Asymmetric NHC-Catalyzed Addition of Enals to Nitroalkenes: Controlling Stereochemistry Via the Homoenolate Reactivity Pathway To Access δ-Lactams

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Materials and Methods

All reactions were carried out under an atmosphere of argon in flame-dried glassware with magnetic stirring. Dichloromethane was degassed with argon and passed through two col- umns of neutral alumina. Toluene was degassed with argon and passed through one column of neutral alumina and one column of Q5 reactant. Methanol was purchased from Fisher Scientific and dried with activated 3Å molecular sieves. N,N-Diisopropylethylamine was purchased from Aldrich and distilled from Calcium hydride prior to use. Column chromatography was performed on SiliCycle®Silica*Flash*® P60, 40-63μm 60A. Thin layer chromatography was performed on SiliCycle® 250μm 60A plates. Visualization was accomplished with UV light or KMnO4 stain followed by heating.

^{1}H NMR spectra were recorded on Varian 300 or 400 MHz spectrometers at ambient temperature. Data is reported as follows: chemical shift in parts per million (δ, ppm) from $CDCl_3$ (7.26 ppm) or acetone-D_6 (2.03 ppm), multiplicity (s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), coupling constants (Hz). ^{13}C NMR were recorded on Varian 300 or 400 MHz spectrometers (at 75 or 100 MHz) at ambient temperature. Chemical shifts are reported in ppm from $CDCl_3$ (77.36 ppm) or acetone-D_6 (205.87, 30.6 ppm).

Aldehydes were either purchased from Aldrich or prepared via literature procedures. Ni-troalkenes were prepared according to the general procedure as described within.

General Procedure for the Synthesis of Nitro-Esters

To a screw cap vial charged with a stirbar was added triazolium salt **5f** (15 mg, 0.025 mmol) and NaOAc (10 mg, .125 mmol). This vial was then fitted with a rubber septum and evacuated and refilled with argon three times. 0.75 ml EtOH was then added via syringe. To this solution was then added (*E*)-1-nitrobut-1-ene **2a** (26 μL, 0.25 mmol, 1 equiv) followed by *trans*-cinnamaldehyde **1a** (49 μL, 0.375 mmol, 1.5 equiv). The septum was then quickly removed and replaced with a screw cap. This was then allowed to stir at ambient temperature for 12 hours. After 12 hours the reaction was concentrated via rotary evaporation and then purified by silica gel chromatography (8:2 hexanes:ether) to yield 49 mg (70 %) (3*S*,4*R*)-ethyl 4-(nitromethyl)-3-phenylhexanoatein **3a** as a colorless oil.

General Procedure for One-Pot Synthesis of δ-Lactams

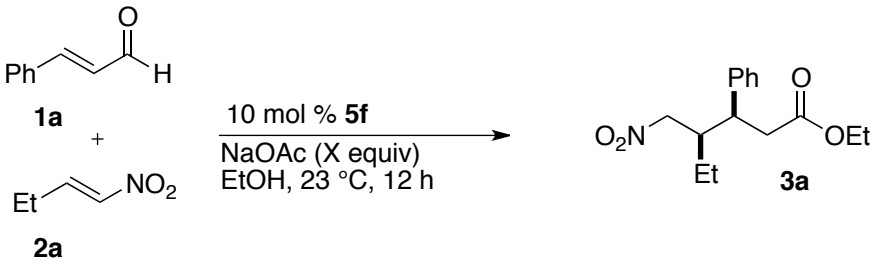
To a screw cap vial charged with a stirbar was added triazolium salt **5f** (15 mg, 0.025 mmol) and NaOAc (10 mg, .125 mmol). This vial was then fitted with a rubber septum and evacuated and refilled with argon three times. 0.75 mL EtOH was then added via syringe. To this solution was then added (*E*)-1-nitrobut-1-ene **2a** (26 μL, 0.25 mmol, 1 equiv) followed by *trans*-cinnamaldehyde **1a** (49 μL, 0.375 mmol, 1.5 equiv). The septum was then quickly removed and replaced with a screw cap. This was then allowed to stir at ambient temperature for 12 hours. After 12 hours the screw cap was removed and Zinc dust (165 mg, 2.5 mmol) was added followed by 0.75 mL AcOH. The screw cap was replaced and the reaction was then heated to reflux in an oil bath. After four hours the vial was removed from the oil bath and allowed to cool. Upon cooling, the reaction was filtered through celite and rinsed with 10 ml EtOAc. The filtrate was then diluted with an additional 10 ml EtOAc and quenched with 20 mL saturated $NaHCO_3$. The organic layer was then separated, washed with brine (1 x 20mL), dried (Na_2SO_4), and concentrated *in vacuo*. The crude residue was then subjected to column chromatography (1:1 hexanes:EtOAc) to yield 32 mg (63 %) (4*S*,5*R*)-5-ethyl-4-phenylpiperidin-2-one **6a** as a white solid.

Reaction Optimization:

Base Screen:

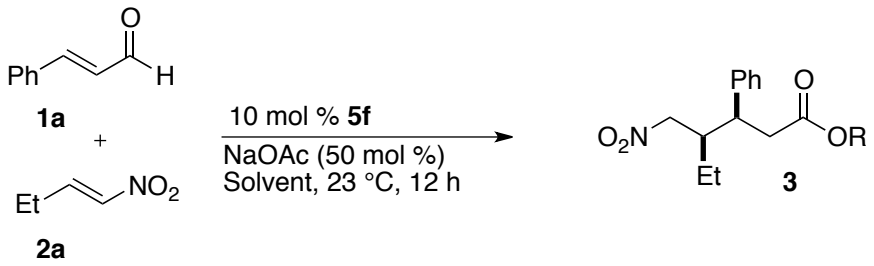
Solvent	Yield
NaOAc	49 %
K_3PO_4	31 %
i-Pr_2NEt	6 %
DBU	trace
Et_3N	8 %
$KHCO_3$	trace

Base Equiv. Screen:



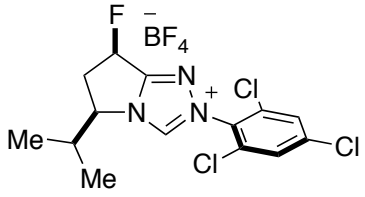
Base Eq.	Yield
0.25	65 %
0.3	66 %
0.5	69 %
0.6	60 %
0.75	46 %
1.0	49 %
1.5	46 %
2.0	57 %
4.0	42 %

Solvent Screen:

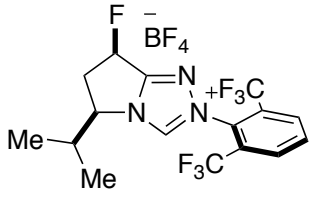


Solvent	Yield
MeOH	56 %
EtOH	70 %
i-PrOH	21 %
EtOH:*t*BuOH (10:1)	9 %
EtOH:DCM (10:1)	trace
EtOH:Toluene (10:1)	trace

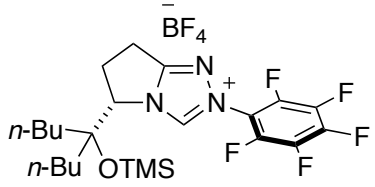
Characterization Data:



Triazolium Salt (**5c**) To a flame-dried flask with magnetic stir bar was added (3*R*,5*R*)-3-fluoro-5-isopropylpyrrolidin-2-one[1] (290.3 mg, 2.0 mmol, 1.0 equiv). The flask was then evacuated and back-filled with argon. Dichloromethane (15 mL) and trimethyloxonium tetrafluoroborate (296 mg, 2.0 mmol, 1.0 equiv) were then added via powder funnel. The heterogeneous mixture was stirred at room temperature until the reaction was homogeneous (about 6 hours). (2,4,6-trichlorophenyl)hydrazine (422.9 mg, 2.0 mmol, 1.0 equiv) was added in one portion and the mixture was stirred for 18 hours at which point dichloromethane was removed *in vacuo*. Trimethylorthoformate (20 mL) was then added and the solution was heated in a 110 °C oil bath for 1 h. After cooling to room temperature, the reaction concentrated *in vacuo* and 20 mL chlorobenzene was added and the solution was refluxed for 10 minutes. Upon cooling in an ice bath the product precipitated out and was filtered to yield triazolium salt (**5c**) (366 mg, 42 %) as an off-white solid. $[\alpha]_D^{21}$ = 11.8 (c = 0.010 g/ml, acetone); **^{1}H-NMR** (400 MHz; aceton-d_6): δ 10.60 (s, 1H), 7.97 (s, 2H), 6.55 (ddd, *J* = 54.7, 7.6, 2.1 Hz, 1H), 5.26-5.20 (m, 1H), 3.72-3.57 (m, 1H), 3.00-2.88 (m, 1H), 2.58 (dq, *J* = 12.8, 6.5 Hz, 1H), 1.10 (dd, *J* = 30.7, 6.8 Hz, 6H). **^{13}C-NMR** (101 MHz; acetone): δ 160.3, 160.1, 143.9, 139.3, 134.1, 130.2, 129.5, 84.4, 82.6, 66.6, 37.1, 36.8, 31.5, 17.3, 16.2 **IR** (ATR, neat) 2960, 1571, 1054, 1034, 825 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 348.0, found 348.0l

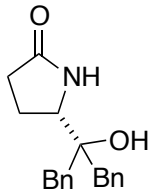


Triazolium Salt (**5d**): To a flame-dried flask with magnetic stir bar was added (3*R*,5*R*)-3-fluoro-5-isopropylpyrrolidin-2-one[1] (290.3 mg, 2.0 mmol, 1.0 equiv). The flask was then evacuated and back-filled with argon. Dichloromethane (15 mL) and trimethyloxonium tetrafluoroborate (296 mg, 2.0 mmol, 1.0 equiv) were then added via powder funnel. The heterogeneous mixture was stirred at room temperature until the reaction was homogeneous (about 6 hours). (2,6-bis(trifluoromethyl)phenyl)hydrazine (488.3 mg, 2.0 mmol, 1.0 equiv) was added in one portion and the mixture was stirred for 18 hours at which point dichloromethane was removed *in vacuo*. Trimethylorthoformate (20 mL) was then added and the solution was heated in a 110 °C oil bath for 1 h. After cooling to room temperature, the reaction concentrated *in vacuo* and purified by column chromatography to yield triazolium salt (**5d**) (234 mg, 25 %) as an off-white solid R_f = 0.41 (19:1 CH_2Cl_2:MeOH) $[\alpha]_D^{21}$ = 20.6 (c = 0.010 g/ml, acetone); **^{1}H-NMR** (400 MHz; aceton-d_6): δ 10.73 (s, 1H), 8.48 (d, *J* = 8.0 Hz, 2H), 8.37-8.32 (m, 1H), 6.60 (ddd, *J* = 54.7, 7.7, 1.9 Hz, 1H), 5.34 (dq, *J* = 8.5, 4.2 Hz, 1H), 3.69 (dddd, *J* = 27.5, 16.0, 8.6, 7.5 Hz, 1H), 2.96 (dddd, *J* = 28.3, 15.8, 3.3, 2.0 Hz, 1H), 2.65-2.57 (m, 1H), 1.07 (dd, *J* = 33.0, 6.9 Hz, 6H). **^{13}C-NMR** (101 MHz; acetone): δ 160.0, 159.7, 144.51, 144.49, 144.46, 134.95, 134.92, 132.34, 132.30, 132.25, 132.21, 132.18, 132.13, 132.09, 132.04, 129.3, 129.06, 129.01, 128.7, 126.0, 123.5, 123.2, 120.8, 120.5, 84.4, 82.6, 66.9, 36.8, 36.6, 31.5, 17.1, 15.6; **IR** (ATR, neat) 2972, 2925, 1513, 1295, 1140, 1052, 1035, 836, 676 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 382.1, found 382.1

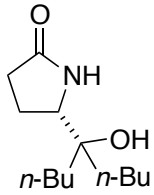


Triazolium Salt (**5f**): (*S*)-5-(5-hydroxynonan-5-yl)pyrrolidin-2-one (**S2**) (1.136 g, 5 mmol, 1 equiv) was dissolved in CH_2Cl_2 (50 mL) and cooled to 0 °C in an ice bath. Trimethylsilyl trifluoromethanesulfonate (2.12 mL, 11.7 mmol, 2.33 equiv) and 2,6-lutidine (1.7 mL, 12 mmol, 3 equiv) were added dropwise to the cooled solution. The solution was allowed to stir at 0 °C for 1.5 hours and then allowed to warm to room temperature and stir for 12 hours. After 12 hours the reaction was cooled to 0 °C and quenched with 50 mL saturated ammonium chloride and extracted 3 x 50 mL EtOAc, dried over sodium sulfate, and concentrated *in vacuo* to quantitatively yield (*S*)-5-(5-((trimethylsilyl)oxy)nonan-5-yl)pyrrolidin-2-one as a colorless oil. To a flame-dried flask with magnetic stir bar was added crude (*S*)-5-(5-((trimethylsilyl)oxy)nonan-5-yl)pyrrolidin-2-one (1.46 g, 4.87 mmol, 1.0 equiv). The flask was then evacuated and back-filled with argon. Dichloromethane (25 mL) and trimethyloxonium tetrafluoroborate (720 mg, 4.87 mmol, 1.0 equiv) were then added via powder funnel. The heterogeneous mixture was stirred at room temperature until the reaction was homogeneous (about 6 hours). Pentafluorophenyl hydrazine (965 mg, 4.87

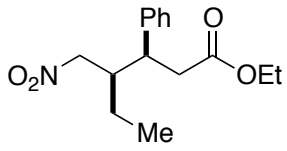
mmol, 1.0 equiv) was added in one portion and the mixture was stirred for 12 hours at which point dichloromethane was removed *in vacuo*. The resulting yellow oil was then dissolved in acetonitrile (25 mL) and trimethylorthoformate (6 mL). This solution was refluxed in an oil bath for 24 hours. After 24 hours the solvent was removed *in vacuo* and the desired product purified by column chromatography to yield triazolium salt (**5f**) (1.1 g, 39 %) as a red amorphous solid. R_f = 0.43 (19:1 CH_2Cl_2:MeOH) $[\alpha]_D^{21}$ = 16.4 (c = 0.010 g/ml, acetone); **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 9.83 (s, 1H), 5.01 (dd, *J* = 8.6, 2.9 Hz, 1H), 3.30-3.00 (m, 3H), 2.68 (d, *J* = 3.6 Hz, 1H), 1.63-1.04 (m, 12H), 0.90 (dt, *J* = 14.9, 7.3 Hz, 6H), 0.10--0.01 (m, 9H). **^{13}C-NMR** (101 MHz; $CDCl_3$): δ 164.0, 143.4, 79.4, 68.9, 37.0, 36.4, 28.4, 25.7, 25.5, 23.2, 22.8, 21.9, 13.81, 13.75 **IR** (ATR, neat) 2958, 2873, 1525, 1065, 1001, 841 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 490.2, found 490.2



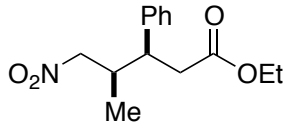
(*S*)-5-(2-hydroxy-1,3-diphenylpropan-2-yl)pyrrolidin-2-one (**S1**): To a flame dried dry 250 ml 3-neck round bottom flask containing a magnetic stirbar and fitted with a reflux condenser was added 1.9 g Magnesium turnings (80 mmols) followed by 15 mL dry THF. To this was added dropwise a solution of 9.5 mL benzyl bromide (80 mmols) in 55 mL dry THF with the use of an addition funnel at a rate sufficient to maintain reflux. After completion of the benzyl bromide addition the reaction was refluxed for 30 minutes. After 30 minutes the heat source was removed and the reaction was cooled to 0 °C in an ice bath. To this mixture was added a solution of 2.8 grams (20 mmols) (*S*)-methyl 5-oxopyrrolidine-2-carboxylate in 80 mL dry THF dropwise over 30 minutes. Upon completion of addition the reaction was allowed to warm to room temperature and stirred overnight. The reaction was cooled to 0 °C in an ice bath and quenched with 80 mL saturated NH_4Cl. The organic layer was separated and the aqueous layer was extracted 3 x 50 mL EtOAc. The organic layers were combined and washed 1 x 100 mL brine. The organic layer was dried over sodium sulfate and concentrated *in vacuo*. The resulting white solid was then triturated with hexanes to yield 2.5 grams (42 %) of the (*S*)-5-(2-hydroxy-1,3-diphenylpropan-2-yl)pyrrolidin-2-one as a white solid. $[\alpha]_D^{21}$ = 52.4 (c = 0.010 g/ml, CH_2Cl_2); **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.34-7.21 (m, 8H), 7.15-7.12 (m, 2H), 6.26 (s, 1H), 3.62 (dd, *J* = 8.2, 6.1 Hz, 1H), 2.97 (d, *J* = 13.6 Hz, 1H), 2.75 (d, *J* = 1.3 Hz, 2H), 2.67 (d, *J* = 13.6 Hz, 1H), 2.43-2.28 (m, 2H), 2.21-2.12 (m, 1H), 2.11-2.01 (m, 1H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 178.2, 135.99, 135.80, 130.8, 130.3, 128.53, 128.49, 126.91, 126.88, 75.4, 59.7, 42.3, 40.3, 30.2, 21.7. **IR** (ATR, neat) 3384, 3298, 1686, 700 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 296.2, found 296.1



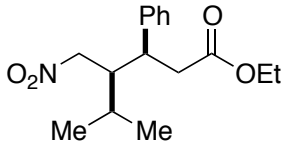
(*S*)-5-(5-hydroxynonan-5-yl)pyrrolidin-2-one (**S2**): To a solution of (*S*)-methyl 5-oxopyrrolidine-2-carboxylate (2.8g, 20 mmol) in THF (60 ml) cooled to 0 °C was added 42.5 ml *n*-Butyl Lithium in hexanes (1.6 M, 68 mmol) dropwise. The solution was allowed to warm to room temperature slowly and stirred for 4 hours at room temp. After four hours the reaction was quenched with 60 ml saturated sodium bicarbonate. The THF was then removed via rotary evaporation and the solution was extracted 3x 50 ml EtOAc and dried over Na_2SO_4. The solvent was removed *in vacuo* to yield a white solid that was triturated with hexanes to yield the product as a white solid (1.15 g, 25 %). $[\alpha]_D^{21}$ = -13.3 (c = 0.010 g/ml, CH_2Cl_2); **^{1}H-NMR** (400 MHz; CDCl3): δ 6.68 (s, 1H), 3.67-3.64 (m, 1H), 2.38-2.22 (m, 2H), 2.05-1.98 (m, 2H), 1.47-1.41 (m, 3H), 1.32-1.16 (m, 9H), 0.90-0.87 (m, 6H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 74.8, 60.7, 36.2, 33.5, 25.6, 25.2, 23.32, 23.23, 21.2, 14.0. **IR** (ATR, neat) 3247, 2954, 2933, 2871, 1691, 1458, 1277 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 228.2, found 228.2



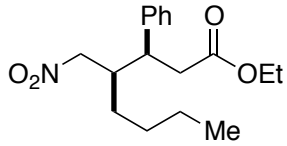
(3*S*,4*R*)-ethyl 4-(nitromethyl)-3-phenylhexanoate (**3a**): Colorless Oil. R_f= 0.28 (8:2 Hexanes:Ether); 70 % yield, 17:1 d.r., 93 % ee;$[\alpha]_D^{21}$ = -4.9 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 97:3 hexanes/*iso*-propanol, 1.0 mL/min. Major: 21.1 min, minor: 22.6 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.32-7.28 (m, 2H), 7.24 (d, *J* = 6.4 Hz, 1H), 7.17-7.15 (m, 2H), 4.31 (dd, *J* = 6.7, 2.1 Hz, 2H), 4.02-3.96 (m, 2H), 3.30 (q, *J* = 7.3 Hz, 1H), 2.72-2.70 (m, 2H), 2.45 (ddd, *J* = 8.5, 6.5, 4.5 Hz, 1H), 1.55-1.48 (m, 1H), 1.30-1.034 (m, 1H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.5, 139.8, 128.5, 128.3, 127.2, 76.8, 60.6, 43.7, 42.4, 37.4, 21.2, 14.0, 11.0. **IR** (ATR, neat) 2966, 2929, 2878, 1730, 1549, 1379, 1217, 702 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 280.2, found 280.1



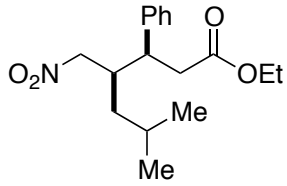
(3*S*,4*R*)-ethyl 4-methyl-5-nitro-3-phenylpentanoate (**3b**): R_f = 0.21 (8:2 Hexanes:Ether); $[\alpha]_D^{21}$ = -0.17 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 97:3 hexanes/*iso*-propanol, 1.0 mL/min. Major: 31.6 min, minor: 28.5 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.32-7.24 (m, 4H), 7.13 (d, *J* = 7.6 Hz, 3H), 4.36 (dd, *J* = 12.1, 6.1 Hz, 1H), 4.08-3.95 (m, 3H), 3.23 (q, *J* = 6.7 Hz, 1H), 2.73 (d, *J* = 7.7 Hz, 2H), 2.80-2.57 (d, *J* = 7.7 Hz, 4H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.4, 139.1, 128.51, 128.41, 127.3, 79.9, 60.6, 43.8, 37.9, 36.7, 14.0, 13.8. **IR** (ATR, neat) 2979, 2924, 1731, 1550, 1378, 1173, 1031, 702 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 266.1, found 266.1



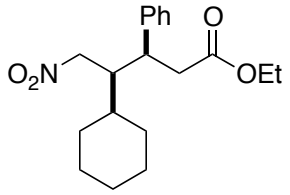
(3*S*,4*R*)-ethyl 5-methyl-4-(nitromethyl)-3-phenylhexanoate (**3c**): Colorless Oil. R_f= 0.29 (8:2 Hexanes:Ether); 57 % yield, 20:1 d.r., 94 % ee; $[\alpha]_D^{21}$ = -29.5 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 97:3 hexanes/*iso*-propanol, 1.0 mL/min. Major: 18.9 min, minor: 16.1 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.29 (t, *J* = 7.3 Hz, 2H), 7.23-7.18 (m, 2H), 4.43-4.33 (m, 2H), 3.92 (q, *J* = 7.1 Hz, 2H), 3.25 (td, *J* = 9.7, 5.1 Hz, 1H), 2.69-2.58 (m, 2H), 2.56-2.50 (m, 1H), 1.66 (dtd, *J* = 13.8, 6.9, 3.5 Hz, 1H), 1.02 (t, *J* = 7.1 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.68 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.7, 141.2, 128.6, 127.8, 127.1, 75.1, 60.5, 47.5, 43.8, 38.4, 27.5, 21.4, 16.4, 13.9. **IR** (ATR, neat) 2959, 2926, 2856, 1732, 1552, 1378, 1163, 1032 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 294.2, found 294.1



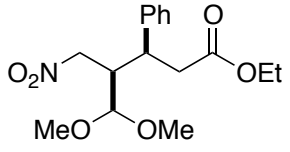
(3*S*,4*R*)-ethyl 4-(nitromethyl)-3-phenyloctanoate (**3d**): Colorless Oil. R_f= 0.26 (8:2 Hexanes:Ether); 72 % yield, 20:1 d.r., 93 % ee; $[\alpha]_D^{21}$ = -2.3 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 97:3 hexanes/*iso*-propanol, 1.0 mL/min. Major: 15.1 min, minor: 16.2 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.32-7.28 (m, 2H), 7.25-7.22 (m, 1H), 7.17-7.15 (m, 2H), 4.28 (d, *J* = 6.8 Hz, 2H), 3.99 (qd, *J* = 7.1, 0.8 Hz, 2H), 3.31 (td, *J* = 7.7, 5.8 Hz, 1H), 2.71 (d, *J* = 7.8 Hz, 2H), 2.51 (dqd, *J* = 8.6, 6.3, 4.3 Hz, 1H), 1.48-1.41 (m, 1H), 1.30-1.23 (m, 4H), 1.08 (t, *J* = 7.1 Hz, 3H), 1.03 (dt, *J* = 9.3, 4.7 Hz, 1H), 0.83 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.5, 139.7, 128.50, 128.33, 127.2, 77.2, 60.6, 42.5, 42.0, 37.2, 28.7, 27.8, 22.5, 13.97, 13.81. **IR** (ATR, neat) 2958, 2931, 2871, 1731, 1550, 1379, 1163, 1032, 702 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 308.2, found 308.1



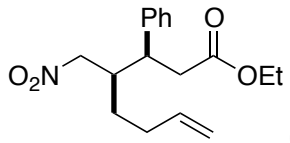
(3*S*,4*R*)-ethyl 6-methyl-4-(nitromethyl)-3-phenylheptanoate (**3e**): Colorless Oil. R_f= 0.24 (8:2 Hexanes:Ether); 67 % yield, 20:1 d.r., 91 % ee; $[\alpha]_D^{21}$ = 0.71 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 97:3 hexanes/*iso*-propanol, 1.0 mL/min. Major: 12.3 min, minor: 15.0 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.30 (tt, *J* = 7.3, 1.6 Hz, 2H), 7.25-7.21 (m, 1H), 7.17-7.15 (m, 2H), 4.24-4.22 (dq, 2H), 4.03-3.98 (m, 2H), 3.34 (td, *J* = 7.8, 4.9 Hz, 1H), 2.72-2.70 (m, 2H), 2.59 (dddd, *J* = 9.2, 6.8, 4.5, 2.1 Hz, 1H), 1.59-1.50 (m, 1H), 1.26 (ddd, *J* = 14.0, 9.3, 4.6 Hz, 1H), 1.10 (d, *J* = 14.3 Hz, 3H), 0.95 (ddd, *J* = 14.3, 9.4, 5.0 Hz, 1H), 0.88 (dd, *J* = 6.5, 2.2 Hz, 6H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.4, 139.4, 128.50, 128.45, 127.2, 77.3, 60.6, 42.4, 39.8, 37.1, 36.7, 25.2, 23.2, 21.7, 14.0. **IR** (ATR, neat) 2958, 2930, 2871, 1732, 1551, 1380, 1170, 738, 703 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 308.2, found 308.2



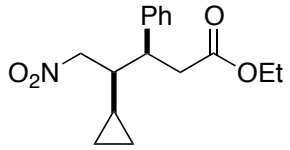
(3*S*,4*R*)-ethyl 4-cyclohexyl-5-nitro-3-phenylpentanoate (**3f**): Colorless Oil. R_f = 0.27 (8:2 Hexanes:Ether); 59 % yield, 20:1 d.r. 96 % ee; $[\alpha]_D^{21}$ = -8.9 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 97:3 hexanes/*iso*-propanol, 1.0 mL/min. Major: 16.6 min, minor: 14.1 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.29 (ddd, *J* = 8.0, 6.4, 1.3 Hz, 2H), 7.24-7.17 (m, 3H), 4.38 (qd, *J* = 13.8, 5.7 Hz, 2H), 3.96-3.91 (m, 2H), 3.36-3.30 (m, 1H), 2.68-2.57 (m, 2H), 2.51-2.45 (m, 1H), 1.69-0.86 (m, 11H), 1.08-0.99 (m, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.7, 141.2, 128.6, 127.8, 127.1, 75.7, 60.5, 47.4, 42.7, 38.0, 37.8, 31.8, 27.7, 26.4, 26.17, 26.16, 13.9. **IR** (ATR, neat) 2925, 2853, 1732, 1551, 1374, 1032 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 334.2, found 334.2



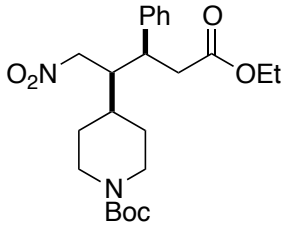
(3*S*,4*R*)-ethyl 5,5-dimethoxy-4-(nitromethyl)-3-phenylpentanoate (**3g**): Colorless Oil. R_f= 0.1 (8:2 Hexanes:Ether); 49 % yield, 8:1 d.r., 79 % ee; $[\alpha]_D^{21}$ = -22.1 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 98:2 hexanes/*iso*-propanol, 1.0 mL/min. Major: 50.6 min, minor: 55.9 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.33-7.19 (m, 5H), 4.69 (dd, *J* = 14.1, 5.0 Hz, 1H), 4.31 (dd, *J* = 14.1, 6.3 Hz, 1H), 3.98-3.91 (m, 2H), 3.81 (d, *J* = 4.0 Hz, 1H), 3.35-3.33 (m, 1H), 3.23 (d, *J* = 6.0 Hz, 6H), 2.96-2.91 (m, 1H), 2.71 (qd, *J* = 14.1, 7.8 Hz, 2H), 1.04 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.4, 144.1, 128.7, 128.0, 127.3, 73.7, 60.5, 55.7, 55.2, 45.0, 41.6, 38.1, 25.3, 13.9 **IR** (ATR, neat) 2923, 1733, 1557, 1065 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 362.2, found 362.2.



