Electronic Supplementary Material (ESI) for Chemical Communications

A donor-acceptor cyclopropene as a dipole source for a silver(I) catalyzed asymmetric catalytic [3+3]-cycloaddition with nitrones

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Supporting Information

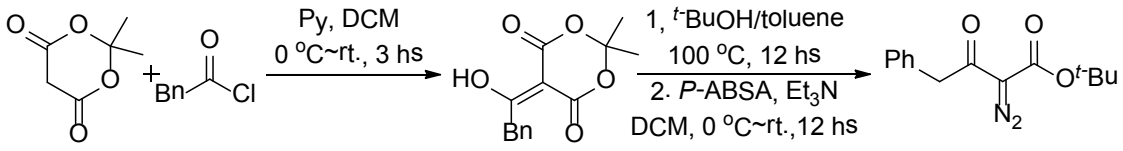
General Information

All reactions were performed in oven-dried (140 °C) glassware under an atmosphere of dry N_2. Dichloromethane (DCM) was passed through a solvent column prior to use and was kept over 3 Å molecular sieves. Thin layer chromatography (TLC) was carried out using EM Science silica gel 60 F254 plates. The developed chromatogram was analyzed by a UV lamp (254 nm). Liquid chromatography was performed using flash chromatography of the indicated system on silica gel (230-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 400 MHz spectrometer; chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (*J*) are given in Hertz. The peak information is described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. Enantioselectivity was determined on an Agilent 1200 Series HPLC instrument using Daicel Chiralcel IB-3, IC-3, OD-H and IA columns. Optical rotations were recorded on a JASCO DIP-1000 digital polarimeter. High-resolution mass spectra (HRMS) were performed on a TOF-CS mass spectrometer using CsI as the standard.

Materials

Rh_2(*S*-PTPA)$_4$ was prepared according to the literature procedure.[1] Rh_2(*S*-DOSP)$_4$ was purchased from Strem Chemicals. $AgSbF_6$ and (*S*)-^{t}BuBox were purchased from Sigma Aldrich. Enoldiazoacetates **1**[2] and nitrones **2**[3] were prepared according to the literature procedures.

General Procedure for the Preparation of Enoldiazoacetate 1c.[2e]

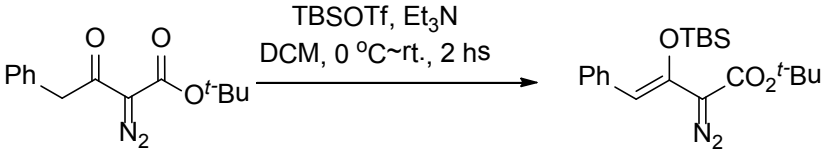


S-1 **S-2**

2-Phenylacetyl chloride (32 g, 0.21 mol) was added slowly over 1 h to a stirred solution of 2,2-dimethyl-1,3-dioxane-4,6-dione (30 g, 0.21 mol) and pyridine (33 g, 0.42 mol) in dichloromethane (150 mL) at 0 °C. Stirring was continued for another 1 h under this

condition and then at room temperature for 2 h (the reaction mixture tuned dark red during this time). After quenching the reaction with HCl (120 mL, 2M), the organic phase was separated: and the aqueous phase was extracted with DCM (50 mL). The combined organic phase was washed with HCl (100 mL, 2M) and diluted saturated brine (100 mL). The organic layer was dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting mixture was purified by crystallization in methanol (100 mL), and the pure product **S-1** was collected as a white solid by filtration and washed with ice-cold methanol (38 g, 68% yield).

Intermediate **S-1** (13 g, 50 mmol) was dissolved in *tert*-butyl alcohol (7.4 g, 100 mmol) and toluene (60 mL), and the reaction mixture was refluxed at 110 ℃ overnight. Then the solvent was removed under reduced pressure, and the reaction mixture was purified by flash column chromatography on silica gel (eluent: hexanes/EtOAc = 90:10 to 70:30). The collected product was dissolved in acetonitrile (150 mL), *p*-ABSA (4-Acetamidobenzenesulfonyl azide, 14.4 g, 60 mmol) and Et_3N (11 mL, 75 mmol) were added in sequence at 0 ℃, then the reaction mixture was slowly warmed to room temperature and stirred overnight. The reaction was quenched with saturated aqueous ammonium chloride solution (100 mL), and the resulting mixture was diluted by ether (200 mL). The separated organic phase was washed with saturated brine (100 mL X 3) and dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The resulting mixture was purified by flash column chromatography on silica gel (eluent: hexanes/EtOAc = 90:10 to 80:20) to give pure diazo compound **S-2** as a pale yellow oil (11 g, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36-7.29 (comp, 5H), 4.22 (s, 2H), 1.58 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 190.7, 160.5, 134.4, 129.8, 128.6, 127.1, 83.4, 45.8, 28.4).



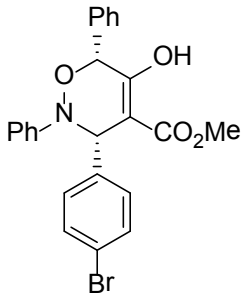
S-2 **1c**

Triethylamine (0.7 mL, 5.0 mmol) was added to a stirring solution of *tert*-butyl 2-diazo-3-oxo-4-phenylbutanoate **S-2** (0.70 g, 3.0 mmol) in dichloromethane (10 mL) at 0 °C

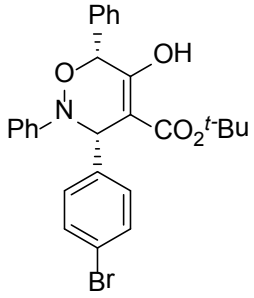
under N_2. *tert*-Butyldimethylsilyl trifluoromethanesulfonate (0.93 mL, 4.0 mmol) was then added over 10 min, and the mixture was stirred for 1 h at room temperature. After dilution with hexanes (20 mL), the organic phase was washed with dilute aqueous sodium bicarbonate (30 mL X 3). The organic layer was dried with anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The crude reaction mixture was purified by flash column chromatography on silica gel (eluent: hexanes/EtOAc = 100:0 to 90:10) to give the pure enoldiazoacetate **1c** as a red oil (0.90 g, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.52 (d, J = 7.3 Hz, 2H), 7.35-7.24 (m, 2H), 7.24-7.01 (m, 1H), 6.39 (s, 1H), 1.57 (s, 9H), 0.98 (s, 9H), -0.04 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): 164.0, 136.7, 134.7, 129.2, 128.0, 126.2, 111.3, 82.3, 28.6, 26.0, 18. 3, -4.6).

General Procedure for the Rh(II)/Ag(I)-catalyzed Enantioselective Formal [3+3]-Cycloaddition of Enoldiazoacetates 1c with Nitrone 5.

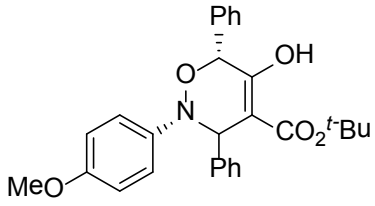
To an oven-dried flask containing a magnetic stirring bar, $Rh_2(OAc)_4$ (1.8 mg 2.0 mol%) in DCM (1.0 mL), was added enoldiazoacetates **1** (90 mg, 0.24 mmol) in DCM (0.5 mL) over 10 min via a syringe pump at room temperature. The reaction mixture was stirred for another 20 min, during which time the diazo compound converted to the cyclopropene (the color of the reaction mixture turned back to green), then the flask was placed in a dry-ice bath (- 78 ℃), and nitrone **2** (0.20 mmol) was added at this temperature. The $AgSbF_6$/(*S*)-^{t}BuBox catalyst in DCM was then added slowly (10 mol% of $AgSbF_6$ + 12 mol% of (*S*)-^{t}BuBox in 0.5 mL DCM was stirred for 0.5 h before added to the reaction mixture). After stirring overnight at - 78 ℃, TBAF (2.0 mL, 1 M in THF) was added to the reaction solution followed by transfering the flask from the dry-ice bath to an ice bath (0 ℃); and stirring was continued for 10 min under this condition. The reaction mixture was purified by column chromatography on silica gel (eluent: hexanes:EtOAc = 100:0 to 90:10) to give the pure 3,6-dihydro-1,2-oxazine derivatives **7**.



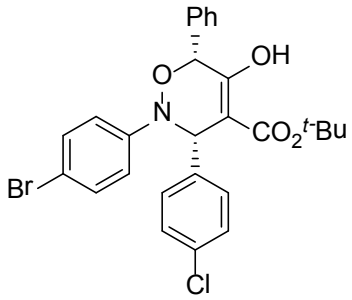
Methyl (3*S*,6*R*)-3-(4-Bromophenyl)-5-hydroxy-2,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (6a). 87% yield. 81% *ee*; HPLC conditions for determination of enantiomeric excess: IC-3 column, 254 nm, 0.7 mL/min, hexanes:IPA = 98:2, t_r = 9.8, 13.6 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.24 (bs, 1H), 7.57-6.98 (comp, 14H), 5.69 (d, *J* = 1.2 Hz, 1H), 5.49 (d, *J* = 1.2 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): 171.12, 171.06, 147.7, 136.9, 134.6, 131.14, 130.97, 129.5, 129.1, 128.91, 128.89, 123.1, 122.0, 117.6, 99.8, 80.1, 62.6, 52.2; HRMS (ESI) calculated for $C_{24}H_{21}BrNO_4$ $[M+H]^+$: 466.0649; found: 466.0661.



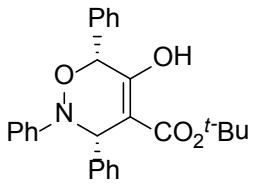
***tert*-Butyl (3*S*,6*R*)-3-(4-Bromophenyl)-5-hydroxy-2,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7a)**. 89% yield. $[\alpha]_D^{20}$ = +114° (c = 1, EtOAc); 93% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.5 mL/min, hexanes:IPA = 98:2, t_r = 8.9, 21.0 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.44 (bs, 1H), 7.60-6.95 (comp, 14H), 5.68 (d, *J* = 1.1 Hz, 1H), 5.40 (d, *J* = 1.1 Hz, 1H), 1.38 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.36, 170.34, 147.9, 137.3, 134.9, 131.2, 130.7, 129.4, 129.1, 128.82, 128.80, 123.0, 121.7, 117.7, 101.1, 82.8, 80.3, 63.4, 28.3; HRMS (ESI) calculated for $C_{27}H_{27}BrNO_4$ $[M+H]^+$: 508.1118; found: 508.1112.



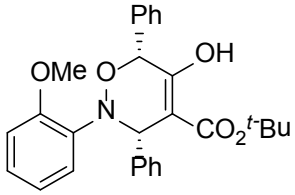
***tert*-Butyl (3*S*,6*R*)-5-Hydroxy-2-(4-methoxyphenyl)-3,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7b)**. 85% yield. 91% *ee*; HPLC conditions for determination of enantiomeric excess: IB-3 column, 254 nm, 0.7 mL/min, hexanes:IPA = 96:4, t_r = 6.6, 7.7 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.40 (bs, 1H), 7.63-6.71 (comp, 14H), 5.64 (s, 1H), 5.25 (s, 1H), 3.75 (s, 3H), 1.32 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.6, 170.1, 156.1, 141.6, 138.3, 135.5, 129.8, 129.2, 128.7, 127.54, 127.51, 120.7, 113.8, 101.7, 82.4, 80.1, 65.1, 55.6, 28.2; HRMS (ESI) calculated for $C_{28}H_{30}NO_5$ $[M+H]^+$: 460.2119; found: 460.2113.



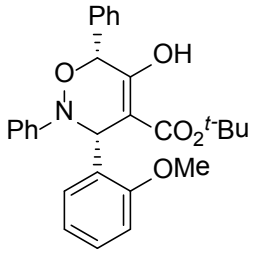
***tert*-Butyl (3*S*,6*R*)-2-(4-Bromophenyl)-3-(4-chlorophenyl)-5-hydroxy-6-phenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7c)**. 92% yield. Mp = 175-178 ℃. $[\alpha]_D^{20}$ = +208° (c = 1, EtOAc, with > 99.5% *ee* sample); 82% *ee* (>99.5% *ee* after recrystalization); HPLC conditions for determination of enantiomeric excess: IB-3 column, 254 nm, 0.7 mL/min, hexanes:IPA = 97:3, t_r = 6.2, 11.0 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.42 (bs, 1H), 7.58-21 (comp, 13H), 5.66 (d, *J* = 1.2 Hz, 1H), 5.33 (d, *J* = 1.2 Hz, 1H), 1.37 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.36, 170.34, 147.9, 137.3, 134.7, 131.2, 130.7, 129.3, 129.1, 128.82, 128.80, 123.0, 121.7, 117.7, 101.1, 82.8, 80.3, 63.4, 28.3; HRMS (ESI) calculated for $C_{27}H_{26}BrClNO_4$ $[M+H]^+$: 542.0729; found: 542.0733.



***tert*-Butyl (3*S*,6*R*)-5-Hydroxy-2,3,6-triphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7d)**. 93% yield. 90% *ee*; HPLC conditions for determination of enantiomeric excess: IB-3 column, 254 nm, 0.7 mL/min, hexanes:IPA = 97:3, t_r = 5.8, 7.1 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.43 (bs, 1H), 7.64-6.95 (comp, 15H), 5.69 (s, 1H), 5.45 (s, 1H), 1.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.6, 170.0, 148.1, 138.2, 135.1, 192.7, 192.28, 129.24, 128.77, 128.68, 128.0, 127.6, 122.7, 117.7, 101.5, 82.6, 80.1, 63.8, 28.2; HRMS (ESI) calculated for $C_{27}H_{28}NO_4$ $[M+H]^+$: 430.2013; found: 430.2011.

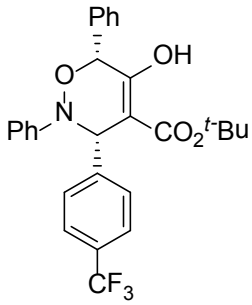


***tert*-Butyl (3*S*,6*R*)-5-Hydroxy-2-(2-methoxyphenyl)-3,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7e)**. 95% yield. 92% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.7 mL/min, hexanes:IPA = 98:2, t_r = 7.4, 8.4 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.36 (bs, 1H), 7.66-6.64 (comp, 14H), 5.79 (d, *J* = 1.5 Hz, 1H), 5.68 (d, *J* = 1.5 Hz, 1H), 4.04 (s, 3H), 1.29 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.60, 169.9, 149.0, 138.1, 137.2, 135.2, 129.5, 129.23, 129.20, 128.73, 128.72, 127.3, 124.5, 120.9, 120.2, 110.5, 101.6, 82.1, 81.2, 62.3, 55.8, 28.2; HRMS (ESI) calculated for $C_{28}H_{30}NO_5$ $[M+H]^+$: 460.2119; found: 460.2132.

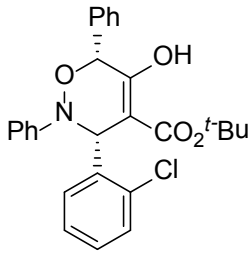


***tert*-Butyl (3*S*,6*R*)-5-Hydroxy-3-(2-methoxyphenyl)-2,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7f)**. 91% yield. 90% *ee*; HPLC

conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.7 mL/min, hexanes:IPA = 98:2, t_r = 6.4, 9.1 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.37 (bs, 1H), 7.67-6.67 (comp, 14H), 6.14 (s, 1H), 5.67 (s, 1H), 3.57 (s, 3H), 1.31 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.7, 169.6, 157.4, 148.1, 130.0, 129.9, 129.2, 129.2, 128.7, 128.6, 128.4, 128.1, 127.3, 122.5, 119.9, 117.8, 109.8, 101.6, 82.2, 79.2, 55.0, 28.1; HRMS (ESI) calculated for $C_{28}H_{30}NO_5$ $[M+H]^+$: 460.2119; found: 460.2137.

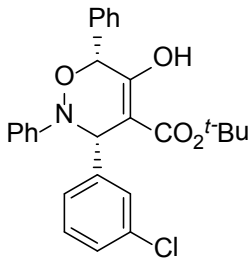


***tert*-Butyl (3*S*,6*R*)-5-Hydroxy-2,6-diphenyl-3-[4-(trifluoromethyl)phenyl]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7g)**. 88% yield. 90% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.7 mL/min, hexanes:IPA = 98:2, t_r = 6.2, 14.2 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.43 (bs, 1H), 7.59-6.95 (comp, 14H), 5.68 (d, *J* = 1.2 Hz, 1H), 5.47 (d, *J* = 1.2 Hz, 1H), 1.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.5, 170.3, 147.7, 142.4, 134.8, 129.9, 129.5, 129.2, 128.9, 125.7, 124.6 (q, *J* = 3.7 Hz), 123.1, 123.0, 117.6, 100.9, 83.0, 80.2, 63.4, 28.3; HRMS (ESI) calculated for $C_{28}H_{27}F_3NO_4$ $[M+H]^+$: 498.1887; found: 498.1876.

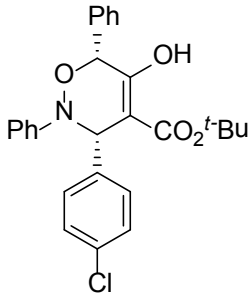


***tert*-Butyl (3*S*,6*R*)-3-(2-Chlorophenyl)-5-hydroxy-2,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7h)**. 77% yield. $[\alpha]_D^{20}$ = +160° (c = 1, EtOAc); 93% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.7 mL/min, hexanes:IPA = 98:2, t_r = 6.2, 11.8 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.48 (bs, 1H), 7.78-7.02 (comp, 14H), 6.08 (s, 1H), 5.63 (s, 1H),

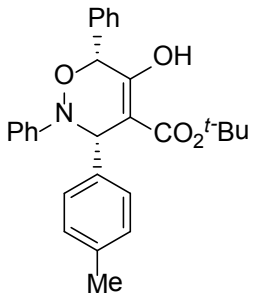
1.36 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.6, 170.0, 147.3, 136.7, 135.1, 130.6, 129.3, 129.1, 128.9, 128.77, 128.69, 126.3, 123.5, 118.7, 100.4, 82.9, 77.8, 58.1, 28.2; HRMS (ESI) calculated for $C_{27}H_{27}ClNO_4$ $[M+H]^+$: 464.1624; found: 464.1629.



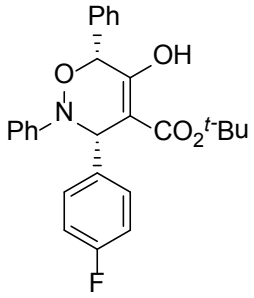
***tert*-Butyl (3*S*,6*R*)-3-(3-Chlorophenyl)-5-hydroxy-2,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7i)**. 80% yield. 90% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.7 mL/min, hexanes:IPA = 98:2, t_r = 6.3, 11.0 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.45 (bs, 1H), 7.62-6.96 (comp, 14H), 5.69 (d, *J* = 1.0 Hz, 1H), 5.41 (d, *J* = 1.0 Hz, 1H), 1.40 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.35, 170.34, 147.8, 140.5, 134.8, 133.5, 129.8, 129.4, 129.2, 128.89, 128.85, 128.8, 127.8, 127.7, 123.0, 117.6, 101.1, 82.9, 80.2, 63.3, 28.3; HRMS (ESI) calculated for $C_{27}H_{27}ClNO_4$ $[M+H]^+$: 464.1624; found: 464.1633.



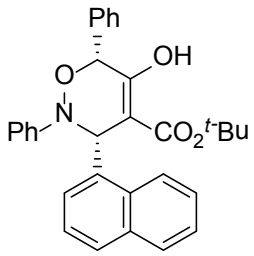
***tert*-Butyl (3*S*,6*R*)-3-(4-Chlorophenyl)-5-hydroxy-2,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7j)**. 91% yield. $[\alpha]_D^{20}$ = +119° (c = 1, EtOAc); 94% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.5 mL/min, hexanes:IPA = 98:2, t_r = 8.7, 20.0 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.45 (bs, 1H), 7.61-6.97 (comp, 14H), 5.70 (d, *J* = 1.1 Hz, 1H), 5.42 (d, *J* = 1.1 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.62, 170.57, 147.9, 136.8, 134.9, 133.4, 130.9, 129.4, 129.1, 128.82, 128.79, 127.8, 123.0, 117.7, 101.2, 82.8, 80.3, 63.4, 28.3; HRMS (ESI) calculated for $C_{27}H_{27}ClNO_4$ $[M+H]^+$: 464.1624; found: 464.1628.



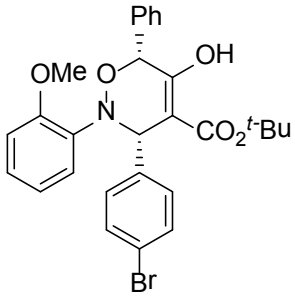
***tert*-Butyl (3*S*,6*R*)-5-Hydroxy-2,6-diphenyl-3-(p-tolyl)-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7k)**. 95% yield. 90% *ee*; HPLC conditions for determination of enantiomeric excess: IB-3 column, 254 nm, 0.5 mL/min, hexanes:IPA:EtOH = 98:1:1, t_r = 8.2, 10.1 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.40 (bs, 1H), 7.62-6.92 (comp, 14H), 5.66 (d, *J* = 0.8 Hz, 1H), 5.42 (d, *J* = 0.8 Hz, 1H), 2.29 (s, 3H), 1.37 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.6, 169.8, 148.2, 137.1, 135.21, 135.18, 129.5, 129.2, 128.75, 128.68, 128.3, 122.6, 117.6, 101.7, 82.5, 80.1, 63.3, 28.3, 21.3; HRMS (ESI) calculated for $C_{28}H_{30}NO_4$ $[M+H]^+$: 444.2170; found: 444.2177.



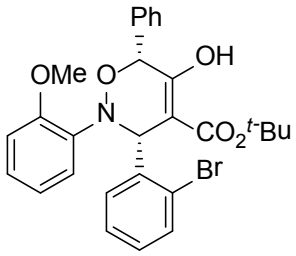
***tert*-Butyl (3*S*,6*R*)-3-(4-Fluorophenyl)-5-hydroxy-2,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7l)**. 92% yield. $[\alpha]_D^{20}$ = +191° (c = 1, EtOAc); 94% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.5 mL/min, hexanes:IPA = 98:2, t_r = 8.7, 20.0 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.46 (bs, 1H), 7.63-6.91 (comp, 14H), 5.72 (d, *J* = 0.9 Hz, 1H), 5.44 (d, *J* = 0.9 Hz, 1H), 1.39 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.4, 170.2, 162.4 (d, *J* = 245.7 Hz), 148.0, 135.0, 134.1 (d, *J* = 3.2 Hz), 131.1 (d, *J* = 8.0 Hz), 129.3, 129.2, 128.8, 128.7, 122.9, 177.8, 114.4 (d, *J* = 21.2 Hz), 101.5, 82.7, 80.3, 63.4, 28.2; HRMS (ESI) calculated for $C_{27}H_{27}FNO_4$ $[M+H]^+$: 448.1919; found: 448.1932.



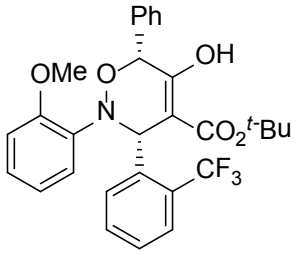
***tert*-Butyl (3*S*,6*R*)-5-Hydroxy-3-(naphthalen-1-yl)-2,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7m)**. 88% yield. $[\alpha]_D^{20}$ = +136° (c = 1, EtOAc); 92% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.5 mL/min, hexanes:IPA = 98:2, t_r = 9.2, 16.6 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.49 (bs, 1H), 7.83-6.91 (comp, 17H), 5.72 (s, 1H), 5.63 (s, 1H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.6, 170.1, 148.1, 136.0, 135.2, 133.04, 132.98, 129.3, 129.2, 128.9, 128.81, 128.77, 128,2, 127.7, 127.1, 125.9, 122.8, 117.6, 101.5, 82.7, 80.0, 63.6, 28.2; HRMS (ESI) calculated for $C_{31}H_{30}NO_4$ $[M+H]^+$: 480.2170; found: 480.2177.



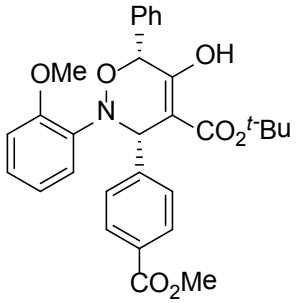
***tert*-Butyl (3*S*,6*R*)-3-(4-Bromophenyl)-5-hydroxy-2-(2-methoxyphenyl)-6-phenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7n)**. 85% yield. $[\alpha]_D^{20}$ = +165° (c = 1, EtOAc); 96% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.7 mL/min, hexanes:IPA = 98:2, t_r = 7.7, 10.6 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.55 (bs, 1H), 7.66-6.59 (comp, 13H), 6.10 (s, 1H), 5.83 (s, 1H), 4.00 (s, 3H), 1.38 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.7, 170.3, 137.6, 136.2, 135.0, 132.3, 131.5, 123.0, 129.2, 128.7, 126.5, 126.2, 125.7, 121.6, 119.9, 110.5, 102.3, 82.6, 81.3, 60.8, 55.8, 28.3; HRMS (ESI) calculated for $C_{28}H_{29}BrNO_5$ $[M+H]^+$: 538.1224; found: 538.1234.



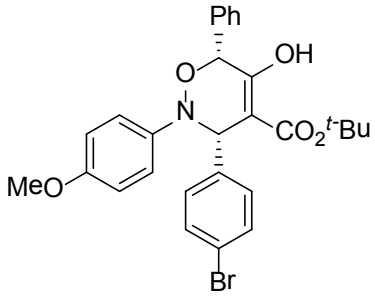
***tert*-Butyl (3*S*,6*R*)-3-(2-Bromophenyl)-5-hydroxy-2-(2-methoxyphenyl)-6-phenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7o)**. 75% yield. $[\alpha]_D^{20}$ = +212 ° (c = 1, EtOAc); 93% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.7 mL/min, hexanes:IPA = 98:2, t_r = 7.8, 9.8 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.34 (bs, 1H), 7.61-6.67 (comp, 13H), 5.75 (d, *J* = 1.5 Hz, 1H), 5.63 (d, *J* = 1.5 Hz, 1H), 4.02 (s, 3H), 1.31 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.4, 170.2, 148.9, 137.3, 136.8, 135.0, 131.0, 130.5, 129.3, 129.1, 128.8, 124.7, 121.5, 121.1, 120.1, 110.7, 101.2, 82.3, 81.2, 61.6, 55.9, 28.2; HRMS (ESI) calculated for $C_{28}H_{29}BrNO_5$ $[M+H]^+$: 538.1224; found: 538.1237.



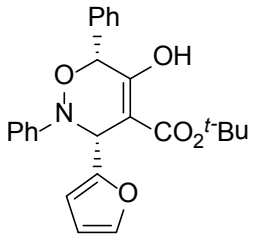
***tert*-Butyl (3*S*,6*R*)-5-Hydroxy-2-(2-methoxyphenyl)-6-phenyl-3-[2-(trifluoromethyl)phenyl]-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7p)**. 85% yield. $[\alpha]_D^{20}$ = +150 ° (c = 1, EtOAc); 94% *ee*; HPLC conditions for determination of enantiomeric excess: IB-3 column, 254 nm, 0.5 mL/min, hexanes:IPA = 98:2, t_r = 9.3, 11.6 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.79 (bs, 1H), 8.05 -6.55 (comp, 13H), 6.10 (s, 1H), 5.72 (s, 1H), 3.94 (s, 3H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.9, 170.7, 137.2, 135.8, 131.4, 130.7, 129.5, 129.24, 129.17, 129.1, 128.7, 128.4, 127.7, 126.5 (q, *J* = 5.5 Hz), 126.00, 123.3, 120.1, 111.0, 102.0, 82.9, 80.4, 57.3, 55.5, 28.2; HRMS (ESI) calculated for $C_{29}H_{29}F_3NO_5$ $[M+H]^+$: 528.1993; found: 528.1982.



***tert*-Butyl (3*S*,6*R*)-5-Hydroxy-3-[4-(methoxycarbonyl)phenyl]-2-(2-methoxyphenyl)-6-phenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7q)**. 82% yield. $[\alpha]_D^{20}$ = +181° (c = 1, EtOAc); 97% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.7 mL/min, hexanes:IPA = 98:2, t_r = 10.9, 13.3 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.37 (bs, 1H), 7.85-6.61 (comp, 13H), 5.78 (d, *J* = 1.4 Hz, 1H), 5.72 (d, *J* = 1.4 Hz, 1H), 4.04 (s, 3H), 3.90 (s, 3H), 1.28 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.4, 170.3, 167.3, 149.0, 143.6, 136.7, 135.0, 129.4, 129.3, 129.2, 129.1, 128.8, 128.7, 124.8, 121.0, 120.0, 110. 7, 101.1, 82.4, 81.2, 61.9, 55.9, 52.2, 28.2; HRMS (ESI) calculated for $C_{30}H_{32}NO_7$ $[M+H]^+$: 518.2174; found: 518.2136.



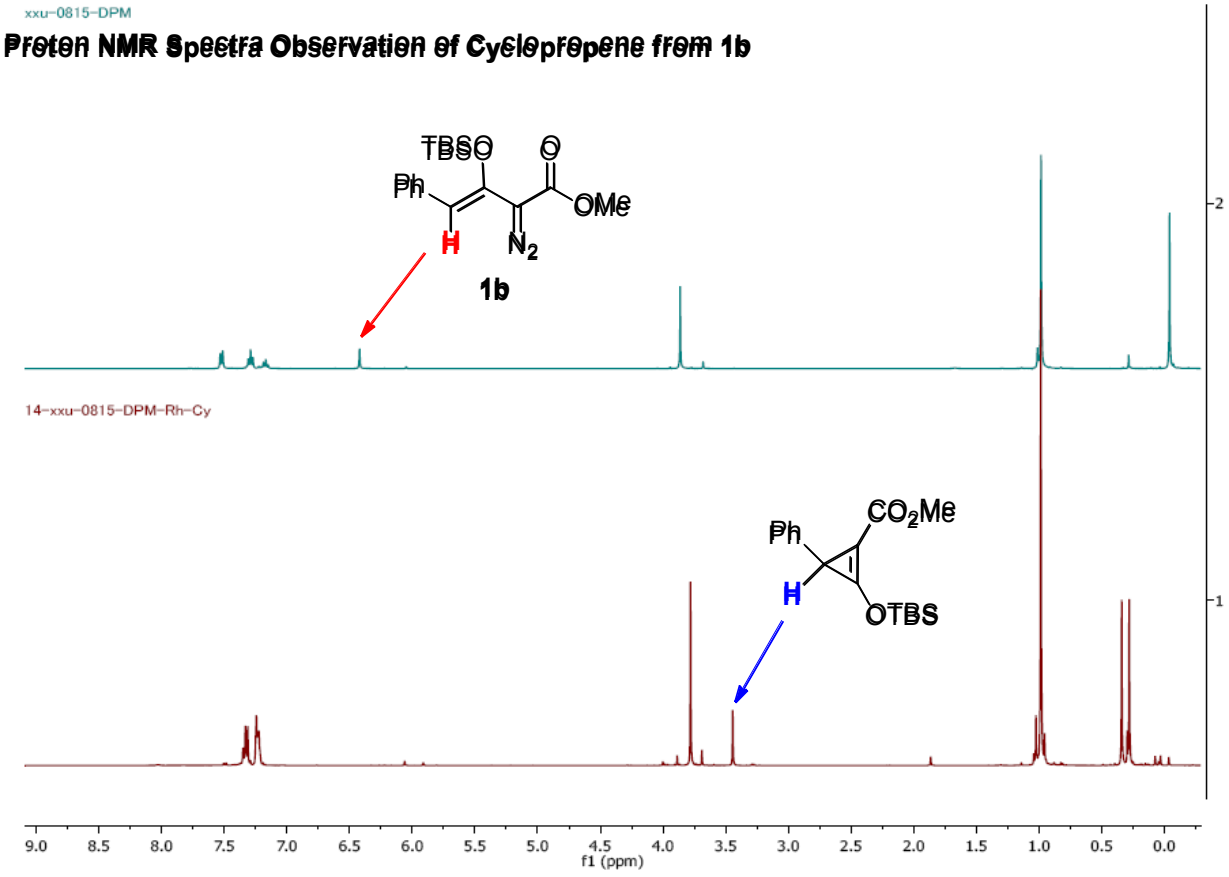
***tert*-Butyl (3*S*,6*R*)-3-(4-Bromophenyl)-5-hydroxy-2-(4-methoxyphenyl)-6-phenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7r)**. 71% yield. $[\alpha]_D^{20}$ = +130° (c = 1, EtOAc); 93% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.7 mL/min, hexanes:IPA = 98:2, t_r = 8.2, 18.5 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.42 (bs, 1H), 7.59-6.74 (comp, 13H), 5.64 (s, 1H), 5.20 (s, 1H), 3.76 (s, 3H), 1.34 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.43, 170.40, 156.1, 141.3, 137.4, 135.2, 131.4, 130.7, 129.2, 129.1, 128.8, 121.6, 120.3, 113.9, 101.3, 82.7, 80.2, 64.7, 55.6, 28.2; HRMS (ESI) calculated for $C_{28}H_{29}BrNO_5$ $[M+H]^+$: 538.1224; found: 538.1245.

