

Supporting Information

Radical Carboazidation: Expedient Assembly of the Core Structure of Various Alkaloid Families

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General Techniques. C₆H₆, CH₂Cl₂, THF, Et₂O were dried and purified through activated alumina columns prior to use. EtOH was distilled from magnesium ethoxide under N₂. Et₃N was distilled from CaH₂. Other reagents were obtained from commercial sources and used as received. Filtration and flash column chromatography (FC): *SdS* silica gel (0.063-0.200 mm) and column chromatography (CC): *SdS* silica gel (0.040-0.063 mm); EtOAc, Et₂O, CH₂Cl₂ and hexane as eluents. Thin-layer chromatography (TLC): *Macherey-Nagel SIL G-25 UV₂₅₄* pre-coated TLC plates; detection either with UV or by dipping in a soln. of KMnO₄ (3 g), K₂CO₃ (20 g), NaOH 5% (3 mL) in H₂O (300 mL) and subsequent heating. M.p.: not corrected. NMR spectroscopy: chemical shifts δ in ppm relative to CHCl₃ for ¹H (δ = 7.26 ppm) and CDCl₃ for ¹³C (δ = 77.0 ppm).

Caution: Since sulfonyl azides are capable of exploding, it is strongly recommended to apply standard safety rules and to use a safety shield.

General Procedure A. DTBHN (5 mg, 0.03 mmol) was added every 2 h to a solution of radical precursor (1.0 mmol), olefin (1.0 or 2.0 mmol), PhSO₂N₃ (550 mg, 3.0 mmol) and Bu₆Sn₂ (0.76 mL, 1.5 mmol) in dry C₆H₆ (2.0 mL) at reflux under N₂. The reaction was monitored by TLC. Upon completion of the reaction (4–12 h), the solvent was removed under reduced pressure and the crude product was filtered through silica gel. Elution with hexane allowed the removal of unchanged Bu₆Sn₂ and further elution with hexane/Et₂O or hexane/EtOAc gave a crude product that was purified by FC (hexane/Et₂O or hexane/EtOAc).

General Procedure B. Indium powder (230 mg, 2.0 mmol) and NH₄Cl (107 mg, 2.0 mmol) were added to a solution of azide (2.0 mmol) in dry EtOH (6.0 mL). The reaction mixture was stirred under reflux for 2 h. Et₃N (1.4 mL, 10.0 mmol) was added and the reaction mixture was further stirred under

reflux for 4 h. The cooled reaction mixture was then diluted with EtOAc (10 mL), stirred for 10 min and filtered through a short pad of Celite[®]. The solvent was removed under reduced pressure and the crude product was purified by FC (CH₂Cl₂/MeOH).

General Procedure C. A solution of azide (2.0 mmol) and 10% Pd/C (10% w/w) in dry EtOH (12.0 mL) was stirred for 36 h at rt under H₂ (30 bars). Et₃N (1.4 mL, 10.0 mmol) was added and the reaction mixture was stirred under reflux for 4 h. The catalyst was filtered off, the solvent removed under reduced pressure and the crude product was purified by CC (EtOAc or CH₂Cl₂/MeOH).

Ethyl 4-azidodecanoate (1a). (a) Prepared according to General Procedure A from ethyl 2-iodoacetate (214 mg, 1.0 mmol), 1-octene (0.31 mL, 2.0 mmol), PhSO₂N₃ (550 mg, 3.0 mmol), Bu₆Sn₂ (0.76 mL, 1.5 mmol) and DTBHN (10 mg, 0.06 mmol). Filtration (hexane then hexane/EtOAc 90:10) and FC (hexane/EtOAc 95:5) gave **1a** (191 mg, 79%) as a colorless oil: ¹H NMR (360 MHz, CDCl₃) δ 4.15 (*q*, *J* = 7.3 Hz, 2H), 3.35–3.27 (*m*, 1H), 2.50–2.31 (*m*, 2H), 1.95–1.81 (*m*, 1H), 1.80–1.64 (*m*, 1H), 1.62–1.21 (*m*, 10H), 1.26 (*t*, *J* = 7.3 Hz, 3H), 0.89 (*t*, *J* = 6.8 Hz, 3H); ¹³C NMR (90 MHz, CDCl₃) 173.0, 62.2, 60.5, 34.4, 31.6, 30.9, 29.5, 29.0, 26.0, 22.5, 14.2, 14.0; IR (film) 2932, 2861, 2099, 1738, 1466, 1377, 1343, 1256, 1179, 1032, 860 cm⁻¹; MS (CI, CH₄) *m/z* (%) 242 (MH⁺, 20), 214 (100), 199 (88), 168 (30), 143 (27), 126 (13), 113 (7), 70 (18). Anal. Calcd for C₁₂H₂₃N₃O₂ (241.33): C, 59.72; H, 9.61; N, 17.41. Found: C, 59.77; H, 9.56; N, 17.36.

(b) Prepared according to General Procedure A from ethyl 2-bromoacetate (167 mg, 1.0 mmol), 1-octene (0.31 mL, 2.0 mmol), PhSO₂N₃ (550 mg, 3.0 mmol), Bu₆Sn₂ (0.76 mL, 1.5 mmol) and DTBHN (16 mg, 0.09 mmol). Filtration (hexane then hexane/EtOAc 90:10) and FC (hexane/EtOAc 95:5) gave **1a** (158 mg, 66%).

(c) Prepared according to General Procedure A from ethyl 2-[(ethyloxy)carbothioyl]sulfanyl}acetate (208 mg, 1.0 mmol, prepared from ethyl 2-iodoacetate and potassium ethyl xanthogenate according to a literature procedure),¹ 1-octene (0.31 mL, 2.0 mmol), PhSO₂N₃ (550 mg, 3.0 mmol), Bu₆Sn₂ (0.76 mL, 1.5 mmol) and DTBHN (31 mg, 0.18 mmol) added by 3% portions every 90 min. Filtration (hexane then hexane/EtOAc 90:10) and FC (hexane/EtOAc 95:5) gave **1a** (168 mg, 70%).

Ethyl 3-(1-azidocyclohexyl)propanoate (1b). (a) Prepared according to General Procedure A from ethyl 2-iodoacetate (856 mg, 4.0 mmol), methylenecyclohexane (0.96 mL, 8.0 mmol), PhSO₂N₃ (2.20 g, 12.0 mmol), Bu₆Sn₂ (3.00 mL, 6.0 mmol) and DTBHN (42 mg, 0.24 mmol). Filtration (hexane then hexane/EtOAc 90:10) and FC (hexane/EtOAc 95:5) gave **1b** (800 mg, 89%) as a colorless oil: ¹H NMR (500 MHz, CDCl₃) δ 4.14 (*q*, *J* = 7.2 Hz, 2H), 2.42–2.38 (*m*, 2H), 1.90–1.87 (*m*, 2H), 1.71–1.65 (*m*, 2H), 1.62–1.51 (*m*, 5H), 1.40–1.24 (*m*, 3H), 1.27 (*t*, *J* = 7.2 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.4, 63.3, 60.6, 34.7, 34.4 (2CH₂), 28.6, 25.3, 22.0 (2CH₂), 14.2; IR (film) 2936, 2861, 2101, 1738, 1451 1377, 1302, 1258, 1174, 1024, 895 cm⁻¹; MS (EI, 70eV) *m/z* (%) 226 (M+1, 8), 198 (37), 183 (100), 168 (7), 152 (17), 137 (21), 125 (20), 109 (14), 96 (37), 82 (10), 67 (13), 56 (20). Anal. Calcd for C₁₁H₁₉N₃O₂ (225.29): C, 58.64; H, 8.50; N, 18.65. Found: C, 58.70; H, 8.47; N, 18.55.

(b) Prepared according to General Procedure A from methylenecyclohexane (96 mg, 1.0 mmol), ethyl 2-iodoacetate (124 mg, 1.0 mmol), PhSO₂N₃ (550 mg, 3.0 mmol), Bu₆Sn₂ (870 mg, 0.76 mL, 1.5 mmol) and DTBHN (10 mg, 0.06 mmol). Filtration (hexane then hexane/EtOAc 90:10) and FC (hexane/EtOAc 95:5) gave **1b** (183 mg, 81%).

Ethyl 4-azido-7-[(1,1-dimethylethyl)(dimethyl)silyloxy]heptanoate (1c). Prepared according to General Procedure A from ethyl 2-iodoacetate (214 mg, 1.0 mmol), (1,1-dimethylethyl)(dimethyl)(4-

pentenyloxy)silane (401 mg, 2.0 mmol, prepared from 4-penten-1-ol and *tert*-butyldimethylchlorosilane according to a literature procedure),² PhSO₂N₃ (550 mg, 3.0 mmol), Bu₆Sn₂ (0.76 mL, 1.5 mmol) and DTBHN (10 mg, 0.06 mmol). Filtration (hexane then hexane/EtOAc 90:10) and FC (hexane/EtOAc 95:5) gave **1c** (252 mg, 77%) as a colorless oil: ¹H NMR (500 MHz, CDCl₃) δ 4.14 (*q*, *J* = 7.2 Hz, 2H), 3.67–3.60 (*m*, 2H), 3.38–3.32 (*m*, 1H), 2.49–2.37 (*m*, 2H), 1.94–1.86 (*m*, 1H), 1.79–1.71 (*m*, 1H), 1.69–1.57 (*m*, 4H), 1.27 (*t*, *J* = 7.2 Hz, 3H), 0.89 (*s*, 9H), 0.05 (*s*, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 172.9, 62.5, 62.1, 60.6, 30.8 (2CH₂), 29.6, 29.1, 25.9 (3CH₃), 18.3, 14.2, -5.3 (2CH₃); IR (film) 2951, 2859, 2099, 1738, 1472, 1256, 1099, 1034, 837, 777 cm⁻¹; MS (CI, CH₄) *m/z* (%) 330 (MH⁺, 31), 302 (78), 287 (100), 272 (79), 229 (36), 170 (60), 144 (18), 124 (18). Anal. Calcd for C₁₅H₃₁N₃O₃Si (329.51): C, 54.68; H, 9.48; N, 12.75. Found: C, 54.66; H, 9.38; N, 12.72.

Ethyl 4-azido-5-(trimethylsilyl)pentanoate (1d). Prepared according to General Procedure A from ethyl 2-[[*(ethyloxy)carbothioyl*]sulfanyl]acetate (208 mg, 1.0 mmol), allyltrimethylsilane (0.31 mL, 2.0 mmol), PhSO₂N₃ (550 mg, 3.0 mmol), Bu₆Sn₂ (0.76 mL, 1.5 mmol) and DTBHN (31 mg, 0.18 mmol) added by 3% portions every 90 min. Filtration (hexane then hexane/EtOAc 90:10) and FC (hexane/EtOAc 95:5) gave **1d** (194 mg, 80%) as a colorless oil: ¹H NMR (500 MHz, CDCl₃) δ 4.14 (*q*, *J* = 7.2 Hz, 2H), 3.46–3.39 (*m*, 1H), 2.48–2.37 (*m*, 2H), 1.94–1.88 (*m*, 1H), 1.79–1.72 (*m*, 1H), 1.26 (*t*, *J* = 7.2 Hz, 3H), 1.00 (*dd*, *J* = 14.7, 7.5 Hz, 1H), 0.88 (*dd*, *J* = 14.7, 7.3 Hz, 1H), 0.08 (*s*, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 173.0, 60.5, 59.8, 32.3, 30.9, 22.3, 14.2, -1.08 (3CH₃); IR (film) 2982, 2957, 2905, 2103, 1740, 1447, 1422, 1375, 1341, 1252, 1181, 1098, 1024, 843, 764, 694 cm⁻¹; MS (CI, CH₄) *m/z* (%) 244 (MH⁺, 1), 228 (10), 201 (100), 142 (11), 119 (5), 83 (9), 55 (3). Anal. Calcd for C₁₀H₂₁N₃O₂Si (243.38): C, 49.35; H, 8.70; N, 17.27. Found: C, 49.41; H, 8.76; N, 17.20.

Ethyl 4-azido-2-methyldecanoate (1e). Prepared according to General Procedure A from ethyl 2-iodopropionate (684 mg, 3.0 mmol, prepared from ethyl 2-bromopropionate and sodium iodide according to a literature procedure),³ 1-octene (0.94 mL, 6.0 mmol), PhSO₂N₃ (1.65 g, 9.0 mmol), Bu₆Sn₂ (2.25 mL, 4.5 mmol) and DTBHN (47 mg, 0.27 mmol). Filtration (hexane then hexane/EtOAc 90:10) and FC (hexane/EtOAc 96:4) gave **1e** (573 mg, 75%) as a colorless liquid (54:46 mixture of two isomers (GC)).

1e-Major: ¹H NMR (300 MHz, CDCl₃) δ 4.15 (*q*, *J* = 7.2 Hz, 2H), 3.34–3.20 (*m*, 1H), 2.68 (*qtd*, *J* = 7.0, 7.0, 4.0 Hz, 1H), 1.87 (*ddd*, *J* = 14.0, 10.3, 3.7 Hz, 1H), 1.60–1.25 (*m*, 11H), 1.28 (*t*, *J* = 7.2 Hz, 3H), 1.19 (*d*, *J* = 7.0 Hz, 3H), 0.89 (*t*, *J* = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 176.0, 61.4, 60.4, 38.7, 36.6, 34.9, 31.6, 29.0, 25.9, 22.5, 18.0, 14.1, 13.9.

1e-Minor: ¹H NMR (300 MHz, CDCl₃) δ 4.14 (*q*, *J* = 7.2 Hz, 2H), 3.34–3.20 (*m*, 1H), 2.58 (*qt*, *J* = 7.0, 7.0 Hz, 1H), 1.90 (*ddd*, *J* = 14.0, 9.6, 6.6 Hz, 1H), 1.60–1.25 (*m*, 11H), 1.26 (*t*, *J* = 7.2 Hz, 3H), 1.19 (*d*, *J* = 7.0 Hz, 3H), 0.89 (*t*, *J* = 6.6 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 176.1, 60.7, 60.4, 38.0, 36.8, 34.5, 31.6, 29.0, 25.9, 22.5, 16.9, 14.1, 14.0.

Mixture of isomers **1e**: GC (180°C) t_r (**5e**-major) = 14.3 min (54%), t_r (**5e**-minor) = 15.8 min (46%); IR (film) 2932, 2859, 2102, 1735, 1466, 1379, 1342, 1256, 1178, 861 cm⁻¹; MS (ESI, MeOH/H₂O/HCOOH 74:25:1) *m/z* (%) 278 (MNa⁺, 37), 256 (MH⁺, 1), 228 (80), 182 (100), 154 (51), 126 (34). Anal. Calcd for C₁₃H₂₅N₃O₂ (255.36): C, 61.15; H, 9.87; N, 16.46. Found: C, 61.20; H, 9.82; N, 16.55.

Diethyl 2-(2-azidoethyl)malonate (1f). (a) Prepared according to General Procedure A from diethyl 2-[(ethoxycarbonothioyl)thio]malonate (561 mg, 2.0 mmol, prepared from diethyl bromomalonate and potassium ethyl xanthogenate following the procedure used for the acetate derivative), 1-octene (0.63

mL, 4.0 mmol), PhSO₂N₃ (1.10 mg, 6.0 mmol), Bu₆Sn₂ (1.50 mL, 3 mmol) and DTBHN (63 mg, 0.36 mmol) added by 3% portions every 90 min. Filtration (hexane then hexane/Et₂O 90:10) and FC (hexane/Et₂O 98:2) gave **1f** (479 mg, 76%) as a colorless liquid: ¹H NMR (300 MHz, CDCl₃) δ 4.27–4.14 (*m*, 4H), 3.56 (*dd*, *J* = 9.2, 5.5 Hz, 1H), 3.37–3.25 (*m*, 1H), 2.15 (*ddd*, *J* = 14.3, 9.6, 3.7 Hz, 1H), 1.92 (*ddd*, *J* = 14.3, 10.3, 5.3 Hz, 1H), 1.70–1.20 (*m*, 16H), 0.89 (*t*, *J* = 6.8 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) 168.9, 168.8, 61.5 (2CH₂), 60.7, 49.0, 34.5, 33.3, 31.5, 28.8, 25.7, 22.4, 13.9 (3CH₃); IR (film) 2958, 2932, 2859, 2103, 1735, 1466, 1369, 1258, 1154, 1097, 1031, 862 cm⁻¹; MS (ESI, H₂O/CH₃CN 1:1) *m/z* (%) 336 (MNa⁺, 100), 314 (MH⁺, 4), 293 (8), 288 (28), 286 (8), 194 (32). Anal. Calcd for C₁₅H₂₇N₃O₄ (313.39): C, 57.49; H, 8.68; N, 13.41. Found: C, 57.55; H, 8.74; N, 13.35.

(b) Prepared according to General Procedure A from diethyl 2-bromomalonate (717 mg, 3.0 mmol), 1-octene (0.94 mL, 6.0 mmol), PhSO₂N₃ (1.65 mg, 9.0 mmol), Bu₆Sn₂ (2.25 mL, 4.5 mmol) and DTBHN (47 mg, 0.27 mmol). Filtration (hexane then hexane/Et₂O 90:10) gave a 19:33:48 unseparable mixture of bromine atom transfer product, PhSO₂N₃ and **1f** (433 mg, 46% according to ¹H NMR).

(c) Prepared according to General Procedure A from diethyl 2-(phenylseleno)malonate **1f** (315 mg, 1.0 mmol, prepared from diethyl malonate and phenylselenyl chloride according to a literature procedure),⁴ 1-octene (0.31 mL, 2.0 mmol), PhSO₂N₃ (550 mg, 3.0 mmol), Bu₆Sn₂ (0.76 mL, 1.5 mmol) and DTBHN (26 mg, 0.15 mmol). Filtration (hexane then hexane/Et₂O 90:10) gave a 22:32:46 unseparable mixture of phenylseleno group transfer product, PhSO₂N₃ and **1f** (157 mg, 50% according to ¹H NMR).

1-(2,2,2-Trichloroethyl)cyclohexyl azide (1g). Prepared according to General Procedure A from bromotrichloromethane (198 mg, 1.0 mmol), methylenecyclohexane (0.24 mL, 2.0 mmol), PhSO₂N₃ (550 mg, 3.0 mmol), Bu₆Sn₂ (0.76 mL, 1.5 mmol) and DTBHN (16 mg, 0.09 mmol). Filtration (hexane

then hexane/EtOAc 90:10) and FC (hexane) gave **1g** (104 mg, 40%) as a colorless liquid. ¹H NMR (400 MHz, CDCl₃) δ 3.02 (*s*, 2H), 2.02–1.91 (*m*, 2H), 1.72–1.52 (*m*, 7H), 1.33–1.20 (*m*, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 95.6, 63.6, 62.2, 35.3 (2CH₂), 25.0, 21.8 (2CH₂); IR (film) 2935, 2858, 2106, 1449, 1262, 1207, 1145, 1105, 1074, 1044, 977, 952, 909, 852 cm⁻¹; MS (EI, 70eV) *m/z* (%) 261 (M⁺, 0.1), 259 (M⁺, 0.2), 258 (M⁺, 0.1), 257 (M⁺, 0.7), 256 (M⁺, 0.1), 255 (M⁺, 0.9), 228 (3), 215 (4), 213 (4), 186 (45), 184 (47), 179 (49), 177 (64), 158 (47), 141 (54), 117 (70), 96 (92), 81 (94), 69 (88), 55 (100), 42 (88). HRMS (ESI) for C₈H₁₃Cl₃N₃: calcd 256.0175, found 256.0180.

