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Supporting Information

The Formation of a Novel Pd/C-Ethylenediamine Complex Catalyst: Chemoselective Hydrogenation without Deprotection of the *O*-Benzyl and *N*-Cbz Groups

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General Procedures. M.p.s were determined on a Yanagimoto melting–point apparatus and are uncorrected. Thin-layer chromatographic (TLC) analyses were carried out on pre-coated Silica gel 60 F_{254} plates (Merck, Art 5715). Flash column chromatography was performed on Merck silica gel (0.040–0.063 mm). ^{1}H NMR spectra were run at 270, 300 or 400 MHz and ^{13}C NMR spectra at either 75 or 100 MHz with the sample solvent being $CDCl_3$ unless otherwise noted. Mass spectra and high-resolution mass spectra were taken on a JEOL JMS-SX 102A machine or carried out at Mass Spectrometry Laboratory, University of California, Berkeley, California, USA. X-ray Photoelectron Spectroscopies were carried out at the Analytical center of Japan Energy Co. Ltd., Toda, Saitama, Japan. Elemental analyses were carried out at the Microanalytical Laboratory of our University. *N*-Boc-*O*-benzyl-L-tyrosine, *N*-Boc-L-tyrosine, *N*-Boc-*O*-benzyl-L-serine and 4-benzyloxy-3-methoxystyrene are commercially available from Sigma Co., Inc. and/or Aldrich Chemical Co., Inc.

The preparation of 5% Pd/C(en) catalyst: A suspension of commercial 5% Pd/C (10 g, 4.74 mmol of Pd metal) and ethylenediamine (22 mL, 0.329 mol) in methanol (200 mL) under a rigorous argon atmosphere to prevent the ignition (Pd/C is highly pyrophoric) was stirred for 48 h at ambient temperature.[6] The solid was filtered, washed vigorously with methanol (20 mL x 5) and ether (20 mL x 2), and dried under vacuum pump at room temperature for 48 h to give the 5% Pd/C(en).

Benzyl Cinnamyl Ether: To a stirring mixture of cinnamyl alcohol (4.03 g, 30.00 mmol) and NaH (60% W/W in mineral oil, 1.44 g, 36.00 mmol) in DMF (30 mL) was added benzyl bromide (3.93 mL, 33.00 mmol) at room temperature. The mixture was stirred at room temperature for 12 h, after which it was concentrated *in vacuo.* The residue was partitioned between ether (100 mL) and water (100 mL). The ethereal layer was washed with water (100 mL) and brine (100 mL), dried over $MgSO_4$ and evaporated *in vacuo.* The residue was applied to a flash silica gel column chromatography (hexane : ether = 20 : 1) to obtain benzyl cinnamyl ether (6.11 g, 91%) as a clear oil: ^{1}H NMR (300 MHz): δ 4.21 (dd, J = 1.5 and 6.3 Hz, 2H), 4.58 (s, 2H), 6.34 (dt, J = 6.1 and 15.9 Hz, 1H), 6.64 (d, J = 15.9 Hz, 1H), 7.19–7.44 (m, 10H); ^{13}C NMR (75 MHz): δ 70.7, 72.1, 126.0, 126.5, 127.6, 127.7, 127.8, 128.4, 128.5, 132.5, 136.7, 138.2; HRMS (EI) calcd for $C_{16}H_{16}O$ (M^+) 224.1201, found 224.1203.

Benzyl Geranyl Ether: was prepared by a procedure similar to that described above using geraniol (5.62 mL, 21.3 mmol), benzyl bromide (2.78 mL, 23.40 mmol) and NaH (60% W/W in mineral oil, 0.94 g, 23.4 mmol) in DMF (30 mL) (3.87 g, 49% as a clear oil): ^{1}H NMR (400 MHz): δ 1.60, 1.65 and 1.68 (each s, 3H), 2.01–2.18 (m, 4H), 4.03 (d, J = 6.8 Hz, 2H), 4.50 (s, 2H), 5.10 (br t, J = 6.6 Hz, 1H), 5.40 (br t, J = 6.8 Hz, 1H), 7.22–7.43 (m, 5H); ^{13}C NMR (100 MHz): δ 16.4, 17.6, 25.6, 26.3, 39.5, 66.5, 71.9, 120.8, 123.9, 127.4, 127.8, 128.3, 131.6, 138.5, 140.3; HRMS (FAB) calcd for $C_{17}H_{25}O$ ($M^+ + H$) 245.1905, found 245.1896.

4-(4-Methoxybenzyloxy)cinnamic Acid Methyl Ester: was prepared by a procedure similar to that described above using 4-hydroxycinnamic acid methyl ester

(1.78 g, 10.00 mmol) and 4-methoxybenzyl chloride (1.49 g, 11.00 mmol) and NaH (60% W/W in mineral oil, 0.44 g, 11.00 mmol) in DMF (15 mL) (2.44 g, 82% as a white solid): mp. 158–159 °C; ^{1}H NMR (400 MHz): δ 3.79 and 3.82 (each s, 3H), 5.02 (s, 2H), 6.31 (d, J = 16.1 Hz, 1H), 6.92, 6.97, 7.35 and 7.47 (each d, J = 8.8 Hz, 2H), 7.65 (d, J = 16.1 Hz, 1H); LRMS (EI) m/z 298 (M^+), 267, 178, 147 (base peak), 121, 91. Anal. calcd for $C_{18}H_{18}O_4$: C, 72.47; H, 6.08. Found: C, 72.42, H, 6.14.

4-Benzyloxyphenylacetic Acid Benzyl Ester was prepared by a procedure similar to that described above using 4-benzyloxyphenylacetic acid (2.42 g, 10.00 mmol) and Et_3N (1.40 mL, 10.00 mmol) in THF (20 mL) was added benzyl bromide (1.19 mL, 10.00 mmol) (2.19 g, 88% as a white solid) : mp. 69–70 °C; ^{1}H NMR (400 MHz): δ 3.60, 5.05 and 5.12 (each s, 3H), 6.93 (d, J = 8.8 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 7.30–7.49 (m, 10H); ^{13}C NMR (100 MHz): δ 42.27, 68.39, 71.83, 129.25, 129.76, 129.95, 130.02, 130.35, 132.18, 132.25, 137.70, 138.76, 138.84, 159.76, 173.55; LRMS (EI) m/z 332 (M^+), 242, 149, 91 (base peak). Anal. calcd for $C_{22}H_{20}O_3$: C, 79.49; H, 6.06. Found: C, 79.21, H, 6.10.

