Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Divergent Pd-Catalyzed Cross-Coupling of Allenyloxazolidinones to give Chiral 1,3-Dienes and Vinyloxazolidinones

Ronald W. Brown, Farzad Zamani, Michael G. Gardiner, Haibo Yu, Stephen G. Pyne and Christopher J. T. Hyland*

Abstract: The divergent reactivity of 5-allenyloxazolidinones has been explored. This novel building block undergoes Pd(0)-catalyzed cross-coupling with boronic acids to form a wide range of chiral 1,3-dienes and pharmaceutically useful vinyloxazolidinones, the chemoselectivity being tightly controlled by a simple switch in additive.

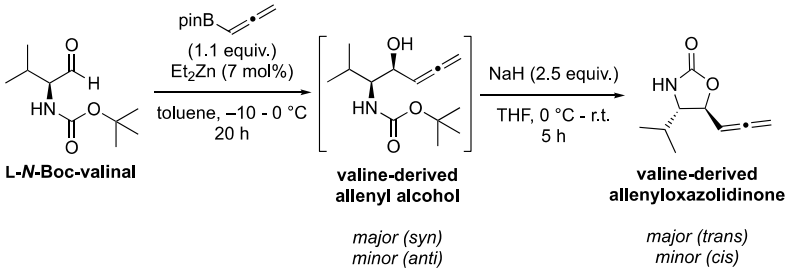
Table of Contents

1. General Experimental

All commercial reagents were used as received, unless otherwise noted. Anhydrous solvents were either purchased from commercial suppliers or passed over activated alumina, before being dried over pre-activated 3, 4 or 5 Å molecular sieves and stored under nitrogen gas. Reaction vessels were oven-dried (120 °C) overnight before use and all reactions were carried out under a nitrogen atmosphere, unless otherwise noted. Reactions were monitored via thin-layer chromatography (TLC) analysis using aluminium-backed silica gel sheets coated with fluorescent indicator F254 and visualized under UV light (254 nm) and anisaldehyde stain (4 mL anisaldehyde, 5 mL concentrated H_2SO_4, 2 mL glacial AcOH in 150 mL EtOH). Column chromatography was performed under compressed air using flash grade silica gel (40 – 60 nm). NMR spectroscopy was conducted using a Bruker 500 (500 MHz, ^{1}H, 125 MHz, ^{13}C) or Bruker 400 (400 MHz, ^{1}H, 100 MHz, ^{13}C) spectrometer. For samples dissolved in $CDCl_3$ (0.1% v/v TMS), chemical shifts (δ) have been reported in parts per million (ppm) and referenced to the $CDCl_3$ signal (7.26 ppm, ^{1}H, 77.0 ppm, ^{13}C) or TMS signal (0.00 ppm, ^{1}H and ^{13}C). Those dissolved in acetone-d6 have been referenced to the $(CD_3)_2CO$ signal (2.05 ppm, ^{1}H, 29.9, ^{13}C). Coupling constants (*J*) are reported in hertz (Hz). Multiplicities of NMR signals have been abbreviated as s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sext (sextet), sept (septet), oct (octet), dd (doublet of doublets), ddd (doublet of doublet of doublets), dt (doublet of triplets), ddt (doublet of doublet of triplets), tt (triplet of triplets), dq (doublet of quartets) or m (multiplet) and some denoted as app. (apparent) or br. (broad), with quaternary carbons denoted as 'QC' when reporting ^{13}C NMR signals. High resolution mass spectrometry (HRMS) was carried out using a Waters Xevo G1 QTof mass spectrometer. Infrared data was collected on either a Shimadzu IRAffinity-1 Miracle 10 Fourier transform infrared (FTIR) or Bruker Vertex 70 FTIR instrument and the intensities of the observed signals assigned as very weak (vw), weak (w), strong (s) or very strong (vs). Melting points (Mp) were obtained using a Buchi M-560 melting point apparatus. Optical rotation data was obtained using a JASCO P-2000 polarimeter at 589 nm and a 0.5 mL cell with a path length of 0.5 decimeters. Chiral high-performance liquid chromatography (HPLC) was conducted using a Shimadzu Nexera X2 UHPLC system equipped with a PDA detector, under normal-phase conditions. Fresh $Pd_2dba_3{\cdot}CHCl_3$ was synthesized at a purity of > 90% (via ^{1}H NMR analysis) using the procedure outlined by Zalesskiy and Ananikov.[1] The L-α-amino aldehydes were prepared via the TEMPO-catalyzed oxidation of L-α-amino alcohols reported in our previous work.[2] The NMR data for all L-α-amino aldehydes matches that previously reported in the literature.[3] The allenyloxazolidinones were prepared via a slightly modified version (detailed herein) of our previously reported method, and the NMR data of these products match that reported therein.[2]

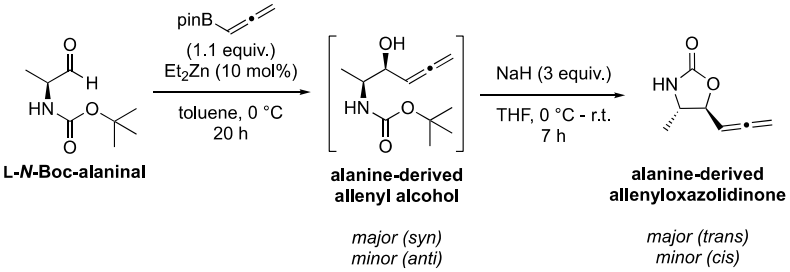
2. Synthesis of 5-allenyloxazolidinones

(4*S*,5*S*)-4-isopropyl-5-(propa-1,2-dien-1-yl)oxazolidin-2-one:



In order to reduce the scale of the reaction to maintain an acceptable diastereoisomeric ratio, a solution of L-*N*-Boc-valinal (1.88 g, 9.35 mmol, 1 equiv.) in toluene (9 mL) was divided into 3×3mL aliquots (0.63 g, 3.12 mmol each) and distributed equally into 3 oven-dried reaction vessels under nitrogen and the vessels cooled to −10 °C with stirring. To each was added allenylboronic acid pinacol ester (0.62 mL, 3.43 mmol, 1.1 equiv.), followed by Et_2Zn (0.22 mmol of a 15% wt. solution in toluene, 7 mol%) dropwise at −10 °C. The homogenous solutions were transferred to a refrigerator and left at approximately 0 °C overnight. After 20 hours, the reactions were warmed to room temperature and diethanolamine (0.56 mL, 5.80 mmol, 2.0 equiv.) was added to each and the mixtures stirred for 1 hour at room temperature. Each organic layer was washed with brine and extracted with EtOAc, before drying with $MgSO_4$, filtration and concentration *in vacuo* to give the crude products. These were combined and subjected to column chromatography (Et_2O/hexane, 50:50) to give the allenyl alcohol as a deep brown oil (Rf = 0.30, Et_2O/hexane, 50:50). The allenyl alcohol was dissolved in THF (15 mL) in an oven-dried Schlenk flask and cooled to 0 °C with stirring, before NaH (60% dispersion in mineral oil, 0.623 g, 2.0 equiv.) was added in one portion. The reaction was warmed to room temperature and stirred for 2 hours, after which an additional portion of NaH (0.5 equiv.) was added for the reaction to proceed to completion. After a further 3 hours, the reaction was cooled to 0 °C and quenched with a saturated aqueous solution of NH_4Cl. The organic layer washed with brine and extracted with CH_2Cl_2 before drying with $MgSO_4$, filtration and concentration *in vacuo* to give the crude allenyloxazolidinone, which was subjected to column chromatography (acetone/pentane, 20:80) to give the pure allenyloxazolidinone as a yellow oil (0.858 g, 5.13 mmol, 55 %, 3.3:1 *dr*). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.97 (s, 1H, NH, *major*), 6.89 (s, 1H, NH, *minor*), 5.34 (app. q, *J* = 6.7 Hz, 1H, =CH, *major*), 5.31 (app. dt, *J* = 8.9, 6.6 Hz, 1H, =CH, *minor*), 5.04 (app. ddt, *J* = 8.7, 7.7, 1.1 Hz, 1H, CH-O, *minor*), 4.99 – 4.87 (m, 2H, $=CH_2$, *minor*), 4.95 (ddd, *J* = 6.5, 3.0, 1.9 Hz, 1H, $=CH_2$, *major*), 4.72 (app. ddt, *J* = 7.3, 5.5, 1.9 Hz, 1H, CH-O, *major*), 3.60 (app. t, *J* = 8.0 Hz, 1H, CH-N, *minor*), 3.43 (ddd, *J* = 6.7, 5.4, 1.1 Hz, 1H, CH-N, *major*), 1.91 – 1.83 (m, 1H, *i*-PrCH, *minor*), 1.74 (app. oct, *J* = 6.7 Hz, 1H, *i*-PrCH, *major*), 0.99 (d, *J* = 6.6 Hz, 3H, *i*-$PrCH_3$, *minor*), 0.94 (d, *J* = 6.7 Hz, 3H, *i*-$PrCH_3$, *major*), 0.90 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$, *major*), 0.88 (d, *J* = 6.7 Hz, 3H, *i*-$PrCH_3$, *minor*) ppm.- **^{13}C NMR** (125 MHz, $CDCl_3$): δ 209.8 (QC, =C=, *minor*), 208.7 (QC, =C=, *major*), 160.0 (QC, CO, *minor*), 159.3 (QC, CO, *major*), 90.4 (CH, =CH, *major*), 85.7 (CH, =CH, *minor*), 78.8 (CH, CH-O, *minor*), 78.6 (CH_2, $=CH_2$, *major*), 78.0 (CH, CH-O, *major*), 77.4 (CH_2, $=CH_2$, *minor*), 63.5 (CH, CH-N, *major*), 62.6 (CH, CH-N, *minor*), 32.3 (CH, *i*-PrCH, *major*), 28.7 (CH, *i*-PrCH, *minor*), 19.2 (CH_3, *i*-$PrCH_3$, *minor*), 19.0 (CH_3, *i*-$PrCH_3$, *minor*), 17.9 (CH_3, *i*-$PrCH_3$, *major*), 17.8 (CH_3, *i*-$PrCH_3$, *major*) ppm. The NMR data match that previously reported.[2]

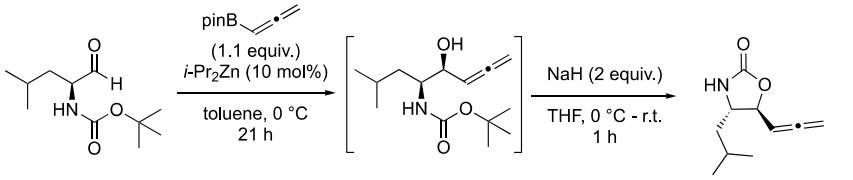
(4*S*,5*S*)-4-methyl-5-(propa-1,2-dien-1-yl)oxazolidin-2-one:



A solution of L-*N*-Boc-alaninal (0.526 g, 3.04 mmol, 1.0 equiv.) in toluene (8 mL) in an oven-dried Schlenk flask was cooled to 0 °C with stirring. To this was added allenylboronic acid pinacol ester (0.65 mL, 3.62 mmol, 1.1 equiv.), followed by Et_2Zn (0.33 mmol of a 1.0 M solution in hexane, 10 mol%) dropwise at 0 °C. The homogenous solution was stirred at 0 °C for 5 minutes before being

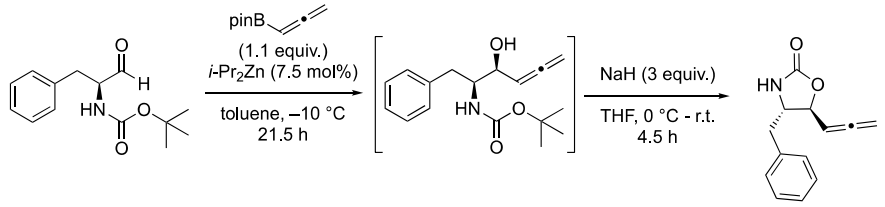
transferred to a refrigerator to be left at approximately 0 °C overnight. After 20 hours, the reaction was quenched with a saturated aqueous solution of NH_4Cl at 0 °C and warmed to room temperature before washing with saturated aqueous $NaHCO_3$ and drying with Na_2SO_4, before filtration and concentration *in vacuo* to give the crude product, which was subjected to column chromatography (EtOAc/hexane, 30:70) to give the allenyl alcohol as a yellow oil (Rf = 0.25, EtOAc/hexane, 30:70). The allenyl alcohol was dissolved in THF (6 mL) in an oven-dried Schlenk flask and cooled to 0 °C with stirring, before NaH (60% dispersion in mineral oil, 0.165 g, 4.13 mmol, 2.0 equiv.) was added in one portion. The reaction was warmed to room temperature and stirred for 2 hours, after which an additional portion of NaH (1.0 equiv.) was added for the reaction to proceed to completion. After a further 5 hours, the reaction was cooled to 0 °C and quenched with a saturated aqueous solution of NH_4Cl. The organic layer was washed with brine and extracted with CH_2Cl_2, dried with $MgSO_4$, filtered and the filtrate concentrated *in vacuo* to give the crude product (2.6:1 *dr*). The *trans* isomer of the allenyl oxazolidinone was isolated via column chromatography (CH_2Cl_2/Et_2O, 2:98) as a colourless oil (0.156 g, 1.12 mmol, 37%, > 99:1 *dr*). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 6.68 (s, 1H, NH), 5.30 (app. q, *J* = 6.7 Hz, 1H, =CH), 5.03 – 4.85 (m, 2H, $=CH_2$), 4.52 (app. tt, *J* = 7.0, 1.8 Hz, 1H, CH-O), 3.76 (app. p, *J* = 6.3 Hz, 1H, CH-N), 1.26 (d, *J* = 6.3 Hz, 3H, Me) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 208.9 (QC, =C=), 159.1 (QC, CO), 88.8 (CH, =CH), 81.4 (CH, CH-O), 78.3 (CH_2, $=CH_2$), 53.8 (CH, CH-N), 19.7 (CH_3, Me) ppm. The NMR data match that previously reported.[2]

(4*S*,5*S*)-4-isobutyl-5-(propa-1,2-dien-1-yl)oxazolidin-2-one:



A solution of L-*N*-Boc-leucinal (0.205 g, 0.95 mmol, 1.0 equiv.) in toluene (2.6 mL) in an oven-dried Schlenk flask was cooled to 0 °C with stirring. To this was added allenylboronic acid pinacol ester (0.19 mL, 1.05 mmol, 1.1 equiv.), followed by *i*-Pr_2Zn (0.10 mmol of a 1.0M solution in toluene, 10 mol%) dropwise at 0 °C. The homogenous solution was stirred at 0 °C for 3 hours before being transferred to a refrigerator to be left at approximately 0 °C overnight. After 18 hours, the reaction was quenched with a saturated aqueous solution of NH_4Cl at 0 °C and warmed to room temperature before washing with saturated aqueous $NaHCO_3$, extracting with EtOAc and drying with Na_2SO_4, then filtration and concentration *in vacuo* to give the crude product, which was subjected to column chromatography (EtOAc/hexane, 20:80) to give the allenyl alcohol as an orange oil (Rf = 0.31, EtOAc/hexane, 20:80). The allenyl alcohol was dissolved in THF (2 mL) in an oven-dried Schlenk flask and cooled to 0 °C with stirring, before NaH (60% dispersion in mineral oil, 64.7 mg, 1.61 mmol, 2.0 equiv.) was added in one portion. The reaction was warmed to room temperature and stirred for 1 hour before cooling to 0 °C and quenching with a saturated aqueous solution of NH_4Cl. The organic layer was washed with brine and extracted with CH_2Cl_2, dried with $MgSO_4$, filtered and the filtrate concentrated *in vacuo* to give the crude product. This was subjected to column chromatography (acetone/pentane, 20:80) to give the pure allenyloxazolidinone as a colourless oil (0.102 g, 0.60 mmol, 63%, 4.7:1 *dr*). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.12 (br. s, 1H, NH, *major* and *minor*), 5.30 (app. q, *J* = 6.7 Hz, 1H, =CH, *major*), 5.21 (app. dt, *J* = 8.8, 6.5 Hz, 1H, =CH, *minor*), 5.04 (app. t, *J* = 8.9 Hz, 1H, CH-O, *minor*), 4.97 – 4.83 (m, 2H, $=CH_2$, *minor*), 4.93 (app. dt, *J* = 6.5, 2.0 Hz, 2H, $=CH_2$, *major*), 4.56 (app. tt, *J* = 6.7, 1.9 Hz, 1H, CH-O, *major*), 3.99 – 3.93 (m, 1H, CH-N, *minor*), 3.73 – 3.68 (m, 1H, CH-N, *major*), 1.71 – 1.57 (m, 1H, *i*-BuCH, *major* and *minor*), 1.52 – 1.21 (m, 2H, *i*-$BuCH_2$, *major* and *minor*), 0.92 – 0.86 (m, 6H, *i*-$BuCH_3$, *major* and *minor*) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 209.5 (QC, =C=, *minor*), 208.8 (QC, =C=, *major*), 159.6 (QC, CO, *minor*), 159.4 (QC, CO, *major*), 89.3 (CH, =CH, *major*), 86.0 (CH, =CH, *minor*), 80.2 (CH, CH-O, *major*), 78.6 (CH, CH-O, *minor*), 78.3 (CH_2, $=CH_2$, *major*), 77.3 (CH_2, $=CH_2$, *minor*), 56.3 (CH, CH-N, *major*), 54.0 (CH, CH-N, *minor*), 43.8 (CH_2, *i*-$BuCH_2$, *major*), 39.6 (CH_2, *i*-$BuCH_2$, *minor*), 24.7 (CH, *i*-BuCH, *major* and *minor*), 23.4 (CH_3, *i*-$BuCH_3$, *minor*), 22.8 (CH_3, *i*-$BuCH_3$, *major*), 21.9 (CH_3, *i*-$BuCH_3$, *major*), 21.3 (CH_3, *i*-$BuCH_3$, *minor*) ppm. The NMR data match that previously reported.[2]

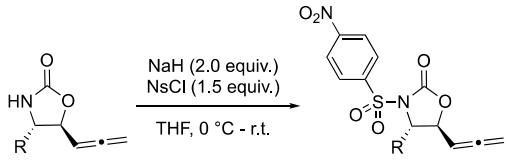
(4*S*,5*S*)-4-benzyl-5-(propa-1,2-dien-1-yl)oxazolidin-2-one:



A solution of L-*N*-Boc-phenylalaninal (0.418 g, 1.68 mmol, 1 equiv.) in toluene (5 mL) in an oven-dried Schlenk flask was cooled to −10 °C with stirring. To this was added allenylboronic acid pinacol ester (0.33 mL, 1.84 mmol, 1.1 equiv.), followed by *i*-Pr_2Zn (0.13 mmol of a 1.0 M solution in toluene, 7.5 mol%) dropwise at −10 °C. The homogenous solution was stirred at −10 °C for 1.5 hours before being transferred to a refrigerator to be left at approximately 0 °C overnight. After 20 hours, the reaction was warmed to room temperature and diethanolamine (0.30 mL, 3.1 mmol, 2.0 equiv.) was added and the mixture stirred for 1 hour at room temperature. The organic layer was washed with brine and extracted with EtOAc, before drying with $MgSO_4$, filtration and concentration *in vacuo* to give the crude product. This was subjected to column chromatography (EtOAc/hexane, 30:70) to give the allenyl alcohol as a white solid (Rf = 0.30, EtOAc/hexane, 30:70). The allenyl alcohol was dissolved in THF (4 mL) in an oven-dried Schlenk flask and cooled to 0 °C with stirring, before NaH (60% dispersion in mineral oil, 0.131 g, 3.26 mmol, 2.0 equiv.) was added in one portion. The reaction was warmed to room temperature and stirred for 2.5 hours, after which an additional portion of NaH (1.0 equiv.) was added for the reaction to proceed to completion. After a further 2 hours, the reaction was cooled to 0 °C and quenched with a saturated aqueous solution of NH_4Cl. The organic layer was washed with brine and extracted with CH_2Cl_2, dried with $MgSO_4$, filtered and the filtrate concentrated *in vacuo* to give the crude product. This was subjected to column chromatography (acetone/pentane, 20:80) to give the pure allenyloxazolidinone as a yellow oil (0.122 g, 0.57 mmol, 34%, 2.9:1 *dr*). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.33 – 7.16 (m, 5H, ArH, *major* and *minor*), 6.29 (s, 1H, NH, *major*), 5.74 (s, 1H, NH, *minor*), 5.36 (app. dt, *J* = 8.6, 6.6 Hz, 1H, =CH, *minor*), 5.25 (app. q, *J* = 6.7 Hz, 1H, =CH, *major*), 5.14 (app. ddt, *J* = 8.9, 7.7, 1.4 Hz, 1H, CH-O, *minor*), 5.01 – 4.84 (m, 2H, $=CH_2$, *major* and *minor*), 4.73 (app. ddt, *J* = 6.8, 5.9, 2.0 Hz, 1H, CH-O, *major*), 4.15 – 4.11 (m, 1H, CH-N, *minor*), 3.93 – 3.89 (m, 1H, CH-N, *major*), 2.91 (dd, *J* = 13.7, 4.6 Hz, 1H, $BnCH_2$, *minor*), 2.88 (d, *J* = 6.8 Hz, 2H, $BnCH_2$, *major*), 2.73 (dd, *J* = 13.7, 10.1 Hz, 1H, $BnCH_2$, *minor*) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 209.6 (QC, =C=, *minor*), 208.6 (QC, =C=, *major*), 158.5 (QC, CO, *major*), 158.4 (QC, CO, *minor*), 136.6 (QC, ArC, *minor*), 135.7 (QC, ArC, *major*), 129.1 (CH, 2×ArCH, *major*), 128.8 (CH, 2×ArCH, *minor*), 128.7 (CH, 2×ArCH, *major* and *minor*), 127.01 (CH, ArCH, *major*), 126.96 (CH, ArCH, *minor*), 89.1 (CH, =CH, *major*), 85.9 (CH, =CH, *minor*), 78.9 (CH, CH-O, *major*), 78.4 (CH_2, $=CH_2$, *major*), 78.0 (CH, CH-O, *minor*), 77.7 (CH_2, $=CH_2$, *minor*), 59.0 (CH, CH-N, *major*), 57.2 (CH, CH-N, *minor*), 40.6 (CH_2, $BnCH_2$, *major*), 37.2 (CH_2, $BnCH_2$, *minor*) ppm. The NMR data match that previously reported.[2]

3. Synthesis of *N*-nosyl-5-allenyloxazolidinones (1a-d)

General procedure:

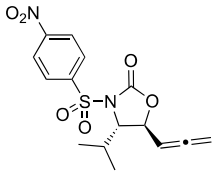


allenyloxazolidinone — **1a-d**

major (syn) / *minor (anti)* — *major (trans)* / *minor (cis)*

A solution of the allenyloxazolidinone in THF (typically approximately 0.2 M) was cooled to 0 °C with stirring, before NaH (60% dispersion in mineral oil, 2.0 equiv.) was added portionwise. After 15 minutes, nosyl chloride (1.5 equiv.) was added portionwise at 0 °C and the reaction warmed to room temperature and stirred for 2 hours, or until the allenyloxazolidinone could no longer be detected via TLC analysis. The reaction was quenched with a saturated aqueous solution of NH_4Cl and extracted with EtOAc before drying with $MgSO_4$, filtration and concentration *in vacuo* to give the crude product, which was purified via column chromatography.

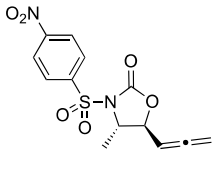
(4*S*,5*S*)-4-isopropyl-3-((4-nitrophenyl)sulfonyl)-5-(propa-1,2-dien-1-yl)oxazolidin-2-one (1a):



1a

Eluent: MeOH/CH_2Cl_2 (2:98). Yellow solid, 95%, 2.8:1 *dr*. The *trans* diastereoisomer was isolated via selective recrystallization in CH_2Cl_2 layered with hexane (white crystals, 54%, > 99:1 *dr*). The enantiopurity was determined via chiral HPLC using a Daicel CHIRALPAK IA-U column, hexane/isopropanol (95:5), 0.2 mL/min, 40 °C, 254 nm, single peak, t_R = 24.91 min, > 99% *ee*. Racemic **1a**, prepared from racemic *N*-Boc-valinal, gave two peaks (t_R = 21.71, 24.08 min, 1:1) under the same conditions. $[\alpha]_D^{22}$ +41.4 (*c* 2.99, $CHCl_3$). Mp 125.9 – 130.9 °C. **HRMS-ESI** (*m*/*z*): $[M+Na]^+$ calcd for $C_{15}H_{16}N_2O_6SNa$, 375.0621; found, 375.0625. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3112 (w, C=CH), 2962 – 2935 (w), 2878 (w), 1955 (w), 1767 (s, CO), 1379 (s), 1352 (s), 1179 (s), 1128 (s), 1011 (s), 855 (s), 745 (s), 737 (s), 615 (vs). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 9.0 Hz, 2H, NsCH), 8.28 (d, *J* = 9.1 Hz, 2H, NsCH), 5.30 (app. q, *J* = 6.6 Hz, 1H, =CH), 5.04 (app. t, *J* = 2.3 Hz, 1H, =CH_2), 5.02 (dd, *J* = 2.4, 1.7 Hz, 1H, =CH_2), 4.79 – 4.76 (m, 1H, CH-O), 4.35 (dd, *J* = 3.9, 2.5 Hz, 1H, CH-N), 2.49 – 2.37 (m, 1H, *i*-PrCH), 0.97 (d, *J* = 7.0 Hz, 3H, *i*-PrCH_3), 0.82 (d, *J* = 6.9 Hz, 3H, *i*-PrCH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 207.9 (QC, =C=), 151.3 (QC, CO), 151.0 (QC, NsC), 143.3 (QC, NsC), 129.9 (CH, 2×NsCH), 124.2 (CH, 2×NsCH), 89.8 (CH, =CH), 80.3 (CH_2, =CH_2), 72.9 (CH, CH-O), 66.6 (CH, CH-N), 30.4 (CH, *i*-PrCH), 17.5 (CH_3, *i*-PrCH_3), 14.8 (CH_3, *i*-PrCH_3) ppm. A crystal structure for **1a** was obtained (CCDC 1919153).

(4*S*,5*S*)-4-methyl-3-((4-nitrophenyl)sulfonyl)-5-(propa-1,2-dien-1-yl)oxazolidin-2-one (1b):

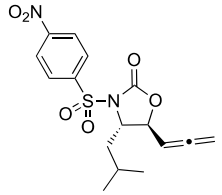


1b

Eluent: EtOAc/hexane (40:60). White crystals, 58%, > 99:1 *dr*. $[\alpha]_D^{23}$ +1.6 (*c* 1.10, $CHCl_3$). Mp 98.9 – 101.5 °C. **HRMS-ESI** (*m*/*z*): $[M+Na]^+$ calcd for $C_{13}H_{12}N_2O_6SNa$, 347.0308; found, 347.0306. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3104 (w, C=CH), 3068 (w), 3029 (w), 2990 (w), 1948 (w), 1782 (s, CO), 1608 (w), 1535 (s), 1362 (s), 1348 (s), 1318 (m), 1287 (m), 1172 (s), 1132 (s), 1110 (s), 1089 (s), 854 (s), 751 (s), 616 (vs). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.41 (d, *J* = 9.0 Hz, 2H, NsCH), 8.27 (d, *J* = 9.1 Hz, 2H, NsCH), 5.30 – 5.25 (m, 1H, =CH), 5.04 (dd, *J* = 2.1, 1.5 Hz, 1H, =CH_2), 5.03 (dd, *J* = 2.1, 1.0 Hz, 1H, =CH_2), 4.59 (app. oct, 1H, CH-O), 4.42 (app. dq, *J* = 6.3, 4.1 Hz,

1H, CH-N), 1.59 (d, *J* = 6.3 Hz, 3H, Me) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 208.6 (QC, =C=), 150.96 (QC, CO), 150.94 (QC, NsC), 143.3 (QC, NsC), 129.9 (CH, 2×NsCH), 124.3 (CH, 2×NsCH), 88.1 (CH, =CH), 80.0 (CH_2, $=CH_2$), 79.1 (CH, CH-O), 58.5 (CH, CH-N), 20.1 (CH_3, Me) ppm.

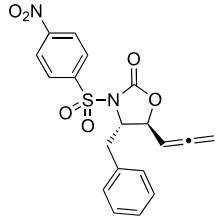
(4*S*,5*S*)-4-isobutyl-3-((4-nitrophenyl)sulfonyl)-5-(propa-1,2-dien-1-yl)oxazolidin-2-one (1c):



1c

Eluent: EtOAc/hexane (20:80). Colourless oil, 93%, 4.9:1 *dr* (after purification). **HRMS-ESI** (*m*/*z*): $[M+Na]^+$ calcd for $C_{16}H_{18}N_2O_6SNa$, 389.0778; found, 389.0796. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3108 (w, C=CH), 2959 – 2872 (w), 1954 (w), 1776 (vs, CO), 1607 (w), 1531 (s), 1348 (s), 1172 (vs), 1139 (s), 1090 (s), 855 (s), 736 (s), 613 (vs). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8.8 Hz, 2H, NsCH, *major* and *minor*), 8.29 – 8.26 (m, 2H, NsCH, *major* and *minor*), 5.29 (app. q, *J* = 6.4 Hz, 1H, =CH, *major*), 5.21 (app. dt, *J* = 8.8, 6.5 Hz, 1H, =CH, *minor*), 5.10 (app. ddt, *J* = 8.4, 6.9, 1.2 Hz, 1H, CH-O, *minor*), 5.05 – 4.96 (m, 2H, $=CH_2$, *minor*), 5.03 (dd, *J* = 6.6, 2.4 Hz, 2H, $=CH_2$, *minor*), 4.74 – 4.72 (m, 1H, CH-O, *major*), 4.56 – 4.52 (m, 1H, CH-N, *minor*), 4.42 (app. ddd, *J* = 10.7, 3.4, 2.4 Hz, 1H, CH-N, *major*), 1.93 – 1.87 (m, 1H, *i*-$BuCH_2$, *major*), 1.81 – 1.76 (m, 1H, *i*-$BuCH_2$, *minor*), 1.72 – 1.61 (m, 2H, *i*-BuCH and *i*-$BuCH_2$, *major* and *minor*), 1.02 (d, *J* = 6.2 Hz, 3H, *i*-$BuCH_3$, *minor*), 1.00 (d, *J* = 6.5 Hz, 6H, *i*-$BuCH_3$, *major*), 0.97 (d, *J* = 6.2 Hz, 3H, *i*-$BuCH_3$, *minor*) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 210.5 (CH, =C=, *minor*), 208.1 (CH, =C=, *major*), 151.2 (QC, CO, *minor*), 151.0 (QC, CO, *major*), 150.9 (QC, NsC, *major* and *minor*), 143.6 (QC, NsC, *minor*), 143.5 (QC, NsC, *major*), 129.93 (CH, 2×NsCH, *minor*), 129.87 (CH, 2×NsCH, *major*), 124.30 (CH, 2×NsCH, *minor*), 124.25 (CH, 2×NsCH, *major*), 89.2 (CH, =CH, *major*), 84.5 (CH, =CH, *minor*), 80.2 (CH_2, $=CH_2$, *major*), 78.5 (CH_2, $=CH_2$, *minor*), 78.2 (CH, CH-O, *minor*), 77.23 (CH, CH-O, *major*), 60.7 (CH, CH-N, *major*), 59.8 (CH, CH-N, *minor*), 42.9 (CH_2, *i*-$BuCH_2$, *major*), 38.9 (CH_2, *i*-$BuCH_2$, *minor*), 24.9 (CH, *i*-BuCH, *minor*), 24.5 (CH, *i*-BuCH, *major*), 23.5 (CH_3, *i*-$BuCH_3$, *major*), 23.0 (CH_3, *i*-$BuCH_3$, *minor*), 21.7 (CH_3, *i*-$BuCH_3$, *minor*), 21.3 (CH_3, *i*-$BuCH_3$, *major*) ppm.

(4*S*,5*S*)-4-benzyl-3-((4-nitrophenyl)sulfonyl)-5-(propa-1,2-dien-1-yl)oxazolidin-2-one (1d):



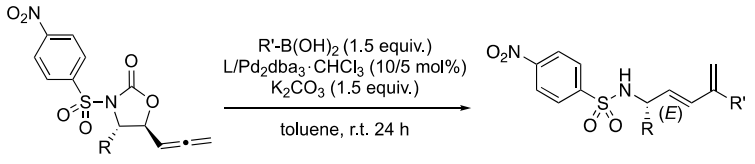
1d

34% conversion. Product was isolated via column chromatography (EtOAc/hexane, 30:70) and reclaimed starting material was resubjected to the reaction conditions and purified separately. Brown gum, combined yield 70%, 2.2:1 *dr* (after purification). **HRMS-ESI** (*m*/*z*): $[M+Na]^+$ calcd for $C_{13}H_{12}N_2O_6SNa$, 423.0621; found, 423.0616. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3107 (w, C=CH), 3069 – 2868 (w), 1955 (w), 1772 (s, CO), 1605 (w), 1527 (s), 1381 (s), 1167 (vs), 1116 (s), 1089 (s), 855 (s), 737 (s), 612 (vs). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8.5 Hz, 2H, NsCH, *major*), 8.30 (d, *J* = 8.9 Hz, 2H, NsCH, *minor*), 8.27 (d, *J* = 8.5 Hz, 2H, NsCH, *major*), 8.09 (d, *J* = 8.5 Hz, 2H, NsCH, *minor*), 7.42 – 7.15 (m, 5H, ArH, *major* and *minor*), 5.22 – 5.14 (m, 2H, =CH and CH-O, *minor*), 5.09 (app. q, *J* = 6.4 Hz, 1H, =CH, *major*), 5.00 – 4.94 (m, 1H, CH-N, *minor*), 4.87 – 4.80 (m, 2H, $=CH_2$, *major* and *minor*), 4.76 – 4.74 (m, 1H, CH-O, *major*), 4.65 – 4.62 (m, 1H, CH-N, *major*), 3.48 (dd, *J* = 13.6, 4.0 Hz, 1H, $BnCH_2$, *major*), 3.21 (dd, *J* = 14.7, 5.6 Hz, 1H, $BnCH_2$, *minor*), 3.12 (dd, *J* = 14.6, 8.4 Hz, 1H, $BnCH_2$, *minor*), 2.94 (dd, *J* = 13.6, 9.8 Hz, 1H, $BnCH_2$, *major*) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 210.0 (QC, =C=, *minor*), 207.8 (QC, =C=, *major*), 151.3 (QC, CO, *minor*), 150.93 (QC, CO, *major*), 150.89 (QC, NsC, *major*), 150.7 (QC, NsC, *minor*), 143.4 (QC, NsC, *minor*), 143.2 (QC, NsC, *major*), 135.2 (QC, ArC, *minor*), 133.8 (QC, ArC, *major*), 129.9 (CH, 2×NsCH, *major*), 129.7 (CH, 2×NsCH, *minor*), 129.4 (CH, 2×ArCH, *major* and *minor*), 129.1 (CH, 2×ArCH, *major*), 128.7 (CH, 2×ArCH, *minor*), 127.7 (CH, ArCH, *major*), 127.2 (CH, ArCH, *minor*), 124.3 (CH, 2×NsCH, *major*), 124.2 (CH, 2×NsCH, *minor*),

88.8 (CH, =CH, *major*), 84.8 (CH, =CH, *minor*), 80.1 (CH_2, $=CH_2$, *major*), 78.7 (CH_2, $=CH_2$, *minor*), 78.0 (CH, CH-O, *minor*), 75.8 (CH, CH-O, *major*), 62.5 (CH, CH-N, *major*), 61.9 (CH, CH-N, *minor*), 39.7 (CH_2, $BnCH_2$, *major*), 36.0 (CH_2, $BnCH_2$, *minor*) ppm.

4. Synthesis of 1,3-dienes (2a-q)

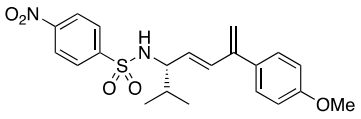
General procedure:



1a-d **2a-q**

A solution of the allenyloxazolidinone (1.0 equiv.), boronic acid (1.5 equiv.), $Pd_2dba_3{\cdot}CHCl_3$ (5 mol%), tris(2,4-di-*tert*-butylphenyl) phosphite (10 mol%) and K_2CO_3 (1.5 equiv.) in toluene (0.06 mM with respect to the allenyloxazolidinone) was stirred under nitrogen for 24 hours at room temperature. The reaction was quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic layer was dried with $MgSO_4$ and concentrated *in vacuo* to give the crude product, which was purified via column chromatography (Et_2O/hexane, 50:50, unless otherwise specified).

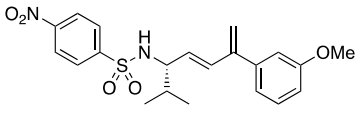
(*S*,*E*)-*N*-(6-(4-methoxyphenyl)-2-methylhepta-4,6-dien-3-yl)-4-nitrobenzenesulfonamide (2a):



2a

Yellow solid, 74%, > 95:5 (*E*:*Z*). The enantiopurity was determined via chiral HPLC using a Daicel CHIRALPAK IA-U column, hexane/isopropanol (97:3), 0.2 mL/min, 40 °C, 254 nm, single peak, t_R = 41.06 min, > 99% *ee*. Racemic **2a**, prepared from racemic *N*-Boc-valinal, gave two peaks (t_R = 41.41, 44.63 min, 1:1) under the same conditions. Mp 85.5 – 89.4 °C. $[\alpha]_D^{22}$ +16.8 (*c* 0.73, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M-H]^-$ calcd for $C_{21}H_{23}N_2O_5S$, 415.1333; found, 415.1342. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3255 (w, NH), 2965 (w), 1607 (m), 1526 (s), 1509 (s), 1346 (s), 1247 (s), 1166 (s), 1030 (s), 84 (s), 736 (vs). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.26 (d, *J* = 8.9 Hz, 2H, NsCH), 7.96 (d, *J* = 8.9 Hz, 2H, NsCH), 6.92 (d, *J* = 8.8 Hz, 2H, ArCH), 6.78 (d, *J* = 8.8 Hz, 2H, ArCH), 6.07 (d, *J* = 15.6 Hz, 1H, =CH), 5.12 (dd, *J* = 15.6, 8.2 Hz, 1H, =C*H*-CH-N), 5.03 (d, *J* = 1.5 Hz, 1H, $=CH_2$), 4.99 (s, 1H, $=CH_2$), 4.68 (d, *J* = 8.4 Hz, 1H, NH), 3.80 (s, 3H, OMe), 3.79 – 3.70 (m, 1H, CH-N), 1.76 (app. oct, *J* = 6.7 Hz, 1H, *i*-PrCH), 0.93 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3), 0.88 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.2 (QC, ArC), 149.8 (QC, NsC), 147.0 (QC, NsC), 145.9 (QC, *C*=CH_2), 134.6 (CH, =CH), 131.5 (QC, ArC) 129.4 (CH, =*C*H-CH-N), 128.9 (CH, 2×ArCH), 128.5 (CH, 2×NsCH), 124.1 (CH, 2×NsCH), 116.9 (CH_2, $=CH_2$), 113.5 (CH, 2×ArCH), 62.3 (CH, CH-N), 55.2 (CH_3, OMe), 33.2 (CH, *i*-PrCH), 18.6 (CH_3, *i*-PrCH_3), 18.5 (CH_3, *i*-PrCH_3) ppm.

(*S*,*E*)-*N*-(6-(3-methoxyphenyl)-2-methylhepta-4,6-dien-3-yl)-4-nitrobenzenesulfonamide (2b):

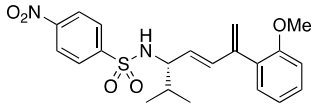


2b

Yellow gum, 62%, > 95:5 (*E*:*Z*). $[\alpha]_D^{23}$ +11.6 (*c* 1.77, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M+Na]^+$ calcd for $C_{21}H_{24}N_2O_5SNa$, 439.1298; found, 439.1320. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3295 (br., w, NH), 2963 – 2874 (w), 1595 (w), 1527 (s), 1345 (vs), 1162 (s), 854 (m), 748 (s), 737 (s), 616 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.27 (d, *J* = 9.0 Hz, 2H, NsCH), 7.97 (d, *J* = 9.0 Hz, 2H, NsCH), 7.17 (app. t, *J* = 7.9 Hz, 1H, ArCH), 6.79 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H, ArCH), 6.57 (ddd, *J* = 7.6, 1.5, 1.1 Hz, 1H, ArCH), 6.51 (dd, *J* = 2.5, 1.6 Hz, 1H, ArCH), 6.07 (d, *J* = 15.7 Hz, 1H, =CH), 5.16 (dd, *J* = 15.7, 8.2 Hz, 1H, =C*H*-CH-N), 5.08 (d, *J* = 1.5 Hz, 1H, $=CH_2$), 5.05 (s, 1H, $=CH_2$), 4.77 (d, *J* = 8.5 Hz, 1H, NH), 3.77 (s, 3H, OCH_3), 3.79 – 3.72 (m, 1H, CH-N), 1.76 (app. oct, *J* = 6.7 Hz, 1H, *i*-PrCH), 0.92 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3), 0.87 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 159.4 (QC, C-OMe), 149.9 (QC, NsC), 147.0 (QC, NsC), 146.3

(QC, *C*=CH_2), 140.7 (QC, ArC), 134.1 (CH, =CH), 129.7 (CH, =*C*H-CH-N), 129.2 (CH, ArCH), 128.4 (CH, 2×NsCH), 124.1 (CH, 2×NsCH), 120.2 (CH, ArCH), 117.6 (CH_2, =CH_2), 113.9 (CH, ArCH), 112.7 (CH, ArCH), 62.3 (CH, CH-N), 55.2 (CH_3, OMe), 33.2 (CH, *i*-PrCH), 18.6 (CH_3, *i*-PrCH_3), 18.5 (CH_3, *i*-PrCH_3) ppm.

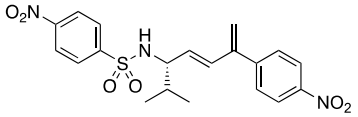
(*S*,*E*)-*N*-(6-(2-methoxyphenyl)-2-methylhepta-4,6-dien-3-yl)-4-nitrobenzenesulfonamide (2c):



2c

Corresponding 5-vinyloxazolidinone **3c** obtained as major product (83%, > 95:5, *E*:*Z*). Yellow gum, 32%, 90:10 (*E*:*Z*). $[\alpha]_D^{23}$ +6.8 (*c* 0.34, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M-H]^-$ calcd for $C_{21}H_{23}N_2O_5S$, 415.1333; found, 415.1319. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3284 (br., w, NH), 2962 – 2837 (w), 1605 (w), 1528 (s), 1347 (s), 1163 (s), 854 (m), 748 (s), 737 (vs), 612 (s). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.27 (d, *J* = 9.0 Hz, 2H, NsCH), 7.94 (d, *J* = 9.0 Hz, 2H, NsCH), 7.30 – 7.19 (m, 1H, ArCH), 6.87 (td, *J* = 7.4, 1.0 Hz, 1H, ArCH), 6.83 (d, *J* = 8.3 Hz, 1H, ArCH), 6.78 (dd, *J* = 7.4, 1.8 Hz, 1H, ArCH), 6.01 (d, *J* = 15.6 Hz, 1H, =CH), 5.14 (d, *J* = 1.7 Hz, 1H, =CH_2), 5.02 (d, *J* = 1.7 Hz, 1H, =CH_2), 4.76 (dd, *J* = 15.5, 8.2 Hz, 1H, =C*H*-CH-N), 4.50 (d, *J* = 8.5 Hz, 1H, NH), 3.76 – 3.66 (m, 1H, CH-N), 3.70 (s, 3H, OMe), 1.72 (app. oct, *J* = 6.8 Hz, 1H, *i*-PrCH), 0.90 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3), 0.84 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 156.3 (QC, ArC), 149.8 (QC, NsC), 147.0 (QC, NsC), 144.4 (QC, *C*=CH_2), 134.0 (CH, =CH), 130.5 (CH, ArCH), 129.1 (CH, =*C*H-CH-N), 128.6 (CH, ArCH), 128.5 (CH, 2×NsCH), 128.3 (QC, ArC), 124.1 (CH, 2×NsCH), 120.5 (CH, ArCH), 119.1 (CH_2, =CH_2), 110.6 (CH, ArCH), 62.1 (CH, CH-N), 55.3 (CH_3, OMe), 33.2 (CH, *i*-PrCH), 18.4 (CH_3, *i*-PrCH_3), 18.3 (CH_3, *i*-PrCH_3) ppm.

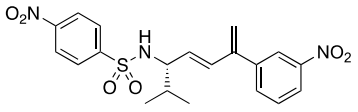
(*S*,*E*)-*N*-(2-methyl-6-(4-nitrophenyl)hepta-4,6-dien-3-yl)-4-nitrobenzenesulfonamide (2d):



2d

Yellow gum, 79%, 90:10 (*E*:*Z*). $[\alpha]_D^{22}$ +16.8 (*c* 0.73, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M-H]^-$ calcd for $C_{20}H_{20}N_3O_6S$, 430.1078; found, 430.1067. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3298 (br., w, NH), 2964 – 2874 (w), 1593 (w), 1516 (s), 1343 (vs), 1163 (m), 854 (m), 738 (vs), 616 (m). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 9.0 Hz, 2H, NsCH), 8.15 (d, *J* = 8.9 Hz, 2H, ArCH), 8.01 (d, *J* = 9.0 Hz, 2H, NsCH), 7.23 (d, *J* = 8.9 Hz, 2H, ArCH), 6.17 (d, *J* = 15.8 Hz, 1H, =CH), 5.23 (s, 1H, =CH_2), 5.19 (s, 1H, =CH_2), 5.16 (dd, *J* = 15.8, 7.8 Hz, 1H, =C*H*-CH-N), 4.77 (d, *J* = 8.4 Hz, 1H, NH), 3.85 – 3.54 (m, 1H, CH-N), 1.75 (app. oct, *J* = 6.7 Hz, 1H, *i*-PrCH), 0.89 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3), 0.84 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.9 (QC, NsC), 147.4 (QC, ArC), 146.9 (QC, NsC), 146.0 (QC, *C*=CH_2), 144.8 (QC, ArC), 133.1 (CH, =CH), 130.9 (CH, =*C*H-CH-N), 128.8 (CH, ArCH), 128.5 (CH, 2×NsCH), 124.1 (CH, 2×NsCH), 123.6 (CH, ArCH), 119.6 (CH_2, =CH_2), 62.0 (CH, CH-N), 33.1 (CH, *i*-PrCH), 18.6 (CH_3, *i*-PrCH_3), 18.4 (CH_3, *i*-PrCH_3) ppm.

(*S*,*E*)-*N*-(2-methyl-6-(3-nitrophenyl)hepta-4,6-dien-3-yl)-4-nitrobenzenesulfonamide (2e):

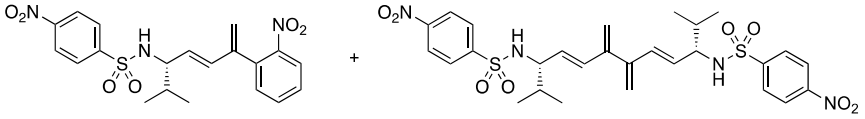


2e

Pale yellow gum, 80%, > 99:1 (*E*:*Z*). $[\alpha]_D^{23}$ –10.3 (*c* 4.03, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M-H]^-$ calcd for $C_{20}H_{20}N_3O_6S$, 430.1078; found, 430.1079. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3287 (br., w, NH), 2964 – 2874 (w), 1527 (s), 1347 (s), 1309 (m), 1161 (s), 854 (m), 748 (vs), 614 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.31 (d, *J* = 9.0 Hz, 2H, NsCH), 8.13 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H, ArCH), 8.02 (d, *J* = 9.0 Hz, 2H, NsCH), 7.88 (app. t, *J* = 1.9 Hz, 1H, ArCH), 7.47 (app. t, *J* = 7.9 Hz, 1H, ArCH), 7.38 (app. dt, *J* = 7.6, 1.3 Hz, 1H, ArCH), 6.17 (d, *J* = 15.8 Hz, 1H, =CH), 5.22 (s, 1H, =CH_2), 5.19 (s, 1H, =CH_2), 5.15 (dd, *J* = 15.8, 7.9 Hz, 1H, =C*H*-CH-N), 4.87 (d, *J* = 8.5 Hz, 1H, NH), 3.84 – 3.66 (m, 1H, CH-N), 1.75 (app. oct, *J* = 6.7 Hz, 1H, *i*-PrCH), 0.90 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3), 0.85 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.9 (QC, NsC), 148.1 (QC, ArC), 146.9 (QC, NsC), 144.4 (QC, *C*=CH_2), 140.9 (QC, ArC), 134.0 (CH,

ArCH), 133.2 (CH, =CH), 130.7 (CH, =*C*H-CH-N), 129.4 (CH, ArCH), 128.5 (CH, 2×NsCH), 124.2 (CH, 2×NsCH), 122.8 (CH, ArCH), 122.7 (CH, ArCH), 119.4 (CH_2, $=CH_2$), 62.0 (CH, CH-N), 33.1 (CH, *i*-PrCH), 18.5 (CH_3, *i*-PrCH_3), 18.4 (CH_3, *i*-PrCH_3) ppm.

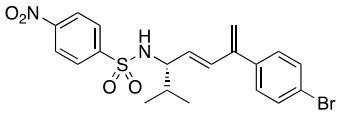
(*S*,*E*)-*N*-(2-methyl-6-(2-nitrophenyl)hepta-4,6-dien-3-yl)-4-nitrobenzenesulfonamide (2f) + *N*,*N*'-((3*S*,4*E*,8*E*,10*S*)-2,11-dimethyl-6,7-dimethylenedodeca-4,8-diene-3,10-diyl)bis(4-nitrobenzenesulfonamide) (4):



2f **4**

Eluent: Et_2O/hexane (60:40). Inseparable mixture (86:14) of **2f** (47%, 90:10, *E*:*Z*) and **4** (> 99:1, *E*:*Z*), respectively, obtained as a yellow gum. **HRMS-ESI** (*m*/*z*) (**2f**): $[M-H]^-$ calcd for $C_{20}H_{20}N_3O_6S$, 430.1078; found, 430.1079. **HRMS-ESI** (*m*/*z*) (**4**): $[M-H]^-$ calcd for $C_{28}H_{33}N_4O_8S_2$, 617.1745; found, 617.1749. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}) (**2f** and **4**): 3280 (br., w, NH, **2f** and **4**), 2960 – 2925 (w), 1716 (w), 1526 (s), 1347 (s), 1279 (s), 1162 (s), 853 (m), 735 (vs), 611 (s). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.35 (d, *J* = 8.8 Hz, 4H, NsCH, **4**), 8.31 (d, *J* = 8.9 Hz, 2H, NsCH, **2f**), 8.06 (d, *J* = 8.9 Hz, 4H, NsCH, **4**), 7.97 (d, *J* = 8.9 Hz, 2H, NsCH, **2f**), 7.85 (dd, *J* = 8.1, 1.1 Hz, 1H, ArCH, **2f**), 7.53 (td, *J* = 7.5, 1.2 Hz, 1H, ArCH, **2f**), 7.45 (td, *J* = 8.0, 1.4 Hz, 1H, ArCH, **2f**), 7.05 (dd, *J* = 7.6, 1.3 Hz, 1H, ArCH, **2f**), 6.15 (d, *J* = 15.6 Hz, 2H, =CH, **4**), 6.06 (d, *J* = 15.8 Hz, 1H, =CH, **2f**), 5.64 (d, *J* = 9.1 Hz, 2H, NH, **4**), 5.41 (dd, *J* = 15.5, 9.2 Hz, 2H, =C*H*-CH-N, **4**), 5.22 (s, 1H, $=CH_2$, **2f**), 5.11 (d, *J* = 2.0 Hz, 2H, $=CH_2$, **4**), 5.09 (s, 1H, $=CH_2$, **2f**), 5.02 (d, *J* = 2.0 Hz, 2H, $=CH_2$, **4**), 4.72 (dd, *J* = 15.8, 7.7 Hz, 1H, =C*H*-CH-N, **2f**), 4.66 (d, *J* = 8.5 Hz, 1H, NH, **2f**), 3.72 – 3.63 (m, 1H, CH-N, **2f** and 2H, CH-N, **4**), 1.73 – 1.61 (m, 1H, *i*-PrCH, **2f** and 2H, *i*-PrCH, **4**), 0.84 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3, **2f**), 0.80 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3, **2f**), 0.77 (d, *J* = 6.7 Hz, 12H, *i*-PrCH_3, **4**) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.88 (QC, NsC, **2f**), 149.85 (QC, 2×NsC, **4**), 148.6 (QC, ArC, **2f**), 147.2 (QC, 2×NsC, **4**), 146.9 (QC, NsC, **2f**), 145.7 (QC, 2×=C, **4**), 143.5 (QC, ArC, **2f**), 134.0 (QC, =C, **2f**), 133.4 (CH, =CH, **2f**), 133.02 (CH, 2×=CH, **4**), 132.97 (CH, ArCH, **2f**), 131.6 (CH, ArCH, **2f**), 131.4 (CH, 2×=*C*H-CH-N, **4**), 128.9 (CH, ArCH and =*C*H-CH-N, **2f**), 128.4 (CH, 2×NsCH, **2f**), 128.0 (CH, 4×NsCH, **4**), 124.3 (CH, 4×NsCH, **4**), 124.2 (CH, 2×NsCH, **2f**), 124.1 (CH, ArCH, **2f**), 119.4 (CH_2, $=CH_2$, **2f**), 119.0 (CH_2, 2×$=CH_2$, **4**), 63.3 (CH, 2×CH-N, **4**) 61.7 (CH, CH-N, **2f**), 33.1 (CH, *i*-PrCH, **2f**), 32.8 (CH, 2×*i*-PrCH, **4**), 18.9 (CH_3, 2×*i*-PrCH_3, **4**), 18.7 (CH_3, 2×*i*-PrCH_3, **4**), 18.3 (CH_3, *i*-PrCH_3, **2f**), 18.1 (CH_3, *i*-PrCH_3, **2f**) ppm.

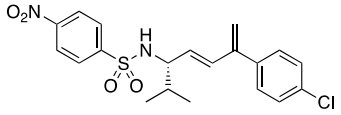
(*S*,*E*)-*N*-(6-(4-bromophenyl)-2-methylhepta-4,6-dien-3-yl)-4-nitrobenzenesulfonamide (2g):



2g

Eluent: MeOH/CH_2Cl_2 (1:99). Yellow gum, 27%, > 95:5 (*E*:*Z*). $[\alpha]_D^{23}$ –4.8 (*c* 1.10, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M-H]^-$ calcd for $C_{20}H_{20}N_2O_4SBr$, 463.0333; found, 463.0344. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3280 (br., w, NH), 2961 – 2872 (w), 1716 (w), 1606 (w), 1527 (s), 1347 (s), 1309 (s), 1162 (s), 1091 (m), 1010 (m), 853 (s), 735 (vs), 612 (s), 463 (s). **^{1}H NMR** (500 MHz,$CDCl_3$): δ 8.28 (d, *J* = 8.9 Hz, 2H, NsCH), 7.98 (d, *J* = 8.9 Hz, 2H, NsCH), 7.40 (d, *J* = 8.4 Hz, 2H, ArCH), 6.88 (d, *J* = 8.4 Hz, 2H, ArCH), 6.09 (d, *J* = 15.7 Hz, 1H, =CH), 5.10 (dd, *J* = 15.7, 8.07 Hz, 1H, =C*H*-CH-N), 5.07 (s, 2H, $=CH_2$), 4.67 (d, *J* = 8.4 Hz, 1H, NH), 3.76 – 3.72 (m, 1H, CH-N), 1.75 (dq, *J* = 13.4, 6.7 Hz, 1H, *i*-PrCH), 0.90 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3), 0.85 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.9 (QC, NsC), 146.9 (QC, NsC), 145.5 (QC, ArC), 138.1 (QC, *C*=CH_2), 133.9 (CH, =CH), 131.4 (CH, 2×ArCH), 130.0 (CH, *C*H=CH-N), 129.5 (CH, 2×ArCH), 128.5 (CH, 2×NsCH), 124.1 (CH, 2×NsCH), 121.8 (QC, ArC), 118.2 (CH_2, $=CH_2$), 62.2 (CH, CH-N), 33.1 (CH, *i*-PrCH), 18.6 (CH_3, *i*-PrCH_3), 18.5 (CH_3, *i*-PrCH_3) ppm.

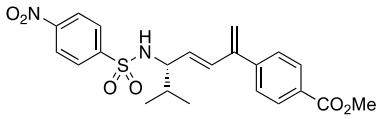
(*S*,*E*)-*N*-(6-(4-chlorophenyl)-2-methylhepta-4,6-dien-3-yl)-4-nitrobenzenesulfonamide (2h):



2h

Yellow gum, 66%, > 95:5 (*E*:*Z*). $[\alpha]_D^{23}$ +52.5 (*c* 0.89, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M-H]^-$ calcd for $C_{20}H_{20}N_2O_4SCl$, 419.0838; found, 419.0846. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3283 (br., w, NH), 2963 – 2873 (w), 1527 (s), 1347 (s), 1309 (s), 1162 (s), 1091 (s), 853 (m), 735 (vs), 611 (s), 463 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.9 Hz, 2H, NsCH), 7.98 (d, *J* = 8.9 Hz, 2H, NsCH), 7.24 (d, *J* = 8.5 Hz, 2H, ArCH), 6.94 (d, *J* = 8.4 Hz, 2H, ArCH), 6.09 (d, *J* = 15.7 Hz, 1H, =CH), 5.10 (dd, *J* = 15.7, 8.1 Hz, 1H, =C*H*-CH-N), 5.07 (s, 2H, $=CH_2$), 4.81 (d, *J* = 8.4 Hz, 1H, NH), 3.76 – 3.71 (m, 1H, CH-N) 1.75 (app. oct, *J* = 6.7 Hz, 1H, *i*-PrCH), 0.90 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$), 0.85 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.9 (QC, NsC), 146.9 (QC, NsC), 145.4 (QC, ArC), 137.7 (QC, *C*=CH_2), 133.9 (CH, =CH), 133.6 (QC, ArC), 129.9 (CH, =*C*H-CH-N), 129.2 (CH, 2×ArCH), 128.5 (CH, 2×ArCH), 128.4 (CH, 2×ArCH), 124.1 (CH, 2×NsCH), 118.1 (CH_2, $=CH_2$), 62.2 (CH, CH-N), 33.1 (CH, *i*-PrCH), 18.54 (CH_3, *i*-$PrCH_3$) , 18.46 (CH_3, *i*-$PrCH_3$) ppm.

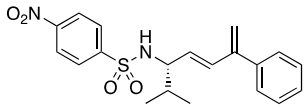
Methyl (*S*,*E*)-4-(6-methyl-5-((4-nitrophenyl)sulfonamido)hepta-1,3-dien-2-yl)benzoate (2i):



2i

Brown solid, 34%, > 95:5 (*E*:*Z*). Mp 73.0 – 75.0 °C. $[\alpha]_D^{22}$ –4.7 (*c* 1.34, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M-H]^-$ calcd for $C_{22}H_{23}N_2O_6S$, 443.1282; found, 443.1277. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3275 (br., w, NH), 2959 – 2923 (m), 1716 (m), 1527 (s), 1347 (s), 1278 (s), 1162 (s), 1107 (s), 1016 (m), 853 (s), 736 (vs), 612 (s), 463 (s). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.28 (d, *J* = 9.0 Hz, 2H, NsCH), 7.98 (d, *J* = 9.0 Hz, 2H, NsCH), 7.94 (d, *J* = 8.5 Hz, 2H, ArCH), 7.08 (d, *J* = 8.5 Hz, 2H, ArCH), 6.12 (d, *J* = 15.7 Hz, 1H, =CH), 5.14 (s, 2H, $=CH_2$), 5.10 (dd, *J* = 15.8, 8.0 Hz, 1H, =C*H*-CH-N), 4.70 (d, *J* = 8.4 Hz, 1H, NH), 3.92 (s, 3H, CO_2Me), 3.78 – 3.73 (m, 1H, CH-N), 1.75 (app. oct, *J* = 6.7 Hz, 1H, *i*-PrCH), 0.90 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$), 0.85 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.7 (QC, *C*O_2Me), 149.9 (QC, NsC), 147.0 (QC, NsC), 145.7 (QC, ArC), 143.9 (QC, *C*=CH_2), 133.7 (CH, =CH), 130.2 (CH, *C*H-CH-N), 129.53 (CH, 2×ArCH), 129.47 (QC, ArC), 128.4 (CH, 2×NsCH) , 127.9 (CH, 2×ArCH), 124.1 (CH, 2×NsCH), 118.7 (CH_2, $=CH_2$), 62.1 (CH, CH-N), 52.2 (CH_3, CO_2*Me*), 33.1 (CH, *i*-PrCH), 18.54 (CH_3, *i*-$PrCH_3$), 18.45 (CH_3, *i*-$PrCH_3$) ppm.

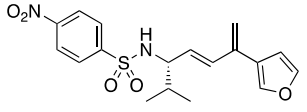
(*S*,*E*)-*N*-(2-methyl-6-phenylhepta-4,6-dien-3-yl)-4-nitrobenzenesulfonamide (2j):



2j

Yellow gum, 61%, > 95:5 (*E*:*Z*). $[\alpha]_D^{23}$ +13.2 (*c* 1.89, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M-H]^-$ calcd for $C_{20}H_{21}N_2O_4S$, 385.1228; found, 385.1227. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3287 (br., w, NH), 2963 – 2874 (w), 1606 (w), 1527 (s), 1347 (s), 1310 (m), 1162 (s), 1092 (m), 854 (m), 752 (s), 736 (vs), 615 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.26 (d, *J* = 9.0 Hz, 2H, NsCH), 7.96 (d, *J* = 9.0 Hz, 2H, NsCH), 7.27 – 7.23 (m, 3H, ArCH), 7.06 – 6.85 (m, 2H, ArCH), 6.09 (d, *J* = 15.7 Hz, 1H, =CH), 5.10 (dd, *J* = 16.1, 7.5 Hz, 1H, =C*H*-CH-N), 5.07 (d, *J* = 1.2 Hz, 1H, $=CH_2$), 5.05 (s, 1H, $=CH_2$), 4.75 (d, *J* = 8.5 Hz, 1H, NH), 3.82 – 3.62 (m, 1H, CH-N), 1.76 (dq, *J* = 13.4, 6.7 Hz, 1H, *i*-PrCH), 0.92 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$), 0.87 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.8 (QC, NsC), 147.0 (QC, NsC), 146.5 (QC, *C*=CH_2), 139.2 (QC, ArC), 134.3 (CH, $=CH_2$), 129.6 (CH, =*C*H-CH-N), 128.4 (CH, 2×NsCH), 128.2 (CH, 2×ArCH), 127.8 (CH, 2×ArCH), 127.7 (CH, ArCH), 124.1 (CH, 2×NsCH), 117.8 (CH_2, $=CH_2$), 62.3 (CH, CH-N), 33.1 (CH, *i*-PrCH), 18.6 (CH_3, *i*-$PrCH_3$), 18.5 (CH_3, *i*-$PrCH_3$) ppm.

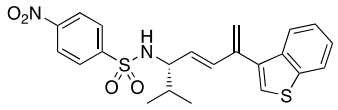
(*S*,*E*)-*N*-(6-(furan-3-yl)-2-methylhepta-4,6-dien-3-yl)-4-nitrobenzenesulfonamide (2k):



2k

Brown gum, 58%, > 95:5 (*E*:*Z*). $[\alpha]_D^{23}$ –11.1 (*c* 3.03, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M–H]^-$ calcd for $C_{18}H_{19}N_2O_5S$, 375.1020; found, 375.1004. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3286 (br., w, NH), 2964 – 2874 (w), 1527 (s), 1347 (s), 1309 (m), 1161 (s), 1091 (m), 854 (m), 735 (vs), 614 (s). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.26 (d, *J* = 9.0 Hz, 2H, NsCH), 7.99 (d, *J* = 9.0 Hz, 2H, NsCH), 7.33 (app. t, *J* = 1.7 Hz, 1H, FurCH), 7.23 – 7.19 (m, 1H, FurCH), 6.23 (dd, *J* = 1.8, 0.9 Hz, 1H, FurCH), 6.02 (d, *J* = 15.7 Hz, 1H, =CH), 5.39 (dd, *J* = 15.7, 8.1 Hz, 1H, =C*H*-CH-N), 5.11 (d, *J* = 1.4 Hz, 1H, $=CH_2$), 4.94 (s, 1H, $=CH_2$), 4.90 (d, *J* = 8.4 Hz, 1H, NH), 3.76 – 3.72 (m, 1H, CH-N), 1.78 (dq, *J* = 13.5, 6.8 Hz, 1H, *i*-PrCH), 0.92 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$), 0.88 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.8 (QC, NsC), 146.9 (QC, NsC), 143.0 (CH, FurCH), 139.5 (CH, FurCH), 136.8 (QC, *C*=CH_2), 133.4 (CH, =CH), 128.9 (CH, =*C*H-CH-N), 128.5 (CH, 2×NsCH), 124.1 (CH, 2×NsCH), 123.9 (QC, FurC), 116.0 (CH_2, =CH_2), 109.7 (CH, FurCH), 62.3 (CH, CH-N), 33.1 (CH, *i*-PrCH), 18.50 (CH_3, *i*-$PrCH_3$), 18.47 (CH_3, *i*-$PrCH_3$) ppm.

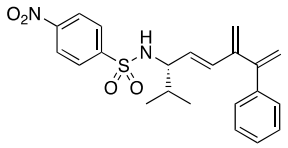
(*S*,*E*)-*N*-(6-(benzo[*b*]thiophen-3-yl)-2-methylhepta-4,6-dien-3-yl)-4-nitrobenzenesulfonamide (2l):



2l

Yellow gum, 76%, > 99:1 (*E*:*Z*). $[\alpha]_D^{23}$ −20.4 (*c* 3.94, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M–H]^-$ calcd for $C_{22}H_{21}N_2O_4S_2$, 441.0948; found, 441.0940. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3283 (br., w, NH), 2964 – 2871 (w), 1527 (s), 1346 (s), 1310 (m), 1163 (s), 1091 (m), 853 (m), 735 (vs), 616 (s). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.24 (d, *J* = 8.9 Hz, 2H, NsCH), 7.94 (d, *J* = 8.9 Hz, 2H, NsCH), 7.83 (d, *J* = 7.5 Hz, 1H, HetCH), 7.45 (d, *J* = 7.5 Hz, 1H, HetCH), 7.36 – 7.27 (m, 2H, HetCH), 7.03 (s, 1H, HetCH) 6.19 (d, *J* = 15.6 Hz, 1H, =CH), 5.31 (d, *J* = 1.3 Hz, 1H, $=CH_2$), 5.22 (d, *J* = 1.6 Hz, 1H, $=CH_2$), 5.01 (dd, *J* = 15.6, 8.0 Hz, 1H, =C*H*-CH-N), 4.66 (d, *J* = 8.6 Hz, 1H, NH), 3.76 – 3.71 (m, 1H, CH-N), 1.70 (app. oct, *J* = 6.7 Hz, 1H, *i*-PrCH), 0.86 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$), 0.81 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.8 (QC, NsC), 147.0 (QC, NsC), 140.6 (QC, *C*=CH_2), 140.0 (QC, HetC), 137.9 (QC, HetC), 135.0 (QC, HetC), 134.0 (CH, =CH), 130.0 (CH, =*C*H-CH-N), 128.4 (CH, 2×NsCH), 124.5 (CH, HetCH) , 124.0 (CH, 2×HetCH), 124.0 (CH, 2×NsCH), 122.9 (CH, HetCH), 122.7 (CH, HetCH), 120.1 (CH_2, =CH_2), 62.0 (CH, CH-N), 33.0 (CH, *i*-PrCH), 18.5 (CH_3, *i*-$PrCH_3$), 18.3 (CH_3, *i*-$PrCH_3$) ppm.

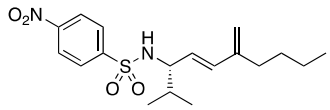
(*S*,*E*)-*N*-(2-methyl-6-methylene-7-phenylocta-4,7-dien-3-yl)-4-nitrobenzenesulfonamide (2m):



2m

Pale yellow solid, 43%, 85:15 (*E*:*Z*). Mp 75.0 – 79.0 °C. $[\alpha]_D^{22}$ +52.3 (*c* 0.81, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M–H]^-$ calcd for $C_{22}H_{23}N_2O_4S$, 411.1384; found, 411.1376. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3323 (w, C=CH), 3266 (w, NH), 2958 – 2924 (m), 1673 (w), 1526 (s), 1348 (s), 1312 (m), 1168 (vs), 1090 (s), 1015 (s), 851 (m), 736 (vs), 614 (vs). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.29 (d, *J* = 8.9 Hz, 2H, NsCH), 7.94 (d, *J* = 9.0 Hz, 2H, NsCH), 7.26 – 7.18 (m, 5H, ArH), 5.87 (d, *J* = 15.7 Hz, 1H, =CH), 5.37 (d, *J* = 1.6 Hz, 1H, Ph-C=C*H*$_2$), 5.14 (d, *J* = 2.0 Hz, 1H, $=CH_2$), 5.07 (d, *J* = 2.0 Hz, 1H, $=CH_2$), 5.00 (d, *J* = 1.6 Hz, 1H, Ph-C=C*H*$_2$), 4.92 (dd, *J* = 15.7, 8.0 Hz, 1H, =C*H*-CH-N), 4.54 (d, *J* = 8.5 Hz, 1H, NH), 3.64 – 3.58 (m, 1H, CH-N), 1.62 – 1.54 (m, 1H, *i*-PrCH), 0.69 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$), 0.58 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.8 (QC, NsC), 147.9 (QC, Ph-*C*=CH_2), 147.0 (QC, NsC), 146.6 (QC, *C*=CH_2), 139.3 (QC, ArC), 132.9 (CH, =CH), 130.2 (CH, *C*H=CH-N), 128.4 (CH, 2×NsCH), 128.3 (CH, 2×ArCH), 127.8 (CH, ArCH), 126.5 (CH, 2×ArCH), 124.0 (CH, 2×NsCH), 119.2 (CH_2, =CH_2), 114.8 (CH_2, =CH_2), 61.9 (CH, CH-N), 33.2 (CH, *i*-PrCH), 18.3 (CH_3, *i*-$PrCH_3$), 17.8 (CH_3, *i*-$PrCH_3$) ppm.

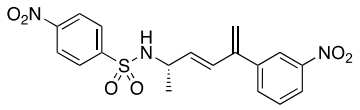
(*S*,*E*)-*N*-(2-methyl-6-methylenedec-4-en-3-yl)-4-nitrobenzenesulfonamide (2n):



2n

67% conversion. Required resubjection to the reaction conditions to consume starting material and enable purification. Off-white needles, 30%, > 95:5 (*E*:*Z*). Mp 72.0 – 73.0 °C. $[\alpha]_D^{23}$ +52.5 (*c* 0.89, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M-H]^-$ calcd for $C_{18}H_{25}N_2O_4S$, 365.1541; found, 365.1545. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3277 (br., w, NH), 2956 – 2870 (w), 1606 (w), 1528 (s), 1348 (s), 1332 (s), 1312 (s), 1161 (s), 1091 (s), 980 (s), 851 (s), 736 (vs), 631 (s), 462 (s). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.28 (d, *J* = 9.0 Hz, 2H, NsCH), 7.98 (d, *J* = 9.0 Hz, 2H, NsCH), 5.80 (d, *J* = 15.8 Hz, 1H, =CH), 5.14 (dd, *J* = 15.8, 8.1 Hz, 1H, =C*H*-CH-N), 4.88 (d, *J* = 1.2 Hz, 1H, $=CH_2$), 4.78 (s, 1H, $=CH_2$), 4.67 (d, *J* = 8.5 Hz, 1H, NH), 3.85 – 3.65 (m, 1H, CH-N), 1.92 – 1.73 (m, 2H, *n*-BuCH_2-C=CH_2 and 1H, *i*-PrCH), 1.26 – 1.18 (m, 4H, *n*-BuCH_2), 0.93 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3), 0.88 (d, *J* = 6.8 Hz, 3H, *i*-PrCH_3), 0.87 – 0.80 (m, 3H, *n*-BuCH_3) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 149.8 (QC, NsC), 147.0 (QC, NsC), 144.7 (QC, *C*=CH_2), 135.3 (CH, =CH), 128.5 (CH, 2×NsCH), 125.2 (CH, =*C*-CH-N), 124.1 (CH, 2×NsCH), 116.5 (CH_2, $=CH_2$), 62.5 (CH, CH-N), 33.2 (CH, *i*-PrCH), 31.4 (CH_2, *n*-Bu*C*H_2-C=CH_2), 30.2 (CH_2, *n*-BuCH_2), 22.5 (CH_2, *n*-BuCH_2), 18.5 (CH_3, 2×*i*-PrCH_3), 13.9 (CH_3, *n*-BuCH_3) ppm.

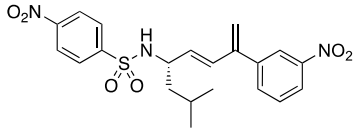
(*S*,*E*)-4-nitro-*N*-(5-(3-nitrophenyl)hexa-3,5-dien-2-yl)benzenesulfonamide (2o):



2o

Off-white gum, 47%, > 95:5 (*E*:*Z*). $[\alpha]_D^{22}$ –0.95 (*c* 2.19, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M-H]^-$ calcd for $C_{18}H_{16}N_3O_6S$, 402.0765; found, 402.0757. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3238 (m, NH), 2963 (w), 1606 (w), 1521 (s), 1345 (s), 1308 (s), 1171 (s), 1089 (s), 1065 (s), 985 (s), 850 (s), 804 (s), 734 (vs), 683 (s), 604 (s), 570 (s). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.32 (d, *J* = 8.9 Hz, 2H, NsCH), 8.14 (ddd, *J* = 8.1, 2.2, 1.2 Hz, 1H, ArCH), 8.03 (d, *J* = 8.9 Hz, 2H, NsCH), 7.91 (app. t, *J* = 1.9 Hz, 1H, ArCH), 7.48 (app. t, *J* = 7.9 Hz, 1H, ArCH), 7.42 (app. dt, *J* = 7.6, 1.4 Hz, 1H, ArCH), 6.32 (d, *J* = 15.8 Hz, 1H, =CH), 5.31 (s, 1H, $=CH_2$), 5.23 (dd, *J* = 15.8, 7.0 Hz, 1H, =C*H*-CH-N), 5.23 (s, 1H, $=CH_2$), 4.79 (d, *J* = 7.6 Hz, 1H, NH), 4.17 – 4.10 (m, 1H, CH-N), 1.25 (d, *J* = 6.8 Hz, 3H, Me) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 150.0 (QC, NsC), 148.1 (QC, ArC), 146.9 (QC, NsC), 144.4 (QC, =C), 141.0 (QC, ArC), 134.1 (CH, ArCH), 133.2 (CH, *C*H=CH-N), 131.8 (CH, =CH), 129.3 (CH, ArCH), 128.4 (CH, 2×NsCH), 124.3 (CH, 2×NsCH), 122.9 (CH, ArCH), 122.7 (CH, ArCH), 119.8 (CH_2, $=CH_2$), 51.9 (CH, CH-N), 21.9 (CH_3, Me) ppm.

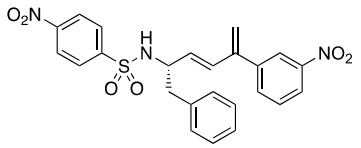
(*S*,*E*)-*N*-(2-methyl-7-(3-nitrophenyl)octa-5,7-dien-4-yl)-4-nitrobenzenesulfonamide (2p):



2p

Deep red gum, 58%, > 95:5 (*E*:*Z*). $[\alpha]_D^{22}$ –30.9 (*c* 2.66, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M-H]^-$ calcd for $C_{21}H_{22}N_3O_6S$, 444.1235; found, 444.1227. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3284 (br., w, NH), 2957 – 2869 (w), 1525 (vs), 1346 (vs), 1308 (s), 1162 (s), 1091 (m), 971 (m), 854 (m), 747 (m), 615 (s). **^{1}H NMR** (400 MHz,$CDCl_3$): δ 8.30 (d, *J* = 8.9 Hz, 2H, NsCH), 8.12 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H, ArCH), 8.01 (d, *J* = 8.9 Hz, 2H, NsCH), 7.84 – 7.83 (m, 1H, ArCH), 7.46 (app. t, *J* = 7.9 Hz, 1H, ArCH), 7.35 (app. dt, *J* = 7.6, 1.2 Hz, 1H, ArCH), 6.24 (d, *J* = 15.7 Hz, 1H, =CH), 5.25 (s, 1H, $=CH_2$), 5.19 (s, 1H, $=CH_2$), 5.08 (dd, *J* = 15.7, 7.9 Hz, 1H, =C*H*-CH-N), 4.75 (d, *J* = 7.9 Hz, 1H, NH), 4.04 (app. p, *J* = 7.6 Hz, 1H, CH-N), 1.66 – 1.56 (m, 1H, *i*-BuCH), 1.44 – 1.25 (m, 2H, *i*-BuCH_2), 0.89 – 0.85 (m, 6H, *i*-BuCH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.9 (QC, NsC), 148.1 (QC, ArC), 147.1 (QC, NsC), 144.5 (QC, =C), 134.0 (CH, ArCH), 132.5 (CH, =CH-CH-N), 132.4 (CH, *i*-BuCH), 129.4 (CH, ArCH), 128.5 (2×NsCH), 124.1 (2×NsCH), 122.8 (CH, ArCH), 122.6 (CH, ArCH), 119.6 (CH_2, $=CH_2$), 54.9 (CH, CH-N), 44.8 (CH_2, *i*-BuCH_2), 24.4 (CH, *i*-BuCH), 22.4 (CH_3, *i*-BuCH_3), 22.1 (CH_3, *i*-BuCH_3) ppm. NMR spectrum showed evidence of inseparable impurity, likely due to polymerization, despite efforts to purify under neutral conditions.

(*S*,*E*)-4-nitro-*N*-(5-(3-nitrophenyl)-1-phenylhexa-3,5-dien-2-yl)benzenesulfonamide (2q):

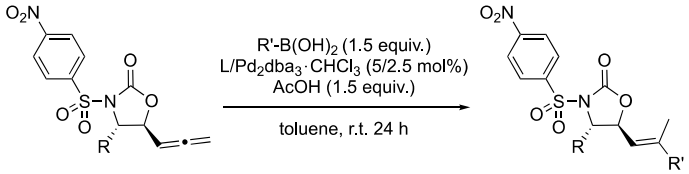


2q

Yellow gum, 46%, > 95:5 (*E*:*Z*). $[\alpha]_D^{22}$ –29.8 (*c* 2.54, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M-H]^-$ calcd for $C_{24}H_{20}N_3O_6S$, 478.1078; found, 478.1074. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3287 (br., w), 3104 – 2865 (w), 1606 (w), 1524 (vs), 1346 (vs), 1309 (s), 1092 (m), 854 (m), 735 (s), 614 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.8 Hz, 2H, NsCH), 8.15 (ddd, *J* = 8.0, 2.7, 1.7 Hz, 1H, ArCH), 7.98 (app. t, *J* = 2.0 Hz, 1H, ArCH), 7.79 (d, *J* = 8.9 Hz, 2H, NsCH), 7.49 (app. t, *J* = 7.8 Hz, 1H, ArCH), 7.43 (app. dt, *J* = 7.6, 1.5 Hz, 1H, ArCH), 7.22 – 7.20 (m, 3H, BnCH), 7.02 – 7.0 (m, 2H, BnCH), 6.32 (d, *J* = 15.7 Hz, 1H, =CH), 5.32 (dd, *J* = 15.7, 7.0 Hz, 1H, =C*H*-CH-N), 5.30 (s, 1H, $=CH_2$), 5.23 (s, 1H, $=CH_2$), 4.72 (d, *J* = 7.4 Hz, 1H, NH), 4.18 (app. p, *J* = 6.7 Hz, 1H, CH-N), 2.87 (dd, *J* = 13.8, 5.9 Hz, 1H, $BnCH_2$), 2.75 (dd, *J* = 13.8, 7.8 Hz, 1H, $BnCH_2$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 149.8 (QC, NsC), 148.1 (QC, ArC), 146.2 (QC, NsC), 144.5 (QC, =CH), 141.0 (QC, ArC), 135.6 (QC, BnC), 134.1 (CH, ArCH), 132.6 (CH, =CH), 132.1 (CH, =*C*H-CH-N), 129.4 (CH, ArCH), 129.3 (CH, 2×BnCH), 128.8 (CH, 2×BnCH), 128.2 (CH, 2×NsCH), 127.3 (CH, BnCH), 124.1 (CH, 2×NsCH), 122.9 (CH, ArCH), 122.7 (CH, ArCH), 119.6 (CH_2, $=CH_2$), 57.2 (CH, CH-N), 42.0 (CH_2, $BnCH_2$) ppm.

5. Synthesis of 5-vinyloxazolidinones (3a-q)

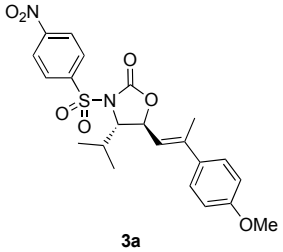
General procedure:



1a-d **3a-q**

A solution of the allenyloxazolidinone (1.0 equiv.), boronic acid (1.5 equiv.), $Pd_2dba_3{\cdot}CHCl_3$ (2.5 mol%), tris(2,4-di-*tert*-butylphenyl) phosphite (5 mol%) and AcOH (1.5 equiv.) in toluene (0.06 mM with respect to the allenyloxazolidinone) was stirred under nitrogen for 24 hours at room temperature. The reaction was quenched with water and extracted with CH_2Cl_2. The organic layer was dried with $MgSO_4$ and concentrated *in vacuo* to give the crude product, which was purified via column chromatography (Et_2O/hexane, 40:60, unless otherwise specified).

(4*S*,5*S*)-4-isopropyl-5-((*E*)-2-(4-methoxyphenyl)prop-1-en-1-yl)-3-((4-nitrophenyl)sulfonyl)oxazolidin-2-one (3a):

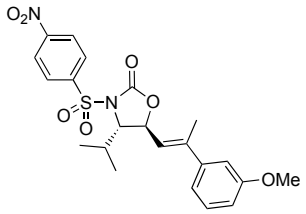


3a

Eluent: Et_2O/hexane (50:50). Pale yellow solid, 93%, > 95:5 (*E*:*Z*). The enantiopurity was determined via chiral HPLC using a Daicel CHIRALPAK IA-U column, hexane/isopropanol (90:10), 0.2 mL/min, 40 °C, 254 nm, single peak, t_R = 21.35 min, > 99% *ee*. Racemic **3a**, prepared from racemic *N*-Boc-valinal, gave two peaks (t_R = 21.45, 24.75 min, 1:1) under the same conditions. Mp 140.0 – 142.1 °C. $[\alpha]_D^{23}$ +4.42 (*c* 2.96, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M+Na]^+$ calcd for $C_{22}H_{24}N_2O_7SNa$, 483.1196; found, 483.1207. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 2964 – 2837 (w), 1772 (s, CO), 1606 (m), 1531 (s), 1511 (s), 1350 (s), 1241 (m), 1168 (vs), 1121 (s), 1090 (s), 1030 (m), 828 (s), 736 (s), 611 (vs), 564 (s). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.39 (d, *J* = 9.0 Hz, 2H, NsCH), 8.30 (d, *J* = 9.0 Hz, 2H, NsCH), 7.27 (d, *J* = 8.9 Hz, 2H, ArCH), 6.87 (d, *J* = 8.9 Hz, 2H, ArCH), 5.51 (dq, *J* = 9.2, 1.3 Hz, 1H, =CH), 5.13 (dd, *J* = 9.2, 2.5 Hz, 1H, CH-O), 4.18 (dd, *J* = 3.9, 2.5 Hz, 1H, CH-N), 3.84 (s, 3H, OMe), 2.50 – 2.40 (m, 1H, *i*-PrCH), 2.12 (d, *J* = 1.3 Hz, 3H, CH_3), 1.03 (d, *J* = 7.0 Hz, 3H, *i*-

$PrCH_3$), 0.89 (d, *J* = 6.9 Hz, 3H, *i*-$PrCH_3$) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 160.0 (QC, ArC), 151.8 (QC, CO), 150.9 (QC, NsC), 143.3 (QC, NsC), 142.6 (QC, ArC), 133.4 (QC, =C), 129.9 (CH, 2×NsCH), 127.1 (CH, 2×ArCH), 124.3 (CH, 2×NsCH), 120.7 (CH, =CH), 113.9 (CH, 2×ArCH), 73.1 (CH, CH-O), 68.5 (CH, CH-N), 55.4 (CH_3, OMe), 30.5 (CH, *i*-PrCH), 17.9 (CH_3, *i*-$PrCH_3$), 16.5 (CH_3, CH_3), 15.1 (CH_3, *i*-$PrCH_3$) ppm. A crystal structure for **3a** was obtained (CCDC 1919154).