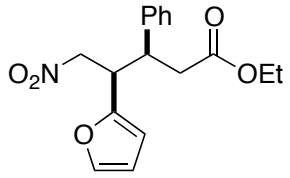
(3*S*,4*R*)-ethyl 4-(nitromethyl)-3-phenyloct-7-enoate (**3h**): Colorless Oil. R_f = 0.24 (8:2 Hexanes:Ether) 72 % yield, 12:1 d.r., 89 % ee; $[\alpha]_D^{21}$ = -3.4 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 97:3 hexanes/*iso*-propanol, 1.0 mL/min. Major: 16.8 min, minor: 23.6 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.30 (td, *J* = 7.2, 1.4 Hz, 2H), 7.25-7.23 (m, 1H), 7.17-7.15 (m, 2H), 5.67 (ddt, *J* = 17.0, 10.3, 6.7 Hz, 1H), 5.02-4.96 (m, 2H), 4.31-4.29 (m, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.33 (td, *J* = 7.7, 5.8 Hz, 1H), 2.71 (d, *J* = 7.7 Hz, 2H), 2.57-2.52 (m, 1H), 2.12-1.99 (m, 2H), 1.56 (dddd, *J* = 12.0, 8.4, 6.2, 3.8 Hz, 1H), 1.15 (dd, *J* = 14.2, 5.5 Hz, 1H), 1.13-1.07 (m, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.4, 139.6, 137.0, 128.6, 128.3, 127.3, 115.9, 76.9, 60.6, 42.4, 41.3, 37.1, 30.7, 27.4, 14.0.**IR** (ATR, neat) 2978, 2927, 1732, 1551, 1379, 1162, 916 cm^{-1}; LRMS (ESI + APCI) *m/z* [M+H] calcd 306.2, found 306.1



(3*S*,4*R*)-ethyl 4-cyclopropyl-5-nitro-3-phenylpentanoate (**3i**): Colorless Oil. R_f= 0.23 (8:2 Hexanes:Ether); 68 % yield, 18:1 d.r., 88 % ee;$[\alpha]_D^{21}$ = -37.5 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 97:3 hexanes/*iso*-propanol, 1.0 mL/min. Major: 16.4 min, minor: 19.2 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.33-7.29 (m, 2H), 7.26-7.20 (m, 3H), 4.31 (dd, *J* = 12.1, 7.9 Hz, 1H), 4.24 (dd, *J* = 12.0, 6.7 Hz, 1H), 4.06-3.98 (m, 2H), 3.39 (td, *J* = 8.0, 3.8 Hz, 1H), 2.89 (d, *J* = 8.0 Hz, 2H), 1.85-1.78 (m, 1H), 1.11 (d, *J* = 14.3 Hz, 3H), 0.67 (tdd, *J* = 8.2, 5.7, 4.0 Hz, 1H), 0.52-0.35 (m, 3H), 0.13-0.08 (m, 1H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.6, 138.9, 128.7, 128.4, 127.3, 78.9, 60.5, 46.9, 43.6, 37.5, 14.0, 10.1, 5.3, 2.6.**IR** (ATR, neat) 2960, 2925, 1731, 1552, 1378, 1175, 1028, 740 cm^{-1}; LRMS (ESI + APCI) *m/z* [M+H] calcd 292.2, found 292.2

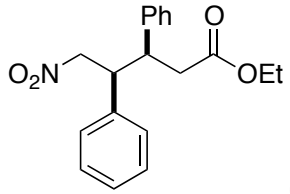


tert-butyl 4-((2*R*,3*S*)-5-ethoxy-1-nitro-5-oxo-3-phenylpentan-2-yl)piperidine-1-carboxylate (**3j**): Colorless Oil. R_f= 0.26 (6:4 Hexanes:Ether); 65 % yield, 19:1 d.r., 94 % ee;$[\alpha]_D^{21}$ = 9.11 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 85:15 hexanes/*iso*-propanol, 1.0 mL/min. Major: 31.4 min, minor: 41.3 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.32-7.29 (m, 2H), 7.22-7.22 (m, 1H), 7.20-7.17 (m, 2H), 4.37 (d, *J* = 5.7 Hz, 2H), 4.04 (m, 2H), 3.95 (qd, *J* = 7.1, 0.9 Hz, 2H), 3.36-3.30 (m, 1H), 2.65-2.63 (m, 2H), 2.55-2.51 (m, 2H), 2.39-2.31 (m, 1H), 1.56-1.31 (m, 5H), 1.39 (s, 9H), 1.04 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.5, 154.5, 140.7, 128.8, 127.7, 127.3, 79.5, 75.3, 60.6, 46.6, 36.6, 28.4, 13.9. **IR** (ATR, neat) 2976, 2927, 2854, 1732, 1688, 1553, 1425, 1366, 1169, 766 cm^{-1}; LRMS (ESI + APCI) *m/z* [M+H] calcd 435.2, found 435.2

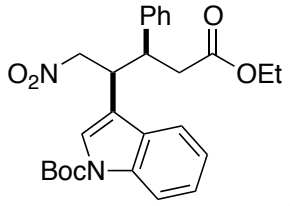


(3*S*,4*R*)-ethyl 4-(furan-2-yl)-5-nitro-3-phenylpentanoate (**3k**): Colorless Oil. R_f= 0.31 (8:2 Hexanes:Ether); 90 % yield, 3:1 d.r., 81 % ee; $[\alpha]_D^{21}$ = -1.9 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 97:3 hexanes/*iso*-propanol, 1.0 mL/min. Major: 23.3 min, minor: 31.6 min. **^{1}H-NMR**, isolated as a 2:1mixture of diastereomers (400 MHz; $CDCl_3$): δ 7.40-7.20 (m, 5H), 6.86 (dd, *J* = 6.7, 2.8 Hz, 1H), 6.31-6.24 (m, 1H), 5.97 (d, *J* = 3.3 Hz, 1H), 4.57-4.47 (m, 2H), 4.18 (dd, *J* = 12.7, 4.2 Hz, 0.33H, minor diastereomer), 4.05 (qt, *J* = 7.2, 3.6 Hz, 2.33H), 3.90-3.80 (m, 1H), 3.53 (td, *J* = 7.7, 4.8 Hz, 0.66H, major diastereomer), 3.46 (td, *J* = 10.4, 5.0 Hz, 0.33H, minor diastereomer), 2.85-2.66 (m, 1.32H, major diastereomer), 2.50 (qd, *J* =

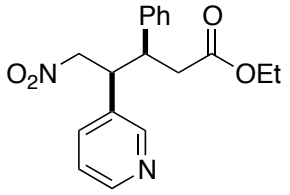
17.1, 7.4 Hz, 0.66H, minor diastereomer), 1.13 (t, *J* = 7.1 Hz, 2H, major diastereomer), 1.01 (t, *J* = 7.1 Hz, 1H, minor diastereomer); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.3, 171.1, 150.4, 150.0, 142.8, 142.2, 139.9, 138.4, 129.1, 127.81, 127.72, 127.5, 110.38, 110.36, 109.5, 108.7, 77.1, 75.8, 60.7, 60.4, 43.7, 43.37, 43.34, 41.6, 39.5, 37.8, 14.03, 13.91.**IR** (ATR, neat) 2981, 2923, 1729, 1553, 1376, 1162, 702 cm^{-1}; LRMS (ESI + APCI) *m/z* [M+H] calcd 318.1, found 318.1



(3*S*,4*S*)-ethyl 5-nitro-3,4-diphenylpentanoate (**3l**): White Solid. R_f= 0.26 (8:2 Hexanes:Ether); 95 % yield, 6:1 d.r., 87 % ee; $[\alpha]_D^{21}$ = -26.8 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralcel OD-H column, 98:2 hexanes/*iso*-propanol, 1.0 mL/min. Major: 43.0 min, minor: 54.6 min. **^{1}H-NMR** (400 MHz; CDCl3): δ 7.38-7.28 (m, 1H), 7.24-7.17 (m, 5H), 6.84-6.79 (m, 4H), 4.65 (ddd, *J* = 56.8, 12.8, 7.8 Hz, 2H), 4.04 (qt, *J* = 7.1, 3.5 Hz, 2H), 3.88 (ddd, *J* = 8.6, 7.0, 5.7 Hz, 1H), 3.55 (td, *J* = 7.7, 5.6 Hz, 1H), 2.75-2.57 (m, 2H), 1.12 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.4, 138.4, 135.7, 128.90, 128.82, 128.22, 128.11, 127.8, 127.4, 77.9, 60.7, 47.8, 44.0, 37.9, 14.0.**IR** (ATR, neat) 2958, 2924, 2854, 1728, 1551, 1377, 1156, 1029 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 328.2, found 328.1

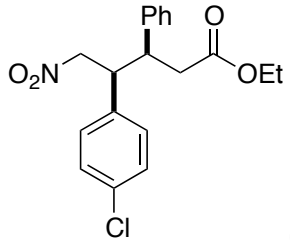


tert-butyl 3-((2*S*,3*S*)-5-ethoxy-1-nitro-5-oxo-3-phenylpentan-2-yl)-1*H*-indole-1-carboxylate (**3m**): Colorless Oil. R_f = 0.61 (6:4 Hexanes:Ether) 86 % yield, 8:1 d.r., 87 % ee; $[\alpha]_D^{21}$ = 12.7 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 96:4 hexanes/*iso*-propanol, 1.0 mL/min. Major: 30.73 min, minor: 31.44 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 8.09 (ddd, *J* = 8.4, 1.6, 0.6 Hz, 1H), 7.41-7.19 (m, 6H), 7.01 (dd, *J* = 6.5, 3.0 Hz, 2H), 6.89-6.88 (m, 1H), 4.71 (dd, *J* = 12.9, 7.2 Hz, 1H), 4.52 (dd, *J* = 12.9, 8.4 Hz, 1H), 4.30-4.25 (m, 1H), 4.07-3.97 (m, 2H), 3.72 (td, *J* = 7.7, 4.8 Hz, 1H), 2.77-2.59 (m, 2H), 1.61 (s, 9H), 1.10 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.5, 138.7, 129.9, 128.7, 128.3, 127.6, 124.7, 124.5, 122.7, 118.9, 115.28, 115.15, 84.0, 60.6, 43.1, 39.1, 37.2, 28.1, 14.0**IR** (ATR, neat) 2924, 2853, 1731, 1553, 1452, 1153 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 466.5, found 466.4

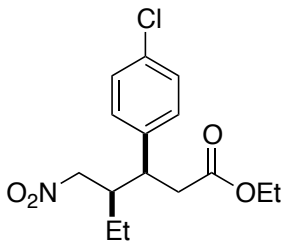


(3*S*,4*S*)-ethyl 5-nitro-3-phenyl-4-(pyridin-3-yl)pentanoate (**3n**): Colorless Oil. R_f = 0.12 (6:4 Hexanes:Ether) 73 % yield, 5:1 d.r., 86 % ee; $[\alpha]_D^{21}$ = -24.9

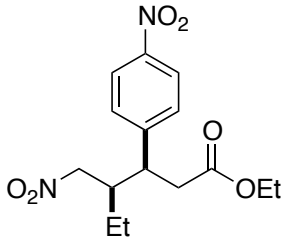
(c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiracel OD-H column, 80:20hexanes/*iso*-propanol, 1.0 mL/min. Major: 27.5 min, minor: 20.7 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 8.47 (s, 1H), 8.17 (s, 1H), 7.24-7.07 (m, 5H), 6.81 (td, *J* = 3.9, 1.6 Hz, 2H), 4.79 (dd, *J* = 13.0, 6.6 Hz, 1H), 4.59 (dd, *J* = 13.0, 9.1 Hz, 1H), 4.11-4.03 (m, 2H), 3.95-3.89 (m, 1H), 3.59-3.53 (m, 1H), 2.67 (qd, *J* = 18.0, 7.6 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.1, 149.9, 148.9, 137.8, 136.4, 128.57, 128.50, 127.8, 123.1, 77.5, 60.9, 45.6, 43.9, 37.9, 14.0. **IR** (ATR, neat) 2980, 2924, 1729, 1553, 1378, 1160, 1026 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 329.2, found 329.1



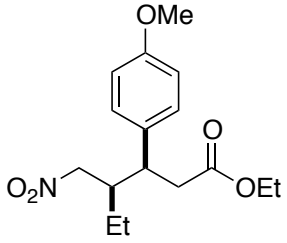
(3*S*,4*S*)-ethyl 4-(4-chlorophenyl)-5-nitro-3-phenylpentanoate (**3o**): White Solid. R_f = 0.62 (6:4 Hexanes:Ether) 75 % yield, 4:1 d.r., 86 % ee; $[\alpha]_D^{21}$ = -49.2 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 90:10 hexanes/*iso*-propanol, 1.0 mL/min. Major: 12.7 min, minor: 20.8 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.24-7.16 (m, 4H), 6.84-6.81 (m, 2H), 6.76-6.74 (m, 2H), 4.71 (dd, *J* = 12.9, 6.6 Hz, 1H), 4.53 (dd, *J* = 12.8, 9.1 Hz, 1H), 4.05 (qd, *J* = 7.1, 2.1 Hz, 2H), 3.86 (dt, *J* = 9.0, 6.2 Hz, 1H), 3.54-3.49 (m, 1H), 2.72-2.57 (m, 2H), 1.13 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.3, 138.2, 134.2, 133.7, 130.2, 128.7, 128.45, 128.28, 127.5, 77.8, 60.8, 47.3, 44.0, 37.9, 14.0.**IR** (ATR, neat) 2981, 2924, 1728, 1552, 1493, 1377, 1014, 828 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 362.1, found 362.2



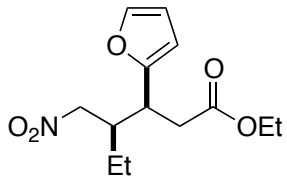
(3*S*,4*R*)-ethyl 3-(4-chlorophenyl)-4-(nitromethyl)hexanoate (**3p**): Colorless Oil. R_f = 0.58 (6:4 Hexanes:Ether) 73 % yield, 20:1 d.r., 82 % ee; $[\alpha]_D^{21}$ = -2.3 (c = 0.010 g/ml, CH_2Cl_2); Could not separate via HPLC, ee inferred from lactam **6e**. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.28 (d, *J* = 8.5 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.30 (qd, *J* = 14.1, 6.6 Hz, 2H), 3.99 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.27 (dt, *J* = 8.9, 6.4 Hz, 1H), 2.68 (dd, *J* = 7.7, 3.9 Hz, 2H), 2.42 (tdd, *J* = 8.7, 4.4, 1.9 Hz, 1H), 1.49 (ddd, *J* = 14.3, 7.4, 4.3 Hz, 1H), 1.12-1.00 (m, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.2, 138.4, 133.0, 129.6, 128.7, 76.6, 60.7, 43.6, 42.0, 37.4, 21.2, 14.0, 11.0. **IR** (ATR, neat) 2966, 2925, 1731, 1549, 1162, 830 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 314.1, found 314.1



(3*S*,4*R*)-ethyl 4-(nitromethyl)-3-(4-nitrophenyl)hexanoate (**3q**): Yellow Solid. R_f = 0.48 (6:4 Hexanes:Ether) 48 % yield, 10:1 d.r., 90 % ee; $[\alpha]_D^{21}$ = -9.5 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 90:10 hexanes/*iso*-propanol, 1.0 mL/min. Major: 32.9 min, minor: 36.5 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 4.42-4.27 (m, 2H), 3.99 (qd, *J* = 7.1, 2.8 Hz, 2H), 3.41 (dt, *J* = 9.0, 6.5 Hz, 1H), 2.75 (dd, *J* = 7.6, 3.7 Hz, 2H), 2.53-2.45 (m, 1H), 1.48 (ddd, *J* = 14.3, 7.4, 4.3 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 1.10-0.98 (m, 1H), 0.93 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 170.7, 147.8, 129.2, 123.8, 98.7, 76.2, 60.9, 43.5, 42.5, 37.2, 21.5, 14.0, 10.9. **IR** (ATR, neat) 2973, 2937, 1731, 1552, 1521, 1347 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 325.1, found 325.1

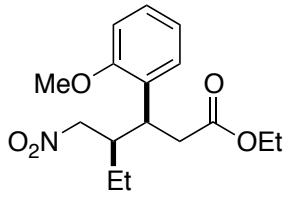


(3*S*,4*R*)-ethyl 3-(4-methoxyphenyl)-4-(nitromethyl)hexanoate (**3r**) White Solid. R_f= 0.27 (7:3 Hexanes:Ether); 35 % yield, 5:1 d.r., 88 % ee; $[\alpha]_D^{21}$ = -3.9 (c = 0.010 g/ml, CH_2Cl_2); **HPLC Analysis** – Chiralpak IC column, 98:2 hexanes/*iso*-propanol, 1.0 mL/min. Major: 43.6 min, minor: 48.8 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.08 (d, *J* = 8.3 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 4.30-4.28 (m, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.77 (d, *J* = 0.9 Hz, 3H), 3.28-3.22 (m, 1H), 2.68-2.66 (m, 2H), 2.43-2.38 (m, 1H), 1.30-1.21 (m, 2H), 1.10 (td, *J* = 7.1, 1.0 Hz, 3H), 1.16-1.02 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.5, 131.6, 129.3, 114.1, 113.9, 76.9, 60.5, 55.2, 43.8, 41.7, 37.6, 21.0, 14.0, 11.1.**IR** (ATR, neat) 2959, 2924, 2854, 1732, 1551, 1513, 1250, 1035 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 310.2, found 310.2

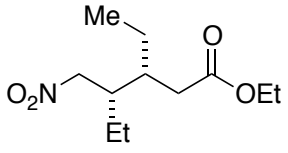


(3*S*,4*R*)-ethyl 3-(furan-2-yl)-4-(nitromethyl)hexanoate (**3s**): Colorless Oil. R_f= 0.22 (8:2 Hexanes:Ether); 83 % yield, 19:1 d.r., 91 % ee ;$[\alpha]_D^{21}$ = 11.3 (c = 0.010 g/ml, CH_2Cl_2); Could not separate via HPLC, ee inferred from lactam **6c**. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.32 (ddd, *J* = 4.0, 2.0, 0.8 Hz, 1H), 6.27 (td, *J* = 3.7, 1.8 Hz, 1H), 6.11-6.09 (m, 1H), 4.34 (qd, *J* = 12.7, 6.9 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.47 (td, *J* = 6.0, 3.1 Hz, 1H), 2.74-2.58 (m, 2H), 2.51-2.46 (m, 1H), 1.54 (ddd, *J* = 14.4, 7.5, 5.2 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.20-1.07 (m, 1H), 0.93 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.2, 153.5, 141.9, 110.1, 107.3, 77.4, 60.8, 42.4, 36.2,

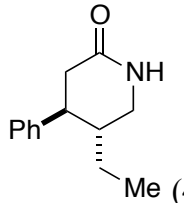
35.2, 21.2, 14.1, 11.6.**IR** (ATR, neat) 2966, 2928, 1731, 1550, 1374, 1162, 1011, 808 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 270.1, found 270.1



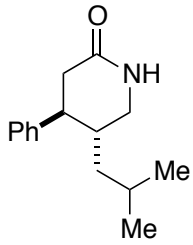
(3*S*,4*R*)-ethyl 3-(2-methoxyphenyl)-4-(nitromethyl) (**3t**): White Solid. R_f=0.29 (8:2 Hexanes:Ether); % yield, 9:1 d.r., 82 % ee; $[\alpha]_D^{21}$ = -15.7 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 97:3 hexanes/*iso*-propanol, 1.0 mL/min. Major: 24.1 min, minor: 30.8 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.22-7.18 (m, 1H), 7.06 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.90-6.84 (m, 2H), 4.29 (qd, *J* = 13.8, 6.7 Hz, 2H), 3.99 (qd, *J* = 7.1, 2.6 Hz, 2H), 3.79 (s, 3H), 3.81-3.76 (m, 1H), 2.76-2.65 (m, 2H), 2.63-2.55 (m, 1H), 1.53-1.41 (m, 1H), 1.16-1.04 (m, 1H), 1.08 (t, *J* = 7.1 Hz, 3H), 0.91 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.9, 157.2, 128.53, 128.36, 128.1, 120.3, 110.7, 76.9, 60.4, 55.2, 41.9, 36.1, 35.9, 21.6, 14.0, 10.9.**IR** (ATR, neat) 2964, 2925, 1731, 1550, 1492, 1242, 1028, 756m cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 310.2, found 310.2



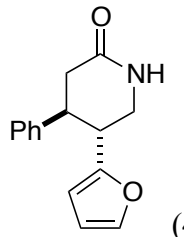
(3*R*,4*S*)-ethyl 3-ethyl-4-(nitromethyl)hexanoate (**3u**): Synthesized by a modified procedure: To a screw cap vial charged with a stirbar was added triazolium salt **6d** (10.5 mg, 0.025 mmol) and NaOAc (10 mg, .125 mmol). This vial was then fitted with a rubber septum and evacuated and refilled with argon three times. 0.75 ml EtOH was then added via syringe. To this solution was then added (*E*)-1-nitrobut-1-ene (26 µL, 0.25 mmol, 1 equiv) followed by *trans*-2-pentenal (31.5 mg, 1.5 equiv). The septum was then quickly removed and replaced with a screw cap. This was then allowed to stir at 50 °C for 12 hours. After 12 hours the reaction was concentrated via rotary evaporation and then purified by silica gel chromatography (8:2 hexanes:ether) to yield 15 mg (25 %) (3*R*,4*S*)-ethyl 3-ethyl-4-(nitromethyl)hexanoate as a colorless oil. R_f= 0.21 in (8:2 Hexanes:Ether); 25 % yield, 20:1 d.r., 91 % ee; $[\alpha]_D^{21}$ = -3.3 (c = 0.010 g/ml, CH_2Cl_2); **GC Analysis** – Varian BDM column, 130 °C, 1mL/min. Major: 39.237 min, minor: 39.836 min. **^{1}H-NMR** (400 MHz; CDCl3): δ 4.35 (dd, *J* = 12.0, 6.2 Hz, 1H), 4.24 (dd, *J* = 12.0, 7.7 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.30-2.26 (m, 1H), 2.28-2.14 (m, 2H), 2.03-1.97 (m, 1H), 1.46-1.41 (m, 1H), 1.37-1.27 (m, 3H), 1.27-1.23 (m, 3H), 0.96-0.92 (m, 6H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 172.7, 77.2, 60.6, 41.3, 37.3, 35.5, 23.8, 21.6, 14.1, 11.8, 11.6. **IR** (ATR, neat) 2963, 2927, 2877, 1733, 1553, 1463, 1377, 1181, 1034 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 232.2, found 232.0



(4*S*,5*R*)-5-ethyl-4-phenylpiperidin-2-one (**6a**): White Solid. R_f = 0.18 (100 % EtOAc)63 % yield, 17:1 d.r., 93 % ee; $[\alpha]_D^{21}$ = 30.0 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 80:20 hexanes/*iso*-propanol, 1.0 mL/min. Major: 37.9 min, minor: 40.3 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.31 (qd, *J* = 5.6, 2.2 Hz, 2H), 7.25-7.20 (m, 1H), 7.15-7.12 (m, *J* = 8.1 Hz, 2H), 6.62 (s, 1H), 3.47 (ddd, *J* = 12.1, 5.0, 3.8 Hz, 1H), 3.04 (t, *J* = 11.1 Hz, 1H), 2.76 (td, *J* = 10.8, 5.5 Hz, 1H), 2.62 (dd, *J* = 17.8, 5.5 Hz, 1H), 2.49 (dd, *J* = 17.8, 11.1 Hz, 1H), 1.96-1.87 (m, 1H), 1.29 (dtd, *J* = 14.3, 7.3, 3.7 Hz, 1H), 1.02 (ddt, *J* = 14.2, 9.3, 7.2 Hz, 1H), 0.77 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 172.2, 142.7, 128.8, 127.4, 126.8, 46.2, 44.5, 39.9, 39.0, 24.0, 11.0. **IR** (ATR, neat) 2960, 2930, 1678, 1495, 701 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 232.2, found 232.1

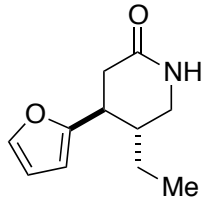


(4*S*,5*R*)-5-isobutyl-4-phenylpiperidin-2-one (**6b**): White Solid. R_f = 0.34 (19:1 EtOAc:MeOH) 65 % yield, 19:1 d.r., 93 % ee; $[\alpha]_D^{21}$ = 55.1 (c = 0.010 g/ml, CH_2Cl_2); HPLC analysis – Chiralpak IC column, 80:20 hexanes/*iso*-propanol, 1.0 mL/min. Major: 31.6 min, minor: 33.8 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.34-7.30 (m, 2H), 7.26-7.22 (m, 1H), 7.14-7.12 (m, 2H), 6.01 (s, 1H), 3.46 (ddd, *J* = 12.1, 4.8, 3.8 Hz, 1H), 3.03-2.97 (m, 1H), 2.74 (td, *J* = 10.5, 5.5 Hz, 1H), 2.67-2.62 (m, 1H), 2.51 (dd, *J* = 17.8, 10.8 Hz, 1H), 2.10-2.01 (m, 1H), 1.50-1.40 (m, 1H), 1.01-0.98 (m, 2H), 0.77 (dd, *J* = 6.5, 3.2 Hz, 6H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 172.1, 142.8, 128.8, 127.3, 126.8, 46.7, 45.1, 40.6, 38.9, 36.1, 25.0, 23.7, 21.1 .**IR** (ATR, neat) 3210, 2955, 2924, 1669, 1495, 1348, 758 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 310.2, found 310.2

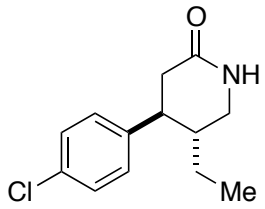


(4*S*,5*R*)-5-(furan-2-yl)-4-phenylpiperidin-2-one (**6c**): White Solid. R_f = 0.42 (19:1 EtOAc:MeOH) 82 % yield, 3:1 d.r., 82 % ee; $[\alpha]_D^{21}$ = 50.6 (c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 85:15 hexanes/*iso*-propanol, 1.0 mL/min. Major: 42.5 min, minor: 46.1 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.31-7.11 (m, 6H), 6.22 (s, 1H), 6.12 (s, 1H), 5.87 (s, 1H), 3.60-3.51 (m, 2H), 3.45-3.32 (m, 2H), 2.82-2.60 (m, 2H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.4, 153.1, 141.8, 141.4, 128.6,

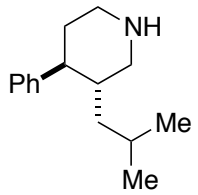
127.01, 126.90, 110.0, 106.9, 45.2, 42.9, 39.6, 38.0**IR** (ATR, neat) 3206, 2923, 2854, 1669, 1495, 1011, 760 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 242.1, found 242.1



(4*S*,5*R*)-5-ethyl-4-(furan-2-yl)piperidin-2-one (**6d**): White Solid. R_f = 0.44 (19:1 EtOAc:MeOH) 60 % yield, 19:1 d.r., 91 % ee $[\alpha]_D^{21}$ = 3.0 (c = 0.010 g/ml, CH_2Cl_2); **GC Analysis** – Varian BDM column, 170 °C, 1mL/min. Major: 16.453 min, minor: 16.594 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.33 (d, *J* = 1.6 Hz, 1H), 6.30 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.06 (dd, *J* = 9.3, 5.8 Hz, 1H), 3.41-3.37 (m, 1H), 3.06-2.93 (m, 2H), 2.63 (dt, *J* = 7.0, 3.6 Hz, 2H), 2.03-1.94 (m, 1H), 1.43-1.34 (m, 1H), 1.28-1.18 (m, 1H), 0.84 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.3, 155.5, 141.5, 110.1, 105.9, 45.5, 44.3, 38.7, 37.5, 24.0, 11.1 **IR** (ATR, neat) 3102, 2962, 2924, 1667, 1495, 1014 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd194.1, found 194.1

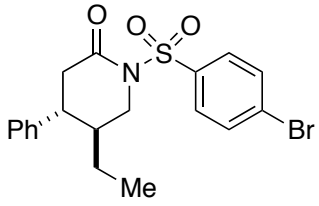


(4*S*,5*R*)-4-(4-chlorophenyl)-5-ethylpiperidin-2-one (**6e**): White Solid. R_f = 0.31 (19:1 EtOAc:MeOH) 70 % yield, 20:1 d.r., 82 % ee; $[\alpha]_D^{21}$ = 28.3(c = 0.010 g/ml, CH_2Cl_2); **HPLC analysis** – Chiralpak IC column, 85:15 hexanes/*iso*-propanol, 1.0 mL/min. Major: 50.9 min, minor: 54.3 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.30-7.28 (m, 2H), 7.09-7.07 (m, 2H), 6.15 (s, 1H), 3.50-3.44 (m, 1H), 3.05 (t, *J* = 11.1 Hz, 1H), 2.79-2.72 (m, 1H), 2.61 (dd, *J* = 17.8, 5.5 Hz, 1H), 2.45 (dd, *J* = 17.8, 11.2 Hz, 1H), 1.93-1.84 (m, 1H), 1.35-1.24 (m, 1H), 1.09-1.00 (m, 1H), 0.78 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 171.8, 141.1, 132.6, 129.0, 128.7, 46.1, 43.9, 39.8, 38.8, 23.9, 11.0. **IR** (ATR, neat) 3212, 2960, 2928, 2874, 1668, 1491, 1089, 837, 818 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 238.1, found 238.1