***N*-Boc-*O*-benzyl-L-serine Benzyl Ester:** To a stirring solution of *N*-Boc-*O*-benzyl-L-serine (2.95 g, 10.00 mmol) in dry DMF (5 mL) was added N,N-dimethylformamide dibenzylacetal (purity 90%, 3.47 mL, 12.00 mmol) at room temperature. The mixture was stirred at room temperature for 15 h, after which it was concentrated *in vacuo*. The residue was applied to a flash silica gel column chromatography (hexane : ether = 5 : 1) to obtain *N*-Boc-*O*-benzyl-L-serine Benzyl Ether (3.43 g, 89%) as a clear oil: ^{1}H NMR (300 MHz): δ 1.44 (s, 9H), 3.60 and 3.91 (each dd, J = 3.0 and 9.2 Hz, 1H), 4.32–4.58 (m, 5H), 5.14 and 5.23 (each d, J = 12.2 Hz, 1H), 5.43 (br d, J = 9.2 Hz, 1H), 7.10–7.43 (m, 10H); ^{13}C NMR (75 MHz): δ 28.3, 54.1, 67.1, 70.1, 73.3, 80.0, 127.5, 127.8, 128.1, 128.3, 128.4, 128.5, 135.4, 137.5, 155.5, 170.6; HRMS (FAB) calcd for

$C_{22}H_{28}NO_5$ ($M^+ + H$) 386.1967, found 386.1960.

***N*-Boc-*O*-benzyl-L-tyrosine Methyl Ester** was prepared by a procedure similar to that described above using *N*-Boc-*O*-benzyl-L-tyrosine (1.71 g, 4.60 mmol) and N,N-dimethylformamide dimethylacetal (3.06 mL, 23.00 mmol) in dry DMF (5 mL) (1.30 g, 73% as a white solid) : mp. 61–64 °C; ^{1}H NMR (400 MHz): δ 1.42 (s, 9H), 2.92–3.14 (m, 2H), 3.70 (s, 3H), 4.48–4.62 (m, 1H), 4.97 (br, 1H), 5.03 (s, 2H), 6.90 and 7.04 (each d, J = 8.8 Hz, 2H), 7.27–7.45 (m, 5H); ^{13}C NMR (100 MHz): δ 28.3, 37.5, 52.2, 54.5, 70.0, 79.9, 114.9, 127.4, 128.0, 128.2, 128.6, 130.3, 137.0, 155.1, 157.9, 172.4; LRMS (EI) m/z 385 (M^+), 268, 197, 91 (base peak). Anal. calcd for $C_{22}H_{27}NO_5$: C, 68.55; H, 7.06; N, 3.63. Found: C, 68.39, H, 7.17; N, 3.66.

***N*-Cbz-*O*-benzyl-L-tyrosine Methyl Ester:** was prepared by a procedure similar to that described above using *N*-Cbz-*O*-benzyl-L-tyrosine (202 mg, 0.50 mmol) and N,N-dimethylformamide dimethylacetal (332 μL, 2.50 mmol) in dry DMF (3 mL) (190 mg, 91% as a waxy solid): ^{1}H NMR (400 MHz): δ 2.94–3.12 (m, 2H), 3.69 (s, 3 H), 4.52–4.68 (m, 1H), 5.01 (s, 2 H), 5.06 and 5.10 (each d, J = 12.2 Hz, 1H), 5.24 (br d, J = 7.8 Hz, 1H), 6.89 and 6.99 (each d, J = 8.8 Hz, 1H), 7.26–7.45 (m, 10H); ^{13}C NMR (100 MHz): δ 37.3, 52.2, 54.9, 66.9, 69.9, 114.9, 127.4, 127.9, 128.0, 128.1, 128.4, 128.5, 130.2, 136.3, 136.9, 155.6, 157.9, 172.0; HRMS (EI) calcd for $C_{25}H_{25}NO_5$ (M^+) 419.1742, found 419.1733.

2-Benzyloxyethyl Azido:[18] To a stirring solution of 2-benzyloxyethanol (Aldrich, 3.81 g, 25.00 mmol) and Et_3N (3.90 mL, 28.00 mmol) in CH_2Cl_2 (50 mL) was added MsCl (2.17 mL, 28.00 mmol) at room temperature. The mixture was stirred at room temperature for 15 h, after which it was concentrated *in vacuo*. The residue was partitioned between AcOEt (30 mL) and water (30 mL). The organic layer was washed with water (30 mL), saturated $NaHCO_3$ solution (30 mL), water (30 mL), 10% $NaHSO_4$

solution (30 mL), water (30 mL), and brine (30 mL), dried over $MgSO_4$ and evaporated *in vacuo*. The residue was used for the next reaction without further purification (5.71 g, 99% crude) as a yellow oil: ^1H NMR (300 MHz): δ 3.04 (s, 3H), 3.75 (t, *J* = 4.7 Hz, 2H), 4.40 (t, *J* = 4.7 Hz, 2H), 4.58 (s, 2H), 7.27–7.39 (m, 5H); ^{13}C NMR (75 MHz): δ 37.7, 67.8, 69.1, 73.3, 127.8, 128.0, 128.5, 137.3.

To a mixture of the above compound (5.71 g, crude) in DMF (50 mL) was added NaN_3 (1.95 g, 30 mmol). The reaction mixture was stirred at room temperature for 48 h. The solvent was evaporated and the residue was partitioned between AcOEt (50 mL) and water (50 mL). The organic layer was washed with water (50 mL) and brine (50 mL), dried over $MgSO_4$ and evaporated *in vacuo*. The residue was applied to a flash silica gel column chromatography (hexane : ether = 20 : 1) to obtain 2-benzyloxyethyl azido (4.21 g, 83% for two steps) as a clear oil: ^1H NMR (300 MHz): δ 3.41 and 3.66 (each t, *J* = 5.0 Hz, 2H), 4.58 (s, 2H), 7.23–7.38 (m, 5H); ^{13}C NMR (75 MHz): δ 50.79, 68.83, 73.25, 127.61, 127.76, 128.44, 137.68.

