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Supporting Information

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Brønsted Acid Catalyzed Asymmetric S_N2-Type O-Alkylations**

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Supporting Information

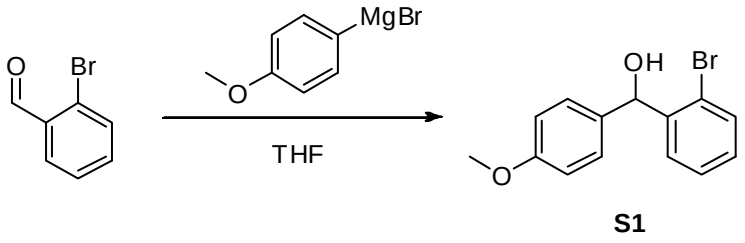
General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents used in the reactions were distilled from appropriate drying agents prior to use. Reactions were monitored by thin layer chromatography on silica gel pre-coated plastic sheets (0.2 mm, Machery-Nagel). Visualization was accomplished by irradiation with UV light at 254 nm and/or phosphomolybdic acid (PMA) stain. Column chromatography was performed on Merck silica gel (60, particle size 0.040-0.063 mm). Proton and carbon NMR spectra were recorded on Bruker AV-500 or Bruker AV-400 spectrometer in deuterated solvent. Proton chemical shifts are reported in ppm (δ) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard (C_6D_6, δ 7.16 ppm; DMSO-d_6, δ 2.49 ppm; $CDCl_3$ δ 7.24). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t= triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. ^{13}C chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (C_6D_6, δ 128.06 ppm; DMSO-d_6, δ 39.5 ppm; $CDCl_3$, δ 77.0). High resolution mass spectra were determined on a Bruker APEX III FTMS (7 T magnet). The enantiomeric ratios were determined by HPLC analysis employing a chiral stationary phase column specified in the individual experiment, by comparing the samples with the appropriate racemic mixtures.

Substrate synthesis

Substrates for Table 1

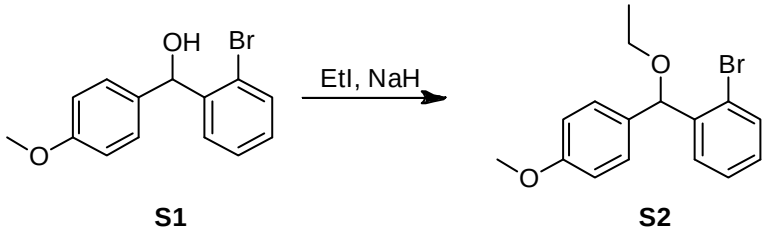
(2-bromophenyl)(4-methoxyphenyl)methanol (S1)



S1

1.0 M Solution of 4-methoxyphenyl-magnesium bromide in THF (11 ml, 11.0 mmol) was added to the solution of 2-bromobenzaldehyde (1.85 g, 10.0 mmol) in THF (10 ml) under an argon atmosphere at -30 °C and the resulting mixture was stirred for 1 hour at -30 °C. The mixture was quenched with water and extracted with EtOAc. The organic layer was washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 2.23 g, 76%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.68 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.54 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 8.7 Hz, 2H), 7.19 (dt, *J* = 7.9, 1.7 Hz, 1H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.97 (d, *J* = 4.3 Hz, 1H), 5.89 (d, *J* = 4.0 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.3, 144.3, 135.7, 132.2, 128.8, 128.5, 128.2, 127.8, 121.7, 113.5, 72.6, 55.0. HRMS (EI (DE)) *m/z* calculated for $C_{14}H_{13}O_2Br$ (M) 292.0099, found 292.0101.

1-bromo-2-(ethoxy(4-methoxyphenyl)methyl)benzene (S2)

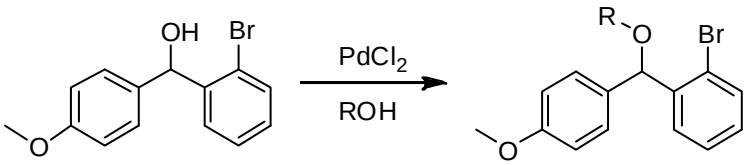


S1 **S2**

Ethyliodide (3.35 g, 21.5 mmol) and sodium hydride (60% dispersion in mineral oil, 258 mg, 6.45 mmol) were added to the solution of alcohol **S1** (1.26 g, 4.3 mmol) in THF (26 ml) under argon and the resulting suspension was stirred overnight at 50 ˚C. The reaction was quenched with addition of water and extracted with ethyl acetate. The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 1.0 g, 74%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.33 (t,

J = 7.1 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 2H), 7.12 (dt, *J* = 7.8, 1.7 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.70 (s, 1H), 3.78 (s, 3H), 3.52 (q, *J* = 7.0 Hz, 2H), 1.25 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 141.7, 133.2, 132.9, 128.9, 128.8, 128.6, 127.8, 123.6, 113.8, 81.5, 64.8, 55.4, 15.5. HRMS (ESI+) *m/z* calculated for $C_{16}H_{17}BrNaO_2$ (M+Na) 343.0304, found 343.0303.

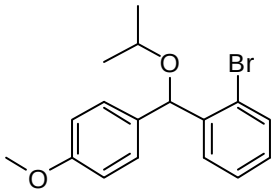
General procedure for S3 and S4[1]



S1

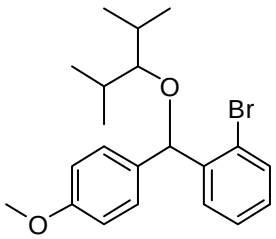
Palladium(II) chloride (10 mol%) was added to the solution of **S1** in the corresponding alcohol (5 ml/mmol) under argon. The resulting suspension was heated to 80 ºC and stirred for 21-23 h until TLC showed full conversion. The reaction mixture was then concentrated and the product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent.

1-bromo-2-(isopropoxy(4-methoxyphenyl)methyl)benzene (S3)



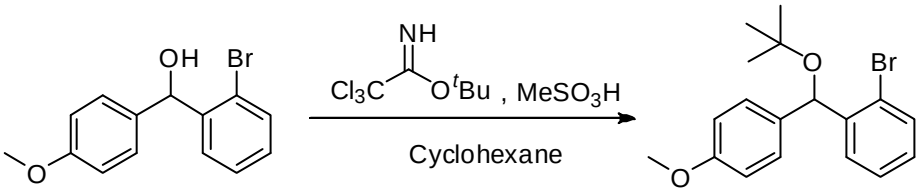
Light yellow oil, 730 mg (from 2.7 mmol of **S1**), 89%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 7.4 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.10 (dt, *J* = 7.8, 1.6 Hz, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.85 (s, 1H), 3.75 (s, 3H), 3.62 (septet, *J* = 6.1 Hz, 1H), 1.24 (d, *J* = 6.1 Hz, 3H), 1.19 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.0, 142.2, 133.8, 132.7, 128.9, 128.8, 128.8, 127.8, 123.4, 113.8, 78.4, 69.5, 55.3, 22.7, 22.2. HRMS (ESI+) *m/z* calculated for $C_{17}H_{19}BrNaO_2$ (M+Na) 357.0461, found 357.0459.

1-bromo-2-(((2,4-dimethylpentan-3-yl)oxy)(4-methoxyphenyl)methyl)benzene (S4)



Colorless oil, 255 mg (from 1.0 mmol of **S1**), 65%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.47 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.32 (t, *J* = 8.1 Hz, 1H), 7.30 (d, *J* = 8.8 Hz, 2H), 7.08 (dt, *J* = 7.7, 1.6 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 2H), 5.80 (s, 1H), 3.77 (s, 3H), 3.06 (t, *J* = 4.9 Hz, 1H), 1.85 (m, 2H), 0.84 (d, *J* = 3.6 Hz, 3H), 0.83 (d, *J* = 3.5 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H), 0.78 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 143.3, 134.4, 132.4, 129.6, 129.1, 128.6, 127.6, 122.9, 113.5, 87.6, 81.1, 55.3, 30.6, 30.5, 20.6, 20.4, 18.5, 18.3. HRMS (ESI+) *m/z* calculated for $C_{21}H_{27}BrNaO_2$ (M+Na) 413.1087, found 413.1091.

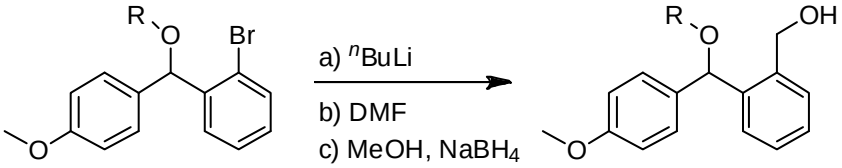
1-bromo-2-(*tert*-butoxy(4-methoxyphenyl)methyl)benzene (S5)[2]



S1 **S5**

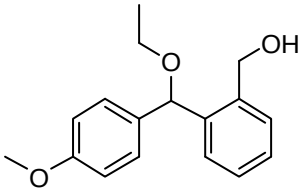
The starting alcohol (2.23 g, 7.61 mmol) was dissolved in cyclohexane (14 ml) and DCM (1 ml) under argon. *tert*-Butyl 2,2,2-trichloroacetimidate (4.98 g, 22.82 mmol, 3 eq.) was added, followed by $MeSO_3H$ (0.05 ml, 0.76 mmol, 10 mol%). The resulting solution was stirred for 22 hours at r.t., forming a white precipitate. Solid $NaHCO_3$ was then added and the suspension was stirred for 30 min. The mixture was then filtered, concentrated, and the product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 1.73 g, 65%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.48 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 8.7 Hz, 2H), 7.09 (dt, *J* = 7.8, 1.7 Hz, 1H), 6.80 (d, *J* = 8.7 Hz, 2H), 5.93 (s, 1H), 3.76 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 144.9, 135.6, 132.4, 129.7, 128.5, 128.4, 127.7, 122.2, 113.7, 75.3, 73.8, 55.3, 28.8. HRMS (ESI+) *m/z* calculated for $C_{18}H_{21}BrNaO_2$ (M+Na) 371.0617, found 371.0615.

General procedure for substrates in Table 1, entries 1, 3-5



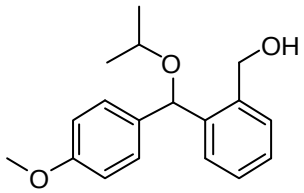
The starting aryl bromide was dissolved in THF (7 ml/mmol) under an argon atmosphere and cooled to -78 ˚C. Subsequently, *n*-butyllithium (2.5 M in hexanes; 1.1 eq.) was added and the resulting mixture was stirred at -78 ˚C for 1 hour. DMF (1.9 eq.) was added and the mixture stirred at -78˚C for 1.5 hour, after which the mixture was warmed to room temperature and stirred for an additional 2-3 hours. To the mixture methanol (7 ml/mmol) and $NaBH_4$ (1.5 eq.) were added. After stirring for 1.5 h the reaction was quenched with water and extracted with diethyl ether. The combined organic extracts were washed with Na_2CO_3 (aq. sat.), dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent.

(2-(ethoxy(4-methoxyphenyl)methyl)phenyl)methanol



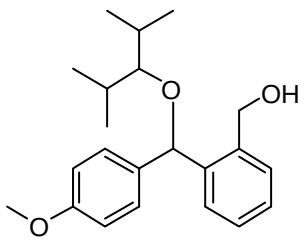
Colorless oil, 144 mg (from 0.7 mmol of bromide **S2**), 76%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.44-7.38 (m, 2H), 7.28-7.24 (m, 2H), 7.21 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 5.94 (s, 1H), 5.15 (t, *J* = 5.5 Hz, 1H), 4.58 (dd, *J* = 13.8, 5.3 Hz, 1H), 4.40 (dd, *J* = 14.1, 5.6 Hz, 1H), 3.72 (s, 3H), 3.40 (q, *J* = 7.1 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.4, 139.5, 139.5, 133.5, 128.5, 126.9, 126.8, 126.6, 126.1, 113.6, 78.2, 63.5, 60.2, 55.0, 15.3. HRMS (ESI+) *m/z* calculated for $C_{17}H_{20}O_3Na$ (M+Na) 295.1305, found 295.1303.

(2-(isopropoxy(4-methoxyphenyl)methyl)phenyl)methanol



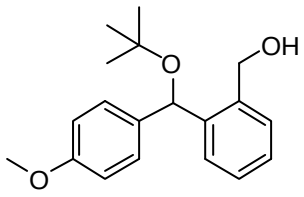
Colorless oil, 163 mg (from 0.75 mmol of bromide **S3**), 76%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.44 (d, *J* = 6.8 Hz, 1H), 7.39 (d, *J* = 6.8 Hz, 1H), 7.28-7.22 (m, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.72 (s, 1H), 5.14 (t, *J* = 5.4 Hz, 1H), 4.56 (dd, *J* = 13.8, 5.3 Hz, 1H), 4.38 (dd, *J* = 13.9, 5.1 Hz, 1H), 3.71 (s, 3H), 3.53 (septet, *J* = 6.1 Hz, 1H), 1.13 (d, *J* = 6.1 Hz, 3H), 1.11 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.3, 140.0, 139.3, 134.1, 128.4, 126.9, 126.8, 126.7, 126.4, 113.5, 75.2, 68.2, 60.3, 55.0, 22.3, 22.2. HRMS (ESI+) *m/z* calculated for $C_{18}H_{22}O_3Na$ (M+Na) 309.1461, found 309.1460.

(2-(((2,4-dimethylpentan-3-yl)oxy)(4-methoxyphenyl)methyl)phenyl)methanol



Light yellow oil, 126 mg (from 0.65 mmol of bromide **S4**), 56%. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.64 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.0, 1H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.23-7.17 (m, 1H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.60 (s, 1H), 5.11 (t, *J* = 5.4 Hz, 1H), 4.45 (dd, *J* = 13.9, 5.6 Hz, 1H), 4.25 (dd, *J* = 14.0, 5.4 Hz, 1H), 3.70 (s, 3H), 3.03 (t, *J* = 4.9 Hz, 1H), 1.83-1.72 (m, 2H), 0.79 (d, *J* = 6.9 Hz, 3H), 0.75 (d, *J* = 6.9 Hz, 3H), 0.74 (d, *J* = 6.7 Hz, 3H), 0.67 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 158.2, 140.8, 138.4, 134.4, 128.9, 126.6, 126.5, 126.4, 126.4, 113.3, 86.4, 78.5, 60.4, 55.0, 30.0, 29.7, 20.2, 20.1, 18.2, 18.0. HRMS (ESI+) *m/z* calculated for $C_{22}H_{30}O_3Na$ (M+Na) 365.2087, found 365.2087.

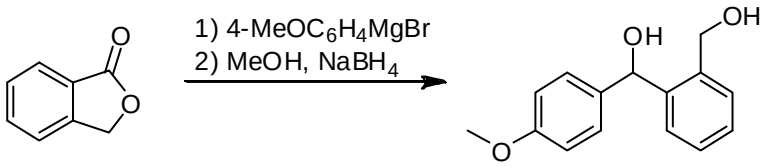
(2-(*tert*-butoxy(4-methoxyphenyl)methyl)phenyl)methanol (*rac*-2a)



Colorless oil, 1.17 g (from 4.94 mmol of bromide **S5**), 79%. For characterization see enantioenriched sample.

Substrate in Table 1, entry 2

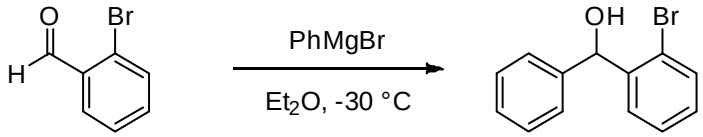
(2-(hydroxymethyl)phenyl)(4-methoxyphenyl)methanol



0.4 M solution of 4-methoxyphenylmagnesium bromide in THF (2.2 mmol, 5.5 ml) was added dropwise to the solution of phthalide (2 mmol) in dry THF (10 ml) at -78 °C under argon. The resulting yellow solution was stirred at -78 °C for 1 h, then warmed to room temperature and stirred for an additional 2 h. MeOH (5 ml) and $NaBH_4$ (151 mg, 4 mmol.) were added and the mixture stirred at room temperature for 3 h. The reaction mixture was diluted with water and extracted with EtOAc. The combined organic extracts were washed with brine, dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 298 mg, 59%. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.46-7.36 (m, 2H), 7.27-7.21 (m, 2H), 7.19 (d, *J* = 8.7 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 5.85 (d, *J* = 4.4 Hz, 1H), 5.66 (d, *J* = 4.4 Hz, 1H), 5.10 (t, *J* = 5.5 Hz, 1H), 4.53 (dd, *J* = 13.9, 5.4 Hz, 1H), 4.38 (dd, *J* = 13.9, 5.5 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.0, 142.3, 138.9, 136.5, 128.0, 126.6, 126.5, 126.4, 126.3, 113.3, 70.1, 60.2, 55.0. HRMS (ESI+) *m/z* calculated for $C_{15}H_{16}O_3Na$ (M+Na) 267.0992, found 267.0990.

*rac-**2b-f***

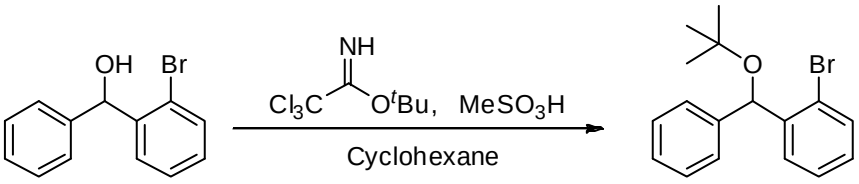
(2-bromophenyl)(phenyl)methanol (S6)[3]



S6

2.8 M Solution of phenylmagnesium bromide in Et_2O (4.4 ml, 12.3 mmol) was added to the solution of 2-bromobenzaldehyde (2.07 g, 11.2 mmol) in Et_2O (10 ml) and THF (5 ml) at -30 °C under an argon atmosphere and the resulting mixture was stirred for 1 hour. The mixture was quenched with water and extracted with EtOAc. The organic layer was washed with conc. aq. Na_2CO_3, dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 2.6 g, 87%. ^{1}H NMR (500 MHz, C_6D_6) δ 7.53 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.38-7.35 (m, 2H), 7.29 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.12-7.07 (m, 2H), 7.04-6.99 (m, 1H), 6.94-6.90 (m, 1H), 6.65 (td, *J* = 7.9, 1.8 Hz, 1H), 6.04 (d, *J* = 3.8 Hz, 1H), 1.71 (d, *J* = 3.9 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6) δ 143.7, 143.1, 132.8, 129.1, 128.6, 127.8, 127.7, 127.4, 123.1, 74.7, 60.1, 20.5, 14.2.

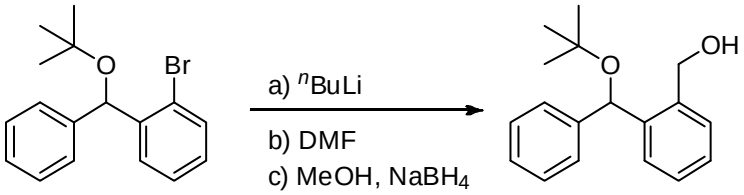
1-bromo-2-(*tert*-butoxy(phenyl)methyl)benzene (S7)



S6 **S7**

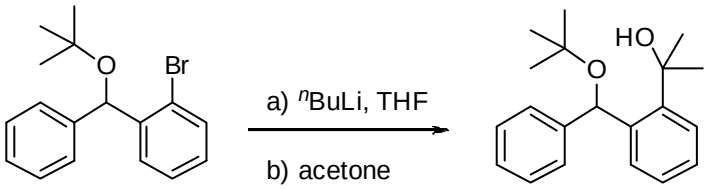
tert-Butyl 2,2,2-trichloroacet-imidate (5.24 ml, 29.3 mmol) and $MeSO_3H$ (0.07 ml, 0.98 mmol) were added to the solution of alcohol **S6** (2.57 g, 9.77 mmol) in cyclohexane (19 ml) under argon. The resulting solution was stirred for 22 hours at r.t., forming a white precipitate. Solid $NaHCO_3$ was then added and the suspension was stirred for 30 min. The mixture was then filtered, concentrated, and the product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 2.5 g, 80%. ^{1}H NMR (500 MHz, C_6D_6) δ 7.75 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.59-7.56 (m, 2H), 7.30 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.16-7.12 (m, 2H), 7.04-7.00 (m, 1H), 6.96-6.92 (m, 1H), 6.63 (td, *J* = 7.9, 1.7 Hz, 1H), 6.20 (s, 1H), 1.14 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6) δ 145.5, 144.2, 132.6, 130.2, 128.7, 128.5, 127.3, 127.2, 122.5, 75.2, 74.5, 28.6. HRMS (EI (DE)) *m/z* calculated for $C_{17}H_{19}OBr$ (M) 318.0619, found 318.0622.

(2-(*tert*-butoxy(phenyl)methyl)phenyl)methanol (*rac*-2b)



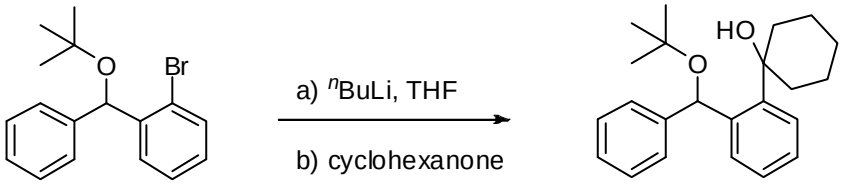
Bromide **S7** (0.64 g, 2 mmol) was dissolved in THF (14 ml) under an argon atmosphere and cooled to -78 ˚C. Subsequently, *n*-butyllithium (2.5 M in hexanes, 0.8 ml, 2.2 mmol) was added and the resulting mixture was stirred at -78 ˚C for 1 hour. DMF (0.29 ml, 3.8 mmol) was added and the mixture stirred at -78 ˚C for 1.5 hour, after which the mixture was warmed to room temperature and stirred for an additional 3 hours. To the mixture methanol (14 ml) and $NaBH_4$ (0.11 g, 3 mmol) were added. After stirring for 1.5 h the reaction was quenched with water and extracted with diethyl ether. The combined organic extracts were washed with Na_2CO_3 (aq. conc.), dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 337 mg, 62%. For characterization see enantioenriched sample.

2-(2-(*tert*-butoxy(phenyl)methyl)phenyl)propan-2-ol (*rac*-2c)



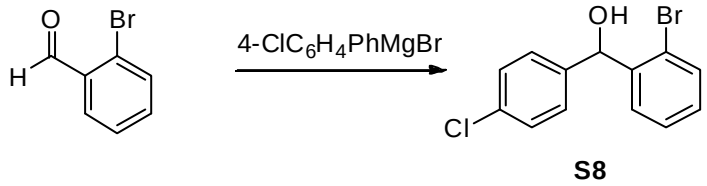
2.5 M Solution of n-BuLi in hexanes (0.88 ml, 2.2 mmol) was added to the solution of bromide **S7** (0.63 g, 2.0 mmol) in THF (15 ml) at -78 °C under an argon atmosphere and the resulting mixture was stirred at -78 °C for 1 hour. Acetone (0.12 g, 2.0 mmol) was added and the mixture was allowed to warm to room temperature overnight. Water was added and the mixture extracted with EtOAc. Combined organic extracts were washed with saturated aqueous Na_2CO_3, dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 0.26 g, 44%. For characterization see enantioenriched sample.

1-(2-(*tert*-butoxy(phenyl)methyl)phenyl)cyclohexanol (*rac*-2d)



2.5 M Solution of n-BuLi in hexanes (0.88 ml, 2.2 mmol) was added to the solution of bromide **S7** (0.63 g, 2.0 mmol) in THF (15 ml) at -78 °C under an argon atmosphere and the resulting mixture was stirred at -78 °C for 1 hour. Cyclohexanone (0.2 g, 2.0 mmol, 1.0 eq.) was added and the mixture was allowed to warm to room temperature overnight. Water was added and the mixture extracted with EtOAc. Combined organic extracts were washed with saturated aqueous Na_2CO_3, dried (MgSO4), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 0.30 g, 45%. For characterization see enantioenriched sample.

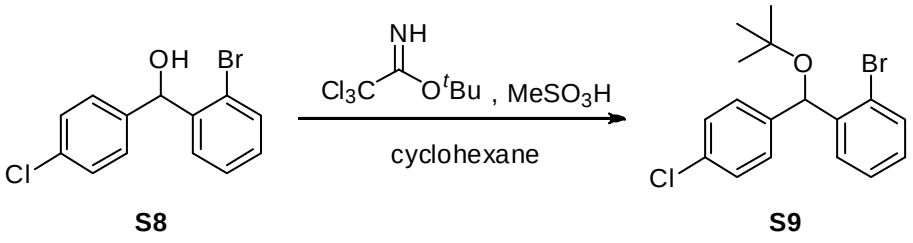
(2-bromophenyl)(4-chlorophenyl)methanol (S8)



S8

1.0 M Solution of 4-chlorophenyl-magnesium bromide in 2-methyl-tetrahydrofuran (11.1 ml, 11.1 mmol) was added to the solution of 2-bromobenzaldehyde (1.85 g, 10 mmol) in THF (15 ml) at -30 °C under an argon atmosphere and the resulting mixture was stirred for 1 hour. The mixture was quenched with water and extracted with EtOAc. The organic layer was washed with Na_2CO_3 dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. 2.67 g, 90%.^{1}H NMR (500 MHz, C_6D_6) δ 7.39 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.08-7.03 (m, 4H), 6.91 (t, *J* = 7.5 Hz, 1H), 6.65 (dt, *J* = 7.9, 1.3 Hz, 1H), 5.86 (d, *J* = 3.9 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6) δ 143.2, 141.5, 133.6, 132.9, 129.3, 128.9, 128.8, 128.7, 123.0, 74.0. HRMS (EI(DE)) *m/z* calculated for $C_{13}H_{10}OBrCl$ (M) 295.9604, found 295.9606.

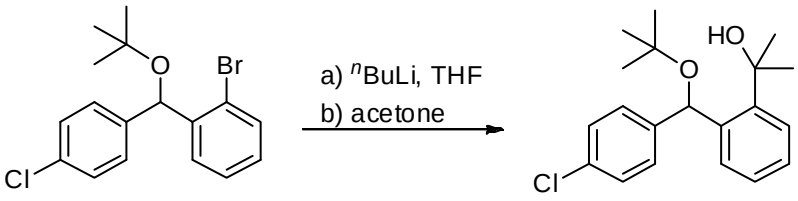
1-bromo-2-(*tert*-butoxy(4-chlorophenyl)methyl)benzene (S9)



S8 **S9**

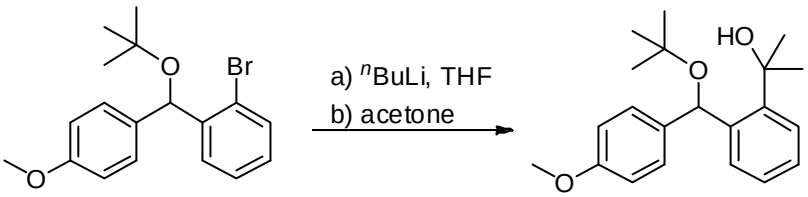
tert-Butyl 2,2,2-trichloro-acetimidate (4.76 ml, 26.6 mmol) and $MeSO_3H$ (0.06 ml, 0.89 mmol) were added to the solution of alcohol **S8** (2.64 g, 8.87 mmol) in cyclohexane (18 ml) under argon. The resulting solution was stirred for 22 hours at r.t., forming a white precipitate. Solid $NaHCO_3$ was then added and the suspension was stirred for 30 min. The mixture was then filtered and the product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. 2.22 g, 71%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.32-7.28 (m, 3H), 7.10-7.08 (m, 2H), 6.94 (dt, *J* = 7.8, 0.8 Hz, 1H), 6.64 (dt, *J* = 8.0, 1.7 Hz, 1H), 6.05 (s, 1H), 1.09 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 142.7, 133.1, 132.6, 130.0, 122.3, 75.4, 73.8, 28.6. HRMS (EI(DE)) *m/z* calculated for $C_{17}H_{18}OBrCl$ (M) 352.0230, found 352.0231.

2-(2-(*tert*-butoxy(4-chlorophenyl)methyl)phenyl)propan-2-ol (*rac*-2e)



2.5 M Solution of n-BuLi in hexanes (0.88 ml, 2.2 mmol) was added to the solution of bromide **S9** (0.7 g, 2.0 mmol) in THF (15 ml) at -78 °C under an argon atmosphere and the resulting mixture was stirred at -78 °C for 1 h. Acetone (145 µl, 2.0 mmol) was added and the mixture was allowed to warm to room temperature overnight. Water was added and the mixture extracted with EtOAc. Combined organic extracts were washed with saturated aqueous Na_2CO_3, dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 288 mg, 43%. For characterization see enantioenriched sample.

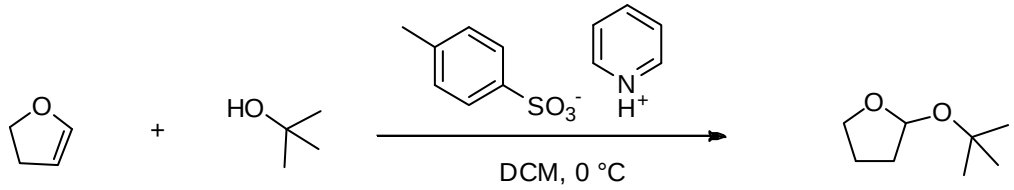
2-(2-(*tert*-butoxy(phenyl)methyl)phenyl)propan-2-ol (*rac*-2f)



2.5 M Solution of n-BuLi in hexanes (0.94 ml, 2.34 mmol) was added to the solution of bromide **S5** (0.63 g, 2.0 mmol) in THF (13 ml) at -78 °C under an argon atmosphere and the resulting mixture was stirred at -78 °C for 15 min. A solution of acetone (286 µl, 3.9 mmol) in THF (2 ml) was added and the mixture was stirred at -78 °C for 1 h. The cooling bath was than removed and the mixture was allowed to warm to room temperature. Water was added and the mixture extracted with EtOAc. Combined organic extracts were washed with saturated aqueous Na_2CO_3, dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 498 mg, 76%. For characterization see enantioenriched sample.

*rac-**2g-i** and rac-**3l***

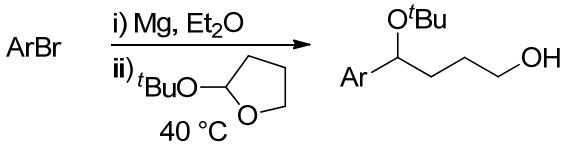
2-(*tert*-butoxy)tetrahydrofuran



Pyridinium *p*-toluenesulfonate (10 mol%) was added to the solution of *tert*-butanol (37.1 g, 500 mmol) and dihydrofuran (52.6 g, 750 mmol) in dry DCM (500 ml) under argon at 0 ˚C. The resulting mixture was stirred for 1.5 hours at 0 ˚C. Saturated aqueous Na_2CO_3 (250 ml) and water (250 ml) were added to the mixture and organic layer was separated, dried ($MgSO_4$), filtered and concentrated. Distillation under reduced pressure gave colorless oil, 41.5 g, 58%.

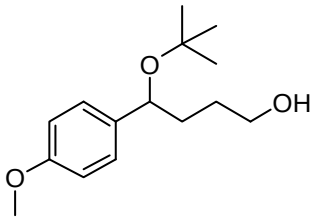
^{1}H NMR (500 MHz, DMSO-d_6) δ 5.35 (dd, *J* = 4.9, 1.8 Hz, 1H), 3.76-.3.71 (m, 1H), 3.69-3.65 (m, 1H), 1.87-1.80 (m, 2H), 1.73-1.59 (m, 2H), 1.15 (s, 9H). ^{13}C NMR (125 MHz, DMSO-d_6) δ 98.0, 73.0, 65.7, 33.0, 28.7, 23.4. HRMS (CI (FE) *i*-butane) *m/z* calculated for $C_8H_{17}O_2$ (M+H) 145.1229, found 145.1227.

General procedure for *rac*-2g-i and *rac*-3l



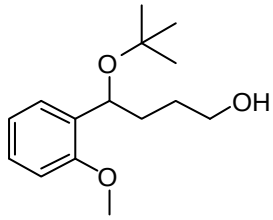
A solution of aryl bromide (5.3 mmol) in Et_2O (2 ml) was added dropwise to the activated magnesium turnings (0.14 g, 5.8 mmol, 1.1 eq., activated with 1,2-dibromoethane) and the resulting mixture was stirred for 0.5-3 h at reflux temperature under argon until most of the magnesium was consumed. 2-(*tert*-Butoxy)tetrahydrofuran (1.1 g, 8.0 mmol, 1.5 eq.) was added and the mixture was stirred for 24 hours at reflux temperature under argon. During time some Et_2O is evaporated possibly resulting in a higher reaction rate of the more concentrated mixture. The mixture was cooled to room temperature, quenched with water and extracted with EtOAc. Combined organic extracts were washed with saturated aqueous Na_2CO_3, dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent.

4-(*tert*-butoxy)-4-(4-methoxyphenyl)butan-1-ol (*rac*-2g)



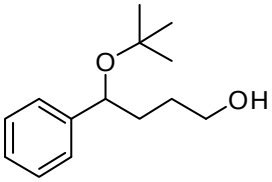
Colorless oil, 0.68 g, 51%. For characterization see enantioenriched sample.

4-(*tert*-butoxy)-4-(2-methoxyphenyl)butan-1-ol (*rac*-2h)



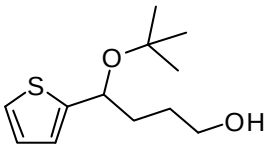
Colorless oil, 0.56 g, 42%. For characterization see enantioenriched sample.

4-(*tert*-butoxy)-4-phenylbutan-1-ol (*rac*-2i)



The reaction was performed on 25.5 mmol scale in 6 ml of Et_2O. Colorless oil, 4.12 g, 73%. For characterization see enantioenriched sample.

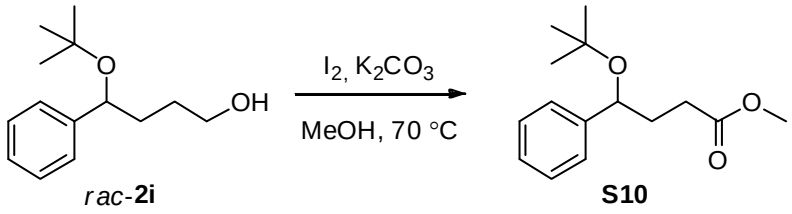
4-(*tert*-butoxy)-4-(thiophen-2-yl)butan-1-ol (*rac*-2l)



The reaction was performed on 10 mmol scale in 2 ml of Et_2O. Colorless oil, 1.6 g, 70%. For characterization see enantioenriched sample.

rac-***2j***

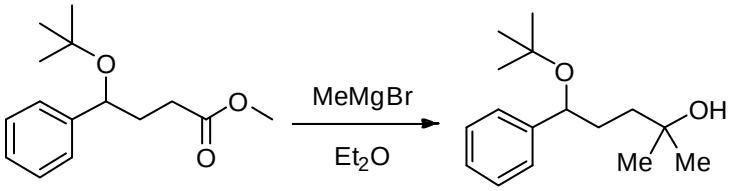
methyl 4-(*tert*-butoxy)-4-phenylbutanoate (S10)



rac-**2i** **S10**

Iodine (7.61 g, 30.0 mmol, 3.0 eq.) and solid K_2CO_3 (4.15 g, 30.0 mmol, 3.0 eq.) were added to the solution of *rac*-**2i** (2.22 g, 10.0 mmol) in MeOH (5 ml) under argon atmosphere. The mixture was stirred at 70 °C for 17 hours, then cooled to 0 °C, treated with saturated aqueous Na_2SO_3, and extracted with Et_2O. Combined organic extracts were dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 1.31 g, 53%. ^{1}H NMR (500 MHz, C_6D_6) δ 7.32-7.30 (m, 2H), 7.18-7.14 (m, 2H), 7.08-7.05 (m, 1H), 4.45 (dd, *J* = 7.32, 5.68 Hz, 1H), 3.34 (s, 3H), 2.40-2.34 (m, 1H), 2.29-2.23 (m, 1H), 1.99-1.95 (m, 2H), 1.02 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6) δ 173.5, 146.7, 128.5, 127.1, 126.4, 74.0, 73.2, 50.9, 35.5, 30.5, 28.7. HRMS (ESI+) *m/z* calculated for $C_{15}H_{22}O_3Na$ (M+Na) 273.1461, found 273.1459.

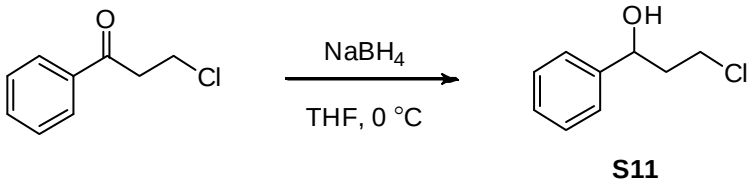
5-(*tert*-butoxy)-2-methyl-5-phenylpentan-2-ol (*rac*-2j)



3 M Solution of MeMgBr in Et_2O (2 ml, 6.0 mmol) was added dropwise to the solution of ester **S10** (0.50 g, 2.0 mmol) in Et_2O (5 ml) at 0 °C under argon atmosphere. After 1 hour water was added and the mixture was extracted with EtOAc. Combined organic layers were washed with concentrated aqueous Na_2CO_3, dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 0.39 g, 79%. For characterization see enantioenriched sample.

*rac-**2k***

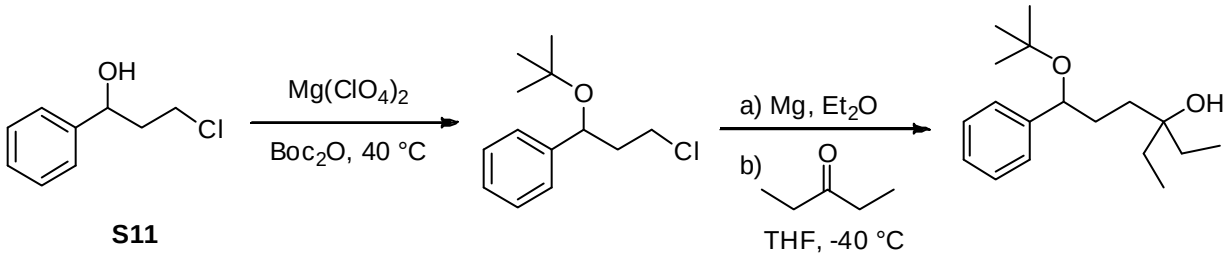
3-chloro-1-phenylpropan-1-ol (S11)[4]



S11

To the solution of 3-chloro-1-phenyl-1-propanone (3.0 g, 17.8 mmol) in THF (74 ml) was added $NaBH_4$ (1.35 g, 35.6 mmol) portionwise at 0 °C. The reaction mixture was stirred at r.t. for 40 min and quenched with water. The resulting mixture was extracted with EtOAc, dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 2.6 g, 85%, containing 20 % of dechlorinated alcohol.

6-(*tert*-butoxy)-3-ethyl-6-phenylhexan-3-ol (*rac*-2k)



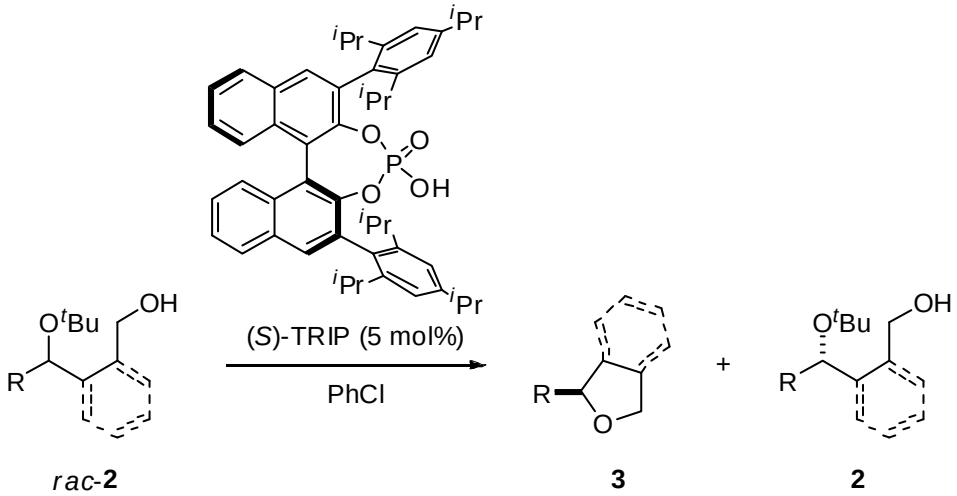
S11

$Mg(ClO_4)_2$ (0.7 g, 3.15 mmol, commercial anhydrous $Mg(ClO_4)_2$ was heated under vacuum at 130 °C for 2 hours before use to enhance its activity) and **S11** (5.37 g of mixture obtained above) were placed in a two necked flask. Boc_2O (22.2 ml, 104 mmol) was added to the flask and gas evolution was immediately observed.[5] The mixture was stirred at 40 °C for 36 h. The crude reaction mixture was diluted with water and extracted with DCM. The organic layer was seperated, dried ($MgSO_4$), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent giving colorless oil, 2.5 g. 2.0 g of the oil was dissolved in Et_2O (4 ml) and added dropwise to the activated magnesium turnings (0.32 g, 13.2 mmol). The resulting mixture was refluxed for 2 hours, diluted with Et_2O (5 ml) and THF (5 ml). Half of the thus formed Grignard reagent solution was transferred to a second flask with a syringe and cooled to -40 °C. Solution of 3-pentanone (0.38 g, 4.41 mmol, 0.5 eq.) in Et_2O (1 ml) was added dropwise at -40 °C and the resulting mixture was allowed to warm to room temperature overnight. Water was added and the mixture extracted with EtOAc. Combined

organic extracts were washed with concentrated aqueous Na_2CO_3, dried (MgSO4), filtered, and concentrated. The product was purified by column chromatography on silica gel using EtOAc/hexane as the eluent. Colorless oil, 0.60 g with regards to ketone, 49%. For characterization see enantioenriched sample.

Asymmetric transetherification

General procedure



rac-**2** **3** **2**

(*S*)-TRIP (7.55 mg, 0.01 mmol) was added to a solution of the substrate (0.2 mmol) in dry chlorobenzene (2 ml) and the resulting solution was stirred at the indicated temperature. In some cases 4 Å molecular sieves (40 mg) were used although similar results could be obtained in their absence. After specified reaction time the reaction was quenched with Et_3N (50 μL) and cooled to room temperature. The product and starting material were isolated by silica gel chromatography using EtOAc/hexane as the eluent. The conversions and s-factors were calculated from enantiomeric excess values of the product and the starting material, based on HPLC traces provided below.[6]

Racemates

p-Toluenesulfonic acid (0.95 mg, 0.005 mmol) or $(PhO)PO_2H$ (1.25 mg, 0.005 mmol) were added to the solution of the substrate (0.1 mmol) in chlorobenzene (1 ml). The mixture was stirred at room or elevated temperature, generally until >50% conversion. A sample of the product for HPLC was isolated by thin layer chromatography using EtOAc/hexanes as the eluent.

Optimization

Molecular sieves 4 Å (10 mg) and a solution of (*S*)-TRIP (20 mol%) in dry chlorobenzene (0.125 ml), were added to a solution of the substrate (0.025 mmol) in dry chlorobenzene (0.125 ml) and stirred at the indicated temperature. Samples (100 μL) were removed from the reaction mixture at

the indicated time intervals and then quenched by a few drops of Et_3N. Samples of the product and recovered starting material for HPLC analysis were isolated by thin layer chromatography using EtOAc/hexanes as the eluent. Conversions in entries 1-4 in Table 1 were determined by ^1H NMR analysis. The conversions in entries 5-6 in Table 1 were calculated from enantiomeric excess values of the product and the starting material.[6]

Products

rac-**2a**

conversion 56 %
s-factor 33

(*S*)-**3a**

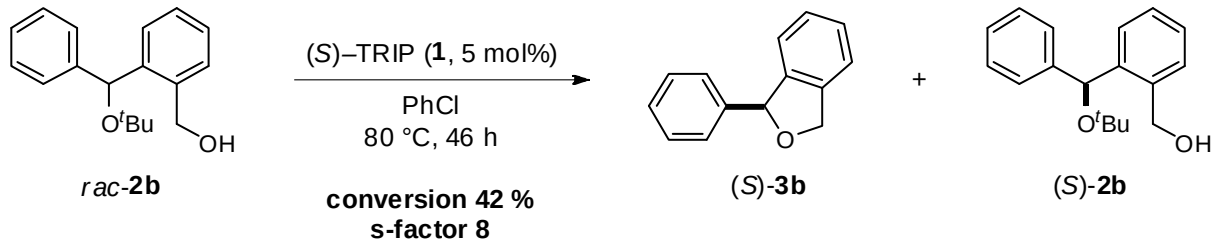
(*S*)-**2a**

(*S*)-1-(4-methoxyphenyl)-1,3-dihydroisobenzofuran (3a)

Colorless oil, 56 %; ^1H NMR (500 MHz, C_6D_6) δ 7.22-7.19 (m, 2H), 7.05 (t, *J* = 7.3 Hz, 1H), 7.00 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.78-6.75 (m, 2H), 6.10 (s, 1H), 5.13 (dd, *J* = 12.3, 2.4 Hz, 1H), 4.98 (d, *J* = 12.3 Hz, 1H), 3.27 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6) δ 160.0, 143.3, 139.9, 135.2, 128.8, 127.6, 127.6, 122.7, 121.1, 114.2, 86.2, 73.0, 54.8. HRMS (EI (DE)) *m/z* calculated for $C_{15}H_{14}O_2$ (M) 226.0994, found 226.0992. HPLC (OD-3), *n*-heptane/*i*-PrOH 99:1, 1.0 ml/min, λ = 220 nm, t_{minor} = 10.7 min, t_{major} = 9.7 min, er = 89:11.

(*S*)-(2-(*tert*-butoxy(4-methoxyphenyl)methyl)phenyl)methanol (2a)

Colorless oil, 33 %; ^1H NMR (500 MHz, C_6D_6) δ 7.47 (d, *J* = 7.5 Hz, 2H), 7.30-7.27 (m, 2H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.18 (td, *J* = 7.6, 1.2 Hz, 1H), 7.11 (td, *J* = 7.5, 1.2 Hz, 1H), 6.75-6.72 (m, 2H), 5.73 (s, 1H), 4.59 (td, *J* = 12.5, 3.3 Hz, 1H), 4.42 (dd, *J* = 12.7, 8.7 Hz, 1H), 3.28 (s, 3H), 2.68 (dd, *J* = 8.5, 3.8 Hz, 1H), 1.12 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6) δ 159.2, 143.6, 139.7, 136.1, 130.4, 129.0, 127.6, 113.9, 75.7, 75.4, 63.7, 54.7, 28.6. HRMS (ESI+) *m/z* calculated for $C_{19}H_{24}O_3Na$ (M+Na) 323.1618, found 323.1615. HPLC (OD-3), *n*-heptane/*i*-PrOH 99:1, 1.0 ml/min, λ = 220 nm, t_{minor} = 16.5 min, t_{major} = 12.9 min, er = 99:1.

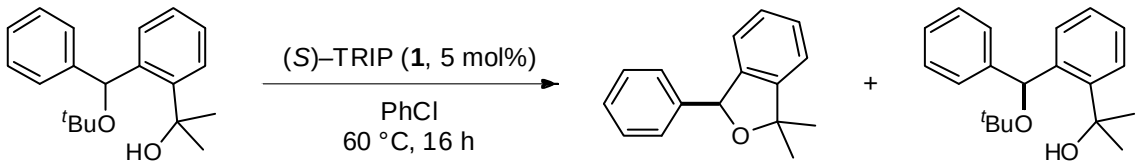


(*S*)-1-phenyl-1,3-dihydroisobenzofuran (3b)

Colorless oil, 42 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.29-7.27 (m, 2H), 7.15-7.13 (m, 2H), 7.10-7.06 (m, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.95 (dt, *J* = 7.4, 0.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.08 (s, 1H), 5.11 (dd, *J* = 12.3, 2.6 Hz, 1H), 4.98 (d, *J* = 12.2 Hz, 1H). ^{13}C NMR (125 MHz, C_6D_6) δ 143.2, 142.9, 139.7, 128.7, 127.7, 127.6, 127.3, 122.6, 121.1, 86.4, 73.3. HRMS (EI (DE)) *m/z* calculated for $C_{14}H_{12}O_1$ (M) 196.0888, found 196.0886. HPLC (OD-3), *n*-heptane/*i*-PrOH 99.9:0.1, 1.0 ml/min, λ = 220 nm, t_{major} = 10.31 min, t_{minor} = 16.75 min, er = 83.5:16.5.

(*S*)-(2-(*tert*-butoxy(phenyl)methyl)phenyl)methanol (2b)

Colorless oil, 47 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.42-7.38 (m, 3H), 7.21 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.15-7.07 (m, 4H), 7.04-7.01 (m, 1H), 5.72 (s, 1H), 4.54 (dd, *J* = 12.6, 3.5 Hz, 1H), 4.35 (dd, *J* = 12.6, 8.6 Hz, 1H), 2.60 (dd, *J* = 8.6, 4.0 Hz, 1H), 1.08 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6) δ 144.1, 143.3, 139.8, 130.5, 129.2, 128.4, 127.9, 127.6, 127.1, 127.0, 75.9, 75.8, 63.7, 28.5. HRMS (ESI+) *m/z* calculated for $C_{18}H_{22}O_2Na$ (M+Na) 293.1512, found 293.1513. HPLC (OD-3), *n*-heptane/*i*-PrOH 99:1, 1.0 ml/min, λ = 220 nm, t_{major}= 8.38 min, t_{minor} = 10.69 min, er = 74:26.



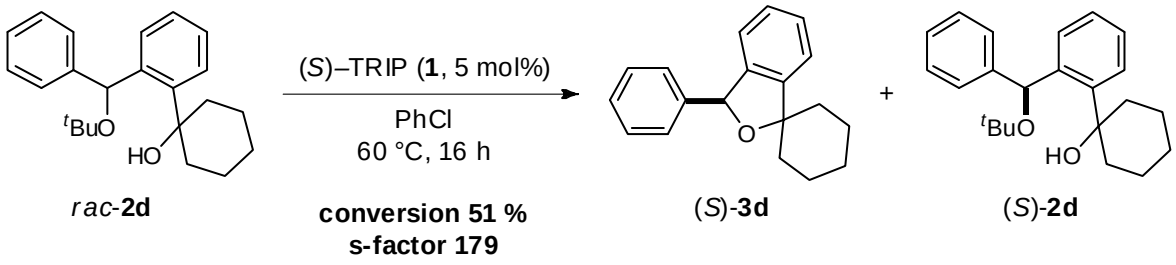
rac-**2c** **conversion 50 %** **s-factor 142** (*S*)-**3c** (*S*)-**2c**

(*S*)-1,1-dimethyl-3-phenyl-1,3-dihydroisobenzofuran (3c)

Colorless oil, 47 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.18-7.16 (m, 2H), 7.18-7.16 (peak overlapped with solvent, 2H), 7.11-7.05 (m, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 7.5 Hz, 1H), 6.11 (s, 1H), 1.60 (s, 3H), 1.47 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6) δ 147.7, 143.2, 142.3, 128.7, 128.0, 127.7, 127.6, 122.7, 120.6, 85.4, 84.0, 29.5, 29.0. HRMS (EI (DE)) *m/z* calculated for $C_{16}H_{16}O_1$ (M) 224.1201, found 224.12103. HPLC (OD-3), *n*-heptane/*i*-PrOH 99.9:0.1, 1.0 ml/min, λ = 220 nm, t_{minor} = 6.01 min, t_{major} = 5.14 min, er = 97.5:2.5.

(*S*)-2-(2-(*tert*-butoxy(phenyl)methyl)phenyl)propan-2-ol (2c)

Colorless oil, 46 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.19-7.13 (m, 3H), 7.08 (d, *J* = 4.2 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.68 (s, 1H), 2.32 (s, 1H), 1.44 (s, 3H), 1.29 (s, 3H), 1.21 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6) δ 146.3, 145.5, 142.3, 131.1, 128.4, 128.2, 127.1, 127.0, 126.8, 126.7, 75.3, 74.6, 74.3, 33.6, 32.7, 29.1. HRMS (ESI+) *m/z* calculated for $C_{20}H_{26}O_2Na$ (M+Na) 321.1825, found 321.1821. HPLC (OD-3), *n*-heptane/*i*-PrOH 99.9:0.1, 1.0 ml/min, λ = 220 nm, t_{minor} = 6.86 min, t_{major} = 6.16 min, er = 98:2.