(3*R*,4*S*)-3-isobutyl-4-phenylpiperidine (**7a**): To a flame dried10 ml round bottom containing a stir bar, 46 mg **6b** (0.2 mmol, 1 equiv.) was dissolved in 6 ml dry THF and cooled to 0 °C in an ice bath. Then 11.3 mg Lithium aluminum hydride (0.3 mmol, 1.5 equiv.) was added in two portions over 5 minutes. This was stoppered with septum and placed under argon and allowed to stir for 1 hour. After 1 hour the ice bath was removed and the flask was fitted with a condenser and the reaction was refluxed for 4 hours. After 4 hours the heat source was removed and the flask was cooled to 0 °C in an ice bath and quenched with 2 ml 1 M HCl. This solution was then transferred to

a separatory funnel and diluted with 15 ml brine and extracted 3x 15 ml DCM. The organic layer was dried over sodium sulfate and the solvent was removed via rotary evaporation to yield 38 mg (89 %) (3*R*,4*S*)-3-isobutyl-4-phenylpiperidine as a colorless oil. Rf = 0.12 (19:1 EtOAc:MeOH) 89 % yield, >20:1 d.r., 93 % ee; $[\alpha]_D^{21}$ = 35.5 (c = 0.010 g/ml, CH_2Cl_2); **HPLC Analysis** - Chiralpak IC column, 60:40 hexanes/*iso*-propanol, 1.0 mL/min. Major: 35.38 min, minor: 33.76 min. **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 9.76-9.63 (m, 1H), 7.30 (t, *J* = 7.3 Hz, 2H), 7.23-7.18 (m, 3H), 3.65-3.56 (m, 2H), 2.96-2.88 (m, 1H), 2.59-2.56 (m, 1H), 2.40-2.23 (m, 3H), 1.95 (d, *J* = 14.2 Hz, 1H), 1.47-1.38 (m, 1H), 0.93 (ddd, *J* = 14.4, 9.9, 4.2 Hz, 2H), 0.72 (d, *J* = 13.6 Hz, 6H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 142.4, 128.7, 127.6, 127.0, 48.7, 47.8, 44.4, 40.5, 36.0, 31.0, 24.7, 23.7, 21.1 **IR** (ATR, neat) 3352, 2955, 2925, 2869, 2721, 2492, 1454, 1066, 758, 702 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 218.2, found 218.2



(4*R*,5*S*)-1-((4-bromophenyl)sulfonyl)-5-ethyl-4-phenylpiperidin-2-one (**S3**): To a flame dried 25 mL round bottom flask containing a stirbar was added 107 mg (4*S*,5*R*)-5-ethyl-4-phenylpiperidin-2-one (**7a**) (synthesized via catalyst **5b**) (0.52 mmol, 1 equiv.) and 10 mL THF and cooled to -78 °C. To this was then added dropwise 0.357 mL *n*-Butyl lithium (1.6 M, hexanes) (0.572 mmol, 1.1 equiv). After stirring at -78 °C for 10 minutes a solution (146 mg 4-bromobenzenesulfonyl chloride (0.572 mmol, 1.1 equiv.) in 5 mL THF) was added dropwise to the reaction. This was stirred at -78 °C for 1 hour and then allowed to warm to room temperature and stir overnight. After 12 hours the reaction was cooled to 0 °C and quenched with 8 mL saturated NH_4Cl. The reaction was extracted 3 x 10 mL CH_2Cl_2, dried with anhydrous Na_2SO_4 and then concentrated *in vacuo*. The resulting crude oil was then purified by column chromatography to yield 180 mg (4*R*,5*S*)-1-((4-bromophenyl)sulfonyl)-5-ethyl-4-phenylpiperidin-2-one (82 %) as a crystalline white solid. Rf = 0.51 (1:1 hexanes:ether) $[\alpha]_D^{21}$ = -11.8 (c = 0.010 g/ml, CH_2Cl_2); **^{1}H-NMR** (400 MHz; $CDCl_3$): δ 7.93-7.90 (m, 2H), 7.69-7.65 (m, 2H), 7.31-7.27 (m, 2H), 7.22 (dt, *J* = 7.2, 1.9 Hz, 1H), 7.06-7.04 (m, 2H), 4.22 (dd, *J* = 12.5, 4.7 Hz, 1H), 3.48 (dd, *J* = 12.5, 9.4 Hz, 1H), 2.75 (dt, *J* = 10.1, 5.0 Hz, 1H), 2.71-2.65 (m, 1H), 2.56 (dd, *J* = 17.4, 10.5 Hz, 1H), 2.05-1.96 (m, 1H), 1.40 (dtd, *J* = 14.4, 7.3, 4.1 Hz, 1H), 1.21-1.14 (m, 1H), 0.88 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (101 MHz; $CDCl_3$): δ 169.9, 141.7, 137.7, 132.0, 130.3, 129.12, 128.95, 127.21, 127.09, 49.8, 44.0, 41.5, 41.1, 24.3, 11.1; **IR** (ATR, neat) 1960, 2923, 1692, 1170 cm^{-1}; **LRMS** (ESI + APCI) *m/z* [M+H] calcd 422.0, found 422.1

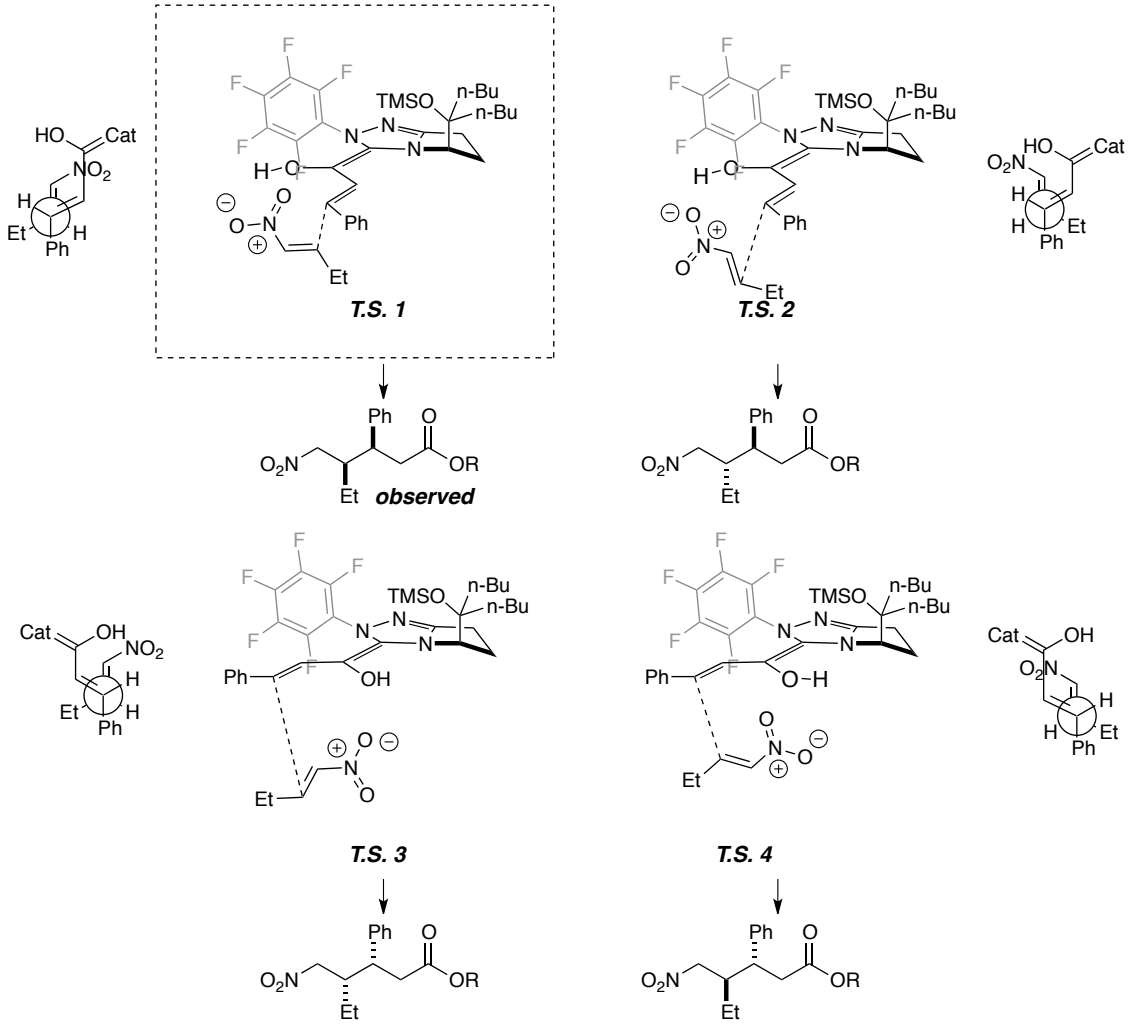
General Procedure for the Synthesis of Nitroalkenes

To a dry round bottom flask was added cyclopentane carboxaldehyde (1.02 g, 10.4 mmol), nitromethane (840 μL, 15.6 mmol), and 1:1 THF/*t*-BuOH (10 mL). This solution was cooled to 0 °C and potassium tert-butoxide (0.233 g, 2.08 mmol) added in one portion. The reaction was then stirred at 0 °C for 1 h then warmed to room temperature and stirred for 12 h. After completion, saturated aqueous NH_4Cl solution (20 mL) was added to quench the reaction and then extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were then dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. After drying the crude residue under vacuum (4 mm) for 1 h, CH_2Cl_2 (20 mL) was added followed by cooling to 0 °C. Trifluoroacetic anhydride (1.52 mL, 10.9 mmol) was added followed by the slow dropwise addition of Et3N (3.04 mL, 21.8 mmol). After stirring for 1 h at 0 °C the reaction was allowed to warm to room temperature and stirred an additional 2 h. The reaction was diluted with CH_2Cl_2 (20 mL) followed by the addition of water (20 mL). The organic layer was separated and washed with saturated aqueous NH_4Cl solution (3 x 20 mL), dried (Na_2SO4) and concentrated *in vacuo* to give a yellow oil that was purified by column chromatography (20:1 hexanes:ether) yielding 0.779 g (53%) of (*E*)-(2- nitrovinyl)cyclopentane as a pale yellow oil.

Proposed Stereochemical Models to Account for Selectivity:

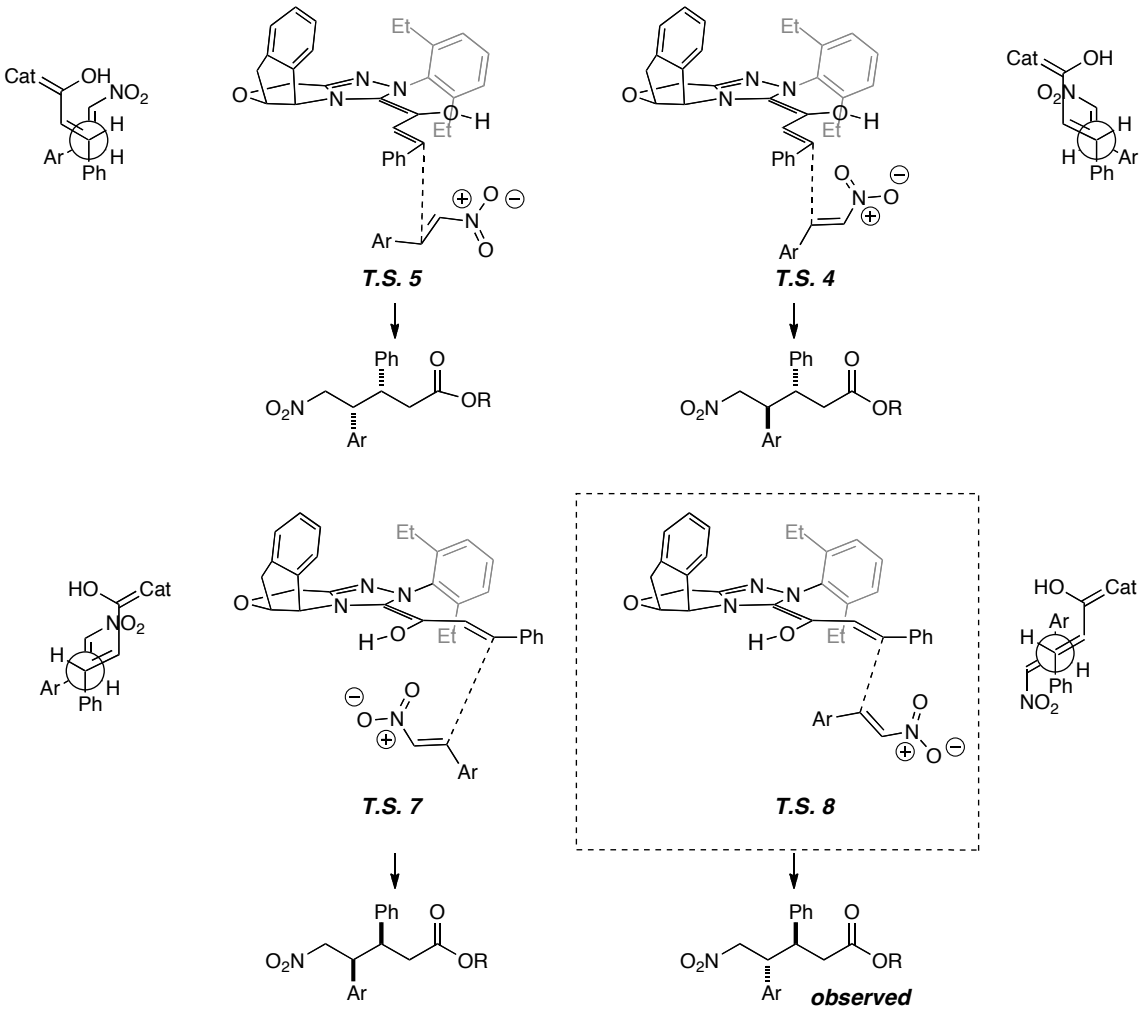
The inversion of diastereoselectivity between our reation and that observed in Liu's reaction is intriguing. Complicating matters is that the same stereochemistry is observed at the beta-position in the product in spite of the fact that the pseudo-enantiomeric catalysts are used. This suggests that the electrophile approaches from the opposite prochiral face of the enal, most likely because of an inversion of Breslow intermediate geometry. The reasons for this are not clear at this time, but may have much to do with the nature of the N-aryl substituent. We present an analysis of the diastereomeric transition states that may be involved in settling these issues of selectivity.

Transition States and Stereoisomers Formed (this work):

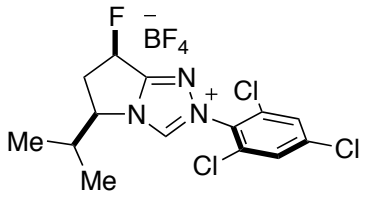


Scheme S1

Transition States and Stereoisomers Formed (Liu et al - reference 7 in text):



