Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Copper(I)/DM-SEGPHOS-Catalyzed Enantio- and Diastereoselective Conjugate Boration to α-Alkylidene-γ-lactams

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General Methods.

All reactions were carried out using oven-dried glassware. The progress of all reactions was monitored by thin-layer chromatography on Dynamic Adsorbent, Inc. precoated silica gel plates (250 μm) and visualized by ultra-violet light or by staining with $KMnO_4$. Unless otherwise specified, all chemicals were purchased from Sigma Aldrich or Alfa Aesar or TCI chemicals and all solvents were purchased from Fischer Scientific. HPLC grade toluene and THF were further dried through alumina columns. The ^{1}H NMR and ^{13}C NMR spectra were obtained on JEOL600 MHz Fourier Transform spectrometers. Chemical Shifts are reported in units of parts per million downfield from tetramethylsilane as standard. The coupling constants are reported in Hertz. The infrared spectra were obtained using a Thermo Nicolet IR 300 Spectrometer. Silica gel (32-64u, Merck KGaA) was used for column chromatography. Melting points were recorded on a Buchi-B-450 melting point apparatus and the melting point values were uncorrected. The absolute configuration of compound **3k** was determined by the single crystal X-ray analysis, and the relative configurations of other compounds were determined accordingly. The enantiomeric excess of chiral compounds was determined by the HPLC analysis on chiral stationary phase.

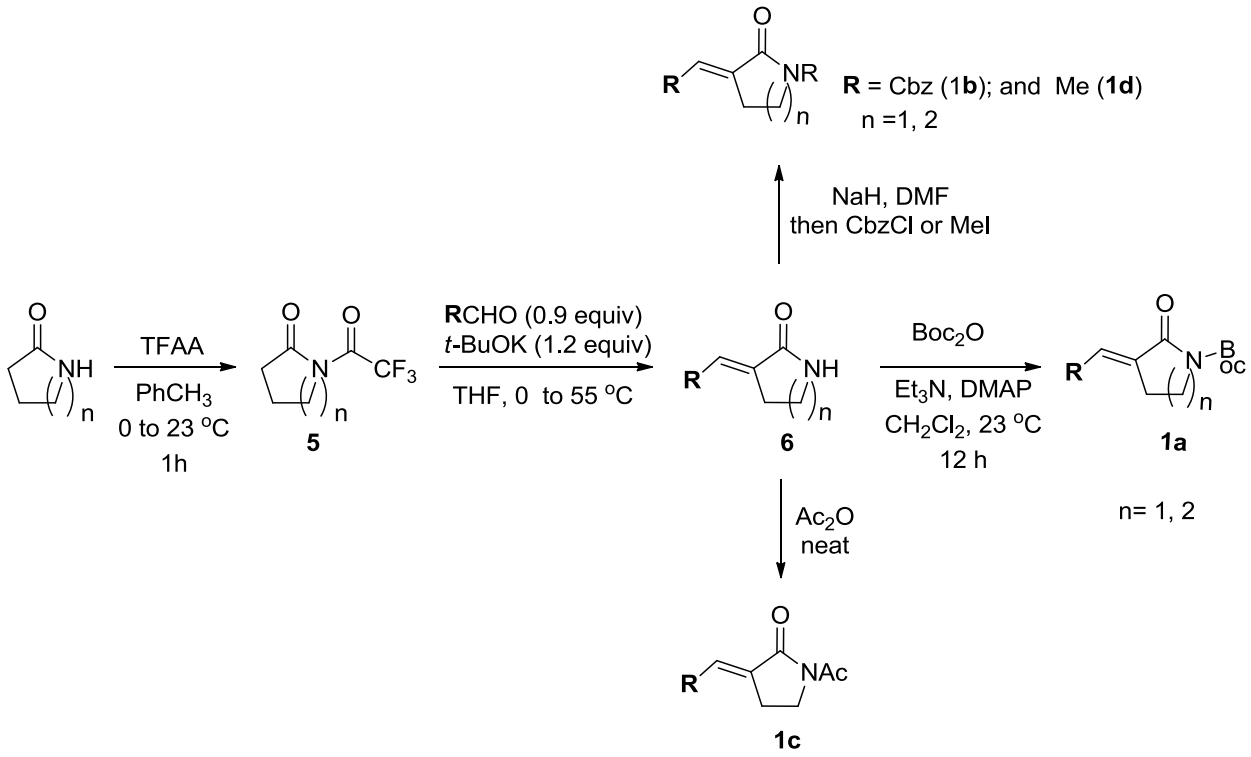
Preparation of Starting Materials

α-Alkylidene-γ-lactams were synthesized from the corresponding 2-pyrrolidinone or 2-piperidinone according to the literature procedures.[1-2] Some new derivatives were synthesized by the Procedure C below and characterized.

A. The Synthesis of Compounds **5**

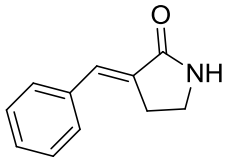
A solution of lactam (20 mmol) in anhydrous toluene (20 mL) was cooled to 0 ^{o}C and stirred for 10 min at this temperature. Trifluoroacetic anhydride (22 mmol) was then added dropwise. After 10 min, the cooling bath was removed, and the reaction was warmed to room temperature and continued to stir for 1 h. After which, all volatiles were removed under reduced pressure and the residue was co-evaporated with toluene

(3x10 mL) to provide the trifluoro acetyl 2-pyrrolidine as pale-yellow oil in quantitative yield. This compound was used in next step without further purification.



B. Procedure A for the Synthesis of Alkylidene Lactam **6**[1]

An oven dried round bottom flask equipped with a magnetic stirrer under argon was charged with potassium *tert*-butoxide (740 mg, 6.5 mmol, 1.3 equiv) in anhydrous THF (7 mL). This solution was cooled to 0 ℃. After stirring for 10 min, a mixture of aldehyde (5.0 mmol) and trifluoroactyl lactam **5** (0.9 g, 5 mmol) was added dropwise and further stirred for 10 min. The reaction temperature was then changed to 55 °C and remained at this temperature for 1 h. The solvent was removed under reduced pressure after cooling down the reaction mixture to room temperature. The residue was suspended in water (20 mL) and extracted with ethyl acetate (3x20 mL). Organic layers were combined and washed with brine, dried and concentrated. The residue obtained was washed with 5% ethyl acetate in hexanes to remove unreacted aldehydes to get the pure product. This compound was directly employed in the next step for the Boc, Cbz, Ac and Me protections.



(*E*)-3-Benzylidenepyrrolidin-2-one (**6**): 0.7g (80%); white solid; m.p. 164-165 ℃. ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.49 (d, *J* = 7.2 Hz, 2H), 7.41 (dd, *J* = 6.6, 7.8 Hz, 2H), 7.37-7.30 (m, 3H), 3.56 (t, *J* = 6.0 Hz, 2H), 3.16 (dt, *J* = 2.4, 6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 172.7, 135.6, 130.3, 130.2, 129.5, 128.6, 128.5, 39.6, 26.3; IR (neat): 3206, 3086, 2918, 1756, 1724, 1710, 1636, 1383, 1366, 1318, 1284, 1256, 1157 cm^{-1}; HRMS (ESI): m/z calcd for $C_{11}H_{11}NNaO$ $[M+Na]^+$ 196.0733; Found 196.0737.

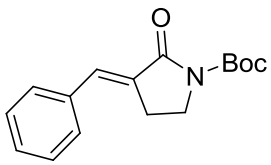
C. Procedure B for Boc Protection of Alkylidene Lactams[1]

To a solution of compound **6** (5 mmol/20 mL of dry DCM) was added DMAP (60 mg, 0.1 equiv) and triethylamine (1.1 mL, 1.5 equiv) at room temperature under argon. $(Boc)_2O$ (2.3 mL, 2.0 equiv) was added and the solution was continued to stir for 6-8 h. After the reaction was complete, all volatiles were removed *in vaccuo*, and the residue was purified by column chromatography on silica gel to provide the corresponding alkylidene lactams.

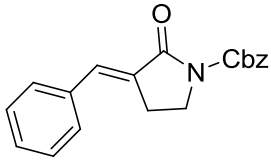
D. Procedure C for Cbz Protection of Alkylidene Lactams

A solution of compound **6** (5 mmol) in dry DMF (20 mL) under argon was cooled to 0 ℃. NaH (220 mg, 1.1 equiv, 60% suspension in mineral oil) was added portionwise to this solution. After 15 min, CbzCl (0.72 mL, 5 mmol) was added dropwise at this temperature. The reaction mixture was slowly warmed to room temperature and stirred for 6 h. The reaction was quenched by the dropwise addition of ice-cold water (25 ml) at 0 ℃, and the aqueous layer was extracted with ethyl acetate (2x25 mL). The combined organic layers were washed with ice cold water (4x25 mL) and brine (25 mL), and then dried over sodium sulfate, filtered and concentrated. The residue was purified by column chromatography on silica gel using 50-100% CH_2Cl_2 in hexanes as eluent.

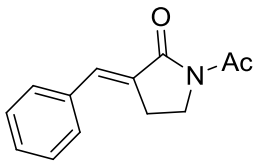
E. Characterization Data for Starting Materials



(*E*)-*tert*-Butyl 3-benzylidene-2-oxopyrrolidine-1-carboxylate (**1a**): This compound was prepared from benzaldehyde (0.53 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using (10-15%) ethyl acetate in hexanes as eluent. 0.91g (67%); white solid; m.p. 131-132 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.53 (t, *J* = 3.0 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.42 (dd, *J* = 7.2, 7.8 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 1H), 3.84 (dd, *J* = 6.6, 7.8 Hz, 2H), 3.05 (td, *J* = 7.8, 3.0 Hz, 2H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.7, 150.8, 135.1, 134.1, 130.0, 129.9, 129.2, 128.7, 82.9, 43.3, 28.0, 23.3; IR (neat): 2978, 2916, 1773, 1712, 1649, 1365, 1312, 1153 cm^{-1}; HRMS (ESI): m/z calcd for $C_{16}H_{19}NNaO_3$ $[M+Na]^+$ 296.1257; Found 296.1261.

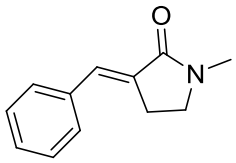


(*E*)-Benzyl 3-benzylidene-2-oxopyrrolidine-1-carboxylate (**1b**): This compound was prepared from benzaldehyde (0.53 g, 5.0 mmol) according to the Procedure A followed by the Procedure C. The compound was purified by column chromatography on silica gel using (50-100 %) CH_2Cl_2 in hexanes as eluent. 820 mg (54%); white solid; m.p. 134-136 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.55 (t, *J* = 3.0 Hz, 1H), 7.51-7.45 (m, 4H), 7.44-7.40 (m, 2H), 7.39 -7.36 (m, 3H), 7.32 (m, 1H), 5.33 (s, 2H), 3.89 (t, *J* = 7.2 Hz, 2H), 3.07 (td, *J* = 7.2, 3.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.5, 152.1, 135.3, 134.9, 134.8, 130.0, 129.4, 129.2, 128.8, 128.5, 128.3, 128.0, 68.0, 43.2, 23.4; IR (neat): 2916, 1774, 1713, 1648, 1383, 1298, 1273 cm^{-1}; HRMS (ESI): m/z calcd for $C_{19}H_{17}NNaO_3$ $[M+Na]^+$ 330.1101; Found 330.1109.

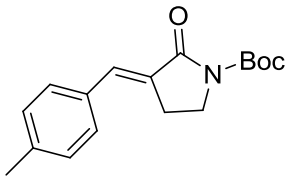


(*E*)-1-Acetyl-3-benzylidenepyrrolidin-2-one (**1c**): This compound was prepared by refluxing the compound **6** (865 mg, 5 mmol) in acetic anhydride (5 mL) for 12 h. After the reaction was complete by TLC, the reaction mixture was cool down to room temperature and all volatiles were removed *in vacuuo*. The residue was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent to obtain the pure product. 0.75g (70%); white solid; m.p. 192-194 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.56 (t, *J* = 3.0 Hz, 1H), 7.52 (d, *J* = 7.2 Hz, 2H), 7.44 (dd, *J* = 7.2, 7.8 Hz, 2H), 7.39 (m, 1H), 3.89 (t, *J* = 7.2 Hz, 2H), 3.08 (dt, *J* = 3.0,

7.2 Hz, 2H), 2.63 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 171.9, 168.8, 135.1, 134.8, 130.2, 130.1, 129.5, 128.8, 42.2, 25.0, 23.0; IR (neat): 2926, 2845, 1708, 1688, 1485, 1380, 1368, 1256 cm^{-1}; HRMS (FAB): HRMS (ESI): m/z calcd $C_{13}H_{14}NO_2$ $[M+H]^+$ 216.1019; Found 216.1023.

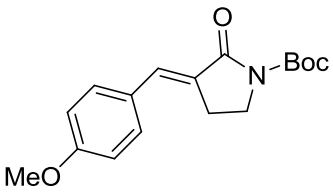


(*E*)-3-Benzylidene-1-methylpyrrolidin-2-one (**1d**): A solution of the compound **6** (865 mg, 5 mmol) in dry DMF (20 mL) under argon was cooled to 0 ℃. NaH (220 mg, 1.1 equiv, 60% suspension in mineral oil) was added portionwise and continued to stir for 15 min. Iodomethane (0.47 mL, 1.5 equiv) was then added and the reaction mixture was warmed to room temperature and allowed to stir for 6 h. After the completion of reaction (by TLC analysis), the reaction was cooled to 0 ℃ and quenched by the dropwise addition of ice-cold water (25 mL). The aqueous layer was extracted with ethyl acetate (2x25 mL). The organic layers were combined, washed with ice-cold water (4x25 mL) and brine (25 mL). After drying over sodium sulfate, the organic layer was filtered and concentrated. The residue was purified by column chromatography on silica gel using 10-20% ethyl acetate in hexanes as eluent. 440 mg (56%); white solid; m.p. 134-136 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.87 (t, *J* = 7.8 Hz, 2H), 7.40 (dd, *J* = 7.2, 7.8 Hz, 2H), 7.36-7.30 (m, 2H), 3.50 (t, *J* = 6.6 Hz, 2H), 3.07 (td, *J* = 6.6, 2.4 Hz, 2H), 3.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 169.2, 135.8, 130.7, 129.6, 129.4, 128.6, 128.2, 46.7, 30.2, 24.3; IR (neat): 3047, 2940, 2885, 1673, 1655, 1645, 1448, 1384, 1290 cm^{-1}; HRMS (ESI): m/z calcd for $C_{12}H_{14}NO$ $[M+H]^+$ 188.1070; Found 188.1072.

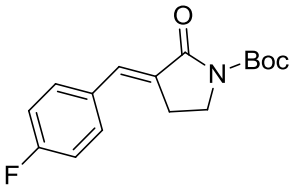


(*E*)-*tert*-Butyl 3-(4-methylbenzylidene)-2-oxopyrrolidine-1-carboxylate (**1e**): This compound was prepared from *p*-tolualdehyde (0.60 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent. 617mg (43%); white solid; m.p. 159-161 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.50 (t, *J* = 3.0 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 2H), 7.23 (dd, *J* = 7.8 Hz, 2H), 3.82 (dd, *J* = 6.6, 7.8 Hz, 2H), 3.02 (td, *J* = 7.8, 3.0 Hz, 2H), 2.38 (s, 3H), 1.56 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.8, 150.9, 139.6, 134.1, 132.3, 130.0, 129.5, 128.8, 82.8, 43.3,

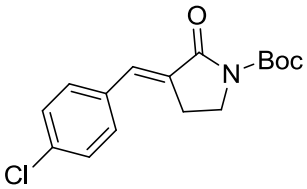
28.0, 23.3, 21.4; IR (neat): 2979, 2918, 1756, 1724, 1710, 1636, 1383, 1366, 1318, 1284, 1256, 1157 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{21}NNaO_3$ $[M+Na]^+$ 310.1414; Found 310.1409.



(*E*)-*tert*-Butyl 3-(4-methoxybenzylidene)-2-oxopyrrolidine-1-carboxylate (**1f**). This compound was prepared from *p*-anisaldehyde (0.68 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent. 575 mg (38%); white solid; m.p. 145-146 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.49 (t, *J* = 3.0 Hz, 1H), 7.46 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 3.85 (s, 3H), 3.83 (t, *J* = 7.8 Hz, 2H), 3.03 (td, *J* = 7.8, 3.0 Hz, 2H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 168.0, 160.3, 150.9, 133.8, 131.7, 127.9, 127.1, 114.2, 82.7, 55.3, 43.2, 28.0, 23.2; IR (neat): 2979, 2933, 1769, 1600, 1514, 1360, 1293, 1280, 1176, 1021 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{21}NNaO_4$ $[M+Na]^+$ 326.1363; Found 326.1363.

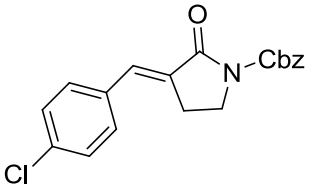


(*E*)-*tert*-Butyl 3-(4-fluorobenzylidene)-2-oxopyrrolidine-1-carboxylate (**1g**): This compound was prepared from 4-fluorobenzaldehyde (0.62 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent. 814 mg (56%); white solid; m.p. 184-186 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.50-7.46 (m, 3H), 7.11 (t, *J* = 7.2 Hz, 2H), 3.84 (t, *J* = 7.2 Hz, 2H), 3.01 (td, *J* = 7.2, 3.0 Hz, 2H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.5, 163.7 (d, *J* = 248.4), 150.7, 132.8, 131.9 (d, *J* = 8.5 Hz), 131.3 (d, *J* = 3.0 Hz), 129.5, 116.0 (d, *J* = 21.4 Hz), 82.9, 43.2, 28.0, 23.2; IR (neat): 2979, 2918, 1762, 1646, 1510, 1367, 1257, 1229, 1160 cm^{-1}; HRMS (ESI): m/z calcd for $C_{16}H_{18}FNNaO_3$ $[M+Na]^+$ 314.1163; Found 314.1161.

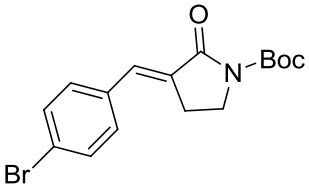


(*E*)-*tert*-Butyl 3-(4-chlorobenzylidene)-2-oxopyrrolidine-1-carboxylate (**1h**): This compound was prepared from 4-chloro benzaldehyde (0.70 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent. 720 mg

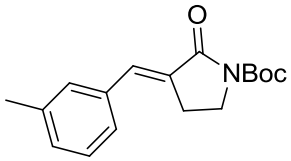
(47%); white solid; m.p. 188-190 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.47 (t, *J* = 3.0 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 3.85 (t, *J* = 7.2 Hz, 2H), 3.04-2.98 (m, 2H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.4, 150.7, 135.2, 133.5, 132.7, 131.1, 130.5, 129.0, 83.0, 43.2, 28.0, 23.3; IR (neat): 2980, 1765, 1727, 1701, 1384, 1367, 1324, 1160 cm^{-1}; HRMS (ESI): m/z calcd for $C_{16}H_{18}ClNNaO_3$ $[M+Na]^+$ 330.0867; Found 330.0866.



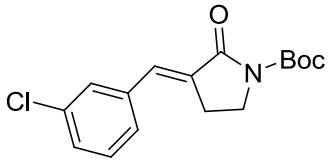
(*E*)-Benzyl 3-(4-chlorobenzylidene)-2-oxopyrrolidine-1-carboxylate (**1i**): This compound was prepared from 4-chloro benzaldehyde (0.70 g, 5.0 mmol) according to the Procedure A followed by the Procedure C. The compound was purified by column chromatography on silica gel using 50-100% CH_2Cl_2 in hexanes as eluent. 600 mg (35%); white solid; m.p. 168-169 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.50 (t, *J* = 3.0 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.44-7.37 (m, 6H), 7.34 (m, 1H), 5.34 (s, 2H), 3.91 (dd, *J* = 6.6, 7.8 Hz, 2H), 3.04 (td, *J* = 7.8, 3.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.2, 152.0, 135.4, 135.3, 133.4, 133.3, 131.2, 129.9, 129.1, 128.5, 128.3, 128.1, 68.1, 43.2, 23.4; IR (neat): 2959, 1765, 1640, 1490, 1379, 1295, 1270, 1253, 1094 cm^{-1}; HRMS (ESI): m/z calcd for $C_{19}H_{16}ClNNaO_3$ $[M+Na]^+$ 364.0711; Found 364.0713.



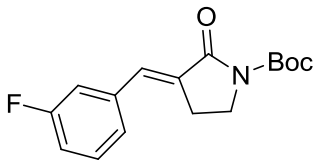
(*E*)-*tert*-Butyl 3-(4-bromobenzylidene)-2-oxopyrrolidine-1-carboxylate (**1j**): This compound was prepared from 4-bromo benzaldehyde (0.92 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent. 1.0 g (58%); white solid; m.p. 170-171 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.55 (d, *J* = 9.0 Hz, 2H), 7.45 (t, *J* = 3.0 Hz, 1H), 7.35 (d, *J* = 9.0 Hz, 2H), 3.84 (dd, *J* = 6.6, 7.8 Hz, 2H), 2.99 (td, *J* = 7.8, 3.0 Hz, 2H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.4, 150.7, 133.9, 132.7, 132.0, 131.3, 130.7, 123.5, 83.0, 43.2, 28.0, 23.3; IR (neat): 2979, 1765, 1728, 1698, 1646, 1367, 1323, 1254, 1159 cm^{-1}; HRMS (ESI): m/z calcd for $C_{16}H_{18}BrNNaO_3$ $[M+Na]^+$ 374.0362; Found 374.0365.



(*E*)-*tert*-Butyl 3-(3-methylbenzylidene)-2-oxopyrrolidine-1-carboxylate (**1k**): This compound was prepared from 3-methyl benzaldehyde (0.60 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent. 745 mg (52%); white solid; m.p. 124-126 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.50 (t, *J* = 3.0 Hz, 1H), 7.34-7.28 (m, 3H), 7.19 (d, *J* = 7.2 Hz, 1H), 3.83 (dd, *J* = 6.6, 7.8 Hz, 2H), 3.05 (td, *J* = 7.8, 3.0 Hz, 2H), 2.93 (s, 3H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.7, 150.8, 138.4, 135.0, 134.3, 130.8, 130.0, 129.6, 128.6, 127.0, 82.8, 43.2, 28.0, 23.3, 21.4; IR (neat): 2979, 2917, 1770, 1732, 1712, 1647, 1365, 1310, 1259, 1154 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{21}NNaO_3$ $[M+Na]^+$ 310.1414; Found 310.1419.

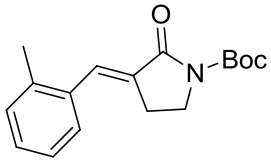


(*E*)-*tert*-Butyl 3-(3-chlorobenzylidene)-2-oxopyrrolidine-1-carboxylate (**1l**): This compound was prepared from 3-chloro benzaldehyde (0.70 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent. 782 mg (51%); white solid; m.p. 128-129 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.47-7.44 (m, 2H), 7.37-7.33 (m, 3H), 3.85 (t, *J* = 7.2 Hz, 2H), 3.04 (td, *J* = 7.2, 2.4 Hz, 2H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.2, 150.7, 136.8, 134.7, 132.5, 131.5, 130.0, 129.4, 129.1, 128.2, 83.1, 43.2, 28.0, 23.3; IR (neat): 2916, 2846, 1776, 1717, 1649, 1384, 1361, 1297, 1275 cm^{-1}; HRMS (ESI): m/z calcd for $C_{16}H_{18}ClNNaO_3$ $[M+Na]^+$ 330.0867; Found 330.0871.

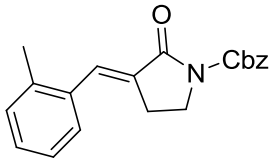


(*E*)-*tert*-Butyl 3-(3-fluorobenzylidene)-2-oxopyrrolidine-1-carboxylate (**1m**): This compound was prepared from 3-fluoro benzaldehyde (0.62 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent. 873 mg (60%); white solid; m.p. 148-150 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.48 (t, *J* = 3.0 Hz, 1H), 7.40 (m, 1H), 7.26 (d, *J* = 7.8 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.07 (m, 1H), 3.86 (t, *J* = 7.2 Hz, 2H), 3.03 (td, *J* = 7.2, 3.0 Hz, 2H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.3, 163.6 (d, *J* = 244.0), 150.7, 137.2 (d,

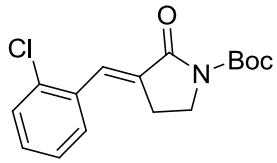
J = 8.5 Hz), 132.7, (d, *J* = 2.85 Hz), 131.3, 130.3 (d, *J* = 8.5 Hz), 126.0, 116.23 (d, *J* = 24.3Hz), 116.21 (d, *J* = 21.4 Hz), 83.1, 43.2, 28.0, 23.2; IR (neat): 2978, 2924, 1763, 1645, 1580, 1367, 1296, 1282, 1156 cm^{-1}; HRMS (ESI): m/z calcd for $C_{16}H_{18}FNNaO_3$ $[M+Na]^+$ 314.1163; Found 314.1168.



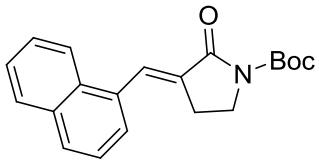
(*E*)-*tert*-Butyl 3-(2-methylbenzylidene)-2-oxopyrrolidine-1-carboxylate (**1n**): This compound was prepared from 2-methyl benzaldehyde (0.60 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent. 830 mg (58%); white solid; m.p. 86-88 ^oC; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.73 (t, *J* = 3.0 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.28-7.21 (m, 3H), 3.80 (dd, *J* = 6.6, 7.8 Hz, 2H), 2.98 (td, *J* = 7.8, 3.0 Hz, 2H), 2.39 (s, 3H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.6, 150.8, 138.4, 133.8, 132.0, 130.7, 130.6, 129.0, 128.0, 125.8, 82.9, 43.4, 28.0, 23.2, 19.9; IR (neat): 2978, 2930, 1773, 1731, 1713, 1647, 1366, 1312, 1292, 1249, 1154 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{21}NNaO_3$ $[M+Na]^+$ 310.1414; Found 310.1418.



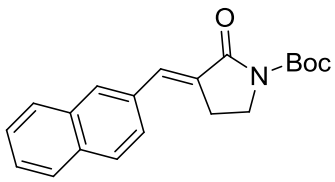
(*E*)-Benzyl 3-(2-methylbenzylidene)-2-oxopyrrolidine-1-carboxylate (**1o**): This compound was prepared from 2-methyl benzaldehyde (0.60 g, 5.0 mmol) according to the Procedure A followed by the Procedure C. The compound was purified by column chromatography on silica gel using 50-100% CH_2Cl_2 in hexanes as eluent. 720 mg (45%); white solid; m.p. 117-119 ^oC; ^1H NMR ($CDCl_3$, 600 MHz): δ 7.57 (t, *J* = 3.0 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.39-7.31 (m, 4H), 7.26-7.20 (m, 3H), 5.33 (s, 2H), 3.85 (t, *J* = 7.2 Hz, 2H), 2.98 (td, *J* = 7.2, 3.0 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.4, 152.2, 138.5, 135.3, 133.6, 132.7, 130.6, 130.1, 129.2, 128.5, 128.3, 128.1 (2C), 125.8, 68.1, 43.4, 23.3, 19.9; IR (neat): 3030, 2916, 1777, 1717, 1644, 1484, 1382, 1297, 1278, 1216, 1096 cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{19}NNaO_3$ $[M+Na]^+$ 344.1257; Found 344.1259.



(E)-tert-Butyl 3-(2-chlorobenzylidene)-2-oxopyrrolidine-1-carboxylate (**1p**): This compound was prepared from 2-chloro benzaldehyde (0.70 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent. 840 mg (55%); white solid; m.p. 171-175 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.85 (t, *J* = 3.0 Hz, 1H), 7.47-7.43 (m, 2H), 7.32-7.28 (m, 2H), 3.81 (dd, *J* = 6.6, 7.8 Hz, 2H), 2.96 (td, *J* = 7.8, 3.0 Hz, 2H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.0, 150.9, 135.4, 133.4, 132.7, 130.5, 130.2, 130.1, 129.4, 126.7, 83.2, 43.4, 28.1, 23.2; IR (neat): 2980, 2932, 1776, 1751, 1716, 1383, 1368, 1312, 1285, 1253, 1153 cm^{-1}; HRMS (ESI): m/z calcd for $C_{16}H_{18}ClNNaO_3$ $[M+Na]^+$ 330.0867; Found 330.0870.

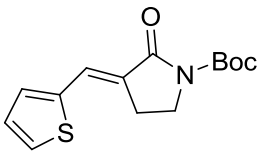


(*E*)-t*ert*-Butyl 3-(naphthalen-1-ylmethylene)-2-oxopyrrolidine-1-carboxylate (**1q**): This compound was prepared from 1-naphthaldehyde (0.78 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent. 516 mg (32%); brownish amorphous solid; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.25 (t, *J* = 3.0 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.88 (dd, *J* = 7.2, 9.0 Hz, 2H), 7.57-7.50 (m, 3H), 7.49 (m, 1H), 3.82 (t, *J* = 6.6 Hz, 2H), 2.96 (td, *J* = 7.8, 3.0 Hz, 2H), 1.59 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.5, 151.0, 133.7, 132.6, 131.9(9), 131.9(6), 131.5, 129.7, 128.7, 126.8, 126.4, 126.3, 125.1, 124.0, 83.0, 43.4, 28.0, 23.3; IR (neat): 2978, 2930, 1772, 1715, 1647, 1475, 1367, 1311, 1292, 1153 cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{21}NNaO_3$ $[M+Na]^+$ 346.1414; Found 346.1422.

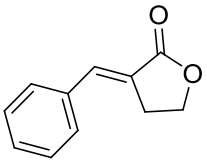


(*E*)-*tert*-Butyl 3-(naphthalen-2-ylmethylene)-2-oxopyrrolidine-1-carboxyl ate (**1r**): This compound was prepared from 2-naphthaldehyde (0.78 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent. 790 mg (49%); white solid; m.p. 187-189 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.94 (s, 1H), 7.88-7.80 (m, 3H), 7.67 (m, 1H), 7.59 (m, 1H), 7.53-7.49 (m, 2H), 3.86 (dd, *J* = 6.6, 7.2 Hz, 2H), 3.15 (td, *J* =

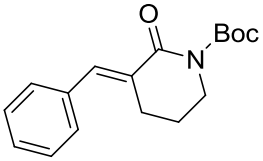
7.8, 3.0 Hz, 2H), 1.57 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.8, 150.9, 134.2, 133.4, 133.3, 132.7, 130.5, 130.2, 128.6, 128.5, 127.7, 127.2, 126.7(6), 126.7(3), 82.9, 43.3, 28.0, 23.4; IR (neat): 3014, 2574, 1758, 1639, 1367, 1304, 1163 cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{21}NNaO_3$ $[M+Na]^+$ 346.1414; Found 346.1421.



(*E*)-*tert*-Butyl 2-oxo-3-(thiophen-2-ylmethylene)pyrrolidine-1-carboxylate (**1s**): This compound was prepared from 2-thiophenecarboxaldehyde (0.56 g, 5.0 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 10-15% ethyl acetate in hexanes as eluent. 0.80 mg (58%); white solid; m.p. 145-147 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.73 (t, *J* = 3.0 Hz, 1H), 7.53 (d, *J* = 6.6 Hz, 1H), 7.32 (d, *J* = 3.2 Hz, 1H), 7.14 (m, 1H), 3.87 (dd, *J* = 7.2, 7.8 Hz, 2H), 2.93 (td, *J* = 7.2, 3.0 Hz, 2H), 1.56 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 167.4, 150.7, 139.3, 131.7, 129.6, 127.9, 127.5, 126.9, 82.9, 43.2, 28.0, 23.0; IR (neat): 3063, 3012, 2976, 2917, 1755, 1721, 1704, 1638, 1363, 1332, 1316, 1253, 1157 cm^{-1}; HRMS (ESI): m/z calcd for $C_{14}H_{17}NNaO_3S$ $[M+Na]^+$ 302.0821; Found 302.0822.

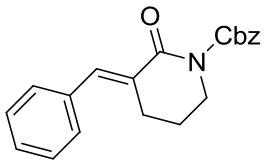


(*E*)-3-Benzylidenedihydrofuran-2(3*H*)-one[2] (**1t**): 320 mg (81%); white solid; m.p. 110-112 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.58 (t, *J* = 3.0 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 2H), 7.48-7.43 (m, 2H), 7.41 (m, 1H), 4.47 (dd, *J* = 6.6, 7.8 Hz, 2H), 3.26 (td, *J* = 7.8, 3.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 172.4, 136.5, 134.5, 129.9, 129.7, 128.8, 123.4, 65.3, 27.3; IR (neat): 3085, 3028, 2994, 1741, 1651, 1452, 1386, 1364, 1226, 1193, 1182, 1060, 1023 cm^{-1}; HRMS (ESI): m/z calcd for $C_{11}H_{10}NaO_2$ $[M+Na]^+$ 197.0573; Found 197.0572.



(*E*)-*tert*-Butyl 3-benzylidene-2-oxopiperidine-1-carboxylate (**1u**): This compound was prepared from benzaldehyde (0.53 g, 5.0 mmol) and trifluoroacetyl piperidinone (0.98g, 5 mmol) according to the Procedure A followed by the Procedure B. The compound was purified by column chromatography on silica gel using 5-10% ethyl acetate in hexanes as eluent. 0.89 g (62%); white solid; m.p. 90-92 ^{o}C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.87

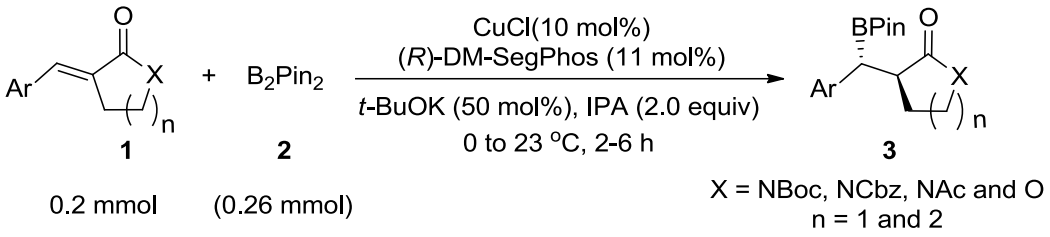
(t, *J* = 3.0 Hz, 1H), 7.41-7.38 (m, 4H), 7.32 (m, 1H), 3.77-3.74 (m, 2H), 2.82-2.78 (m, 2H), 1.91-1.84 (m, 2H), 1.56 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 165.7, 153.1, 138.4, 135.6, 130.7, 129.9, 128.5, 128.3, 82.9, 45.9, 28.0, 26.2, 25.4; IR (neat): 2978, 2938, 1762, 1713, 1615, 1392, 1368, 1295, 1270, 1149 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{21}NNaO_3$ $[M+Na]^+$ 310.1414; Found 310.1417.



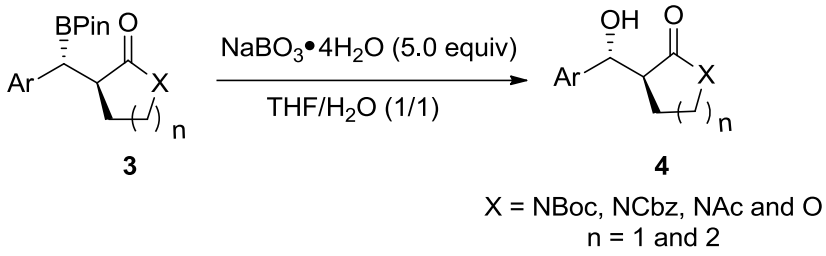
(*E*)-Benzyl 3-benzylidene-2-oxopiperidine-1-carboxylate (**1v**): This compound was prepared from benzaldehyde (0.53g, 5.0 mmol) and trifluoroacetyl piperidinone (0.98g, 5 mmol) according to the Procedure A followed by the Procedure C. The compound was purified by column chromatography on silica gel using 50-100% CH_2Cl_2 in hexanes as eluent. 860 mg (54%); white solid; m.p. 150-152 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.89 (t, *J* = 1.8 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.41-7.30 (m, 8H), 5.33 (s, 2H), 3.85-3.31 (m, 2H), 2.83-2.78 (m, 2H), 1.92-1.86 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 165.6, 154.4, 139.0, 135.4(8), 135.4(4), 130.4, 129.9, 128.6, 128.5, 128.3, 128.2, 128.0, 68.5, 46.3, 26.1, 22.4; IR (neat): 2940, 2870, 1710, 1686, 1608, 1383, 1288, 1255, 1168 cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{19}NNaO_3$ $[M+Na]^+$ 344.1257; Found 344.1259.

Procedure D for Catalytic Asymmetric Boronate Conjugate Addition to Alkylidene Lactams

An oven dried Schlenk flask charged with Cu(I)Cl (0.02 mmol, 10 mol%), (*R*)-DM-Segphos (0.022 mmol, 11 mol%), bis(pinacolato)diboron **2** (0.26 mmol) was purged with argon (evacuated and backfilled with argon three times). Anhydrous THF (2 mL) was added to this flask and allowed to stir at room temperature for 30 min. The reaction was then cooled to 0 °C and potassium *tert*-butoxide (0.1 mmol, 50 mol%) was carefully added under argon flow. After 5 min, alkylidene lactam (**1**, 0.2 mmol) was added and continued to stir for 5 min followed by the addition of anhydrous isopropyl alcohol (30 µL, 0.4 mmol). After stirring for 15 min, the reaction was warmed to room temperature and stirred until the starting material was fully consumed by TLC (for 2-6 h, TLC eluent: 20% acetone in hexanes). The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel.



Procedure E for Oxidation of Boronate Adducts to Alcohols



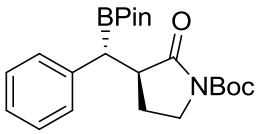
To a solution of pinacolatoboron **3** (0.1 mmol) in 2 mL of THF/water (1/1) was added sodium perborate tetrahydrate (0.5 mmol, 5 equiv) and stirred for 2 h. The reaction was then diluted with water (5 mL) and ethyl acetate (5 mL). The organic layer was separated, and aqueous layer was extracted with ethyl acetate (2x5 mL). Organic layers were combined, dried over sodium sulfate, concentrated and the corresponding alcohol product was isolated by column chromatography on silica gel with 100% CH_2Cl_2 as eluent.

1.0 mmol Scale Reaction for the Synthesis of Compound 3a

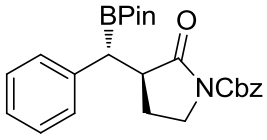
An argon purged oven dried two-neck round bottom flask was filled with Cu(I)Cl (9.8 mg, 0.1 mmol, 10 mol%), (*R*)-DM-SegPhos (79 mg, 0.11 mmol, 11 mol%) and bis(pinacolato)diboron **2** (330 mg, 1.3 mmol) and then the flask was evacuated and backfilled with argon three time. Anhydrous THF (10 mL) was added to this flask and the solution was stirred for 30 min. The reaction was cooled down to 0 ℃ and a solution of potassium *tert*-butoxide (0.5 mL, 1M in THF) was added dropwise. After 5 min, a solution of **1a** (273 mg, 1.0 mmol) in 1.0 mL dry THF was added and the solution was stirred for 10 min followed by the addition of anhydrous isopropyl alcohol (0.15 mL, 2 mmol). After 15 min stirring at this temperature, the solution was warmed to room temperature and stirred for 3 h. The solvent was removed under reduced

pressure and the residue was purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 352 mg (88%), dr 95:5, 92% ee. The NMR data are consistent with the characterization data of **3a** from the 0.2 mmol scale.

Characterization Data for the Compounds in Scheme 3

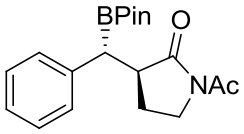


(*S*)-*tert*-Butyl 2-oxo-3-((*R*)-phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl)pyrrolidine-1-carboxylate (**3a**): The compound was synthesized using **1a** (55 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 73 mg (91%); dr 95:5; 94% ee; white solid; m.p. 145-147 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.26-7.20 (m, 4H), 7.15 (m, 1H), 3.65 (m, 1H), 3.43 (td, *J* = 11.4, 7.2 Hz, 1H), 3.18 (td, *J* = 11.4, 8.4 Hz, 1H), 2.36 (d, *J* = 11.4 Hz, 1H), 1.86 (m, 1H), 1.49-1.51 (m, 1H), 1.50 (s, 9H), 1.22 (s, 6H), 1.19 (s, 6H);^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.8, 150.0, 139.6, 128.6, 128.4, 125.8, 83.5, 82.4, 47.0, 44.6, 27.9, 24.9, 24.7, 24.3; HPLC conditions: IA column, 2-propanol/hexanes = 3/97, flow rate 1.0 mL/min, retention time = 8.07 min (minor) and 8.84 min (major); IR (neat): 2979, 2932, 1781, 1746, 1717, 1508, 1369, 1317, 1153, 1233 cm^{-1}; HRMS (ESI): m/z calcd for $C_{22}H_{32}BNO_5Na$ $[M+Na]^+$ 424.2266; Found 424.2270.



(*S*)-Benzyl 2-oxo-3-((*R*)-phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) methyl)pyrrolidine-1-carboxylate (**3b**): The compound was synthesized using **1b** (62 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 78 mg (89%); dr 96:4; 94% ee; white solid; m.p. 117-118 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.42 (d, *J* = 7.2 Hz, 2H), 7.38-7.30 (m, 3H), 7.27-7.20 (m, 4H), 7.16 (m, 1H), 5.28 (d, *J* = 12.6 Hz, 1H), 5.25 (d, *J* = 12.6 Hz, 1H), 3.73 (m, 1H), 3.52 (m, 1H), 3.21 (td, *J* = 10.8, 8.4 Hz, 1H), 2.40 (d, *J* = 10.8 Hz, 1H), 1.90 (m, 1H), 1.54 (m, 1H), 1.23 (s, 6H), 1.20 (m, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.6, 151.3, 139.3, 135.4, 128.7, 128.4 (2C), 128.2, 128.1, 125.9, 83.6, 67.7, 46.9, 44.6, 24.8, 24.6, 24.4; HPLC conditions: AD-H column, 2-propanol/hexanes = 3/97, flow rate 1.0

mL/min, 220 nm, retention time = 21.04 min (major) and 29.15 min (minor); IR (neat): 2977, 2930, 1787, 1748, 1723, 1453, 1359, 1302, 1277, 1141, 1037 cm^{-1}; HRMS (ESI): m/z calcd for $C_{25}H_{31}BNO_5$ $[M+H]^+$ 436.2290; Found 436.2295.



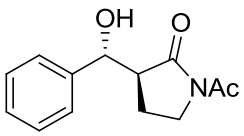
(*S*)-1-Acetyl-3-((*R*)-phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl) pyrrolidin-2-one (**3c**): The compound was synthesized using **1c** (43 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 60 mg (87%); dr 66:34;

NMR data for major diastereomer ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.30-7.10 (m, 5H), 3.83 (m, 1H), 3.44 (m, 1H), 3.28 (m, 1H), 2.51 (s, 3H), 2.41 (d, *J* = 10.2 Hz, 1H), 1.98 (m, 1H), 1.55 (m, 1H), 1.24 (s, 6H), 1.21 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 177.2, 171.4 139.3, 129.7, 128.7, 126.1, 83.7, 47.8, 43.4, 24.9, 24.7, 24.5(9), 24.5(3).

NMR data for minor diastereomer

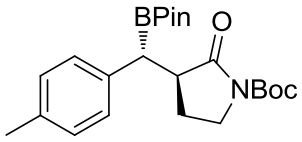
^{1}H NMR ($CDCl_3$, 600 MHz): 7.30-7.10 (m, 5 H), 3.82 (m, 1 H), 3.42 (m, 1 H), 3.08 (m, 1H), 2.87 (d, *J* = 5.4 Hz, 1H), 2.49 (s, 3 H), 2.0-1.94 (m, 2 H), 1.26 (s, 6 H), 1.23 (s, 6 H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 177.0, 171.5, 139.7, 130.2, 128.6, 126.2, 83.9, 47.9, 43.3, 24.9(5), 24.7, 24.53, 22.7.

HPLC conditions: AD-H column, 2-propanol/hexanes = 3/97, flow rate 0.5 mL/min, 220 nm. retention time for major diastereomer = 12.01 (major) and 14.31 (minor), 71% ee; retention time for minor diastereomer = 15.36 min (minor) and 16.28 min (major), 78% ee; IR (neat): 2978, 2932, 1735, 1697, 1495, 1372, 1298, 1142 cm^{-1}; HRMS (ESI): m/z calcd for $C_{19}H_{27}BNO_4$ $[M+H]^+$ 344.2028; Found 344.2026.

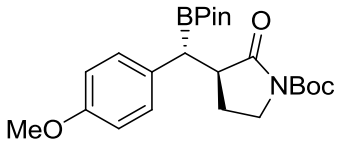


(*S*)-1-Acetyl-3-((*R*)-hydroxy(phenyl)methyl)pyrrolidin-2-one (**4a**): The compound was synthesized using **3c** (35 mg, 0.1 mmol) by the Procedure E and purified by column chromatography on silica gel using CH_2Cl_2 as eluent. 10 mg (43% yield); colorless amorphous solid; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.39-7.36 (m, 4H), 7.30 (m, 1H), 5.41 (d, *J* =

3.6 Hz, 1H), 3.85 (m, 1H), 3.50 (m, 1H), 2.98 (td, *J* = 9.0, 3.6 Hz, 1H), 2.55 (s, 3H), 2.37 (d, *J* = 6.6 Hz, 1H), 2.18 (m, 1H), 1.78 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.6, 171.2, 141.5, 128.5, 127.7, 125.4, 71.2, 51.9, 43.2, 25.0, 16.8; IR (neat): 3480, 2982, 1731, 1488, 1378, 1166, 1051 cm^{-1}; HRMS (ESI): m/z calcd for $C_{13}H_{16}NO_3$ $[M+H]^+$ 234.1125; Found 234.1128.

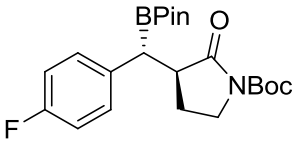


(*S*)-*tert*-Butyl 2-oxo-3-((*R*)-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(*p*-tolyl)methyl)pyrrolidine-1-carboxylate (**3d**): The compound was synthesized using **1e** (58 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 68 mg (82%); dr 94:6; 94% ee; white solid; m.p. 120-123 ℃; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.10 (d, *J* = 8.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 3.63 (m, 1H), 3.42 (m, 1H), 3.12 (td, *J* = 10.8, 7.8 Hz, 1H), 2.31 (d, *J* = 10.8 Hz, 1H), 2.76 (s, 3H), 1.84 (m, 1H), 1.48 (s, 9H), 1.48-1.49 (m, 1H), 1.20 (s, 6H), 1.18 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.9, 150.0, 136.3, 135.2, 129.1, 128.5, 83.4, 82.4, 47.0, 44.6, 29.7, 24.8, 24.7, 24.3, 20.9; HPLC conditions: AD-H column, 2-propanol/hexanes = 2/98, flow rate 1.0 mL/min, 220 nm, retention time = 11.04 min (major) and 13.52 min (minor); IR (neat): 2978, 2930, 1778, 1745, 1716, 1511, 1368, 1317, 1153 cm^{-1}; HRMS (ESI): m/z calcd for $C_{23}H_{34}BNO_5Na$ $[M+Na]^+$ 438.2422; Found 438.2423.

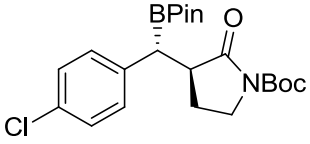


(*S*)-*tert*-Butyl 2-oxo-3-((*R*)-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(*p*-tolyl)methyl)pyrrolidine-1-carboxylate (**3e**): The compound was synthesized using **1f** (61 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 71 mg (82%); dr 95:5; 92% ee; pale yellow amorphous solid; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.15 (d, *J* = 9.0 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 3.77 (s, 3H), 3.64 (m, 1H), 3.44 (td, *J* = 10.8, 6.0 Hz, 1H), 3.10 (m, 1H), 2.33 (d, *J* = 10.8 Hz, 1H), 1.86 (m, 1H), 1.50-1.51 (m, 1H), 1.50 (s, 9H), 1.23 (s, 6H), 1.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): 175.8, 157.7, 149.9, 131.3, 129.6, 113.8, 83.4, 82.4, 55.0, 47.1, 44.6, 27.9, 24.7 (2C), 24.3; HPLC conditions: AD-H column, 2-propanol/hexanes = 2/98, flow rate 1.0 mL/min, 220 nm, retention time =

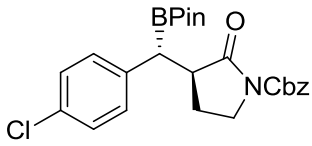
17.40 min (major) and 19.26 min (minor); IR (neat): 2978, 2933, 1718, 1716, 1602, 1510, 1455, 1369, 1317, 1251, 1151 cm^{-1}; HRMS (ESI): m/z calcd for $C_{23}H_{34}BNO_6Na$ $[M+Na]^+$ 432.2552; Found 432.2554.



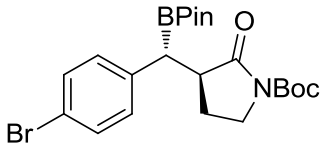
(S)-*tert*-Butyl 3-((*R*)-(4-fluorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2-oxopyrrolidine-1-carboxylate (**3f**): The compound was synthesized using **1g** (58 mg, 0.2 mmol) by the Procedure D and purified column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 73 mg (87%); dr 95:5; 96% ee; white solid; m.p. 168-170 ℃; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.20-7.15 (m, 2H), 6.96-6.90 (m, 2H), 3.65 (m, 1H), 3.42 (m, 1H), 3.09 (m, 1H), 2.34 (d, *J* = 10.8 Hz, 1H), 1.85 (m, 1H), 1.48 (s, 9H), 1.47-1.48 (m, 1H), 1.20 (s, 6H), 1.18 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.7, 162.2 (d, *J* = 242.7 Hz), 150.0, 135.3, 130.1 (d, *J* = 24.1 Hz), 115.4 (d, *J* = 21.6 Hz), 83.7, 82.7, 47.2, 44.7, 28.0, 24.8(8), 24.8(5), 24.4; HPLC conditions: AD-H column, 2-propanol/hexanes = 1/99, flow rate 1.0 mL/min, 220 nm, retention time = 20.38 min (major) and 23.88 min (minor); IR (neat): 2978, 2932, 1781, 1745, 1717, 1508, 1369, 1318, 1153 cm^{-1}; HRMS (ESI): m/z calcd for $C_{22}H_{31}BFNO_5Na$ $[M+Na]^+$ 442.2172; Found 442.2174.



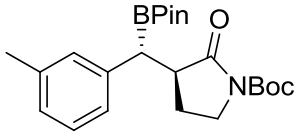
(*S*)-*tert*-Butyl 3-((*R*)-(4-chlorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2-oxopyrrolidine-1-carboxylate (**3g**): The compound was synthesized using **1h** (62 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 76 mg (87%); dr 93:7; 94% ee; white solid; m.p.132-134 ℃; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.25-7.21 (m, 2H), 7.19-7.16 (m, 2H), 3.68 (m, 1H), 3.48 (m, 1H), 3.14 (m, 1H), 2.35 (d, *J* = 10.8 Hz, 1H), 1.87 (m, 1H), 1.50 (s, 9H), 1.48-1.50 (m, 1H), 1.22 (s, 6H), 1.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.5, 149.9, 138.2, 131.6, 130.0, 128.5, 83.7, 82.6, 47.0, 44.6, 27.9, 24.8, 24.7, 24.3; HPLC conditions: IA column, 2-propanol/hexanes = 2/98, flow rate 1.0 mL/min, 220 nm, retention time = 10.38 min (major) and 11.67 min (minor); IR (neat): 2978, 29321, 1781, 1745, 1716, 1490, 1369, 1317, 1141 cm^{-1}; HRMS (ESI): m/z calcd for $C_{22}H_{31}BClNO_5Na$ $[M+Na]^+$ 458.1876; Found 458.1886.



