₄Cl/NH₃ solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (CH₂Cl₂:*i*-hexane 8:1) to afford **5h** (182 mg, 0.76 mmol, 76%) as a white solid.

m.p.: 55 – 56 °C

¹H-NMR (400 MHz, CDCl₃, ppm): δ = 8.23 - 8.33 (m, 1 H), 8.20 (ddd, *J* = 8.6, 4.2, 1.7 Hz, 1 H), 7.19 - 7.33 (m, 1 H), 4.15 (s, 2 H), 1.45 (s, 6 H).

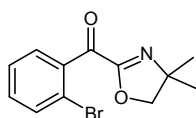
¹³C-NMR (100 MHz, CDCl₃, ppm): δ = 180.90, 157.20, 155.77, 155.64, 153.19, 153.06, 151.33, 151.20, 148.84, 148.71, 131.74, 131.70, 131.65, 128.22, 128.19, 128.14, 128.11, 120.28, 120.09, 117.54, 117.36, 78.84, 69.41, 28.14, 24.59.

FT-IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2971, 2361, 1721, 1689, 1679, 1617, 1602, 1515, 1469, 1432, 1420, 1399, 1382, 1366, 1330, 1283, 1272, 1257, 1242, 1216, 1198, 1146, 1119, 1056, 1035, 998, 979, 958, 947, 932, 920, 889, 871, 864, 828, 798, 787, 774, 758, 704, 668, 656.

MS (EI, 70 eV): *m/z* (%) = 240 (5), 239 (10), 225 (4), 211 (4), 196 (4), 190 (4), 158 (4), 142 (8), 141 (100), 140 (4), 113 (28), 109 (4), 97 (6), 95 (4), 91 (4), 83 (5), 81 (4), 73 (9), 69 (7), 63 (5), 57 (7), 56 (4), 55 (6), 42 (5), 40 (4).

HR-MS (EI, 70 eV): [C₁₂H₁₁F₂NO₂], calc.: 239.0758; found: 239.0744.

Synthesis of (2-bromophenyl)(4,4-dimethyloxazoliny)methanone (5j):



4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl·LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1**. The reaction mixture is cooled to -40 °C, CuCN·2LiCl (1.4 mL, 1.4 mmol, 1 M solution in THF) is added and the reaction is stirred for 15 min at this temperature. Then, 2-bromobenzoyl chloride (219 mg, 1.0 mmol) is added, the reaction is allowed to warm to r.t. over 4 h and is then quenched with sat. aq. NH₄Cl/NH₃ solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (CH₂Cl₂:*i*-hexane 8:1) to afford **5j** (200 mg, 0.71 mmol, 71%) as a yewollish solid.

m.p.: 57 – 59 °C

¹H-NMR (400 MHz, CDCl₃, ppm): δ = 7.63 (dd, *J* = 7.7, 1.3 Hz, 1 H), 7.58 - 7.61 (m, 1 H), 7.35 - 7.45 (m, 2 H), 4.19 (s, 2 H), 1.40 (s, 6 H).

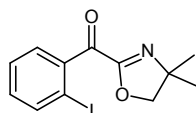
¹³C-NMR (100 MHz, CDCl₃, ppm): δ = 186.4, 157.9, 138.0, 133.5, 132.9, 130.7, 127.3, 120.7, 79.9, 69.0, 27.7.

FT-IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2973, 1740, 1691, 1636, 1586, 1461, 1435, 1386, 1364, 1324, 1284, 1262, 1227, 1186, 1165, 1064, 1048, 1023, 981, 970, 955, 934, 905, 873, 860, 819, 782, 754, 724, 688.

MS (ESI, 70 eV): *m/z* (%) = 285 (11), 284 (88), 283 (12), 282 (86), 185 (100), 183 (82), 170 (5).

HR-MS (ESI, 70 eV): [C₁₂H₁₂BrNO₂], calc.: 282.0130; found: 282.0125 [M+H⁺].

Synthesis of (2-iodophenyl)(4,4-dimethyloxazoliny)methanone (**5k**):



4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl·LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1**. The reaction mixture is cooled to -40 °C, CuCN·2LiCl (1.4 mL, 1.4 mmol, 1 M solution in THF) is added and the reaction is stirred for 15 min at this temperature. Then, 2-iodobenzoyl chloride (266 mg, 1.0 mmol) is added, the reaction is allowed to warm to r.t. over 6 h and is then quenched with sat. aq. NH₄Cl/NH₃ solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (CH₂Cl₂:*i*-hexane 8:2) to afford **5k** (241 mg, 0.65 mmol, 65%) as a yellowish solid.

m.p.: 69 – 72 °C

¹H-NMR (400 MHz, CDCl₃, ppm): δ = 7.89 - 7.95 (m, 1 H), 7.58 (dd, J = 7.7, 1.6 Hz, 1 H), 7.46 (td, J = 7.6, 1.0 Hz, 1 H), 7.20 (td, J = 7.7, 1.7 Hz, 1 H), 4.19 (s, 2 H), 1.41 (s, 6 H).

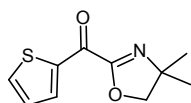
¹³C-NMR (100 MHz, CDCl₃, ppm): δ = 187.3, 157.4, 141.2, 140.2, 132.8, 130.5, 127.9, 92.8, 79.8, 69.1, 27.7.

FT-IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2971, 1737, 1693, 1625, 1581, 1462, 1431, 1386, 1380, 1366, 1324, 1301, 1283, 1259, 1227, 1216, 1187, 1166, 1118, 1062, 1046, 1017, 986, 968, 949, 939, 903, 860, 816, 793, 781, 748, 723, 680.

MS (EI, 70 eV): m/z (%) = 330 (1), 315 (1), 314 (1), 286 (1), 271 (1), 260 (1), 257 (1), 247 (1), 245 (1), 232 (7), 231 (100), 203 (10), 202 (67), 174 (27), 1448 (28), 76 (32), 55 (10), 50 (10).

HR-MS (EI, 70 eV): [C₁₂H₁₂INO₂], calc.: 329.9985; found: 329.9984 [M+H⁺].

Synthesis of (4,4-dimethyloxazoliny)(thiophen-2-yl)methanone (5I):



4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl·LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1**. The reaction mixture is cooled to -40 °C, CuCN·2LiCl (1.4 mL, 1.4 mmol, 1 M solution in THF) is added and the reaction is stirred for 15 min at this temperature. Then, thiophene-2-carbonyl chloride (147 mg, 1.0 mmol) is added, the reaction is allowed to warm to r.t. over 2 h and is then quenched with sat. aq. NH₄Cl/NH₃ solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (CH₂Cl₂ 100%) to afford **5I** (134 mg, 0.64 mmol, 64%) as a yellow liquid.

¹H-NMR (400 MHz, CDCl₃, ppm): δ = 8.38 (dd, J = 3.9, 1.2 Hz, 1 H), 7.77 (dd, J = 4.9, 1.0 Hz, 1 H), 7.18 (td, J = 4.9, 3.9 Hz, 1 H), 4.16 (s, 2 H), 1.44 (s, 6 H).

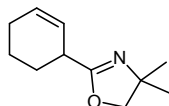
¹³C-NMR (100 MHz, CDCl₃, ppm): δ = 175.3, 157.6, 140.7, 137.3, 136.8, 128.5, 79.2, 69.1, 28.1.

FT-IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2974, 2931, 1736, 1689, 1681, 1649, 1614, 1582, 1548, 1525, 1513, 1501, 1467, 1440, 1430, 1407, 1380, 1360, 1344, 1301, 1277, 1257, 1233, 1220, 1187, 1153, 1079, 1049, 990, 972, 944, 915, 879, 846, 833, 794, 782, 714, 664.

MS (EI, 70 eV): m/z (%) = 209 (9), 112 (6), 111 (100), 83 (5), 83 (10), 71 (5), 70 (19), 69 (7), 57 (12), 56 (8), 55 (11), 43 (9), 43 (5), 41 (14).

HR-MS (EI, 70 eV): $[C_{10}H_{11}NO_2S]$, calc.: 209.0510; found: 209.0505.

Synthesis of 2-(cyclohex-2-en-1-yl)-4,4-dimethyloxazoline (5m):



4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl·LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1**. The reaction mixture is cooled to -40 °C, CuCN·2LiCl (1.4 mL, 1.4 mmol, 1 M solution in THF) is added and the reaction is stirred for 15 min at this temperature. Then, 3-bromocyclohex-1-ene (161 mg, 1.0 mmol) is added, the reaction is allowed to warm to r.t. over 4 h and is then quenched with sat. aq. NH_4Cl/NH_3 solution, extracted with CH_2Cl_2 and dried over Na_2SO_4 . The crude product is purified by column chromatography on silica (*i*-hexane:ethyl acetate 6:1) to afford **5m** (142 mg, 0.79 mmol, 79%) as colorless crystals.

m.p.: 40 – 42 °C

1H -NMR (400 MHz, $CDCl_3$, ppm): δ = 5.93 – 5.81 (m, 1H), 5.74 (d, J = 10.3 Hz, 1H), 3.92 (s, 2H), 3.17 – 2.98 (m, 1H), 2.13 – 1.46 (m, 6H), 1.28 (s, 6H).

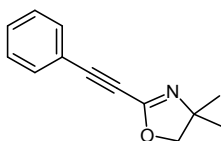
^{13}C -NMR (100 MHz, $CDCl_3$, ppm): δ = 167.9, 129.4, 125.2, 79.0, 66.8, 35.2, 28.4, 28.3, 26.4, 24.7, 20.8.

FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3110, 2964, 2944, 2926, 2909, 2866, 2834, 1659, 1611, 1477, 1463, 1450, 1437, 1428, 1399, 1367, 1351, 1315, 1301, 1286, 1251, 1208, 1189, 1156, 1138, 1118, 1104, 1068, 1037, 996, 980, 958, 950, 915, 898, 878, 857, 843, 832, 823, 736, 702, 657.

MS (EI, 70 eV): m/z (%) = 180 (20), 179 (100), 178 (87), 165 (6), 164 (66), 152 (5), 151 (8), 150 (57), 148 (8), 138 (5), 134 (5), 124 (6), 113 (8), 108 (6), 95 (5), 81 (13) 79 (6).

HR-MS (EI, 70 eV): $[C_{11}H_{17}NO]$, calc.: 179.1310; found: 179.1294.

Synthesis of 4,4-dimethyl-2-(phenylethynyl)oxazoline (5n):



4,4-Dimethyloxazoline (**1**, 119 mg, 1.2 mmol) is metalated with TMPZnCl·LiCl (**3**, 1.21 mL, 1.4 mmol, 1.16 M solution) according to **TP 1**. Iodine (355 mg, 1.4 mmol) dissolved in dry THF (1 mL) is then added dropwise at 0 °C and the resulting mixture is stirred for 1 h at 0 °C. To the solution of the 2-iodo-4,4-dimethyloxazoline, CuI (8 mg, 0.04 mmol), Pd(dba)₂ (17 mg, 0.03 mmol), P(*o*-furyl) (14 mg, 0.06 mmol), NEt₃ (2 mL) and phenylacetylene (206 mg, 2.0 mmol) are successively added. The reaction mixture is stirred at 25 °C for 1 h and is then quenched with sat. aq. NH₄Cl solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (*i*-hexane:diethyl ether 6:1) to afford **5n** (141 mg, 0.85 mmol, 71%) as yellowish liquid.

¹H-NMR (400 MHz, CDCl₃, ppm): δ = 7.53 - 7.58 (m, 2 H), 7.33 - 7.44 (m, 3 H), 4.04 (s, 2 H), 1.35 (s, 6 H).

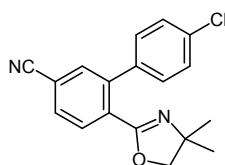
¹³C-NMR (100 MHz, CDCl₃, ppm): δ = 148.2, 132.4, 130.0, 128.4, 120.4, 89.2, 78.9, 77.7, 67.9, 28.1.

FT-IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2969, 2929, 2896, 2231, 1627, 1597, 1574, 1491, 1474, 1460, 1444, 1385, 1364, 1352, 1312, 1248, 1230, 1187, 1143, 1097, 1070, 999, 974, 928, 896, 820, 786, 755, 688.

MS (EI, 70 eV): *m/z* (%) = 200 (3), 199 (16), 185 (13), 184 (100), 170 (6), 169 (41), 157 (4), 156 (32), 129 (14), 128 (81), 127 (38), 115 (5), 101 (8), 100 (7), 84 (16), 77 (15), 75 (11), 74 (6), 63 (5), 57 (6), 54 (9), 51 (12), 50 (5), 42 (9).

HR-MS (EI, 70 eV): [C₁₃H₁₃NO], calc.: 199.0997; found: 199.0990.

Synthesis of 4'-chloro-6-(4,4-dimethyloxazoliny)-[1,1'-biphenyl]-3-carbonitrile (**7**):



4-(4,4-Dimethyloxazoliny)benzonitrile (**5c**, 200 mg, 1.0 mmol) is dissolved in THF (1.0 mL) and the solution is cooled to 0 °C. TMPMgCl·LiCl (**6**, 1.09 mL, 1.2 mmol, 1.1 M) is added and the reaction mixture is stirred for 1 h at 0 °C. Then, 1-chloro-4-iodobenzene (215 mg, 0.9 mmol), Pd(dba)₂ (17 mg, 3 mol%) and tris(*o*-furyl)phosphine (14 mg, 6 mol%) are added. The reaction mixture is stirred for 4 h at r.t. and is then quenched with sat. aq. NH₄Cl solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (*i*-hexane:diethyl ether 1:1) to afford **7** (260 mg, 0.84 mmol, 93%) as a yellowish solid.

m.p.: 92 – 94 °C

¹H-NMR (400 MHz, CDCl₃, ppm): δ = 7.87 (d, *J* = 8.1 Hz, 1 H), 7.68 (dd, *J* = 7.9, 1.3 Hz, 1 H), 7.64 (s, 1 H), 7.40 (d, *J* = 8.3 Hz, 2 H), 7.29 (d, *J* = 8.3 Hz, 2 H), 3.86 (s, 2 H), 1.30 (s, 6 H).

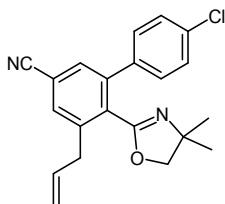
¹³C-NMR (100 MHz, CDCl₃, ppm): δ = 161.7, 141.6, 137.3, 134.4, 133.5, 132.2, 131.1, 130.7, 129.5, 128.5, 117.9, 114.3, 79.7, 68.0, 27.9.