Scheme S2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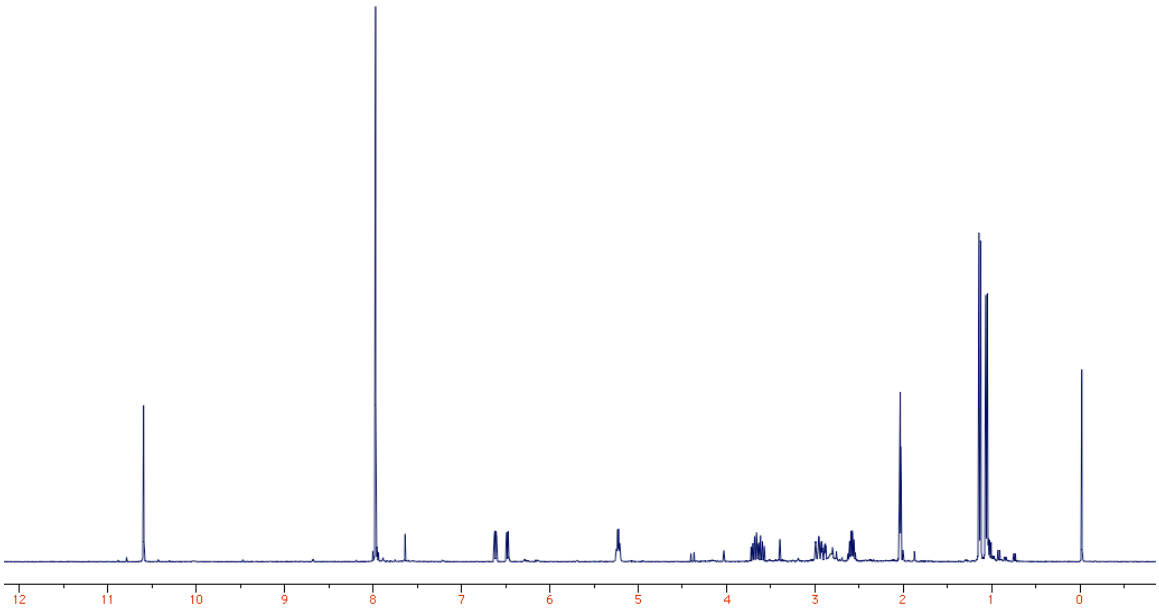
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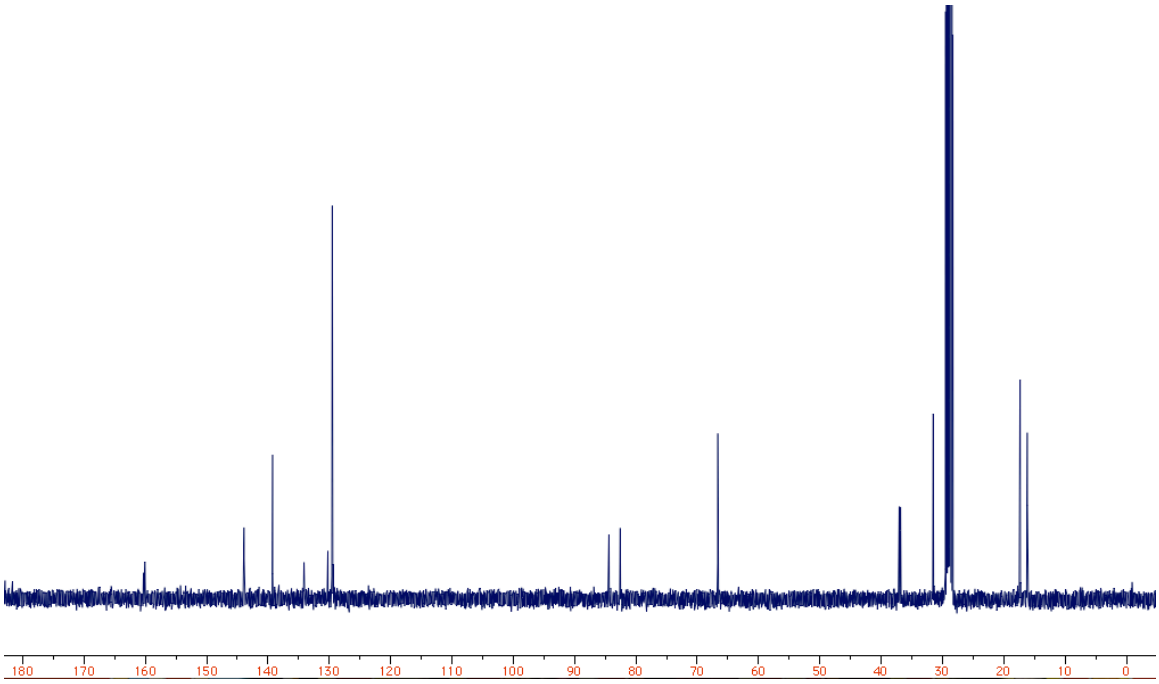
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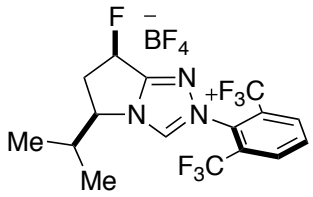
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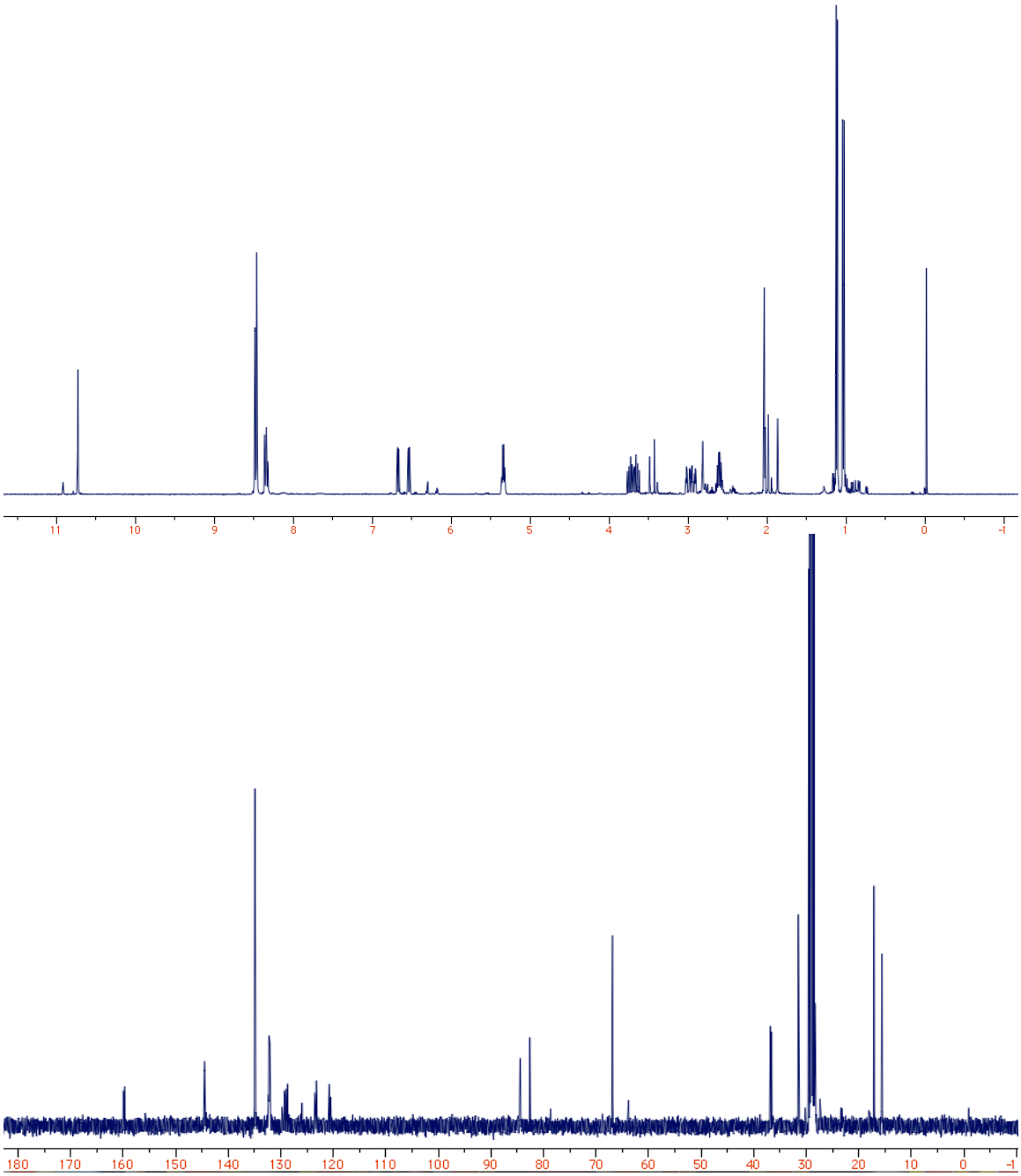
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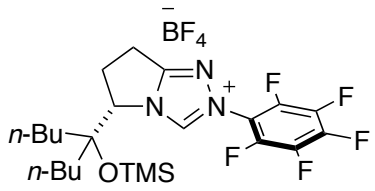
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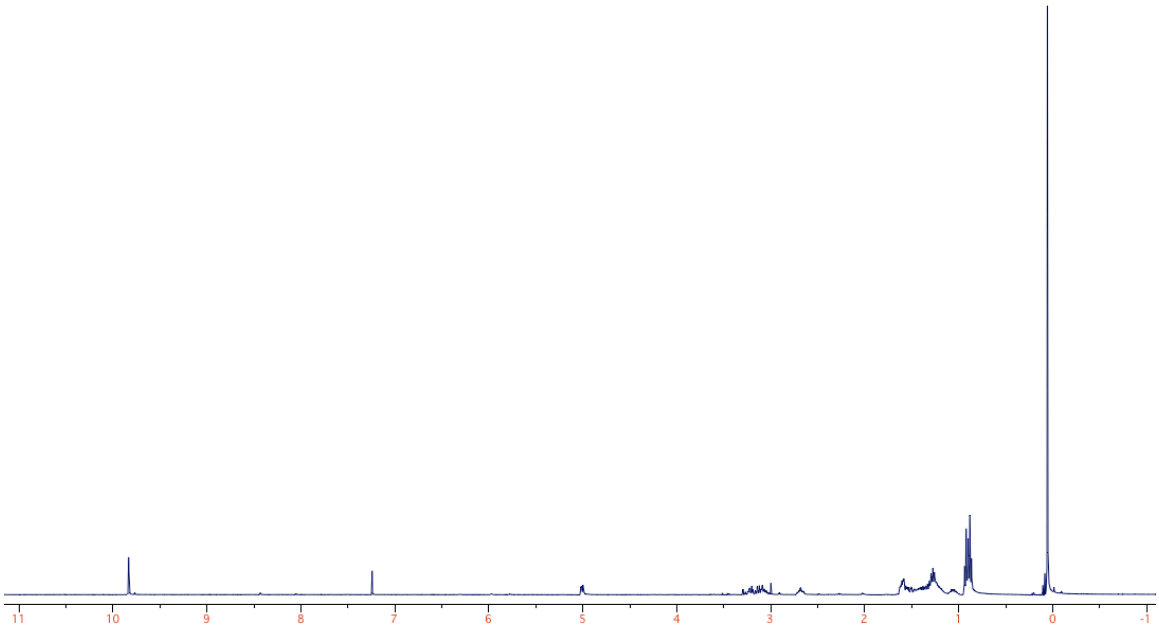
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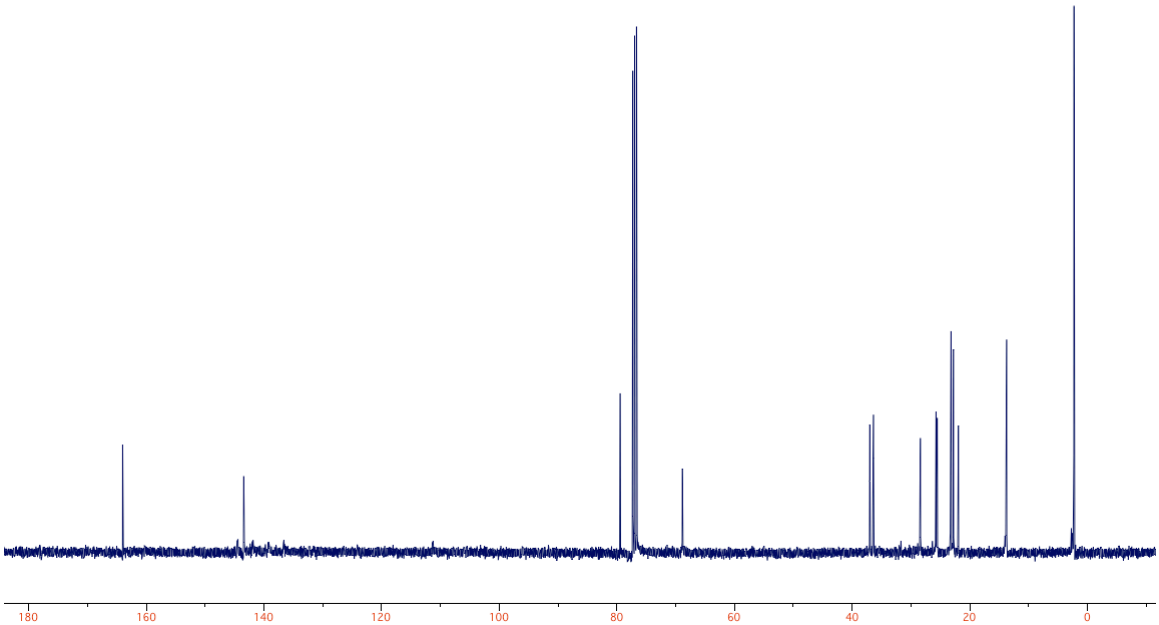
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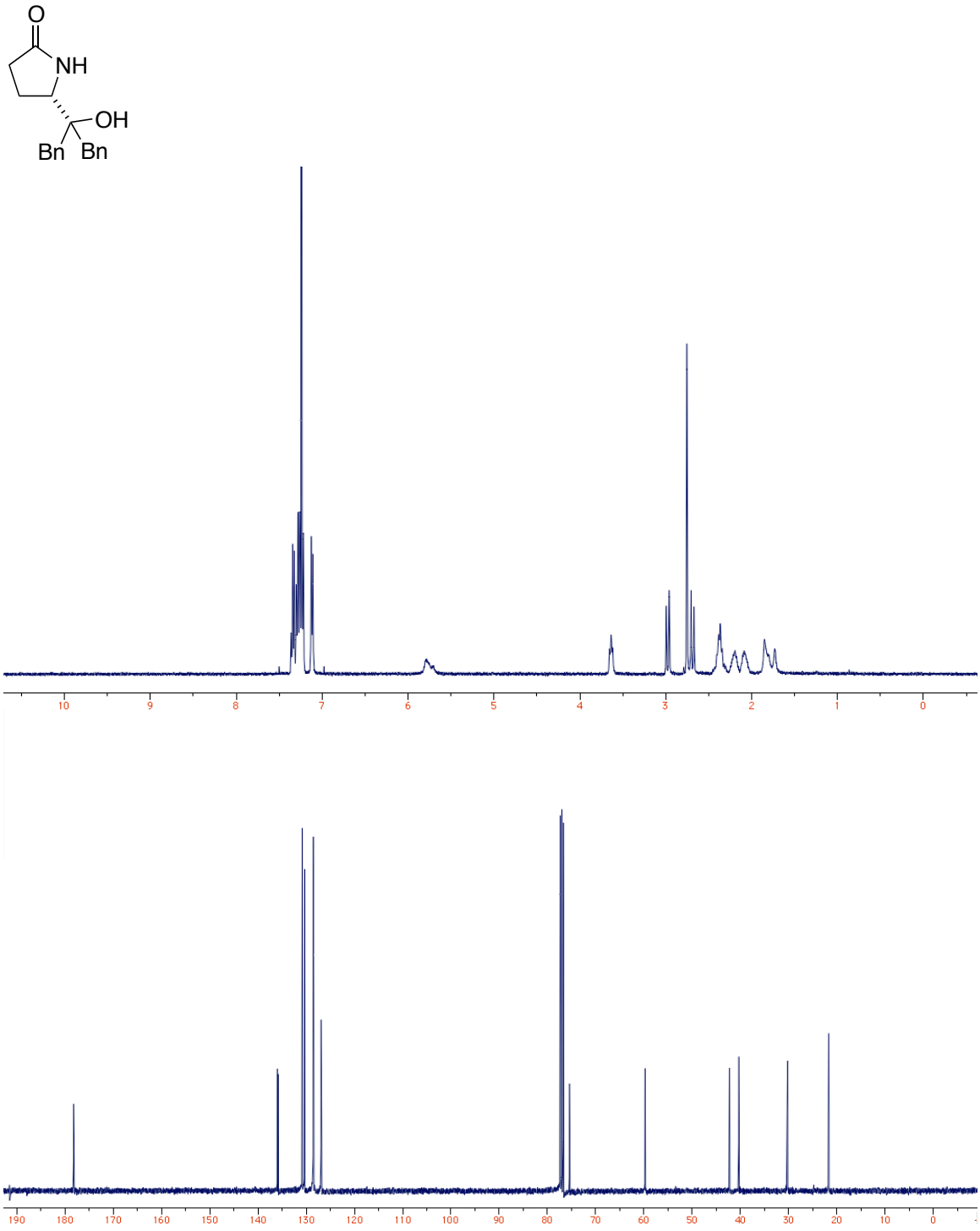
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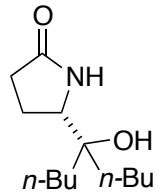
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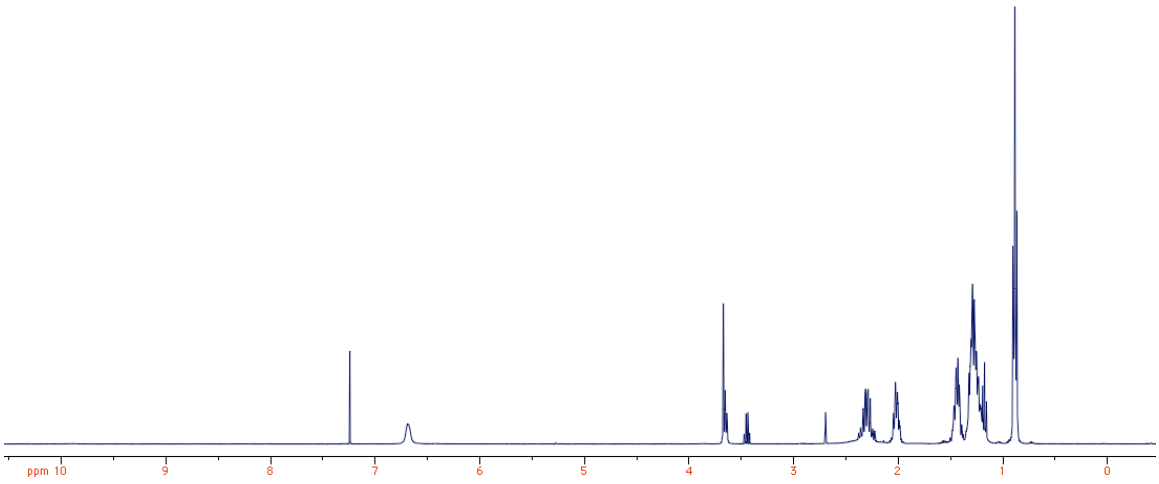
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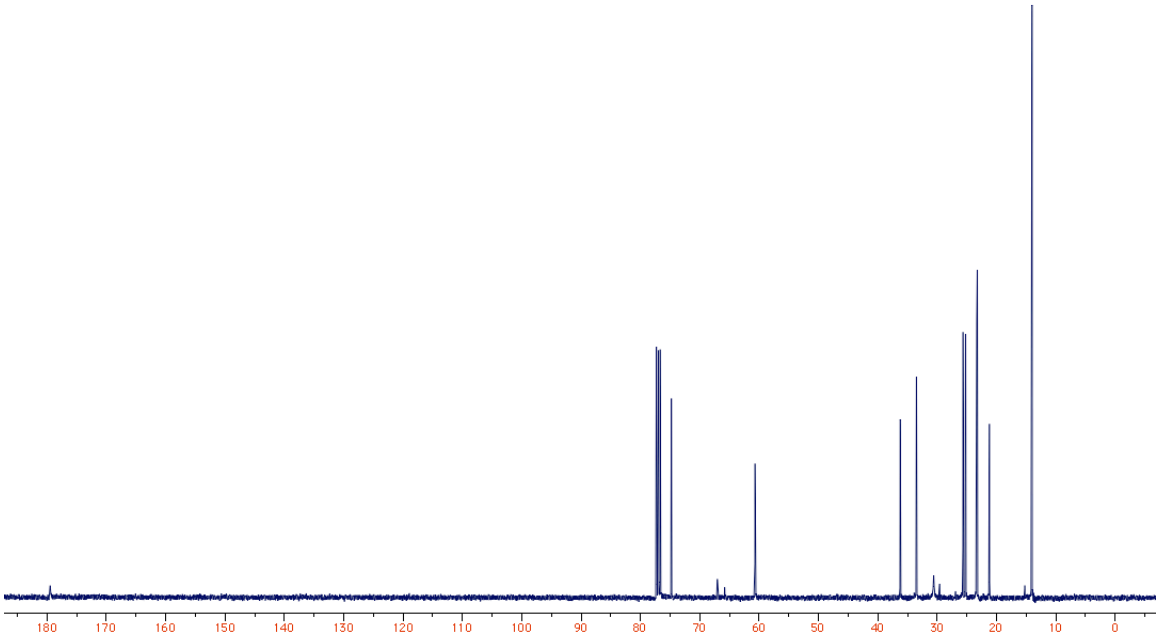
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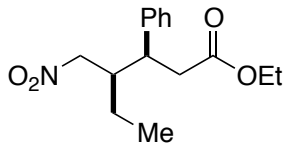
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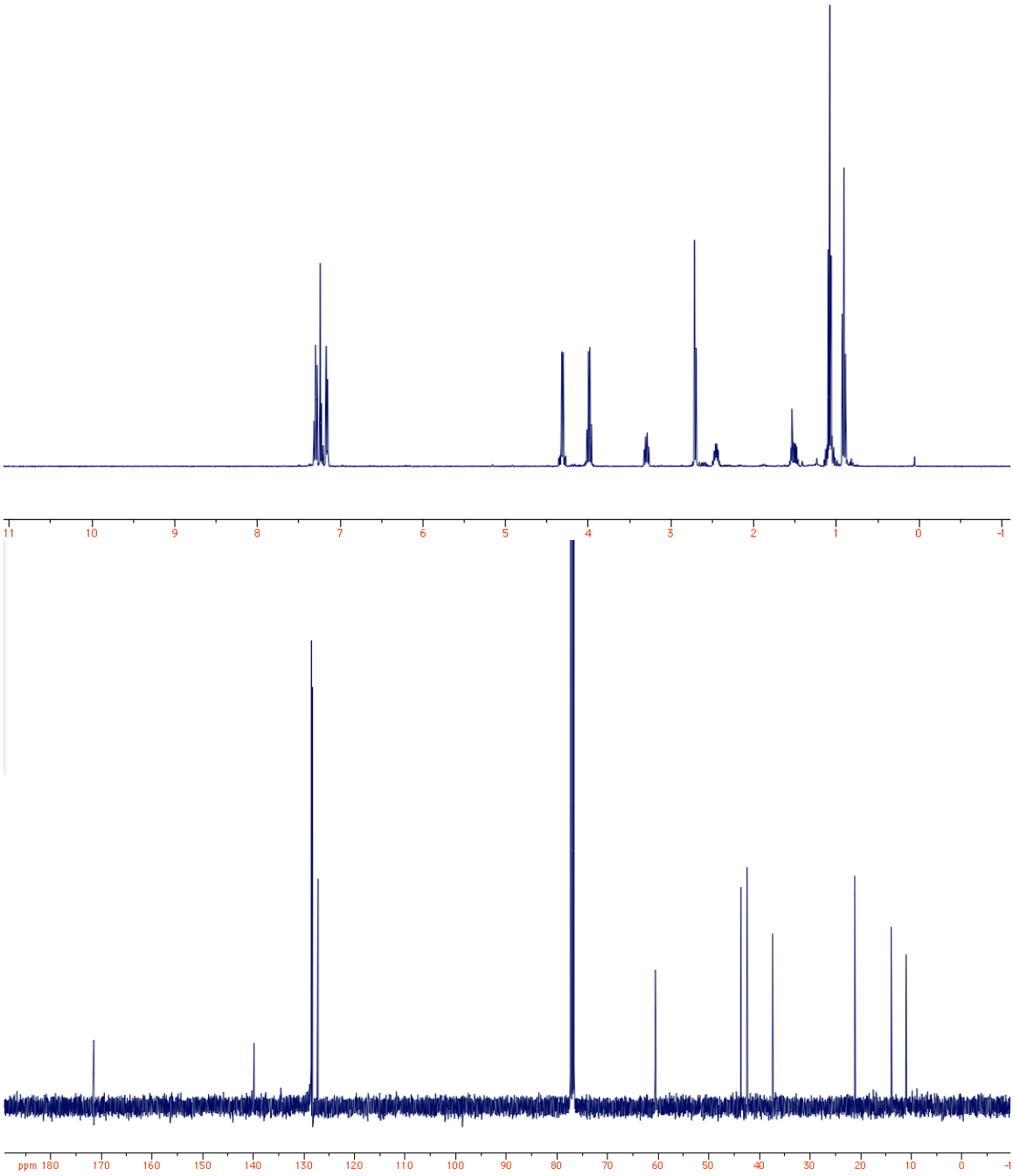
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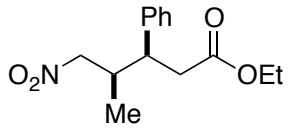
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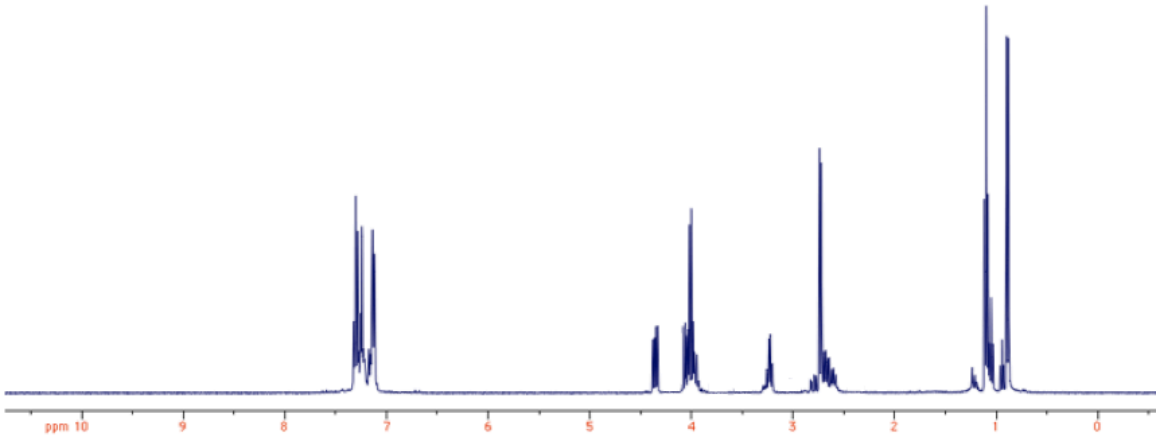
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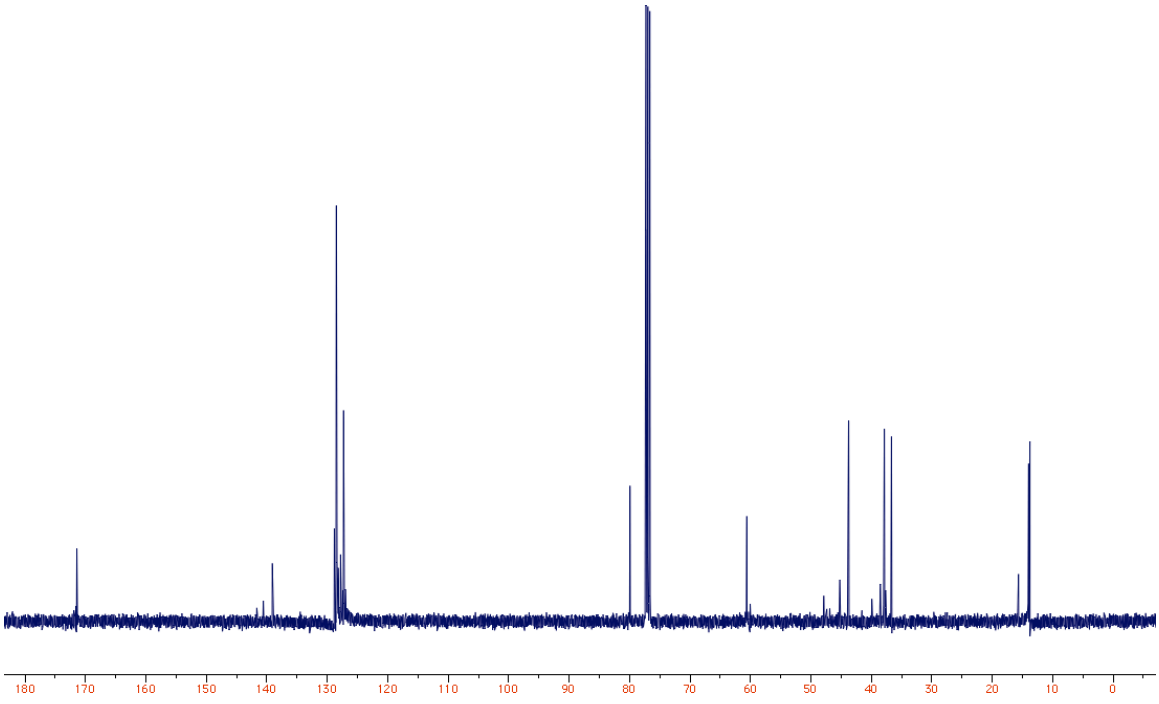
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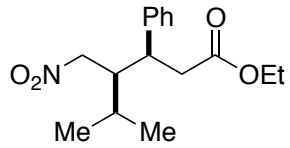
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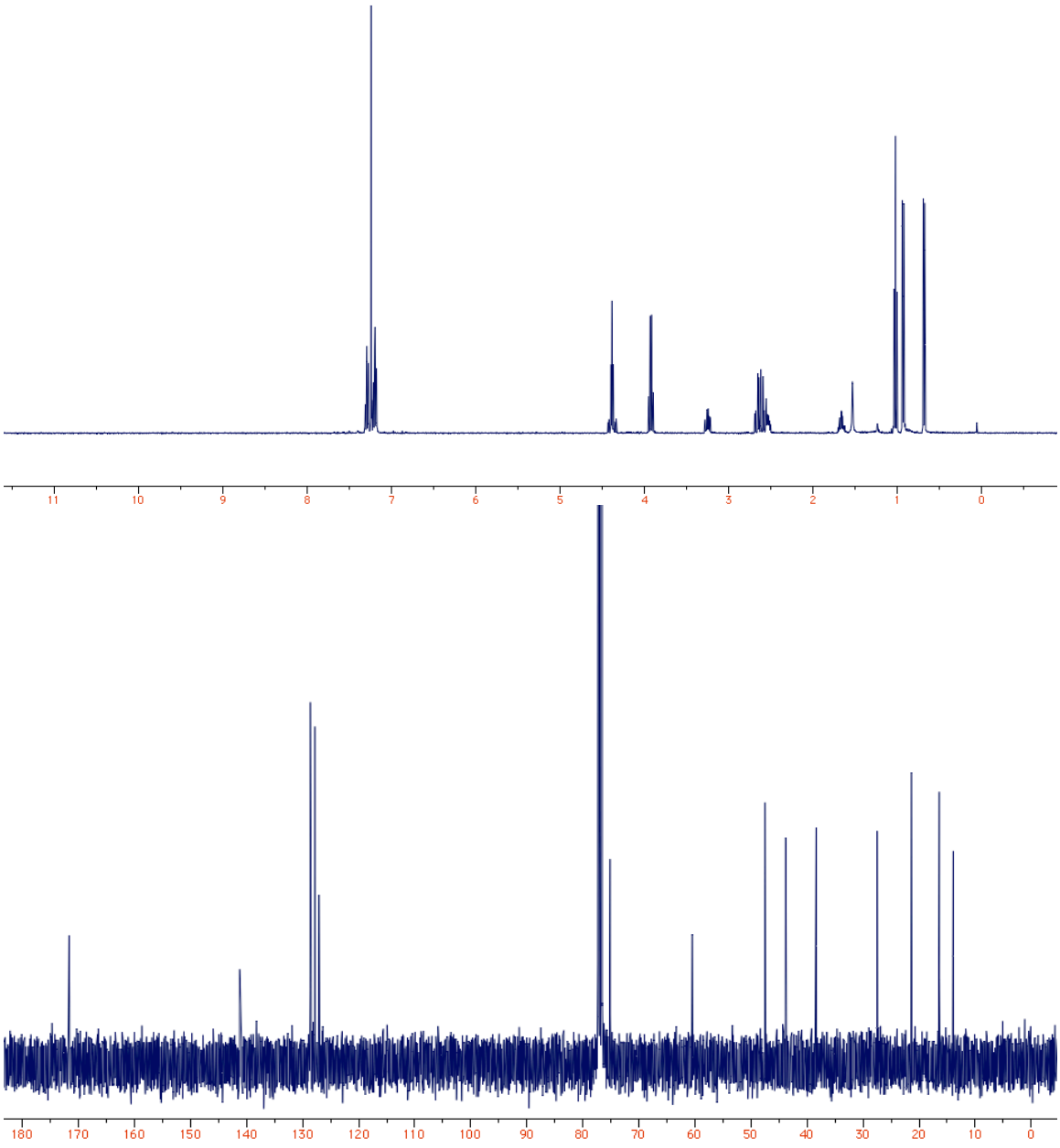
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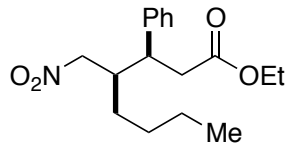
