Electronic Supplementary Information

Secondary Stereocontrolling Interactions in Chiral Brønsted Acid Catalysis: Study of a Petasis-Ferrier-Type Rearrangement Catalyzed by Chiral Phosphoric Acids

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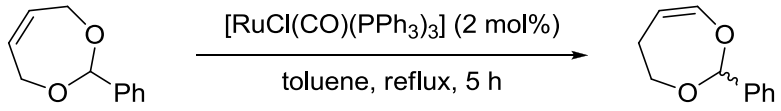
Contents

1. General Information

Infrared spectra were recorded on a Jasco FT/IR-4100 spectrometer. ^{1}H NMR spectra were recorded on a JEOL ECA-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sext = sextet, sept = septet, br = broad, m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL ECA-600 (150.9 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 77.0 ppm). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on silica gel 60 N (Merck 230-400 mesh). Optical rotations were measured on a JASCO P-1020 digital polarimeter with a sodium lamp and reported as follows; $[\alpha]^{T\,^{\circ}C}_{D}$ (*c* = g/100 mL, solvent). Mass spectra analyses were performed on a Bruker Daltonics solariX 9.4T spectrometer at the Research and Analysis Center for Giant Molecules, Graduate School of Science, Tohoku University. X-ray crystallographic analyses were performed on a Rigaku XtaLAB mini diffractometer using graphite monochromated Mo-Kα radiation at the Research and Analysis Center for Giant Molecules, Graduate School of Science, Tohoku University.

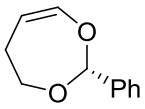
Unless otherwise noted, all reactions were carried out under argon or nitrogen atmosphere in dried glassware. All substrates were purified by column chromatography or HPLC to use. Dichloromethane (CH_2Cl_2), diethyl ether (Et_2O), tetrahydrofuran (THF) and toluene were supplied from Kanto Chemical Co., Inc. as “Dehydrated solvent system”. Other solvents were dried over activated MS4A and used under nitrogen atmosphere. Reagents were purchased from commercial suppliers and used without further purification. The other simple chemicals were used as such.

2. Preparation of Cyclic Acetal 2a



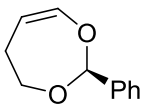
S1 (±)-**2a**

Representative Procedure: To a solution of **S1**[1] (3.0 mmol, 528.6 mg) in toluene (15 mL) was added [RuCl(CO)(PPh_3)$_3$] (2 mol%, 57.1 mg, 0.060 mmol) and the atmosphere was replaced with argon. The reaction mixture was heated to the reflux temperature and stirred for 5 h. After the mixture was cooled to 0 °C, 30% aqueous H_2O_2 (0.3 mL) was added and the resultant mixture was stirred for 10 min. The reaction mixture was diluted with saturated aqueous Na_2SO_3 and extracted with EtOAc (×3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc as eluent) to give (±)-**2a** in 93% yield as colorless oil. The racemate (±)-**2a** was separated by preparative HPLC with a chiral column (CHIRALCEL OD (2 cmφ × 25 cm), hexane/IPA = 99/1, 10.0 mL/min, 220 nm, 20 °C, t_R = 13.9 (*R*), 16.2 (*S*) min) to afford enantiomerically pure products (>99% ee for each enantiomer).



(*R*)-2-phenyl-4,5-dihydro-1,3-dioxepine ((*R*)-2a):

Colorless oil; R_f = 0.47 (Hexane/EtOAc = 10/1); HPLC analysis: CHIRALCEL OD-3 (hexane/IPA = 98/2, 1.0 mL/min, 220 nm, 30 °C) 5.9 (major), 7.6 (minor) min (>99% ee); $[\alpha]^{19}_D$ = 1.2 (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 2.25 (1H, ddt, *J* = 16.8, 7.8, 2.4 Hz), 2.59-2.66 (1H, m), 3.49 (1H, td, *J* = 11.4, 2.4 Hz), 4.29 (1H, ddd, *J* = 11.4, 4.8, 2.4 Hz), 5.00 (1H, td, *J* = 7.8, 3.0 Hz), 5.42 (1H, s), 6.51 (1H, dd, *J* = 6.6, 3.0 Hz), 7.33-7.39 (3H, m), 7.52-7.54 (2H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 30.0, 69.5, 105.9, 108.2, 125.9, 128.2, 128.6, 138.9, 146.1; IR (ATR): 3039, 2959, 2925, 2871, 1647, 1453, 1397, 1365, 1346, 1269, 1110, 1058, 1012, 973, 925, 893 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{12}O_2Na$ ([M + Na]$^+$) 199.0730, found 199.0729.

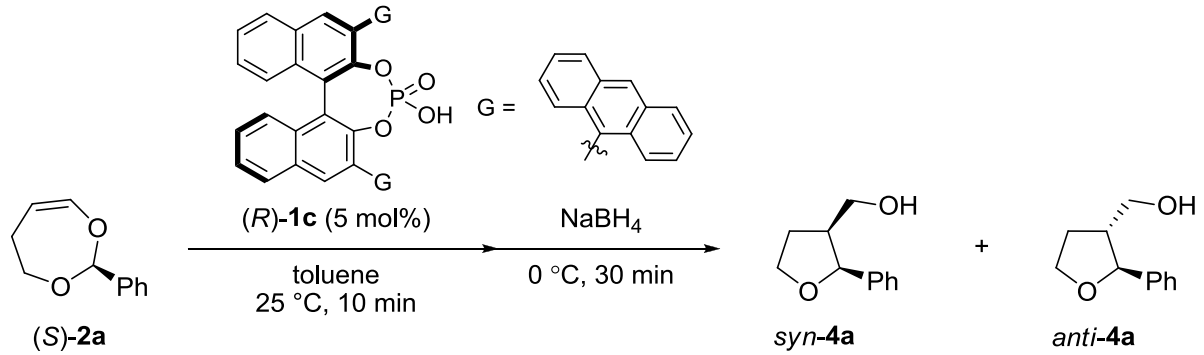


(*S*)-2-phenyl-4,5-dihydro-1,3-dioxepine ((*S*)-2a):

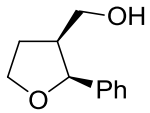
HPLC analysis: CHIRALCEL OD-3 (hexane/IPA = 98/2, 1.0 mL/min, 220 nm, 30 °C) 5.9 (minor), 7.6 (major) min (>99% ee); $[\alpha]^{20}_D$ = -1.4 (*c* 1.0, CH_2Cl_2).

(1) E. Wolf and I. D. Spense, *J. Org. Chem*., 1995, **60**, 6937.

3. Chiral Phosphoric Acid-Catalyzed Petasis-Ferrier-Type Rearrangement

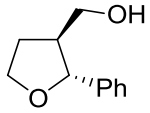


Representative Procedure: To a solution of (*R*)-**1c** (5 mol%, 0.0050 mmol, 3.5 mg) in toluene (0.5 mL) was added (*S*)-**2** (0.10 mmol, 17.6 mg) and the resultant mixture was stirred at 25 °C for 10 min. The reaction mixture was cooled to 0 °C and MeOH (0.5 mL) was added. $NaBH_4$ (0.30 mmol, 11.3 mg) was added and the resultant reaction mixture was stirred at 0 °C for 30 min. The reaction mixture was diluted with saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2 (×3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc as eluent) to give **4a** in 90% yield (*anti*:*syn* = 7:93 mixture) as colorless oil.



((2*S*,3*S*)-2-phenyltetrahydrofuran-3-yl)methanol (*syn*-4a):

Anti:*syn* = 7:93 mixture; colorless oil; R_f = 0.33 (Hexane/EtOAc = 1/1); HPLC analysis: CHIRALPAK IA-3 (hexane/IPA = 93/7, 1.0 mL/min, 220 nm, 15 °C) 11.1 (*anti*), 12.9 (*syn*-minor), 14.7 (*anti*), 16.0 (*syn*-minor) min (98% ee for *syn*-**4a**); $[\alpha]^{16}_D$ = -61.7 (*c* 1.1, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.95 (1H, brs), 1.90-1.95 (1H, m), 2.16-2.21 (1H, m), 2.65 (1H, sext, *J* = 6.6 Hz), 3.22-3.25 (1H, m), 3.30-3.34 (1H, m), 3.91 (1H, q, *J* = 8.4 Hz), 4.21 (1H, td, *J* = 8.4, 4.8 Hz), 5.01 (1H, d, *J* = 6.6 Hz), 7.25-7.28 (1H, m), 7.32-7.36 (4H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 28.9, 45.5, 62.7, 67.5, 81.9, 125.9, 127.3, 128.3, 139.4; IR (ATR): 3396, 2923, 2874, 2851, 1492, 1453, 1083, 1050, 1028 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{14}O_2Na$ ($[M + Na]^+$) 201.0886, found 201.0885.



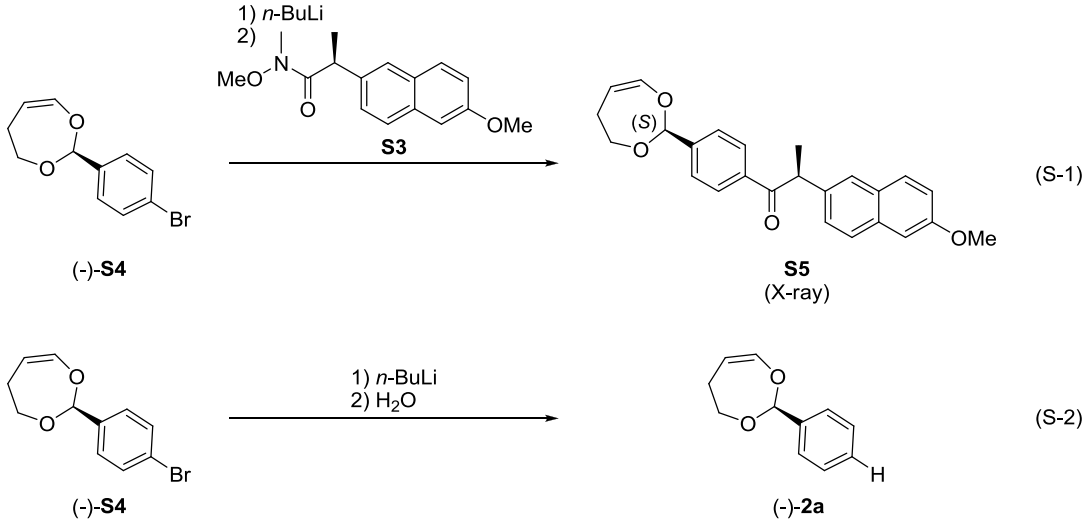
((2*R*,3*S*)-2-phenyltetrahydrofuran-3-yl)methanol (*anti*-4a):

Anti:*syn* = 99:1 mixture; colorless oil; R_f = 0.33 (Hexane/EtOAc = 1/1); HPLC analysis: CHIRALPAK IA-3 (hexane/IPA = 93/7, 1.0 mL/min, 220 nm, 15 °C) 11.1 (*anti*-minor), 12.9 (*syn*), 14.7 (*anti*-major), 16.0 (*syn*) min (95% ee for *anti*-**4a**); $[\alpha]^{18}_D$ = -1.3 (*c* 0.9, $CHCl_3$); ^{1}H NMR

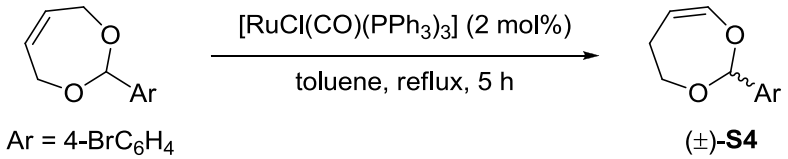
($CDCl_3$, 600 MHz): δ 1.42 (1H, brs), 1.85-1.90 (1H, m), 2.16-2.22 (1H, m), 2.32-2.38 (1H, m), 3.69-3.72 (1H, m), 3.75-3.79 (1H, m), 3.99 (1H, td, *J* = 7.8, 6.0 Hz), 4.11-4.15 (1H, m), 4.65 (1H, d, *J* = 7.2 Hz), 7.25-7.28 (1H, m), 7.32-7.36 (4H, m); ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 29.5, 50.2, 63.8, 68.0, 83.1, 125.9, 127.4, 128.4, 142.5; IR (ATR): 3411, 3063, 3030, 2940, 2873, 1603, 1493, 1454, 1365, 1209, 1052, 1027, 972, 907, 808 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{14}O_2Na$ ($[M + Na]^+$) 201.0886, found 201.0885.

4. Determination of Absolute and Relative Configurations

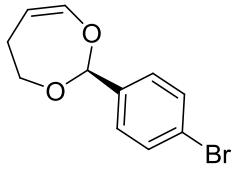
4.1 Determination of Absolute Configuration of **2a**



(±)-**S4**, which is a brominated analog of (±)-**2a**, was synthesized by the same procedure for the synthesis of (±)-**2a** and separated by preparative HPLC with a chiral column to afford enantiomerically pure (-)-**S4**. (-)-**S4** was coupled with enantiomerically pure **S3** to afford **S5**, whose relative configuration of the acetal carbon was unambiguously determined to be (*S*) by X-ray crystallographic analysis (Scheme S-1). Thus, the absolute configuration of the acetal carbon of (-)-**S4** was deduced to be (*S*). On the other hand, debromination of (-)-**S4** afforded (-)-**2a**, concluding that the absolute configuration of the acetal carbon of (-)-**2a** to be (*S*) (Scheme S-2).



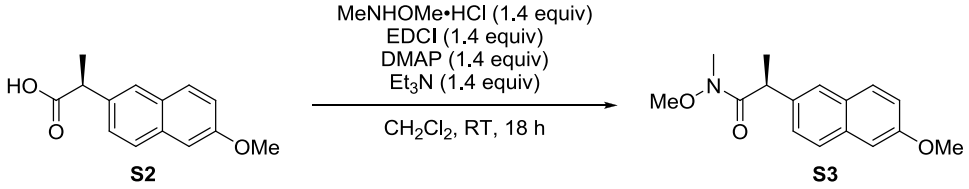
(±)-**S4** was synthesized by the same procedure for the synthesis of (±)-**2a** and separated by preparative HPLC with a chiral column (CHIRALCEL OJ-H (2 cmφ × 25 cm), hexane/IPA = 70/30, 10.0 mL/min, 220 nm, 20 °C, t_R = 16.6 (*S*), 21.3 (*R*) min) to afford enantiomerically pure products (>99% ee for each enantiomer).



(*S*)-2-(4-bromophenyl)-4,5-dihydro-1,3-dioxepine ((-)-S4):

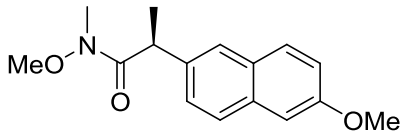
Pale yellow solid; R_f = 0.53 (Hexane/EtOAc = 10/1); HPLC analysis: CHIRALCEL OJ-H (hexane/IPA = 90/10, 1.0 mL/min, 220 nm, 30 °C) 11.6 (major), 15.2 (minor) min (>99% ee); $[\alpha]^{23}_{D}$

= -8.8 (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 2.25 (1H, ddt, *J* = 16.2, 7.2, 2.4 Hz), 2.58-2.63 (1H, m), 3.47 (1H, td, *J* = 11.4, 2.4 Hz), 4.28 (1H, ddd, *J* = 11.4, 4.8, 2.4 Hz), 5.01 (1H, td, *J* = 7.2, 3.0 Hz), 5.36 (1H, s), 6.50 (1H, dd, *J* = 7.2, 2.4 Hz), 7.41 (2H, d, *J* = 9.0 Hz), 7.50 (2H, d, *J* = 9.0 Hz); ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 29.9, 69.5, 105.0, 108.5, 122.7, 127.8, 131.3, 137.8, 146.0; IR (ATR): 3045, 2969, 2946, 2921, 2878, 2824, 1652, 1594, 1489, 1463, 1401, 1346, 1283, 1274, 1114, 1090, 1069, 1058, 1018, 969, 947, 807 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{11}BrO_2Na$ ($[M + Na]^+$) 276.9834, found 276.9834.



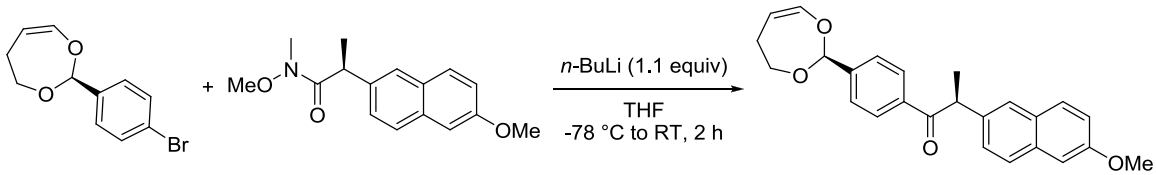
S2 **S3**

To a solution of (*S*)-(+)-6-Methoxy-α-methyl-2-naphthaleneacetic Acid (**S2**) (1.3 mmol, 299.3 mg), *N,O*-dimethylhydroxyamine hydrochloride (1.8 mmol, 117.5 mg), EDCI (1.8 mmol, 345.0 mg), and DMAP (1.8 mmol, 219.9 mg) in CH_2Cl_2 (6.5 mL)was added Et_3N (1.8 mmol, 250 μL) and the resultant mixture was stirred at room temperature for 18 h. The reaction was quenched with saturated aqueous NH_4Cl solution and extracted with CH_2Cl_2 (×3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc as eluent) to give **S3**[2] in 96% yield as pale yellow solid.



(*S*)-2-(6-methoxynaphthalen-2-yl)-*N*,*N*-dimethylpropanamide (S3):

White solid; ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.51 (3H, d, *J* = 7.2 Hz), 3.17 (3H, s), 3.39 (3H, brs), 3.90 (3H, s), 4.27 (1H, brs), 7.10 (1H, d, *J* = 2.4 Hz), 7.13 (1H, dd, *J* = 8.4, 2.4 Hz), 7.42 (1H, dd, *J* = 8.4, 1.8 Hz), 7.67 (1H, d, *J* = 1.8 Hz), 7.69 (2H, d, *J* = 8.4 Hz).



(-)-**S4** **S3** **S5**

To a solution of (-)-**S4** (0.31 mmol, 69.8 mg) in THF (1.5 mL) was added *n*-BuLi (1.64 M in hexane, 0.34 mmol, 207 μL) at -78 °C. The resultant mixture was stirred at -78 °C for 30 min and **S3** (0.37 mmol, 101.6 mg) in THF (1.0 mL) was added. The reaction mixture was allowed to warm to room

(2) Analytical data matched the literature values. See; H. A. Duong, R. E. Gilligan, M. L. Cooke, R. J. Phipps and M. J. Gaunt, *Angew. Chem. Int. Ed.*, 2011, **50**, 463.

temperature and stirred for 2 h. The reaction was quenched with water and extracted with CH_2Cl_2 (×3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc as eluent) to give **S5** in 56% yield as white solid.

S5 was recrystallized from EtOAc/hexane to give a clear needle crystal and the relative configuration was unambiguously determined by X-ray crystallographic analysis. CCDC-985709 contains the crystallographic data of this compound. The data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

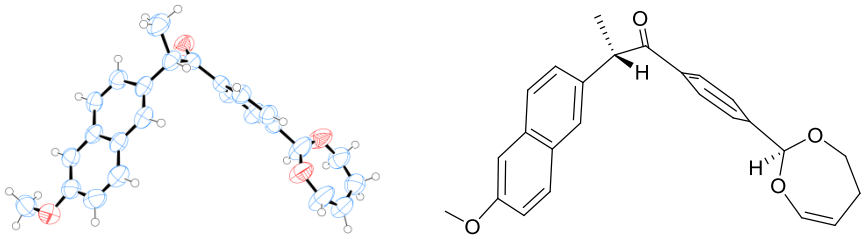
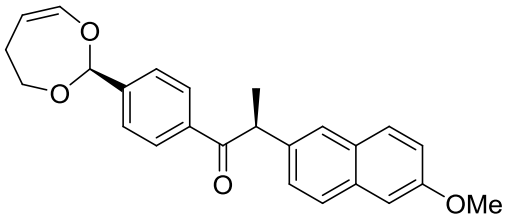
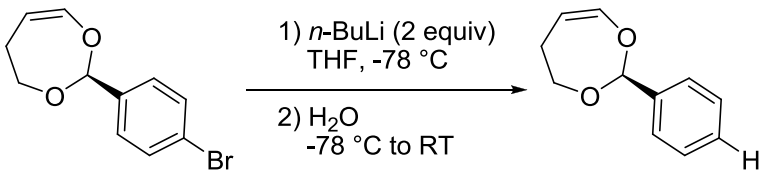


Fig. S1 ORTEP (left) and its schematic (right) drawings of **S5**



(*S*)-1-(4-((*S*)-4,5-dihydro-1,3-dioxepin-2-yl)phenyl)-2-(6-methoxynaphthalen-2-yl)propan-1-one (S5):

White solid; R_f = 0.33 (Hexane/EtOAc = 4/1); $[\alpha]^{18}_D$ = 74.1 (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 1.60 (3H, d, *J* = 7.2 Hz), 2.22 (1H, ddt, *J* = 16.8, 7.8, 2.4 Hz), 2.54-2.61 (1H, m), 3.43 (1H, td, *J* = 12.0, 2.4 Hz), 3.88 (3H, s), 4.24 (1H, ddd, *J* = 12.0, 5.4, 2.4 Hz), 4.80 (1H, q, *J* = 7.2 Hz), 4.99 (1H, td, *J* = 7.8, 2.4 Hz), 5.34 (1H, s), 6.46 (1H, dd, *J* = 7.8, 3.6 Hz), 7.06 (1H, d, *J* = 1.8 Hz), 7.11 (1H, dd, *J* = 8.4, 1.8 Hz), 7.35 (1H, dd, *J* = 8.4, 1.8 Hz), 7.52 (2H, d, *J* = 8.4 Hz), 7.61 (1H, d, *J* = 1.8 Hz), 7.65 (2H, t, *J* = 8.4 Hz), 7.99 (2H, d, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 19.4, 29.9, 47.9, 55.3, 69.6, 105.0, 105.5, 108.6, 119.0, 126.2_2, 126.2_4, 126.4, 127.6, 128.8, 129.1_2, 129.1_4, 133.4, 136.5, 136.6, 143.0, 146.0, 157.6, 200.0; IR (ATR): 3048, 2970, 2931, 2871, 2840, 1681, 1650, 1633, 1605, 1575, 1505, 1483, 1462, 1416, 1392, 1366, 1346, 1268, 1227, 1208, 1173, 1108, 1058, 1019, 964, 953, 922, 896, 851, 813 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{24}O_4Na$ ([M + Na]$^+$) 411.1567, found 411.1567.

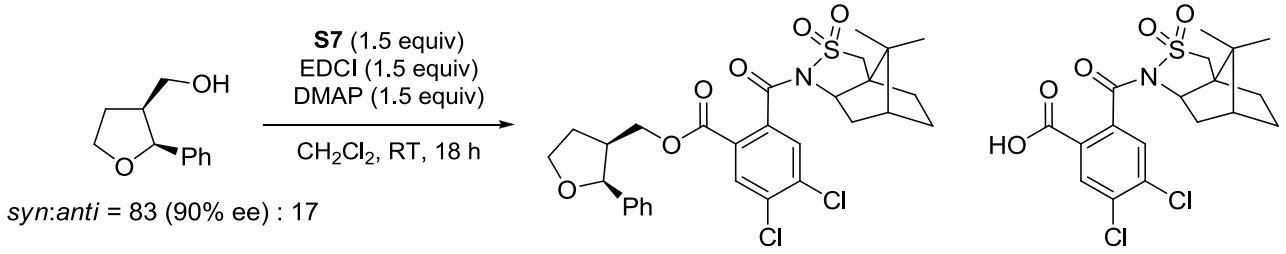


(-)-**S4** (-)-**2a**

To a solution of (-)-**S4** (0.20 mmol, 51.0 mg) in THF (2.0 mL) was added *n*-BuLi (1.64 *M* in hexane, 0.40 mmol, 260 μL) at -78 °C. The resultant mixture was stirred at -78 °C for 30 min and H_2O (1.4 mmol, 25 μL) was added. The reaction mixture was allowed to warm to room temperature and stirred for 1 h. The reaction was quenched with water and extracted with CH_2Cl_2 (×3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc as eluent) to give (-)-**2a** in 79% yield (>99% ee) as colorless oil. The optical rotation of this product was compared to that described in section 2 to determine the absolute configuration.