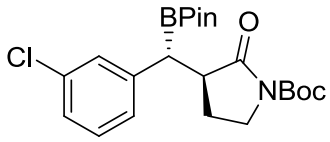
(*S*)-Benzyl 3-((*R*)-(4-chlorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2-oxopyrrolidine-1-carboxylate (**3h**): The compound was synthesized using **1i** (68 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 84 mg (89%); dr 95:5; 95% ee; white solid; m.p.111-113 ℃; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.44-7.39 (m, 2H), 7.38-7.31 (m, 3H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 5.27 (d, *J* = 12.0 Hz, 1H), 5.25 (d, *J* = 12.0 Hz, 1H), 3.74 (m, 1H), 3.52 (m, 1H), 3.17 (m, 1H), 2.38 (d, *J* = 10.8 Hz, 1H), 1.90 (m, 1H), 1.54 (m, 1H), 1.23 (s, 6H), 1.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.3, 151.2, 137.9, 135.3, 131.7, 130.0, 128.6, 128.5, 128.3, 128.1, 83.8, 67.8, 46.8, 44.5, 24.7, 24.6, 24.4; HPLC conditions: IE column, 2-propanol/hexanes = 1/9, flow rate 1.0 mL/min, 220 nm, retention time = 19.11 min (major) and 26.69 min (minor); IR (neat): 2977, 2931, 1787, 1747, 1722, 1490, 1380, 1304, 1141 cm^{-1}; HRMS (ESI): m/z calcd for $C_{25}H_{29}BClNO_5Na$ $[M+Na]^+$ 492.1720; Found 492.1726.



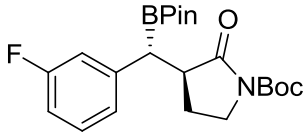
(*S*)-*tert*-Butyl 3-((*R*)-(4-bromophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaboro lan-2-yl)methyl)-2-oxopyrrolidine-1-carboxylate (**3i**): The compound was synthesized using **1j** (70 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 88 mg (91%); dr 94:6; 96% ee; white solid; m.p. 116-118 ℃; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.40-7.36 (m, 2H), 7.14-7.10 (m, 2H), 3.68 (m, 1H), 3.46 (m, 1H), 3.13 (m, 1H), 2.34 (d, *J* = 11.4 Hz, 1H), 1.87 (m, 1H), 1.50 (s, 9H), 1.49-1.50 (m, 1H), 1.22 (s, 6H), 1.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.5, 149.9, 138.7, 131.5, 130.4, 119.6, 83.7, 82.6, 46.9, 44.6, 27.9, 24.8, 24.7, 24.3; HPLC conditions: IA column, 2-propanol/hexanes = 2/98, flow rate 1.0 mL/min, 220 nm, retention time = 10.83 min (major) and 12.80 min (minor); IR (neat): 2977, 2932, 1780, 1745, 1717, 1468, 1368, 1317, 1141 cm^{-1}; HRMS (ESI): m/z calcd for $C_{22}H_{31}BBrNO_5Na$ $[M+Na]^+$ 502.1371; Found 502.1376.



(*S*)-*tert*-Butyl 2-oxo-3-((*R*)-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) (*m*-tolyl)methyl)pyrrolidine-1-carboxylate (**3j**): The compound was synthesized using **1k** (58 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 75 mg (90%); dr 94:6; 90% ee; white solid; m.p. 62-64 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.14 (m, 1H), 7.04 (s, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.2 Hz, 1H), 3.66 (m, 1H), 3.44 (m, 1H), 3.17 (m, 1H), 2.31 (d, *J* = 10.8 Hz, 1H), 2.30 (s, 3H), 1.88 (m, 1H), 1.50 (s, 9H), 1.49-1.50 (m, 1H), 1.22 (s, 6H), 1.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.9, 150.0, 139.4, 137.9, 129.5, 128.2, 126.5, 125.9, 83.5, 82.4, 47.0, 44.6, 27.9, 24.9, 24.7, 24.3, 21.3; HPLC conditions: IA column, 2-propanol/hexanes = 2/98, flow rate 1.0 mL/min, 220 nm, retention time = 8.67 min (minor) and 10.09 min (major); IR (neat): 2978, 2931, 1781, 1747, 1716, 1479, 1369, 1318, 1251, 1141 cm^{-1}; HRMS (ESI): m/z calcd for $C_{23}H_{34}BNO_5Na$ $[M+Na]^+$ 438.2422; Found 438.2433.

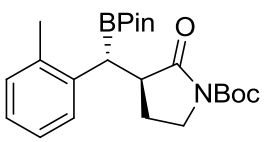


((*S*)-*tert*-Butyl 3-((*R*)-(3-chlorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxa borolan-2-yl)methyl)-2-oxopyrrolidine-1-carboxylate (**3k**): The compound was synthesized using **1l** (68 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 80 mg (92%); dr 94:6; 89% ee; white solid; m.p. 120-123 °C; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.24 (t, *J* = 2.4 Hz, 1H), 7.19 (dd, *J* = 7.2, 7.8 Hz, 1H), 7.16-7.11 (m, 2H), 3.69 (m, 1H), 3.46 (m, 1H), 3.15 (m, 1H), 2.33 (d, *J* = 10.8 Hz, 1H), 1.88 (m, 1H), 1.50 (s, 9H), 1.49-1.50 (m, 1H), 1.23 (s, 6H), 1.21 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.4, 149.8, 141.8, 134.1, 129.6, 128.6, 126.8, 126.0, 83.7, 82.6, 46.9, 44.6, 27.9, 24.8, 24.7, 24.2; HPLC conditions: IA column, 2-propanol/hexanes = 2/98, flow rate 1.0 mL/min, 220 nm, retention time = 9.47 min (minor) and 11.09 min (major); IR (neat): 2978, 2931, 1781, 1747, 1716, 1479, 1369, 1318, 1251, 1141 cm^{-1}; HRMS (ESI): m/z calcd for $C_{22}H_{32}BClNO_5$ $[M+H]^+$ 436.2057; Found 436.2059.



(*S*)-*tert*-Butyl 3-((*R*)-(3-fluorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaboro lan-2-yl)methyl)-2-oxopyrrolidine-1-carboxylate (**3l**): The compound was synthesized using **1m** (58 mg, 0.2 mmol) by the Procedure D and purified by

column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 75mg (90%); dr 95:5; 94% ee; colorless amorphous solid; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.22 (m, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.96 (m, 1H), 6.86 (m, 1H), 3.69 (m, 1H), 3.47 (m, 1H), 3.15 (m, 1H), 2.36 (d, *J* = 10.8 Hz, 1H), 1.89 (m, 1H), 1.51-1.52 (m, 1H), 1.51 (s, 9H), 1.23 (s, 6H), 1.20 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.4, 163.6 (d, *J* = 244.2 Hz), 149.9, 142.3 (d, *J* = 7.2 Hz), 129.8 (d, *J* = 8.7 Hz), 124.4, 115.3 (d, *J* = 20.1Hz), 112.8 (d, *J* = 20.1Hz), 83.7, 82.5, 47.0, 44.6, 27.9, 24.8, 24.7, 24.3; HPLC conditions: IA column, 2-propanol/hexanes = 2/98, flow rate 1.0 mL/min, 220 nm, retention time = 9.68 min (minor) and 11.54 min (major); IR (neat): 2979, 2932, 1781, 1746, 1716, 1612, 1586, 1485, 1370, 1317, 1255, 1141 cm^{-1}; HRMS (ESI): m/z calcd for $C_{22}H_{31}BFNO_5Na$ $[M+Na]^+$ 442.2172; Found 442.2177.



((S)-*tert*-Butyl 2-oxo-3-((*R*)-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) (*o*-tolyl)methyl)pyrrolidine-1-carboxylate (**3m**): The compound was synthesized using **1n** (58 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 76 mg (92%); colorless amorphous solid; dr 74:26.

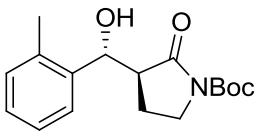
NMR data for major diastereomer

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.24 (m, 1H), 7.17-7.07 (m, 2H), 7.03 (m, 1H), 3.69 (m, 1H), 3.47 (m, 1H), 3.30 (m, 1H), 2.65 (d, *J* = 11.4 Hz, 1H), 2.33 (s, 3H), 1.96 (m, 1H), 1.51 (s, 9H), 1.40 (m, 1H), 1.18 (s, 6H), 1.16 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 176.1, 150.0, 137.9, 136.4, 130.2, 127.3, 125.8, 125.2, 83.3, 82.4, 46.7, 44.6, 27.9, 25.1, 24.6, 24.2, 20.3

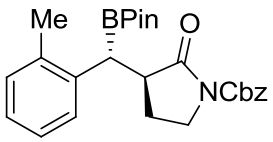
NMR data for minor diastereomer

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.17-7.06 (m, 4H), 3.75 (m, 1H), 3.43 (m, 1H), 3.13 (d, *J* = 4.8 Hz, 1H), 2.92 (m, 1H), 2.32 (s, 3H), 2.01 (m, 1H), 1.51 (s, 9H), 1.44 (m, 1H), 1.25 (s, 6H), 1.22 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.3, 150.4, 138.4, 136.6, 130.3, 129.6, 126.0, 125.8, 83.5, 82.1, 46.2, 44.4, 29.9, 24.8, 24.4, 22.4, 19.7

HPLC conditions: IA column, 2-propanol/hexanes = 2/98, flow rate 1.0 mL/min, 220 nm. retention time for major diastereomer = 6.35 min (minor) and 7.23 min (major), 98% ee; retention time for minor diastereomer: 8.70 (major) and 13.65 (minor), 92% ee; IR (neat): 2978, 2932, 1781, 1746, 1716, 1480, 1369, 1318, 1248, 1142 cm^{-1}; HRMS (ESI): m/z calcd for $C_{23}H_{34}BNO_5Na$ $[M+Na]^+$ 438.2422; Found 438.2433.



(*S*)-*tert*-Butyl 3-((*R*)-hydroxy(*o*-tolyl)methyl)-2-oxopyrrolidine-1-carboxylate (**4b**): The compound was synthesized using **3m** (42mg, 0.1 mmol) by the Procedure E. The crude NMR of the reaction mixture **3m** showed 74/26 dr. The major isomer was obtained by column chromatography on silica gel using 100% CH_2Cl_2 as eluent. 21 mg (69%); colorless amorphous solid; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.41 (d, *J* = 7.2 Hz, 1H), 7.23 (m, 1H), 7.19 (td, J = 7.2, 1.2 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 5.10 (d, *J* = 9.0 Hz, 1H), 4.82 (s, 1H), 3.75 (m, 1H), 3.51 (td, *J* = 10.8, 7.2 Hz, 1H), 3.01 (m, 1H), 2.41 (s, 3H), 1.74 (m, 1H), 1.55 (s, 9H), 1.51 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 177.0, 149.8, 138.1, 135.7, 130.6, 127.9, 126.8, 126.4, 83.5, 71.2, 49.2, 44.5, 27.9, 21.4, 19.5; IR (neat): 3475, 2979, 2931, 1774, 1719, 1369, 1304, 1256, 1152 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{23}NO_4Na$ $[M+Na]^+$ 328.1519; Found 328.1523.



(*S*)-Benzyl 2-oxo-3-((*R*)-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(*o*-tolyl) methyl)pyrrolidine-1-carboxylate (**3n**): The compound was synthesized using **1o** (64 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 53 mg (59%); dr 83:17; colorless amorphous solid;

Data for major diastereomer

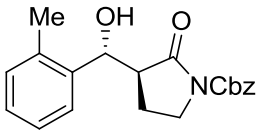
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.42 (d, *J* = 7.8 Hz, 2H), 7.34-7.29 (m, 3H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.19 (dd, *J* = 6.0, 7.2 Hz, 2H), 7.03 (t, *J* = 7.2 Hz, 1H), 5.28 (d, *J* = 12.6 Hz, 1H), 5.25 (d, *J* = 12.6, 1H), 3.75 (m, 1H), 3.53 (m, 1H), 3.32 (m, 1H), 2.65 (d, *J* = 10.8 Hz, 1H), 2.32 (s, 3H), 1.97 (m, 1H), 1.46 (m, 1H),

1.18 (s, 6H), 1.15 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 176.1, 151.5, 137.9, 136.6, 135.6, 130.5, 128.6, 128.4, 128.3, 127.5, 126.1, 125.5, 83.6, 67.9, 46.8, 44.8, 25.3, 24.7, 24.5, 20.6.

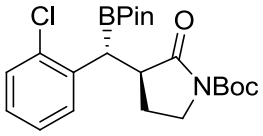
Data for minor diastereomer

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.44-7.40 (m, 2H), 7.34-7.29 (m, 2H), 7.14-7.06 (m, 5H), 5.29-5.22 (m, 2H), 3.81 (m, 1H), 3.50 (m, 1H), 3.13 (d, *J* = 5.4 Hz, 1H), 2.95 (m, 1H), 2.32 (s, 3H), 2.05 (m, 1H), 1.84 (m, 1H), 1.23 (s, 6H), 1.19 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.4, 151.9, 138.3, 136.8, 135.8, 130.7, 129.7, 128.6, 128.3(7), 128.1, 128.2, 126.1, 83.9, 67.8, 46.3, 44.6, 24.9, 24.6, 22.9, 20.0;

HPLC conditions: AD-H column, 2-propanol/hexanes = 5/95, flow rate 1.0 mL/min, 220 nm. retention time for major diastereomer = 8.78 (major) and 12.40 (minor), 99% ee; retention time for minor diastereomer = 10.10 min (major) and 15.53 min (minor), 91% ee; IR (neat): 2975, 2932, 1780, 1740, 1715, 1480, 1368, 1315, 1251, 1142 cm^{-1}; HRMS (ESI): m/z calcd for $C_{26}H_{33}BNO_5$ $[M+H]^+$ 450.2446; Found 450.2448.



(*S*)-Benzyl 3-((*R*)-hydroxy(*o*-tolyl)methyl)-2-oxopyrrolidine-1-carboxylate (**4c**): The compound was synthesized using **3u** (45 mg, 0.1 mmol) by the Procedure E. The crude NMR of the reaction mixture **3u** showed 83/17 dr. The major diastereomer was obtained by column chromatography on silica gel using 100% CH_2Cl_2 as eluent. 27 mg (80%); colorless amorphous solid; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.44 (d, *J* = 7.2 Hz, 2H), 7.42-7.34 (m, 4H), 7.23 (dd, *J* = 6.6, 7.8 Hz, 1H), 7.19 (m, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 5.31 (d, *J* = 12.6 Hz, 1H), 5.30 (d, *J* = 12.6 Hz, 1H), 5.10 (d, *J* = 9.6 Hz, 1H), 4.66 (s, 1H), 3.81 (m, 1H), 3.58 (m, 1H), 3.05 (m, 1H), 2.40 (s, 3H), 1.78 (m, 1H), 1.56 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 176.8, 151.1, 138.0, 135.6, 134.9, 130.7, 128.6, 128.5, 128.3, 128.0, 126.8, 126.5, 71.2, 68.4, 49.1, 44.5, 21.6, 19.5; IR (neat): 3475, 2979, 2920, 1782, 1719, 1456, 1380, 1295 cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{22}NO_4$ $[M+H]^+$ 340.1543; Found 340.1547.



(*S*)-*tert*-Butyl 3-((*R*)-(2-chlorophenyl)(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2-oxopyrrolidine-1-carboxylate (**3o**): The compound was synthesized using **1p** (62mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 76 mg (87 %); dr 62:38; colorless amorphous solid;

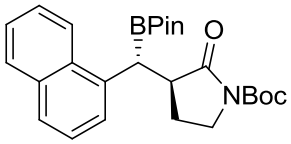
NMR data for major diastereomer

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.45 (m, 1H), 7.33 (m, 1H), 7.18 (m, 1H), 7.09 (m, 1H), 3.71 (m, 1H), 3.45 (m, 1H), 3.18 (m, 1H), 3.06 (d, *J* = 10.2 Hz, 1H), 1.86 (m, 1H), 1.65 (m, 1H), 1.51 (s, 9H), 1.23 (s, 6H), 1.21 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.5, 150.0, 137.8, 134.4, 129.9, 129.6, 126.9, 126.7, 83.6, 82.4, 47.3, 44.5, 27.9, 24.9, 24.7, 24.3.

NMR data for minor diastereomer

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.39 (m, 1H), 7.33 (m, 1H), 7.16 (m, 1H), 7.13 (m, 1H), 3.63 (m, 1H), 3.43 (m, 1H), 3.34 (d, *J* = 4.8 Hz, 1H), 3.15 (m, 1H), 1.95 (m, 1H), 1.76 (m, 1H), 1.49 (s, 9H), 1.27 (s, 12H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.1, 150.1, 137.4, 135.1, 132.0, 129.2, 127.4, 126.8, 83.8, 82.7, 46.4, 44.5, 29.9(8), 24.5, 24.4, 22.3.

HPLC conditions: AD-H column, 2-propanol/hexanes = 2/98, flow rate 1.0 mL/min, 220 nm. retention time for major diastereomer = 7.26 min (minor) and 12.15 min (major), 99% ee; retention time for minor diastereomer = 8.59 (major) and 11.44 (minor), 92% ee; IR (neat): 2979, 2932, 1781, 1746, 1716, 1480, 1368, 1315, 1251, 1142 cm^{-1}; HRMS (ESI): m/z calcd for $C_{22}H_{31}BClNO_5Na$ $[M+Na]^+$ 458.1876; Found 458.1877. (Note: Attempts to separate diastereomers after conversion to alcohol were unsuccessful)



(*S*)-*tert*-Butyl 3-((*R*)-naphthalen-1-yl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2-oxopyrrolidine-1-carboxylate (**3p**): The compound was synthesized using **1q** (65 mg, 0.2 mmol) by the Procedure D and purified by

column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 51 mg (56 %); dr 83:17; colorless amorphous solid;

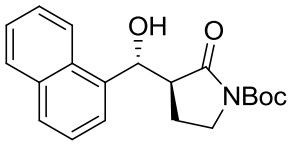
NMR Data for major diastereomer

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.23 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 7.2 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.50-7.42 (m, 3H), 7.39 (t, *J* = 7.8 Hz, 1H), 3.62 (m, 1H), 3.48-3.30 (m, 2H), 3.21 (d, *J* = 10.8 Hz, 1H), 1.82 (m, 1H), 1.50 (s, 9H), 1.46 (m, 1H), 1.18 (s, 6H), 1.12 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 176.1, 150.0, 136.3, 133.9, 132.4, 128.6, 126.3, 125.6, 125.5 (2C), 125.4, 124.2, 83.6, 82.5, 47.1, 44.6, 27.9, 24.9, 24.6, 24.3

NMR Data for minor diastereomer

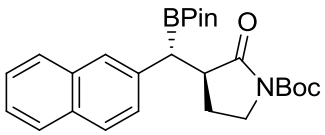
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.11 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.70 (m, 1H), 7.50-7.42 (m, 3H), 7.37 (t, *J* = 7.8 Hz, 1H), 3.80 (m, 1H), 3.70 (m, 1H), 3.63 (m, 1H), 3.09 (m, 1H), 2.01 (m, 1H), 1.58 (s, 9H), 1.45 (m, 1H), 1.28 (s, 6H), 124 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.4, 150.4, 136.2, 134.1, 132.3, 128.9, 128.6, 127.3, 126.9, 126.0, 125.4, 123.4, 83.7, 82.2, 46.7, 44.5, 28.0, 24.6, 24.4, 22.5.

HPLC conditions: IA column, 2-propanol/hexanes = 2/98, flow rate 1.0 mL/min, 220 nm. retention time for major diastereomer = 9.52 min (minor) and 11.31 min (major), 99% ee; retention time for minor diastereomer = 12.40 (major) and 21.05 (minor), 92% ee; IR (neat): 2978, 2931, 1719, 1745, 1716, 1369, 1318, 1260, 1152 cm^{-1}; HRMS (ESI): m/z calcd for $C_{26}H_{34}BNO_5Na$ $[M+Na]^+$ 474.2422; Found 474.2432.

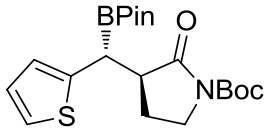


(*S*)-*tert*-Butyl 3-((*R*)-hydroxy(naphthalen-1-yl)methyl)-2-oxopyrrolidine-1-carboxylate (**4d**): The compound was synthesized using **3q** (45 mg, 0.1 mmol) by the Procedure E. The crude NMR of the reaction mixture **3q** showed 83/17 dr. The major isomer was obtained by column chromatography on silica gel using 100% CH_2Cl_2 as eluent. 24 mg (72%) colorless amorphous solid; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.39 (d, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.55-7.45 (m, 3H), 5.52 (d, *J* = 9.6 Hz,

1H), 5.08 (s, 1H), 3.71 (m, 1H), 3.47 (m, 1H), 3.25 (m, 1H), 1.65-1.52 (m, 2H), 1.55 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): 177.0, 149.8, 135.7, 134.0, 131.1, 128.9(4), 128.9 (2C), 126.1, 125.6, 125.2, 123.7, 83.5, 73.0, 49.3, 44.5, 27.9, 21.8; IR (neat): 3464, 2979, 2928, 1773, 1718, 13658, 1309, 1257, 1151 cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{23}NO_4Na$ $[M+Na]^+$ 364.1519; Found 364.1514.

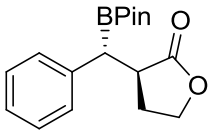


(*S*)-*tert*-Butyl 3-((*R*)-naphthalen-2-yl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2-oxopyrrolidine-1-carboxylate (**3q**): The compound was synthesized using **1r** (65 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 76 mg (87%); dr 95:05; 93% ee (major); white solid; m.p. 78-80 ℃; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.78 (d, *J* = 8.4 Hz, 1H), 7.75 (dd, *J* = 6.0, 8.4 Hz, 2 H), 7.67 (s, 1H), 7.46-7.38 (m, 3H), 3.67 (m, 1H), 3.45 (td, *J* = 10.8, 6.6 Hz, 1H), 3.31 (m, 1H), 2.53 (d, *J* = 12.0 Hz, 1H), 1.85 (m, 1H), 1.53 (m, 1H), 1.51 (s, 9H), 1.22 (s, 6H), 1.19 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.8, 149.9, 137.2, 133.6, 131.9, 127.9, 127.5, 127.4, 127.0(9), 127.0(1), 125.8, 125.1, 83.6, 82.5, 47.0, 44.7, 27.9, 25.0, 24.7, 24.3; HPLC conditions: IC column, 2-propanol/hexanes = 1/9, flow rate 1.0 mL/min, 220 nm, retention time = 8.26 min (minor) and 10.47 min (major); IR (neat): 2978, 2931, 1778, 1744, 1716, 1599, 1477, 1455, 1370, 1317, 1256, 1151 cm^{-1}; HRMS (ESI): m/z calcd for $C_{26}H_{34}BNO_5Na$ $[M+Na]^+$ 474.2422; Found 474.2432.



(*S*)-*tert*-Butyl 2-oxo-3-((*R*)-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)(thiophen-2-yl)methyl)pyrrolidine-1-carboxylate (**3r**): The compound was synthesized using **1s** (56 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 44 mg (54 %); dr 86:14; 74% ee (major); colorless oil; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.11 (d, *J* = 4.8 Hz, 1H), 6.91(m, 1H), 6.85 (d, *J* = 3.6 Hz, 1H), 3.67 (m, 1H), 3.47 (m, 1H), 3.07 (m, 1H), 2.74 (d, *J* = 10.2 Hz, 1H), 1.99 (m, 1H), 1.63 (m, 1H), 1.50 (s, 9H), 1.27 (s, 6H), 1.24 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.3, 150.0, 141.9, 126.9, 125.3, 123.6, 84.0, 82.7, 47.9, 44.7, 28.1, 24.9, 24.7, 24.5; HPLC conditions: IC column, 2-propanol/hexanes = 1/9, flow rate 1.0 mL/min, 220 nm, retention time = 9.22 min (minor) and 14.36 min

(major); IR (neat): 2977, 2918, 1769, 1361, 1326, 1215, 1140 cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{30}BNO_5SNa$ $[M+Na]^+$ 430.1830; Found 430.1840.



(*S*)-3-((*R*)-Phenyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)dihydrofuran-2(3*H*)-one (**3s**): The compound was synthesized using **1t** (35 mg, 0.2 mmol) by the Procedure D and purified by column chromatography on silica gel using 4-6% acetone in hexanes as eluent. 34 mg (56 %); dr 76:24; 56% ee (major); colorless oil.

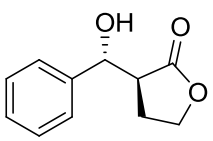
NMR data for major diastereomer

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.33-7.16 (m, 5H), 4.24 (m, 1H), 4.12 (m, 1H), 3.20 (m, 1H), 2.44 (d, *J* = 10.8 Hz, 1H), 2.11 (m, 1H), 1.83 (m, 1H), 1.24 (s, 6H), 1.21 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 179.2, 139.4, 128.7, 128.6, 126.1, 83.9, 67.0, 42.7, 29.1, 24.7, 24.5.

NMR data for minor diastereomer

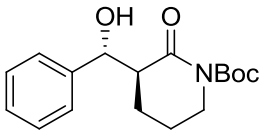
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.33-7.16 (m, 5H), 4.21 (m, 1H), 4.08 (m, 1H), 3.02 (m, 1H), 2.86 (d, *J* = 4.8 Hz, 1H), 2.27 (m, 1H), 2.14 (m, 1H), 1.27 (s, 6H), 1.25 (s, 6H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 178.8, 139.7, 129.7, 128.6(6), 126.3, 84.0, 67.1, 43.1, 27.1, 24.8, 24.6.

HPLC conditions: IA column, 2-propanol/hexanes = 3/97, flow rate 1.0 mL/min, 220 nm, retention time = 19.68 min (minor) and 20.75 min (major); IR (neat): 2977, 2918, 1769, 1361, 1326, 1215, 1140 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{24}BO_4$ $[M+H]^+$ 303.1762; Found 303.1766.

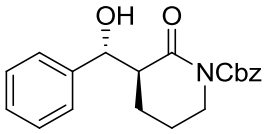


(*S*)-3-((*R*)-Hydroxy(phenyl)methyl)dihydrofuran-2(3*H*)-one (**4e**): The compound was synthesized using **3s** (0.2 mmol) by the Procedure E. The crude NMR of the reaction mixture **3s** showed 76/24 dr. The major diastereomer was obtained by column chromatography on silica gel using 100% CH_2Cl_2 as eluent. 13 mg (66%); colorless amorphous solid; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.41-7.31 (m, 5H), 4.83 (d, *J* = 9.0 Hz, 1H), 4.32 (m, 1H), 4.29 (m, 1H), 4.16 (m, 1H), 2.98 (m, 1H), 2.03-1.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 179.2, 140.2, 128.7, 128.4, 126.5,

74.6, 67.0, 46.2, 25.8; IR (neat): 3468, 2983, 2916, 1757, 1453, 1378, 1214, 1171, 1017 cm^{-1}; HRMS (ESI): m/z calcd for $C_{11}H_{13}O_3$ $[M+H]^+$ 193.0859; Found 193.0861.



(*S*)-*tert*-Butyl 3-((*R*)-hydroxy(phenyl)methyl)-2-oxopiperidine-1-carboxylate (**4f**): The compound was synthesized using **1u** (58 mg, 0.2 mmol) according to the Procedure D followed by The Procedure E. Due to the stability issue of the borylated product during column chromatography, the reaction mixture was directly subjected to the oxidation condition after the reaction was completed. The crude NMRs of the reaction mixtures for both borylation step as well as oxidation step showed 90/10 dr. The major diastereomer was obtained by column chromatography on silica gel using 100% CH_2Cl_2 as eluent. 38 mg (62%); 74% ee; colorless amorphous solid; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.37-7.28 (m, 5H), 4.95 (s, 1H), 4.83 (d, *J* = 9.0 Hz, 1H), 3.77 (m, 1H), 3.54 (m, 1H), 2.64 (m, 1H), 1.77 (m, 1H), 1.71 (m, 1H), 1.40-1.28 (m, 2H), 1.55 (s, 9H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.5, 152.2, 140.7, 128.5, 128.1, 127.2, 83.6, 75.5, 50.1, 45.4, 28.0, 23.3, 21.6; HPLC conditions: OD-H column, 2-propanol/hexanes = 1/9, flow rate 1.0 mL/min, 220 nm, retention time = 8.70 min (major) and 11.35 min (minor); IR (neat): 3482, 3027, 2956, 2922, 1768, 1716, 1454, 1378, 1287, 1251, 1168 cm^{-1}; HRMS (ESI): m/z calcd for $C_{17}H_{23}NO_4Na$ $[M+Na]^+$ 328.1519; Found 328.1525.



(*S*)-Benzyl 3-((*R*)-hydroxy(phenyl)methyl)-2-oxopiperidine-1-carboxylate (**4g**): The compound was synthesized using **1v** (64 mg, 0.2 mmol) according to The Procedure D followed by the Procedure E. Due to the stability issue of the borylated product during column chromatography, the reaction mixture was directly subjected to the oxidation condition after the reaction was completed. The crude NMRs of the reaction mixtures for both borylation step as well as oxidation step showed 76/24 dr. The major diastereomer was isolated by column chromatography on silica gel using 100% CH_2Cl_2 as eluent. 40 mg (58%); 80% ee; colorless amorphous solid; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.44 (d, *J* = 7.8 Hz, 2H), 7.38 (dd, *J* = 7.2, 7.8 Hz, 2H), 7.36-7.27 (m, 6H), 5.30 (s, 2H), 4.84 (dd, *J* = 2.4, 9.0 Hz, 1H), 4.73 (d, *J* = 2.4 Hz, 1H), 3.87 (m, 1H), 3.62 (m, 1H), 2.68 (m, 1H), 1.80 (m, 1H), 1.68 (m, 1H), 1.37 (m, 1H), 1.29 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz): δ 175.3,

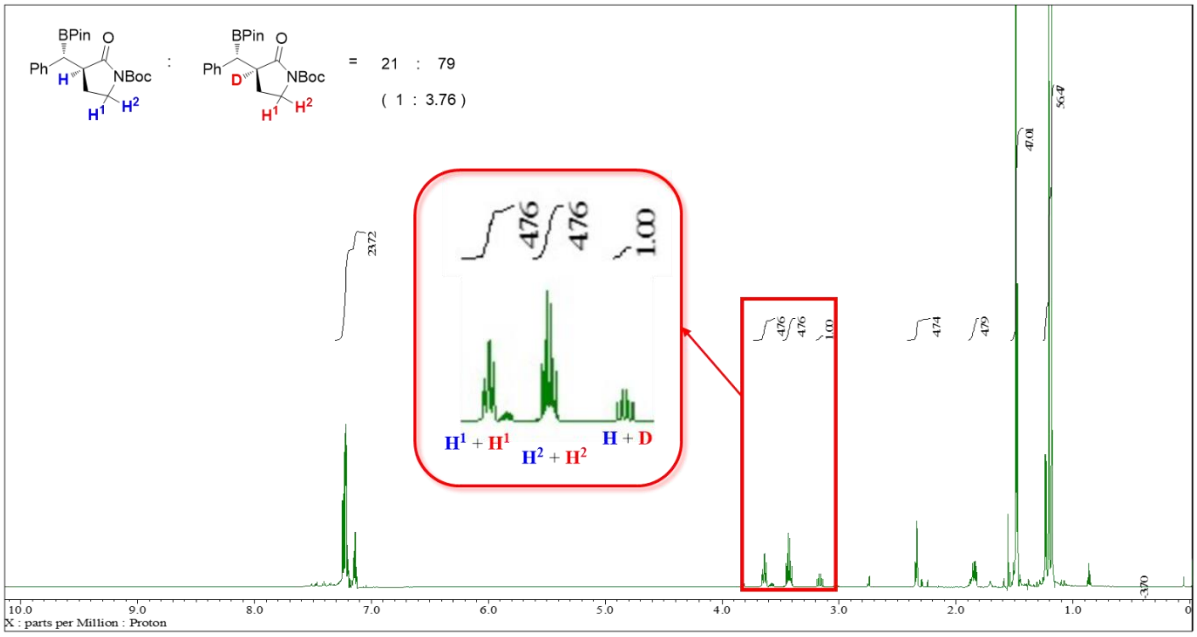
153.5, 140.4, 135.1, 128.6, 128.4 (2C), 128.2, 128.1, 127.0, 75.2, 68.8, 50.2, 45.5, 23.1, 21.4; HPLC conditions: OD-H column, 2-propanol/hexanes = 2/8, flow rate 1.0 mL/min, 220 nm, retention time = 8.07 min (minor) and 9.80 min (major); IR (neat): 3482, 3027, 2956, 2922, 1768, 1716, 1454, 1378, 1287, 1251, 1168 cm^{-1}; HRMS (ESI): m/z calcd for $C_{20}H_{22}NO_4$ $[M+H]^+$ 340.1543; Found 340.1546.

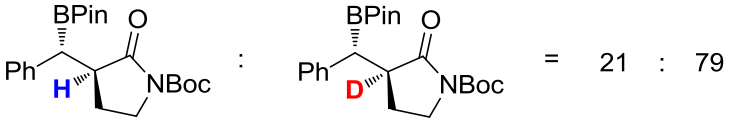
References

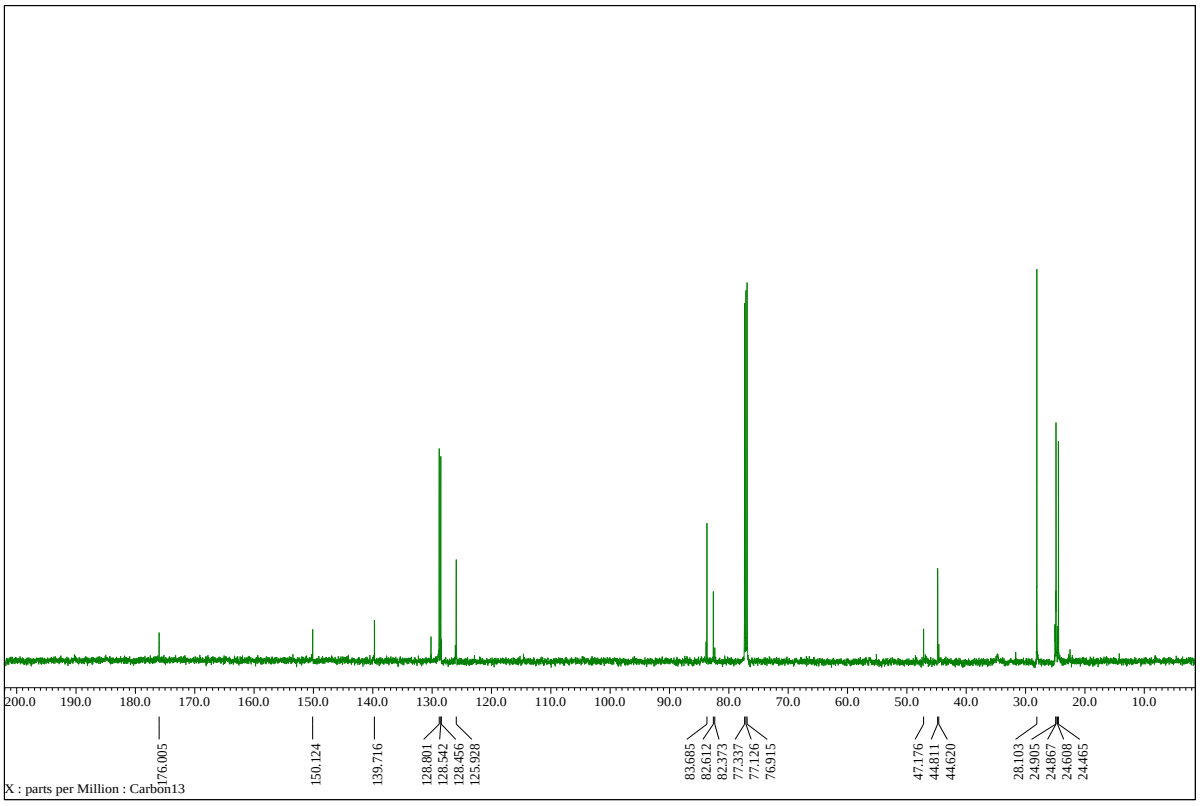
1. Liu, X.; Han, Z.; Wang, Z.; Ding, K. *Angew. Chem. Int. Ed.* **2014**, *53*, 1978-1982.

2. Tian, F.; Yao, D.; Liu, Y.; Xie, F.; Zhang, W. *Adv. Synth. Catal.* **2010**, *352*, 1841-1845.

Control Experiment with Isopropanol-D_8



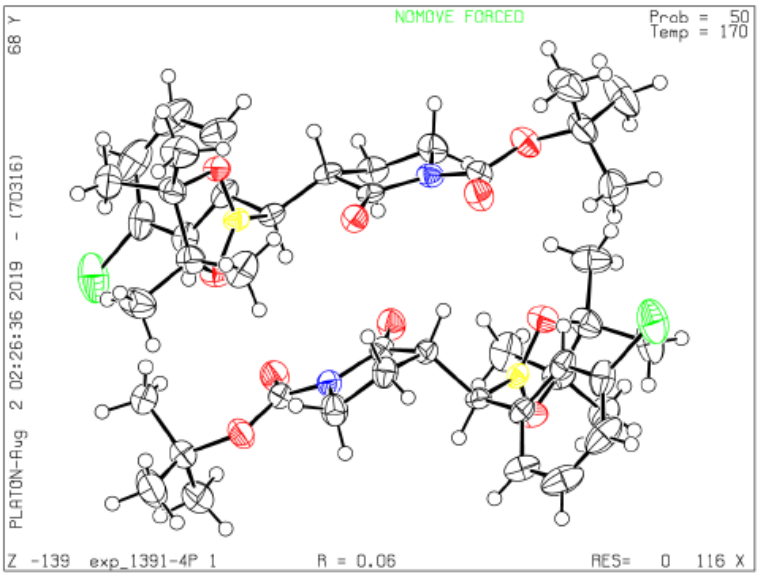




X-Ray Analysis of Compound 3k

X-Ray Crystal Data of Compound **3k** (**CCDC 1949071**)

Bond precision:	C-C = 0.0069 A	Wavelength=0.71073	
Cell:	a=9.0828(2)	b=9.6899(3)	c=14.3986(3)
	alpha=80.540(2)	beta=81.788(2)	gamma=71.284(2)
Temperature: 170 K			
	Calculated		Reported
Volume	1178.39(5)		1178.39(5)
Space group	P 1		P 1
Hall group	P 1		P 1
Moiety formula	C_{22} H_{31} B Cl N O_5		2(C_{22} H_{31} B Cl N O_5)
Sum formula	C_{22} H_{31} B Cl N O_5		C_{44} H_{62} B_2 Cl_2 N_2 O_{10}
Mr	435.74		871.47
Dx, g cm^{-3}	1.228		1.228
Z	2		1
Mu (mm^{-1})	0.193		0.193
F000	464.0		464.0
F000’	464.51		
h,k,l max	12,13,20		12,12,19
Nref	13346[6673]		11142
Tmin,Tmax	0.939,0.949		0.849,1.000
Tmin’ 0.939			
Correction method=	# Reported T Limits:	Tmin=0.849	Tmax=1.000
AbsCorr = MULTI-SCAN			
Data completeness	=	1.67/0.83	Theta(max)= 29.671
R(reflections)= 0.0602(9128)		wR2(reflections)= 0.1509(11142)	
S = 1.053		Npar= 555	


NOMOVE FORCED
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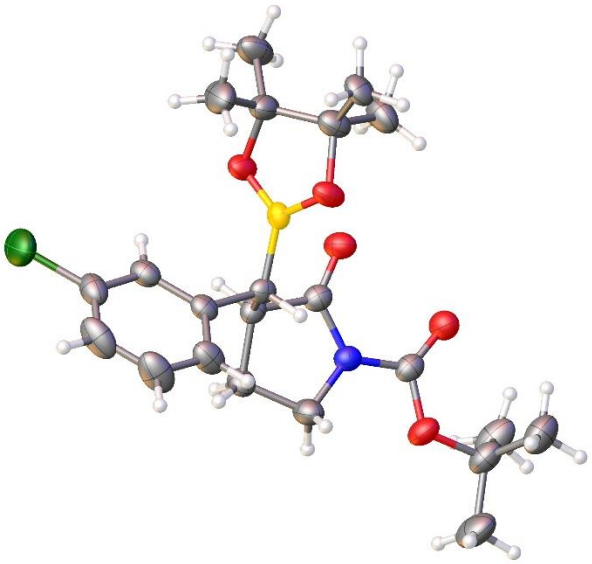
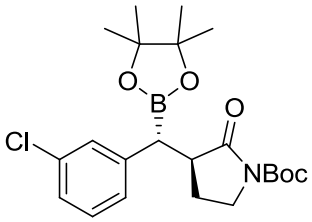
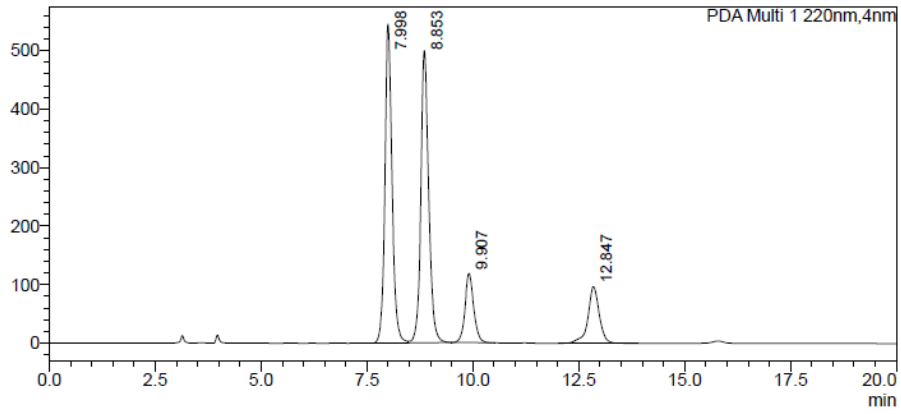
68 Y
PLATON-Aug 2 02:26:36 2019 - (70316)
Z -139 exp_1391-4P 1
R = 0.06
RES= 0 116 X




O
B
O
O
Cl
NBoc

HPLC Traces of Enantioenriched Compounds



<Peak Table>

PDA Ch1 220nm

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3	9.907	1683941	118227	10.291
4	12.847	1810322	96933	11.063
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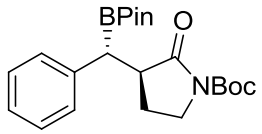
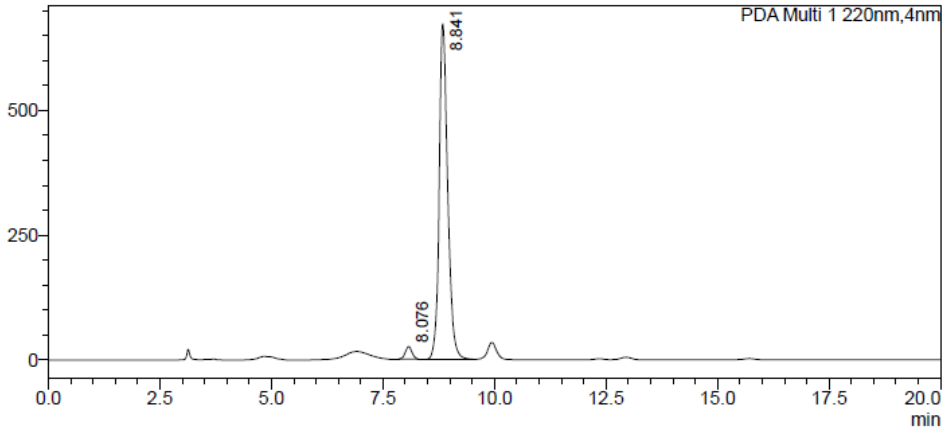


3a

(IA column, IPA/hexanes: 2/98, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 220nm

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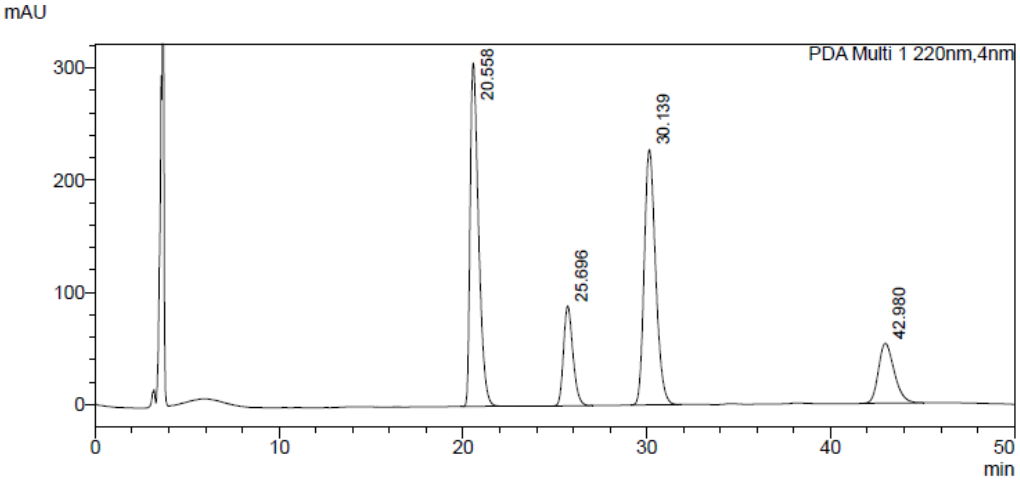

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PDA Ch1 220nm

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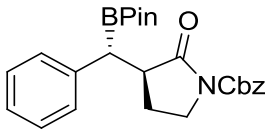
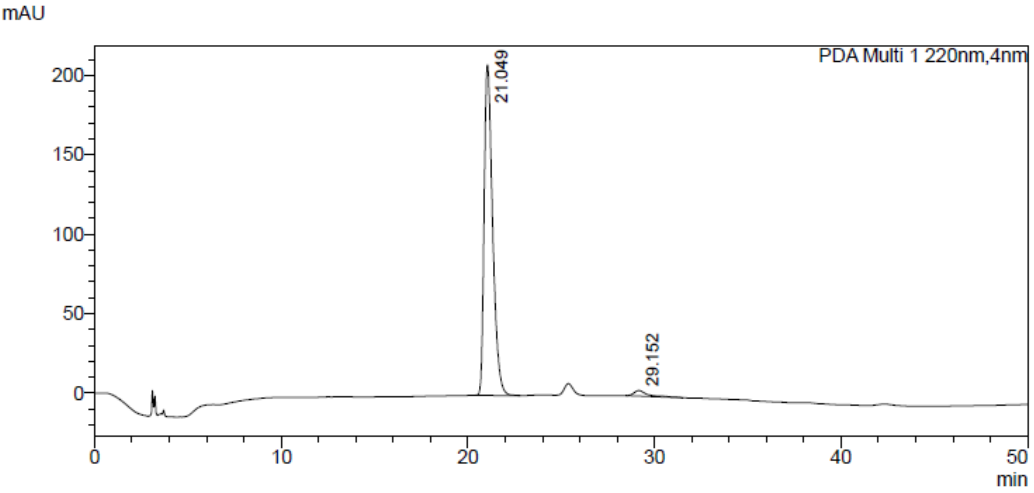


3b

(AD-H column, IPA/hexanes: 3/97, flow rate 1.0 mL/min)



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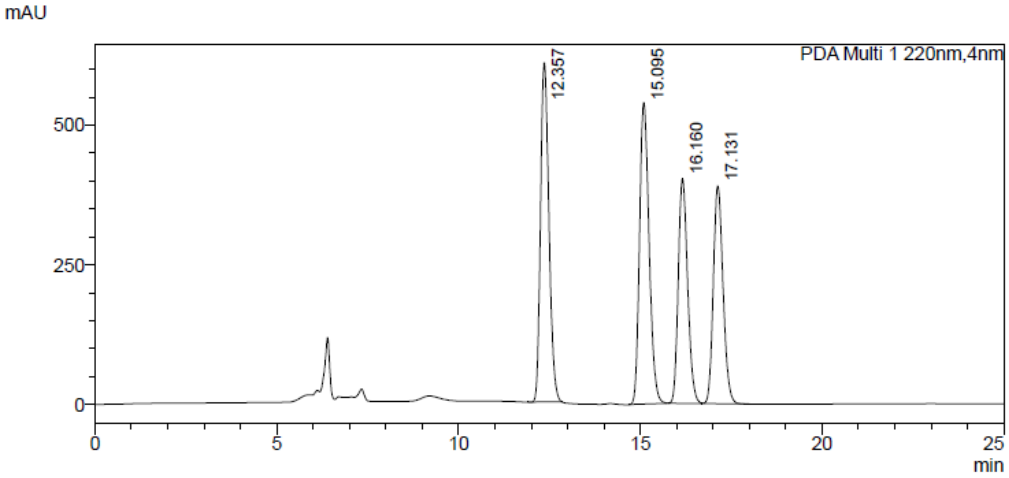

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PDA Ch1 220nm

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1	12.357	9769589	606781	28.451
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3	16.160	7195180	402597	20.954
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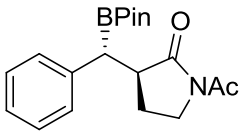
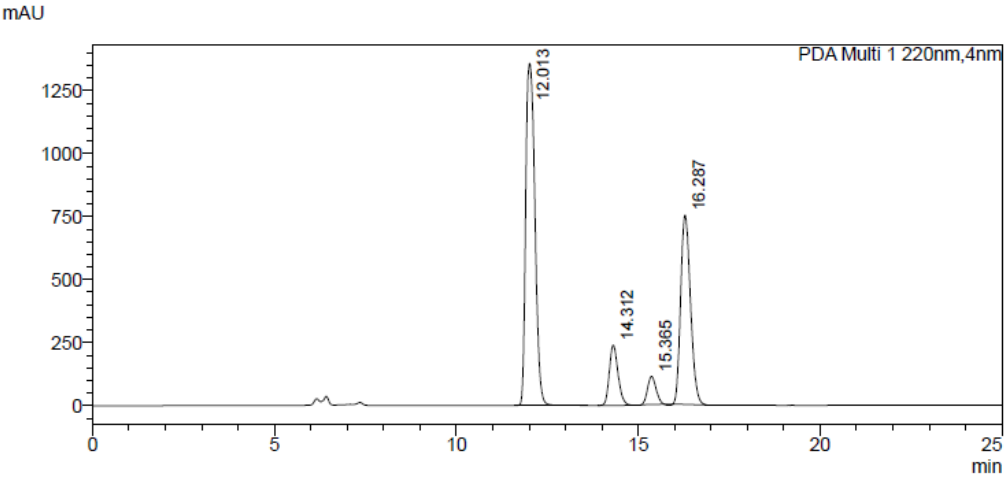
5	48.733	223094	2412	0.650
Total		34338052	1941934	100.000



3c

(AD-H column, IPA/hexanes: 3/97, flow rate 0.5 mL/min)



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1	12.013	23787742	1356795	54.414
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4	16.287	14154600	750537	32.378
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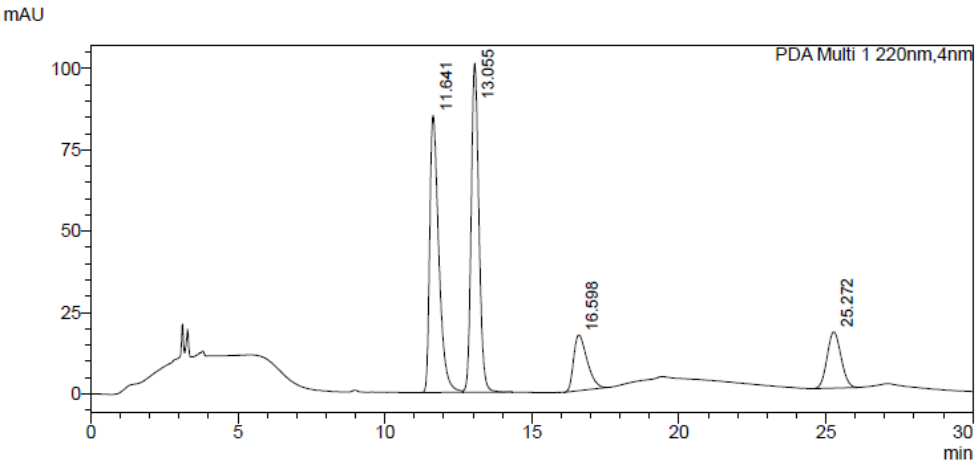