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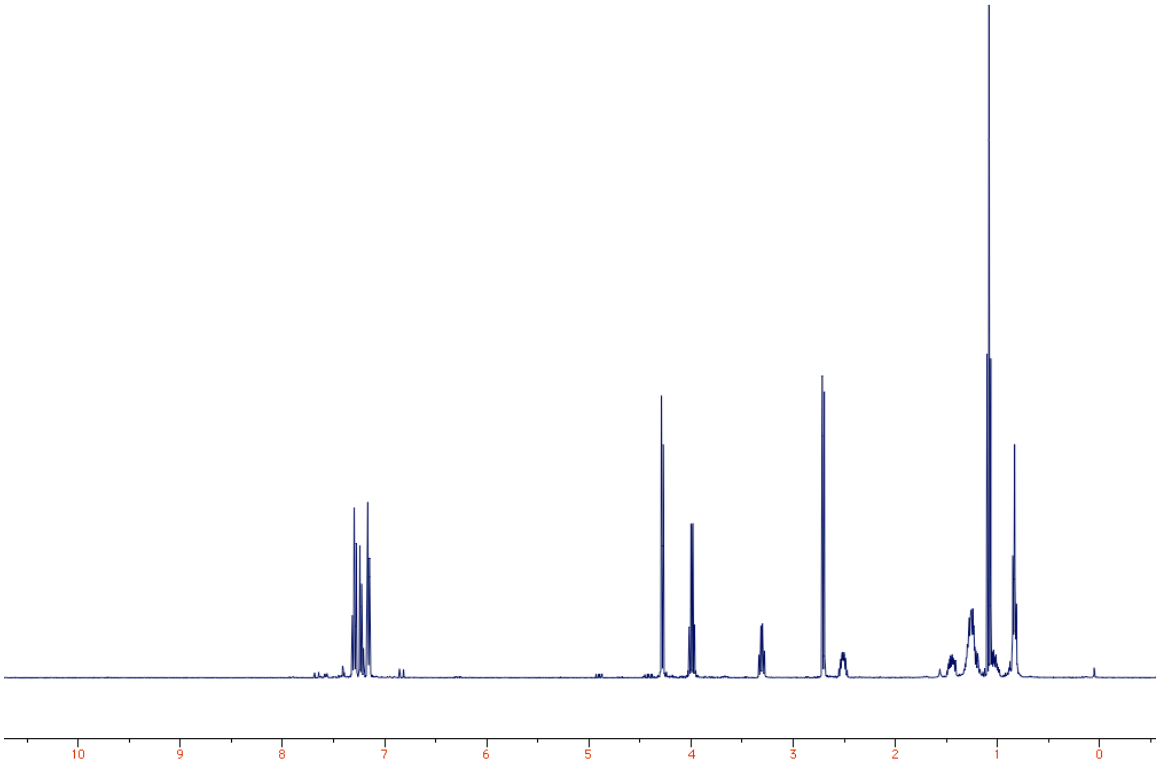
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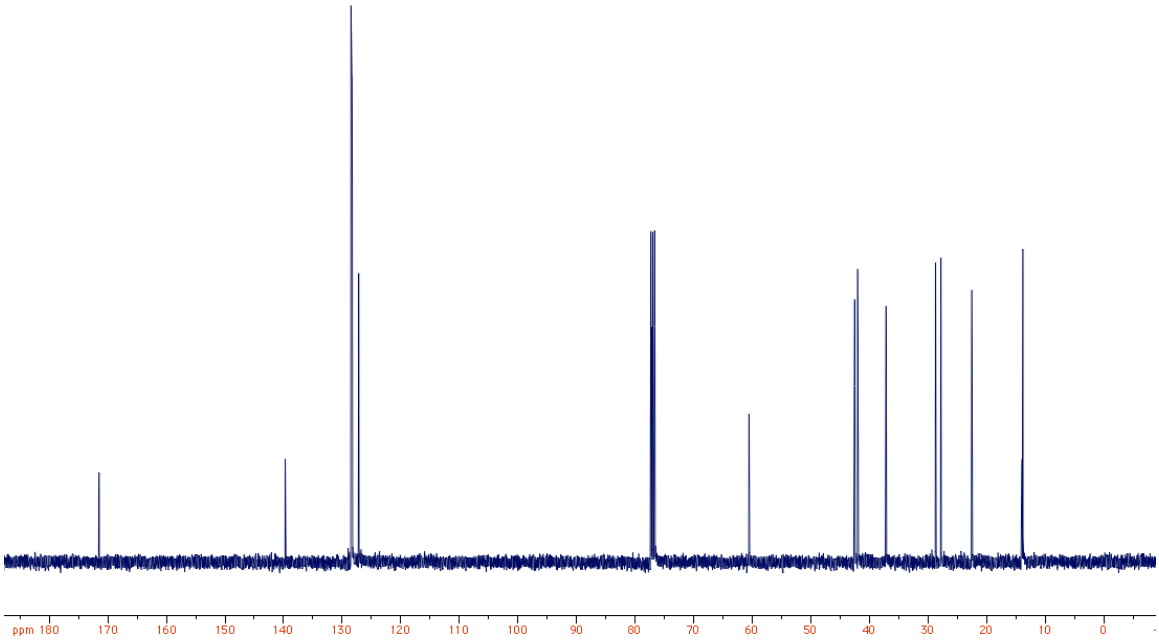
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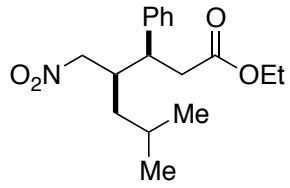
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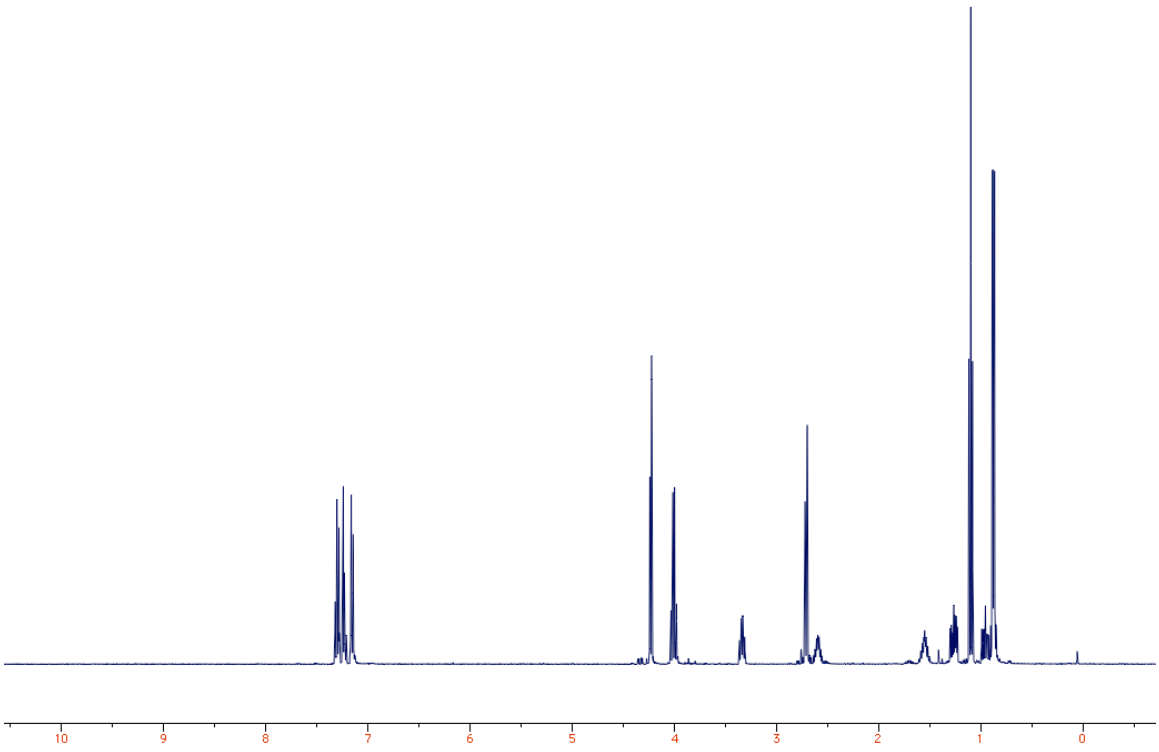
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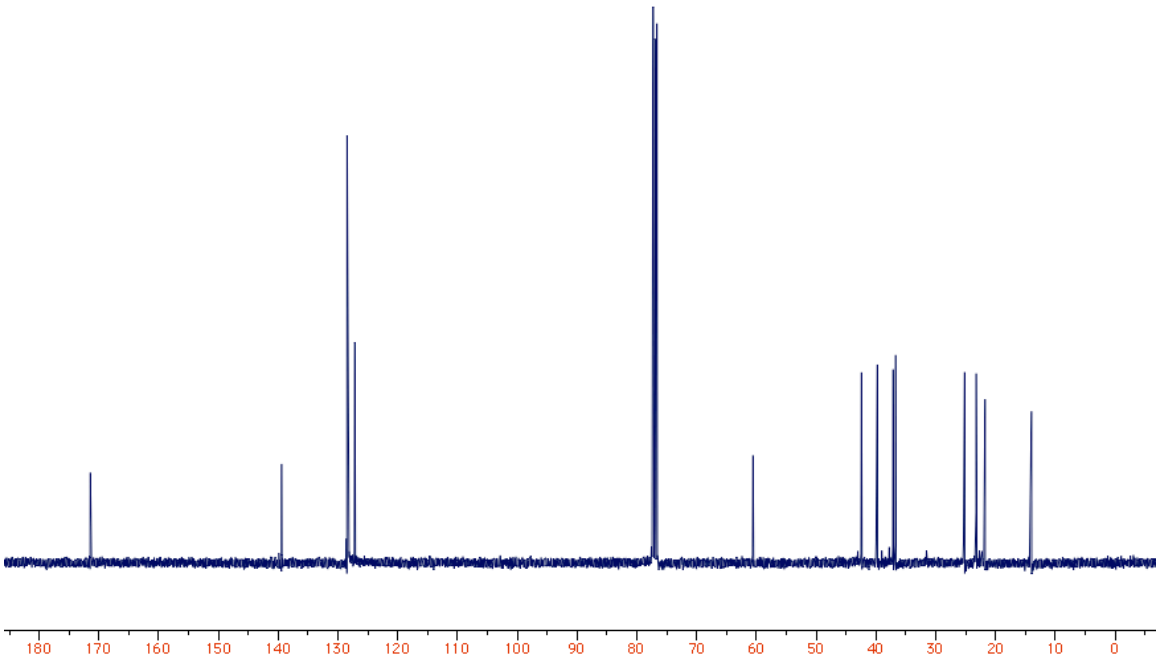
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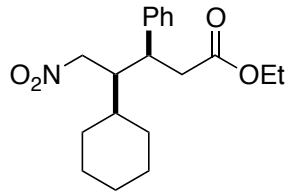
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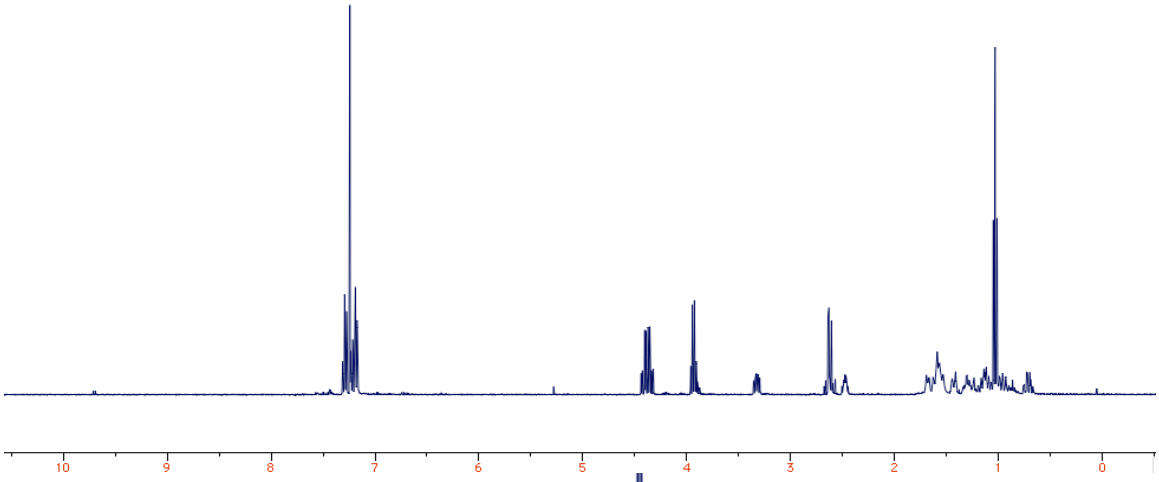
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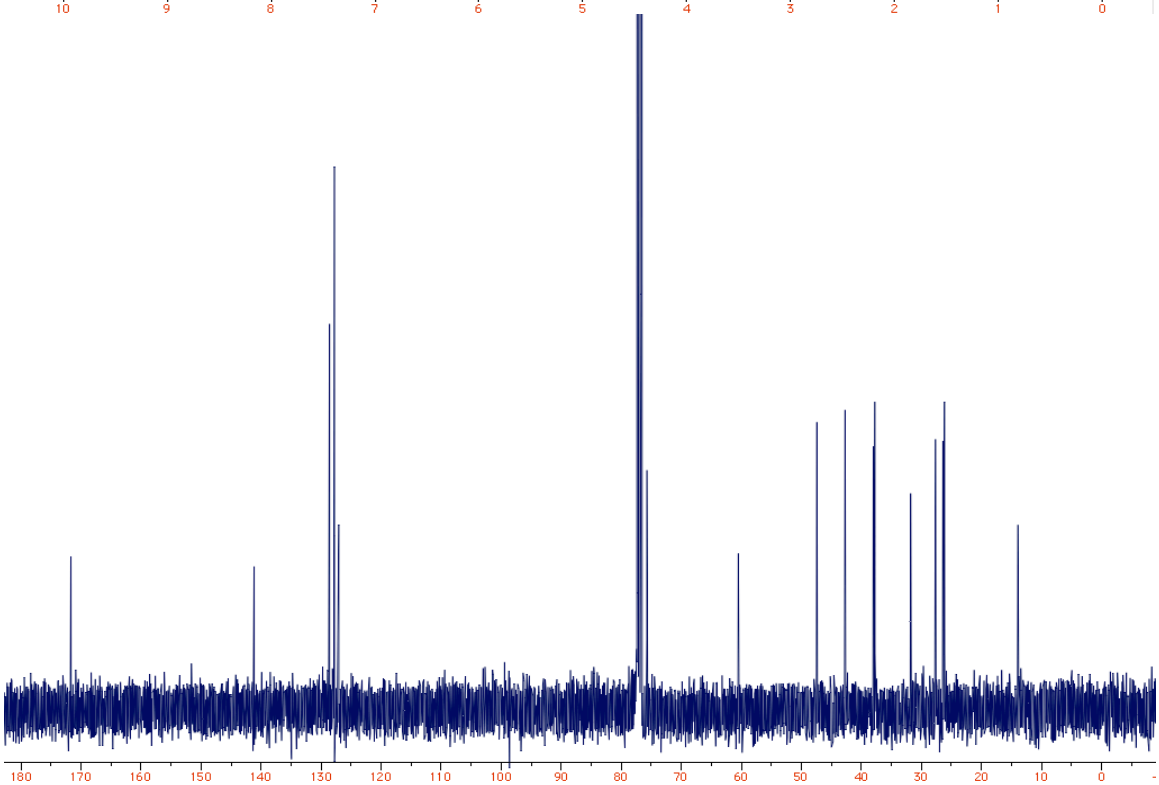
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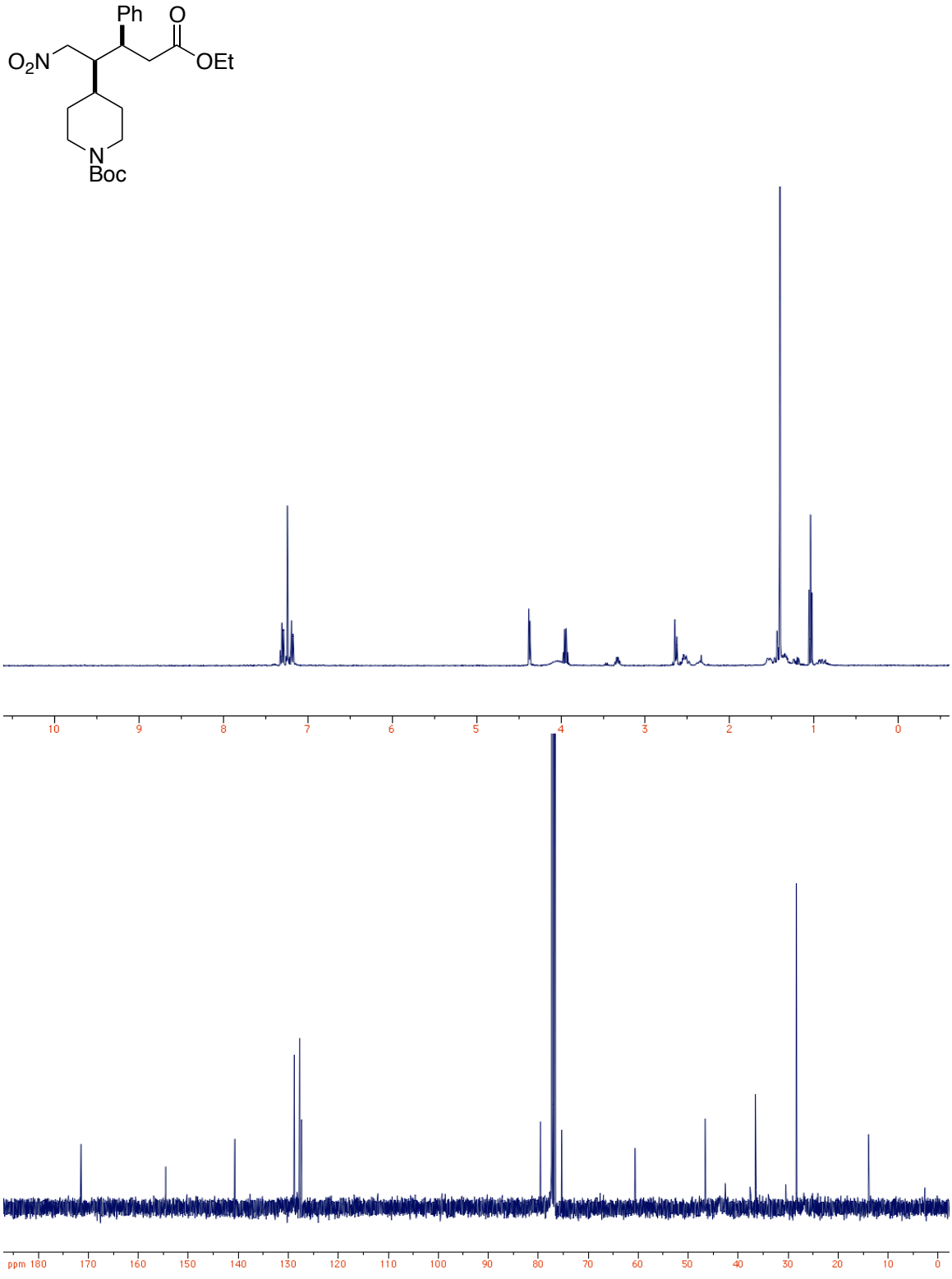
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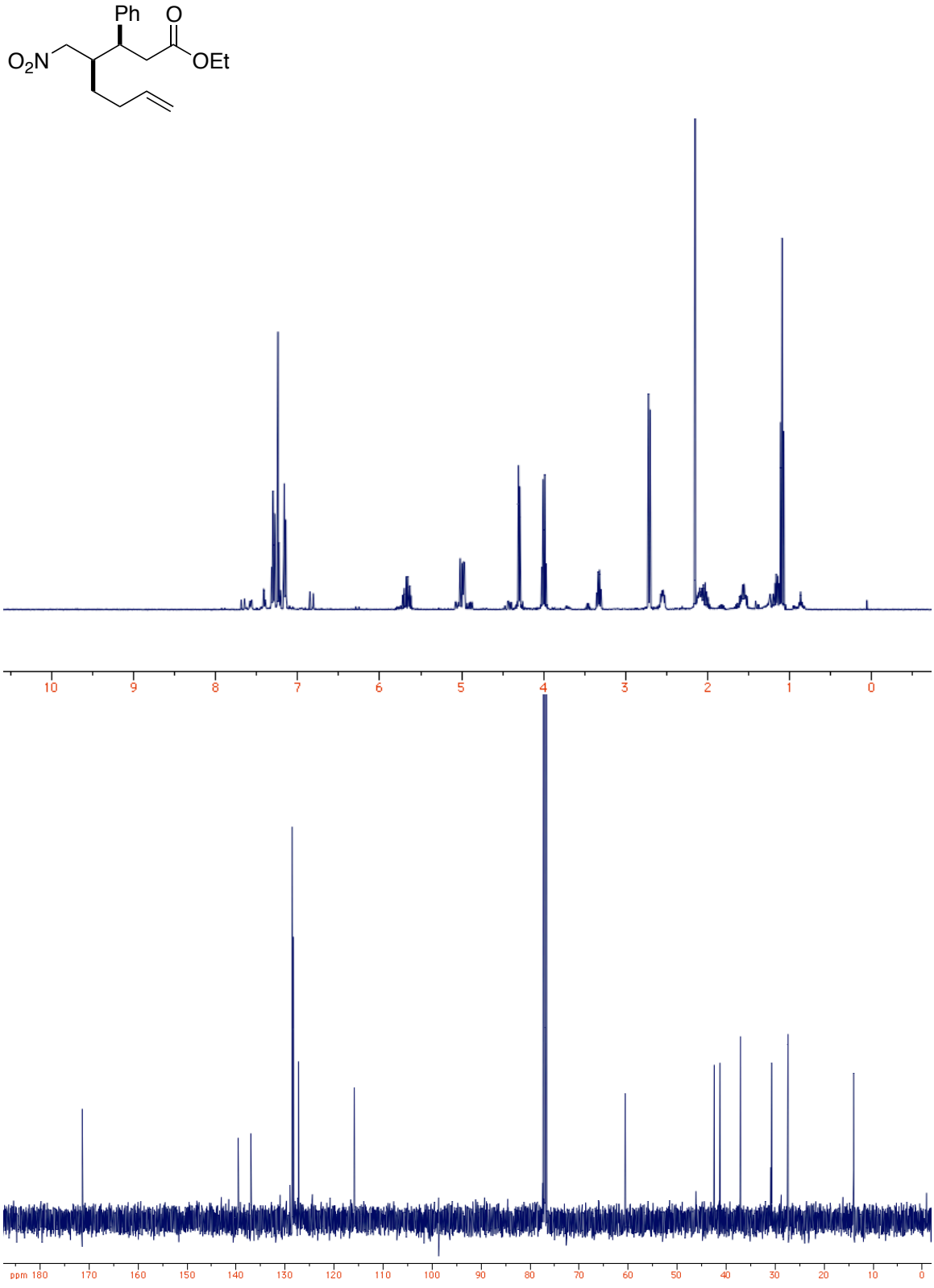
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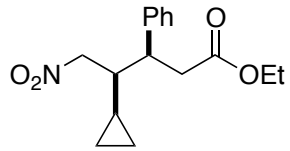
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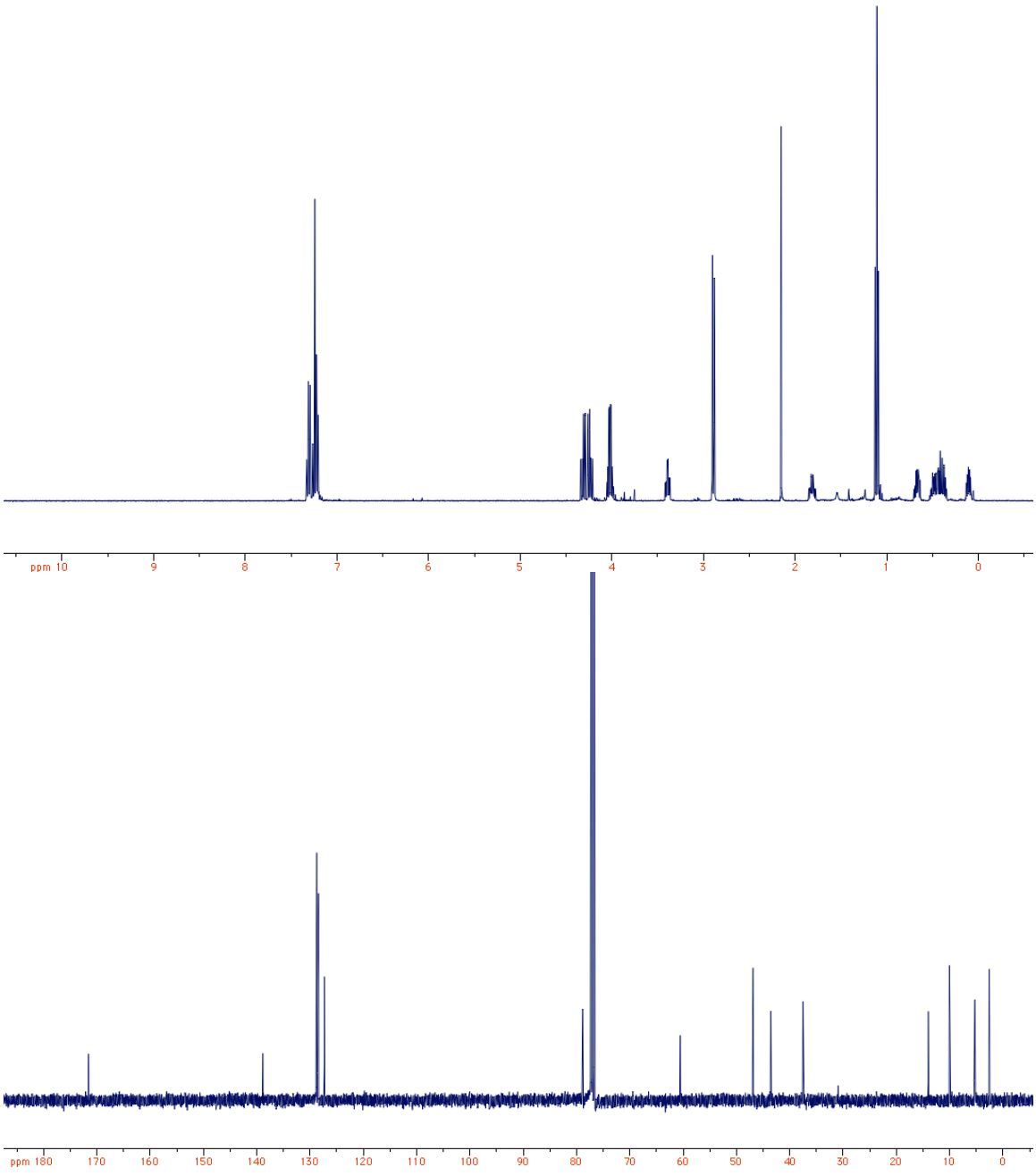
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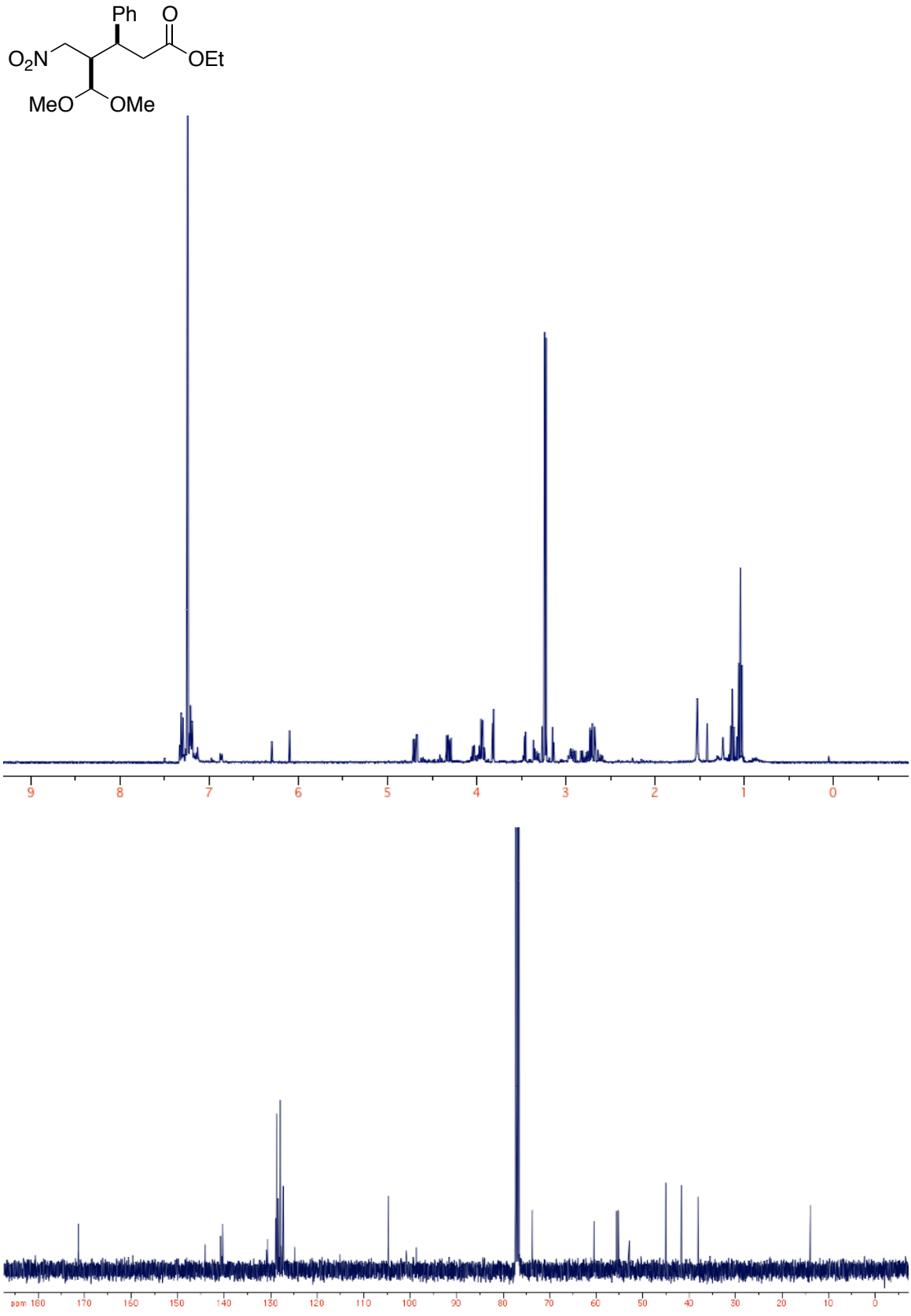
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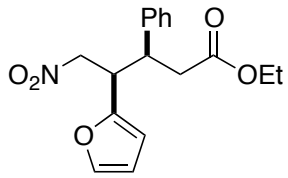
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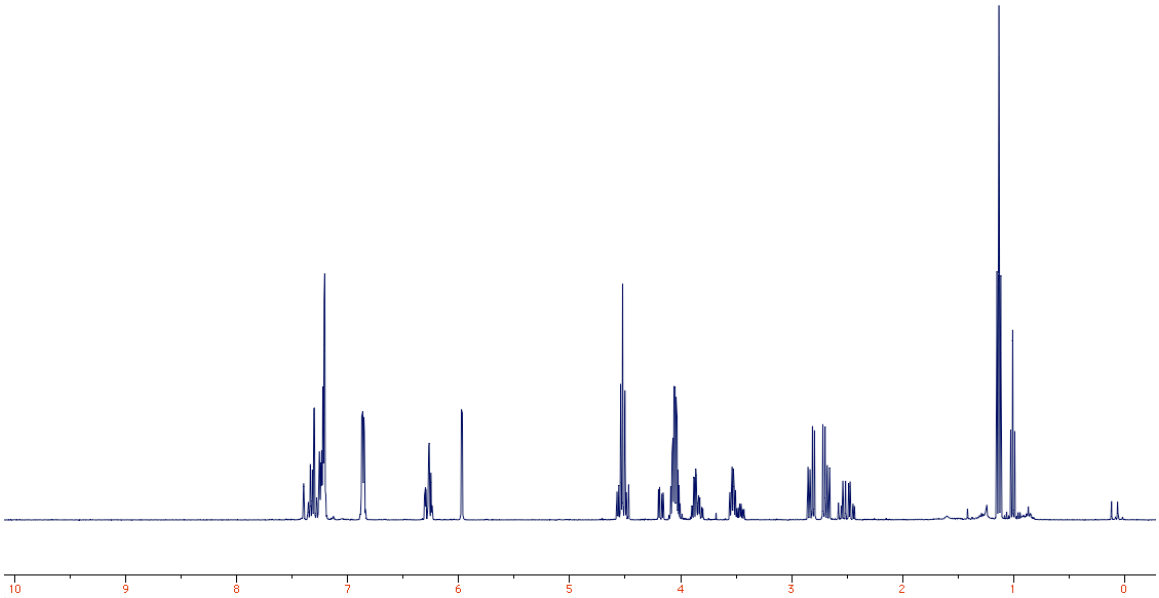
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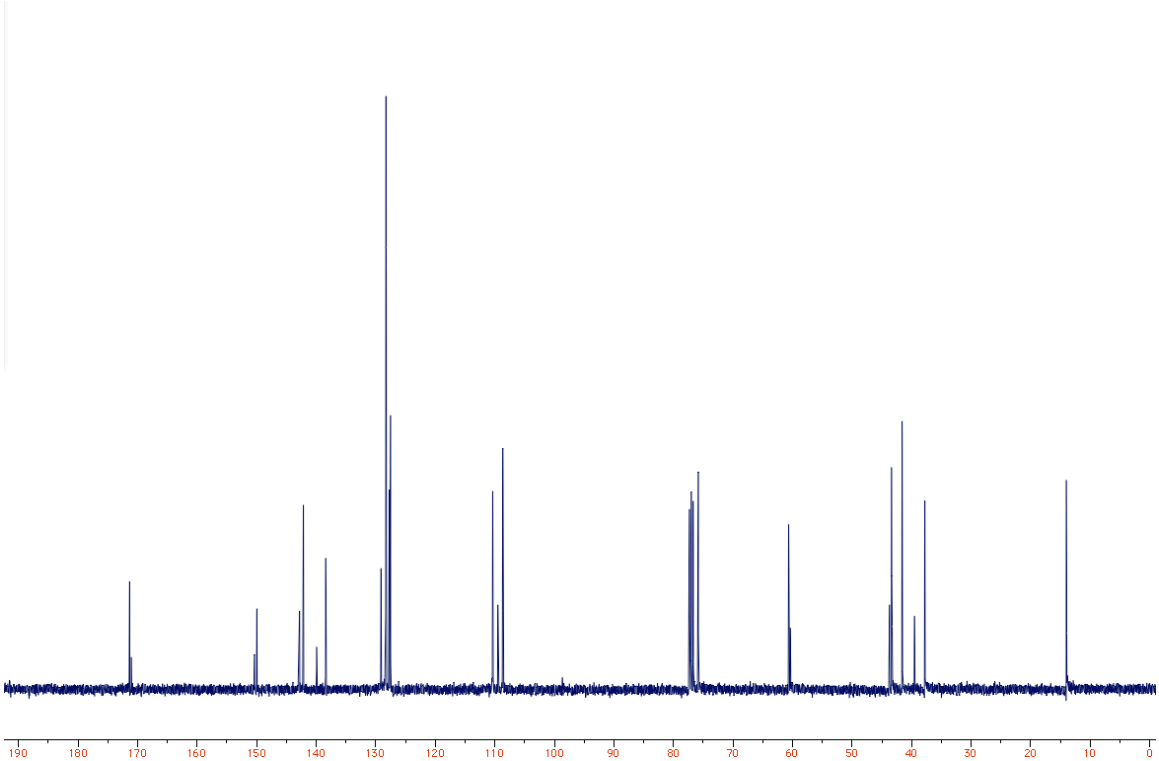
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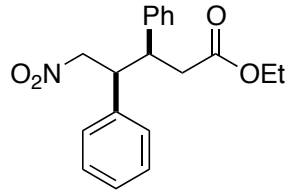
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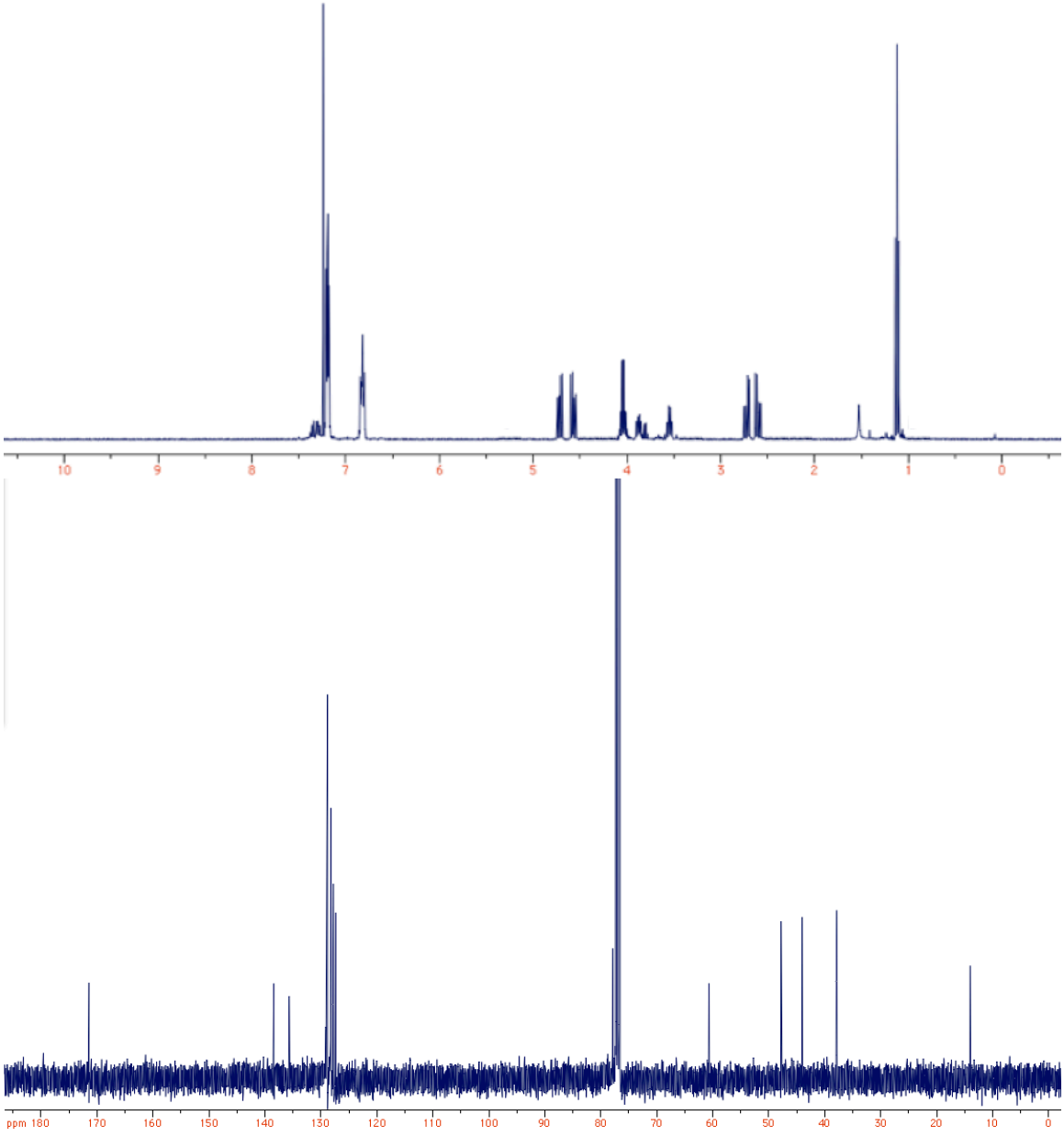
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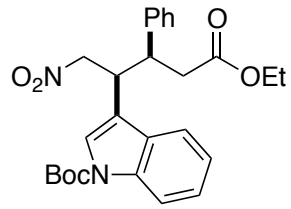