Ethyl 2-(3-azidobicyclo[2.2.1]hept-2-yl)acetate (2). Prepared according to General Procedure A from ethyl 2-iodoacetate (214 mg, 1.0 mmol), norbornene (188 mg, 2.0 mmol), PhSO₂N₃ (550 mg, 3.0 mmol), Bu₆Sn₂ (0.76 mL, 1.5 mmol) and DTBHN (10 mg, 0.06 mmol). Filtration (hexane then hexane/EtOAc 90:10) and FC (hexane/EtOAc 95:5) gave **2** (166 mg, 74%) as a colorless oil (85:15 mixture of *exo/endo* isomers (¹H NMR)).

2-Major (*exo*-azide): ¹H NMR (500 MHz, CDCl₃) δ 4.20–4.10 (*m*, 2H), 3.64 (*br. d*, *J* = 7.3 Hz, 1H), 2.44–2.18 (*m*, 4H), 1.95 (*br. dd*, *J* = 3.6, 1.4 Hz, 1H), 1.63–1.45 (*m*, 4H), 1.29–1.10 (*m*, 2H), 1.26 (*t*, *J* = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.1, 67.8, 60.4, 43.2, 42.2, 41.1, 35.3, 32.9, 29.5, 25.3, 14.2.

2-Minor (*endo*-azide): ¹H NMR (500 MHz, CDCl₃) δ 3.49 (*ddd*, *J* = 6.0, 4.2, 1.8 Hz 1H), 2.00 (*br. d*, *J* = 3.7 Hz, 1H), 1.76–1.66 (*m*, 2H), 1.43–1.30 (*m*, 2H), 1.27 (*t*, *J* = 7.1 Hz, 3H) characteristic signals; ¹³C NMR (125 MHz, CDCl₃) δ 173.1, 69.2, 60.6, 45.3, 41.9, 41.6, 39.9, 34.9, 29.2, 21.1, 14.2.

Mixture of isomers **2**: IR (film) 2961, 2876, 2101, 1730, 1456, 1414, 1377, 1329, 1271, 1179, 1151, 1030 cm⁻¹; MS (EI, 70eV) *m/z* (%) 224 (M+1, 22), 196 (47), 181 (51), 167 (34), 150 (89), 149 (17), 122

(58), 108 (91), 94 (76), 80 (87), 67 (100), 54 (46). Anal. Calcd for C₁₁H₁₇N₃O₂ (223.27): C, 59.17; H, 7.67; N, 18.82. Found: C, 59.26; H, 7.67; N, 18.82.

5-Hexyl-2-pyrrolidinone (3). Prepared according to General Procedure B from azide **1a** (483 mg, 2.0 mmol). CC (EtOAc/MeOH 99:1) gave **3** (288 mg, 85%) as a white solid. Physical and spectral data were in accordance with literature data.⁵

Ethyl 4-azido-7-bromoheptanoate (4a). Prepared according to General Procedure A from ethyl 2-iodoacetate (642 mg, 3.0 mmol), 5-bromo-1-pentene (0.71 mL, 6.0 mmol), PhSO₂N₃ (1.65 g, 9.0 mmol), Bu₆Sn₂ (2.25 mL, 4.5 mmol) and DTBHN (31 mg, 0.18 mmol). Filtration (hexane then hexane/EtOAc 90:10) and CC (hexane/Et₂O 95:5) gave **4a** (645 mg, 77%) as a colorless liquid: ¹H NMR (300 MHz, CDCl₃) δ 4.15 (*q*, *J* = 7.3 Hz, 2H), 3.44 (*t*, *J* = 6.4 Hz, 2H), 3.41–3.32 (*m*, 1H), 2.53–2.36 (*m*, 2H), 2.12–1.60 (*m*, 6H), 1.27 (*t*, *J* = 7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 172.7, 61.2, 60.5, 33.0, 32.8, 30.6, 29.4, 29.0, 14.1; IR (film) 2980, 2938, 2102, 1732, 1446, 1375, 1344, 1259, 1181, 1097, 1032, 862 cm⁻¹; MS (EI, 70eV) *m/z* (%) 280 (M⁺, 0.1), 278 (M⁺, 0.1), 232 (2), 189 (1), 162 (10), 143 (17), 124 (18), 100 (15), 81 (39), 70 (100), 55 (45), 41 (98). Anal. Calcd for C₉H₁₆BrN₃O₂ (278.15): C, 38.86; H, 5.80; N, 15.11. Found: C, 38.94; H, 5.87; N, 15.17.

Ethyl 4-azido-7-bromo-2-methylheptanoate (4b). Prepared according to General Procedure A from ethyl 2-iodopropionate (684 mg, 3.0 mmol), 5-bromo-1-pentene (0.71 mL, 6.0 mmol), PhSO₂N₃ (1.65 g, 9.0 mmol), Bu₆Sn₂ (2.25 mL, 4.5 mmol) and DTBHN (47 mg, 0.27 mmol). Filtration (hexane then hexane/Et₂O 90:10) and FC (hexane/Et₂O 95:5) gave **4b** (628 mg, 72%) as a colorless liquid (54:46 mixture of two isomers (GC)).

4b-Major: ^1H NMR (300 MHz, CDCl_3) δ 4.16 (*q*, $J = 7.2$ Hz, 2H), 3.43 (*t*, $J = 6.4$ Hz, 2H), 3.38–3.27 (*m*, 1H), 2.68 (*qtd*, $J = 7.0, 7.0, 4.0$ Hz, 1H), 2.12–1.83 (*m*, 3H), 1.79–1.60 (*m*, 2H), 1.59–1.44 (*m*, 1H), 1.27 (*t*, $J = 7.2$ Hz, 3H), 1.20 (*d*, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 175.8, 60.6, 60.5, 38.5, 36.5, 33.3, 32.9, 29.0, 18.0, 14.1.

4b-Minor: ^1H NMR (300 MHz, CDCl_3) δ 4.15 (*q*, $J = 7.2$ Hz, 2H), 3.43 (*t*, $J = 6.4$ Hz, 2H), 3.38–3.27 (*m*, 1H), 2.58 (*qt*, $J = 7.0, 7.0$ Hz, 1H), 2.12–1.83 (*m*, 3H), 1.82–1.44 (*m*, 3H), 1.25 (*t*, $J = 7.2$ Hz, 3H), 1.20 (*d*, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 175.8, 60.5, 59.9, 37.8, 36.7, 33.0, 32.9, 29.0, 17.0, 14.1.

Mixture of isomers **4b**: GC (180°C) t_r (**4b**-major) = 10.0 min (54%), t_r (**4b**-minor) = 11.0 min (46%); IR (film) 2979, 2940, 2101, 1732, 1455, 1378, 1339, 1258, 1181, 1027, 859 cm^{-1} ; MS (EI, 70eV) m/z (%) 248 (3), 234 (2), 190 (10), 162 (10), 138 (10), 95 (22), 84 (24), 68 (32), 57 (85), 41 (100). Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{BrN}_3\text{O}_2$ (292.17): C, 41.11; H, 6.21; N, 14.38. Found: C, 41.15; H, 6.29; N, 14.36.

Ethyl 4-azido-8-bromooctanoate (4c). Prepared according to General Procedure A from ethyl 2-iodoacetate (642 mg, 3.0 mmol), 6-bromo-1-hexene (0.80 mL, 6.0 mmol), PhSO_2N_3 (1.65 g, 9.0 mmol), Bu_6Sn_2 (2.25 mL, 4.5 mmol) and DTBHN (31 mg, 0.18 mmol). Filtration (hexane then hexane/EtOAc 90:10) and CC (hexane/Et₂O 95:5) gave **4c** (648 mg, 74%) as a colorless liquid: ^1H NMR (300 MHz, CDCl_3) δ 4.15 (*q*, $J = 7.3$ Hz, 2H), 3.42 (*t*, $J = 6.8$ Hz, 2H), 3.38–3.29 (*m*, 1H), 2.52–2.36 (*m*, 2H), 1.96–1.83 (*m*, 3H), 1.81–1.69 (*m*, 1H), 1.66–1.49 (*m*, 4H), 1.27 (*t*, $J = 7.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 172.6, 61.8, 60.4, 33.4, 33.1, 32.2, 30.6, 29.3, 24.5, 14.1; IR (film) 2980, 2942, 2868, 2103, 1734, 1447, 1375, 1343, 1252, 1181, 1098, 1034, 860 cm^{-1} ; MS (EI, 70eV) m/z (%) 294 (M^+ , 0.6), 292 (M^+ , 0.6), 218 (11), 184 (82), 139 (93), 110 (57), 96 (33), 82 (52), 56 (100). Anal. Calcd for $\text{C}_{10}\text{H}_{18}\text{BrN}_3\text{O}_2$ (292.18): C, 41.11; H, 6.21; N, 14.38. Found: C, 41.19; H, 6.24; N, 14.35.

Ethyl 4-azido-8-bromo-2-methyloctanoate (4d). Prepared according to General Procedure A from ethyl 2-iodopropionate (684 mg, 3.0 mmol), 6-bromo-1-hexene (0.80 mL, 6.0 mmol), PhSO₂N₃ (1.65 g, 9.0 mmol), Bu₆Sn₂ (2.25 mL, 4.5 mmol) and DTBHN (47 mg, 0.27 mmol). Filtration (hexane then hexane/Et₂O 90:10) and CC (hexane/Et₂O 97:3) gave **4d** (635 mg, 69%) as a colorless liquid (54:46 mixture of two isomers (GC)).

4d-Major: ¹H NMR (300 MHz, CDCl₃) δ 4.15 (*q*, *J* = 7.2 Hz, 2H), 3.41 (*t*, *J* = 6.6 Hz, 2H), 3.34–3.24 (*m*, 1H), 2.68 (*qtd*, *J* = 7.0, 7.0, 4.0 Hz, 1H), 1.94–1.82 (*m*, 3H), 1.64–1.41 (*m*, 5H), 1.27 (*t*, *J* = 7.2 Hz, 3H), 1.19 (*d*, *J* = 7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 175.9, 61.1, 60.5, 38.6, 36.5, 34.0, 33.2, 32.3, 24.6, 18.0, 14.2.

4d-Minor: ¹H NMR (300 MHz, CDCl₃) δ 4.14 (*q*, *J* = 7.2 Hz, 2H), 3.41 (*t*, *J* = 6.6 Hz, 2H), 3.34–3.24 (*m*, 1H), 2.58 (*qt*, *J* = 7.0, 7.0 Hz, 1H), 1.99–1.84 (*m*, 3H), 1.64–1.48 (*m*, 5H), 1.26 (*t*, *J* = 7.2 Hz, 3H), 1.19 (*d*, *J* = 7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 176.0, 60.5, 60.4, 37.9, 36.8, 33.6, 33.2, 32.3, 24.6, 17.0, 14.2.

Mixture of isomers **4d**: GC (180°C) *t*_r (**4d**-major) = 11.9 min (54%), *t*_r (**4d**-minor) = 12.9 min (46%); IR (film) 2977, 2940, 2103, 1732, 1460, 1378, 1341, 1254, 1180, 1096, 1025, 861 cm⁻¹; MS (EI, 70eV) *m/z* (%) 309 (M+1, 0.1), 307 (M+1, 0.01), 262 (3), 248 (2), 198 (59), 152 (63), 124 (40), 98 (41), 82 (40), 73 (41), 55 (100), 41 (82). Anal. Calcd for C₁₁H₂₀BrN₃O₂ (306.20): C, 43.15; H, 6.58; N, 13.72. Found: C, 43.16; H, 6.60; N, 13.74.

Hexahydro-3H-pyrrolizin-3-one (5a). Prepared according to General Procedure B from azide **4a** (556 mg, 2.0 mmol). CC (CH₂Cl₂/MeOH 97:3) gave **5a** (205 mg, 82%) as a yellowish oil. Physical and spectral data were in accordance with literature data.⁶

2-Methylhexahydro-3H-pyrrolizin-3-one (5b). Prepared according to General Procedure B from azide **4b** (584 mg, 2.0 mmol). CC (CH₂Cl₂/MeOH 99:1) gave **5b** (234 mg, 84%) as a yellowish oil (1:1 mixture of two isomers (GC)). Physical and spectral data were in accordance with literature data.⁶

Hexahydro-3(2H)-indolizinone (5c). Prepared according to General Procedure B from azide **4c** (584 mg, 2.0 mmol). CC (CH₂Cl₂/MeOH 98:2) gave **5c** (201 mg, 72%) as a yellowish oil. Physical and spectral data were in accordance with literature data.⁷

2-Methylhexahydroindolizin-3(2H)-one (5d). Prepared according to General Procedure B from azide **4d** (612 mg, 2.0 mmol). CC (CH₂Cl₂/MeOH 99:1) gave **5d** (201 mg, 83%) as a yellowish oil (1:1 mixture of two isomers (GC)). Physical and spectral data were in accordance with literature data.⁸

Ethyl 3-(1-azidocyclopentyl)propanoate (6). Prepared according to General Procedure A from methylenecyclopentane (411 mg, 5.0 mmol), ethyl 2-iodoacetate (1.07 g, 5.0 mmol), PhSO₂N₃ (2.75 g, 15.0 mmol), Bu₆Sn₂ (3.79 mL, 7.5 mmol) and DTBHN (52 mg, 0.30 mmol). Filtration (hexane then hexane/EtOAc 90:10) and FC (hexane/EtOAc 98:2) gave **6** (790 mg, 75%) as a yellowish oil: ¹H NMR (300 MHz, CDCl₃) δ 4.09 (*q*, *J* = 7.0 Hz, 2H), 2.39–2.36 (*m*, 2H), 1.95–1.89 (*m*, 2H), 1.81–1.65 (*m*, 6H), 1.55–1.48 (*m*, 2H), 1.22 (*t*, *J* = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 173.2, 72.7, 60.4, 36.7 (2CH₂), 33.9, 30.3, 23.6 (2CH₂), 14.1; IR (film) 2101, 1727 cm⁻¹; HRMS (ESI) for C₁₀H₁₇N₃O₂Na: calcd 234.1218, found 234.1228.

1-Azaspiro[4.4]nonan-2-one (7). Prepared according to General Procedure C from azide **6** (211 mg, 1 mmol) and 10% Pd/C (63 mg, 30% w/w). FC (EtOAc) gave **7** (115 mg, 84%) as a pale brown solid:

mp 142-144 °C; ¹H NMR (300 MHz, CDCl₃) δ 6.72 (*br. s*, 1H), 2.41–2.36 (*m*, 2H), 2.04–1.98 (*m*, 2H), 1.72–1.65 (*m*, 8H); ¹³C NMR (75 MHz, CDCl₃) δ 66.9, 39.1 (2CH₂), 33.8, 30.7, 29.7, 23.1 (2CH₂); HRMS (ESI) for C₈H₁₄NO: calcd 140.1075, found 140.1071.

1-Azaspiro[4.5]decan-2-one (8). Prepared according to General Procedure C from azide **1b** (550 mg, 2.0 mmol) and 10% Pd/C (50 mg, 10% w/w). CC (CH₂Cl₂/MeOH 98:2) gave **8** (264 mg, 86%) as a white solid. Physical and spectral data were in accordance with literature data.⁹

8-Methylene-1,4-dioxaspiro[4.5]decane (10). *t*-BuOK (3.67 g, 30.0 mmol) was added to a solution of CH₃PPh₃Br (10.72 g, 30.0 mmol) in Et₂O (60.0 mL) at rt under N₂. The resulting deep yellow suspension was stirred for 0.5 h at rt. Then a solution of ketone **9** (3.12 g, 20.0 mmol) in Et₂O (40.0 mL) was added dropwise to the reaction mixture. The suspension was stirred under reflux for 1h, cooled to rt and further stirred for 18 h. The reaction mixture was then washed with brine (2 x 20 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The residue was dissolved in EtOAc and Ph₃P=O was precipitated by adding hexane slowly. The mixture was filtered through a short silica pad and the solvent removed under reduced pressure. FC (hexane/EtOAc 93:7) gave **10** (2.62 g, 85%) as a yellowish oil. Physical and spectral data were in accordance with literature data.¹⁰

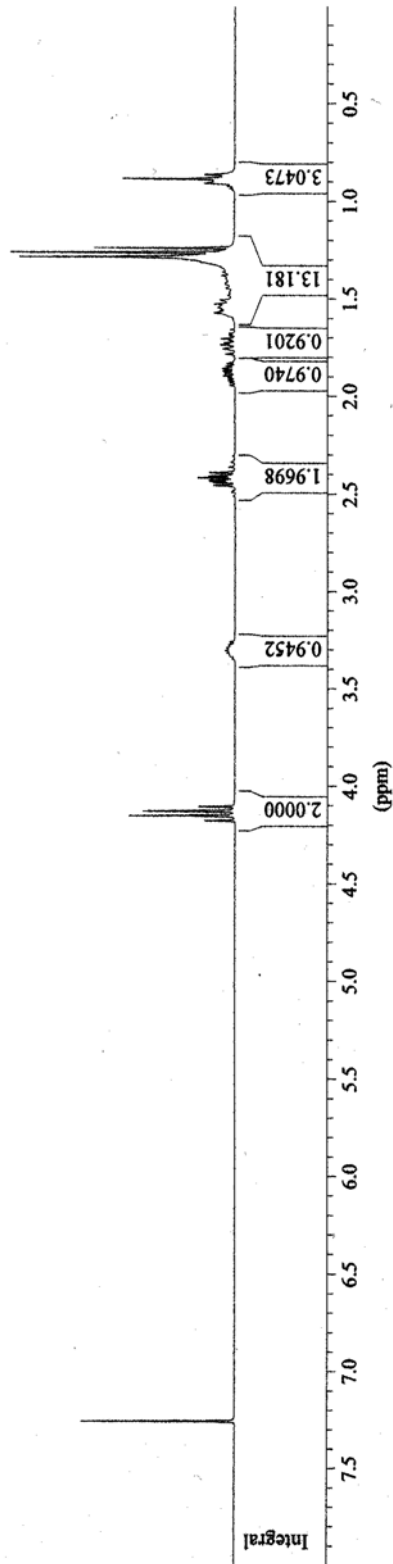
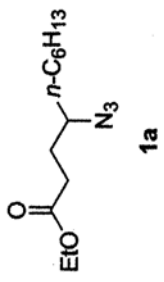
Ethyl 3-(8-azido-dioxaspiro[4.5]dec-8-yl)propanoate (11). Prepared according to General Procedure A from **10** (462 mg, 3.0 mmol), ethyl 2-iodoacetate (642 mg, 3.0 mmol), PhSO₂N₃ (1.65 g, 9.0 mmol), Bu₆Sn₂ (2.27 mL, 4.5 mmol) and DTBHN (32 mg, 0.18 mmol). Filtration (hexane then hexane/EtOAc 80:20) and FC (hexane/ EtOAc 85:15) gave **11** (678 mg, 80%) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 4.13 (*q*, *J* = 7.0 Hz, 2H), 3.97–3.87 (*m*, 4H), 2.42–2.37 (*m*, 2H), 1.94–1.88

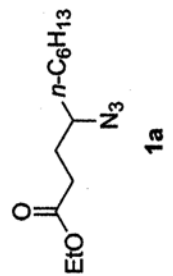
(*m*, 2H), 1.82–1.57 (*m*, 8H), 1.25 (*t*, *J* = 7.0 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 173.0, 107.9, 64.3, 64.2, 62.3, 60.6, 34.4, 31.8 (2CH₂), 30.6 (2CH₂), 28.9, 14.1; IR (film) 2094, 1735 cm⁻¹; HRMS (ESI) for C₁₃H₂₁N₃O₄Na: calcd 306.1429, found 306.1410.