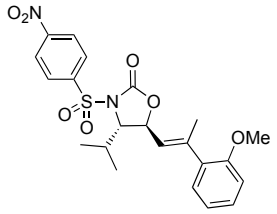
(4*S*,5*S*)-4-isopropyl-5-((*E*)-2-(3-methoxyphenyl)prop-1-en-1-yl)-3-((4-nitrophenyl)sulfonyl)oxazolidin-2-one (3b):



3b

93% conversion. Starting material was removed via recrystallisation in $CHCl_3$ layered with hexane, following column chromatography. Pale yellow crystals, 63%, > 95:5 (*E*:*Z*). Mp 116.5 – 118.0 °C. $[\alpha]_D^{24}$ +8.4 (*c* 1.55, $CHCl_3$). **HRMS-ASAP** (*m*/*z*): $[M+H]^+$ calcd for $C_{22}H_{25}N_2O_7S$, 461.1377; found, 461.1380. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 2961 – 2839 (w), 1771 (s, CO), 1529 (s), 1375 (s), 1349 (s), 1176 (vs), 1116 (s), 1045 (s), 856 (s), 739 (s), 680 (s), 615 (vs), 563 (vs). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.39 (d, *J* = 9.0 Hz, 2H, NsCH), 8.30 (d, *J* = 9.0 Hz, 2H, NsCH), 7.28 (app. t, *J* = 8.0 Hz, 1H, ArCH), 6.91 – 6.86 (m, 2H, ArCH), 6.81 – 6.80 (m, 1H, ArCH), 5.55 (dq, *J* = 9.1, 1.3 Hz, 1H, =CH), 5.12 (dd, *J* = 9.2, 2.4 Hz, 1H, CH-O), 4.18 (dd, *J* = 4.0, 2.4 Hz, 1H, CH-N), 3.83 (s, 3H, OMe), 2.49 – 2.42 (m, 1H, *i*-PrCH), 2.13 (d, *J* = 1.3 Hz, 3H, CH_3), 1.04 (d, *J* = 7.0 Hz, 3H, *i*-$PrCH_3$), 0.90 (d, *J* = 6.9 Hz, 3H, *i*-$PrCH_3$) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 159.7 (QC, ArC), 151.7 (QC, CO), 150.9 (QC, NsC), 143.3 (QC, NsC), 143.1 (QC, ArC), 142.7 (QC, =C), 129.8 (CH, 2×NsCH), 129.6 (CH, ArCH), 124.3 (CH, 2×NsCH), 122.5 (CH, =CH), 118.3 (CH, ArCH), 113.3 (CH, ArCH), 112.3 (CH, ArCH), 72.9 (CH, CH-O), 68.5 (CH, CH-N), 55.3 (CH_3, OMe), 30.5 (CH, *i*-PrCH), 17.9 (CH_3, *i*-$PrCH_3$), 16.7 (CH_3, CH_3), 15.1 (CH_3, *i*-$PrCH_3$) ppm.

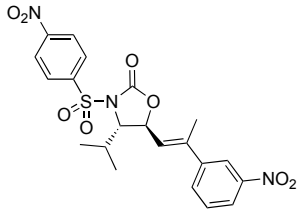
(4*S*,5*S*)-4-isopropyl-5-((*E*)-2-(2-methoxyphenyl)prop-1-en-1-yl)-3-((4-nitrophenyl)sulfonyl)oxazolidin-2-one (3c):



3c

Yellow solid, 69%, > 95:5 (*E*:*Z*). Mp 122.2 – 123.8 °C. $[\alpha]_D^{24}$ +15.0 (*c* 2.63, $CHCl_3$). **HRMS-ASAP** (*m*/*z*): $[M+H]^+$ calcd for $C_{22}H_{25}N_2O_7S$, 461.1377; found, 461.1370. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 2971 – 2835 (w), 1789 (s, CO), 1521 (s), 1346 (s), 1164 (vs), 1133 (s), 1118 (s), 856 (m), 736 (vs), 684 (s), 636 (s), 569 (vs). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.35 (d, *J* = 9.0 Hz, 2H, NsCH), 8.27 (d, *J* = 9.0 Hz, 2H, NsCH), 7.29 (ddd, *J* = 8.9, 7.8, 2.2 Hz, 1H, ArCH), 7.01 (dd, *J* = 7.4, 1.8 Hz, 1H, ArCH), 6.93 – 6.87 (m, 2H, ArCH), 5.34 (dq, *J* = 9.2, 1.4 Hz, 1H, =CH), 5.12 (dd, *J* = 9.2, 2.6 Hz, 1H, CH-O), 4.19 (dd, *J* = 3.9, 2.6 Hz, 1H, CH-N), 3.80 (s, 3H, OMe), 2.50 – 2.42 (m, 1H, *i*-PrCH), 2.08 (d, *J* = 1.3 Hz, 3H, CH_3), 1.06 (d, *J* = 7.0 Hz, 3H, *i*-$PrCH_3$), 0.91 (d, *J* = 6.9 Hz, 3H, *i*-$PrCH_3$) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 156.4 (QC, ArC), 151.8 (QC, CO), 150.9 (QC, NsC), 143.7 (QC, ArC), 143.3 (QC, NsC), 132.0 (QC, =C), 129.8 (CH, 2×NsCH), 129.4 (CH, ArCH), 128.9 (CH, ArCH), 124.3 (CH, =CH), 124.2 (CH, 2×NsCH), 120.6 (CH, ArCH), 110.9 (CH, ArCH), 72.8 (CH, CH-O), 68.5 (CH, CH-N), 55.4 (CH_3, OMe), 30.5 (CH, *i*-PrCH), 17.8 (CH_3, *i*-$PrCH_3$), 17.8 (CH_3, CH_3), 15.1 (CH_3, *i*-$PrCH_3$) ppm.

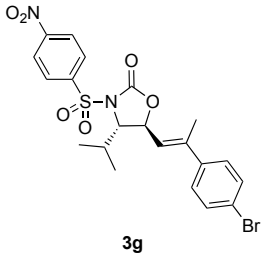
(4*S*,5*S*)-4-isopropyl-5-((*E*)-2-(3-nitrophenyl)prop-1-en-1-yl)-3-((4-nitrophenyl)sulfonyl)oxazolidin-2-one (3e):



3e

Ligand/catalyst loading increased to 10/5 mol%, respectively. 84% conversion. Required resubjection to the reaction conditions to consume starting material and enable purification. Eluent: Et_2O/hexane (50:50). Pale yellow solid, 62%, > 95:5 (*E*:*Z*). Mp 153.1 – 154.0 °C. $[\alpha]_D^{24}$ +9.0 (*c* 2.44, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M+Na]^+$ calcd for $C_{21}H_{21}N_3O_8SNa$, 498.0942; found, 498.0952. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 2962 – 2853 (w),1779 (s, CO), 1524 (s), 1347 (vs), 1170 (vs), 1138 (s), 1120 (s), 1088 (s), 854 (m), 736 (vs), 683 (s), 614 (vs), 561 (s). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.41 (d, *J* = 9.0 Hz, 2H, NsCH), 8.32 (d, *J* = 9.0 Hz, 2H, NsCH), 8.21 – 8.19 (m, 2H, ArCH), 7.69 (ddd, *J* = 7.8, 1.8, 1.1 Hz, 1H, ArCH), 7.56 (dd, *J* = 8.8, 7.8 Hz, 1H, ArCH), 5.77 (dq, *J* = 9.1, 1.3 Hz, 1H, =CH), 5.14 (dd, *J* = 9.1, 2.5 Hz, 1H, CH-O), 4.25 (dd, *J* = 3.8, 2.6 Hz, 1H, CH-N), 2.52 – 2.46 (m, 1H, *i*-PrCH), 2.21 (d, *J* = 1.3 Hz, 3H, CH_3), 1.04 (d, *J* = 7.0 Hz, 3H, *i*-PrCH_3), 0.87 (d, *J* = 6.9 Hz, 3H, *i*-PrCH_3) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.5 (QC, CO), 160.0 (QC, NsC), 148.4 (QC, ArC), 143.2 (QC, NsC), 142.9 (QC, =C), 141.2 (QC, ArC), 131.9 (CH, ArCH), 129.9 (CH, 2×NsCH), 129.7 (CH, ArCH), 124.7 (CH, =CH), 124.3 (CH, 2×NsCH), 123.3 (CH, ArCH), 120.9 (CH, ArCH), 72.3 (CH, CH-O), 68.1 (CH, CH-N), 30.3 (CH, *i*-PrCH), 17.9 (CH_3, *i*-PrCH_3), 16.7 (CH_3, CH_3), 14.9 (CH_3, *i*-PrCH_3) ppm.

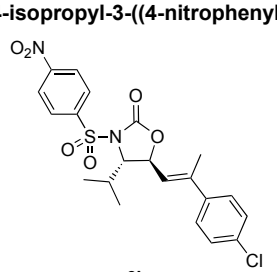
(4*S*,5*S*)-5-((*E*)-2-(4-bromophenyl)prop-1-en-1-yl)-4-isopropyl-3-((4-nitrophenyl)sulfonyl)oxazolidin-2-one (3g):



3g

Off-white solid, 73%, > 95:5 (*E*:*Z*). 129.4 – 132.8 °C. $[\alpha]_D^{24}$ +15.6 (*c* 0.85, $CHCl_3$). **HRMS-ASAP** (*m*/*z*): $[M+H]^+$ calcd for $C_{21}H_{22}N_2O_6SBr$, 509.0376; found, 509.0391. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 2963 – 2853 (w), 1768 (s, CO), 1530 (s), 1365 (s), 1347 (s), 1170 (s), 1118 (s), 1008 (s), 800 (s), 736 (s), 681 (s), 615 (vs), 555 (s). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.40 (d, *J* = 8.9 Hz, 2H, NsCH), 8.31 (d, *J* = 8.9 Hz, 2H, NsCH), 7.49 (d, *J* = 8.5 Hz, 2H, ArCH), 7.21 (d, *J* = 8.5 Hz, 2H, ArCH), 5.64 (app. dd, *J* = 9.1, 1.2 Hz, 1H, =CH), 5.11 (dd, *J* = 9.2, 2.5 Hz, 1H, CH-O), 4.21 (dd, *J* = 3.7, 2.6 Hz, 1H, CH-N), 2.49 – 2.43 (m, 1H, *i*-PrCH), 2.13 (d, *J* = 1.2 Hz, 3H, CH_3), 1.02 (d, *J* = 7.0 Hz, 3H, *i*-PrCH_3), 0.86 (d, *J* = 6.9 Hz, 3H, *i*-PrCH_3) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 151.6 (QC, CO), 150.9 (QC, NsC), 143.2 (QC, Ns), 142.3 (QC, ArC), 140.1 (QC, ArC), 131.7 (CH, 2×ArCH), 129.9 (CH, 2×NsCH), 127.5 (CH, 2×ArCH), 124.3 (CH, 2×NsCH), 122.8 (CH, =C), 122.7 (QC, ArC), 72.6 (CH, CH-O), 68.2 (CH, CH-N), 30.3 (CH, *i*-PrCH), 17.8 (CH_3, *i*-PrCH_3), 16.6 (CH_3, CH_3), 14.9 (CH_3, *i*-PrCH_3) ppm.

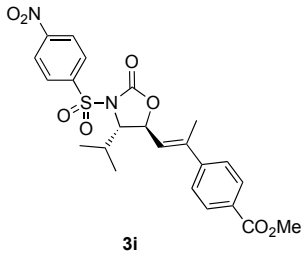
(4*S*,5*S*)-5-((*E*)-2-(4-chlorophenyl)prop-1-en-1-yl)-4-isopropyl-3-((4-nitrophenyl)sulfonyl)oxazolidin-2-one (3h):



3h

Off-white solid, 81%, > 95:5 (*E*:*Z*). Mp 140.7 – 141.4 °C. $[\alpha]_D^{24}$ +15.4 (*c* 1.79, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M+Na]^+$ calcd for $C_{21}H_{21}N_2O_6SCl$, 487.0701; found, 487.0720. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 2964 (w), 1779 (s, CO), 1526 (s), 1365 (m), 1348 (s), 1250 (m), 1168 (s), 1085 (s), 1012 (vs), 797 (s), 614 (s), 550 (s). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.39 (d, *J* = 9.0 Hz, 2H, NsCH), 8.31 (d, *J* = 9.0 Hz, 2H, NsCH), 7.33 (d, *J* = 8.7 Hz, 2H, ArCH), 7.27 (d, *J* = 8.7 Hz, 2H, ArCH), 5.64 (dq, *J* = 9.2, 1.3 Hz, 1H, =CH), 5.12 (dd, *J* = 9.2, 2.5 Hz, 1H, CH-O), 4.22 (dd, *J* = 3.8, 2.6 Hz, 1H, CH-N), 2.49 – 2.43 (m, 1H, *i*-PrCH), 2.13 (d, *J* = 1.3 Hz, 3H, CH_3), 1.02 (d, *J* = 7.0 Hz, 3H, *i*-PrCH_3), 0.86 (d, *J* = 6.9 Hz, 3H, *i*-PrCH_3) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.6 (QC, CO), 150.9 (QC, NsC), 143.3 (QC, NsC), 142.2 (QC, ArC), 139.6 (QC, =C), 134.5 (QC, ArC), 129.9 (CH, 2×NsCH), 128.7 (CH, 2×ArCH), 127.2 (CH, 2×ArCH), 124.3 (CH, 2×NsCH), 122.7 (CH, =CH), 72.6 (CH, CH-O), 68.2 (CH, CH-N), 30.3 (CH, *i*-PrCH), 17.8 (CH_3, *i*-PrCH_3), 16.6 (CH_3, CH_3), 14.9 (CH_3, *i*-PrCH_3) ppm.

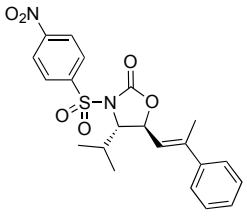
Methyl 4-((*E*)-1-((4*S*,5*S*)-4-isopropyl-3-((4-nitrophenyl)sulfonyl)-2-oxooxazolidin-5-yl)prop-1-en-2-yl)benzoate (3i):



3i

71% conversion. Required resubjection to the reaction conditions to consume starting material and enable purification. Eluent: Et_2O/hexane (50:50). Brown solid, 89%, > 95:5 (*E*:*Z*). Mp 167.0 – 169.5 °C. $[\alpha]_D^{24}$ +19.6 (*c* 2.61, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M+Na]^+$ calcd for $C_{23}H_{24}N_2O_8SNa$, 511.1146; found, 511.1167. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 2962 – 2852 (w), 1768 (s, CO), 1713 (s, *CO*-OMe), 1527 (s), 1348 (s), 1281 (s), 1173 (s), 1110 (s), 1087 (s), 1004 (s), 853 (s), 734 (s), 682 (s), 614 (vs), 556 (vs). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.39 (d, *J* = 8.9 Hz, 2H, NsCH), 8.31 (d, *J* = 8.9 Hz, 2H, NsCH), 8.02 (d, *J* = 8.5 Hz, 2H, ArCH), 7.40 (d, *J* = 8.5 Hz, 2H, ArCH), 5.73 (app. dd, *J* = 9.1, 1.3 Hz, 1H, =CH), 5.14 (dd, *J* = 9.1, 2.5 Hz, 1H, CH-O), 4.24 (dd, *J* = 3.7, 2.6 Hz, 1H, CH-N), 3.93 (s, 3H, CO_2Me), 2.50 – 2.44 (m, 1H, *i*-PrCH), 2.17 (d, *J* = 1.2 Hz, 3H, CH_3), 1.03 (d, *J* = 7.0 Hz, 3H, *i*-PrCH_3), 0.86 (d, *J* = 6.9 Hz, 3H, *i*-PrCH_3) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 166.5 (QC, ArC), 151.6 (QC, CO), 150.9 (QC, NsC), 145.6 (QC, =C), 143.2 (QC, NsC), 142.5 (QC, ArC), 129.9 (CH, 2×ArCH), 129.8 (CH, 2×ArCH), 125.9 (CH, 2×ArCH), 124.3 (CH, 2×NsCH), 123.9 (CH, =CH), 72.5 (CH, CH-O), 68.2 (CH, CH-N), 52.2 (CH_3, CO_2*Me*), 30.3 (CH, *i*-PrCH), 17.8 (CH_3, *i*-PrCH_3), 16.6 (CH_3, CH_3), 14.9 (CH_3, *i*-PrCH_3) ppm.

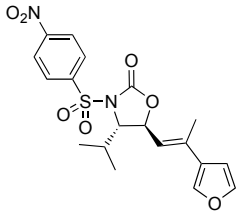
(4*S*,5*S*)-4-isopropyl-3-((4-nitrophenyl)sulfonyl)-5-((*E*)-2-phenylprop-1-en-1-yl)oxazolidin-2-one (3j):



3j

Off-white solid, 75%, > 95:5 (*E*:*Z*). Mp 122.9 – 124.5 °C. $[\alpha]_D^{23}$ +9.6 (*c* 2.76, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M+Na]^+$ calcd for $C_{21}H_{22}N_2O_6SNa$, 453.1091; found, 453.1118. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 2960 – 2851 (w), 1770 (s, CO), 1529 (s), 1374 (s), 1348 (s), 1167 (vs), 1108 (s), 1002 (m), 854 (m), 753 (s), 740 (s), 615 (vs), 565 (vs). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.38 (d, *J* = 8.9 Hz, 2H, NsCH), 8.30 (d, *J* = 8.9 Hz, 2H, NsCH), 7.39 – 7.30 (m, 5H, ArCH), 5.59 (app. dd, *J* = 9.2, 1.3 Hz, 1H, =CH), 5.14 (dd, *J* = 9.2, 2.5 Hz, 1H, CH-O), 4.20 (dd, *J* = 3.8, 2.6 Hz, 1H, CH-N), 2.49 – 2.43 (m, 1H, *i*-PrCH), 2.15 (d, *J* = 1.2 Hz, 3H, CH_3), 1.04 (d, *J* = 7.0 Hz, 3H, *i*-PrCH_3), 0.89 (d, *J* = 6.9 Hz, 3H, *i*-PrCH_3) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.7 (QC, CO), 150.9 (QC, NsC), 143.29 (QC, ArC), 143.26 (QC, ArC), 141.2 (QC, =C), 129.9 (CH, 2×NsCH), 128.6 (CH, ArCH), 128.5 (CH, 2×ArCH), 125.9 (CH, 2×ArCH), 124.3 (CH, 2×NsCH), 122.3 (CH, =CH), 72.9 (CH, CH-O), 68.4 (CH, CH-N), 30.4 (CH, *i*-PrCH), 17.9 (CH_3, *i*-PrCH_3), 16.6 (CH_3, CH_3), 15.0 (CH_3, *i*-PrCH_3) ppm.

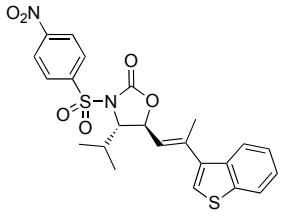
(4*S*,5*S*)-5-((*E*)-2-(furan-3-yl)prop-1-en-1-yl)-4-isopropyl-3-((4-nitrophenyl)sulfonyl)oxazolidin-2-one (3k):



3k

76% conversion. Required resubjection to the reaction conditions to consume starting material and enable purification. Eluent: Et_2O/hexane (50:50). Off-white solid, 81%, > 95:5 (*E*:*Z*). Mp 152.0 – 153.3 °C. $[\alpha]_D^{23}$ –5.4 (*c* 2.56, $CHCl_3$). **HRMS-ASAP** (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{21}N_2O_7S$, 421.1064; found, 421.1057. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 2962 – 2876 (w), 1772 (s, CO), 1530 (s), 1349 (s), 1170 (s), 1120 (s), 1088 (s), 737 (s), 615 (vs), 558 (s). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.41 (d, *J* = 8.9 Hz, 2H, NsCH), 8.32 (d, *J* = 9.0 Hz, 2H, NsCH), 7.50 (s, 1H, FurCH), 7.41 (app. t, *J* = 1.7 Hz, 1H, FurCH), 6.44 (dd, *J* = 1.8, 0.8 Hz, 1H, FurCH), 5.60 (app. dd, *J* = 9.3, 1.1 Hz, 1H, =CH), 5.13 (dd, *J* = 9.3, 2.5 Hz, 1H, CH-O), 4.20 (dd, *J* = 3.7, 2.7 Hz, 1H, CH-N), 2.48 – 2.42 (m, 1H, *i*-PrCH), 2.03 (d, *J* = 1.2 Hz, 3H, CH_3), 1.00 (d, *J* = 7.0 Hz, 3H, *i*-$PrCH_3$), 0.84 (d, *J* = 6.9 Hz, 3H, *i*-$PrCH_3$) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.7 (QC, CO), 150.9 (QC, NsC), 144.0 (CH, FurCH), 143.4 (QC, NsC), 140.4 (CH, FurCH), 134.3 (QC, =C), 129.9 (CH, 2×NsCH), 127.1 (QC, FurC), 124.3 (CH, 2×NsCH), 119.6 (CH, =CH), 107.1 (CH, FurCH), 72.5 (CH, CH-O), 68.2 (CH, CH-N), 30.3 (CH, *i*-PrCH), 17.8 (CH_3, *i*-$PrCH_3$), 15.5 (CH_3, CH_3), 14.9 (CH_3, *i*-$PrCH_3$) ppm.

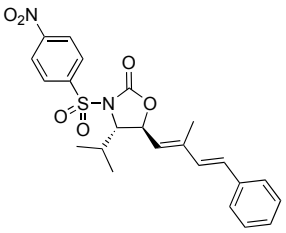
(4*S*,5*S*)-5-((*E*)-2-(benzo[*b*]thiophen-3-yl)prop-1-en-1-yl)-4-isopropyl-3-((4-nitrophenyl)sulfonyl)oxazolidin-2-one (3l):



3l

89% conversion. Required resubjection to the reaction conditions to consume starting material and enable purification. Eluent: Et_2O/hexane (50:50). Brown solid, 98%, > 95:5 (*E*:*Z*). Mp 171.6 – 174.5 °C. $[\alpha]_D^{24}$ –21.4 (*c* 1.91, $CHCl_3$). **HRMS-ASAP** (*m*/*z*): $[M+Na]^+$ calcd for $C_{23}H_{22}N_2O_6S_2Na$, 509.0811; found, 509.0805. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 2963 – 2876 (w), 1776 (s, CO), 1529 (s), 1363 (s), 1348 (s), 1169 (s), 1118 (s), 1085 (s), 752 (s), 736 (s), 615 (vs), 548 (s). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.31 (d, *J* = 9.0 Hz, 2H, NsCH), 8.26 (d, *J* = 9.0 Hz, 2H, NsCH), 7.90 – 7.87 (m, 1H, HetCH), 7.72 – 7.69 (m, 1H, HetCH), 7.41 – 7.35 (m, 1H, HetCH), 7.31 (s, 1H, HetCH), 5.65 (dq, *J* = 9.3, 1.3 Hz, 1H, =CH), 5.22 (dd, *J* = 9.3, 2.6 Hz, 1H, CH-O), 4.23 (dd, *J* = 3.9, 2.6 Hz, 1H, CH-N), 2.54 – 2.47 (m, 1H, *i*-PrCH), 2.23 (d, *J* = 1.3 Hz, 3H, CH_3), 1.09 (d, *J* = 7.0 Hz, 3H, *i*-$PrCH_3$), 0.94 (d, *J* = 6.9 Hz, 3H, *i*-$PrCH_3$) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.7 (QC, CO), 150.9 (QC, NsC), 143.1 (QC, NsC), 140.6 (QC, HetC), 138.5 (QC, =C), 138.2 (QC, HetC), 136.7 (QC, HetC), 129.8 (CH, 2×NsCH), 124.7 (CH, HetCH), 124.49 (CH, =CH or HetCH), 124.47 (CH, =CH or HetCH), 124.3 (CH, 2×NsCH), 124.0 (CH, HetCH), 123.2 (CH, HetCH), 122.6 (CH, HetCH), 72.6 (CH, CH-O), 68.5 (CH, CH-N), 30.5 (CH, *i*-PrCH), 18.3 (CH_3, CH_3), 17.9 (CH_3, *i*-$PrCH_3$), 15.1 (CH_3, *i*-$PrCH_3$) ppm.

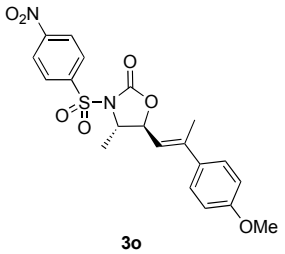
(4*S*,5*S*)-4-isopropyl-5-((1*E*,3*E*)-2-methyl-4-phenylbuta-1,3-dien-1-yl)-3-((4-nitrophenyl)sulfonyl)oxazolidin-2-one (3m):



3m

53% conversion. Required resubjection to the reaction conditions to consume starting material and enable purification. Eluent: Et_2O/hexane (30:70). Yellow gum, 65%, > 99:1 (*E*:*Z*). $[\alpha]_D^{22}$ +24.1 (*c* 1.86, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M+Na]^+$ calcd for $C_{23}H_{24}N_2O_6S$, 479.1247; found, 479.1248. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3106 (w), 3026 (w), 2964 – 2876 (w), 1773 (s, CO), 1531 (s), 1348 (s), 1170 (vs), 1118 (s), 1088 (s), 960 (s), 855 (m), 747 (s), 682 (s), 613 (vs), 554 (s). **^{1}H NMR** (500 MHz,$CDCl_3$): δ 8.43 (d, *J* = 8.8 Hz, 2H, NsCH), 8.33 (d, *J* = 8.8 Hz, 2H, NsCH), 7.42 (d, *J* = 7.5 Hz, 2H, ArCH), 7.36 (app. t, *J* = 7.5 Hz, 2H, ArCH), 7.28 (t, *J* = 7.3 Hz, 1H, ArCH), 6.71 (app. dd, *J* = 19.7, 16.2 Hz, 2H, styryl =CH), 5.52 (d, *J* = 9.4 Hz, 1H, =CH), 5.15 (dd, *J* = 9.4, 2.3 Hz, 1H, CH-O), 4.21 – 4.20 (m, 1H, CH-N), 2.49 – 2.43 (m, 1H, *i*-PrCH), 1.98 (s, 3H, CH_3), 1.00 (d, *J* = 7.0 Hz, 3H, *i*-PrCH_3), 0.84 (d, *J* = 6.9 Hz, 3H, *i*-PrCH_3) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 151.6 (QC, CO), 150.9 (QC, NsC), 143.2 (QC, NsC), 140.6 (QC, =C) 136.3 (QC, ArC), 131.5 (CH, styryl =CH), 130.9 (CH, styryl =CH), 129.9 (CH, 2×NsCH), 128.8 (CH, 2×ArCH), 128.3 (CH, ArCH), 126.7 (CH, 2×ArCH), 125.5 (CH, =CH), 124.3 (CH, 2×NsCH), 72.5 (CH, CH-O), 68.2 (CH, CH-N), 30.2 (CH, *i*-PrCH), 17.8 (CH_3, *i*-PrCH_3), 14.8 (CH_3, *i*-PrCH_3), 13.1 (CH_3, CH_3) ppm.

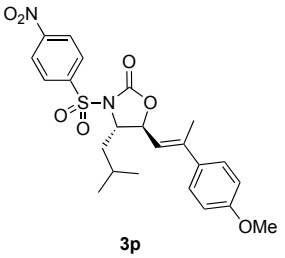
(4*S*,5*S*)-5-((*E*)-2-(4-methoxyphenyl)prop-1-en-1-yl)-4-methyl-3-((4-nitrophenyl)sulfonyl)oxazolidin-2-one (3o):



3o

Purified via recrystallization in CH_2Cl_2 layered with hexane. Yellow solid, 80%, 92:8 (*E*:*Z*). Mp 153.4 – 153.8 °C. $[\alpha]_D^{23}$ +0.4 (*c* 1.54, $CHCl_3$). **HRMS-ESI** (*m*/*z*): $[M+H]^+$ calcd for $C_{20}H_{21}N_2O_6S$, 433.1064; found, 433.1088. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 3108 9w), 1777 (s, CO), 1605 (m), 1529 (s), 1369 (s), 1346 (s), 1170 (s), 1141 (s), 741 (s), 616 (vs), 560 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.40 (d, *J* = 9.0 Hz, 2H, NsCH), 8.28 (d, *J* = 9.1 Hz, 2H, NsCH), 7.29 (d, *J* = 8.9 Hz, 2H, ArCH), 6.87 (d, *J* = 8.9 Hz, 2H, ArCH), 5.56 (dq, *J* = 8.9, 1.3 Hz, 1H, =CH), 4.95 (dd, *J* = 8.9, 5.2 Hz, 1H, CH-O), 4.28 – 4.22 (m, 1H, CH-N), 3.82 (s, 3H, OMe), 2.12 (d, *J* = 1.3 Hz, 3H, =C-CH_3), 1.64 (d, *J* = 6.2 Hz, 3H, Me) ppm. **^{13}C NMR** (125 MHz, $CDCl_3$): δ 160.0 (QC, ArC), 151.6 (QC, CO), 151.0 (QC, NsC), 144.3 (QC, =C), 143.2 (QC, NsC), 133.3 (QC, ArC), 129.9 (CH, 2×NsCH), 127.1 (CH, 2×ArCH), 124.3 (CH, 2×NsCH), 119.2 (CH, =CH), 113.8 (CH, 2×ArCH), 79.2 (CH, CH-O), 60.2 (CH, CH-N), 55.3 (CH_3, OMe), 19.9 (CH_3, Me), 16.7 (CH_3, =C-CH_3) ppm.

(4*S*,5*S*)-4-isobutyl-5-((*E*)-2-(4-methoxyphenyl)prop-1-en-1-yl)-3-((4-nitrophenyl)sulfonyl)oxazolidin-2-one (3p):

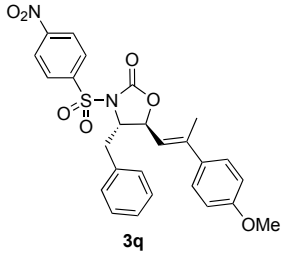


3p

Starting material 4.9:1 *dr*. 90% conversion. Required resubjection to the reaction conditions to consume starting material and enable purification. Yellow gum, 81%, 8.0:1 *dr* (crude), 15.3:1 *dr* (after purification), > 95:5 (*E*:*Z*). **HRMS-ASAP** (*m*/*z*): $[M+H]^+$ calcd for $C_{23}H_{27}N_2O_7S$, 475.1533; found, 475.1531. **FTIR $\bar{\nu}_{max}$** (cm^{-1}): 2959 – 2839 (w), 1773 (s, CO), 1606 (m), 1531 (s), 1513 (s), 1368 (s), 1247 (s), 1172 (vs), 1139 (s), 1120 (s), 1089 (s), 744 (s), 682 (s), 612 (vs), 561 (s). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.38 (d, *J* = 9.0 Hz, 2H, NsCH, *major* and *minor*), 8.32 (d, *J* = 9.0 Hz, 2H, NsCH, *minor*), 8.28 (d, *J* = 9.0 Hz, 2H, NsCH, *major* and *minor*), 7.32 (d, *J* = 8.8 Hz, 2H, ArCH, *minor*), 7.26 (d, *J* = 8.9 Hz, 2H, ArCH, *major*), 6.87 (d, *J* = 8.8 Hz, 2H, ArCH, *major* and *minor*), 5.70 (app. dd, *J* = 9.1, 1.2 Hz, 1H, =CH, *minor*), 5.51 (app. dd, *J* = 9.2, 1.2 Hz, 1H, =CH, *major*), 5.07 (dd, *J* = 9.2, 2.9 Hz, 1H, CH-O, *major* and *minor*), 4.61 – 4.56 (m, 1H, CH-N, *minor*), 4.26 (app. dt, *J* = 10.2, 3.2 Hz, 1H, CH-N, *major*), 3.83 (s, 3H, OMe, *major*), 3.82 (s, 3H, OMe, *minor*), 2.11 (d, *J* = 1.2 Hz, 3H, CH_3, *major* and *minor*), 2.05 – 1.90 (m, 1H, *i*-BuCH_2, *major*), 1.83 – 1.60 (m, 2H, *i*-BuCH_2, *major* and *minor* and *i*-BuCH, *major* and *minor*), 1.03 (d, *J* = 6.4 Hz, 3H, *i*-BuCH_3, *major*), 1.00 (d, *J* = 6.4 Hz, 3H, *i*-BuCH_3, *major* and *minor*), 0.91 (d, *J*

= 6.2 Hz, 3H, *i*-BuCH$_3$, *minor*) ppm. **^{13}C NMR** (100 MHz, CDCl$_3$): δ 160.0 (QC, ArC, *major* and *minor*), 151.5 (QC, CO, *major* and *minor*), 150.9 (QC, NsC, *major* and *minor*), 143.59 (QC, =C, *major*), 143.56 (QC, =C, *minor*), 143.5 (QC, NsC, *major* and *minor*), 133.4 (QC, ArC, *major* and *minor*), 130.0 (CH, 2×NsCH, *minor*) 129.8 (CH, 2×NsCH, *major*), 127.06 (CH, 2×ArCH, *major*), 126.98 (CH, 2×ArCH, *minor*), 124.30 (CH, 2×NsCH, *major*), 124.27 (CH, 2×NsCH, *minor*), 120.0 (CH, =CH, *major*), 116.1 (CH, =CH, *minor*), 113.91 (CH, 2×ArCH, *minor*), 113.85 (CH, 2×ArCH, *major*), 77.5 (CH, CH-O, *major*), 77.2 (CH, CH-O, *minor*), 62.6 (CH, CH-N), 59.96 (CH, CH-N, *minor*), 55.33 (CH$_3$, OMe, *major*), 55.31 (CH$_3$, OMe, *minor*), 43.1 (CH$_2$, *i*-BuCH$_2$, *major*), 39.0 (CH$_2$, *i*-BuCH$_2$, *minor*), 25.0 (CH, *i*-BuCH, *minor*), 24.6 (CH, *i*-BuCH, *major*), 23.6 (CH$_3$, *i*-BuCH$_3$, *major*), 23.0 (CH$_3$, *i*-BuCH$_3$, *minor*), 21.8 (CH$_3$, *i*-BuCH$_3$, *minor*), 21.4 (CH$_3$, *i*-BuCH$_3$, *minor*), 16.8 (CH$_3$, CH$_3$, *minor*), 16.6 (CH$_3$, CH$_3$, *major*) ppm.

(4*S*,5*S*)-4-benzyl-5-((*E*)-2-(4-methoxyphenyl)prop-1-en-1-yl)-3-((4-nitrophenyl)sulfonyl)oxazolidin-2-one (3q):

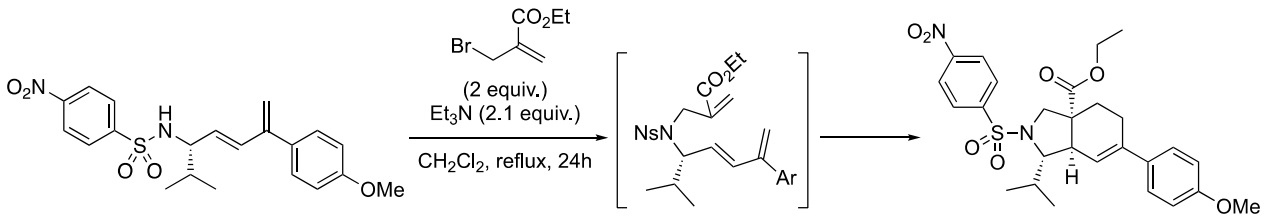


3q

Starting material 2.2:1 *dr*. Pale yellow crystals, 79%, 3.2:1 *dr* (crude), 9.7:1 (after purification), > 95:5 (*E*:*Z*). Mp 68.9 – 72.4 °C. **HRMS-ASAP** (*m*/*z*): [M+H]$^+$ calcd for $C_{26}H_{25}N_2O_7SNa$, 509.1377; found, 509.1369. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 2959 – 2839 (w), 1774 (s, CO), 1606 (m), 1531 (s), 1513 (s), 1369 (m), 1348 (s), 1246 (m), 1173 (s), 1124 (s), 736 (s), 612 (s), 559 (s). **^{1}H NMR** (500 MHz,CDCl$_3$): δ 8.39 (d, *J* = 9.0 Hz, 2H, NsCH, *major*), 8.33 (d, *J* = 9.0 Hz, 2H, NsCH, *minor*), 8.31 (d, *J* = 9.0 Hz, 2H, NsCH, *major*), 8.16 (d, *J* = 9.0 Hz, 2H, NsCH, *minor*), 7.38 – 7.19 (m, 5H, BnCH, *major* and *minor*), 7.14 (d, *J* = 8.9 Hz, 2H, ArCH, *minor*), 7.11 (d, *J* = 8.9 Hz, 2H, ArCH, *major*), 6.84 (d, *J* = 8.9 Hz, 2H, ArCH, *minor*), 6.81 (d, *J* = 8.9 Hz, 2H, ArCH, *major*), 5.71 (app. dd, *J* = 8.4, 1.3 Hz, 1H, =CH, *minor*), 5.54 (dd, *J* = 8.5, 7.0 Hz, 1H, CH-O, *minor*), 5.35 (dq, *J* = 9.1, 1.3 Hz, 1H, =CH, *major*), 5.09 (dd, *J* = 9.1, 2.7 Hz, 1H, CH-O, *major*), 5.03 (ddd, *J* = 8.9, 7.0, 5.1 Hz, 1H, CH-N, *minor*), 4.45 (ddd, *J* = 10.3, 4.0, 2.6 Hz, 1H, CH-N, *major*), 3.82 (s, 3H, OMe, *minor*), 3.80 (s, 3H, OMe, *major*), 3.57 (dd, *J* = 13.4, 4.0 Hz, 1H, BnCH$_2$, *major*), 3.18 (dd, *J* = 14.5, 5.1 Hz, 1H, BnCH$_2$, *minor*), 3.05 (dd, *J* = 14.5, 8.8 Hz, 1H, BnCH$_2$, *minor*), 2.92 (dd, *J* = 13.4, 10.3 Hz, 1H, BnCH$_2$, *major*), 1.74 (d, *J* = 1.1 Hz, 3H, CH$_3$, *minor*), 1.54 (d, *J* = 1.2 Hz, 3H, CH$_3$, *major*) ppm. **^{13}C NMR** (100 MHz, CDCl$_3$): δ 159.8 (QC, ArC, *major*), 159.7 (QC, ArC, *minor*), 151.6 (QC, CO, *minor*), 151.4 (QC, CO, *major*), 151.0 (QC, NsC, *major*), 150.8 (QC, NsC, *minor*), 143.6 (QC, NsC, *minor*), 143.5 (QC, =C, *minor*), 143.3 (QC, NsC, *major*), 142.6 (QC, =C, *major*), 135.5 (QC, BnC, *minor*), 134.2 (QC, BnC, *major*), 133.43 (QC, ArC, *minor*), 133.37 (QC, ArC, *major*), 129.9 (CH, 2×NsCH, *major* and *minor*), 129.5 (CH, 2×BnCH, *major* and *minor*), 129.3 (CH, 2×BnCH, *minor*), 129.2 (CH, 2×BnCH, *major*), 128.7 (CH, BnCH, *minor*), 127.8 (CH, BnCH, *major*), 127.1 (CH, 2×ArCH, *minor*), 126.9 (CH, 2×ArCH, *major*), 124.4 (CH, 2×NsCH, *major*), 124.2 (CH, 2×NsCH, *minor*), 119.8 (CH, =CH, *major*), 116.4 (CH, =CH, *minor*), 113.72 (CH, 2×ArCH, *major*), 113.67 (CH, 2×ArCH, *minor*), 77.7 (CH, CH-O, *minor*), 76.2 (CH, CH-O, *major*), 64.6 (CH, CH-N, *major*), 62.1 (CH, CH-N, *minor*), 55.3 (CH$_3$, OMe, *major* and *minor*), 39.9 (CH$_2$, BnCH$_2$, *major*), 36.1 (CH$_2$, BnCH$_2$, *minor*), 16.5 (CH$_3$, CH$_3$, *minor*), 15.7 (CH$_3$, CH$_3$, *major*) ppm.

6. Synthesis of isoindoline 5a:

Ethyl (1*S*,3a*R*,7a*R*)-1-isopropyl-6-(4-methoxyphenyl)-2-((4-nitrophenyl)sulfonyl)-1,2,3,4,5,7a-hexahydro-3a*H*-isoindole-3a-carboxylate (5a):

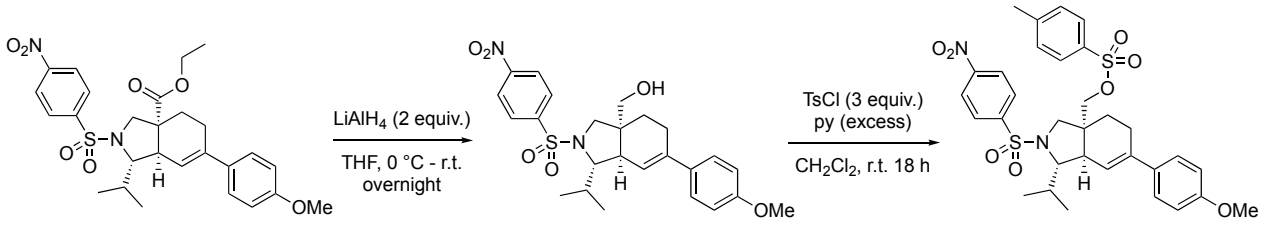


2a **5a** (*major*)

To a solution of the 1,3-diene **2a** (50.3 mg, 0.12 mmol, 1.0 equiv.) and Et_3N (36.0 µL, 0.26 mmol, 2.1 equiv.) in CH_2Cl_2 (2 mL) was added ethyl 2-(bromomethyl)acrylate (34 µL, 0.25 mmol, 2.0 equiv.) and the reaction mixture heated at reflux with stirring. After 24 hours, the reaction mixture was concentrated *in vacuo* and subjected to column chromatography (EtOAc/hexane, 20:80) to give the pure product **5a** as deep yellow crystals (35.3 mg, 66.8 µmol, 55%, 10:3:1 *dr*). Mp 60.6 – 63.1 °C. **HRMS-ESI** (*m*/*z*): $[M+Na]^+$ calcd for $C_{27}H_{32}N_2O_7SNa$, 551.1822; found, 551.1813. **FTIR** $\bar{\nu}_{max}$ (cm^{-1}): 2957 – 2855 (s), 1725 (s, *CO*-OEt), 1607 (m), 1530 (s), 1512 (s), 1463 (s), 1347 (s), 1160 (vs), 1089 (s), 1033 (s), 735 (s), 685 (s), 615 (vs). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.32 (d, *J* = 9.0 Hz, 2H, NsCH, *minor*), 8.14 (d, *J* = 8.8 Hz, 2H, NsCH, *major*), 7.97 (d, *J* = 8.8 Hz, 2H, NsCH, *minor*), 7.93 (d, *J* = 8.7 Hz, 2H, NsCH, *major*), 7.19 (d, *J* = 8.8 Hz, 2H, ArCH, *minor*), 6.81 – 6.78 (m, 2H, ArCH, *major* and *minor*), 6.06 – 6.05 (m, 1H, =CH, *minor*), 5.66 – 5.65 (m, 1H, =CH, *major*), 4.27 – 4.14 (m, 1H, CH-N, *minor* and 2H, $EtCH_2$, *major*), 3.98 (d, *J* = 11.4 Hz, 1H, CH_2-N, *minor*), 3.84 (d, *J* = 11.0 Hz, 1H, CH_2-N, *major*), 3.81 (s, 3H, OMe, *major*), 3.78 (s, 3H, OMe, *minor*), 3.70 – 3.65 (m, 2H, $EtCH_2$, *minor*), 3.56 (dd, *J* = 6.8, 4.8 Hz, 1H, CH-N, *major*), 3.48 (d, *J* = 11.0 Hz, 1H, CH_2-N, *major*), 3.30 – 3.28 (m, 1H, C*H*-CH-N, *major*), 3.20 (d, *J* = 11.3 Hz, 1H, CH_2-N, *minor*), 2.73 (dd, *J* = 10.8, 2.7 Hz, 1H, C*H*-CH-N, *minor*), 2.69 – 2.64 (m, 1H, *i*-PrCH, *minor*), 2.63 – 2.57 (m, 1H, CH_2, *minor*), 2.50 (dd, *J* = 12.4, 7.9 Hz, 1H, CH_2, *minor*), 2.46 – 2.32 (m, 1H, CH_2, *minor*), 2.27 – 2.21 (m, 1H, CH_2, *major*), 2.13 (dt, *J* = 17.4, 5.8 Hz, 1H, CH_2, *major*), 2.05 – 1.96 (m, 2H, *i*-PrCH and CH_2, *major*), 1.81 – 1.71 (m, CH_2, *minor*), 1.63 – 1.58 (m, 1H, CH_2, *major*), 1.29 – 1.25 (m, 3H, $EtCH_3$, *major* and *minor*), 1.08 (d, *J* = 7.6 Hz, 3H, *i*-$PrCH_3$, *minor*), 1.06 (d, *J* = 7.0 Hz, 3H, *i*-$PrCH_3$, *major*), 0.88 (d, *J* = 6.7 Hz, 3H, *i*-$PrCH_3$, *major*), 0.86 (d, *J* = 6.8 Hz, 3H, *i*-$PrCH_3$, *minor*) ppm. **^{13}C NMR** (100 MHz, $CDCl_3$): δ 174.0 (QC, CO, *major*), 172.3 (QC, CO, *minor*), 159.1 (QC, ArC, *major*), 159.0 (QC, ArC, *minor*), 149.5 (QC, NsC, *major* and *minor*), 146.0 (QC, NsC, *minor*), 145.0 (QC, NsC, *major*), 136.4 (QC, =C, *minor*), 135.4 (QC, =C, *major*), 133.4 (QC, ArC, *minor*), 132.5 (QC, ArC, *major*), 128.23 (CH, 2×NsCH, *major*), 128.18 (CH, 2×NsCH, *minor*), 126.32 (CH, 2×ArCH, *minor*), 125.8 (CH, 2×ArCH, *major*), 124.1 (CH, 2×NsCH, *major* and *minor*), 122.1 (CH, =CH, *minor*), 122.0 (CH, =CH, *major*), 113.71 (CH, 2×ArCH, *major*), 113.66 (CH, 2×ArCH, *minor*), 72.7 (CH, CH-N, *major*), 67.6 (CH, CH-N, *minor*), 61.5 (CH_2, $EtCH_2$, *major*), 60.7 (CH_2, $EtCH_2$, *minor*), 57.28 (CH_3, OMe, *minor*), 55.3 (CH_3, OMe, *major*), 54.4 (CH_2, CH_2-N, *major*), 52.7 (CH_2, CH_2-N, *minor*), 50.9 (QC, *C*-CO_2Et, *minor*), 50.2 (QC, *C*-CO_2Et, *major*), 46.1 (CH, C*H*-CH-N, *minor*), 42.8 (CH, C*H*-CH-N, *major*), 32.2 (CH, *i*-PrCH, *major*), 30.9 (CH, *i*-PrCH, *minor*), 29.6 (CH_2, CH_2, *minor*), 27.1 (CH_2, CH_2, *major*), 26.1 (CH_2, CH_2, *minor*), 23.5 (CH_2, CH_2, *major*), 19.8 (CH_3, *i*-$PrCH_3$, *major*), 19.3 (CH_3, *i*-$PrCH_3$, *minor*), 17.4 (CH_3, *i*-$PrCH_3$, *major*), 15.2 (CH_3, *i*-$PrCH_3$, *minor*), 14.1 (CH_3, $EtCH_3$, *major*), 14.0 (CH_3, $EtCH_3$, *minor*) ppm. Note: NMR data for the second minor isomer has not been reported.

7. Elucidation of Stereochemistry of Isoindoline Scaffold 5:

2-Step reduction and *O*-tosylation of isoindoline 5a to 5b:



5a
(*major*)
10:3:1 *dr*

5b
(*major*)
single isomer

To an oven-dried Schlenk flask was added $LiAlH_4$ (6.1 mg, 0.16 mmol, 2.0 equiv.) and the vessel cooled to 0 °C, before THF (1 mL) was added. To the resulting solution was added the isoindoline **5b** (35.3 mg, 66.8 µmol, 1.0 equiv.) in THF (0.5 mL) dropwise with stirring and the reaction mixture warmed to room temperature. The reaction was stirred overnight, after which a Fieser workup was employed in which the reaction was diluted with Et_2O and quenched by adding water (1 drop), followed by an aqueous 15 % wt. solution of NaOH (1 drop), then further water (3 drops). $MgSO_4$ was then added and the mixture was stirred before filtration of the resulting white solid. The filtrate was washed with brine and extracted with EtOAc before being dried with $MgSO_4$ and concentrated *in vacuo*. The crude residue was subjected to column chromatography (EtOAc/hexane, 60:40, pre-washed with Et_3N) to give the alcohol as a yellow solid (Rf = 0.49, EtOAc/hexane, 60:40, 10.6 mg, 21.8 µmol, 33%). The alcohol was dissolved in CH_2Cl_2 (0.75 mL) in an oven-dried reaction vial and a molar excess of pyridine (0.1 mL) added. Tosyl chloride (14.2 mg, 74.5 µmol, 3.0 equiv.) was then added and the mixture stirred at room temperature. After 18 hours, the reaction was diluted with CH_2Cl_2 and washed with an aqueous 10% wt. solution of $CuSO_4$, then water. The organic layer was dried with $MgSO_4$, filtered and the filtrate concentrated *in vacuo* to give the crude product, which was subjected to column chromatography (CH_2Cl_2/hexane, 40:60), through which the major isomer of the *O*-tosyl derivative **5b** was able to be isolated as a yellow solid (3.1 mg, 4.8 µmol, 22%). **HRMS-ESI** (*m*/*z*): $[M+Na]^+$ calcd for $C_{32}H_{36}N_2O_8S_2Na$, 663.1805; found, 663.1808. **^{1}H NMR** (400 MHz, $(CD_3)_2CO$): δ 8.41 (d, *J* = 8.9 Hz, 2H, NsCH), 8.15 (d, *J* = 8.8 Hz, 2H, NsCH), 7.81 (d, *J* = 8.4 Hz, 2H, TsCH), 7.47 (d, *J* = 8.0 Hz, 2H, TsCH), 7.18 (d, *J* = 8.9 Hz, 2H, ArCH), 6.85 (d, *J* = 8.9 Hz, 2H, ArCH), 5.73 (d, *J* = 5.1 Hz, 1H, =CH), 3.99 (app. q, *J* = 10.1 Hz, 2H, CH_2-OTs), 3.78 (s, 3H, OMe), 3.63 (dd, *J* = 7.4, 4.8 Hz, 1H, CH-N), 3.56 (d, *J* = 11.3 Hz, 1H, CH_2-N), 3.35 (d, *J* = 11.3 Hz, 1H, CH_2-N), 2.54 (app. t, *J* = 6.3 Hz, 1H, C*H*-CHN), 2.44 (s, 3H, $TsCH_3$), 2.39 – 2.31 (m, 1H, *i*-PrCH), 2.13 – 1.92 (m, 2H, CH_2), 1.62 – 1.57 (m, 1H, CH_2), 1.20 – 1.12 (m, 1H, CH_2), 0.99 (d, *J* = 7.1 Hz, 3H, *i*-PrCH_3), 0.82 (d, *J* = 6.7 Hz, 3H, *i*-PrCH_3) ppm.

Analysis of 1D NOE spectra and supporting evidence from computational data:

The 1D NOE spectra of **5b** revealed strong correlations between the CH_2-OTs protons 'f' (see pp. 25 – 26) and the bridgehead proton 'b', indicating that these were positioned on the same face of the molecule. Two possible isomers **5b** and **5b'** (Figure S1C) were therefore possible, depending on the relationship (*cis* or *trans*) between the protons 'a' and 'b'. The 1D NOE spectra implied that this was a *trans* relationship (i.e. **5b**) due to the significant correlation between proton 'b' and the *i*-PrCH_3 protons, as well as a comparitavely weak correlation between protons 'a' and 'b'. In order to justify this inference, both **5b** and **5b'** were modelled computationally to compare the interproton distances for each isomer and relate this to the observed NOE signals. An exhaustive conformational sampling of compounds **5b** and **5b'** was carried out with the MMFF force field and RDkit as implemented in the script *genConf.py*.[4,5] Both the energy-based (< 5.0 kcal/mol) and root-mean-square deviation (RMSD)-based (> 0.5 Å) cleaning were applied. Only those conformers, which differed from the others by more than 0.5 Å RMSD and had an energy less than 5 kcal/mol higher than the lowest energy, were kept for further analyses. In total, 52 and 108 conformers were generated for **5b** and **5b'**, respectively. Those conformers were subjected to geometry optimization in the gas phase with B3LYP/6-31G(d) and the optimized structures were verified with vibrational frequency calculations.[6] The lowest energy conformers are shown in Figure S1A.

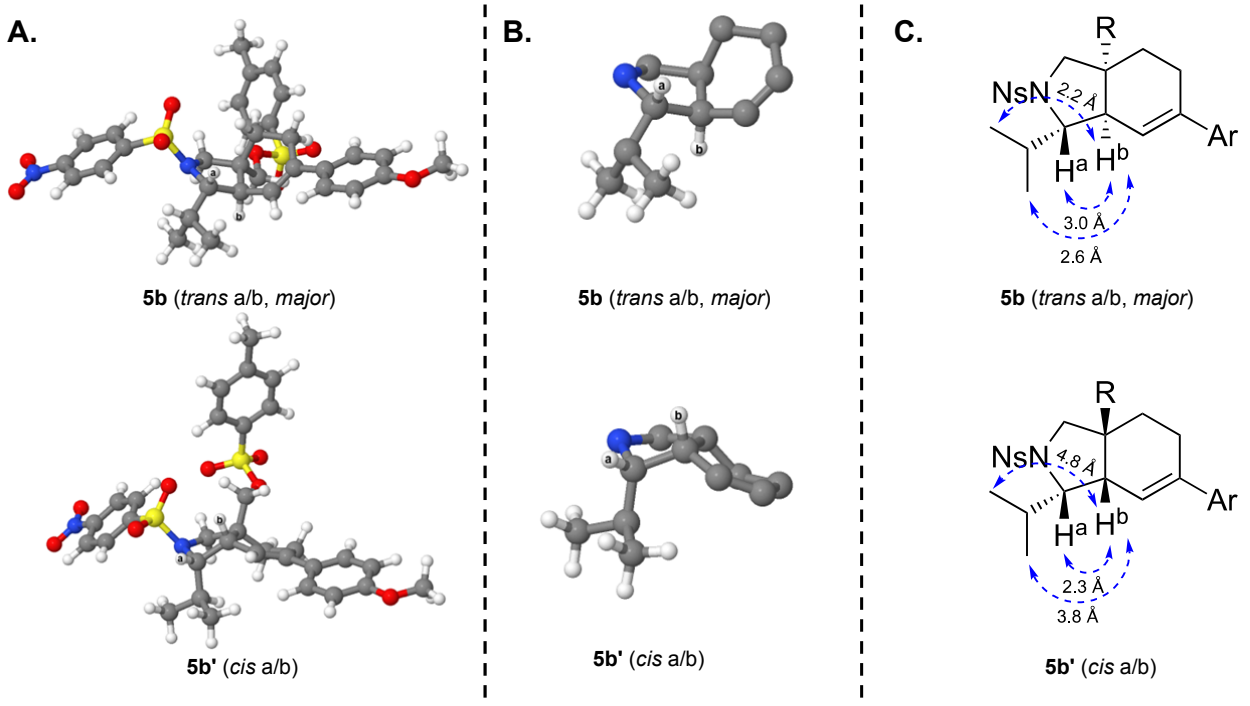
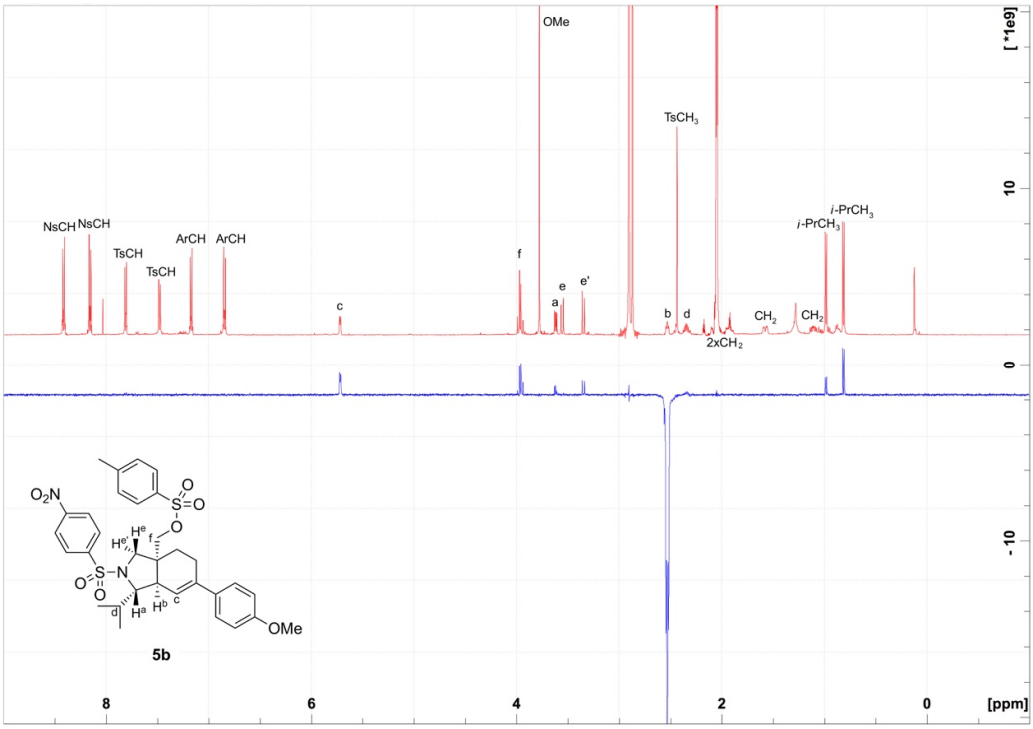


Figure S1. A. Lowest energy conformers of **5b** and **5b'**. **B.** Lowest energy conformers of **5b** and **5b'** showing only isoindoline core and key protons. **C.** Key interproton distances estimated via density functional theory calculations, where R = CH_2OTs and Ar = *p*-methoxyphenyl.

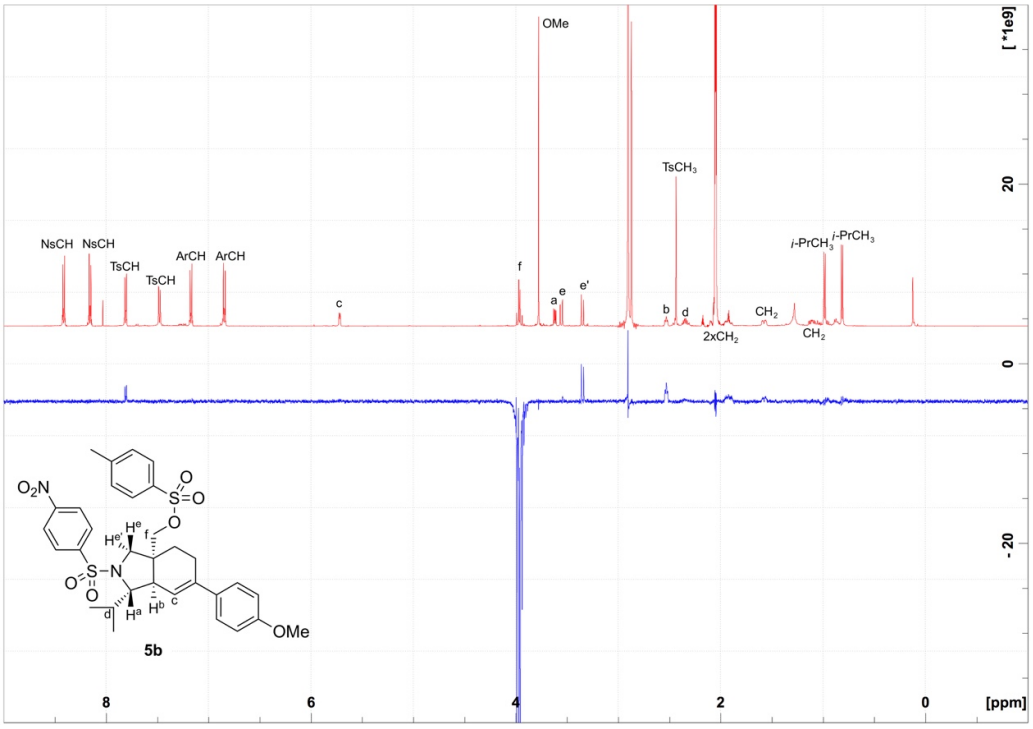
The indicative interproton distances for **5b** and **5b'** were measured from these conformers and revealed that the distance between 'a' and 'b' is 2.3 Å in the *cis* conformation (**5b'**) and 3.0 Å in the *trans* conformation (**5b**). The *trans* conformation better supports the comparatively weak correlation observed in the 1D NOE spectra. The measured interproton distances between 'b' and the *i*-PrCH_3 protons were more conclusive, as the distances of 3.8 Å and 4.8 Å for the *cis* conformation (**5b'**) do not justify the comparatively strong correlations observed in the 1D NOE spectra, where as the distances of 2.2 Å and 2.6 Å in the *trans* conformation (**5b**) do. These results were deemed to justify the signal strengths observed in the 1D NOE spectra, leading to our assignment of the stereochemistry of the derivatized isoindoline system, and therefore the parent scaffold **5a**, to be as per **5b**.

1D NOE Spectra:

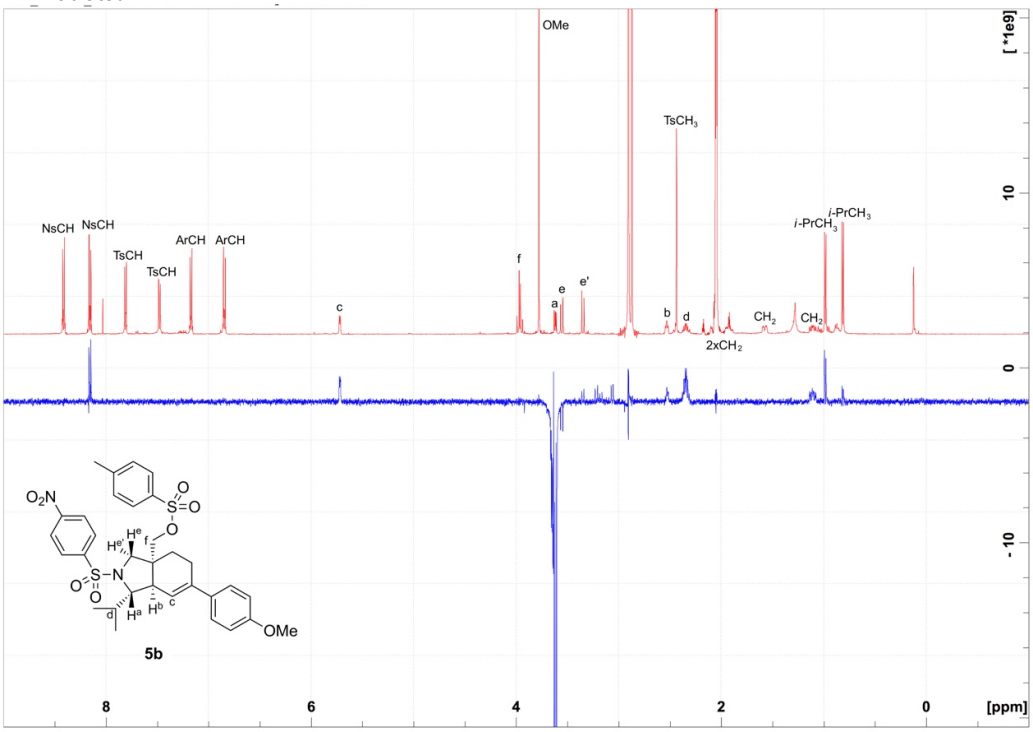
'H^{b}' irradiated:



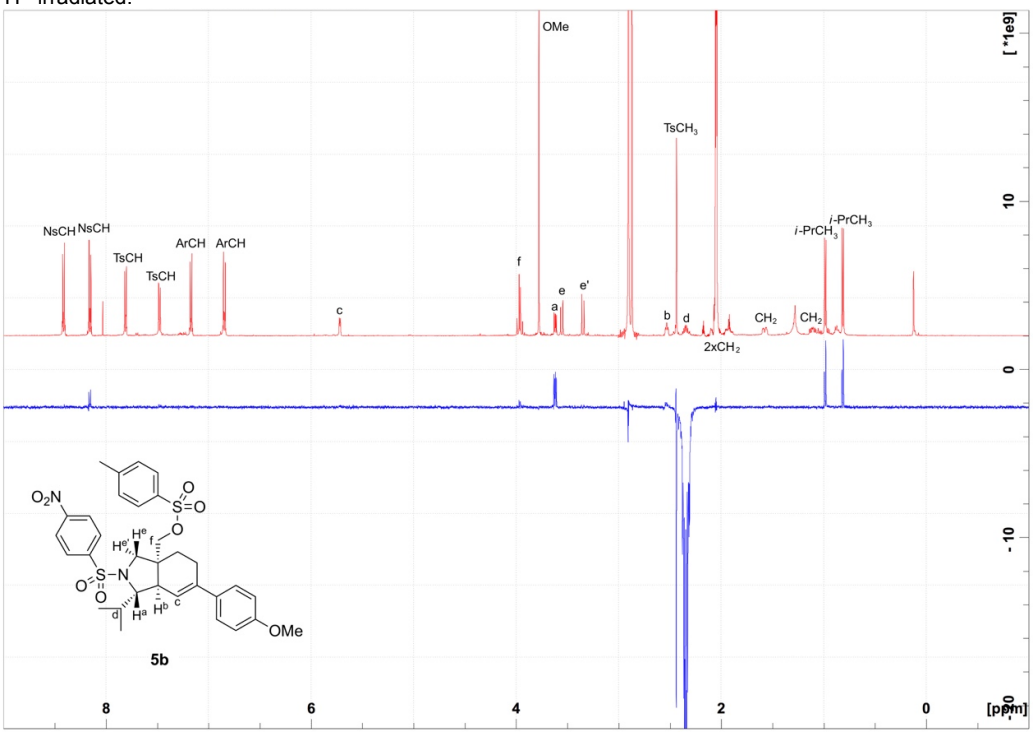
'H^{f}' irradiated:



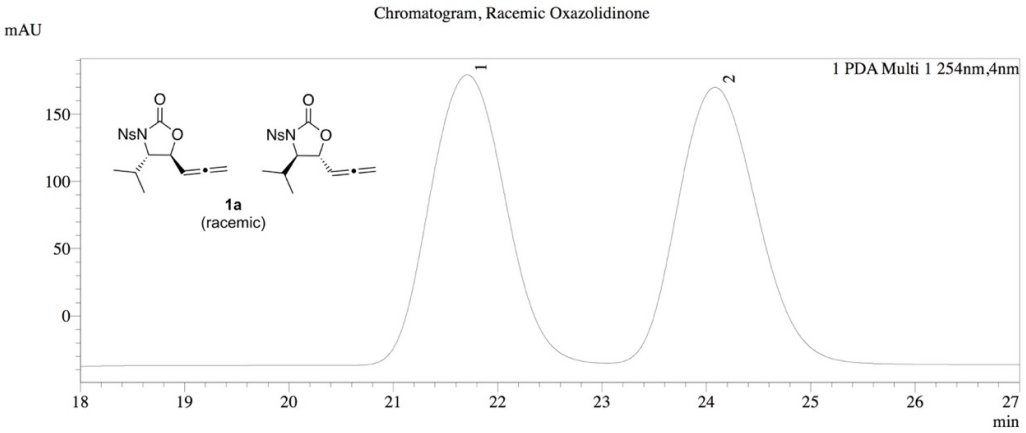
'H^{a}' irradiated:



'H^{d}' irradiated:

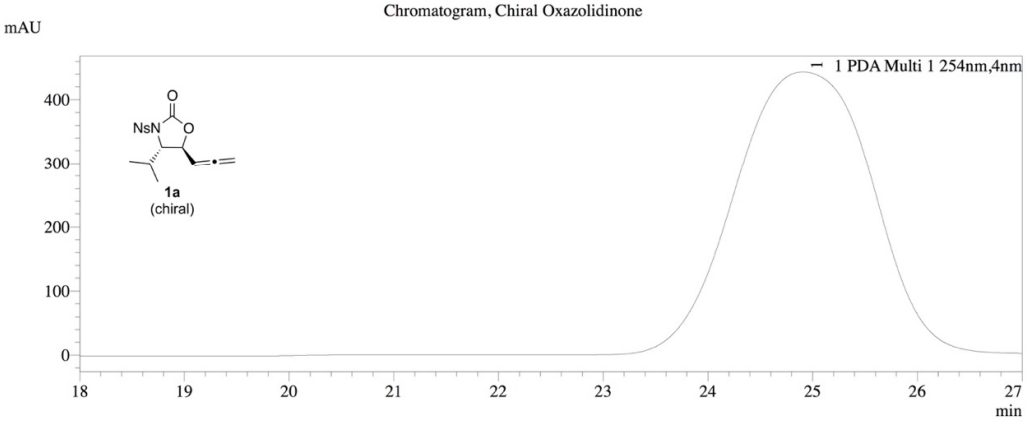


8. Chiral HPLC Data:



Peak Table, Racemic Oxazolidinone
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	21.708	49.897
2	24.083	50.103
Total		100.000

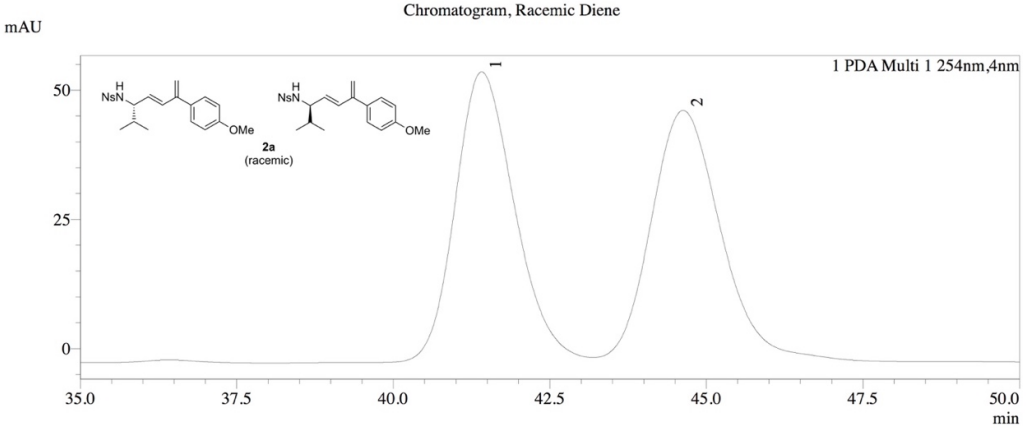


Peak Table, Chiral Oxazolidinone
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	24.908	100.000
Total		100.000

Conditions: Daicel CHIRALPAK IA-U column, hexane/isopropanol (95:5), 0.2 mL/min, 40 °C.

Chromatogram, Racemic Diene

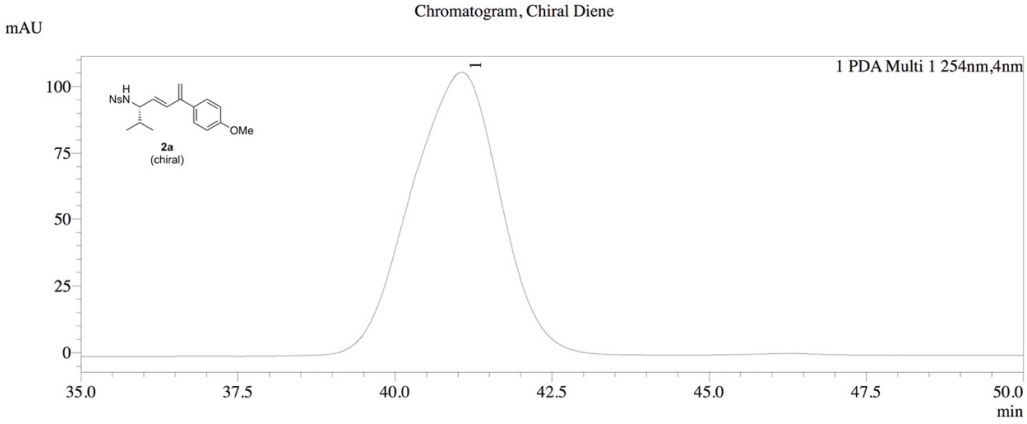


Peak Table, Racemic Diene

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	41.410	49.539
2	44.626	50.461
Total		100.000

Chromatogram, Chiral Diene



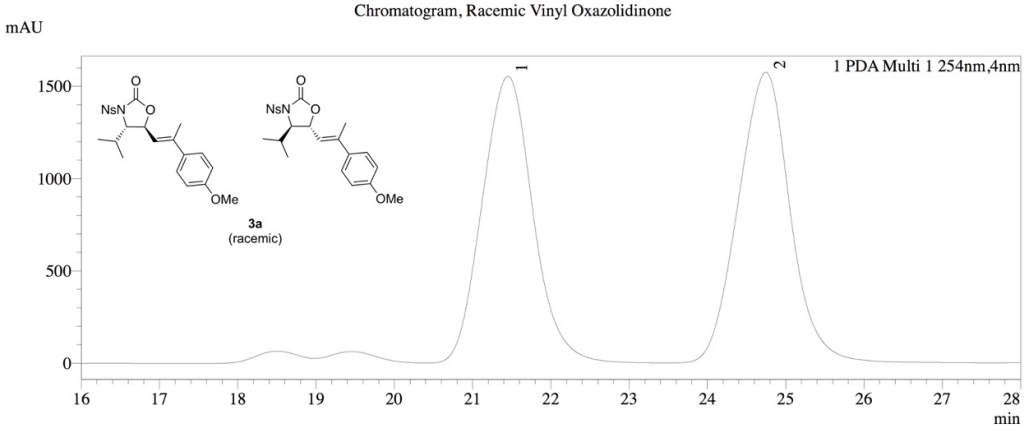
Peak Table, Chiral Diene

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	41.058	100.000
Total		100.000

Conditions: Daicel CHIRALPAK IA-U column, hexane/isopropanol (97:3), 0.2 mL/min, 40 °C.

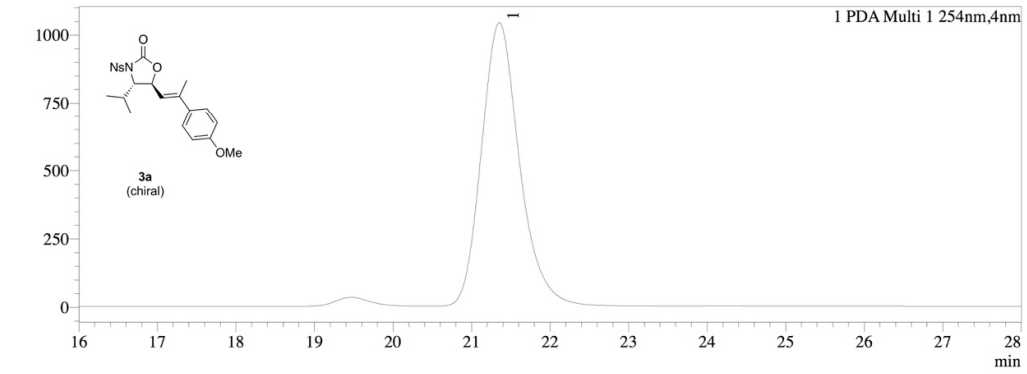
Chromatogram, Racemic Vinyl Oxazolidinone



Peak Table, Racemic Vinyl Oxazolidinone
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	21.452	48.990
2	24.747	51.010
Total		100.000

Chromatogram, Chiral Vinyl Oxazolidinone



Peak Table, Chiral Vinyl Oxazolidinone
PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	21.353	100.000
Total		100.000

Conditions: Daicel CHIRALPAK IA-U column, hexane/isopropanol (90:10), 0.2 mL/min, 40 °C.

9. References:

[1] S. S. Zalesskiy, V. P. Ananikov, *Organometallics* **2012**, *31*, 2302.

[2] F. Zamani, S. G. Pyne, C. J. T. Hyland, *J. Org. Chem.* **2017**, *82*, 6819.

[3] J. Ivkovic, C. Lembacher-Fadum, R. Breinbauer, *Org. Biomol. Chem.* **2015**, *13*, 10456.

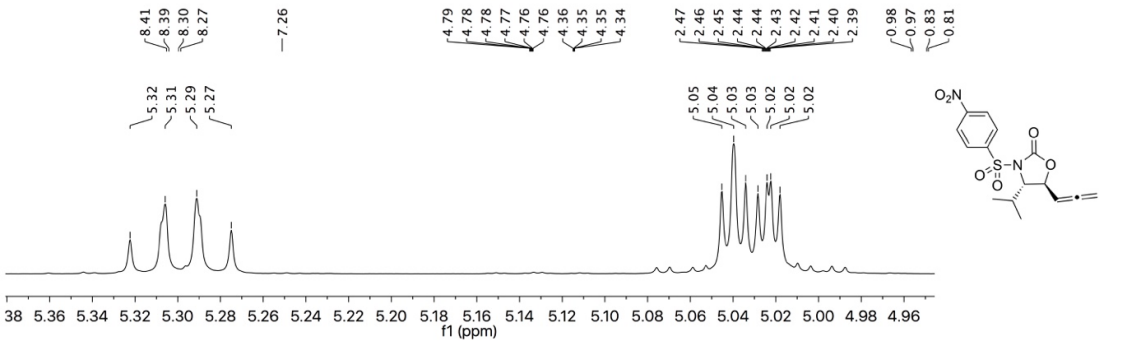
[4] RdKit Conformational Generation Script. Available at: https://www.pharmacelera.com/scripts/rdkit-conformation-generation-script/.

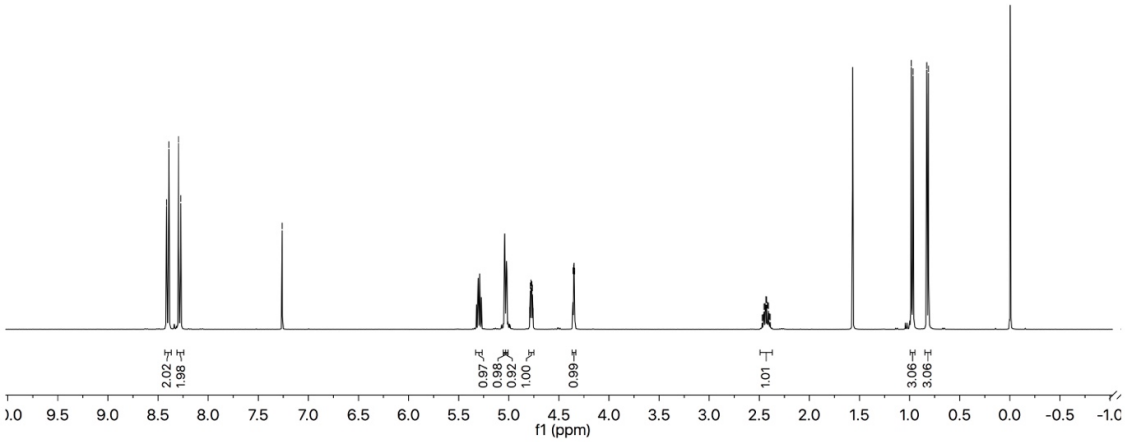
[5] RDKit: Open-source cheminformatics; Available at: http://www.rdkit.org.

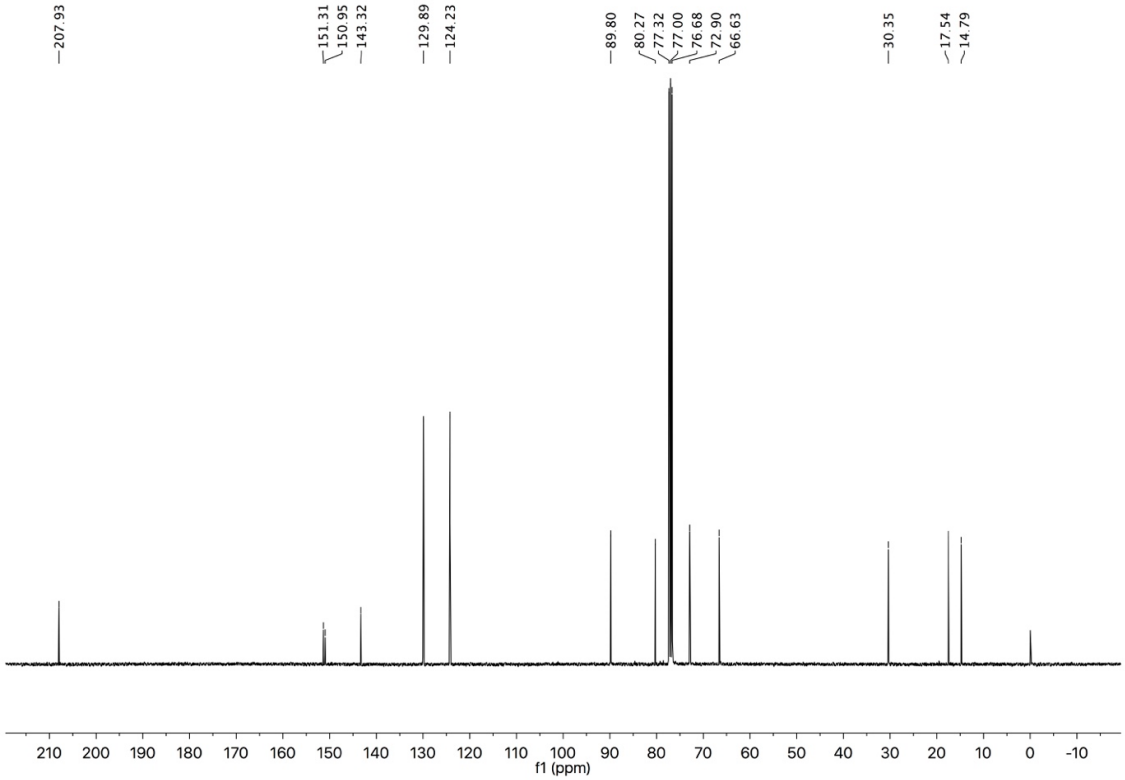
[6] M. J. Frisch *et al.* Gaussian 09 Revision E.01.

