Asymmeric Formal [3+3]-Cycloaddition Reactions of Nitrones with Electrophilic Vinylcarbene Intermediates

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Supporting Information

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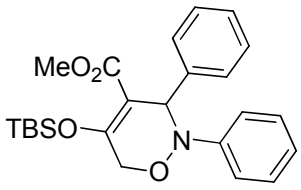
General Information. All reactions, unless noted, were carried out under an inert atmosphere of dried nitrogen in flame-dried or oven-dried glassware with magnetic stirring. Analytical thin layer chromatography (TLC) was performed on Dynamic Adsorbents precoated (0.25 mm thickness) silica gel plates with F_{254} indicator. Visualization was accomplished by UV light (254 nm) or phosphomolybdic acid (PMA) solution in ethanol. Flash chromatography was performed with silica gel (32-63 μm) supplied by Dynamic Adsorbents. ^{1}H NMR spectra were recorded on a Bruker DRX-400 (400 MHz) spectrometer and chemical shifts were reported in ppm. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite; coupling constant(s) in Hz. ^{13}C NMR spectra were recorded on a Bruker DRX-400 (100 MHz) or a Bruker DRX-500 (125 MHz) spectrometer with complete proton decoupling. Enantioselectivity was determined on an Agilent 1200 Series HPLC using a Daicel Chiralcel OD-H column or an AD-H column. High-resolution mass spectra (HRMS) were performed on JEOL AccuTOF-CS mass spectrometer using CsI as the standard.

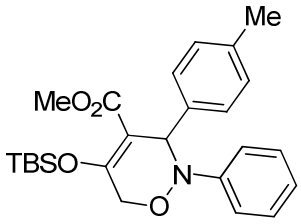
Materials. Rh_2(*S*-PTA)$_4$[1], Rh_2(*S*-PTV)$_4$[1], Rh_2(*S*-PTTL)$_4$[1], Rh_2(*S*-PTPA)$_4$[1], Rh_2(*S*-NTA)$_4$[2], and Rh_2(*S*-NTTL)$_4$[2] were prepared according to the literature procedures. Rh_2(*S*-PTAD)$_4$[3] and Rh_2(*S*-DOSP)$_4$[4] were purchased from Strem Chemicals, Inc. Nitrones[5] and the TBSO-substituted vinyldiazoacetate **5**[6] were prepared according to the literature procedures. Solvents were dried with 4 Å MS before use. All the other chemicals were obtained from commercial sources and used without further purification.

General Procedure for the Asymmetric Formal [3+3] Cycloaddition Reactions of Nitrones with the TBSO-Substituted Vinyldiazoacetate 5. A 10 mL Schlenk flask charged with a magnetic stir bar and 4 Å molecular sieves (100 mg) was placed under high vacuum and heated by Bunsen burner to dryness. After cooling to room temperature, Rh_2(*S*-PTA)$_4$ (5.4 mg, 2.0 mol%), *N*,α-diphenylnitrone (49.3 mg, 0.250 mmol) and 1.0 mL of *tert*-butyl methyl ether (TBME) were added under the flow of N_2. The resulting green solution was stirred for 5 min and then cooled to -30 °C. Methyl 3-(*tert*-butyldimethylsilyloxy)-2-diazobut-3-enoate (**5**, 96 mg, 0.38 mmol) in 1.0 mL of TBME was added into the flask *via* a syringe pump over a time period of 1 h. After the addition, the mixture was stirred for another one hour at -30 °C. The reaction mixture was then allowed to warm to room temperature. The solution was evaporated to dryness. The obtained mixture was dissolved in a minimal amount of dichloromethane and loaded onto a silica gel column. Column chromatography with hexane/ethyl acetate provided the cycloaddition product which was later analyzed for enantiomeric excess by HPLC (AD-H or OD-H column).



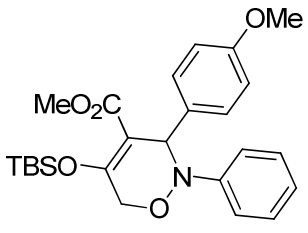
11a

Methyl 5-(*tert*-Butyldimethylsilyloxy)-2,3-diphenyl-3,6-dihydro-*2H*-1,2-oxazine-4-carboxylate (11a). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.19-7.26 (comp, 7H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 7.2 Hz, 1H), 5.61 (d, *J* = 1.6 Hz, 1H), 4.51 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H), 4.31 (d, *J* = 16.0 Hz, 1H), 3.67 (s, 3H), 1.01 (s, 9H), 0.27 (s, 3H), 0.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ165.79, 158.50, 147.98, 138.00, 129.80, 128.98, 127.95, 122.91, 117.76, 109.69, 68.81, 63.55, 51.66, 26.01, 18.80, -3.58, -3.65; HRMS (ESI) calculated for $C_{24}H_{32}NO_4Si$ $[M+H]^+$: 426.2095; found: 426.2088. HPLC conditions for determination of the enantiomeric excess: AD-H column, 254 nm, 1.0 mL/min, hexane:IPA = 95:5, t_r = 5.9, 6.6 min; 93% ee.



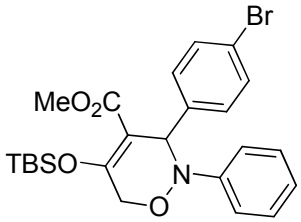
11b

Methyl 5-(*tert*-Butyldimethylsilyloxy)-2-phenyl-3-*p*-tolyl-3,6-dihydro-*2H*-1,2-oxazine-4-carboxylate (11b). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.93-7.30 (comp, 9H), 5.61 (d, *J* = 1.6 Hz, 1H), 4.50 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H), 4.31 (d, *J* = 16.0 Hz, 1H), 3.68 (s, 3H), 2.28 (s, 3H), 1.02 (s, 9H), 0.28 (s, 3H), 0.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.81, 158.33, 148.06, 137.51, 135.05, 129.69, 129.00, 128.76, 122.80, 117.69, 109.93, 68.86, 63.13, 51.66, 26.07, 21.55, 18.83, -3.56, -3.61; HRMS (ESI) calculated for $C_{25}H_{34}NO_4Si$ $[M+H]^+$: 440.2252; found: 440.2233. HPLC conditions for determination of the enantiomeric excess: AD-H column, 254 nm, 1.0 mL/min, hexane:IPA = 97:3, t_r = 6.1, 8.0 min; 87% ee.



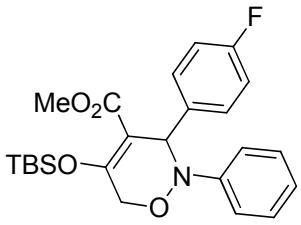
11c

Methyl 5-(*tert*-Butyldimethylsilyloxy)-3-(4-methoxyphenyl)-2-phenyl-3,6-dihydro-*2H*-1,2-oxazine-4-carboxylate (11c). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.19-7.26 (comp, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 2H), 5.57 (d, *J* = 1.6 Hz, 1H), 4.51 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H), 4.32 (d, *J* = 16.0 Hz, 1H), 3.71 (s, 3H), 3.68 (s, 3H), 1.02 (s, 9H), 0.28 (s, 3H), 0.24 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.85, 159.34, 158.30, 148.13, 130.93, 130.18, 128.99, 122.85, 117.77, 113.35, 110.08, 69.07, 63.15, 55.16, 51.67, 26.07, 18.83, -3.55, -3.63; HRMS (ESI) calculated for $C_{25}H_{34}NO_5Si$ $[M+H]^+$: 456.2201; found: 456.2186. HPLC conditions for determination of the enantiomeric excess: AD-H column, 254 nm, 0.7 mL/min, hexane:IPA = 97:3, t_r = 14.0, 16.2 min; 78% ee.



11d

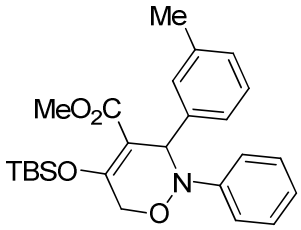
Methyl 3-(4-Bromophenyl)-5-(*tert*-butyldimethylsilyloxy)-2-phenyl-3,6-dihydro-*2H*-1,2-oxazine-4-carboxylate (11d). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.16-7.30 (comp, 4H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.90-6.96 (comp, 3H), 5.51 (d, *J* = 1.6 Hz, 1H), 4.48 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H), 4.28 (d, *J* = 16.0 Hz, 1H), 3.64 (s, 3H), 0.97 (s, 9H), 0.24 (s, 3H), 0.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.23, 158.60, 147.38, 136.67, 131.05, 130.68, 128.65, 122.73, 121.70, 117.27, 108.96, 68.75, 62.89, 51.26, 25.58, 18.38, -3.99, -4.06; HRMS (ESI) calculated for $C_{24}H_{31}BrNO_4Si$ $[M+H]^+$: 504.1200; found: 504.1201. HPLC conditions for determination of the enantiomeric excess: AD-H column, 254 nm, 1.0 mL/min, hexane:IPA = 97:3, t_r = 8.0, 11.3 min; 80% ee.



11e

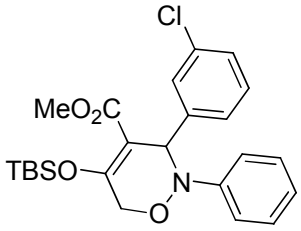
Methyl 5-(*tert*-Butyldimethylsilyloxy)-3-(4-fluorophenyl)-2-phenyl-3,6-dihydro-*2H*-1,2-oxazine-4-carboxylate (11e). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.80-7.23 (comp, 9H), 5.53 (d, *J* = 1.6 Hz, 1H), 4.48 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H), 4.28 (d, *J* = 16.0 Hz, 1H), 3.64 (s, 3H),

0.98 (s, 9H), 0.24 (s, 3H), 0.20 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.27, 162.19 (d, *J* = 244.0 Hz), 158.35, 147.45, 133.32 (d, *J* = 3.2 Hz), 130.92 (d, *J* = 8.0 Hz), 128.56, 122.65, 117.32, 114.30 (d, *J* = 21.1 Hz), 109.22, 68.69, 62.80, 51.22, 25.57, 18.35, -4.02, -4.08; HRMS (ESI) calculated for $C_{24}H_{31}FNO_4Si$ [M+H] $^+$: 444.2001; found: 444.1988. HPLC conditions for determination of the enantiomeric excess: AD-H column, 254 nm, 0.8 mL/min, hexane:IPA = 97:3, t_r = 10.0, 11.0 min; 77% ee.



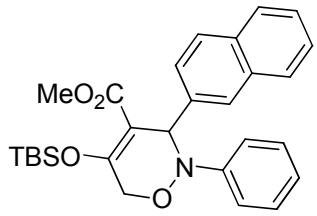
11f

Methyl 5-(*tert*-Butyldimethylsilyloxy)-2-phenyl-3-*m*-tolyl-3,6-dihydro-*2H*-1,2-oxazine-4-carboxylate (11f). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.89-7.24 (comp, 9H), 5.55 (d, *J* = 1.6 Hz, 1H), 4.42 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H), 4.23 (d, *J* = 16.0 Hz, 1H), 3.63 (s, 3H), 2.22 (s, 3H), 0.95 (s, 9H), 0.21 (s, 3H), 0.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.38, 157.81, 147.48, 137.60, 136.97, 130.01, 128.54, 128.34, 127.36, 126.41, 122.43, 117.34, 109.25, 67.91, 62.58, 51.20, 25.58, 21.39, 18.35, -1.08, -1.17; HRMS (ESI) calculated for $C_{25}H_{34}NO_4Si$ [M+H] $^+$: 440.2252; found: 440.2253. HPLC conditions for determination of the enantiomeric excess: AD-H column, 254 nm, 0.5 mL/min, hexane:IPA = 98:2, t_r = 12.4, 18.5 min; 90% ee.



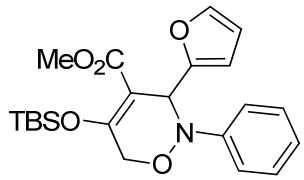
11g

Methyl 5-(*tert*-Butyldimethylsilyloxy)-3-(3-chlorophenyl)-2-phenyl-3,6-dihydro-*2H*-1,2-oxazine-4-carboxylate (11g). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.90-7.24 (comp, 9H), 5.51 (d, *J* = 1.6 Hz, 1H), 4.44 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H), 4.25 (d, *J* = 16.0 Hz, 1H), 3.64 (s, 3H), 0.96 (s, 9H), 0.22 (s, 3H), 0.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 165.17, 158.69, 147.24, 139.75, 133.45, 129.30, 128.67, 128.63, 127.70, 122.77, 117.29, 108.67, 68.42, 62.78, 51.24, 25.55, 18.35, -4.03, -4.10; HRMS (ESI) calculated for $C_{24}H_{31}ClNO_4Si$ [M+H] $^+$: 460.1705; found: 460.1691. HPLC conditions for determination of the enantiomeric excess: OD-H column, 254 nm, 0.4 mL/min, hexane:IPA = 98:2, t_r = 11.8, 13.7 min; 85% ee.



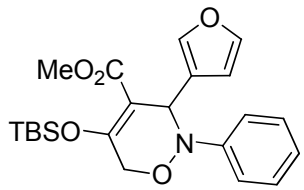
11h

Methyl 5-(*tert*-Butyldimethylsilyloxy)-3-(naphthalen-2-yl)-2-phenyl-3,6-dihydro-*2H*-1,2-oxazine-4-carboxylate (11h). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.31-7.74 (comp, 7H), 7.17 (t, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.88 (m, 1H), 5.75 (s, 1H), 4.50 (d, *J* = 16.0 Hz, 1H), 4.32 (d, *J* = 16.0 Hz, 1H), 3.61 (s, 3H), 0.98 (s, 9H), 0.26 (s, 3H), 0.21 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.32, 158.20, 147.50, 132.88, 132.83, 128.61, 128.51, 128.19, 127.53, 127.42, 127.08, 125.65,125.55, 122.53, 117.31, 109.37, 68.39, 63.01, 51.23, 25.55, 18.10, -1.01, -1.11; HRMS (ESI) calculated for $C_{28}H_{34}NO_4Si$ $[M+H]^+$: 476.2252; found: 476.2234. HPLC conditions for determination of the enantiomeric excess: AD-H column, 254 nm, 1.0 mL/min, hexane:IPA = 95:5, t_r = 7.6, 10.7 min; 80% ee.



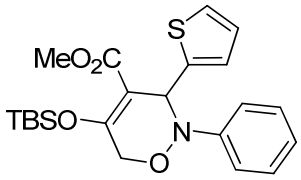
11i

Methyl 5-(*tert*-Butyldimethylsilyloxy)-3-(furan-2-yl)-2-phenyl-3,6-dihydro-*2H*-1,2-oxazine-4-carboxylate (11i). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.20-7.30 (comp, 3H), 7.09 (d, *J* = 7.6 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.21 (m, 1H), 6.13 (d, *J* = 3.6 Hz, 1H), 5.72 (d, *J* = 1.6 Hz, 1H), 4.49 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H), 4.28 (d, *J* = 16.0 Hz, 1H), 3.73 (s, 3H), 1.00 (s, 9H), 0.26 (s, 3H), 0.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.50, 159.10, 152.27, 147.82, 142.38, 129.01, 123.07, 117.31, 110.38, 109.65, 107.95, 69.09, 57.25, 51.76, 26.03, 18.82, -3.57, -3.61; HRMS (ESI) calculated for $C_{22}H_{30}NO_5Si$ $[M+H]^+$: 416.1888; found: 416.1863. HPLC conditions for determination of the enantiomeric excess: AD-H column, 254 nm, 0.5 mL/min, hexane:IPA = 97:3, t_r = 12.8, 13.7 min; 90% ee.



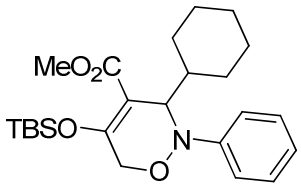
11j

Methyl 5-(*tert*-Butyldimethylsilyloxy)-3-(furan-3-yl)-2-phenyl-3,6-dihydro-*2H*-1,2-oxazine-4-carboxylate (11j). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.21-7.38 (comp, 4H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.19 (m, 1H), 5.59 (d, *J* = 1.6 Hz, 1H), 4.53 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H), 4.2 (d, *J* = 16.0 Hz, 1H), 3.74 (s, 3H), 1.00 (s, 9H), 0.26 (s, 3H), 0.23 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.01, 158.73, 147.95, 142.31, 141.79, 129.23, 122.70, 122.51, 117.01, 111.43, 111.00, 69.11, 55.43, 51.36, 26.02, 18.97, -3.59, -3.63; HRMS (ESI) calculated for $C_{22}H_{30}NO_5Si$ $[M+H]^+$: 416.1888; found: 416.1876. HPLC conditions for determination of the enantiomeric excess: AD-H column, 254 nm, 0.5 mL/min, hexane:IPA = 97:3, t_r = 12.8, 15.2 min; 89% ee.



11k

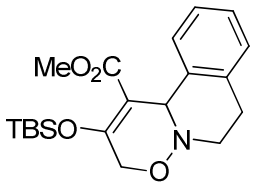
Methyl 5-(*tert*-Butyldimethylsilyloxy)-2-phenyl-3-(thiophen-2-yl)-3,6-dihydro-*2H*-1,2-oxazine-4-carboxylate (11k). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.11-7.28 (comp, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.97 (t, *J* = 8.0 Hz, 1H), 6.78-6.83 (comp, 2H), 5.89 (d, *J* = 1.6 Hz, 1H), 4.57 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H), 4.35 (d, *J* = 16.0 Hz, 1H), 3.72 (s, 3H), 1.01 (s, 9H), 0.28 (s, 3H), 0.26 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.59, 158.93, 147.88, 140.58, 129.03, 127.75, 126.21, 125.80, 122.98, 117.27, 110.90, 69.75, 59.60, 51.71, 26.06, 18.81, -3.47, -3.49; HRMS (ESI) calculated for $C_{22}H_{30}NO_4SSi$ $[M+H]^+$: 432.1659; found: 432.1644. HPLC conditions for determination of the enantiomeric excess: OD-H column, 254 nm, 0.5 mL/min, hexane:IPA = 97:3, t_r = 9.6, 10.5 min; 80% ee.



11l

Methyl 5-(*tert*-Butyldimethylsilyloxy)-3-cyclohexyl-2-phenyl-3,6-dihydro-*2H*-1,2-oxazine-4-carboxylate (11l). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.23-7.27 (comp, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 6.91 (t, *J* = 7.2 Hz, 1H), 4.35 (d, *J* = 8.0 Hz, 1H), 4.03 (d, *J* = 16.0 Hz, 1H), 3.83 (d, *J* = 16.0 Hz, 1H), 3.76 (s, 3H), 2.08 (m, 1H), 1.84 (m, 1H), 1.69 (m, 2H), 1.61 (m, 2H), 1.00-1.25 (comp, 5H), 0.79 (s, 9H), -0.07 (s, 3H), -0.17 (s, 3H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.91, 153.83, 147.28, 129.10, 121.79, 116.72, 109.83, 62.60, 59.59, 51.47, 42.61, 30.96, 29.93, 26.56,

26.42, 26.29, 25.42, 25.32, 18.08, -4.60, -4.65; HRMS (ESI) calculated for $C_{24}H_{38}NO_4Si$ $[M+H]^+$: 432.2565; found: 432.2564. HPLC conditions for determination of the enantiomeric excess: AD-H column, 254 nm, 0.4 mL/min, hexane:IPA = 99:1, t_r = 9.7, 10.1 min; 77% ee.