Ethylene Glycol Benzyl Ether 2-Bromobenzoate: To a stirring mixture of 2-(benzyloxy)ethanol (1.52 g, 10.00 mmol), Et_3N (1.67 mL, 12.00 mmol) and DMAP (0.12 g, 1.00 mmol) in THF (10 mL) was added 2-bromobenzoyl chloride (2.41 mL, 11.00 mmol) at room temperature. The mixture was stirred at room temperature for 24 h, after which it was concentrated *in vacuo*. The residue was partitioned between AcOEt (50 mL) and water (50 mL). The organic layer was washed with water (30 mL), saturated $NaHCO_3$ solution (30 mL), water (30 mL), 10% $NaHSO_4$ solution (30 mL), water (30 mL), and brine (30 mL), dried over $MgSO_4$ and evaporated *in vacuo*. The residue was applied to a flash silica gel column chromatography (hexane : ether = 4 : 1) to obtain ethylene glycol benzyl ether 2-bromobenzoate (2.86 g, 78%) as a white wax: ^1H NMR (400 MHz): δ 3.81 and 4.52 (each t, *J* = 4.8 Hz, 2H), 4.61 (s, 2H), 7.22–7.39 (m, 7H), 7.66 (dd, $J = 1.7$ and 7.6 Hz, 1H), 7.81 (dd, $J = 2.2$ and 7.6 Hz, 1H); ^{13}C NMR (100 MHz): δ 64.6, 67.8, 73.1, 121.8, 127.1, 127.5, 127.7, 128.4, 131.4, 132.0, 132.6, 134.3, 137.8, 166.0; HRMS (EI) calcd for $C_{16}H_{15}O_3Br$ (M^+) 334.0205, found 334.0211.

Ethylene Glycol Benzyl Ether 4-Nitrobenzoate was prepared by a procedure similar to that described above using 2–(benzyloxy)ethanol (3.04 g, 20.00 mmol), 4-nitrobenzoyl chloride (3.90 g, 21.00 mmol), Et_3N (3.07 mL, 22.00 mmol) and DMAP (0.24 g, 2.00 mmol) in THF (20 mL) (92% as a pale yellow oil): ^{1}H NMR (270 MHz): δ 3.83 and 4.55 (each t, $J = 4.6$ Hz, 2H), 4.61 (s, 2H), 7.22–7.48 (m, 5H), 8.22 and 8.30 (each d, $J = 8.8$ Hz, 2H); ^{13}C NMR (100 MHz): δ 65.0, 67.7, 73.2, 123.5, 127.7, 127.9, 128.5, 130.8, 135.5, 137.7, 150.6, 164.7; HRMS (EI) calcd for $C_{16}H_{15}NO_5$ ($M^+ + H$) 301.0950, found 301.0939.

1-Benzyloxycarbonyl-*trans*-4-cinnamylpiperazine: A mixture of *trans*-1-cinnamylpiperazine (3.00 g, 14.80 mmol) and *N*-(benzyloxycarbonyloxy)succinimide (3.69 g, 22.20 mmol) in CH_2Cl_2 (25 mL) was stirred at room temperature for 17 h, after which it was concentrated *in vacuo*. The residue was partitioned between AcOEt (50 mL) and water (50 mL). The organic layer was washed with water (30 mL), saturated $NaHCO_3$ solution (30 mL), water (30 mL) and brine (30 mL), dried over $MgSO_4$ and evaporated *in vacuo*. The residue was applied to a flash silica gel column chromatography ($CHCl_3$: MeOH = 50 : 1) to obtain 1-Benzyloxycarbonyl-*trans*-4-cinnamylpiperazine (4.24 g, 85%) as a pale yellow oil: ^{1}H NMR (400 MHz): δ 2.23–2.50 (m, 4H), 3.16 (d, $J = 6.6$ Hz, 2H), 3.54 (t, $J = 4.9$ Hz, 4H), 5.13 (s, 2H), 6.24 (dt, $J = 6.6$ and 15.9 Hz, 1H), 6.52 (d, $J = 15.9$ Hz, 1H), 7.21–7.38 (m, 10H); ^{13}C NMR (100 MHz): δ 43.8, 52.8, 61.0, 67.1, 126.0, 126.3, 127.6, 127.8, 128.0, 128.4, 133.4, 136.7, 155.2; HRMS (EI) calcd for $C_{21}H_{24}N_2O_2$ (M^+) 336.1838, found

336.1844.

N-(Benzyloxycarbonyl)diallylamine was prepared by a procedure similar to that described above using diallylamine (1.94 g, 20.00 mmol) and *N*-(benzyloxycarbonyloxy)succinimide (5.48 g, 22.00 mmol) in CH_2Cl_2 (10 mL) (2.52 g, 55% as a clear oil): ^{1}H NMR (400 MHz): δ 3.87–3.90 and 5.05–5.19 (each m, 4H), 5.15 (s, 2H), 5.70–5.83 (m, 2H), 7.30–7.36 (m, 5H); ^{13}C NMR (100 MHz): δ 48.2, 48.8, 66.8, 116.4, 116.8, 127.5, 127.6, 128.1, 133.2, 136.6, 155.7; HRMS (FAB) calcd for $C_{14}H_{18}NO_2$ ($M^+ + H$) 232.1337, found 232.1346.

N-(Benzyloxycarbonyl)propargylamine was prepared by a procedure similar to that described above using propargylamine (1.10 g, 20.00 mmol) and *N*-(benzyloxycarbonyloxy)succinimide (5.48 g, 22.00 mmol) in CH_2Cl_2 (10 mL) (2.90 g, 77% as a white solid): ^{1}H NMR (400 MHz): δ 2.24 (t, *J* = 2.4 Hz, 1H), 3.98–4.02 (m, 2H), 4.92 (br, 1H), 5.13 (s, 2H), 7.32–7.36 (m, 5H); ^{13}C NMR (100 MHz): δ 30.8, 67.1, 71.6, 79.6, 128.1, 128.2, 128.5, 136.1, 155.8; LRMS (EI) m/z 189 (M^+), 128, 108, 91 (base peak). Anal. calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.81; H, 5.96; N, 7.40.