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PDA Ch1 220nm

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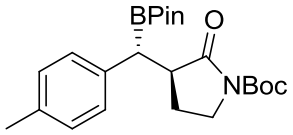
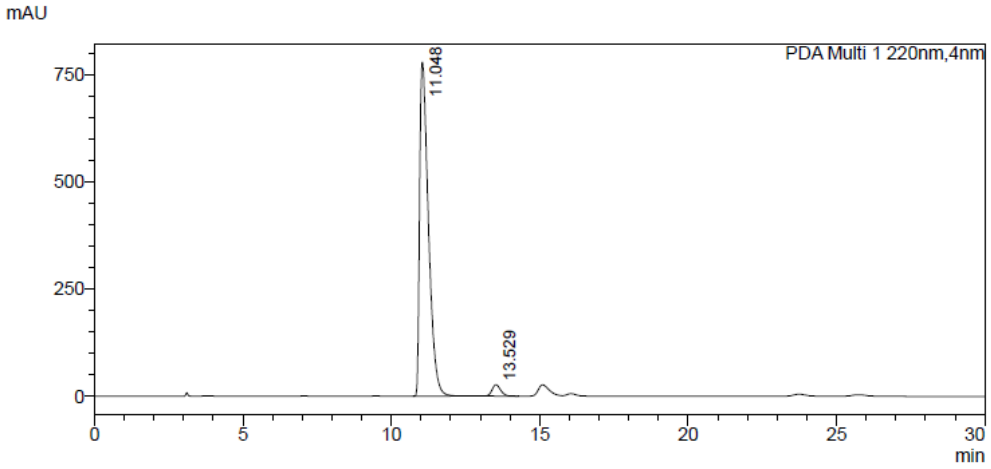
3	16.598	544486	17113	11.362
4	25.272	566834	17265	11.828
Total		4792248	220554	100.000



3d

(AD-H column, IPA/hexanes: 2/98, flow rate 1.0 mL/min)



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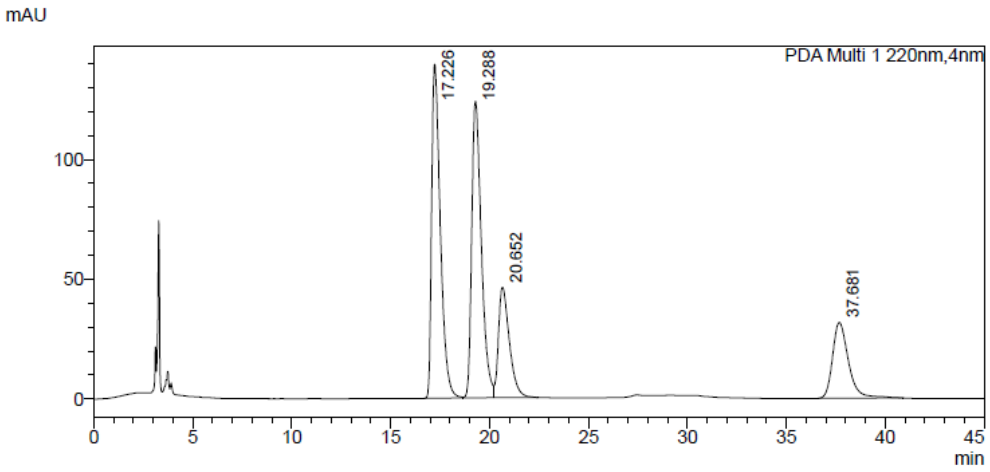

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PDA Ch1 220nm

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1	17.226	4250146	139299	35.465
2	19.288	4185601	123731	34.927
3	20.652	1774894	46079	14.810
4	37.681	1773387	31688	14.798
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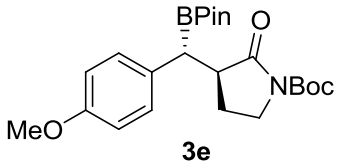
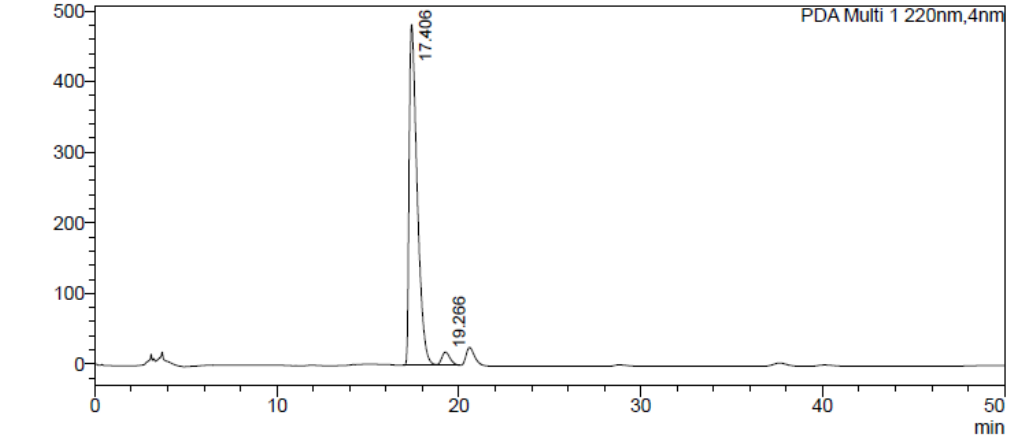


3e

(AD-H column, IPA/hexanes: 2/98, flow rate 1.0 mL/min)



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PDA Ch1 220nm

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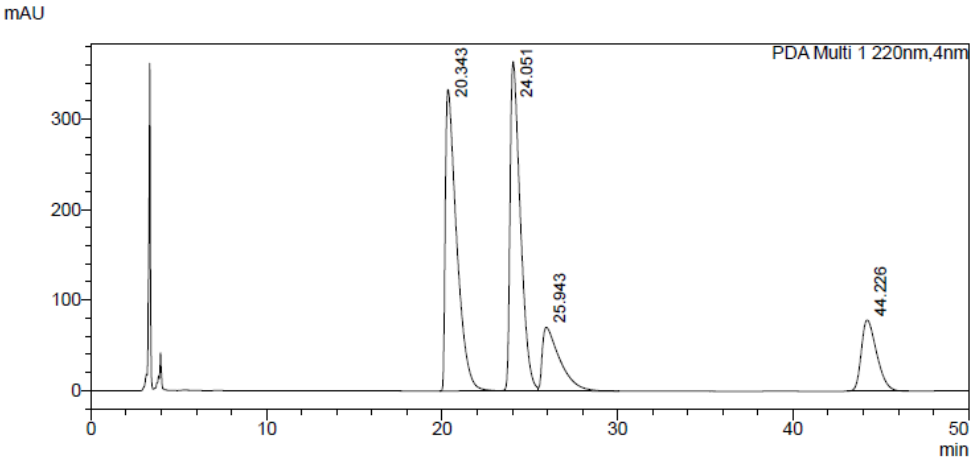

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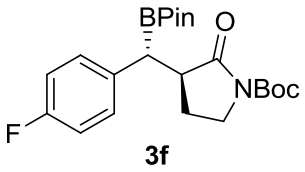
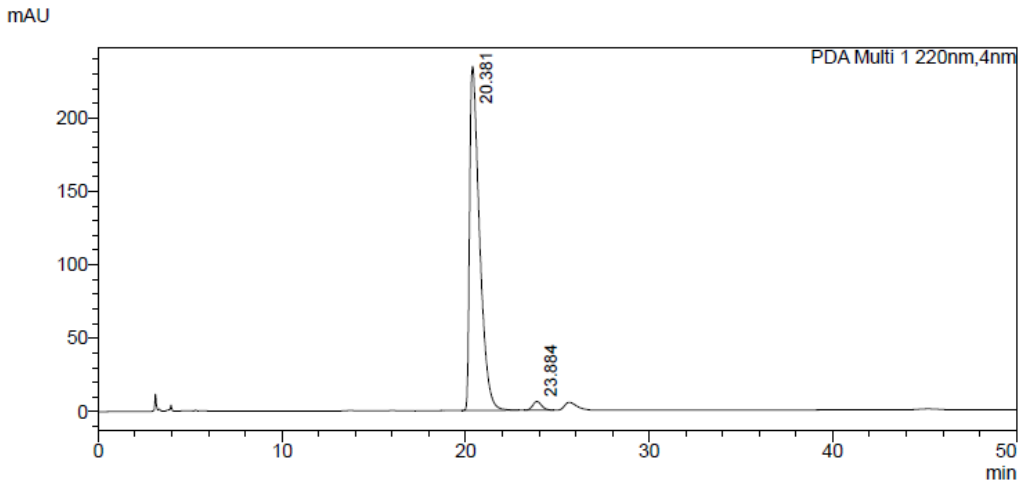


3f

(AD-H column, IPA/hexanes: 1/99, flow rate 1.0 mL/min)



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PDA Ch1 220nm

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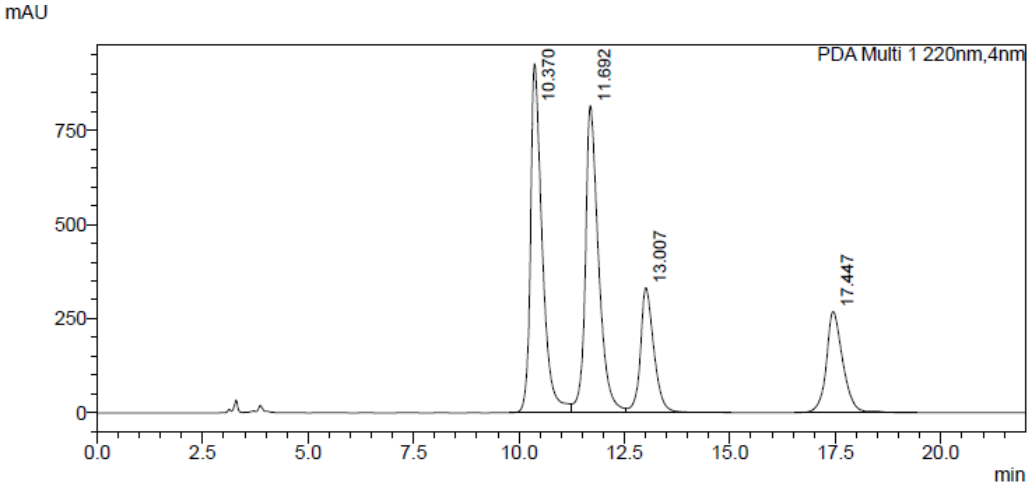

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PDA Ch1 220nm

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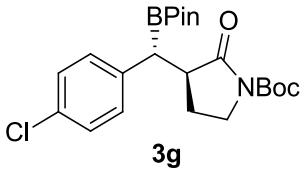
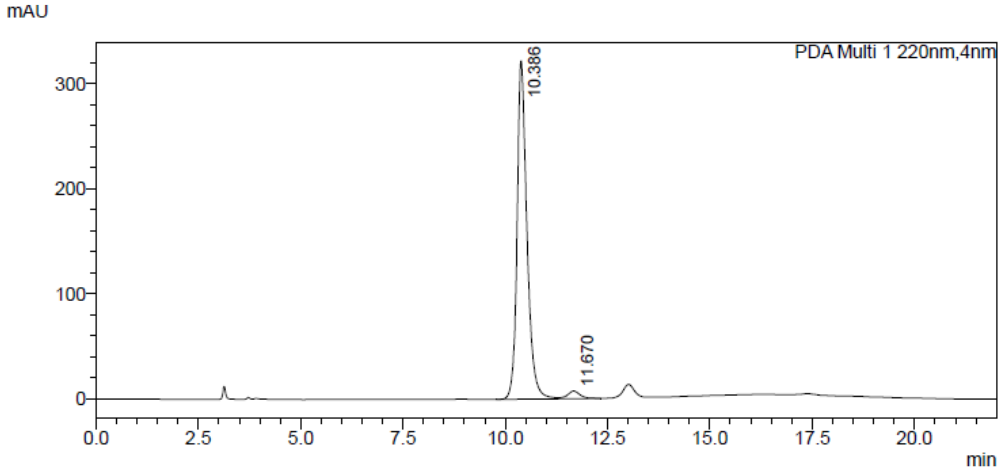


3g

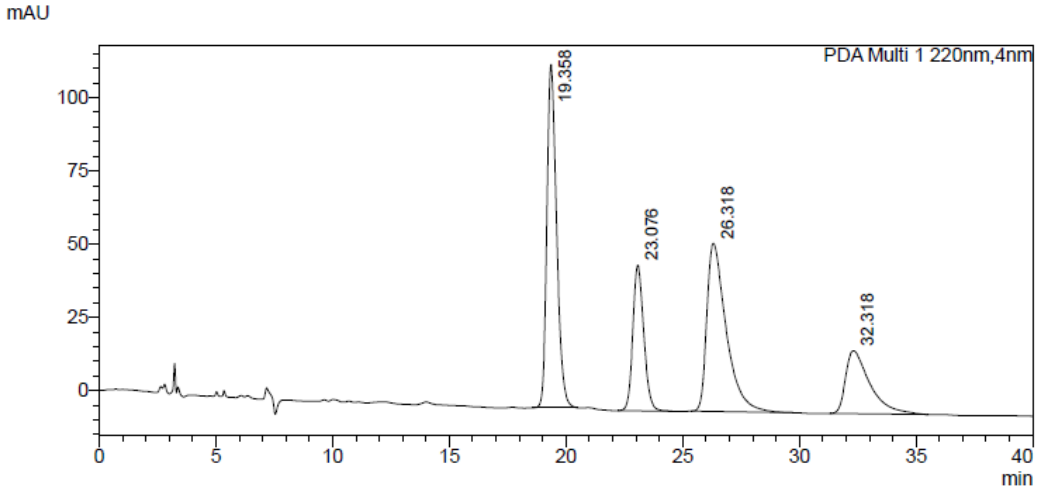
(IA column, IPA/hexanes: 2/98, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 220nm

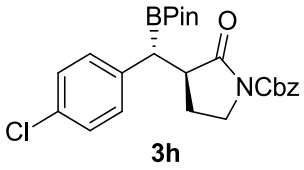
Peak#	Ret. Time	Area	Height	Area%
1	10.386	5397982	321868	97.201
2	11.670	155418	7286	2.799
Total		5553401	329153	100.000



<Peak Table>

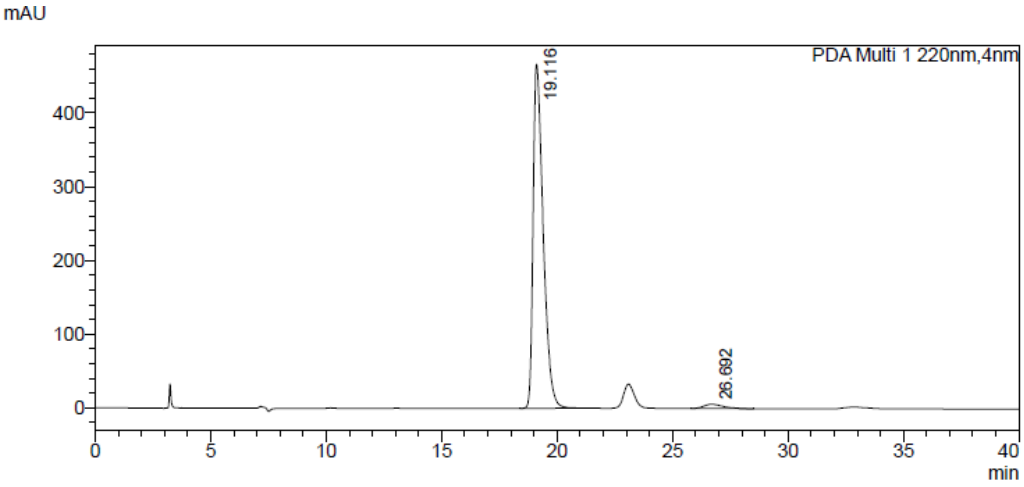
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	19.358	3383230	117139	34.238
2	23.076	1624034	49697	16.435
3	26.318	3318047	57377	33.579
4	32.318	1556086	21475	15.748
Total		9881397	245687	100.000



3h

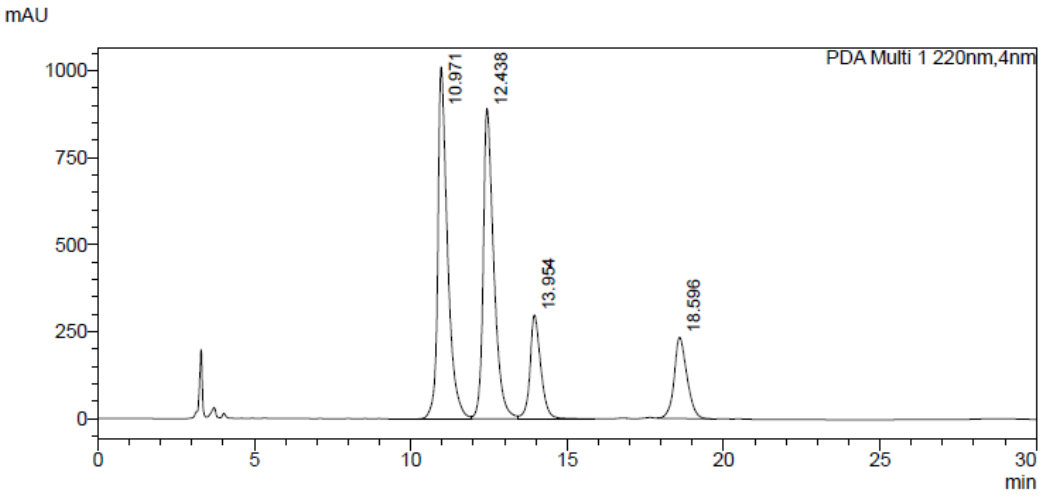
(IE column, IPA/hexanes: 10/90, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 220nm

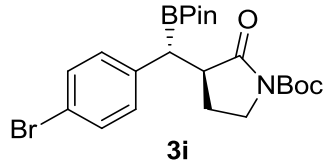
Peak#	Ret. Time	Area	Height	Area%
1	19.116	14158957	466292	97.687
2	26.692	335300	5789	2.313
Total		14494257	472081	100.000



<Peak Table>

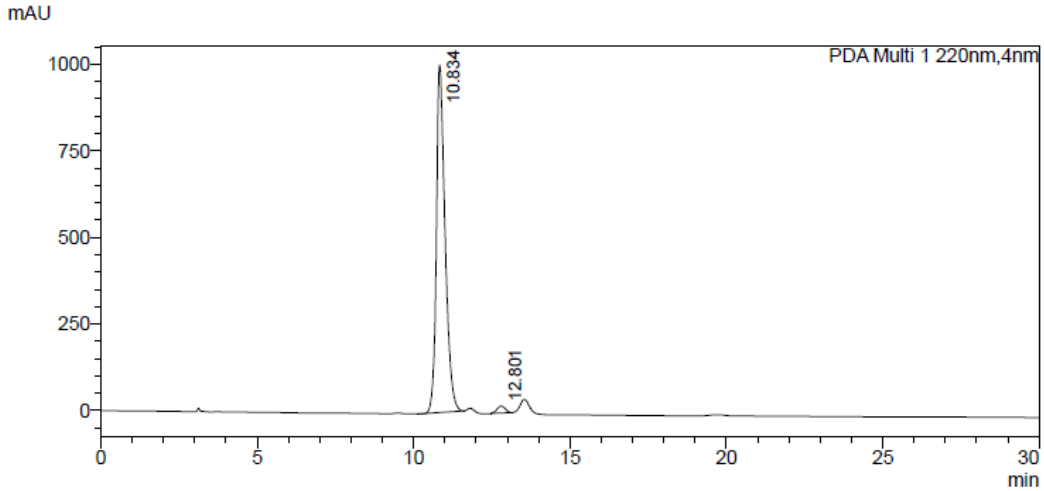
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	10.971	21909971	1010422	38.675
2	12.438	20995333	892040	37.060
3	13.954	7137786	298044	12.599
4	18.596	6608779	233040	11.666
Total		56651869	2433546	100.000



3i

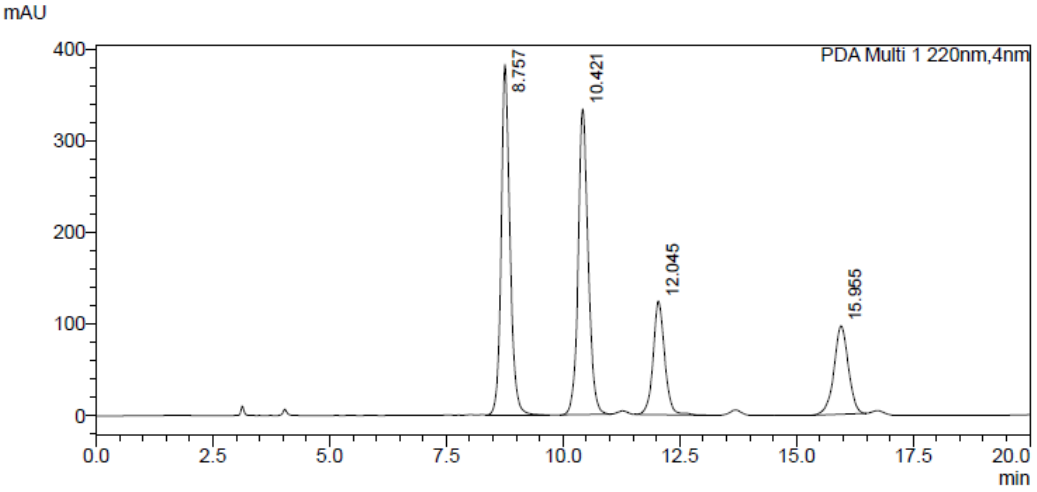
(IA column, IPA/hexanes: 2/98, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 220nm

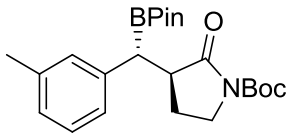
Peak#	Ret. Time	Area	Height	Area%
1	10.834	19356955	1003352	98.133
2	12.801	368312	19948	1.867
Total		19725267	1023300	100.000



<Peak Table>

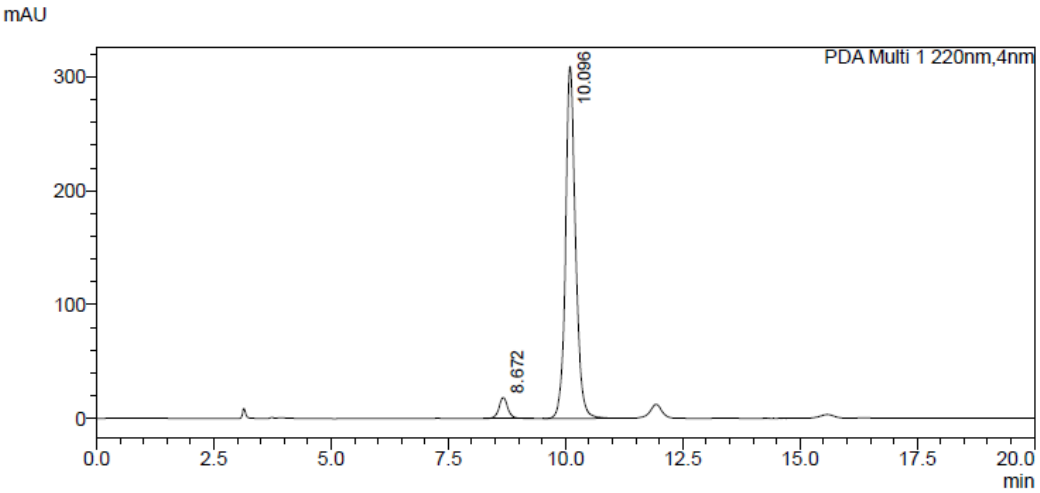
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	8.757	4995269	382214	35.255
2	10.421	4962151	333337	35.021
3	12.045	2142868	123838	15.124
4	15.955	2068720	96442	14.600
Total		14169008	935831	100.000



3j

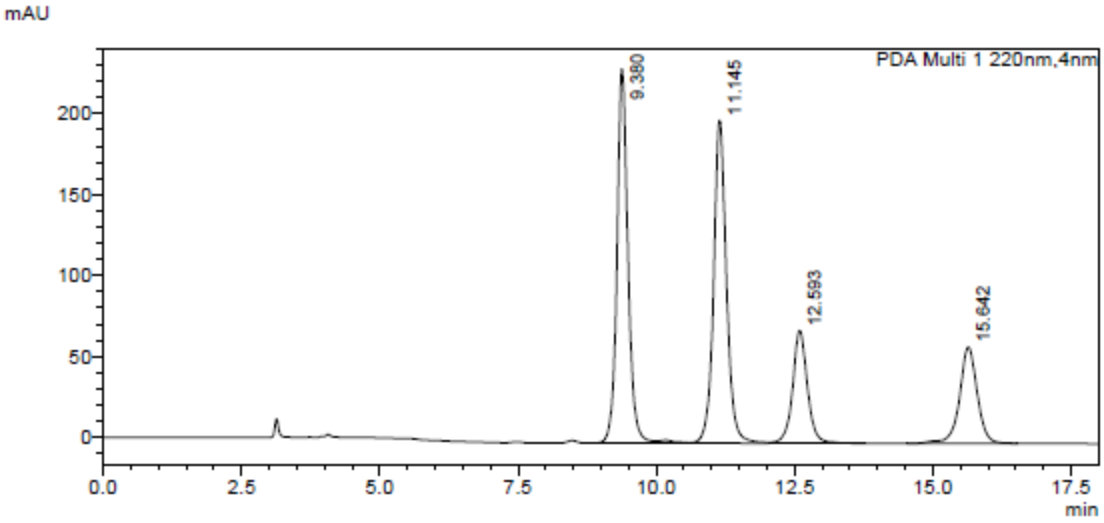
(IA column, IPA/hexanes: 2/98, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 220nm

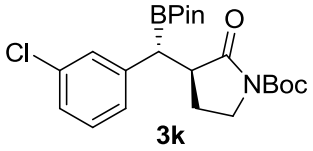
Peak#	Ret. Time	Area	Height	Area%
1	8.672	245637	18521	5.083
2	10.096	4586565	309411	94.917
Total		4832202	327932	100.000



<Peak Table>

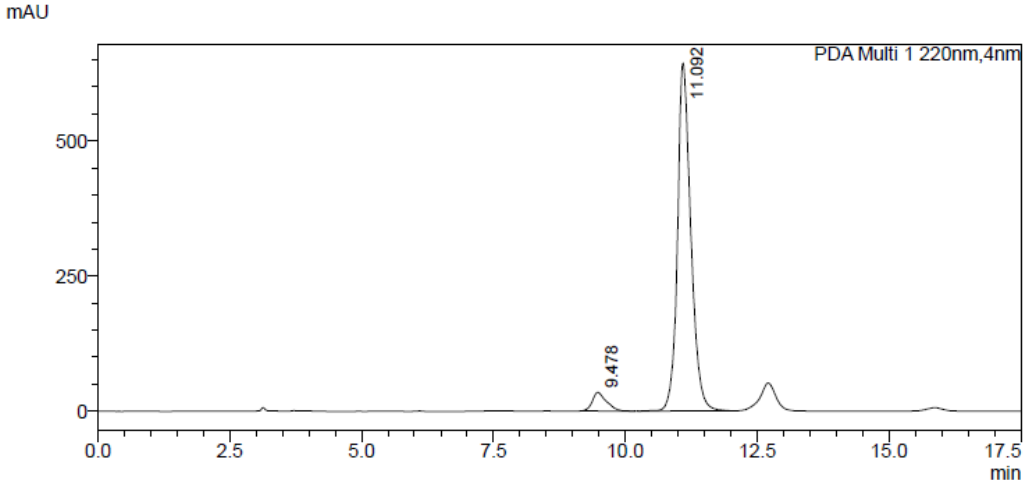
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	9.380	3206711	231121	35.438
2	11.145	3216546	199592	35.547
3	12.593	1295052	69671	14.312
4	15.642	1330492	59504	14.704
Total		9048801	559888	100.000



3k

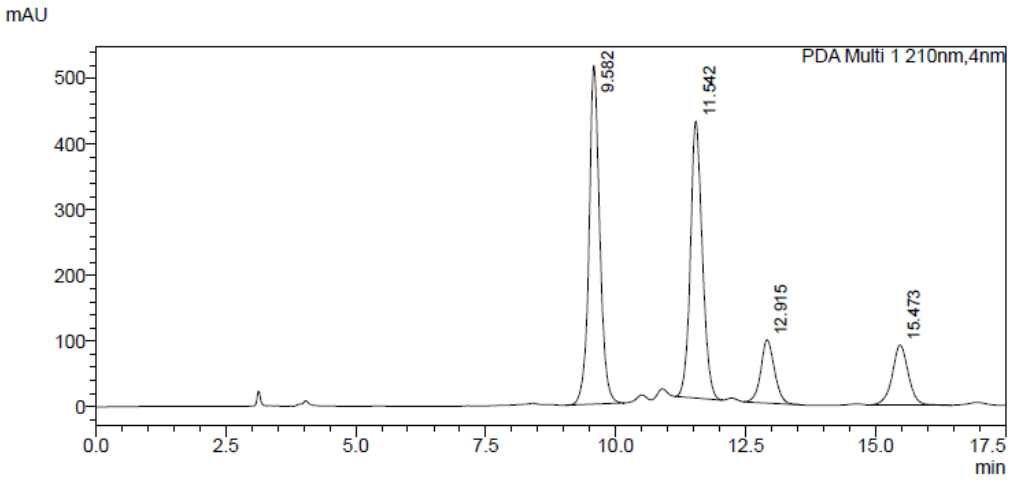
(IA column, IPA/hexanes: 2/98, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 220nm

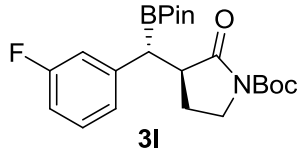
Peak#	Ret. Time	Area	Height	Area%
1	9.478	642334	34542	5.363
2	11.092	11334838	642904	94.637
Total		11977172	677446	100.000



<Peak Table>

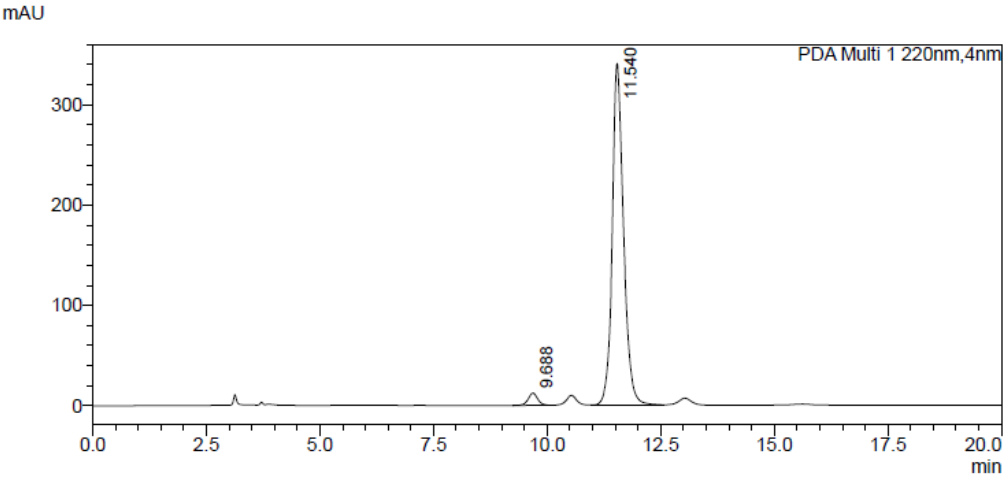
PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	9.582	7396395	516120	41.431
2	11.542	6736726	421940	37.736
3	12.915	1762245	96339	9.871
4	15.473	1957042	91342	10.962
Total		17852407	1125741	100.000



3l

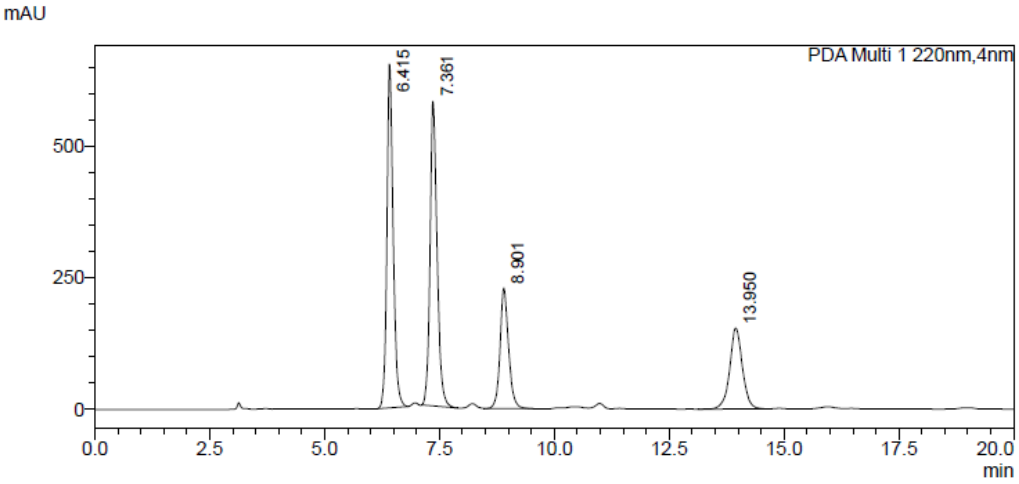
(IA column, IPA/hexanes: 2/98, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 220nm

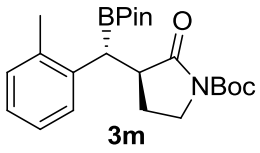
Peak#	Ret. Time	Area	Height	Area%
1	9.688	175243	12227	2.900
2	11.540	5867082	340194	97.100
Total		6042326	352421	100.000



<Peak Table>

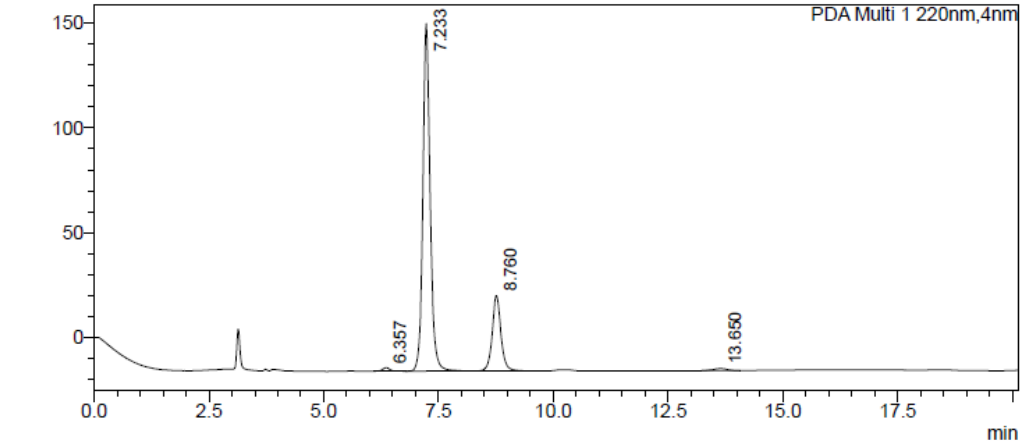
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	6.415	6217100	653482	33.956
2	7.361	6194409	579307	33.832
3	8.901	2958053	228981	16.156
4	13.950	2939815	153746	16.056
Total		18309377	1615515	100.000



3m

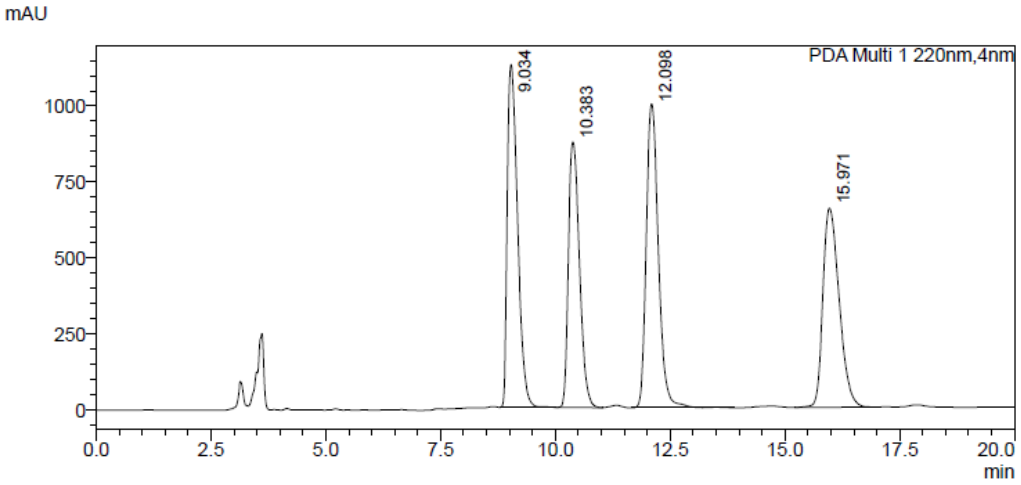
(IA column, IPA/hexanes: 2/98, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 220nm

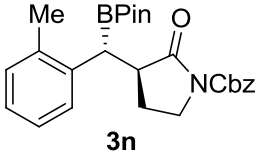
Peak#	Ret. Time	Area	Height	Area%
1	6.357	17838	1686	0.765
2	7.233	1824570	165544	78.217
3	8.760	470263	35890	20.160
4	13.650	20038	1012	0.859
Total		2332709	204132	100.000



<Peak Table>

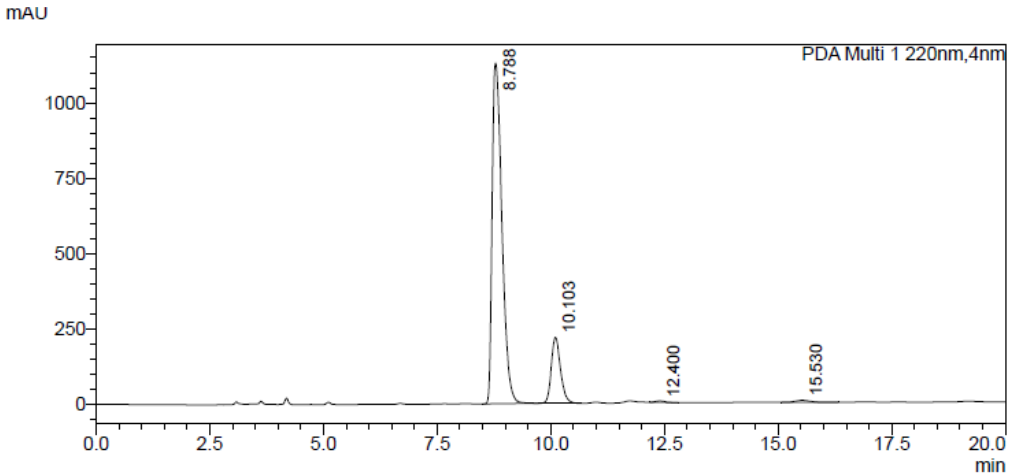
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	9.034	17612347	1127657	26.409
2	10.383	14597270	873418	21.888
3	12.098	18324780	999736	27.477
4	15.971	16156457	654824	24.226
Total		66690855	3655634	100.000



3n

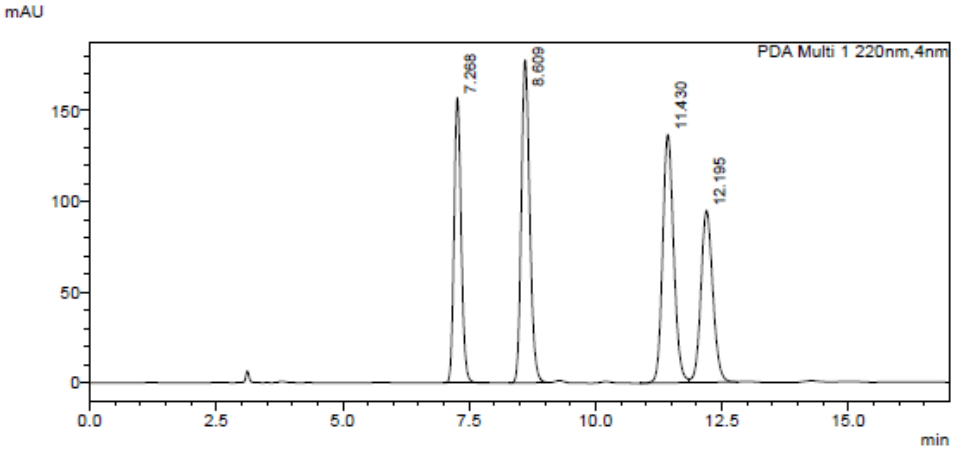
(AD-H column, IPA/hexanes: 5/95, flowrate 1.0 mL/min)



<Peak Table>

PDA Ch1 220nm

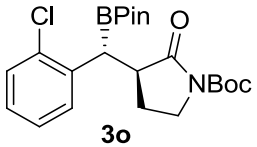
Peak#	Ret. Time	Area	Height	Area%
1	8.788	16892729	1129458	83.751
2	10.103	3064038	218325	15.191
3	12.400	66313	4755	0.329
4	15.530	147062	6995	0.729
Total		20170142	1359533	100.000



<Peak Table>

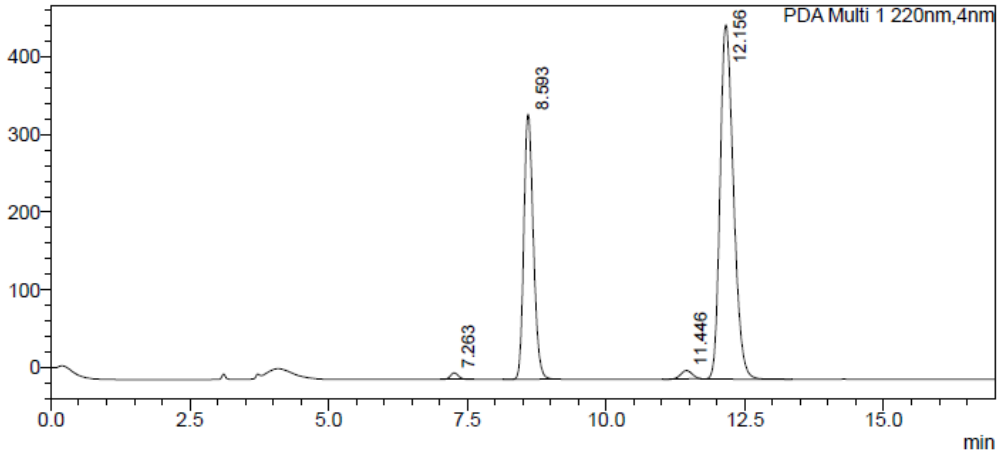
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	7.268	1538005	157337	21.261
2	8.609	2063672	178103	28.528
3	11.430	2081169	136784	28.770
4	12.195	1551055	94680	21.441
Total		7233900	566904	100.000



3o

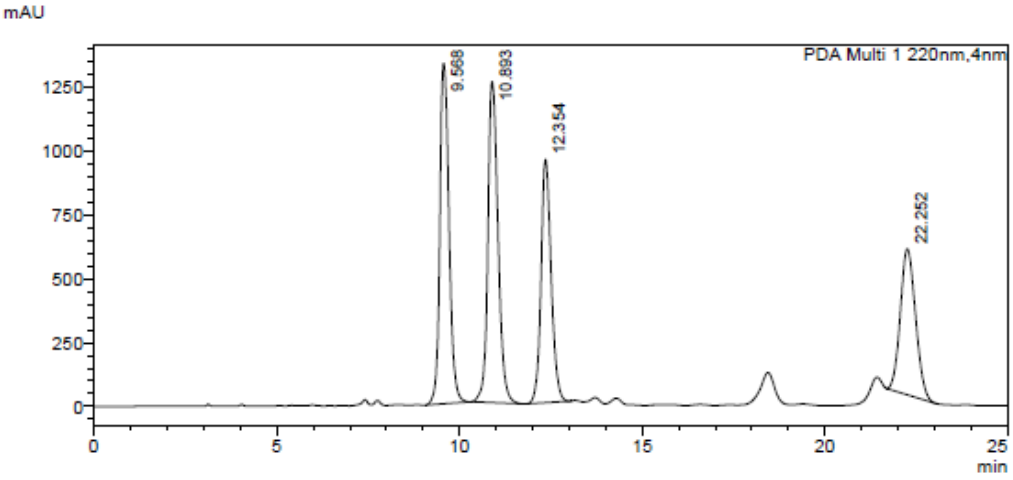
(AD-H column, IPA/hexanes: 2/98, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 220nm

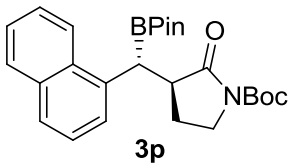
Peak#	Ret. Time	Area	Height	Area%
1	7.263	83897	8405	0.701
2	8.593	4061547	341273	33.943
3	11.446	152984	10731	1.279
4	12.156	7667329	456021	64.077
Total		11965758	816430	100.000



<Peak Table>

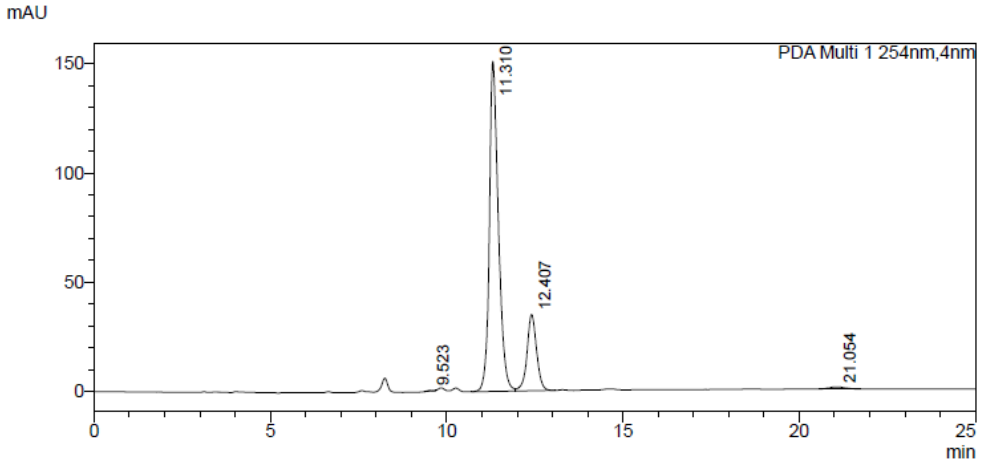
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	9.568	23288198	1334429	28.231
2	10.893	24337071	1257840	29.503
3	12.354	18300917	953056	22.185
4	22.252	16564351	571990	20.080
Total		82490537	4117315	100.000



3p

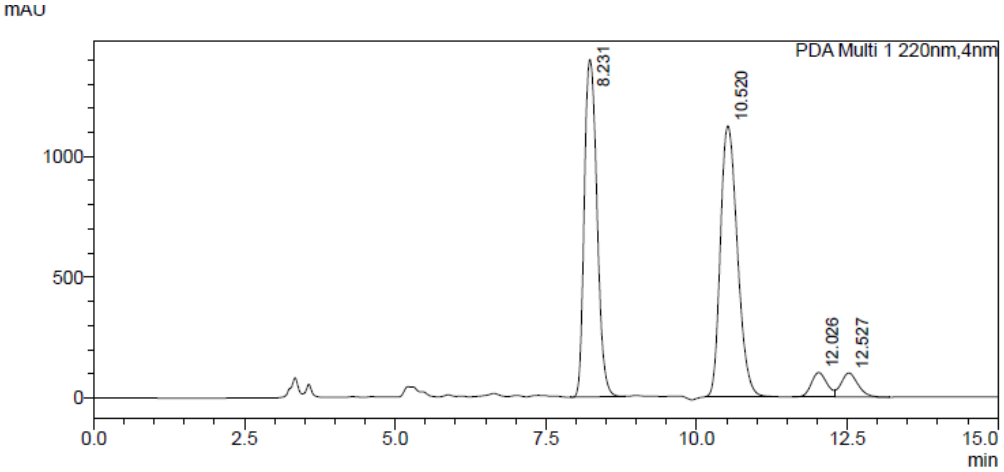
(IA column, IPA/hexanes: 2/98, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 254nm

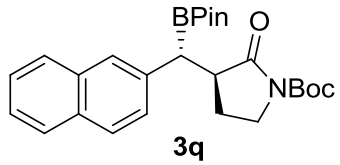
Peak#	Ret. Time	Area	Height	Area%
1	9.523	2245	320	0.067
2	11.310	2685279	150842	79.618
3	12.407	657987	34879	19.509
4	21.054	27172	950	0.806
Total		3372683	186991	100.000



<Peak Table>

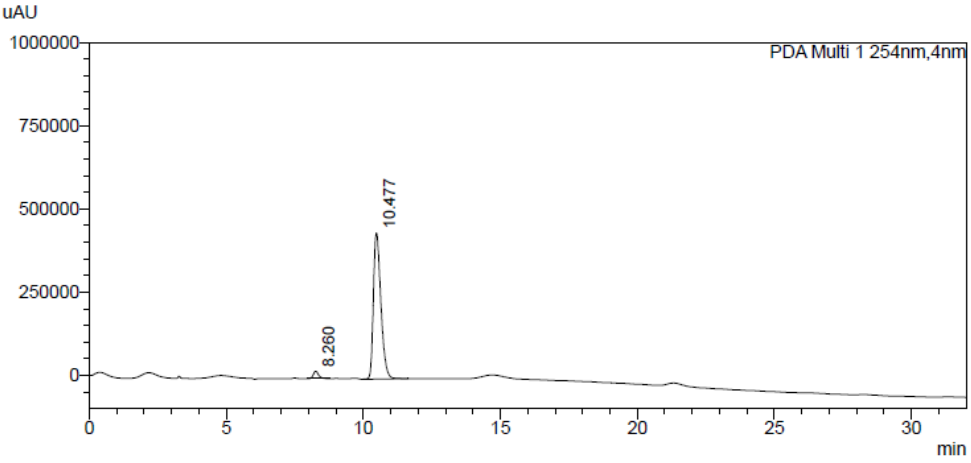
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	8.231	20479446	1397310	44.339
2	10.520	21953566	1121137	47.531
3	12.026	1820140	101129	3.941
4	12.527	1935135	99374	4.190
Total		46188286	2718950	100.000



3q

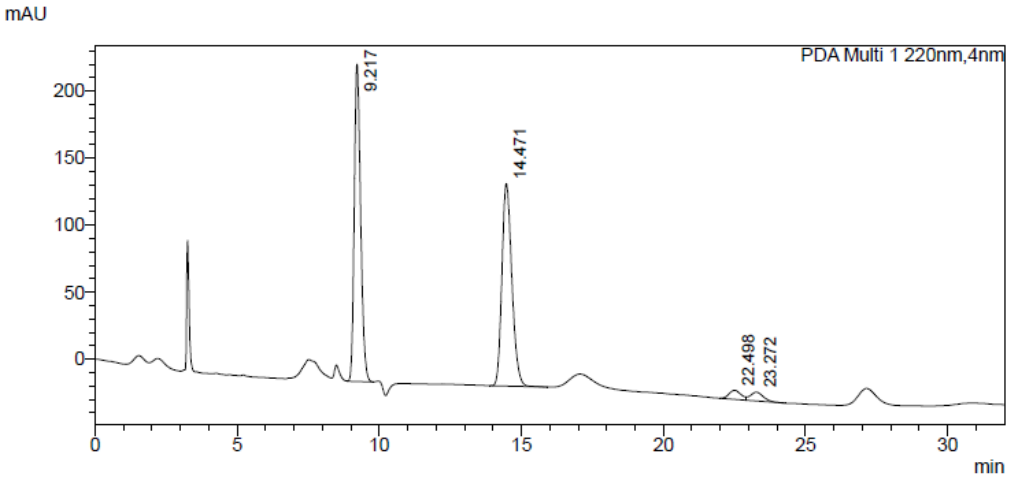
(IC column, IPA/hexanes: 10/90, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 254nm

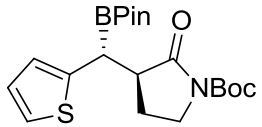
Peak#	Ret. Time	Area	Height	Area%
1	8.260	294624	21994	3.416
2	10.477	8331210	438928	96.584
Total		8625834	460922	100.000