1,4-dioxa-9-azadispiro[4.2.4.2]tetradecan-10-one (12). Prepared according to General Procedure C from azide **11** (283 mg, 1 mmol) and 10% Pd/C (90 mg, 30% w/w). FC (EtOAc/MeOH 99:1) gave **12** (177 mg, 84%) as a white solid. Physical and spectral data were in accordance with literature data.¹¹

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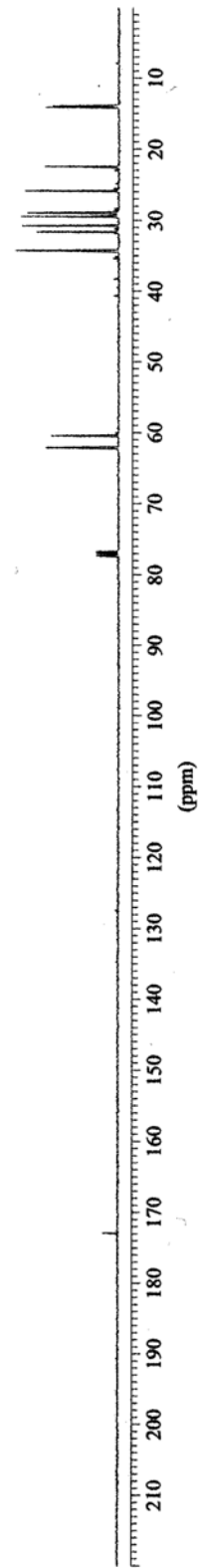


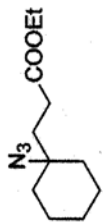
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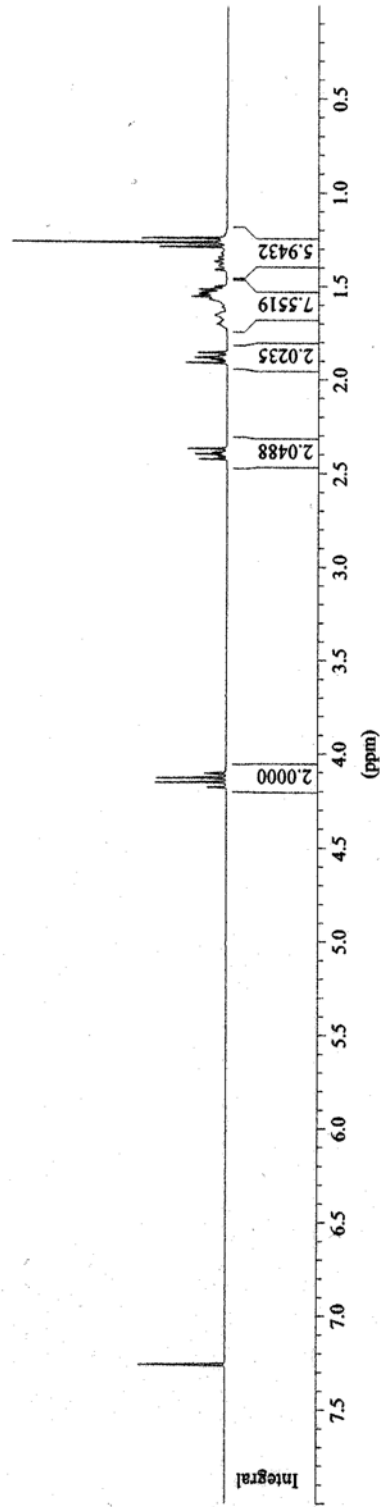
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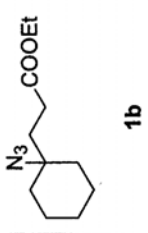
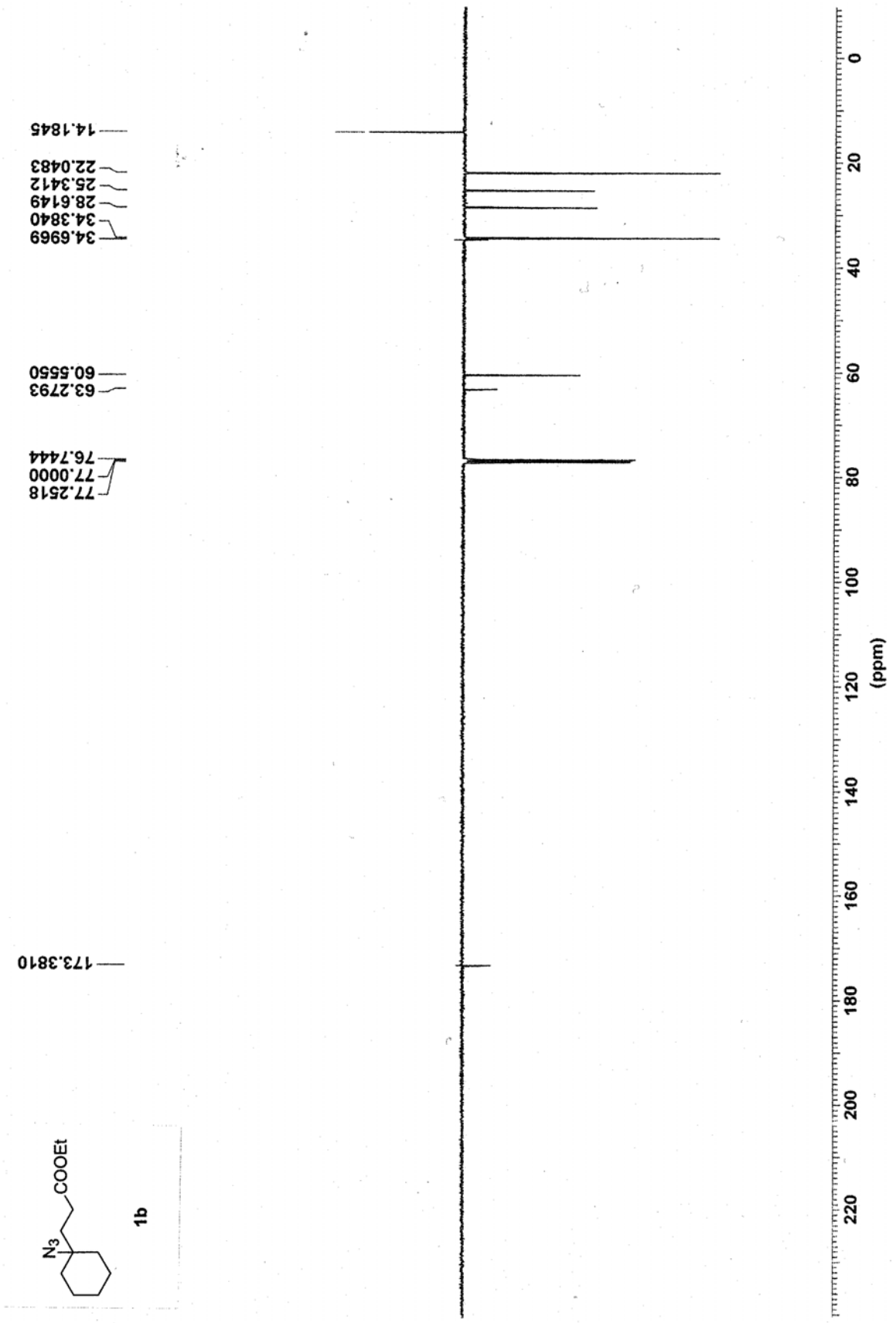
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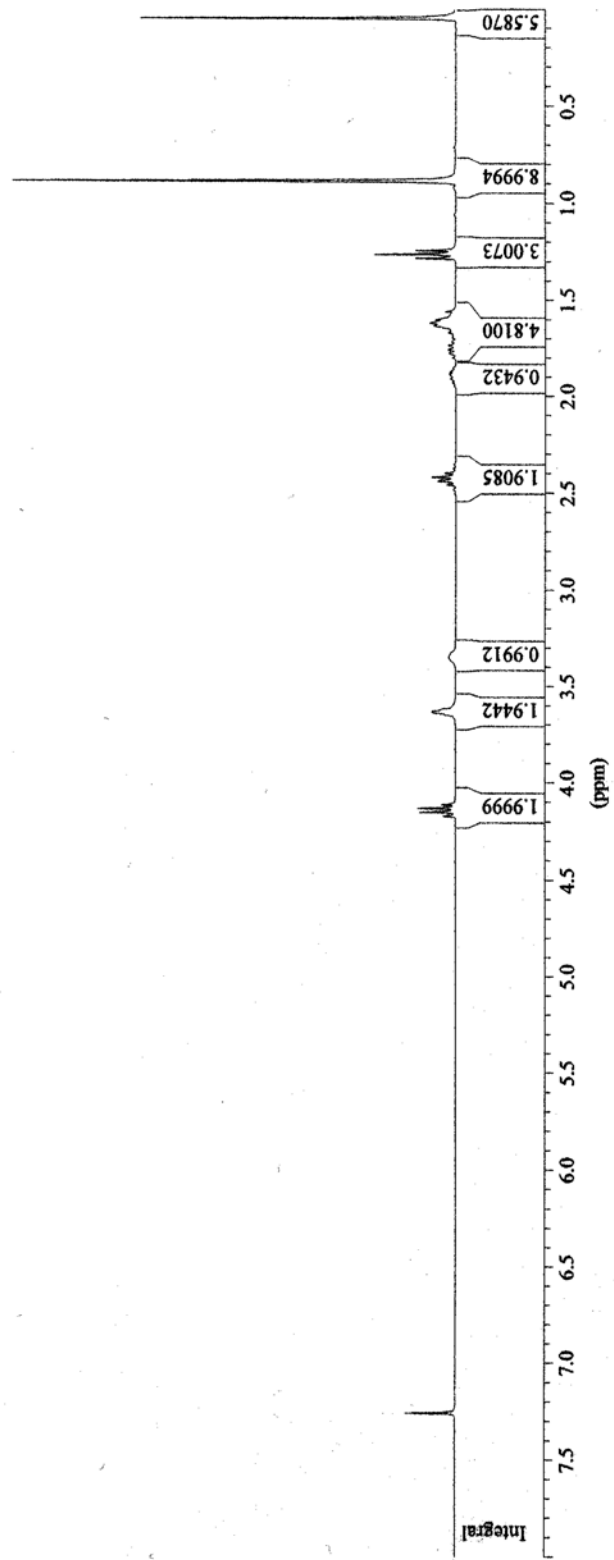
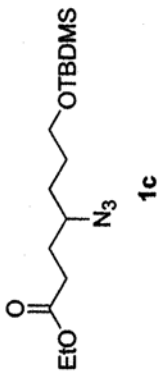


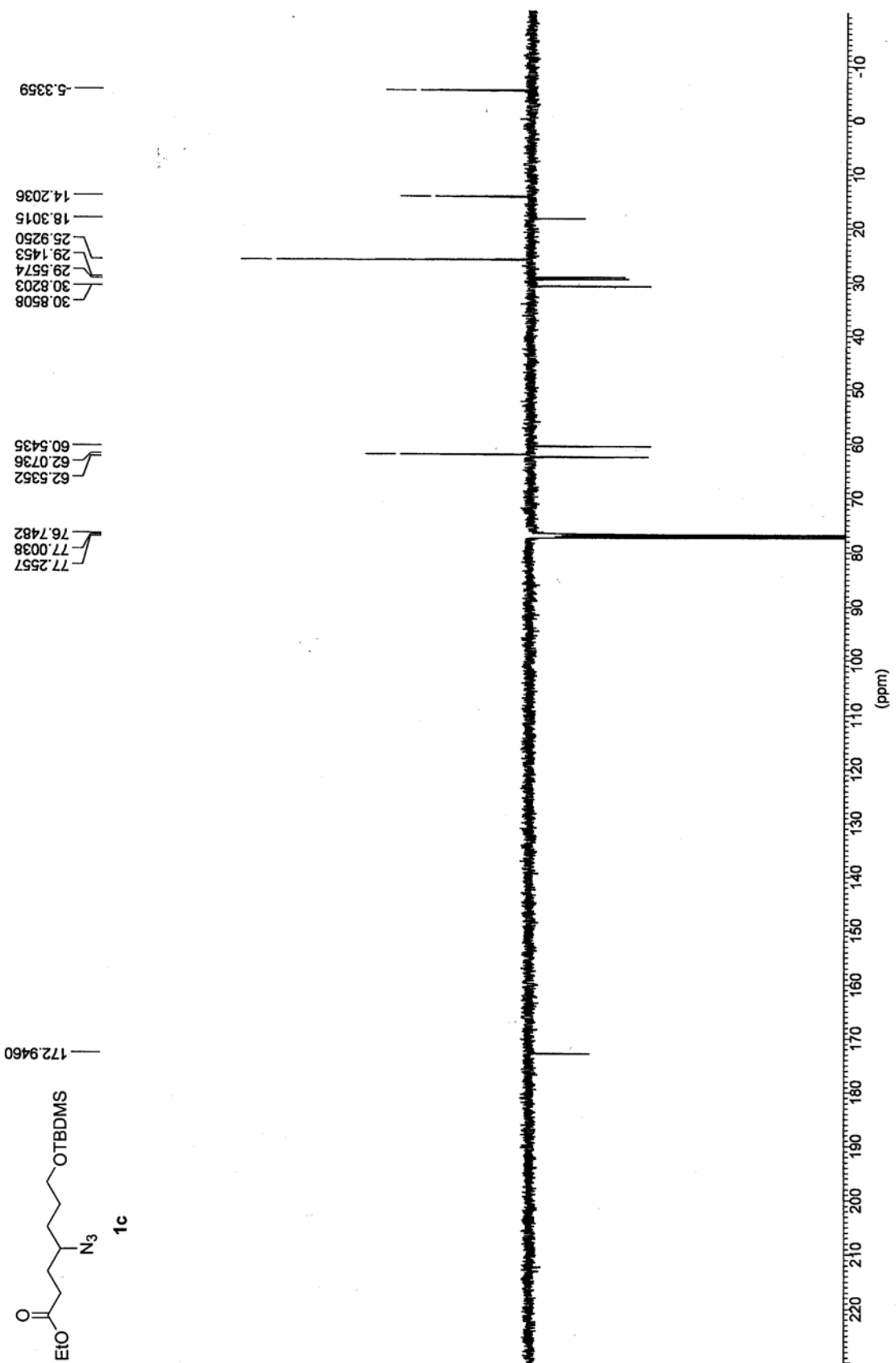


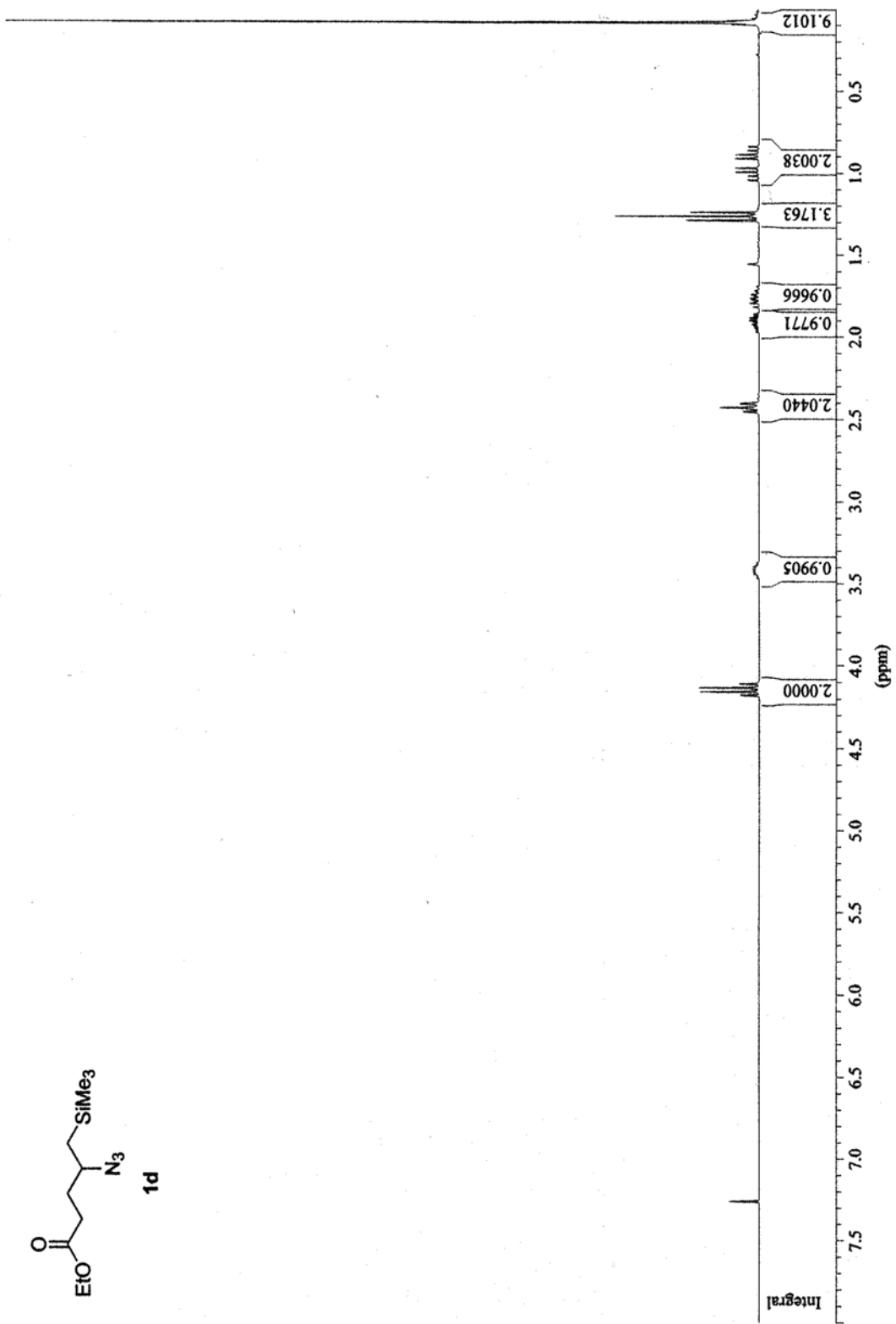
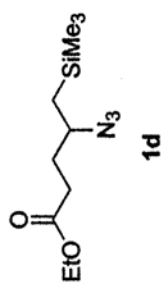
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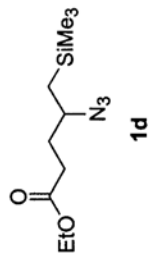