FT-IR (ATR, cm⁻¹): $\tilde{\nu}$ = 2967, 2928, 2231, 1653, 1484, 1462, 1410, 1392, 1365, 1350, 1308, 1213, 1179, 1091, 1065, 1034, 1013, 986, 959, 920, 901, 828, 814, 763, 734, 724, 698, 668.

MS (EI, 70 eV): *m/z* (%) = 312 (6), 311 (38), 310 (23), 309 (100), 295 (6), 255 (8), 245 (12), 240 (6), 239 (11), 238 (9), 226 (8), 226 (8), 224 (23), 203 (13), 202 (8), 177 (11), 176 (12).

HR-MS (EI, 70 eV): [C₁₈H₁₅ClN₂O], calc.: 309.0795; found: 309.0797 [M-H⁺].

Synthesis of 5-allyl-4'-chloro-6-(4,4-dimethyloxazoliny)-[1,1'-biphenyl]-3-carbonitrile (**9**):



4'-Chloro-6-(4,4-dimethyloxazoliny)-[1,1'-biphenyl]-3-carbonitrile (**7**, 131 mg, 0.5 mmol) is dissolved in THF (1.0 mL) and the solution is cooled to -20 °C. TMP₂Mg·2LiCl (**8**, 1.11 mL, 0.6 mmol, 0.54 M) is added and the reaction mixture is stirred for 1.5 h at -20 °C. Then, CuCN·2LiCl (0.6 mL, 0.6 mmol) is added, the reaction is stirred for 0.5 h and allyl bromide (49 mg, 0.45 mmol) is added. The reaction is allowed to warm to r.t. over 4 h and is then quenched with sat. aq. NH₄Cl/NH₃ solution, extracted with CH₂Cl₂ and dried over Na₂SO₄. The crude product is purified by column chromatography on silica (CH₂Cl₂ 100%) to afford **9** (123 mg, 0.35 mmol, 78%) as a yellowish solid.

m.p.: 170 – 173 °C

¹H-NMR (400 MHz, CDCl₃, ppm): δ = 7.56 (d, *J* = 1.5 Hz, 1 H), 7.49 (d, *J* = 1.7 Hz, 1 H), 7.40 - 7.45 (m, 2 H), 7.35 - 7.40 (m, 2 H), 6.00 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 1 H), 5.18 - 5.23 (m, 1 H), 5.11 - 5.18 (m, 1 H), 3.68 (s, 2 H), 3.57 (d, *J* = 6.6 Hz, 2 H), 1.19 (s, 6 H).

¹³C-NMR (100 MHz, CDCl₃, ppm): δ = 166.9, 140.3, 139.5, 139.4, 136.6, 135.6, 134.8, 132.2, 131.0, 130.1, 128.8, 118.0, 117.7, 113.1, 54.9, 51.1, 36.9, 24.5.

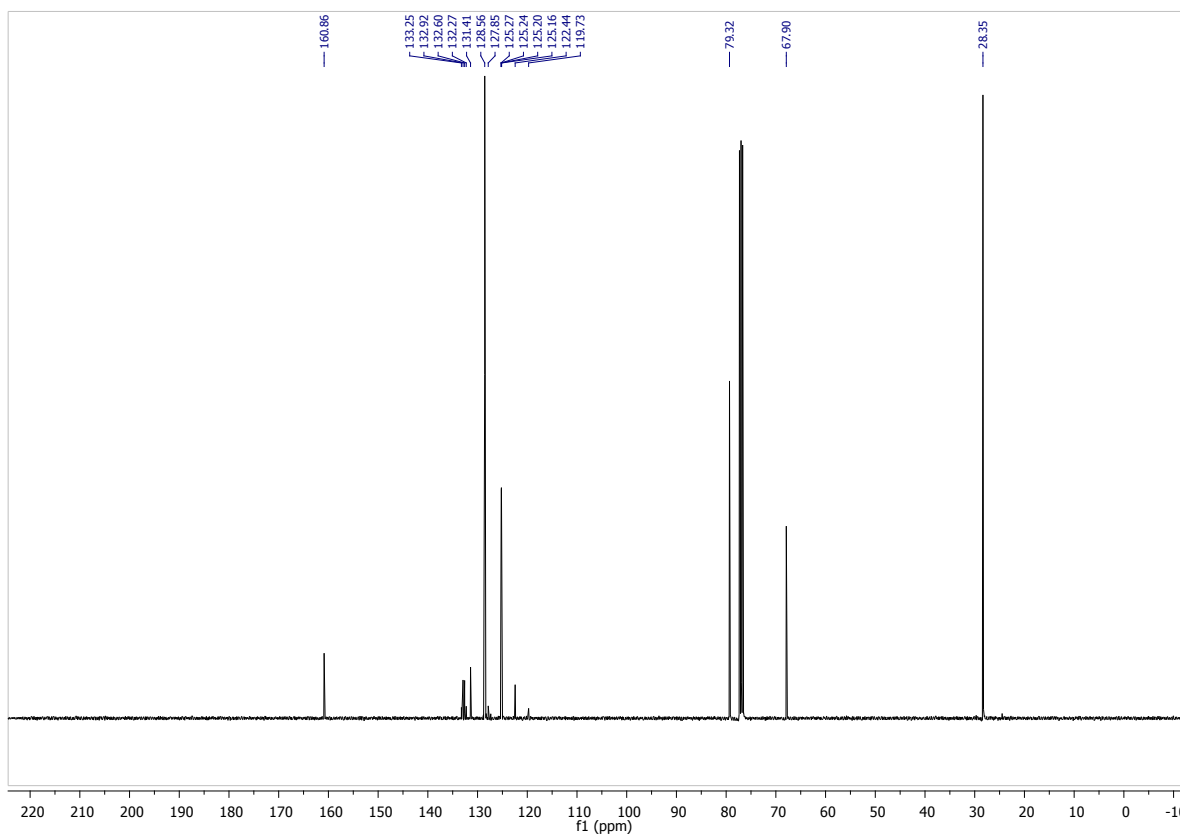
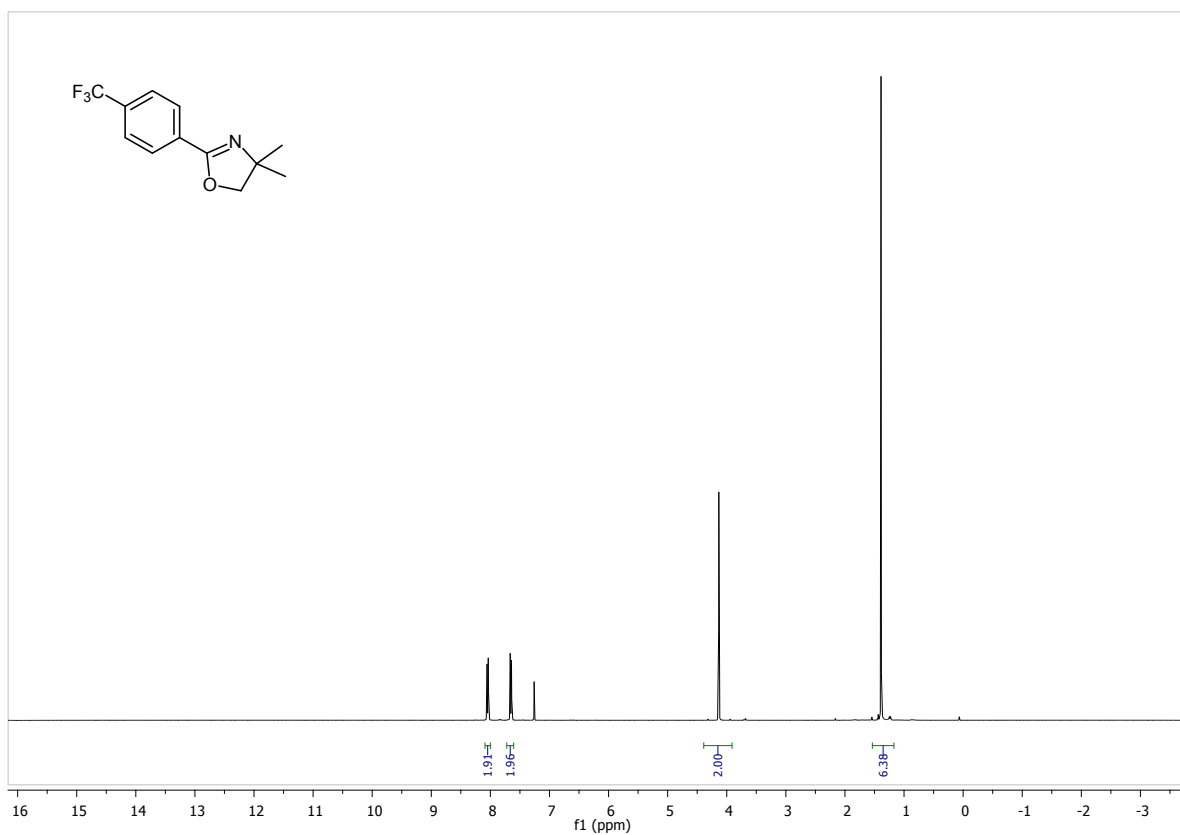
FT-IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3264, 2924, 2237, 1630, 1603, 1555, 1494, 1470, 1455, 1445, 1432, 1416, 1387, 1364, 1327, 1300, 1262, 1238, 1092, 1016, 994, 927, 913, 891, 872, 844, 837, 831, 801, 758, 733, 714, 700, 677.

MS (EI, 70 eV): m/z (%) = 352 (20), 351 (42), 350 (53), 349 (100), 346 (39), 337 (21), 335 (62), 278 (20), 220 (32), 219 (77), 216 (20), 214 (22), 191 (48), 190 (59), 105 (20), 85 (19), 77 (79), 71 (23), 69 (22), 57 (40), 55 (50), 51 (26), 43 (27), 43 (20), 41 (37).

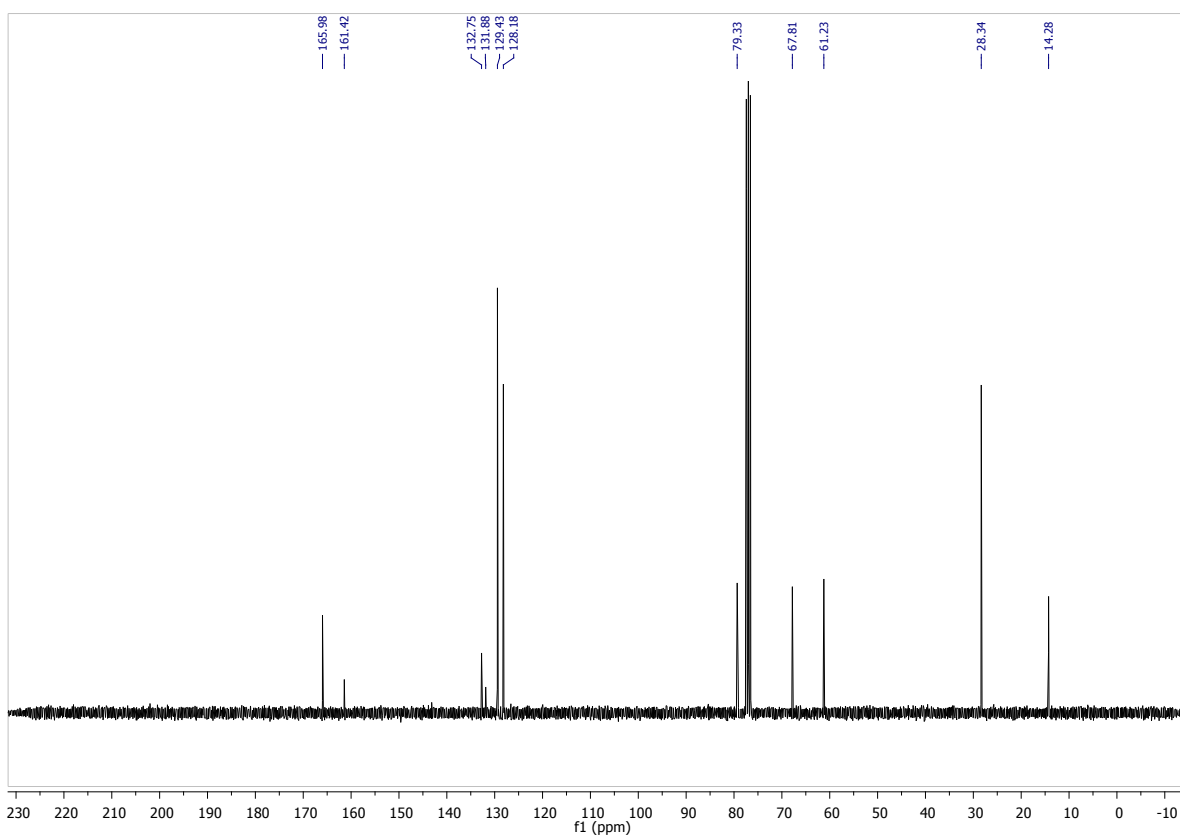
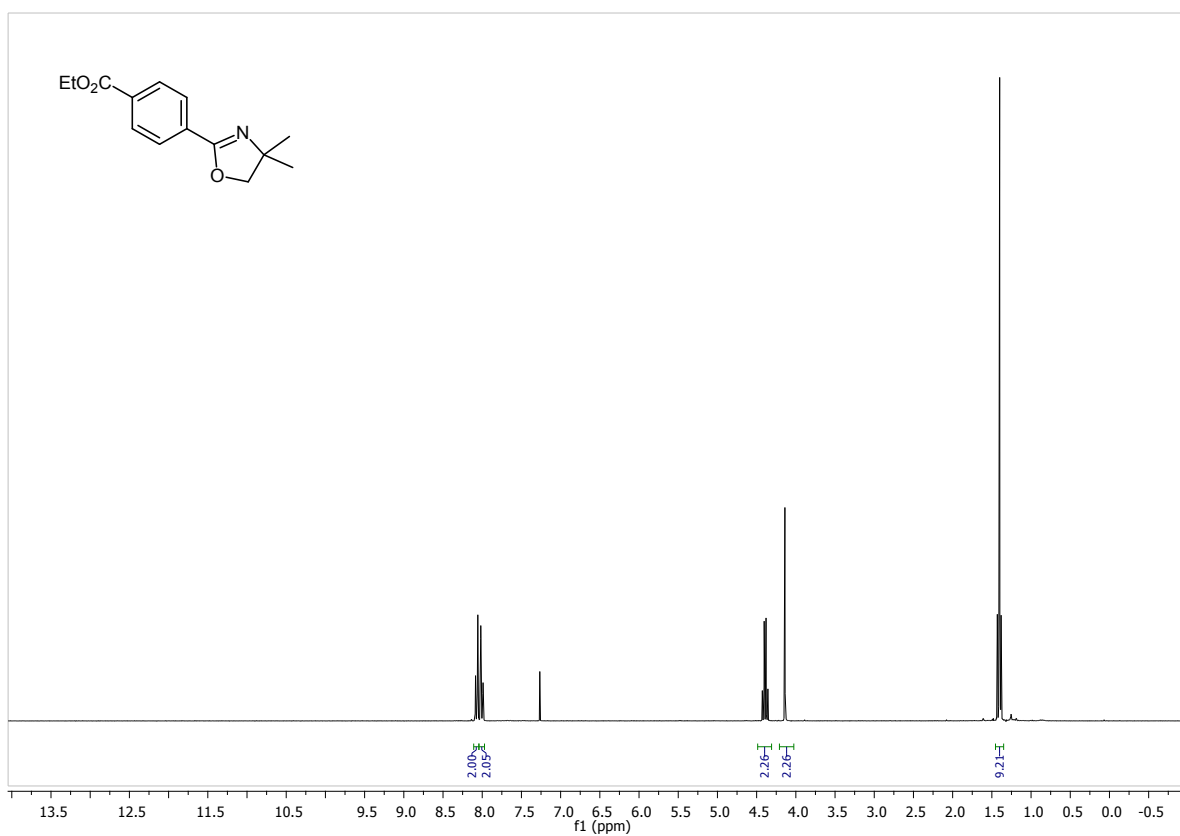
HR-MS (EI, 70 eV): $[\text{C}_{21}\text{H}_{18}\text{ClN}_2\text{O}]$, calc.: 349.1108; found: 349.1098 $[\text{M}-\text{H}^+]$.

