

Supporting Information

Palladium Pincer-Complex Catalyzed Allylic Stannylation with Hexaalkylditin Reagents

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All reactions were conducted under an argon atmosphere by employing standard manifold techniques. All solvents were freshly distilled prior to use. NMR spectra were recorded in CDCl_3 on Varian spectrometers with ^1H at 300 or 400 MHz and ^{13}C at 75 or 100.5 MHz with CDCl_3 ($\delta[^1\text{H}] = 7.26$, $\delta[^{13}\text{C}] = 77.26$) as internal standard. For column chromatography, Merck silica gel 60 (230-400 mesh) was used. All eluents for silica gel chromatography are given as volume/volume ratios.

Complex $[\text{PdCl}]\{\text{C}_6\text{H}_3(\text{C}_{12}\text{H}_5\text{OP})_2\}$ (2): Resorcinolbis(diphenyl)phosphinite¹ (0.68 g, 1.43 mmol) and $\{(\text{Pd}(\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2)\text{Cl})_2\}^2$ (0.20g, 0.36 mmol) were dissolved in 8.5 ml benzene followed by drop wise addition of glacial acetic acid (0.21 ml). The reaction mixture was stirred at 75°C for 5h, and after filtration the solvent was evaporated. The crude product was purified by silica gel flash chromatography using CH_2Cl_2 : pentane (2 : 1) as eluent affording the product as a white solid. Yield 95%. ^1H -NMR: δ 8.02-7.94 (m, 8H), 7.52-7.45 (m, 12H), 7.09 (tt, 8.1 Hz, 1.3 Hz, 1H), 6.76 (d, 8.1 Hz, 2H). ^{31}P -NMR: δ 144.8.

Synthesis of allyl stannanes (general procedure A). The corresponding allylic substrate (0.25 mmol) and catalyst **1** (1.9 mg, 0.005 mmol) were dissolved in 1.25 ml THF followed by addition of the hexaalkylditin reagent (0.25 mmol). The reaction mixture was stirred for the allotted times and temperatures (Table 1). After evaporation of the solvent the crude product was purified by silica gel chromatography.

Cinnamyl-tributyl-stannane (5a). The product obtained by procedure A was purified by silica gel chromatography using pentane as eluent. ^1H -NMR: δ 7.31-7.23 (m, 4H), 7.17-7.10 (m, 1H), 6.43 (dt, $^3J(\text{H-H}) = 15.6$ Hz, 8.8 Hz, $^3J(\text{H-Sn}) = 9.5$ Hz, 1H), 6.21 (dt, $^3J(\text{H-H}) = 15.6$ Hz, 1.1 Hz, $^4J(\text{H-Sn}) = 10.3$ Hz, 1H), 1.98 (dd, $^3J(\text{H-H}) = 8.8$ Hz, 1.1 Hz, $^2J(\text{H-Sn}) = 30.2$ Hz, 2H), 1.67-1.39 (m, 6H), 1.39-1.26 (m, 6H), 1.05-0.81 (m, 15H). ^{13}C -NMR: δ 139.1, 131.4 ($J(\text{C-Sn}) = 23.9$ Hz), 128.6, 125.9, 125.4 ($J(\text{C-Sn}) = 4.3$ Hz), 125.2, 29.4 ($J(\text{C-Sn}) = 10.4$ Hz), 27.6 ($J(\text{C-Sn}) = 26.1$ Hz), 16.3, 14.0, 9.8 ($^2J(\text{C-}^{117}\text{Sn}) = 150.4$ Hz, $^2J(\text{C-}^{119}\text{Sn}) = 157.5$ Hz).

Ethyl-5-(tributylstannyl)-pent-3-eneoate (5b). The product obtained by procedure A was purified by silica gel chromatography using pentane : diethyl ether (40:1) as eluent affording the product as a 9:1 mixture of E and Z isomers. NMR-data is given for the E-isomer. ^1H -NMR: δ 5.67 (dtt, 15.0 Hz, 8.6 Hz, 1.3 Hz, 1H), 5.29 (dtt, 15.0 Hz, 7.1 Hz, 1.2 Hz, 1H), 4.11

(q, 7.1 Hz, 2H), 2.97 (d, $^3J(\text{H-H}) = 7.1$ Hz, $^5J(\text{H-Sn}) = 8.2$ Hz, 2H), 1.73 (d, $^3J(\text{H-H}) = 8.6$ Hz, $^2J(\text{H-Sn}) = 29.2$ Hz, 2H), 1.58-1.37 (m, 6H), 1.34-1.22 (m, 9H), 0.95-0.77 (m, 15H). ^{13}C -NMR: δ 172.7, 134.1, 116.7, 60.6, 38.6, 29.3 ($J(\text{C-Sn}) = 10.4$ Hz), 27.5 ($J(\text{C-Sn}) = 25.7$ Hz), 14.7, 14.5, 13.9, 9.4 ($^2J(\text{C-}^{117}\text{Sn}) = 151.6$ Hz, $^2J(\text{C-}^{119}\text{Sn}) = 159.0$ Hz).

