

Intermolecular Non-Reductive Alkylation of Enamides via Radical–Polar Crossover

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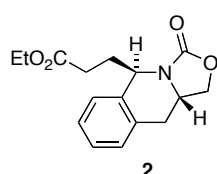
Supporting Information

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Materials and Methods. Reactions employed oven- or flame-dried glassware under argon unless otherwise noted. THF, diethyl ether, benzene and toluene were distilled from sodium/benzophenone ketyl under argon. CH₂Cl₂ was distilled from CaH₂ under argon or nitrogen. Alternatively, these solvents were purchased inhibitor-free and were sparged with argon and passed through columns of activated alumina prior to use (dropwise addition of blue benzophenone ketyl solution revealed the THF purified in this manner sustained the blue color more readily than the control sample purified by distillation). Argon was passed successively through columns of anhydrous CaSO₄ and R3-11 catalyst for removal of water and oxygen, respectively. All other materials were used as received from commercial sources unless otherwise noted. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates with UV indicator. Flash chromatography columns were packed with 230-400 mesh silica gel as a slurry in the hexane. Gradient flash chromatography was conducted by adsorption of product mixtures on silica gel, packing over a short pad of clean silica gel as a slurry in hexane, and eluting with a continuous gradient from hexane to the indicated solvent. Melting points were determined on a Meltemp apparatus and uncorrected. Nuclear magnetic resonance (NMR) data were obtained at operating frequencies of 600 or 300 MHz for ¹H and 75 MHz for ¹³C. Infrared spectra were recorded using a single beam FT-IR spectrophotometer by standard transmission methods or by use of an attenuated total reflectance (ATR) probe. Optical rotations were determined using a digital polarimeter operating at ambient temperature. Low resolution mass spectra were obtained using sample introduction by dip,

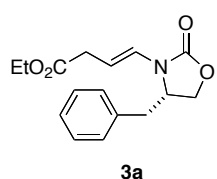
liquid chromatography or gas chromatography. Stereoisomer ratio analyses employed HPLC with Microsorb-MV Si 8um 100A or Chiralcel OD columns (2-propanol/hexane as mobile phase).



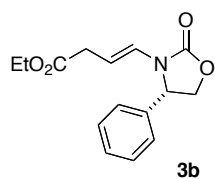
Ethyl 3-((5R,10aS)-3-oxo-3,5,10,10a-tetrahydro-1H-oxazolo[3,4-b]isoquinolin-5-yl)propanoate (2). To a solution of **1a**¹ (120 mg, 0.59 mmol) and ethyl iodoacetate (0.72 mL, 6.1 mmol) in CH₂Cl₂ (0.2 M) at –78° was added O₂ (4.2 mL) and a solution of Et₃B (1 M in hexane, 1.2 mL, 1.2 mmol) in CH₂Cl₂ (3 mL) by syringe pump concurrently over 5 h, using two syringes. The reaction mixture was allowed to warm slowly to room temperature. After 12 h, the reaction mixture was partitioned between CH₂Cl₂ and saturated sodium thiosulfate solution, and the organic phase was washed with brine and dried over NaSO₄. Concentration and flash chromatography (petroleum ether/EtOAc) afforded **2** (82 mg, 48% yield) as a colorless oil; [α]_D²³ –138 (c 0.56, CHCl₃); IR (film) 2974, 2929, 1752, 1724, 1413, 1270, 1176, 1147, 1062 cm^{–1}; ¹H NMR (600 MHz, CDCl₃) δ 7.25–7.09 (m, 4H), 4.91 (dd, *J* = 10.6, 3.5 Hz, 1H), 4.50 (dd, *J* = 8.5, 7.8 Hz, 1H), 4.17 (dd, *J* = 8.8, 2.8 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 1H), 4.08 (m, apparent qd, *J* = 8, 2.7 Hz, 1H), 2.90 (d, *J* = 7.84 Hz, 2H), 2.53 (ABX₂, Δ*v*_{AB} = 32.5 Hz, *J*_{AB} = 19.1 Hz, *J*_{AX} = 7.3, 7.3 Hz, *J*_{BX} = 7.3, 6.8 Hz, 2H), 2.27 (dddd, *J* = 14.5, 7.4, 7.4, 3.5 Hz, 1H), 2.06 (dddd, *J* = 14.3, 10.6, 7.5, 6.8 Hz, 1H), 1.28 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 173.2, 157.3, 135.4, 131.3, 129.4, 127.1, 127.0, 126.9, 68.3, 60.6, 52.5, 48.1, 33.7, 31.8, 31.1, 14.2; MS (EI) *m/z* (relative intensity) 289 (M⁺, 1%), 244 ([M–OEt]⁺, 5%), 188 (100%); Anal. Calcd. for C₁₆H₁₉NO₄: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.59; H, 6.70; N, 4.69.

General Procedure: Synthesis of Substituted *N*-Vinyloxazolidinone Derivatives

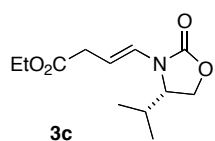
A solution of the *N*-vinyl oxazolidinone (**1a–1d**), α-iodoester or α-iodoacetonitrile (3 equiv), NEt₃ (0.5 equiv) in benzene (0.01 M) was deoxygenated by sparging with argon through a syringe needle. The mixture was heated to reflux, and solutions of AIBN (0.05 equiv) in benzene (0.05 M) and Bu₃SnH (2 equiv) in benzene (0.2 M) were added simultaneously via syringe pump over 10 h. Heating was continued for ca. 12 h. For reactions employing α-bromoesters, NBu₄I (1 equiv) was included in the initial reaction mixture. In certain cases, and as indicated below, *i*-Pr₂NEt was substituted for NEt₃.



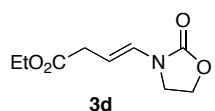
Ethyl (S,E)-4-(4-benzyl-2-oxooxazolidin-3-yl)but-3-enoate (3a). From **1a** (60 mg, 0.29 mmol), AIBN (24 mg, 0.15 mmol), Bu₃SnH (0.16 mL, 0.59 mmol), ethyl iodoacetate (0.10 mL, 0.845 mmol) and NEt₃ (0.02 mL, 0.14 mmol), following the General Procedure, was obtained **3a** (64 mg, 76% yield) as a colorless oil; [α]_D²⁵ +40.5 (c 0.65, CHCl₃); IR (film) 2970, 1752, 1735, 1670, 1417, 1241, 1172, 1100, 1032 cm^{–1}; ¹H NMR (300 MHz, CDCl₃) δ 7.39–7.18 (m, 5H) 6.70 (dd, *J* = 14.7, 1.1 Hz, 1H), 5.20 (ddd, *J* = 14.7, 7.3, 7.3 Hz, 1H), 4.34–4.15 (m, 5H) 3.25 (dd, *J* = 13.9, 2.9 Hz, 1H), 3.16 (m, apparent d, *J* = 7.3 Hz, 2H), 2.80 (dd, *J* = 13.9, 8.6 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 171.8, 154.9, 135.1, 129.3, 128.9, 127.3, 125.6, 103.3, 66.5, 60.9, 54.8, 35.9, 35.4, 14.2; MS (EI) *m/z* (relative intensity) 289 (M⁺, 15%), 243 (13%), 198 (100%); Anal. Calcd. for C₁₆H₁₉NO₄: C, 66.42; H, 6.62; N, 4.84. Found: C, 66.35; H, 6.77; N, 4.78.

**Ethyl (S,E)-4-(2-oxo-4-phenyloxazolidin-3-yl)but-3-enoate (3b).**

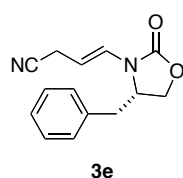
From **1b**¹ (100 mg, 0.53 mmol), AIBN (42 mg, 0.26 mmol), Bu₃SnH (0.29 mL, 1.08 mmol), ethyl iodoacetate (0.19 mL, 1.6 mmol) and NEt₃ (0.08 mL, 0.58 mmol), following the General Procedure, was obtained **3b** (100 mg, 69% yield) as a colorless oil; $[\alpha]_D^{25} +99.6$ (*c* 0.48, CHCl₃); IR (film) 2981, 2919, 1761, 1732, 1675, 1405, 1221, 1192, 1159, 1103, 1035 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.43-7.24 (m, 5 H), 6.70 (ddd, *J* = 14.6, 1.1, 1.1 Hz, 1H), 5.05 (dd, *J* = 9.0, 5.2 Hz, 1H), 4.75-4.65 (m, 2H), 4.12 (dd, *J* = 8.7, 5.3 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 2.91 (dd, *J* = 7.4, 1.1 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 171.5, 155.6, 137.9, 129.4, 128.8, 125.9, 125.6, 104.7, 70.6, 60.7, 58.5, 35.5, 14.1; MS (EI) *m/z* (relative intensity) 275 (M⁺, 7%), 229 (12%), 202 (67%), 91 (100%); Anal. Calcd. for C₁₅H₁₇NO₄: C, 65.44; H, 6.22; N, 5.09. Found: C, 65.40; H, 6.52; N, 4.86.

**Ethyl (S,E)-4-(4-isopropyl-2-oxooxazolidin-3-yl)but-3-enoate (3c).**

From **1c**¹ (45 mg, 0.29 mmol), AIBN (24 mg, 0.15 mmol), Bu₃SnH (0.16 mL, 0.59 mmol), ethyl iodoacetate (0.10 mL, 0.845 mmol) and *i*-Pr₂NEt (0.05 mL, 0.29 mmol), following the General Procedure, was obtained **3c** (50 mg, 72% yield) as a colorless oil; $[\alpha]_D^{22} +28.0$ (*c* 1.1, CHCl₃); IR (film) 2964, 1754, 1726, 1673, 1413, 1159, 1104, 1051, 1027 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.63 (d, *J* = 15.0 Hz, 1H), 5.04 (ddd, *J* = 14.7, 7.3, 7.3 Hz, 1H), 4.31-4.20 (m, 2H), 4.15 (q, *J* = 7.14 Hz, 2H), 4.05 (ddd, *J* = 8.4, 3.4, 3.4 Hz, 1H), 3.12-3.04 (m, 2H), 2.44 (m, apparent septet of doublets, *J* = 6.9, 3.4 Hz, 1H), 1.26 (t, *J* = 7.14 Hz, 3H), 0.92 (d, *J* = 7.08 Hz, 3H), 0.83 (d, *J* = 6.82 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 171.9, 155.5, 125.6, 103.2, 62.9, 60.8, 58.2, 35.4, 25.9, 17.8, 14.1, 13.8; MS (EI) *m/z* (relative intensity) 241.1 (M⁺, 25%), 198 (32%), 195 (12%), 168 (100%); HRMS, calculated for C₁₂H₁₉NO₄: 241.1314, found: 241.1311.

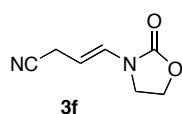
**Ethyl (E)-4-(2-oxooxazolidin-3-yl)but-3-enoate (3d).**

From **1d**¹ (59 mg, 0.52 mmol), AIBN (48 mg, 0.29 mmol), Bu₃SnH (0.28 mL, 1.04 mmol), ethyl iodoacetate (0.19 mL, 1.6 mmol) and NEt₃ (0.04 mL, 0.29 mmol), following the General Procedure, was obtained **3d** (70 mg, 68% yield) as a colorless oil; IR (film) 2984, 2925, 1755, 1726, 1674, 1481, 1423, 1245, 1200, 1107, 1067, 1031 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.76 (d, *J* = 14.4 Hz, 1H), 4.91 (ddd, *J* = 14.4, 7.3, 7.3 Hz, 1H), 4.44 (dd, *J* = 9.4, 7.8 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.73 (dd, *J* = 8.5, 7.7 Hz, 2H), 3.09 (d, *J* = 7.3 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (300 MHz, CDCl₃) δ 171.8, 155.2, 126.7, 102.4, 62.2, 60.8, 42.4, 35.1, 14.1; MS (EI) *m/z* (relative intensity) 199 (M⁺, 15%), 153 (7%), 126 (100%); Anal. Calcd. for C₉H₁₃NO₄: C, 54.26; H, 6.58; N, 7.03. Found: C, 53.79; H, 6.80; N, 6.64.

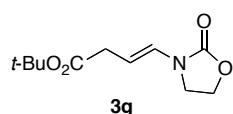
**(S,E)-4-(4-Benzyl-2-oxooxazolidin-3-yl)but-3-enenitrile (3e).**

From **1a** (100 mg, 0.49 mmol), AIBN (40 mg, 0.24 mmol), Bu₃SnH (0.26 mL, 0.97 mmol), iodoacetone nitrile (0.1 mL, 1.4 mmol) and NEt₃ (0.03 mL, 0.22 mmol), following the General Procedure B, was obtained **3e** (80 mg, 67% yield) as a colorless solid; mp 80–82 °C, $[\alpha]_D^{25} +6.0$ (*c* 1.5, CHCl₃); IR (film) 2920, 2252, 1755, 1674, 1413, 1238, 1100 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.16 (m, 5H), 6.85 (ddd, *J* = 14.5, 1.4, 1.4 Hz, 1H), 5.00 (ddd, *J* = 14.5, 6.5, 6.5 Hz, 1H), 4.29-4.20 (m, 3H), 3.23-3.17 (m, 3H), 2.84-2.76 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 154.8, 134.7, 129.2, 129.0, 127.5, 127.5, 117.5, 98.8, 66.7, 54.9, 36.4, 18.5; MS (EI) *m/z*

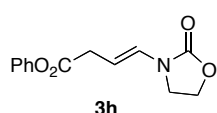
(relative intensity) 242 (M^+ , 17%), 171 (9%), 151 (100%); Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.14; H, 5.83; N, 11.49.



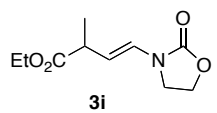
(E)-4-(2-Oxooxazolidin-3-yl)but-3-enitrile (3f). From **1d** (50 mg, 0.44 mmol), AIBN (36 mg, 0.22 mmol), Bu_3SnH (0.24 mL, 0.89 mmol), iodoacetonitrile (0.10 mL, 1.4 mmol) and NEt_3 (0.03 mL, 0.22 mmol), following the General Procedure, was obtained **3f** (44 mg, 66% yield) as a colorless solid; mp 90–93 °C; IR (film) 2925, 2250, 1754, 1478, 1424, 1228, 1102, 1041, 958 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 6.94 (dt, $J = 14.3, 1.4$ Hz, 1H), 4.73 (dt, $J = 14.2, 6.6$ Hz, 1H), 4.51–4.45 (m, 2H), 3.72 (dd, $J = 8.9, 7.2$ Hz, 2H), 3.16 (dd, $J = 6.6, 1.4$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.0, 128.5, 117.5, 98.0, 62.2, 42.3, 18.2; MS (EI) m/z (relative intensity) 152 (M^+ , 86%), 107 (71%), 93 (100%); HRMS, calculated for $C_7H_8N_2O_2$: 152.0586, found: 152.0584.