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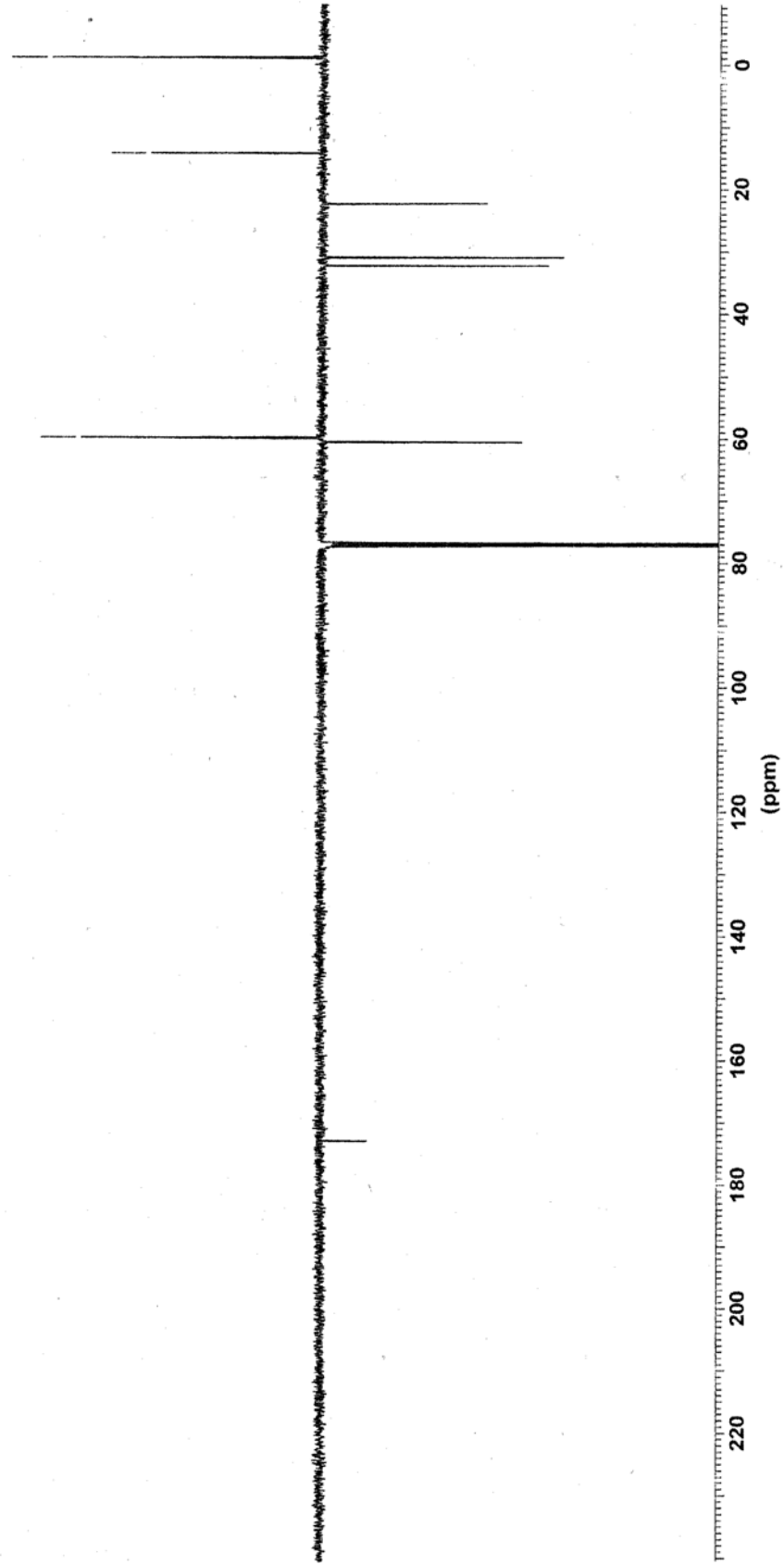
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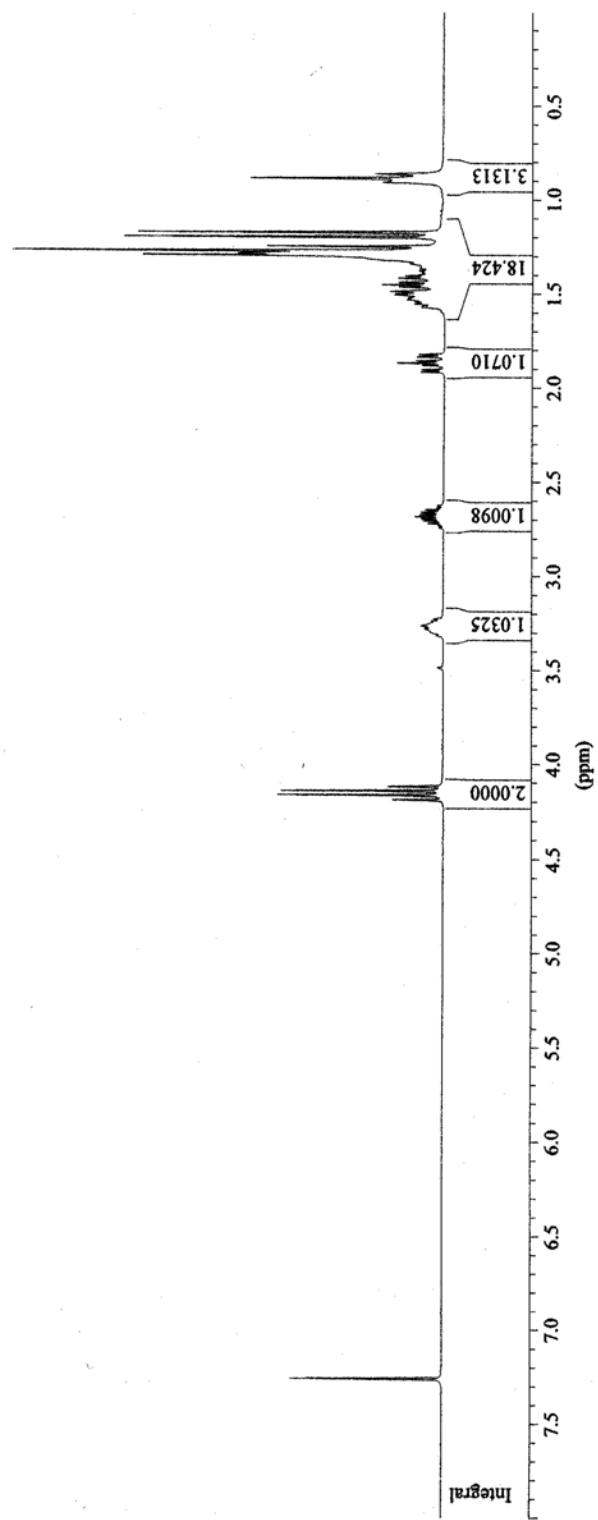
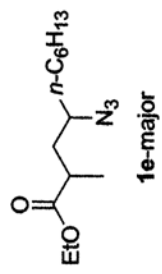
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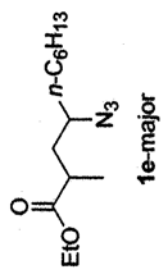
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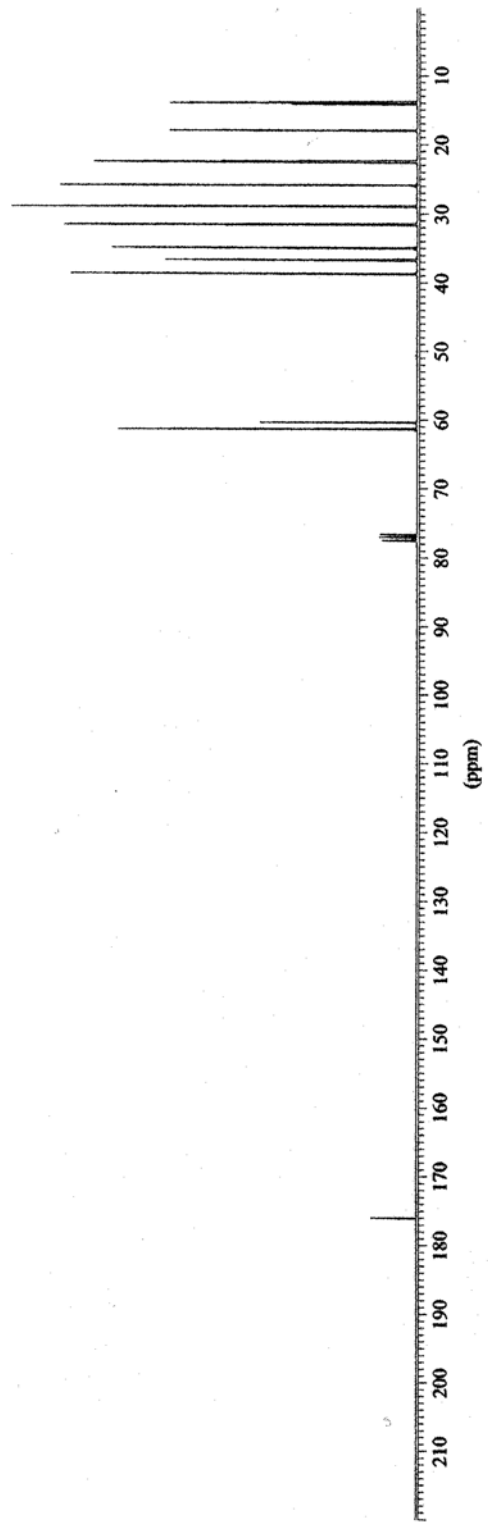


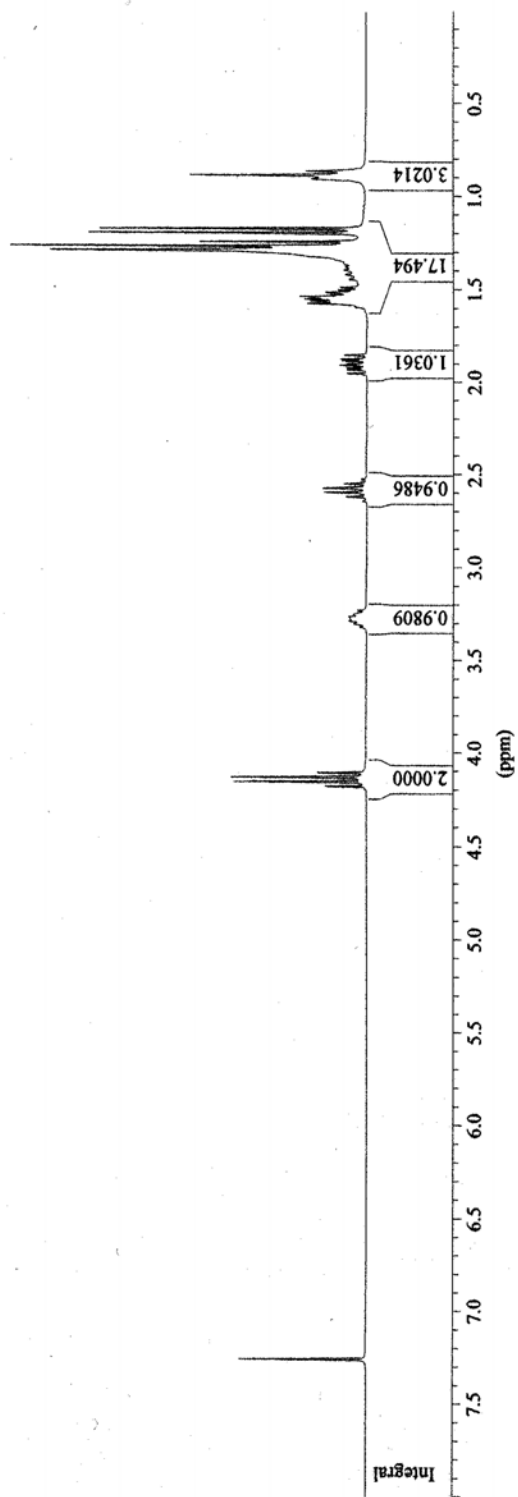
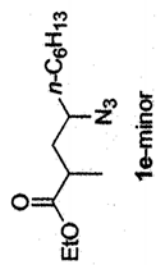
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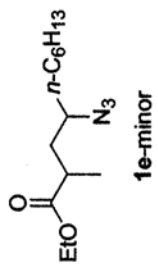
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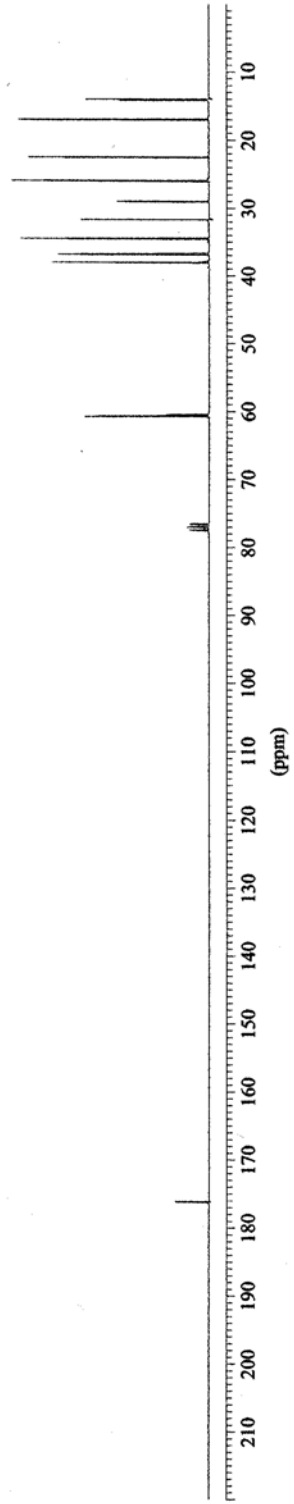


