Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Base-promoted diastereoselective α-alkylation of borane *N*-((*S*)-1'-phenylethyl)azetidine-2-carboxylic acid ester complexes

Eiji Tayama, Ryotaro Nishio and Yoshiaki Kobayashi*

Department of Chemistry, Faculty of Science, Niigata University 950-2181, Japan

E-mail: tayama@chem.sc.niigata-u.ac.jp

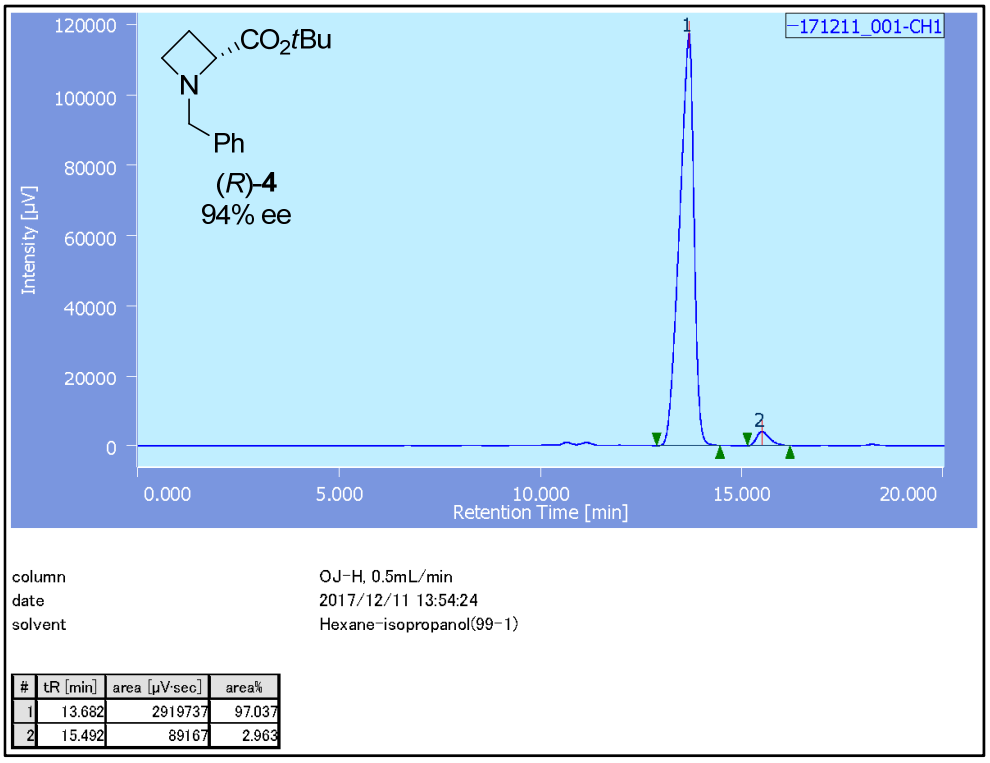
Electronic Supplementary Information

Contents:

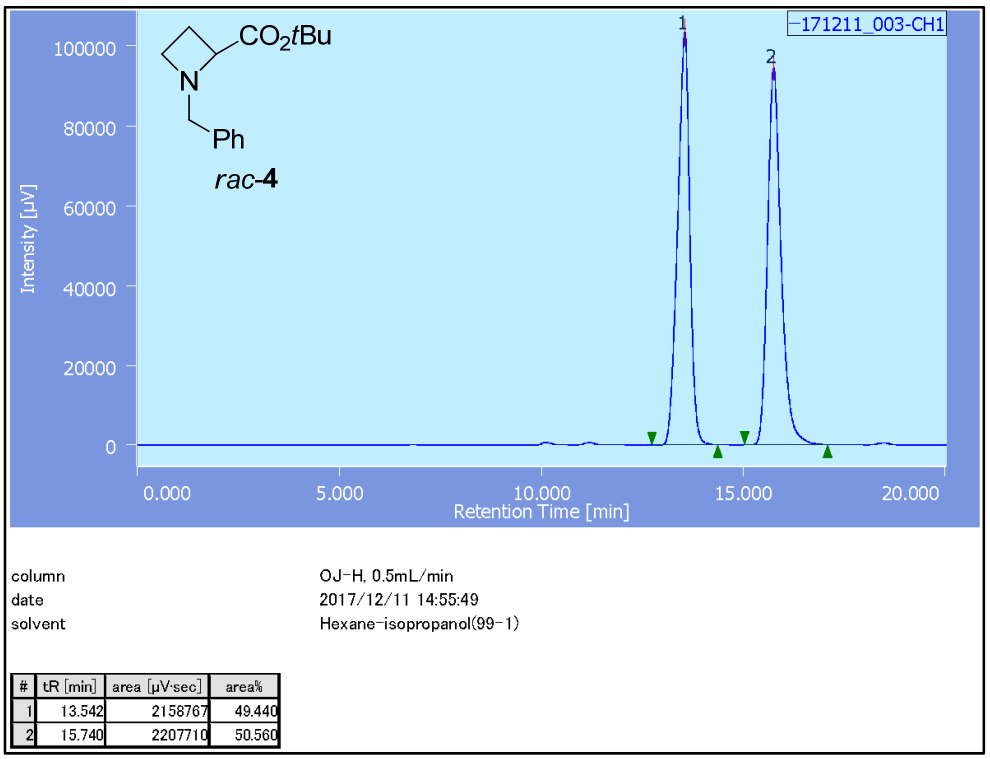
1. HPLC chromatogram for determination of enantiomeric excess (ee)

The ee were determined by HPLC analysis using chiral column in comparison with the racemic compounds.

(*R*)-**4**: 94% ee, Daicel Chiralcel OJ-H column (25 cm), *n*-hexane/2-PrOH = 99/1 as the eluent, flow rate = 0.50 mL/min, t_R = 13.7 min for (*R*)-**4** (97.0%) and 15.5 min for (*S*)-**4** (3.0%).

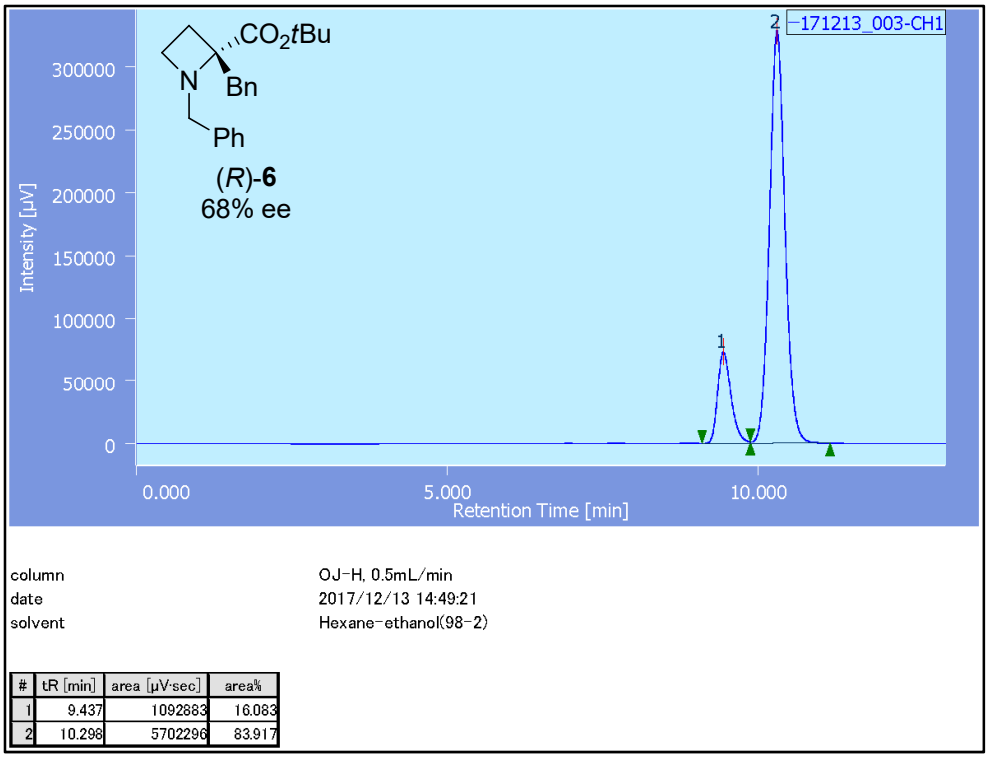


#	tR [min]	area [μV·sec]	area%
1	13.682	2919737	97.037
2	15.492	89167	2.963



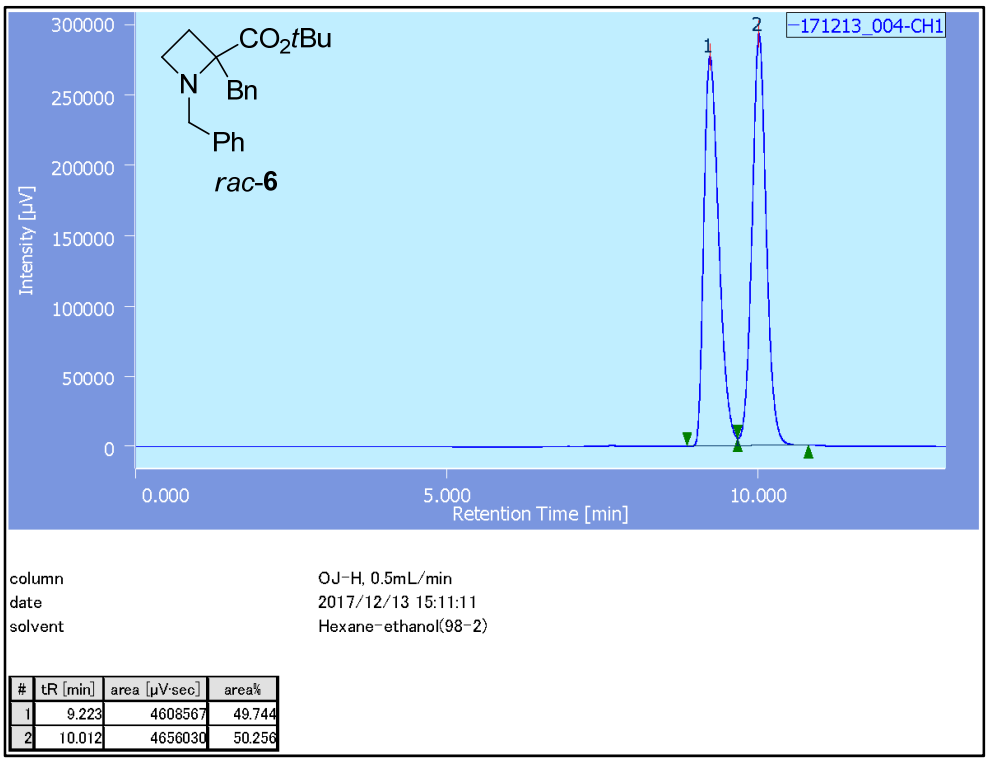
#	tR [min]	area [μV·sec]	area%
1	13.542	2158767	49.440
2	15.740	2207710	50.560

(*R*)-**6**: 68% ee, Daicel Chiralcel OJ-H column (25 cm), *n*-hexane/EtOH = 98/2 as the eluent, flow rate = 0.50 mL/min, t_R = 9.4 min for (*S*)-**6** (16.1%) and 10.3 min for (*R*)-**6** (83.9%).



column	OJ-H, 0.5mL/min
date	2017/12/13 14:49:21
solvent	Hexane-ethanol(98-2)

#	tR [min]	area [μV·sec]	area%
1	9.437	1092883	16.083
2	10.298	5702296	83.917

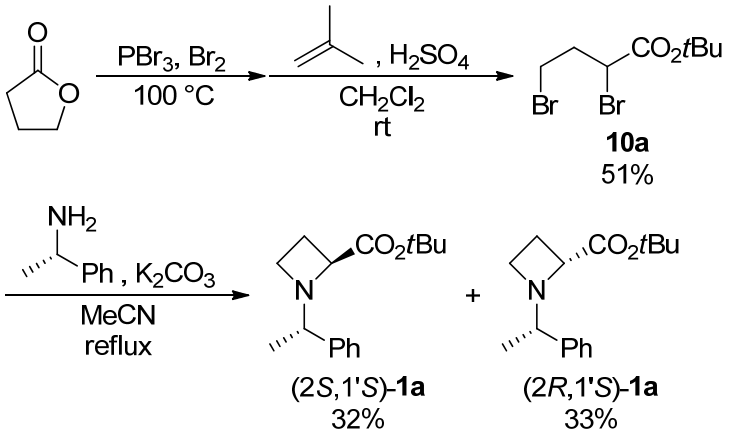


column	OJ-H, 0.5mL/min
date	2017/12/13 15:11:11
solvent	Hexane-ethanol(98-2)

#	tR [min]	area [μV·sec]	area%
1	9.223	4608567	49.744
2	10.012	4656030	50.256

2. Preparation of substrates

***tert*-Butyl 1-((*S*)-1´-phenylethyl)azetidine-2-carboxylate [(2*S*,1´*S*)-1a and (2*R*,1´*S*)-1a]**

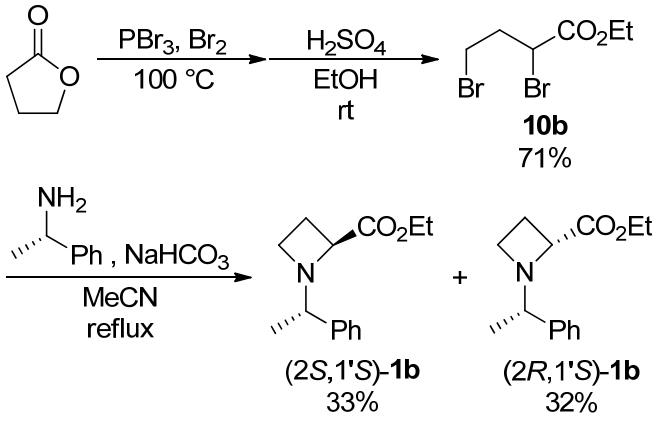


(Step 1) γ-Butyrolactone (3.0 mL, 39 mmol) and PBr_3 (0.07 mL, 0.7 mmol) was stirred at 100 °C under an argon atmosphere. Br_2 (2.2 mL, 43 mmol) was added dropwise to the mixture over 30 min with stirring. After stirring for 5 min at 100 °C, the resulting mixture was cooled to room temperature and the excess Br_2 was removed by flow of nitrogen. The residue was dissolved in CH_2Cl_2 (13 mL) and treated with *conc*. H_2SO_4 (0.2 mL) and isobutene (excess) at room temperature. The mixture was stirred for 20 h the same temperature and treated with saturated aqueous $NaHCO_3$. The mixture was extracted with CH_2Cl_2 and the combined extracts were washed with saturated aqueous NaBr, dried over Na_2SO_4, and evaporated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 30/1 as the eluent) gave *tert*-butyl 2,4-dibromobutanoate (**10a**) (5.97 g, 51% yield) as a colorless oil. (Step 2) A mixture of (*S*)-1-phenylethylamine (400 μL, 3.10 mmol), **10a** (937 mg, 3.10 mmol), and K_2CO_3 (1.29 g, 9.3 mmol) in MeCN (16 mL) was refluxed for 6 h. The resulting mixture was cooled to room temperature followed by filtered. The filtrate was evaporated and the residue was purified by chromatography on silica gel [*n*-hexane/EtOAc = 7/1 to 4/1 as the eluent, R_f: (2*S*,1´*S*) > (2*R*,1´*S*)] to obtain (2*S*,1´*S*)-**1a** (261 mg, 32% yield) as a colorless oil and (2*R*,1´*S*)-**1a** (270 mg, 33% yield) as a colorless oil. The stereochemistry of each diastereomers were clarified in our previous work.[1] (2*S*,1´*S*)-**1a**: $[\alpha]^{22}_{589}$ –111.1 (*c* 1.0 in EtOH); IR (film) ν_{max}/cm^{-1} 3061, 3025, 3003, 2973, 2930, 2869, 2837, 2779, 1742, 1718, 1493, 1478, 1453, 1391, 1366, 1319, 1284, 1232, 1213, 1152, 1101, 1071, 1042, 1031, 975, 945, 847, 763, 701; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.27 (4H, m, Ph), 7.22 (1H, dddd, *J* = 7.4, 6.6, 1.6, 1.6 Hz, Ph), 3.62 (1H, dd, *J* = 8.6, 8.2 Hz, 2-H), 3.43 (1H, q, *J* = 6.6 Hz, 1´-H), 3.08 (1H, dddd, *J* = 8.4, 7.0, 2.8, 0.8 Hz, 4-H), 2.73 (1H, ddd, *J* = 8.9, 8.2, 7.0 Hz, 4-H), 2.21 (1H, dddd, *J* = 10.6, 8.9, 8.6, 8.4 Hz, 3-H), 2.12 (1H, dddd, *J* = 10.6, 8.2, 8.2, 2.8 Hz, 3-H), 1.49 (9H, s, *t*Bu), 1.23 (3H, d, *J* = 6.6 Hz, 1´-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 142.9, 128.2, 127.4, 127.0, 80.6, 67.3, 64.8, 49.5, 28.0, 21.2, 20.7; HRMS (ESI): calcd. for $C_{16}H_{24}NO_2$ $[M + H]^+$ 262.1802, found 262.1794. (2*R*,1´*S*)-**1a**: $[\alpha]^{22}_{589}$ +56.8 (*c* 1.0 in EtOH); IR (film) ν_{max}/cm^{-1} 3062, 3026, 3003, 2973, 2930, 2870, 2827, 2784, 1735, 1493, 1477, 1453, 1391, 1366, 1302, 1276, 1233, 1208, 1153, 1114, 1081, 1057, 1030, 1012, 975, 947, 846, 762, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.29 (2H, m, Ph), 7.26 (2H, dddd, *J* = 7.2, 7.2, 1.6, 1.6 Hz, Ph), 7.20 (1H, tt, *J* = 7.2, 1.6 Hz, Ph), 3.54 (1H, dddd, *J* = 8.2, 6.6, 2.6, 0.6 Hz, 4-H), 3.50 (1H, dd, *J* = 8.2, 8.2 Hz,

[1] E. Tayama, K. Watanabe and Y. Matano, *Eur. J. Org. Chem.*, **2016**, 3631.

2-H), 3.36 (1H, q, J = 6.6 Hz, 1′-H), 2.96 (1H, ddd, J = 9.2, 8.2, 6.6 Hz, 4-H), 2.22 (1H, dddd, J = 10.5, 9.2, 8.2, 8.2 Hz, 3-H), 2.11 (1H, dddd, J = 10.5, 8.2, 8.2, 2.6 Hz, 3-H), 1.26 (3H, d, J = 6.6 Hz, 1′-CH_3), 1.16 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 142.2, 128.2, 128.1, 127.3, 80.1, 68.0, 65.3, 50.7, 27.7, 20.8, 20.0; HRMS (ESI): calcd. for $C_{16}H_{24}NO_2$ $[M + H]^+$ 262.1802, found 262.1792.