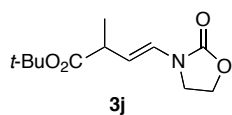
tert-Butyl (E)-4-(2-oxooxazolidin-3-yl)but-3-enoate (3g). From **1d** (40 mg, 0.35 mmol), AIBN (29 mg, 0.18 mmol), Bu_3SnH (0.19 mL, 0.71 mmol), *tert*-butyl 2-bromoacetate (0.15 mL, 1.0 mmol), NBu_4I (0.13 g, 0.35 mmol) and NEt_3 (0.03 mL, 0.22 mmol), following the General Procedure, was obtained **3g** (51 mg, 63% yield) as a colorless oil; IR (film) 2978, 2930, 1764, 1727, 1674, 1481, 1422, 1242, 1149 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 6.73 (d, $J = 14.4$ Hz, 1H), 4.90 (dt, $J = 14.5, 7.3$ Hz, 1H), 4.46–4.41 (m, 2H), 3.73 (dd, $J = 8.9, 7.2$ Hz, 2H), 3.01 (dd, $J = 7.3, 1.3$ Hz, 2H), 1.45 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 155.3, 126.4, 103.0, 80.9, 62.2, 42.4, 36.2, 28.0; MS (EI) m/z (relative intensity) 227 (M^+ , 6%), 126 (100%), 57 (88%); Anal. Calcd. for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54; N, 6.16. Found: C, 58.42; H, 7.72; N, 5.98.



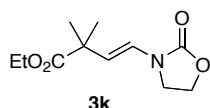
Phenyl (E)-4-(2-oxooxazolidin-3-yl)but-3-enoate (3h). From **1d** (40 mg, 0.35 mmol), AIBN (29 mg, 0.18 mmol), Bu_3SnH (0.19 mL, 0.71 mmol), phenyl 2-bromoacetate (226 mg, 1.05 mmol), NBu_4I (129 mg, 0.35 mmol) and NEt_3 (0.02 mL, 0.14 mmol), following the General Procedure, was obtained **3h** (56 mg, 65% yield) as a colorless oil; IR (film) 1749, 1673, 1481, 1420, 1193, 1133 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 7.41–7.07 (m, 5H), 6.87 (d, $J = 14.4$ Hz, 1H), 4.99 (dt, $J = 14.4, 7.3$ Hz, 1H), 4.49–4.43 (m, 2H), 3.76 (dd, $J = 8.9, 7.2$ Hz, 2H), 3.36 (dd, $J = 7.3, 1.3$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.3, 155.3, 150.6, 129.4, 127.4, 125.9, 121.4, 101.6, 62.2, 42.4, 35.2; MS (EI) m/z (relative intensity) 247 (M^+ , 1%), 154 ($[M-OPh]^+$, 61%), 126 (100%); HRMS, calculated for $C_{13}H_{13}NO_4$: 247.0845, found: 247.0841.



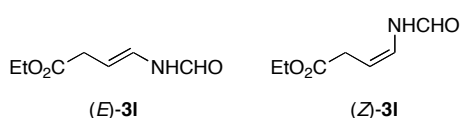
Ethyl (E)-2-methyl-4-(2-oxooxazolidin-3-yl)but-3-enoate (3i). From **1d** (60 mg, 0.52 mmol), AIBN (43 mg, 0.26 mmol), Bu_3SnH (0.28 mL, 1.04 mmol), ethyl 2-bromopropionate (0.20 mL, 1.54 mmol), NBu_4I (192 mg, 0.52 mmol) and NEt_3 (0.04 mL, 0.29 mmol), following the General Procedure, was obtained **3i** (64 mg, 58% yield) as a colorless oil; IR (film) 2979, 2930, 1758, 1731, 1670, 1481, 1416, 1225, 1081, 1034 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 6.76 (d, $J = 14.4$ Hz, 1H), 4.90 (dd, $J = 14.4, 8.4$ Hz, 1H), 4.47–4.41 (m, 2H), 4.13 (m, apparent q, $J = 7.1$ Hz, 2H), 3.73–3.68 (m, 2H), 3.16 (m, apparent quintet, $J = 8$ Hz, 1H), 1.30 (d, $J = 7.1$ Hz, 3H), 1.26 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.8, 155.4, 125.2, 109.8, 62.2, 60.8, 42.4, 40.6, 18.1, 14.2; MS (EI) m/z (relative intensity) 213 (M^+ , 9%), 140 ($[M-CO_2Et]^+$, 100%); HRMS, calculated for $C_{10}H_{15}NO_4$: 213.1001, found: 213.1000.

**tert-Butyl (E)-2-methyl-4-(2-oxooxazolidin-3-yl)but-3-enoate (3j).**

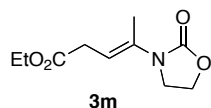
From **1d** (60 mg, 0.52 mmol), AIBN (43 mg, 0.26 mmol), Bu₃SnH (0.28 mL, 1.04 mmol), *tert*-butyl 2-bromopropanoate (0.26 mL, 1.56 mmol), NBu₄I (192 mg, 0.52 mmol) and NEt₃ (0.04 mL, 0.29 mmol), following the General Procedure, was obtained **3j** (75 mg, 60% yield) as a colorless oil; IR (film) 2977, 2929, 1758, 1726, 1670, 1415, 1228, 1150, 1081, 1032 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.74 (d, *J* = 14.3 Hz, 1H), 4.90 (dd, *J* = 14.4, 8.3 Hz, 1H), 4.44 (dd, *J* = 8.9, 7.3 Hz, 2H), 3.71 (dd, *J* = 9.0, 7.2 Hz, 2H), 3.11–3.01(m, apparent quintet, *J* = 8 Hz, 1H), 1.44 (s, 9H), 1.26 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 174.2, 155.4, 124.9, 110.3, 80.7, 62.2, 42.5, 41.5, 28.0, 18.3; MS (EI) *m/z* (relative intensity) 241.1 (M⁺, 20%), 140 ([M–CO₂*t*-Bu]⁺, 100%); HRMS, calculated for C₁₂H₁₉NO₄: 241.1314, found: 241.1315.

**Ethyl (E)-2,2-dimethyl-4-(2-oxooxazolidin-3-yl)but-3-enoate (3k).**

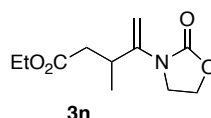
From **1d** (60 mg, 0.52 mmol), AIBN (43 mg, 0.26 mmol), Bu₃SnH (0.28 mL, 1.04 mmol), ethyl 2-bromo-2-methylpropionate (0.23 mL, 1.6 mmol), NBu₄I (192 mg, 0.52 mmol) and NEt₃ (0.04 mL, 0.29 mmol), following the General Procedure, was obtained **3k** (26 mg, 22% yield) as a colorless oil; IR (film) 2978, 2925, 1754, 1726, 1667, 1481, 1415, 1223, 1144, 1084, 1031 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.74 (d, *J* = 14.7 Hz, 1H), 5.05 (d, *J* = 14.7 Hz, 1H), 4.44 (dd, *J* = 8.9, 7.2 Hz, 2H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.71 (dd, *J* = 9.0, 7.1 Hz, 2H), 1.35 (s, 6H), 1.25 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 176.4, 155.5, 123.4, 115.8, 62.1, 60.9, 42.7, 42.5, 25.5, 14.1; MS (EI) *m/z* (relative intensity) 227 (M⁺, 4%), 154 ([M–CO₂Et]⁺, 100%); Anal. Calcd. for C₁₁H₁₇NO₄: C, 58.14; H, 7.54; N, 6.16. Found: C, 58.21; H, 7.83; N, 5.78.

**Ethyl 4-formamidobut-3-enoate (3l).**

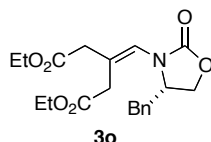
From *N*-vinylformamide (**1e**, 0.04 mL, 0.57 mmol), AIBN (46 mg, 0.28 mmol), Bu₃SnH (0.31 mL, 1.15 mmol), ethyl iodoacetate (0.20 mL, 1.7 mmol), *i*-Pr₂NEt (0.10 mL, 0.57 mmol), following the General Procedure, was obtained **3l** (73 mg, *E/Z* = 1:1.4, 82% yield). The *E* and *Z* isomers were separated by rotary thin-layer chromatography to afford analytical samples, each of which exhibited two rotamers in its NMR spectra. (E)-**3l**: Colorless oil; IR (film) 1731, 1667, 1515, 1274, 1177, 1026 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, mixture of rotamers, 2.7:1) major rotamer δ 8.26 (d, *J* = 11.4 Hz, 1H), 8.10 (s, 1H), 6.93–6.84 (dd, *J* = 14.3, 11.3 Hz, 1H), 5.35 (dt, *J* = 14.3, 7.4 Hz, 1H), 4.20–4.09 (m, 2H), 3.09–3.02 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); minor rotamer δ 8.28 (d, *J* = 11.1 Hz, 1H), 8.19 (s, 1H), 6.44 (dd, *J* = 13.9, 11.1 Hz, 1H), 5.22 (ddd, *J* = 14.5, 7.2, 6.6 Hz, 1H), 4.20–4.09 (m, 2H), 3.12–3.09 (m, 2H), 1.29–1.22 (m, 3H), some resonances were not resolved from the major rotamer; ¹³C NMR (75 MHz, CDCl₃) major rotamer δ 171.8, 158.5, 123.3, 103.1, 61.4, 32.0, 14.1; minor rotamer δ 171.0, 163.0, 125.0, 102.2, 61.2, 31.4, 14.1; MS (EI) *m/z* (relative intensity) 157 (M⁺, 18%), 84 (100%); HRMS calculated for C₇H₁₁NO₃: 157.0739, found: 157.0743. (Z)-**3l**: Colorless oil; IR (film) 1730, 1665, 1510, 1397, 1260, 1179, 1031 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, mixture of rotamers, 2.2:1) major rotamer δ 8.22 (s, 1H), 8.10 (br s, 1H), 6.94 (dd, *J* = 9.9, 9.6 Hz, 1H), 4.97 (ddd, apparent q, *J* = 8.1 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.07–3.03 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 3H); minor rotamer δ 8.30 (d, *J* = 11.0 Hz, 1H), 8.10 (br s, 1H), 6.46 (dd, *J* = 11.1, 8.7 Hz, 1H), 4.91 (ddd, apparent q, *J* = 8.1 Hz, 1H), some resonances were not resolved from the major rotamer; ¹³C NMR (75 MHz, C₆D₆) major rotamer δ 171.4, 157.5, 123.9, 105.5, 60.5, 35.0, 14.1; minor rotamer δ 171.1, 161.9, 126.4, 103.5, 60.5, 35.0, 14.2; MS (EI) *m/z* (relative intensity) 157 (M⁺, 14%), 84 (100%); HRMS, calculated for M⁺: 157.0739, found: 158.0741.



Ethyl (E)-4-(2-oxooxazolidin-3-yl)pent-3-enoate (3m). From **1f**² (64 mg, 0.50 mmol), AIBN (48 mg, 0.29 mmol), Bu₃SnH (0.28 mL, 1.04 mmol), ethyl iodoacetate (0.19 mL, 1.6 mmol) and NEt₃ (0.04 mL, 0.29 mmol), following the General Procedure, was obtained **3m** (76 mg, 71% yield) as a colorless oil; IR (film) 2982, 2923, 1764, 1725, 1659, 1481, 1408, 1176, 1051 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.10 (m, apparent t, *J* = 7.2 Hz, 1H), 4.35 (dd, *J* = 8.7, 7.1 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.81 (dd, *J* = 8.7, 7.2 Hz, 2H), 3.11 (d, *J* = 7.2 Hz, 2H), 2.13 (d, *J* = 0.9 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 171.7, 155.1, 135.9, 105.9, 61.3, 60.8, 45.8, 32.6, 14.3, 14.2; MS (EI) *m/z* (relative intensity) 213 (M⁺, 10%), 167 (18%), 140 (100%); HRMS, calculated for C₁₀H₁₅NO₄: 213.1001, found: 213.1002.



Ethyl 3-methyl-4-(2-oxooxazolidin-3-yl)pent-4-enoate (3n). From **1g**² (60 mg, 0.43 mmol), AIBN (35 mg, 0.21 mmol), Bu₃SnH (0.23 mL, 0.86 mmol), ethyl iodoacetate (0.16 mL, 1.4 mmol) and NEt₃ (0.02 mL, 0.14 mmol), following the General Procedure, was obtained a mixture of alkene isomers³ (40 mg, 34% yield), from which **3n** was separated as a colorless oil; IR (film) 2974, 2922, 1753, 1728, 1401, 1275, 1179, 1052 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.65 (s, 2H), 4.36 (t, *J* = 8.0 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.89-3.71 (m, 2H), 3.60 (m, apparent sextet, *J* = 7.1 Hz, 1H), 2.56 (dd, *J* = 15.3, 6.3 Hz, 1H), 2.36 (dd, *J* = 15.3, 7.8 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.18 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 172.1, 155.0, 148.6, 98.8, 61.3, 60.4, 46.3, 40.5, 31.1, 19.3, 14.2; MS (EI) *m/z* (relative intensity) 227 (M⁺, 12%), 182 ([M-OEt]⁺, 65%), 137 (100%); HRMS, calculated for C₁₁H₁₇NO₄: 227.1158, found: 227.1156.



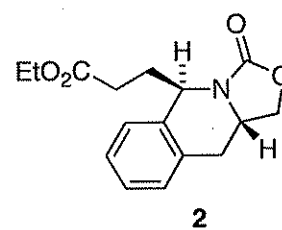
Diethyl (S)-3-((4-benzyl-2-oxooxazolidin-3-yl)methylene)-pentanedioate (3o). From **3a** (53 mg, 0.18 mmol), AIBN (15 mg, 0.091 mmol), Bu₃SnH (0.10 mL, 0.37 mmol), ethyl iodoacetate (0.060 mL, 0.51 mmol) and NEt₃ (0.01 mL, 0.07 mmol), following the General Procedure, was obtained **3o** (20 mg, 30% yield) as a colorless oil; [α]_D²⁵ -48 (c 0.7, CHCl₃); IR (film) 2980, 2922, 1754, 1737, 1726, 1407, 1368, 1257, 1174, 1092, 1029 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.35-7.15 (m, 5H), 6.06 (s, 1H), 4.3-4.10 (m, 7H), 3.33 (s, 2H), 3.28 (s, 2H), 3.16 (dd, *J* = 13.6, 3.4 Hz, 1H), 2.68 (dd, *J* = 13.7, 8.9 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 170.7, 170.2, 156.2, 135.1, 129.3, 128.9, 127.2, 124.3, 124.1, 66.5, 61.0, 60.9, 58.5, 40.1, 38.1, 36.0, 14.1 (2C); MS (EI) *m/z* (relative intensity) 375 (M⁺, 4%), 329 (41%), 91 (100%); HRMS, calculated for C₂₀H₂₅NO₆: 375.1682, found: 375.1680.