13

Methyl 2-(*tert*-Butyldimethylsilyloxy)-3,6,7,11*b*-tetrahydro-[1,2]oxazino[3,2-*a*]isoquinoline-1-carboxylate (13). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.07-7.24 (comp, 3H), 6.05 (d, *J* = 6.8 Hz, 1H), 5.08 (d, *J* = 1.6 Hz, 1H), 4.40 (dd, *J* = 16.0 Hz, 1.6 Hz, 1H), 3.95 (d, *J* = 16.0 Hz, 1H), 3.81 (s, 3H), 3.63 (m, 1H), 3.40 (m, 1H), 3.20 (m, 1H), 2.57 (m, 1H), 0.93 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 167.25, 159.88, 136.61, 133.79, 128.73, 127.83, 126.81, 126.68, 110.45, 69.82, 58.37, 51.90, 51.24, 26.00, 23.81, 18.76, -3.38, -3.46; HRMS (ESI) calculated for $C_{20}H_{30}NO_4Si$ $[M+H]^+$: 376.1939; found: 376.1930. HPLC conditions for determination of the enantiomeric excess: AD-H column, 254 nm, 1.0 mL/min, hexane:IPA = 97:3, t_r = 6.3, 8.4 min; 80% ee.

References

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(2) (b) (a) Liang, C.; Collet, F.; Robert-Peillard, F.; Müller, P.; Dodd, R. H.; Dauban, P. *J. Am. Chem. Soc.* **2008**, *130*, 343. (b) Müller, P.; Allenbach, Y.; Robert, E. *Tetrahedron: Asymmetry* **2003**, *14*, 779.

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(4) Davies, H. M. L.; Bruzinski, P. R.; Lake, D. H.; Kong, N.; Fall, M. J. *J. Am. Chem. Soc.* **1996**, *118*, 6897.

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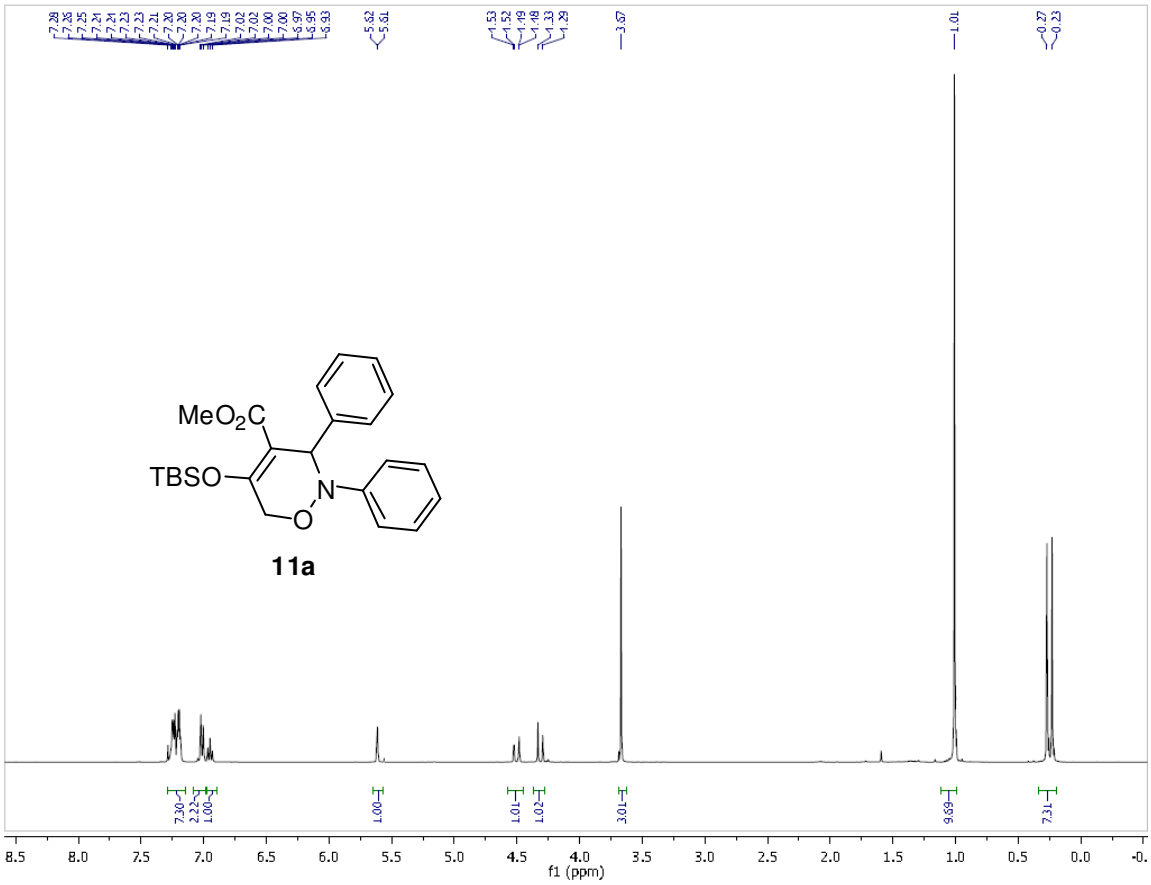
(6) Davies, H. M. L.; Ahmed, G.; Churchill, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 10774.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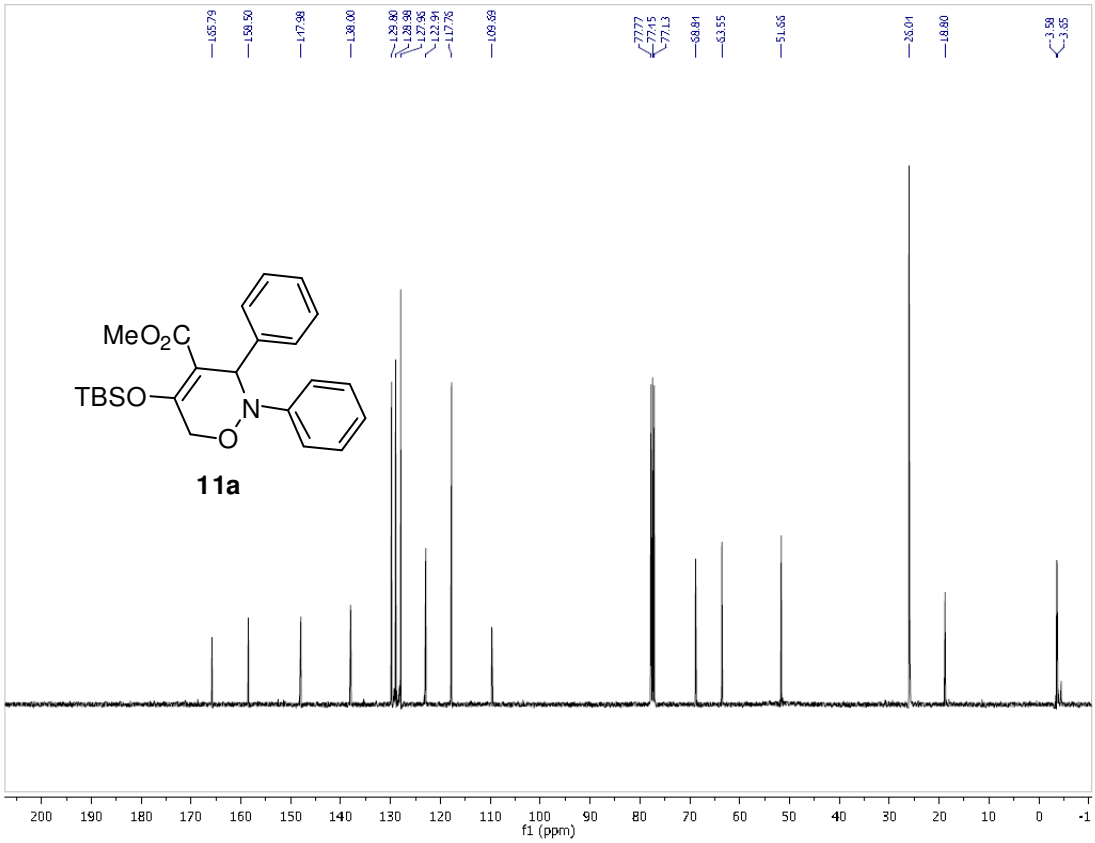
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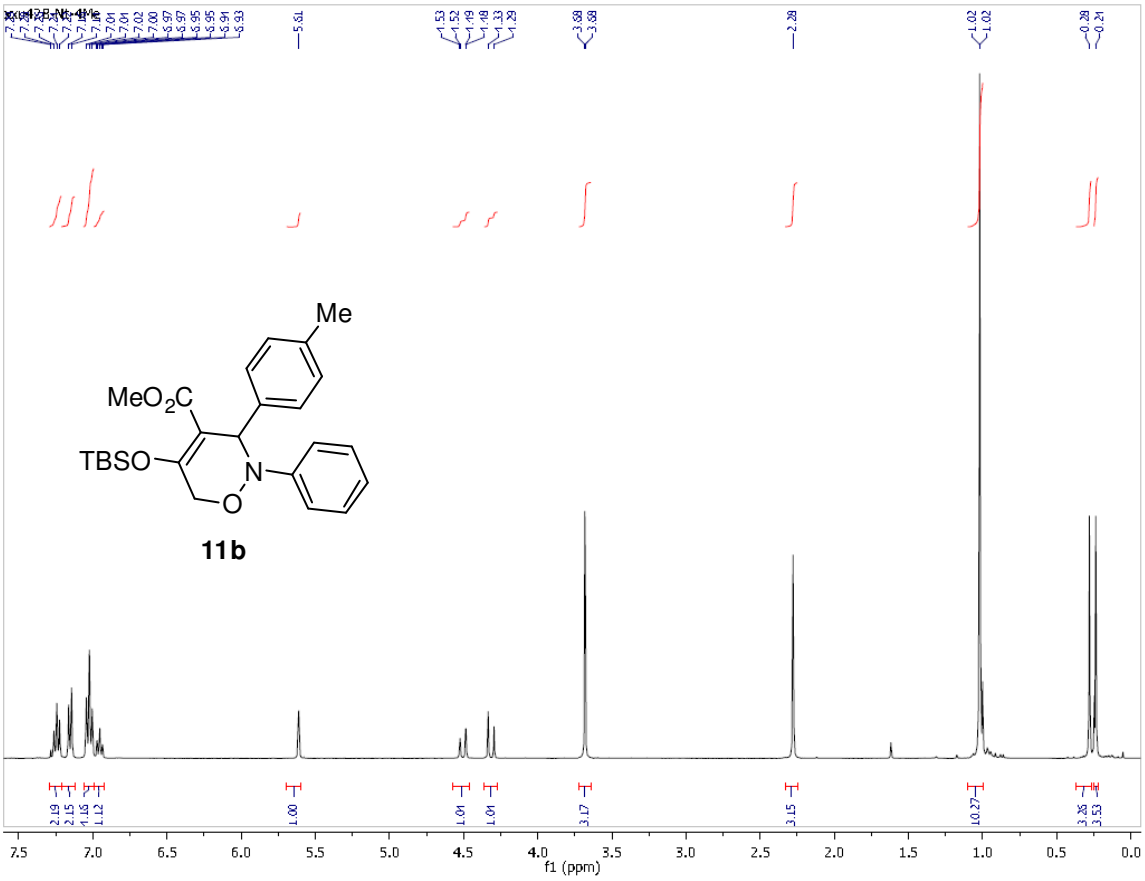
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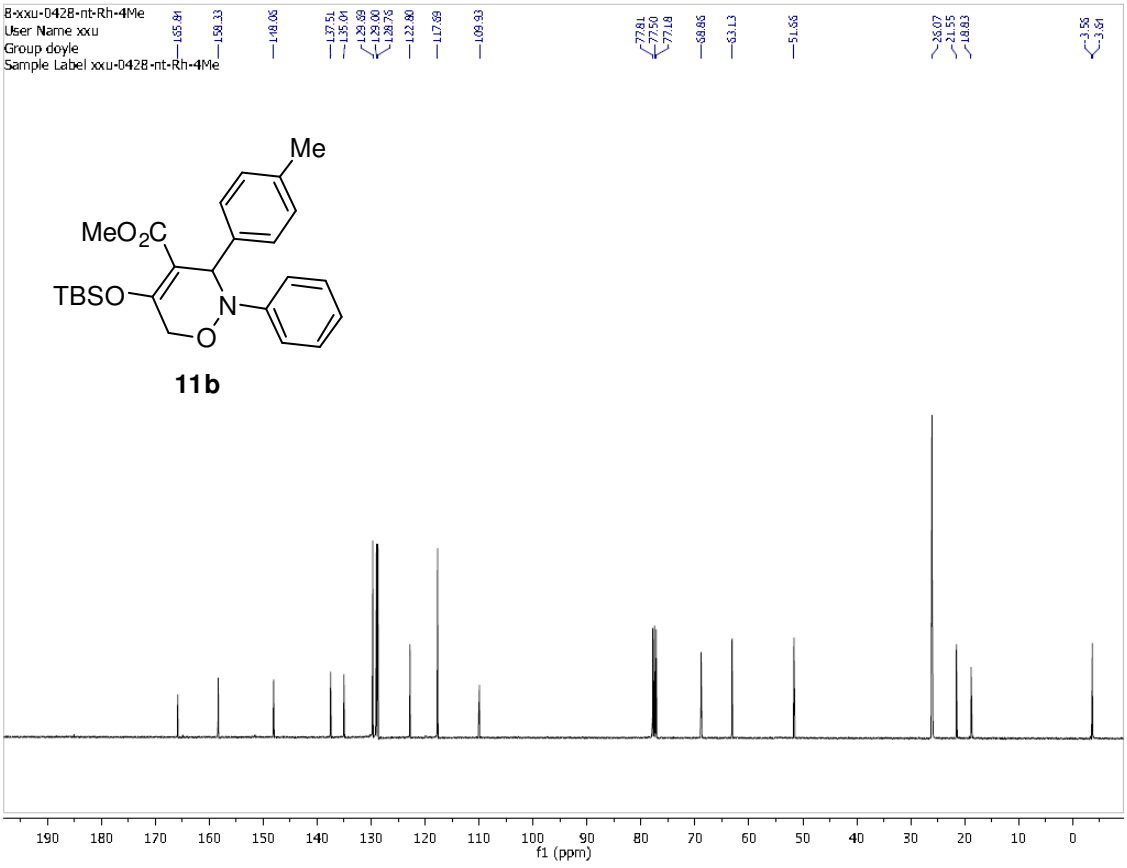
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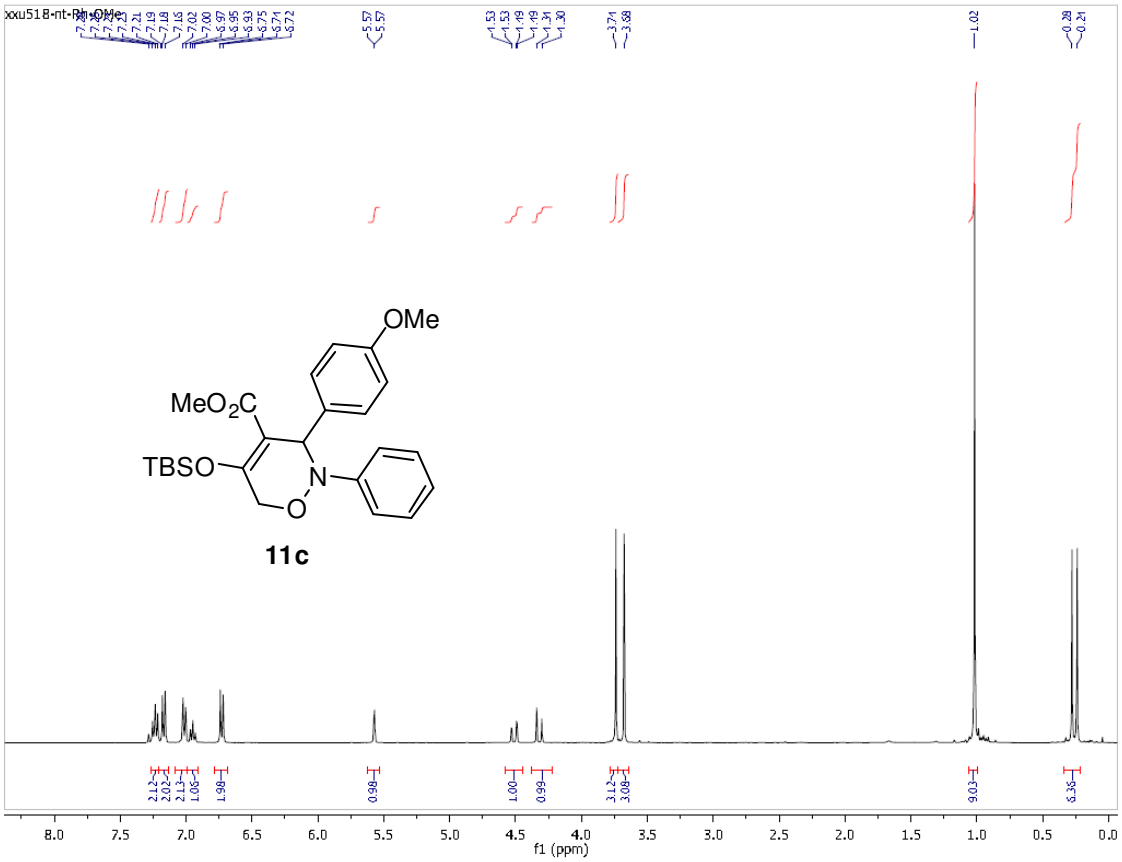
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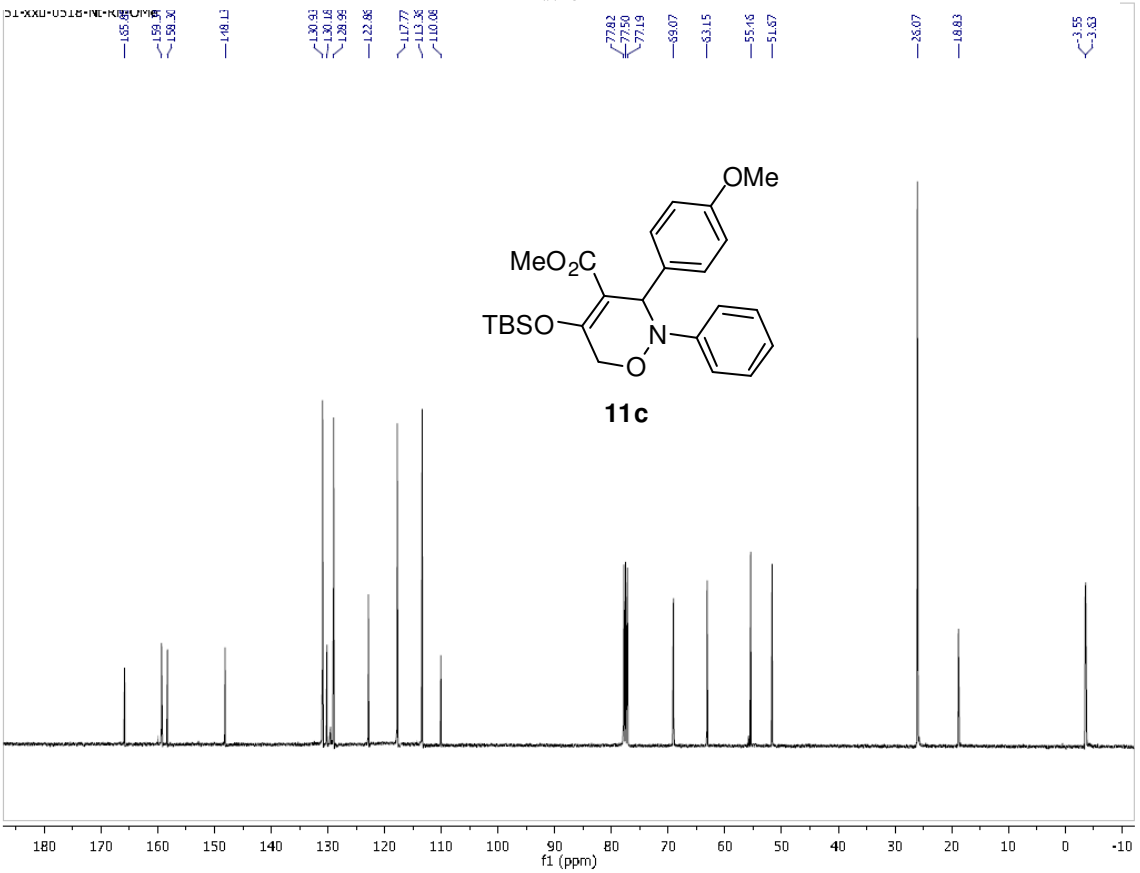
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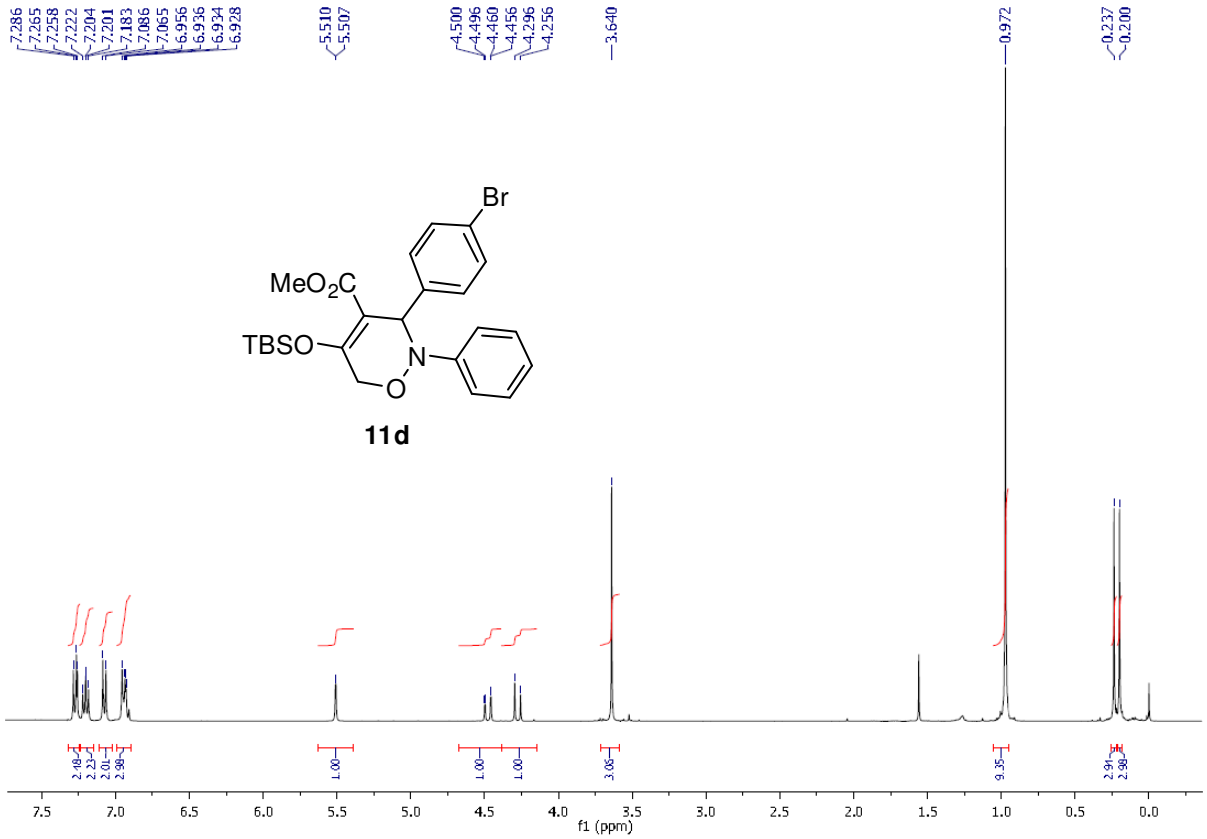
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5.510
5.507
4.500
4.496
4.460
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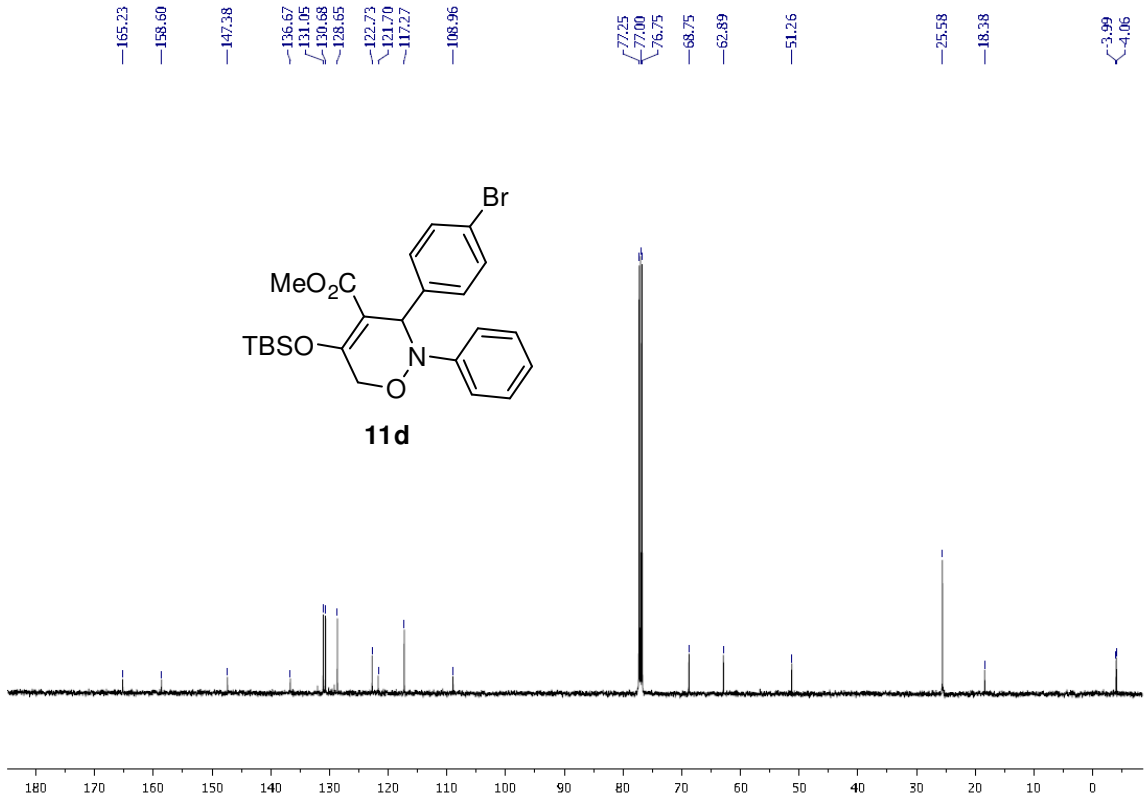
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Br
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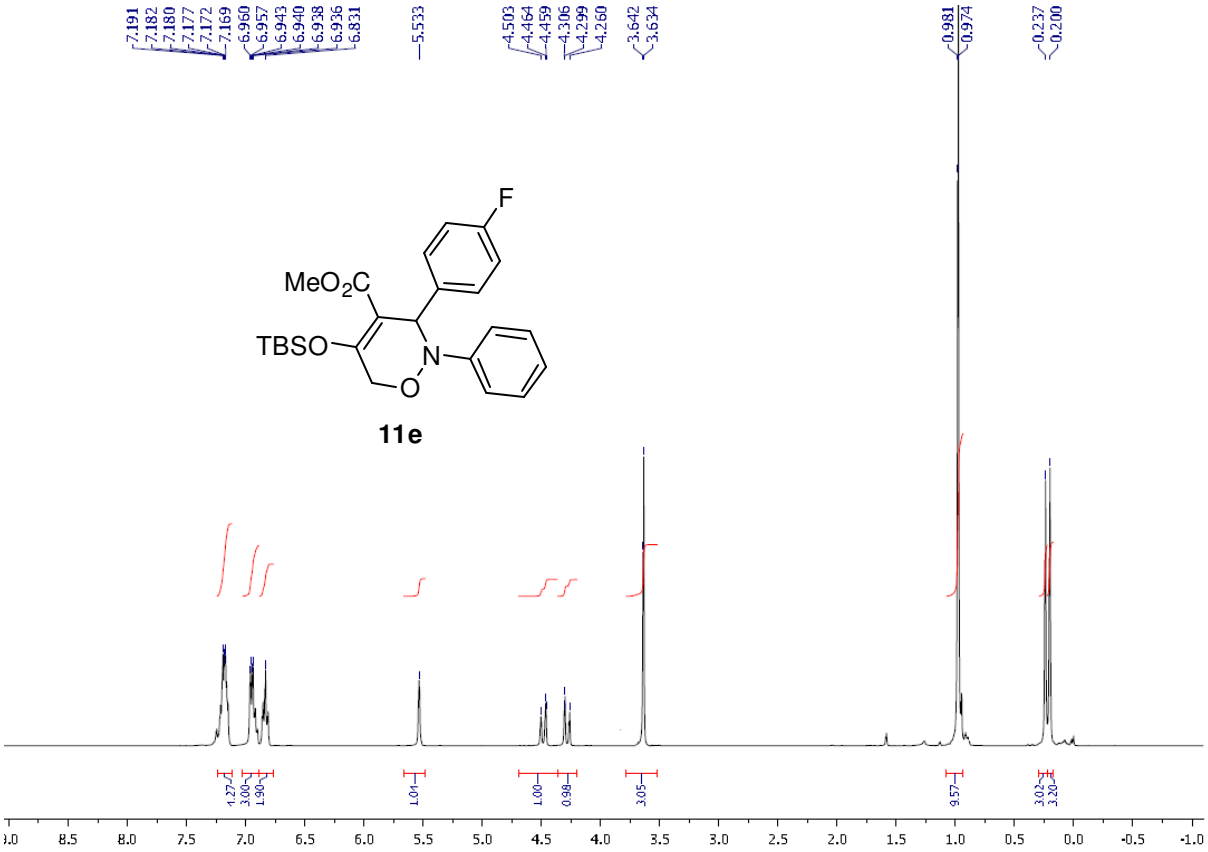
O
11d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F
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TBSO
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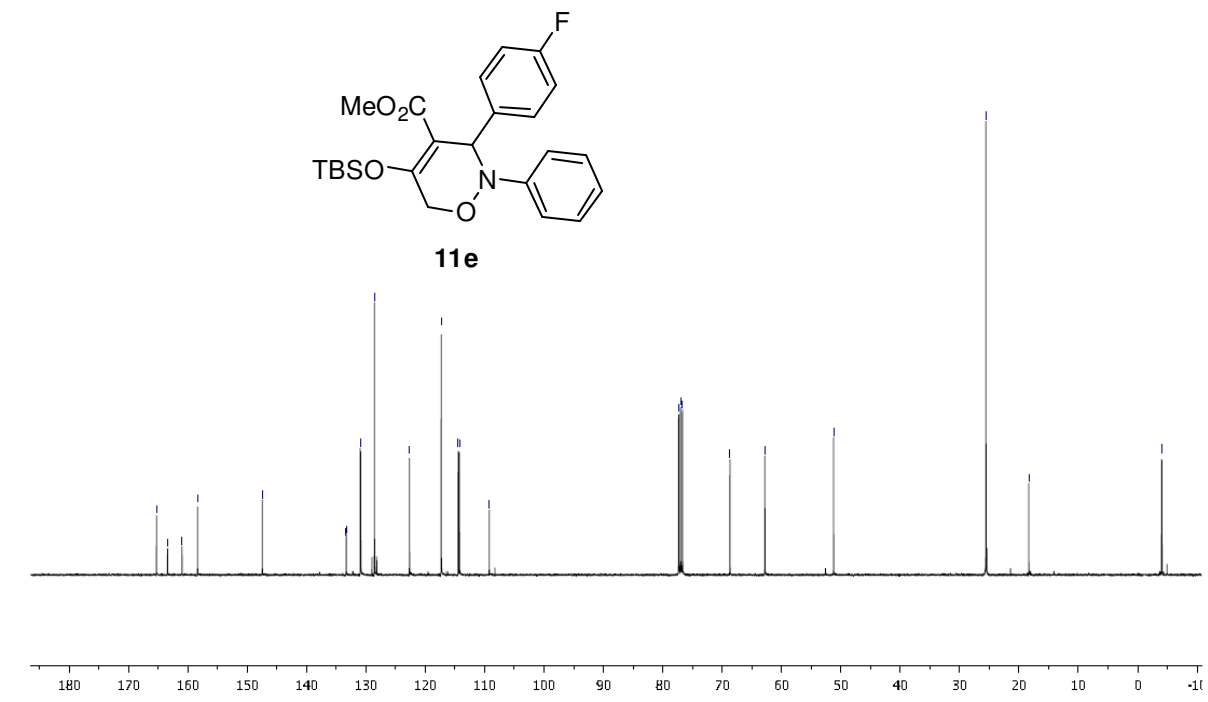
O