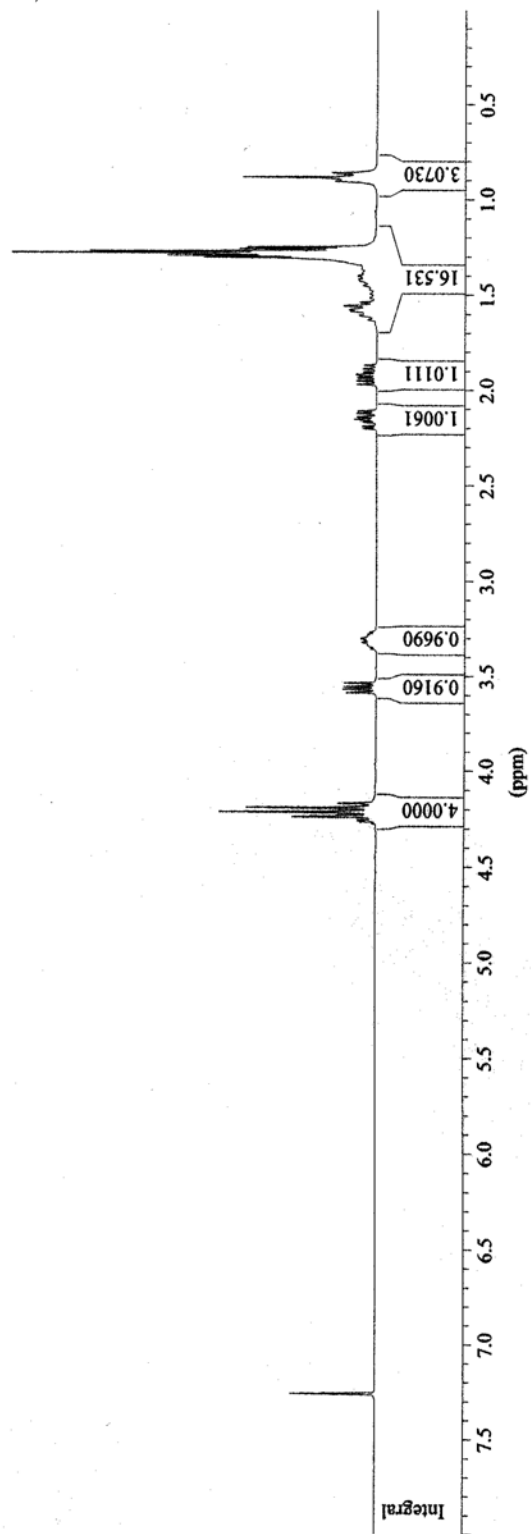
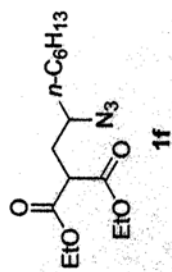
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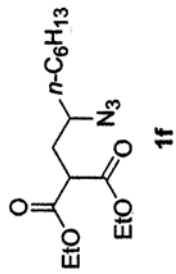
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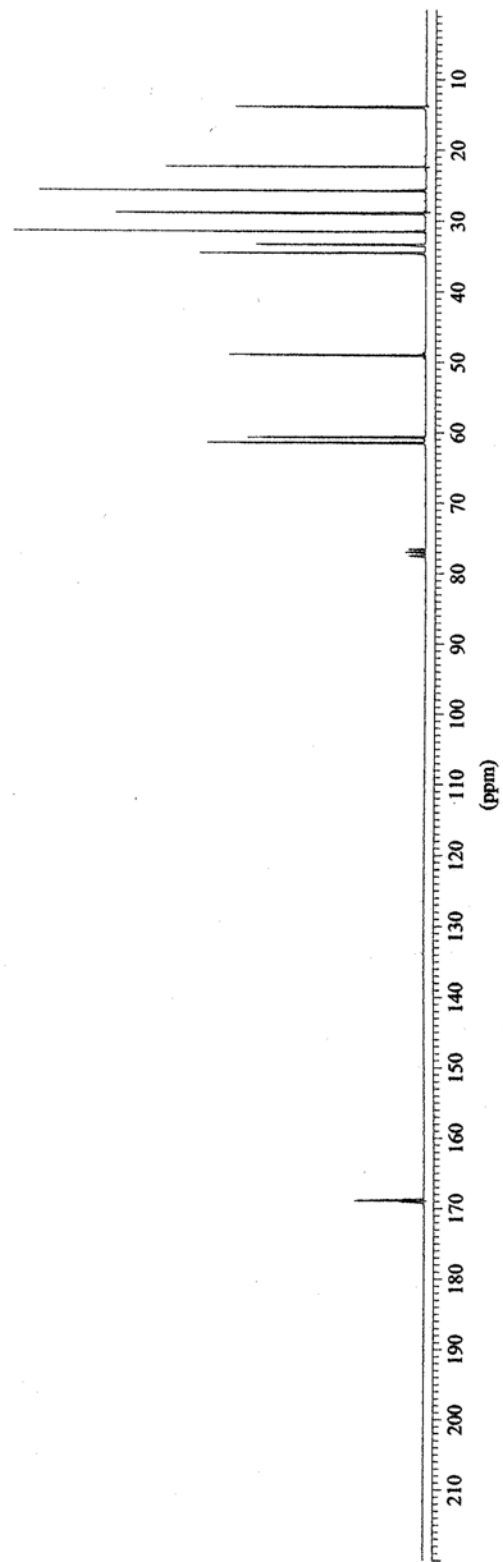
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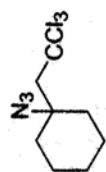
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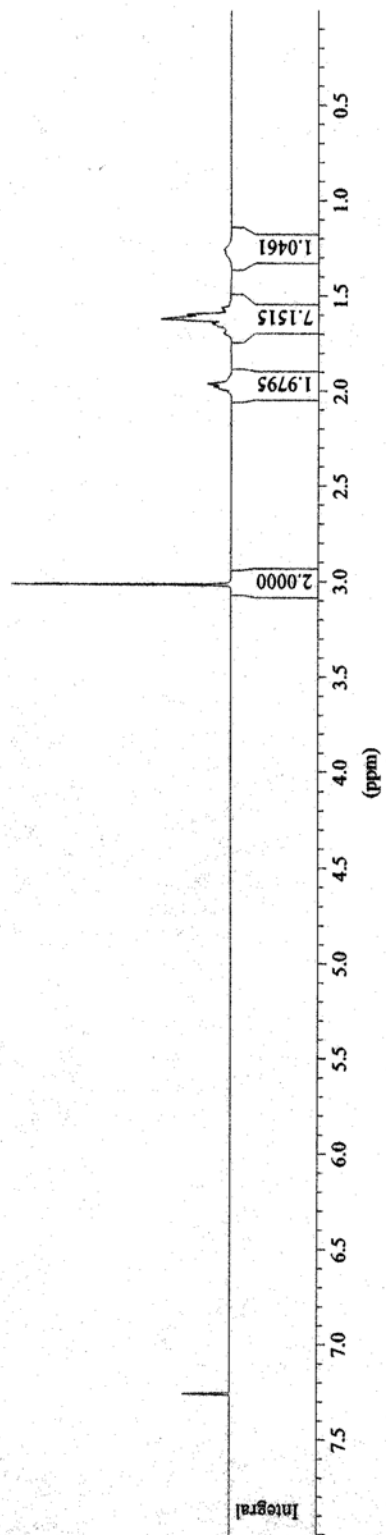
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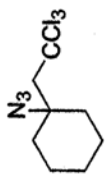
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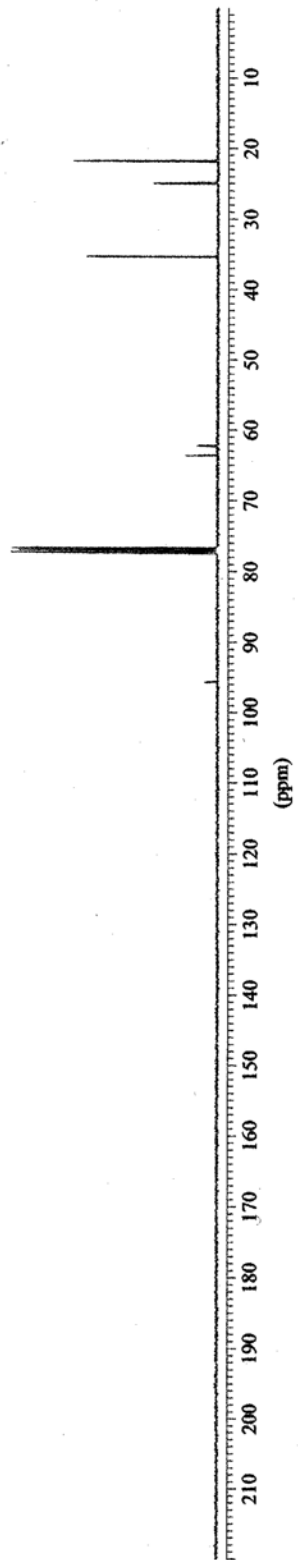
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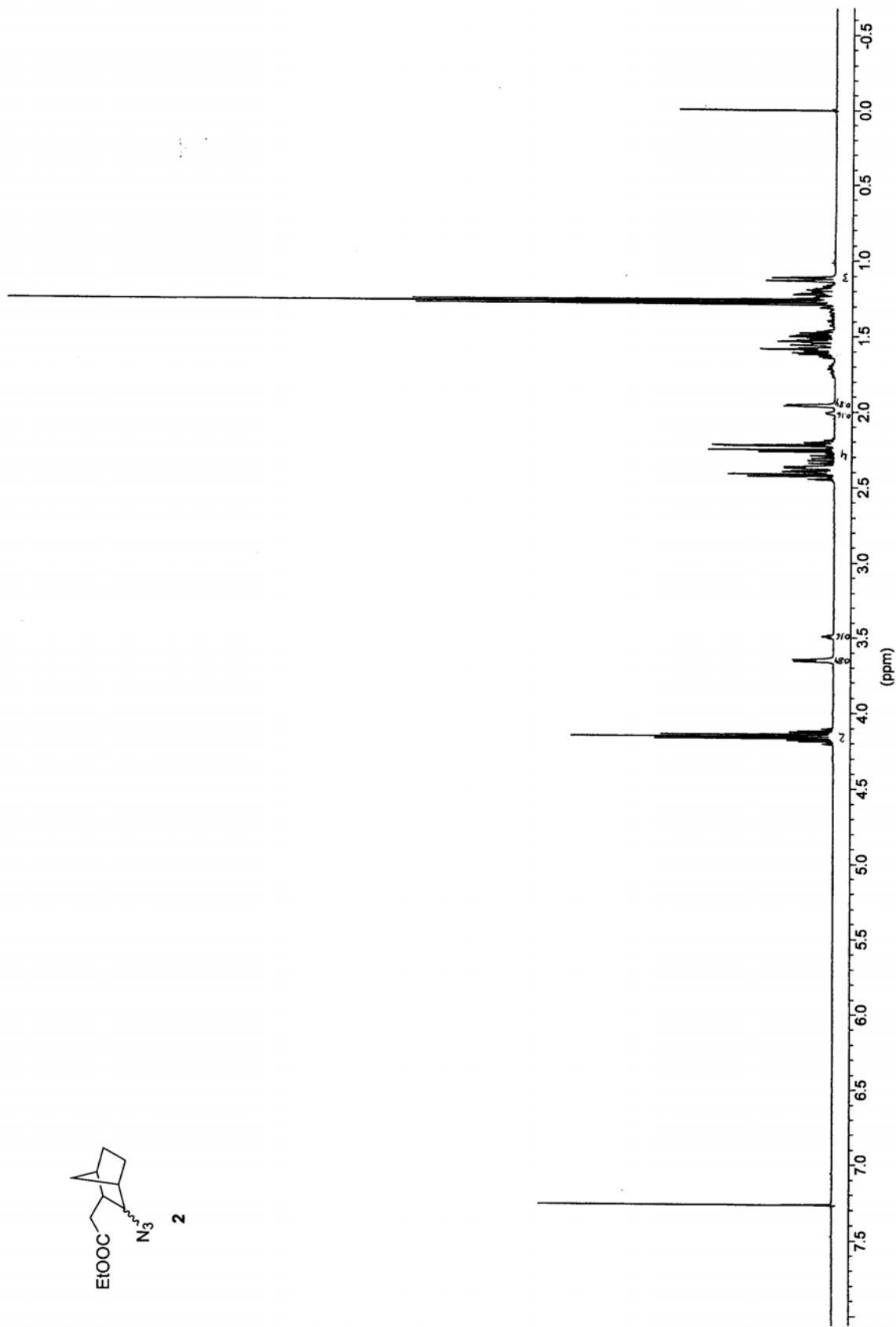
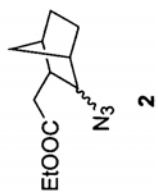




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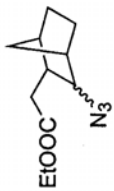
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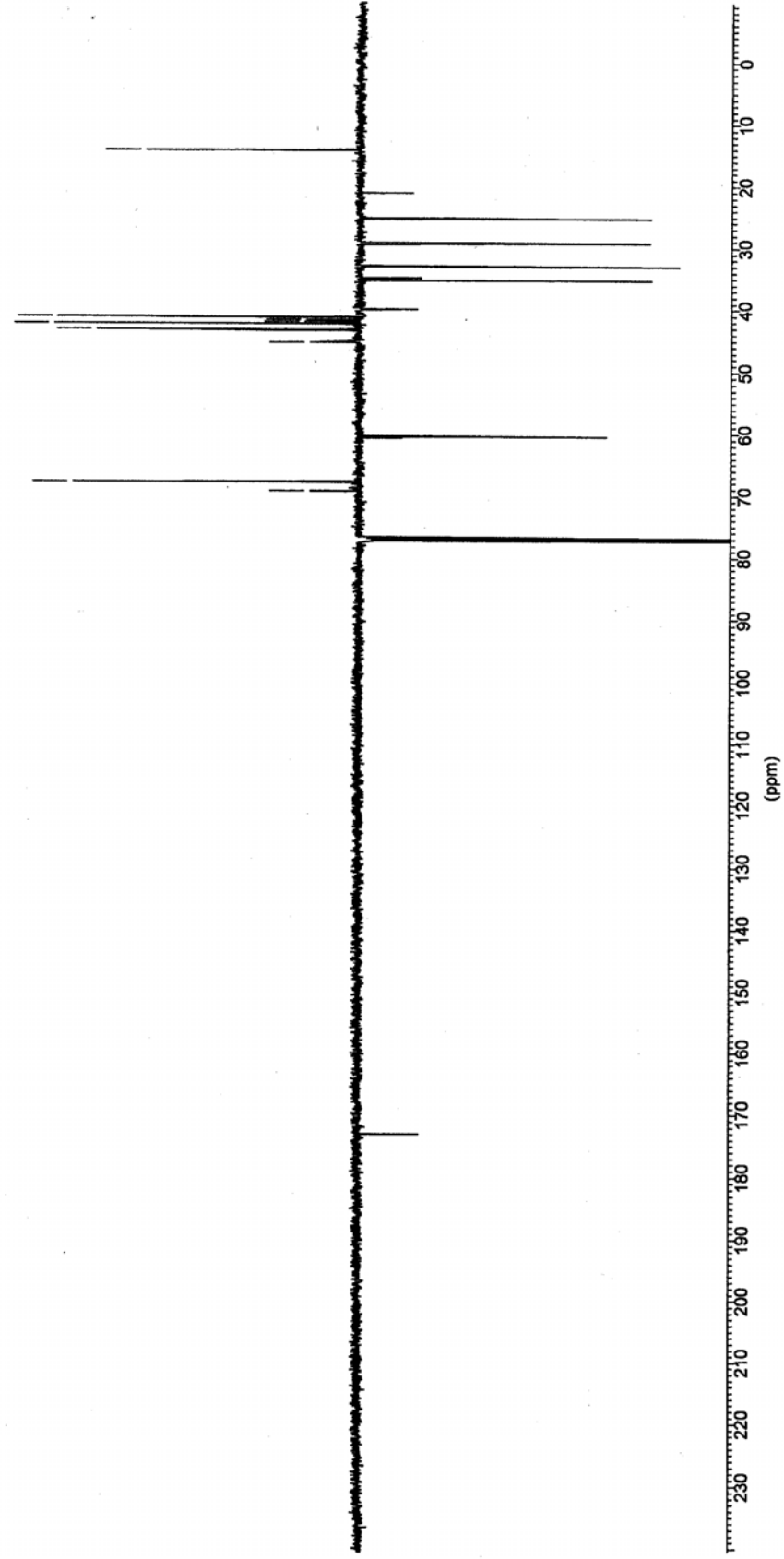


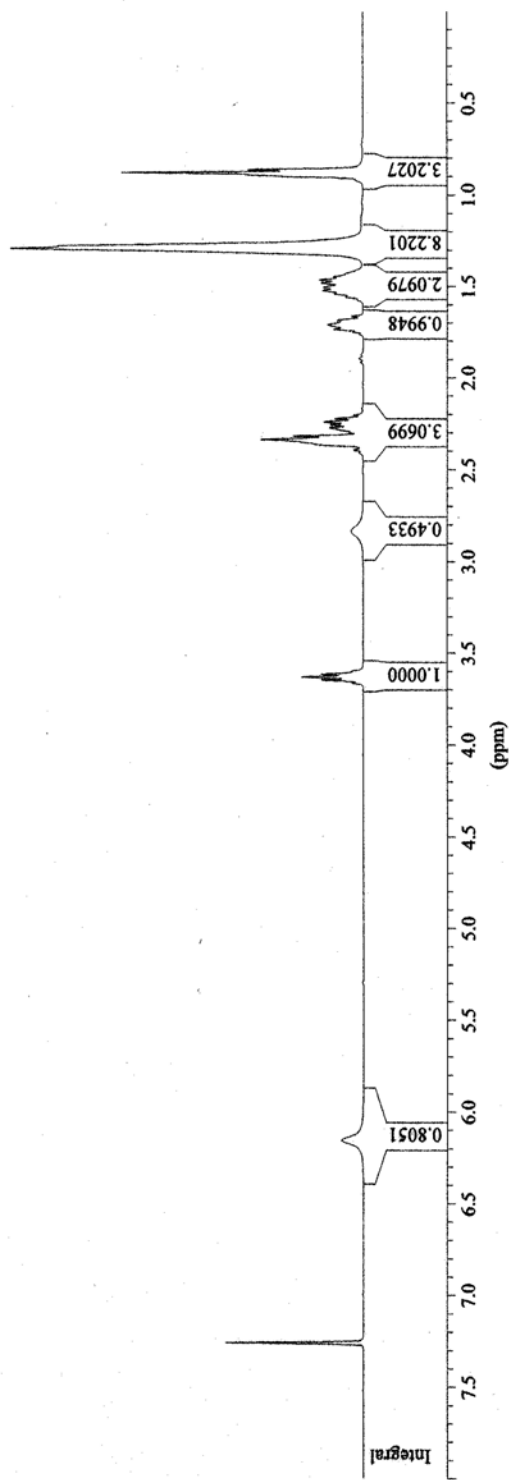
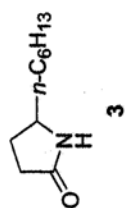
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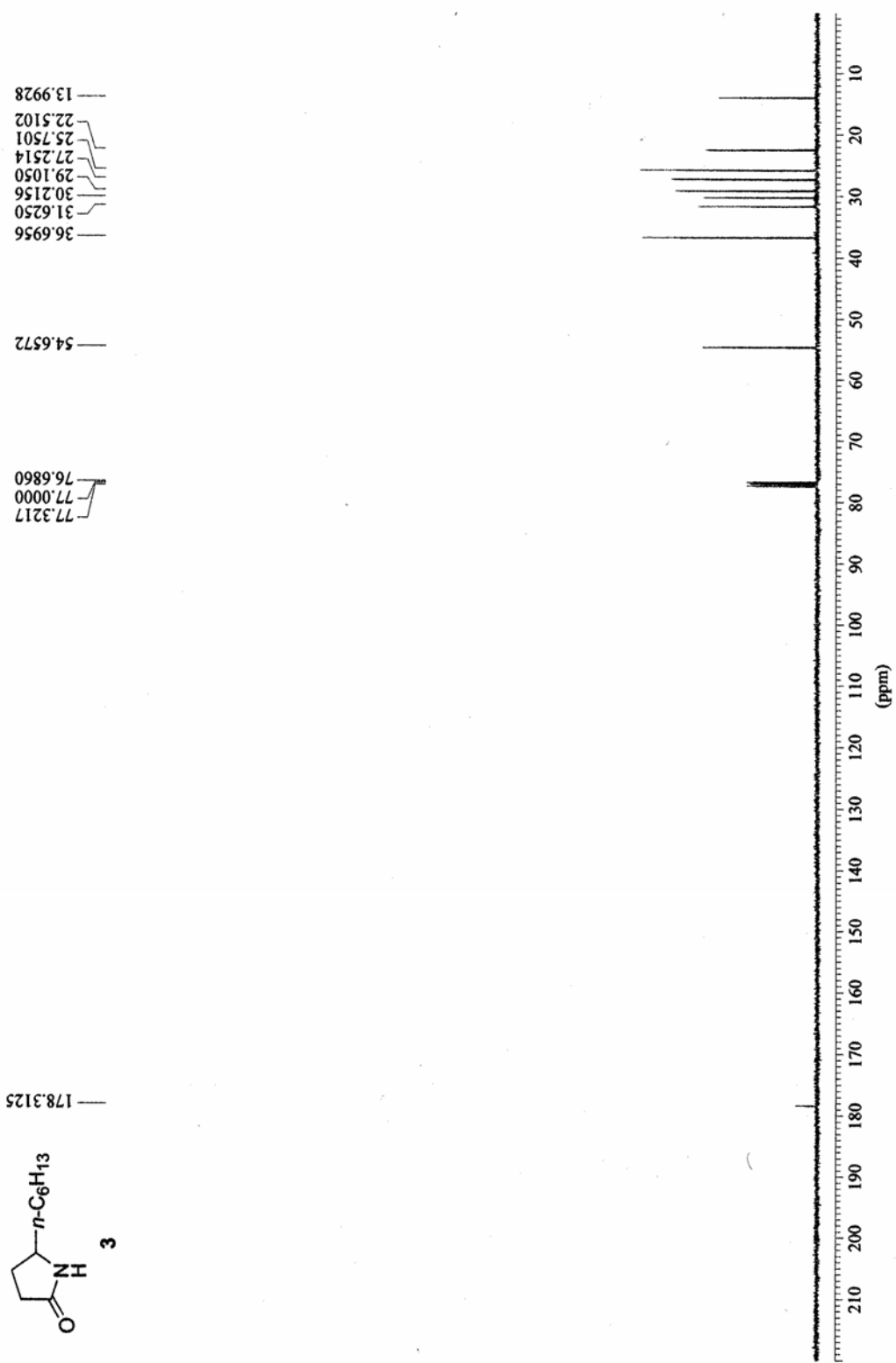
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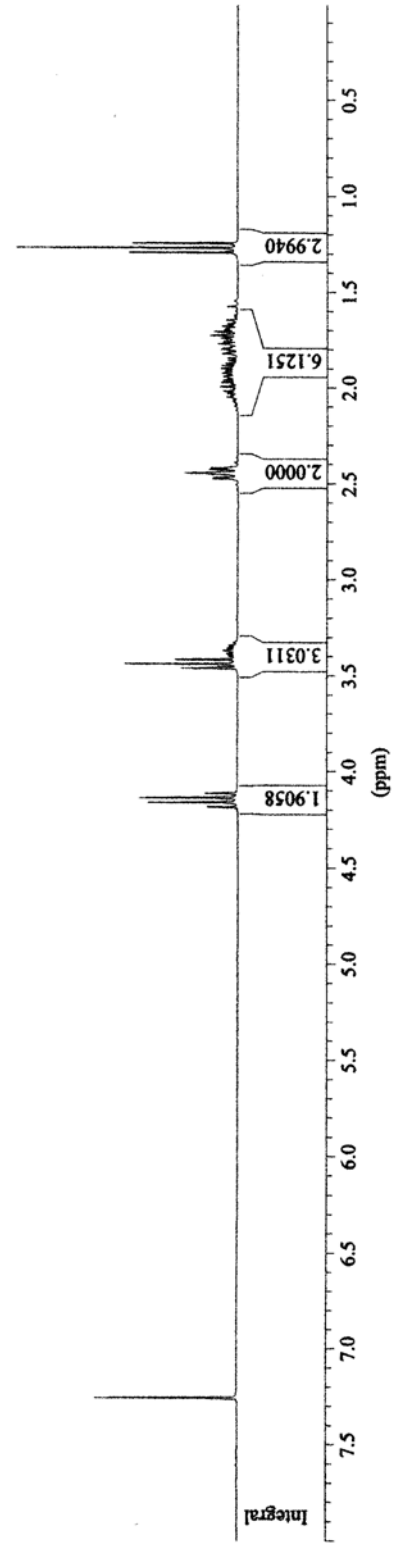
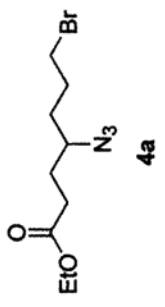


