Supporting Information for:

Stannylcyclopropanes by Diastereoselective Cyclopropanations with (Tributylstannyl)-Diazoacetate Esters Catalyzed by Cu(I) *N*-Heterocyclic Carbene.

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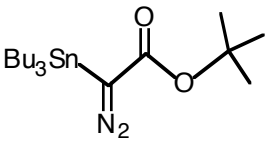
Proton NMR were recorded at 300 MHz, carbon at 75 MHz, in $CDCl_3$, unless otherwise noted. The 1D proton and carbon spectra are reproduced here. Other spectra that were obtained, and which aided the chemical shift assignments, are indicated for each compound.

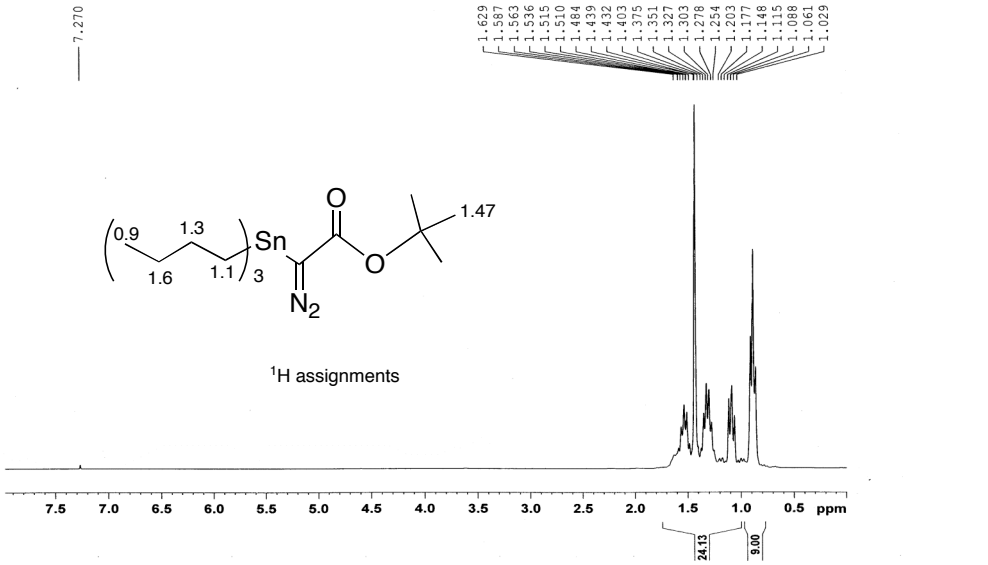
Reagents were used as received. Dichloroethane was distilled from calcium hydride under a nitrogen atmosphere. Hexane was distilled to remove high boiling impurities. All reactions were conducted under an atmosphere of dry nitrogen.

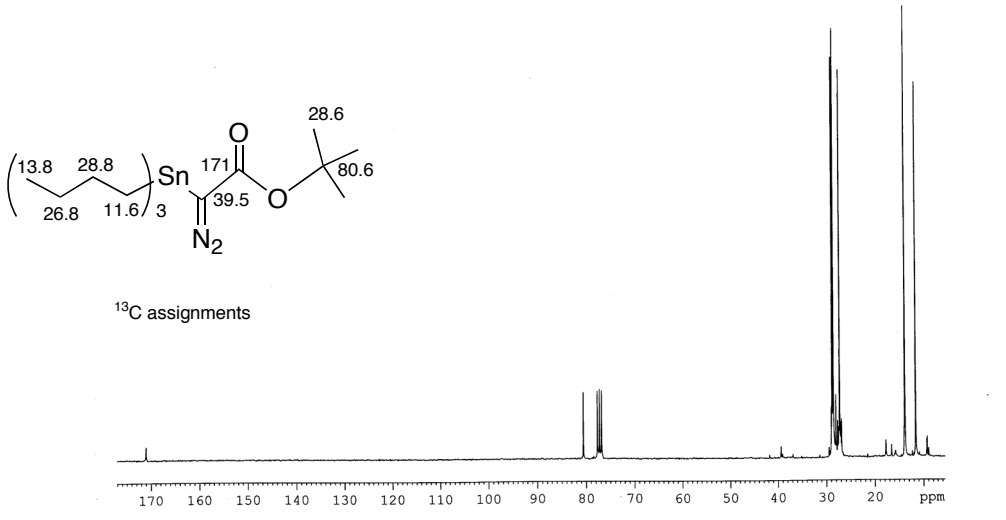
Cyclopropanations were conducted as described in the general procedure in the manuscript. Diastereomer ratios (dr) were determined by integration of the proton NMR signals, and are probably accurate to ±5%. The chemical shifts listed are for the major diastereomer.

***tert*-Butyl 2-(Tributylstannyl)diazoacetate, 1d.** Following the procedure of Lorberth,[1] to a solution of *N*-(tributylstannyl)-*N*-ethylethanamine) (4.4 g, 12 mmol) in pentane under nitrogen, was slowly added *tert*-butyl diazoacetate (1.8 g, 13 mmol); after addition, the reaction mixture was refluxed overnight. The solvent was removed by distillation at atmospheric pressure, and the product was purified by distillation under reduced pressure (0.1/142 °C), to give a clear yellow liquid (4.09 g, 79 %).

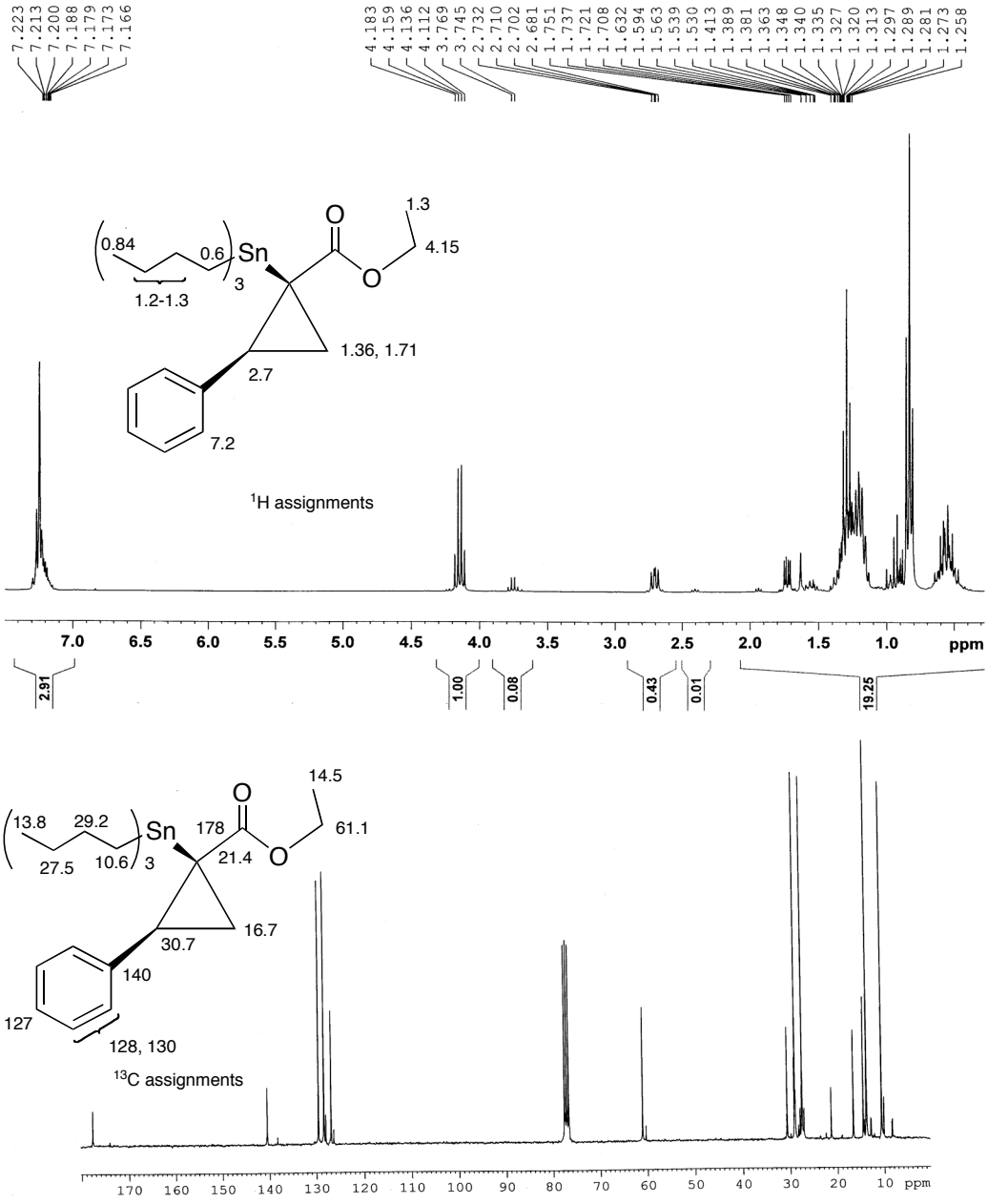


1) J. Lorberth, *J. Organomet. Chem.*, 1968, **15**, 251.