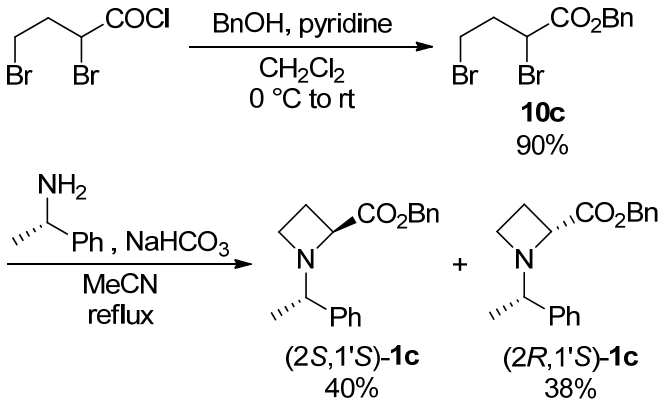
Ethyl 1-((*S*)-1′-phenylethyl)azetidine-2-carboxylate [(2*S*,1′*S*)-1b and (2*R*,1′*S*)-1b]



(Step 1) γ-Butyrolactone (3.0 mL, 39 mmol) and PBr_3 (0.07 mL, 0.7 mmol) was stirred at 100 °C under an argon atmosphere. Br_2 (2.2 mL, 43 mmol) was added dropwise to the mixture over 30 min with stirring. After stirring for 5 min at 100 °C, the resulting mixture was cooled to room temperature and the excess Br_2 was removed by flow of nitrogen. The residue was dissolved in EtOH (15 mL) and treated with *conc*. H_2SO_4 (0.6 mL) at room temperature. The mixture was stirred for 20 h the same temperature and treated with saturated aqueous $NaHCO_3$ followed by saturated aqueous Na_2SO_3. The mixture was extracted with EtOAc and the combined extracts were washed with saturated aqueous $NaHCO_3$ followed by saturated aqueous NaBr. The solution was dried over Na_2SO_4 and evaporated. The residue was purified by chromatography on silica gel (*n*-hexane/EtOAc = 30/1 to 20/1 as the eluent) to afford ethyl 2,4-dibromobutanoate (**10b**) (7.56 g, 71% yield) with impurities as a colorless oil. (Step 2) A mixture of (*S*)-1-phenylethylamine (1.29 mL, 10.0 mmol), **10b** (2.74 g, 10.0 mmol), and $NaHCO_3$ (5.04 g, 60.0 mmol) in MeCN (50 mL) was refluxed for 12 h. The resulting mixture was cooled to room temperature followed by filtered. The filtrate was evaporated and the residue was purified by chromatography on silica gel [*n*-hexane/EtOAc = 15/1, 10/1, 5/1, to 2/1 as the eluent, R_f: (2*S*,1′*S*) > (2*R*,1′*S*)] to obtain (2*S*,1′*S*)-**1b** (762 mg, 33% yield) as a pale yellow oil and (2*R*,1′*S*)-**1b** (754 mg, 32% yield) as a colorless oil. The stereochemistry of each diastereomers were determined by analogy with **1a**. (2*S*,1′*S*)-**1b**: $[\alpha]^{24}_{589}$ –111.4 (*c* 1.0 in EtOH); IR (film) ν_{max}/cm^{-1} 3061, 3025, 2969, 2931, 2838, 2780, 1749, 1727, 1602, 1493, 1453, 1371, 1357, 1344, 1319, 1280, 1230, 1183, 1143, 1096, 1071, 1042, 974, 941, 913, 863, 764, 702; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.21 (5H, m, Ph), 4.24 (1H, dq, J = 10.8, 7.2 Hz, OCH_2CH$_3$), 4.19 (1H, dq, J = 10.8, 7.2 Hz, OCH_2CH$_3$), 3.74 (1H, dd, J = 8.4, 8.4 Hz, 2-H), 3.45 (1H, q, J = 6.8 Hz, 1′-H), 3.11 (1H, dddd, J = 8.3, 7.1, 2.8, 0.8 Hz, 4-H), 2.79 (1H, ddd, J = 8.9, 8.3, 7.1 Hz, 4-H), 2.26 (1H, dddd, J = 10.6, 8.9, 8.4, 8.3 Hz, 3-H), 2.17 (1H, dddd, J = 10.6, 8.4, 8.3, 2.8 Hz, 3-H), 1.29 (3H, t, J = 7.2 Hz, OCH$_2$CH_3), 1.23 (3H, d, J = 6.8 Hz, 1′-CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.2, 142.6, 128.3, 127.4, 127.1, 67.3, 64.1, 60.6, 49.7, 20.92, 20.88, 14.2; HRMS (ESI): calcd. for $C_{14}H_{20}NO_2$ $[M + H]^+$ 234.1489, found 234.1483. (2*R*,1′*S*)-**1b**: $[\alpha]^{24}_{589}$ +51.1 (*c* 1.0 in EtOH); IR (film) ν_{max}/cm^{-1} 3061, 3026, 2968, 2930, 2901, 2870, 2827, 2785, 1743, 1601, 1493, 1453, 1377, 1350, 1305, 1276, 1230, 1180, 1112, 1096, 1082, 1056, 1032, 973, 943, 913, 865, 763, 700; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.18 (5H, m, Ph), 3.83 (1H, dq, J = 10.8,

7.0 Hz, OCH_2CH$_3$), 3.76 (1H, dq, J = 10.8, 7.2 Hz, OCH_2CH$_3$), 3.61-3.54 (1H, m, 4-H), 3.57 (1H, dd, J = 8.4, 8.4 Hz, 2-H), 3.36 (1H, q, J = 6.4 Hz, 1′-H), 3.00 (1H, ddd, J = 9.2, 8.1, 6.8 Hz, 4-H), 2.29 (1H, dddd, J = 10.5, 9.2, 8.8, 8.4 Hz, 3-H), 2.13 (1H, dddd, J = 10.5, 8.4, 8.1, 2.4 Hz, 3-H), 1.28 (3H, d, J = 6.4 Hz, 1′-CH$_3$), 0.97 (3H, t, J = 7.0 Hz, OCH$_2$CH_3); ^{13}C NMR (100 MHz, CDCl$_3$) δ 172.3, 141.8, 128.1, 128.0, 127.4, 68.3, 64.7, 60.4, 50.8, 20.8, 19.9, 13.9; HRMS (ESI): calcd. for $C_{14}H_{20}NO_2$ [M + H]$^+$ 234.1489, found 234.1483.

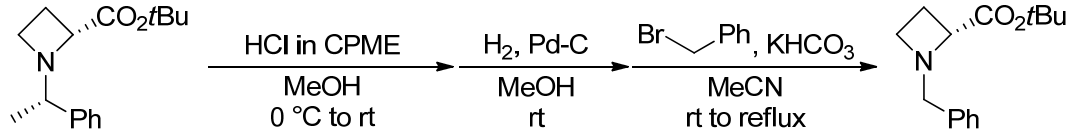
Benzyl 1-((*S*)-1′-phenylethyl)azetidine-2-carboxylate [(2*S*,1′*S*)-1c and (2*R*,1′*S*)-1c]



(Step 1) A solution of benzyl alcohol (1.03 mL, 10 mmol) and pyridine (0.81 mL, 10 mmol) in CH_2Cl_2 (20 mL) was treated with 2,4-dibromobutyryl chloride (1.32 mL, 10 mmol) at 0 °C under an argon atmosphere. After stirring for 1 h at room temperature, the resulting mixture was diluted with water and extracted with CH_2Cl_2. The combined extracts were washed saturated aqueous NaBr, dried over Na_2SO_4, and evaporated. Purification of the residue by chromatography on silica gel (*n*-hexane/EtOAc = 20/1 to 15/1 as the eluent) gave benzyl 2,4-dibromobutanoate (**10c**) (3.04 g, 90% yield) as a colorless oil. (Step 2) A mixture of (*S*)-1-phenylethylamine (773 μL, 6.00 mmol), **10c** (2.02 g, 6.01 mmol) and $NaHCO_3$ (3.02 g, 35.9 mmol) in MeCN (30 mL) was refluxed for 12 h. The resulting mixture was cooled to room temperature followed by filtered. The filtrate was evaporated and the residue was purified by chromatography on silica gel [*n*-hexane/EtOAc = 15/1, 7/1, to 4/1 as the eluent, R_f: (2*S*,1′*S*) > (2*R*,1′*S*)] to obtain (2*S*,1′*S*)-**1c** (703 mg, 40% yield) as a colorless oil and (2*R*,1′*S*)-**1c** (679 mg, 38% yield) as a colorless oil. The stereochemistry of each diastereomers were determined by analogy with **1a**. (2*S*,1′*S*)-**1c**: $[\alpha]^{23}_{589}$ –91.3 (*c* 1.0 in EtOH); IR (film) ν_{max}/cm^{-1} 3062, 3030, 3005, 2966, 2930, 2839, 2781, 1749, 1493, 1453, 1371, 1360, 1319, 1271, 1230, 1212, 1169, 1094, 1071, 1040, 1028, 976, 911, 763, 699; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40-7.20 (10H, m, Ph), 5.22 (1H, d, J = 12.2 Hz, CH_2Ph), 5.16 (1H, d, J = 12.2 Hz, CH_2Ph), 3.80 (1H, dd, J = 8.4, 8.4 Hz, 2-H), 3.45 (1H, q, J = 6.8 Hz, 1′-H), 3.12 (1H, dddd, J = 8.2, 7.2, 2.6, 0.6 Hz, 4-H), 2.80 (1H, ddd, J = 8.7, 8.2, 7.2 Hz, 4-H), 2.28 (1H, dddd, J = 10.6, 8.7, 8.4, 8.2 Hz, 3-H), 2.18 (1H, dddd, J = 10.6, 8.4, 8.2, 2.6 Hz, 3-H), 1.19 (3H, d, J = 6.8 Hz, 1′-CH$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 173.0, 142.5, 135.8, 128.5, 128.23, 128.21, 128.18, 127.4, 127.1, 67.1, 66.3, 63.9, 49.7, 21.0, 20.8; HRMS (ESI): calcd. for $C_{19}H_{22}NO_2$ [M + H]$^+$ 296.1645, found 296.1635. (2*R*,1′*S*)-**1c**: $[\alpha]^{24}_{589}$ +49.4 (*c* 1.0 in EtOH); IR (film) ν_{max}/cm^{-1} 3062, 3030, 3005, 2966, 2929, 2869, 2828, 2784, 1743, 1493, 1454, 1384, 1370, 1351, 1307, 1275, 1230, 1211, 1167, 1112, 1081, 1056, 1030, 1017, 976, 909, 763, 746, 698; ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34-7.15 (8H, m, Ph), 7.13-7.06 (2H, m, Ph), 4.81 (1H, d, J = 12.0 Hz, CH_2Ph), 4.70 (1H, d, J = 12.0 Hz, CH_2Ph), 3.63 (1H, dd, J = 8.4, 8.4 Hz, 2-H), 3.62-3.56 (1H, m, 4-H), 3.38 (1H, q, J = 6.4 Hz, 1′-H), 3.01 (1H, ddd, J = 9.2, 8.0, 6.8 Hz, 4-H), 2.31 (1H, dddd, J = 10.4, 9.2, 8.4, 8.2 Hz, 3-H), 2.14 (1H, dddd, J = 10.4, 8.4, 8.0, 2.8 Hz, 3-H), 1.27 (3H, d, J = 6.4 Hz, 1′-CH$_3$); ^{13}C NMR (100

MHz, $CDCl_3$) δ 172.2, 141.8, 135.5, 128.25, 128.18, 128.04, 127.95, 127.91, 127.4, 68.1, 66.1, 64.3, 50.8, 20.8, 20.0; HRMS (ESI): calcd. for $C_{19}H_{22}NO_2$ $[M + H]^+$ 296.1645, found 296.1638.

(*R*)-*tert*-Butyl 1-benzylazetidine-2-carboxylate [(*R*)-4][1]



(2*R*,1'*S*)-**1a** (*R*)-**4**
67%, 94% ee

A solution of (2*R*,1′*S*)-**1a** (632 mg, 2.42 mmol) in MeOH (12 mL) was treated with ca. 4 M HCl in cyclopentyl methyl ether (CPME) (0.73 mL, 2.9 mmol) at 0 °C. After stirring for 20 min at room temperature, the solution was evaporated. A mixture of the residue and palladium on activated carbon (loading: 10 wt.%, 0.13 g) in MeOH (12 mL) was stirred at room temperature for 3 days under a hydrogen atmosphere. The resulting mixture was filtered through a pad of Celite and the filtrate was evaporated. A mixture of the residual oil, benzyl bromide (288 μL, 2.42 mmol), and $KHCO_3$ (1.21 g, 12.1 mmol) in MeCN (12 mL) was stirred for 1 h at room temperature and refluxed for 0.5 h. The resulting mixture was cooled to room temperature and filtered. The filtrate was evaporated and the residue was purified by chromatography on silica gel (CH_2Cl_2/EtOAc = 20/1 to 10/1 as the eluent) to obtain (*R*)-**4** (403 mg, 67% yield) as a colorless oil. $[\alpha]^{24}_{589}$ +77.9 (*c* 1.0 in EtOH); 94% ee [determined by HPLC analysis: Daicel Chiralcel OJ-H column (25 cm), *n*-hexane/2-PrOH = 99/1 as the eluent, flow rate = 0.50 mL/min, t_R = 13.7 min for (*R*)-**4** (97.0%) and 15.5 min for (*S*)-**4** (3.0%)]; IR (film) ν_{max}/cm^{-1} 3085, 3062, 3027, 3004, 2975, 2932, 2829, 2702, 1735, 1604, 1494, 1477, 1453, 1391, 1366, 1295, 1238, 1157, 1096, 1052, 1021, 979, 941, 847, 797, 784, 737, 702; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.20 (5H, m, Ph), 3.83 (1H, d, *J* = 12.6 Hz, CH_2Ph), 3.62 (1H, ddd, *J* = 8.4, 8.2, 0.6 Hz, 2-H), 3.54 (1H, d, *J* = 12.6 Hz, CH_2Ph), 3.28 (1H, dddd, *J* = 8.4, 6.6, 2.4, 0.6 Hz, 4-H), 2.88 (1H, ddd, *J* = 9.3, 7.9, 6.6 Hz, 4-H), 2.32 (1H, dddd, *J* = 10.4, 9.3, 8.4, 8.4 Hz, 3-H), 2.14 (1H, dddd, *J* = 10.4, 8.2, 7.9, 2.4 Hz, 3-H), 1.41 (9H, s, *t*Bu); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 137.4, 129.1, 128.3, 127.1, 80.7, 65.1, 62.5, 50.6, 28.0, 21.4; HRMS (ESI): calcd. for $C_{15}H_{22}NO_2$ $[M + H]^+$ 248.1645, found 248.1640.

3. Copies of ^{1}H and ^{13}C NMR spectra of substrates and products

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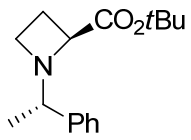
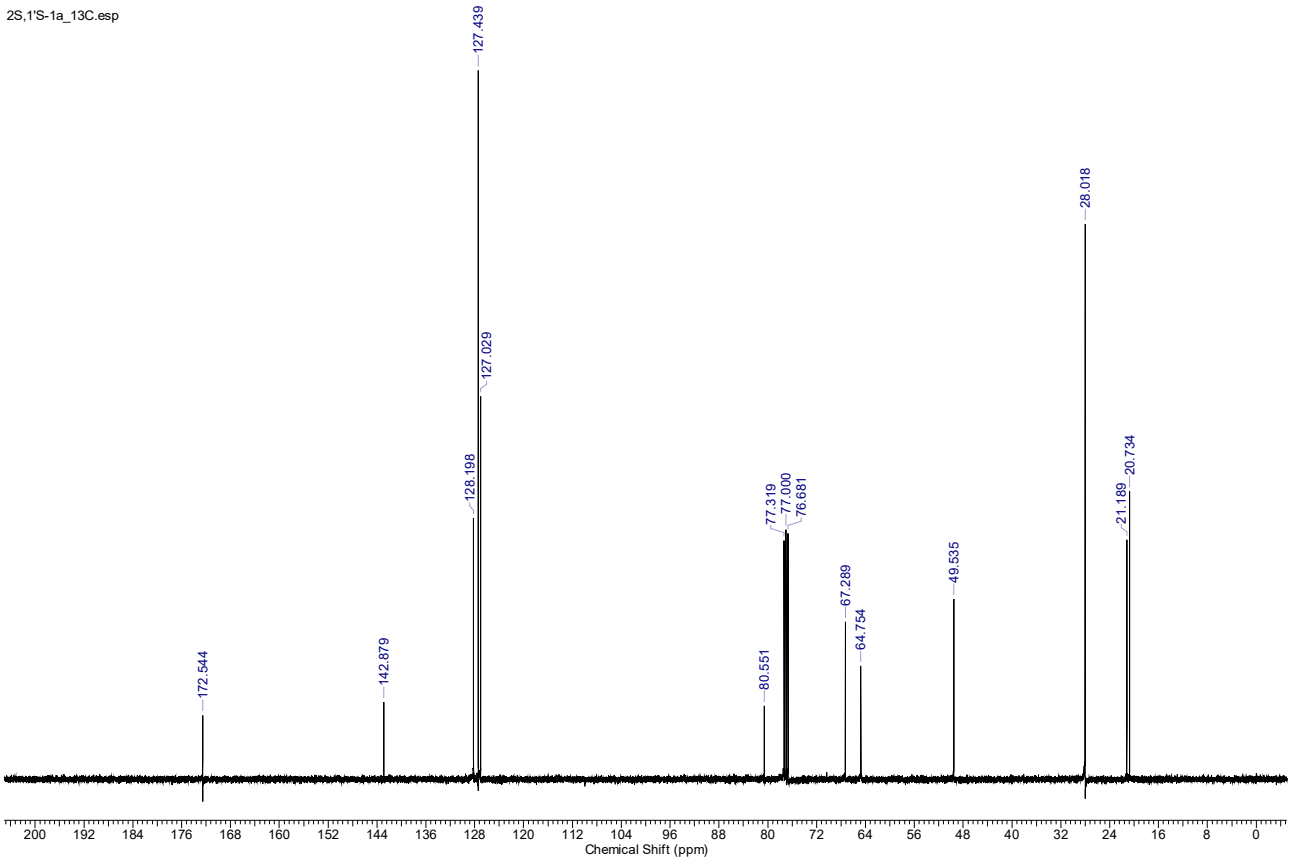


(2*S*,1'*S*)-**1a**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

2S,1'S-1a_13C.esp



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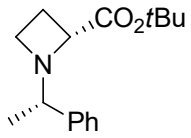
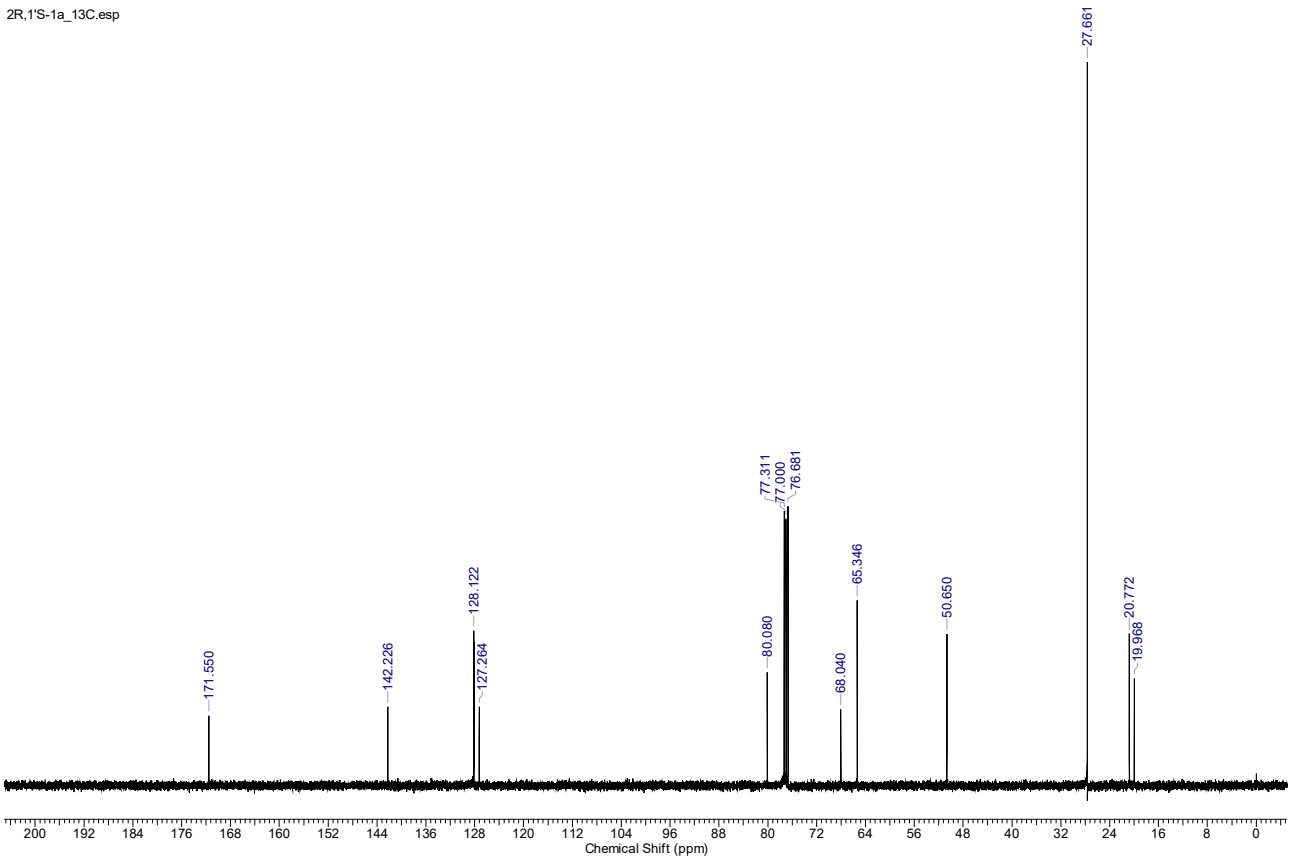


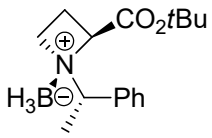
(2*R*,1'*S*)-**1a**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