4.2 Determination of Absolute Configuration of *syn*-**4a**

Syn-**4a** was coupled with enantiomerically pure **S7** to give **S6**, whose relative configuration was unambiguously determined by X-ray crystallographic analysis.



syn:*anti* = 83 (90% ee) : 17

S6 **S7**

To a stirred solution of *N*-(2-carboxy-4,5-dichlorobenzoyl)-(-)-10,2-camphorsultam (**S7**) (0.30 mmol, 129.7 mg), EDCI (0.30 mmol, 57.5 mg), and DMAP (0.30 mmol, 36.7 mg) in CH_2Cl_2 (3.0 mL) was added CH_2Cl_2 (1.0 mL) solution of the alcohol **4a** (0.20 mmol, 36.0 mg, *anti*:*syn* = 17:83 mixture, 90% ee for *syn*-**4a**). The reaction mixture was stirred for 16 h at room temperature and then quenched with saturated aqueous NH_4Cl solution. The aqueous layer was extracted with CH_2Cl_2 (×3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography (silica gel, hexane/EtOAc as eluent) and preparative HPLC (GL Science Inc. Inertsil® SIL-100A (2 cmφ × 25 cm), hexane/EtOAc = 6.5/3.5, 10.0 mL/min, 254 nm, 20 °C, t_R = 14.5 min) to give S**6** (single diastereomer) as white solid in 49% yield.

S6 was recrystallized from MeOH to give a clear needle crystal and the relative configuration was unambiguously determined by X-ray crystallographic analysis. CCDC-985710 contains the

crystallographic data of this compound. The data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

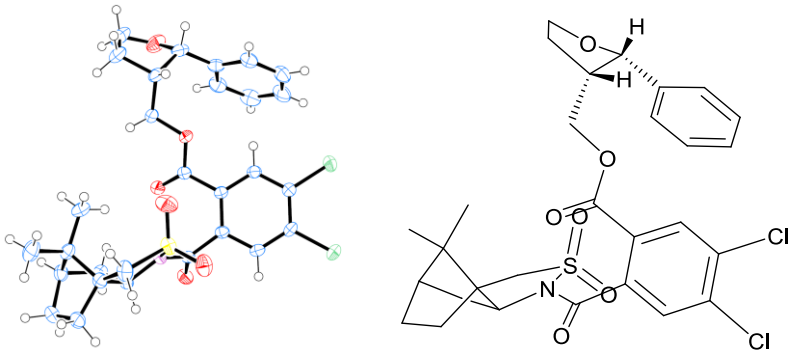
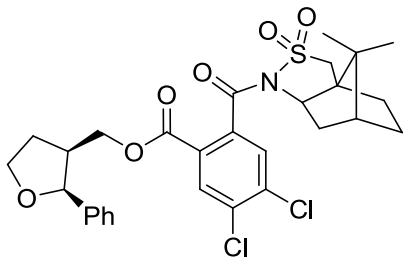


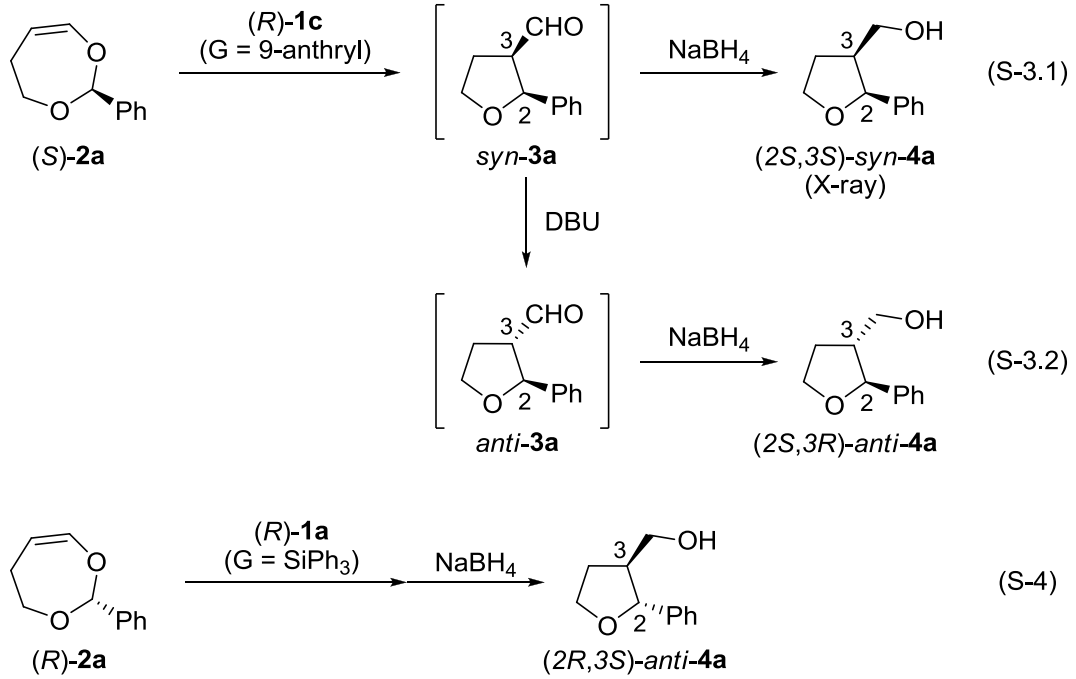
Fig. S2 ORTEP (left) and its schematic (right) drawings of **S6**



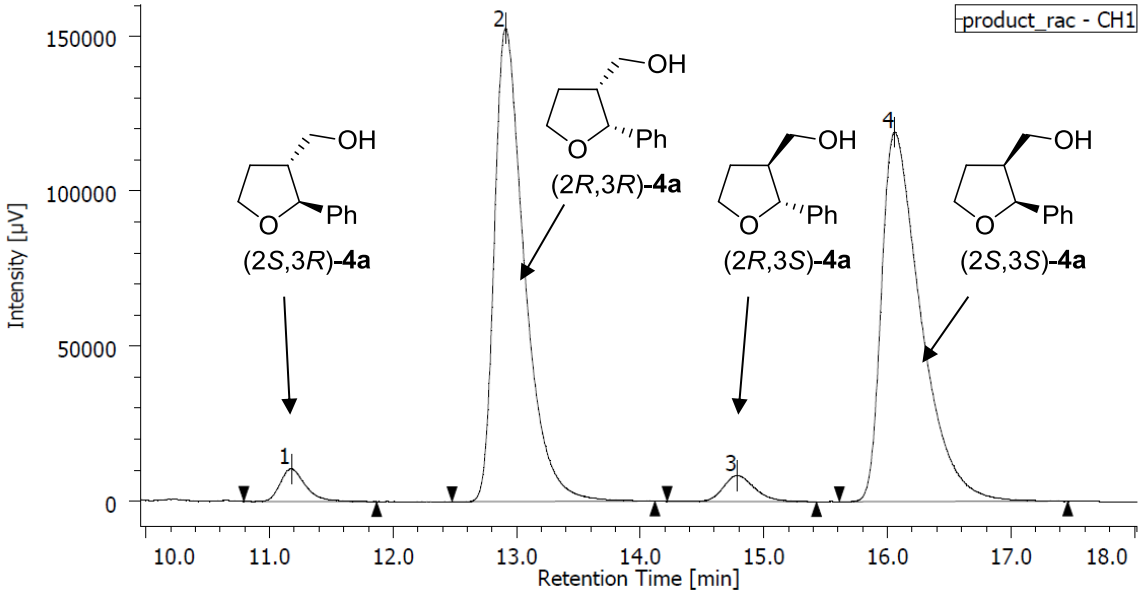
S6:

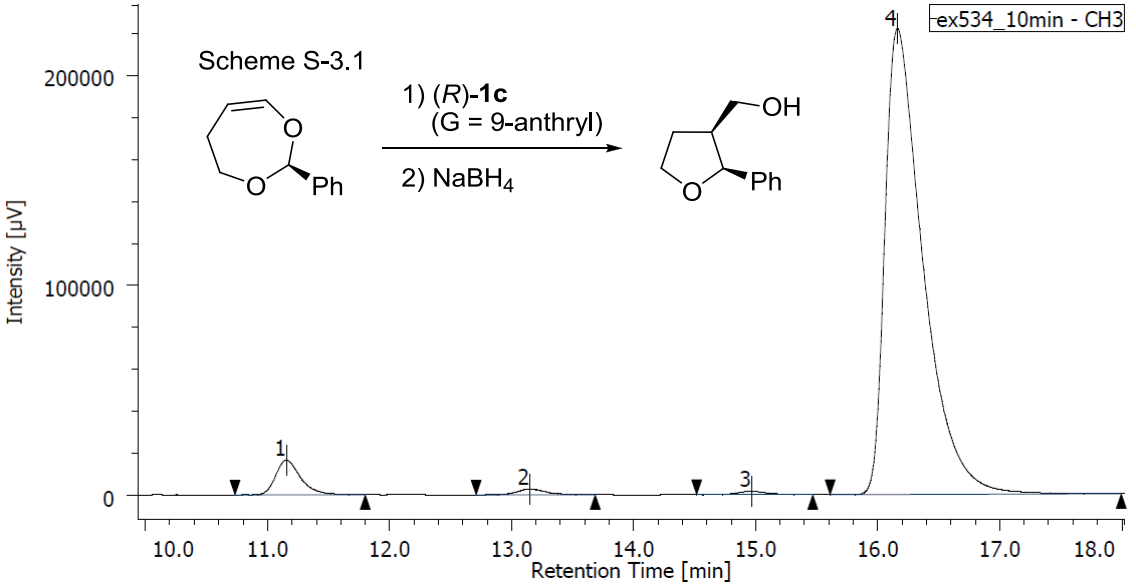
White solid; R_f = 0.40 (Hexane/EtOAc = 2/1); $[\alpha]^{16}_D$ = -103.2 (*c* 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 600 MHz): δ 0.97 (3H, s), 1.13 (3H, s), 1.36-1.45 (2H, m), 1.88-1.94 (4H, m), 2.14 (1H, brs), 2.22-2.27 (1H, m), 2.41 (1H, brs), 2.89 (1H, sext, *J* = 6.0 Hz), 3.37 (1H, d, *J* = 13.8 Hz), 3.41 (1H, d, *J* = 13.8 Hz), 3.84-3.87 (1H, m), 3.91-3.95 (2H, m), 4.03 (1H, brs), 4.22 (1H, td, *J* = 8.4, 5.4 Hz), 5.04 (1H, d, *J* = 6.0 Hz), 7.23-7.25 (1H, m), 7.30-7.34 (4H, m), 7.46 (1H, s), 7.59 (1H, s); ^{13}C NMR ($CDCl_3$, 150.9 MHz): δ 20.0, 20.6, 26.4, 29.4, 33.1, 37.5, 42.2, 44.7, 47.7, 48.4, 53.0, 65.4, 65.7, 67.1, 81.8, 126.1, 127.6, 128.3, 128.4, 131.0, 131.2, 134.6, 134.7, 136.7, 138.8, 163.2, 165.2; IR (ATR): 2959, 2881, 1726, 1686, 1588, 1553, 1454, 1412, 1375, 1335, 1296, 1266, 1246, 1167, 1141, 1116, 1096, 1064, 1027, 1009, 976, 906 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{31}Cl_2NO_6SNa$ ($[M + Na]^+$) 614.1141, found 614.1141.

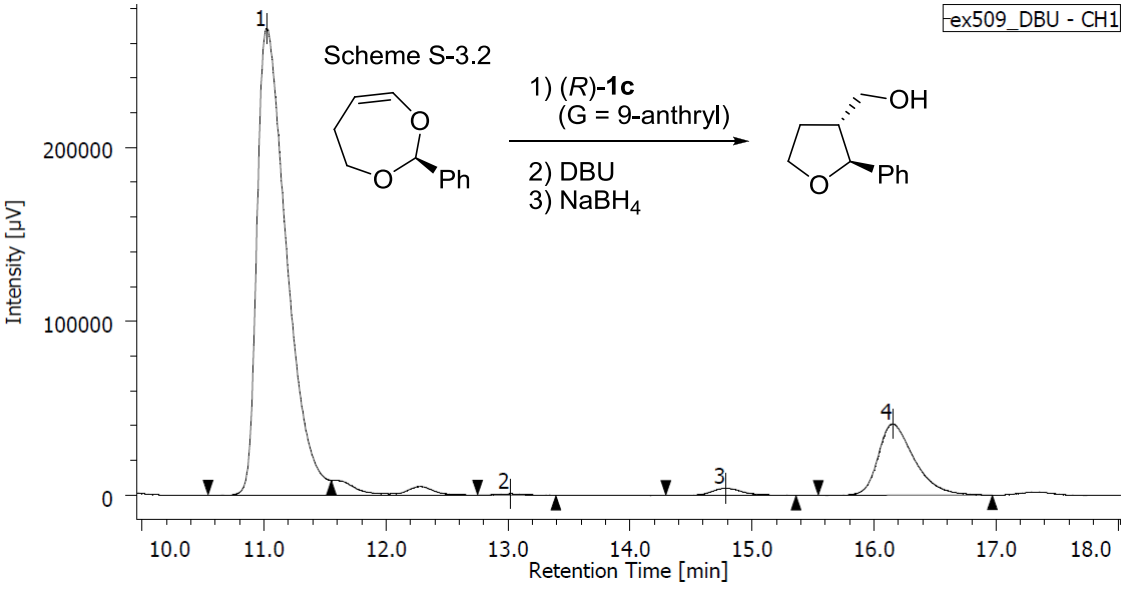
4.3 Determination of Absolute Configuration of *anti*-**4a**

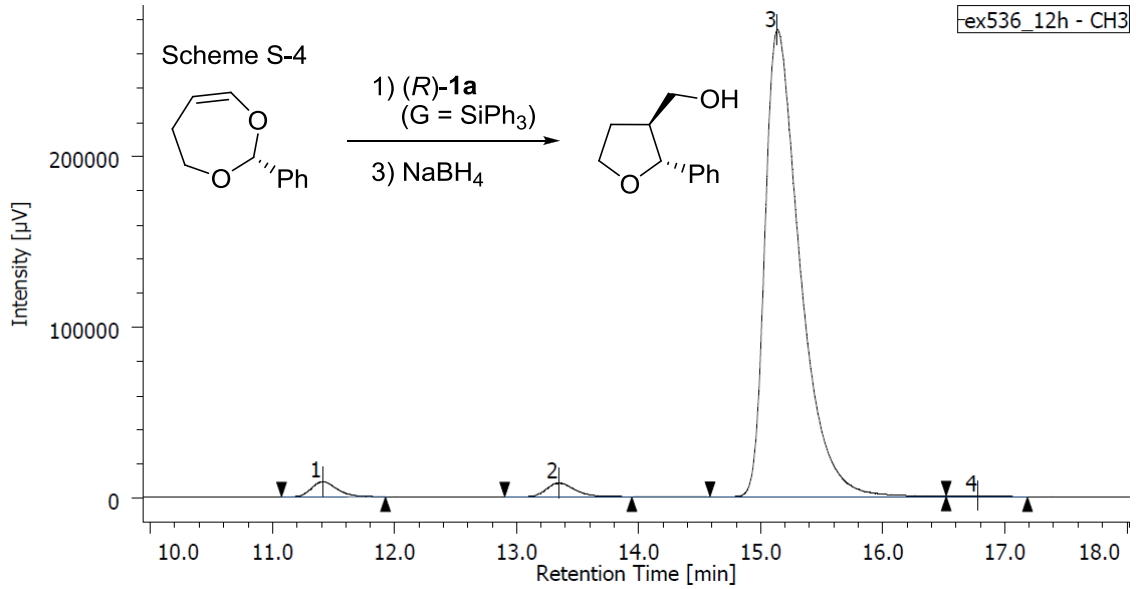


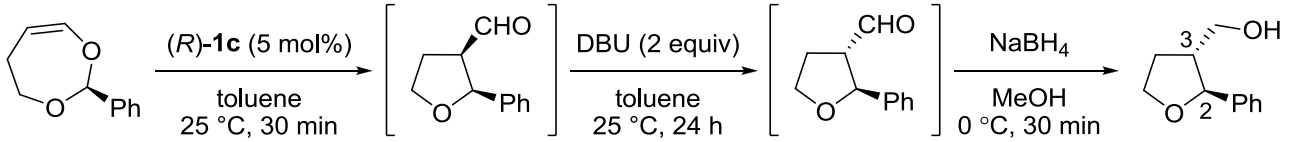
The reaction of (*S*)-**2a** catalyzed by (*R*)-**1c** afforded (2*S*,3*S*)-*syn*-**4a**, whose absolute configuration was unambiguously determined by X-ray crystallographic analysis (Scheme S-3.1, see section 4.2 for details). (2*S*,3*R*)-*anti*-**4a** was independently synthesized by epimerization of intermediary aldehyde *syn*-**3a** to *anti*-**3a** at C3 position by treatment with DBU, followed by the reduction with sodium borohydride (Scheme S-3.2). Chiral HPLC analysis revealed that thus obtained (2*S*,3*R*)-*anti*-**4a** is the opposite enantiomer of the reaction product of (*R*)-**2a** catalyzed by (*R*)-**1a**. Thus, the product obtained by the reaction of (*R*)-**2a** catalyzed by (*R*)-**1a** was determined to be (2*R*,3*S*)-*anti*-**4a** (Scheme S-4).




ex534_10min - CH3
Scheme S-3.1
1) (R)-1c
(G = 9-anthryl)
2) NaBH4
OH
Ph
Intensity [µV]
Retention Time [min]


ex509_DBU - CH1
Scheme S-3.2
1) (R)-1c
(G = 9-anthryl)
2) DBU
3) NaBH4
OH
Ph
Intensity [µV]
Retention Time [min]


ex536_12h - CH3
Scheme S-4
1) (R)-1a
(G = SiPh3)
3) NaBH4
OH
Ph
Intensity [µV]
Retention Time [min]

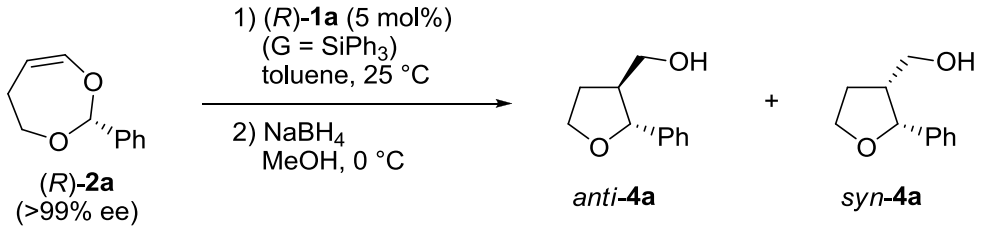


To a solution of (*R*)-**1c** (5 mol%, 0.010 mmol, 7.0 mg) in toluene (1.0 mL) was added (*S*)-**2a** (0.20 mmol, 35.2 mg) and the resultant mixture was stirred at 25 °C for 30 min. DBU (0.40 mmol, 60 μL) was added to the reaction mixture and the resultant mixture was stirred at 25 °C for 24 h. The reaction mixture was cooled to 0 °C and MeOH (1.0 mL) was added. $NaBH_4$ (0.60 mmol, 22.6 mg) was added and the mixture was stirred at 0 °C for 30 min. The reaction was quenched with saturated aqueous NH_4Cl solution and extracted with CH_2Cl_2 (×3). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc as eluent) to give *anti*-**4a** in 82% yield (*anti*:*syn* = 84:16, 97% ee for *anti*-**4a**) as colorless oil ((*2S,3R*) as the major diastereomer).

4.4 Epimerization Experiments of the Product

Anti-product was confirmed to be a kinetically formed product for Table 1, entry 4 and Table 2, entry 1 (both of the reactions are catalyzed by (*R*)-**1a**) by the following experiments, although epimerization from *syn*-**3a** to *anti*-**3a** was observed in a reaction catalyzed by (*R*)-**1c**.

Table S1 Petasis-Ferrier-type rearrangement of (*R*)-**2a** catalyzed by (*R*)-**1**

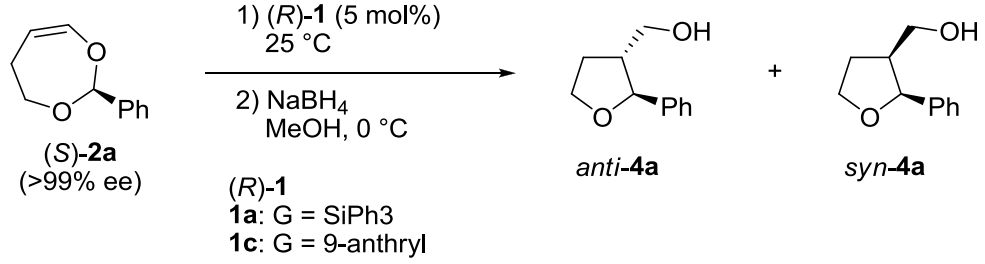


Entry	time	conversion (%)[a]	*anti*-**4a**/*syn*-**4a**
1 (Table 1, entry 4)	12 h	>99 (95)	99:1
2	10 min	20	99:1

[a] Isolate yield in parentheses.

The reaction of (*R*)-**2a** catalyzed by (*R*)-**1a** in toluene required 12 h to complete and the resultant *anti*:*syn* ratio was 99:1 (Table S1, entry 1). When the reaction was conducted for 10 min in the identical conditions, the *anti*:*syn* ratio was exactly the same as those after full conversion (Table S1, entry 1 vs. entry 2). These results show that aldehyde *anti*-**3a** was kinetically formed product and did not epimerize for 12 h under the present reaction conditions.

Table S2 Petasis-Ferrier-type rearrangement of (*S*)-**2a** catalyzed by (*R*)-**1**



Entry	(*R*)-**1**	solvent	time	conversion (%)[a]	*anti*-**4a**/*syn*-**4a**
1 (Table 2, entry 1)	**1a**	CH_2Cl_2	5 h	>99 (86)	89:11
2	**1a**	CH_2Cl_2	10 min	29	89:11
3 (Table 2, entry 4)	**1c**	toluene	10 min	>99 (90)	7:93
4	**1c**	toluene	1 h	>99 (90)	11:89

[a] Isolate yield in parentheses.

The reaction of (*S*)-**2a** catalyzed by (*R*)-**1a** in toluene required 5 h to complete and the resultant *anti*:*syn* ratio was 89:11 (Table S2, entry 1). When the reaction was conducted for 10 min in the identical conditions, the *anti*:*syn* ratio was exactly the same as those after full conversion (Table S2, entry 1 vs. entry 2). These results show that aldehyde *anti*-**3a** was kinetically formed product and did not epimerize for 5 h under the present reaction conditions. On the other hand, epimerization of the product was observed in the reaction of (*S*)-**2a** catalyzed by (*R*)-**1c** in CH_2Cl_2. The reaction required 10 min to complete and the resultant *anti*:*syn* ratio was 7:93 (Table S2, entry 3). When the reaction was conducted for 1 h in the identical conditions, the *anti*:*syn* ratio decreased to 11:89 (Table S2, entry 3 vs.4). These results show that kinetically formed aldehyde *syn*-**3a** gradually epimerized to *anti*-**3a** under the present reaction conditions.