<Peak Table>

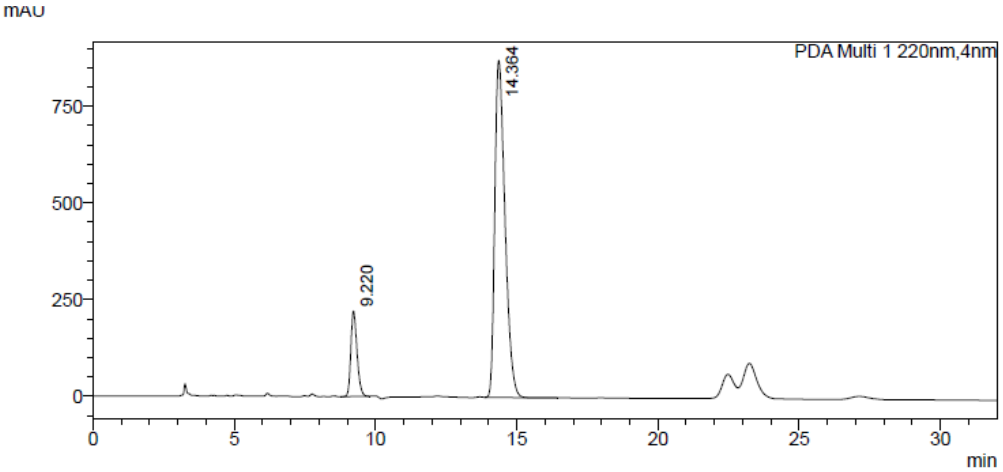
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	9.217	3685283	236677	47.436
2	14.471	3679810	150976	47.366
3	22.498	199002	6746	2.562
4	23.272	204847	6510	2.637
Total		7768942	400909	100.000



3r

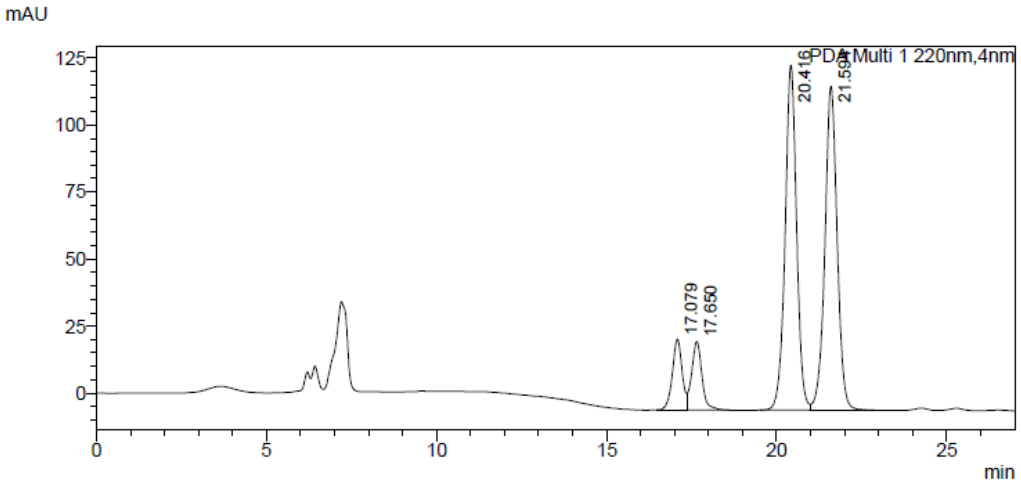
(IC column, IPA/hexanes: 10/90, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 220nm

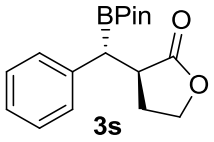
Peak#	Ret. Time	Area	Height	Area%
1	9.220	3364207	221163	13.296
2	14.364	21938308	872400	86.704
Total		25302515	1093563	100.000



<Peak Table>

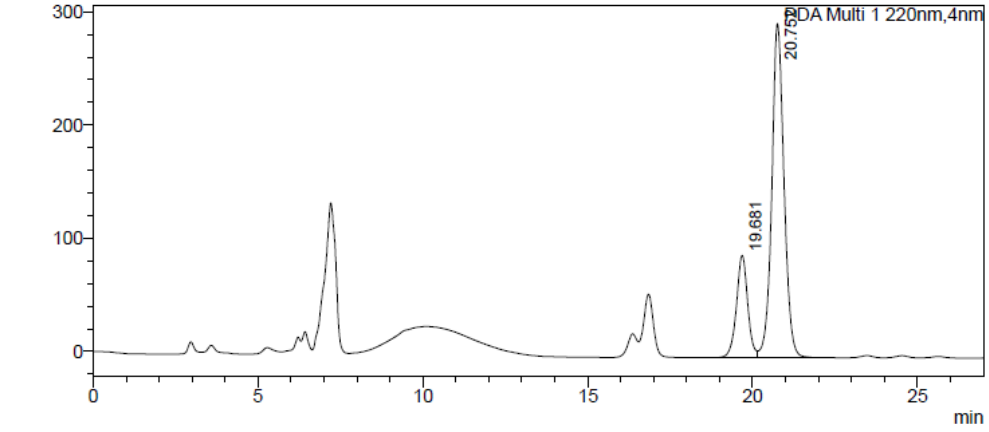
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	17.079	525959	26360	7.400
2	17.650	537295	25537	7.560
3	20.416	3016395	128585	42.441
4	21.594	3027673	120715	42.599
Total		7107322	301198	100.000



3s

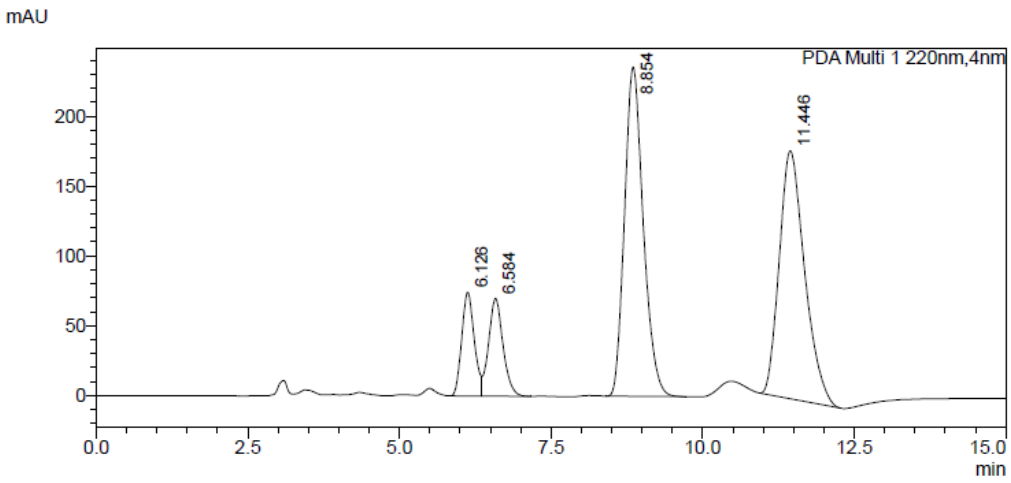
(IA column, IPA/hexanes: 3/97, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 220nm

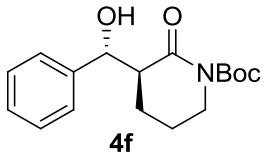
Peak#	Ret. Time	Area	Height	Area%
1	19.681	2149536	90325	22.084
2	20.752	7583853	294884	77.916
Total		9733389	385209	100.000



<Peak Table>

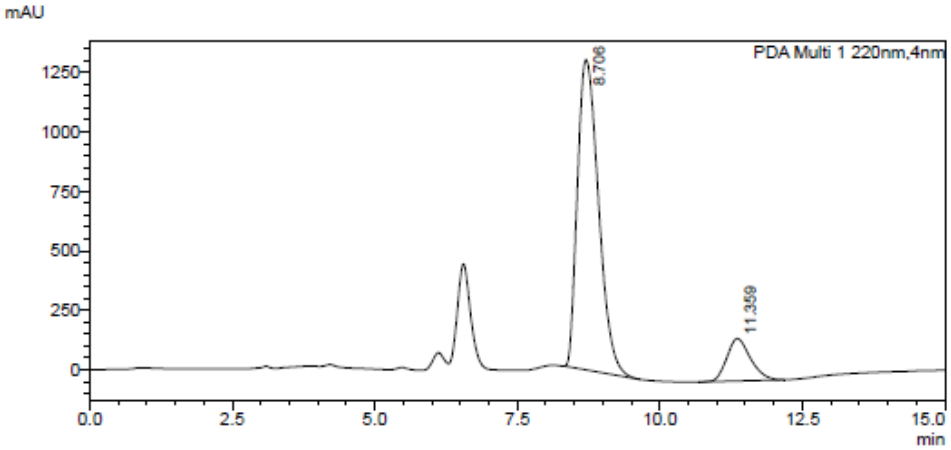
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	6.126	1075526	74444	8.610
2	6.584	1156764	70175	9.261
3	8.854	5086598	236043	40.722
4	11.446	5172110	177670	41.407
Total		12490998	558331	100.000



4f

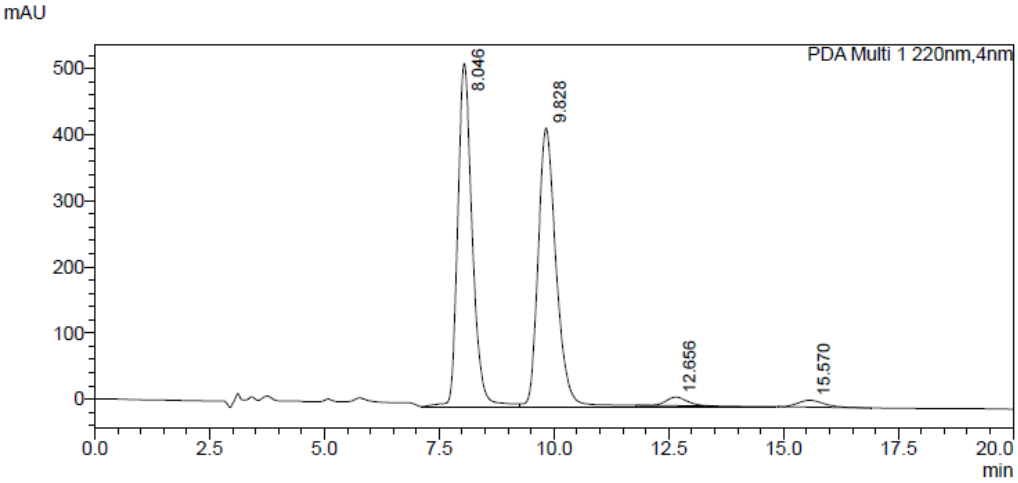
(OD-H column, IPA/hexanes: 10/90, flow rate 1.0 mL/min)



<Peak Table>

PDA Ch1 220nm

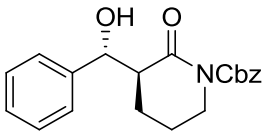
Peak#	Ret. Time	Area	Height	Area%
1	8.706	33605376	1304078	86.720
2	11.359	5146291	178328	13.280
Total		38751668	1482406	100.000



<Peak Table>

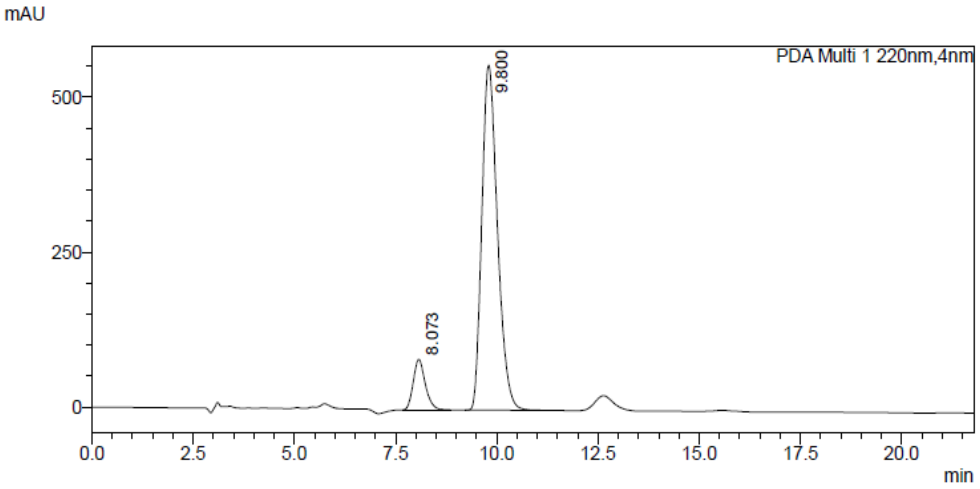
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%
1	8.046	11418158	519116	47.622
2	9.828	11727827	421545	48.913
3	12.656	411789	12917	1.717
4	15.570	418976	10506	1.747
Total		23976751	964084	100.000



4g

(OD-H column, IPA/hexanes: 20/80, flow rate 1.0 mL/min)

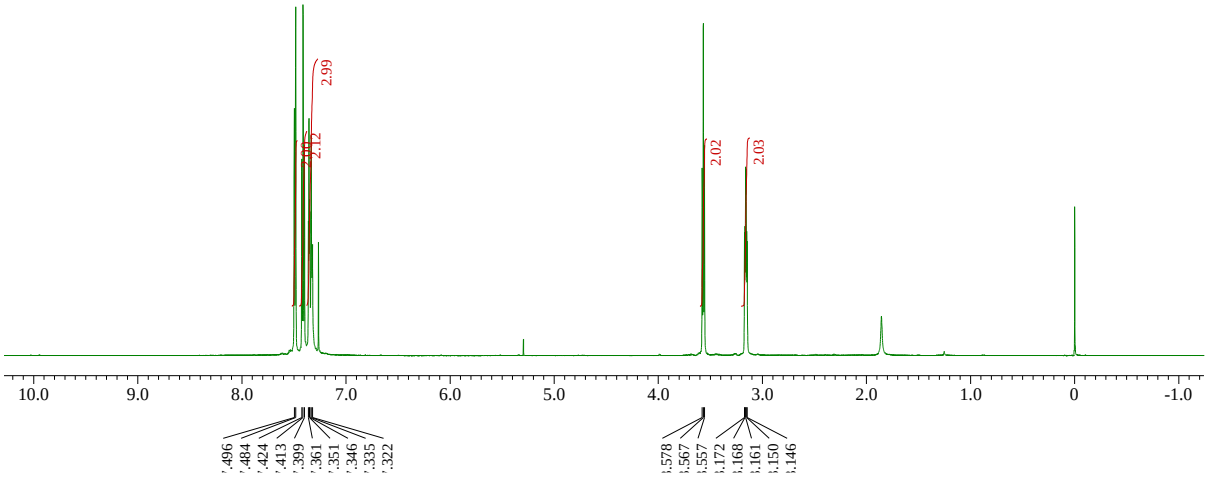


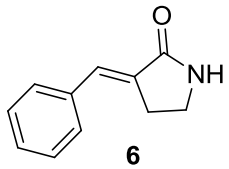
<Peak Table>

PDA Ch1 220nm

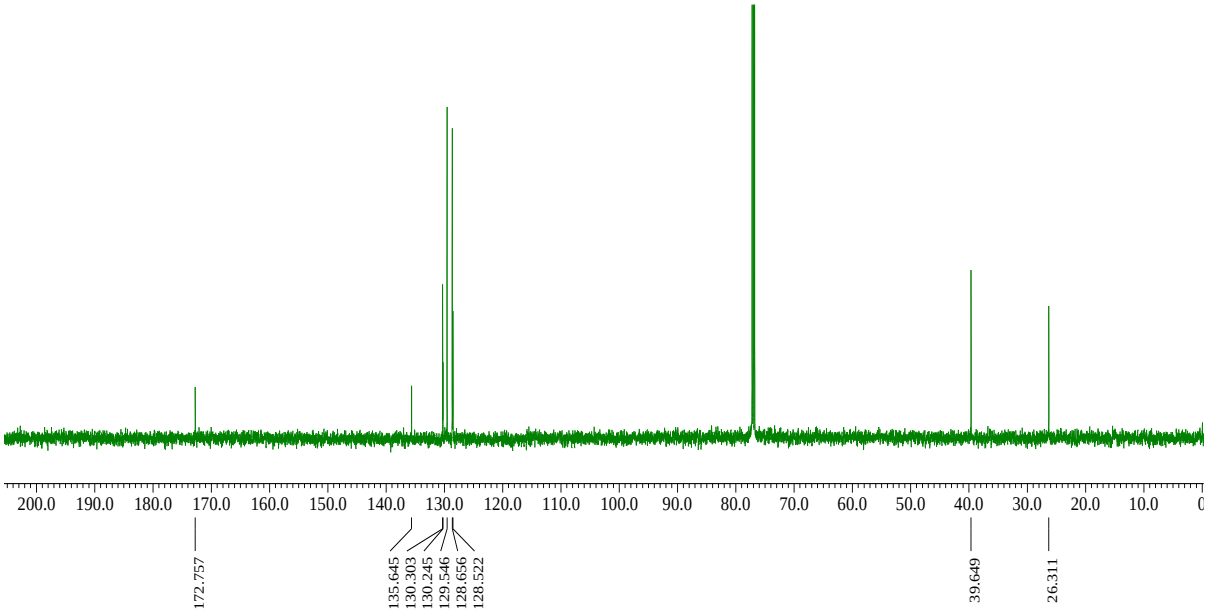
Peak#	Ret. Time	Area	Height	Area%
1	8.073	1677651	81569	10.097
2	9.800	14938168	556155	89.903
Total		16615819	637724	100.000

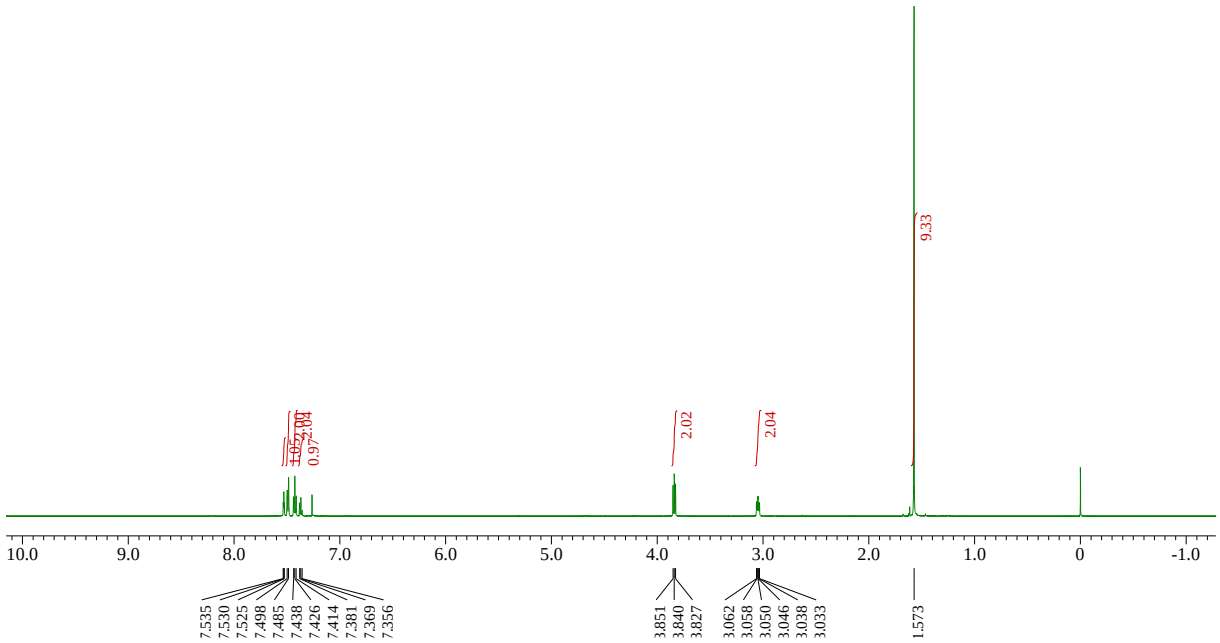
NMR Spectra





6

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3.0
2.0
1.0
0
-1.0
7.535
7.530
7.525
7.498
7.485
7.438
7.426
7.414
7.381
7.369
7.356
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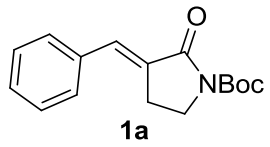
3.840
3.827
3.062
3.058
3.050
3.046
3.038
3.033
1.573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NBoc

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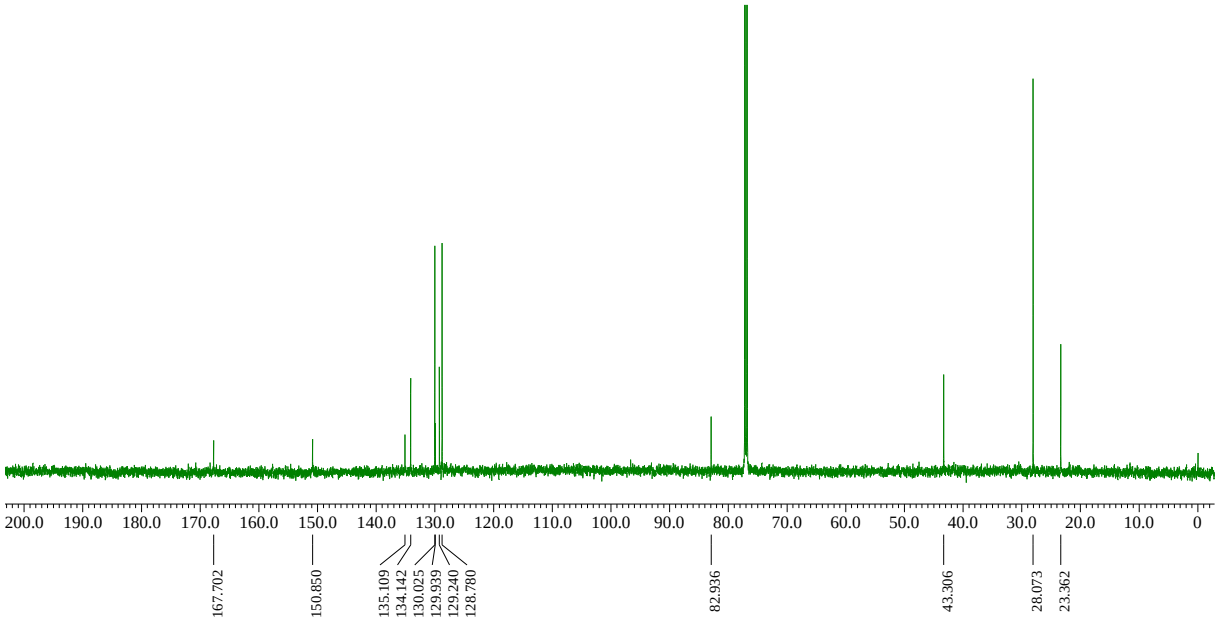
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10.0
0
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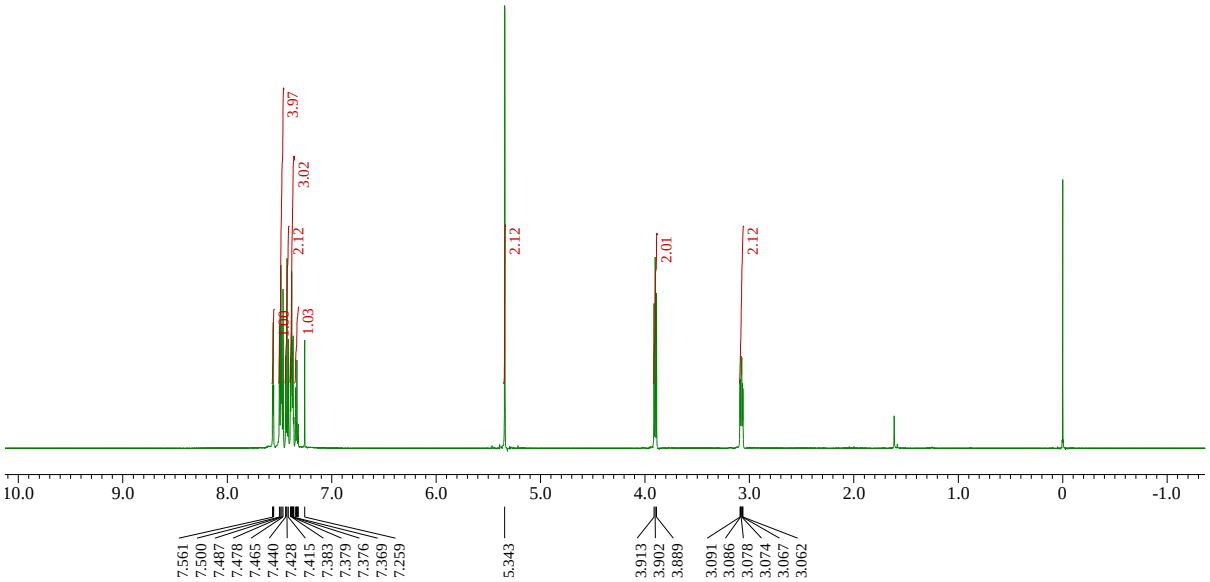
23.362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2.12
2.01
2.12
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
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7.500
7.487
7.478
7.465
7.440
7.428
7.415
7.383
7.379
7.376
7.369
7.259
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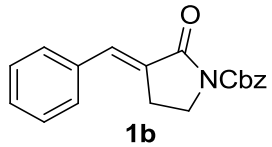
3.902
3.889
3.091
3.086
3.078
3.074
3.067
3.062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NCbz

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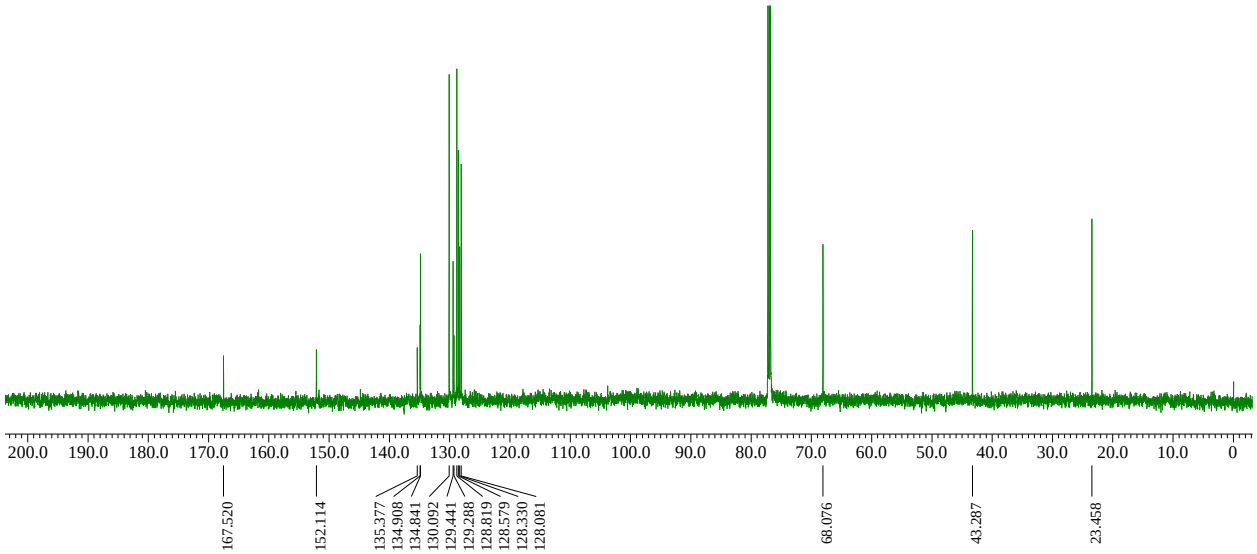
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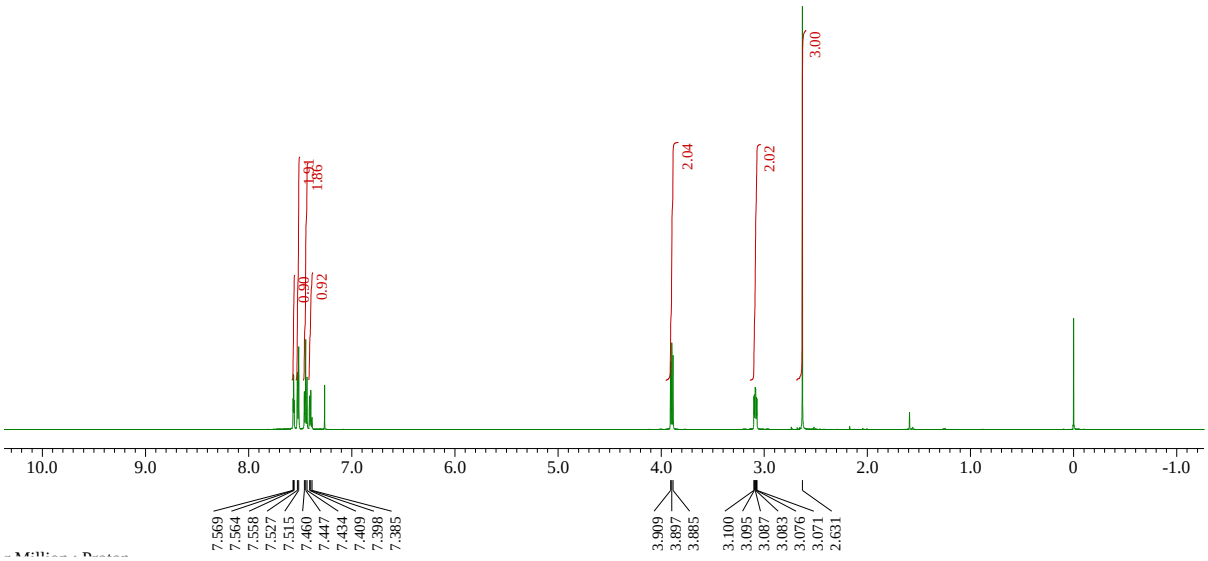
128.330
128.081
68.076
43.287
23.458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5.0
4.0
3.0
2.0
1.0
0
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7.527
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7.434
7.409
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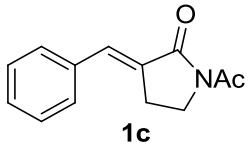
3.076
3.071
2.631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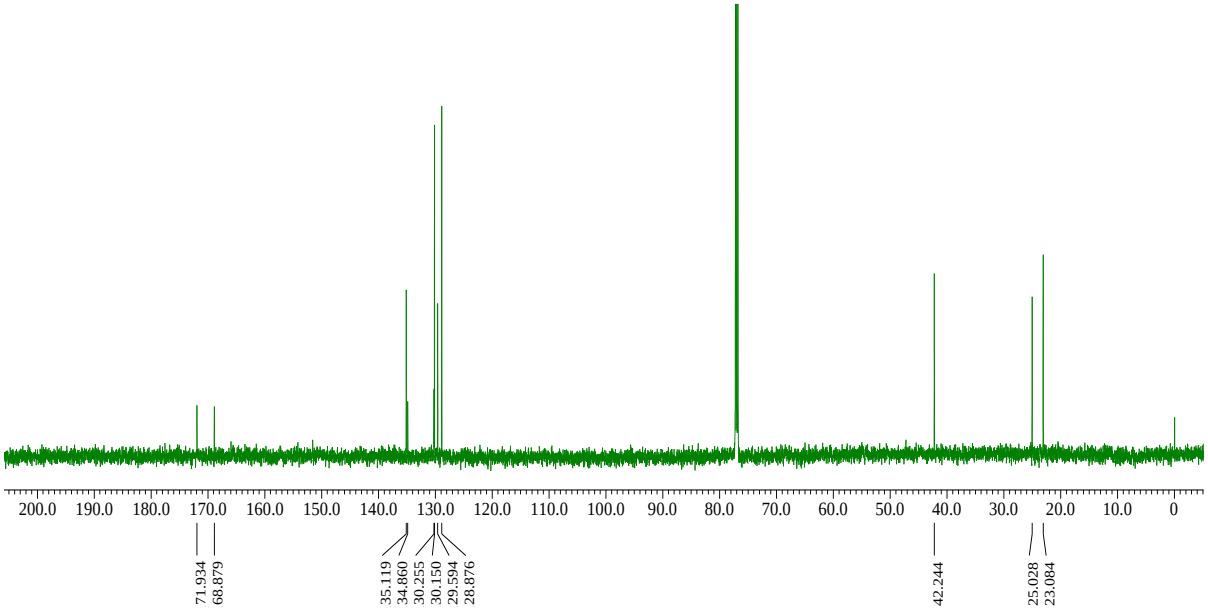
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110.0
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50.0
40.0
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20.0
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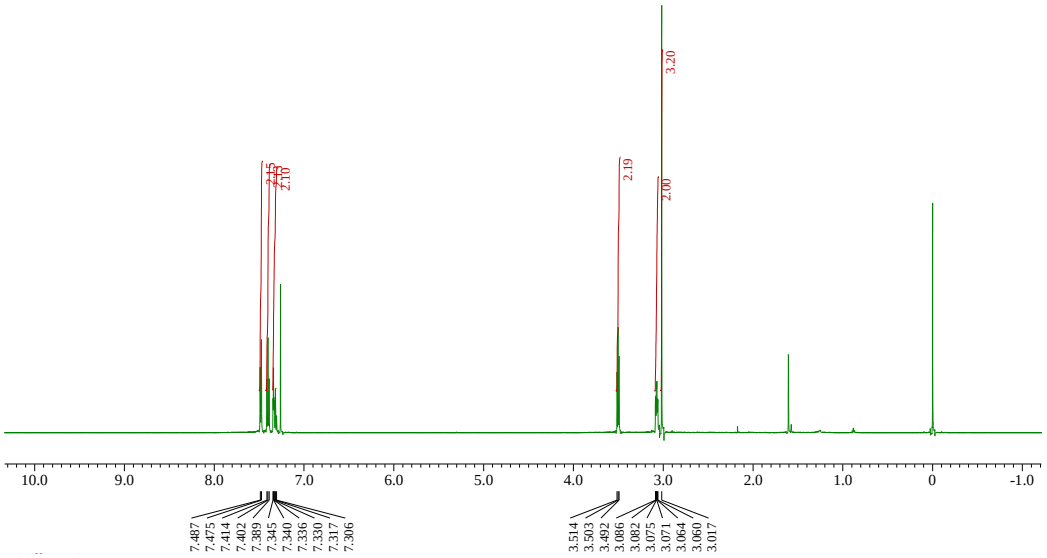
23.084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2.0
1.0
0
-1.0
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7.414
7.402
7.389
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7.340
7.336
7.330
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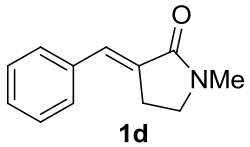
3.075
3.071
3.064
3.060
3.017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NMe

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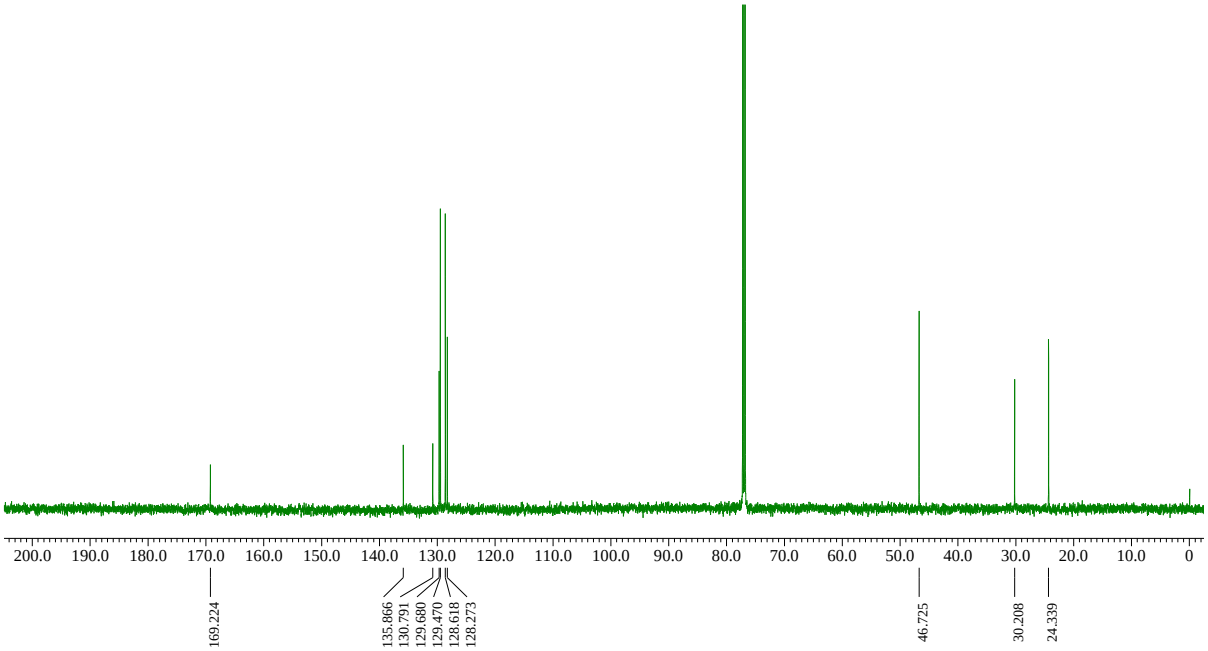
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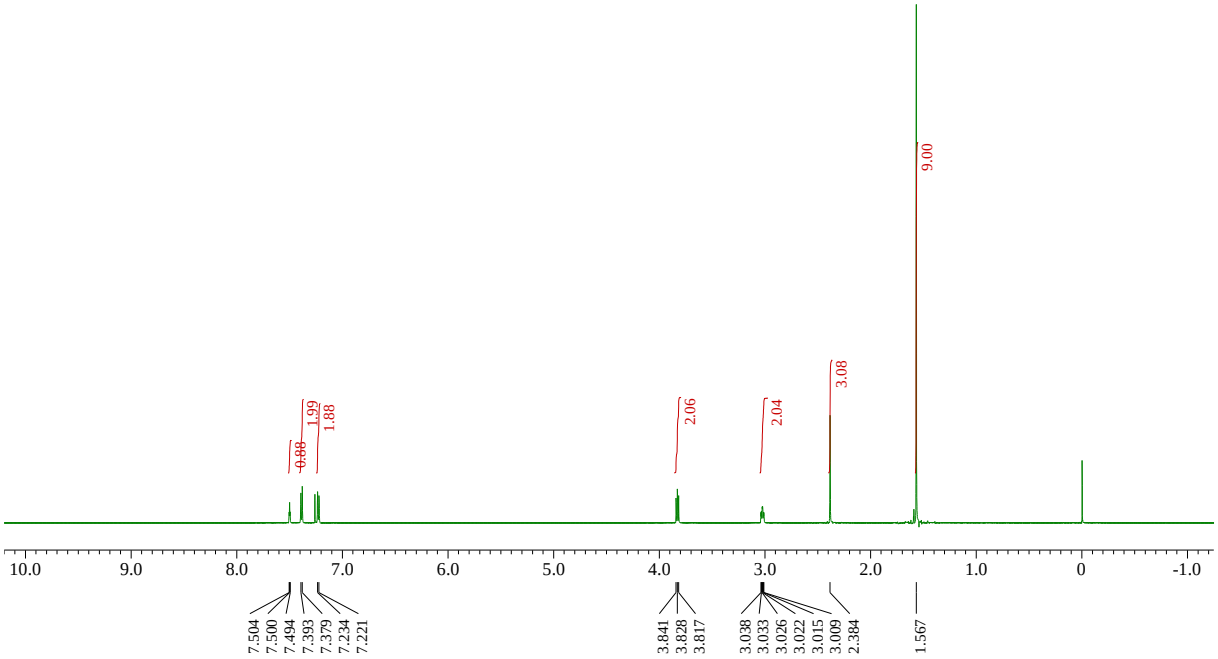
24.339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5.0
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1.0
0
-1.0
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7.393
7.379
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3.022
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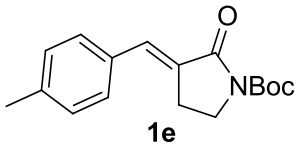
1.567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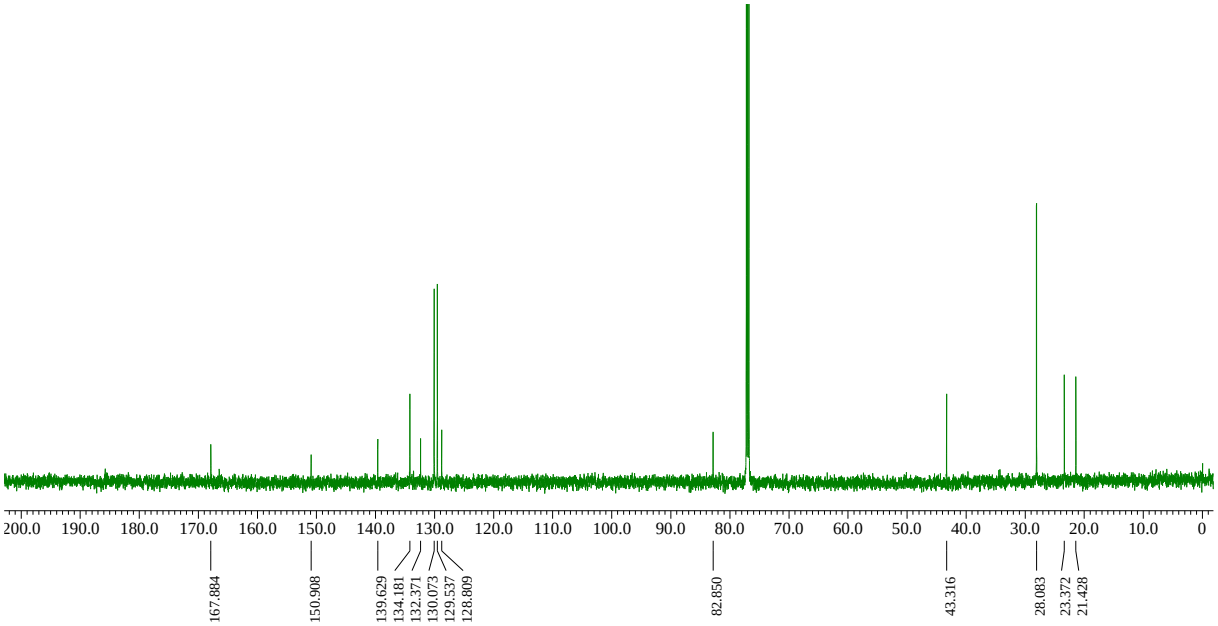
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40.0
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20.0
10.0
0
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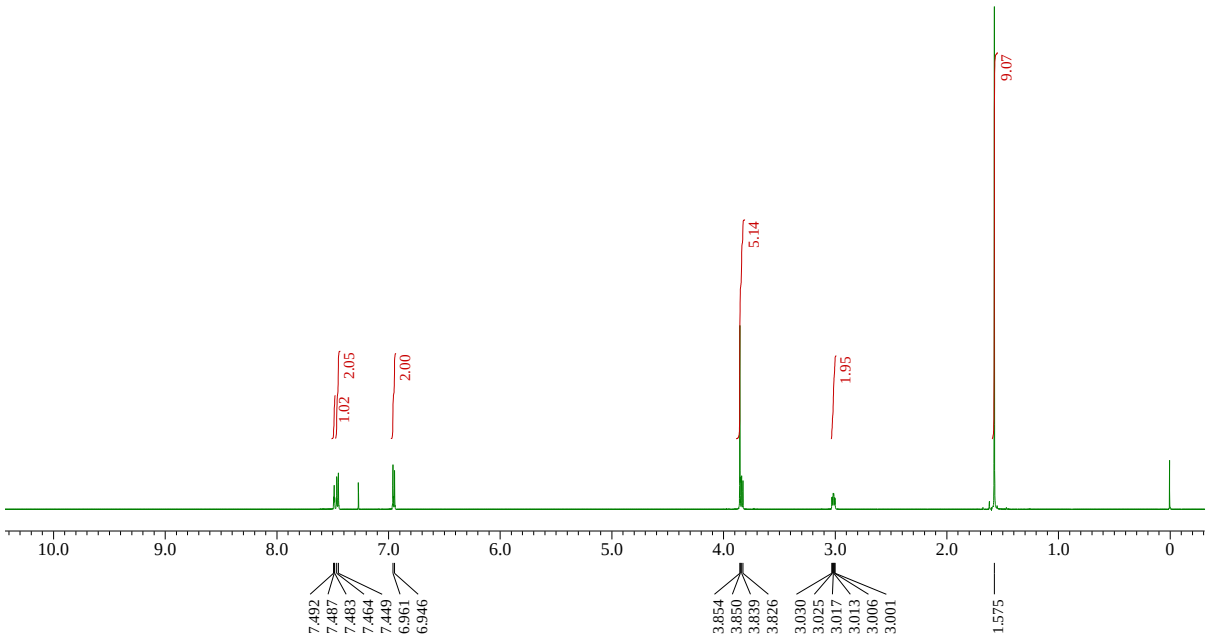
21.428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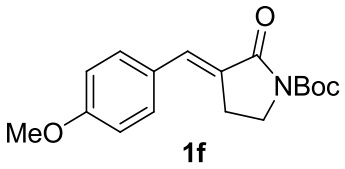
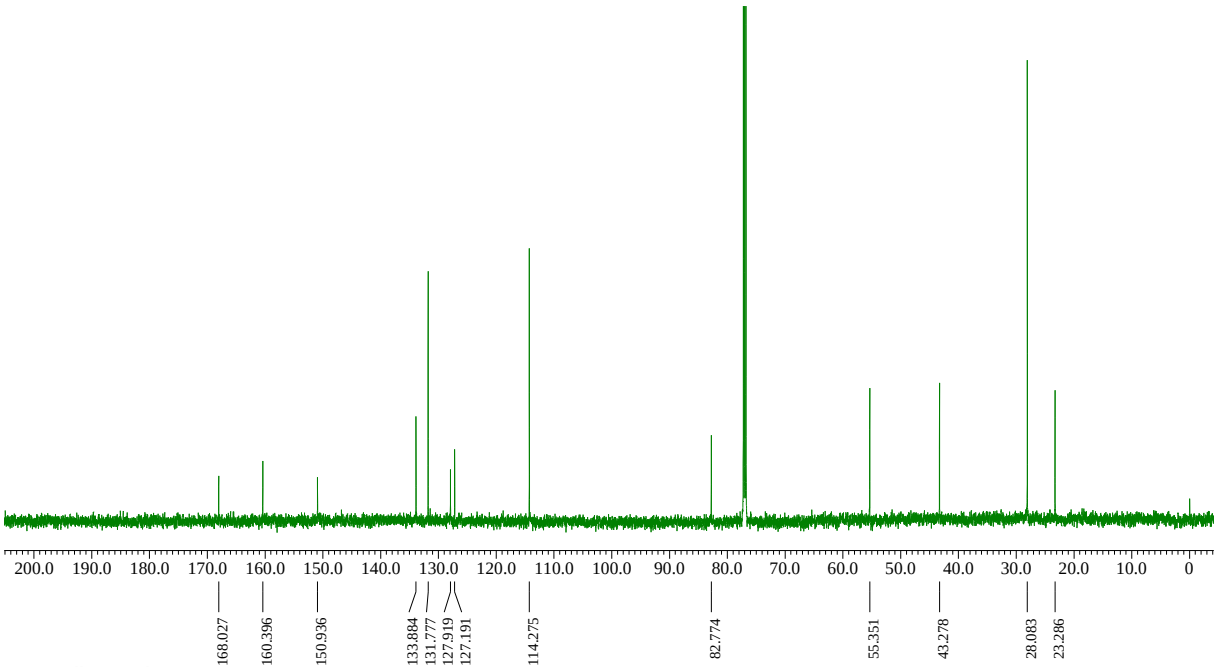
1.575


O
NBoc
MeO

1f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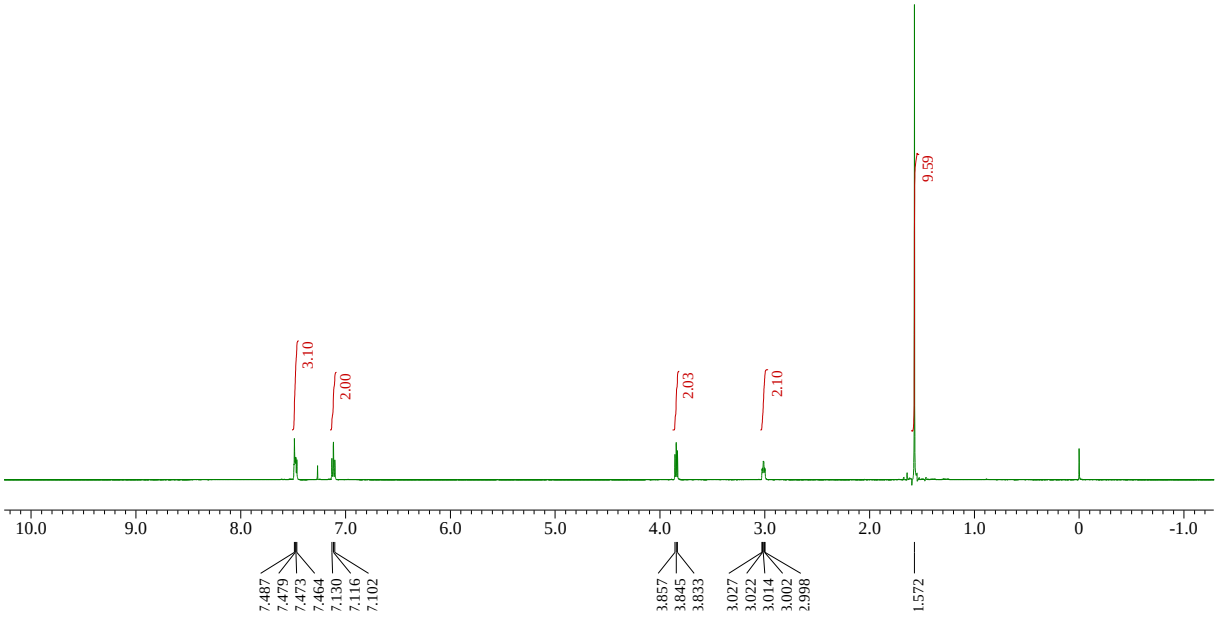
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3.022
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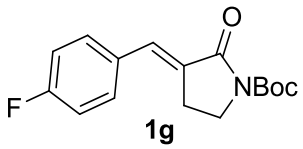
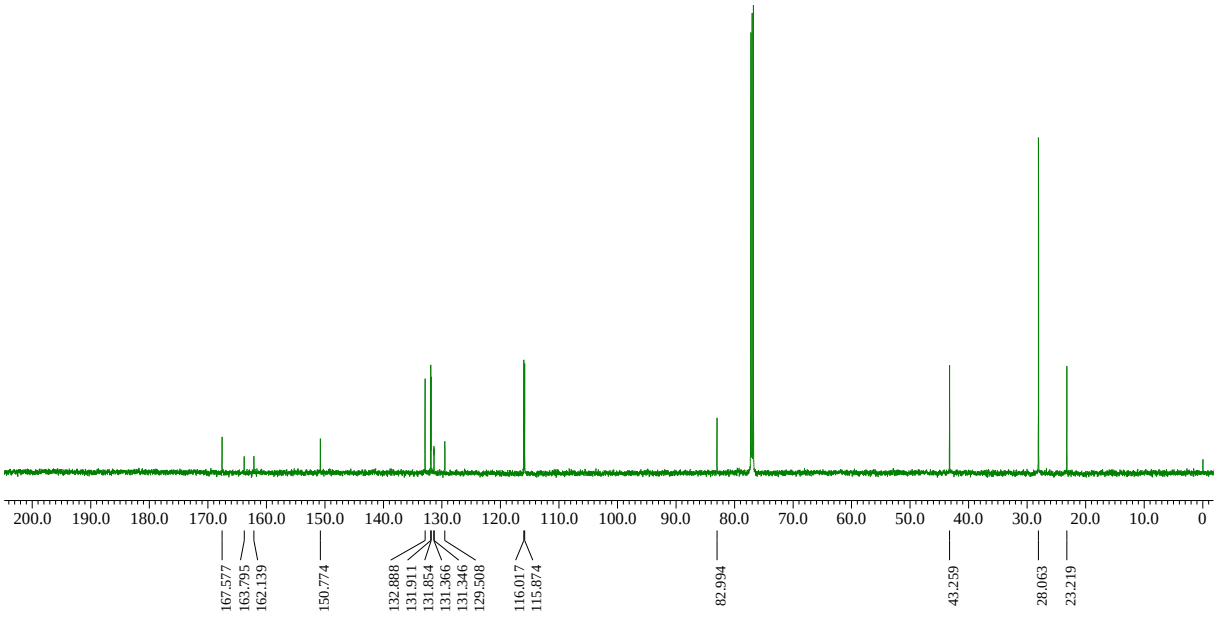
1.572