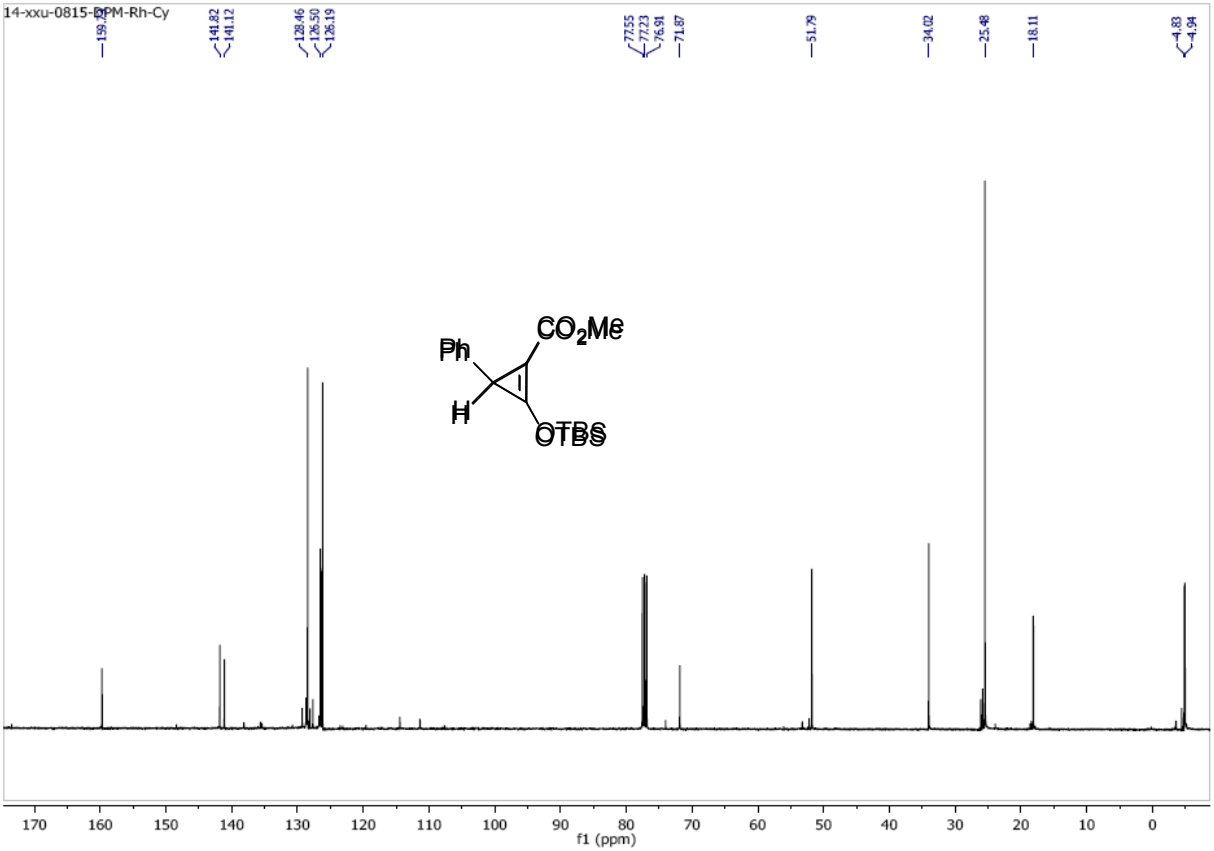


***tert*-Butyl (3*S*,6*R*)-3-(Furan-2-yl)-5-hydroxy-2,6-diphenyl-3,6-dihydro-2*H*-1,2-oxazine-4-carboxylate (7s)**. 95% yield. 79% *ee*; HPLC conditions for determination of enantiomeric excess: OD-H column, 254 nm, 0.7 mL/min, hexanes:IPA = 98:2, t_r = 6.5, 12.2 min. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 12.35 (bs, 1H), 7.57-6.97 (comp, 12H), 6.31-6.30 (m, 1H), 5.68 (d, *J* = 1.1 Hz, 1H), 5.45 (d, *J* = 1.1 Hz, 1H), 1.52 (s, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): 170.4, 170.1, 148.2, 142.2, 141.6, 135.1, 129.4, 129.3, 128.82, 128.81, 123.1, 122.5, 116.9, 111.3, 102.0, 82.8, 80.8, 55.5, 28.4; HRMS (ESI) calculated for $C_{25}H_{26}NO_5$ $[M+H]^+$: 420.1806; found: 420.1812.

References

1. (a) S. Hashimoto, N. Watanabe, T. Sato, M. Shiro and S. Ikegami, *Tetrahedron lett.*, 1993, **34**, 5109; (b) H. Tsutsui, T. Abe, S. Nakamura, M. Anada and S. Hashimoto, *Chem. Pharm. Bull.*, 2005, **53**, 1366; (c) S. Kitagaki, M. Anada, O. Kataoka, K. Matsuno, C. Umeda, N. Watanabe and S. Hashimoto, *J. Am. Chem. Soc.*, 1999, **121**, 1417.
2. For **1a**: (a) H. M. L. Davies, Z.-Q. Peng and J. H. Houser, *Tetrahedron Lett.*, 1994, **35**, 8939; (b) Y. Ueda, G. Roberge and V. Vinet, *Can. J. Chem.*, 1984, **62**, 2936; (c) H. M. L. Davies, G. Ahmed and M. R. Churchill, *J. Am. Chem. Soc.*, 1996, **118**, 10774; (d) K. Kundu and M. P. Doyle, *Tetrahedron: Asymmetry*, 2006, **17**, 574. For **1b** and **1c**: (e) Y. Qian, X. Xu, X. Wang, P. J. Zavalij, W. Hu and M. P. Doyle, *Angew. Chem. Int. Ed.*, 2012, **51**, 5900.
3. M. M. Lo and G. C. Fu, *J. Am. Chem. Soc.*, 2002, **124**, 4572.


xxu-0815-DPM
Proton NMR Spectra Observation of Cyclopropene from 1b
TBSO
O
Ph
OMe
H
N2
1b
14-xxu-0815-DPM-Rh-Cy
CO2Me
Ph
H
OTBS
f1 (ppm)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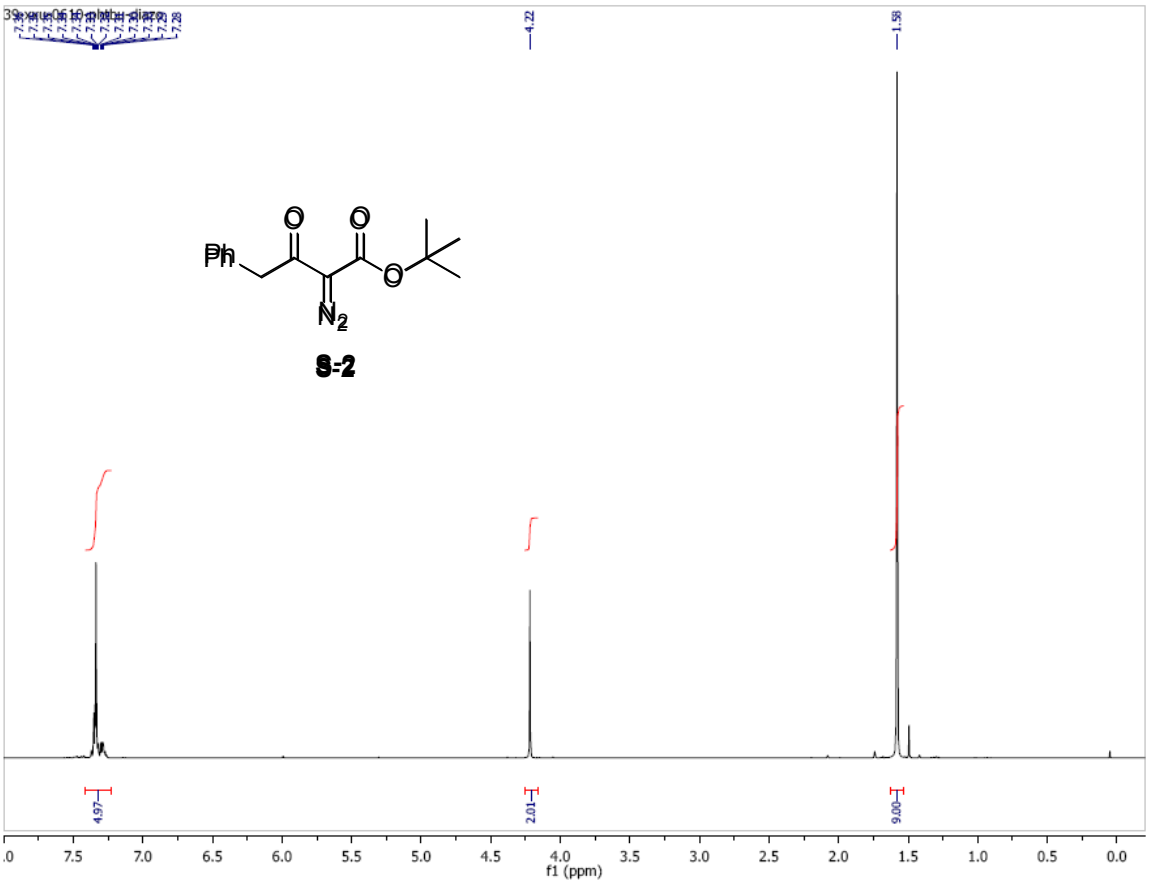
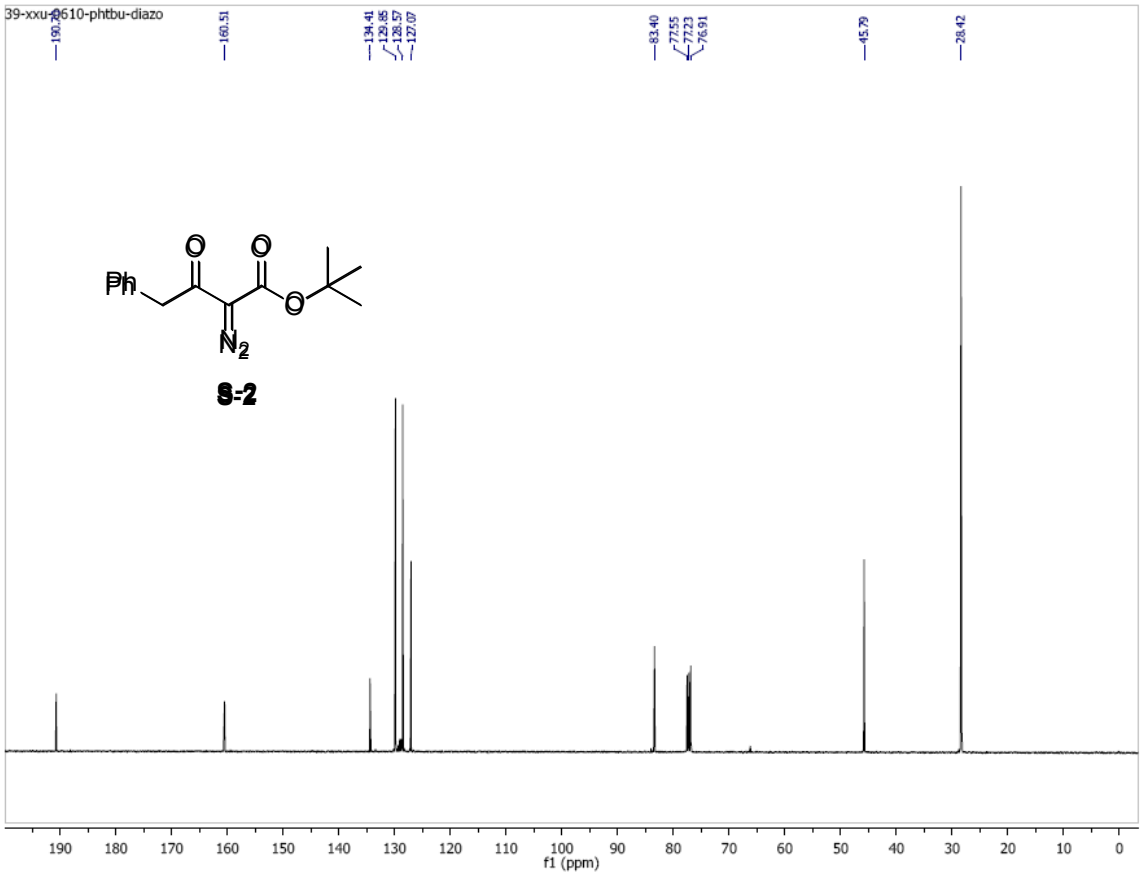
141.82
141.12
128.46
126.50
126.19
77.55
77.23
76.91
71.87
51.79
34.02
25.48
18.11
-4.83
-4.94
CO2Me
Ph
H
OTBS
f1 (ppm)


4.22
1.58
4.97
2.01
9.00
f1 (ppm)

S-2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127.07
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77.23
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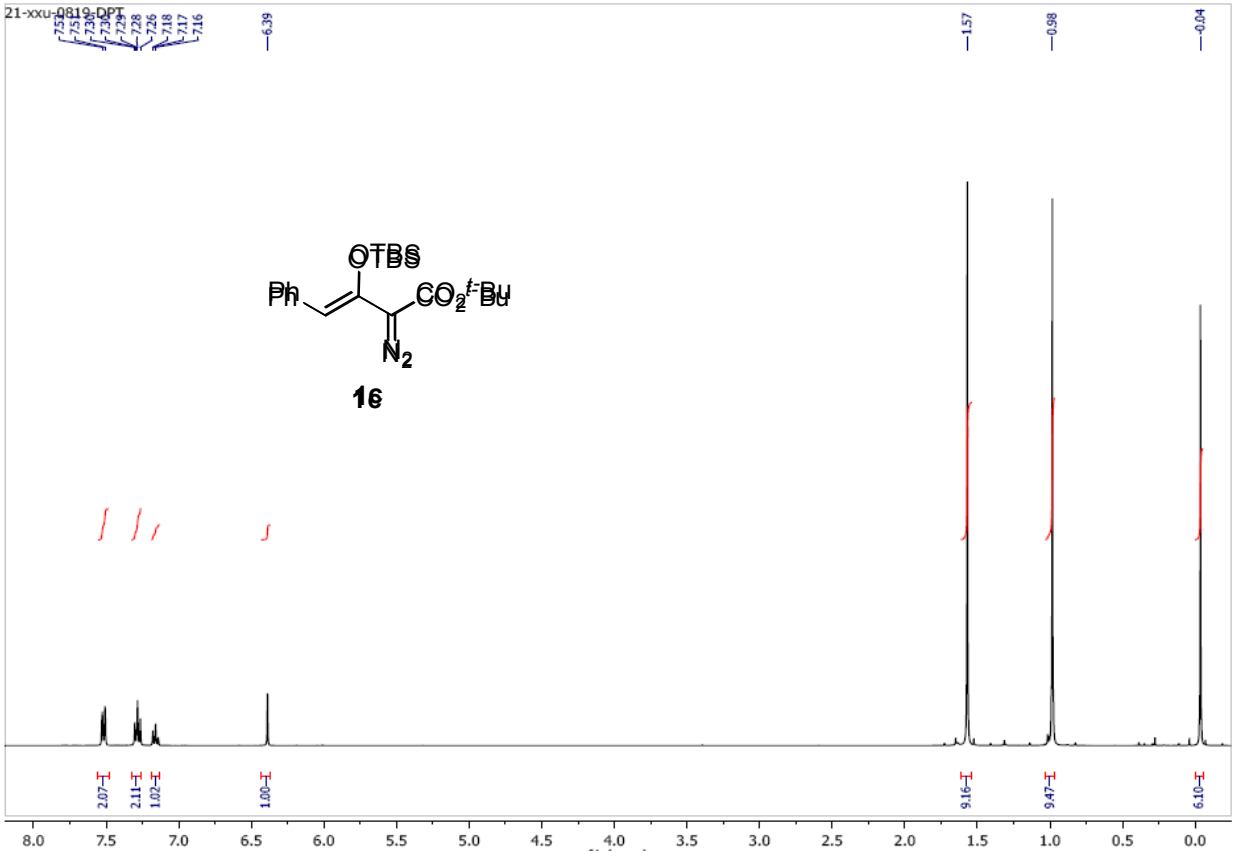
45.79
28.42
f1 (ppm)

S-2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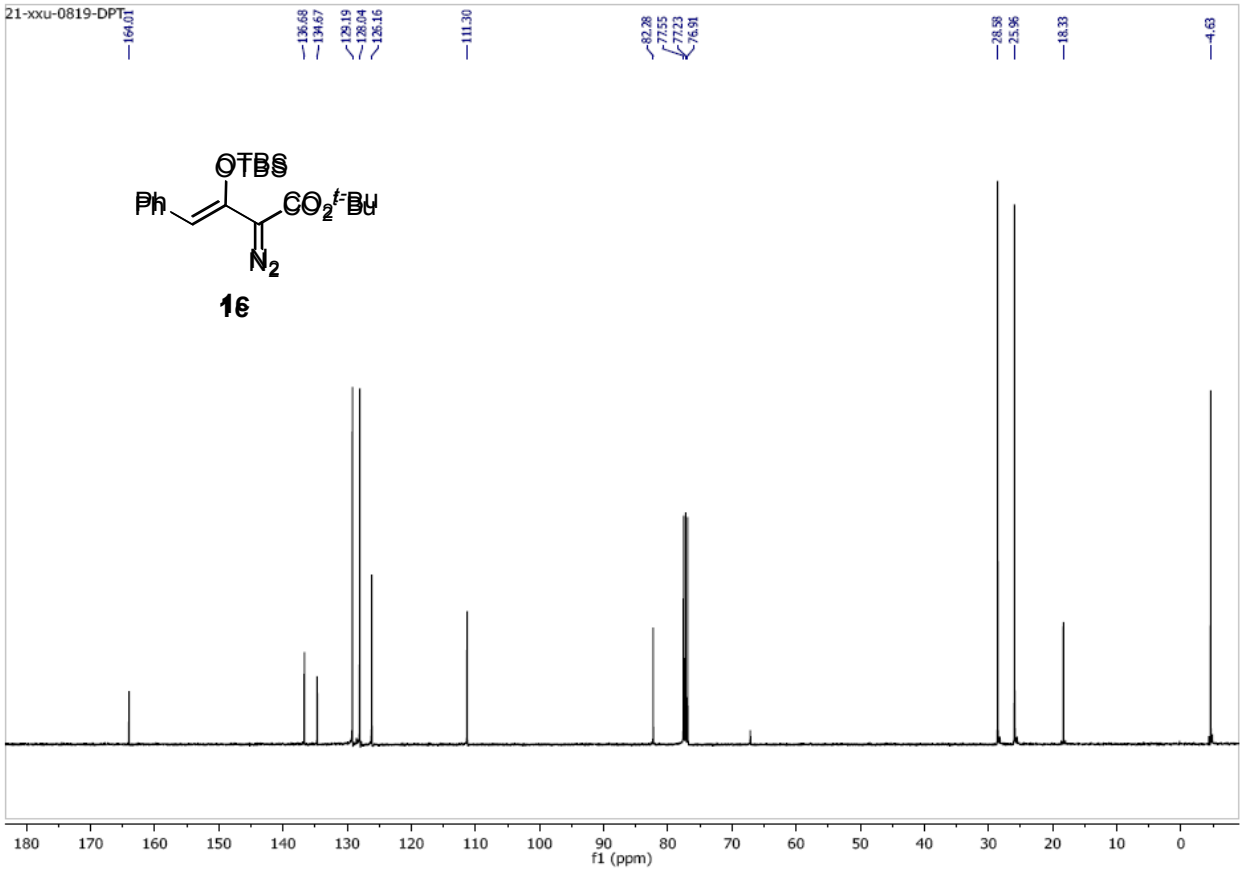
CO2t-Bu
N2
16e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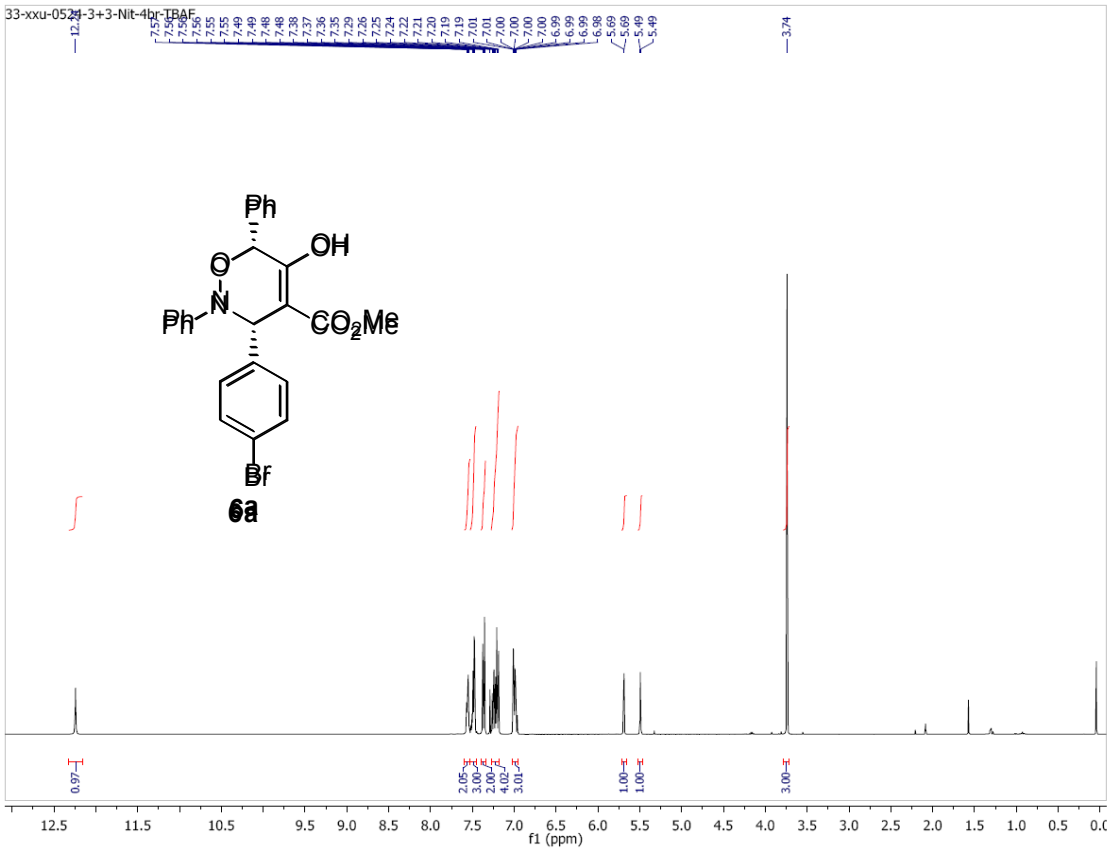
OTBS
Ph
CO2t-Bu
N2
16e
f1 (ppm)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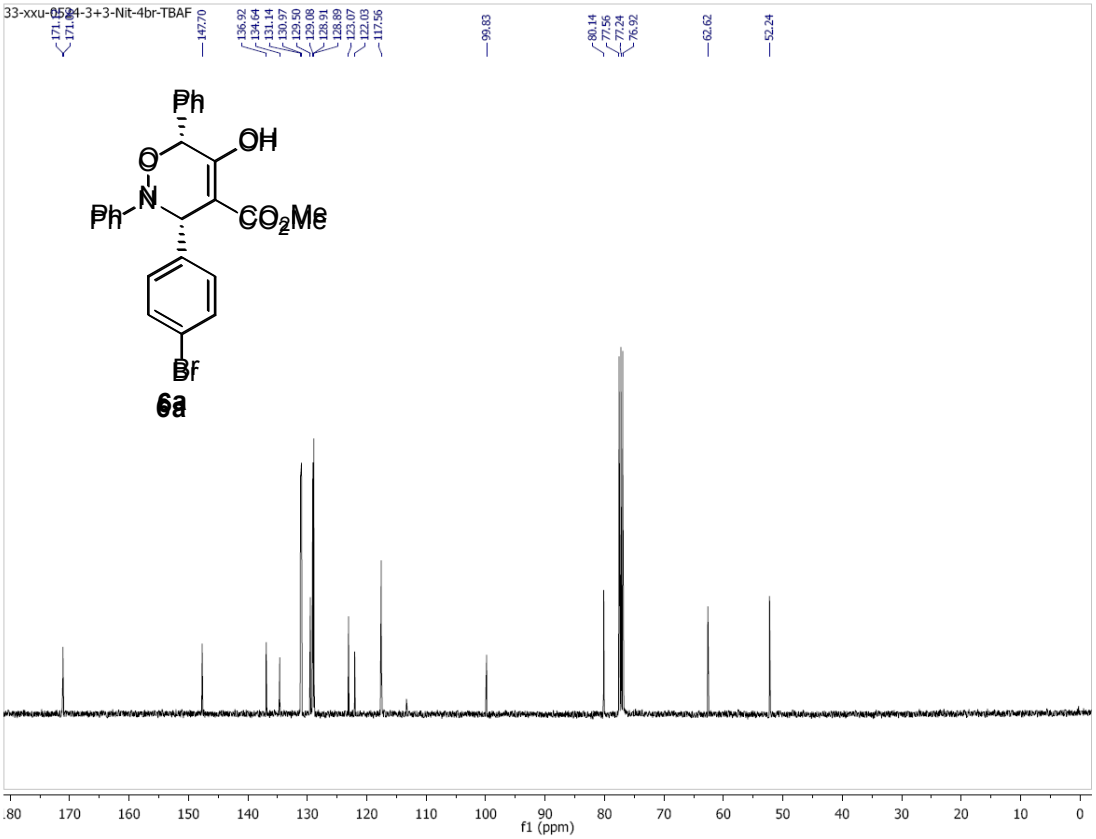
OH
O
N
Ph
CO2Me
Br
6a
f1 (ppm)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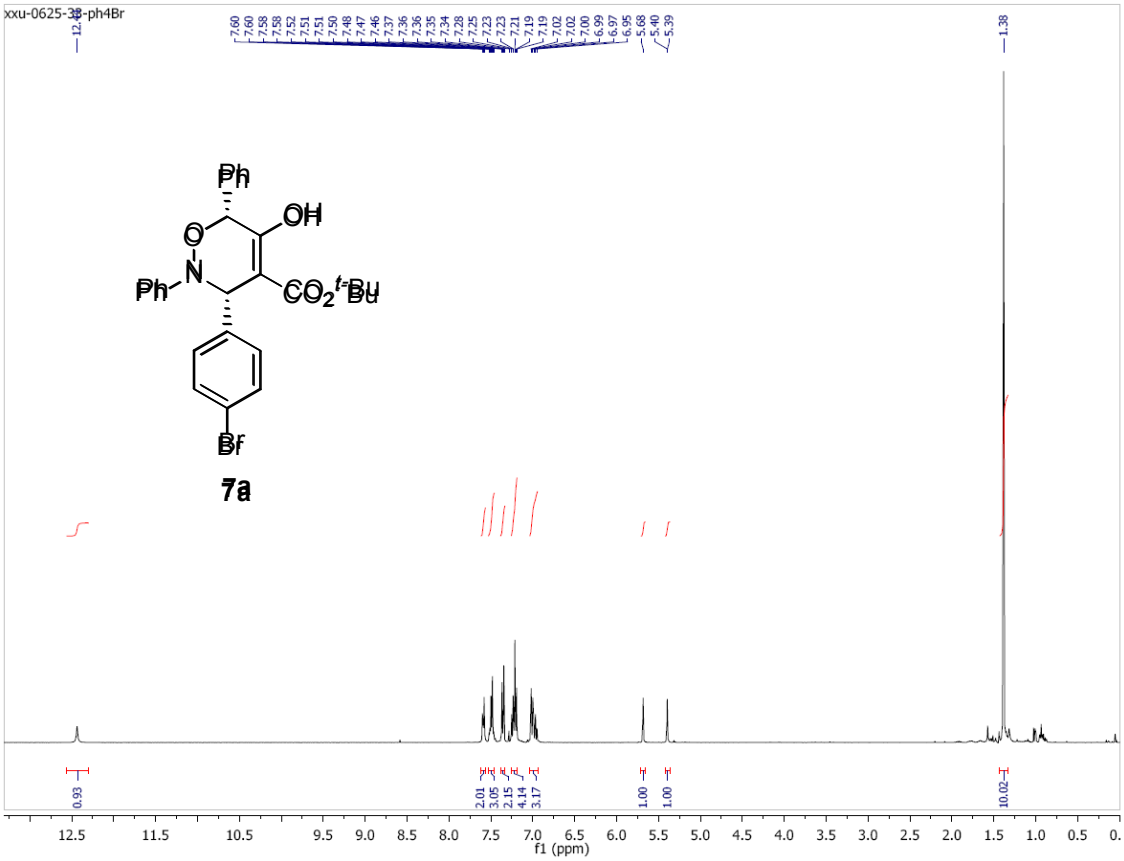
OH
O
N
Ph
CO2Me
Br
6a
f1 (ppm)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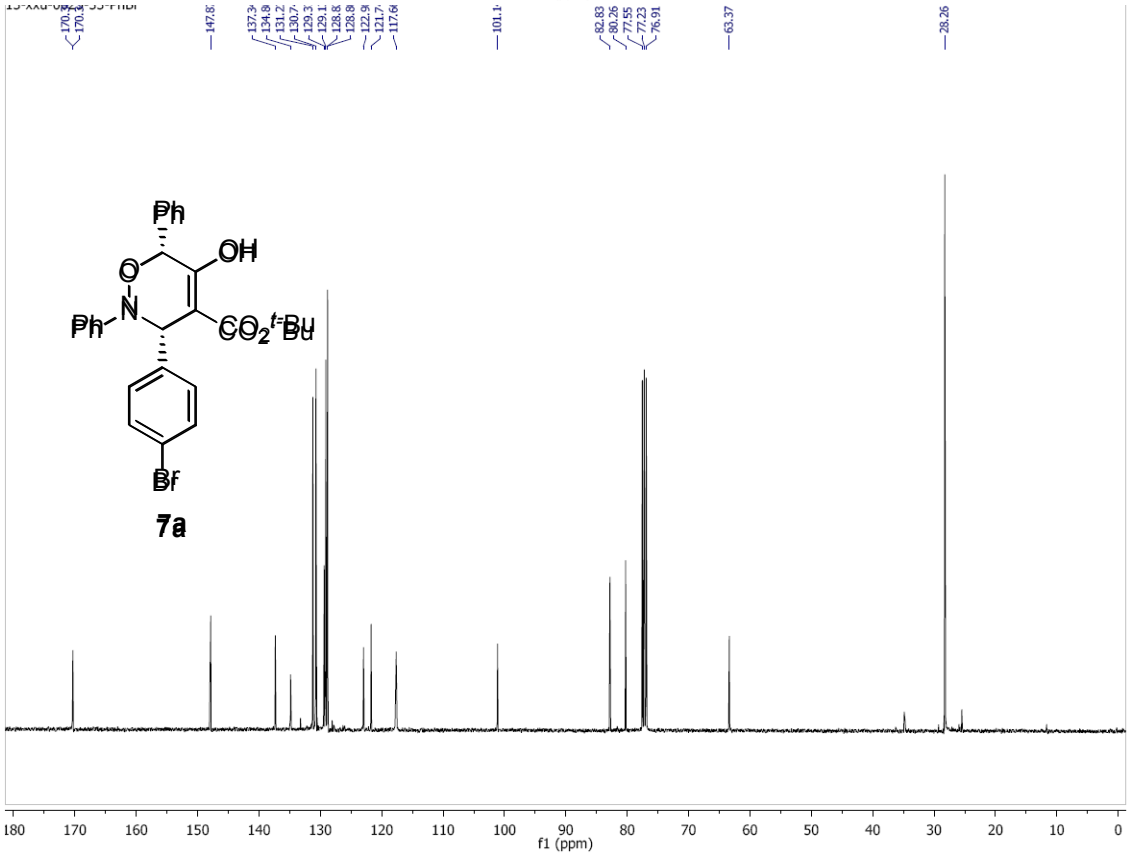
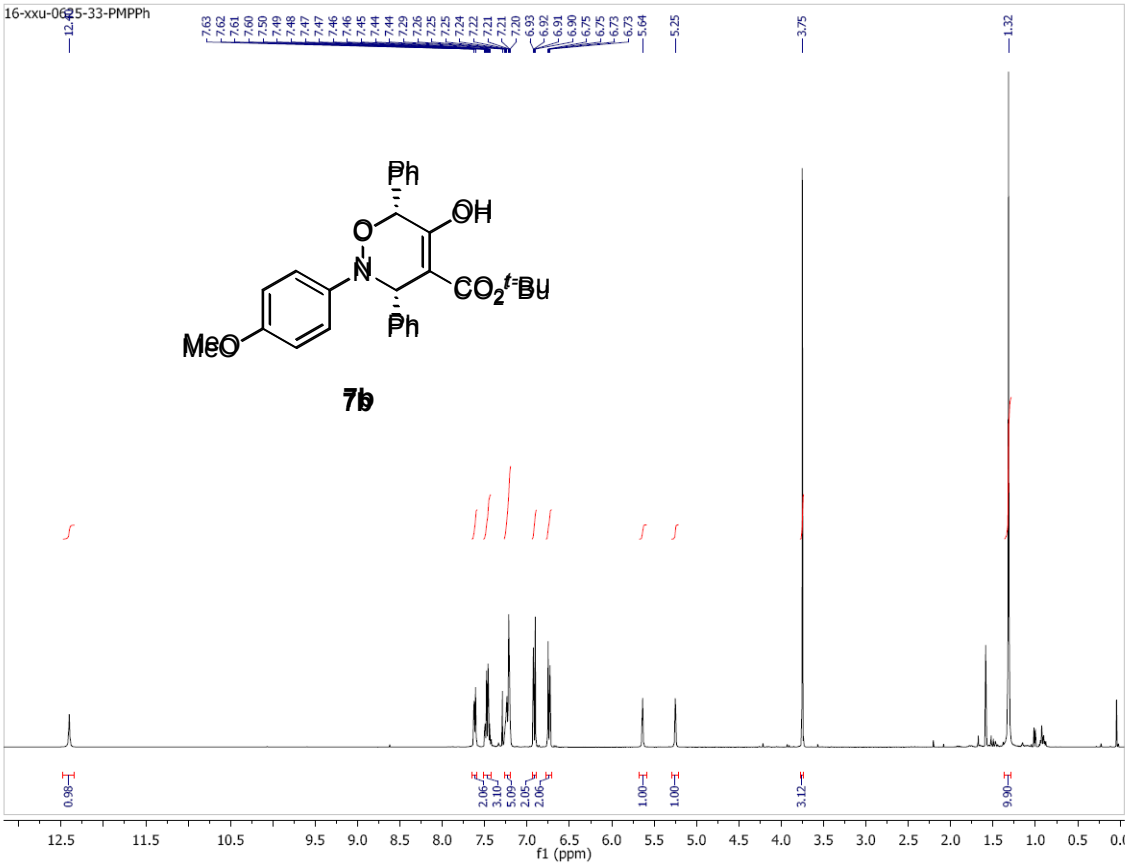

