Supporting Information for:

Asymmetric Fe^{II}-Catalyzed Thia-Michael Addition Reaction to α,β-Unsaturated Oxazolidin-2-one Derivatives

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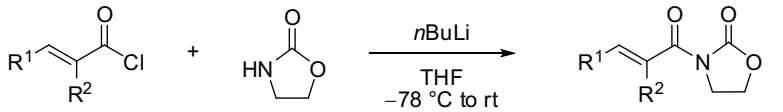
Content

General Information

All reactions were performed in flame-dried glass and tubes under an atmosphere of argon. All solvents (MeCN, CH_2Cl_2, THF, Et_2O, PhMe) were commercially available and they were distilled prior to use from the indicated drying agents. $Fe(ClO_4)_2 \cdot 6H_2O$ was purchased from Alfa Aesar® (reagent grade purity). Bolm's ligand was prepared according to reported procedures.[1] All thiols were purchased directly from commercial suppliers (Alfa Aesar®, VWR® and Sigma-Aldrich®) and they were used without further purifications. Michael acceptors **1h** and **1k** were purchased from Sigma-Aldrich® and they were used without further purifications. Powdered 4 Å MS was preactivated for 15 hours at 150 °C under vacuum prior to use. Thin-layer chromatography (TLC) was carried out on commercial silica gel plates (250 μm; Silicycle F254) and compounds were visualized using UV light absorbance (254 nm) and/or aqueous $KMnO_4$. Flash column chromatography was performed on silica gel (Silicycle, 230–400 mesh) or Biotage® Isolera™ One automated chromatography system using a normal phase cartridge (Biotage®SNAP Ultra 25g packed with Biotage®HP-Sphere™ 25 μm). ^1H, $^{13}C\{H\}$, and ^{19}F NMR spectra were recorded on a Varian Inova 400 MHz and Agilent Technologies DD2 500 MHz spectrometers in $CDCl_3$. For ^1H NMR, chemical shifts were reported in ppm downfield from tetramethylsilane (TMS) served as internal standard (δ = 0 ppm). Coupling constant are measured in hertz (Hz). For $^{13}C\{H\}$ NMR, $CDCl_3$ was used as internal standard (δ = 77.23 ppm) and spectra were obtained with complete proton decoupling. For ^{19}F NMR, $CFCl_3$ was used as the external standard. High-resolution mass spectra (HRMS) were recorded on an LC/MS-TOF (time of flight) Agilent 6210 mass spectrometer using electrospray ionization (ESI). IR spectra were recorded on a Thermo Scientific Nicolet 380 FT-IR spectrometer with ZnSe ATR accessory and they were reported in reciprocal centimeters (cm^{-1}). Melting point (mp) are uncorrected and they were recorded on a MEL-TEMP® capillary melting point apparatus. Enantiomeric ratios were determined on an Agilent 1100 Series HPLC system (hexane/*i*PrOH solvent mixture) using Daicel ChiralCel® OD–H and OJ–H, and Daicel ChiralPak® AD–H and AS–H columns. Optical rotations were measured on a Jasco DIP-360 digital polarimeter using a sodium lamp at ambient temperature.

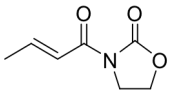
General Procedure for the Preparation of α,β-Unsaturated Oxazolidin-2-ones 1a, 1e



1a: $R^1 = CH_3$, $R^2 = H$
1e: $R^1 = H$, $R^2 = CH_3$

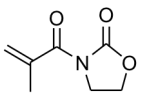
To an appropriate vacuum flame-dried flask under argon, the oxazolidin-2-one (5.0 g, 57.0 mmol, 1.0 equiv) was added to THF (111 mL). The flask was cooled to −78 °C before *n*-butyllithium (22.80 mL, 57.0 mmol, 1.0 equiv, 2.5 M in hexane) was added dropwise. The reaction was stirred at −78 °C for 2 hours. Then, the α,β-unsaturated acyl chloride (62.2 mmol, 1.1 equiv) was added dropwise at −78 °C. The mixture was stirred at −78 °C for 2 hours. The reaction was allowed to warm to room temperature and it was stirred overnight. Upon complete consumption of starting materials, the reaction mixture was quenched with an aqueous solution of saturated NH_4Cl (30 mL), and extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with aqueous saturated $NaHCO_3$ (50 mL), brine (50 mL), and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 38 ºC). The crude product was purified by silica gel chromatography to afford the corresponding α,β-unsaturated oxazolidin-2-ones.

(*E*)-3-(But-2-enoyl)oxazolidin-2-one (1a):[2]



Product was obtained as a white solid (8.13 g, 42.4 mmol, 92% yield). mp = 30–31 °C (litt. mp = 30 °C).[2] R_f = 0.22 (Hexane/EtOAc = 70:30). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.27 (dq, J = 15.3, 1.3 Hz, 1H), 7.19 (dq, J = 15.3, 6.6 Hz, 1H), 4.43 (t, J = 8.0 Hz, 2H), 4.08 (t, J = 8.0 Hz, 2H), 1.97 (dd, J = 6.6, 1.3 Hz, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 165.1, 153.5, 146.8, 121.4, 62.0, 42.7, 18.5 ppm. IR (ZnSe): 2996, 2925, 1773, 1681, 1637, 1338, 1216, 970, 705 cm^{-1}.

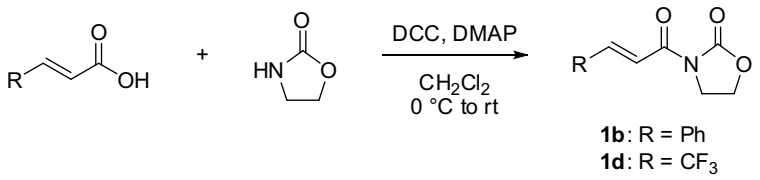
3-Methacryloyloxazolidin-2-one (1e):[3]



Product was obtained as a white solid (7.25 g, 46.7 mmol, 82% yield). mp = 51–53 °C (litt. mp = 56–57 °C).[3] R_f = 0.20 (Hexane/EtOAc = 70:30). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 5.47 (qd, J = 1.6, 0.6 Hz, 1H), 5.44 (m, 1H), 4.46 (t, J = 7.9 Hz, 2H), 4.05 (t, J = 7.9 Hz, 2H), 2.05 (dd, J = 1.6, 1.0 Hz, 3H)

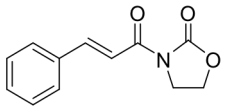
ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 171.0, 152.8, 139.1, 120.9, 62.3, 43.0, 19.1 ppm. IR (ZnSe): 2959, 2923, 1770, 1681, 1379, 1317, 1187, 1006, 762 cm^{-1}.

General Procedure for the Preparation of α,β-Unsaturated Oxazolidin-2-ones 1b, 1d



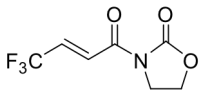
To vacuum flame-dried 50 mL flask under argon, the oxazolidin-2-one (0.98 g, 11.3 mmol, 1.0 equiv), DMAP (179 mg, 1.50 mmol, 0.13 equiv) and the α,β-unsaturated acid (14.7 mmol, 1.3 equiv) was added to CH_2Cl_2 (15 mL). The flask was cooled to 0 °C before DCC (3.03 g, 14.7 mmol, 1.3 equiv) was added in one portion. The reaction was stirred at 0 °C for 10 minutes. The reaction was allowed to warm to room temperature, and it was stirred overnight. Upon the complete consumption of starting materials, the formed dicyclohexylurea was filtered, and the precipitate was washed with portions of CH_2Cl_2 (3 x 30 mL). The filtrate was washed with aqueous saturated $NaHCO_3$ (100 mL), brine (100 mL), and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 30 ºC). The crude product was purified by silica gel chromatography to afford the corresponding α,β-unsaturated oxazolidin-2-ones.

(*E*)-3-Cinnamoyloxazolidin-2-one (1b):[4]



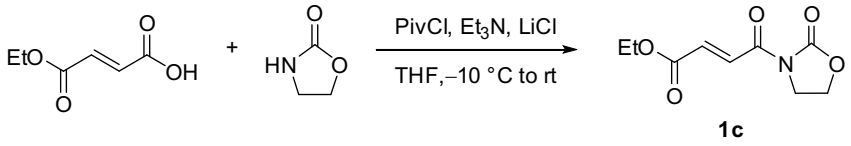
Product was obtained as a white solid (2.14 g, 9.83 mmol, 87% yield). mp = 144–145 °C (litt. mp = 151.0–151.5 °C).[5] R_f = 0.21 (Hexane/EtOAc = 70:30). ^1H NMR (500 MHz, $CDCl_3$): δ_H 7.93 (d, J = 15.8 Hz, 1H), 7.88 (d, J = 15.8 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.43 – 7.39 (m, 3H), 4.48 (m, 2H), 4.15 (m, 2H) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 165.3, 153.6, 146.2, 134.5, 130.7, 128.9, 128.6, 116.6, 62.1, 42.8 ppm. IR (ZnSe): 3096, 2928, 1762, 1675, 1614, 1351, 1209, 1036, 752 cm^{-1}.

(*E*)-3-(4,4,4-Trifluorobut-2-enoyl)oxazolidin-2-one (1d):[4]



Product was obtained as a yellow solid (1.44 g, 6.89 mmol, 61% yield). mp = 78–80 °C (litt. mp = 82–85 °C).[6] R_f = 0.23 (Hexane/EtOAc = 70:30). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.92 (dq, J = 15.6, 2.0 Hz, 1H), 6.91 (dq, J = 15.6, 6.6 Hz, 1H), 4.51 (t, J = 8.0 Hz, 2H), 4.13 (t, J = 8.0 Hz, 2H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 162.5, 153.1, 131.8 (q, J = 35.6 Hz), 127.2 (q, J = 6.2 Hz), 122.1 (q, J = 270.2 Hz), 62.4, 42.5 ppm. ^{19}F NMR (470 MHz, $CDCl_3$): δ_F –65.34 (d, J = 6.5 Hz, 3F) ppm. IR (ZnSe): 3103, 2929, 1771, 1690, 1375, 1213, 1112, 984, 752 cm^{-1}.

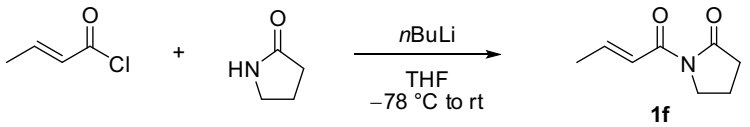
Procedure for the Preparation of (*E*)-Ethyl 4-oxo-4-(2-oxooxazolidin-3-yl)but-2-enoate (1c):[7]



To a vacuum flame-dried 250 mL flask under argon, the mono-ethyl fumarate (1.97 g, 13.7 mmol, 1.2 equiv) was added to THF (100 mL). The mixture was cooled to –10 °C before the triethylamine (4.00 mL, 28.7 mmol, 2.5 equiv) and the pivaloyl chloride (1.70 mL, 13.7 mmol, 1.2 equiv) were added subsequently. The white suspension was stirred at –10 °C for 1 hour. Then, the lithium chloride (533 mg, 12.6 mmol, 1.1 equiv), and the oxazolidin-2-one (1.00 g, 11.5 mmol, 1.0 equiv) were added to the mixture at –10 °C. The reaction was allowed to warm to room temperature, and it was stirred for 5 hours. An aqueous solution of HCl (20 mL, 1 M) was added by portions, and the slurry was stirred for 1 hour. The reaction was extracted with EtOAc (9 x 75 mL). The organic layer was washed with aqueous saturated $NaHCO_3$ (2 x 100 mL), brine (1 x 200 mL), and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 38 ºC). The crude product was purified by silica gel chromatography to give the compound **1c** as a white solid (1.42 g, 6.67 mmol, 58% yield). mp = 65–66 °C (litt. mp = 62–63 °C).[8] R_f = 0.49 (Hexane/EtOAc = 50:50). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.16 (d, J = 15.6 Hz, 1H), 6.97 (d, J = 15.6 Hz, 1H), 4.49 (t, J = 8.1 Hz, 2H), 4.29 (q, J = 7.1 Hz, 2H), 4.12 (t, J = 8.0 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 164.8, 163.8, 153.1,

134.3, 131.7, 62.4, 61.4, 42.6, 14.1 ppm. IR (ZnSe): 3096, 2990, 1768, 1716, 1677, 1367, 978, 752, 668 cm^{-1}.

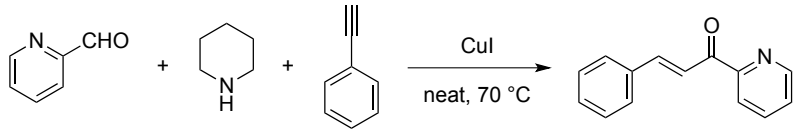
Procedure for the Preparation of (*E*)-1-But-2-enoylpyrrolidin-2-one (1f):[9]



1f

To a vacuum flame-dried 100 mL flask under argon, the pyrrolidin-2-one (1,50 g, 17.6 mmol, 1.0 equiv) was added to THF (34 mL). The flask was cooled to −78 °C before the *n*-butyllithium (7.05 mL, 17.6 mmol, 1.0 equiv, 2.5 M in hexane) was added dropwise. The reaction was stirred at −78 °C for 1 hour. Then, the (*E*)-crotonoyl chloride (1.89 mL, 19.4 mmol, 1.1 equiv) was added dropwise at −78 °C. The mixture was stirred at −78 °C for 0.5 hour. The reaction was allowed to warm to room temperature, and it was stirred for an additional 3 hours. The reaction mixture was quenched with an aqueous solution of saturated NH_4Cl (18 mL), and extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with aqueous saturated $NaHCO_3$ (30 mL), brine (30 mL), and dried over $MgSO_4$. The drying agent was removed by filtration, and the filtrate was concentrated *in vacuo* (bath temperature 38 ºC). The crude product was purified by silica gel chromatography to give the compound **1f** as a colorless oil (1.92 g, 12.5 mmol, 71% yield). R_f = 0.29 (Hexane/EtOAc = 70:30) ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 7.27 (dq, J = 15.3, 1.6 Hz, 1H), 7.14 (dq, J = 15.3, 6.8 Hz, 1H), 3.86 (t, J = 7.2, 2H), 2.62 (t, J = 8.1 Hz, 2H), 2.05 (m, 2H), 1.95 (dd, J = 6.8, 1.6 Hz, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 175.5, 166.1, 145.7, 123.5, 45.7, 33.9, 18.5, 17.2 ppm. IR (ZnSe): 2970, 2912, 1729, 1673, 1634, 1330, 1215, 968, 670 cm^{-1}.

Procedure for the Preparation of (*E*)-3-Phenyl-1-(pyridin-2-yl)prop-2-en-1-one (1g):[10]

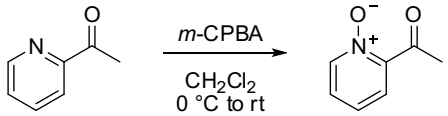


1g

The copper iodide was added to a 10 mL flask equipped with a mechanical stirrer. Then, the 2-pyridinecarboxaldehyde (1.43 mL, 15.0 mmol, 1.0 equiv), the piperidine (1.78 mL, 18.0 mmol, 1.2 equiv), and the phenylacetylene (1.98 mL, 18.0 mmol, 1.2 equiv) were added

to the flask. The mixture was warmed to 70 °C, and was stirred with opened cap for 24 hours. The reaction was filtered through a plug of Celite®, washed 3 times with EtOAc, and the filtrate was concentrated *in vacuo* (bath temperature 38 ºC). The crude product was purified by silica gel chromatography to give the compound **1g** as a brown-orange solid (1.69 g, 8.10 mmol, 54% yield). mp = 54–55 °C (litt. mp = 65.4–67.5 °C).[10] R_f = 0.59 (Hexane/EtOAc = 70:30). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.76 (ddd, J = 4.8, 1.7, 0.9 Hz, 1H), 8.32 (d, J = 16.0 Hz, 1H), 8.21 (dt, J = 7.8, 1.1 Hz, 1H), 7.96 (d, J = 16.0 Hz, 1H), 7.89 (td, J = 7.7, 1.7 Hz, 1H), 7.77 – 7.73 (m, 2H), 7.51 (ddd, J = 7.5, 4.7, 1.2 Hz, 1H), 7.46 – 7.41 (m, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 189.4, 154.2, 148.8, 144.7, 137.0, 135.1, 130.6, 128.9, 128.8, 126.9, 122.9, 120.8 ppm. IR (ZnSe): 3058, 2929, 2797, 1668, 1602, 1447, 1333, 975, 750 cm^{-1}.

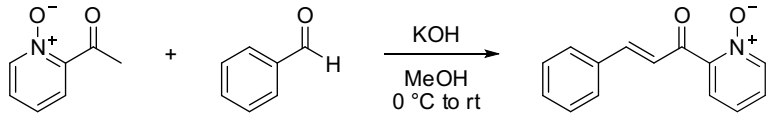
Procedure for the Preparation of 2-Acetylpyridine 1-oxide (5):[11]



5

To a 100 mL flask equipped with a mechanical stirrer, the 2-acetylpyridine (0.56 mL, 5.0 mmol, 1.0 equiv) was added to CH_2Cl_2 (50 mL). The mixture was cooled to 0 °C before the 3-chloroperbenzoic acid (50 %w/w; 5.17 g, 15.0 mmol, 3.0 equiv) was added portionwise. The reaction was stirred overnight at 0 °C, and it was allowed to reach room temperature. The reaction was quenched with water (5 mL) and aqueous saturated $NaHCO_3$ (15 mL) subsequently. The reaction was extracted with CH_2Cl_2 (2 x 20 mL). The combine organic layer was washed with brine (20 mL), dried with $MgSO_4$, and the filtrate was concentrated *in vacuo* (bath temperature 30 ºC). The crude product was purified by silica gel chromatography to give the compound **5** as a yellow solid (0.481 g, 3.51 mmol, 70% yield). mp = 32–33 °C. R_f = 0.38 (CH_2Cl_2/Acetone = 50:50). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.21 (ddd, J = 6.5, 1.2, 0.6 Hz, 1H), 7.71 (ddd, J = 7.9, 2.2, 0.6 Hz, 1H), 7.38 (ddd, J = 7.9, 6.5, 2.2 Hz, 1H), 7.32 (td, J = 7.9, 1.2 Hz, 1H), 2.83 (s, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 194.9, 146.8, 140.6, 128.0, 126.8, 125.4, 30.6 ppm. IR (ZnSe): 3096, 3076, 3056, 1679, 1433, 1357, 1159, 849, 778 cm^{-1}.

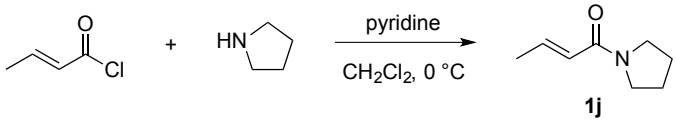
Procedure for the Preparation of (*E*)-2-Cinnamoylpyridine 1-oxide (1i):[12]



5 **1i**

To a 25 mL flask equipped with a mechanical stirrer, the 2-acetylpyridine 1-oxide (450 mg, 3.3 mmol, 1.0 equiv) was added to MeOH (10 mL). The mixture was cooled to 0 °C before the potassium hydroxide (184 mg, 4.9 mmol, 1.5 equiv) was added portionwise. After stirring at 0 °C for 0.5 hour, the benzaldehyde (0.50 mL, 3.3 mmol, 1.0 equiv) was added to the reaction. The mixture was stirred at 0 °C for 3 hours. The mixture was neutralized with HCl 1M (5 mL), and methanol was evaporated *in vacuo*. The residue was extracted with CH_2Cl_2 (3 x 20 mL). The combine organic layer was washed with brine (20 mL), dried over $MgSO_4$, and the filtrate was concentrated *in vacuo* (bath temperature 30 ºC). The crude product was purified by silica gel chromatography to give the compound **1i** as a yellow solid (0.293 g, 1.30 mmol, 39% yield). mp = 99–102 °C (litt. mp = 104–107 °C).[12] R_f = 0.48 (CH_2Cl_2/Acetone = 50:50). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 8.25 (ddd, J = 6.5, 1.2, 0.6 Hz, 1H), 7.83 (d, J = 15.8 Hz, 1H), 7.74 (d, J = 15.8 Hz, 1H), 7.70 (ddd, J = 7.9, 2.2, 0.6 Hz, 1H), 7.66 – 7.64 (m, 2H), 7.43 – 7.35 (m, 5H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 186.3, 147.2, 144.2, 140.4, 134.6, 130.8, 128.8, 128.8, 127.7, 127.2, 125.6, 124.3 ppm. IR (ZnSe): 3111, 3022, 1668, 1610, 1423, 1194, 968, 845, 759 cm^{-1}.

Procedure for the Preparation of (*E*)-1-(Pyrrolidin-1-yl)but-2-en-1-one (1j):[13]

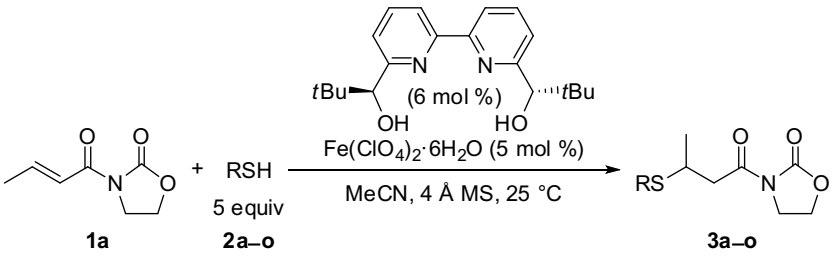


1j

To a vacuum flame-dried 25 mL flask equipped with a mechanical stirrer, the pyrrolidine (1.04 mL, 12.5 mmol, 1.0 equiv) was added to CH_2Cl_2 (6 mL). The mixture was cooled to 0 °C before the pyridine (1.01 mL, 12.5 mmol, 1.0 equiv) was added portionwise. After stirring at 0 °C for 0.5 hour, the (*E*)-crotonoyl chloride (1.34 mL, 13.8 mmol, 1.1 equiv) was added to the reaction. The mixture was stirred at 0 °C for 0.25 hour. The reaction was allowed to warm to room temperature, and it was stirred for an additional 3 hours. The reaction was diluted with CH_2Cl_2 (20 mL), and the resulting mixture was washed with H_2O (10 mL), HCl

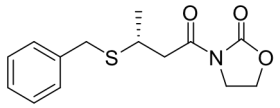
5% (10 mL), NaOH 5% (10 mL), and brine (10 mL). The organic layer was dried over $MgSO_4$, and the filtrate was concentrated *in vacuo* (bath temperature 30 ºC). The crude product was purified by silica gel chromatography to give the compound **1j** as colorless crystals (1.23 g, 8.87 mmol, 71% yield). mp = 29 °C. R_f = 0.10 (Hexane/EtOAc = 40:60). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H 6.92 (dq, J = 15.0, 6.9 Hz, 1H), 6.13 (dq, J = 15.0, 1.7 Hz, 1H), 3.54 – 3.50 (m, 4H), 1.99 – 1.94 (m, 2H), 1.89 – 1.84 (m, 2H), 1.88 (dd, J = 6.9, 1.8 Hz, 3H) ppm. ^{13}C{H} NMR (100 MHz, CDCl3): δ_C 164.7, 140.4, 123.1, 46.4, 45.6, 26.0, 24.2, 17.9 ppm. IR (ZnSe): 2967, 2870, 1664, 1607, 1414, 1226, 962, 824, 675 cm^{-1}.

General Procedure for the Asymmetric Thia-Michael Addition Reaction to (*E*)-3-Crotonoyloxazolidin-2-one Catalyzed by $Fe(ClO_4)_2{\cdot}6H_2O$/(*S*,*S*)-Bolm's Ligand complex:



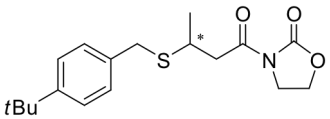
Under argon atmosphere, a mixture of 1,1'-(2,2'-bipyridine-6,6'-diyl)bis(2,2-dimethylpropan-1-ol) ((*S*,*S*)-Bolm's ligand, 9.9 mg, 0.030 mmol, 0.06 equiv), $Fe(ClO_4)_2{\cdot}6H_2O$ (9.1 mg, 0.025 mmol, 0.05 equiv), and activated 4 Å molecular sieves (50 mg) in MeCN (0.5 mL) were stirred at 25 °C for 2 hours (pre-complexation) during in which time the Fe^{II} salt was completely dissolved to give a yellow solution. (*E*)-3-Crotonoyloxazolidin-2-one **1a** (77.6 mg, 0.50 mmol, 1 equiv) was introduced, and thiol **2a–o** (2.5 mmol, 5 equiv) was added subsequently. The mixture was stirred at 25 °C, and monitored by TLC. After completion of the reaction, the mixture was filtered through a plug of Celite®, washed 3 times with Et_2O, and the filtrate was concentrated *in vacuo* (bath temperature 35 °C). The crude residue was purified by a normal phase chromatography (Biotage®SNAP Ultra 25g/Biotage®HP-Sphere™ 25 μm) using a gradient elution of hexane/EtOAc = 90:10–60:40 to give thioethers **3a–o**. Bolm's ligand **L*** was recovered quantitatively in the purification process by eluting with hexane/EtOAc = 80:20 (R_f = 0.27).

(+)-(*R*)-3-(3-(Benzylthio)butanoyl)oxazolidin-2-one (3a):[14]



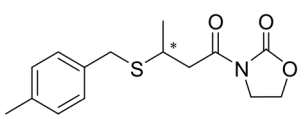
Product was obtained as a colorless oil (131 mg, 0.469 mmol, 94% yield). Reaction time: 24 h. 96:4 *er* determined by HPLC (Daicel ChiralCel® OD-H, hexane/*i*PrOH = 70:30, flow rate = 0.5 mL/min, λ = 220 nm, t_R(*R*) = 23.3 min, t_R(*S*) = 27.0 min. $[\alpha]_D^{25}$ = +13.0 (*c* = 0.25, $CHCl_3$) (litt.[14] $[\alpha]_D^{25}$ = –15.0 (*c* = 0.5, $CHCl_3$), 94% *ee* of (*S*)-**3a**; litt.[15] $[\alpha]_D^{25}$ = –15.7 (*c* = 1.0, $CHCl_3$), 97% *ee* of (*S*)-**3a**). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.35 – 7.28 (m, 4H), 7.23 (tt, *J* = 7.1, 1.6 Hz, 1H), 4.39 – 4.35 (m, 2H), 4.01 – 3.94 (m, 2H), 3.81 (d, *J* = 13.3 Hz, 1H), 3.77 (d, *J* = 13.3 Hz, 1H), 3.31 – 3.20 (m, 2H), 3.07 (m, 1H), 1.33 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 171.0, 153.4, 138.4, 128.8, 128.5, 126.9, 62.0, 42.5, 42.4, 35.6, 35.3, 21.6 ppm. IR (ZnSe): 2963, 2921, 1770, 1693, 1383, 1219, 1028, 757, 702 cm^{-1}.

(+)-3-(3-(4-Tert-butylbenzylthio)butanoyl)oxazolidin-2-one (3b):



Product was obtained as a colorless oil (126 mg, 0.375 mmol, 75% yield). Reaction time: 15 h. 95:5 *er* determined by HPLC (Daicel ChiralPak® AD-H, hexane/*i*PrOH = 90:10, flow rate = 0.5 mL/min, λ = 220 nm, t_R(major) = 27.0 min, t_R(minor) = 29.3 min. $[\alpha]_D^{25}$ = +10.3 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.32 (dt, *J* = 8.3, 2.0 Hz, 2H), 7.26 (dt, *J* = 8.3, 2.0 Hz, 2H), 4.41 – 4.37 (m, 2H), 4.02 – 3.98 (m, 2H), 3.79 (d, *J* = 13.2 Hz, 1H), 3.75 (d, *J* = 13.2 Hz, 1H), 3.33 – 3.23 (m, 2H), 3.08 (m, 1H), 1.34 (d, *J* = 6.8 Hz, 3H), 1.30 (s, 9H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 171.0, 153.4, 149.8, 135.2, 128.5, 125.4, 62.1, 42.5, 42.4, 35.6, 34.8, 34.5, 31.4, 21.6 ppm. IR (ZnSe): 2960, 2866, 1772, 1694, 1383, 1188, 1098, 1028, 703 cm^{-1}. HRMS (ESI) calcd for $C_{18}H_{26}NO_3S$ $(M+H)^+$ 336.1628, found 336.1637.

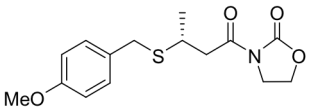
(+)-3-(3-(4-Methylbenzylthio)butanoyl)oxazolidin-2-one (3c):



Product was obtained as a white solid (137 mg, 0.467 mmol, 93% yield). mp = 44–45 °C. Reaction time: 21 h. 95:5 *er* determined by HPLC (Daicel ChiralCel® OD-H, hexane/*i*PrOH = 70:30, flow rate = 0.5 mL/min, λ = 220 nm, t_R(major) = 24.5 min, t_R(minor)

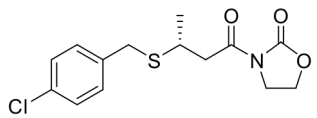
= 29.6 min. $[\alpha]_D^{25}$ = +8.5 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.21 (dt, *J* = 8.0, 1.8 Hz, 2H), 7.10 (dt, *J* = 8.0, 1.8 Hz, 2H), 4.38 – 4.34 (m, 2H), 4.02 – 3.91 (m, 2H), 3.77 (d, *J* = 13.3 Hz, 1H), 3.73 (d, *J* = 13.3 Hz, 1H), 3.30 – 3.19 (m, 2H), 3.06 (m, 1H), 2.31 (s, 3H), 1.33 (d, *J* = 6.8 Hz, 3H) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 171.0, 153.4, 136.5, 135.2, 129.1, 128.7, 62.0, 42.5, 42.4, 35.5, 35.0, 21.6, 21.1 ppm. IR (ZnSe): 2958, 2919, 1756, 1698, 1369, 1222, 1033, 759, 711 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{20}NO_3S$ $(M+H)^+$ 294.1158, found 294.1162.

(+)-(*R*)-3-(3-(4-Methoxybenzylthio)butanoyl)oxazolidin-2-one (3d):[14]



Product was obtained as a white solid (144 mg, 0.465 mmol, 93% yield). mp = 78–80 °C. Reaction time: 24 h. 96:4 *er* determined by HPLC (Daicel ChiralCel® OD-H, hexane/*i*PrOH = 70:30, flow rate = 0.5 mL/min, λ = 220 nm, $t_R(R)$ = 32.9 min, $t_R(S)$ = 38.5 min. $[\alpha]_D^{25}$ = +8.4 (*c* = 0.5, $CHCl_3$) (litt.[14] $[\alpha]_D^{25}$ = –16.6 (*c* = 0.5, $CHCl_3$), 96% *ee* of (*S*)-**3d**; litt.[15] $[\alpha]_D^{25}$ = –14.7 (*c* = 1.0, $CHCl_3$), 97% *ee* of (*S*)-**3d**). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.25 (dt, *J* = 8.8, 2.1 Hz, 2H), 6.83 (dt, *J* = 8.8, 2.1 Hz, 2H), 4.40 – 4.36 (m, 2H), 4.01 – 3.94 (m, 2H), 3.78 (s, 3H), 3.76 (d, *J* = 13.3 Hz, 1H), 3.72 (d, *J* = 13.3 Hz, 1H), 3.29 – 3.18 (m, 2H), 3.06 (m, 1H), 1.33 (d, *J* = 6.8 Hz, 3H) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 171.0, 158.5, 153.4, 130.3, 129.9, 113.8, 62.0, 55.3, 42.5, 42.4, 35.4, 34.6, 21.6 ppm. IR (ZnSe): 2976, 2924, 1783, 1690, 1364, 1188, 1025, 753, 653 cm^{-1}.

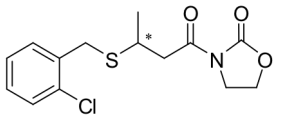
(+)-(*R*)-3-(3-(4-Chlorobenzylthio)butanoyl)oxazolidin-2-one (3e):[14]



Product was obtained as a white solid (144 mg, 0.459 mmol, 92% yield). mp = 42–43 °C. Reaction time: 63 h. 94:6 *er* determined by HPLC (Daicel ChiralPak® AD-H, hexane/*i*PrOH = 70:30, flow rate = 0.5 mL/min, λ = 220 nm, $t_R(R)$ = 22.1 min, $t_R(S)$ = 23.8 min. $[\alpha]_D^{25}$ = +6.0 (*c* = 0.5, $CHCl_3$) (litt.[14] $[\alpha]_D^{25}$ = –13.2 (*c* = 0.5, $CHCl_3$), 97% *ee* of (*S*)-**3e**; litt.[15] $[\alpha]_D^{25}$ = –16.5 (*c* = 1.0, $CHCl_3$), 93% *ee* of (*S*)-**3e**). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.29 – 7.24 (m, 4H), 4.41 – 4.36 (m, 2H), 4.01 – 3.94 (m, 2H), 3.77 (d, *J* = 13.5 Hz, 1H), 3.72 (d, *J* = 13.5 Hz, 1H), 3.28 (dd, *J* = 16.2, 6.8 Hz, 1H), 3.20 (m, 1H), 3.03 (dd, *J* = 16.2, 6.8 Hz, 1H), 1.31 (d, *J* = 6.7 Hz, 3H) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 170.8, 153.4,

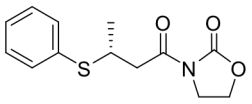
137.0, 132.6, 130.2, 128.6, 62.1, 42.5, 42.4, 35.6, 34.6, 21.6 ppm. IR (ZnSe): 2971, 2917, 1767, 1696, 1384, 1221, 1012, 758, 706 cm^{-1}.

(+)-3-(3-(2-Chlorobenzylthio)butanoyl)oxazolidin-2-one (3f):



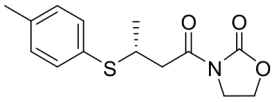
Product was obtained as a white solid (118 mg, 0.376 mmol, 75% yield). mp = 36–37 °C. Reaction time: 15 h. 94:6 *er* determined by HPLC (Daicel ChiralPak® AD-H, hexane/*i*PrOH = 70:30, flow rate = 0.5 mL/min, λ = 220 nm, t_R(minor) = 16.3 min, t_R(major) = 17.4 min. $[\alpha]_D^{25}$ = +12.2 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.38 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.32 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.19 (td, *J* = 7.4, 1.7 Hz, 1H), 7.15 (td, *J* = 7.5, 2.0 Hz, 1H), 4.37 – 4.32 (m, 2H), 3.97 – 3.93 (m, 2H), 3.91 – 3.84 (m, 2H), 3.33 – 3.24 (m, 2H), 3.05 (m, 1H), 1.33 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 170.9, 153.4, 136.2, 133.9, 130.8, 129.7, 128.4, 126.9, 62.1, 42.5, 42.5, 36.0, 32.7, 21.7 ppm. IR (ZnSe): 3015, 2969, 2918, 1763, 1692, 1381, 1202, 1041, 759 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{17}ClNO_3S$ $(M+H)^+$ 314.0612, found 314.0618.

(+)-(*R*)-3-(3-(Phenylthio)butanoyl)oxazolidin-2-one (3g):[15]



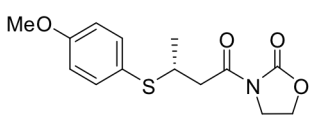
Product was obtained as a white solid (119 mg, 0.449 mmol, 90% yield). mp = 40–41 °C. Reaction time: 20 h. 81:19 *er* determined by HPLC (Daicel ChiralPak® AD-H, hexane/*i*PrOH = 85:15, flow rate = 1.0 mL/min, λ = 254 nm, t_R(*S*) = 13.9 min, t_R(*R*) = 15.6 min. $[\alpha]_D^{25}$ = +28.6 (*c* = 1.0, $CHCl_3$) (litt.[15] $[\alpha]_D^{25}$ = –11.5 (*c* = 1.0, $CHCl_3$), 86% *ee* of (*S*)-**3d**; litt.[16] $[\alpha]_D^{24}$ = –12.70 (*c* = 1.26, $CHCl_3$), 90% *ee* of (*S*)-**3d**). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.45 – 7.42 (m, 2H), 7.31 – 7.26 (m, 2H), 7.23 (tt, *J* = 7.2, 1.5 Hz, 1H), 4.36 – 4.31 (m, 2H), 3.97 – 3.87 (m, 2H), 3.76 (m, 1H), 3.25 (dd, *J* = 17.0, 6.6 Hz, 1H), 3.11 (dd, *J* = 17.0, 7.4 Hz, 1H), 1.34 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 171.0, 153.4, 134.1, 132.8, 128.9, 127.3, 62.1, 42.4, 42.3, 38.9, 21.3 ppm. IR (ZnSe): 2964, 2922, 1770, 1693, 1383, 1219, 1038, 746, 691 cm^{-1}.

(+)-(*R*)-3-(3-(4-Methylphenylthio)butanoyl)oxazolidin-2-one (3h):[15]



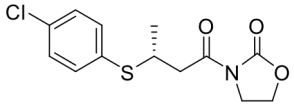
Product was obtained as a white solid (137 mg, 0.490 mmol, 98% yield). mp = 46–47 °C. Reaction time: 20 h. 83:17 *er* determined by HPLC (Daicel ChiralCel® OD-H, hexane/*i*PrOH = 95:5, flow rate = 1.0 mL/min, λ = 254 nm, t_R(*R*) = 38.3 min, t_R(*S*) = 48.6 min. $[\alpha]_D^{25}$ = +18.7 (*c* = 1.0, $CHCl_3$) (litt.[15] $[\alpha]_D^{25}$ = –20.1 (*c* = 1.0, $CHCl_3$), 90% *ee* of (*S*)-**3h**). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.35 (dt, *J* = 8.0, 1.7 Hz, 2H), 7.10 (dt, *J* = 8.0, 1.7 Hz, 2H), 4.37 – 4.33 (m, 2H), 3.96 – 3.91 (m, 2H), 3.67 (m, 1H), 3.23 (dd, *J* = 17.0, 6.5 Hz, 1H), 3.08 (dd, *J* = 17.0, 7.4 Hz, 1H), 2.31 (s, 3H), 1.32 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 171.1, 153.4, 137.7, 133.6, 130.1, 129.7, 62.1, 42.4, 42.3, 39.3, 21.2, 21.1 ppm. IR (ZnSe): 2969, 2922, 1771, 1693, 1384, 1220, 1038, 809, 757 cm^{-1}.