3) NMR Spectra

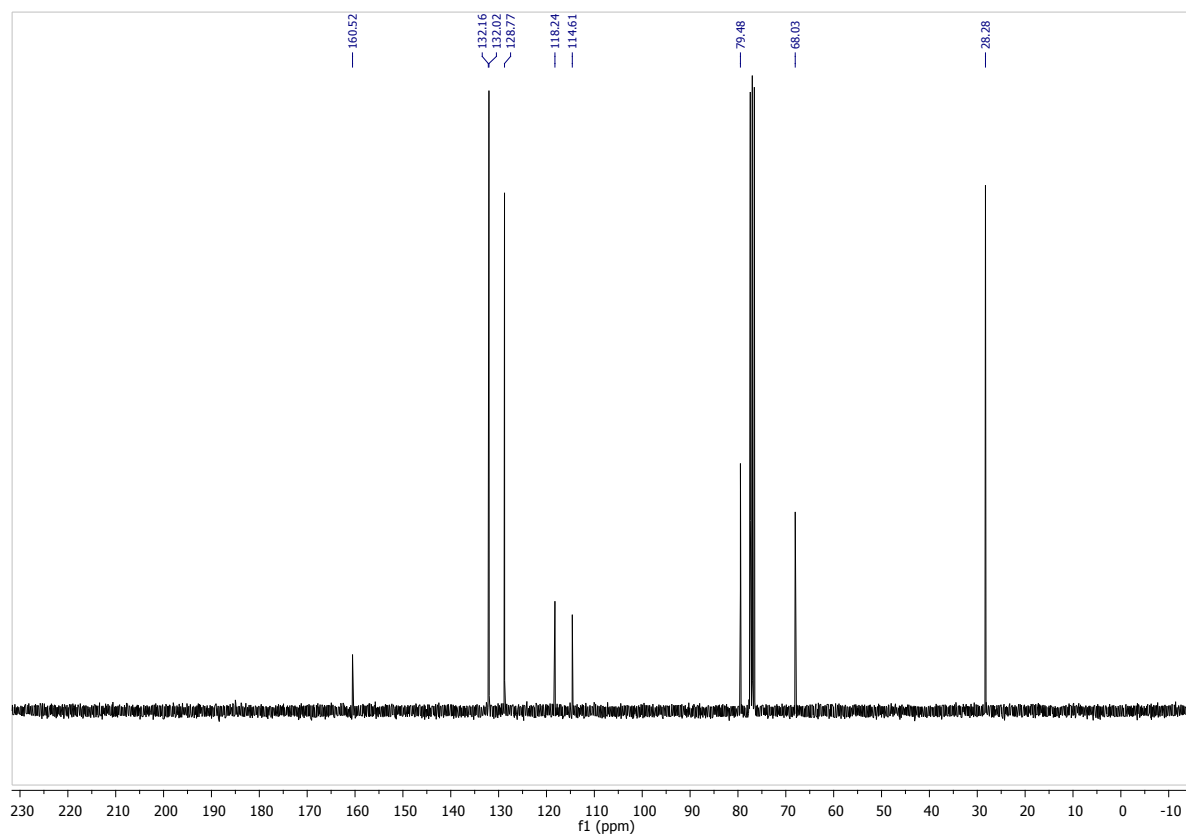
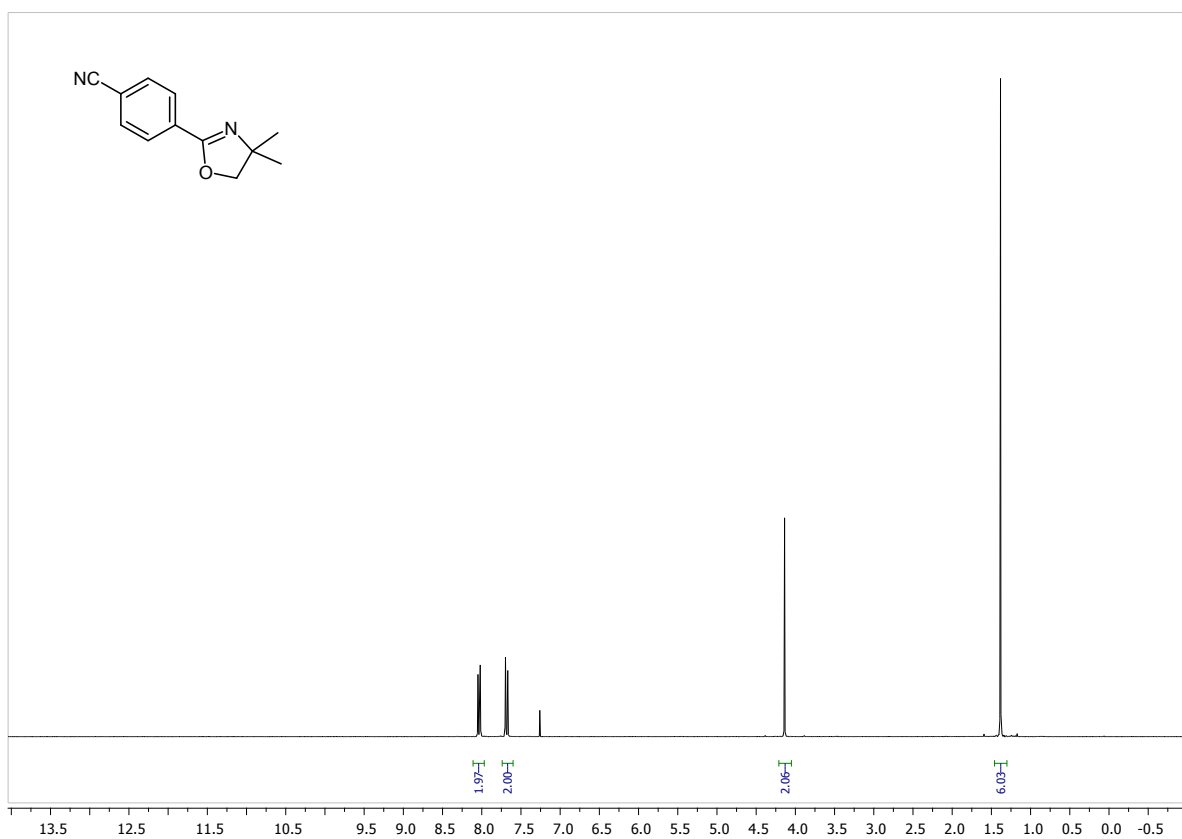
4,4-dimethyl-2-(4-(trifluoromethyl)phenyl)oxazoline (5a):



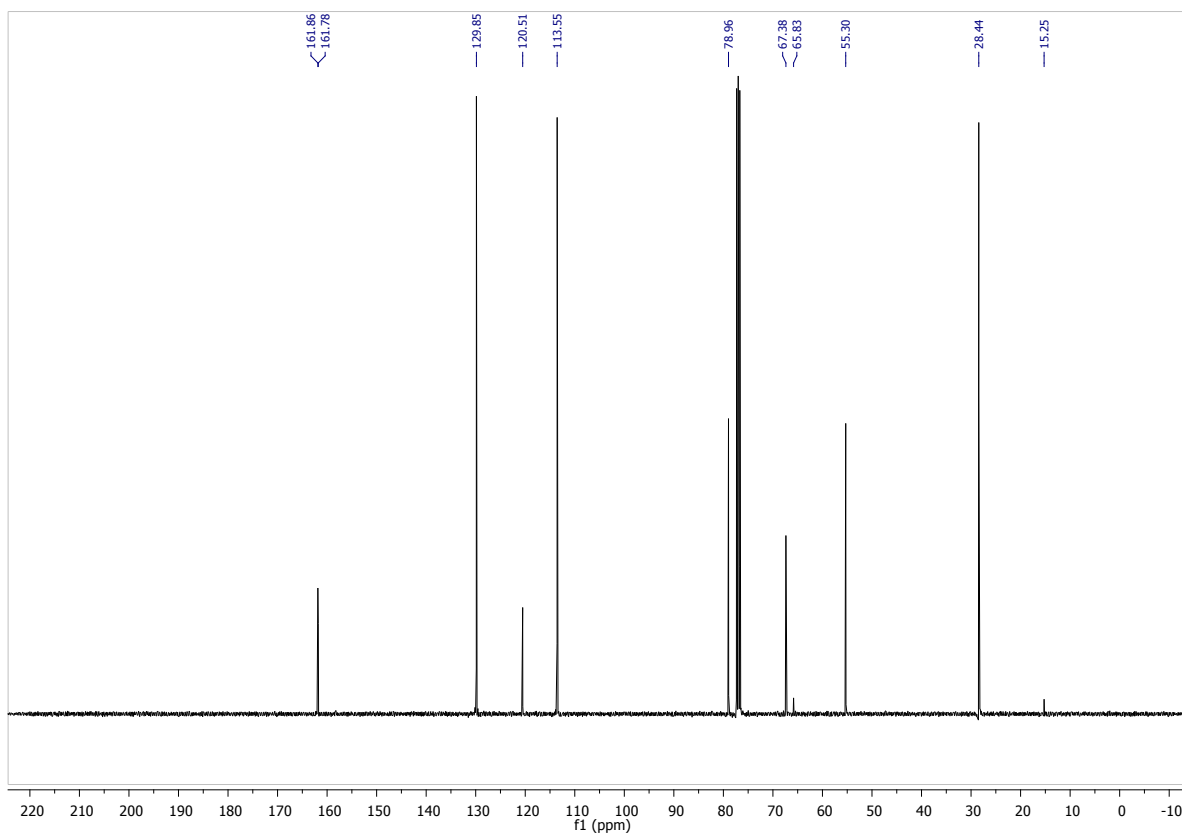
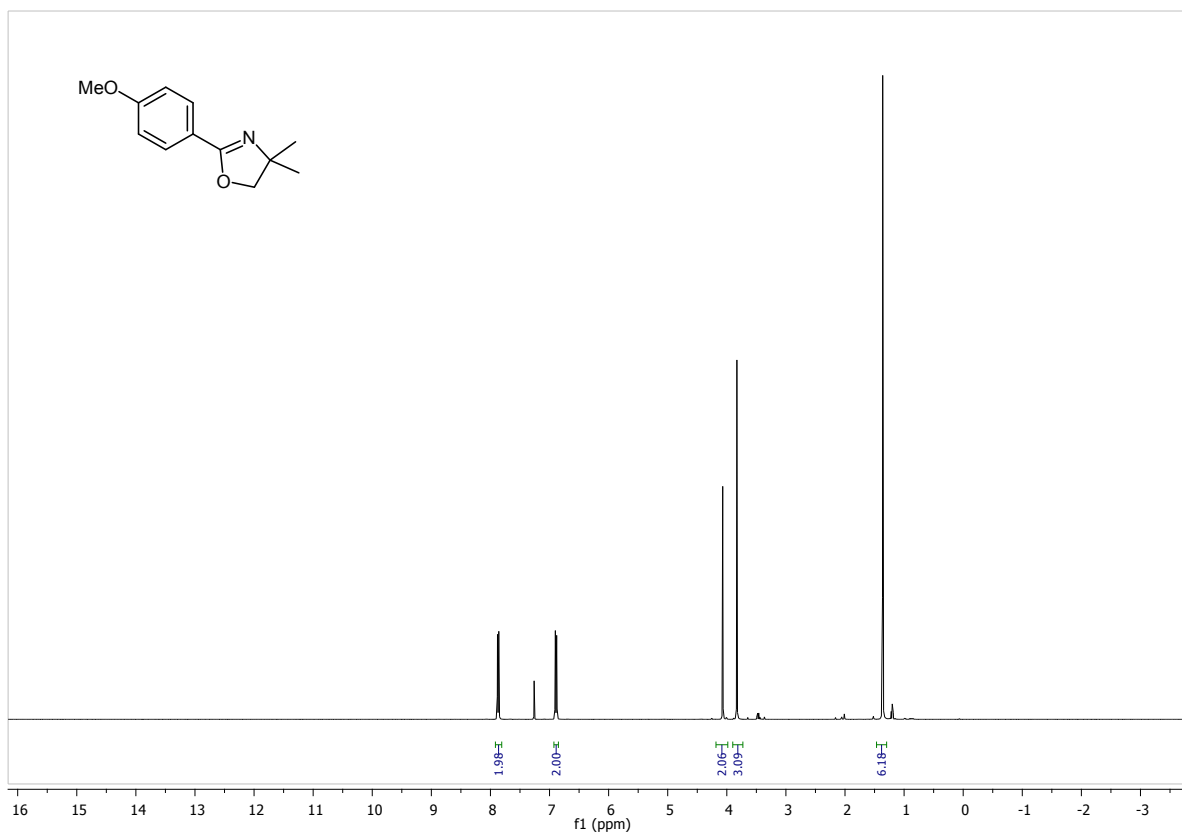
ethyl 4-(4,4-dimethyloxazoliny)benzoate (5b):