O
NBoc
F

1g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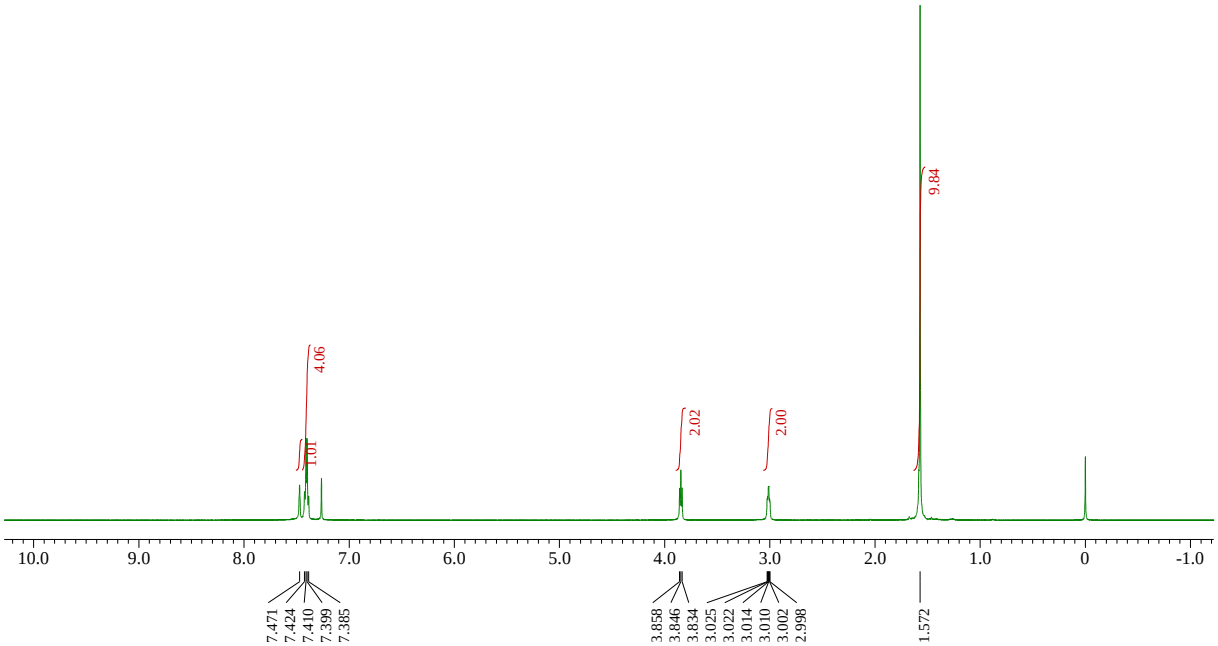
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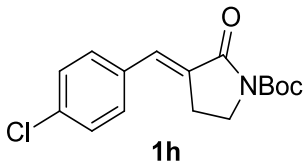
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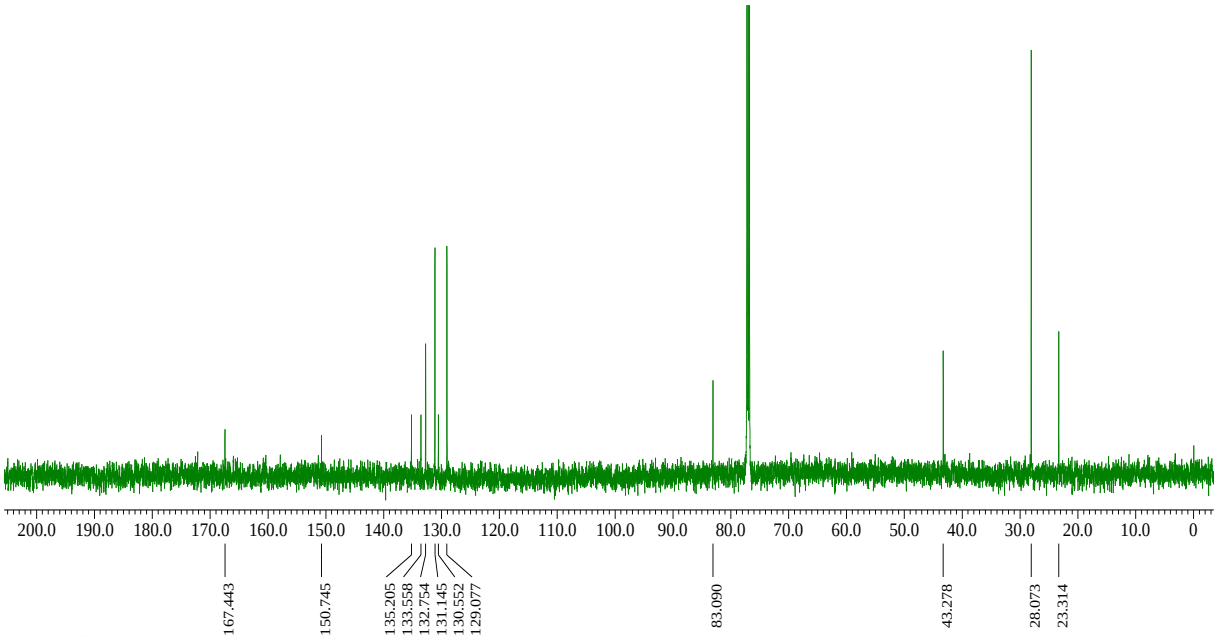
NBoc
Cl

1h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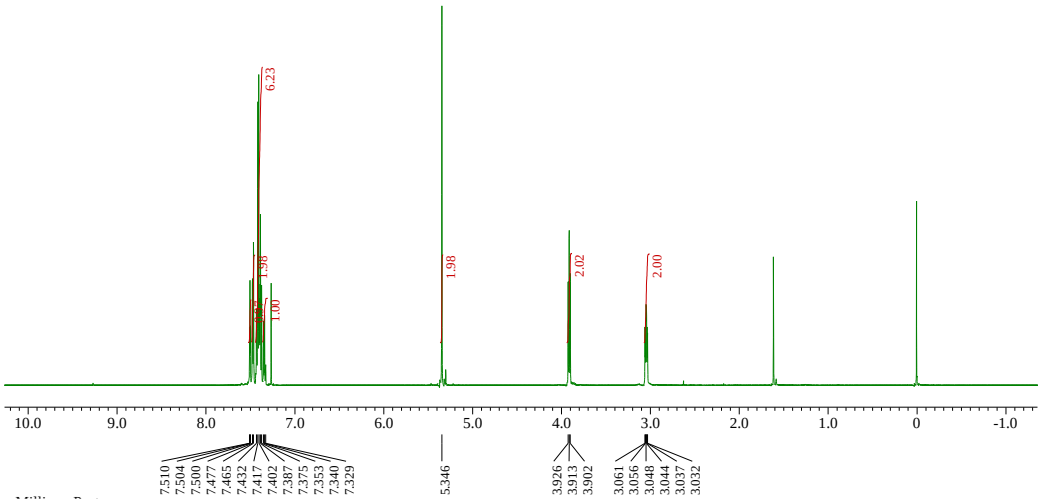
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2.0
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7.500
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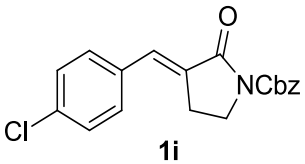
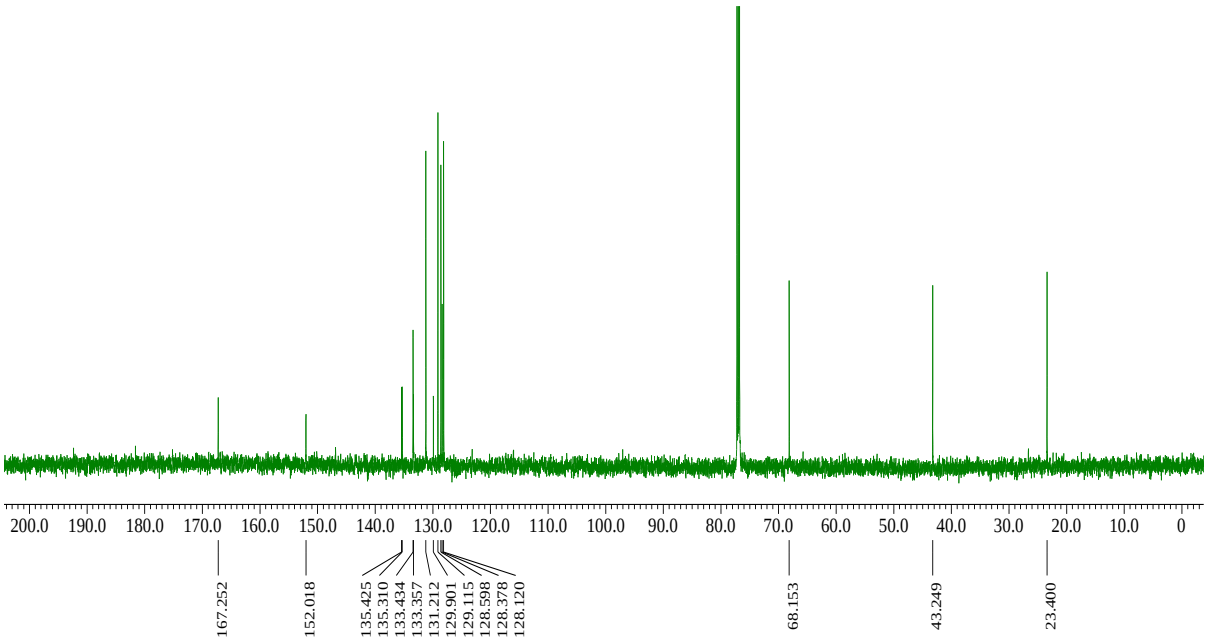
3.044
3.037
3.032


O
NCbz
Cl

1i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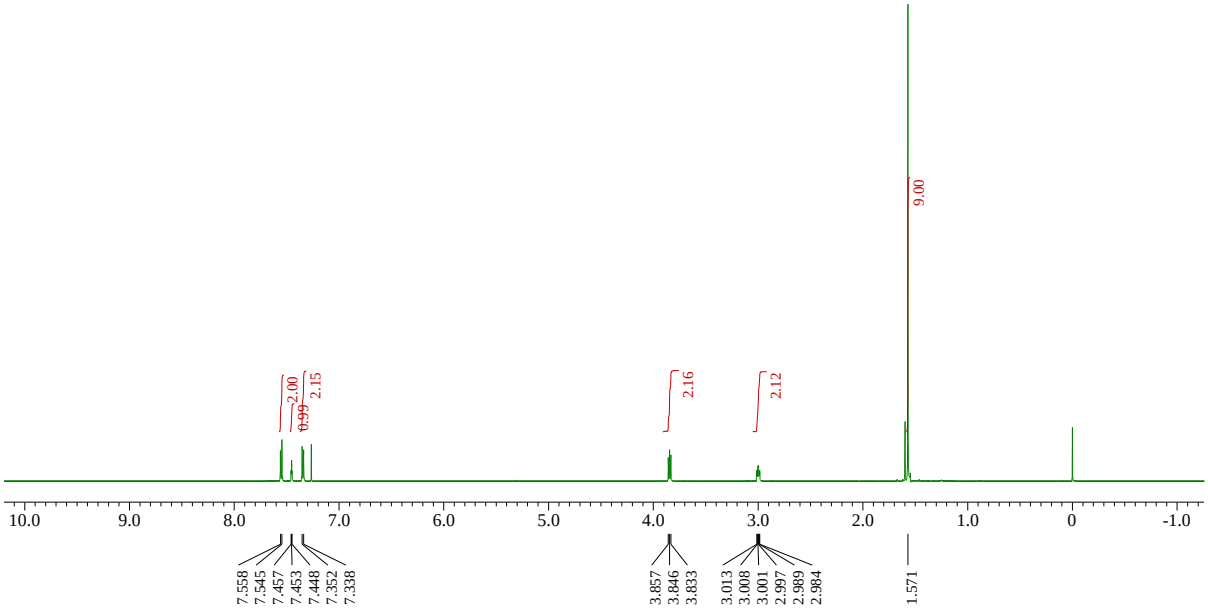
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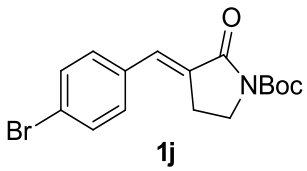
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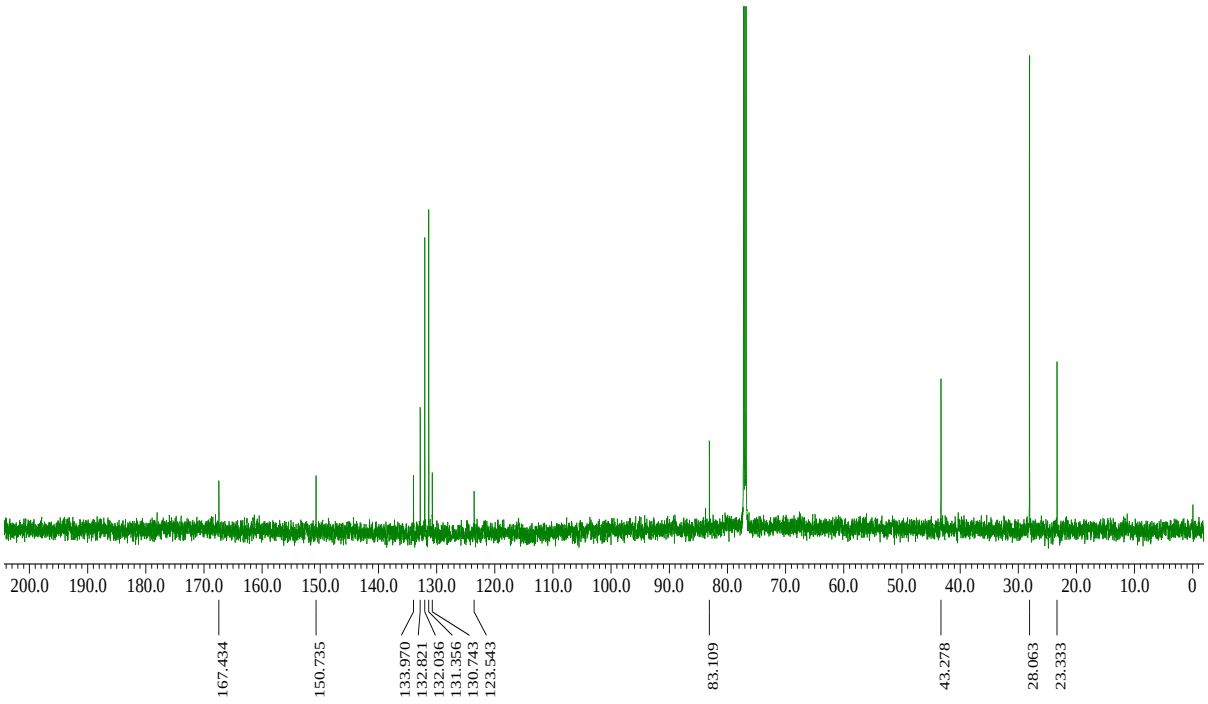
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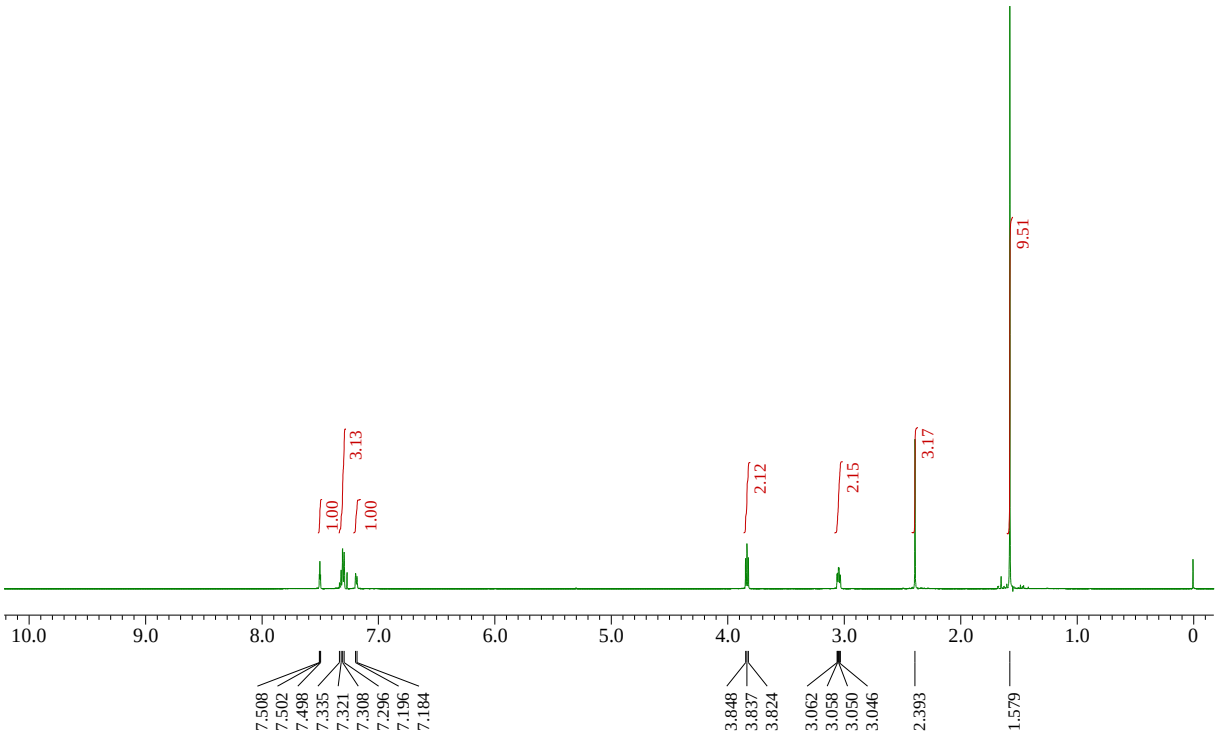
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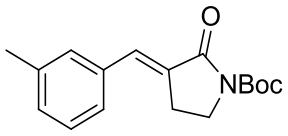
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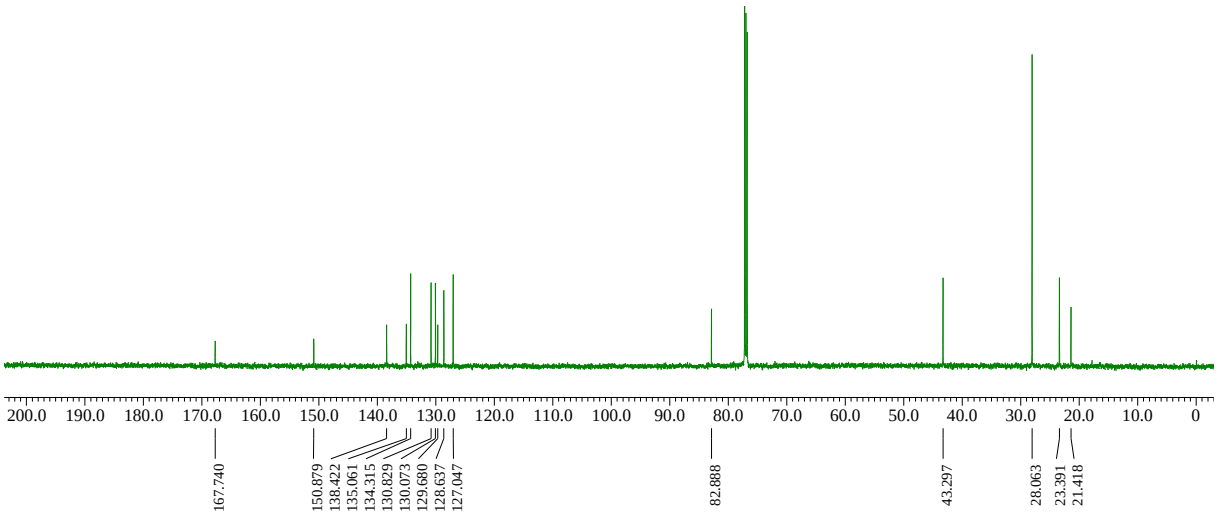
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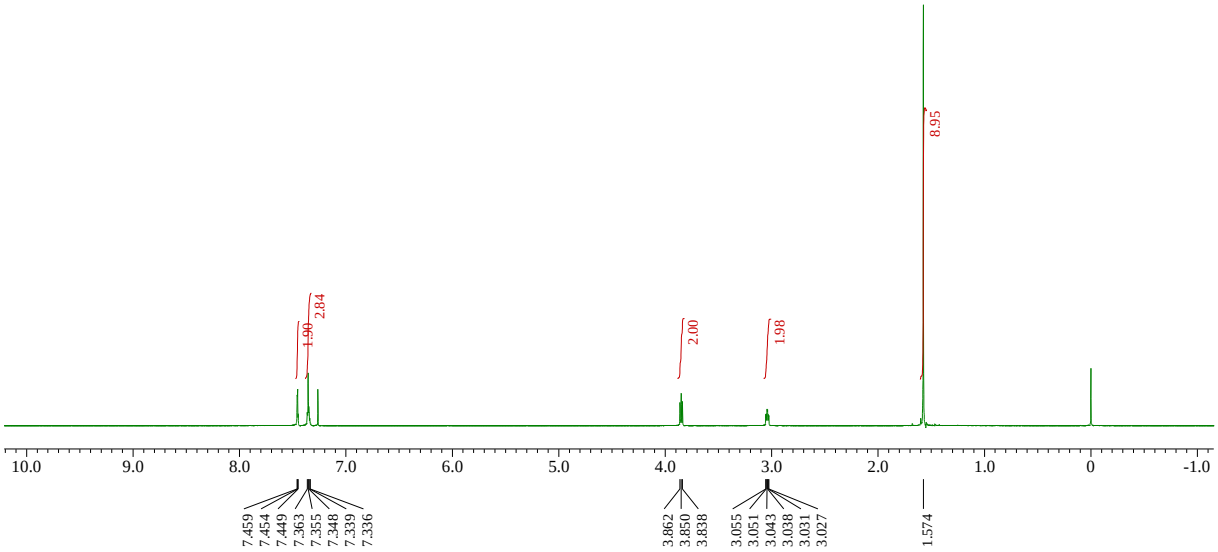
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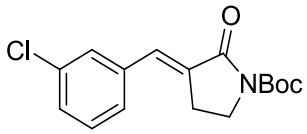
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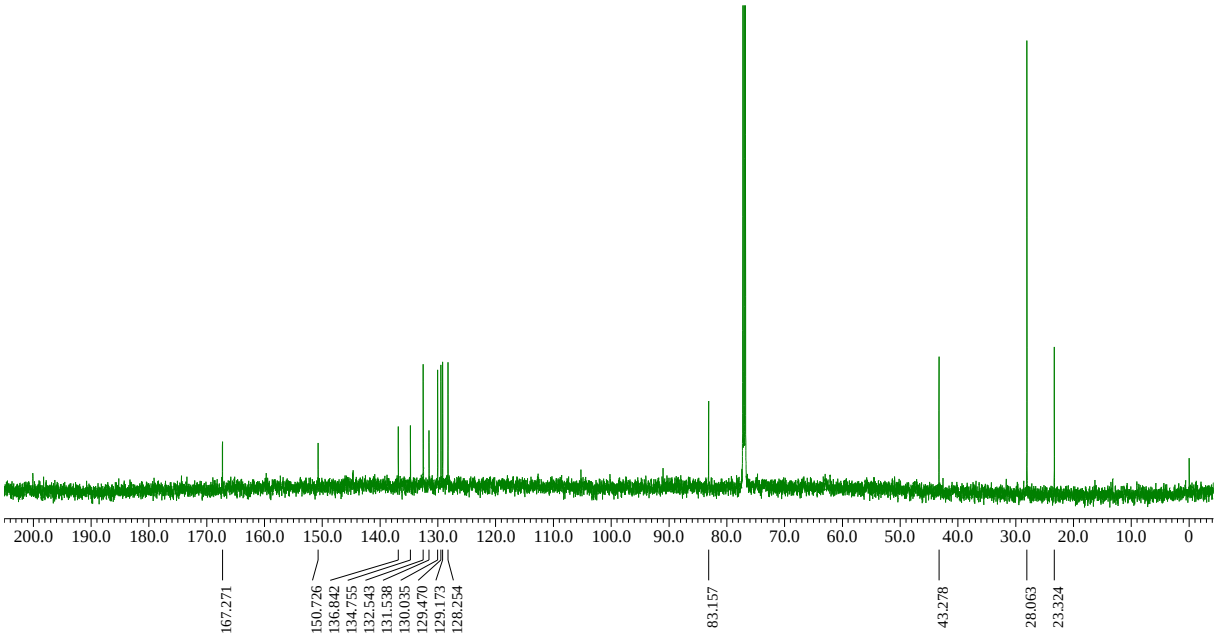
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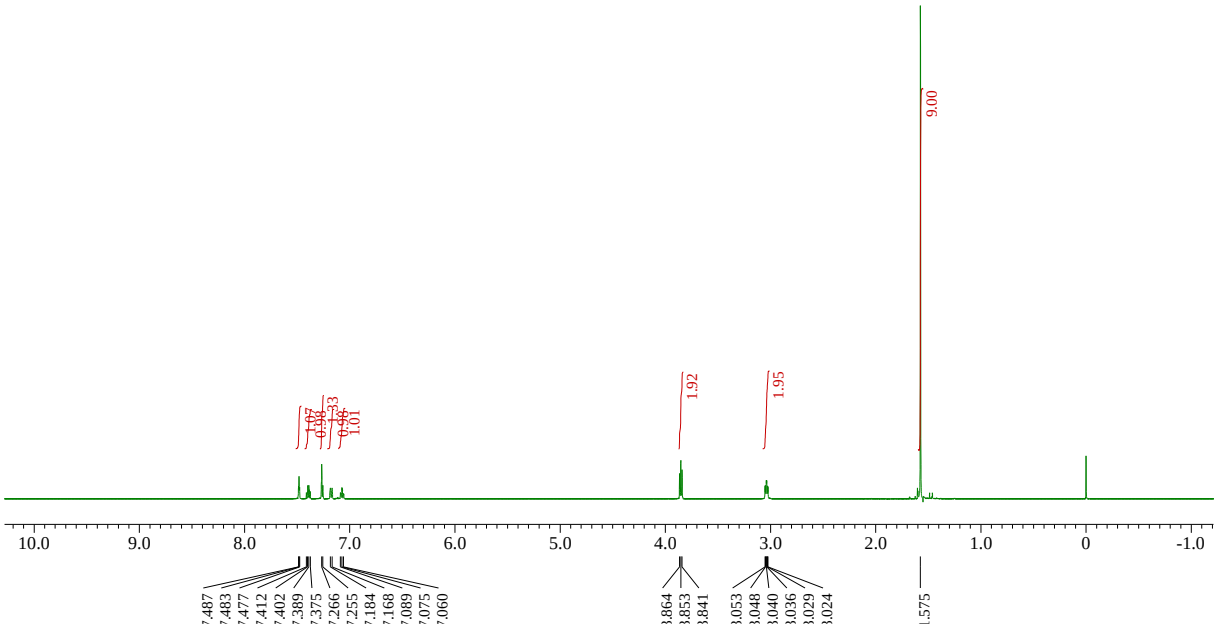
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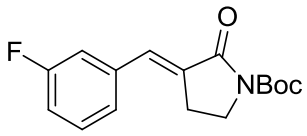
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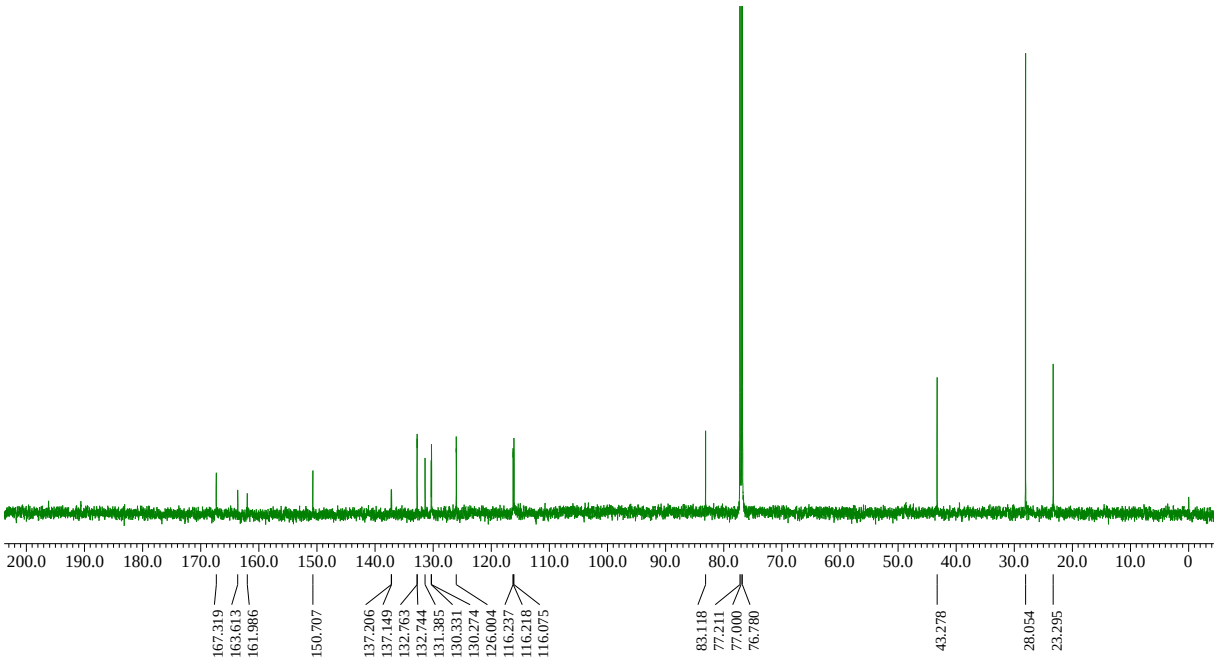
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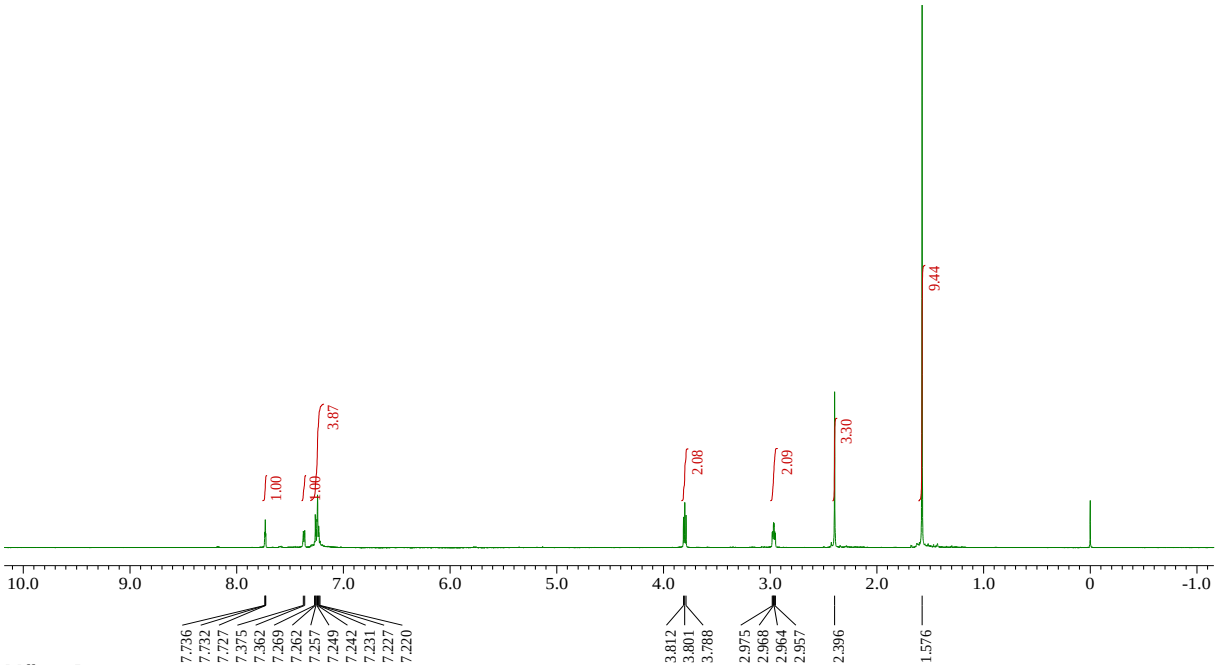
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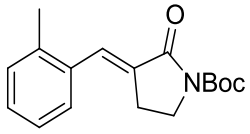
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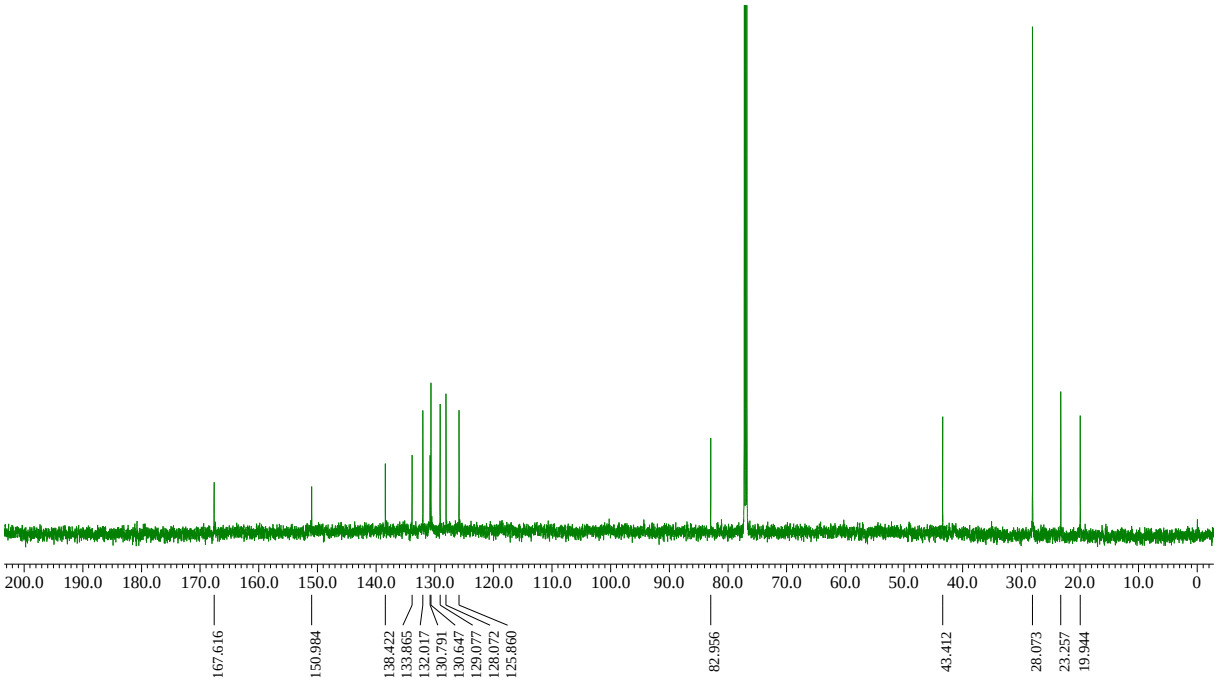
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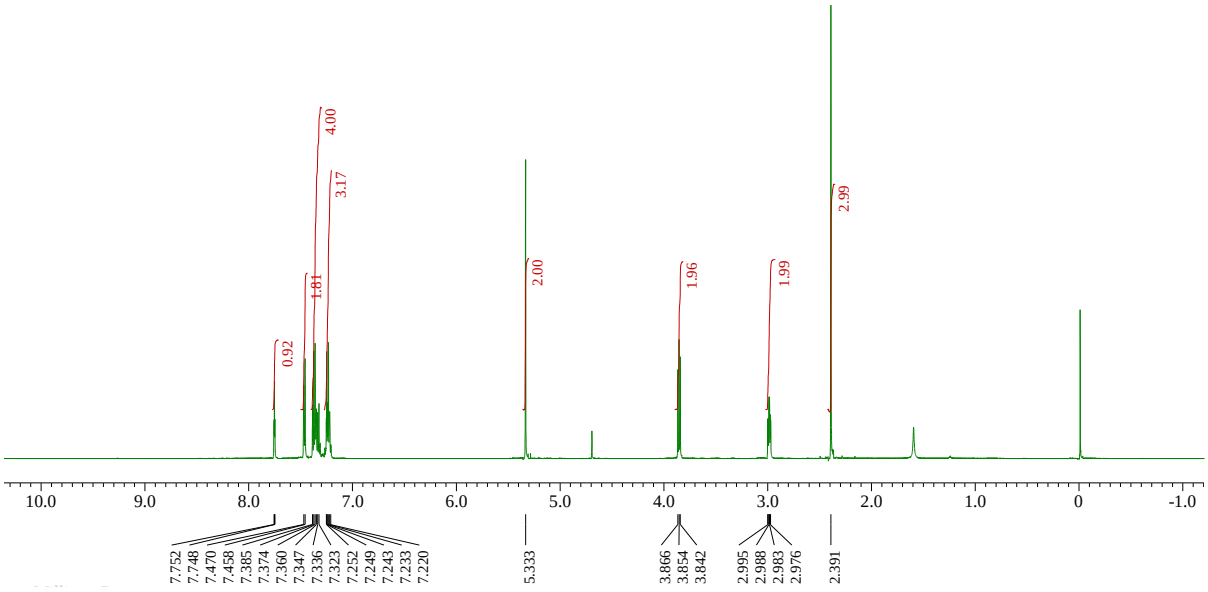
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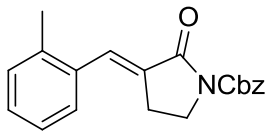
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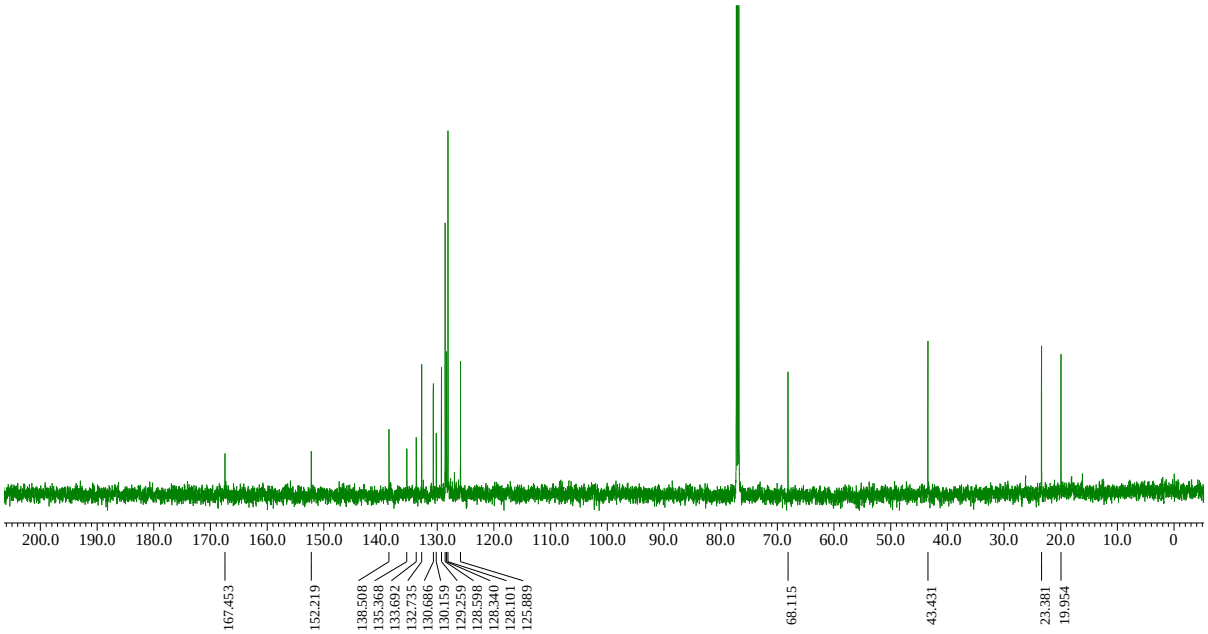
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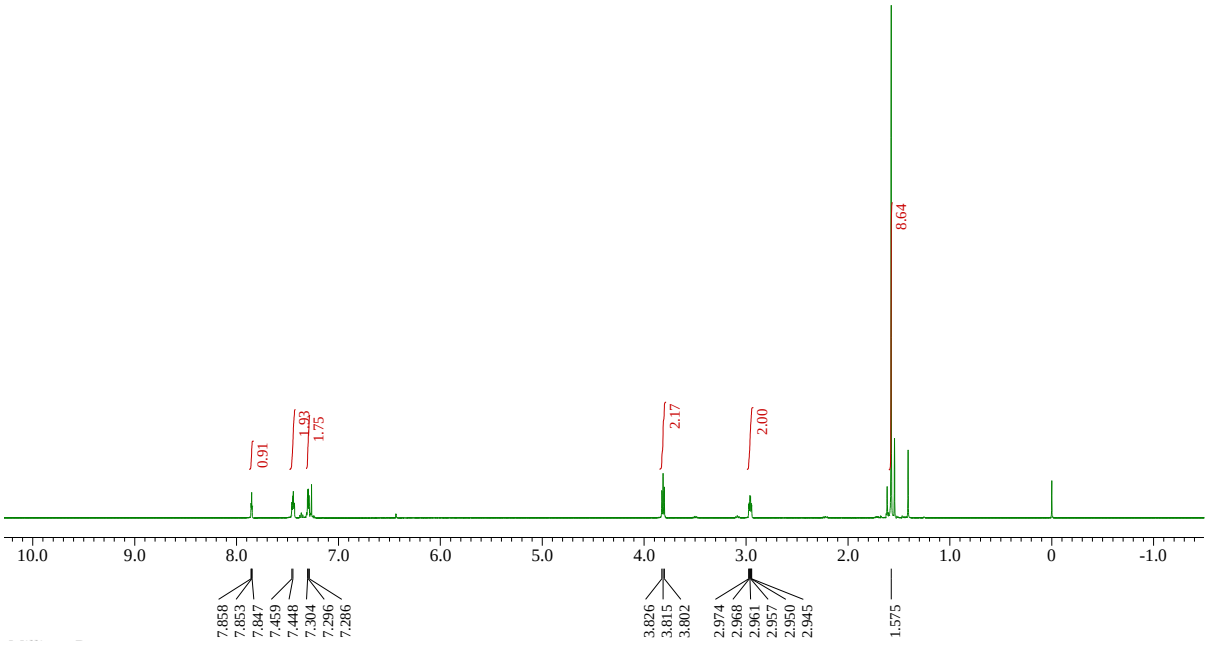
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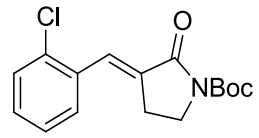
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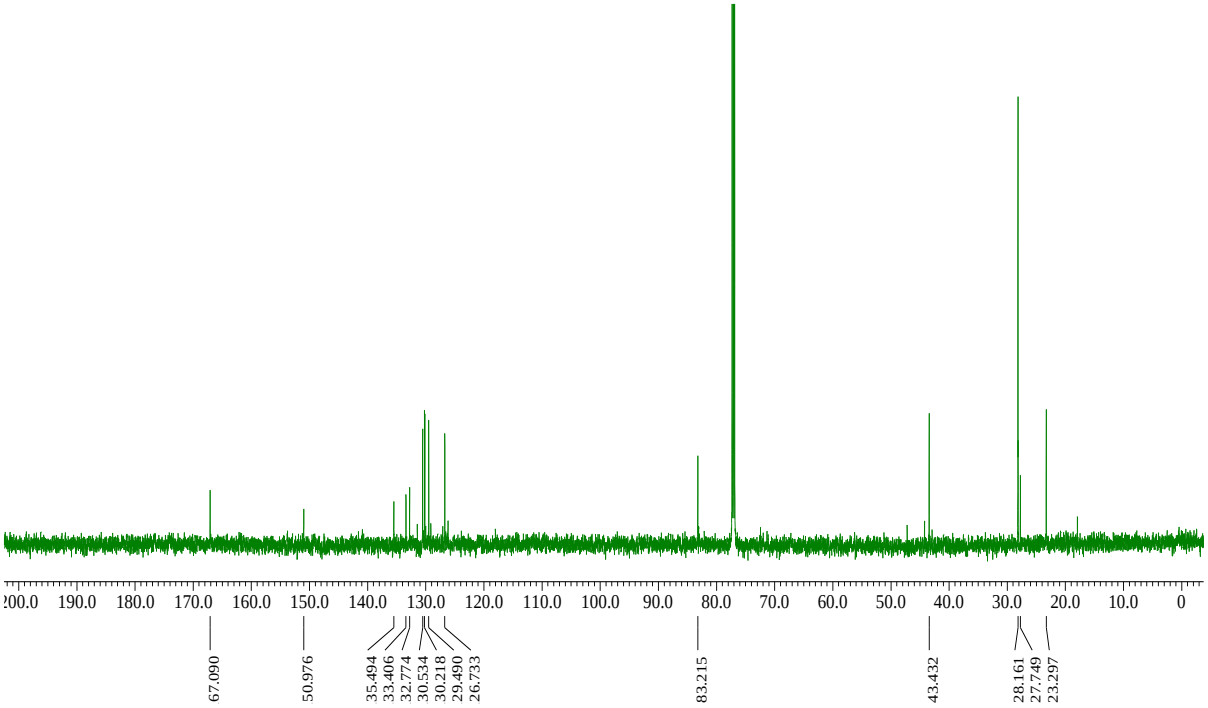
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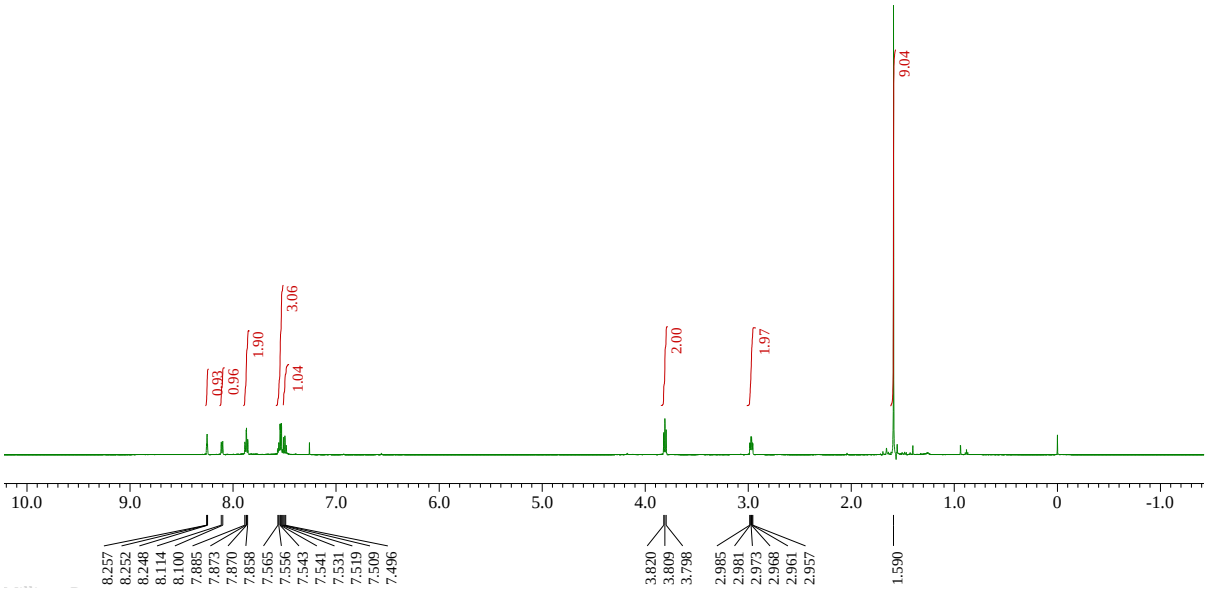
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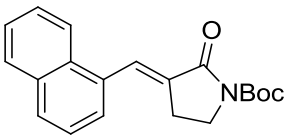
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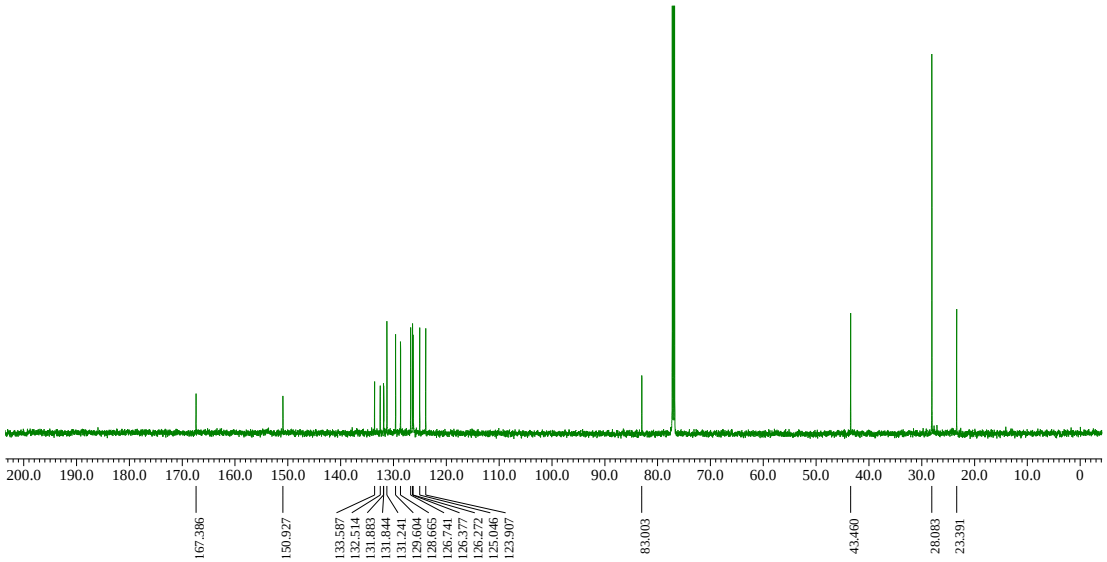
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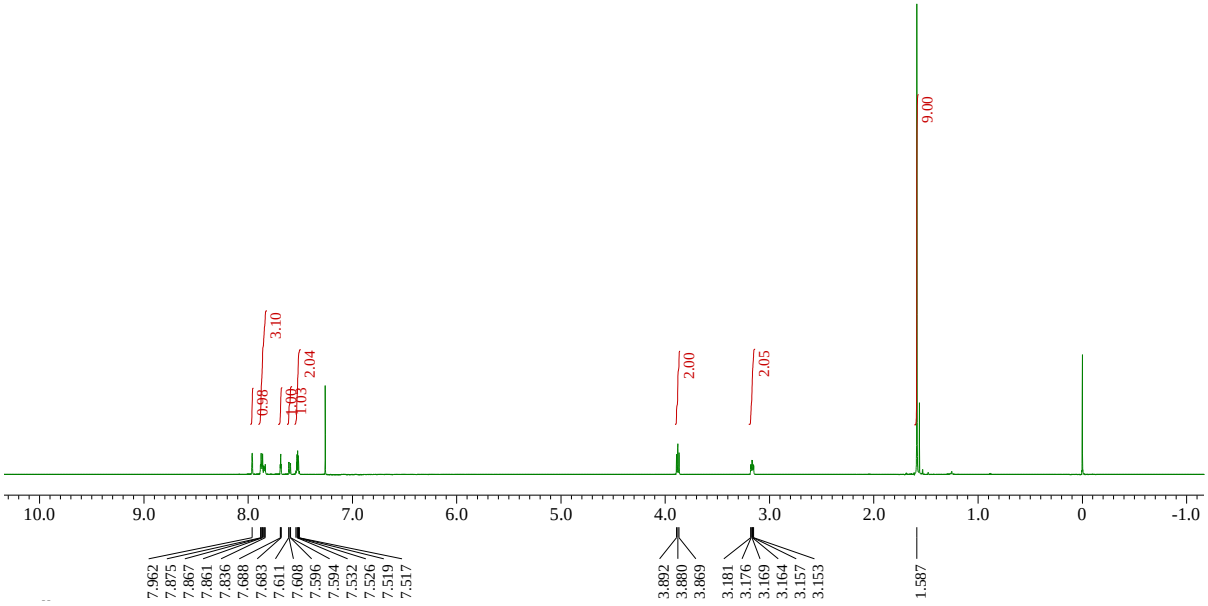
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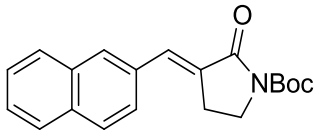
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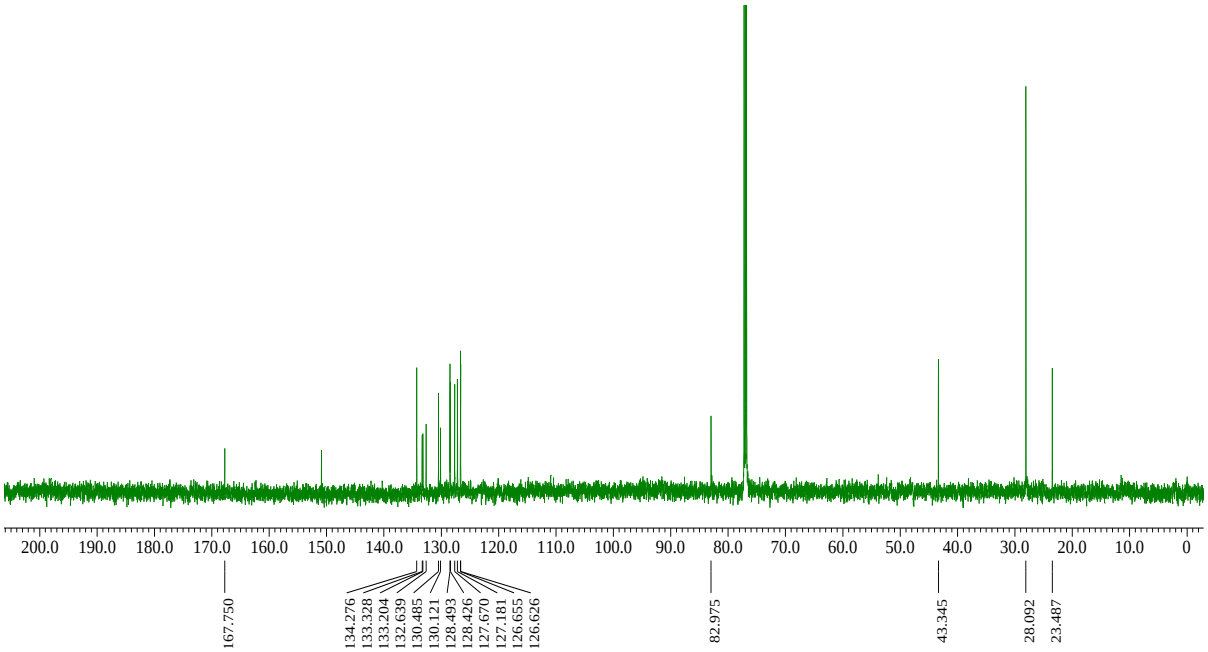
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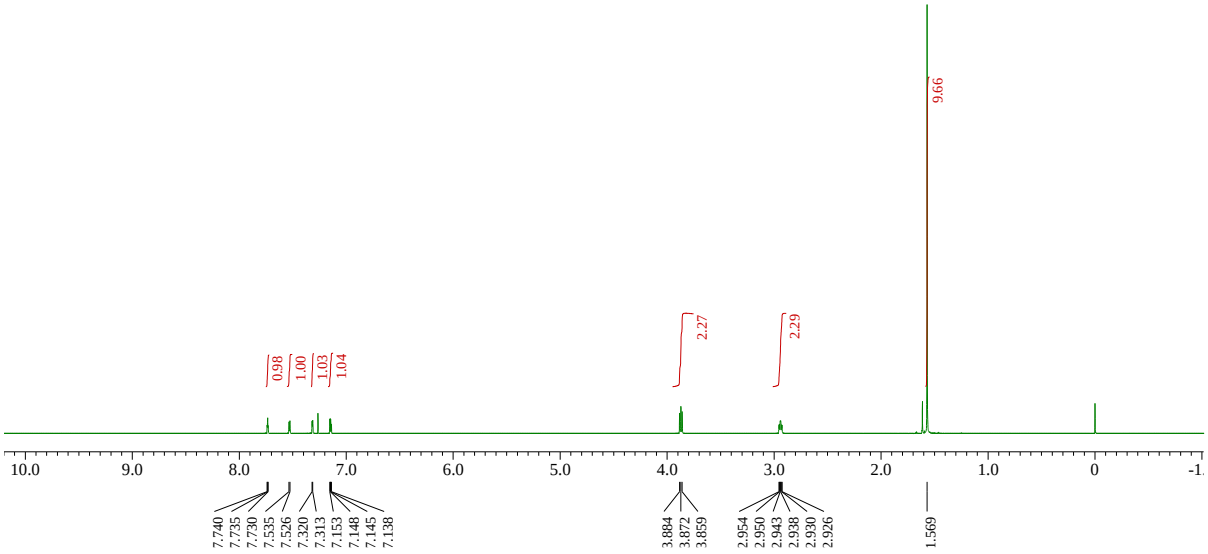
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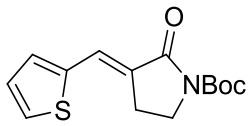
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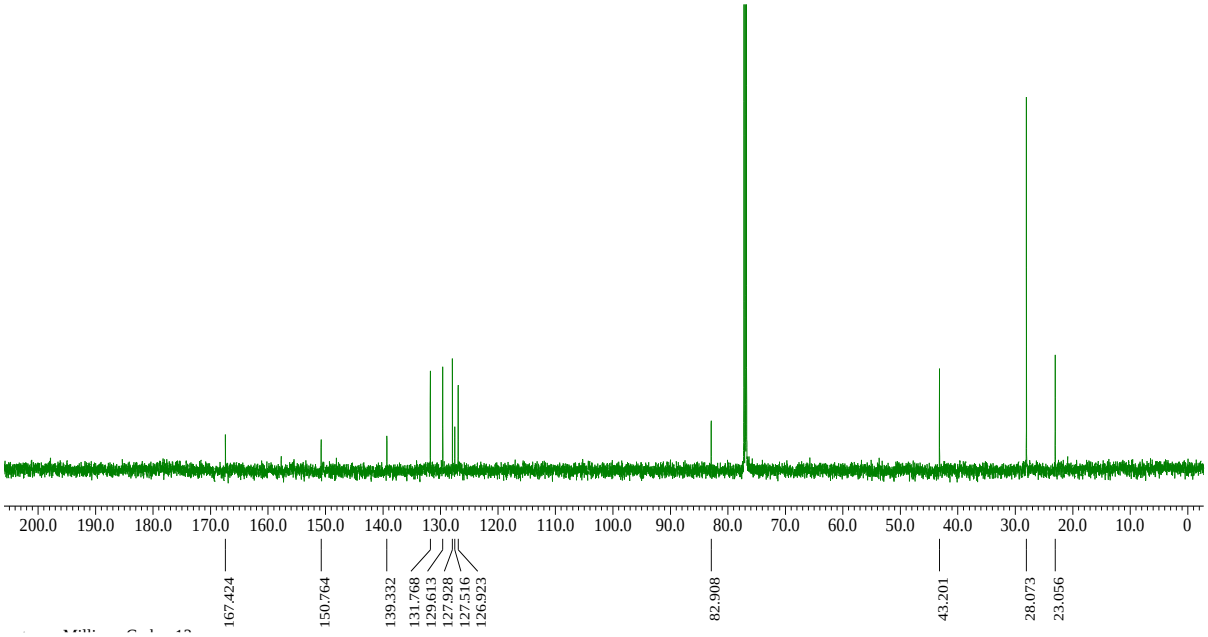
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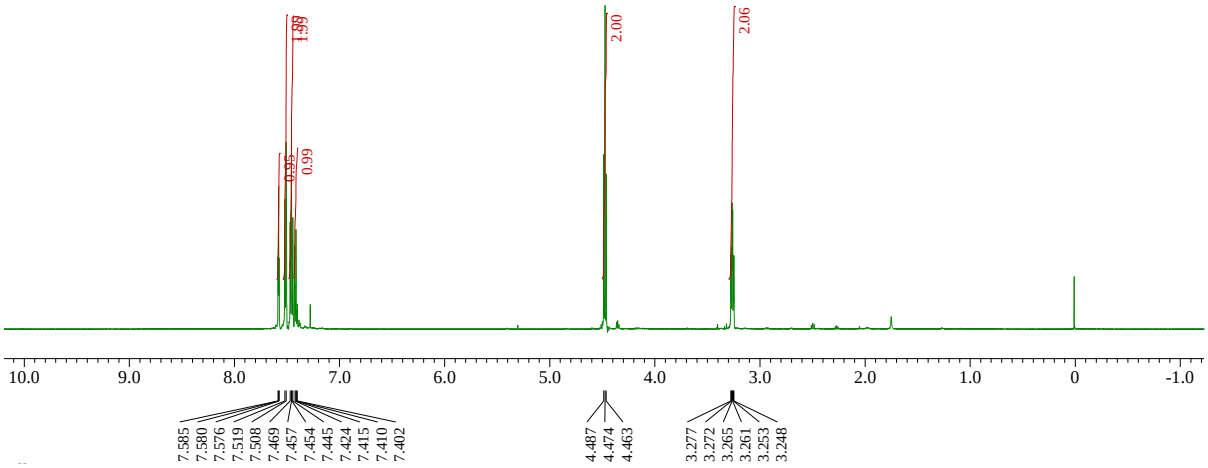
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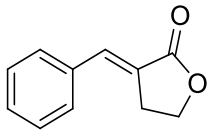
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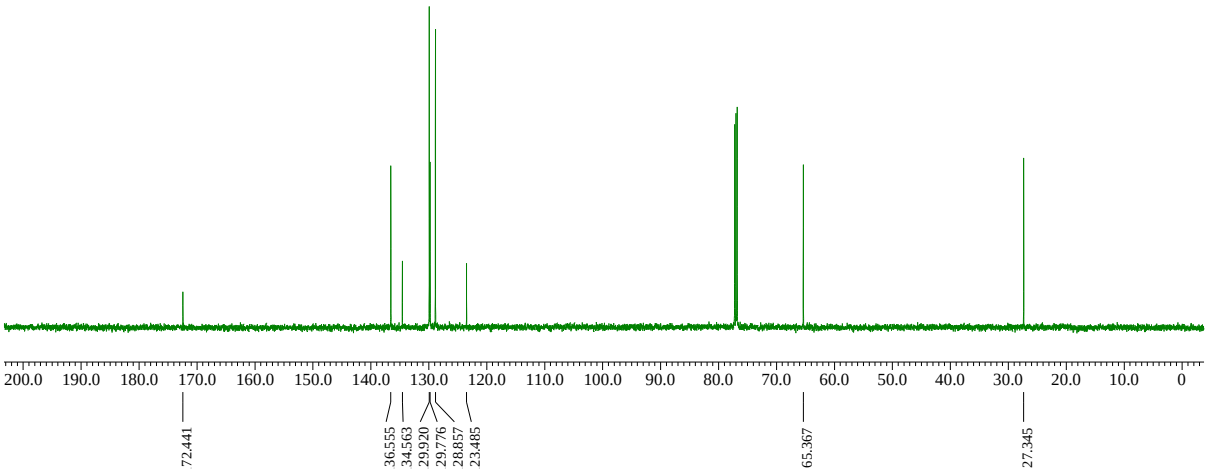
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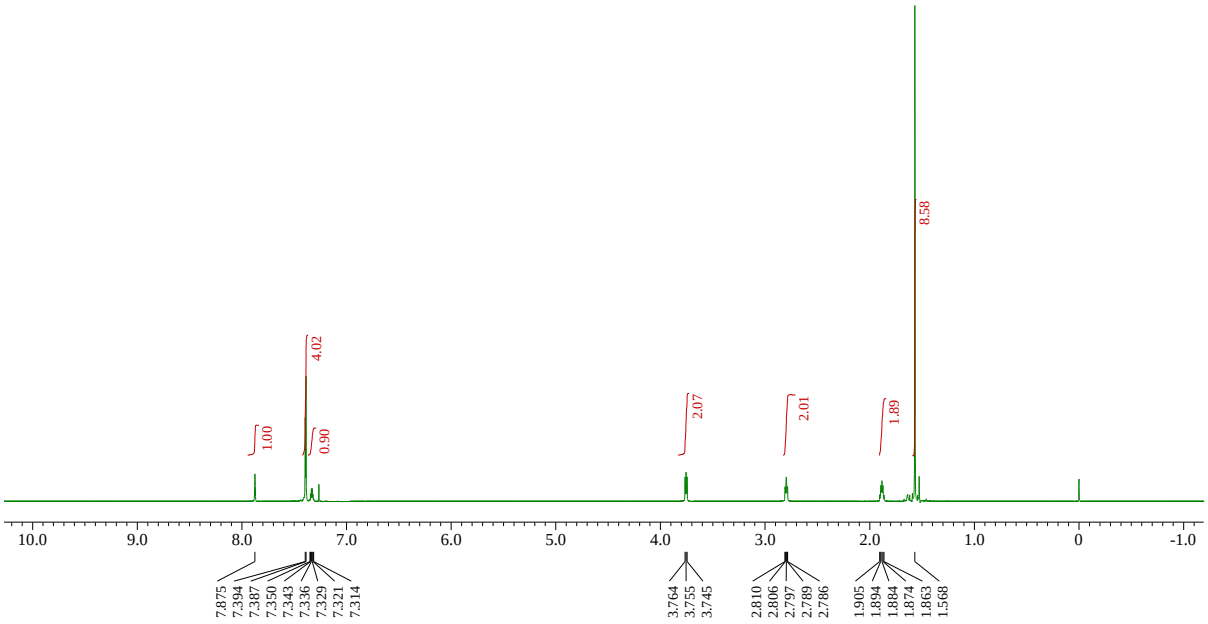
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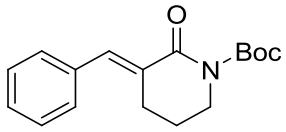
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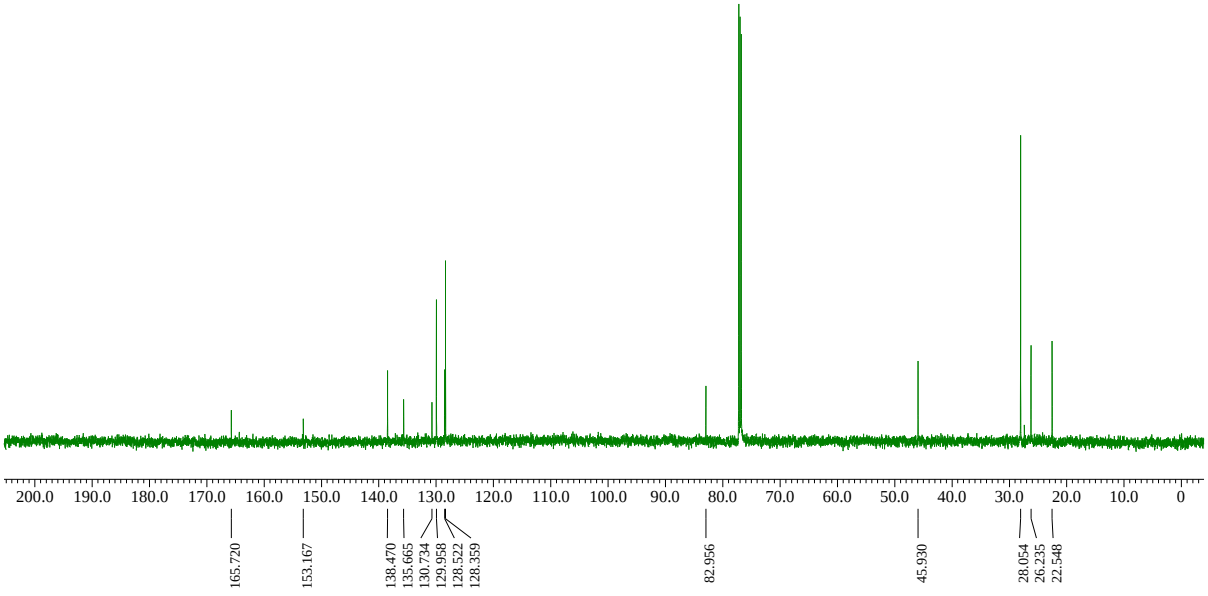
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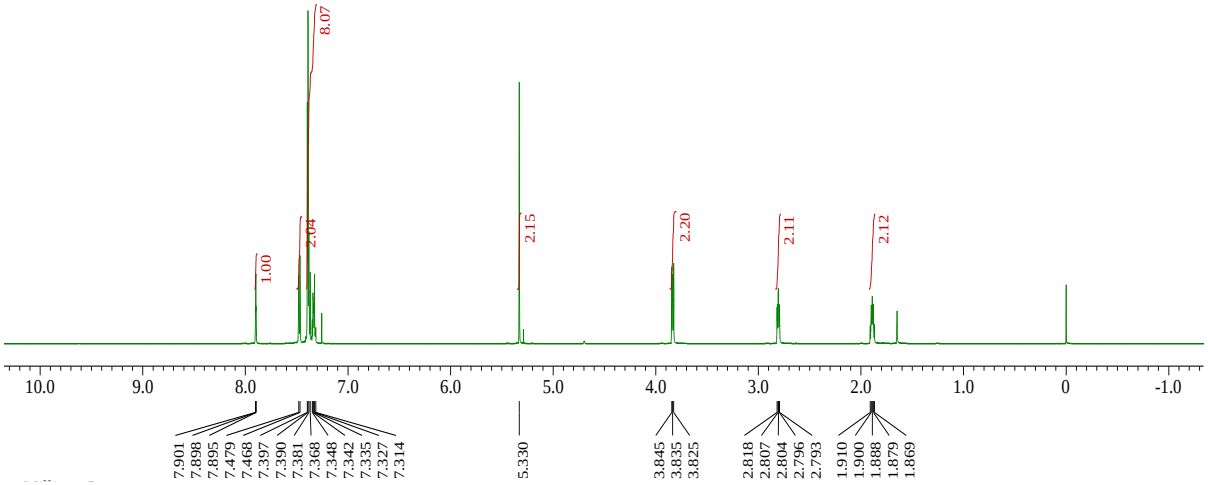
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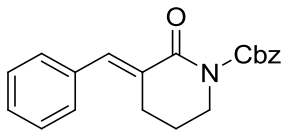
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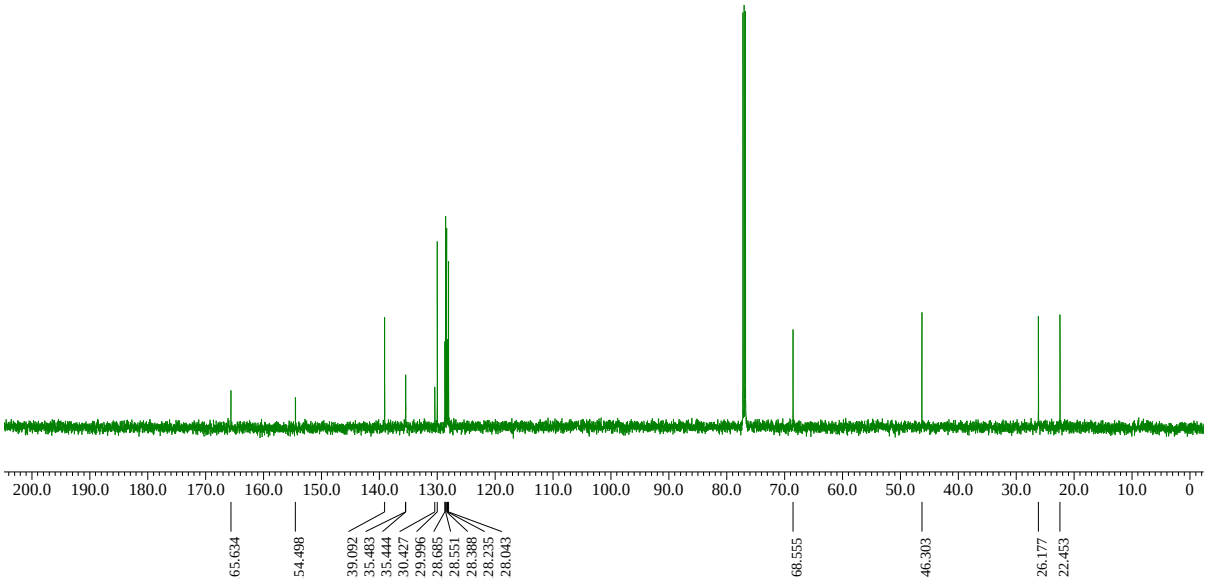
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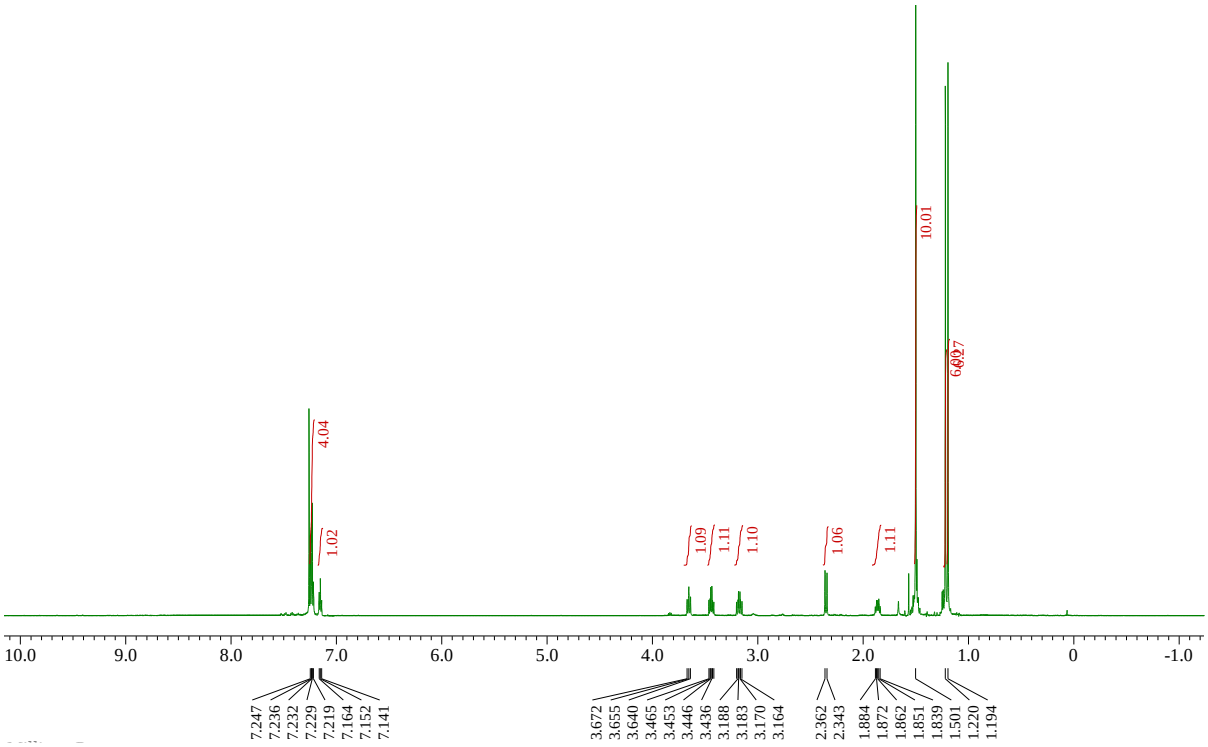
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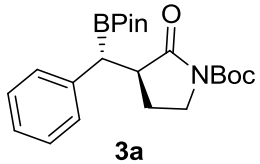
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NBoc