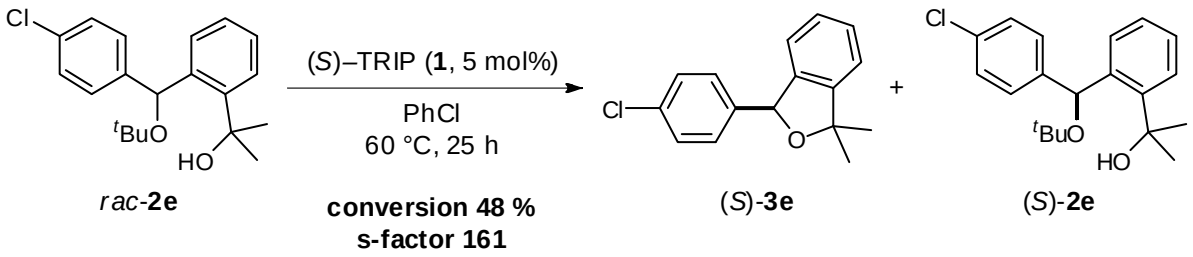
rac-**2d** **conversion 51 %** **s-factor 179** (*S*)-**3d** (*S*)-**2d**

(*S*)-3'-phenyl-3'H-spiro[cyclohexane-1,1'-isobenzofuran] (3d)

Colorless oil, 49 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.37 (d, *J* = 7.7 Hz, 2H), 7.19-7.16 (overlapped with solvent, 2H), 7.11-7.07 (m, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 7.6 Hz, 1H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.11 (s, 1H), 2.06-1.95 (m, 3H), 1.91 (d, *J* = 13.5 Hz, 1H), 1.77-1.59 (m, 4H), 1.50 (td, *J* = 13.0, 4.1 Hz, 1H), 1.29-1.20 (m, 1H). ^{13}C NMR (125 MHz, C_6D_6) δ 147.5, 143.5, 142.6, 128.7, 128.0, 127.8, 127.6, 122.8, 120.9, 86.6, 84.0, 38.6, 37.6, 25.8, 23.3, 22.7. HRMS (EI (DE)) *m/z* calculated for $C_{19}H_{20}O_1$ (M) 264.1514, found 264.1513. HPLC (OJ-H), *n*-heptane/*i*-PrOH 95:5, 0.5 ml/min, λ = 220 nm, t_{minor} = 18.6 min, t_{major} = 24.0 min, er = 97:3.

(*S*)-1-(2-(*tert*-butoxy(phenyl)methyl)phenyl)cyclohexanol (2d)

Colorless oil, 48 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.88 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.20-7.12 (overlapped with solvent, 5H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.63 (s, 1H), 2.46 (s, 1H), 1.96 (d, *J* = 12.6 Hz, 1H), 1.86-1.77 (m, 1H), 1.66-1.55 (m, 5H), 1.44 (d, *J* = 12.8 Hz, 1H), 1.38-1.29 (m, 1H), 1.20 (s, 9H), 1.13-1.02 (m, 1H). ^{13}C NMR (125 MHz, C_6D_6) δ 146.5, 146.4, 142.4, 131.3, 127.2, 127.1, 126.7, 126.6, 75.4, 75.2, 75.1, 40.2, 39.4, 29.0, 25.9, 22.4, 22.0. HRMS (ESI+) *m/z* calculated for $C_{23}H_{30}O_2Na$ (M+Na) 361.2138, found 361.2134. HPLC (OD-3), *n*-heptane/*i*-PrOH 99.9:0.1, 1.0 ml/min, λ = 220 nm, t_{minor} = 5.2 min, t_{major} = 4.6 min, er = 99.7:0.3.

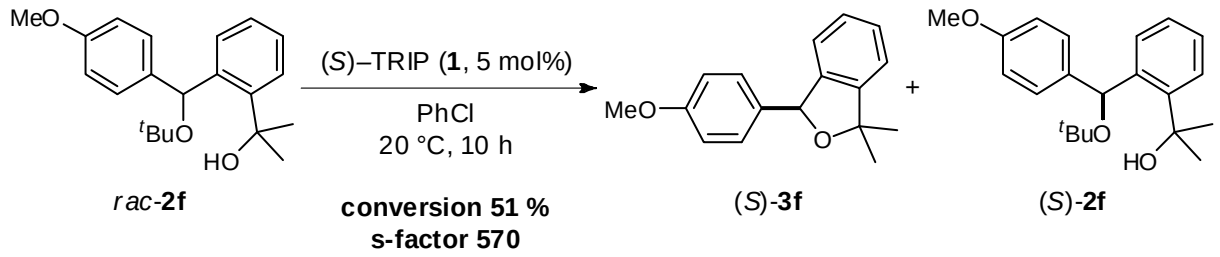


(*S*)-3-(4-chlorophenyl)-1,1-dimethyl-1,3-dihydroisobenzofuran (3e)

Colorless oil, 45 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.13-7.11 (m, 2H), 7.08-7.04 (m, 3H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 5.93 (s, 1H), 1.54 (s, 3H), 1.44 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6) δ 147.5, 141.7, 141.6, 133.8, 128.9, 128.9, 127.8, 122.5, 120.7, 85.5, 83.2, 29.4, 28.9. HRMS (EI (DE)) *m/z* calculated for $C_{16}H_{15}OCl$ (M) 258.0811, found 258.0809. HPLC (OD-3), *n*-heptane/*i*-PrOH 99.9:0.1, 1.0 ml/min, λ = 220 nm, t_{major} = 4.01 min, t_{minor} = 4.27 min, er = 98:2.

(*S*)-2-(2-(*tert*-butoxy(4-chlorophenyl)methyl)phenyl)propan-2-ol (2e)

Colorless oil, 50 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.21-7.19 (m, 2H), 7.14-7.11 (m, 3H), 7.08-7.03 (m, 2H), 6.55 (s, 1H), 2.15 (s, 1H), 1.41 (s, 3H), 1.26 (s, 3H), 1.16 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6) δ 145.3, 144.9, 141.9, 132.5, 130.9, 129.7, 127.3, 127.0, 126.8, 75.4, 74.3, 73.9, 33.6, 32.7, 29.0. HRMS (ESI+) *m/z* calculated for $C_{20}H_{25}O_2ClNa$ (M+Na) 355.1435, found 355.1432. HPLC (OD-3), *n*-heptane/*i*-PrOH 99.9:0.1, 1.0 ml/min, λ = 220 nm, t_{minor} = 6.54 min, t_{major} = 6.81 min, er = 94.5:5.5.

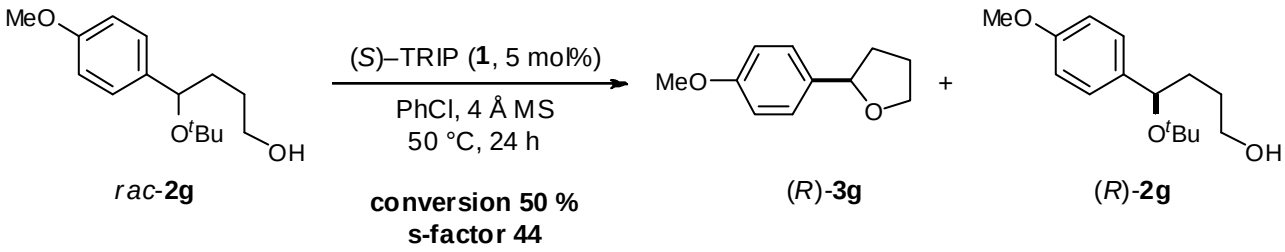


(*S*)-3-(4-methoxyphenyl)-1,1-dimethyl-1,3-dihydroisobenzofuran (3f)

Colorless solid, 45%; ^{1}H NMR (500 MHz, C_6D_6) δ 7.26 (d, *J* = 8.5 Hz, 2H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.5 Hz, 2H), 6.12 (s, 1H), 3.28 (s, 3H), 1.62 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6) δ 159.9, 147.9, 142.7, 135.3, 129.1, 127.7, 122.8, 120.6, 114.2, 85.1, 83.8, 54.8, 29.6, 29.0 (one aromatic carbon signal ovelapped). HRMS (ESI+) *m/z* calculated for $C_{17}H_{18}O_2Na$ (M+Na) 277.1199, found 277.1195. HPLC (OJ-3), *n*-heptane/*i*-PrOH 80:20, 1.0 ml/min, λ = 220 nm, t_{minor} = 19.2 min, t_{major} = 64.6 min, er = 98.8:1.2.

(*S*)-2-(2-(*tert*-butoxy(4-methoxyphenyl)methyl)phenyl)propan-2-ol (2f)

Colorless oil, 50 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.99 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.22-1.19 (m, 1H), 7.13-7.09 (m, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 6.68 (s, 1H), 3.27 (s, 3H), 2.45 (s, 1H), 1.48 (s, 3H), 1.34 (s, 3H), 1.24 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 145.4, 142.7, 138.3, 130.9, 129.7, 127.1, 127.0, 126.7, 113.7, 75.1, 74.3, 74.2, 54.7, 33.5, 32.7, 29.1. HRMS (ESI+) *m/z* calculated for $C_{21}H_{28}O_3Na$ (M+Na) 351.1931, found 351.1928. HPLC (OD-3), *n*-heptane/*i*-PrOH 99:1, 1.0 ml/min, λ = 200 nm, t_{major} = 4.67 min, t_{minor} = 5.51 min, er = 99.9:0.1.

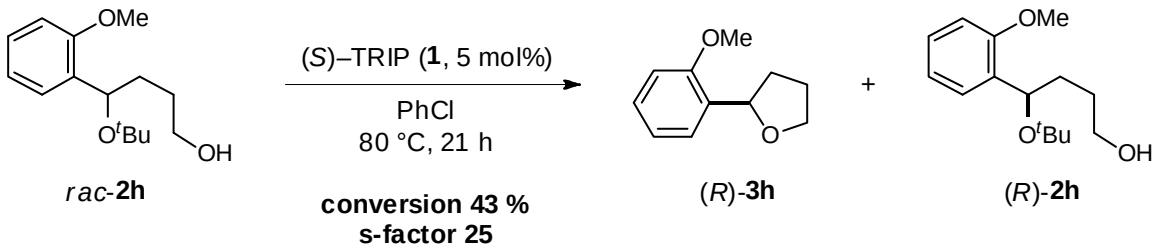


(*R*)-2-(4-methoxyphenyl)tetrahydrofuran (3g)

Colorless oil, 45%; ^{1}H NMR (500 MHz, C_6D_6) δ 7.30-7.27 (m, 2H), 6.85-6.82 (m, 2H), 4.73 (t, *J* = 6.9 Hz, 1H), 3.93-3.89 (m, 1H), 3.72-3.68 (m, 1H), 3.32 (s, 3H), 1.94-1.86 (m, 1H), 1.65-1.49 (m, 3H). ^{13}C NMR (125 MHz, C_6D_6) δ 159.4, 136.2, 127.2, 114.0, 80.5, 63.0, 68.3, 54.8, 35.0, 26.2. HRMS (EI (FE)) *m/z* calculated for $C_{11}H_{14}O_2$ (M) 178.0994, found 178.0992. HPLC (OD-3), *n*-heptane/*i*-PrOH 90:10, 1.0 ml/min, λ = 220 nm, t_{minor} = 4.0 min, t_{major} = 3.6 min, er = 94:6.

(*R*)-4-(*tert*-butoxy)-4-(4-methoxyphenyl)butan-1-ol (2g)

Colorless oil, 39 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.31-7.28 (m, 2H), 6.91-6.88 (m, 2H), 4.42 (dd, *J* = 7.4, 4.7 Hz, 1H), 3.54-3.49 (m, 2H), 3.41 (s, 3H), 1.87-1.78 (m, 1H), 1.76-1.63 (m, 2H), 1.61-1.52 (m, 1H), 1.47 (bs, 1H), 1.16 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6) δ 159.1, 139.0, 127.5, 113.9, 74.1, 63.0, 54.8, 37.6, 29.7, 28.8. HRMS (ESI+) *m/z* calculated for $C_{15}H_{24}O_3Na$ (M+Na) 275.1618, found 275.1618. HPLC (OD-3), *n*-heptane/*i*-PrOH 90:10, 1.0 ml/min, λ = 220 nm, t_{minor} = 4.4 min, t_{major} = 3.5 min, er = 94:6.

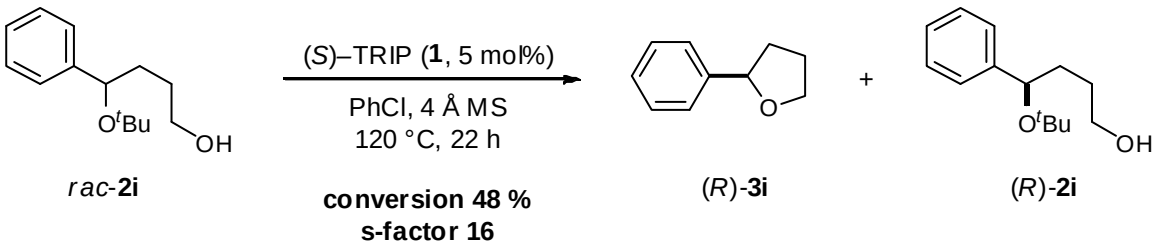


(*R*)-2-(2-methoxyphenyl)tetrahydrofuran (3h)

Colorless oil, 38 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.79 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.11 (td, *J* = 7.8, 1.7 Hz, 1H), 6.98 (td, *J* = 7.6, 0.7 Hz, 1H), 6.53 (d, *J* = 8.1 Hz, 1H), 5.40-35 (m, 1H), 3.98-3.94 (m, 1H), 3.75-3.71 (m, 1H), 3.28 (s, 3H), 2.36-2.27 (m, 1H), 1.64-1.55 (m, 3H). ^{13}C NMR (125 MHz, C_6D_6) δ 156.4, 133.3, 126.2, 120.9, 110.2, 76.2, 68.4, 54.8, 33.8, 26.1. HRMS (EI (FE)) *m/z* calculated for $C_{11}H_{14}O_2$ (M) 178.0994, found 178.0992. HPLC (OD-3), *n*-heptane/*i*-PrOH 98:2, 1.0 ml/min, λ = 220 nm, t_{minor} = 3.9 min, t_{major} = 4.6 min, er = 93:7.

(*R*)-4-(*tert*-butoxy)-4-(2-methoxyphenyl)butan-1-ol (2h)

Colorless oil, 48 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.77 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.08 (td, *J* = 7.9, 1.3 Hz, 1H), 6.97 (t, *J* = 7.5, 1.6 Hz, 1H), 6.53 (d, *J* = 8.3 Hz, 1H), 5.15 (dd, *J* = 7.2, 4.7 Hz, 1H), 3.52-3.49 (m, 2H), 3.33 (s, 3H), 1.87-1.78 (m, 3H), 1.77-1.59 (m, 2H), 1.11 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6) δ 155.5, 135.3, 127.7, 121.0, 110.2, 74.1, 67.6, 63.1, 54.9, 35.8, 29.7, 28.6. HRMS (ESI+) *m/z* calculated for $C_{15}H_{24}O_3Na$ (M+Na) 275.1618, found 275.1618. HPLC (OD-3), *n*-heptane/*i*-PrOH 98:2, 1.0 ml/min, λ = 220 nm, t_{minor} = 10.4 min, t_{major} = 7.7 min, er = 82:18.



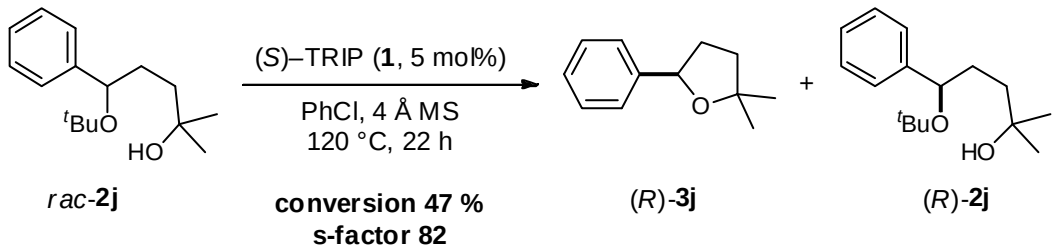
(*R*)-2-phenyltetrahydrofuran (3i)

Colorless oil, 42 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.34 (d, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.6 Hz, 2H), 7.10 (t, *J* = 7.5 Hz, 1H), 4.73 (t, *J* = 6.8 Hz, 1H), 3.89-3-85 (m, 1H), 3.71-3.66 (m, 1H), 1.92-1.85 (m, 1H), 1.58-1.46 (m, 3H). ^{13}C NMR (125 MHz, C_6D_6) δ 144.4, 128.5, 127.2, 125.9, 80.7, 68.5, 35.0, 26.1. HRMS (EI (FE)) *m/z* calculated for $C_{10}H_{12}O_1$ (M) 148.0888, found 148.0890. HPLC (OD-3), *n*-heptane/*i*-PrOH 90:10, 1.0 ml/min, λ = 210 nm, t_{minor} = 3.7 min, t_{major} = 2.9 min, er = 89:11. α_D^{25} = 27.1 °, c 0.199, CH_2Cl_2. (literature value[7] for (*S*)-**3i**: α_D^{25} = –37.6, c 1.62, $CHCl_3$, e.r. > 99:1)

(*R*)-4-(*tert*-butoxy)-4-phenylbutan-1-ol (2i)

Colorless oil, 43 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.29 (d, *J* = 7.7 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 2H), 7.08 (t, *J* = 7.3 Hz, 1H), 4.33 (dd, *J* = 7.6, 4.4 Hz, 1H), 3.39 (d, *J* = 5.3 Hz, 2H), 1.74-1.66 (m, 1H), 1.64-1.35 (m, 2H), 1.49-1.40 (m, 1H), 1.32 (bs, 1H), 1.05 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6) δ 147.0, 128.4, 126.9, 126.4, 74.4, 74.2, 62.9, 37.4, 29.6, 28.8. HRMS (ESI+) *m/z* calculated for $C_{14}H_{22}O_2Na$ (M+Na) 245.1512, found 245.1513. HPLC (OD-3), *n*-heptane/*i*-PrOH 90:10, 1.0 ml/min, λ = 210 nm, t_{minor} = 4.9 min, t_{major} = 3.4 min, er = 85:15. α_D^{25} = 58.4 °, c 0.576, CH_2Cl_2.

The absolute configuration was assigned by comparison of HPLC retention times with a sample of known configuration which was obtained by alternative synthesis (see Determination of absolute configurations section).



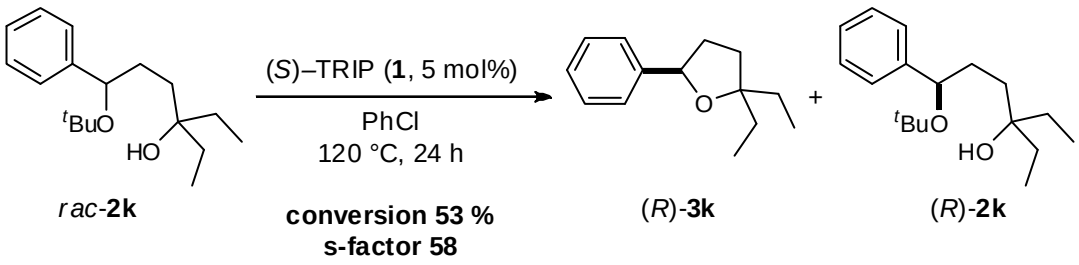
rac-**2j** **conversion 47 %** **s-factor 82** (*R*)-**3j** (*R*)-**2j**

(*R*)-2,2-dimethyl-5-phenyltetrahydrofuran (3j)

Colorless oil, 43%; ^{1}H NMR (500 MHz, C_6D_6) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 4.88 (dd, *J* = 8.4, 6.4 Hz, 1H), 2.02-1.96 (m, 1H), 1.72-1.62 (m, 1H), 1.57-1.47 (m, 2H), 1.28 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6) δ 144.7, 128.5, 127.2, 126.0, 80.9, 80.4, 39.1, 35.9, 29.2, 28.5. HRMS (EI (FE)) *m/z* calculated for $C_{12}H_{16}O_1$ (M) 176.1201, found 176.1200. HPLC (OD-3), *n*-heptane/*i*-PrOH 99.9:0.1, 1.0 ml/min, λ = 210 nm, t_{minor} = 7.2 min, t_{major} = 4.0 min, er = 97:3.

(*R*)-5-(*tert*-butoxy)-2-methyl-5-phenylpentan-2-ol (2j)

Colorless oil, 48%; ^{1}H NMR (500 MHz, C_6D_6) δ 7.33 (d, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 4.35 (dd, *J* = 7.7, 4.8 Hz, 1H), 1.86-1.78 (m, 1H), 1.74-1.60 (m, 2H), 1.45-1.39 (m, 2H), 1.07 (s, 9H), 1.05 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.3, 128.4, 126.9, 126.5, 75.0, 74.1, 69.8, 40.3, 35.4, 29.69, 29.67, 28.8. HRMS (ESI+) *m/z* calculated for $C_{16}H_{26}O_2Na$ (M+Na) 273.1825, found 273.1826. HPLC (AD-3), *n*-heptane/*i*-PrOH 99:1, 1.0 ml/min, λ = 210 nm, t_{minor} = 8.6 min, t_{major} = 7.6 min, er = 92:8.



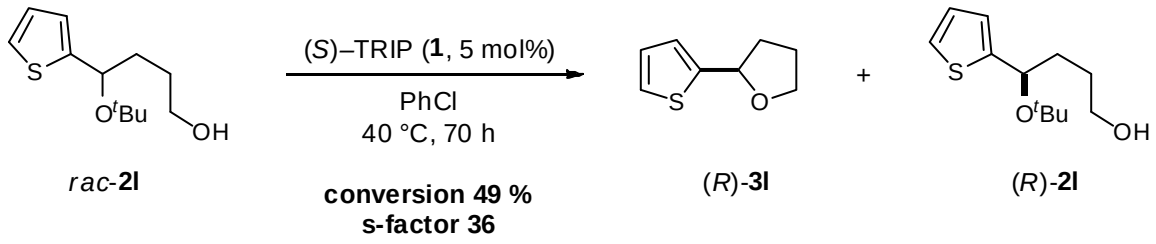
rac-**2k** **conversion 53 %** **s-factor 58** (*R*)-**3k** (*R*)-**2k**

(*R*)-2,2-diethyl-5-phenyltetrahydrofuran (3k)

Colorless oil, 52 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.42 (d, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.4 Hz, 2H), 7.11 (t, *J* = 7.3 Hz, 1H), 4.81 (dd, *J* = 9.2, 5.9 Hz, 1H), 1.97-1.93 (m, 1H), 1.67-1.47 (m, 7H), 0.93 (t, *J* = 3.0 Hz, 3H overlapped), 0.90 (t, *J* = 3.0 Hz, 3H overlapped). ^{13}C NMR (125 MHz, C_6D_6) δ 144.4, 128.5, 127.2, 126.1, 85.9, 80.5, 36.0, 35.2, 31.6, 31.3, 9.0, 8.8. HRMS (ESI+) *m/z* calculated for $C_{14}H_{20}ONa$ (M+Na) 227.1406, found 227.1407. HPLC (OD-3), *n*-heptane/*i*-PrOH 99.9:0.1, 1.0 ml/min, λ = 220 nm, t_{minor} = 4.5 min, t_{major} = 2.9 min, er = 93:7.

(*R*)-6-(*tert*-butoxy)-3-ethyl-6-phenylhexan-3-ol (2k)

Colorless oil, 37 %; ^{1}H NMR (500 MHz, C_6D_6) δ 7.33 (d, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 4.36-4.32 (m, 1H), 1.77-1.70 (m, 1H), 1.65-1.58 (m, 2H), 1.45-1.30 (m, 5H), 1.22 (bs, 1H), 1.07 (s, 9H), 0.82-0.78 (m, 6H). ^{13}C NMR (125 MHz, C_6D_6) δ 147.3, 128.4, 126.9, 126.4, 75.0, 74.1, 73.6, 34.6, 31.61, 31.57, 28.8, 8.1, 8.0. HRMS (ESI+) *m/z* calculated for $C_{18}H_{30}O_2Na$ (M+Na) 301.2138, found 301.2139. HPLC (AD-3), *n*-heptane/*i*-PrOH 99:1, 1.0 ml/min, λ = 220 nm, t_{minor} = 7.4 min, t_{major} = 6.6 min, er = 98:2.



(*R*)-2-(thiophen-2-yl)tetrahydrofuran (3l)

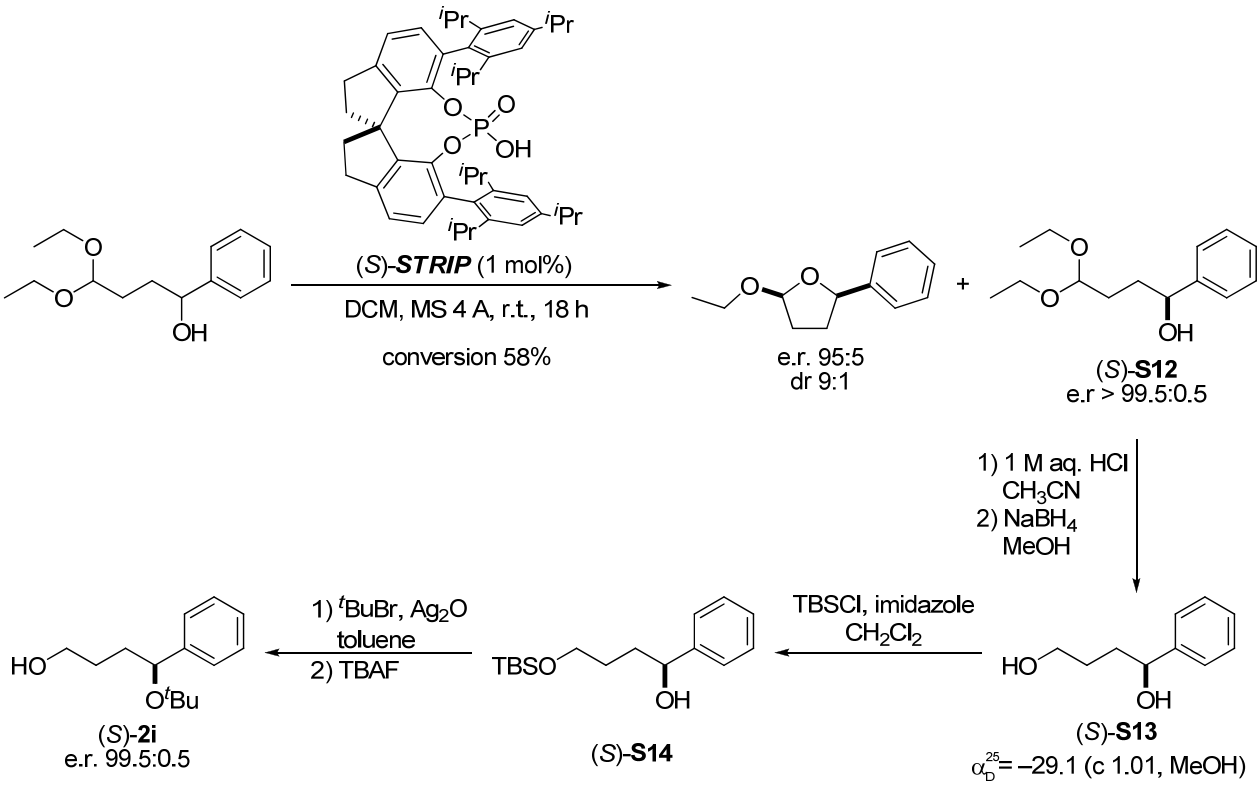
Colorless oil, 47 %; ^{1}H NMR (500 MHz, C_6D_6) δ 6.87 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.78 (td, *J* = 3.5, 1.0 Hz, 1H), 6.75-6.73 (m, 1H), 4.94 (t, *J* = 6.5 Hz, 1H), 3.82 (td, *J* = 7.8, 6.1 Hz, 1H), 3.59 (td, *J* = 7.9, 6.3 Hz, 1H), 1.86-1.79 (m, 1H), 1.70-1.64 (m, 1H), 1.62-1.54 (m, 1H), 1.47-1.38 (m, 1H). ^{13}C NMR (125 MHz, C_6D_6) δ 148.2, 126.7, 124.3, 123.4, 77.0, 68.2, 35.0, 26.0. HRMS (EI (FE)) *m/z* calculated for $C_8H_{10}OS$ (M) 154.0452, found 154.0451. HPLC (OJ-H), *n*-heptane/*i*-PrOH 90:10, 0.5 ml/min, λ = 220 nm, t_{minor} = 17.7 min, t_{major} = 21.8 min, er = 93:7.

(*R*)-4-(*tert*-butoxy)-4-(thiophen-2-yl)butan-1-ol (2l)

Colorless oil, 47 %; ^{1}H NMR (500 MHz, C_6D_6) δ 6.87 (dd, *J* = 5.0, 1.0 Hz, 1H), 6.75 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.72 (d, *J* = 3.2 Hz, 1H), 4.61 (dd, *J* = 6.8, 5.5 Hz, 1H), 3.36-3.33 (m, 2H), 1.85-1.78 (m, 1H), 1.73-1.66 (m, 1H), 1.57-1.40 (m, 2H), 1.13 (s, 1H), 1.08 (s, 9H). ^{13}C NMR (125 MHz, C_6D_6) δ 151.5, 126.5, 123.9, 122.9, 74.6, 70.6, 62.7, 37.8, 29.3, 28.5. HRMS (ESI+) *m/z* calculated for $C_{12}H_{20}O_2SNa$ (M+Na) 251.1076, found 251.1074. HPLC (OJ-H), *n*-heptane/*i*-PrOH 90:10, 0.5 ml/min, λ = 220 nm, t_{minor} = 12.5 min, t_{major} = 9.9 min, er = 91:9.

Determination of absolute configurations

*For (R)-**2i***



(*S*)-4,4-diethoxy-1-phenylbutan-1-ol ((*S*)-S12)

Prepared according to the literature procedure starting with 1 mmol of *rac*-**S12** at room temperature.[8] Colorless oil, 41%, enantiomeric ratio determined as described previously.[8]

(*S*)-1-phenylbutane-1,4-diol ((*S*)-S13)

A solution of (*S*)-**S12** (93 mg, 0.39 mmol, e.r. > 99.5:0.5) in MeCN (12 ml) was treated with 1 M HCl (4 ml). After being stirred at room temperature for 50 min the mixture was diluted with water and extracted with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, and concentrated under reduced pressure. The residue was dissolved in methanol (4 ml) and treated with $NaBH_4$ (29.5 mg, 0.78 mmol). After being stirred at room temperature for 1 h the mixture was concentrated and the residue was purified by column chromatography on silica gel using hexane/EtOAc as the eluent. Colorless solid, 22 mg. $\alpha_D^{25} = -29.1$ (c 1.01, methanol), (literature[9]: $\alpha_D^{25} = -28.0$, c 1.27, methanol, e.r. > 98.5:1.5). ^{1}H NMR (500 MHz, C_6D_6) δ 7.23 (d, J = 7.7 Hz,

2H), 7.17 (t, *J* = 7.4 Hz, 2H), 7.11-7.08 (m, 1H), 4.40 (dd, *J* = 6.9, 5.6 Hz, 1H), 3.30-3.28 (m, 2H), 1.66-1.61 (m, 2H), 1.48-1.33 (m, 2H), 0.43 (s, 1H), 0.30 (s, 1H). ^{13}C NMR (125 MHz, C_6D_6) δ 145.9, 128.5, 127.4, 126.1, 74.2, 62.7, 36.9, 29.5.

(*S*)-4-(*tert*-butyldimethylsilyloxy)-1-phenylbutan-1-ol ((*S*)-S14)

A mixture of (*S*)-**S13** (10 mg, 0.06 mmol), imidazole (8.2 mg, 0.12 mmol), and TBSCl (8.95 mg, 0.059 mmol) in CH_2Cl_2 (0.2 ml) was stirred at room temperature for 1 h. The product was isolated by column chromatography on silica gel using EtOAc/hexane as eluent. ^{1}H NMR (500 MHz, C_6D_6) δ 7.30 (d, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.11-7.08 (m, 1H), 4.50 (t, *J* = 6.2 Hz, 1H), 3.47 (t, *J* = 6.1 Hz, 2H), 2.11 (s, 1H), 1.77 (q, *J* = 7.0 Hz, 2H), 1.63-1.49 (m, 2H), 0.96 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (125 MHz, C_6D_6) δ 146.0, 128.5, 127.3, 126.2, 74.1, 63.4, 36.9, 29.5, 26.1, 18.5, -5.2.

(*S*)-4-*tert*-butoxy-4-phenylbutan-1-ol ((*S*)-2i)

A mixture of (*S*)-**S14** (6.1 mg, 0.0217 mmol), Ag_2O (25.2 mg, 0.109 mmol), and *tert*-butyl bromide (15 mg, 0.109 mmol) in toluene (0.5 ml) was stirred at room temperature until starting material was almost completely consumed as determined by TLC. The TBS protected product **S15** was isolated by column chromatography on silica gel using EtOAc/hexane as eluent. ^{1}H NMR (500 MHz, C_6D_6) δ 7.35 (d, *J* = 7.4 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.09-7.06 (m, 1H), 4.40 (dd, *J* = 7.6, 4.6 Hz, 1H), 3.58-3.50 (m, 2H), 1.86-1.80 (m, 1H), 1.78-1.70 (m, 2H), 1.65-1.55 (m, 1H), 1.08 (s, 9H), 0.97 (s, 9H), 0.044 (s, 3H), 0.037 (s, 3H). ^{13}C NMR (125 MHz, C_6D_6) δ 147.4, 128.4, 126.9, 126.5, 74.5, 73.8, 63.5, 37.2, 29.9, 28.9, 26.2, 18.5, -5.1. The TBS protected alcohol **S15** thus obtained (3.2 mg) was treated with 0.1 M solution of TBAF (0.25 ml) and stirred at room temperature until starting material was completely consumed as determined by TLC. The product was isolated by column chromatography on silica gel using EtOAc/hexane as eluent. Colorless oil, e.r. 99.5:0.5, NMR and HPLC analysis conditions as given above for (*R*)-**2i**.

Absolute configuration of (*R*)-2i

A comparison of HPLC retention times of (*S*)-**2i** obtained above with a sample recovered after our transetherification reaction from ether *rac*-**2i** revealed that they are of opposite configurations. Therefore, the recovered material after our (*S*)-TRIP catalyzed transetherification reaction of *rac*-**2i** is (*R*)-**2i**.

*Single crystal data for (S)-**3f***

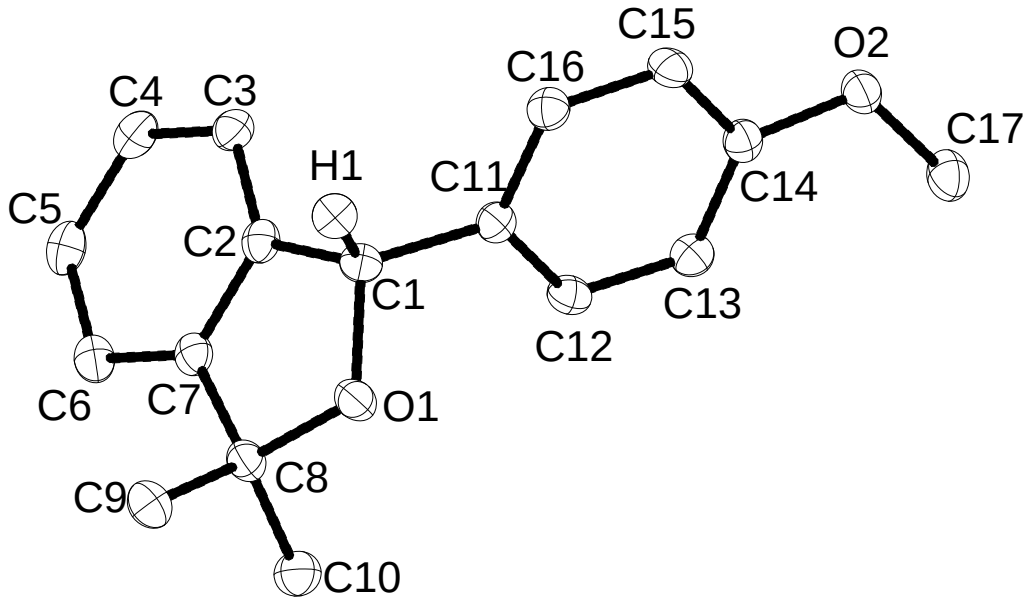


Figure S1. Single crystal structure of (*S*)-**3f**. The crystals were grown from a diethyl ether solution at 4 °C in an open flask. X-ray crystallographic data have been deposited in the Cambridge Crystallographic Data Centre database (http://www.ccdc.cam.ac.uk/) under accession code CCDC 915236.

Crystal data and structure refinement for (*S*)-3f.

Empirical formula	$C_{17} H_{18} O_2$	
Color	colourless	
Formula weight	254.31 g·mol^{-1}	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	ORTHORHOMBIC	
Space group	p 2_1 2_1 2_1, (no. 19)	
Unit cell dimensions	a = 7.0097 (5) Å	α = 90°.
	b = 11.1321 (8) Å	β = 90°.
	c = 17.6150(12) Å	γ = 90°.

Volume	1374.55(17) $Å^3$	
Z	4	
Density (calculated)	1.229 $Mg \cdot m^{-3}$	
Absorption coefficient	0.625 mm^{-1}	
F(000)	544 e	
Crystal size	0.38 x 0.31 x 0.22 mm^3	
θ range for data collection	4.70 to 67.15°.	
Index ranges	$-8 \leq h \leq 8, -13 \leq k \leq 13, -21 \leq l \leq 20$	
Reflections collected	55633	
Independent reflections	2441 [R_{int} = 0.0563]	
Reflections with I>2σ(I)	2385	
Completeness to θ = 27.50°	99.5 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.89405 and 0.80636	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2441 / 0 / 176	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2σ(I)]	R_1 = 0.0247	w R^2 = 0.0660
R indices (all data)	R_1 = 0.0280	w R^2 = 0.0663
Absolute structure parameter	-0.04(15)	
Extinction coefficient	0.0032(5)	
Largest diff. peak and hole	0.122 and -0.127 e $\cdot Å^{-3}$	

Selected bond lengths [Å] and angles [°] for (*S*)-3f.

C(1)-O(1)	1.4415(14)	C(1)-C(2)	1.5089(15)
C(1)-C(11)	1.5129(15)	C(2)-C(7)	1.3820(15)
C(2)-C(3)	1.3882(16)	C(3)-C(4)	1.3913(16)
C(4)-C(5)	1.3945(18)	C(5)-C(6)	1.3881(17)
C(6)-C(7)	1.3925(16)	C(7)-C(8)	1.5077(15)
C(8)-O(1)	1.4577(13)	C(8)-C(10)	1.5182(15)
C(8)-C(9)	1.5219(15)	C(11)-C(16)	1.3889(15)
C(11)-C(12)	1.3963(15)	C(12)-C(13)	1.3899(15)
C(13)-C(14)	1.3944(16)	C(14)-O(2)	1.3689(13)
C(14)-C(15)	1.3917(16)	C(15)-C(16)	1.3843(16)
C(17)-O(2)	1.4363(13)		
O(1)-C(1)-C(2)	103.90(9)	O(1)-C(1)-C(11)	110.79(8)
C(2)-C(1)-C(11)	114.39(9)	C(7)-C(2)-C(3)	121.05(10)
C(7)-C(2)-C(1)	109.58(9)	C(3)-C(2)-C(1)	129.37(10)
C(2)-C(3)-C(4)	118.52(10)	C(3)-C(4)-C(5)	120.47(11)
C(6)-C(5)-C(4)	120.69(11)	C(5)-C(6)-C(7)	118.56(11)
C(2)-C(7)-C(6)	120.68(10)	C(2)-C(7)-C(8)	110.15(9)
C(6)-C(7)-C(8)	129.17(10)	O(1)-C(8)-C(7)	103.28(8)
O(1)-C(8)-C(10)	107.78(9)	C(7)-C(8)-C(10)	112.52(9)
O(1)-C(8)-C(9)	108.78(8)	C(7)-C(8)-C(9)	112.31(9)
C(10)-C(8)-C(9)	111.67(9)	C(16)-C(11)-C(12)	118.36(10)
C(16)-C(11)-C(1)	120.37(9)	C(12)-C(11)-C(1)	121.23(9)
C(13)-C(12)-C(11)	121.11(10)	C(12)-C(13)-C(14)	119.69(10)
O(2)-C(14)-C(15)	115.94(10)	O(2)-C(14)-C(13)	124.54(10)
C(15)-C(14)-C(13)	119.51(10)	C(16)-C(15)-C(14)	120.17(10)
C(15)-C(16)-C(11)	121.14(10)	C(1)-O(1)-C(8)	112.27(8)
C(14)-O(2)-C(17)	117.10(9)		

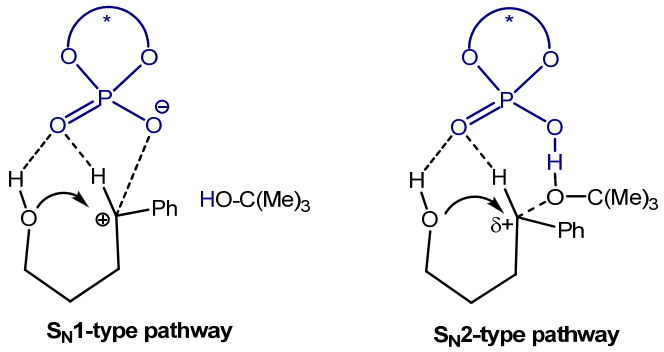
Density functional calculations

All calculations were performed with the Gaussian09 quantum chemical program.[10] Geometry optimizations were done using the hybrid B3LYP functional[11] and the 6-31G* basis set. [12] The optimized stationary points were characterized as local minima or transition structures by harmonic force constant analysis, and intrinsic reaction coordinate (IRC) calculations were performed to verify the transition state structures. [13]

For single-point calculations, the B3LYP functional was used in combination with the 6-31+G** basis set. Solvation effects were treated by the polarizable continuum model (PCM) and chlorobenzene as solvent.[14] Empirical dispersion corrections for B3LYP were also included.[15,16] The Gibbs free energies were in all cases computed by adding to these single-point energies both the zero-point vibrational energies and thermal corrections (300K) obtained at the level of theory employed in the geometry optimization (B3LYP/6-31G*). Relative free energies are reported in Table S1 for all relevant diastereomeric transition states at the following DFT level: $PCM_{(chlorobenzene)}$/B3LYP-D/6-31+G**//B3LYP/6-31G*

Further single-point solvent-phase calculations at the B3LYP gas-phase optimized structures were carried out with other DFT functionals (M06-2X[17] and ωB97X-D[18]). The corresponding results are collected in Table S2. The activation barriers obtained from these DFT approaches show the same trends as those at the B3LYP level. Natural orbital analyses were performed at the B3LYP/6-31G* level. [19]

We investigated two different pathways (see Scheme S1). For substrate **2i**, the barrier to nucleophilic substitution via the S_N1-type pathway is found to be 6.5 kcal/mol higher than the barrier to cyclization via the S_N2-type pathway. In the main paper, only the lowest energy transition state for the S_N2-type pathway is presented and discussed. It should be noted, however, that there are further conformationally distinct diastereomeric transition states. The forming five-membered ring assumes an '*envelope*' form during the S_N2-type nucleophilic substitution in **2i**. In the '*envelope*'-like transition structure, the phenyl group at the C1 atom can be placed *syn* or *anti* with respect to the adjacent out-of-plane methylene group of the substrate, and the corresponding diastereomeric transition states are thus labeled as ***syn*** or ***anti***. The structures of all relevant transition states (***syn*** and ***anti***) are shown in Figure S2, and numerical results are provided in Tables S1-S3. The data given in the main paper refer to the ***syn*** transition states only.



Scheme S1. Two possible pathways for the intramolecular transetherification reaction

Table S1. Activation parameters[a,b] relative to the separated reactants for the intramolecular transetherification reaction at the $PCM_{(chlorobenzene)}$/B3LYP/6-31+G**//B3LYP/6-31G* level.

	B3LYP-D	
	$\Delta E^{\dagger}$	$\Delta G^{\dagger}$
RC	–23.0	–9.7
(R)-3i – syn	–7.8 (0.0)	4.9 (0.0)
(R)- 3i – anti	–7.0 (0.8)	6.8 (2.1)
(S)- 3i – syn	–7.3 (0.5)	7.3 (2.4)
(S)- 3i – anti	–6.9 (0.9)	7.6 (2.7)

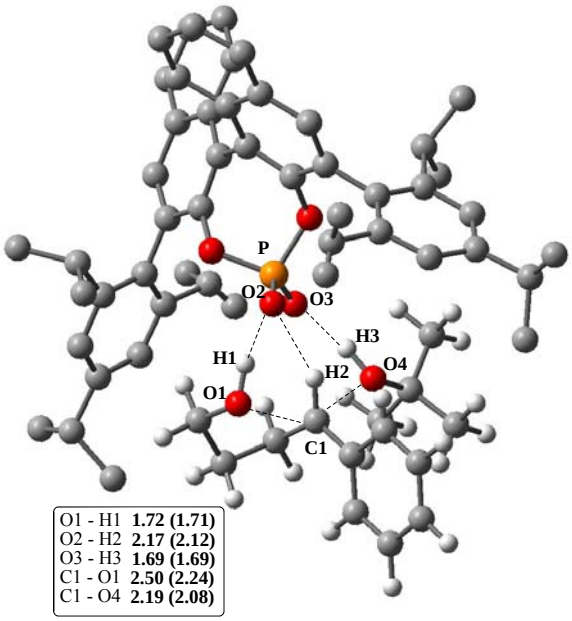
[a]Relative energies for the reactant complex **RC**. [b]Values in parentheses indicate the energy relative to the lowest-energy transition state.

Table S2. Activation parameters[a,b] relative to the separated reactants for the intramolecular transetherification reaction computed with different functionals.

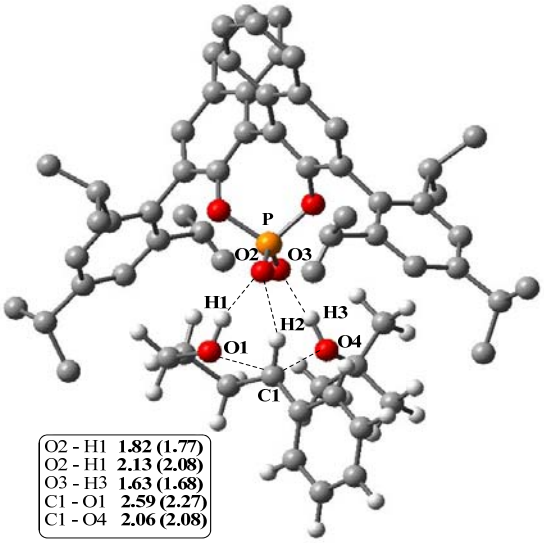
	M1		M2	
	$\Delta E^{\dagger}$	$\Delta G^{\dagger}$	$\Delta E^{\dagger}$	$\Delta G^{\dagger}$
RC	–16.6	–3.3	–22.3	–9.0
(R)-3i – syn	6.4	19.2 (0.0)	–2.9	9.8 (0.0)
(R)- 3i – anti	6.6	20.4 (1.2)	–2.3	11.5 (1.7)
(S)- 3i – syn	6.7	21.3 (2.1)	–2.1	12.4 (2.6)
(S)- 3i – anti	6.6	21.3 (2.1)	–2.3	12.4 (2.6)

[a]Relative energies for the reactant complex **RC**. [b]Values in parentheses indicate the energy relative to the lowest-energy transition state.

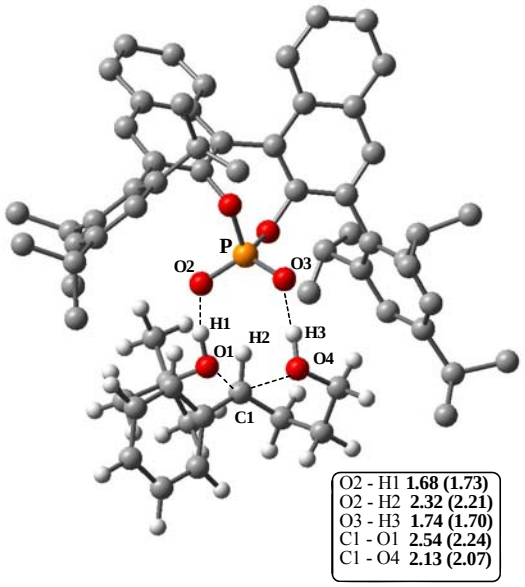
M1: $PCM_{(chlorobenzene)}$/M06-2X/6-31+G**//B3LYP/6-31G*
M2: $PCM_{(chlorobenzene)}$/ωB97X-D/6-31+G**//B3LYP/6-31G*



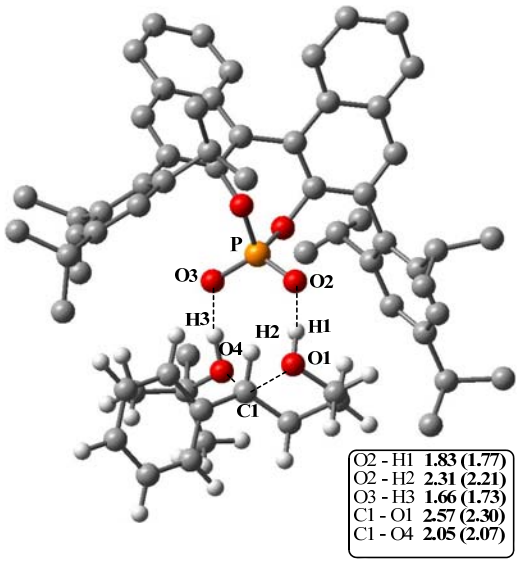
(R)-3i – syn



(R)-3i – anti



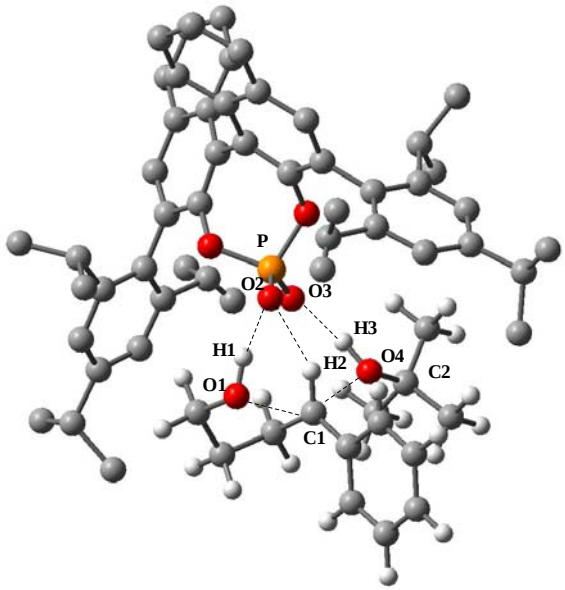
(S)-3i – syn



(S)-3i - anti

Figure S2. Optimized transition states for the S_N2-type pathway of intramolecular transetherification reaction.

Table S3. Natural population analysis of diastereoisomeric transition states performed at the B3LYP/6-31G* level of theory.



Atom	(*R*)-*3i-syn*	(*R*)-*3i-anti*	(*S*)-*3i-syn*	(*S*)-*3i-anti*
P	2.58	2.58	2.58	2.58
O1	-0.75	-0.75	-0.76	-0.75
O2	-1.14	-1.14	-1.14	-1.14
O3	-1.13	-1.13	-1.13	-1.14
O4	-0.74	-0.72	-0.76	-0.71
C1	0.14	0.13	0.14	0.13
C2	0.28	0.29	0.28	0.28
H1	0.52	0.54	0.52	0.51
H2	0.29	0.28	0.28	0.28
H3	0.52	0.53	0.53	0.53

Table S4. Optimized geometries (B3LYP, Cartesian coordinates in Å) and single-point energies of reactants, intermediates and transition states (B3LYP-D, in a.u.). Notation: E = total electronic energy, Tc = thermal correction at 298 K to obtain the Gibbs free energy, Nimag = number of imaginary frequencies (value in parenthesis, in cm^{-1}).