7a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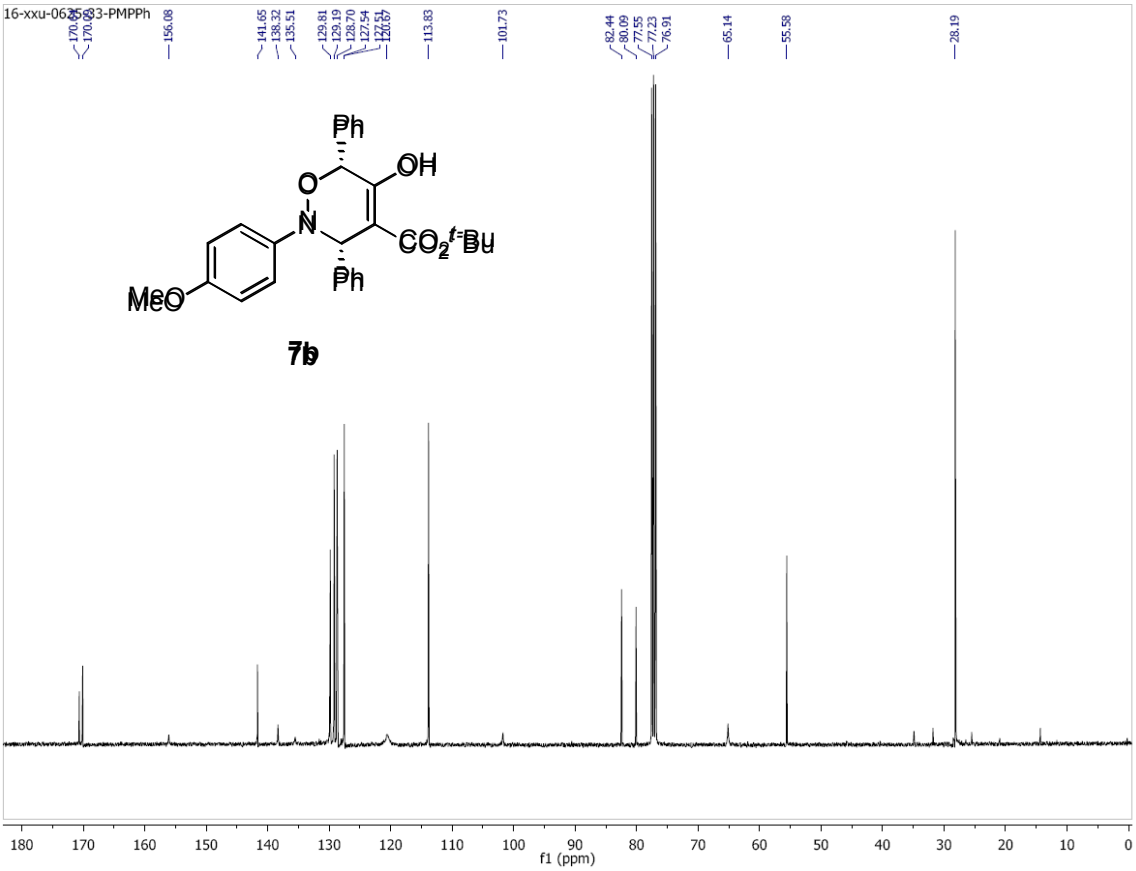
OH
O
N
CO2tBu
Ph
MeO
7b
f1 (ppm)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OH
O
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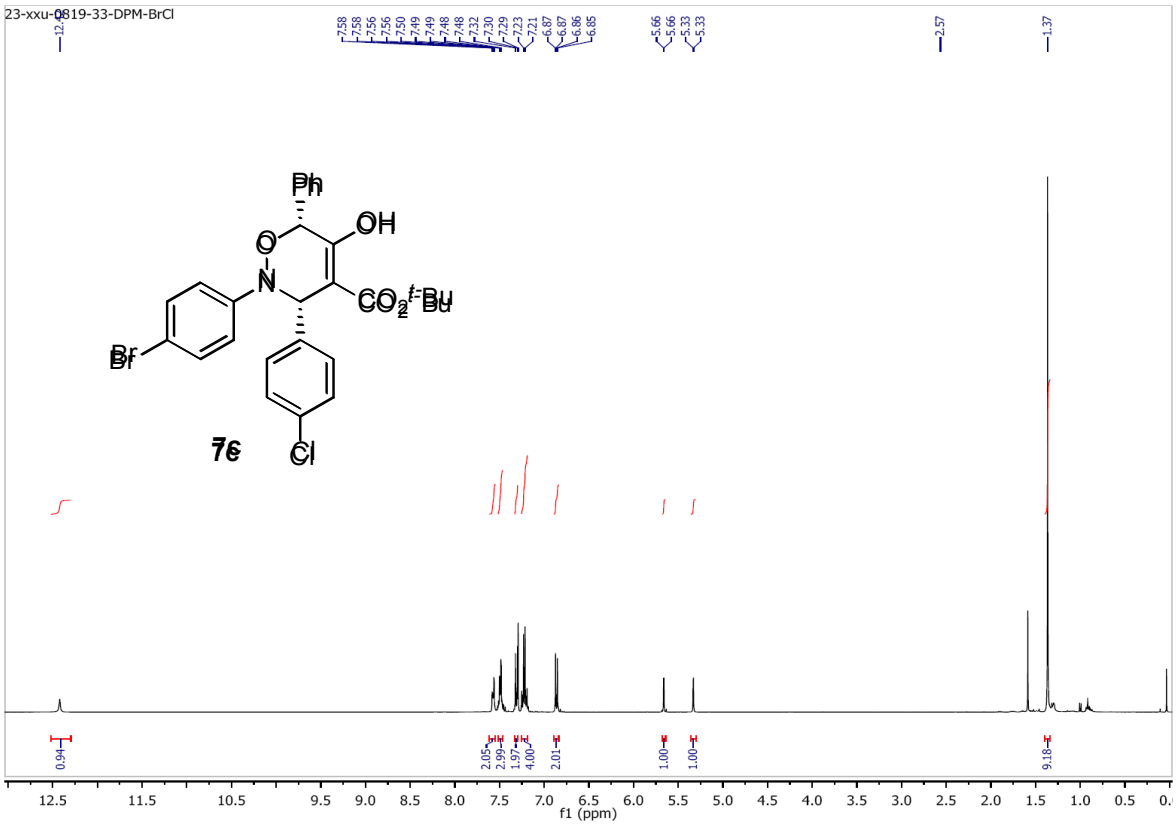
MeO
7b
f1 (ppm)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O
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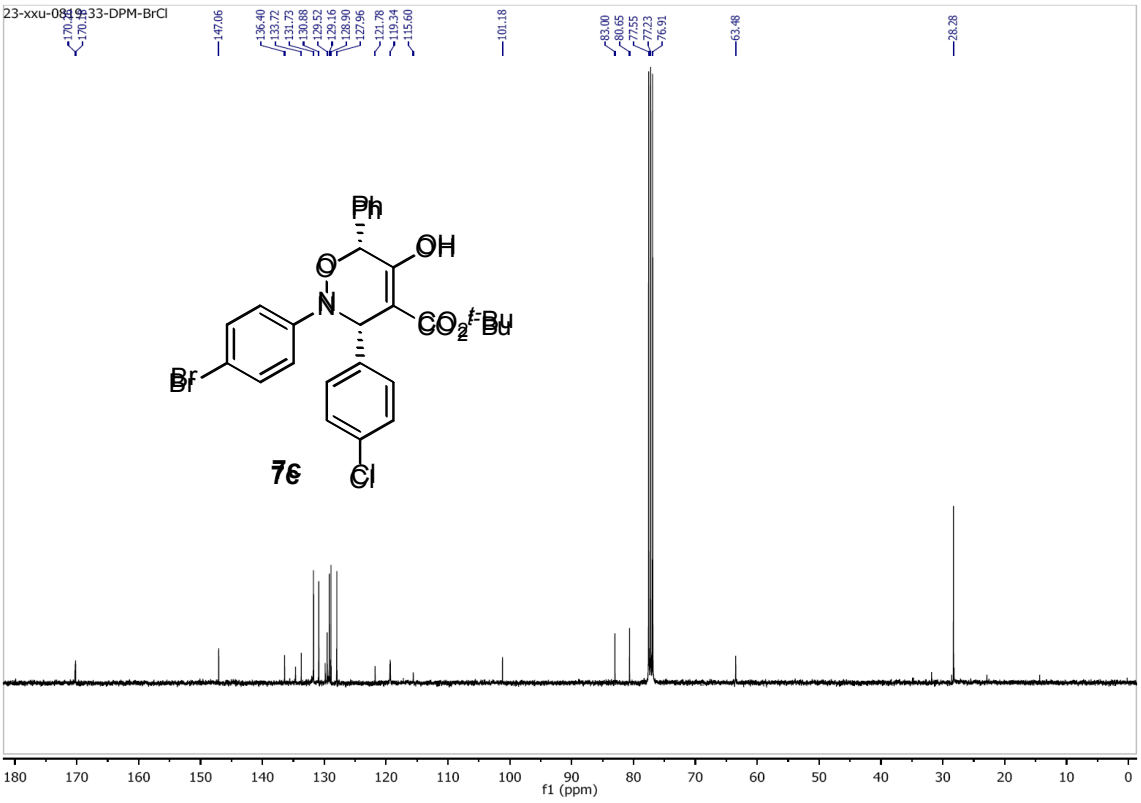
CO2t-Bu
Br
Cl
7e
f1 (ppm)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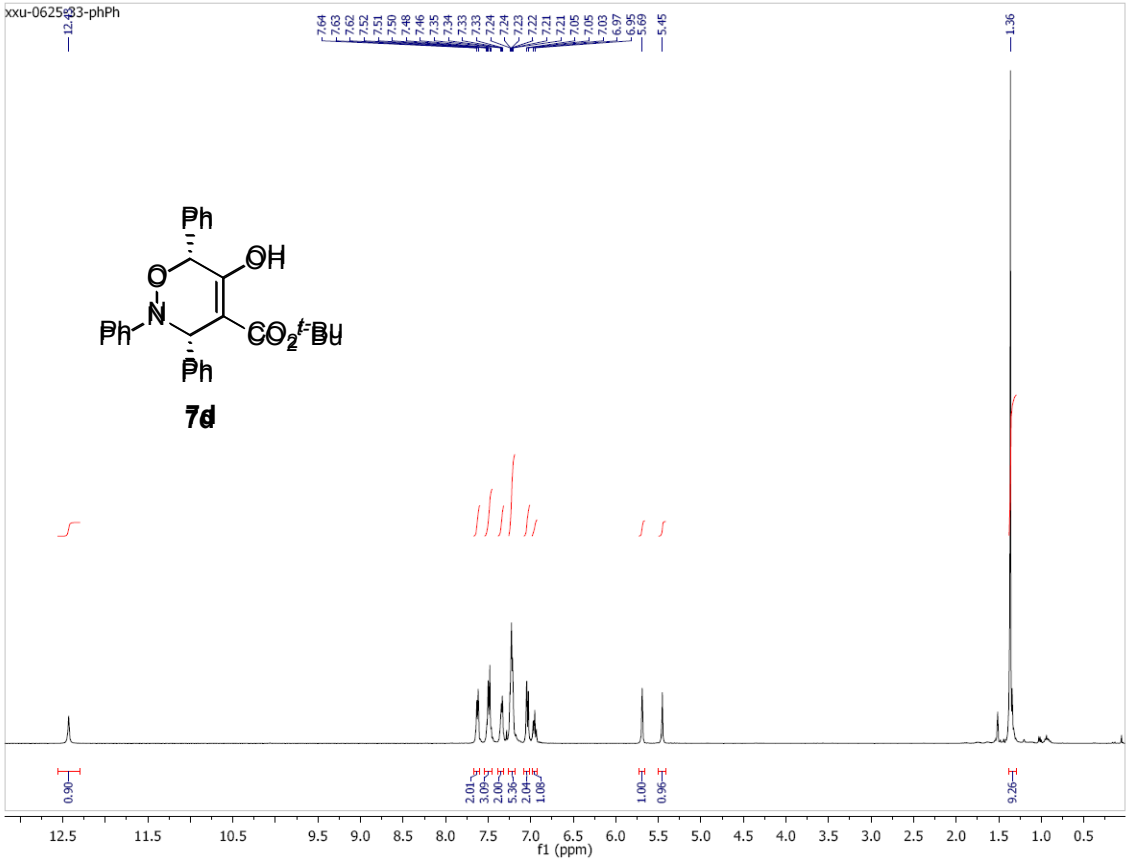
Ph
OH
O
N
CO2t-Bu
Br
Cl
7e
f1 (ppm)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7.03
6.97
6.95
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5.45
1.36
Ph
OH
O
N
Ph
CO2t-Bu
Ph
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1.00
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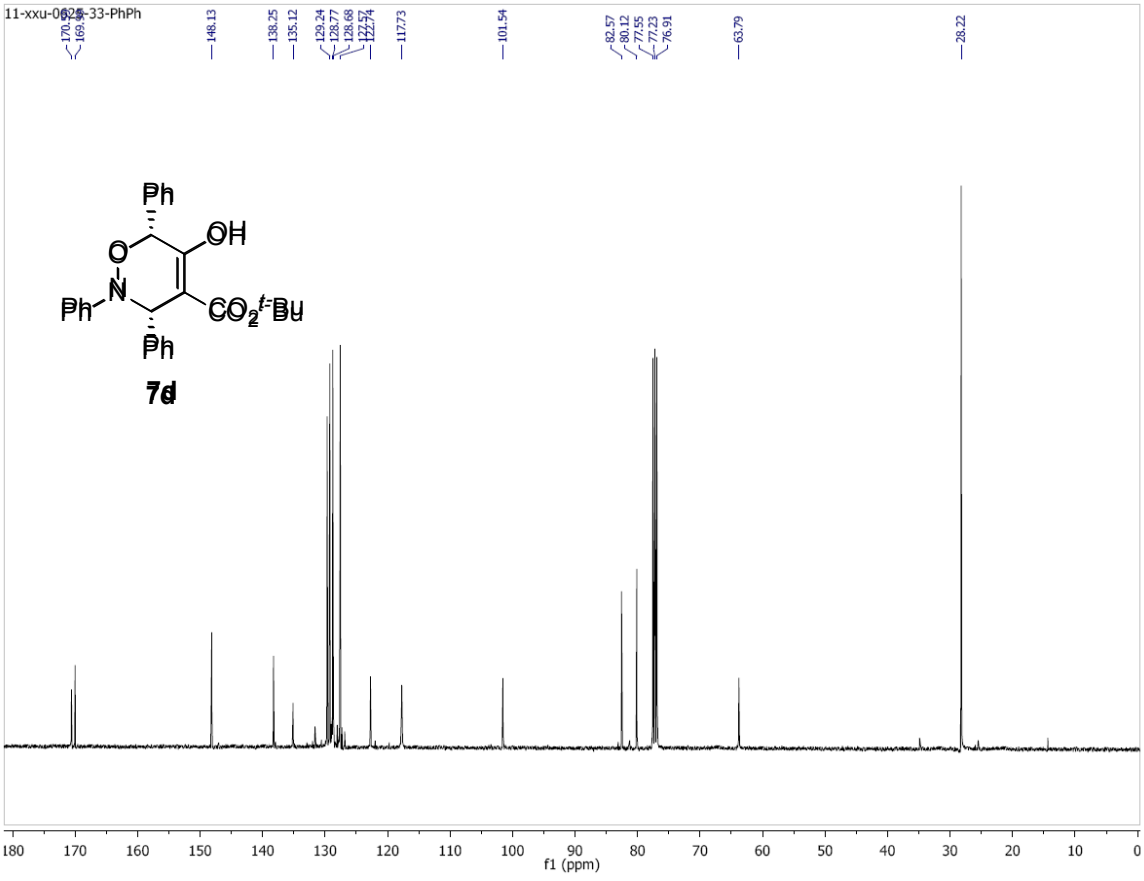
9.26
f1 (ppm)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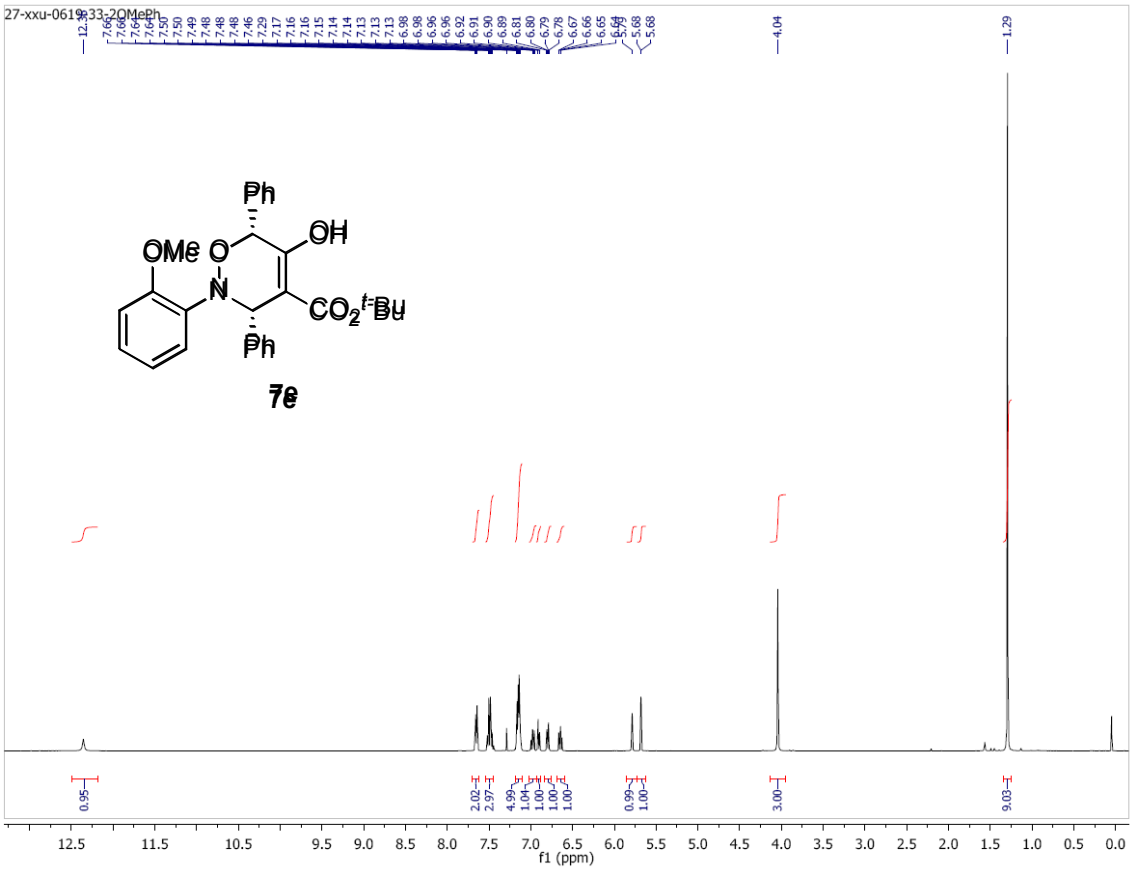
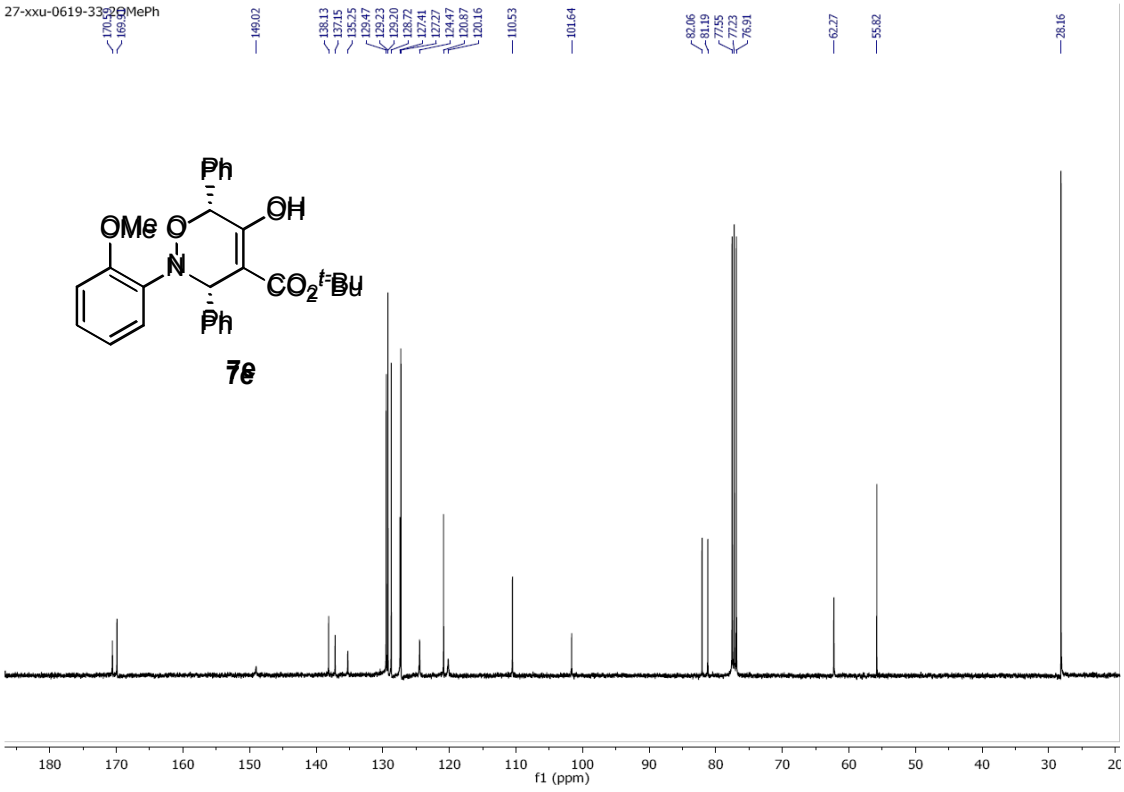
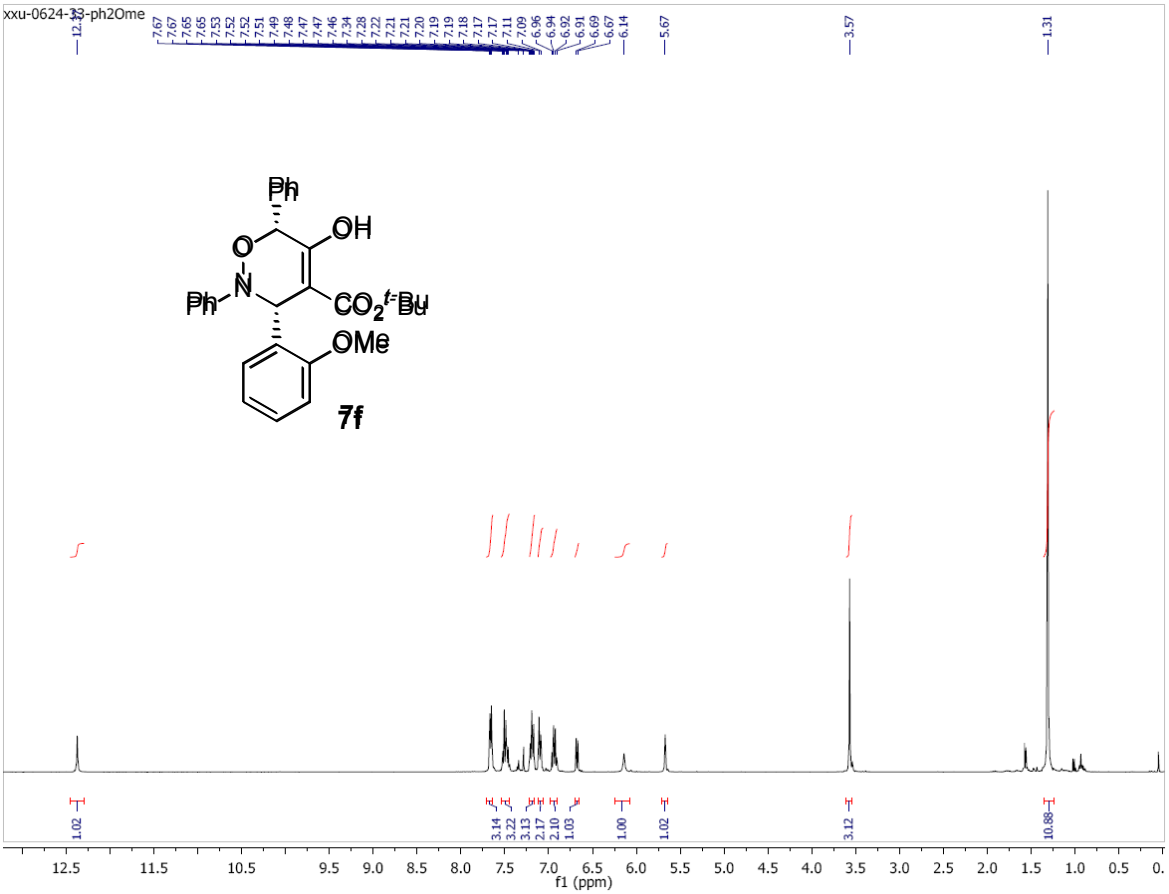
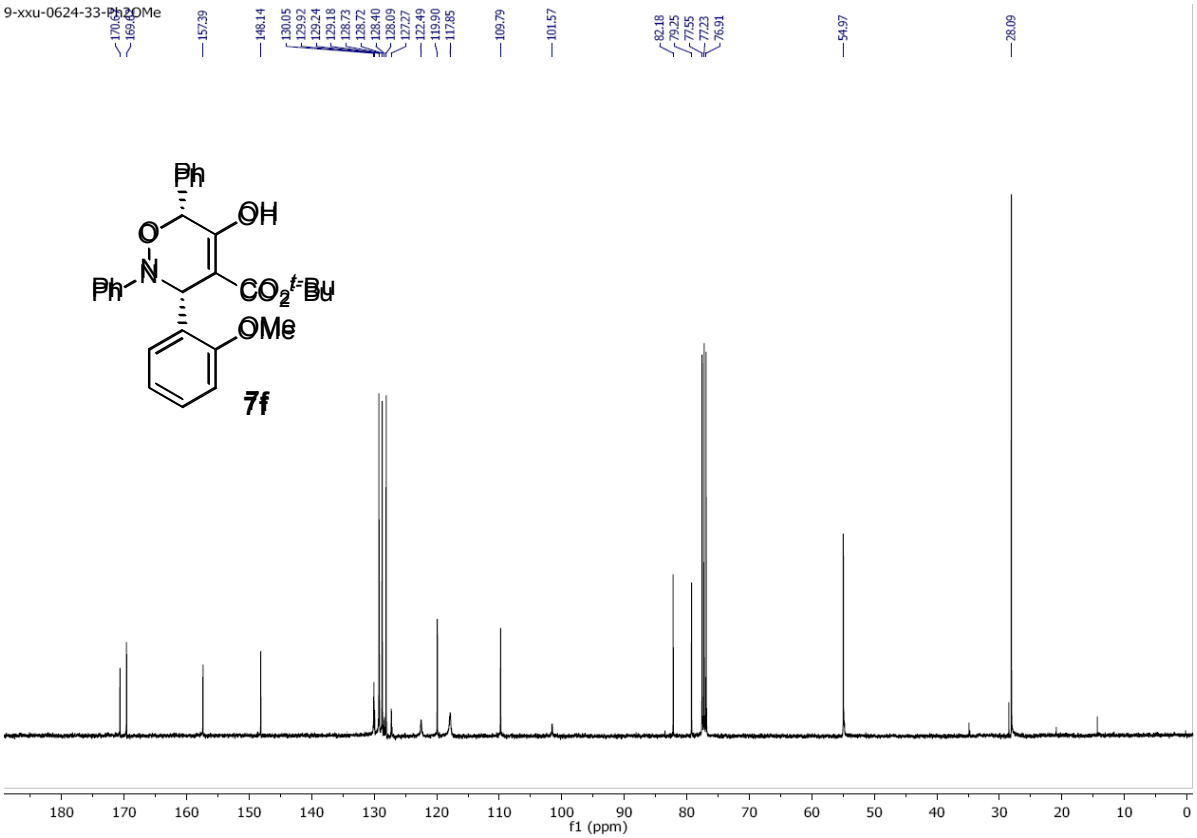
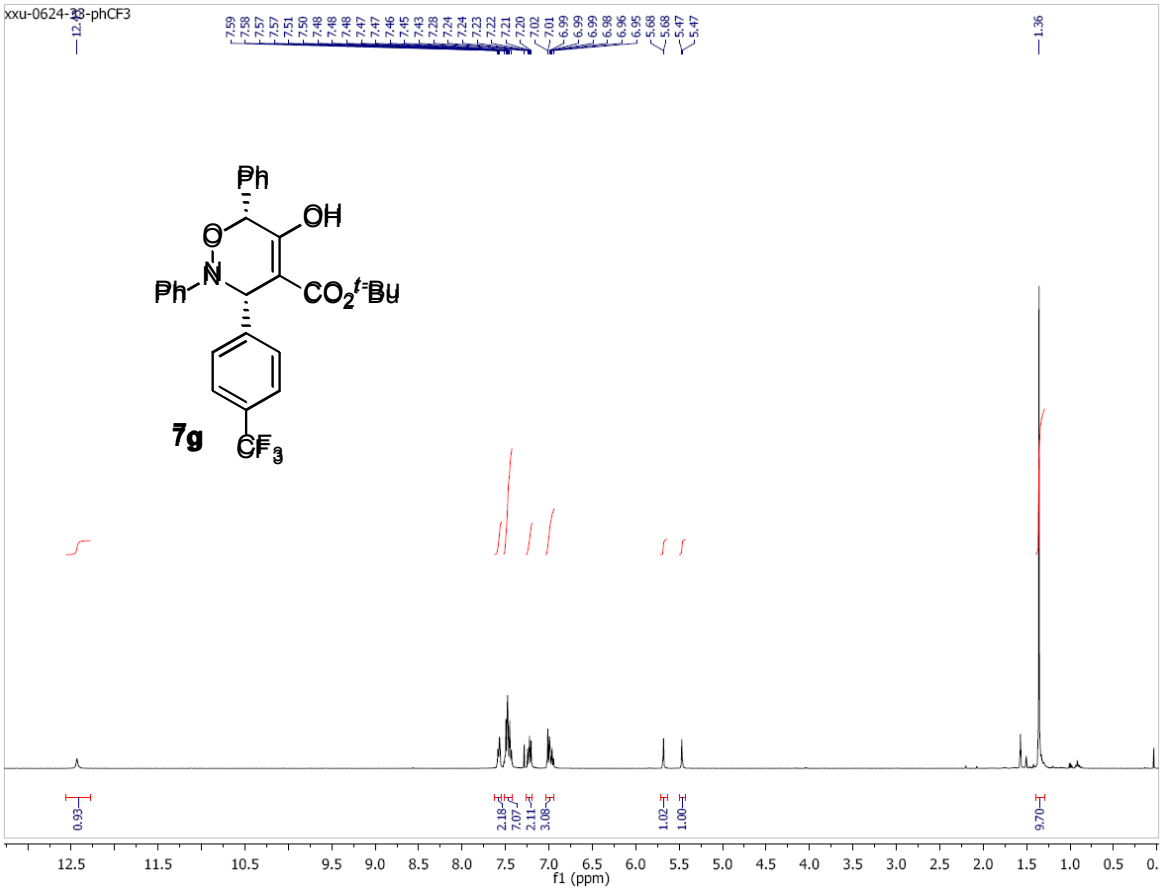
77.55
77.23
76.91
63.79
28.22
Ph
OH
O
N
Ph
CO2t-Bu
Ph
7d
f1 (ppm)

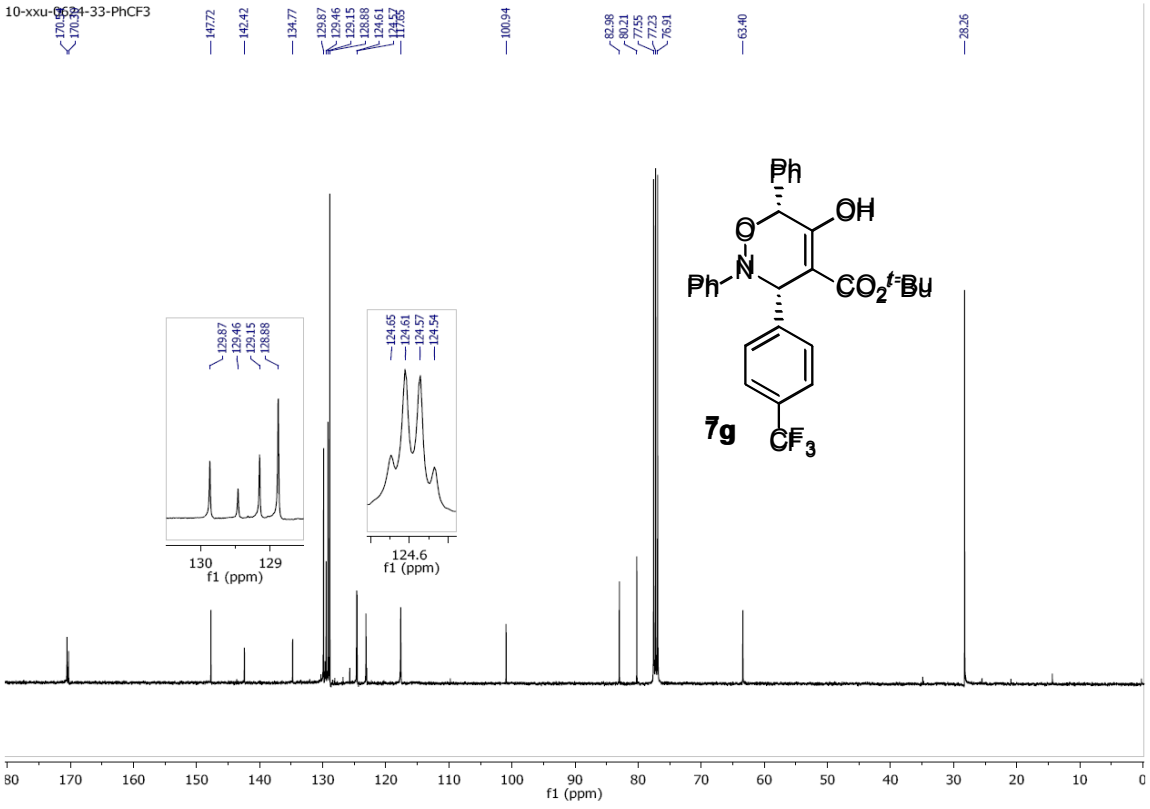

27-xxu-0619-33-2OMePh
Ph
OMe
O
OH
N
CO2tBu
Ph
7e
f1 (ppm)

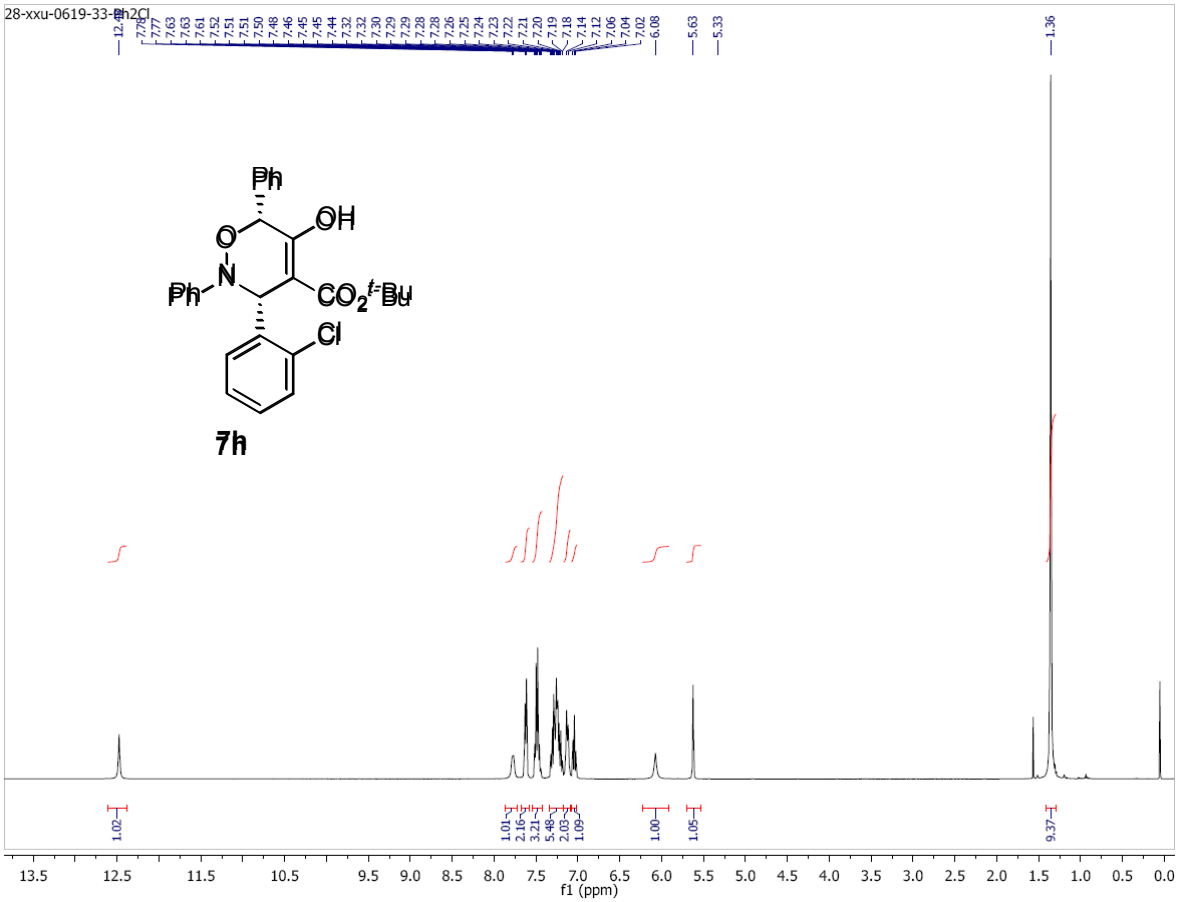

27-xxu-0619-33-2OMePh
Ph
OMe
O
OH
N
CO2tBu
Ph
7e
f1 (ppm)