Citations and Notes

¹ (a) Gaulon, C.; Gizecki, P.; Dhal, R.; Dujardin, G. *Synlett* **2002**, 952-956. (b) Gaulon, C.; Dhal, R.; Dujardin, G. *Synthesis* **2003**, 2269-2272.

² Pan, X.; Cai, Q.; Ma, D. *Org. Lett.* **2004**, 6, 1809-1812.

³ Other alkene isomer(s) were not be obtained in pure form suitable for full characterization. One alkene isomer exhibited the following data in spectra obtained from mixtures: ¹H NMR (300 MHz, CDCl₃) δ 4.39 (dd, *J* = 9.2, 7.8 Hz, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.68 (dd, *J* = 9.2, 8.1 Hz, 2H), 3.11 (s, 2H), 1.86 (s, 3H), 1.76 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H).



(¹H NMR, 300 MHz)



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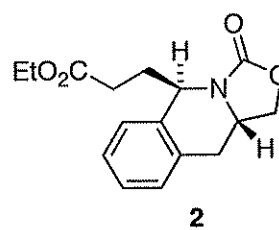
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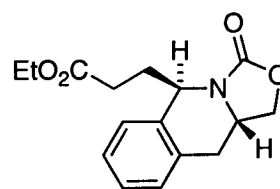
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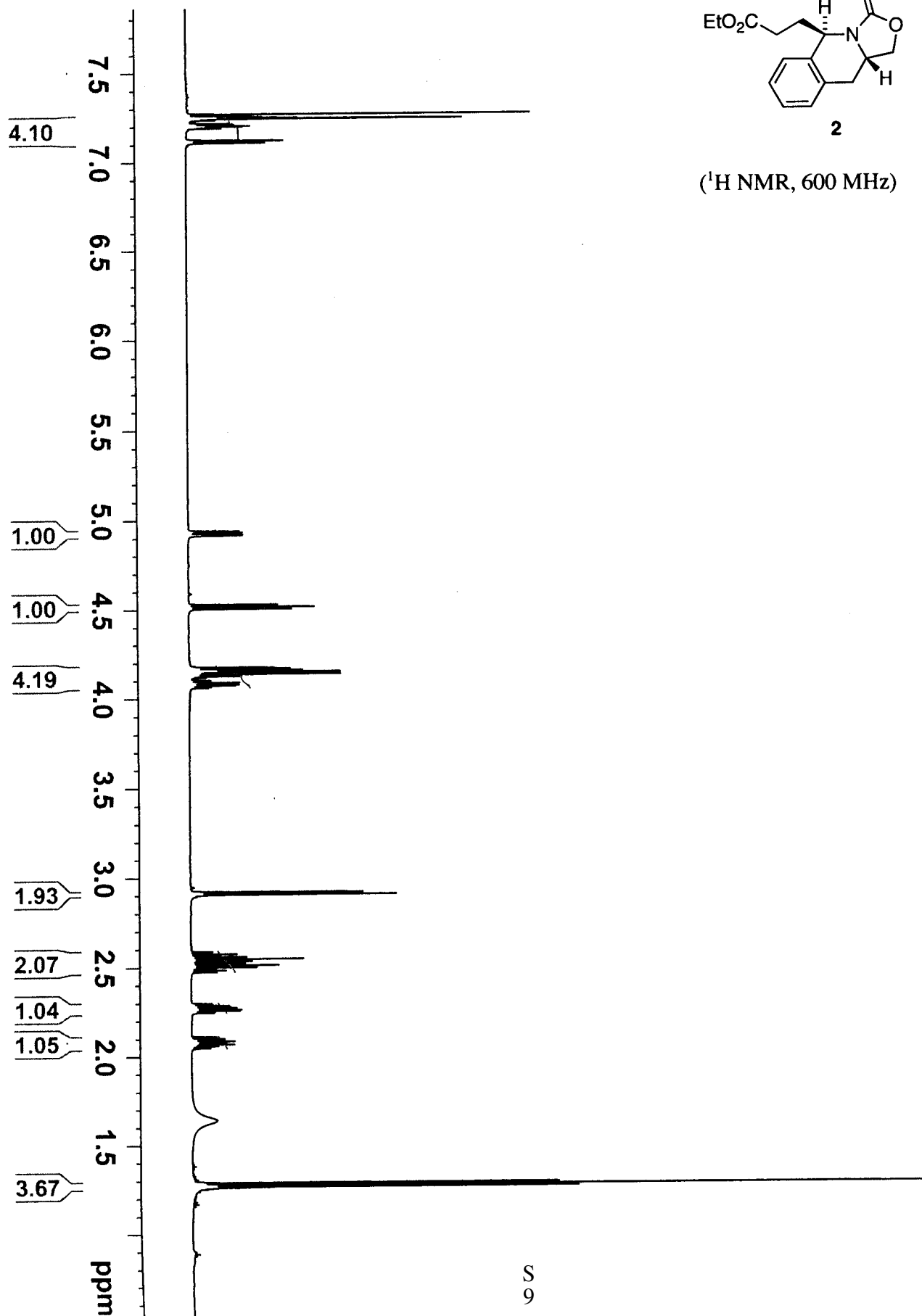
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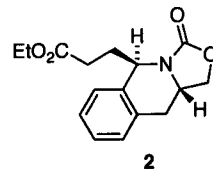




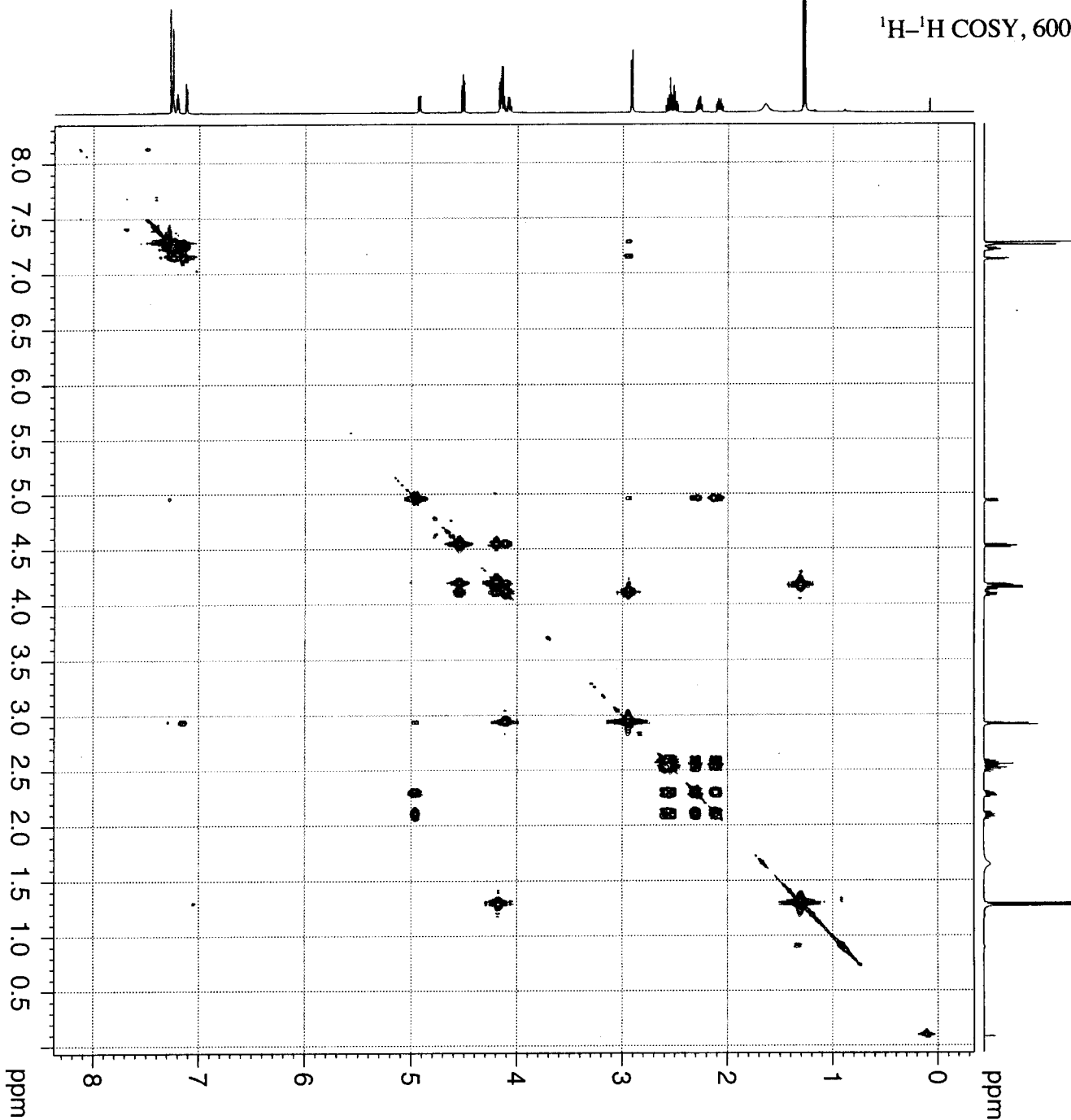
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(¹H NMR, 600 MHz)