2R,1'S-1a_13C.esp



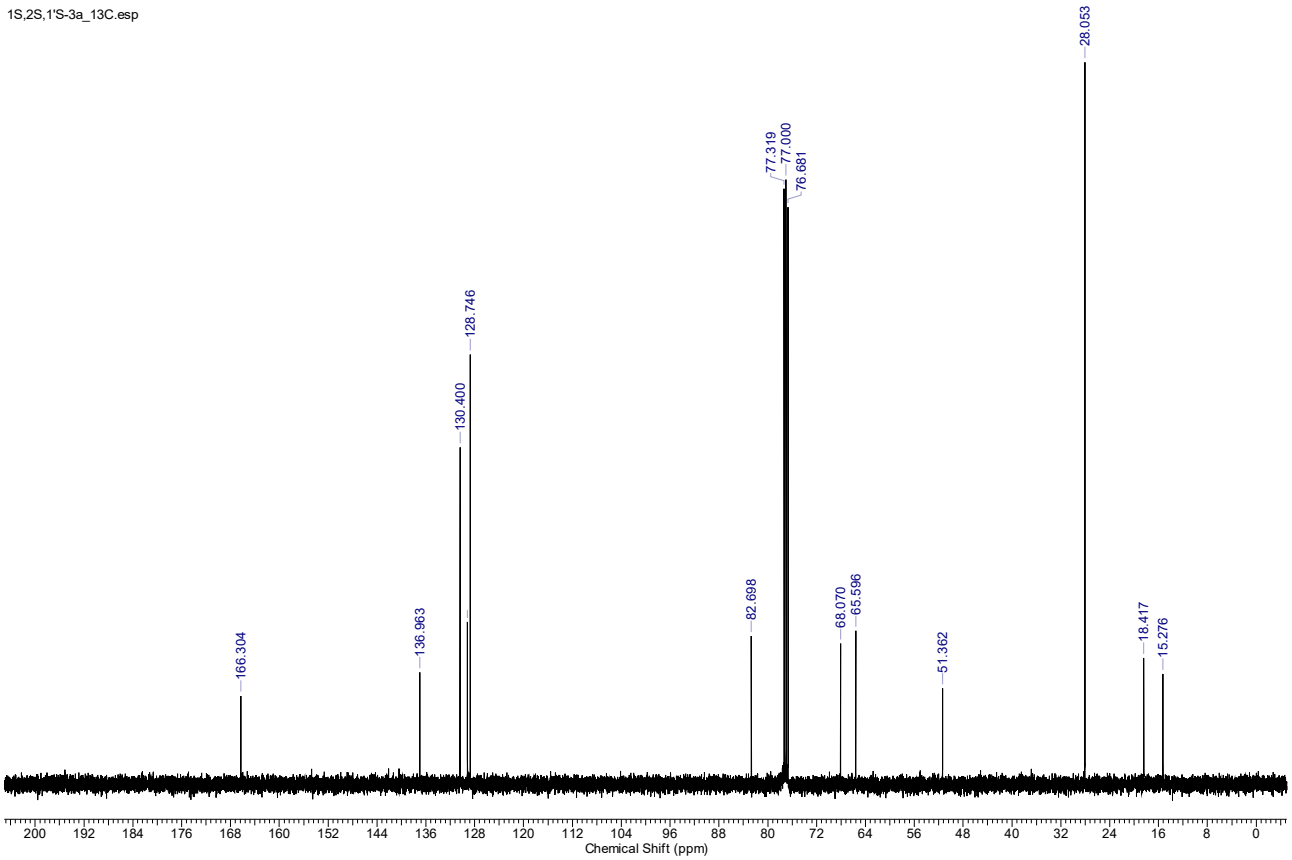
1S,2S,1'S-3a_1H.esp



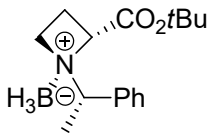
(1*S*,2*S*,1'*S*)-**3a**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

1S,2S,1'S-3a_13C.esp



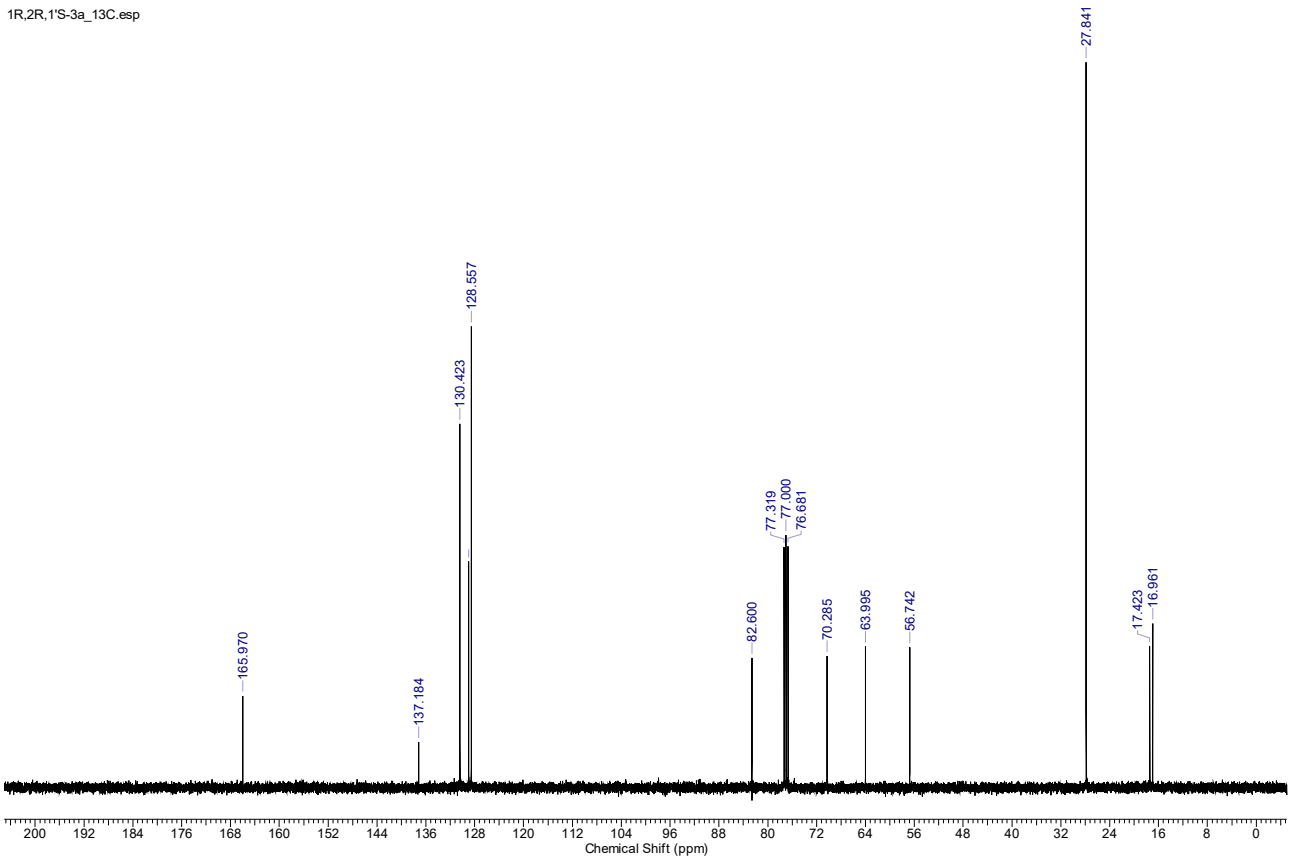
1R,2R,1'S-3a_1H.esp

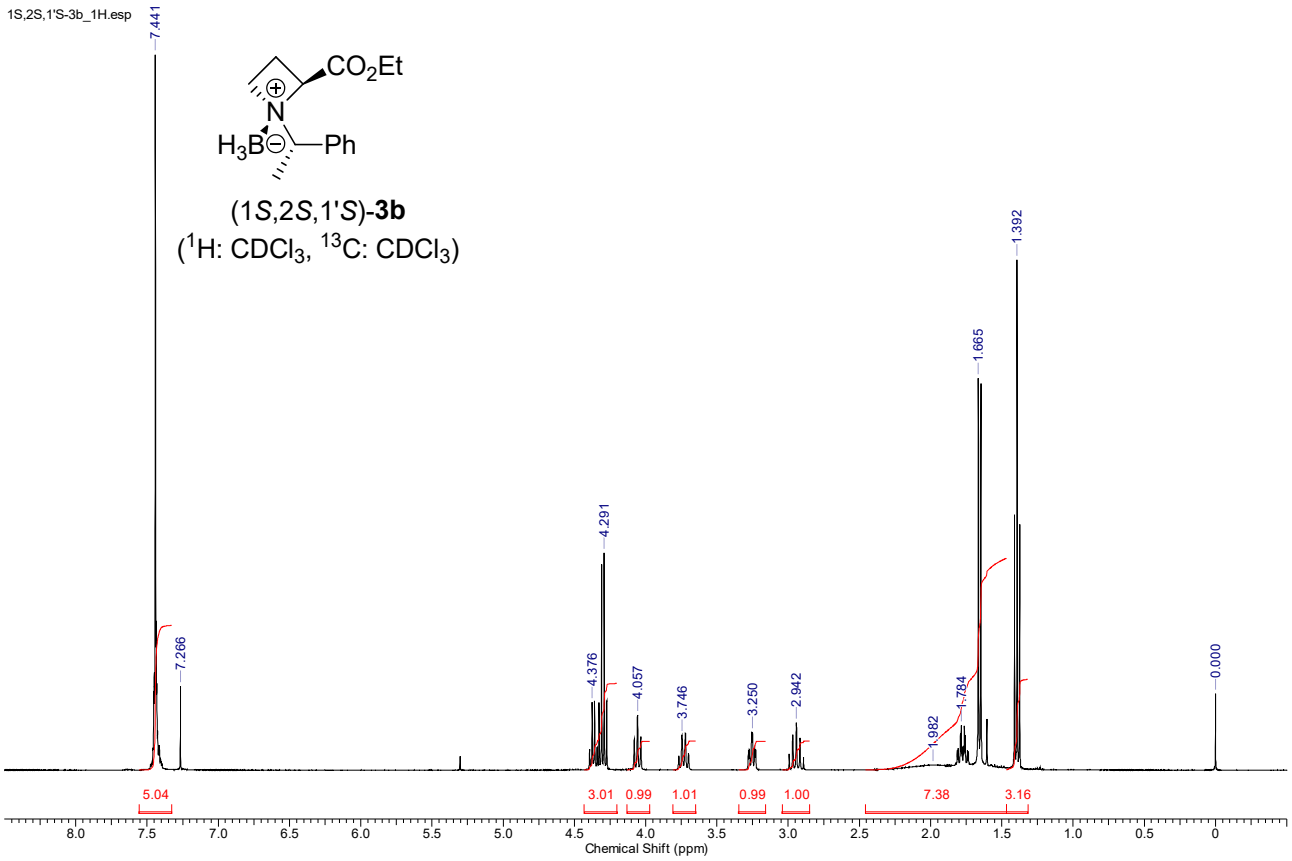


(1*R*,2*R*,1'*S*)-**3a**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

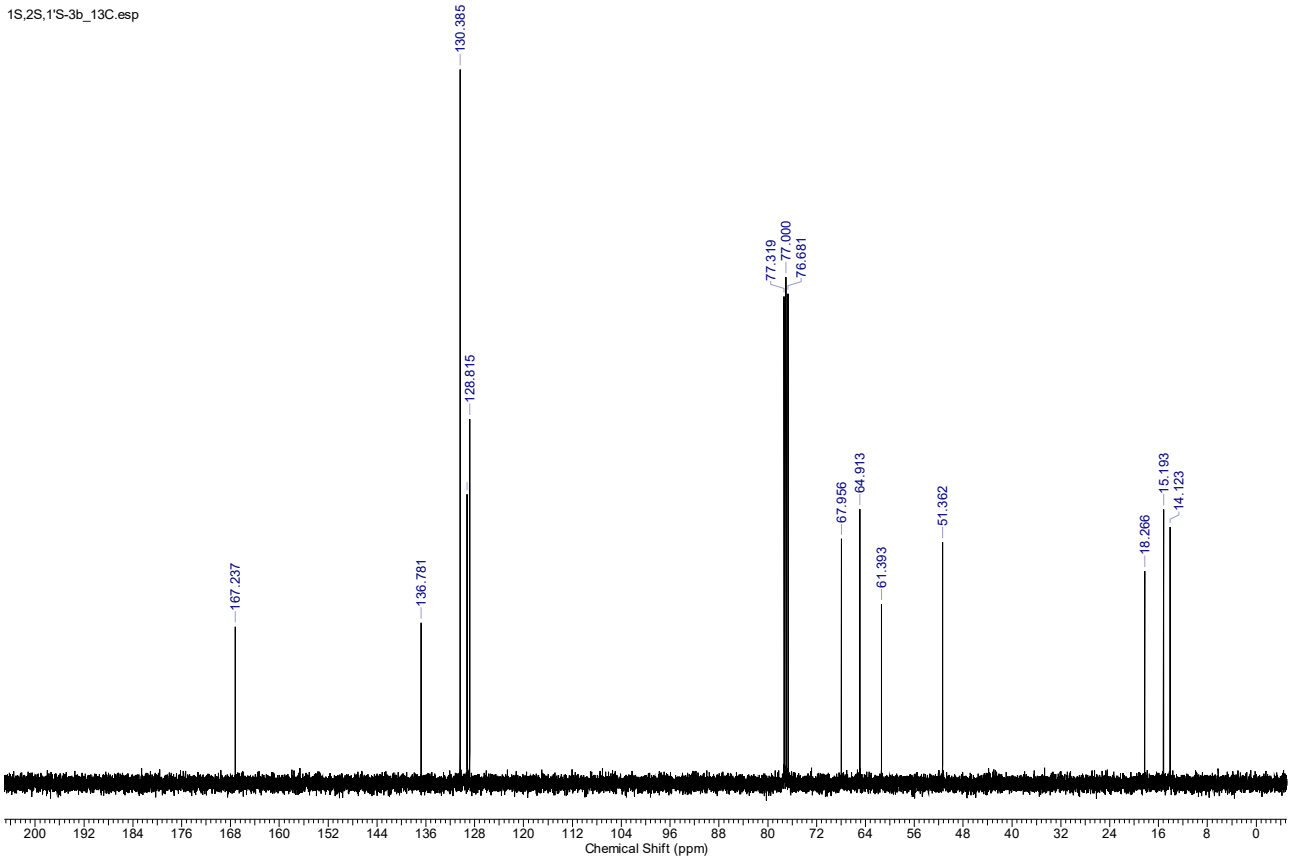
1R,2R,1'S-3a_13C.esp



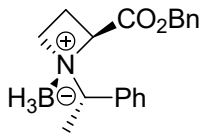


$(1S,2S,1'S)$-**3b**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)



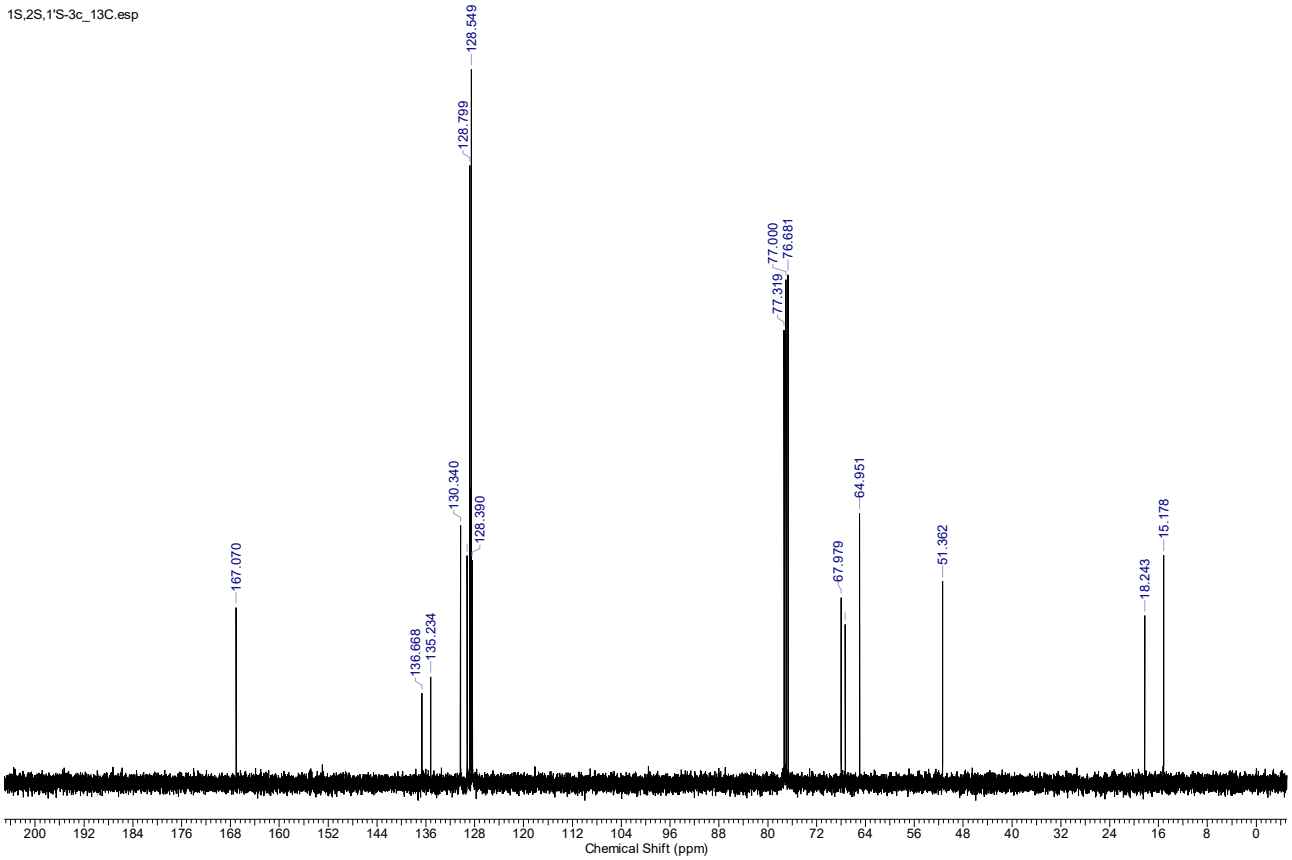
1S,2S,1'S-3c_1H.esp



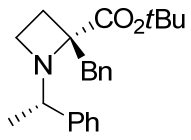
(1*S*,2*S*,1'*S*)-**3c**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

1S,2S,1'S-3c_13C.esp



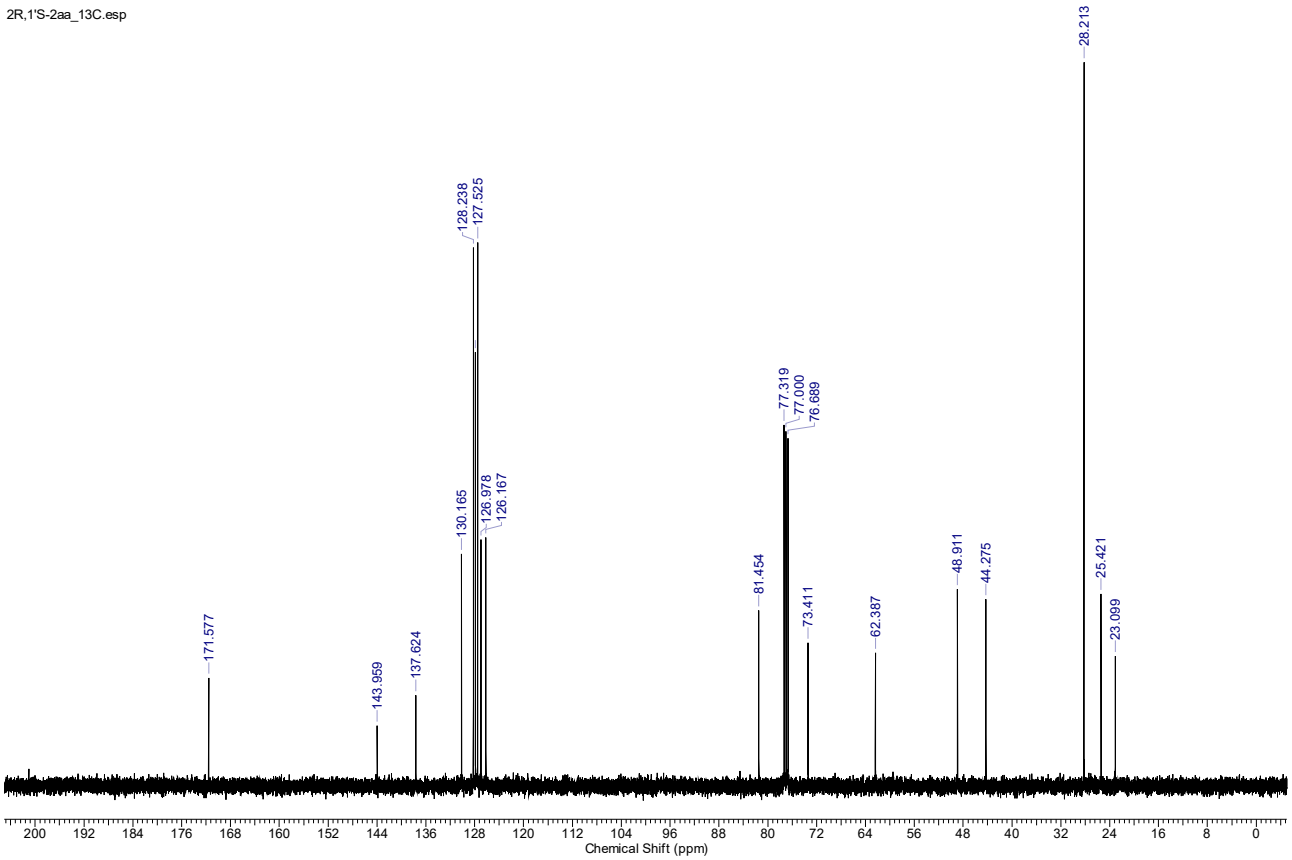
2R,1'S-2aa_1H.esp



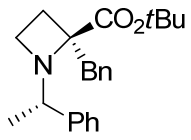
(2*R*,1'*S*)-**2aa**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