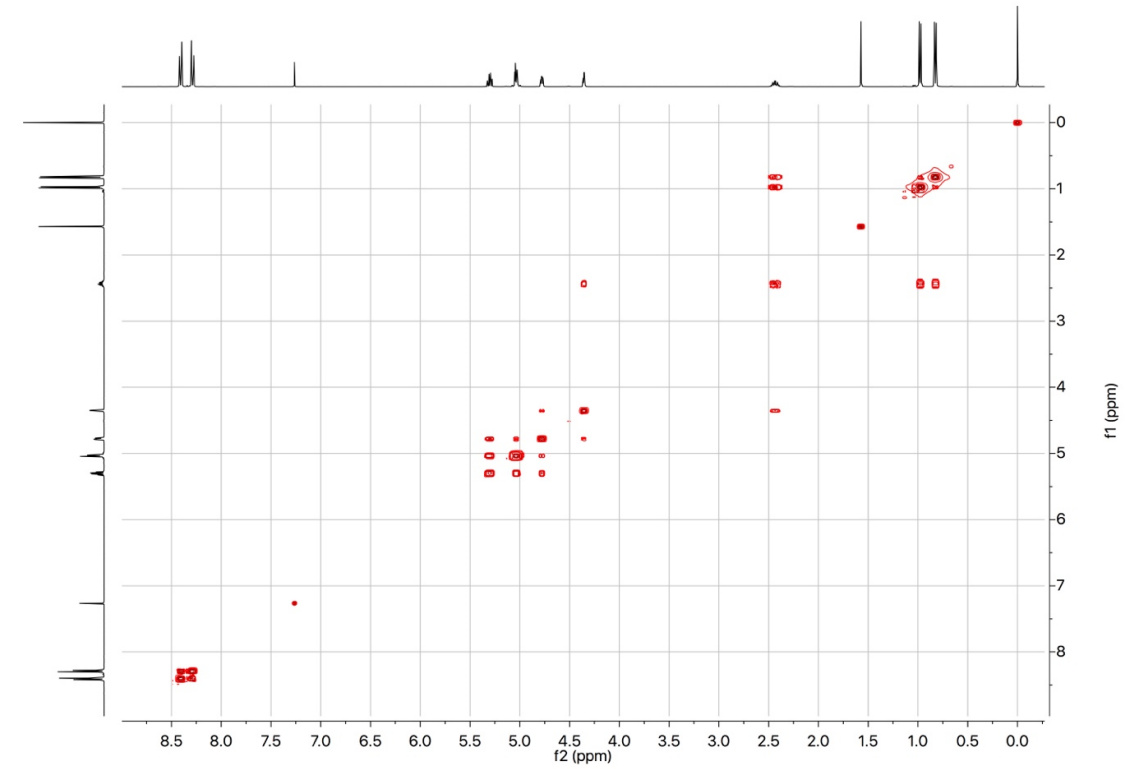
10. NMR Spectra

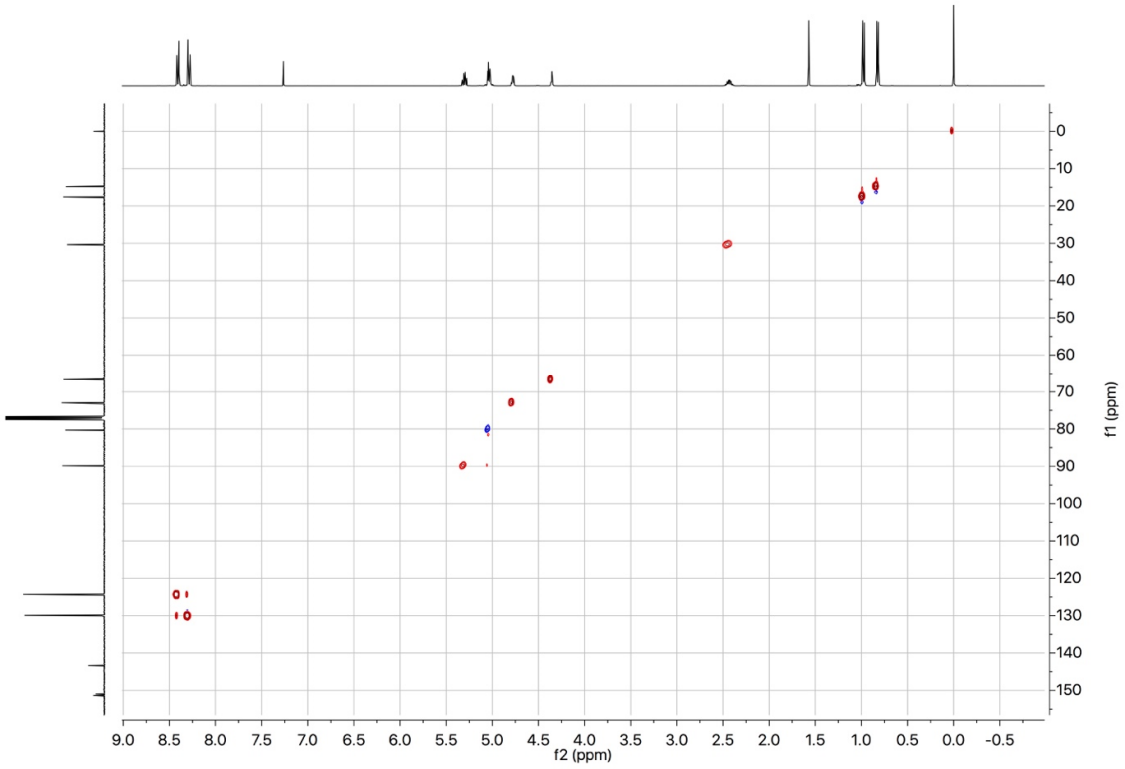
1a

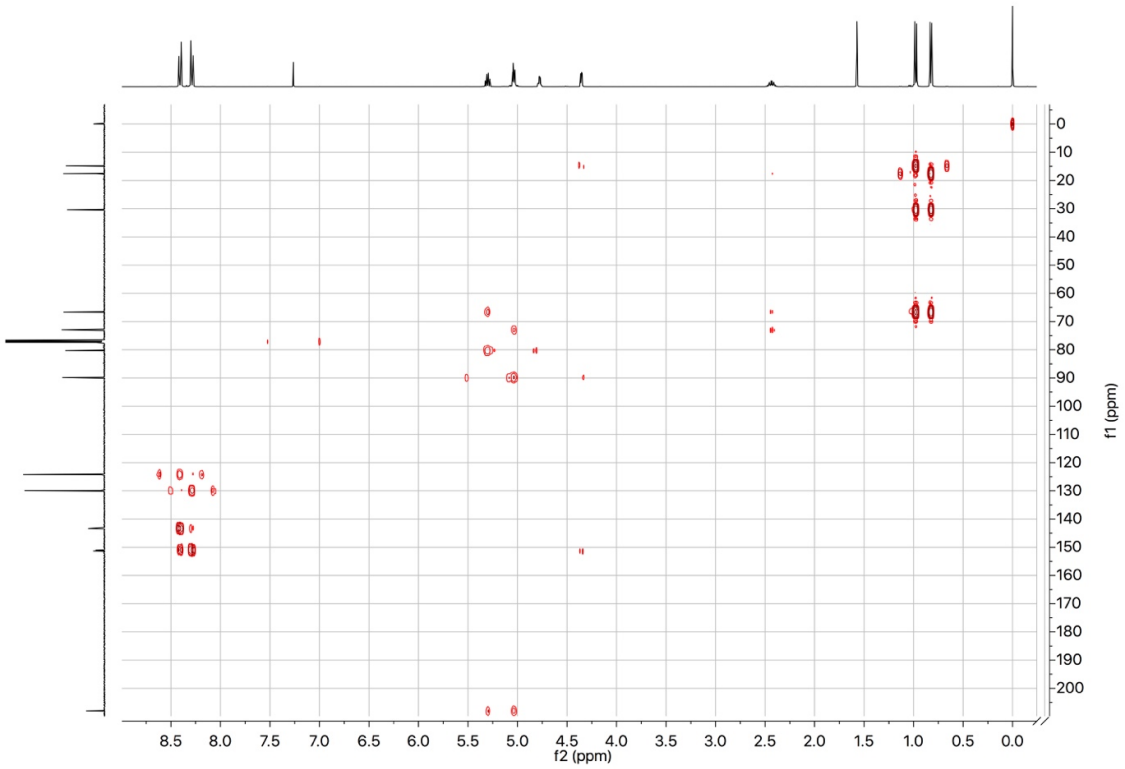




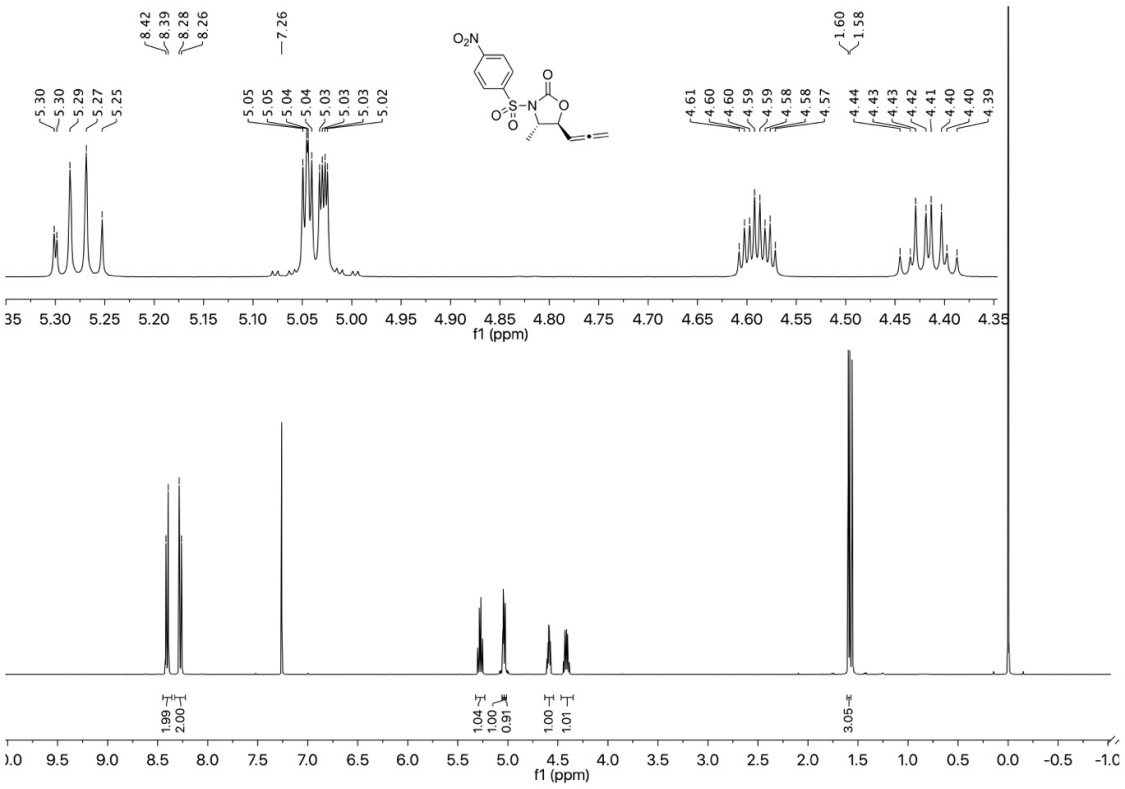


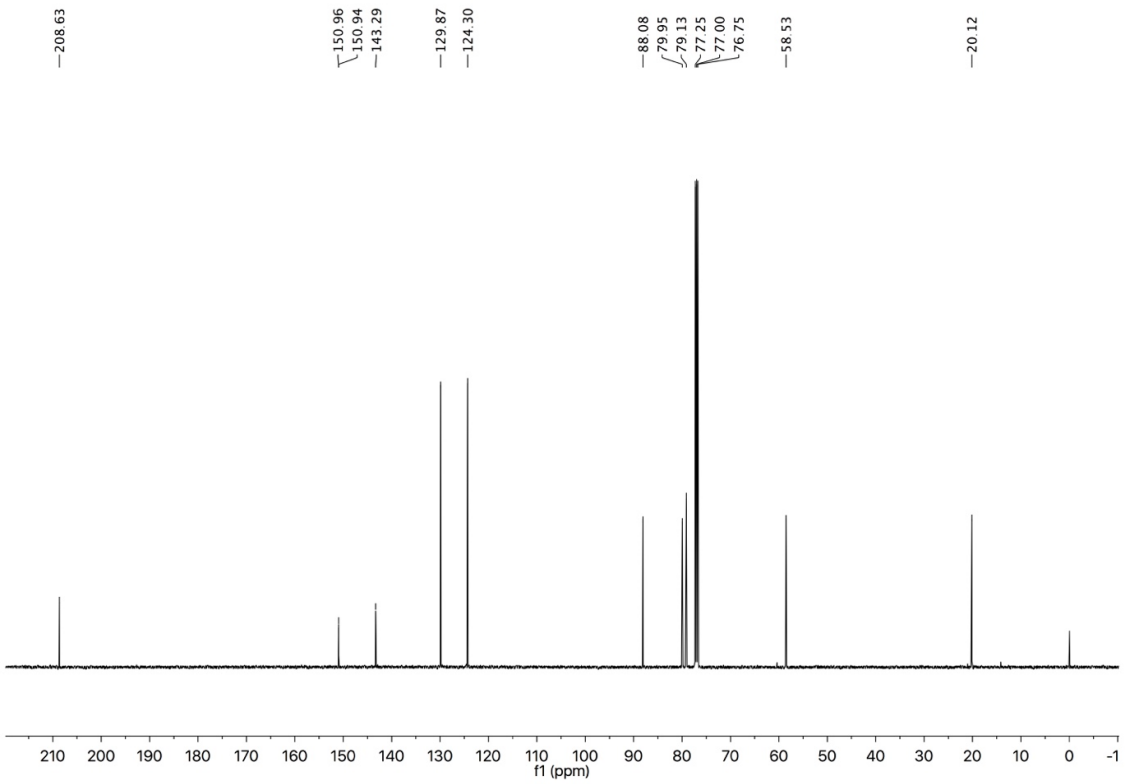

f2 (ppm)
f1 (ppm)

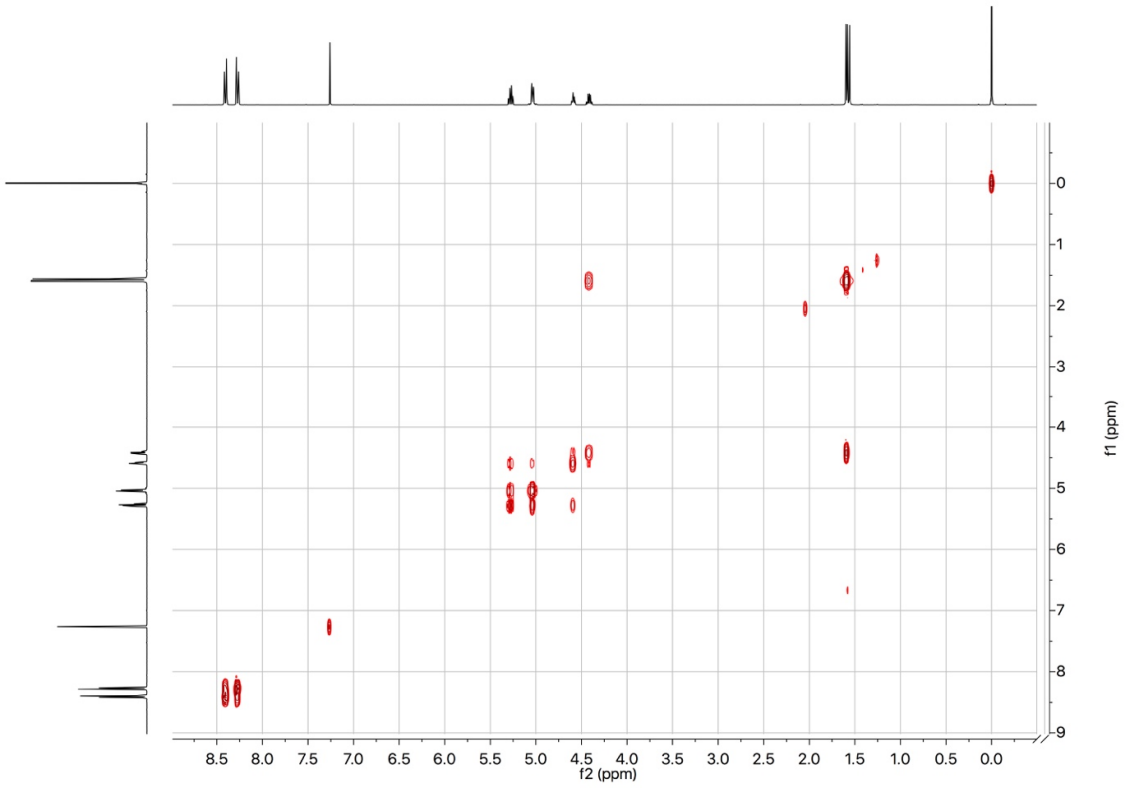

f2 (ppm)
f1 (ppm)

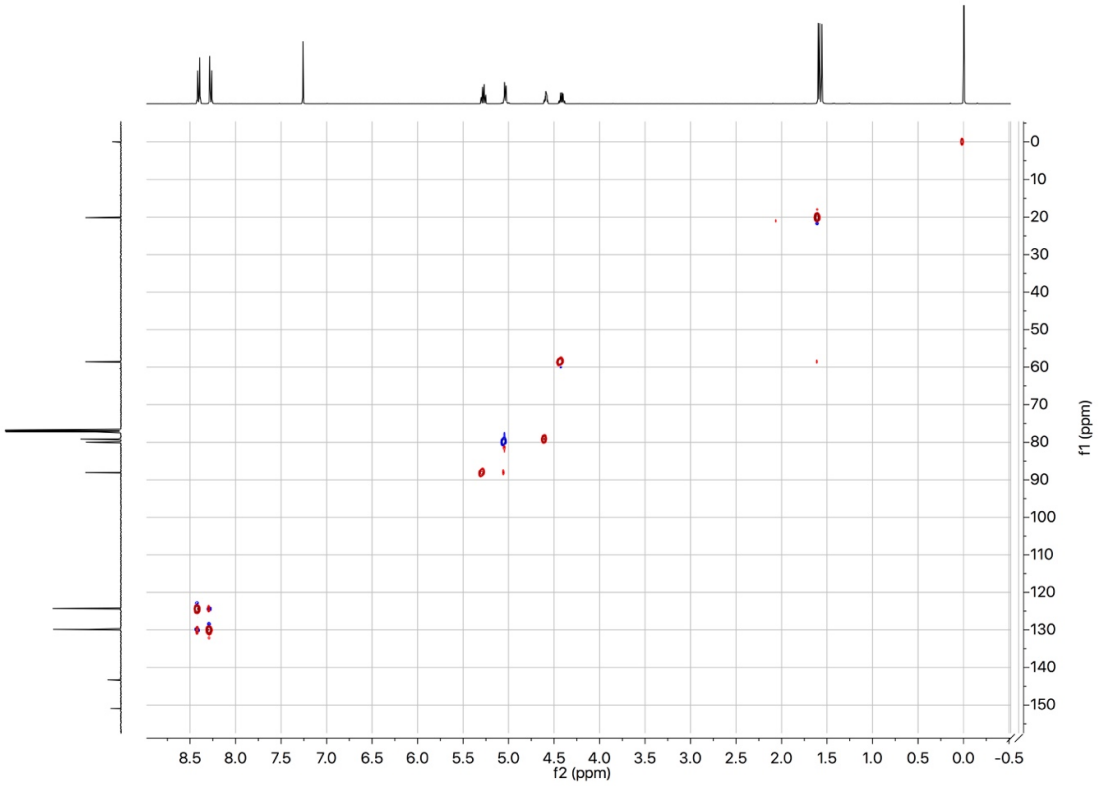


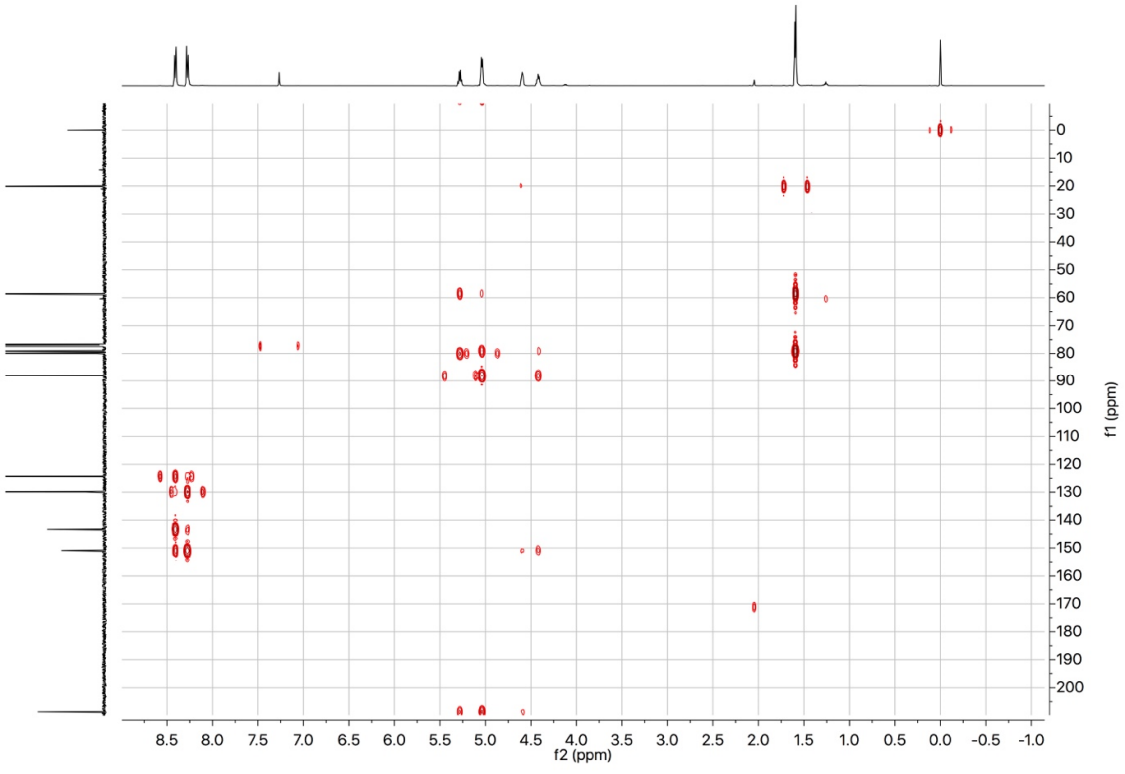
1b



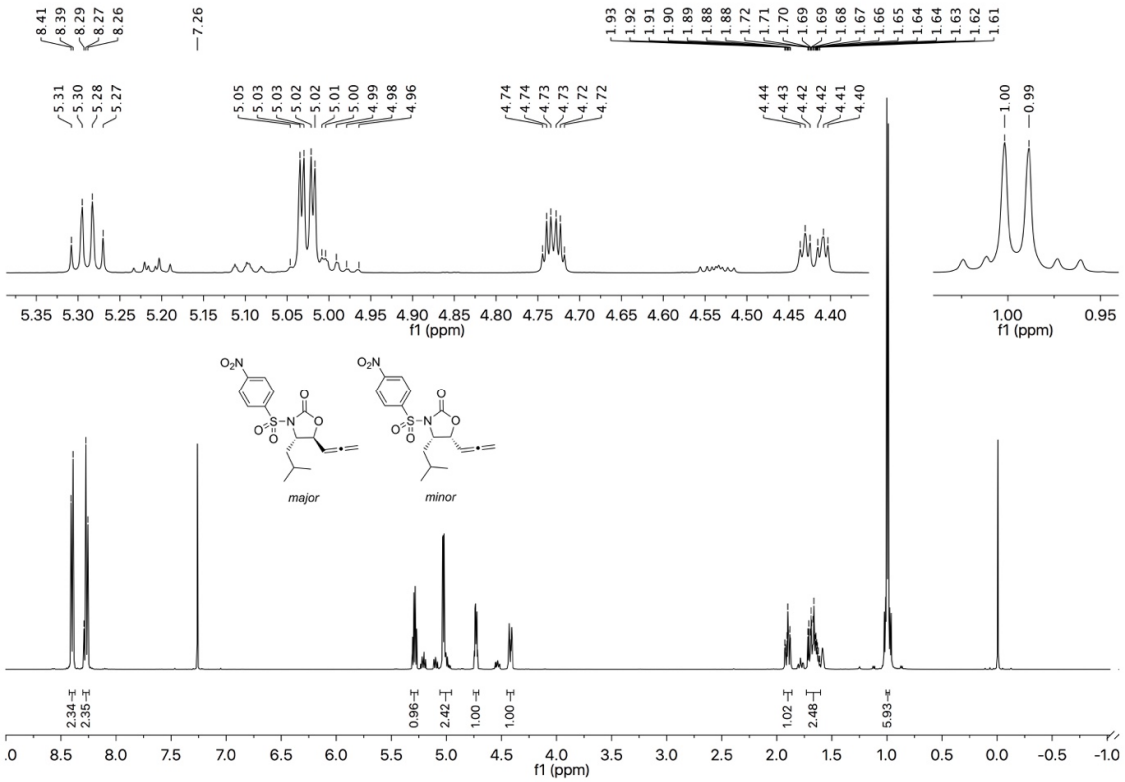

208.63
150.96
150.94
143.29
129.87
124.30
88.08
79.95
79.13
77.25
77.00
76.75
58.53
20.12
f1 (ppm)

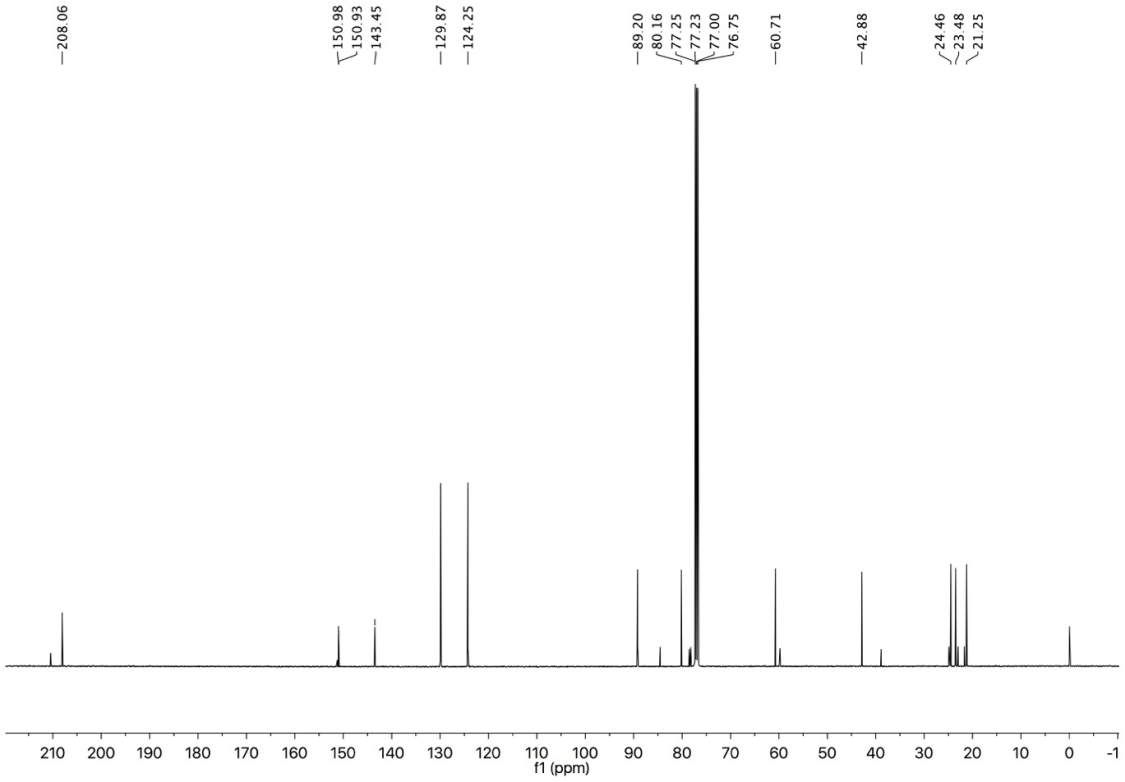

f2 (ppm)
f1 (ppm)

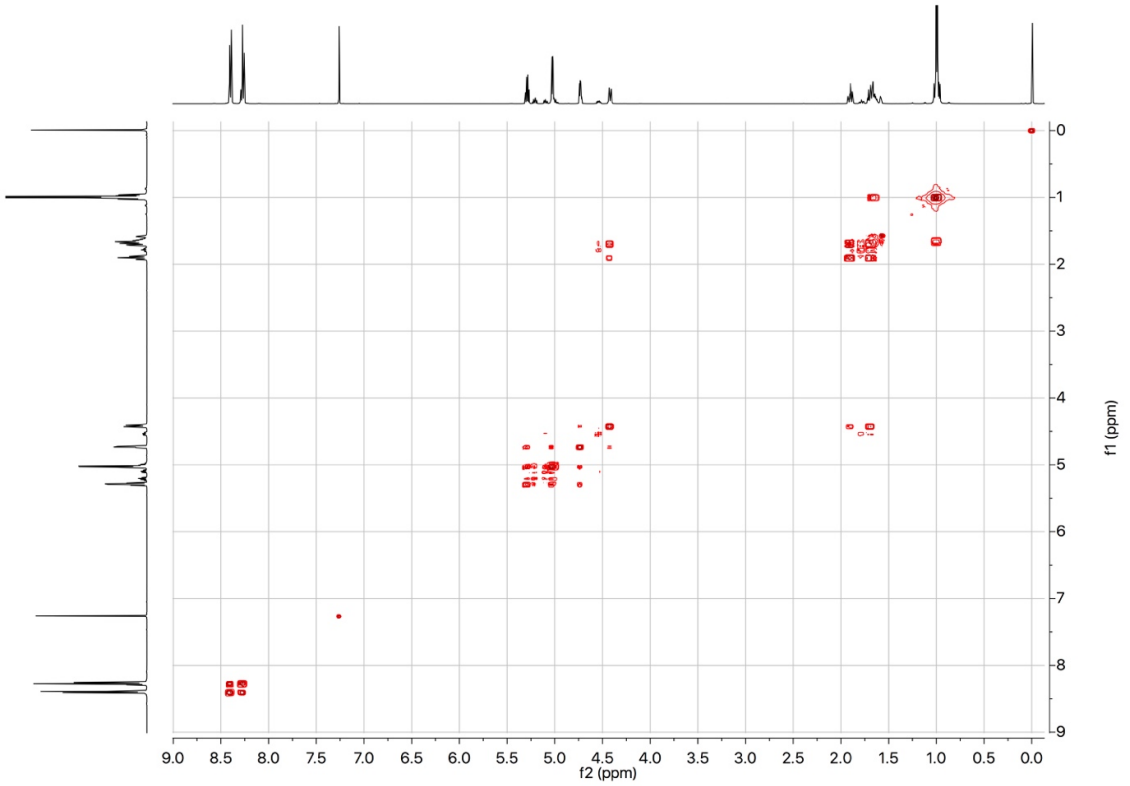

f2 (ppm)
f1 (ppm)

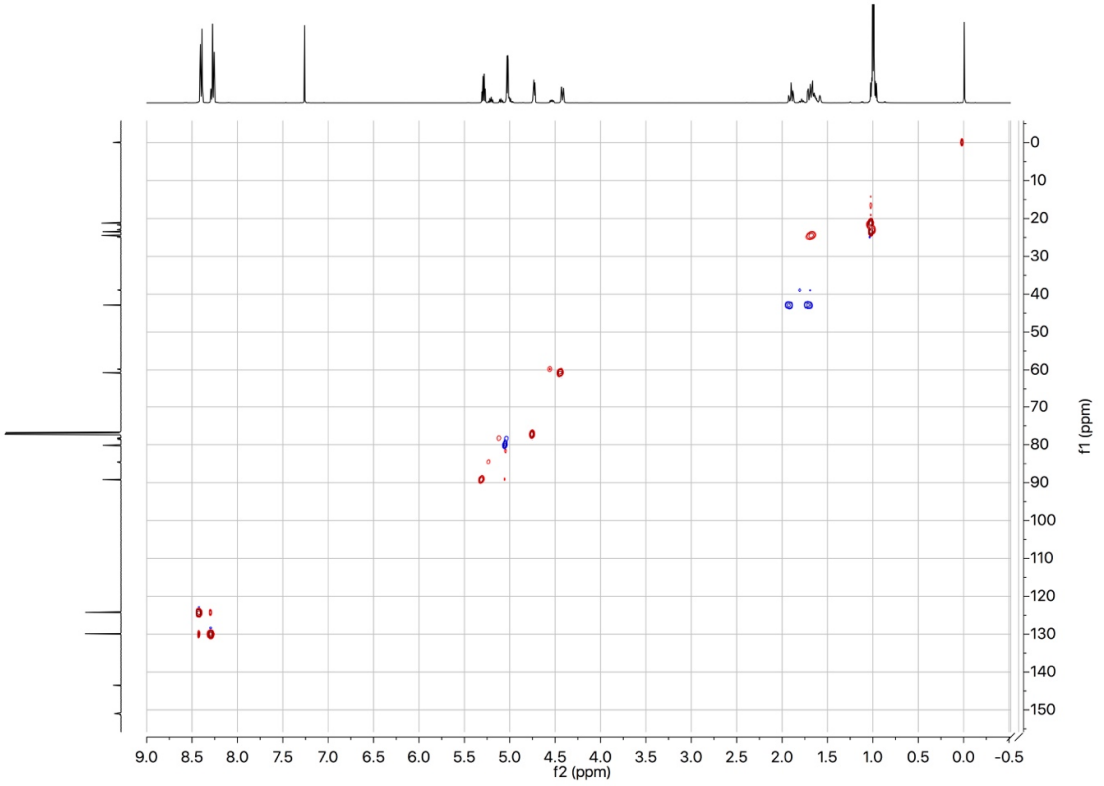

f2 (ppm)
f1 (ppm)

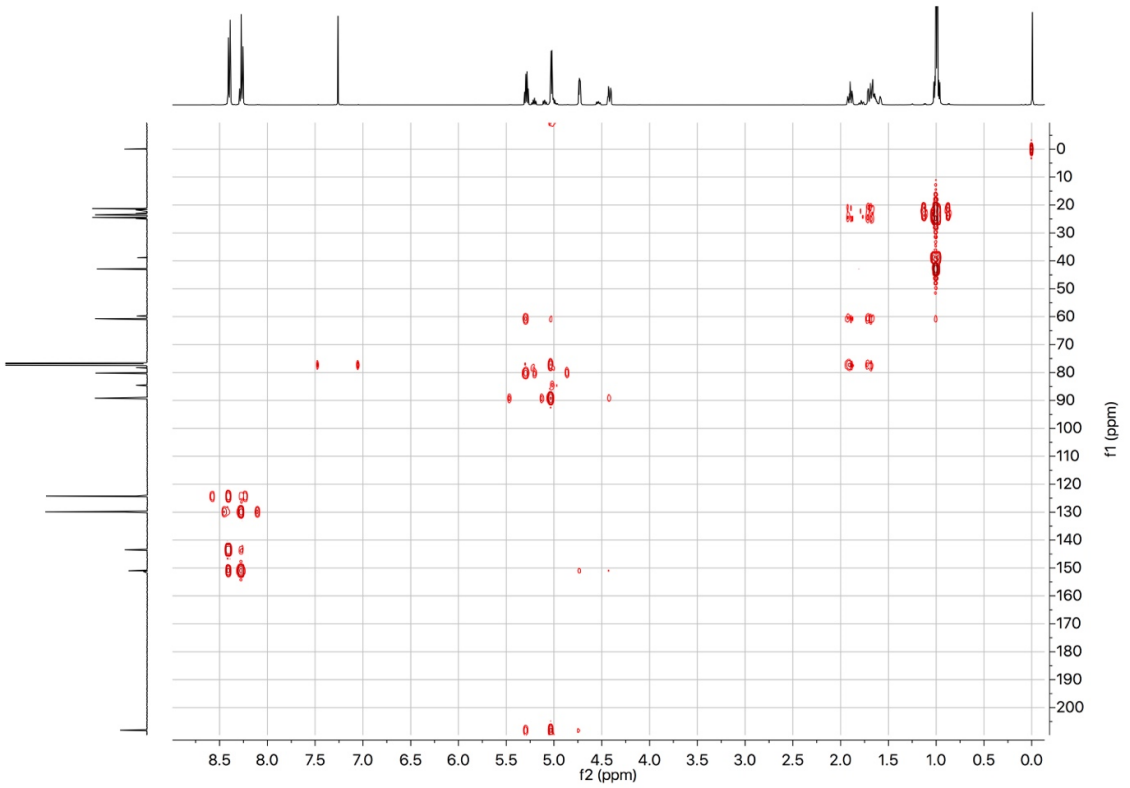
1c



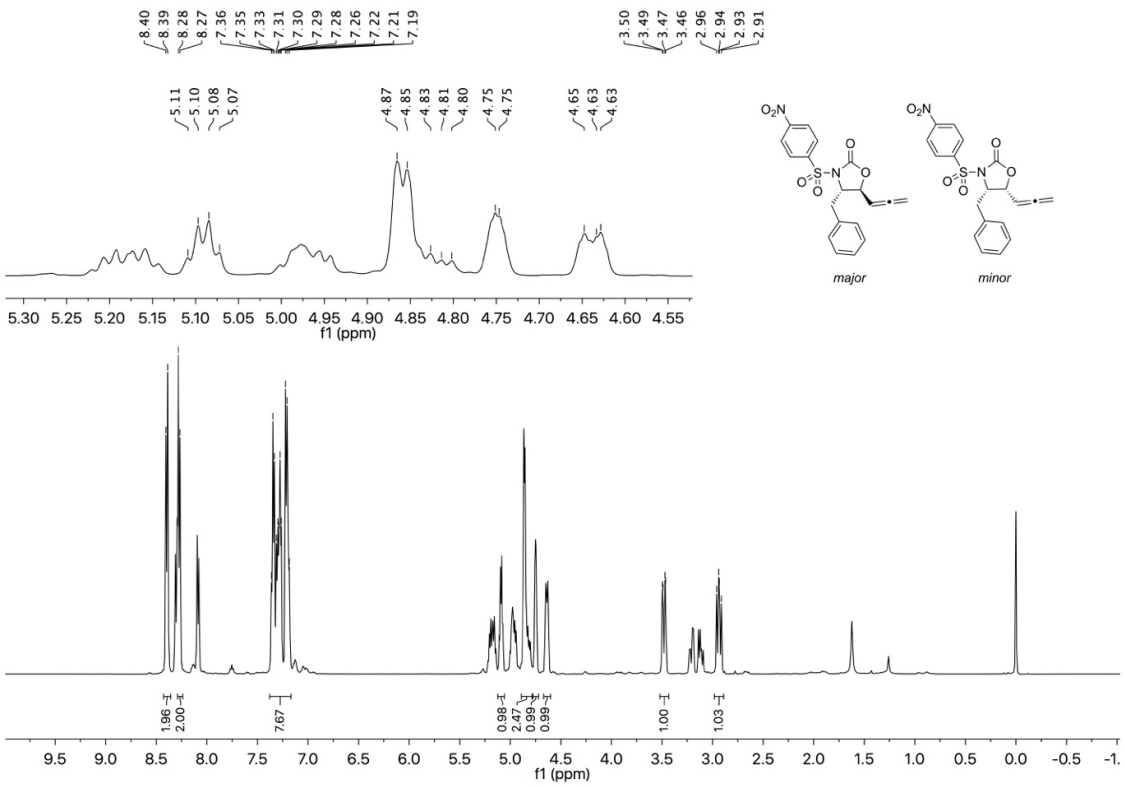


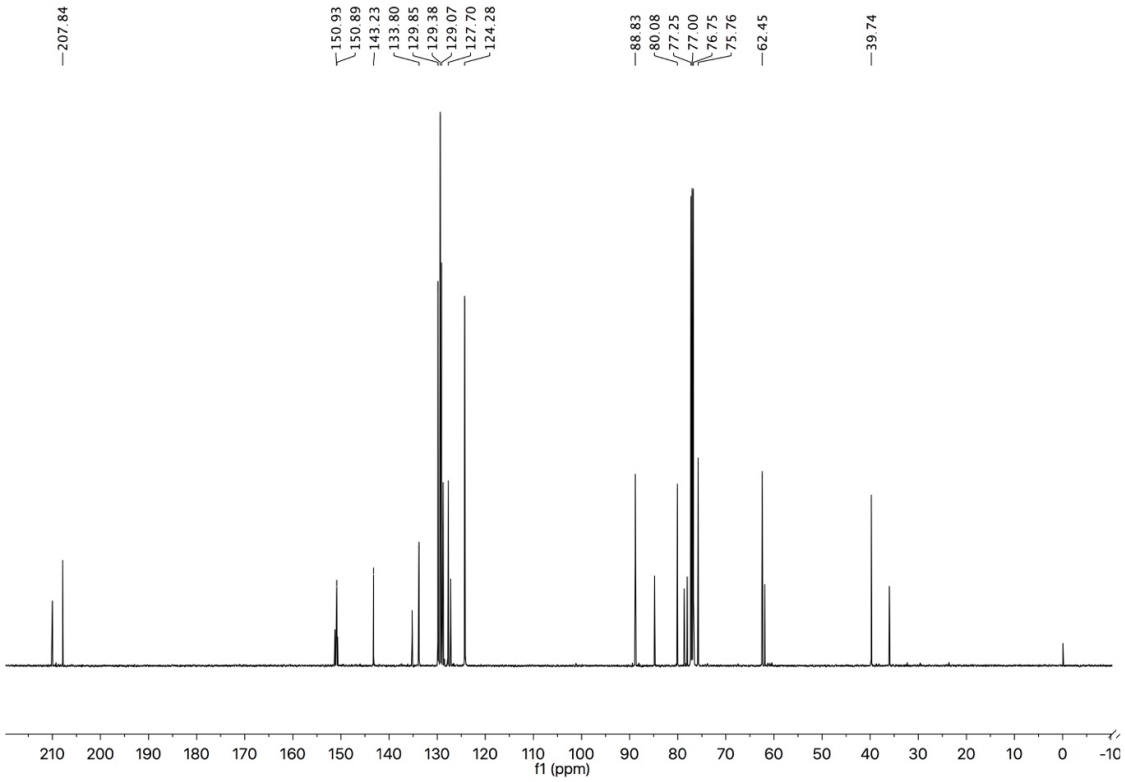

f2 (ppm)
f1 (ppm)

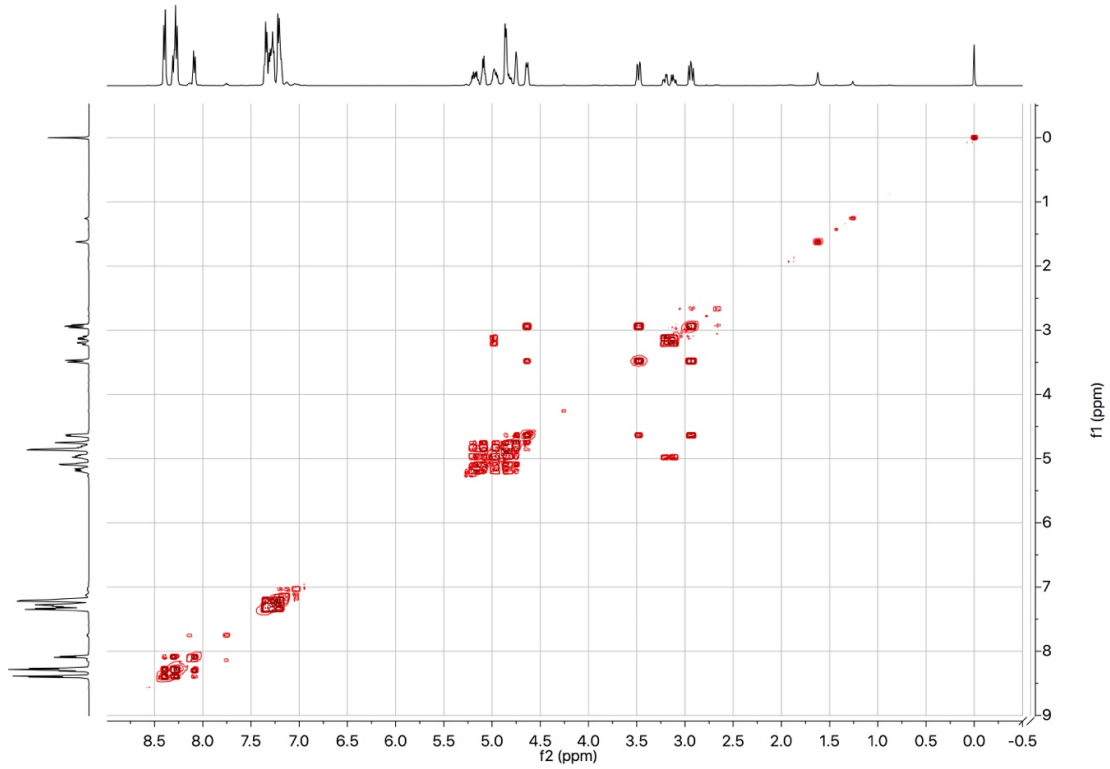

f2 (ppm)
f1 (ppm)

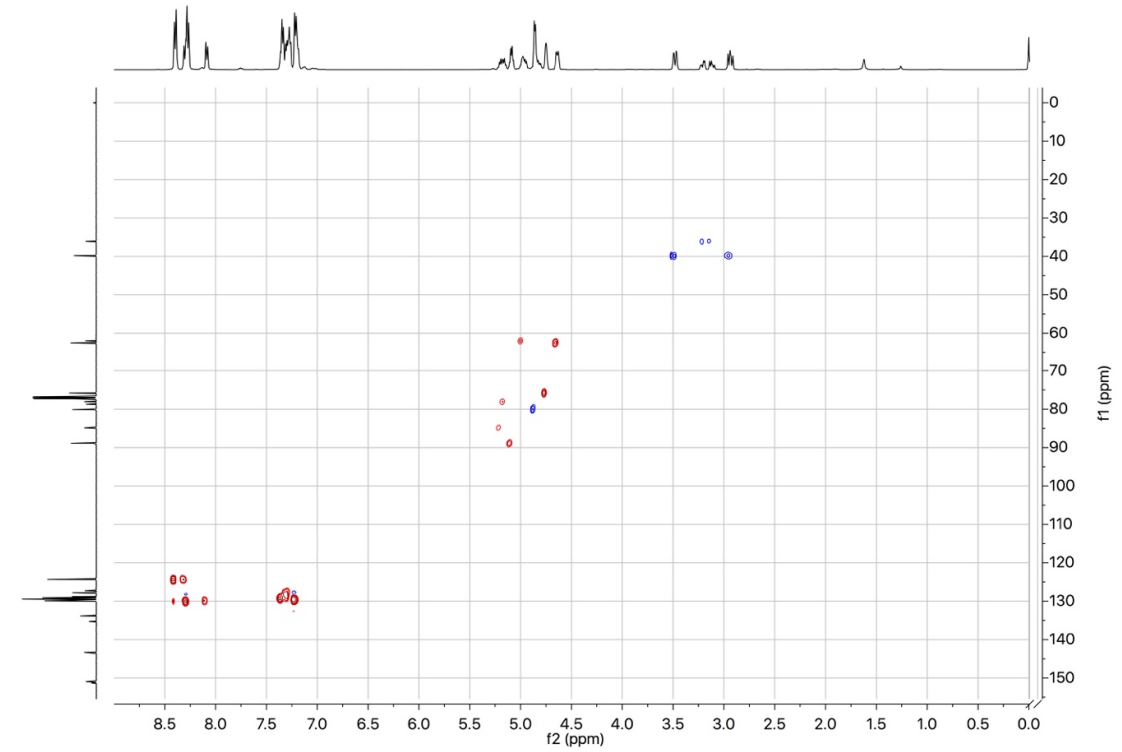

f2 (ppm)
f1 (ppm)

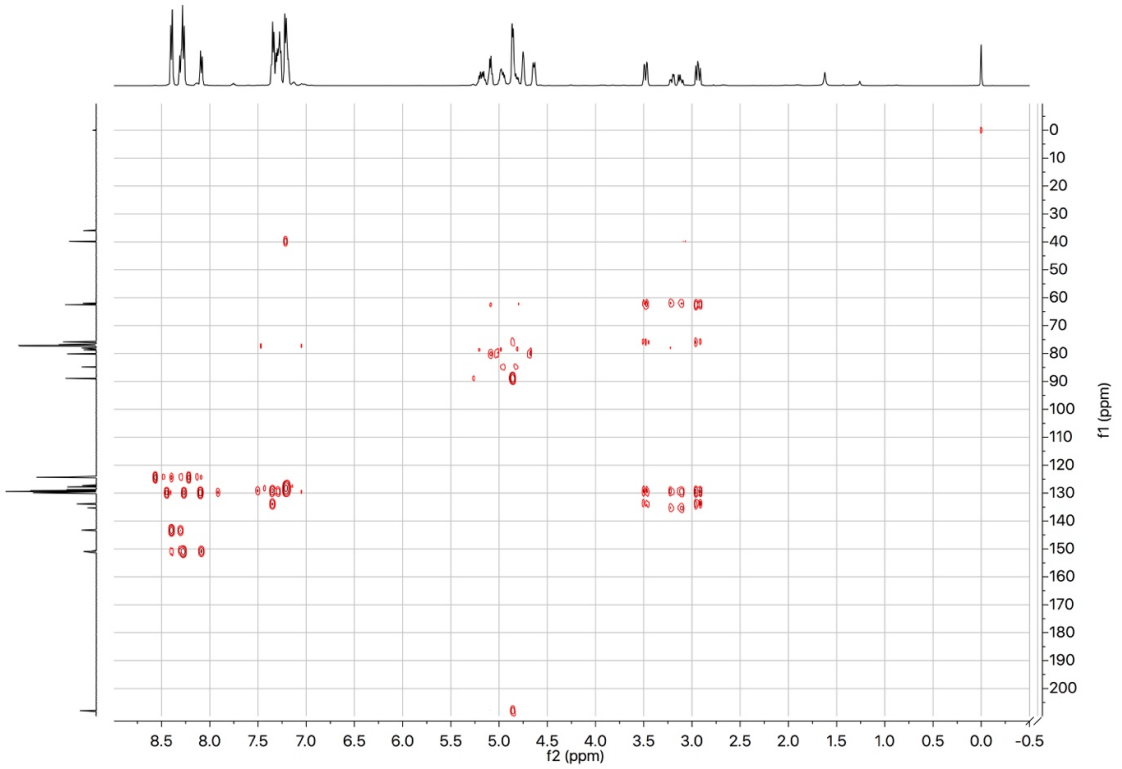
1d


8.40
8.39
8.28
8.27
7.36
7.35
7.33
7.31
7.30
7.29
7.28
7.26
7.22
7.21
7.19
3.50
3.49
3.47
3.46
2.96
2.94
2.93
2.91
5.11
5.10
5.08
5.07
4.87
4.85
4.83
4.81
4.80
4.75
4.75
4.65
4.63
4.63
major
minor
f1 (ppm)
1.96
2.00
7.67
0.98
2.47
0.99
0.99
1.00
1.03
f1 (ppm)

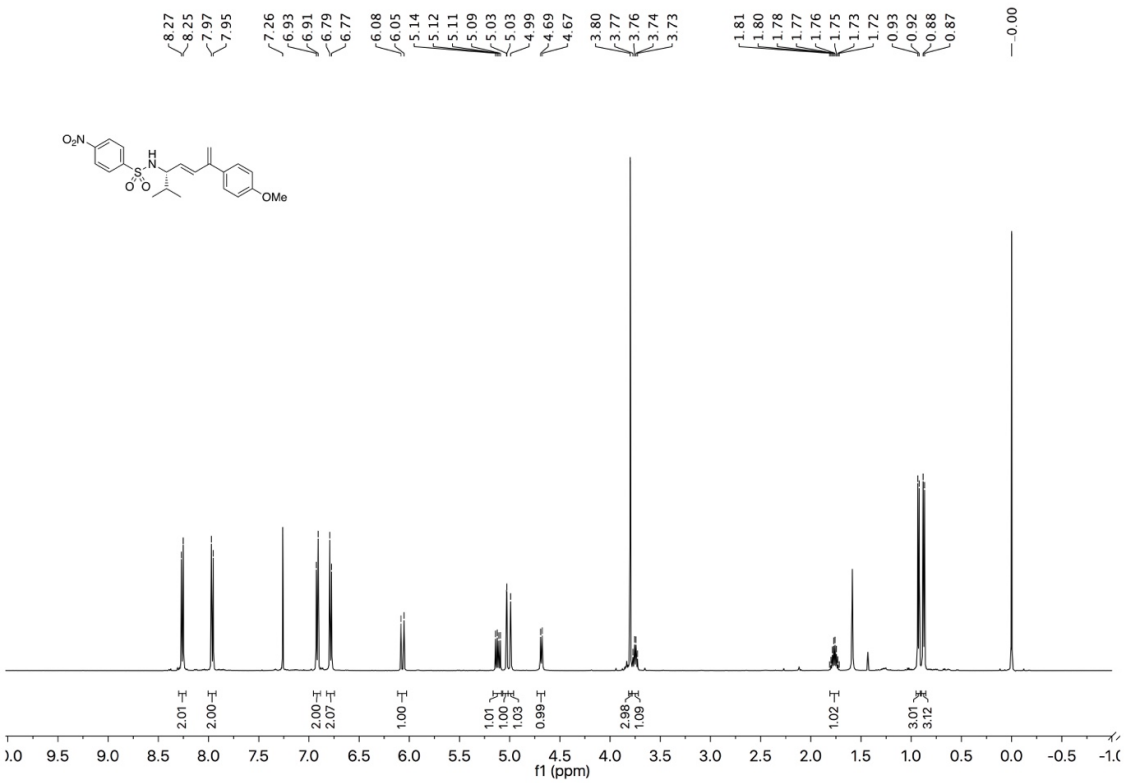

207.84
150.93
150.89
143.23
133.80
129.85
129.38
129.07
127.70
124.28
88.83
80.08
77.25
77.00
76.75
75.76
62.45
39.74
f1 (ppm)

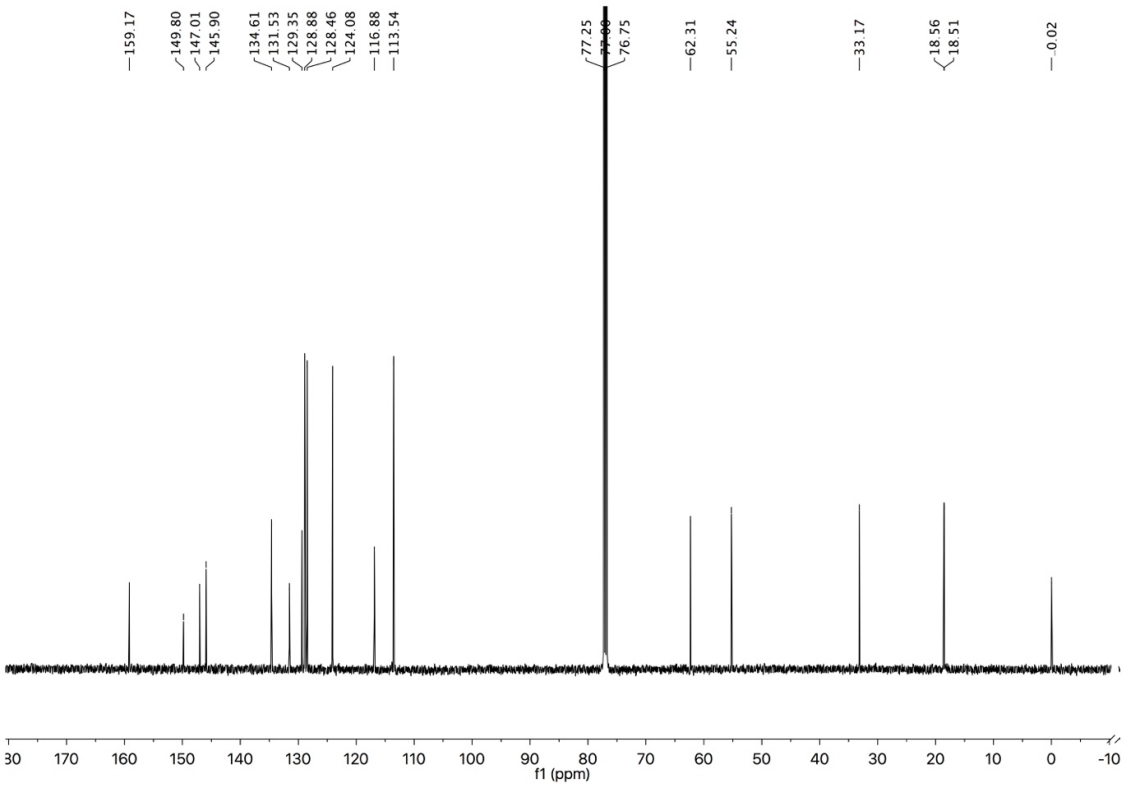

f2 (ppm)
f1 (ppm)

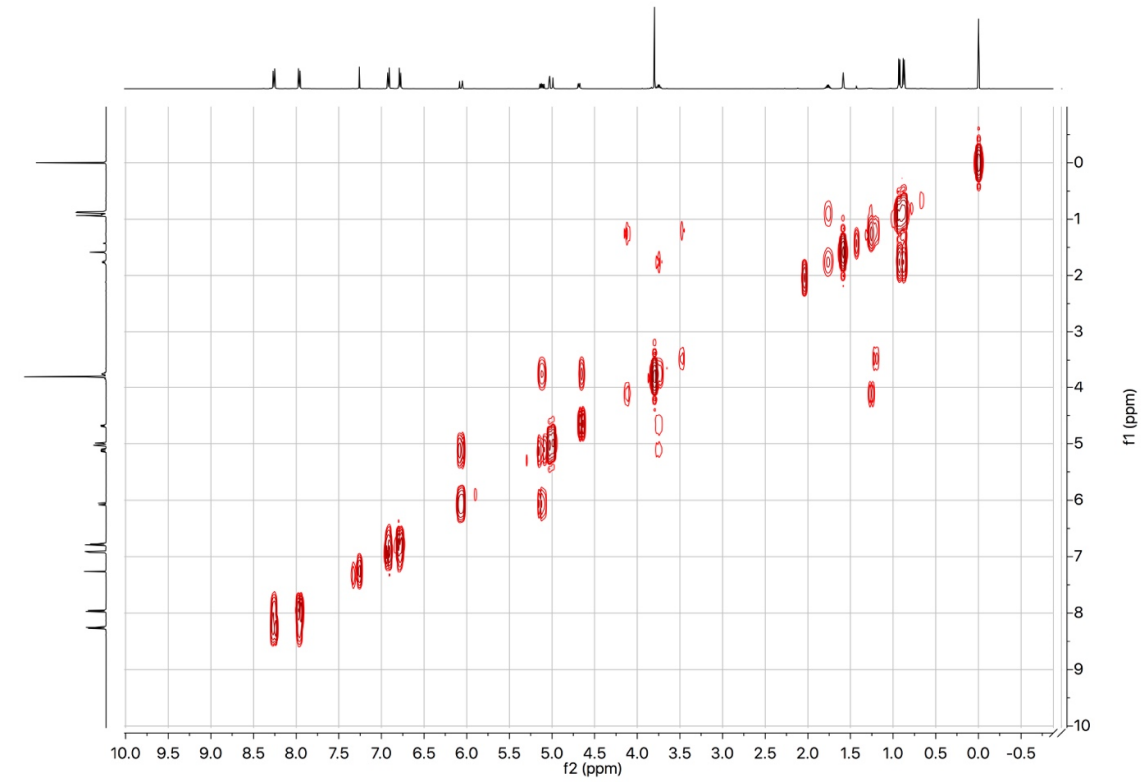

f2 (ppm)
f1 (ppm)

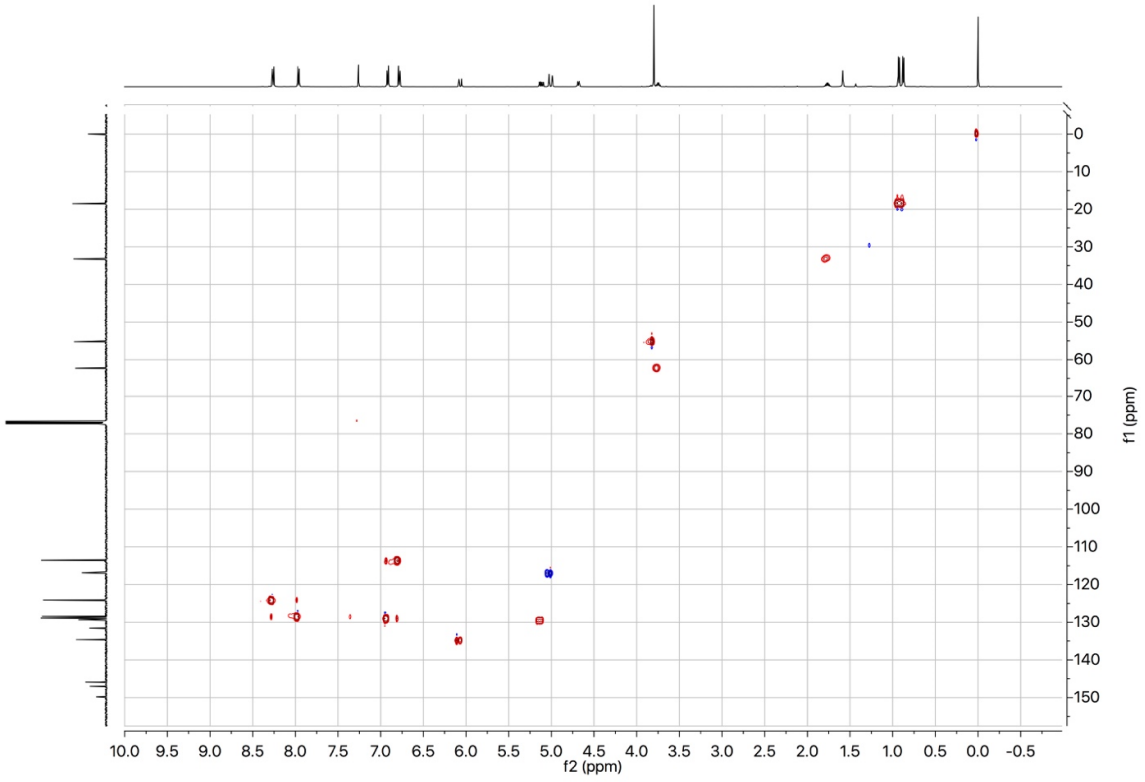

f2 (ppm)
f1 (ppm)

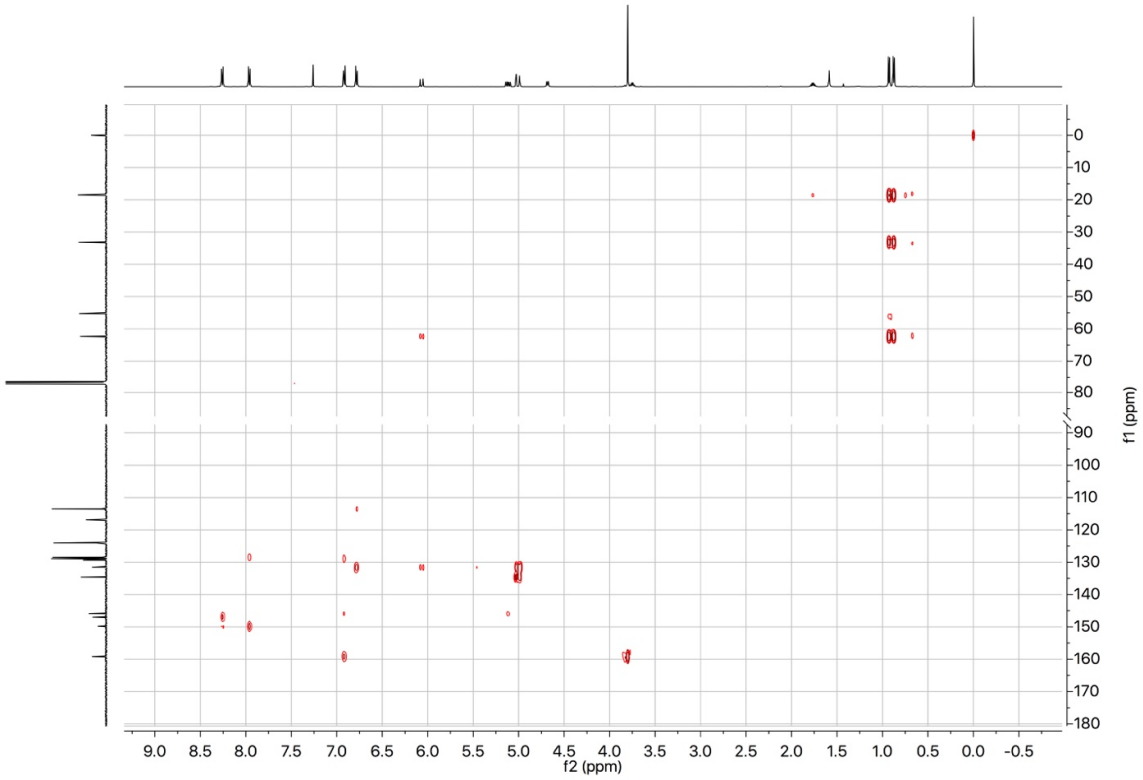
2a


8.27
8.25
7.97
7.95
7.26
6.93
6.91
6.79
6.77
6.08
6.05
5.14
5.12
5.11
5.09
5.03
5.03
4.99
4.69
4.67
3.80
3.77
3.76
3.74
3.73
1.81
1.80
1.78
1.77
1.76
1.75
1.73
1.72
0.93
0.92
0.88
0.87
0.00
O2N
NH
O
O
OMe
2.01
2.00
2.00
2.07
1.00
1.01
1.00
1.03
0.99
2.98
1.09
1.02
3.01
3.12
f1 (ppm)

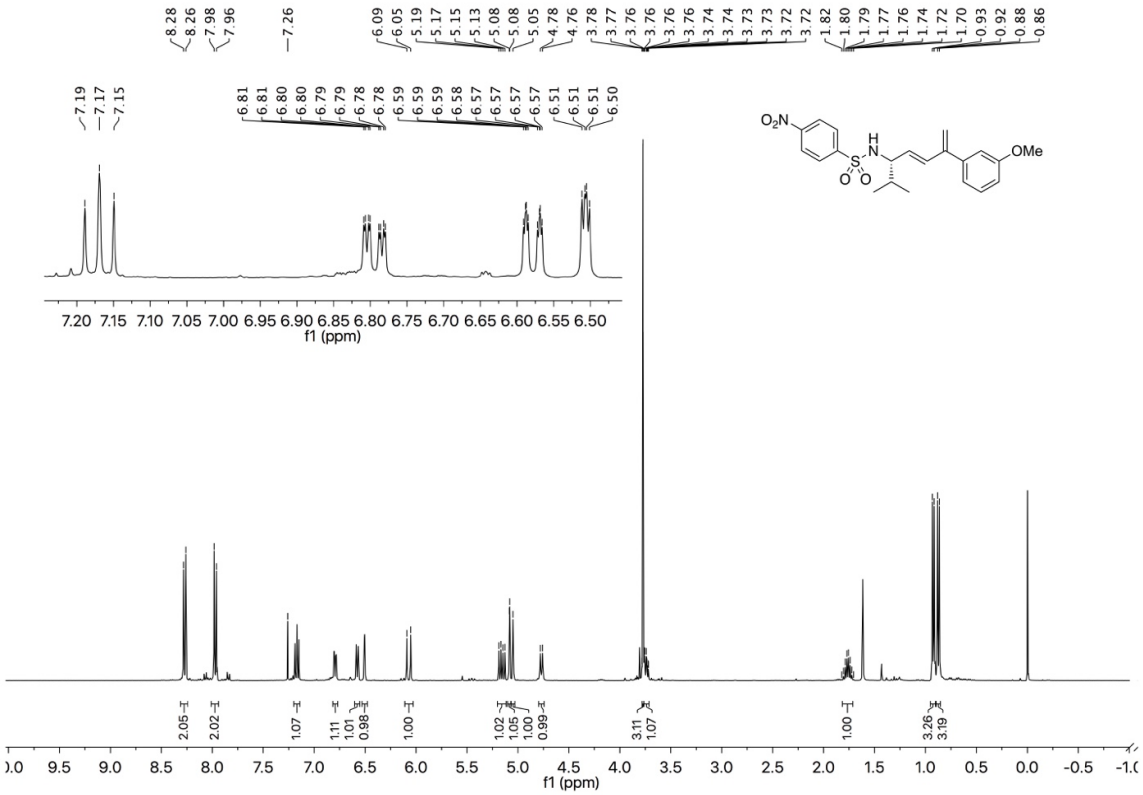

159.17
149.80
147.01
145.90
134.61
131.53
129.35
128.88
128.46
124.08
116.88
113.54
77.25
77.00
76.75
62.31
55.24
33.17
18.56
18.51
0.02
f1 (ppm)

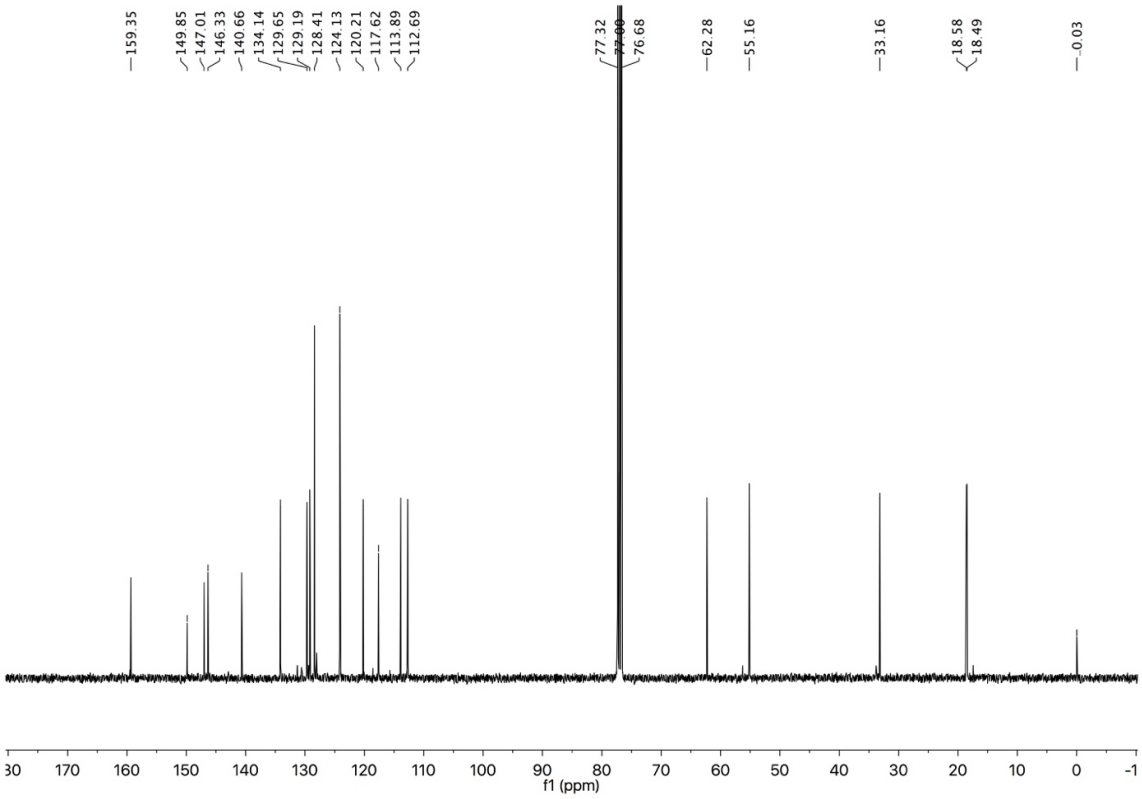

f1 (ppm)
f2 (ppm)

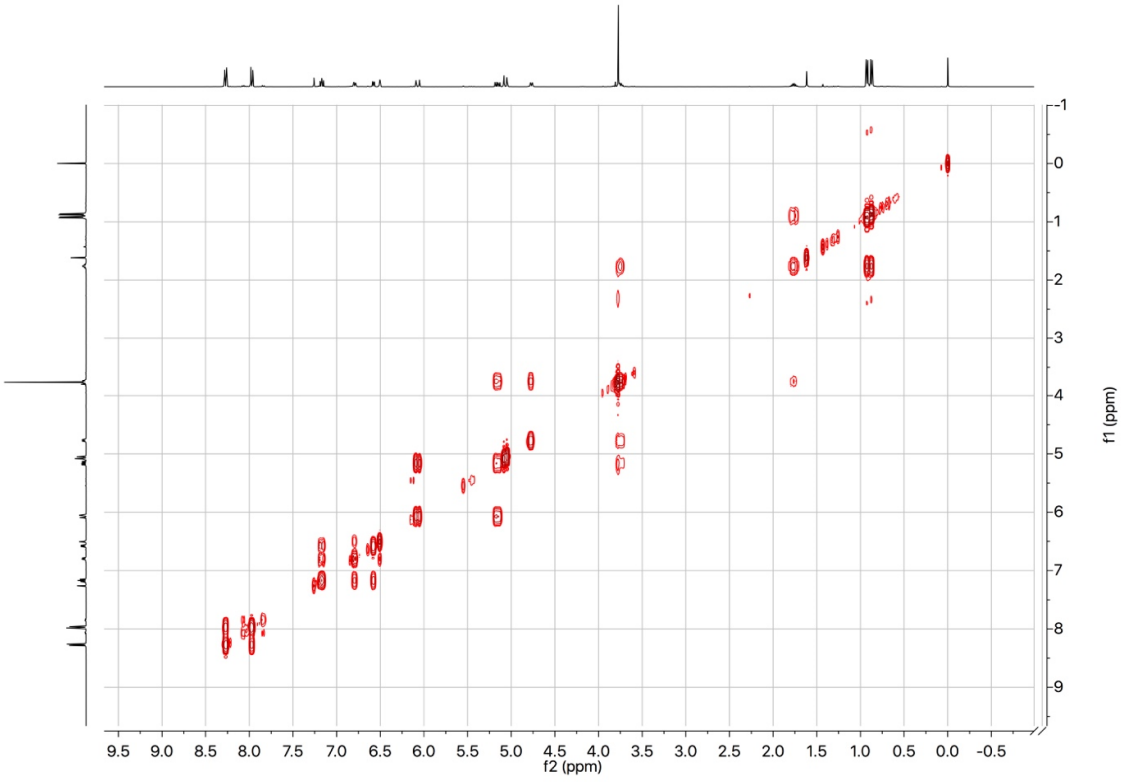

f1 (ppm)
f2 (ppm)

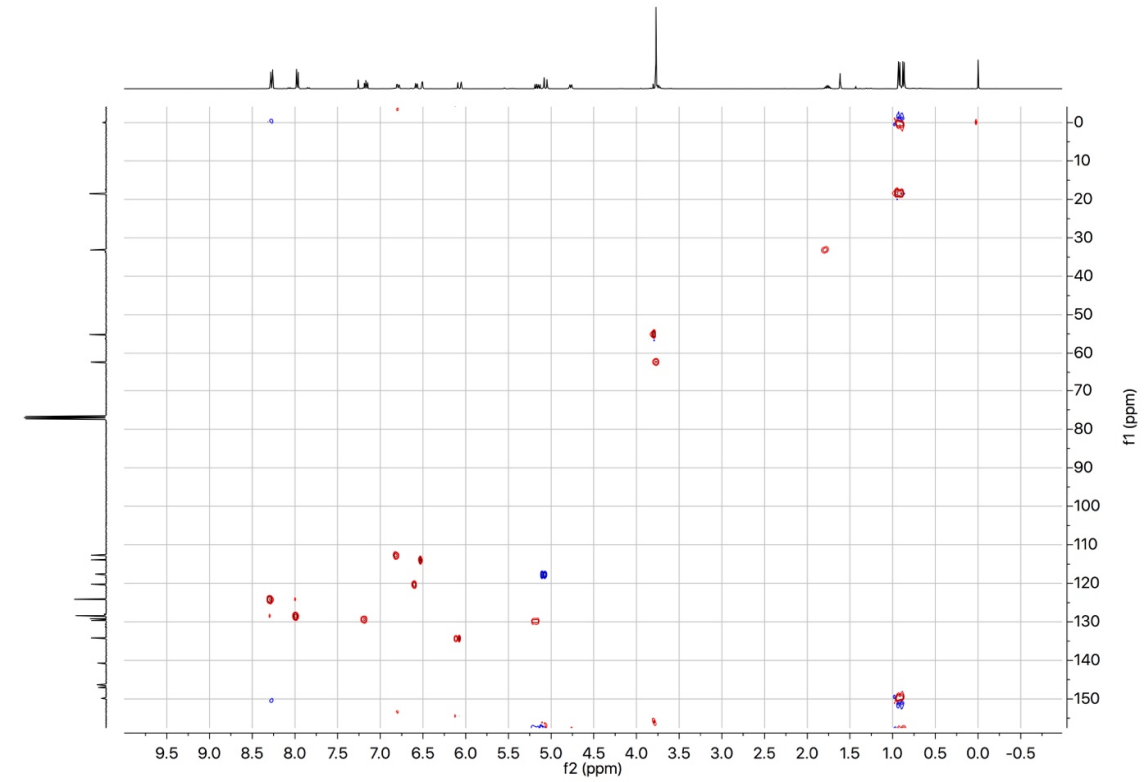

f2 (ppm)
f1 (ppm)

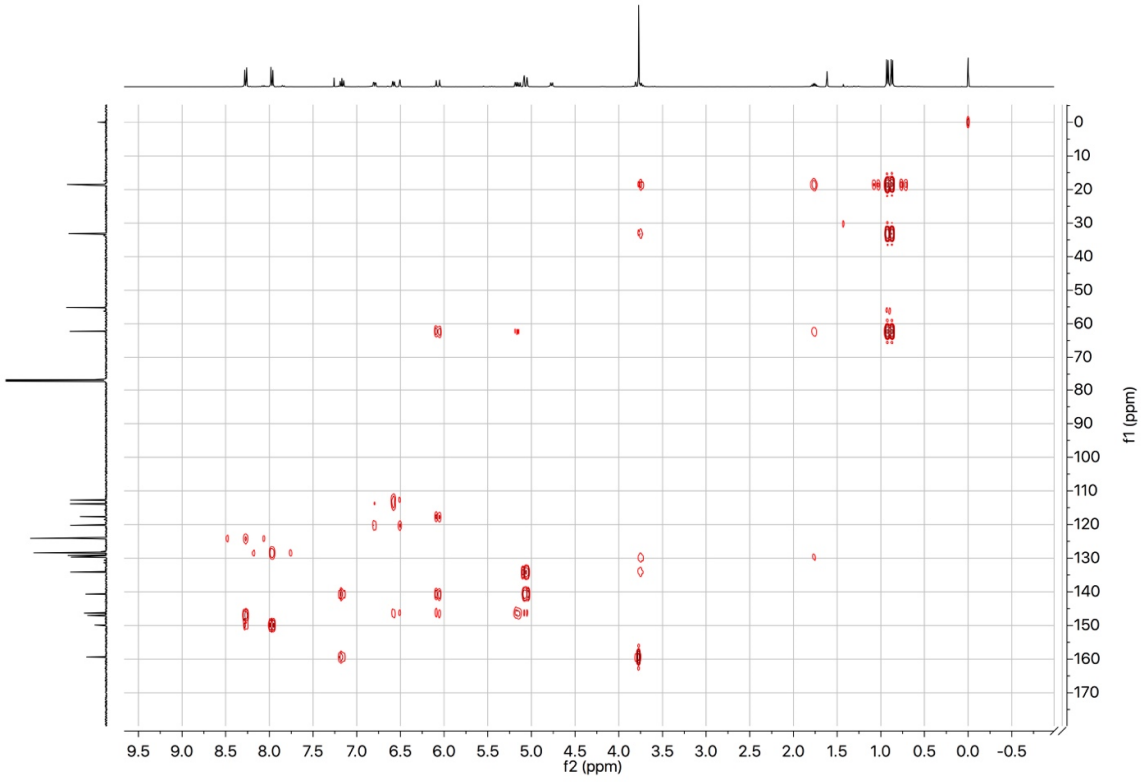
2b


8.28
8.26
7.98
7.96
7.26
6.09
6.05
5.19
5.17
5.15
5.13
5.08
5.08
5.05
4.78
4.76
3.78
3.77
3.76
3.76
3.76
3.76
3.74
3.74
3.73
3.73
3.72
3.72
1.82
1.80
1.79
1.77
1.76
1.74
1.72
1.70
0.93
0.92
0.88
0.86
7.19
7.17
7.15
6.81
6.81
6.80
6.80
6.79
6.79
6.78
6.78
6.59
6.59
6.59
6.58
6.57
6.57
6.57
6.57
6.51
6.51
6.51
6.50
O2N
OMe
f1 (ppm)
2.05
2.02
1.07
1.11
1.01
0.98
1.00
1.02
1.05
1.00
0.99
3.11
1.07
1.00
3.26
3.19
f1 (ppm)

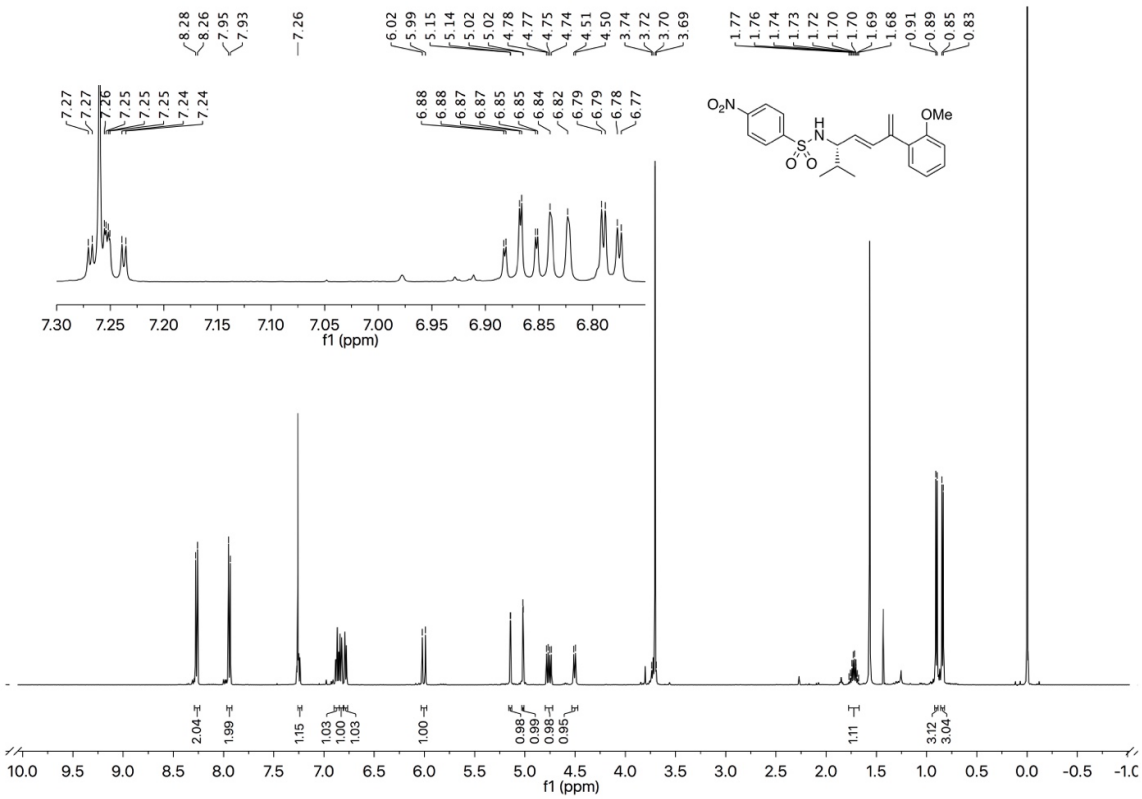

159.35
149.85
147.01
146.33
140.66
134.14
129.65
129.19
128.41
124.13
120.21
117.62
113.89
112.69
77.32
77.00
76.68
62.28
55.16
33.16
18.58
18.49
0.03
f1 (ppm)

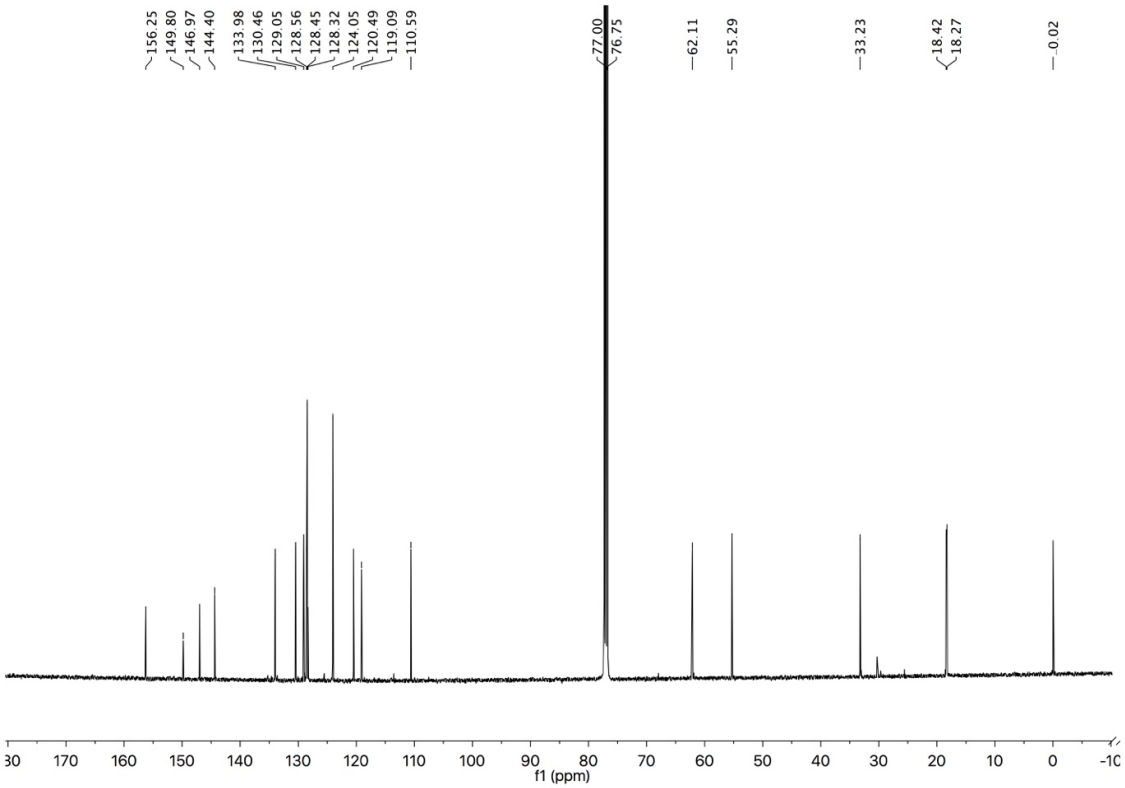

f2 (ppm)
f1 (ppm)