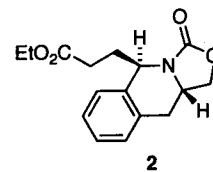




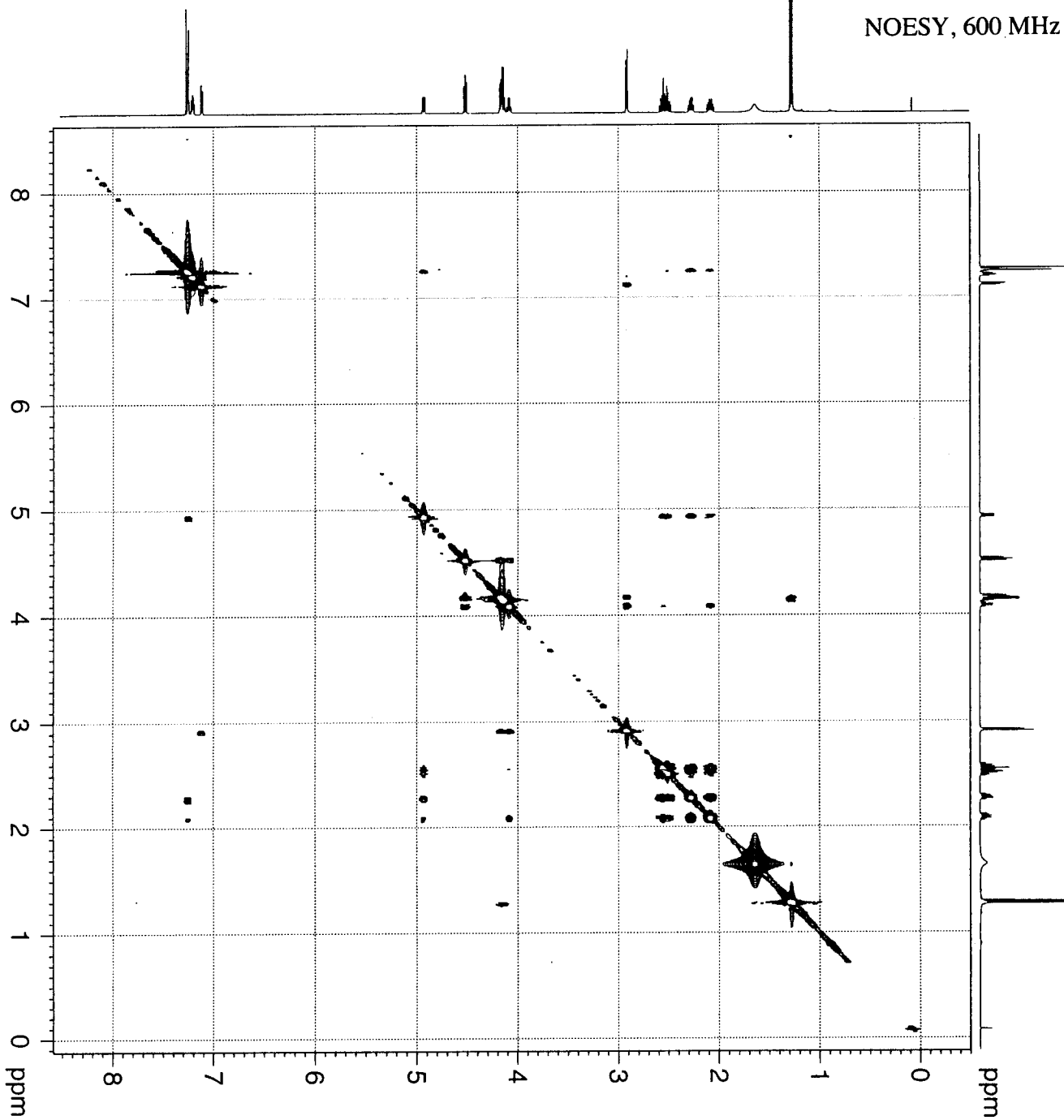
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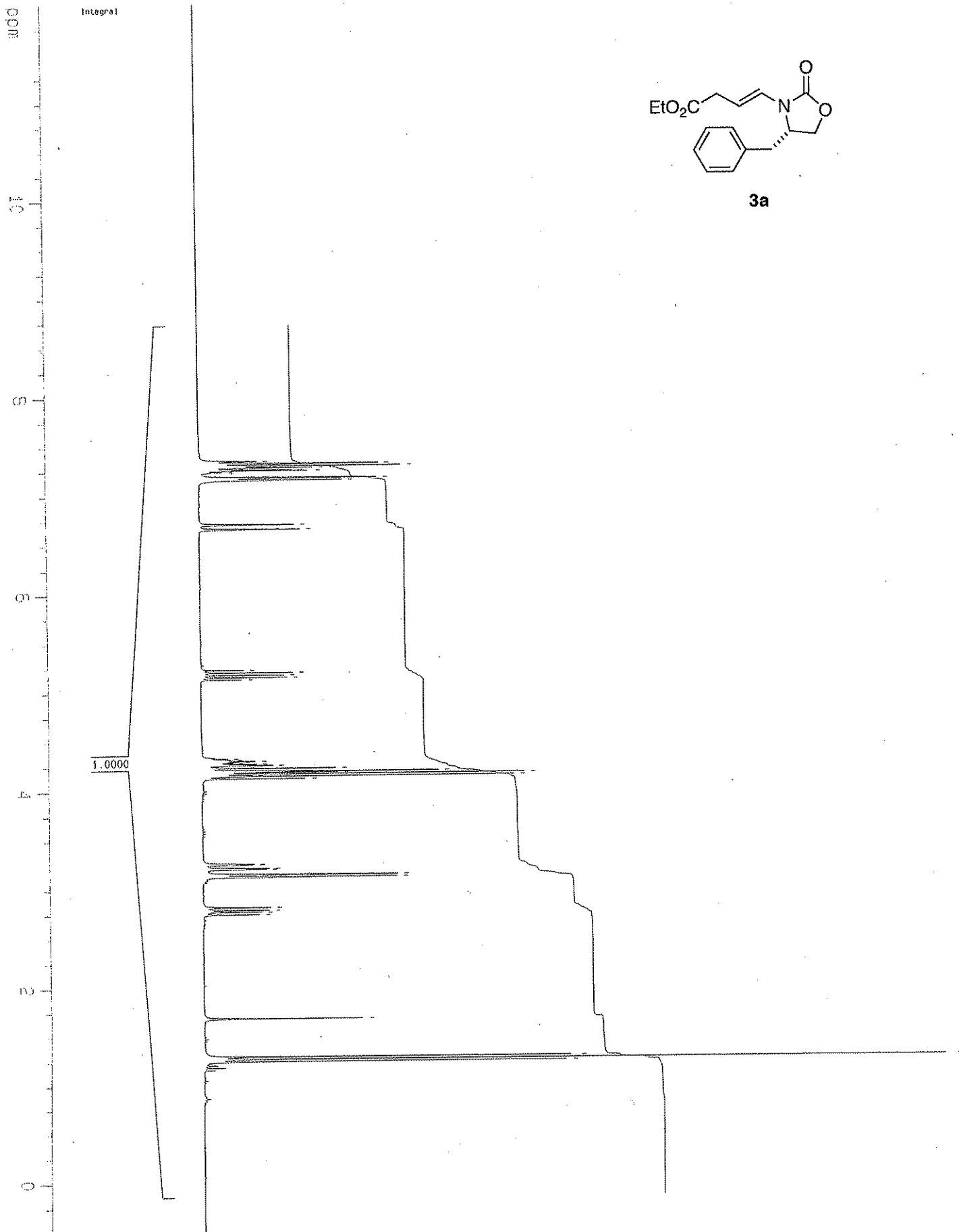
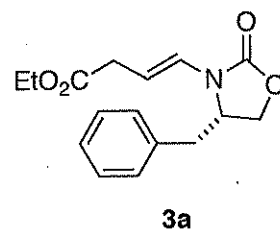
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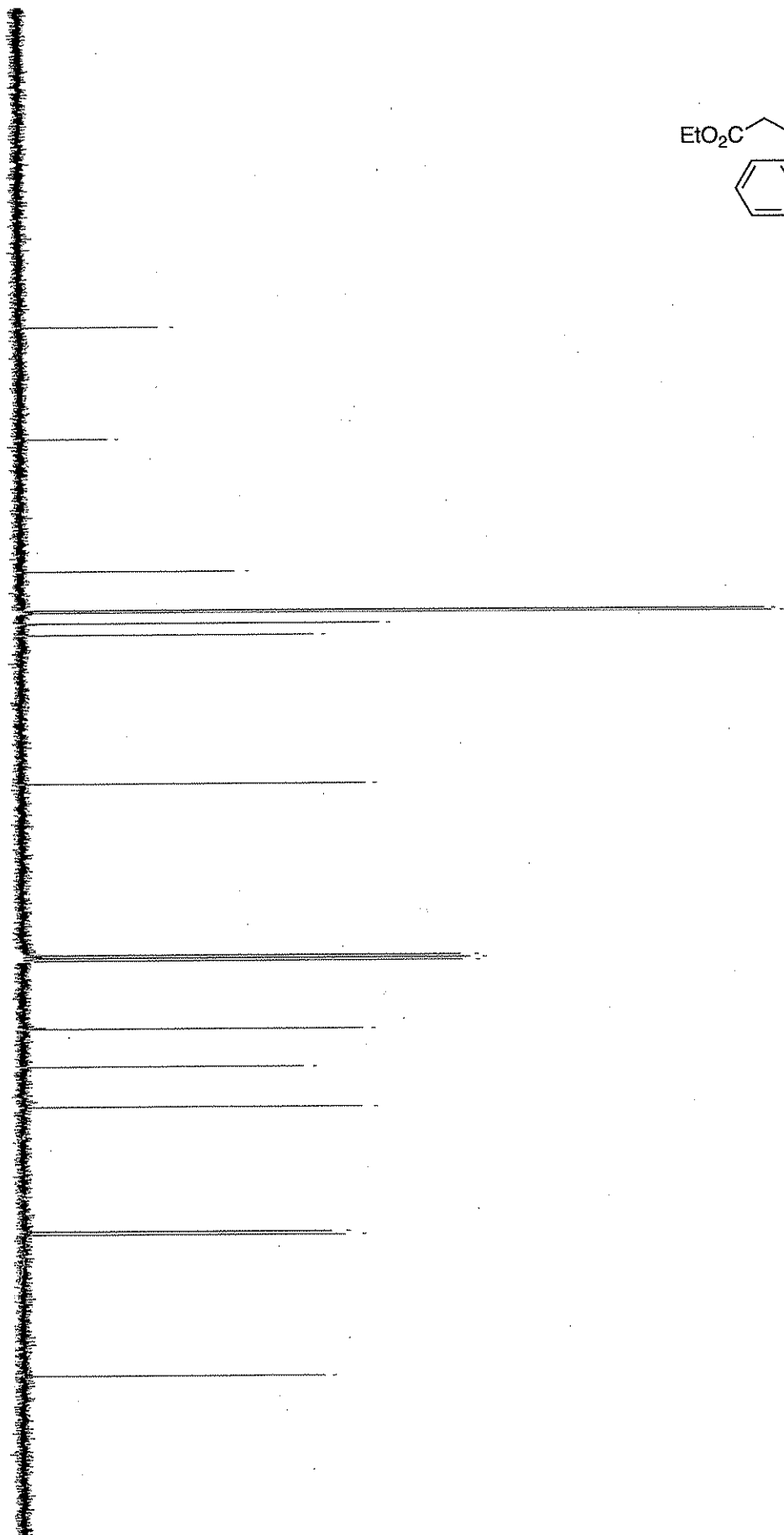
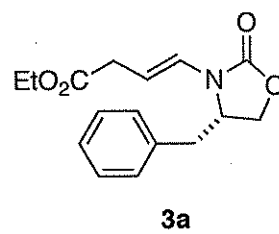
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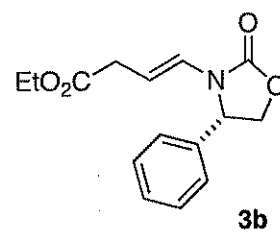