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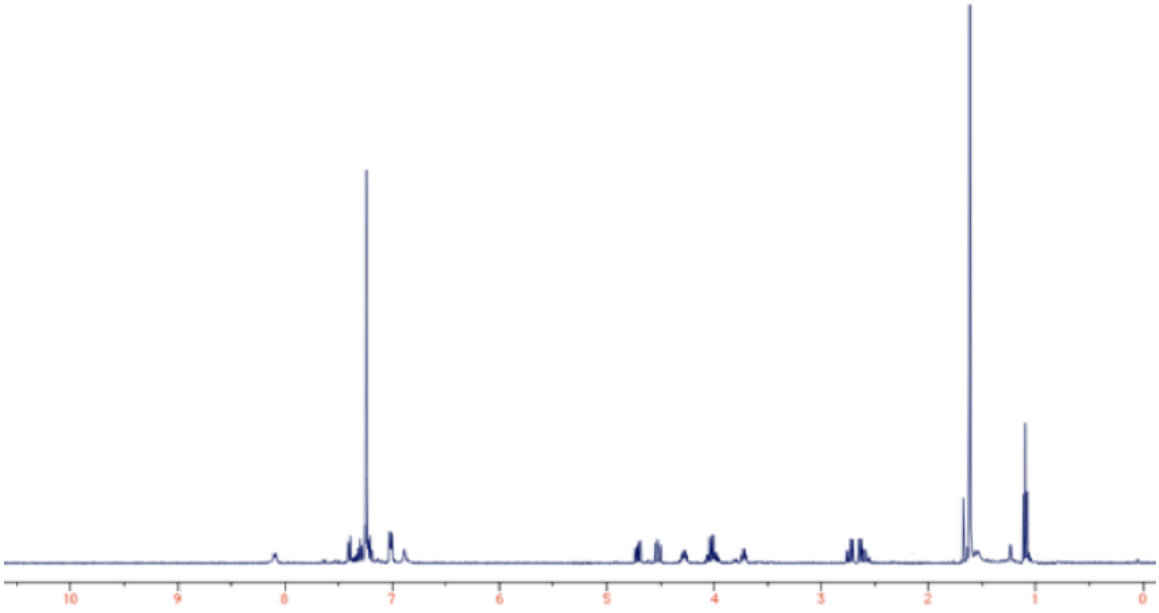
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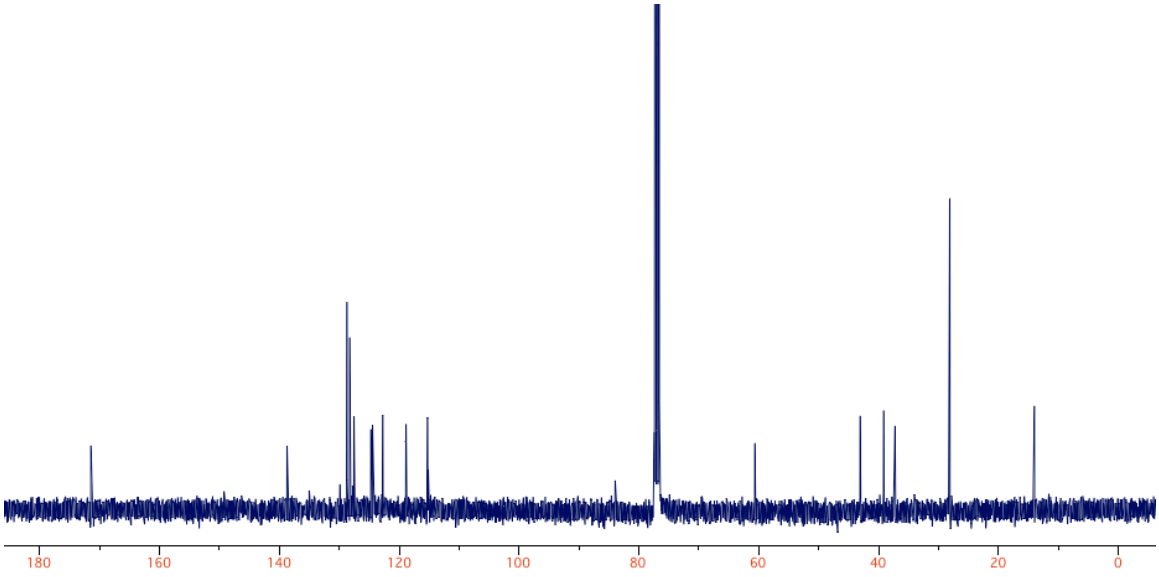
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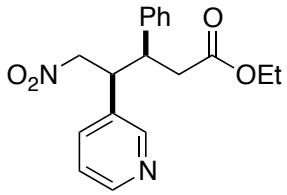
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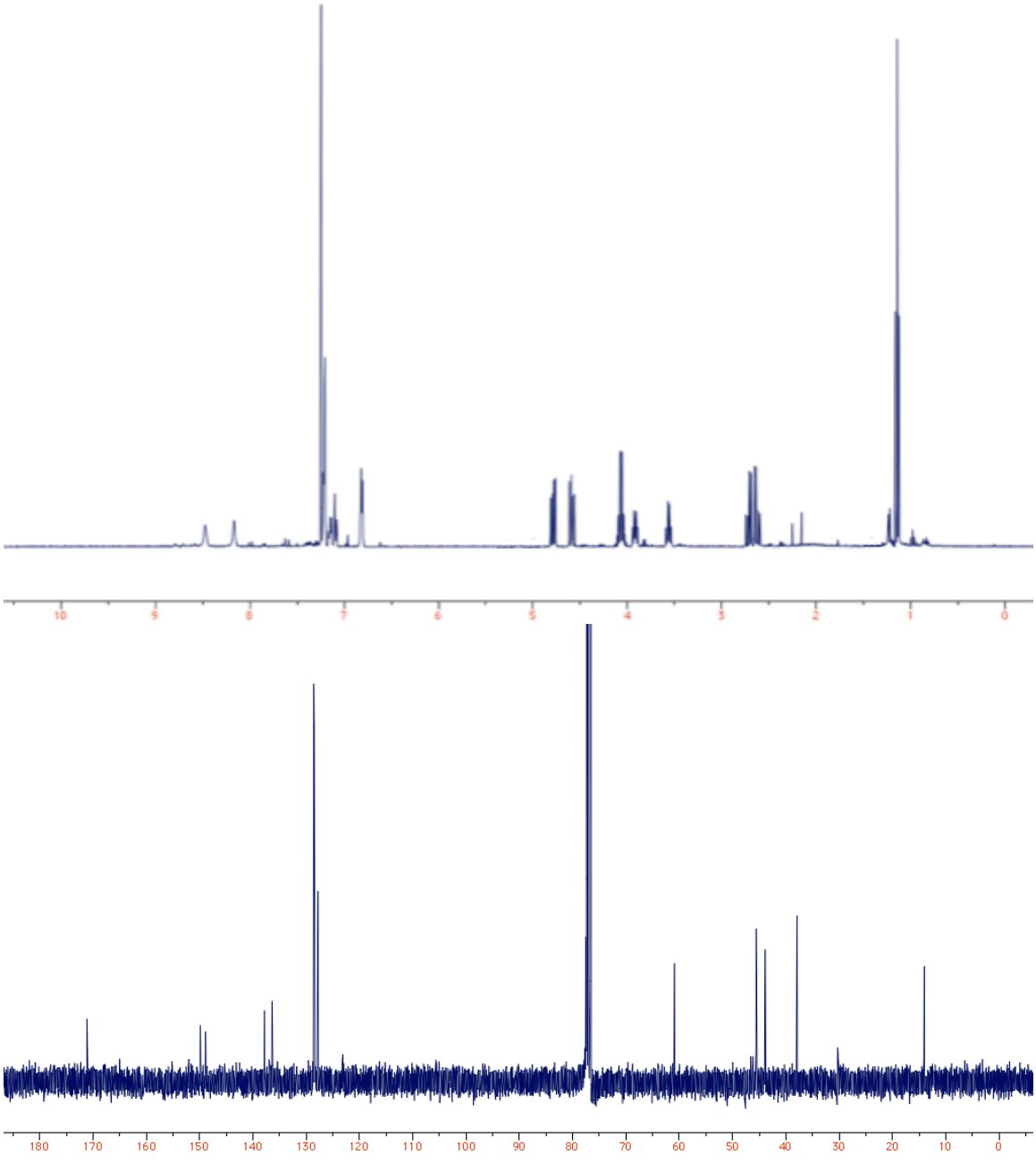
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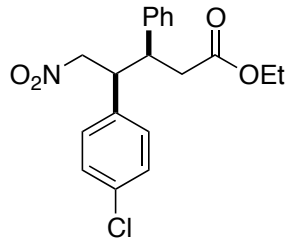
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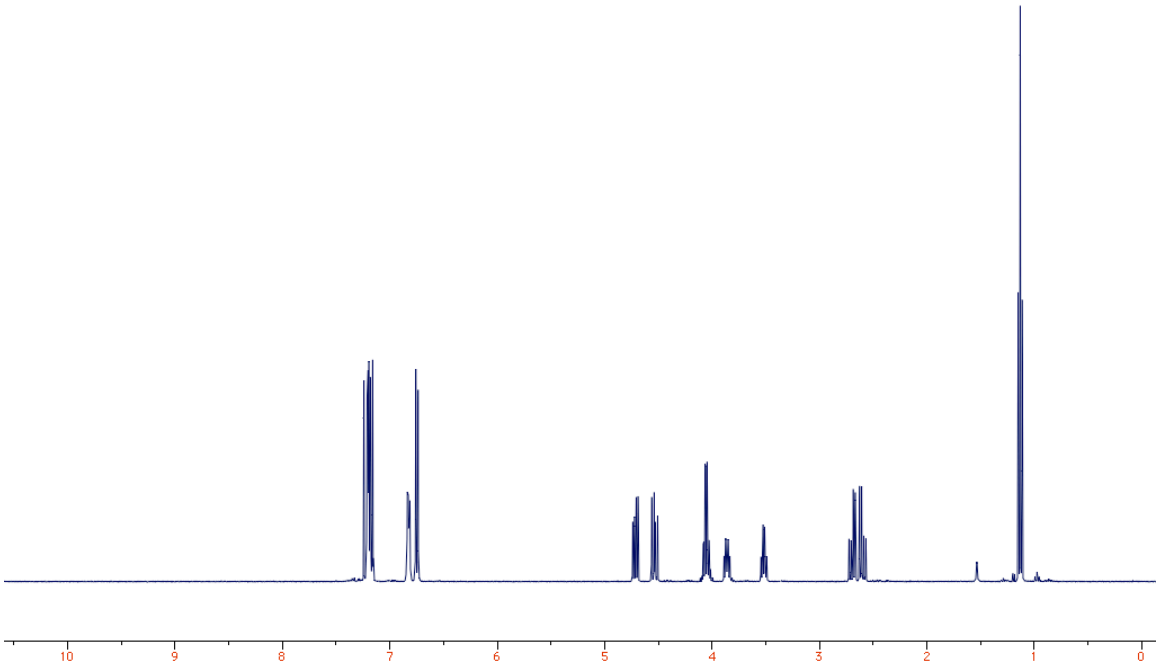
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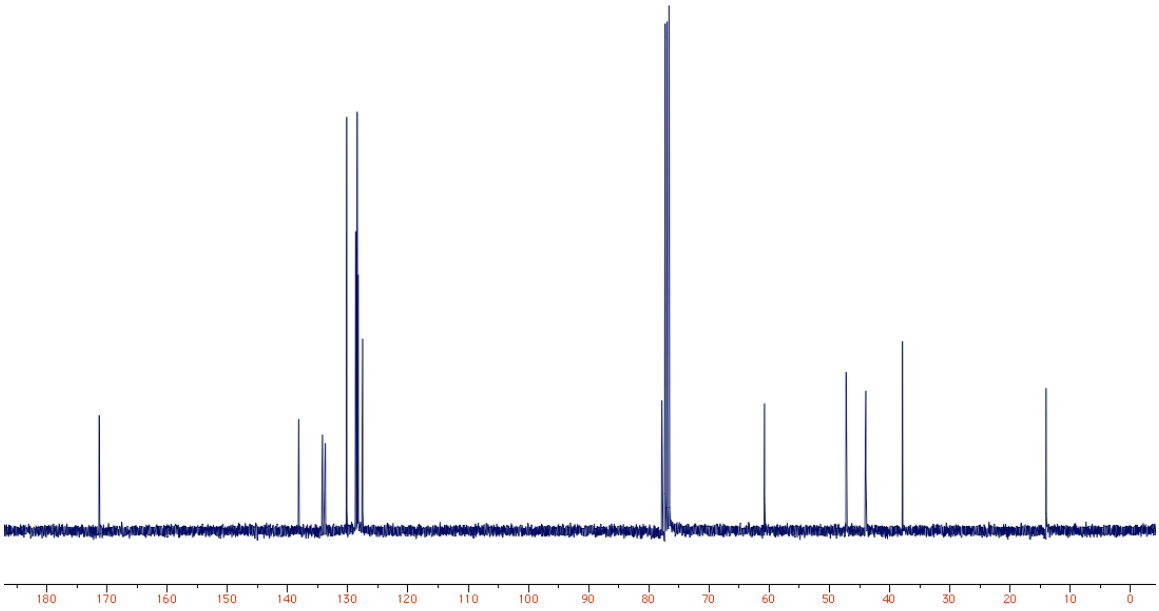
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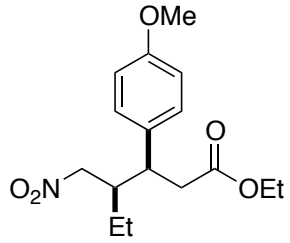
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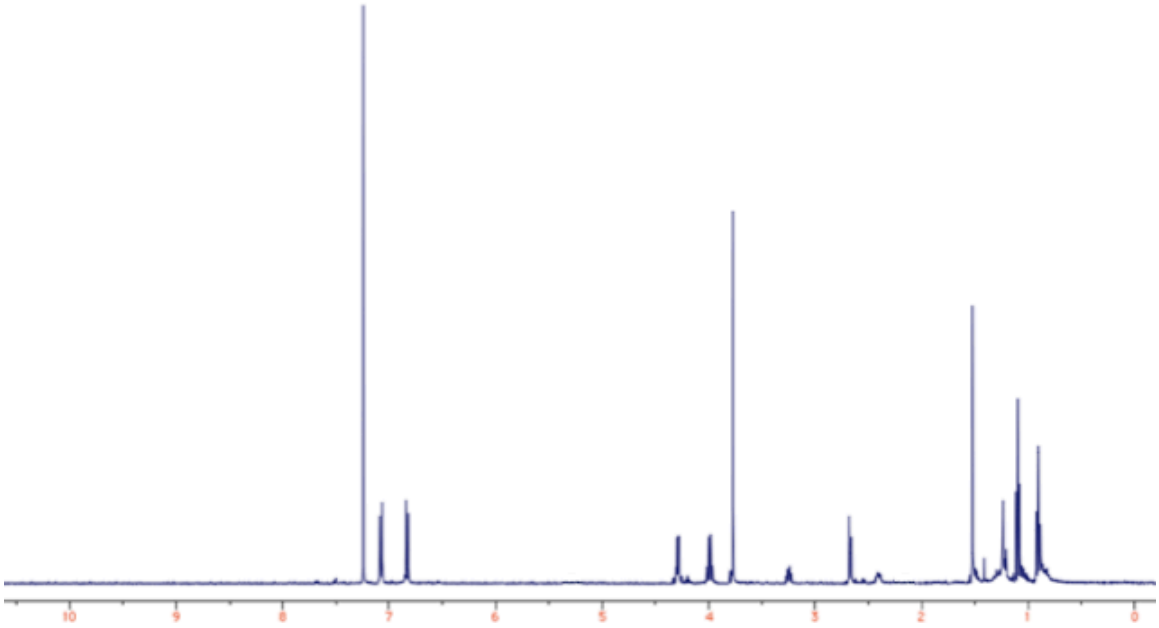
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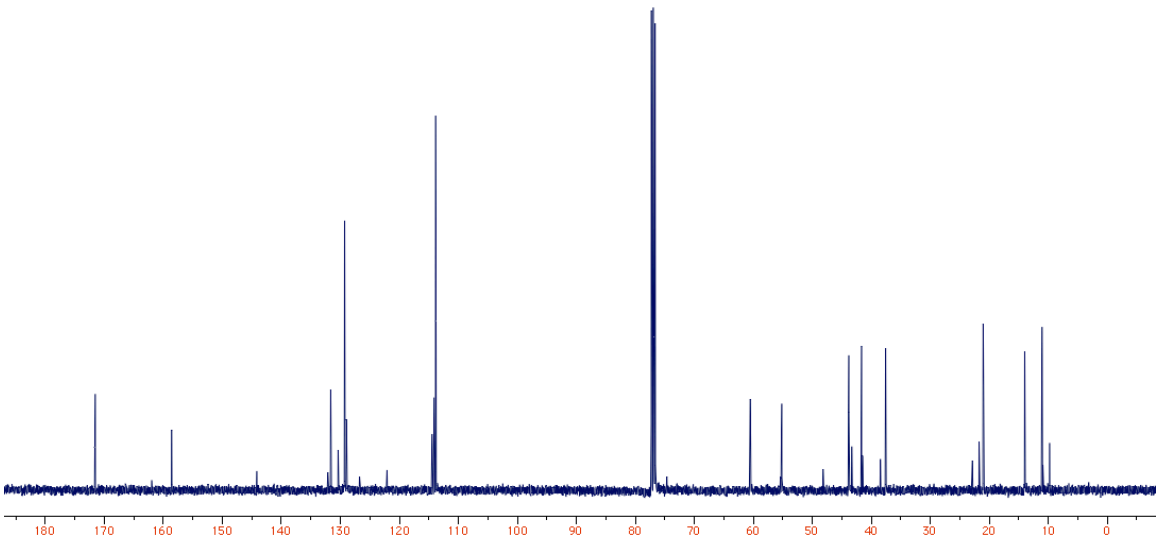
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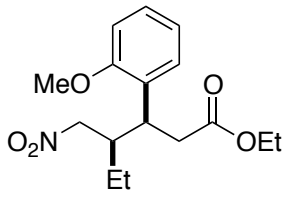
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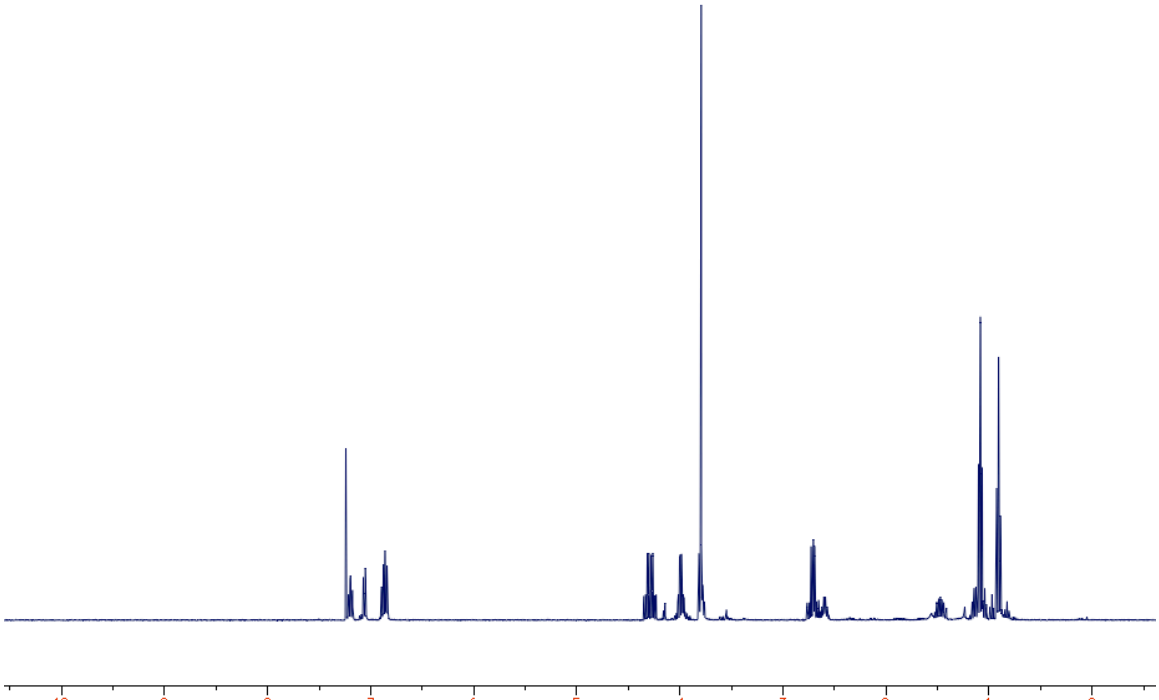
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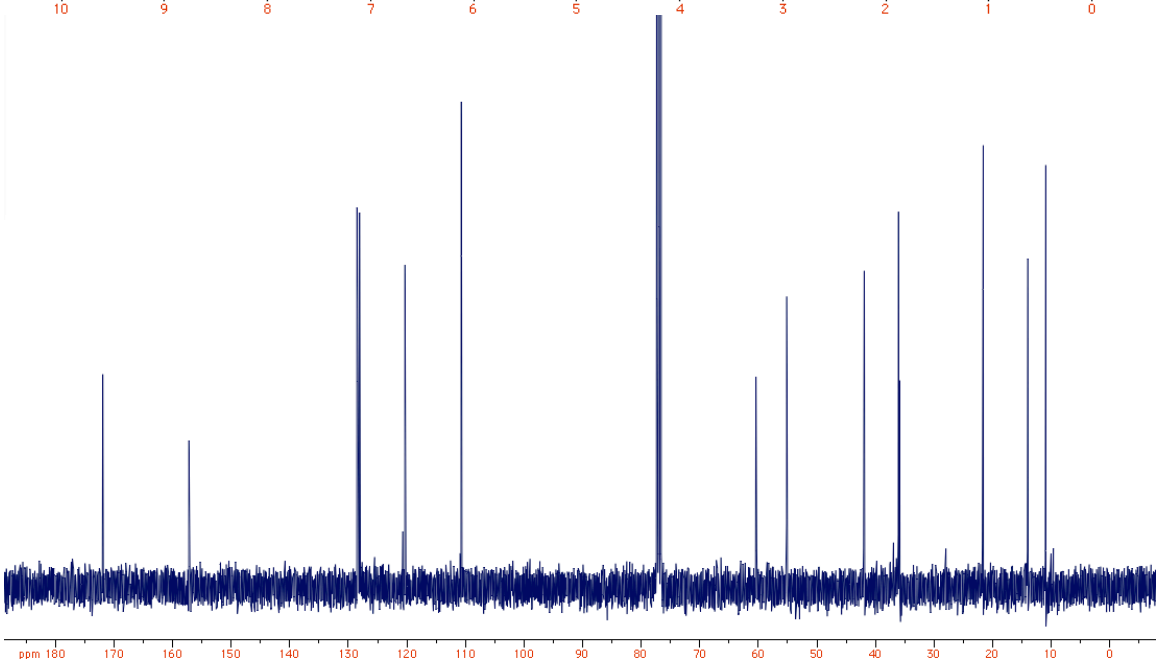
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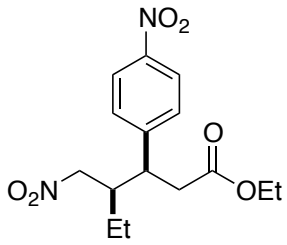
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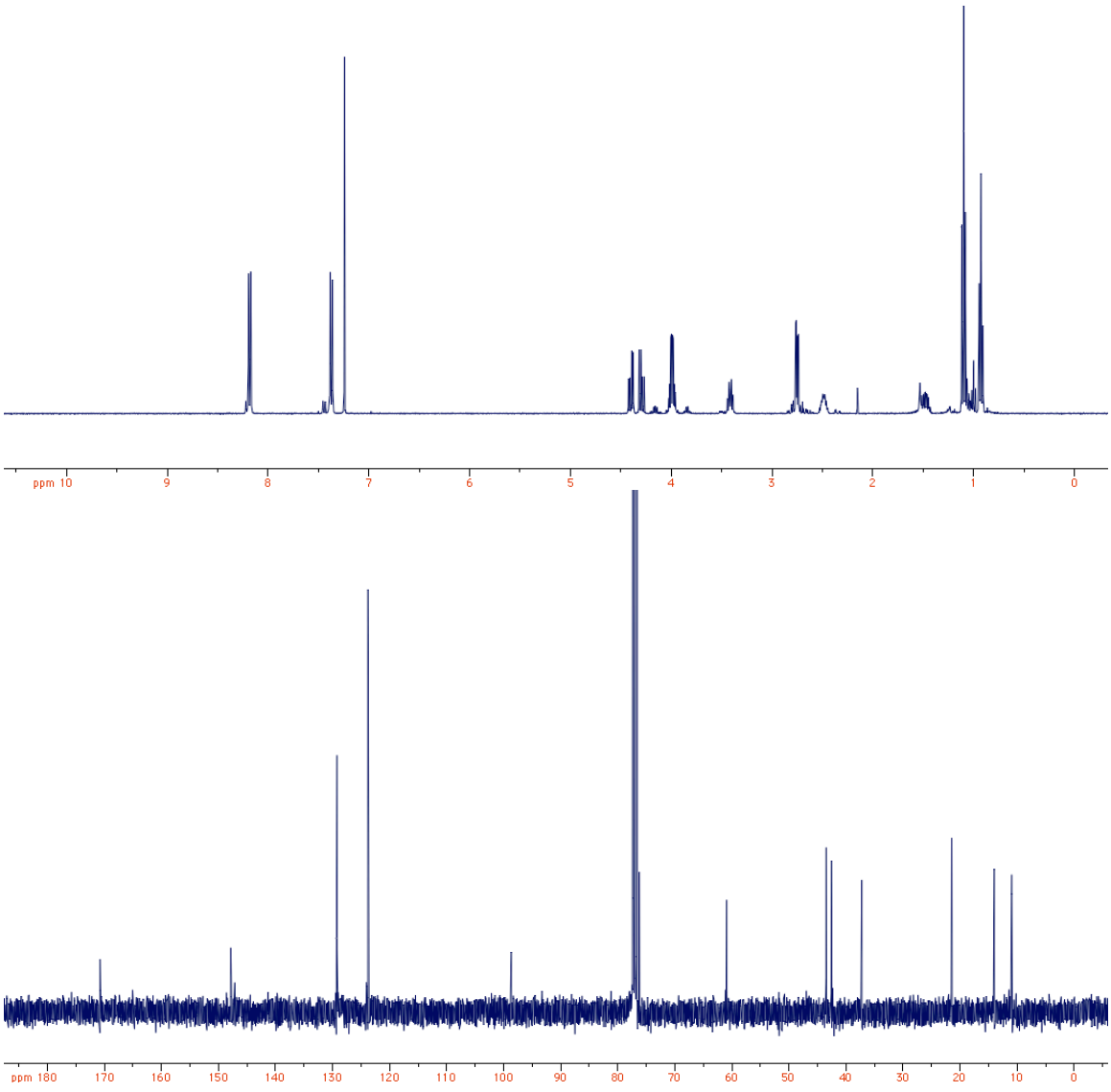
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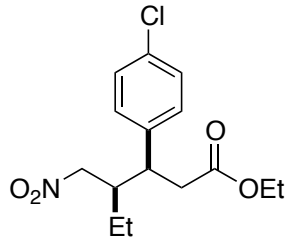
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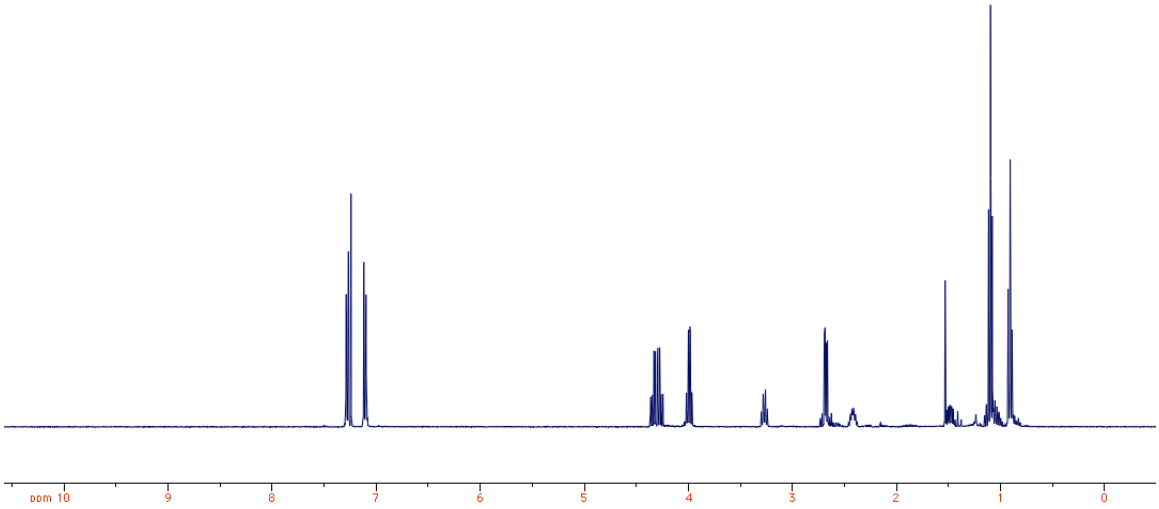
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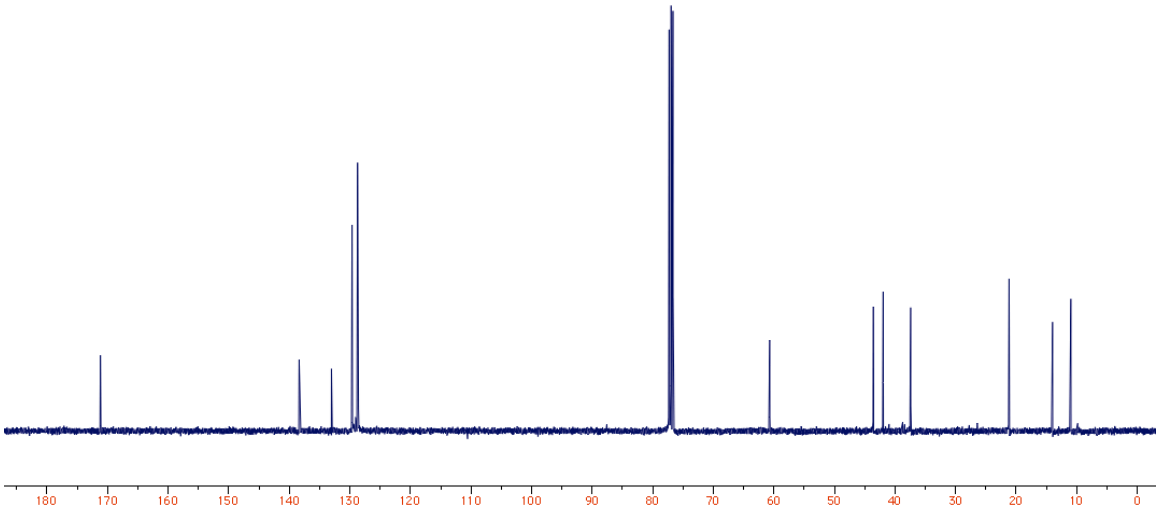
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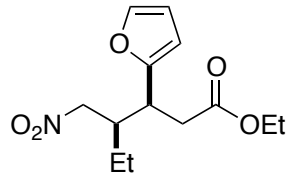