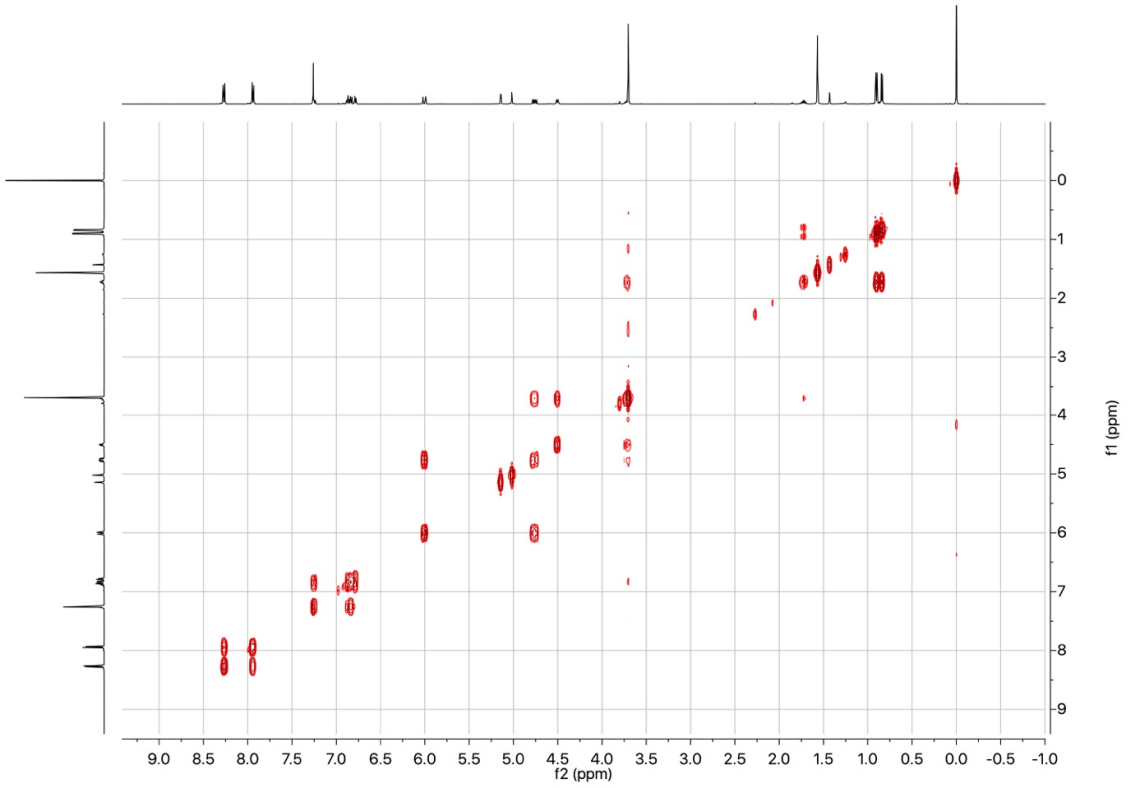

f1 (ppm)
f2 (ppm)

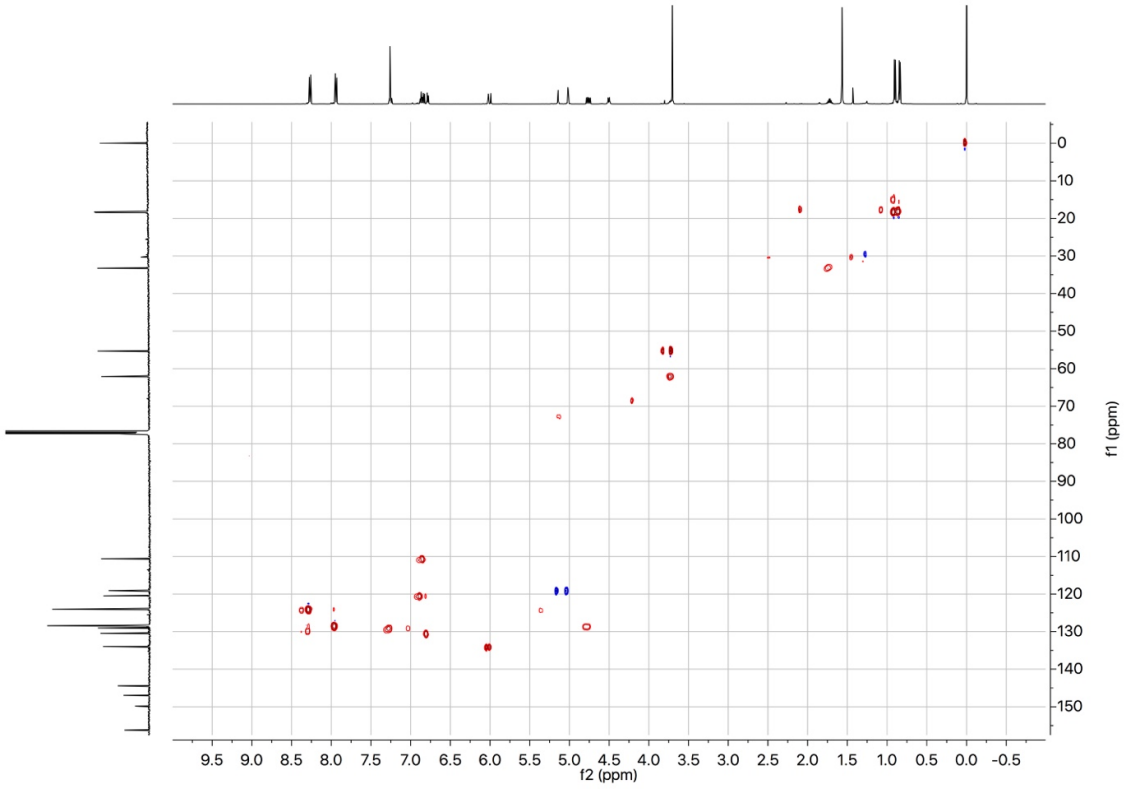

f1 (ppm)
f2 (ppm)

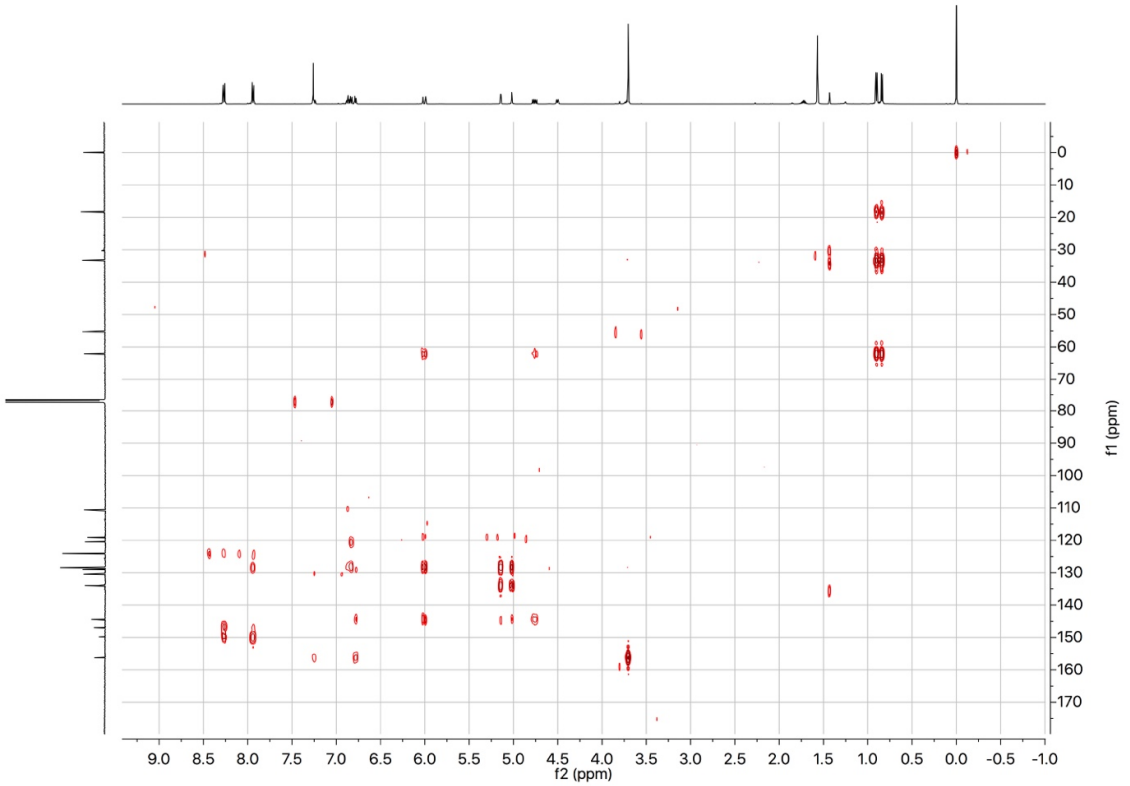
2c


8.28
8.26
7.95
7.93
7.26
6.02
5.99
5.15
5.14
5.02
5.02
4.78
4.77
4.75
4.74
4.51
4.50
3.74
3.72
3.70
3.69
1.77
1.76
1.74
1.73
1.72
1.70
1.70
1.69
1.68
0.91
0.89
0.85
0.83
7.27
7.27
7.26
7.25
7.25
7.25
7.24
7.24
6.88
6.88
6.87
6.87
6.85
6.85
6.84
6.82
6.79
6.79
6.78
6.77
O2N
H
N
S
O
O
OMe
7.30 7.25 7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85 6.80
f1 (ppm)
2.04
1.99
1.15
1.03
1.00
1.03
1.00
0.98
0.99
0.98
0.95
1.11
3.12
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

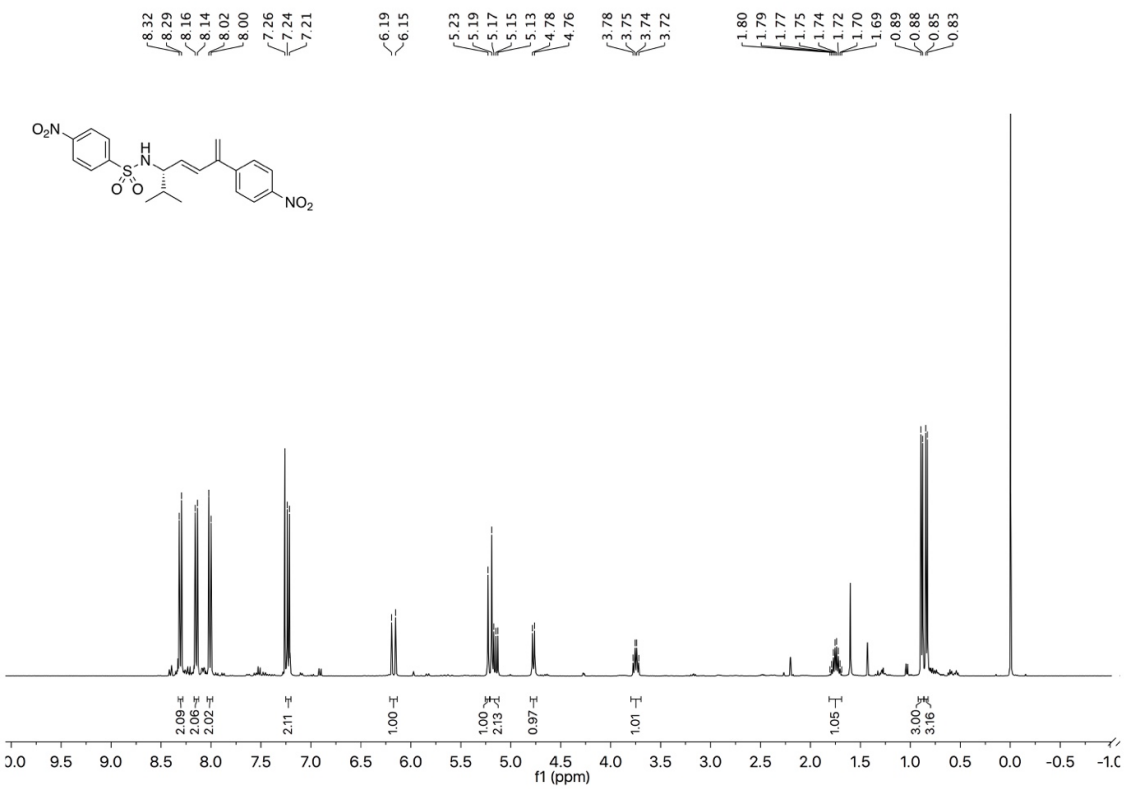

156.25
149.80
146.97
144.40
133.98
130.46
129.05
128.56
128.45
128.32
124.05
120.49
119.09
110.59
77.00
76.75
62.11
55.29
33.23
18.42
18.27
0.02
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

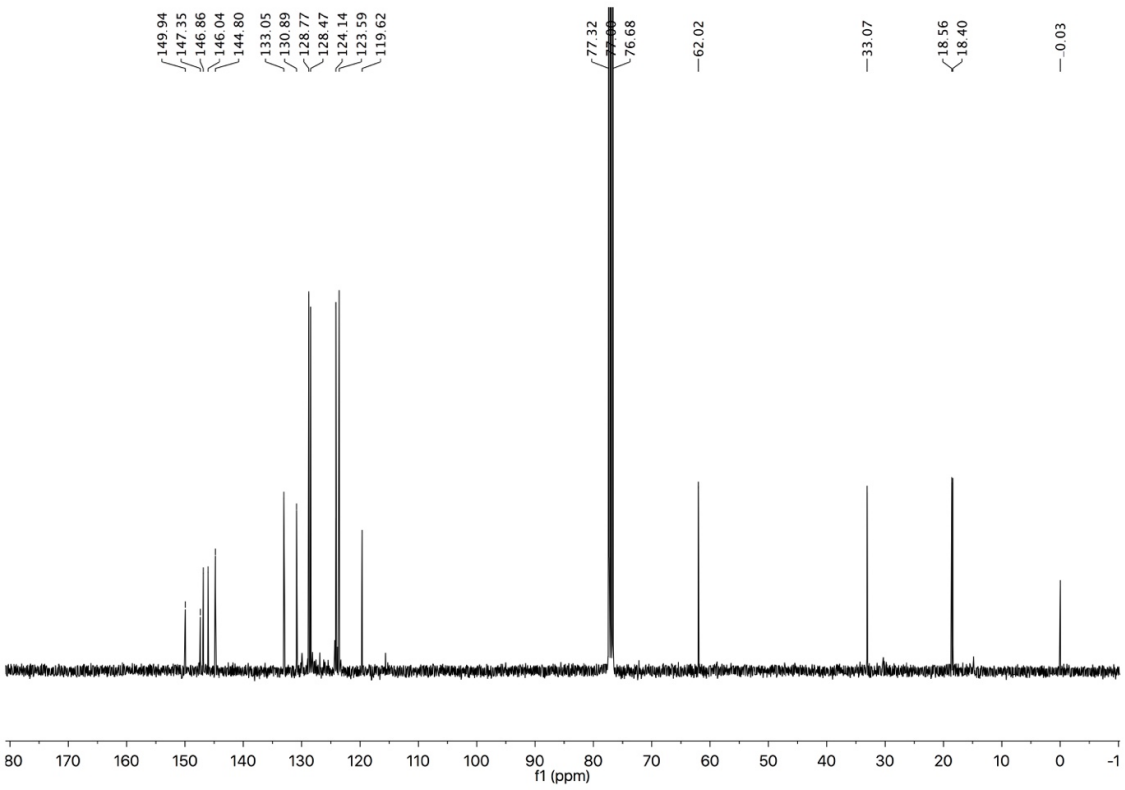

f2 (ppm)
f1 (ppm)

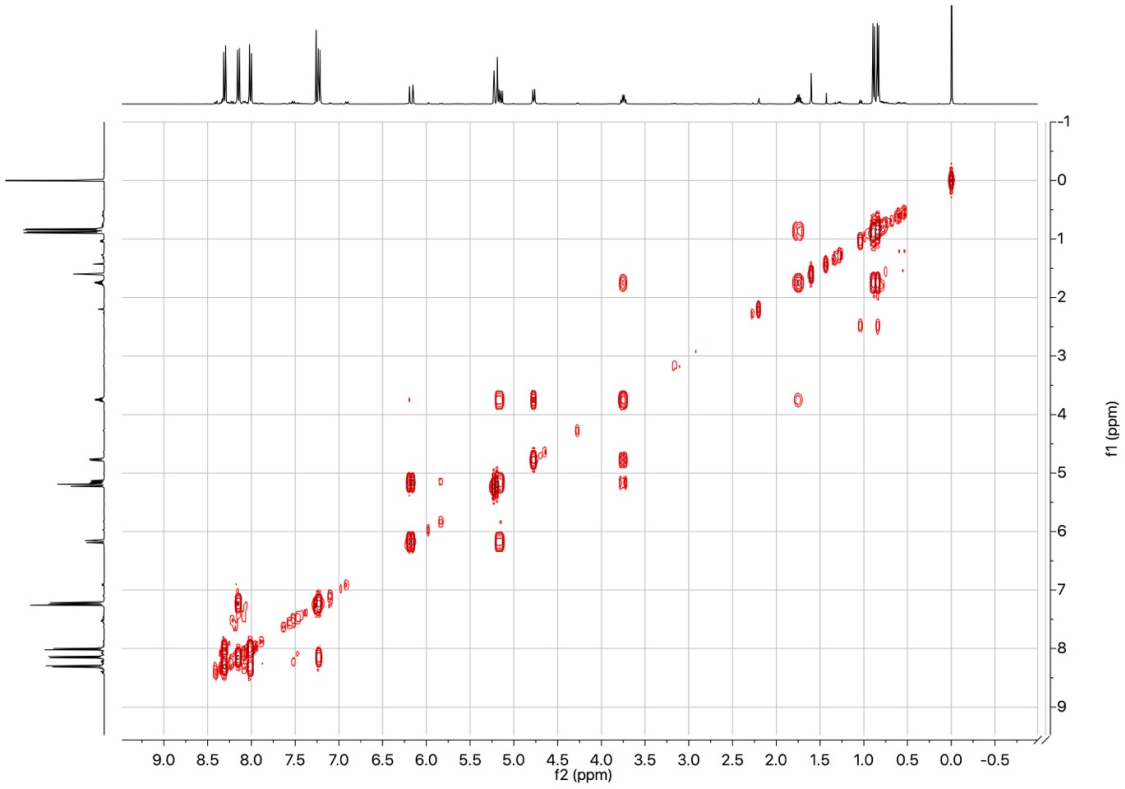

f2 (ppm)
f1 (ppm)

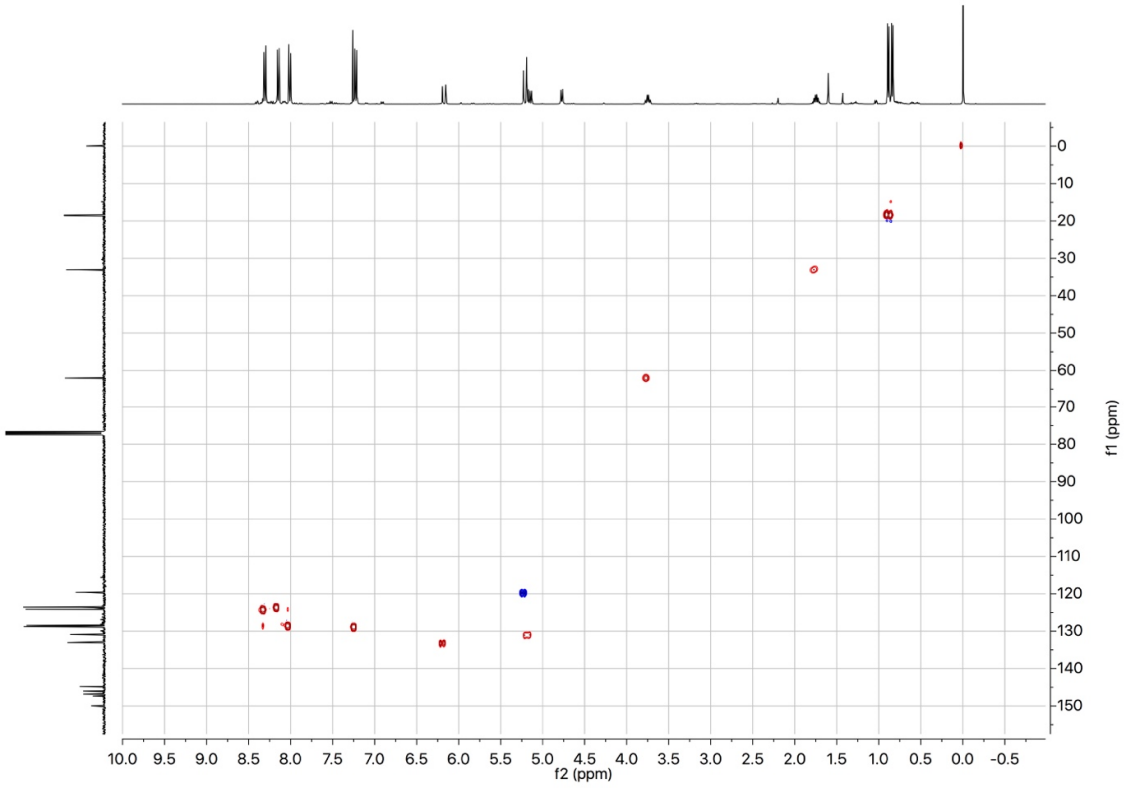

f2 (ppm)
f1 (ppm)

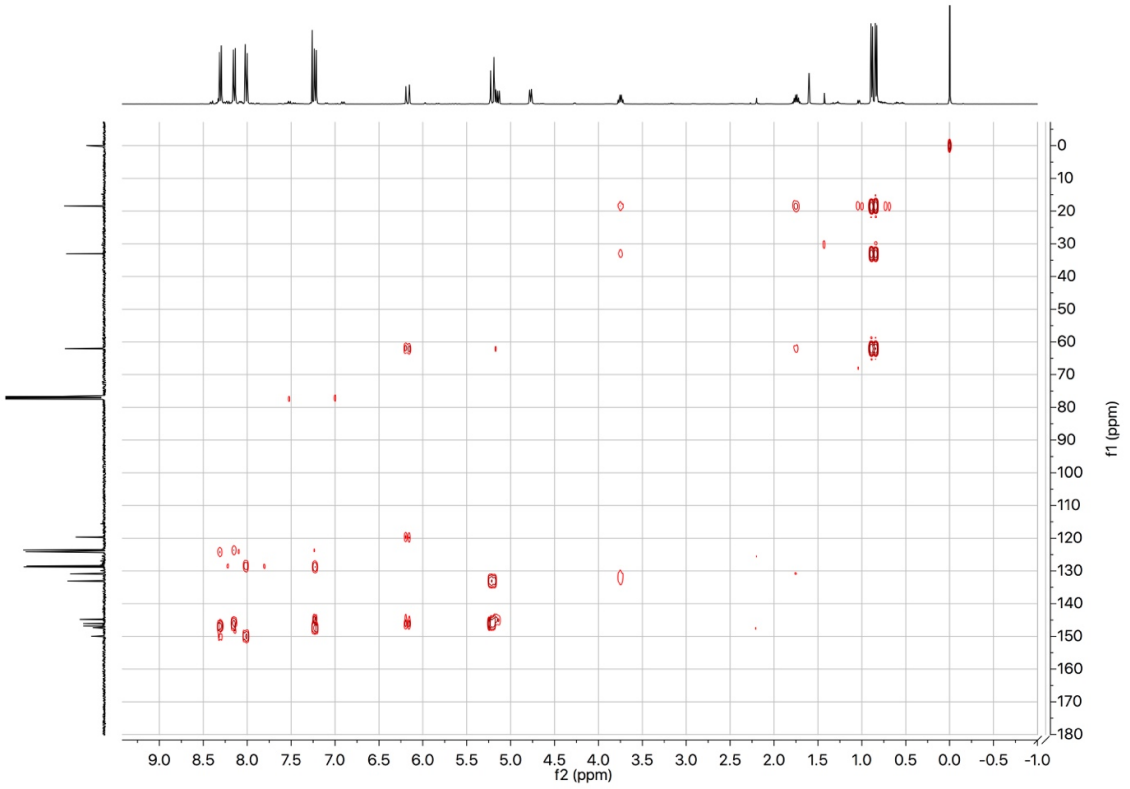
2d


8.32
8.29
8.16
8.14
8.02
8.00
7.26
7.24
7.21
6.19
6.15
5.23
5.19
5.17
5.15
5.13
4.78
4.76
3.78
3.75
3.74
3.72
1.80
1.79
1.77
1.75
1.74
1.72
1.70
1.69
0.89
0.88
0.85
0.83
O2N
NO2
f1 (ppm)

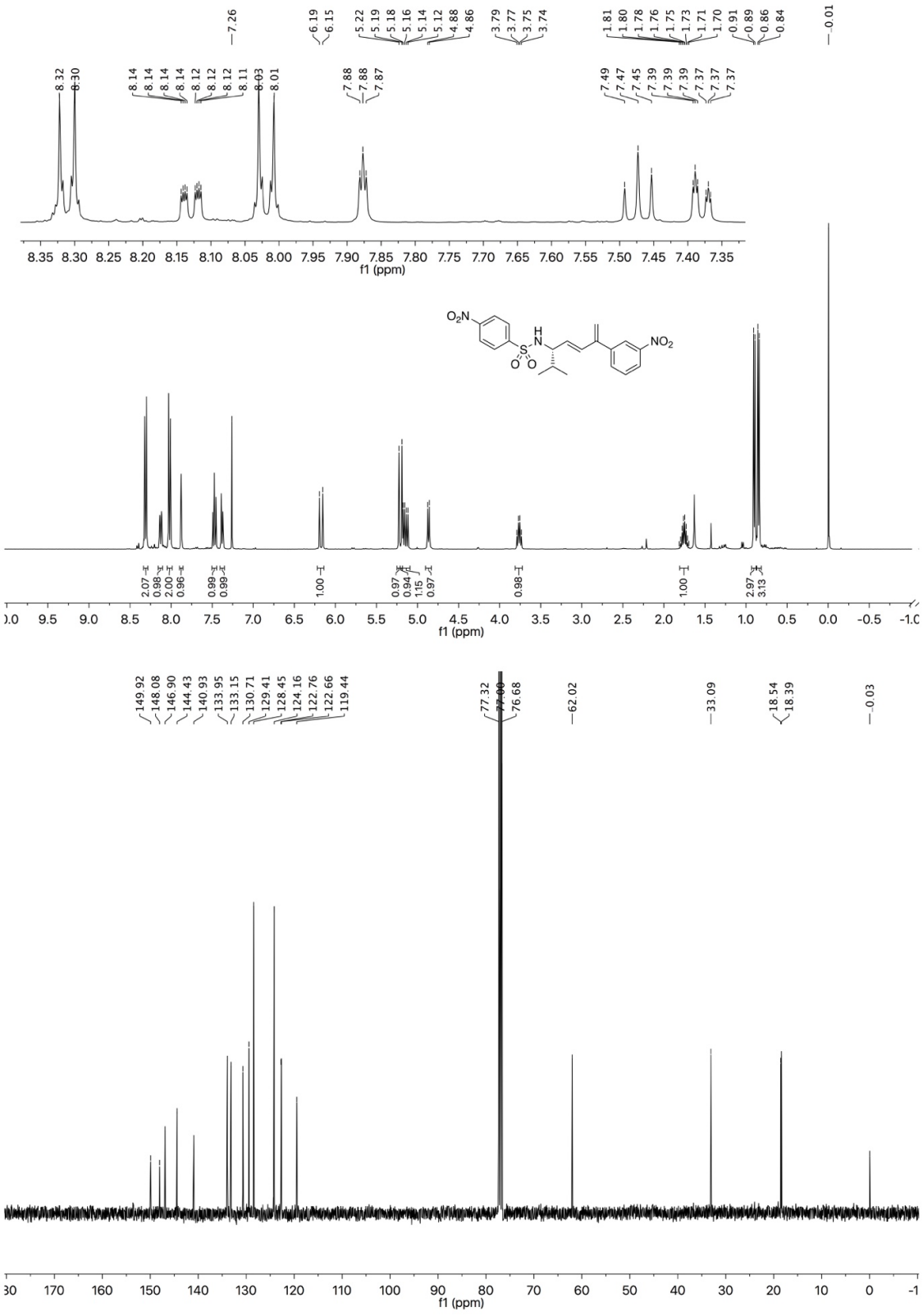

149.94
147.35
146.86
146.04
144.80
133.05
130.89
128.77
128.47
124.14
123.59
119.62
77.32
77.00
76.68
62.02
33.07
18.56
18.40
0.03
f1 (ppm)

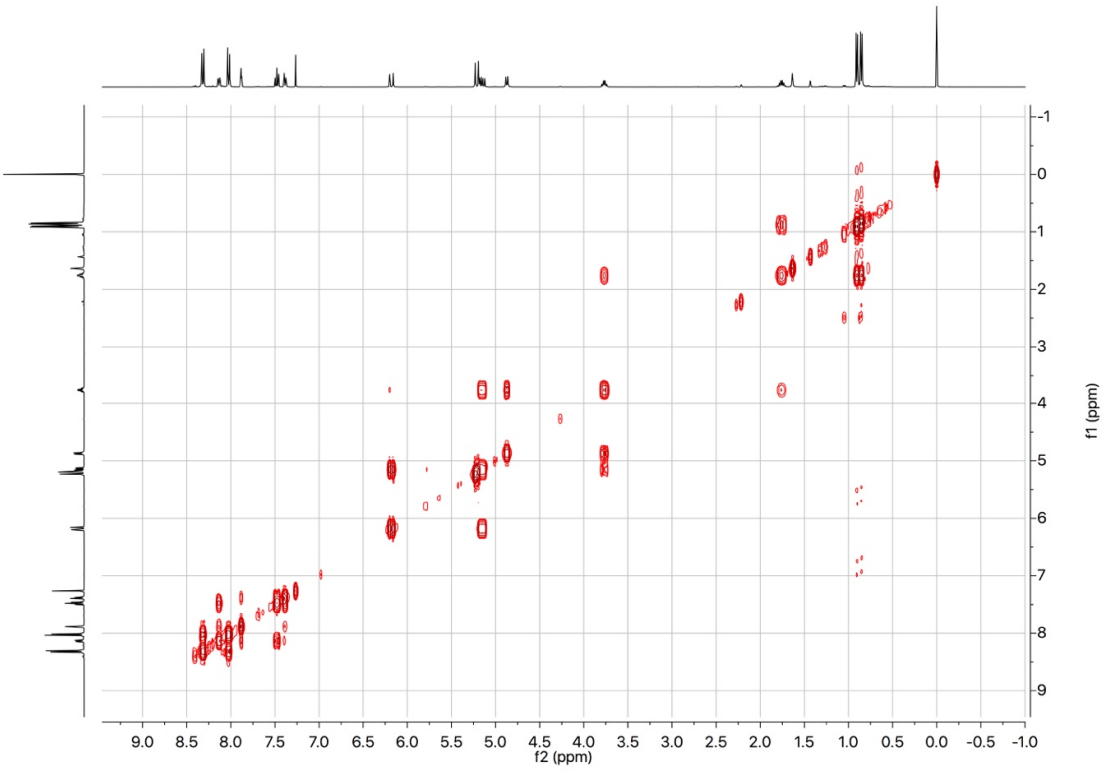

f2 (ppm)
f1 (ppm)

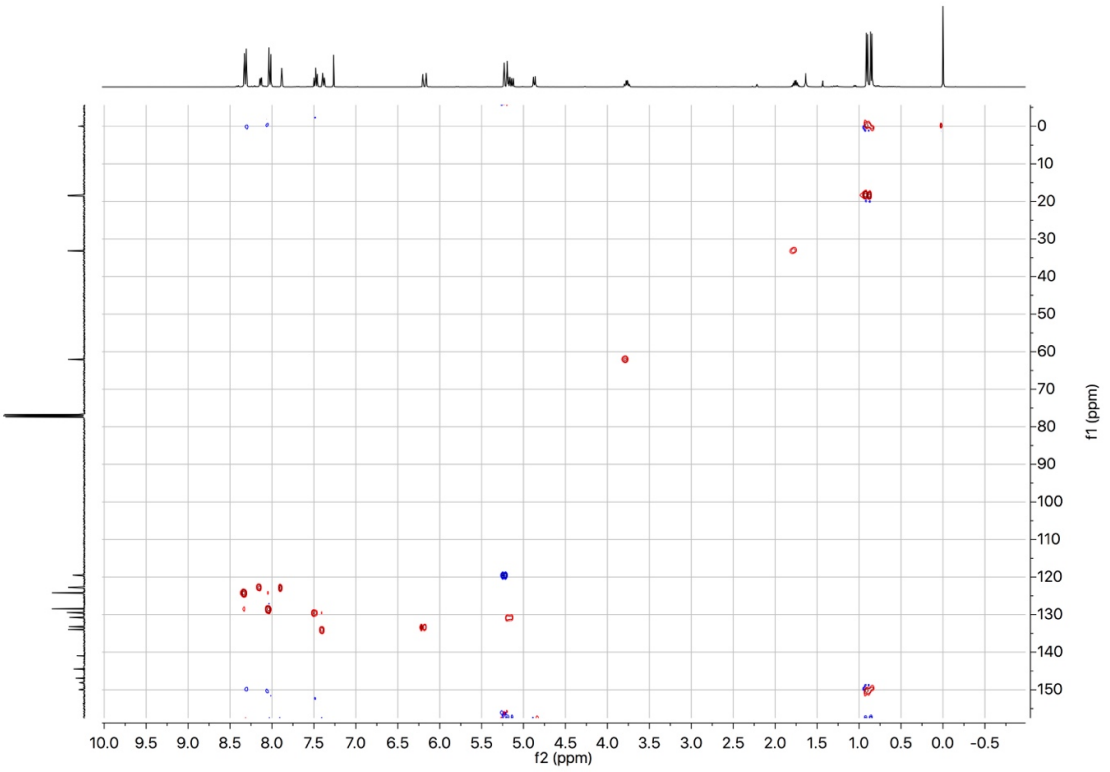

f2 (ppm)
f1 (ppm)

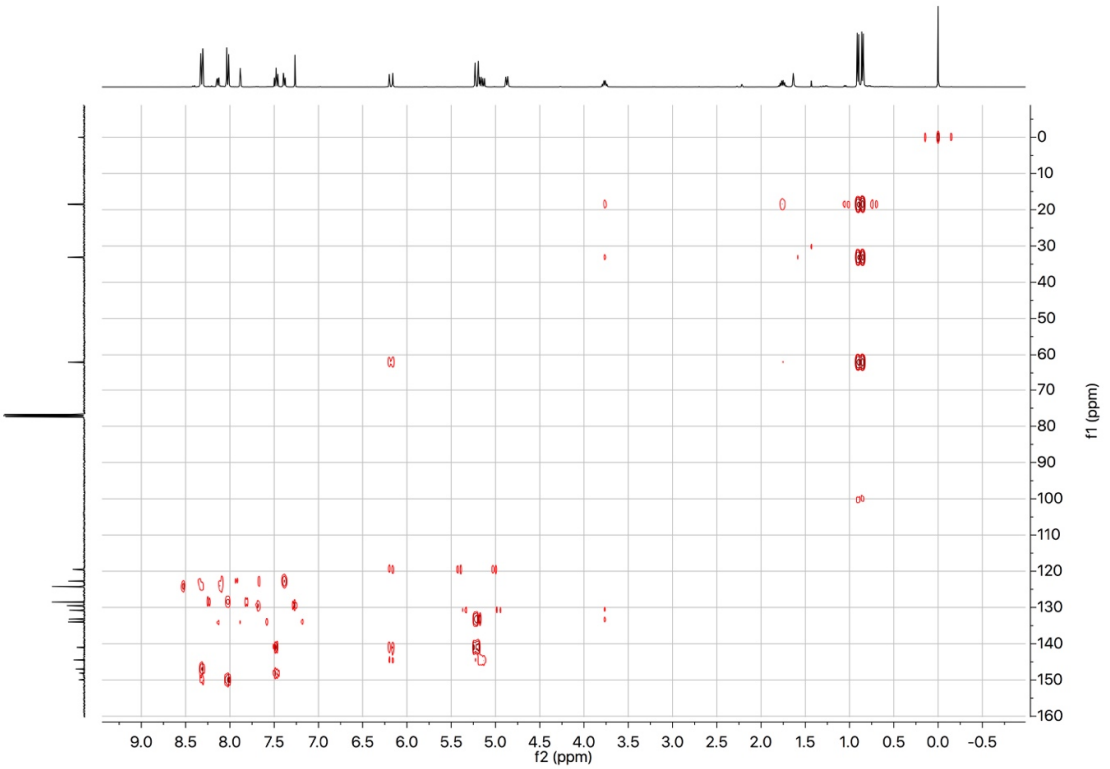

f2 (ppm)
f1 (ppm)

2e

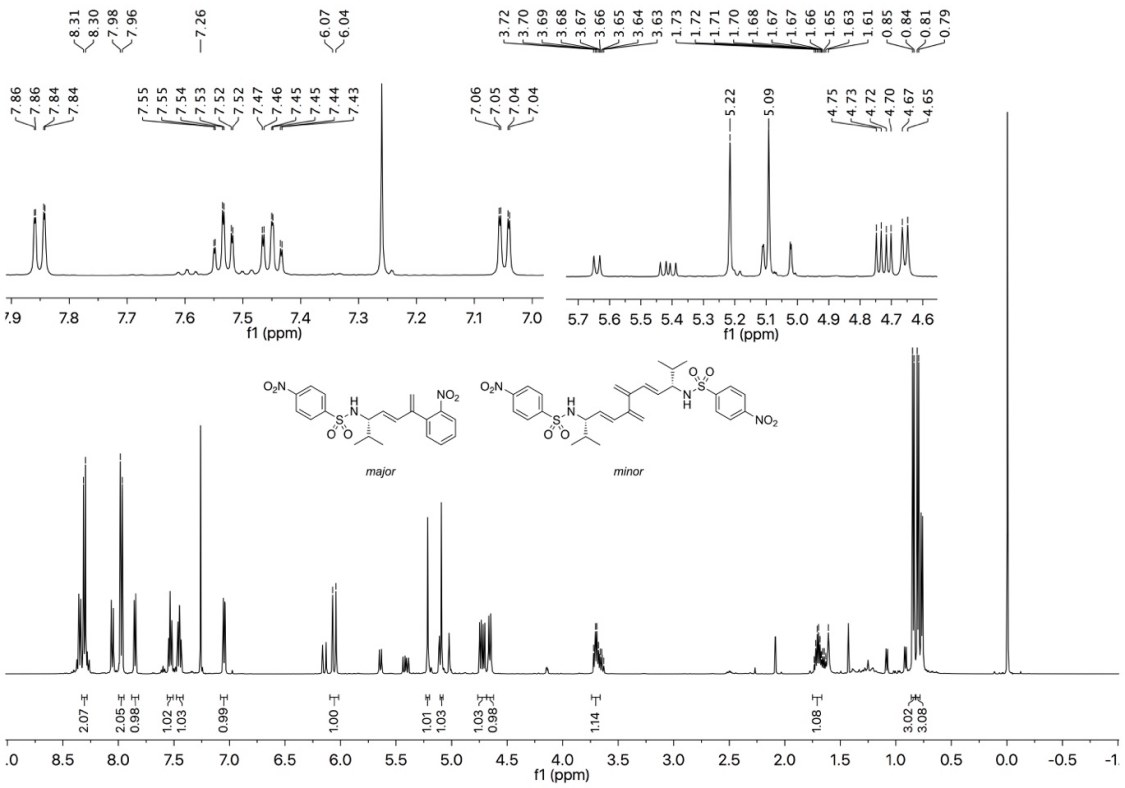


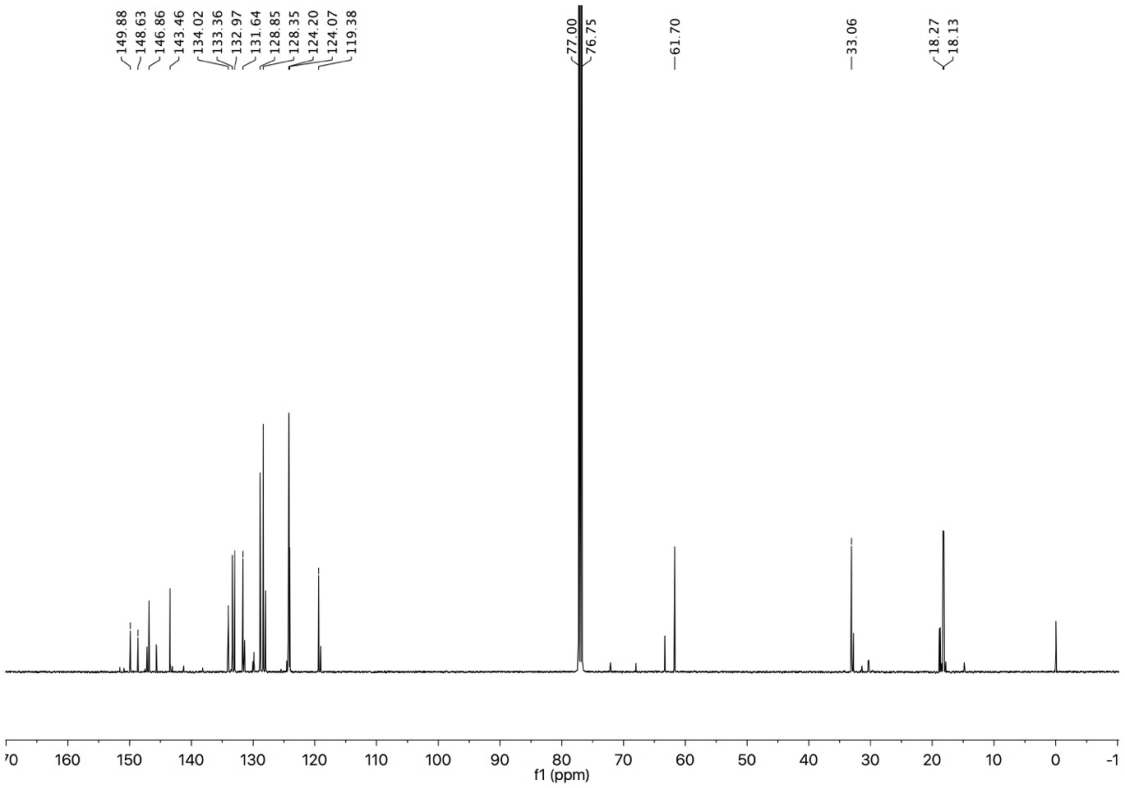

f2 (ppm)
f1 (ppm)

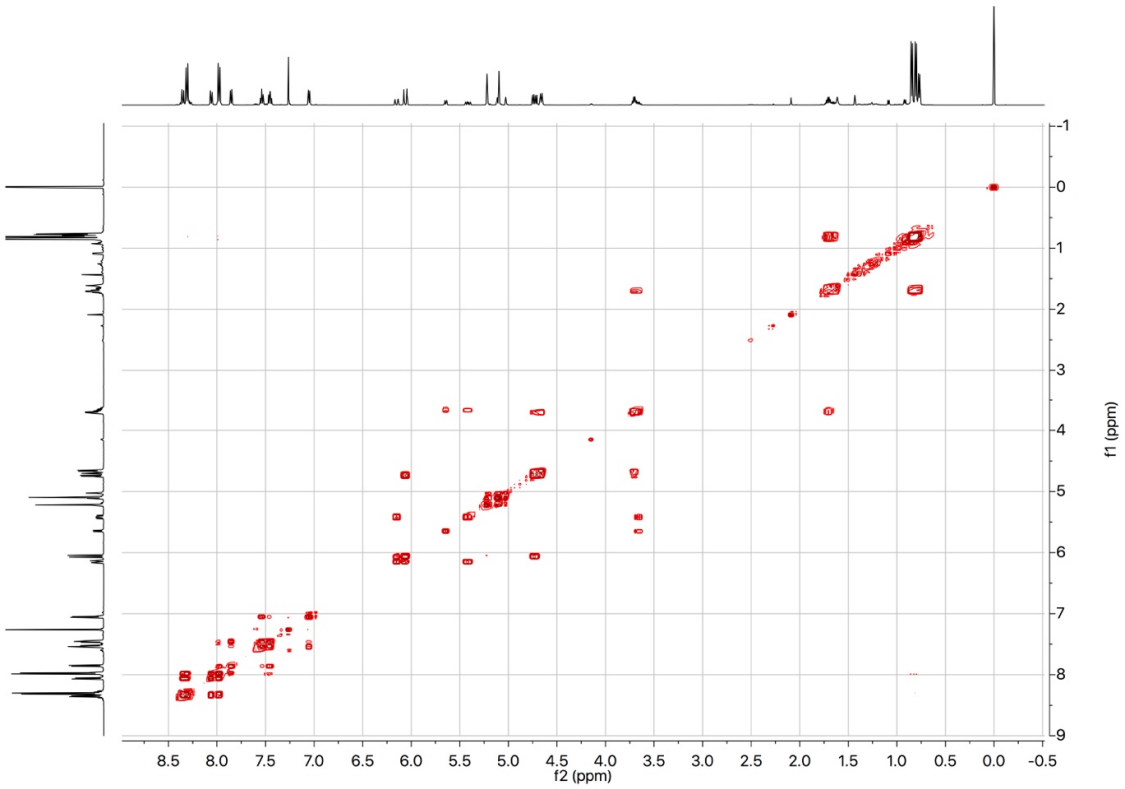

f2 (ppm)
f1 (ppm)

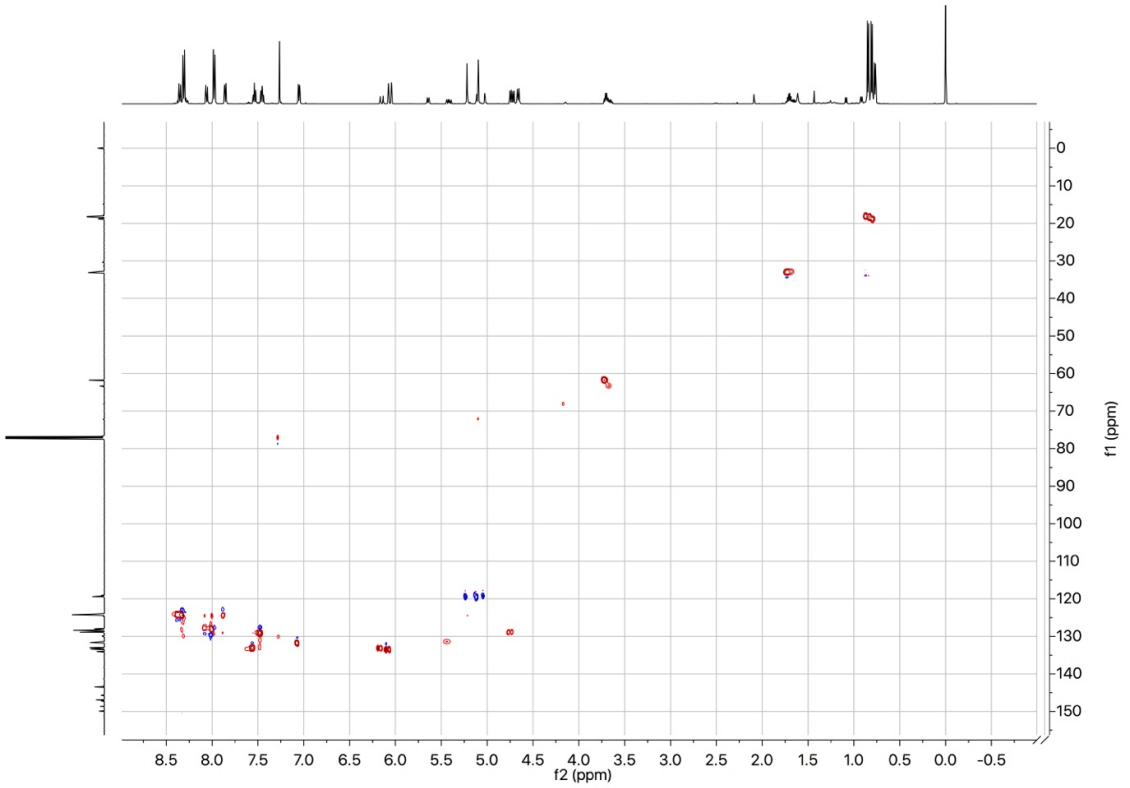


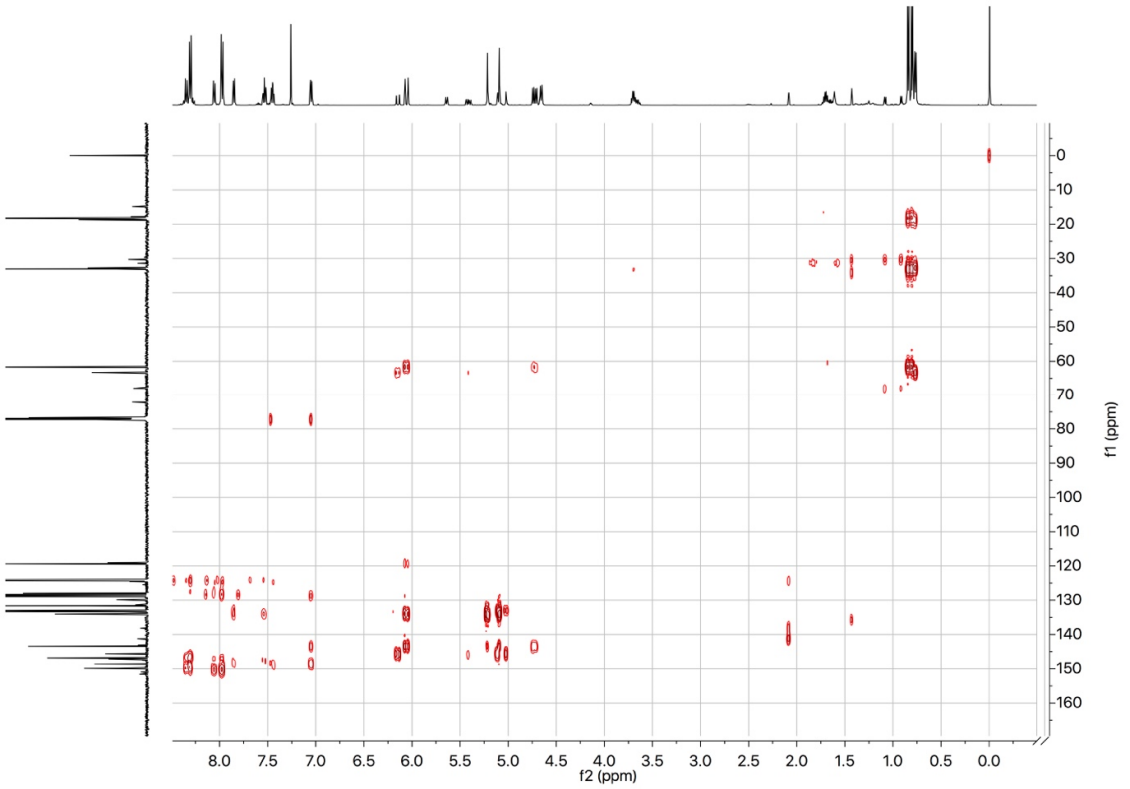
2f + 4



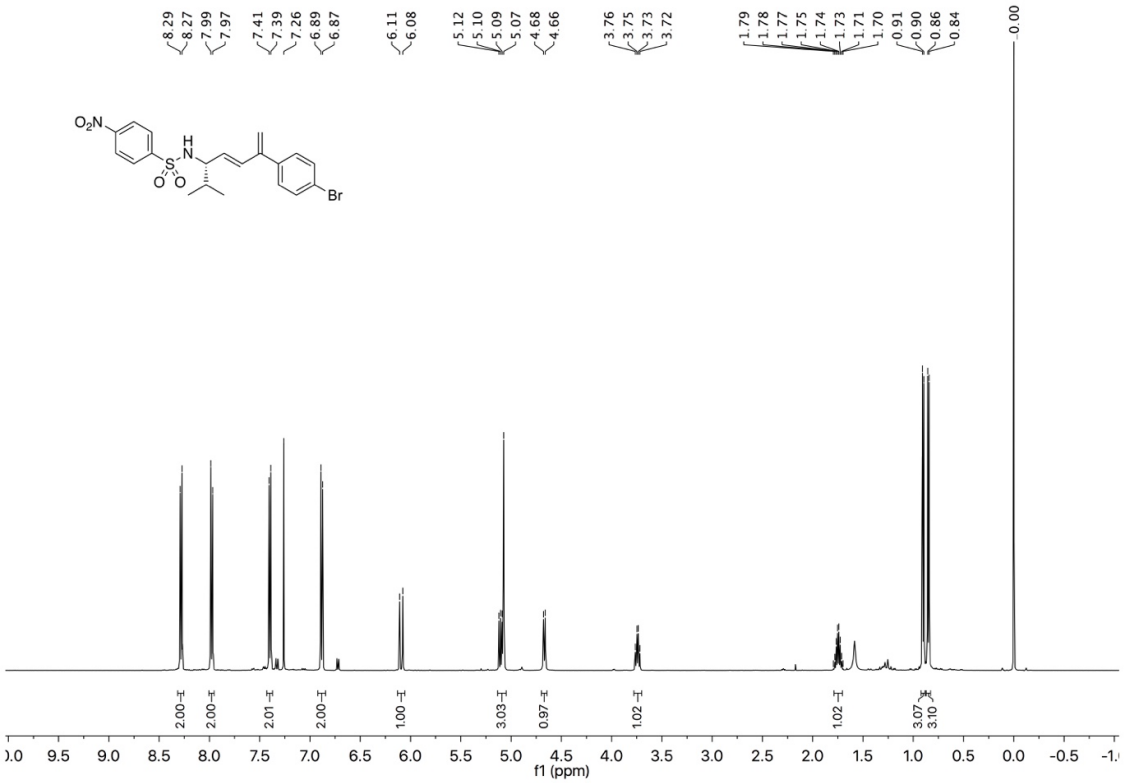

149.88
148.63
146.86
143.46
134.02
133.36
132.97
131.64
128.85
128.35
124.20
124.07
119.38
77.00
76.75
61.70
33.06
18.27
18.13
f1 (ppm)

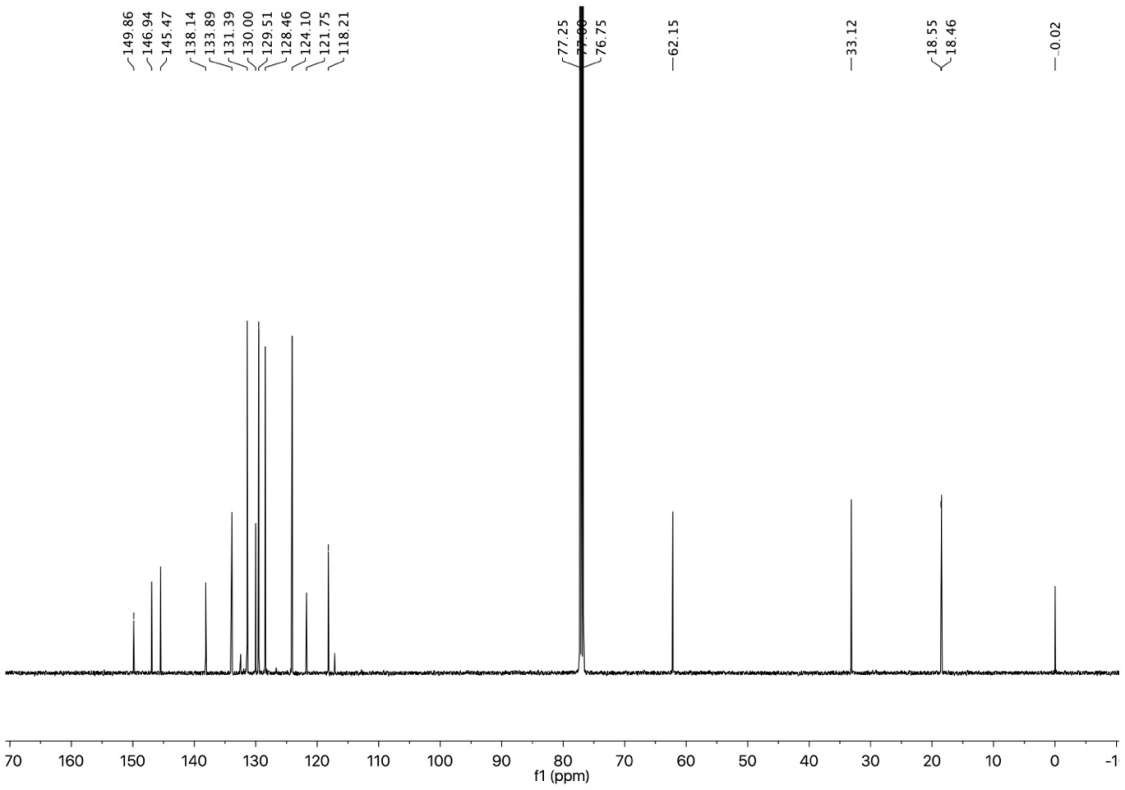

f2 (ppm)
f1 (ppm)

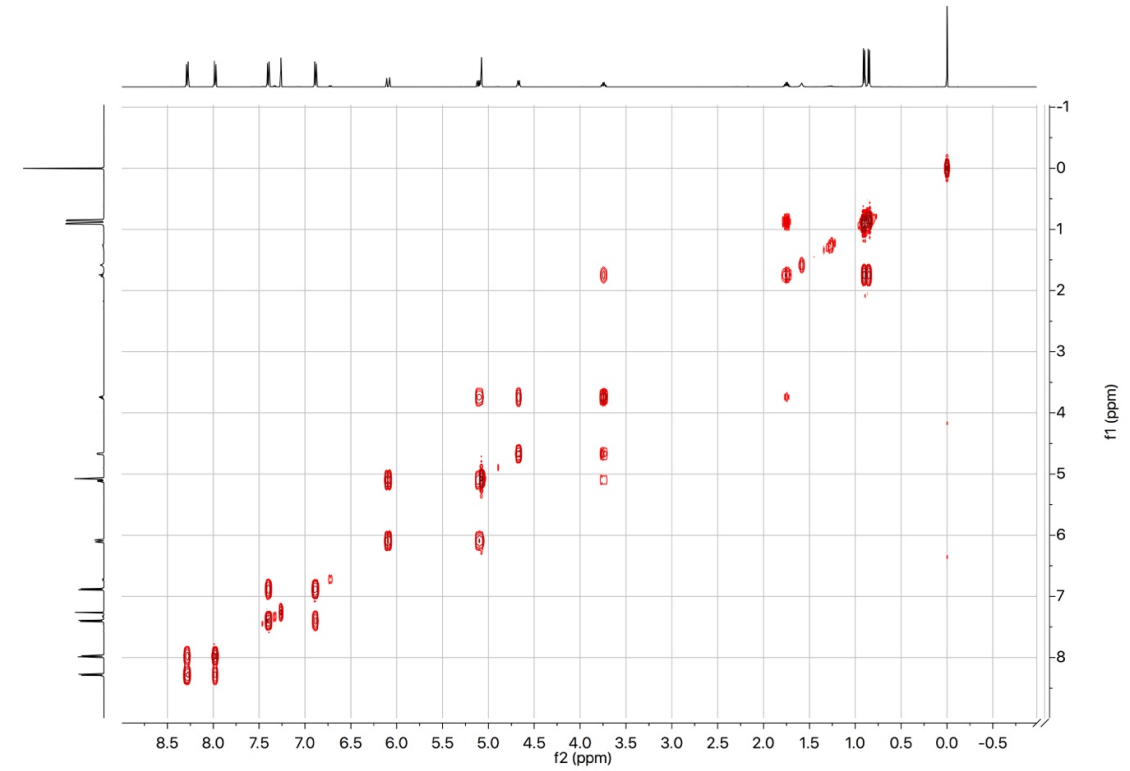

f2 (ppm)
f1 (ppm)

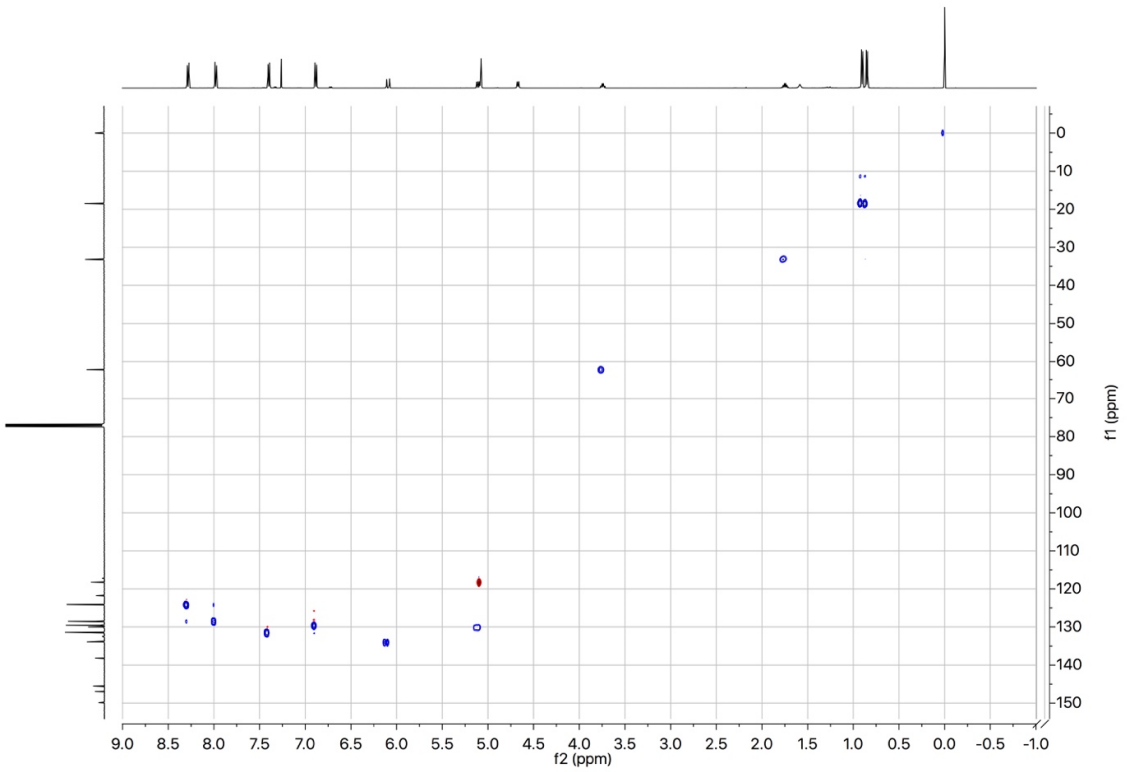

f2 (ppm)
f1 (ppm)

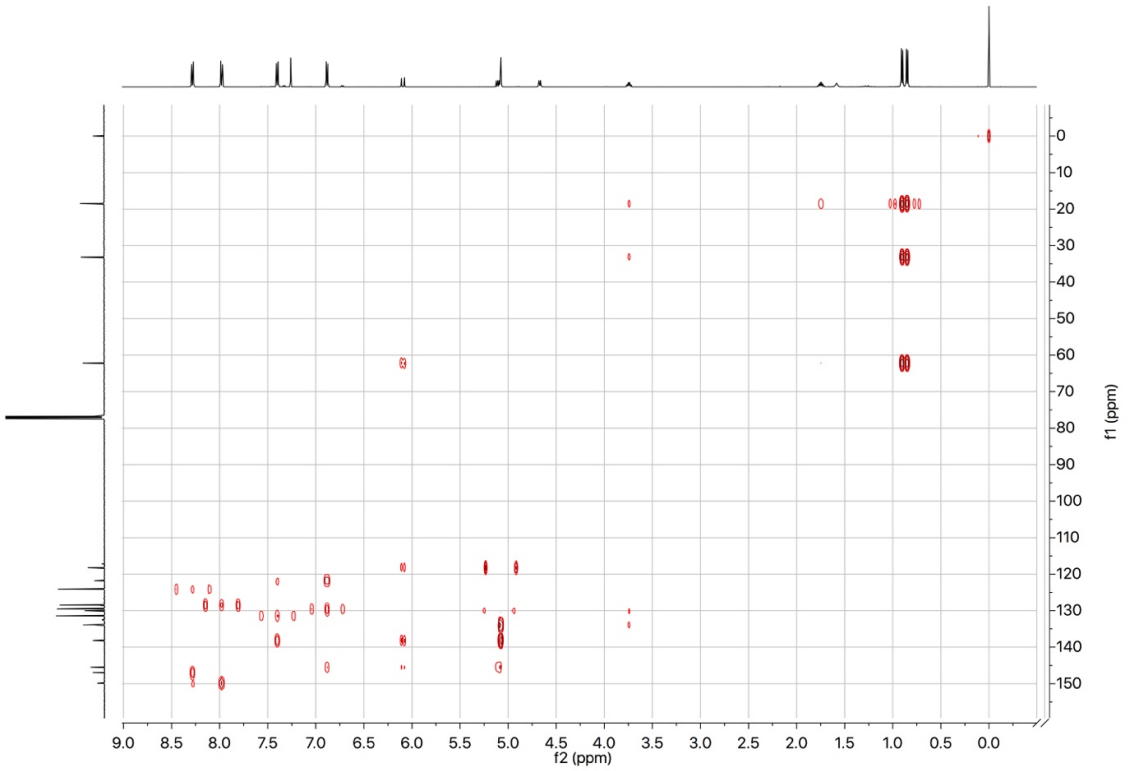
2g


8.29
8.27
7.99
7.97
7.41
7.39
7.26
6.89
6.87
6.11
6.08
5.12
5.10
5.09
5.07
4.68
4.66
3.76
3.75
3.73
3.72
1.79
1.78
1.77
1.75
1.74
1.73
1.71
1.70
0.91
0.90
0.86
0.84
0.00
O2N
H
N
S
O
O
Br
2.00
2.00
2.01
2.00
1.00
3.03
0.97
1.02
1.02
3.07
3.10
f1 (ppm)

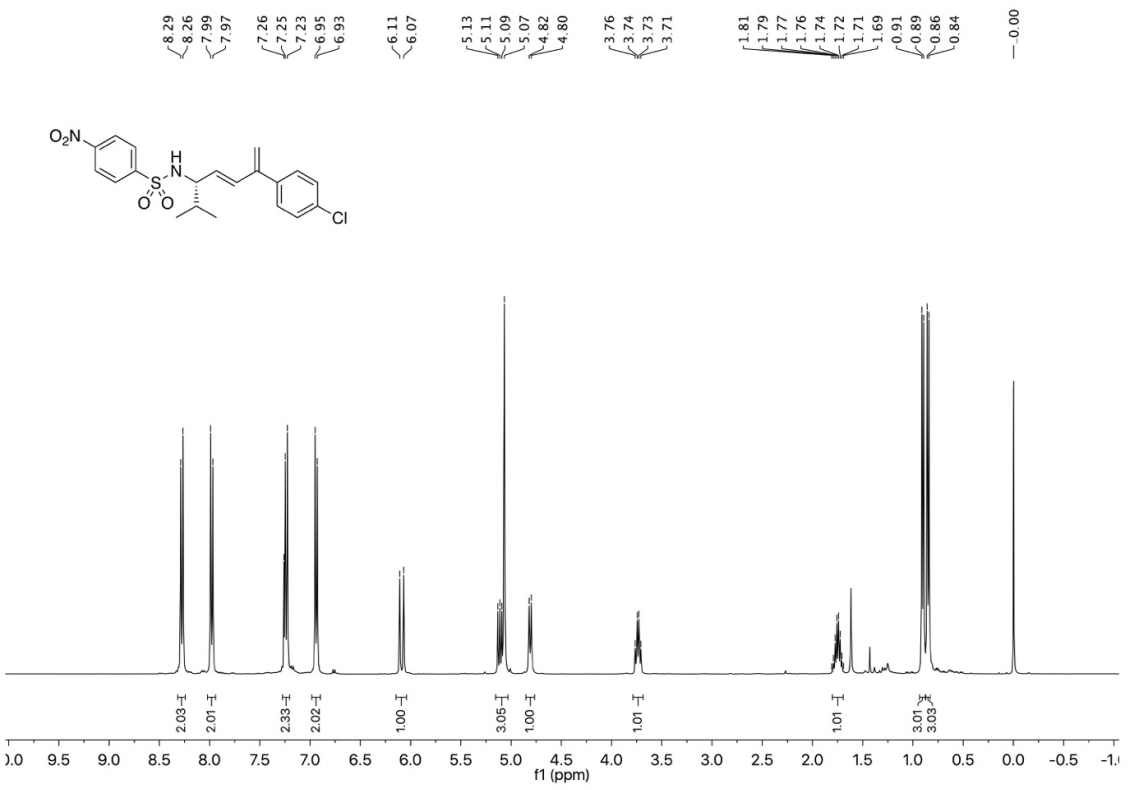

149.86
146.94
145.47
138.14
133.89
131.39
130.00
129.51
128.46
124.10
121.75
118.21
77.25
77.00
76.75
62.15
33.12
18.55
18.46
0.02
f1 (ppm)

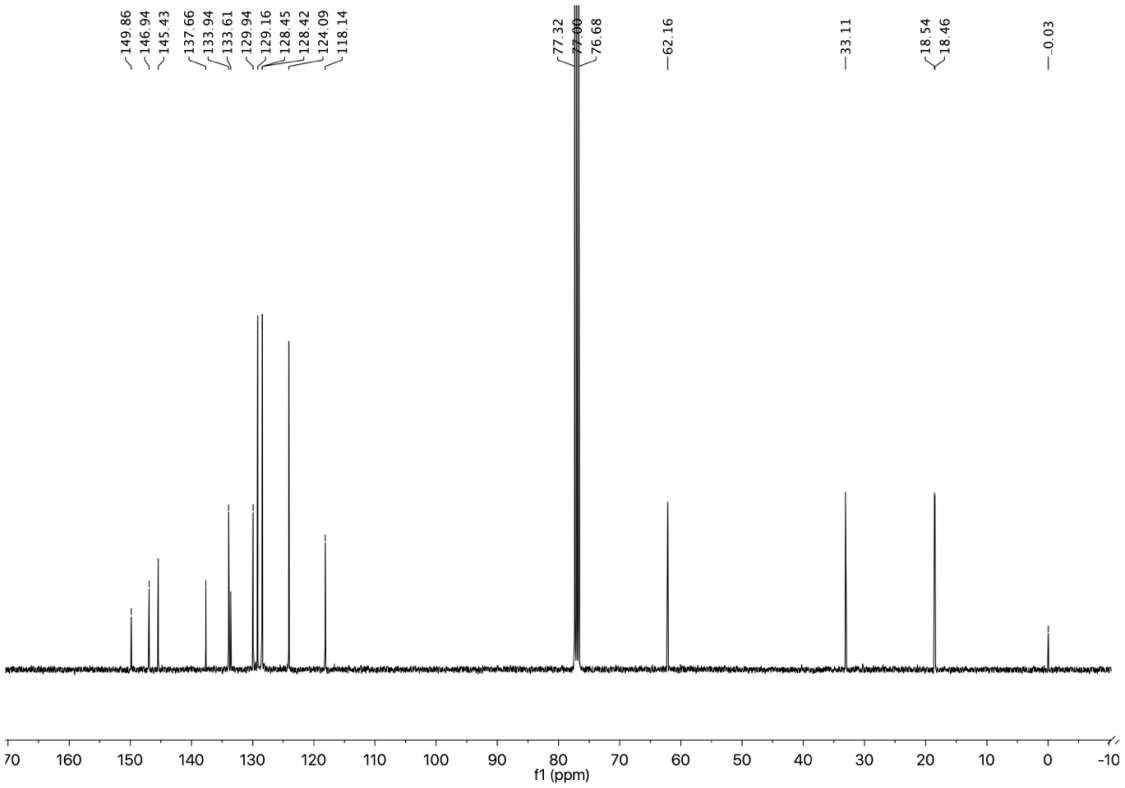

f2 (ppm)
f1 (ppm)

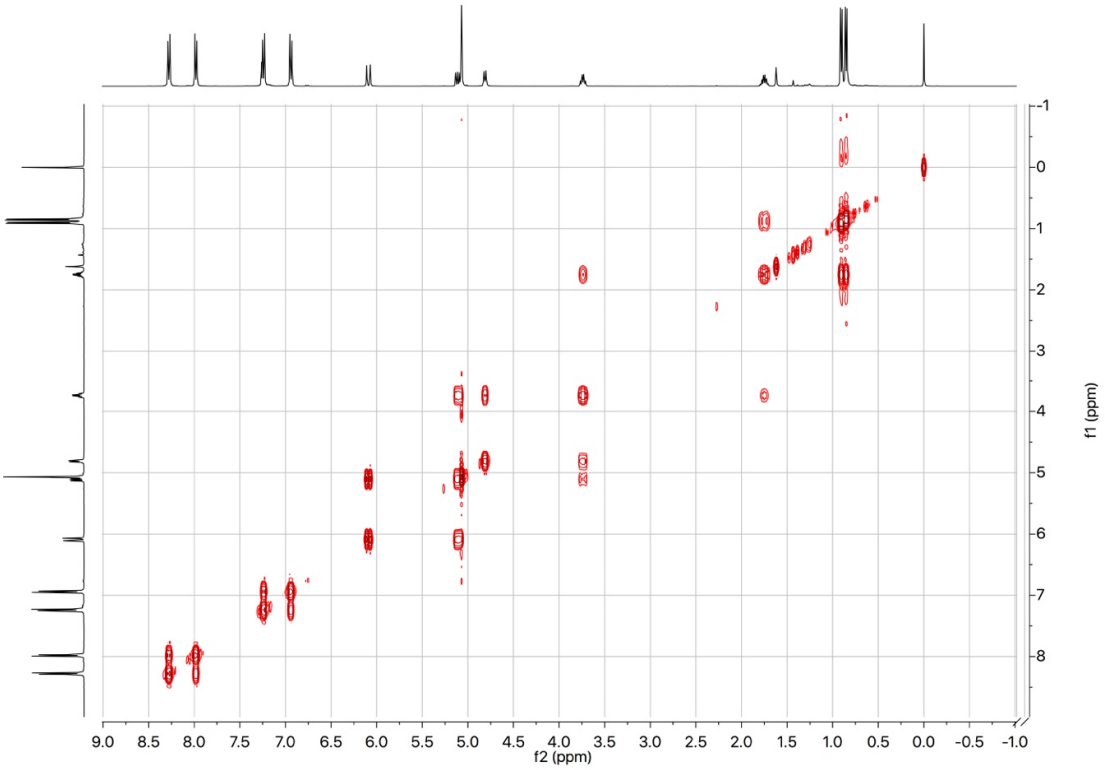

f2 (ppm)
f1 (ppm)

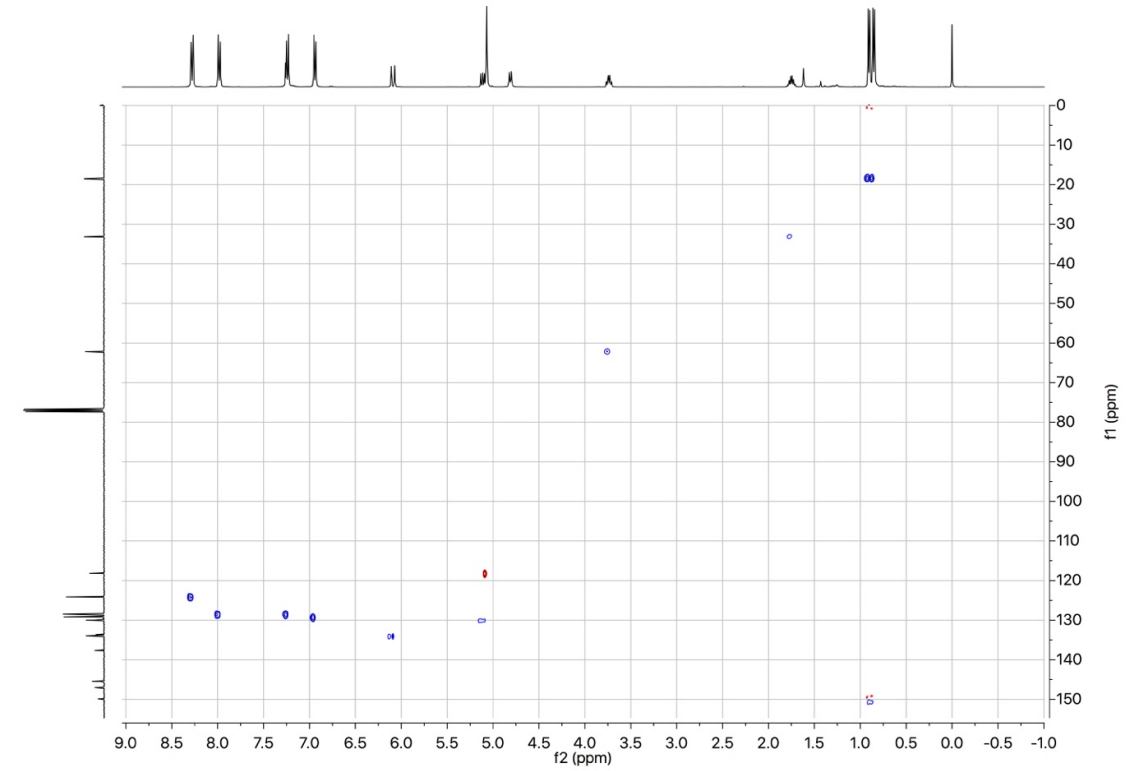

f2 (ppm)
f1 (ppm)

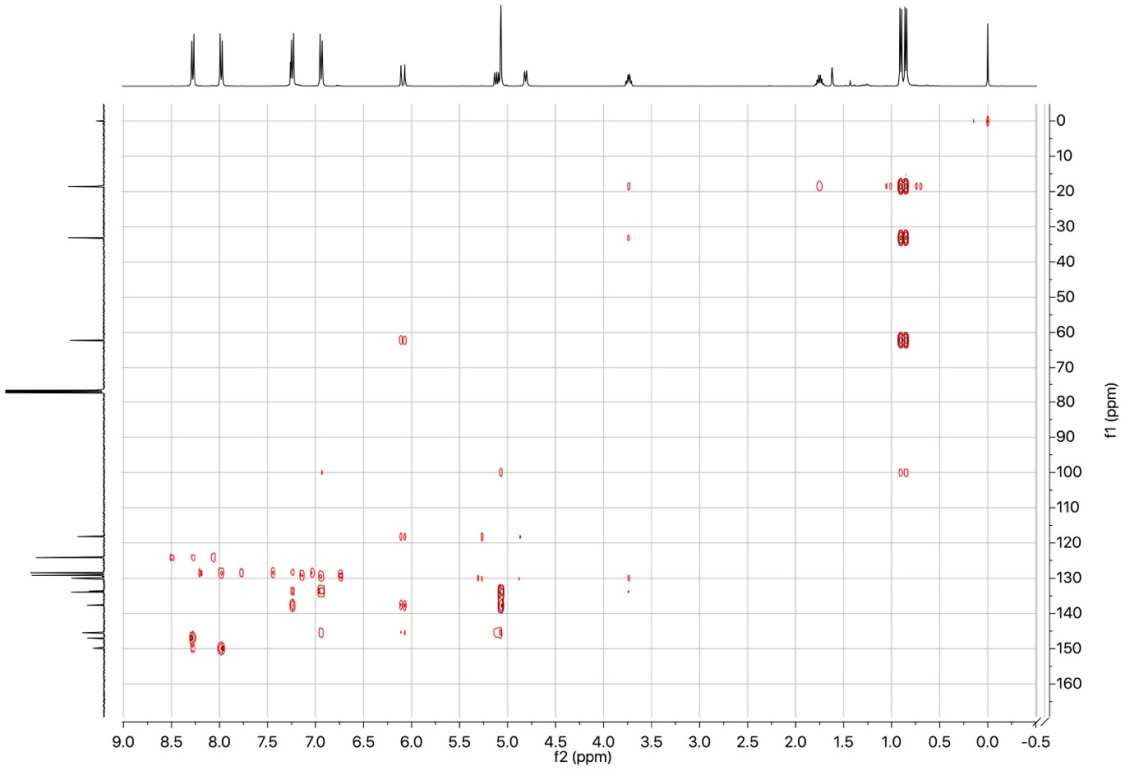
2h


8.29
8.26
7.99
7.97
7.26
7.25
7.23
6.95
6.93
6.11
6.07
5.13
5.11
5.09
5.07
4.82
4.80
3.76
3.74
3.73
3.71
1.81
1.79
1.77
1.76
1.74
1.72
1.71
1.69
0.91
0.89
0.86
0.84
0.00
O2N
H
N
S
O
O
Cl
2.03
2.01
2.33
2.02
1.00
3.05
1.00
1.01
1.01
3.01
3.03
f1 (ppm)

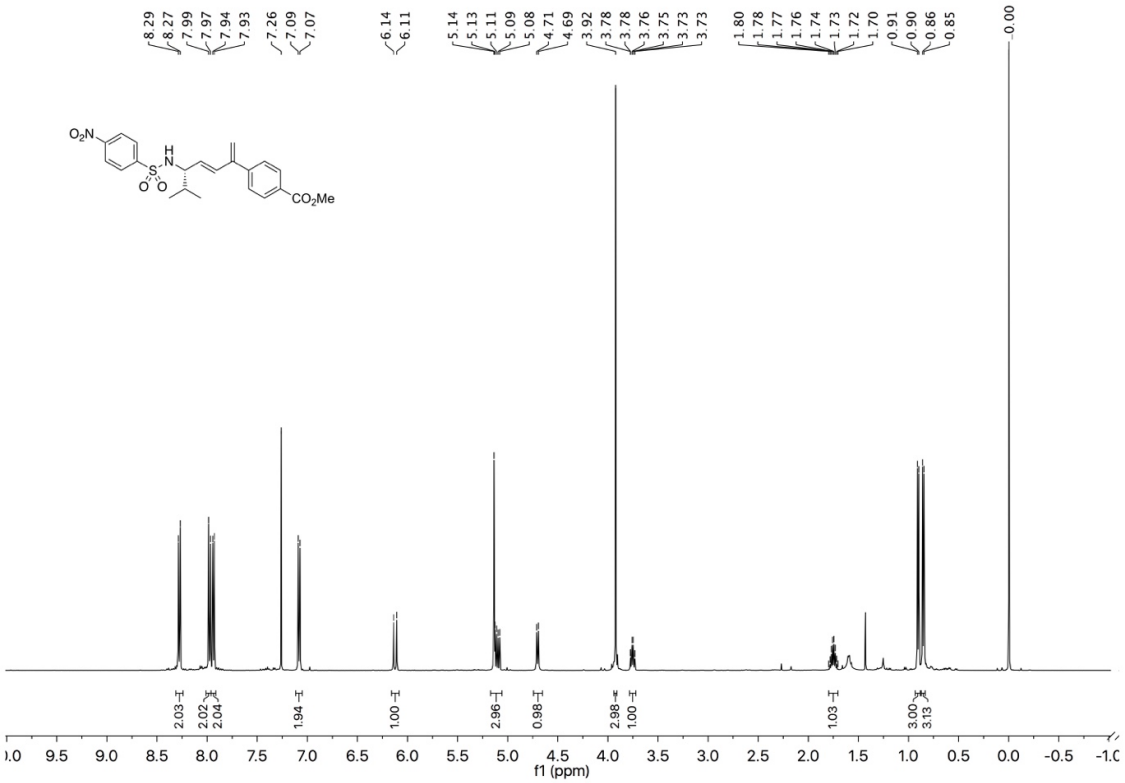

149.86
146.94
145.43
137.66
133.94
133.61
129.94
129.16
128.45
128.42
124.09
118.14
77.32
77.00
76.68
62.16
33.11
18.54
18.46
0.03
f1 (ppm)

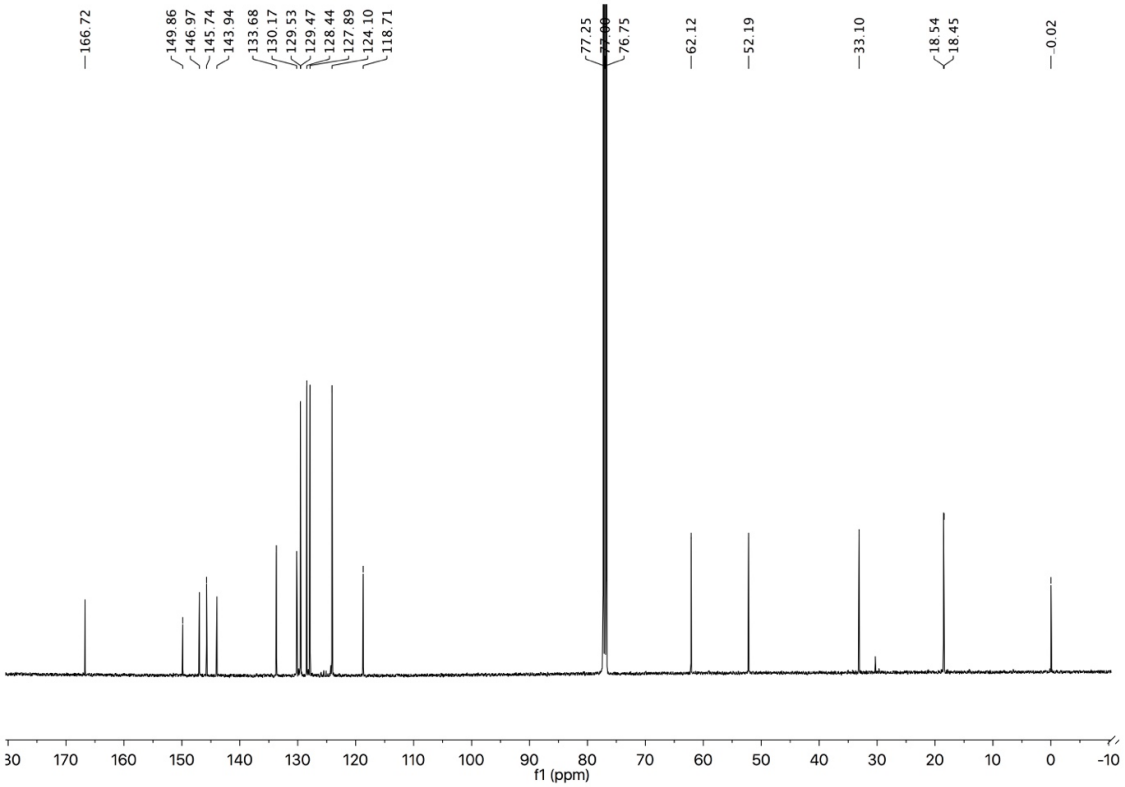

f2 (ppm)
f1 (ppm)