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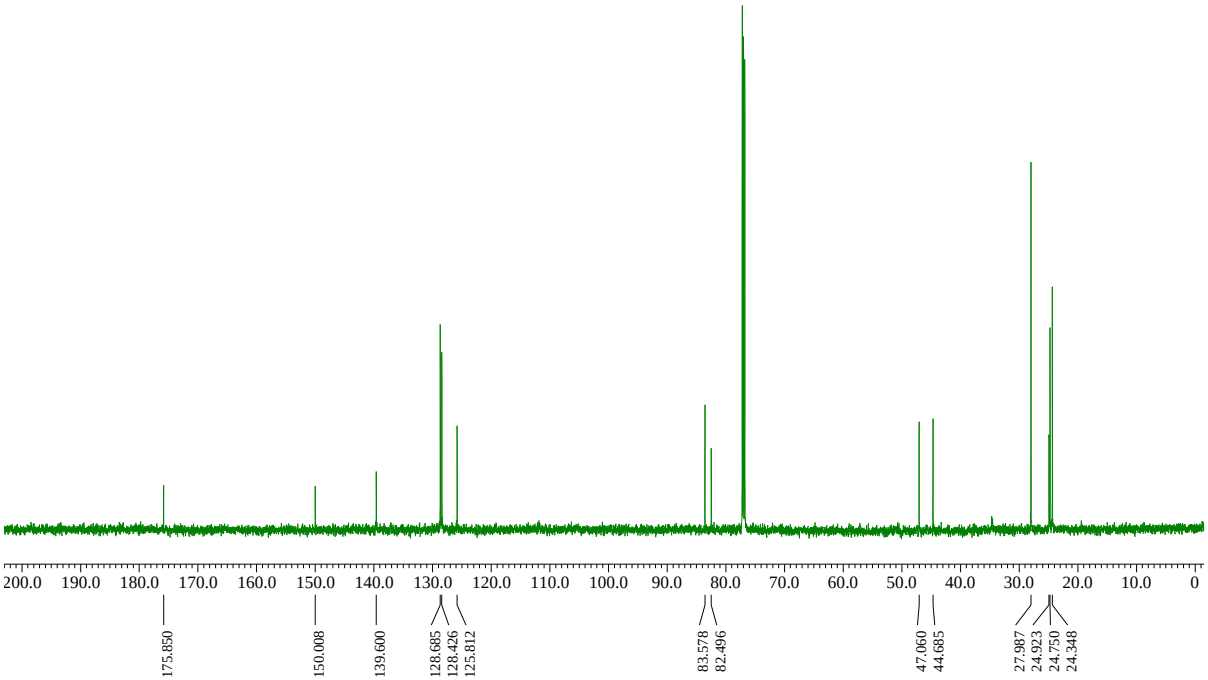
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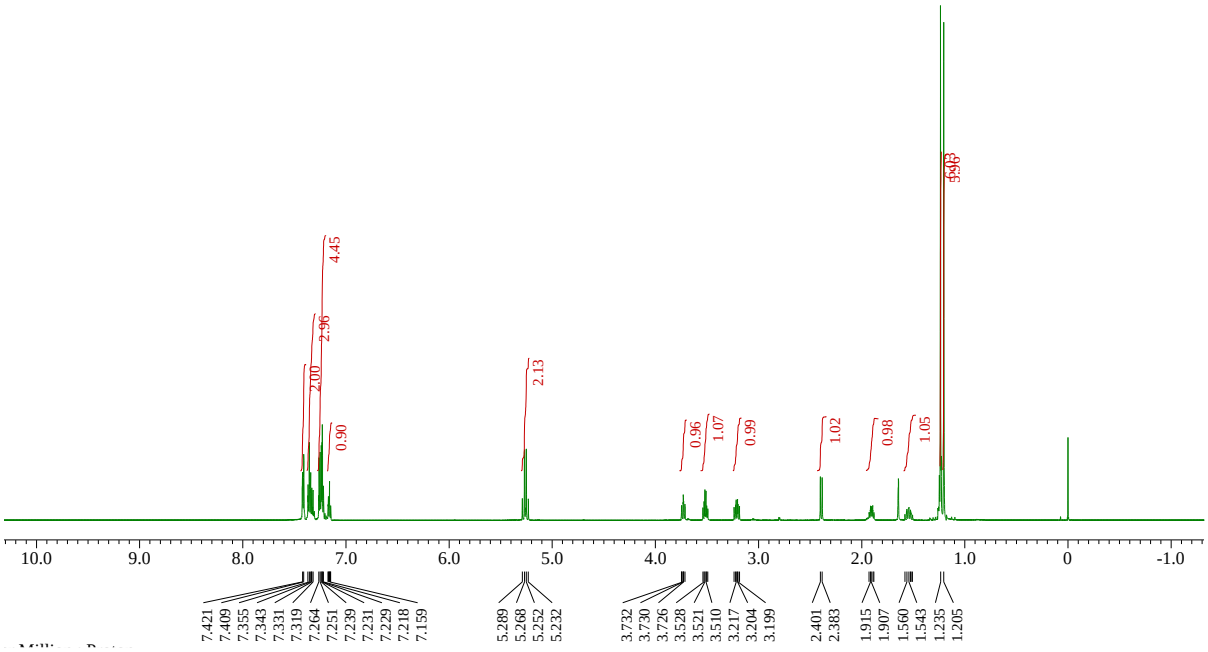
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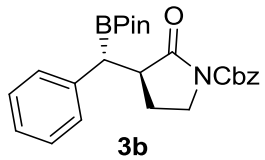
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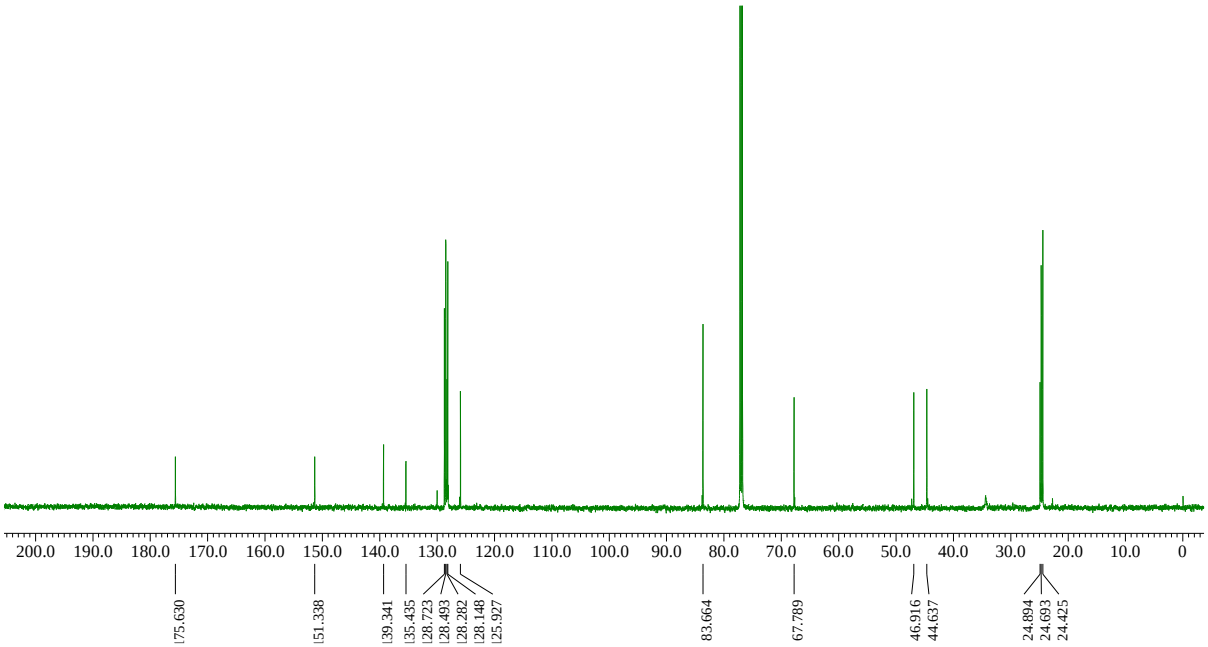
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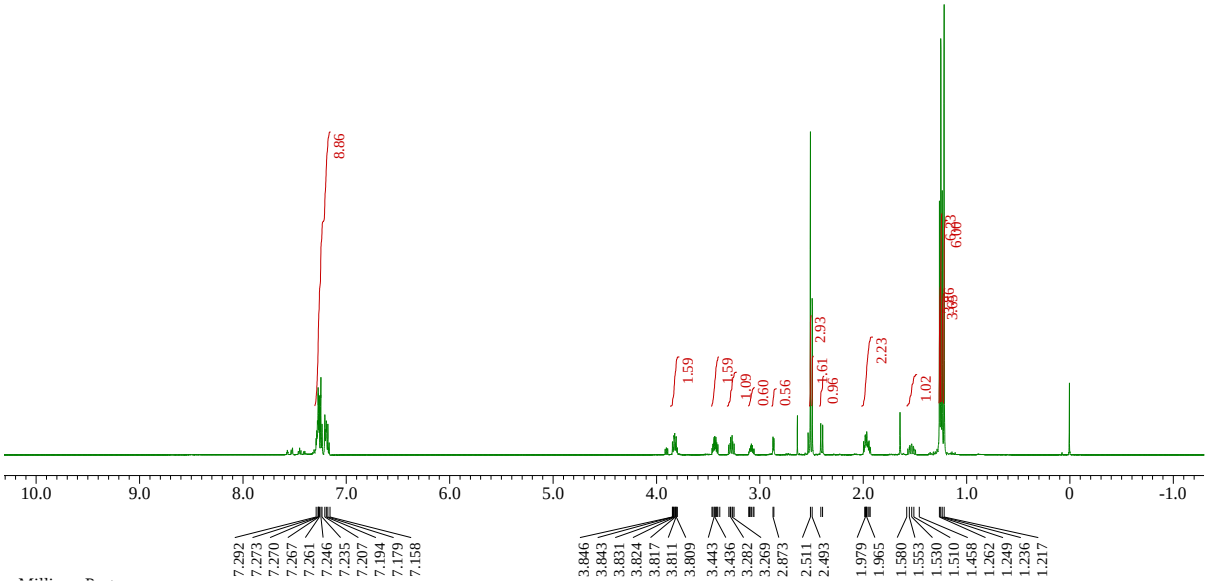

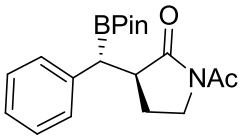

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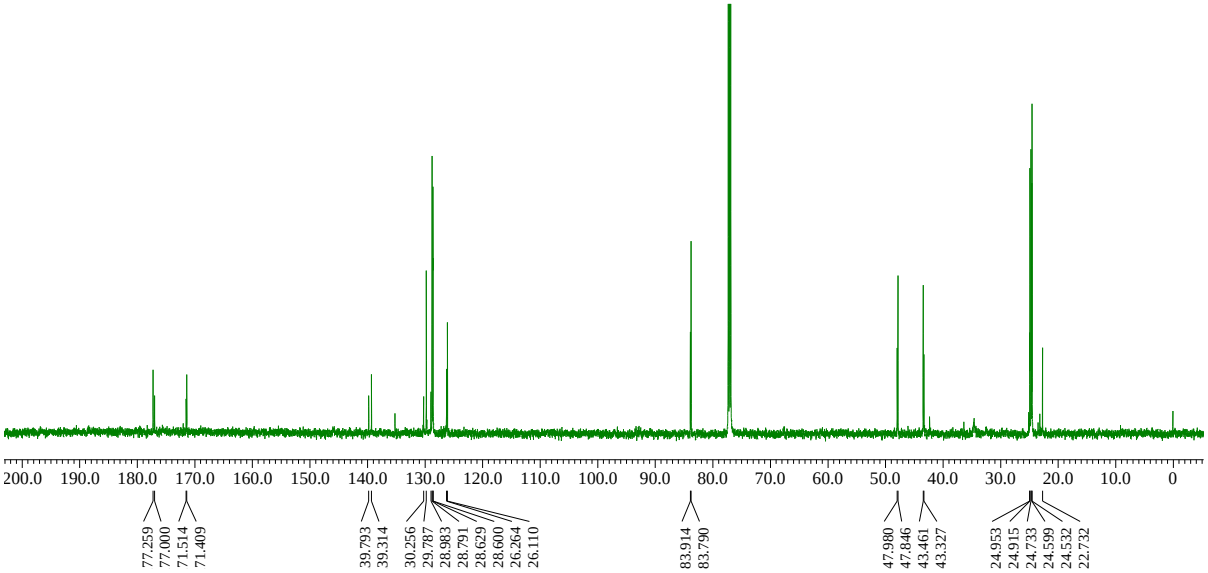

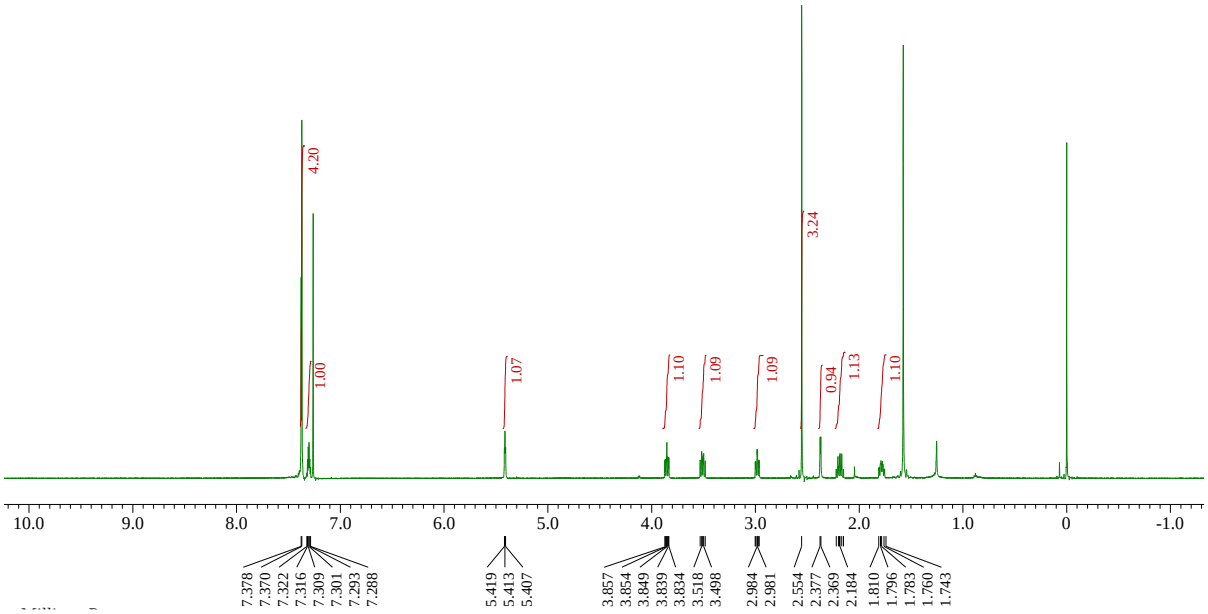
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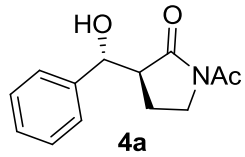
HO
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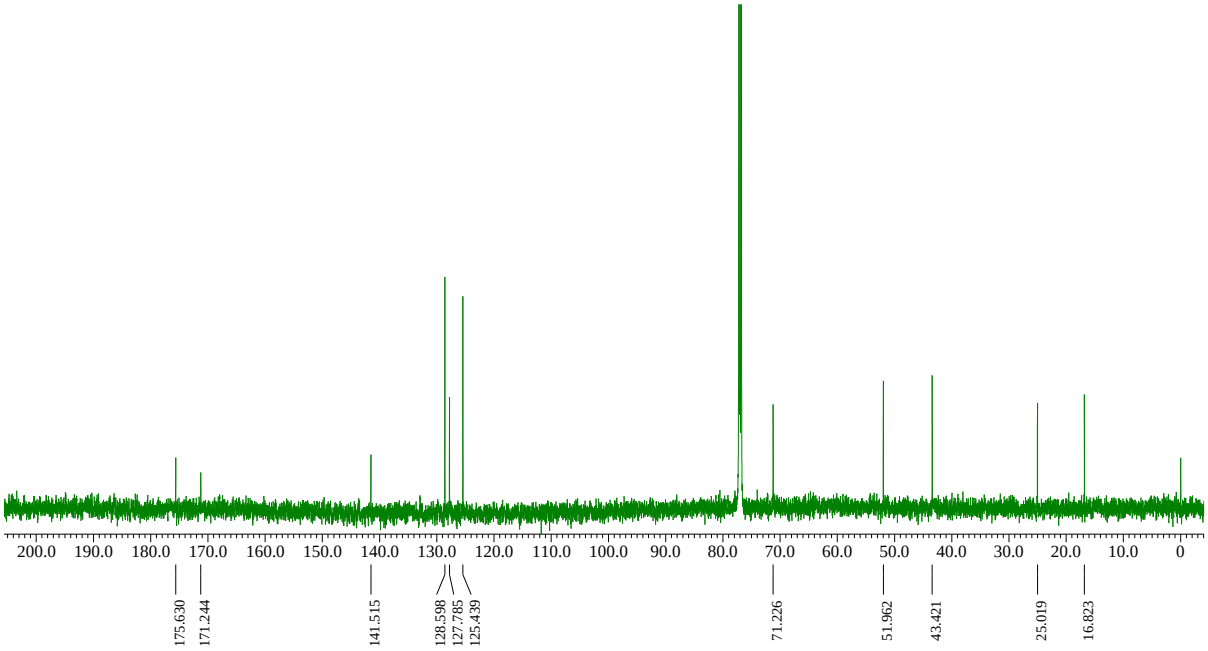
NAc

4a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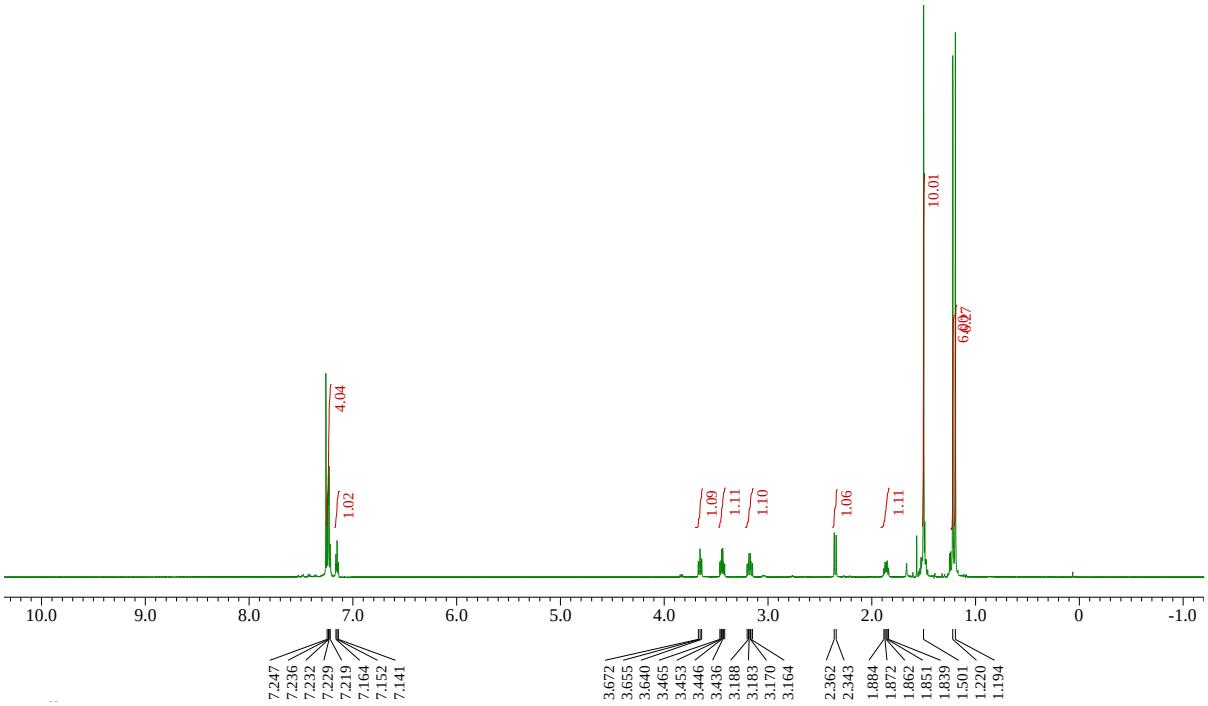
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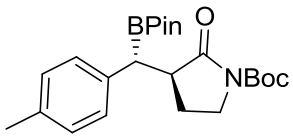
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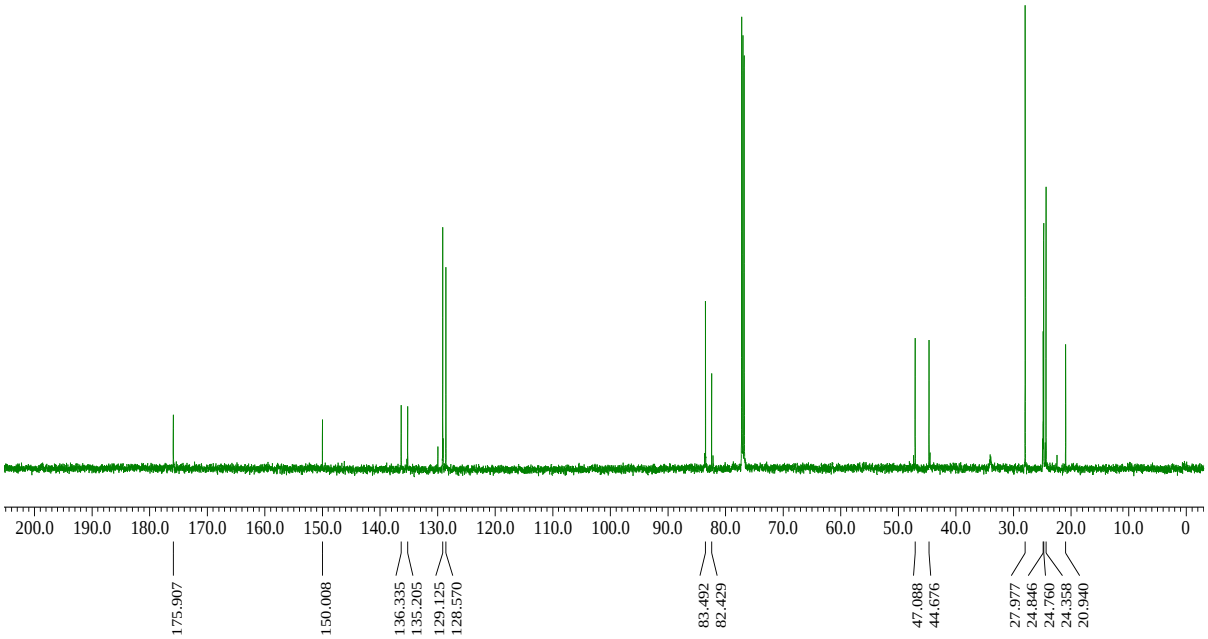
NBoc