N-(Benzyloxycarbonyl)-L-proline Benzyl Ester was prepared by a procedure similar to that described above using L-proline Benzyl Ester Hydrochloride (2.42 g, 10.00 mmol), Et_3N (1.30 mL, 9.30 mmol) and *N*-(benzyloxycarbonyloxy)succinimide (2.99 g, 12.00 mmol) in CH_2Cl_2 (20 mL) (2.75 g, 81% as a clear oil): ^{1}H NMR (400 MHz): δ 1.86–2.02 (m, 3H), 2.17–2.26, 3.44–3.56 and 3.58–3.67 (each m, 1H), 4.38 and 4.45 (each dd, *J* = 3.7 and 8.5 Hz, 0.5 H), 4.99–5.09 and 5.11–5.23 (each m, 2H), 7.22–7.36 (m, 10H); ^{13}C NMR (100 MHz): δ 23.5, 24.3, 29.9, 30.9, 46.4, 46.9, 58.9, 59.3, 66.7, 66.8, 66.9, 67.0, 85.3, 127.77, 127.84, 127.9, 128.0, 128.1, 128.2, 128.28, 128.37, 128.42, 128.5, 135.5, 135.7, 136.6, 136.7, 154.3, 154.9, 172.4, 172.6 ; HRMS (EI) calcd for $C_{20}H_{21}NO_4$ (M^+) 339.1471, found 339.1456.

Chemoselective Hydrogenation of *O*-Benzyl Ether and *N*-Cbz Derivatives: After two vacuum/H_2 cycles to remove air from the reaction tube, the stirred mixture of the substrate (0.2 mmol), 5% Pd/C(en) (10% of the weight of the substrate) in MeOH, 1,4-dioxane or THF (1 mL) was hydrogenated at ordinary pressure (balloon) and temperature (*ca.* 20 °C) for the appropriate time (see Table 1). The reaction mixture was filtered using a membrane filter (Millipore Dimex-13, 0.22 µm) and the filtrate was concentrated *in vacuo*. The resulting product was purified by flash silica gel column chromatography, if necessary.

1-Benzyloxy-3-phenylpropane:[8] 95% as a clear oil; ^{1}H NMR (400 MHz): δ 1.88–2.02 (m, 2H), 2.72 (d, *J* = 7.7 Hz, 2H), 3.49 (dt, *J* = 1.4 and 6.5 Hz, 2H), 4.51 (s, 2H), 7.14–7.20 (m, 10H); ^{13}C NMR (100 MHz): δ 31.3, 32.3, 69.4, 72.9, 125.7, 127.5, 127.6, 128.2, 128.3 128.4 141.9 ; HRMS (EI) calcd for $C_{16}H_{18}O$ (M^+) 226.1358, found 226.1356.

Benzyl 3,7-Dimethyl-1-octyl Ether: 91% as a clear oil; ^{1}H NMR (400 MHz): δ 0.86 (d, *J* = 6.8 Hz, 6H), 0.86 (d, *J* = 6.4 Hz, 3H), 1.05–1.35 (m, 6H), 1.37–1.74 (m, 4H), 3.45–3.55 (m, 2H), 4.50 (s, 2H), 7.24–7.36 (m, 5H); HRMS (FAB) calcd for $C_{17}H_{29}O$ ($M^+ + H$) 249.2218, found 249.2225.

2-Benzyloxyethylamine:[10] 93% as a pale yellow oil; ^{1}H NMR (270 MHz): δ 1.48 (br, 2H), 2.90 and 3.52 (each t, *J* = 5.3 Hz, 2H), 4.54 (s, 2H), 7.25–7.43 (m, 5H).

Ethylene Glycol Benzyl Ether Benzoate: 93% as a white solid; ^{1}H NMR (400 MHz): δ 3.81 and 4.51 (each t, *J* = 4.9 Hz, 2H), 4.62 (s, 2H), 7.28–7.35 (m, 5H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 8.07 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz): δ 64.1, 68.0, 73.2, 127.7, 127.8, 128.3, 128.4, 129.7, 130.1, 133.0, 138.0, 166.6; HRMS (EI) calcd for $C_{16}H_{16}O_3$ (M^+) 256.1099, found 256.1107.

***N*-Boc-*O*-benzyl-L-serine:** 91% as a white solid; commercially available; ^{1}H NMR (300 MHz): δ 1.45 (s, 9H), 43.71 (dd, *J* = 3.8 and 9.5 Hz, 1H), 3.93 (br dd, *J* = 3.8

and 7.5 Hz, 1H), 4.43–4.55 (m, 1H), 4.55 (s, 2H), 5.41 (br d, *J* = 7.8 Hz, 1H), 7.24–7.37 (m, 5H).

Ethylene Glycol Benzyl Ether 4-Aminobenzoate: 98% as a pale yellow oil; ^{1}H NMR (400 MHz): δ 3.78 (t, *J* = 4.9 Hz, 2H), 3.97 (br, 2H), 4.44 (t, *J* = 4.9 Hz, 2H), 4.60 (s, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 7.30–7.41 (m, 5H), 7.86 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (100 MHz): δ 63.5, 68.1, 73.1, 113.7, 119.5, 127.7, 128.4, 131.7, 138.0, 150.9, 166.6; HRMS (EI) calcd for $C_{16}H_{17}NO_3$ (M^+) 271.1208, found 271.1216.

4-(4-Methoxybenzyloxy)dihydrocinnamic Acid Methyl Ether: 97% as a white wax; ^{1}H NMR (270 MHz): δ 2.60 and 2.89 (each t, *J* = 7.7 Hz, 2H), 3.67 and 3.82 (each s, 3H), 496 (s, 2H), 6.89, 6.91, 7.11 and 7.35 (each d, *J* = 8.8 Hz, 2H); LRMS (EI) m/z 298 (M^+), 267, 178, 147 (base peak), 121, 91; HRMS (EI) calcd for $C_{18}H_{20}O_4$ (M^+) 300.1362, found 300.1356.

4-Benzyloxy-3-methoxyethylbenzene: 96% as a white solid; ^{1}H NMR (400 MHz): δ 1.21 (t, *J* = 7.8 Hz, 3H), 2.59 (q, *J* = 7.8 Hz, 2H), 3.88 (s, 3H), 5.12 (s, 2H), 6.67 (dd, *J* = 2.0 and 8.1 Hz, 1H), 6.75 (d, *J* = 2.0 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.44 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz): δ 15.7, 28.5, 55.9, 71.2, 111.9, 114.3, 119.5, 127.2, 127.7, 128.5, 137.5, 137.6, 146.2, 149.5; HRMS (FAB) calcd for $C_{16}H_{19}O_2$ ($M^+ + H$) 243.1385, found 243.1384.