2R,1'S-2aa_13C.esp



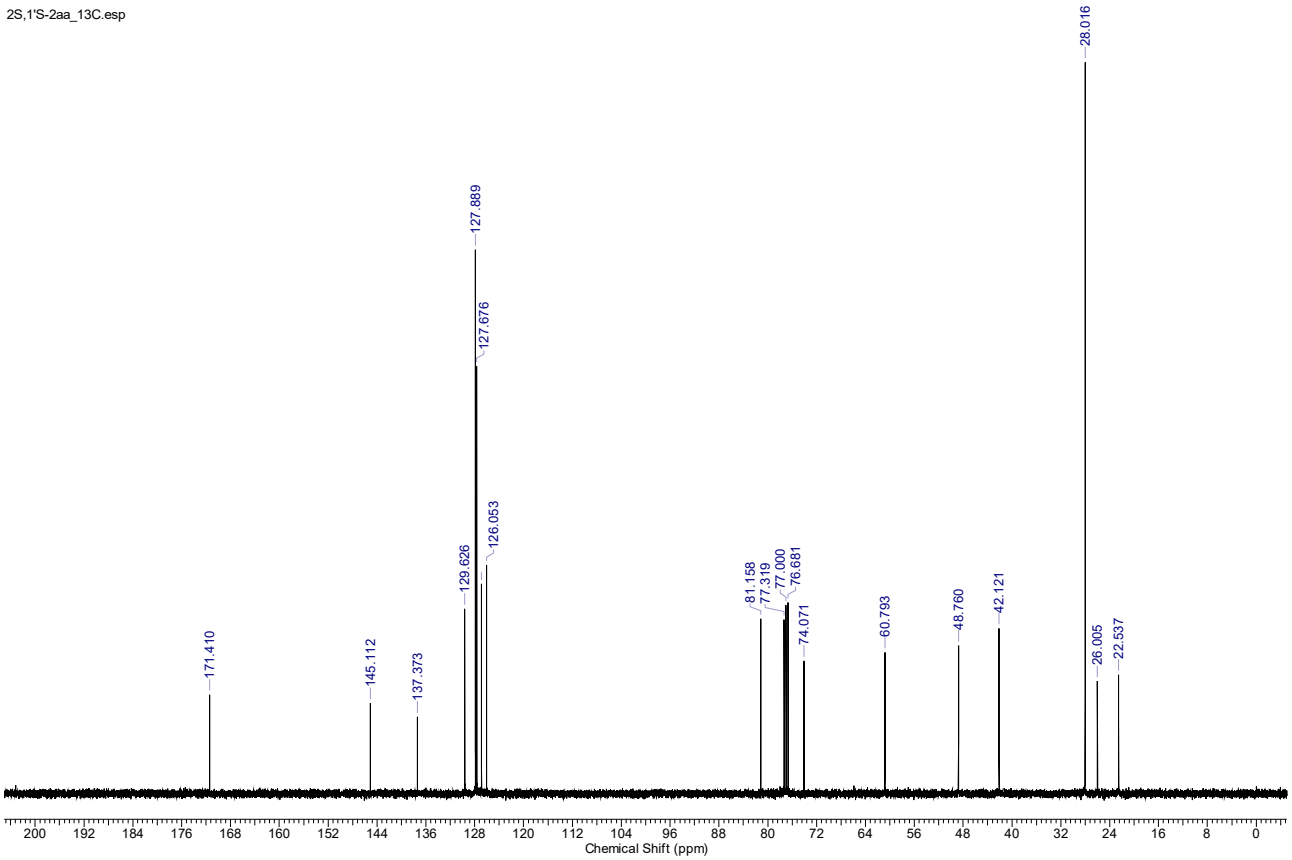
2S,1'S-2aa_1H.esp



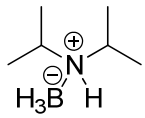
(2*S*,1'*S*)-**2aa**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

2S,1'S-2aa_13C.esp



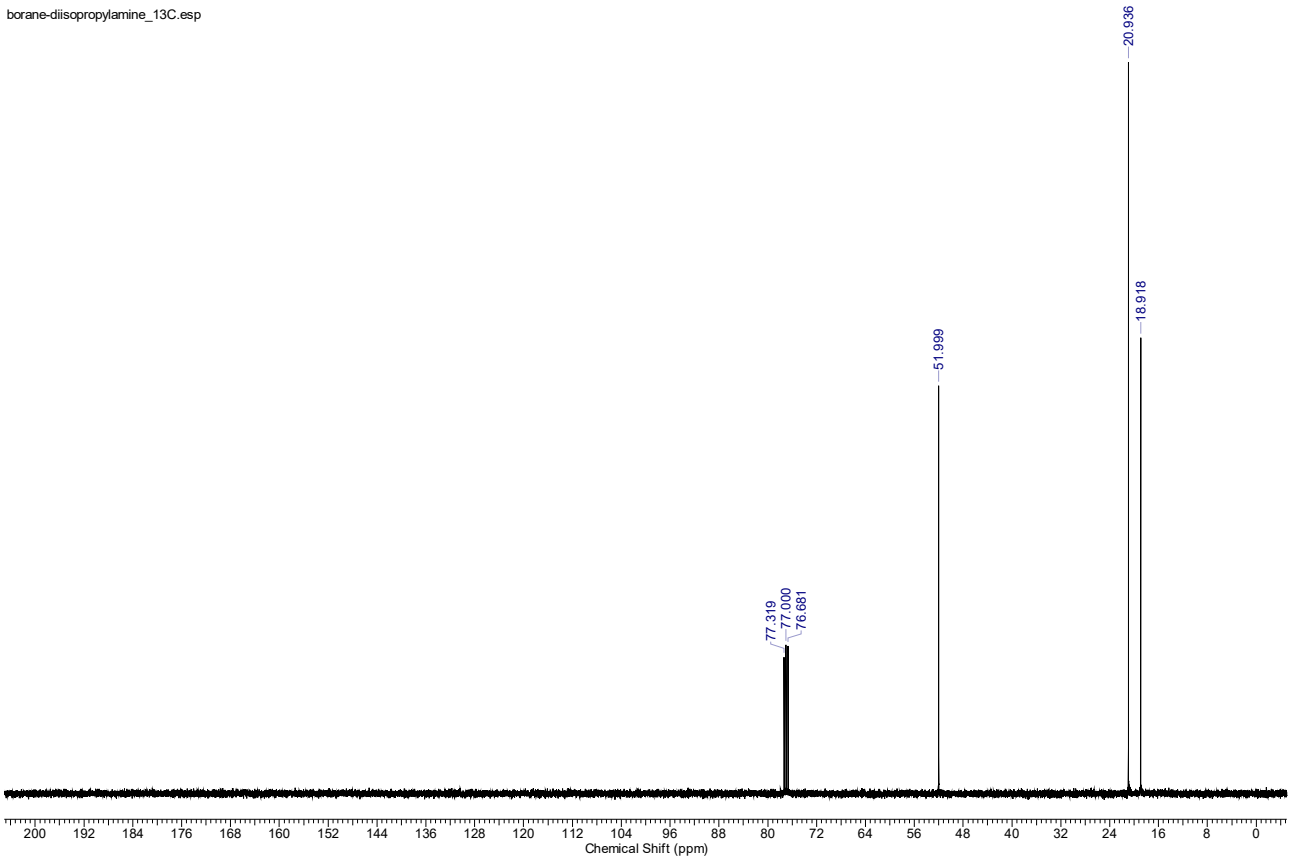
borane-diisopropylamine_1H.esp



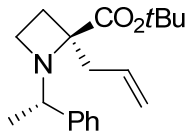
borane–diisopropylamine

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

borane-diisopropylamine_13C.esp



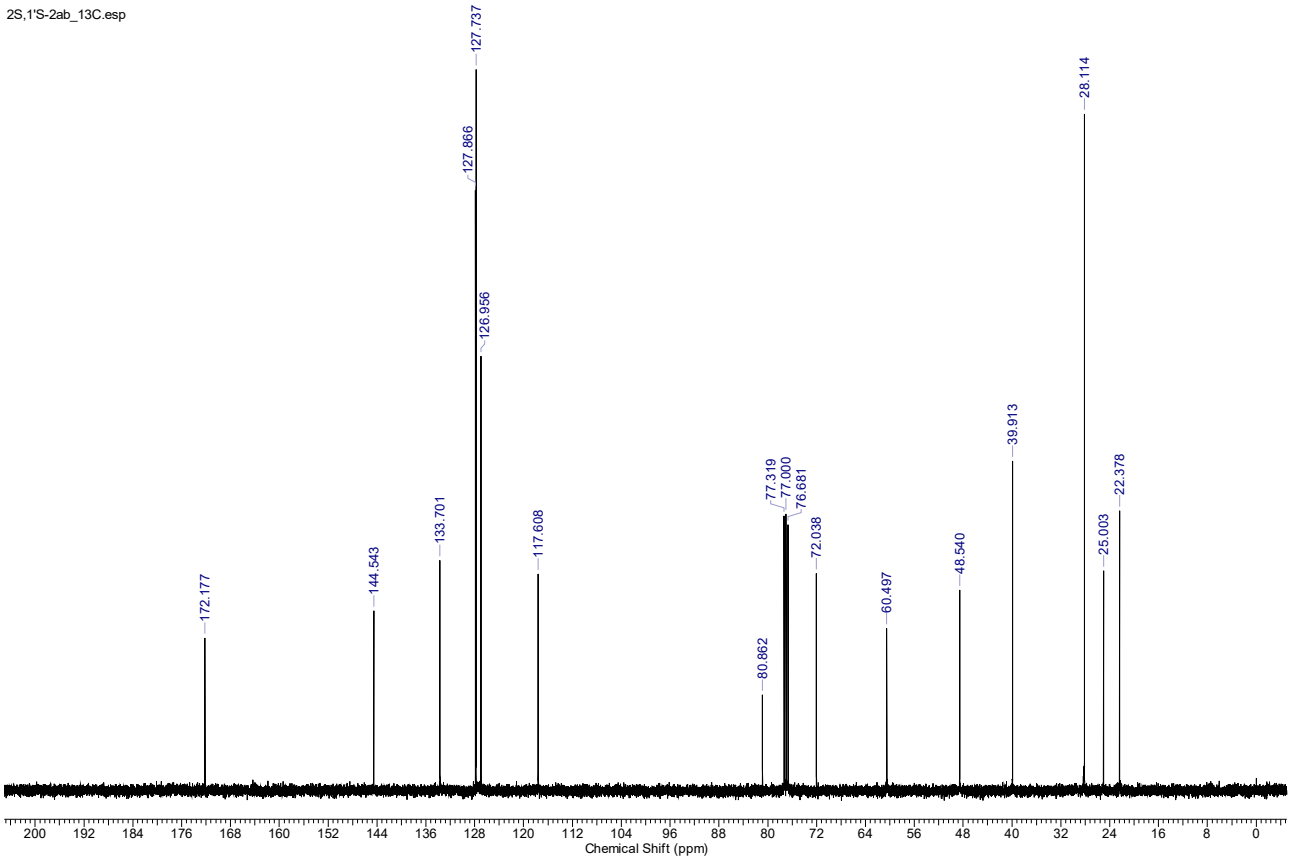
2S,1'S-2ab_1H.esp



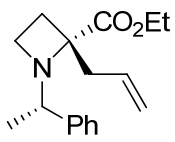
(2*S*,1'*S*)-**2ab**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

2S,1'S-2ab_13C.esp



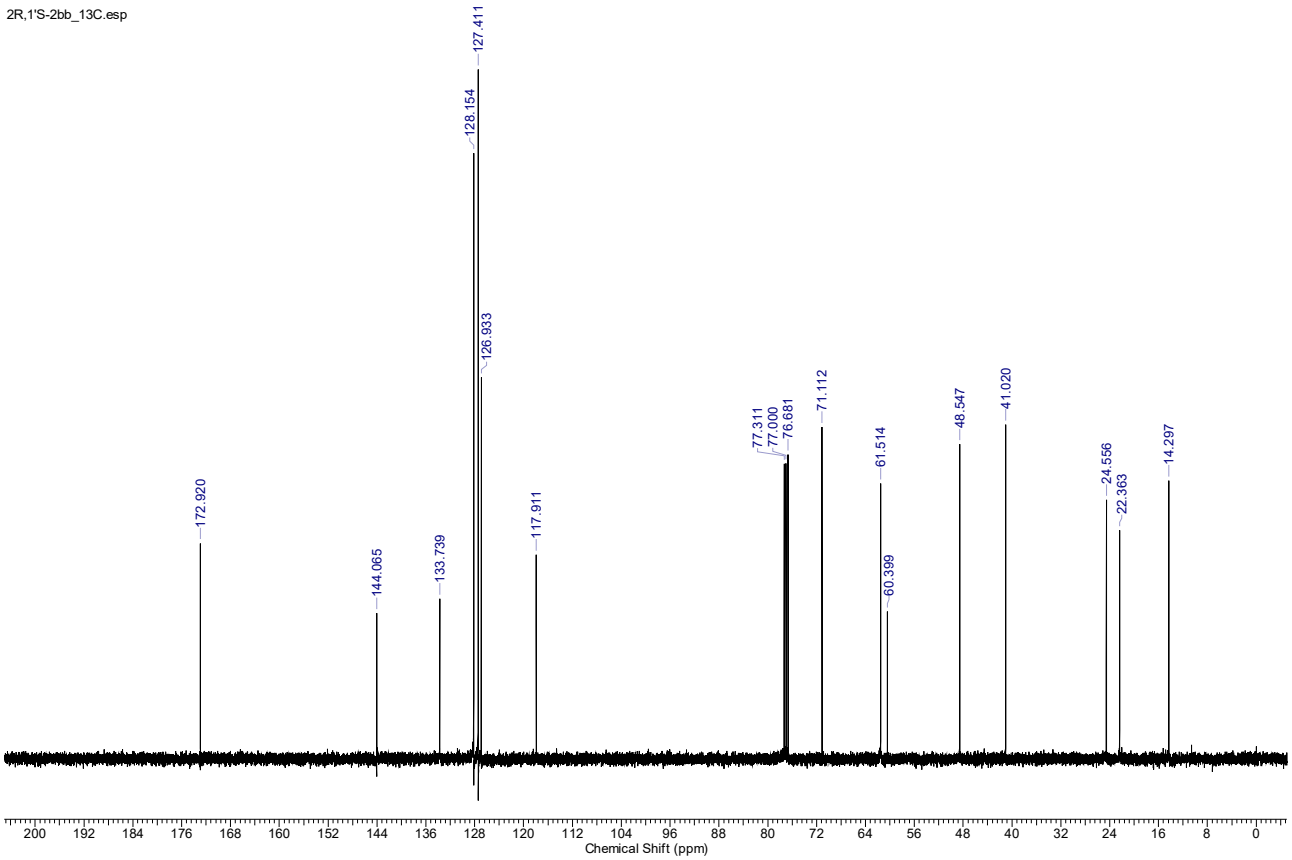
2R,1'S-2bb_1H.esp



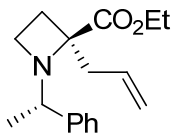
(2*R*,1'*S*)-**2bb**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