RC E = -3279.2603257 (-3279.764815) Tc = 1.181022 Nimag = 0				***(R)-3i – syn*** E = -3279.2339739 (-3279.7388467) Tc = 1.178242 NImag = 1 (136.08*i*)			
6	-0.325321	5.030001	-1.386757	6	-0.798639	4.850644	-1.519377
6	-1.557528	4.405441	-1.066823	6	-1.961667	4.142916	-1.123505
6	-1.621114	3.179974	-0.436373	6	-1.897990	2.949058	-0.436028
6	-0.384536	2.589978	-0.050950	6	-0.605475	2.470374	-0.067730
6	0.851109	3.194522	-0.221441	6	0.563819	3.177420	-0.311286
6	0.903801	4.416723	-0.980852	6	0.488821	4.360395	-1.128162
1	-2.481419	4.902867	-1.348755	1	-2.933485	4.547862	-1.393753
6	4.199116	2.755151	1.630136	6	3.981049	3.127177	1.461592
6	4.540986	1.454237	1.181741	6	4.423986	1.840119	1.066454
6	3.674230	0.679764	0.439034	6	3.610266	0.960613	0.383540
6	2.428552	1.268819	0.076642	6	2.305244	1.410093	0.019724
6	2.083629	2.582190	0.358982	6	1.860780	2.705187	0.256591
6	2.949269	3.330734	1.233292	6	2.676161	3.568701	1.070282
1	5.512477	1.049119	1.451670	1	5.430923	1.530031	1.334966
6	3.464695	5.289285	2.590872	6	3.048427	5.631398	2.319532
6	2.606977	4.609044	1.754688	6	2.235711	4.837486	1.540319
1	3.174250	6.259803	2.983825	1	2.681645	6.591587	2.672555
1	1.649030	5.045713	1.498244	1	1.237243	5.176475	1.290277
6	4.716145	4.734941	2.947509	6	4.351481	5.207219	2.670054
6	5.070649	3.492115	2.476933	6	4.802502	3.977693	2.249735
1	5.386791	5.285789	3.601146	1	4.985254	5.846154	3.279046
1	6.020907	3.044295	2.757920	1	5.794326	3.627706	2.526631
6	2.121902	6.202855	-2.107626	6	1.516793	6.182433	-2.383010
6	2.121767	5.031937	-1.382021	6	1.637150	5.054335	-1.601409
1	3.066417	6.647009	-2.409784	1	2.411123	6.687016	-2.738922
1	3.063063	4.562432	-1.122064	1	2.622111	4.677591	-1.351808
6	0.905994	6.828475	-2.469362	6	0.242118	6.686298	-2.732396
6	-0.290306	6.248501	-2.117457	6	-0.889246	6.028174	-2.309457
1	0.920663	7.755723	-3.035399	1	0.160790	7.581320	-3.343220
1	-1.233364	6.705837	-2.406877	1	-1.876459	6.390784	-2.586580
8	1.570816	0.487005	-0.696743	8	1.507648	0.535105	-0.692271
8	-0.434842	1.359100	0.610185	8	-0.535902	1.288385	0.648009
15	0.098093	0.049005	-0.189406	15	0.093946	-0.058377	-0.070144
8	0.315398	-0.979274	0.986286	8	0.341842	-1.037437	1.051839
8	-0.723070	-0.397724	-1.340731	8	-0.715376	-0.480731	-1.269740
1	-0.766836	-1.839927	-2.522783	1	-0.638305	-1.780075	-2.404933
6	4.056085	-0.703939	-0.000608	6	4.107061	-0.406246	0.015414
6	4.157694	-1.752827	0.946770	6	4.310929	-1.384655	1.019092
6	4.368303	-0.950740	-1.358309	6	4.431158	-0.702285	-1.329492

6	4.574321	-3.016201	0.513571	6	4.831018	-2.631176	0.652840
6	4.767841	-2.237845	-1.736316	6	4.940879	-1.968802	-1.639856
6	4.881819	-3.285642	-0.822358	6	5.155226	-2.947918	-0.668484
6	-2.943851	2.534739	-0.137370	6	-3.152611	2.215085	-0.061603
6	-3.703582	1.945286	-1.178209	6	-3.933874	1.578467	-1.057721
6	-3.458309	2.571720	1.178845	6	-3.590627	2.210802	1.283115
6	-4.965533	1.422959	-0.874516	6	-5.133459	0.961607	-0.682994
6	-4.722918	2.024923	1.425682	6	-4.793046	1.569422	1.602126
6	-5.497341	1.450531	0.417643	6	-5.584044	0.941942	0.639617
8	-0.903262	-2.680056	-2.999268	8	-0.661991	-2.692005	-2.791924
1	-5.124074	2.058074	2.436617	1	-5.132869	1.570994	2.635958
1	-5.551202	0.981863	-1.676550	1	-5.736573	0.488652	-1.454276
1	5.011829	-2.427450	-2.779329	1	5.200617	-2.193366	-2.672522
1	4.658791	-3.815996	1.244809	1	4.994186	-3.374020	1.429920
6	-2.703625	3.220208	2.339027	6	-2.826356	2.922258	2.398905
1	-1.738340	3.573232	1.965017	1	-1.913456	3.345198	1.971600
6	-3.210544	1.883973	-2.625059	6	-3.534330	1.560816	-2.534442
1	-2.141541	2.116426	-2.626669	1	-2.514666	1.946371	-2.611785
6	-6.883297	0.896154	0.722666	6	-6.906286	0.291520	1.026939
1	-7.028848	0.972656	1.809133	1	-6.977988	0.336810	2.122413
6	-2.408816	2.217245	3.470104	6	-2.392808	1.954164	3.515203
1	-1.837937	1.362901	3.092622	1	-1.778007	1.145961	3.108678
1	-1.821104	2.696189	4.262651	1	-1.802447	2.485651	4.271565
1	-3.331687	1.838500	3.925337	1	-3.257277	1.509905	4.023981
6	-3.452676	4.456903	2.873884	6	-3.639822	4.102140	2.967534
1	-3.621963	5.191538	2.078644	1	-3.909486	4.813801	2.179010
1	-4.430072	4.186143	3.290430	1	-4.568473	3.761228	3.440559
1	-2.874296	4.942920	3.669086	1	-3.057489	4.639590	3.725987
6	-3.361203	0.486034	-3.252970	6	-3.513121	0.140058	-3.126254
1	-4.413049	0.201370	-3.376502	1	-4.508837	-0.320628	-3.129236
1	-2.904556	0.475650	-4.249538	1	-3.166781	0.171484	-4.166348
1	-2.861509	-0.273804	-2.648137	1	-2.827881	-0.497317	-2.562843
6	-3.922533	2.939747	-3.495990	6	-4.447603	2.481642	-3.368876
1	-3.539934	2.911774	-4.523412	1	-4.123892	2.497029	-4.416744
1	-5.002584	2.752021	-3.534798	1	-5.488513	2.135934	-3.345345
1	-3.777452	3.954141	-3.108589	1	-4.434085	3.511612	-2.995521
6	-7.015720	-0.590563	0.344639	6	-6.971538	-1.193050	0.624987
1	-6.909017	-0.735864	-0.737088	1	-6.944286	-1.308224	-0.465713
1	-6.251170	-1.198361	0.840765	1	-6.129696	-1.755298	1.044282
1	-8.000480	-0.976104	0.635190	1	-7.901920	-1.651212	0.982005
6	-7.987585	1.734644	0.050141	6	-8.107723	1.068267	0.454279
1	-8.981281	1.358325	0.322199	1	-9.054295	0.623647	0.785602
1	-7.925255	2.785770	0.352399	1	-8.089976	2.114820	0.777005
1	-7.903127	1.696510	-1.042519	1	-8.098021	1.058253	-0.642257
6	3.838251	-1.560028	2.429947	6	3.998521	-1.132958	2.494989
1	3.375080	-0.576738	2.551265	1	3.556484	-0.137446	2.582572
6	4.338360	0.142708	-2.426233	6	4.305185	0.329228	-2.450779
1	3.977207	1.065528	-1.964016	1	3.889303	1.246160	-2.024958
6	5.337775	-4.667133	-1.273666	6	5.759070	-4.296511	-1.041379

1	5.489218	-4.616983	-2.360659	1	5.873337	-4.307728	-2.134179
6	6.685836	-5.058803	-0.638818	6	7.162726	-4.475312	-0.430835
1	7.026838	-6.029002	-1.019951	1	7.610611	-5.422298	-0.756035
1	7.458433	-4.314307	-0.859990	1	7.830082	-3.660225	-0.730873
1	6.603134	-5.139732	0.451654	1	7.119230	-4.484073	0.664738
6	4.269375	-5.744107	-1.007750	6	4.844914	-5.475889	-0.662185
1	4.079114	-5.860793	0.065811	1	4.689256	-5.529135	0.421778
1	3.319511	-5.485644	-1.488903	1	3.861081	-5.382323	-1.136242
1	4.595139	-6.716801	-1.395519	1	5.286688	-6.427548	-0.981688
6	3.373972	-0.191975	-3.579847	6	3.341928	-0.127162	-3.562049
1	3.688587	-1.090594	-4.123567	1	3.690660	-1.046527	-4.048154
1	2.357885	-0.356273	-3.208932	1	2.341201	-0.305781	-3.157732
1	3.343983	0.634749	-4.299689	1	3.261093	0.645273	-4.336463
6	5.756073	0.437959	-2.956339	6	5.688225	0.693281	-3.027390
1	6.432772	0.724117	-2.143229	1	6.361017	1.057834	-2.242943
1	6.187814	-0.436527	-3.457196	1	6.167878	-0.170720	-3.502605
1	5.729546	1.259110	-3.682890	1	5.592320	1.479860	-3.785722
6	5.118801	-1.582917	3.288322	6	5.279426	-1.143855	3.352418
1	4.879158	-1.411707	4.344866	1	5.043519	-0.908830	4.397444
1	5.627115	-2.551610	3.211704	1	5.767755	-2.125733	3.333980
1	5.830401	-0.811791	2.973663	1	6.007813	-0.406688	2.995522
6	2.824928	-2.596489	2.950509	6	2.956766	-2.126461	3.041540
1	2.542670	-2.360406	3.983800	1	2.730460	-1.896060	4.090311
1	1.920041	-2.592487	2.336567	1	2.031548	-2.051010	2.463360
1	3.237358	-3.612373	2.948762	1	3.319475	-3.161332	3.002476
6	0.192295	-3.543185	-2.730299	6	0.646008	-3.241316	-2.698632
6	-0.163525	-4.696252	-1.780408	6	0.583203	-4.486235	-1.821831
1	0.659908	-5.424174	-1.821896	1	1.580219	-4.924327	-1.689265
1	-1.051032	-5.206181	-2.174939	1	-0.048439	-5.238901	-2.308717
6	-0.377778	-4.311510	-0.302300	6	0.004840	-4.139330	-0.420910
1	-0.353570	-5.217245	0.313593	1	-0.052083	-5.055745	0.174339
1	0.470382	-3.697938	0.027939	1	0.679495	-3.443179	0.083903
6	-1.658337	-3.502095	-0.038266	6	-1.340647	-3.500543	-0.518342
1	-1.657269	-2.667539	-0.738057	1	-1.383664	-2.424672	-0.588709
1	-0.434048	-1.657790	1.102161	1	-0.863427	-2.138278	1.504782
8	-1.579897	-2.776526	1.243178	8	-1.590019	-2.825767	1.551590
6	-1.918928	-3.290850	2.574931	6	-1.701839	-3.366621	2.893019
6	-3.443031	-3.351968	2.762546	6	-3.026411	-4.132208	2.933007
1	-3.670585	-3.529351	3.820301	1	-3.201206	-4.543733	3.933109
1	-3.897645	-2.400216	2.469980	1	-3.858107	-3.467143	2.679290
1	-3.904489	-4.150237	2.179874	1	-3.020596	-4.961470	2.217875
1	0.515751	-3.978267	-3.686869	1	1.000333	-3.509481	-3.703883
1	1.052069	-2.984231	-2.328890	1	1.350866	-2.513793	-2.276501
6	-2.974449	-4.231302	-0.259283	6	-2.570947	-4.209515	-0.777418
6	-4.098329	-3.472125	-0.618489	6	-3.743465	-3.452864	-0.986746
6	-3.119141	-5.620180	-0.150074	6	-2.643925	-5.617247	-0.836185
6	-5.336039	-4.076122	-0.829699	6	-4.951022	-4.086512	-1.254776
1	-3.995077	-2.395661	-0.730256	1	-3.689111	-2.369602	-0.935494
6	-4.357450	-6.230945	-0.363317	6	-3.852875	-6.246984	-1.105424

1	-2.262559	-6.241444	0.094102	1	-1.753110	-6.214822	-0.671458
6	-5.471000	-5.460415	-0.697308	6	-5.006194	-5.482240	-1.314880
1	-6.193183	-3.468161	-1.106251	1	-5.848573	-3.497526	-1.415269
1	-4.447576	-7.310461	-0.274038	1	-3.902498	-7.330823	-1.152679
1	-6.433884	-5.935329	-0.866020	1	-5.950440	-5.977556	-1.524562
6	-1.342535	-2.227303	3.520836	6	-1.727093	-2.174269	3.860191
1	-1.593510	-2.475881	4.557335	1	-1.847587	-2.518638	4.893965
1	-0.253337	-2.166113	3.438846	1	-0.795315	-1.602273	3.794265
1	-1.762963	-1.242067	3.294391	1	-2.557079	-1.504308	3.615192
6	-1.270384	-4.649910	2.863300	6	-0.519536	-4.295412	3.203474
1	-0.186500	-4.608243	2.717467	1	0.432277	-3.765562	3.094988
1	-1.461457	-4.928143	3.906114	1	-0.584098	-4.669686	4.231785
1	-1.684800	-5.439749	2.232125	1	-0.513560	-5.161354	2.532362

(R)-3i – anti				***(S)-3i – syn***			
E = -3279.2309696 (-3279.7378934)				E = -3279.2309384 (-3279.738771)			
Tc = 1.180445 NImag = 1 (180.23*i*)				Tc = 1.182593 NImag = 1 (179.65*i*)			
6	-1.131355	4.788453	-1.460183	6	2.128223	4.188249	1.832231
6	-2.251847	4.002544	-1.090778	6	3.062140	3.321751	1.211865
6	-2.121673	2.804111	-0.420681	6	2.672571	2.280218	0.394448
6	-0.806097	2.399651	-0.046181	6	1.277061	2.136606	0.129176
6	0.319325	3.182747	-0.263186	6	0.331118	3.056328	0.565330
6	0.179642	4.373382	-1.060186	6	0.737851	4.053044	1.520281
1	-3.244199	4.349984	-1.366564	1	4.120981	3.471587	1.407943
6	3.720036	3.316253	1.534895	6	-3.010357	4.183044	-0.966612
6	4.250452	2.072997	1.109209	6	-3.766812	3.001896	-0.768397
6	3.501475	1.156865	0.400054	6	-3.203209	1.837340	-0.291091
6	2.169479	1.526329	0.044138	6	-1.825224	1.870736	0.082972
6	1.638933	2.782975	0.308543	6	-1.059712	3.028133	0.026780
6	2.390361	3.679578	1.146973	6	-1.628639	4.198585	-0.592255
1	5.276450	1.827458	1.372213	1	-4.821086	3.007925	-1.034088
6	2.619485	5.732333	2.445247	6	-1.465017	6.468315	-1.474358
6	1.864174	4.904758	1.643673	6	-0.876330	5.370380	-0.886193
1	2.188620	6.657631	2.818463	1	-0.862655	7.345295	-1.696042
1	0.845889	5.181348	1.396463	1	0.181811	5.392115	-0.655189
6	3.946619	5.387342	2.792833	6	-2.841628	6.463586	-1.798885
6	4.480118	4.200592	2.347018	6	-3.593715	5.338944	-1.552202
1	4.534099	6.052671	3.419713	1	-3.295508	7.339347	-2.254746
1	5.491995	3.910950	2.620986	1	-4.648149	5.308772	-1.817051
6	1.105225	6.279807	-2.268482	6	0.249973	5.838569	3.108472
6	1.287394	5.147378	-1.505364	6	-0.182998	4.898438	2.199289
1	1.970028	6.846599	-2.603093	1	-0.475861	6.463279	3.622271
1	2.291234	4.829493	-1.249188	1	-1.243678	4.785986	2.006174
6	-0.194427	6.708216	-2.626520	6	1.628781	5.995161	3.384025
6	-1.286844	5.971944	-2.231014	6	2.545219	5.182550	2.757965
1	-0.324727	7.607403	-3.222545	1	1.957784	6.746532	4.096776
1	-2.291591	6.276119	-2.515243	1	3.607175	5.277690	2.972688
8	1.429153	0.618404	-0.688431	8	-1.275967	0.722170	0.622760
8	-0.671527	1.211013	0.649880	8	0.886442	1.101070	-0.697817

15	0.063548	-0.080312	-0.068141	15	-0.080030	-0.122699	-0.148559
8	0.401237	-1.028702	1.060315	8	-0.583998	-0.826540	-1.378463
8	-0.701962	-0.586870	-1.261455	8	0.601246	-0.921920	0.943100
1	-0.483308	-1.930328	-2.468922	1	-0.114873	-2.260216	-2.410094
6	4.107354	-0.155009	-0.006276	6	-4.035824	0.596435	-0.164693
6	4.409164	-1.133764	0.972516	6	-4.463425	-0.092353	-1.326972
6	4.456633	-0.385645	-1.358067	6	-4.449081	0.147042	1.110204
6	5.062114	-2.307565	0.578822	6	-5.270739	-1.226575	-1.180541
6	5.101244	-1.581551	-1.696224	6	-5.259752	-0.990279	1.197315
6	5.423821	-2.553643	-0.747892	6	-5.681467	-1.696234	0.069983
6	-3.336067	1.995163	-0.069091	6	3.708569	1.384708	-0.219227
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1	-3.381082	4.341877	3.775628	1	3.488161	4.105893	-3.807039
6	-3.517258	-0.077093	-3.135492	6	3.869048	-1.006194	2.500832
1	-4.476018	-0.610058	-3.135745	1	4.638358	-1.743355	2.239247
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6	4.203375	0.642032	-2.461006	6	-4.088234	0.890522	2.395450
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6	6.184399	-3.811061	-1.151297	6	-6.576587	-2.921144	0.211105
1	6.275226	-3.795633	-2.246237	1	-6.767344	-3.057582	1.284623
6	7.613021	-3.810952	-0.572127	6	-7.940963	-2.721815	-0.475462
1	8.175351	-4.685710	-0.921235	1	-8.590417	-3.589554	-0.307122
1	8.160122	-2.910631	-0.871982	1	-8.451156	-1.832978	-0.088868
1	7.594611	-3.839945	0.523926	1	-7.827448	-2.596227	-1.558774
6	5.441519	-5.104431	-0.770593	6	-5.888537	-4.201835	-0.297784
1	5.320456	-5.192833	0.315475	1	-5.673699	-4.137075	-1.371292
1	4.443474	-5.136745	-1.222221	1	-4.939967	-4.373613	0.223710
1	5.997374	-5.985098	-1.114468	1	-6.529299	-5.077817	-0.138419
6	3.265224	0.098561	-3.554702	6	-3.271527	0.014324	3.361575
1	3.700508	-0.768927	-4.066060	1	-3.846840	-0.856666	3.699774
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1	6.175082	1.581445	-2.292030	1	-5.899941	2.121724	2.409698
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1	5.328695	1.933325	-3.811654	1	-5.063141	2.040637	3.972534
6	5.313463	-0.886153	3.333521	6	-5.368150	0.819443	-3.511143
1	5.037736	-0.713682	4.381007	1	-5.094843	1.208115	-4.499628
1	5.893068	-1.816320	3.290721	1	-6.064922	-0.014047	-3.661939
1	5.974741	-0.070627	3.019138	1	-5.908726	1.607719	-2.974580
6	3.101643	-2.072428	2.937928	6	-3.327848	-0.692610	-3.533310
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6	0.354811	-4.282857	-0.505174	6	-2.023465	-3.932109	-1.737034
1	0.289938	-5.326140	-0.831400	1	-2.934537	-4.506117	-1.947859
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1	-0.613944	-2.246830	1.447041	1	-1.905031	-4.565861	0.312710
8	-1.266626	-3.017729	1.479226	1	-1.087391	-5.667560	-0.796396
6	-1.360395	-3.593866	2.814932	6	0.014086	-3.898087	-0.251241
6	-2.690033	-4.349774	2.870303	1	0.004511	-2.351881	1.563810
1	-2.849886	-4.760795	3.873185	8	-0.364674	-3.283758	1.671120
1	-3.519911	-3.677272	2.632562	6	-0.099280	-3.820458	3.002658
1	-2.704372	-5.178486	2.155644	6	-0.851345	-5.150180	3.084510
1	1.513019	-2.722974	-3.412199	1	-0.727220	-5.593819	4.078095
6	-2.251484	-4.360941	-0.710940	1	-1.921745	-5.002424	2.906525
6	-3.417739	-3.592581	-0.906735	1	-0.468633	-5.864751	2.347860
6	-2.341429	-5.765339	-0.772943	1	-1.715286	-3.294500	-3.783145
6	-4.634187	-4.211771	-1.168300	1	-0.905512	-4.817488	-3.377586

1	-3.351428	-2.510034	-0.855143	6	-0.672393	-2.802439	3.997467
6	-3.562099	-6.382158	-1.026897	1	-0.532257	-3.155775	5.025618
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6	-4.708138	-5.606719	-1.227349	1	-1.741201	-2.651126	3.821306
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1	-1.456534	-2.781603	4.827493	1	0.007030	-2.830832	-0.397086
1	-0.429820	-1.842119	3.722372	6	1.325903	-4.519403	-0.212827
1	-2.195050	-1.741740	3.587673	6	2.455768	-3.675306	-0.213882
6	-0.180383	-4.536429	3.086233	6	1.513955	-5.915287	-0.178310
1	0.774791	-4.009215	2.990864	6	3.736133	-4.214527	-0.183608
1	-0.242160	-4.938593	4.103853	1	2.310154	-2.599584	-0.225278
1	-0.186152	-5.384584	2.392871	6	2.797216	-6.450830	-0.140864
6	1.341929	-3.501812	-1.400507	1	0.659019	-6.583501	-0.175678
1	0.766136	-4.291745	0.506985	6	3.908624	-5.601596	-0.145062
1	1.520558	-2.518317	-0.956794	1	4.597001	-3.554432	-0.189514
1	2.306853	-4.023219	-1.399966	1	2.934262	-7.527965	-0.113022
1	0.776522	-4.332465	-3.325881	1	4.910202	-6.022654	-0.120744

(*S*)-*3i – anti*			
E = -3279.2321078 (-3279.7391263)			
Tc = 1.182501 NImag = 1 (149.34*i*)			
6	2.466092	3.994032	1.873742
6	3.323700	3.130880	1.146560
6	2.840939	2.161641	0.290876
6	1.428187	2.101016	0.095996
6	0.549022	3.023065	0.650568
6	1.054677	3.935494	1.641171
1	4.397254	3.220277	1.292570
6	-2.812194	4.355457	-0.658456
6	-3.589130	3.176790	-0.549104
6	-3.044067	1.963408	-0.182678
6	-1.665766	1.941976	0.188846
6	-0.868247	3.080520	0.187988
6	-1.420810	4.308492	-0.325258
1	-4.644138	3.224021	-0.807037
6	-1.223672	6.635409	-1.036037
6	-0.646658	5.480842	-0.554574
1	-0.604798	7.511819	-1.209214
1	0.418365	5.459390	-0.358862
6	-2.609394	6.690144	-1.314272
6	-3.382663	5.567692	-1.132835
1	-3.053442	7.609888	-1.685303
1	-4.444599	5.582726	-1.367281
6	0.738819	5.627558	3.368812
6	0.212802	4.767952	2.429606
1	0.072445	6.244225	3.966107

1	-0.861214	4.709324	2.294244
6	2.137180	5.711529	3.566946
6	2.979110	4.907721	2.833883
1	2.540324	6.400026	4.304691
1	4.055037	4.947391	2.988167
8	-1.141179	0.751519	0.657699
8	0.941593	1.140969	-0.771612
15	0.002862	-0.089629	-0.195120
8	-0.590361	-0.762310	-1.400387
8	0.747140	-0.909483	0.837121
1	-0.588446	-2.335464	-2.151333
6	-3.907997	0.736311	-0.211230
6	-4.346676	0.220473	-1.457448
6	-4.368864	0.152477	0.989740
6	-5.247393	-0.851344	-1.465027
6	-5.271087	-0.916224	0.923356
6	-5.735762	-1.427670	-0.288839
6	3.785247	1.239636	-0.422650
6	4.566943	0.313823	0.313019
6	3.951745	1.333957	-1.825413
6	5.490526	-0.487631	-0.367887
6	4.887834	0.504884	-2.453508
6	5.671152	-0.410515	-1.750693
8	-0.677944	-3.302414	-2.343183
1	5.020017	0.583919	-3.530347
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1	-5.643854	-1.350451	1.848924
1	-5.591430	-1.232391	-2.423885
6	3.188603	2.340290	-2.686475
1	2.492180	2.884067	-2.043878
6	4.444465	0.140931	1.827770
1	3.656731	0.808336	2.184390
6	6.697732	-1.272875	-2.474029
1	6.611554	-1.045492	-3.545368
6	2.350414	1.649793	-3.778693
1	1.646829	0.937938	-3.338293
1	1.775877	2.395474	-4.341753
1	2.983986	1.112733	-4.495126
6	4.142774	3.388410	-3.294360
1	4.705139	3.913778	-2.513951
1	4.868479	2.927197	-3.974806
1	3.577131	4.133909	-3.866327
6	4.008939	-1.286899	2.202922
1	4.741948	-2.037755	1.882826
1	3.899825	-1.375728	3.291446
1	3.045559	-1.515020	1.738007
6	5.745585	0.533168	2.554513
1	5.619499	0.447939	3.640833
1	6.580705	-0.115800	2.264546

1	6.037402	1.564940	2.327476
6	6.419588	-2.777784	-2.302742
1	6.516379	-3.080982	-1.252527
1	5.408120	-3.032703	-2.638480
1	7.132563	-3.374098	-2.885077
6	8.136601	-0.927787	-2.044223
1	8.865222	-1.517751	-2.613713
1	8.353052	0.133407	-2.208014
1	8.294099	-1.138951	-0.979756
6	-3.898130	0.800878	-2.801305
1	-3.167624	1.588723	-2.603944
6	-3.961275	0.682849	2.362340
1	-3.197742	1.451093	2.217570
6	-6.769659	-2.546970	-0.314815
1	-6.983259	-2.812108	0.729959
6	-8.093924	-2.080898	-0.949883
1	-8.848134	-2.875961	-0.903667
1	-8.491574	-1.201541	-0.431858
1	-7.955661	-1.812422	-2.003827
6	-6.245267	-3.815656	-1.011581
1	-6.002109	-3.622047	-2.063053
1	-5.338787	-4.186754	-0.520113
1	-6.997272	-4.613616	-0.984958
6	-3.332323	-0.415314	3.238619
1	-4.058226	-1.197892	3.491646
1	-2.487962	-0.885625	2.725494
1	-2.969186	0.013281	4.181021
6	-5.149010	1.355286	3.078334
1	-5.561027	2.172807	2.476232
1	-5.958463	0.640700	3.270203
1	-4.832495	1.769850	4.043331
6	-5.077290	1.446964	-3.555677
1	-4.728306	1.907274	-4.487840
1	-5.842173	0.705625	-3.816710
1	-5.562717	2.224713	-2.955159
6	-3.186835	-0.243133	-3.681894
1	-2.876813	0.213826	-4.629783
1	-2.293150	-0.618813	-3.176988
1	-3.841790	-1.089391	-3.923897
6	-2.052043	-3.653831	-2.268564
6	-1.724173	-4.377952	0.142926
6	-0.329881	-3.846645	0.113612
1	0.112286	-2.152554	1.771034
8	-0.342388	-2.995829	2.068549
6	0.089105	-3.390431	3.404641
6	-0.989579	-4.340315	3.930054
1	-0.754479	-4.658698	4.951473
1	-1.966517	-3.846900	3.935075
1	-1.057471	-5.238020	3.305174

6	0.160796	-2.113451	4.253525
1	0.472820	-2.356502	5.275668
1	0.884850	-1.407387	3.833039
1	-0.814121	-1.619725	4.296147
6	1.457128	-4.084083	3.361285
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1	1.781632	-4.332928	4.378270
1	1.417149	-5.011480	2.783219
1	-0.201098	-2.802681	-0.113728
6	0.859212	-4.661129	0.004564
6	2.083725	-4.012506	-0.262893
6	0.836343	-6.065768	0.127872
6	3.252211	-4.751543	-0.405585
1	2.097505	-2.929875	-0.347105
6	2.007431	-6.800300	-0.015149
1	-0.097420	-6.578933	0.335030
6	3.214834	-6.143722	-0.281018
1	4.189313	-4.245106	-0.614679
1	1.985258	-7.882146	0.078036
1	4.128472	-6.721500	-0.392652
6	-2.198815	-4.800939	-1.275722
1	-1.795107	-5.238604	0.815907
1	-2.383520	-3.596631	0.529685
1	-1.604281	-5.653944	-1.624244
1	-3.243181	-5.129883	-1.210034
1	-2.406596	-3.974928	-3.259272
1	-2.661951	-2.797836	-1.955128

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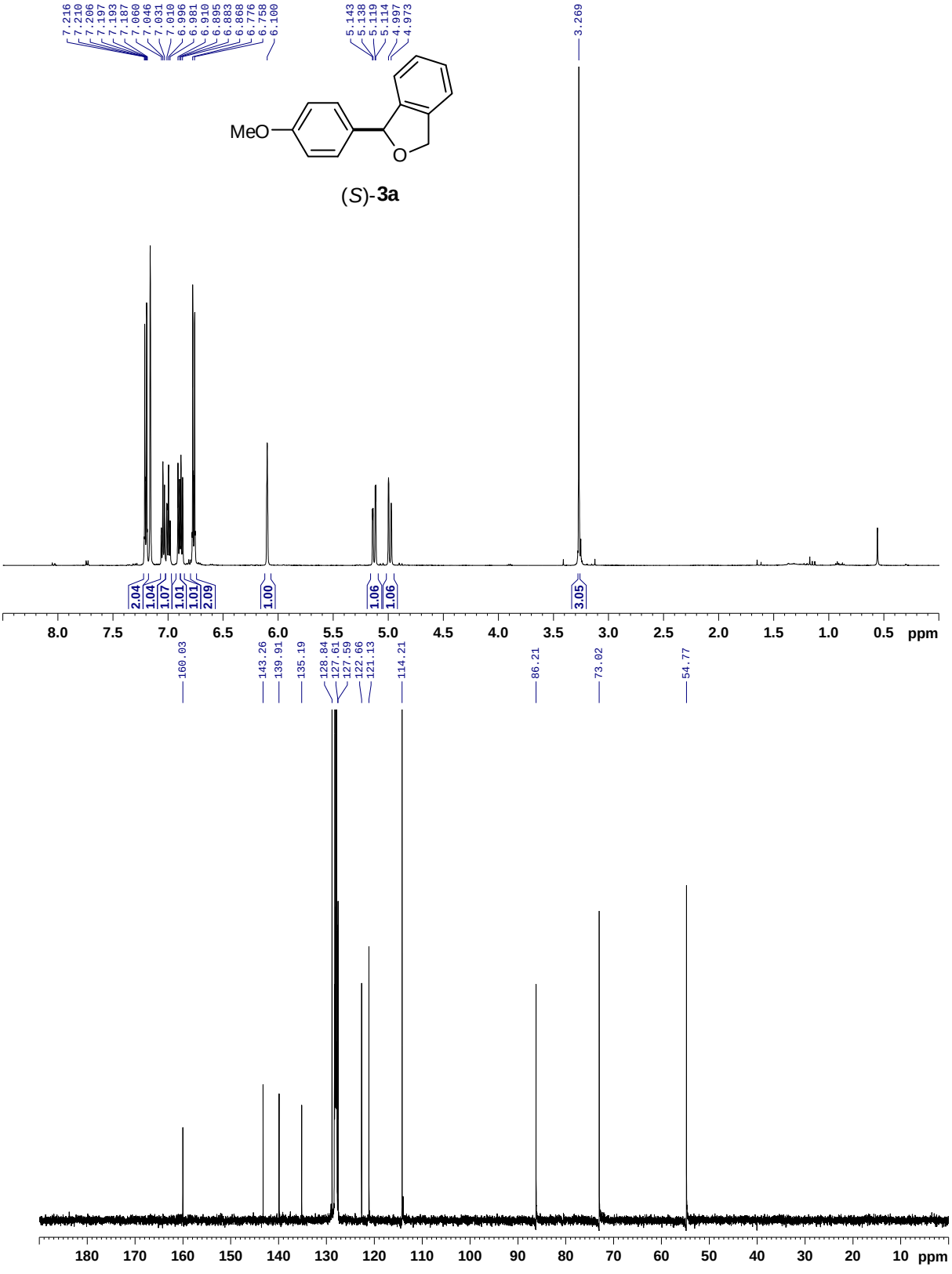
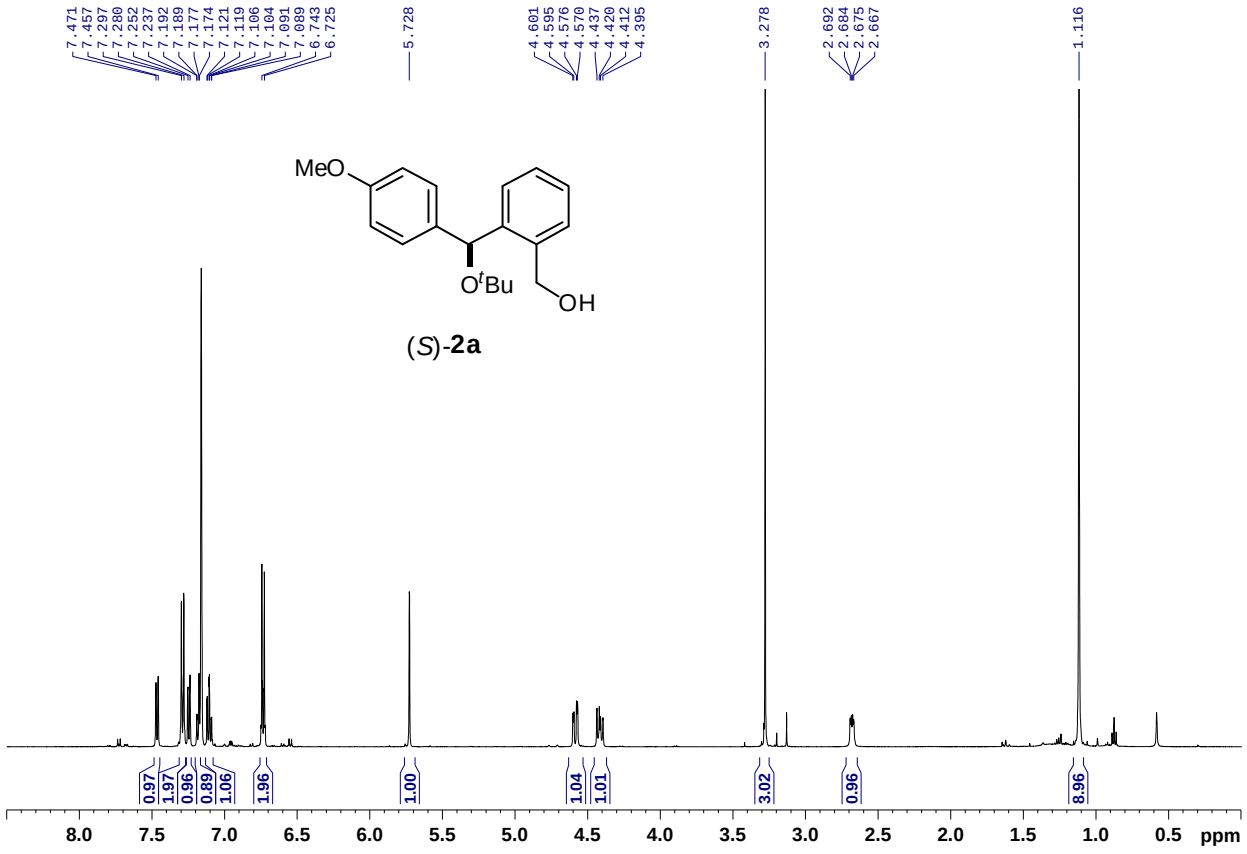
Copies of NMR spectra

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7.104
7.091
7.089
6.743
6.725
5.728
4.601
4.595
4.576
4.570
4.437
4.420
4.412
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3.278
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2.684
2.675
2.667
1.116
MeO
O^{t}Bu
OH
0.97
1.97
0.96
0.89
1.06
1.96
1.00
1.04
1.01
3.02
0.96
8.96
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
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1.0
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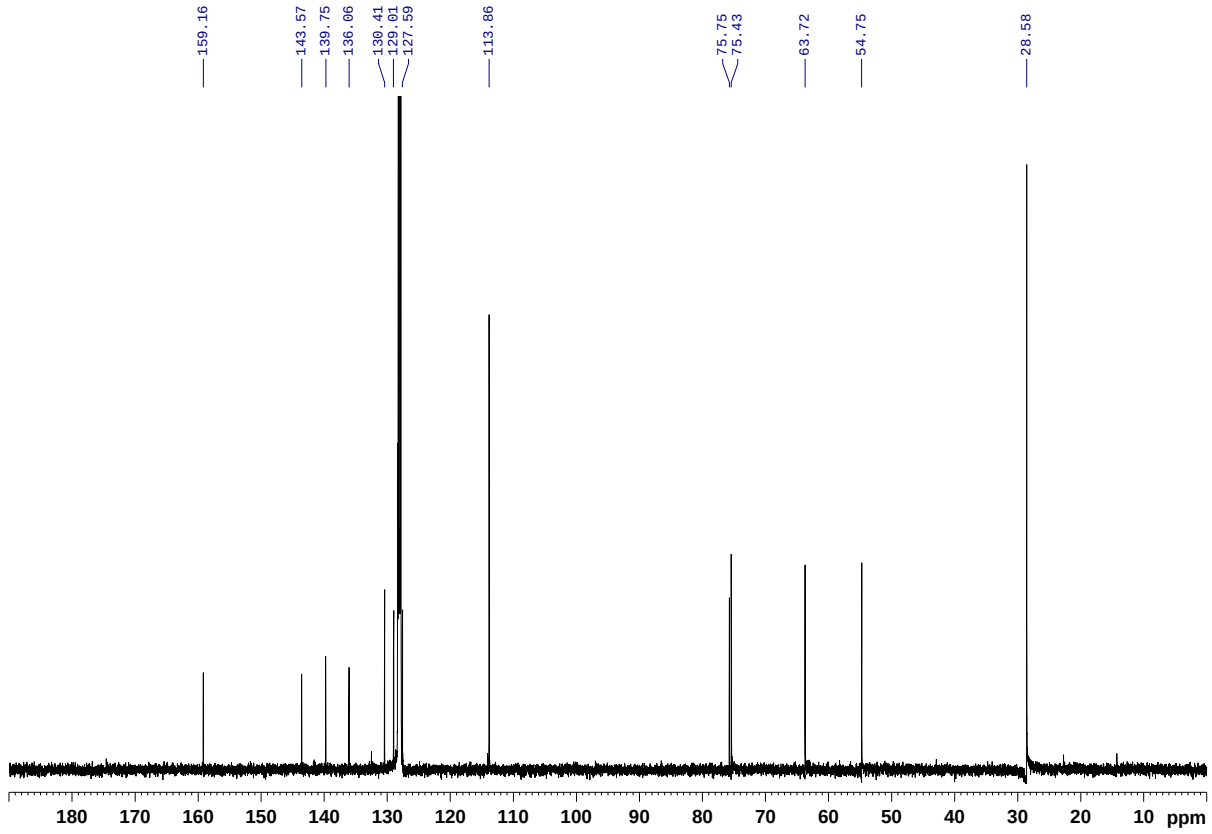
ppm

(*S*)-**2a**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130.41
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63.72
54.75
28.58
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150
140
130
120
110
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90
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70
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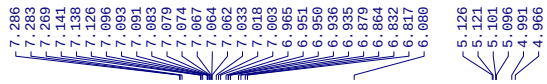
50
40
30
20
10
ppm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7.079
7.074
7.067
7.064
7.062
7.033
7.018
7.003
6.965
6.951
6.950
6.936
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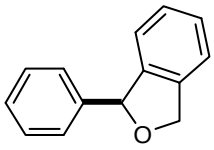
5.096
4.991
4.966


O

(*S*)-**3b**

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1.03
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1.03
1.00
1.09
1.07
8.0
7.5
7.0
6.5
6.0
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5.0
4.5
4.0
3.5
3.0
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2.0
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1.0
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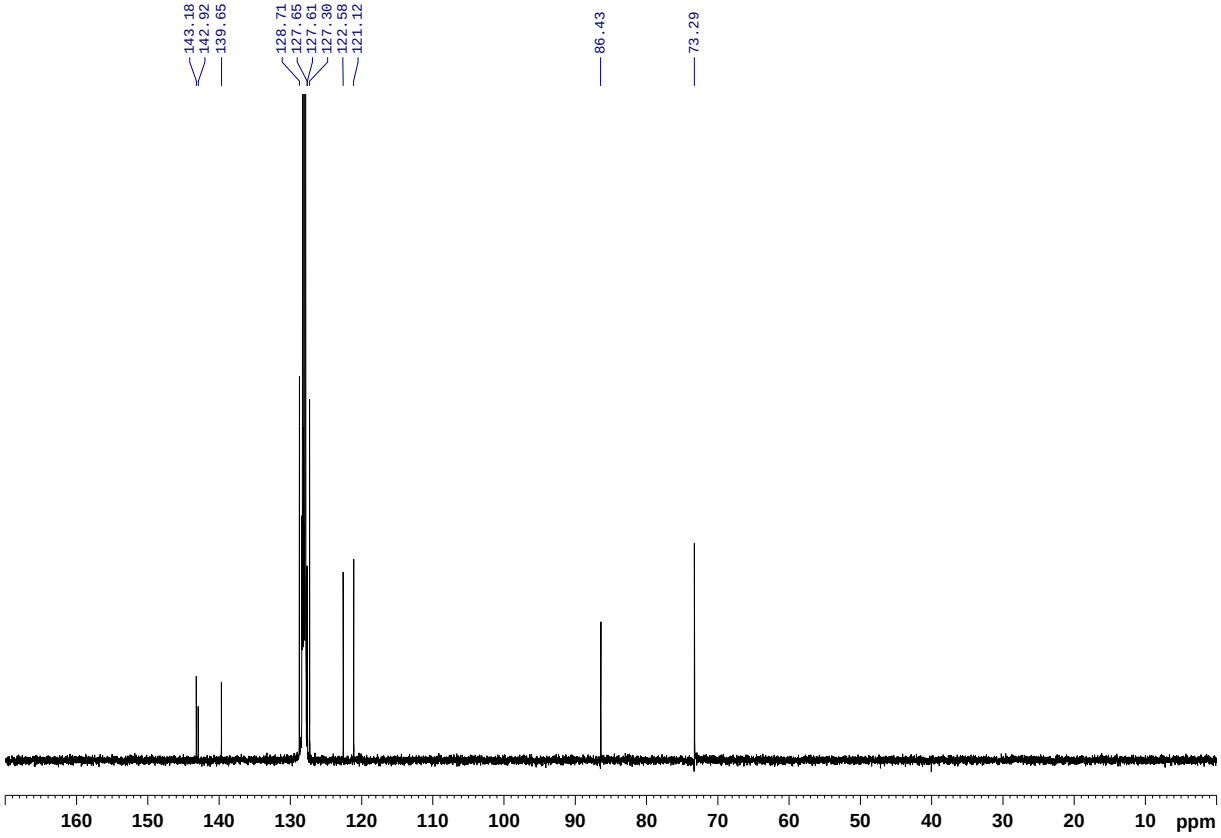
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140
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70
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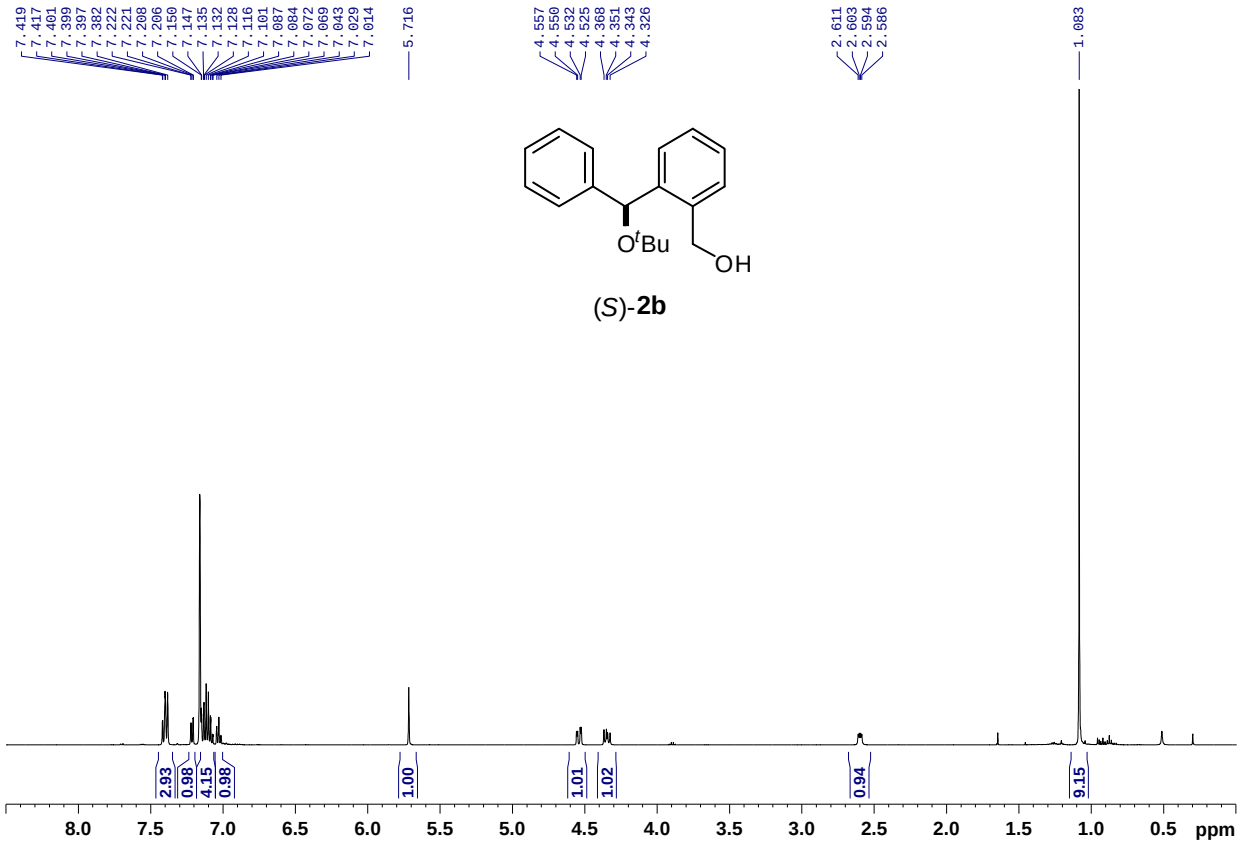
30
20
10
ppm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7.135
7.132
7.128
7.116
7.101
7.087
7.084
7.072
7.069
7.043
7.029
7.014
5.716
4.557
4.550
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4.525
4.368
4.351
4.343
4.326
2.611
2.603
2.594
2.586
1.083
O^{t}Bu
OH
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0.98
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0.98
1.00
1.01
1.02
0.94
9.15
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7.0
6.5
6.0
5.5
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2.5
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1.0
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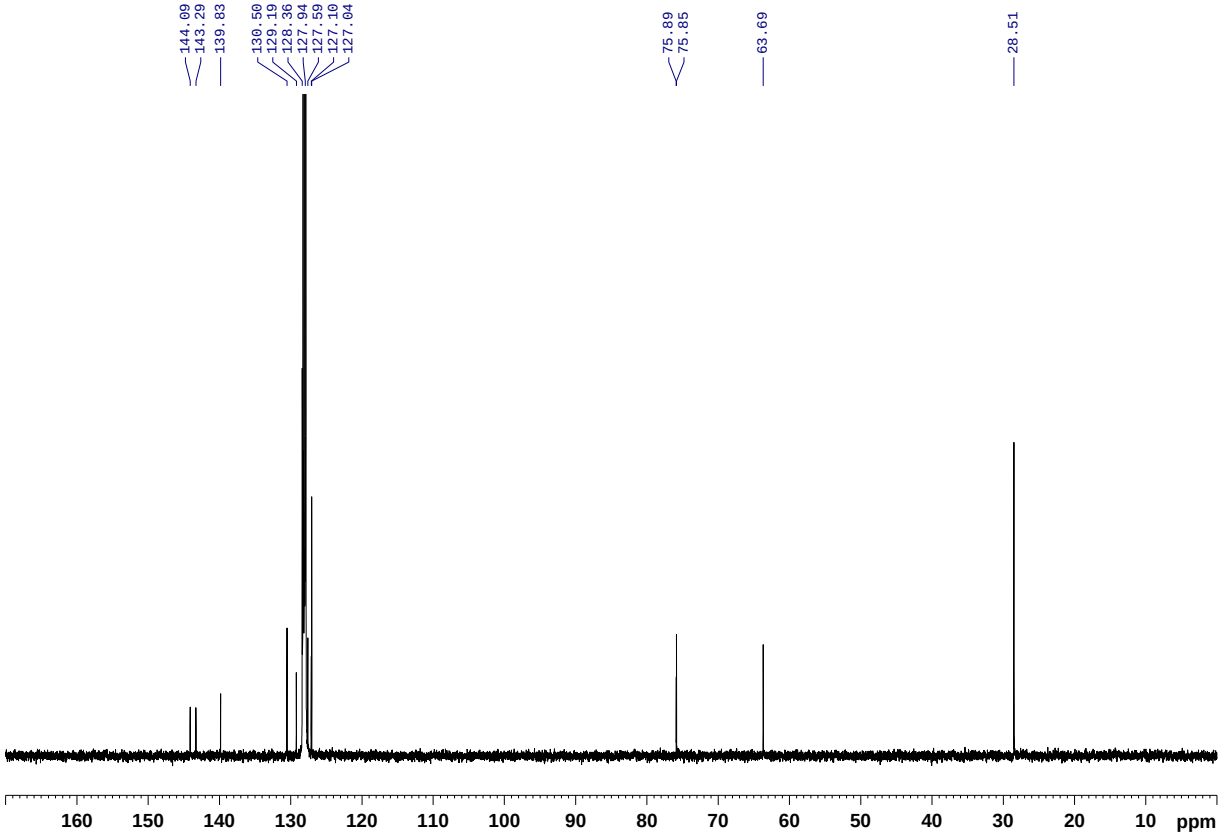
ppm