Cyclohex-2-enyltributylstannane (5c). The product obtained by procedure A was purified by silica gel chromatography using cyclohexane as eluent. ^1H -NMR: δ 5.76 (ddt, $^3J(\text{H-H}) = 9.9$ Hz, 4.3 Hz, 2.1 Hz, $^3J(\text{H-Sn}) = 9.5$ Hz, 1H), 5.40 (ddt, $^3J(\text{H-H}) = 9.9$ Hz, 3.7 Hz, 2.0 Hz, $^4J(\text{H-Sn}) = 9.6$ Hz, 1H), 2.19-2.12 (m, $^2J(\text{H-Sn}) = 39.4$ Hz, 1H), 2.10-1.94 (m, 2H), 1.84-1.76 (m, 1H), 1.72-1.63 (m, 1H), 1.61-1.40 (m, 7H), 1.36-1.25 (m, 7H), 0.93-0.84 (m, 15H). ^{13}C -NMR: δ 131.8, 121.7, 29.5 ($J(\text{C-Sn}) = 10.0$ Hz), 27.8 ($J(\text{C-Sn}) = 26.6$ Hz), 27.1 ($J(\text{C-Sn}) = 8.0$ Hz), 26.3, 25.3 ($J(\text{C-Sn}) = 6.5$ Hz), 23.5 ($J(\text{C-Sn}) = 10.0$ Hz), 14.0, 9.2 ($^2J(\text{C-}^{117}\text{Sn}) = 142.8$ Hz, $^2J(\text{C-}^{119}\text{Sn}) = 149.3$ Hz).

1-Trimethylstannyl-4-hydroxybut-2-ene (5d). The product obtained by procedure A was purified by silica gel chromatography using pentane:diethyl ether (1:1) as eluent affording the product as a 5:3 mixture of E and Z isomers. The NMR-data is given separately for the two isomers. E-isomer: ^1H -NMR: δ 5.81 (dt, 15.0 Hz, 8.6 Hz, 1.1 Hz, 1H), 5.46 (dt, 15.0 Hz, 6.6 Hz, 1.3 Hz, 1H), 4.03 (d, $^3J(\text{H-H}) = 6.6$ Hz, $^5J(\text{H-Sn}) = 7.8$ Hz, 2H), 1.73 (d, $^3J(\text{H-H}) = 8.6$ Hz, $^2J(\text{H-Sn}) = 32.8$ Hz, 2H), 1.30-1.20 (bs, 1H), 0.09 (s, $^2J(\text{H-}^{117}\text{Sn}) = 25.6$, $^2J(\text{H-}^{119}\text{Sn}) = 26.8$ Hz, 9H). ^{13}C -NMR: δ 133.7, 124.7, 64.4, 16.4, -9.9 ($^2J(\text{C-}^{117}\text{Sn}) = 157.2$ Hz, $^2J(\text{C-}^{119}\text{Sn}) = 164.5$ Hz). Z-isomer: ^1H -NMR: δ 5.72 (dt, 10.6 Hz, 9.4 Hz, 1.3 Hz, 1H), 5.34 (dt, 10.6 Hz, 6.8 Hz, 1.1 Hz, 1H), 4.15 (d, $^3J(\text{H-H}) = 6.8$ Hz, $^5J(\text{H-Sn}) = 6.8$ Hz, 2H), 1.78 (d, $^3J(\text{H-H}) = 9.4$ Hz, $^2J(\text{H-Sn}) = 34.2$ Hz, 2H), 1.30-1.20 (bs, 1H), 0.10 (s, $^2J(\text{H-}^{117}\text{Sn}) = 25.4$ Hz, $^2J(\text{H-}^{119}\text{Sn}) = 26.8$ Hz, 9H). ^{13}C -NMR: δ 132.2, 123.2, 58.6, 13.0, -9.8 ($^2J(\text{C-}^{117}\text{Sn}) = 157.2$ Hz, $^2J(\text{C-}^{119}\text{Sn}) = 164.5$ Hz).