2R,1'S-2bb_13C.esp



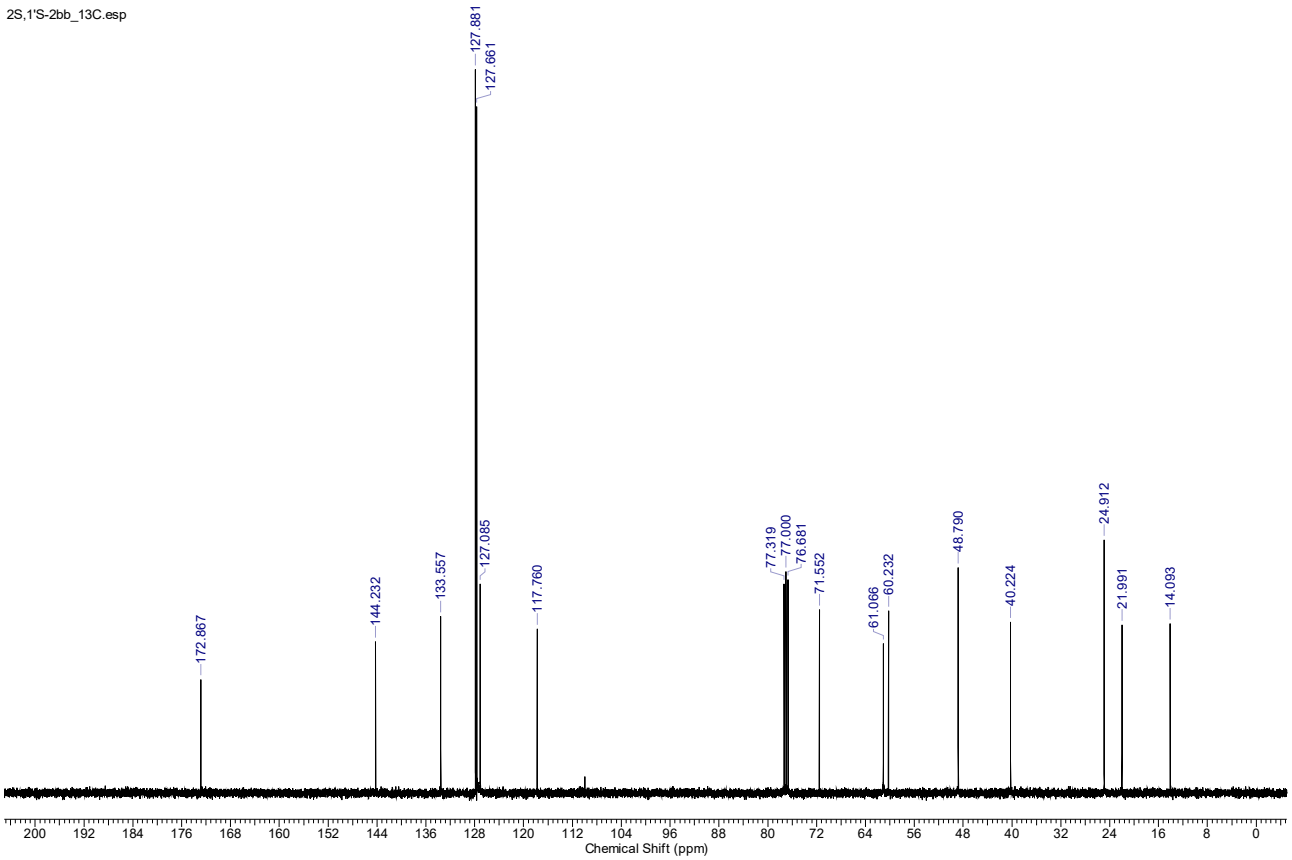
2S,1'S-2bb_1H.esp

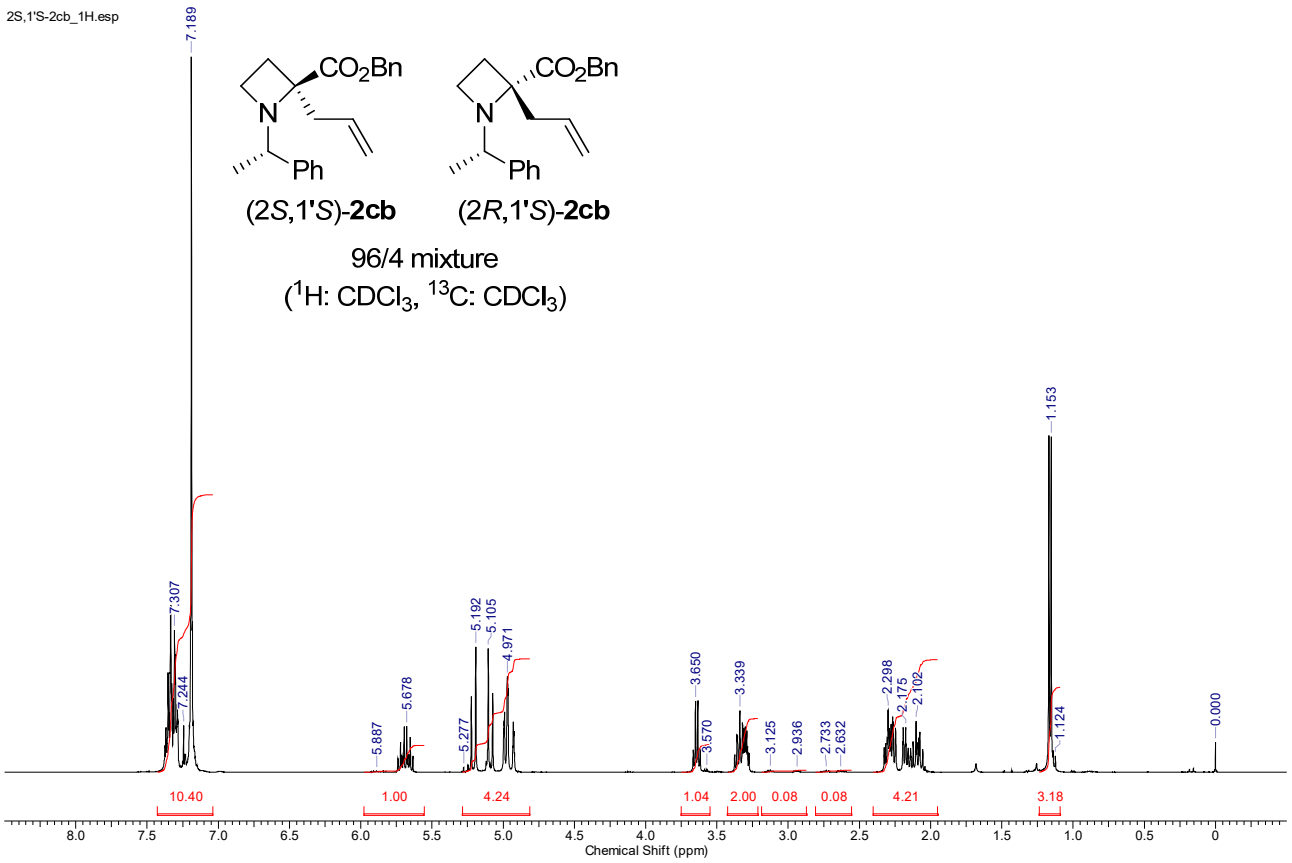


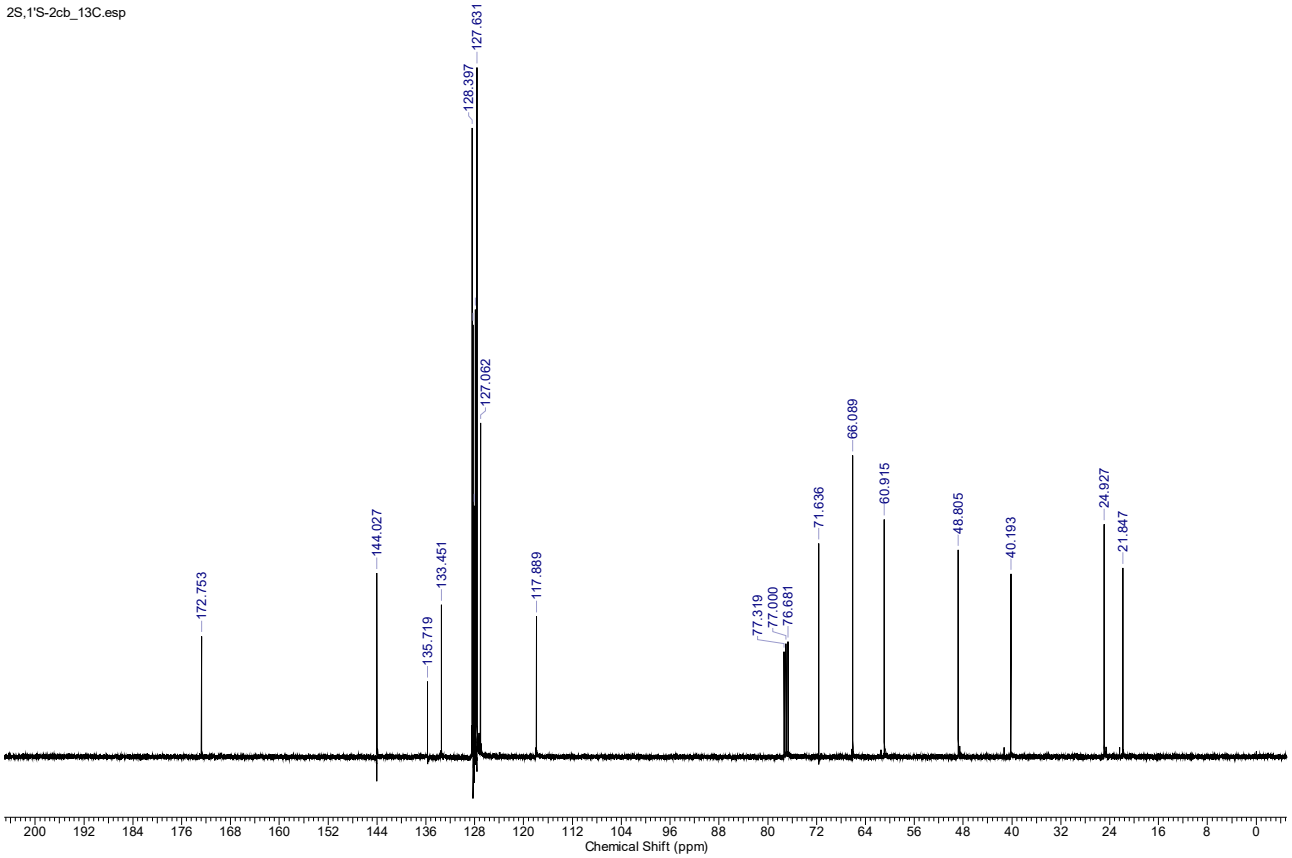
(2*S*,1'*S*)-**2bb**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

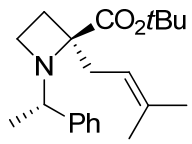
2S,1'S-2bb_13C.esp




2S,1'S-2cb_1H.esp
7.189
CO2Bn
N
Ph
(2S,1'S)-2cb
(2R,1'S)-2cb
96/4 mixture
(1H: CDCl3, 13C: CDCl3)
7.307
7.244
5.887
5.678
5.277
5.192
5.105
4.971
3.650
3.570
3.339
3.125
2.936
2.733
2.632
2.298
2.175
2.102
1.153
1.124
0.000
10.40
1.00
4.24
1.04
2.00
0.08
0.08
4.21
3.18
Chemical Shift (ppm)

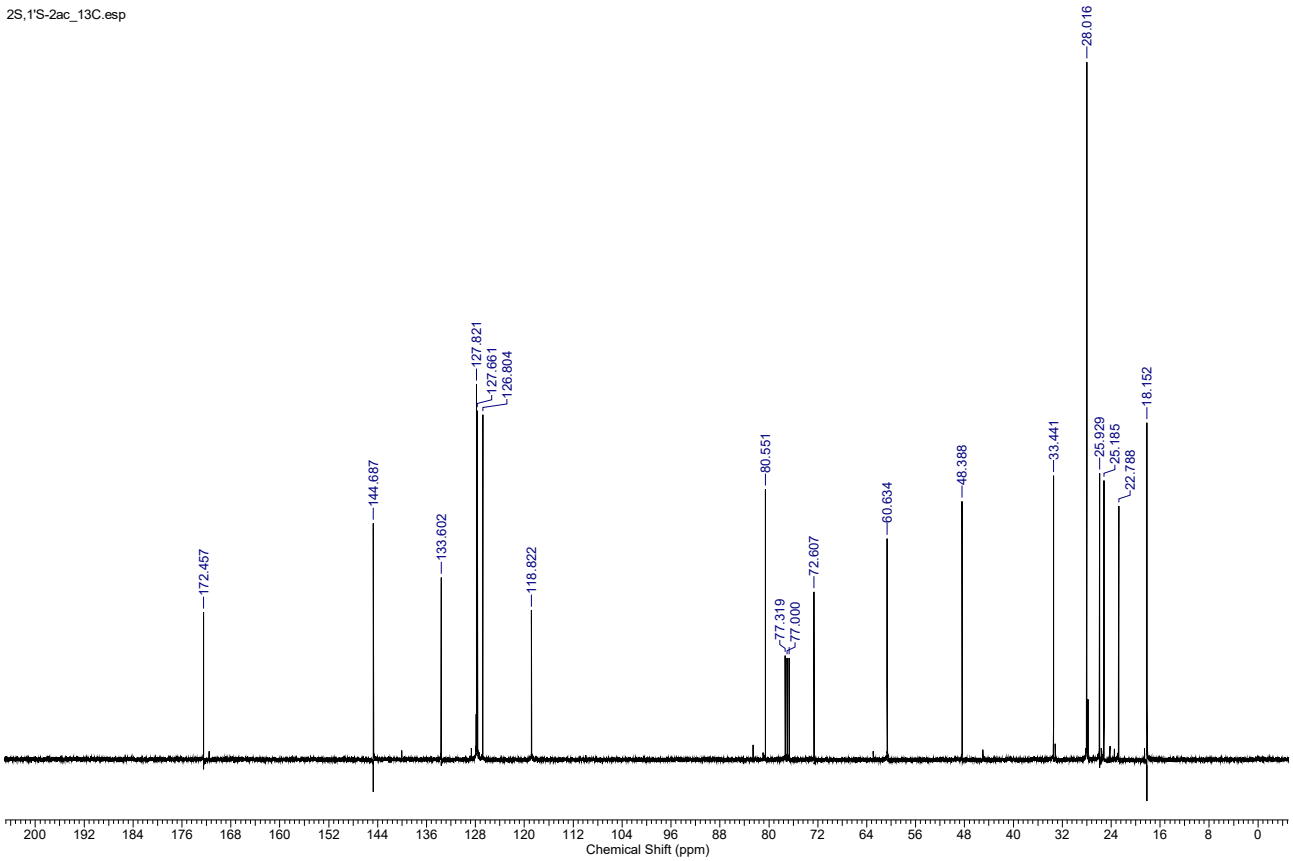

2S,1'S-2cb_13C.esp
127.631
128.397
127.062
172.753
144.027
135.719
133.451
117.889
77.319
77.000
76.681
71.636
66.089
60.915
48.805
40.193
24.927
21.847
Chemical Shift (ppm)

2S,1'S-2ac_1H.esp

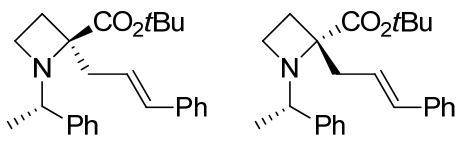


(2*S*,1'*S*)-**2ac**
(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

2S,1'S-2ac_13C.esp



2S,1'S-2ad_1H.esp



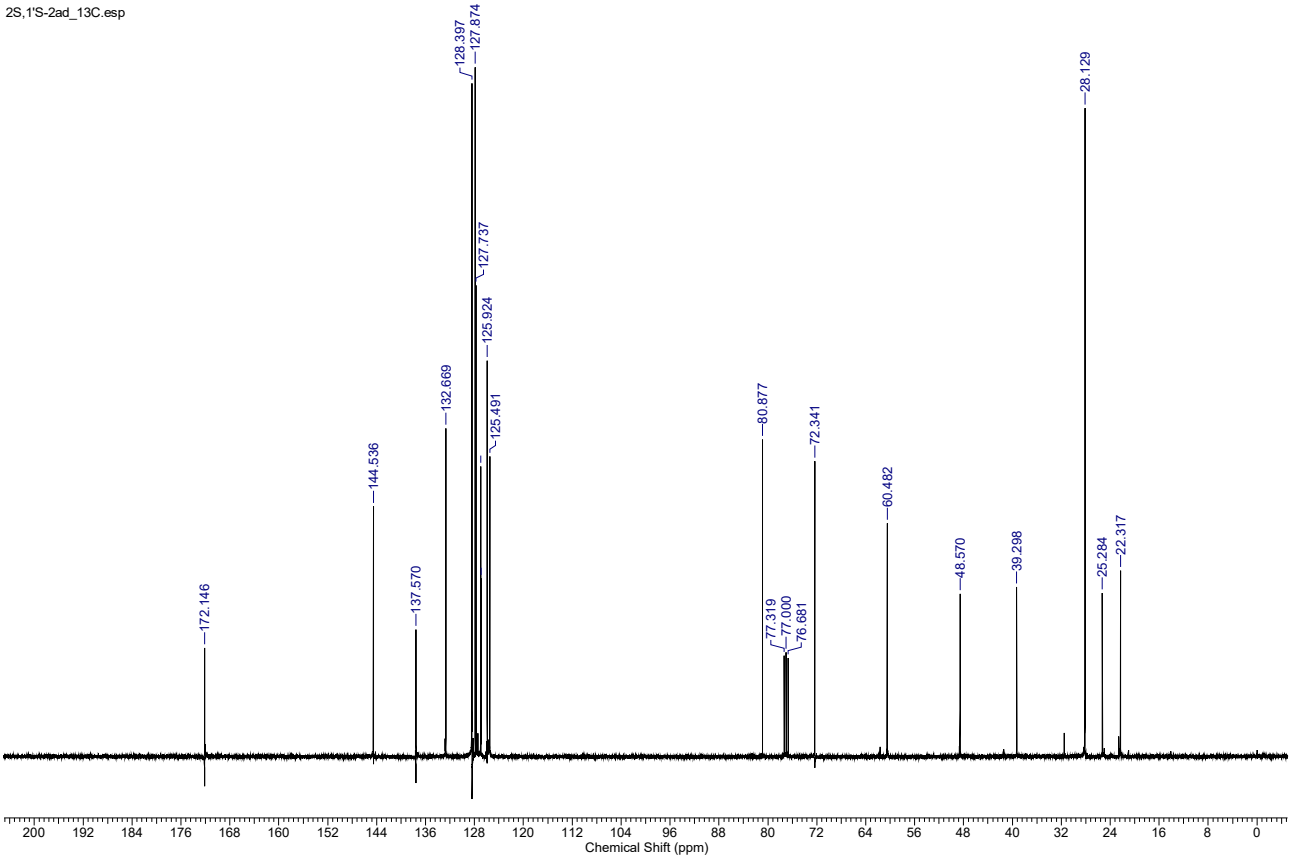
(2*S*,1'*S*)-**2ad**

(2*R*,1'*S*)-**2ad**

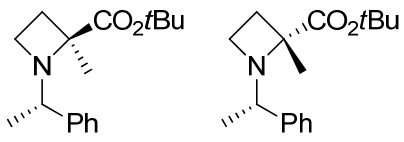
94/6 mixture

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

2S,1'S-2ad_13C.esp



2ae_1H.esp

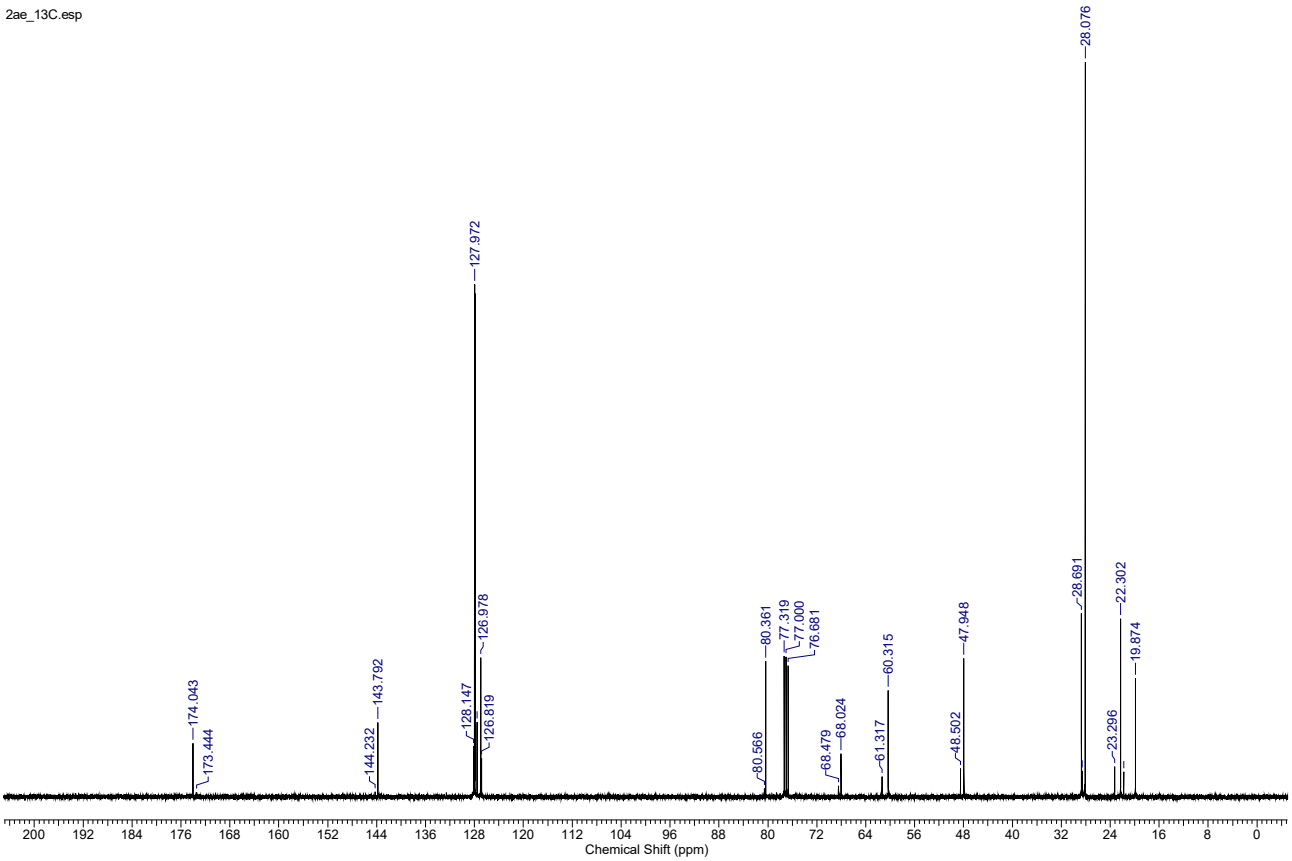


(2*S*,1'*S*)-**2ae** (2*R*,1'*S*)-**2ae**

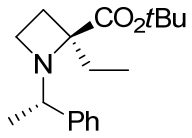
89/11 mixture

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

2ae_13C.esp



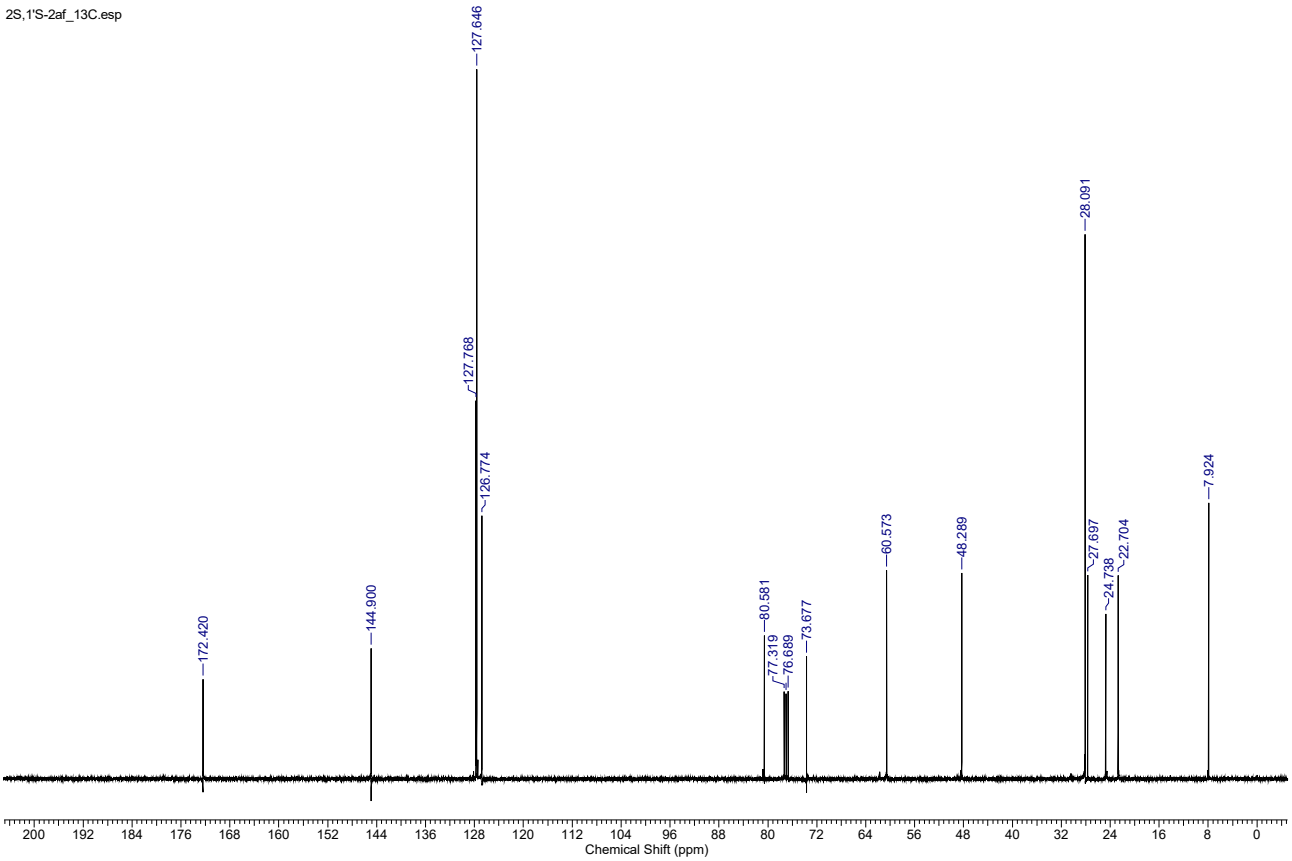
2S,1'S-2af_1H.esp



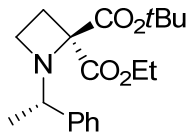
(2*S*,1'*S*)-**2af**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