(*S*)-**2b**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150
140
130
120
110
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90
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70
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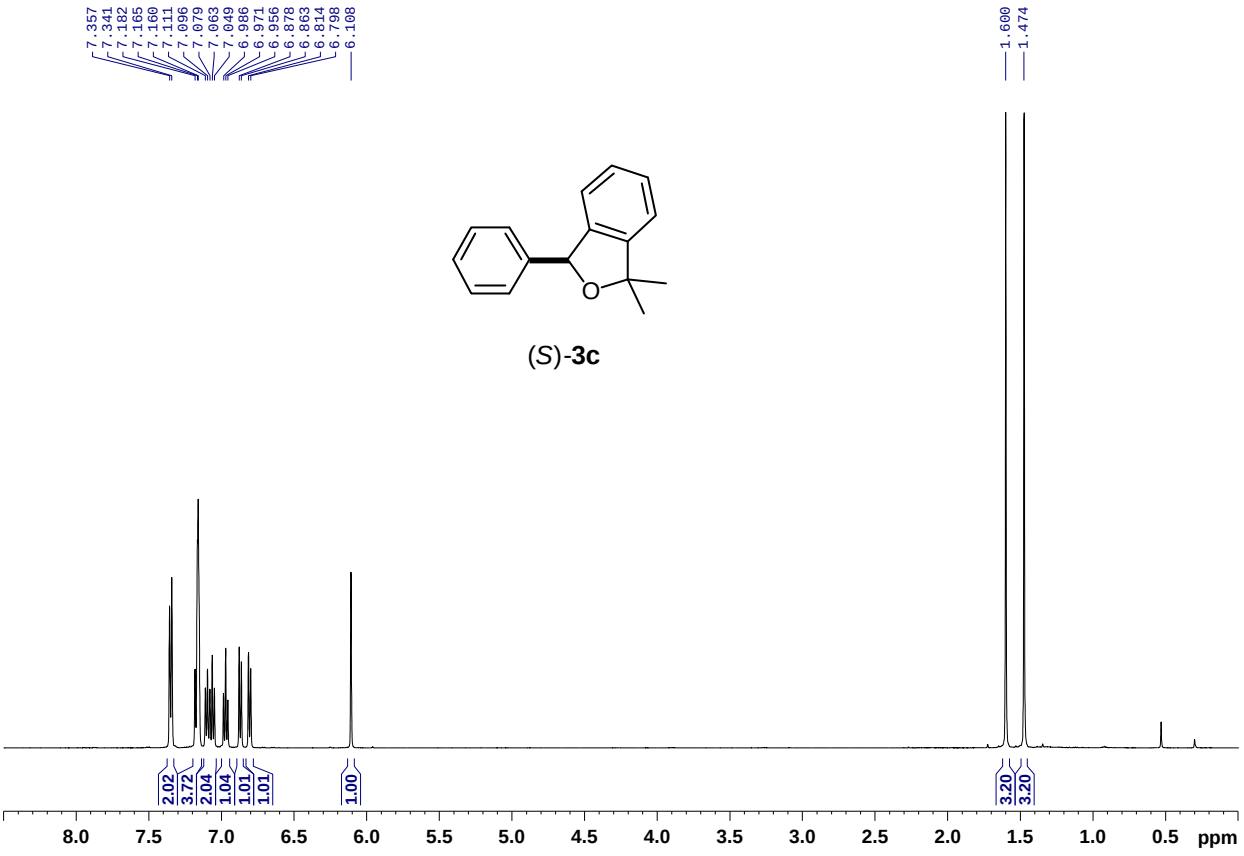
50
40
30
20
10
ppm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7.049
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6.956
6.878
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6.814
6.798
6.108
1.600
1.474
O
2.02
3.72
2.04
1.04
1.01
1.01
1.00
3.20
3.20
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7.5
7.0
6.5
6.0
5.5
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3.0
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1.0
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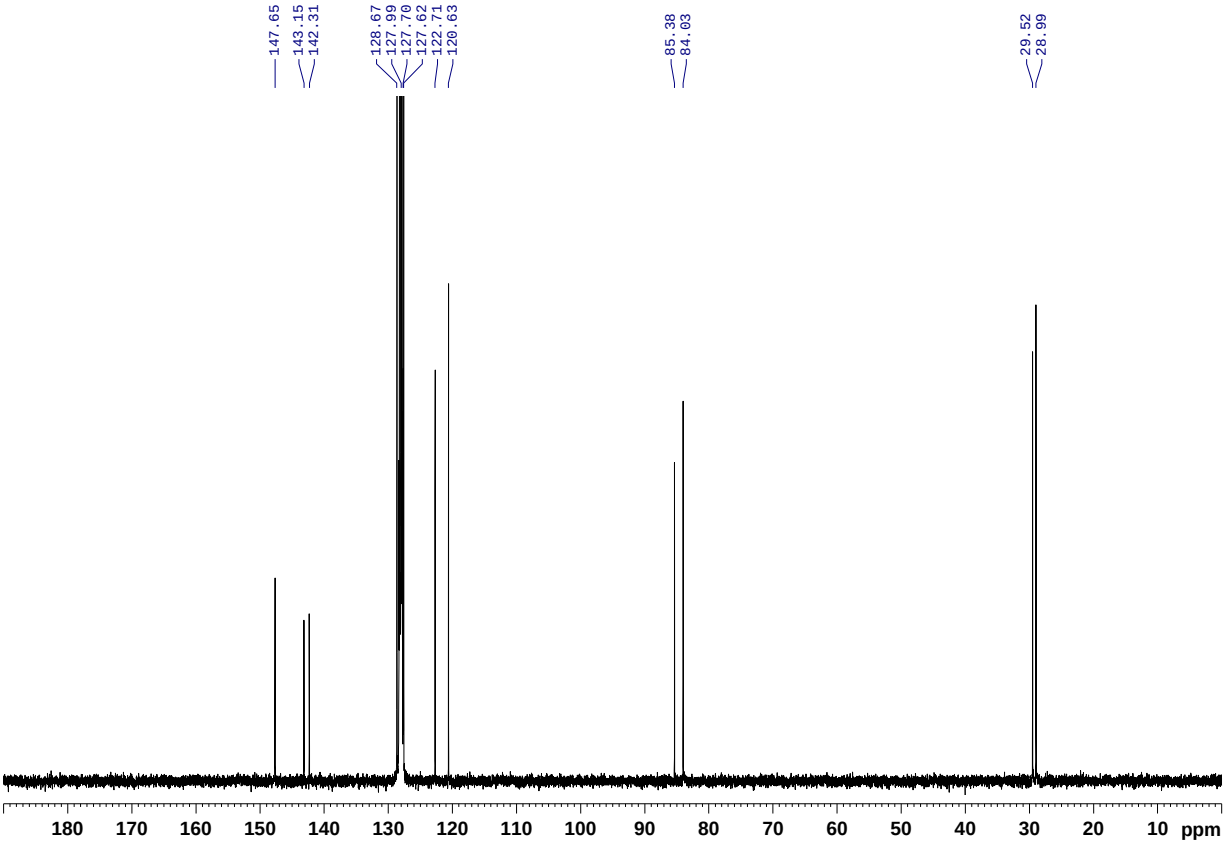
ppm

(*S*)-**3c**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150
140
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120
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70
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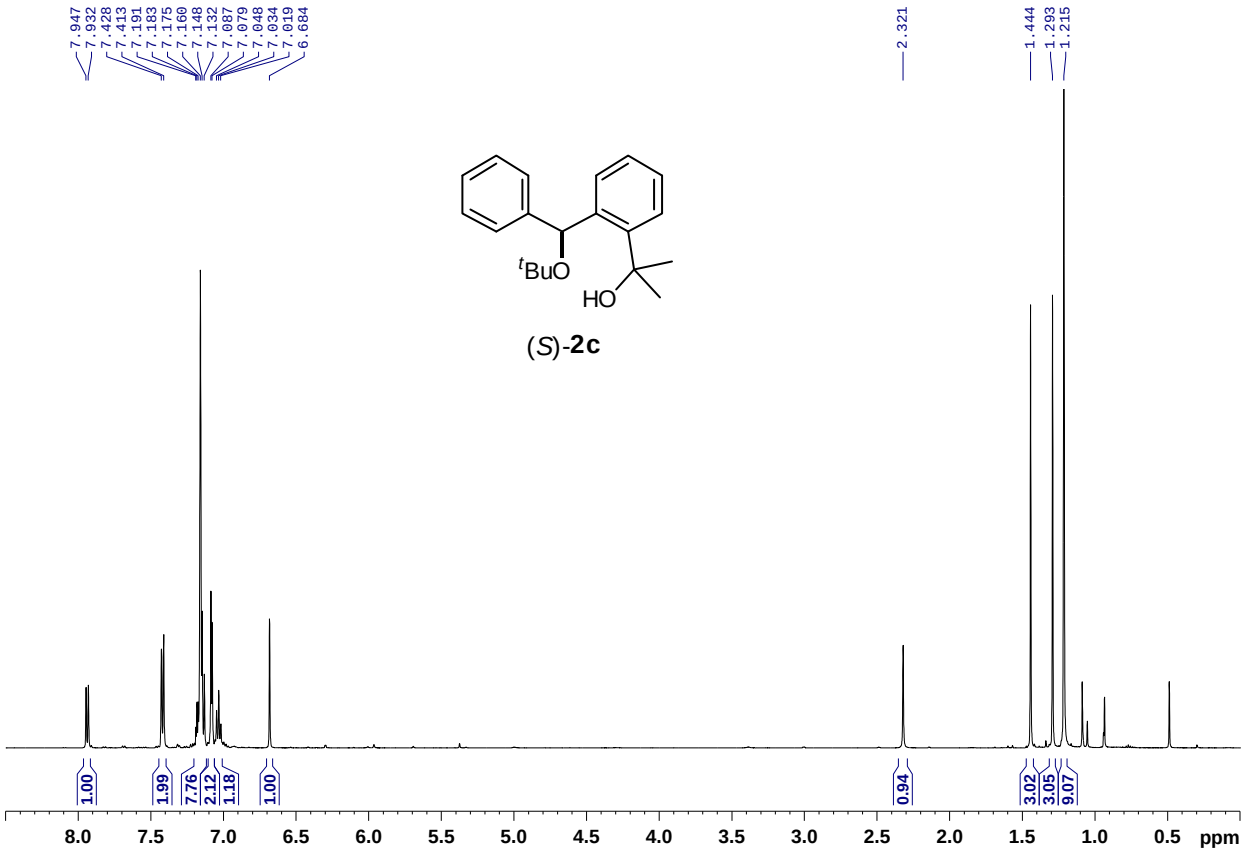
40
30
20
10
ppm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7.034
7.019
6.684
2.321
1.444
1.293
1.215
tBuO
HO
1.00
1.99
7.76
2.12
1.18
1.00
0.94
3.02
3.05
9.07
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
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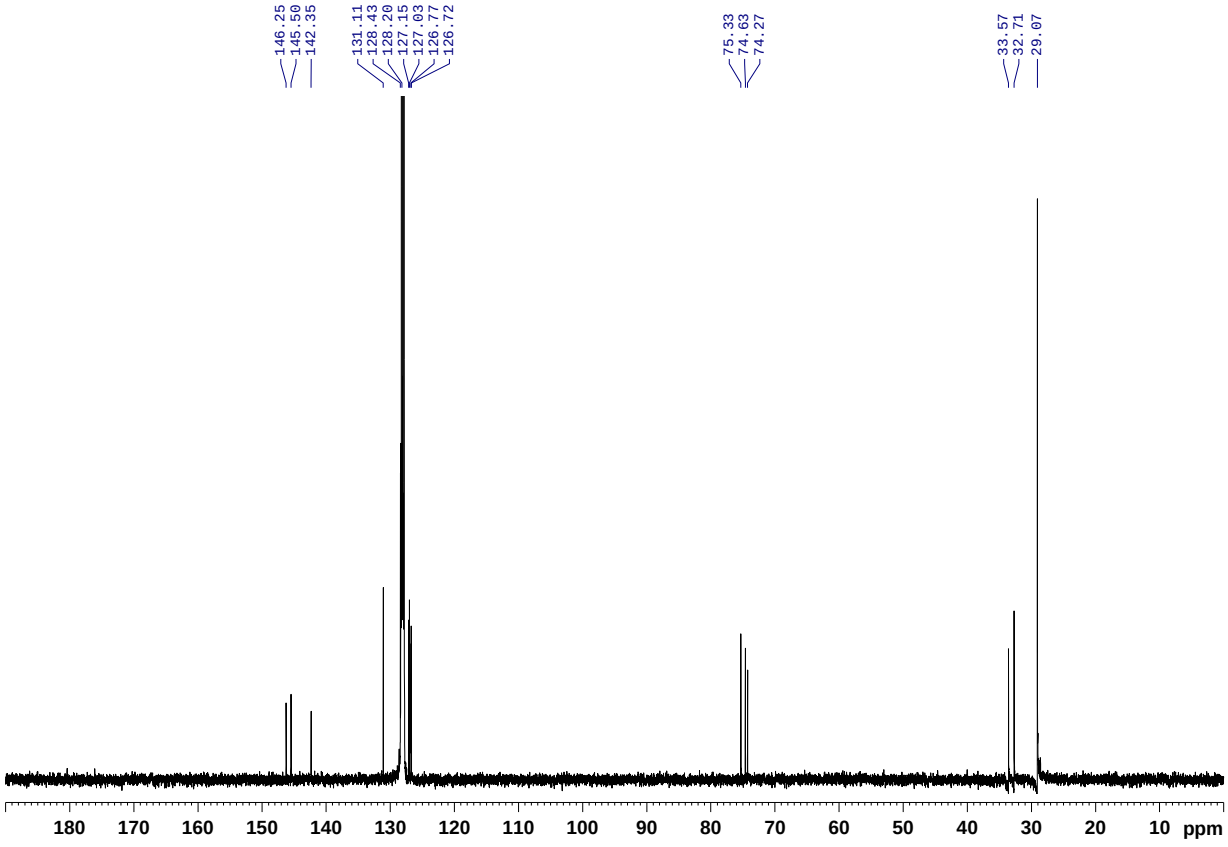
ppm

(*S*)-**2c**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74.27
33.57
32.71
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140
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10
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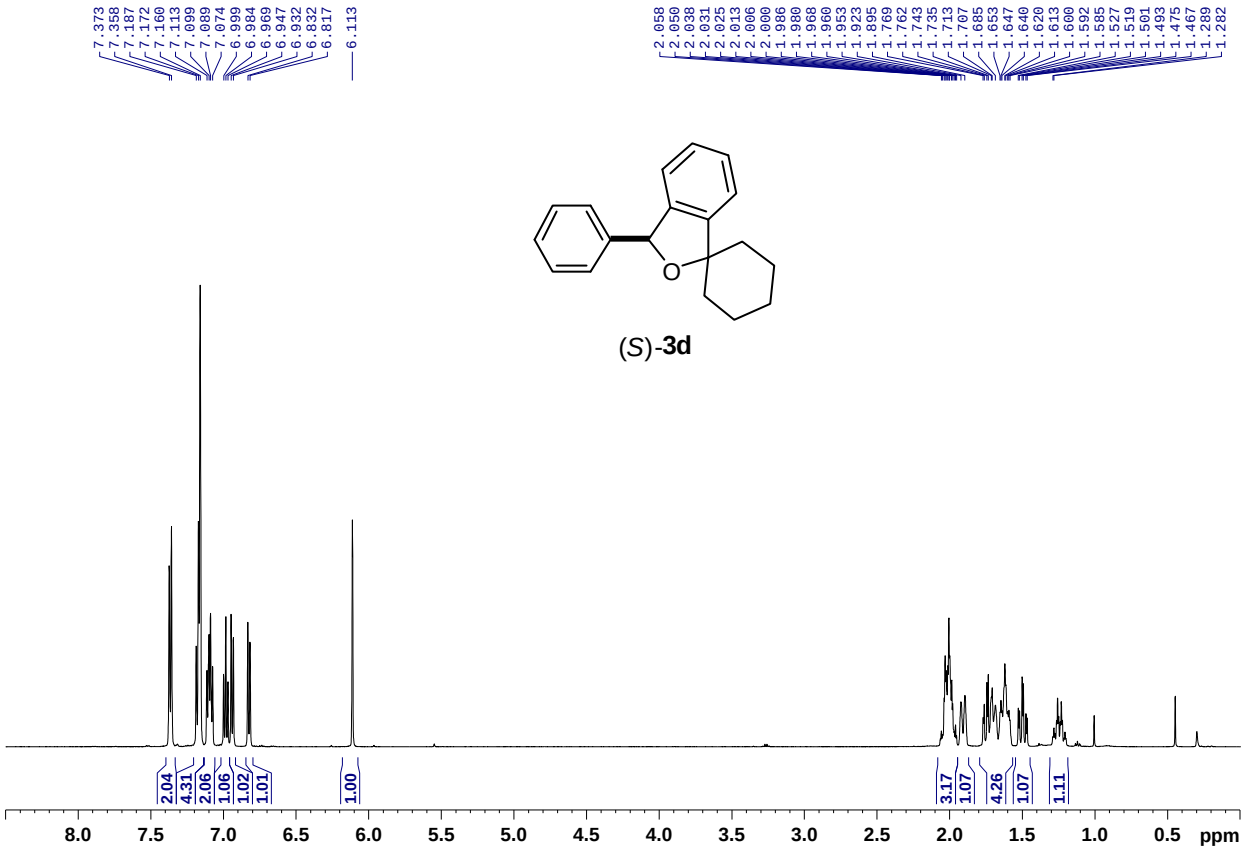
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1.06
1.02
1.01
1.00
3.17
1.07
4.26
1.07
1.11
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6.0
5.5
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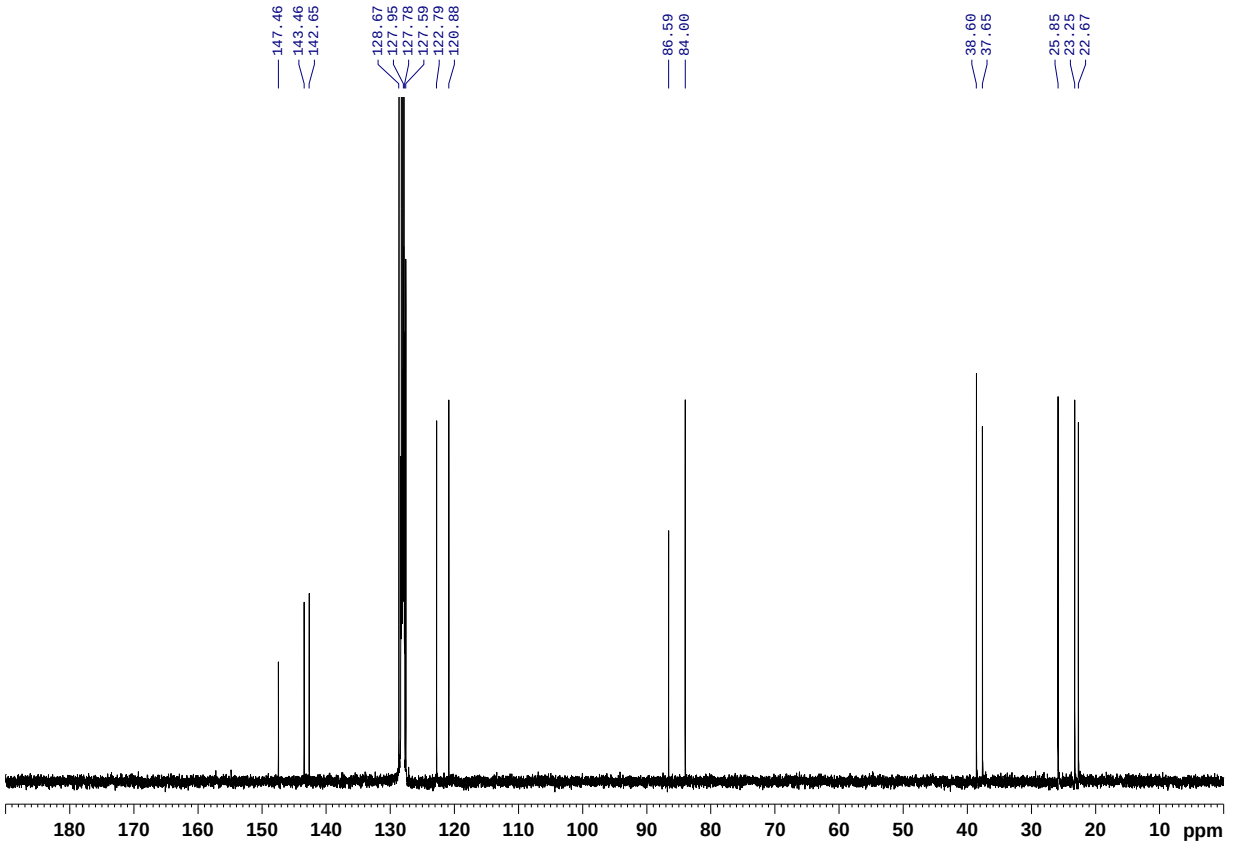
ppm

(*S*)-**3d**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23.25
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70
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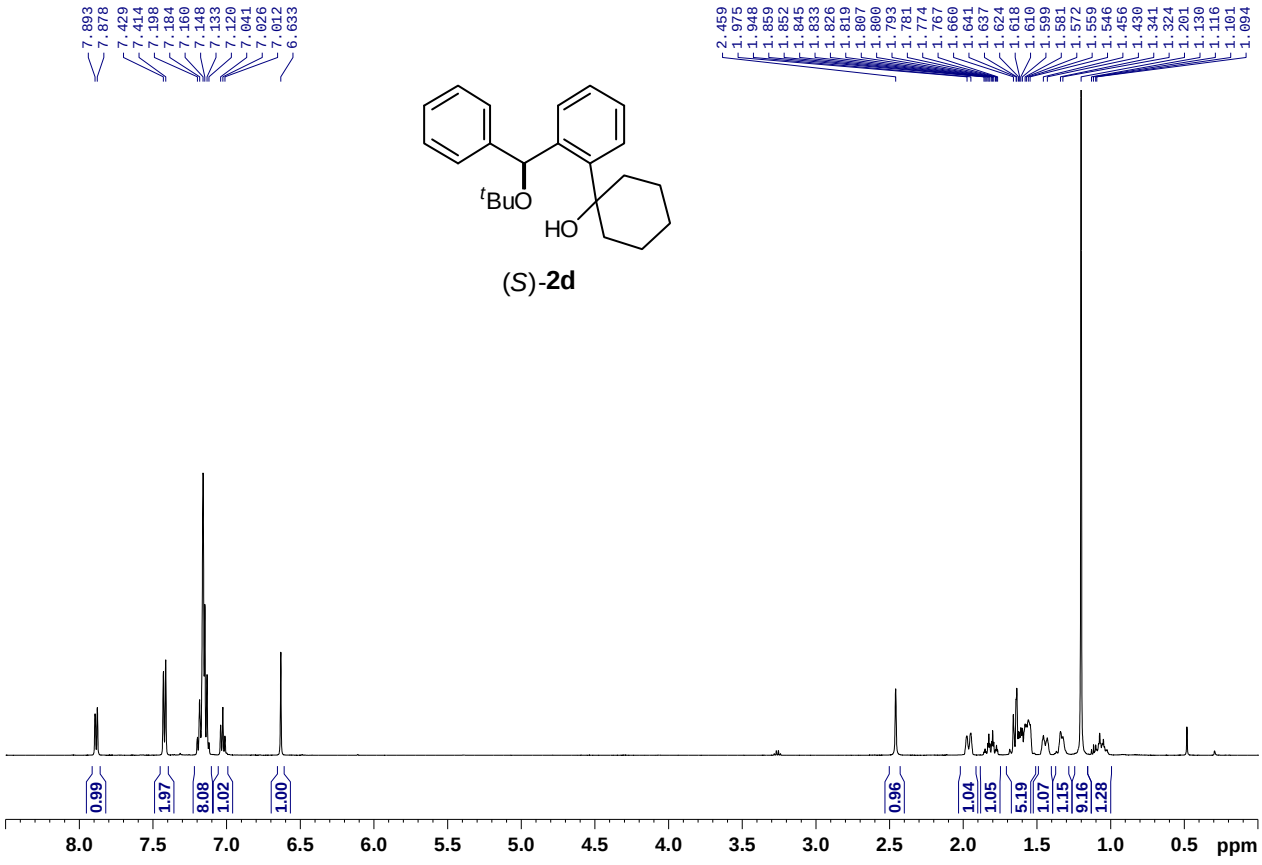
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6.633
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1.859
1.852
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1.826
1.819
1.807
1.800
1.793
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1.660
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1.130
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1.094
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HO
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8.08
1.02
1.00
0.96
1.04
1.05
5.19
1.07
1.15
9.16
1.28
8.0
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7.0
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6.0
5.5
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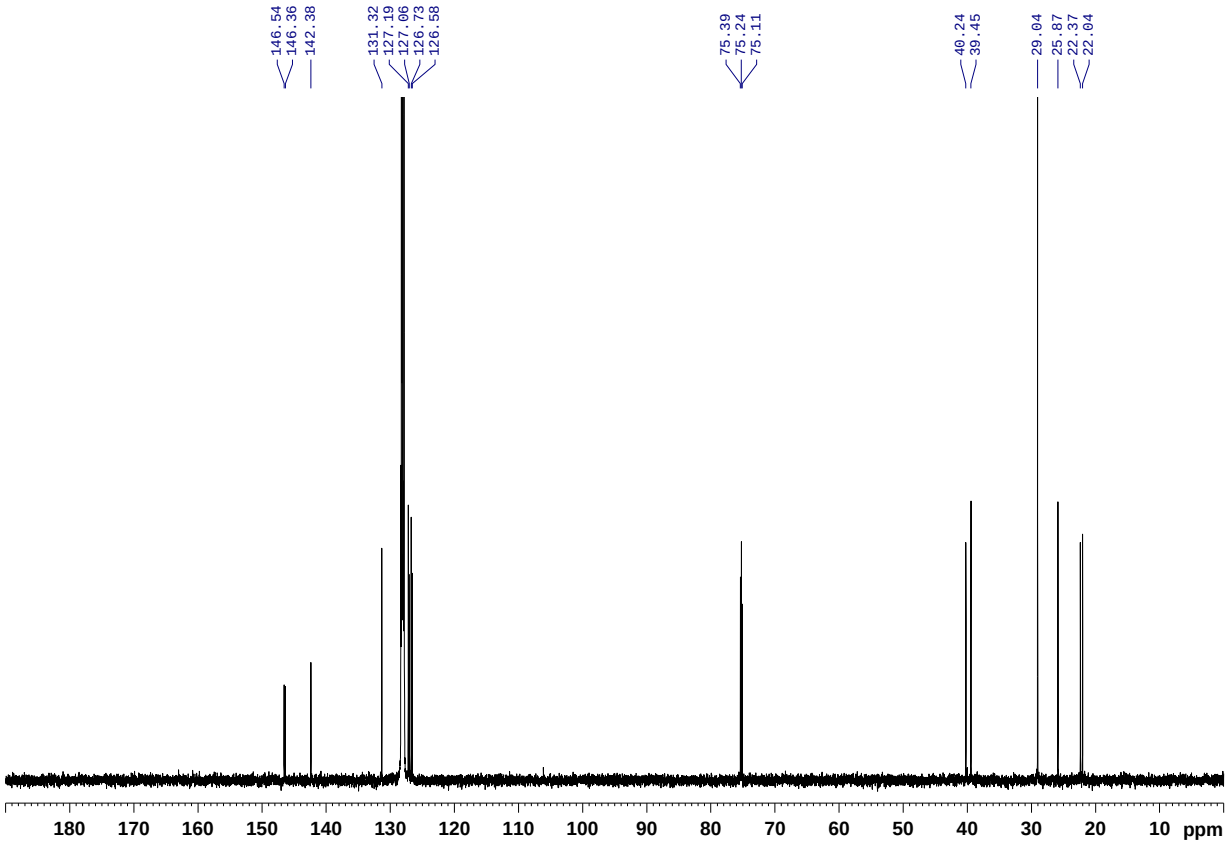
ppm

(*S*)-**2d**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22.37
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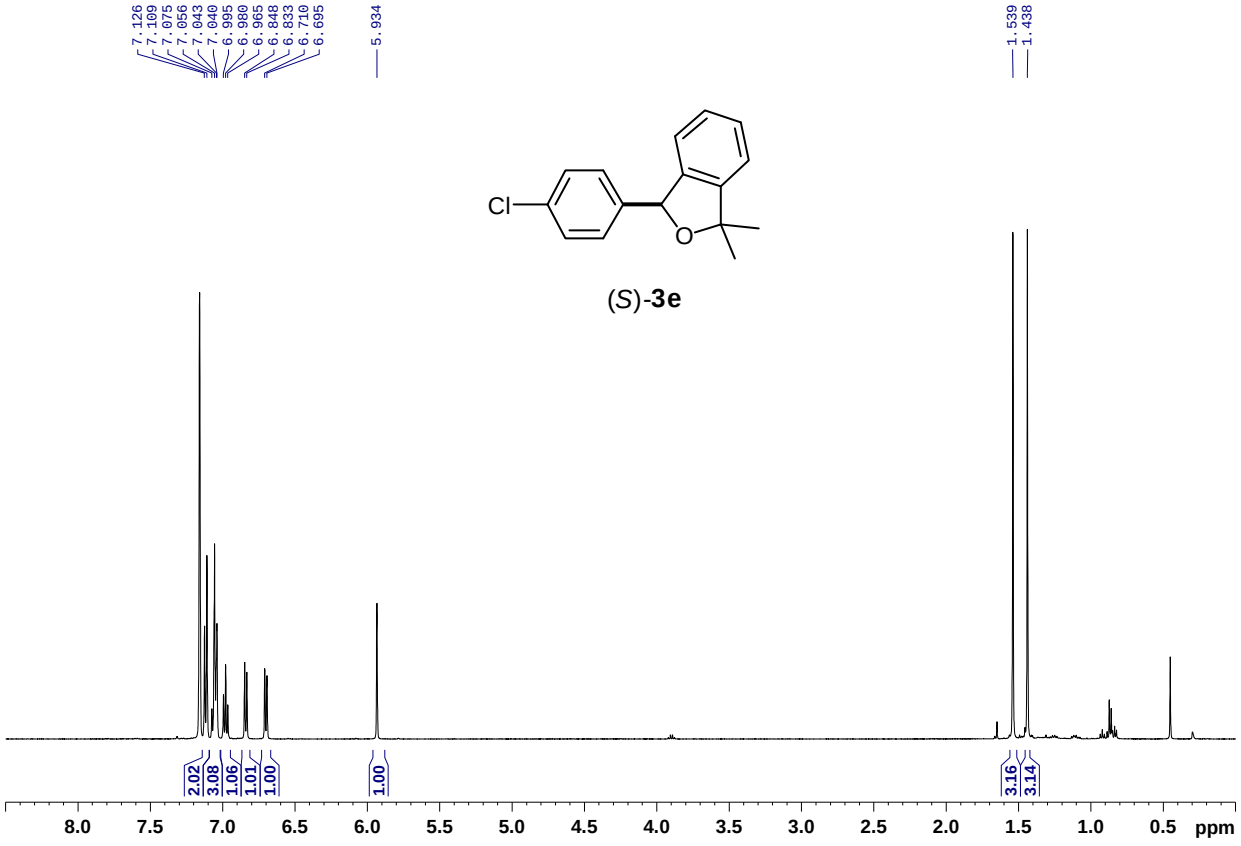
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6.710
6.695
5.934
1.539
1.438
Cl
O
2.02
3.08
1.06
1.01
1.00
1.00
3.16
3.14
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.5
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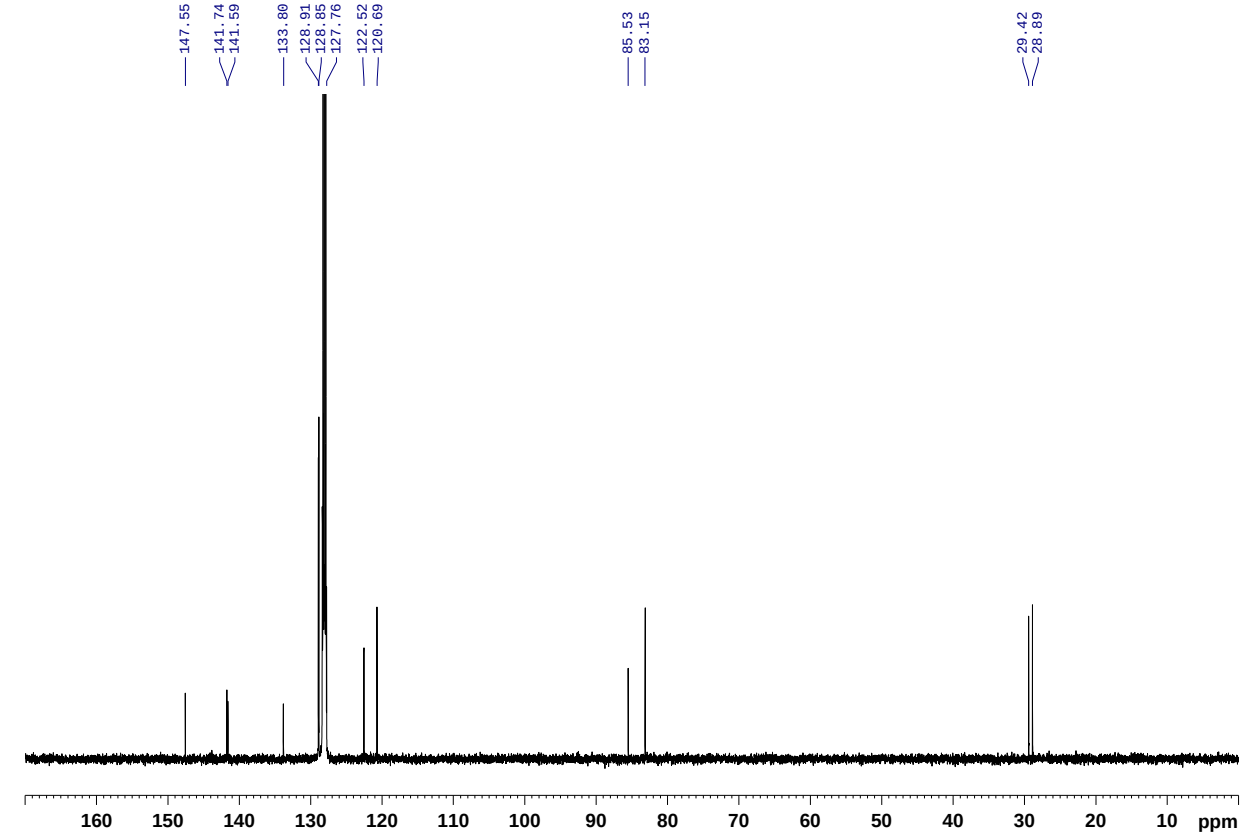
1.0
0.5
ppm

(*S*)-**3e**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110
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80
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30
20
10
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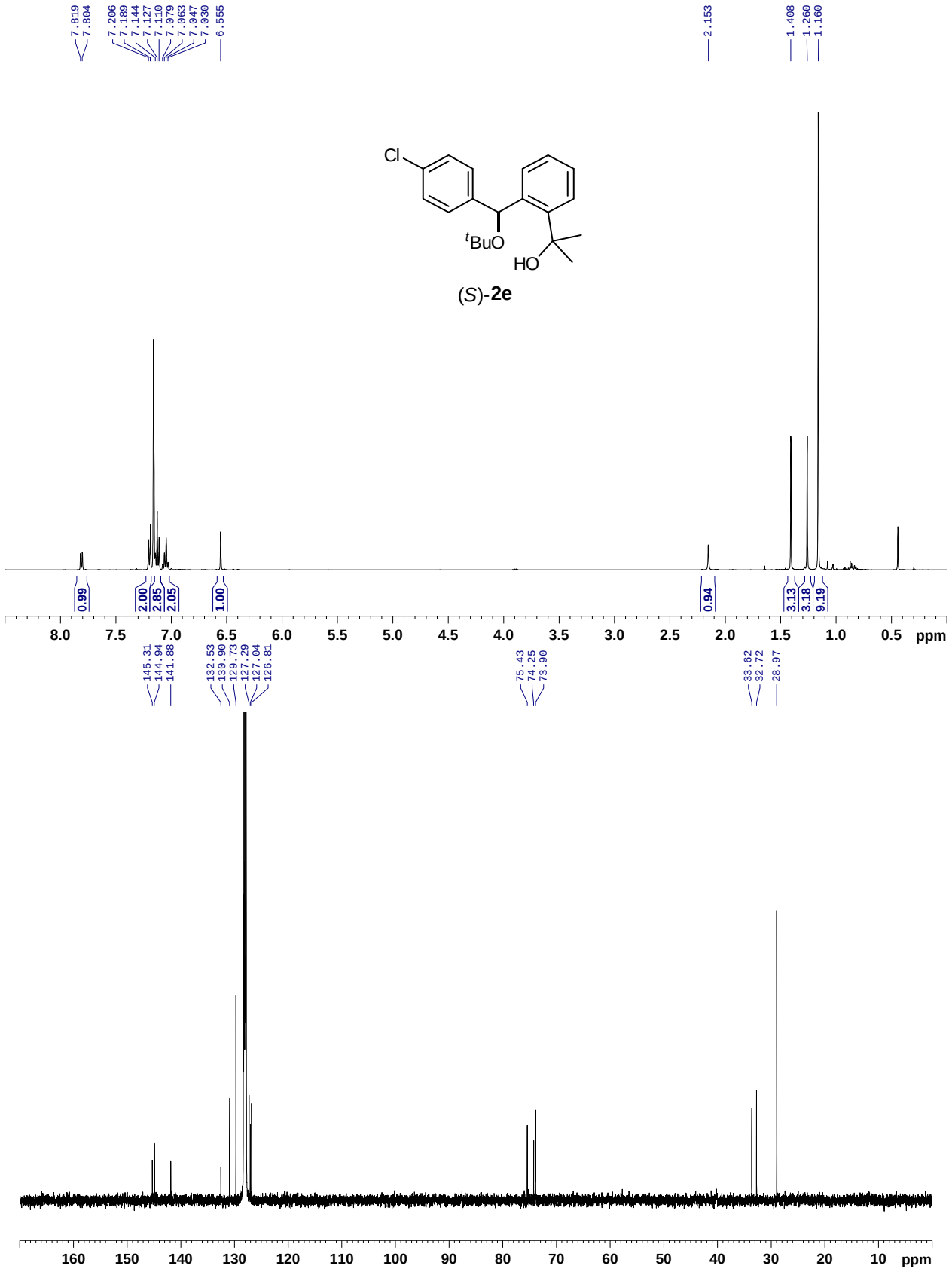
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7.047
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1.408
1.260
1.160
Cl
tBuO
HO
(S)-2e
0.99
2.00
2.85
2.05
1.00
0.94
3.13
3.18
9.19
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
145.31
144.94
141.88
132.53
130.90
129.73
127.29
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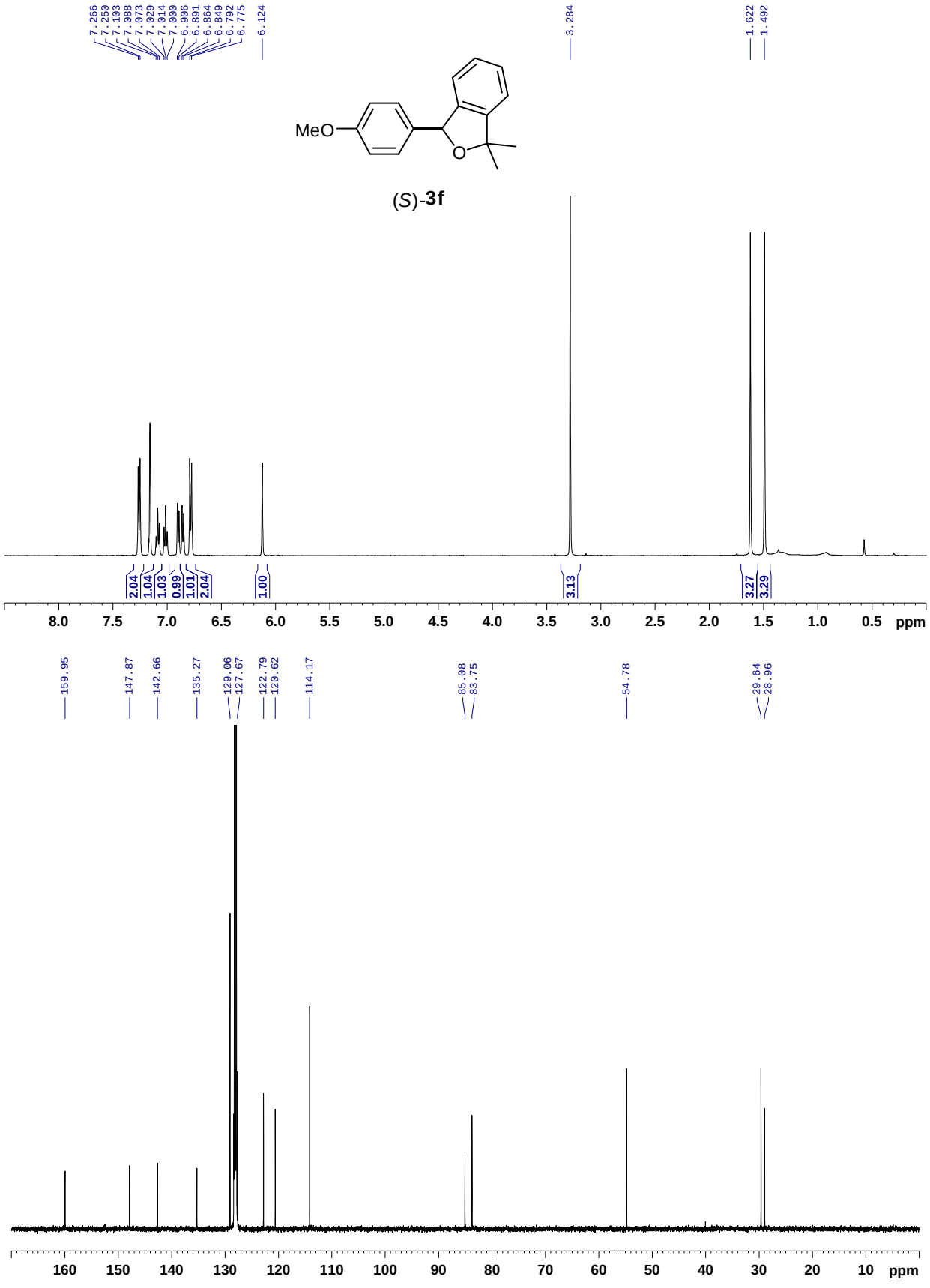
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7.000
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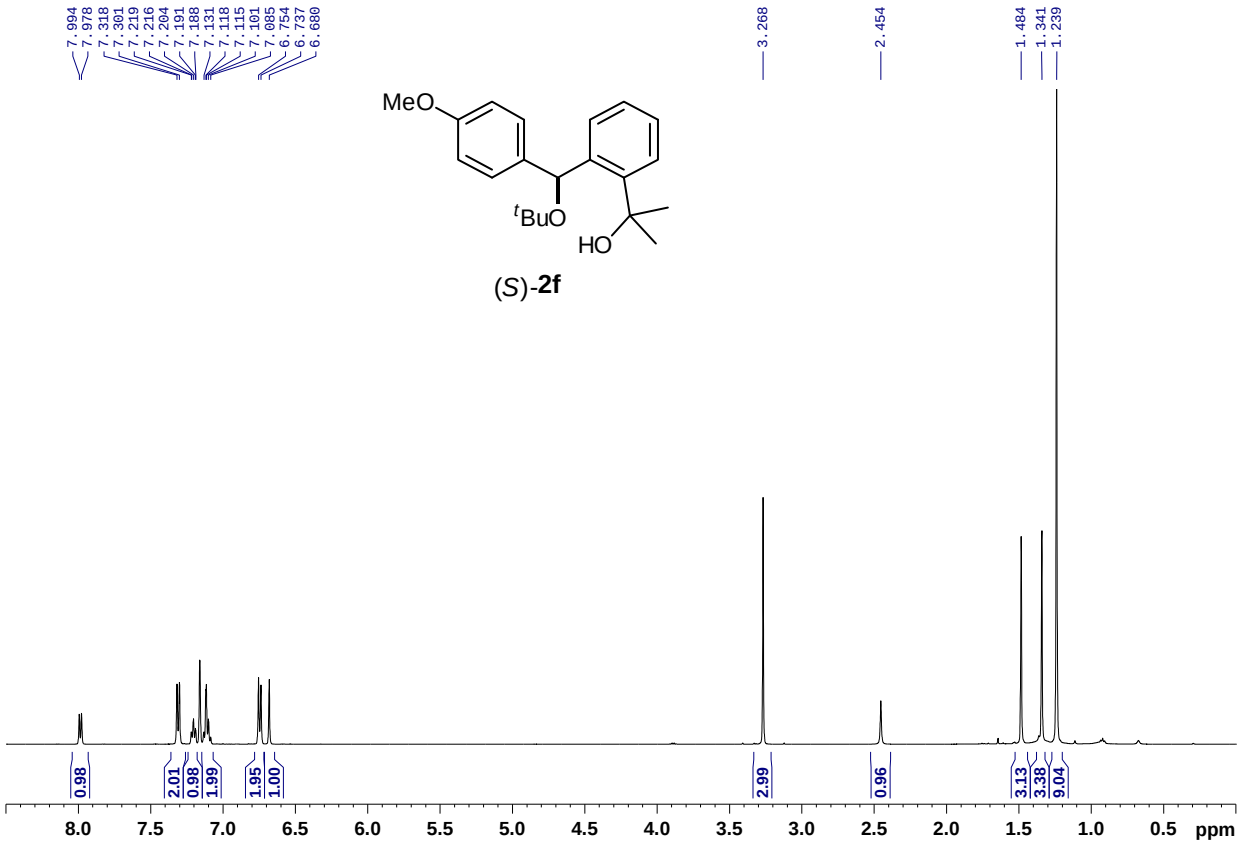
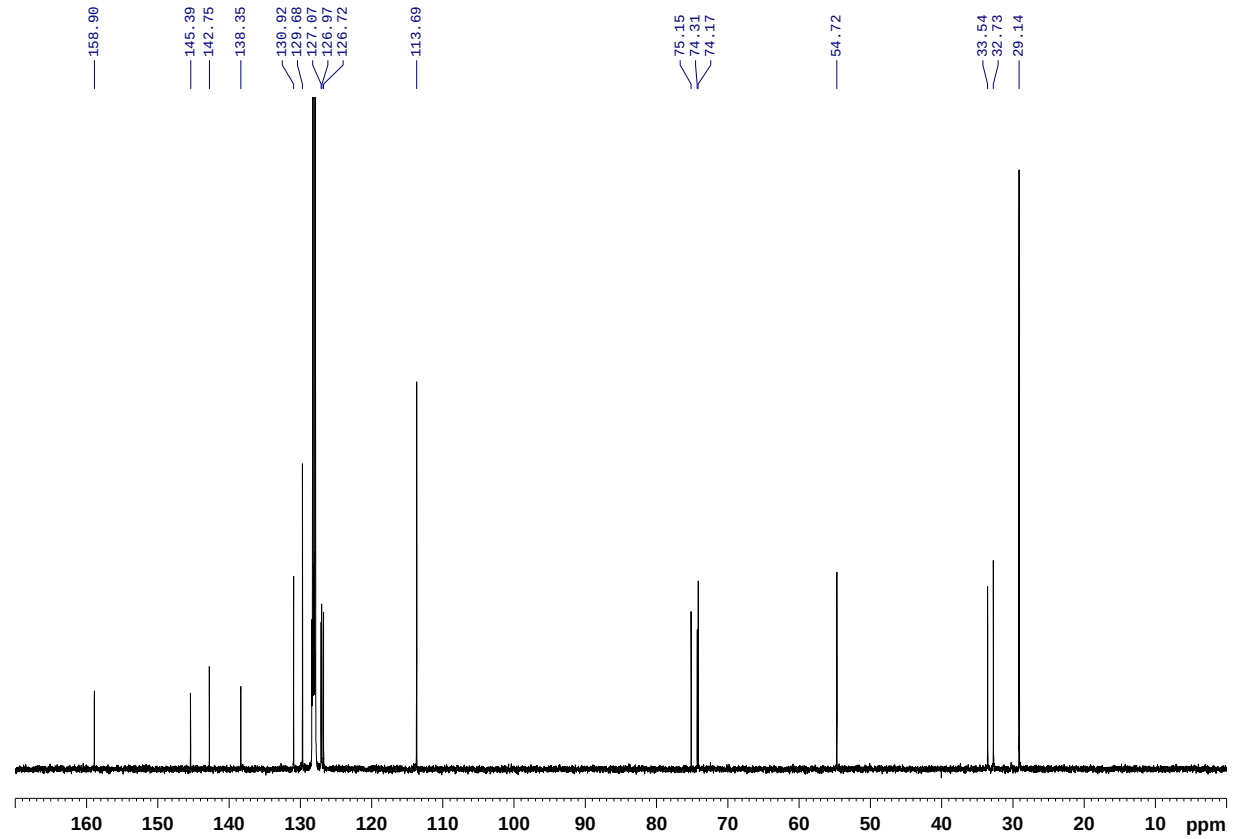
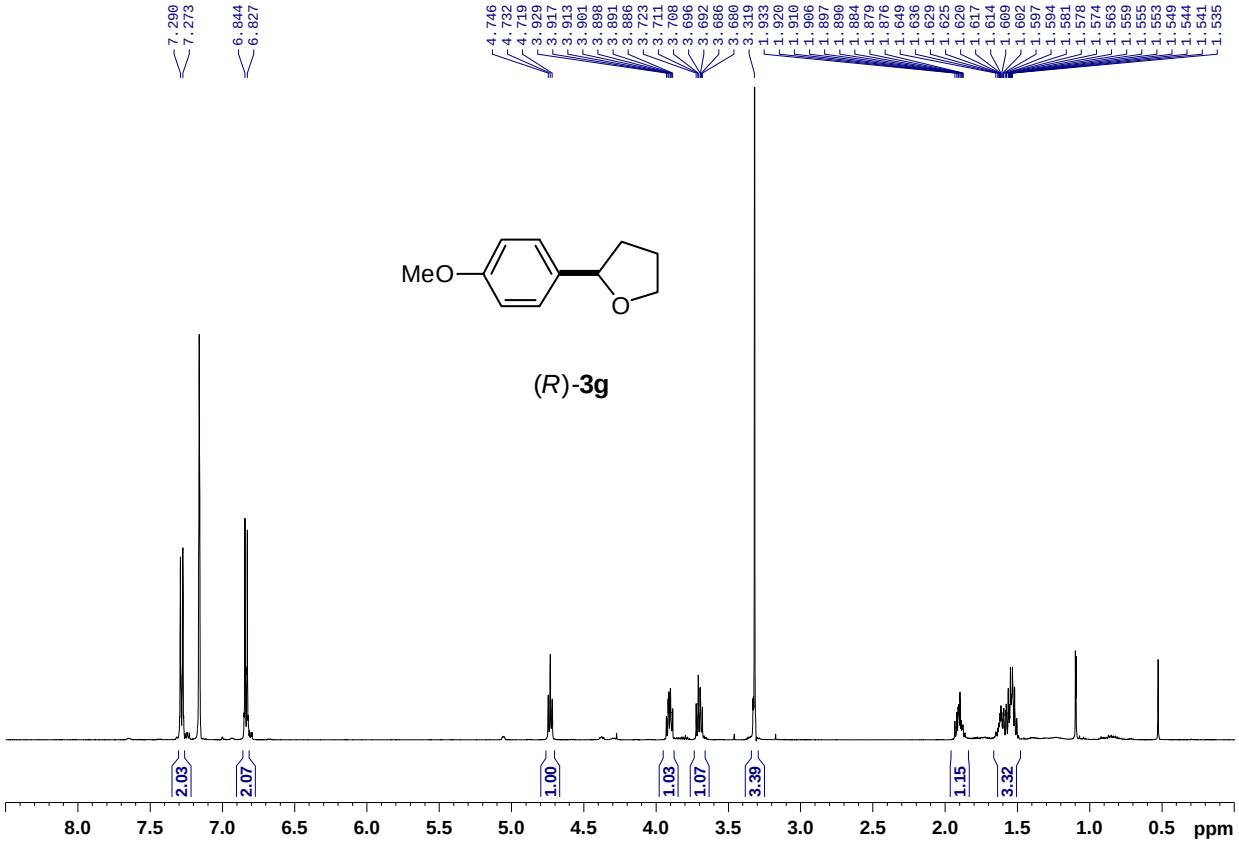
6.891
6.864
6.849
6.792
6.775
6.124
3.284
1.622
1.492
MeO
O
(S)-3f
2.04
1.04
1.03
0.99
1.01
2.04
1.00
3.13
3.27
3.29
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
159.95
147.87
142.66
135.27
129.06
127.67
122.79
120.62
114.17
85.08
83.75
54.78
29.64
28.96
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