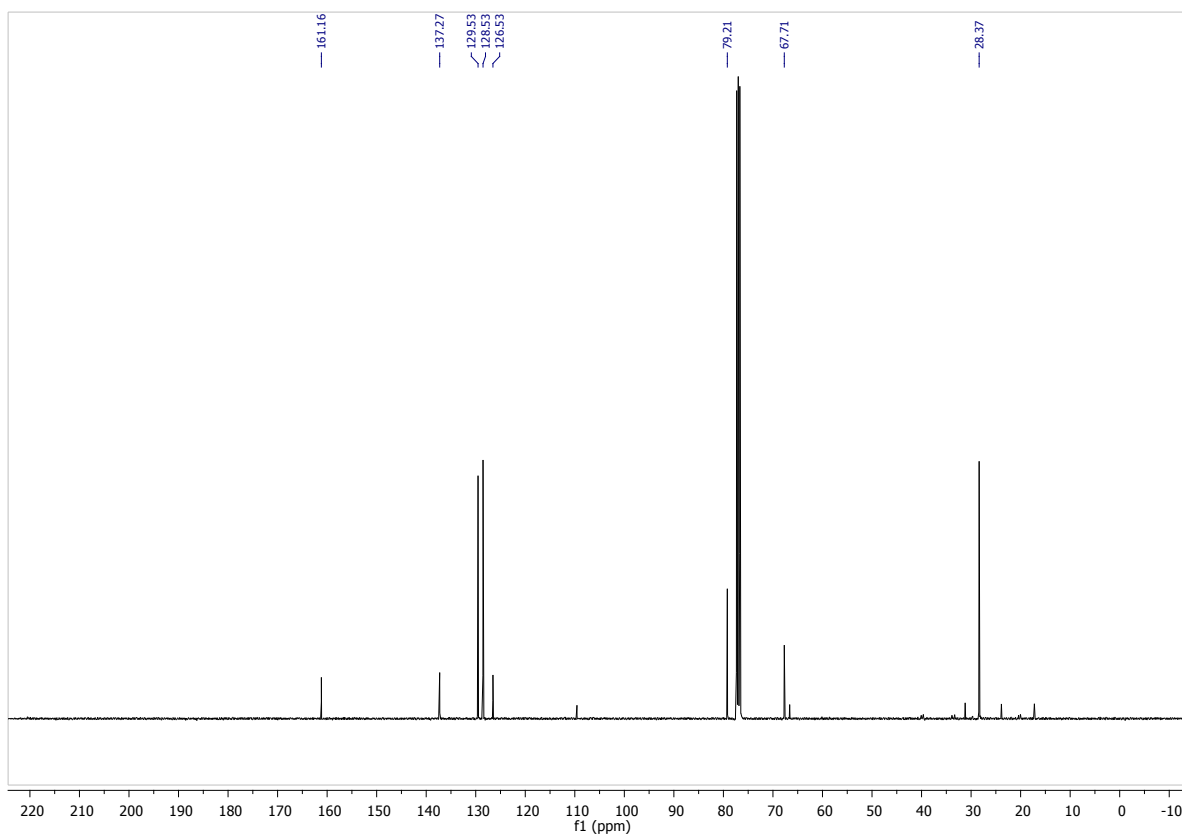
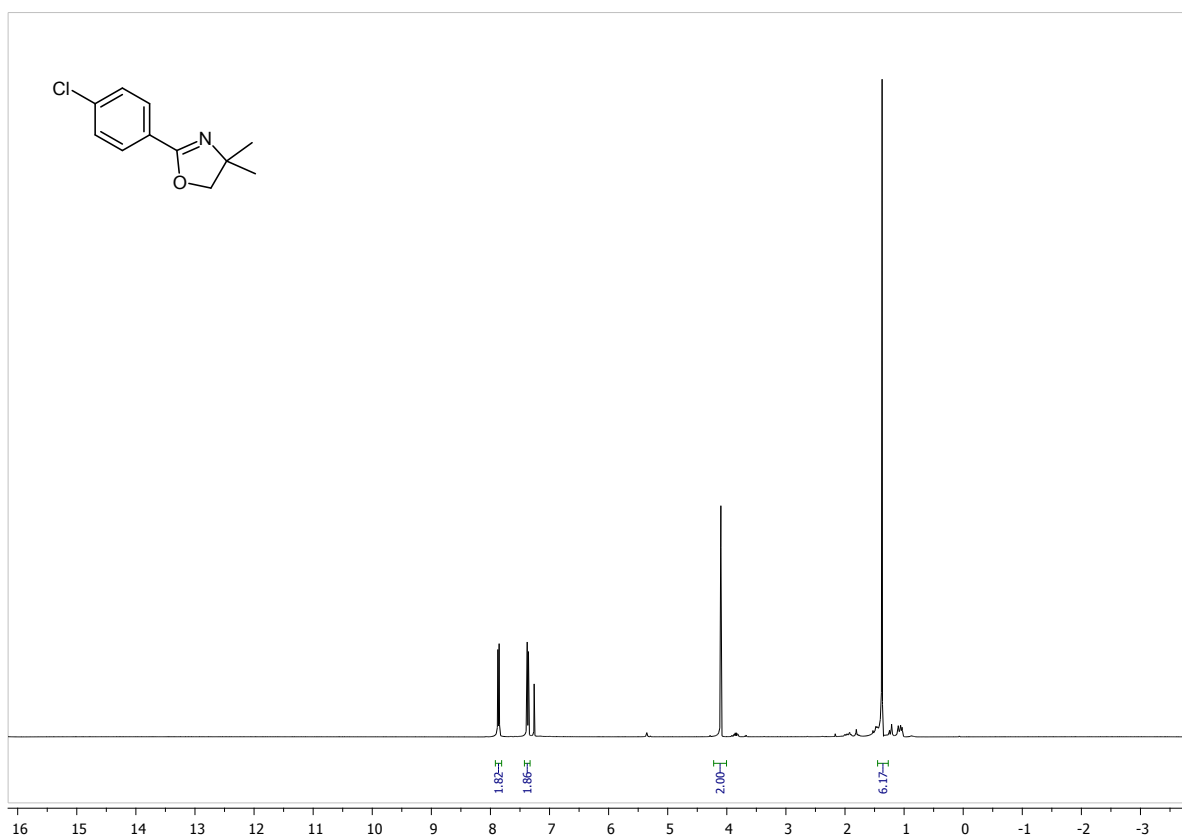
4-(4,4-dimethyloxazoliny)benzonitrile (5c):



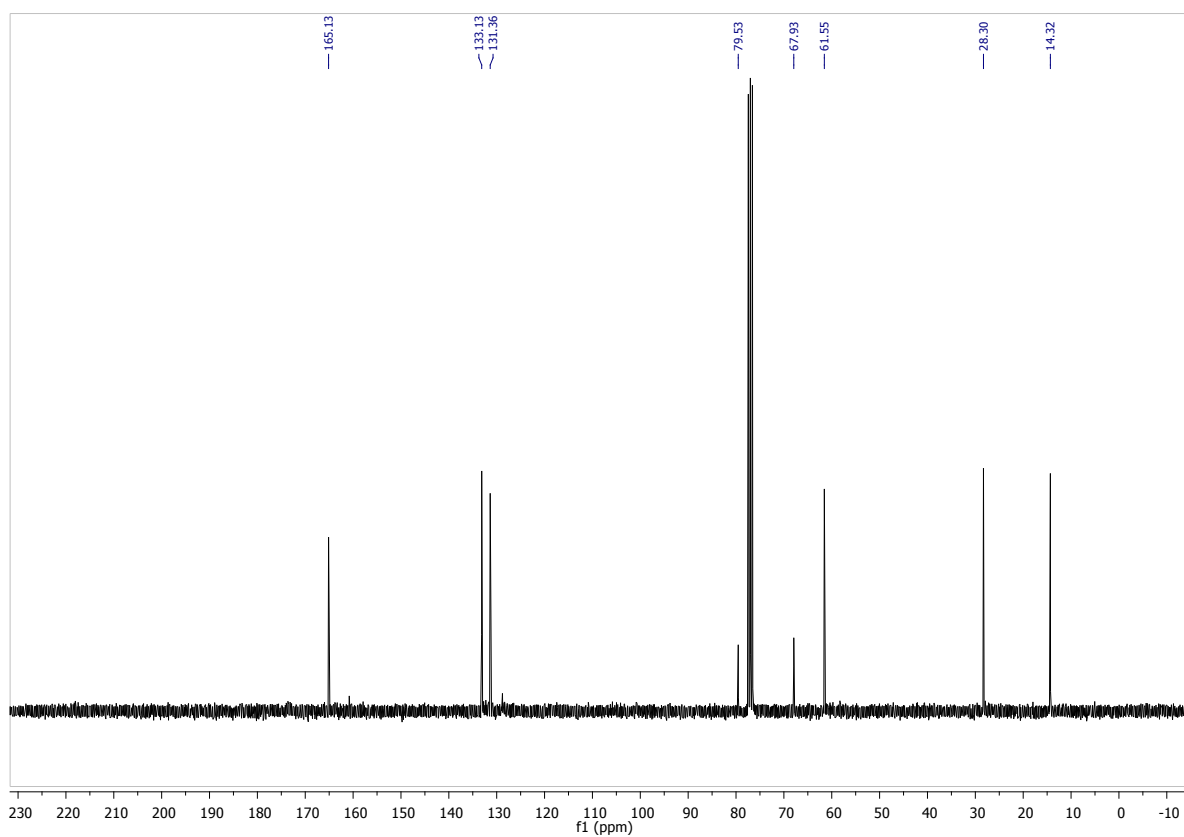
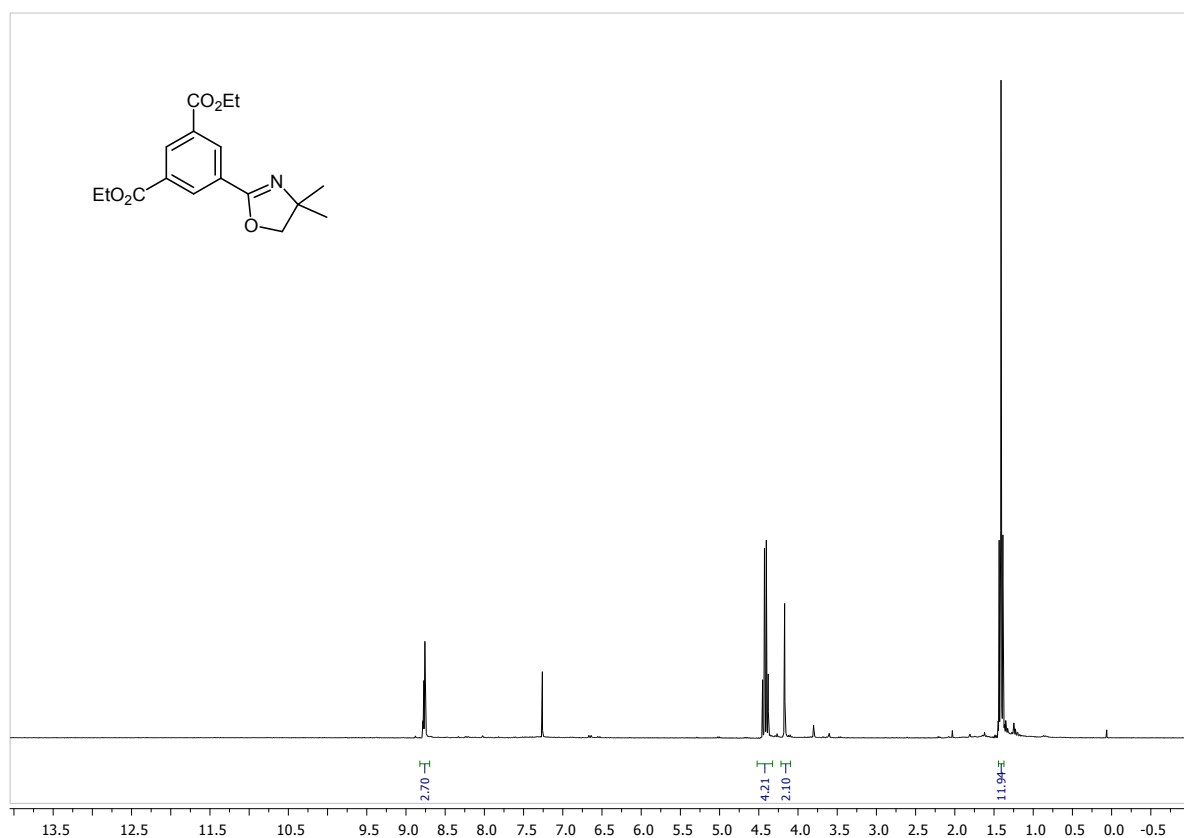
2-(4-methoxyphenyl)-4,4-dimethyloxazoline (5d):