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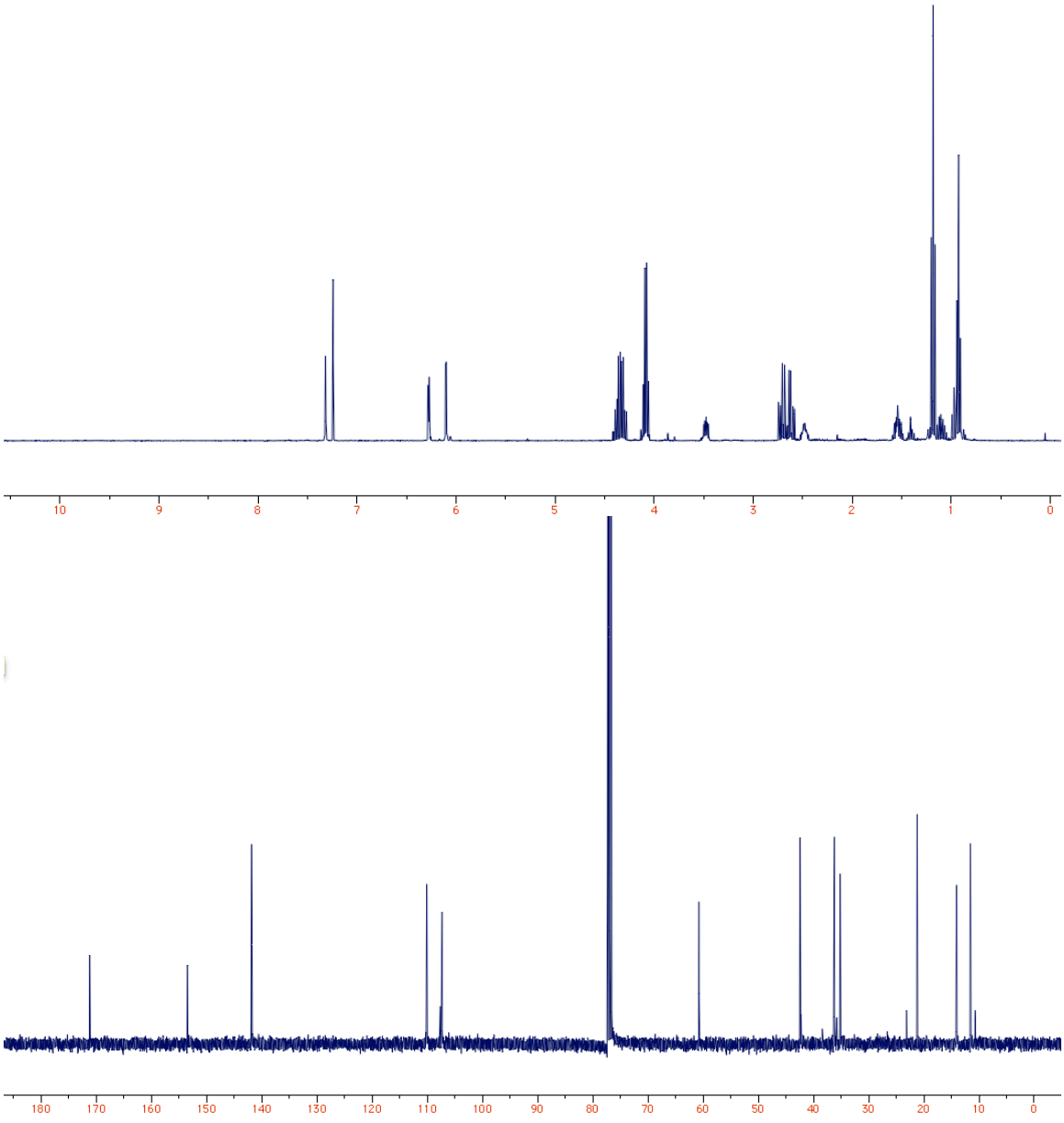
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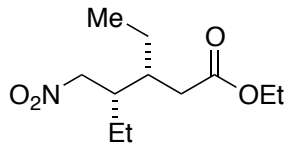
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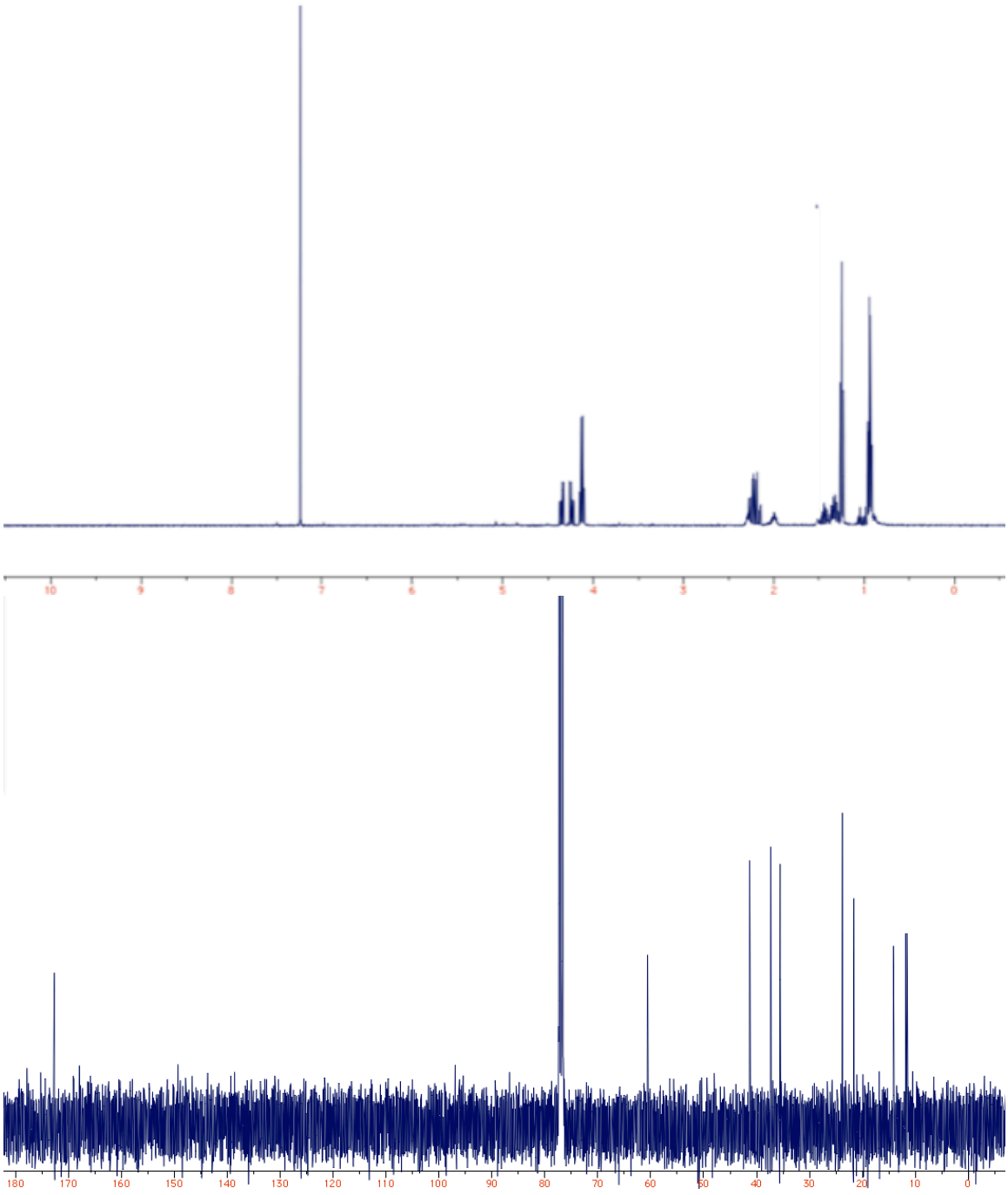
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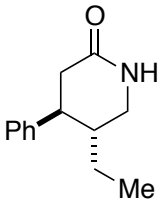
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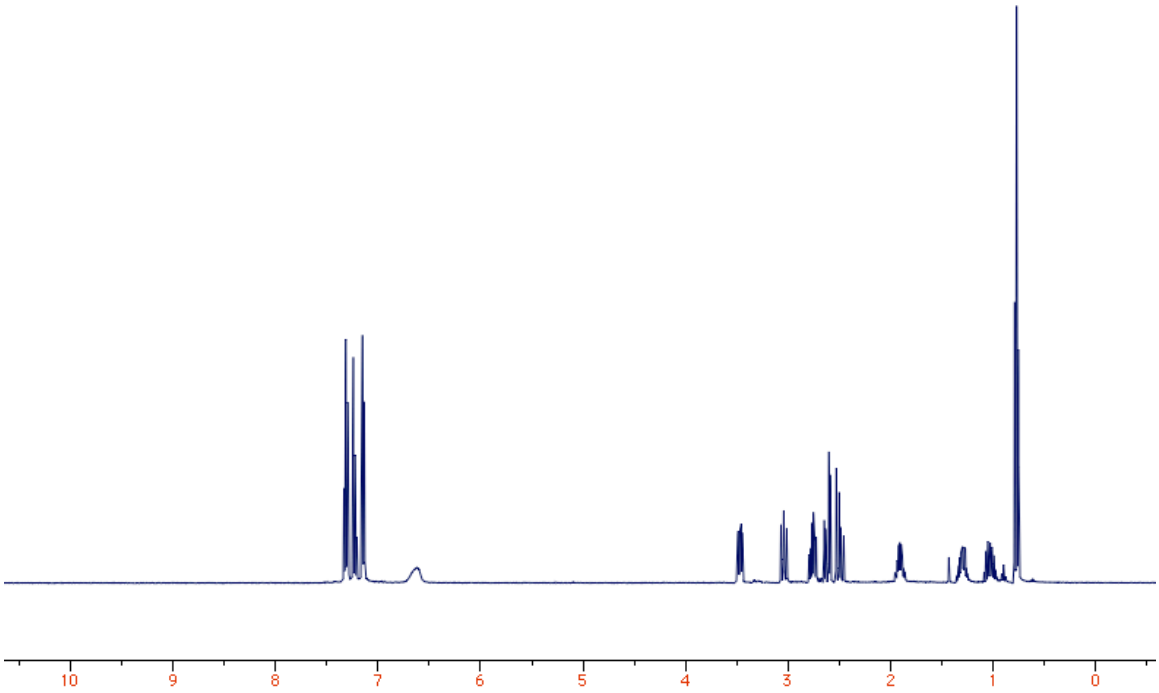
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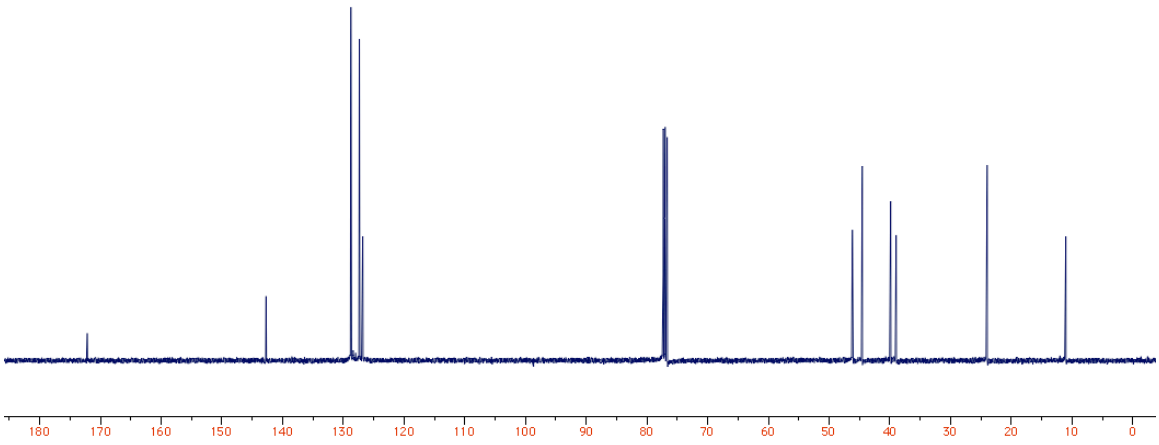
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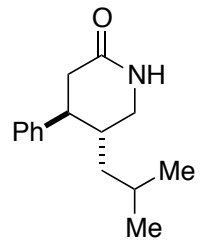
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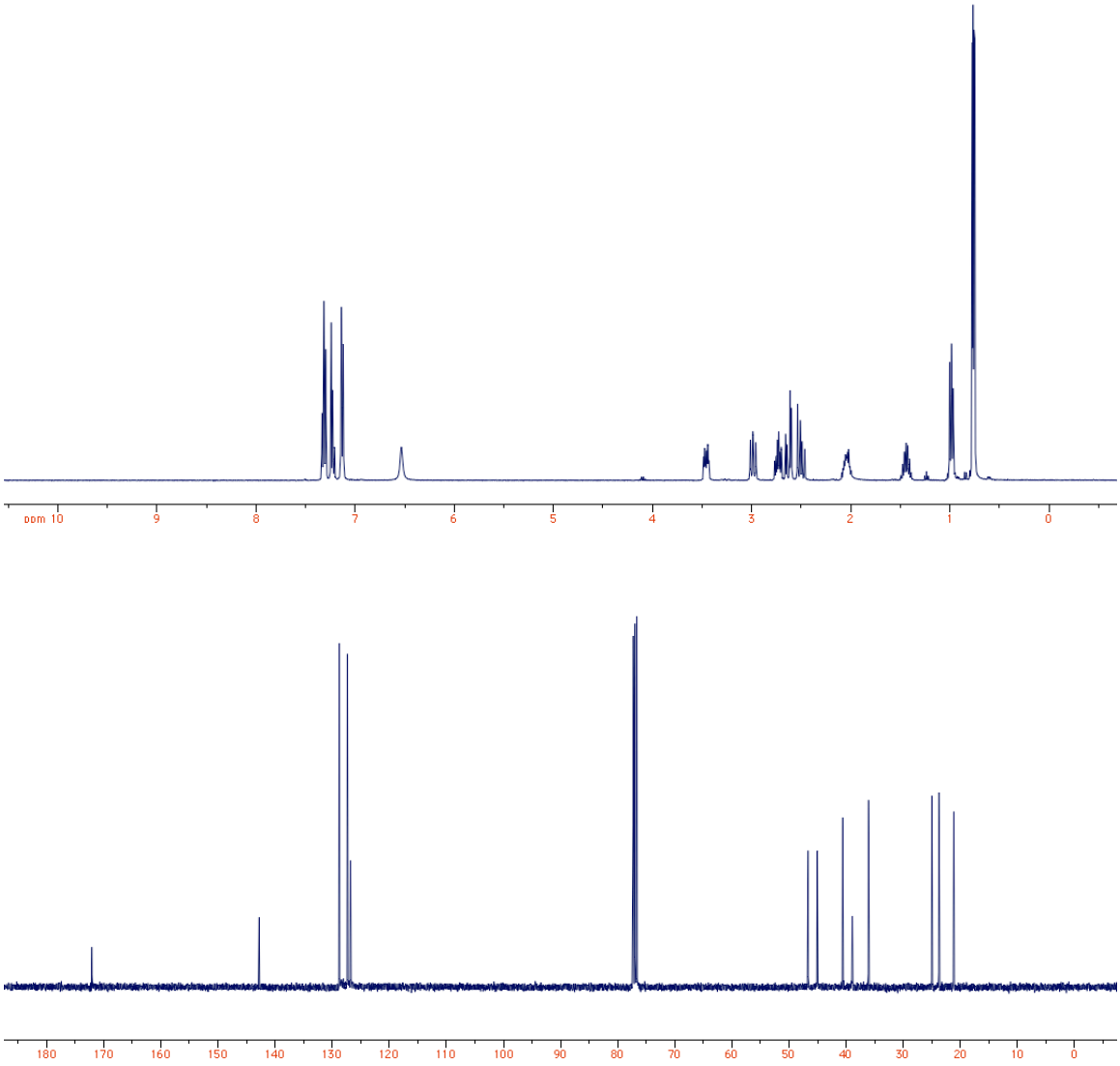
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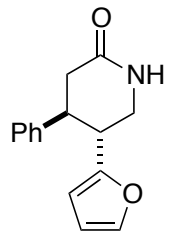
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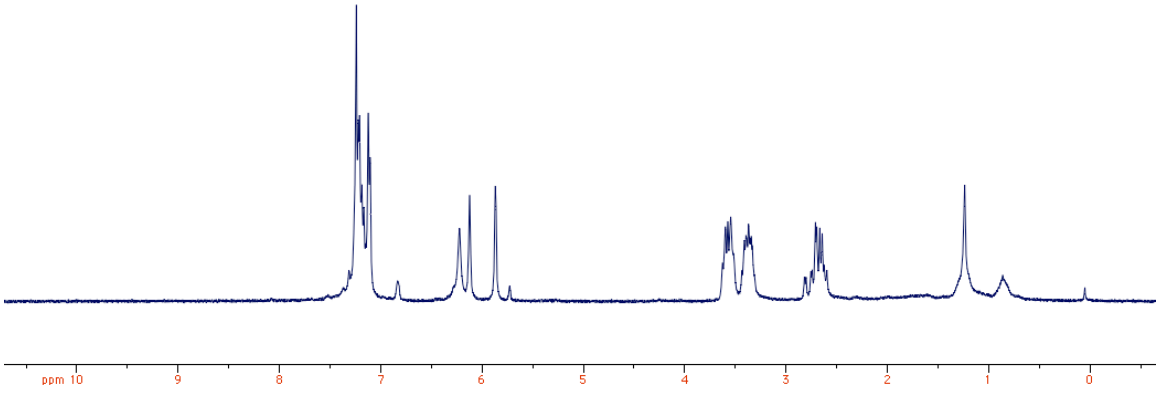
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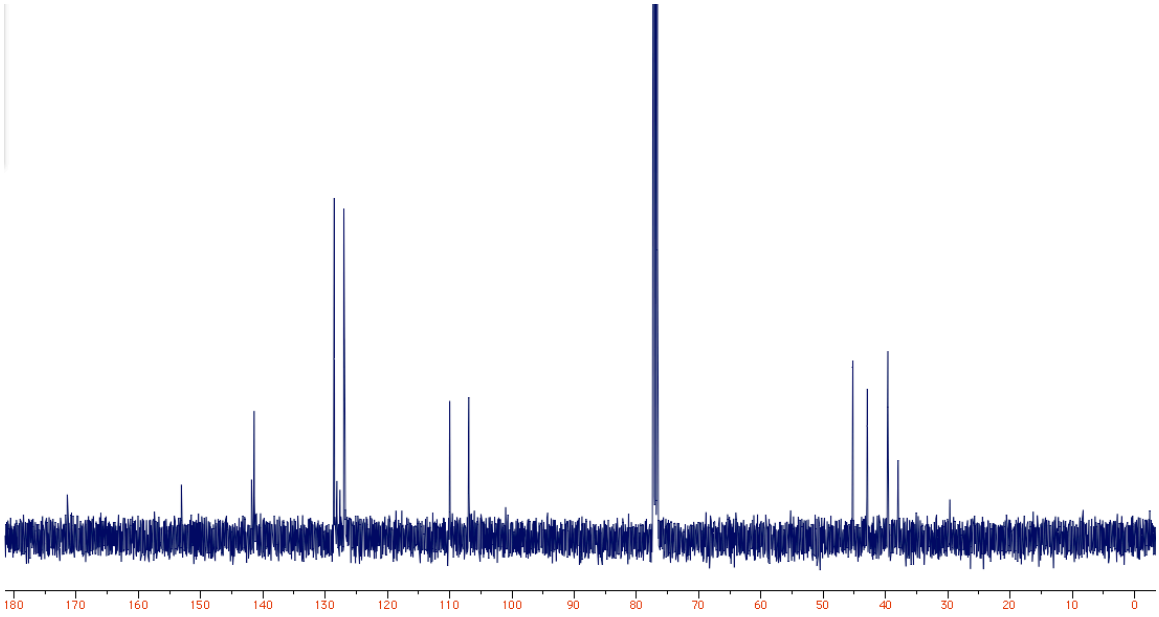
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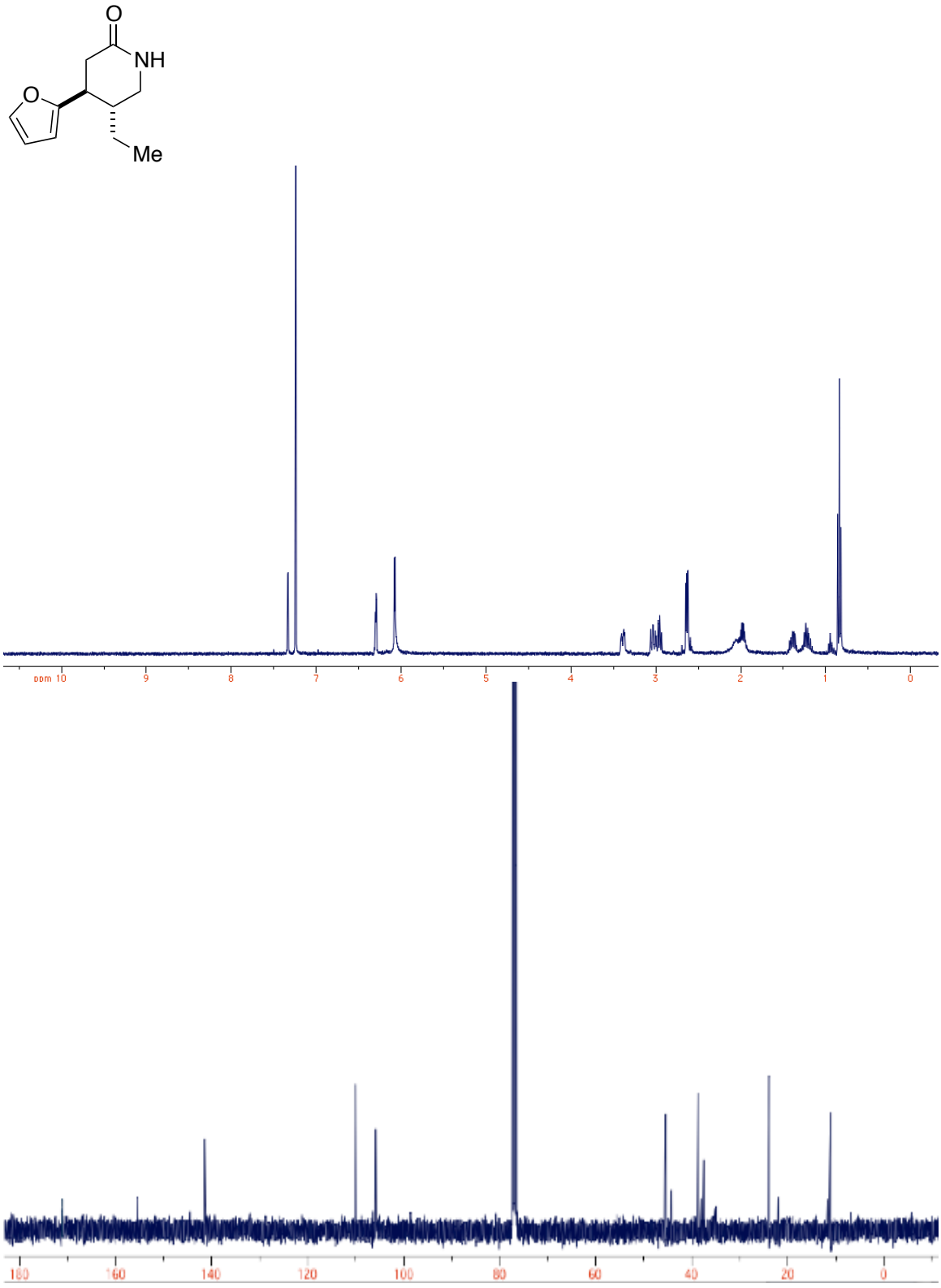
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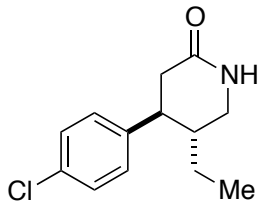
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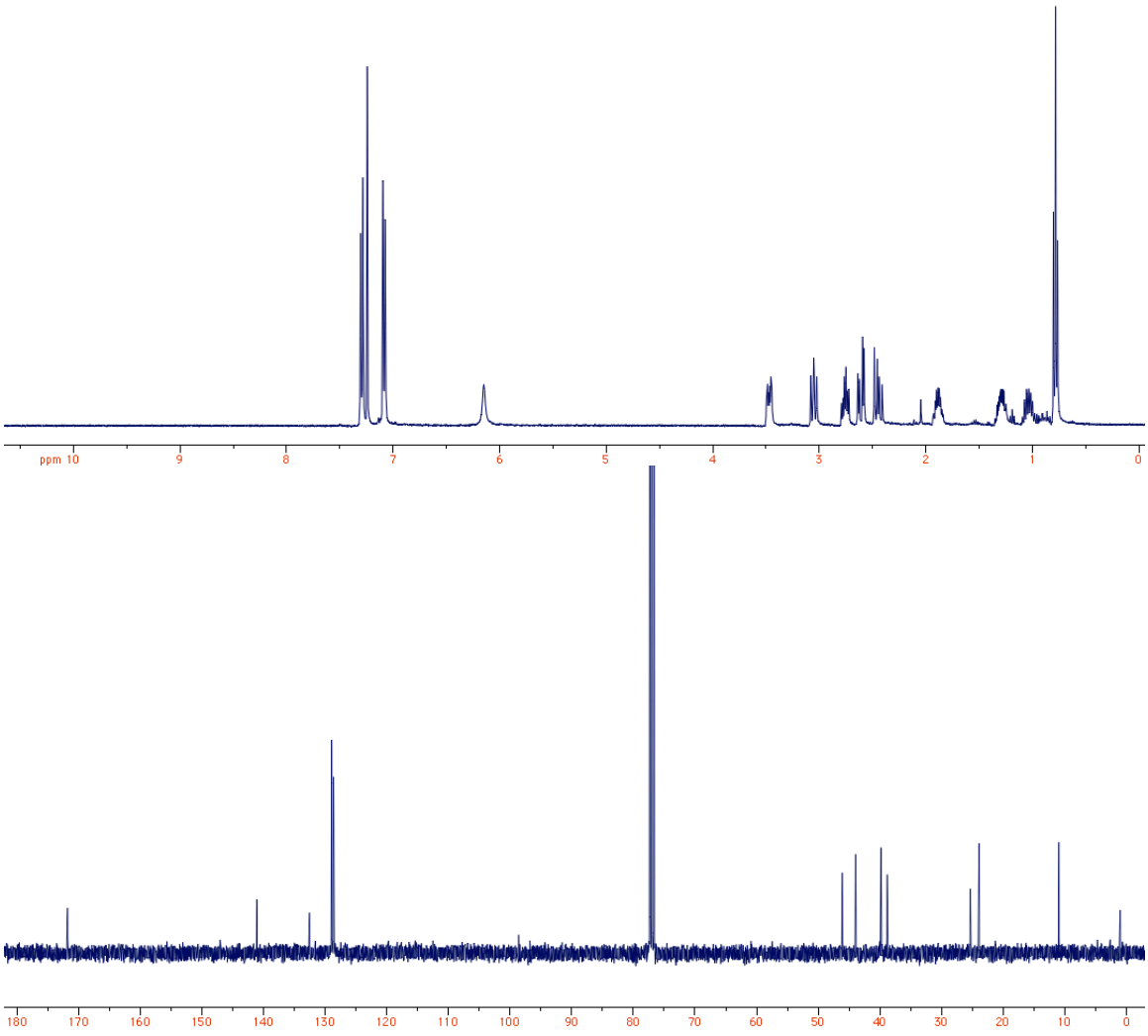
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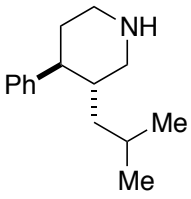
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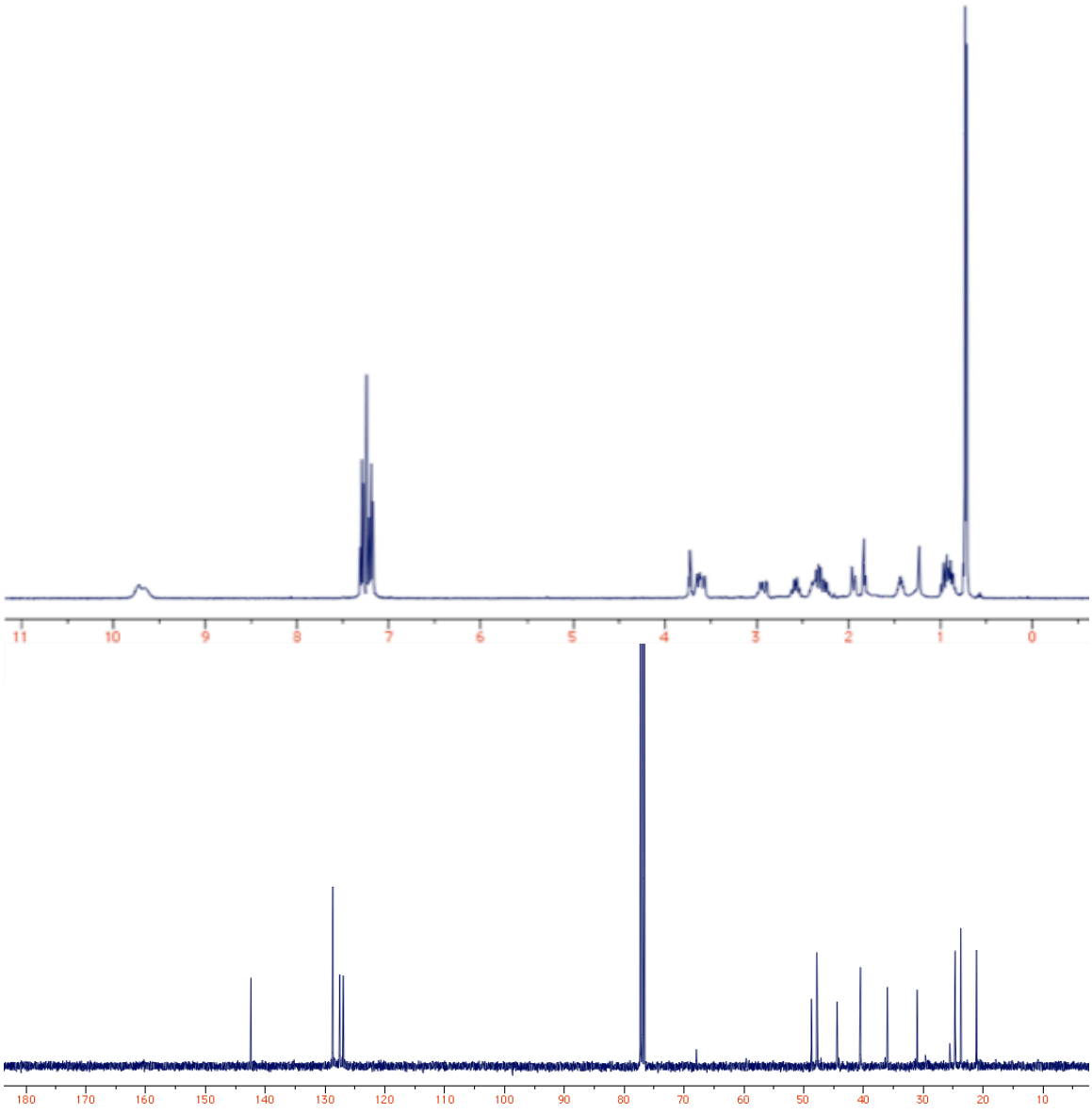
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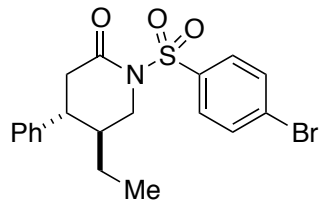
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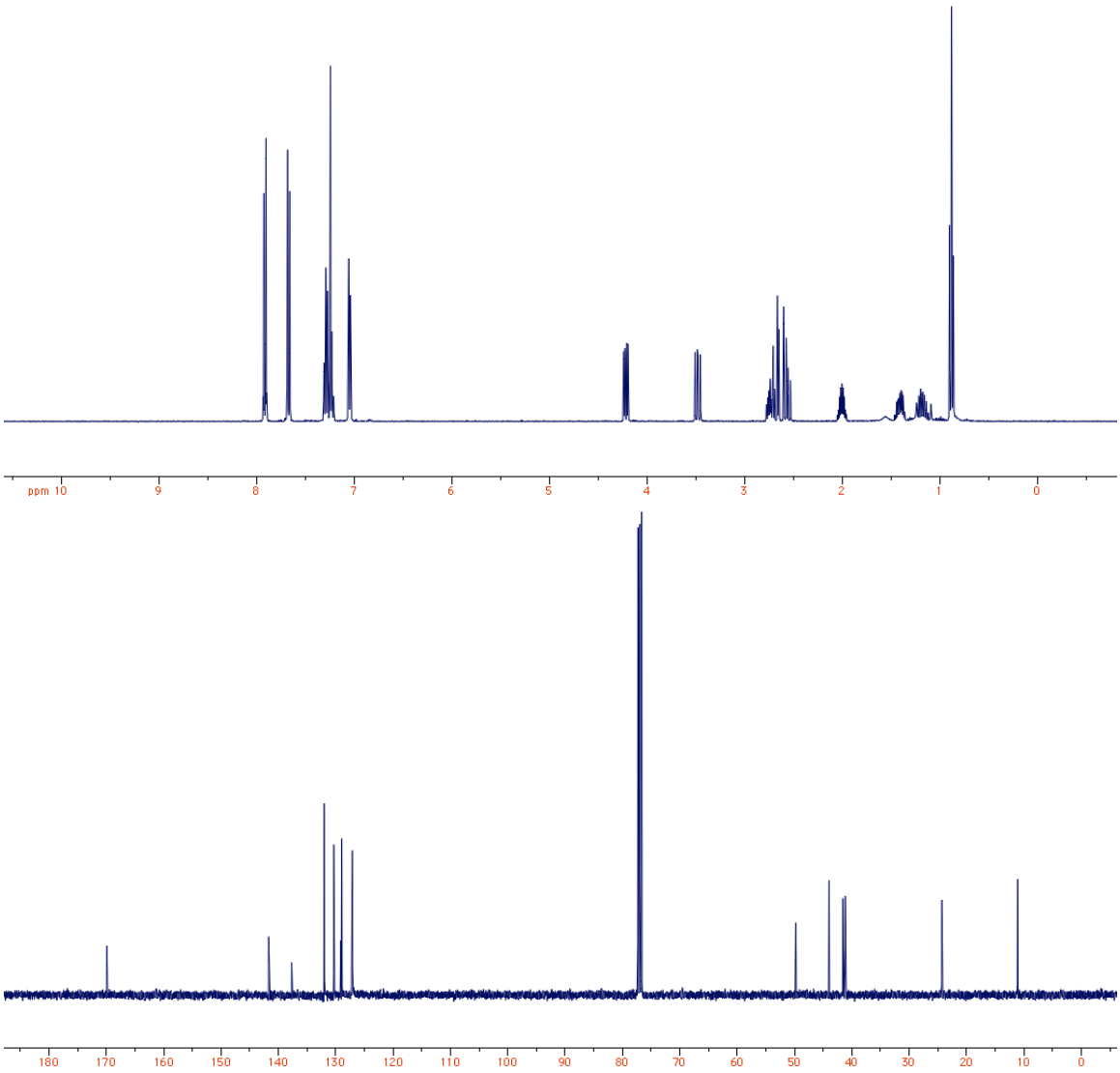
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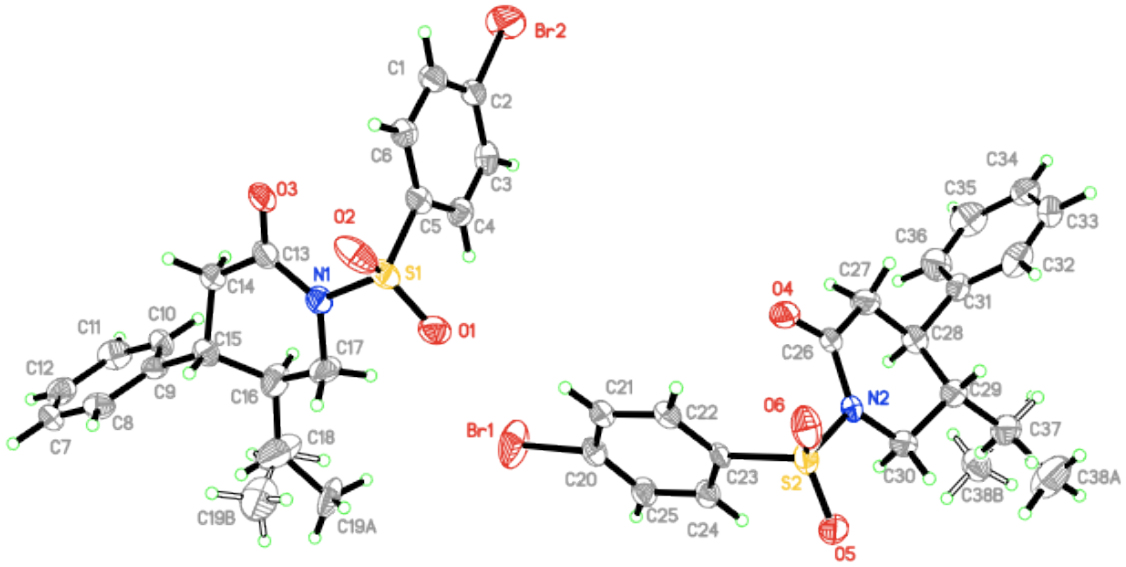