(+)-(*R*)-3-(3-(4-Methoxyphenylthio)butanoyl)oxazolidin-2-one (3i):[16]



Product was obtained as a colorless oil (139 mg, 0.471 mmol, 94% yield). Reaction time: 20 h. 82:18 *er* determined by HPLC (Daicel ChiralCel® OD-H, hexane/*i*PrOH = 90:10, flow rate = 1.0 mL/min, λ = 254 nm, t_R(*R*) = 36.3 min, t_R(*S*) = 43.4 min. $[\alpha]_D^{25}$ = +14.7 (*c* = 2.13, $CHCl_3$) (litt.[16] $[\alpha]_D^{25}$ = –6.7 (*c* = 2.13, $CHCl_3$), 86% *ee* of (*S*)-**3i**; litt.[17] $[\alpha]_D^{25}$ = –5.9 (*c* = 2.05, $CHCl_3$), 78% *ee* of (*S*)-**3i**). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.42 (dt, *J* = 8.8, 2.1 Hz, 2H), 6.84 (dt, *J* = 8.8, 2.1 Hz, 2H), 4.39 – 4.35 (m, 2H), 3.98 – 3.93 (m, 2H), 3.79 (s, 3H), 3.58 (m, 1H), 3.23 (dd, *J* = 17.0, 6.6 Hz, 1H), 3.05 (dd, *J* = 17.0, 7.3 Hz, 1H), 1.30 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 171.0, 159.7, 153.4, 136.3, 123.8, 114.4, 62.1, 55.3, 42.4, 42.2, 39.8, 21.1 ppm. IR (ZnSe): 2960, 2922, 1771, 1693, 1383, 1241, 1025, 828, 756 cm^{-1}.

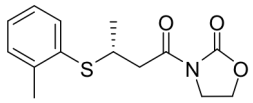
(+)-(*R*)-3-(3-(4-Chlorophenylthio)butanoyl)oxazolidin-2-one (3j):[16]



Product was obtained as a white solid (142 mg, 0.474 mmol, 95% yield). mp = 66–68 °C. Reaction time: 20 h. 81:19 *er* determined by HPLC (Daicel ChiralPak® AD-H, hexane/*i*PrOH = 80:20, flow rate = 1.0 mL/min, λ = 254 nm, t_R(*S*) = 12.0 min, t_R(*R*) = 14.1 min. $[\alpha]_D^{25}$ = +24.8 (*c* = 2.15, $CHCl_3$) (litt.[16] $[\alpha]_D^{25}$ = –16.47 (*c* = 2.15, $CHCl_3$), 87% *ee* of (*S*)-**3j**; litt.[18] $[\alpha]_D^{20}$ = –21.0 (*c* = 1.0, CH_2Cl_2), 86% *ee* of (*S*)-**3j**). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.38

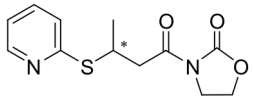
(dt, J = 8.4, 2.0 Hz, 2H), 7.27 (dt, J = 8.4, 2.0 Hz, 2H), 4.41 – 4.37 (m, 2H), 3.99 – 3.95 (m, 2H), 3.73 (m, 1H), 3.25 (dd, J = 17.1, 6.5 Hz, 1H), 3.11 (dd, J = 17.1, 7.4 Hz, 1H), 1.34 (d, J = 6.8 Hz, 3H) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 170.8, 153.4, 134.1, 133.4, 132.6, 129.0, 62.1, 42.4, 42.1, 39.2, 21.2 ppm. IR (ZnSe): 2961, 2921, 1778, 1689, 1381, 1204, 1011, 819, 758 cm^{-1}.

(+)-(*R*)-3-(3-(2-Methylphenylthio)butanoyl)oxazolidin-2-one (3k):[16]



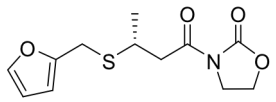
Product was obtained as a white solid (137 mg, 0.490 mmol, 98% yield). mp = 33–34 °C. Reaction time: 16 h. 86:14 *er* determined by HPLC (Daicel ChiralCel® OD-H, hexane/*i*PrOH = 95:5, flow rate = 1.0 mL/min, λ = 254 nm, t_R(*R*) = 32.2 min, t_R(*S*) = 45.1 min. $[\alpha]_D^{25}$ = +30.1 (*c* = 2.13, $CHCl_3$) (litt.[16] $[\alpha]_D^{26}$ = –29.95 (*c* = 2.13, $CHCl_3$), 95% *ee* of (*S*)-**3k**; litt.[17] $[\alpha]_D^{26}$ = –30.33 (*c* = 2.09, $CHCl_3$), 89% *ee* of (*S*)-**3k**). ^1H NMR (400 MHz, $CDCl_3$): δ_H 7.43 (m, 1H), 7.19 (m, 1H), 7.16 – 7.12 (m, 2H), 4.35 – 4.31 (m, 2H), 3.91 – 3.87 (m, 2H), 3.77 (m, 1H), 3.25 (dd, J = 17.1, 6.3 Hz, 1H), 3.13 (dd, J = 17.1, 7.5 Hz, 1H), 2.42 (s, 3H), 1.36 (d, J = 6.8 Hz, 3H) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 171.0, 153.3, 140.3, 133.7, 132.6, 130.3, 127.3, 126.3, 62.1, 42.4, 42.4, 38.3, 21.1, 20.8 ppm. IR (ZnSe): 2970, 2922, 1771, 1693, 1384, 1220, 1037, 751, 706 cm^{-1}.

(+)-3-(3-(Pyridin-2-ylthio)butanoyl)oxazolidin-2-one (3l):



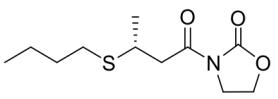
Product was obtained as a colorless oil (103 mg, 0.387 mmol, 77% yield). Reaction time: 24 h. 53:47 *er* determined by HPLC (Daicel ChiralPak® AD-H, hexane/*i*PrOH = 90:10, flow rate = 0.5 mL/min, λ = 254 nm, t_R(minor) = 49.5 min, t_R(major) = 52.4 min. $[\alpha]_D^{25}$ = +3.6 (*c* = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ_H 8.39 (ddd, J = 4.9, 1.9, 1.0 Hz, 1H), 7.45 (m, 1H), 7.14 (dt, J = 8.1, 1.0 Hz, 1H), 6.95 (ddd, J = 7.4, 4.9, 1.0 Hz, 1H), 4.46 (m, 1H), 4.40 – 4.36 (m, 2H), 4.04 – 3.91 (m, 2H), 3.37 (dd, J = 17.1, 6.4 Hz, 1H), 3.31 (dd, J = 17.1, 7.2 Hz, 1H), 1.48 (d, J = 7.0 Hz, 3H) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C 171.0, 158.5, 153.5, 149.4, 135.9, 122.6, 119.5, 62.1, 42.4, 42.2, 35.1, 21.2 ppm. IR (ZnSe): 2966, 2923, 1769, 1691, 1576, 1383, 1218, 1036, 755 cm^{-1}. HRMS (ESI) calcd for $C_{12}H_{15}N_2O_3S$ $(M+H)^+$ 267.0798, found 267.0798.

(+)-(*R*)-3-(3-(Furan-2-ylmethylthio)butanoyl)oxazolidin-2-one (3m):[15]



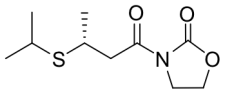
Product was obtained as a yellow solid (100 mg, 0.371 mmol, 74% yield). mp = 32–33 °C. Reaction time: 15 h. 95:5 *er* determined by HPLC (Daicel ChiralPak® AD-H, hexane/*i*PrOH = 90:10, flow rate = 0.5 mL/min, λ = 220 nm, t_R(*S*) = 43.8 min, t_R(*R*) = 48.2 min. $[\alpha]_D^{25}$ = +29.4 (*c* = 0.5, $CHCl_3$) (litt.[15] $[\alpha]_D^{25}$ = –26.4 (*c* = 1.0, $CHCl_3$), 96% *ee* of (*S*)-**3m**). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.30 (dd, *J* = 1.8, 0.9 Hz, 1H), 6.25 (dd, *J* = 3.2, 1.9 Hz, 1H), 6.16 (dd, *J* = 3.2, 0.9 Hz, 1H), 4.37 – 4.33 (m, 2H), 3.98 – 3.92 (m, 2H), 3.78 (d, *J* = 14.9 Hz, 1H), 3.73 (d, *J* = 14.9 Hz, 1H), 3.31 – 3.21 (m, 2H), 3.01 (m, 1H), 1.28 (d, *J* = 6.8 Hz, 3H) ppm. ^{13}C{H} NMR (400 MHz, $CDCl_3$): δ_C 170.9, 153.4, 151.7, 142.0, 110.4, 107.4, 62.1, 42.5, 42.4, 35.7, 27.4, 21.4 ppm. IR (ZnSe): 3513, 3371, 3112, 2976, 2924, 1758, 1691, 1369, 1005, 748 cm^{-1}.

(+)-(*R*)-3-(3-(Butylthio)butanoyl)oxazolidin-2-one (3n):[18]



Product was obtained as a colorless oil (102 mg, 0.416 mmol, 83% yield). Reaction time: 21 h. 91:9 *er* determined by HPLC (Daicel ChiralPak® AS-H, hexane/*i*PrOH = 95:5, flow rate = 0.5 mL/min, λ = 220 nm, t_R(*R*) = 43.0 min, t_R(*S*) = 45.8 min. $[\alpha]_D^{25}$ = +7.0 (*c* = 1.0, CH_2Cl_2) (litt.[18] $[\alpha]_D^{20}$ = –1.0 (*c* = 1.0, CH_2Cl_2), 68% *ee* of (*S*)-**3n**). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.38 – 4.34 (m, 2H), 3.99 – 3.95 (m, 2H), 3.27 – 3.21 (m, 2H), 2.96 (m, 1H), 2.52 – 2.48 (m, 2H), 1.51 – 1.45 (m 2H), 1.36 – 1.30 (m, 2H), 1.28 (d, *J* = 6.7 Hz, 3H), 0.84 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C{H} NMR (400 MHz, $CDCl_3$): δ_C 171.1, 153.4, 62.1, 42.5, 42.5, 35.5, 31.7, 30.2, 22.0, 21.6, 13.6 ppm. IR (ZnSe): 2958, 2926, 1773, 1695, 1384, 1220, 1039, 758, 706 cm^{-1}.

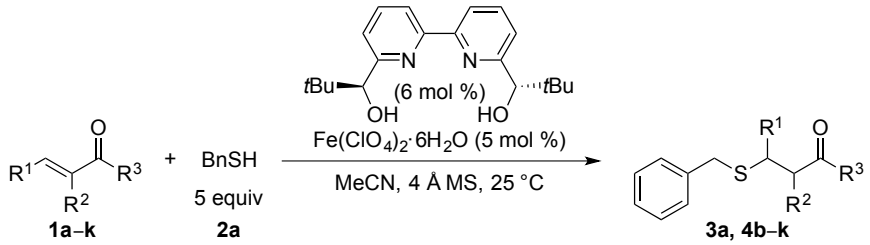
(+)-(*R*)-3-(3-(Isopropylthio)butanoyl)oxazolidin-2-one (3o):[15]



Product was obtained as a white solid (102 mg, 0.441 mmol, 88% yield). mp = 26–27 °C. Reaction time: 43 h. 83:17 *er* determined by HPLC (Daicel ChiralPak® AD-H, hexane/*i*PrOH = 80:20, flow rate = 0.5 mL/min, λ = 220 nm, t_R(*S*) = 16.9 min, t_R(*R*) = 20.2 min. $[\alpha]_D^{25}$ = +6.0 (*c* = 1.0, $CHCl_3$) (litt.[15] $[\alpha]_D^{25}$ = –11.5 (*c* = 1.0, $CHCl_3$), 97% *ee* of (*S*)-**3o**). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 4.40 – 4.36 (m, 2H), 4.01 – 3.97 (m, 2H), 3.32 – 3.22 (m, 2H), 3.01

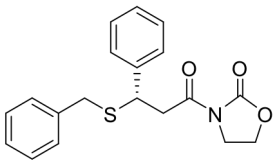
(m, 1H), 2.97 (m, 1H), 1.30 (d, J = 6.7 Hz, 3H), 1.23 (d, J = 6.7 Hz, 3H), 1.21 (d, J = 6.7 Hz, 3H) ppm. $^{13}C\{H\}$ NMR (100 MHz, $CDCl_3$): δ_C ^{13}C 171.1, 153.4, 62.1, 42.8, 42.5, 34.3, 34.3, 23.8, 23.6, 22.1 ppm. IR (ZnSe): 2961, 2923, 1771, 1693, 1383, 1219, 1038, 757, 658 cm^{-1}.

General Procedure for the Michael Addition Reaction of Benzyl Thiol to α,β-Unsaturated Carbonyl Compounds Catalyzed by $Fe(ClO_4)_2{\cdot}6H_2O$/(*S*,*S*)-Bolm's Ligand complex:



Under argon atmosphere, a mixture of 1,1'-(2,2'-bipyridine-6,6'-diyl)bis(2,2-dimethylpropan-1-ol) ((*S*,*S*)-Bolm's ligand, 9.9 mg, 0.030 mmol, 0.06 equiv), $Fe(ClO_4)_2{\cdot}6H_2O$ (9.1 mg, 0.025 mmol, 0.05 equiv), and activated 4 Å molecular sieves (50 mg) in MeCN (0.5 mL) were stirred at 25 °C for 2 hours (pre-complexation) during in which time the Fe^{II} salt was completely dissolved to give a yellow solution. α,β-Unsaturated carbonyl compound **1b–k** (0.5 mmol, 1 equiv) was introduced, and benzyl thiol **2a** (293 μL, 2.5 mmol, 5 equiv) was added subsequently. The mixture was stirred at 25 °C, and monitored by TLC. After completion of the reaction, the mixture was filtered through a plug of Celite®, washed 3 times with Et_2O, and the filtrate was concentrated *in vacuo* (bath temperature 35 °C). The crude residue was purified by a normal phase chromatography (Biotage®SNAP Ultra 25g/Biotage®HP-Sphere™ 25 μm) using a gradient elution of hexane/EtOAc = 90:10–40:60 (**4b–g**), 99:1–90:10 (**4h**), or 90:10–20:80 (**4i**), to give thioethers **4b–k**. Bolm's ligand **L*** was recovered quantitatively in the purification process by eluting with hexane/EtOAc = 80:20 (R_f = 0.27).

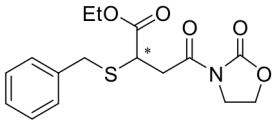
(–)-(*S*)-3-(3-(Benzylthio)-3-phenylpropanoyl)oxazolidin-2-one (4b):[15]



Product was obtained as a white solid (117 mg, 0.343 mmol, 67% yield). mp = 83–85 °C. Reaction time: 118 h. 85:15 *er* determined by HPLC (Daicel ChiralPak® AD-H, hexane/*i*PrOH = 90:10, flow rate = 0.5 mL/min, λ = 220 nm, t_R(*S*) = 44.0 min, t_R(*R*) = 47.9

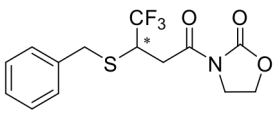
min. $[\alpha]_D^{25}$ = –80.0 (*c* = 1.0, $CHCl_3$) (litt.[15] $[\alpha]_D^{25}$ = +201.0 (*c* = 1.0, $CHCl_3$), 98% *ee* of (*R*)-**4b**). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.39 – 7.20 (m, 10H), 4.34 (m, 1H), 4.32 – 4.25 (m, 2H), 3.93 (ddd, *J* = 11.0, 9.3, 7.0 Hz, 1H), 3.85 (ddd, *J* = 11.0, 9.3, 6.8 Hz, 1H), 3.58 (d, *J* = 13.3 Hz, 1H), 3.58 (dd, *J* = 17.0, 8.0 Hz, 1H), 3.47 (d, *J* = 13.3 Hz, 1H), 3.46 (dd, *J* = 17.0, 7.0 Hz, 1H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 170.1, 153.4, 141.4, 137.9, 129.0, 128.6, 128.4, 128.1, 127.4, 127.0, 62.1, 44.2, 42.4, 41.6, 35.7 ppm. IR (ZnSe): 3060, 2921, 1776, 1690, 1381, 1205, 1037, 757, 695 cm^{-1}.

(–)-Ethyl 2-(benzylthio)-4-oxo-4-(2-oxooxazolidin-3-yl)butanoate (4c):



Product was obtained as a white solid (165 mg, 0.489 mmol, 98% yield). mp = 63–64 °C. Reaction time: 15 h. 95:5 *er* determined by HPLC (Daicel ChiralPak® AD-H, hexane/*i*PrOH = 85:15, flow rate = 1.0 mL/min, λ = 254 nm, t_R(minor) = 22.2 min, t_R(major) = 27.4 min. $[\alpha]_D^{25}$ = –61.1 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.34 – 7.27 (m, 4H), 7.22 (tt, *J* = 7.0, 1.5 Hz, 1H), 4.34 (t, *J* = 8.1 Hz, 2H), 4.18 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.92 – 3.88 (m, 3H), 3.83 (d, *J* = 13.3 Hz, 1H), 3.62 – 3.53 (m, 2H), 3.16 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 171.8, 170.4, 153.3, 137.2, 129.1, 128.5, 127.3, 62.3, 61.4, 42.2, 40.3, 37.5, 35.9, 14.2 ppm. IR (ZnSe): 2983, 2925, 1767, 1725, 1689, 1376, 1170, 1008, 709 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{20}NO_5S$ $(M+H)^+$ 338.1057, found 338.1060.

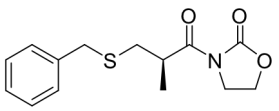
(+)-3-(3-(Benzylthio)-4,4,4-trifluorobutanoyl)oxazolidin-2-one (4d):



Product was obtained as a white solid (158 mg, 0.474 mmol, 95% yield). mp = 77–78 °C. Reaction time: 20 h. 75:25 *er* determined by HPLC (Daicel ChiralCel® OD-H, hexane/*i*PrOH = 85:15, flow rate = 0.5 mL/min, λ = 220 nm, t_R(major) = 36.4 min, t_R(minor) = 45.7 min. $[\alpha]_D^{25}$ = +18.7 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.36 – 7.31 (m, 4H), 7.28 (m, 1H), 4.42 – 4.33 (m, 2H), 3.98 (ddd, *J* = 11.0, 8.9, 6.9 Hz, 1H), 3.95 – 3.88 (m, 3H), 3.73 (m, 1H), 3.37 (dd, *J* = 17.5, 10.0 Hz, 1H), 3.29 (dd, *J* = 17.5, 4.0 Hz, 1H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 168.4, 153.2, 136.7, 129.2, 128.6, 127.5, 126.8 (q, *J* = 278.7 Hz), 62.2, 42.4, 42.2 (q, *J* = 30.2 Hz), 37.4, 35.3(q, *J* = 2.1 Hz) ppm. ^{19}F NMR (470 MHz, $CDCl_3$):

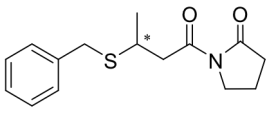
δ_F –70.64 (d, J = 8.4 Hz, 3F) ppm. IR (ZnSe): 2929, 1792, 1687, 1392, 1223, 1120, 954, 709, 653 cm^{-1}. HRMS (ESI) calcd for $C_{14}H_{15}F_3NO_3S$ $(M+H)^+$ 334.0719, found 334.0721.

(+)-(*R*)-3-(3-(Benzylthio)-2-methylpropanoyl)oxazolidin-2-one (4e):[19]



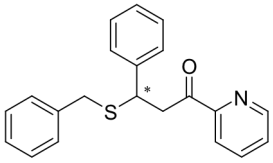
Product was obtained as a white solid (92 mg, 0.329 mmol, 66% yield). mp = 46–47 °C. Reaction time: 130 h. 64:36 *er* determined by HPLC (Daicel ChiralCel® OD-H, hexane/*i*PrOH = 70:30, flow rate = 1.0 mL/min, λ = 254 nm, t_R(*S*) = 12.6 min, t_R(*R*) = 16.1 min. $[\alpha]_D^{25}$ = +20.2 (*c* = 1.0, $CHCl_3$) (litt.[19] $[\alpha]_D^{25}$ = +60.2 (*c* = 1.0, $CHCl_3$), 82% *ee*; litt.[20] $[\alpha]_D^{20}$ = +58.8 (*c* = 1.09, $CHCl_3$), 68% *ee*). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.32 – 7.28 (m, 4H), 7.23 (m, 1H) 4.40 – 4.35 (m, 2H), 4.10 – 3.94 (m, 3H), 3.75 (d, J = 13.7 Hz, 1H), 3.71 (d, J = 13.7 Hz, 1H), 2.81 (dd, J = 13.4, 8.5 Hz, 1H), 2.44 (dd, J = 13.4, 5.8 Hz, 1H), 1.20 (d, J = 6.9 Hz, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 175.8, 153.2, 138.2, 128.9, 128.5, 127.0, 62.0, 42.7, 37.6, 36.4, 34.3, 17.4 ppm. IR (ZnSe): 2968, 2923, 1766, 1690, 1380, 1182, 1000, 753, 696 cm^{-1}.

(+)-1-(3-(Benzylthio)butanoyl)pyrrolidin-2-one (4f):



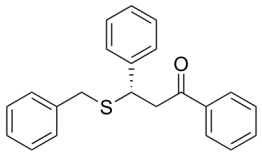
Product was obtained as a colorless oil (129 mg, 0.465 mmol, 93% yield). Reaction time: 20 h. 93:7 *er* determined by HPLC (Daicel ChiralPak® AS-H, hexane/*i*PrOH = 98:2, flow rate = 0.5 mL/min, λ = 220 nm, t_R(major) = 53.5 min, t_R(minor) = 57.8 min. $[\alpha]_D^{25}$ = +25.9 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.34 – 7.26 (m, 4H), 7.21 (tt, J = 7.3, 1.4 Hz, 1H), 3.82 – 3.71 (m, 4H), 3.27 – 3.19 (m, 2H), 3.05 (m, 1H), 2.57 – 2.52 (m, 2H), 2.03 – 1.95 (m, 2H), 1.31 (d, J = 6.6 Hz, 3H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 175.3, 171.8, 138.5, 128.8, 128.4, 126.8, 45.4, 44.1, 35.5, 35.3, 33.6, 21.6, 17.1 ppm. IR (ZnSe): 3027, 2926, 1734, 1685, 1359, 1248, 1189, 1025, 699 cm^{-1}. HRMS (ESI) calcd for $C_{15}H_{20}NO_2S$ $(M+H)^+$ 278.1209, found 278.1212.

(−)-3-(Benzylthio)-3-phenyl-1-(pyridin-2-yl)propan-1-one (4g):



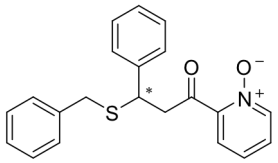
Product was obtained as a yellow oil (140 mg, 0.420 mmol, 84% yield). Reaction time: 15 h. 52:48 *er* determined by HPLC (Daicel ChiralPak® AD-H, hexane/*i*PrOH = 85:15, flow rate = 0.5 mL/min, λ = 220 nm, t_R(major) = 13.1 min, t_R(minor) = 14.6 min. $[\alpha]_D^{25}$ = –8.9 (*c* = 0.25, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.64 (ddd, *J* = 4.7, 1.7, 0.9 Hz, 1H), 7.95 (dt, *J* = 7.8, 1.1 Hz, 1H), 7.77 (td, *J* = 7.7, 1.7 Hz, 1H), 7.44 – 7.41 (m, 3H), 7.34 – 7.29 (m, 2H), 7.27 – 7.19 (m, 6H), 4.51 (m, 1H), 3.88 (dd, *J* = 17.4, 7.9 Hz, 1H), 3.80 (dd, *J* = 17.4, 6.9 Hz, 1H), 3.59 (d, *J* = 13.3 Hz, 1H), 3.50 (d, *J* = 13.3 Hz, 1H) ppm. ^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 198.4, 153.0, 148.9, 142.0, 137.9, 136.8, 129.0, 128.4, 128.4, 128.2, 127.2, 127.2, 126.7, 121.9, 44.2, 44.1, 35.7 ppm. IR (ZnSe): 3058, 3025, 2917, 1694, 1331, 1224, 994, 760, 693 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{19}NOSNa$ $(M+Na)^+$ 356.1080, found 356.1088.

(−)-(*S*)-3-(benzylthio)-1,3-diphenylpropan-1-one (4h):[20]



Product was obtained as a white solid (120 mg, 0.361 mmol, 72% yield) mp = 63–65 °C (litt. mp = 60–62 °C).[20] Reaction time: 26 h. 65:35 *er* determined by HPLC (Daicel ChiralCel® OJ-H, hexane/*i*PrOH = 80:20, flow rate = 1.0 mL/min, λ = 225 nm, t_R(*S*) = 18.7 min, t_R(*R*) = 28.5 min. $[\alpha]_D^{25}$ = –53.3 (*c* = 0.5, CH_2Cl_2) (litt.[21] $[\alpha]_D^{25}$ = –193.1 (*c* = 0.5, CH_2Cl_2), >99% *ee*; litt.[22] $[\alpha]_D^{25}$ = –67.5 (*c* = 1.0, CH_2Cl_2), 54% *ee*). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 7.88 – 7.85 (m, 2H), 7.54 (m, 1H), 7.44 – 7.39 (m, 4H), 7.35 – 7.21 (m, 8H), 4.48 (dd, *J* = 7.8, 6.4 Hz, 1H), 3.58 (d, *J* = 13.5, Hz, 1H), 3.55 (dd, *J* = 17.0, 8.0 Hz, 1H), 3.52 (d, *J* = 13.5 Hz, 1H), 3.48 (dd, *J* = 17.0, 6.3 Hz, 1H) ppm.^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 196.7, 141.8, 137.9, 136.7, 133.2, 128.9, 128.6, 128.5, 128.4, 128.1, 128.1, 127.3, 127.0, 45.3, 44.2, 35.9 ppm. IR (ZnSe): 3025, 2928, 1680, 1595, 1448, 1226, 981, 766, 686 cm^{-1}.

(−)-2-(3-(Benzylthio)-3-phenylpropanoyl)pyridine 1-oxide (4i):

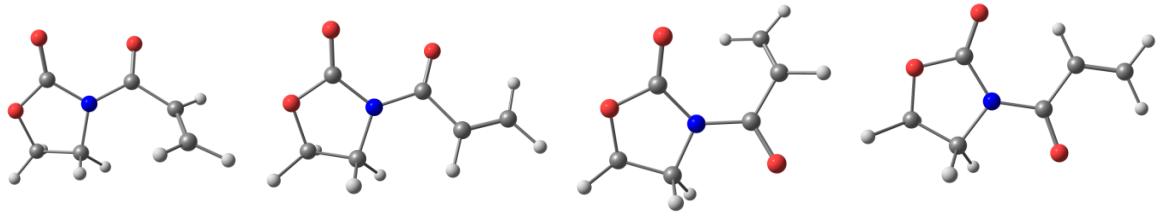


Product was obtained as a yellow solid (158 mg, 0.452 mmol, 90% yield) mp = 92–94 °C. Reaction time: 15 h. 62:38 *er* determined by HPLC (Daicel ChiralPak® AD-H, hexane/*i*PrOH = 70:30, flow rate = 0.5 mL/min, λ = 220 nm, t_R(major) = 17.6 min, t_R(minor) = 21.1 min. $[\alpha]_D^{25}$ = –45.5 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 8.09 (ddd, *J* = 6.5, 1.2, 0.6 Hz, 1H), 7.38 – 7.15 (m, 13H), 4.33 (m, 1H), 3.85 (dd, *J* = 16.9, 7.5 Hz, 1H), 3.70 (dd, *J* = 16.9, 7.8 Hz, 1H), 3.55 (d, *J* = 13.4 Hz, 1H), 3.46 (d, *J* = 13.4 Hz, 1H) ppm.^{13}C{H} NMR (100 MHz, $CDCl_3$): δ_C 194.9, 146.6, 141.3, 140.2, 137.8, 128.9, 128.5, 128.4, 128.0, 127.8, 127.3, 127.0, 126.9, 125.3, 49.1, 44.3, 35.6 ppm. IR (ZnSe): 3057, 3026, 2920, 1684, 1427, 1246, 1075, 759, 696 cm^{-1}. HRMS (ESI) calcd for $C_{21}H_{19}NO_2SNa$ $(M+Na)^+$ 372.1029, found 372.1038.

Computational Study

Structure optimizations were carried out without restrictions using the B3LYP functional [23] as implemented in the Gaussian09 software package.[24] Unless otherwise stated, the doubly charged iron complexes were treated in their quintet spin state.[25] The SDD basis set and associate effective core potential was used for iron,[26] and the 6-31+G(d) basis set for the other elements.[27] Vibrational frequency calculations were performed to establish that the stationary points are minima. Single point energies of the optimized structures were recalculated with the SDD basis set for iron and cc-pVTZ basis set [28] for other atoms. The results presented are Gibbs free energies at 298.15 K under 1 atm (ΔG_{298}) in kcal/mol.

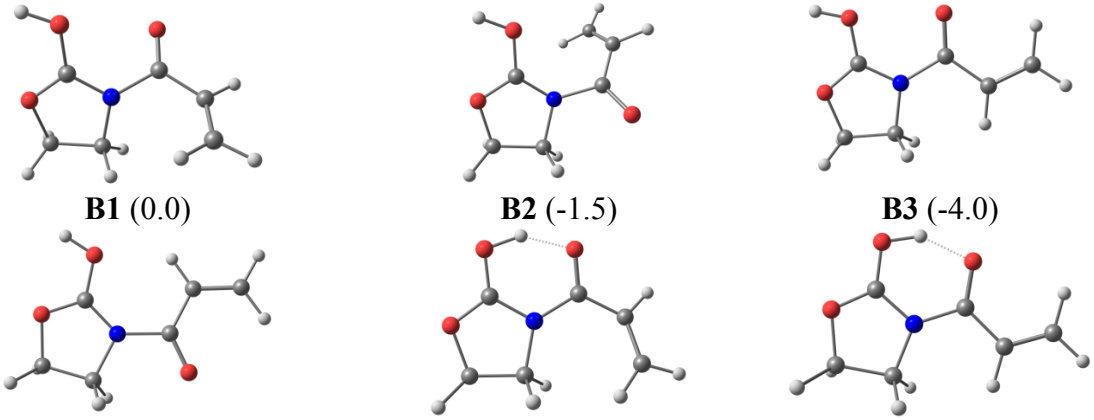
To validate the level of theory, a first set of computations was carried out using 3-acryloyloxazolidin-2-one **A** as model substrate (Figure S1). The expected preferred conformation for this compound is the one with the two carbonyls pointing in opposite directions to avoid electronic repulsion between them, and a *s-cis* conformation of the enone fragment to avoid electronic repulsion between the oxazolidinone carbonyl and the π cloud of the C=C bond. This isomer (**A4**) is indeed the most stable one.



A1 (0.0) **A2** (-2.9) **A3** (-5.8) **A4** (-11.0)

Figure S1. Computed isomers of 3-acryloyloxazolidin-2-one (**A1-4**) and their relative free energies

3-Acryloyloxazolidin-2-one was then protonated (Figure S2, isomers **B1-6**). In this case, one expects the two carbonyls to point in the same direction and a *s-cis* conformation of the enone fragment. This is again respected at our level of theory.

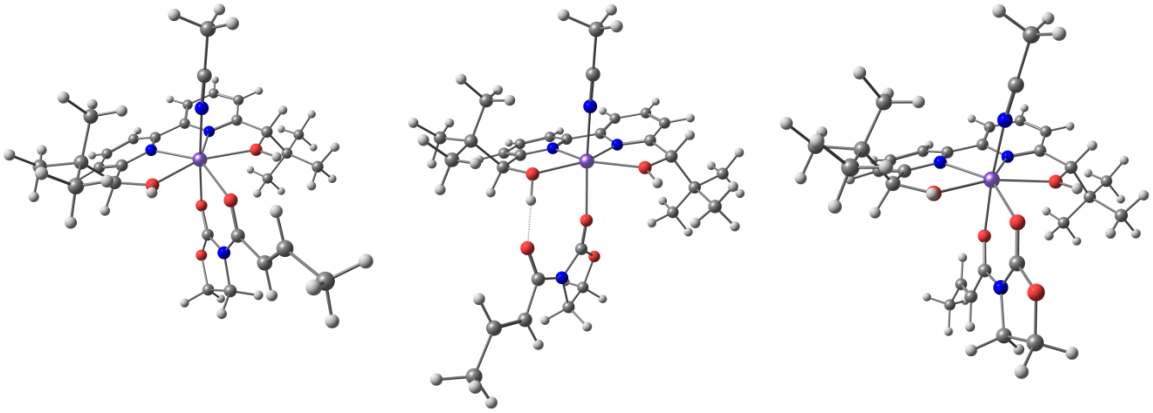


B1 (0.0) **B2** (-1.5) **B3** (-4.0)

B4 (-5.8) **B5** (-8.8) **B6** (-14.9)

Figure S2. Computed isomers of protonated 3-acryloyloxazolidin-2-one (**B1-6**) and their relative free energies.

The **B6**-type conformation was thus chosen for the iron complexes **IIa-c** exhibiting the (*E*)-3-but-2-enoyloxazolidin-2-one ligand (Figure S3). Complex **IIc** is the most stable one (see manuscript for the associated discussion).



IIa (3.0) **IIb** (3.5) **IIc** (0.0)

Figure S3. Computed isomers of the dicationic quintet spin state iron complexes **IIa-c** and their relative free energies.

Of note, the dicationic complex **IIc** was reoptimized at the singlet and triplet states, but the obtained structures proved far less stable ($\Delta\Delta G_{298}$ = 32.7 and 23.8 kcal/mol respectively).