1-Hydroxy-2-(trimethylstannyl)-cyclohex-3-ene (5e). The product obtained by procedure A was purified by silica gel chromatography using pentane : diethyl ether (2:1) as eluent affording two diastereomers in a ratio of 4:1. The reaction also afforded 1-(Trimethylstannyl)-4-hydroxy-cyclohex-2-ene as a minor product. Major diastereomer: ^1H -NMR: δ 5.67-5.57 (m, 1H), 5.52-5.41 (m, 1H), 4.17-4.05 (m, 1H), 2.31-2.18 (m, 1H), 2.14-1.97 (m, 2H), 1.85-1.72 (m, 2H), 1.70-1.60 (m, 1H), 0.11 (s, $^2J(\text{H-}^{117}\text{Sn}) = 25.0$ Hz, $^2J(\text{H-}^{119}\text{Sn}) = 26.2$ Hz, 9H). ^{13}C -

NMR: δ 127.4 ($^3J(\text{C-Sn}) = 19.7$ Hz), 121.5, 69.0, 35.2, 29.1 ($^4J(\text{C-Sn}) = 5.8$ Hz), 20.8 ($^5J(\text{C-Sn}) = 6.1$ Hz), -10.2 ($^2J(\text{C-}^{117}\text{Sn}) = 153.0$ Hz, $^2J(\text{C-}^{119}\text{Sn}) = 159.9$ Hz). Minor diastereomer: $^1\text{H-NMR}$: δ 5.66 (ddt, $^3J(\text{H-H}) = 9.9$ Hz, 4.8 Hz, 2.0 Hz, $^3J(\text{H-Sn}) = 9.1$ Hz, 1H), 5.45-5.33 (m, 1H), 4.31 (ddt, $^3J(\text{H-H}) = 9.8$ Hz, 6.1 Hz, 3.4 Hz, $^3J(\text{H-Sn}) = 39.5$ Hz, 1H), 2.62-2.38 (m, 1H), 2.24-2.08 (m, 2H), 1.85-1.77 (m, 1H), 1.66-1.56 (m, 2H), 0.13 (s, $^2J(\text{H-}^{117}\text{Sn}) = 25.3$ Hz, $^2J(\text{H-}^{119}\text{Sn}) = 26.3$ Hz, 9H). $^{13}\text{C-NMR}$: δ 128.7, 120.8, 70.2, 37.9, 31.7, 24.0, -8.3.

1-(Trimethylstannyl)-4-hydroxy-cyclohex-2-ene. $^1\text{H-NMR}$: δ 5.99 (dd, $^3J(\text{H-H}) = 9.7$ Hz, 4.8 Hz, $^3J(\text{H-Sn}) = 8.4$ Hz, 1H), 5.59 (dd, 9.7 Hz, 4.3 Hz, 1H), 4.18-4.09 (m, 1H), 2.21-2.05 (m, 2H), 1.85-1.78 (m, 1H), 1.76-1.68 (m, 1H), 1.60-1.50 (m, 1H), 1.42 (d, 6.8 Hz, 1H), 0.10 (s, $^2J(\text{H-}^{117}\text{Sn}) = 24.9$ Hz, $^2J(\text{H-}^{119}\text{Sn}) = 25.9$ Hz, 9H). $^{13}\text{C-NMR}$: δ 136.2, 122.9, 64.0, 31.6, 28.0, 21.1, -9.8.