11e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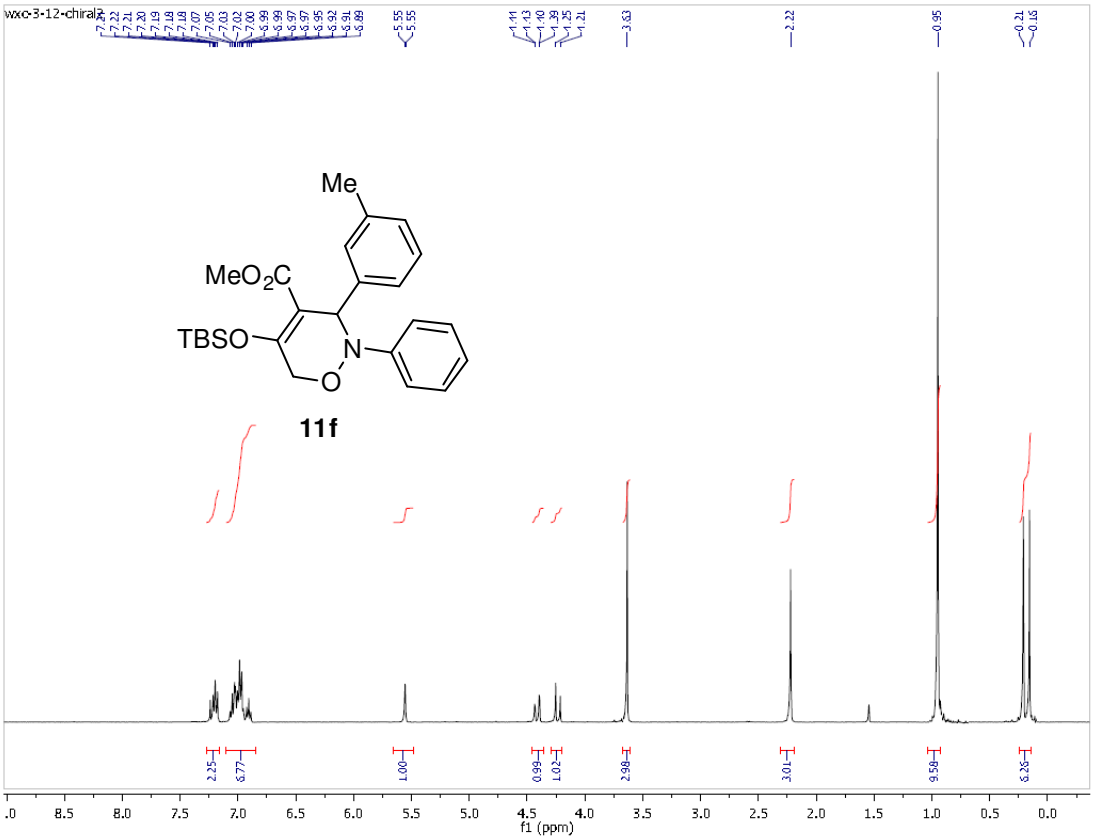
O