Coordinates (x,y,z) and energies of complexes IIa–c:

IIa E(UB3LYP) = -1847.92842990				**IIb** E(UB3LYP) = -1847.92658394			
C	0.741747	1.652183	-2.129969	C	1.430672	-2.002635	-0.980518
C	1.062285	2.935616	-0.03383	C	3.641231	-1.640803	0.091741
C	1.432476	3.894467	-2.379501	C	3.181762	-3.340301	-1.787046
C	1.034448	3.274099	-3.730685	C	1.998809	-3.32642	-2.76675
C	1.532494	4.213636	0.511314	C	4.923504	-2.304916	0.333244
C	1.536228	4.446676	1.84155	C	5.850855	-1.739915	1.136863
C	2.000957	5.70524	2.488428	C	7.173285	-2.334918	1.473465
H	0.891364	4.821986	-2.184739	H	4.127201	-3.108471	-2.280058
H	2.508851	4.078379	-2.309401	H	3.270007	-4.295323	-1.258485
H	1.815063	3.33757	-4.48827	H	1.6452	-4.318192	-3.046308
H	0.098721	3.675529	-4.126274	H	2.193461	-2.731203	-3.66248
H	1.888527	4.980334	-0.167895	H	5.115589	-3.270173	-0.124404
H	1.170291	3.657622	2.498464	H	5.616803	-0.771235	1.577777
H	2.352167	6.447862	1.766881	H	7.33645	-3.306368	0.998584
H	2.812086	5.488896	3.197358	H	7.266752	-2.451414	2.562057
H	1.190554	6.14614	3.085128	H	7.980981	-1.652543	1.174716
N	1.030409	2.831391	-1.430612	N	2.789295	-2.263591	-0.853282
O	0.705871	1.989507	0.688418	O	0.730002	-1.31298	-0.253578
O	0.472991	0.551145	-1.676084	O	3.293243	-0.598631	0.651229
O	0.81734	1.868385	-3.439839	O	0.931353	-2.669586	-2.026055
C	-3.749816	-1.206327	-1.931259	C	0.598316	3.159528	-2.511512
C	-2.888691	-0.62236	-0.995198	C	0.52245	2.422884	-1.321715
C	-4.349009	2.316326	1.172179	C	3.284929	3.185805	1.371762
C	-1.498118	-2.497412	-1.028723	C	-1.688913	1.796862	-1.8069
C	-2.342535	-3.157668	-1.924341	C	-1.690062	2.547153	-2.98299
C	-3.472788	-2.490226	-2.394686	C	-0.521199	3.223177	-3.339642
C	-0.236359	-3.091477	-0.522134	C	-2.83302	0.977401	-1.332497
C	5.026321	-2.617228	0.13035	C	-4.559144	-3.680461	0.683272
C	1.843491	-2.643722	0.439578	C	-3.472685	-0.71264	0.16262
C	2.137582	-4.010366	0.513923	C	-4.813564	-0.577736	-0.217084
C	1.210309	-4.927596	0.024479	C	-5.143045	0.341149	-1.212162
C	0.012946	-4.466067	-0.5213	C	-4.141951	1.11954	-1.795454
C	-3.154976	0.758059	-0.414832	C	1.683598	2.28541	-0.337671
C	-4.32994	0.869514	0.6226	C	2.123022	3.579371	0.433533
C	4.891753	-0.172517	0.619649	C	-2.443646	-4.06229	1.950183
C	2.822542	-1.578577	0.910355	C	-3.014458	-1.717913	1.211672

C	4.11362	-1.376282	0.03826	C	-3.08635	-3.23482	0.810573
C	3.755983	-1.105686	-1.433826	C	-2.347799	-3.502664	-0.512327
C	-5.680091	0.616912	-0.081759	C	2.63648	4.655938	-0.545655
C	-4.162713	-0.125865	1.784042	C	0.9608	4.155468	1.261344
H	5.110465	-0.303074	1.688016	H	-2.890652	-3.836233	2.926979
H	3.091817	-0.241743	-1.536413	H	-1.300885	-3.189191	-0.466362
H	3.260487	-1.966333	-1.897123	H	-2.819953	-2.98115	-1.352868
H	4.666998	-0.904025	-2.008135	H	-2.370333	-4.574466	-0.738542
H	-4.610363	-0.66173	-2.301378	H	1.516332	3.659551	-2.794135
H	-2.103994	-4.150883	-2.287075	H	-2.560169	2.579387	-3.629081
H	-4.123969	-2.962804	-3.123979	H	-0.481164	3.787657	-4.266576
H	3.065357	-4.351156	0.957407	H	-5.585997	-1.166723	0.262008
H	1.414659	-5.992991	0.07409	H	-6.176466	0.459246	-1.524287
H	-0.722567	-5.167807	-0.89771	H	-4.38964	1.846405	-2.56084
H	-3.391901	1.437205	-1.245998	H	2.557573	1.933418	-0.901862
H	-2.020734	1.959452	0.711636	H	2.051082	0.558964	0.631781
H	3.143889	-1.833083	1.93027	H	-3.631432	-1.580225	2.110288
H	2.541879	0.346247	1.409109	H	-1.270729	-1.999272	2.147049
H	-6.498761	0.845507	0.608443	H	3.109468	5.46214	0.024664
H	-5.810612	1.25618	-0.964051	H	3.394506	4.262594	-1.235593
H	-5.802148	-0.427272	-0.383897	H	1.831379	5.113039	-1.12921
H	-4.983051	-0.002519	2.499865	H	1.294473	5.055857	1.788921
H	-3.22187	0.034518	2.319524	H	0.614695	3.436008	2.008753
H	-4.184339	-1.164193	1.434152	H	0.109841	4.441156	0.630698
H	-5.234254	2.462319	1.799463	H	3.63958	4.069818	1.912479
H	-4.394679	3.060309	0.366634	H	4.13593	2.782044	0.808281
H	-3.488753	2.547128	1.817444	H	2.978366	2.441361	2.11234
H	5.988927	-2.395678	-0.342227	H	-4.598614	-4.769038	0.572291
H	4.608957	-3.481124	-0.394926	H	-5.048619	-3.257784	-0.19882
H	5.233846	-2.90241	1.169731	H	-5.14894	-3.423822	1.572409
H	5.852742	-0.067934	0.105585	H	-2.599884	-5.129578	1.763752
H	4.363485	0.780068	0.480403	H	-1.354175	-3.931536	2.01906
N	-1.771682	-1.248265	-0.588674	N	-0.595083	1.748204	-1.01383
N	0.663167	-2.210124	-0.032104	N	-2.526699	0.076322	-0.369851
O	-1.892066	1.181041	0.148084	O	1.331113	1.241012	0.607573
O	2.044576	-0.363254	0.976265	O	-1.656297	-1.331186	1.55847
Fe	-0.070446	-0.138742	0.321405	Fe	-0.590354	0.311516	0.576152
N	-0.537149	-0.551293	2.430861	N	-1.359607	1.536825	2.203649
C	-0.723752	-0.830453	3.539084	C	-1.749325	2.147048	3.10701
C	-0.970421	-1.183116	4.932973	C	-2.229143	2.925523	4.24239
H	-2.048451	-1.23328	5.118778	H	-1.634369	3.839728	4.341515
H	-0.527988	-2.159319	5.156831	H	-3.278804	3.199174	4.093553
H	-0.529842	-0.431842	5.596366	H	-2.138746	2.340677	5.163599

IIc E(UB3LYP) = -1847.92932447				
C	-0.476993	2.790433	-1.493179	
C	-0.594088	2.547781	0.971173	
C	-0.793187	4.781508	-0.268674	
C	-0.965325	5.018861	-1.78072	
C	-0.695904	3.291713	2.228864	
C	-0.748479	2.647768	3.414954	
C	-0.85434	3.312122	4.743549	
H	-1.669546	5.107739	0.294059	
H	0.09913	5.273514	0.129682	
H	-0.311497	5.794163	-2.179311	
H	-1.999307	5.221887	-2.067666	
H	-0.73015	4.375264	2.203751	
H	-0.718373	1.558632	3.404889	
H	-0.874683	4.403035	4.672032	
H	-0.01311	3.014314	5.384522	
H	-1.761756	2.974147	5.262879	
N	-0.640607	3.310236	-0.207419	
O	-0.260516	1.631259	-1.820205	
O	-0.483007	1.313285	0.9317	
O	-0.581371	3.760649	-2.397848	
C	3.384815	-0.871348	2.339353	
C	2.684514	-0.551954	1.169806	
C	4.755891	1.128914	-1.720703	
C	0.9897	-2.065817	1.713062	
C	1.663414	-2.467258	2.869084	
C	2.867838	-1.843262	3.192634	
C	-0.324208	-2.62486	1.308011	
C	-5.385245	-1.733222	-0.146624	
C	-2.232289	-2.290728	0.004162	
C	-2.746911	-3.535753	0.385615	
C	-2.02119	-4.322379	1.277107	
C	-0.79992	-3.856809	1.763475	
C	3.218507	0.460562	0.167207	
C	4.448609	0.00639	-0.700014	
C	-4.788454	0.312908	-1.450367	
C	-2.980532	-1.361058	-0.940597	
C	-4.280687	-0.681014	-0.380259	
C	-3.995134	0.067661	0.934008	
C	5.693507	-0.164561	0.19637	
C	4.169771	-1.312028	-1.443569	

H	-4.943534	-0.175228	-2.42192	
H	-3.197889	0.807947	0.812865	
H	-3.700748	-0.620132	1.735338	
H	-4.897809	0.591535	1.267529	
H	4.310033	-0.362597	2.582909	
H	1.242517	-3.218495	3.527497	
H	3.393952	-2.108167	4.105021	
H	-3.687066	-3.890353	-0.019204	
H	-2.397656	-5.29415	1.582446	
H	-0.216583	-4.464035	2.446237	
H	3.528416	1.357935	0.721191	
H	2.385957	1.21904	-1.483343	
H	-3.262349	-1.93637	-1.833575	
H	-2.300733	0.118174	-2.118858	
H	6.575066	-0.323143	-0.433371	
H	5.887774	0.72561	0.807935	
H	5.615594	-1.034094	0.855569	
H	5.036194	-1.580007	-2.058079	
H	3.30162	-1.229332	-2.104723	
H	3.990647	-2.139856	-0.7482	
H	5.681438	0.896582	-2.257107	
H	4.8964	2.100656	-1.231062	
H	3.985793	1.237634	-2.498755	
H	-6.328355	-1.225781	0.081904	
H	-5.165573	-2.386887	0.702574	
H	-5.558811	-2.354644	-1.034478	
H	-5.753095	0.729862	-1.143193	
H	-4.109894	1.164172	-1.587534	
N	1.495493	-1.114738	0.894815	
N	-1.030326	-1.873091	0.434622	
O	2.084153	0.824574	-0.649921	
O	-2.008852	-0.367088	-1.332662	
Fe	0.072327	-0.208911	-0.548889	
N	0.579302	-1.431869	-2.308416	
C	0.762569	-2.057695	-3.265347	
C	1.003303	-2.84301	-4.470701	
H	2.066702	-3.09348	-4.545756	
H	0.423596	-3.771211	-4.436704	
H	0.709574	-2.27059	-5.356662	

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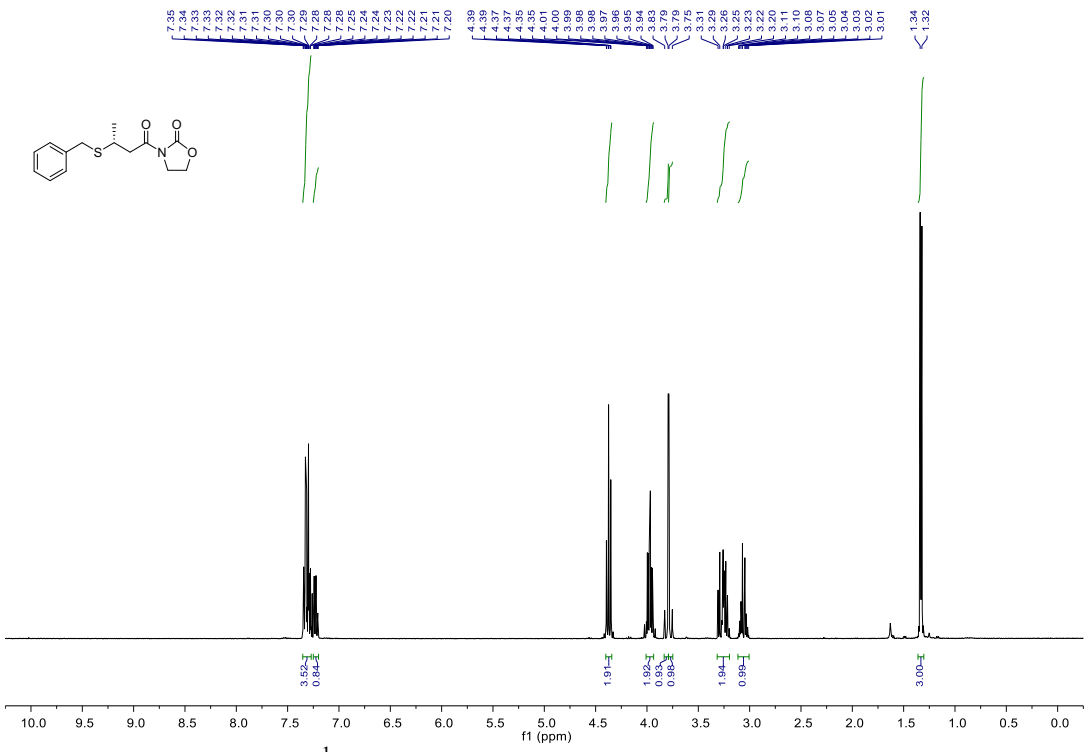
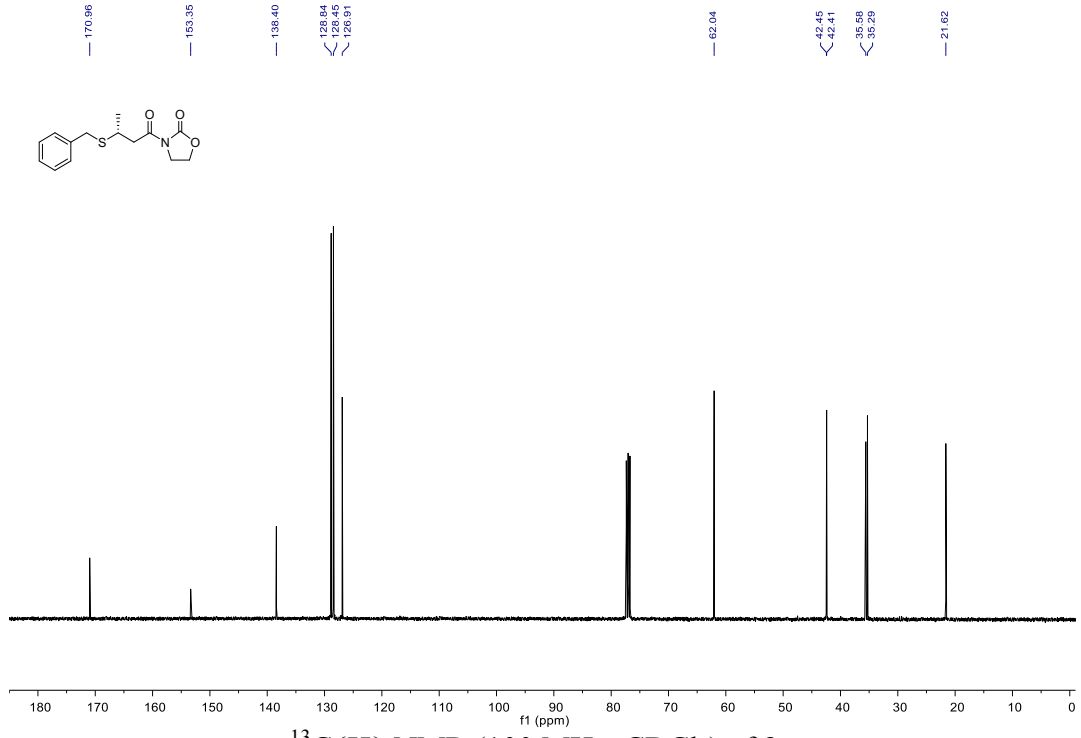
^{1}H and ^{13}C{H} NMR Spectra



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



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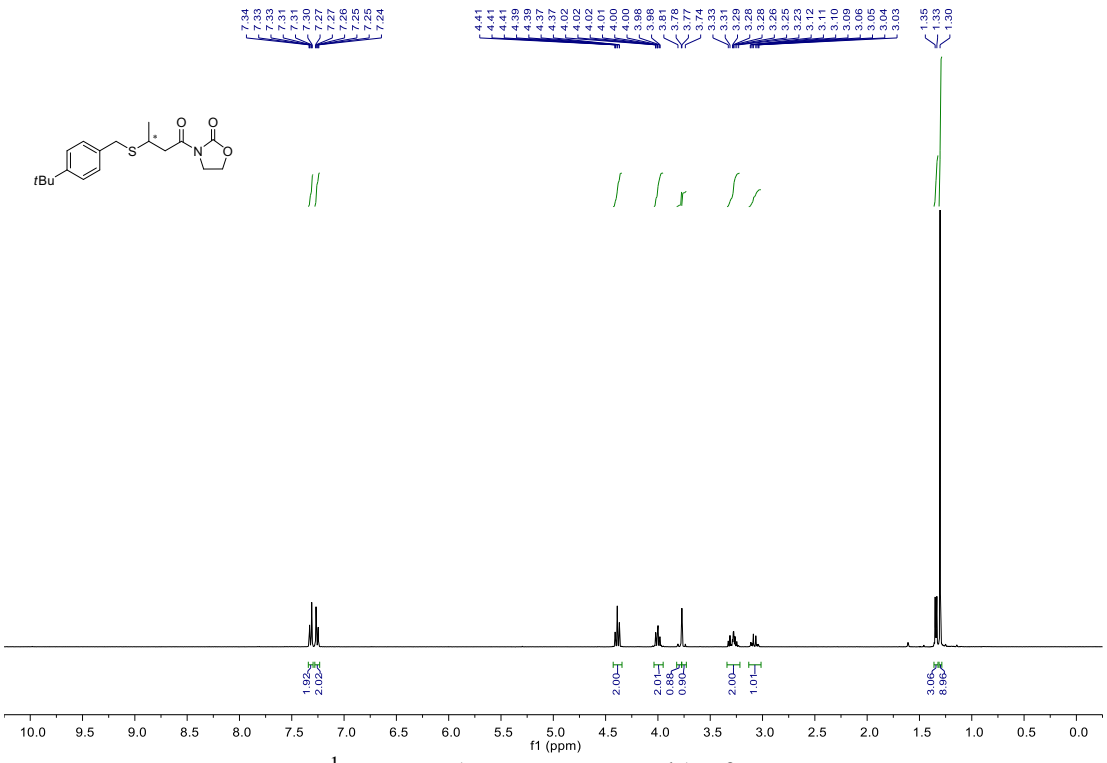

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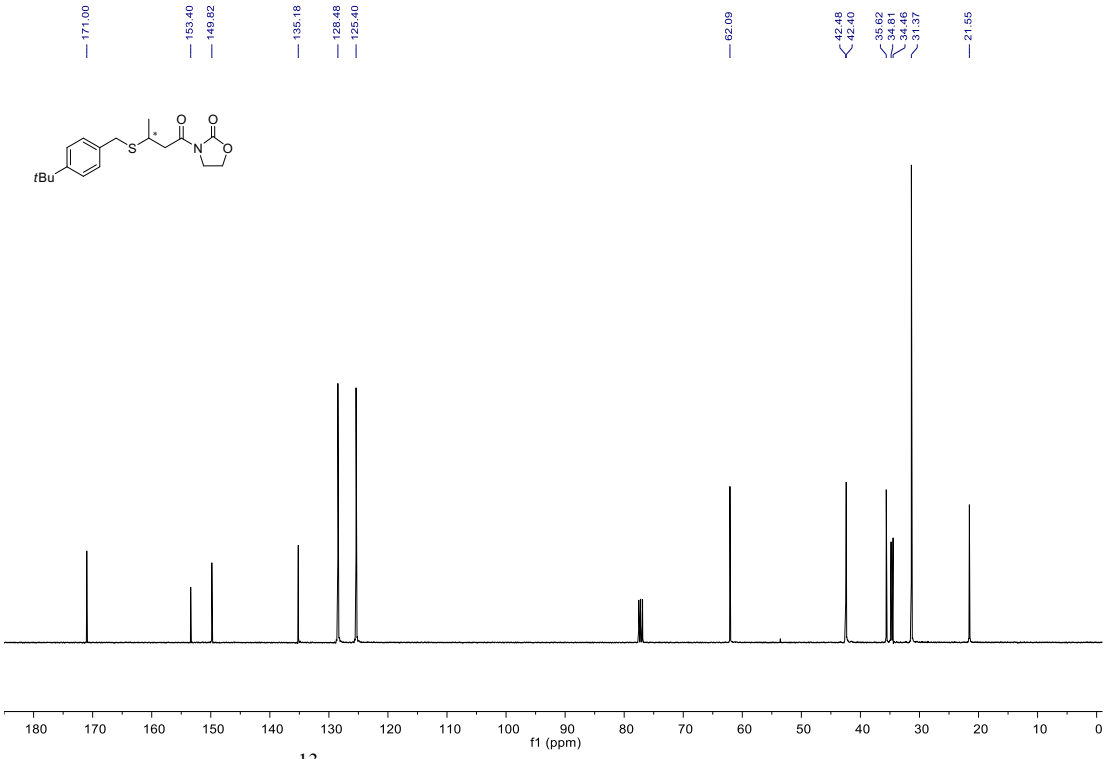

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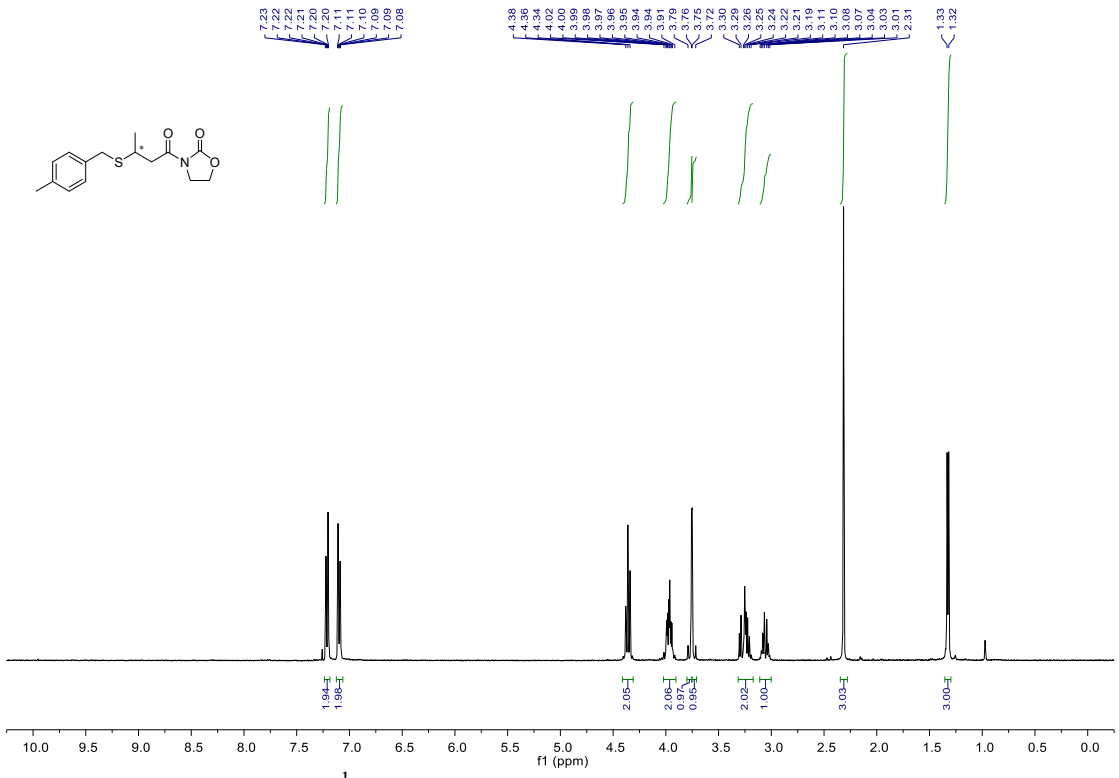

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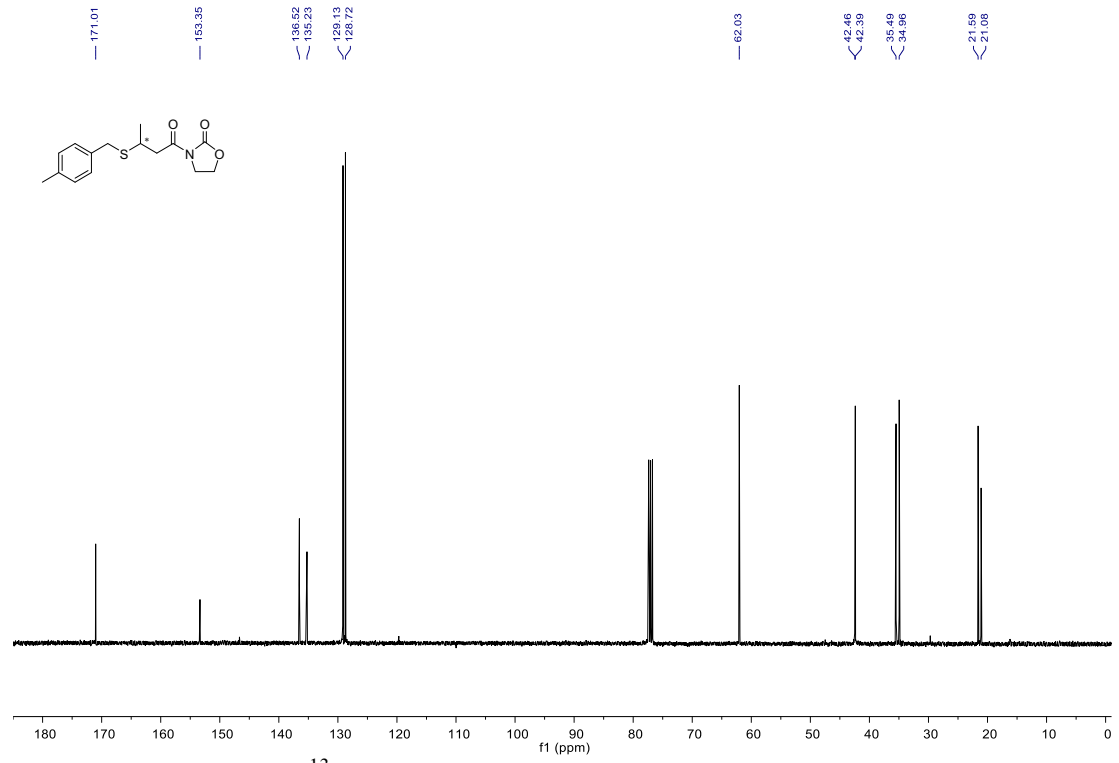

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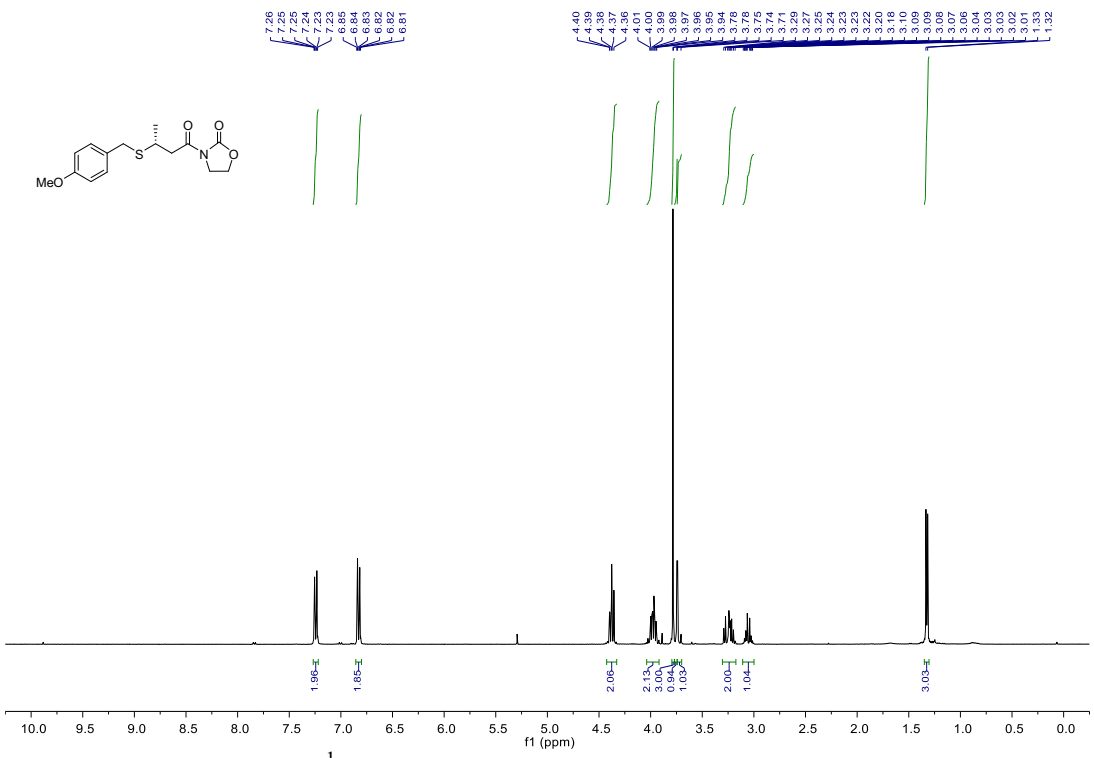

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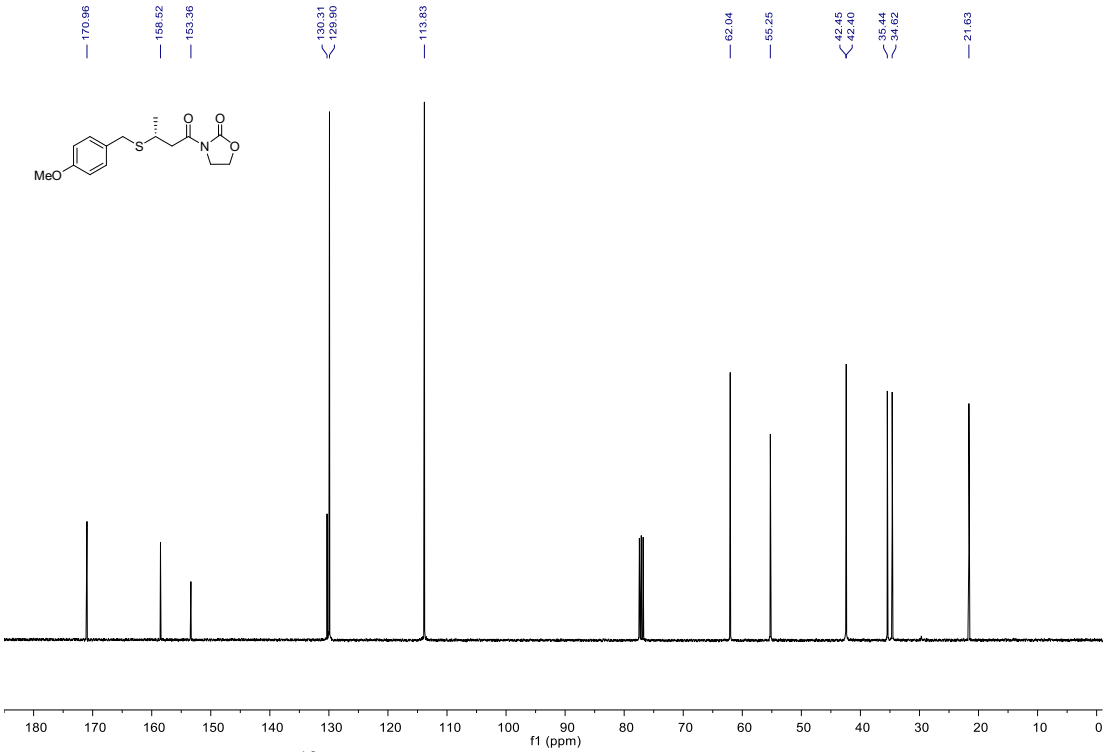

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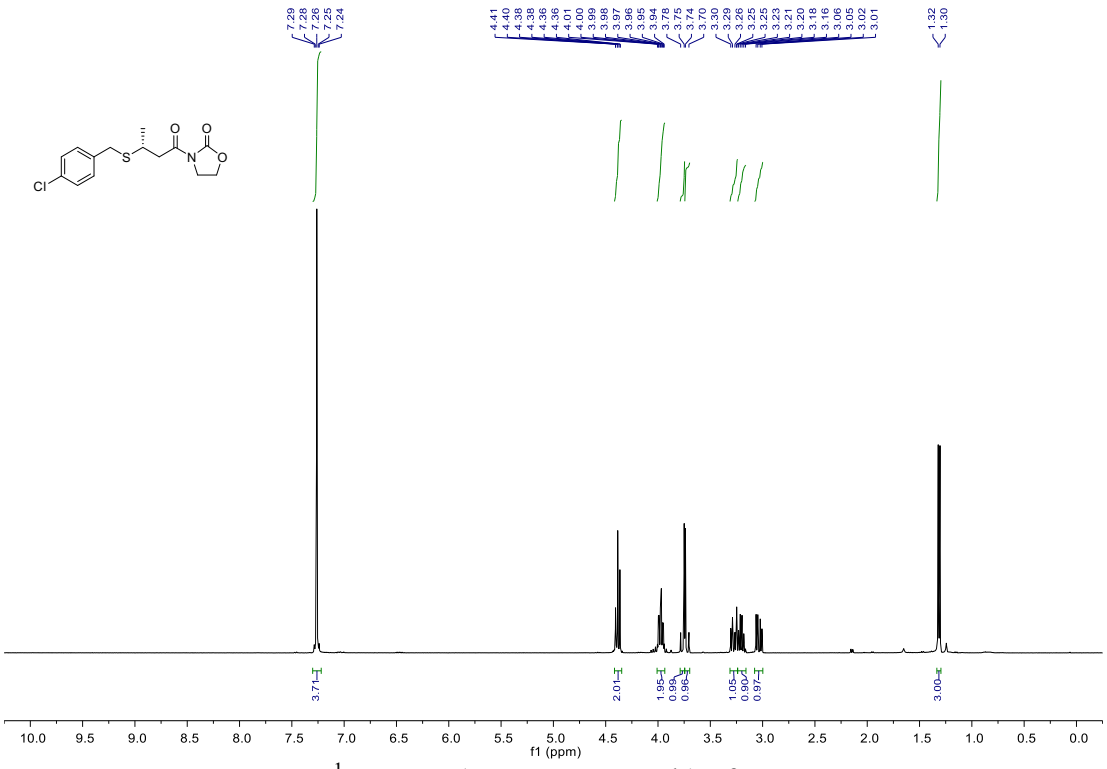

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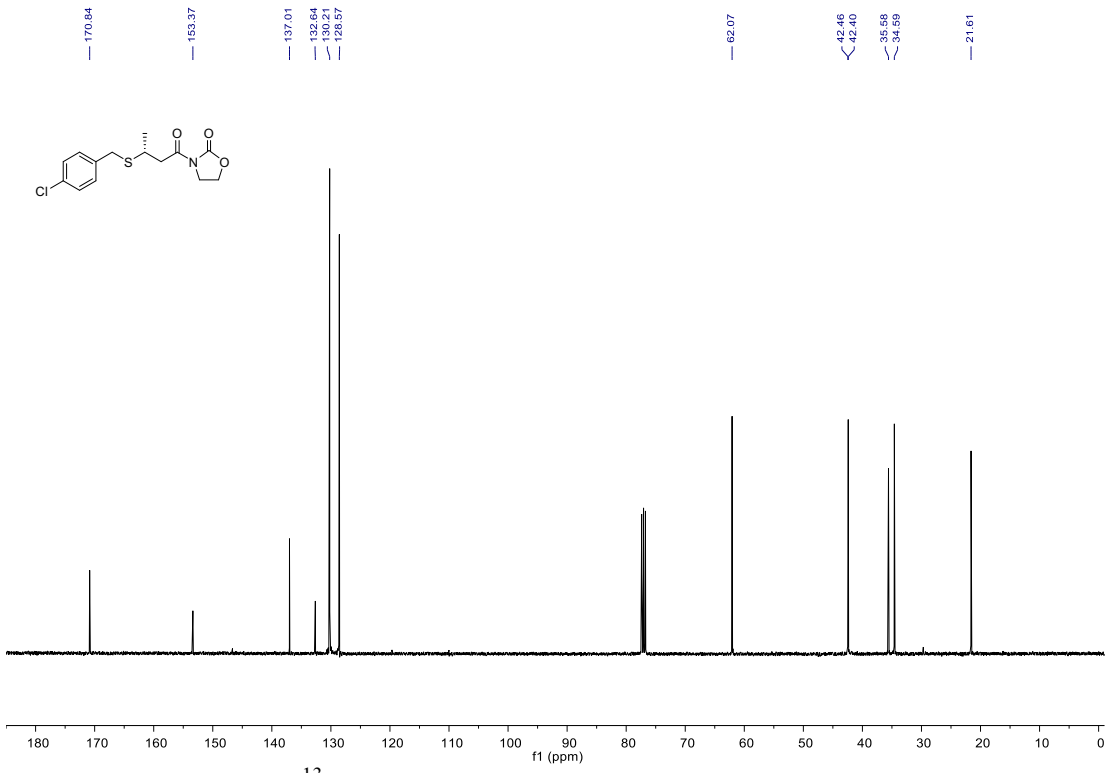

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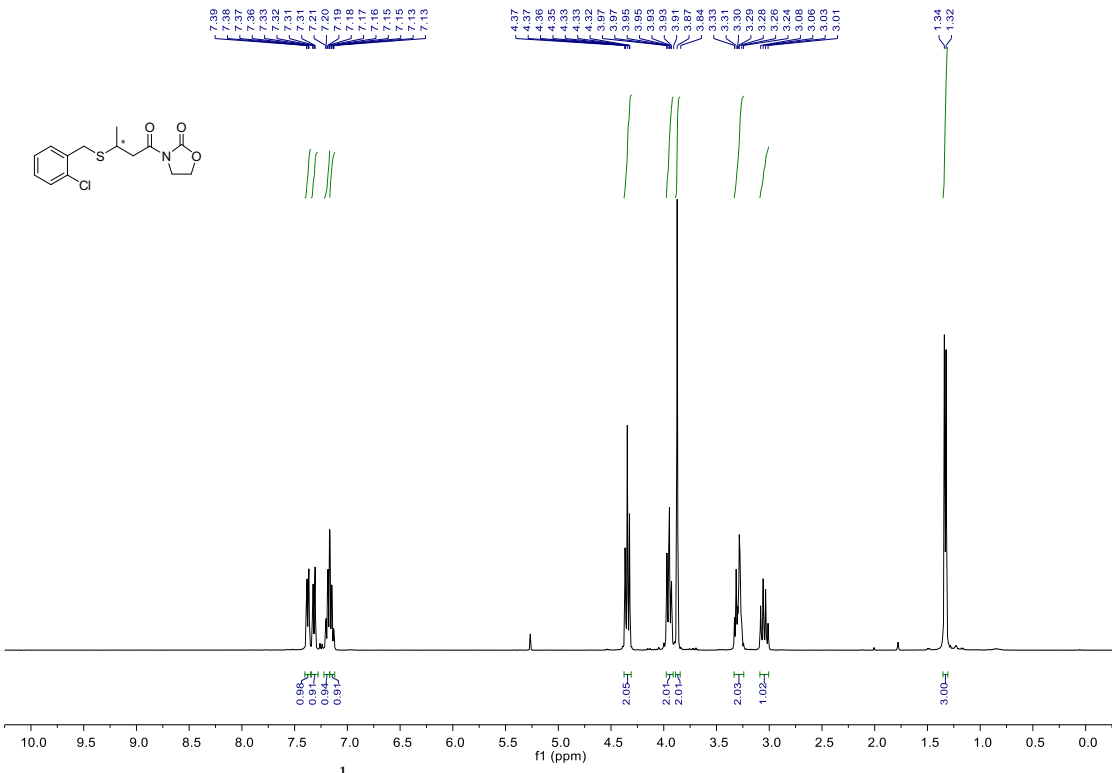