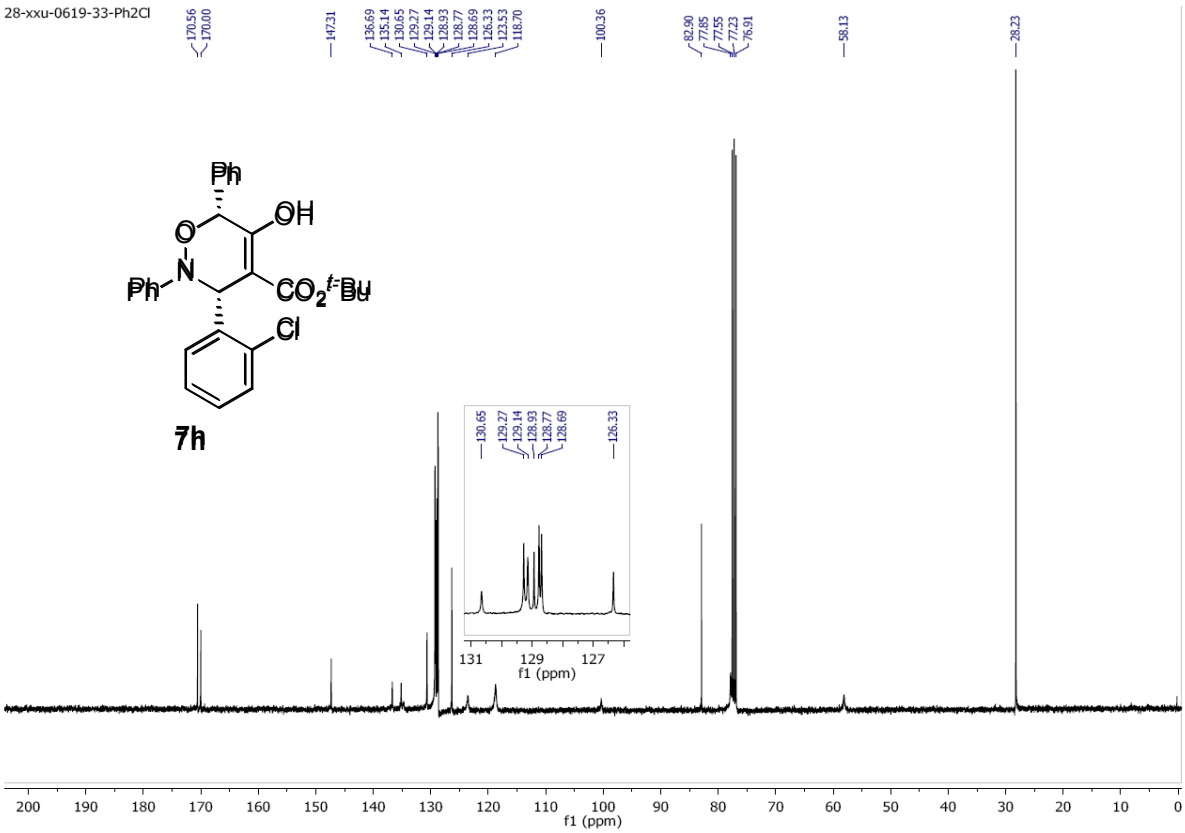

xxu-0624-33-ph2Ome
12.43
7.67
7.67
7.65
7.65
7.53
7.52
7.52
7.51
7.49
7.48
7.47
7.47
7.47
7.46
7.34
7.28
7.22
7.21
7.21
7.20
7.19
7.19
7.18
7.17
7.17
7.11
7.09
6.96
6.94
6.92
6.91
6.69
6.67
6.14
5.67
3.57
1.31
Ph
OH
O
N
Ph
CO2t-Bu
OMe
7f
1.02
3.14
3.22
3.13
2.17
2.10
1.03
1.00
1.02
3.12
10.88
f1 (ppm)

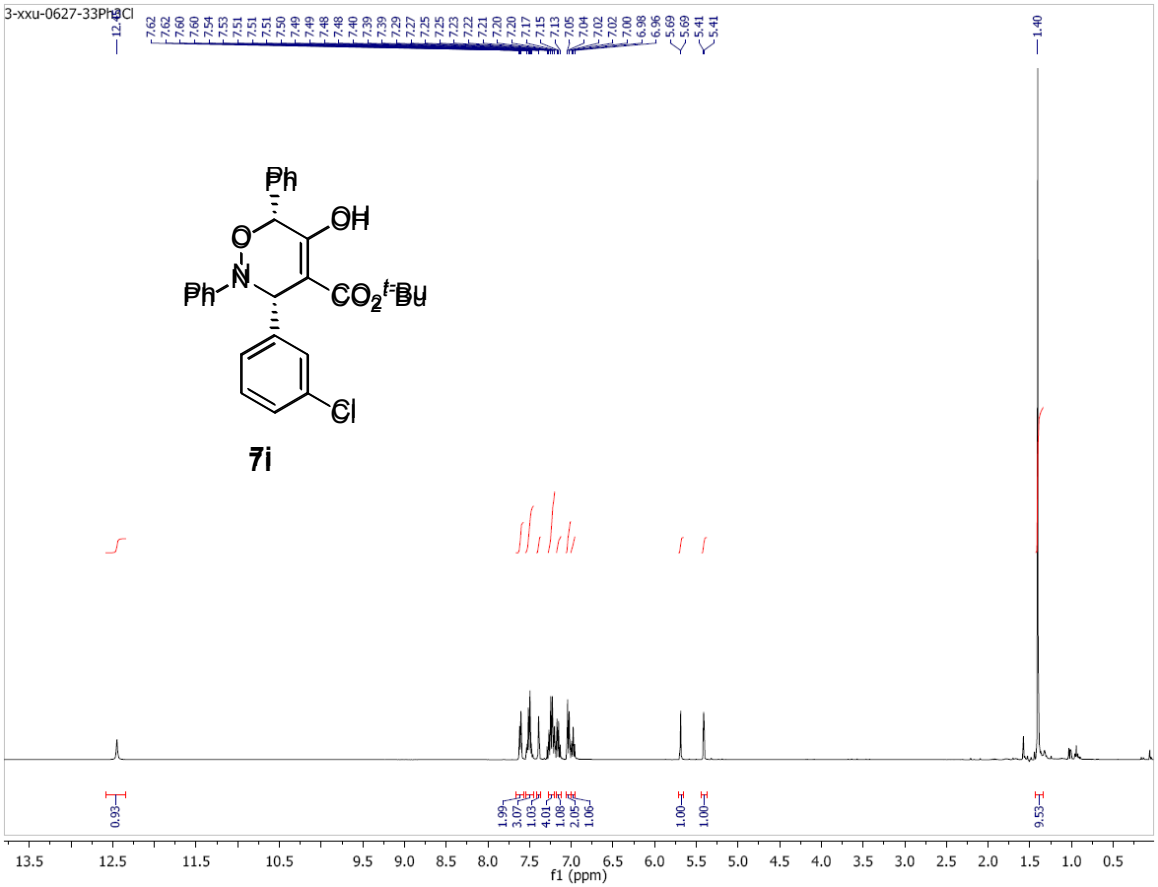

9-xxu-0624-33-Ph2OMe
170.62
169.61
157.39
148.14
130.05
129.92
129.24
129.18
128.73
128.72
128.40
128.09
127.27
122.49
119.90
117.85
109.79
101.57
82.18
79.25
77.55
77.23
76.91
54.97
28.09
Ph
OH
O
N
Ph
CO2t-Bu
OMe
7f
f1 (ppm)

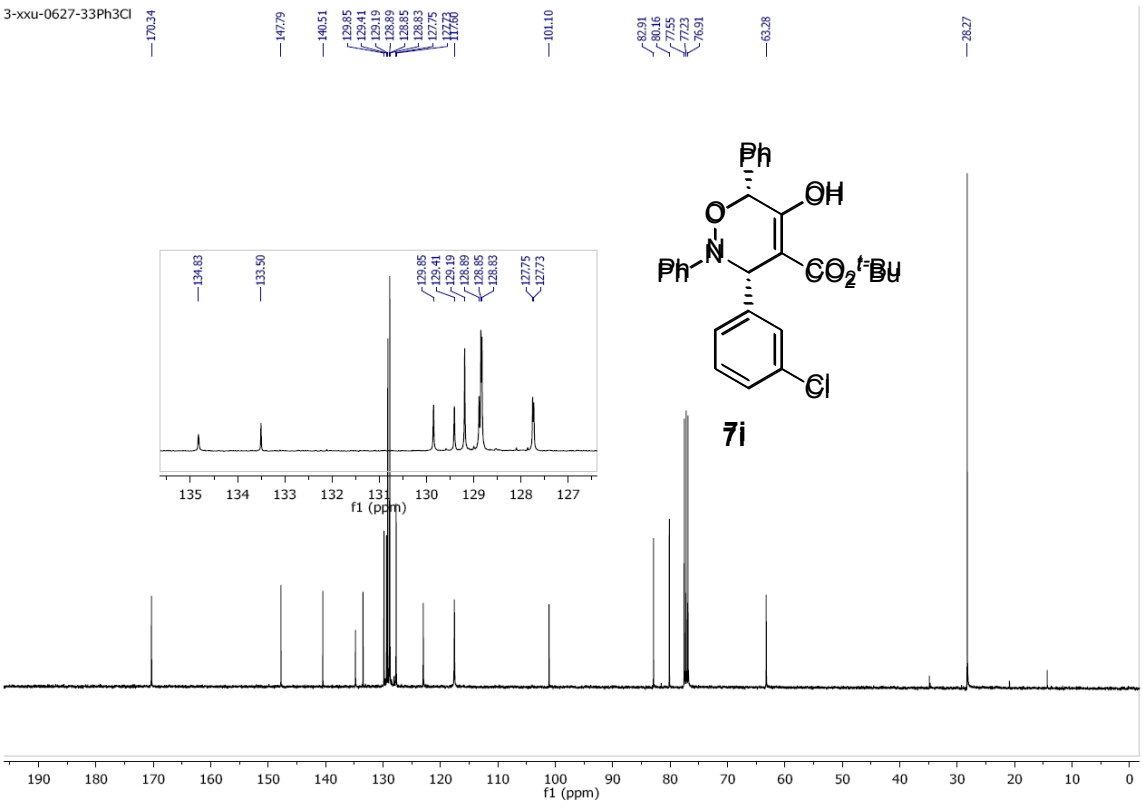

xxu-0624-33-phCF3
Ph
OH
O
N
Ph
CO2tBu
7g
CF3
f1 (ppm)

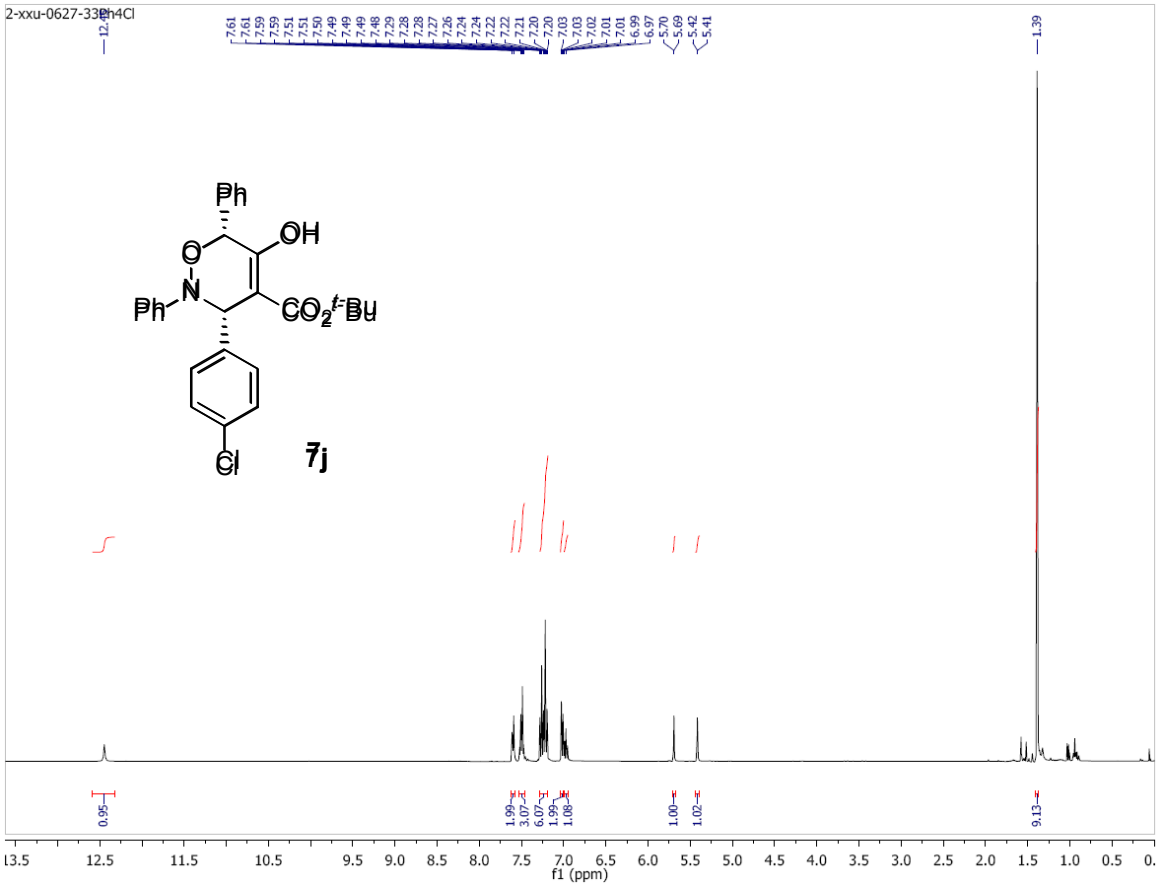

10-xxu-0624-33-PhCF3
Ph
OH
O
N
Ph
CO2tBu
7g
CF3
130
129
f1 (ppm)
124.6
f1 (ppm)
f1 (ppm)


28-xxu-0619-33-Ph2Cl
12.49
7.78
7.77
7.63
7.63
7.61
7.52
7.51
7.51
7.50
7.48
7.46
7.45
7.45
7.44
7.32
7.32
7.30
7.29
7.29
7.28
7.28
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.18
7.14
7.12
7.06
7.04
7.02
6.08
5.63
5.33
1.36
Ph
OH
O
N
Ph
CO2t-Bu
Cl
7h
1.02
1.01
2.16
3.21
5.48
2.03
1.09
1.00
1.05
9.37
f1 (ppm)

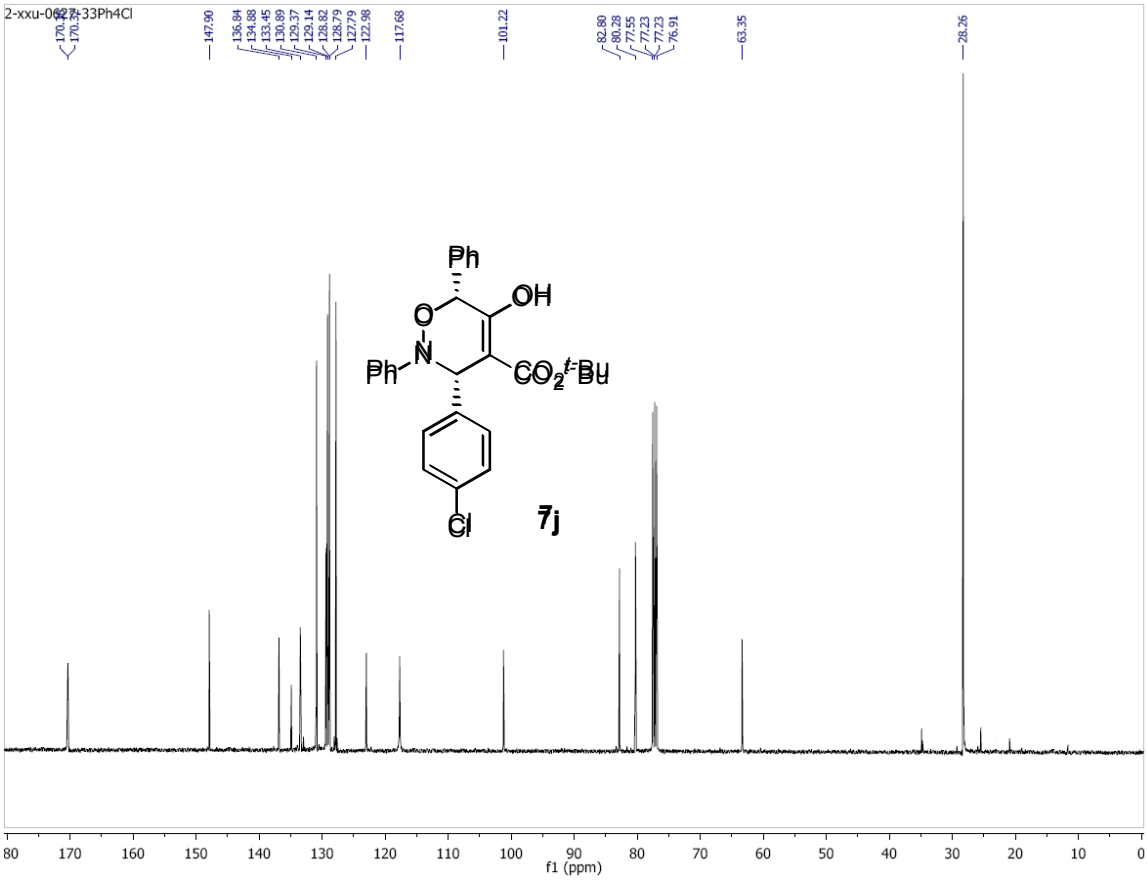

28-xxu-0619-33-Ph2Cl
170.56
170.00
147.31
136.69
135.14
130.65
129.27
129.14
128.93
128.77
128.69
126.33
123.53
118.70
100.36
82.90
77.85
77.55
77.23
76.91
58.13
28.23
Ph
OH
O
N
Ph
CO2t-Bu
Cl
7h
130.65
129.27
129.14
128.93
128.77
128.69
126.33
131
129
127
f1 (ppm)
f1 (ppm)


3-xxu-0627-33Ph3Cl
Ph
OH
O
N
Ph
CO2tBu
Cl
7i
f1 (ppm)

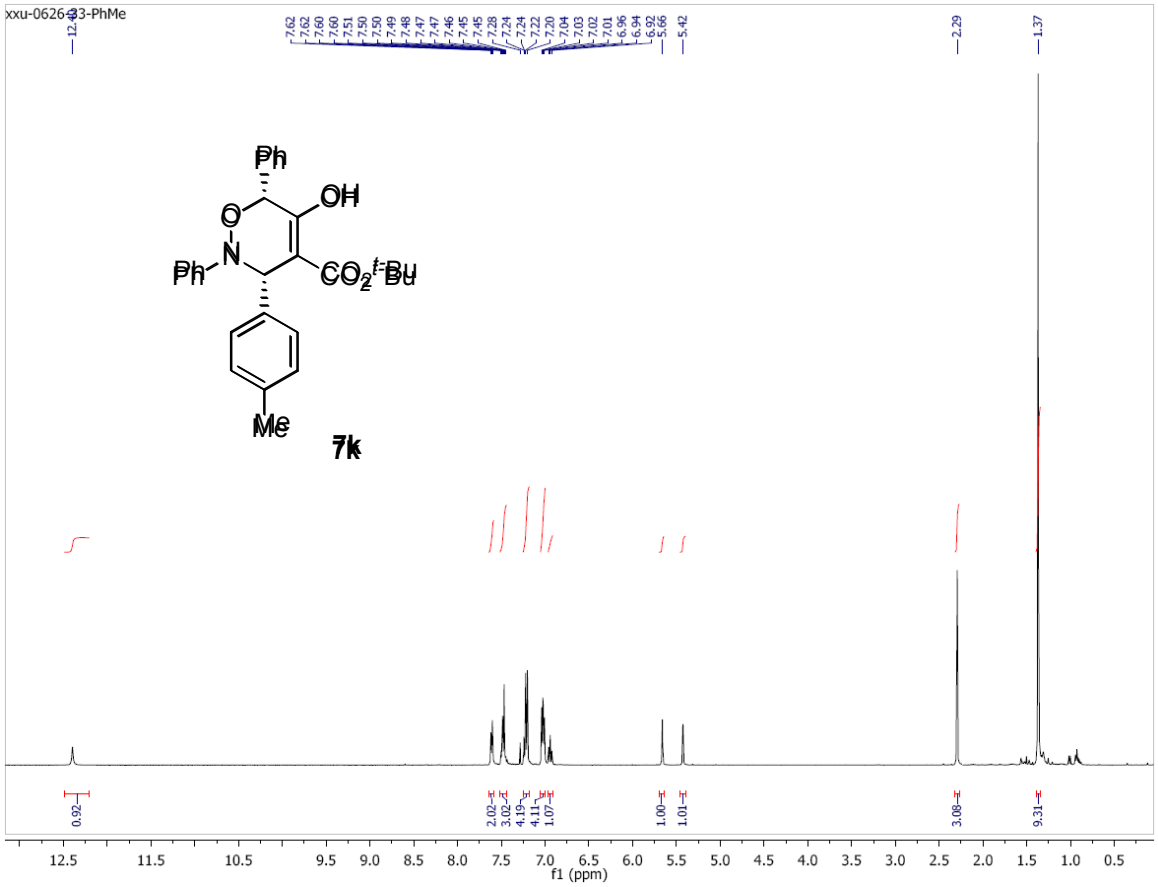

3-xxu-0627-33Ph3Cl
Ph
OH
O
N
Ph
CO2tBu
Cl
7i
f1 (ppm)

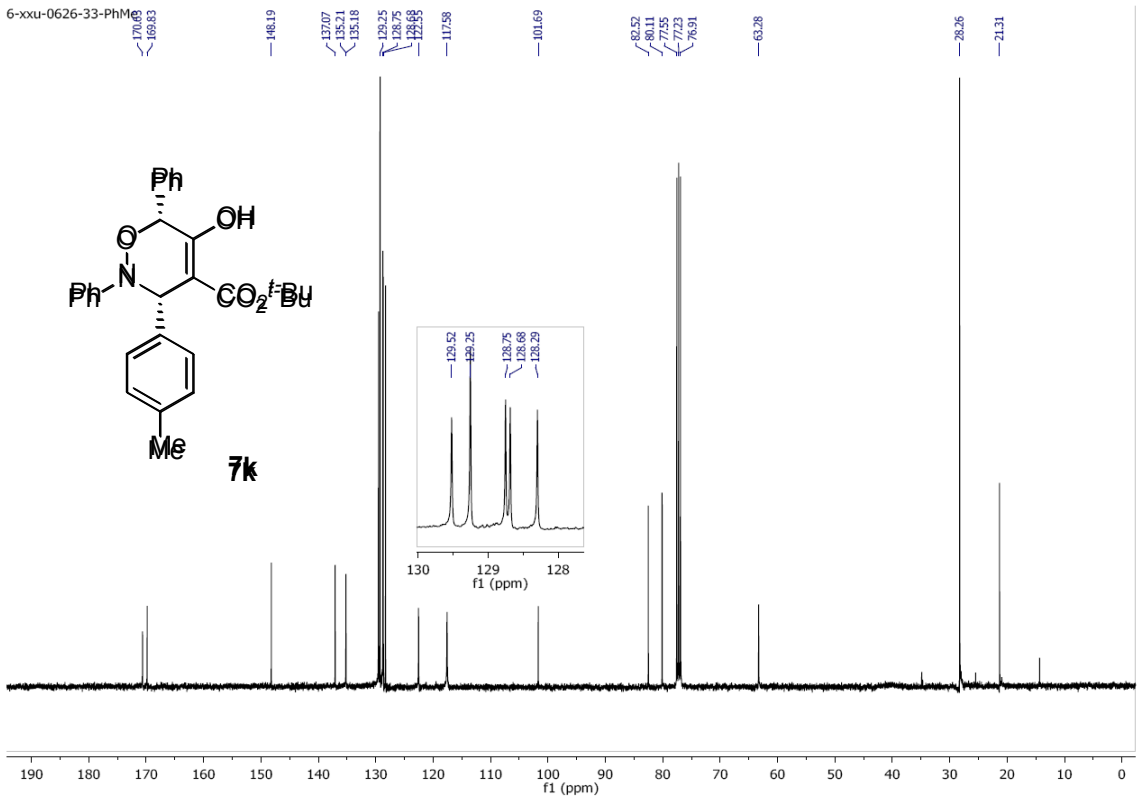


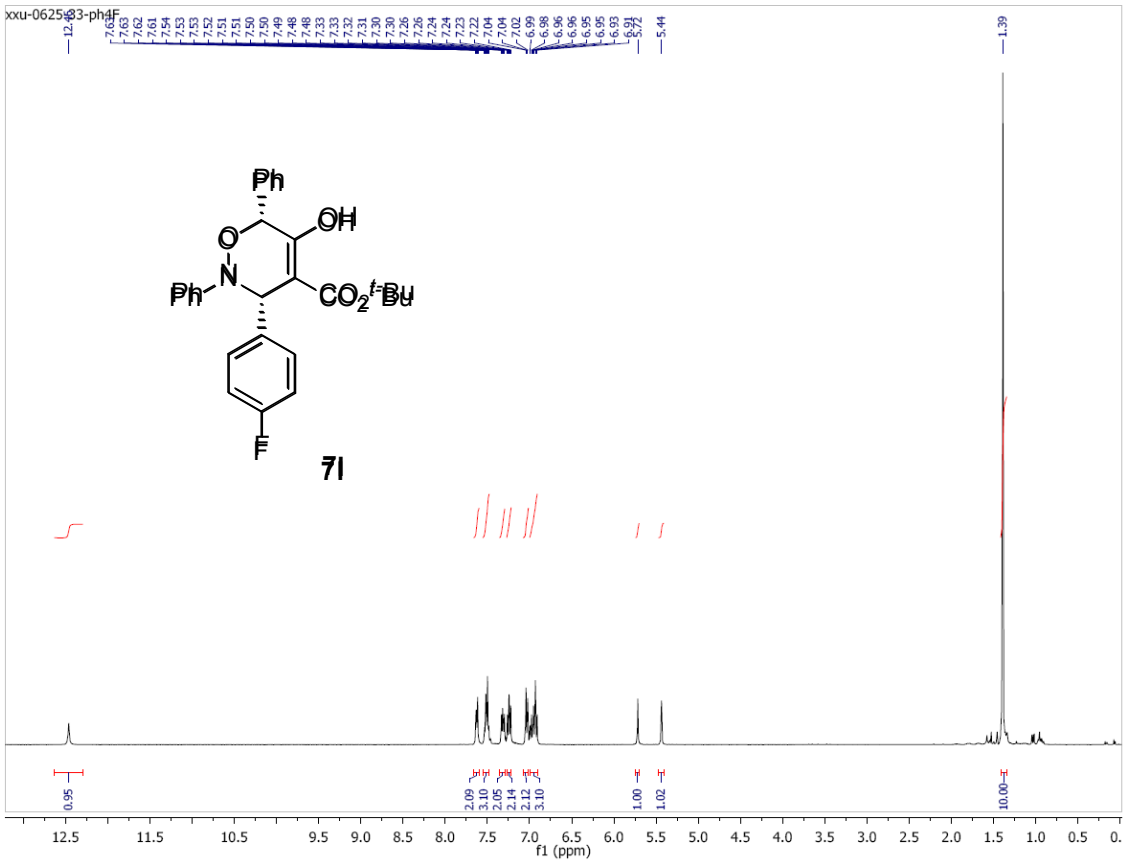
7j

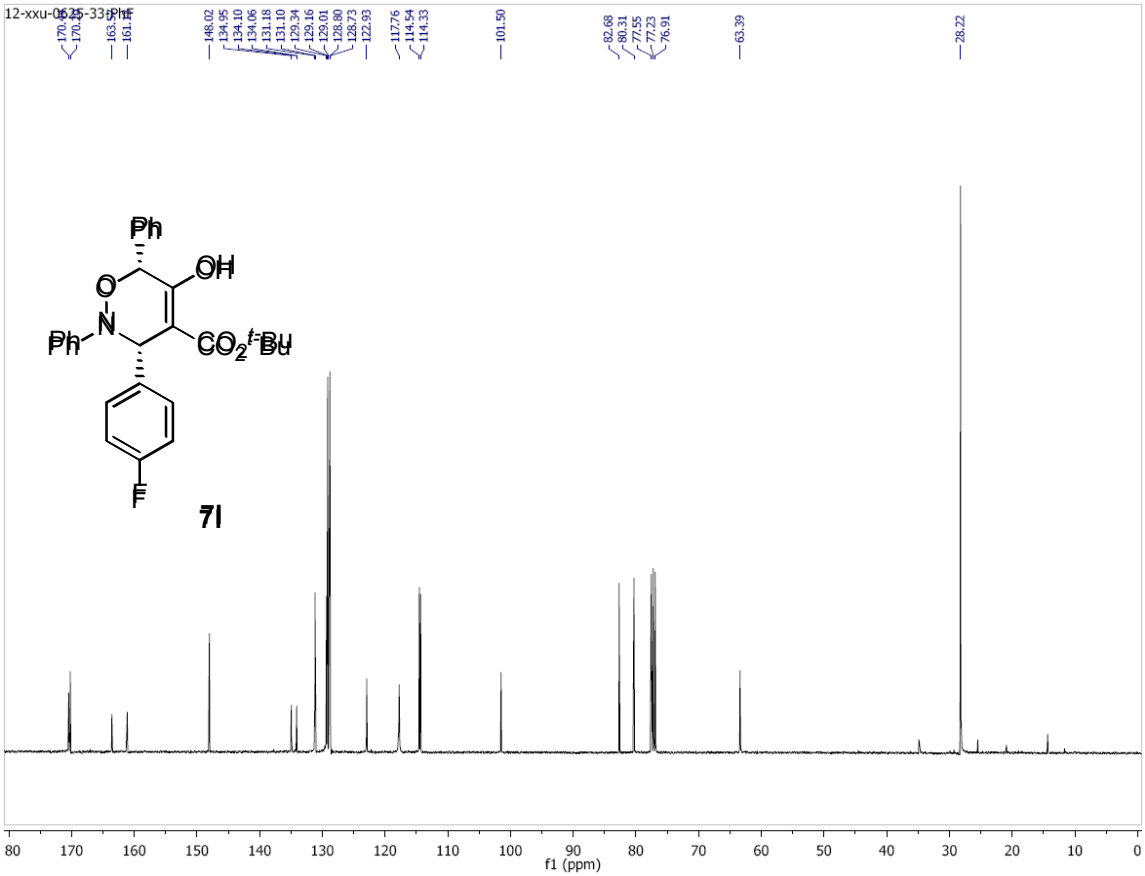


7j


xxu-0626-33-PhMe
12.43
7.62
7.62
7.60
7.60
7.51
7.50
7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.28
7.24
7.24
7.22
7.20
7.04
7.03
7.02
7.01
6.96
6.94
6.92
5.66
5.42
2.29
1.37
Ph
OH
O
N
Ph
CO2t-Bu
Me
7k
0.92
2.02
3.02
4.19
4.11
1.07
1.00
1.01
3.08
9.31
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


6-xxu-0626-33-PhMe
170.68
169.83
148.19
137.07
135.21
135.18
129.25
128.75
128.68
128.29
117.58
101.69
82.52
80.11
77.55
77.23
76.91
63.28
28.26
21.31
Ph
OH
O
N
Ph
CO2t-Bu
Me
7k
129.52
129.25
128.75
128.68
128.29
130
129
128
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


xxu-0625-33-ph4F
12.43
7.63
7.62
7.61
7.54
7.53
7.52
7.51
7.50
7.49
7.48
7.33
7.32
7.31
7.30
7.26
7.24
7.23
7.22
7.04
7.02
6.99
6.98
6.96
6.95
6.93
6.91
5.72
5.44
1.39
Ph
OH
O
N
Ph
CO2t-Bu
F
7l
0.95
2.09
3.10
2.05
2.14
2.12
3.10
1.00
1.02
10.00
f1 (ppm)