4-Benzyloxyphenylacetic Acid: 94% as a white solid; commercially available; ^{1}H NMR (400 MHz): δ 3.58 and 5.05 (each s, 2H), 6.94 and 7.19 (each d, *J* = 8.5 Hz, 2H), 7.27–7.51 (m, 5H).

1-Benzyloxycarbonyl-4-(3-phenylpropyl)piperazine: 77% as a pale yellow oil; ^{1}H NMR (400 MHz): δ 1.81 (p, *J* = 7.6 Hz, 2H), 2.34–2.38 (m, 6H), 2.64 (t, *J* = 7.6 Hz, 2H), 3.52 (t, *J* = 4.9 Hz, 4H), 5.13 (s, 2H), 7.16–7.36 (m, 10H); ^{13}C NMR (100 MHz): δ 28.4, 33.5, 43.8, 52.8, 57.8, 67.0, 125.8, 127.8, 128.0, 128.28, 128.33, 128.4, 136.7, 142.0, 155.2; HRMS (EI) calcd for $C_{21}H_{26}N_2O_2$ (M^+) 338.1994, found 338.2009.

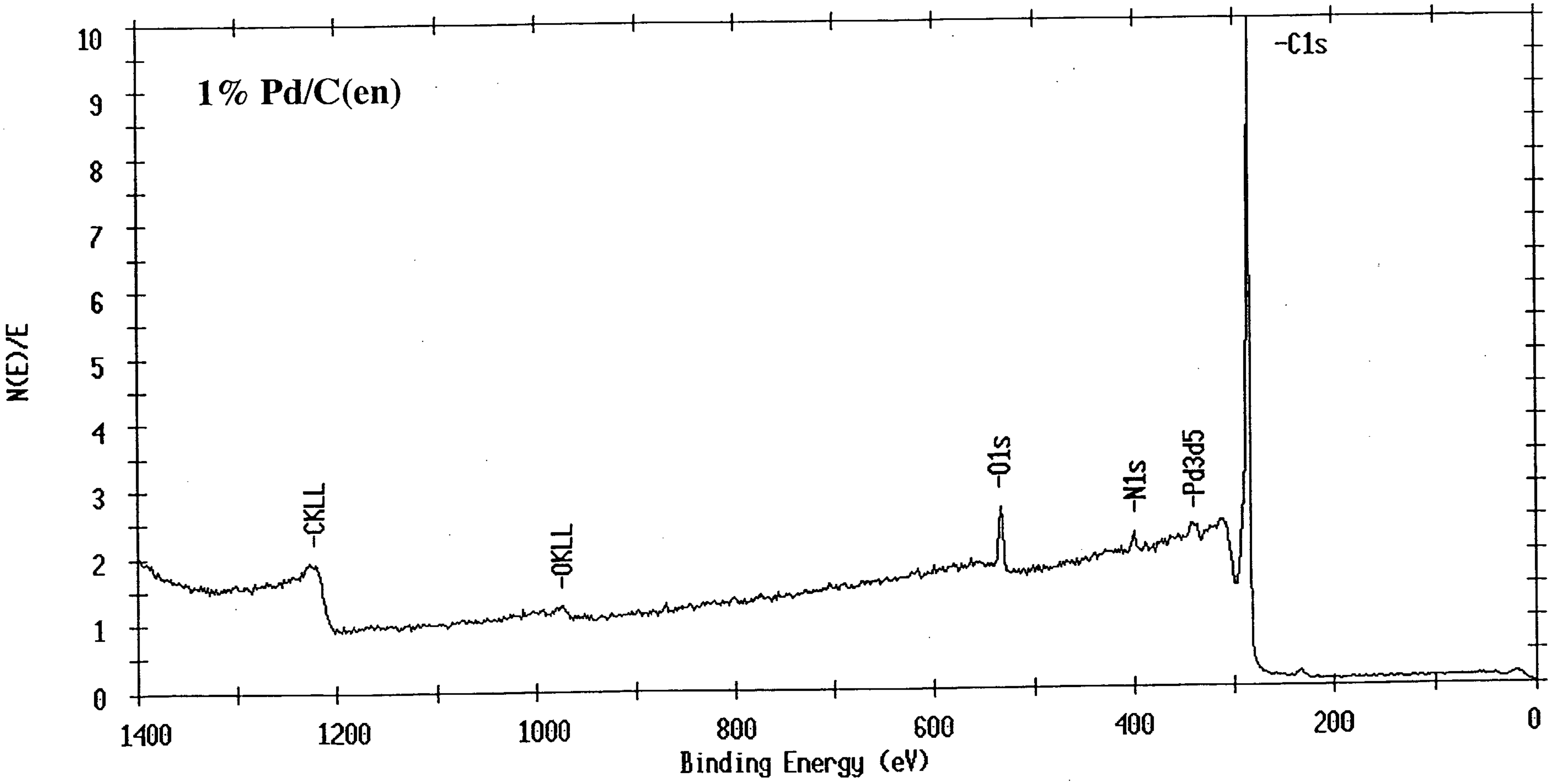
***N*-Benzyloxycarbonyl(dipropyl)amine:** 92% as a clear oil; ^{1}H NMR (400 MHz): δ 0.86–0.89 (m, 6H), 1.49–1.61 and 3.12–3.25 (each m, 4H), 5.12 (s, 2H), 7.28–7.36 (m, 5H); ^{13}C NMR (100 MHz): δ 11.2, 21.3, 21.8, 48.6, 49.2, 66.7, 127.6, 127.7, 128.4, 137.1, 156.2; HRMS (FAB) calcd for $C_{14}H_{21}NO_2$ ($M^+ + H$) 236.1650, found 236.1648.

***N*-Benzyloxycarbonyl(propyl)amine:** 77% as a clear oil; ^{1}H NMR (400 MHz): δ 0.91 (t, *J* = 7.6 Hz, 3H), 1.45–1.56 and 3.10–3.20 (each m, 2H), 4.78 (br, 1H), 5.09 (s, 2H), 7.31–7.36 (m, 5H); ^{13}C NMR (100 MHz): δ 11.2, 23.2, 42.8, 66.5, 128.0, 128.5, 136.7, 156.4; HRMS (EI) calcd for $C_{11}H_{15}NO_2$ (M^+) 193.1103, found 193.1098.