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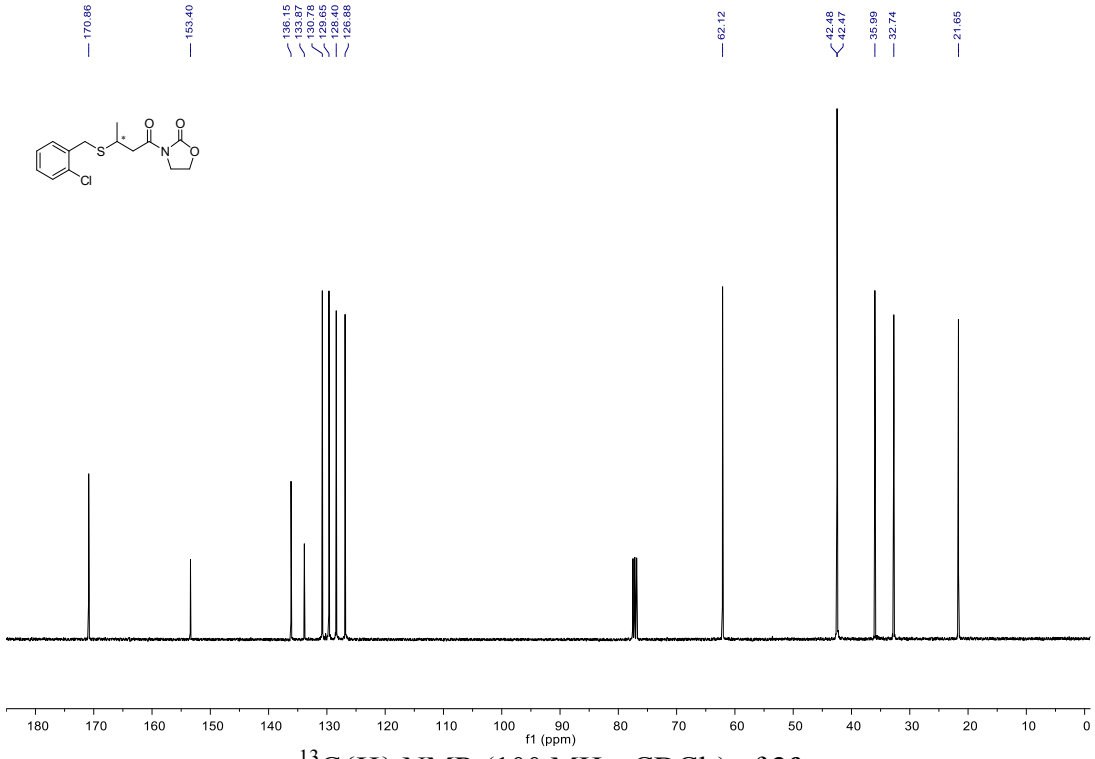

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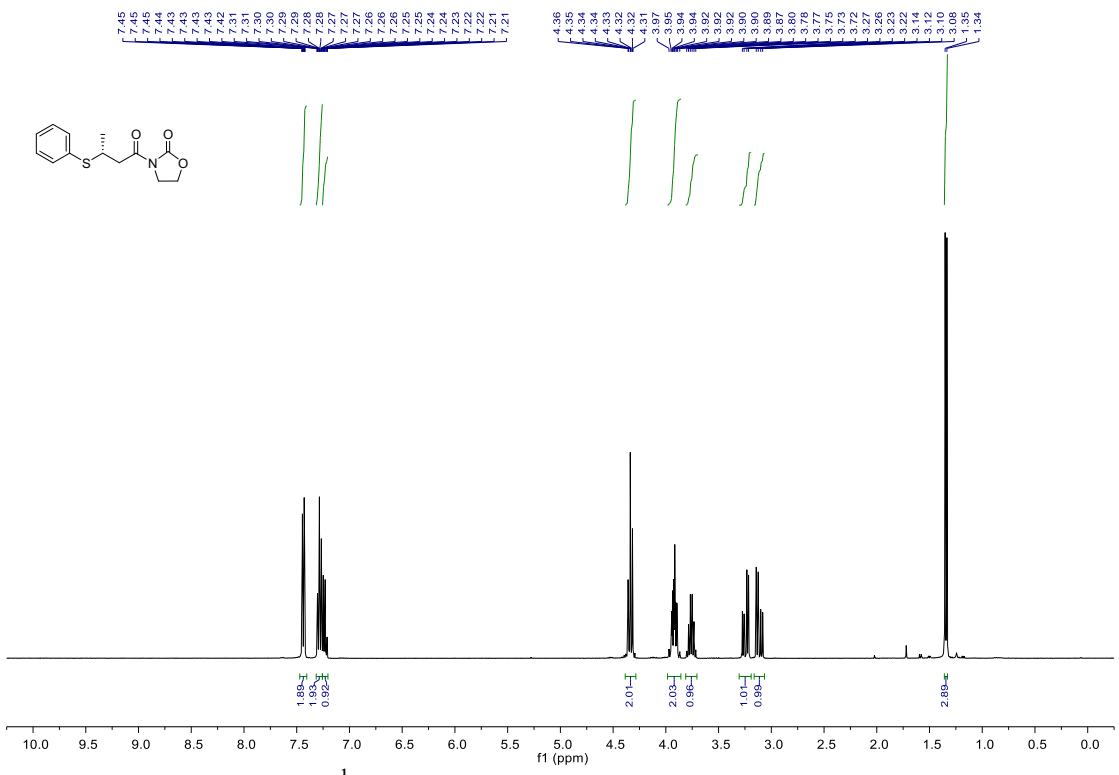

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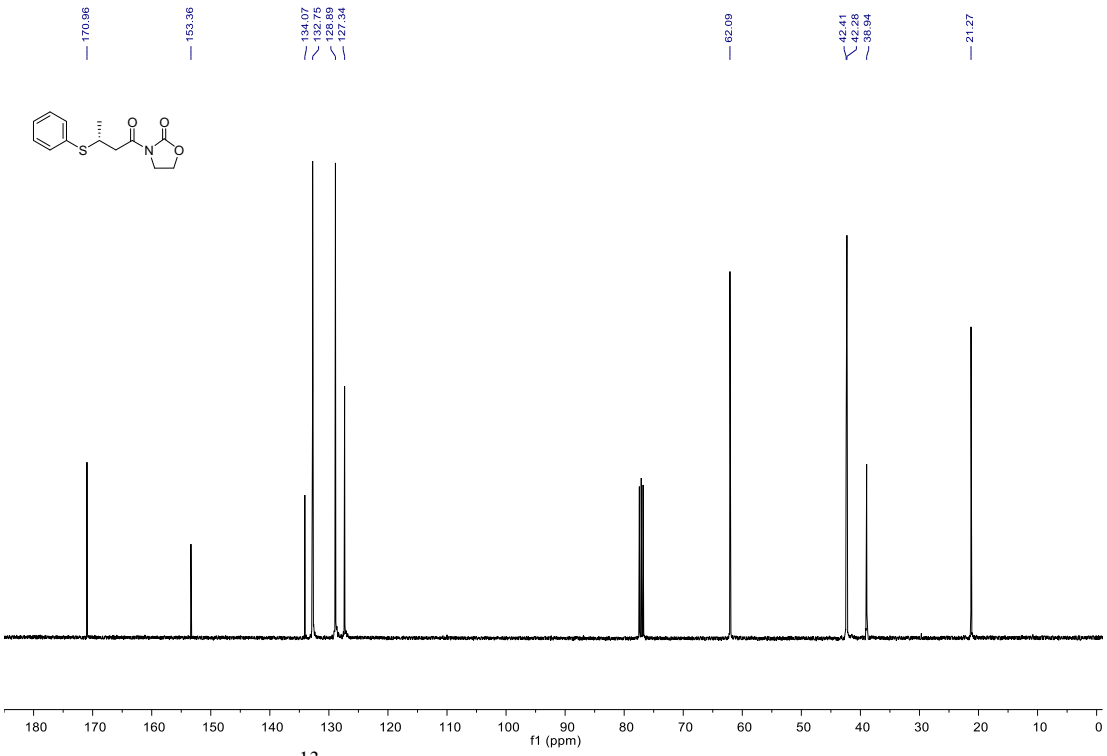

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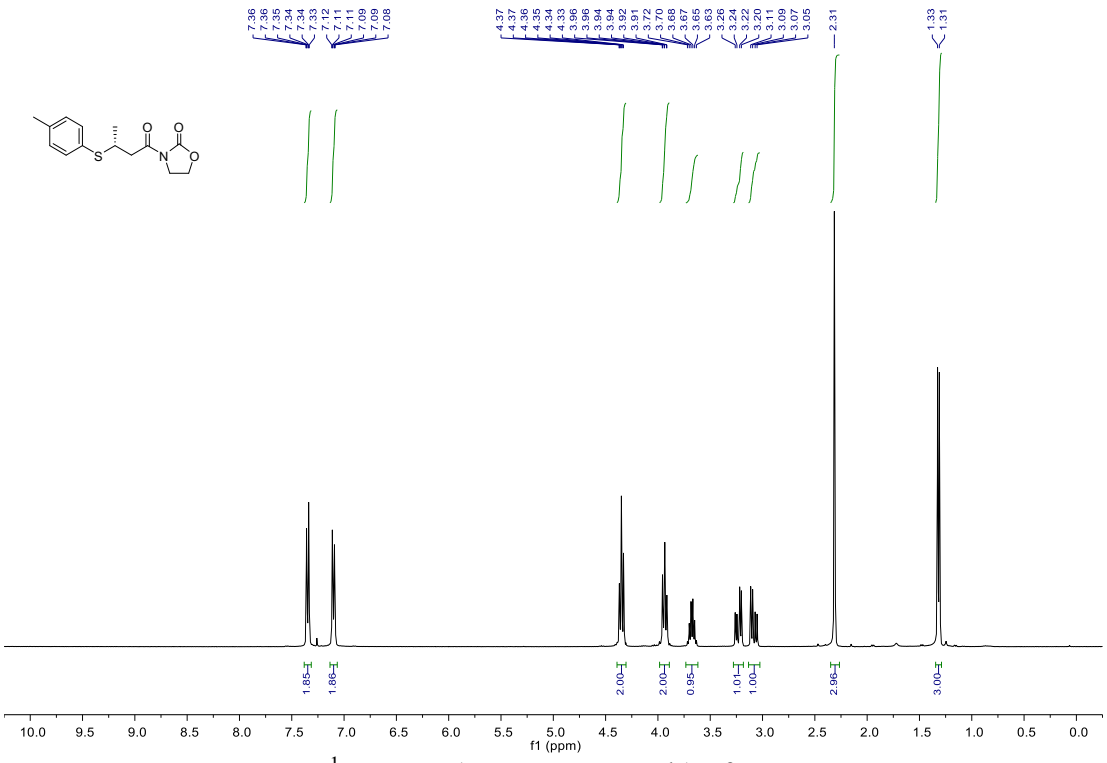

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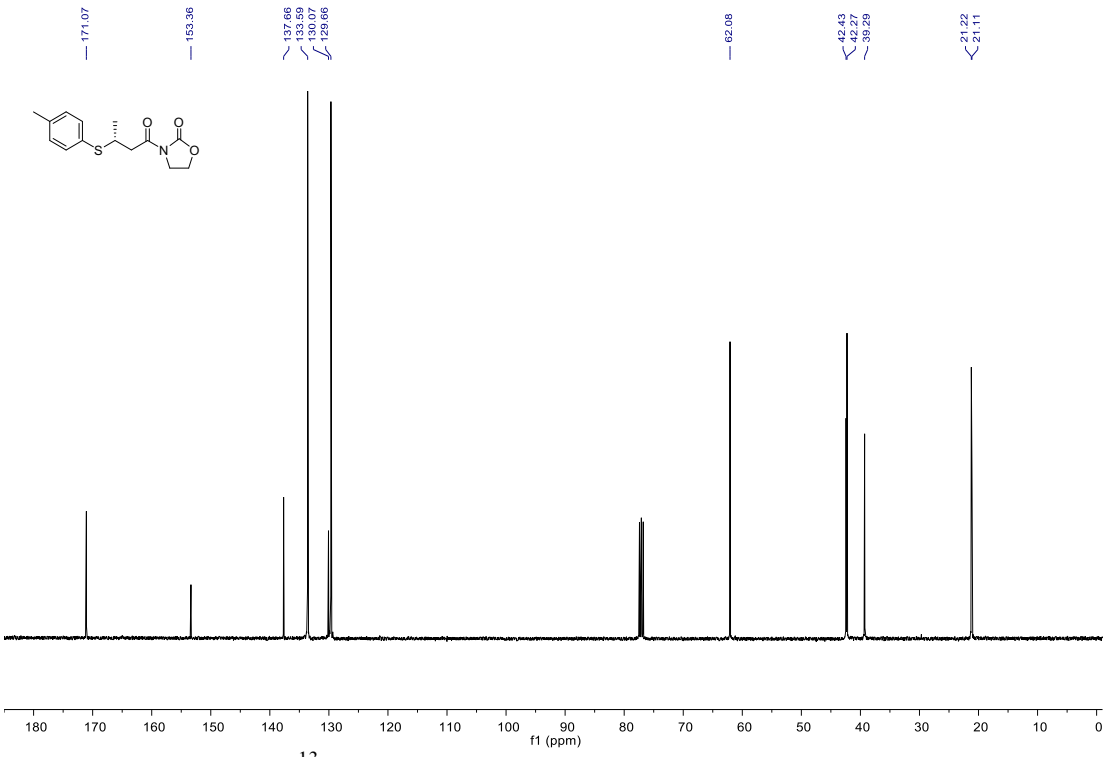

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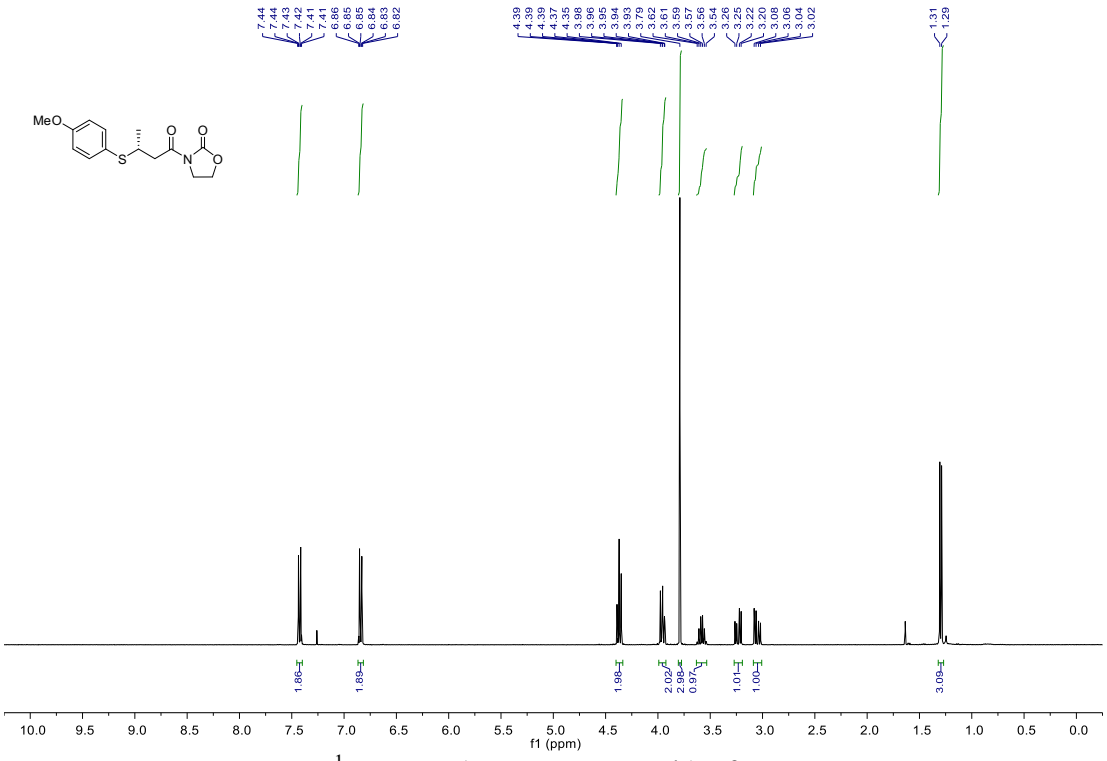

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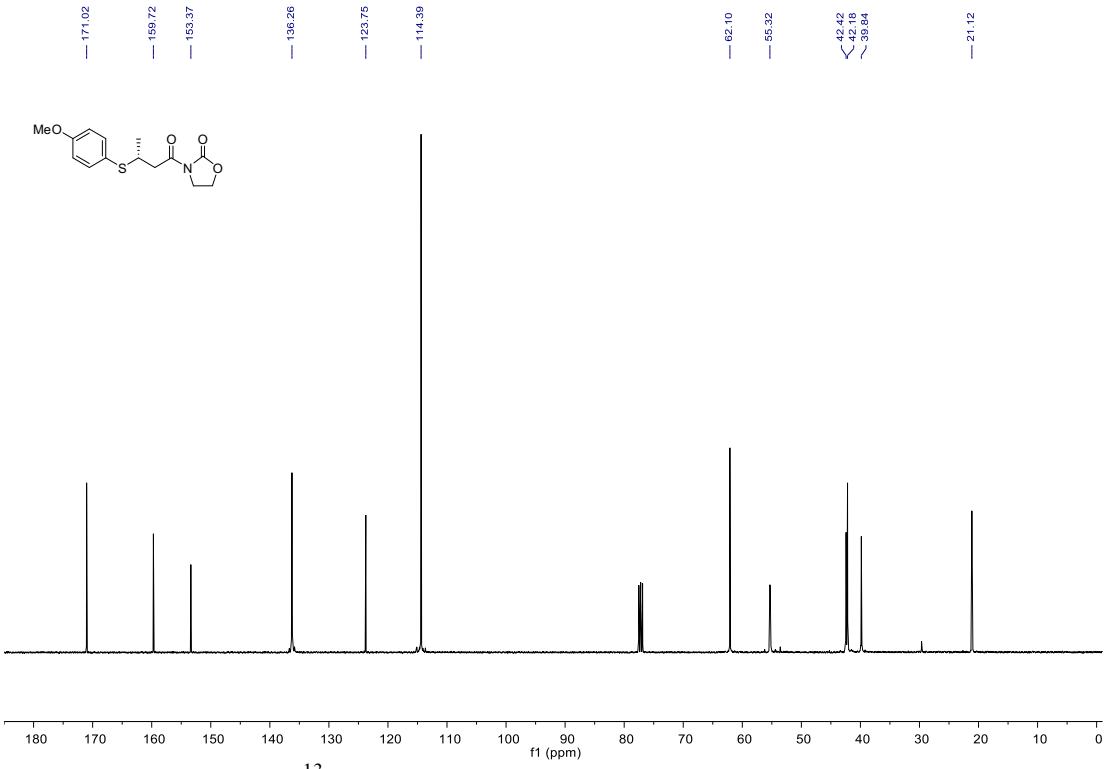

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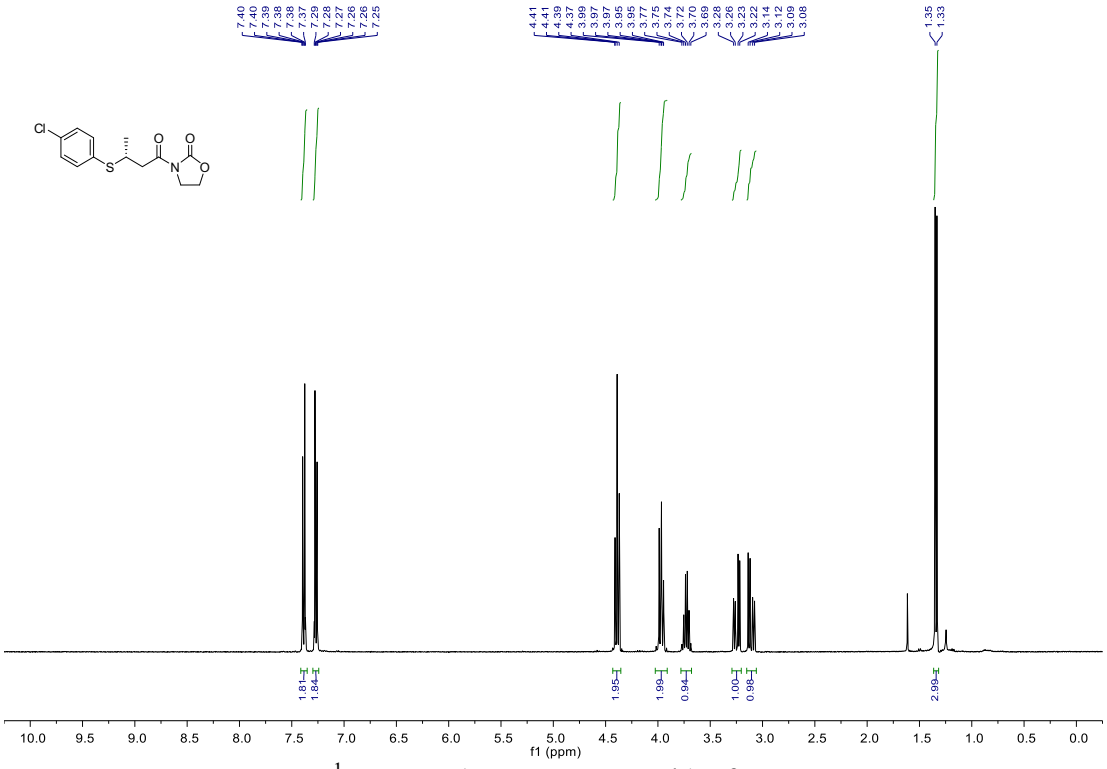

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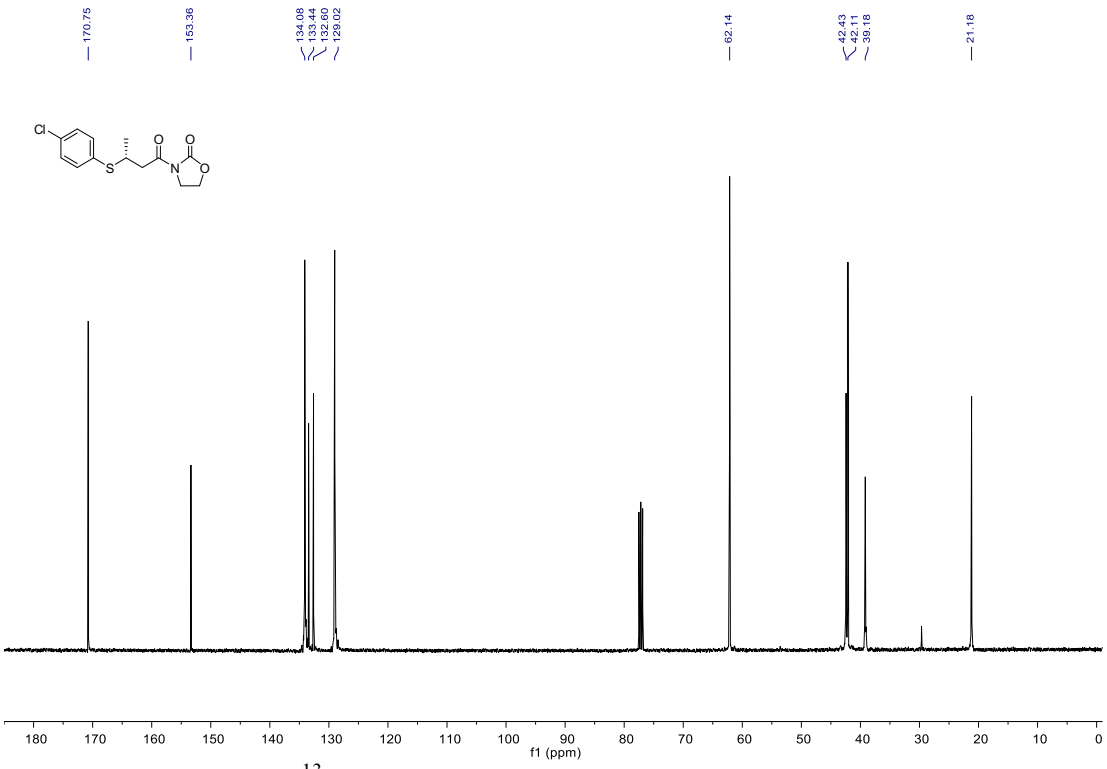

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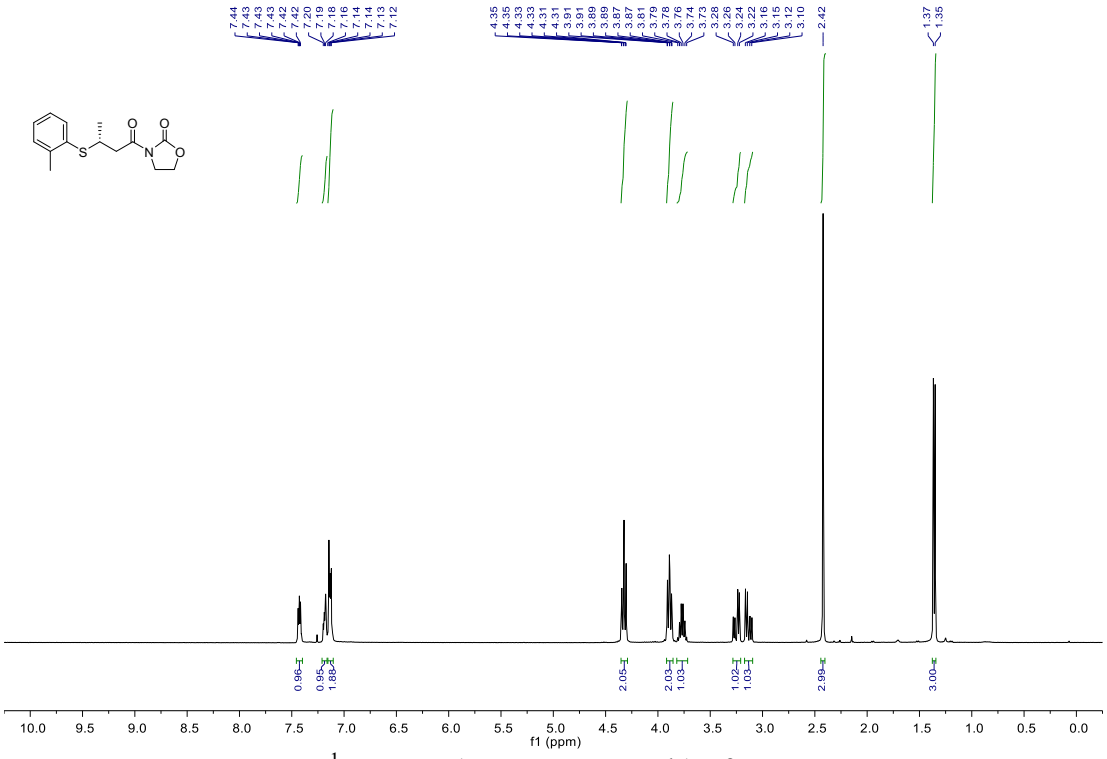

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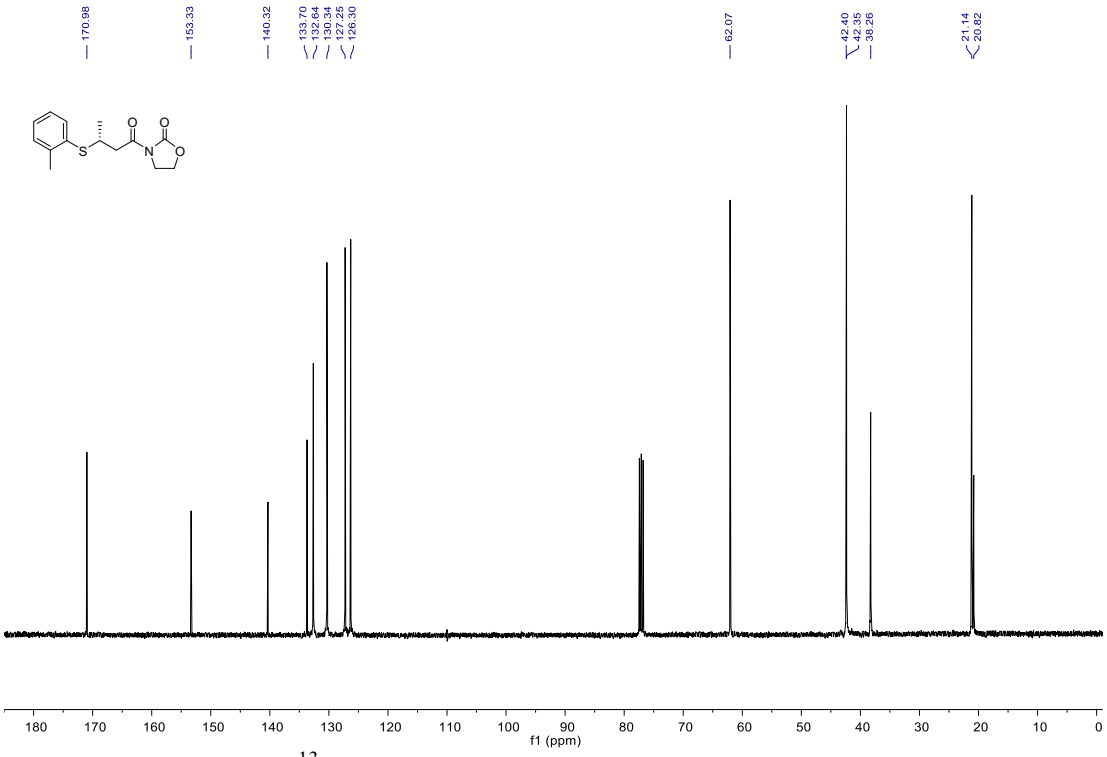

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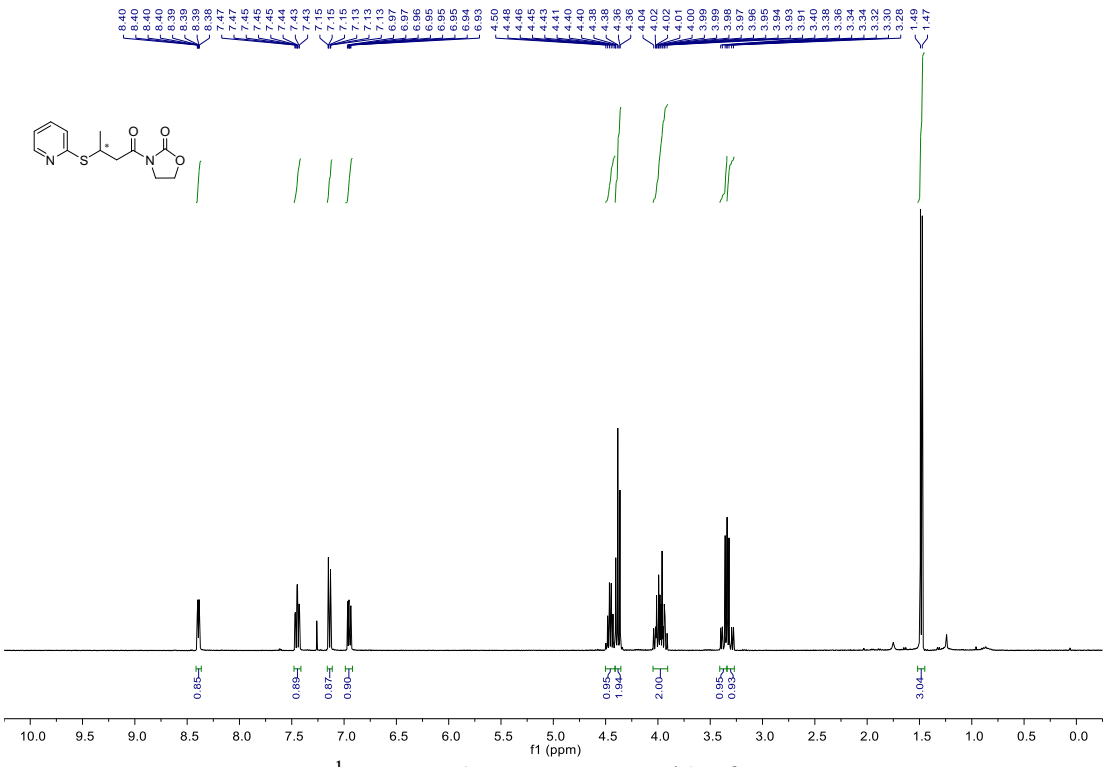

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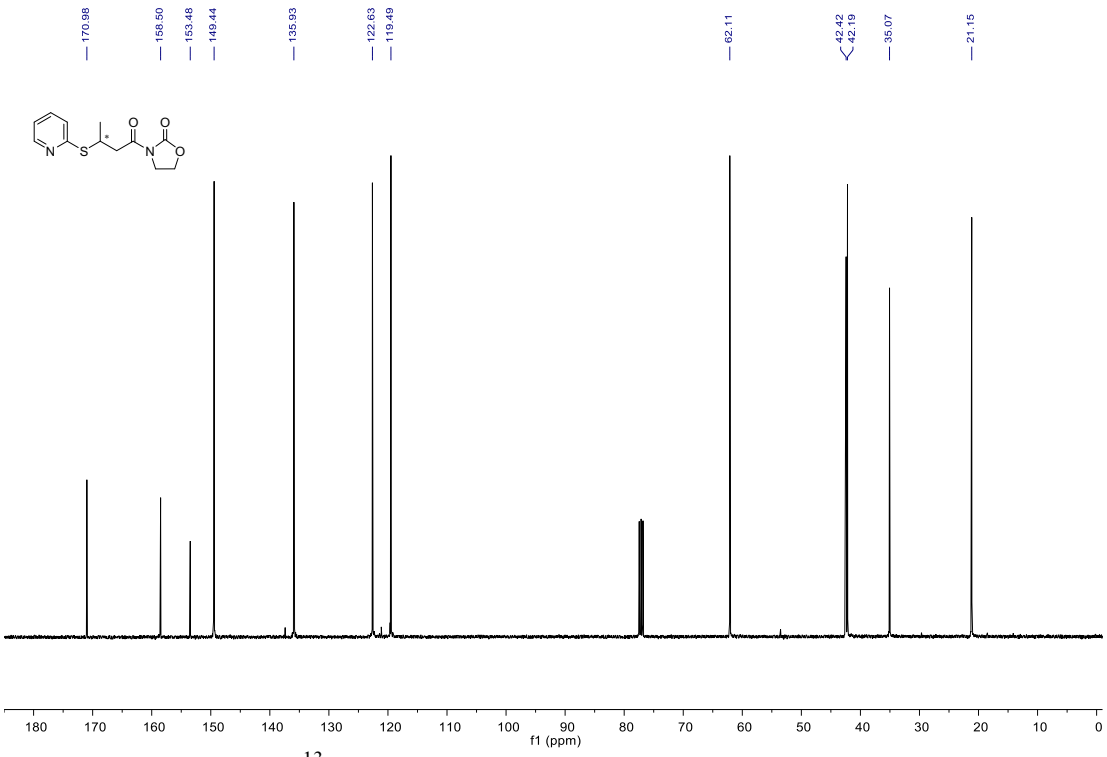

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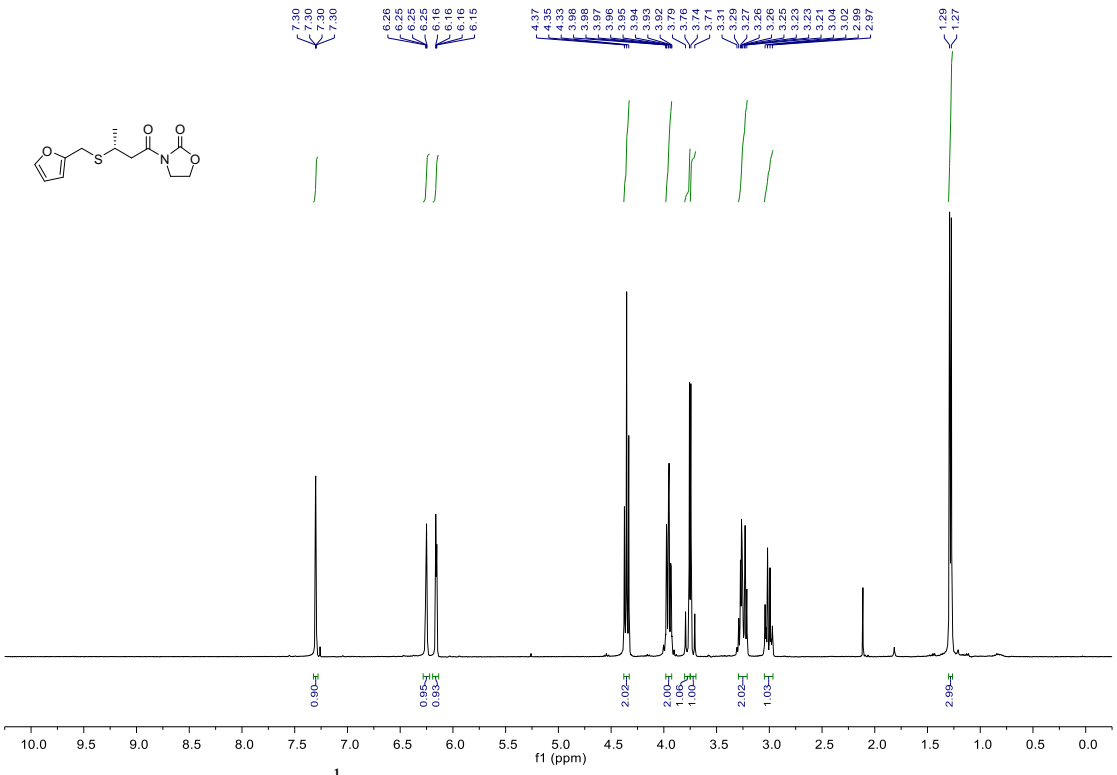