12-xxu-0625-33-PhF
170.25
170.11
163.57
161.64
148.02
134.95
134.10
134.06
131.18
131.10
129.34
129.16
129.01
128.80
128.73
122.93
117.76
114.54
114.33
101.50
82.68
80.31
77.55
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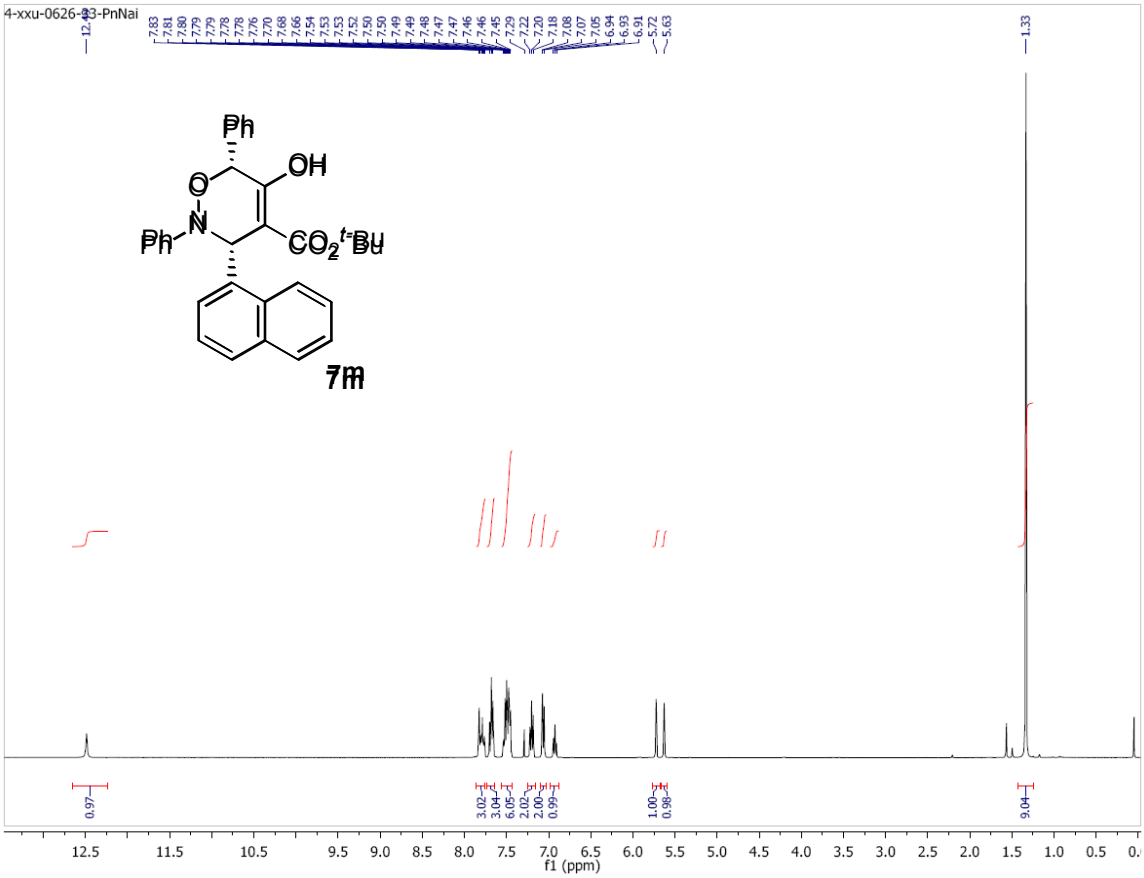
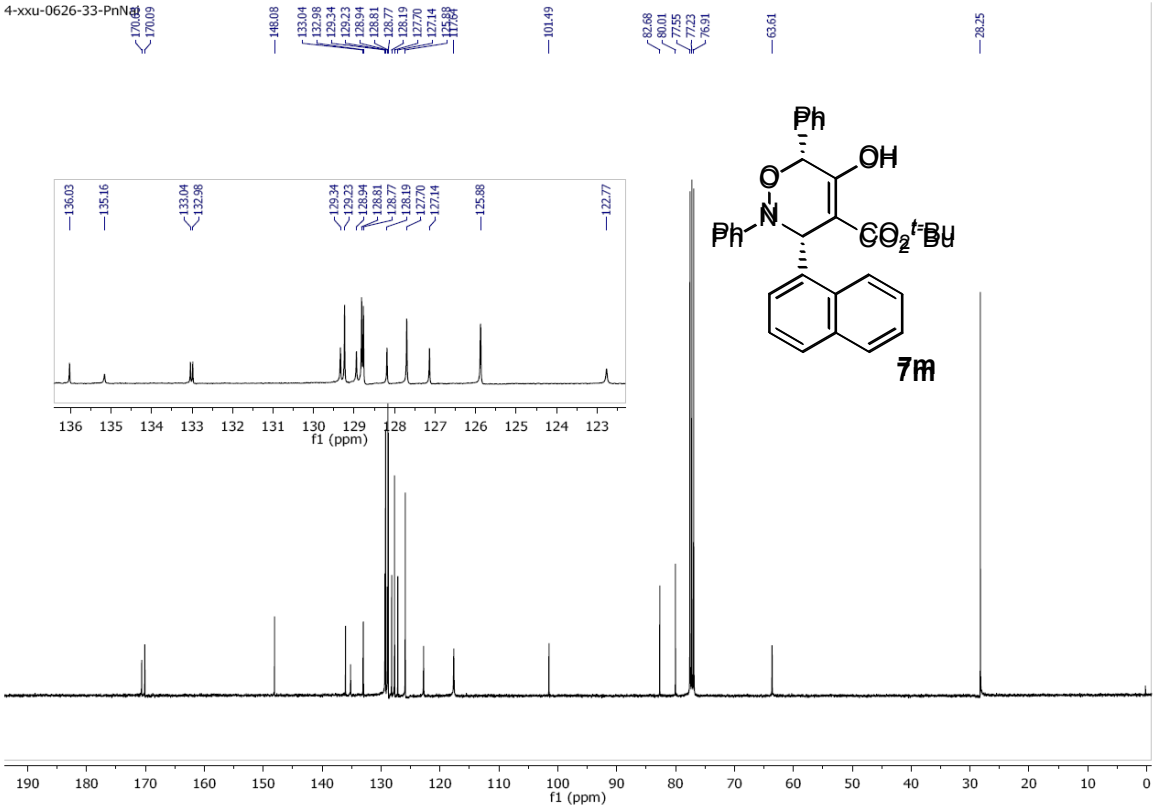
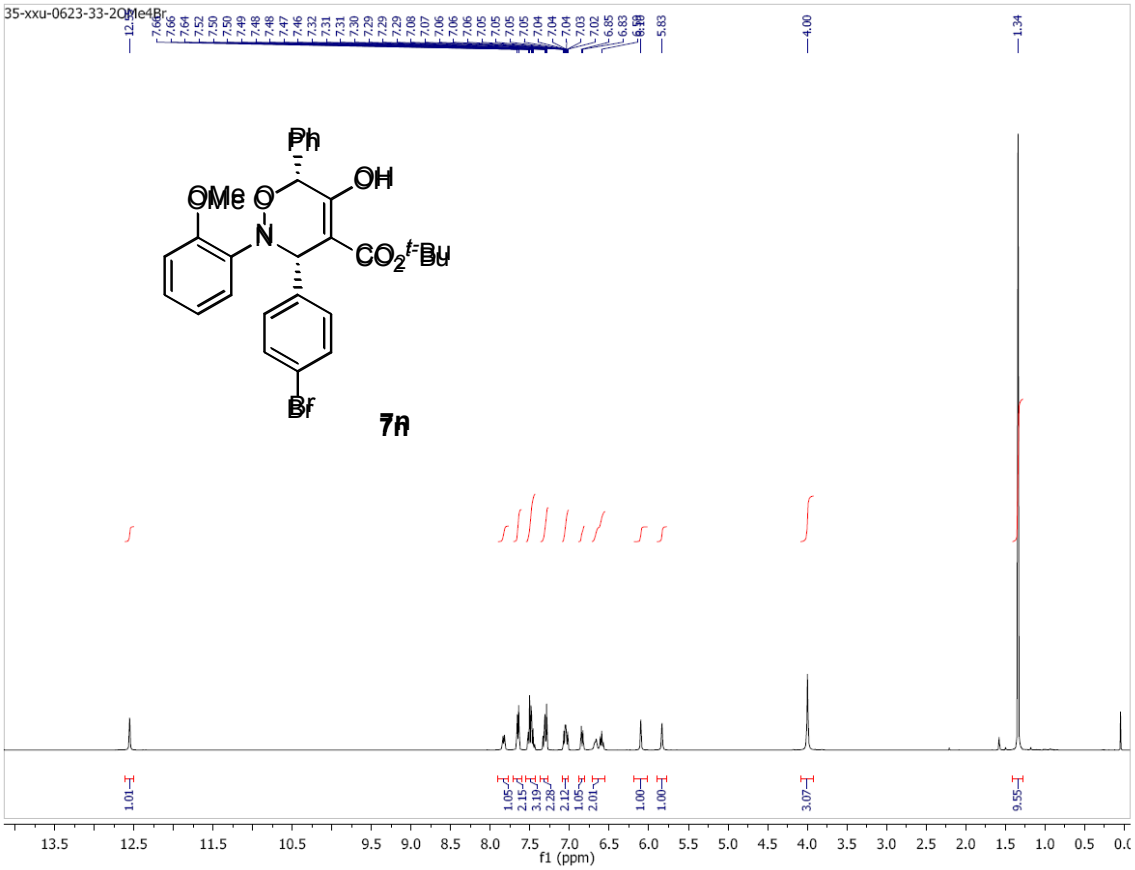
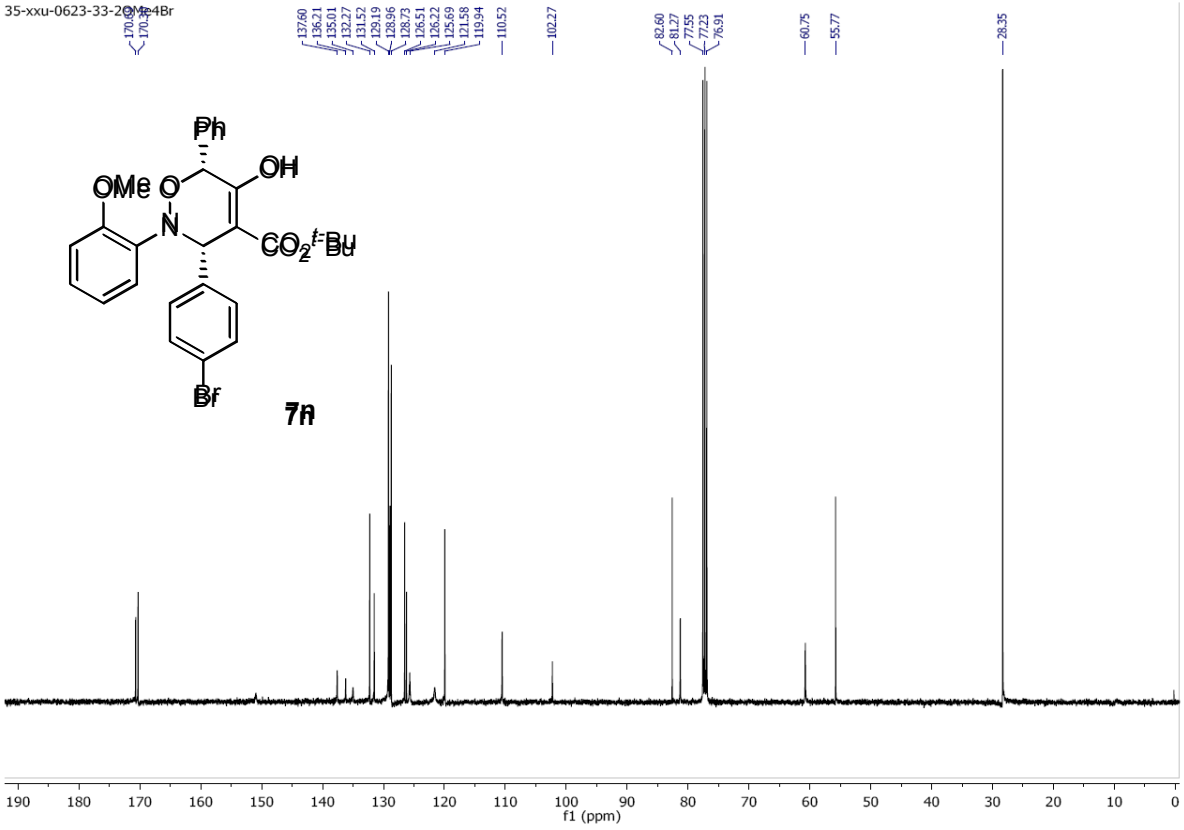
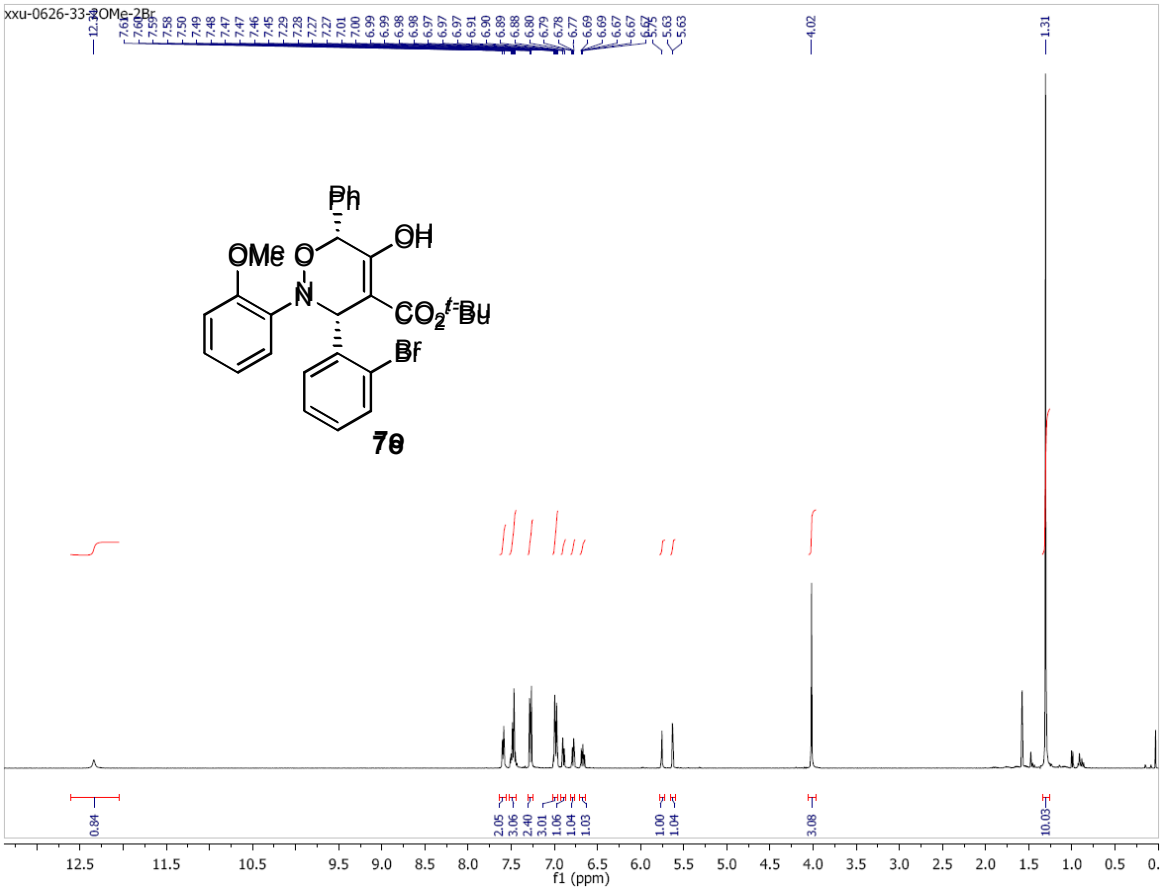
63.39
28.22
Ph
OH
O
N
Ph
CO2t-Bu
F
7l
f1 (ppm)

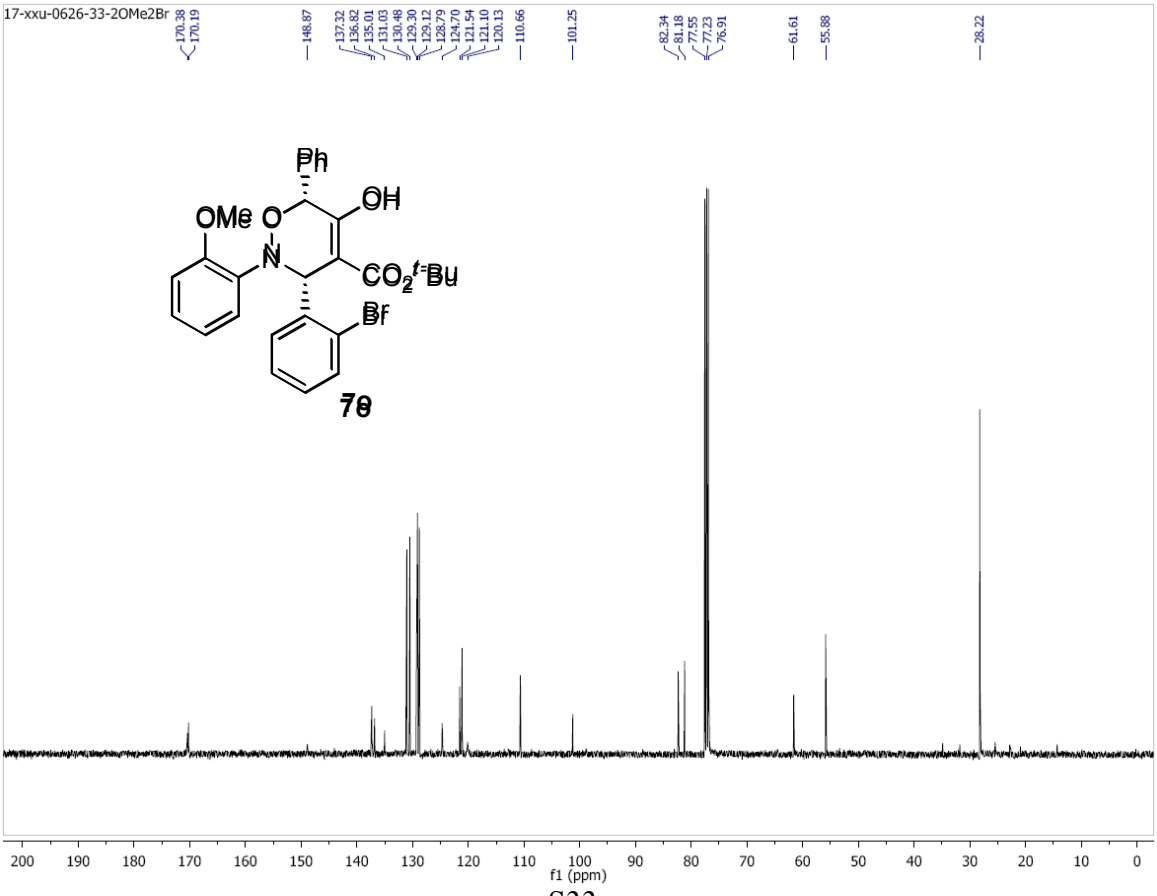

4-xxu-0626-33-PnNai
7m

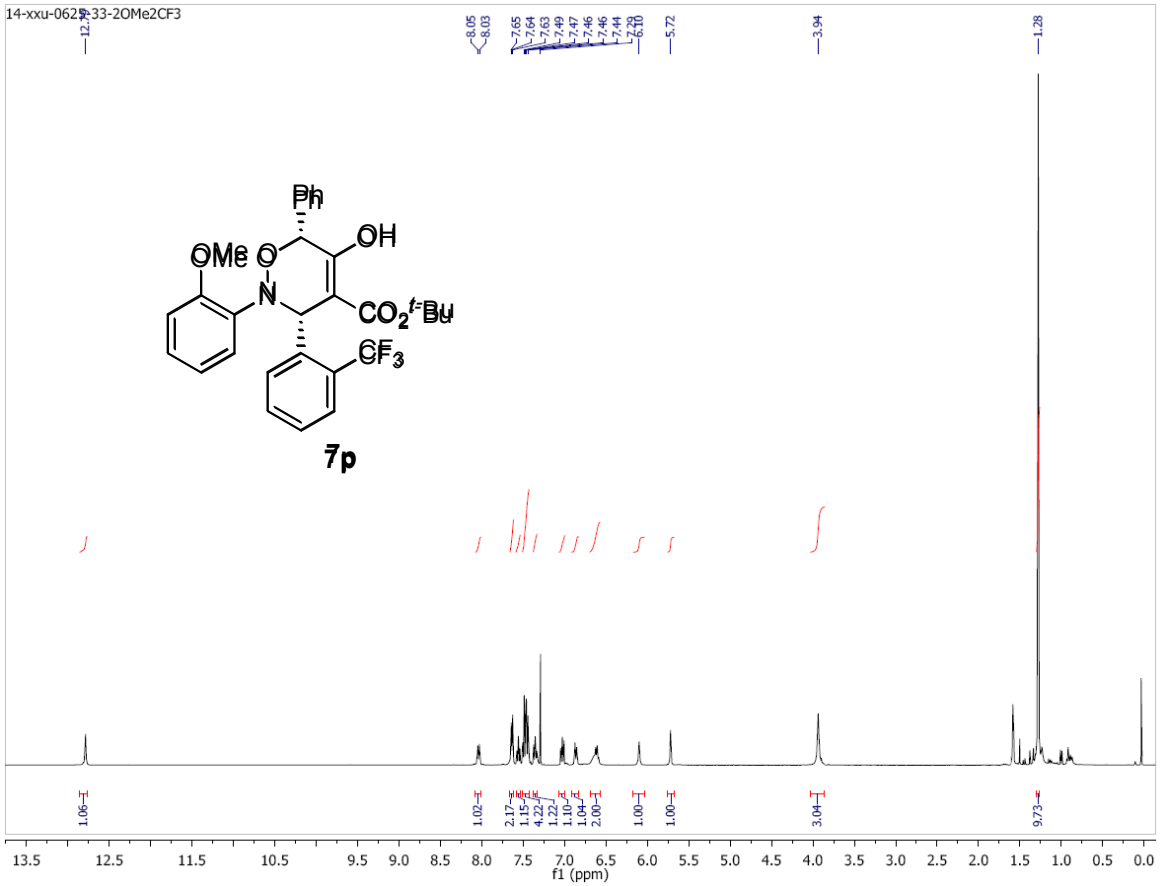

4-xxu-0626-33-PnNai
7m

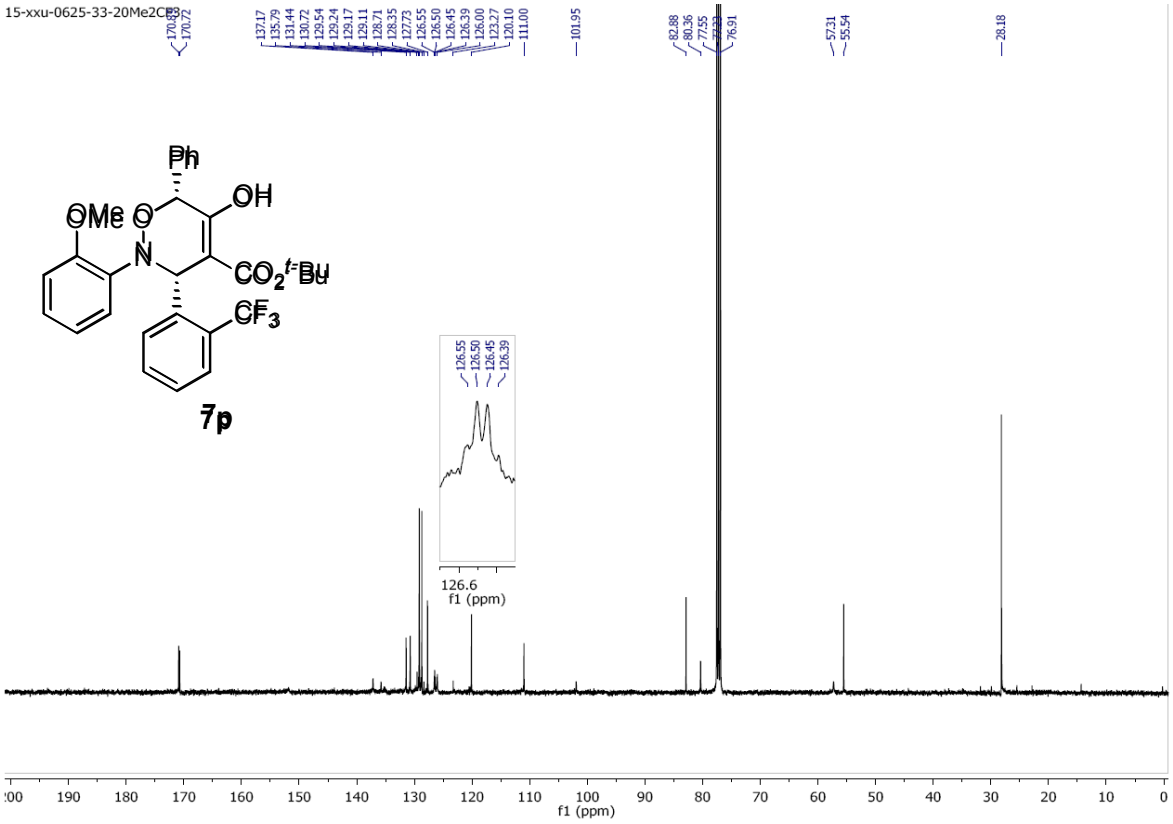

35-xxu-0623-33-2OMe4Br
Ph
OH
OMe O
N
CO2tBu
Br
7n
f1 (ppm)

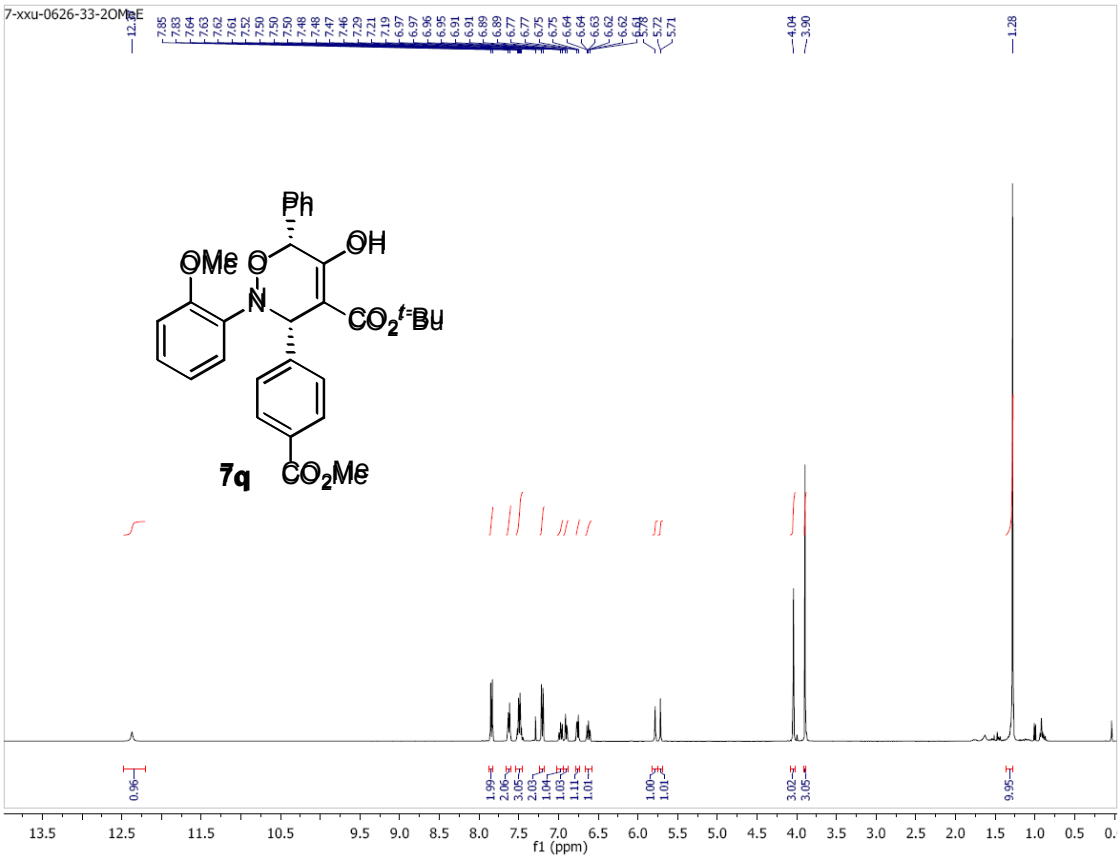

35-xxu-0623-33-2OMe4Br
Ph
OH
OMe O
N
CO2tBu
Br
7n
f1 (ppm)

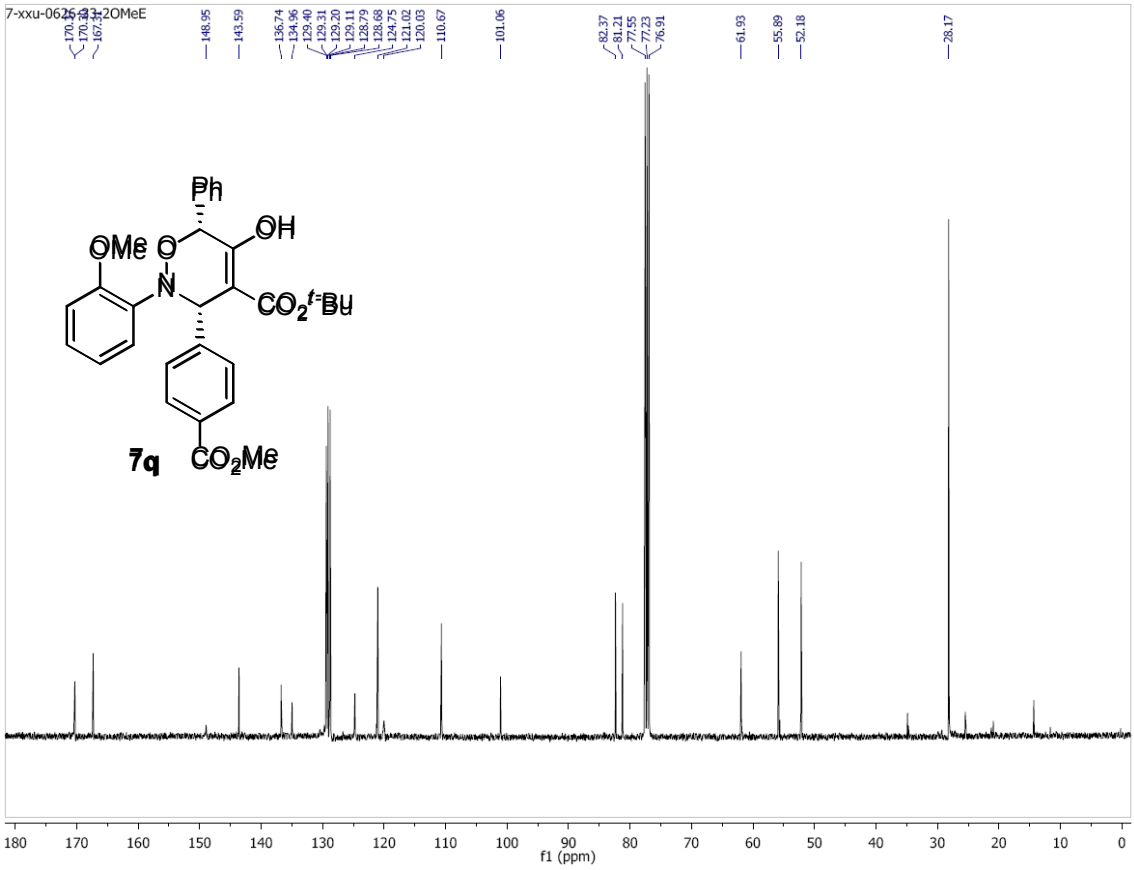

xxu-0626-33-2OMe-2Br
12.32
7.61
7.60
7.59
7.58
7.50
7.49
7.48
7.47
7.47
7.46
7.45
7.29
7.28
7.27
7.27
7.01
7.00
6.99
6.99
6.98
6.97
6.97
6.91
6.90
6.89
6.88
6.80
6.79
6.78
6.77
6.69
6.69
6.67
6.67
5.65
5.63
5.63
4.02
1.31
Ph
OH
OMe
O
N
CO2tBu
Br
7θ
0.84
2.05
3.06
2.40
3.01
1.06
1.04
1.03
1.00
1.04
3.08
10.03
f1 (ppm)

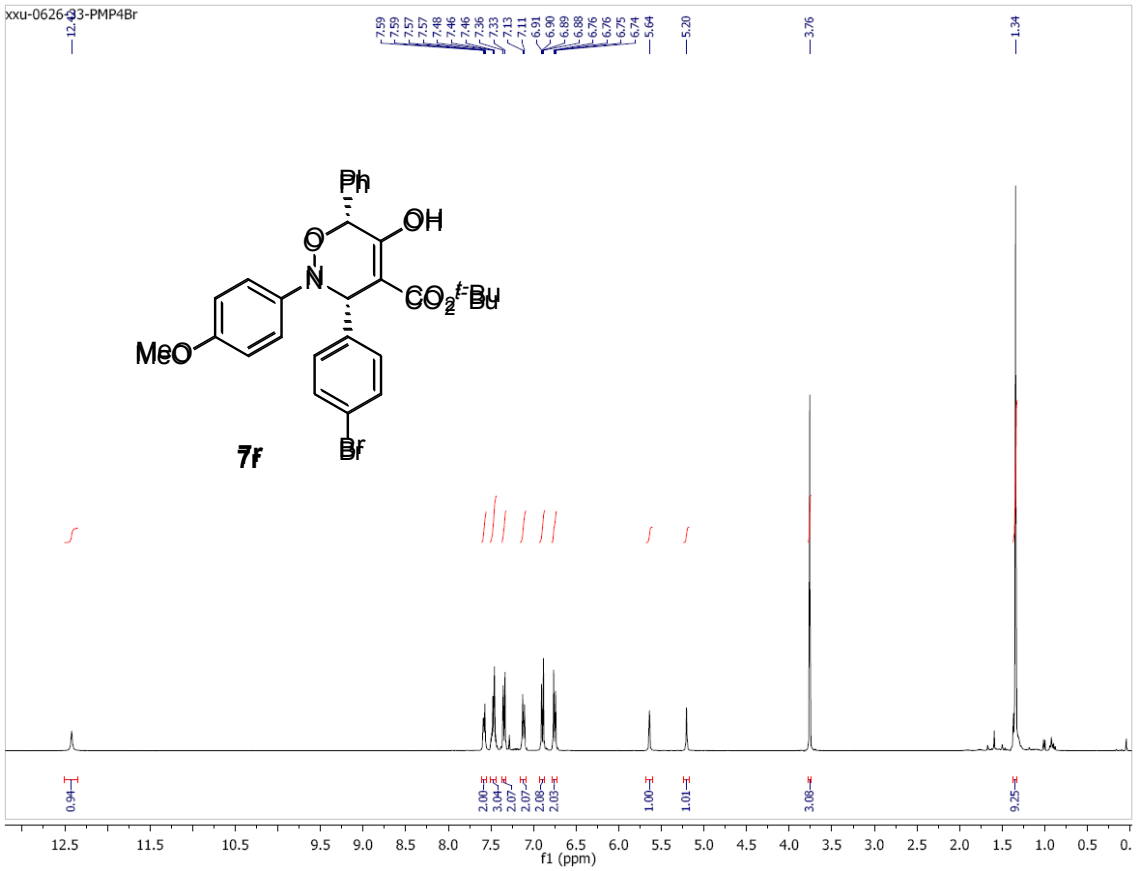

17-xxu-0626-33-2OMe2Br
170.38
170.19
148.87
137.32
136.82
135.01
131.03
130.48
129.30
129.12
128.79
124.70
121.54
121.10
120.13
110.66
101.25
82.34
81.18
77.55
77.23
76.91
61.61
55.88
28.22
Ph
OH
OMe
O
N
CO2tBu
Br
7θ
f1 (ppm)