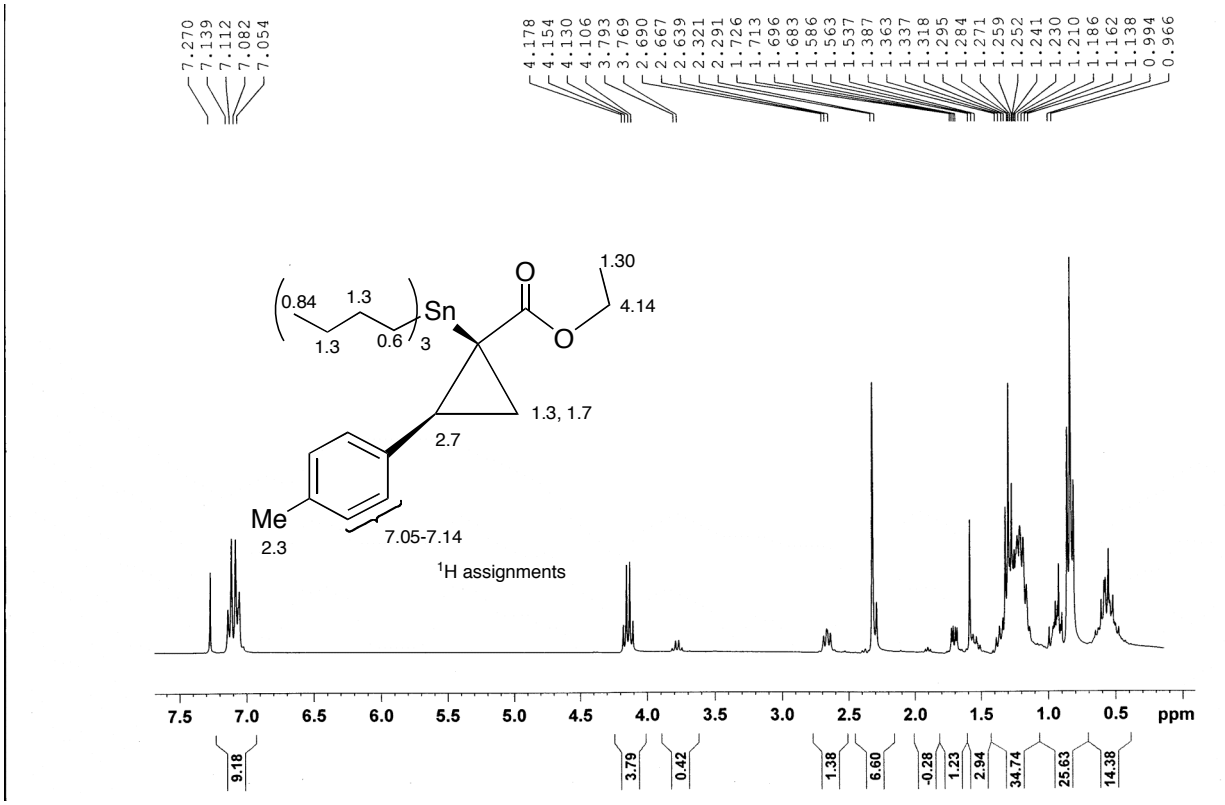


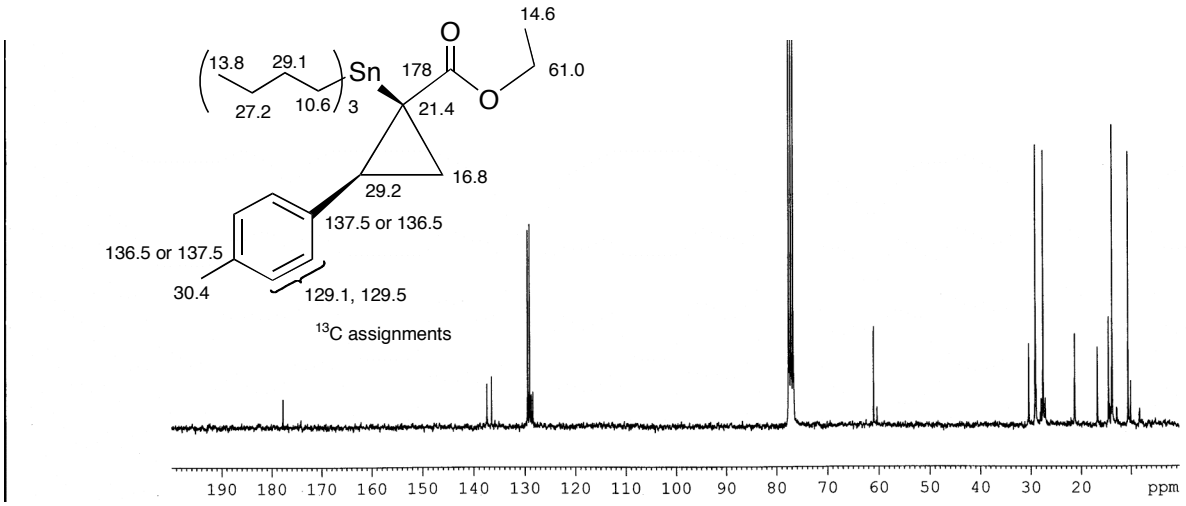


Ethyl 2-phenyl-1-(tributylstannyl)cyclopropanecarboxylate. The ratio of products (NMR) and combined yield were determined after purification by column chromatography, collecting all cyclopropane-containing fractions (hexane:ethylacetate=50:1) afforded the product as a clear liquid (335 mg, 67%). The diastereoselectivity is 91:9 dr. FT-IR (neat) ν 2955, 2925, 1709 (C=O), 1456, 1373, 1228, 1121, 964, 865, 764, 699 cm^{-1}; HRMS $[M+Na]^+$ calcd for $C_{24}H_{40}O_2SnNa$ 503.1942, found 503.1961; Mass $[M+Na]^+$ calcd for $C_{24}H_{40}O_2SnNa$ 503.2, found 503.2; Elemental analysis found (calcd), C 60.38 (60.14), H 8.58 (8.56). Other spectra: DEPT-135, COSY, HMQC, NOESY