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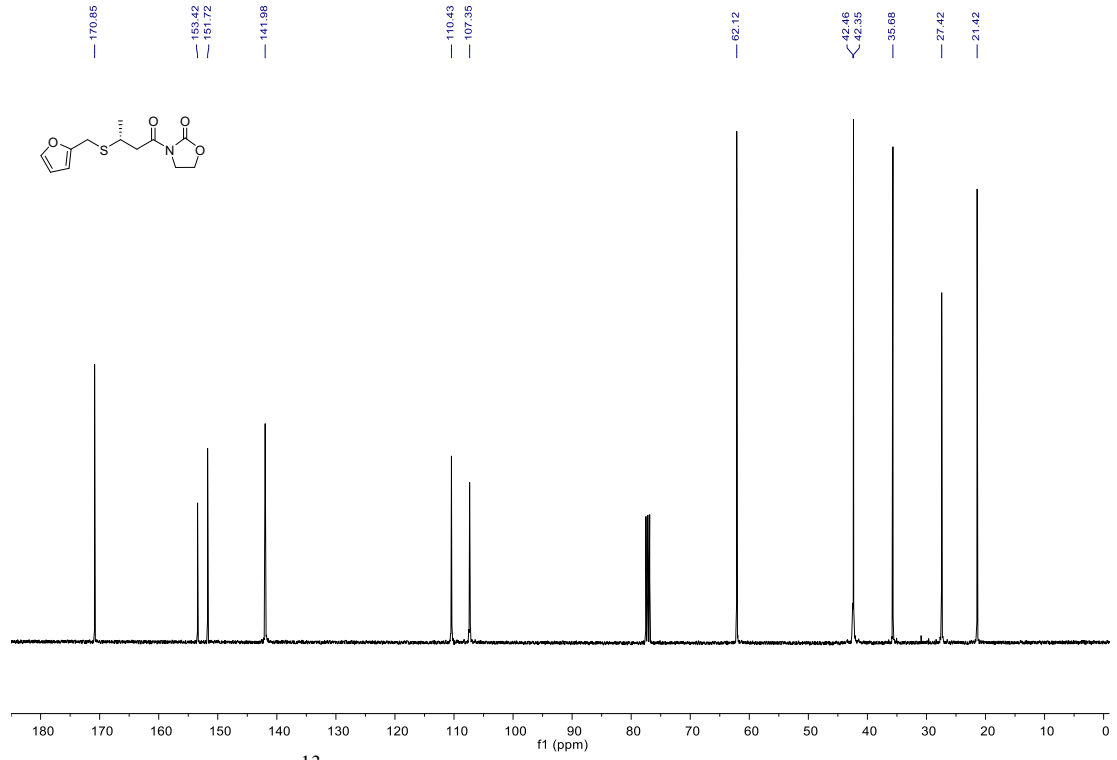

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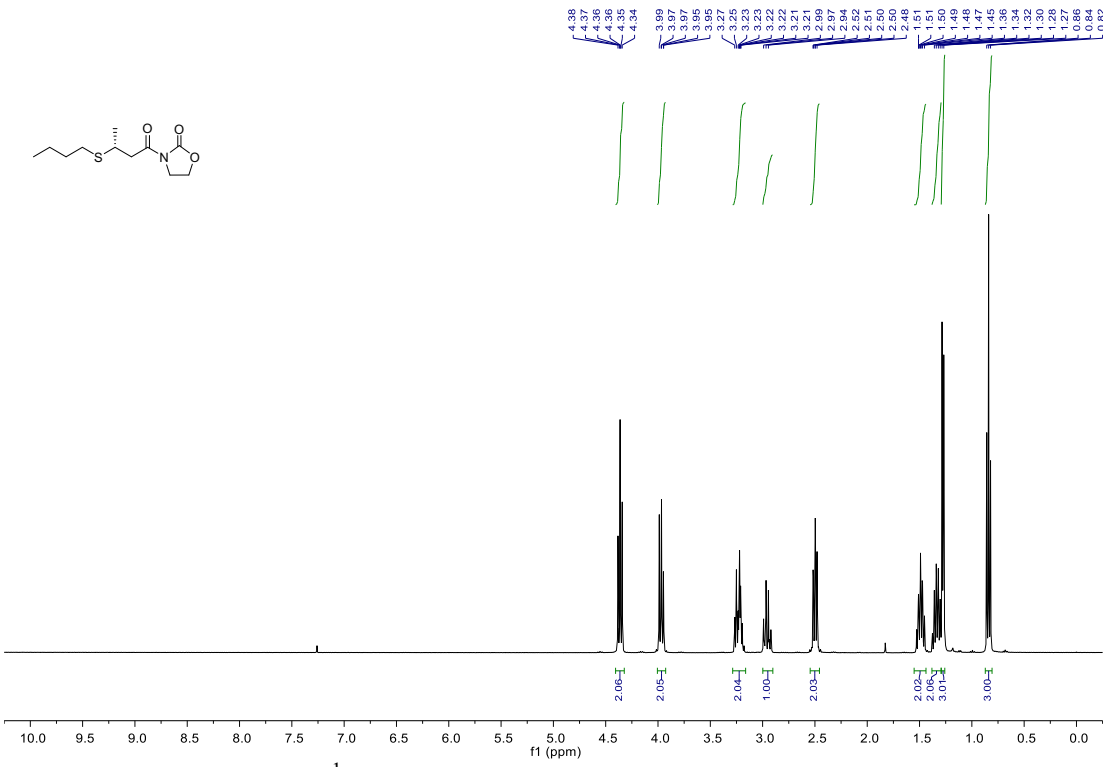

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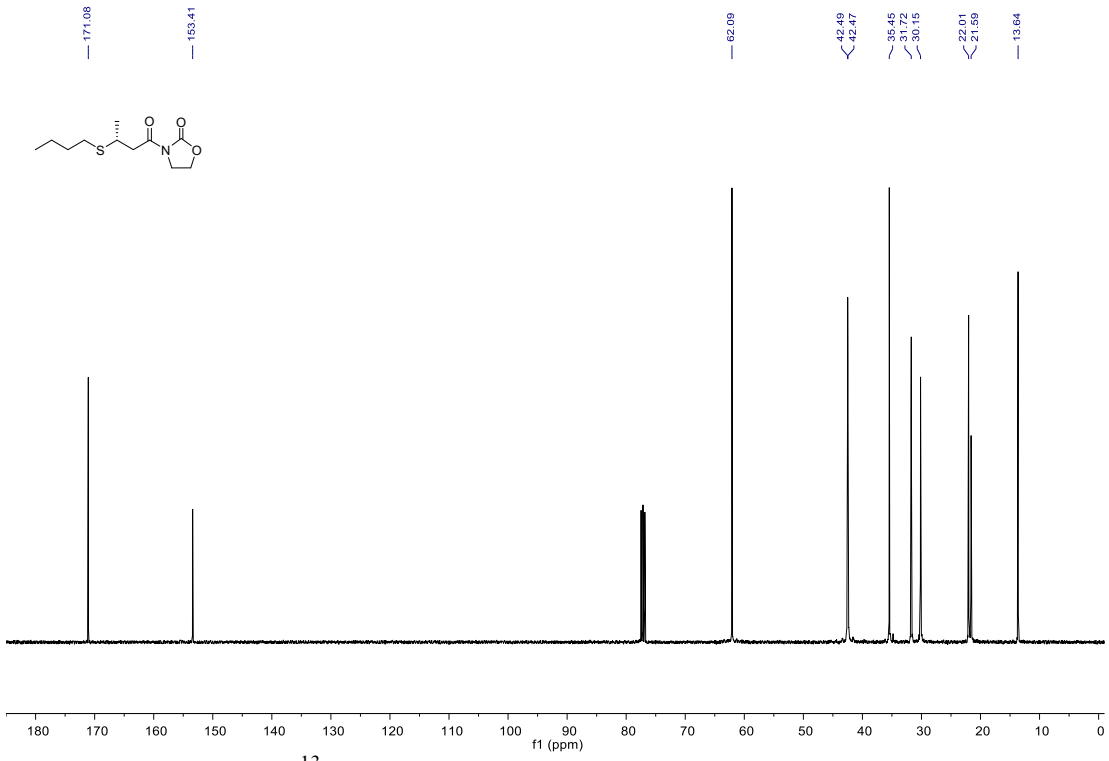

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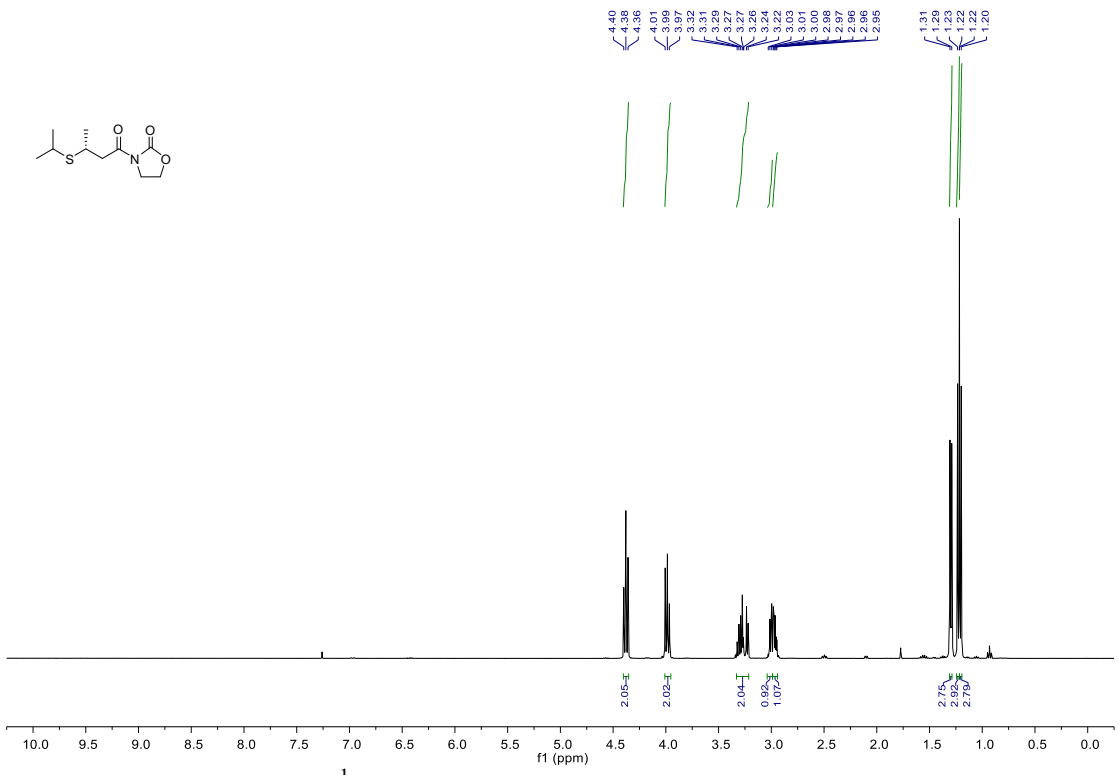

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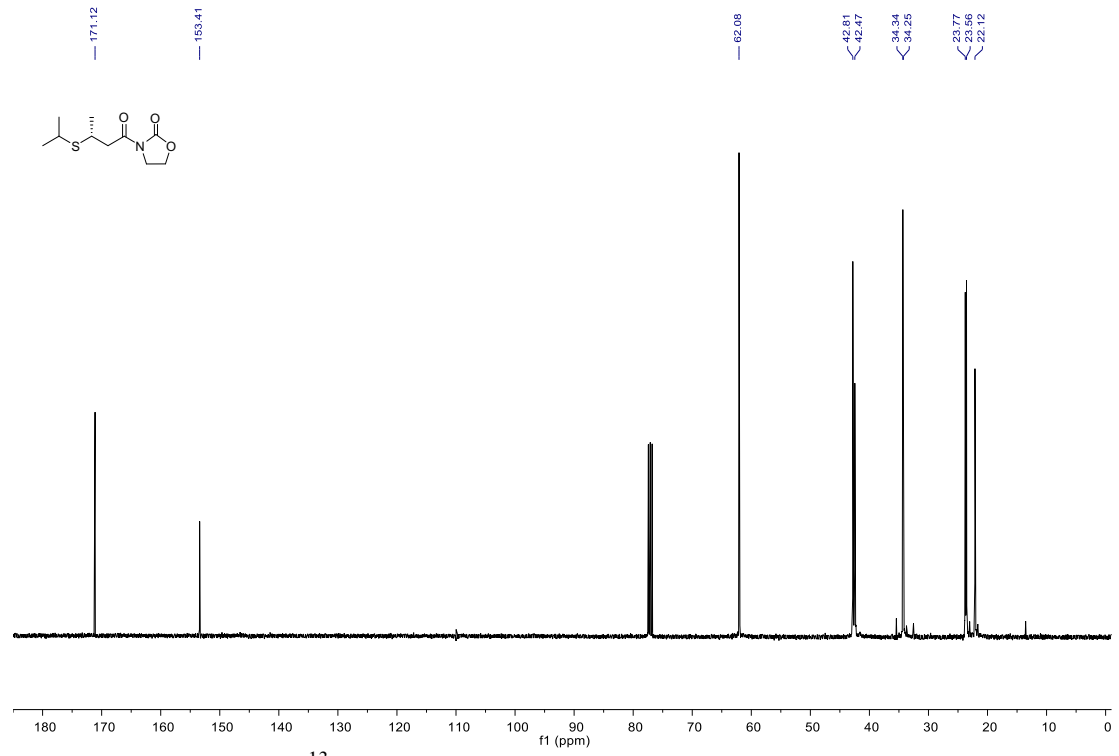

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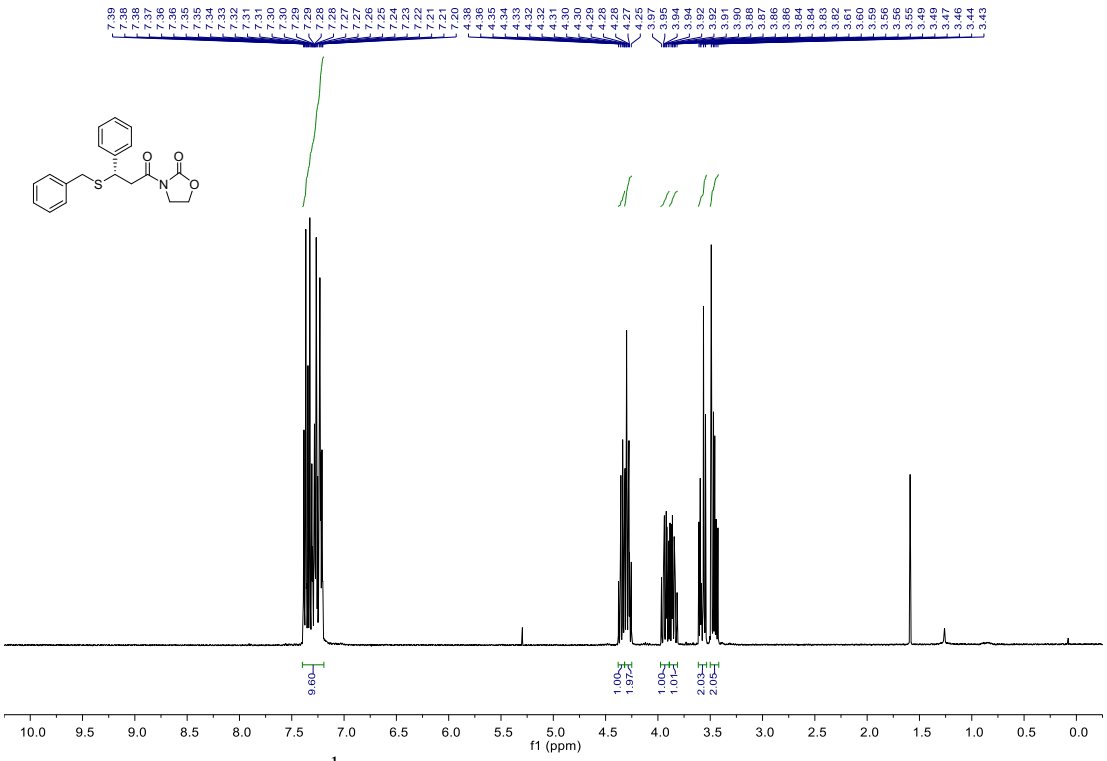

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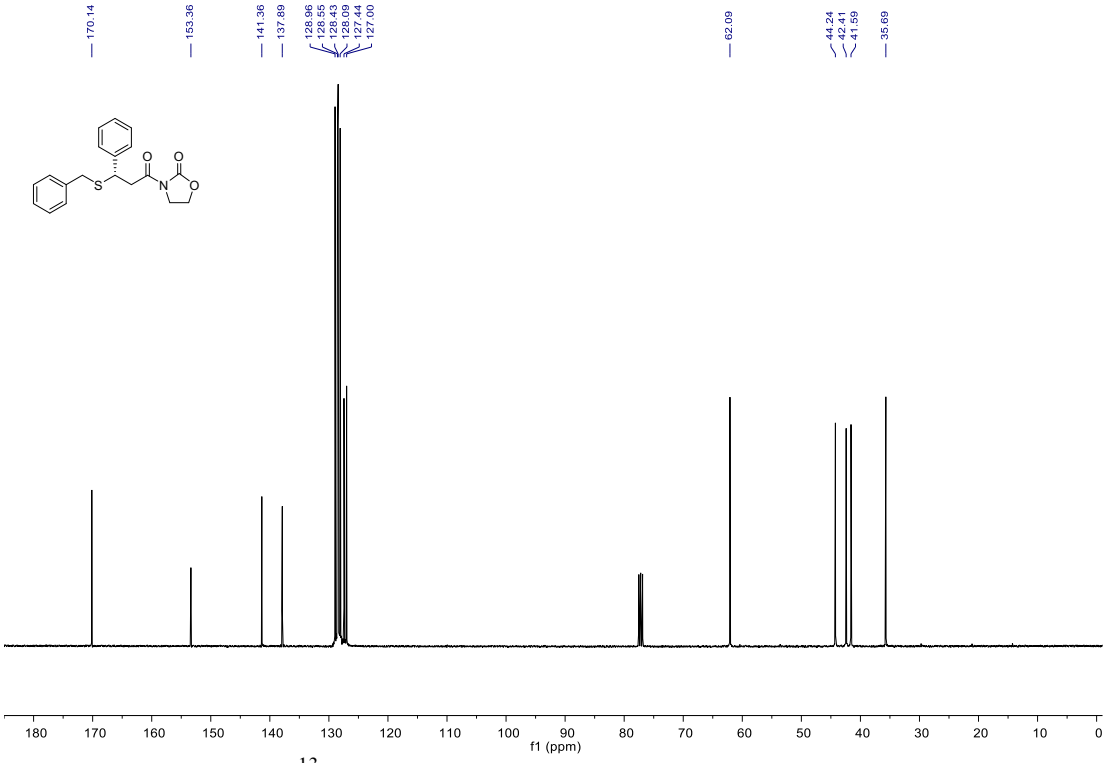

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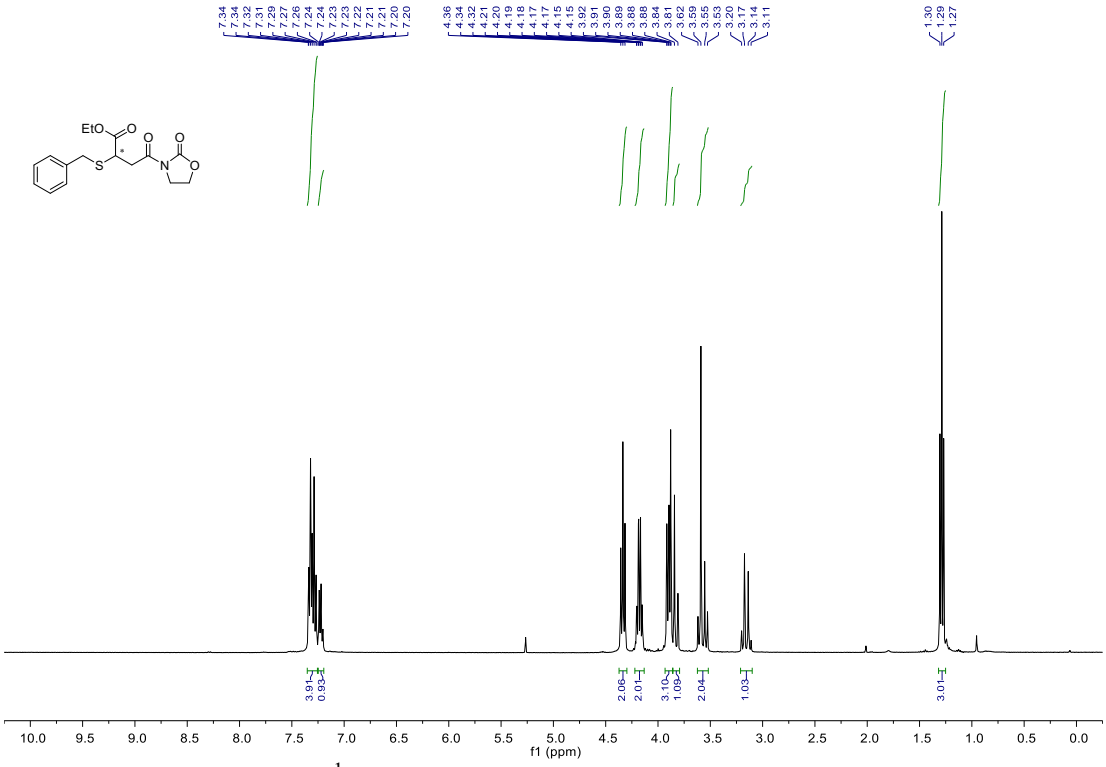

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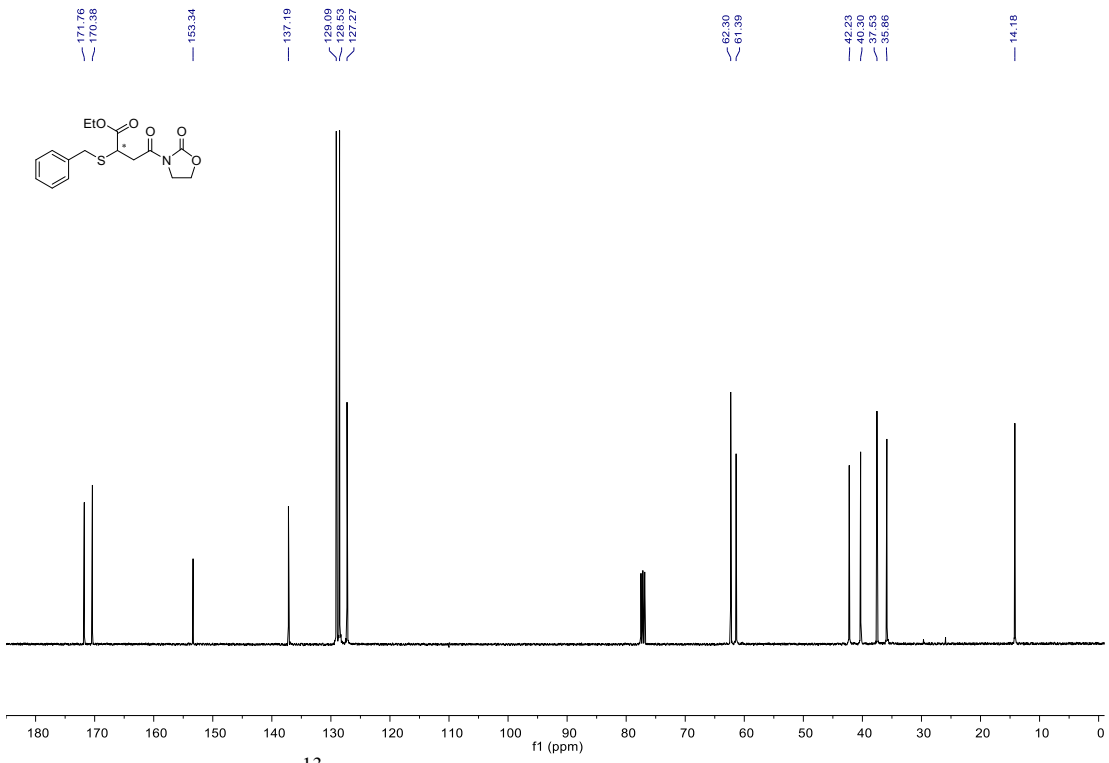

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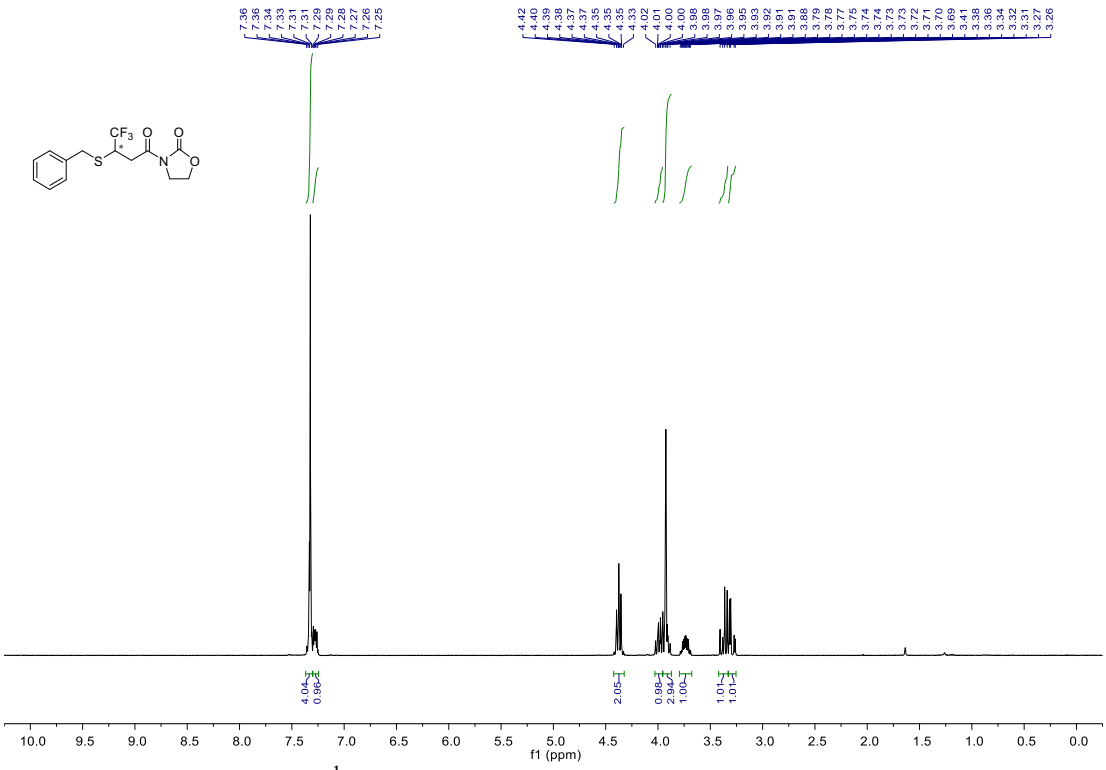

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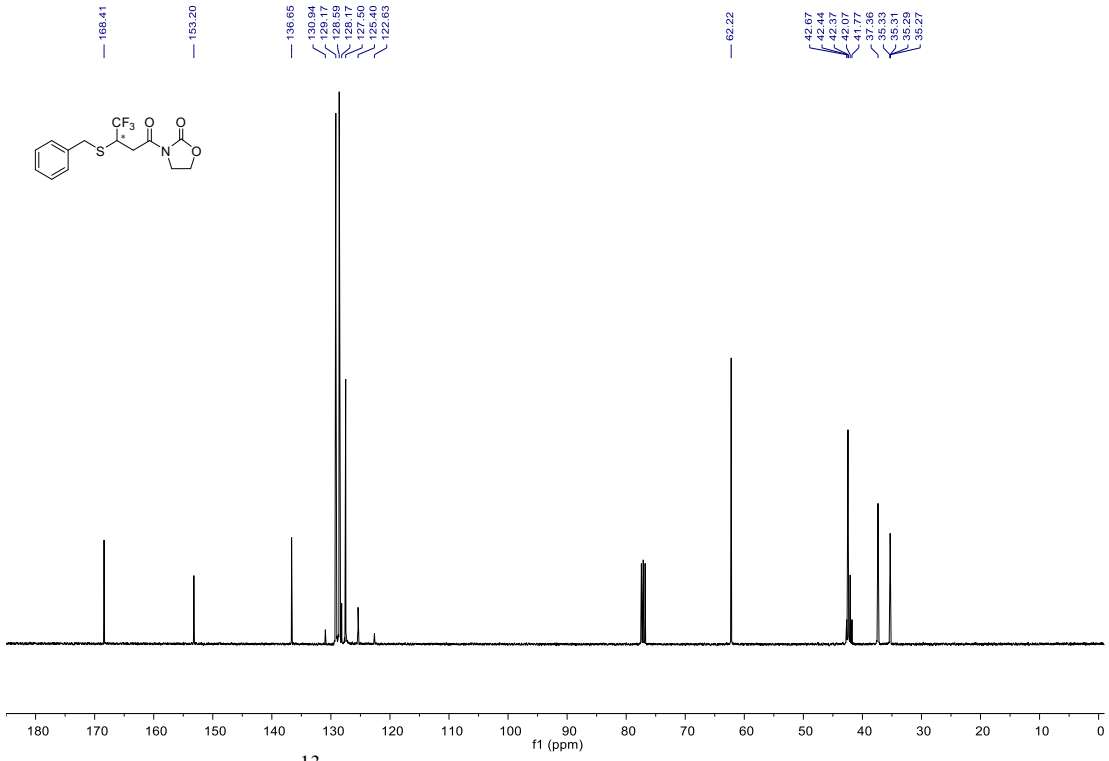

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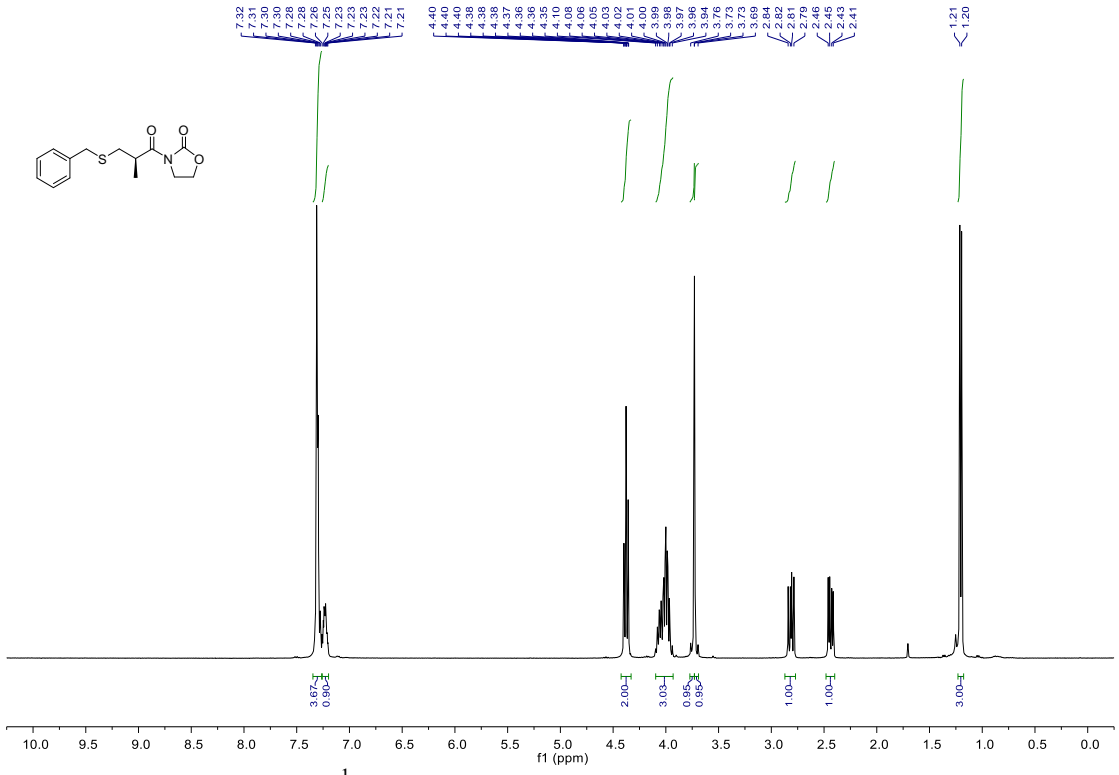

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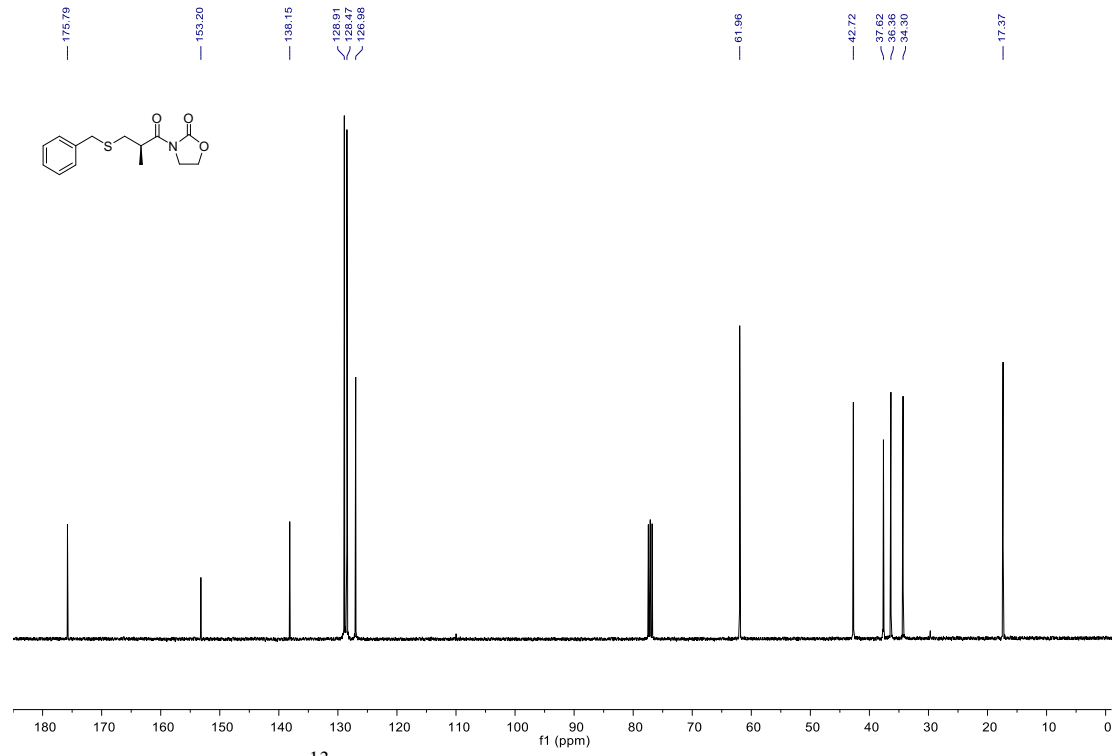

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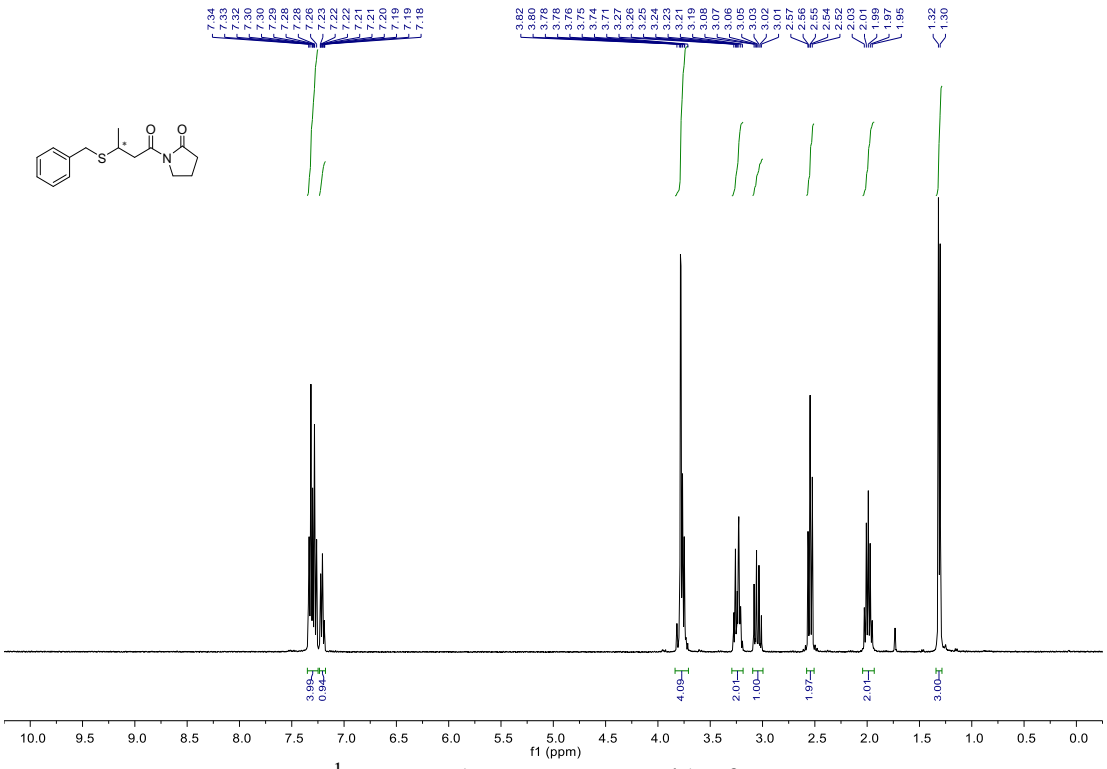