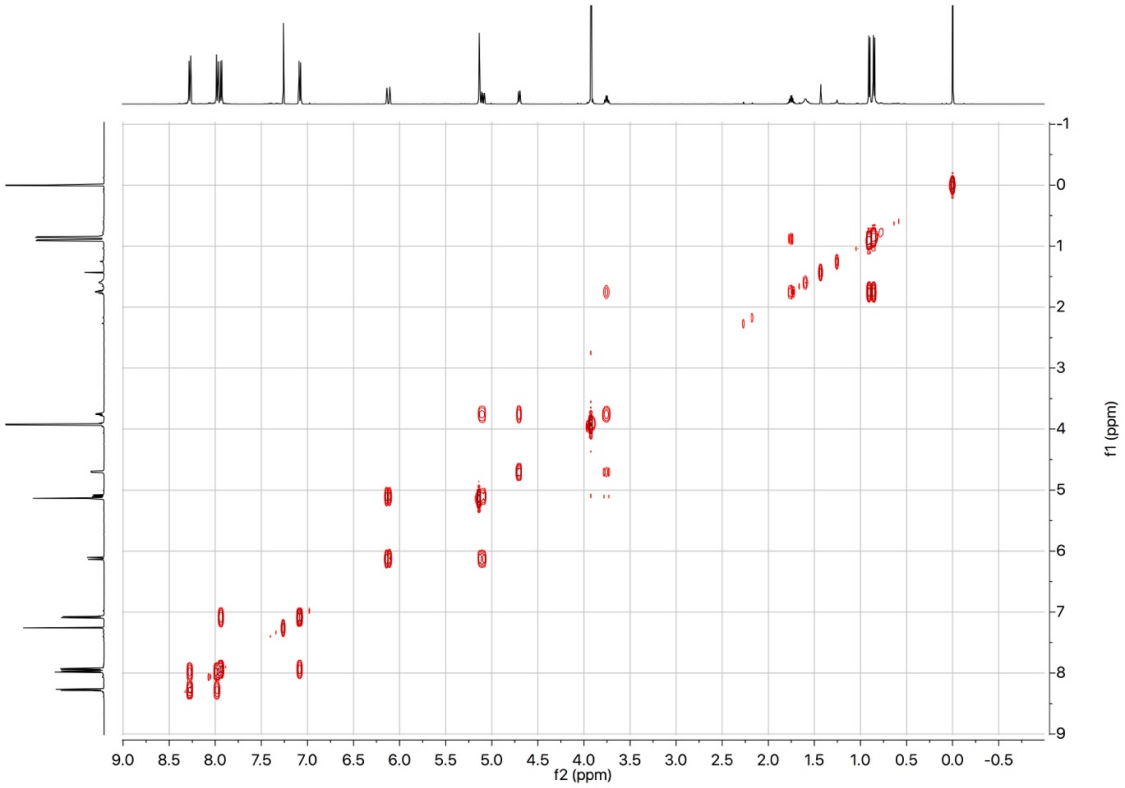

f2 (ppm)
f1 (ppm)

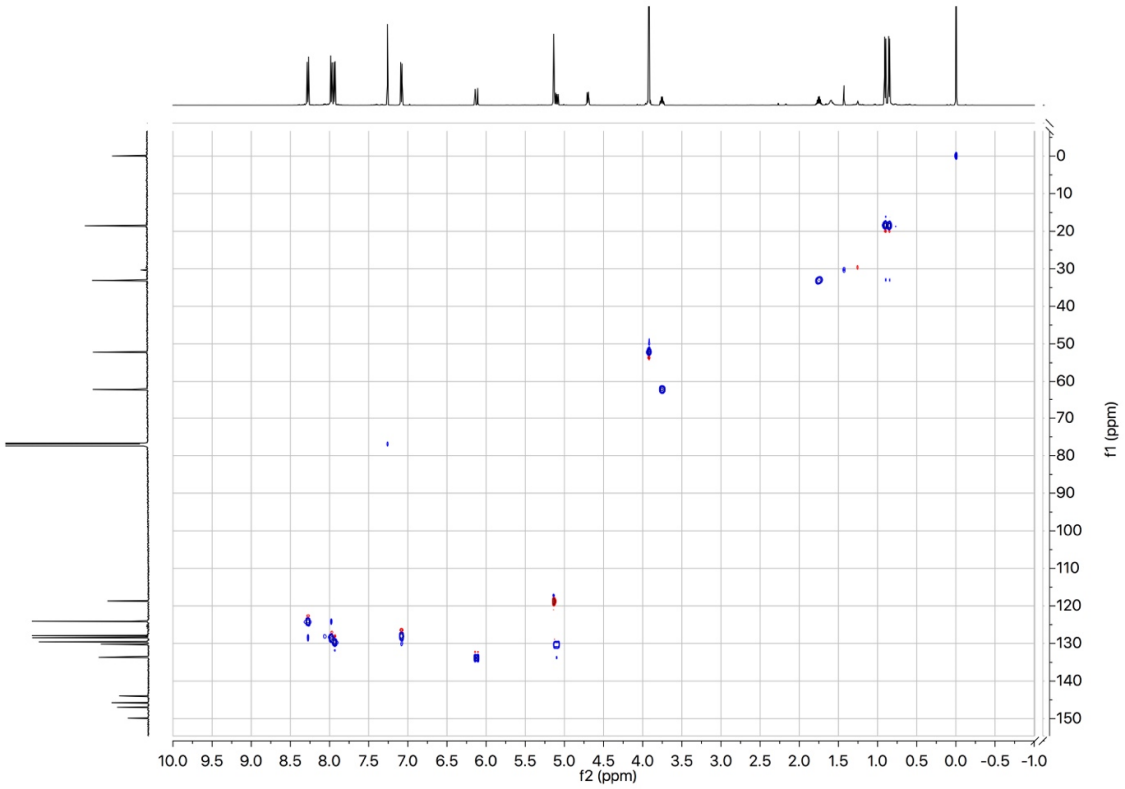

f2 (ppm)
f1 (ppm)

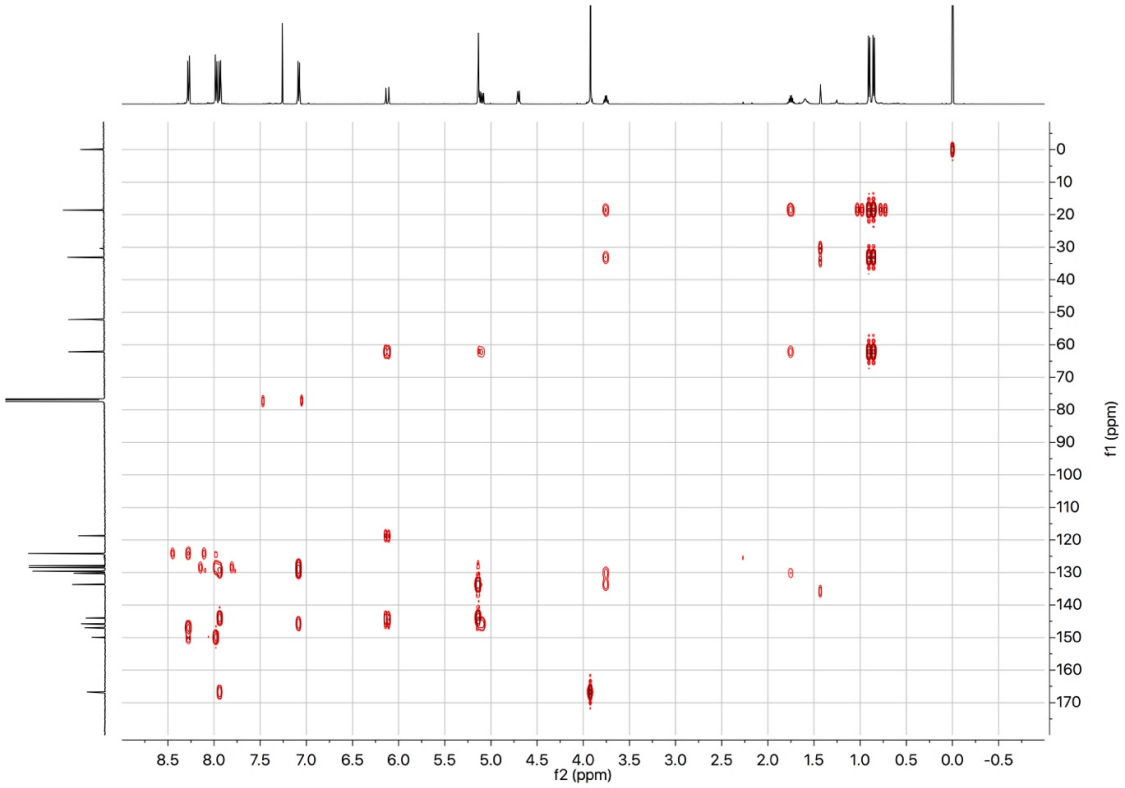
2i


8.29
8.27
7.99
7.97
7.94
7.93
7.26
7.09
7.07
6.14
6.11
5.14
5.13
5.11
5.09
5.08
4.71
4.69
3.92
3.78
3.78
3.76
3.75
3.73
3.73
1.80
1.78
1.77
1.76
1.74
1.73
1.72
1.70
0.91
0.90
0.86
0.85
0.00
O2N
CO2Me
2.03
2.02
2.04
1.94
1.00
2.96
0.98
2.98
1.00
1.03
3.00
3.13
f1 (ppm)

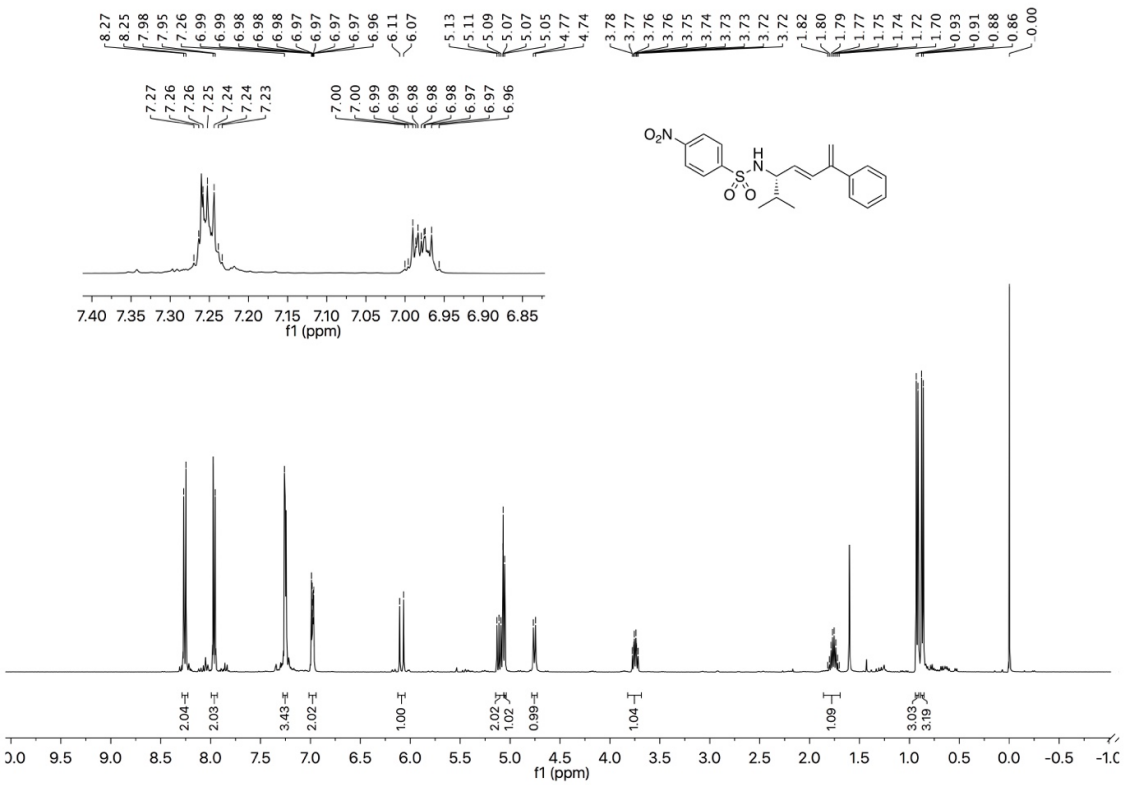

166.72
149.86
146.97
145.74
143.94
133.68
130.17
129.53
129.47
128.44
127.89
124.10
118.71
77.25
77.00
76.75
62.12
52.19
33.10
18.54
18.45
0.02
f1 (ppm)

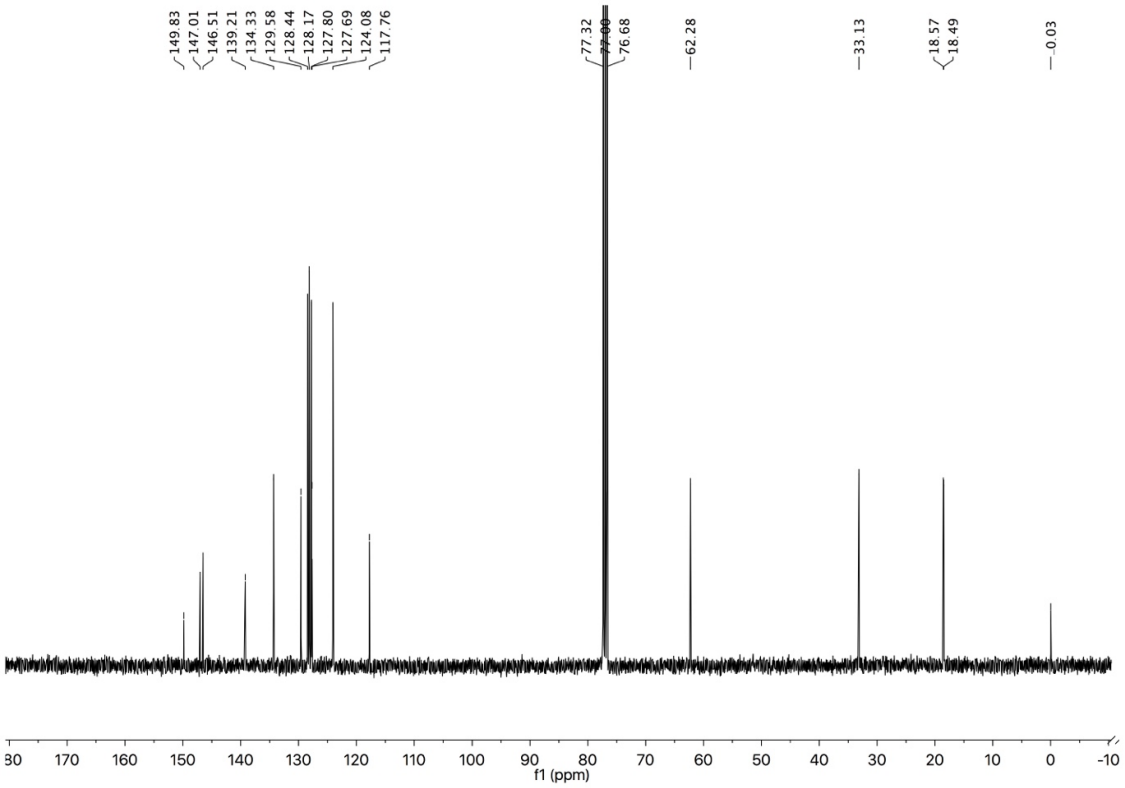

f2 (ppm)
f1 (ppm)

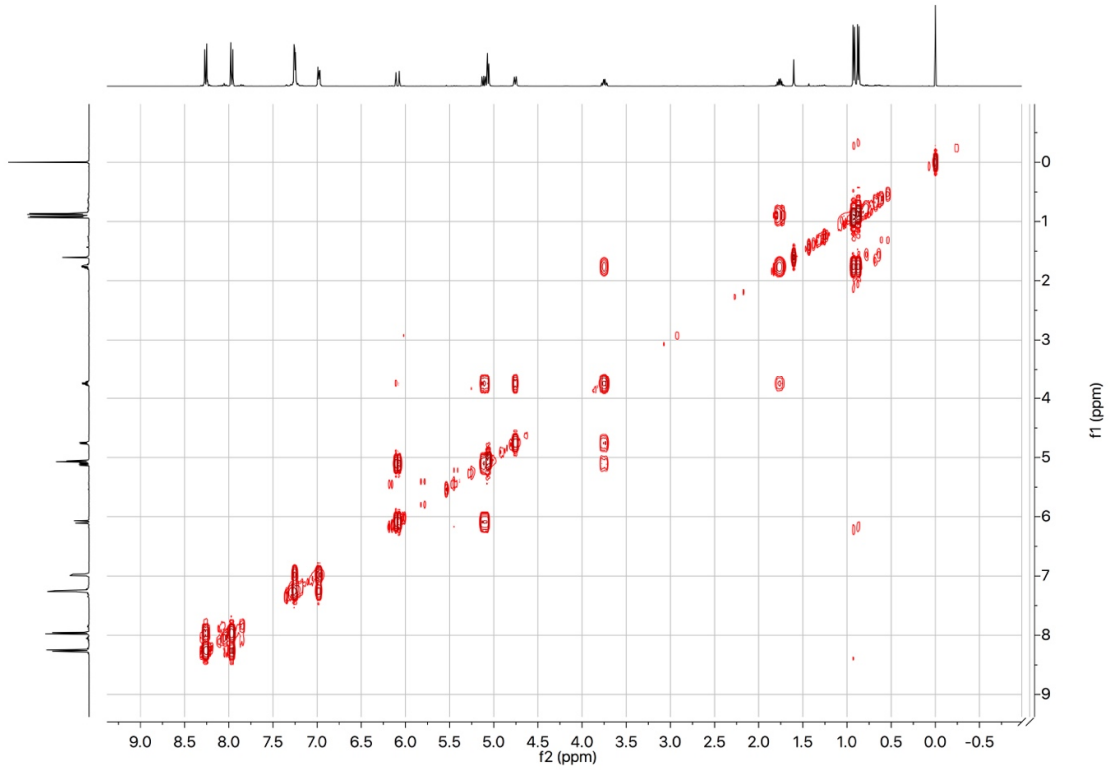

f2 (ppm)
f1 (ppm)

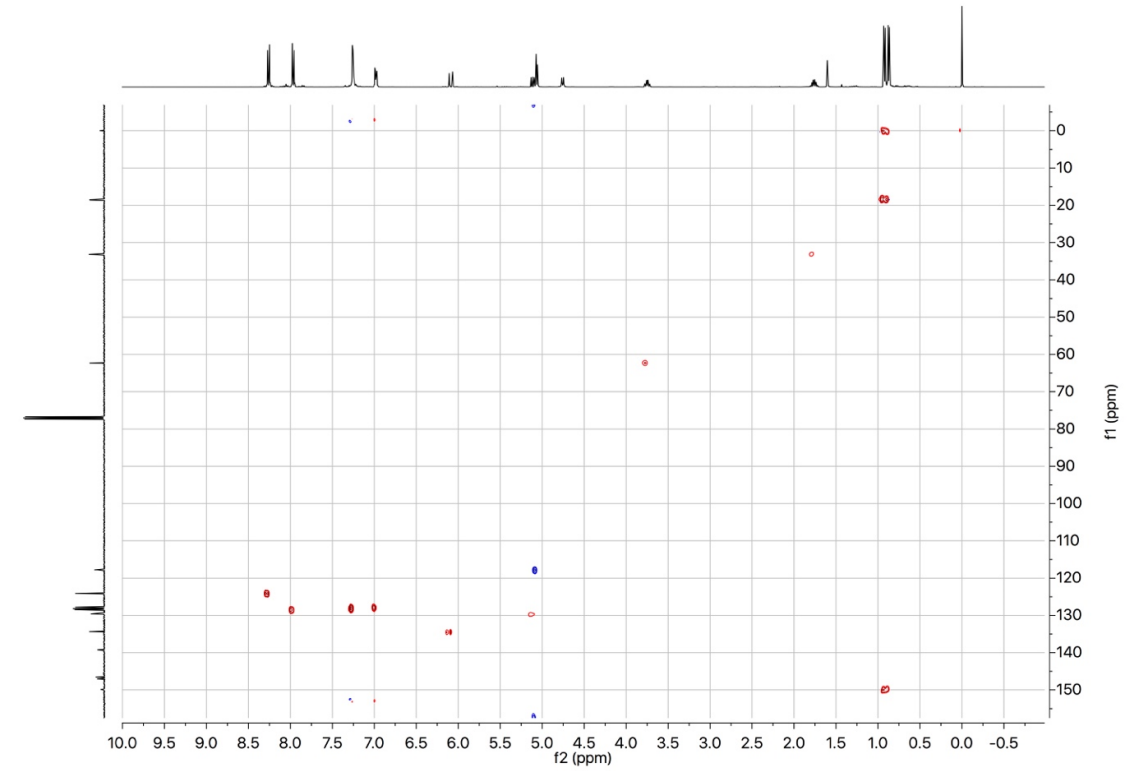


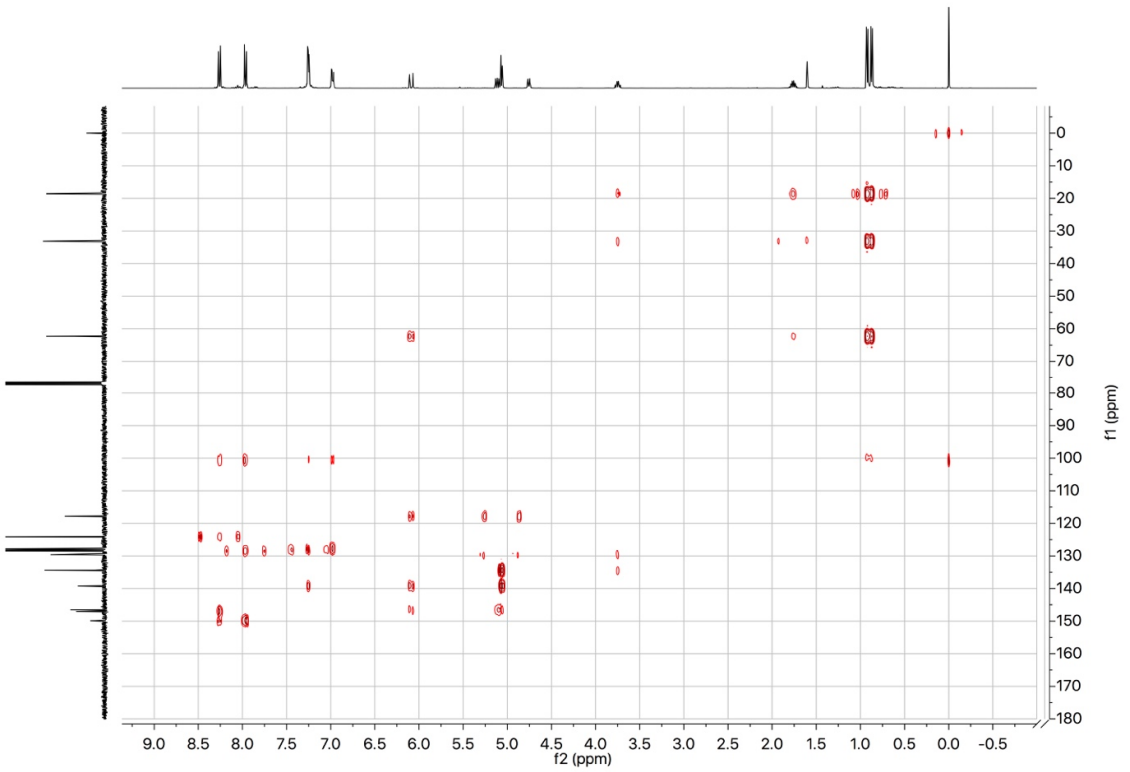
2j



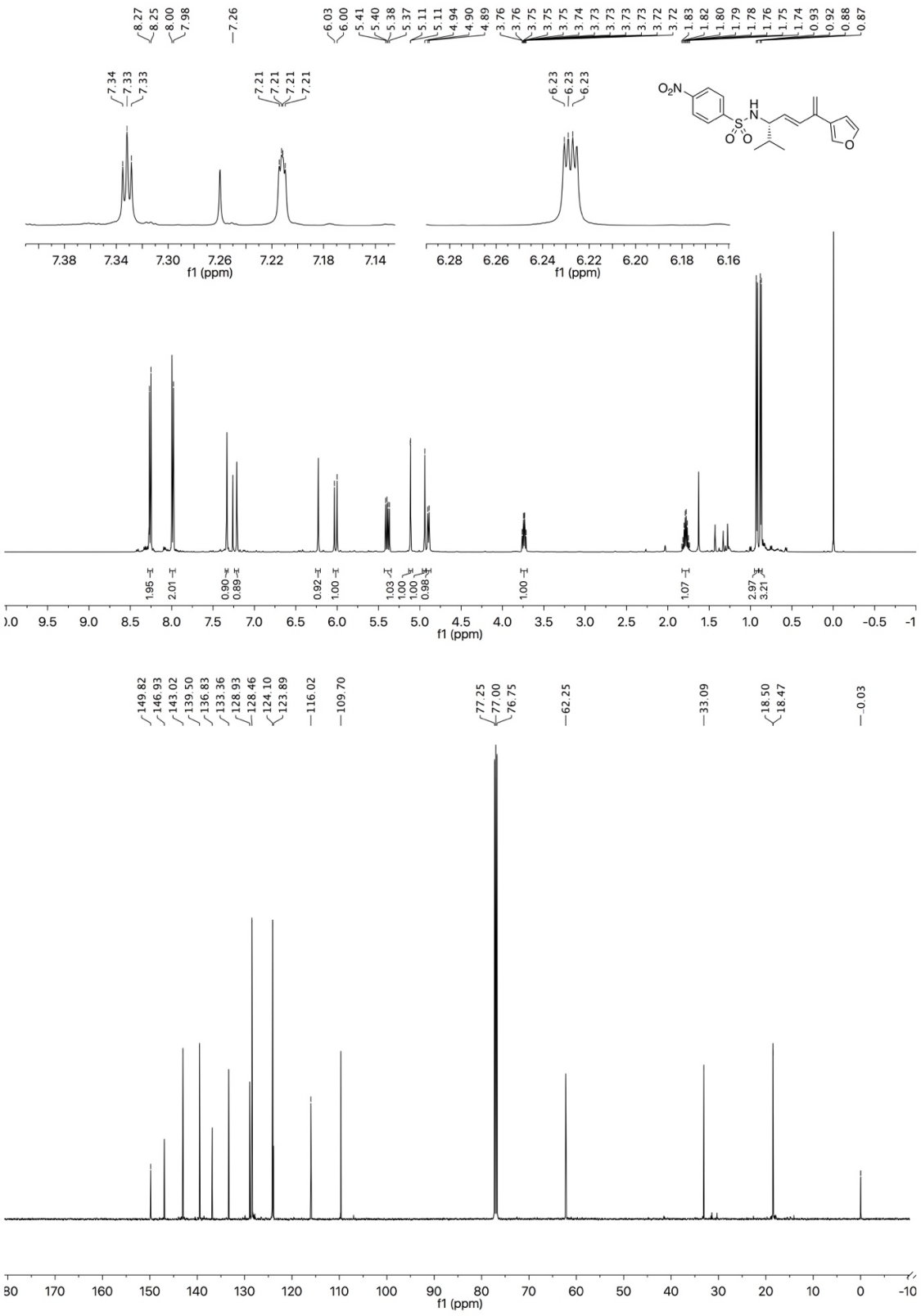

149.83
147.01
146.51
139.21
134.33
129.58
128.44
128.17
127.80
127.69
124.08
117.76
77.32
77.00
76.68
62.28
33.13
18.57
18.49
-0.03
f1 (ppm)

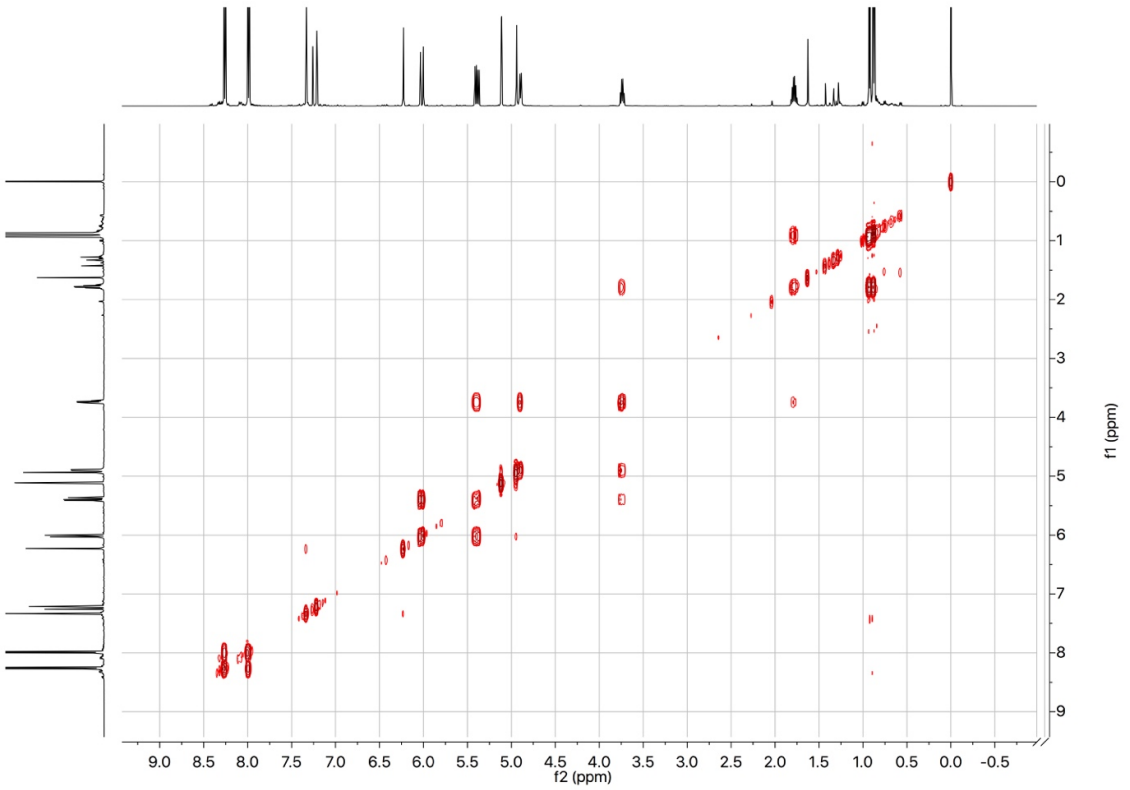

f2 (ppm)
f1 (ppm)

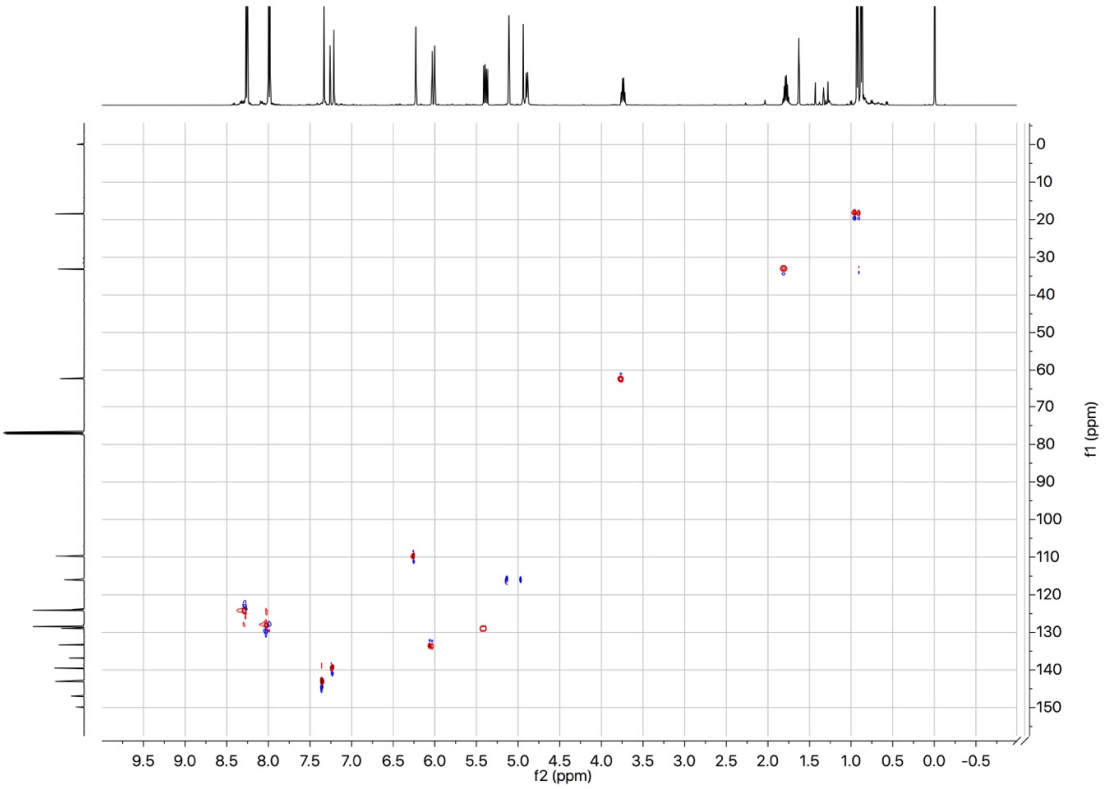

f2 (ppm)
f1 (ppm)

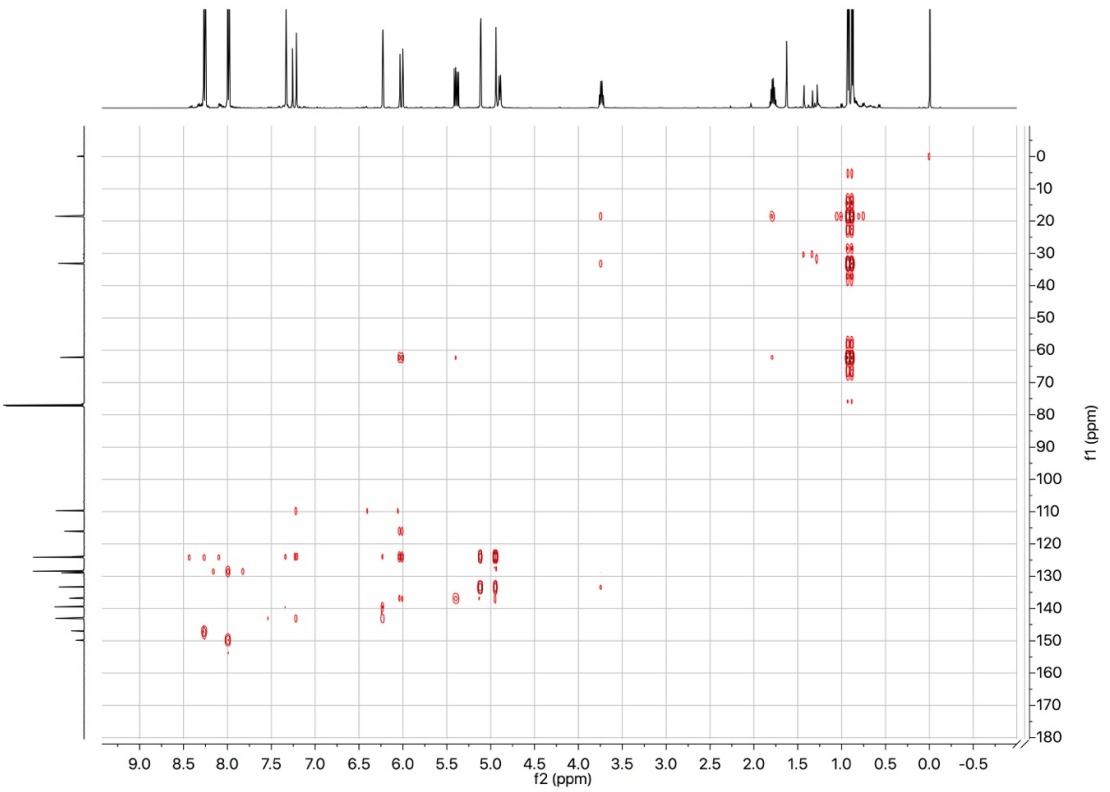

f2 (ppm)
f1 (ppm)

2k

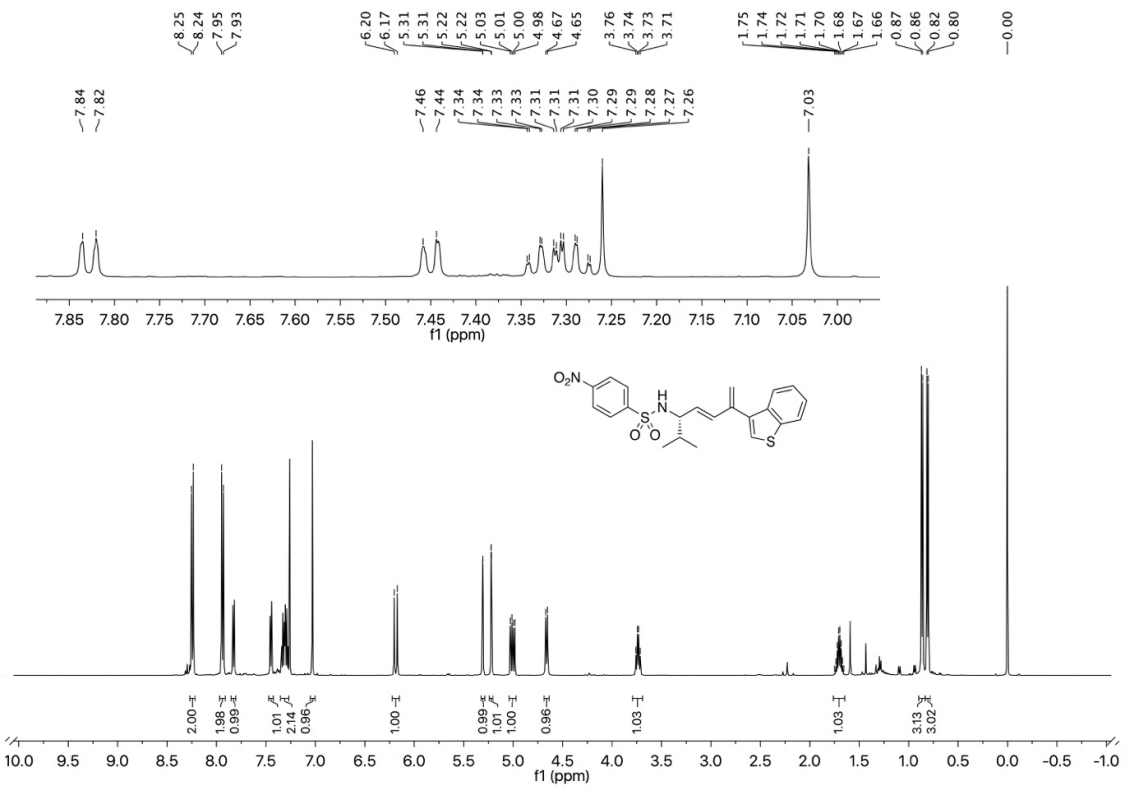

8.27
8.25
8.00
7.98
7.26
6.03
6.00
5.41
5.40
5.38
5.37
5.11
5.11
4.94
4.90
4.89
3.76
3.76
3.75
3.75
3.75
3.74
3.73
3.73
3.73
3.73
3.72
3.72
1.83
1.82
1.80
1.79
1.78
1.76
1.75
1.74
0.93
0.92
0.88
0.87
7.34
7.33
7.33
7.21
7.21
7.21
7.21
6.23
6.23
6.23
O2N
H
N
S
O
O
O
7.38
7.34
7.30
7.26
7.22
7.18
7.14
f1 (ppm)
6.28
6.26
6.24
6.22
6.20
6.18
6.16
f1 (ppm)
1.95
2.01
0.90
0.89
0.92
1.00
1.03
1.00
1.00
0.98
1.00
1.07
2.97
3.21
f1 (ppm)
149.82
146.93
143.02
139.50
136.83
133.36
128.93
128.46
124.10
123.89
116.02
109.70
77.25
77.00
76.75
62.25
33.09
18.50
18.47
0.03
f1 (ppm)

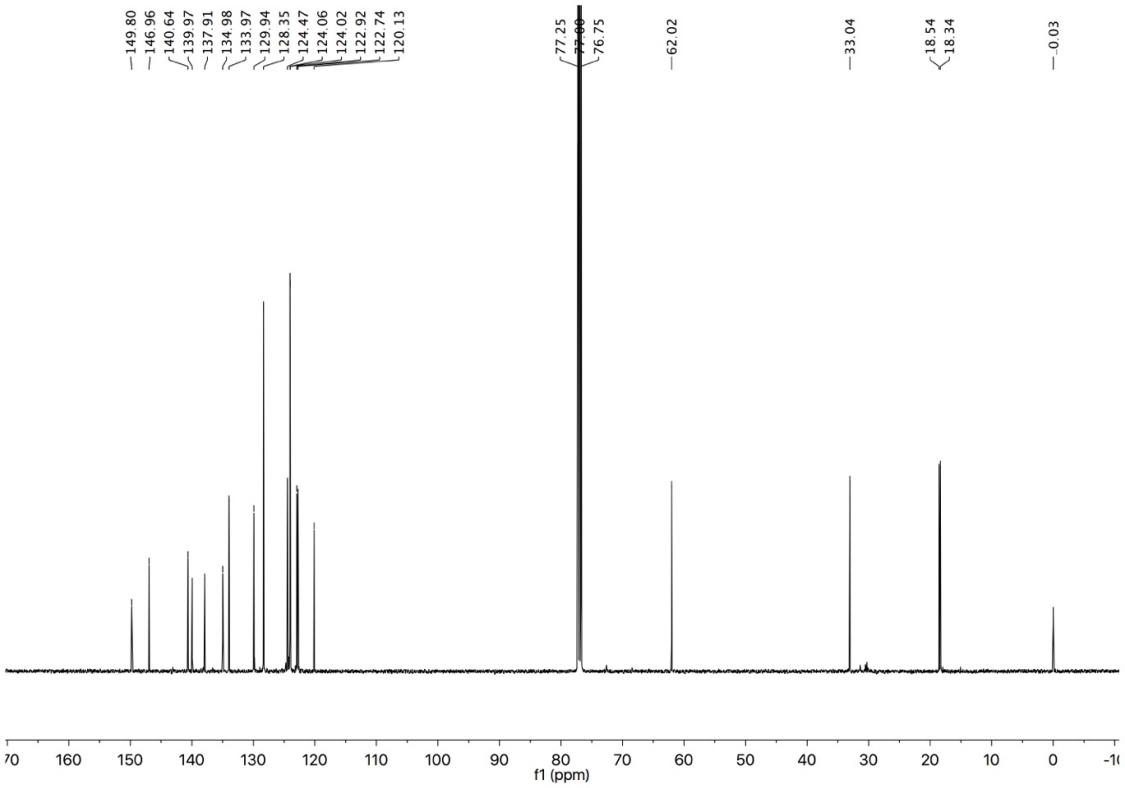

f2 (ppm)
f1 (ppm)

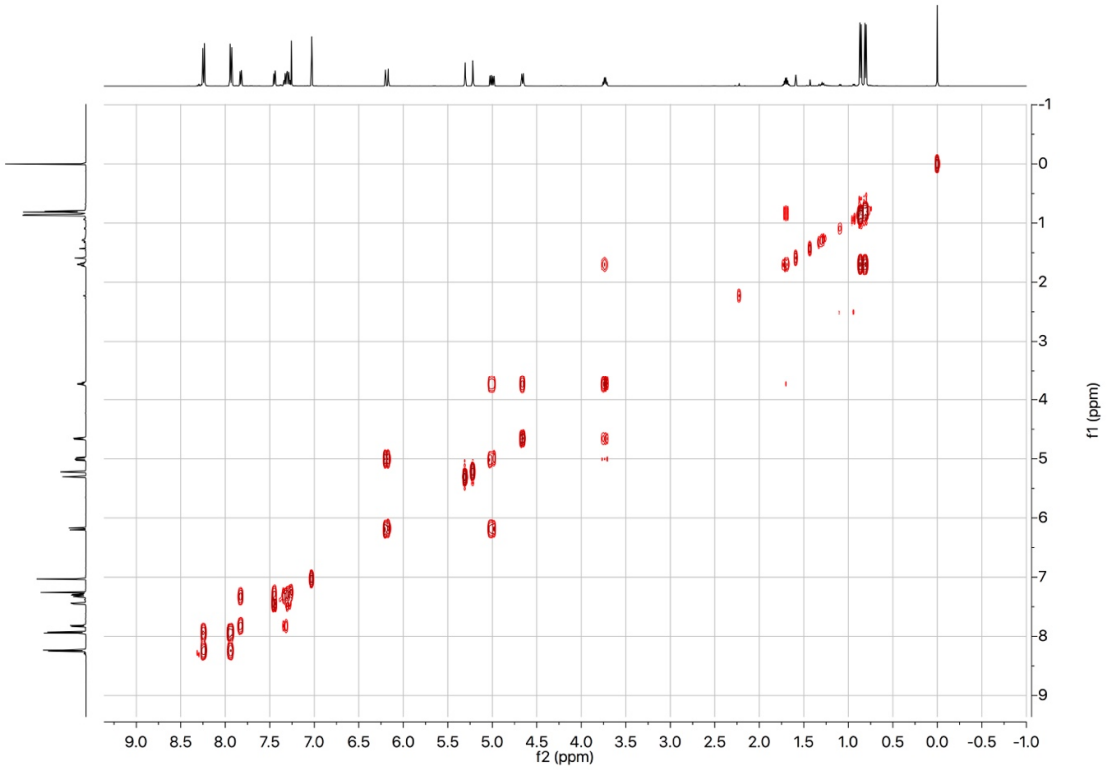

f2 (ppm)
f1 (ppm)

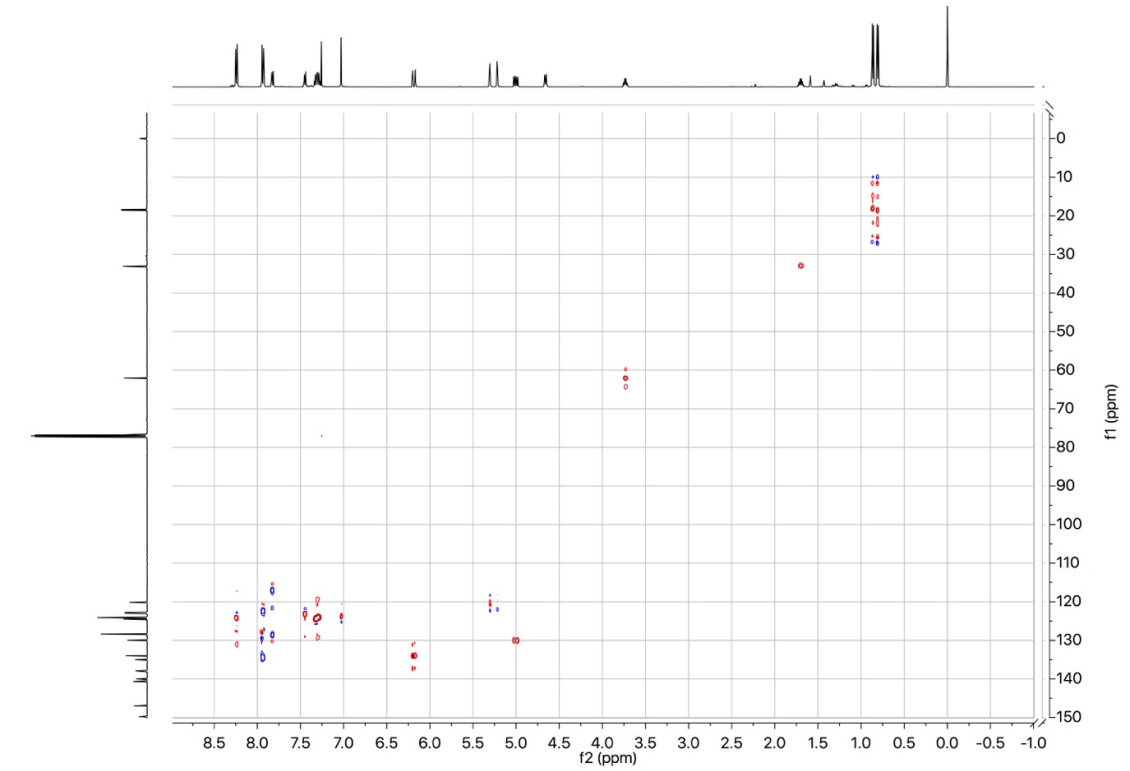

f2 (ppm)
f1 (ppm)

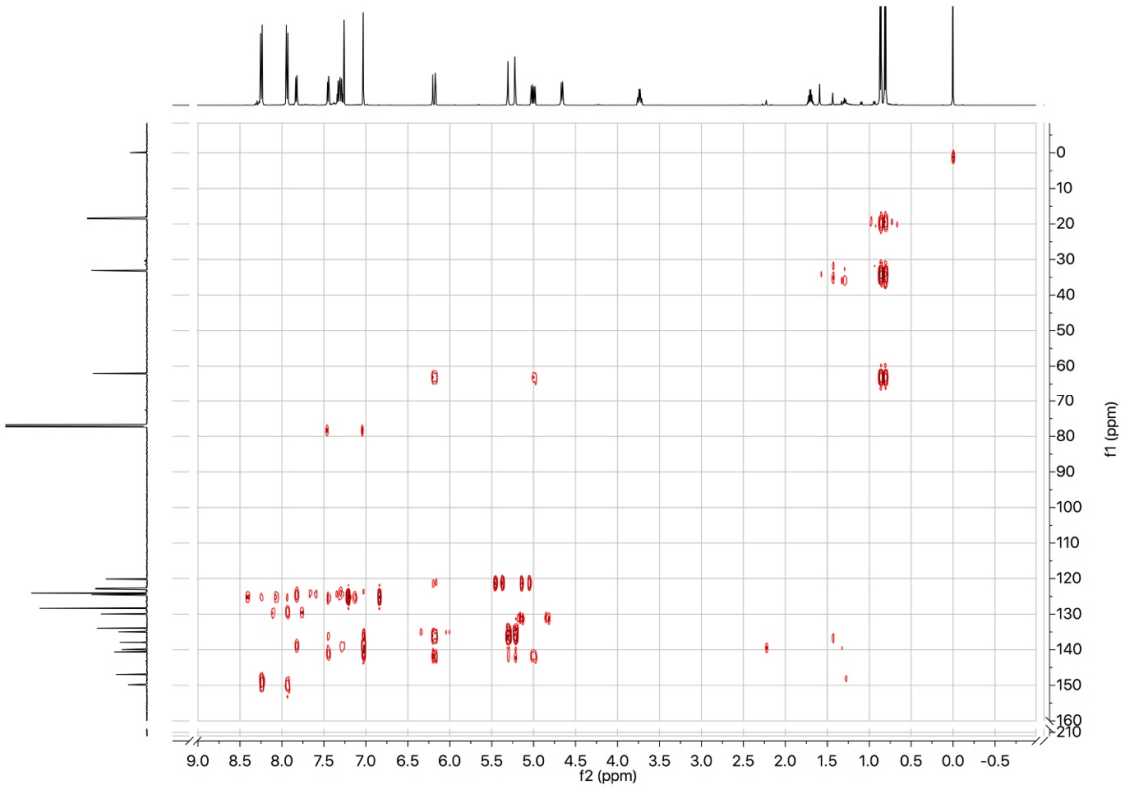
2l


8.25
8.24
7.95
7.93
6.20
6.17
5.31
5.31
5.22
5.22
5.03
5.01
5.00
4.98
4.67
4.65
3.76
3.74
3.73
3.71
1.75
1.74
1.72
1.71
1.70
1.68
1.67
1.66
0.87
0.86
0.82
0.80
0.00
7.84
7.82
7.46
7.44
7.34
7.34
7.33
7.33
7.31
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.26
7.03
f1 (ppm)
O2N
H
N
S
O
O
S
2.00
1.98
0.99
1.01
2.14
0.96
1.00
0.99
1.01
1.00
0.96
1.03
1.03
3.13
3.02
f1 (ppm)

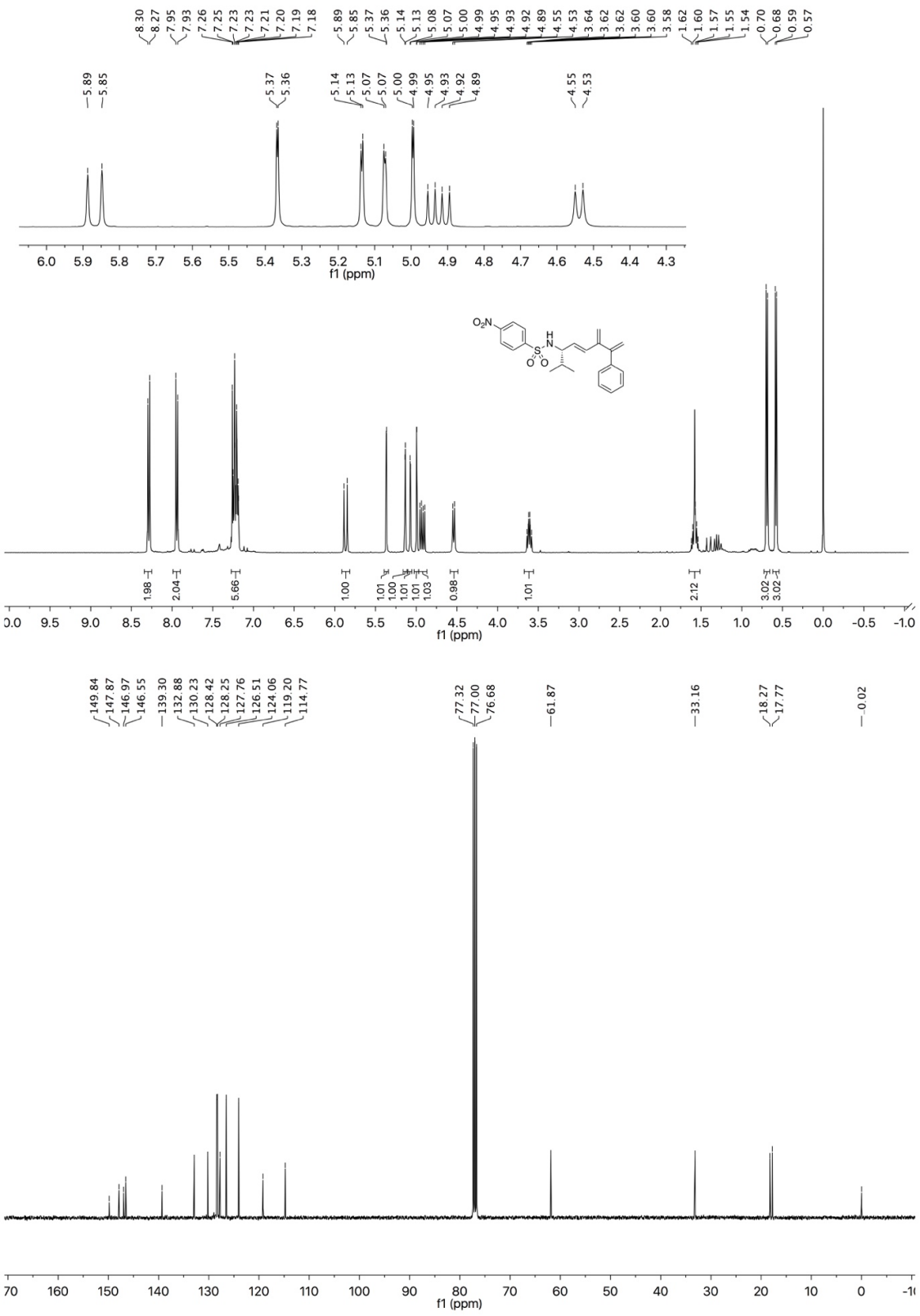

149.80
146.96
140.64
139.97
137.91
134.98
133.97
129.94
128.35
124.47
124.06
124.02
122.92
122.74
120.13
77.25
77.00
76.75
62.02
33.04
18.54
18.34
0.03
f1 (ppm)

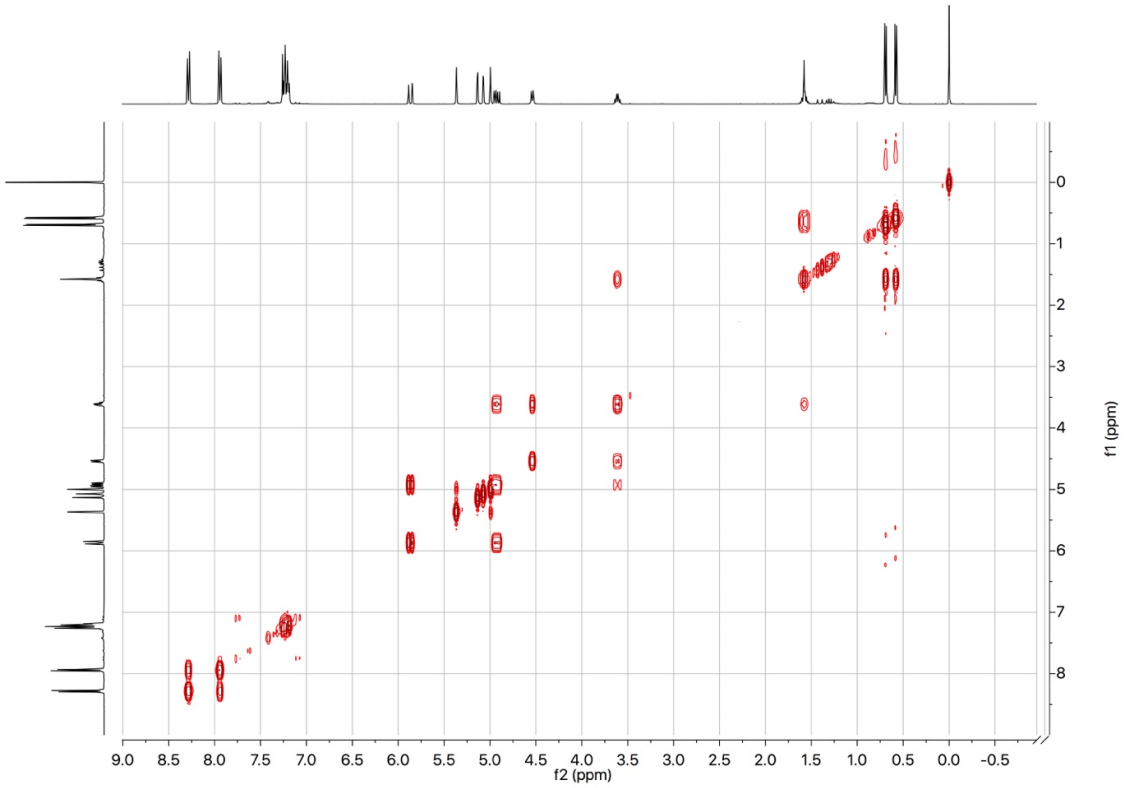

f2 (ppm)
f1 (ppm)

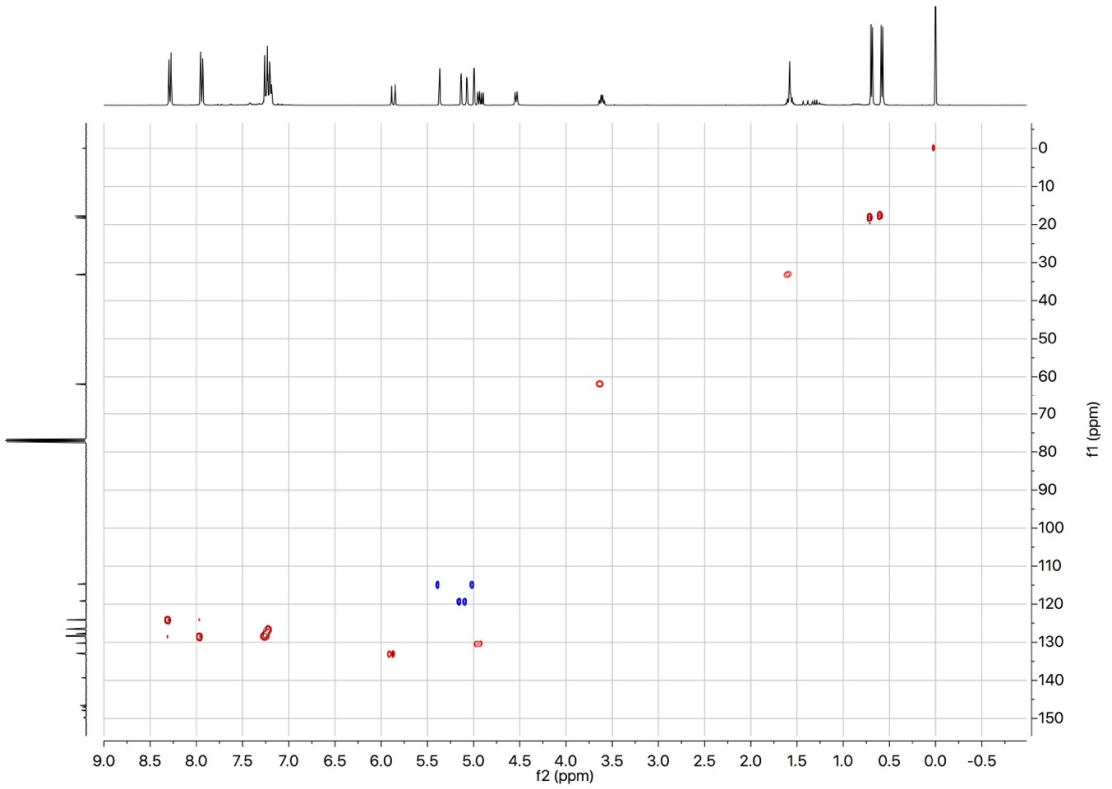

f2 (ppm)
f1 (ppm)

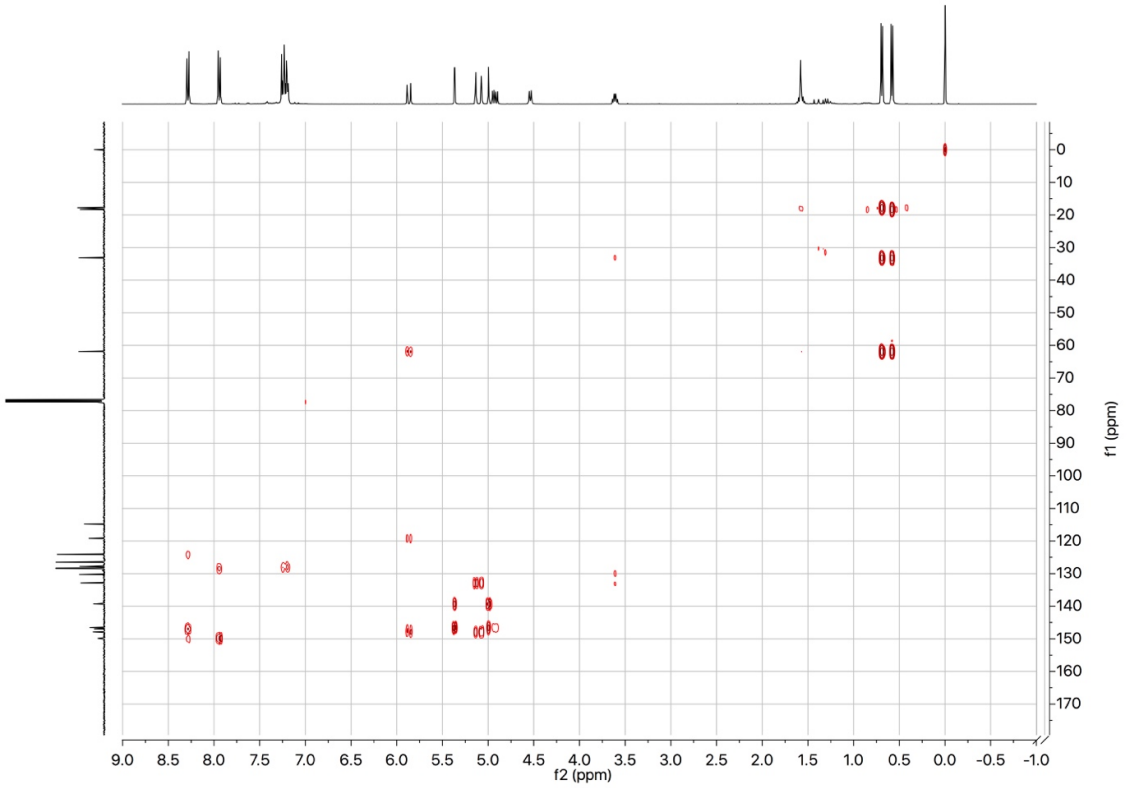

f2 (ppm)
f1 (ppm)

2m

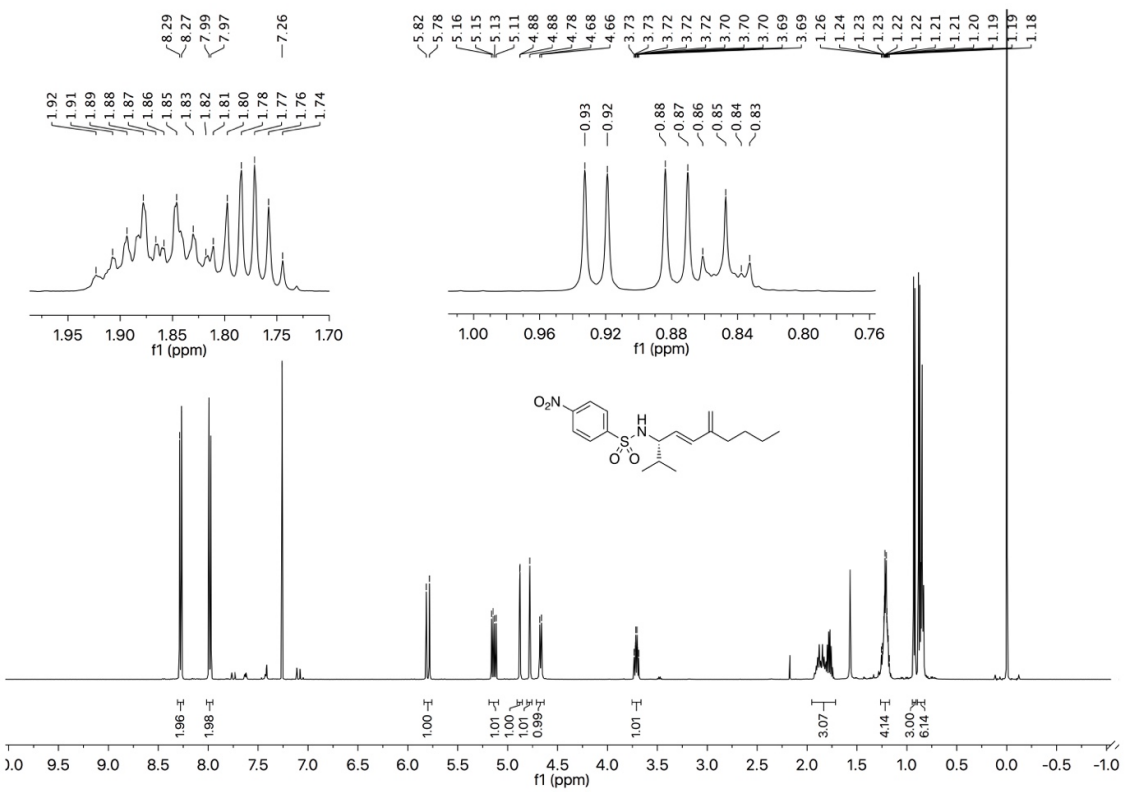


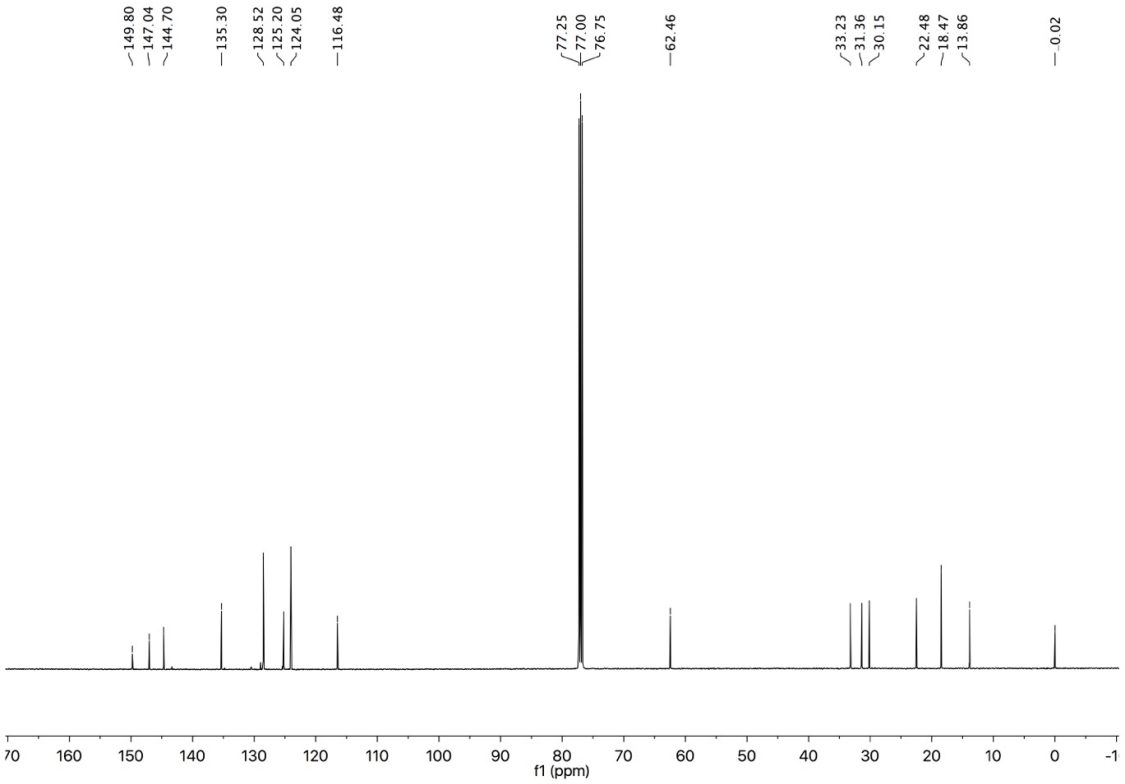

f2 (ppm)
f1 (ppm)

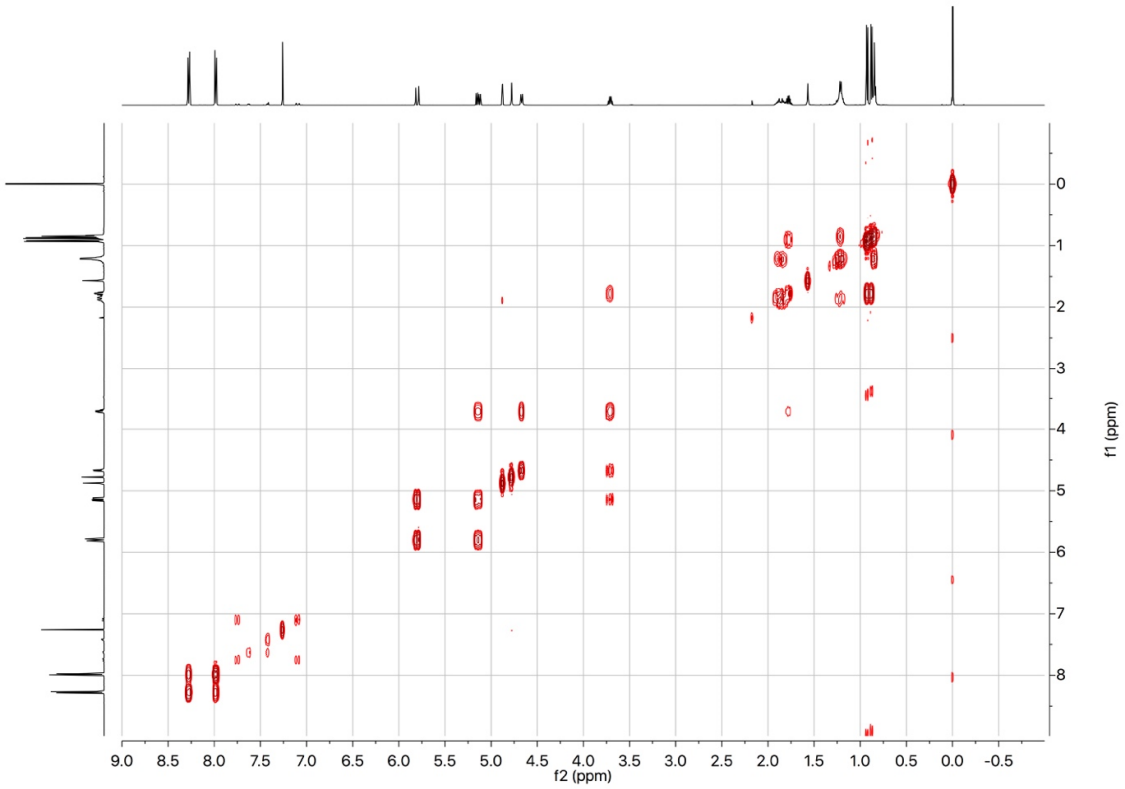

f2 (ppm)
f1 (ppm)

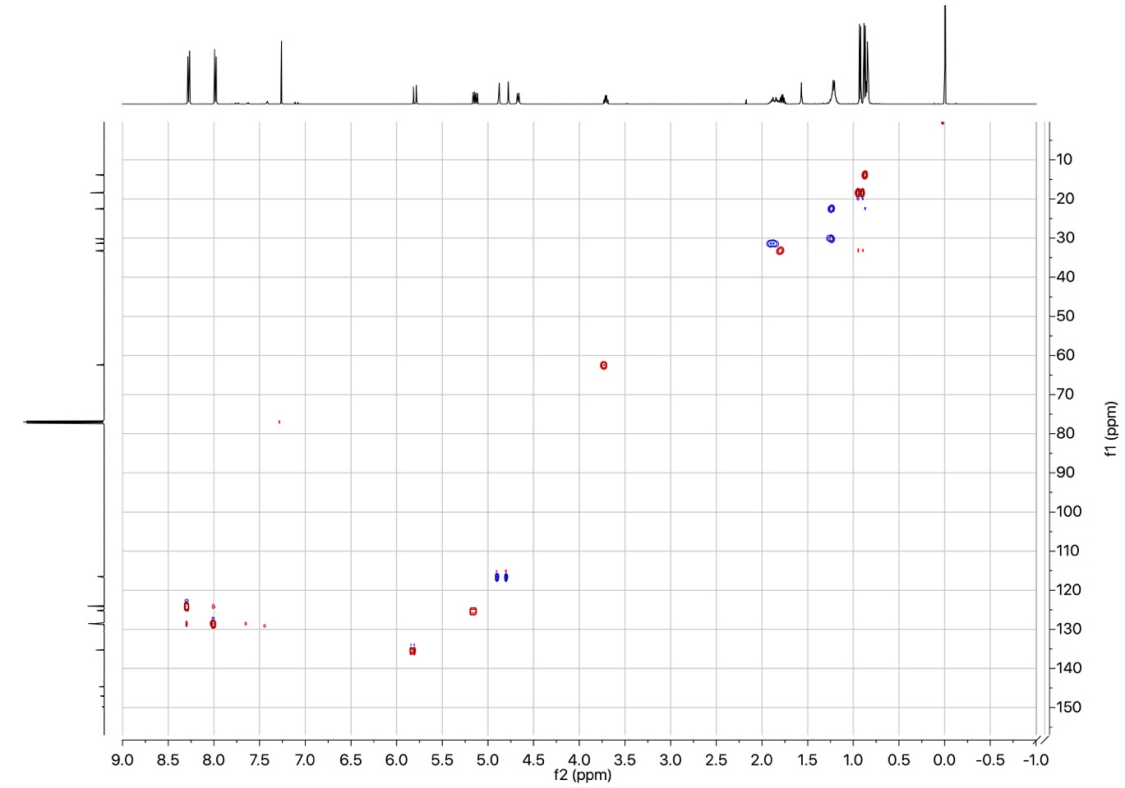


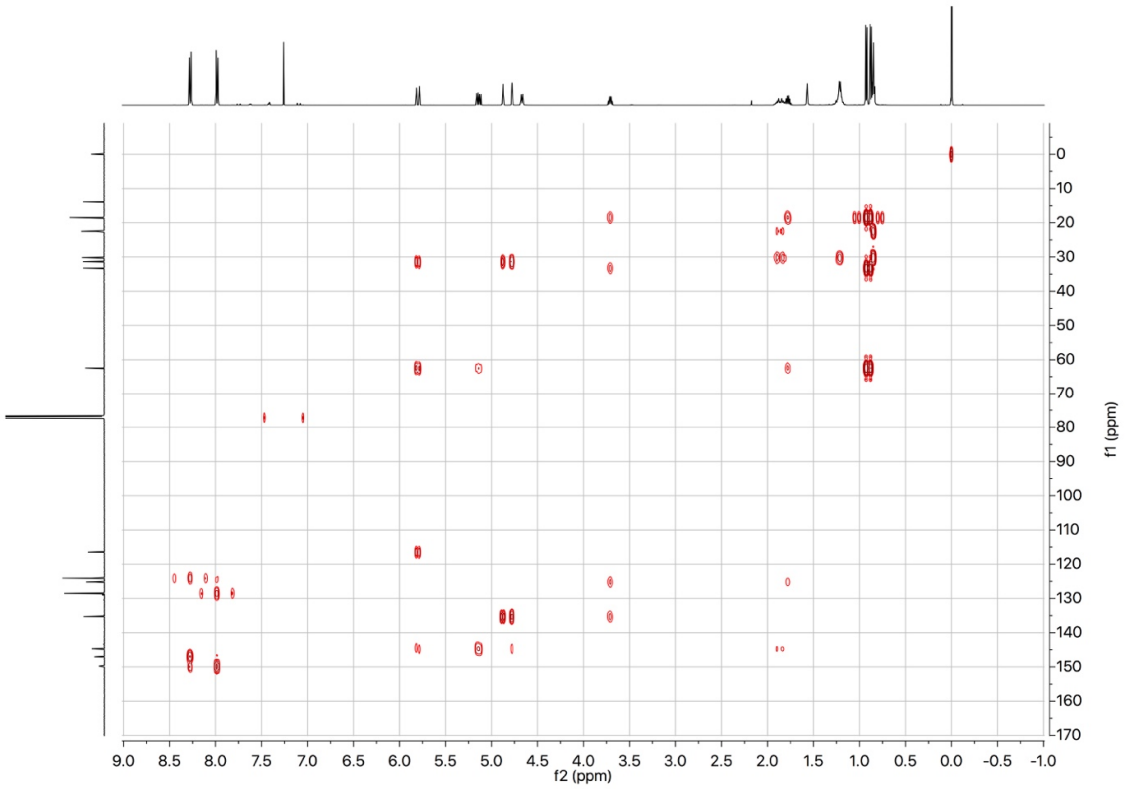
2n



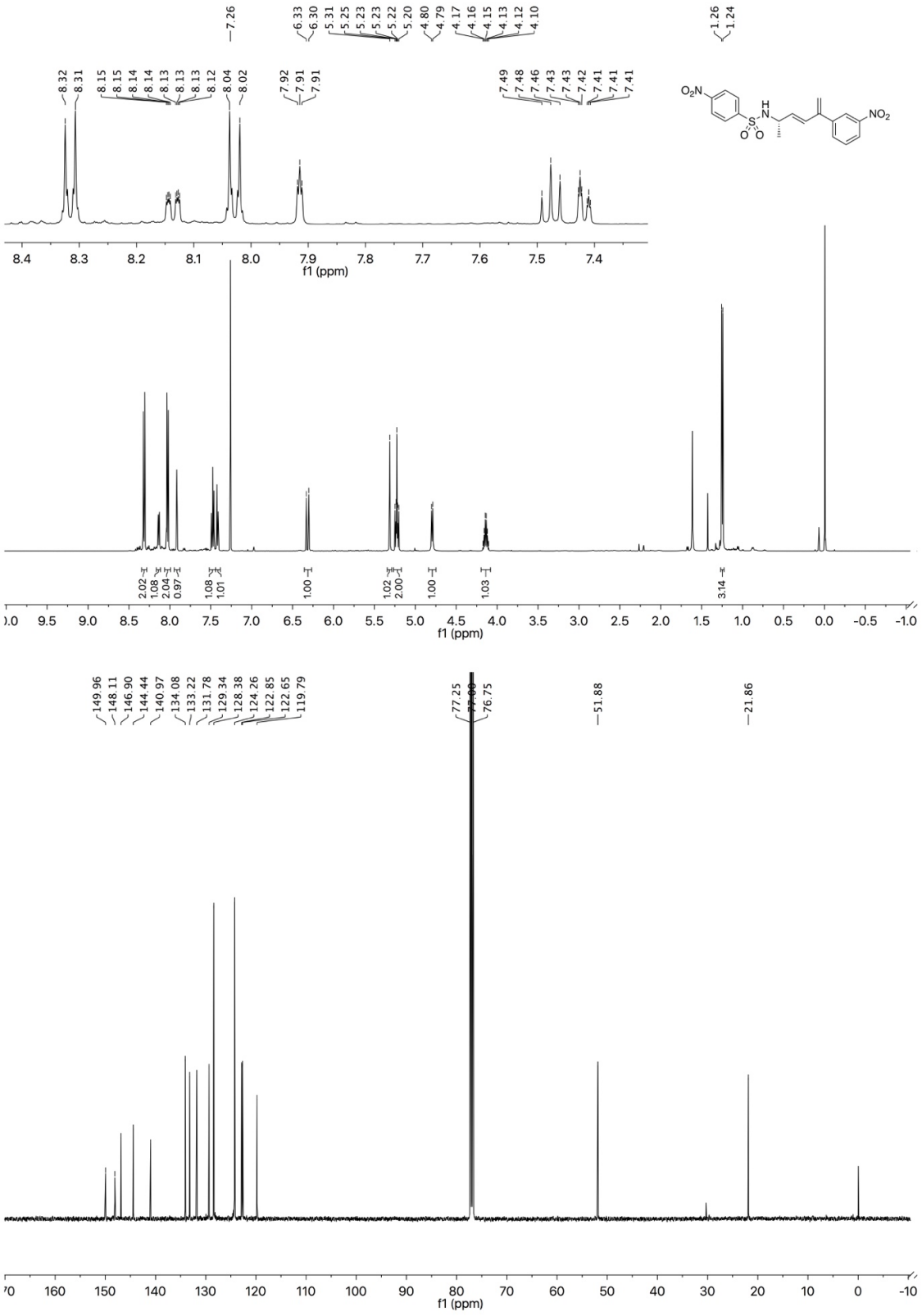

149.80
147.04
144.70
135.30
128.52
125.20
124.05
116.48
77.25
77.00
76.75
62.46
33.23
31.36
30.15
22.48
18.47
13.86
0.02
f1 (ppm)