11e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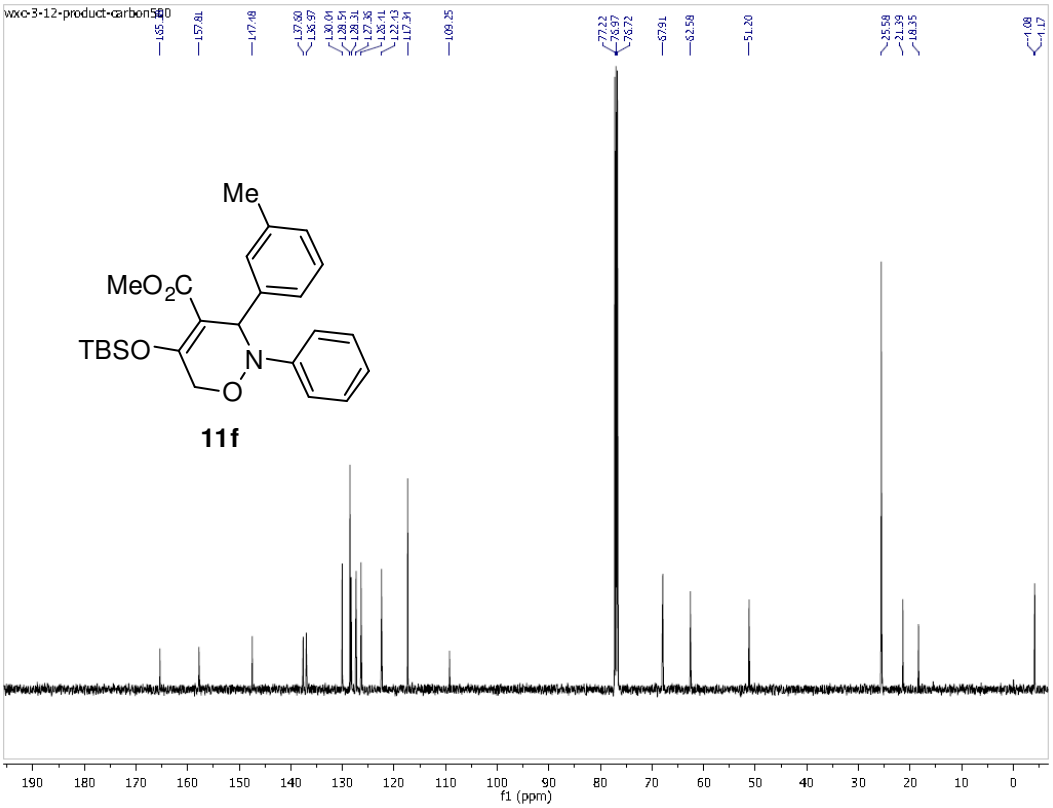
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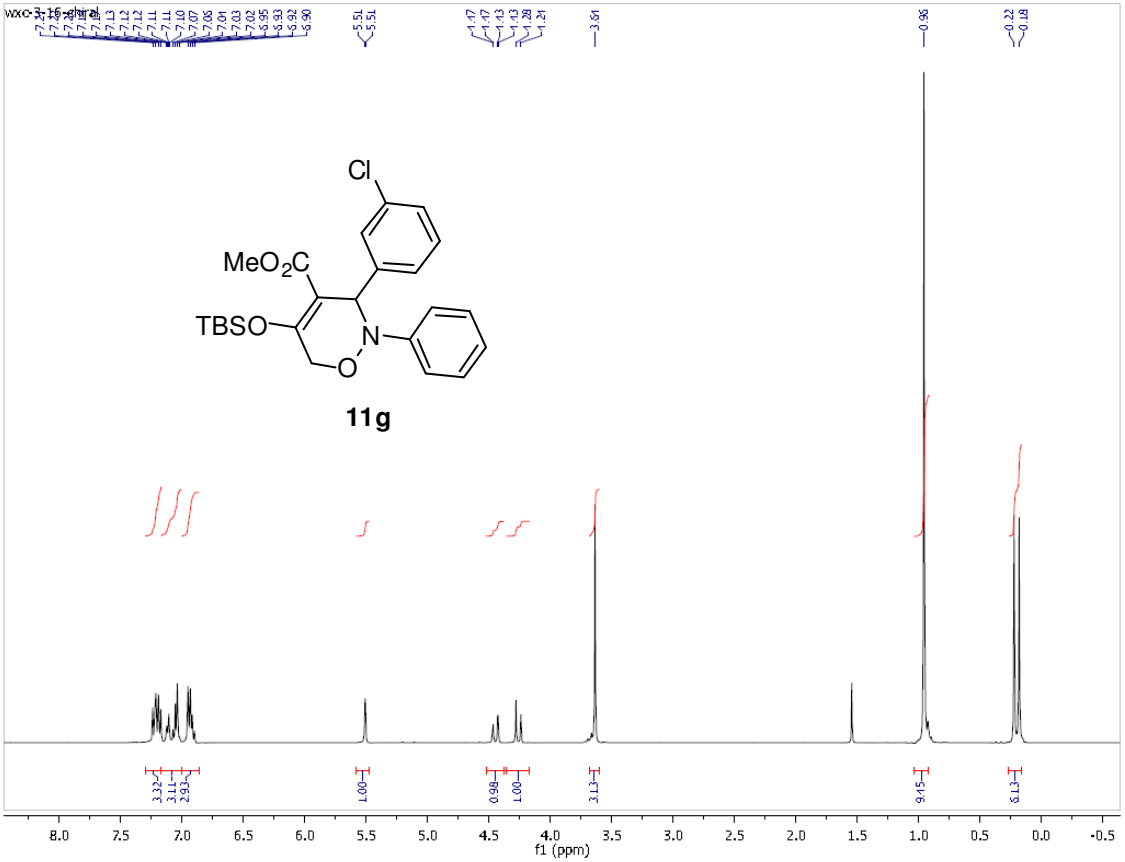
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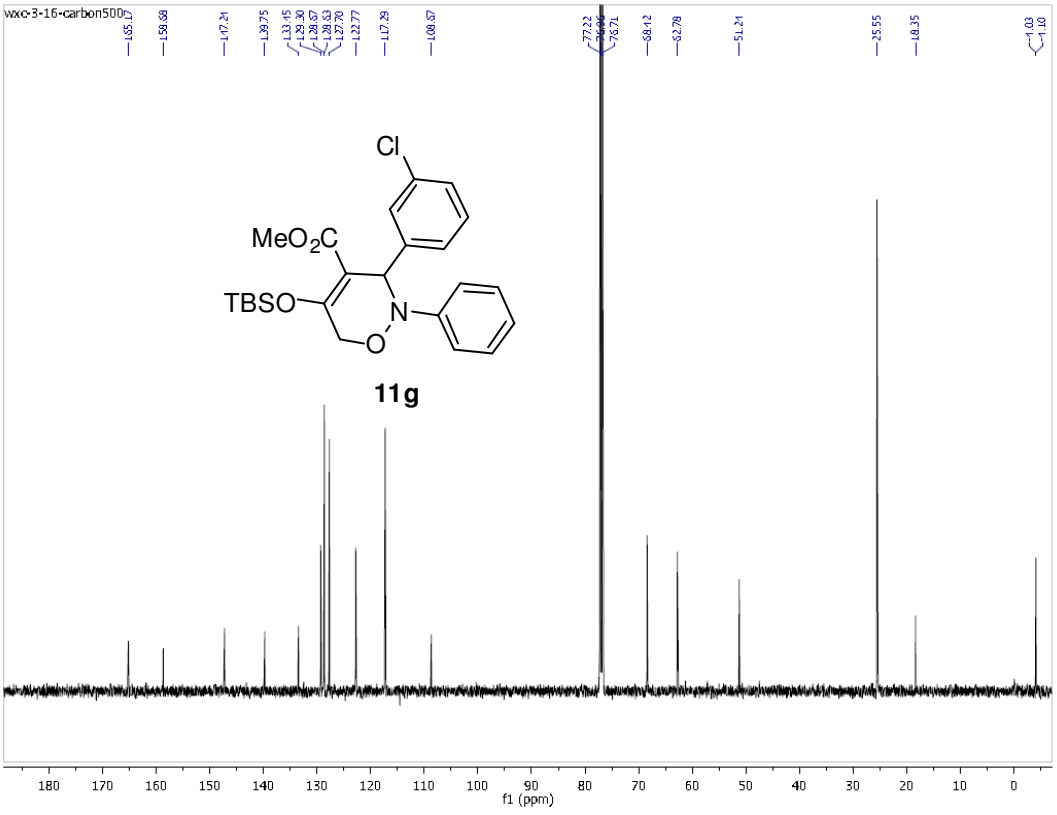
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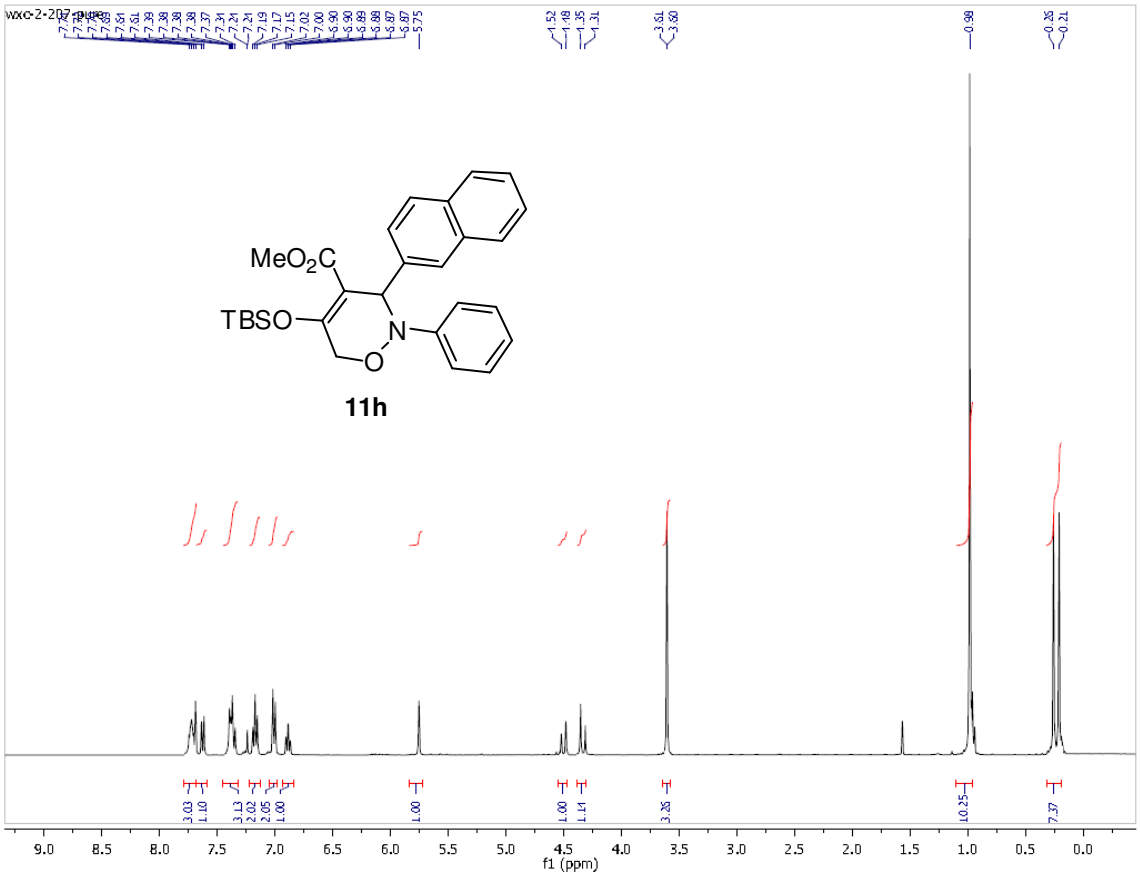
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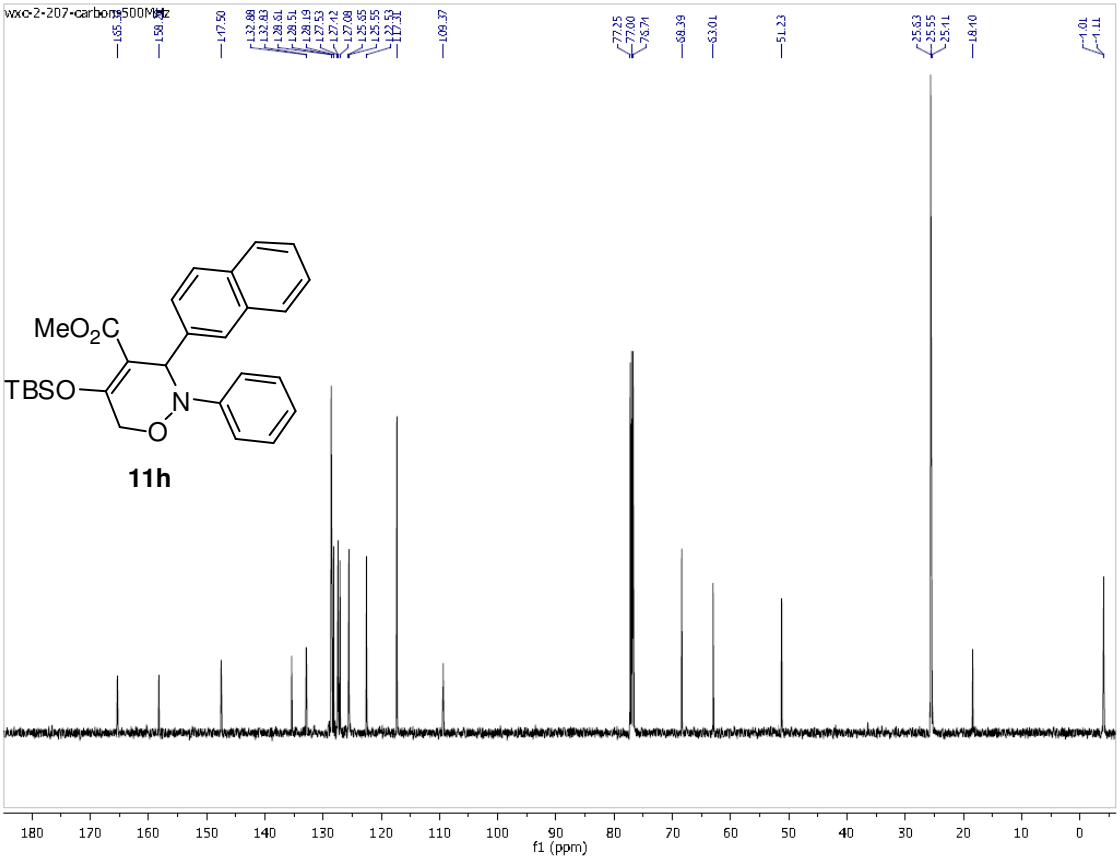
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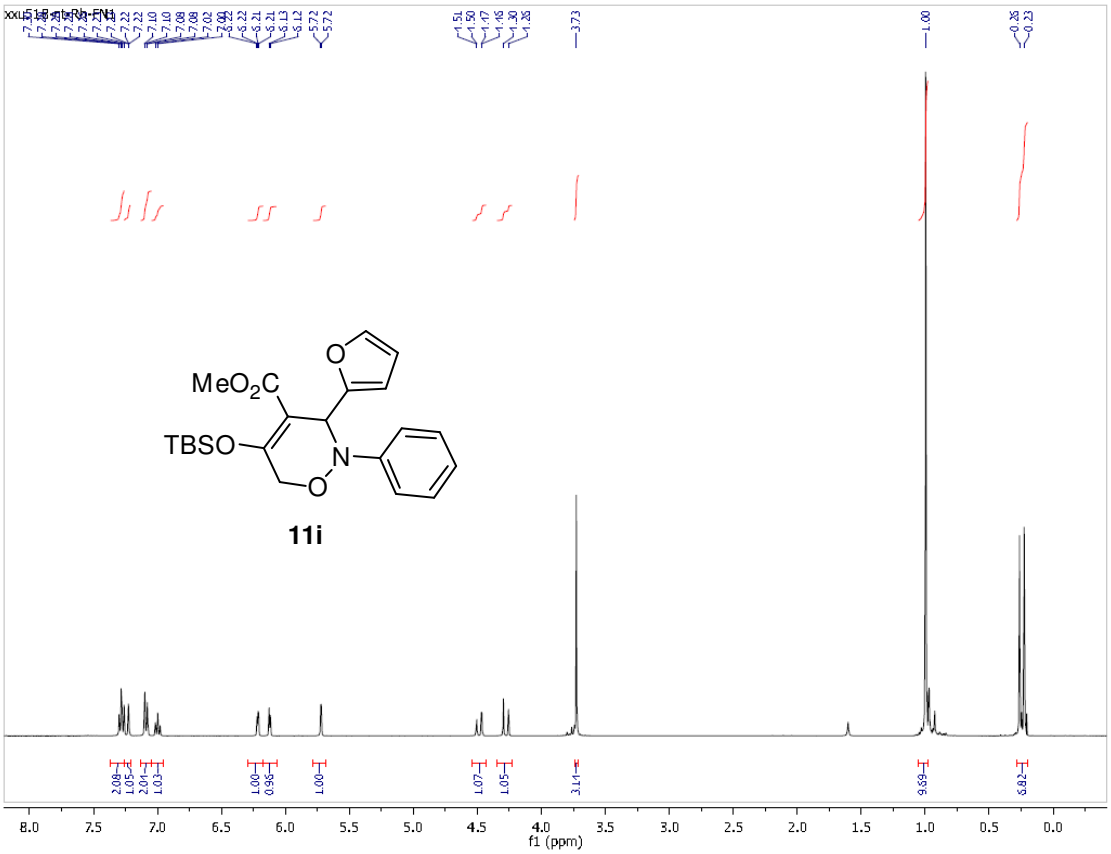

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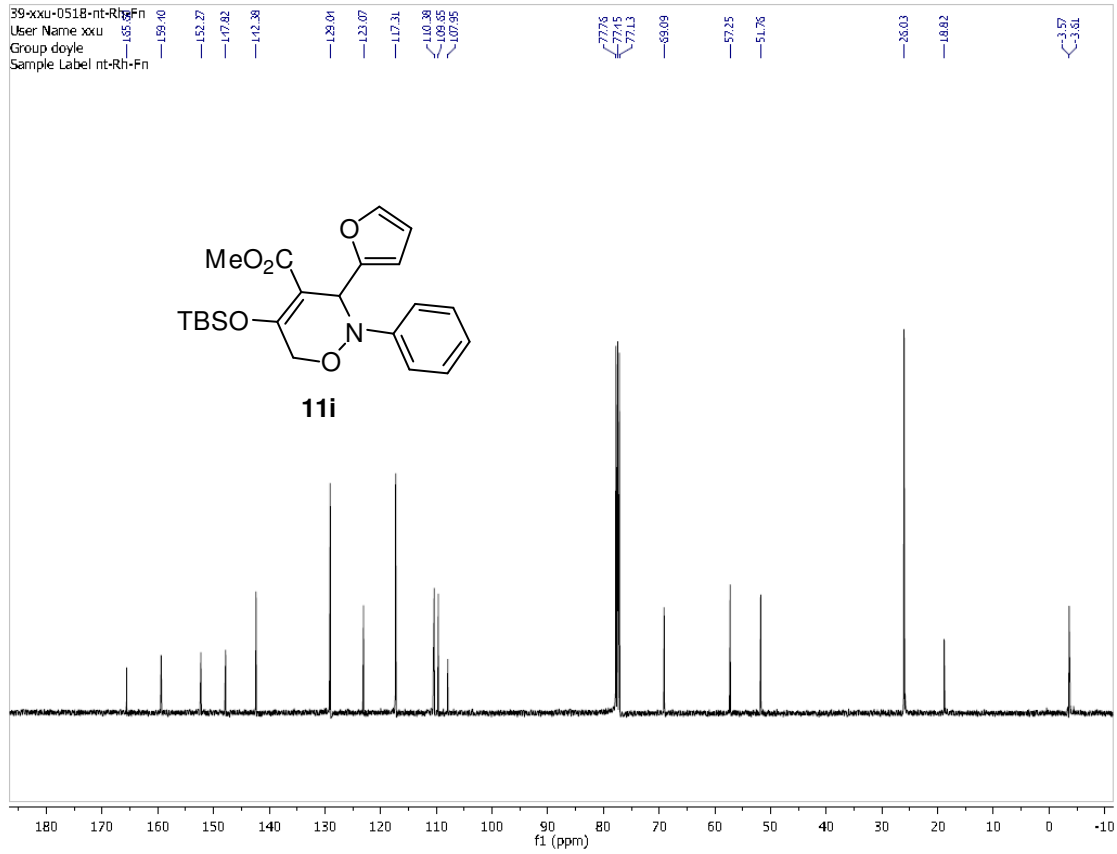