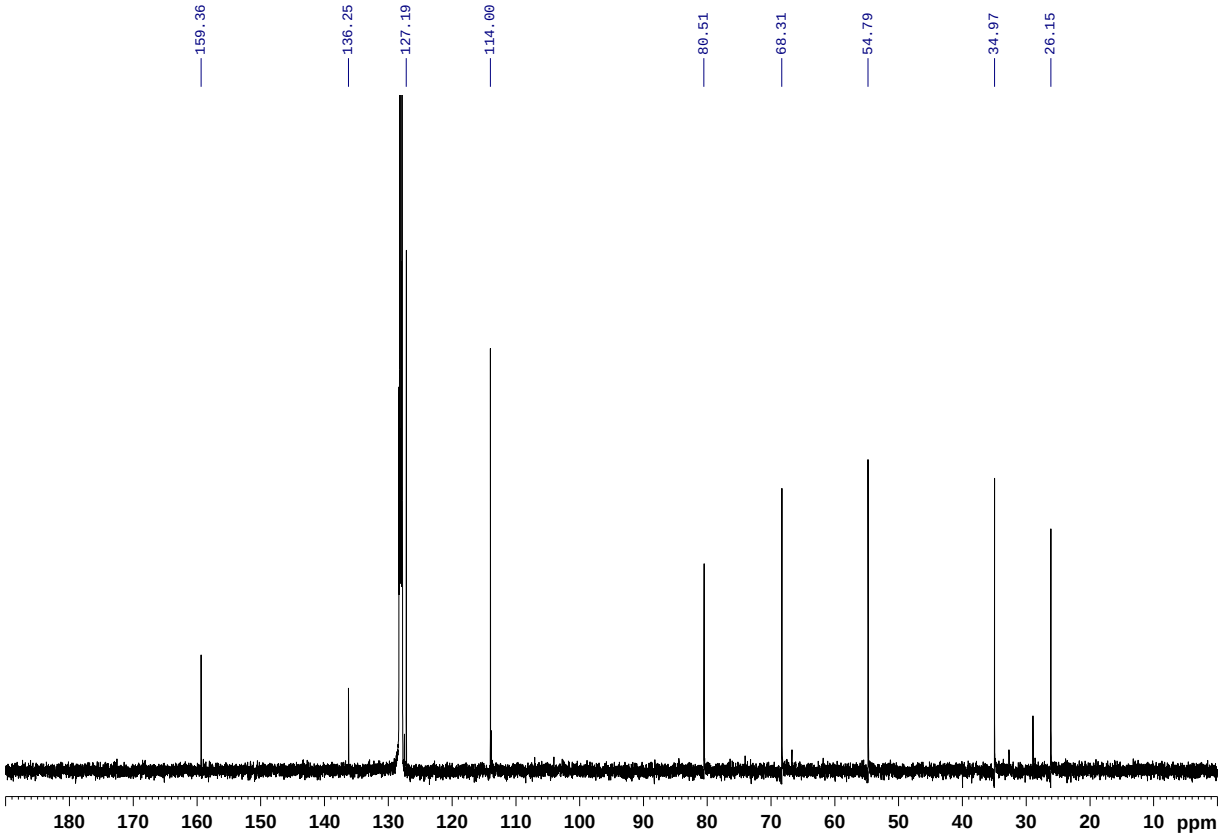

7.994
7.978
7.318
7.301
7.219
7.216
7.204
7.191
7.188
7.131
7.118
7.115
7.101
7.085
6.754
6.737
6.680
3.268
2.454
1.484
1.341
1.239
MeO
tBuO
HO
0.98
2.01
0.98
1.99
1.95
1.00
2.99
0.96
3.13
3.38
9.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

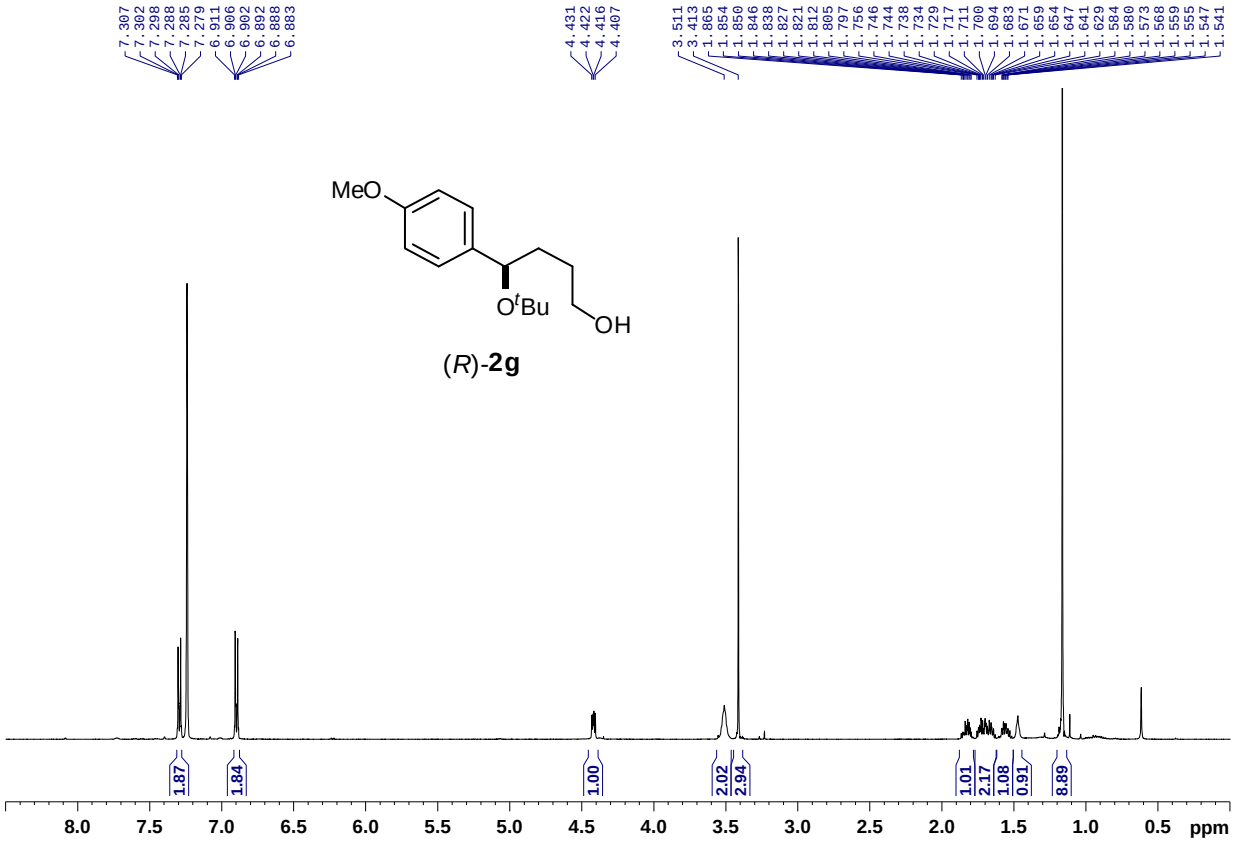
(*S*)-**2f**

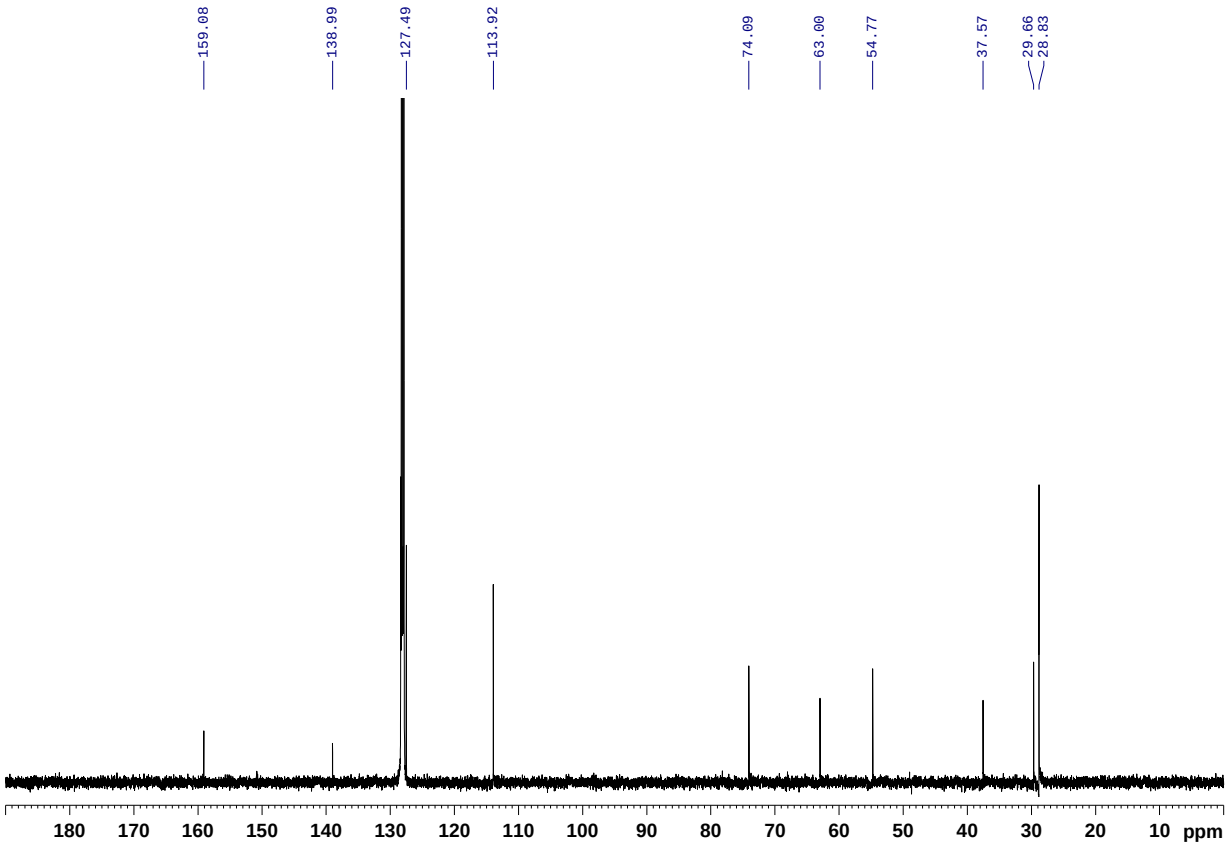

158.90
145.39
142.75
138.35
130.92
129.68
127.07
126.97
126.72
113.69
75.15
74.31
74.17
54.72
33.54
32.73
29.14
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

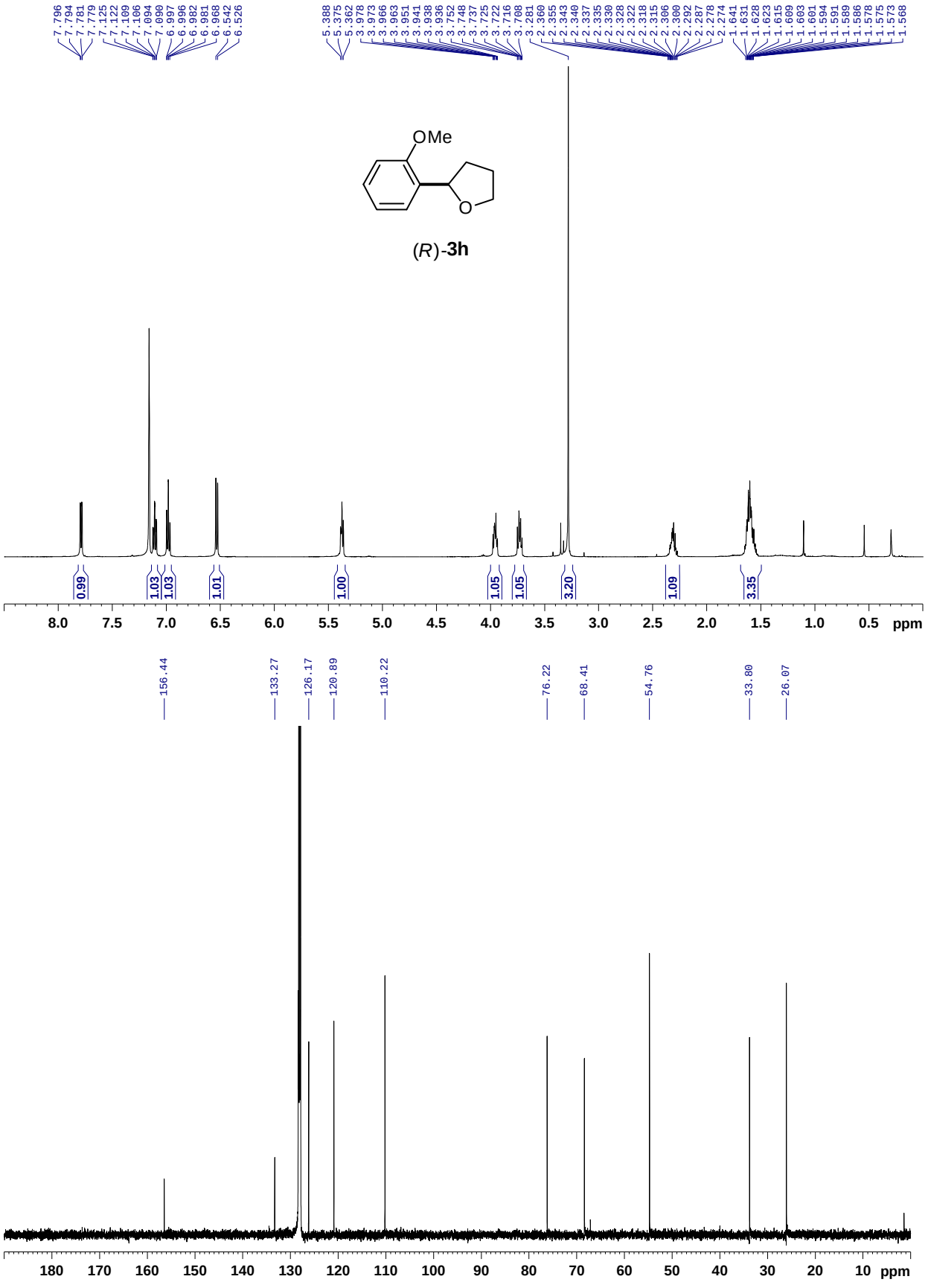

7.290
7.273
6.844
6.827
4.746
4.732
4.719
3.929
3.917
3.913
3.901
3.898
3.891
3.886
3.723
3.711
3.708
3.696
3.692
3.686
3.680
3.319
1.933
1.920
1.910
1.906
1.897
1.890
1.884
1.879
1.876
1.649
1.636
1.629
1.625
1.620
1.617
1.614
1.609
1.602
1.597
1.594
1.581
1.578
1.574
1.563
1.559
1.555
1.553
1.549
1.544
1.541
1.535
MeO
O
2.03
2.07
1.00
1.03
1.07
3.39
1.15
3.32
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
ppm

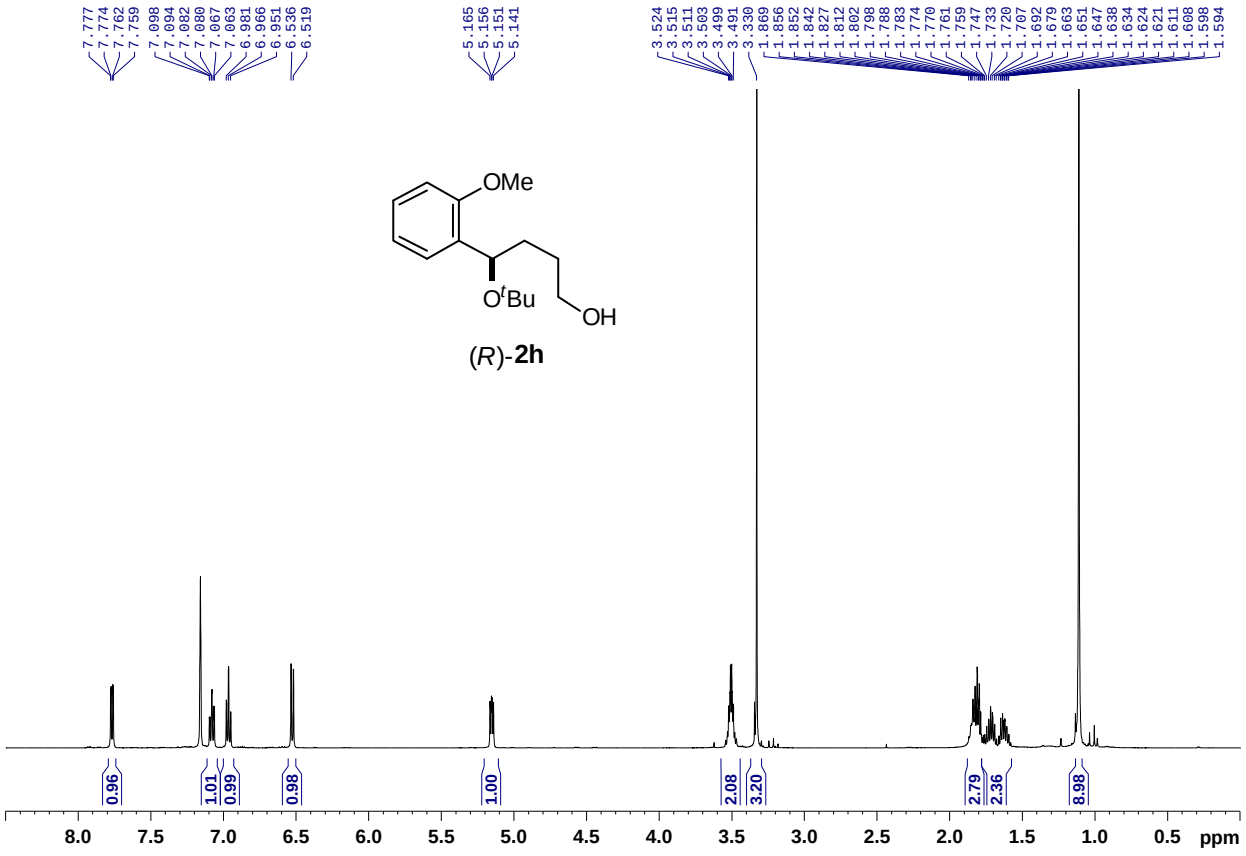
(*R*)-**3g**


159.36
136.25
127.19
114.00
80.51
68.31
54.79
34.97
26.15
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

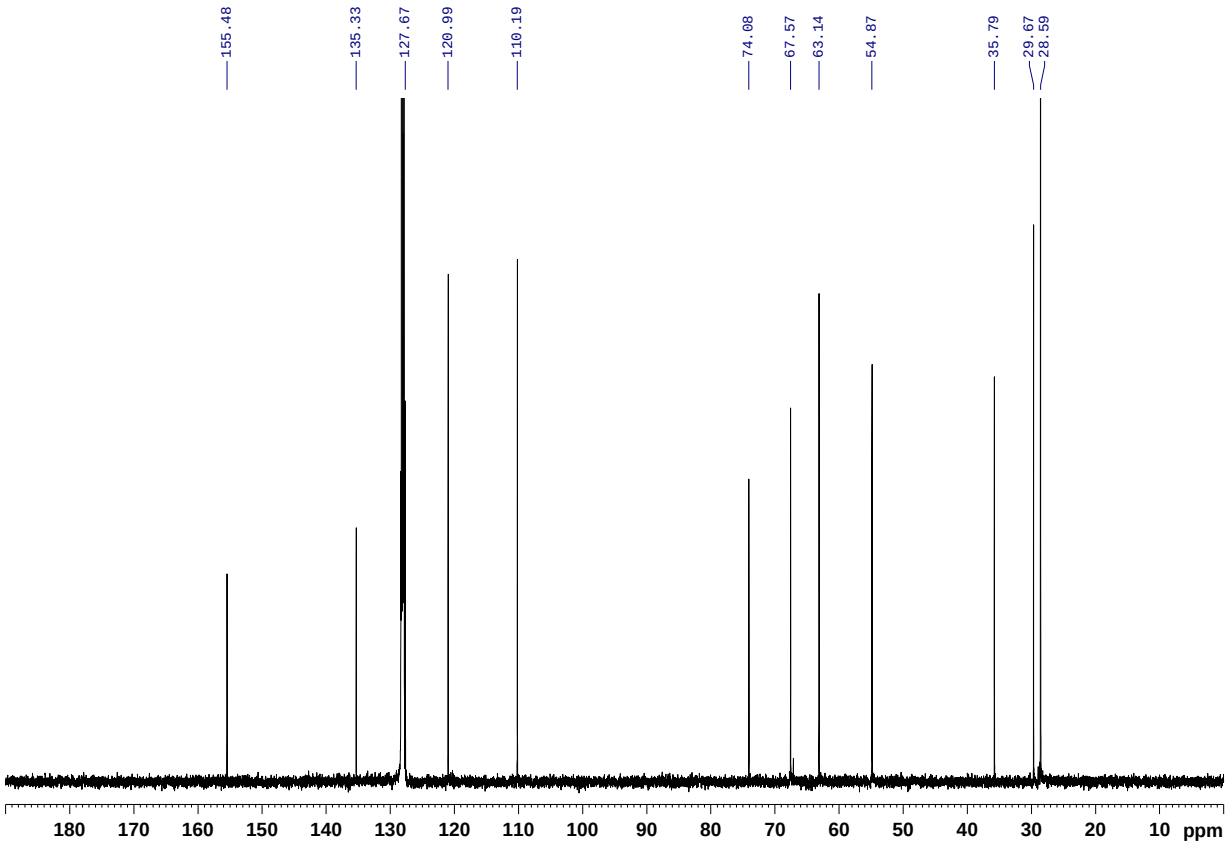

7.307
7.302
7.298
7.288
7.285
7.279
6.911
6.906
6.902
6.892
6.888
6.883
4.431
4.422
4.416
4.407
3.511
3.413
1.865
1.854
1.850
1.846
1.838
1.827
1.821
1.812
1.805
1.797
1.756
1.746
1.744
1.738
1.734
1.729
1.717
1.711
1.700
1.694
1.683
1.671
1.659
1.654
1.647
1.641
1.629
1.584
1.580
1.573
1.568
1.559
1.555
1.547
1.541
MeO
O^{t}Bu
OH
(*R*)-**2g**
1.87
1.84
1.00
2.02
2.94
1.01
2.17
1.08
0.91
8.89
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
ppm

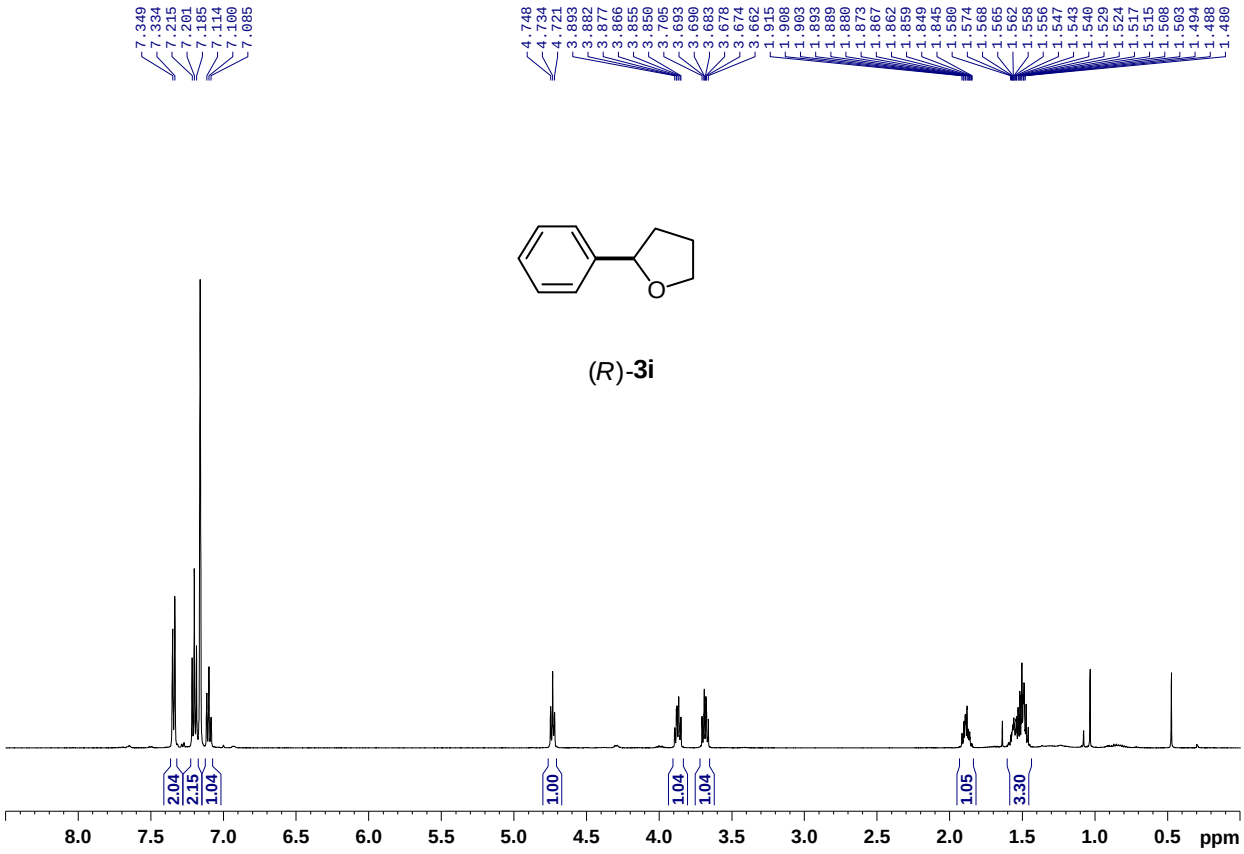

159.08
138.99
127.49
113.92
74.09
63.00
54.77
37.57
29.66
28.83
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OMe
O
(R)-3h
7.796 7.794 7.781 7.779 7.125 7.122 7.109 7.106 7.094 7.090 6.997 6.996 6.982 6.981 6.968 6.542 6.526
5.388 5.375 5.362 3.978 3.973 3.966 3.963 3.951 3.941 3.938 3.936 3.752 3.748 3.737 3.725 3.722 3.716 3.708 3.281 2.360 2.355 2.343 2.340 2.337 2.335 2.330 2.328 2.322 2.318 2.315 2.306 2.300 2.292 2.287 2.278 2.274 1.641 1.631 1.628 1.623 1.615 1.609 1.603 1.601 1.594 1.591 1.589 1.586 1.578 1.575 1.573 1.568
0.99 1.03 1.03 1.01 1.00 1.05 1.05 3.20 1.09 3.35
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 ppm
156.44 133.27 126.17 120.89 110.22 76.22 68.41 54.76 33.80 26.07
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

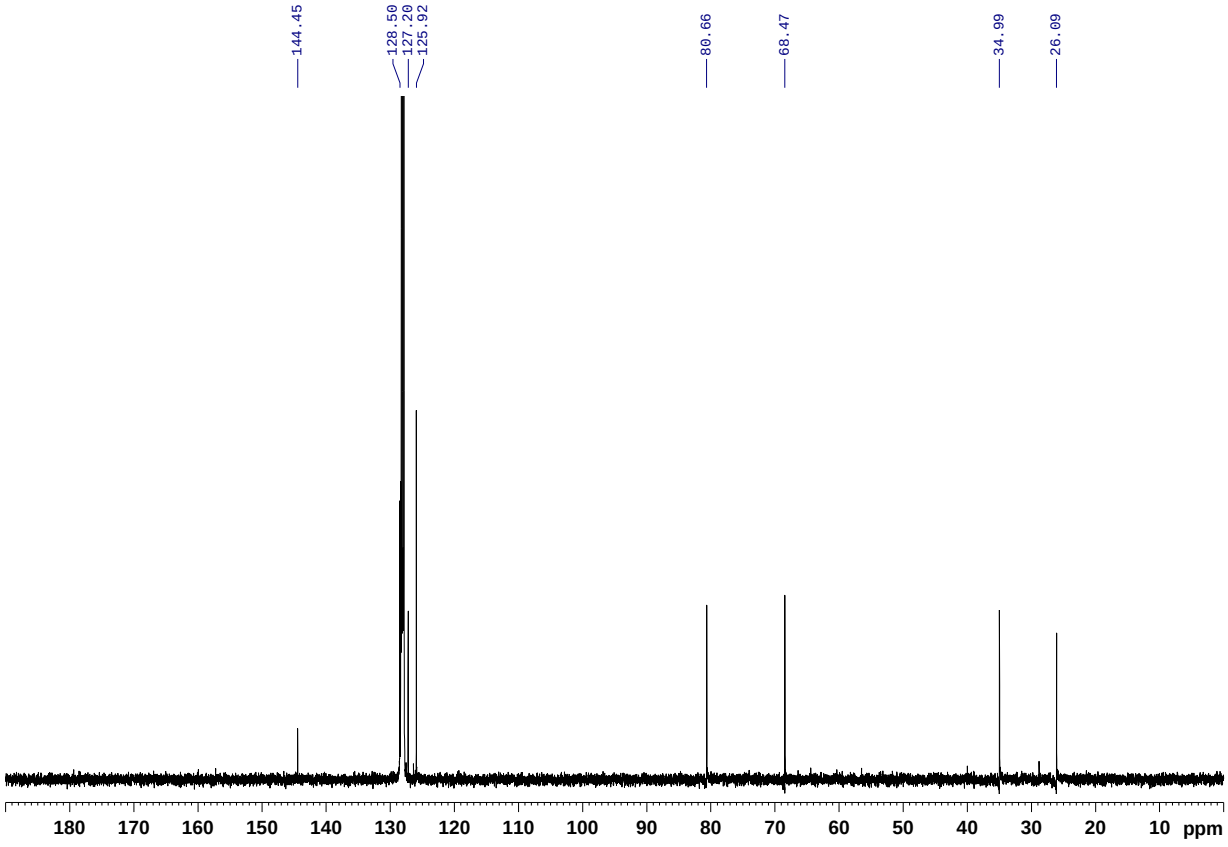

7.777
7.774
7.762
7.759
7.098
7.094
7.082
7.080
7.067
7.063
6.981
6.966
6.951
6.536
6.519
5.165
5.156
5.151
5.141
3.524
3.515
3.511
3.503
3.499
3.491
3.330
1.869
1.856
1.852
1.842
1.827
1.812
1.802
1.798
1.788
1.783
1.774
1.770
1.761
1.759
1.747
1.733
1.720
1.707
1.692
1.679
1.663
1.651
1.647
1.638
1.634
1.624
1.621
1.611
1.608
1.598
1.594
OMe
O^tBu
OH
0.96
1.01
0.99
0.98
1.00
2.08
3.20
2.79
2.36
8.98
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
ppm

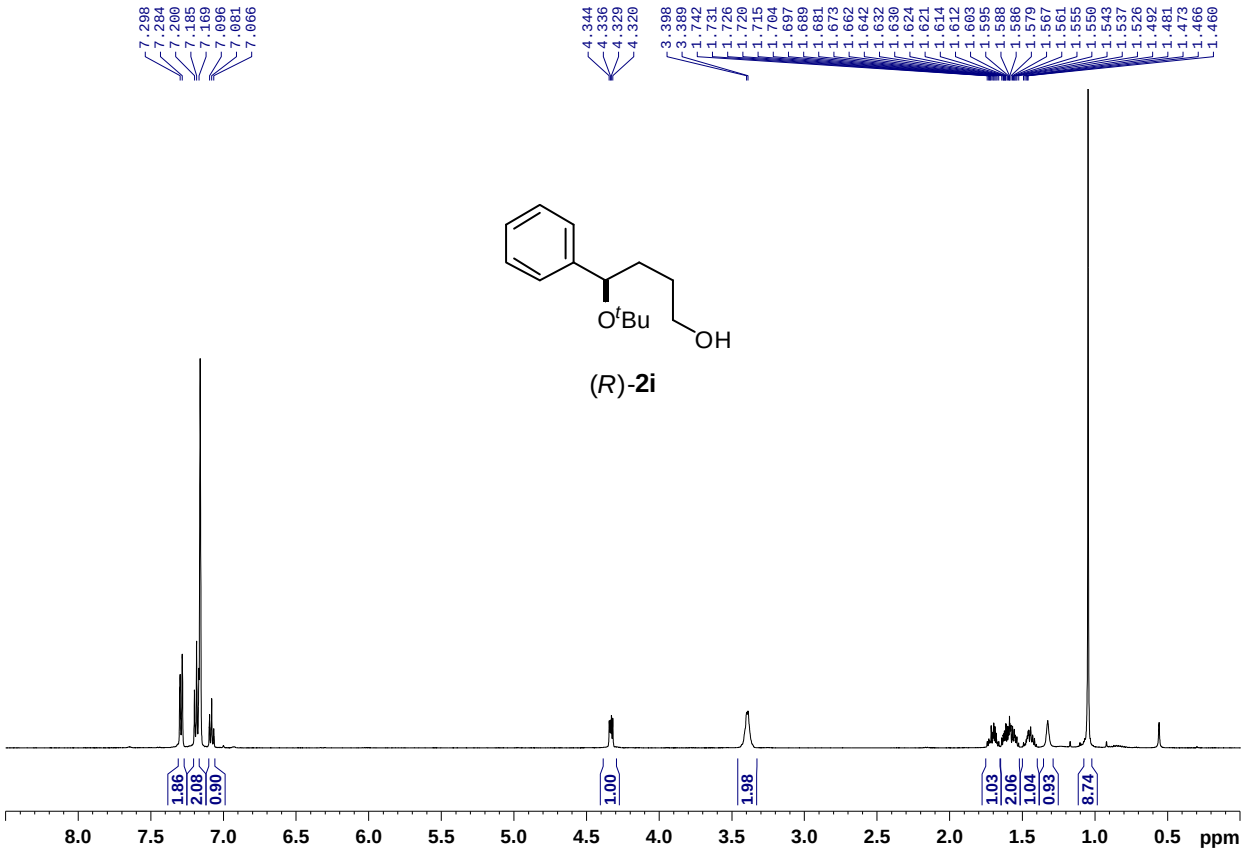
(*R*)-**2h**


155.48
135.33
127.67
120.99
110.19
74.08
67.57
63.14
54.87
35.79
29.67
28.59
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

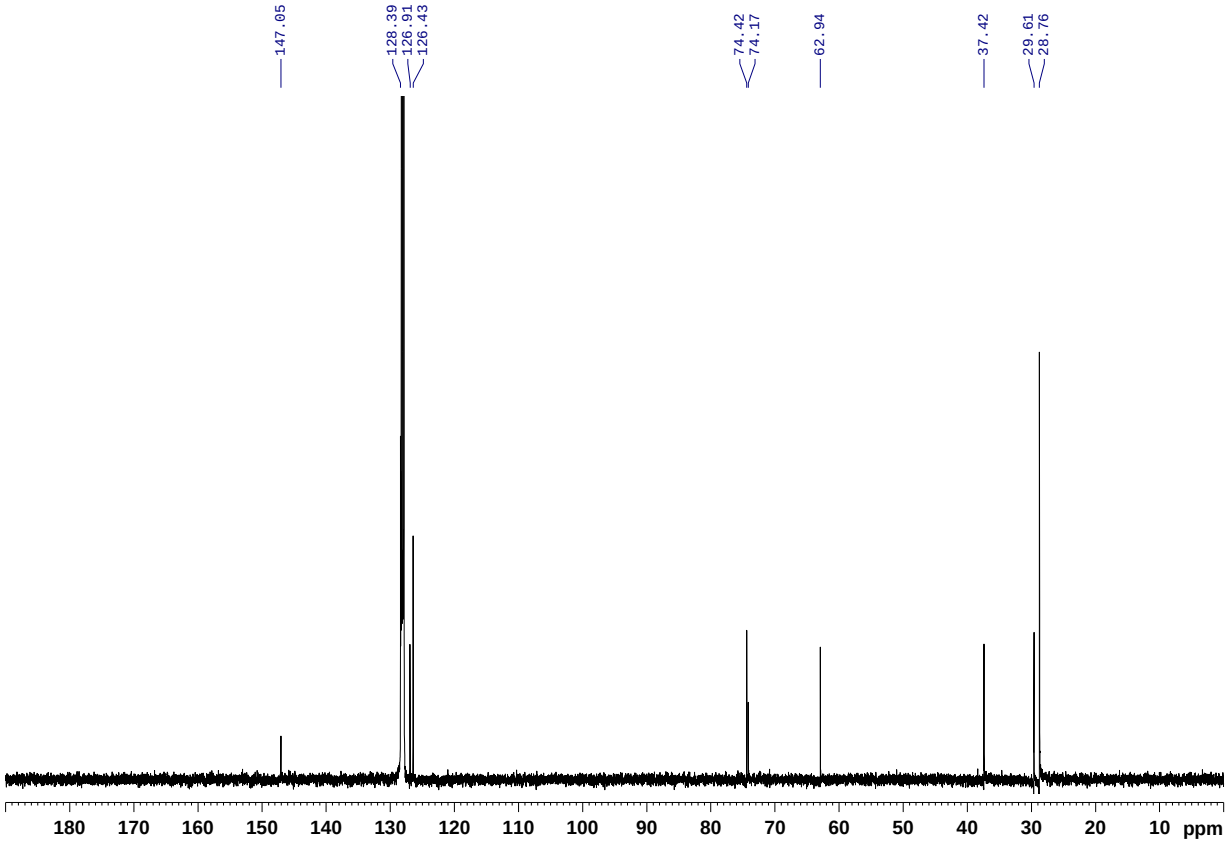

7.349
7.334
7.215
7.201
7.185
7.114
7.100
7.085
4.748
4.734
4.721
3.893
3.882
3.877
3.866
3.855
3.850
3.705
3.693
3.690
3.683
3.678
3.674
3.662
1.915
1.908
1.903
1.893
1.889
1.880
1.873
1.867
1.862
1.859
1.849
1.845
1.580
1.574
1.568
1.565
1.562
1.558
1.556
1.547
1.543
1.540
1.529
1.524
1.517
1.515
1.508
1.503
1.494
1.488
1.480
2.04
2.15
1.04
1.00
1.04
1.04
1.05
3.30
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
ppm

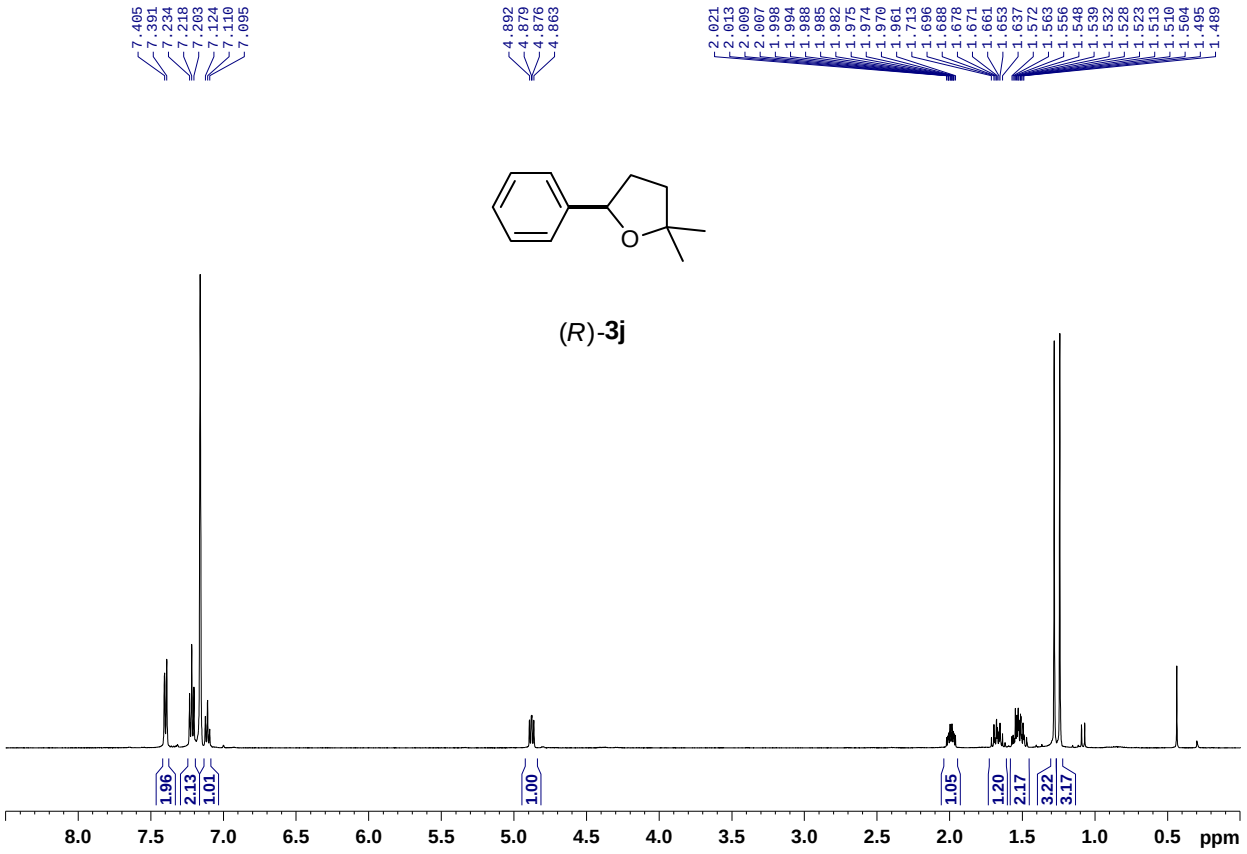
(*R*)-**3i**

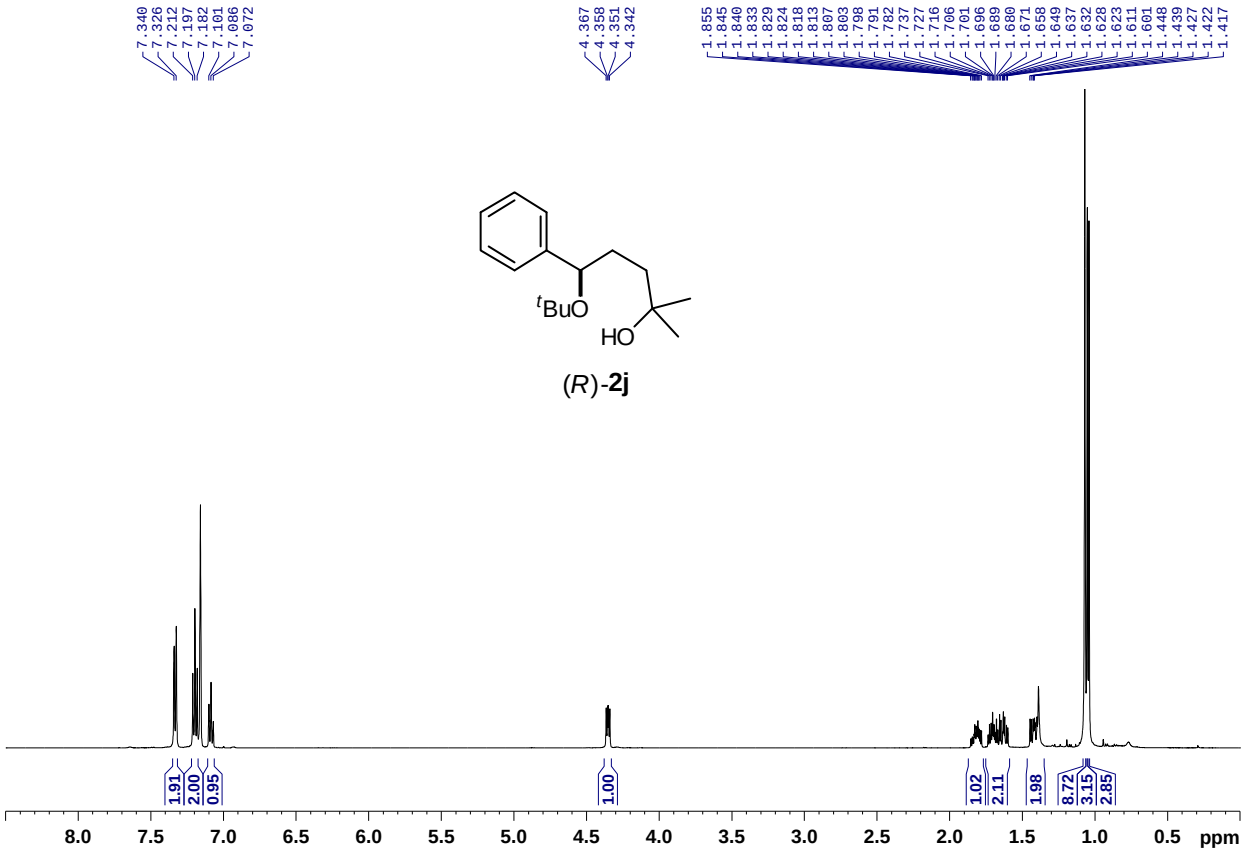

144.45
128.50
127.20
125.92
80.66
68.47
34.99
26.09
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.298
7.284
7.200
7.185
7.169
7.096
7.081
7.066
4.344
4.336
4.329
4.320
3.398
3.389
1.742
1.731
1.726
1.720
1.715
1.704
1.697
1.689
1.681
1.673
1.662
1.642
1.632
1.630
1.624
1.621
1.614
1.612
1.603
1.595
1.588
1.586
1.579
1.567
1.561
1.555
1.550
1.543
1.537
1.526
1.492
1.481
1.473
1.466
1.460
O^{t}Bu
OH
1.86
2.08
0.90
1.00
1.98
1.03
2.06
1.04
0.93
8.74
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
ppm

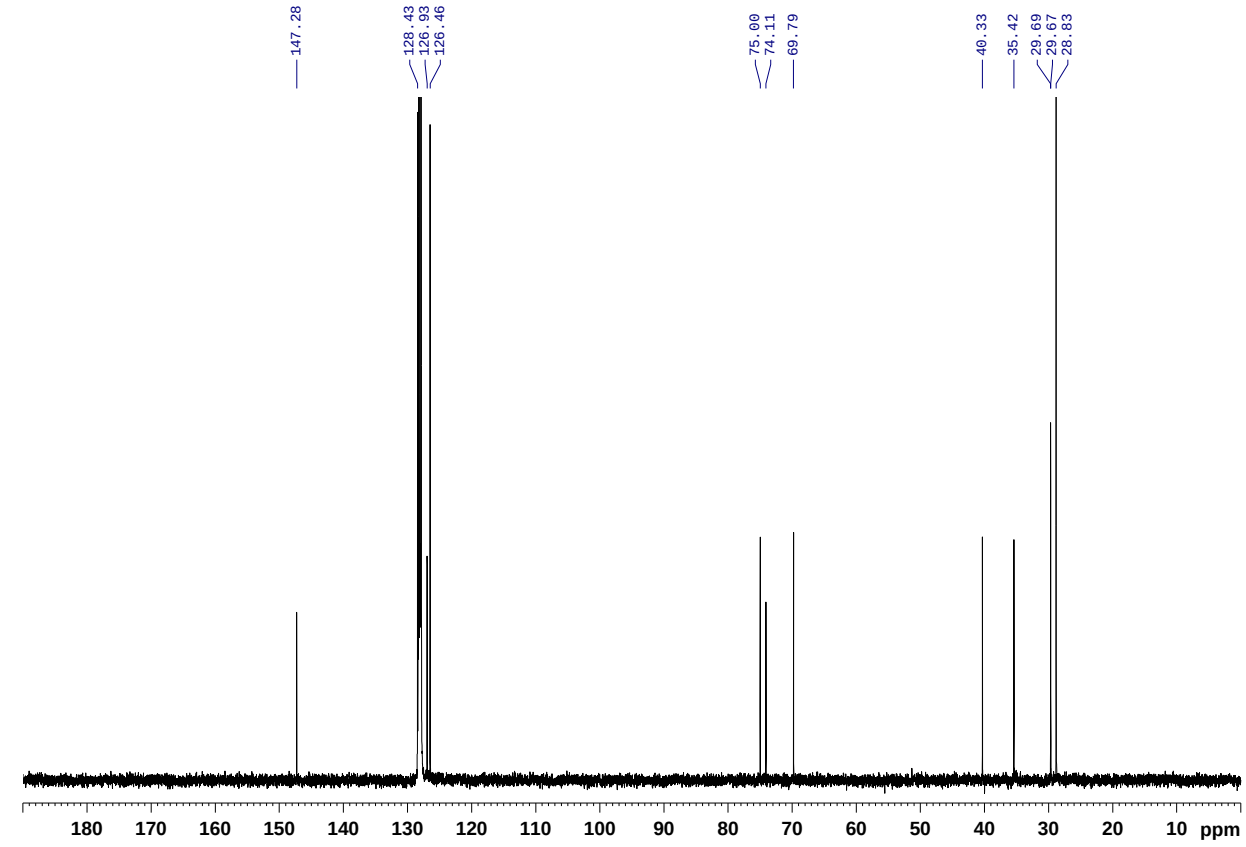
(*R*)-**2i**


147.05
128.39
126.91
126.43
74.42
74.17
62.94
37.42
29.61
28.76
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

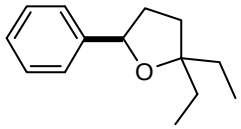

7.405
7.391
7.234
7.218
7.203
7.124
7.110
7.095
4.892
4.879
4.876
4.863
2.021
2.013
2.009
2.007
1.998
1.994
1.988
1.985
1.982
1.975
1.974
1.970
1.961
1.713
1.696
1.688
1.678
1.671
1.661
1.653
1.637
1.572
1.563
1.556
1.548
1.539
1.532
1.528
1.523
1.513
1.510
1.504
1.495
1.489
O
(R)-3j
1.96
2.13
1.01
1.00
1.05
1.20
2.17
3.22
3.17
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
ppm
144.74
128.46
127.16
125.99
80.92
80.35
39.12
35.89
29.23
28.53
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.340
7.326
7.212
7.197
7.182
7.101
7.086
7.072
4.367
4.358
4.351
4.342
1.855
1.845
1.840
1.833
1.829
1.824
1.818
1.813
1.807
1.803
1.798
1.791
1.782
1.737
1.727
1.716
1.706
1.701
1.696
1.689
1.680
1.671
1.658
1.649
1.637
1.632
1.628
1.623
1.611
1.601
1.448
1.439
1.427
1.422
1.417
tBuO
HO
1.91
2.00
0.95
1.00
1.02
2.11
1.98
8.72
3.15
2.85
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
ppm