2S,1'S-2af_13C.esp



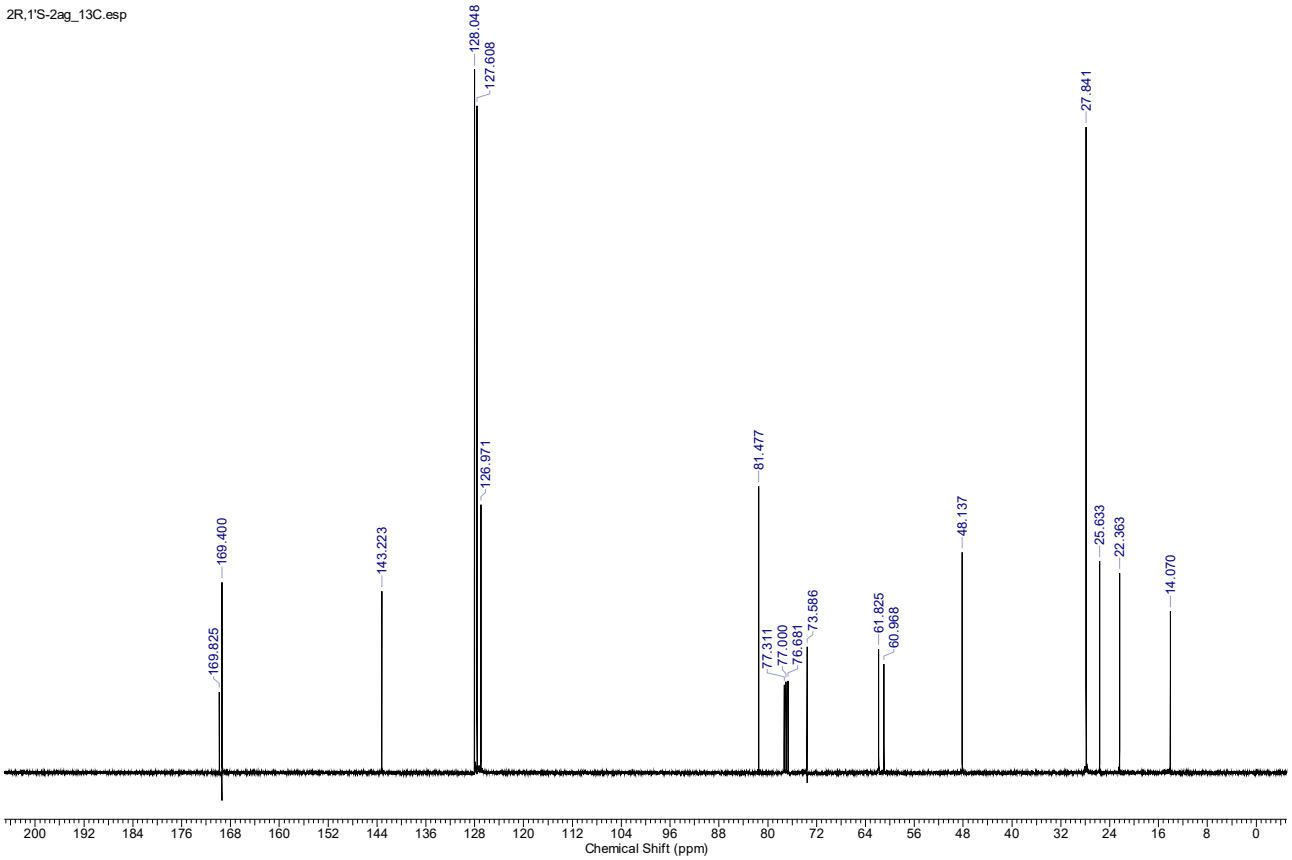
2R,1'S-2ag_1H.esp



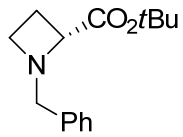
(2*R*,1'*S*)-**2ag**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

2R,1'S-2ag_13C.esp



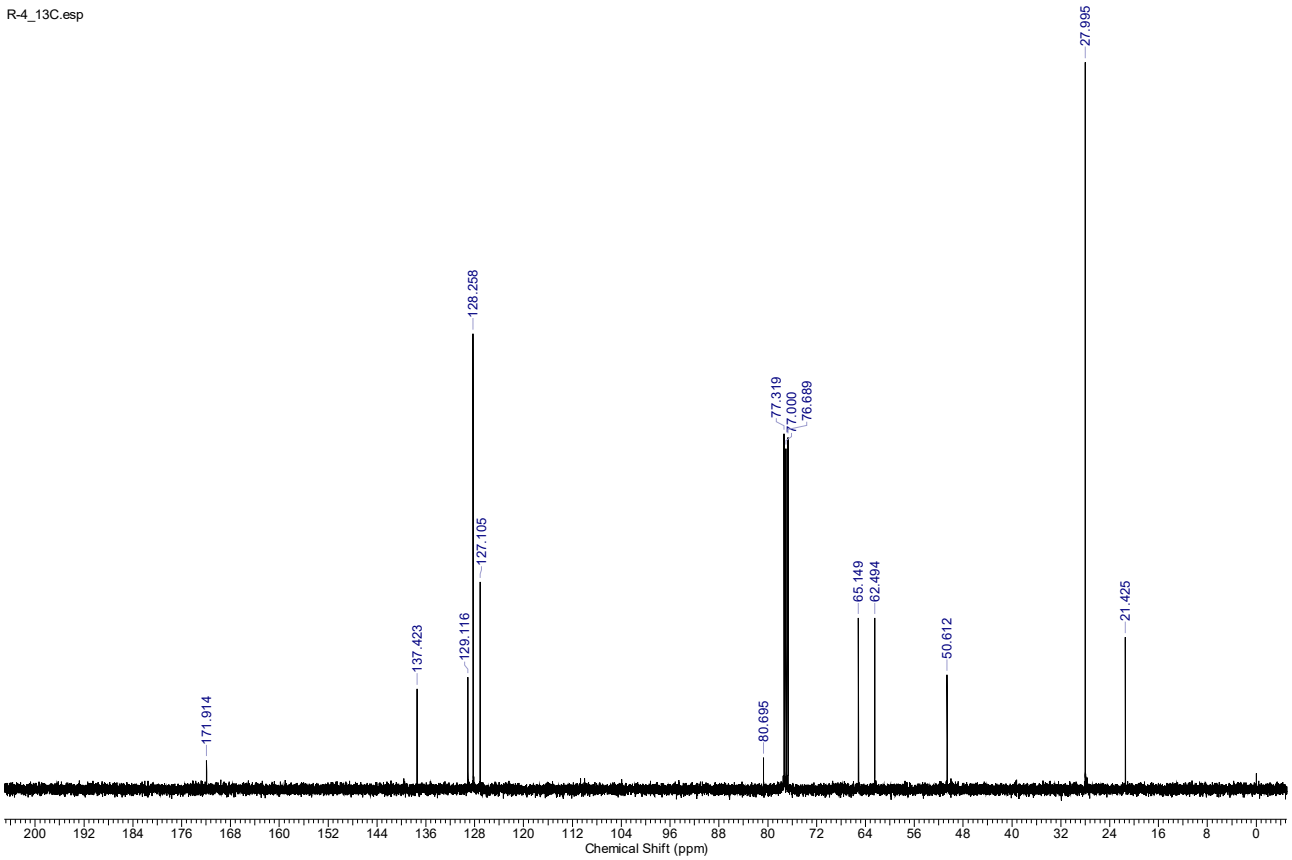
R-4_1H.esp



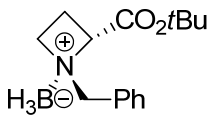
(*R*)-**4**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

R-4_13C.esp



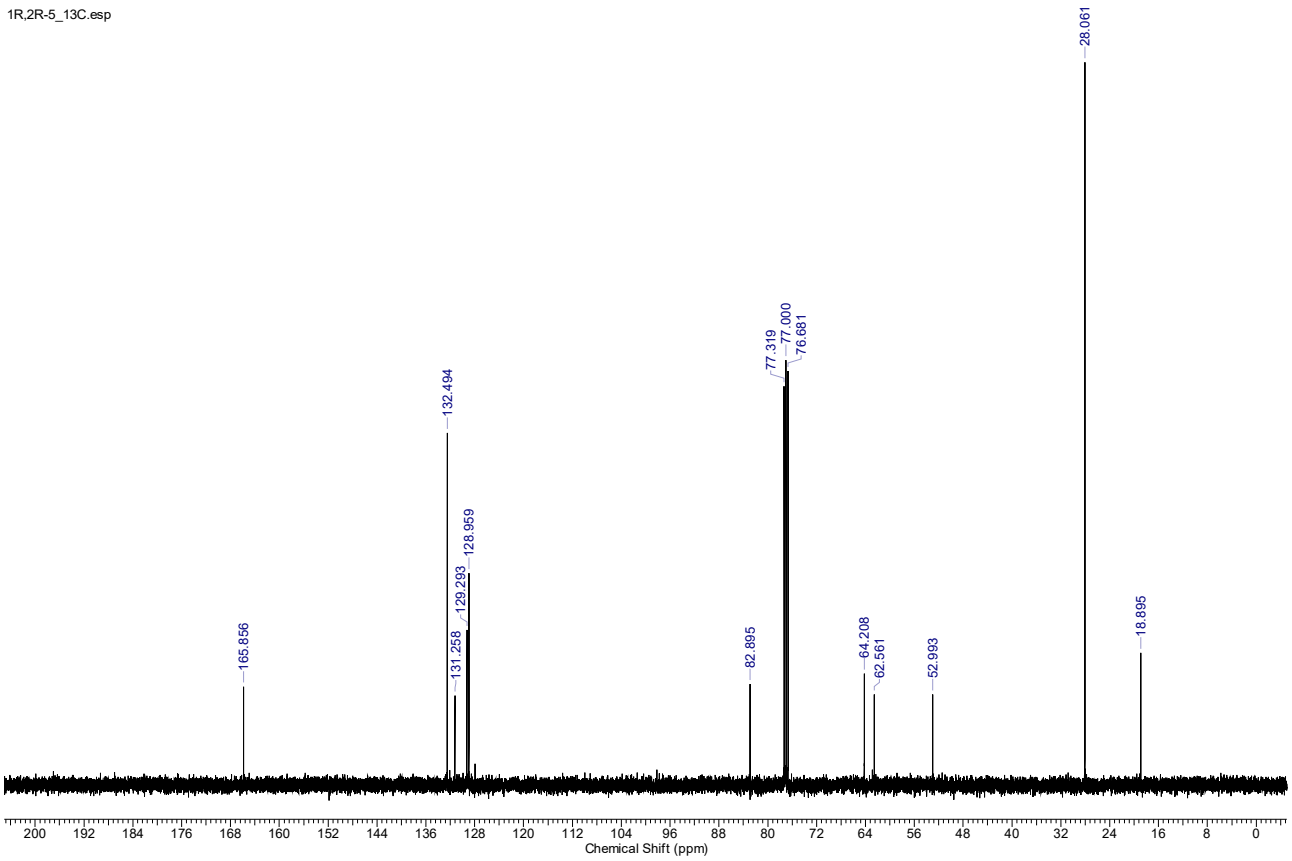
1R,2R-5_1H.esp



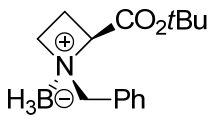
(1*R*,2*R*)-**5**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

1R,2R-5_13C.esp



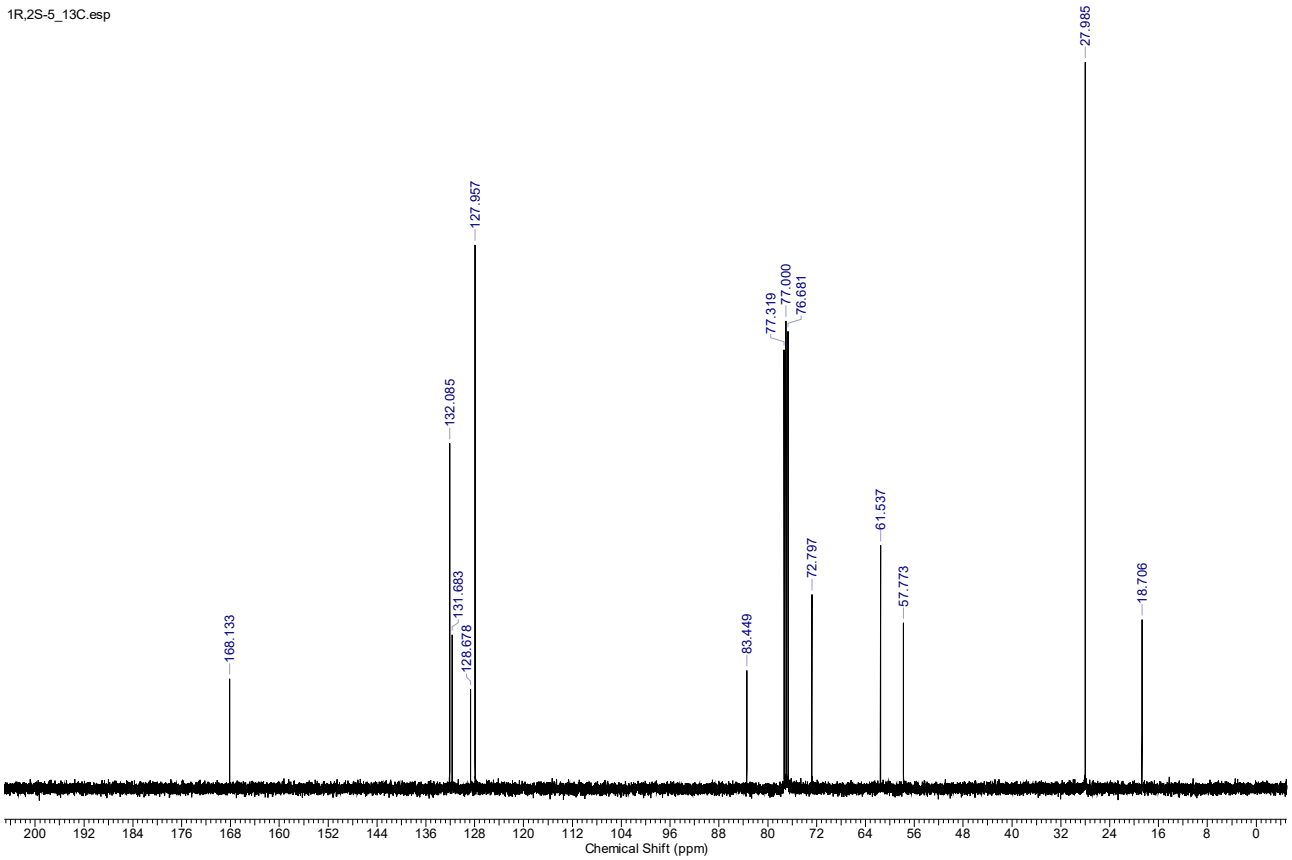
1R,2S-5_1H.esp



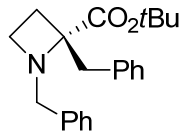
(1*R*,2*S*)-**5**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

1R,2S-5_13C.esp



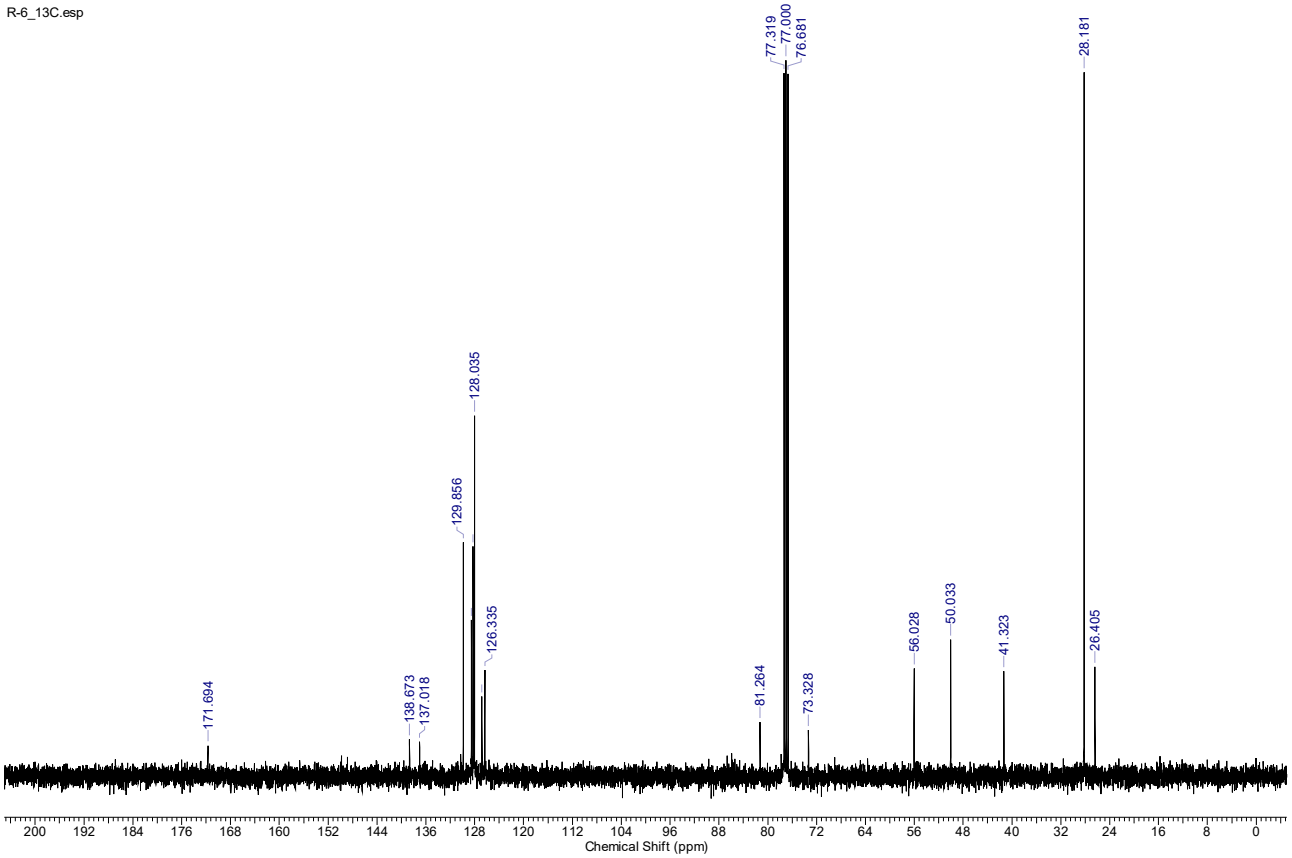
R-6_1H.esp



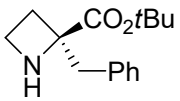
(*R*)-**6**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