3d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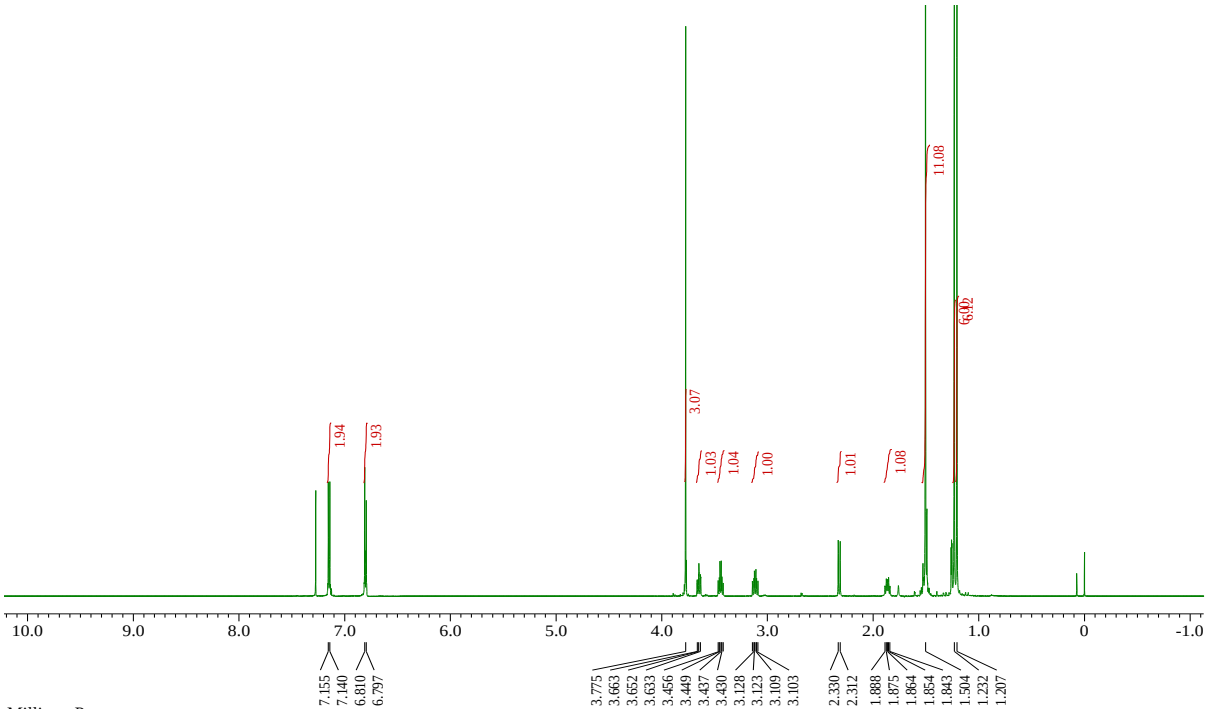
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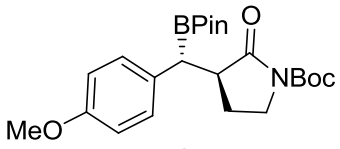
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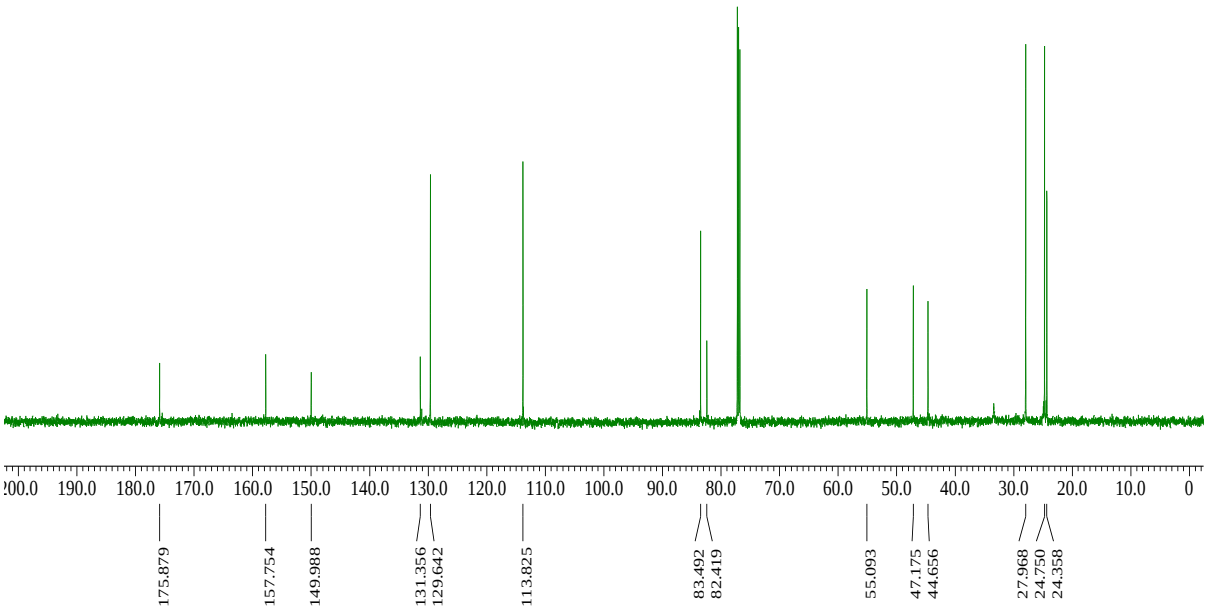
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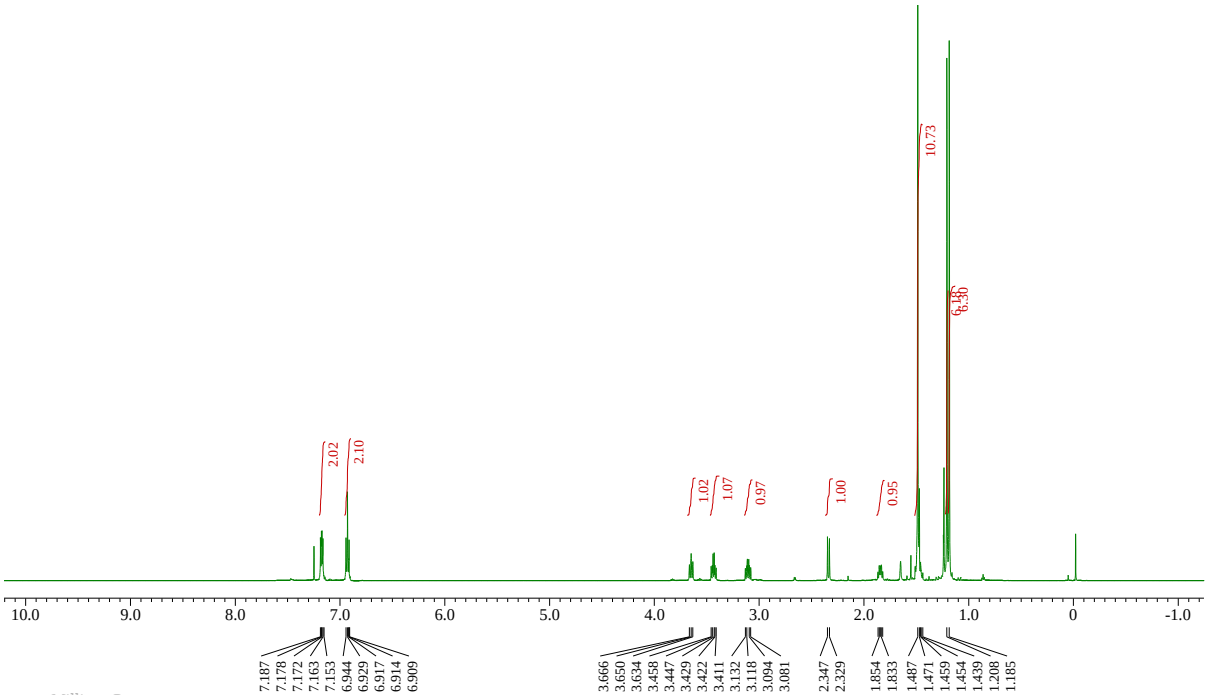
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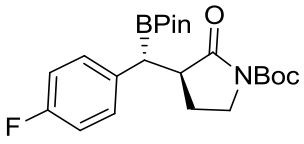
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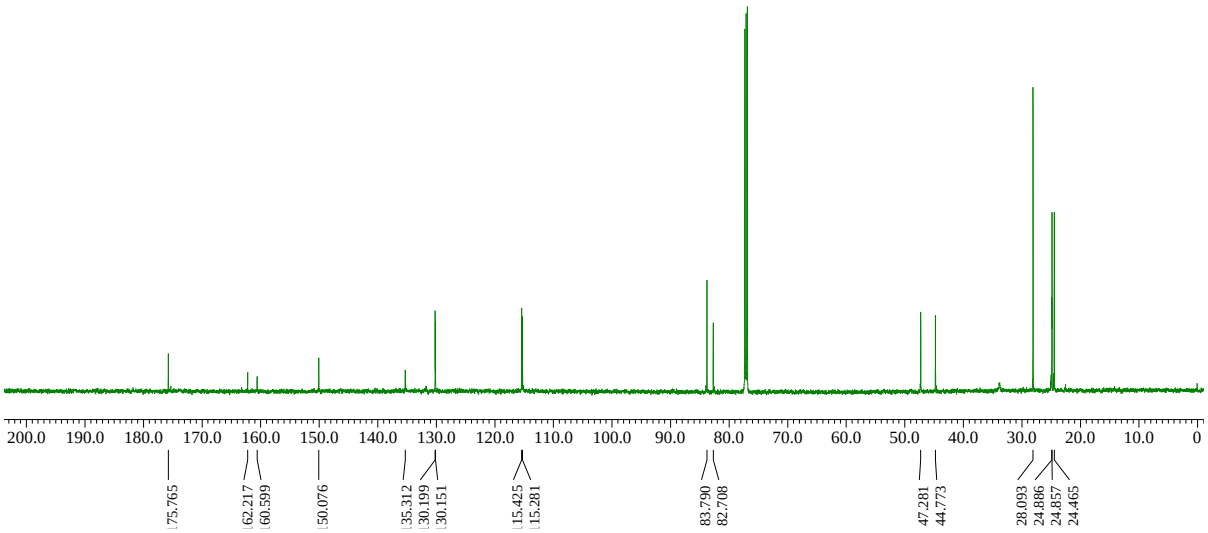
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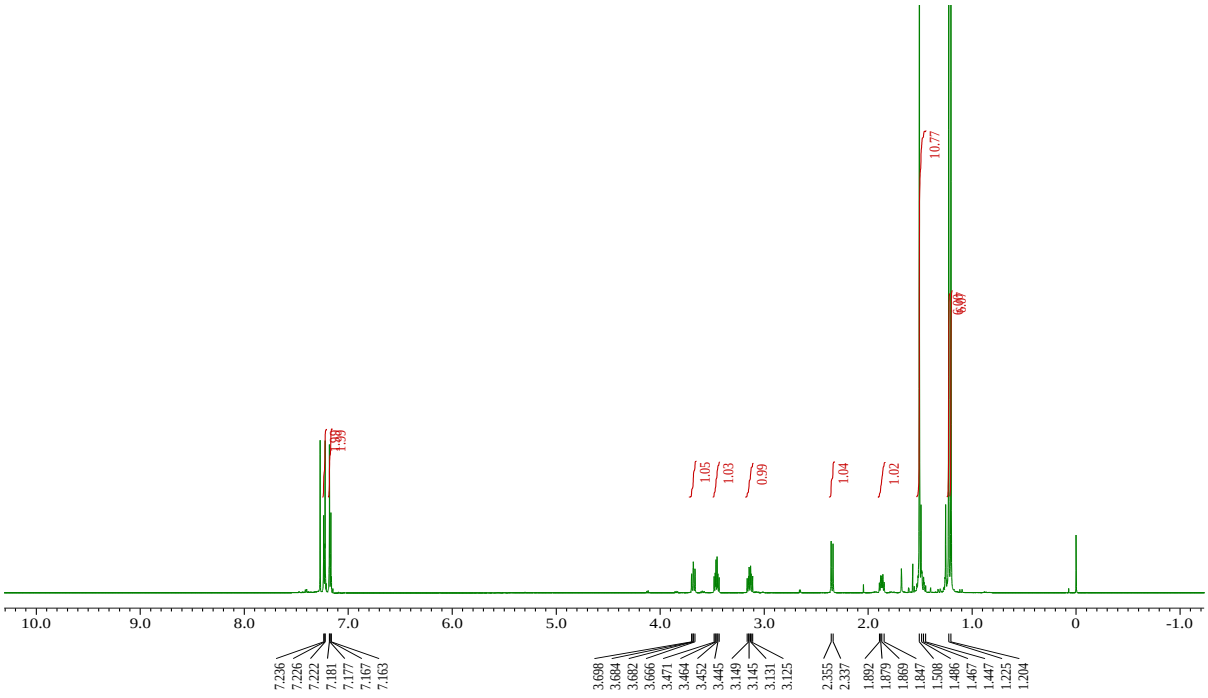
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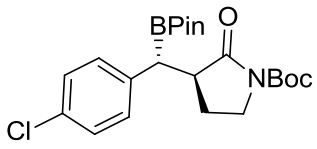
BPin
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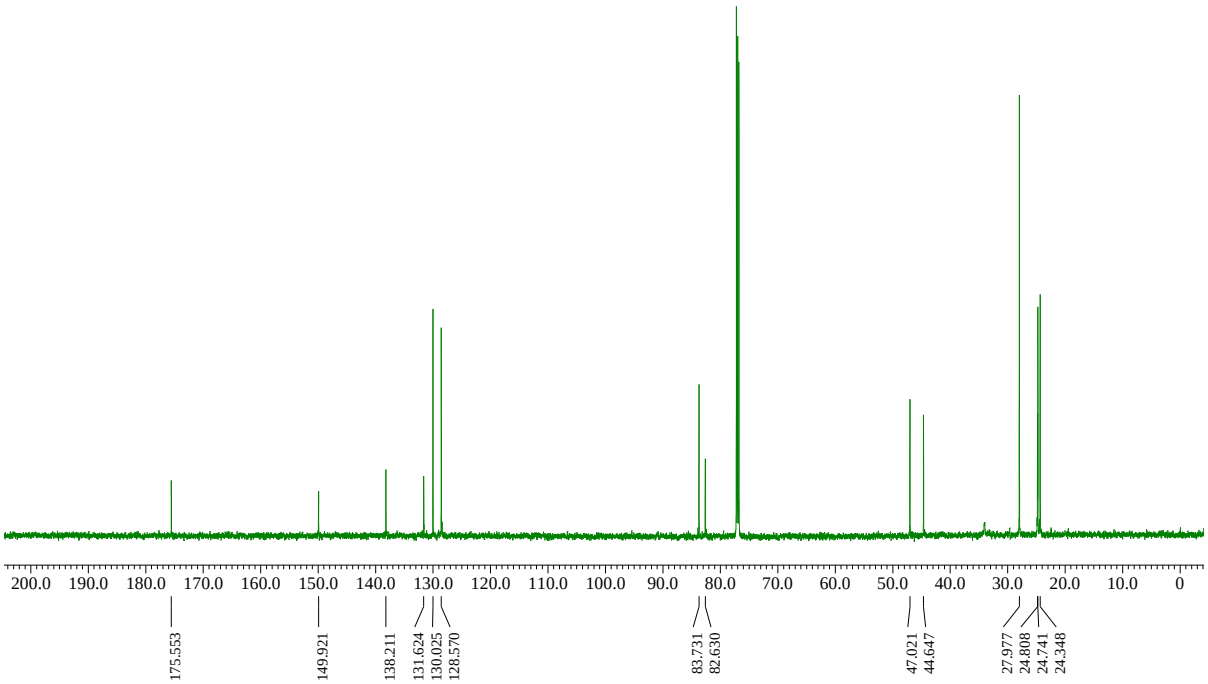
NBoc
Cl

3g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30.0
20.0
10.0
0
175.553
149.921
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27.977
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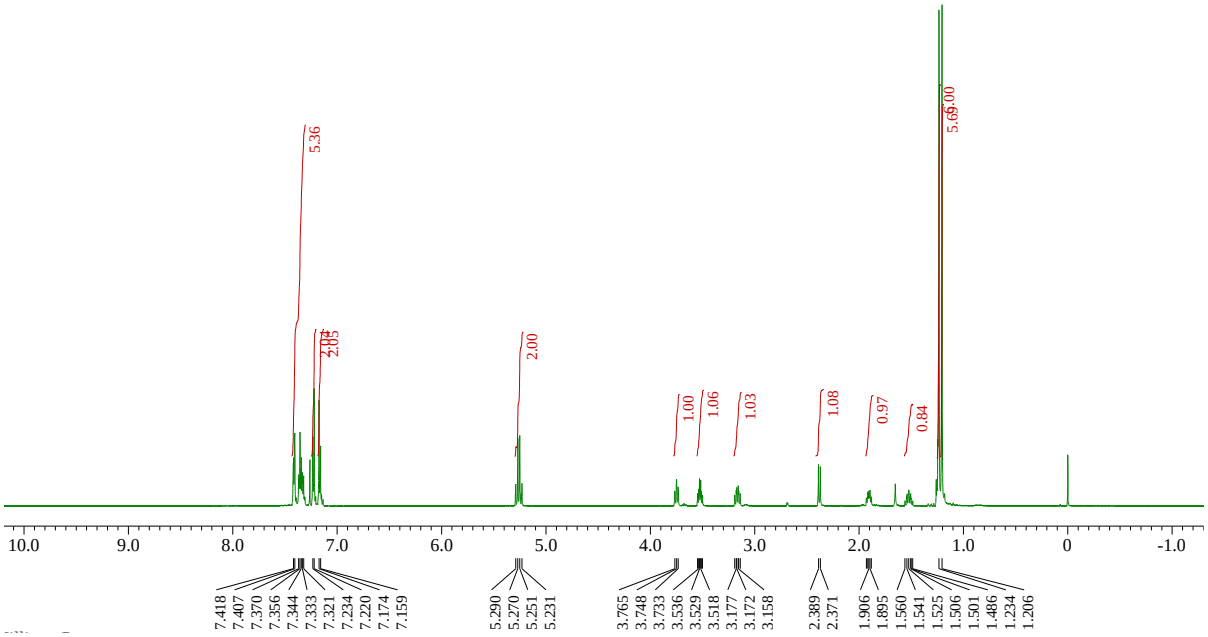
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-1.0
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7.356
7.344
7.333
7.321
7.234
7.220
7.174
7.159
5.290
5.270
5.251
5.231
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3.748
3.733
3.536
3.529
3.518
3.177
3.172
3.158
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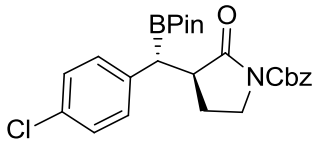
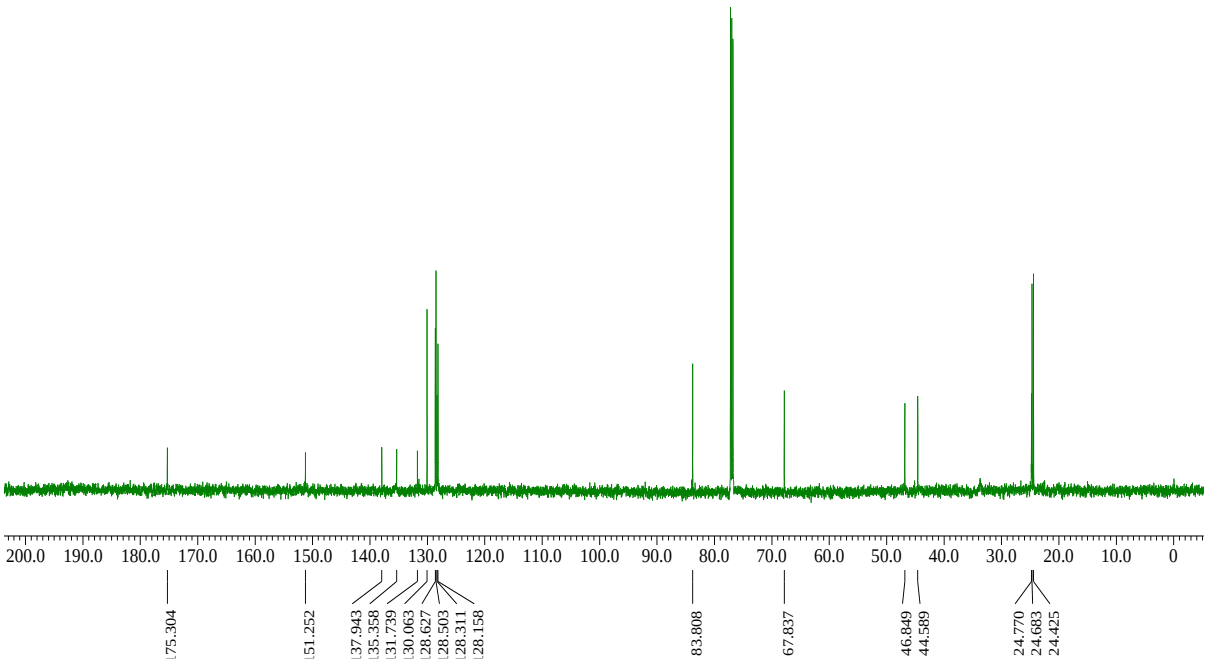

BPin
O
NCbz
Cl

3h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51.252
37.943
35.358
31.739
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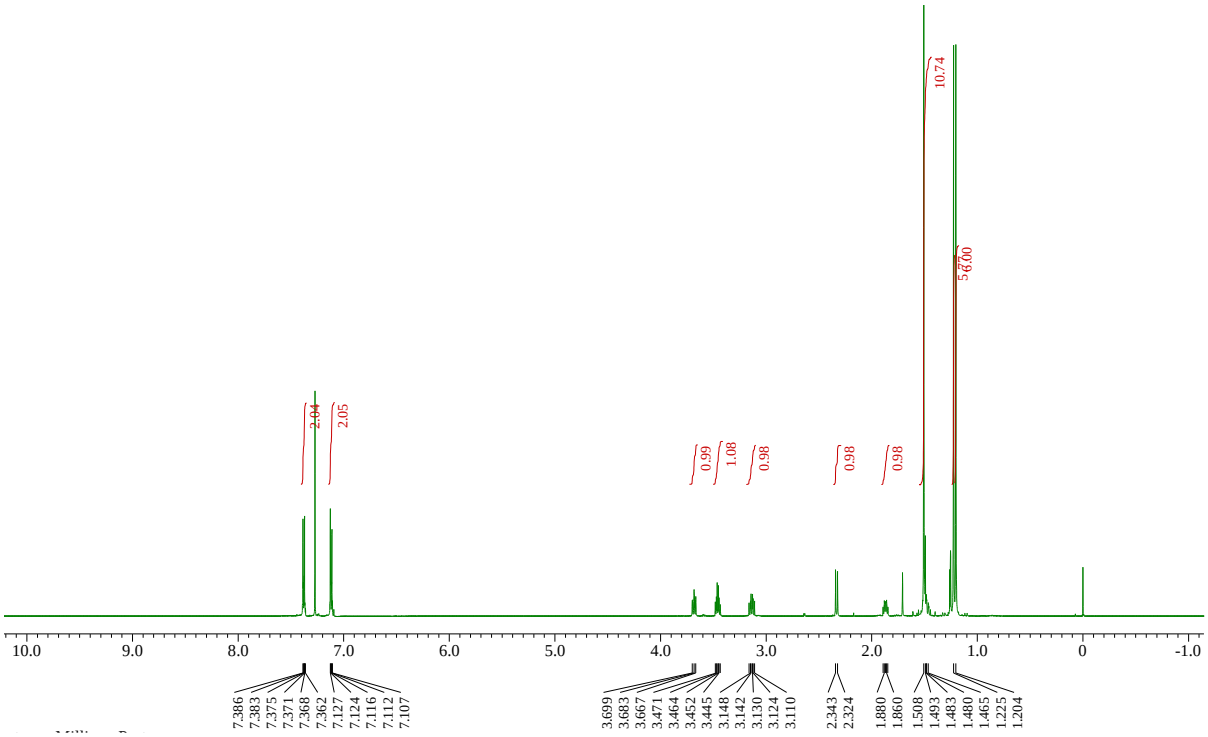
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3.0
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0
-1.0
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7.375
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7.124
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7.112
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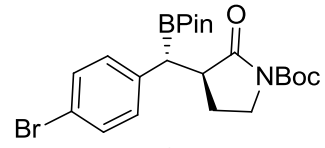
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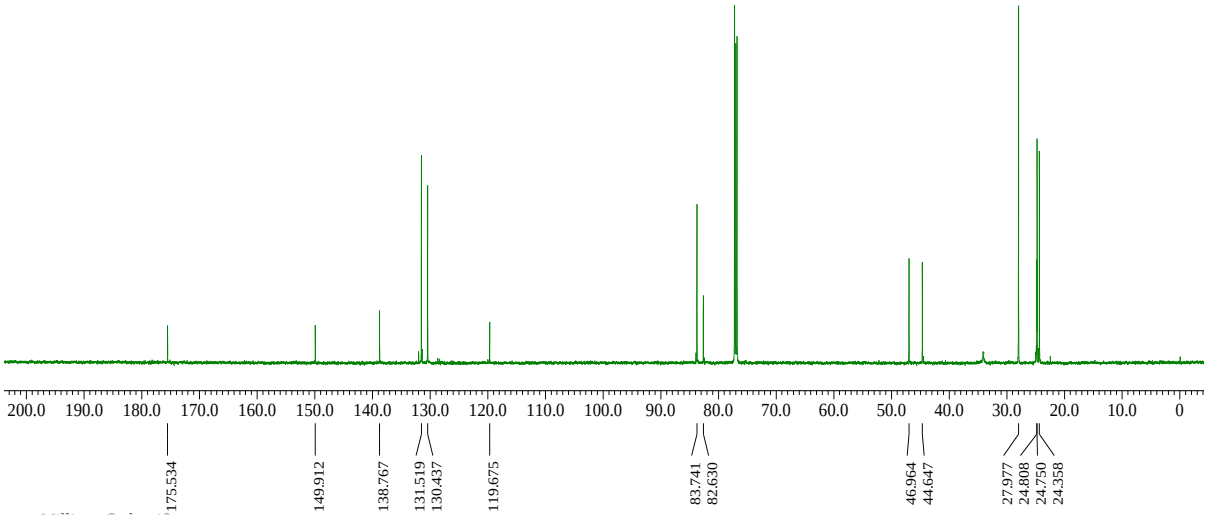
NBoc
Br

3i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10.0
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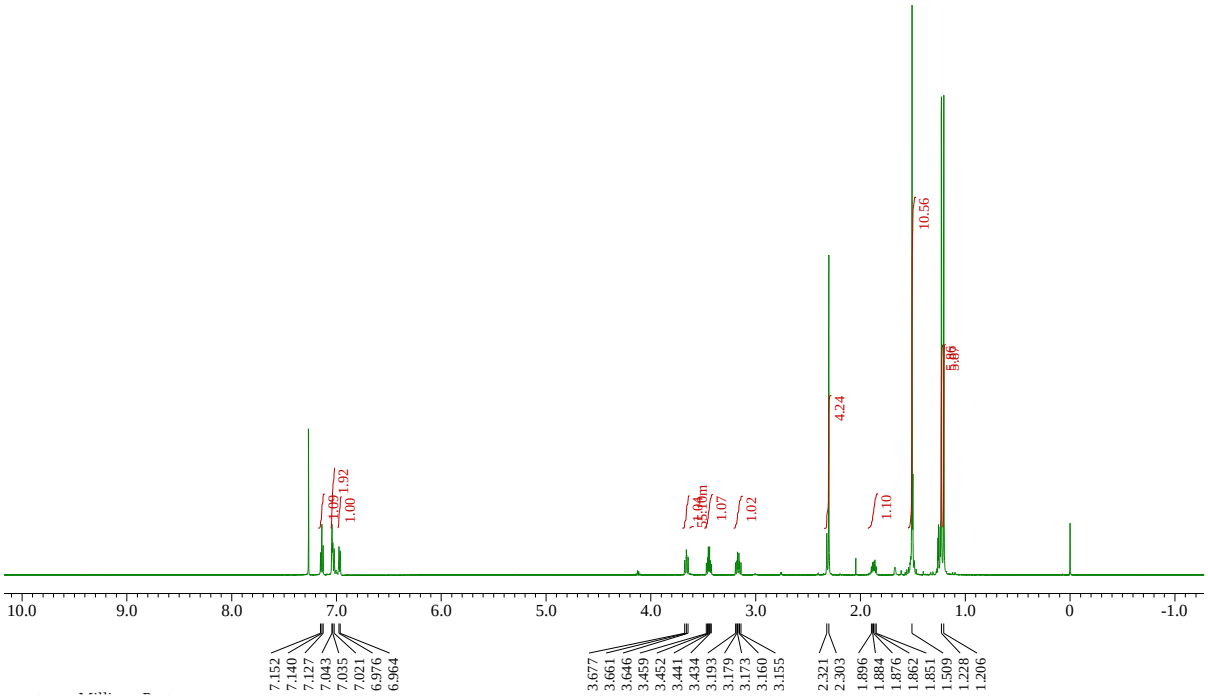
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1.10
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
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7.140
7.127
7.043
7.035
7.021
6.976
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3.661
3.646
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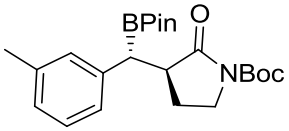
BPin
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NBoc

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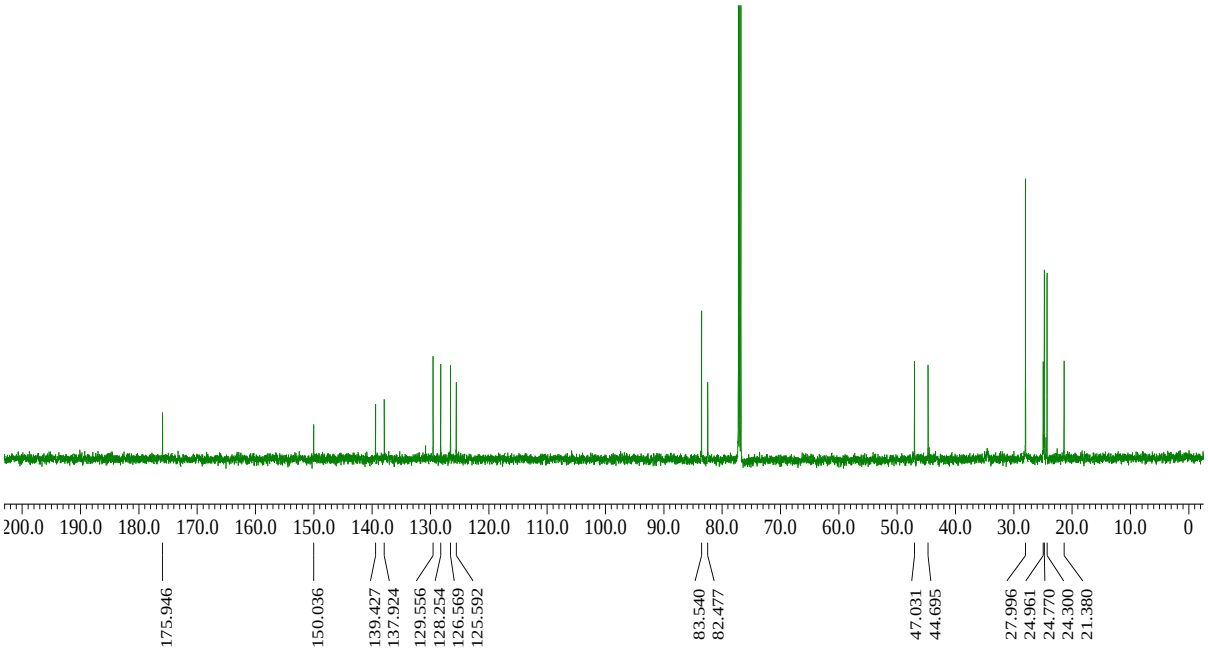
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20.0
10.0
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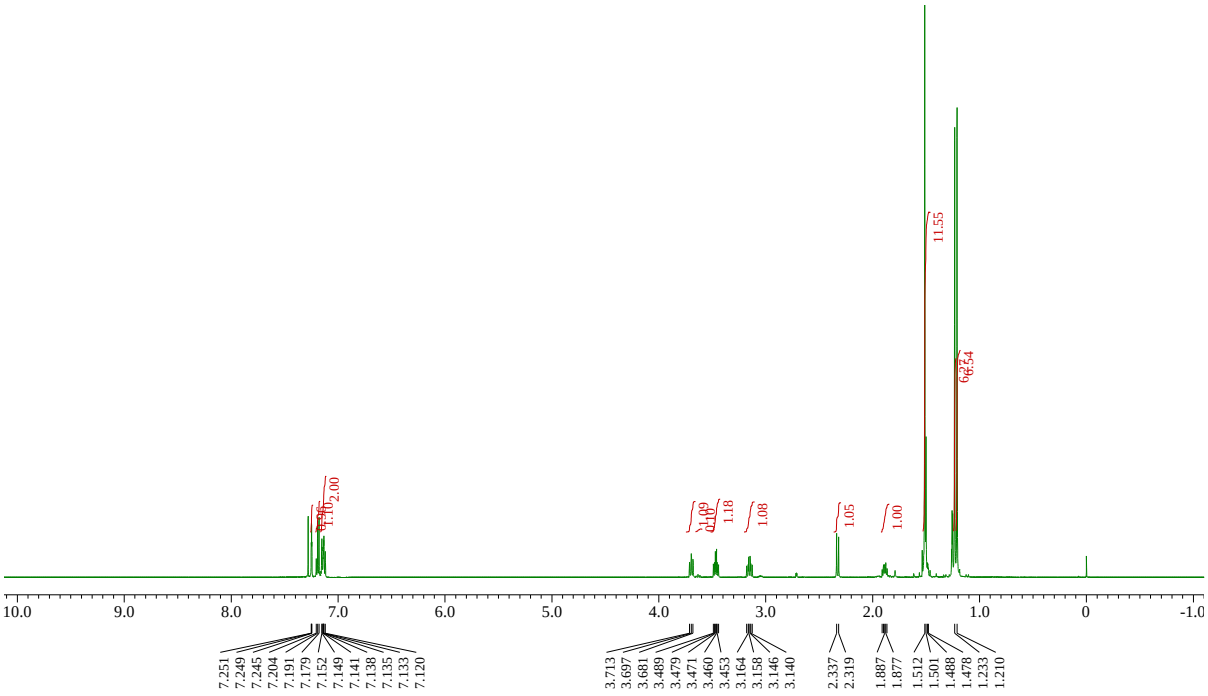
21.380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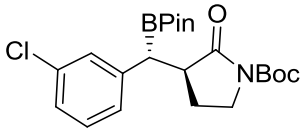
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NBoc

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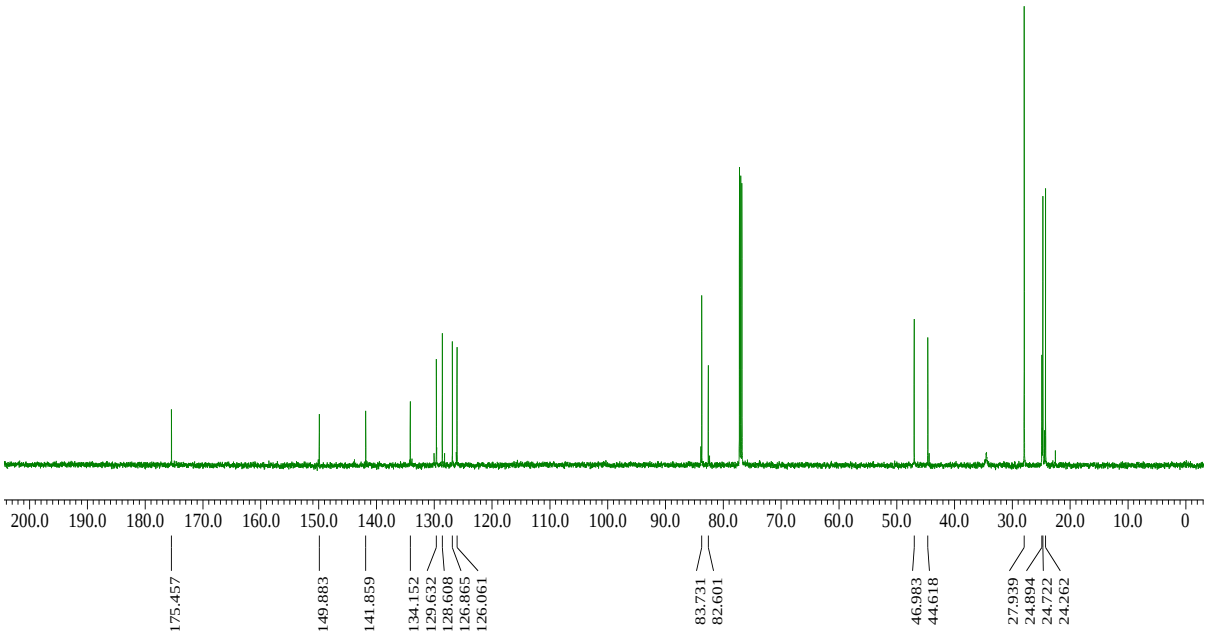
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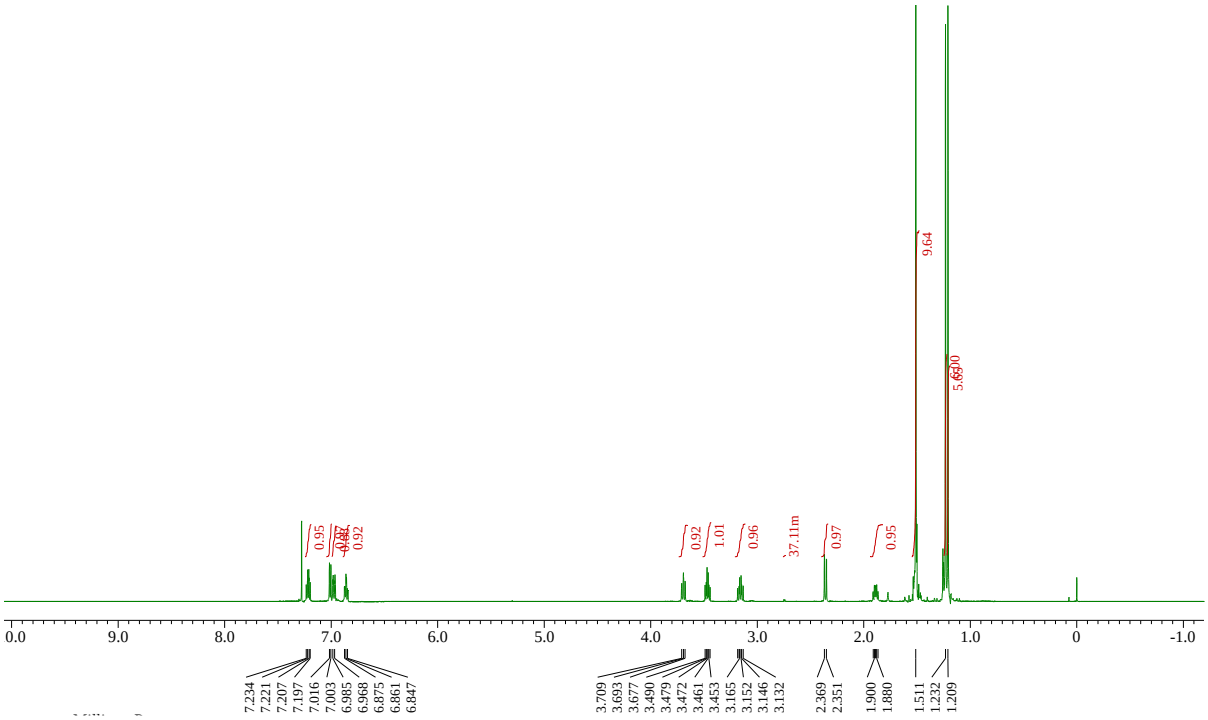

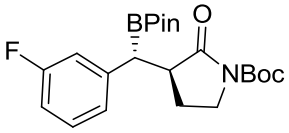

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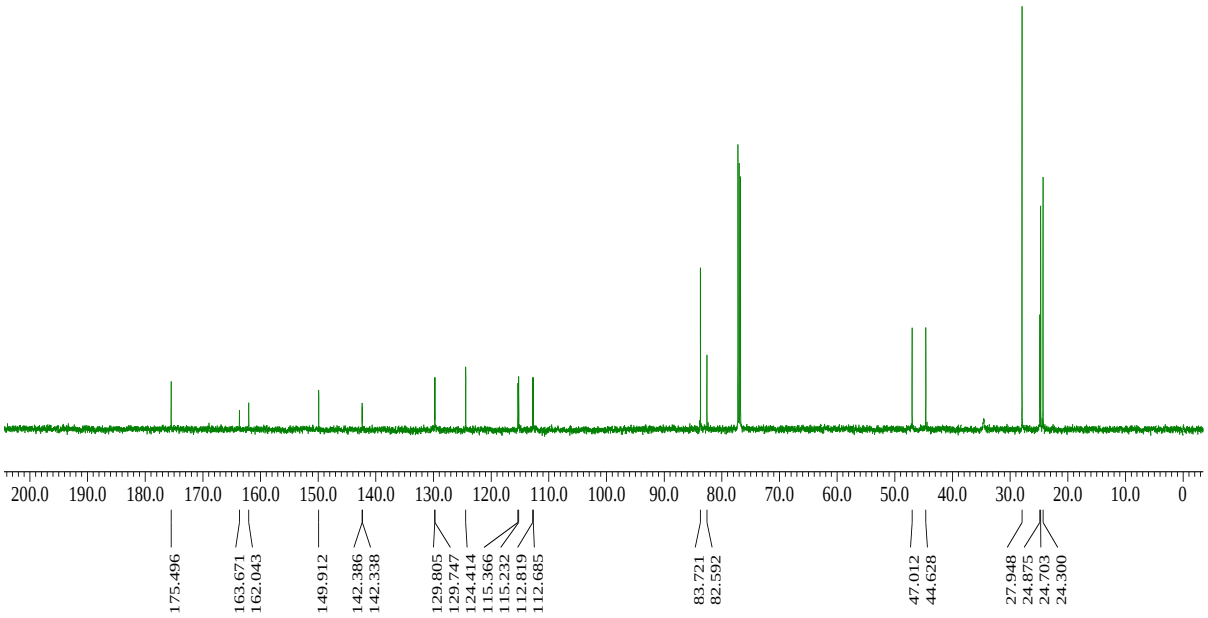
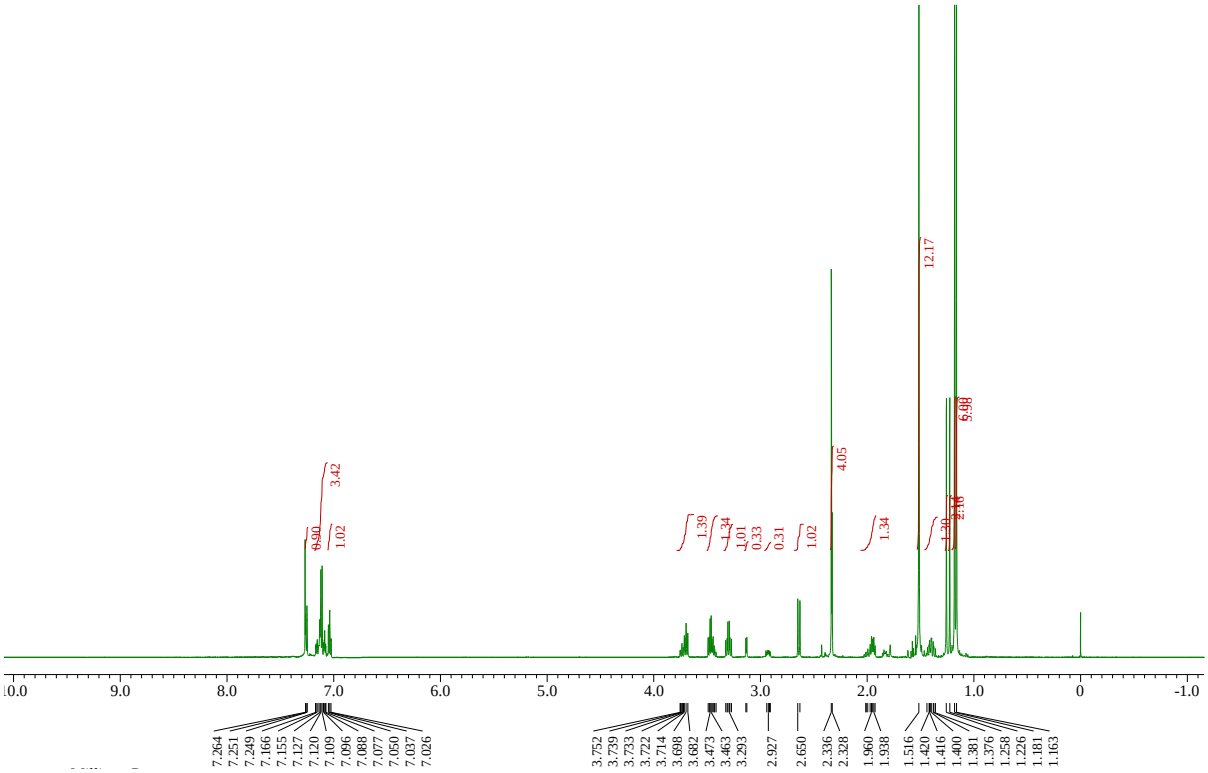
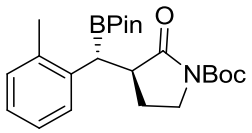
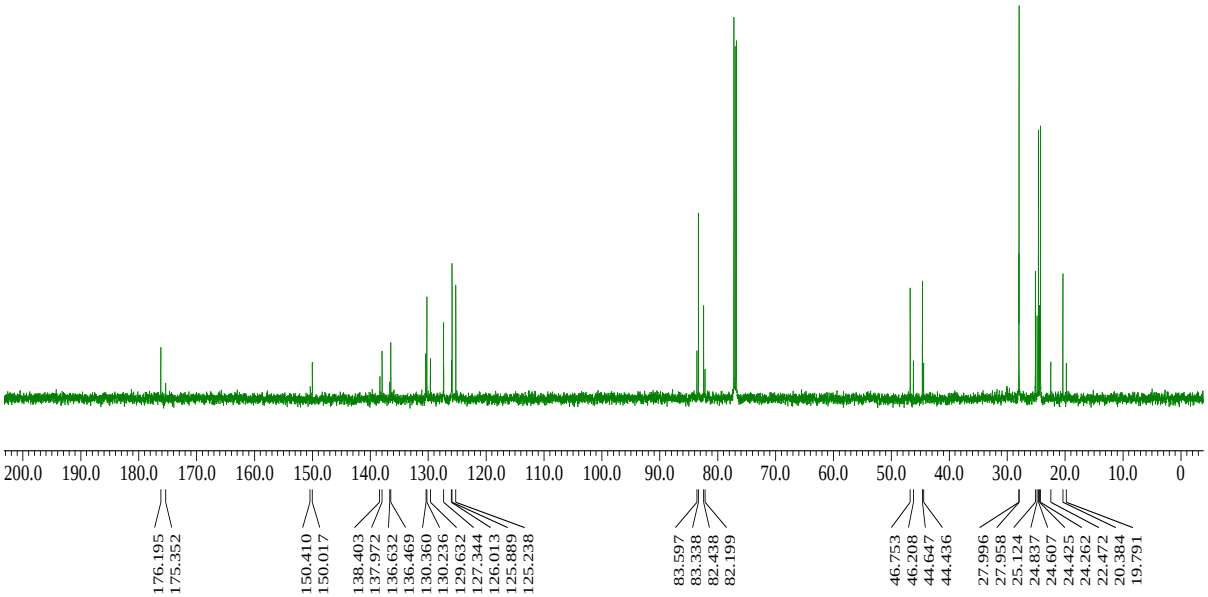
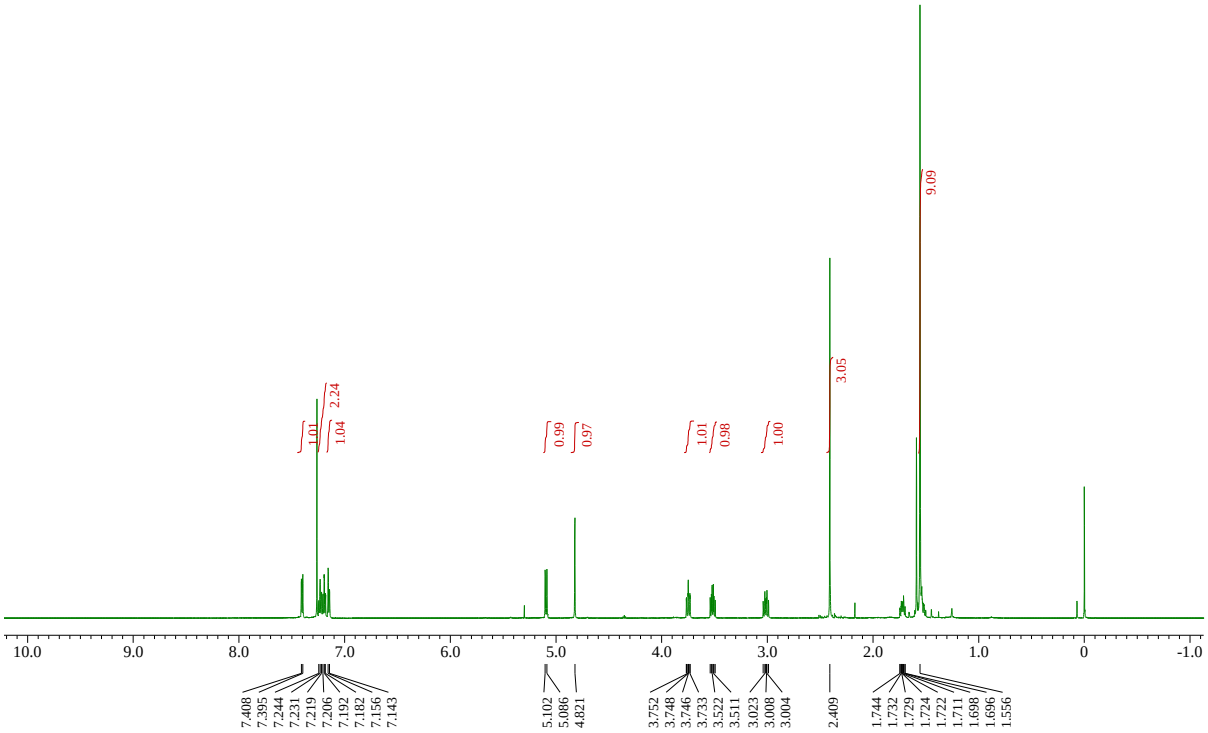






3m, dr 74:26

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5.086
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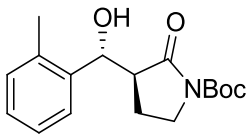
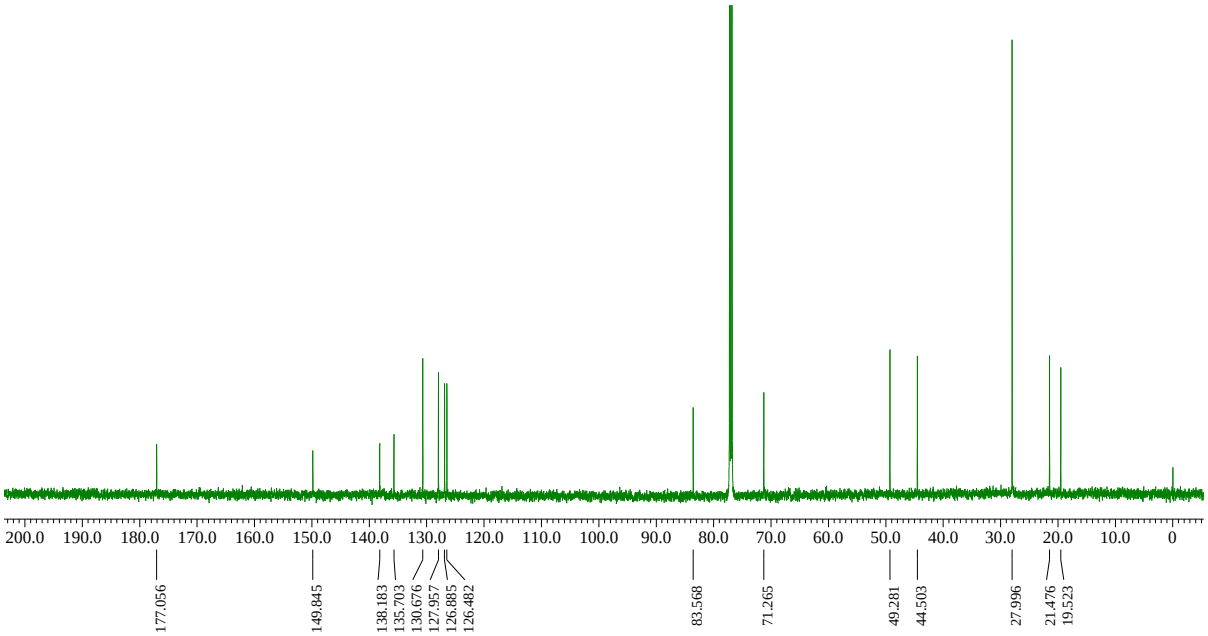

OH
O
NBoc

4b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10.0
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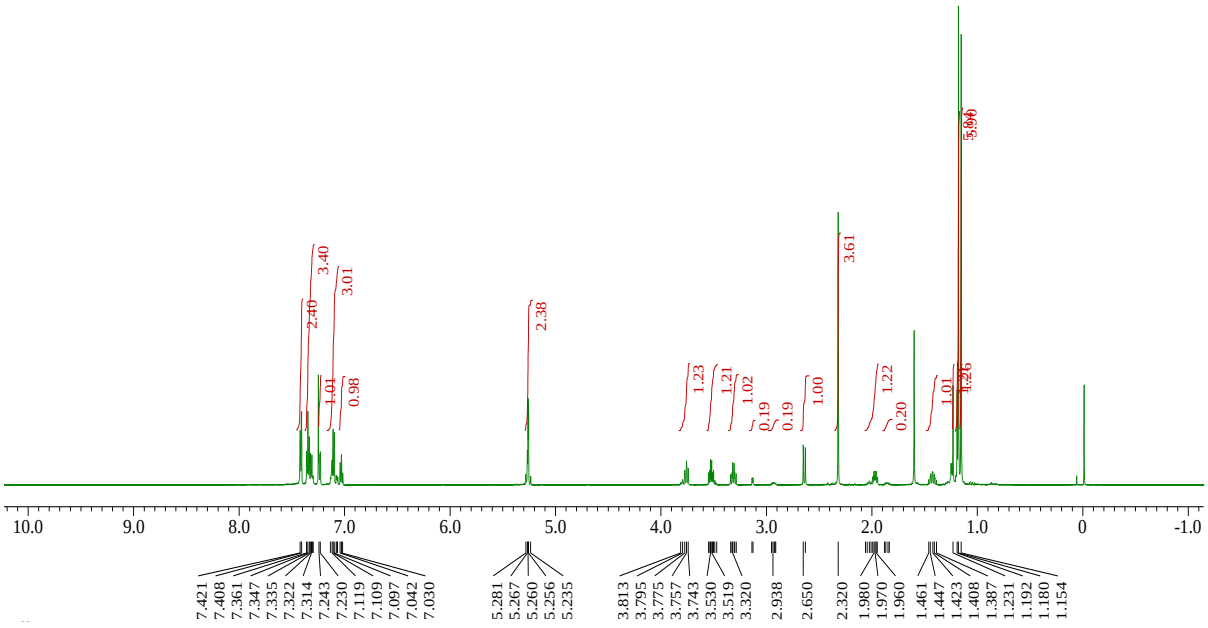
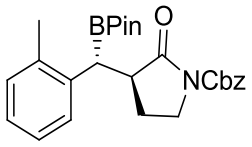
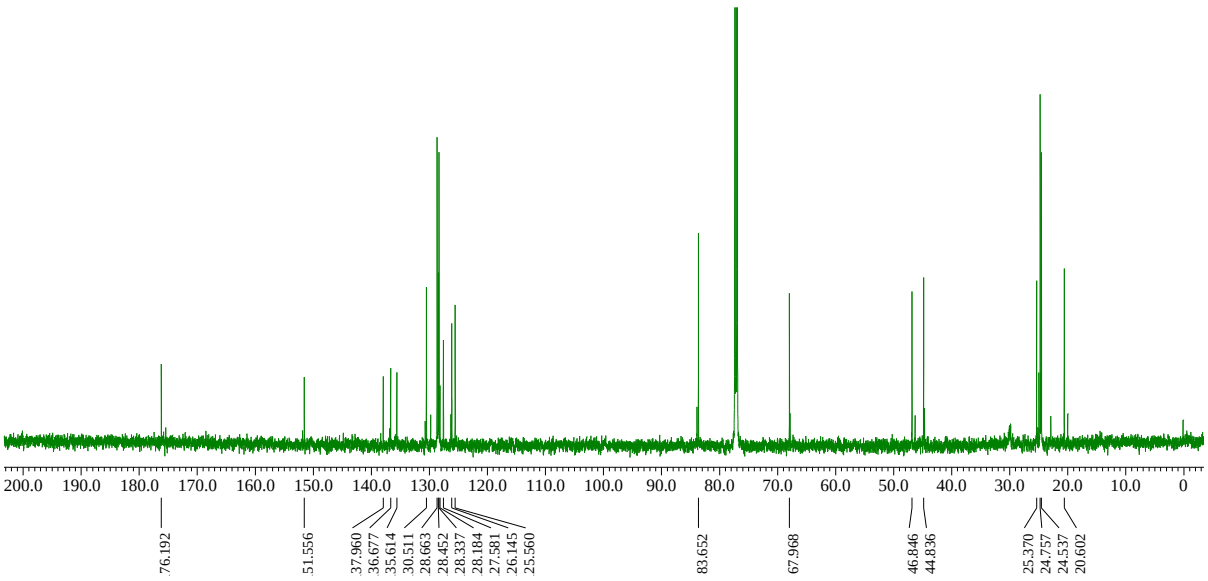
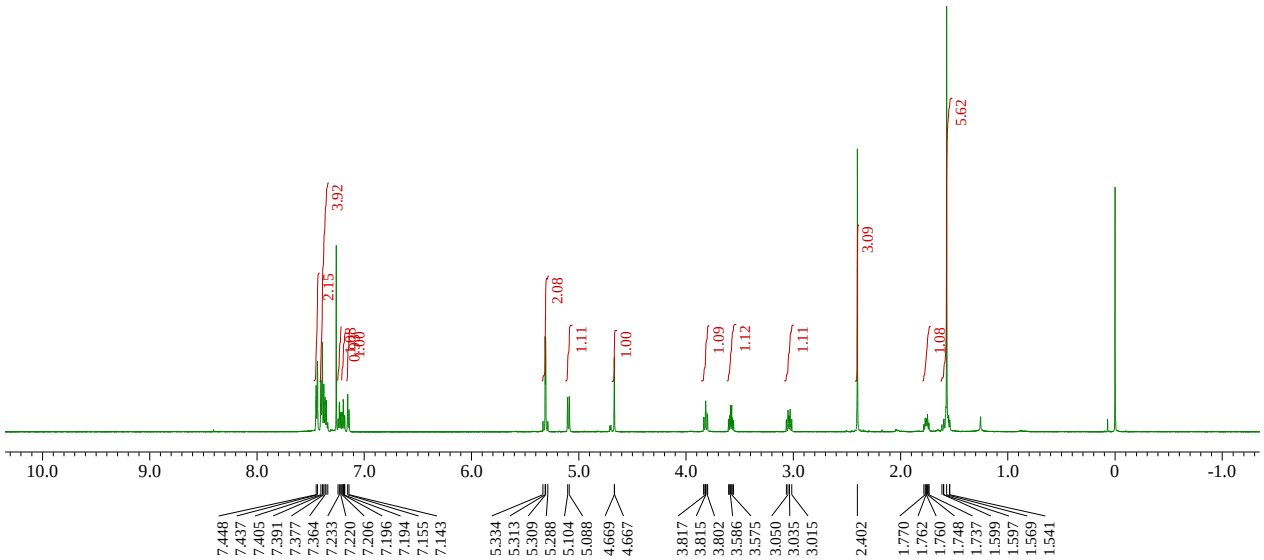