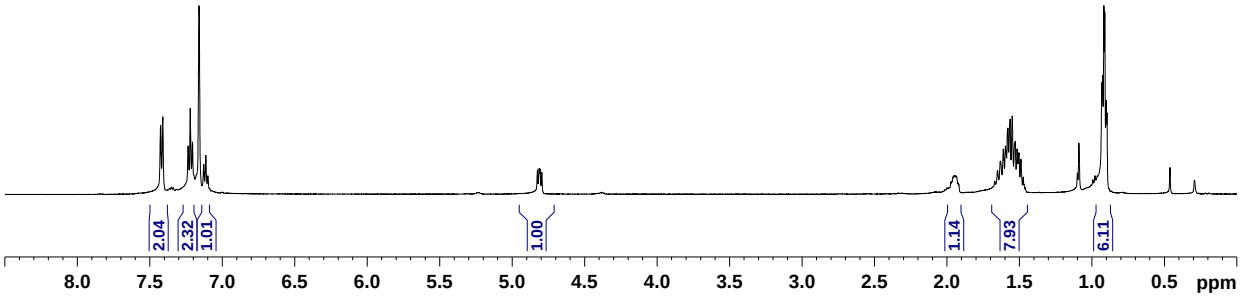
(*R*)-**2j**

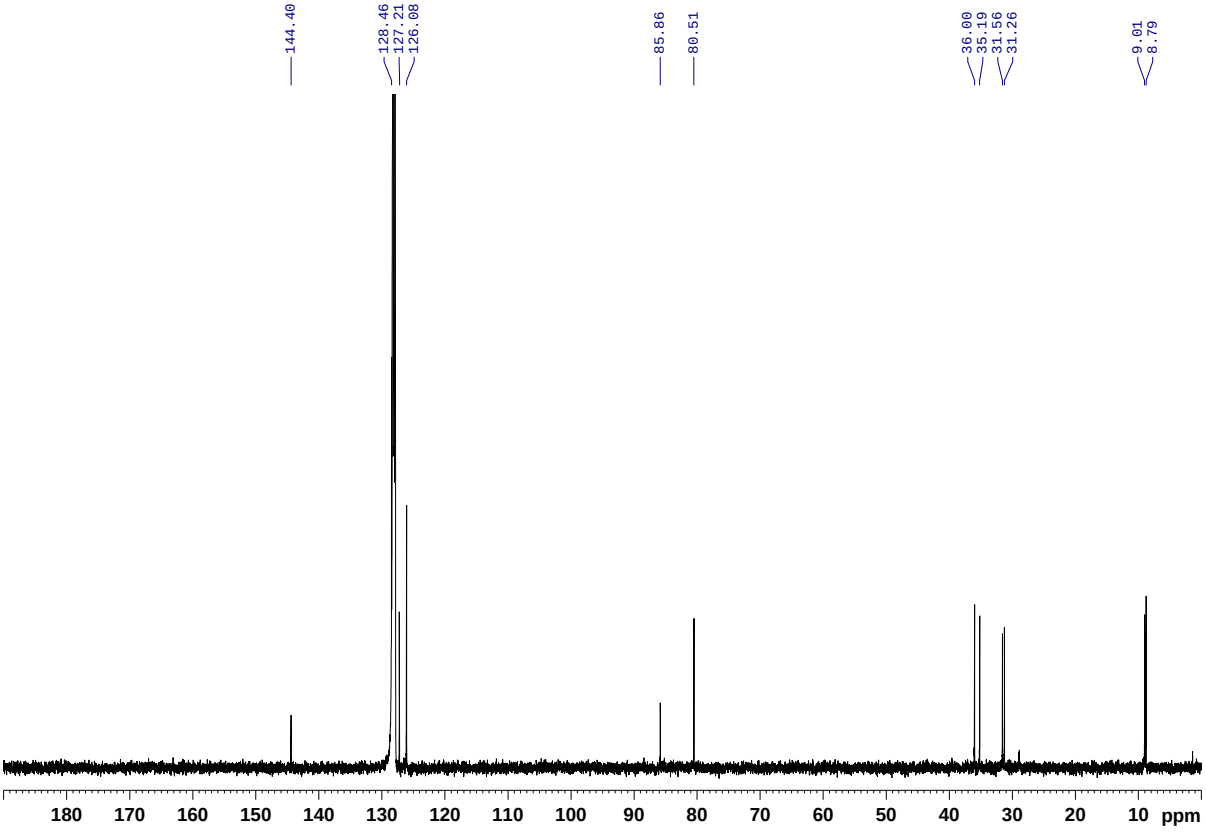

147.28
128.43
126.93
126.46
75.00
74.11
69.79
40.33
35.42
29.69
29.67
28.83
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

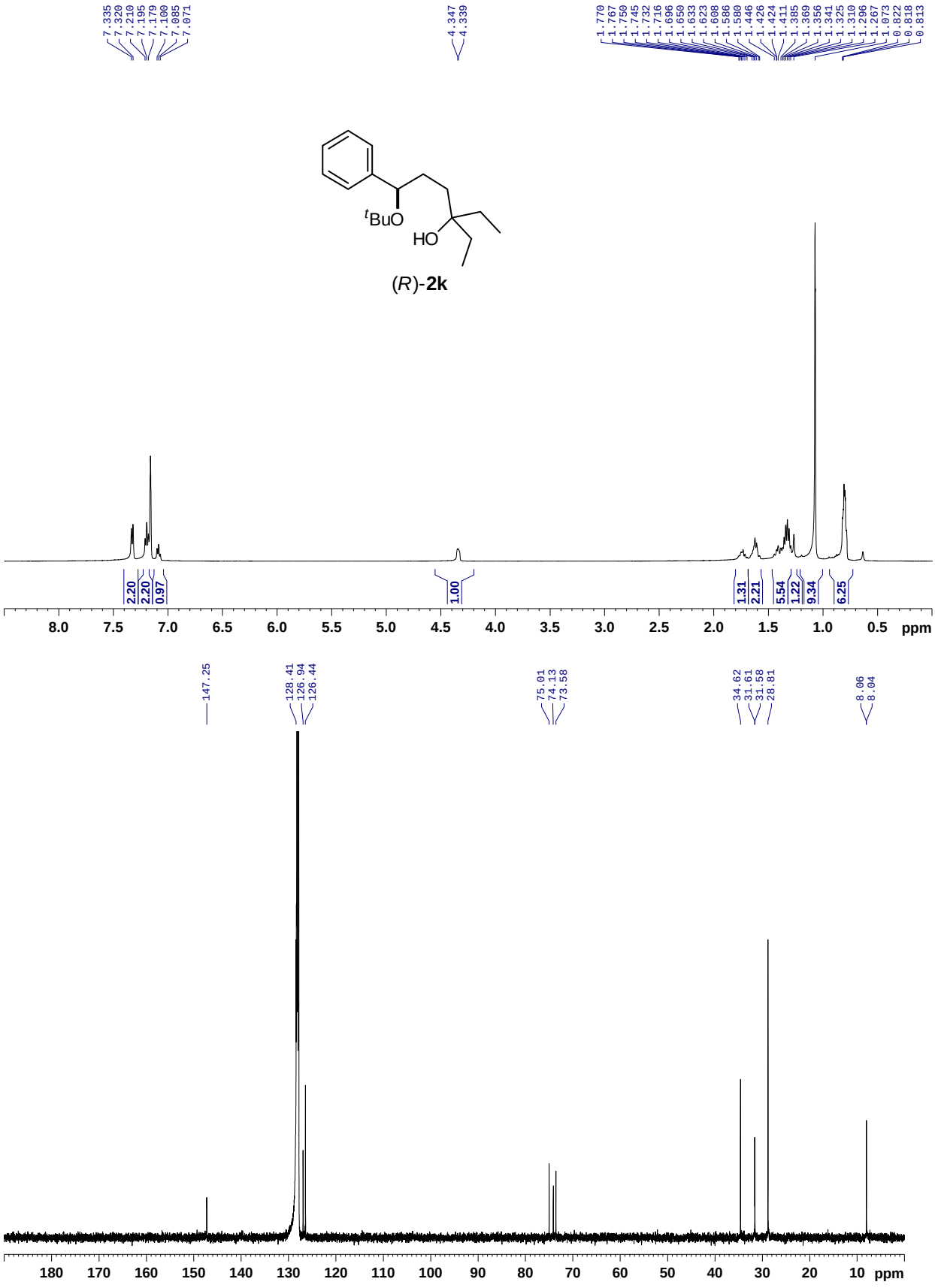

7.426
7.410
7.236
7.221
7.205
7.128
7.113
7.099
4.825
4.814
4.807
4.795
1.974
1.967
1.950
1.944
1.935
1.671
1.651
1.631
1.612
1.597
1.581
1.565
1.550
1.535
1.529
1.517
1.504
1.490
1.474
0.933
0.926
0.918
0.911
0.903
0.897

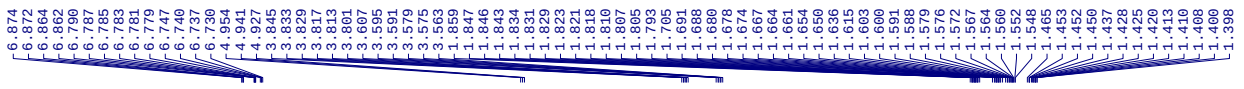

O

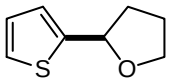
(*R*)-**3k**


2.04
2.32
1.01
1.00
1.14
7.93
6.11
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
ppm


144.40
128.46
127.21
126.08
85.86
80.51
36.00
35.19
31.56
31.26
9.01
8.79
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

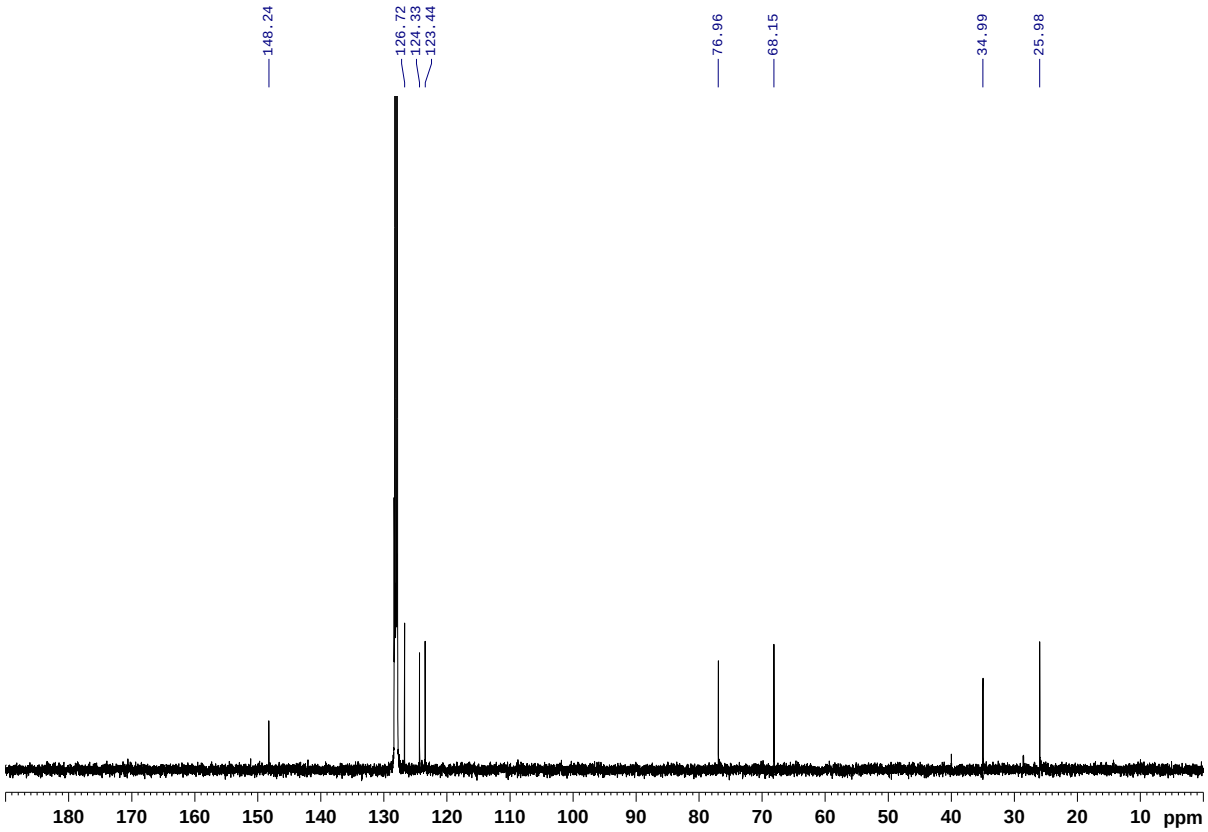

7.335
7.320
7.210
7.195
7.179
7.100
7.085
7.071
4.347
4.339
1.770
1.767
1.750
1.745
1.732
1.716
1.696
1.650
1.633
1.623
1.608
1.586
1.580
1.446
1.426
1.424
1.411
1.385
1.369
1.356
1.341
1.325
1.310
1.296
1.267
1.073
0.822
0.818
0.813
tBuO
HO
(R)-2k
2.20
2.20
0.97
1.00
1.31
2.21
5.54
1.22
9.34
6.25
8.0 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 ppm
147.25
128.41
126.94
126.44
75.01
74.13
73.58
34.62
31.61
31.58
28.81
8.06
8.04
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

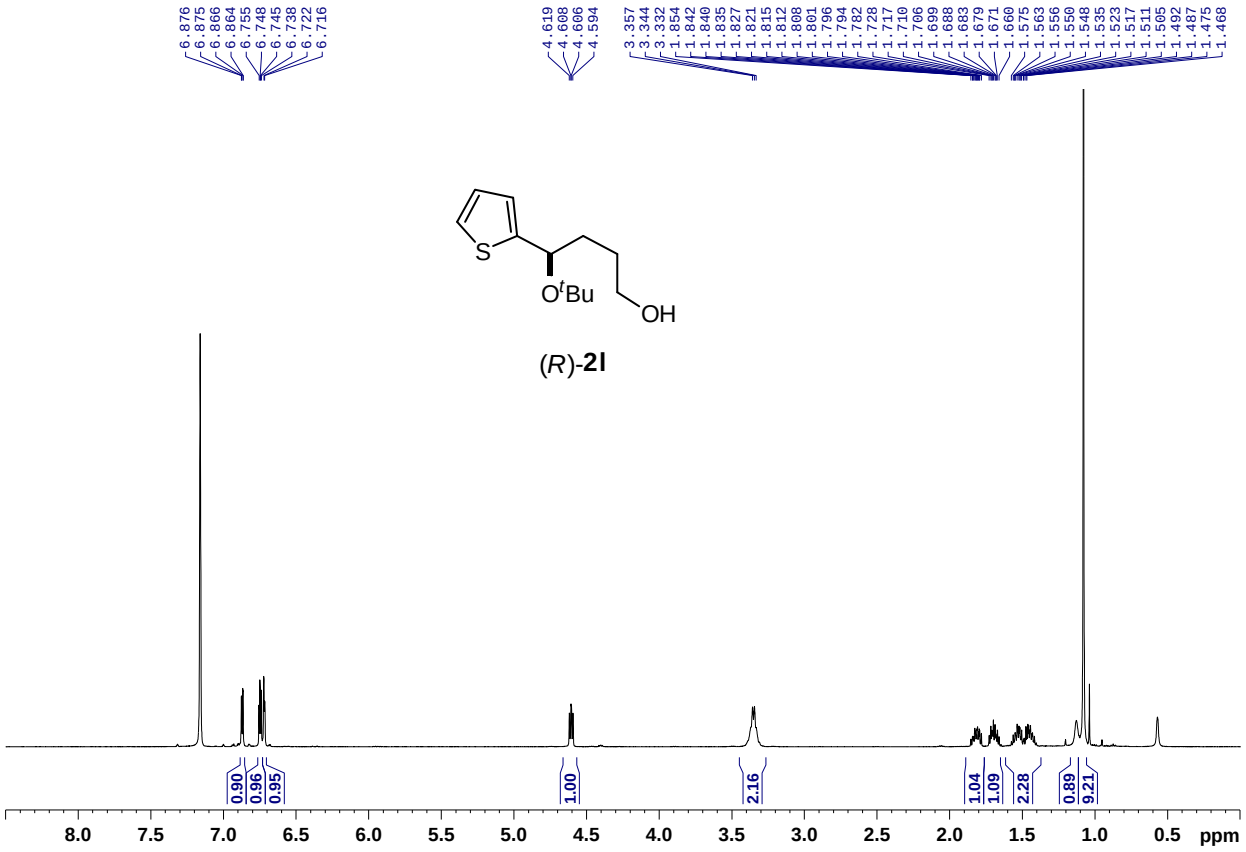

6.874
6.872
6.864
6.862
6.790
6.787
6.785
6.783
6.781
6.779
6.747
6.740
6.737
6.730
4.954
4.941
4.927
3.845
3.833
3.829
3.817
3.813
3.801
3.607
3.595
3.591
3.579
3.575
3.563
1.859
1.847
1.846
1.843
1.834
1.831
1.829
1.823
1.821
1.818
1.810
1.807
1.805
1.793
1.705
1.691
1.688
1.680
1.678
1.674
1.667
1.664
1.661
1.654
1.650
1.636
1.615
1.603
1.600
1.591
1.588
1.579
1.576
1.572
1.567
1.564
1.560
1.552
1.548
1.465
1.453
1.452
1.450
1.437
1.428
1.425
1.420
1.413
1.410
1.408
1.400
1.398

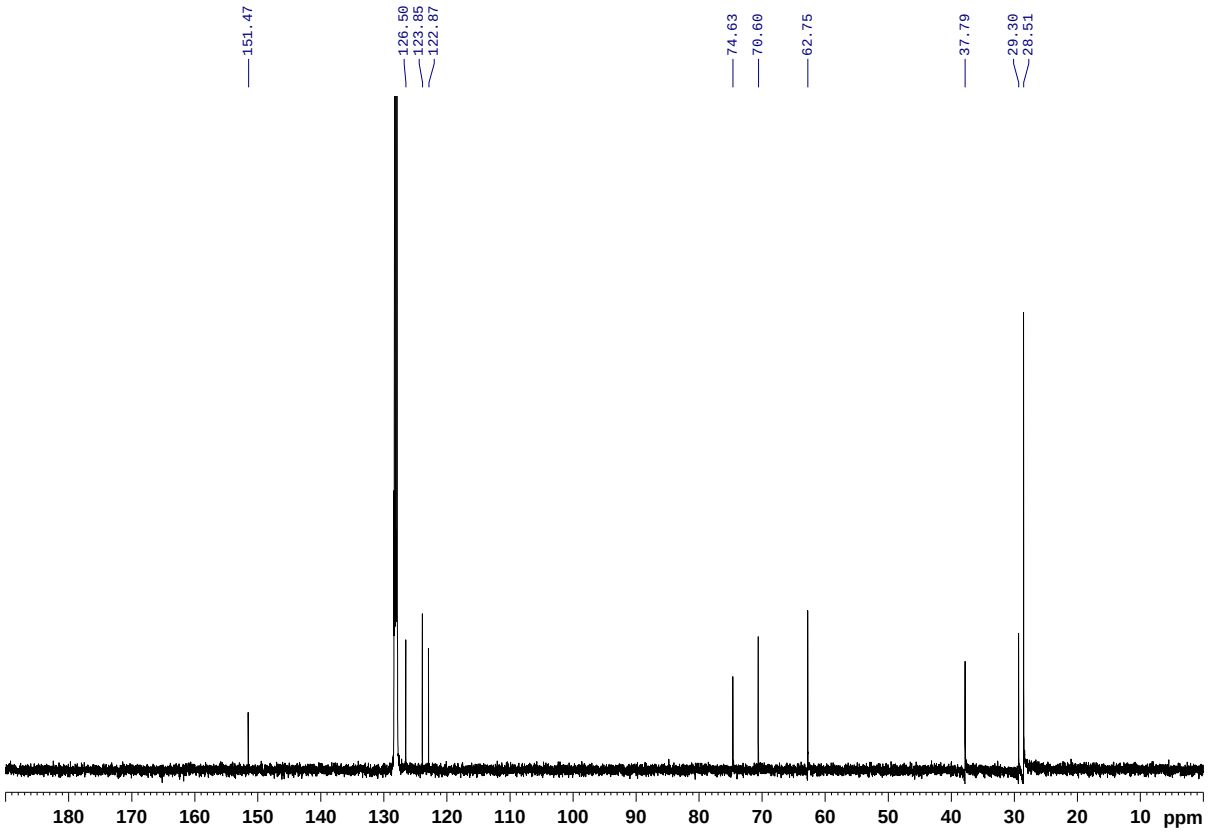

S
O

(*R*)-**3l**

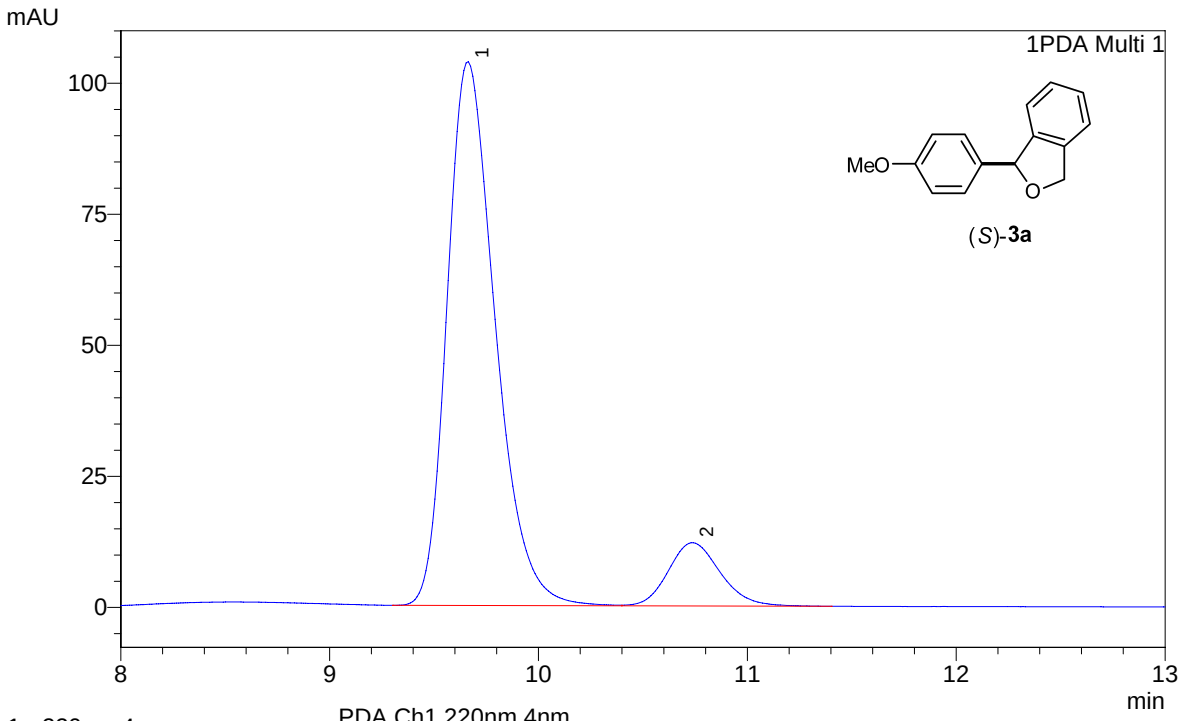
1.03
0.99
1.08
1.00
1.06
1.04
1.14
1.26
1.16
1.12
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


148.24
126.72
124.33
123.44
76.96
68.15
34.99
25.98
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


6.876
6.875
6.866
6.864
6.755
6.748
6.745
6.738
6.722
6.716
4.619
4.608
4.606
4.594
3.357
3.344
3.332
1.854
1.842
1.840
1.835
1.827
1.821
1.815
1.812
1.808
1.801
1.796
1.794
1.782
1.728
1.717
1.710
1.706
1.699
1.688
1.683
1.679
1.671
1.660
1.575
1.563
1.556
1.550
1.548
1.535
1.523
1.517
1.511
1.505
1.492
1.487
1.475
1.468
S
O^{t}Bu
OH
(R)-2l
0.90
0.96
0.95
1.00
2.16
1.04
1.09
2.28
0.89
9.21
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
ppm


151.47
126.50
123.85
122.87
74.63
70.60
62.75
37.79
29.30
28.51
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

HPLC traces

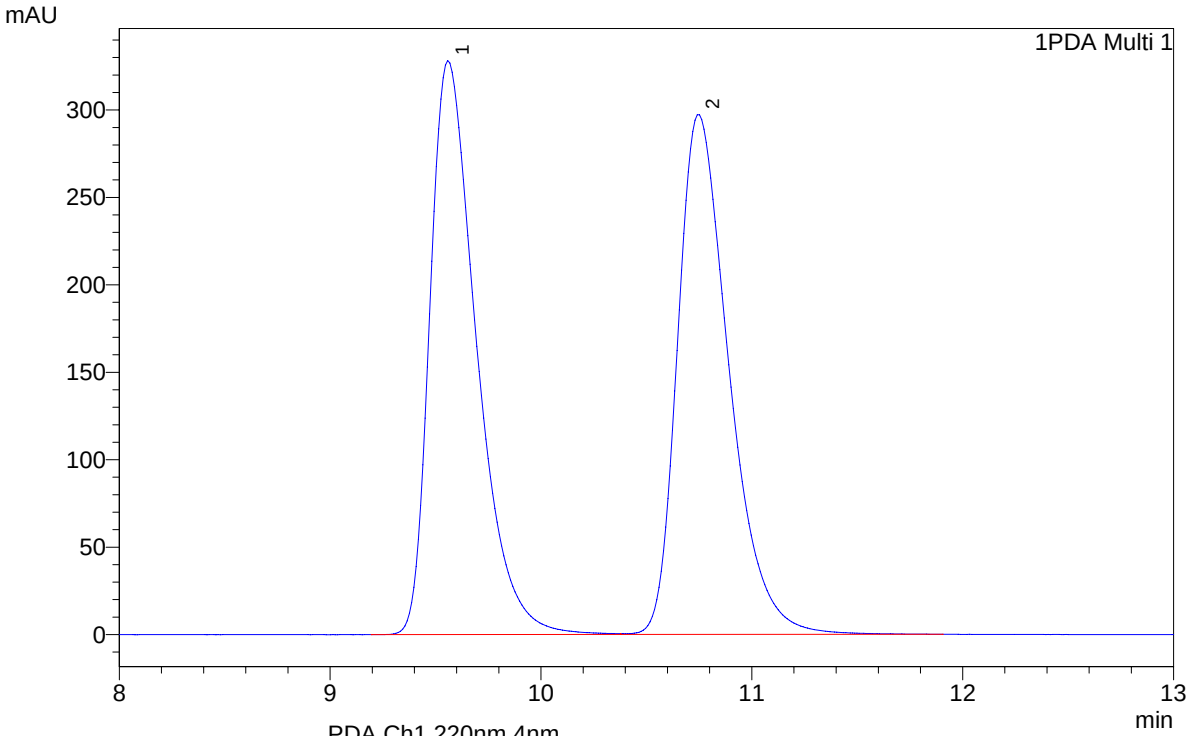


(*S*)-**3a**

1 220nm 4nm

PDA Ch1 220nm 4nm

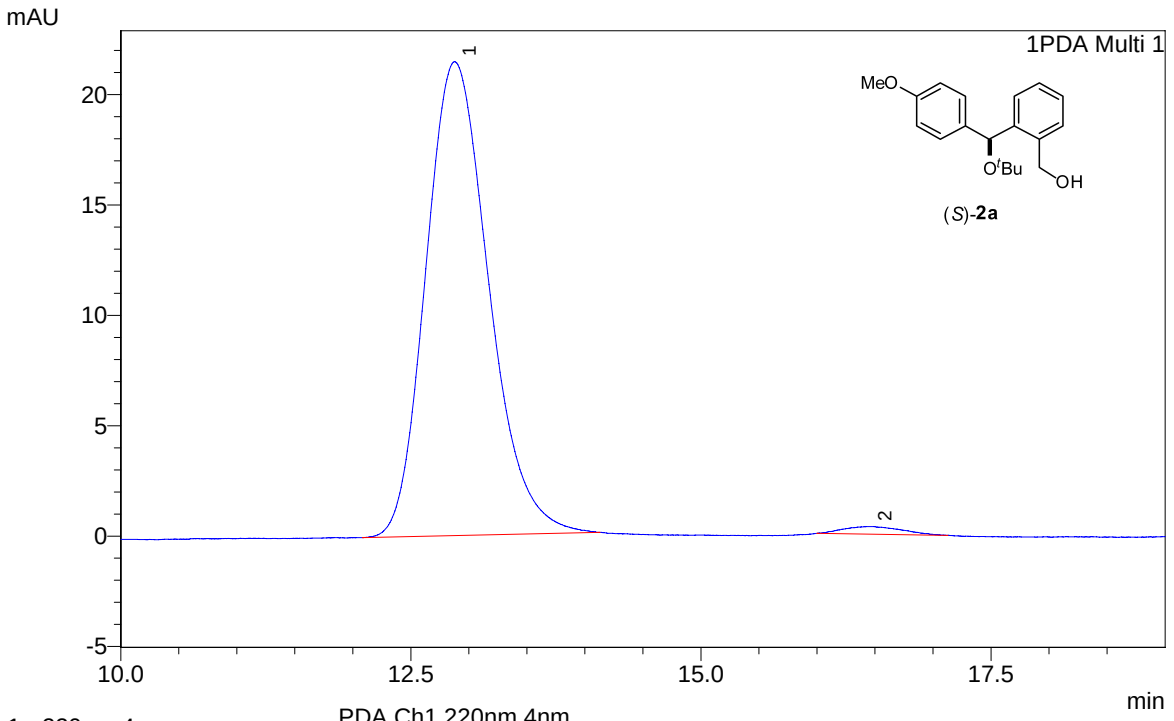
Peak #	Ret. Time	Area %
1	9.66	88.82
2	10.73	11.18
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

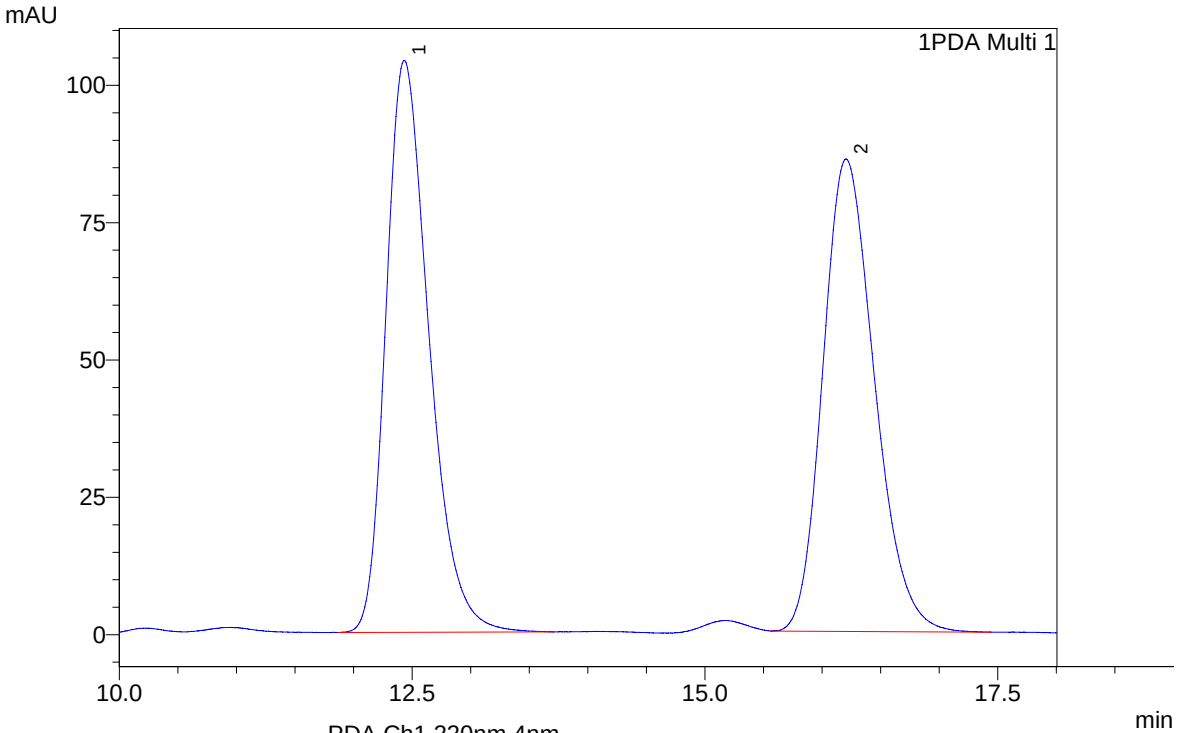
Peak #	Ret. Time	Area %
1	9.55	49.97
2	10.74	50.03
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

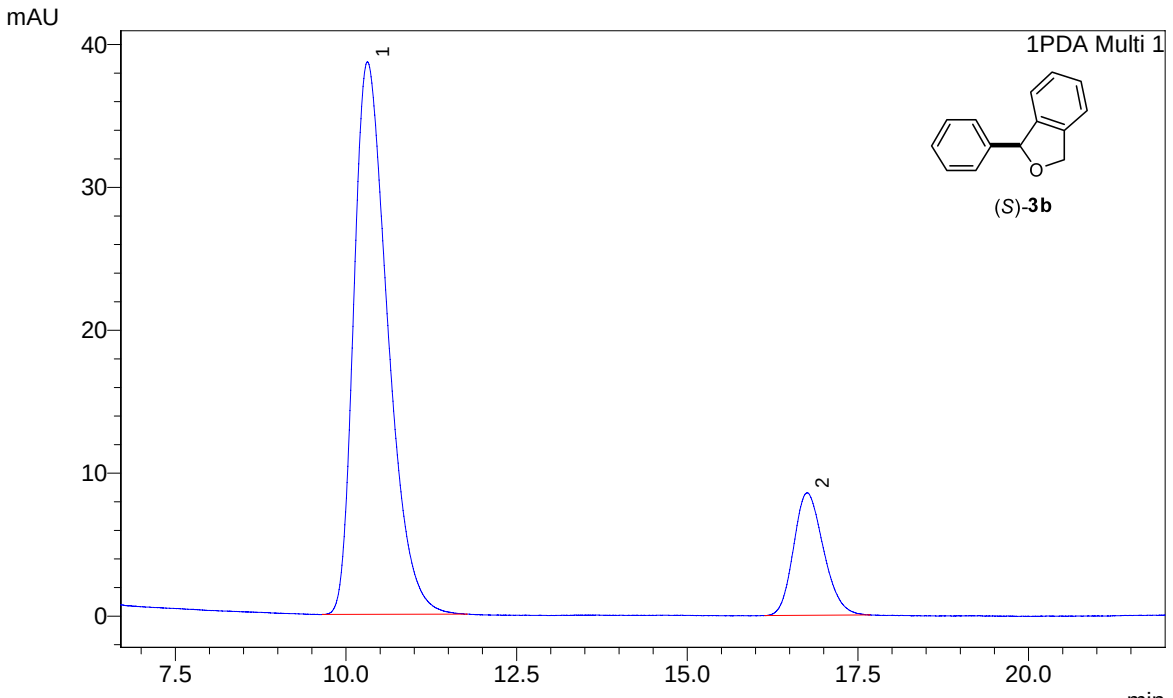
Peak #	Ret. Time	Area %
1	12.87	98.53
2	16.45	1.47
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

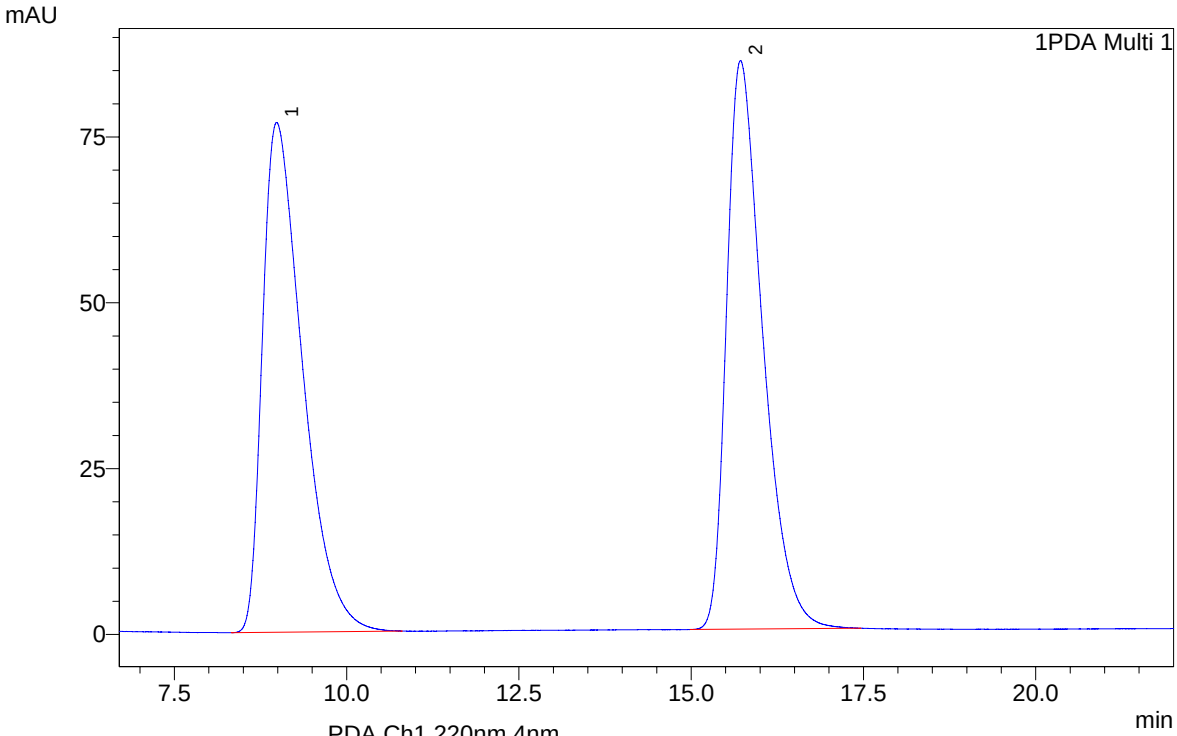
Peak #	Ret. Time	Area %
1	12.43	50.28
2	16.20	49.72
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

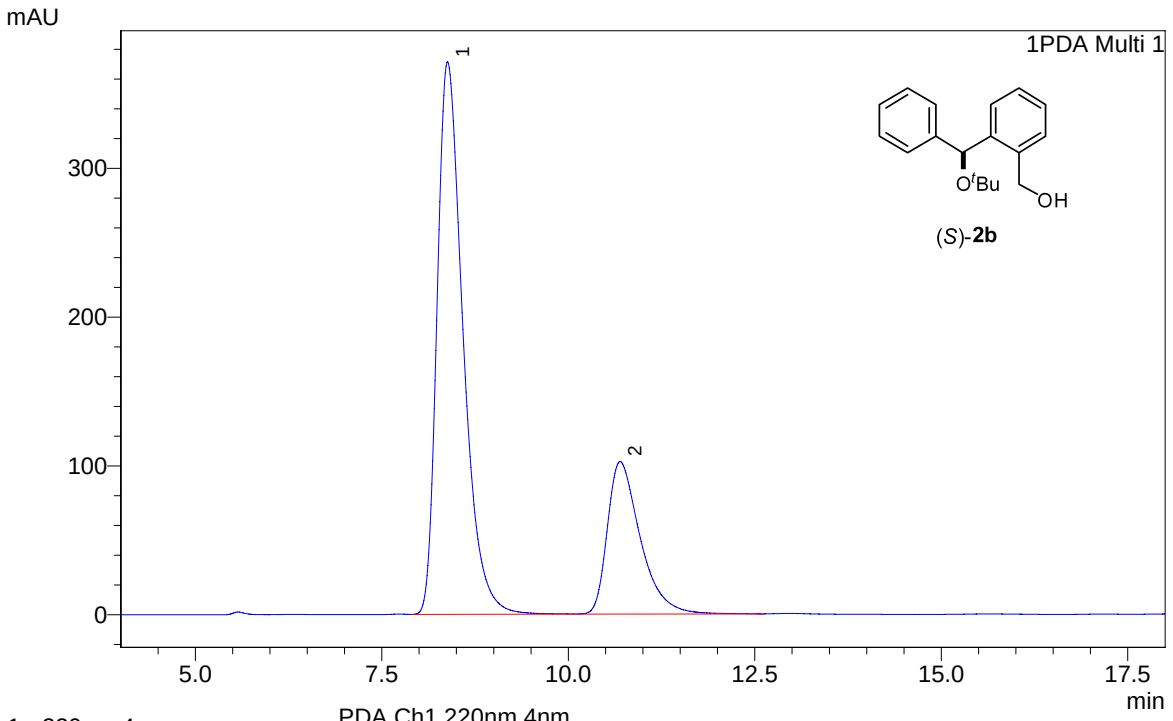
Peak #	Ret. Time	Area %
1	10.31	83.62
2	16.75	16.38
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

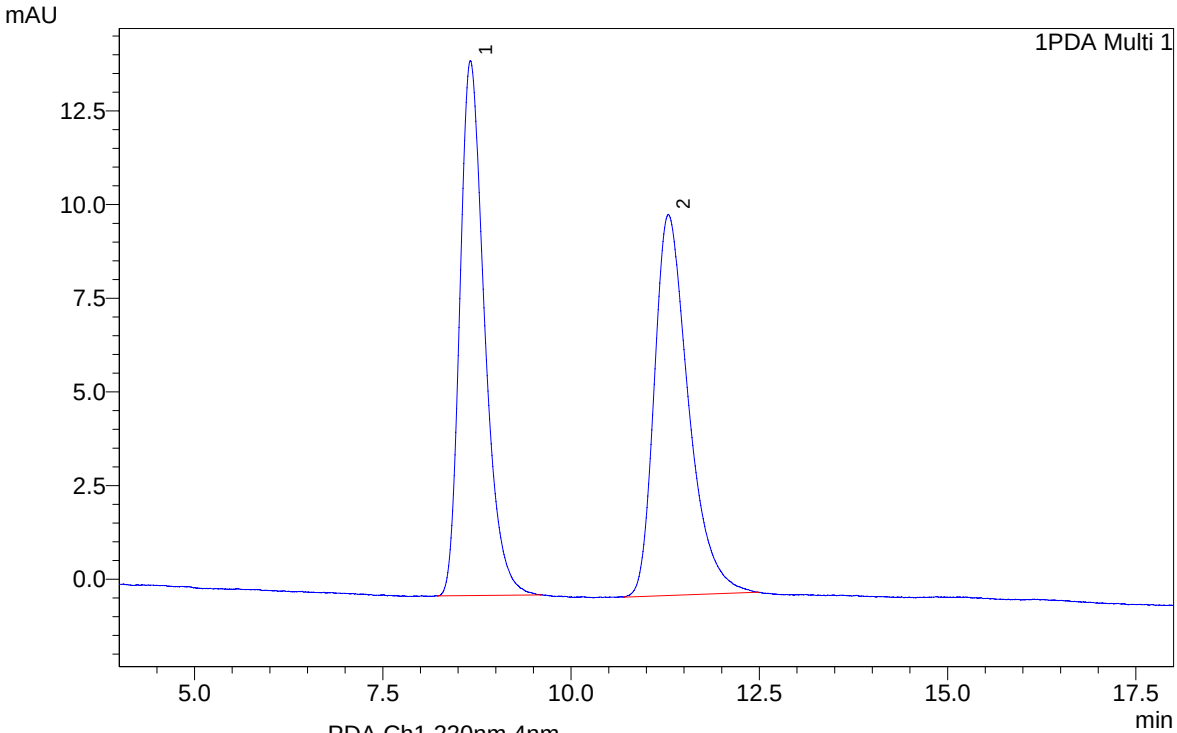
Peak #	Ret. Time	Area %
1	8.98	49.84
2	15.71	50.16
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

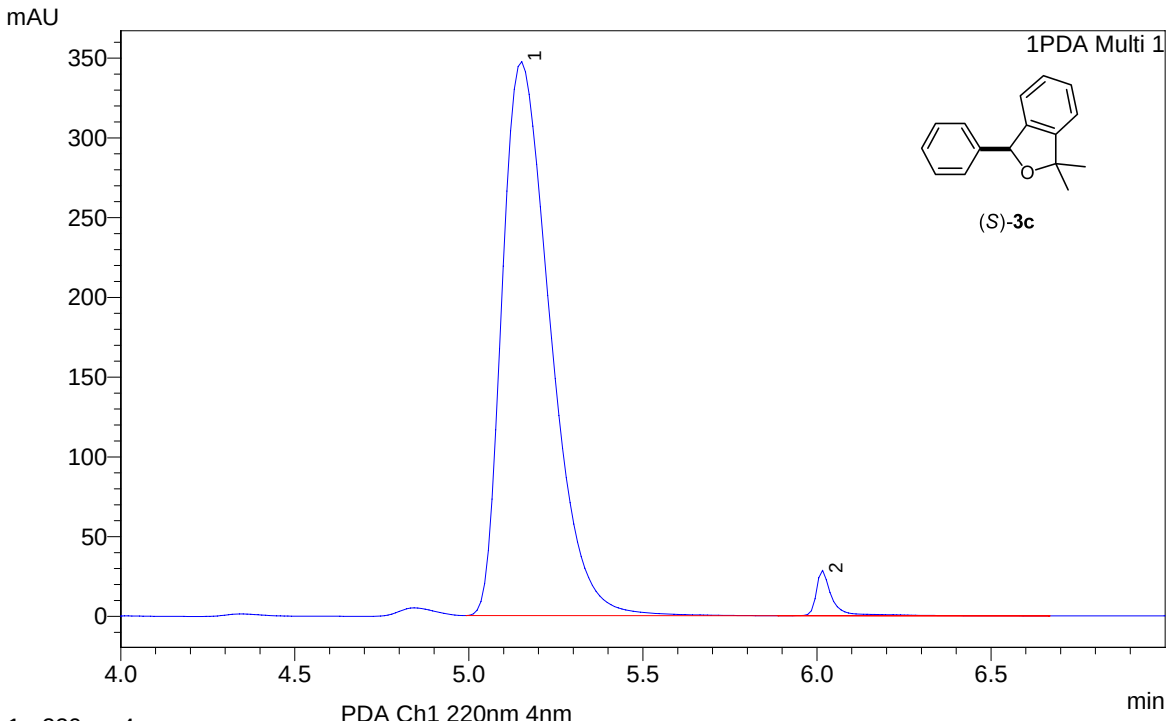
Peak #	Ret. Time	Area %
1	8.38	74.04
2	10.69	25.96
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

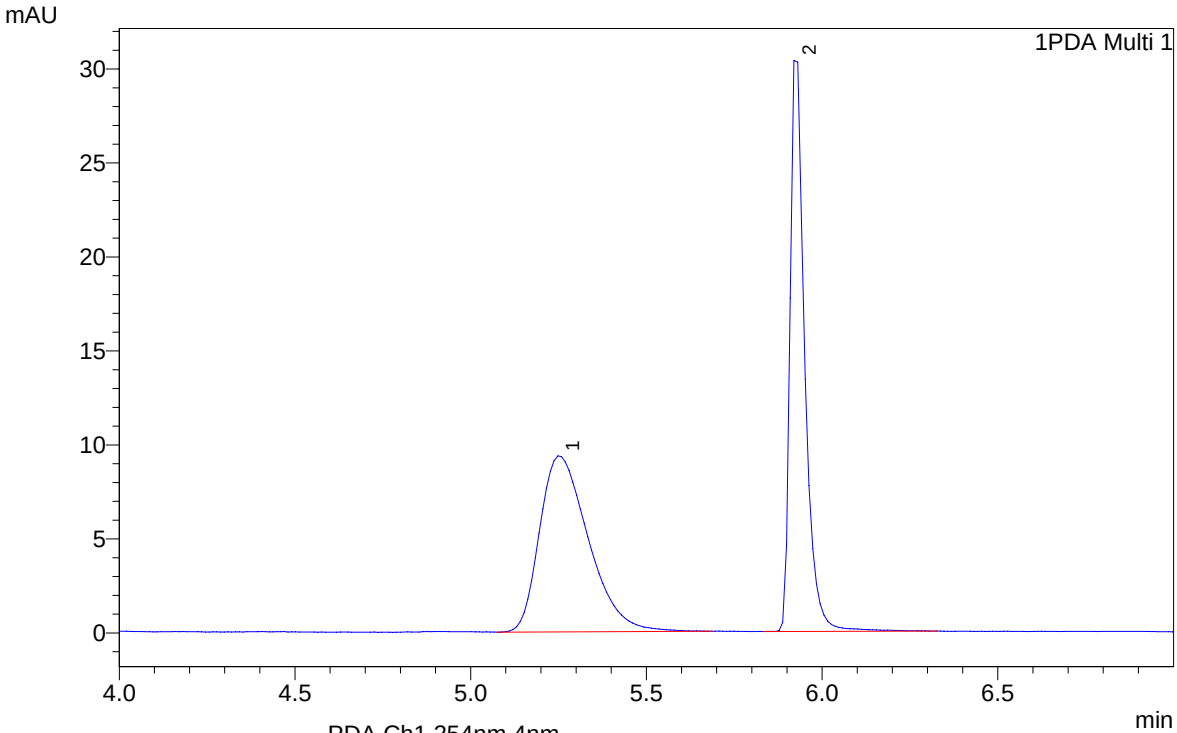
Peak #	Ret. Time	Area %
1	8.66	50.32
2	11.29	49.68
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

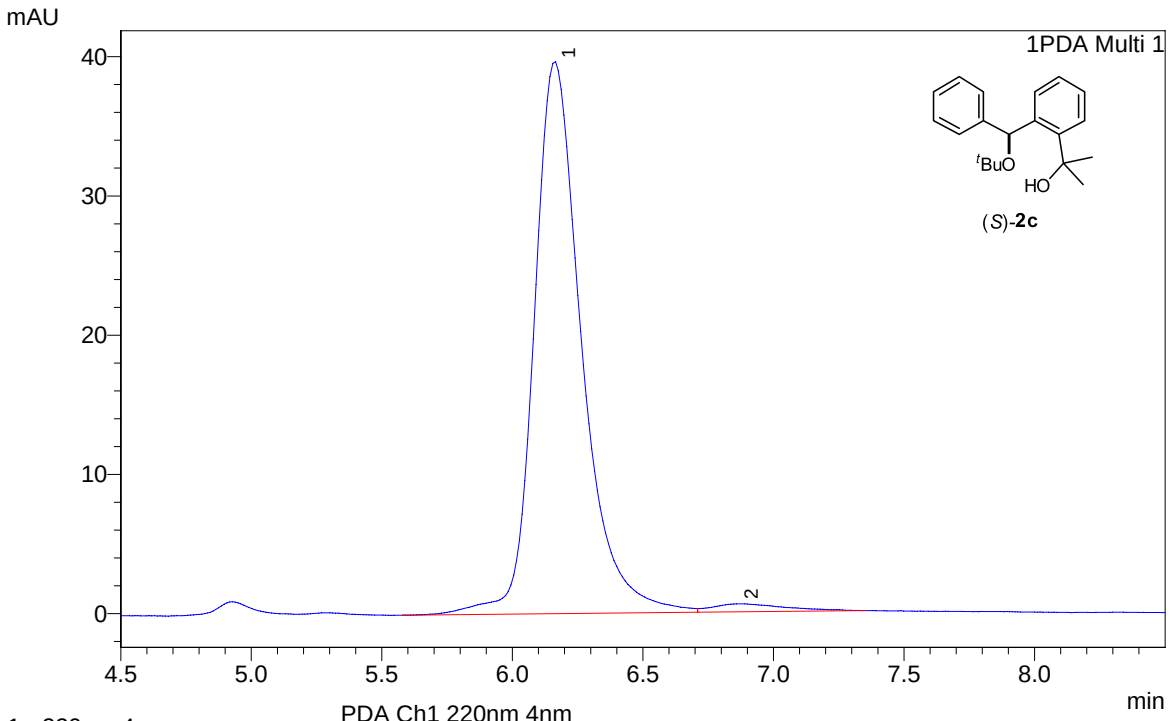
Peak #	Ret. Time	Area %
1	5.14	97.34
2	6.01	2.66
Total		100.00



1 254nm 4nm

PDA Ch1 254nm 4nm

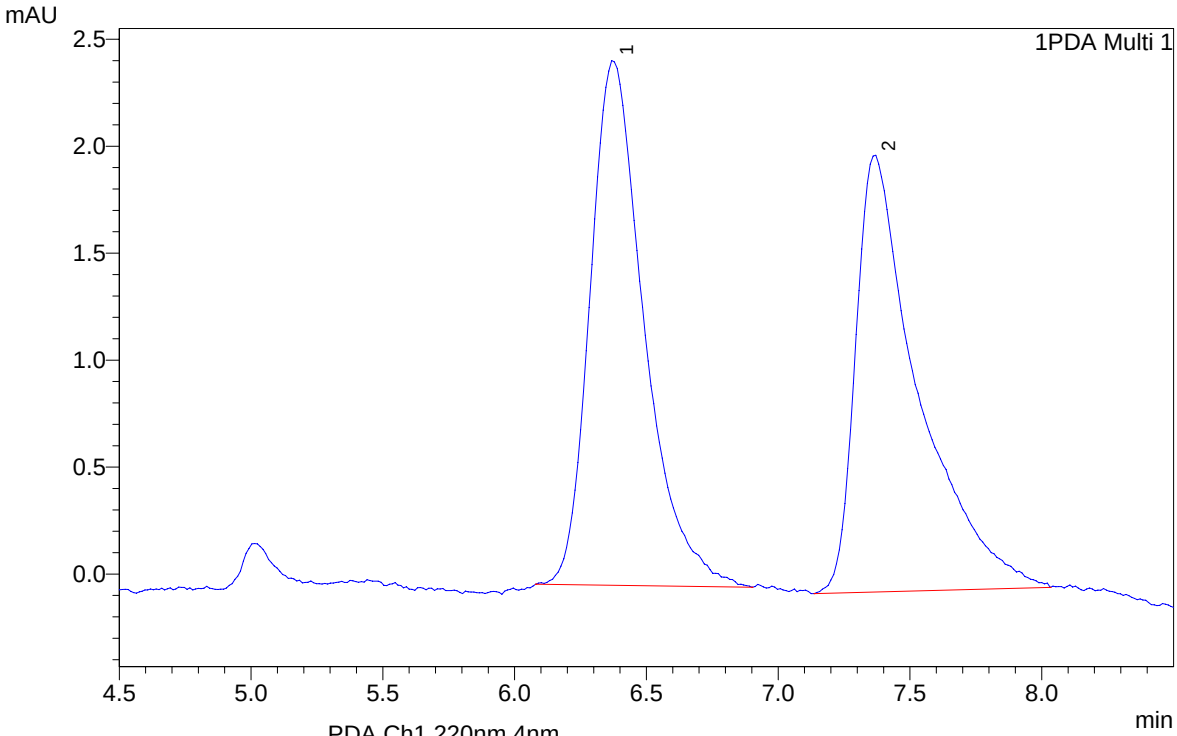
Peak #	Ret. Time	Area %
1	5.25	50.45
2	5.92	49.55
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