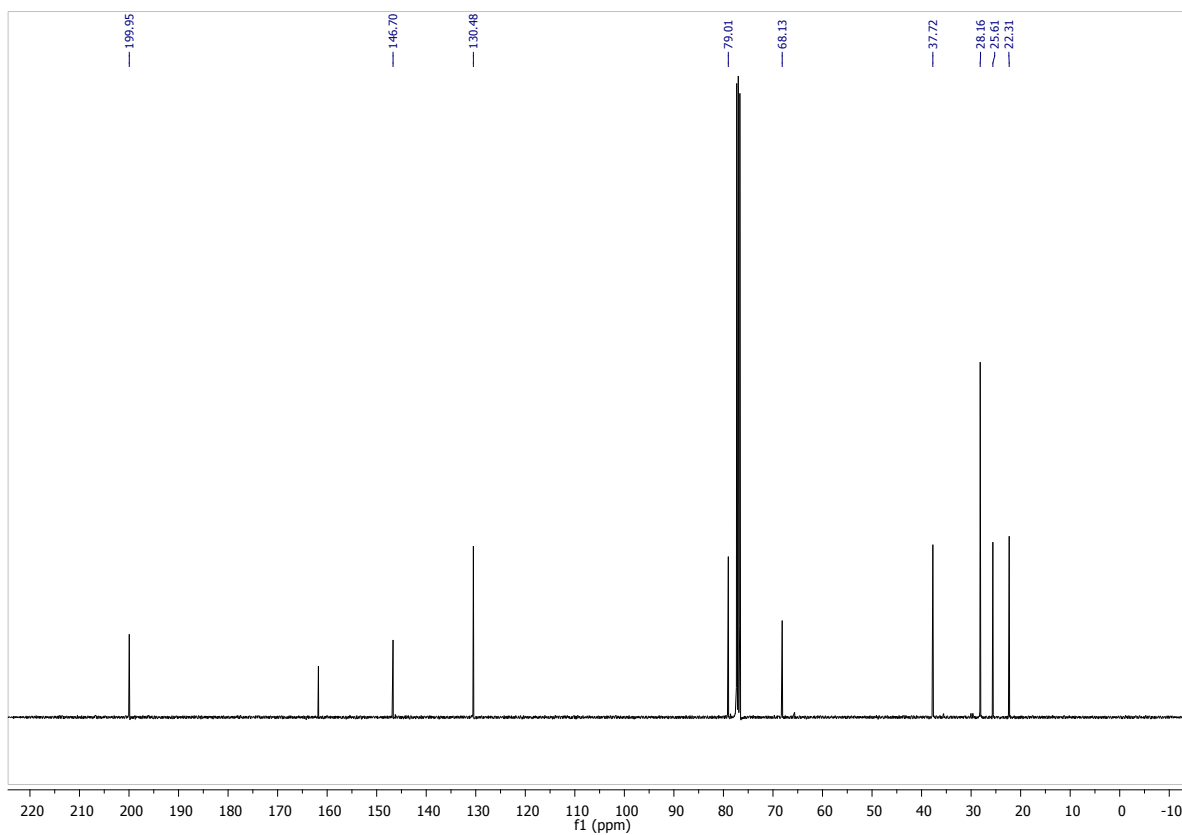
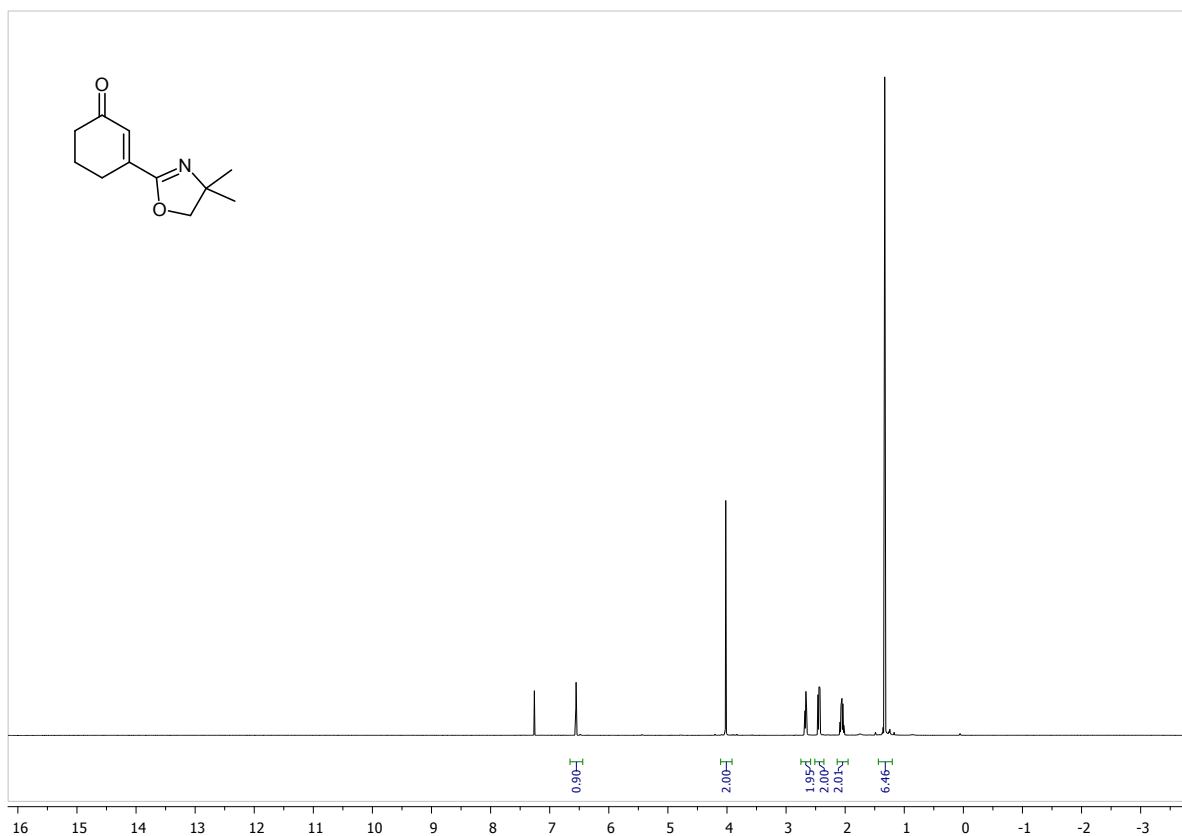
2-(4-chlorophenyl)-4,4-dimethyloxazoline (5e):



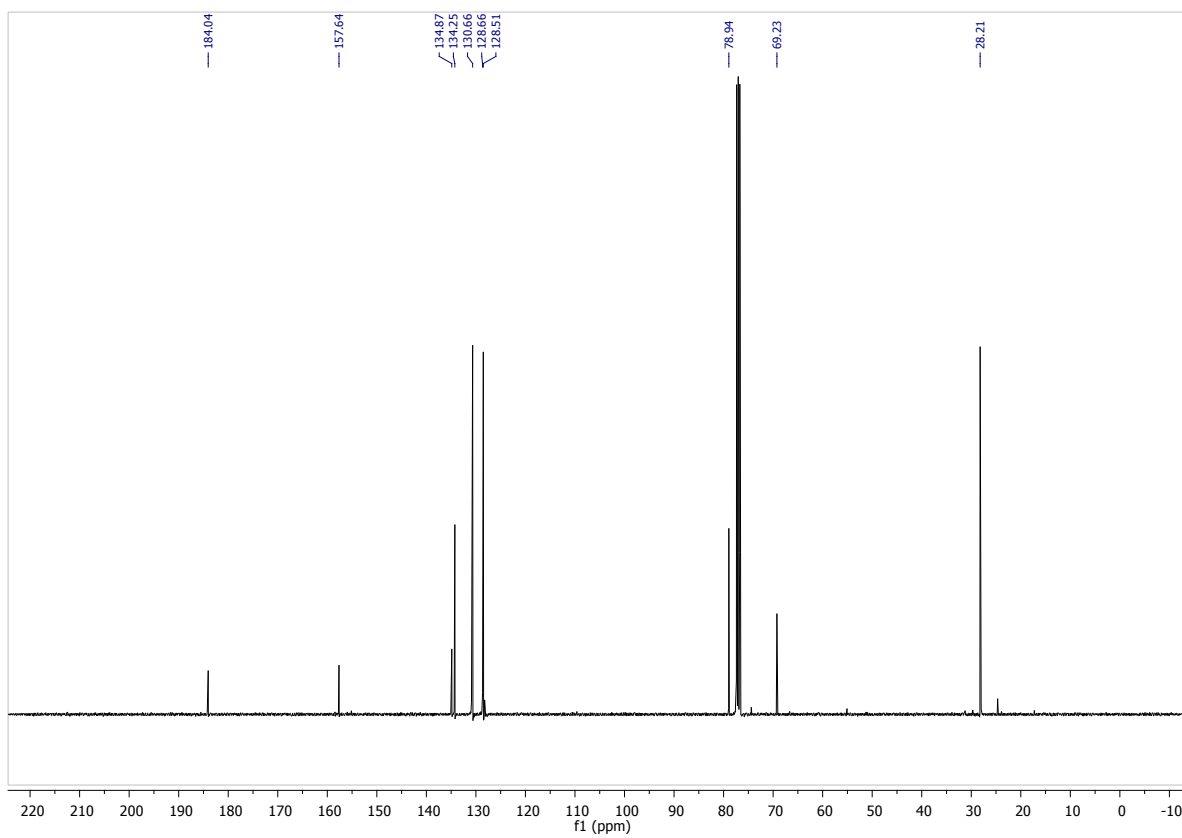
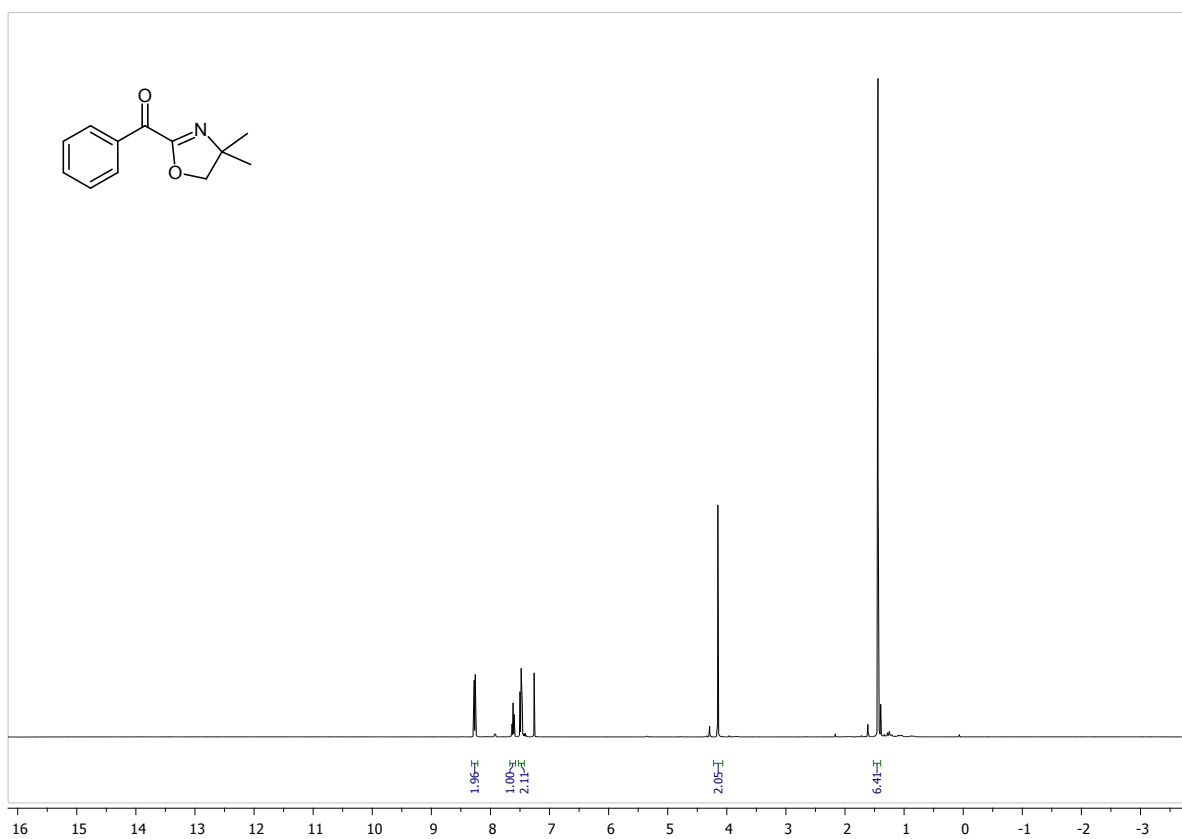
diethyl 5-(4,4-dimethyloxazoliny)isophthalate (5f):