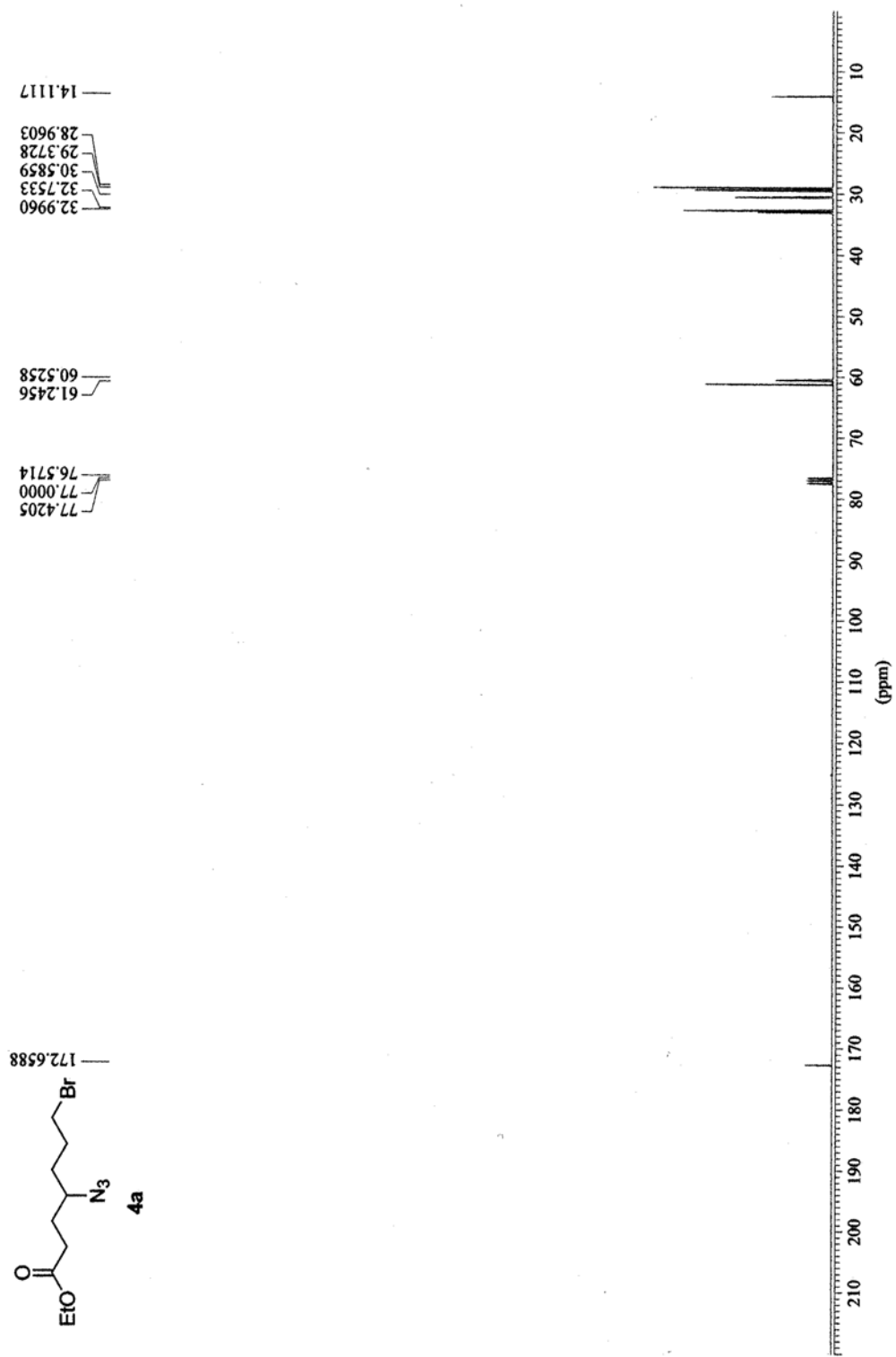
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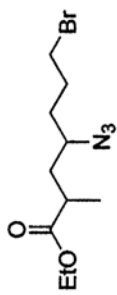




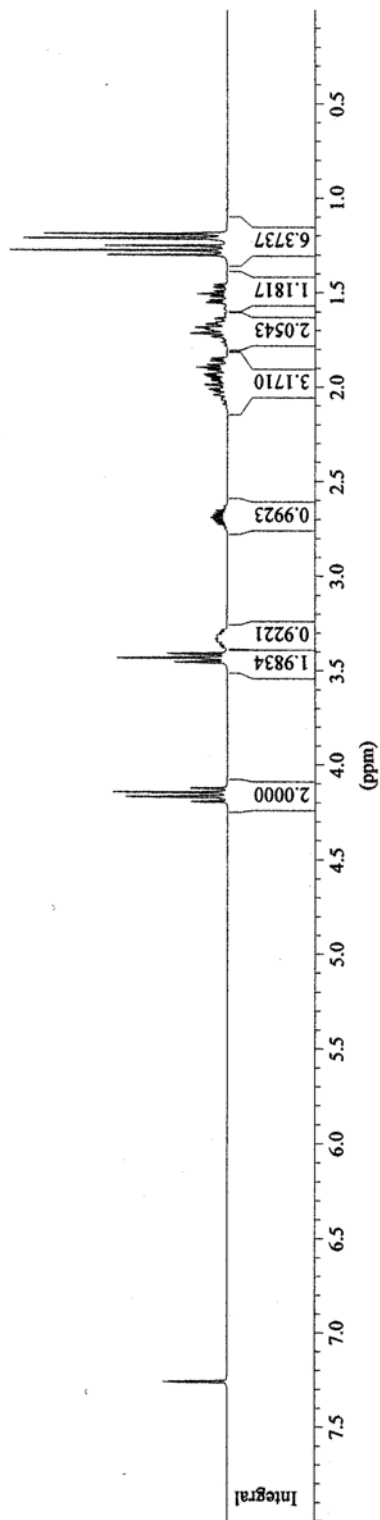


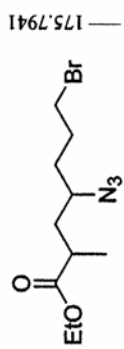






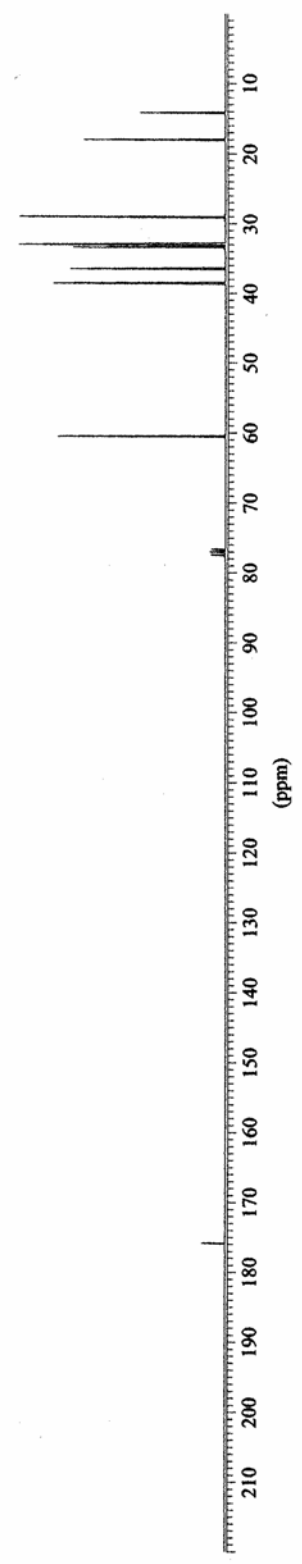
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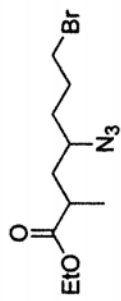




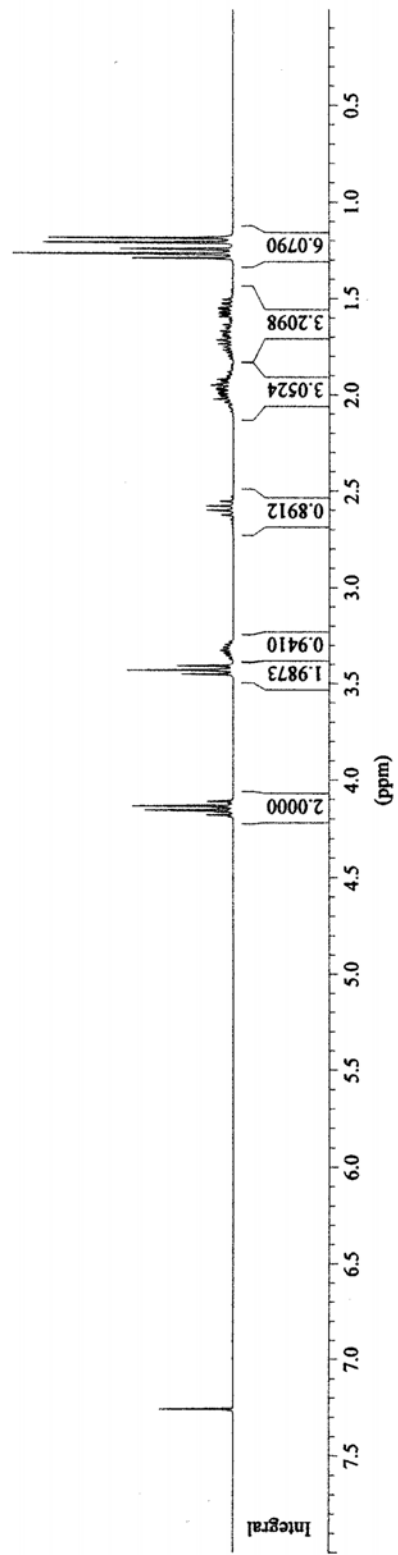
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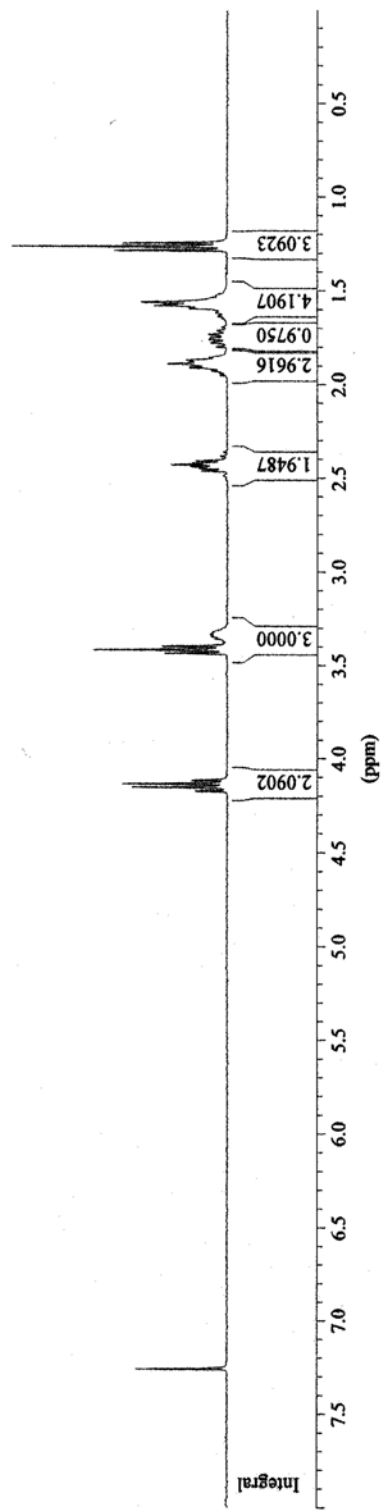
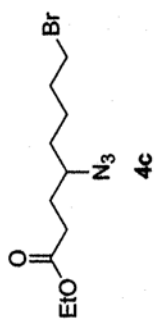
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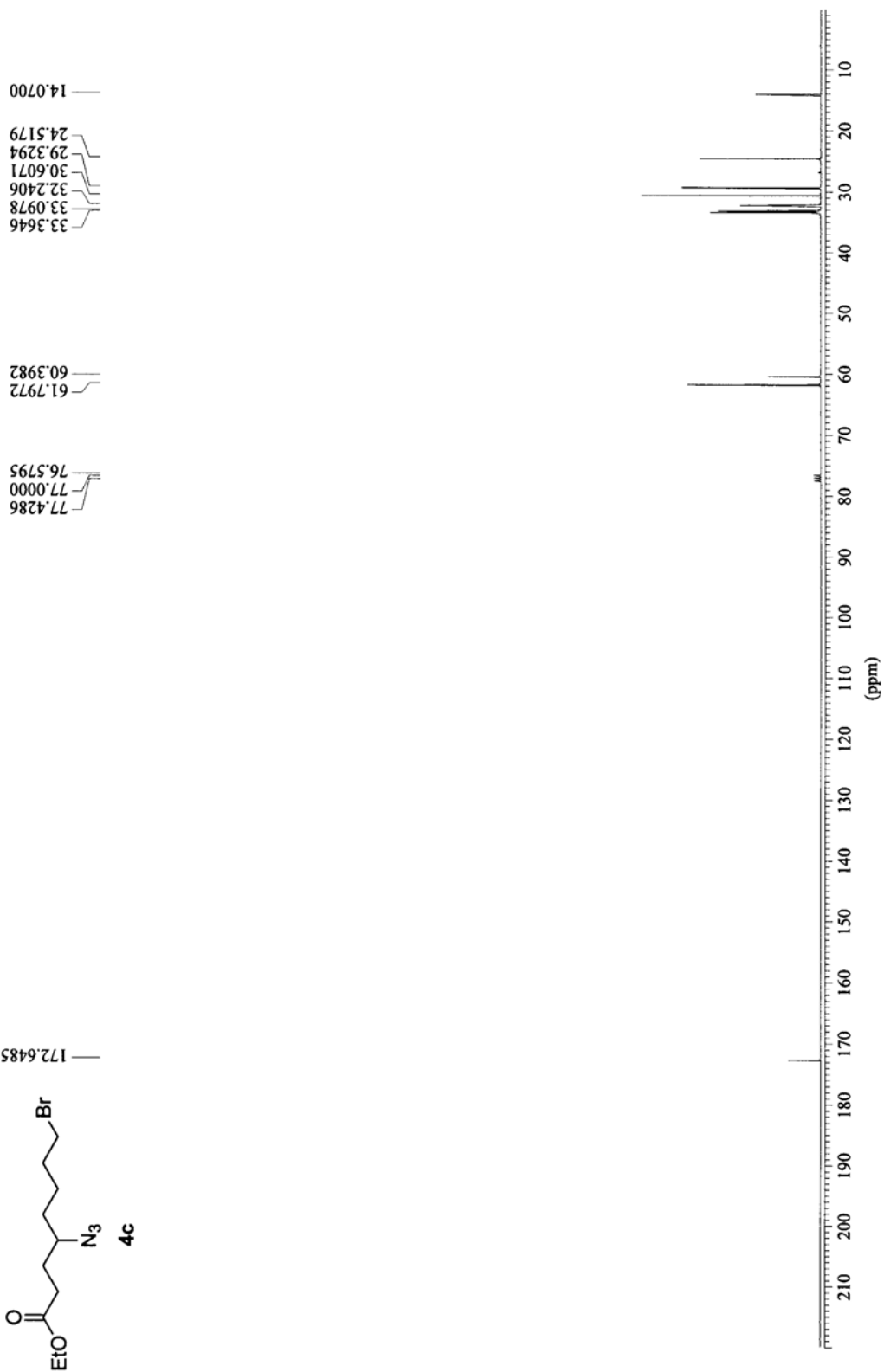