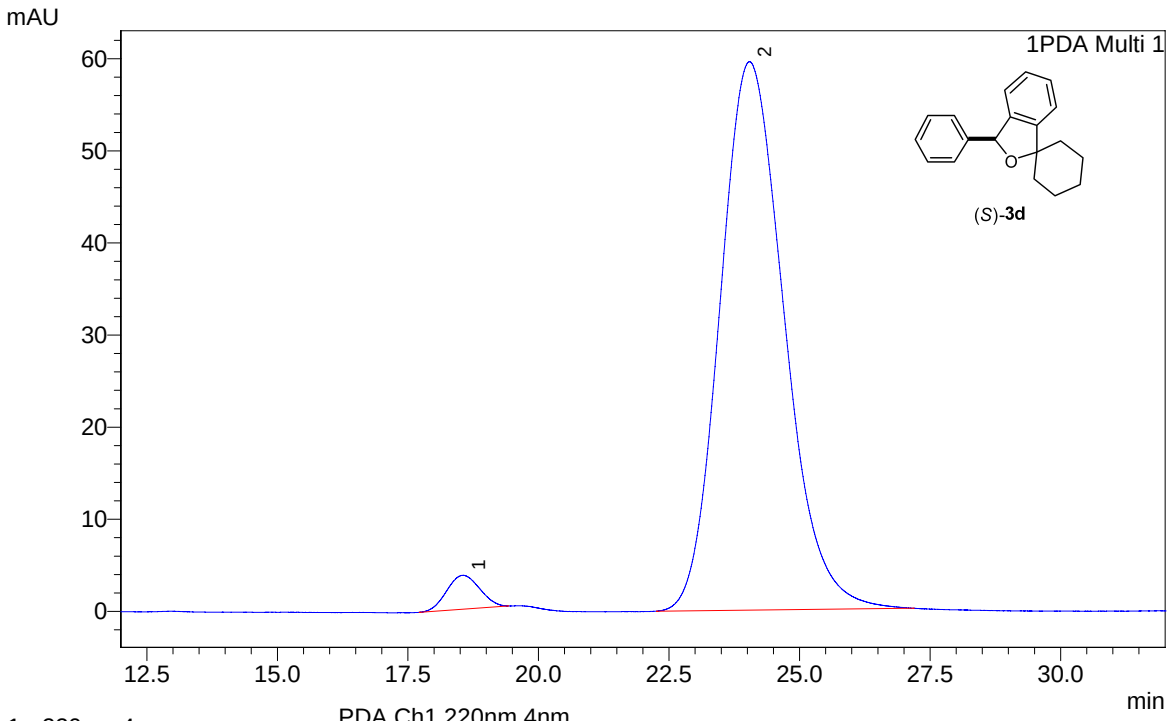
Peak #	Ret. Time	Area %
1	6.16	97.87
2	6.86	2.13
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

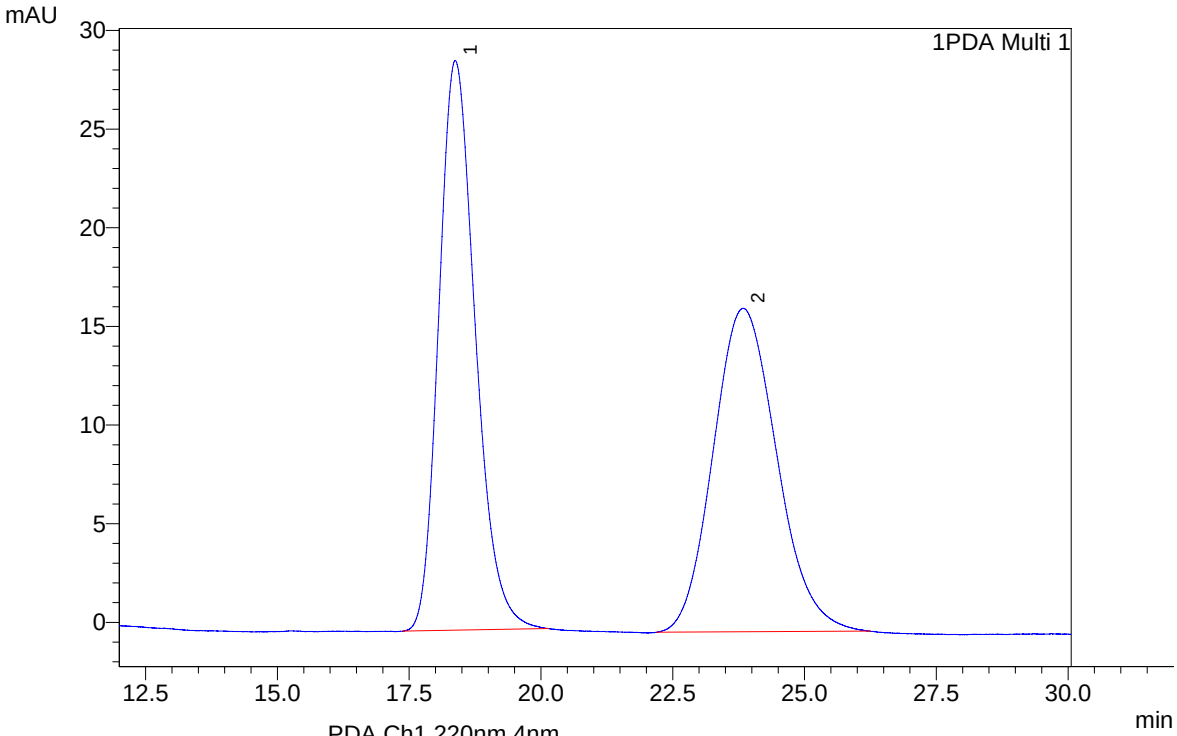
Peak #	Ret. Time	Area %
1	6.37	50.90
2	7.36	49.10
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

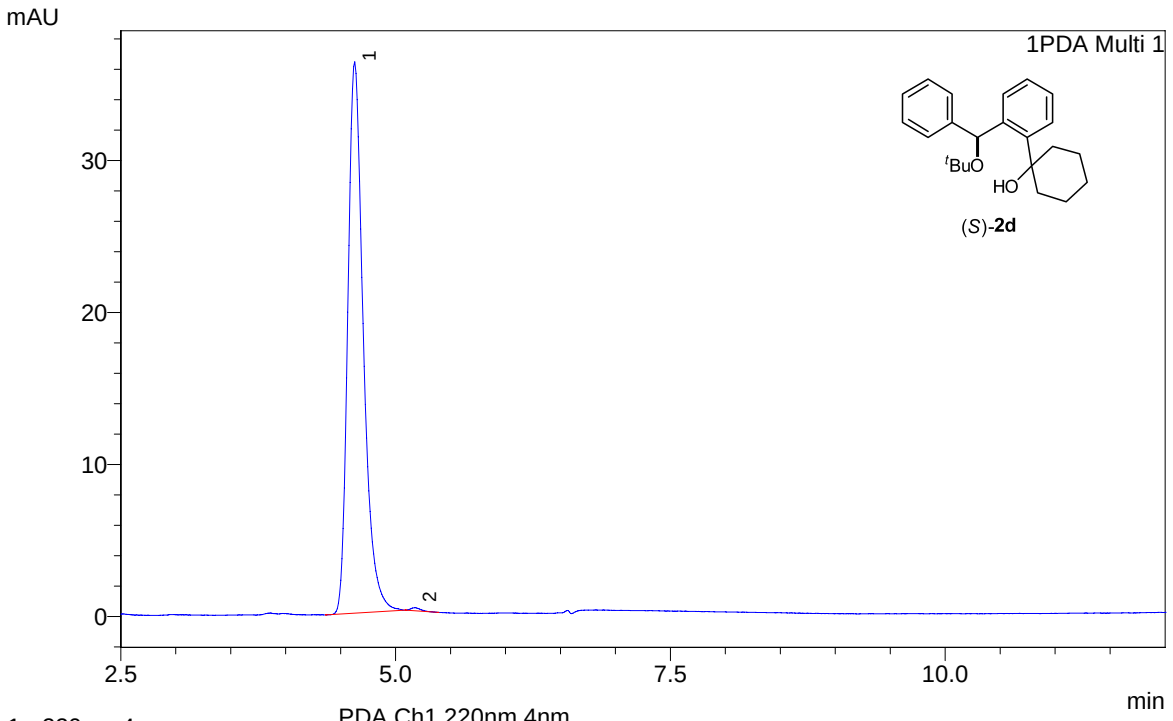
Peak #	Ret. Time	Area %
1	18.56	3.08
2	24.04	96.92
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

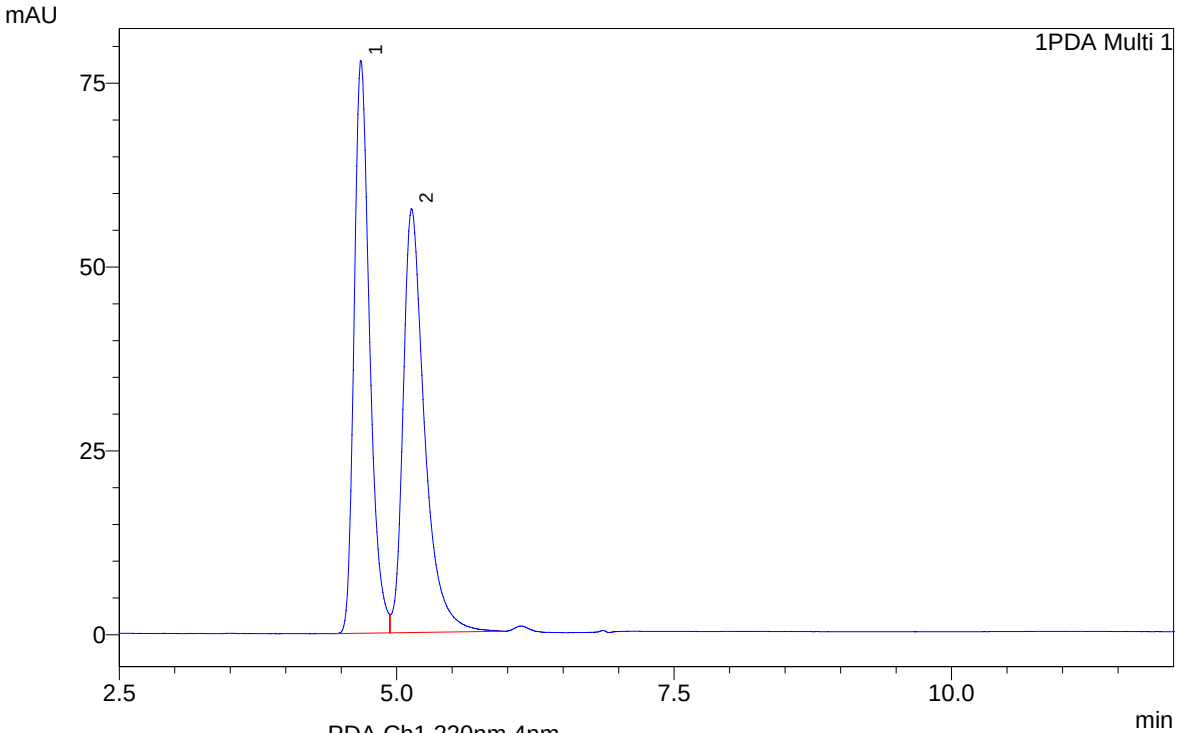
Peak #	Ret. Time	Area %
1	18.37	50.33
2	23.82	49.67
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

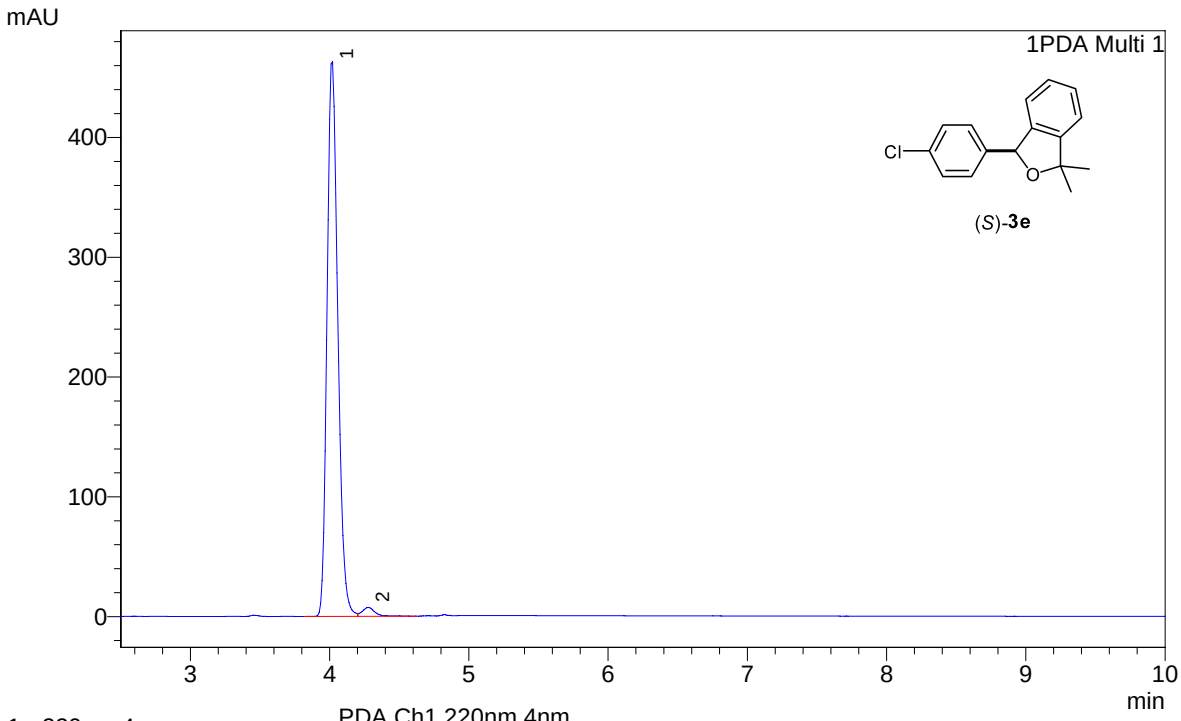
Peak #	Ret. Time	Area %
1	4.62	99.68
2	5.17	0.32
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

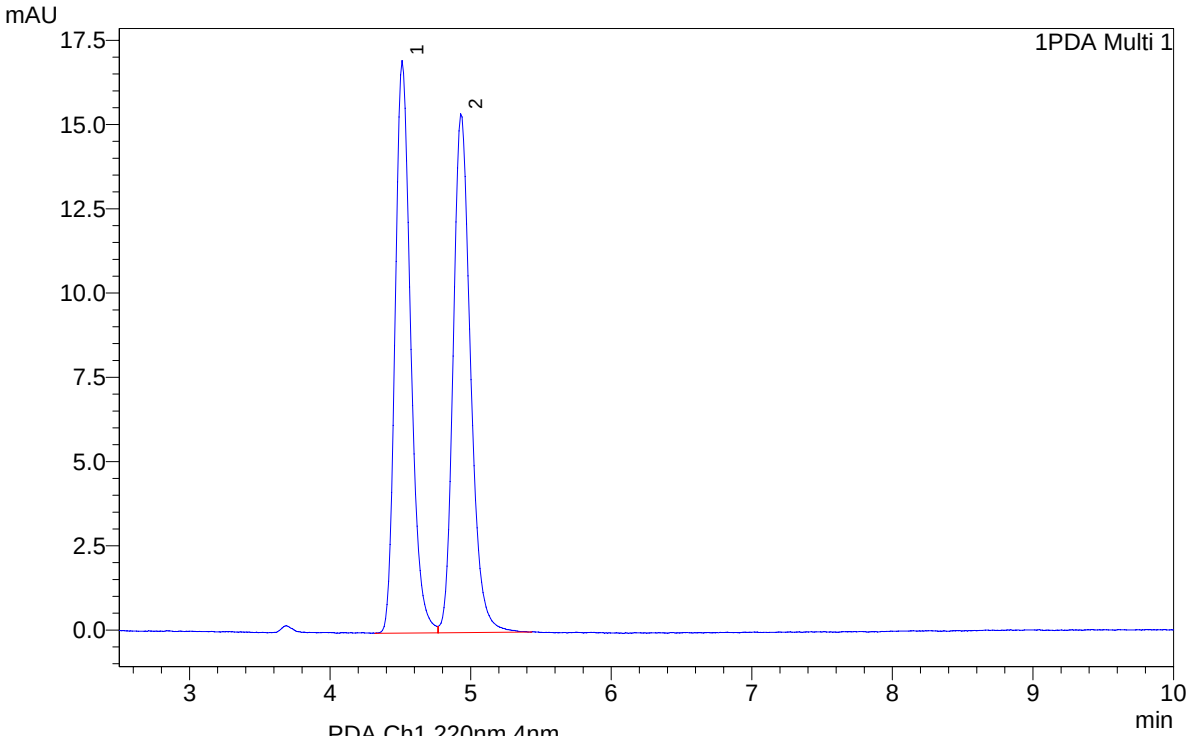
Peak #	Ret. Time	Area %
1	4.67	49.52
2	5.13	50.48
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

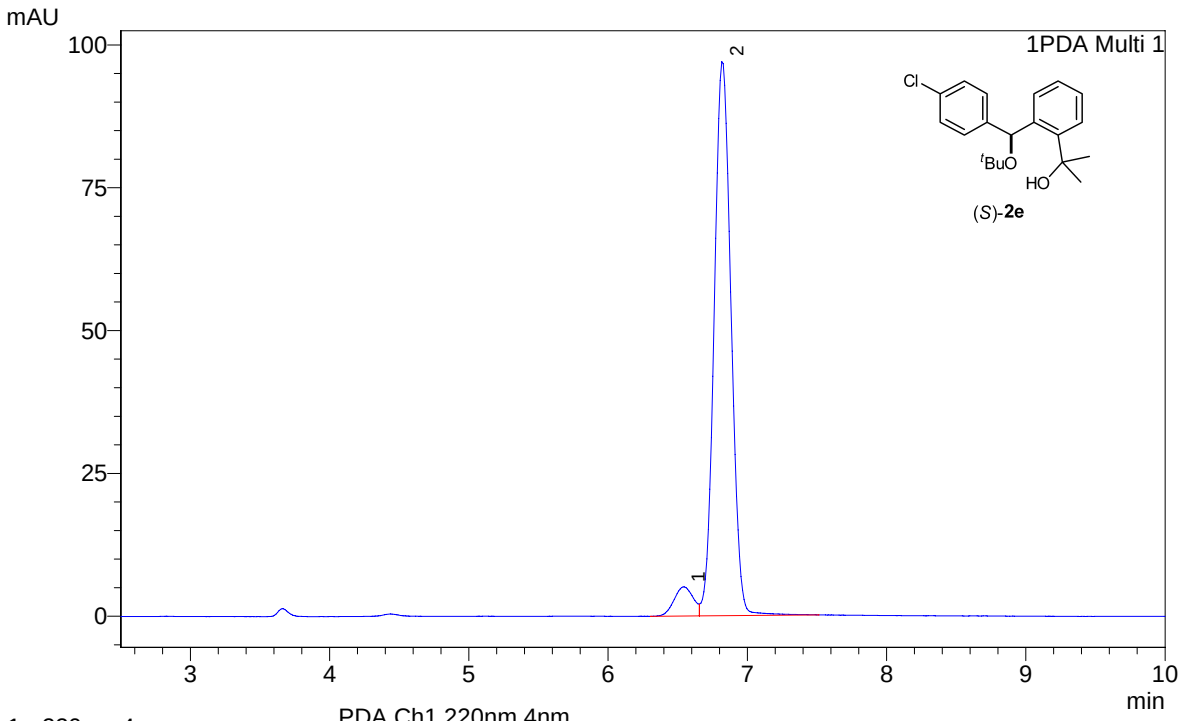
Peak #	Ret. Time	Area %
1	4.01	98.19
2	4.27	1.81
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

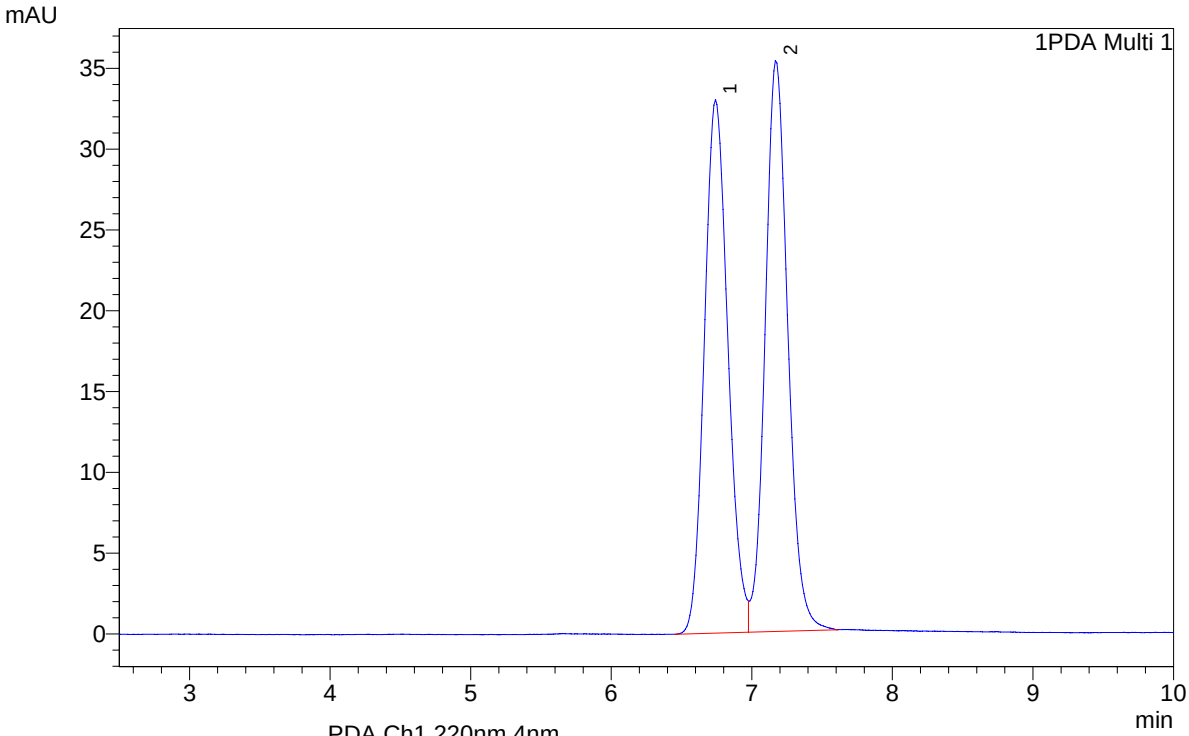
Peak #	Ret. Time	Area %
1	4.51	49.80
2	4.93	50.20
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

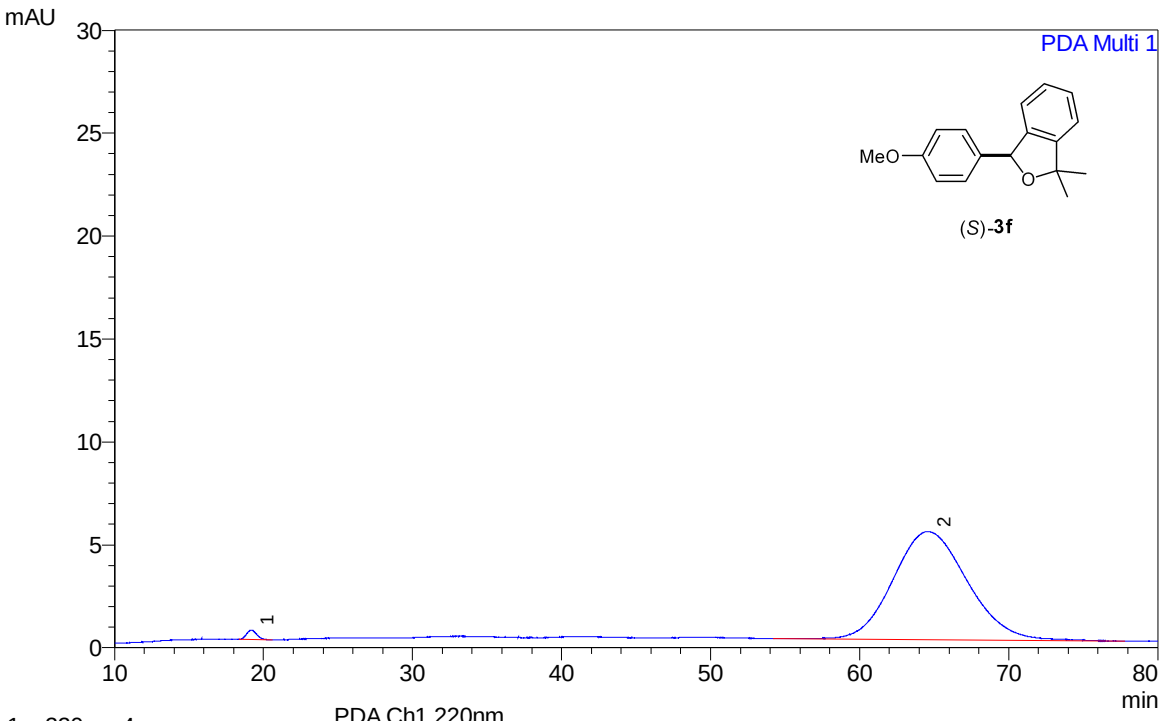
Peak #	Ret. Time	Area %
1	6.54	5.75
2	6.81	94.25
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

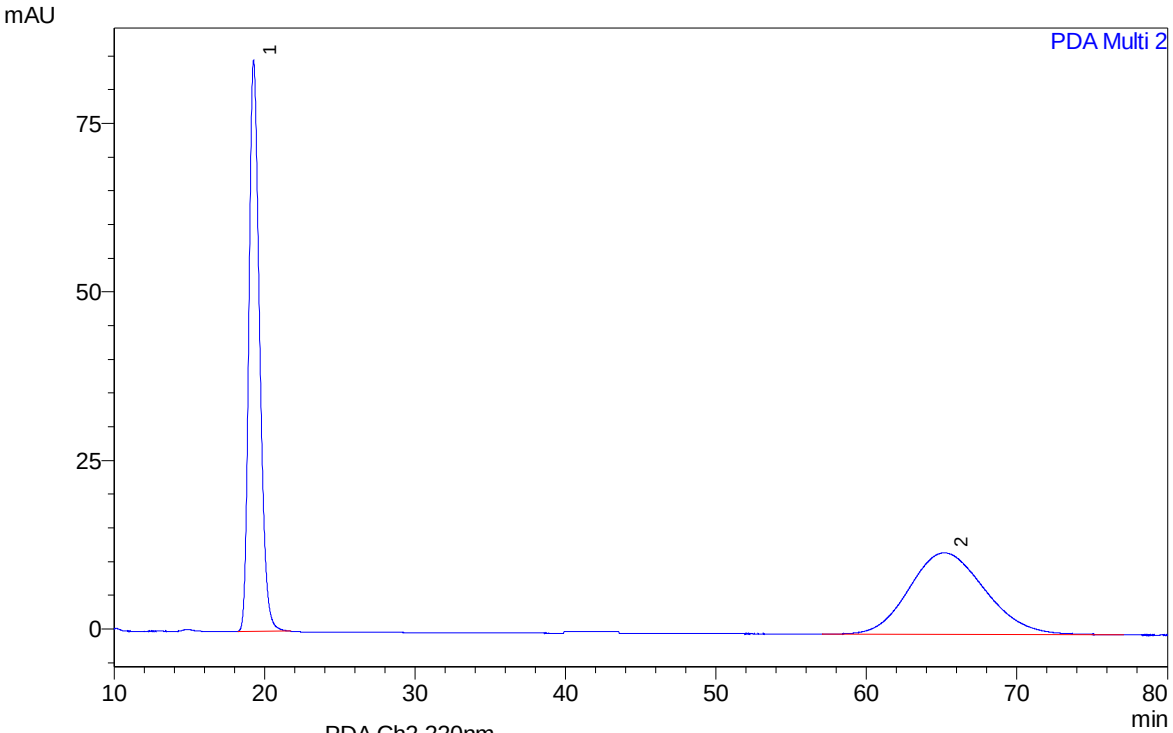
Peak #	Ret. Time	Area %
1	6.74	49.39
2	7.17	50.61
Total		100.00



1 220nm,4nm

PDA Ch1 220nm

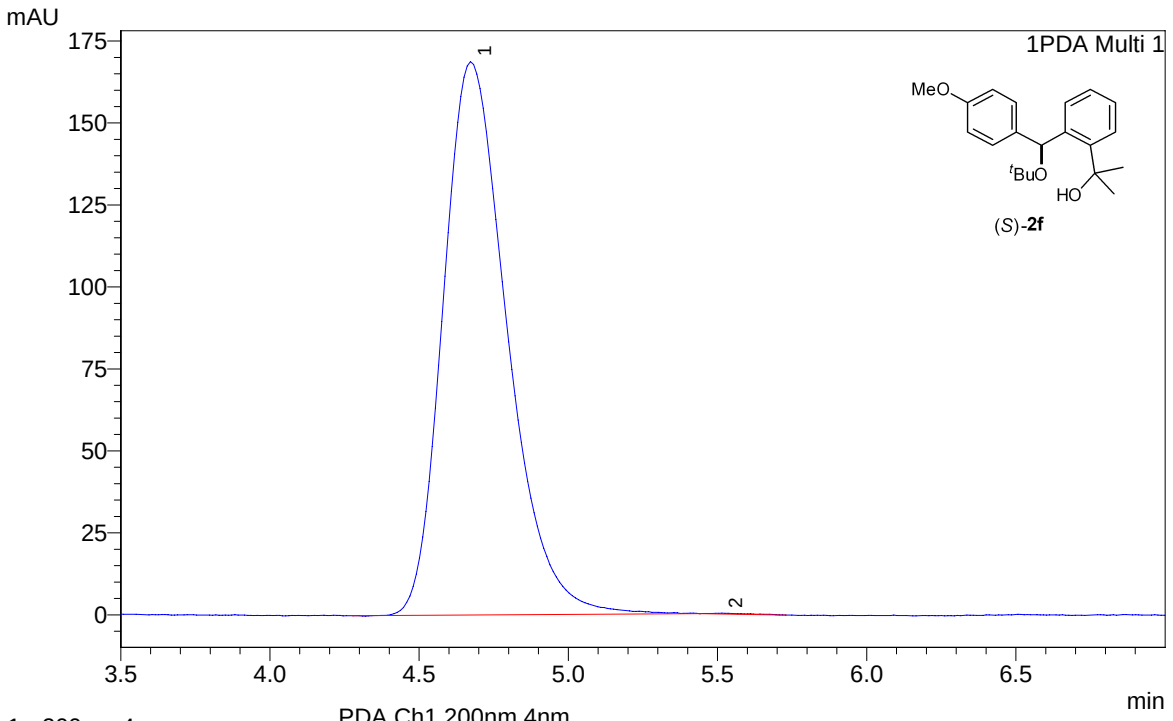
Peak #	Ret. Time	Area %
1	19,18	1,21
2	64,60	98,79
Total		100,00



1 220nm,4nm

PDA Ch2 220nm

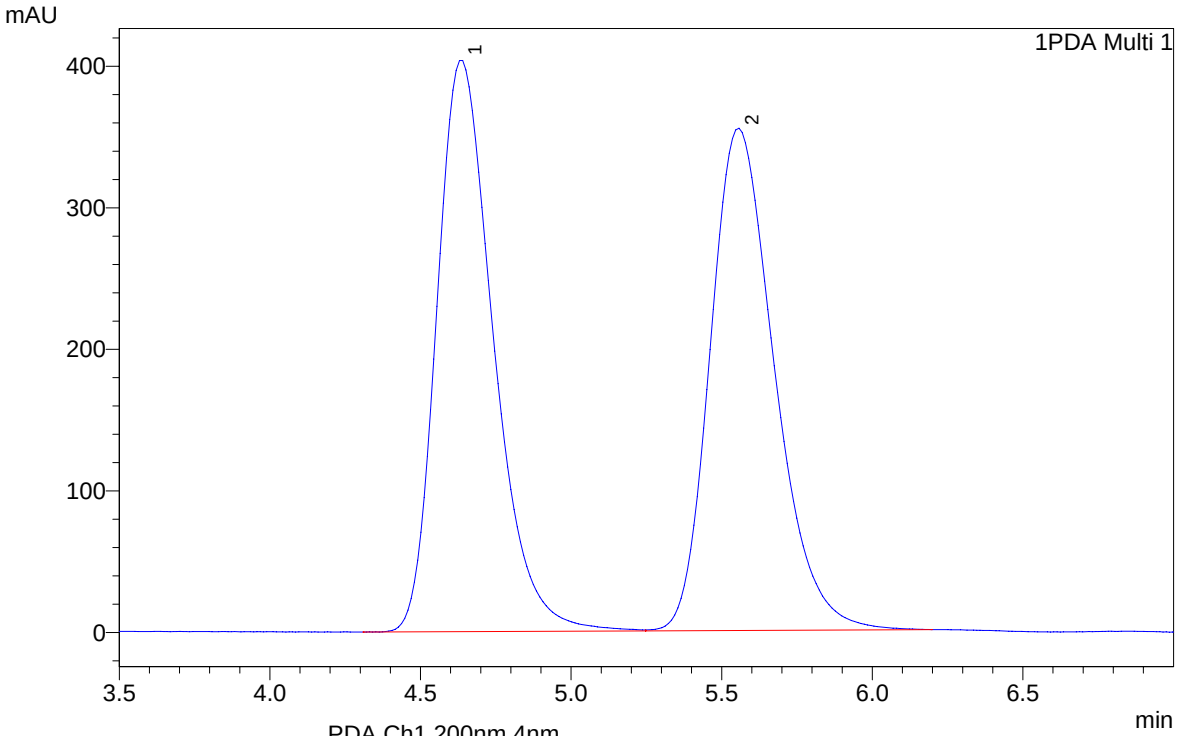
Peak #	Ret. Time	Area %
1	19,27	49,81
2	65,22	50,19
Total		100,00



1 200nm 4nm

PDA Ch1 200nm 4nm

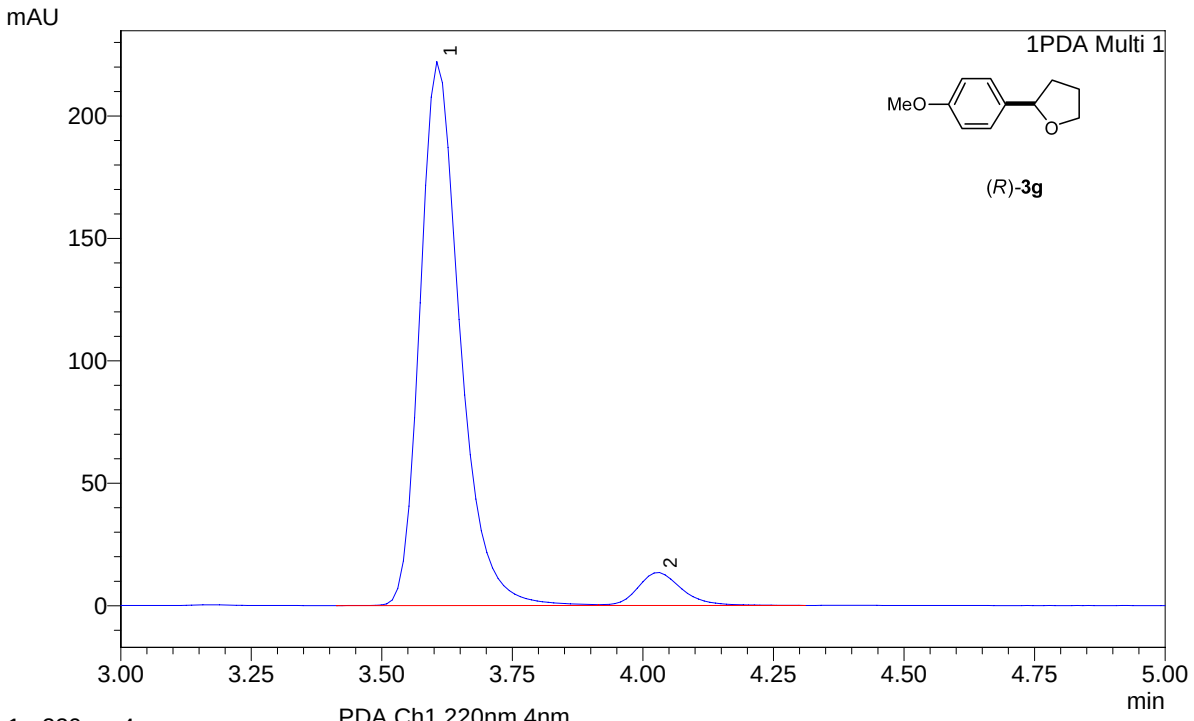
Peak #	Ret. Time	Area %
1	4.67	99.91
2	5.51	0.09
Total		100.00



1 200nm 4nm

PDA Ch1 200nm 4nm

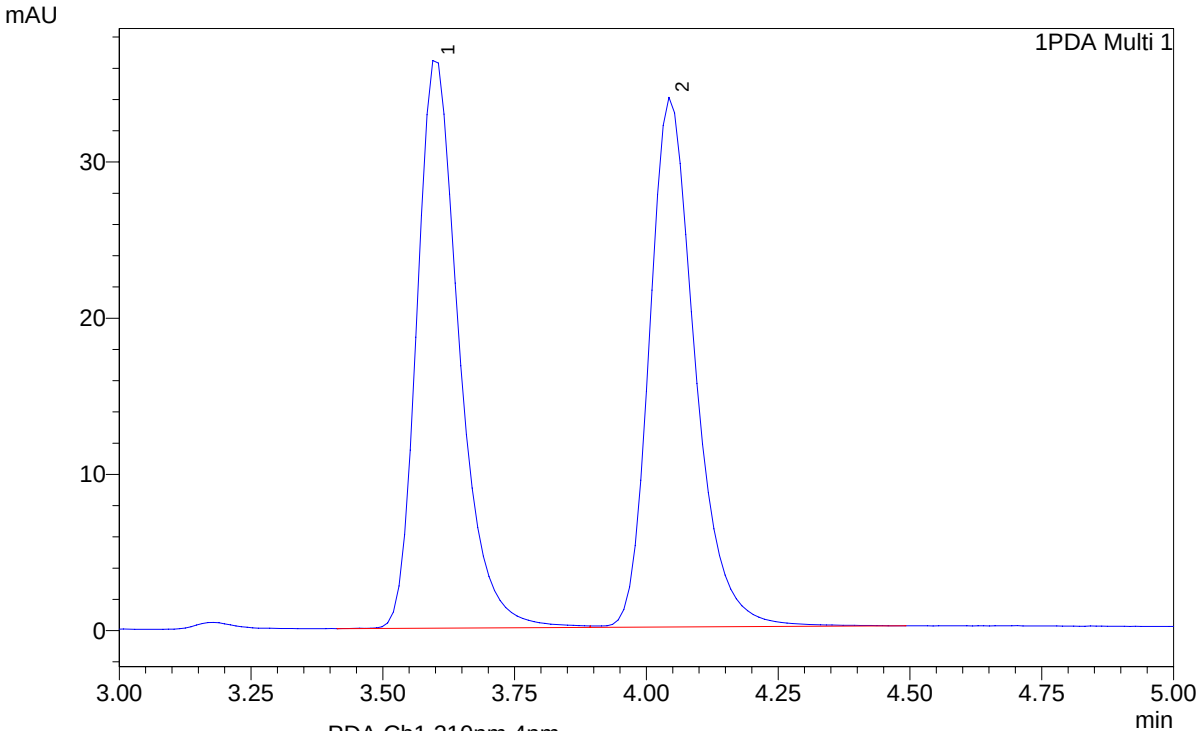
Peak #	Ret. Time	Area %
1	4.63	50.10
2	5.55	49.90
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

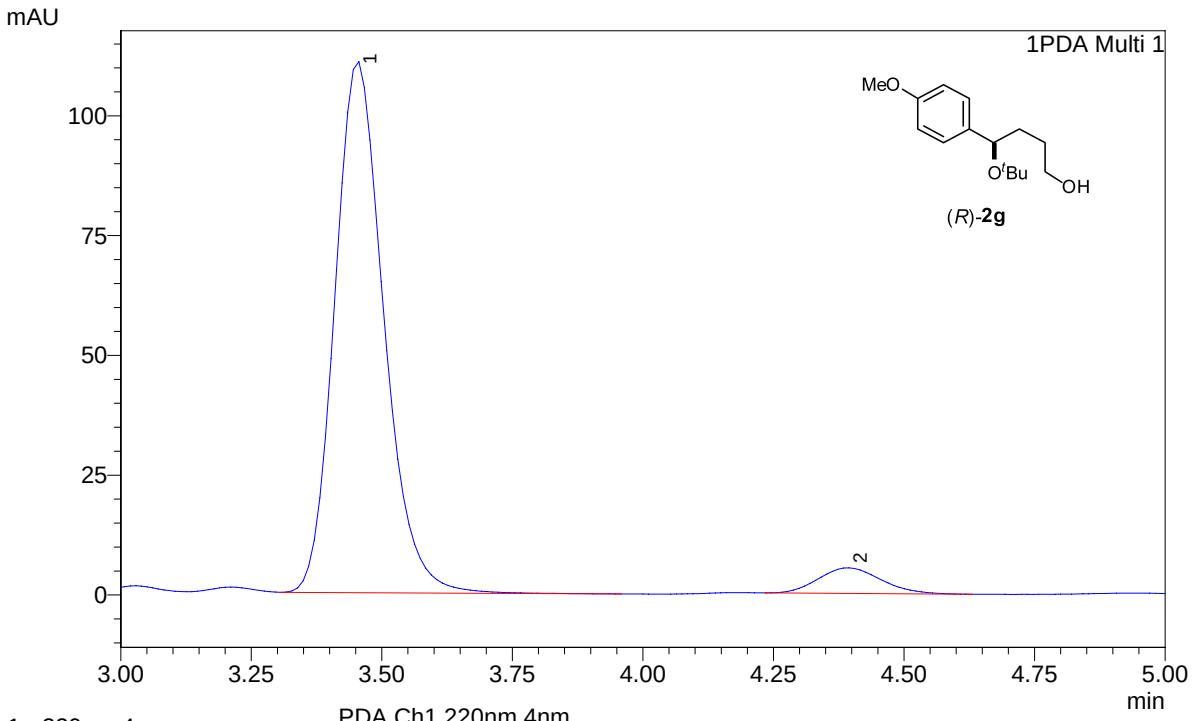
Peak #	Ret. Time	Area %
1	3.60	93.78
2	4.02	6.22
Total		100.00



1 210nm 4nm

PDA Ch1 210nm 4nm

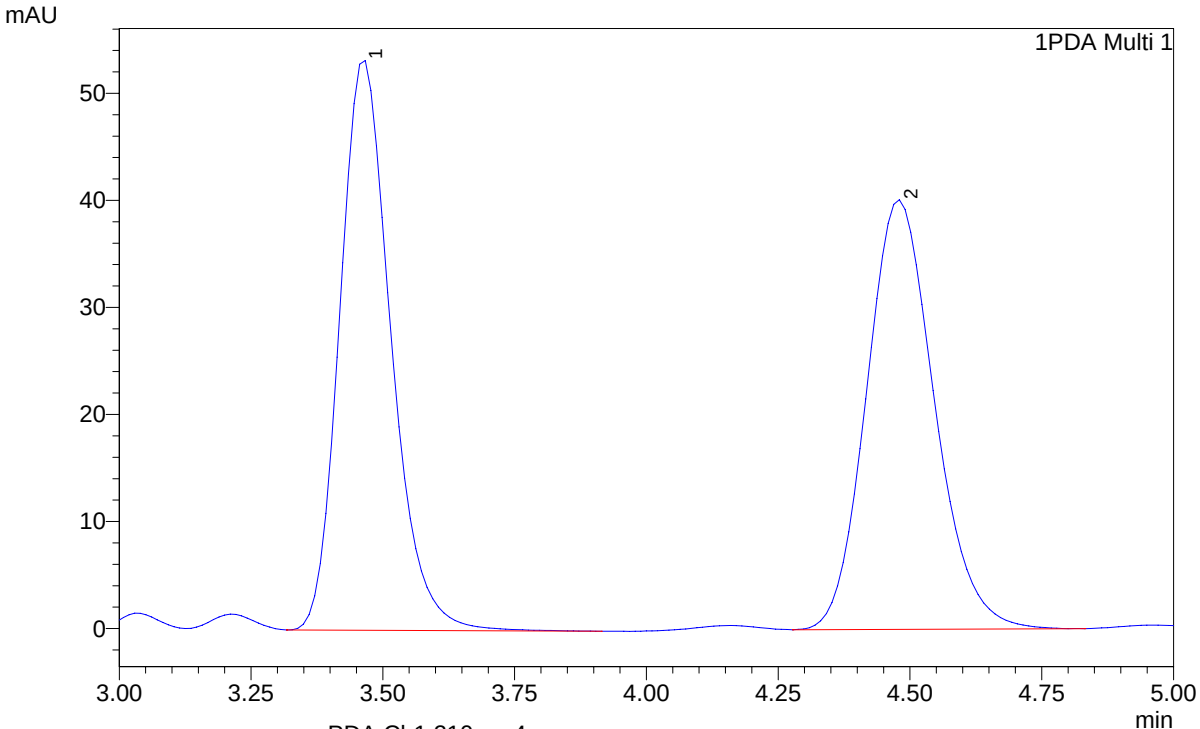
Peak #	Ret. Time	Area %
1	3.59	49.95
2	4.04	50.05
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

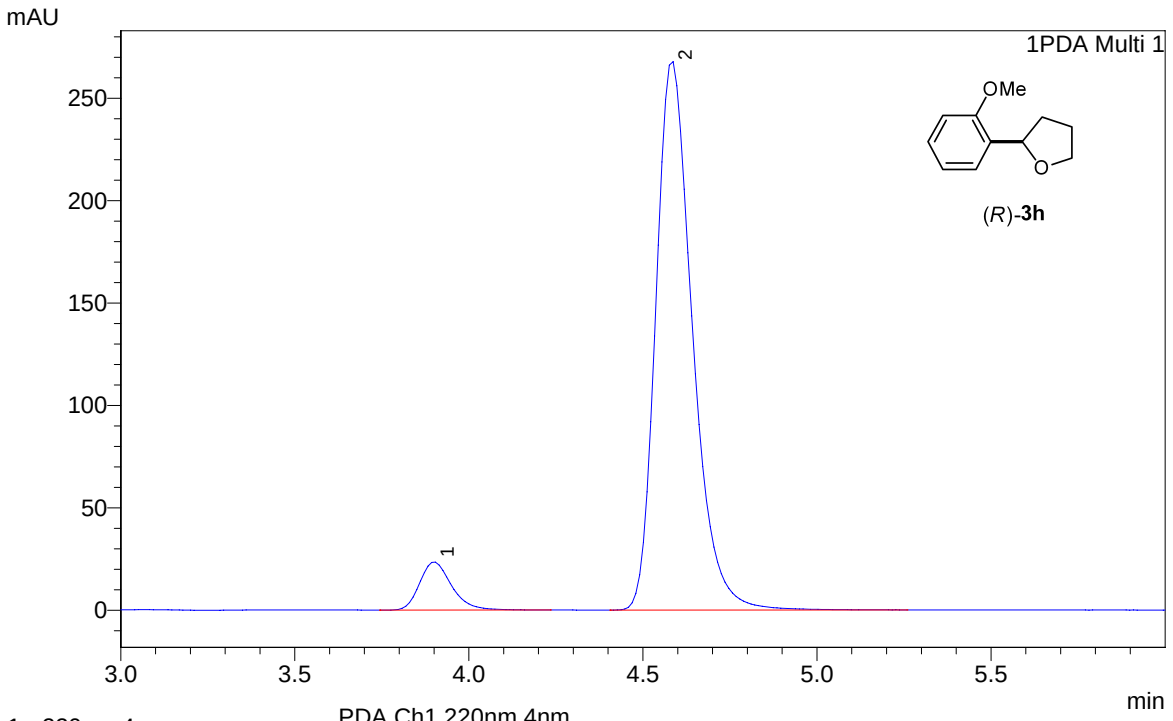
Peak #	Ret. Time	Area %
1	3.45	94.21
2	4.39	5.79
Total		100.00



1 210nm 4nm

PDA Ch1 210nm 4nm

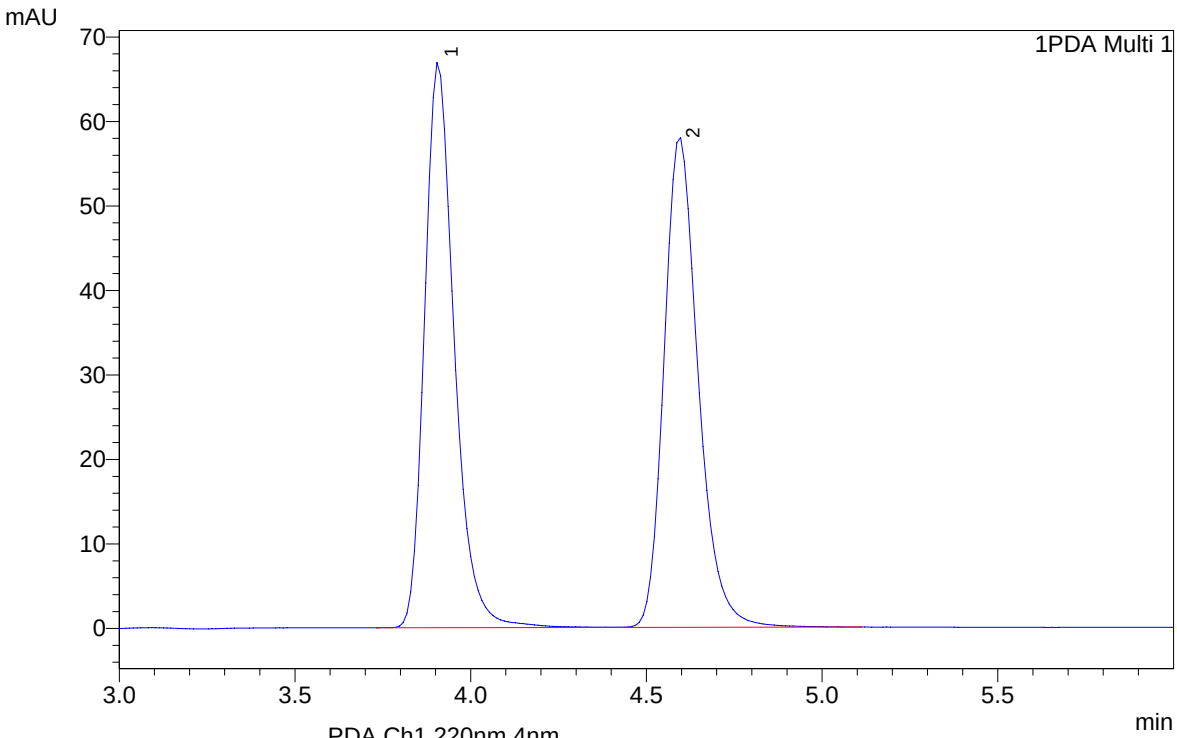
Peak #	Ret. Time	Area %
1	3.46	50.09
2	4.47	49.91
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