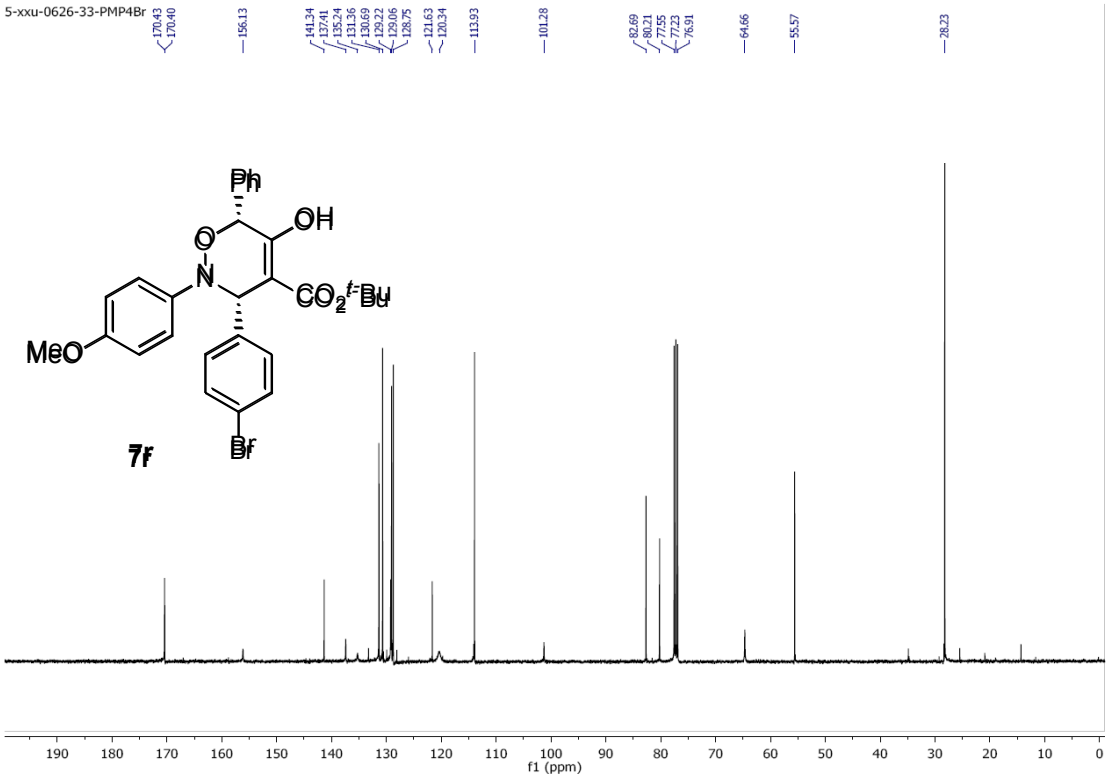

14-xxu-0625-33-2OMe2CF3
Ph
OMe
O
OH
N
CO2t-Bu
CF3
7p
f1 (ppm)

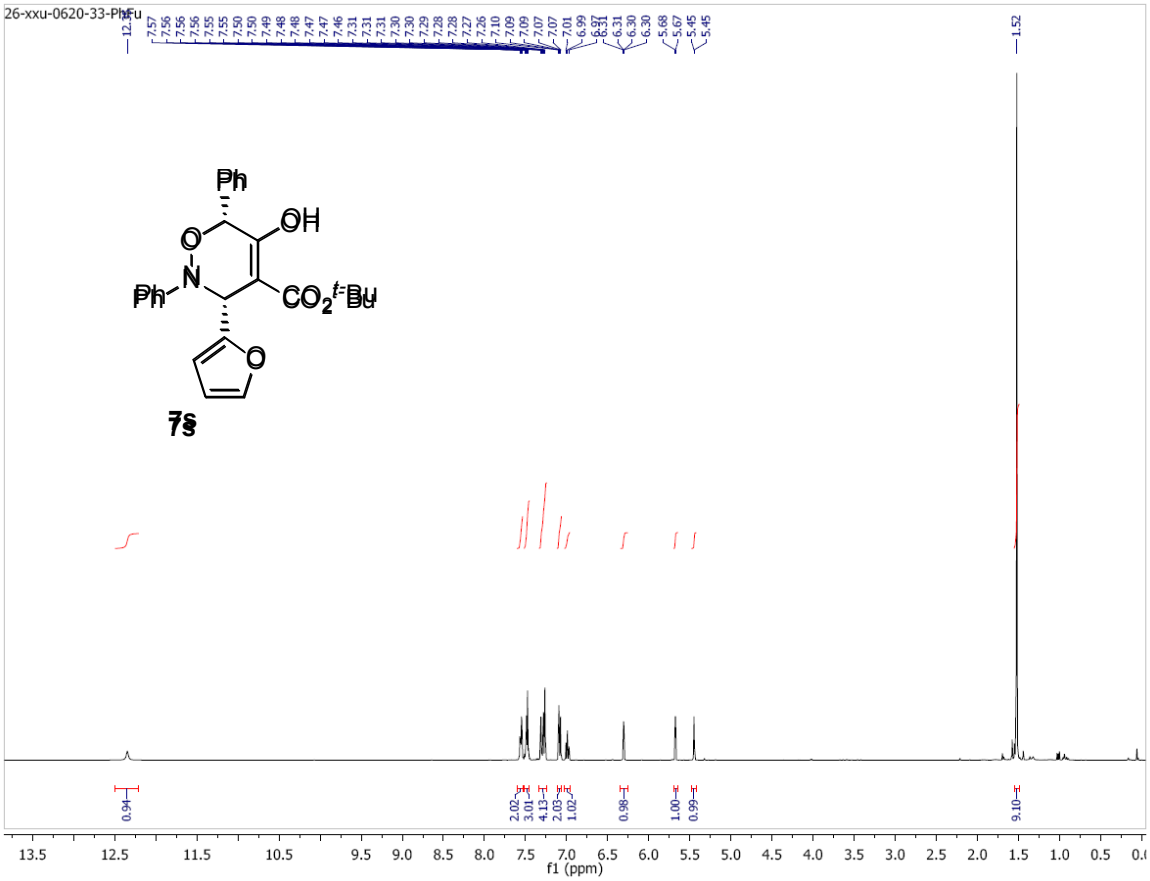

15-xxu-0625-33-20Me2CF3
Ph
OMe
O
OH
N
CO2t-Bu
CF3
7p
126.6
f1 (ppm)

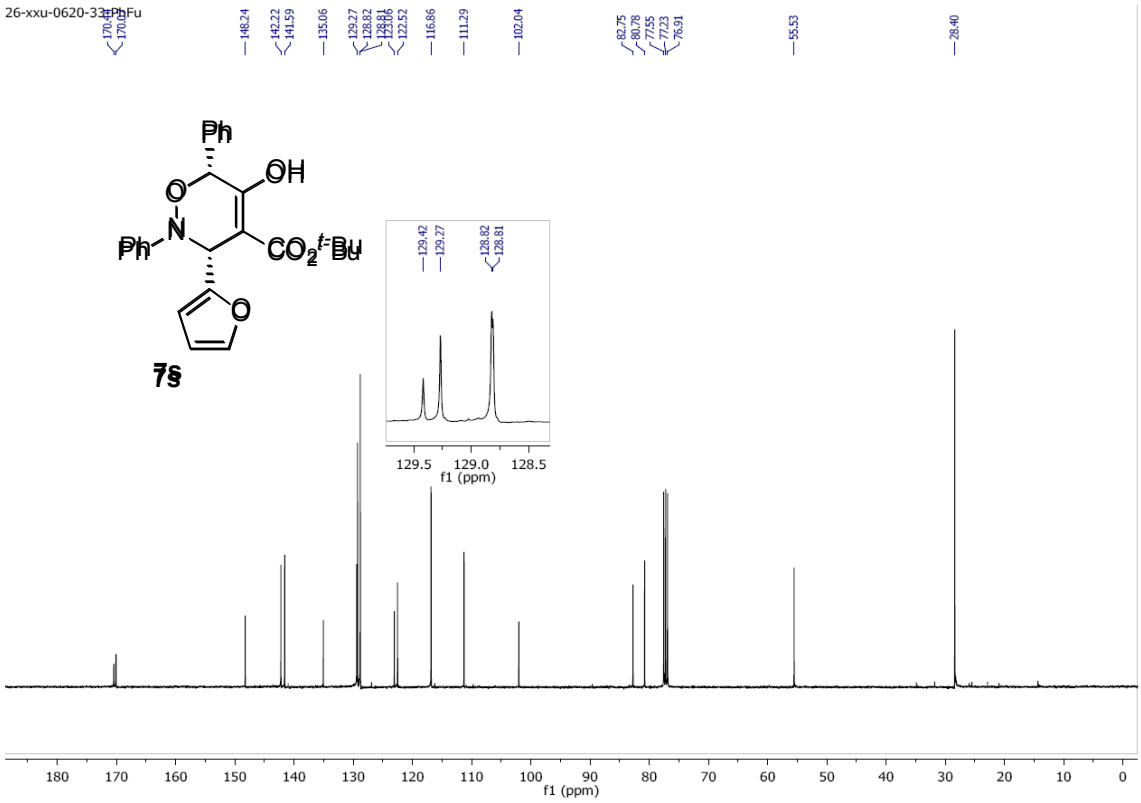

7-xxu-0626-33-2OMeE
Ph
OMe
O
OH
N
CO2tBu
7q
CO2Me
f1 (ppm)

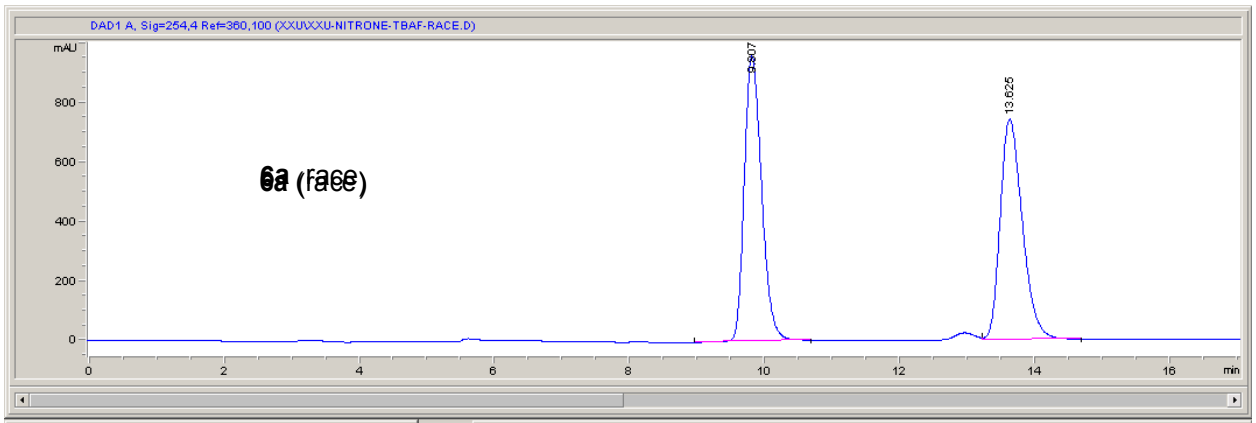

Ph
OMe
O
OH
N
CO2tBu
7q
CO2Me
f1 (ppm)


xxu-0626-33-PMP4Br
12.43
7.59
7.59
7.57
7.57
7.48
7.46
7.46
7.36
7.33
7.13
7.11
6.91
6.90
6.89
6.88
6.76
6.76
6.75
6.74
5.64
5.20
3.76
1.34
Ph
OH
O
N
CO2t-Bu
MeO
Br
7f
0.94
2.00
3.04
2.07
2.07
2.08
2.03
1.00
1.01
3.08
9.25
f1 (ppm)


5-xxu-0626-33-PMP4Br
170.43
170.40
156.13
141.34
137.41
135.24
131.36
130.69
129.22
129.06
128.75
121.63
120.34
113.93
101.28
82.69
80.21
77.55
77.23
76.91
64.66
55.57
28.23
Ph
OH
O
N
CO2t-Bu
MeO
Br
7f
f1 (ppm)

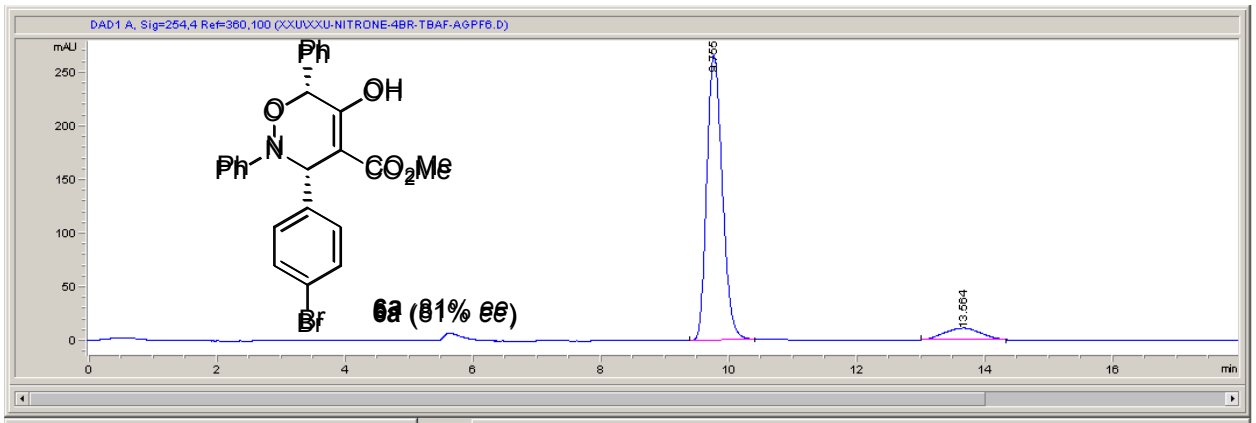

26-xxu-0620-33-PhFu
Ph
OH
O
N
Ph
CO2t-Bu
O
7s
f1 (ppm)


26-xxu-0620-33-PhFu
Ph
OH
O
N
Ph
CO2t-Bu
O
7s
129.42
129.27
128.82
128.81
129.5
129.0
128.5
f1 (ppm)
f1 (ppm)



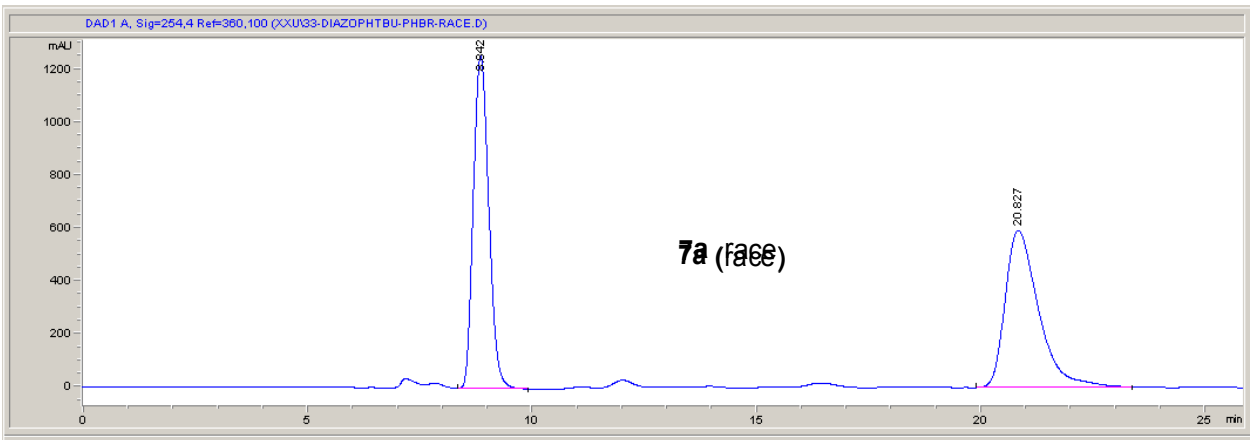
File Information	
LC-File	XXU-NITRONE-TBAF-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	20-May-13, 13:15:01
Sample	IC-3,98:2,0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	34.46 min
Sampling Rate	0.0067 min (0.402 sec), 5170 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.807	17197.9	959.7	0.2791	50.383	0.751
2	13.625	16936.7	741.5	0.3545	49.617	0.698



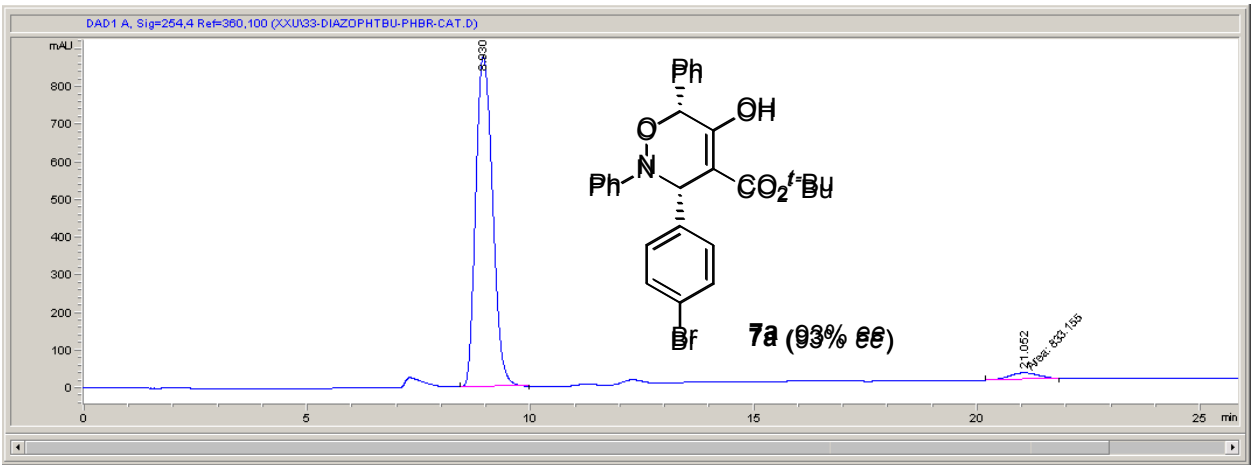
File Information	
LC-File	XXU-NITRONE-4BR-TBAF-AGPF6.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	22-May-13, 10:53:06
Sample	IC-3,98:2,0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	22.493 min
Sampling Rate	0.0067 min (0.402 sec), 3375 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.755	4502.1	265.8	0.2656	90.446	0.784
2	13.564	475.5	11.5	0.6893	9.554	1.114



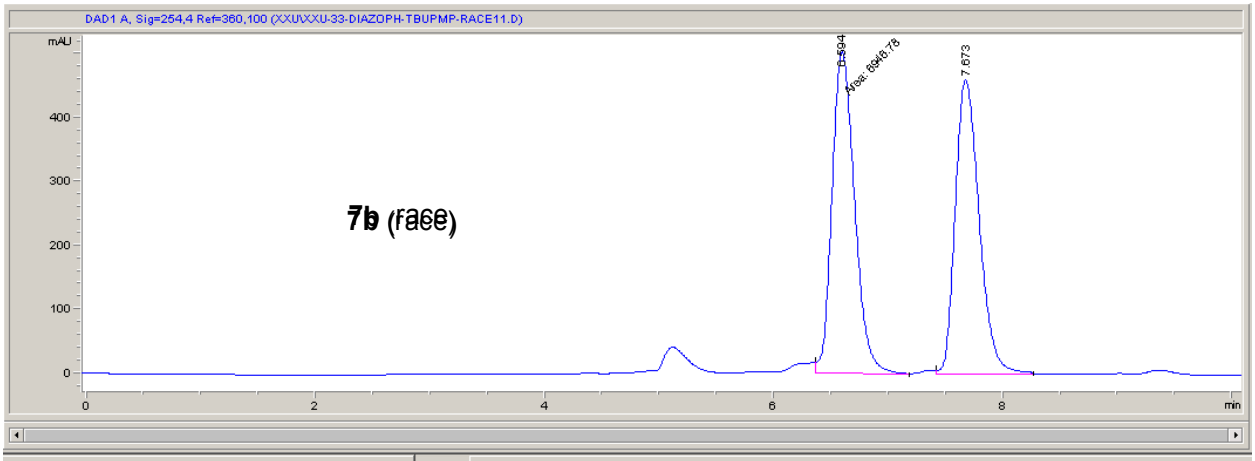
File Information	
LC-File	33-DIAZOPHTBU-PHBR-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	17-Jun-13, 12:26:46
Sample	OD-H,98:2, 0.5
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	44.32 min
Sampling Rate	0.0067 min (0.402 sec), 6649 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	8.842	30107.9	1255.8	0.3797	49.590	0.825
2	20.827	30606.1	592.8	0.7844	50.410	0.595



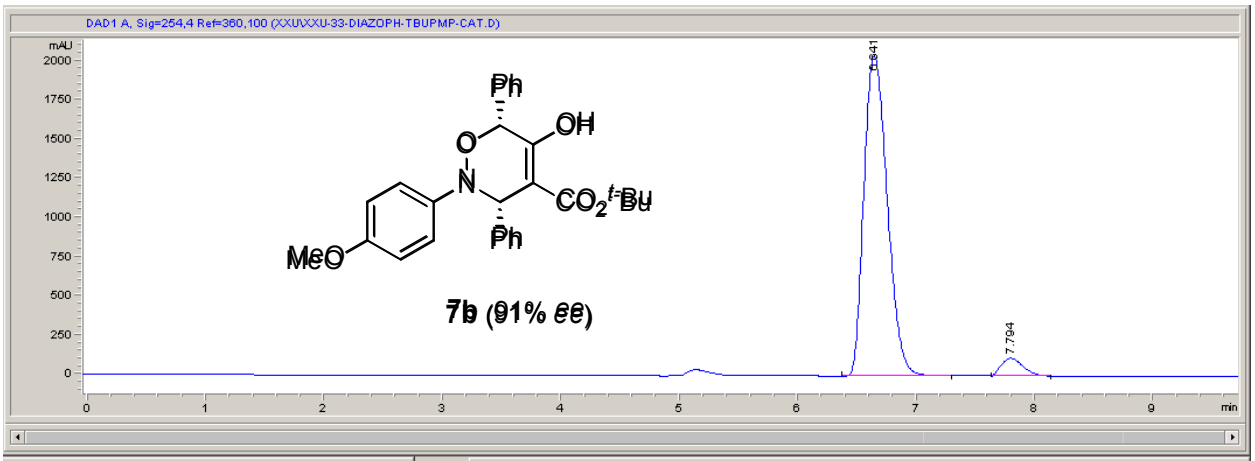
File Information	
LC-File	33-DIAZOPHTBU-PHBR-CAT.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	17-Jun-13, 11:01:11
Sample	OD-H,98:2, 0.5
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	28.633 min
Sampling Rate	0.0067 min (0.402 sec), 4296 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	8.93	23201.8	878.2	0.4242	96.534	0.786
2	21.052	833.2	17.7	0.7824	3.466	0.935



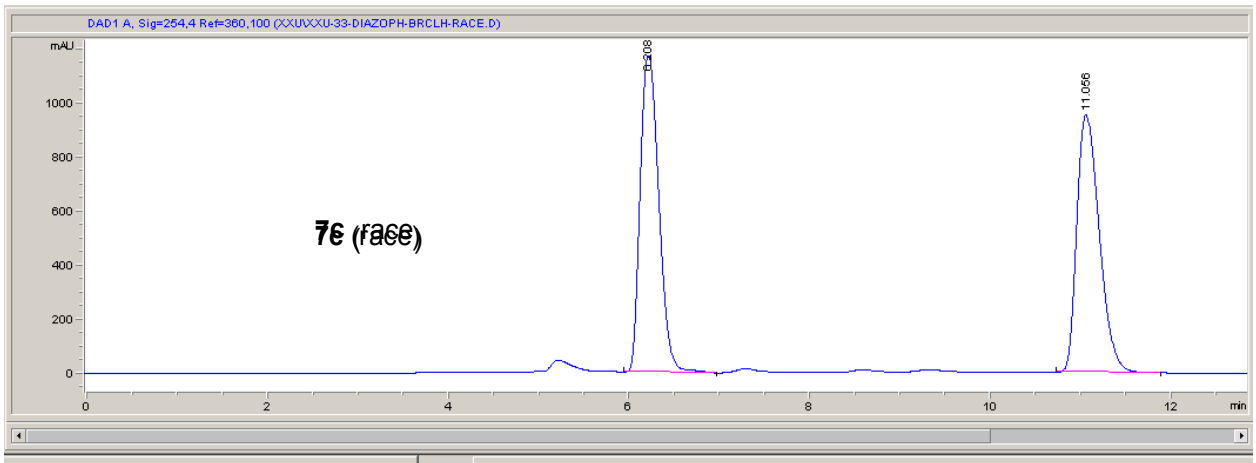
File Information	
LC-File	XXU-33-DIAZOPH-TBUPMP-RACE11.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	07-Jun-13, 11:08:23
Sample	IB-3,96:4, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	10.127 min
Sampling Rate	0.0067 min (0.402 sec), 1520 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.594	6946.8	505.9	0.2289	50.765	0.774
2	7.673	6737.4	461	0.2285	49.235	0.711



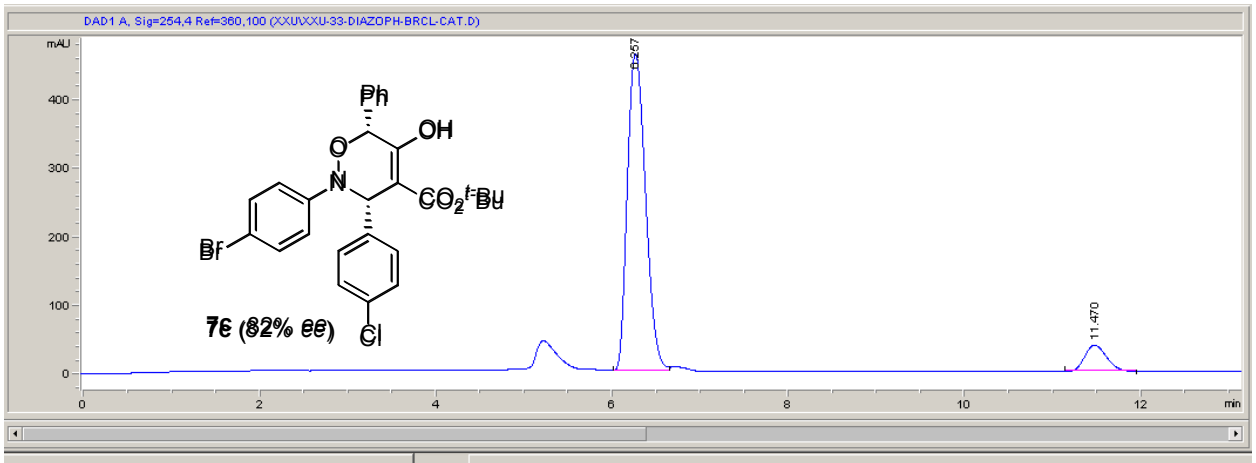
File Information	
LC-File	XXU-33-DIAZOPH-TBUPMP-CAT.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	07-Jun-13, 10:29:04
Sample	IB-3,96:4, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	9.72 min
Sampling Rate	0.0067 min (0.402 sec), 1459 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.641	27983.9	2043	0.2178	95.301	0.722
2	7.794	1379.9	110.4	0.2084	4.699	0.728



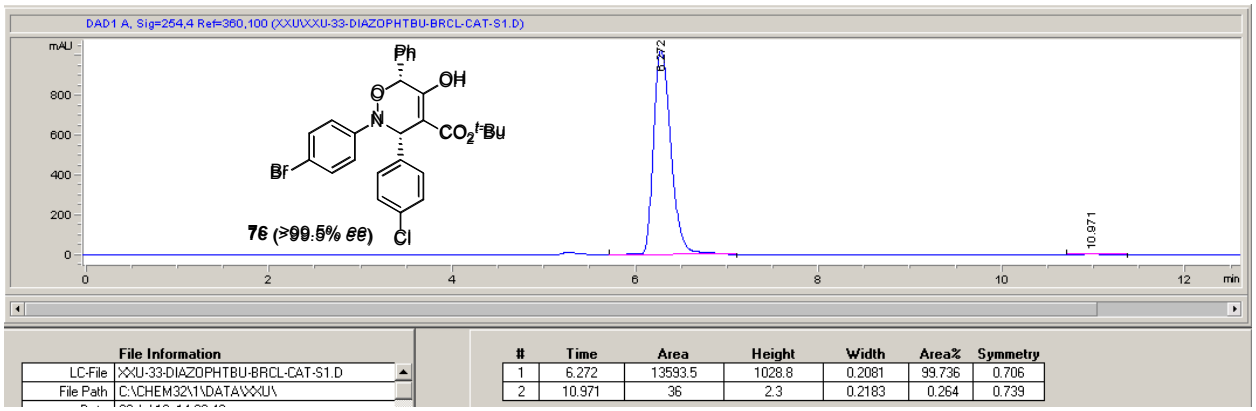
File Information	
LC-File	XXU-33-DIAZOPH-BRCLH-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	11-Jun-13, 17:06:36
Sample	IB-3, 97:3, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	16.127 min
Sampling Rate	0.0067 min (0.402 sec), 2420 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.208	16724.8	1169	0.2289	50.384	0.732
2	11.056	16469.7	951.1	0.272	49.616	0.659



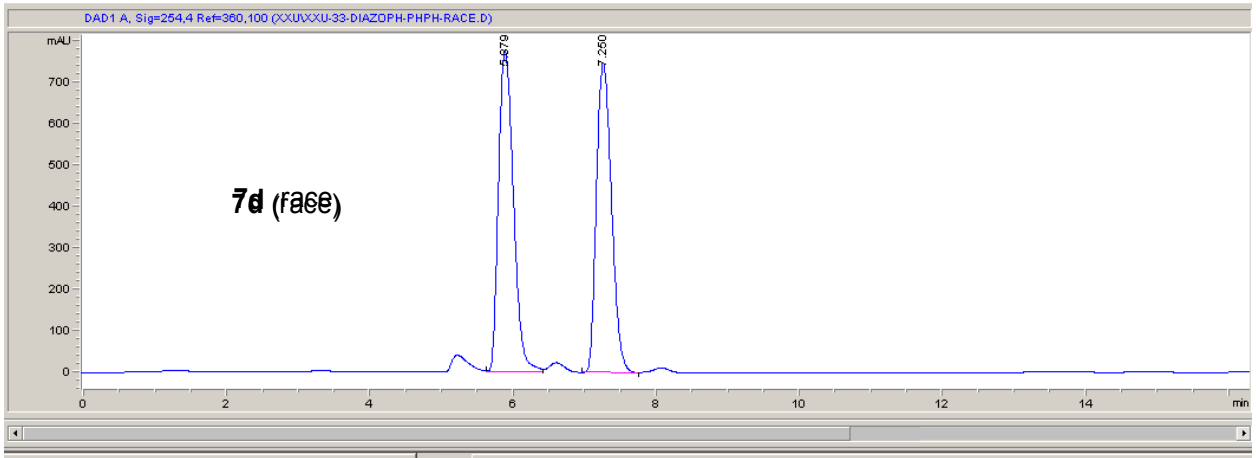
File Information	
LC-File	XXU-33-DIAZOPH-BRCL-CAT.D
File Path	C:\CHEM32\1\DATA\XXU\

#	Time	Area	Height	Width	Area%	Symmetry
1	6.257	6663.3	462.1	0.2302	91.100	0.752
2	11.47	650.9	38	0.2699	8.900	0.805



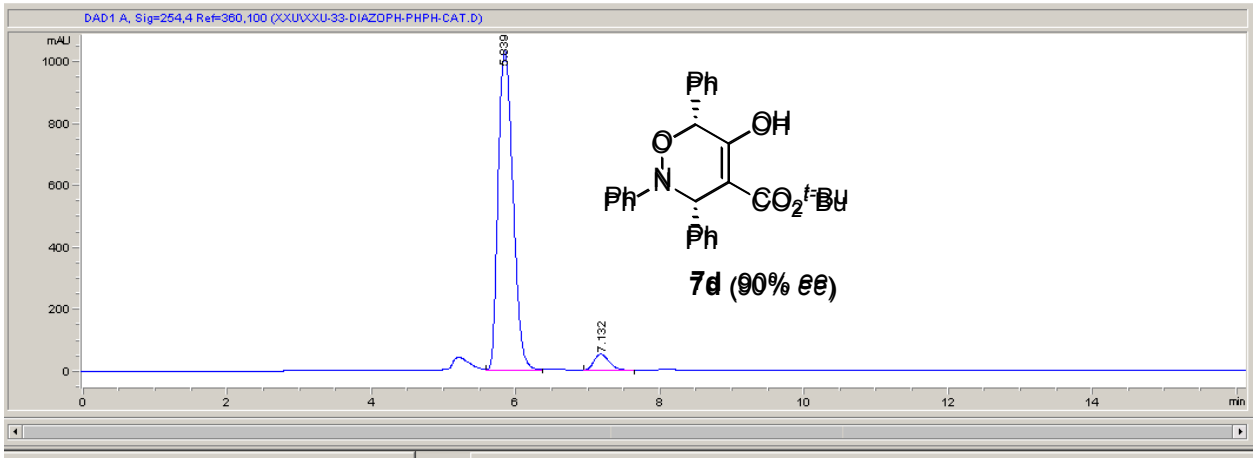
File Information	
LC-File	XXU-33-DIAZOPHTBU-BRCL-CAT-S1.D
File Path	C:\CHEM32\1\DATA\XXU\

#	Time	Area	Height	Width	Area%	Symmetry
1	6.272	13593.5	1028.8	0.2081	99.736	0.706
2	10.971	36	2.3	0.2183	0.264	0.739



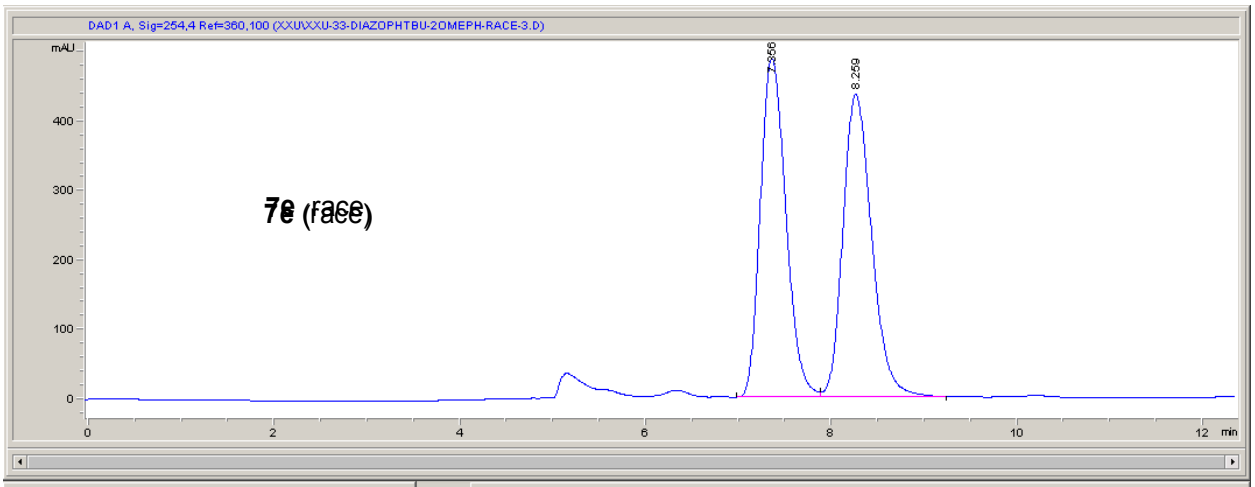
File Information	
LC-File	XXU-33-DIAZOPH-PHPH-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	12-Jun-13, 11:11:31
Sample	IB-3, 97:3, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	23.953 min
Sampling Rate	0.0067 min (0.402 sec), 3594 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	5.879	11291.5	776	0.2318	50.845	0.724
2	7.25	10916.2	747.9	0.2323	49.155	0.754