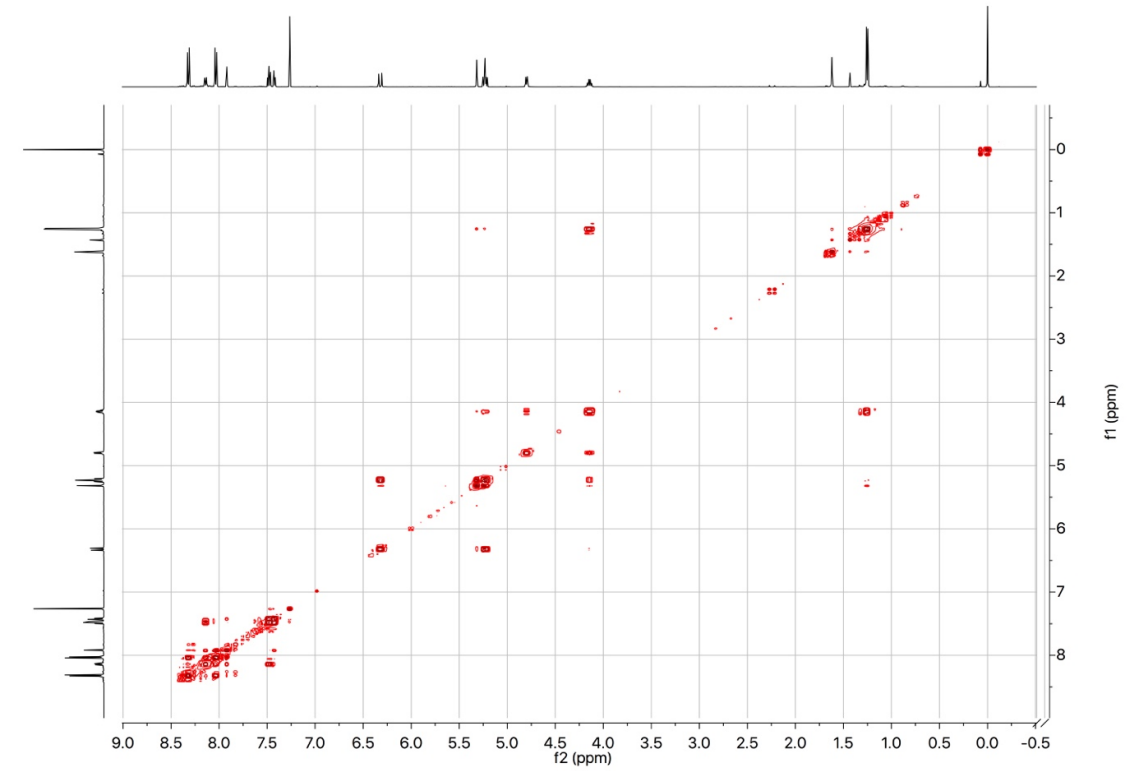

f2 (ppm)
f1 (ppm)

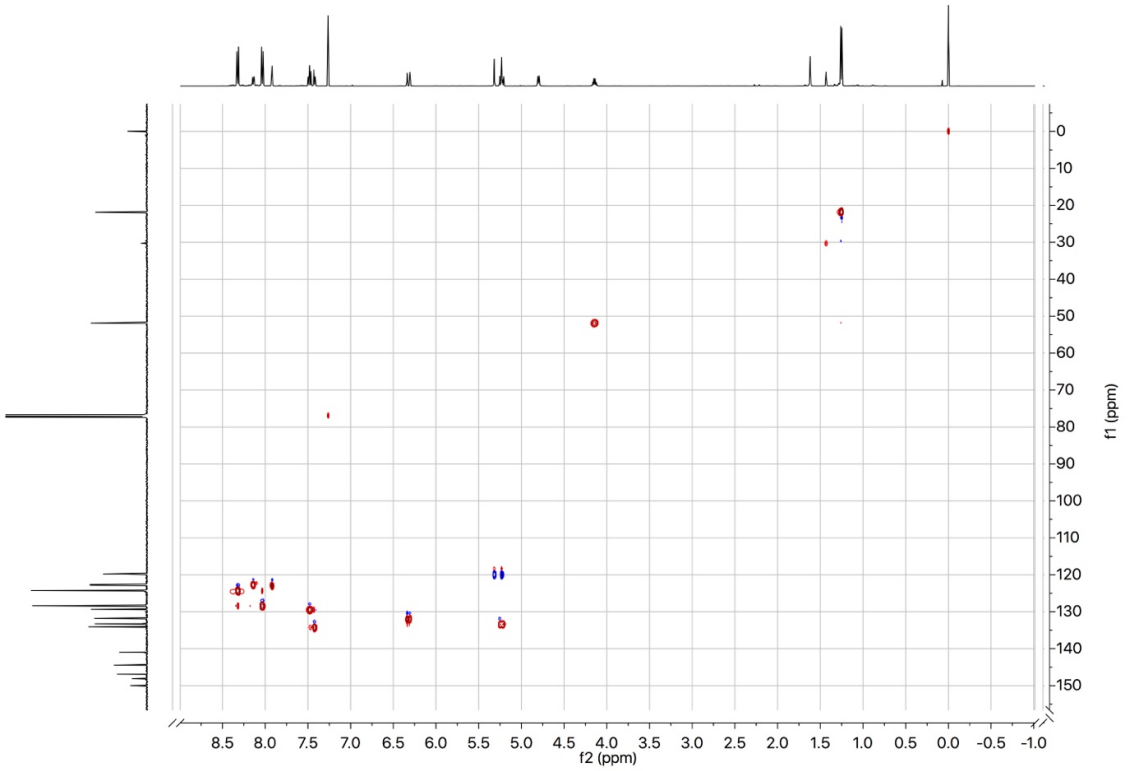

f2 (ppm)
f1 (ppm)

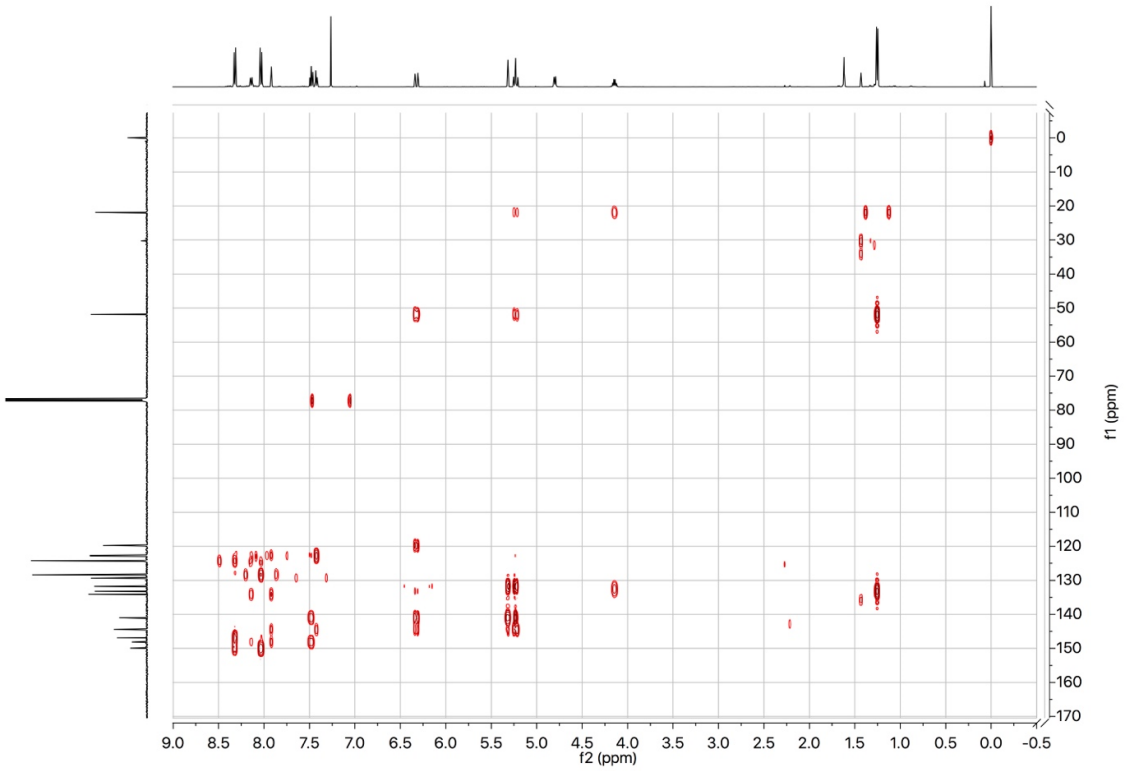

f2 (ppm)
f1 (ppm)

2o

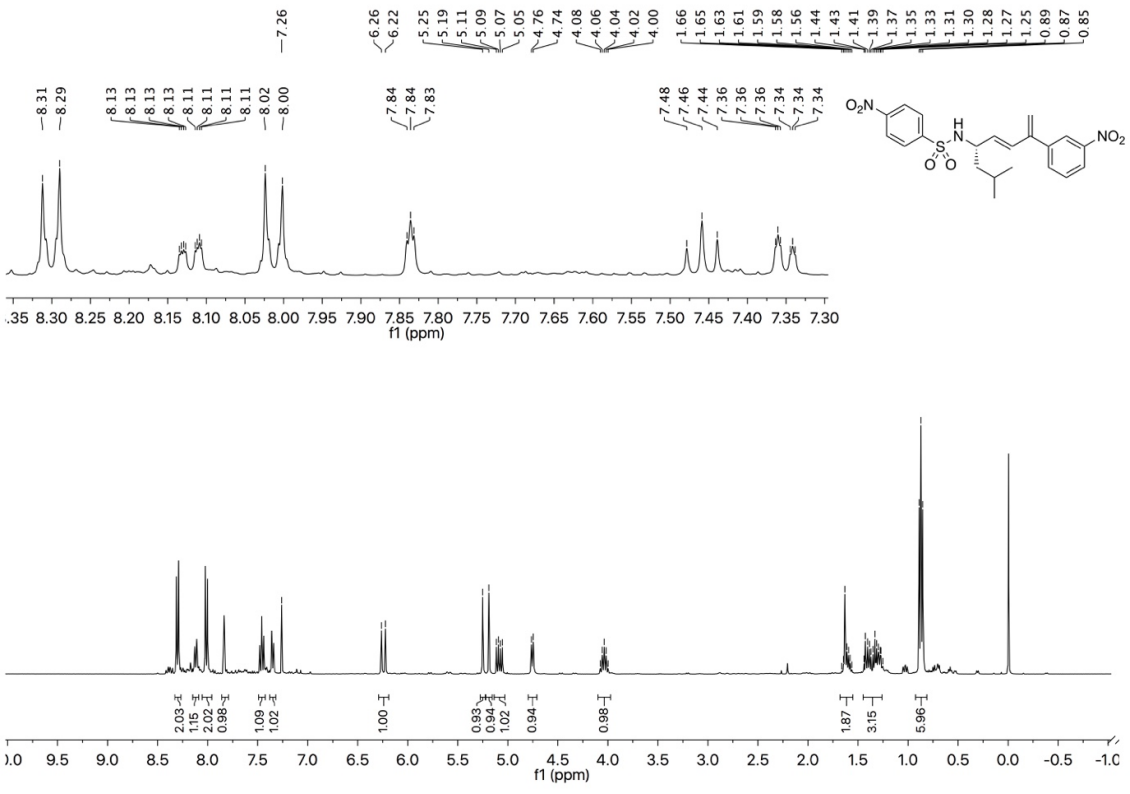

7.26
6.33
6.30
5.31
5.25
5.23
5.23
5.22
5.20
4.80
4.79
4.17
4.16
4.15
4.13
4.12
4.10
1.26
1.24
8.32
8.31
8.15
8.15
8.14
8.14
8.13
8.13
8.13
8.12
8.04
8.02
7.92
7.91
7.91
7.49
7.48
7.46
7.43
7.43
7.42
7.41
7.41
7.41
O2N
NO2
f1 (ppm)
2.02
1.08
2.04
0.97
1.08
1.01
1.00
1.02
2.00
1.00
1.03
3.14
f1 (ppm)
149.96
148.11
146.90
144.44
140.97
134.08
133.22
131.78
129.34
128.38
124.26
122.85
122.65
119.79
77.25
77.00
76.75
51.88
21.86
f1 (ppm)

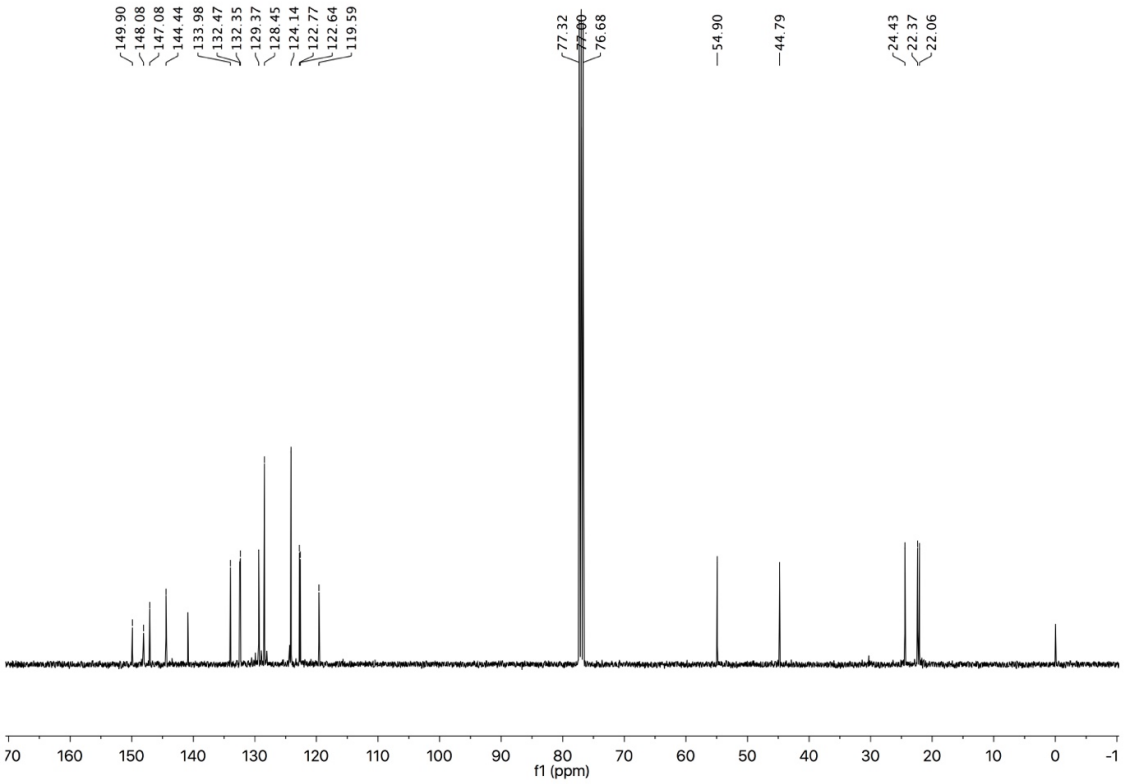

f1 (ppm)
f2 (ppm)

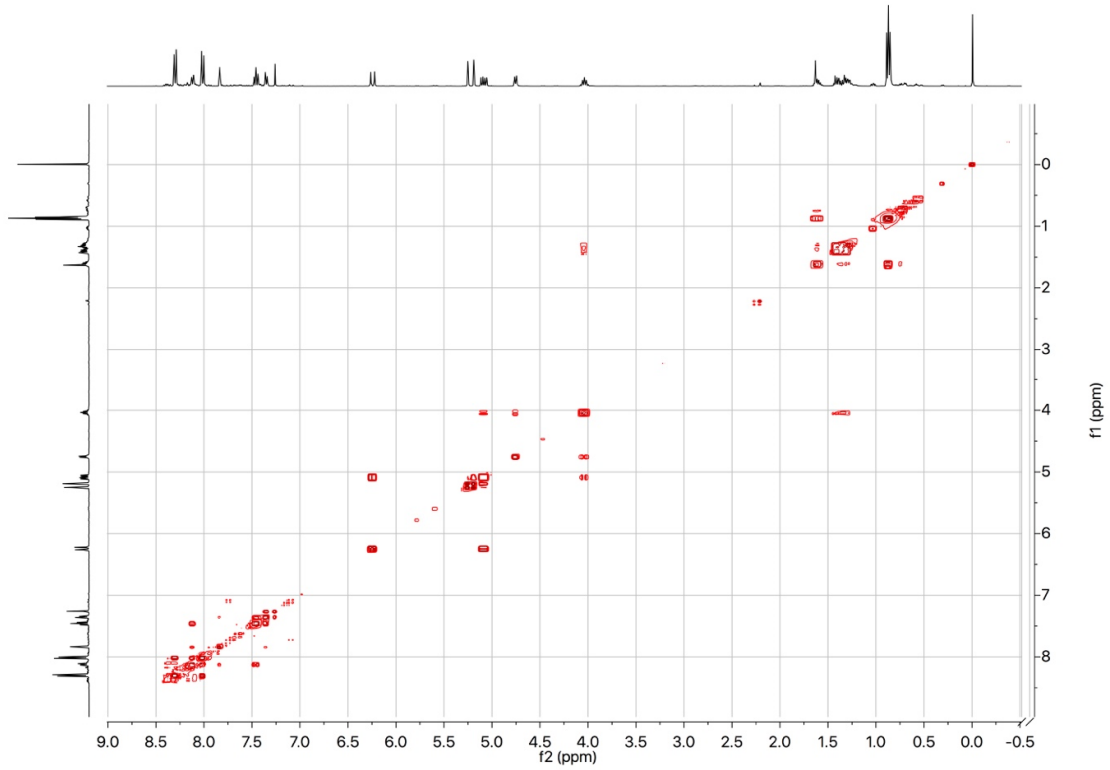

f1 (ppm)
f2 (ppm)

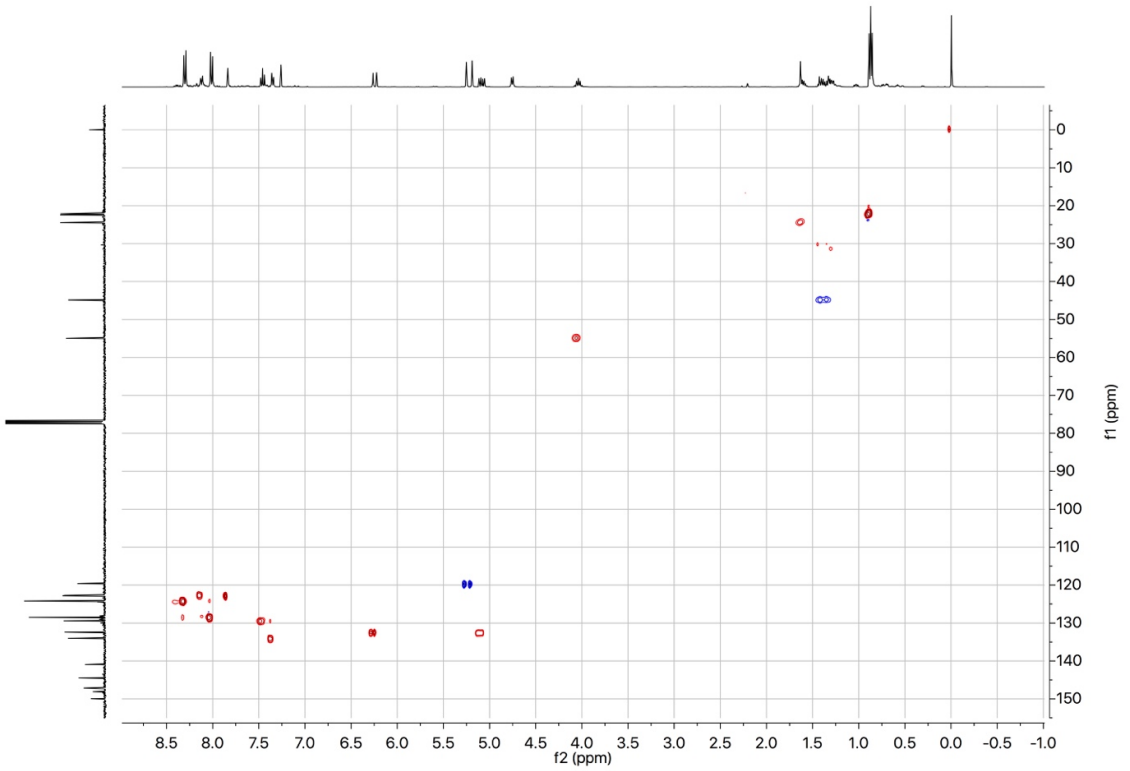


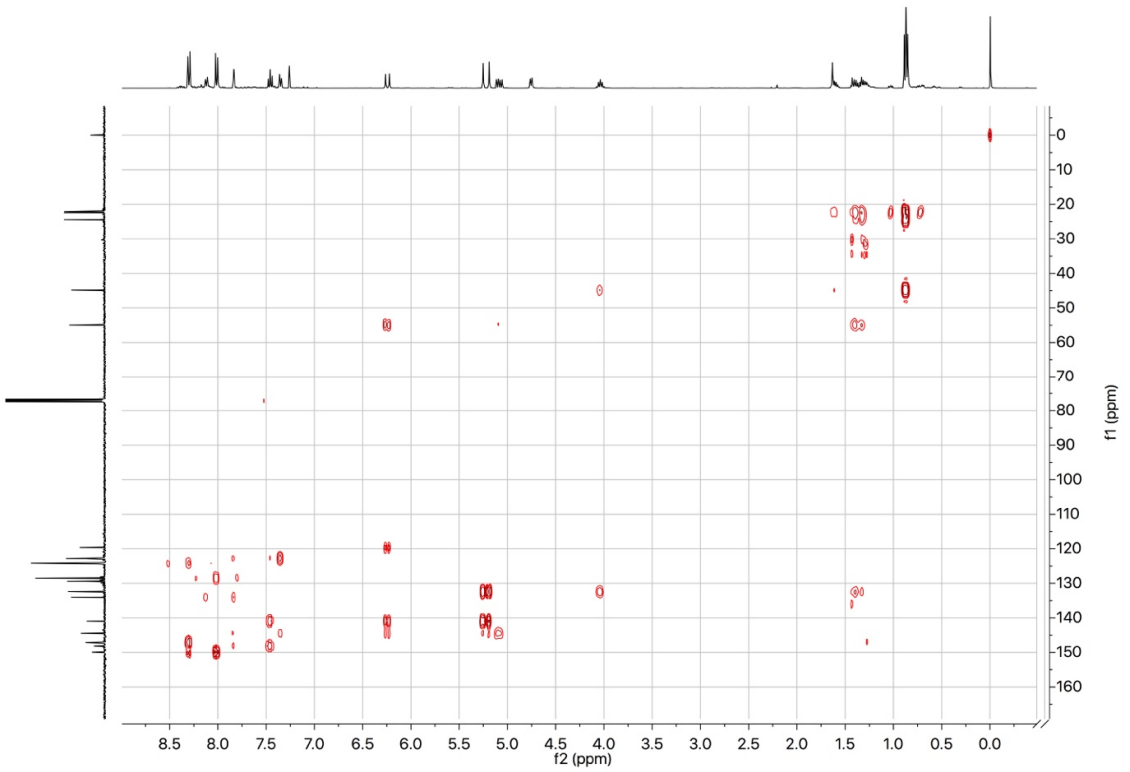
2p



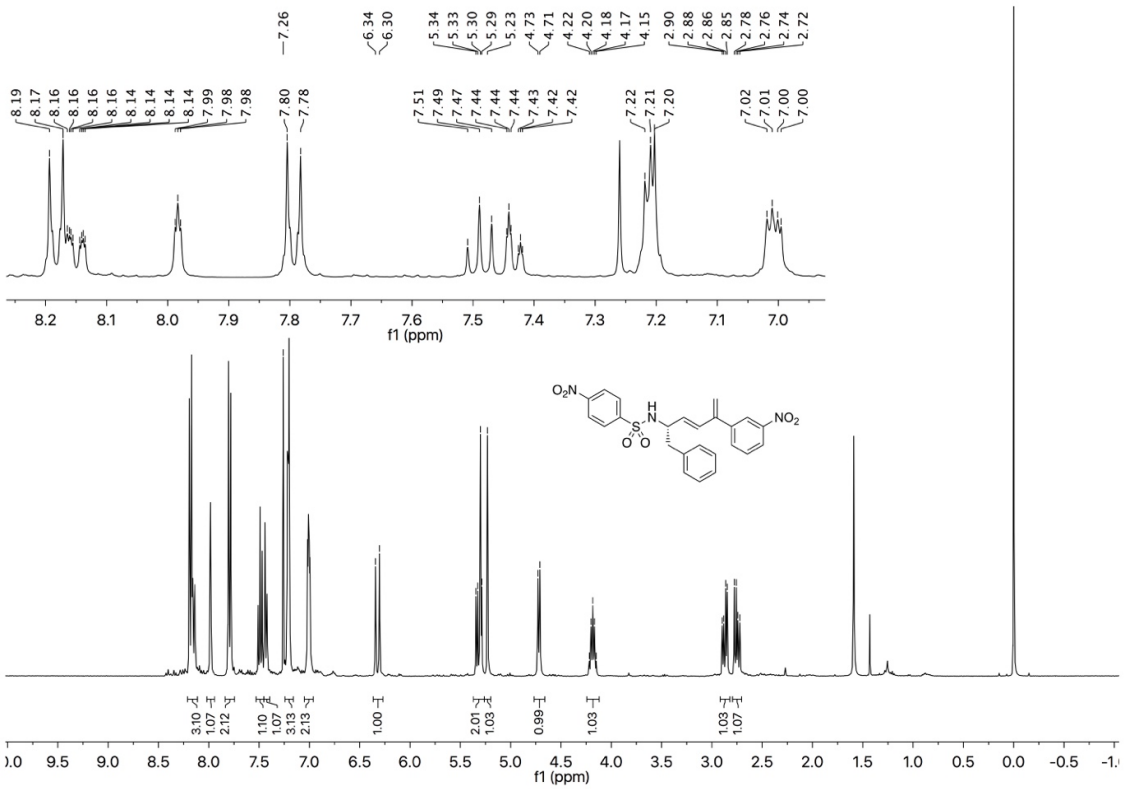

149.90
148.08
147.08
144.44
133.98
132.47
132.35
129.37
128.45
124.14
122.77
122.64
119.59
77.32
77.00
76.68
54.90
44.79
24.43
22.37
22.06
f1 (ppm)

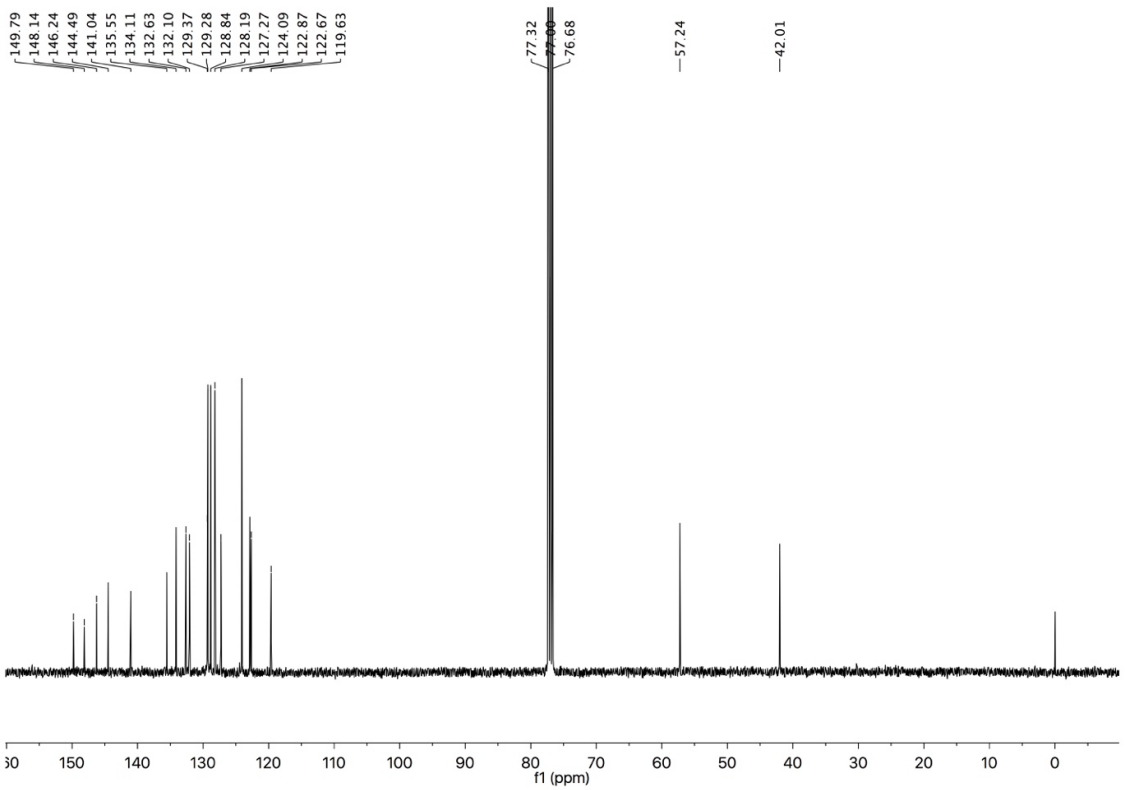

f2 (ppm)
f1 (ppm)

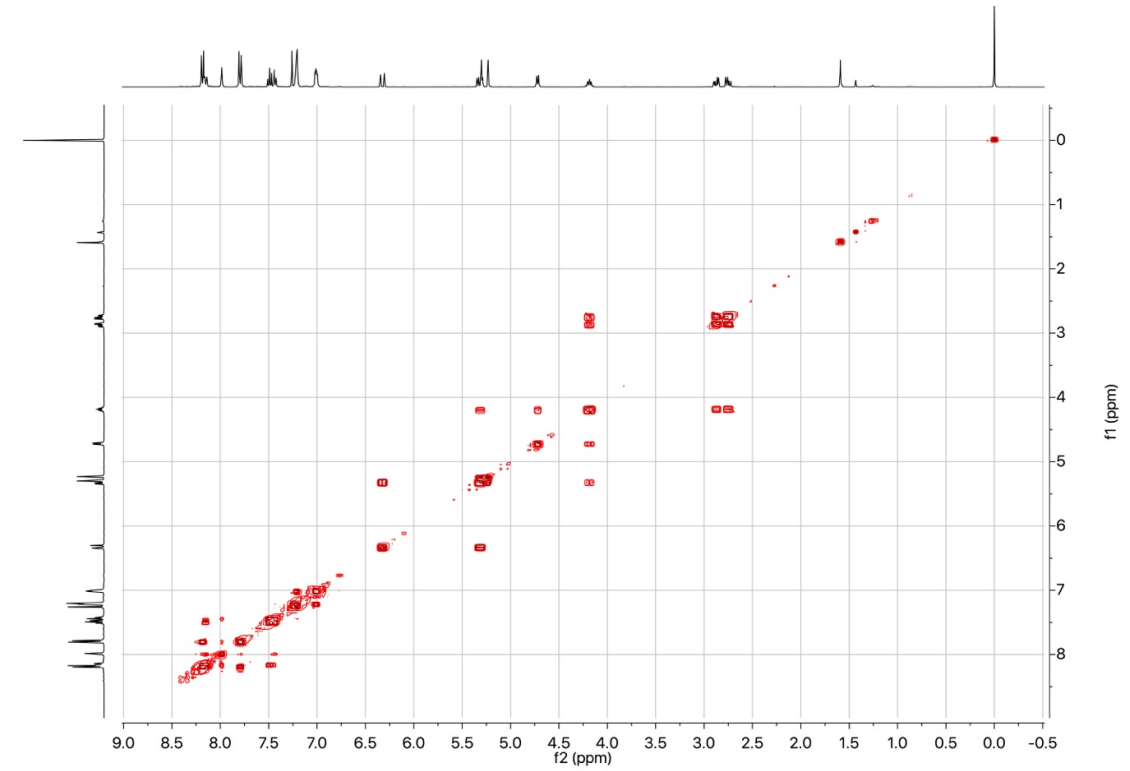

f2 (ppm)
f1 (ppm)

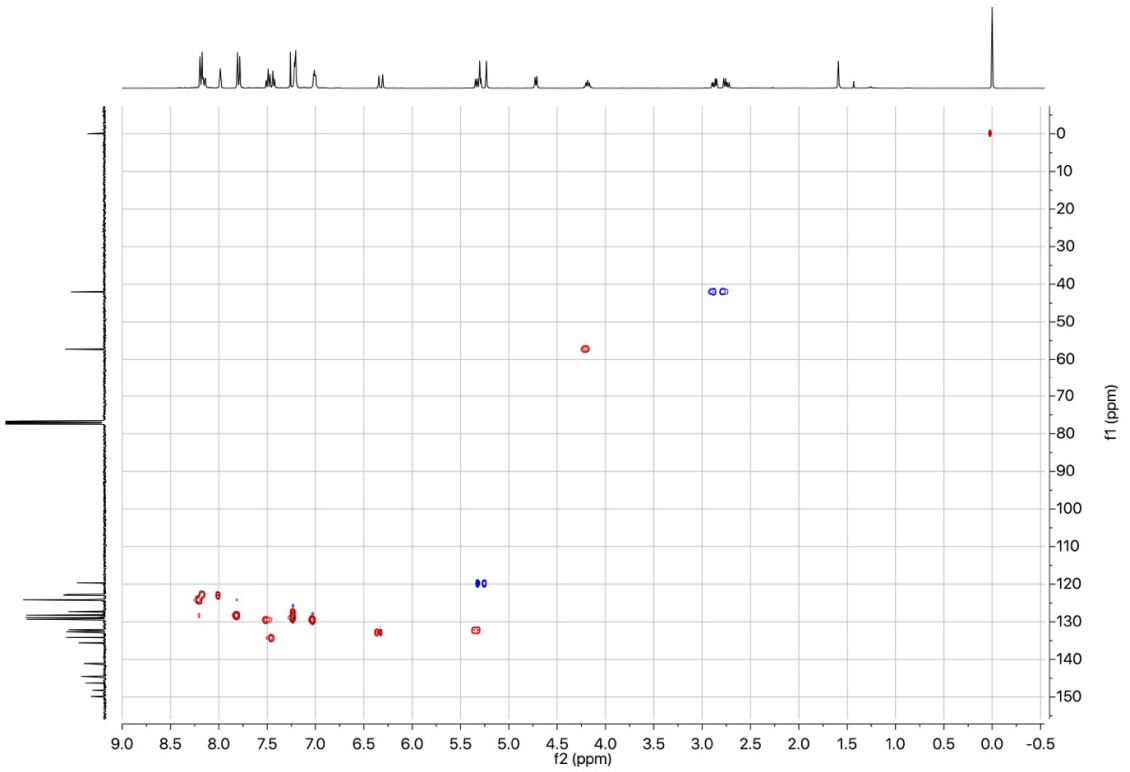

f2 (ppm)
f1 (ppm)

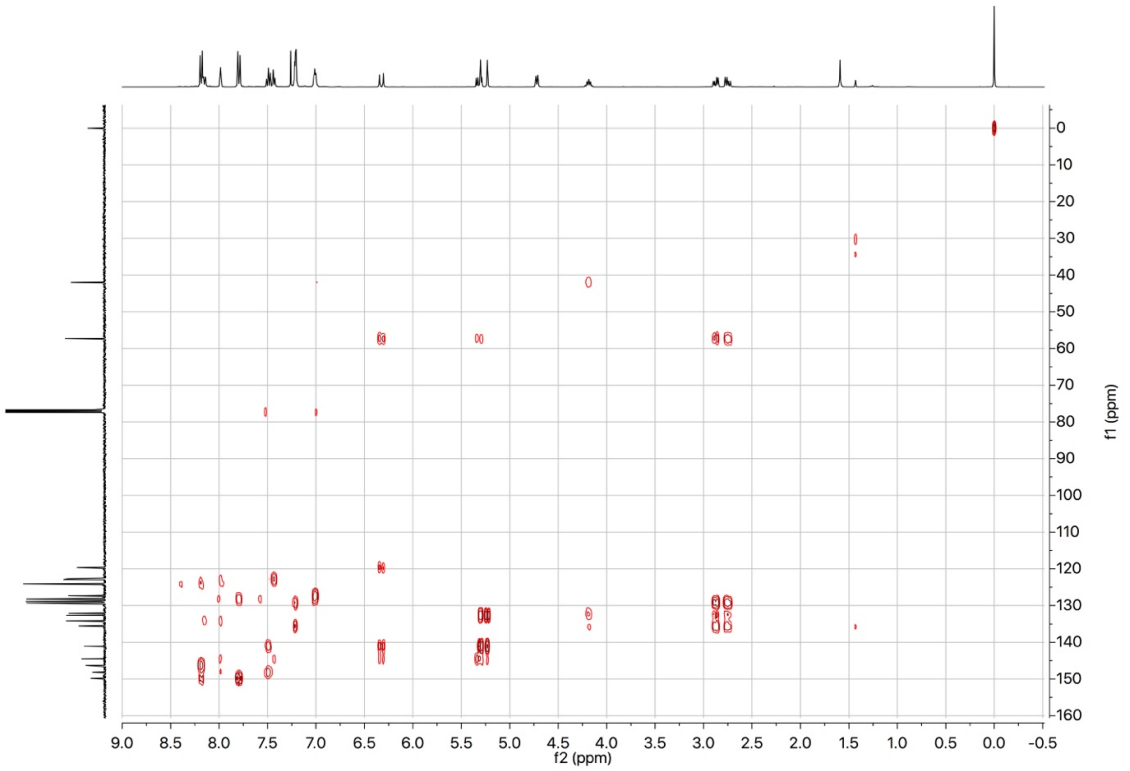
2q


7.26
6.34
6.30
5.34
5.33
5.30
5.29
5.23
4.73
4.71
4.22
4.20
4.18
4.17
4.15
2.90
2.88
2.86
2.85
2.78
2.76
2.74
2.72
8.19
8.17
8.16
8.16
8.16
8.16
8.14
8.14
8.14
8.14
7.99
7.98
7.98
7.80
7.78
7.51
7.49
7.47
7.44
7.44
7.44
7.43
7.42
7.42
7.22
7.21
7.20
7.02
7.01
7.00
7.00
f1 (ppm)
3.10
1.07
2.12
1.10
1.07
3.13
2.13
1.00
2.01
1.03
0.99
1.03
1.03
1.07
f1 (ppm)

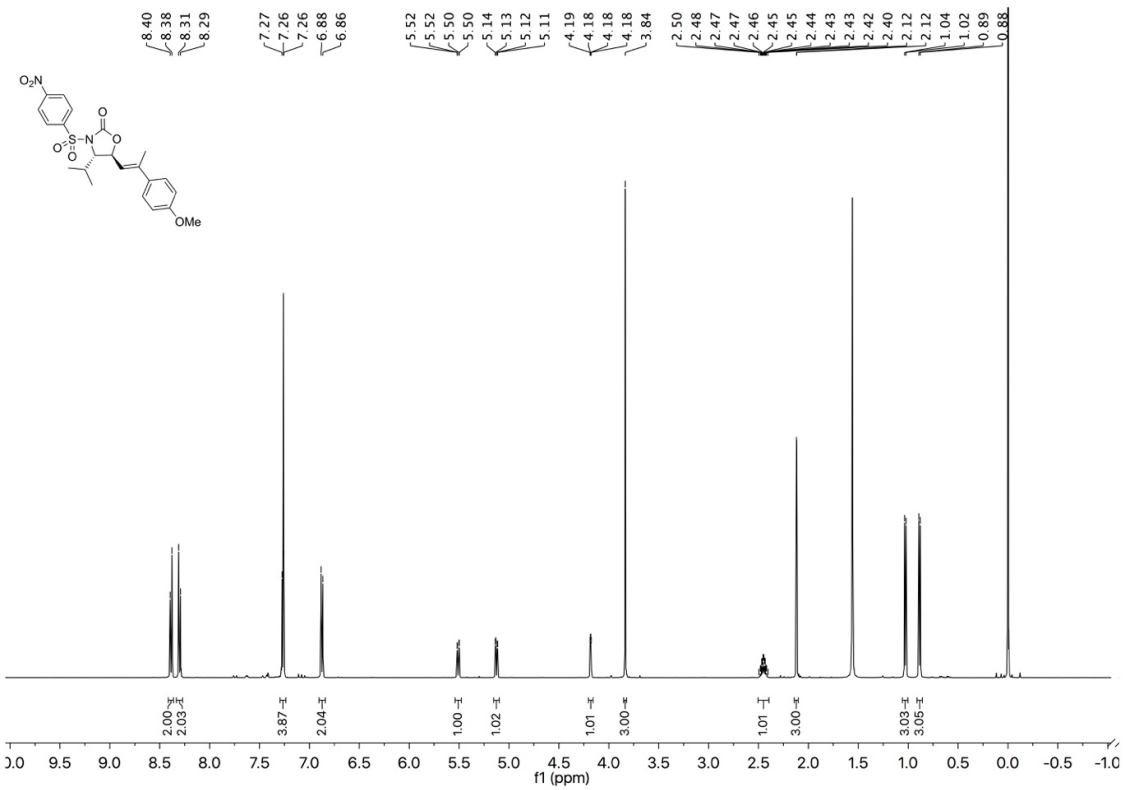

149.79
148.14
146.24
144.49
141.04
135.55
134.11
132.63
132.10
129.37
129.28
128.84
128.19
127.27
124.09
122.87
122.67
119.63
77.32
77.06
76.68
57.24
42.01
f1 (ppm)

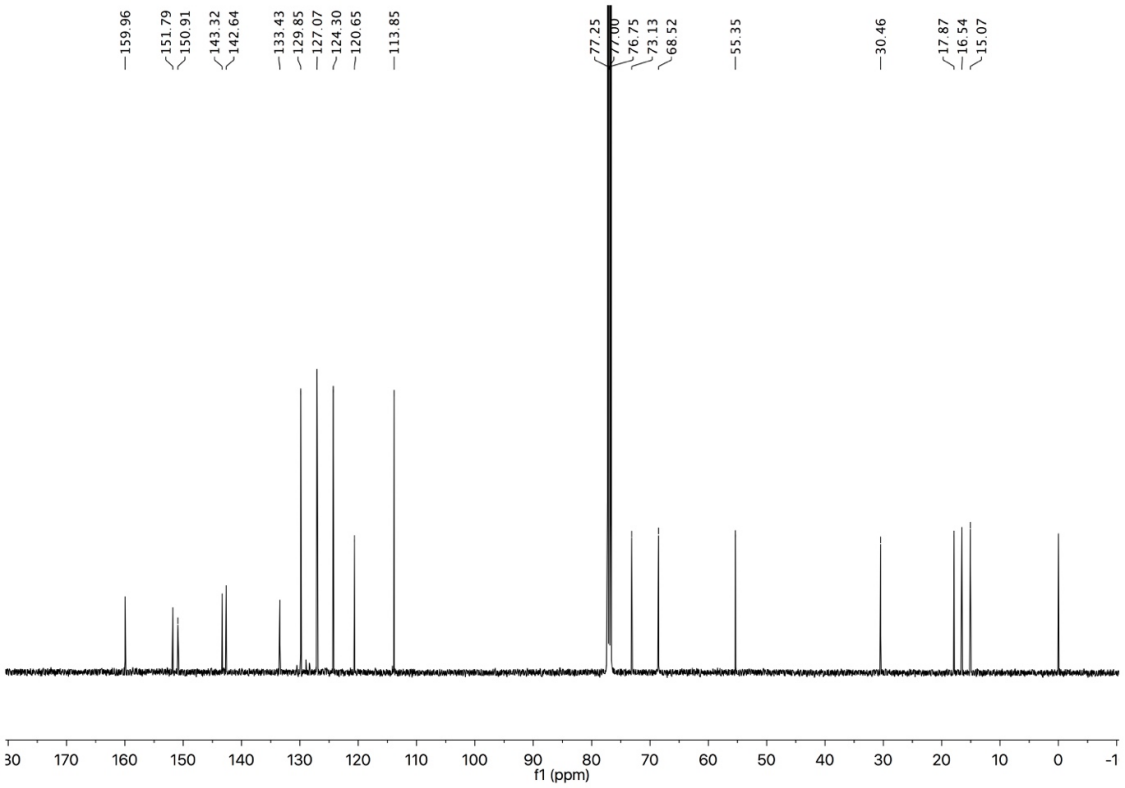

f1 (ppm)
f2 (ppm)

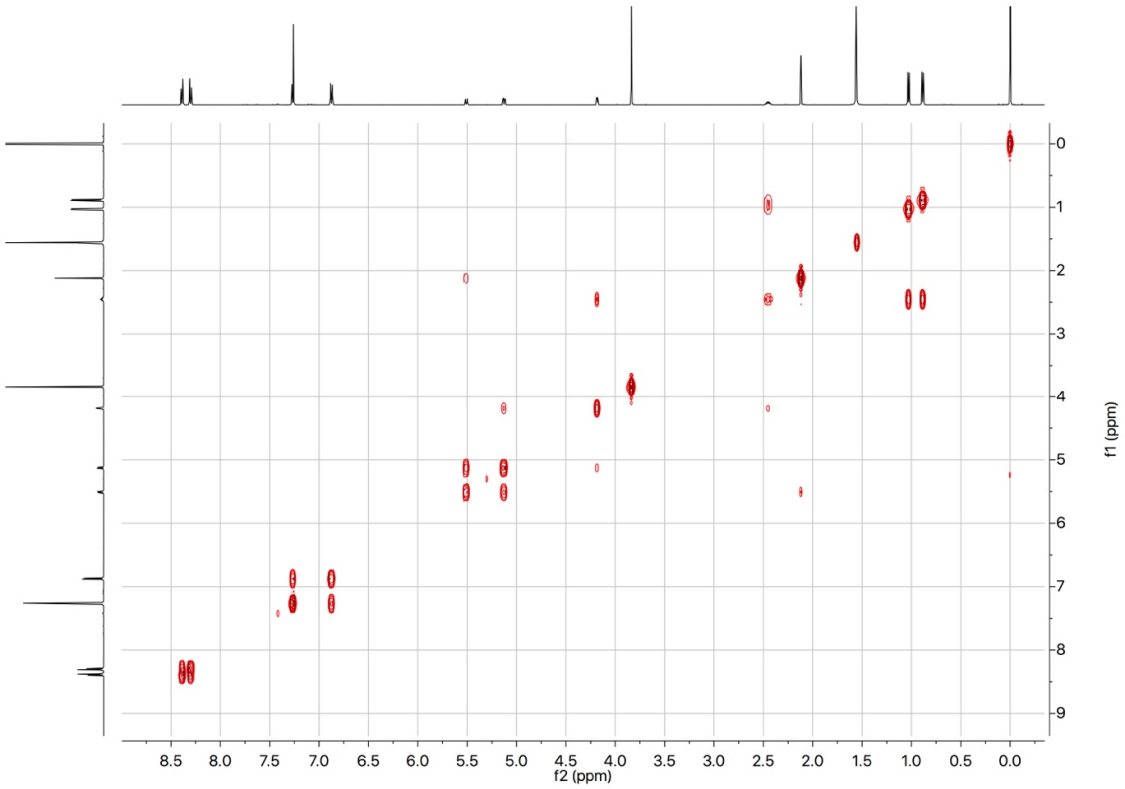

f1 (ppm)
f2 (ppm)

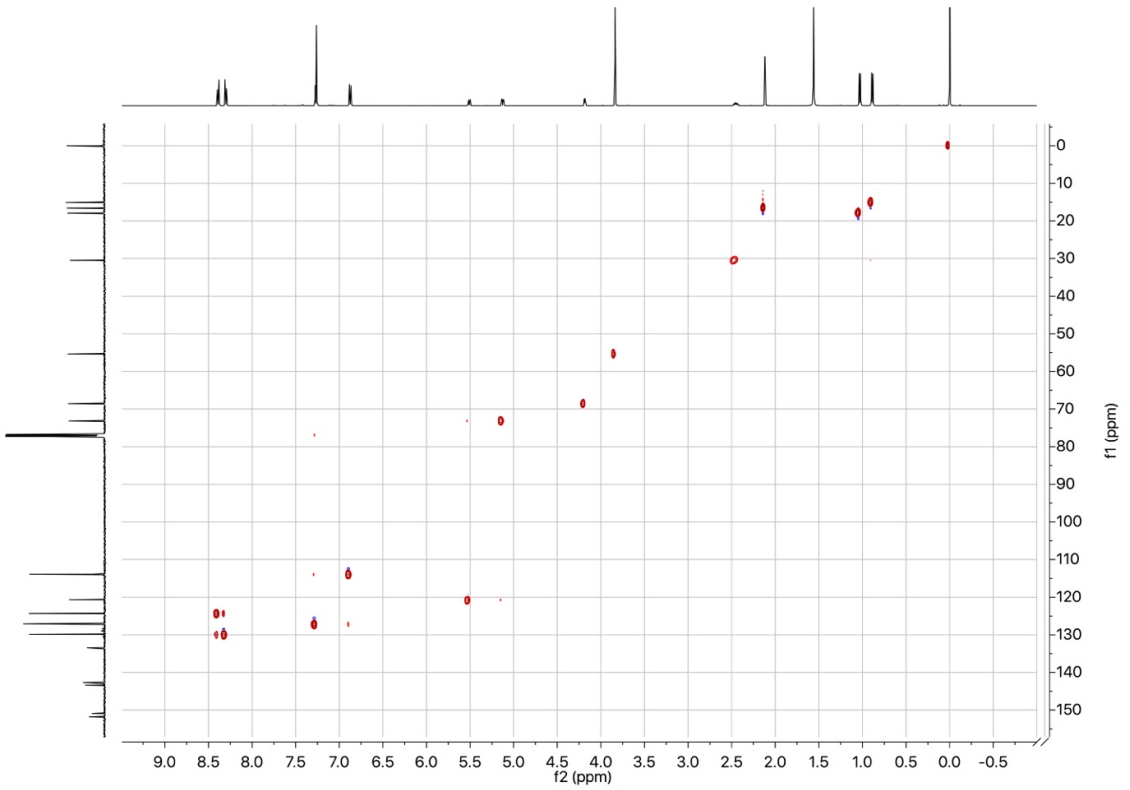

f2 (ppm)
f1 (ppm)

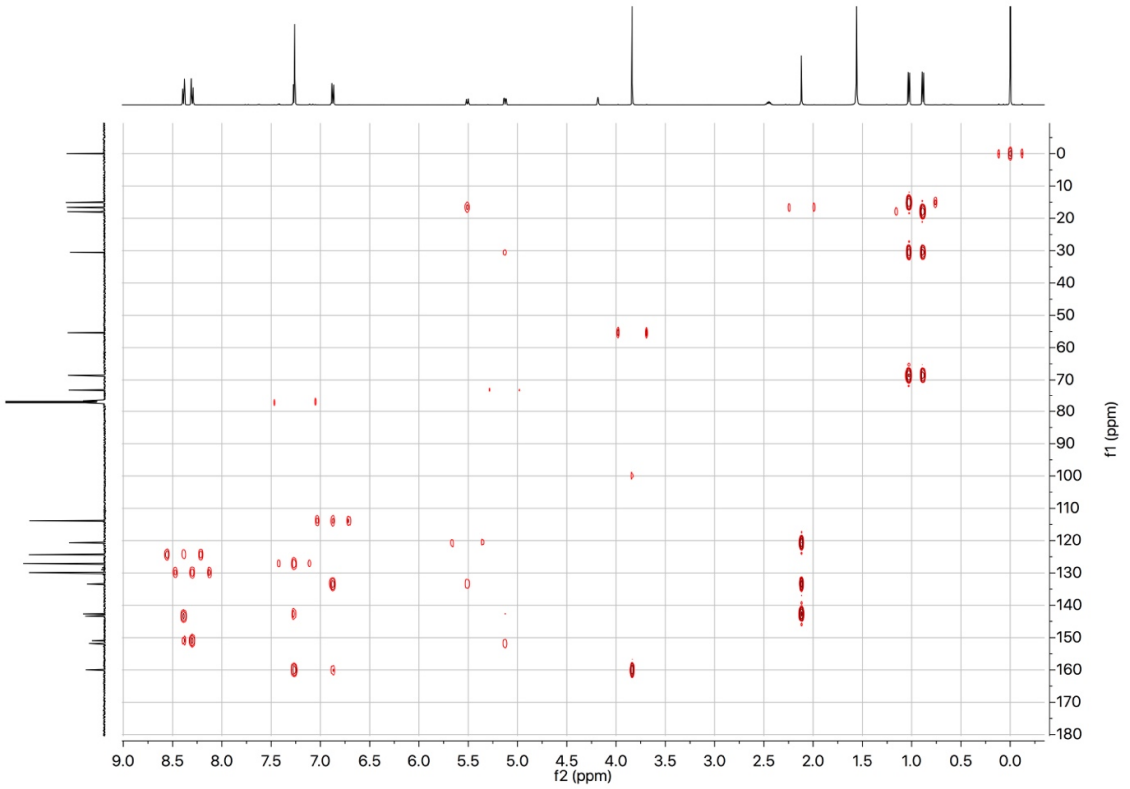
3a


8.40
8.38
8.31
8.29
7.27
7.26
7.26
6.88
6.86
5.52
5.52
5.50
5.50
5.14
5.13
5.12
5.11
4.19
4.18
4.18
4.18
3.84
2.50
2.48
2.47
2.47
2.46
2.45
2.45
2.44
2.43
2.43
2.42
2.40
2.12
2.12
1.04
1.02
0.89
0.88
O2N
OMe
2.00
2.03
3.87
2.04
1.00
1.02
1.01
3.00
1.01
3.00
3.03
3.05
f1 (ppm)

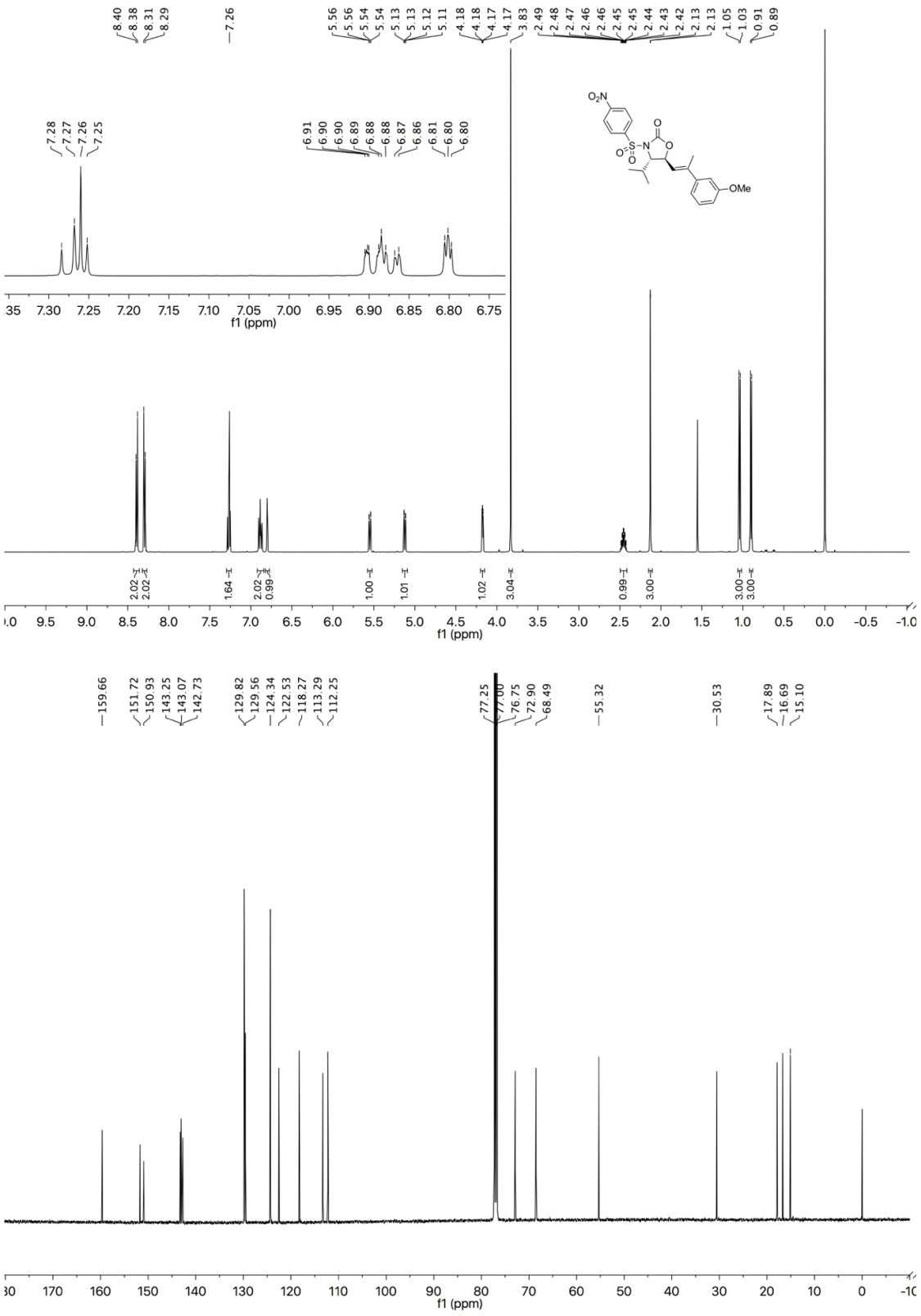

159.96
151.79
150.91
143.32
142.64
133.43
129.85
127.07
124.30
120.65
113.85
77.25
77.00
76.75
73.13
68.52
55.35
30.46
17.87
16.54
15.07
f1 (ppm)

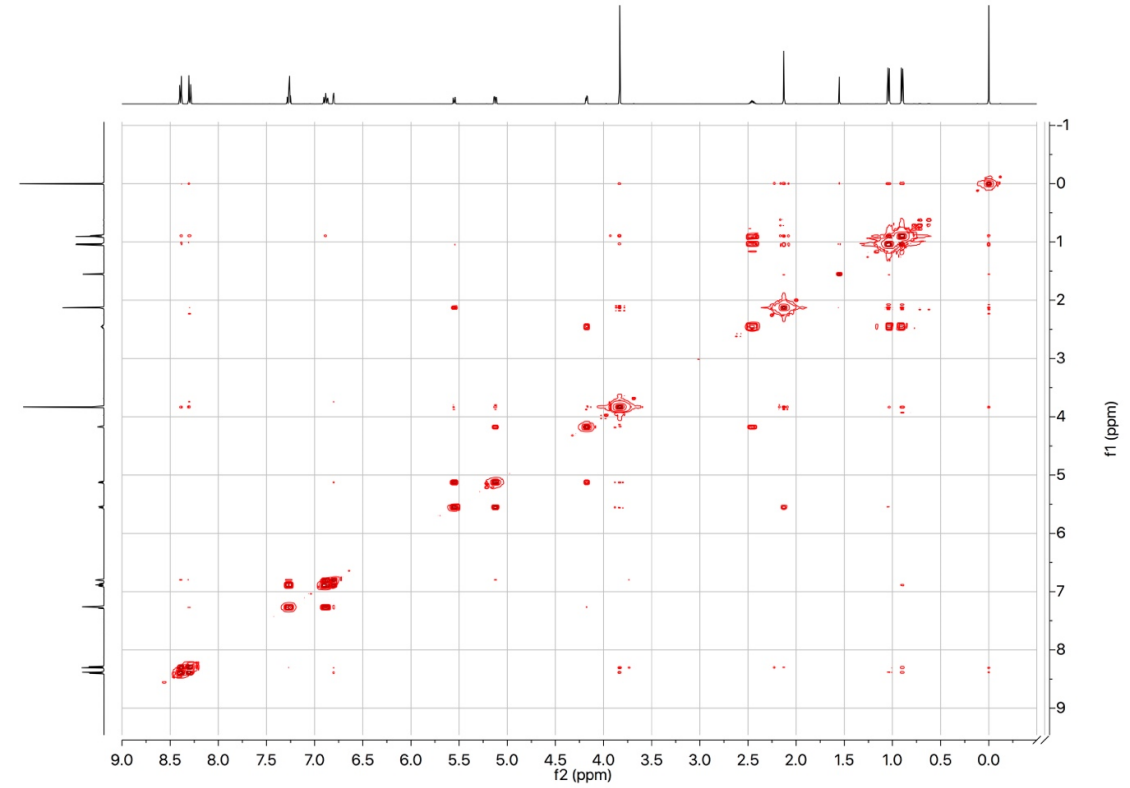

f2 (ppm)
f1 (ppm)

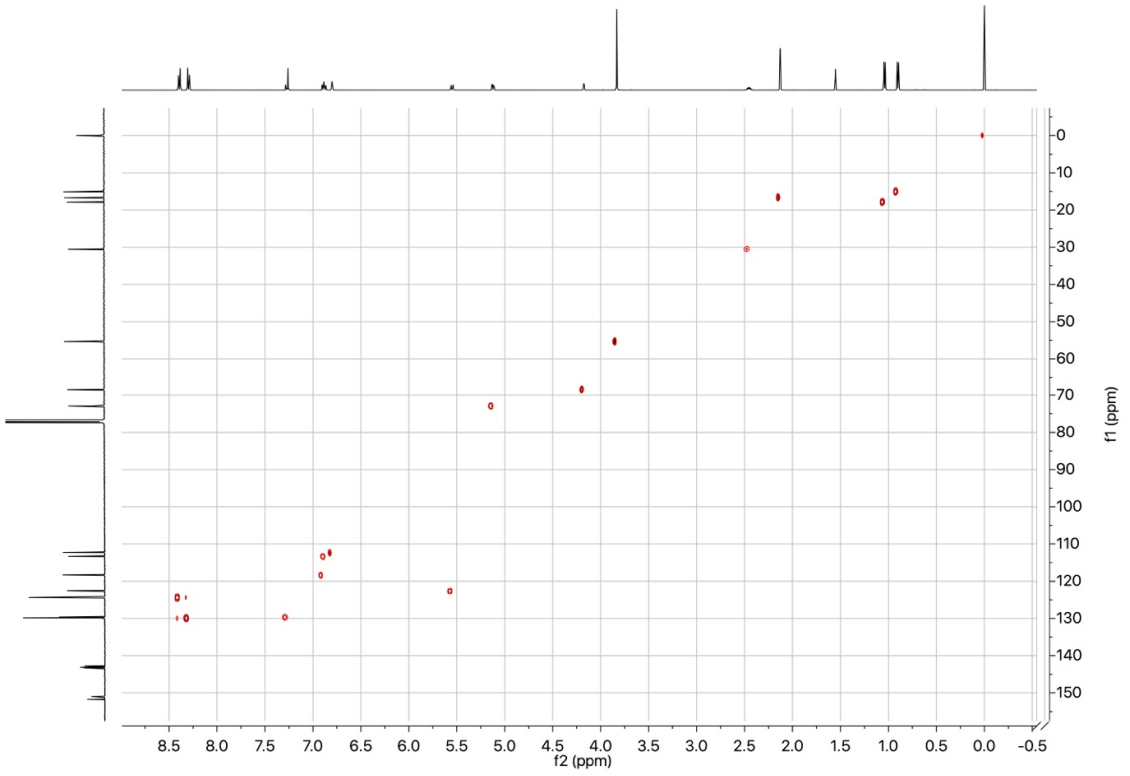

f2 (ppm)
f1 (ppm)

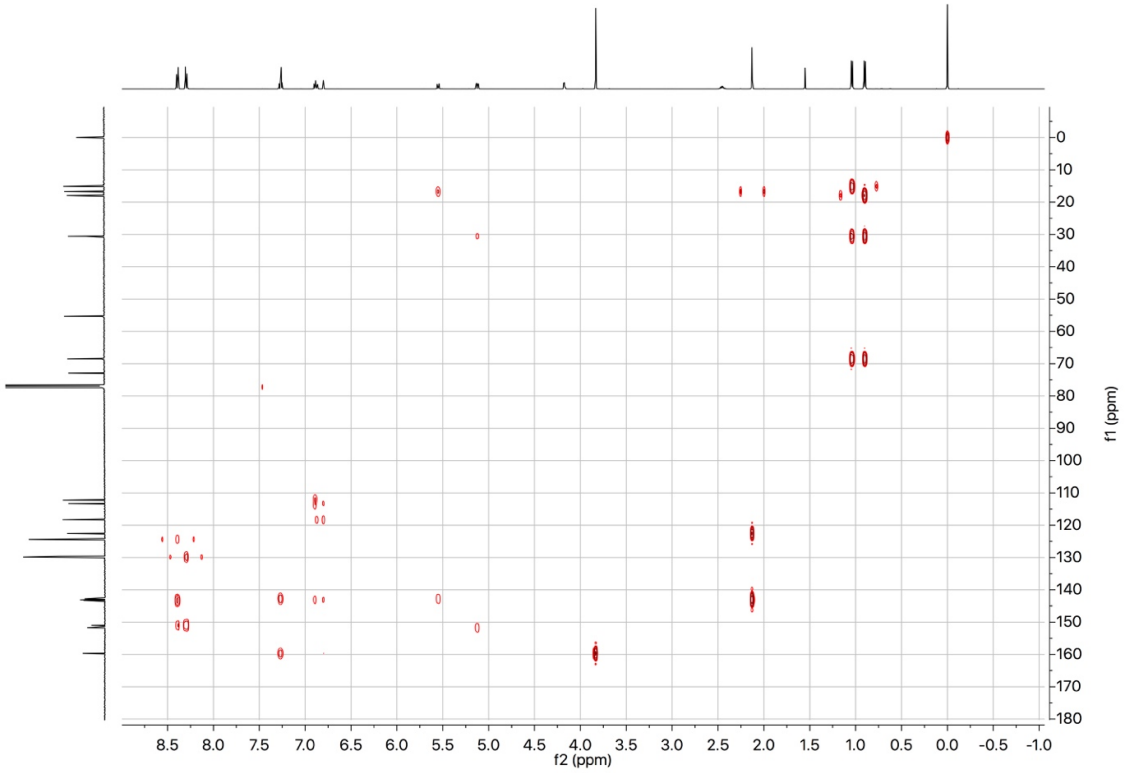

f2 (ppm)
f1 (ppm)

3b

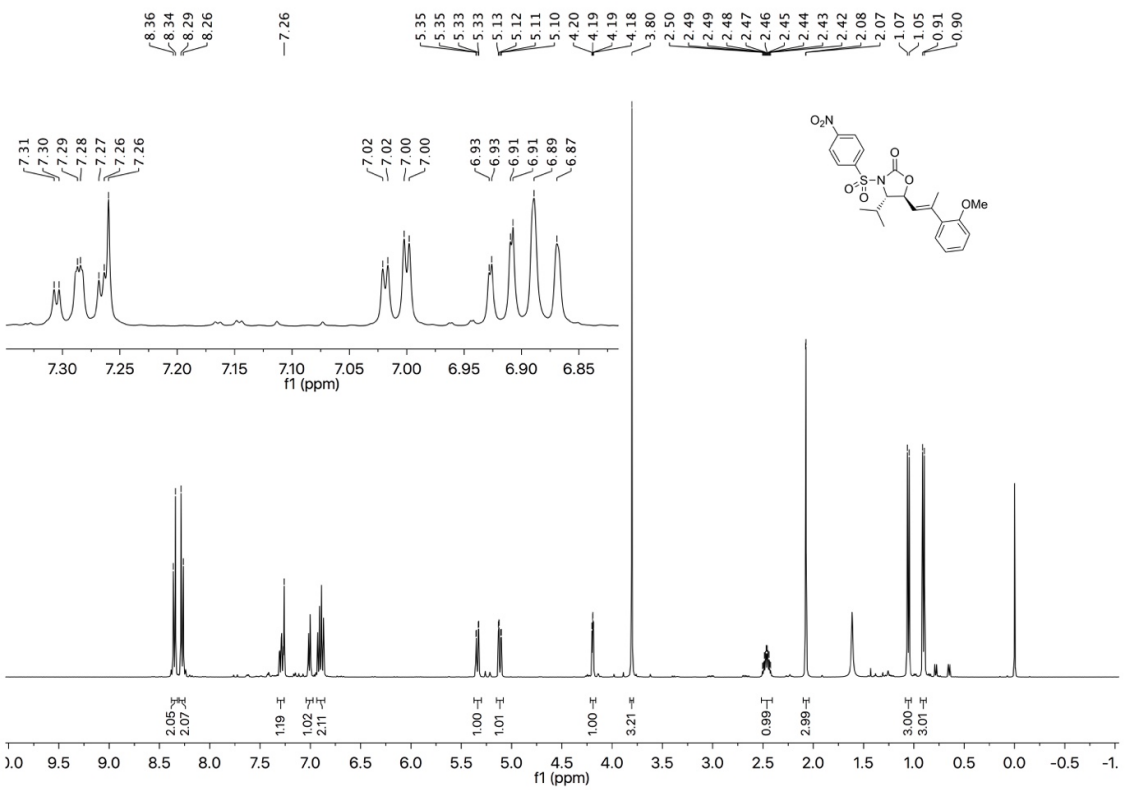

8.40
8.38
8.31
8.29
7.26
5.56
5.56
5.54
5.54
5.13
5.13
5.12
5.11
4.18
4.18
4.17
4.17
3.83
2.49
2.48
2.47
2.46
2.46
2.45
2.45
2.44
2.43
2.42
2.13
2.13
1.05
1.03
0.91
0.89
7.28
7.27
7.26
7.25
6.91
6.90
6.90
6.89
6.88
6.88
6.87
6.86
6.81
6.80
6.80
O2N
OMe
f1 (ppm)
2.02
2.02
1.64
2.02
0.99
1.00
1.01
1.02
3.04
0.99
3.00
3.00
3.00
f1 (ppm)
159.66
151.72
150.93
143.25
143.07
142.73
129.82
129.56
124.34
122.53
118.27
113.29
112.25
77.25
77.00
76.75
72.90
68.49
55.32
30.53
17.89
16.69
15.10
f1 (ppm)

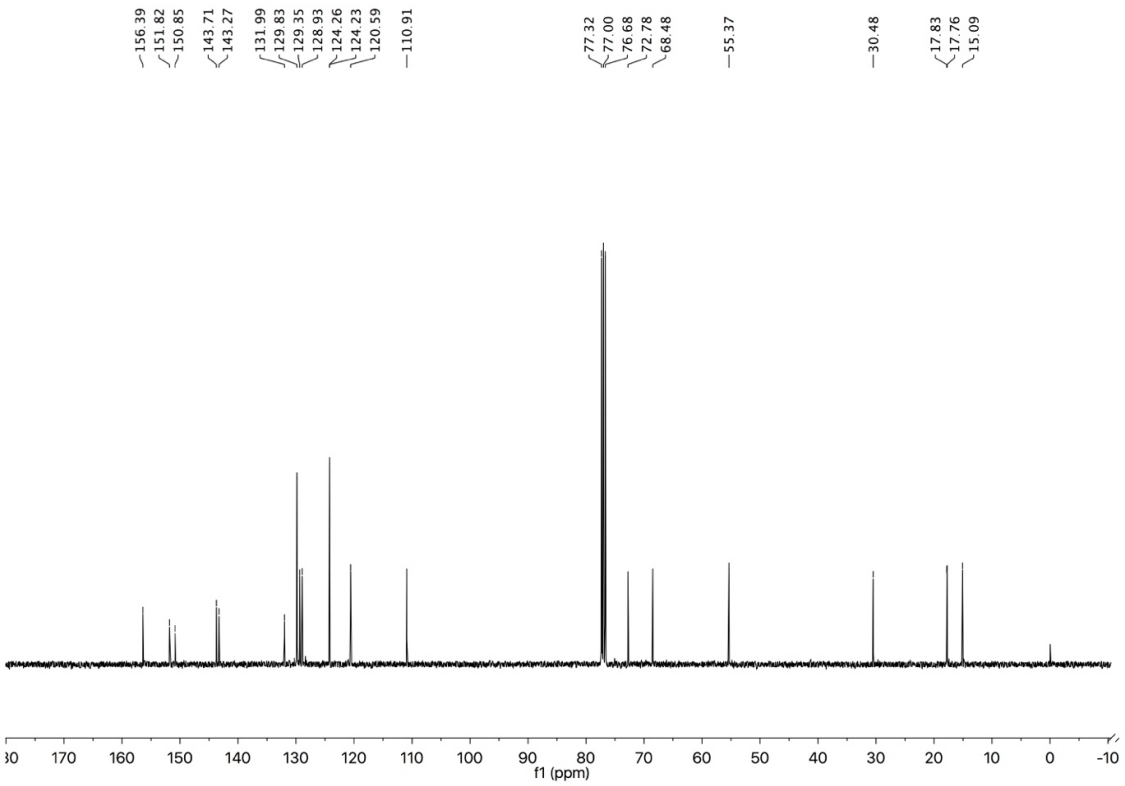

f2 (ppm)
f1 (ppm)

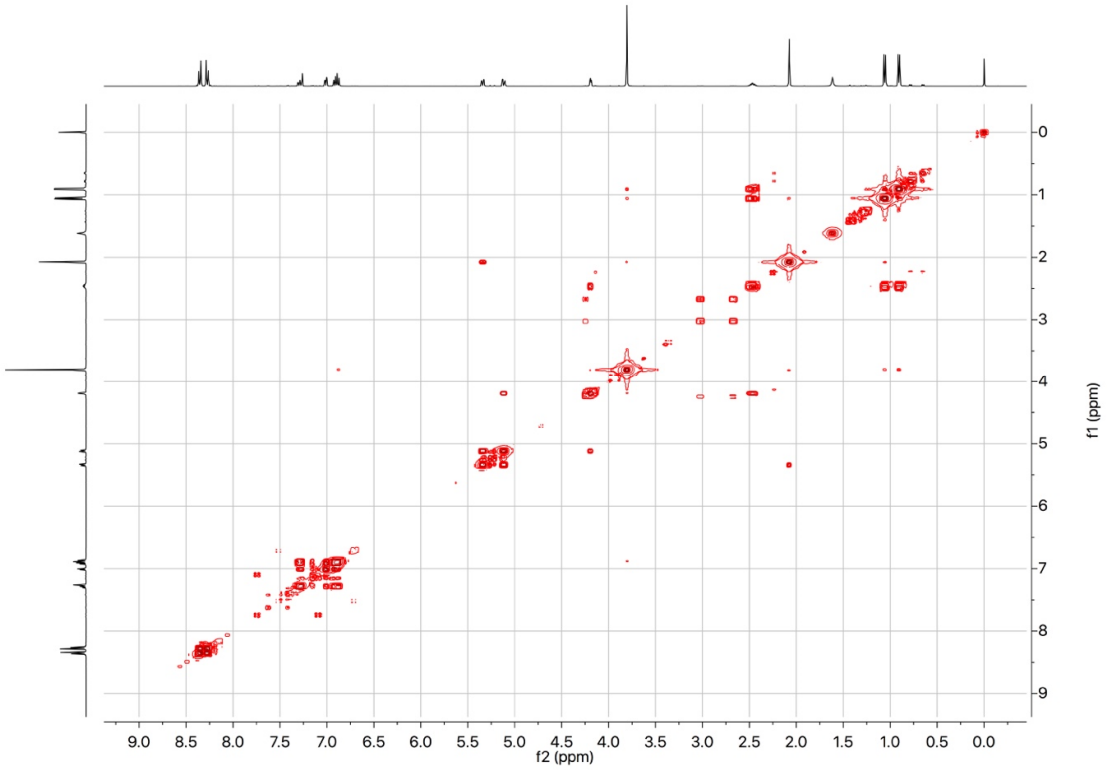

f2 (ppm)
f1 (ppm)

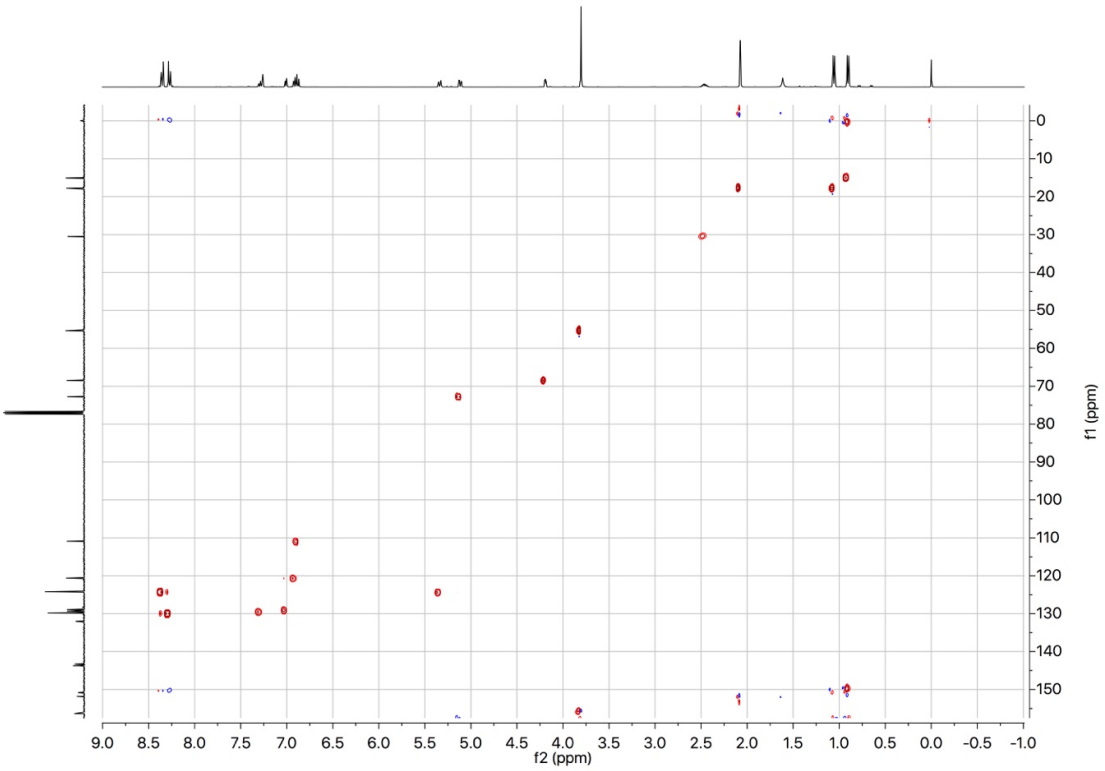

f2 (ppm)
f1 (ppm)

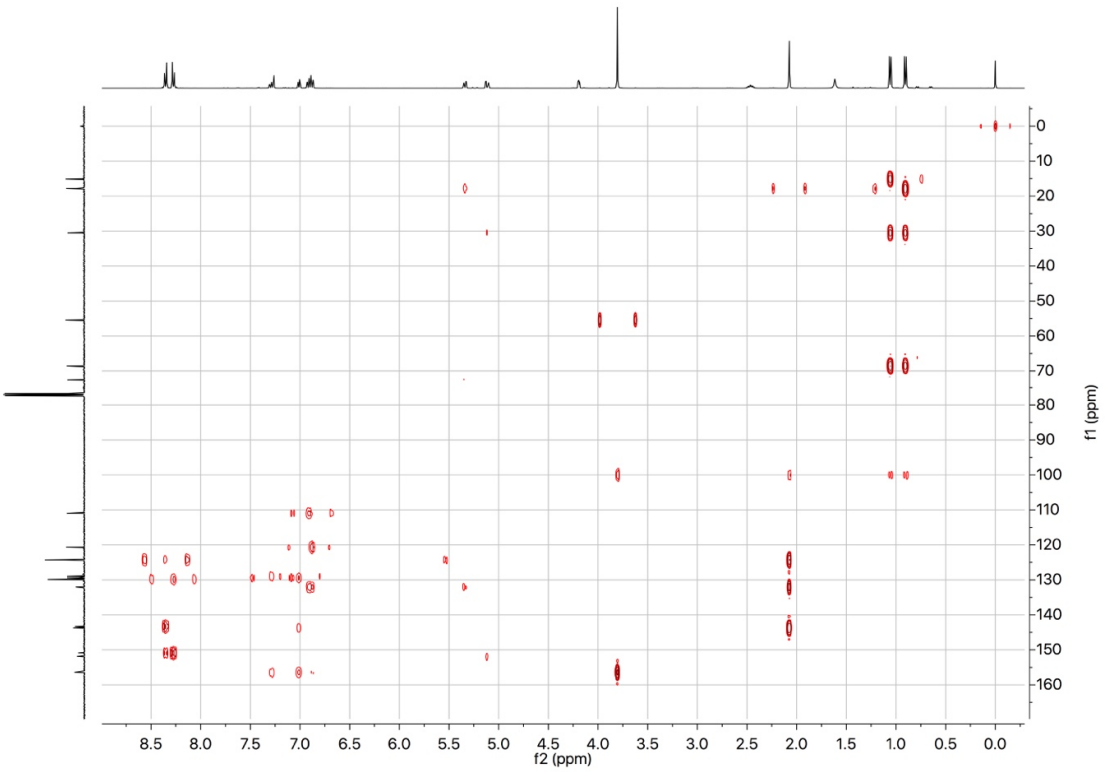
3c


8.36
8.34
8.29
8.26
7.26
5.35
5.33
5.13
5.12
5.11
5.10
4.20
4.19
4.18
3.80
2.50
2.49
2.48
2.47
2.46
2.45
2.44
2.43
2.42
2.08
2.07
1.07
1.05
0.91
0.90
7.31
7.30
7.29
7.28
7.27
7.26
7.26
7.02
7.02
7.00
7.00
6.93
6.93
6.91
6.91
6.89
6.87
OMe
f1 (ppm)
2.05
2.07
1.19
1.02
2.11
1.00
1.01
1.00
3.21
0.99
2.99
3.00
3.01
f1 (ppm)

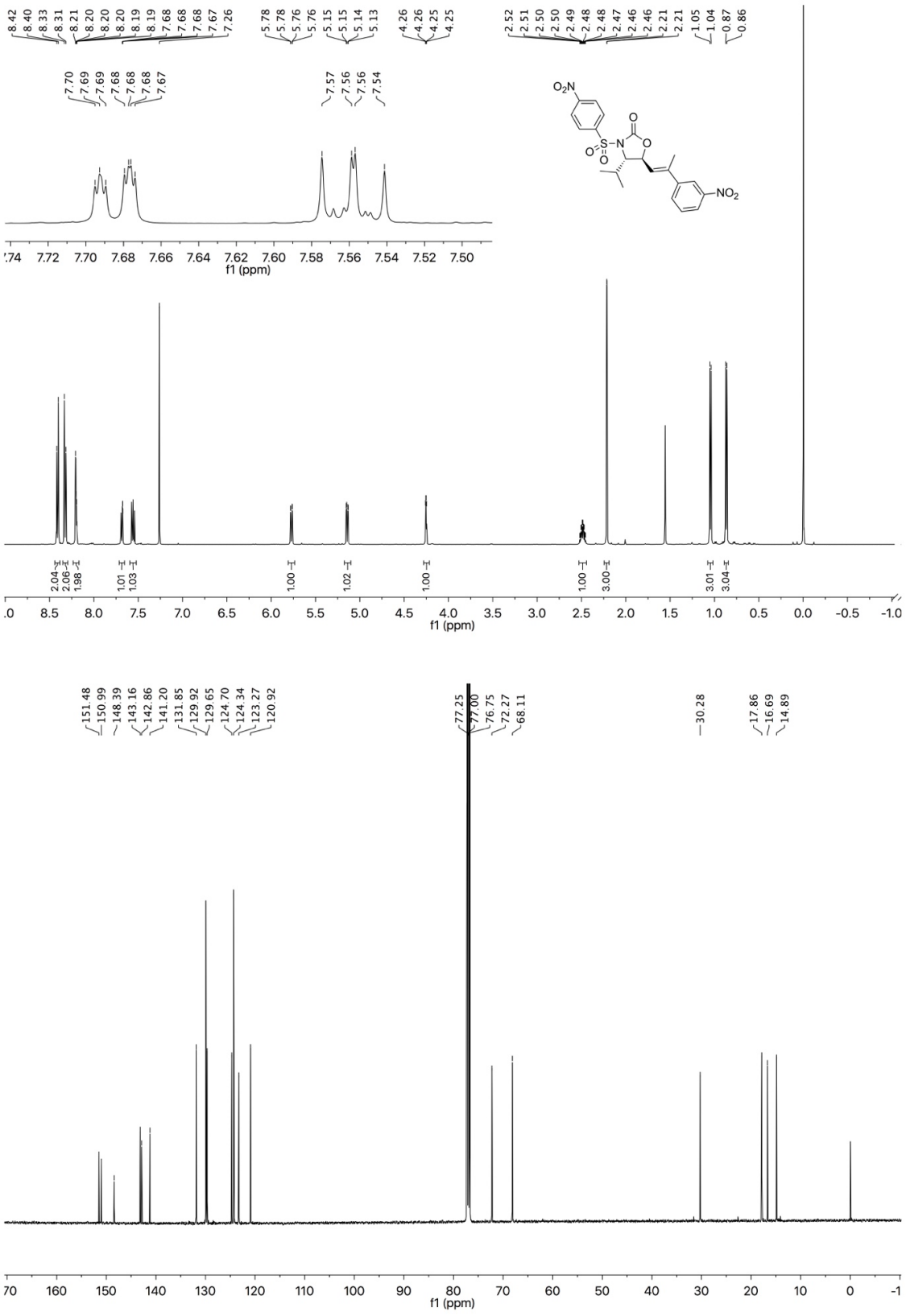

156.39
151.82
150.85
143.71
143.27
131.99
129.83
129.35
128.93
124.26
124.23
120.59
110.91
77.32
77.00
76.68
72.78
68.48
55.37
30.48
17.83
17.76
15.09
f1 (ppm)