5. Computational Studies

5.1 Structure of **CPr**, **TSr-int**, **INTr1**, and **INTr2**

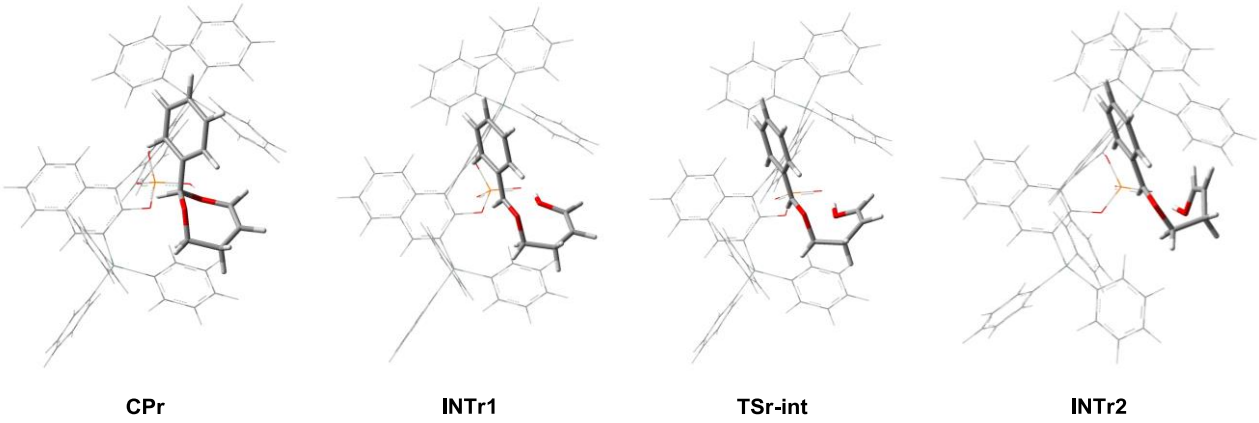


Fig. S3 3D Structure of **CPr**, **TSr-int**, **INTr1**, and **INTr2**

5.2 Energy Profile of the reaction of (S)-**2a** and the Structure of Stable Intermediates

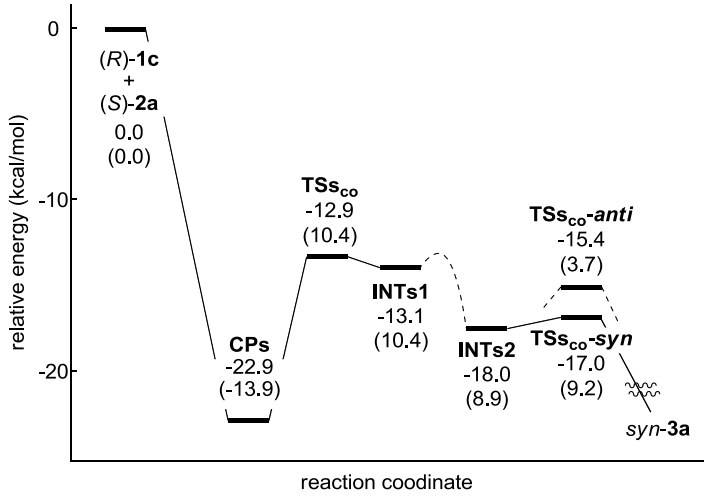


Fig. S4 Energy Profile for the reaction of (*S*)-**2a** catalyzed by (*R*)-**1c**. The potential energy of the sum of (*S*)-**1a** and (*R*)-**2c** was set to zero. The energies for single-point calculations in the solution phase are shown. The energies for frequency calculations with the BHandHLYP/6-31G* level are indicated in parentheses.

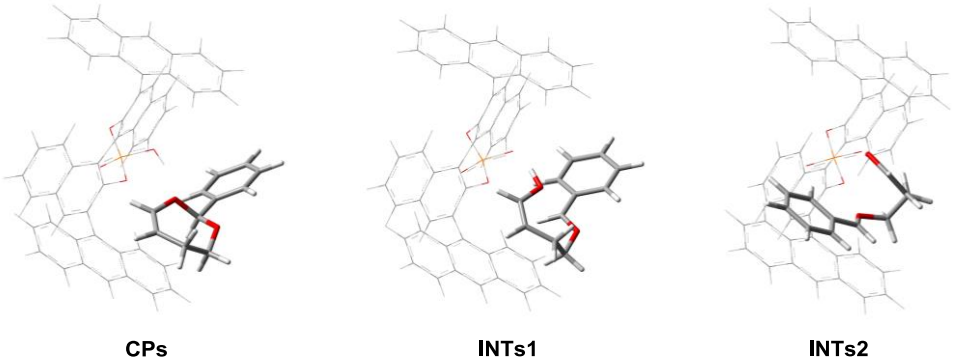


Fig. S5 3D Structures of **CPs**, **INTs1**, and **INTs2**

5.3 Structural Comparison between Transition States

(a) Comparison between **TSr_{cc}-*anti*** and **TSs_{cc}-*anti***

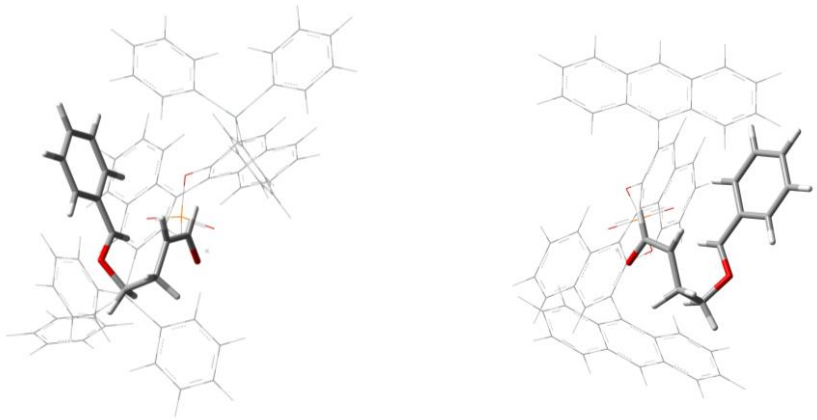


Fig. S6 Comparison of 3D Structures between **TSr_{cc}-*anti*** and **TSs_{cc}-*anti***

(b) Comparison between **TSr_{cc}-*syn*** and **TSs_{cc}-*syn***

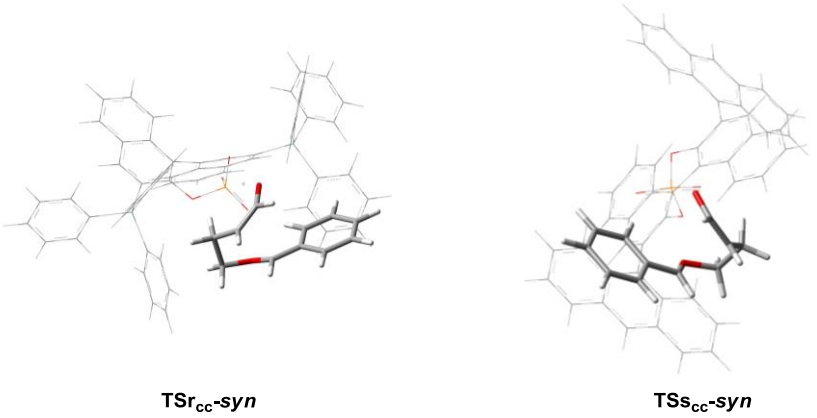


Fig. S7 Comparison of 3D Structures between **TSr_{cc}-*syn*** and **TSs_{cc}-*syn***

5.4 Structure of **F1** and **F2**

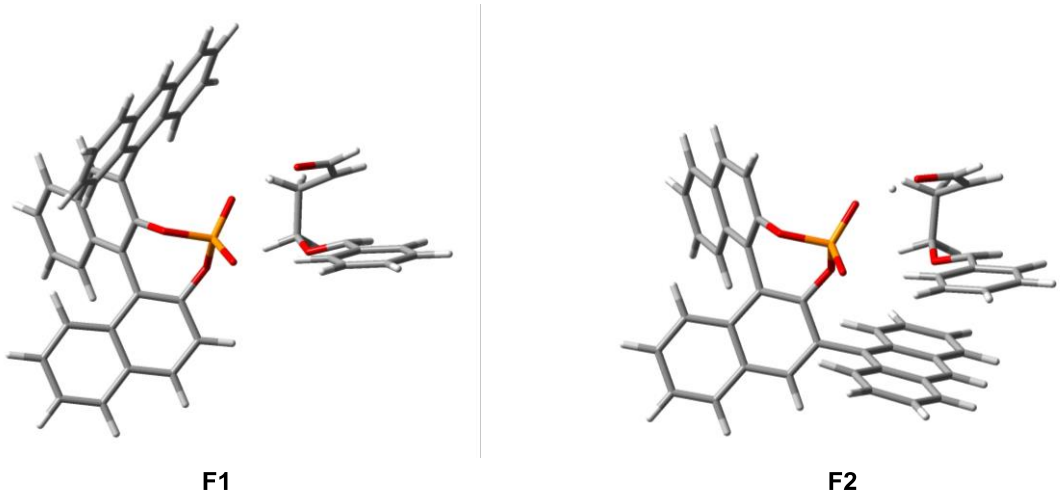


Fig. S8 3D Structures of **F1** and **F2**

The initial structures of **F1** and **F2** were generated by replacing the corresponding 9-anthryl group with the hydrogen atom. These initial structures were partially optimized with respect to the newly introduced hydrogen atom (all the other atoms were fixed during the structural optimization) to afford **F1** and **F2**.

6. Cartesian Coordinates of Each Transition State

CPr
BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −3955.04533474 a.u.
Sum of electronic and thermal Free Energies = −3954.088661 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −3957.95348597 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.800705	5.402185	−2.449550
2	6	0	0.001659	4.455229	−1.985284
3	6	0	2.071227	5.908080	−1.836554
4	6	0	0.450836	4.262857	0.422486
5	6	0	2.364336	5.311973	−0.468749
6	1	0	0.474115	5.890969	−3.355018
7	1	0	−0.908914	4.176274	−2.488896
8	1	0	1.990141	6.990305	−1.731721
9	1	0	0.971926	3.469572	0.947567
10	1	0	2.693290	4.279307	−0.541948
11	8	0	0.253956	3.668583	−0.888078
12	6	0	−0.863815	4.573647	1.079433
13	6	0	−1.454959	3.617274	1.894398
14	6	0	−1.508921	5.784864	0.858206
15	6	0	−2.689104	3.864022	2.477366
16	1	0	−0.947859	2.681614	2.068627
17	6	0	−2.742308	6.029025	1.438985
18	1	0	−1.035313	6.532623	0.245867
19	6	0	−3.334891	5.068566	2.247157
20	1	0	−3.141870	3.115404	3.107291
21	1	0	−3.237492	6.971974	1.269447
22	1	0	−4.293364	5.263059	2.701638
23	8	0	1.204770	5.410006	0.334103
24	1	0	3.145184	5.875958	0.031401
25	1	0	2.913452	5.731475	−2.507565
26	6	0	0.948146	−5.746749	2.738696
27	6	0	0.456684	−4.835232	1.848844
28	6	0	1.283173	−3.814109	1.323616
29	6	0	2.626288	−3.749318	1.766486
30	6	0	3.110244	−4.717766	2.675241
31	6	0	2.292851	−5.698686	3.152137
32	1	0	0.297089	−6.509996	3.133209
33	1	0	−0.575633	−4.882908	1.552362
34	6	0	0.813292	−2.822528	0.405827
35	6	0	3.463908	−2.713989	1.296878
36	1	0	4.139572	−4.656886	2.991817
37	1	0	2.666708	−6.429763	3.850169
38	6	0	3.013432	−1.707814	0.480051
39	6	0	1.651623	−1.782165	0.100047
40	1	0	4.494608	−2.727247	1.612361
41	6	0	−0.547360	−2.900923	−0.189657
42	6	0	−0.953546	−4.050971	−0.940024
43	6	0	−1.449952	−1.878044	−0.050076
44	6	0	−0.060712	−5.084505	−1.308299
45	6	0	−2.298795	−4.150349	−1.367253
46	6	0	−2.815840	−1.961800	−0.418767
47	6	0	−0.490760	−6.158418	−2.033918
48	1	0	0.973717	−5.013766	−1.024331
49	6	0	−2.717996	−5.281681	−2.102933
50	6	0	−3.203749	−3.111923	−1.056173
51	6	0	−1.836722	−6.269091	−2.429451
52	1	0	0.210756	−6.928434	−2.311454
53	1	0	−3.750397	−5.341776	−2.409548
54	1	0	−4.231856	−3.240447	−1.351526
55	1	0	−2.161833	−7.126135	−2.996247
56	8	0	1.135934	−0.746357	−0.658373
57	15	0	0.119093	0.255139	0.066755
58	8	0	−1.055897	−0.709539	0.573721
59	8	0	0.653918	1.048286	1.172625
60	8	0	−0.438725	1.057042	−1.151756
61	1	0	−0.278557	2.020299	−1.057223
62	14	0	−4.103407	−0.609373	−0.082746
63	14	0	4.238345	−0.364398	−0.074447
64	6	0	−5.779676	−1.348112	−0.548181
65	6	0	−6.450387	−1.008739	−1.724010
66	6	0	−6.391303	−2.279593	0.297801
67	6	0	−7.673747	−1.578289	−2.047548
68	1	0	−6.018417	−0.285307	−2.396526
69	6	0	−7.610499	−2.853733	−0.020144
70	1	0	−5.912103	−2.556045	1.224528
71	6	0	−8.255318	−2.503356	−1.197250
72	1	0	−8.171868	−1.295662	−2.961401
73	1	0	−8.059698	−3.569075	0.650396
74	1	0	−9.206705	−2.946038	−1.446133
75	6	0	−4.247599	−0.107197	1.728410
76	6	0	−5.418750	0.547650	2.128137
77	6	0	−3.278300	−0.342116	2.705438
78	6	0	−5.608866	0.961745	3.436291
79	1	0	−6.202618	0.730421	1.409411
80	6	0	−3.467100	0.062189	4.019064
81	1	0	−2.358564	−0.834359	2.446068
82	6	0	−4.630637	0.717416	4.388079
83	1	0	−6.521391	1.465398	3.713242
84	1	0	−2.701914	−0.135712	4.752615
85	1	0	−4.776928	1.030573	5.409704
86	6	0	−3.786571	0.878587	−1.183767
87	6	0	−3.932691	2.184156	−0.715477
88	6	0	−3.458682	0.702148	−2.531064
89	6	0	−3.774582	3.273173	−1.560044
90	1	0	−4.164413	2.362446	0.321377
91	6	0	−3.309113	1.783504	−3.382554
92	1	0	−3.309890	−0.292753	−2.922444
93	6	0	−3.473313	3.073272	−2.897912
94	1	0	−3.883049	4.271611	−1.168045
95	1	0	−3.060745	1.621821	−4.419415
96	1	0	−3.366340	3.917601	−3.561367
97	6	0	5.938059	−1.189808	−0.048259
98	6	0	7.036159	−0.573111	0.553525
99	6	0	6.154770	−2.427017	−0.665457
100	6	0	8.294246	−1.157627	0.534860
101	1	0	6.910324	0.375570	1.049461
102	6	0	7.408452	−3.015263	−0.689938
103	1	0	5.329663	−2.948851	−1.126093
104	6	0	8.484025	−2.378997	−0.088799
105	1	0	9.123781	−0.658890	1.010456
106	1	0	7.545367	−3.969480	−1.173529
107	1	0	9.461032	−2.835193	−0.103831
108	6	0	4.232021	1.078392	1.127910
109	6	0	4.902002	2.262205	0.801310
110	6	0	3.613388	1.006589	2.375569
111	6	0	4.960850	3.325204	1.688284
112	1	0	5.381093	2.359170	−0.161297
113	6	0	3.664070	2.068864	3.265094
114	1	0	3.065945	0.121069	2.651654
115	6	0	4.339101	3.229158	2.924450
116	1	0	5.488112	4.225992	1.415881
117	1	0	3.168250	1.992375	4.219323
118	1	0	4.377259	4.056420	3.615185
119	6	0	3.918328	0.295161	−1.809073
120	6	0	4.558175	−0.238751	−2.928428
121	6	0	3.042480	1.364856	−2.015485
122	6	0	4.324736	0.262200	−4.200594
123	1	0	5.258790	−1.049470	−2.811686
124	6	0	2.806089	1.872159	−3.281725
125	1	0	2.534601	1.811146	−1.175840
126	6	0	3.447569	1.318281	−4.379498
127	1	0	4.832218	−0.169968	−5.048460
128	1	0	2.119545	2.694018	−3.409331
129	1	0	3.265846	1.710075	−5.367824

TSr$_{oo}$
BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −3955.01577722 a.u.
Sum of electronic and thermal Free Energies = −3954.060807 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −3957.94013460 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.986707	−5.157591	2.515776
2	6	0	0.119689	−4.201041	2.208795
3	6	0	2.199068	−5.609578	1.751370
4	6	0	0.488098	−4.141850	−0.683334
5	6	0	2.396717	−4.969268	0.392483
6	1	0	0.788993	−5.697729	3.428537
7	1	0	−0.728656	−3.986578	2.840173
8	1	0	2.141912	−6.689283	1.611509
9	1	0	0.972307	−3.198961	−0.894155
10	1	0	2.602719	−3.908885	0.452231
11	8	0	0.196448	−3.429894	1.101917
12	6	0	−0.813478	−4.394767	−1.270536
13	6	0	−1.429216	−3.371094	−1.988541
14	6	0	−1.431156	−5.639751	−1.137332
15	6	0	−2.659788	−3.598491	−2.581970
16	1	0	−0.941482	−2.412418	−2.062975
17	6	0	−2.659342	−5.855957	−1.727140
18	1	0	−0.943026	−6.418630	−0.577550
19	6	0	−3.270078	−4.835884	−2.449679
20	1	0	−3.140911	−2.810212	−3.136031
21	1	0	−3.142973	−6.814119	−1.630872
22	1	0	−4.229478	−5.009625	−2.910204
23	8	0	1.192373	−5.178518	−0.367389
24	1	0	3.193456	−5.453597	−0.157997
25	1	0	3.101235	−5.432754	2.339489
26	6	0	0.828101	5.610653	−2.835421
27	6	0	0.363016	4.722769	−1.908332
28	6	0	1.205519	3.717773	−1.375834
29	6	0	2.536858	3.645742	−1.851608
30	6	0	2.993711	4.588895	−2.800150
31	6	0	2.161638	5.554323	−3.283328
32	1	0	0.164591	6.361794	−3.232851
33	1	0	−0.661307	4.776019	−1.585935
34	6	0	0.762433	2.751981	−0.419917
35	6	0	3.390382	2.630620	−1.368493
36	1	0	4.015222	4.522100	−3.140614
37	1	0	2.515073	6.266755	−4.010841
38	6	0	2.964846	1.652126	−0.505558
39	6	0	1.608344	1.720345	−0.096394
40	1	0	4.413416	2.640577	−1.707610
41	6	0	−0.589766	2.835036	0.192927
42	6	0	−0.997563	3.990906	0.930455
43	6	0	−1.479189	1.796517	0.075230
44	6	0	−0.112367	5.042805	1.264894
45	6	0	−2.336788	4.081072	1.379649
46	6	0	−2.841592	1.877157	0.463466
47	6	0	−0.542947	6.123038	1.980613
48	1	0	0.917240	4.979713	0.961634
49	6	0	−2.756609	5.218480	2.105594
50	6	0	−3.234448	3.028654	1.095605
51	6	0	−1.882705	6.222403	2.400361
52	1	0	0.153138	6.907090	2.231808
53	1	0	−3.784155	5.270614	2.430046
54	1	0	−4.259653	3.149921	1.404420
55	1	0	−2.208631	7.084135	2.959757
56	8	0	1.124731	0.718836	0.704703
57	15	0	0.070195	−0.344849	0.075574
58	8	0	−1.074222	0.638352	−0.538513
59	8	0	0.642772	−1.106553	−1.057410
60	8	0	−0.468127	−1.102399	1.255225
61	1	0	−0.179270	−2.433650	1.199022
62	14	0	−4.117385	0.520707	0.126326
63	14	0	4.228910	0.367126	0.086340
64	6	0	−5.801399	1.238678	0.604248
65	6	0	−6.459744	0.882380	1.782086
66	6	0	−6.428642	2.172671	−0.227297
67	6	0	−7.685992	1.436833	2.120750
68	1	0	−6.014225	0.158208	2.445027
69	6	0	−7.651120	2.731567	0.105236
70	1	0	−5.958246	2.464429	−1.153800
71	6	0	−8.283633	2.363697	1.283654
72	1	0	−8.173499	1.141612	3.036422
73	1	0	−8.111866	3.449666	−0.554550
74	1	0	−9.237182	2.795007	1.544213
75	6	0	−4.269718	0.055677	−1.698326
76	6	0	−5.444718	−0.577344	−2.120704
77	6	0	−3.301029	0.322380	−2.668611
78	6	0	−5.641385	−0.938633	−3.444081
79	1	0	−6.229098	−0.780647	−1.408096
80	6	0	−3.497234	−0.026431	−3.997521
81	1	0	−2.377040	0.796221	−2.390339
82	6	0	−4.666049	−0.659595	−4.389435
83	1	0	−6.558755	−1.423813	−3.738145
84	1	0	−2.734475	0.199903	−4.725610
85	1	0	−4.819077	−0.926933	−5.423175

86	6	0	−3.813597	−0.990271	1.200365
87	6	0	−4.042335	−2.284611	0.733808
88	6	0	−3.424179	−0.838469	2.532854
89	6	0	−3.902413	−3.384910	1.565632
90	1	0	−4.327830	−2.441915	−0.293387
91	6	0	−3.294570	−1.931235	3.373529
92	1	0	−3.206804	0.144991	2.919572
93	6	0	−3.538079	−3.208653	2.891152
94	1	0	−4.078613	−4.375747	1.177855
95	1	0	−2.997412	−1.786975	4.400117
96	1	0	−3.445068	−4.061722	3.545599
97	6	0	5.910424	1.223778	−0.064013
98	6	0	6.982927	0.641202	−0.740254
99	6	0	6.129247	2.473172	0.528472
100	6	0	8.218688	1.268271	−0.816133
101	1	0	6.855705	−0.314595	−1.221566
102	6	0	7.360331	3.103530	0.459832
103	1	0	5.321852	2.969890	1.044837
104	6	0	8.411502	2.499524	−0.213925
105	1	0	9.028089	0.794169	−1.348439
106	1	0	7.498497	4.065606	0.927255
107	1	0	9.370937	2.988549	−0.271565
108	6	0	4.237983	−1.159483	−1.016911
109	6	0	5.043365	−2.252010	−0.676636
110	6	0	3.512379	−1.234626	−2.205457
111	6	0	5.138116	−3.364108	−1.498752
112	1	0	5.609253	−2.233960	0.242764
113	6	0	3.593550	−2.350180	−3.026771
114	1	0	2.856273	−0.427842	−2.482267
115	6	0	4.410158	−3.414177	−2.679140
116	1	0	5.780177	−4.186088	−1.222092
117	1	0	3.018694	−2.385309	−3.938450
118	1	0	4.481710	−4.276192	−3.323832
119	6	0	4.024099	−0.204491	1.871288
120	6	0	4.837511	0.283076	2.895602
121	6	0	3.083458	−1.182755	2.207925
122	6	0	4.711398	−0.174108	4.199468
123	1	0	5.589682	1.023271	2.678294
124	6	0	2.954147	−1.646341	3.505537
125	1	0	2.431029	−1.584834	1.451527
126	6	0	3.769335	−1.140184	4.507045
127	1	0	5.352682	0.222706	4.970589
128	1	0	2.213856	−2.396850	3.732193
129	1	0	3.669644	−1.497683	5.519847