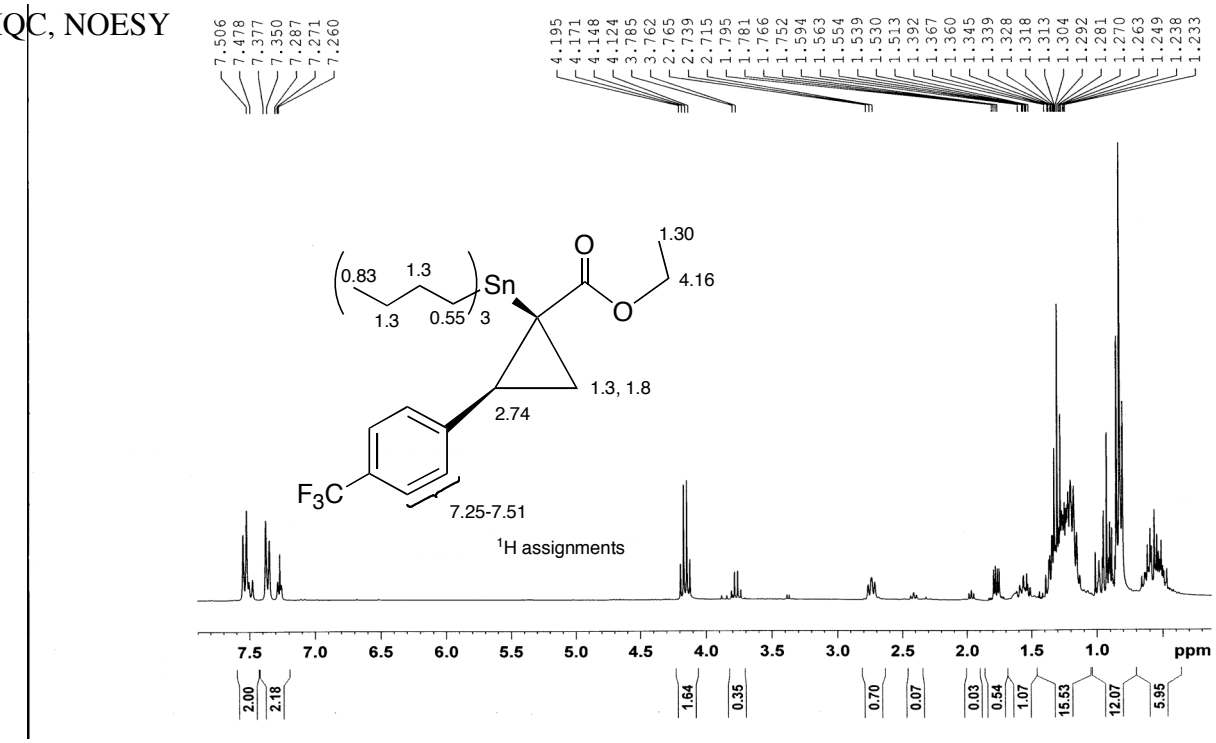


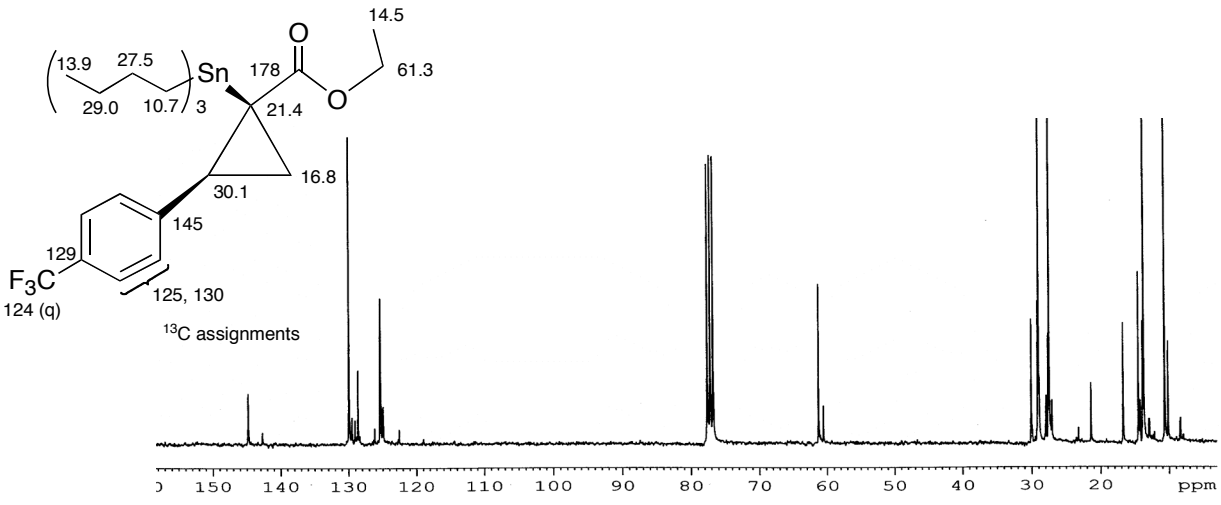
Ethyl 2-(*p*-methylphenyl)-1-(tributylstannyl)cyclopropane-carboxylate. The ratio of products (NMR) and combined yield were determined after purification by column chromatography, collecting all cyclopropane-containing fractions (hexane:ethylacetate=50:1) afforded the product as a clear liquid (320 mg, 65%, 90:10 dr). FT-IR (neat) 2955, 2925, 1709 (C=O), 1457, 1373, 1228, 1118, 963, 822, 667; HRMS $[M-Bu]^+$ calcd for $C_{21}H_{33}O_2Sn$ 437.1503, found 437.1464; ESI/MS $[M+Na]^+$ 517.1 (517.2), $[M-Bu]^+$, 437.1 (437.2); Elemental analysis found (Calcd), C 60.98 (60.87), H 8.65 (8.58). Other spectra: DEPT-135, COSY, HMQC, NOESY