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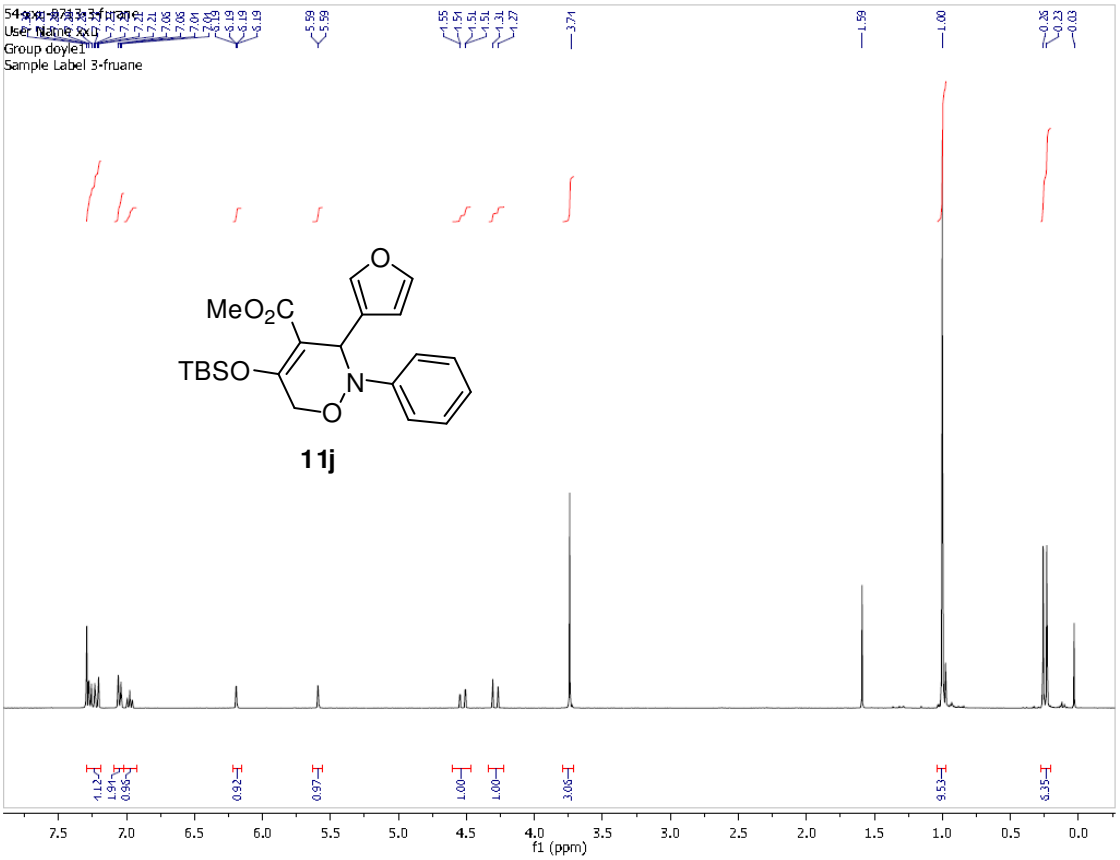
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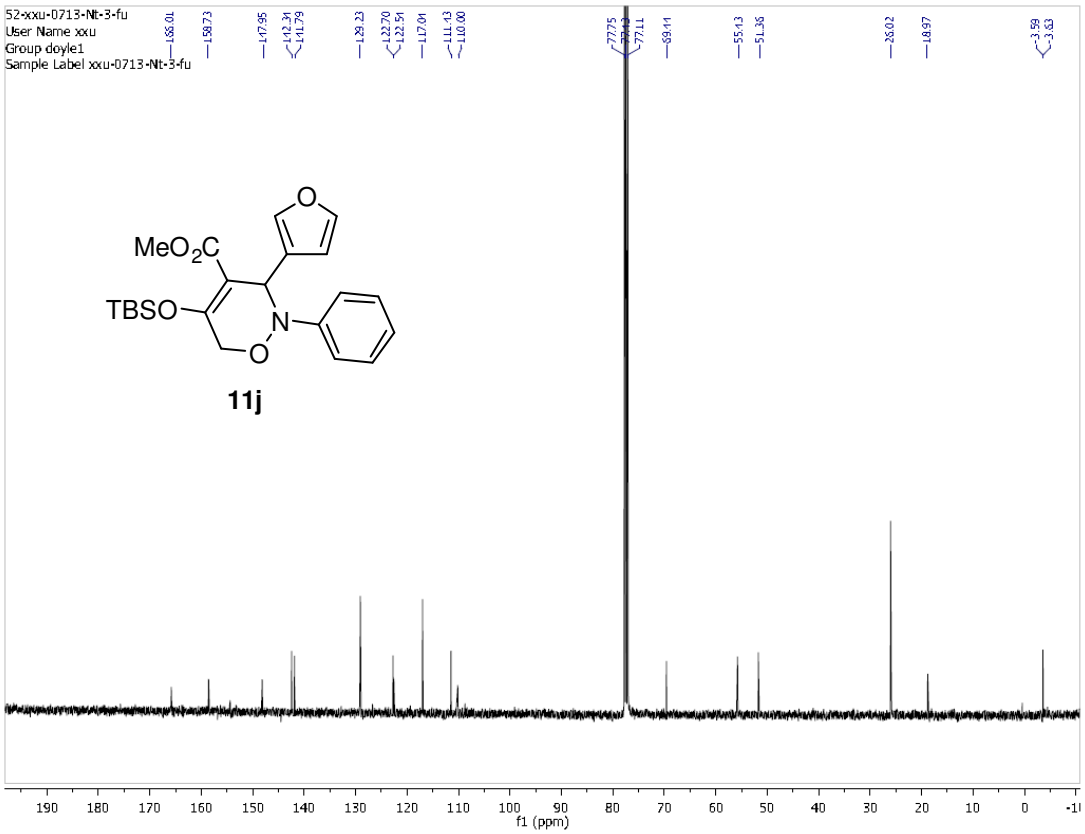
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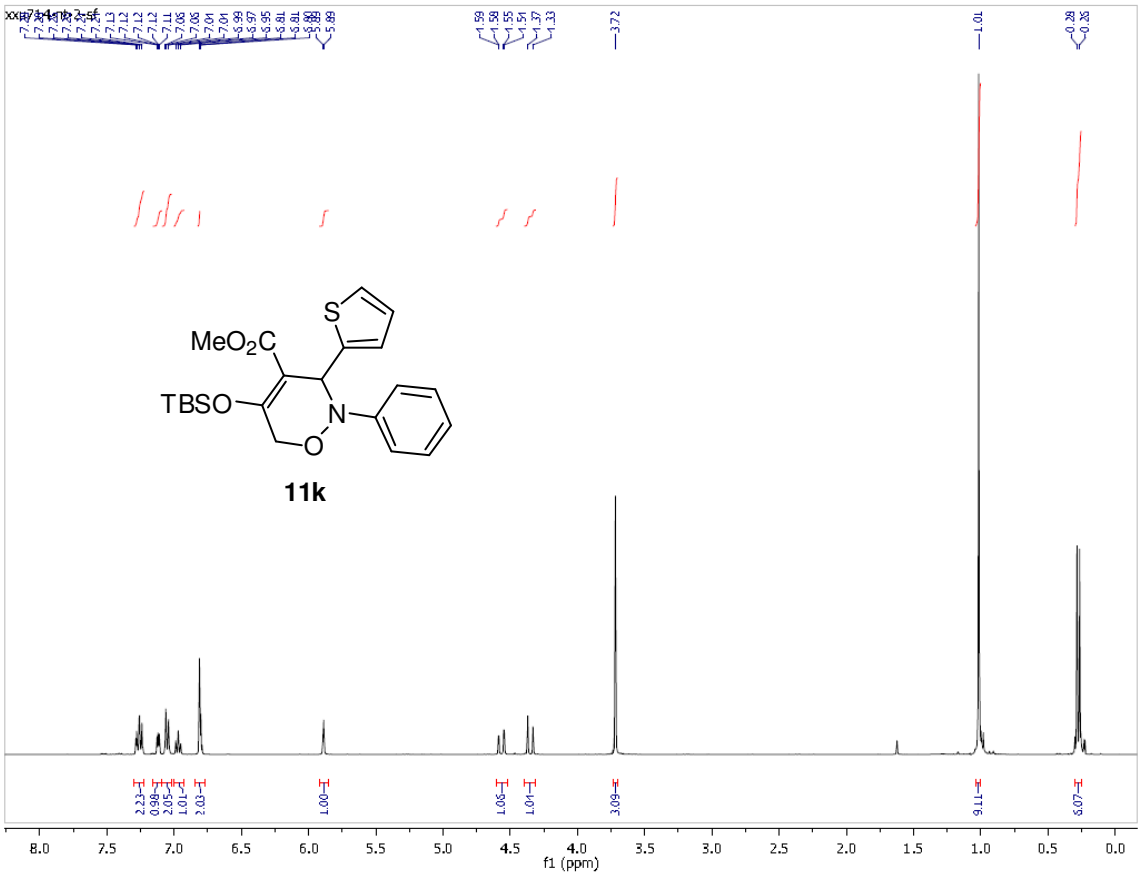
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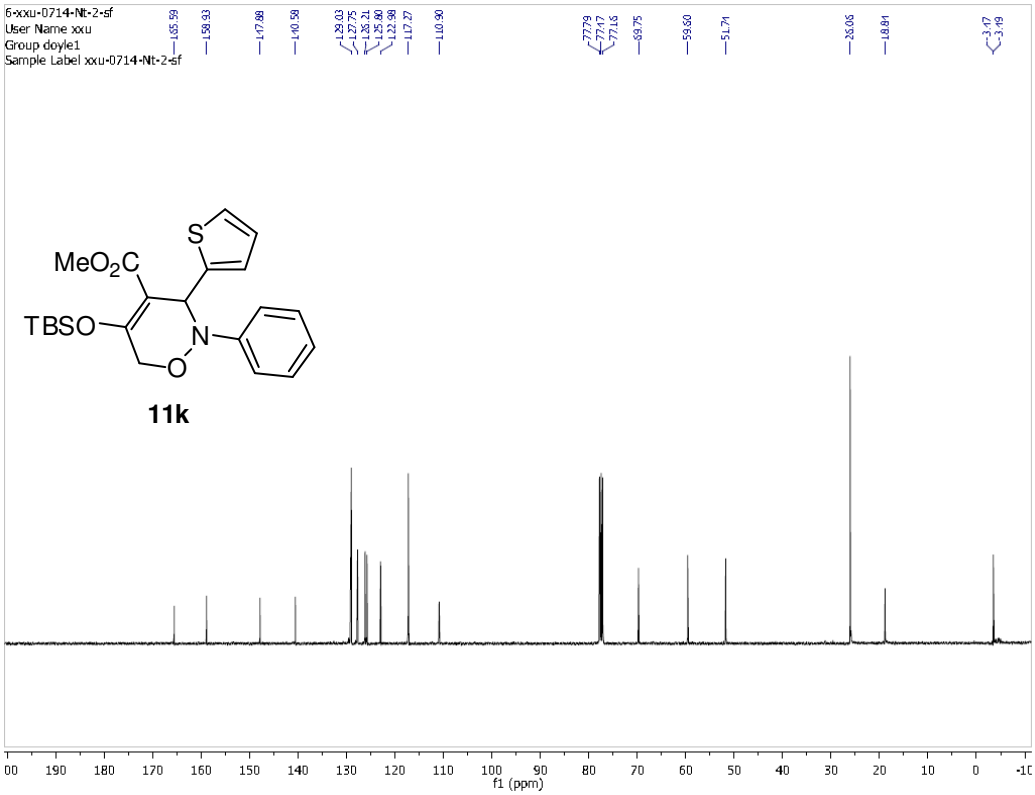
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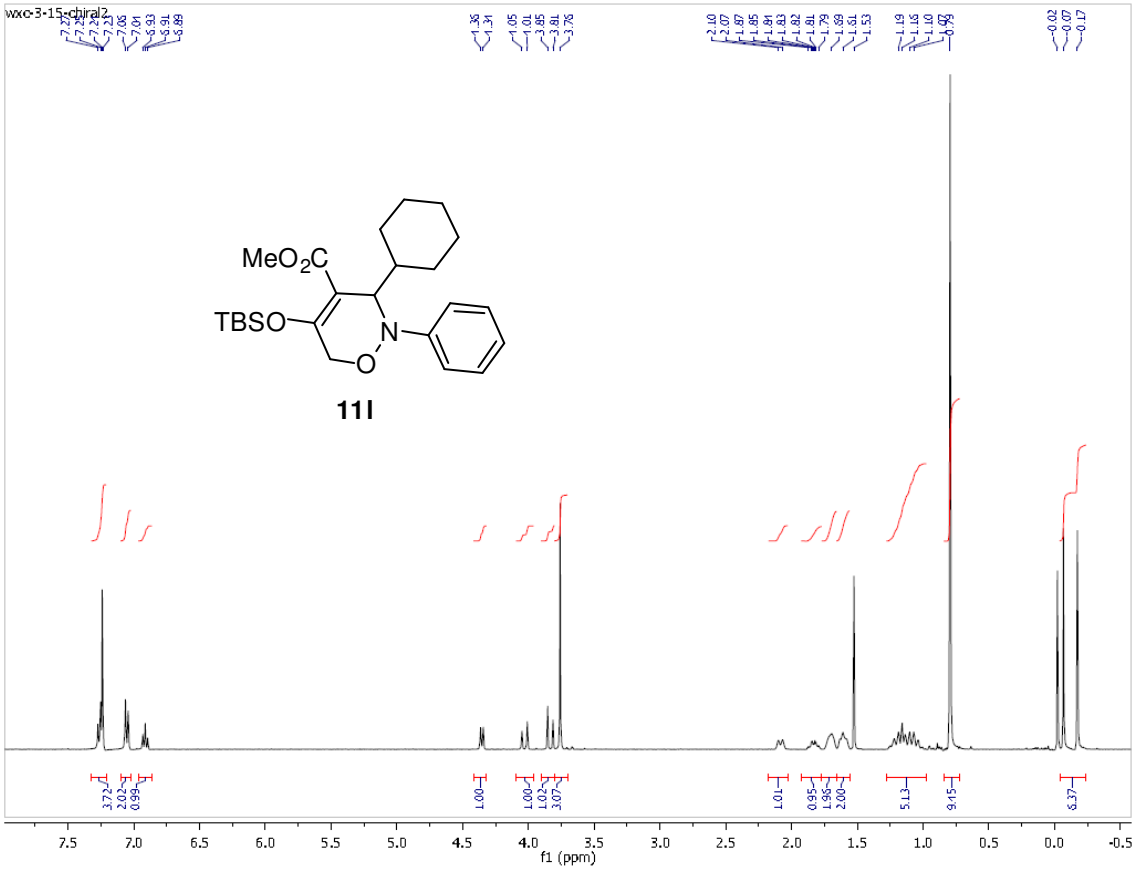
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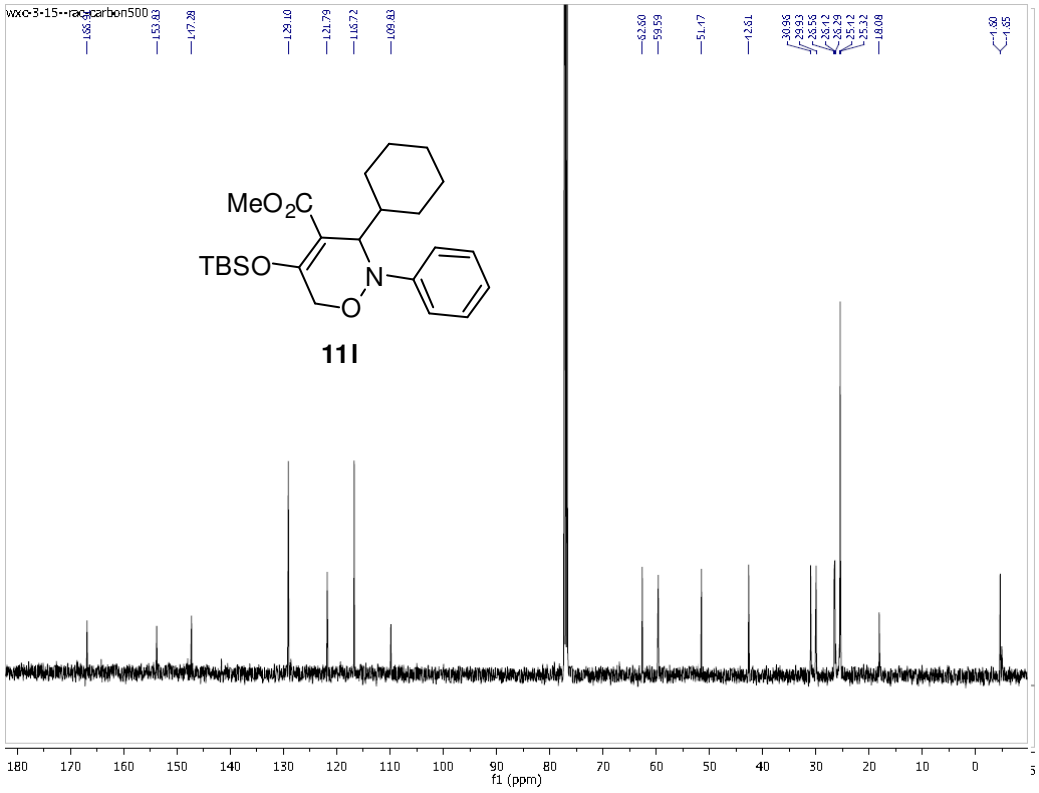
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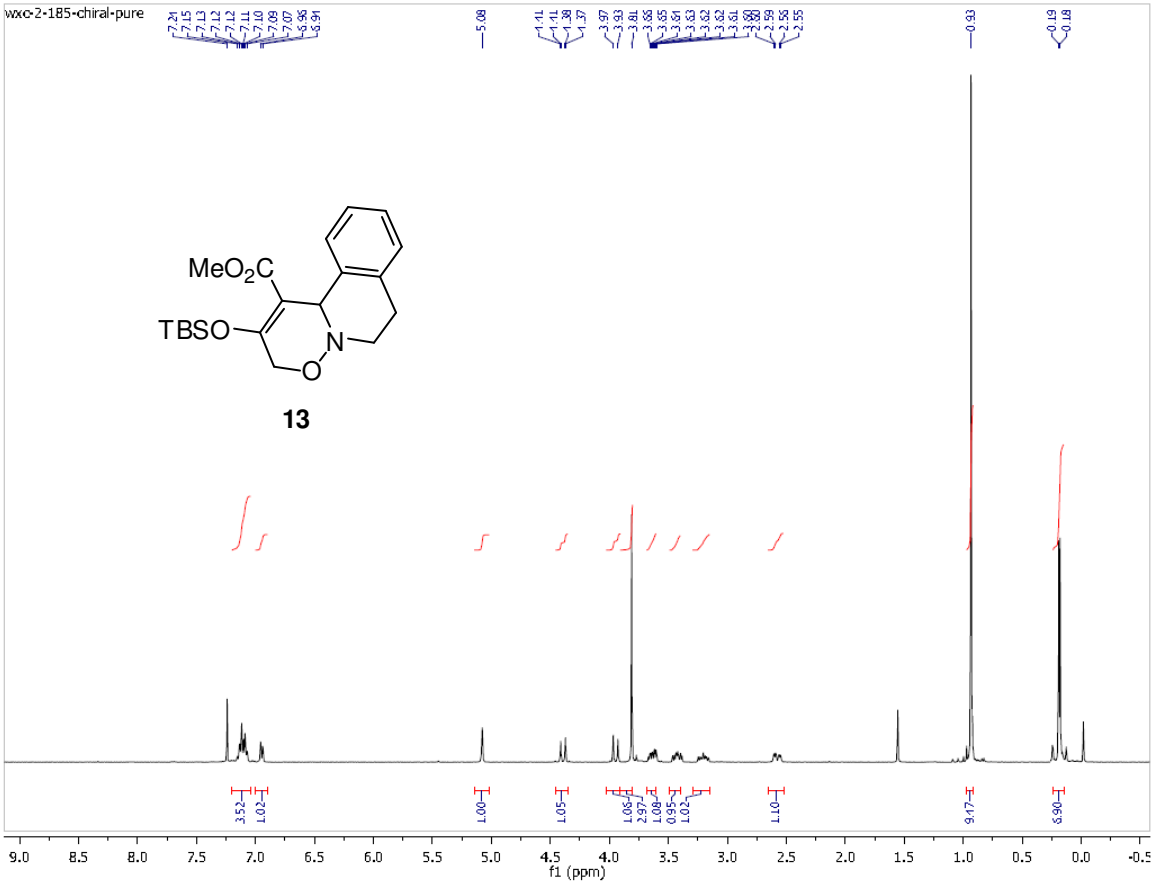
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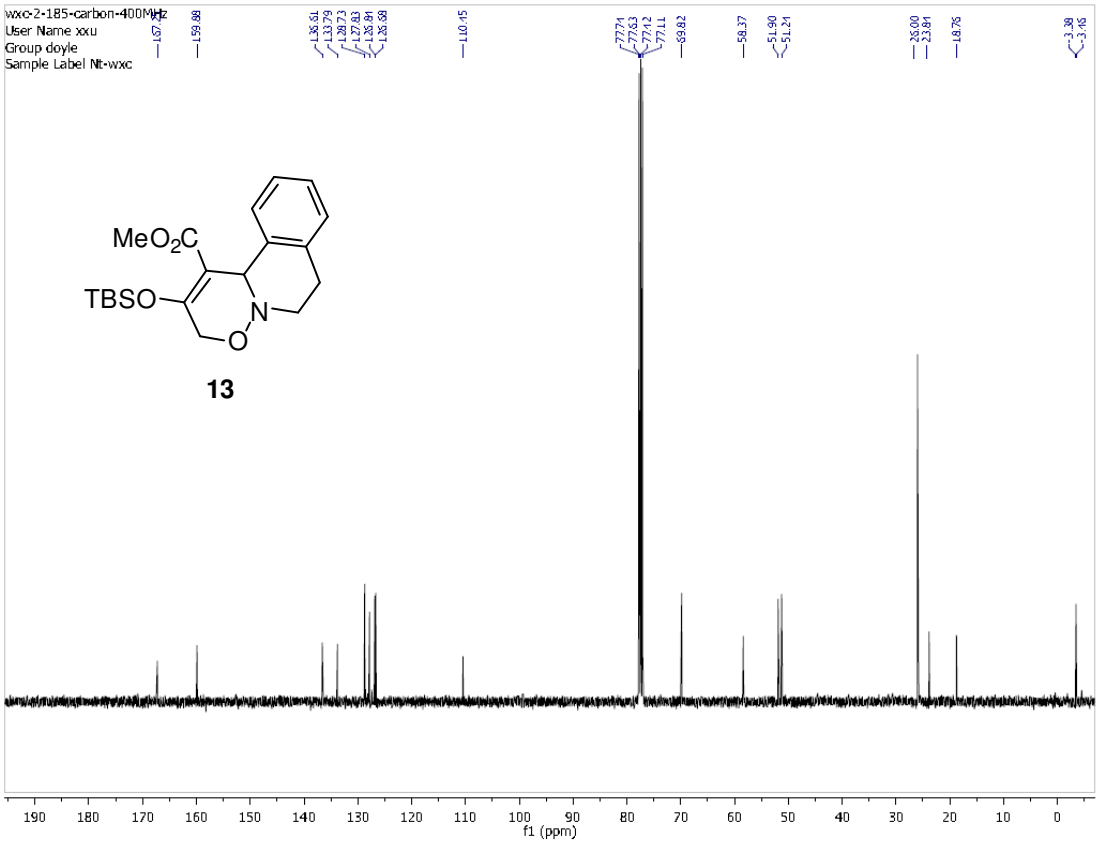
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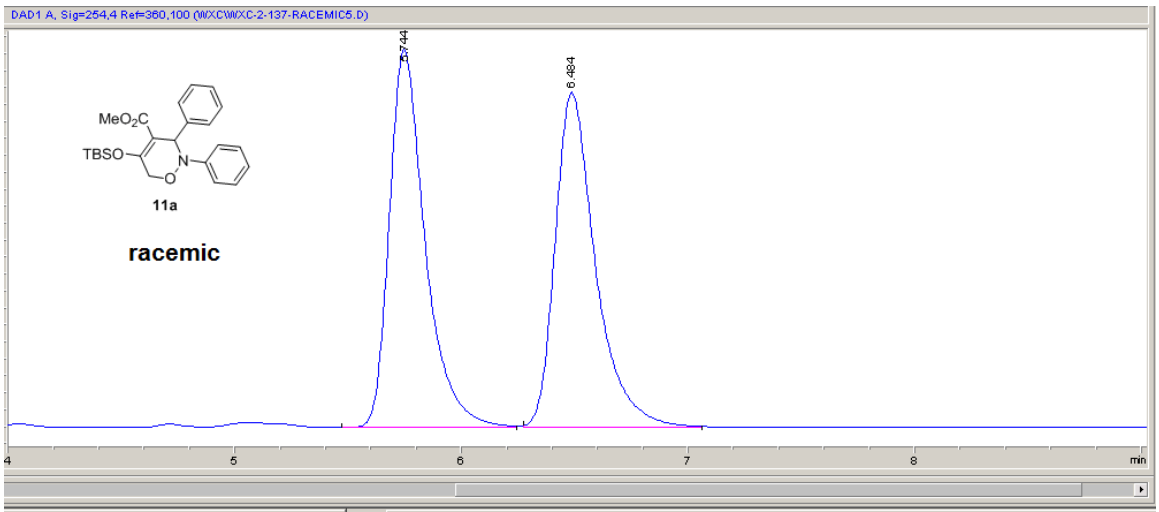