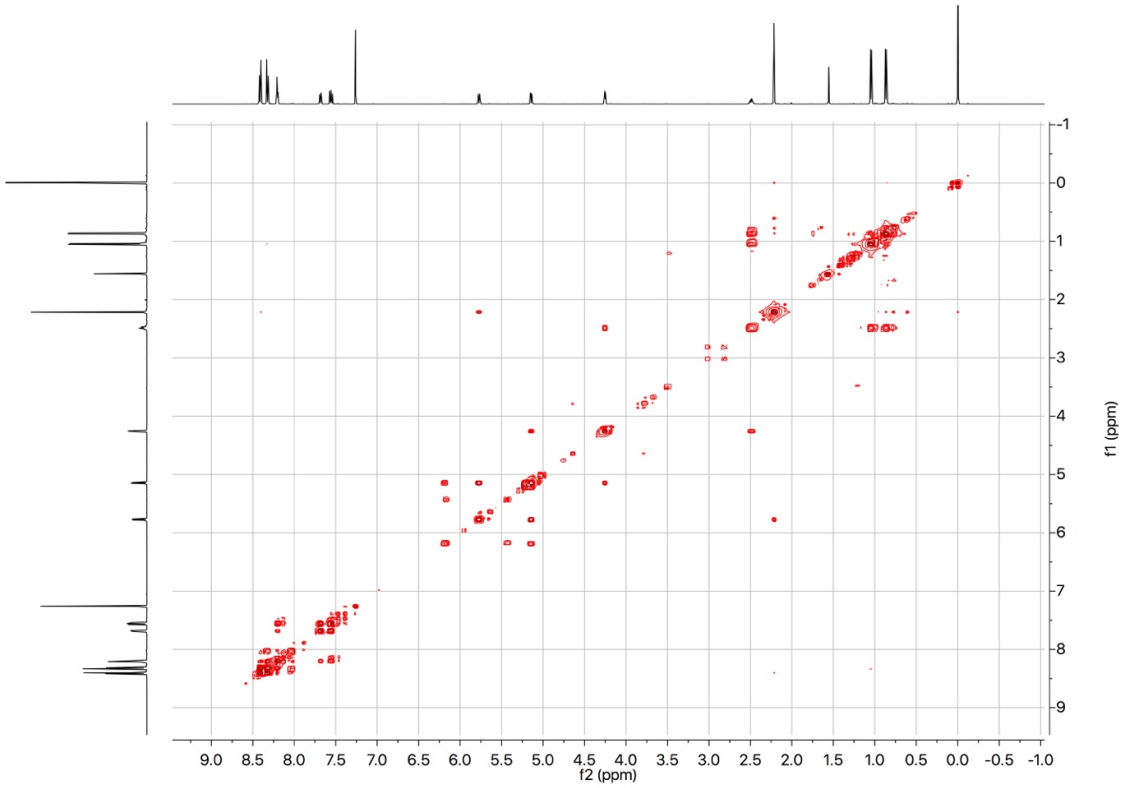

f2 (ppm)
f1 (ppm)

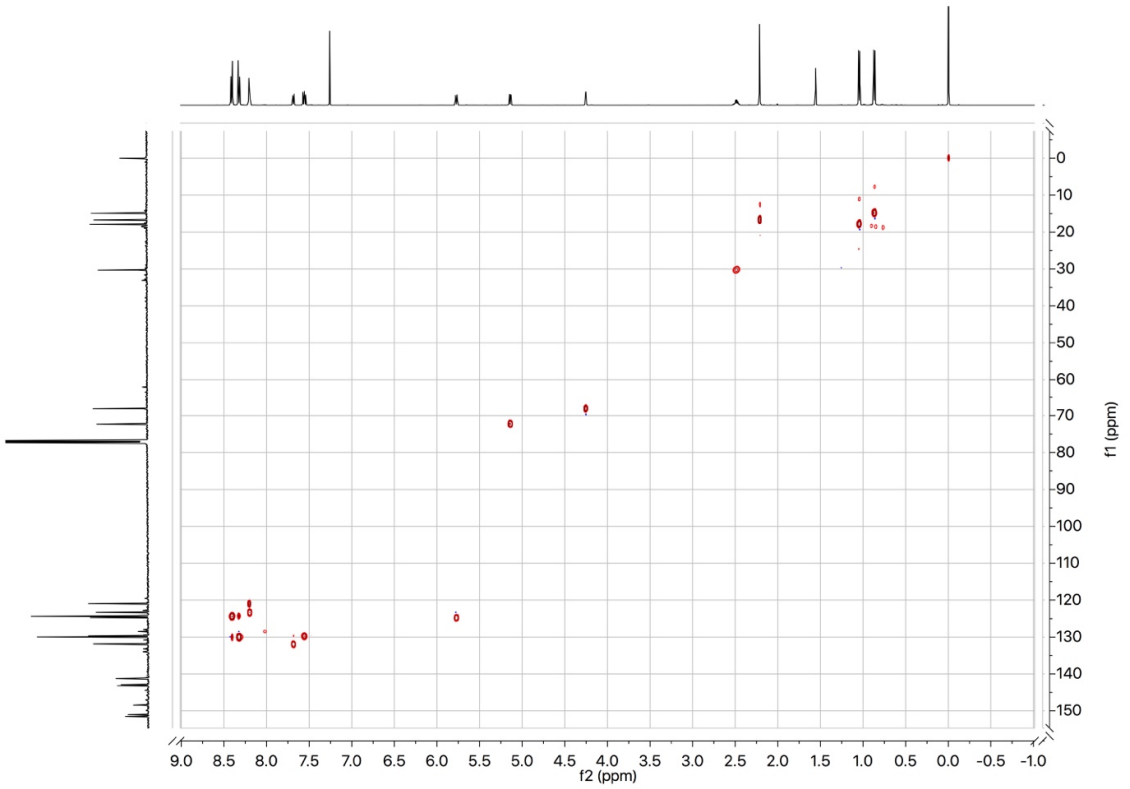

f1 (ppm)
f2 (ppm)

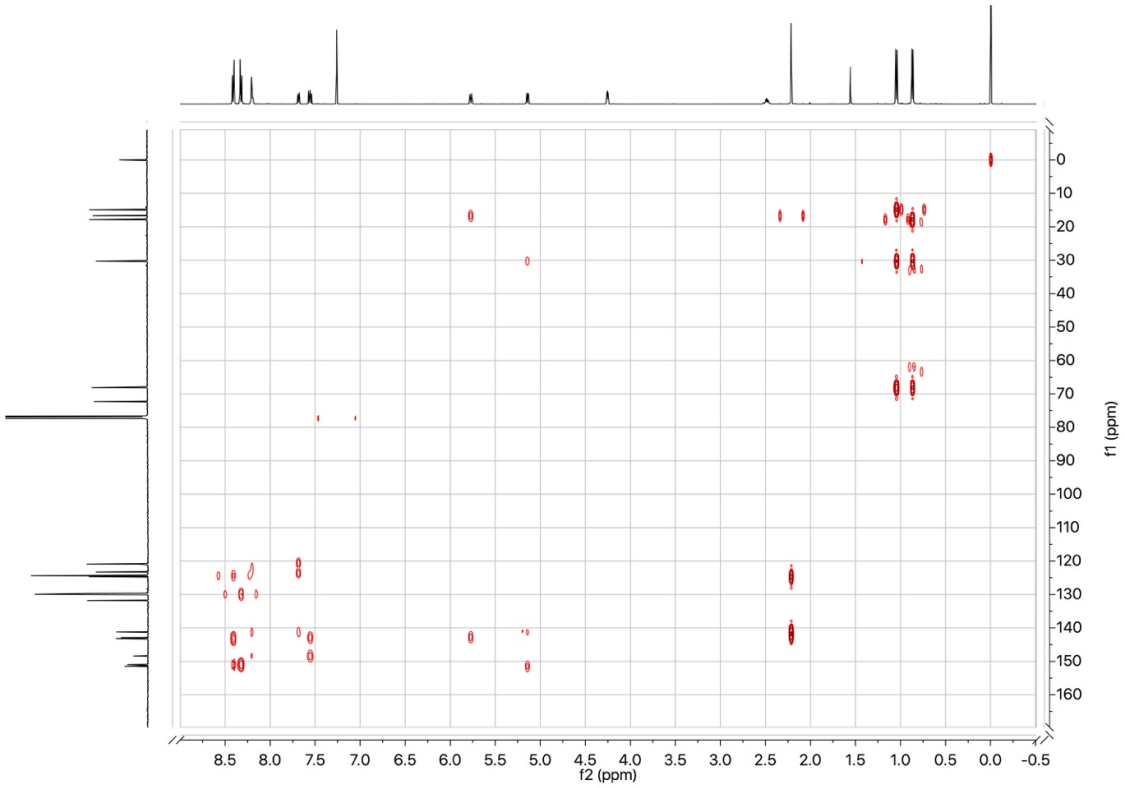

f1 (ppm)
f2 (ppm)

3e

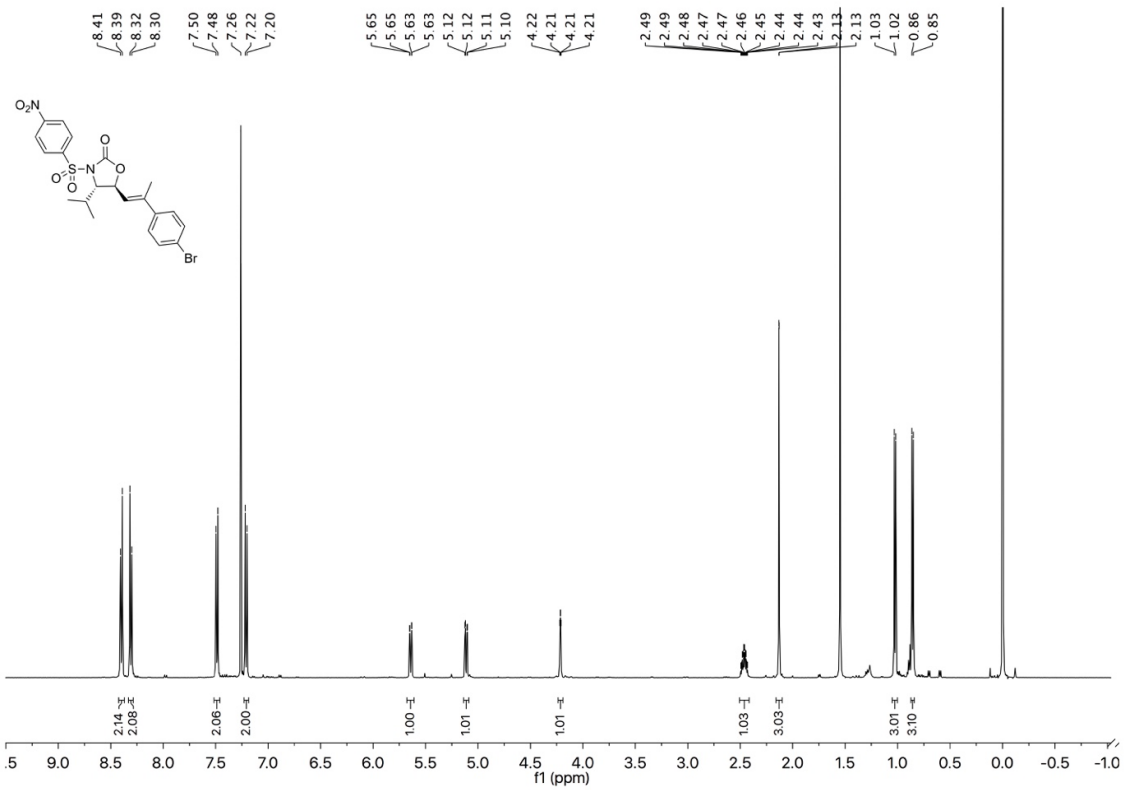

8.42 8.40 8.33 8.31 8.21 8.20 8.20 8.20 8.19 8.19 7.68 7.68 7.68 7.67 7.26
5.78 5.78 5.76 5.76 5.15 5.15 5.14 5.13
4.26 4.26 4.25 4.25
2.52 2.51 2.50 2.50 2.49 2.48 2.48 2.47 2.46 2.46 2.21 2.21
1.05 1.04 0.87 0.86
7.70 7.69 7.69 7.68 7.68 7.68 7.67
7.57 7.56 7.56 7.54
O2N
NO2
f1 (ppm)
2.04 2.06 1.98 1.01 1.03 1.00 1.02 1.00 1.00 3.00 3.01 3.04
151.48 150.99 148.39 143.16 142.86 141.20 131.85 129.92 129.65 124.70 124.34 123.27 120.92
77.25 77.00 76.75 72.27 68.11
30.28
17.86 16.69 14.89

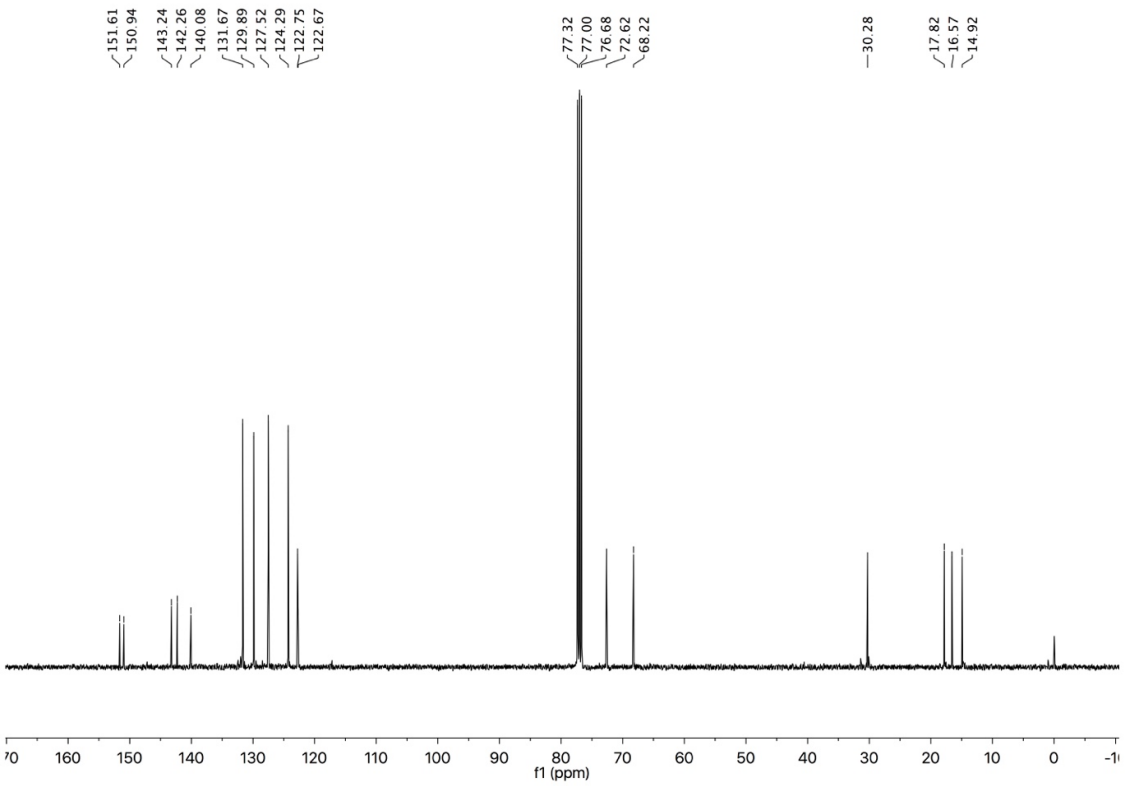

f2 (ppm)
f1 (ppm)

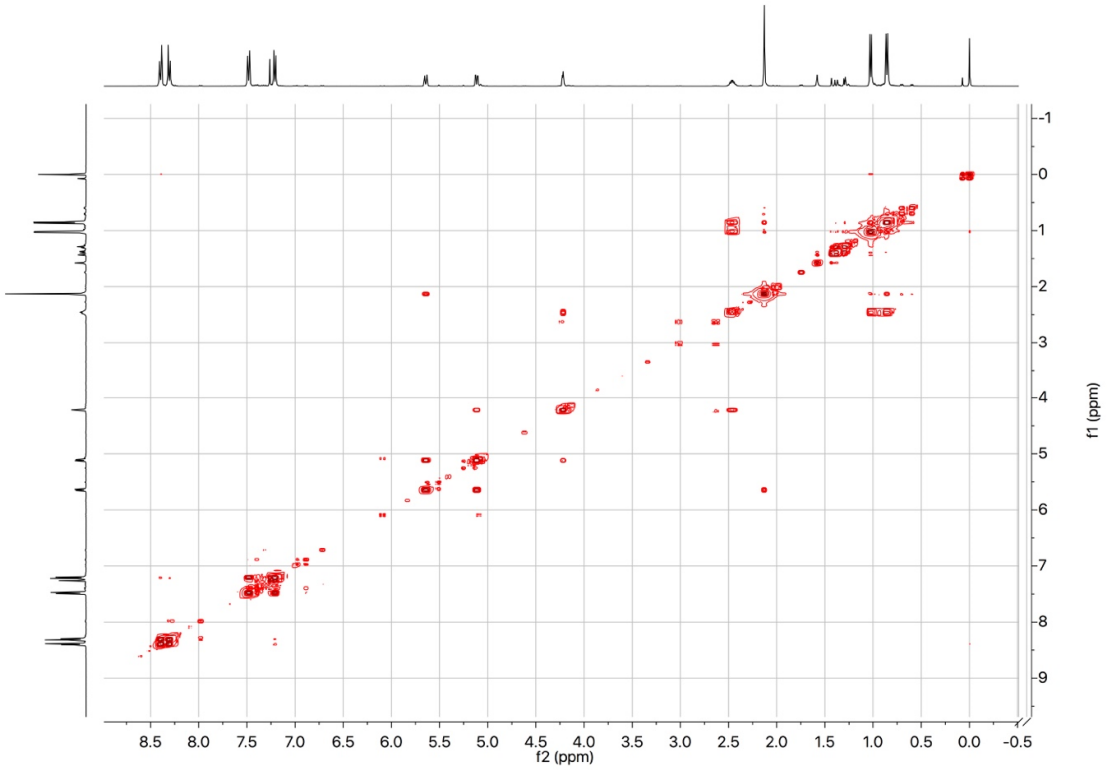

f2 (ppm)
f1 (ppm)

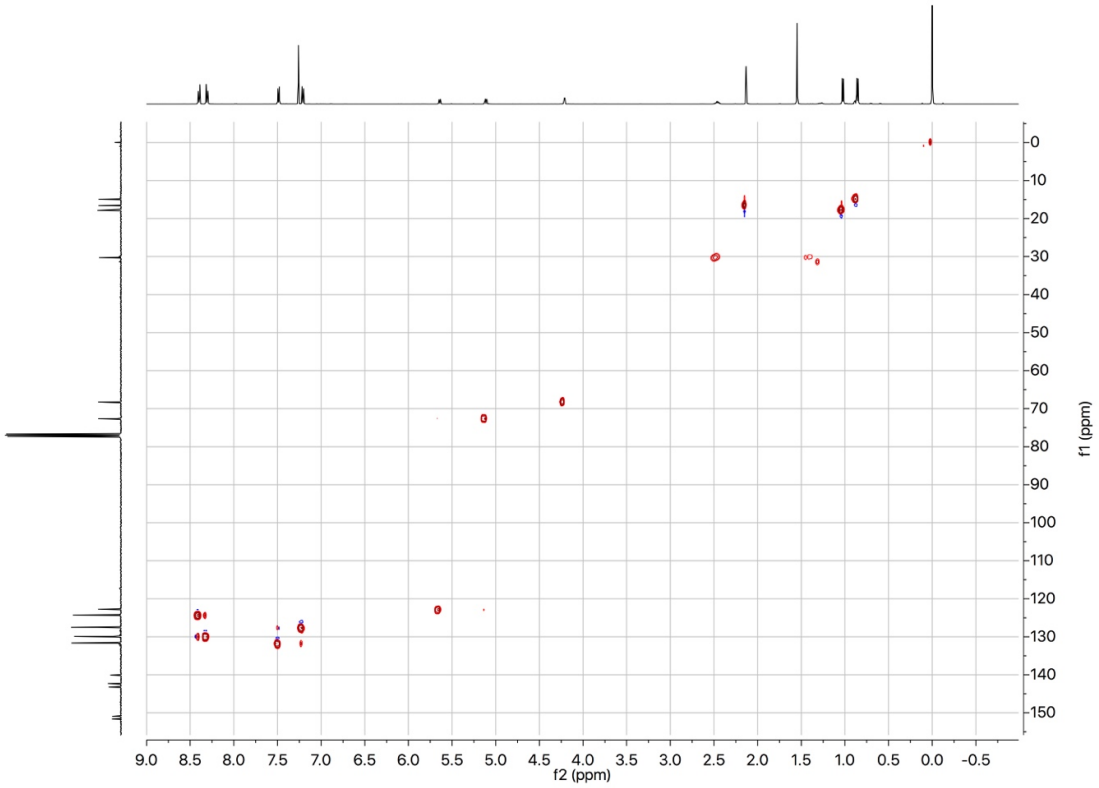


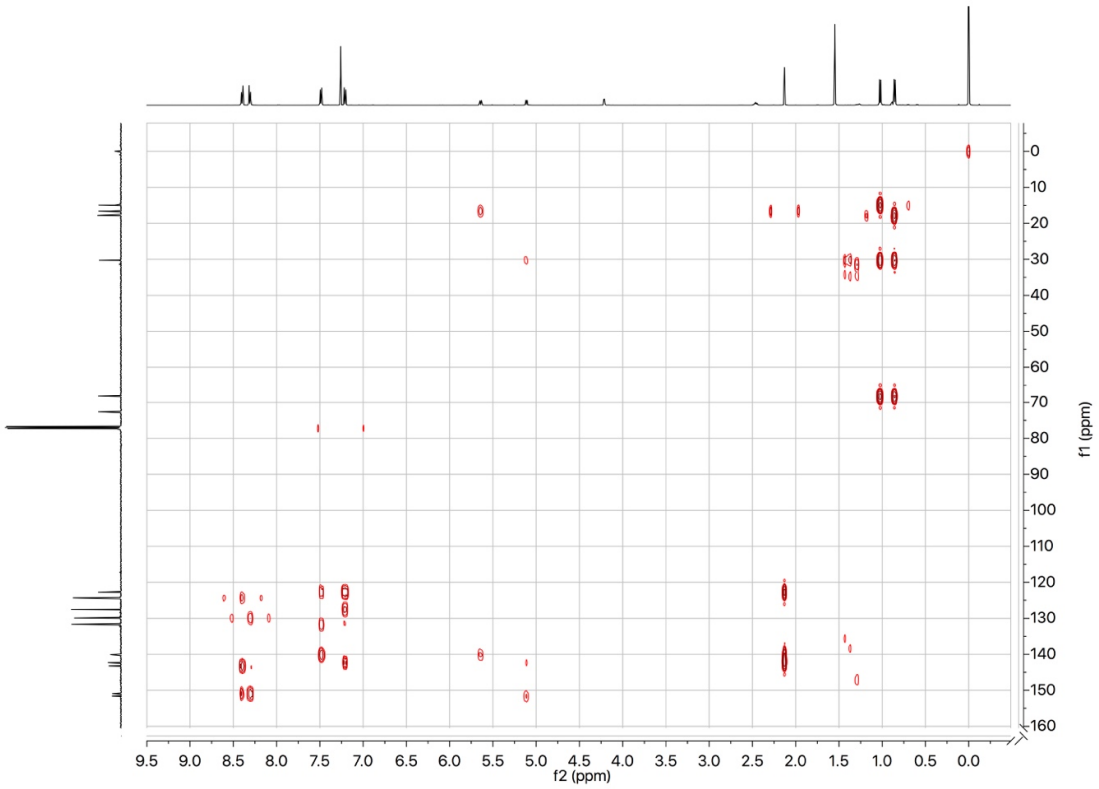
3g



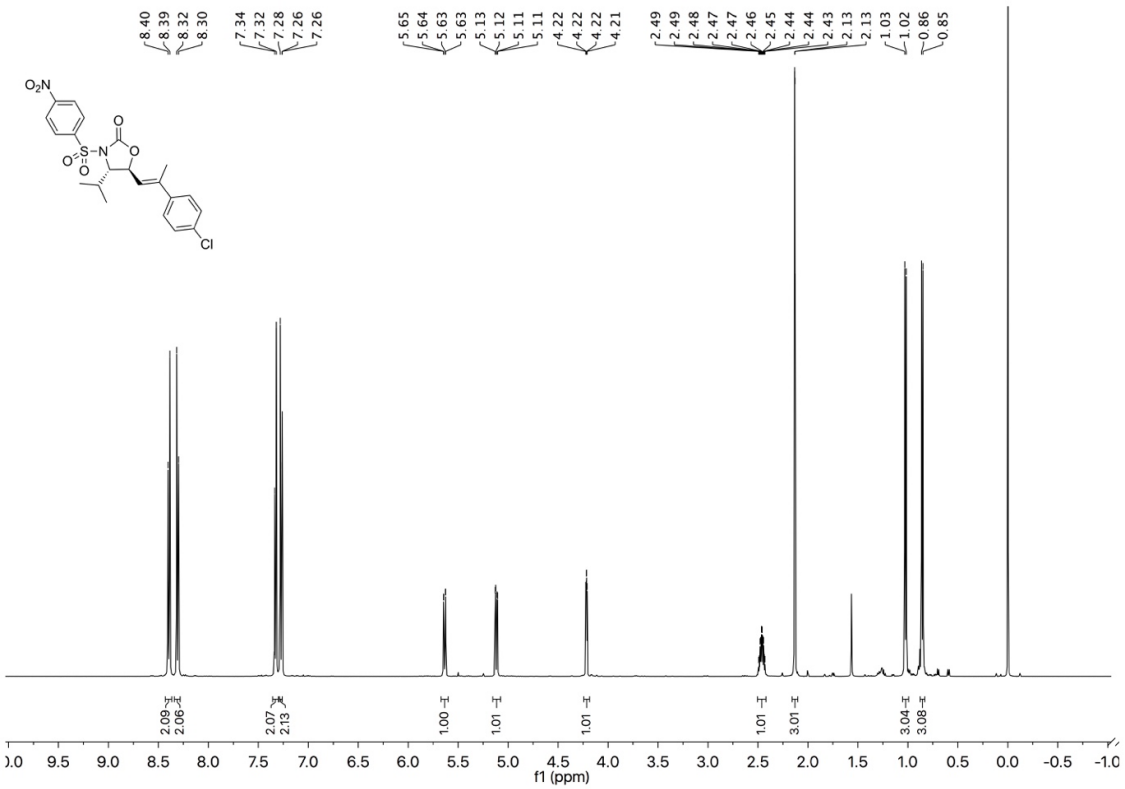

151.61
150.94
143.24
142.26
140.08
131.67
129.89
127.52
124.29
122.75
122.67
77.32
77.00
76.68
72.62
68.22
30.28
17.82
16.57
14.92
f1 (ppm)

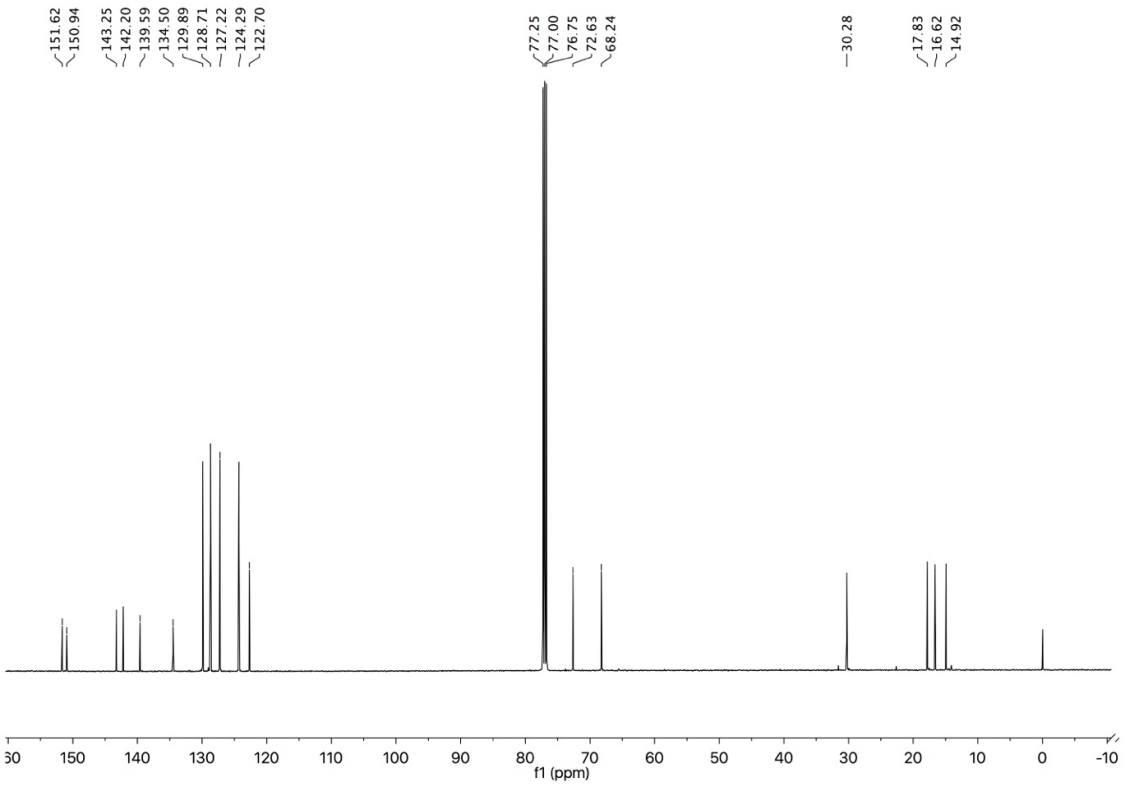

f2 (ppm)
f1 (ppm)

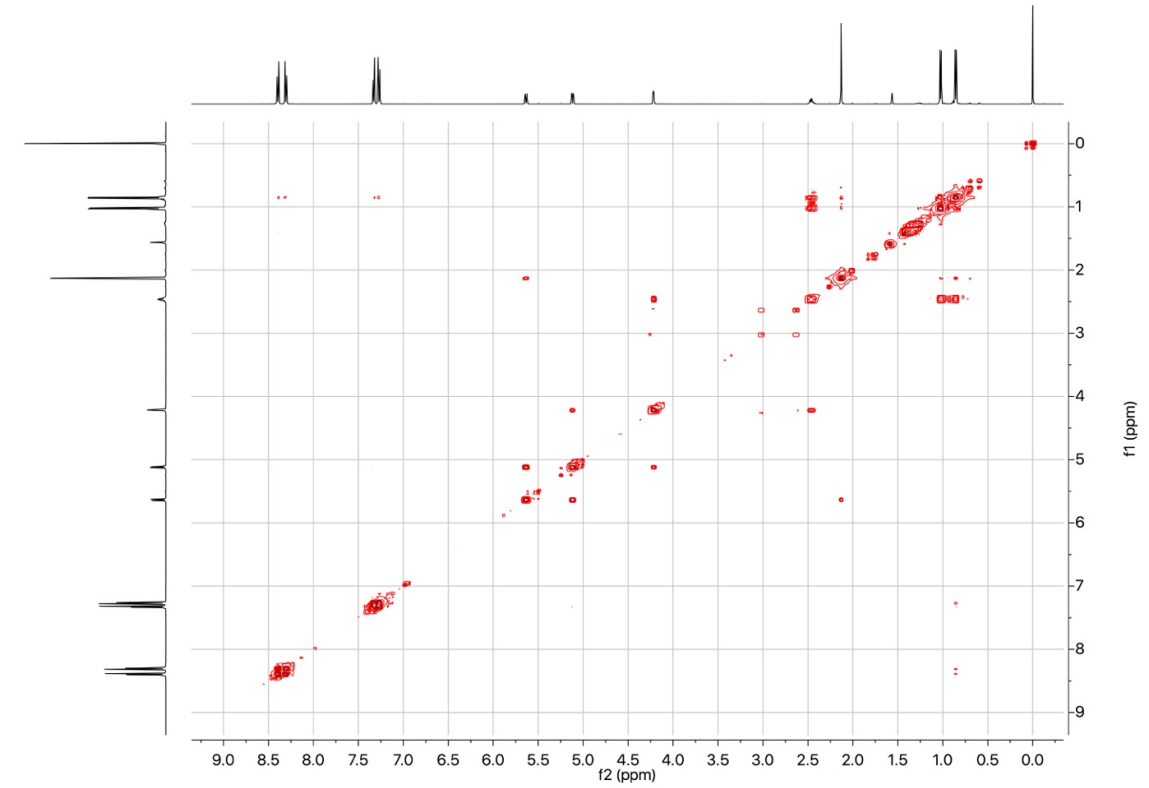

f2 (ppm)
f1 (ppm)

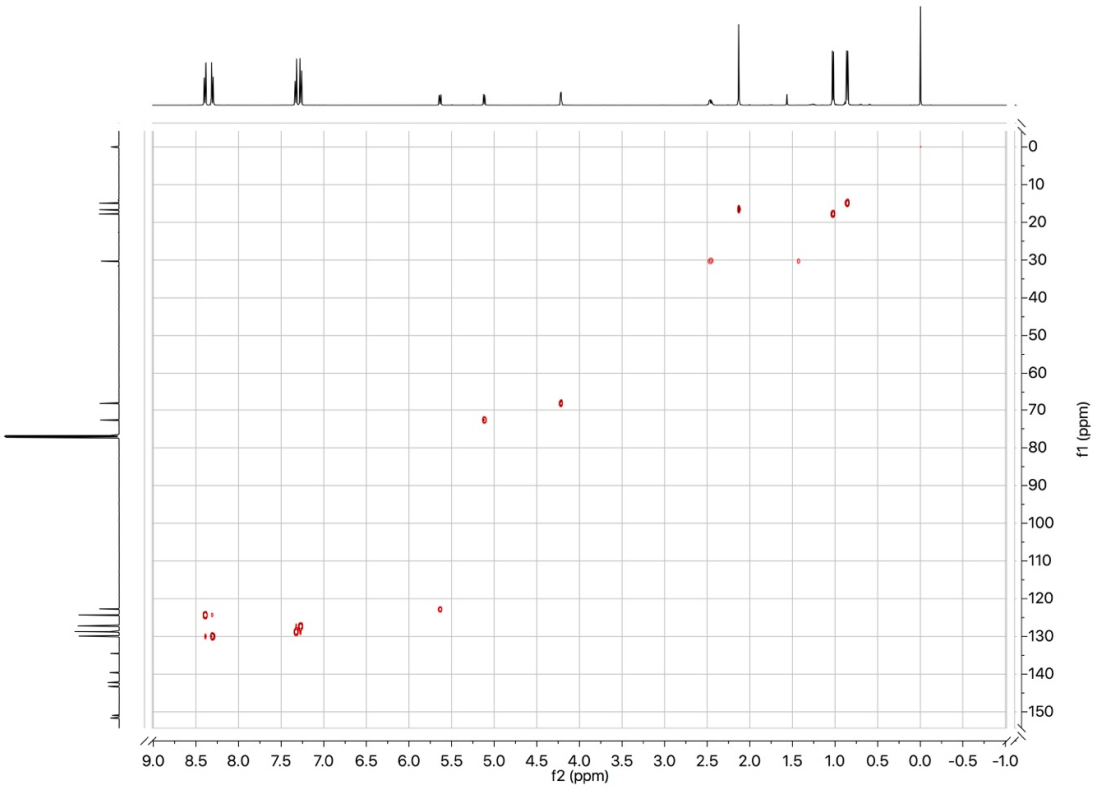

f2 (ppm)
f1 (ppm)

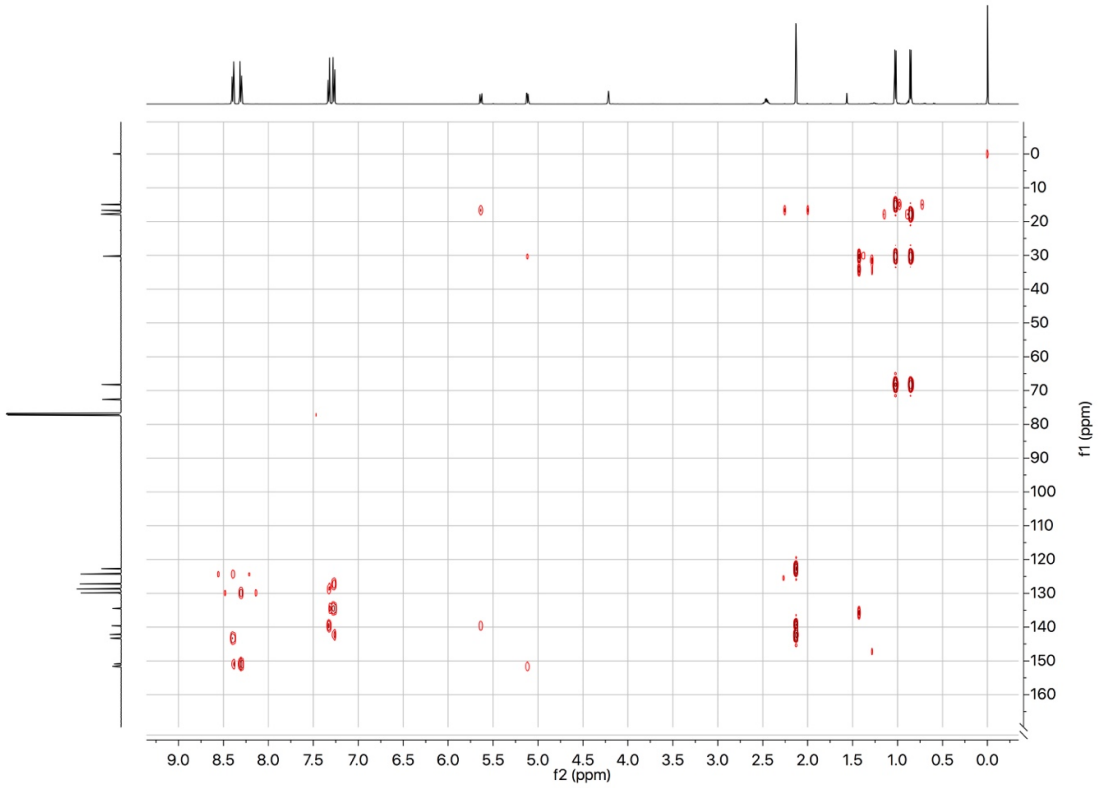
3h


8.40
8.39
8.32
8.30
7.34
7.32
7.28
7.26
7.26
5.65
5.64
5.63
5.63
5.13
5.12
5.11
5.11
4.22
4.22
4.22
4.21
2.49
2.49
2.48
2.47
2.47
2.46
2.45
2.44
2.44
2.43
2.13
2.13
1.03
1.02
0.86
0.85
O2N
O
O
S
N
O
O
Cl
2.09
2.06
2.07
2.13
1.00
1.01
1.01
1.01
3.01
3.04
3.08
f1 (ppm)

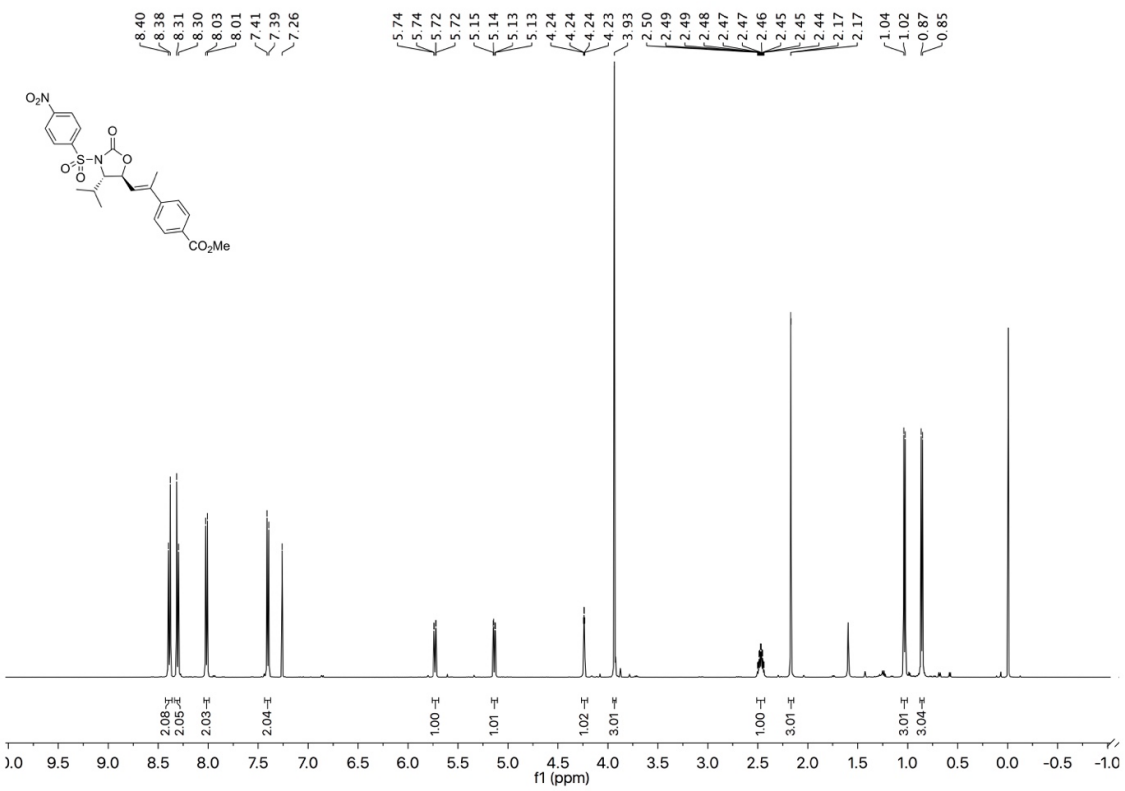

151.62
150.94
143.25
142.20
139.59
134.50
129.89
128.71
127.22
124.29
122.70
77.25
77.00
76.75
72.63
68.24
30.28
17.83
16.62
14.92
f1 (ppm)

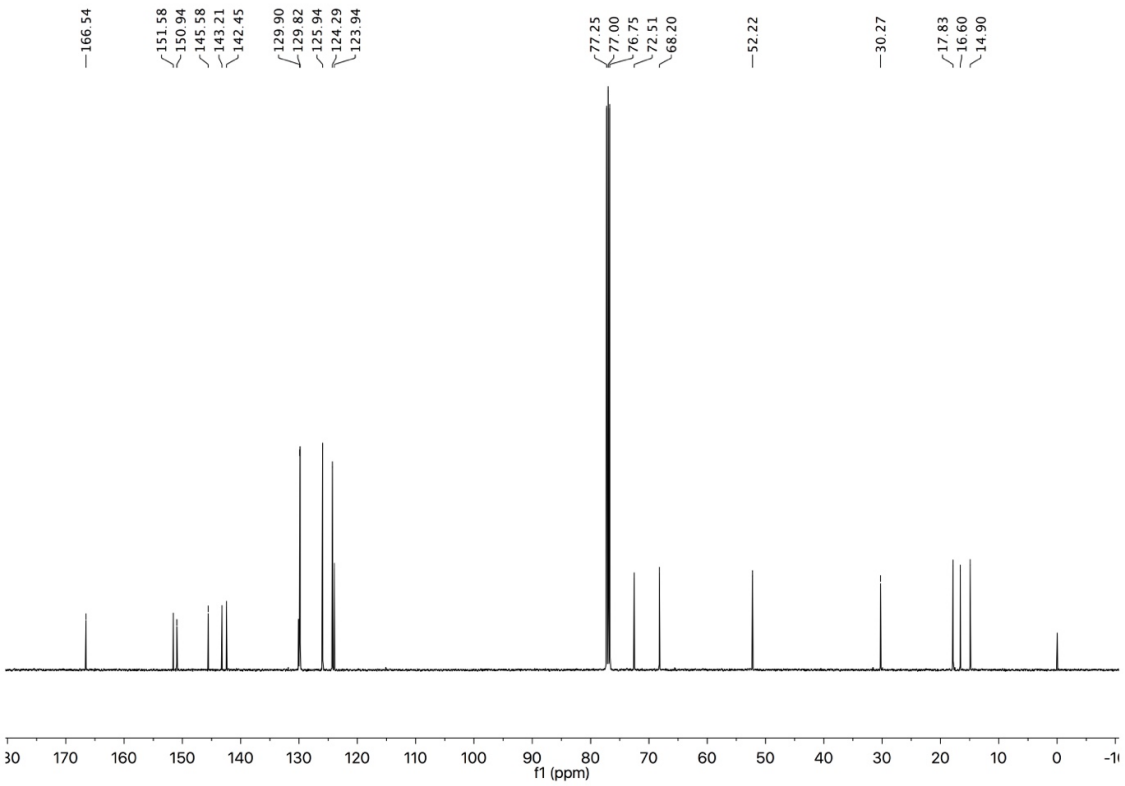

f2 (ppm)
f1 (ppm)

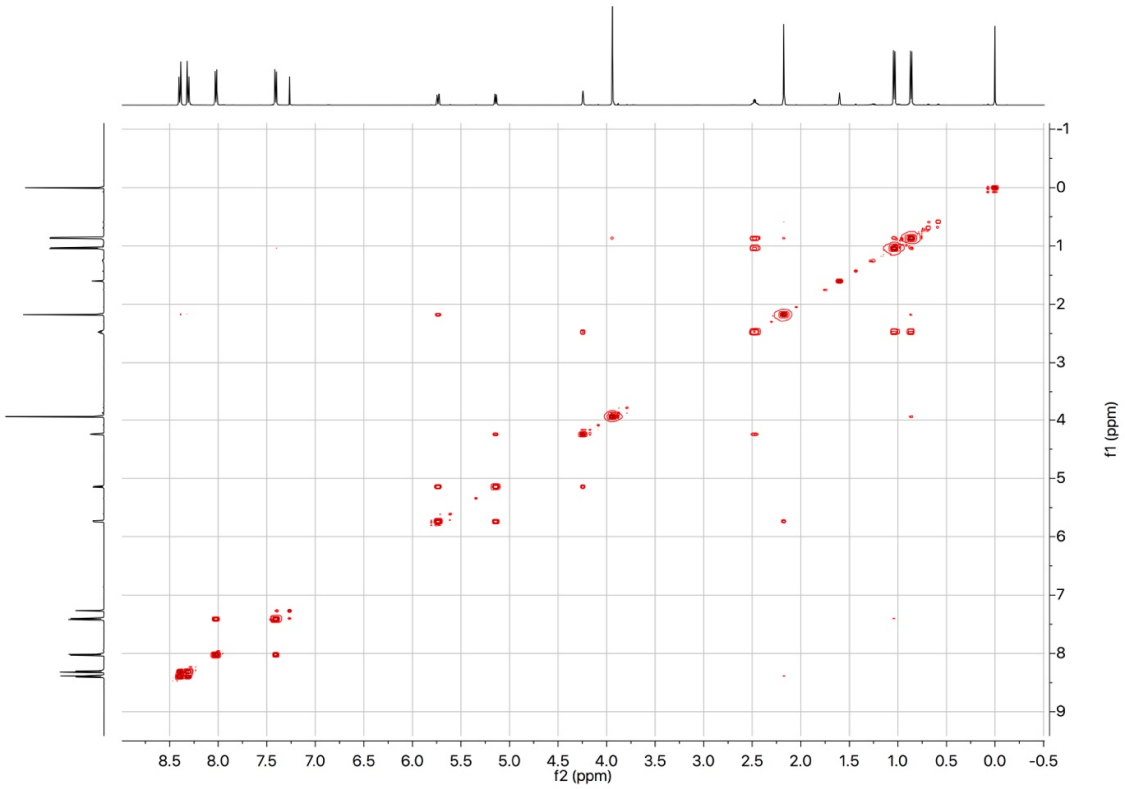

f2 (ppm)
f1 (ppm)

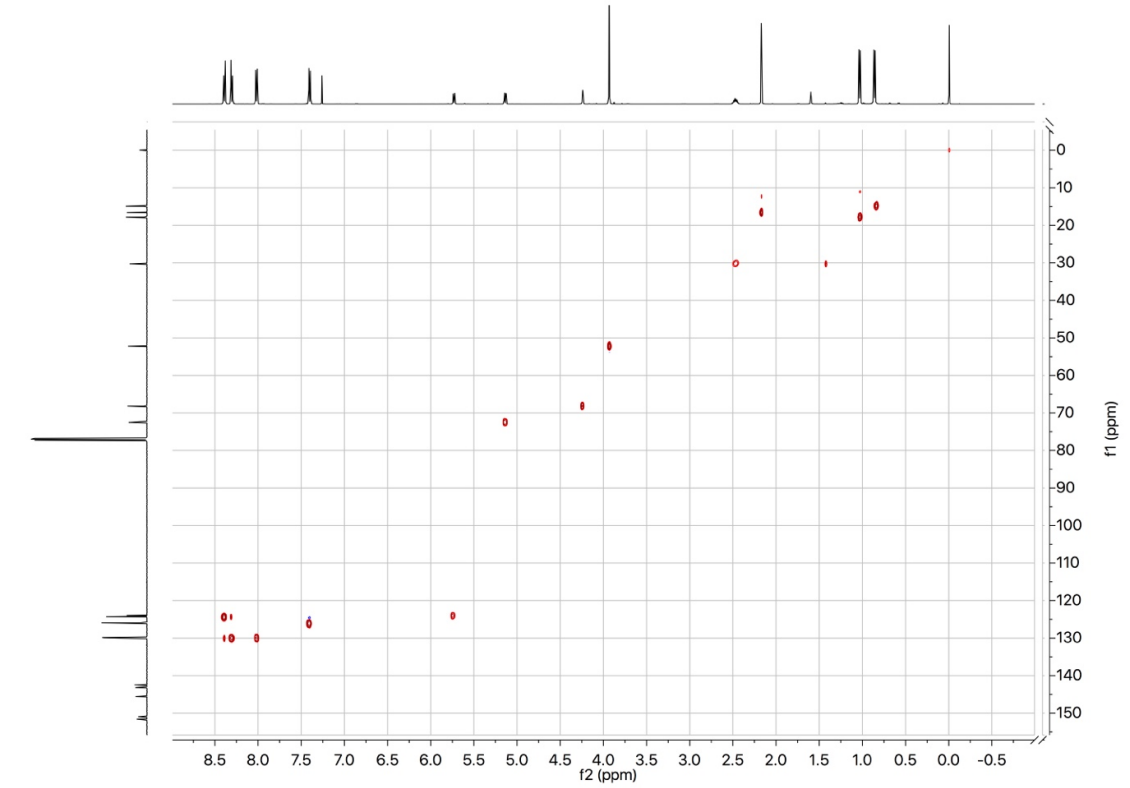

f2 (ppm)
f1 (ppm)

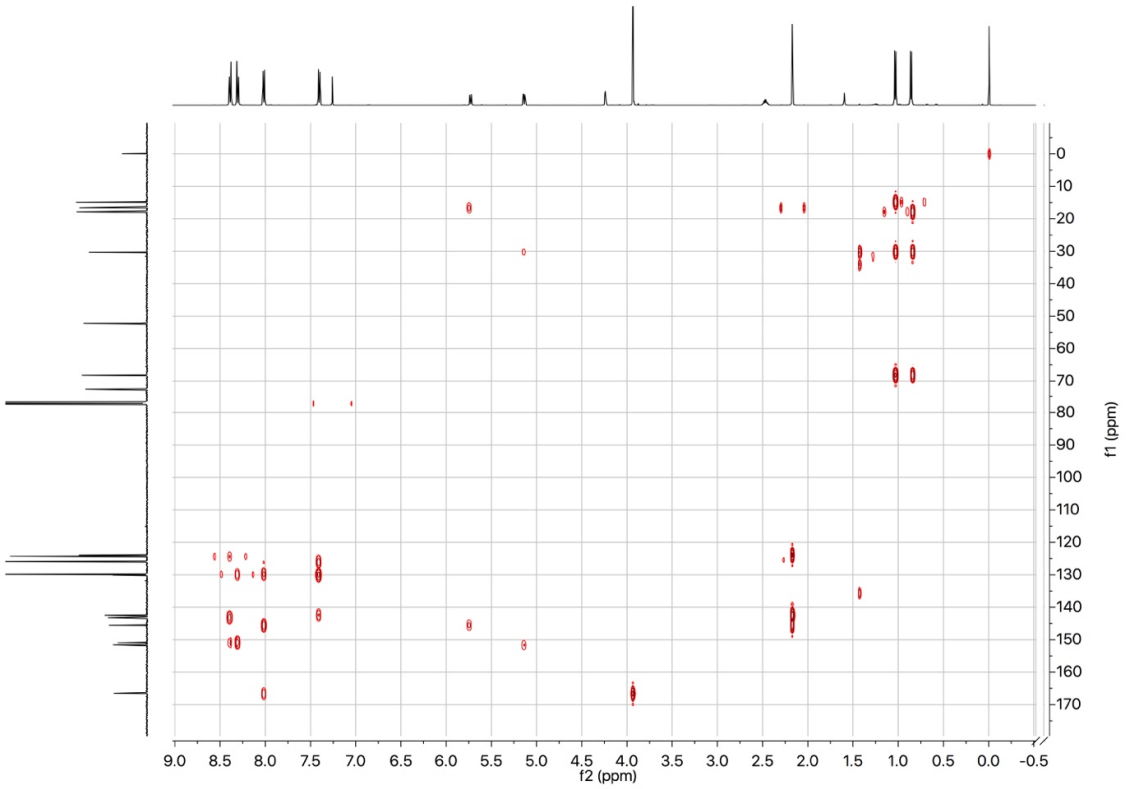
3i


8.40
8.38
8.31
8.30
8.03
8.01
7.41
7.39
7.26
5.74
5.74
5.72
5.72
5.15
5.14
5.13
4.24
4.24
4.23
3.93
2.50
2.49
2.49
2.48
2.47
2.47
2.46
2.45
2.45
2.44
2.17
2.17
1.04
1.02
0.87
0.85
O2N
CO2Me
f1 (ppm)

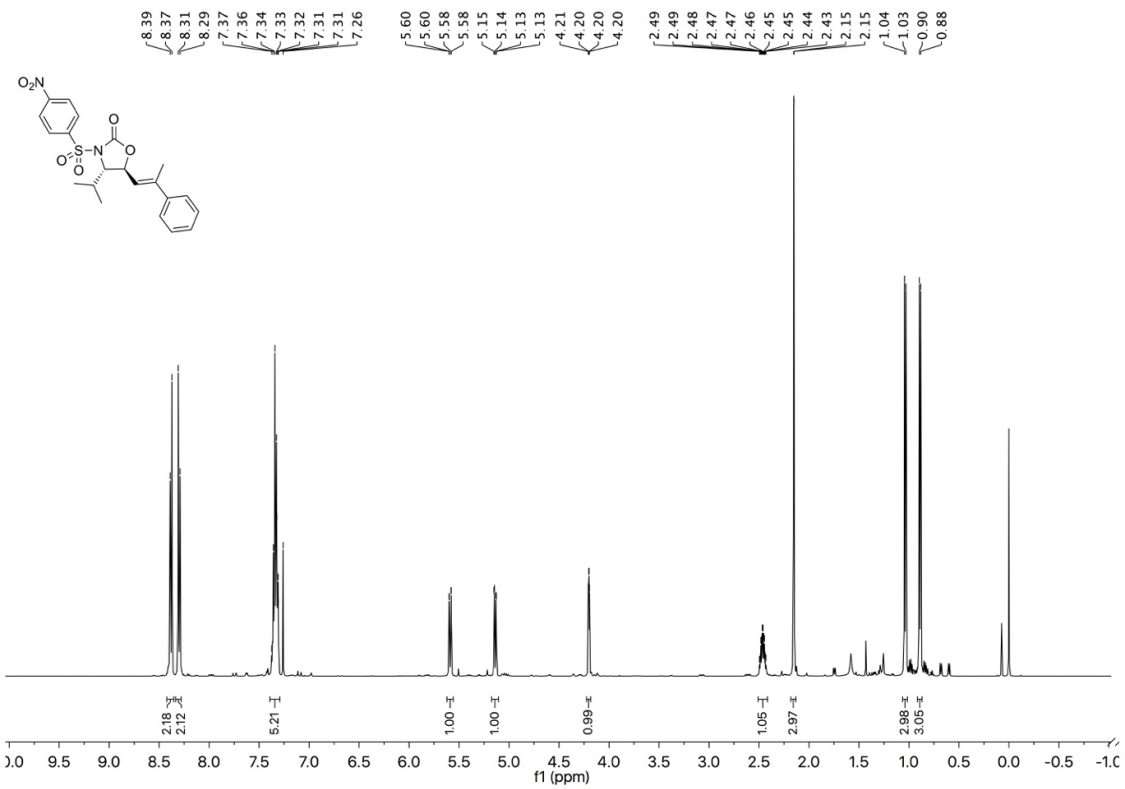

166.54
151.58
150.94
145.58
143.21
142.45
129.90
129.82
125.94
124.29
123.94
77.25
77.00
76.75
72.51
68.20
52.22
30.27
17.83
16.60
14.90
f1 (ppm)

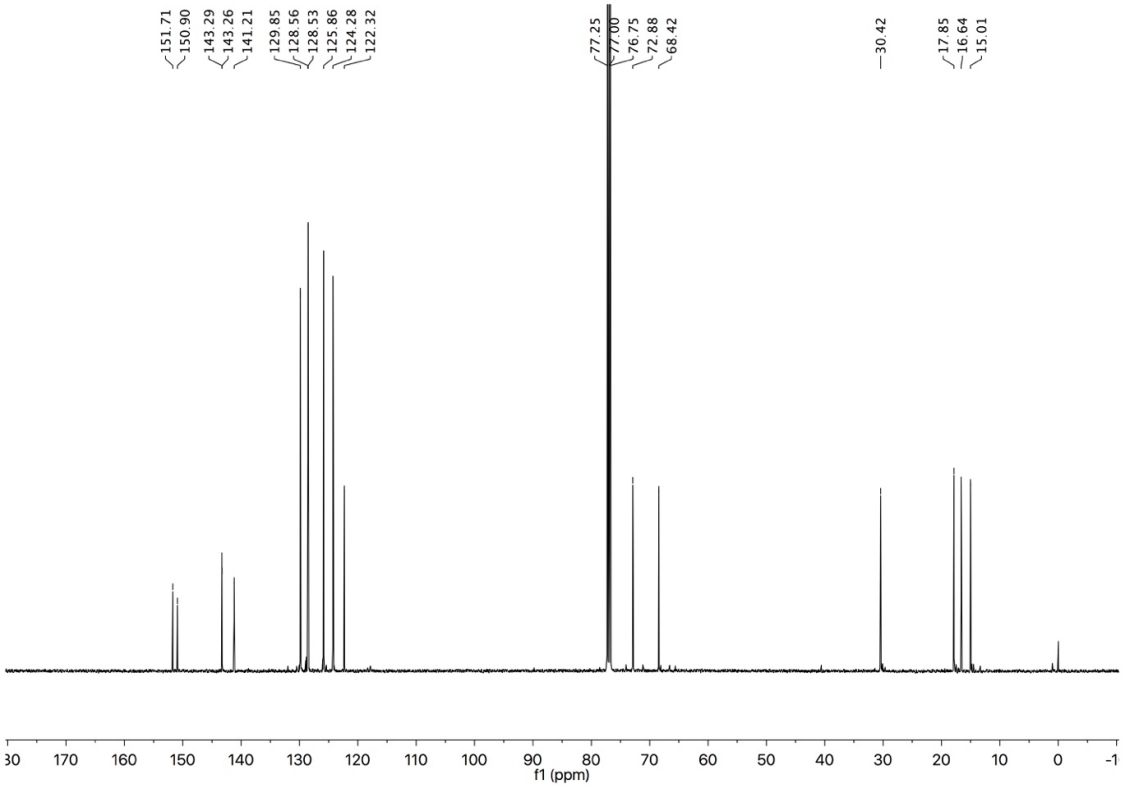

f2 (ppm)
f1 (ppm)

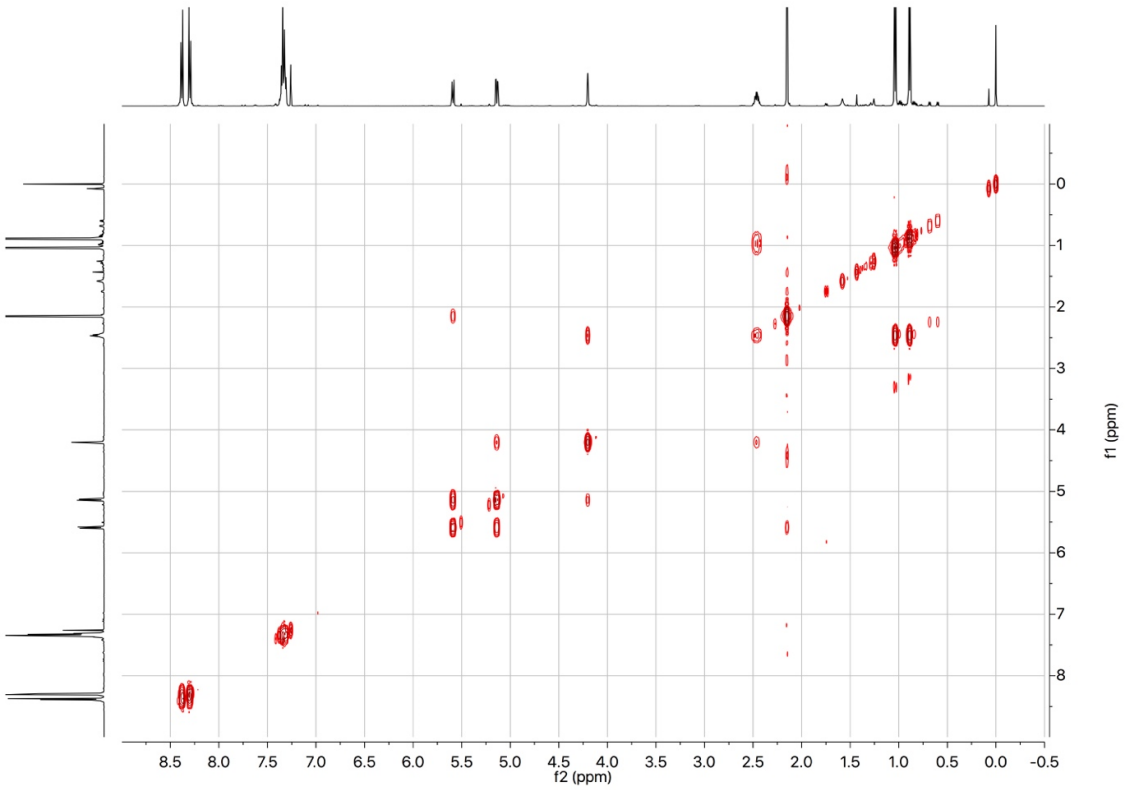

f2 (ppm)
f1 (ppm)

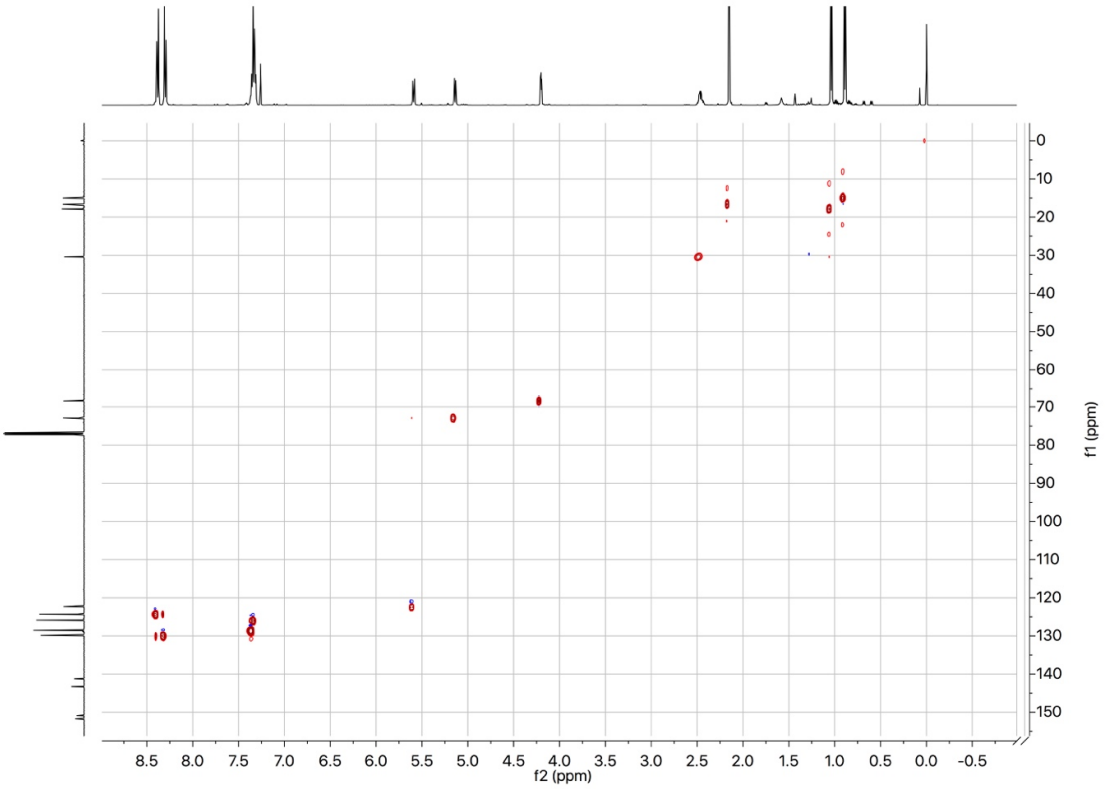

f2 (ppm)
f1 (ppm)

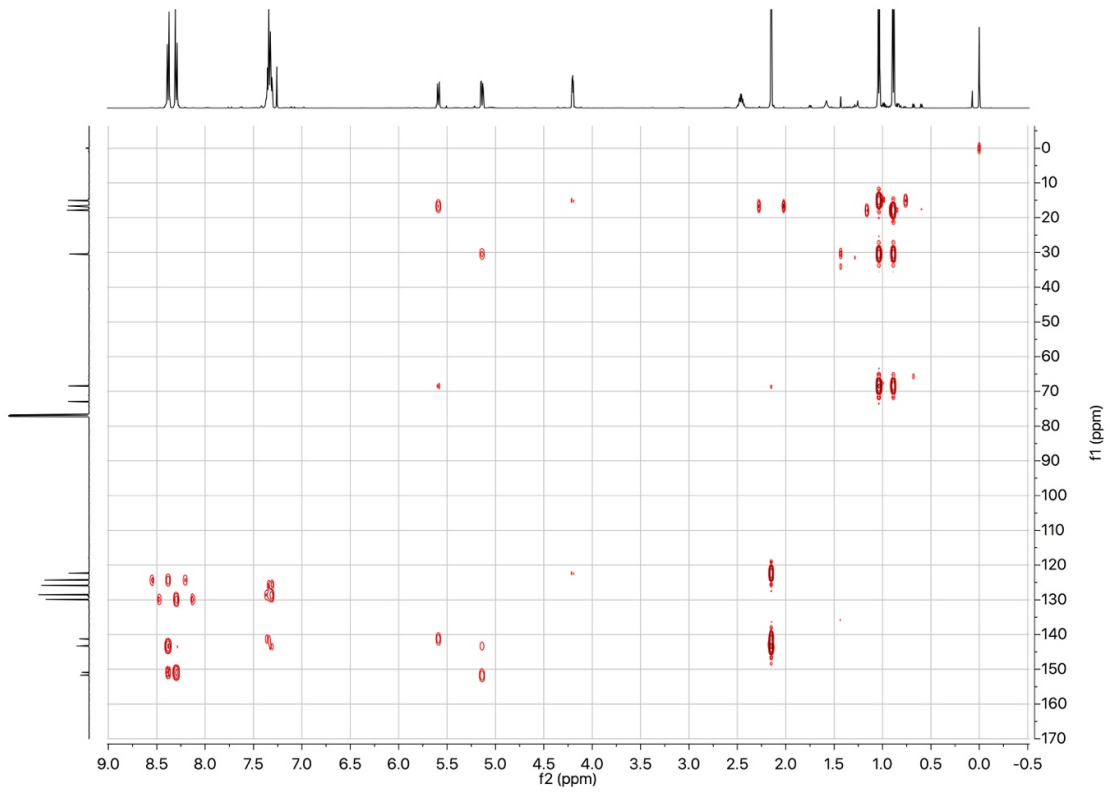
3j


8.39
8.37
8.31
8.29
7.37
7.36
7.34
7.33
7.32
7.31
7.31
7.26
5.60
5.60
5.58
5.58
5.15
5.14
5.13
5.13
4.21
4.20
4.20
4.20
2.49
2.49
2.48
2.47
2.47
2.46
2.45
2.45
2.44
2.43
2.15
2.15
1.04
1.03
0.90
0.88
O2N
O
S
N
O
O
O
2.18
2.12
5.21
1.00
1.00
0.99
1.05
2.97
2.98
3.05
f1 (ppm)

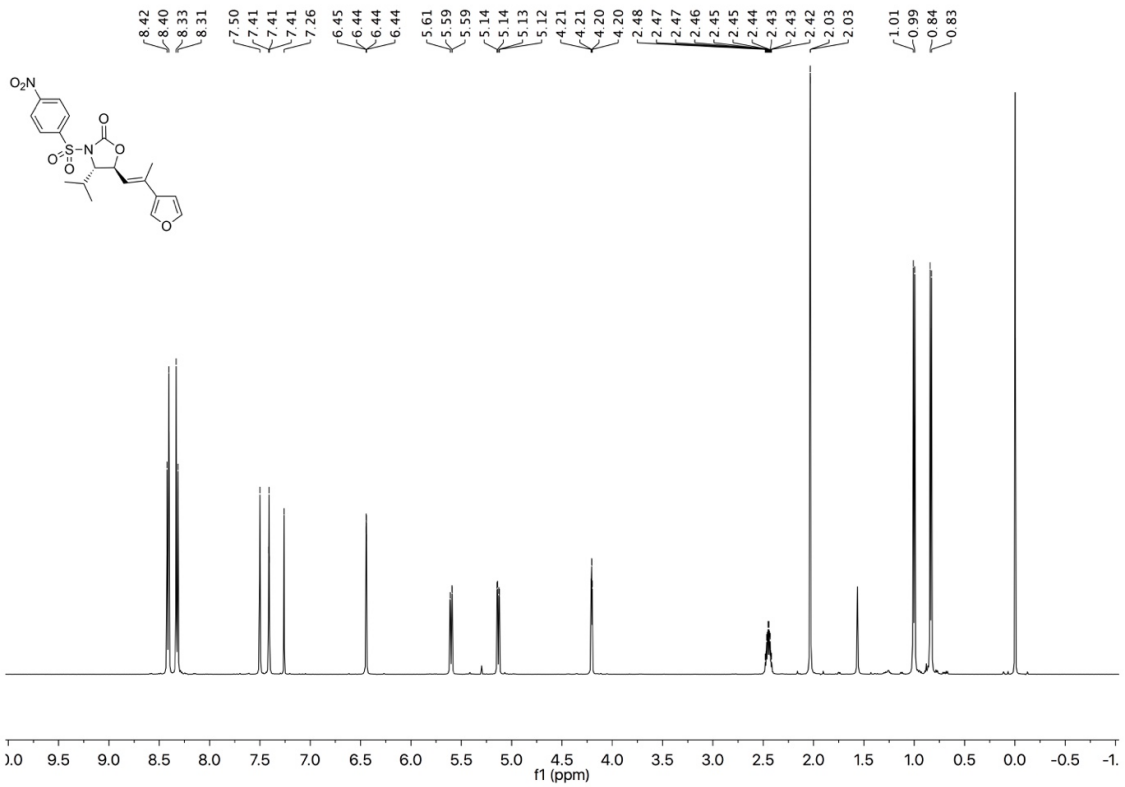

151.71
150.90
143.29
143.26
141.21
129.85
128.56
128.53
125.86
124.28
122.32
77.25
77.00
76.75
72.88
68.42
30.42
17.85
16.64
15.01
f1 (ppm)

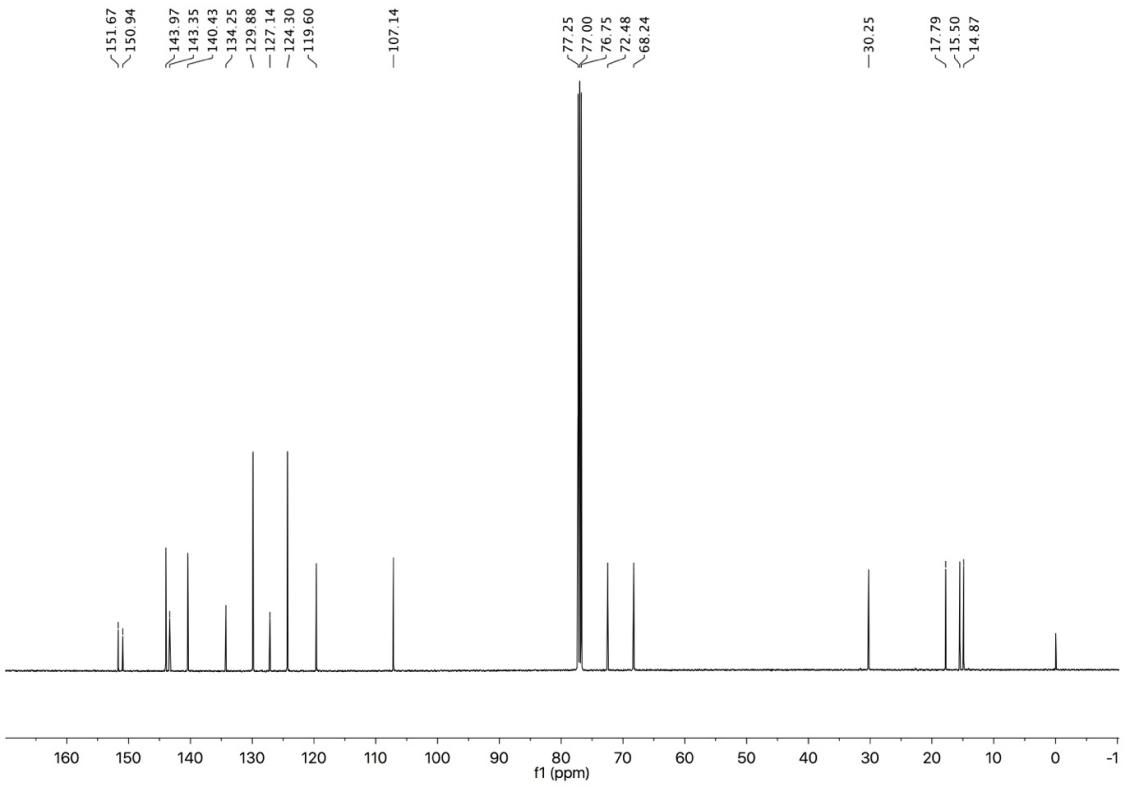

f2 (ppm)
f1 (ppm)

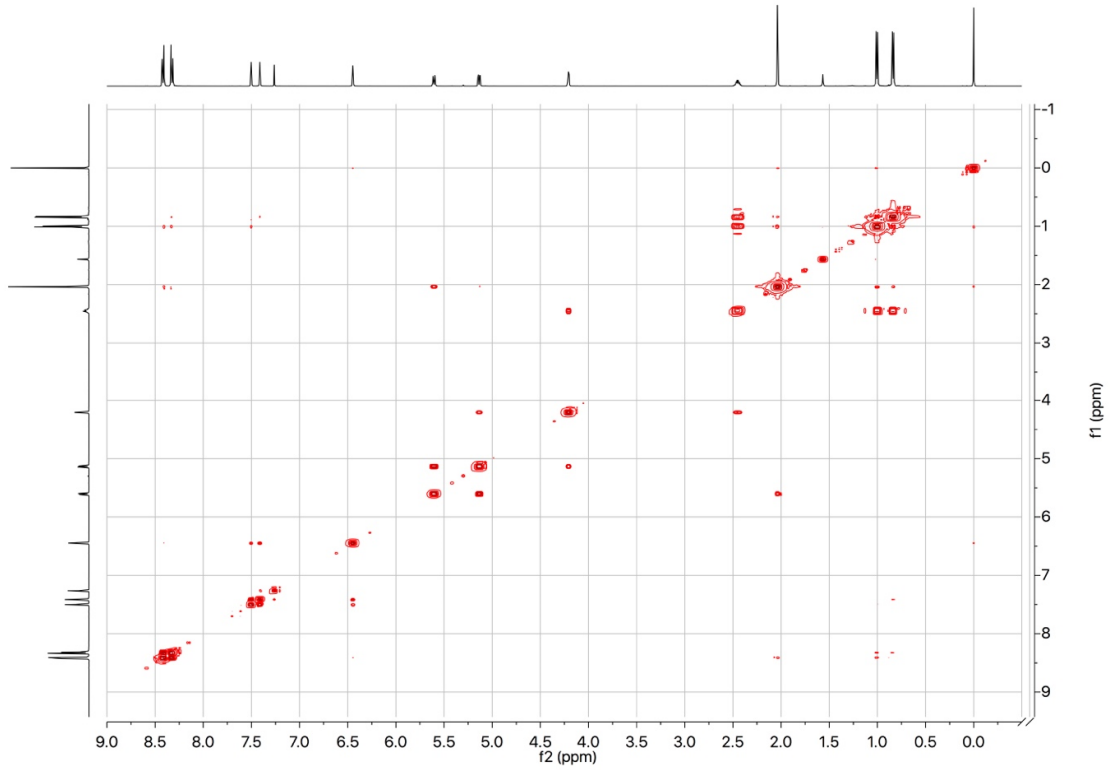

f2 (ppm)
f1 (ppm)

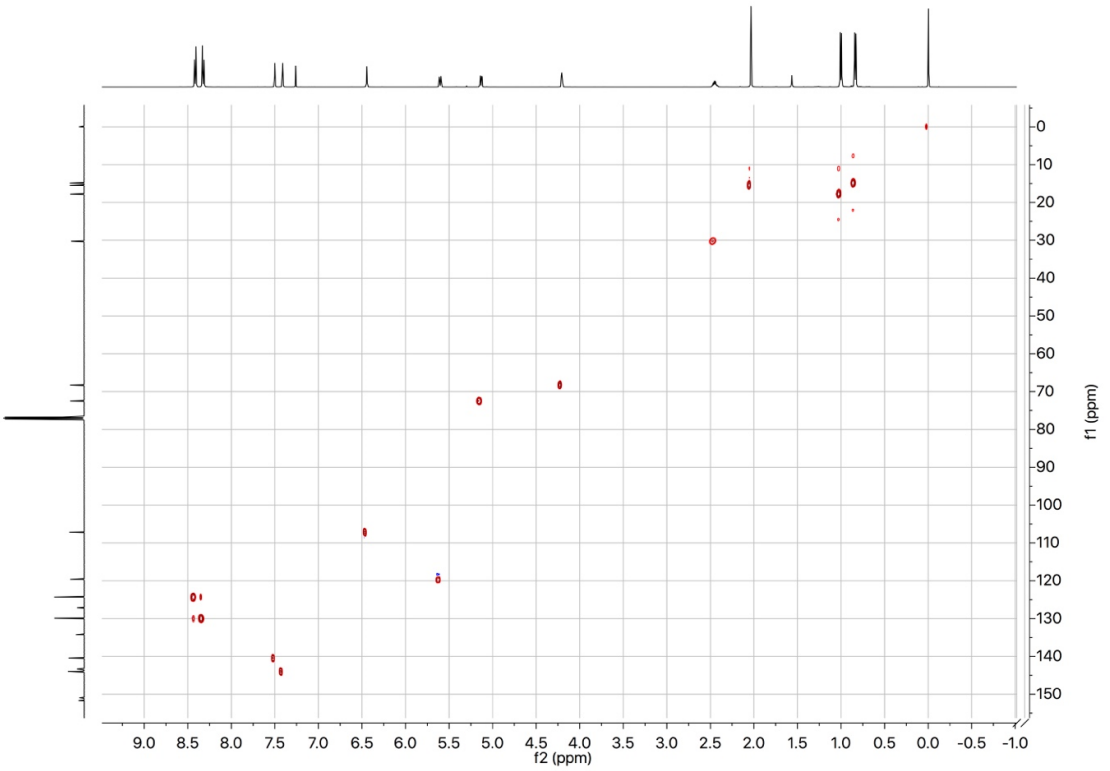

f2 (ppm)
f1 (ppm)

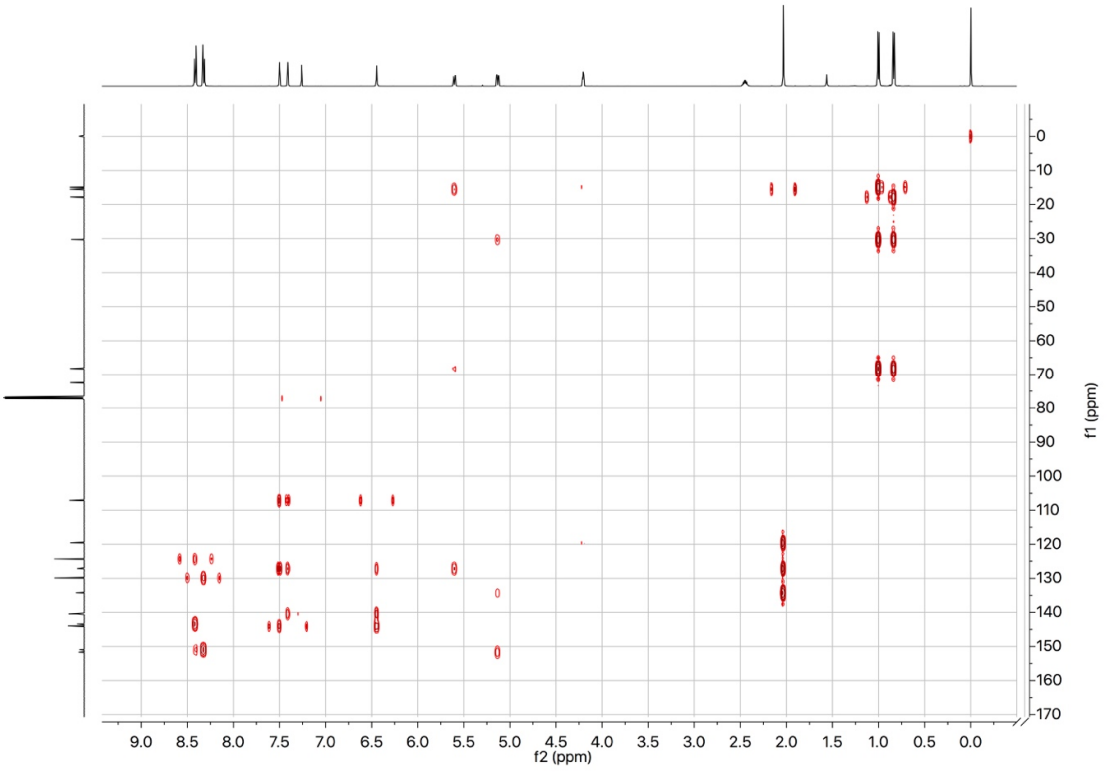
3k


8.42
8.40
8.33
8.31
7.50
7.41
7.41
7.41
7.26
6.45
6.44
6.44
6.44
5.61
5.59
5.59
5.14
5.14
5.13
5.12
4.21
4.21
4.20
4.20
2.48
2.47
2.47
2.46
2.45
2.45
2.44
2.43
2.43
2.42
2.03
2.03
1.01
0.99
0.84
0.83
f1 (ppm)

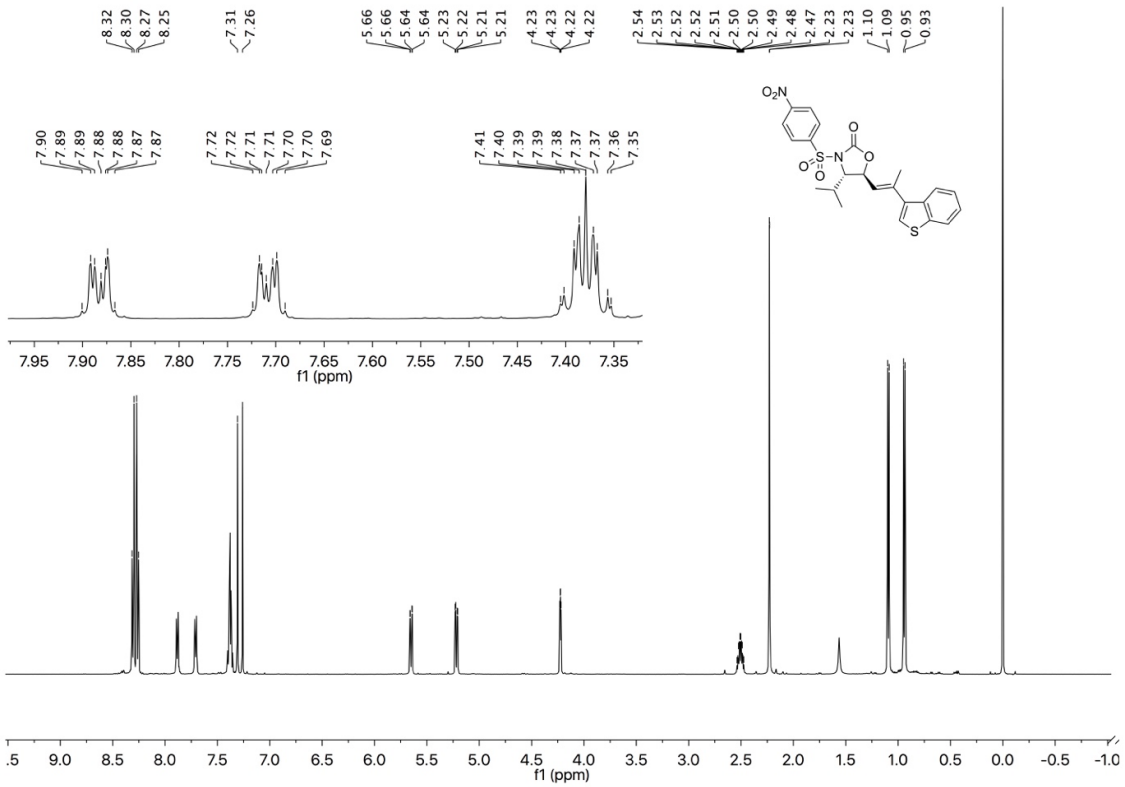

151.67
150.94
143.97
143.35
140.43
134.25
129.88
127.14
124.30
119.60
107.14
77.25
77.00
76.75
72.48
68.24
30.25
17.79
15.50
14.87
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