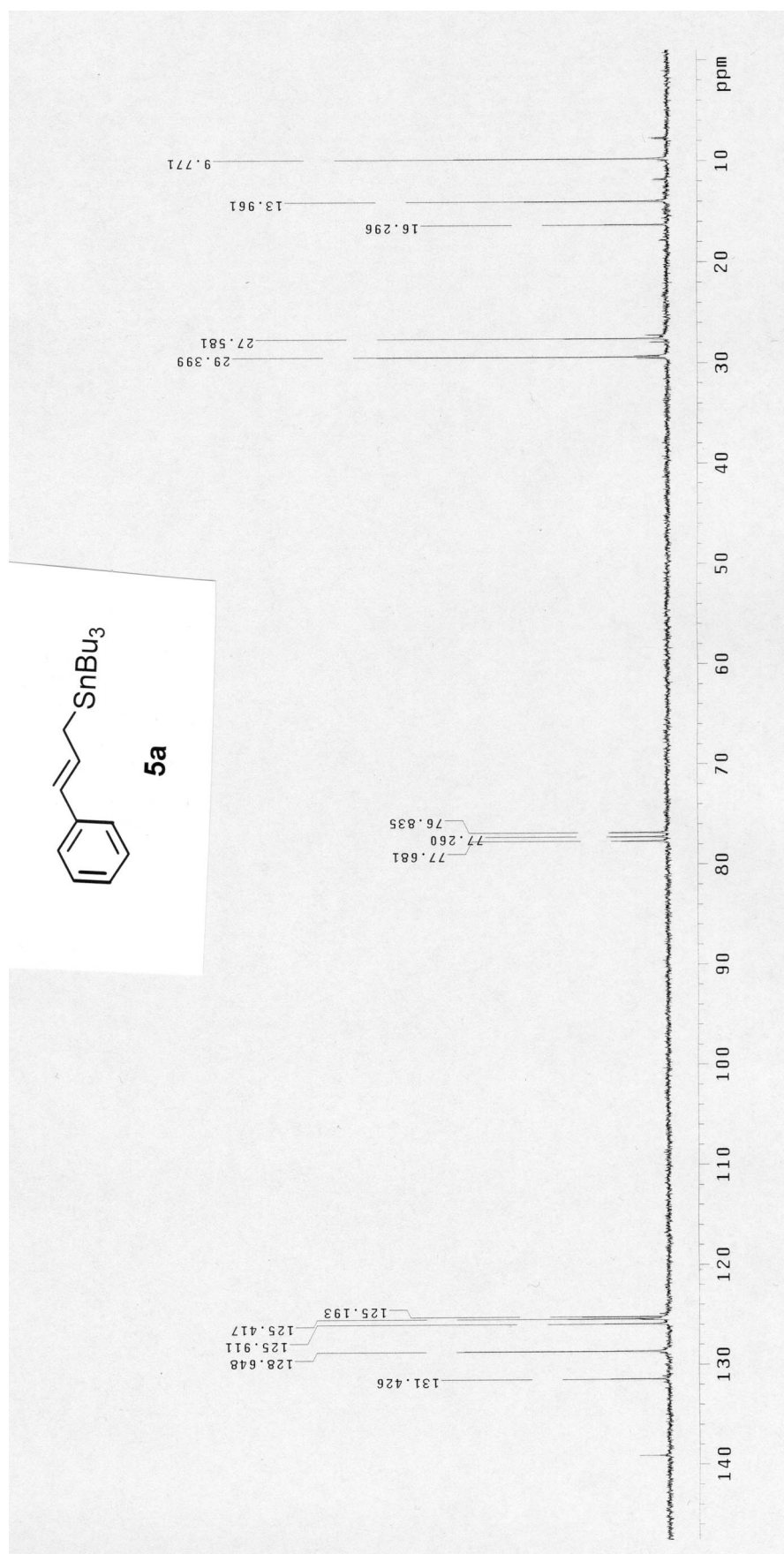
Electrophilic allylation with Allyl Chlorides (general procedure B). The corresponding electrophile (0.25 mmol), catalyst **1** (0.90 mg, 0.0025 mmol) and catalyst **2** (3.1 mg, 0.005 mmol) were dissolved in THF (1.25 ml) containing 4Å molecular sieves (70 mg). After addition of the corresponding allyl chloride (0.30 mmol), the reaction mixture was stirred for 10 min, followed by addition of $(\text{SnMe}_3)_2$ (98 mg, 0.30 mmol). The reaction mixture was then stirred for the allotted times and temperatures (Table 1). After evaporation of the solvent the crude product was purified by silica gel chromatography. The NMR spectra of products **5f-h** and **5j** are identical with those reported in the literature.³