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code	
erator	wxc
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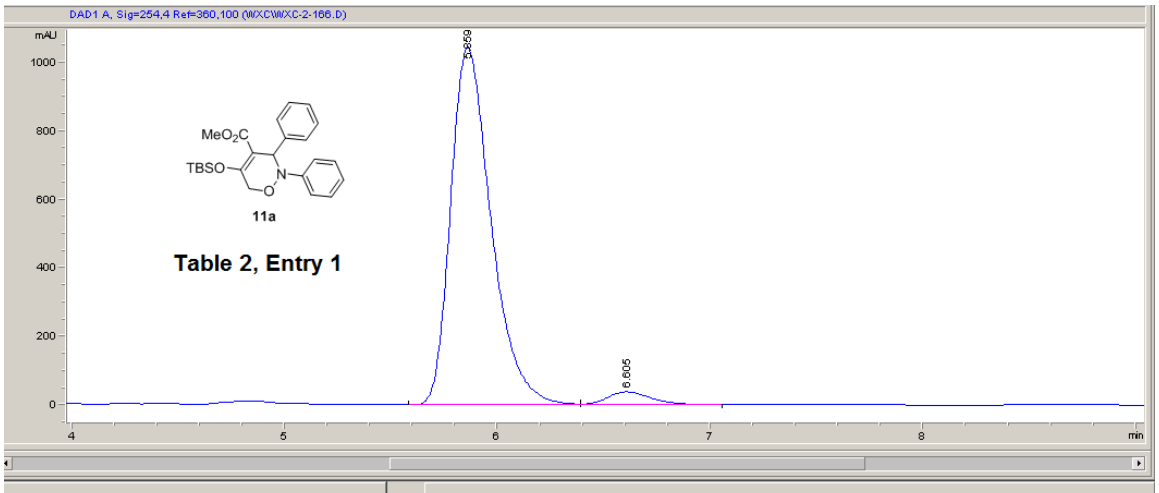

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Barcode	
Operator	wxc
Method	DEF_LC.M
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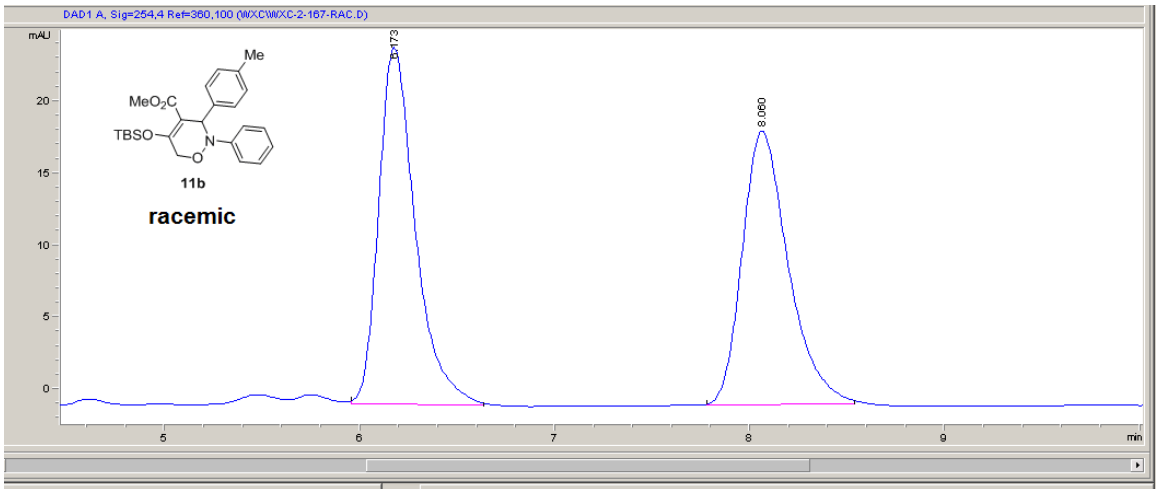

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Barcode	
Operator	wxc
Method	DEF_LC.M
Analysis Time	14.067 min
Sampling Rate	0.0067 min (0.402 sec), 2111 datapoints

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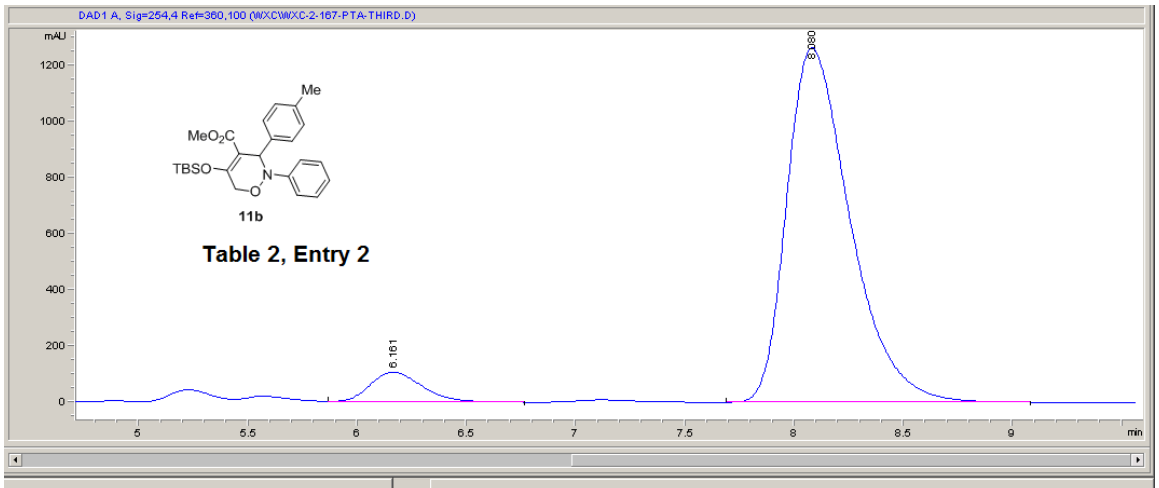

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Barcode	
Operator	wxc
Method	DEF_LC.M
Analysis Time	9.607 min
Sampling Rate	0.0067 min (0.402 sec), 1442 datapoints

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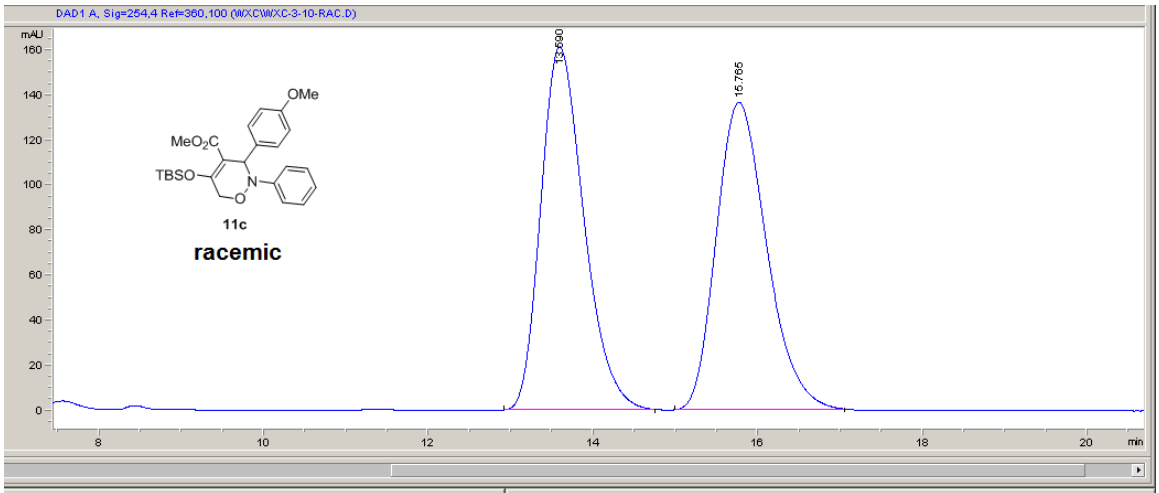

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Barcode	
Operator	wxc
Method	XXU.M
Analysis Time	21.613 min
Sampling Rate	0.0067 min (0.402 sec), 3243 datapoints

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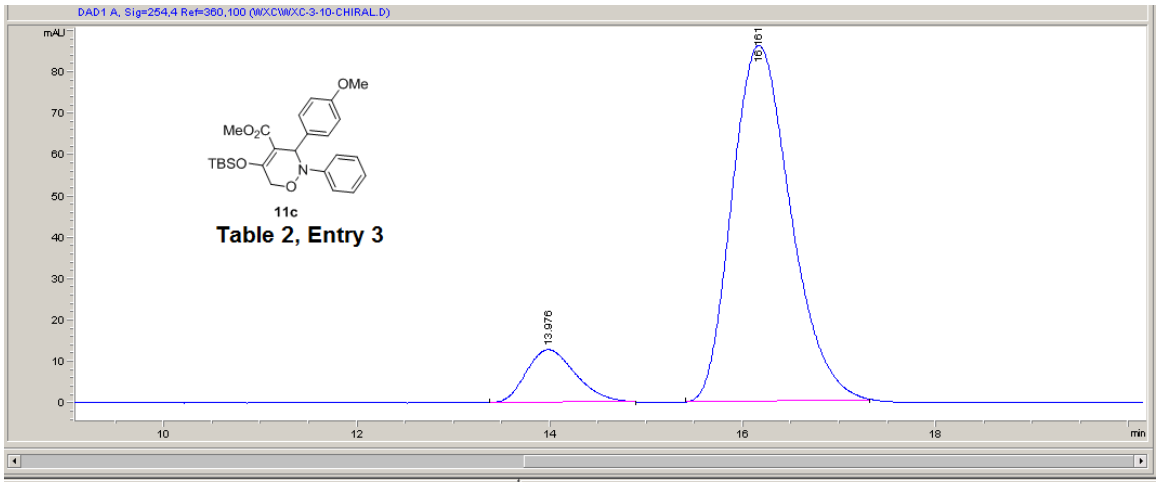

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Barcode	
Operator	wxc
Method	XXU.M
Analysis Time	20.193 min
Sampling Rate	0.0067 min (0.402 sec), 3030 datapoints

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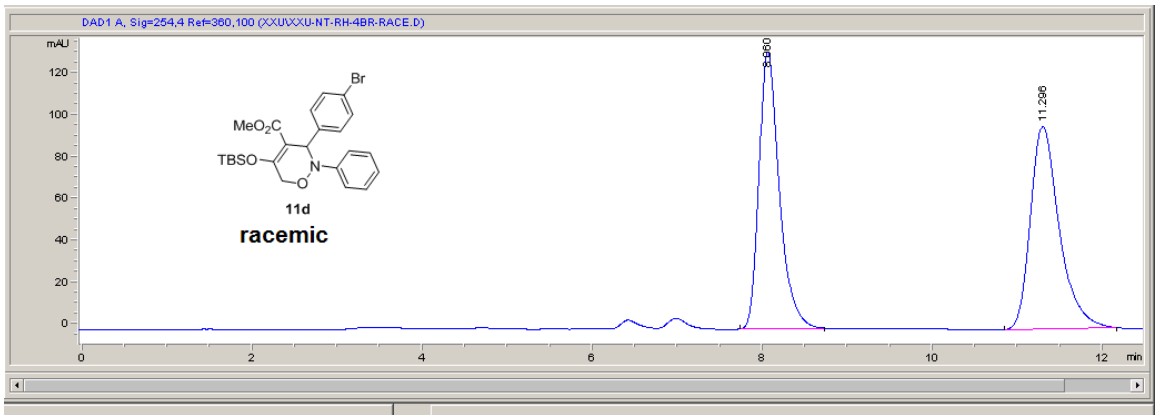

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Analysis Time	13.3 min
Sampling Rate	0.0067 min (0.402 sec), 1996 datapoints

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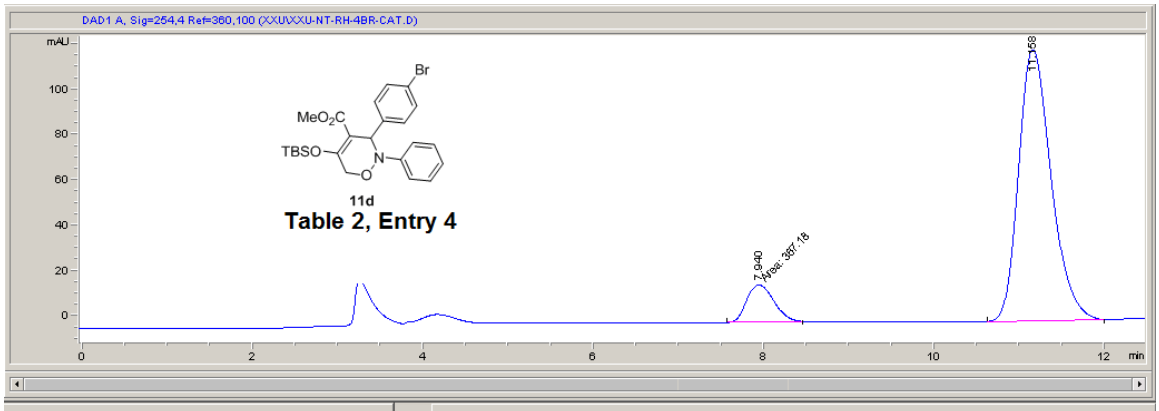
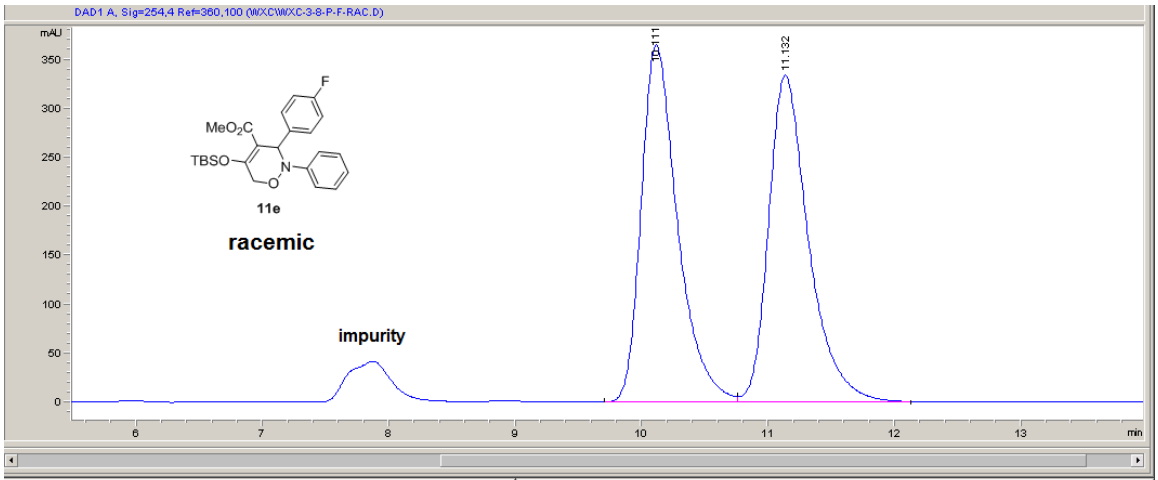
1	8.06	2212.2	132.6	0.2526	48.956	0.692
2	11.296	2306.6	97.2	0.357	51.044	0.687



File Information	
LC-File	XXU-NT-RH-4BR-CAT.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	03-Jun-11, 15:28:02
Sample	xxu-nt-Rh-4Br-Cat
Sample Info	97:3
Barcode	
Operator	xxu
Method	DEF_LC.M
Analysis Time	12.52 min
Sampling Rate	0.0067 min (0.402 sec), 1879 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.94	367.2	16.4	0.3721	10.300	0.771
2	11.158	3197.8	119.8	0.4093	89.700	0.738