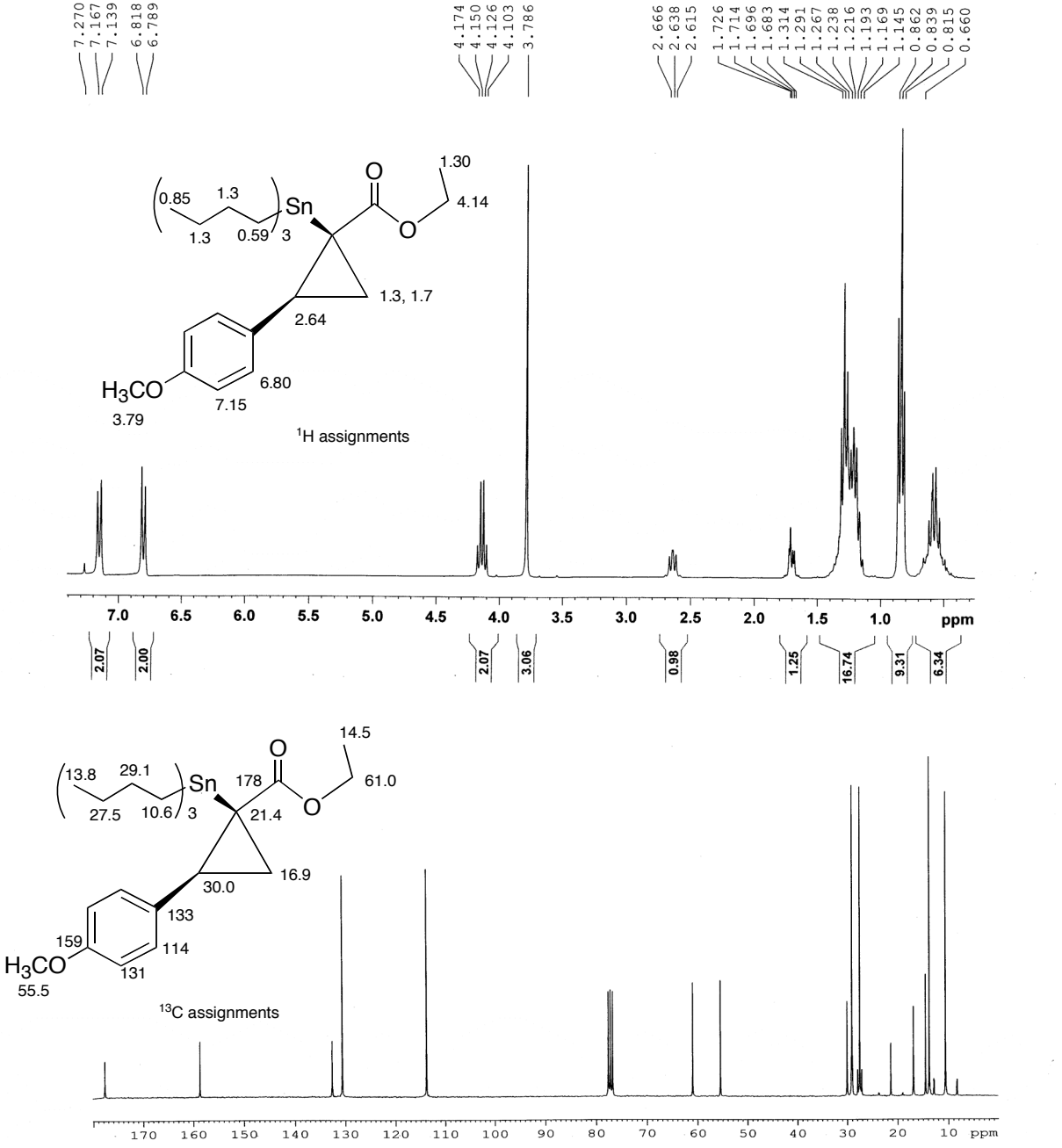


Ethyl 2-(*p*-trifluoromethylphenyl)-1-(tributylstannyl)cyclopropane-carboxylate. The ratio of products (NMR) and combined yield were determined after purification by column chromatography, collecting all cyclopropane-containing fractions (hexane:ethylacetate=50:1) afforded the product as a clear liquid (322 mg, 58%, dr 82:18). FT-IR (neat) 2956, 2926, 1710 (C=O), 1459, 1326, 1229, 1126, 964, 848, 667; HRMS $[M\text{-}Bu]^+$ calcd for $C_{21}H_{30}F_3O_2Sn$ 491.1218, found 491.1220; ESI/MS $[M+Na]^+$ 571.2 (571.1), $[M\text{-}Bu]^+$, 491.1 (491.1); Elemental analysis found (Calcd), C 54.72 (54.87), H 7.25 (7.18). Other spectra: DEPT-135, COSY, HMQC, NOESY

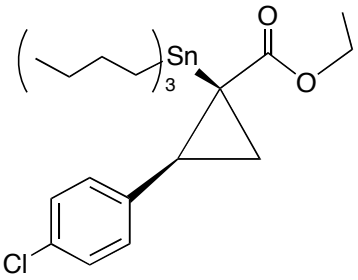




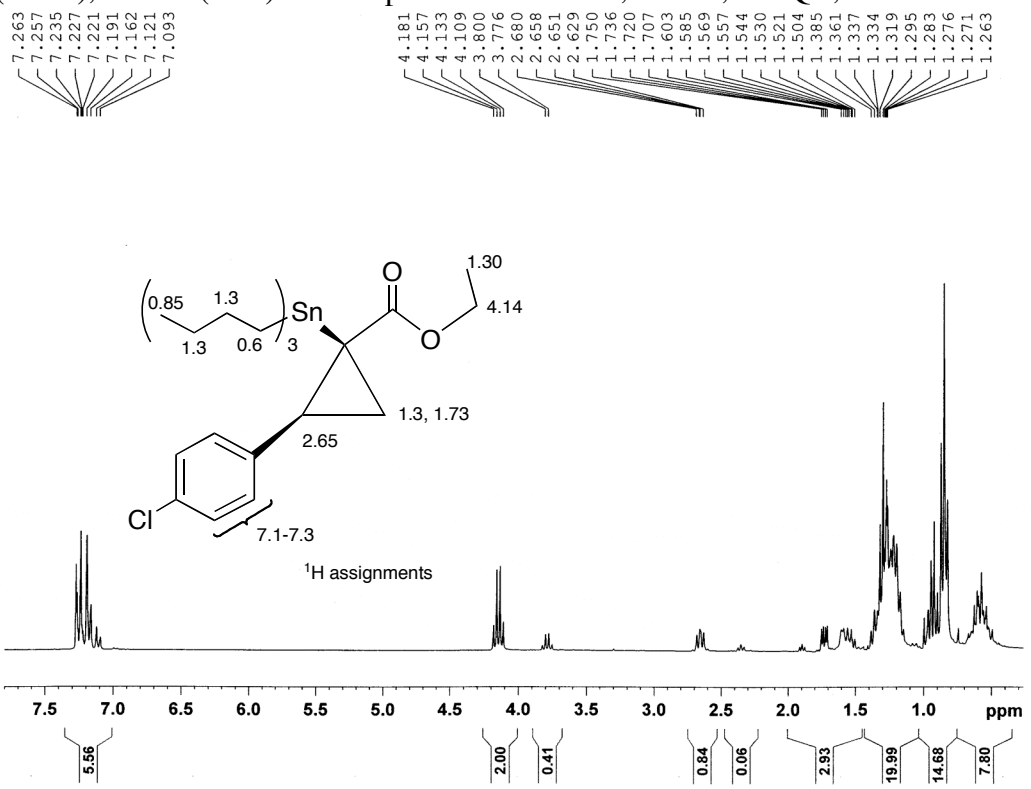
Ethyl 2-(*p*-methoxyphenyl)-1-(tributylstannyl)cyclopropanecarboxylate. The ratio of products (NMR) and combined yield were determined after purification by column chromatography, collecting all cyclopropane-containing fractions (hexane:ethyl acetate=50:1) afforded the product as a clear liquid (331 mg, 64%, single diastereomer). FT-IR (neat) □ 2954, 2925, 1707 (C=O), 1513.8, 1459, 1373, 1239, 1173, 1120, 1036, 964, 834, 667 cm^{-1}; HRMS $[M-Bu]^+$ calcd for $C_{21}H_3O_3Sn$ 453.1452, found 453.1477; ESI/MS $[M+Na]^+$ 533.1 (533.1), $[M-Bu]^+$, 453.1 (453.1); Elemental analysis found (Calcd), C 59.24 (58.96), H 8.63 (8.31). Other spectra: DEPT-135, COSY, HMQC, NOESY

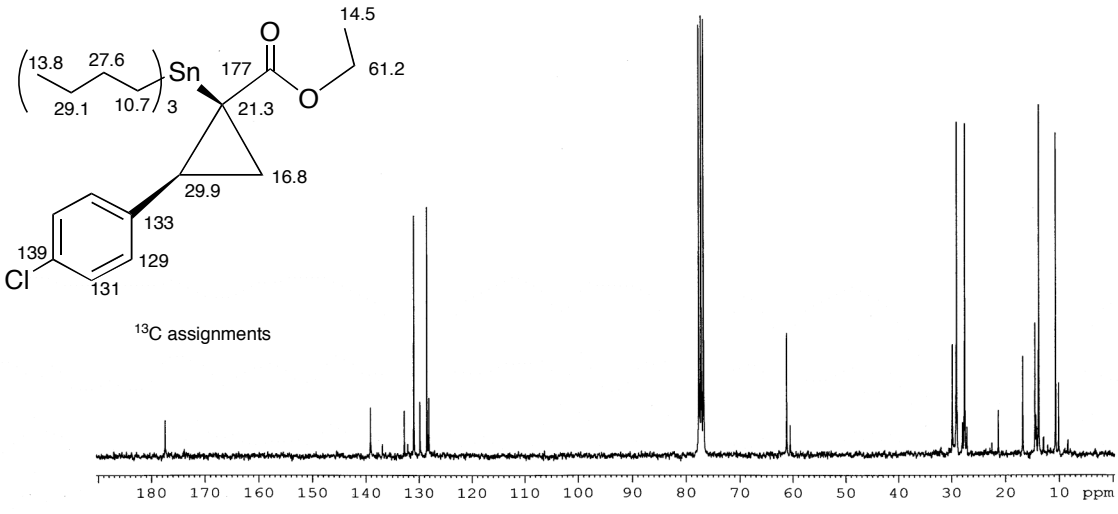


Ethyl 2-(*p*-chlorophenyl)-1-(tributylstannyl)cyclopropanecarboxylate.