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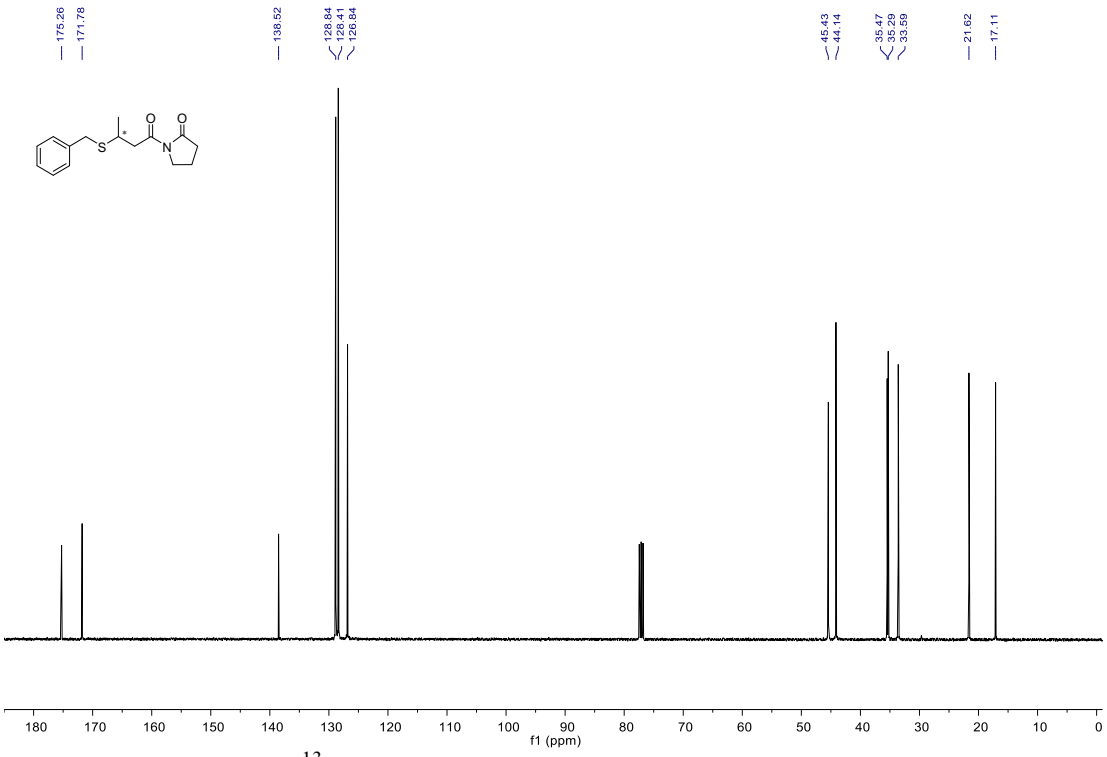

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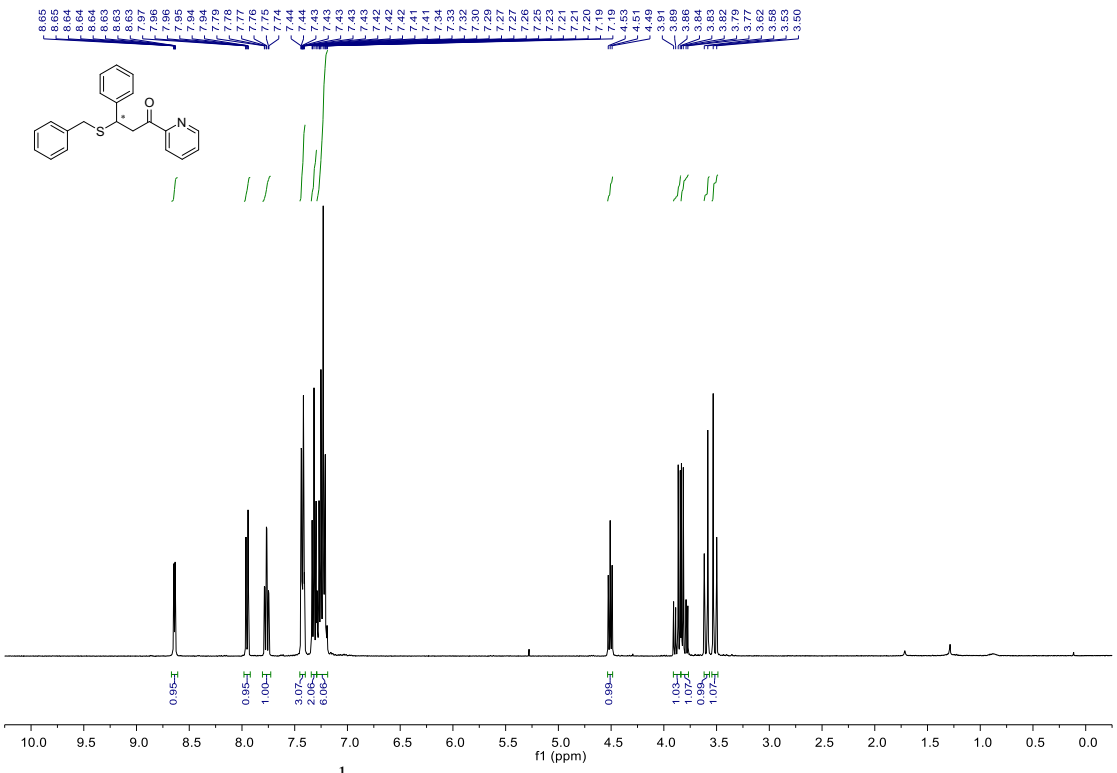

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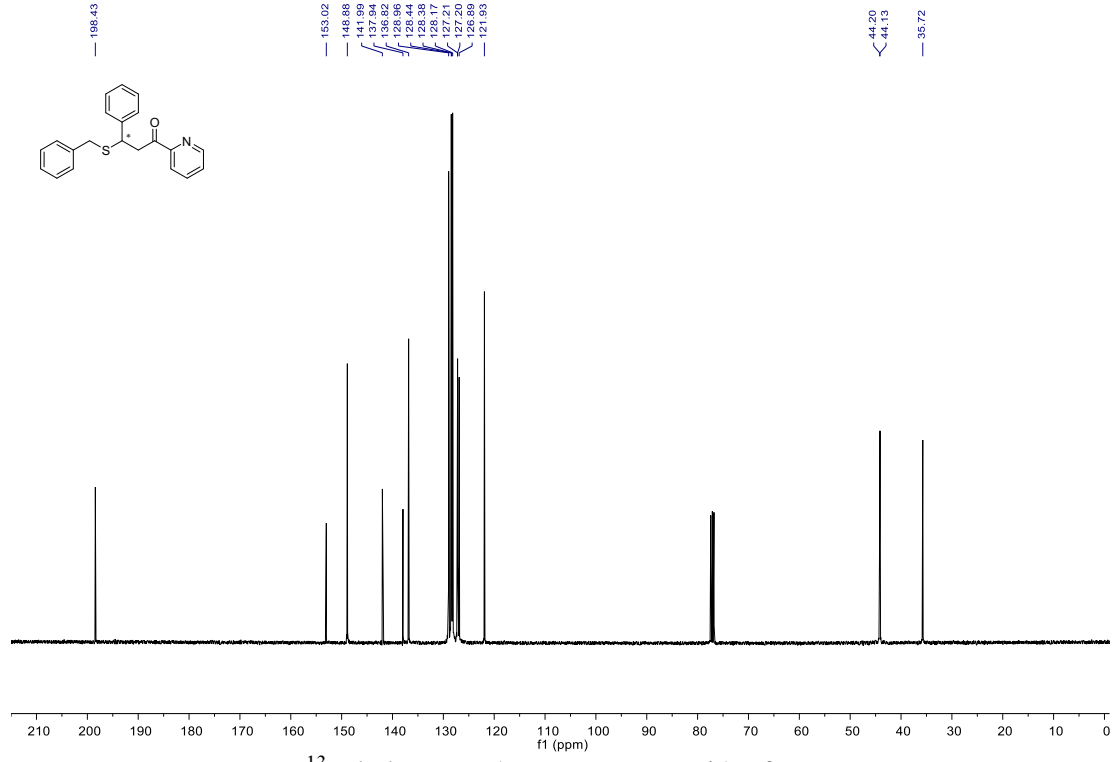

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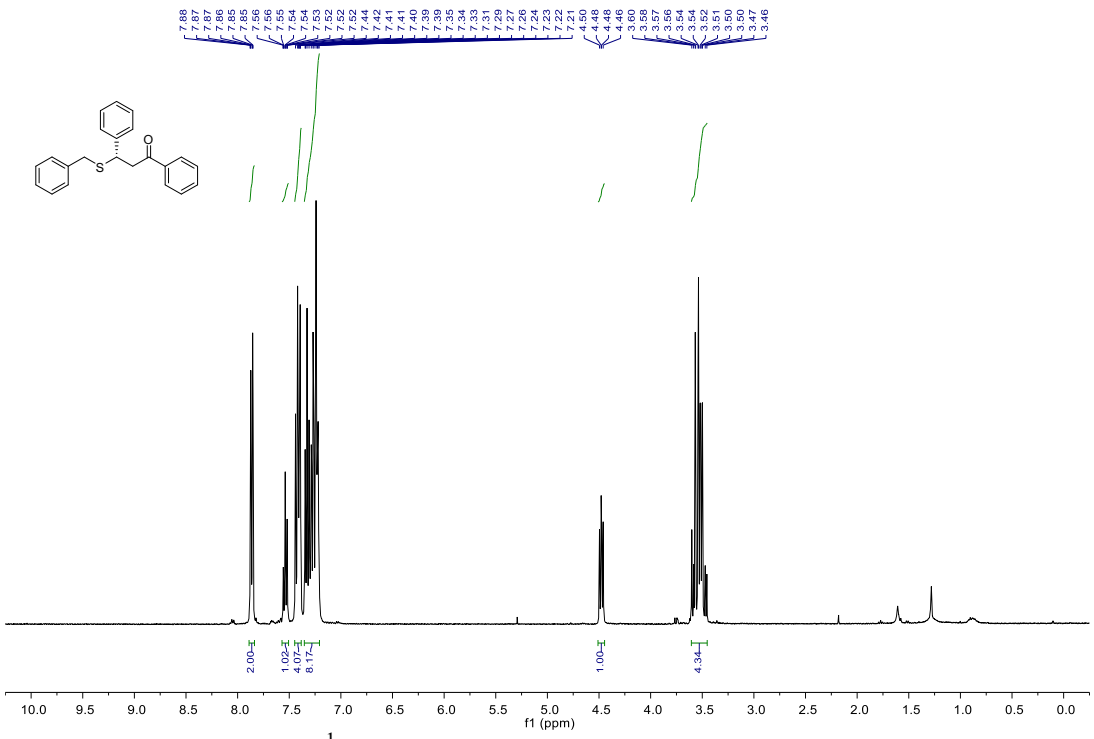

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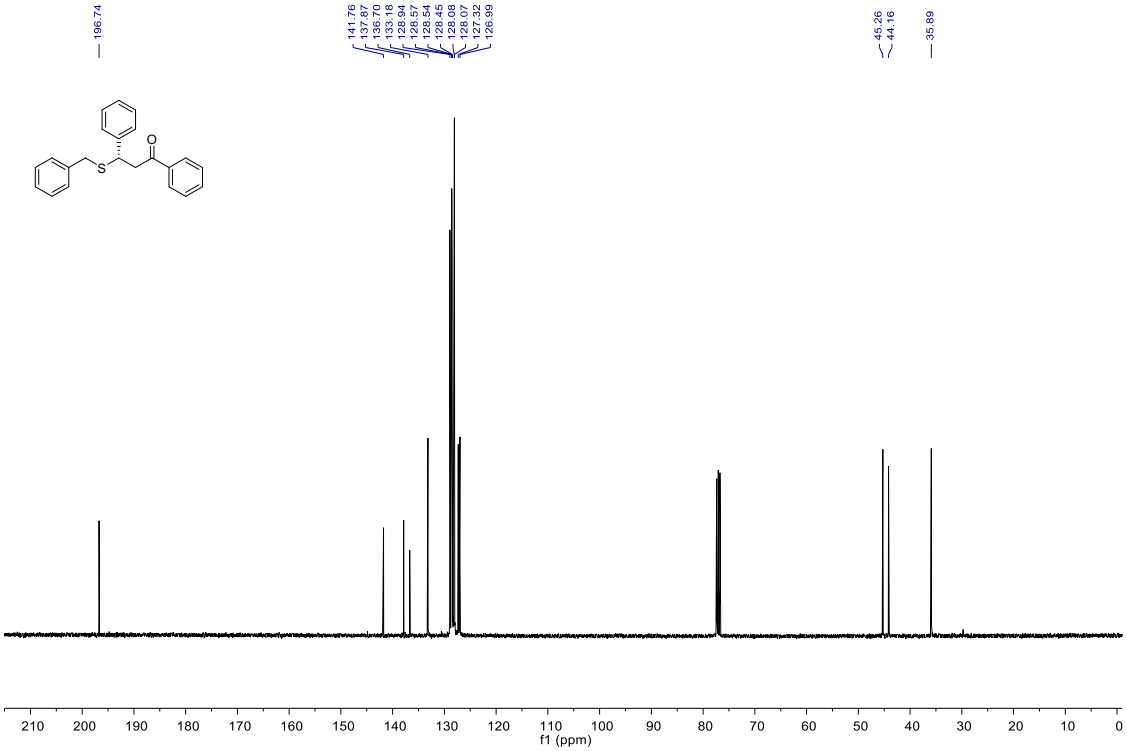

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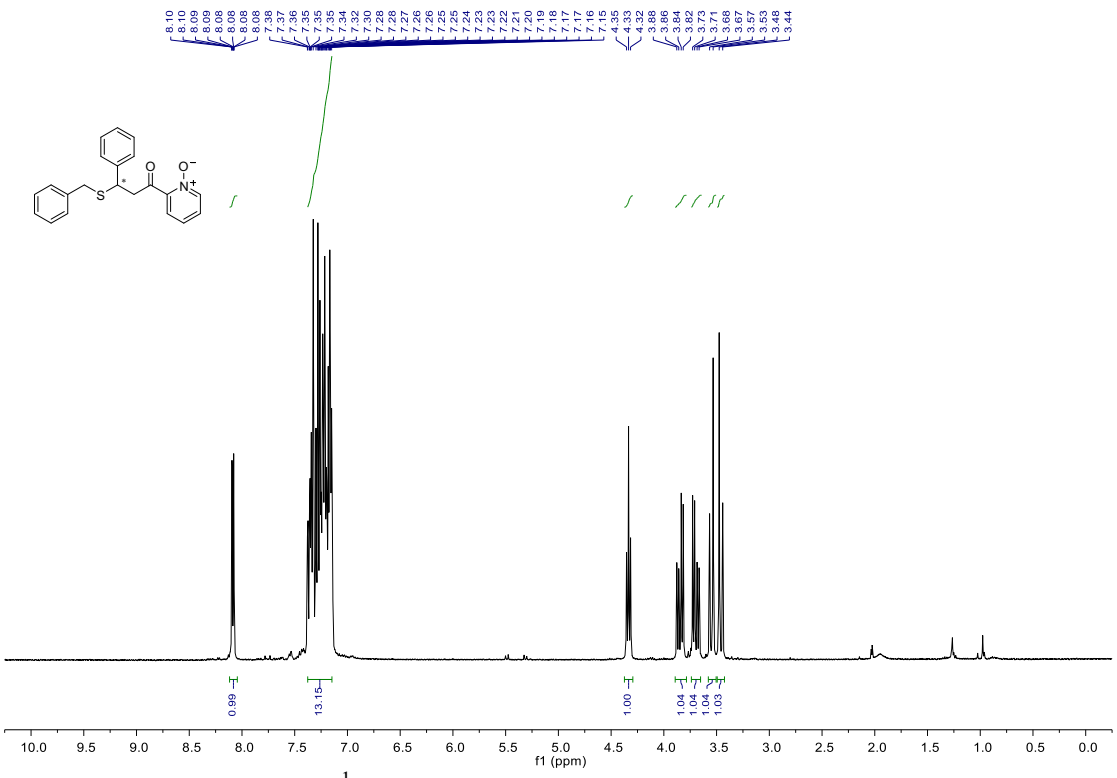
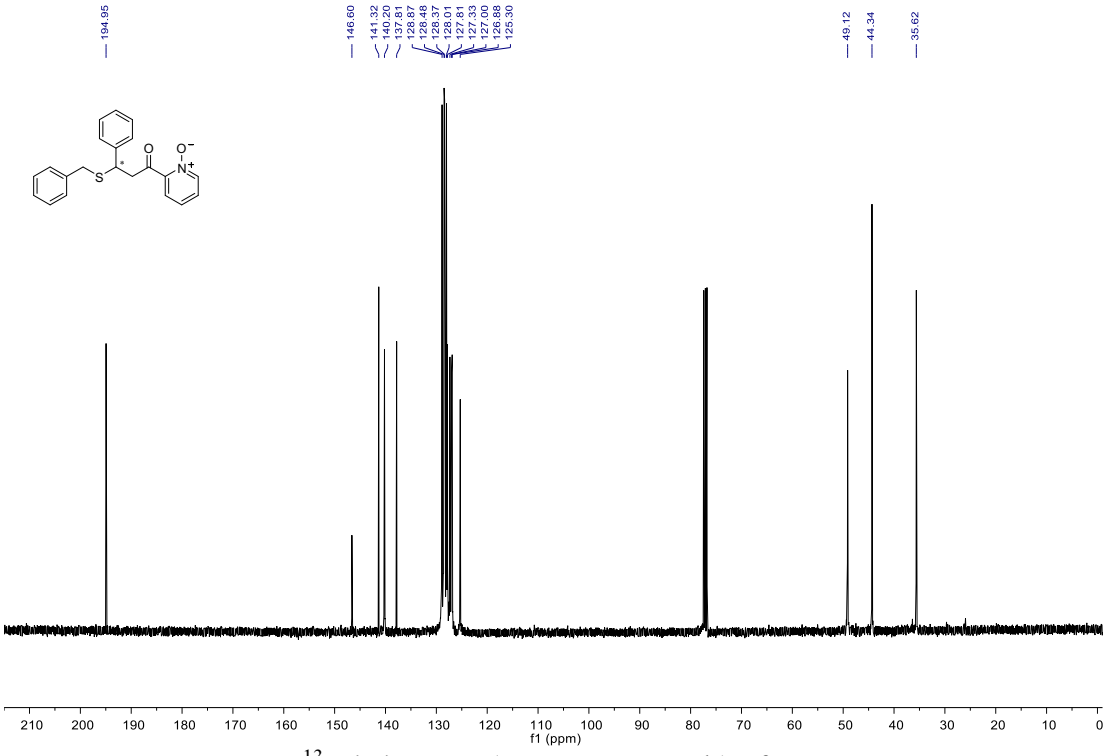
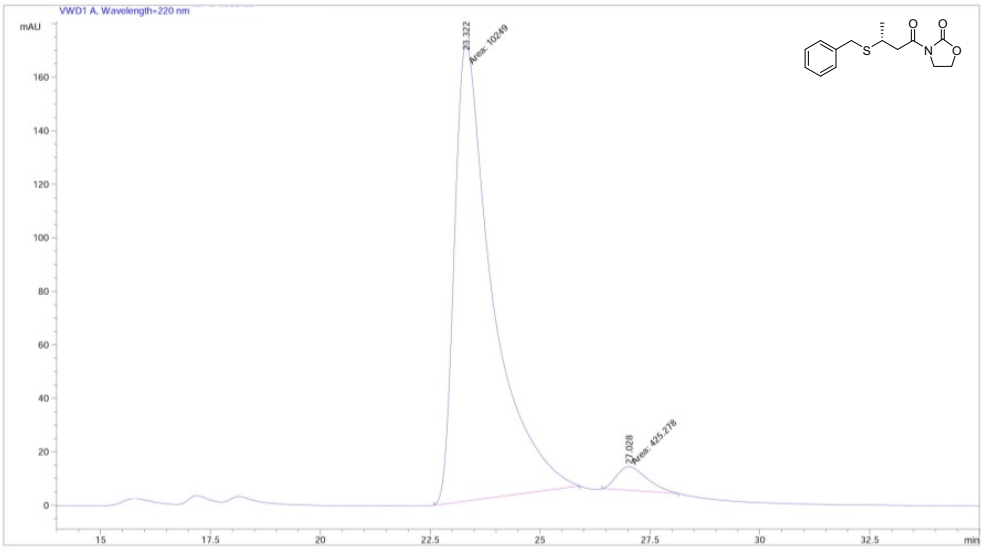


^{1}H NMR (400 MHz, $CDCl_3$) of **4i**



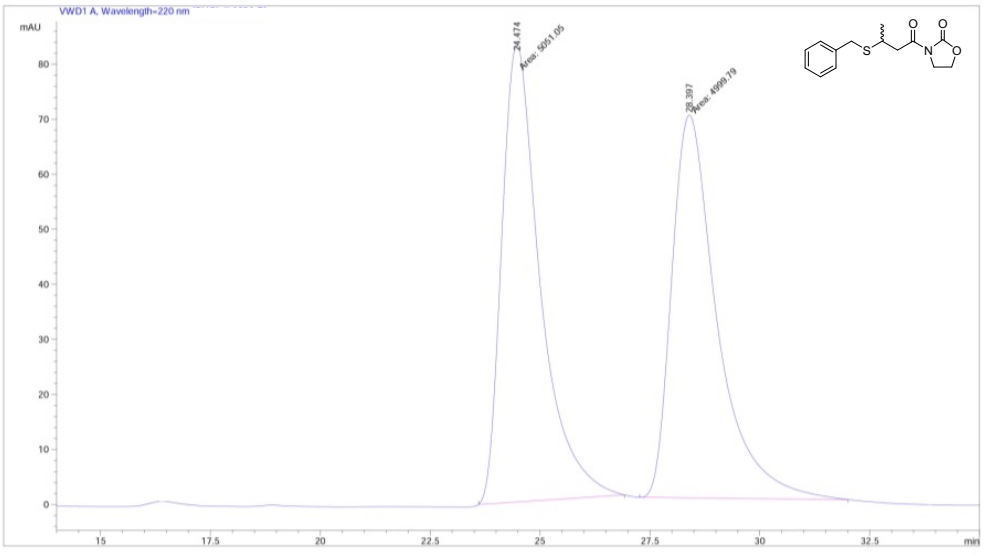
^{13}C{H} NMR (100 MHz, $CDCl_3$) of **4i**

HPLC Chromatograms



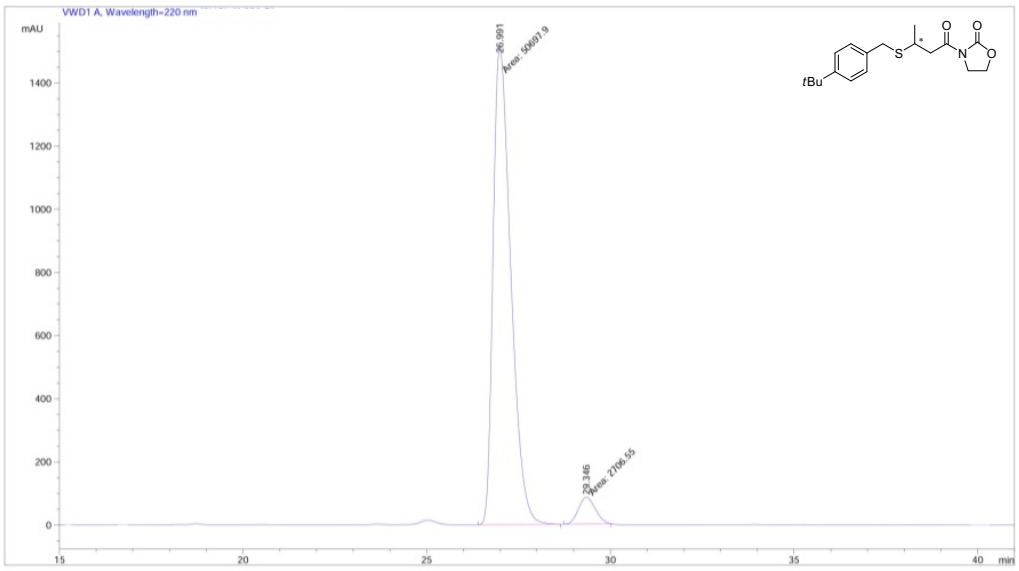
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.322	MM	1.0006	1.02490e4	170.70749	96.0159
2	27.028	MM	0.8013	425.27823	8.84589	3.9841
Totals :				1.06743e4	179.55338	

96:4 *er* of **3a**



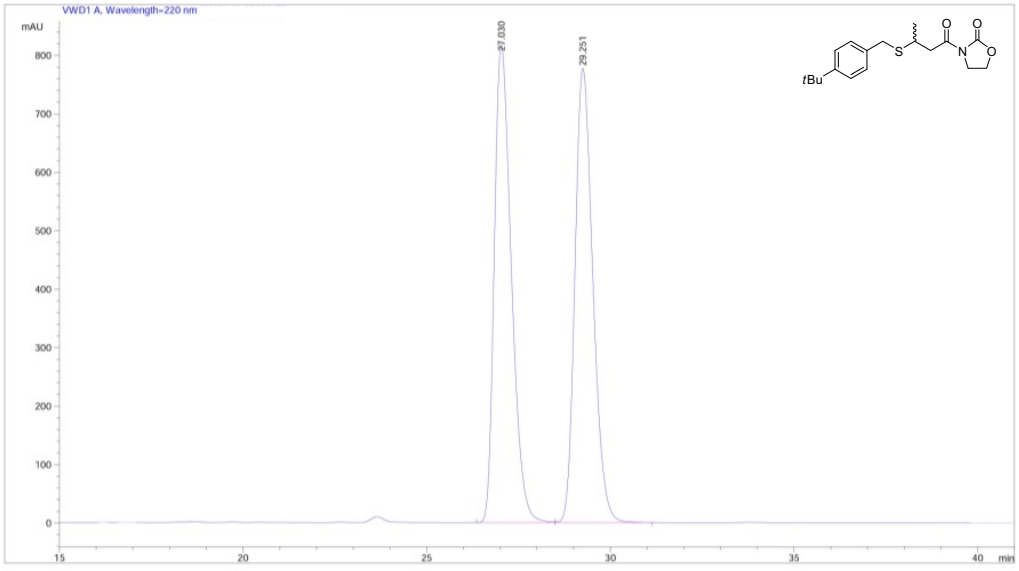
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.474	MM	1.0134	5051.05273	83.07200	50.2550
2	28.397	MM	1.1980	4999.79297	69.55843	49.7450
Totals :				1.00508e4	152.63043	

Racemate of **3a**



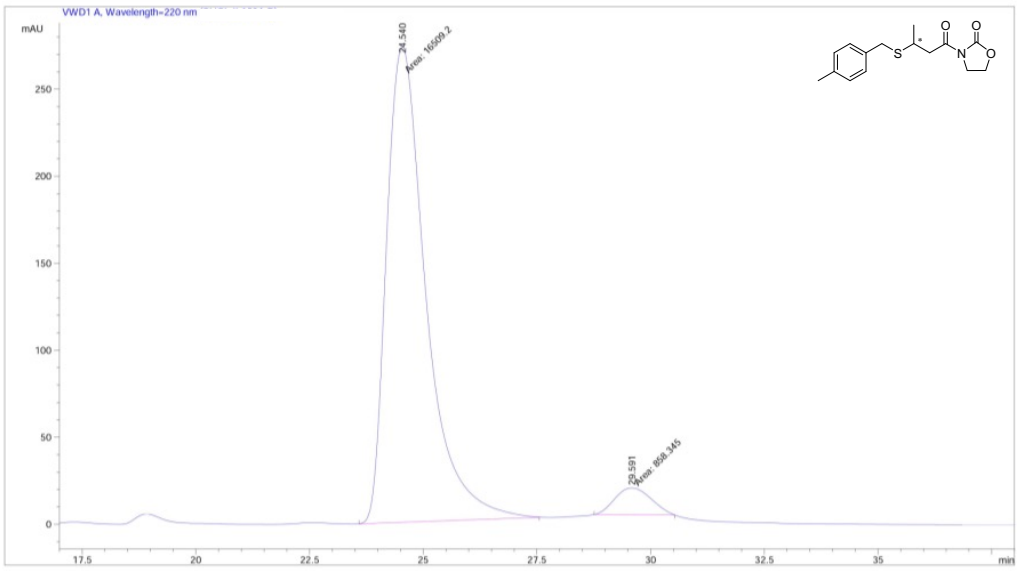
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	26.991	MM	0.5582	5.06935e4	1513.50732	94.9695
2	29.346	MM	0.5304	2685.23047	84.37992	5.0305
Totals :				5.33787e4	1597.88725	

95:5 *er* of **3b**



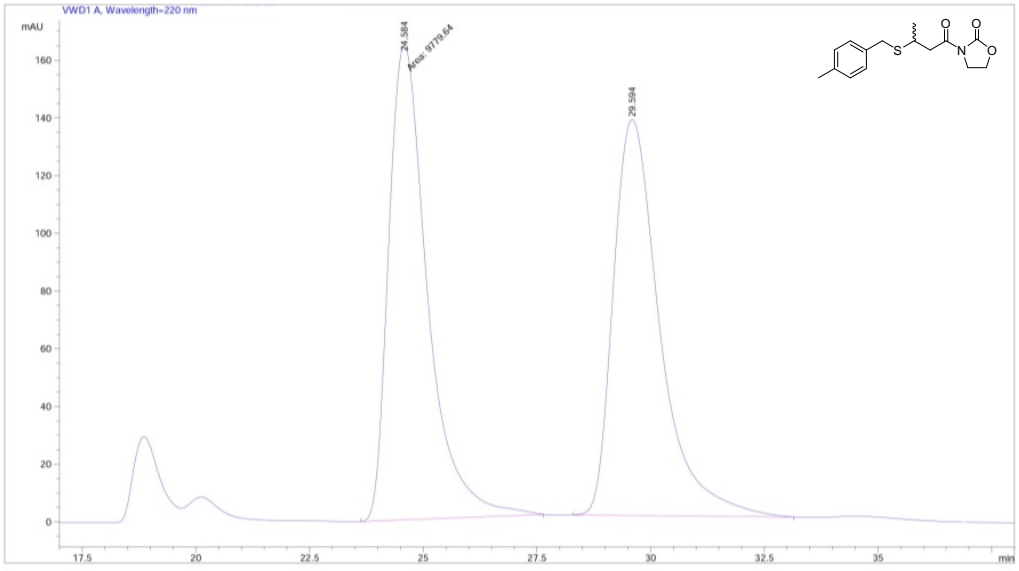
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	27.030	BV	0.4997	2.63469e4	817.58478	50.0130
2	29.251	VB	0.5234	2.63331e4	777.27081	49.9870
Totals :				5.26800e4	1594.85559	

Racemate of **3b**



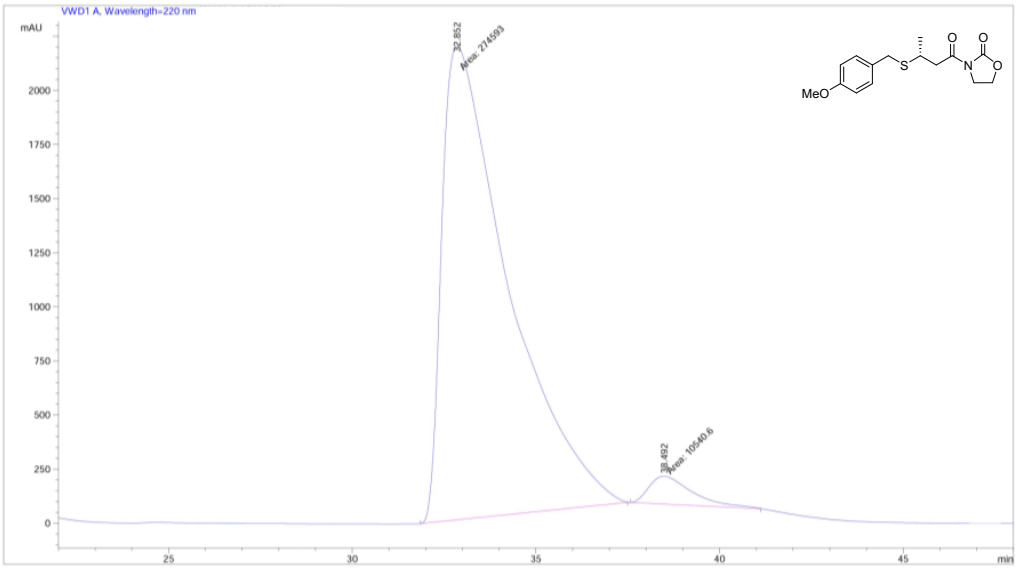
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.540	MM	1.0071	1.65092e4	273.22058	95.0578
2	29.591	MM	0.9235	858.34460	15.48999	4.9422
Totals :				1.73675e4	288.71057	

95:5 *er* of **3c**



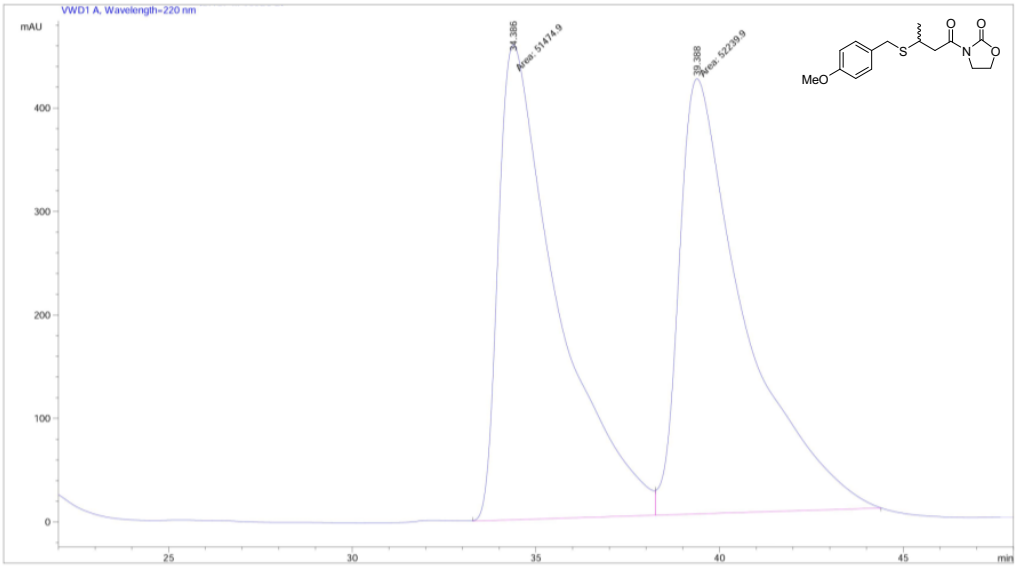
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	24.584	MM	0.9901	9779.64063	164.62575	50.0521
2	29.594	BB	1.0945	9759.27246	137.26799	49.9479
Totals :				1.95389e4	301.89374	

Racemate of **3c**



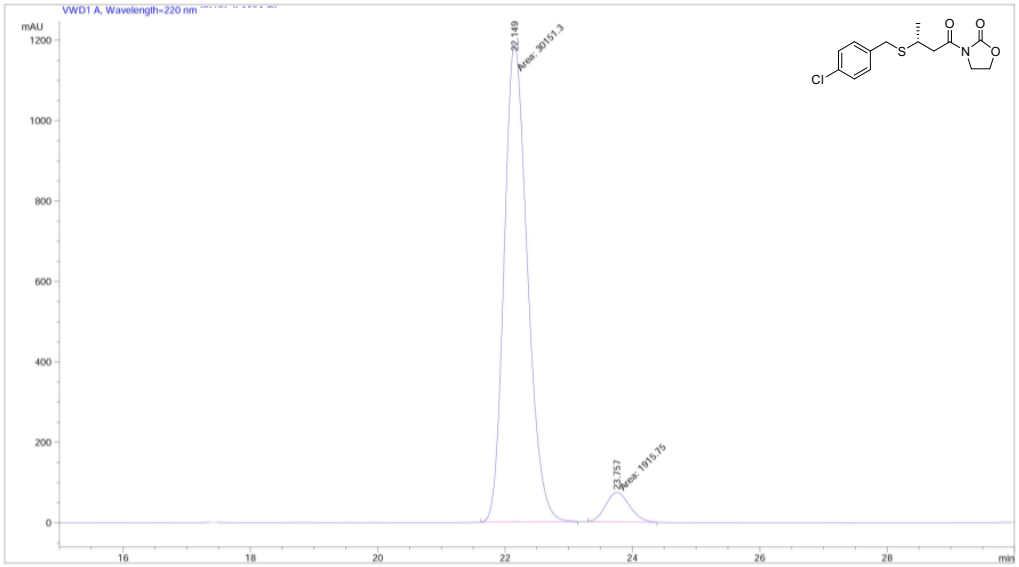
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.852	MM	2.0895	2.74593e5	2190.26782	96.3033
2	38.492	MM	1.3612	1.05406e4	129.05786	3.6967
Totals :				2.85134e5	2319.32568	

96:4 *er* of **3d**



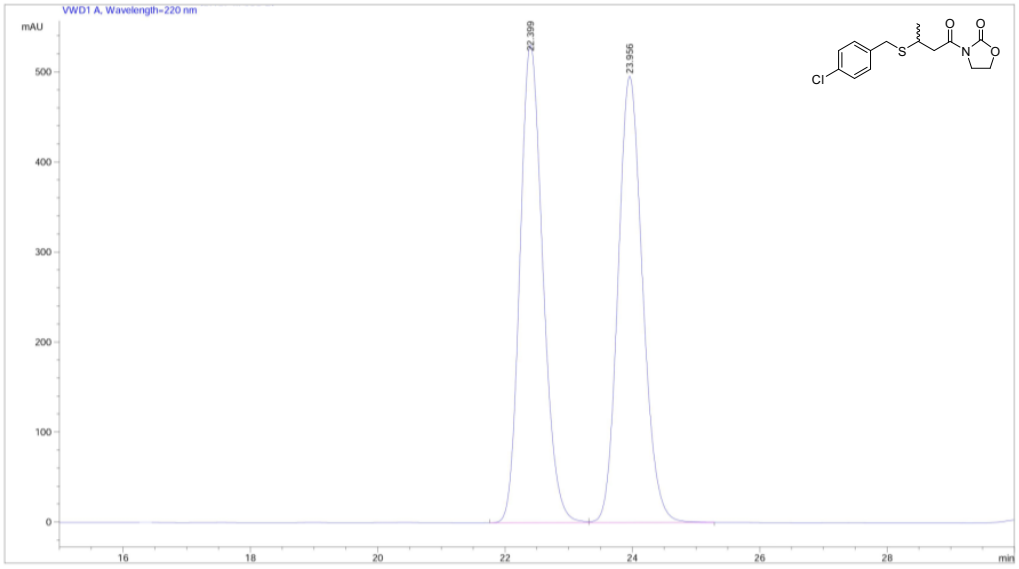
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.386	MF	1.8698	5.14749e4	458.83914	49.6312
2	39.388	FM	2.0713	5.22399e4	420.33963	50.3688
Totals :				1.03715e5	879.17877	