R-6_13C.esp



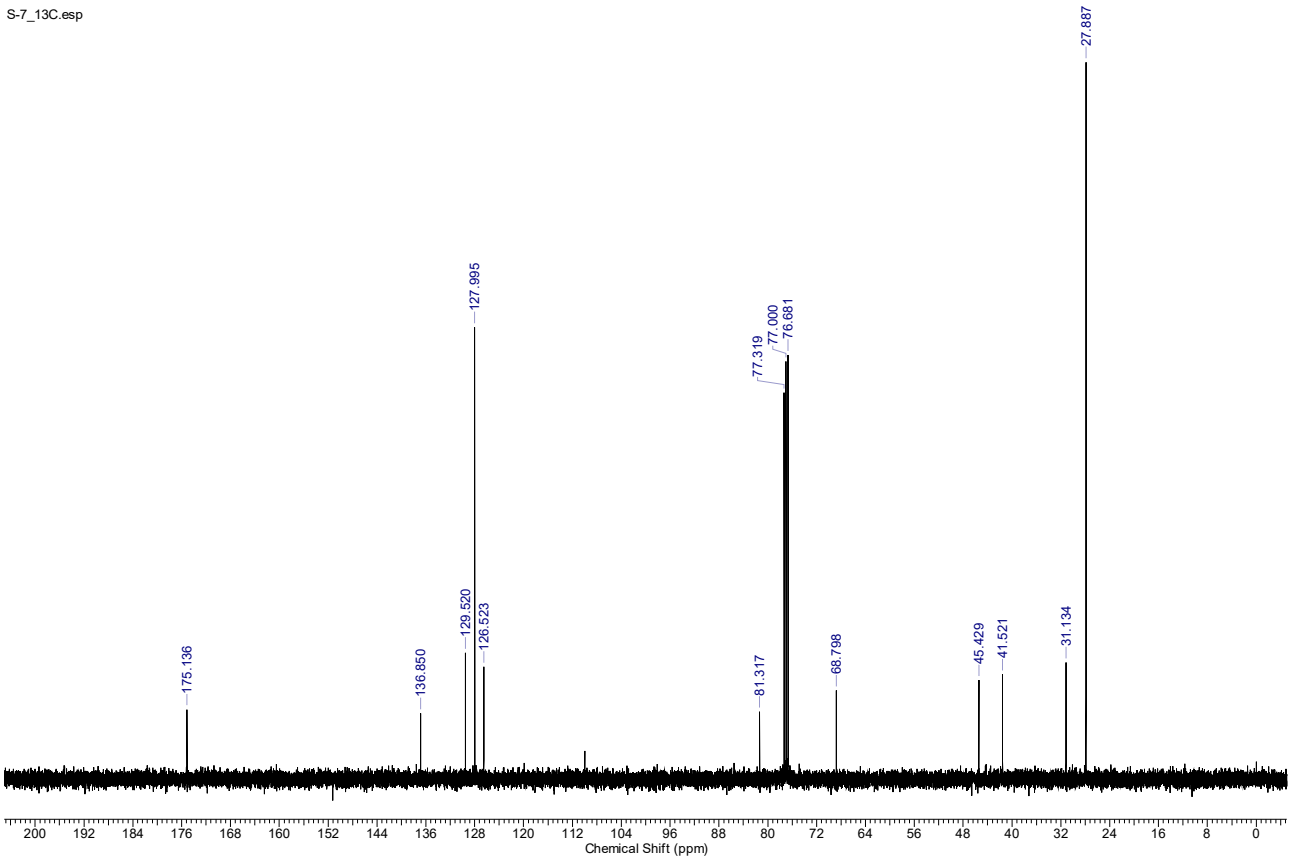
S-7_1H.esp



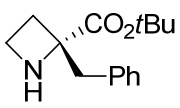
(*S*)-**7**

(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

S-7_13C.esp



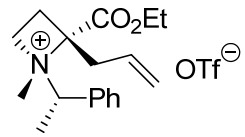
R-7_1H.esp



(*R*)-**7**

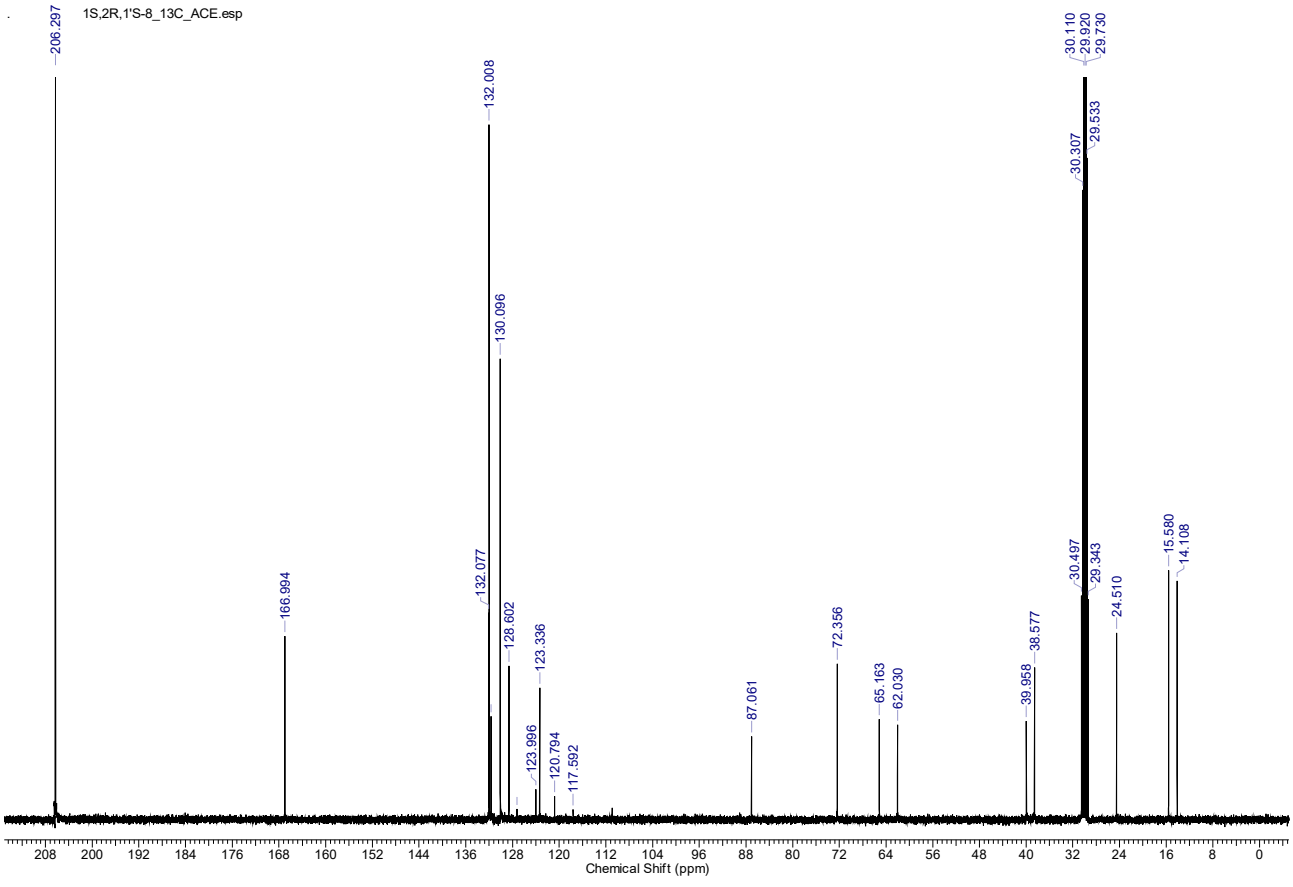
(^{1}H: $CDCl_3$)

1S,2R,1'S-8_1H_ACE.esp

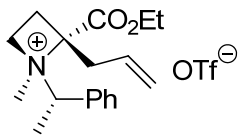


(1*S*,2*R*,1'*S*)-**8**

(^{1}H: Acetone-d_6, ^{13}C: Acetone-d_6)

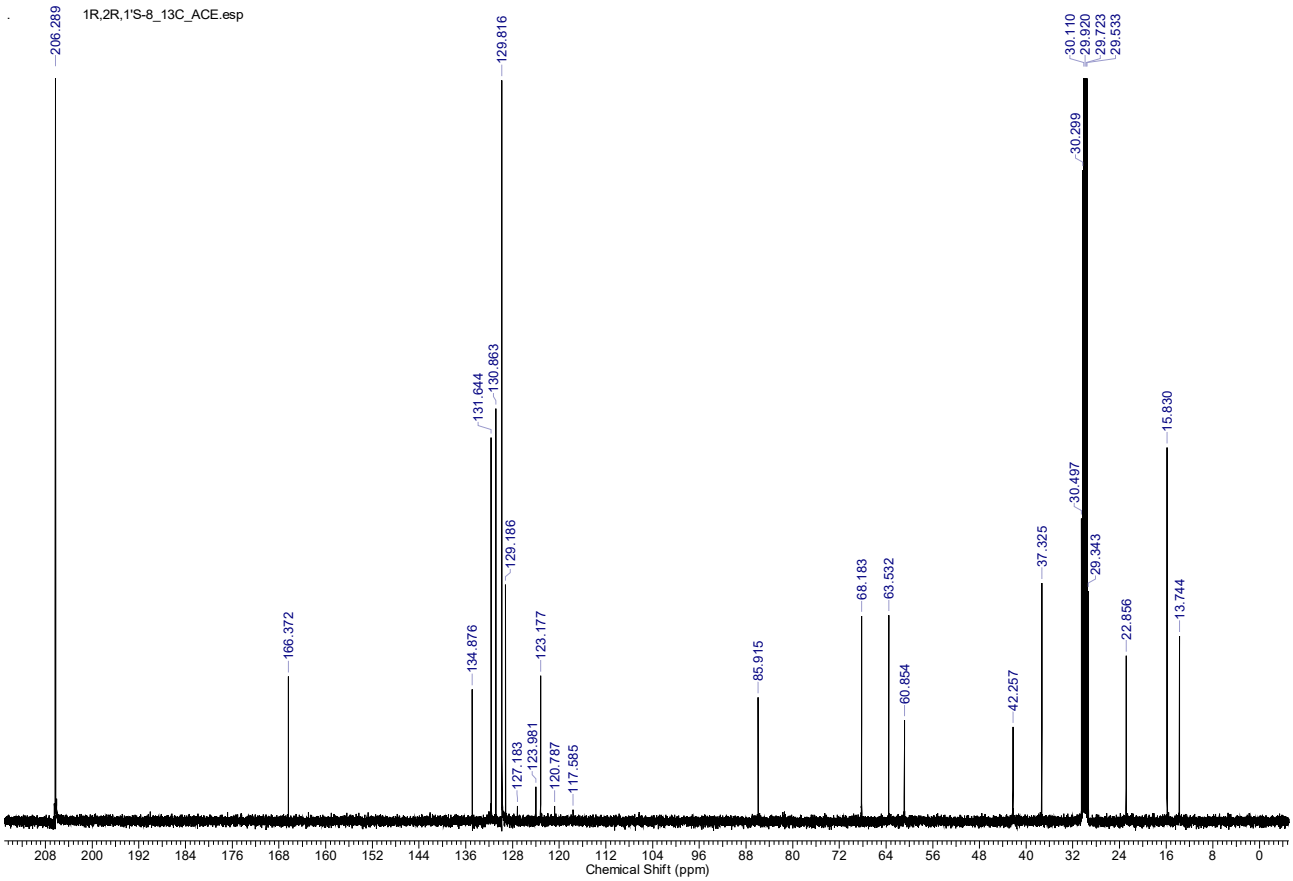


1R,2R,1'S-8_1H_ACE.esp

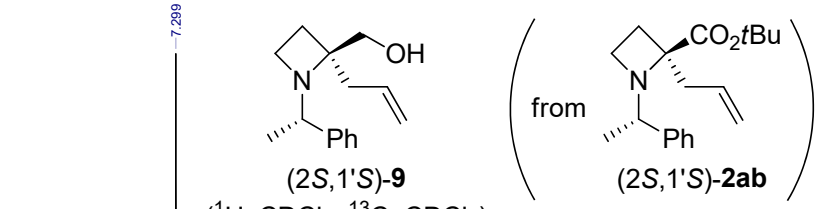


(1*R*,2*R*,1'*S*)-**8**

(^{1}H: Acetone-d_6, ^{13}C: Acetone-d_6)



2S,1'S-9_1H_from_2S,1'S-2ab.esp

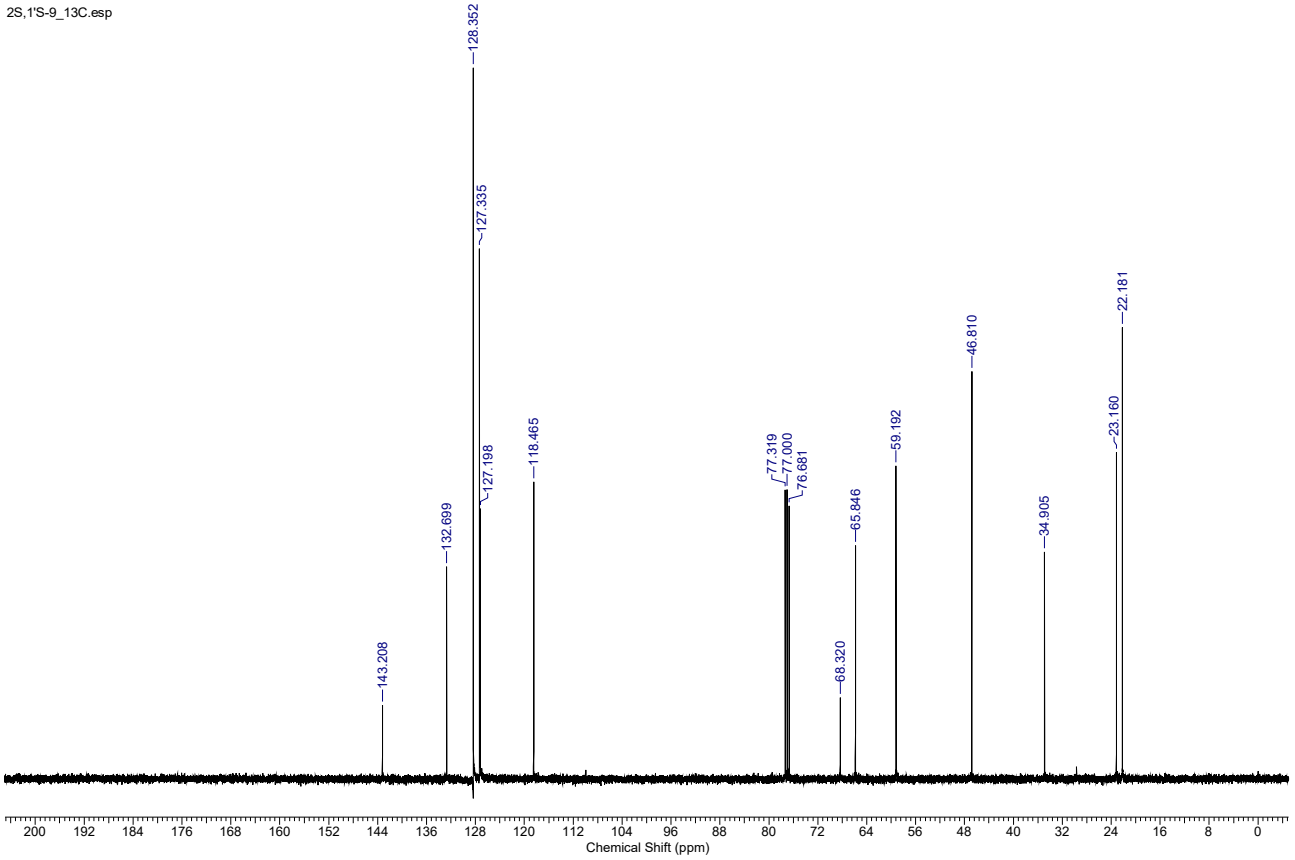


(2*S*,1'*S*)-**9**

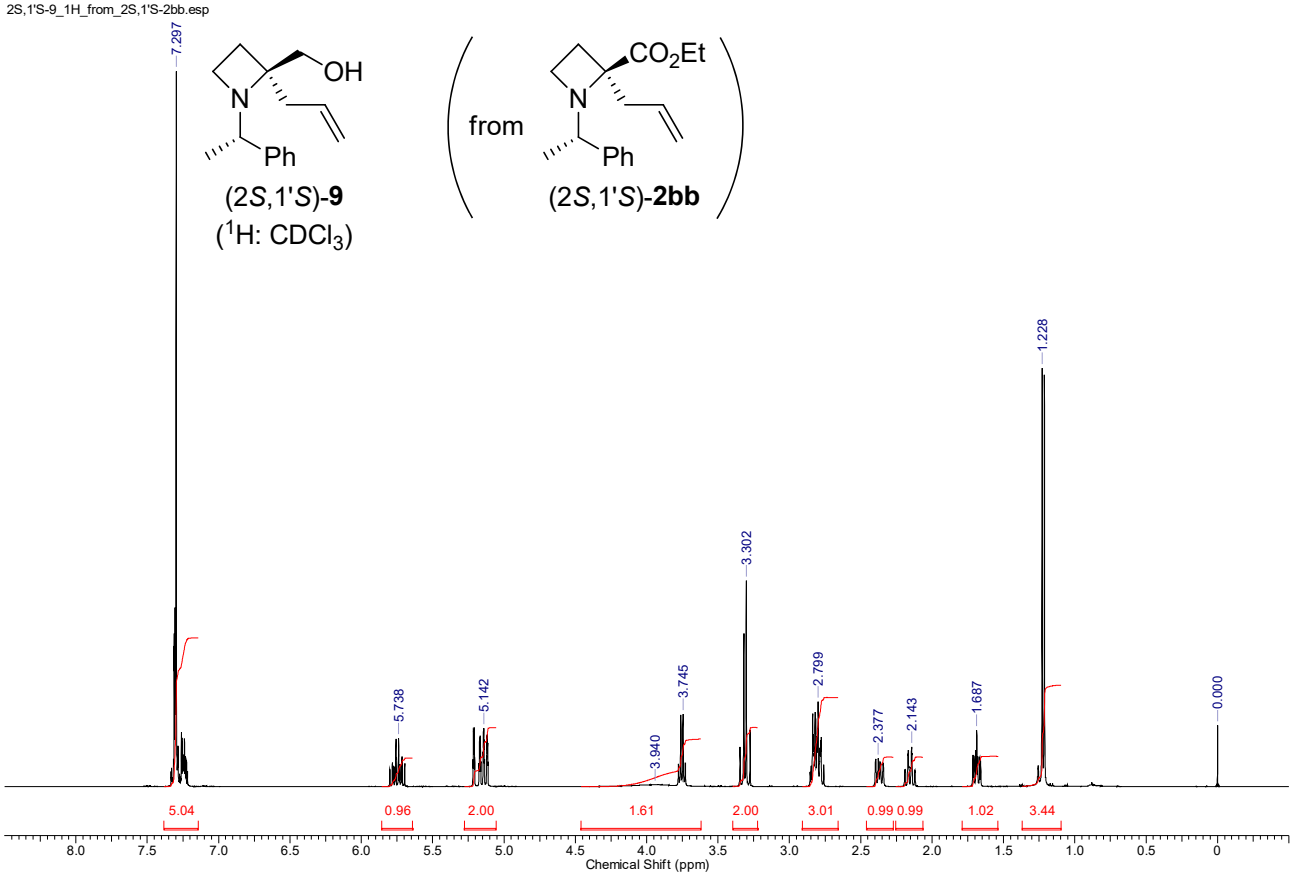
(^{1}H: $CDCl_3$, ^{13}C: $CDCl_3$)

(2*S*,1'*S*)-**2ab**

2S,1'S-9_13C.esp

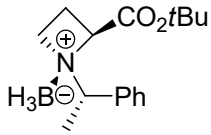


2S,1'S-9_1H_from_2S,1'S-2bb.esp



4. Copies of ^{11}B NMR spectra of borane complexes

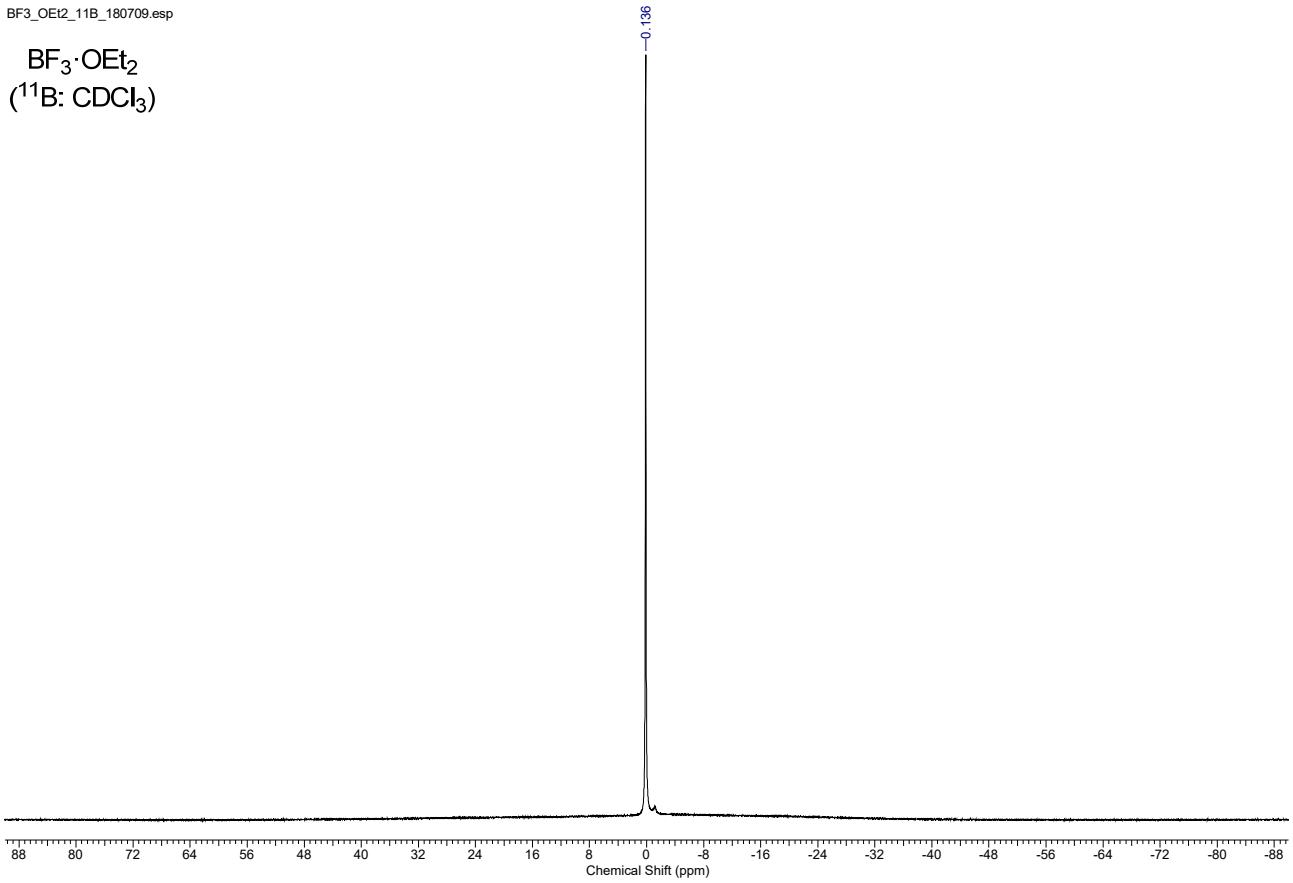
1S,2S,1'S-3a_11B_180709.esp



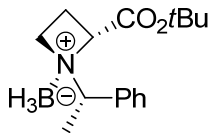
(1*S*,2*S*,1'*S*)-**3a**
(^{11}B: $CDCl_3$)
–13.4 ppm (br)