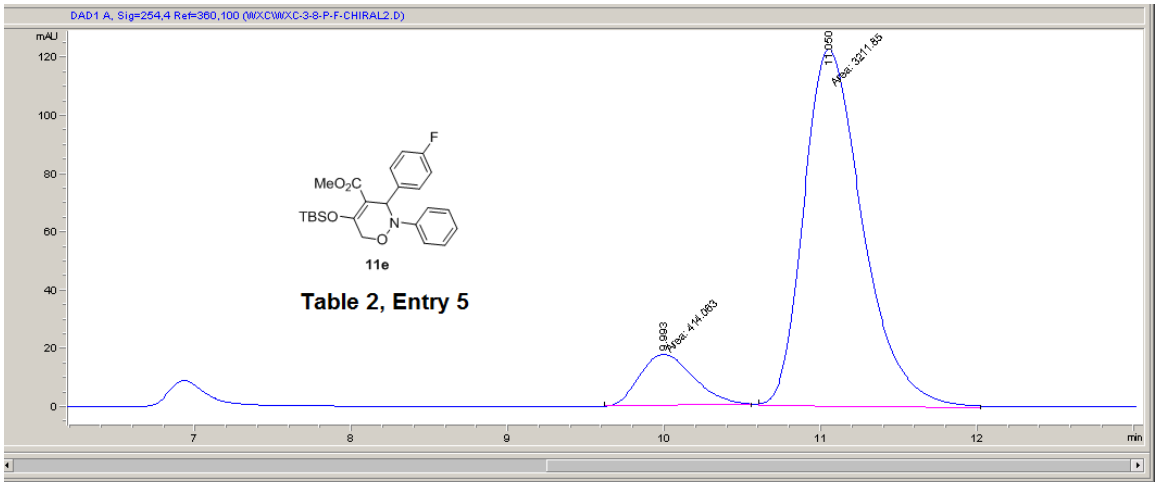


11e

racemic

File Information	
LC-File	WXC-3-8-P-F-RAC.D
File Path	C:\CHEM32\1\DATA\WXC\
Date	21-Jul-11, 16:27:20
Sample	WXC-3-8-P-F-rac.D
Sample Info	Ad-H, 97:3, 0.8 ml/min
Barcode	
Operator	wxc
Method	XXU.M
Analysis Time	14.593 min
Sampling Rate	0.0067 min (0.402 sec), 2190 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	10.111	7292.1	364.8	0.3012	49.786	0.658
2	11.132	7354.8	333.9	0.333	50.214	0.664

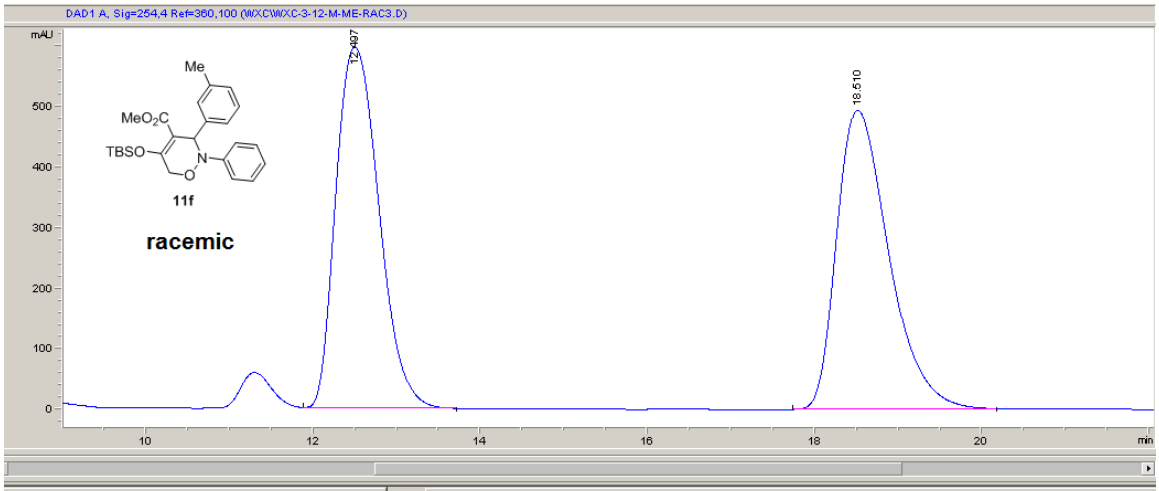


11e

Table 2, Entry 5

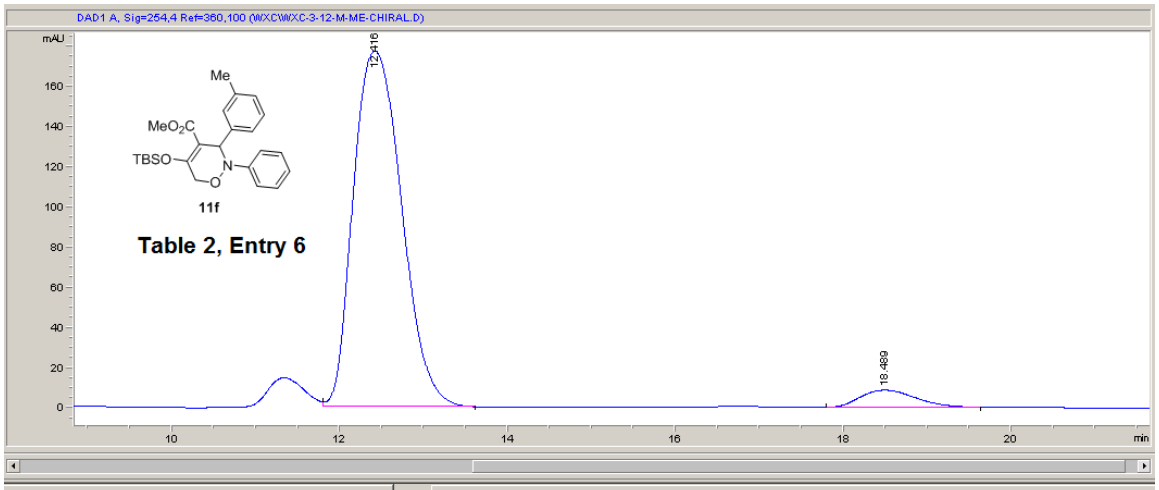
File Information	
LC-File	WXC-3-8-P-F-CHIRAL2.D
File Path	C:\CHEM32\1\DATA\WXC\
Date	21-Jul-11, 16:43:45
Sample	WXC-3-8-P-F-chiral2.D
Sample Info	Ad-H, 97:3, 0.8 ml/min
Barcode	
Operator	wxc
Method	XXU.M
Analysis Time	13.053 min
Sampling Rate	0.0067 min (0.402 sec), 1959 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.993	414.1	17.4	0.3974	11.420	0.765
2	11.05	3211.9	122.8	0.4358	88.580	0.715



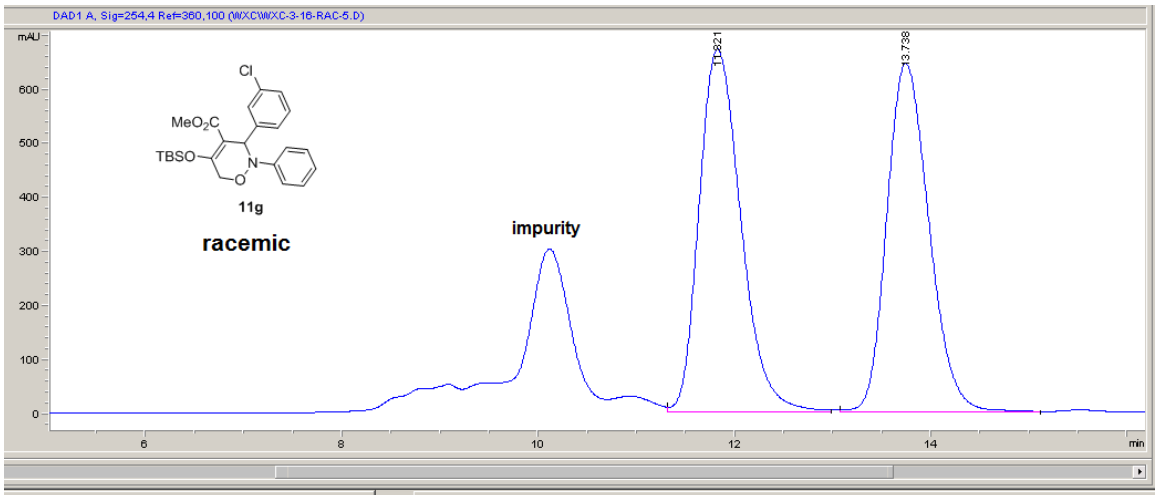
File Information	
LC-File	WXC-3-12-M-ME-RAC3.D
File Path	C:\CHEM32\1\DATA\WXC\
Date	28-Jul-11, 15:44:18
Sample	WXC-3-12-m-Me-rac3
Sample Info	98:2,0.5ml/min, ad-h
Barcode	
Operator	wxc
Method	XXU.M
Analysis Time	28.02 min
Sampling Rate	0.0067 min (0.402 sec), 4204 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	12.497	21367.3	596	0.5743	50.002	0.748
2	18.51	21365.5	492.9	0.6697	49.998	0.628



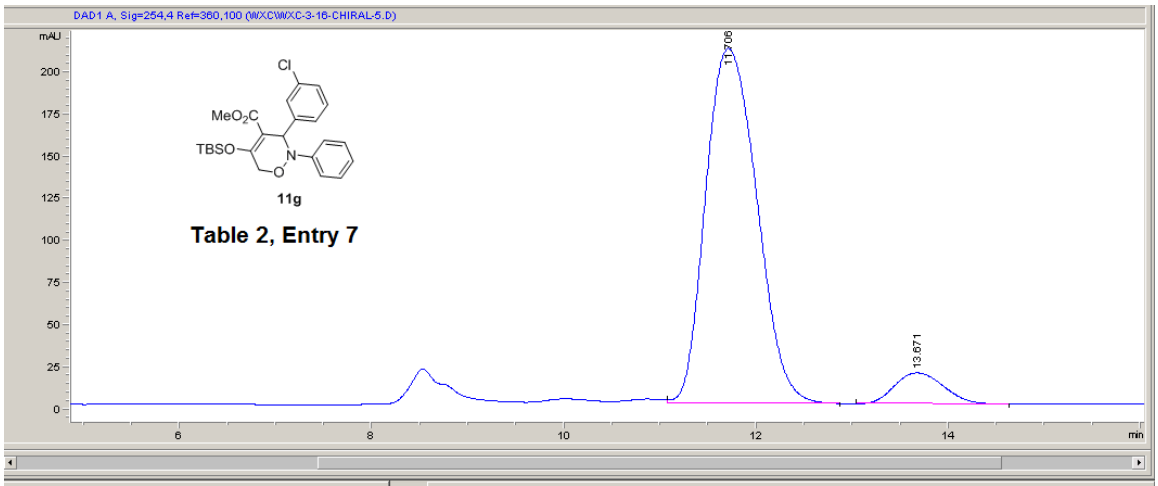
File Information	
LC-File	WXC-3-12-M-ME-CHIRAL.D
File Path	C:\CHEM32\1\DATA\WXC\
Date	28-Jul-11, 15:16:54
Sample	WXC-3-12-m-Me-chiral
Sample Info	98:2,0.5ml/min, ad-h
Barcode	
Operator	wxc
Method	XXU.M
Analysis Time	21.92 min
Sampling Rate	0.0067 min (0.402 sec), 3289 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	12.416	7095.4	177.3	0.647	94.731	0.769
2	18.489	394.6	8.5	0.6509	5.269	0.73



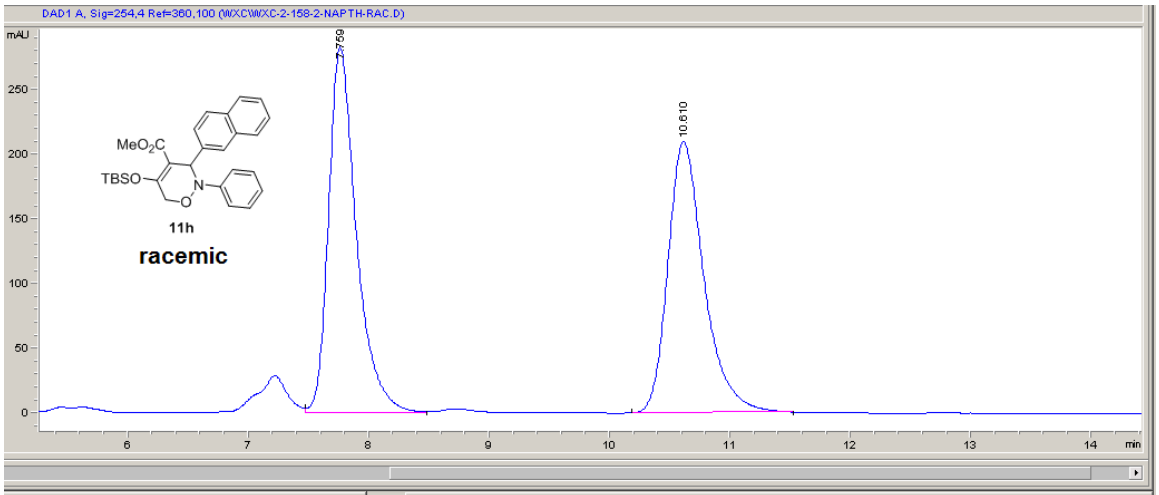
File Information	
LC-File	WXC-3-16-RAC-5.D
File Path	C:\CHEM32\1\DATA\WXC\
Date	04-Aug-11, 19:06:38
Sample	WXC-3-16-rac5
Sample Info	od-h, 0.4ml/min, 254 nm, 98:2,rac-4 is actually the chi
	ral sample with 85% ee
Barcode	
Operator	wxc
Method	XXU.M
Analysis Time	20.54 min
ampling Rate	0.0067 min (0.402 sec), 3082 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	11.821	19951.4	671.9	0.4664	50.764	0.735
2	13.738	19350.5	645.6	0.4697	49.236	0.768



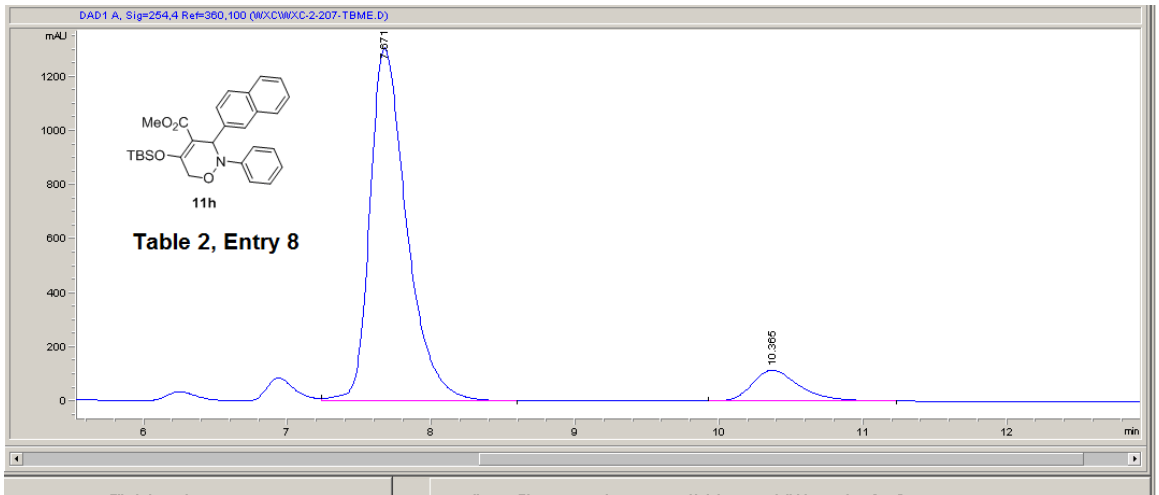
File Information	
LC-File	WXC-3-16-CHIRAL-5.D
File Path	C:\CHEM32\1\DATA\WXC\
Date	04-Aug-11, 19:28:42
Sample	WXC-3-16-chiral5
Sample Info	od-h, 0.4ml/min, 254 nm, 98:2
Barcode	
Operator	wxc
Method	XXU.M
Analysis Time	18.193 min
Sampling Rate	0.0067 min (0.402 sec), 2730 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	11.706	7796.5	210.6	0.6059	92.260	0.762
2	13.671	654.1	18.4	0.5583	7.740	0.819



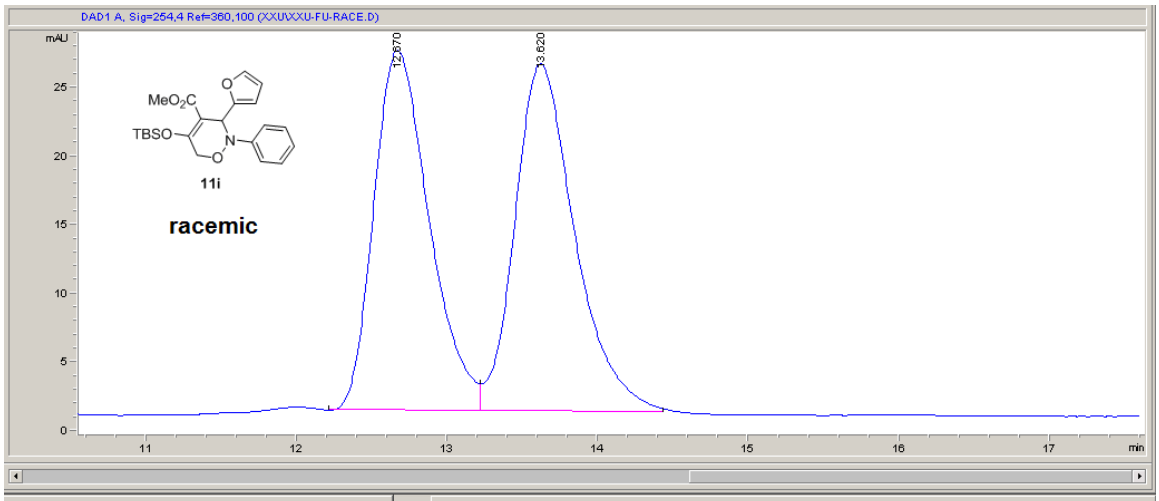
File Information	
LC-File	WXC-2-158-2-NAPTH-RAC.D
File Path	C:\CHEM32\1\DATA\WXC\
Date	03-May-11, 16:03:09
Sample	wxc-2-158-2-napth-rac
Sample Info	95:5
Barcode	
Operator	wxc
Method	DEF_LC.M
Analysis Time	14.947 min
Sampling Rate	0.0067 min (0.402 sec), 2243 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.759	4547.6	282.8	0.2396	50.921	0.658
2	10.61	4383	209.8	0.3157	49.079	0.706



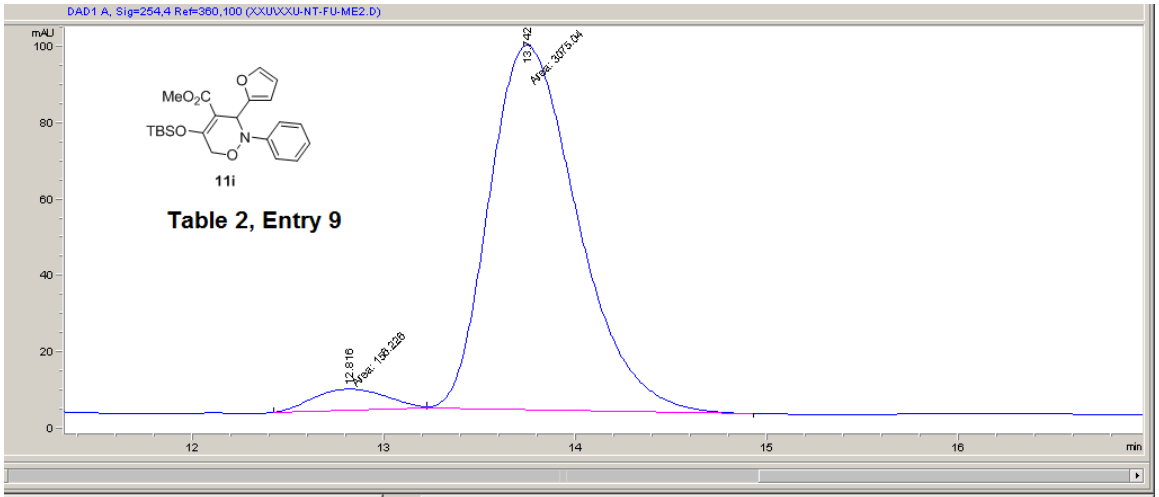
File Information	
LC-File	WXC-2-207-TBME.D
File Path	C:\CHEM32\1\DATA\WXC\
Date	07-Jul-11, 16:04:24
Sample	wxc-2-207-tbme
Sample Info	95:5, 1 ml/min, ad-H
Barcode	
Operator	wxc
Method	XXU.M
Analysis Time	13.5 min
Sampling Rate	0.0067 min (0.402 sec), 2026 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.671	23139	1305.4	0.2668	89.832	0.634
2	10.365	2619.2	114.7	0.3444	10.168	0.685