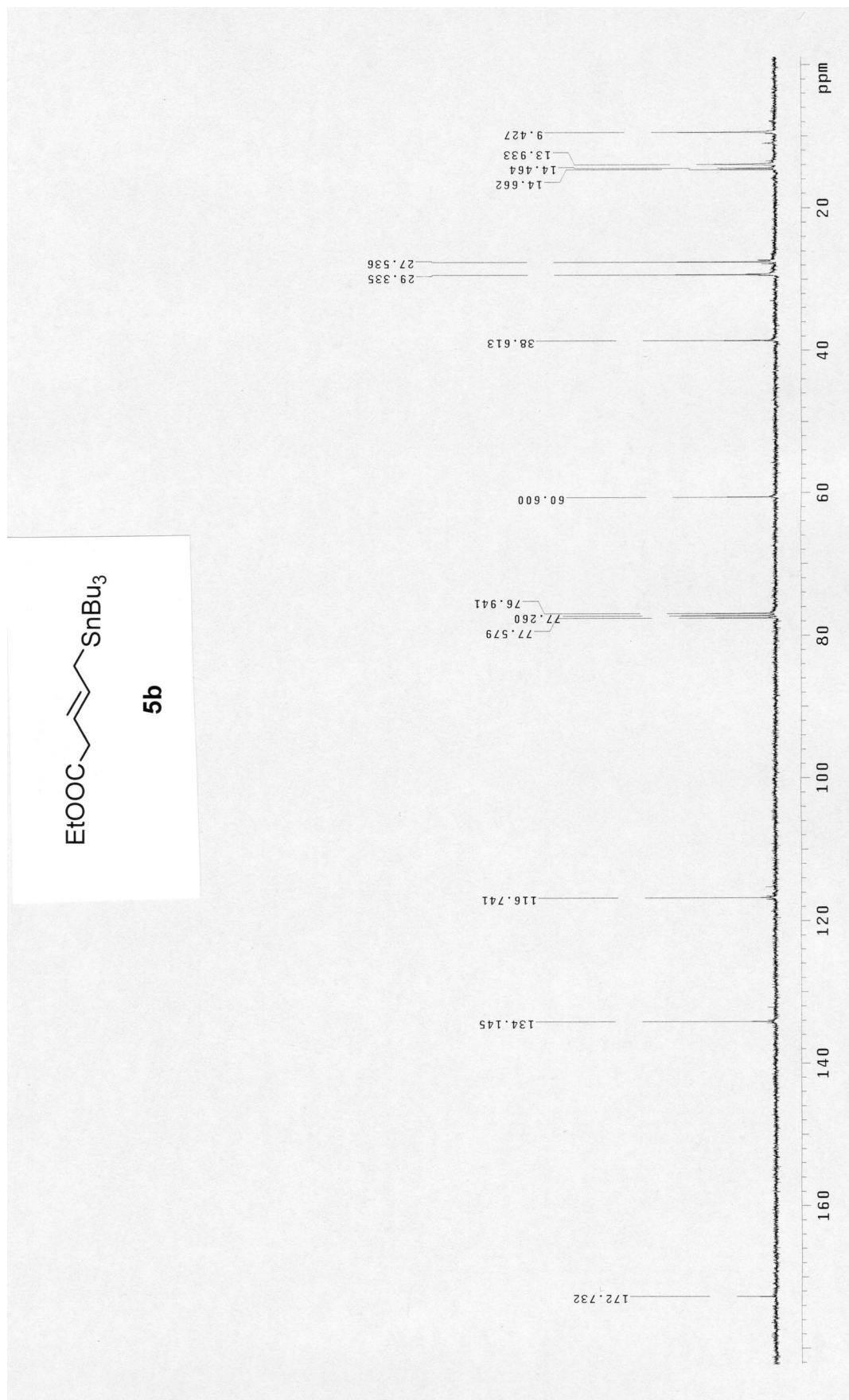
Ethyl-2-{Hydroxy-(4-nitrophenyl)-methyl}-pent-3-enoate (5i). The product obtained by procedure B was purified by silica gel chromatography using pentane : ethyl acetate (4:1) as eluent providing two diastereomers in a ratio of 1:1. The two diastereomers were formed as a 1:3 mixture of E and Z isomers. Yield 95%. Diastereomer A, Z-isomer: $^1\text{H-NMR}$: δ 8.18 (dm, 9.1 Hz, 2H), 7.56-7.44 (m, 2H), 5.61-5.50 (m, 2H), 5.09 (bd, 5.3 Hz, 1H), 4.10 (q, 7.1 Hz, 2H), 3.29 (bs, 1H), 3.23-3.18 (m, 1H), 1.67 (bd, 4.6 Hz, 3H), 1.18 (t, 7.1 Hz, 3H). Diastereomer A, E-isomer: δ 8.01-7.93 (m, 2H), 7.56-7.44 (m, 2H), 5.75 (ddq, 10.6 Hz, 6.8 Hz, 0.9 Hz, 1H), 5.61-5.50 (m, 1H), 5.20 (bd, 4.6 Hz, 1H), 4.13 (q, 7.3 Hz, 2H), 3.62 (ddd, 9.9 Hz, 4.6 Hz, 0.8 Hz, 1H), 3.43 (bs, 1H), 1.41 (dd, 6.9 Hz, 1.8 Hz, 3H), 1.21 (t, 7.3 Hz, 3H). Diastereomer A: $^{13}\text{C-NMR}$: δ 173.1, 148.4, 148.4, 133.3, 131.9, 131.4, 127.6, 127.5, 123.6, 123.6, 123.2, 122.1, 73.3, 73.3, 61.6, 61.5, 57.0, 51.1, 18.3, 14.3, 13.4. Diastereomer B, Z-isomer: $^1\text{H-NMR}$: δ 8.22-8.16 (m, 2H), 7.55-7.46 (m, 2H), 5.65-5.33 (m, 2H), 4.99 (d, 7.7 Hz,