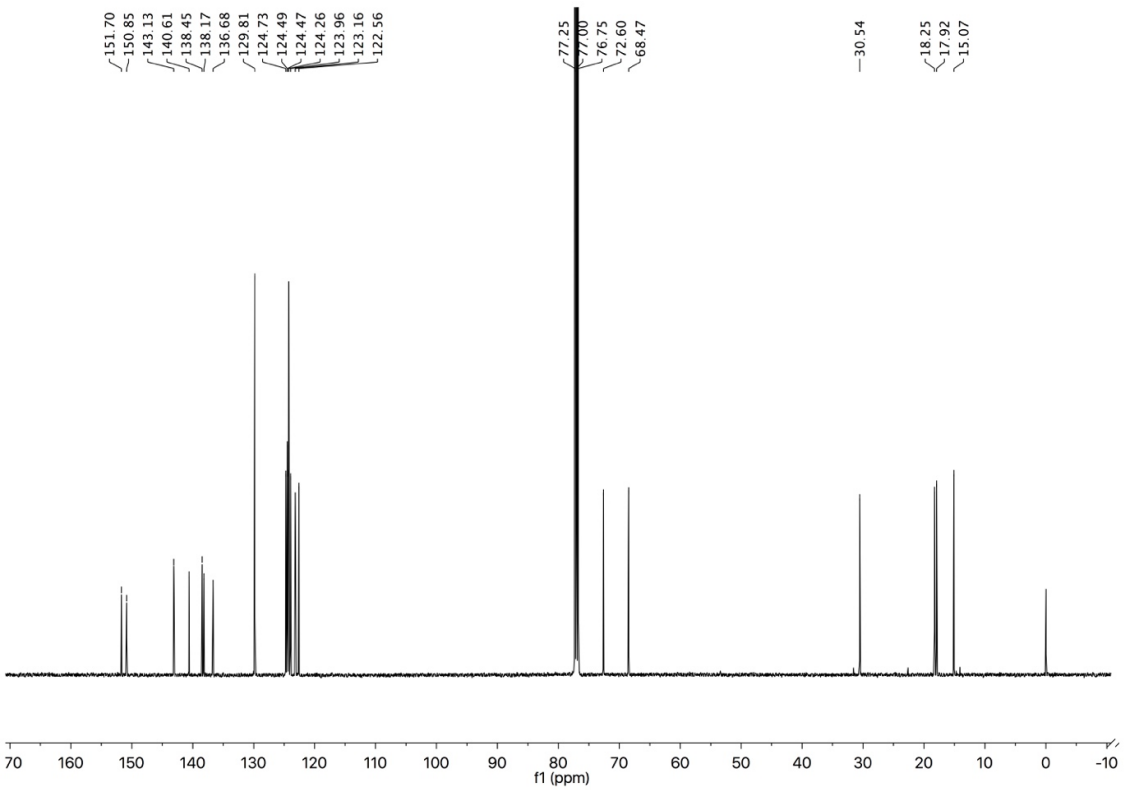

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f2 (ppm)
-1 0 1 2 3 4 5 6 7 8 9
f1 (ppm)

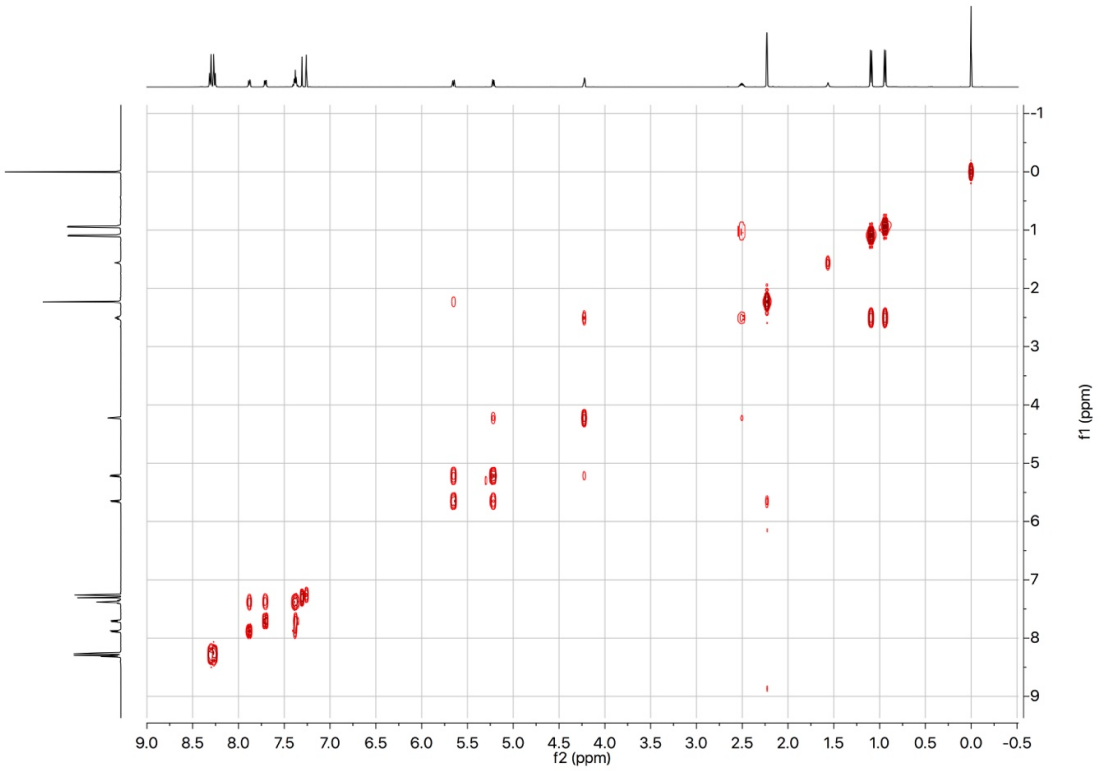

f2 (ppm)
f1 (ppm)

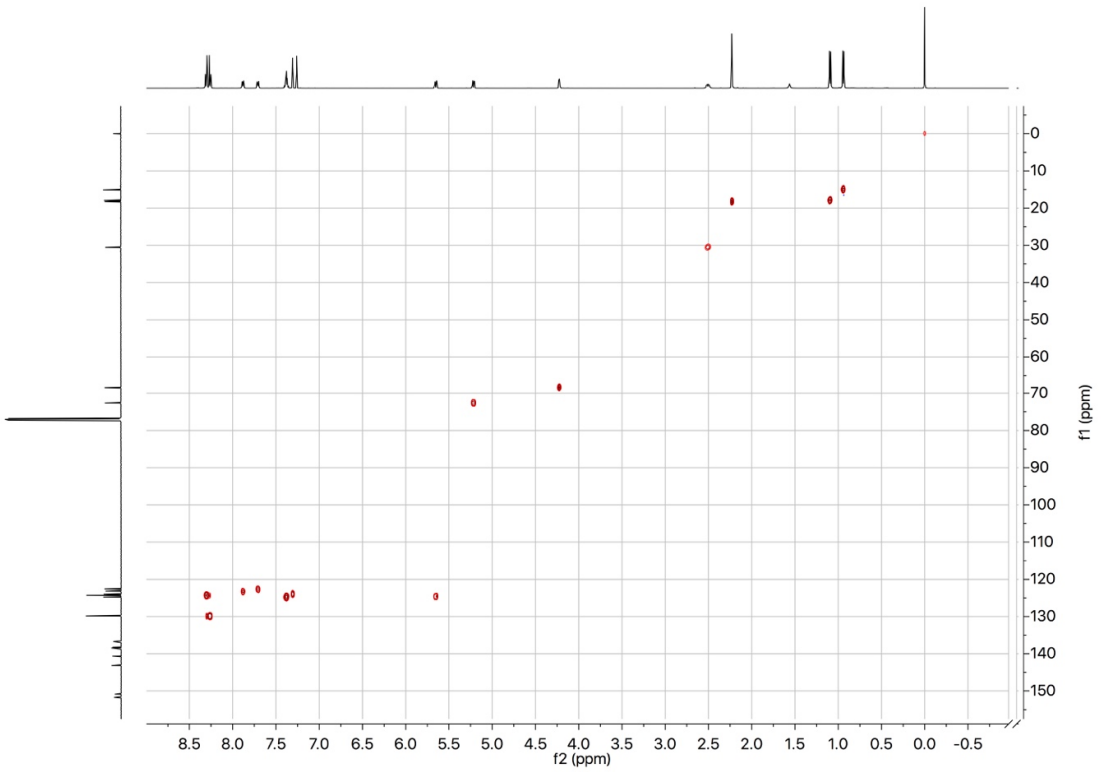

f2 (ppm)
f1 (ppm)

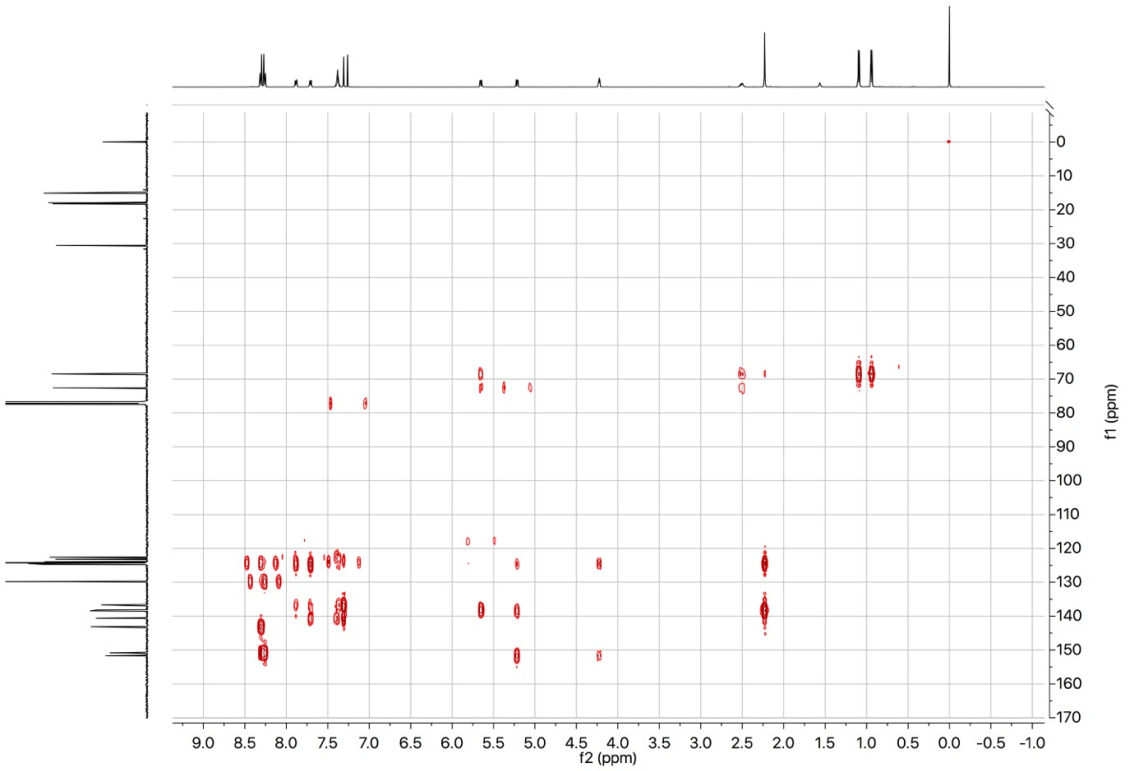
3l


8.32
8.30
8.27
8.25
7.31
7.26
5.66
5.66
5.64
5.64
5.23
5.22
5.21
5.21
4.23
4.23
4.22
4.22
2.54
2.53
2.52
2.52
2.51
2.50
2.50
2.49
2.48
2.47
2.23
2.23
1.10
1.09
0.95
0.93
7.90
7.89
7.89
7.88
7.88
7.87
7.87
7.72
7.72
7.71
7.71
7.70
7.70
7.69
7.41
7.40
7.39
7.39
7.38
7.37
7.37
7.36
7.35
O2N
O
O
S
N
O
O
O
S
7.95 7.90 7.85 7.80 7.75 7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

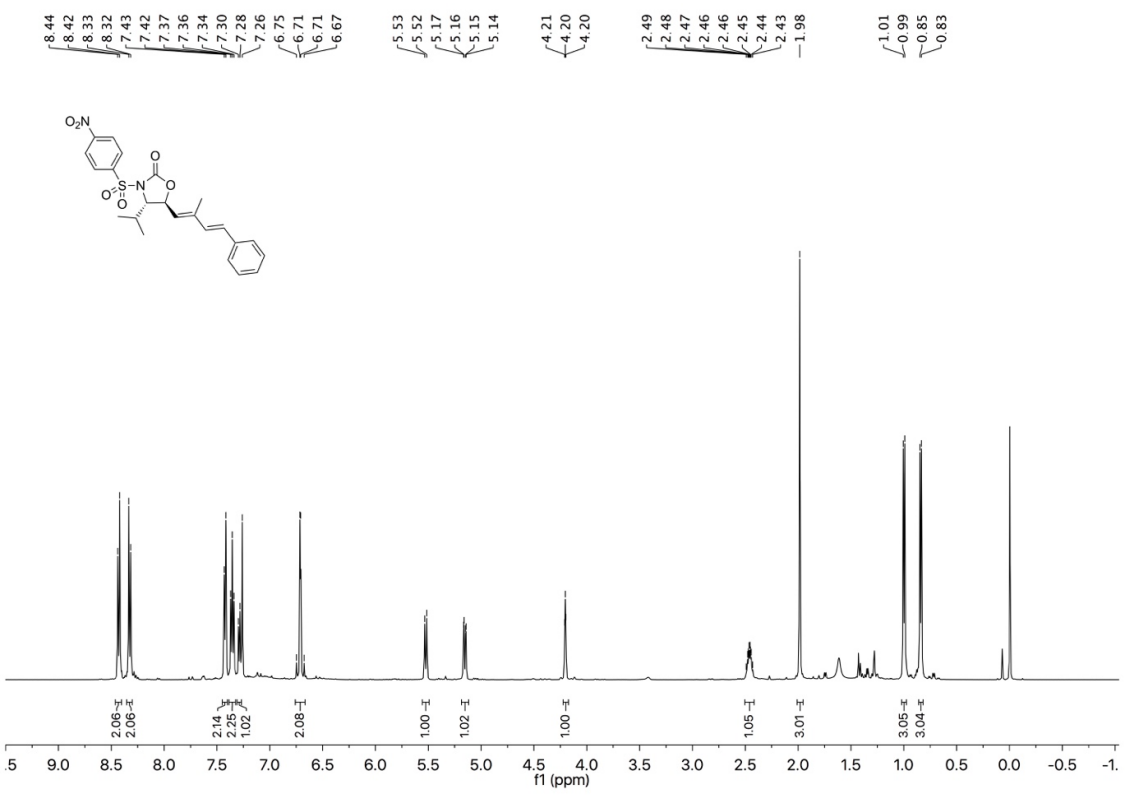

151.70
150.85
143.13
140.61
138.45
138.17
136.68
129.81
124.73
124.49
124.47
124.26
123.96
123.16
122.56
77.25
77.00
76.75
72.60
68.47
30.54
18.25
17.92
15.07
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

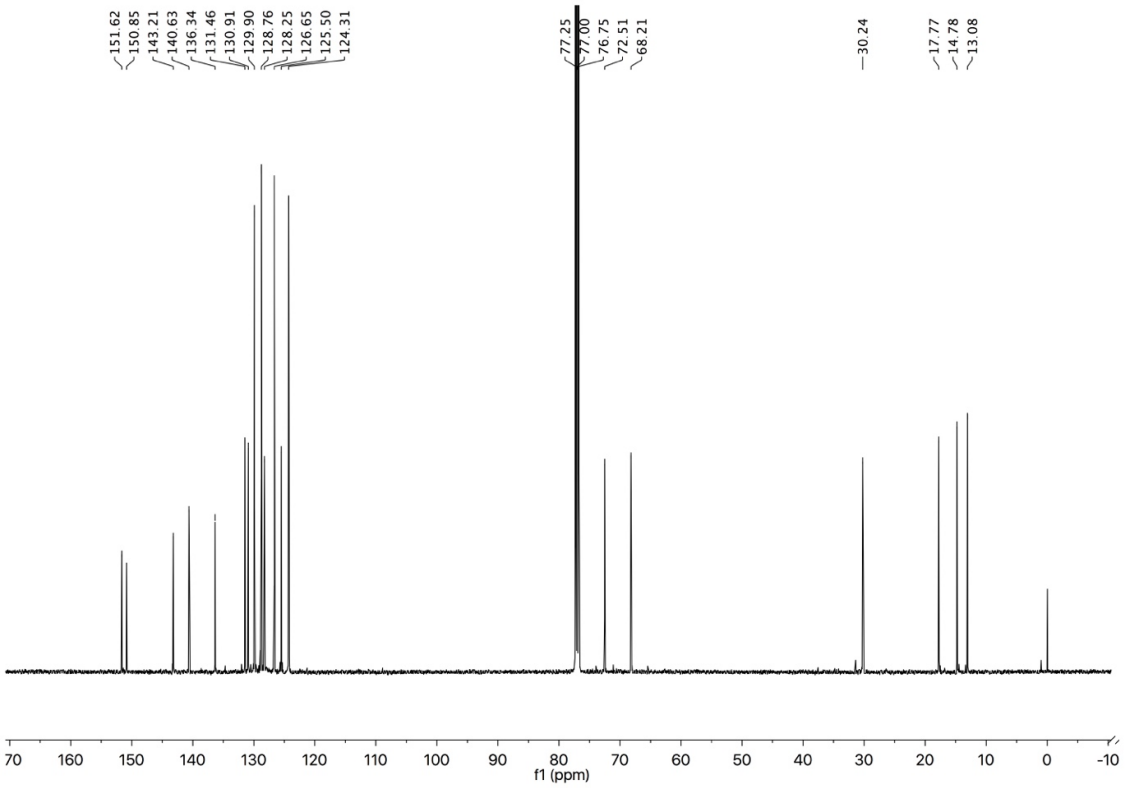

f2 (ppm)
f1 (ppm)

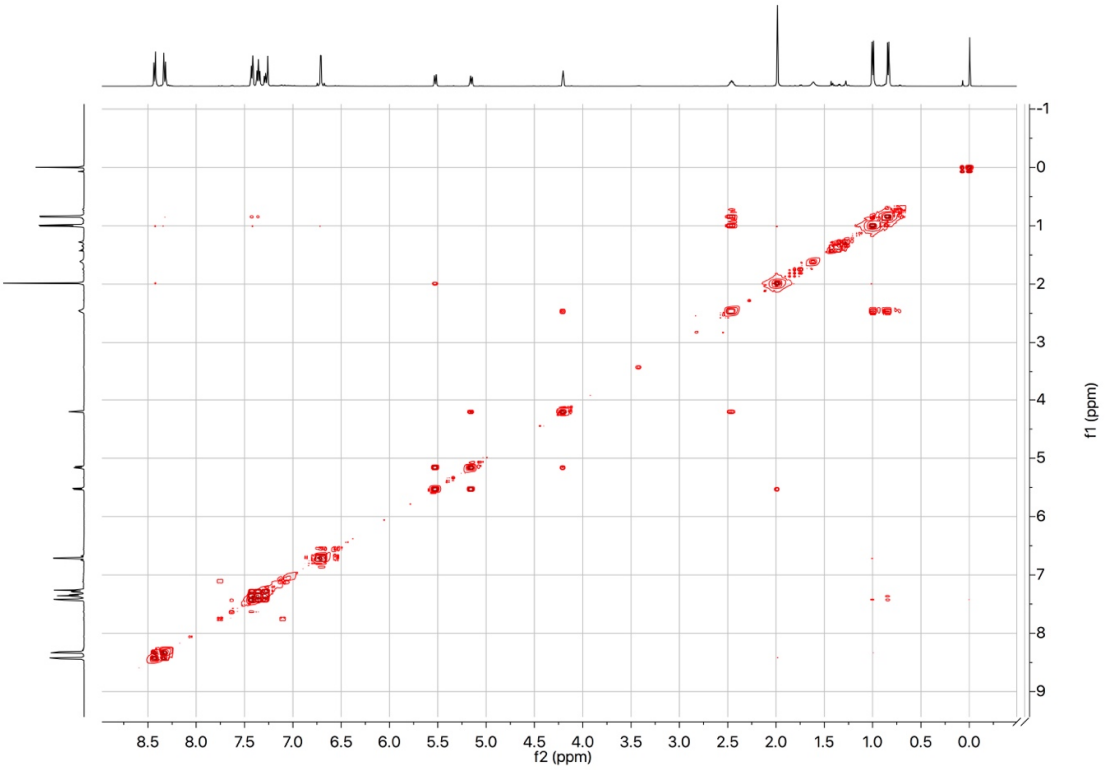

f2 (ppm)
f1 (ppm)

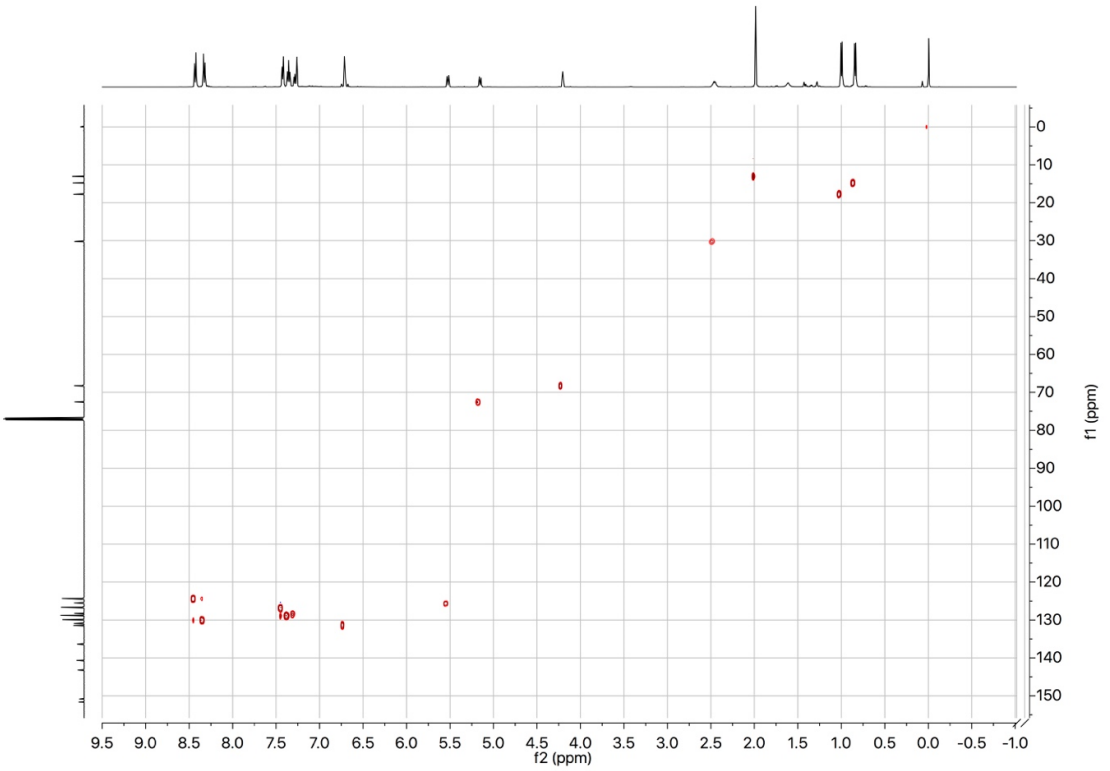

f2 (ppm)
f1 (ppm)

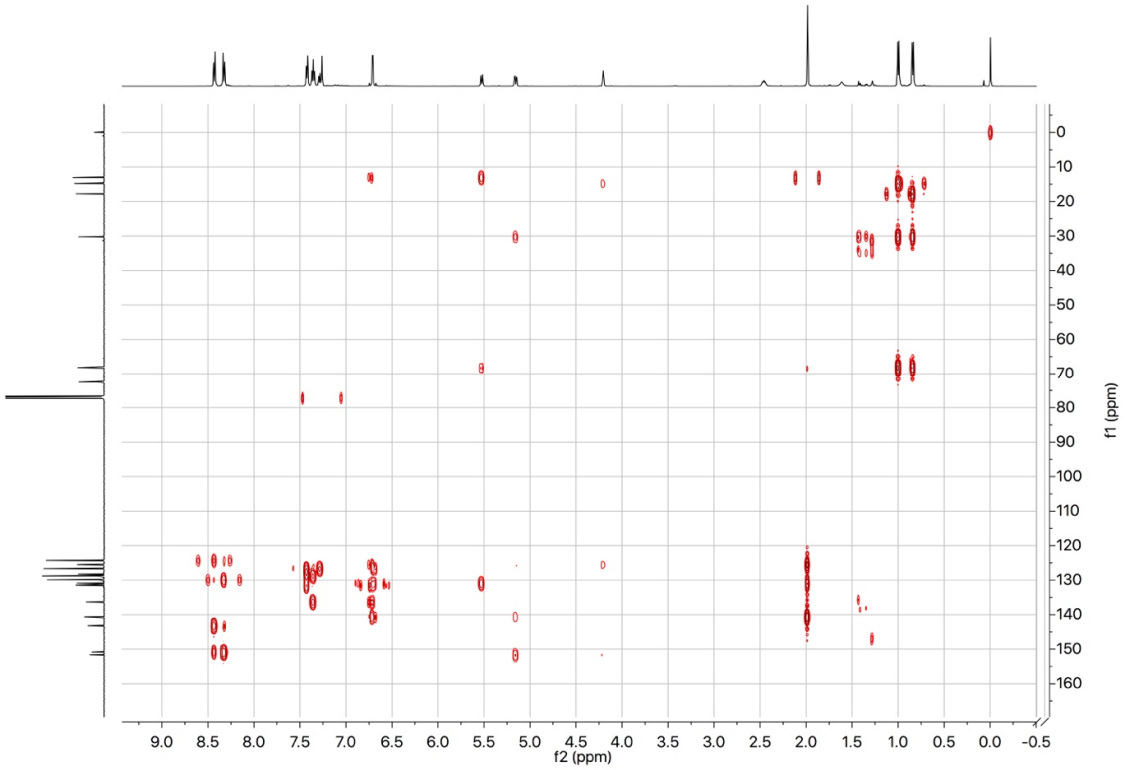
3m


8.44
8.42
8.33
8.32
7.43
7.42
7.37
7.36
7.34
7.30
7.28
7.26
6.75
6.71
6.71
6.67
5.53
5.52
5.17
5.16
5.15
5.14
4.21
4.20
4.20
2.49
2.48
2.47
2.46
2.46
2.45
2.44
2.43
1.98
1.01
0.99
0.85
0.83
O2N
O
O
S
N
O
O
2.06
2.06
2.14
2.25
1.02
2.08
1.00
1.02
1.00
1.05
3.01
3.05
3.04
f1 (ppm)

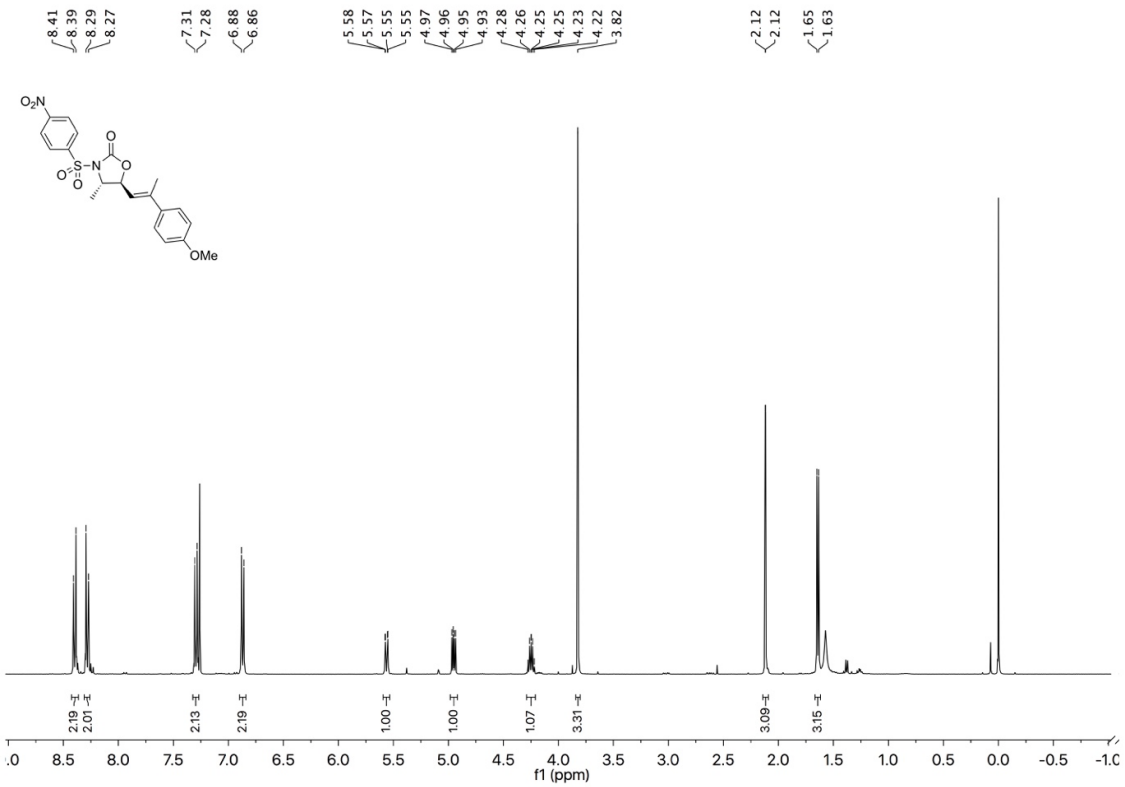

151.62
150.85
143.21
140.63
136.34
131.46
130.91
129.90
128.76
128.25
126.65
125.50
124.31
77.25
77.00
76.75
72.51
68.21
30.24
17.77
14.78
13.08
f1 (ppm)

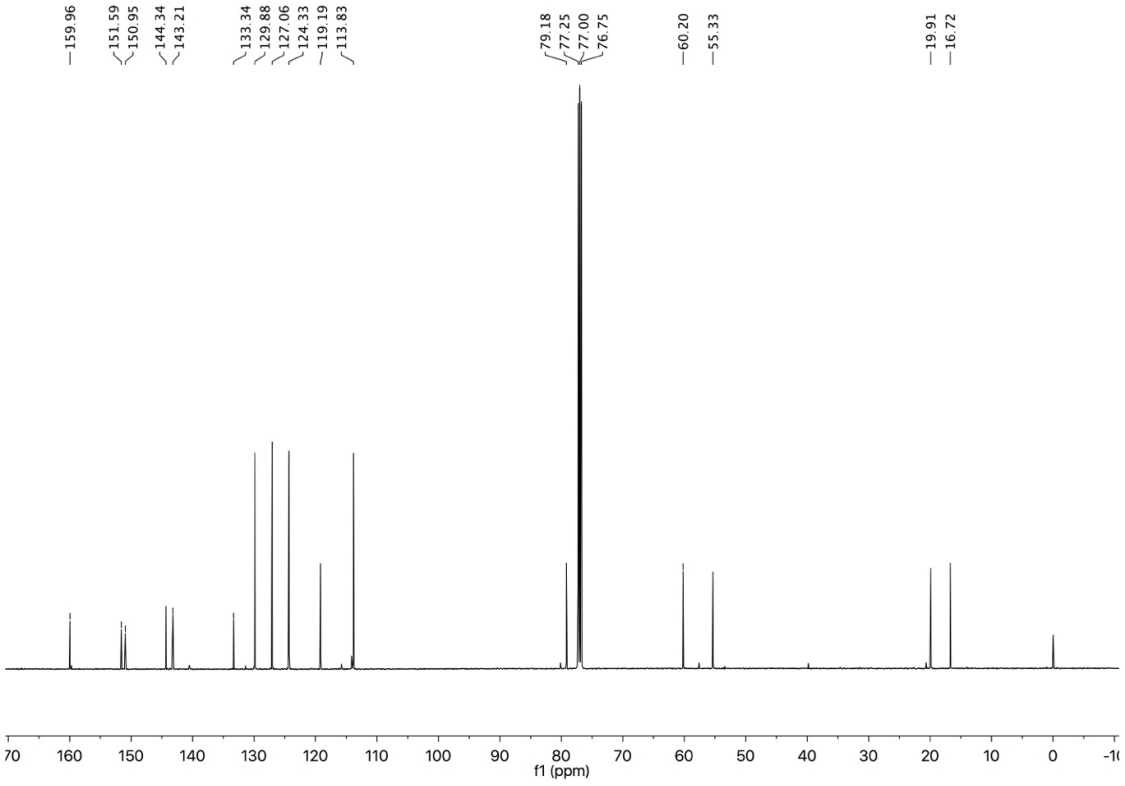

f2 (ppm)
f1 (ppm)

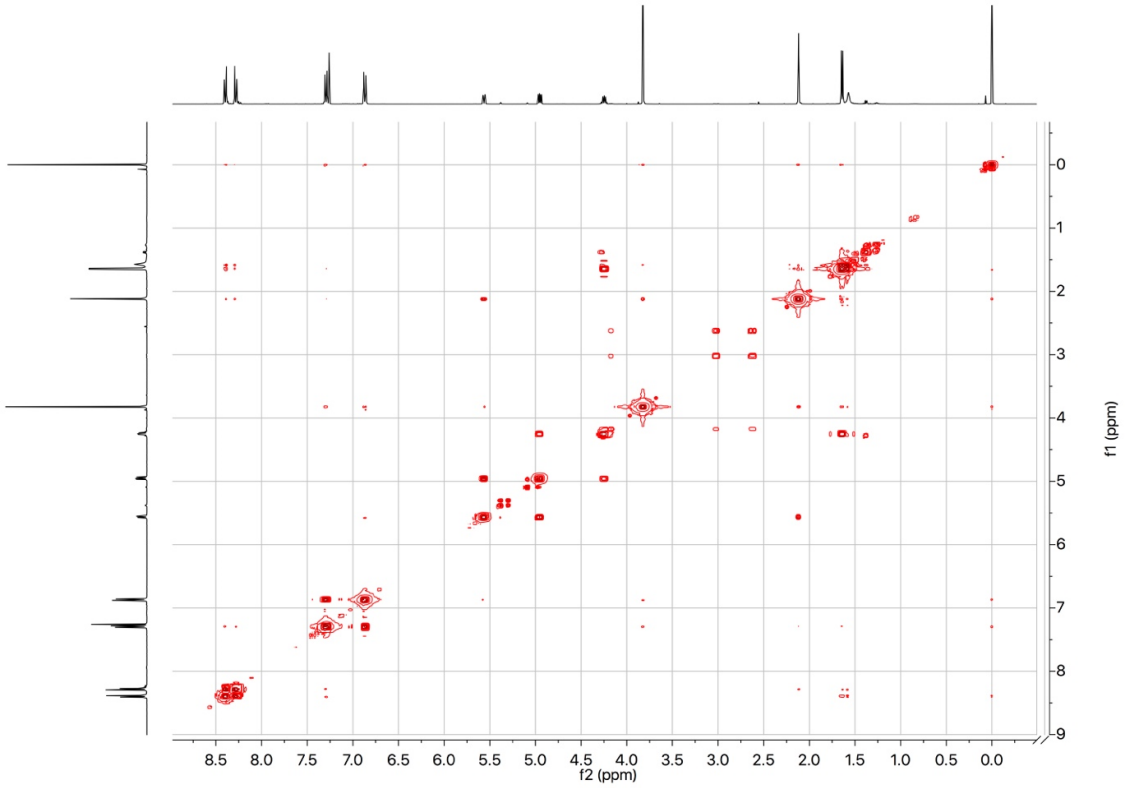

f2 (ppm)
f1 (ppm)

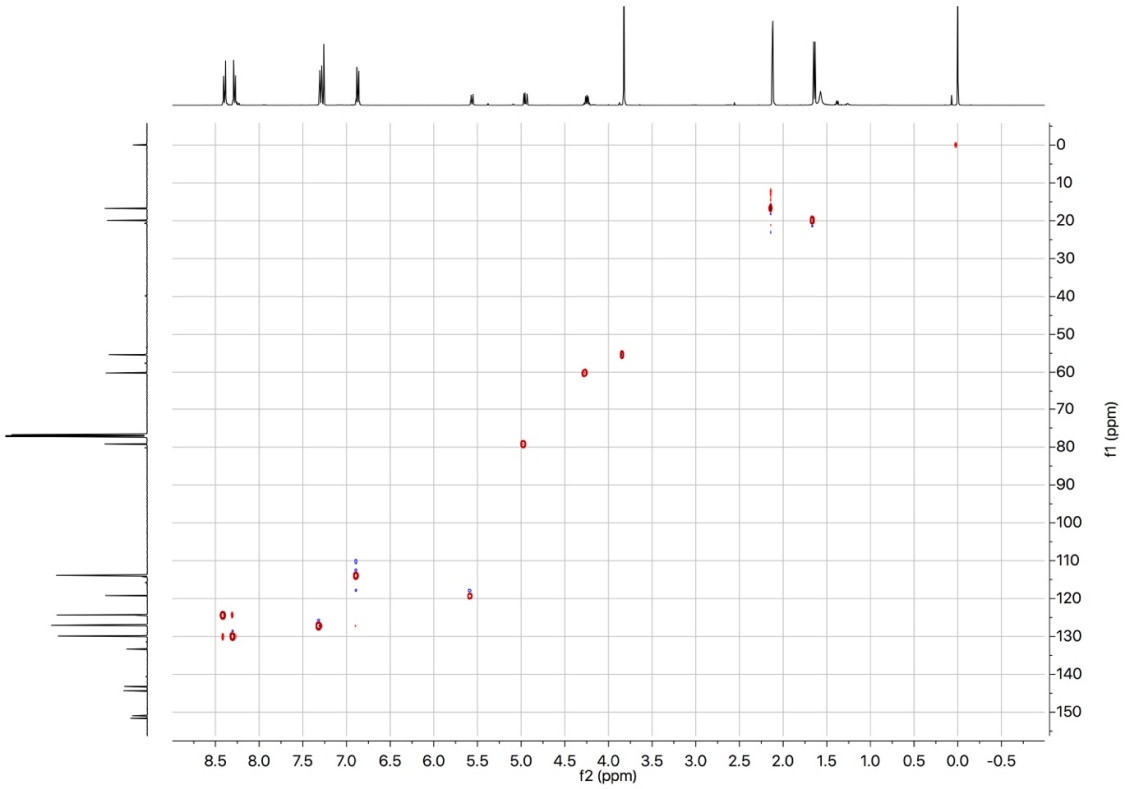

f2 (ppm)
f1 (ppm)

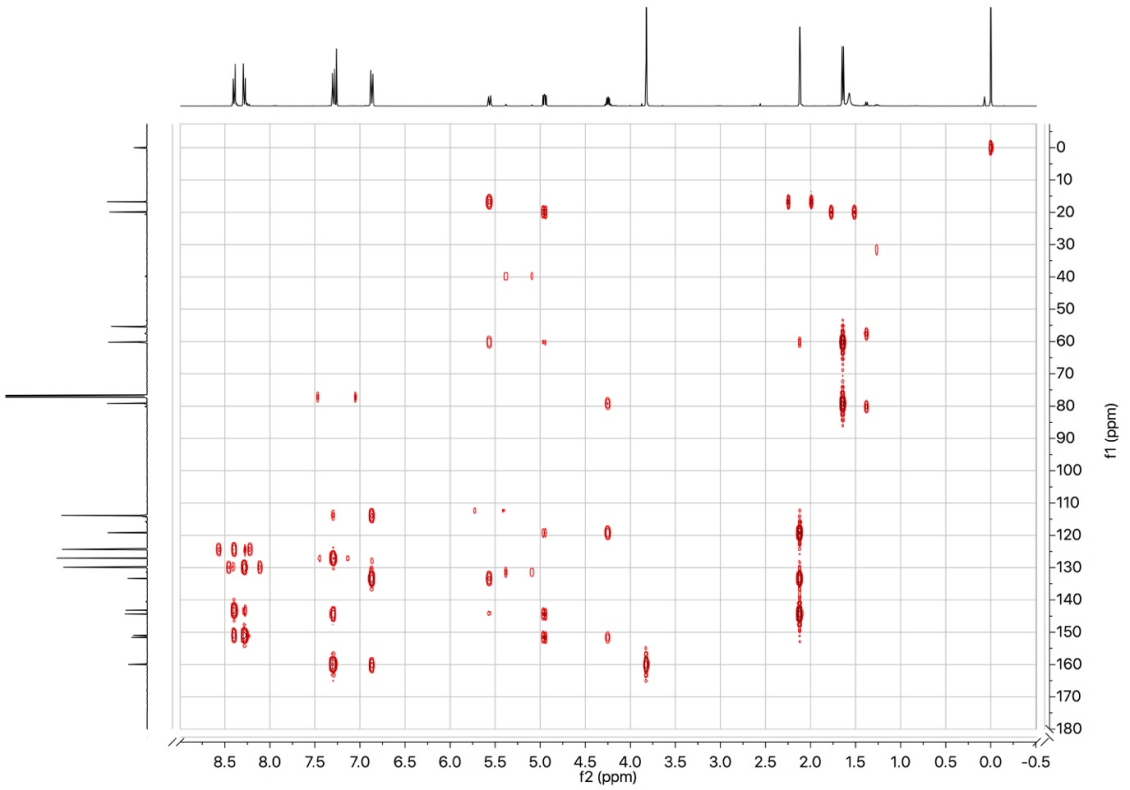
3o


8.41
8.39
8.29
8.27
7.31
7.28
6.88
6.86
5.58
5.57
5.55
5.55
4.97
4.96
4.95
4.93
4.28
4.26
4.25
4.25
4.23
4.22
3.82
2.12
2.12
1.65
1.63
O2N
O
S
N
O
O
O
OMe
2.19
2.01
2.13
2.19
1.00
1.00
1.07
3.31
3.09
3.15
f1 (ppm)

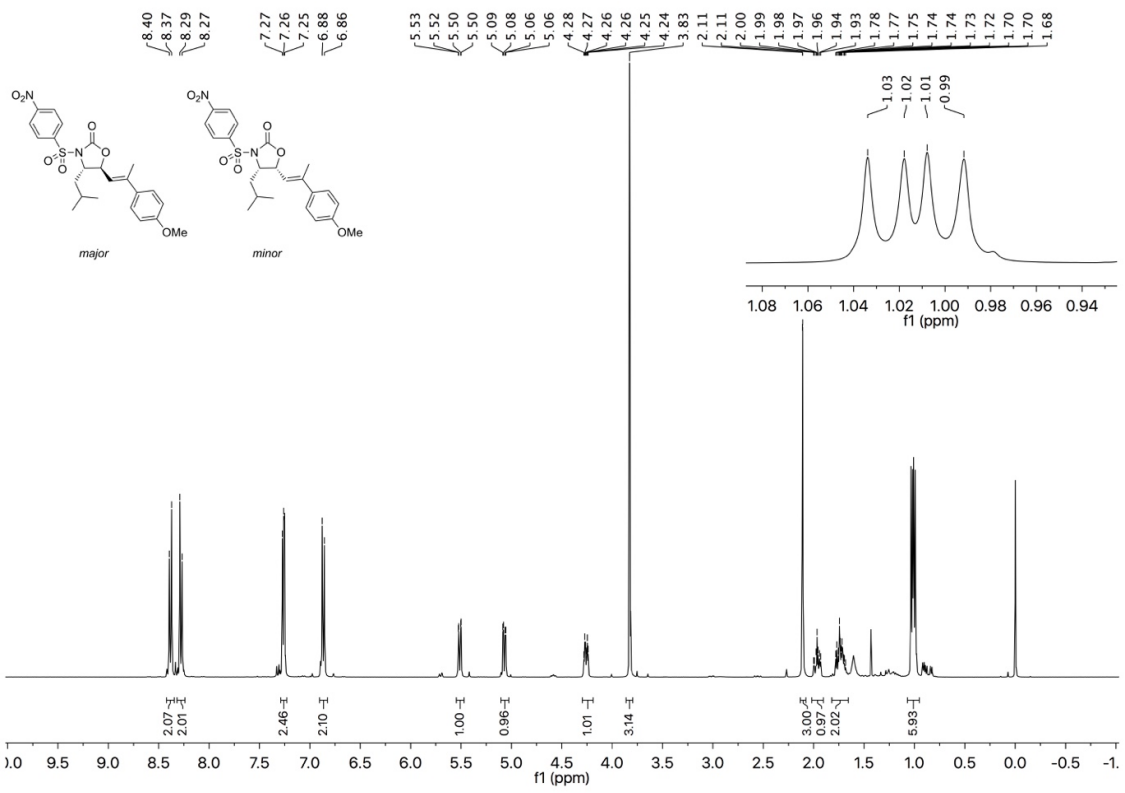

159.96
151.59
150.95
144.34
143.21
133.34
129.88
127.06
124.33
119.19
113.83
79.18
77.25
77.00
76.75
60.20
55.33
19.91
16.72
f1 (ppm)

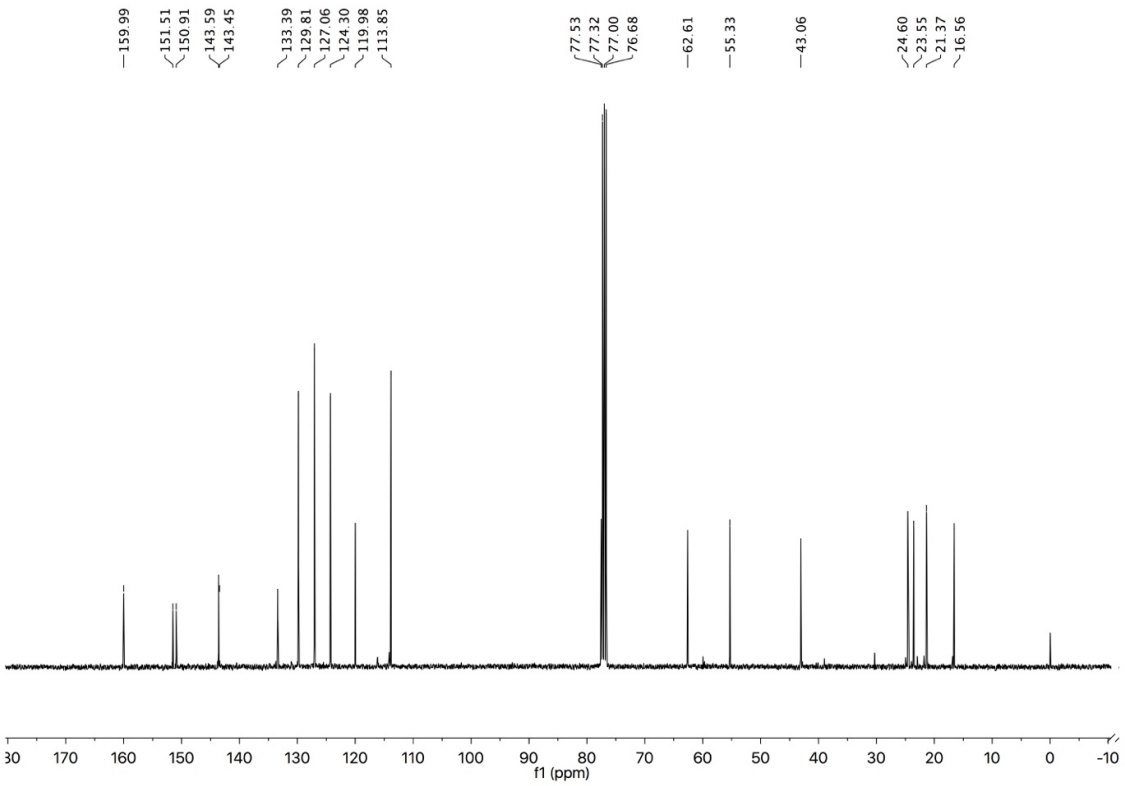

f2 (ppm)
f1 (ppm)

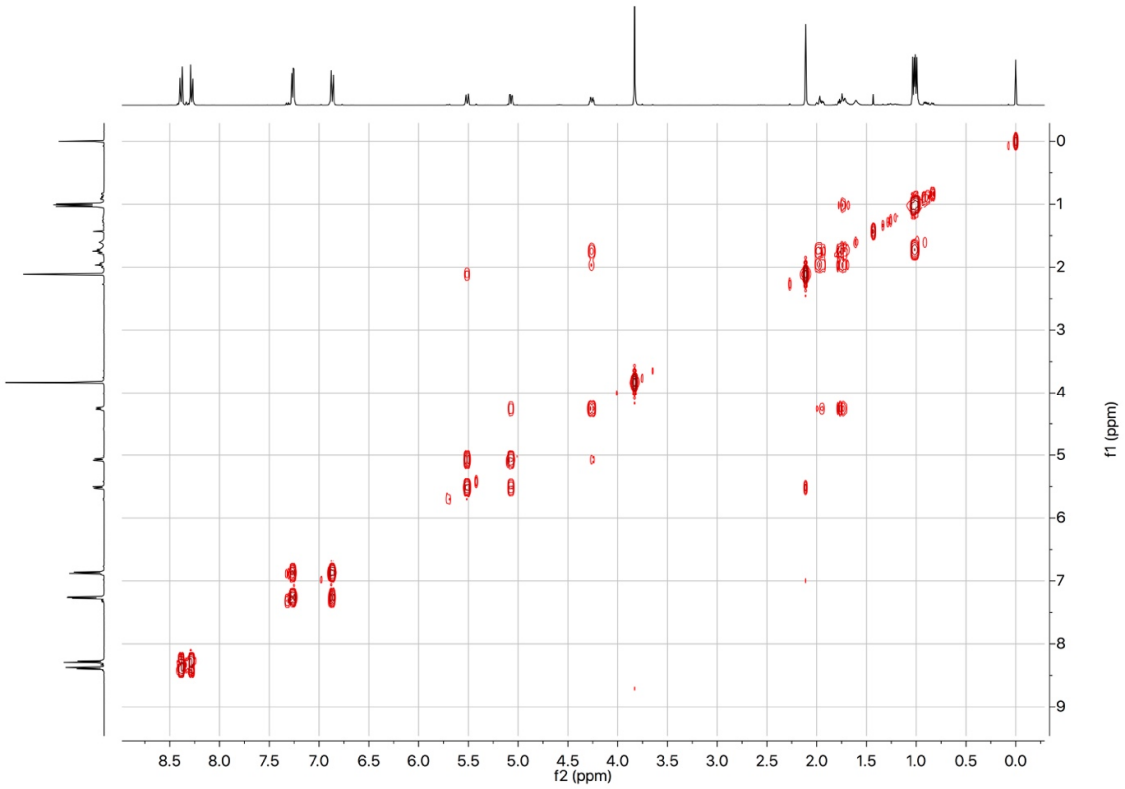

f2 (ppm)
f1 (ppm)

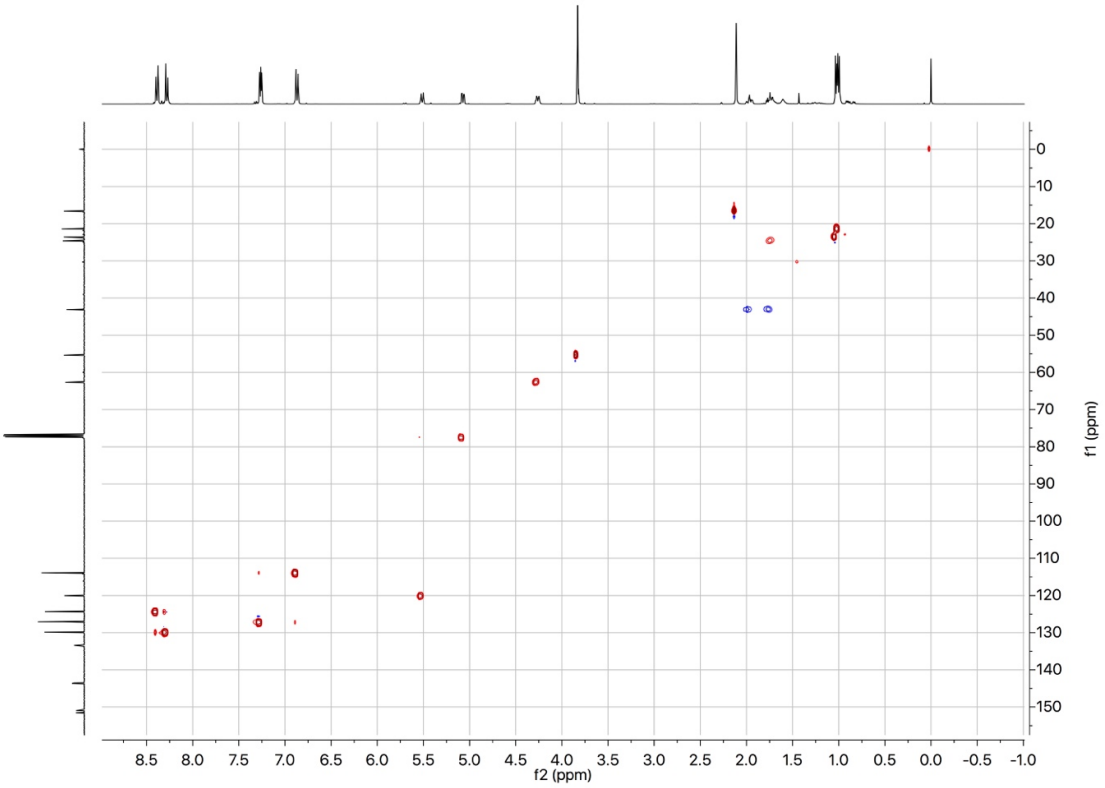


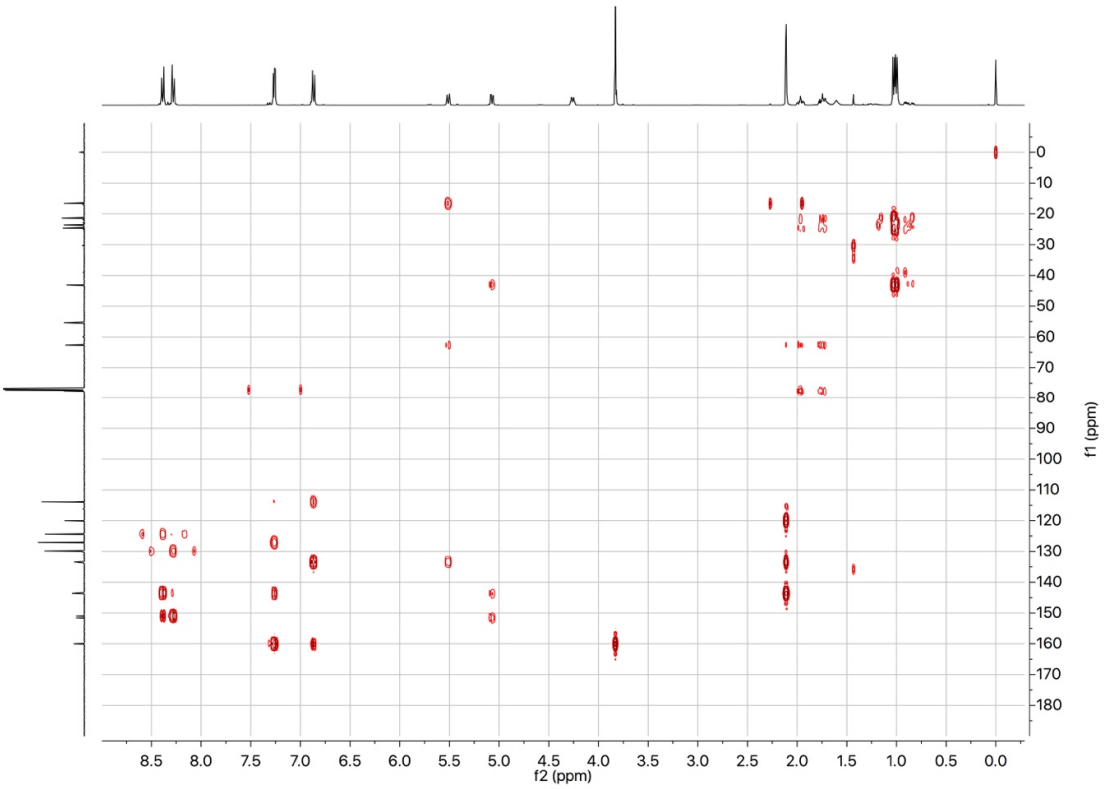
3p



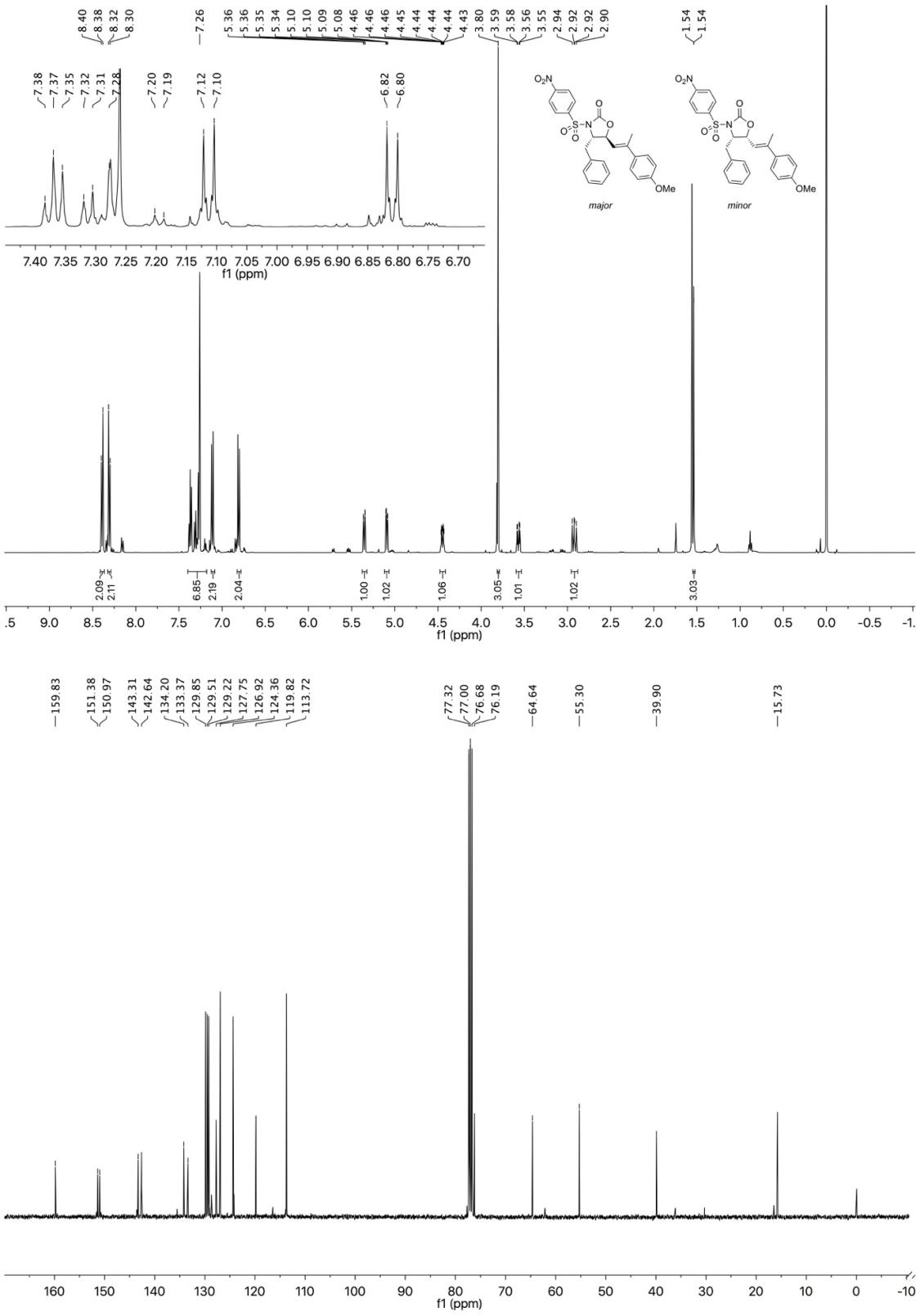

159.99
151.51
150.91
143.59
143.45
133.39
129.81
127.06
124.30
119.98
113.85
77.53
77.32
77.00
76.68
62.61
55.33
43.06
24.60
23.55
21.37
16.56
f1 (ppm)

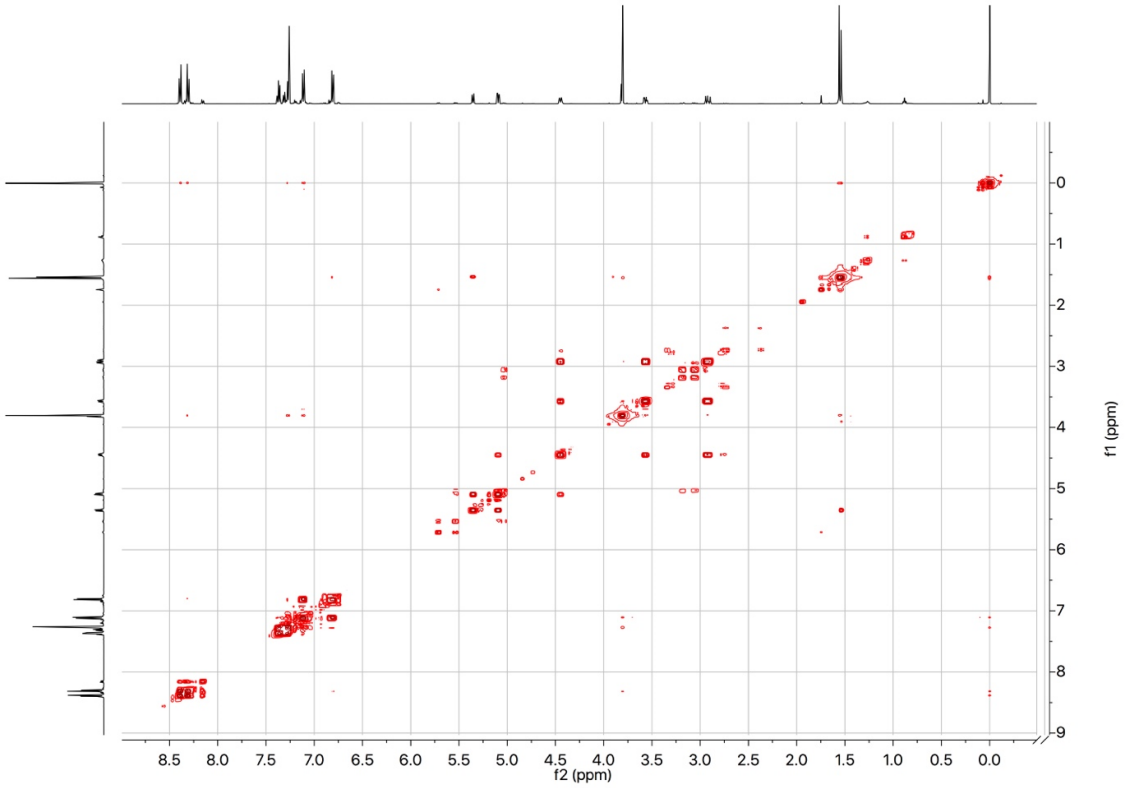

f2 (ppm)
f1 (ppm)

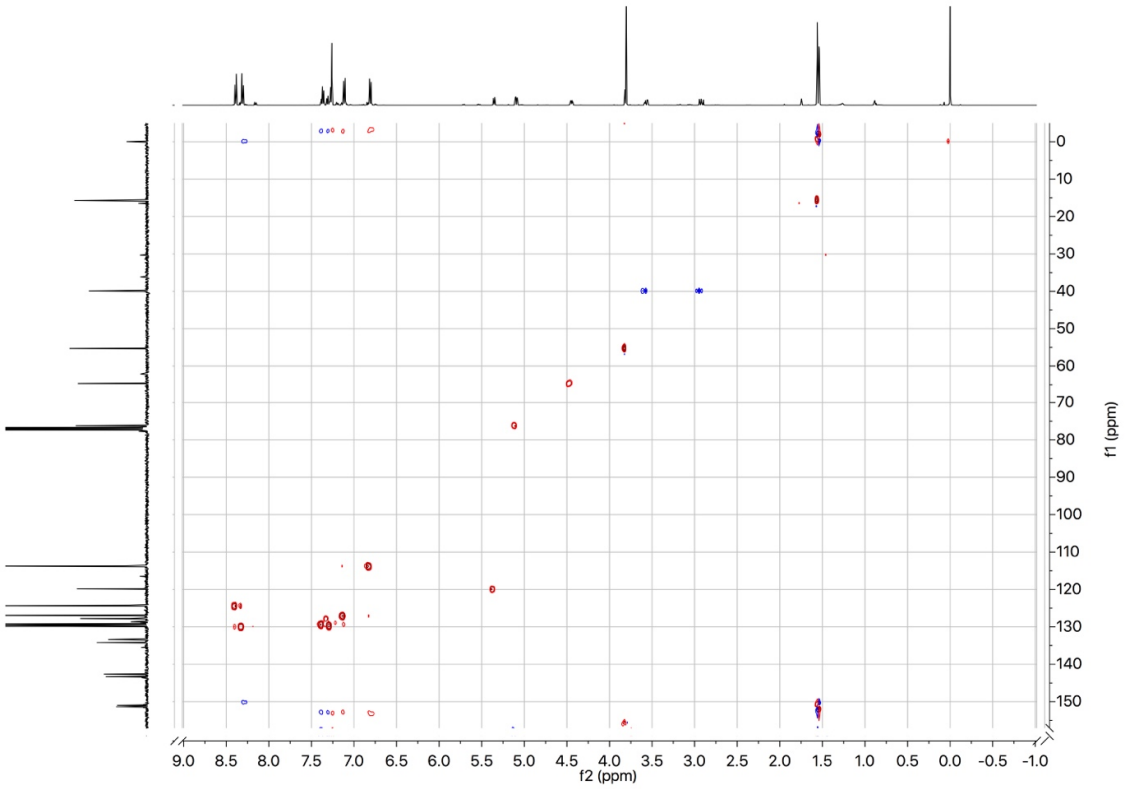

f2 (ppm)
f1 (ppm)

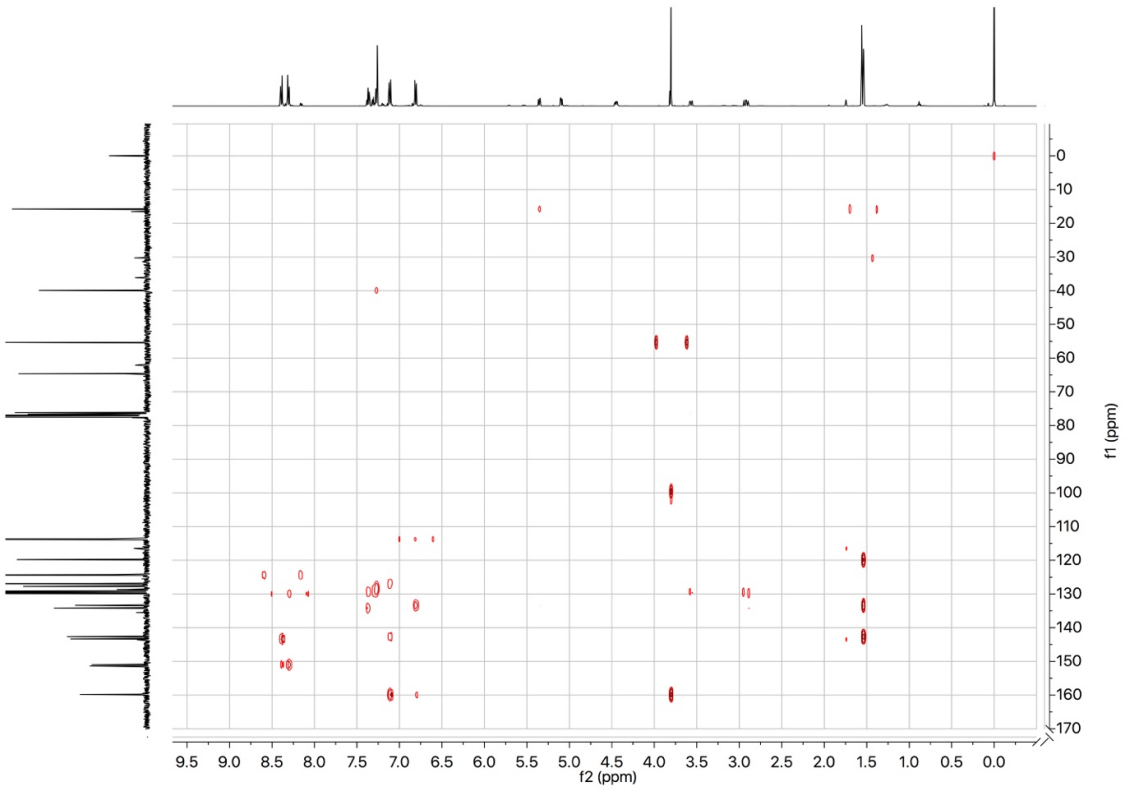

f2 (ppm)
f1 (ppm)

3q

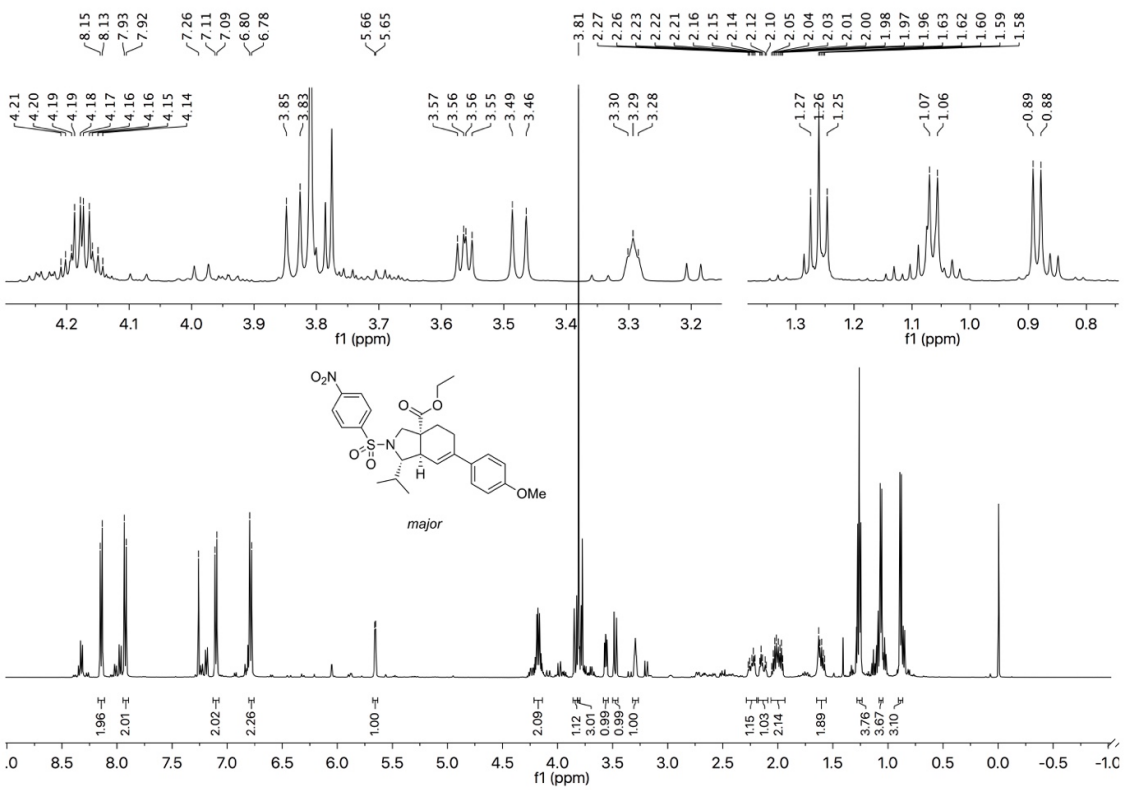


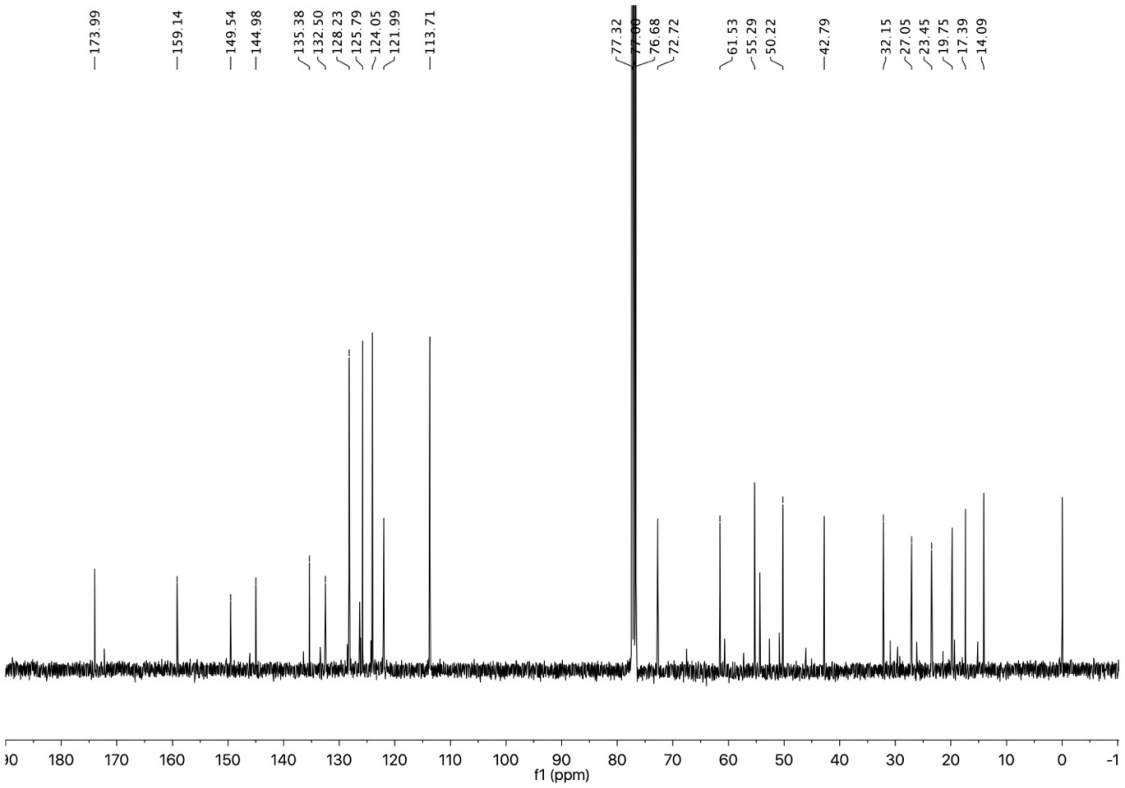

f2 (ppm)
f1 (ppm)

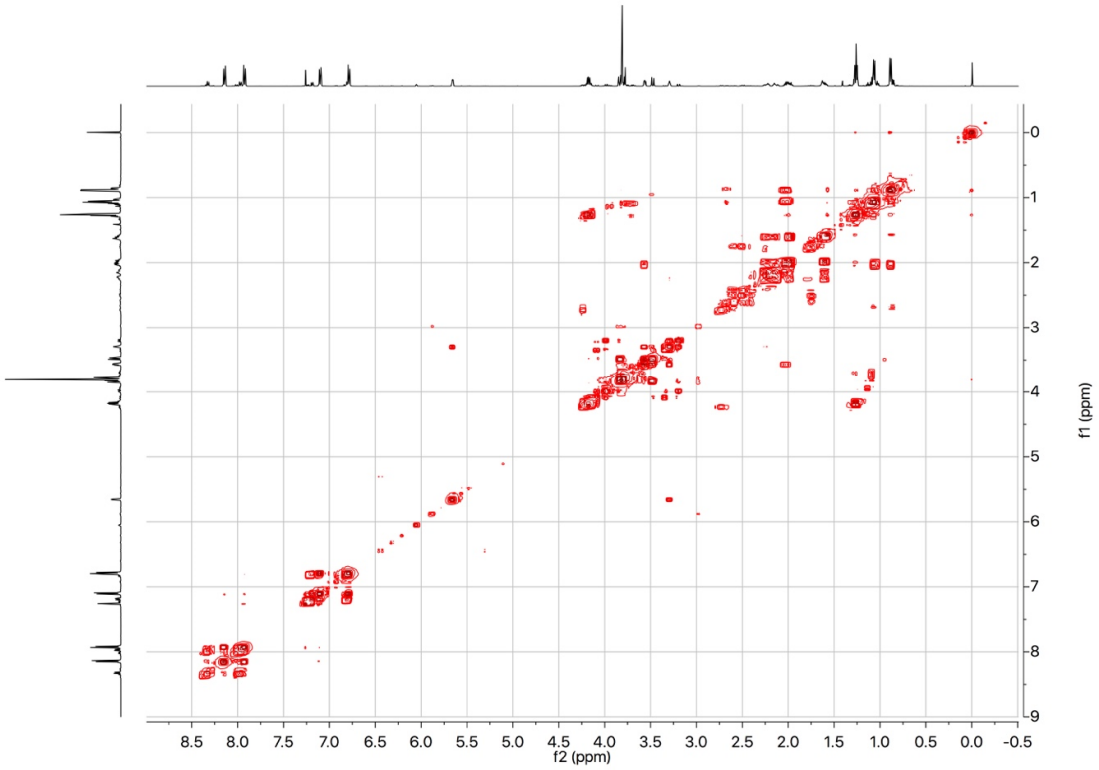

f2 (ppm)
f1 (ppm)

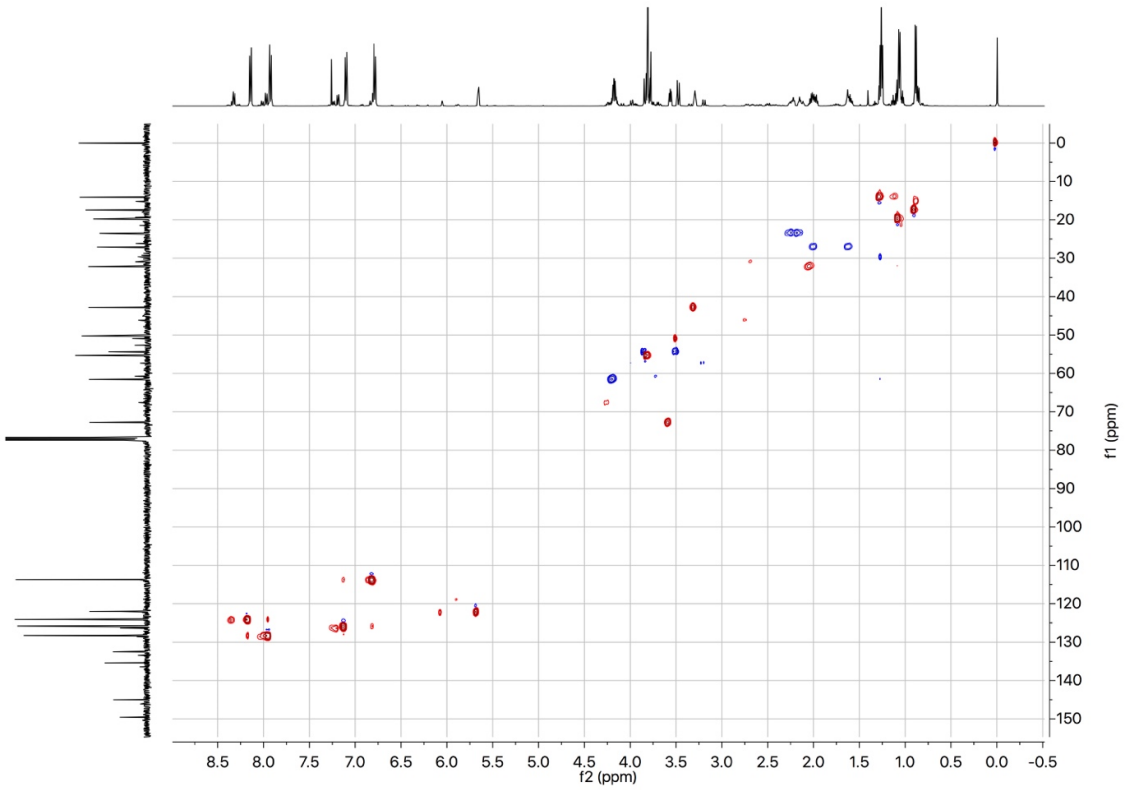


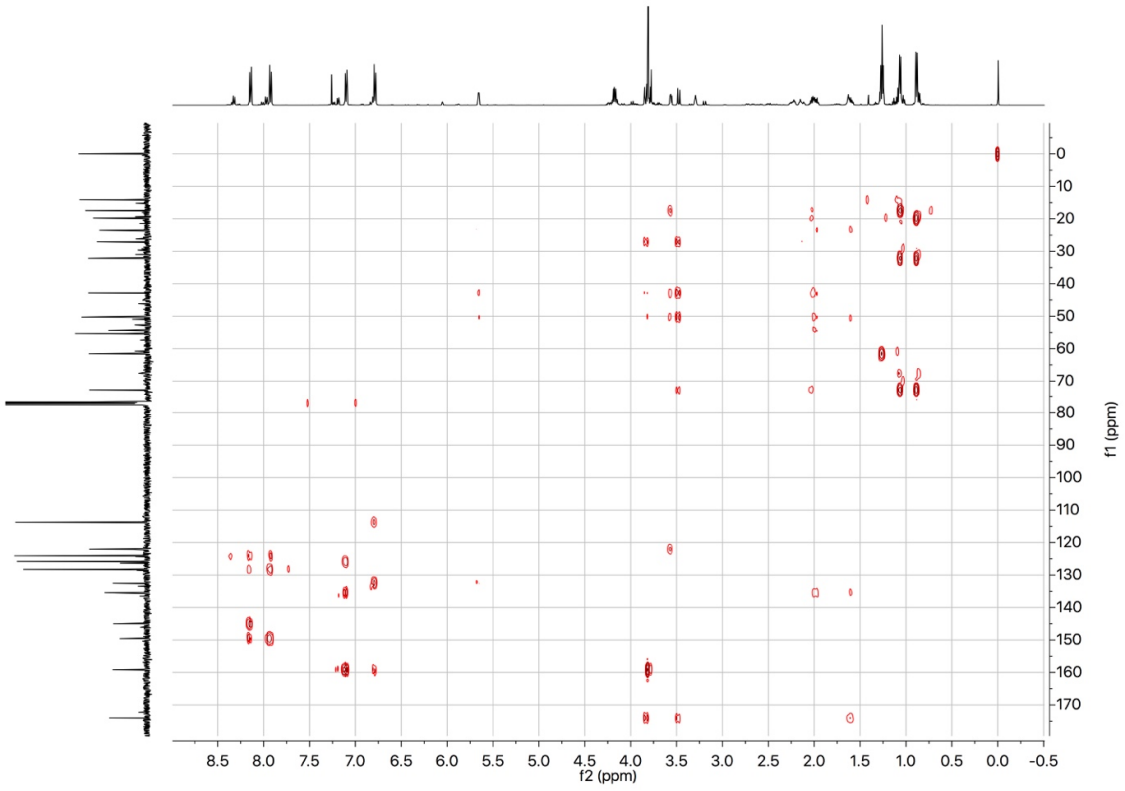
5a




173.99
159.14
149.54
144.98
135.38
132.50
128.23
125.79
124.05
121.99
113.71
77.32
77.00
76.68
72.72
61.53
55.29
50.22
42.79
32.15
27.05
23.45
19.75
17.39
14.09
f1 (ppm)


f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)


f2 (ppm)
f1 (ppm)

5b