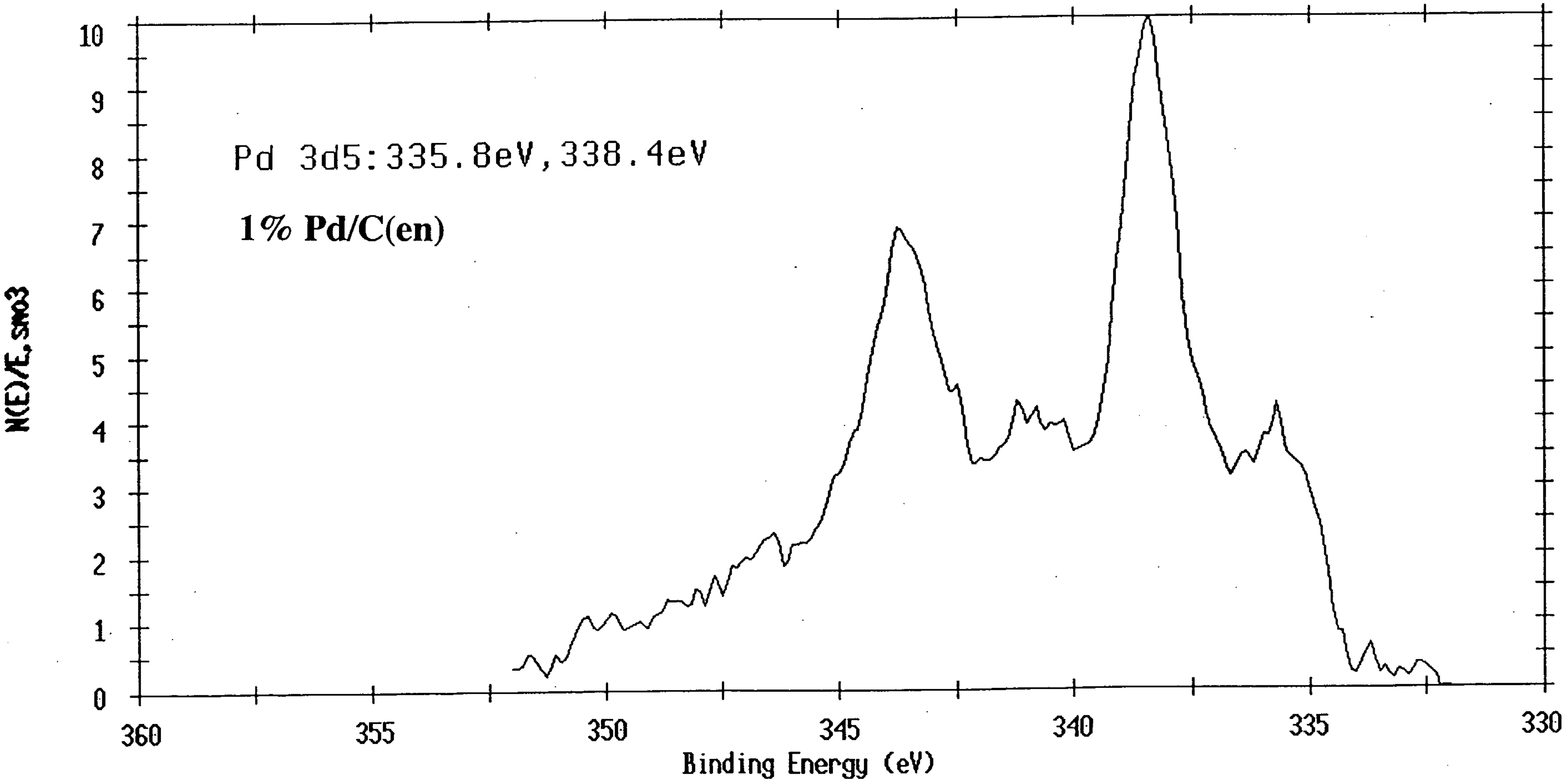
***N*-(Benzyloxycarbonyl)-L-proline:** 75% as a clear oil; commercially available; ^{1}H NMR (400 MHz): δ 1.92–1.98 (m, 3H), 2.05–2.13 and 2.23–2.38 (each m, 1H), 3.45–3.55 (m, 2H), 4.41–4.44 (m, 1H), 5.19 (dd, *J* = 15.1 and 18.6 Hz, 2H), 7.31–7.38 (m, 5H); ^{13}C NMR (100 MHz): δ 23.3, 24.2, 29.5, 30.8, 46.5, 46.8, 58.6, 59.1, 67.1, 67.3, 127.0, 127.5, 127.8, 128.0, 128.3, 128.4, 136.2 136.3, 154.4, 155.4, 176.7, 177.6; HRMS (EI) calcd for $C_{13}H_{15}NO_4$ (M^+) 249.1001, found 249.0993.

Time course of the hydrogenolysis of *N*–Boc–*O*–benzyltyrosine (1): commercial 5% Pd/C (2 mg, 1 μmol of Pd) was stirred with ethylenediamine (0.7 mL of 0.1 M solution in methanol, 70 μmol) at ambient temperature. After being stirred for appropriate time (0 h, 6 h, 12 h, 16 h, 22h, 30 h), the substrate **1** (19 mg, 50 μmol) was added to a stirred suspension. The mixture was hydrogenated (balloon) and the reaction was monitored by TLC scanner (Shimadzu CS-9000).