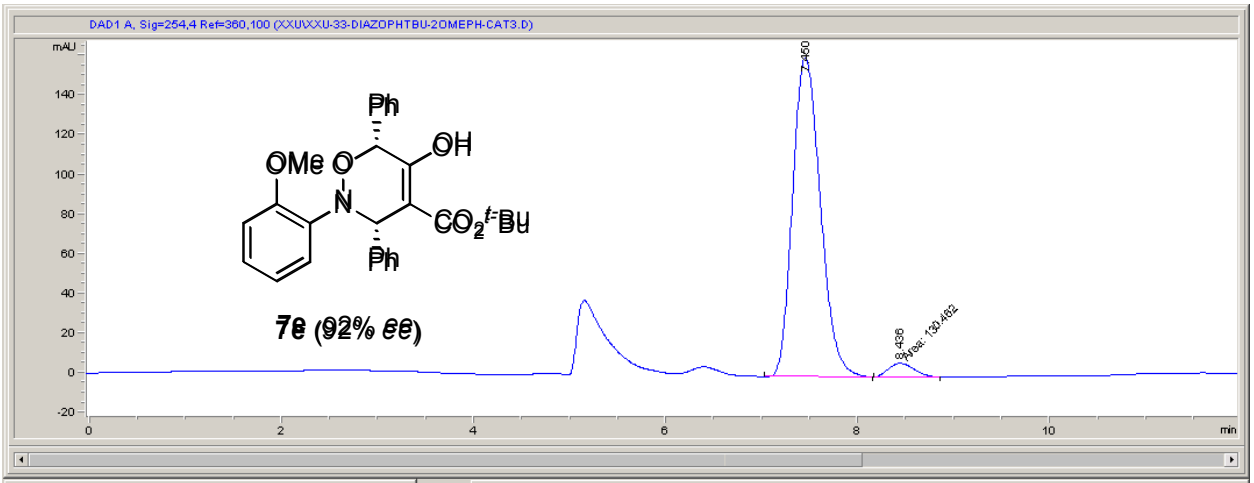
File Information	
LC-File	XXU-33-DIAZOPH-PHPH-CAT.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	12-Jun-13, 10:22:49
Sample	IB-3, 97:3, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	13.987 min
Sampling Rate	0.0067 min (0.402 sec), 2099 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	5.839	14853.3	1034.8	0.2295	94.924	0.743
2	7.132	794.3	52.3	0.253	5.076	0.742



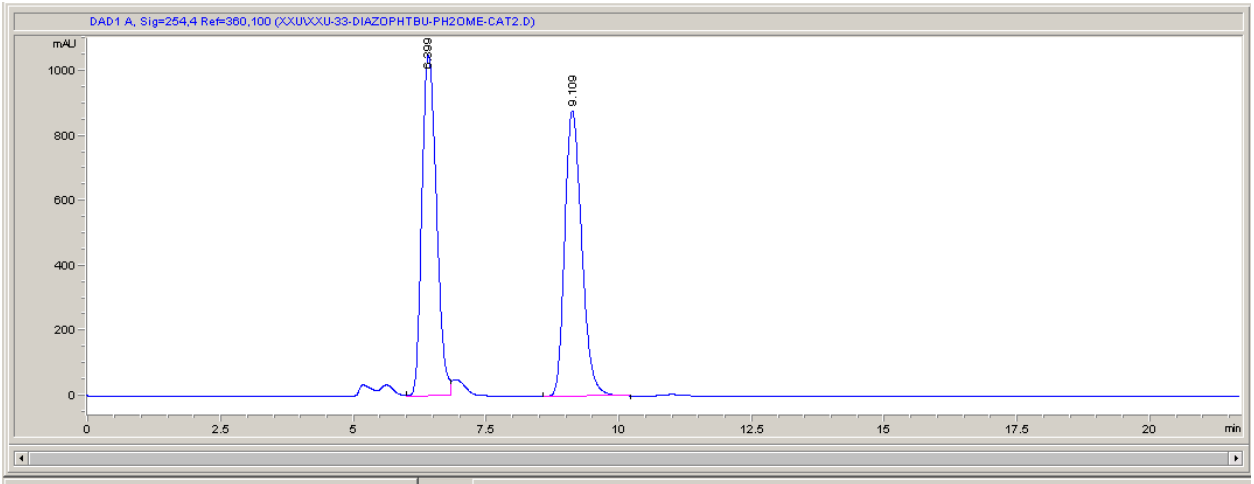
File Information	
LC-File	XXU-33-DIAZOPHTBU-2OMEPH-RACE-3.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	13-Jun-13, 14:25:32
Sample	OD-H, 98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	12.387 min
Sampling Rate	0.0067 min (0.402 sec), 1859 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.356	9324	487.3	0.3012	49.810	0.782
2	8.259	9395.2	436.4	0.3352	50.190	0.754



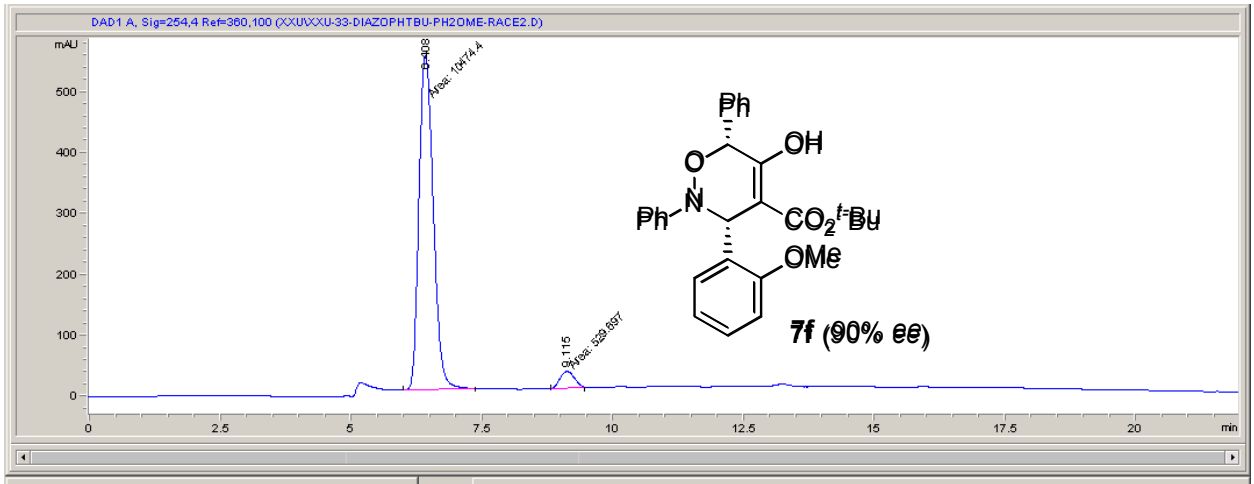
File Information	
LC-File	XXU-33-DIAZOPHTBU-2OMEPH-CAT3.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	13-Jun-13, 14:06:06
Sample	OD-H, 98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	17.18 min
Sampling Rate	0.0067 min (0.402 sec), 2578 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.45	3235.8	160.9	0.3186	96.124	0.791
2	8.436	130.5	7	0.3125	3.876	0.813



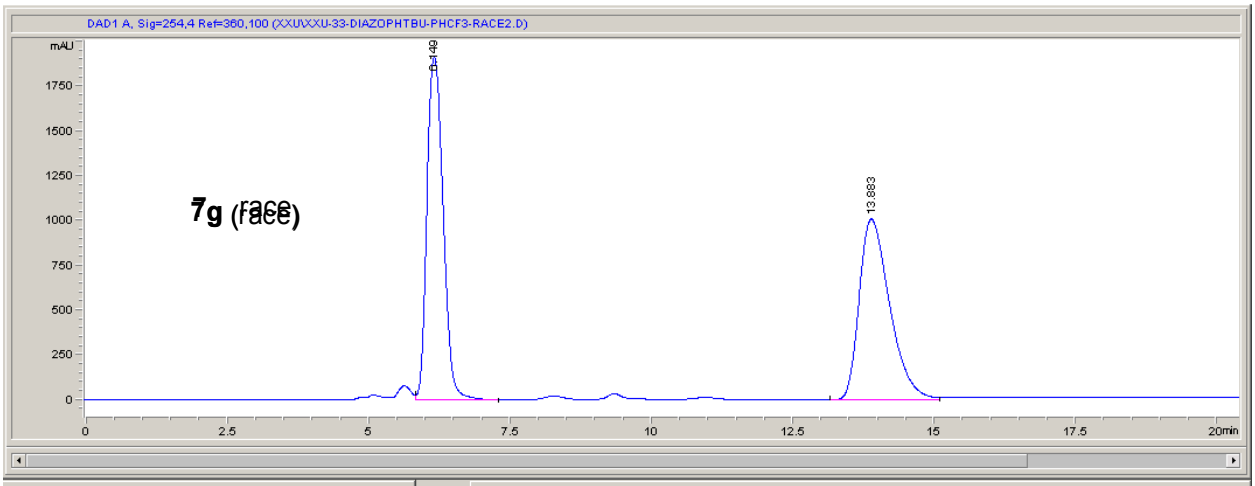
File Information	
LC-File	XXU-33-DIAZOPHTBU-PH2OME-CAT2.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	13-Jun-13, 15:00:35
Sample	OD-H, 98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	21.733 min
Sampling Rate	0.0067 min (0.402 sec), 3261 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.399	20165.7	1052.8	0.3055	50.627	0.758
2	9.109	19665.9	879.9	0.3487	49.373	0.748



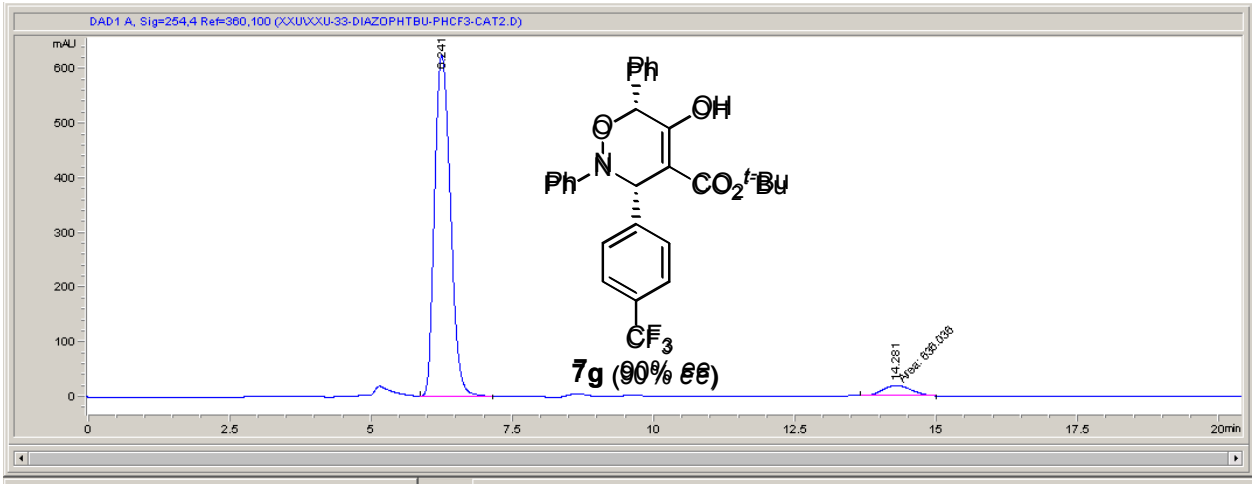
File Information	
LC-File	XXU-33-DIAZOPHTBU-PH2OME-RACE2.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	13-Jun-13, 13:40:48
Sample	OD-H, 98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	22 min
Sampling Rate	0.0067 min (0.402 sec), 3301 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.408	10474.4	548.8	0.3181	95.186	0.774
2	9.115	529.7	27.5	0.321	4.814	0.906



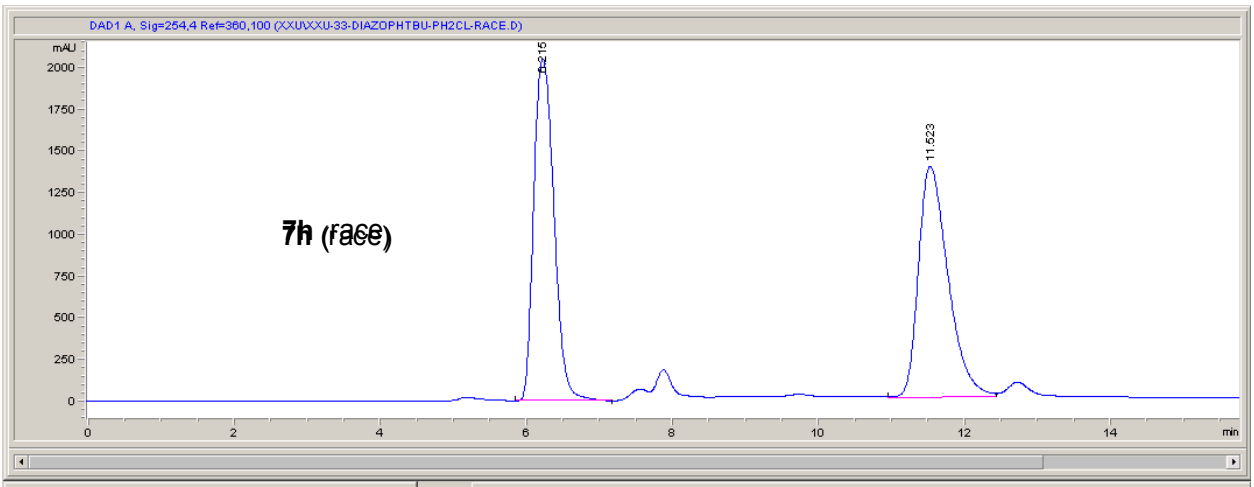
File Information	
LC-File	XXU-33-DIAZOPHTBU-PHCF3-RACE2.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	13-Jun-13, 13:15:04
Sample	OD-H, 98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	24.48 min
Sampling Rate	0.0067 min (0.402 sec), 3673 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.149	38173.6	1913.3	0.3208	50.170	0.748
2	13.883	37914.9	1008.9	0.5784	49.830	0.616



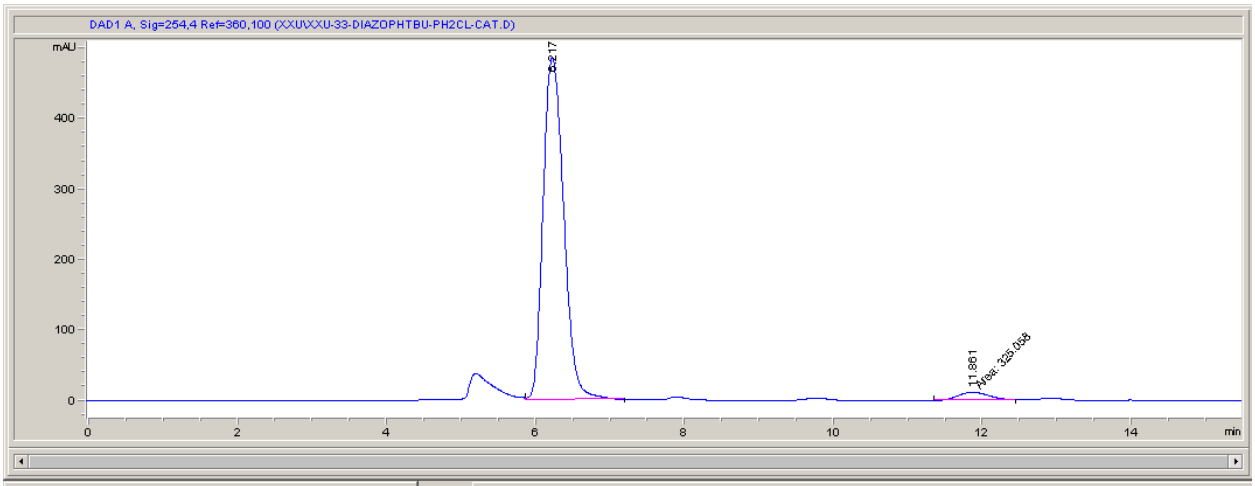
File Information	
LC-File	XXU-33-DIAZOPHTBU-PHCF3-CAT2.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	13-Jun-13, 12:53:45
Sample	OD-H, 98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	20.4 min
Sampling Rate	0.0067 min (0.402 sec), 3061 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.241	12226.3	625.8	0.3119	95.055	0.764
2	14.281	636	18.5	0.5721	4.945	0.859



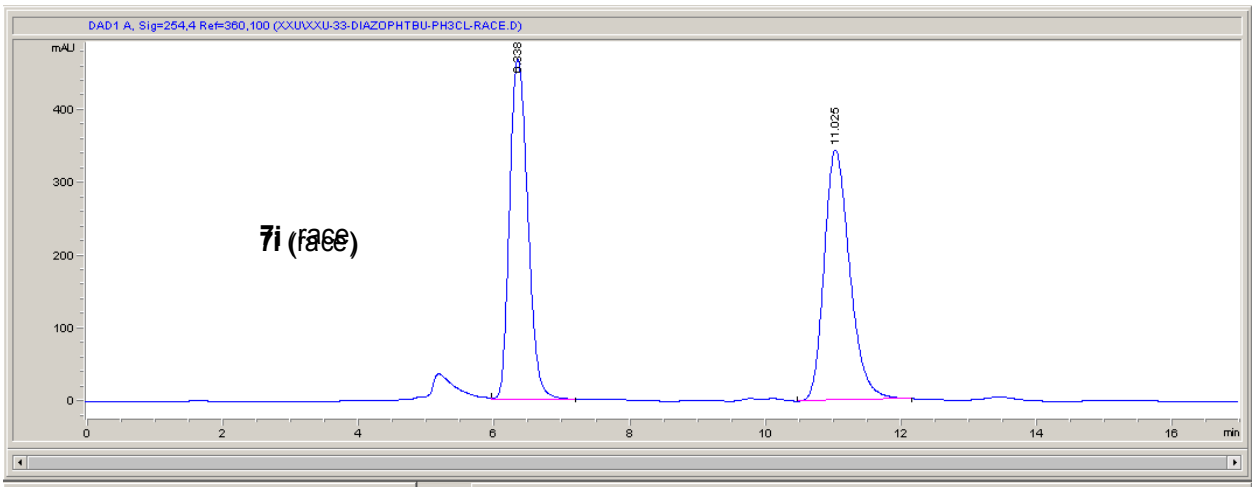
File Information	
LC-File	XXU-33-DIAZOPHTBU-PH2CL-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	14-Jun-13, 10:15:34
Sample	OD-H, 98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	18.647 min
Sampling Rate	0.0067 min (0.402 sec), 2798 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.215	39438.1	2048.9	0.3086	50.072	0.75
2	11.523	39325.1	1387.9	0.4346	49.928	0.617



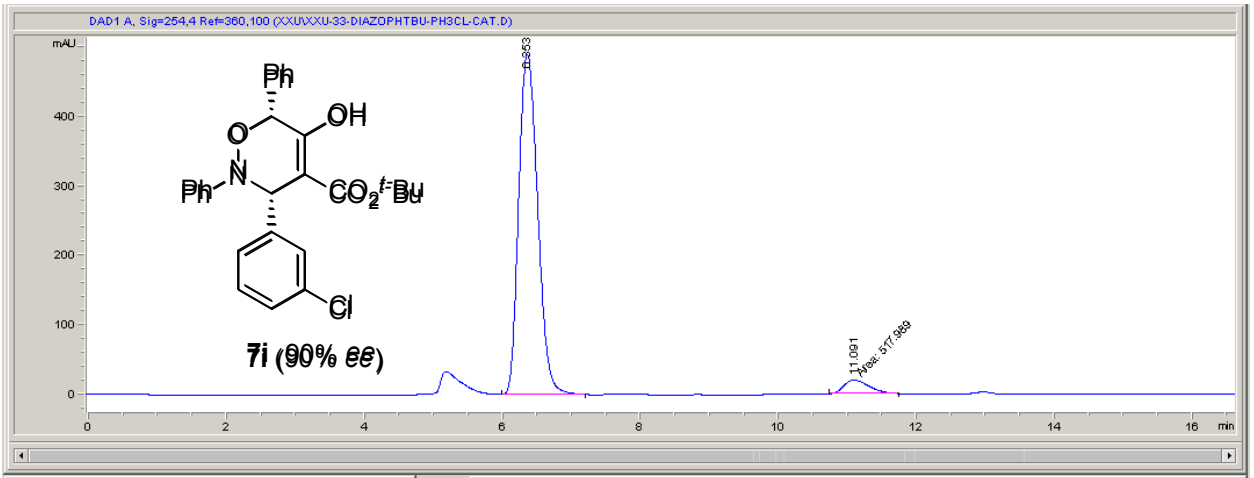
File Information	
LC-File	XXU-33-DIAZOPHTBU-PH2CL-CAT.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	14-Jun-13, 11:35:24
Sample	OD-H, 98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	15.52 min
Sampling Rate	0.0067 min (0.402 sec), 2329 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.217	9367.1	485.2	0.3093	96.646	0.75
2	11.861	325.1	11.4	0.4769	3.354	0.917



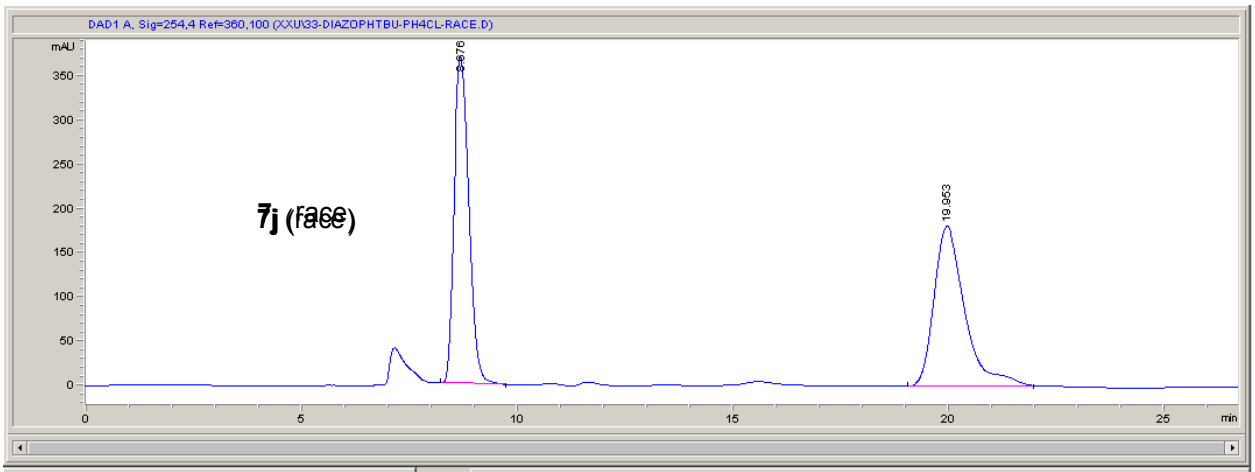
File Information	
LC-File	XXU-33-DIAZOPHTBU-PH3CL-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	14-Jun-13, 10:35:35
Sample	OD-H, 98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	17.007 min
Sampling Rate	0.0067 min (0.402 sec), 2552 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.338	8759.3	467.9	0.2964	49.138	0.77
2	11.025	9066.6	344.2	0.4053	50.862	0.732



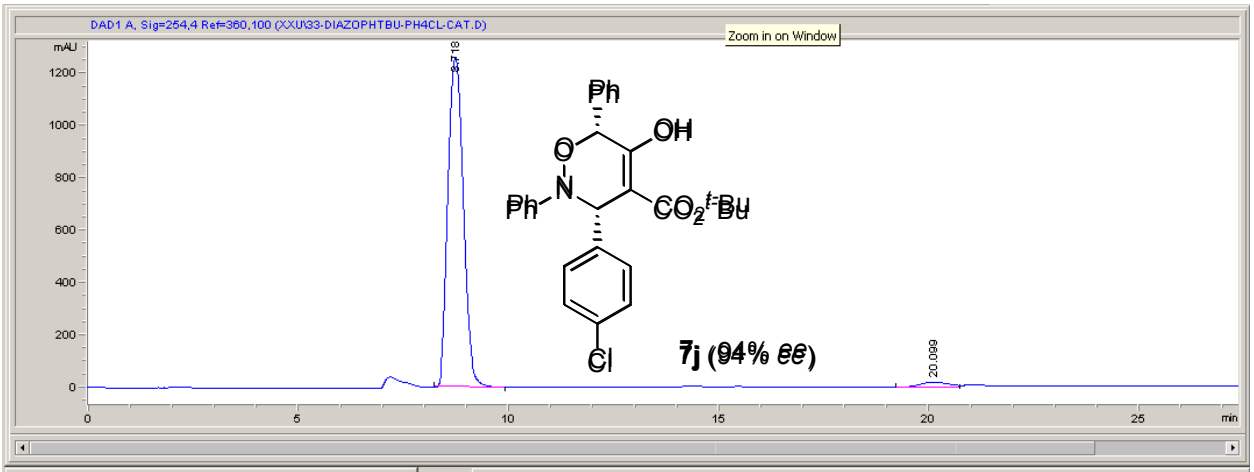
File Information	
LC-File	XXU-33-DIAZOPHTBU-PH3CL-CAT.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	14-Jun-13, 11:52:28
Sample	OD-H, 98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	16.66 min
Sampling Rate	0.0067 min (0.402 sec), 2500 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.353	9412.7	490.3	0.306	94.784	0.768
2	11.091	518	20.1	0.4302	5.216	0.663



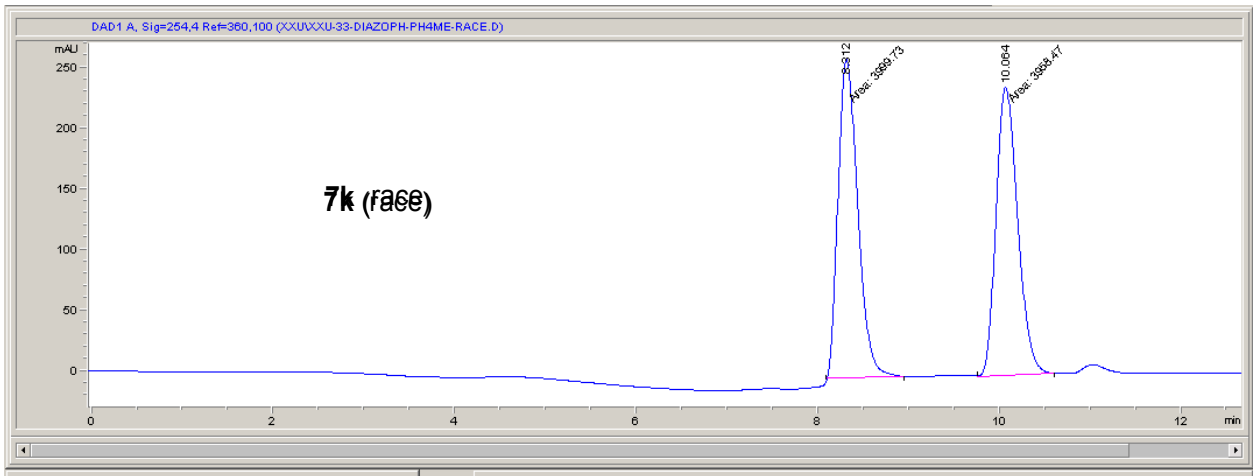
File Information	
LC-File	33-DIAZOPHTBU-PH4CL-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	17-Jun-13, 13:47:15
Sample	OD-H,98:2, 0.5
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	26.773 min
Sampling Rate	0.0067 min (0.402 sec), 4017 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	8.676	9086.7	369.1	0.3952	50.077	0.784
2	19.953	9058.9	180.6	0.7591	49.923	0.659



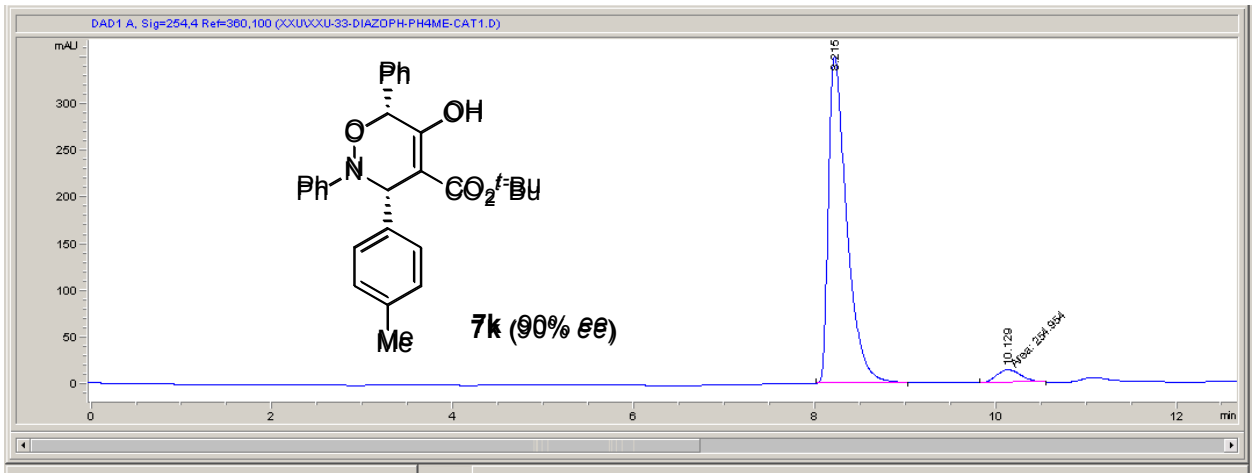
File Information	
LC-File	33-DIAZOPHTBU-PH4CL-CAT.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	17-Jun-13, 13:12:06
Sample	OD-H,98:2, 0.5
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	30.747 min
Sampling Rate	0.0067 min (0.402 sec), 4613 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	8.718	31523.3	1259.9	0.4019	96.982	0.883
2	20.099	981.1	20.5	0.5971	3.018	0.931



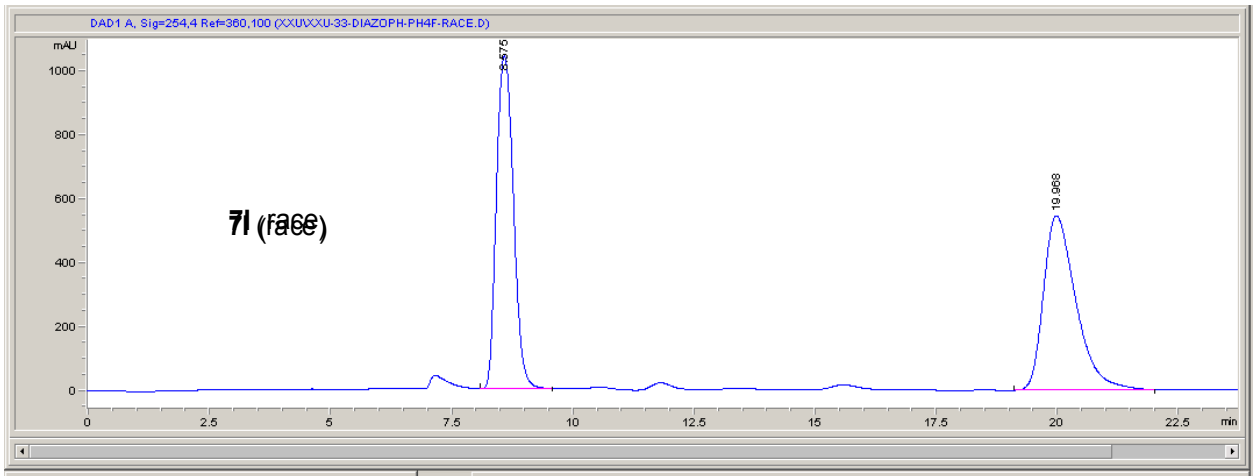
File Information	
LC-File	XXU-33-DIAZOPH-PH4ME-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	20-Jun-13, 13:59:09
Sample	IB-3, 98:1:1, 0.5
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	13.84 min
Sampling Rate	0.0067 min (0.402 sec), 2077 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	8.312	3999.7	263.1	0.2534	50.259	0.717
2	10.064	3958.5	237.9	0.2773	49.741	0.765



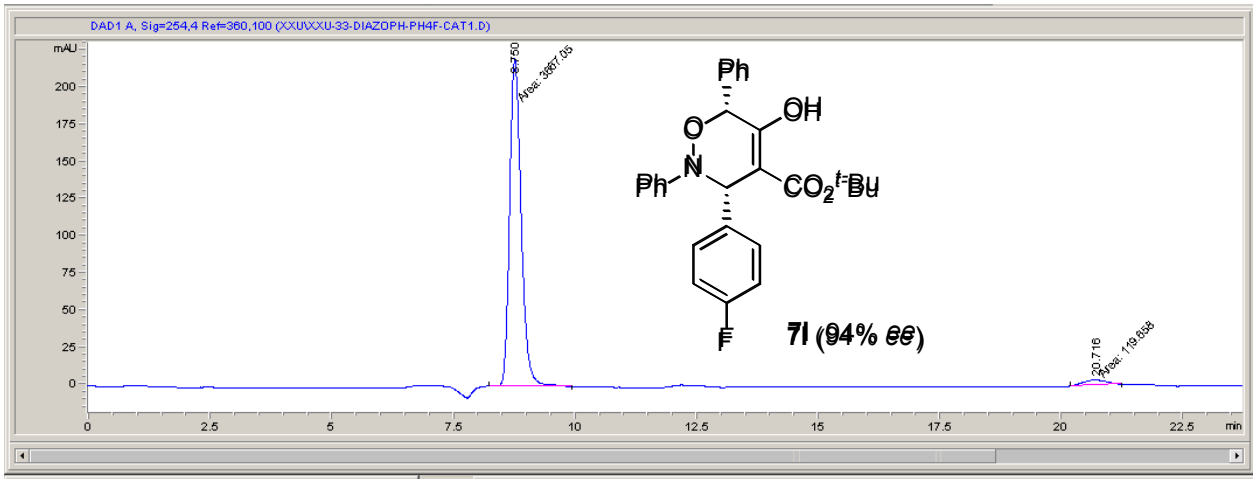
File Information	
LC-File	XXU-33-DIAZOPH-PH4ME-CAT1.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	20-Jun-13, 13:10:56
Sample	IB-3, 98:1:1, 0.5
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	22.627 min
Sampling Rate	0.0067 min (0.402 sec), 3395 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	8.215	4929.3	350.2	0.2122	95.082	0.472
2	10.129	255	13.6	0.3132	4.918	0.794