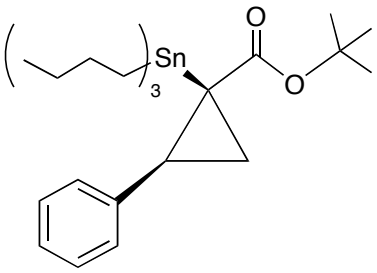


The ratio of products (NMR) and combined yield were determined after purification by column chromatography, collecting all cyclopropane-containing fractions (hexane:ethylacetate=50:1) afforded the product as a clear liquid (262 mg, 50%, dr 83:17). FT-IR (neat) □ 2955, 2925, 1709 (C=O), 1459, 1373, 1229, 1172, 965, 8335, 666 cm^{-1}; HRMS $[M\text{-}Bu]^+$ calcd for $C_{21}H_{33}O_3Sn$ 457.0956, found 457.0924; ESI/MS $[M+Na]^+$ 537.0 (537.2), $[M\text{-}Bu]^+$, 457.1 (457.1); Elemental analysis found (Calcd), C 56.33 (56.11), H 7.59 (7.65). Other spectra: DEPT-135, COSY, HMQC, NOESY

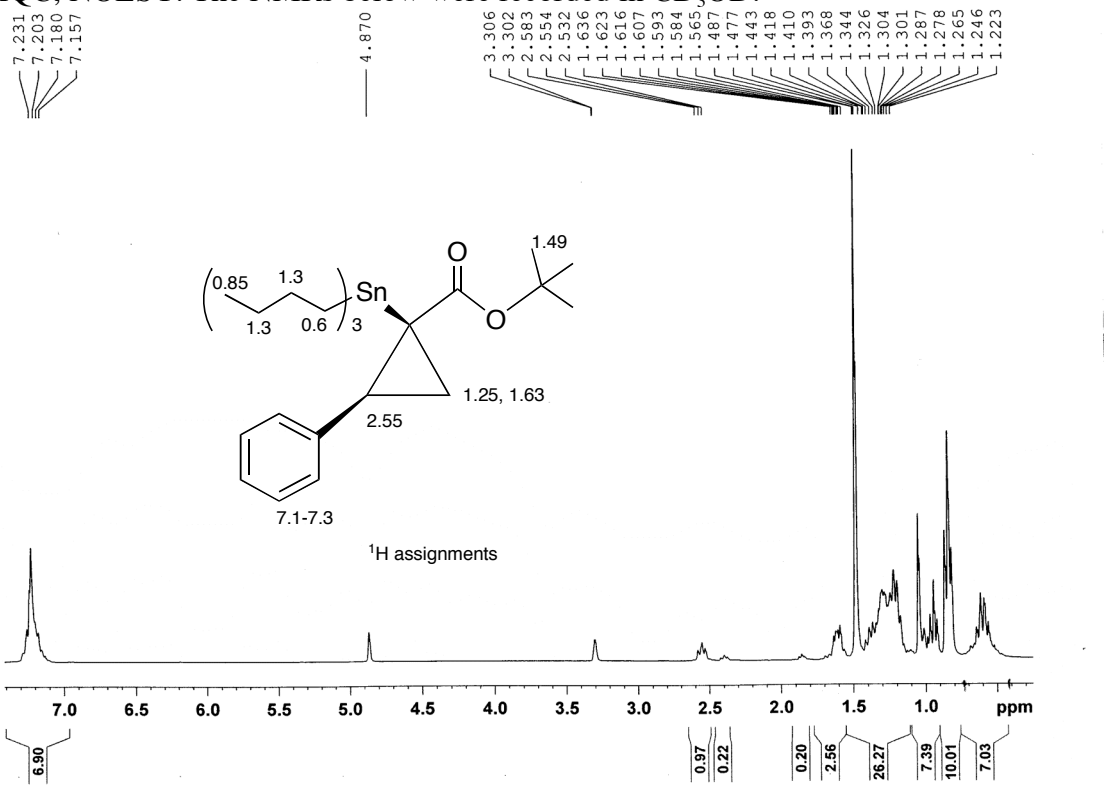


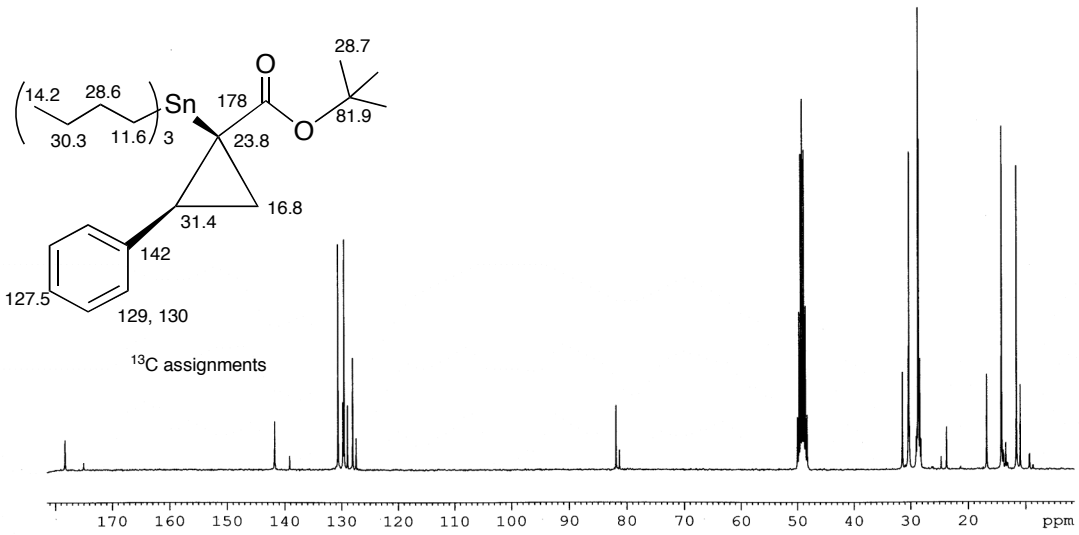


***Tert*-Butyl 2-(phenyl)-1-(tributylstannyl)cyclopropanecarboxylate**.

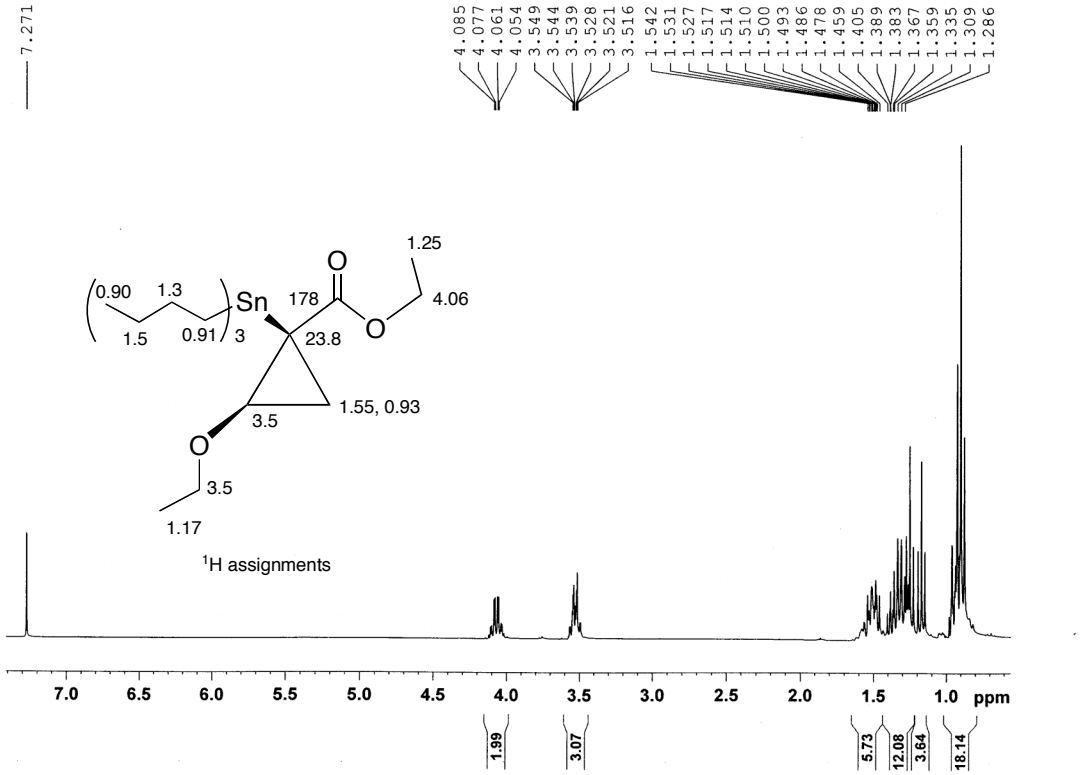


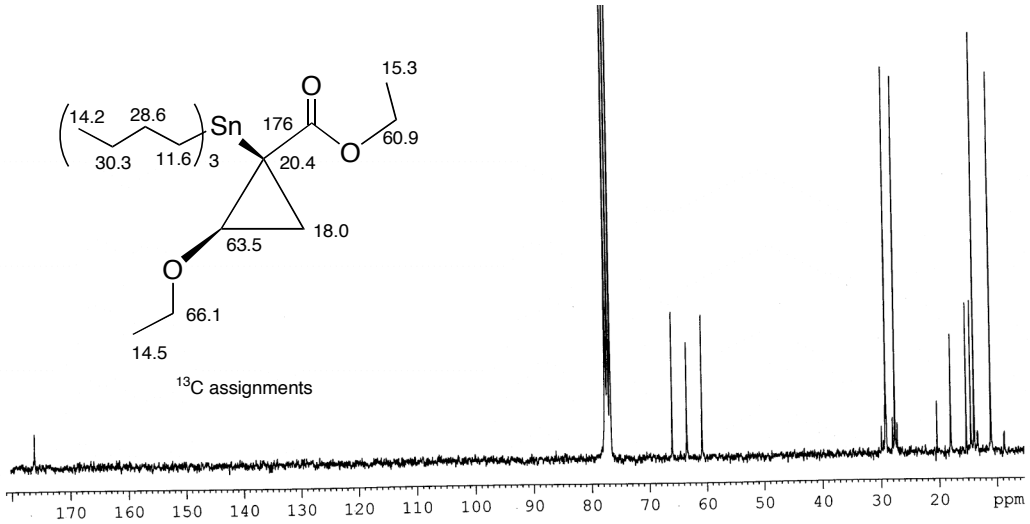
The ratio of products (NMR) and combined yield were determined after purification by column chromatography, collecting all cyclopropane-containing fractions (hexane:ethylacetate=50:1) afforded the product as a clear