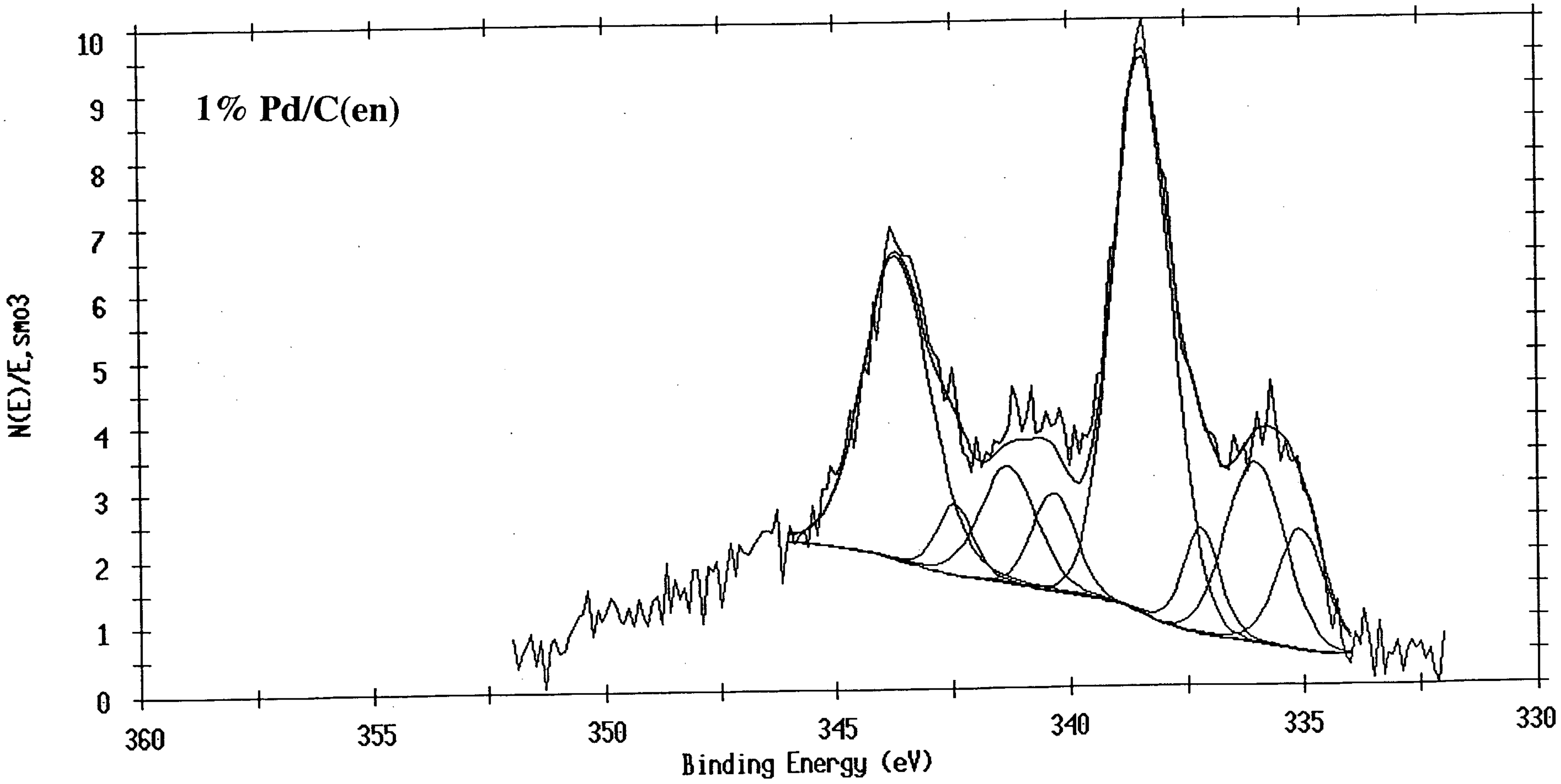
ESCA Survey 9 Apr 97 Area: 1 Angle: 65 degrees Acquisition Time: 4.38 min
File: 7566 No.4:HS-1-179:Pd/C(EDI)
Scale Factor: 5.081 kc/s Offset: 0.050 kc/s Pass Energy: 187.850 eV Aperture: 4 Al 300 W



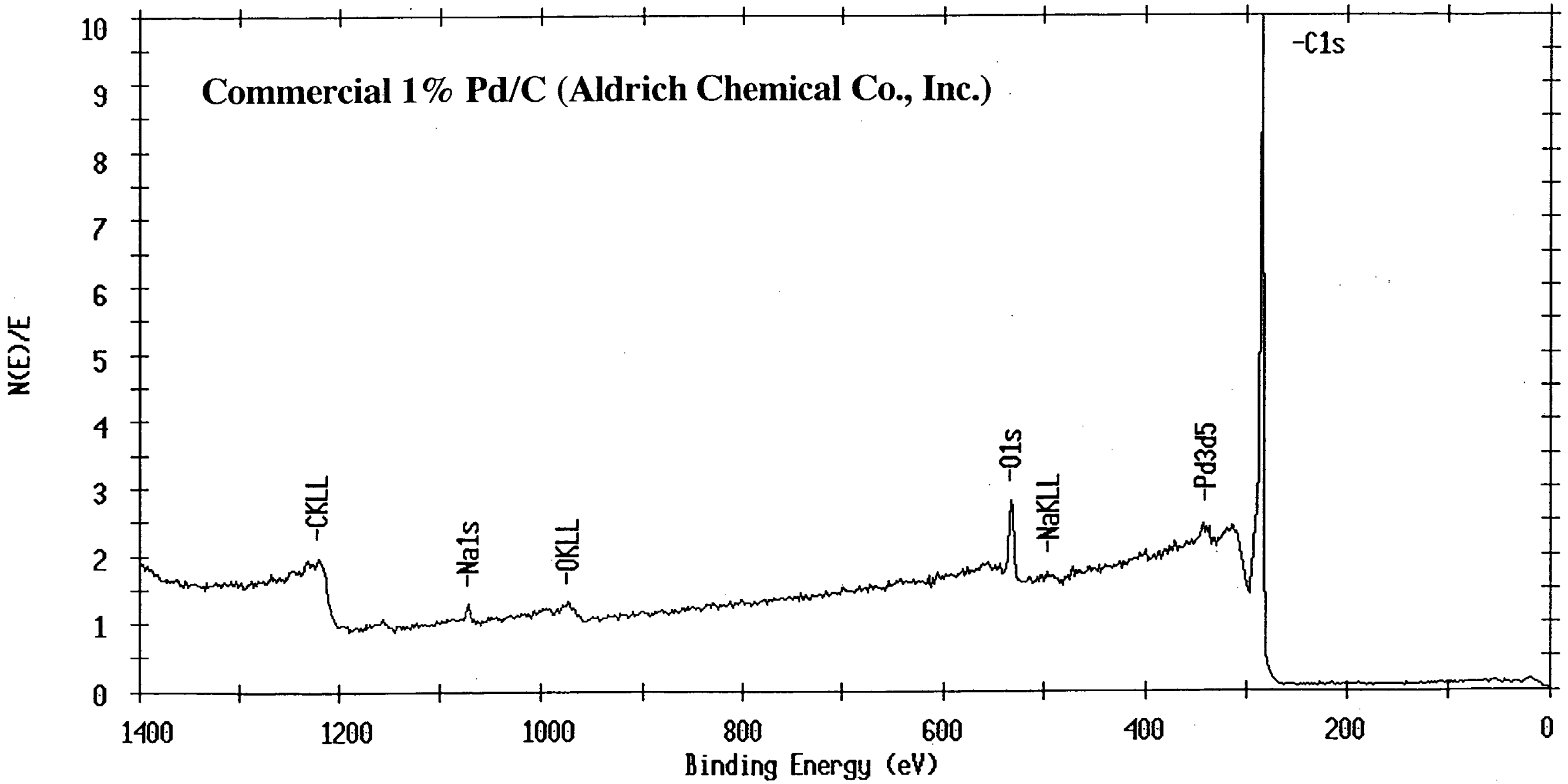
ESCA Multiplex 9 Apr 97 Area: 1 Species: Pd1 Region: 3 Angle: 65 degrees Acquisition Time: 167.50 min
File: 7567 No.4:HS-1-179:Pd/C(EDI)
Scale Factor: 0.016 kc/s Offset: 0.940 kc/s Pass Energy: 23.500 eV Aperture: 4 Al 300 W