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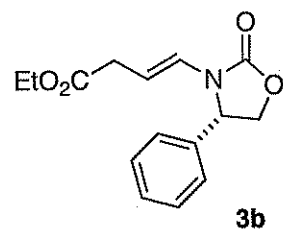
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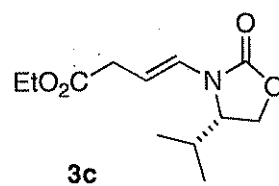
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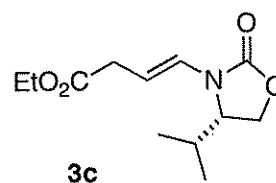
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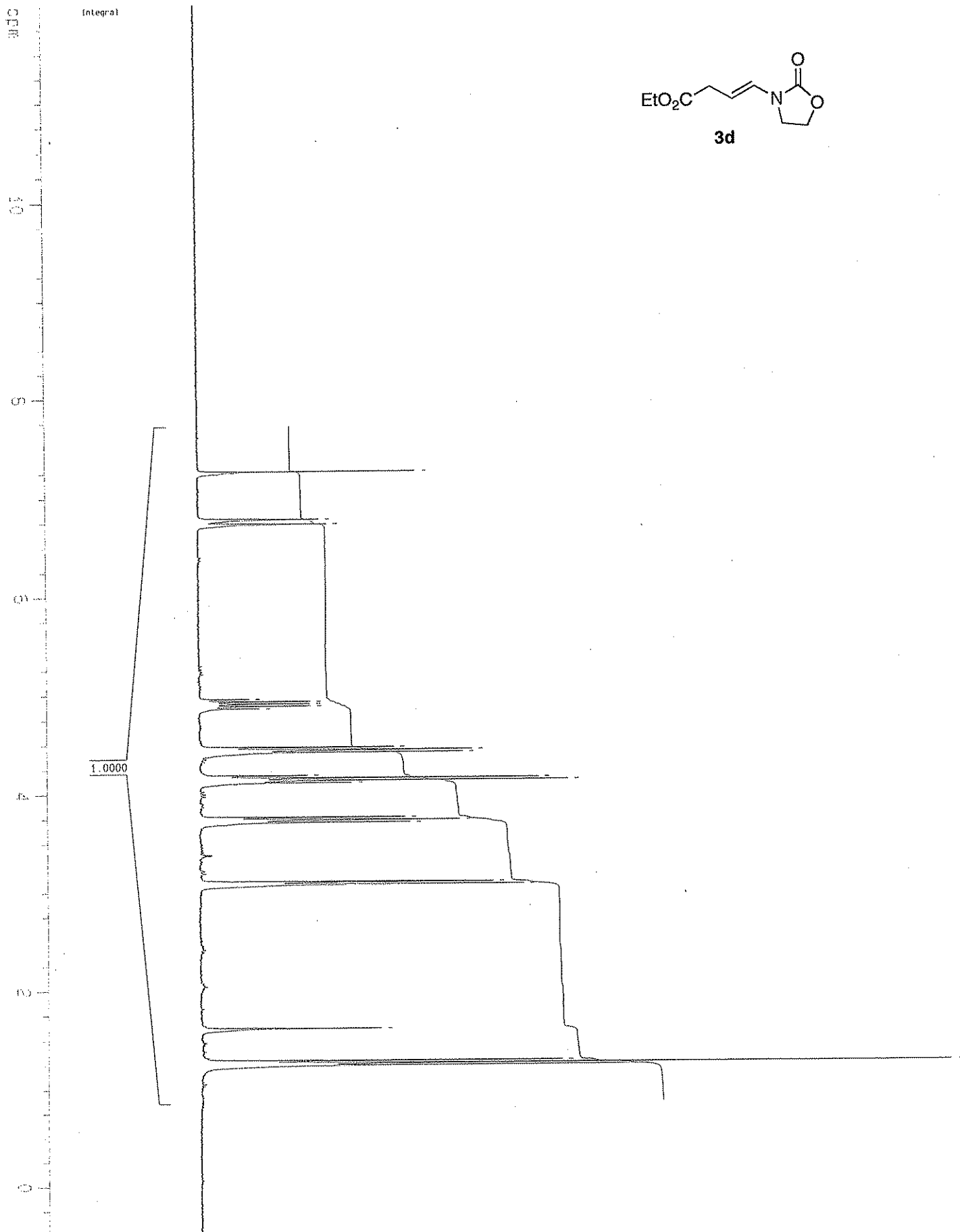
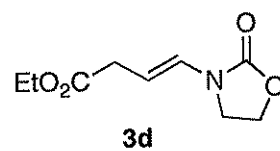
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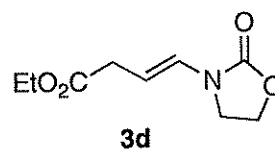
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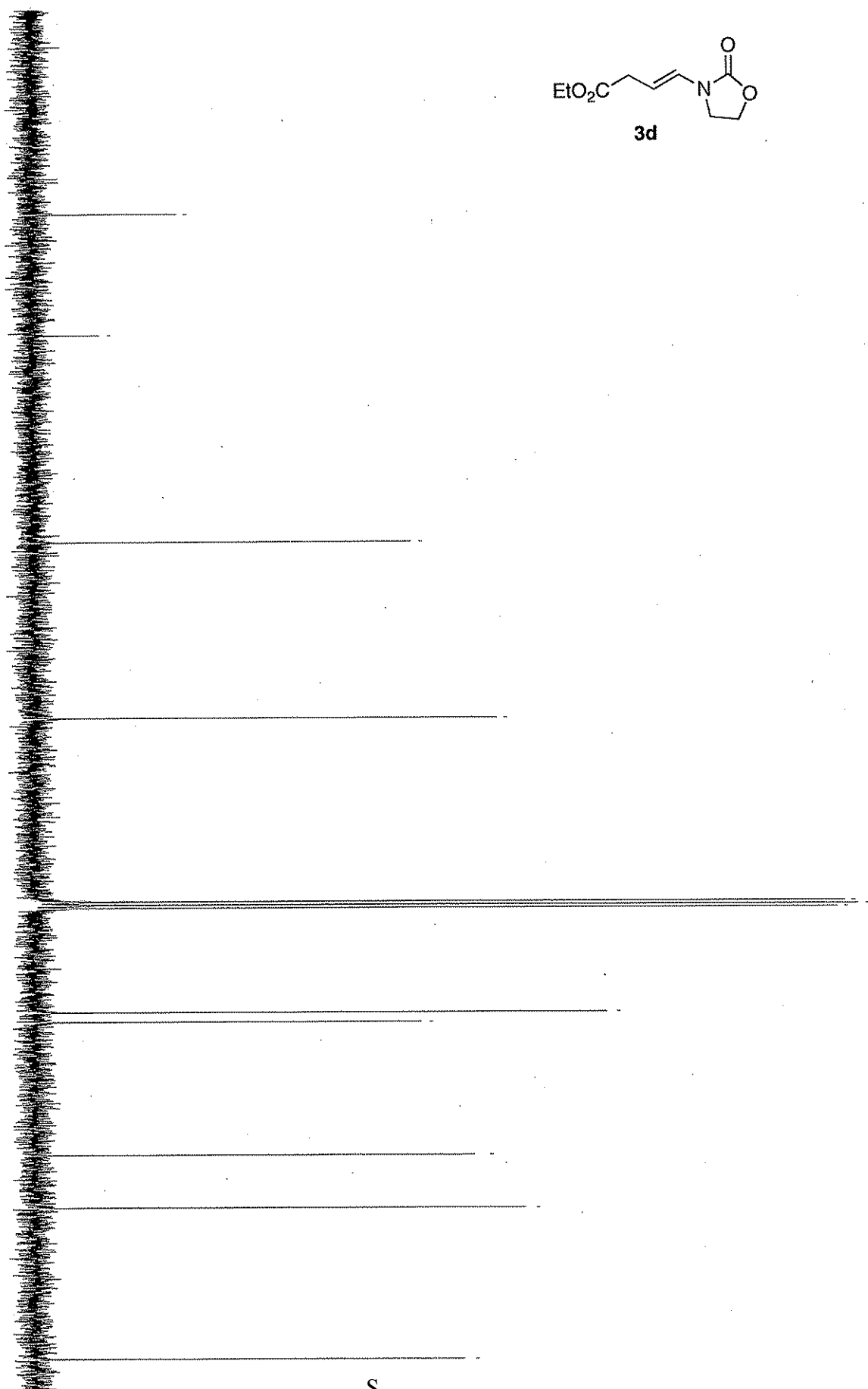
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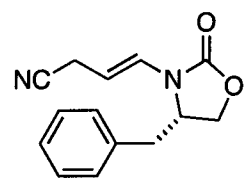
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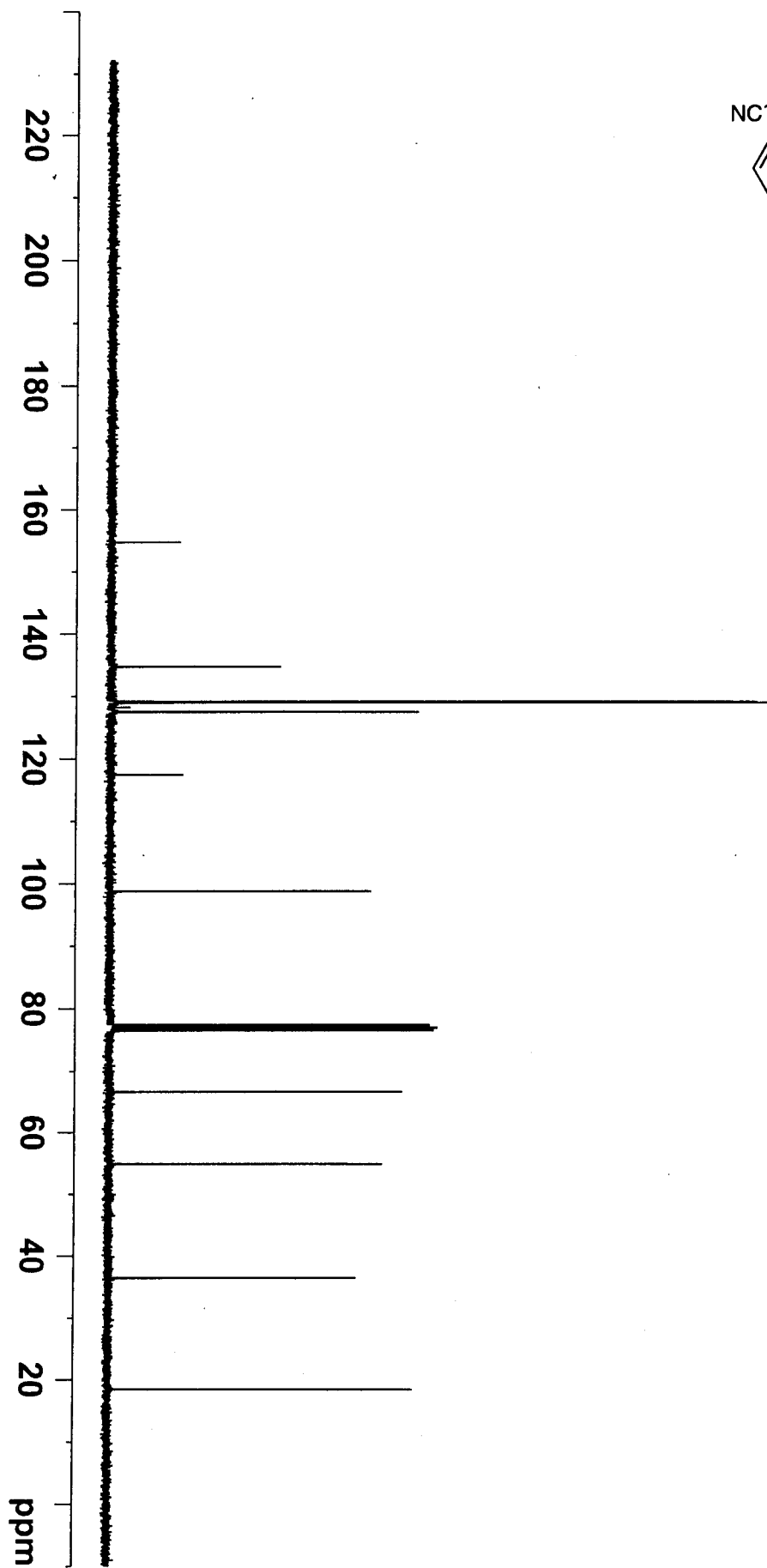
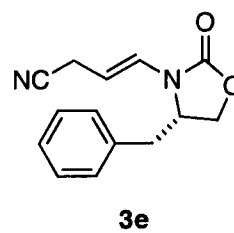
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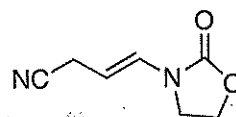
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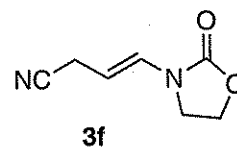
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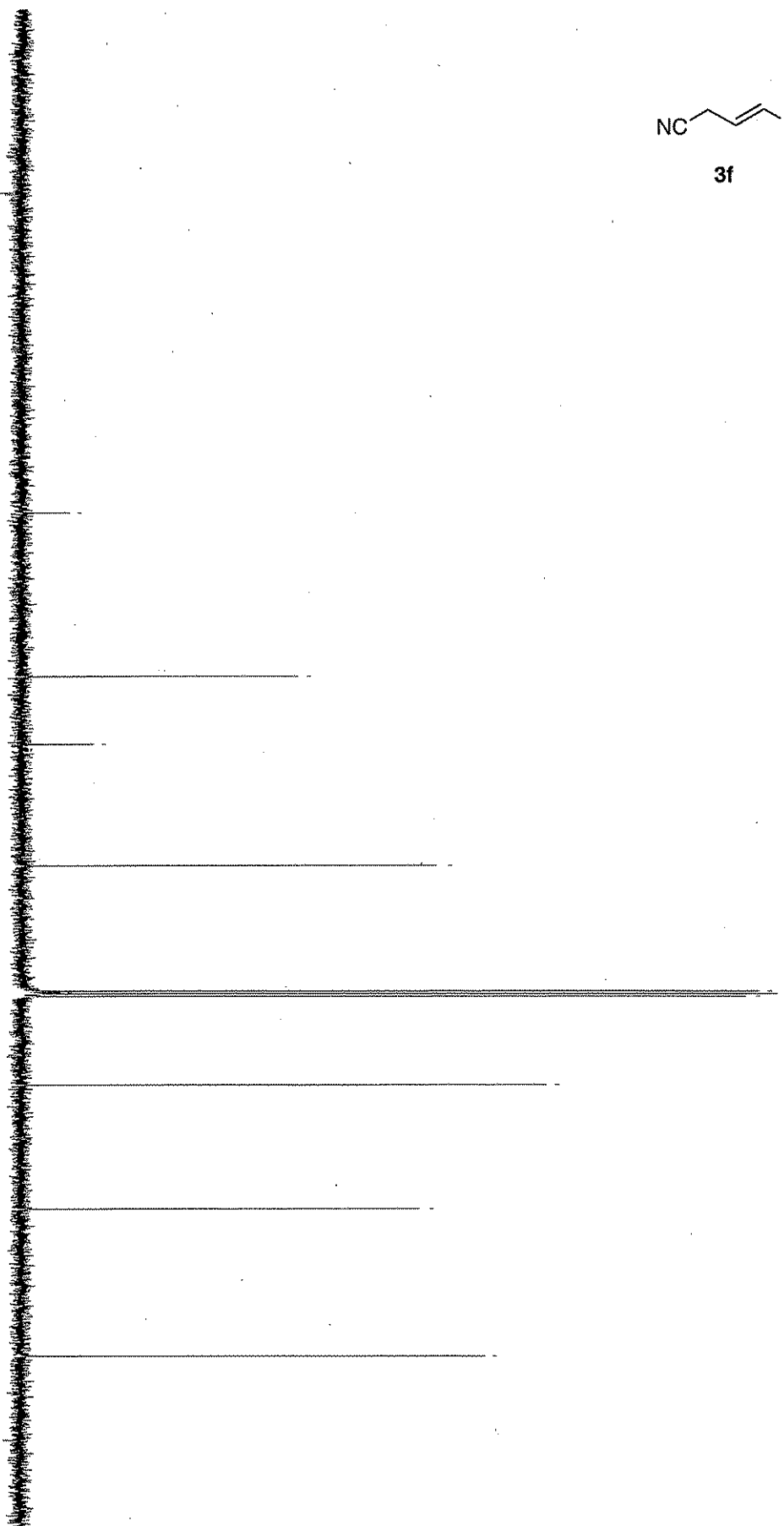
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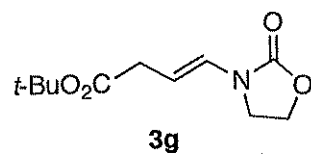
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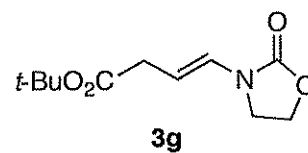
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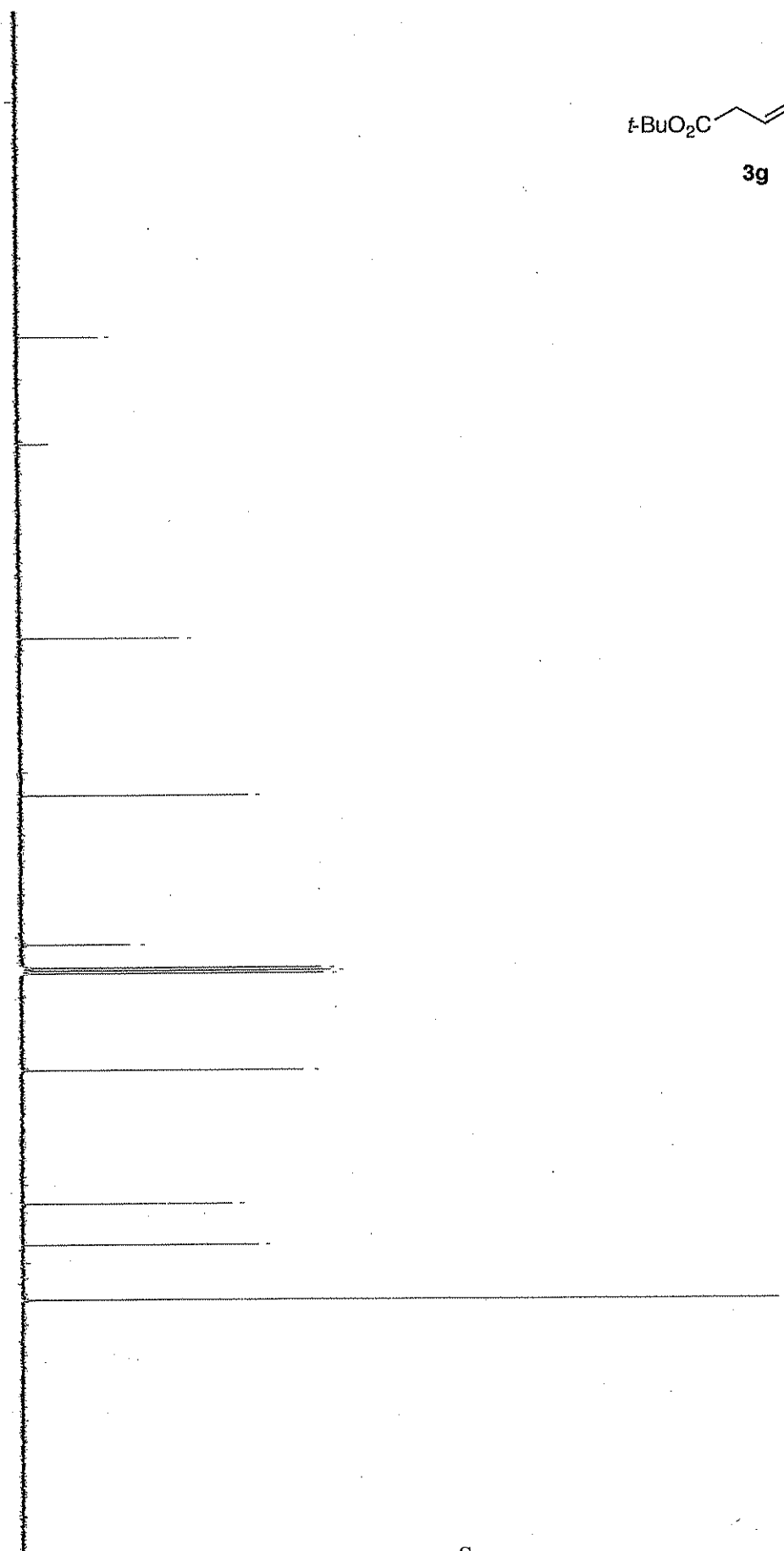
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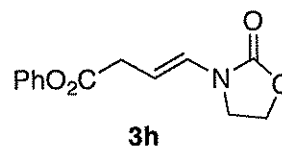
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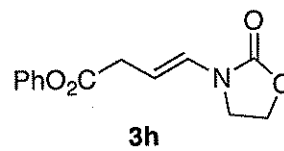
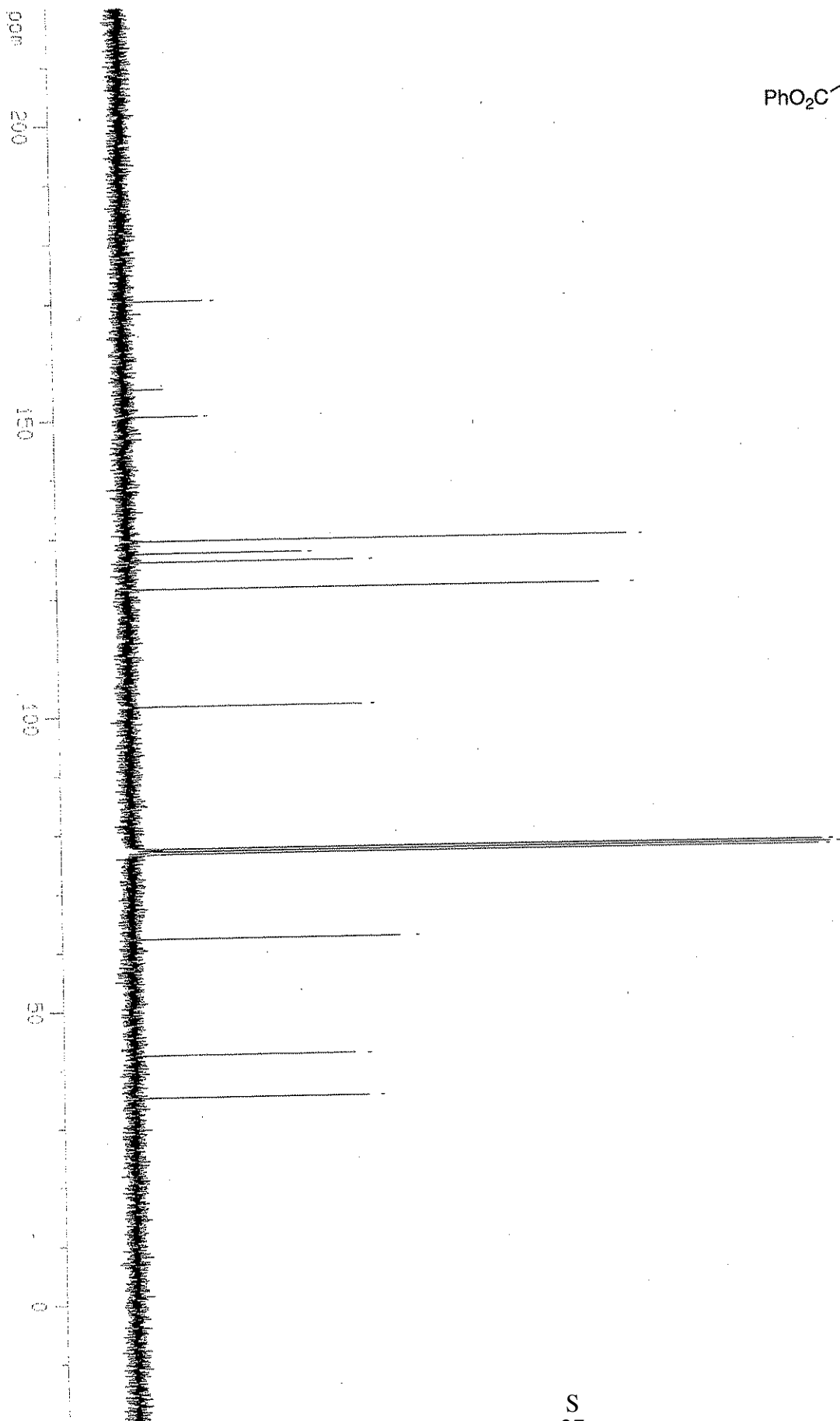
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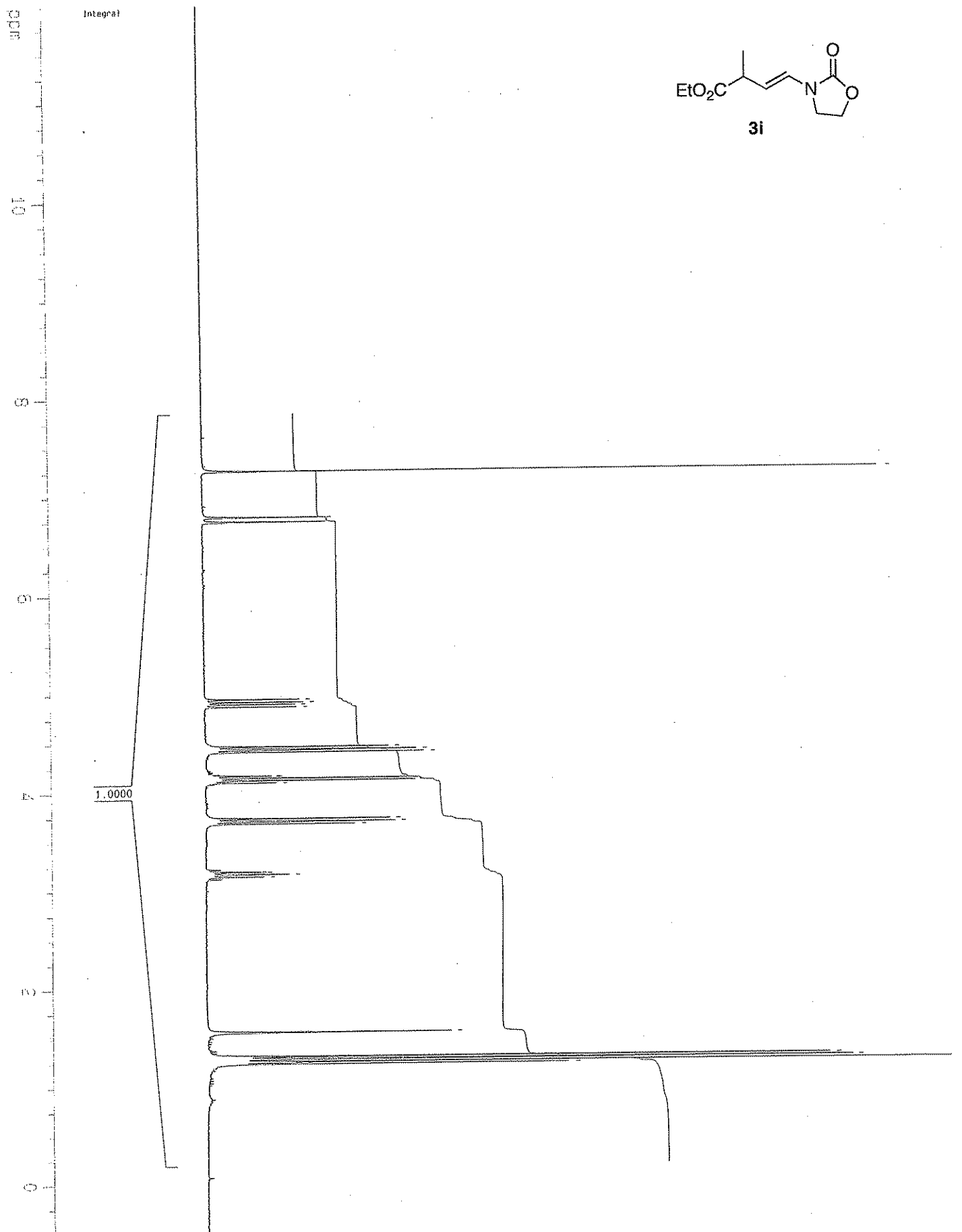
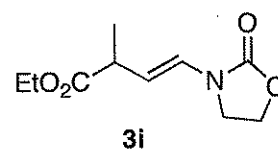
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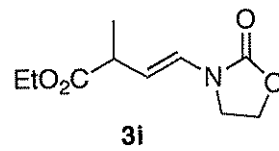
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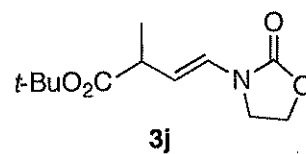
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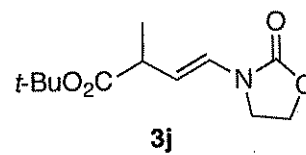
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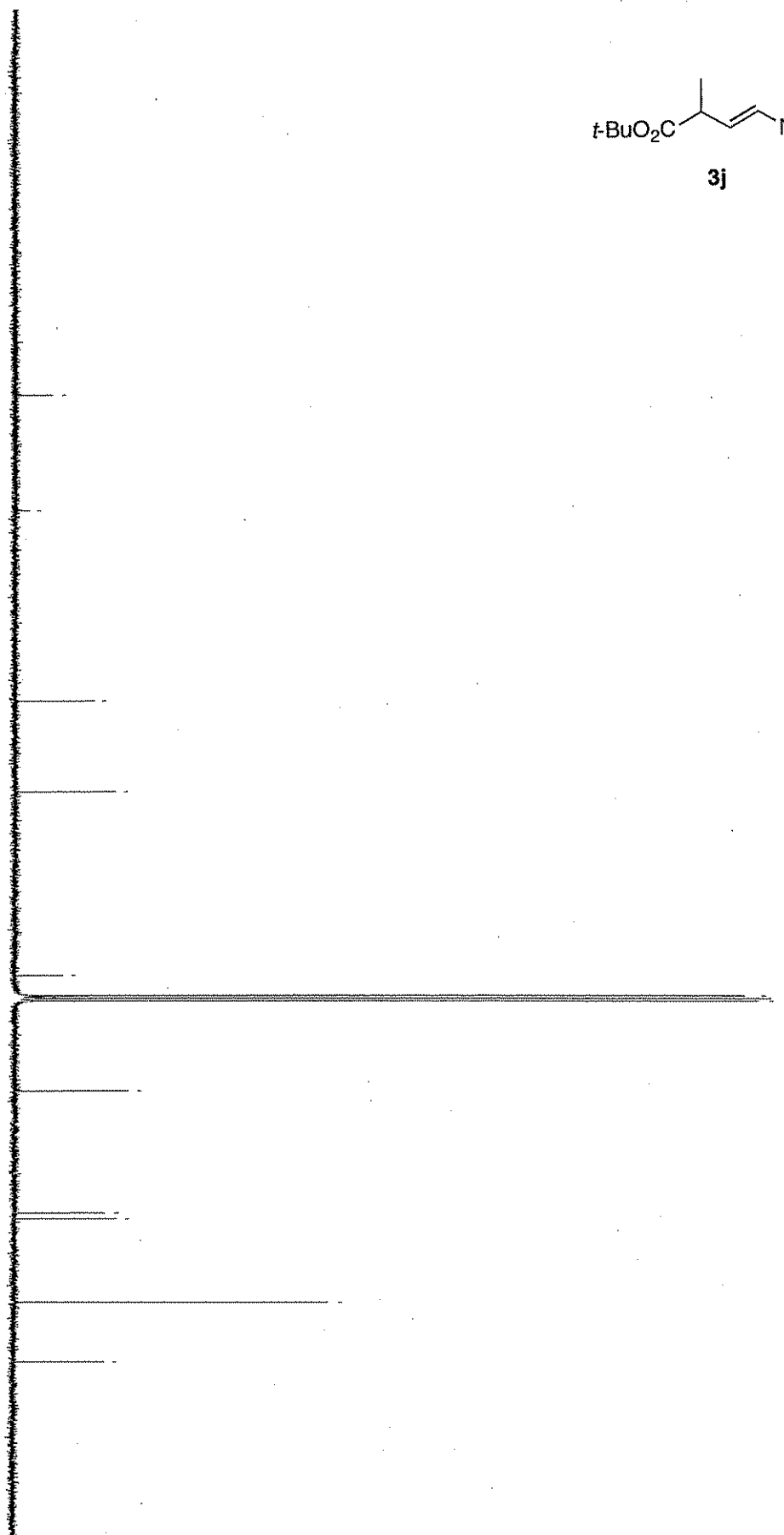
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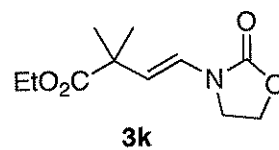
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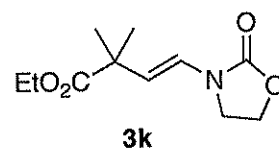
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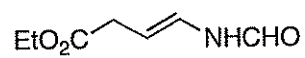
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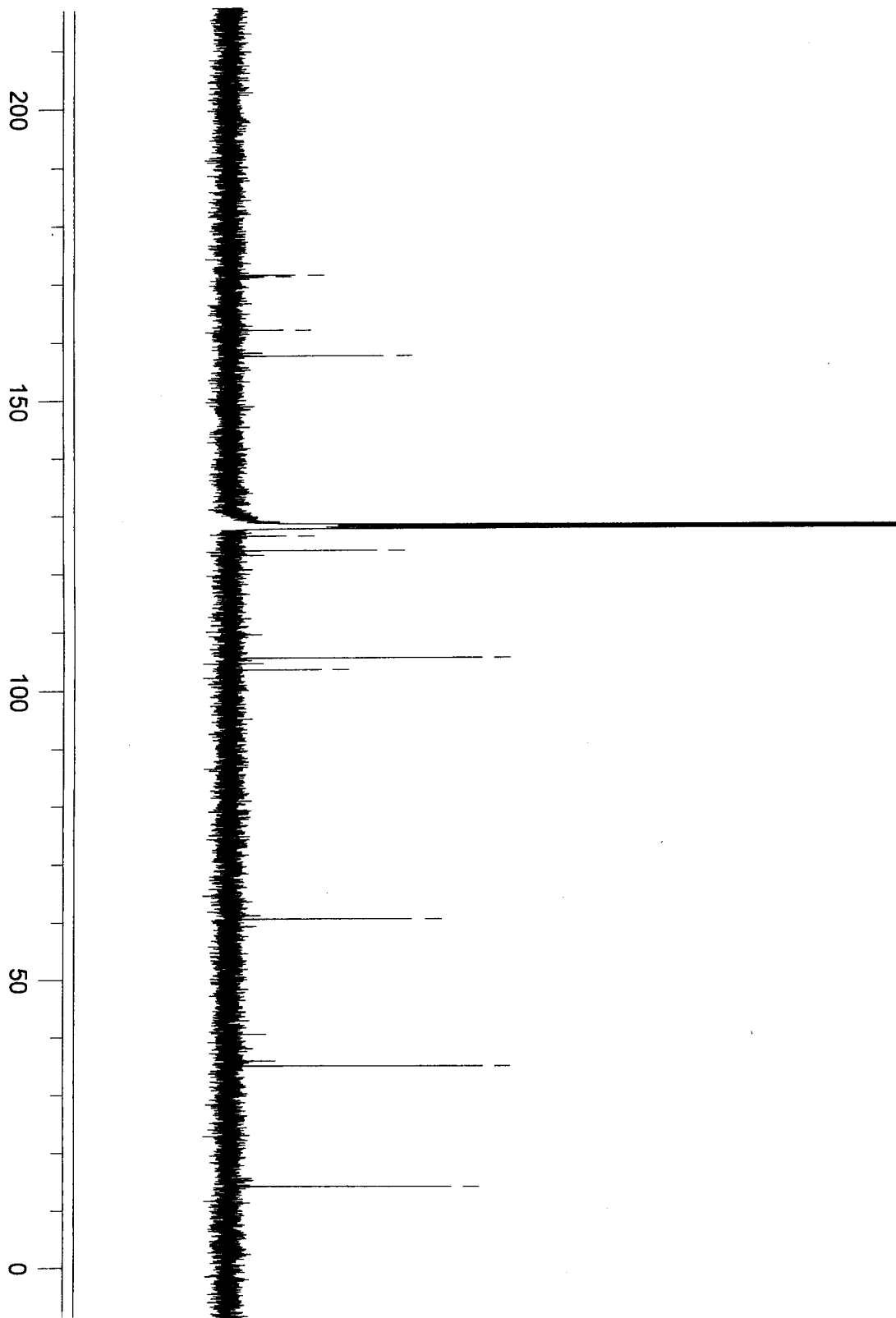
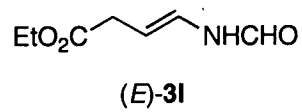
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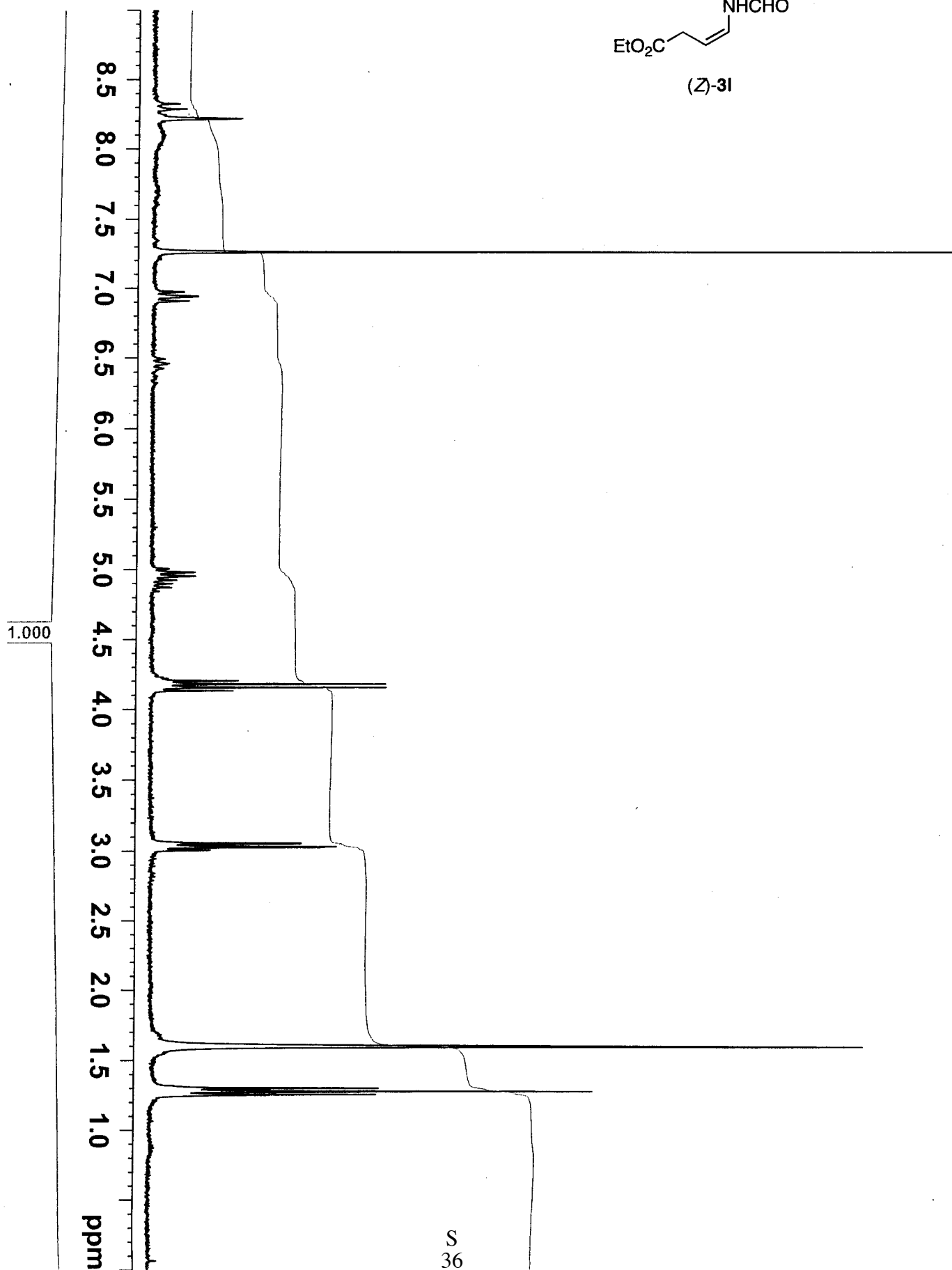
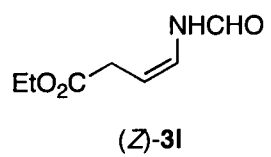
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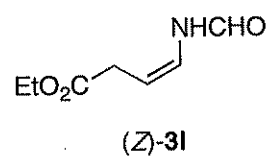
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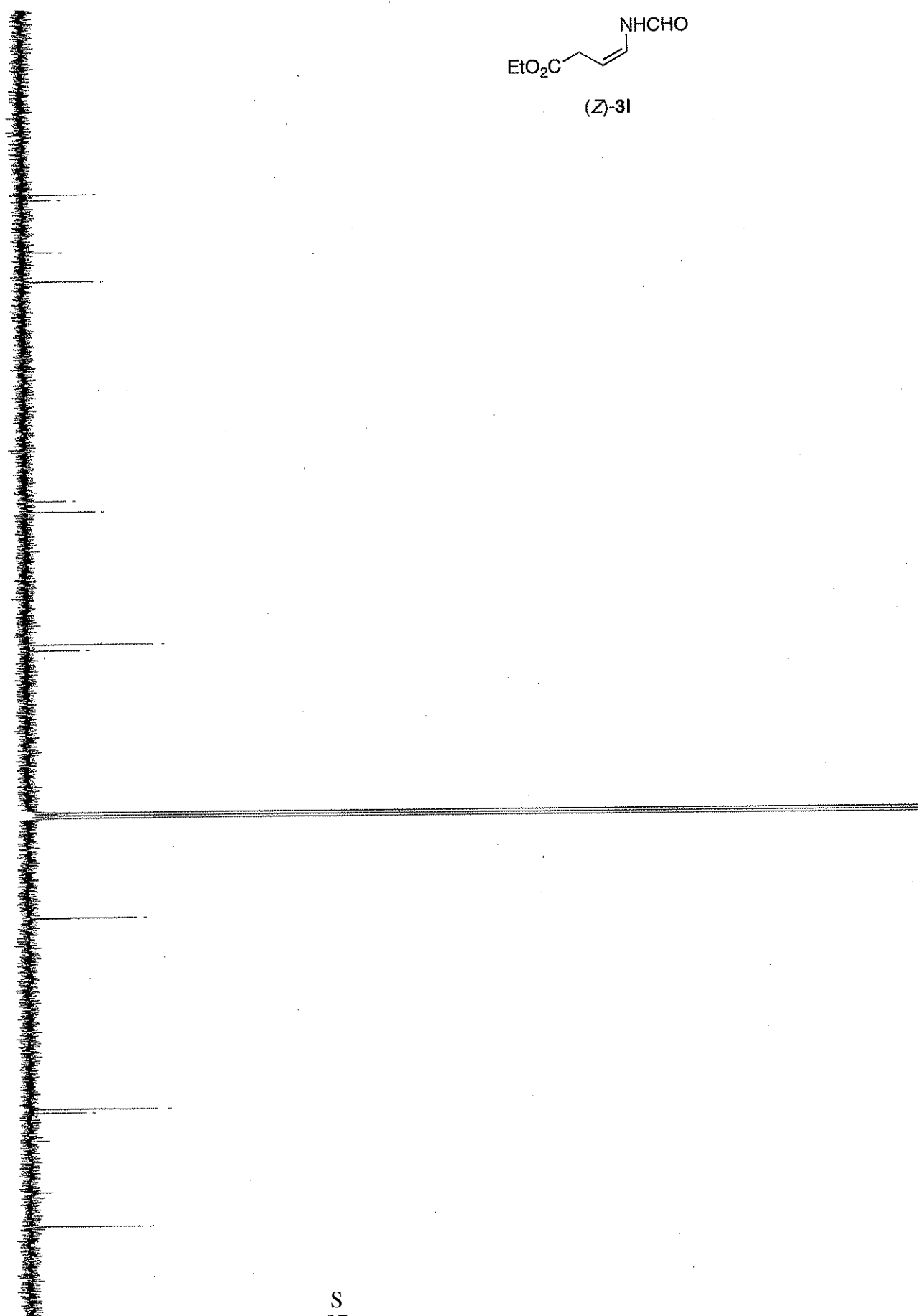
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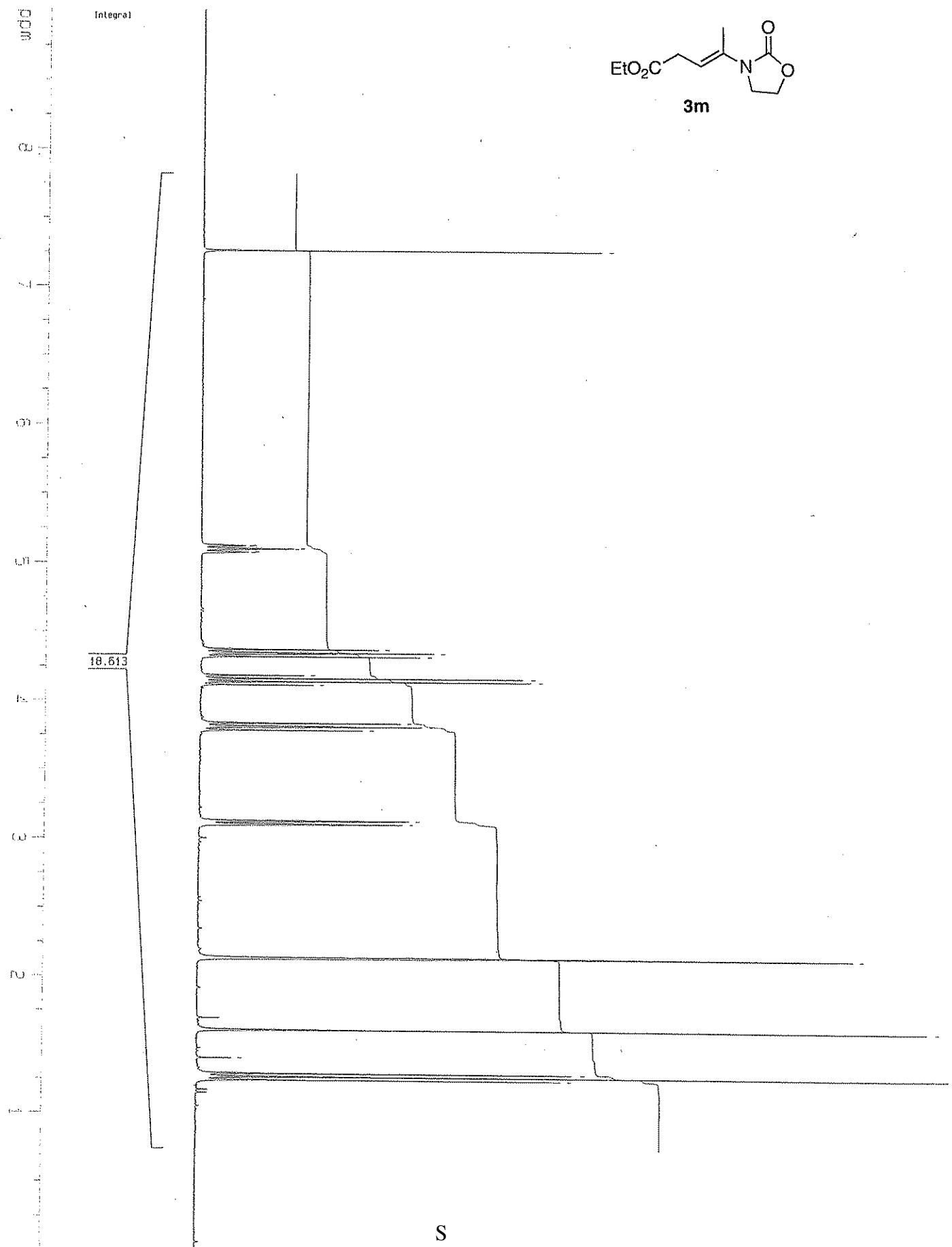