Racemate of **3d**



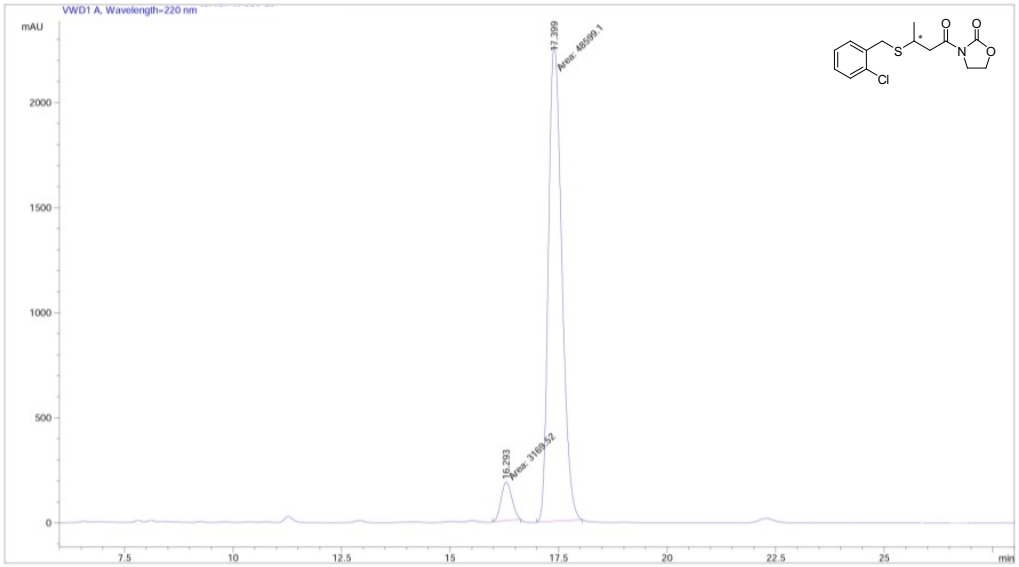
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.149	MM	0.4234	3.01513e4	1186.79016	94.0258
2	23.757	MM	0.4361	1915.74561	73.22240	5.9742
Totals :				3.20670e4	1260.01256	

94:6 *er* of **3e**



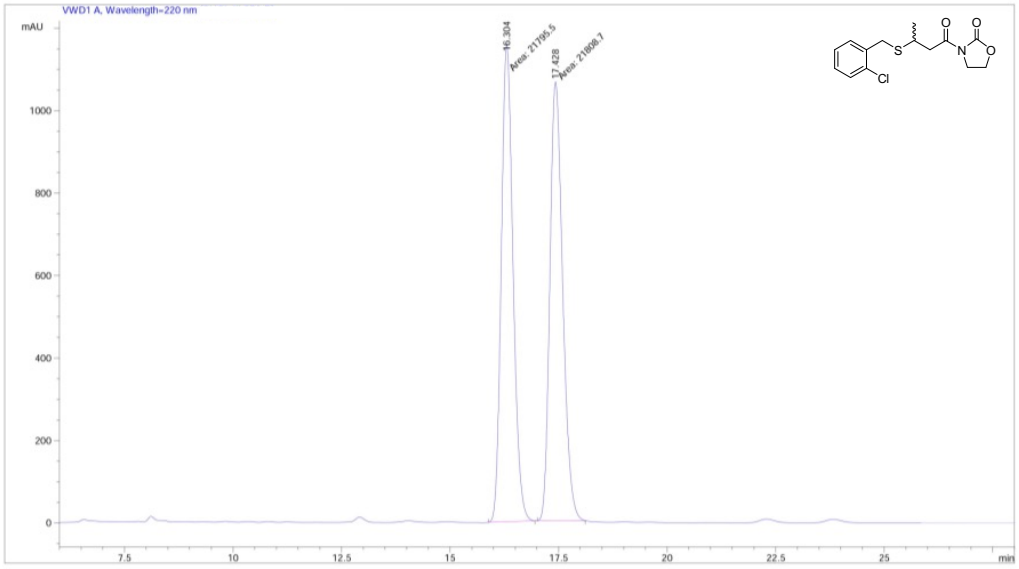
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.399	BV	0.3868	1.32861e4	530.62769	49.9784
2	23.956	VB	0.4150	1.32976e4	495.55350	50.0216
Totals :				2.65838e4	1026.18118	

Racemate of **3e**



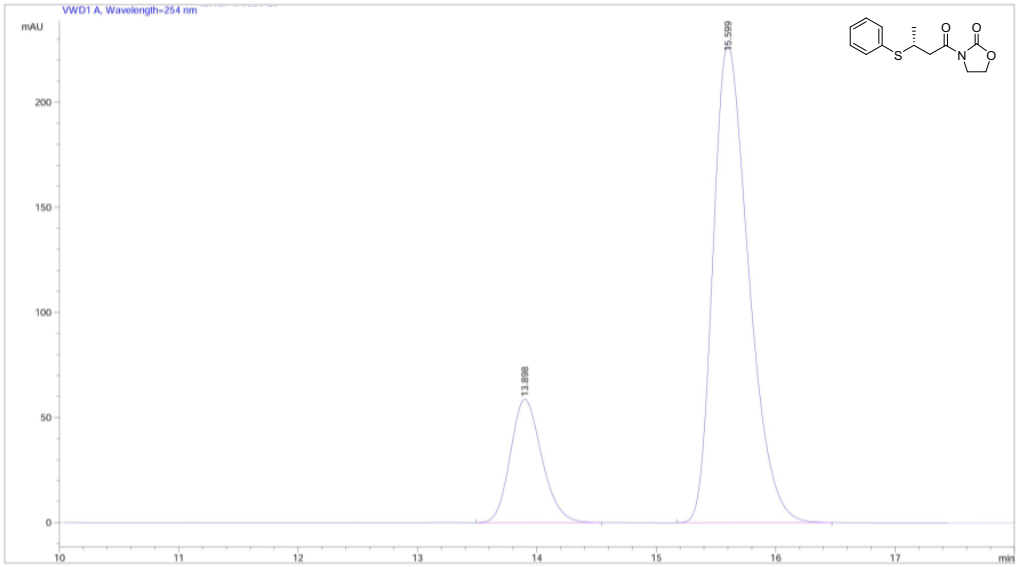
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.293	MM	0.2873	3169.52124	183.87326	6.1225
2	17.399	MM	0.3575	4.85991e4	2265.94507	93.8775
Totals :				5.17686e4	2449.81833	

94:6 *er* of **3f**



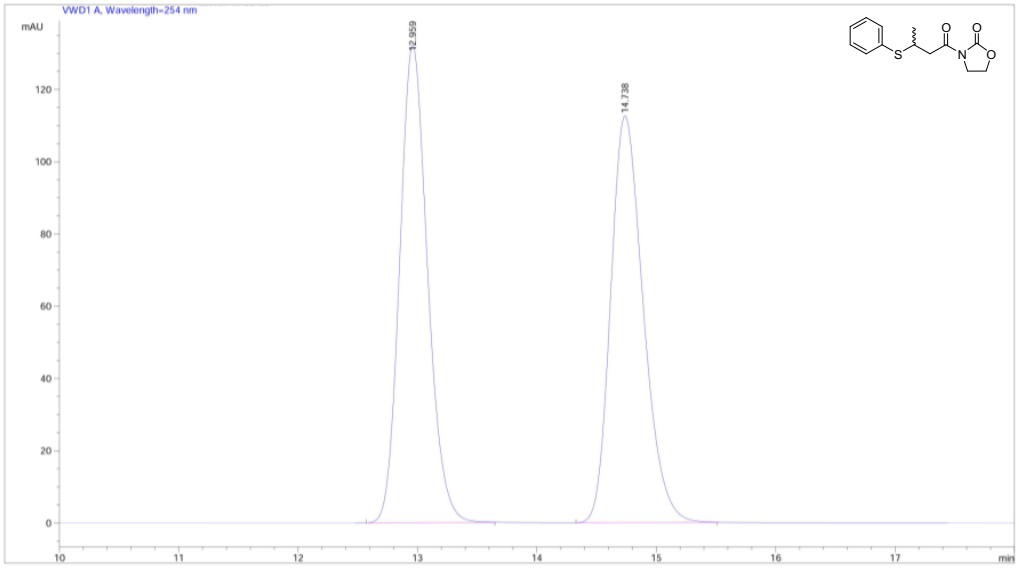
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.304	MM	0.3140	2.17955e4	1156.72473	49.9849
2	17.428	MM	0.3415	2.18087e4	1064.41504	50.0151
Totals :				4.36042e4	2221.13977	

Racemate of **3f**



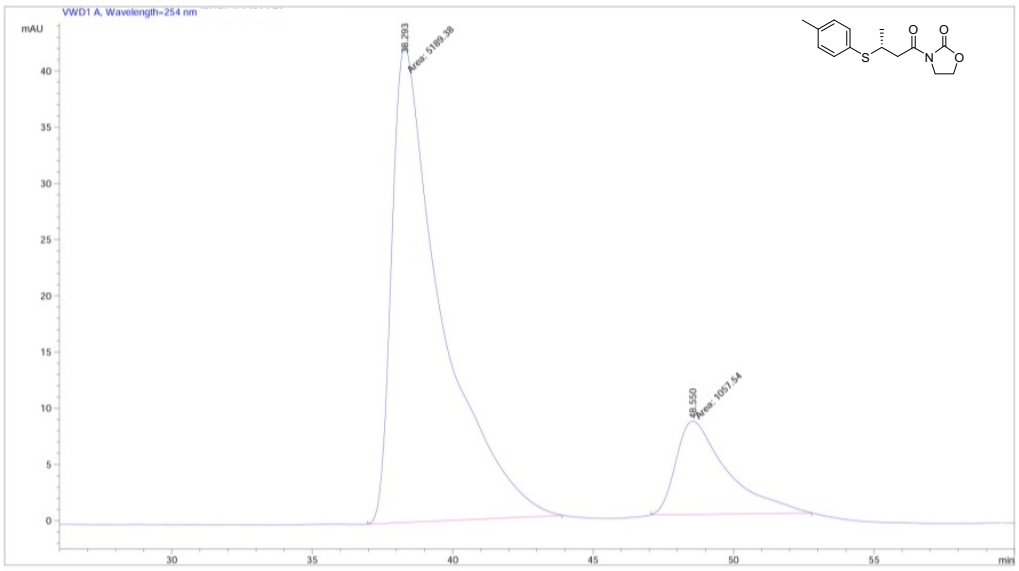
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.898	BB	0.2821	1076.06970	58.74781	18.5911
2	15.599	BB	0.3204	4712.00586	227.34315	81.4089
Totals :				5788.07556	286.09097	

81:19 *er* of **3g**



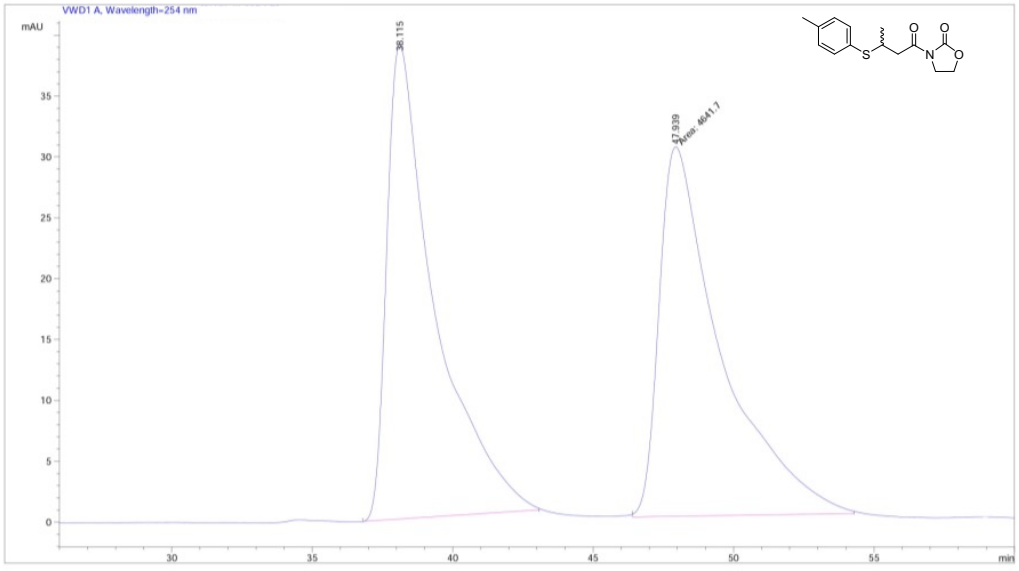
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.959	BB	0.2485	2139.99561	132.26431	50.0044
2	14.738	BB	0.2930	2139.62085	112.62573	49.9956
Totals :				4279.61646	244.89005	

Racemate of **3g**



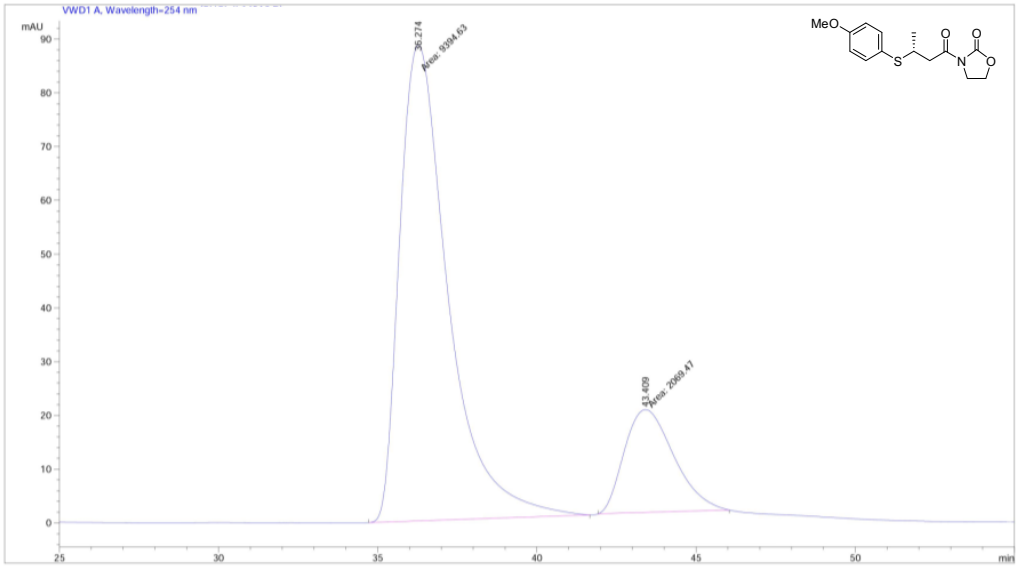
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.293	MM	2.0453	5189.38477	42.28749	83.0710
2	48.550	MM	2.1254	1057.54321	8.29294	16.9290
Totals :				6246.92798	50.58043	

83:17 *er* of **3h**



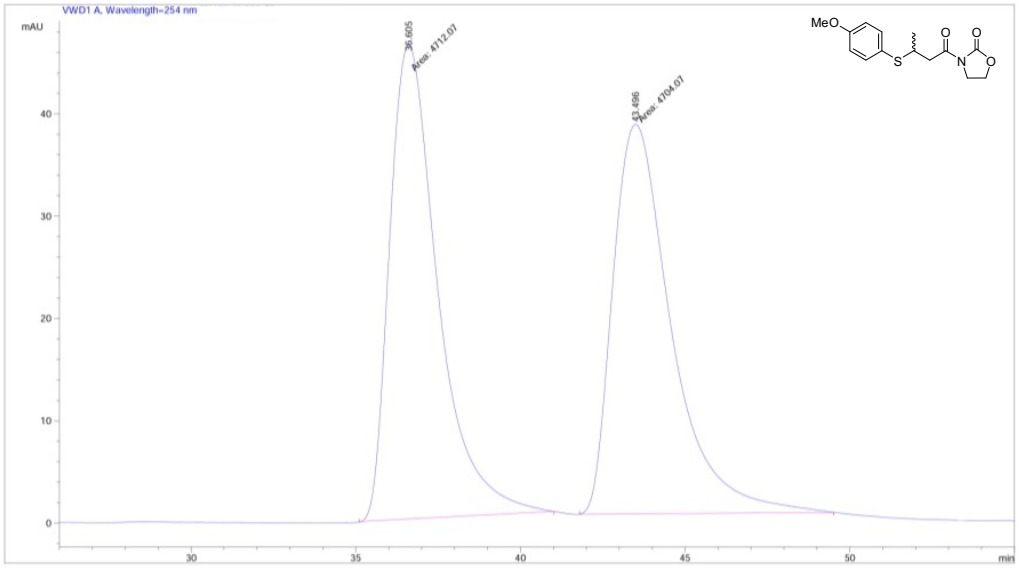
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.115	BB	1.6644	4629.08545	38.95718	49.9320
2	47.939	MM	2.5484	4641.69824	30.35699	50.0680
Totals :				9270.78369	69.31417	

Racemate of **3h**



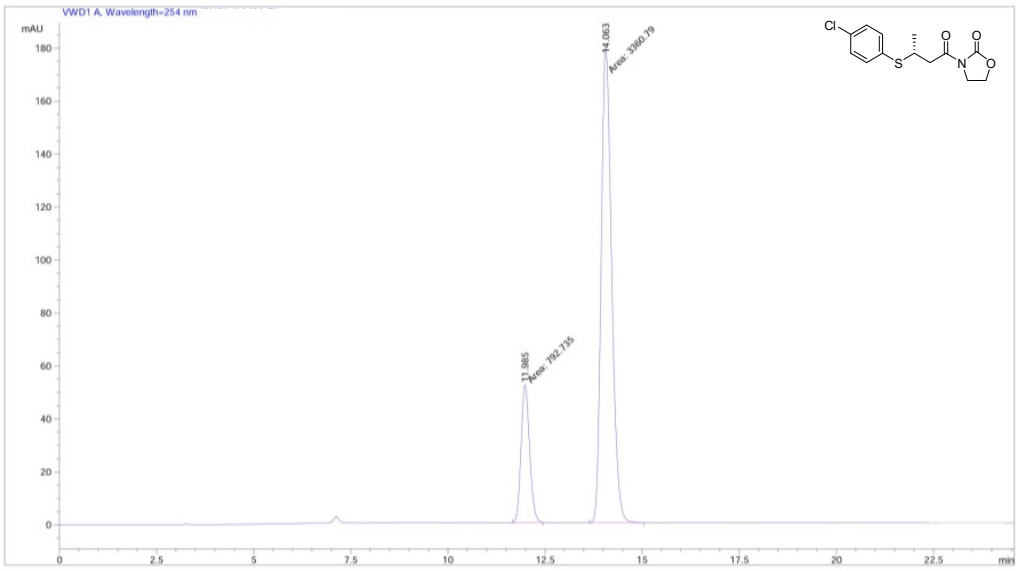
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	36.274	MM	1.7683	9394.62598	88.54430	81.9482
2	43.409	MM	1.8034	2069.47070	19.12585	18.0518
Totals :				1.14641e4	107.67015	

82:18 *er* of **3i**



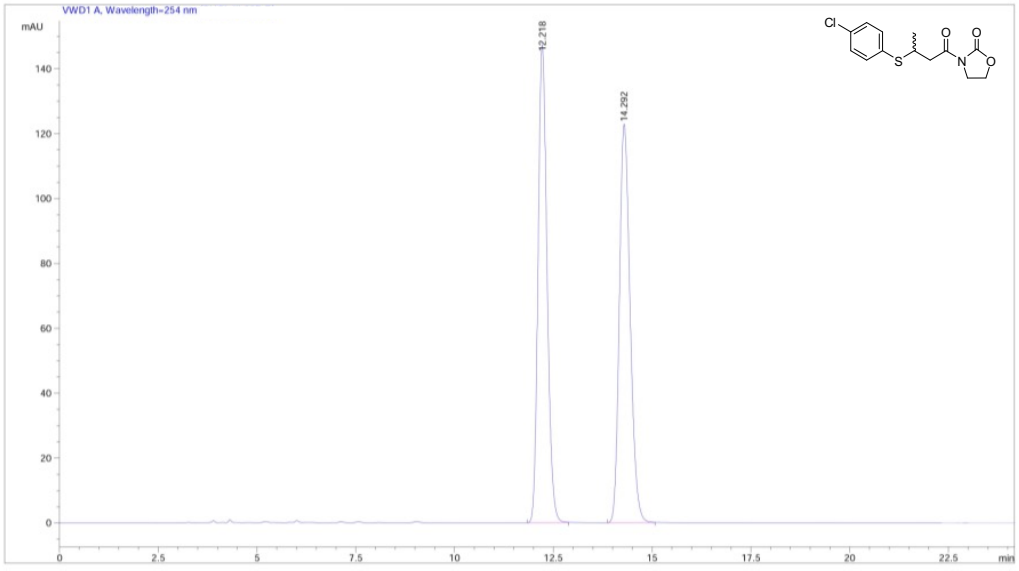
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	36.605	MM	1.6956	4712.06543	46.31523	50.0424
2	43.496	MM	2.0611	4704.07178	38.03822	49.9576
Totals :				9416.13721	84.35345	

Racemate of **3i**



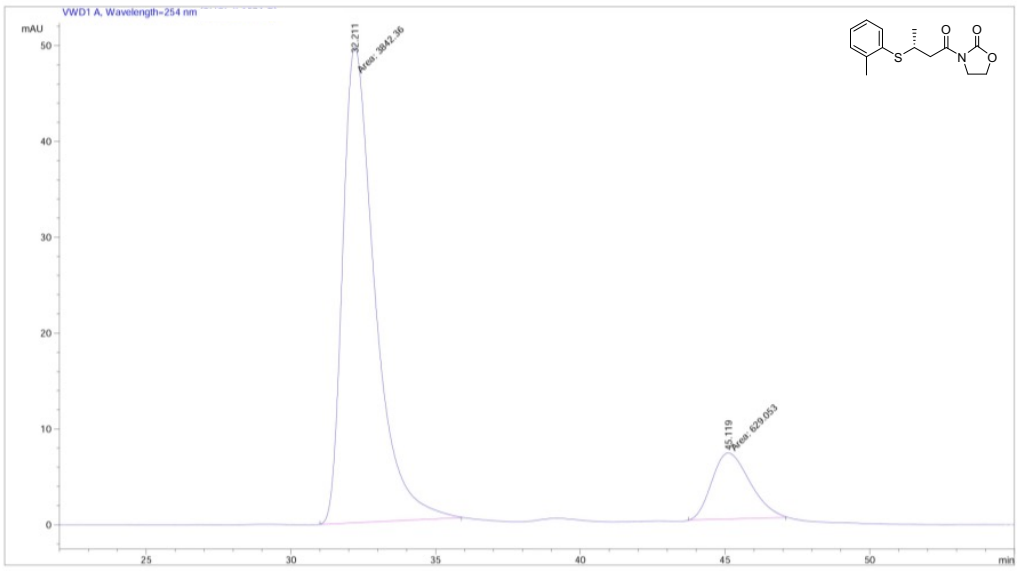
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.985	MM	0.2545	792.73523	51.92241	19.0858
2	14.063	MM	0.3117	3360.79395	179.70496	80.9142
Totals :				4153.52917	231.62737	

81:19 *er* of **3j**



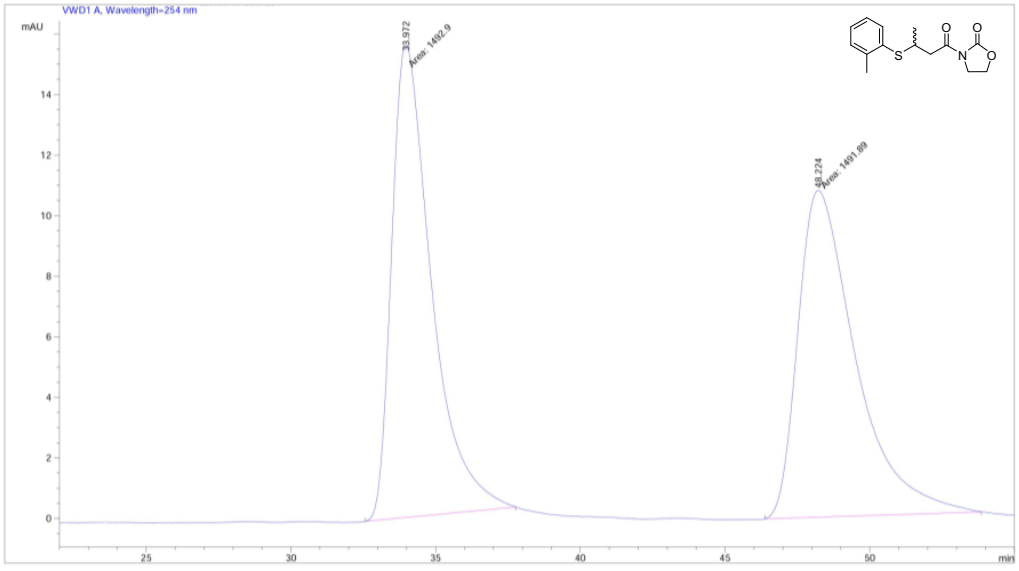
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.218	BB	0.2455	2328.10010	147.33142	50.0060
2	14.292	BB	0.2938	2327.54443	122.85639	49.9940
Totals :				4655.64453	270.18781	

Racemate of **3j**



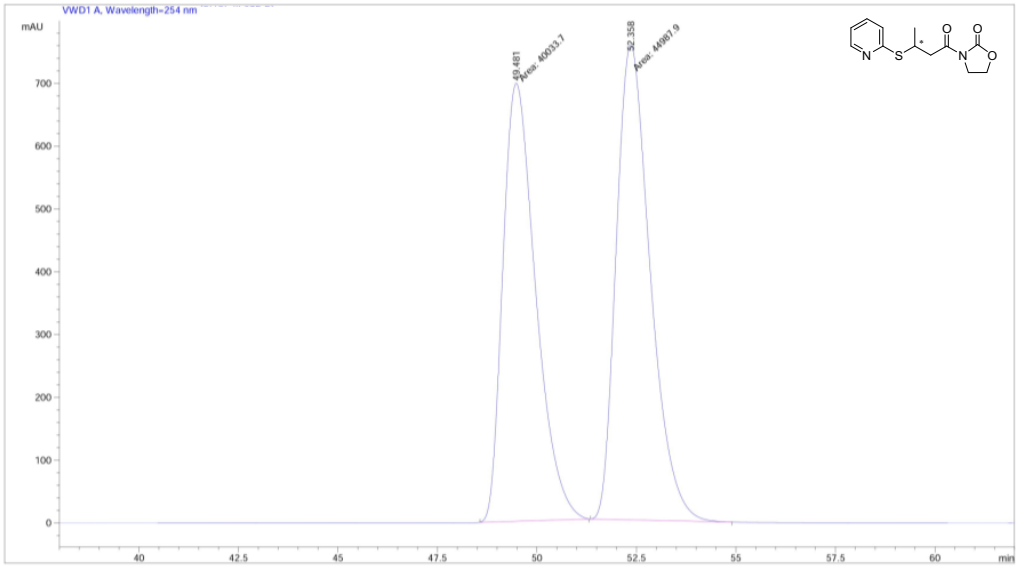
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	32.211	MM	1.2893	3842.36304	49.67105	85.9317
2	45.119	MM	1.5237	629.05304	6.88058	14.0683
Totals :				4471.41608	56.55163	

86:14 *er* of **3k**



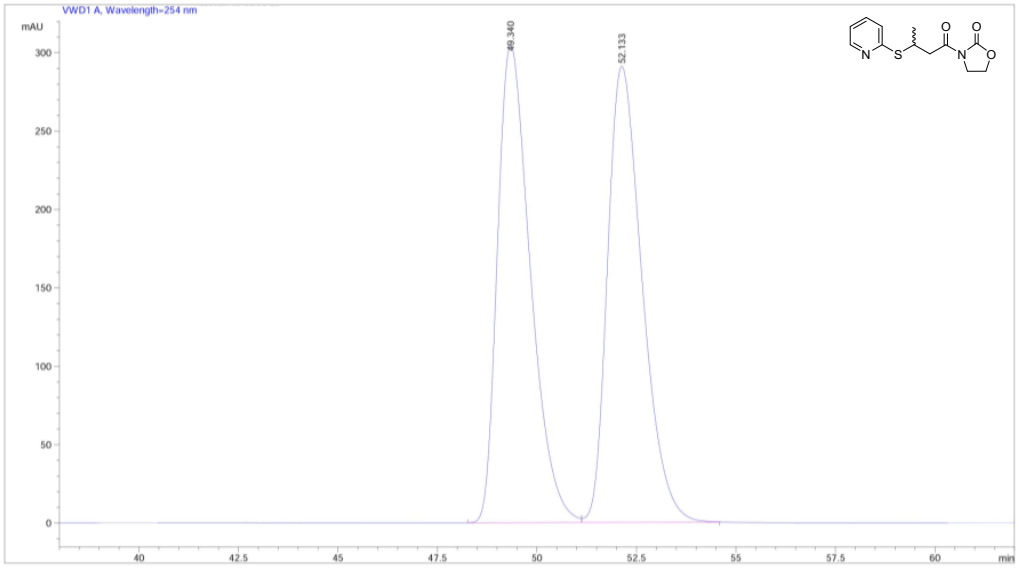
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	33.972	MM	1.5942	1492.90149	15.60715	50.0169
2	48.224	MM	2.3050	1491.89221	10.78726	49.9831
Totals :				2984.79370	26.39441	

Racemate of **3k**



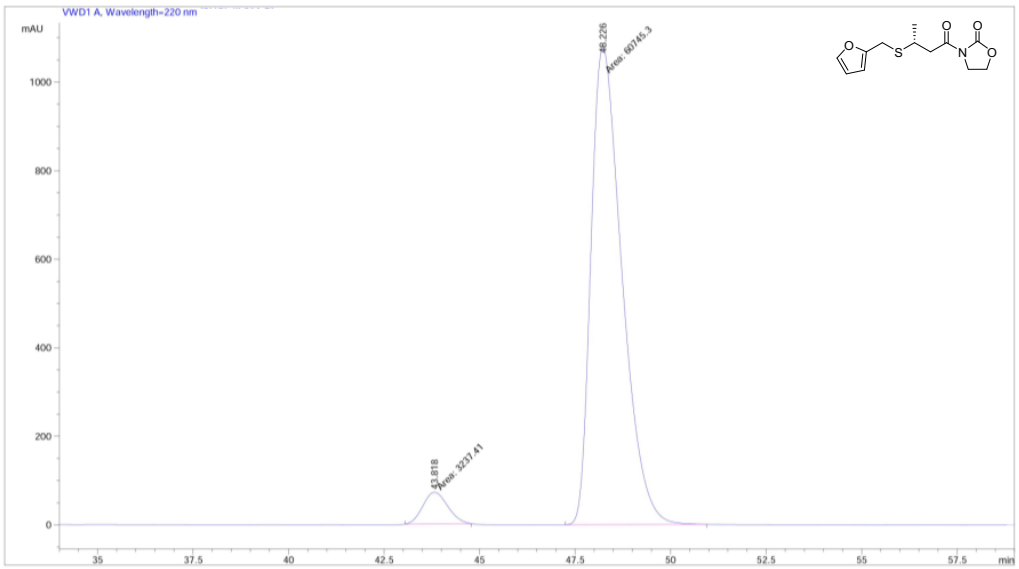
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	49.481	MM	0.9574	4.00337e4	696.90668	47.0865
2	52.358	MM	0.9916	4.49879e4	756.18768	52.9135
Totals :				8.50216e4	1453.09436	

53:47 *er* of **3l**



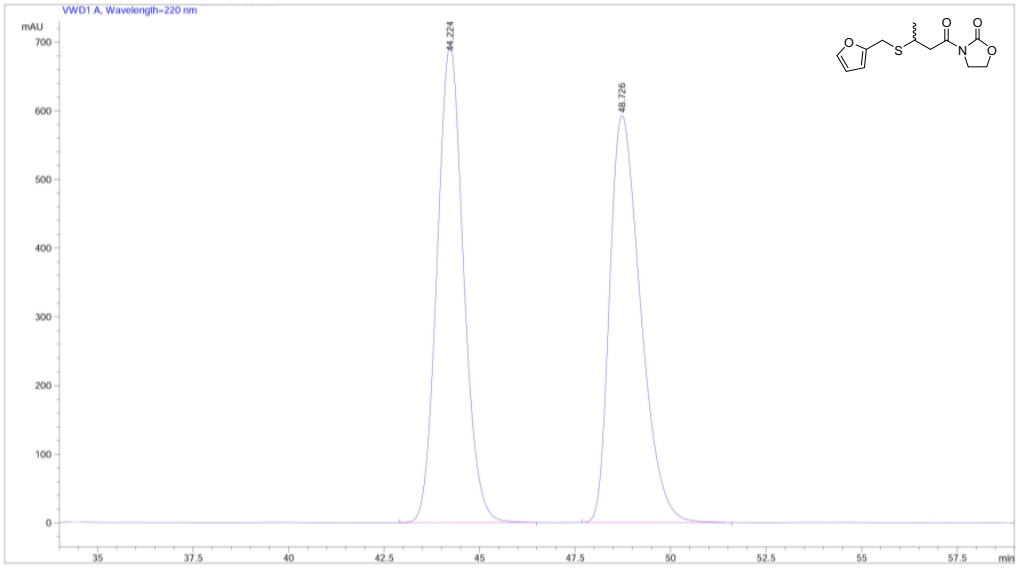
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	49.340	BV	0.8856	1.75466e4	304.83435	49.9251
2	52.133	VB	0.9373	1.75992e4	290.92288	50.0749
Totals :				3.51458e4	595.75723	

Racemate of **3l**



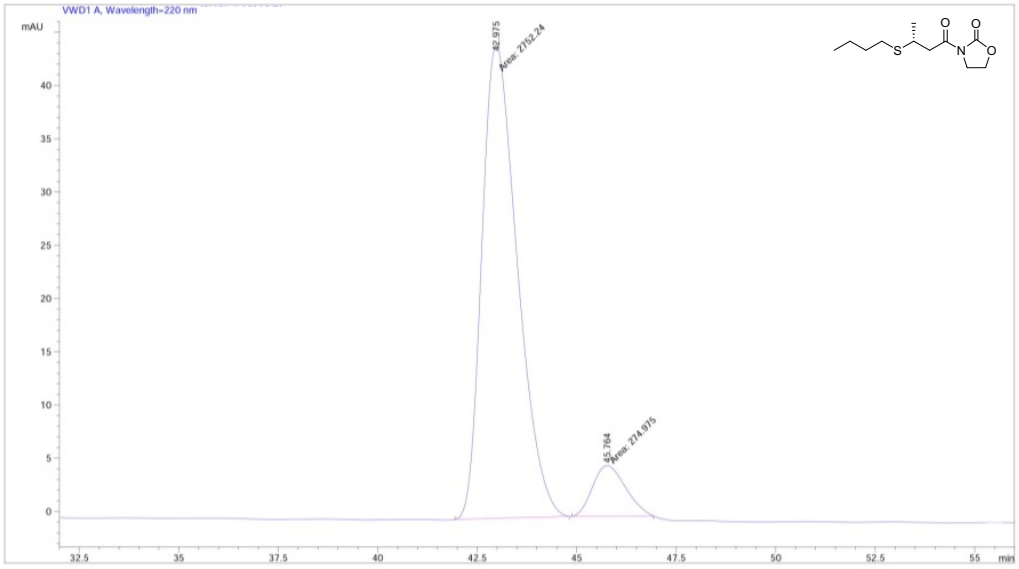
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	43.818	MM	0.7531	3237.41406	71.64645	5.0598
2	48.226	MM	0.9382	6.07453e4	1079.15674	94.9402
Totals :				6.39827e4	1150.80318	

95:5 *er* of **3m**



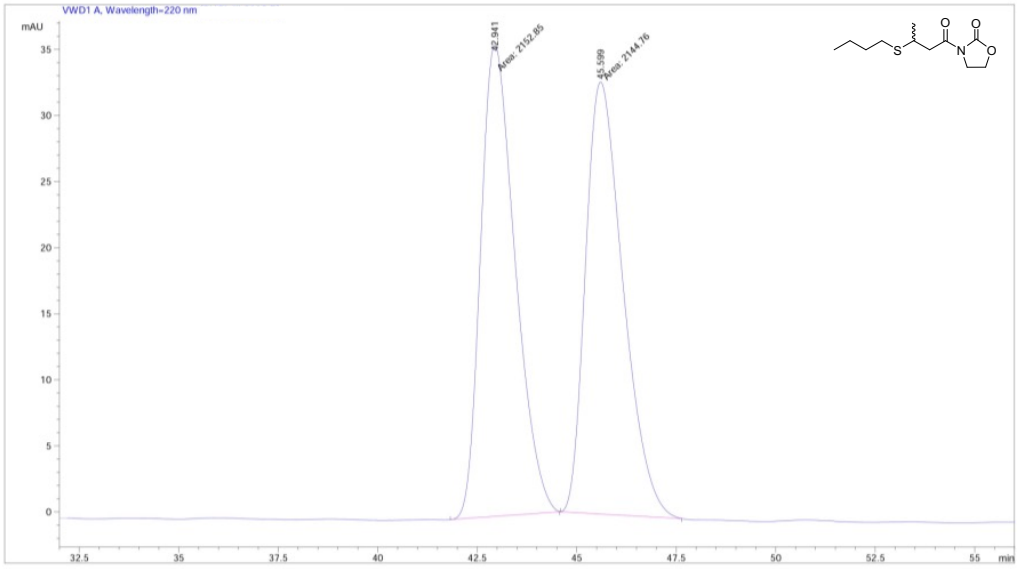
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	44.224	BB	0.7411	3.34239e4	695.64026	50.0466
2	48.726	BB	0.8693	3.33617e4	592.64679	49.9534
Totals :				6.67856e4	1288.28705	