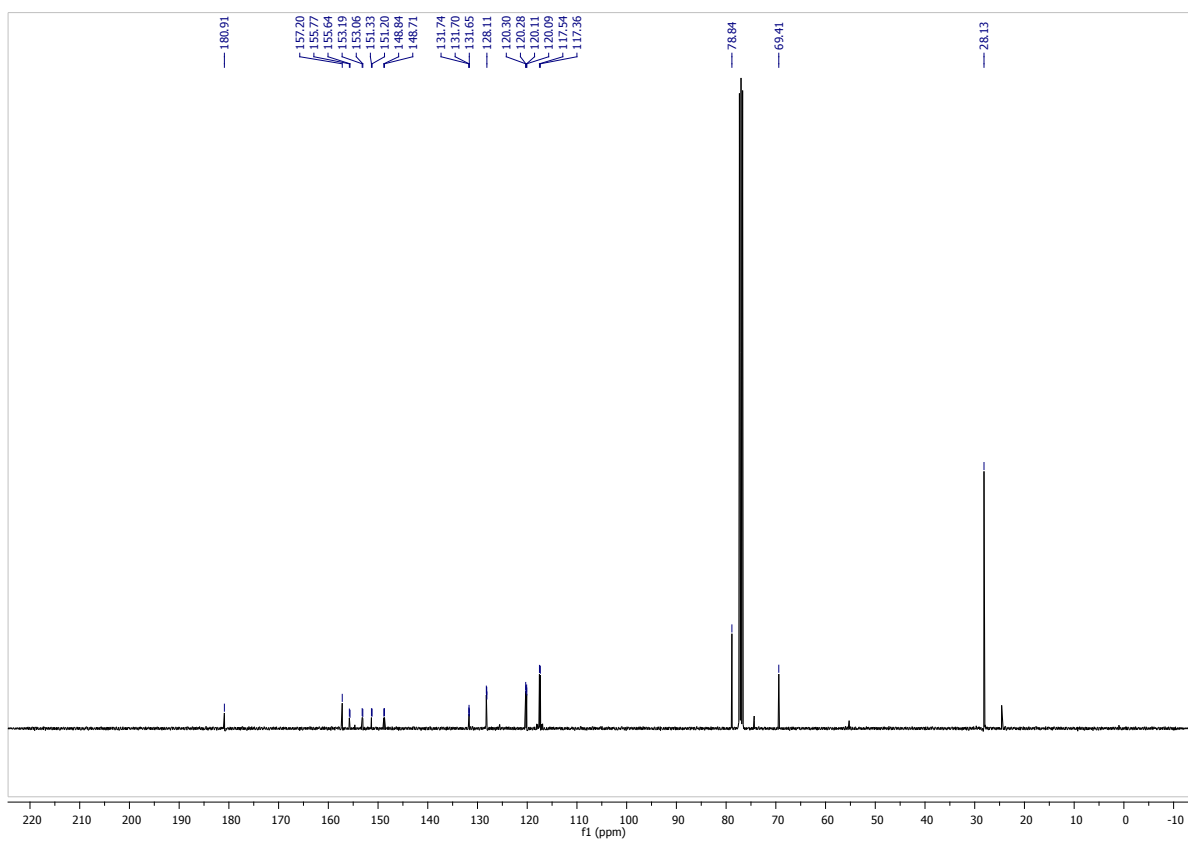
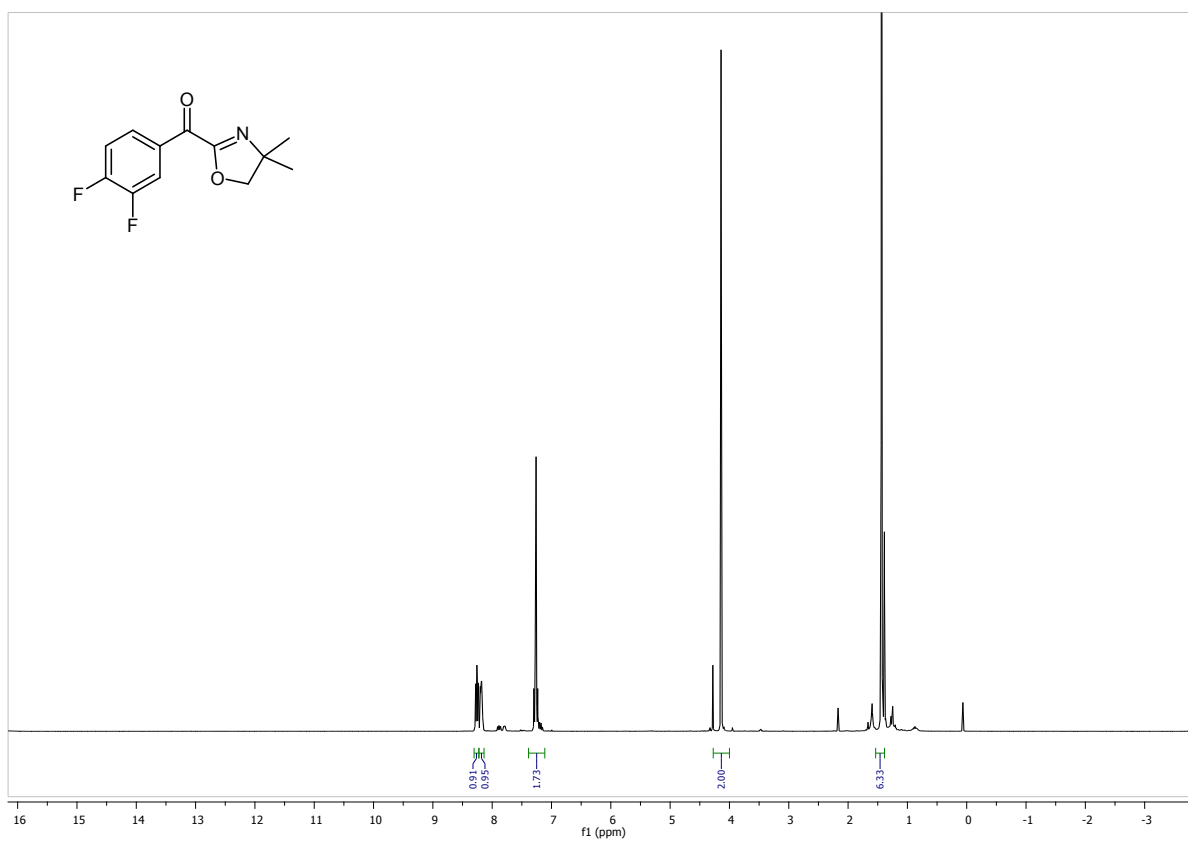
3-(4,4-dimethyloxazoliny)cyclohex-2-en-1-one (5g):



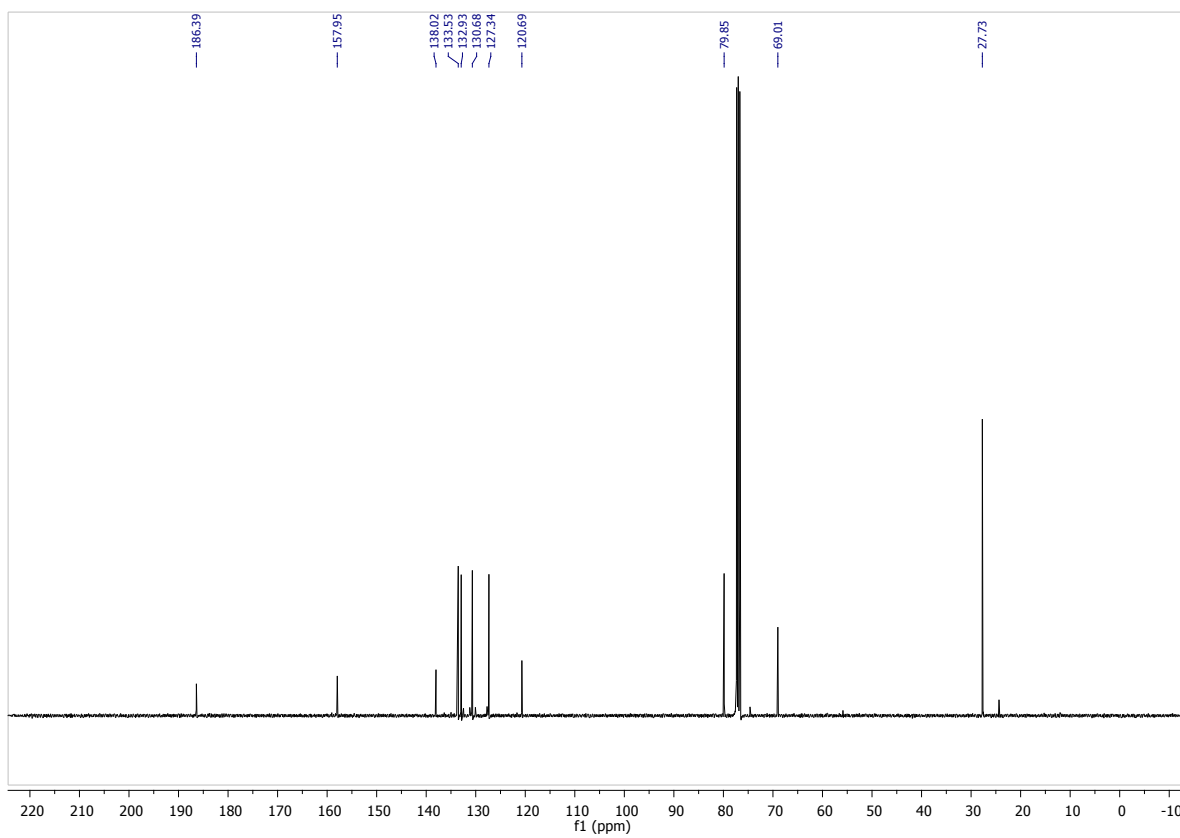
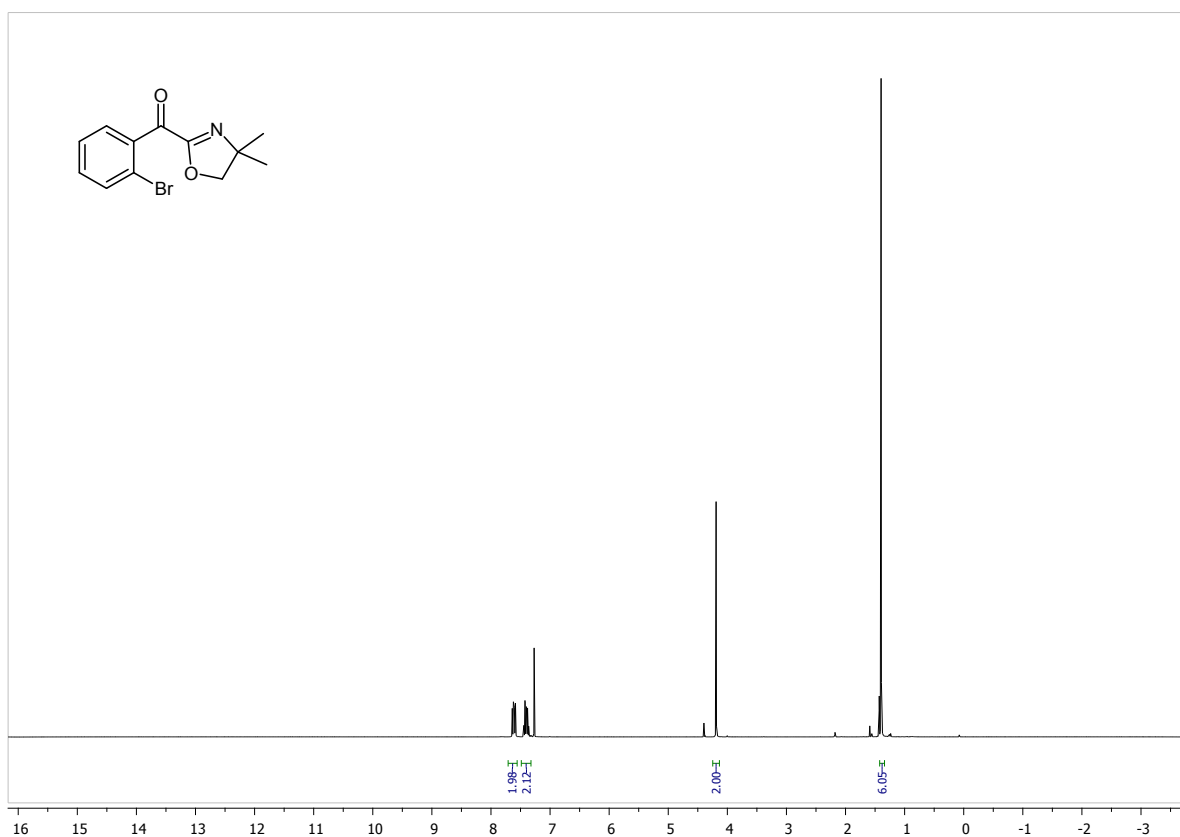
(4,4-dimethyloxazolinyl)(phenyl)methanone (5h):



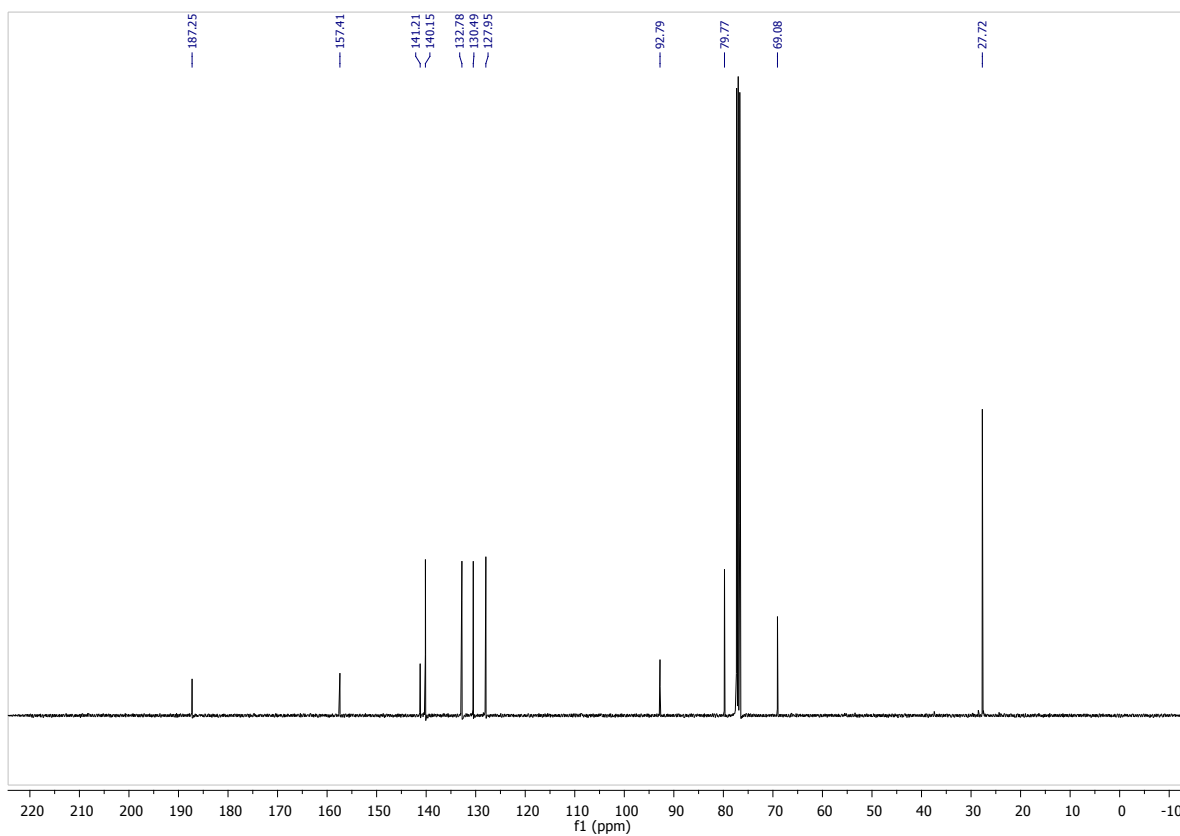
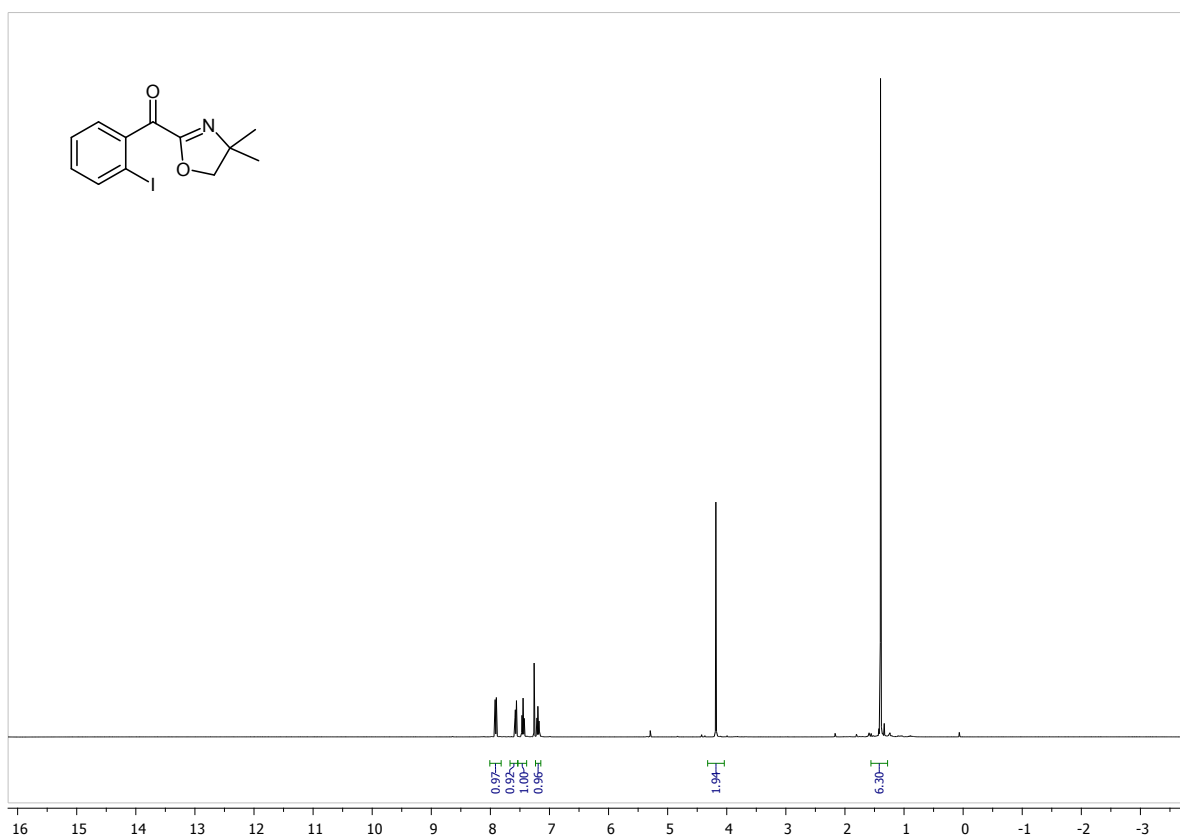
(3,4-difluorophenyl)(4,4-dimethyloxazoliny)methanone (5i):