INTr1

BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −3955.01807854 a.u.
Sum of electronic and thermal Free Energies = −3954.065224 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −3957.94457004 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.012017	−5.219748	2.557966
2	6	0	0.178276	−4.205765	2.352530
3	6	0	2.195740	−5.637441	1.728353
4	6	0	0.509104	−4.189182	−0.825152
5	6	0	2.378993	−4.944147	0.394131
6	1	0	0.828672	−5.824165	3.431960
7	1	0	−0.639415	−4.011317	3.030827
8	1	0	2.141535	−6.710715	1.543685
9	1	0	0.941216	−3.196878	−0.886676
10	1	0	2.534327	−3.878930	0.482409
11	8	0	0.261539	−3.385254	1.297529
12	6	0	−0.785583	−4.429998	−1.378761
13	6	0	−1.423372	−3.375706	−2.038817
14	6	0	−1.413790	−5.674994	−1.240455
15	6	0	−2.679691	−3.577894	−2.582772
16	1	0	−0.932033	−2.416777	−2.092210
17	6	0	−2.668899	−5.860139	−1.772568
18	1	0	−0.912883	−6.467101	−0.711466
19	6	0	−3.294710	−4.812819	−2.446942
20	1	0	−3.180654	−2.772979	−3.093174
21	1	0	−3.167064	−6.809711	−1.669464
22	1	0	−4.277931	−4.963855	−2.863047
23	8	0	1.182621	−5.177391	−0.392902
24	1	0	3.191412	−5.385437	−0.169161
25	1	0	3.120036	−5.482394	2.289010
26	6	0	0.830127	5.618397	−2.839377
27	6	0	0.366130	4.729251	−1.913137
28	6	0	1.208759	3.722669	−1.383325
29	6	0	2.539924	3.651651	−1.860207
30	6	0	2.995667	4.596350	−2.807706
31	6	0	2.163191	5.562417	−3.288981
32	1	0	0.166291	6.370348	−3.234855
33	1	0	−0.657799	4.781953	−1.589347
34	6	0	0.764917	2.755814	−0.429789
35	6	0	3.393526	2.635996	−1.378444
36	1	0	4.016963	4.530242	−3.149142
37	1	0	2.515989	6.275796	−4.015926
38	6	0	2.966207	1.656089	−0.518084
39	6	0	1.608489	1.719708	−0.110248
40	1	0	4.417250	2.647324	−1.715619
41	6	0	−0.586913	2.840602	0.183684
42	6	0	−0.993599	3.992463	0.927341
43	6	0	−1.475387	1.802026	0.058097
44	6	0	−0.109535	5.044845	1.263645
45	6	0	−2.331985	4.078821	1.380074
46	6	0	−2.835997	1.877667	0.455584
47	6	0	−0.540705	6.122551	1.982803
48	1	0	0.919549	4.984102	0.958022
49	6	0	−2.752423	5.213604	2.109911
50	6	0	−3.228113	3.025253	1.095821
51	6	0	−1.879979	6.218633	2.405174
52	1	0	0.154454	6.907253	2.234676
53	1	0	−3.779416	5.262929	2.436687
54	1	0	−4.251762	3.142765	1.411285
55	1	0	−2.206461	7.078520	2.967142
56	8	0	1.133191	0.720752	0.690483
57	15	0	0.042062	−0.345067	0.112031
58	8	0	−1.062218	0.653834	−0.566052
59	8	0	0.605561	−1.156713	−0.996973
60	8	0	−0.529088	−1.011404	1.316391
61	1	0	−0.173819	−2.481105	1.404753
62	14	0	−4.112999	0.521320	0.127471
63	14	0	4.225166	0.371066	0.081621
64	6	0	−5.797512	1.239698	0.606250
65	6	0	−6.455004	0.881933	1.784226
66	6	0	−6.426187	2.174068	−0.223747
67	6	0	−7.681378	1.435248	2.124427
68	1	0	−6.008354	0.157719	2.446321
69	6	0	−7.649012	2.731545	0.110031
70	1	0	−5.956312	2.467846	−1.149902
71	6	0	−8.280485	2.362255	1.288574
72	1	0	−8.167681	1.139122	3.040467
73	1	0	−8.110621	3.450094	−0.548688
74	1	0	−9.234081	2.792799	1.550283
75	6	0	−4.270465	0.052389	−1.697036
76	6	0	−5.446542	−0.579788	−2.117587
77	6	0	−3.303249	0.318479	−2.669214
78	6	0	−5.645915	−0.940973	−3.440809
79	1	0	−6.230112	−0.781617	−1.403661
80	6	0	−3.502162	−0.030042	−3.997953
81	1	0	−2.378448	0.791176	−2.391868
82	6	0	−4.672109	−0.662438	−4.388076
83	1	0	−6.564779	−1.424294	−3.733515
84	1	0	−2.740963	0.196901	−4.727559
85	1	0	−4.827644	−0.928629	−5.421782
86	6	0	−3.815539	−0.990619	1.201989
87	6	0	−4.050019	−2.284480	0.737652
88	6	0	−3.421554	−0.839229	2.532907
89	6	0	−3.908461	−3.384978	1.568864
90	1	0	−4.342372	−2.440566	−0.287938
91	6	0	−3.291638	−1.931880	3.373456
92	1	0	−3.196673	0.143297	2.917075
93	6	0	−3.537817	−3.209207	2.892508
94	1	0	−4.088960	−4.376033	1.183113
95	1	0	−2.989663	−1.787658	4.398640
96	1	0	−3.441704	−4.062374	3.546277
97	6	0	5.909508	1.223055	−0.070116
98	6	0	6.981770	0.640381	−0.746516
99	6	0	6.129115	2.472276	0.522576
100	6	0	8.217774	1.267044	−0.822600
101	1	0	6.854333	−0.315256	−1.228172
102	6	0	7.360407	3.102230	0.453919
103	1	0	5.321948	2.969214	1.039035
104	6	0	8.411243	2.498113	−0.220227
105	1	0	9.026888	0.792773	−1.355250
106	1	0	7.498892	4.064180	0.921521
107	1	0	9.370834	2.986838	−0.278076
108	6	0	4.232481	−1.159092	−1.019362
109	6	0	5.040595	−2.250319	−0.681818
110	6	0	3.501199	−1.236921	−2.204233
111	6	0	5.134662	−3.362624	−1.503991
112	1	0	5.609964	−2.230677	0.235337
113	6	0	3.582185	−2.352105	−3.026314
114	1	0	2.842912	−0.430786	−2.478485
115	6	0	4.403109	−3.414217	−2.682238
116	1	0	5.780694	−4.182521	−1.230149
117	1	0	3.005840	−2.387417	−3.937216
118	1	0	4.476823	−4.274785	−3.328817
119	6	0	4.022572	−0.200876	1.866486
120	6	0	4.839795	0.283246	2.889434
121	6	0	3.081349	−1.178732	2.203142
122	6	0	4.716853	−0.176860	4.192585
123	1	0	5.592250	1.023077	2.671820
124	6	0	2.956746	−1.646453	3.499791
125	1	0	2.424493	−1.576935	1.448658
126	6	0	3.775315	−1.143463	4.500158
127	1	0	5.360493	0.217768	4.962912
128	1	0	2.218605	−2.398954	3.726521
129	1	0	3.678732	−1.503955	5.512236

TSr−int

BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −3955.01947267 a.u.
Sum of electronic and thermal Free Energies = −3954.064115 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −3957.94408726 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.604917	−4.140268	0.768409
2	8	0	−0.653017	−3.241376	−1.902780
3	6	0	−0.533737	5.510151	2.871882
4	6	0	−0.138106	4.650949	1.887262
5	6	0	−1.035135	3.697983	1.347006
6	6	0	−2.346215	3.645595	1.878991
7	6	0	−2.730536	4.558007	2.887872
8	6	0	−1.847943	5.475060	3.375651
9	1	0	0.170566	6.222034	3.271553
10	1	0	0.872715	4.688113	1.522992
11	6	0	−0.667463	2.765784	0.328099
12	6	0	−3.249888	2.674619	1.396568
13	1	0	−3.738110	4.506704	3.270247
14	1	0	−2.146620	6.164654	4.148370
15	6	0	−2.896254	1.728096	0.468032
16	6	0	−1.562153	1.781692	−0.014764
17	1	0	−4.252756	2.692239	1.791641
18	6	0	0.674978	2.813617	−0.309070
19	6	0	1.135696	3.975777	−1.002022
20	6	0	1.513749	1.729419	−0.235978
21	6	0	0.298152	5.078242	−1.292528
22	6	0	2.477167	4.020442	−1.452827
23	6	0	2.884560	1.772616	−0.600206
24	6	0	0.774349	6.161806	−1.973429
25	1	0	−0.731882	5.049335	−0.984474
26	6	0	2.944603	5.161983	−2.142111
27	6	0	3.330626	2.924947	−1.194230
28	6	0	2.115374	6.213546	−2.398204
29	1	0	0.114225	6.985419	−2.193250
30	1	0	3.972338	5.179706	−2.469807
31	1	0	4.364498	3.016599	−1.484318
32	1	0	2.477732	7.077978	−2.930434
33	8	0	−1.159632	0.832286	−0.910011
34	15	0	−0.102230	−0.326050	−0.464243
35	8	0	1.043813	0.561974	0.306040
36	8	0	−0.690644	−1.200461	0.584784
37	8	0	0.426080	−0.907848	−1.726114
38	14	0	4.107195	0.398474	−0.168844
39	14	0	−4.207817	0.475006	−0.083655
40	6	0	5.826003	1.014768	−0.663342
41	6	0	6.474084	0.560243	−1.812878
42	6	0	6.490158	1.967326	0.116786
43	6	0	7.725486	1.038334	−2.174088
44	1	0	5.999658	−0.181956	−2.434487
45	6	0	7.738847	2.449861	−0.238241

46	1	0	6.028117	2.334856	1.020190
47	6	0	8.360146	1.985112	−1.387869
48	1	0	8.203811	0.668429	−3.067181
49	1	0	8.228112	3.184379	0.381769
50	1	0	9.333604	2.357088	−1.665730
51	6	0	4.188808	0.100907	1.697270
52	6	0	5.318102	−0.530356	2.230940
53	6	0	3.196711	0.504437	2.594047
54	6	0	5.447907	−0.761710	3.591524
55	1	0	6.120570	−0.833300	1.576115
56	6	0	3.326276	0.287754	3.958855
57	1	0	2.307488	0.987940	2.230846
58	6	0	4.450476	−0.348603	4.461735
59	1	0	6.332174	−1.248302	3.972093
60	1	0	2.548437	0.620619	4.627771
61	1	0	4.553129	−0.512281	5.522997
62	6	0	3.796022	−1.201492	−1.102478
63	6	0	4.051115	−2.446762	−0.525621
64	6	0	3.404980	−1.173945	−2.442123
65	6	0	3.939384	−3.617349	−1.259384
66	1	0	4.340055	−2.507736	0.511393
67	6	0	3.305502	−2.338684	−3.185785
68	1	0	3.157908	−0.234508	−2.909771
69	6	0	3.576831	−3.563737	−2.595912
70	1	0	4.140130	−4.567793	−0.790334
71	1	0	3.008528	−2.289104	−4.221410
72	1	0	3.503856	−4.472054	−3.173658
73	6	0	−5.874727	1.321705	0.211154
74	6	0	−6.913027	0.691228	0.897916
75	6	0	−6.124893	2.603290	−0.292772
76	6	0	−8.146153	1.304220	1.068926
77	1	0	−6.760030	−0.292449	1.311236
78	6	0	−7.353965	3.220332	−0.128872
79	1	0	−5.343649	3.135273	−0.814106
80	6	0	−8.370661	2.569282	0.553626
81	1	0	−8.928891	0.792902	1.606704
82	1	0	−7.517210	4.208352	−0.529355
83	1	0	−9.328240	3.047608	0.685126
84	6	0	−4.137169	−1.085748	0.973058
85	6	0	−4.897642	−2.204303	0.618505
86	6	0	−3.380570	−1.162588	2.141938
87	6	0	−4.917046	−3.345587	1.406319
88	1	0	−5.484464	−2.186350	−0.287363
89	6	0	−3.387616	−2.303603	2.930560
90	1	0	−2.759661	−0.331209	2.428956
91	6	0	−4.158491	−3.396983	2.567055
92	1	0	−5.527504	−4.188027	1.119359
93	1	0	−2.792597	−2.336974	3.829589
94	1	0	−4.175268	−4.279646	3.187512
95	6	0	−4.126884	−0.037994	−1.892444
96	6	0	−4.954141	0.532680	−2.861134
97	6	0	−3.249900	−1.045075	−2.304372
98	6	0	−4.899554	0.126096	−4.186267
99	1	0	−5.659986	1.298361	−2.583543
100	6	0	−3.191412	−1.457021	−3.624107
101	1	0	−2.594722	−1.514273	−1.590887
102	6	0	−4.017086	−0.869306	−4.570494
103	1	0	−5.548817	0.585509	−4.914878
104	1	0	−2.494253	−2.228861	−3.906786
105	1	0	−3.972747	−1.185899	−5.600757
106	6	0	−0.779944	−5.460626	−2.633071
107	6	0	−0.203092	−4.263624	−2.637577
108	6	0	−2.002133	−5.864613	−1.854468
109	6	0	−2.310985	−5.060189	−0.609074
110	1	0	−0.348716	−6.218435	−3.265933
111	1	0	0.678094	−4.071218	−3.231211
112	1	0	−1.914103	−6.911751	−1.567192
113	1	0	−0.967120	−3.140175	0.539517
114	1	0	−2.492262	−4.015706	−0.805241
115	6	0	0.530333	−4.304571	1.611775
116	6	0	1.135727	−3.148730	2.121637
117	6	0	1.042283	−5.576642	1.918138
118	6	0	2.247454	−3.269295	2.937454
119	1	0	0.728407	−2.186127	1.853135
120	6	0	2.145004	−5.682084	2.730338
121	1	0	0.567857	−6.452951	1.511277
122	6	0	2.743655	−4.527364	3.237160
123	1	0	2.725513	−2.387473	3.328297
124	1	0	2.549313	−6.650247	2.974079
125	1	0	3.611712	−4.617151	3.870508
126	8	0	−1.174304	−5.166800	0.297907
127	1	0	−3.140237	−5.488338	−0.059577
128	1	0	−2.898881	−5.804791	−2.476531
129	1	0	−0.122690	−2.403488	−1.967527

INTr2

BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −3955.01978592 a.u.
Sum of electronic and thermal Free Energies = −3954.067887 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −3957.94963361 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.677574	4.061063	0.529253
2	6	0	0.533237	5.112089	−2.017085
3	6	0	−0.181039	−5.023389	3.331079
4	6	0	−0.489315	−4.245669	2.252107
5	6	0	0.508672	−3.494939	1.585173
6	6	0	1.831798	−3.558518	2.085461
7	6	0	2.122501	−4.383871	3.195639
8	6	0	1.141132	−5.104672	3.808154
9	1	0	−0.960444	−5.580392	3.825903
10	1	0	−1.506007	−4.192801	1.906439
11	6	0	0.236028	−2.653579	0.462891
12	6	0	2.842224	−2.792094	1.465877
13	1	0	3.139625	−4.424928	3.553196
14	1	0	1.369383	−5.728408	4.657085
15	6	0	2.587001	−1.926960	0.431494
16	6	0	1.241693	−1.850332	−0.013064
17	1	0	3.847735	−2.903739	1.838715
18	6	0	−1.115771	−2.611376	−0.153997
19	6	0	−1.714494	−3.790021	−0.697108
20	6	0	−1.823894	−1.434708	−0.207127
21	6	0	−1.008130	−5.004678	−0.863209
22	6	0	−3.062485	−3.740162	−1.123878
23	6	0	−3.207550	−1.375762	−0.530733
24	6	0	−1.615069	−6.100818	−1.405901
25	1	0	0.026196	−5.054545	−0.572959
26	6	0	−3.668477	−4.895534	−1.666474
27	6	0	−3.786561	−2.538289	−0.972204
28	6	0	−2.963882	−6.054206	−1.806387
29	1	0	−1.053243	−7.012089	−1.533905
30	1	0	−4.700444	−4.838211	−1.975586
31	1	0	−4.837332	−2.557820	−1.210576
32	1	0	−3.430074	−6.929875	−2.227858
33	8	0	0.941604	−0.972686	−1.014484
34	15	0	0.029577	0.346025	−0.728606
35	8	0	−1.199737	−0.270200	0.157861
36	8	0	0.741793	1.300562	0.161199
37	8	0	−0.447784	0.788933	−2.069335
38	1	0	0.322208	2.061397	−2.667718
39	14	0	−4.332826	0.099761	−0.154300
40	14	0	4.034584	−0.947046	−0.297647
41	6	0	−6.108693	−0.488207	−0.444814
42	6	0	−6.804432	−0.130256	−1.603368
43	6	0	−6.763406	−1.318283	0.467676
44	6	0	−8.089872	−0.589087	−1.846174
45	1	0	−6.339915	0.523463	−2.325022
46	6	0	−8.049975	−1.777920	0.233185
47	1	0	−6.265720	−1.606399	1.379956
48	6	0	−8.715980	−1.415588	−0.926613
49	1	0	−8.602951	−0.297449	−2.748960
50	1	0	−8.532759	−2.415587	0.956811
51	1	0	−9.717512	−1.770885	−1.110683
52	6	0	−4.197137	0.536779	1.676335
53	6	0	−5.217881	1.219163	2.340268
54	6	0	−3.118672	0.086785	2.441922
55	6	0	−5.178996	1.421473	3.711356
56	1	0	−6.058698	1.599181	1.782403
57	6	0	−3.071330	0.285754	3.812707
58	1	0	−2.298248	−0.425380	1.964221
59	6	0	−4.108492	0.946503	4.453289
60	1	0	−5.986637	1.944187	4.199528
61	1	0	−2.228394	−0.077390	4.378996
62	1	0	−4.083325	1.086945	5.523012
63	6	0	−4.096253	1.600952	−1.257998
64	6	0	−3.581643	1.511530	−2.551436
65	6	0	−4.477824	2.865970	−0.793927
66	6	0	−3.440787	2.643696	−3.343611
67	1	0	−3.263591	0.563021	−2.947141
68	6	0	−4.332004	3.997580	−1.578726
69	1	0	−4.912326	2.970541	0.188700
70	6	0	−3.810687	3.887311	−2.859379
71	1	0	−3.042765	2.546085	−4.341356
72	1	0	−4.633017	4.960313	−1.196674
73	1	0	−3.701939	4.765016	−3.476986
74	6	0	5.573688	−2.002238	0.016456
75	6	0	6.737909	−1.462750	0.565104
76	6	0	5.598294	−3.356514	−0.335601
77	6	0	7.876590	−2.233816	0.749596
78	1	0	6.759588	−0.425703	0.858546
79	6	0	6.732173	−4.131742	−0.157263
80	1	0	4.714242	−3.818967	−0.747497
81	6	0	7.877284	−3.569875	0.386927
82	1	0	8.760913	−1.789838	1.178749
83	1	0	6.721273	−5.172786	−0.438824
84	1	0	8.761080	−4.171161	0.529632
85	6	0	4.248041	0.685277	0.622470
86	6	0	5.094648	1.675481	0.115146
87	6	0	3.646378	0.919998	1.858878
88	6	0	5.347737	2.841861	0.821761
89	1	0	5.565822	1.533838	−0.845458
90	6	0	3.892730	2.085006	2.570280
91	1	0	2.969290	0.188536	2.268137
92	6	0	4.748288	3.046778	2.055735
93	1	0	6.017553	3.583827	0.415304
94	1	0	3.416203	2.241333	3.525043
95	1	0	4.946886	3.949481	2.612025
96	6	0	3.946911	−0.585126	−2.141590
97	6	0	4.654458	−1.347280	−3.072446
98	6	0	3.200430	0.493246	−2.624703
99	6	0	4.608618	−1.054578	−4.427745
100	1	0	5.258224	−2.176467	−2.741542
101	6	0	3.152519	0.794255	−3.974714
102	1	0	2.638281	1.104539	−1.939323
103	6	0	3.857374	0.016214	−4.881171
104	1	0	5.162448	−1.662175	−5.125934
105	1	0	2.556009	1.626764	−4.310676
106	1	0	3.820029	0.244215	−5.934776
107	6	0	1.972872	5.462780	−2.246599
108	6	0	2.916774	4.656979	−1.361793
109	1	0	−0.131628	5.862415	−1.625135
110	1	0	2.274134	5.253818	−3.272949
111	1	0	2.141052	6.522362	−2.073527
112	1	0	2.866686	3.599443	−1.584031
113	1	0	3.939680	5.004726	−1.411711
114	8	0	2.526712	4.854661	0.018531
115	6	0	0.037261	3.902094	−2.285928
116	1	0	−0.995679	3.655392	−2.085869
117	8	0	0.779629	2.932223	−2.811559
118	6	0	1.087129	4.368071	1.787057
119	6	0	1.356229	5.571316	2.458199
120	6	0	0.217411	3.418580	2.337958
121	6	0	0.759354	5.814024	3.671960
122	1	0	2.024650	6.289669	2.015367
123	6	0	−0.379013	3.678259	3.559121
124	1	0	0.038007	2.499482	1.800676
125	6	0	−0.107220	4.866349	4.218082
126	1	0	0.955208	6.732382	4.199667
127	1	0	−1.057867	2.959459	3.984002
128	1	0	−0.574133	5.066085	5.169347
129	1	0	1.440250	3.116494	0.044847

TSr_{ac}−*anti*

BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −3955.02262262 a.u.
Sum of electronic and thermal Free Energies = −3954.065550 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −3957.94974037 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.223900	−4.232926	−0.431087
2	6	0	0.136354	−4.915477	1.618303
3	6	0	0.273480	5.150622	−3.348224
4	6	0	−0.100374	4.390033	−2.277787
5	6	0	0.833799	3.562736	−1.608817

6	6	0	2.160556	3.527966	−2.102410
7	6	0	2.520819	4.337994	−3.203451
8	6	0	1.601470	5.136627	−3.815444
9	1	0	−0.458923	5.766644	−3.844791
10	1	0	−1.121705	4.408747	−1.942980
11	6	0	0.491465	2.737321	−0.492933
12	6	0	3.103811	2.674384	−1.491358
13	1	0	3.540190	4.303133	−3.555081
14	1	0	1.882069	5.747817	−4.657762
15	6	0	2.777569	1.821884	−0.466836
16	6	0	1.431646	1.855549	−0.019040
17	1	0	4.114445	2.703611	−1.865690
18	6	0	−0.868174	2.784955	0.107226
19	6	0	−1.410885	3.995610	0.639724
20	6	0	−1.645798	1.655033	0.151960
21	6	0	−0.642423	5.170459	0.813041
22	6	0	−2.765693	4.017898	1.049525
23	6	0	−3.028910	1.663476	0.467910
24	6	0	−1.196520	6.299409	1.345121
25	1	0	0.396694	5.163216	0.535814
26	6	0	−3.314567	5.205825	1.582543
27	6	0	−3.552219	2.853614	0.904046
28	6	0	−2.550736	6.325812	1.728081
29	1	0	−0.588422	7.179647	1.478438
30	1	0	−4.351376	5.204752	1.880638
31	1	0	−4.598430	2.923331	1.151803
32	1	0	−2.974824	7.226247	2.141770
33	8	0	1.068864	1.002693	0.984337
34	15	0	0.058985	−0.243355	0.719813
35	8	0	−1.090289	0.454497	−0.214073
36	8	0	0.686349	−1.292494	−0.122034
37	8	0	−0.487005	−0.600363	2.063081
38	1	0	0.075775	−1.922669	2.582886
39	14	0	−4.183309	0.198207	0.151882
40	14	0	4.133092	0.692958	0.227164
41	6	0	−5.936095	0.801471	0.528999
42	6	0	−6.596765	0.460303	1.710318
43	6	0	−6.611815	1.633528	−0.369879
44	6	0	−7.872210	0.931208	1.987015
45	1	0	−6.113281	−0.185580	2.425531
46	6	0	−7.884742	2.107783	−0.100000
47	1	0	−6.139182	1.911652	−1.299293
48	6	0	−8.518771	1.756522	1.082507
49	1	0	−8.359670	0.650405	2.907183
50	1	0	−8.382627	2.747512	−0.811422
51	1	0	−9.510922	2.122271	1.294666
52	6	0	−4.187556	−0.312469	−1.668316
53	6	0	−5.314415	−0.962854	−2.184262
54	6	0	−3.130926	−0.066497	−2.548566
55	6	0	−5.382473	−1.359750	−3.510390
56	1	0	−6.163121	−1.150292	−1.545040
57	6	0	−3.199257	−0.448421	−3.881008
58	1	0	−2.239808	0.422221	−2.197151
59	6	0	−4.323344	−1.099127	−4.365358
60	1	0	−6.265371	−1.858916	−3.877207
61	1	0	−2.374320	−0.229580	−4.540870
62	1	0	−4.377927	−1.391246	−5.402341
63	6	0	−3.866901	−1.282094	1.266815
64	6	0	−3.429994	−1.110545	2.581703
65	6	0	−4.198687	−2.575590	0.855432
66	6	0	−3.355352	−2.181268	3.459489
67	1	0	−3.122832	−0.135524	2.921592
68	6	0	−4.122863	−3.651196	1.727306
69	1	0	−4.527012	−2.747807	−0.157552
70	6	0	−3.708441	−3.453108	3.035943
71	1	0	−3.012870	−2.022389	4.469355
72	1	0	−4.391708	−4.639203	1.387694
73	1	0	−3.653795	−4.286037	3.719107
74	6	0	5.761445	1.603976	−0.085351
75	6	0	6.858277	0.971615	−0.672314
76	6	0	5.921738	2.939263	0.301620
77	6	0	8.062634	1.635081	−0.858269
78	1	0	6.773521	−0.053233	−0.995509
79	6	0	7.121871	3.607074	0.122228
80	1	0	5.092610	3.472706	0.741189
81	6	0	8.198240	2.953712	−0.458963
82	1	0	8.892439	1.121282	−1.317317
83	1	0	7.216092	4.636044	0.431322
84	1	0	9.133321	3.471427	−0.602572
85	6	0	4.165495	−0.937734	−0.715208
86	6	0	4.948912	−2.000391	−0.254091
87	6	0	3.467108	−1.119895	−1.908421
88	6	0	5.044418	−3.188175	−0.962744
89	1	0	5.491914	−1.900903	0.673512
90	6	0	3.553375	−2.307420	−2.620049
91	1	0	2.835606	−0.330951	−2.281705
92	6	0	4.345179	−3.343124	−2.150728
93	1	0	5.665002	−3.989022	−0.591585
94	1	0	2.999619	−2.423761	−3.538069
95	1	0	4.415981	−4.265923	−2.704600
96	6	0	4.025504	0.307423	2.066846
97	6	0	4.783348	1.001660	3.010732
98	6	0	3.205482	−0.725273	2.530963
99	6	0	4.716337	0.689330	4.360879
100	1	0	5.444367	1.791962	2.694370
101	6	0	3.134926	−1.043993	3.875899
102	1	0	2.604364	−1.284471	1.833640
103	6	0	3.891395	−0.333610	4.796111
104	1	0	5.311132	1.244149	5.069230
105	1	0	2.480900	−1.837463	4.199805
106	1	0	3.837156	−0.576686	5.845612
107	6	0	1.428640	−5.478374	2.120704
108	6	0	2.586271	−4.962666	1.254350
109	1	0	−0.559658	−5.557456	1.107560
110	1	0	1.619465	−5.181144	3.148937
111	1	0	1.410752	−6.563463	2.083434
112	1	0	2.809050	−3.922568	1.467346
113	1	0	3.485873	−5.557756	1.332953
114	8	0	2.145932	−5.079585	−0.099322
115	6	0	−0.278113	−3.665099	1.938467
116	1	0	−1.210079	−3.273670	1.557074
117	8	0	0.435809	−2.864303	2.678236
118	6	0	0.390507	−4.528022	−1.563875
119	6	0	0.391682	−5.793609	−2.161776
120	6	0	−0.436921	−3.513336	−2.055075
121	6	0	−0.428244	−6.036800	−3.241847
122	1	0	1.034565	−6.564503	−1.772416
123	6	0	−1.263131	−3.772126	−3.134265
124	1	0	−0.411927	−2.543240	−1.583330
125	6	0	−1.257240	−5.027274	−3.723450
126	1	0	−0.431710	−7.007231	−3.710006
127	1	0	−1.911011	−2.997343	−3.508699
128	1	0	−1.902846	−5.225740	−4.563897
129	1	0	1.270834	−3.216014	−0.062505