liquid (330 mg, 65%, dr 82:18. FT-IR (neat) □ 2956, 2925, 1705 (C=O), 1457, 1369, 1249, 1165, 1123, 966, 849, 763, 698 cm^{-1}; Mass $[M+Na]^+$ 531, [MH-Bu] 451.1, {MH-Bu-tBu] 395.2; Elemental analysis: C 61.70 (61.55), H 8.74 (8.74). Other spectra: DEPT-135, COSY, HMQC, NOESY. The NMRs below were recorded in CD_3OD.



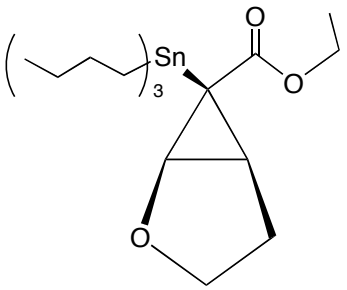


Ethyl 2-ethoxy-1-(tributylstannyl)cyclopropanecarboxylate. The ratio of products (NMR) and yield were determined after purification by column chromatography, collecting all cyclopropane-containing fractions (hexane:ethylacetate=50:1) affording the product as a clear liquid (322 mg, 71%, single diastereoisomer). FT-IR (neat) □ 2956, 2926, 1710 (C=O), 1458, 1373, 1249, 1116, 1073, 909, 666 cm^{-1}; ESI/MS $[M+Na]^+$ 471.1 (471.2), $[M-Bu]^+$, 391.1 (391.1); Elemental analysis found (Calcd), C 53.80 (53.71), H 9.16 (9.01). Other spectra: DEPT-135, COSY, HMQC, NOESY

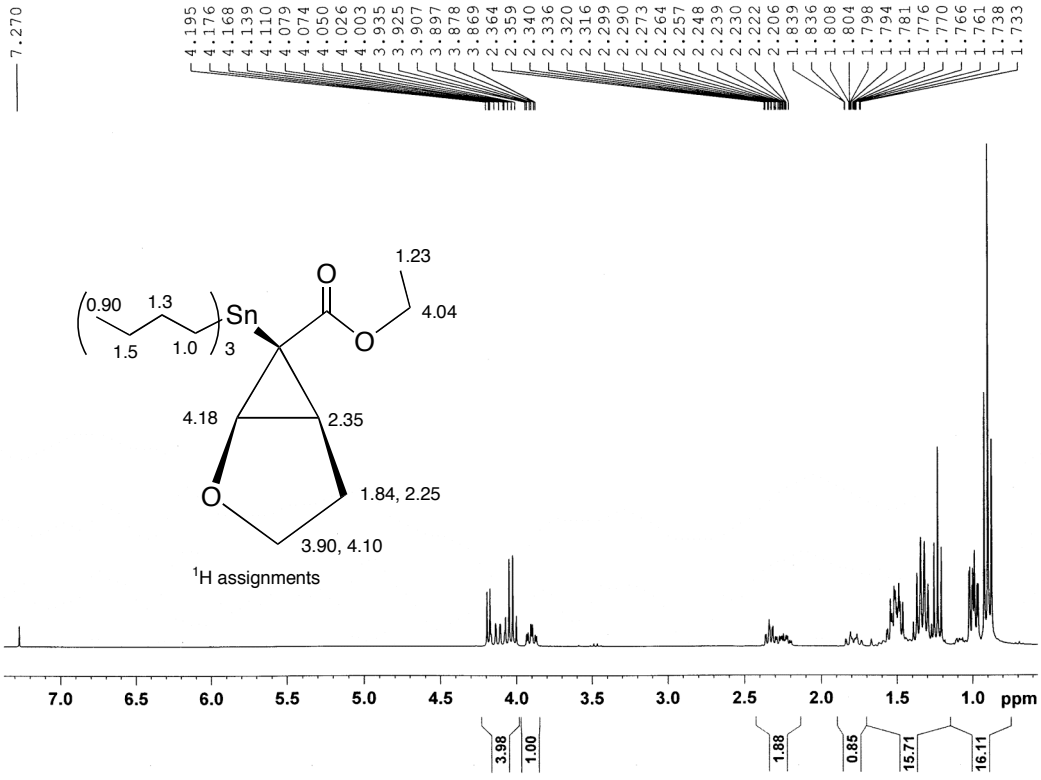


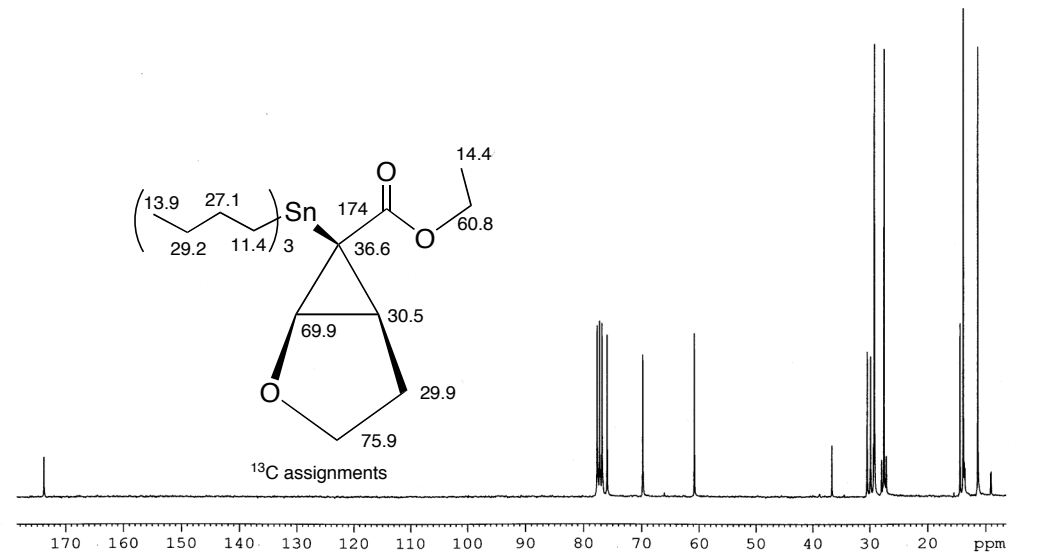


Ethyl 6-(tributylstannyl)-2-oxabicyclo[3.1.0]hexane-6-carboxylate.