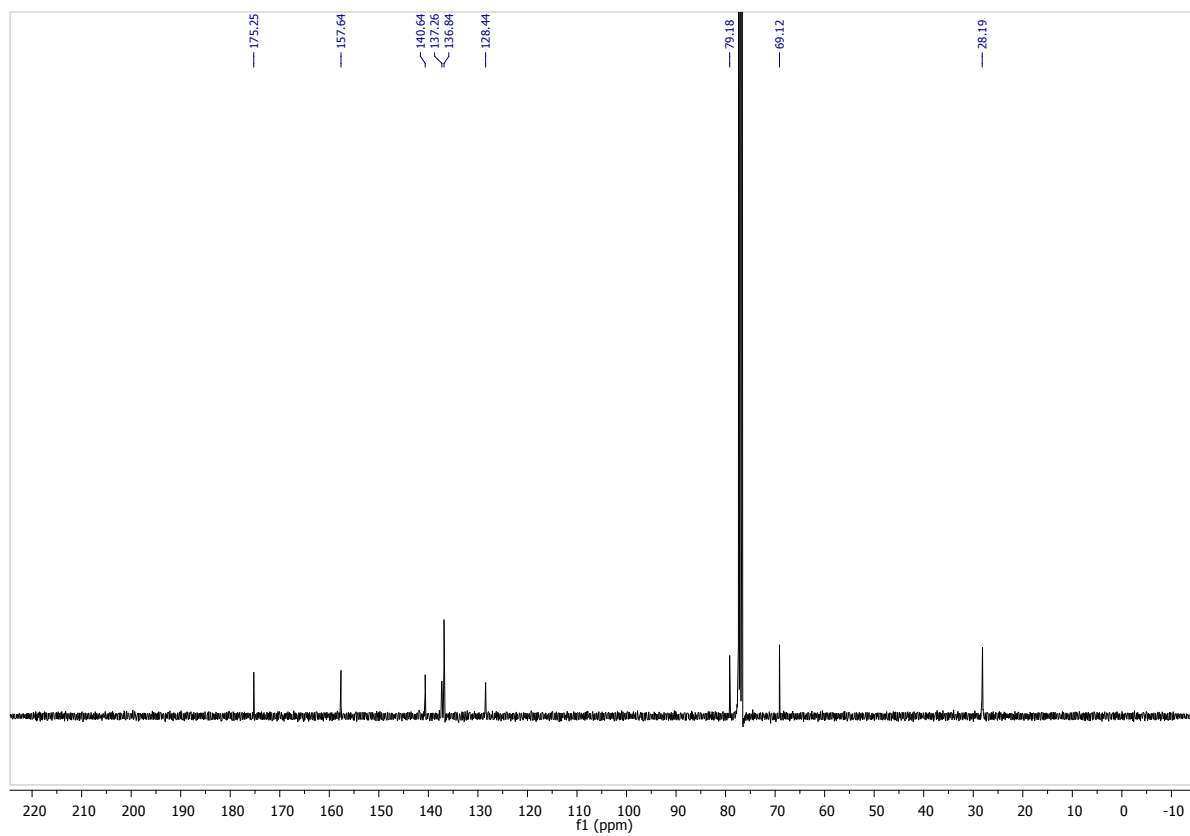
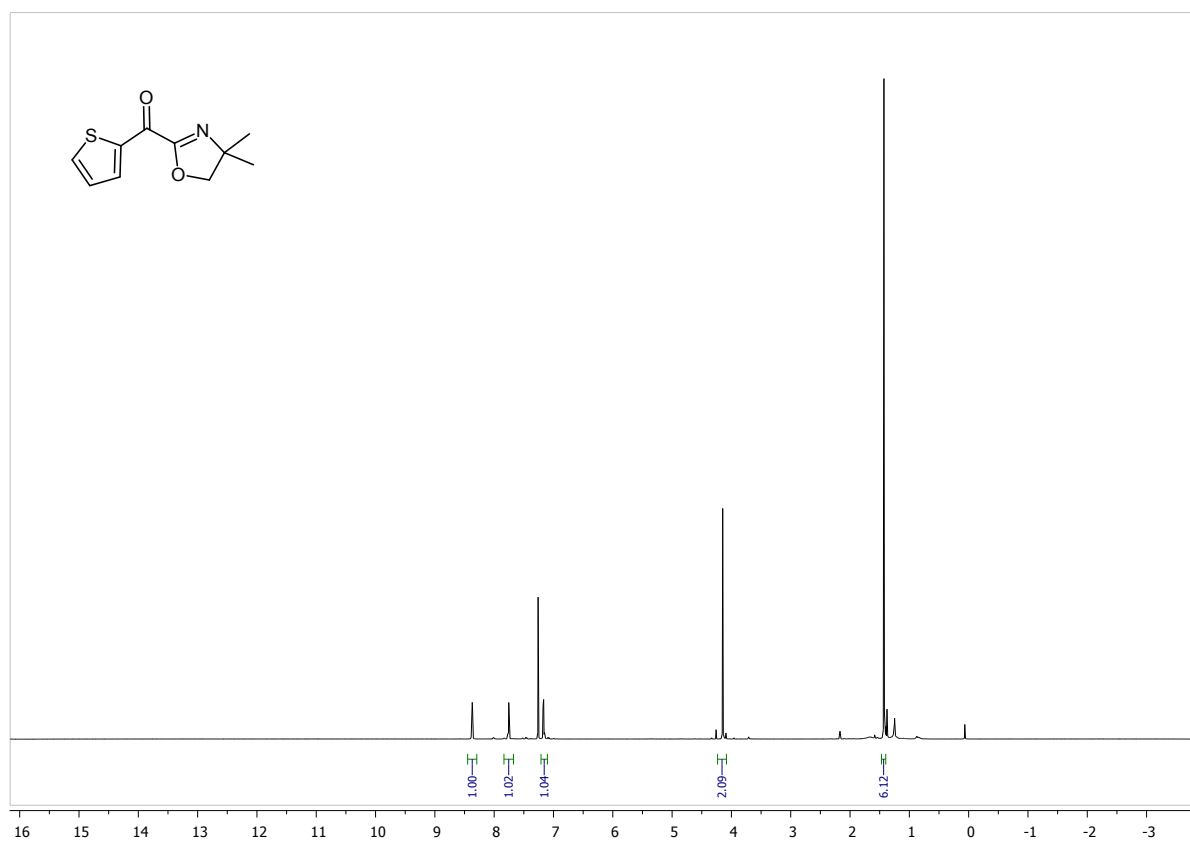
(2-bromophenyl)(4,4-dimethyloxazoliny)methanone (5j):



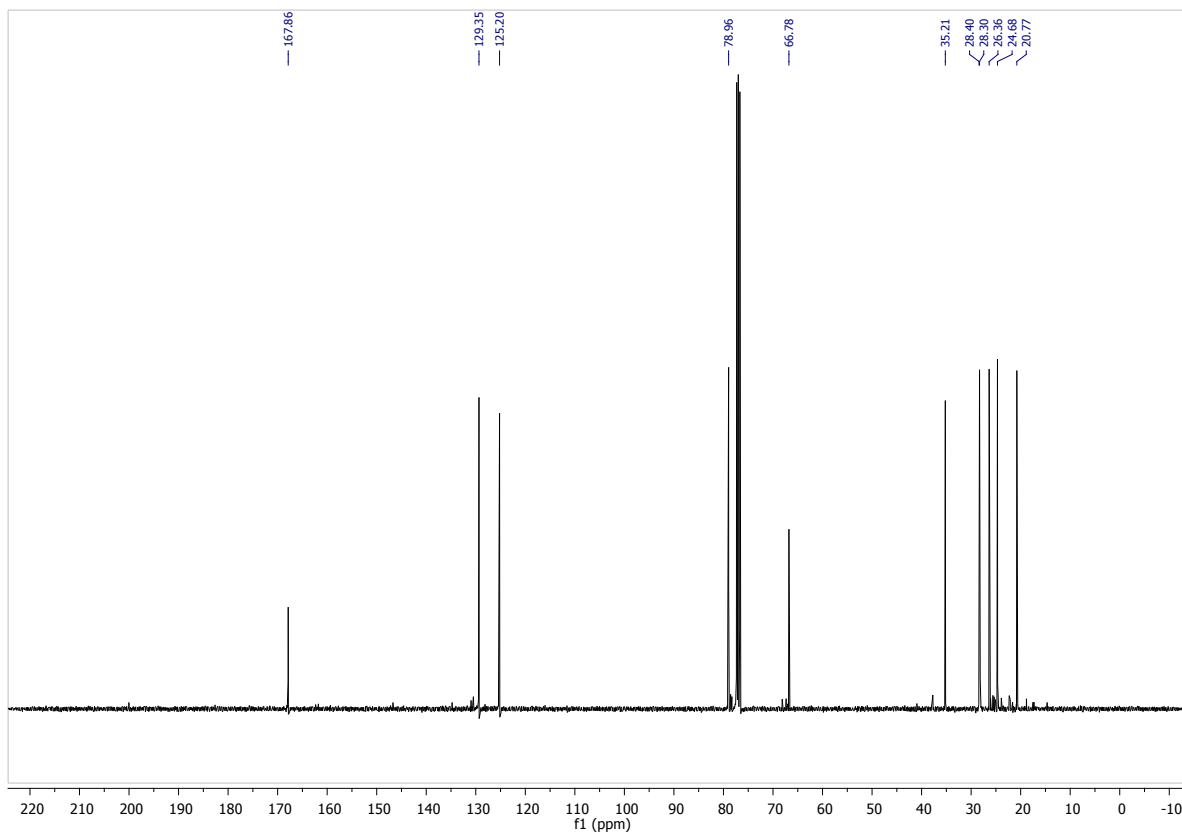
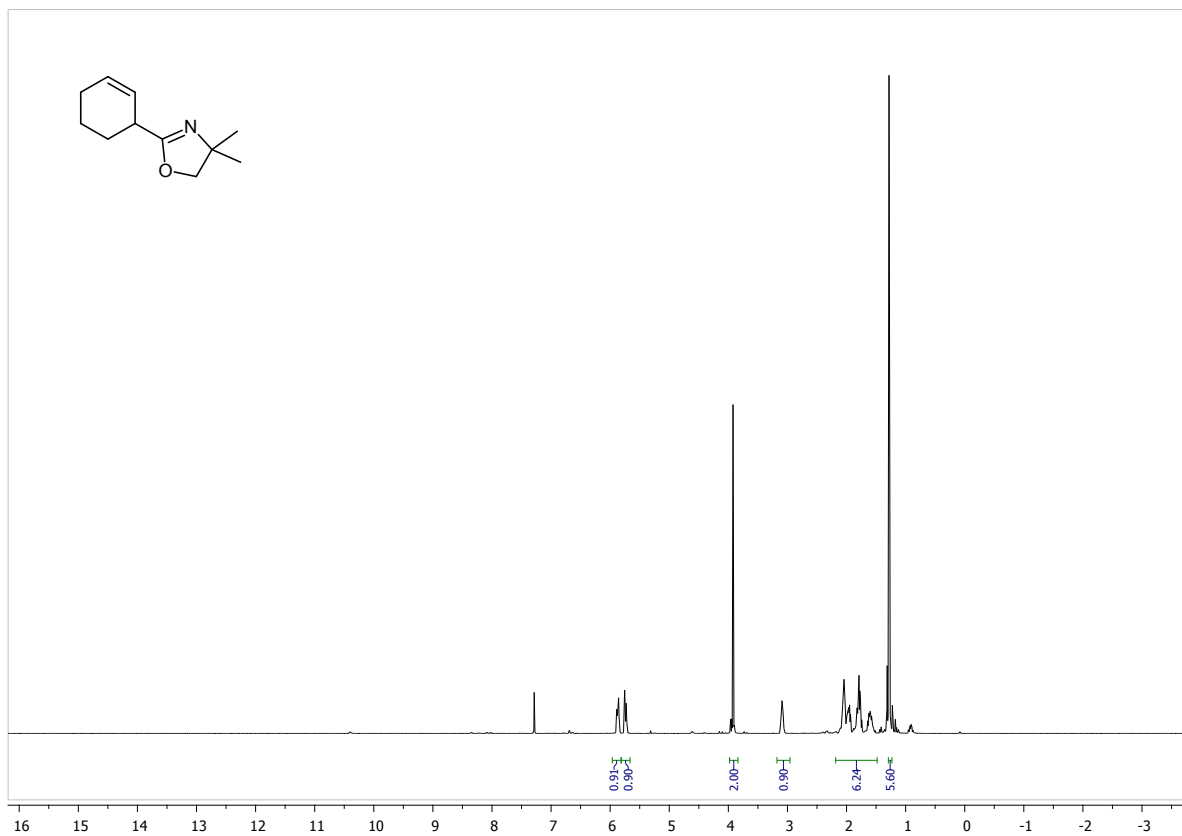
(2-iodophenyl)(4,4-dimethyloxazoliny)methanone (5k):