TSr_{ac}-*syn*

BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −3955.00494940 a.u.
Sum of electronic and thermal Free Energies = −3954.047610 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −3957.94392272 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.603762	4.758420	0.768823
2	6	0	0.537055	4.621869	1.607824
3	6	0	2.278979	3.663644	0.017117
4	6	0	0.147760	5.123023	−1.082375
5	6	0	1.998866	3.816241	−1.481311
6	1	0	2.080140	5.727032	0.796180
7	1	0	0.175558	5.510212	2.109472
8	1	0	1.924729	2.694095	0.340170
9	1	0	0.750567	6.015072	−1.177026
10	1	0	2.522171	4.667840	−1.912173
11	8	0	−0.182970	3.586346	1.886529
12	6	0	−1.255344	5.247184	−0.821797
13	6	0	−1.789364	6.519916	−0.588454
14	6	0	−2.071632	4.111515	−0.791634
15	6	0	−3.135286	6.659403	−0.332583
16	1	0	−1.146132	7.386292	−0.611782
17	6	0	−3.421810	4.266914	−0.533967
18	1	0	−1.648706	3.132380	−0.968317
19	6	0	−3.947891	5.529658	−0.305506
20	1	0	−3.556017	7.635342	−0.156282
21	1	0	−4.061479	3.402528	−0.510126
22	1	0	−5.001362	5.637396	−0.103655
23	8	0	0.593811	4.033524	−1.603493
24	1	0	2.215312	2.924030	−2.047860
25	1	0	3.354272	3.686496	0.172283
26	1	0	0.124064	2.664337	1.561319
27	6	0	−0.355780	−5.420338	−2.979303
28	6	0	0.058035	−4.524323	−2.036347
29	6	0	−0.859325	−3.637018	−1.423303
30	6	0	−2.212955	−3.693572	−1.831439
31	6	0	−2.614525	−4.643642	−2.798413
32	6	0	−1.709309	−5.491952	−3.362376
33	1	0	0.362777	−6.079553	−3.439384
34	1	0	1.096931	−4.478770	−1.762414
35	6	0	−0.477024	−2.668147	−0.447209
36	6	0	−3.140323	−2.801114	−1.255989
37	1	0	−3.653636	−4.676556	−3.086612
38	1	0	−2.020843	−6.209992	−4.103489
39	6	0	−2.777733	−1.811819	−0.375115
40	6	0	−1.403138	−1.741323	−0.036442
41	1	0	−4.175458	−2.916986	−1.536677
42	6	0	0.896771	−2.650501	0.115208
43	6	0	1.406673	−3.797106	0.798174
44	6	0	1.695087	−1.536398	−0.000450
45	6	0	0.607011	−4.917238	1.130907
46	6	0	2.764253	−3.812280	1.191020
47	6	0	3.080613	−1.546532	0.328099
48	6	0	1.138028	−5.986663	1.792452
49	1	0	−0.436270	−4.914829	0.871292
50	6	0	3.291114	−4.940768	1.859672
51	6	0	3.571832	−2.695551	0.897930
52	6	0	2.498651	−6.009235	2.155141
53	1	0	0.506567	−6.823362	2.044730
54	1	0	4.333050	−4.933400	2.139294
55	1	0	4.617994	−2.767511	1.145383
56	1	0	2.903444	−6.864481	2.671356
57	8	0	−0.967969	−0.730004	0.779323
58	15	0	−0.071000	0.454356	0.107800
59	8	0	1.168357	−0.399290	−0.551441
60	8	0	−0.788376	1.134305	−0.988164
61	8	0	0.471052	1.246621	1.261012
62	14	0	4.350823	−0.178327	0.016516
63	14	0	−4.197295	−0.746964	0.292922
64	6	0	4.131357	0.707706	−1.638862
65	6	0	3.287280	0.247707	−2.650944
66	6	0	4.932986	1.818083	−1.926842
67	6	0	3.242724	0.869083	−3.891996
68	1	0	2.642402	−0.594354	−2.472416
69	6	0	4.896614	2.441007	−3.164015
70	1	0	5.604395	2.204388	−1.176114
71	6	0	4.047842	1.965620	−4.152991
72	1	0	2.576328	0.493567	−4.651806
73	1	0	5.533314	3.290056	−3.358058
74	1	0	4.016713	2.444617	−5.118809
75	6	0	4.425014	1.041356	1.450017
76	6	0	5.545599	1.860423	1.634394
77	6	0	3.375635	1.167596	2.361374
78	6	0	5.606735	2.780594	2.668390
79	1	0	6.395994	1.765825	0.976658
80	6	0	3.432747	2.086764	3.399538
81	1	0	2.486811	0.571949	2.251340
82	6	0	4.545326	2.896660	3.554042
83	1	0	6.483714	3.397047	2.789126
84	1	0	2.602958	2.165775	4.083496
85	1	0	4.591275	3.608491	4.363256
86	6	0	6.051280	−1.002008	−0.086203
87	6	0	6.549600	−1.458555	−1.308874
88	6	0	6.841091	−1.208727	1.048089
89	6	0	7.776139	−2.097724	−1.396599
90	1	0	5.974851	−1.308164	−2.209166
91	6	0	8.069329	−1.847280	0.967899
92	1	0	6.496561	−0.860744	2.009308
93	6	0	8.539423	−2.293977	−0.256612
94	1	0	8.136723	−2.439387	−2.353886
95	1	0	8.658703	−1.992436	1.859451
96	1	0	9.495297	−2.788992	−0.322607
97	6	0	−5.615265	−1.983531	0.515323
98	6	0	−6.851483	−1.863003	−0.119506
99	6	0	−5.425849	−3.098402	1.340640
100	6	0	−7.858033	−2.800329	0.069441
101	1	0	−7.035965	−1.032609	−0.780812
102	6	0	−6.426517	−4.034318	1.538700
103	1	0	−4.476290	−3.244255	1.833162
104	6	0	−7.650085	−3.885673	0.902406

105	1	0	−8.802507	−2.681136	−0.437719
106	1	0	−6.250899	−4.881138	2.183079
107	1	0	−8.431073	−4.614336	1.051273
108	6	0	−4.690986	0.535769	−0.997050
109	6	0	−5.850872	1.298854	−0.816434
110	6	0	−3.951992	0.746527	−2.162084
111	6	0	−6.277360	2.204630	−1.774739
112	1	0	−6.434828	1.181712	0.084170
113	6	0	−4.368947	1.661362	−3.119440
114	1	0	−3.030859	0.210262	−2.315725
115	6	0	−5.536430	2.382904	−2.934326
116	1	0	−7.183166	2.769232	−1.617675
117	1	0	−3.777984	1.808324	−4.009316
118	1	0	−5.864142	3.086349	−3.683453
119	6	0	−3.908719	0.128424	1.932491
120	6	0	−4.532569	−0.283100	3.111347
121	6	0	−3.101945	1.268319	1.992331
122	6	0	−4.347359	0.403732	4.302400
123	1	0	−5.178454	−1.145404	3.106347
124	6	0	−2.910476	1.957184	3.177170
125	1	0	−2.608624	1.622522	1.102375
126	6	0	−3.533851	1.522987	4.337606
127	1	0	−4.839864	0.062634	5.199456
128	1	0	−2.265277	2.819909	3.189669
129	1	0	−3.385595	2.055814	5.263864

CPs

BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −3064.18567114 a.u.
Sum of electronic and thermal Free Energies = −3063.398355 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −3066.68631141 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.751957	−3.154986	0.734941
2	8	0	2.106668	−2.758923	−0.475205
3	6	0	−1.777955	6.094811	0.686363
4	6	0	−1.784241	4.730856	0.732967
5	6	0	−0.595437	3.989679	0.532326
6	6	0	0.597013	4.702617	0.249343
7	6	0	0.573473	6.116043	0.223576
8	6	0	−0.584850	6.800551	0.439967
9	1	0	−2.697163	6.637860	0.834614
10	1	0	−2.705911	4.207390	0.913738
11	6	0	−0.554421	2.561610	0.562498
12	6	0	1.786146	3.992731	−0.022411
13	1	0	1.492057	6.642109	0.016712
14	1	0	−0.594497	7.877853	0.411853
15	6	0	1.818317	2.627931	−0.070936
16	6	0	0.614693	1.938894	0.205794
17	1	0	2.689016	4.548112	−0.220157
18	6	0	−1.736914	1.738343	0.930859
19	6	0	−2.386943	1.878960	2.196862
20	6	0	−2.202128	0.777706	0.067022
21	6	0	−1.897918	2.720952	3.224651
22	6	0	−3.549568	1.112309	2.460775
23	6	0	−3.371751	0.016518	0.300834
24	6	0	−2.544153	2.816588	4.423139
25	1	0	−0.998285	3.285884	3.058912
26	6	0	−4.205274	1.245750	3.706234
27	6	0	−4.027001	0.215024	1.482404
28	6	0	−3.719076	2.080503	4.667542
29	1	0	−2.148590	3.459898	5.192318
30	1	0	−5.095215	0.662679	3.883395
31	1	0	−4.926418	−0.344358	1.684054
32	1	0	−4.222551	2.171697	5.616083
33	8	0	0.629473	0.562462	0.143425
34	15	0	−0.093264	−0.128826	−1.128437
35	8	0	−1.536093	0.556761	−1.120390
36	8	0	0.609843	0.030075	−2.394489
37	6	0	−3.901379	−0.942305	−0.709569
38	6	0	−4.578196	−0.451105	−1.836435
39	6	0	−3.773434	−2.323336	−0.502670
40	6	0	−4.745620	0.943097	−2.089512
41	6	0	−5.145057	−1.369700	−2.774814
42	6	0	−4.355694	−3.232195	−1.443746
43	6	0	−3.068379	−2.879058	0.607676
44	6	0	−5.408264	1.385378	−3.187353
45	1	0	−4.335801	1.652910	−1.392503
46	6	0	−5.833217	−0.863733	−3.914891
47	6	0	−5.023777	−2.733882	−2.551913
48	6	0	−4.234934	−4.634929	−1.222531
49	1	0	−2.587055	−2.217487	1.305051
50	6	0	−2.969154	−4.220613	0.777482
51	6	0	−5.961492	0.469415	−4.119549
52	1	0	−5.517454	2.444208	−3.357772
53	1	0	−6.251025	−1.571422	−4.613726
54	1	0	−5.458892	−3.423794	−3.259011
55	6	0	−3.568048	−5.116834	−0.146779
56	1	0	−4.685548	−5.304419	−1.938453
57	1	0	−2.413781	−4.611274	1.614290
58	1	0	−6.482994	0.841376	−4.986476
59	1	0	−3.479360	−6.179965	0.008565
60	6	0	3.079992	1.900609	−0.385714
61	6	0	3.580185	1.899051	−1.696348
62	6	0	3.783991	1.255362	0.642541
63	6	0	2.887145	2.501521	−2.789405
64	6	0	4.830570	1.257652	−1.972695
65	6	0	5.019849	0.597509	0.348654
66	6	0	3.325837	1.231523	1.994189
67	6	0	3.408612	2.494889	−4.040656
68	1	0	1.924970	2.946547	−2.612973
69	6	0	5.344887	1.278835	−3.301709
70	6	0	5.515045	0.623392	−0.947146
71	6	0	5.721043	−0.065957	1.397205
72	1	0	2.410820	1.740735	2.242597
73	6	0	4.020815	0.585526	2.964842
74	6	0	4.661832	1.881944	−4.303711
75	1	0	2.860662	2.946639	−4.851201
76	1	0	6.293332	0.800271	−3.489727
77	1	0	6.453865	0.136125	−1.162653
78	6	0	5.238228	−0.079888	2.664256
79	1	0	6.652911	−0.554503	1.157803
80	1	0	3.650291	0.578460	3.976965
81	1	0	5.058455	1.891033	−5.306006
82	1	0	5.777106	−0.584801	3.449401
83	8	0	−0.362319	−1.575392	−0.595714
84	1	0	0.435367	−2.137420	−0.529437
85	6	0	3.990343	−2.960771	−1.982388
86	6	0	4.698563	−4.169807	−1.445591
87	6	0	4.712848	−4.287518	0.064060
88	6	0	2.869961	−2.397844	−1.559096
89	1	0	4.235843	−5.068834	−1.855318
90	1	0	5.250112	−3.448370	0.508037
91	1	0	4.405226	−2.510596	−2.870315
92	1	0	5.730183	−4.170030	−1.794155
93	1	0	5.206008	−5.206277	0.364652
94	1	0	2.418919	−1.576222	−2.090429
95	1	0	3.461115	−2.363747	0.979318
96	8	0	3.413918	−4.355772	0.608393
97	6	0	1.684782	−3.269546	1.791623
98	6	0	1.103753	−2.112458	2.294790
99	6	0	1.272601	−4.506304	2.266676
100	6	0	0.114995	−2.190836	3.261597
101	1	0	1.420372	−1.149577	1.928757
102	6	0	0.285880	−4.583707	3.237114
103	1	0	1.733726	−5.398894	1.882769
104	6	0	−0.295327	−3.427821	3.735619
105	1	0	−0.331172	−1.287189	3.644372
106	1	0	−0.024734	−5.547687	3.607342
107	1	0	−1.059405	−3.489900	4.493984

TSs_{oo}

BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −3064.14698247 a.u.
Sum of electronic and thermal Free Energies = −3063.360532 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −3066.67038525 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.466016	−2.983028	1.042192
2	8	0	1.470028	−3.240160	−0.819687
3	6	0	−1.215494	6.117054	0.907648
4	6	0	−1.332909	4.757280	0.904764
5	6	0	−0.219564	3.928727	0.625210
6	6	0	1.015206	4.554050	0.316719
7	6	0	1.107745	5.964493	0.341482
8	6	0	0.020631	6.732895	0.633377
9	1	0	−2.079766	6.726760	1.116109
10	1	0	−2.286731	4.303219	1.105972
11	6	0	−0.297433	2.502987	0.603621
12	6	0	2.130242	3.759185	−0.024025
13	1	0	2.057741	6.421732	0.112891
14	1	0	0.099410	7.807796	0.643615
15	6	0	2.044035	2.398955	−0.112064
16	6	0	0.799236	1.791176	0.180149
17	1	0	3.069594	4.245523	−0.234716
18	6	0	−1.532273	1.764036	0.977309
19	6	0	−2.129979	1.888148	2.269247
20	6	0	−2.089957	0.888361	0.074554
21	6	0	−1.548304	2.638541	3.320342
22	6	0	−3.339070	1.196536	2.536297
23	6	0	−3.311608	0.210535	0.316774
24	6	0	−2.146714	2.719436	4.544784
25	1	0	−0.616208	3.146576	3.147989
26	6	0	−3.941822	1.312643	3.810155
27	6	0	−3.913703	0.391789	1.529029
28	6	0	−3.364476	2.058346	4.794708
29	1	0	−1.681219	3.294113	5.329270
30	1	0	−4.868659	0.790243	3.989228
31	1	0	−4.847877	−0.107135	1.732960
32	1	0	−3.830566	2.137773	5.763394
33	8	0	0.709360	0.435506	0.083008
34	15	0	−0.126895	−0.224079	−1.197065
35	8	0	−1.477216	0.691815	−1.125947
36	8	0	0.560699	0.033868	−2.467392
37	6	0	−3.948808	−0.649412	−0.720441
38	6	0	−4.603978	−0.050533	−1.807460
39	6	0	−3.950560	−2.044022	−0.574369
40	6	0	−4.638473	1.362337	−2.003112
41	6	0	−5.285020	−0.870677	−2.761074
42	6	0	−4.650500	−2.853002	−1.525619
43	6	0	−3.267663	−2.710336	0.487347
44	6	0	−5.284152	1.911719	−3.061887
45	1	0	−4.136944	1.998670	−1.295510
46	6	0	−5.951207	−0.253751	−3.858888
47	6	0	−5.297315	−2.247873	−2.592257
48	6	0	−4.670246	−4.268014	−1.354744
49	1	0	−2.689736	−2.124292	1.177469
50	6	0	−3.307174	−4.059477	0.612398
51	6	0	−5.951875	1.092673	−4.009167
52	1	0	−5.290117	2.982032	−3.190285
53	1	0	−6.456690	−0.888073	−4.570288
54	1	0	−5.822276	−2.861992	−3.308311
55	6	0	−4.027297	−4.855124	−0.317379
56	1	0	−5.209722	−4.861067	−2.076728
57	1	0	−2.770749	−4.538075	1.416106
58	1	0	−6.457610	1.548595	−4.844949
59	1	0	−4.047798	−5.926686	−0.199169
60	6	0	3.242730	1.586900	−0.465008
61	6	0	3.726094	1.575501	−1.781006
62	6	0	3.923713	0.883280	0.541474
63	6	0	3.035848	2.212098	−2.855973
64	6	0	4.948820	0.891933	−2.081042
65	6	0	5.133837	0.186219	0.226635
66	6	0	3.464076	0.836003	1.892582
67	6	0	3.541375	2.204352	−4.113444
68	1	0	2.084856	2.671595	−2.660226
69	6	0	5.449049	0.917078	−3.415222
70	6	0	5.622484	0.219390	−1.072534
71	6	0	5.816292	−0.520222	1.260761
72	1	0	2.567086	1.370201	2.152975
73	6	0	4.132391	0.136096	2.845570
74	6	0	4.772924	1.557742	−4.398472
75	1	0	2.995398	2.677530	−4.912797
76	1	0	6.378640	0.410460	−3.622973
77	1	0	6.547246	−0.288219	−1.303093
78	6	0	5.330772	−0.555662	2.527298
79	1	0	6.738658	−1.022870	1.011754
80	1	0	3.760527	0.114509	3.857116
81	1	0	5.157935	1.568932	−5.405405
82	1	0	5.858279	−1.091841	3.299731
83	8	0	−0.429044	−1.605883	−0.705425
84	1	0	0.623873	−2.676299	−0.779272
85	6	0	3.396652	−3.330215	−2.163102
86	6	0	4.125735	−4.330137	−1.306427

87	6	0	4.459866	−3.848837	0.090917
88	6	0	2.184498	−2.859802	−1.910346
89	1	0	3.560485	−5.258265	−1.215239
90	1	0	4.811391	−2.823066	0.102145
91	1	0	3.888528	−2.968900	−3.049892
92	1	0	5.070471	−4.591453	−1.778353
93	1	0	5.185631	−4.490846	0.574681
94	1	0	1.704475	−2.121721	−2.534657
95	1	0	2.740538	−2.016957	0.646405
96	8	0	3.306666	−3.941073	0.967029
97	6	0	1.383150	−3.098432	1.980079
98	6	0	0.606955	−1.970243	2.246495
99	6	0	1.128297	−4.308976	2.634116
100	6	0	−0.410260	−2.049324	3.181271
101	1	0	0.785277	−1.053109	1.712369
102	6	0	0.110122	−4.378835	3.558420
103	1	0	1.730895	−5.172078	2.410773
104	6	0	−0.655537	−3.247691	3.832253
105	1	0	−1.013079	−1.181251	3.389900
106	1	0	−0.093566	−5.305220	4.068929
107	1	0	−1.450650	−3.307447	4.557897

INTs1
BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −3064.14608884 a.u.
Sum of electronic and thermal Free Energies = −3063.362175 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −3066.67078908 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.493582	−2.977306	1.068341
2	8	0	1.448636	−3.241321	−0.880631
3	6	0	−1.226159	6.111330	0.927022
4	6	0	−1.341395	4.751388	0.919490
5	6	0	−0.227092	3.925620	0.635549
6	6	0	1.006265	4.554014	0.327647
7	6	0	1.096573	5.964508	0.357270
8	6	0	0.008614	6.730124	0.653305
9	1	0	−2.091132	6.718905	1.138770
10	1	0	−2.294221	4.295085	1.120345
11	6	0	−0.302701	2.499841	0.609027
12	6	0	2.122125	3.762152	−0.017367
13	1	0	2.045532	6.424079	0.129047
14	1	0	0.085681	7.805108	0.667235
15	6	0	2.037984	2.402104	−0.110096
16	6	0	0.794549	1.791295	0.181603
17	1	0	3.060416	4.250742	−0.227572
18	6	0	−1.535860	1.757589	0.981724
19	6	0	−2.132060	1.876178	2.274876
20	6	0	−2.093328	0.884210	0.076615
21	6	0	−1.550203	2.623791	3.327850
22	6	0	−3.339686	1.181683	2.541070
23	6	0	−3.313570	0.203568	0.318044
24	6	0	−2.147127	2.699401	4.553355
25	1	0	−0.619152	3.133931	3.156068
26	6	0	−3.940942	1.292323	3.816120
27	6	0	−3.914355	0.379573	1.531721
28	6	0	−3.363495	2.035474	4.802542
29	1	0	−1.681520	3.272053	5.339254
30	1	0	−4.866703	0.767803	3.994564
31	1	0	−4.847457	−0.121571	1.735116
32	1	0	−3.828434	2.110731	5.772114
33	8	0	0.706720	0.435834	0.079793
34	15	0	−0.130163	−0.220574	−1.201503
35	8	0	−1.481857	0.692889	−1.125377
36	8	0	0.555340	0.042962	−2.471813
37	6	0	−3.950757	−0.653737	−0.721364
38	6	0	−4.608320	−0.052079	−1.805400
39	6	0	−3.950078	−2.048855	−0.580217
40	6	0	−4.645340	1.361415	−1.996015
41	6	0	−5.289303	−0.869947	−2.761009
42	6	0	−4.649973	−2.855597	−1.533398
43	6	0	−3.264713	−2.717812	0.478241
44	6	0	−5.293296	1.913491	−3.051994
45	1	0	−4.143900	1.996053	−1.286829
46	6	0	−5.957926	−0.250223	−3.855761
47	6	0	−5.299165	−2.247748	−2.597041
48	6	0	−4.667223	−4.271233	−1.367496
49	1	0	−2.686817	−2.133279	1.169669
50	6	0	−3.301894	−4.067448	0.598578
51	6	0	−5.960953	1.096720	−4.001283
52	1	0	−5.301148	2.984240	−3.176603
53	1	0	−6.463329	−0.882842	−4.568733
54	1	0	−5.824084	−2.860180	−3.314570
55	6	0	−4.021965	−4.860966	−0.333056
56	1	0	−5.206699	−4.862602	−2.090861
57	1	0	−2.763642	−4.548016	1.399886
58	1	0	−6.468521	1.554775	−4.834784
59	1	0	−4.040590	−5.932970	−0.218605
60	6	0	3.237514	1.593230	−0.467480
61	6	0	3.719160	1.587255	−1.784144
62	6	0	3.920953	0.887159	0.535615
63	6	0	3.026475	2.226530	−2.855948
64	6	0	4.942584	0.906719	−2.088198
65	6	0	5.131777	0.193162	0.216727
66	6	0	3.463175	0.834373	1.887150
67	6	0	3.530355	2.224037	−4.114102
68	1	0	2.075006	2.683803	−2.657331
69	6	0	5.441012	0.937378	−3.422937
70	6	0	5.618656	0.231705	−1.082958
71	6	0	5.816729	−0.515826	1.247454
72	1	0	2.565673	1.366205	2.150606
73	6	0	4.133869	0.132183	2.836781
74	6	0	4.762563	1.580420	−4.403029
75	1	0	2.982565	2.699154	−4.911061
76	1	0	6.371140	0.432993	−3.633697
77	1	0	6.543927	−0.273598	−1.316523
78	6	0	5.332937	−0.556518	2.514494
79	1	0	6.739571	−1.016107	0.995462
80	1	0	3.763375	0.106427	3.848732
81	1	0	5.146227	1.595784	−5.410421
82	1	0	5.862322	−1.094570	3.284335
83	8	0	−0.429446	−1.604589	−0.714350
84	1	0	0.625089	−2.673042	−0.793360
85	6	0	3.397086	−3.317606	−2.183132
86	6	0	4.128902	−4.319371	−1.330952
87	6	0	4.464104	−3.842469	0.067643
88	6	0	2.184513	−2.850039	−1.927124
89	1	0	3.565263	−5.248724	−1.242300
90	1	0	4.813997	−2.816180	0.082032
91	1	0	3.887212	−2.952372	−3.069285
92	1	0	5.073433	−4.577499	−1.805039
93	1	0	5.191535	−4.485013	0.548183
94	1	0	1.702484	−2.110533	−2.548193
95	1	0	2.766031	−2.009404	0.675609
96	8	0	3.312210	−3.939653	0.944938
97	6	0	1.412141	−3.097763	2.007236
98	6	0	0.634488	−1.971772	2.278655
99	6	0	1.160093	−4.311017	2.657328
100	6	0	−0.381364	−2.055789	3.214481
101	1	0	0.810634	−1.052472	1.747538
102	6	0	0.143252	−4.385776	3.582716
103	1	0	1.763780	−5.172354	2.430147
104	6	0	−0.623859	−3.256840	3.861548
105	1	0	−0.985300	−1.189429	3.426966
106	1	0	−0.058276	−5.314284	4.090217
107	1	0	−1.417917	−3.320436	4.588020