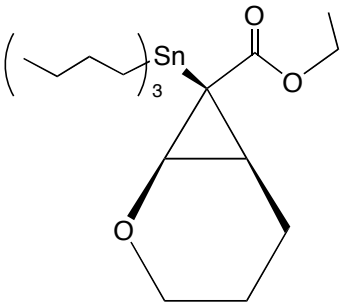


The ratio of products (NMR) and yield were determined after purification by column chromatography, collecting all cyclopropane-containing fractions (hexane:ethylacetate=50:1) affording the product as a clear liquid (254 mg, 56%, single diastereoisomer). FT-IR (neat) □ 2954, 2926, 1704 (C=O), 1458, 1367, 1221, 1058, 940, 861, 671 cm^{-1}; ESI/MS $[M+Na]^+$ 469.1 (469.2), $[MH]^+$ 447.1, $[M-Bu]^+$, 389.1 (389.1); Elemental analysis found (Calcd), C 54.12 (53.95), H 8.71 (8.60). Other spectra: DEPT-135, COSY, HMQC, NOESY

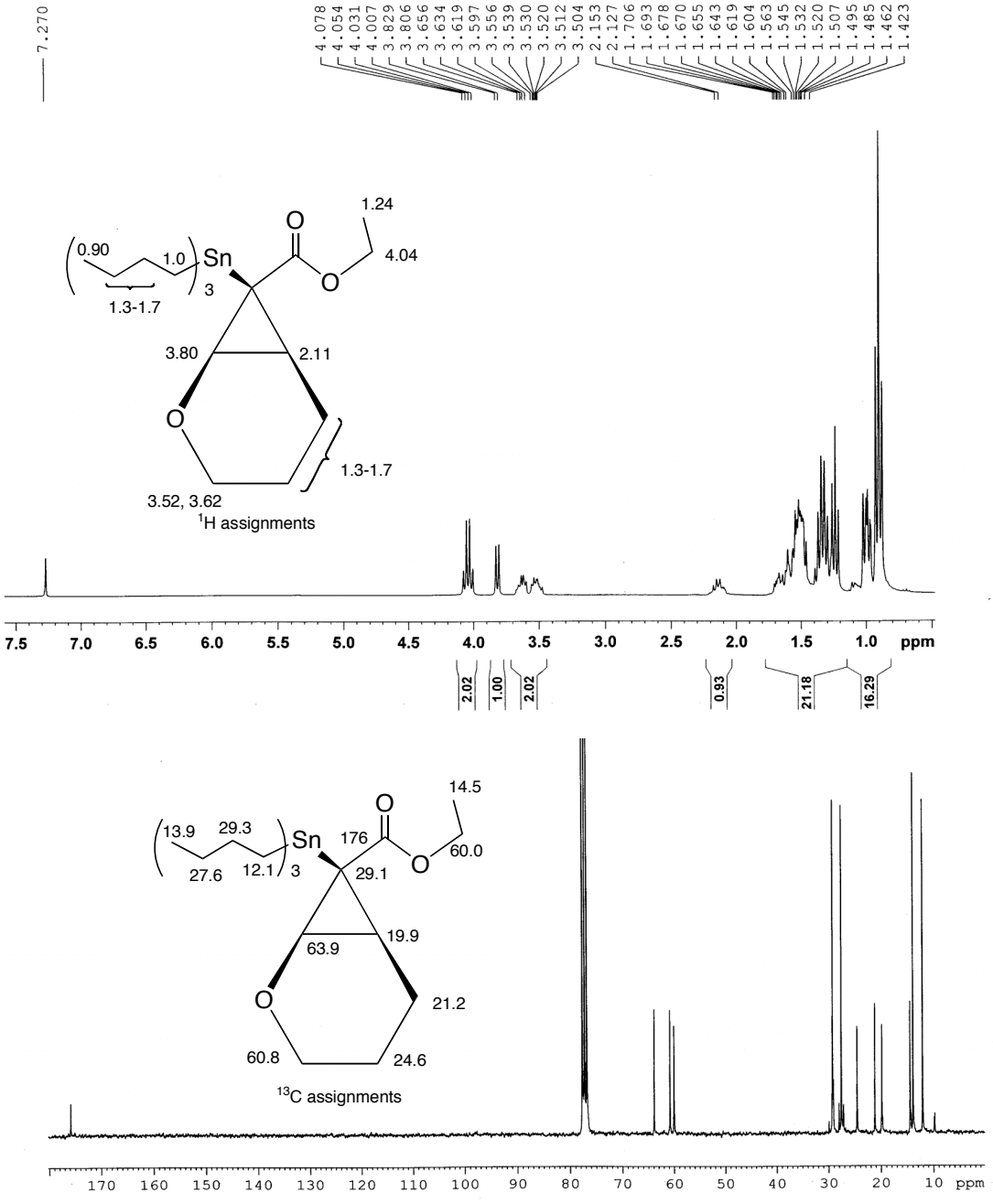




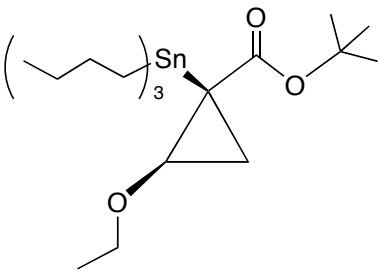
Ethyl 7-(tributylstannyl)-2-oxabicyclo[4.1.0]heptane-7-carboxylate.



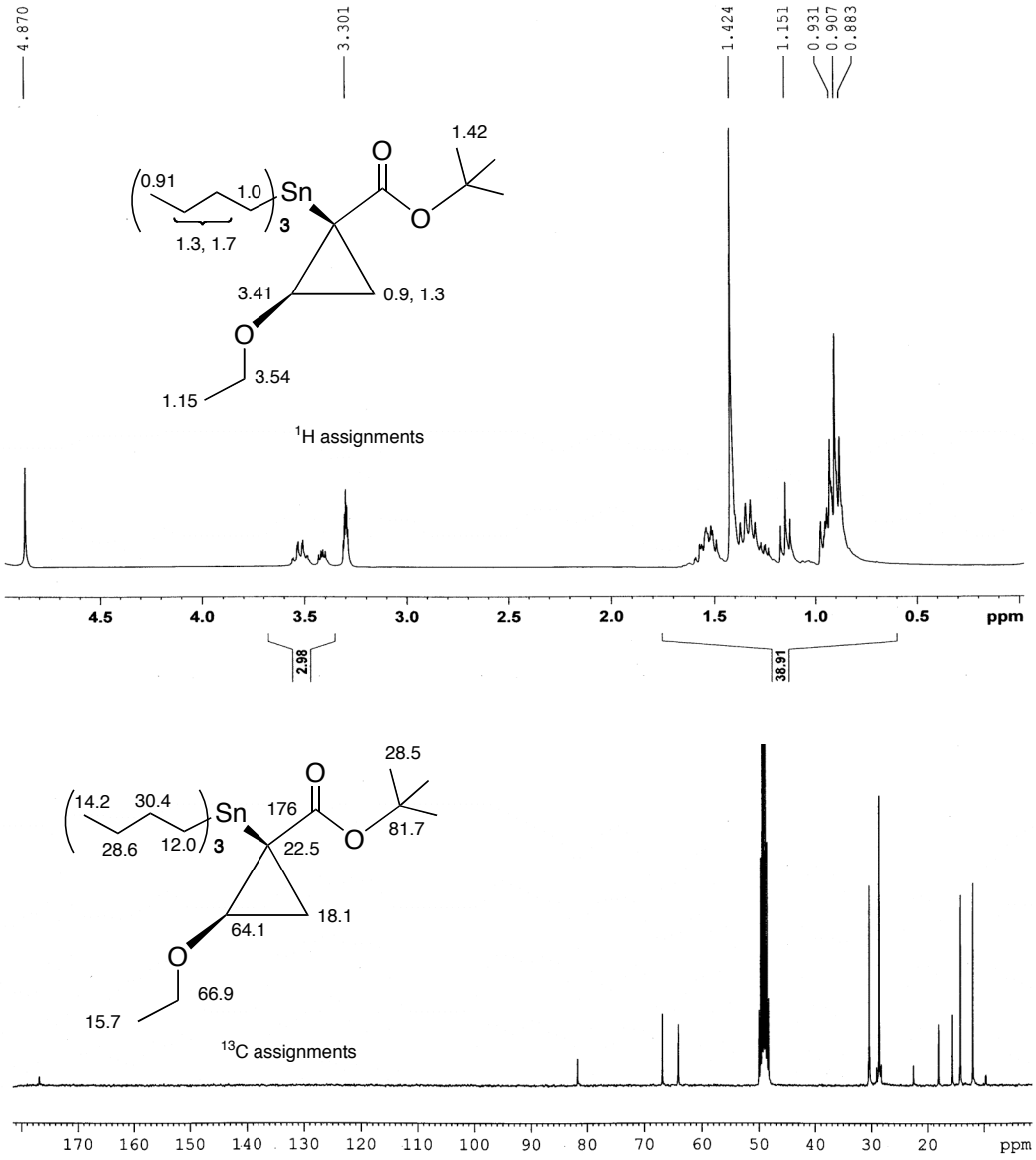
The ratio of products (NMR) and yield were determined after purification by column chromatography, collecting all cyclopropane-containing fractions (hexane:ethylacetate=50:1) affording the product as a clear liquid (290 mg, 63%, single diastereomer). FT-IR (neat) ν 2954, 2926, 1705 (C=O), 1458, 1381, 1222, 1063, 943, 865, 670 cm^{-1}; ESI/MS $[M+Na]^+$ 483.1 (483.2), $[M-Bu]^+$, 403.1 (403.2); Elemental analysis found (Calcd), C 55.04 (54.92), H 8.86(8.78). Other spectra: DEPT-135, COSY, HMQC