ESCA CURVE FIT 9 Apr 97 Angle: 65 degrees Acquisition Time: 167.50 min
File: Curve_Fit No.4:HS-1-179:Pd/C(EDI)
Scale Factor: 0.017 kc/s Offset: 0.937 kc/s Pass Energy: 23.500 eV Aperture: 4 Al 300 W

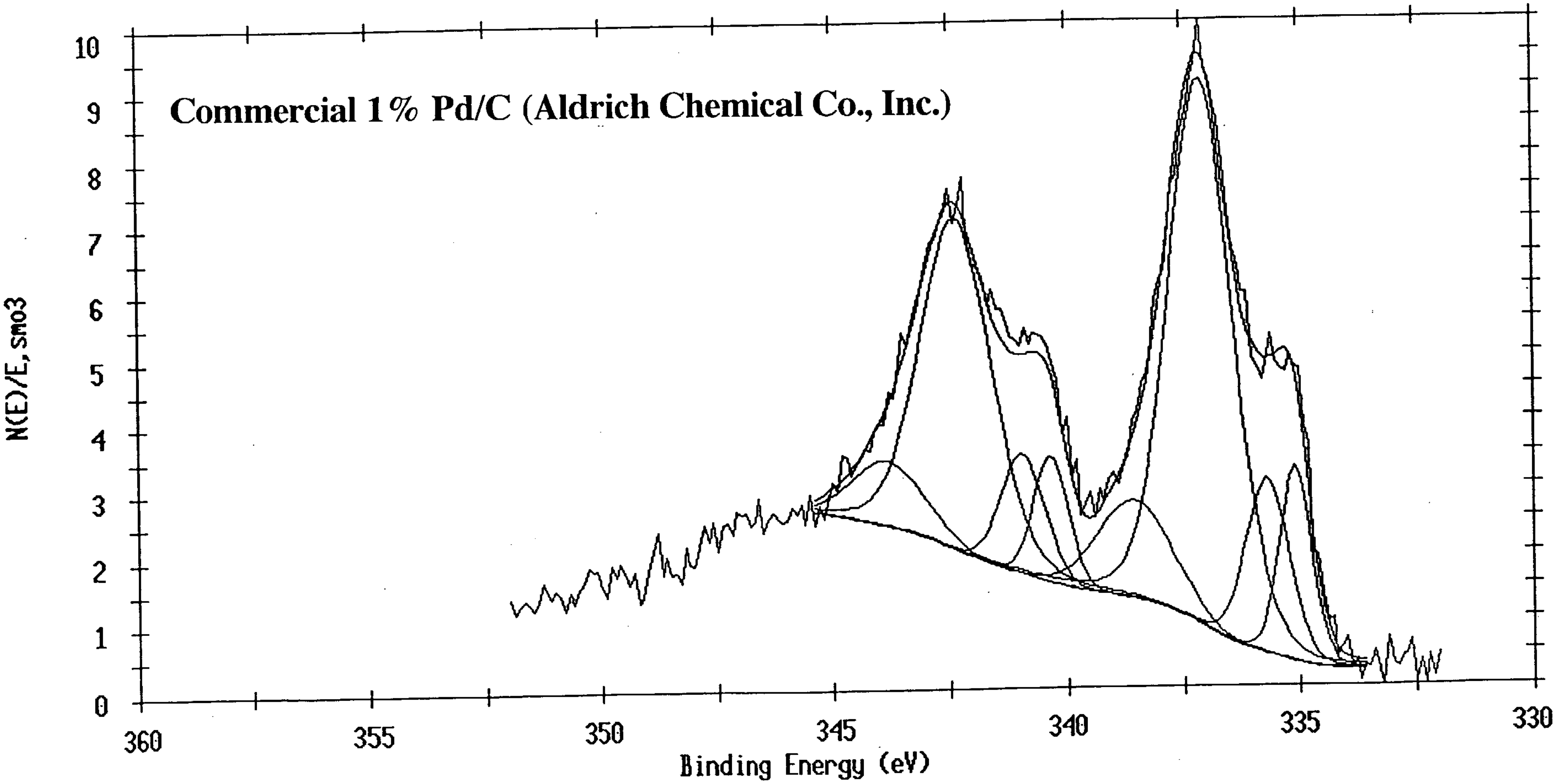


ESCA Survey 9 Apr 97 Area: 1 Angle: 65 degrees Acquisition Time: 4.38 min
File: 7568 No.1:1%Pd/C(Aldrich)
Scale Factor: 4.404 kc/s Offset: 0.057 kc/s Pass Energy: 187.850 eV Aperture: 4 Al 300 W



Commercial 1% Pd/C (Aldrich Chemical Co., Inc.)

ESCA CURVE FIT 9 Apr 97 Angle: 65 degrees Acquisition Time: 194.30 min
File: Curve_Fit No.1:1%Pd/C(Aldrich)
Scale Factor: 0.018 kc/s Offset: 0.759 kc/s Pass Energy: 23.500 eV Aperture: 4 Al 300 W


Commercial 1% Pd/C (Aldrich Chemical Co., Inc.)

ESCA Multiplex 9 Apr 97 Area: 1 Species: Pd1 Region: 3 Angle: 65 degrees Acquisition Time: 194.30 min
File: 7569 No.1:1%Pd/C(Aldrich)
Scale Factor: 0.017 kc/s Offset: 0.763 kc/s Pass Energy: 23.500 eV Aperture: 4 Al 300 W