INTs2
BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −3064.14934160 a.u.
Sum of electronic and thermal Free Energies = −3063.361628 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −3066.67852723 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.960204	−3.430173	−2.791035
2	6	0	−1.641595	−4.185816	−1.717210
3	6	0	−1.384318	−2.084350	−3.084315
4	6	0	−3.593629	−2.186902	−1.127443
5	6	0	−2.247431	−0.938944	−2.532703
6	1	0	−2.622111	−3.884295	−3.511910
7	1	0	−2.088949	−5.165491	−1.620899
8	1	0	−0.396210	−1.981824	−2.654788
9	1	0	−4.216163	−2.360413	−1.993401
10	1	0	−3.131301	−0.753501	−3.136065
11	8	0	−0.855547	−3.919073	−0.706444
12	6	0	−3.933977	−2.798911	0.110476
13	6	0	−5.048647	−3.651573	0.132501
14	6	0	−3.180939	−2.573820	1.270163
15	6	0	−5.409920	−4.275444	1.303227
16	1	0	−5.615348	−3.817860	−0.770640
17	6	0	−3.560035	−3.207762	2.439051
18	1	0	−2.325268	−1.911672	1.264958
19	6	0	−4.659805	−4.051315	2.456075
20	1	0	−6.263177	−4.932153	1.329776
21	1	0	−2.988326	−3.038782	3.335432
22	1	0	−4.941590	−4.542521	3.373675
23	8	0	−2.691484	−1.296798	−1.211968
24	1	0	−1.687188	−0.027599	−2.400272
25	1	0	−1.304876	−1.930228	−4.158654
26	1	0	−0.396626	−3.030045	−0.715037
27	6	0	2.316886	5.625478	2.008725
28	6	0	2.285084	4.445249	1.324153
29	6	0	1.055706	3.836716	0.973294
30	6	0	−0.142151	4.473491	1.384536
31	6	0	−0.076697	5.703025	2.079203
32	6	0	1.123604	6.272215	2.383572
33	1	0	3.265896	6.064808	2.270600
34	1	0	3.205543	3.959493	1.053999
35	6	0	0.976919	2.598660	0.265041
36	6	0	−1.382205	3.861945	1.104152
37	1	0	−0.999883	6.177021	2.374118
38	1	0	1.164159	7.206738	2.919160
39	6	0	−1.461237	2.643178	0.493350
40	6	0	−0.254559	2.006446	0.108971
41	1	0	−2.288855	4.367866	1.396623
42	6	0	2.181080	1.911701	−0.271012
43	6	0	3.057762	2.537171	−1.210171
44	6	0	2.432500	0.612408	0.101745
45	6	0	2.806420	3.812217	−1.772539
46	6	0	4.216369	1.840498	−1.636815
47	6	0	3.588585	−0.095132	−0.312634
48	6	0	3.668737	4.369161	−2.672342
49	1	0	1.915753	4.343802	−1.489034
50	6	0	5.097707	2.450208	−2.558747
51	6	0	4.460345	0.538341	−1.151384
52	6	0	4.836588	3.688264	−3.065482
53	1	0	3.451391	5.339351	−3.089440
54	1	0	5.979652	1.907784	−2.861830
55	1	0	5.351859	0.023322	−1.472704
56	1	0	5.512294	4.142674	−3.771769
57	8	0	−0.334513	0.778910	−0.478757
58	15	0	0.124463	−0.546903	0.402850
59	8	0	1.569457	−0.014686	0.948121
60	8	0	−0.747949	−0.735638	1.575029
61	6	0	3.862283	−1.482374	0.156468
62	6	0	4.309093	−1.699186	1.468759
63	6	0	3.724566	−2.559968	−0.730448
64	6	0	4.473865	−0.639543	2.409651
65	6	0	4.632432	−3.025201	1.896142
66	6	0	4.065259	−3.880655	−0.295808
67	6	0	3.244082	−2.404534	−2.066224
68	6	0	4.911835	−0.878881	3.670807
69	1	0	4.240843	0.365885	2.106488
70	6	0	5.089191	−3.233727	3.229442
71	6	0	4.507974	−4.079783	1.002954
72	6	0	3.944606	−4.967034	−1.210714
73	1	0	2.945091	−1.426461	−2.396489
74	6	0	3.142744	−3.464837	−2.905346
75	6	0	5.224393	−2.197703	4.091986
76	1	0	5.022945	−0.061374	4.364680
77	1	0	5.325757	−4.240810	3.535867
78	1	0	4.761696	−5.077909	1.326785
79	6	0	3.504660	−4.769172	−2.476077
80	1	0	4.212269	−5.954263	−0.867561
81	1	0	2.775201	−3.321830	−3.908937
82	1	0	5.569726	−2.367351	5.099109
83	1	0	3.418207	−5.598423	−3.159773
84	6	0	−2.791659	2.036350	0.201711
85	6	0	−3.539474	1.439854	1.227160
86	6	0	−3.321267	2.127204	−1.095299
87	6	0	−3.036075	1.291686	2.554798
88	6	0	−4.857443	0.951145	0.950855
89	6	0	−4.627093	1.608460	−1.368144
90	6	0	−2.607231	2.731287	−2.174110

91	6	0	−3.796932	0.743533	3.534078
92	1	0	−2.027060	1.595908	2.761939
93	6	0	−5.623159	0.383449	2.010322
94	6	0	−5.365051	1.041534	−0.337612
95	6	0	−5.146360	1.699276	−2.692893
96	1	0	−1.630635	3.140585	−1.983354
97	6	0	−3.134571	2.794610	−3.423382
98	6	0	−5.114855	0.290380	3.262661
99	1	0	−3.393931	0.635701	4.527730
100	1	0	−6.619260	0.031801	1.790677
101	1	0	−6.361562	0.677033	−0.539338
102	6	0	−4.425632	2.268087	−3.691097
103	1	0	−6.136318	1.312583	−2.881300
104	1	0	−2.574144	3.254782	−4.220927
105	1	0	−5.704222	−0.137127	4.057995
106	1	0	−4.832245	2.335398	−4.687385
107	8	0	0.317194	−1.605214	−0.632375

TSs_{oo}-*syn*
BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −3064.14890712 a.u.
Sum of electronic and thermal Free Energies = −3063.361383 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −3066.67691233 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.041797	3.466331	−2.574680
2	6	0	1.645774	4.164588	−1.468470
3	6	0	1.426664	2.184560	−3.035355
4	6	0	3.563246	2.281723	−1.220969
5	6	0	2.241670	0.969391	−2.550000
6	1	0	2.703153	3.997038	−3.241317
7	1	0	2.100201	5.129655	−1.286531
8	1	0	0.419838	2.080911	−2.653003
9	1	0	4.204066	2.435908	−2.077172
10	1	0	3.085694	0.753085	−3.199699
11	8	0	0.820508	3.833160	−0.536385
12	6	0	3.955880	2.849614	0.039029
13	6	0	5.045607	3.728817	0.056724
14	6	0	3.275347	2.536266	1.219088
15	6	0	5.453909	4.293823	1.244281
16	1	0	5.562415	3.962685	−0.861629
17	6	0	3.701377	3.107891	2.405452
18	1	0	2.437470	1.853809	1.219263
19	6	0	4.776964	3.981347	2.419876
20	1	0	6.292295	4.970103	1.263627
21	1	0	3.183483	2.865165	3.317662
22	1	0	5.096276	4.423172	3.350138
23	8	0	2.750013	1.284817	−1.254490
24	1	0	1.637588	0.085919	−2.419163
25	1	0	1.386744	2.154432	−4.121306
26	1	0	0.364271	2.918892	−0.602288
27	6	0	−2.429191	−5.612248	1.993047
28	6	0	−2.375878	−4.429561	1.314045
29	6	0	−1.135717	−3.846544	0.958121
30	6	0	0.050661	−4.511038	1.358637
31	6	0	−0.037421	−5.742412	2.047536
32	6	0	−1.247967	−6.286777	2.356806
33	1	0	−3.385895	−6.031981	2.259046
34	1	0	−3.287254	−3.922421	1.052456
35	6	0	−1.033800	−2.606948	0.255443
36	6	0	1.302172	−3.924383	1.075506
37	1	0	0.877007	−6.237812	2.334336
38	1	0	−1.305536	−7.222893	2.888029
39	6	0	1.404951	−2.704143	0.471160
40	6	0	0.209713	−2.042362	0.094939
41	1	0	2.199231	−4.450147	1.362313
42	6	0	−2.225251	−1.889894	−0.269373
43	6	0	−3.123007	−2.490628	−1.204816
44	6	0	−2.443038	−0.586232	0.108848
45	6	0	−2.905828	−3.769204	−1.773356
46	6	0	−4.267427	−1.764952	−1.621224
47	6	0	−3.581606	0.152419	−0.299346
48	6	0	−3.787671	−4.302466	−2.668504
49	1	0	−2.025792	−4.322593	−1.498600
50	6	0	−5.170004	−2.350646	−2.538239
51	6	0	−4.474985	−0.457690	−1.132778
52	6	0	−4.942114	−3.592926	−3.050526
53	1	0	−3.596247	−5.275941	−3.090553
54	1	0	−6.040918	−1.786411	−2.833279
55	1	0	−5.354304	0.080906	−1.449006
56	1	0	−5.633652	−4.028934	−3.753064
57	8	0	0.313053	−0.813008	−0.488821
58	15	0	−0.106248	0.512699	0.401510
59	8	0	−1.559877	0.017455	0.953281
60	8	0	0.779421	0.698817	1.561243
61	6	0	−3.811760	1.548782	0.165922
62	6	0	−4.237728	1.785488	1.481645
63	6	0	−3.651800	2.617640	−0.728182
64	6	0	−4.425003	0.735653	2.429274
65	6	0	−4.515702	3.122812	1.905798
66	6	0	−3.947183	3.950165	−0.296532
67	6	0	−3.191796	2.441651	−2.068767
68	6	0	−4.841852	0.994246	3.693727
69	1	0	−4.226537	−0.277842	2.128455
70	6	0	−4.951277	3.351519	3.242880
71	6	0	−4.368789	4.168933	1.006131
72	6	0	−3.804362	5.028101	−1.218331
73	1	0	−2.927609	1.453301	−2.398152
74	6	0	−3.068510	3.494437	−2.914668
75	6	0	−5.108903	2.324048	4.111756
76	1	0	−4.970786	0.183801	4.392732
77	1	0	−5.153398	4.366764	3.546923
78	1	0	−4.588317	5.175828	1.327738
79	6	0	−3.385788	4.811251	−2.487916
80	1	0	−4.038949	6.024442	−0.877287
81	1	0	−2.719593	3.334975	−3.922500
82	1	0	−5.437814	2.508824	5.121679
83	1	0	−3.284116	5.634193	−3.177190
84	6	0	2.745030	−2.118120	0.183068
85	6	0	3.509062	−1.557370	1.216539
86	6	0	3.264222	−2.189109	−1.119100
87	6	0	3.016356	−1.425670	2.549974
88	6	0	4.834029	−1.087224	0.942432
89	6	0	4.578065	−1.689729	−1.388140
90	6	0	2.533052	−2.755252	−2.206832
91	6	0	3.792258	−0.909941	3.534982
92	1	0	2.003654	−1.716871	2.758417
93	6	0	5.615970	−0.554424	2.008162
94	6	0	5.332721	−1.160845	−0.350044
95	6	0	5.087943	−1.759923	−2.717541
96	1	0	1.550103	−3.150960	−2.019940
97	6	0	3.052283	−2.800844	−3.460264
98	6	0	5.116901	−0.475728	3.264984
99	1	0	3.396535	−0.813781	4.532824
100	1	0	6.616343	−0.215182	1.788638
101	1	0	6.333492	−0.807862	−0.550546
102	6	0	4.351431	−2.292568	−3.724142
103	1	0	6.083550	−1.386555	−2.902902
104	1	0	2.478781	−3.232777	−4.264374
105	1	0	5.718046	−0.073570	4.064691
106	1	0	4.751127	−2.344961	−4.724171
107	8	0	−0.292258	1.577887	−0.636609

TSs_{oo}-*anti*
BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −3064.15767026 a.u.
Sum of electronic and thermal Free Energies = −3063.370463 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −3066.67444302 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.008699	4.061157	−0.746525
2	6	0	1.899213	4.482163	1.460610
3	6	0	3.267001	4.641377	0.874967
4	6	0	3.295118	4.001691	−0.518643
5	1	0	1.283184	5.344085	1.645944
6	1	0	4.019409	4.144373	1.482955
7	1	0	3.533065	5.691097	0.794831
8	1	0	3.239017	2.920699	−0.454621
9	1	0	4.147128	4.295714	−1.116317
10	8	0	2.141678	4.504670	−1.196916
11	6	0	1.497167	3.277496	1.943761
12	1	0	0.505315	3.134224	2.350902
13	8	0	2.270693	2.237777	1.877991
14	6	0	−0.167296	4.855416	−0.971933
15	6	0	−0.067639	6.187077	−1.394905
16	6	0	−1.419170	4.271594	−0.756489
17	6	0	−1.212441	6.924324	−1.599349
18	1	0	0.904200	6.620634	−1.557027
19	6	0	−2.562078	5.025033	−0.960817
20	1	0	−1.472608	3.241393	−0.440592
21	6	0	−2.458079	6.342553	−1.378487
22	1	0	−1.144856	7.948740	−1.926349
23	1	0	−3.528587	4.579784	−0.798275
24	1	0	−3.351552	6.925515	−1.535597
25	1	0	0.900995	3.012437	−0.501386
26	6	0	−1.529623	−4.833728	−3.659764
27	6	0	−0.911634	−4.190084	−2.626935
28	6	0	−1.623325	−3.294426	−1.792303
29	6	0	−2.989433	−3.060232	−2.085159
30	6	0	−3.606524	−3.754883	−3.150867
31	6	0	−2.897458	−4.626613	−3.921739
32	1	0	−0.963059	−5.504978	−4.284798
33	1	0	0.135448	−4.355143	−2.447519
34	6	0	−1.017010	−2.598920	−0.700249
35	6	0	−3.707758	−2.121710	−1.317328
36	1	0	−4.651042	−3.570725	−3.348110
37	1	0	−3.374039	−5.147776	−4.736025
38	6	0	−3.113207	−1.382725	−0.333467
39	6	0	−1.741186	−1.619082	−0.060563
40	1	0	−4.753856	−1.969758	−1.530594
41	6	0	0.378074	−2.888676	−0.277397
42	6	0	0.797370	−4.199550	0.109232
43	6	0	1.292718	−1.865880	−0.224363
44	6	0	−0.098396	−5.286529	0.251140
45	6	0	2.164983	−4.422465	0.407612
46	6	0	2.666105	−2.074139	0.053762
47	6	0	0.344935	−6.519998	0.632086
48	1	0	−1.145995	−5.130807	0.065952
49	6	0	2.596102	−5.715288	0.783294
50	6	0	3.073780	−3.345151	0.342008
51	6	0	1.710206	−6.745354	0.891143
52	1	0	−0.358795	−7.329428	0.740689
53	1	0	3.642919	−5.866692	0.995541
54	1	0	4.115767	−3.532162	0.548059
55	1	0	2.046994	−7.726208	1.184885
56	8	0	−1.166585	−0.893344	0.940020
57	15	0	0.023136	0.185785	0.670986
58	8	0	0.877286	−0.592371	−0.488694
59	8	0	−0.450422	1.445581	0.053449
60	6	0	3.655701	−0.960595	0.006790
61	6	0	4.062229	−0.441918	−1.233447
62	6	0	4.232142	−0.484265	1.193954
63	6	0	3.509740	−0.886443	−2.471694
64	6	0	5.082886	0.560022	−1.282319
65	6	0	5.264022	0.507076	1.132129
66	6	0	3.820819	−0.936683	2.484763
67	6	0	3.924237	−0.370008	−3.655728
68	1	0	2.747244	−1.644804	−2.457954
69	6	0	5.492443	1.073830	−2.547083
70	6	0	5.664187	1.000812	−0.100588
71	6	0	5.862732	0.964111	2.342112
72	1	0	3.008897	−1.636902	2.552952
73	6	0	4.409505	−0.467665	3.612654
74	6	0	4.931913	0.628453	−3.697787
75	1	0	3.486924	−0.720047	−4.576622
76	1	0	6.268067	1.824070	−2.566612
77	1	0	6.451652	1.738897	−0.143134
78	6	0	5.455088	0.490338	3.543536
79	1	0	6.651030	1.698147	2.276640
80	1	0	4.073860	−0.815735	4.575886
81	1	0	5.250783	1.023692	−4.648800
82	1	0	5.913892	0.843564	4.453008
83	6	0	−3.916526	−0.388951	0.431727
84	6	0	−4.443652	0.733598	−0.227398
85	6	0	−4.222583	−0.619367	1.783267
86	6	0	−4.145115	1.043480	−1.590226
87	6	0	−5.320234	1.621335	0.475757
88	6	0	−5.070901	0.295186	2.483794
89	6	0	−3.742564	−1.756515	2.498880
90	6	0	−4.713840	2.104902	−2.215013
91	1	0	−3.448675	0.420985	−2.122114
92	6	0	−5.899871	2.723593	−0.218641
93	6	0	−5.603781	1.385997	1.812070
94	6	0	−5.375365	0.053928	3.854610

95	1	0	−3.115772	−2.466566	1.990514
96	6	0	−4.058383	−1.953724	3.802915
97	6	0	−5.621404	2.952603	−1.525329
98	1	0	−4.471901	2.313907	−3.244484
99	1	0	−6.577339	3.366273	0.322025
100	1	0	−6.261896	2.060036	2.339317
101	6	0	−4.884629	−1.032541	4.497613
102	1	0	−6.011441	0.758345	4.367530
103	1	0	−3.677351	−2.818328	4.321560
104	1	0	−6.078187	3.780054	−2.044776
105	1	0	−5.120878	−1.206148	5.534990
106	8	0	0.800478	0.222975	1.948480
107	1	0	1.741896	1.376274	2.016188

F1

BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −2526.13905818 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −2528.17169712 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.422184	−0.151858	−2.449190
2	6	0	4.649105	0.523830	−1.282978
3	6	0	3.068759	−0.487344	−2.986998
4	6	0	4.468644	−2.168371	−1.231752
5	6	0	2.663814	−1.928123	−2.617382
6	1	0	5.281040	−0.260261	−3.092666
7	1	0	5.668736	0.794628	−1.042187
8	1	0	2.317992	0.180081	−2.585092
9	1	0	5.036639	−2.492675	−2.091819
10	1	0	3.076523	−2.661565	−3.305136
11	8	0	3.823689	0.867108	−0.355326
12	6	0	5.106342	−2.184932	0.055619
13	6	0	6.482378	−2.439038	0.108244
14	6	0	4.379663	−1.956857	1.227699
15	6	0	7.130902	−2.464228	1.322746
16	1	0	7.031984	−2.613340	−0.804285
17	6	0	5.044819	−1.991073	2.441006
18	1	0	3.316243	−1.766641	1.200489
19	6	0	6.407398	−2.237987	2.490340
20	1	0	8.189237	−2.660219	1.368937
21	1	0	4.488041	−1.821275	3.346778
22	1	0	6.914488	−2.257819	3.441668
23	8	0	3.184850	−2.198857	−1.316814
24	1	0	1.596141	−2.054670	−2.536044
25	1	0	3.061449	−0.400276	−4.070583
26	1	0	2.836845	0.622536	−0.476596
27	6	0	−5.538067	−2.993012	1.550274
28	6	0	−4.582996	−2.216655	0.960575
29	6	0	−3.318339	−2.750827	0.614320
30	6	0	−3.061038	−4.108595	0.930108
31	6	0	−4.076016	−4.890995	1.527009
32	6	0	−5.290315	−4.350816	1.828817
33	1	0	−6.490636	−2.560808	1.811092
34	1	0	−4.784931	−1.179024	0.763678
35	6	0	−2.287578	−1.972578	0.003909
36	6	0	−1.789000	−4.654113	0.656362
37	1	0	−3.864175	−5.925078	1.749830
38	1	0	−6.056074	−4.953248	2.289810
39	6	0	−0.776074	−3.896023	0.142491
40	6	0	−1.042144	−2.535026	−0.149031
41	1	0	−1.611465	−5.694796	0.877407
42	6	0	−2.503694	−0.568051	−0.431696
43	6	0	−3.508642	−0.213535	−1.383694
44	6	0	−1.674713	0.417627	0.049183
45	6	0	−4.311770	−1.169046	−2.052382
46	6	0	−3.691662	1.153383	−1.711927
47	6	0	−1.844414	1.787975	−0.270056
48	6	0	−5.256847	−0.785540	−2.959609
49	1	0	−4.165783	−2.213961	−1.844937
50	6	0	−4.689093	1.520028	−2.644291
51	6	0	−2.857494	2.125904	−1.121197
52	6	0	−5.459931	0.576050	−3.254492
53	1	0	−5.851710	−1.533527	−3.458683
54	1	0	−4.820143	2.566521	−2.871401
55	1	0	−3.012611	3.163579	−1.371110
56	1	0	−6.214513	0.865244	−3.967836
57	8	0	−0.022748	−1.772885	−0.641715
58	15	0	0.671658	−0.656469	0.356994
59	8	0	−0.673585	0.082480	0.911098
60	8	0	1.346625	−1.287182	1.501831
61	6	0	−0.956749	2.837149	0.304888
62	6	0	−1.106399	3.220679	1.646198
63	6	0	−0.009843	3.473961	−0.510776
64	6	0	−2.058814	2.613131	2.517415
65	6	0	−0.293043	4.270544	2.177091
66	6	0	0.788224	4.533349	0.027724
67	6	0	0.208904	3.105904	−1.873284
68	6	0	−2.183995	3.007601	3.809002
69	1	0	−2.683976	1.825264	2.135982
70	6	0	−0.455835	4.654638	3.539365
71	6	0	0.628360	4.902836	1.354549
72	6	0	1.731856	5.190979	−0.814379
73	1	0	−0.353217	2.286673	−2.283170
74	6	0	1.117853	3.756620	−2.641064
75	6	0	−1.368956	4.044743	4.332917
76	1	0	−2.907773	2.529051	4.448680
77	1	0	0.168139	5.446181	3.924246
78	1	0	1.233976	5.700884	1.756805
79	6	0	1.889924	4.822704	−2.108003
80	1	0	2.318910	5.992190	−0.393112
81	1	0	1.263791	3.459926	−3.667500
82	1	0	−1.482763	4.342611	5.362768
83	1	0	2.604968	5.329319	−2.736271
84	8	0	1.395275	0.249844	−0.592686
85	1	0	0.212916	−4.282592	−0.027767