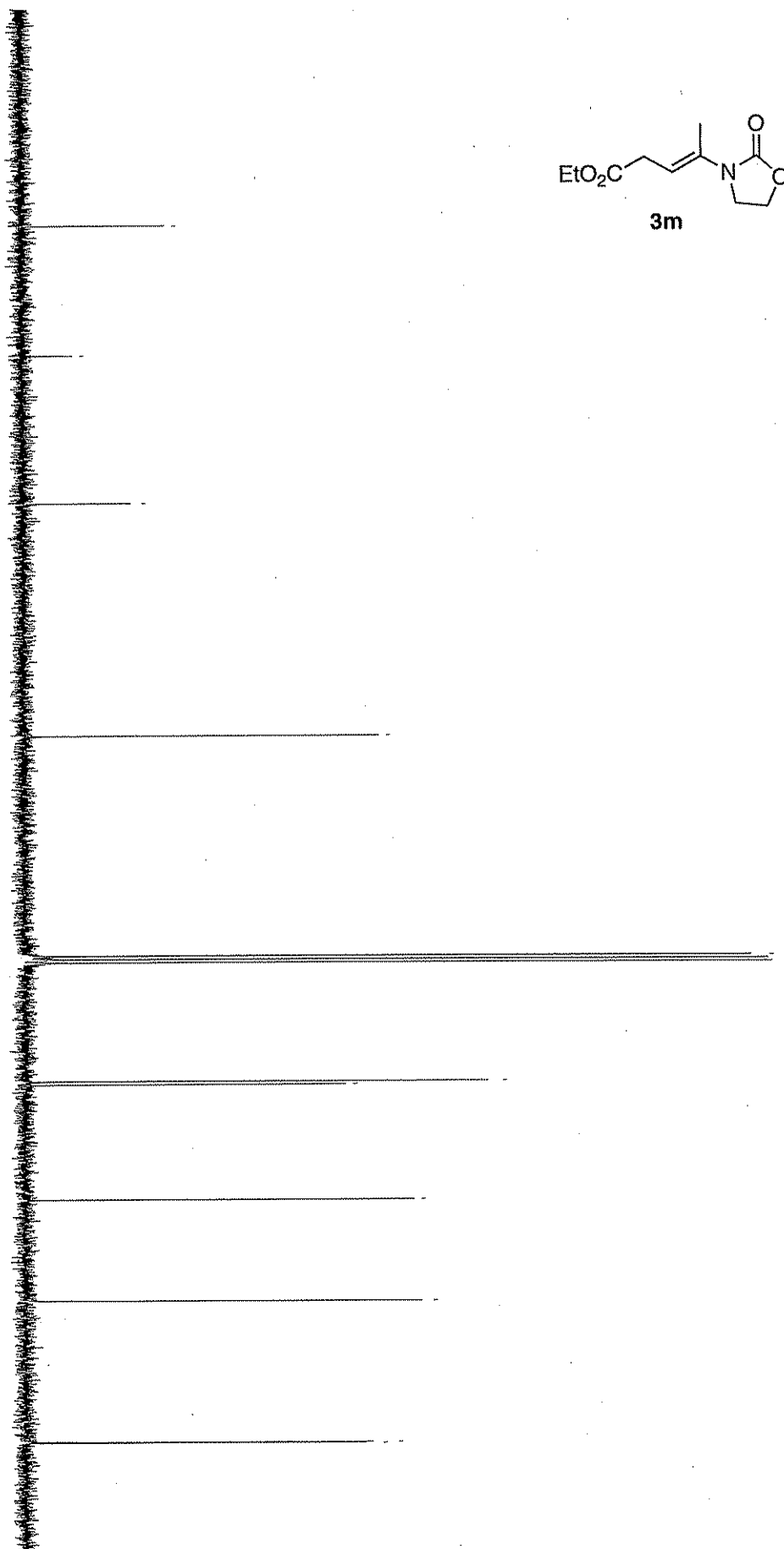
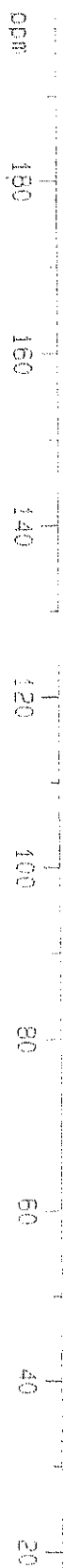
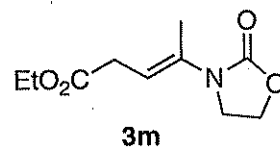