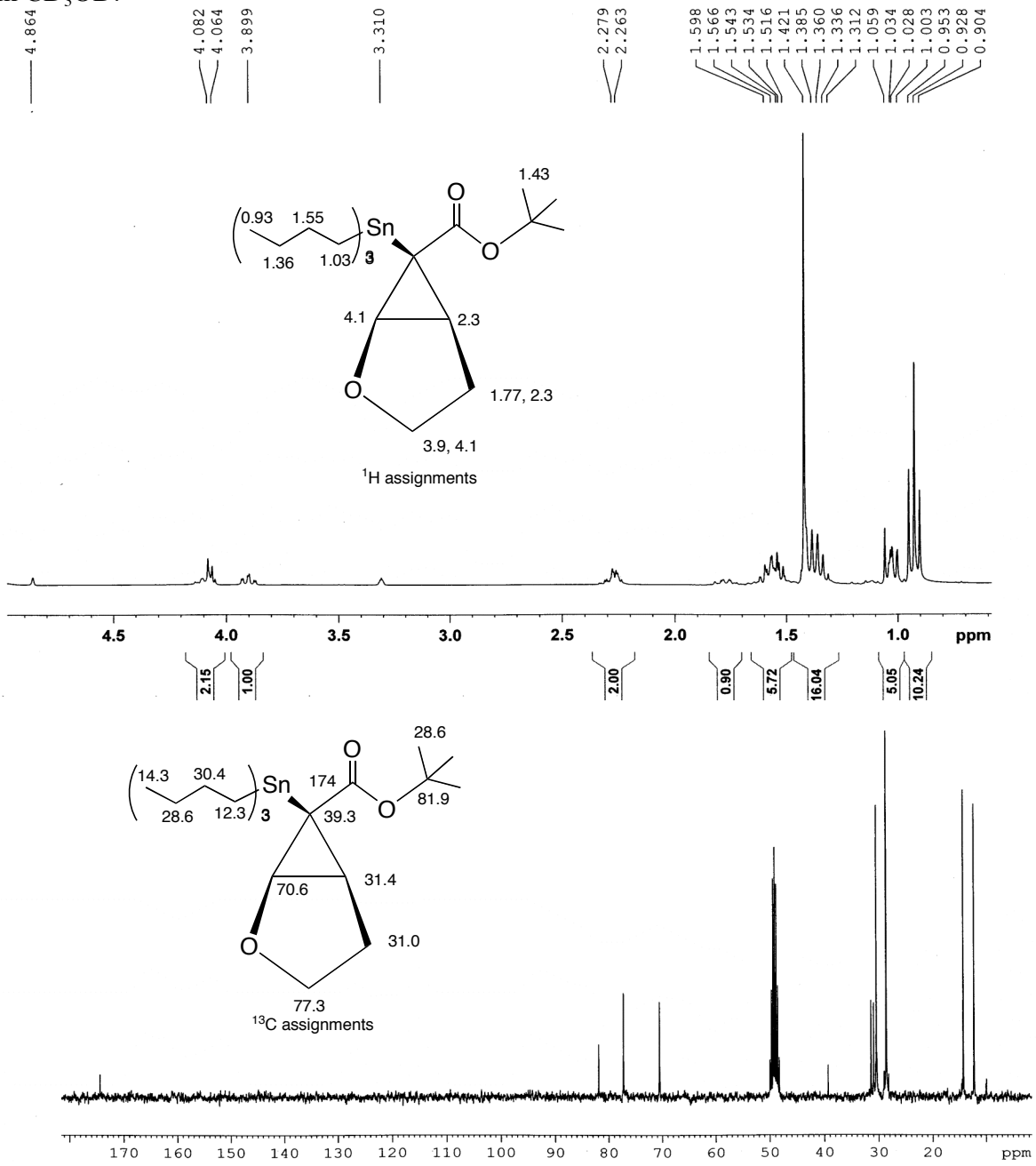
***Tert*-Butyl 2-ethoxy-1-(tributylstannyl)cyclopropanecarboxylate**.



The ratio of products (NMR) and yield were determined after purification by column chromatography, collecting all cyclopropane-containing fractions (hexane:ethylacetate=50:1) affording the product as a clear liquid (314 mg, 66%, single diastereomer). FT-IR (neat) 2958, 2925, 1707 (C=O), 1458, 1369, 1258, 1168, 1118, 1073, 910, 853, 667 cm^{-1}; ESI/MS $[M+Na]^+$ 499.1 (499.2), $[M-Bu]^+$, 419.2 (419.2), {MH-Bu-tBu] 363; Elemental analysis found (Calcd), C 55.69 (55.59), H 9.46 (9.39). Other spectra: DEPT-135, COSY, HMQC, NOESY. The NMRs below were recorded in CD_3OD.



***Tert*-Butyl 6-(tributylstannyl)-2-oxabicyclo[3.1.0]hexane-6-carboxylate**. The ratio of products (NMR) and yield were determined after purification by column chromatography, collecting all cyclopropane-containing fractions (hexane:ethylacetate=50:1) affording the product as a clear liquid (275 mg, 58%, single major diastereisomer. FT-IR (neat) 2956, 2926, 1698 (C=O), 1459, 1366, 1243, 1160, 1053, 943, 843, 671 cm^{-1}; ESI/MS $[M+Na]^+$ 537.0 (537.2), $[M-Bu]^+$, 457.1 (457.1); Elemental analysis found (Calcd) C 55.70 (55.83), H 9.06 (8.94). Other spectra: DEPT-135, COSY, HMQC, NOESY. The NMRs below were run in CD_3OD.



***Tert*-Butyl 7-(tributylstannyl)-2-oxabicyclo[4.1.0]heptane-7-carboxylate**. The ratio of products (NMR) and yield were determined after purification by column chromatography, collecting all cyclopropane containing fractions (hexane:ethylacetate=50:1) affording the product as a clear liquid (299 mg, 62%, as a single diastereomer). FT-IR (neat) 2955, 2926, 1700 (C=O), 1459, 1368, 1245, 1158, 1065, 947, 864, 670 cm^{-1}; ESI/MS $[M+Na]^+$ 537.0 (537.2), $[M-Bu]^+$, 457.1 (457.1); Elemental analysis found (Calcd), C 56.72 (56.69), H 9.15 (9.10). Other spectra: DEPT-135, COSY, HMQC, NOESY. The NMRs below were recorded in CD_3OD.