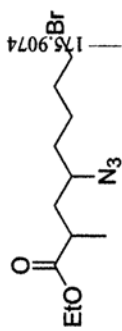


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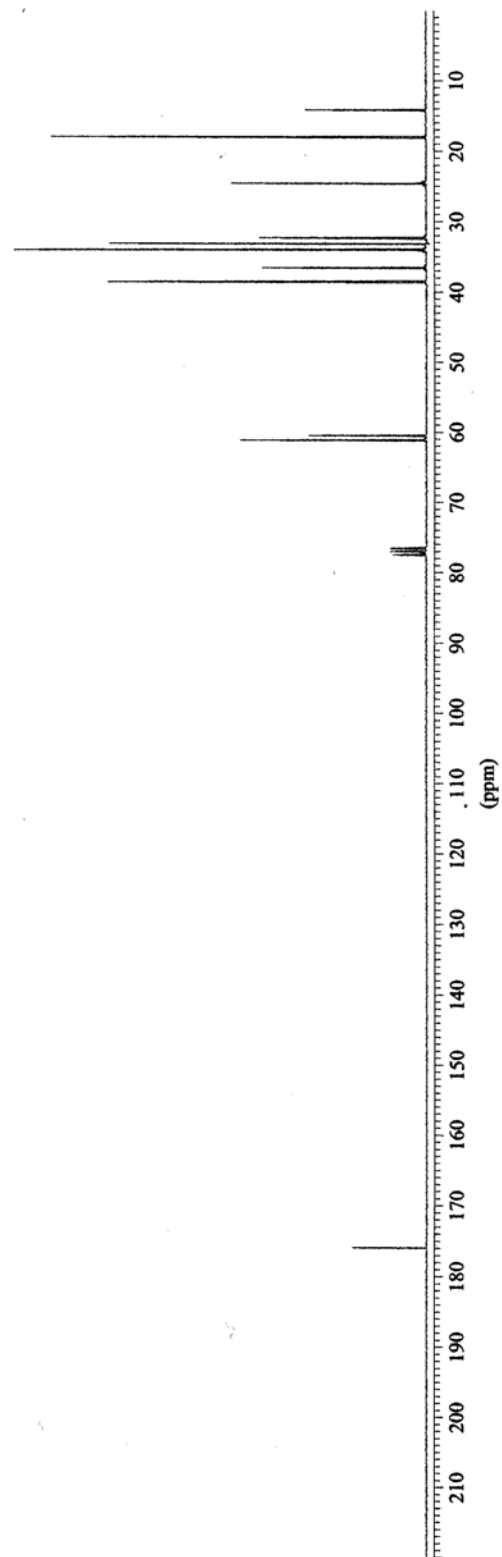


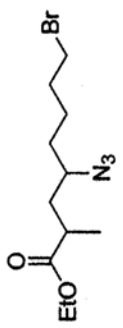




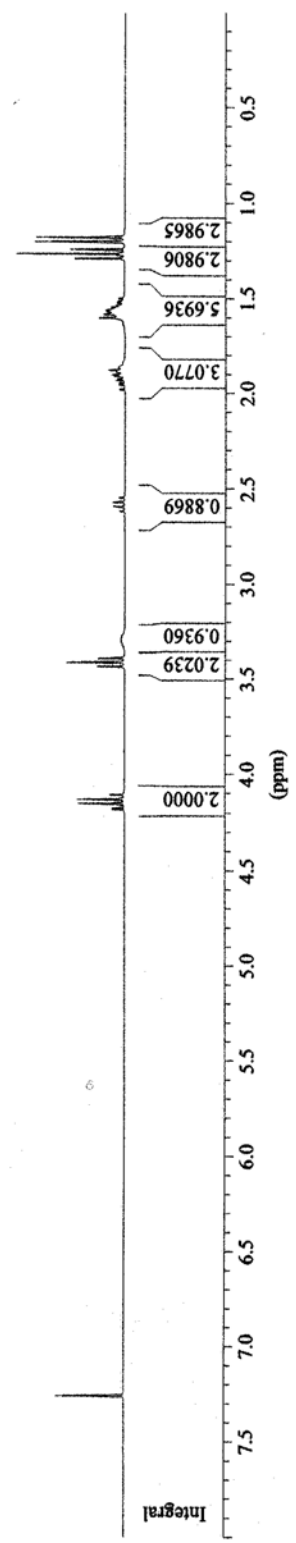
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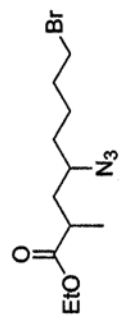
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4d-minor





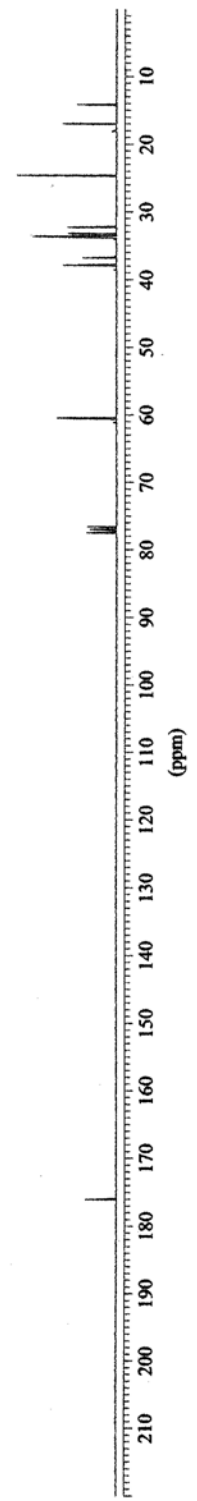
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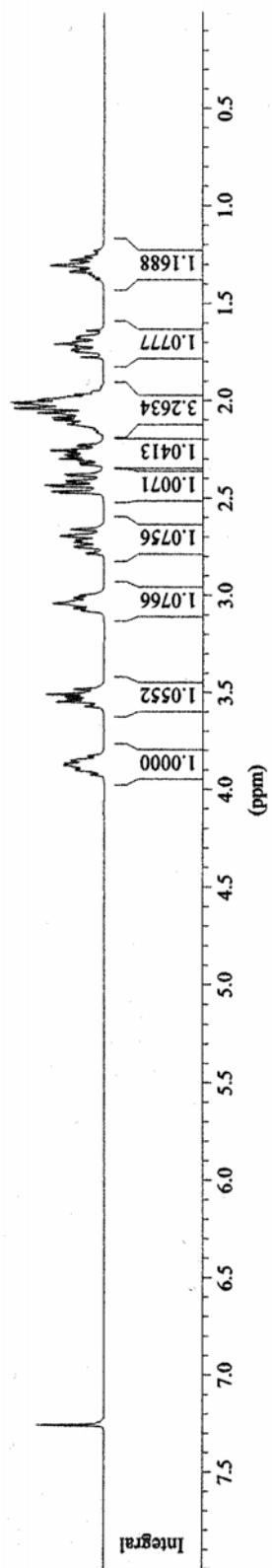
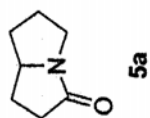
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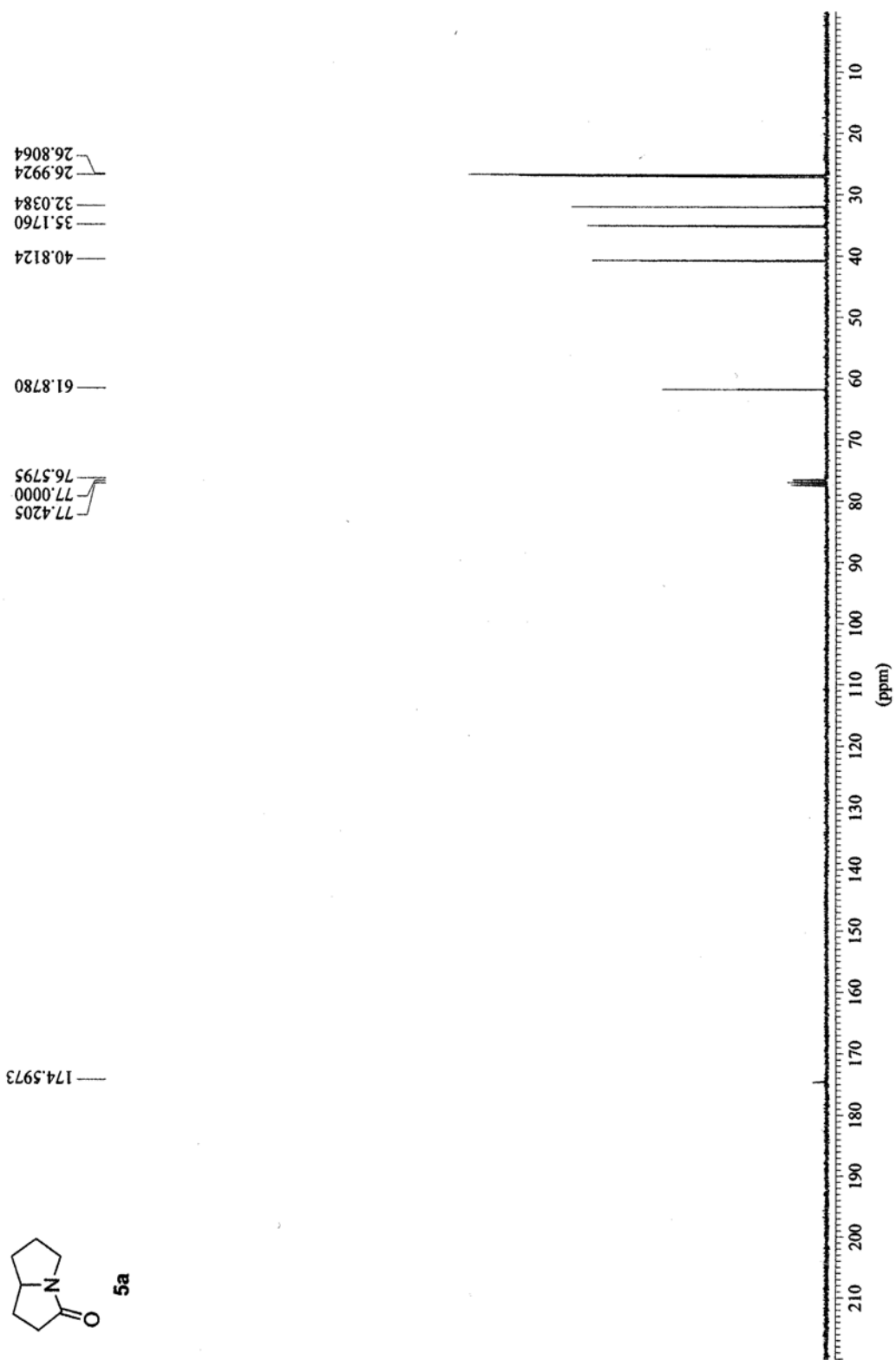
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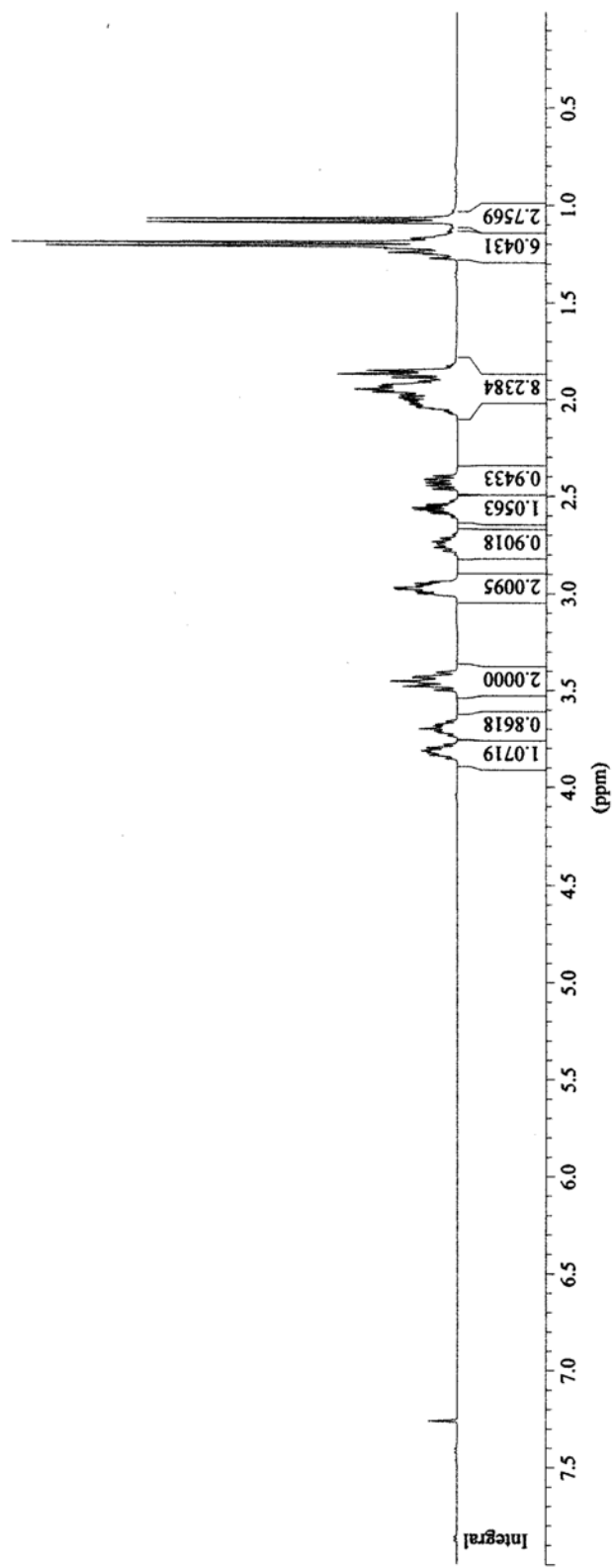
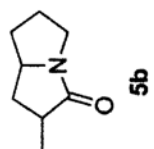
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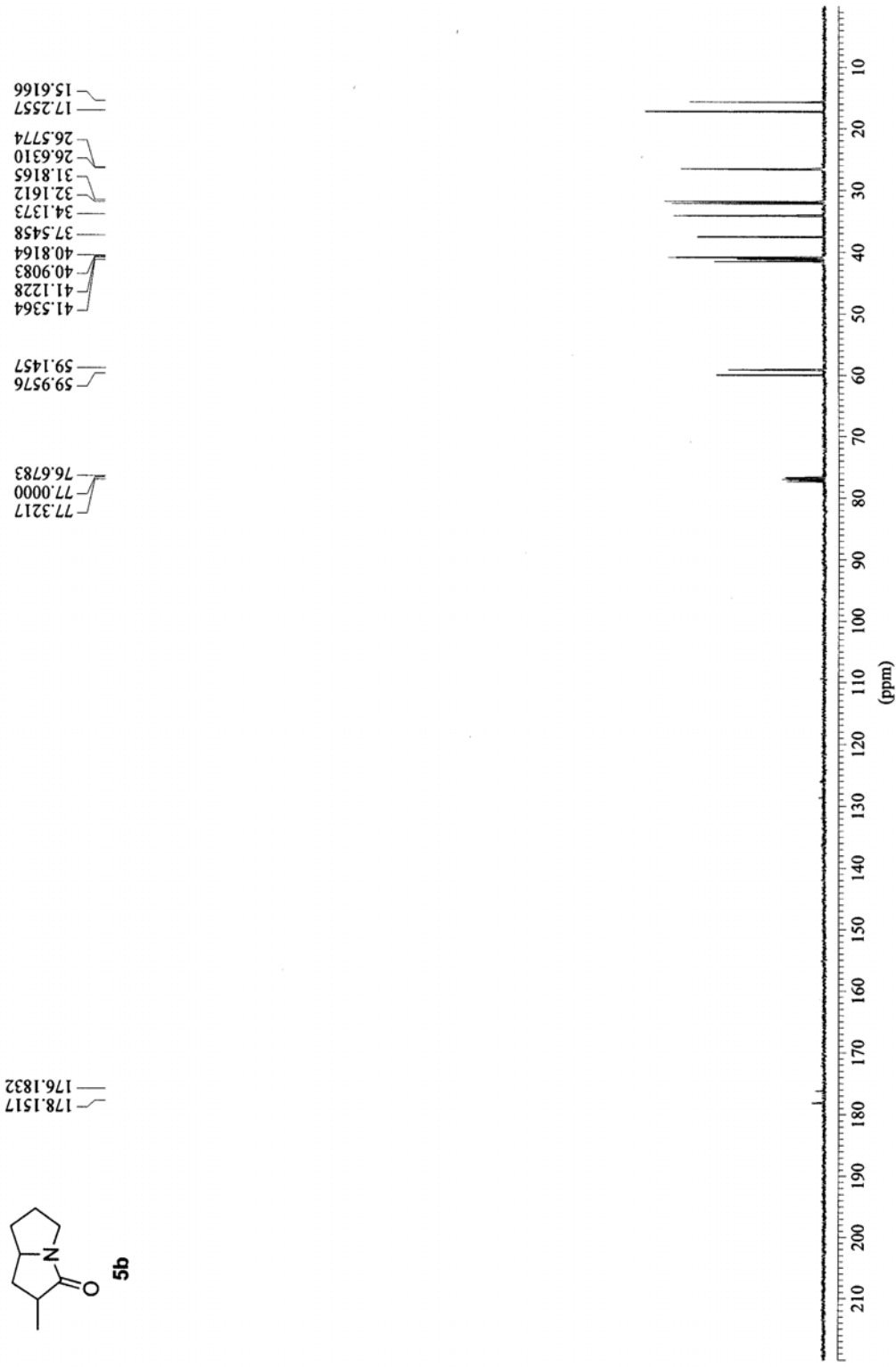
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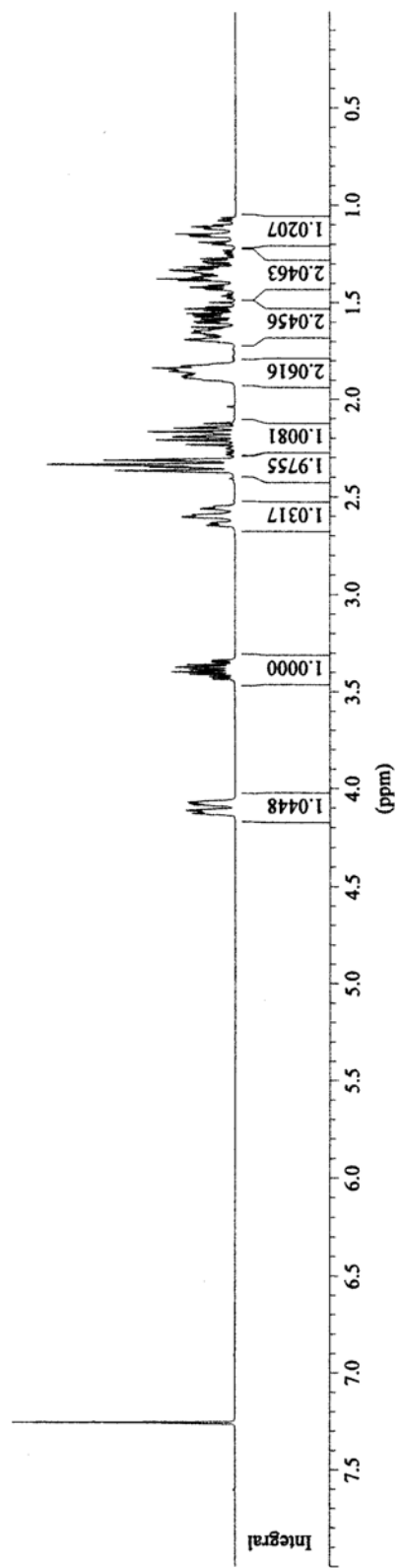
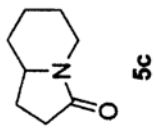