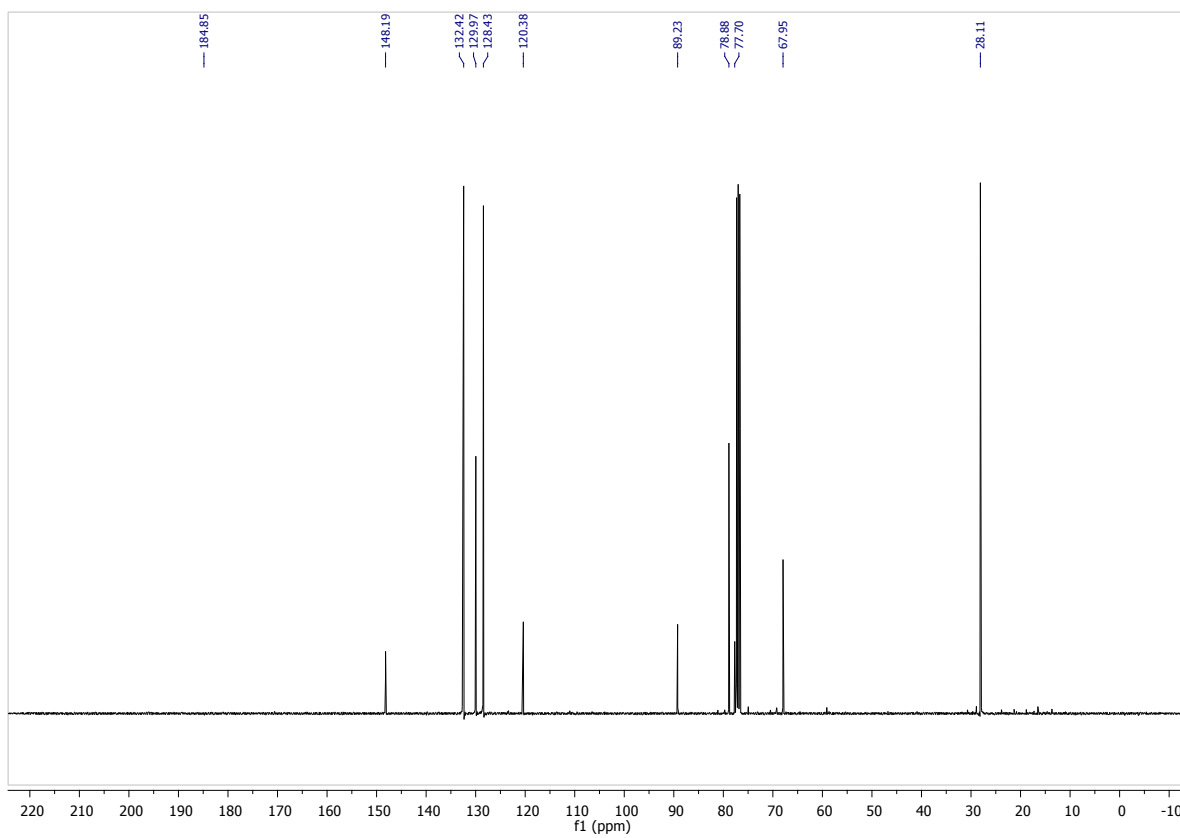
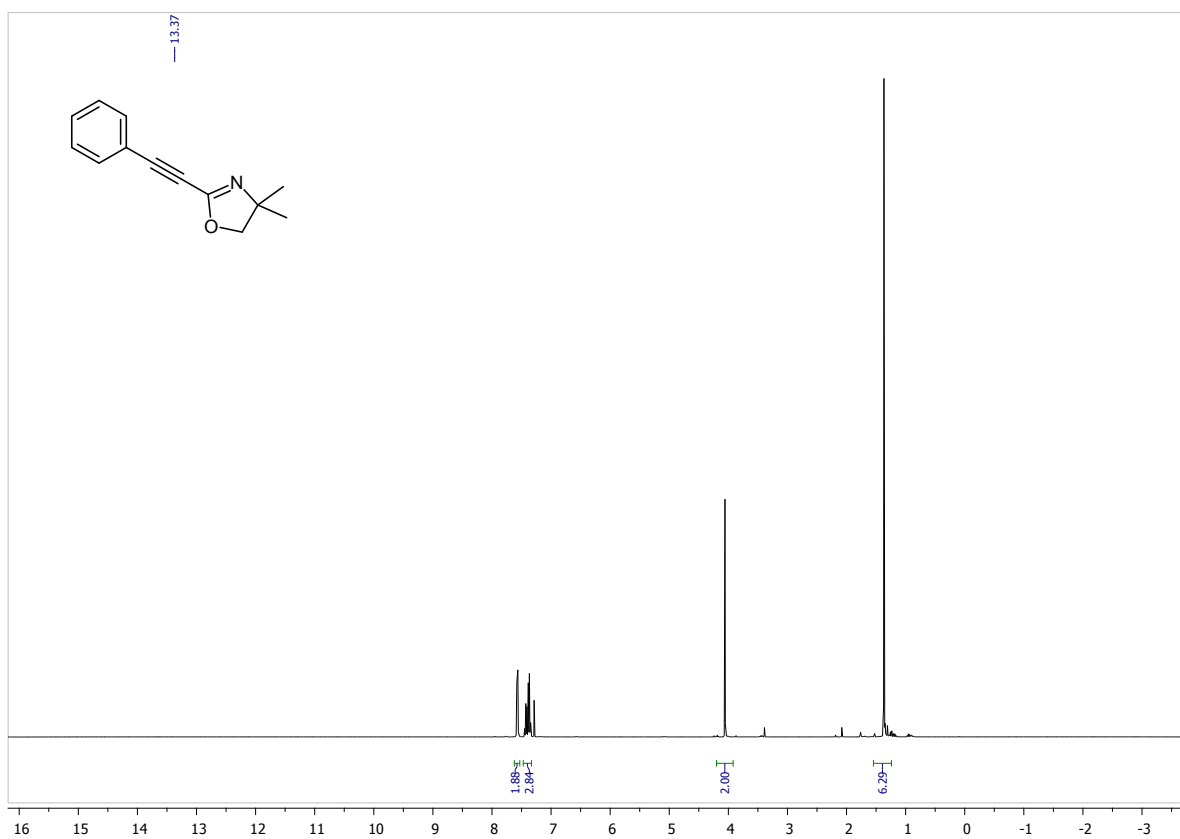
(4,4-dimethyloxazoliny)(thiophen-2-yl)methanone (5I):



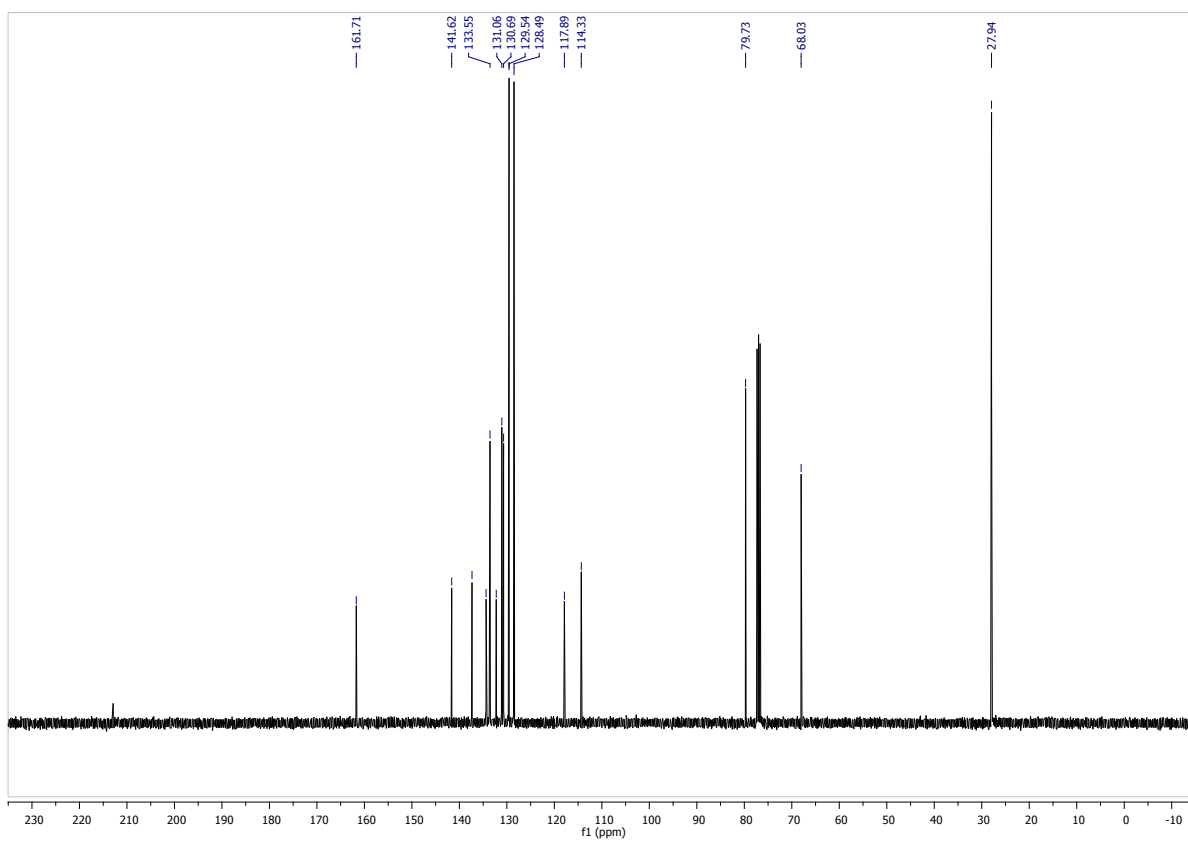
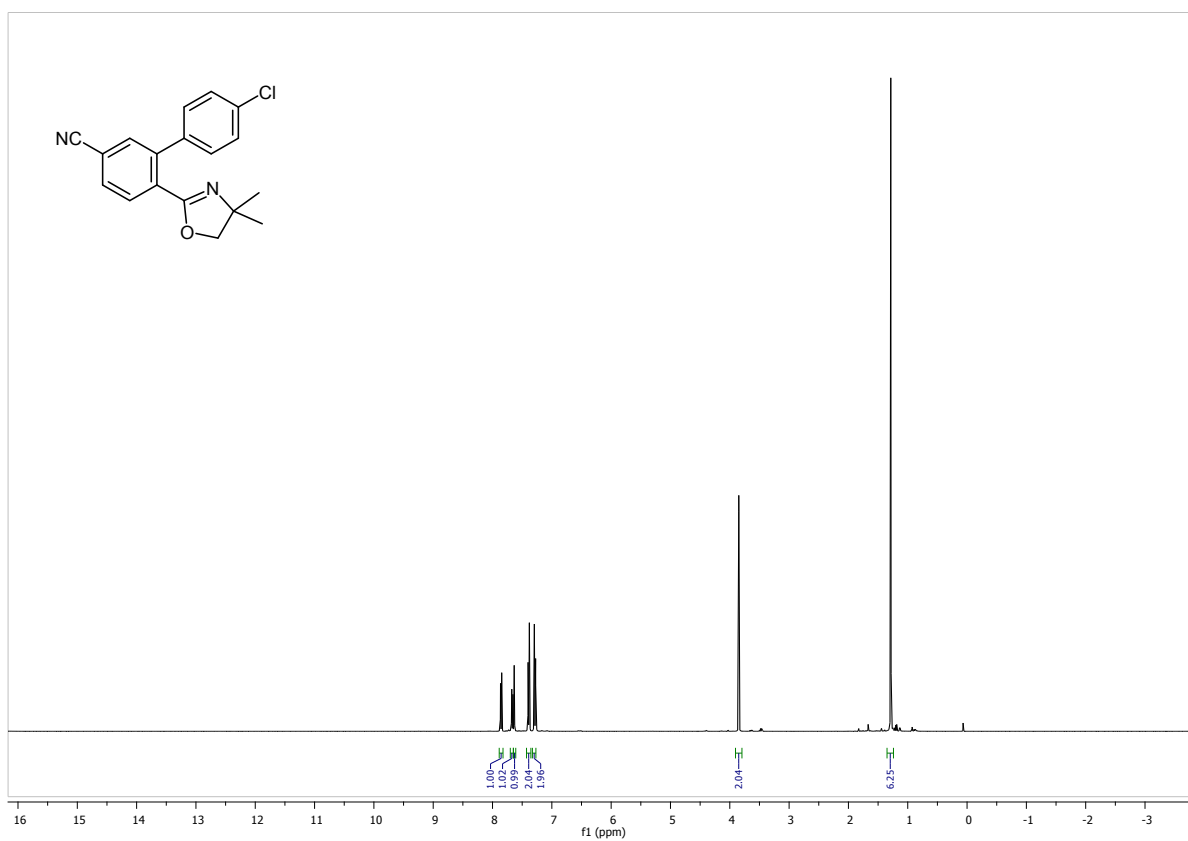
2-(cyclohex-2-en-1-yl)-4,4-dimethyloxazoline (5m):



4,4-dimethyl-2-(phenylethynyl)oxazoline (5n):



4'-chloro-6-(4,4-dimethyloxazoliny)-[1,1'-biphenyl]-3-carbonitrile (7):



5-allyl-4'-chloro-6-(4,4-dimethyloxazolynyl)-[1,1'-biphenyl]-3-carbonitrile (9):