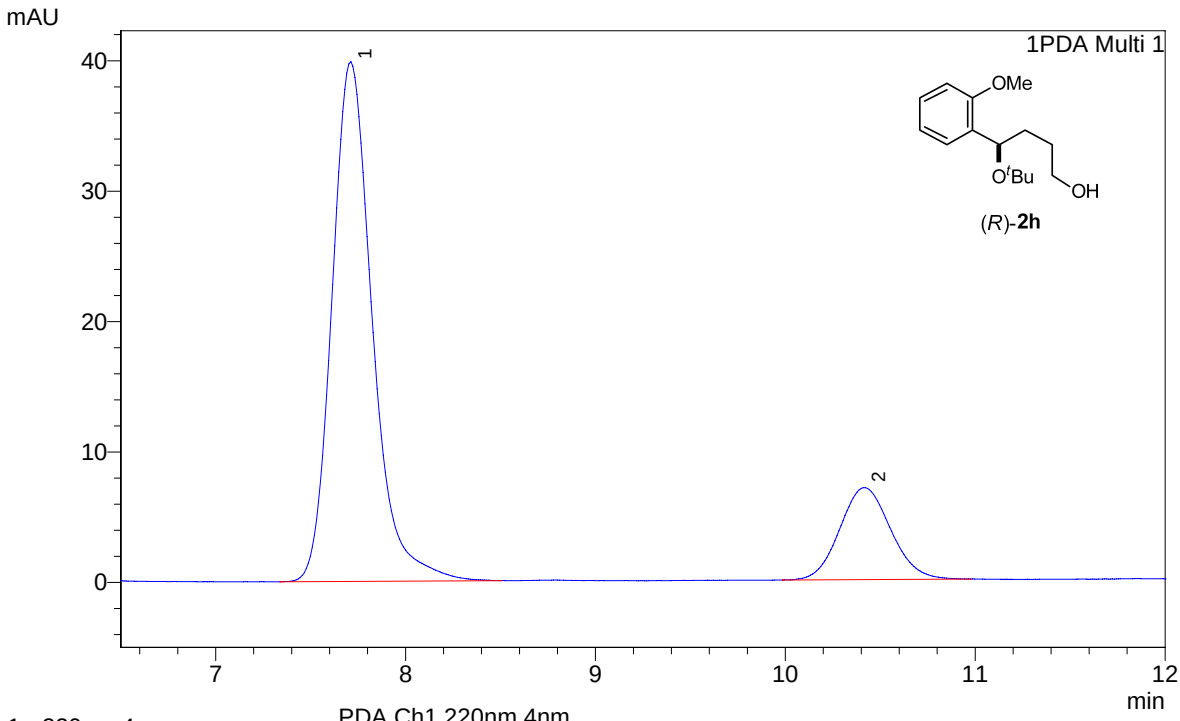
Peak #	Ret. Time	Area %
1	3.89	7.12
2	4.58	92.88
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

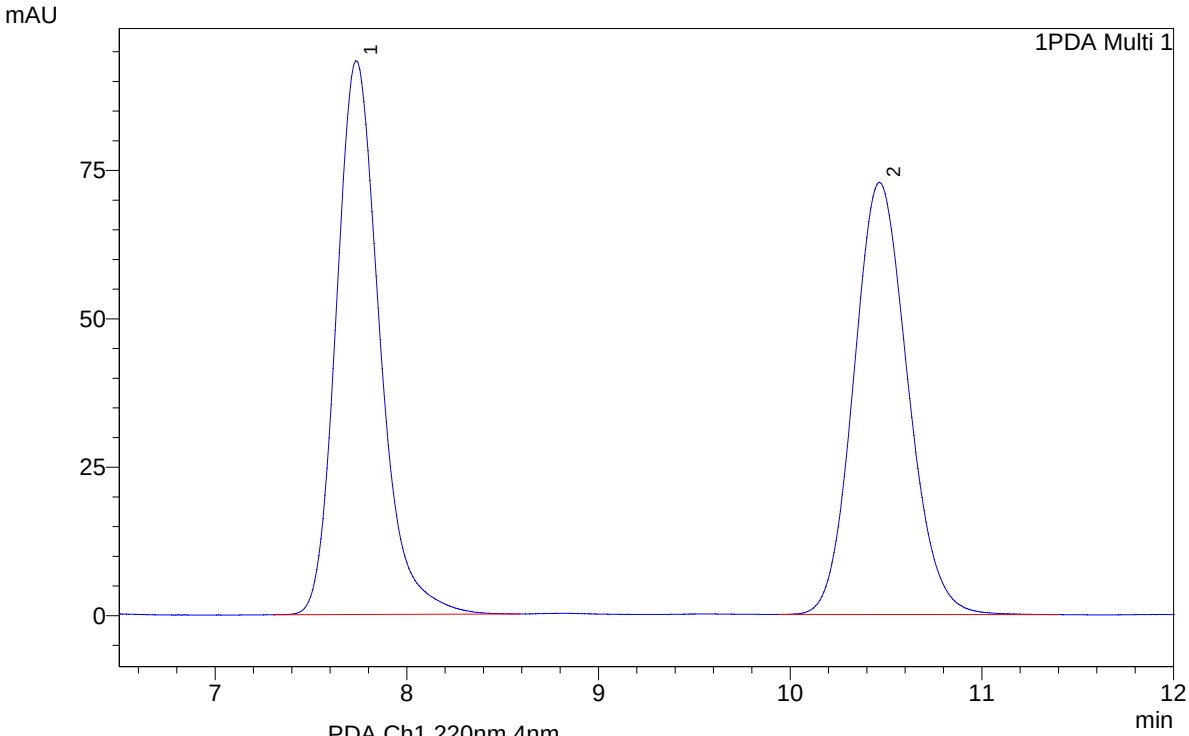
Peak #	Ret. Time	Area %
1	3.90	50.09
2	4.59	49.91
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

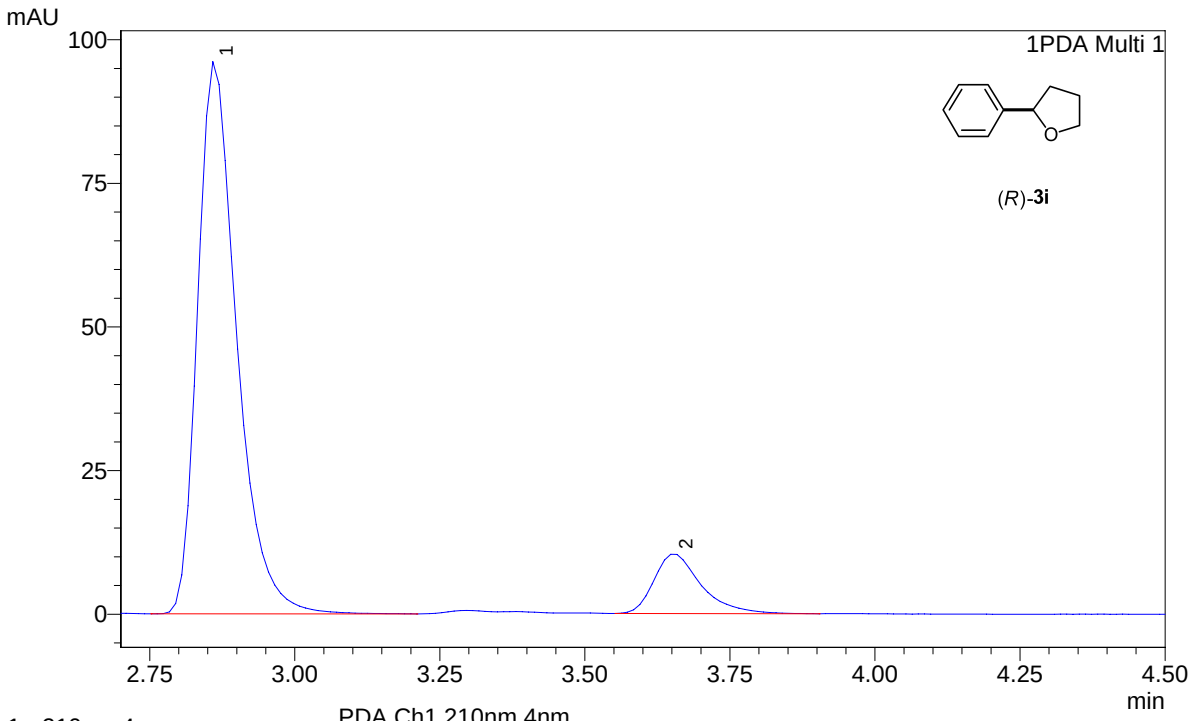
Peak #	Ret. Time	Area %
1	7.70	81.75
2	10.41	18.25
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

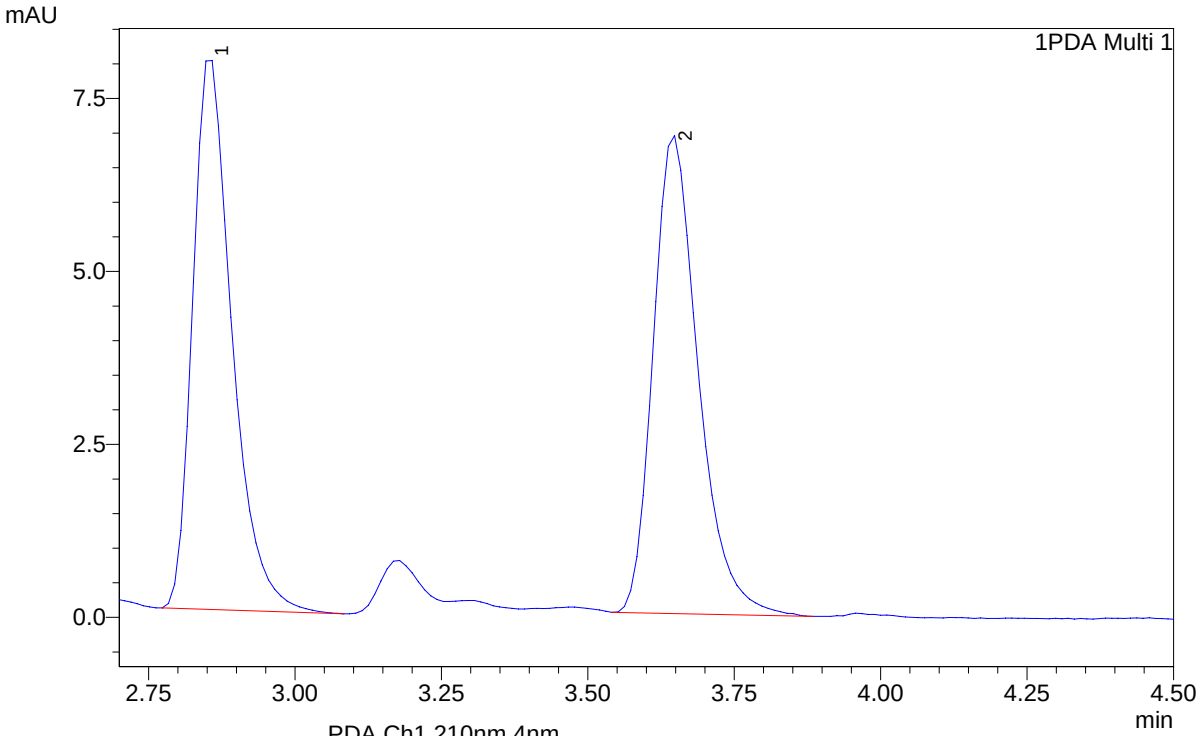
Peak #	Ret. Time	Area %
1	7.73	50.75
2	10.46	49.25
Total		100.00



1 210nm 4nm

PDA Ch1 210nm 4nm

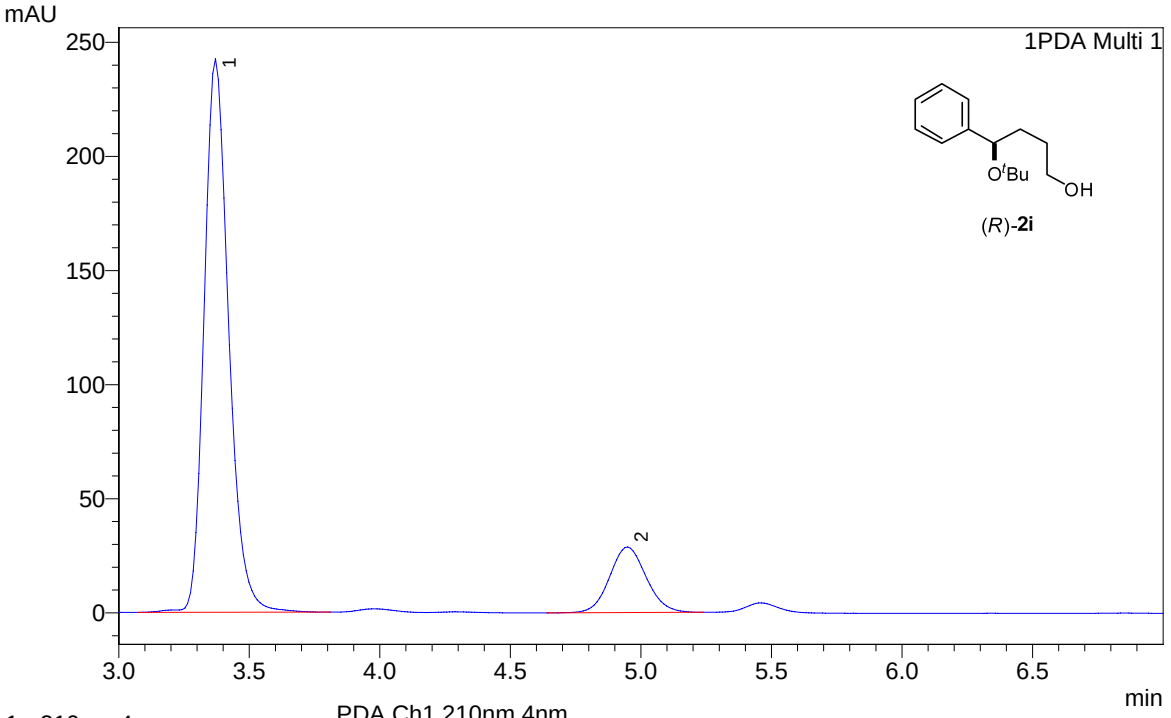
Peak #	Ret. Time	Area %
1	2.86	88.51
2	3.65	11.49
Total		100.00



1 210nm 4nm

PDA Ch1 210nm 4nm

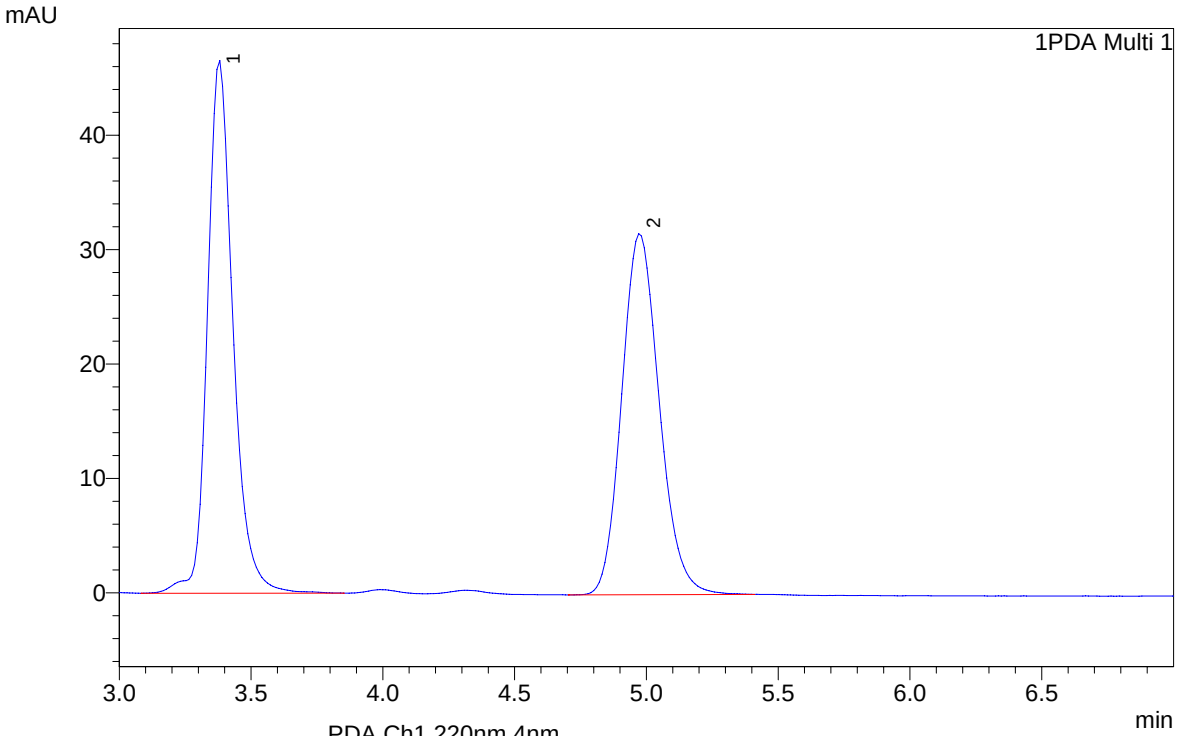
Peak #	Ret. Time	Area %
1	2.85	50.05
2	3.64	49.95
Total		100.00



1 210nm 4nm

PDA Ch1 210nm 4nm

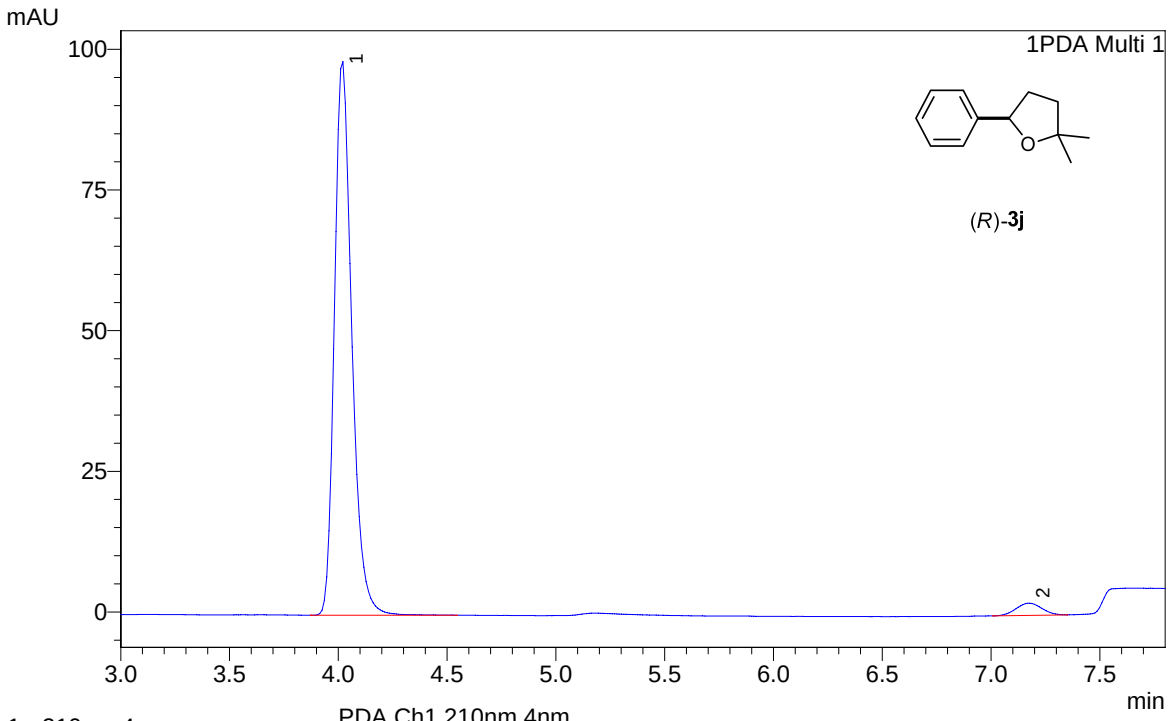
Peak #	Ret. Time	Area %
1	3.36	85.02
2	4.94	14.98
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

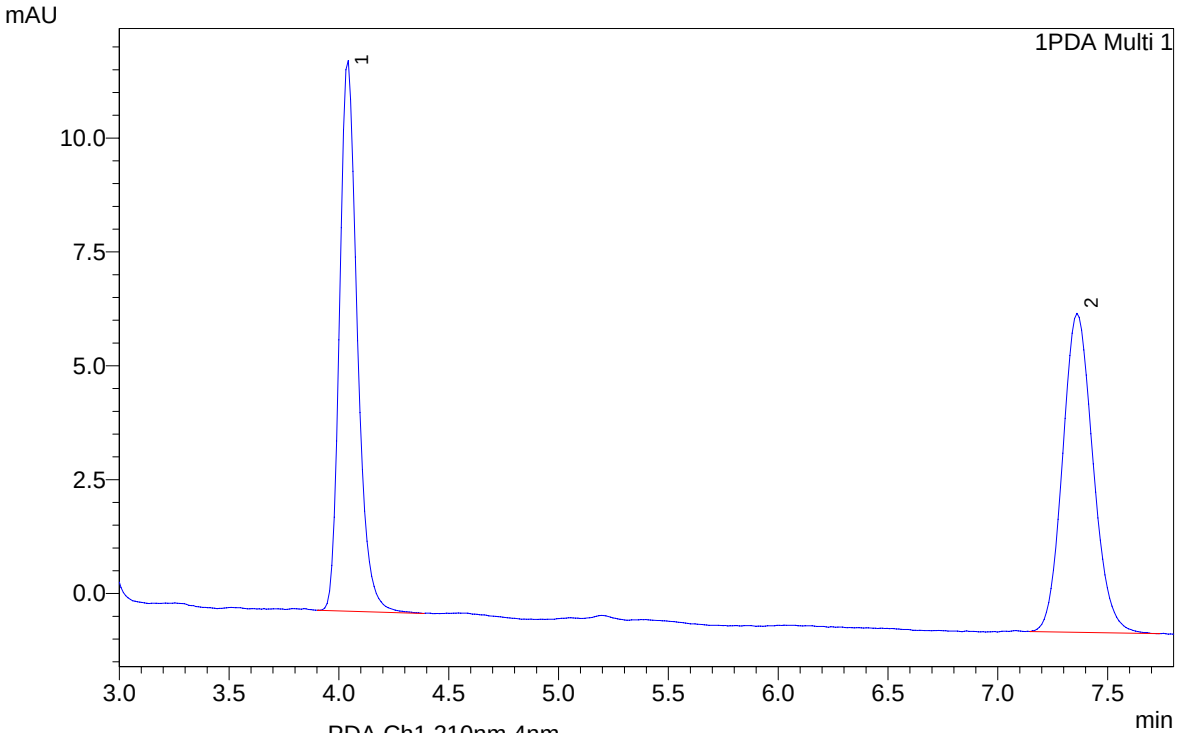
Peak #	Ret. Time	Area %
1	3.37	50.17
2	4.97	49.83
Total		100.00



1 210nm 4nm

PDA Ch1 210nm 4nm

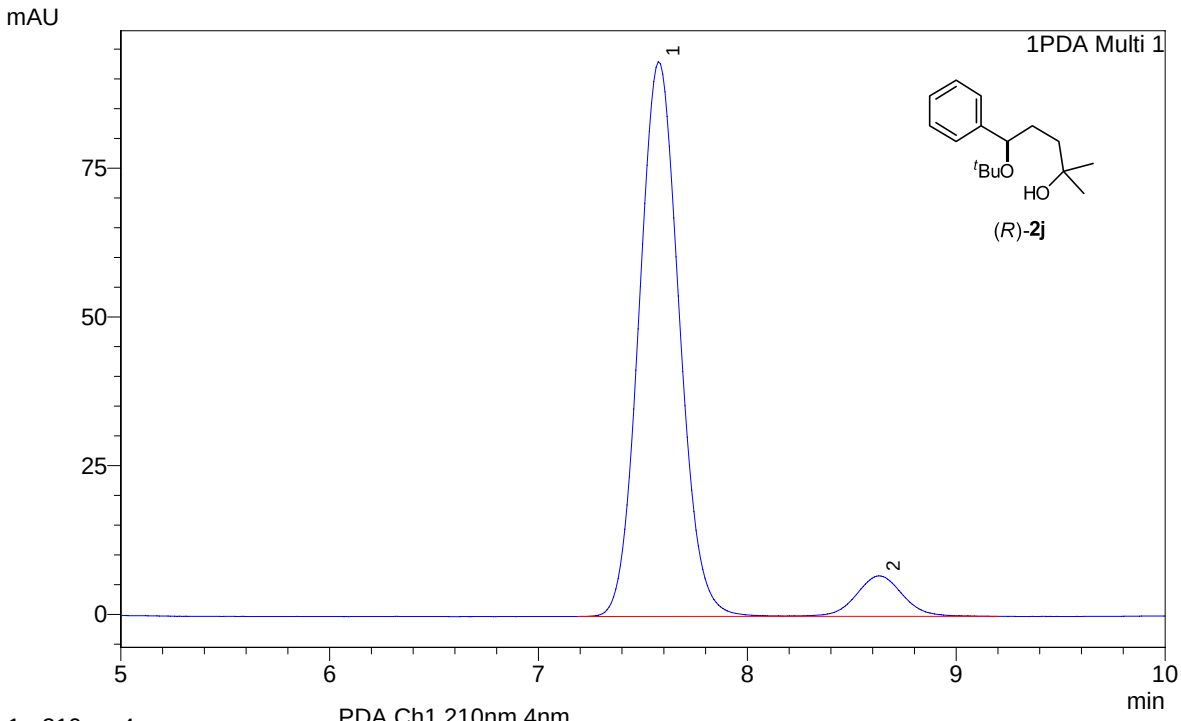
Peak #	Ret. Time	Area %
1	4.01	96.84
2	7.17	3.16
Total		100.00



1 210nm 4nm

PDA Ch1 210nm 4nm

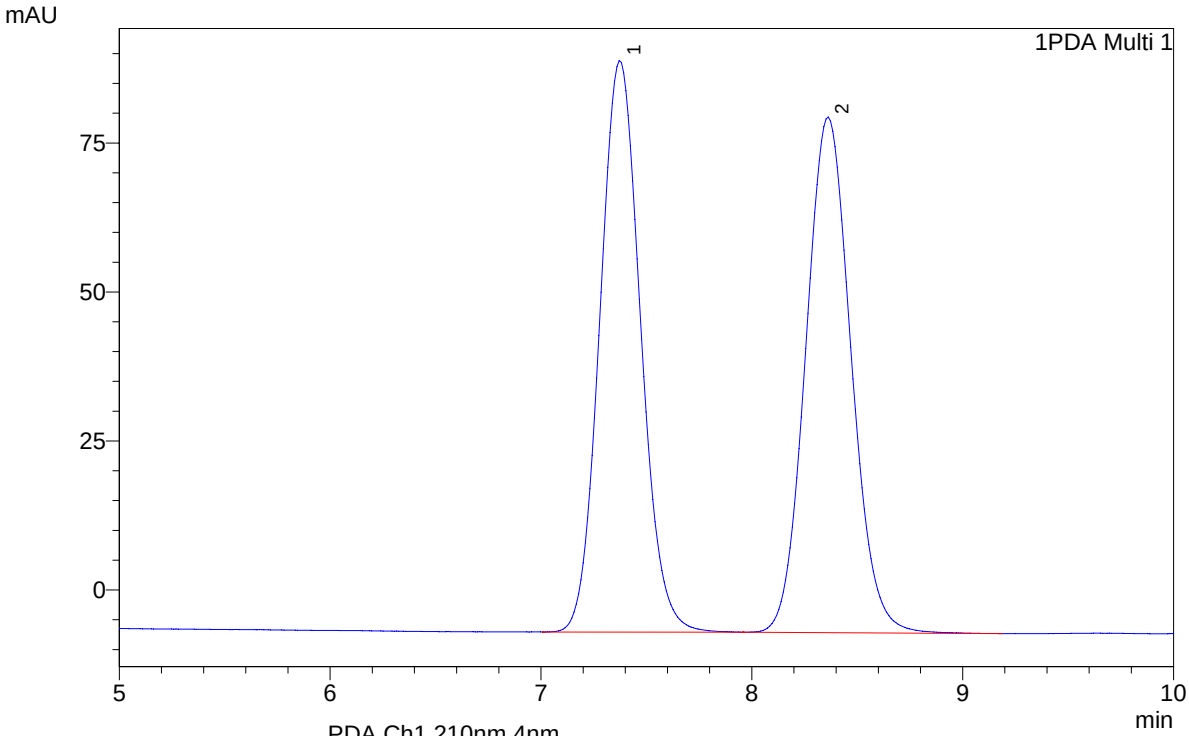
Peak #	Ret. Time	Area %
1	4.03	50.24
2	7.36	49.76
Total		100.00



1 210nm 4nm

PDA Ch1 210nm 4nm

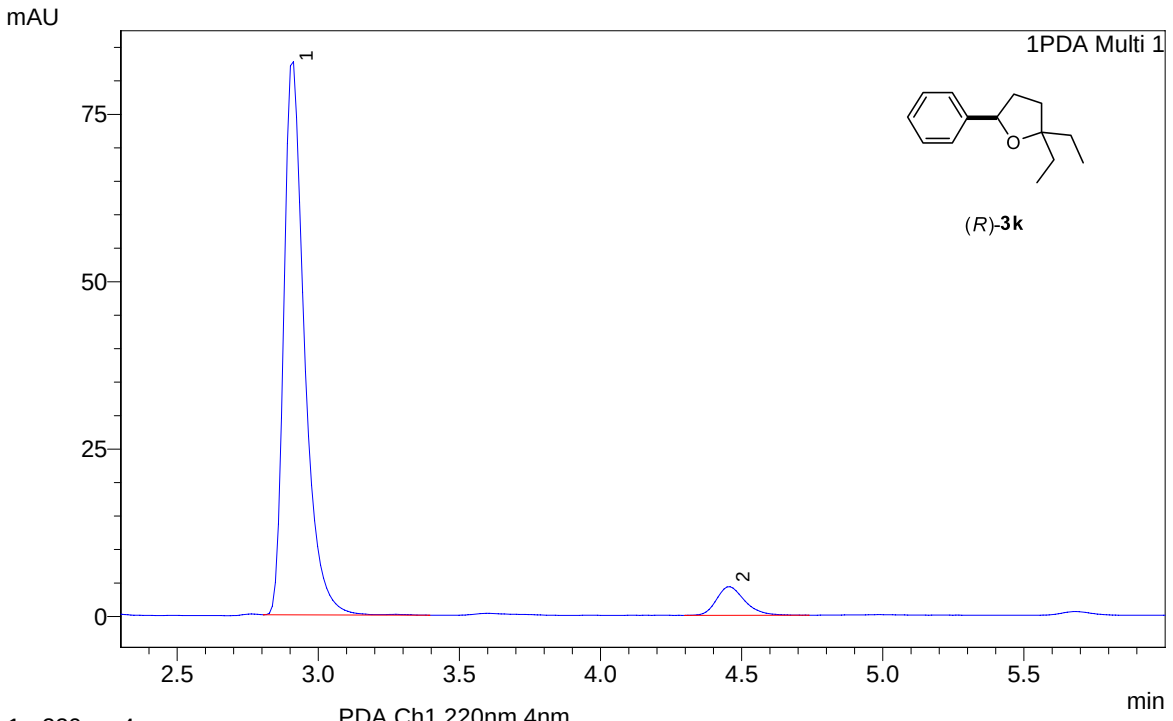
Peak #	Ret. Time	Area %
1	7.57	92.16
2	8.63	7.84
Total		100.00



1 210nm 4nm

PDA Ch1 210nm 4nm

Peak #	Ret. Time	Area %
1	7.37	49.90
2	8.36	50.10
Total		100.00

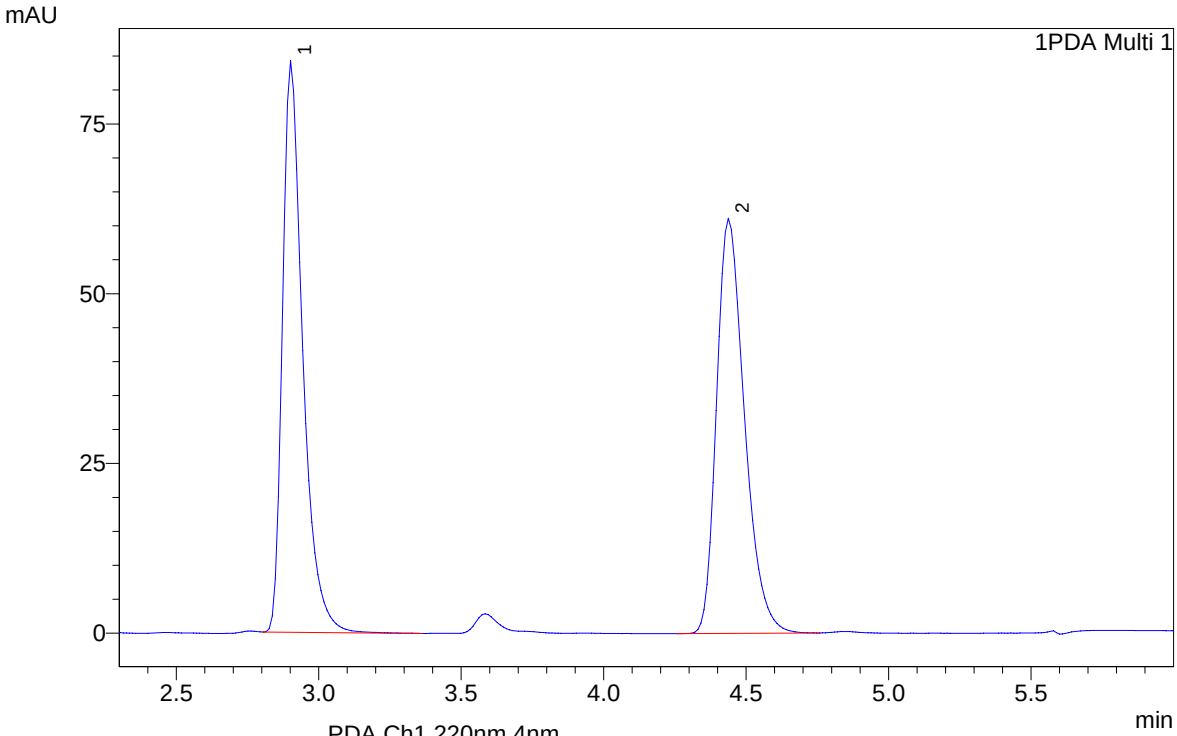


(*R*)-**3k**

1 220nm 4nm

PDA Ch1 220nm 4nm

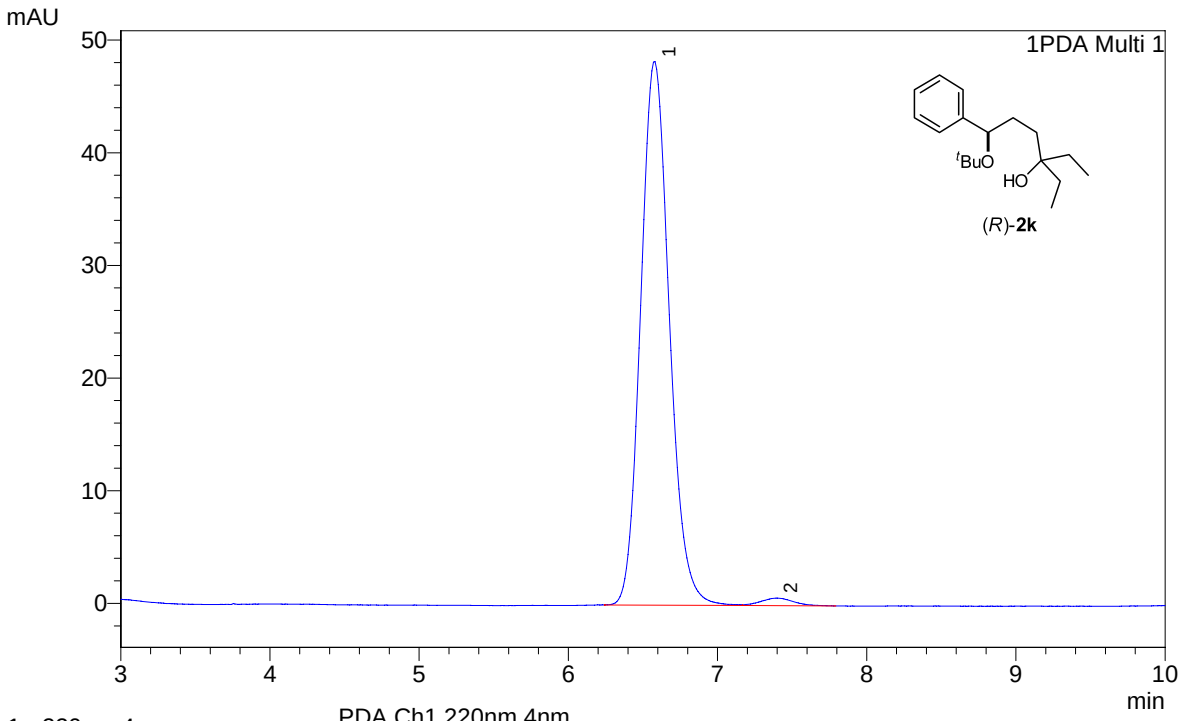
Peak #	Ret. Time	Area %
1	2.90	93.39
2	4.45	6.61
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

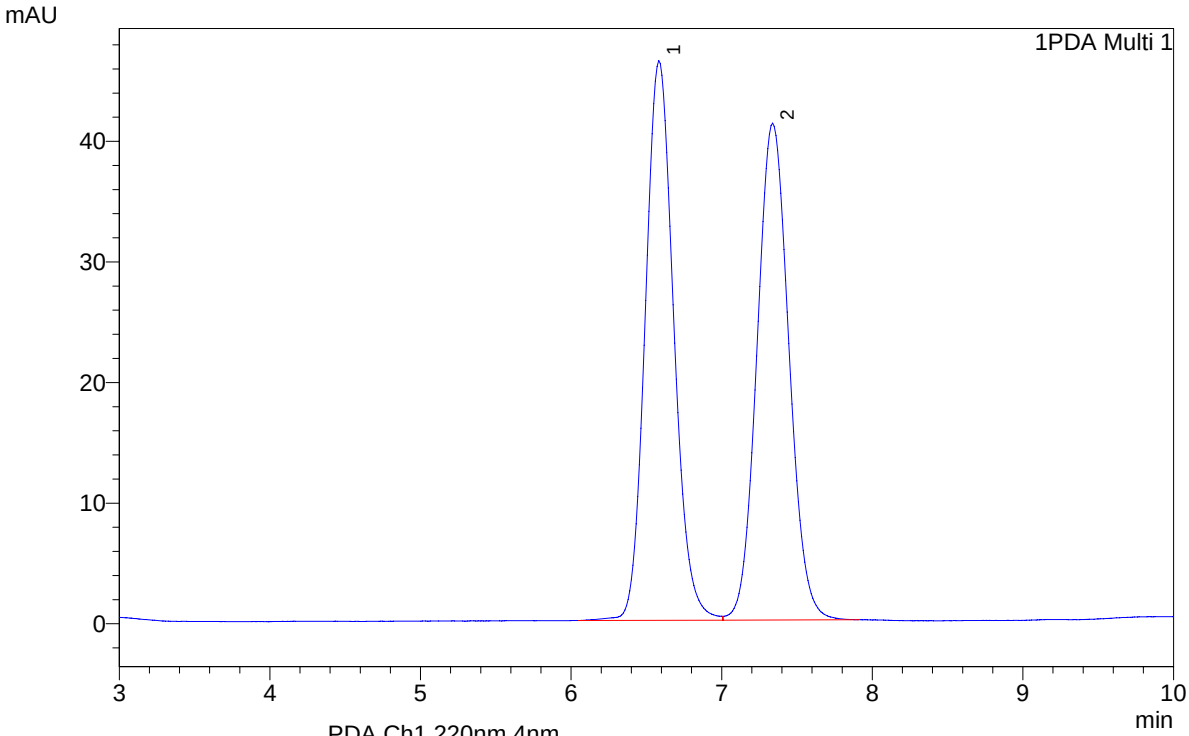
Peak #	Ret. Time	Area %
1	2.90	50.01
2	4.43	49.99
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

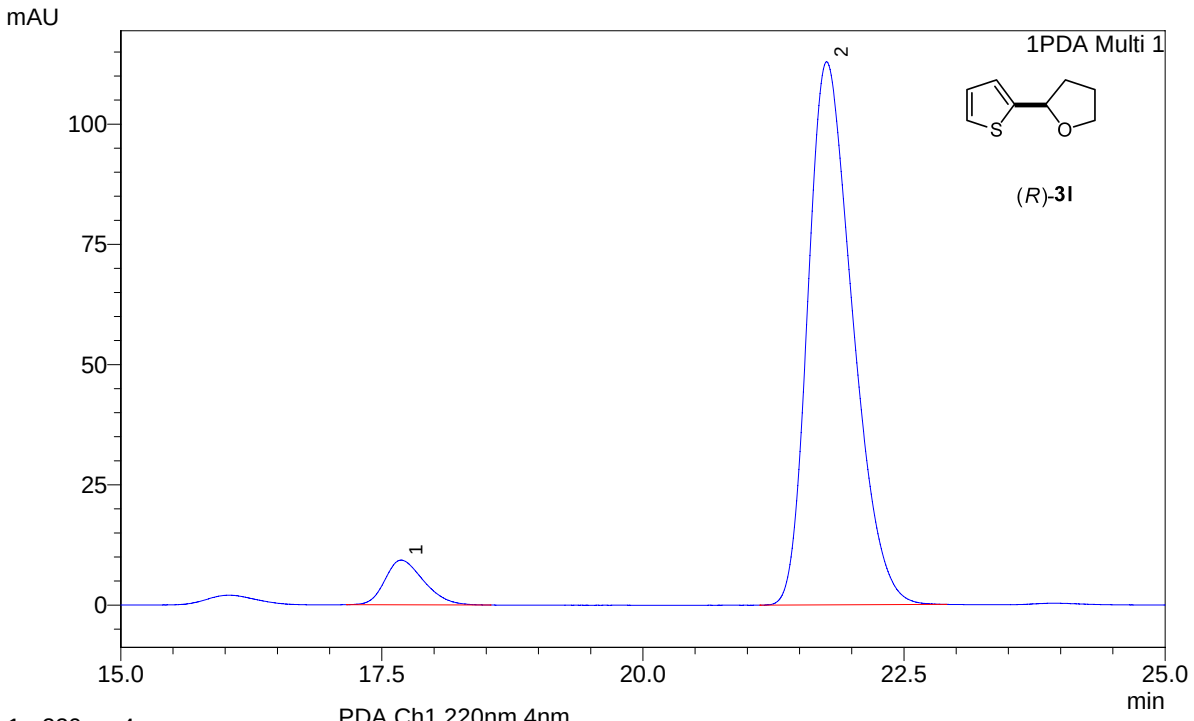
Peak #	Ret. Time	Area %
1	6.57	98.44
2	7.39	1.56
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

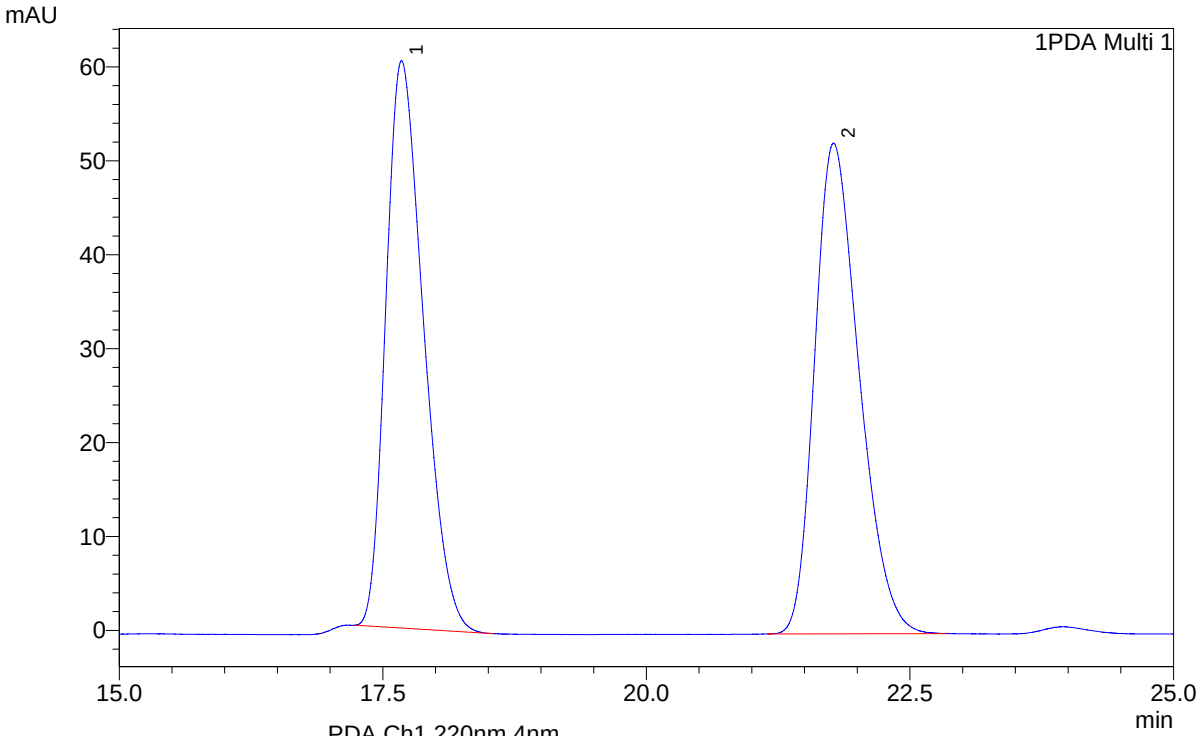
Peak #	Ret. Time	Area %
1	6.58	50.14
2	7.33	49.86
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

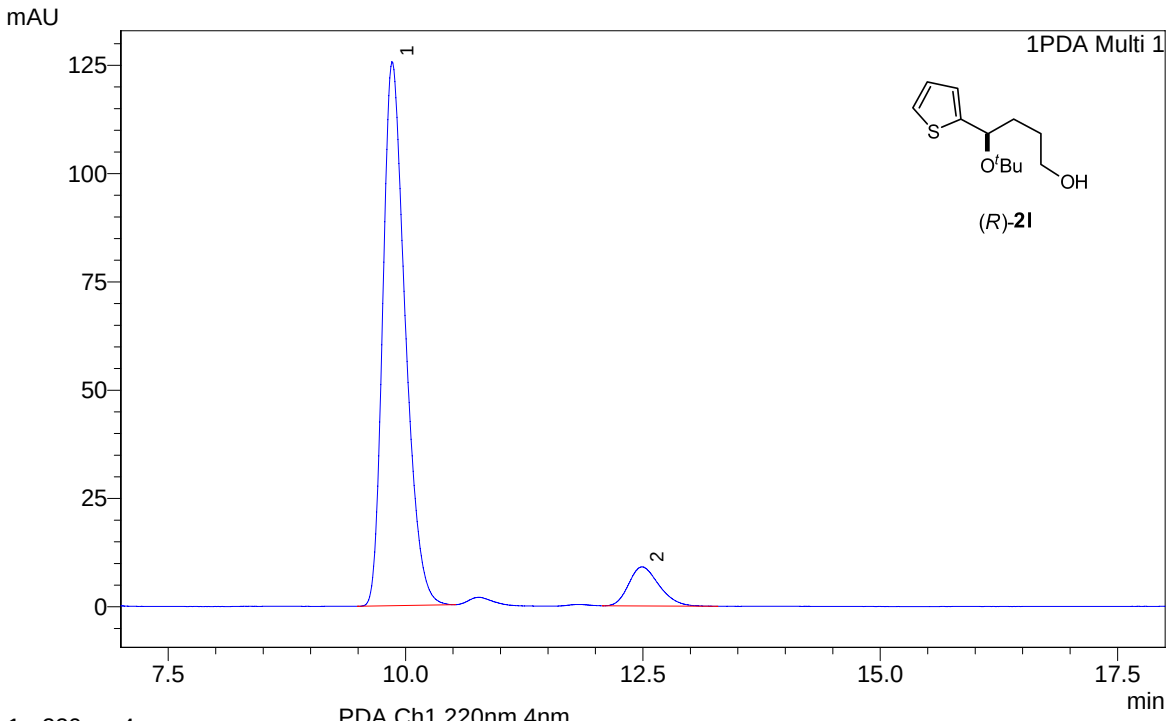
Peak #	Ret. Time	Area %
1	17.68	6.68
2	21.75	93.32
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

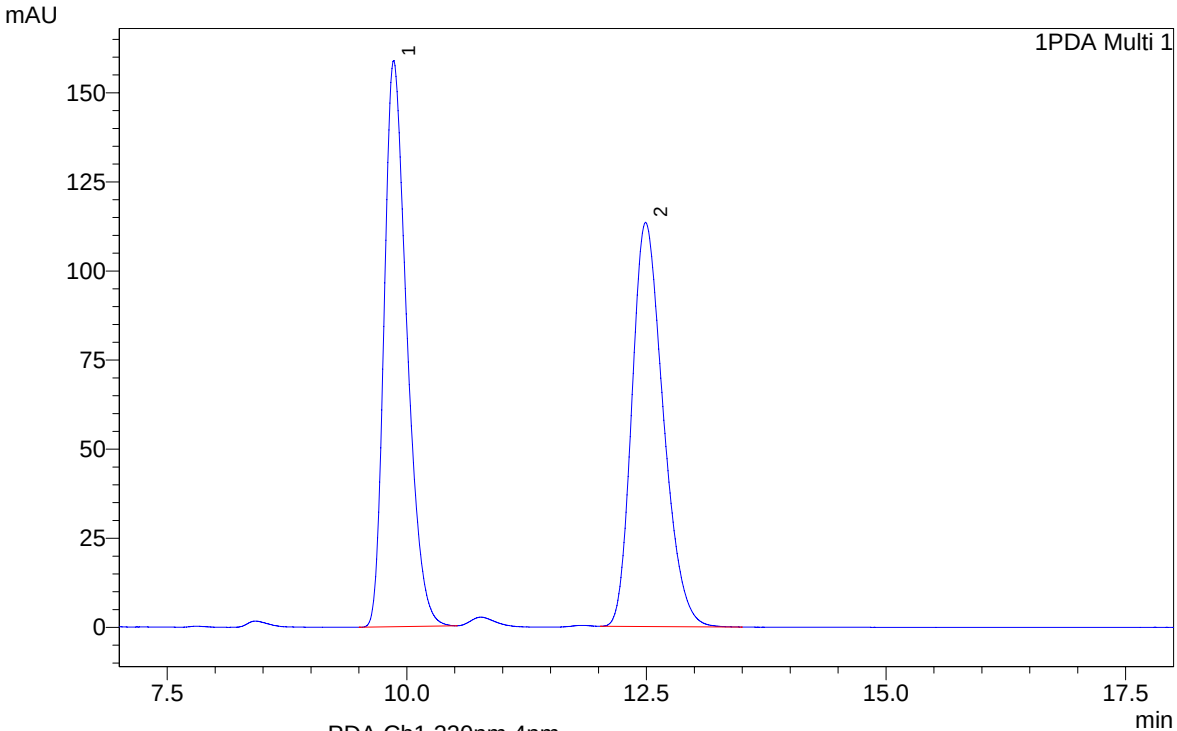
Peak #	Ret. Time	Area %
1	17.67	49.45
2	21.77	50.55
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

Peak #	Ret. Time	Area %
1	9.85	91.12
2	12.49	8.88
Total		100.00



1 220nm 4nm

PDA Ch1 220nm 4nm

Peak #	Ret. Time	Area %
1	9.86	50.44
2	12.49	49.56
Total		100.00