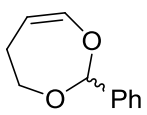
F2

BHandHLYP/6−31G*; SCF Done: E(RBHandHLYP) = −2526.14413856 a.u.
CPCM(toluene)/B3LYP−D/6−311+G**; SCF Done: E(RB3LYP) = −2528.18172615 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.109953	−3.615399	1.343267
2	6	0	3.319324	−3.886934	0.020191
3	6	0	1.807205	−3.167431	1.922679
4	6	0	3.726937	−1.379375	0.930759
5	6	0	1.765553	−1.634573	2.080955
6	1	0	3.892321	−3.943100	2.009570
7	1	0	4.278020	−4.296814	−0.269396
8	1	0	0.982160	−3.456094	1.285019
9	1	0	4.248534	−1.514524	1.867337
10	1	0	2.243978	−1.301782	2.998361
11	8	0	2.551730	−3.683952	−0.994348
12	6	0	4.496989	−1.079567	−0.244567
13	6	0	5.892228	−1.162435	−0.159389
14	6	0	3.877940	−0.712440	−1.442835
15	6	0	6.666257	−0.882215	−1.263286
16	1	0	6.357823	−1.447338	0.771852
17	6	0	4.669898	−0.428434	−2.541862
18	1	0	2.802546	−0.638215	−1.519016
19	6	0	6.050165	−0.515715	−2.456613
20	1	0	7.740137	−0.943501	−1.202910
21	1	0	4.197535	−0.140010	−3.465410
22	1	0	6.655612	−0.295907	−3.321294
23	8	0	2.478415	−1.071160	0.980661
24	1	0	0.766371	−1.234484	2.016779
25	1	0	1.656940	−3.613869	2.902426
26	1	0	1.632955	−3.265099	−0.824654
27	6	0	−5.483188	2.729909	−1.684843
28	6	0	−4.790861	1.593284	−1.382518
29	6	0	−3.489496	1.655922	−0.828338
30	6	0	−2.912740	2.935361	−0.628720
31	6	0	−3.661054	4.094374	−0.937486
32	6	0	−4.919966	3.998998	−1.450757
33	1	0	−6.469800	2.655603	−2.112964
34	1	0	−5.231665	0.631925	−1.576700
35	6	0	−2.726536	0.492275	−0.504981
36	6	0	−1.593453	3.031228	−0.137908
37	1	0	−3.208422	5.058950	−0.768454
38	1	0	−5.480711	4.888090	−1.689304
39	6	0	−0.832380	1.923082	0.102019
40	6	0	−1.415545	0.651088	−0.121674
41	1	0	−1.172888	4.009467	0.034065
42	6	0	−3.287130	−0.880396	−0.608239
43	6	0	−4.447278	−1.284568	0.121558
44	6	0	−2.638929	−1.812208	−1.383854
45	6	0	−5.098446	−0.450373	1.062440
46	6	0	−4.955372	−2.594468	−0.067386
47	6	0	−3.133804	−3.125373	−1.582000
48	6	0	−6.201584	−0.880072	1.741962
49	1	0	−4.709140	0.534686	1.247627
50	6	0	−6.108570	−3.004786	0.639984
51	6	0	−4.286697	−3.478157	−0.940634
52	6	0	−6.724167	−2.168934	1.523174
53	1	0	−6.675705	−0.226904	2.456807
54	1	0	−6.485986	−4.001577	0.473052
55	1	0	−4.688189	−4.468899	−1.083886
56	1	0	−7.600041	−2.492811	2.061538
57	8	0	−0.646629	−0.455083	0.097235
58	15	0	−0.097469	−1.296888	−1.212647
59	8	0	−1.496988	−1.455401	−2.036646
60	8	0	0.823930	−0.496486	−2.033872
61	6	0	0.556261	2.063465	0.625662
62	6	0	1.595396	2.468395	−0.224325
63	6	0	0.804477	1.849298	1.990492
64	6	0	1.407659	2.663864	−1.626002
65	6	0	2.903506	2.693311	0.314164
66	6	0	2.121861	2.048662	2.512699
67	6	0	−0.216885	1.443107	2.901600
68	6	0	2.424580	3.088626	−2.415742
69	1	0	0.448817	2.440576	−2.055626
70	6	0	3.942972	3.141769	−0.551564
71	6	0	3.134785	2.474443	1.664429
72	6	0	2.360655	1.817814	3.899023
73	1	0	−1.217134	1.304534	2.530116
74	6	0	0.051180	1.230088	4.215197
75	6	0	3.711154	3.341932	−1.871056
76	1	0	2.261235	3.222630	−3.472574
77	1	0	4.919975	3.318154	−0.129220
78	1	0	4.122147	2.648614	2.065830
79	6	0	1.362757	1.417285	4.725572
80	1	0	3.357612	1.980307	4.279376
81	1	0	−0.738088	0.922671	4.881991
82	1	0	4.503975	3.684176	−2.516767
83	1	0	1.555430	1.251727	5.773440
84	8	0	0.301138	−2.618430	−0.628221
85	1	0	−2.590775	−3.796118	−2.223234