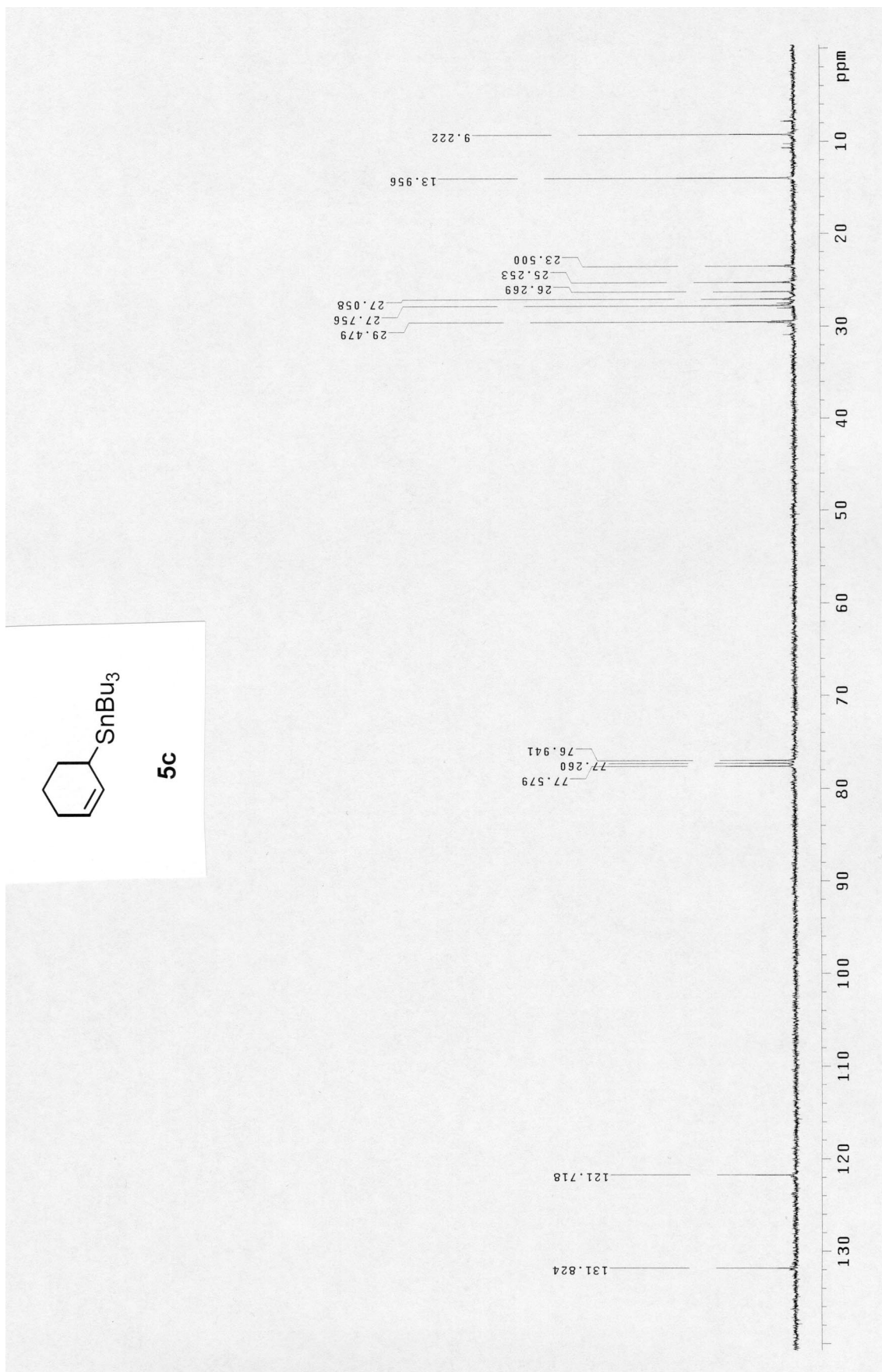
1H), 4.16 (q, 7.2 Hz, 2H), 3.44-3.16 (bs, 1H), 3.31 (bt, 7.7 Hz, 1H), 1.61 (bd, 5.7 Hz, 3H), 1.23 (t, 7.2 Hz, 3H). Diastereomer B, E-isomer: δ 8.22-8.16 (m, 2H), 7.55-7.46 (m, 2H), 5.65-5.33 (m, 2H), 5.00 (d, 8.3 Hz, 1H), 4.18 (q, 7.2 Hz, 2H), 3.67 (ddd, 10.0 Hz, 8.3 Hz, 0.8 Hz, 1H), 3.44-3.16 (bs, 1H), 1.35 (dd, 6.9 Hz, 1.8 Hz, 3H), 1.25 (t, 7.2 Hz, 3H). Diastereomer B: ^{13}C -NMR: δ 172.8, 149.0, 132.0, 127.8, 127.7, 124.4, 123.7, 123.6, 123.4, 74.8, 61.5, 56.9, 52.0, 18.2, 14.3.