BF3_OEt2_11B_180709.esp

$BF_3{\cdot}OEt_2$
(^{11}B: $CDCl_3$)



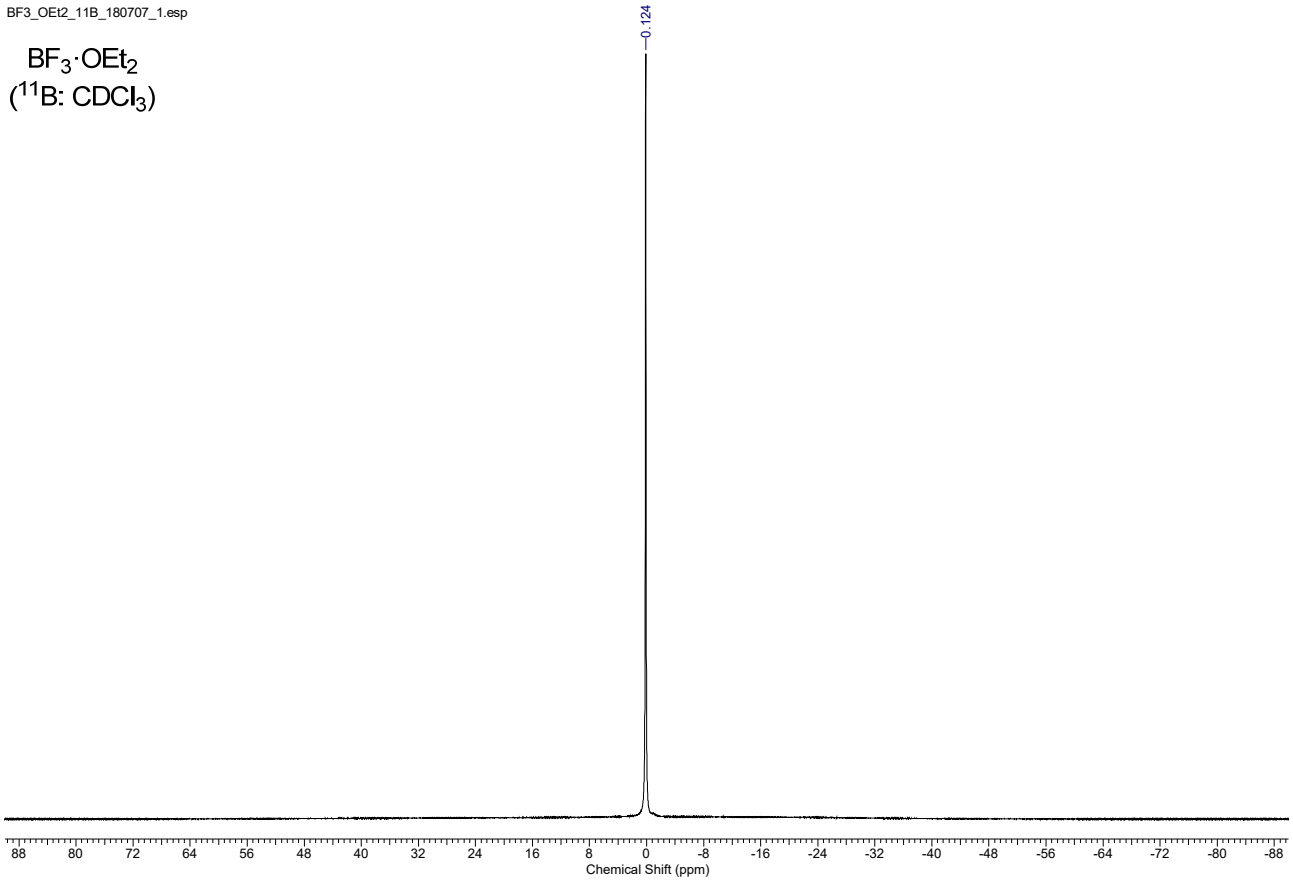
1R,2R,1'S-3a_11B_180707_1.esp



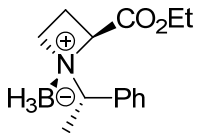
(1*R*,2*R*,1'*S*)-**3a**
(^{11}B: $CDCl_3$)
–14.3 ppm (br)

BF3_OEt2_11B_180707_1.esp

$BF_3{\cdot}OEt_2$
(^{11}B: $CDCl_3$)



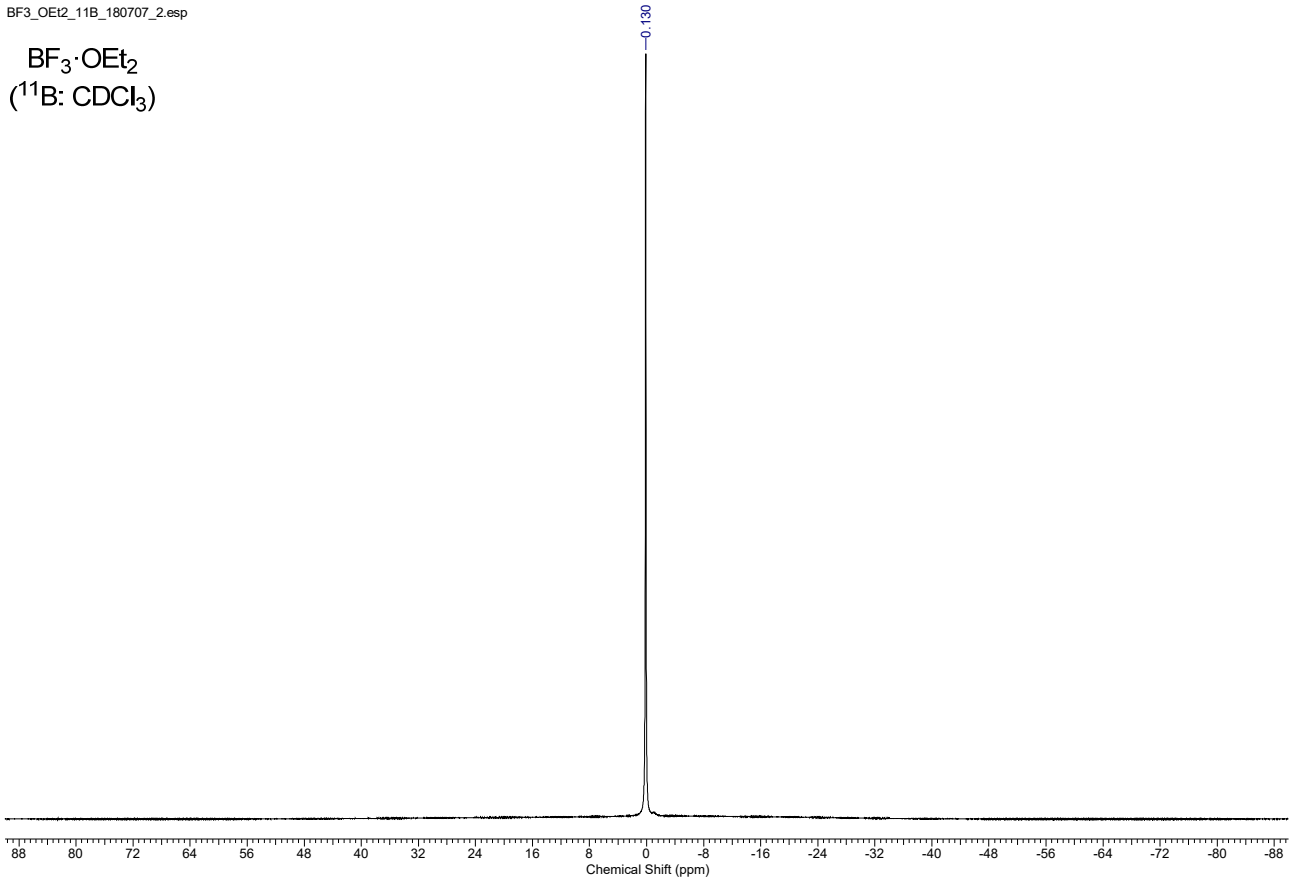
1S,2S,1'S-3b_11B_180707_2.esp



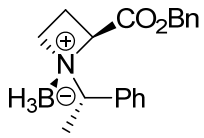
(1*S*,2*S*,1'*S*)-**3b**
(^{11}B: $CDCl_3$)
–13.4 ppm (br)

BF3_OEt2_11B_180707_2.esp

$BF_3{\cdot}OEt_2$
(^{11}B: $CDCl_3$)



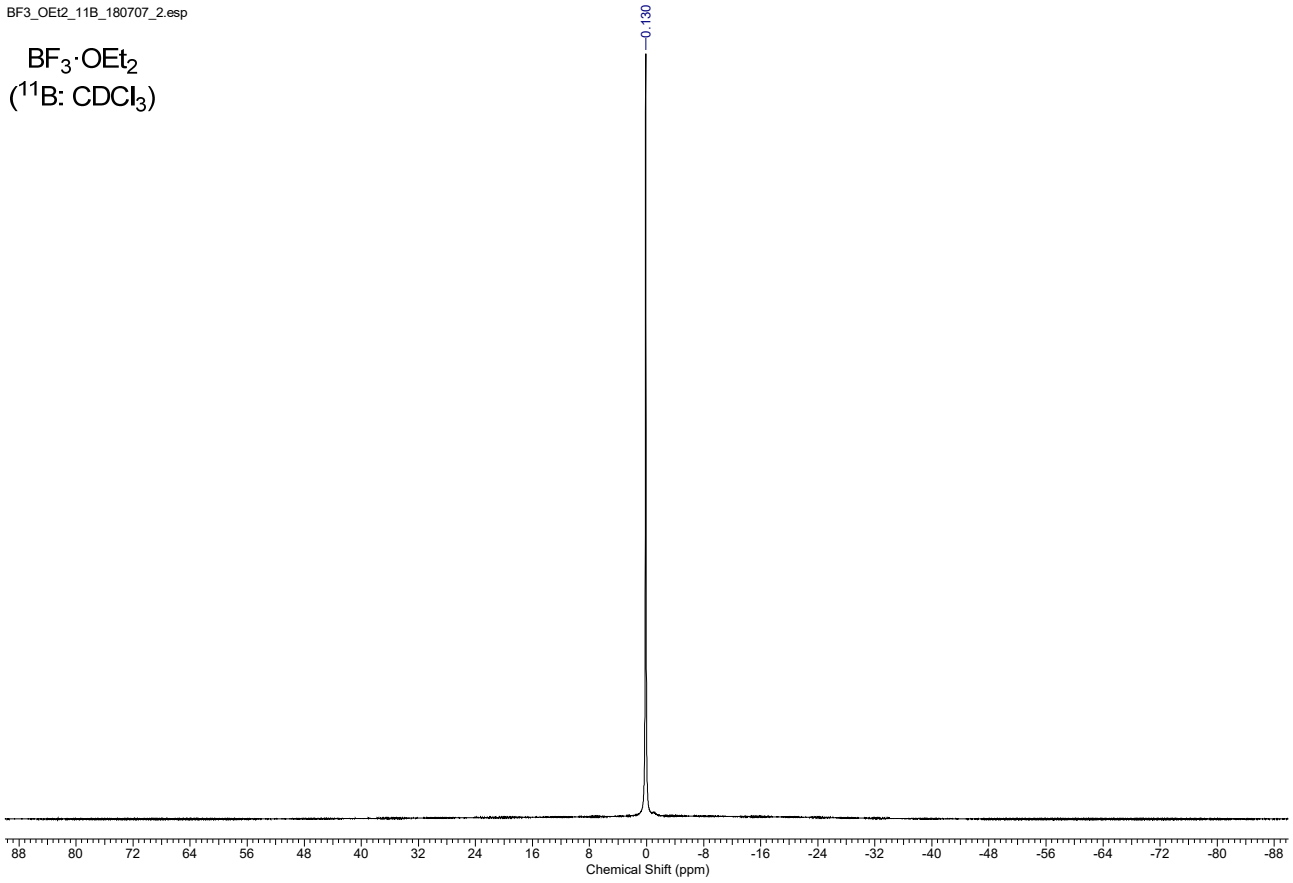
1S,2S,1'S-3c_11B_180707_2.esp



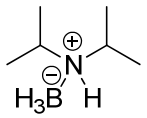
(1*S*,2*S*,1'*S*)-**3c**
(^{11}B: $CDCl_3$)
–13.2 ppm (br)

BF3_OEt2_11B_180707_2.esp

$BF_3{\cdot}OEt_2$
(^{11}B: $CDCl_3$)



borane-diisopropylamine_11B_180709.esp



borane–diisopropylamine

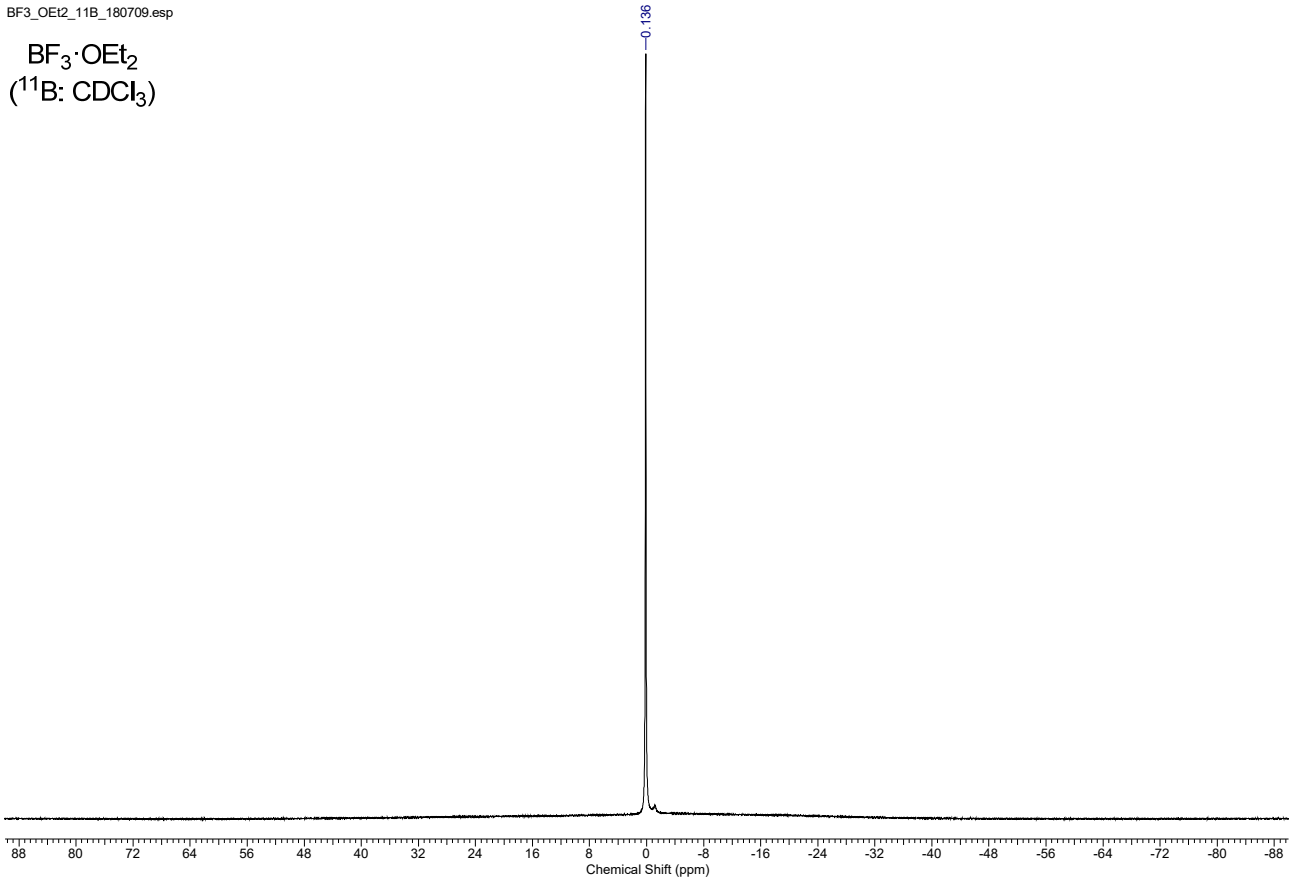
(^{11}B: $CDCl_3$)

–21.5 ppm (q, *J* = 97 Hz)

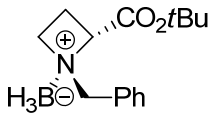
BF3_OEt2_11B_180709.esp

$BF_3 \cdot OEt_2$

(^{11}B: $CDCl_3$)



1R,2R-5_11B_180707.esp



(1*R*,2*R*)-**5**

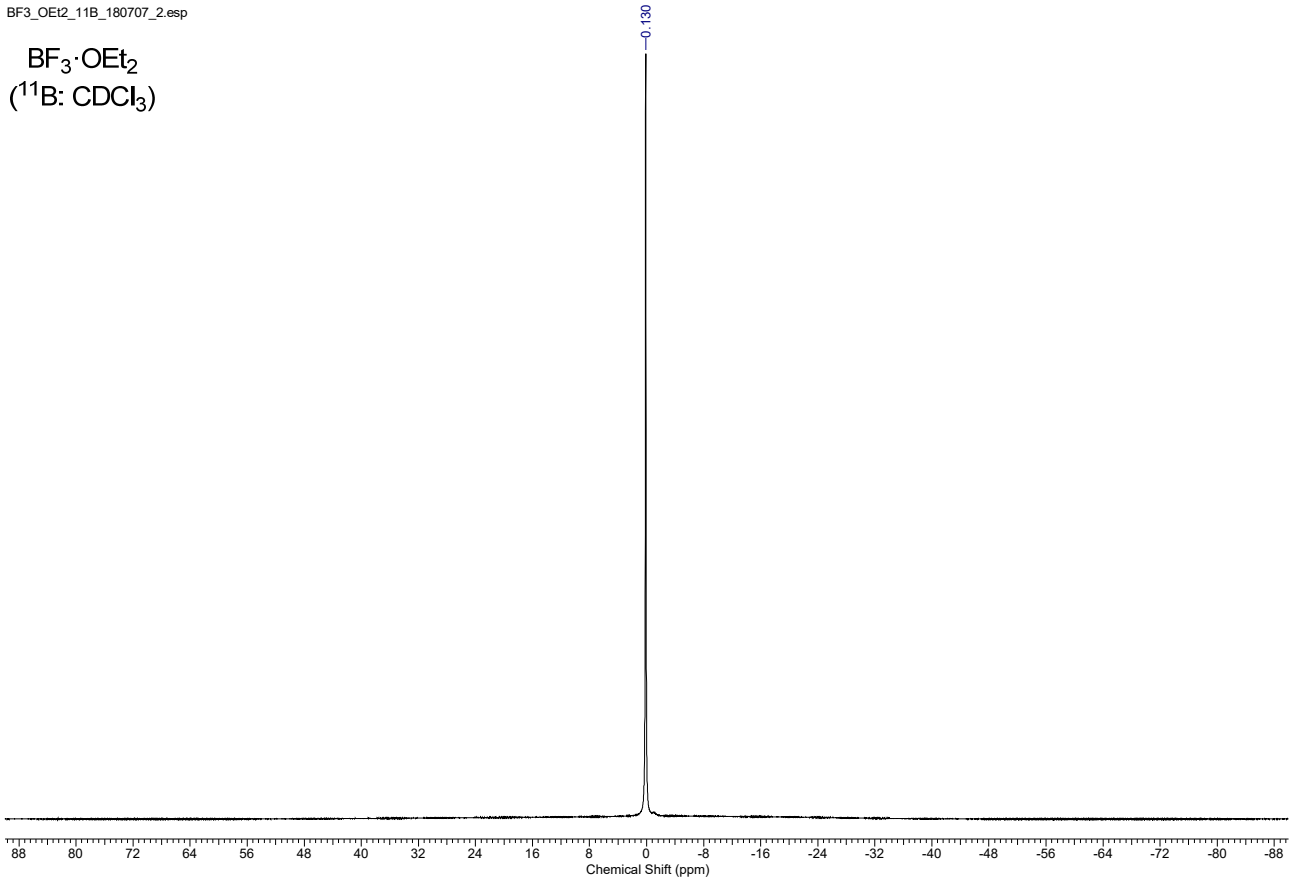
(^{11}B: $CDCl_3$)

–12.7 ppm (br)

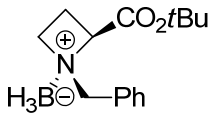
BF3_OEt2_11B_180707_2.esp

$BF_3{\cdot}OEt_2$

(^{11}B: $CDCl_3$)



1R,2S-5_11B_180707.esp



(1*R*,2*S*)-**5**

(^{11}B: $CDCl_3$)

–10.1 ppm (br)

BF3_OEt2_11B_180707_3.esp

$BF_3{\cdot}OEt_2$

(^{11}B: $CDCl_3$)