Table 1. Crystal data and structure refinement for Rovis161. **S3**

Identification code	rovis161	
Empirical formula	C_{19} H_{20} Br N O_3 S	
Formula weight	422.33	
Temperature	120 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	*P* 2_1	
Unit cell dimensions	*a* = 5.8036(5) Å	α = 90°.
	b = 21.9511(18) Å	β = 95.263(5)°.
	c = 14.3746(12) Å	ɣ = 90°.
Volume	1823.5(3) $Å^3$	
Z	4	
Density (calculated)	1.538 Mg/m^3	
Absorption coefficient	2.387 mm^{-1}	
F_{000}	864	
Crystal size	0.37 x 0.11 x 0.10 mm^3	
Theta range for data collection	1.70 to 26.39°.	
Index ranges	-7≤h≤7, -27≤k≤27, -17≤l≤17	
Reflections collected	32881	
Independent reflections	7371 [R_{int} = 0.0412]	
Completeness to theta = 26.39°	99.9 %	
Absorption correction	Semi-empirical from equivalents	

Max. and min. transmission	0.8015 and 0.4721
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7371 / 35 / 472
Goodness-of-fit on F^2	1.046
Final R indices [I>2sigma(I)]	R1 = 0.0453, wR2 = 0.0880
R indices (all data)	R1 = 0.0659, wR2 = 0.0964
Absolute structure parameter	0.013(10)
Largest diff. peak and hole	0.927 and -1.456 e.Å^{-3}

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3)
for Rovis161. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	1838(1)	7724(1)	7695(1)	72(1)
Br(2)	2151(1)	5738(1)	2630(1)	61(1)
C(1)	5687(9)	6608(3)	3097(4)	32(1)
C(2)	3664(10)	6352(2)	3371(4)	31(1)
C(3)	2684(9)	6552(3)	4154(4)	32(1)
C(4)	3729(8)	7022(2)	4682(4)	30(1)
C(5)	5750(9)	7278(2)	4396(4)	26(1)
C(6)	6737(9)	7081(2)	3612(4)	28(1)
C(7)	1001(11)	11231(3)	3885(4)	38(1)
C(8)	2398(8)	10745(3)	4210(3)	33(1)
C(9)	1637(9)	10157(2)	4109(3)	26(1)
C(10)	-544(9)	10054(3)	3687(4)	34(1)
C(11)	-1920(9)	10536(3)	3358(4)	40(2)
C(12)	-1153(11)	11120(3)	3465(4)	41(2)
C(13)	5245(9)	8686(3)	3886(4)	32(1)
C(14)	3688(10)	9218(2)	3634(4)	34(1)
C(15)	3238(8)	9639(2)	4433(3)	31(1)
C(17)	4235(11)	8793(3)	5565(4)	43(2)
C(20)	3572(9)	7136(2)	8433(4)	31(1)

C(21)	5562(9)	6907(3)	8119(4)	30(1)
C(22)	6695(9)	6437(2)	8623(4)	28(1)
C(23)	5795(9)	6226(2)	9425(3)	23(1)
C(24)	3840(8)	6477(2)	9743(4)	28(1)
C(25)	2700(9)	6943(3)	9240(4)	32(1)
C(26)	5094(9)	4847(2)	8895(3)	30(1)
C(27)	3370(10)	4348(3)	8663(4)	39(1)
C(28)	2005(8)	4101(2)	9432(3)	35(1)
C(30)	4225(9)	4763(2)	10582(3)	32(1)
C(31)	1101(9)	3467(2)	9118(4)	32(1)
C(32)	2362(9)	2932(3)	9256(4)	38(1)
C(33)	1462(10)	2390(3)	8912(4)	40(1)
C(34)	-708(11)	2366(3)	8428(4)	44(2)
C(35)	-1948(10)	2902(3)	8298(4)	49(2)
C(36)	-1023(10)	3437(3)	8627(4)	43(1)
C(16)	2435(10)	9260(2)	5213(4)	47(2)
C(18)	1577(17)	9596(4)	6026(5)	85(3)
C(19A)	1410(30)	9419(6)	6948(9)	63(5)
C(19B)	2960(20)	9930(6)	6518(9)	65(3)
C(29)	3412(9)	4113(2)	10364(3)	36(1)
C(37)	2178(10)	3845(3)	11165(4)	43(1)
C(38A)	3430(20)	3780(7)	12034(8)	73(4)
C(38B)	29(17)	4166(4)	11370(8)	41(3)
N(1)	5379(7)	8492(2)	4801(3)	29(1)
N(2)	5506(7)	5021(2)	9829(3)	28(1)
O(1)	6672(6)	7760(2)	6045(2)	41(1)
O(2)	9311(6)	7972(2)	4846(3)	47(1)
O(3)	6287(7)	8431(2)	3302(3)	41(1)
O(4)	6143(7)	5100(2)	8309(3)	36(1)
O(5)	7009(6)	5750(2)	11052(2)	41(1)
O(6)	9431(6)	5533(2)	9774(3)	42(1)
S(1)	7023(2)	7873(1)	5087(1)	33(1)
S(2)	7204(2)	5630(1)	10083(1)	31(1)

Table 3. Bond lengths [Å] and angles [°] for Rovis161.

Br(1)-C(20)	1.900(5)	C(26)-C(27)	1.499(8)
Br(2)-C(2)	1.886(6)	C(27)-C(28)	1.519(7)
C(1)-C(6)	1.384(8)	C(28)-C(29)	1.504(6)
C(1)-C(2)	1.391(7)	C(28)-C(31)	1.540(7)
C(2)-C(3)	1.378(7)	C(30)-N(2)	1.480(6)
C(3)-C(4)	1.388(8)	C(30)-C(29)	1.527(7)
C(4)-C(5)	1.396(7)	C(31)-C(36)	1.365(8)
C(5)-C(6)	1.379(7)	C(31)-C(32)	1.387(7)
C(5)-S(1)	1.762(6)	C(32)-C(33)	1.374(8)
C(7)-C(12)	1.360(9)	C(33)-C(34)	1.382(9)
C(7)-C(8)	1.394(8)	C(34)-C(35)	1.383(9)
C(8)-C(9)	1.367(8)	C(35)-C(36)	1.359(9)
C(9)-C(10)	1.372(8)	C(16)-C(18)	1.506(8)
C(9)-C(15)	1.515(6)	C(18)-C(19B)	1.257(14)
C(10)-C(11)	1.383(8)	C(18)-C(19A)	1.394(13)
C(11)-C(12)	1.362(9)	C(29)-C(37)	1.530(7)
C(13)-O(3)	1.215(6)	C(37)-C(38A)	1.394(12)
C(13)-N(1)	1.377(7)	C(37)-C(38B)	1.485(11)
C(13)-C(14)	1.502(8)	N(1)-S(1)	1.690(4)
C(14)-C(15)	1.515(6)	N(2)-S(2)	1.681(4)
C(15)-C(16)	1.505(6)	O(1)-S(1)	1.432(4)
C(17)-N(1)	1.489(6)	O(2)-S(1)	1.419(4)
C(17)-C(16)	1.517(8)	O(5)-S(2)	1.433(3)
C(20)-C(21)	1.374(7)	O(6)-S(2)	1.421(4)
C(20)-C(25)	1.374(7)		
C(21)-C(22)	1.392(7)	C(6)-C(1)-C(2)	119.6(5)
C(22)-C(23)	1.387(7)	C(3)-C(2)-C(1)	121.7(5)
C(23)-C(24)	1.377(7)	C(3)-C(2)-Br(2)	118.9(4)
C(23)-S(2)	1.769(5)	C(1)-C(2)-Br(2)	119.3(4)
C(24)-C(25)	1.385(7)	C(2)-C(3)-C(4)	119.4(5)
C(26)-O(4)	1.218(6)	C(3)-C(4)-C(5)	118.3(5)
C(26)-N(2)	1.396(6)	C(6)-C(5)-C(4)	122.6(5)
		C(6)-C(5)-S(1)	120.6(4)
		C(4)-C(5)-S(1)	116.9(4)
		C(5)-C(6)-C(1)	118.4(5)
		C(12)-C(7)-C(8)	119.7(6)

C(9)-C(8)-C(7)	120.9(5)	C(33)-C(32)-C(31)	120.2(5)
C(8)-C(9)-C(10)	118.6(5)	C(32)-C(33)-C(34)	120.9(5)
C(8)-C(9)-C(15)	119.6(5)	C(33)-C(34)-C(35)	118.3(5)
C(10)-C(9)-C(15)	121.8(5)	C(36)-C(35)-C(34)	120.3(6)
C(9)-C(10)-C(11)	120.4(5)	C(35)-C(36)-C(31)	122.1(6)
C(12)-C(11)-C(10)	120.7(5)	C(15)-C(16)-C(18)	117.0(5)
C(7)-C(12)-C(11)	119.7(6)	C(15)-C(16)-C(17)	111.8(4)
O(3)-C(13)-N(1)	122.0(5)	C(18)-C(16)-C(17)	109.9(5)
O(3)-C(13)-C(14)	121.2(5)	C(19B)-C(18)-C(19A)	74.0(10)
N(1)-C(13)-C(14)	116.8(4)	C(19B)-C(18)-C(16)	118.8(10)
C(13)-C(14)-C(15)	115.6(4)	C(19A)-C(18)-C(16)	131.2(8)
C(16)-C(15)-C(14)	108.4(4)	C(28)-C(29)-C(30)	109.4(4)
C(16)-C(15)-C(9)	114.9(4)	C(28)-C(29)-C(37)	114.2(5)
C(14)-C(15)-C(9)	111.6(4)	C(30)-C(29)-C(37)	111.2(4)
N(1)-C(17)-C(16)	113.2(4)	C(38A)-C(37)-C(38B)	104.6(9)
C(21)-C(20)-C(25)	123.4(5)	C(38A)-C(37)-C(29)	118.1(7)
C(21)-C(20)-Br(1)	118.9(4)	C(38B)-C(37)-C(29)	115.2(6)
C(25)-C(20)-Br(1)	117.7(4)	C(13)-N(1)-C(17)	125.3(4)
C(20)-C(21)-C(22)	118.1(5)	C(13)-N(1)-S(1)	117.5(3)
C(23)-C(22)-C(21)	119.0(5)	C(17)-N(1)-S(1)	117.2(3)
C(24)-C(23)-C(22)	121.8(5)	C(26)-N(2)-C(30)	123.0(4)
C(24)-C(23)-S(2)	118.2(4)	C(26)-N(2)-S(2)	118.2(3)
C(22)-C(23)-S(2)	120.0(4)	C(30)-N(2)-S(2)	118.0(3)
C(23)-C(24)-C(25)	119.4(5)	O(2)-S(1)-O(1)	118.7(2)
C(20)-C(25)-C(24)	118.2(5)	O(2)-S(1)-N(1)	109.7(2)
O(4)-C(26)-N(2)	119.2(5)	O(1)-S(1)-N(1)	104.2(2)
O(4)-C(26)-C(27)	123.0(5)	O(2)-S(1)-C(5)	109.2(2)
N(2)-C(26)-C(27)	117.8(4)	O(1)-S(1)-C(5)	108.9(3)
C(26)-C(27)-C(28)	118.7(4)	N(1)-S(1)-C(5)	105.1(2)
C(29)-C(28)-C(27)	111.4(4)	O(6)-S(2)-O(5)	119.1(2)
C(29)-C(28)-C(31)	114.8(4)	O(6)-S(2)-N(2)	110.2(2)
C(27)-C(28)-C(31)	107.3(4)	O(5)-S(2)-N(2)	105.1(2)
N(2)-C(30)-C(29)	112.0(4)	O(6)-S(2)-C(23)	109.4(2)
C(36)-C(31)-C(32)	118.2(5)	O(5)-S(2)-C(23)	108.1(2)
C(36)-C(31)-C(28)	117.5(5)	N(2)-S(2)-C(23)	103.8(2)
C(32)-C(31)-C(28)	124.1(5)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for Rovis161. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	84(1)	65(1)	72(1)	37(1)	33(1)	50(1)
Br(2)	75(1)	55(1)	54(1)	-19(1)	10(1)	-37(1)
C(1)	33(3)	28(3)	35(3)	-3(2)	6(2)	1(2)
C(2)	41(3)	23(3)	28(3)	0(2)	-1(2)	1(2)
C(3)	23(3)	29(3)	43(3)	10(2)	3(2)	0(2)
C(4)	29(3)	31(3)	31(3)	5(2)	3(2)	5(2)
C(5)	22(3)	25(3)	31(3)	1(2)	-6(2)	8(2)
C(6)	25(3)	27(3)	31(3)	2(2)	1(2)	4(2)
C(7)	57(4)	23(3)	35(3)	-4(2)	11(3)	-8(2)
C(8)	28(3)	38(3)	32(2)	-7(2)	2(2)	-2(2)
C(9)	29(3)	26(3)	22(2)	-3(2)	3(2)	4(2)
C(10)	40(3)	26(3)	34(3)	-2(2)	1(2)	-12(2)
C(11)	25(3)	54(4)	40(3)	-7(3)	-3(2)	-7(3)
C(12)	55(4)	40(3)	28(3)	4(3)	3(3)	16(3)
C(13)	36(3)	23(3)	37(3)	-1(2)	12(2)	-1(2)
C(14)	47(3)	25(3)	32(3)	0(2)	12(2)	3(2)
C(15)	36(3)	23(2)	34(2)	-1(2)	4(2)	8(2)
C(17)	59(4)	42(3)	28(3)	0(3)	14(3)	20(3)
C(20)	35(3)	23(3)	36(3)	1(2)	3(2)	10(2)
C(21)	39(3)	21(3)	31(3)	-1(2)	6(2)	-2(2)
C(22)	27(3)	22(3)	34(3)	-3(2)	5(2)	1(2)
C(23)	29(3)	13(2)	26(3)	1(2)	-1(2)	0(2)
C(24)	29(3)	24(3)	31(3)	2(2)	7(2)	-5(2)
C(25)	34(3)	26(3)	37(3)	3(2)	9(2)	6(2)
C(26)	47(3)	18(3)	26(3)	1(2)	8(2)	6(2)

C(27)	58(4)	30(3)	29(3)	-5(2)	8(2)	-11(3)
C(28)	43(3)	28(2)	35(2)	1(2)	5(2)	4(2)
C(30)	41(3)	28(3)	27(3)	-2(2)	4(2)	-3(2)
C(31)	42(3)	29(3)	26(2)	5(2)	4(2)	-2(2)
C(32)	20(2)	56(4)	37(3)	8(2)	-6(2)	-4(2)
C(33)	51(4)	33(3)	37(3)	7(2)	2(3)	8(3)
C(34)	69(4)	31(3)	31(3)	-2(3)	4(3)	-24(3)
C(35)	35(3)	63(5)	48(4)	-4(3)	-6(3)	-16(3)
C(36)	36(3)	44(3)	47(3)	0(3)	-3(3)	9(3)
C(16)	63(4)	40(3)	42(3)	13(2)	22(3)	27(3)
C(18)	129(7)	93(6)	35(4)	7(3)	17(4)	70(5)
C(19A)	105(13)	46(8)	45(7)	30(6)	43(8)	48(8)
C(19B)	61(8)	68(8)	68(8)	15(6)	24(6)	24(5)
C(29)	49(3)	30(3)	28(2)	1(2)	5(2)	-3(2)
C(37)	62(4)	36(3)	34(3)	2(2)	12(3)	-14(3)
C(38A)	89(10)	82(9)	43(6)	14(6)	-13(6)	-44(8)
C(38B)	41(6)	33(5)	49(6)	4(5)	12(5)	-6(4)
N(1)	31(2)	25(2)	32(2)	1(2)	6(2)	8(2)
N(2)	42(3)	17(2)	26(2)	3(2)	2(2)	-2(2)
O(1)	55(2)	32(2)	32(2)	-5(2)	-8(2)	14(2)
O(2)	27(2)	36(2)	78(3)	-21(2)	-1(2)	-4(2)
O(3)	58(3)	21(2)	47(2)	-2(2)	24(2)	6(2)
O(4)	49(2)	31(2)	30(2)	-3(2)	15(2)	-3(2)
O(5)	59(2)	32(2)	29(2)	0(2)	-13(2)	-12(2)
O(6)	29(2)	34(2)	61(2)	11(2)	-2(2)	2(2)
S(1)	31(1)	25(1)	41(1)	-5(1)	-4(1)	7(1)
S(2)	34(1)	23(1)	35(1)	5(1)	-5(1)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Rovis161.

	x	y	z	U(eq)

H(1)	6329	6462	2571	38
H(3)	1335	6373	4327	38
H(4)	3099	7164	5214	36
H(6)	8078	7262	3435	33
H(7)	1541	11629	3955	45
H(8)	3868	10822	4501	40
H(10)	-1100	9657	3621	40
H(11)	-3383	10460	3061	48
H(12)	-2099	11442	3251	49
H(14A)	2214	9064	3358	41
H(14B)	4364	9456	3159	41
H(15)	4726	9820	4663	37
H(17A)	5405	8992	5985	51
H(17B)	3500	8484	5919	51
H(21)	6136	7062	7584	36
H(22)	8035	6267	8426	33
H(24)	3289	6335	10290	34
H(25)	1380	7120	9443	38
H(27A)	4189	4010	8411	47
H(27B)	2268	4496	8165	47
H(28)	662	4366	9474	42
H(30A)	2893	5018	10665	39
H(30B)	5217	4765	11163	39
H(32)	3822	2941	9583	46
H(33)	2323	2035	9006	48
H(34)	-1317	1998	8196	52
H(35)	-3421	2896	7983	59
H(36)	-1864	3794	8515	51
H(16)	1110	9025	4935	56
H(18A)	2494	9966	6076	102
H(18B)	23	9724	5803	102
H(18C)	286	9849	5784	102
H(18D)	970	9297	6435	102

H(19A)	762	9747	7283	95
H(19B)	2916	9321	7237	95
H(19C)	421	9068	6959	95
H(19D)	2183	10110	7010	97
H(19E)	3531	10245	6136	97
H(19F)	4239	9689	6784	97
H(29)	4797	3865	10305	43
H(37A)	846	4099	11249	52
H(37B)	1594	3446	10971	52
H(37C)	1796	3423	11019	52
H(37D)	3244	3847	11726	52
H(38A)	2455	3609	12470	109
H(38B)	3983	4171	12253	109
H(38C)	4727	3514	11976	109
H(38D)	-636	3965	11874	61
H(38E)	-1056	4162	10824	61
H(38F)	390	4580	11543	61

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