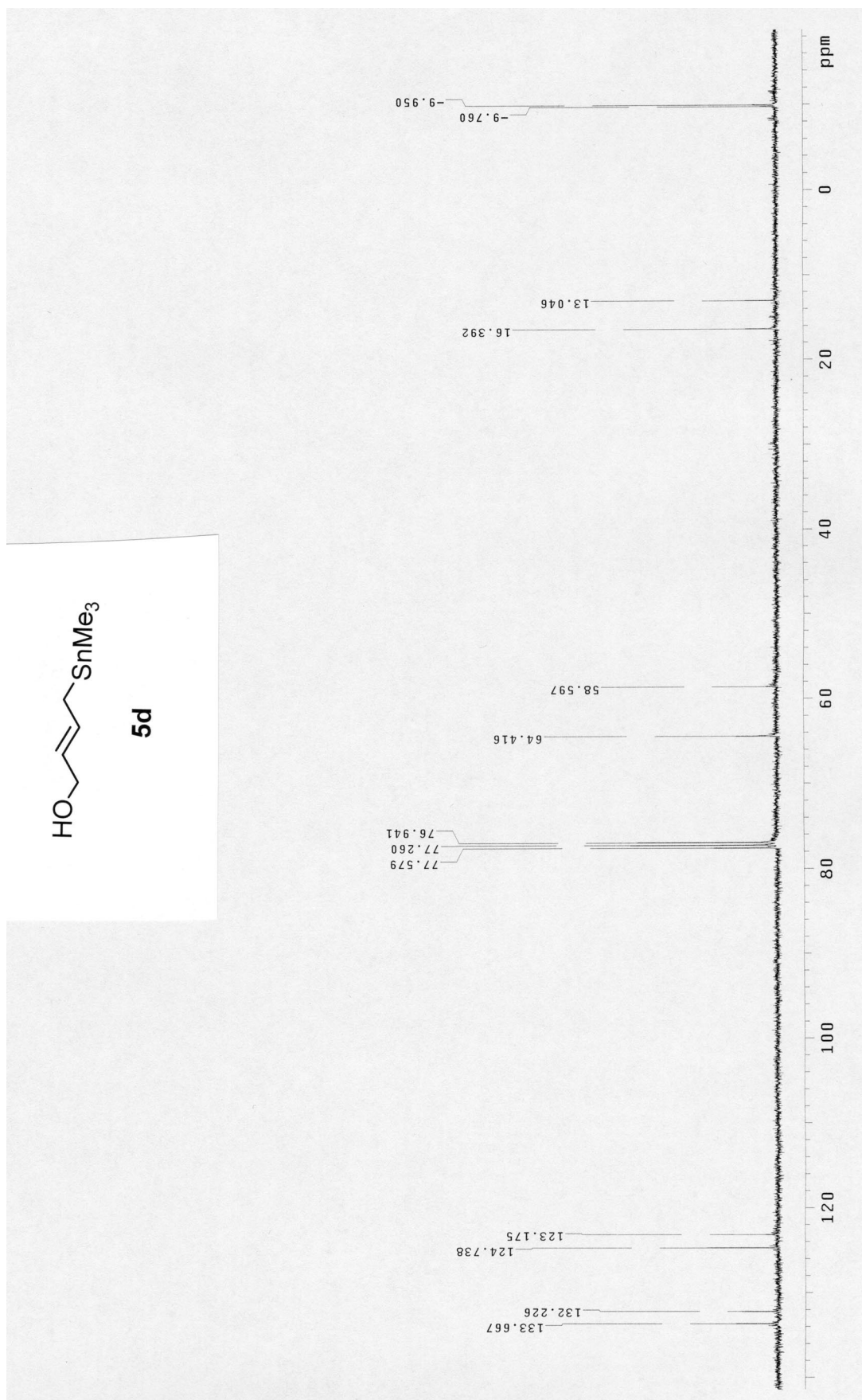
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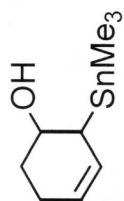
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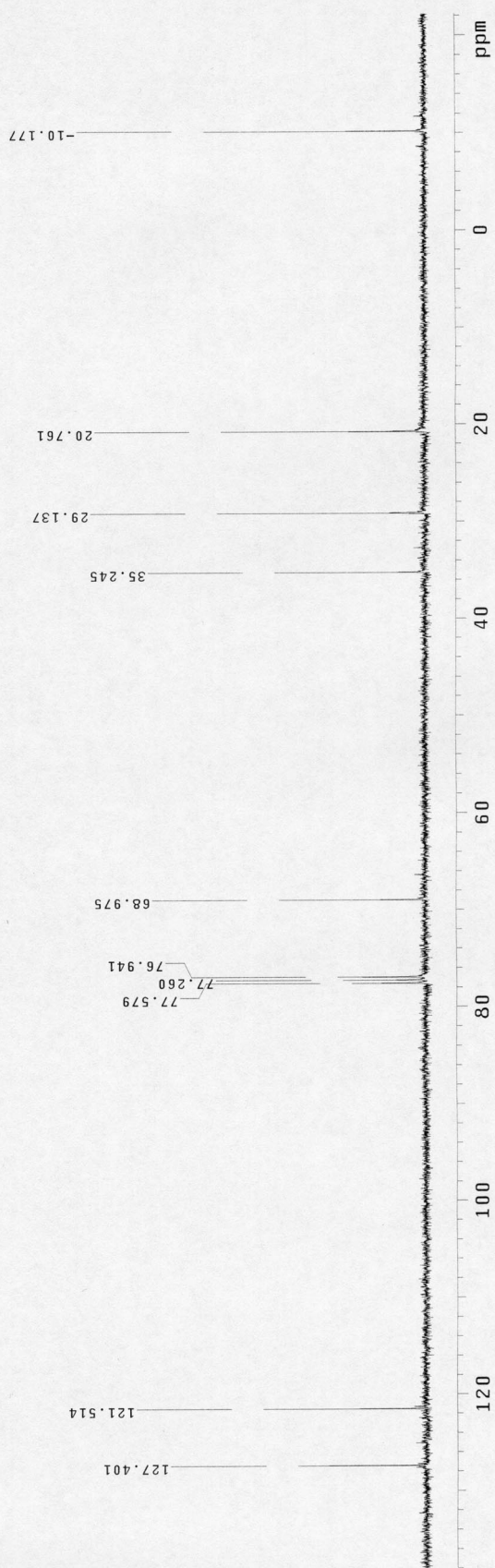