3n, dr 83:17

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2.08
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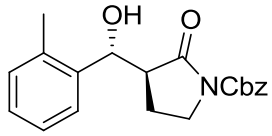
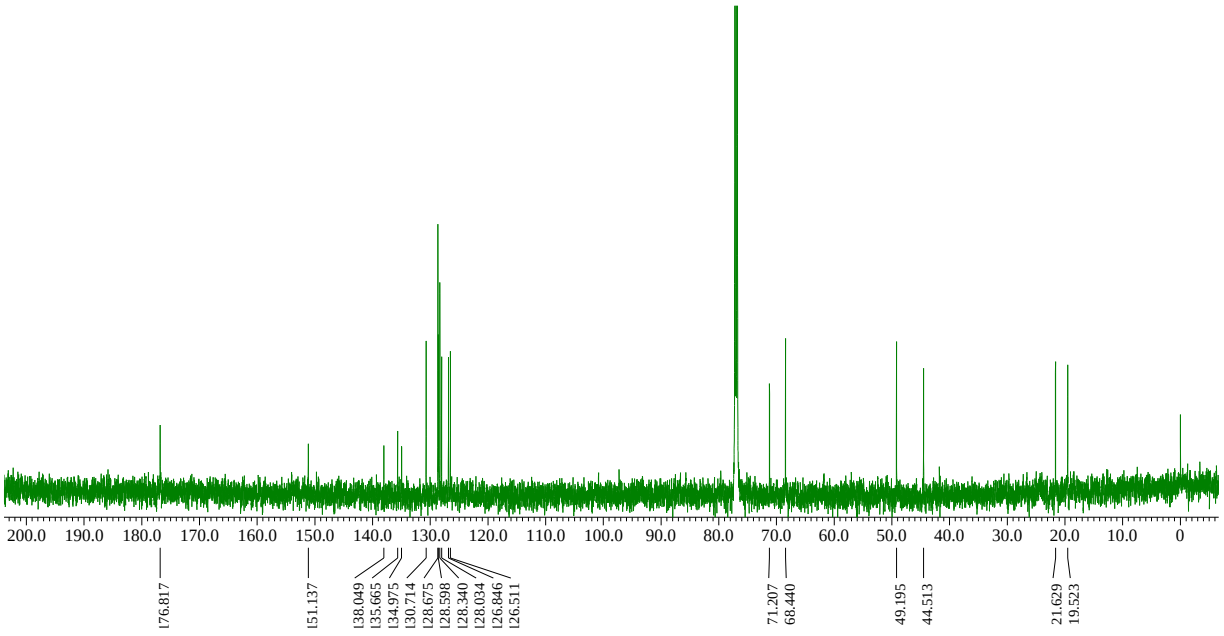

OH
O
NCbz

4c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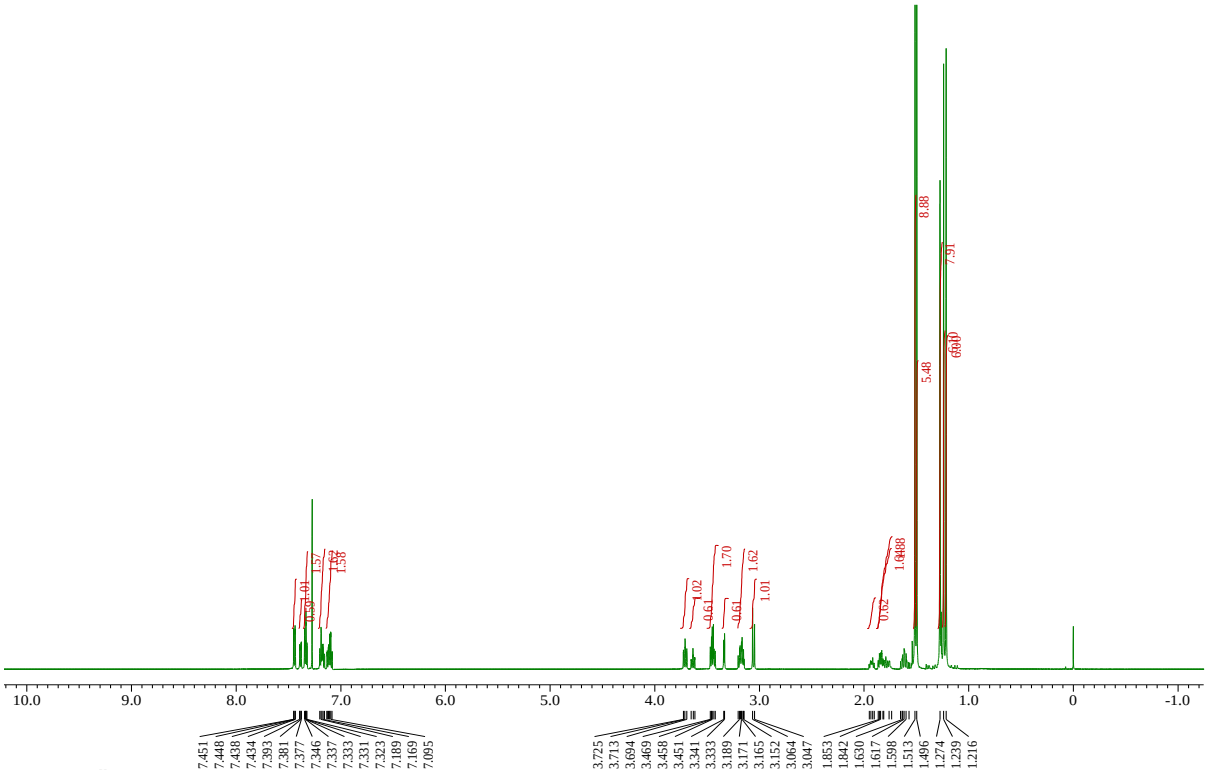
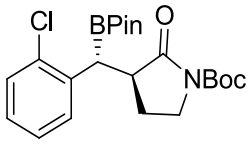
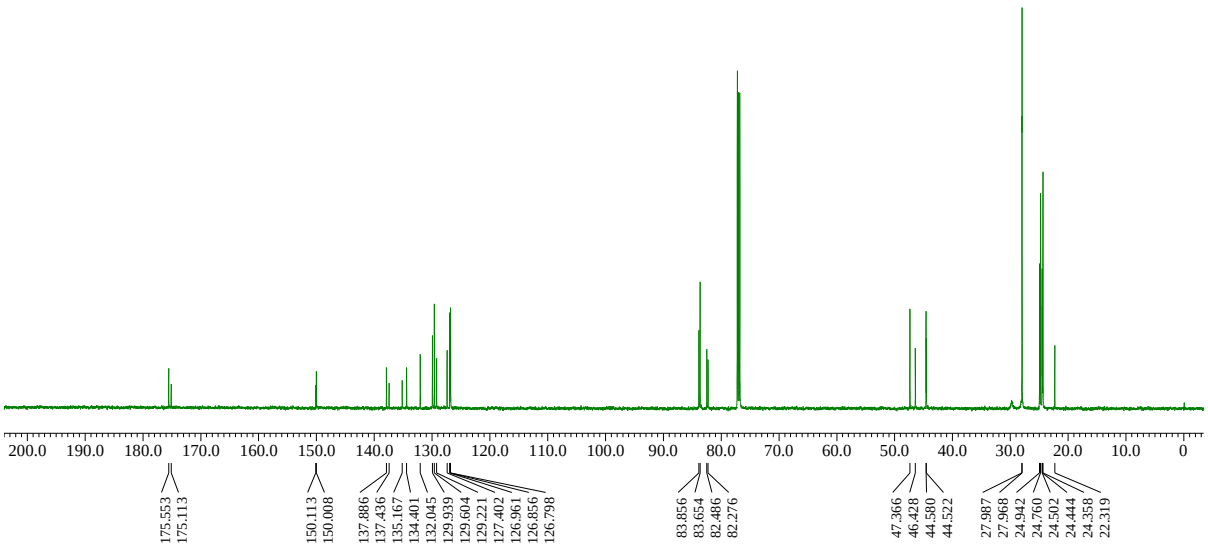
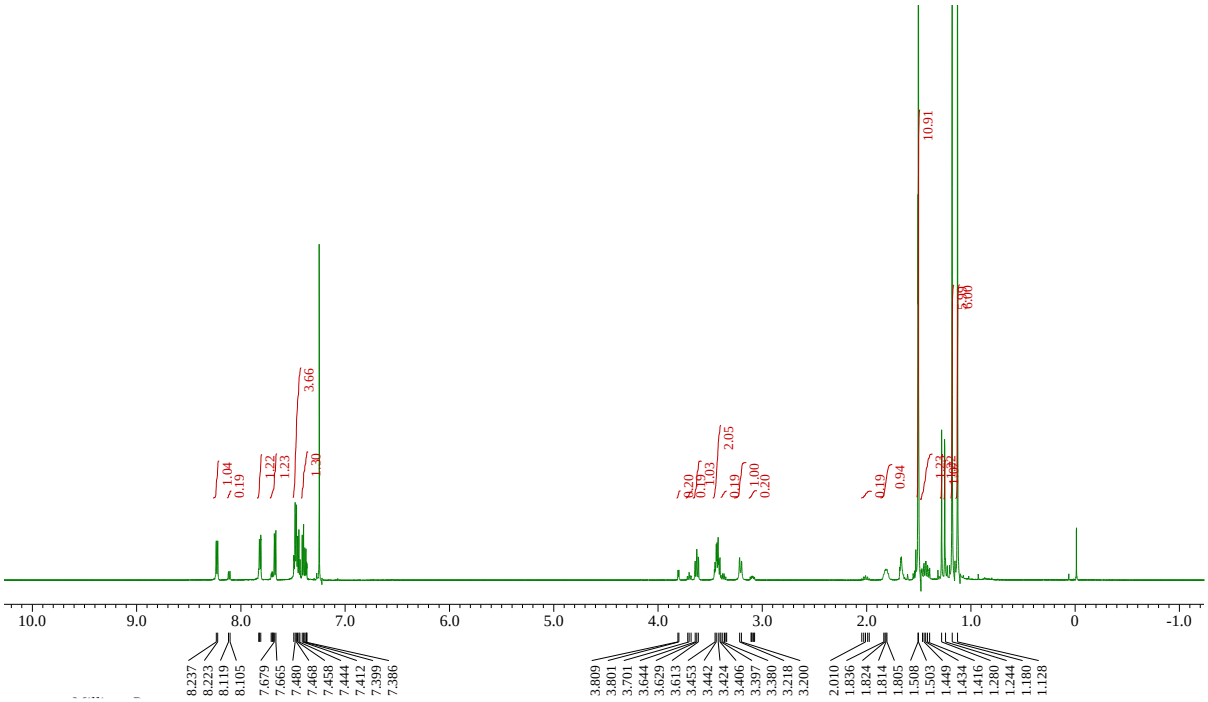
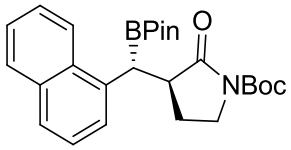




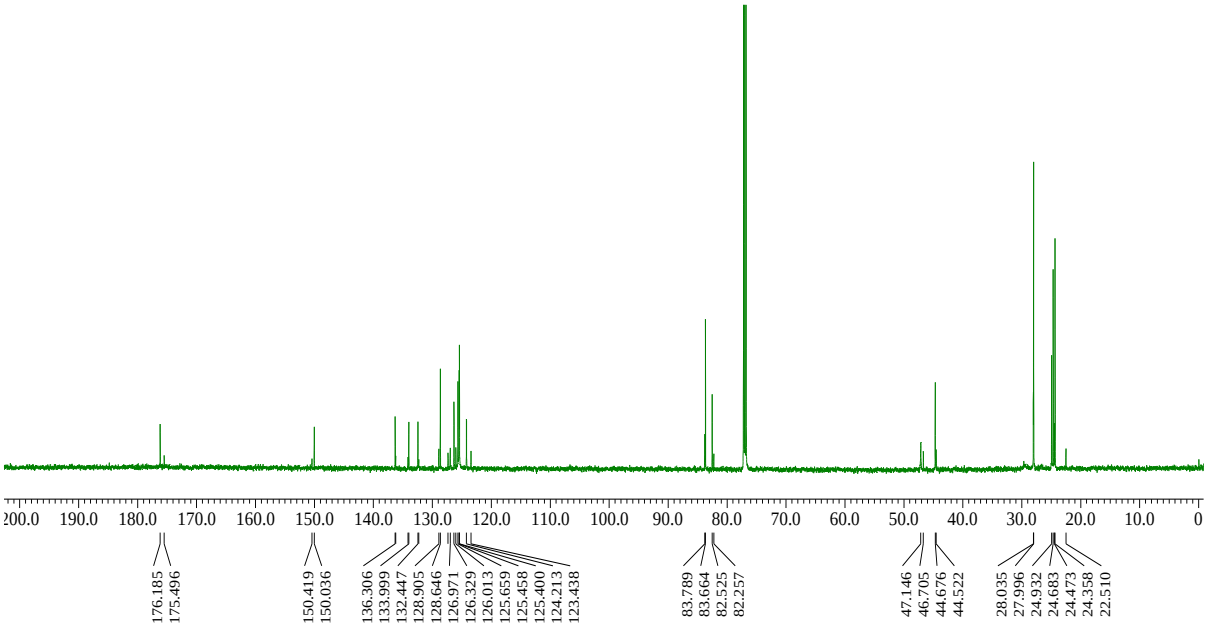
3o, dr 62:38

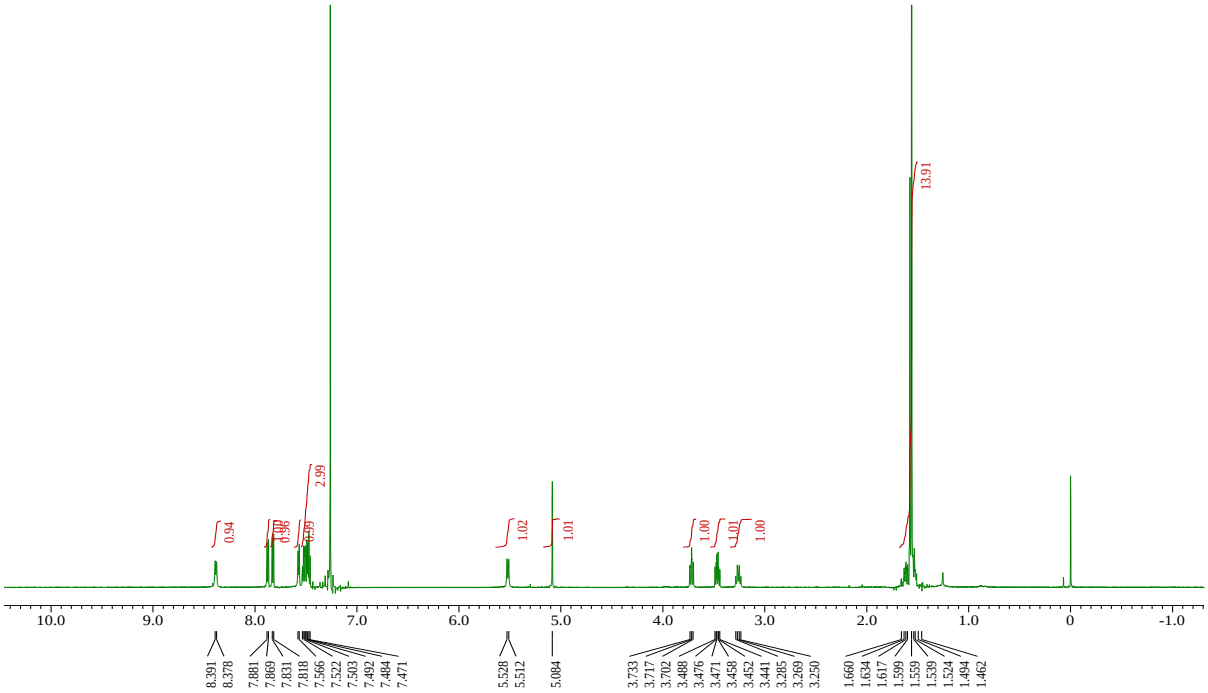


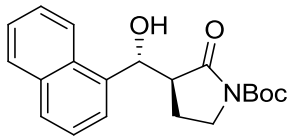




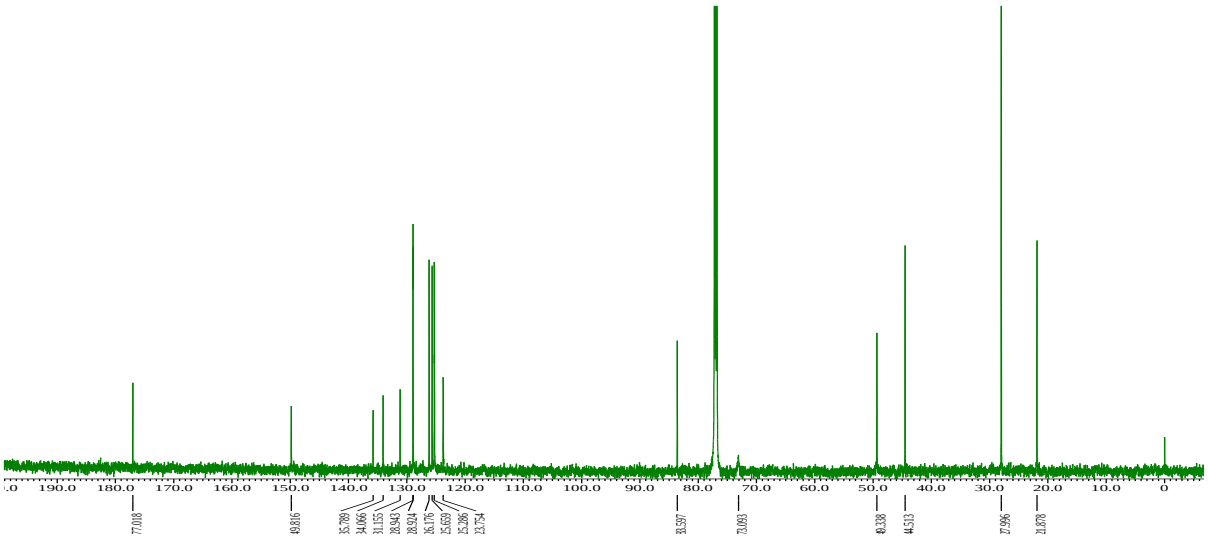
3p, dr 83:17

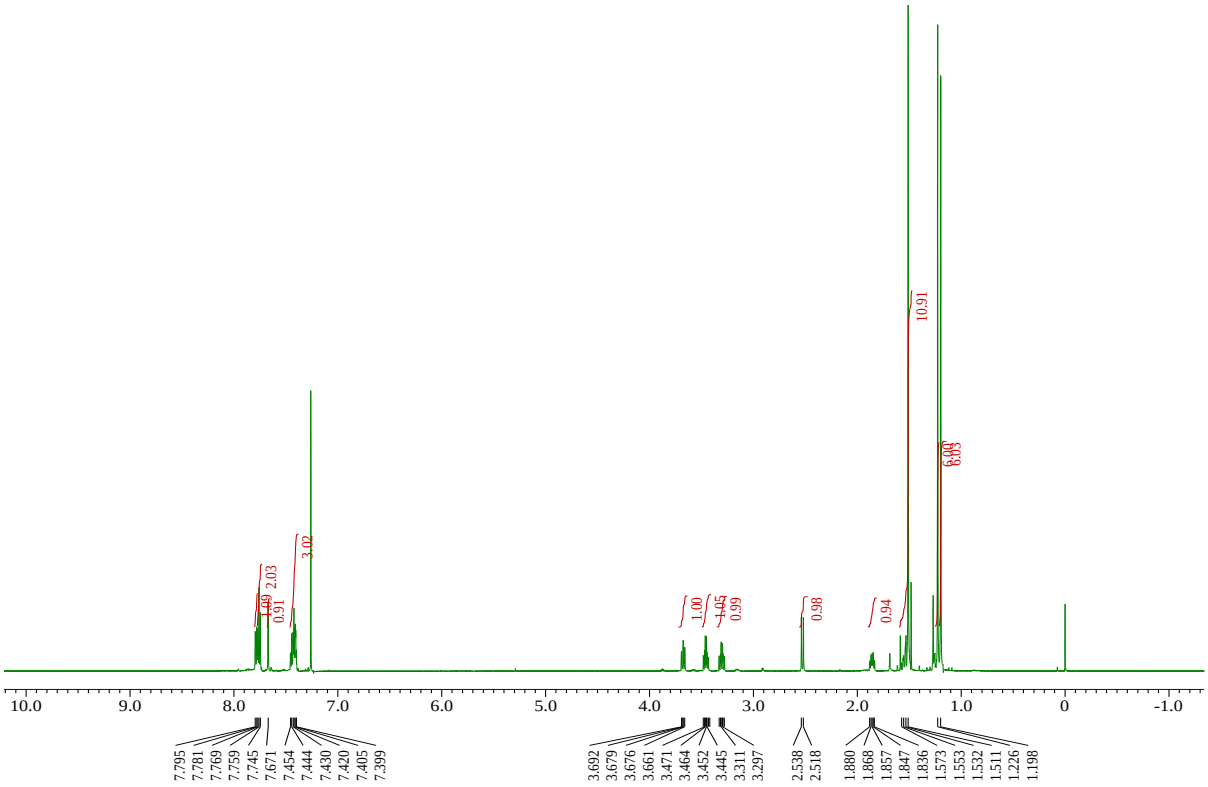






4d

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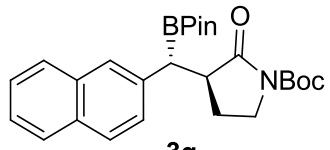
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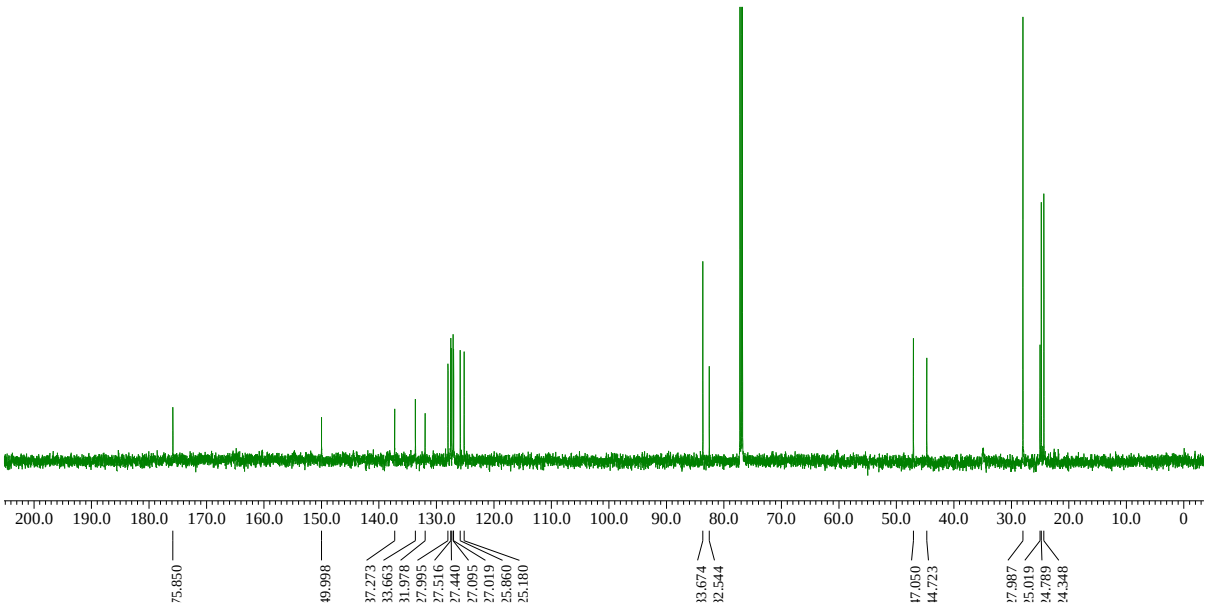
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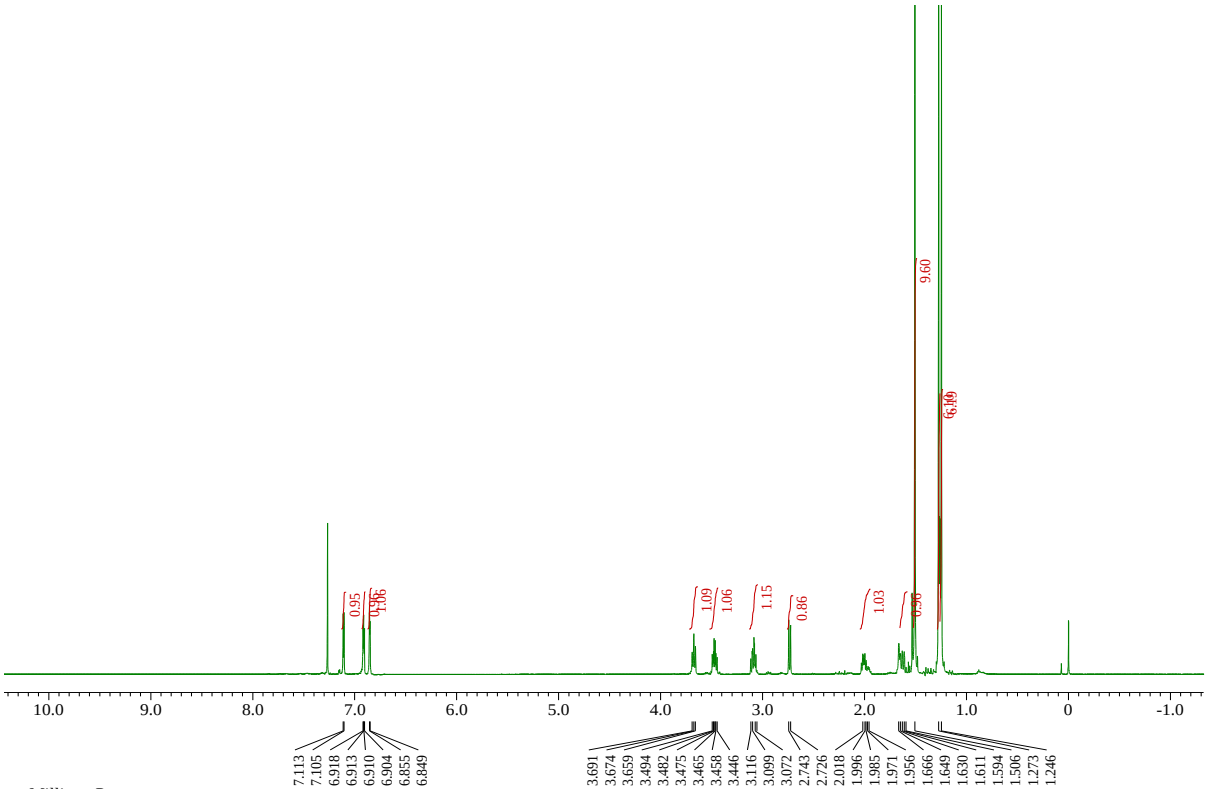
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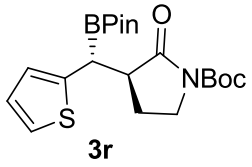
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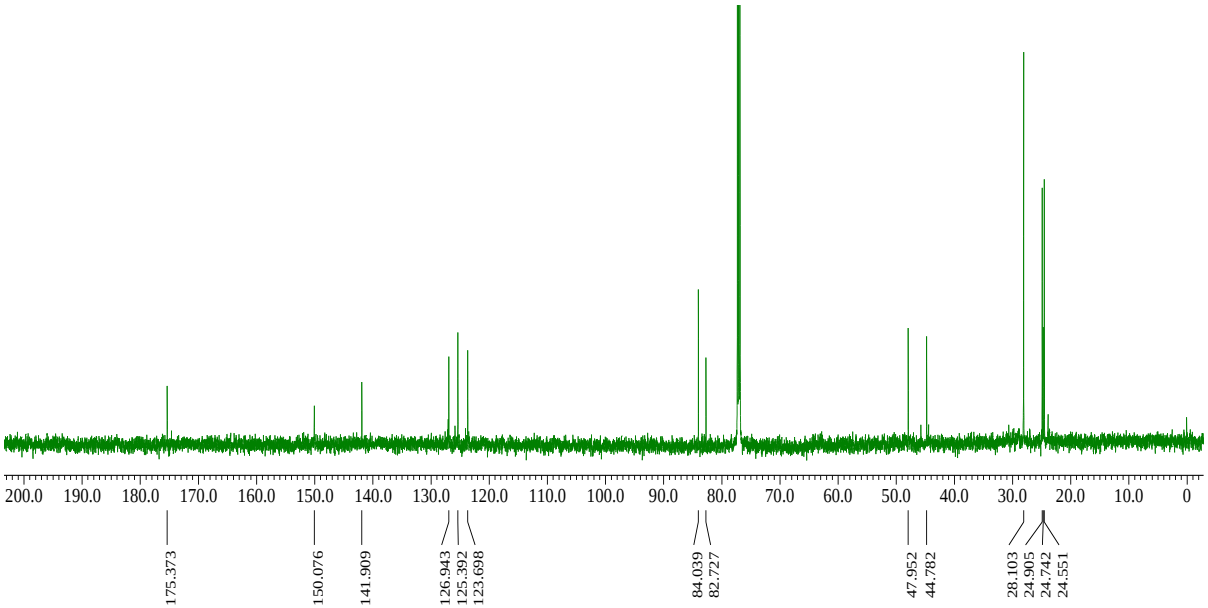
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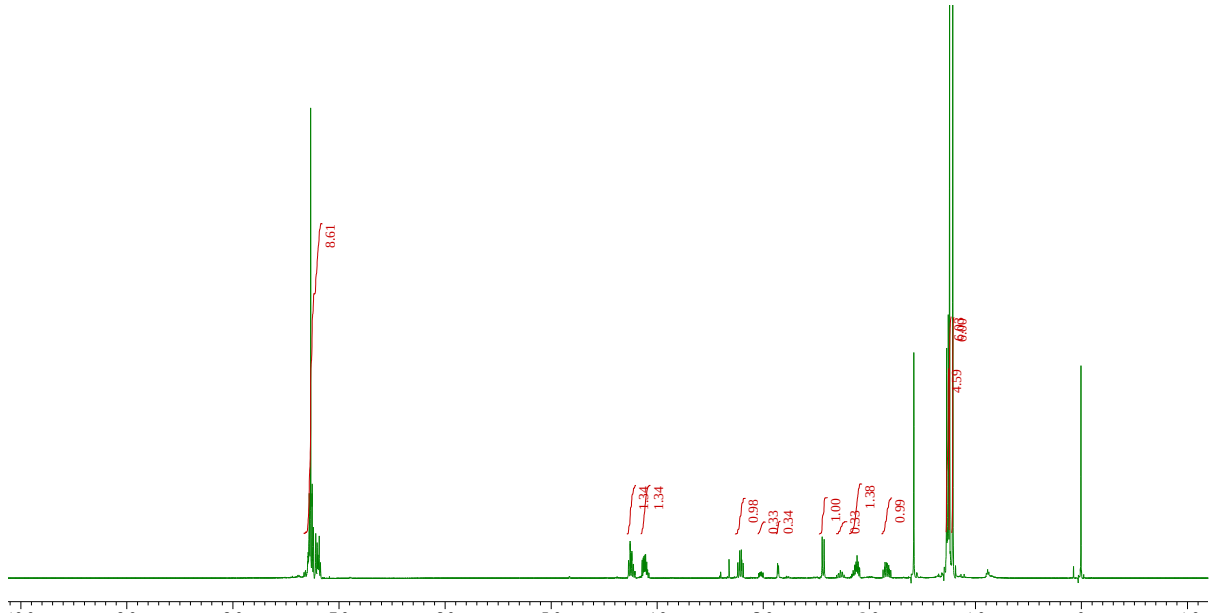
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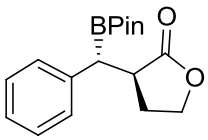
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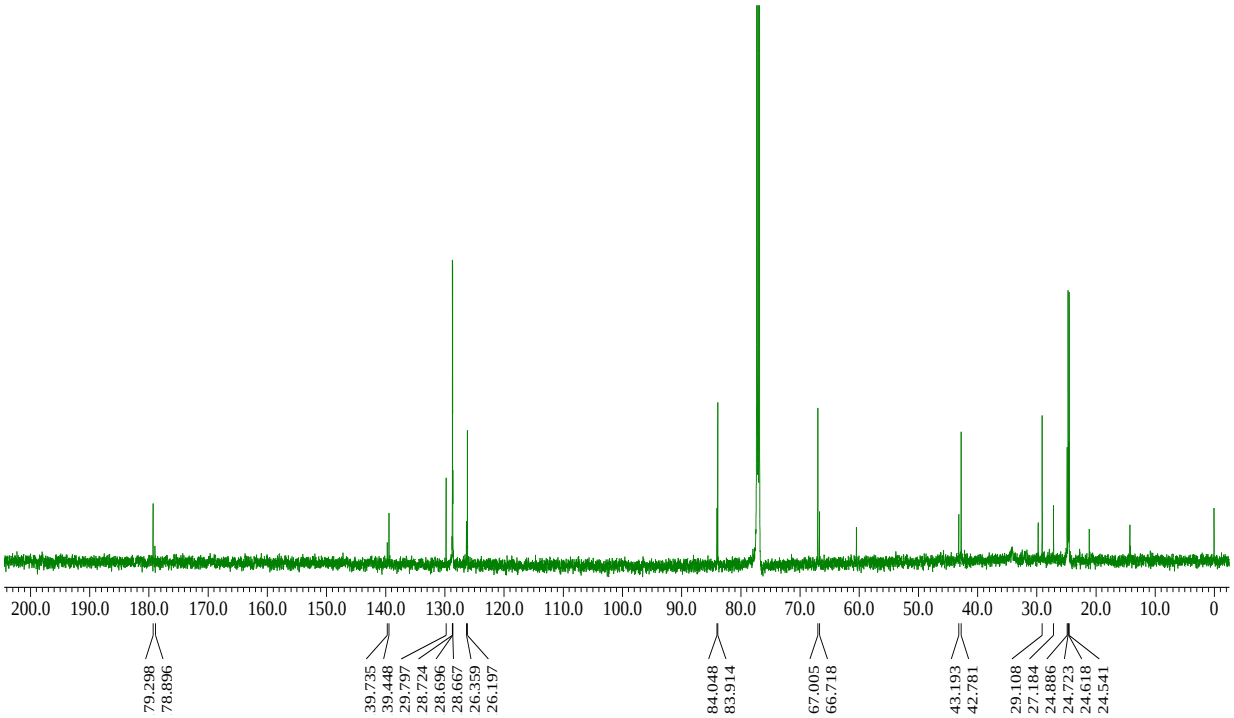
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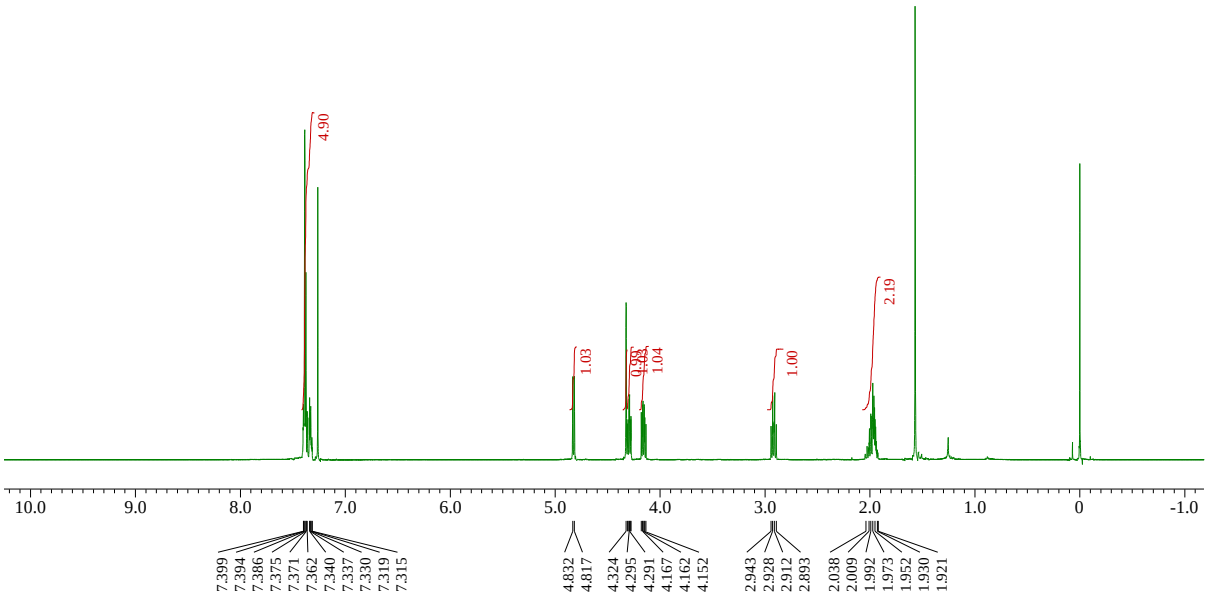
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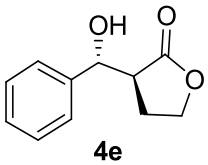
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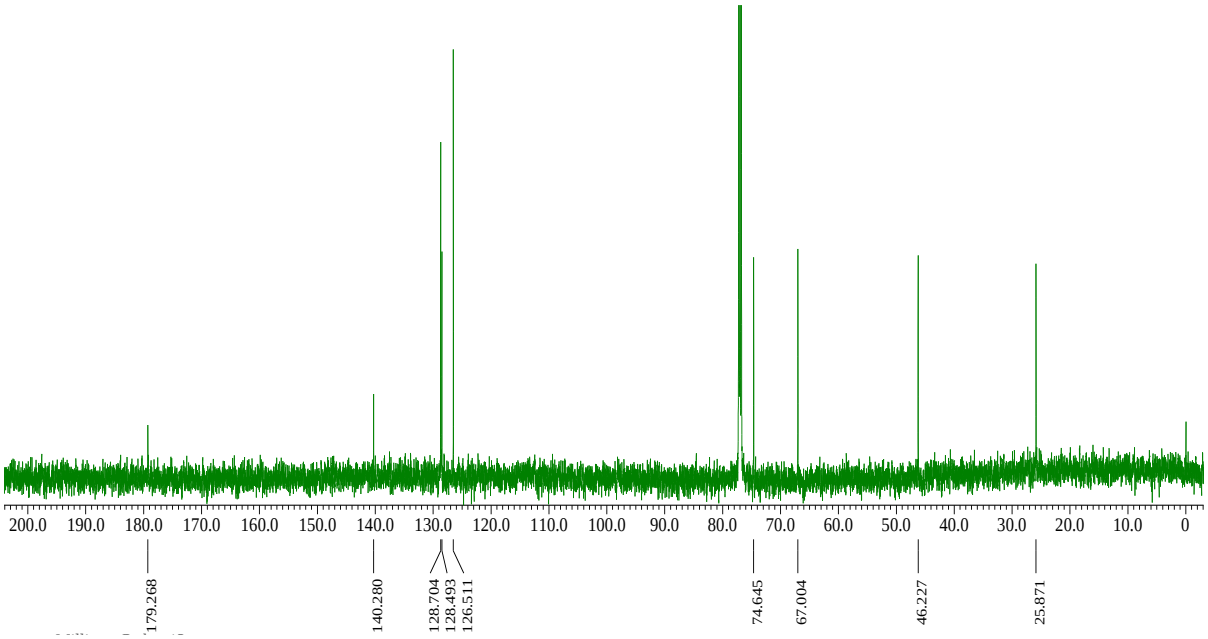
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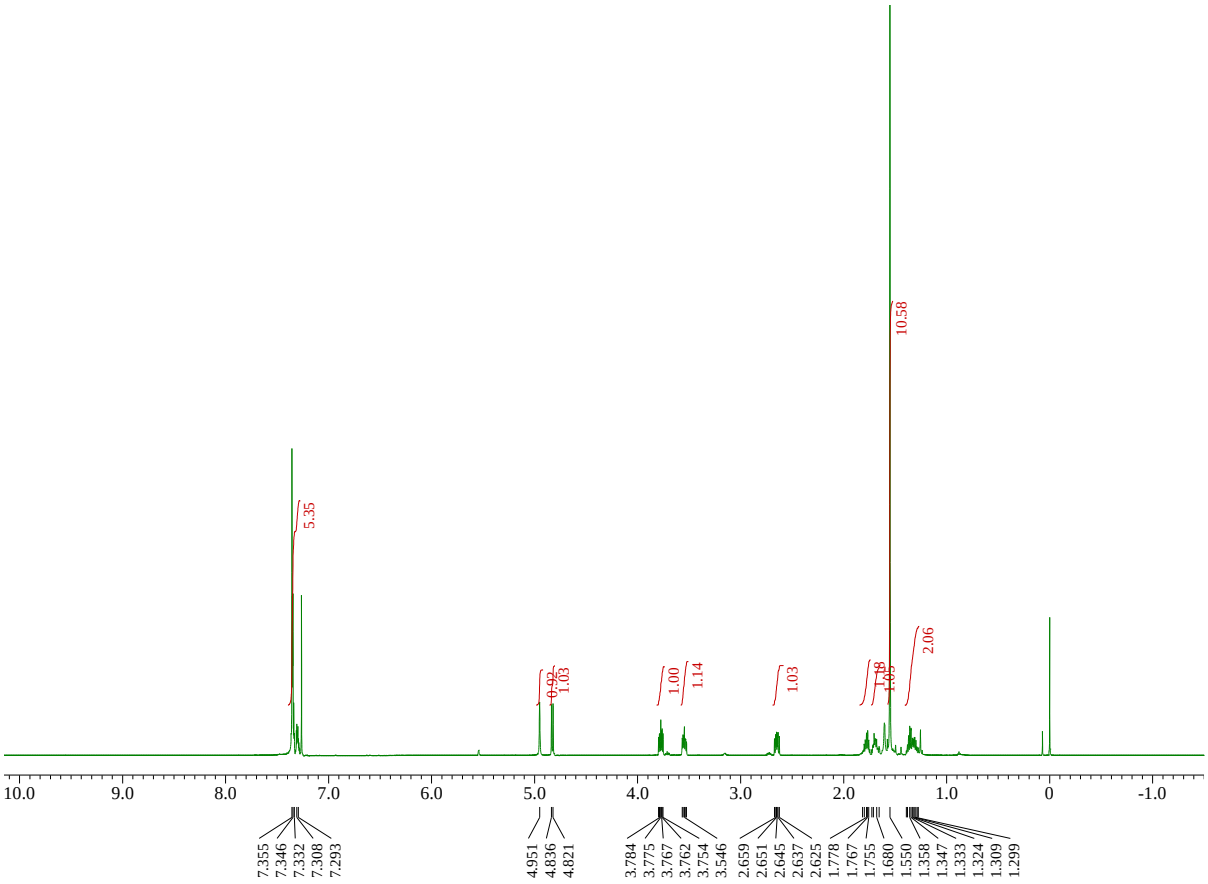
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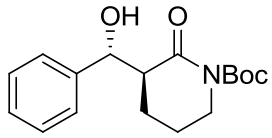
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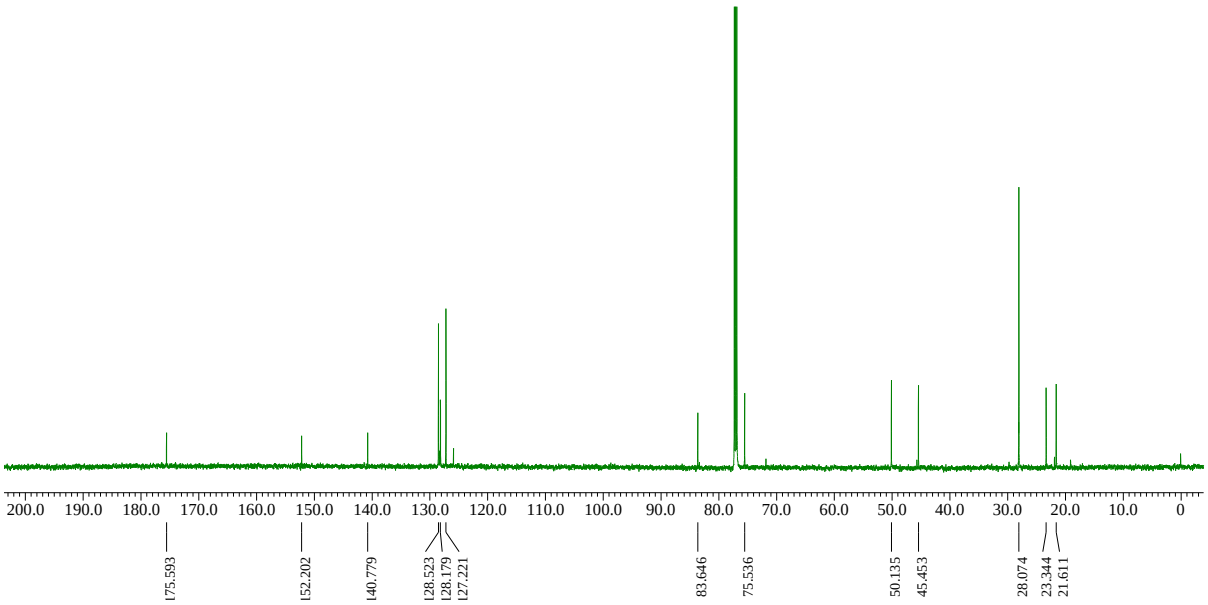
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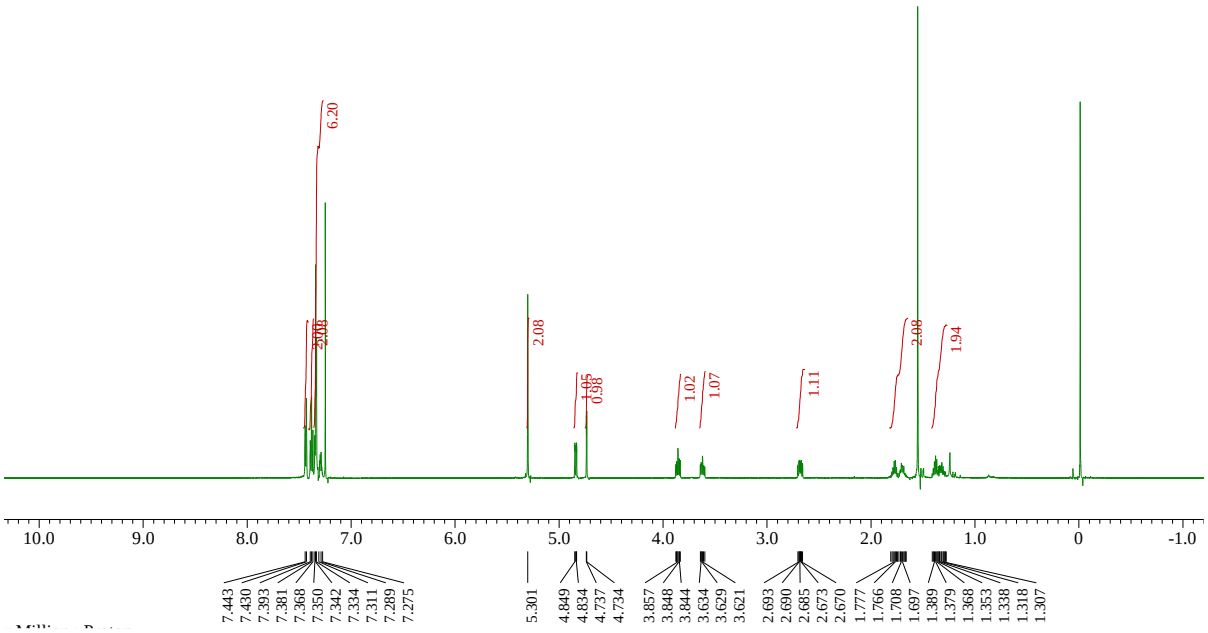
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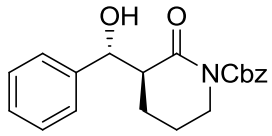
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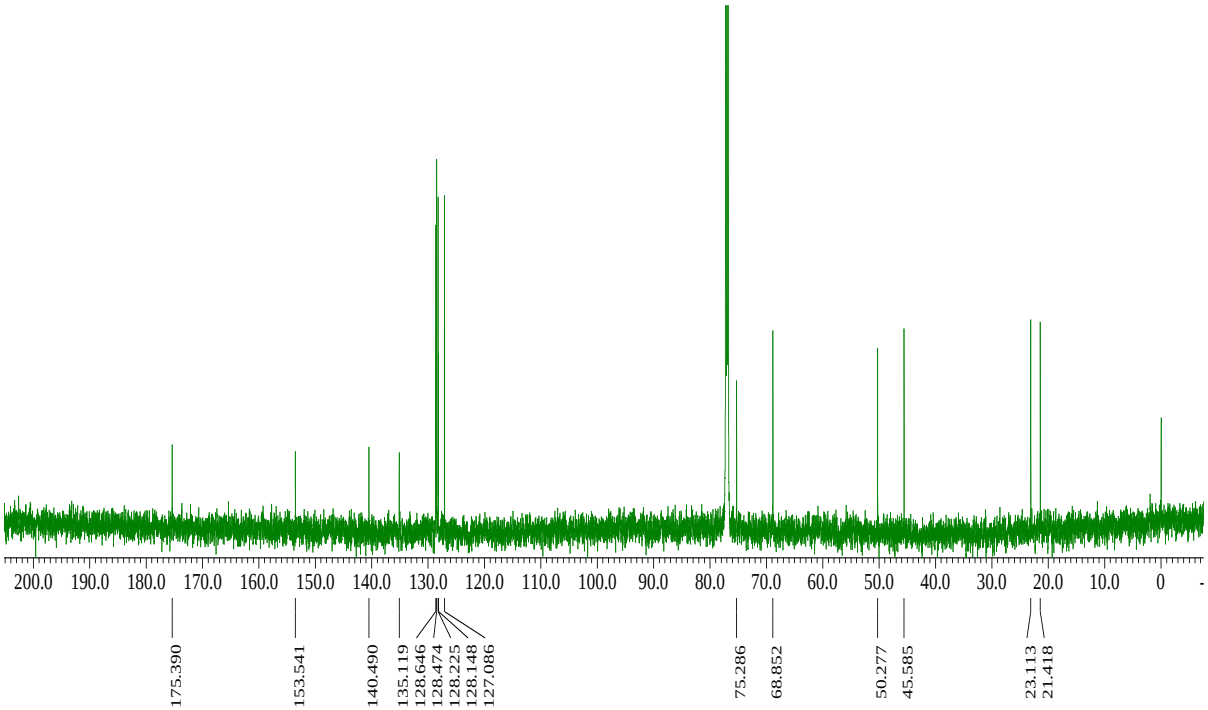
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