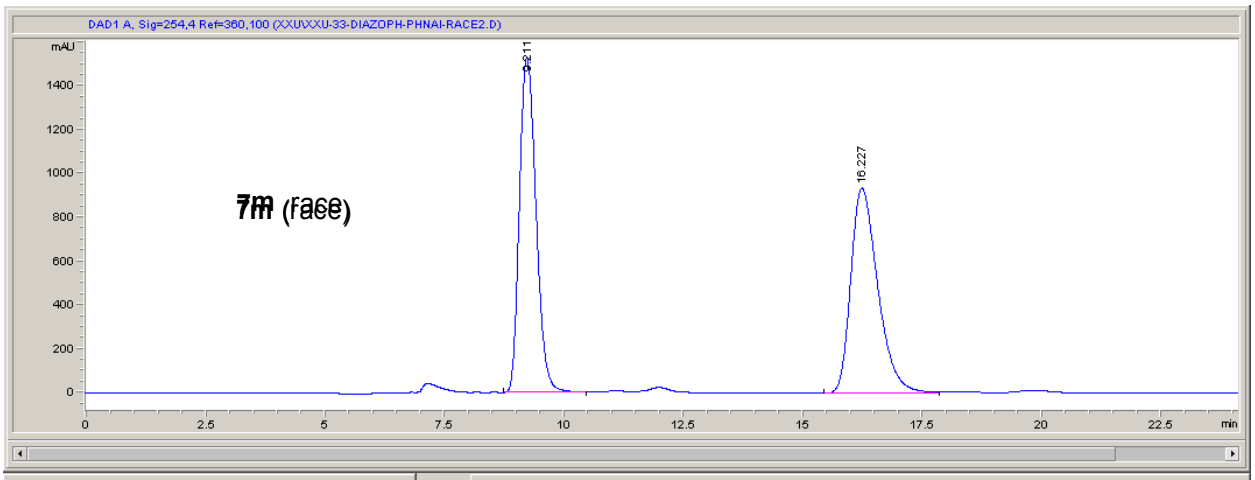
File Information	
LC-File	XXU-33-DIAZOPH-PH4F-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	19-Jun-13, 13:04:24
Sample	OD-H, 98:2. 0.5
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	26.213 min
Sampling Rate	0.0067 min (0.402 sec), 3933 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	8.575	25431.3	1040.2	0.3952	50.056	0.835
2	19.968	25374.6	545.3	0.6989	49.944	0.617



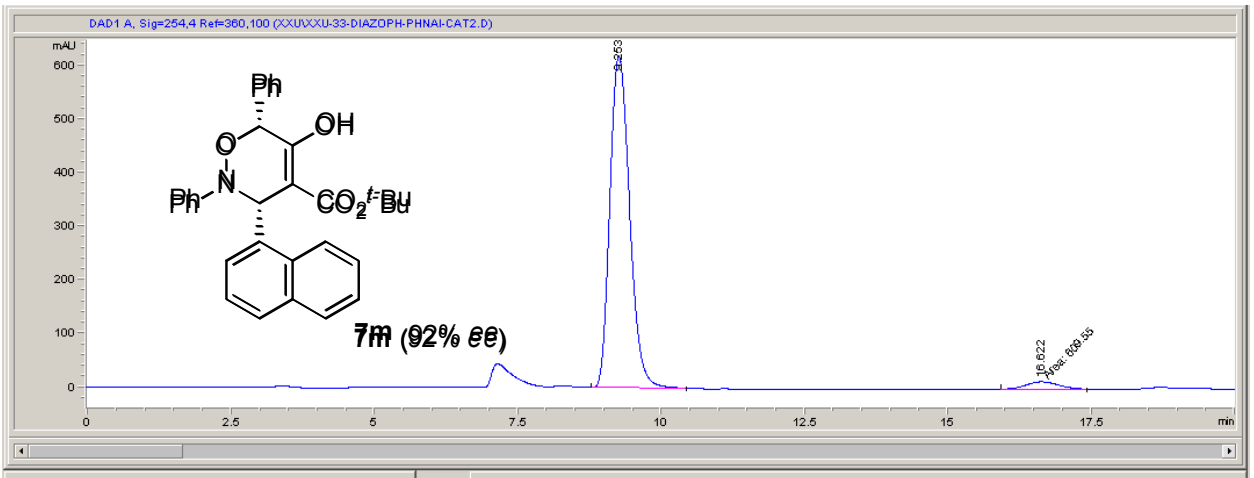
File Information	
LC-File	XXU-33-DIAZOPH-PH4F-CAT1.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	19-Jun-13, 12:30:37
Sample	OD-H, 98:2. 0.5
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	29.48 min
Sampling Rate	0.0067 min (0.402 sec), 4423 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	8.75	3667.1	220.4	0.2773	96.840	0.765
2	20.716	119.7	3.5	0.5745	3.160	1.381



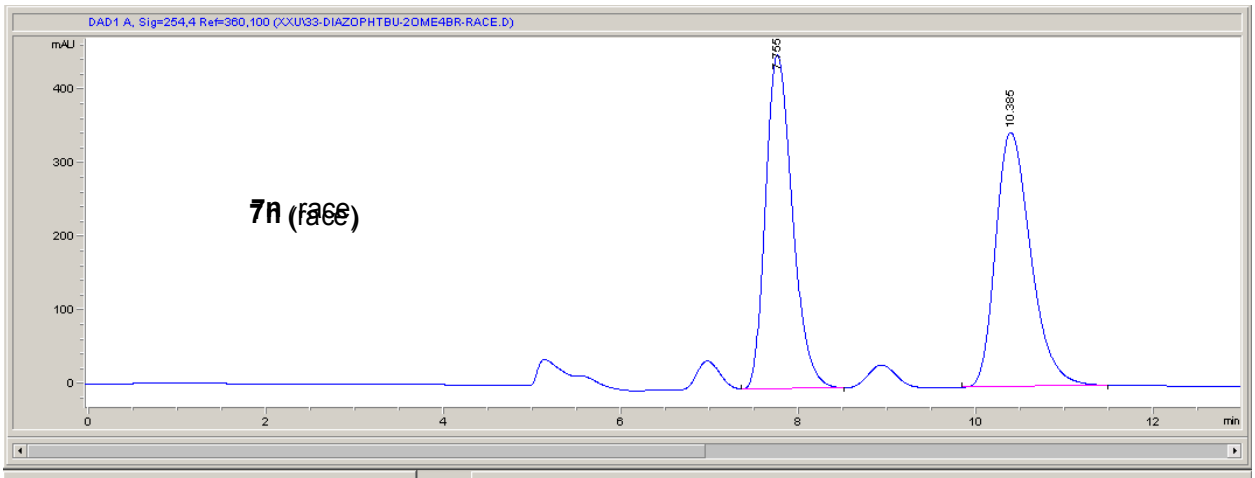
File Information	
LC-File	XXU-33-DIAZOPH-PHNAI-RACE2.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	19-Jun-13, 17:31:49
Sample	OD-H, 98:2. 0.5
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	26.567 min
Sampling Rate	0.0067 min (0.402 sec), 3986 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.211	37062.7	1528.9	0.3848	50.087	0.759
2	16.227	36933.6	936	0.6083	49.913	0.651



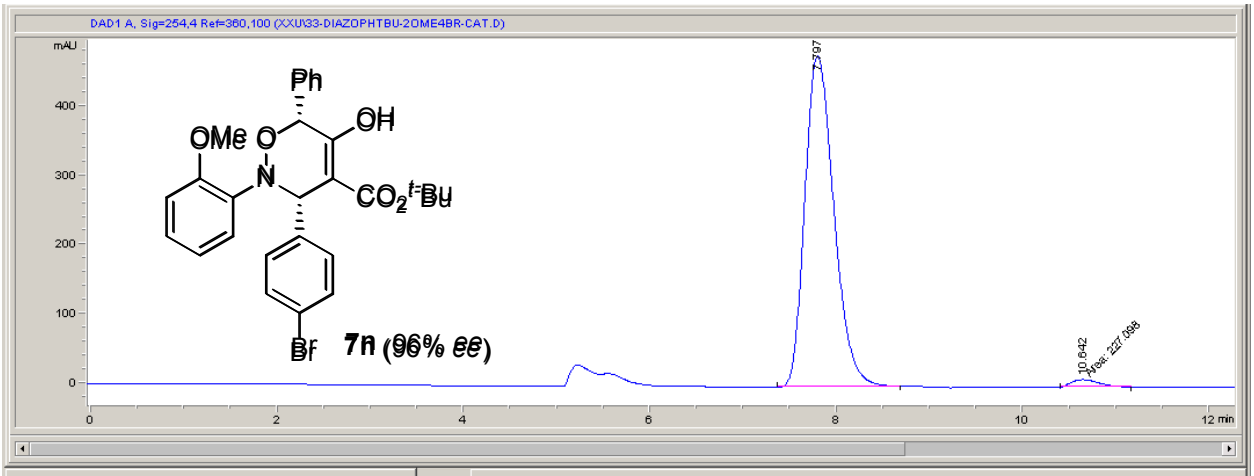
File Information	
LC-File	XXU-33-DIAZOPH-PHNAI-CAT2.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	19-Jun-13, 14:54:13
Sample	OD-H, 98:2. 0.5
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	155 min
Sampling Rate	0.0067 min (0.402 sec), 23251 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.253	14799.2	618.9	0.375	96.044	0.765
2	16.622	609.6	14.6	0.6974	3.956	0.87



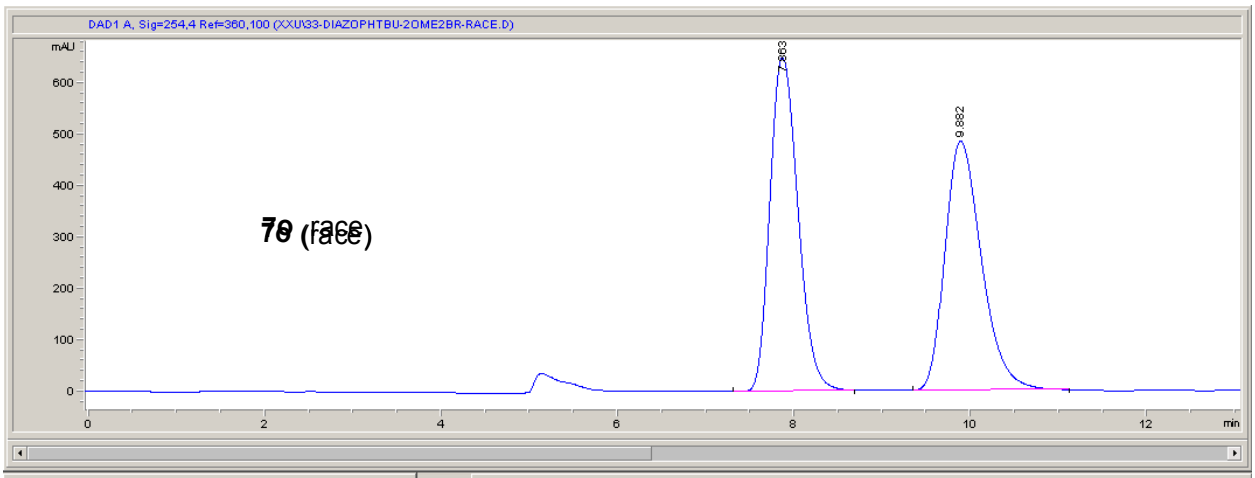
File Information	
LC-File	33-DIAZOPHTBU-2OME4BR-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	17-Jun-13, 15:42:59
Sample	OD-H,98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	23.013 min
Sampling Rate	0.0067 min (0.402 sec), 3453 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.755	9620.1	453.7	0.3314	50.261	0.744
2	10.385	9520.1	344.9	0.428	49.739	0.708



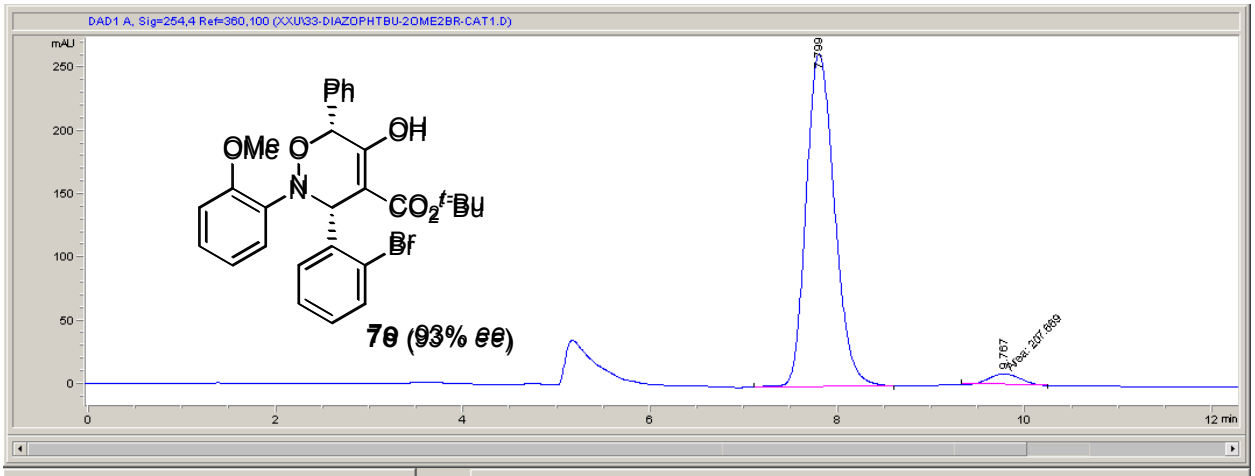
File Information	
LC-File	33-DIAZOPHTBU-2OME4BR-CAT.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	18-Jun-13, 10:54:21
Sample	OD-H,98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	16.767 min
Sampling Rate	0.0067 min (0.402 sec), 2516 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.797	10351.9	476.8	0.3393	97.853	0.736
2	10.642	227.1	10.8	0.3493	2.147	0.66



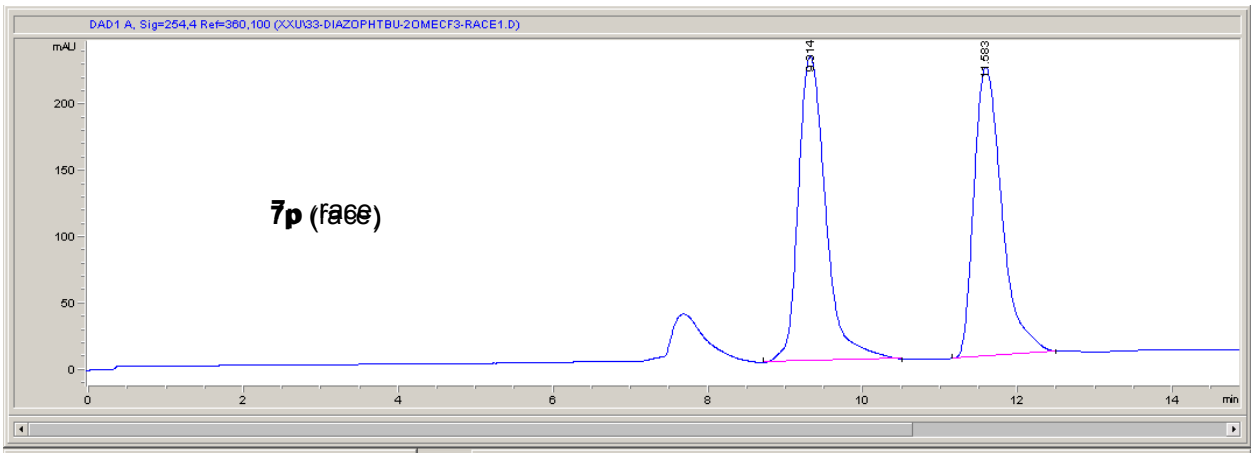
File Information	
LC-File	33-DIAZOPHTBU-2OME2BR-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	17-Jun-13, 16:08:33
Sample	OD-H,98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	25.153 min
Sampling Rate	0.0067 min (0.402 sec), 3774 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.863	14178	648.7	0.341	50.302	0.771
2	9.882	14007.5	484.2	0.4455	49.698	0.703



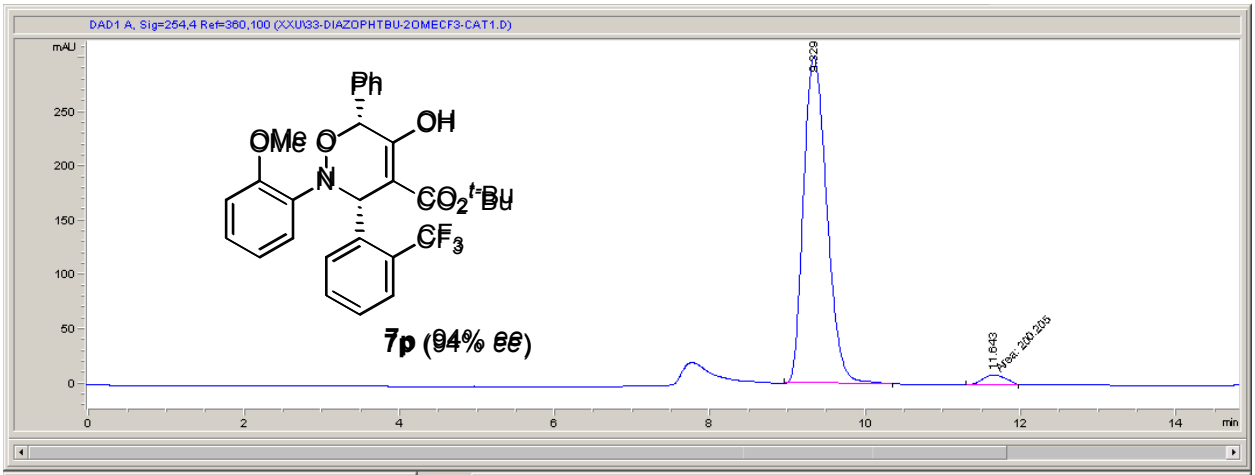
File Information	
LC-File	33-DIAZOPHTBU-2OME2BR-CAT1.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	18-Jun-13, 10:38:15
Sample	OD-H,98:2, 0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	14.76 min
Sampling Rate	0.0067 min (0.402 sec), 2215 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.799	5566.4	263	0.333	96.403	0.8
2	9.767	207.7	8.6	0.4017	3.597	0.82



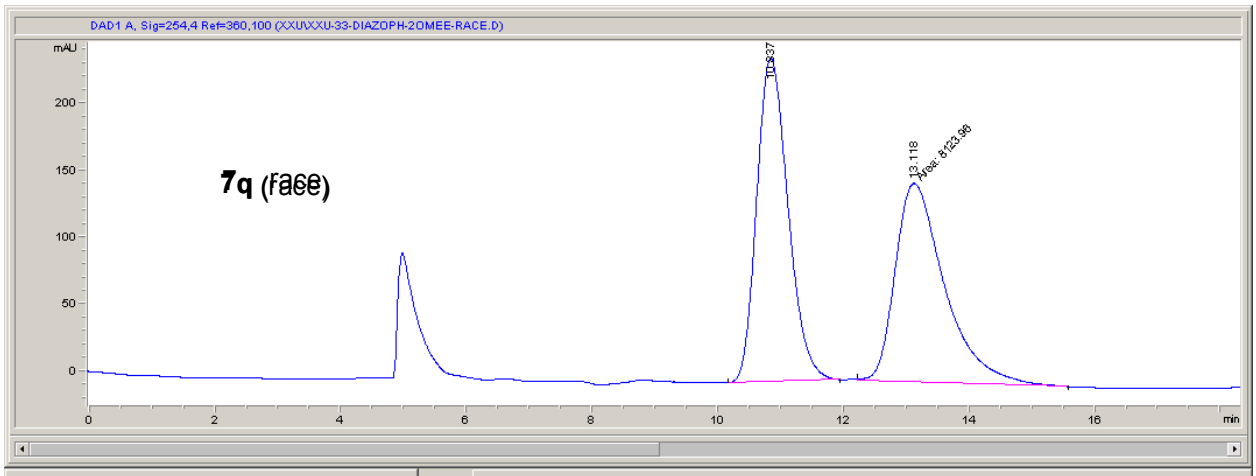
File Information	
LC-File	33-DIAZOPHTBU-2OMECF3-RACE1.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	18-Jun-13, 13:04:52
Sample	IB-3,98:2, 0.5
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	20.173 min
Sampling Rate	0.0067 min (0.402 sec), 3027 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.314	5675.7	230	0.3859	51.019	0.715
2	11.583	5449	217.7	0.392	48.981	0.681



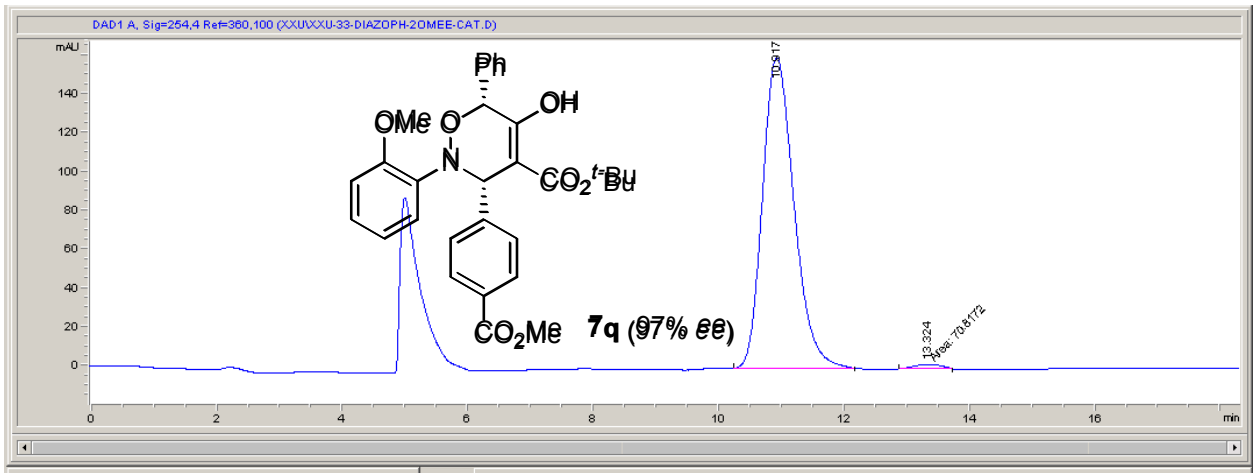
File Information	
LC-File	33-DIAZOPHTBU-2OMECF3-CAT1.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	18-Jun-13, 12:44:36
Sample	IB-3,98:2, 0.5
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	18.18 min
Sampling Rate	0.0067 min (0.402 sec), 2728 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.329	6269.5	299.8	0.3319	96.906	0.751
2	11.643	200.2	9.4	0.3546	3.094	0.861



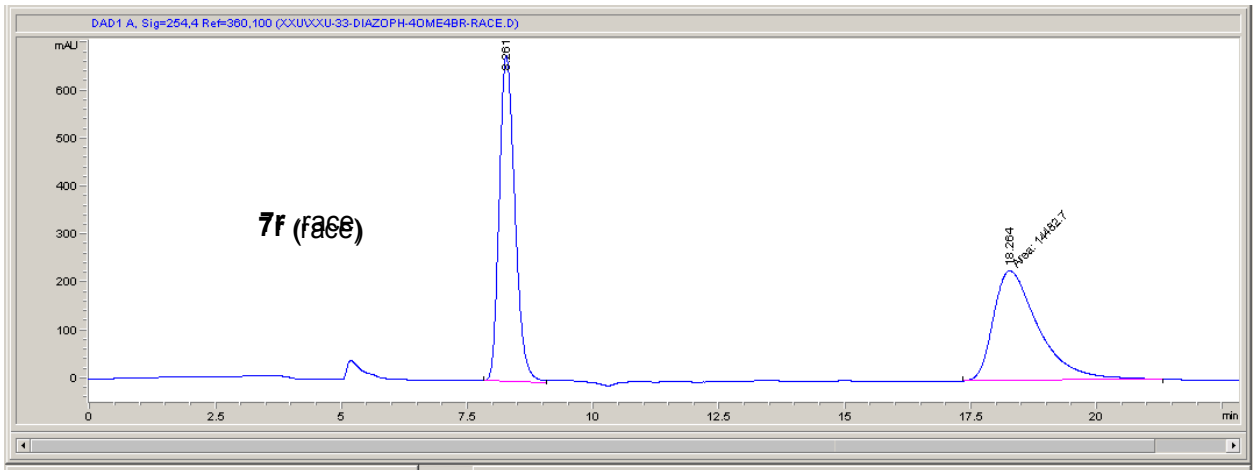
File Information	
LC-File	XXU-33-DIAZOPH-2OMEE-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	20-Jun-13, 16:40:55
Sample	OD-H, 98:2,0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	34.88 min
Sampling Rate	0.0067 min (0.402 sec), 5233 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	10.837	8369.5	241.3	0.5407	50.744	0.768
2	13.118	8124	148.2	0.9134	49.256	0.58



File Information	
LC-File	XXU-33-DIAZOPH-2OMEE-CAT.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	21-Jun-13, 10:39:28
Sample	OD-H, 98:2,0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	18.32 min
Sampling Rate	0.0067 min (0.402 sec), 2749 datapoints

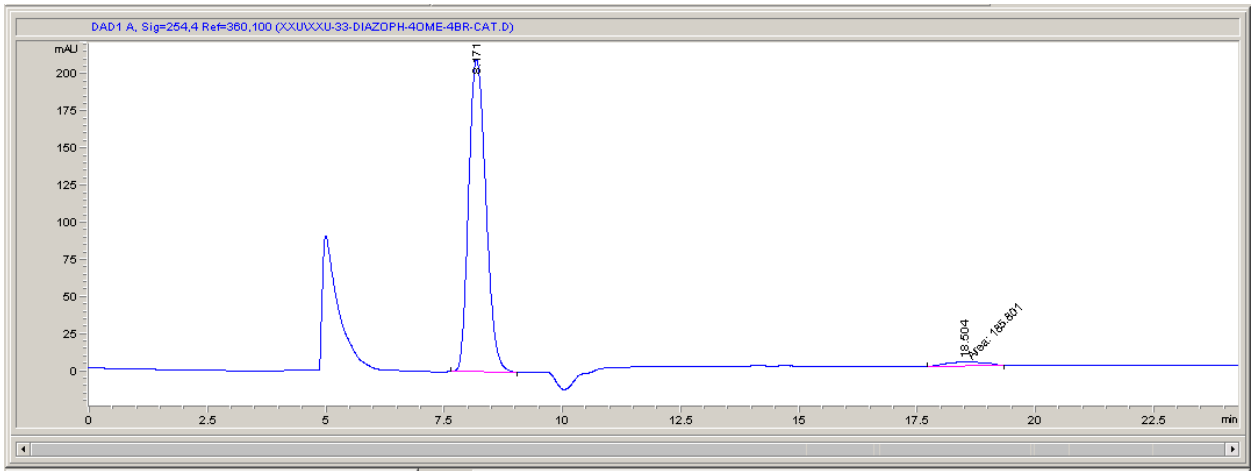
#	Time	Area	Height	Width	Area%	Symmetry
1	10.917	5604.9	160.2	0.5382	98.752	0.763
2	13.324	70.8	2.3	0.5033	1.248	0.995



7f (race)

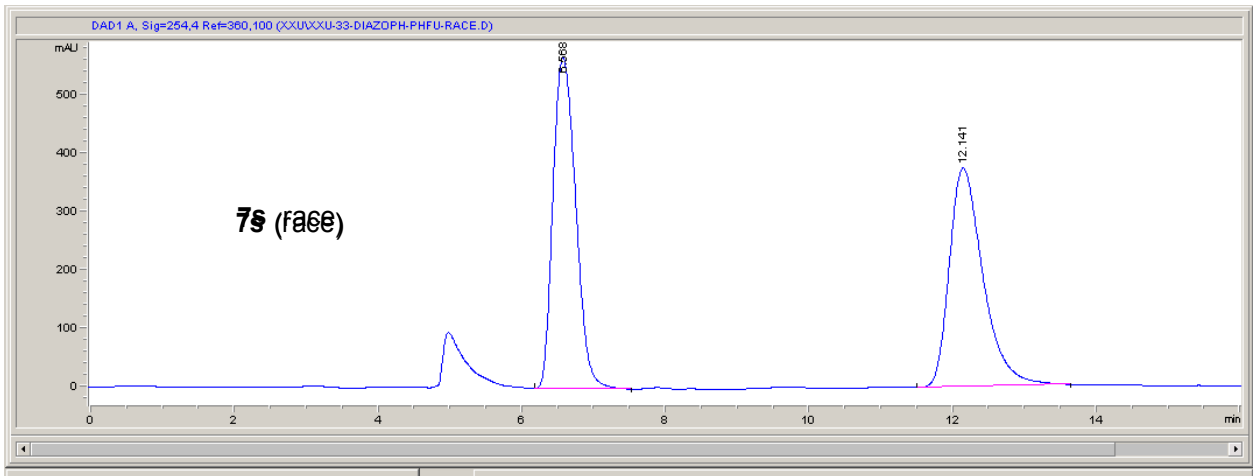
File Information	
LC-File	XXU-33-DIAZOPH-4OME4BR-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	20-Jun-13, 15:54:13
Sample	OD-H, 98:2,0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	24.293 min
Sampling Rate	0.0067 min (0.402 sec), 3645 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	8.261	14759.8	679.4	0.3375	50.474	0.753
2	18.264	14482.7	229.7	1.051	49.526	0.544



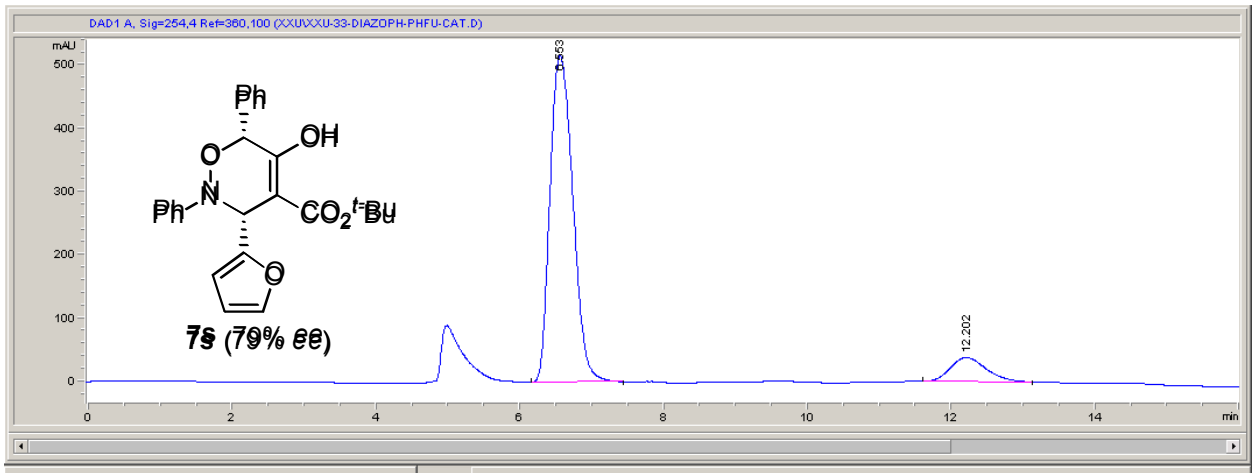
File Information	
LC-File	XXU-33-DIAZOPH-4OME-4BR-CAT.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	21-Jun-13, 10:10:51
Sample	OD-H, 98:2,0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	24.327 min
Sampling Rate	0.0067 min (0.402 sec), 3650 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	8.171	5351.2	210.7	0.4042	96.644	0.785
2	18.504	185.8	3	1.0394	3.356	0.976



File Information	
LC-File	XXU-33-DIAZOPH-PHFU-RACE.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	20-Jun-13, 16:21:50
Sample	OD-H, 98:2,0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	17.727 min
Sampling Rate	0.0067 min (0.402 sec), 2660 datapoints

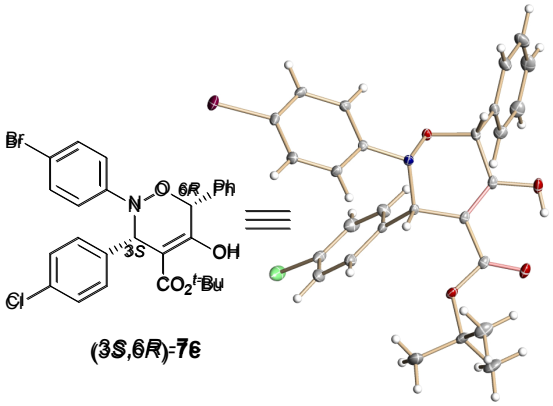
#	Time	Area	Height	Width	Area%	Symmetry
1	6.568	12504.9	566.6	0.3575	50.481	0.736
2	12.141	12266.6	375.1	0.4975	49.519	0.639



File Information	
LC-File	XXU-33-DIAZOPH-PHFU-CAT.D
File Path	C:\CHEM32\1\DATA\XXU\
Date	21-Jun-13, 11:31:18
Sample	OD-H, 98:2,0.7
Sample Info	
Barcode	
Operator	xxu
Method	PHONG.M
Analysis Time	20.813 min
Sampling Rate	0.0067 min (0.402 sec), 3123 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.553	11403.8	515.8	0.3579	89.460	0.743
2	12.202	1343.5	38.3	0.5153	10.540	0.757

Data collection and structure refinement for (3*S*, 6*R*)-7c (UM-2483)



A colorless prism-like specimen of $C_{27}H_{25}BrClNO_4$, approximate dimensions 0.40 mm × 0.46 mm × 0.49 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker APEX-II CCD system equipped with a graphite monochromator and a MoKα sealed tube (λ = 0.71073 Å). Data collection temperature was 150 K.

The total exposure time was 4.04 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using an orthorhombic unit cell yielded a total of 42520 reflections to a maximum θ angle of 29.99° (0.71 Å resolution), of which 7377 were independent (average redundancy 5.764, completeness = 100.0%, R_{int} = 2.57%) and 6754 (91.55%) were greater than $2\sigma(F^2)$.The final cell constants of *a* = 9.7782(6) Å, *b* = 10.1868(6) Å, *c* = 25.4096(14) Å, *V* = 2531.0(3) $Å^3$, are based upon the refinement of the XYZ-centroids of 9895 reflections above 20 σ(I) with 5.125° < 2θ < 60.50°.Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.4400 and 0.4940.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P212121, with Z = 4 for the formula unit, $C_{27}H_{25}BrClNO_4$.The final anisotropic full-matrix least-squares refinement on F^2 with 340 variables converged at R_1 = 2.54%, for the observed data and wR_2 = 4.98% for all data. The goodness-of-fit was 1.000. The largest peak in the final difference electron density synthesis was 0.380 $e^-/Å^3$ and the largest hole was -0.425 $e^-/Å^3$ with an RMS deviation of 0.041 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.425 g/cm^3 and F(000), 1112 e^-.