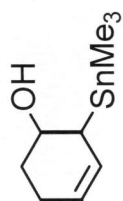




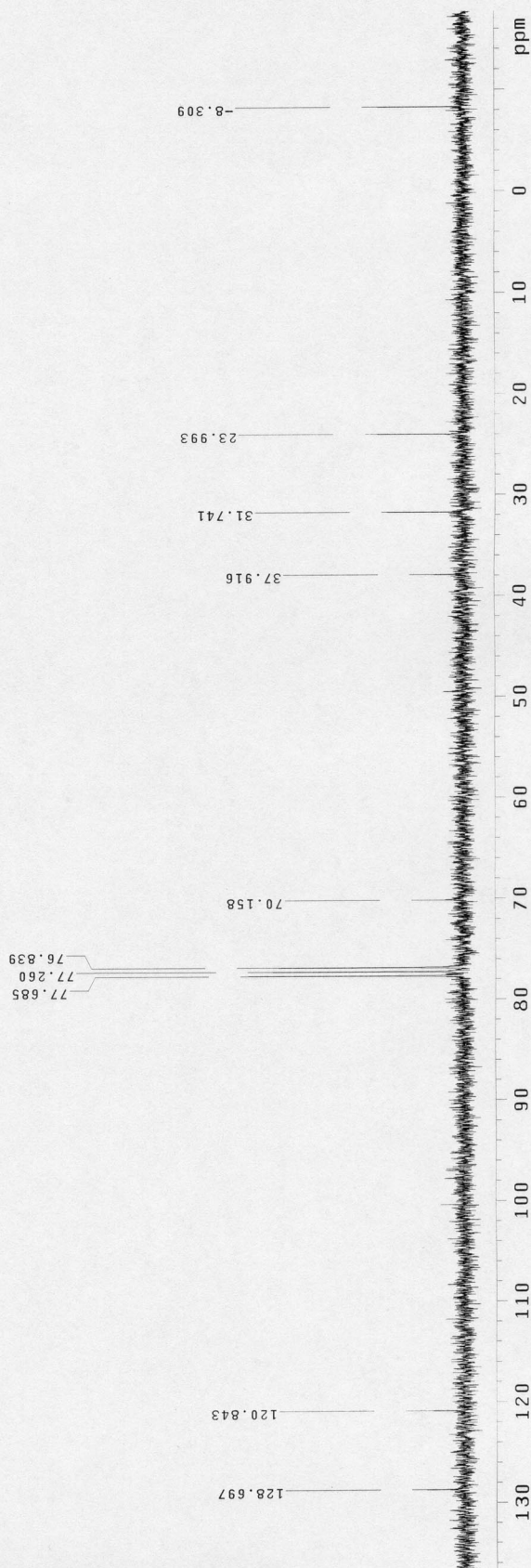


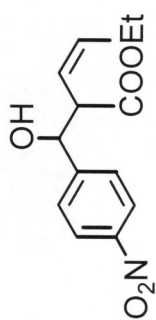
5e, major diastereomer





5e, minor diastereomer



**5i, diastereomer A**