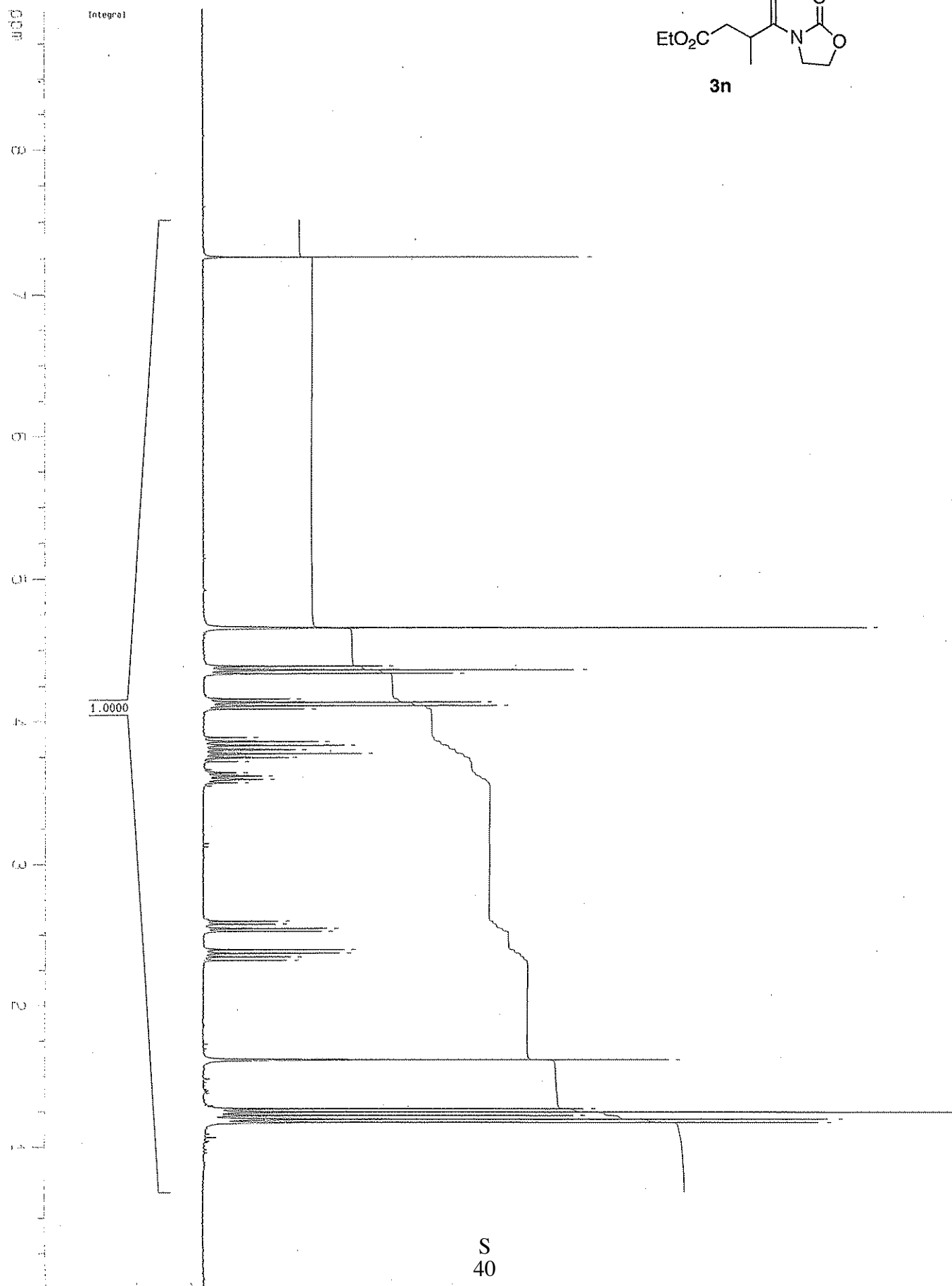
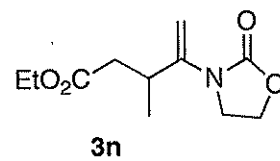