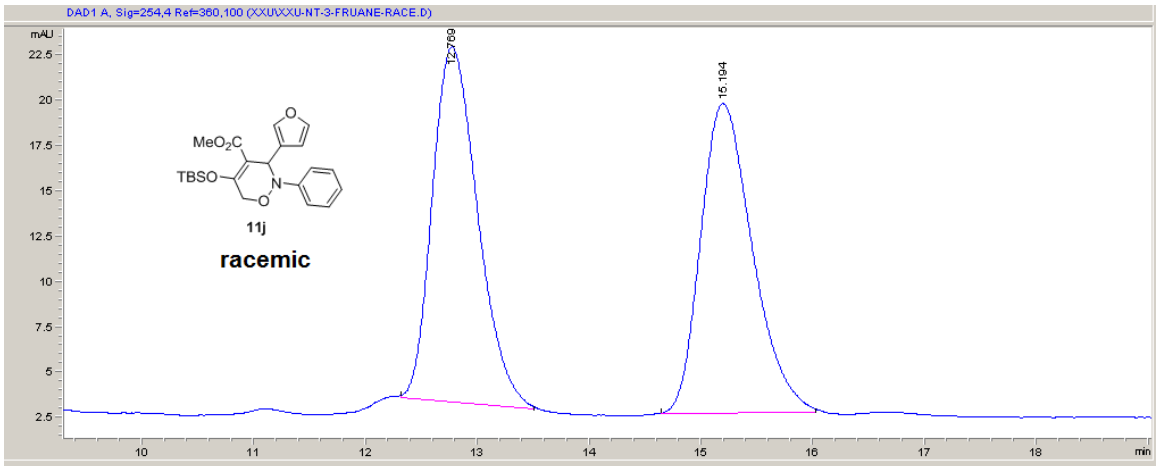
File Information	
LC-File	XXU-FU-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	07-Jul-11, 13:13:36
Sample	xxu-fu-race
Sample Info	93:7, 0.5 ml/min, ad-H
Barcode	
Operator	xxu
Method	XXU.M
Analysis Time	17.64 min
Sampling Rate	0.0067 min (0.402 sec), 2647 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	12.67	671	26.2	0.3945	48.898	0.706
2	13.62	701.3	25.3	0.4171	51.102	0.712



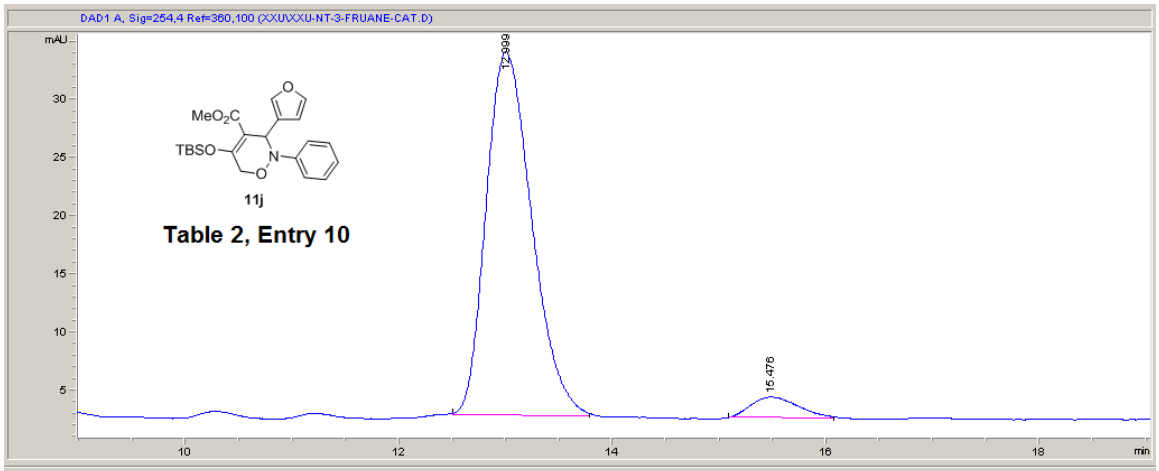
File Information	
LC-File	XXU-NT-FU-ME2.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	06-Jul-11, 14:45:08
Sample	xxu-Nt-Fu-Me2
Sample Info	97:3, 0.5ml/min, ad-h
Barcode	
Operator	xxu
Method	XXU.M
Analysis Time	17 min
Sampling Rate	0.0067 min (0.402 sec), 2551 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	12.816	156.2	5.7	0.456	4.835	0.996
2	13.742	3075	95.5	0.5366	95.165	0.721



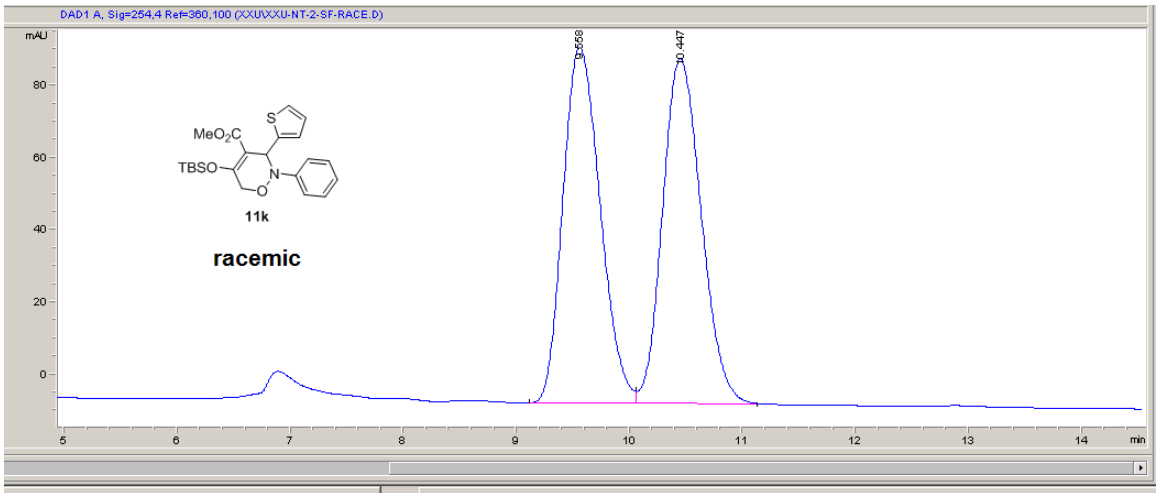
File Information	
LC-File	XXU-NT-3-FRUANE-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	13-Jul-11, 16:07:52
Sample	xxu-Nt-3-fruane-race
Sample Info	97:3, 0.5 ml/min, ad-h
Barcode	
Operator	xxu
Method	XXU.M
Analysis Time	19.233 min
Sampling Rate	0.0067 min (0.402 sec), 2886 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	12.769	555.4	19.6	0.434	50.216	0.725
2	15.194	550.6	17.1	0.4919	49.784	0.721



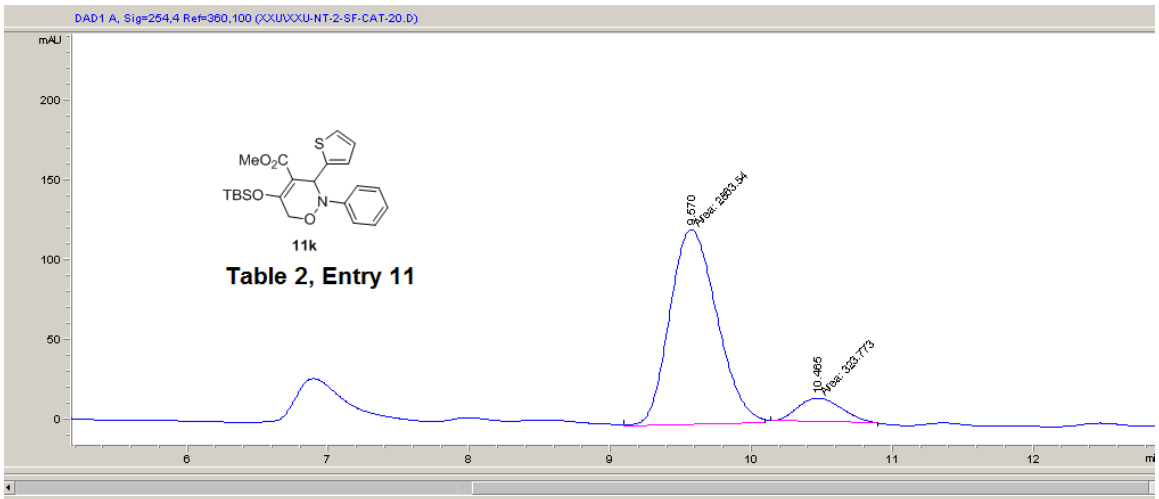
File Information	
LC-File	XXU-NT-3-FRUANE-CAT.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	13-Jul-11, 16:28:05
Sample	xxu-Nt-3-fruane-cat
Sample Info	97:3, 0.5 ml/min, ad-h
Barcode	
Operator	xxu
Method	XXU.M
Analysis Time	36.587 min
Sampling Rate	0.0067 min (0.402 sec), 5489 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	12.999	931.8	31.2	0.4659	94.259	0.735
2	15.476	56.8	1.8	0.3745	5.741	0.694



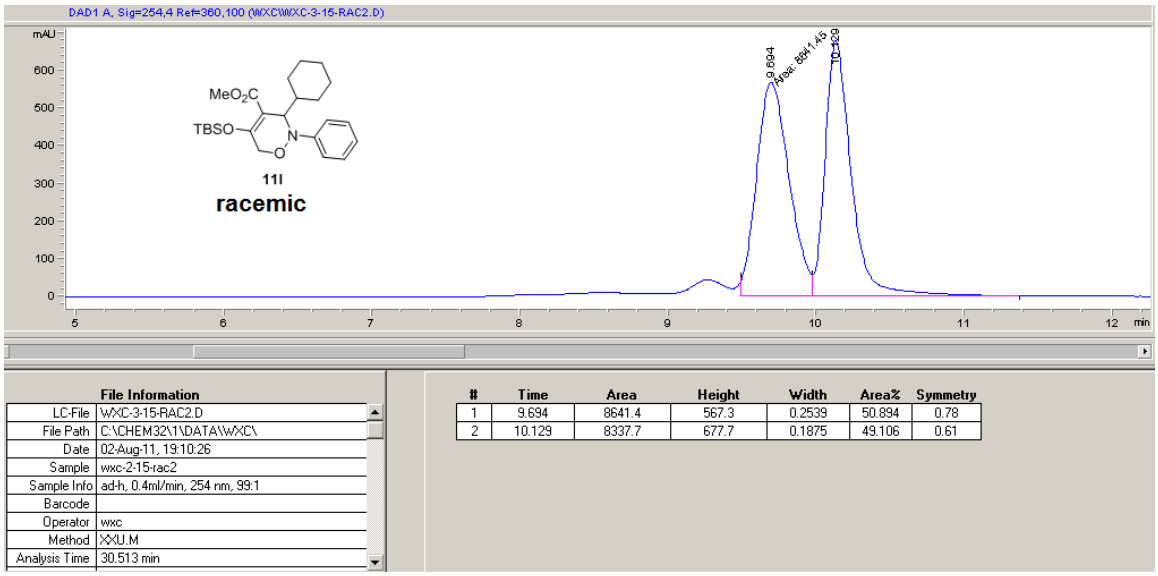
File Information	
LC-File	XXU-NT-2-SF-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	14-Jul-11, 17:00:51
Sample	xxu-nt-2-sf-race
Sample Info	97:3, 0.5 ml/min, OD-H,chiral
Barcode	
Operator	xxu
Method	XXU.M
Analysis Time	14.573 min
Sampling Rate	0.0067 min (0.402 sec), 2187 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.558	2260	98.5	0.3618	49.827	0.781
2	10.447	2275.7	95.6	0.3756	50.173	0.808



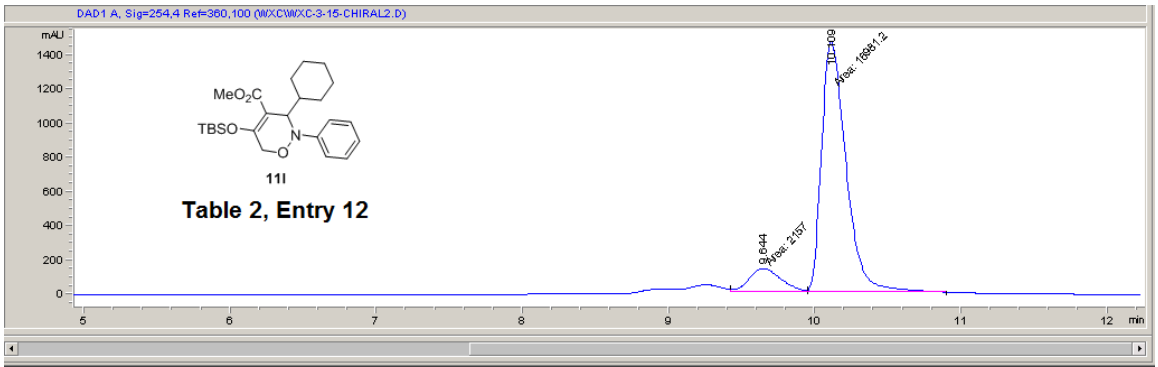
File Information	
LC-File	XXU-NT-2-SF-CAT-20.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	14-Jul-11, 16:46:45
Sample	xxu-nt-2-sf-cat-20
Sample Info	97:3, 0.5 ml/min, OD-H,chiral
Barcode	
Operator	xxu
Method	XXU.M
Analysis Time	12.953 min
Sampling Rate	0.0067 min (0.402 sec), 1944 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.57	2863.5	122.5	0.3894	89.842	0.815
2	10.465	323.8	14.9	0.3614	10.158	0.831



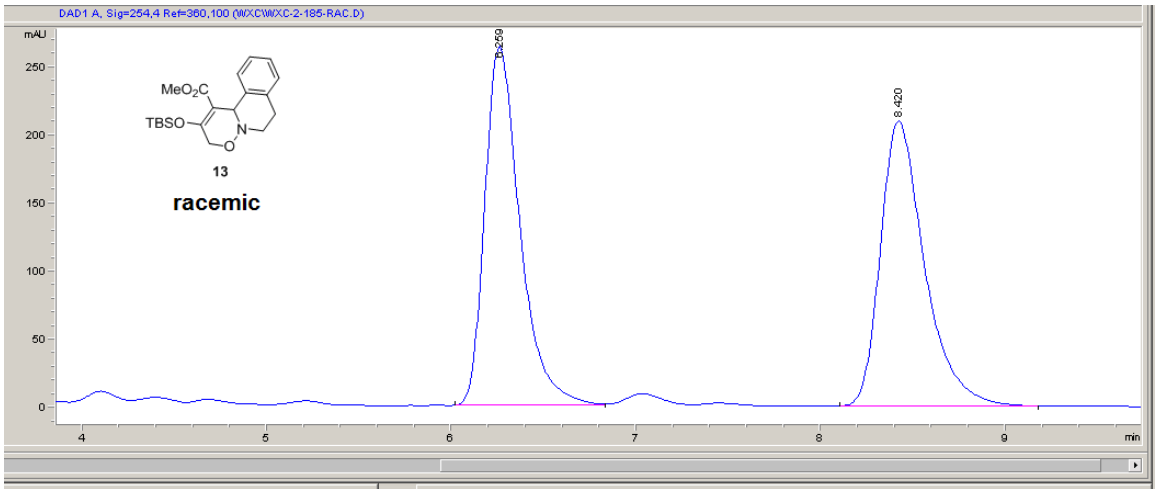
File Information	
LC-File	WXC-3-15-RAC2.D
File Path	C:\CHEM32\1\DATA\WXC\
Date	02-Aug-11, 19:10:26
Sample	wxc-2-15-rac2
Sample Info	ad-h, 0.4ml/min, 254 nm, 99:1
Barcode	
Operator	wxc
Method	XXU.M
Analysis Time	30.513 min

#	Time	Area	Height	Width	Area%	Symmetry
1	9.694	8641.4	567.3	0.2539	50.894	0.78
2	10.129	8337.7	677.7	0.1875	49.106	0.61



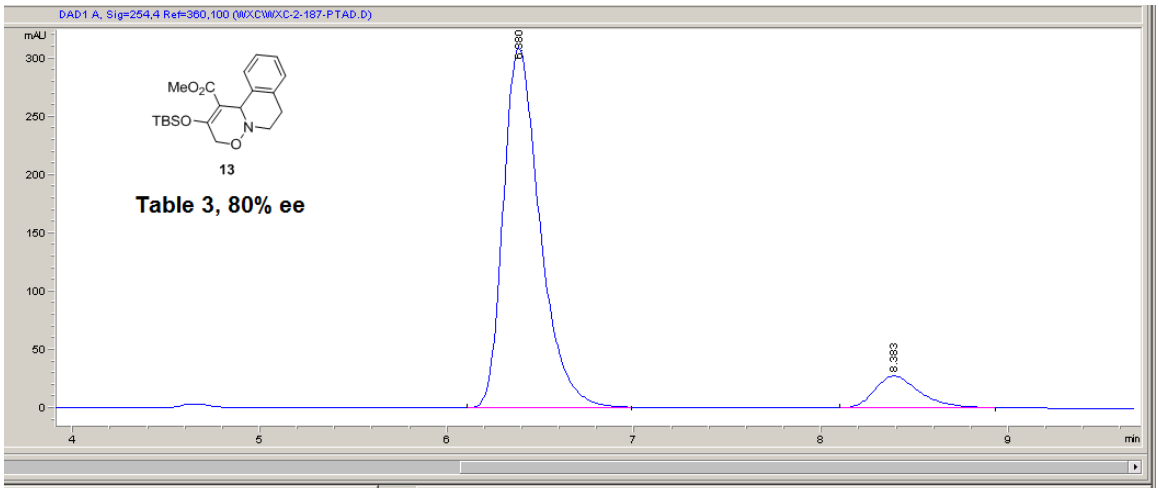
File Information	
LC-File	WXC-3-15-CHIRAL2.D
File Path	C:\CHEM32\1\DATA\WXC\
Date	02-Aug-11, 19:53:00
Sample	wxc-2-15-chiral2
Sample Info	ad-h, 0.4ml/min, 254 nm, 99:1
Barcode	
Operator	wxc
Method	XXU.M
Analysis Time	12.273 min
Sampling Rate	0.0067 min (0.402 sec), 1842 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.644	2157	139.3	0.2581	11.271	0.779
2	10.109	16981.2	1464.4	0.1933	88.729	0.613



File Information	
LC-File	WXC-2-185-RAC.D
File Path	C:\CHEM32\1\DATA\WXC\
Date	08-Jun-11, 20:05:17
Sample	wxc-2-185-rac
Sample Info	97:3
Barcode	
Operator	wxc
Method	DEF_LC.M
Analysis Time	10.013 min
Sampling Rate	0.0067 min (0.402 sec), 1503 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.259	3502.3	263.6	0.203	50.164	0.655
2	8.42	3479.5	209.4	0.2519	49.836	0.651



File Information	
LC-File	WXC-2-187-PTAD.D
File Path	C:\CHEM32\1\DATA\WXC\
Date	10-Jun-11, 16:19:48
Sample	wxc-2-187-ptad
Sample Info	97:3
Barcode	
Operator	wxc
Method	XXU.M
Analysis Time	9.707 min
Sampling Rate	0.0067 min (0.402 sec), 1457 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.38	4202	309.1	0.2066	90.072	0.67
2	8.383	463.2	27.5	0.2543	9.928	0.678