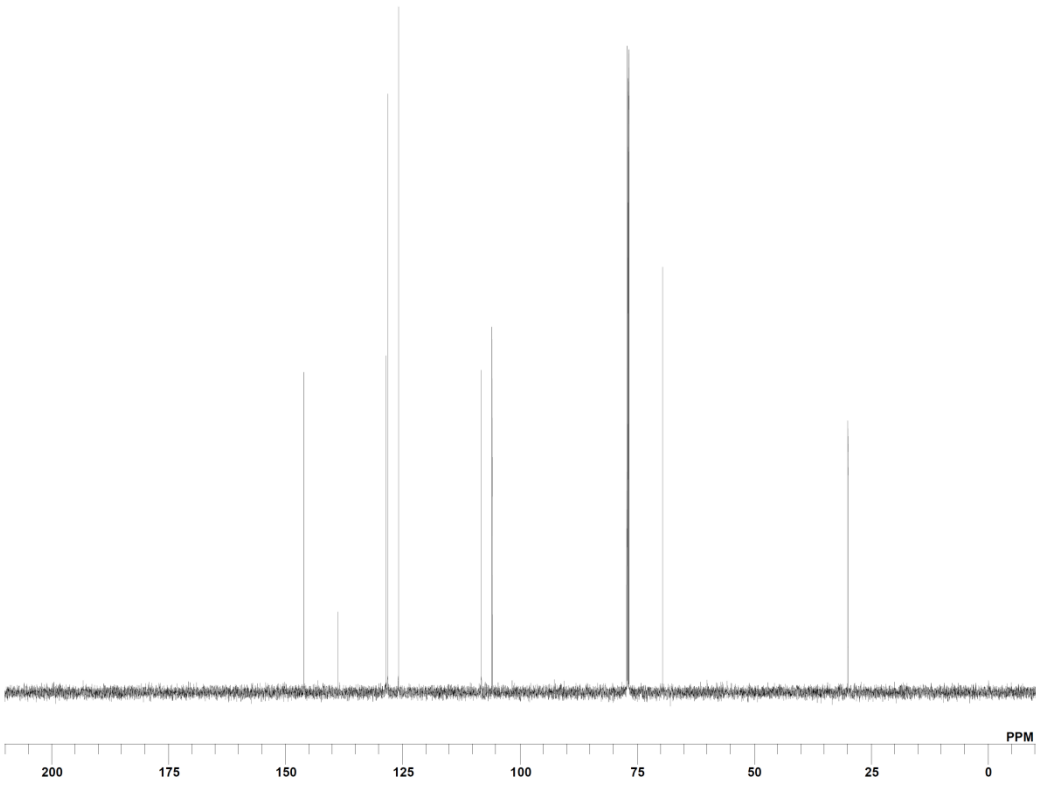
7. ^{1}H and ^{13}C NMR, HPLC Charts

Ph_sm_H

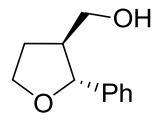


(±)-**2a**

Ph_sm_H

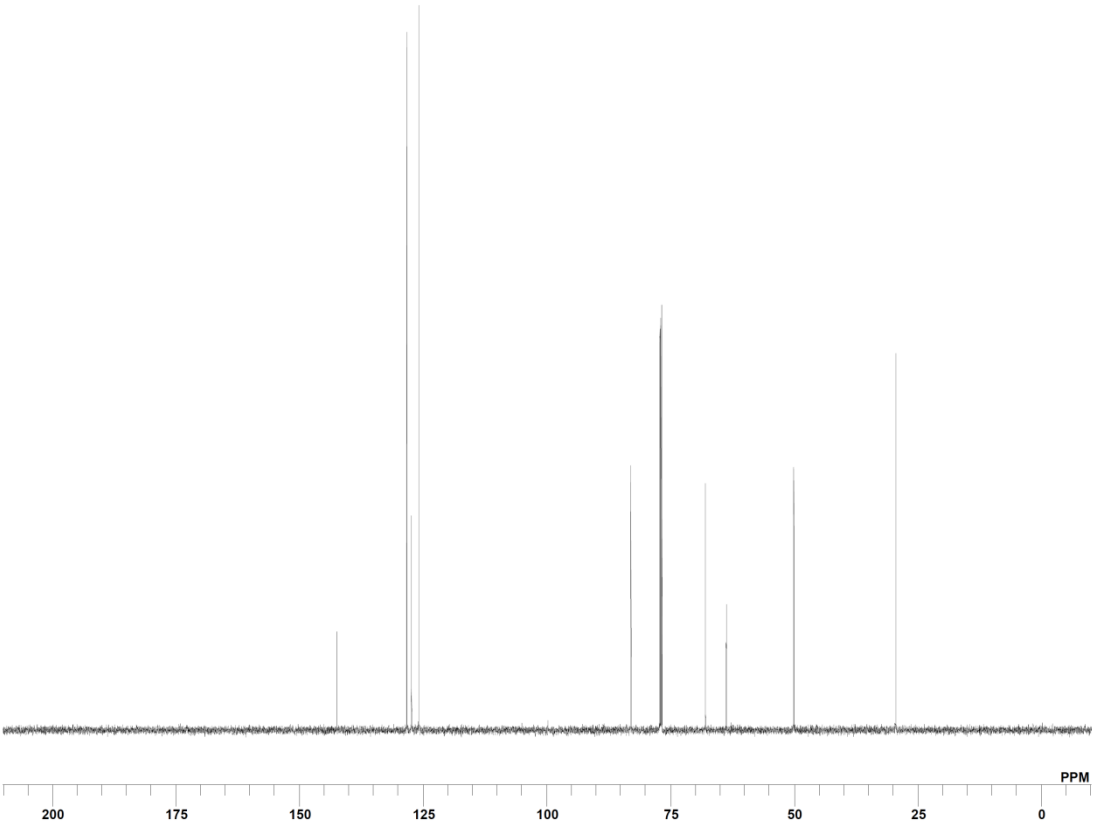


product_anti_H

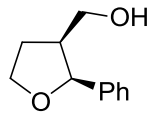


anti-**4a**

product_anti_C

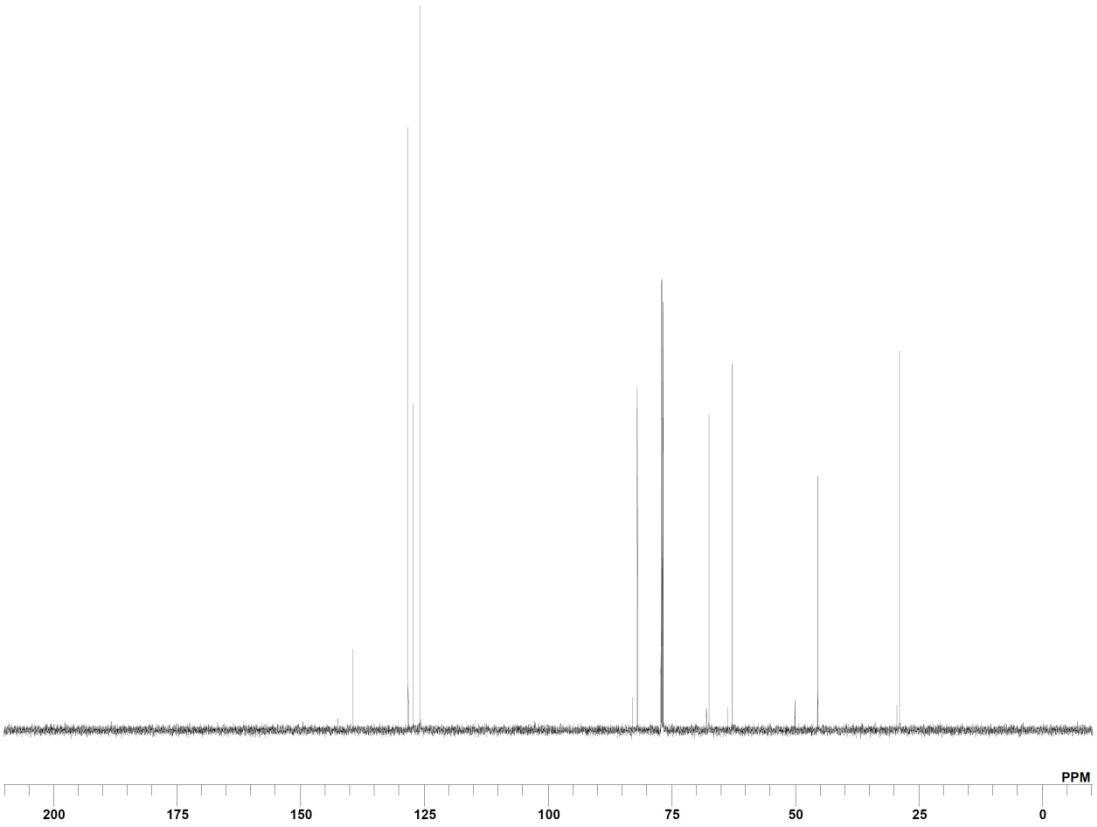


product_syn_H

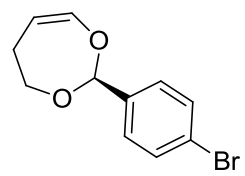


syn-**4a**

product_syn_C



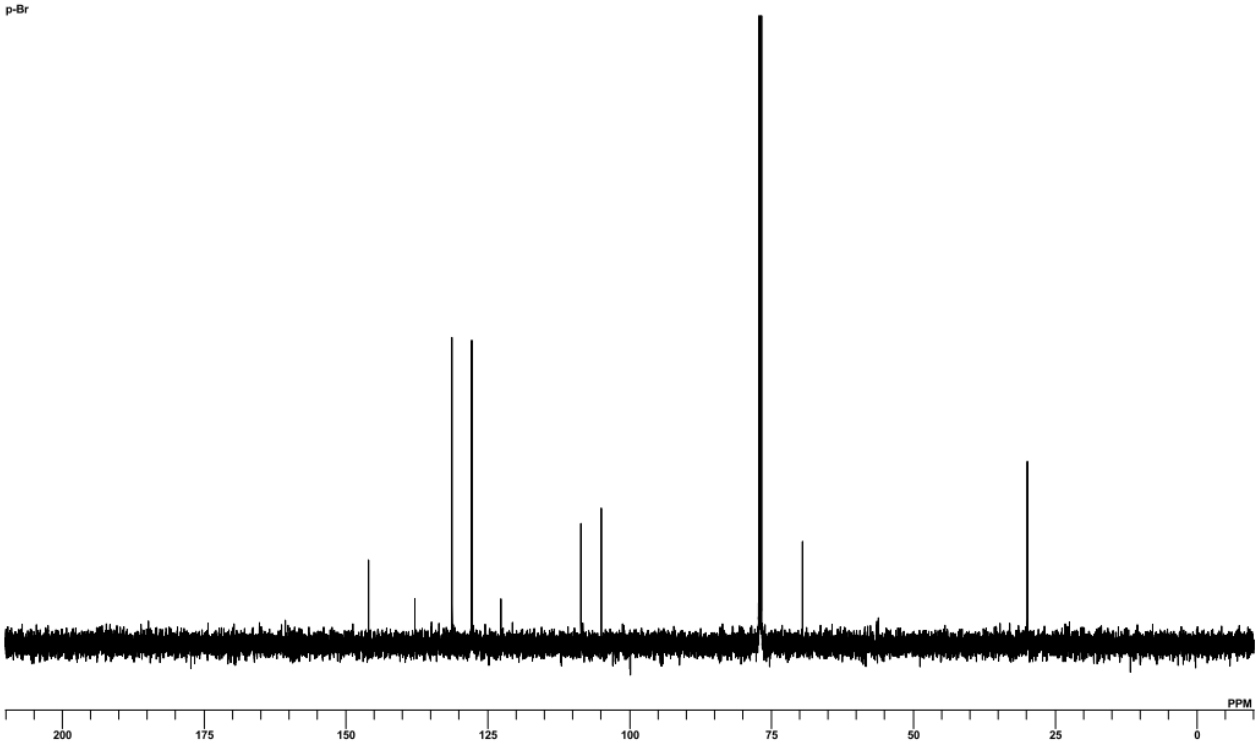
p-Br


O
O
Br

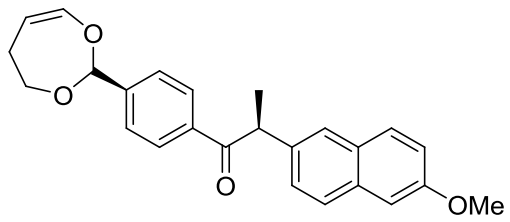
(±)-**S4**

2.03
2.01
1.00
1.01
1.01
1.01
1.01
1.01
1.00
PPM
10
8
6
4
2
0

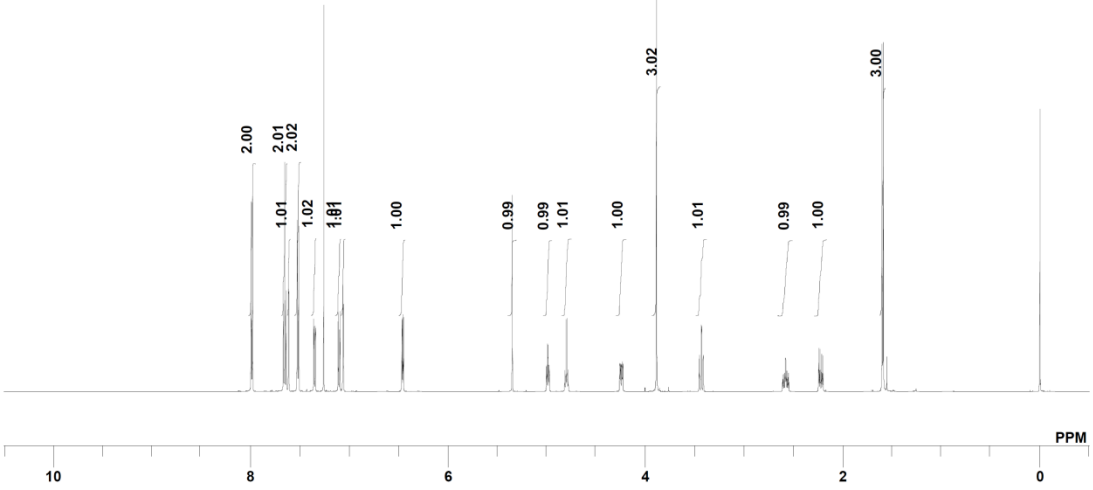
p-Br


PPM
200
175
150
125
100
75
50
25
0

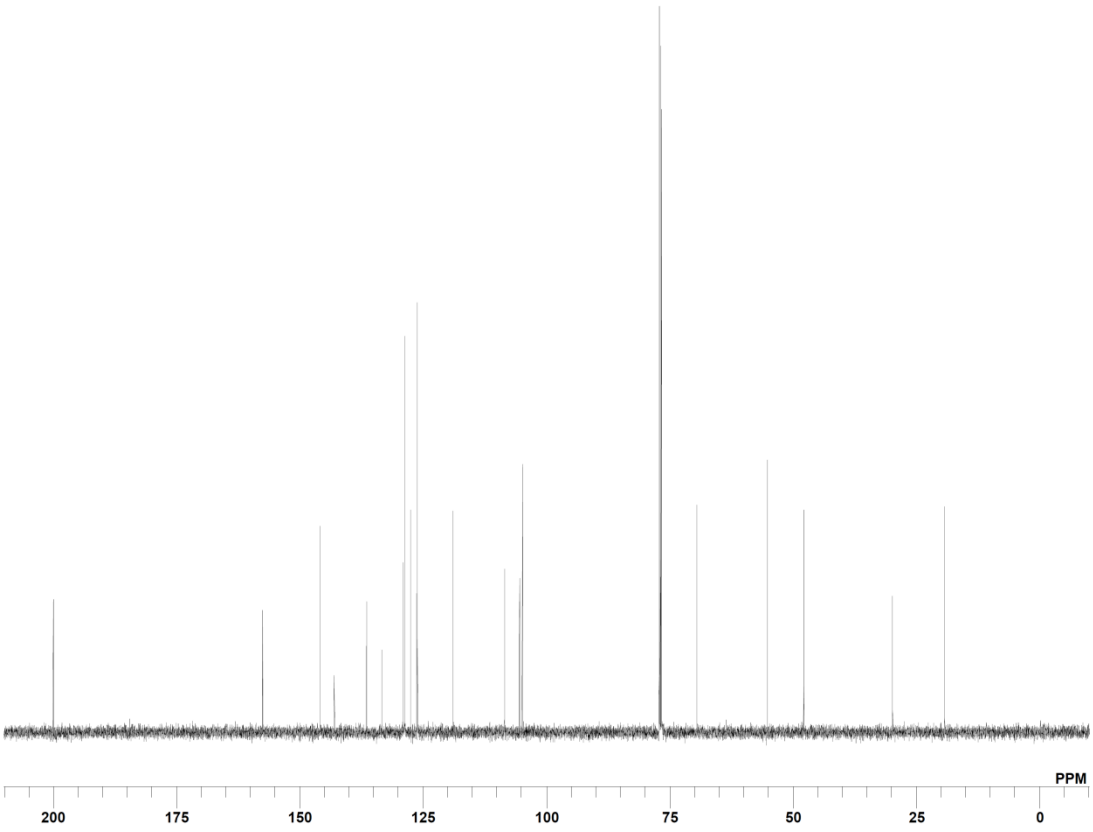
X-ray_sm_H



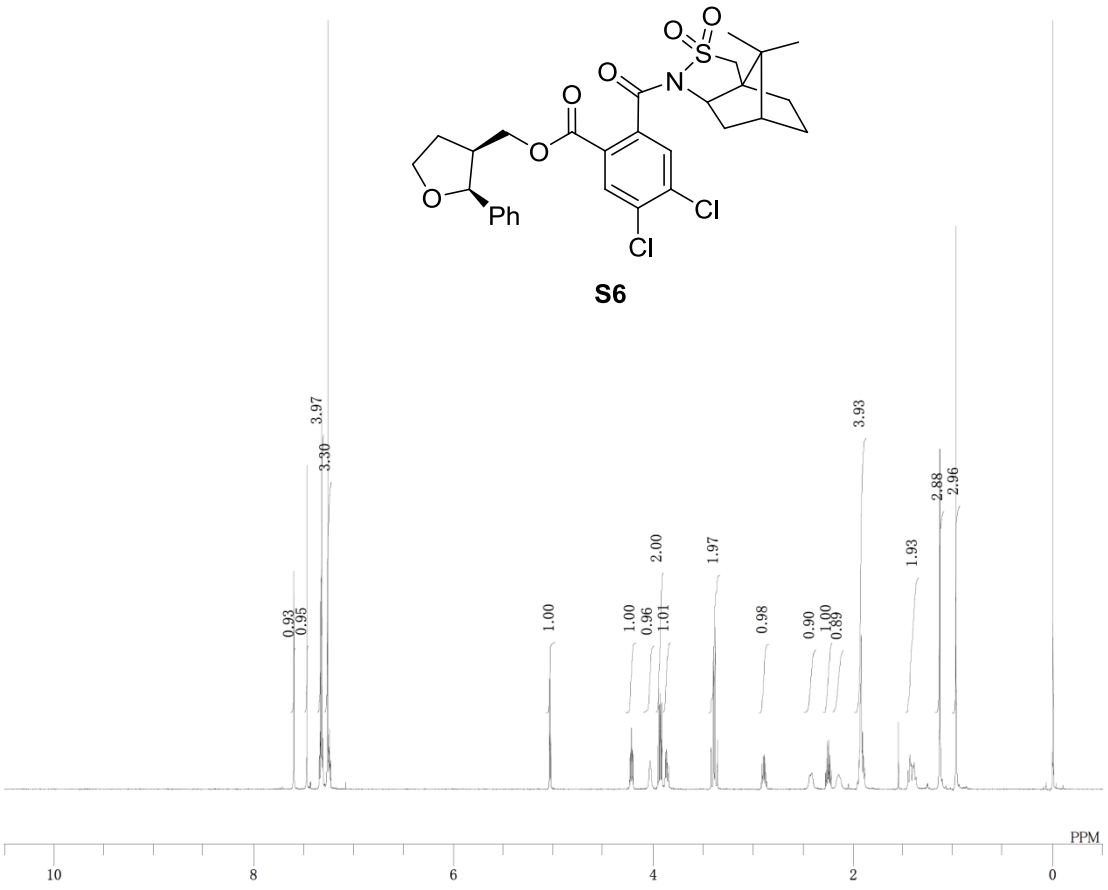
S5



X-ray_sm_C

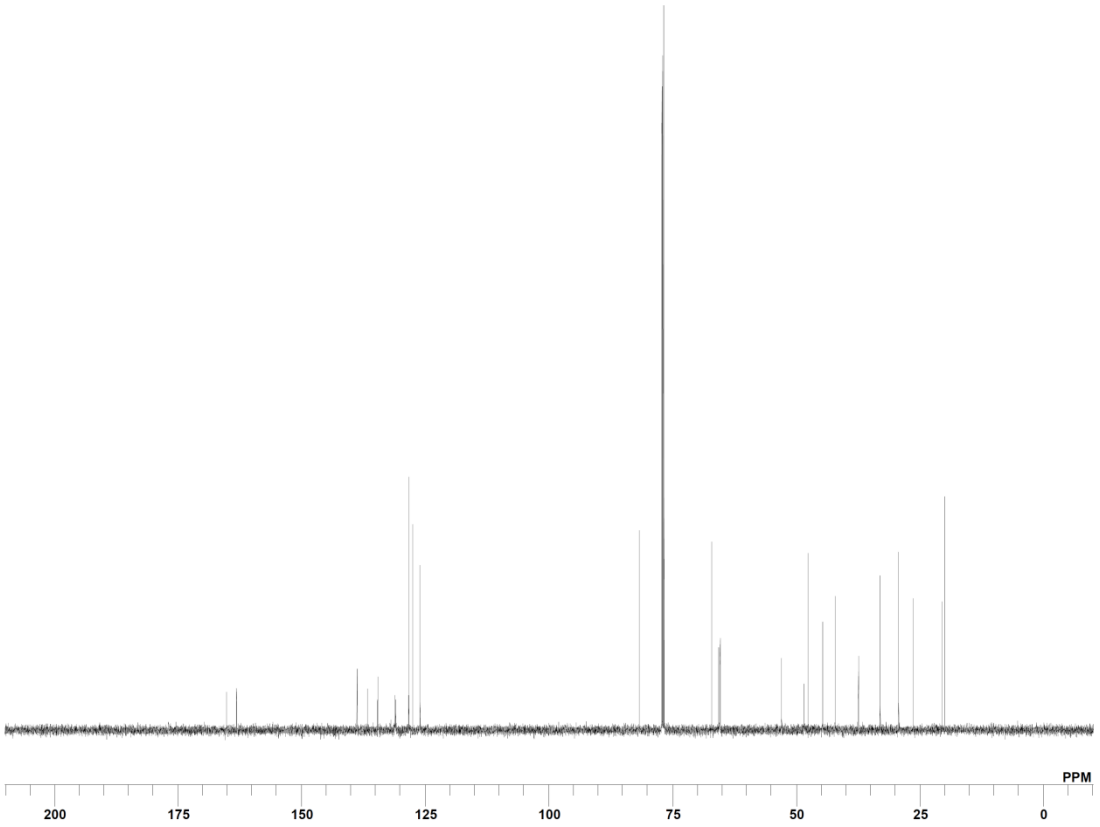


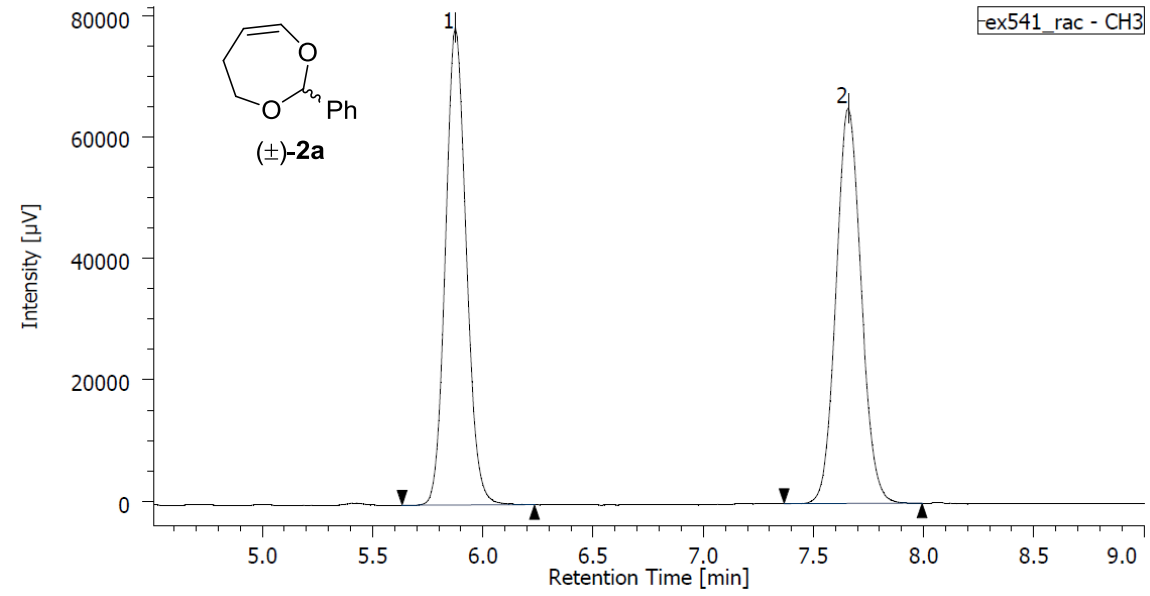
X-ray_syn_1H

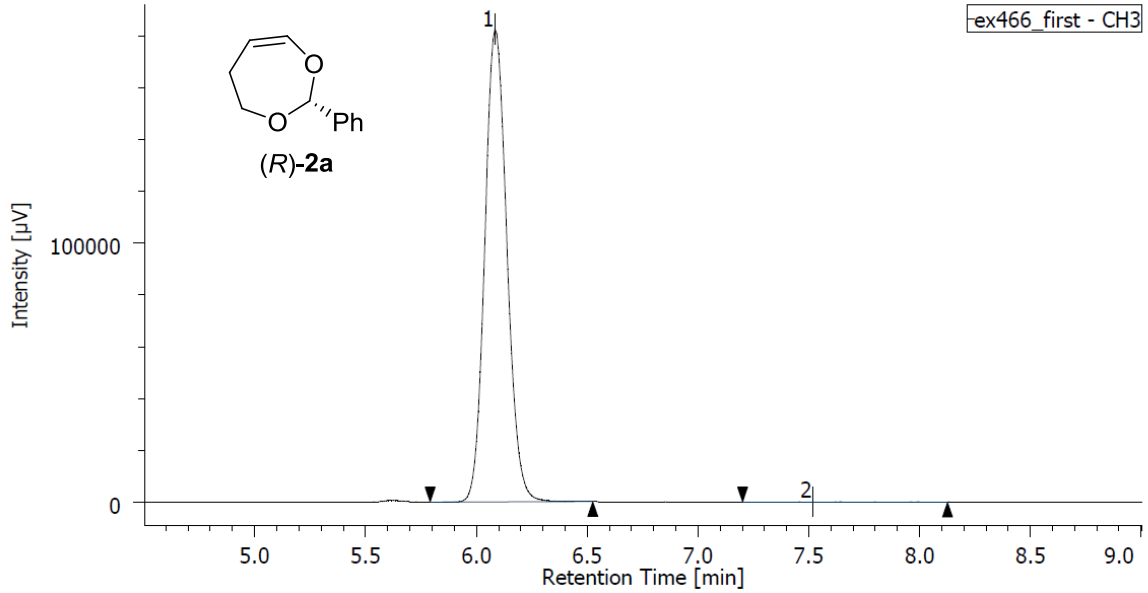


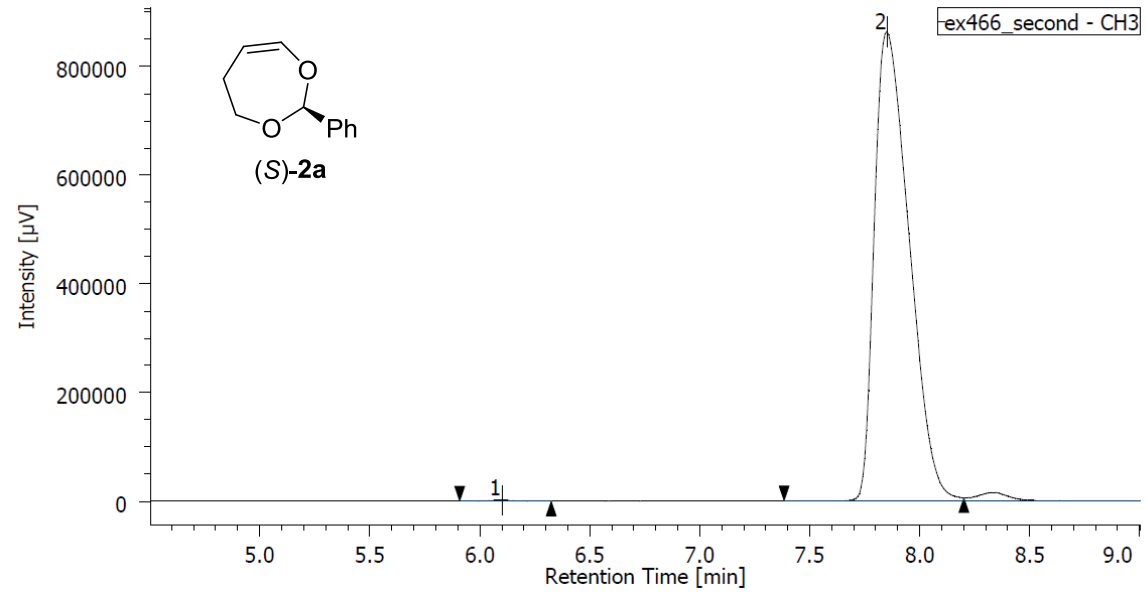
S6

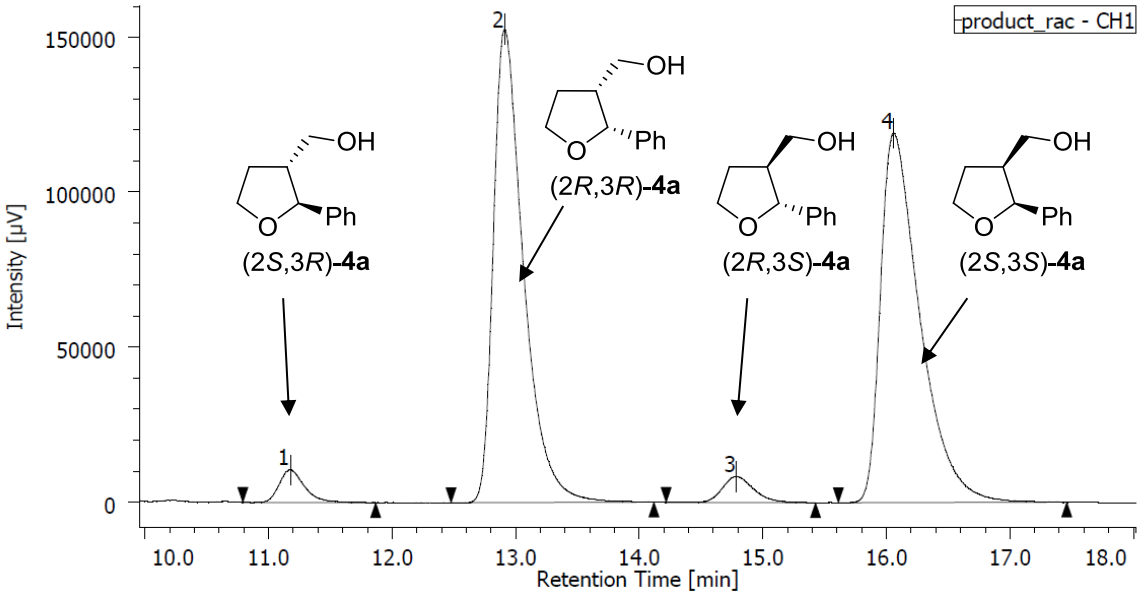
X-ray_syn_C

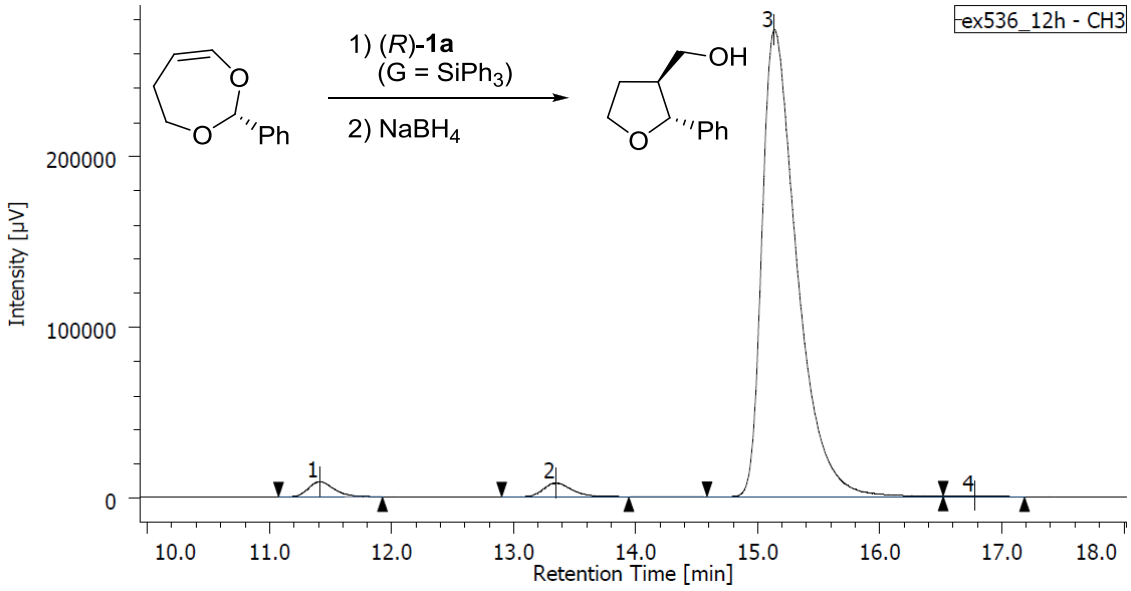


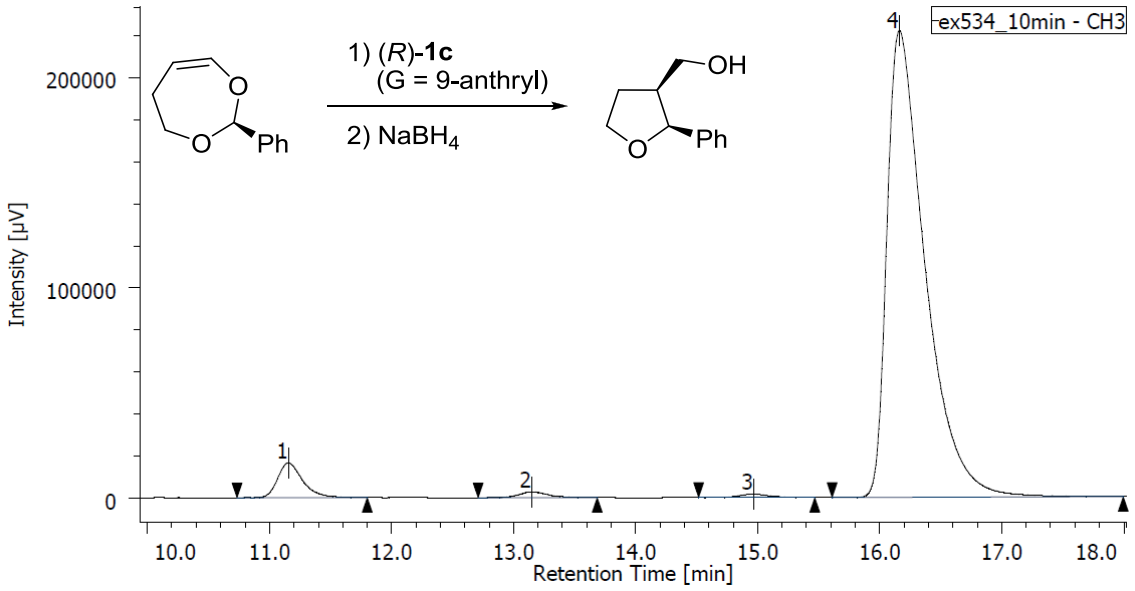

ex541_rac - CH3
(±)-2a
Intensity [µV]
Retention Time [min]

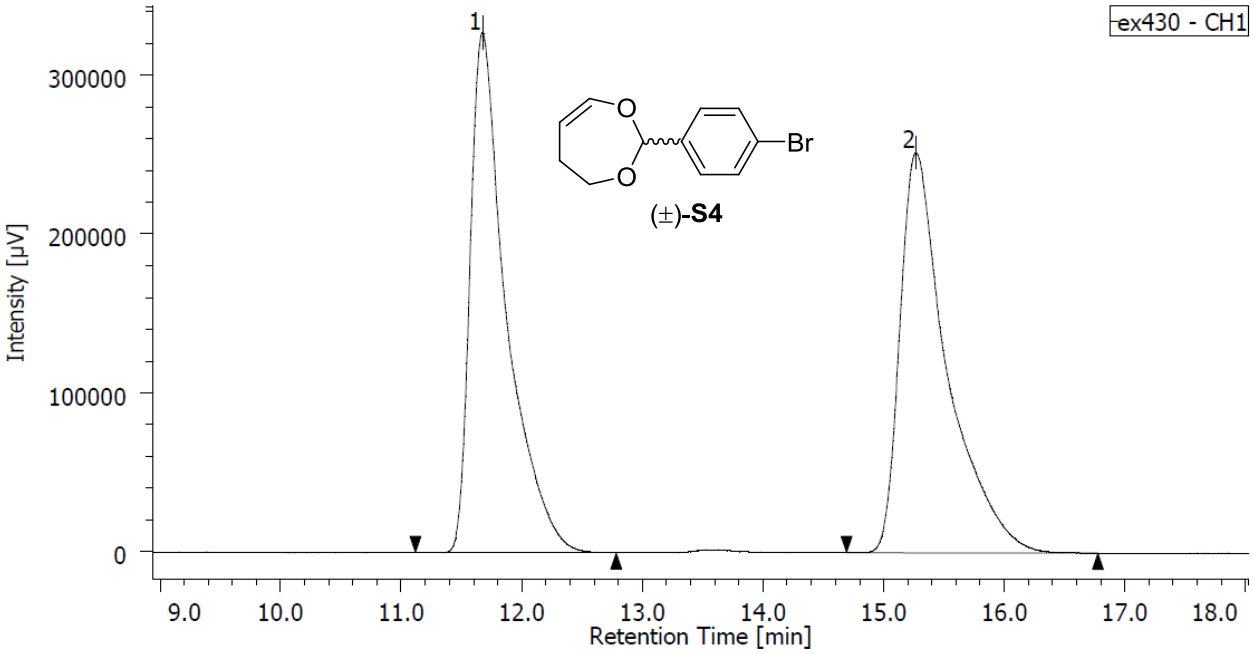

ex466_first - CH3
(R)-2a
Intensity [µV]
Retention Time [min]

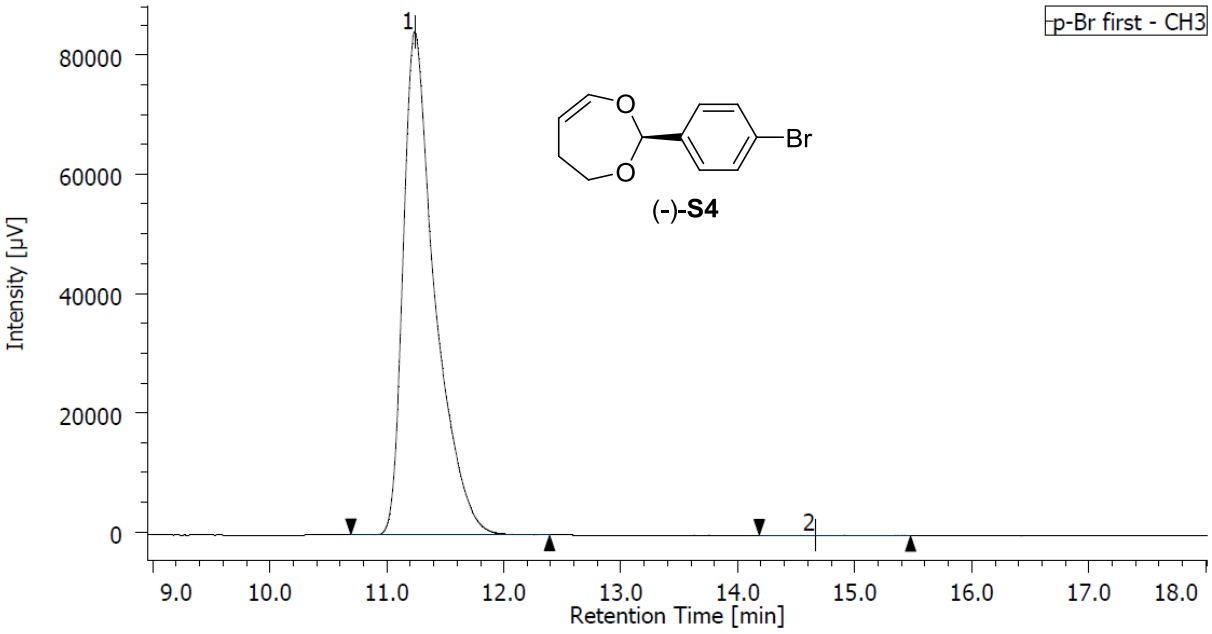

ex466_second - CH3
(S)-2a
Intensity [µV]
Retention Time [min]


product_rac - CH1
Intensity [µV]
150000
100000
50000
0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
Retention Time [min]
1
2
3
4
OH
Ph
O
(2S,3R)-4a
(2R,3R)-4a
(2R,3S)-4a
(2S,3S)-4a


ex536_12h - CH3
Intensity [µV]
200000
100000
0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
Retention Time [min]
1
2
3
4
1) (R)-1a
(G = SiPh3)
2) NaBH4
O
Ph
OH


ex534_10min - CH3
Intensity [µV]
200000
100000
0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
Retention Time [min]
1
2
3
4
1) (R)-1c
(G = 9-anthryl)
2) NaBH4
O
Ph
OH


ex430 - CH1
1
2
Br
(±)-S4
Intensity [µV]
300000
200000
100000
0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
Retention Time [min]


p-Br first - CH3
1
2
Br
(-)-S4
Intensity [µV]
80000
60000
40000
20000
0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
Retention Time [min]