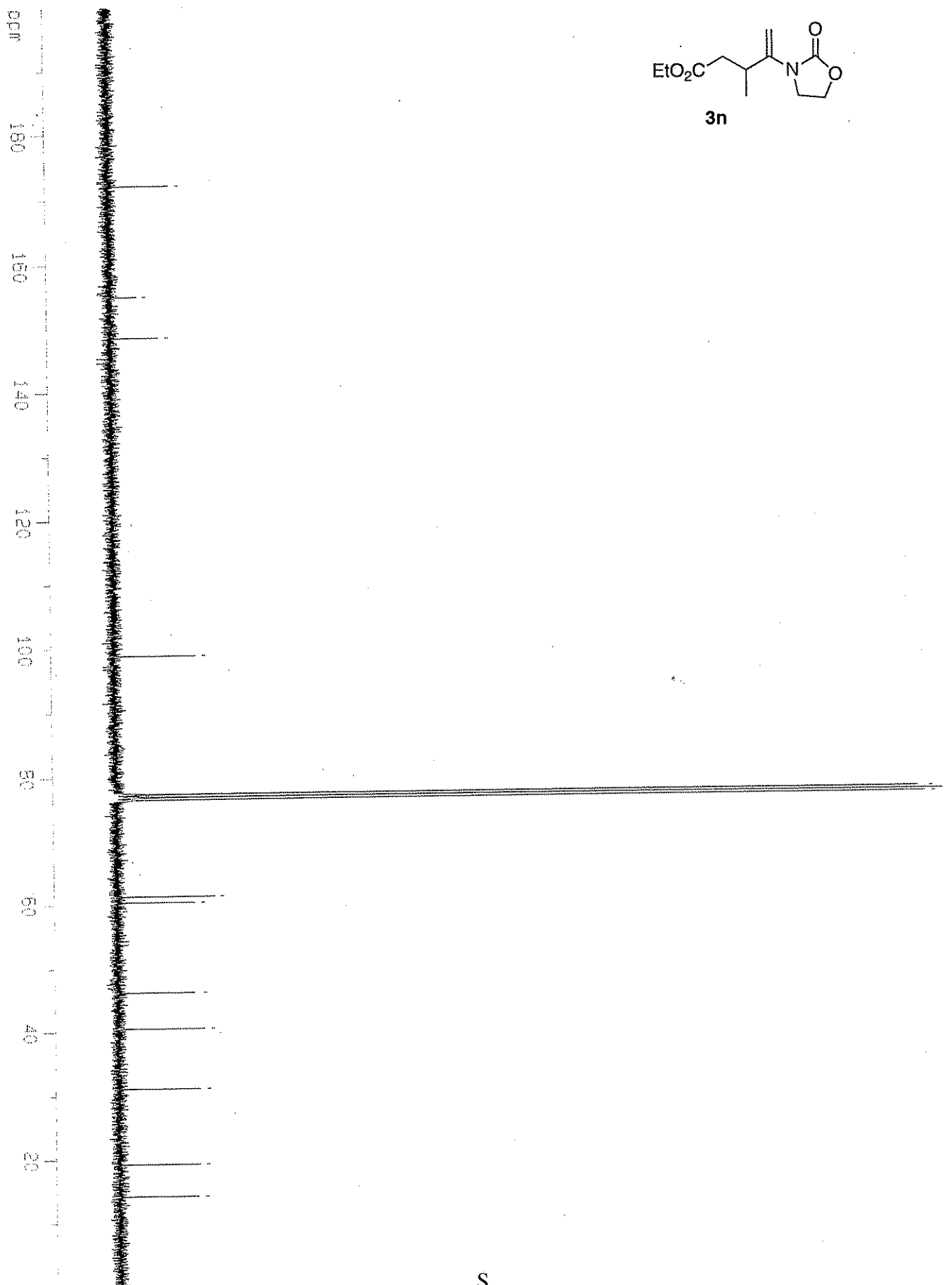
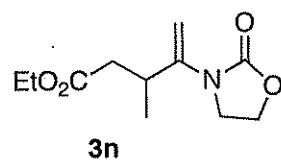
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 180
 160
 140
 120
 100
 80
 60
 40
 20

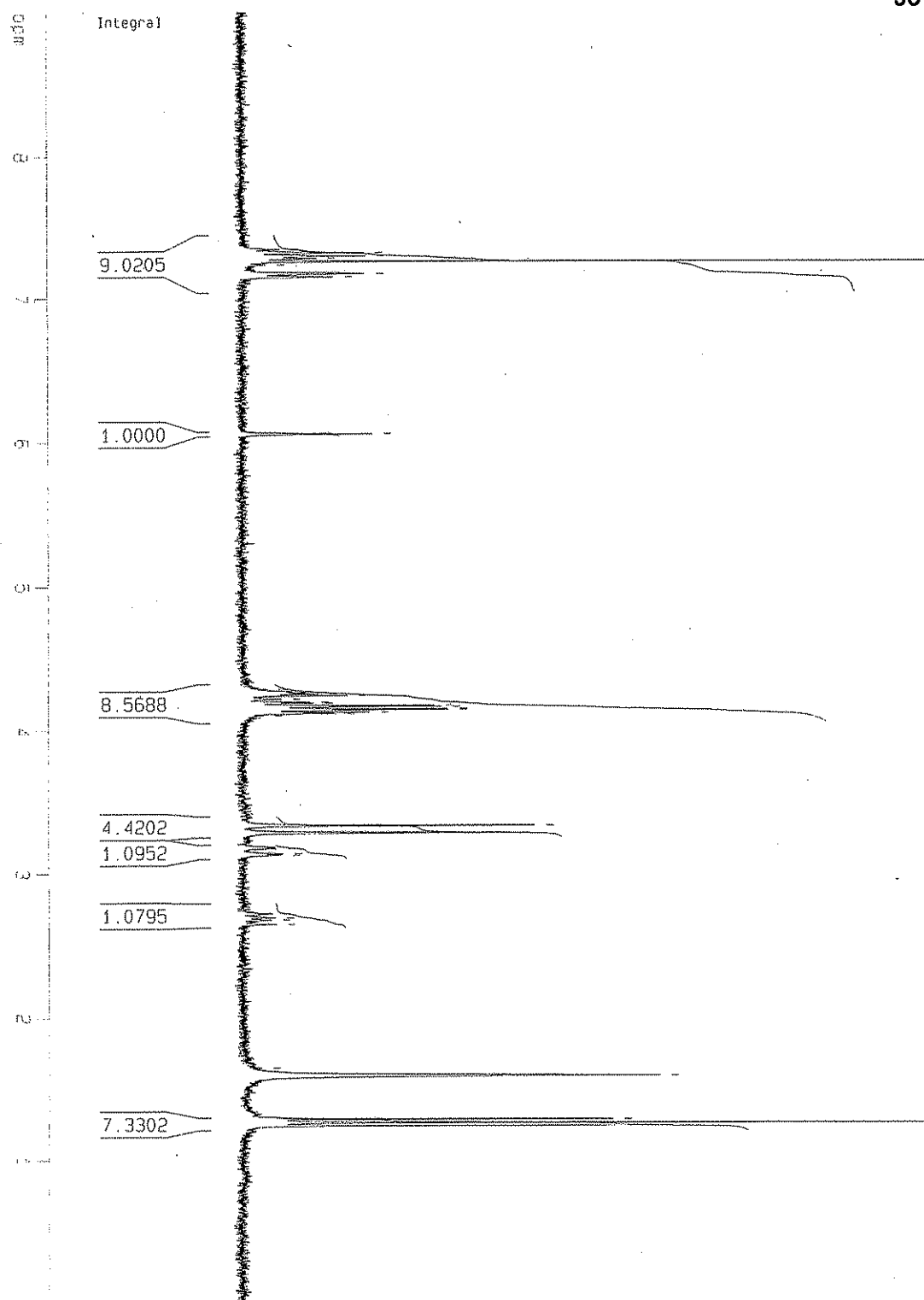
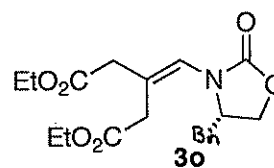












ppm 180 160 140 120 100 80 60 40 20