Racemate of **3m**



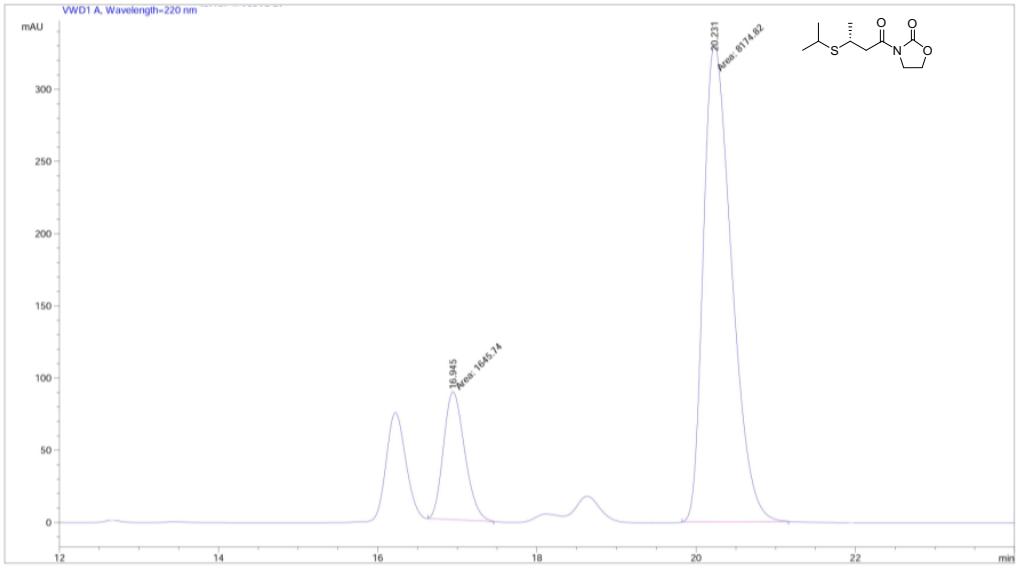
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	42.975	MM	1.0320	2752.24121	44.44815	90.9166
2	45.764	MM	0.9630	274.97513	4.75886	9.0834
Totals :				3027.21634	49.20702	

91:9 *er* of **3n**



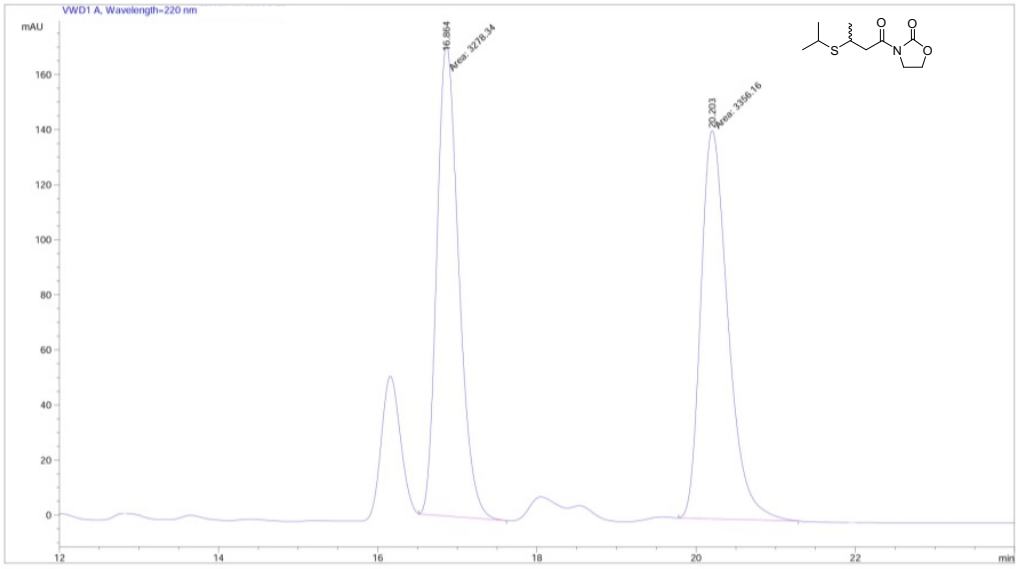
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	42.941	MM	1.0058	2152.84595	35.67539	50.0941
2	45.599	MM	1.0934	2144.75806	32.69350	49.9059
Totals :				4297.60400	68.36889	

Racemate of **3n**



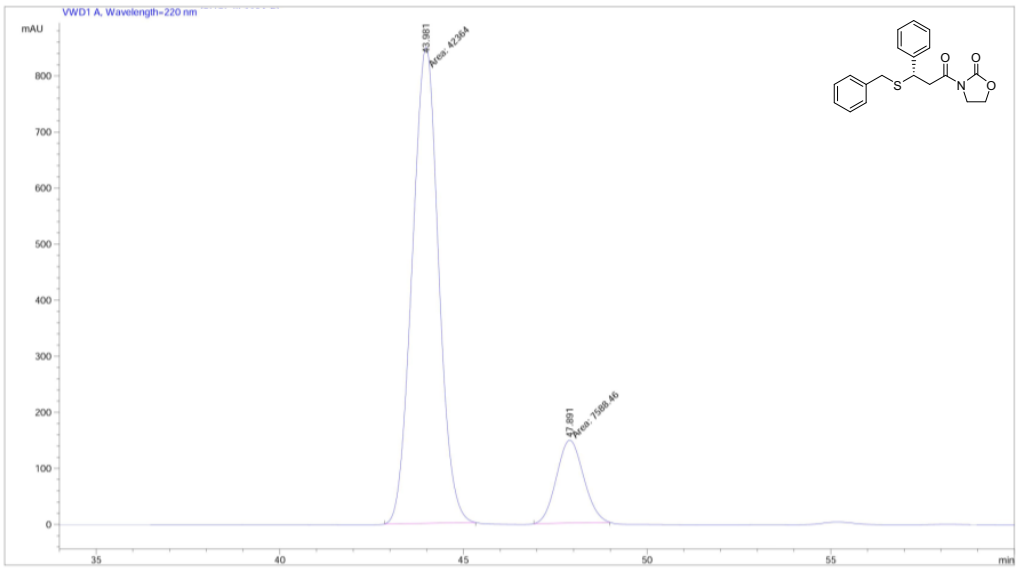
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.945	MM	0.3100	1645.73975	88.47187	16.7581
2	20.231	MM	0.4123	8174.82227	330.43857	83.2419
Totals :				9820.56201	418.91044	

83:17 *er* of **3o**



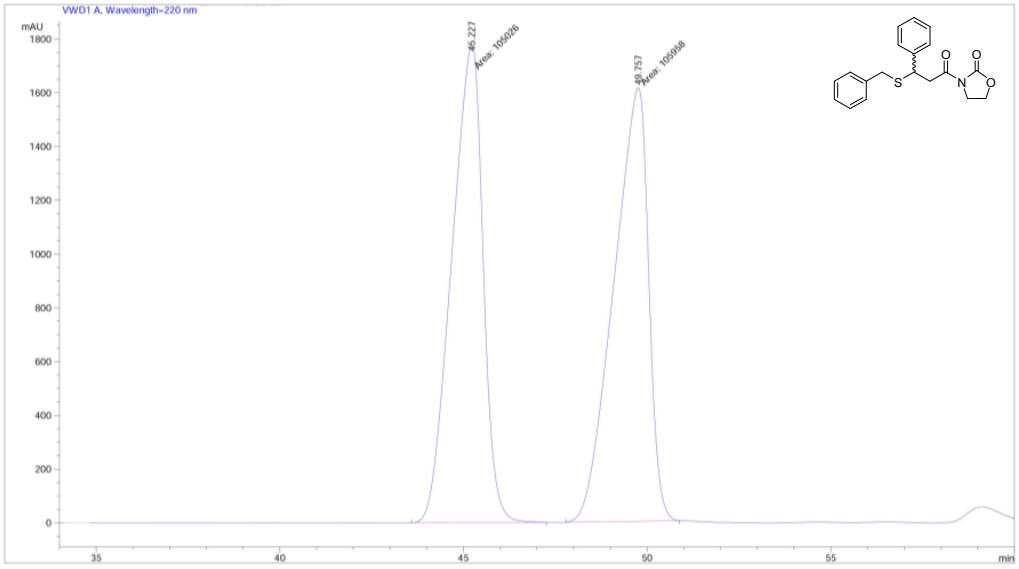
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.864	MM	0.3193	3278.33838	171.14581	49.4135
2	20.203	MM	0.3969	3356.16016	140.94955	50.5865
Totals :				6634.49854	312.09537	

Racemate of **3o**



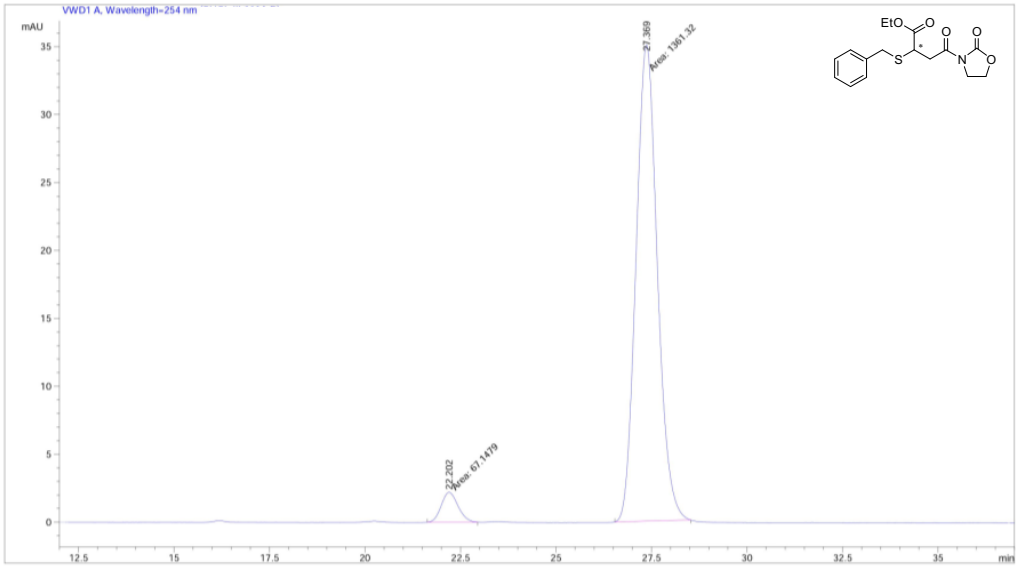
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	43.981	MM	0.8312	4.23640e4	849.48468	84.8086
2	47.891	MM	0.8561	7588.45947	147.73875	15.1914
Totals :				4.99525e4	997.22343	

85:15 *er* of **4b**



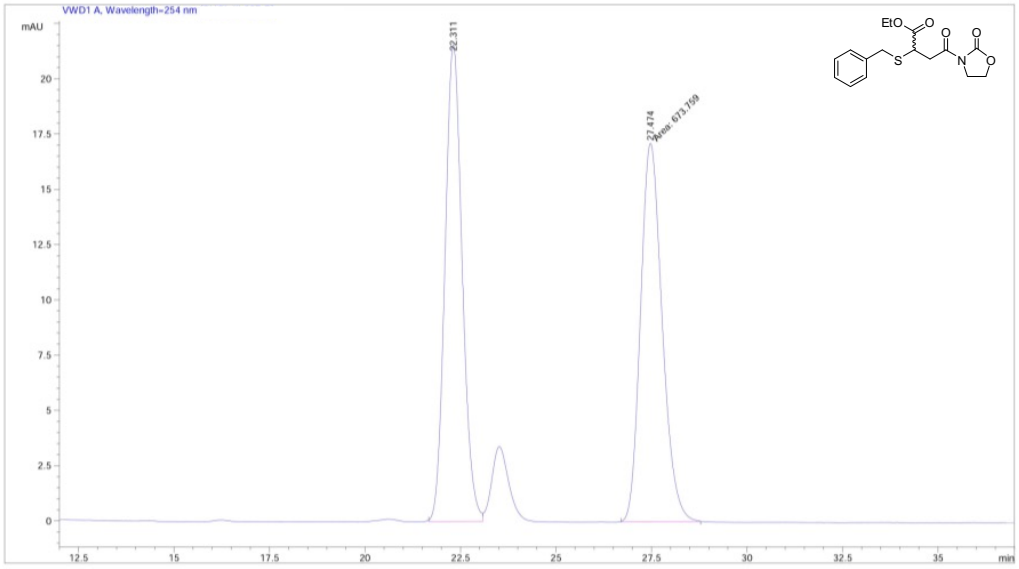
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	45.227	MM	0.9852	1.05026e5	1776.66772	49.7790
2	49.757	MM	1.0951	1.05958e5	1612.66394	50.2210
Totals :				2.10984e5	3389.33167	

Racemate of **4b**



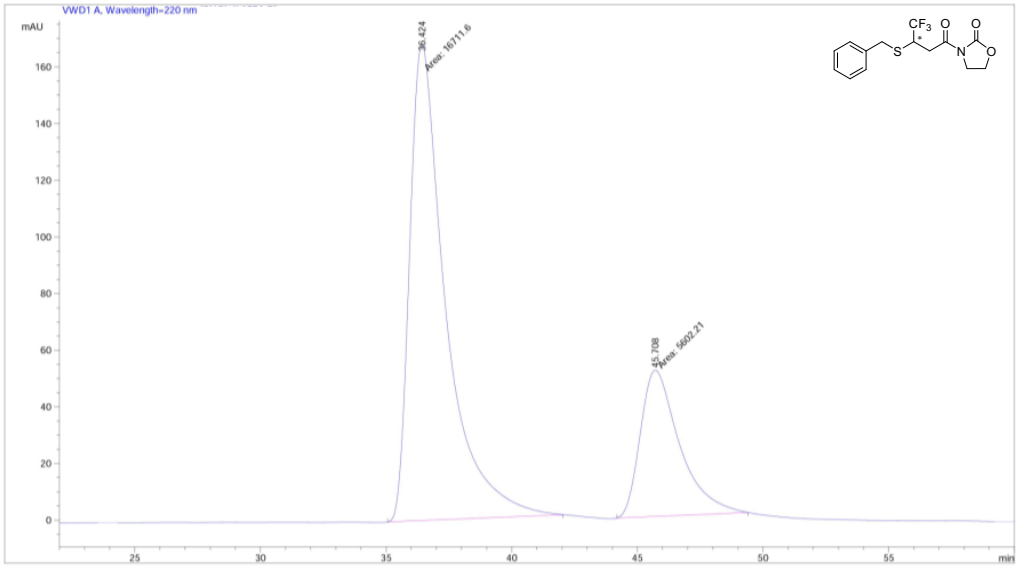
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.202	MM	0.5091	67.14787	2.19815	4.7007
2	27.369	MM	0.6473	1361.31628	35.05354	95.2993
Totals :				1428.46416	37.25170	

95:5 *er* of **4c**



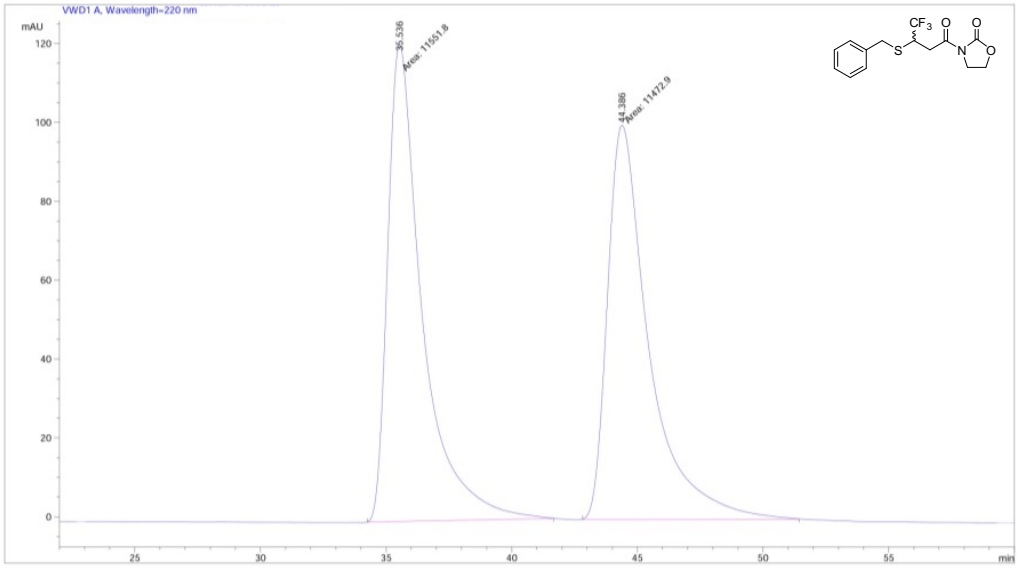
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	22.311	BV	0.4816	674.58514	21.55212	50.0306
2	27.474	MM	0.6564	673.75879	17.10721	49.9694
Totals :				1348.34393	38.65933	

Racemate of **4c**



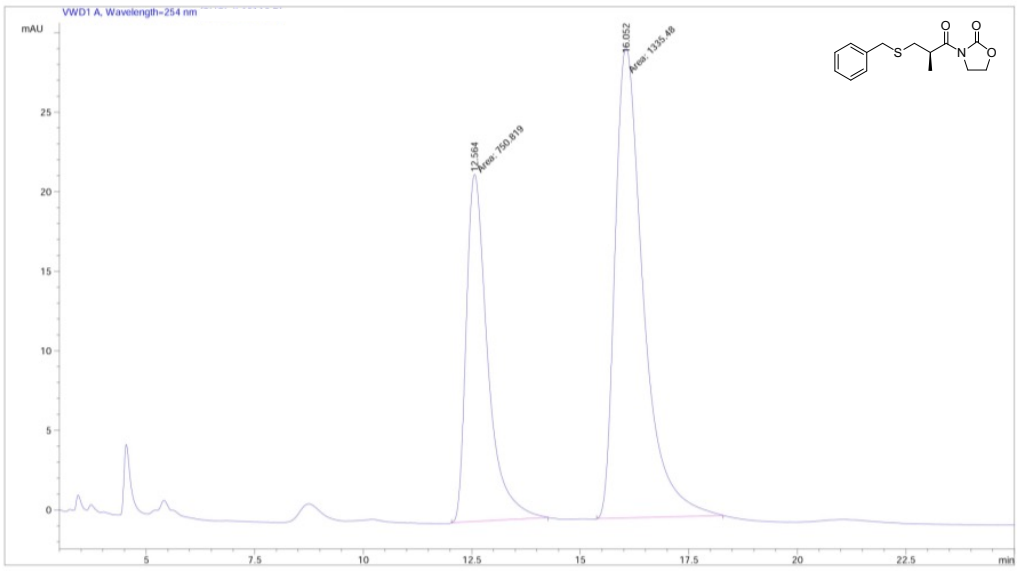
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	36.424	MM	1.6592	1.67116e4	167.86414	74.8935
2	45.708	MM	1.8105	5602.21143	51.57206	25.1065
Totals :				2.23138e4	219.43620	

75:25 *er* of **4d**



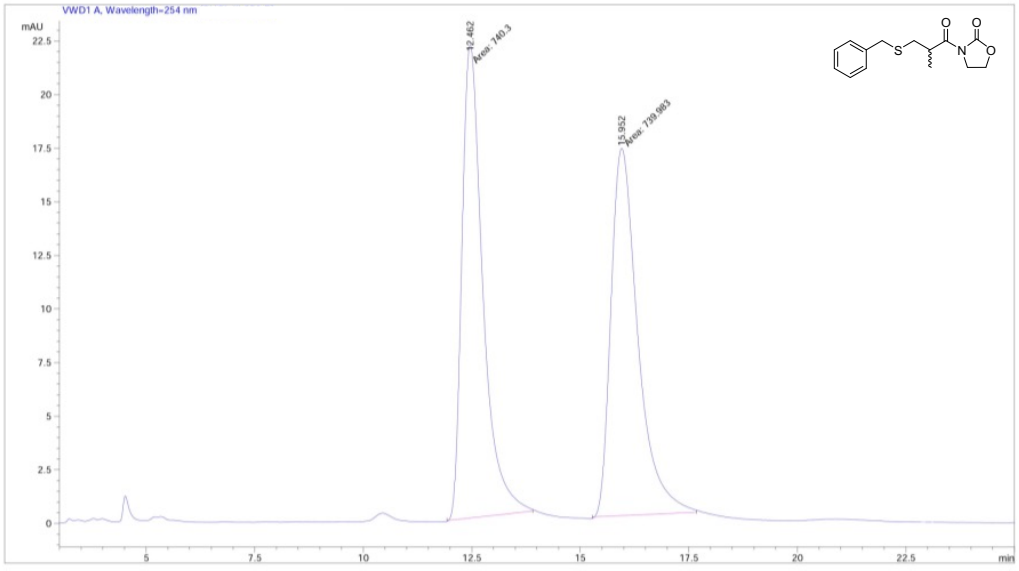
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	35.536	MM	1.5934	1.15518e4	120.82728	50.1713
2	44.386	MM	1.9134	1.14729e4	99.93286	49.8287
Totals :				2.30246e4	220.76014	

Racemate of **4d**



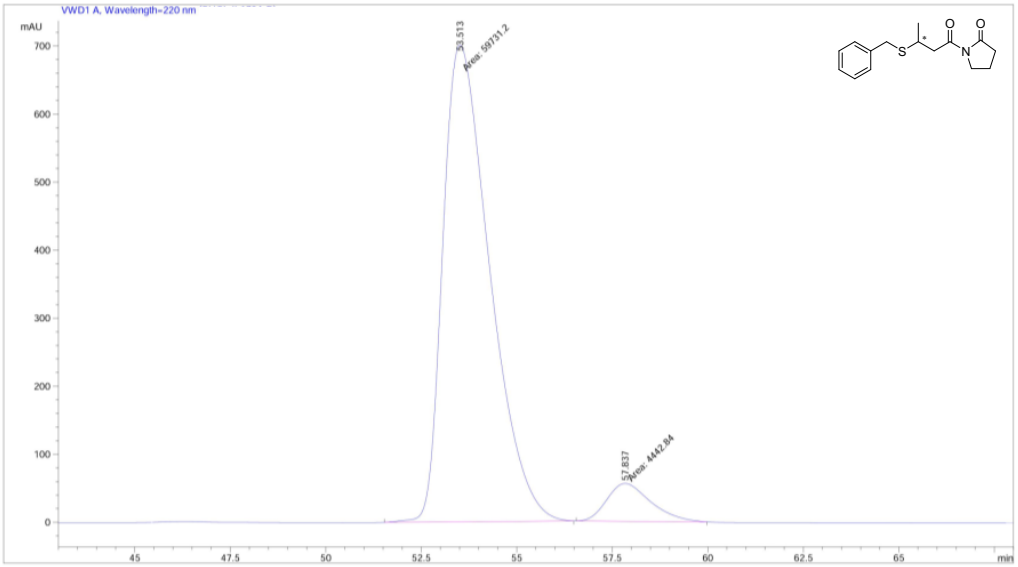
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.564	MM	0.5735	750.81934	21.82145	35.9881
2	16.052	MM	0.7516	1335.48145	29.61594	64.0119
Totals :				2086.30078	51.43739	

64:36 *er* of **4e**



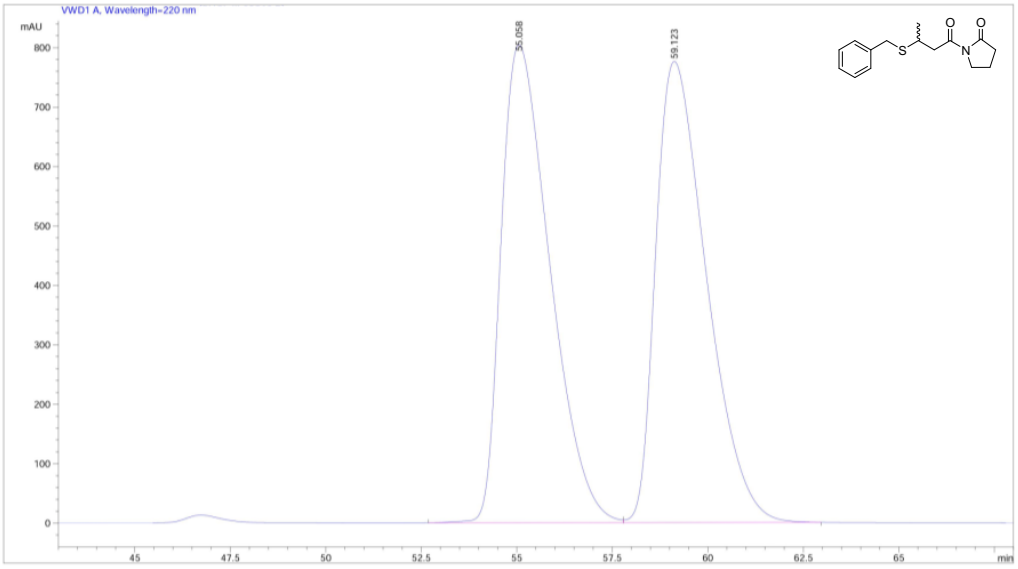
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.462	MM	0.5592	740.30048	22.06325	50.0107
2	15.952	MM	0.7200	739.98315	17.12854	49.9893
Totals :				1480.28363	39.19179	

Racemate of **4e**



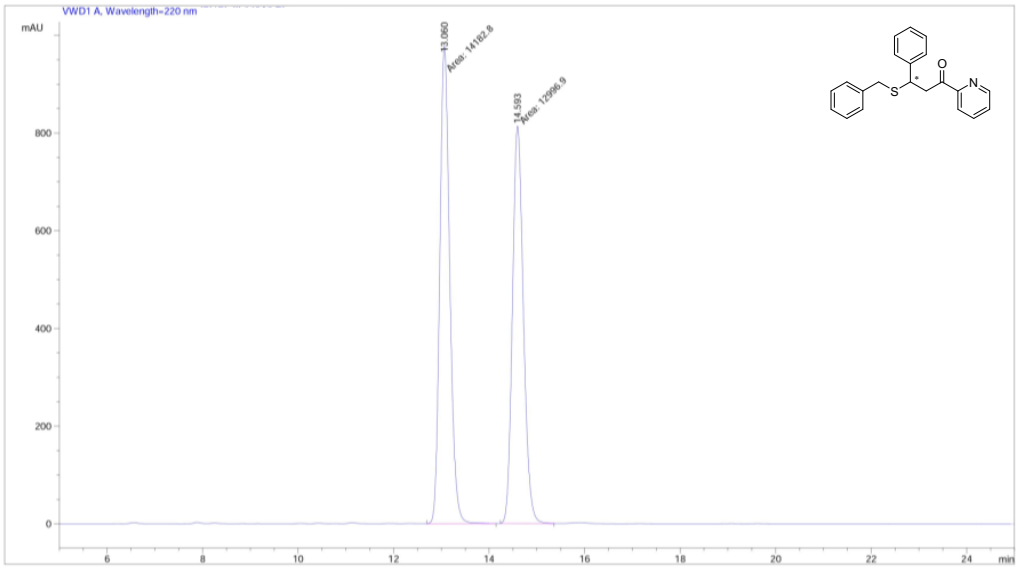
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	53.513	MM	1.4201	5.97312e4	701.01361	93.0769
2	57.837	MM	1.3293	4442.83838	55.70242	6.9231
Totals :				6.41740e4	756.71603	

93:7 *er* of **4f**



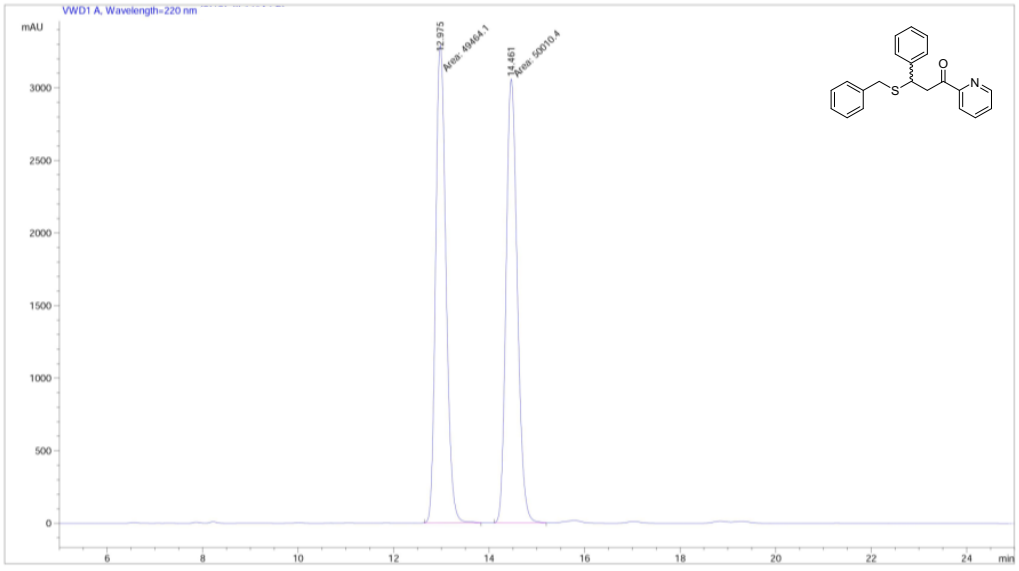
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	55.058	BV	1.3683	7.13914e4	803.69928	49.9365
2	59.123	VB	1.4129	7.15730e4	775.66827	50.0635
Totals :				1.42964e5	1579.36755	

Racemate of **4f**



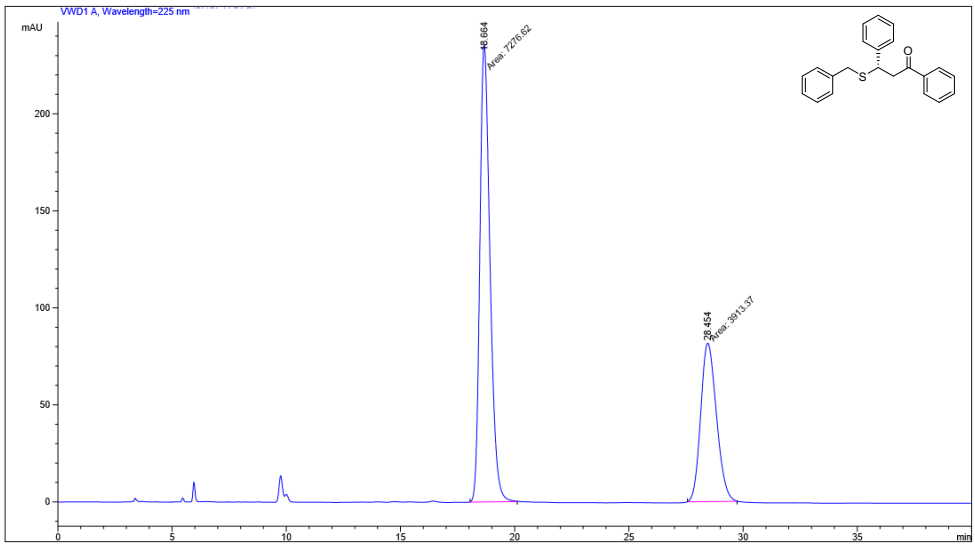
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.060	MM	0.2417	1.41828e4	978.16180	52.1816
2	14.593	MM	0.2662	1.29969e4	813.66882	47.8184
Totals :				2.71797e4	1791.83063	

52:48 *er* of **4g**



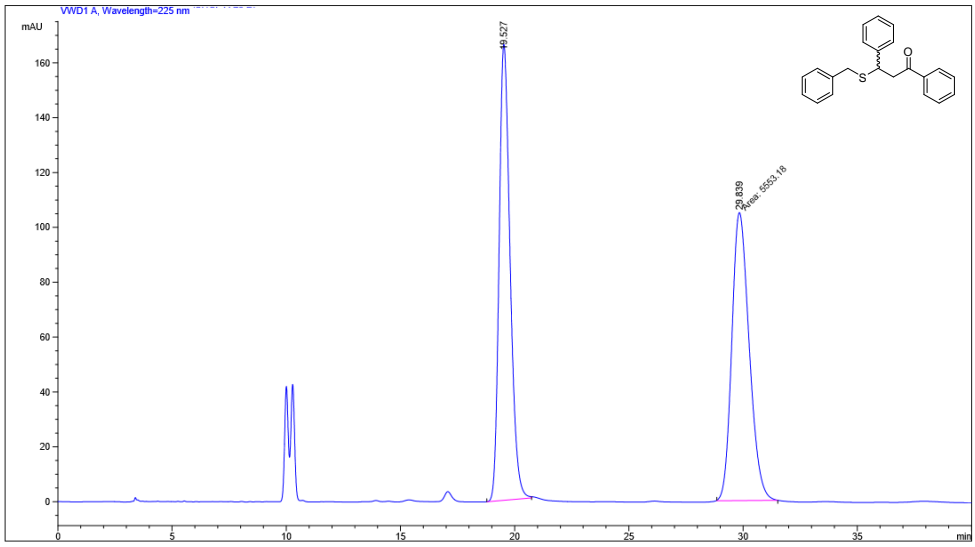
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.975	MM	0.2504	4.94641e4	3291.93115	49.7254
2	14.461	MM	0.2726	5.00104e4	3058.03345	50.2746
Totals :				9.94745e4	6349.96460	

Racemate of **4g**



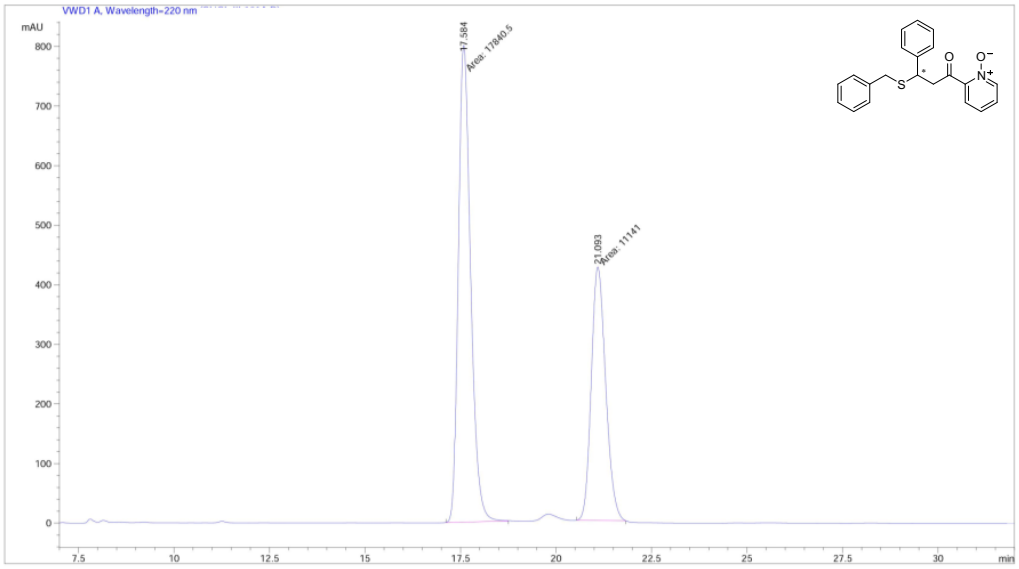
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.664	MM	0.5149	7276.62402	235.51611	65.0279
2	28.454	MM	0.7992	3913.37085	81.61155	34.9721
Totals :				1.11900e4	317.12766	

65:35 *er* of **4h**



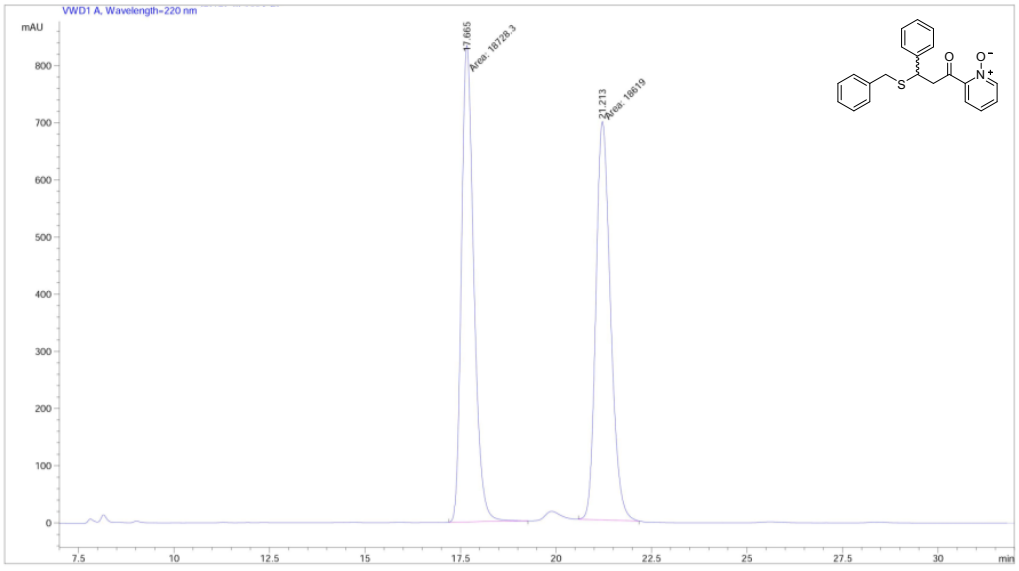
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.527	BB	0.5146	5550.88525	166.29572	49.9897
2	29.839	MM	0.8813	5553.18262	105.02449	50.0103
Totals :				1.11041e4	271.32021	

Racemate of **4h**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.584	MM	0.3717	1.78405e4	799.90369	61.5584
2	21.093	MM	0.4367	1.11410e4	425.21680	38.4416
Totals :				2.89815e4	1225.12048	

62:38 *er* of **4i**



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.665	MM	0.3744	1.87283e4	833.61224	50.1464
2	21.213	MM	0.4452	1.86190e4	696.97461	49.8536
Totals :				3.73473e4	1530.58685	

Racemate of **4i**