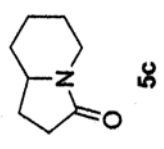
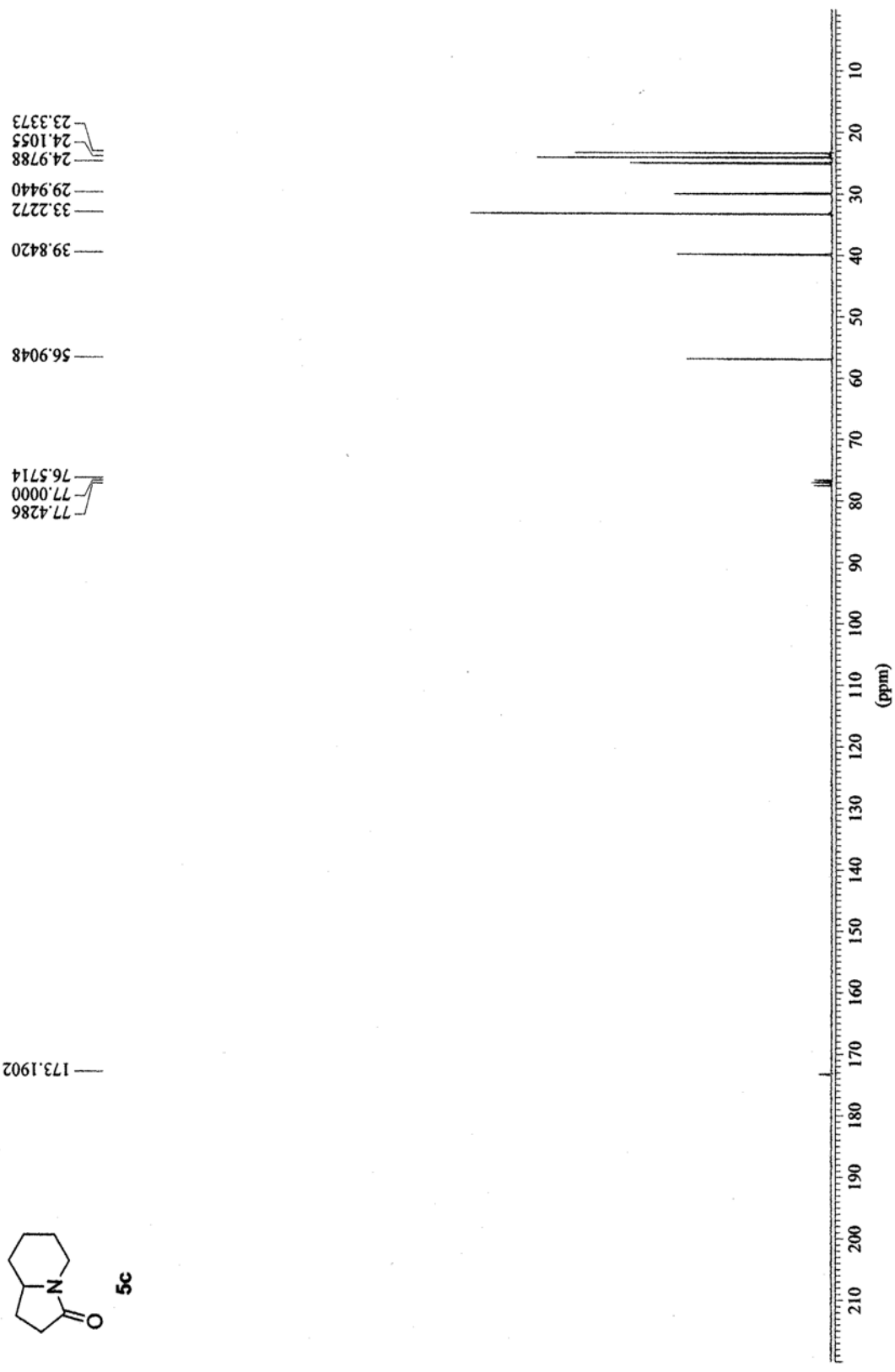


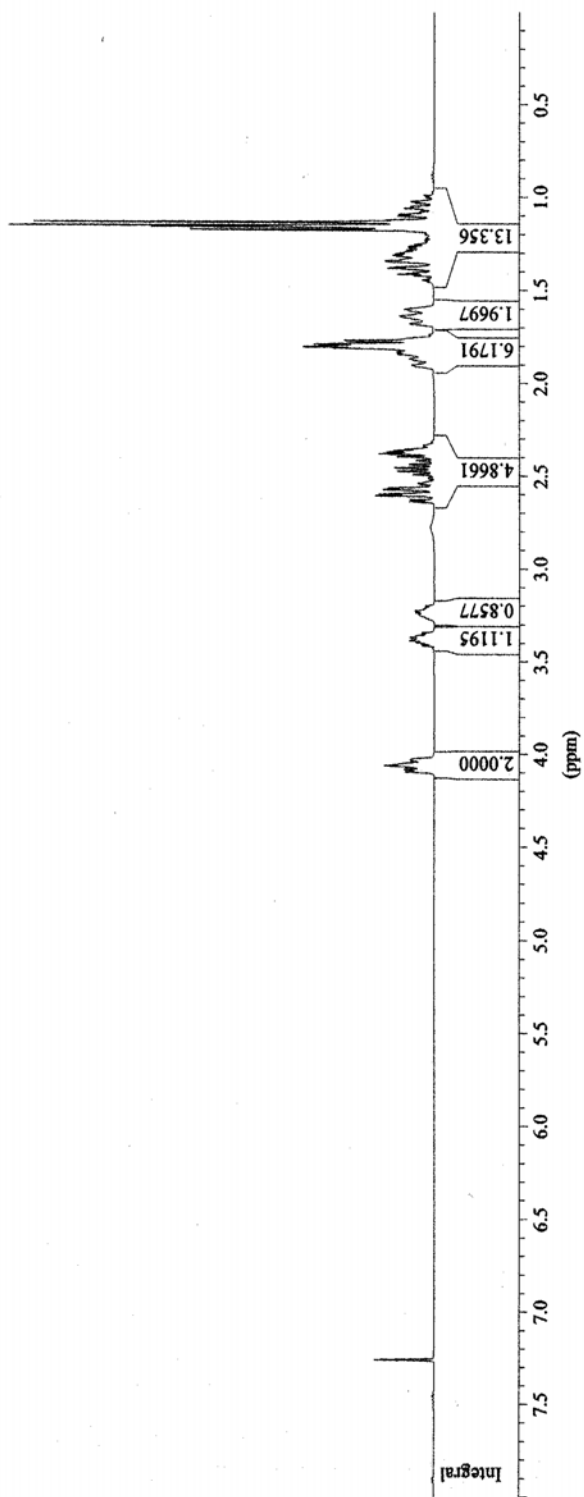
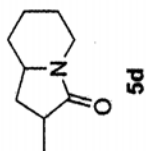


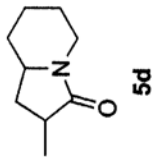






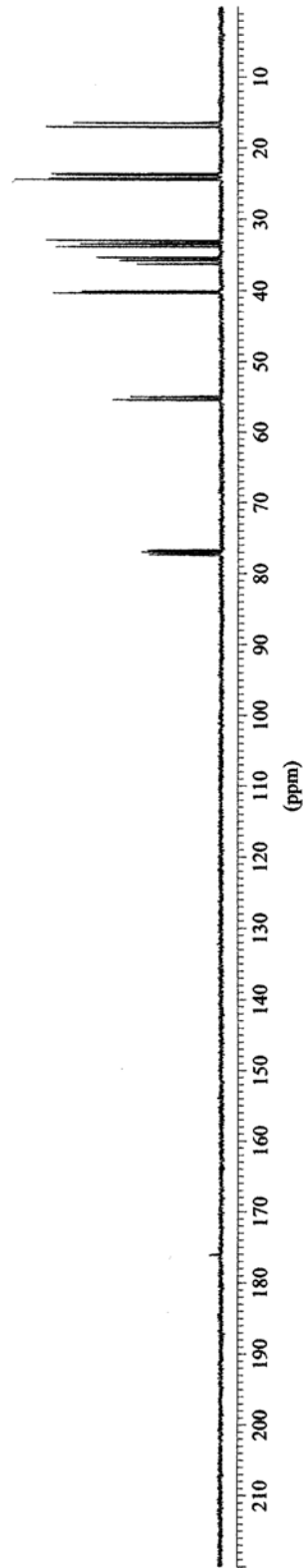


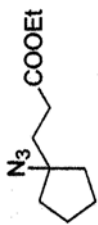




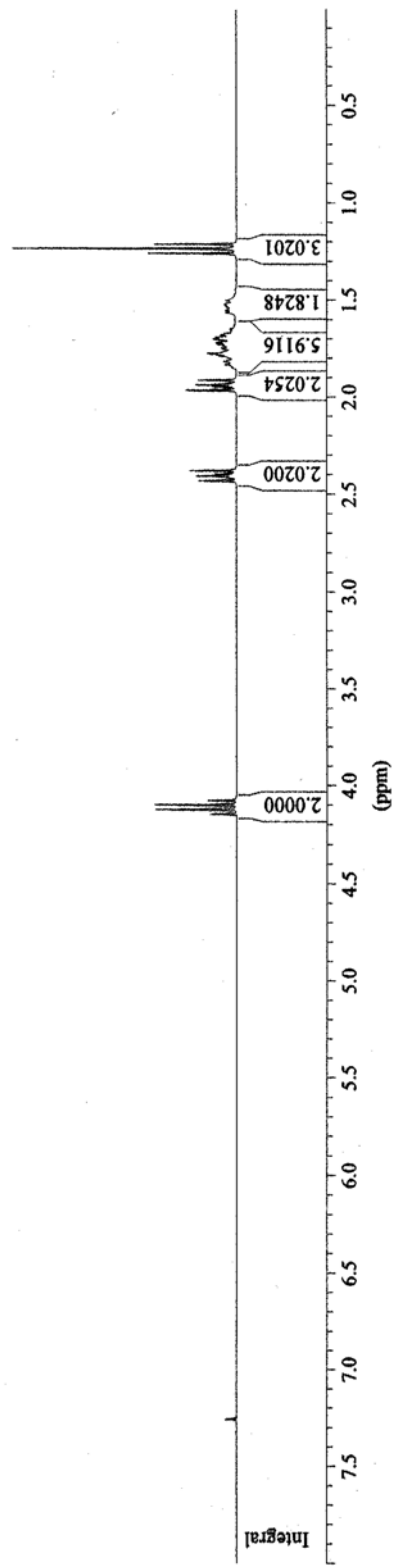
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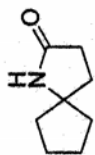




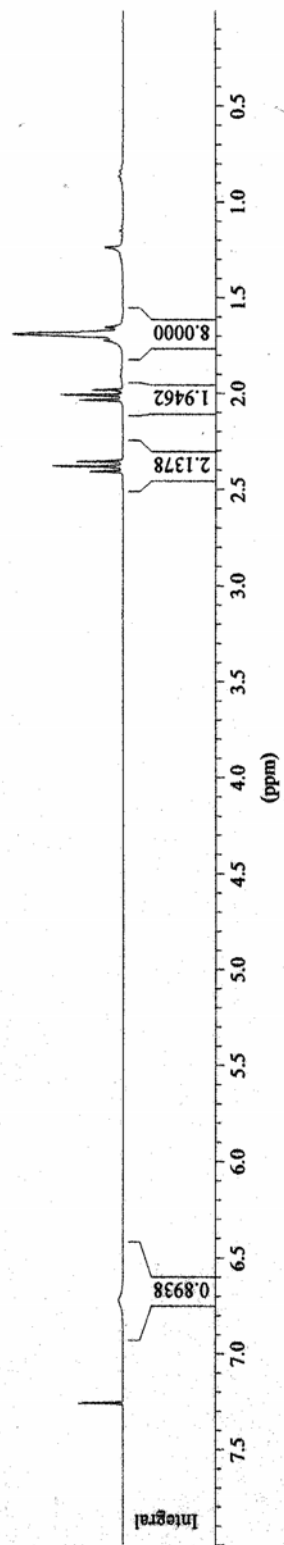
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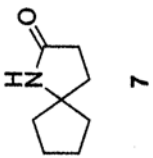
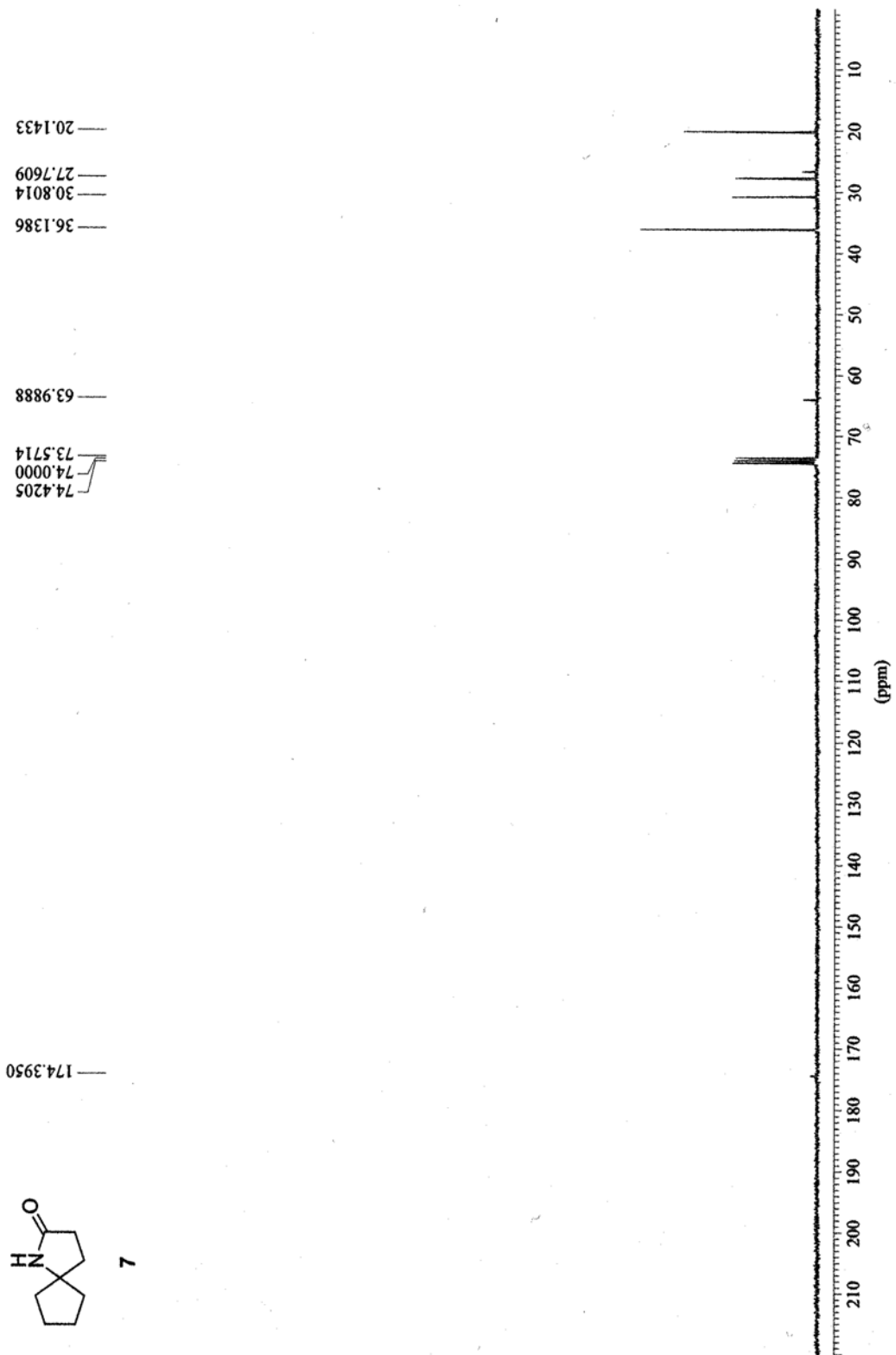


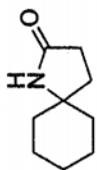




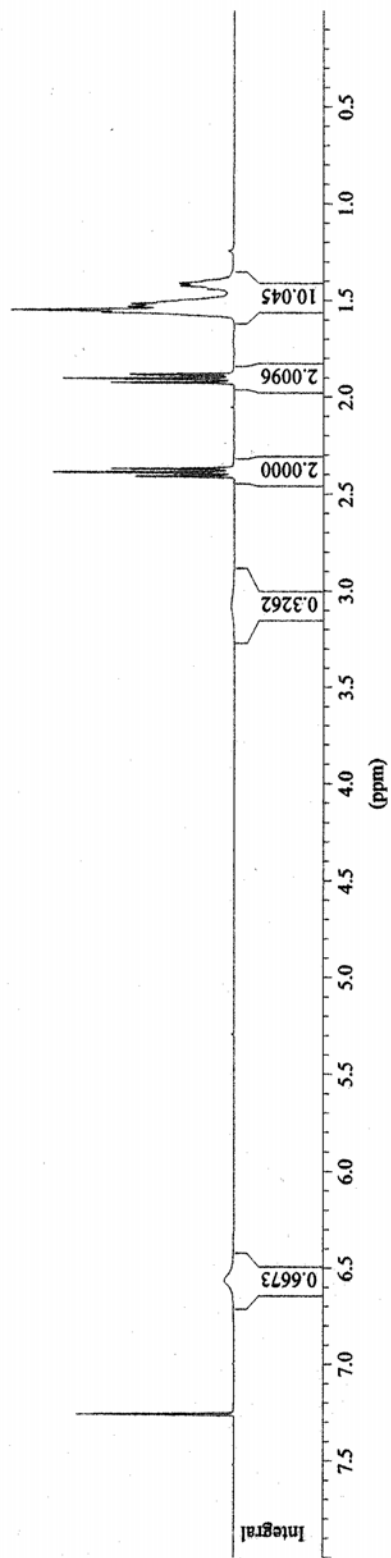
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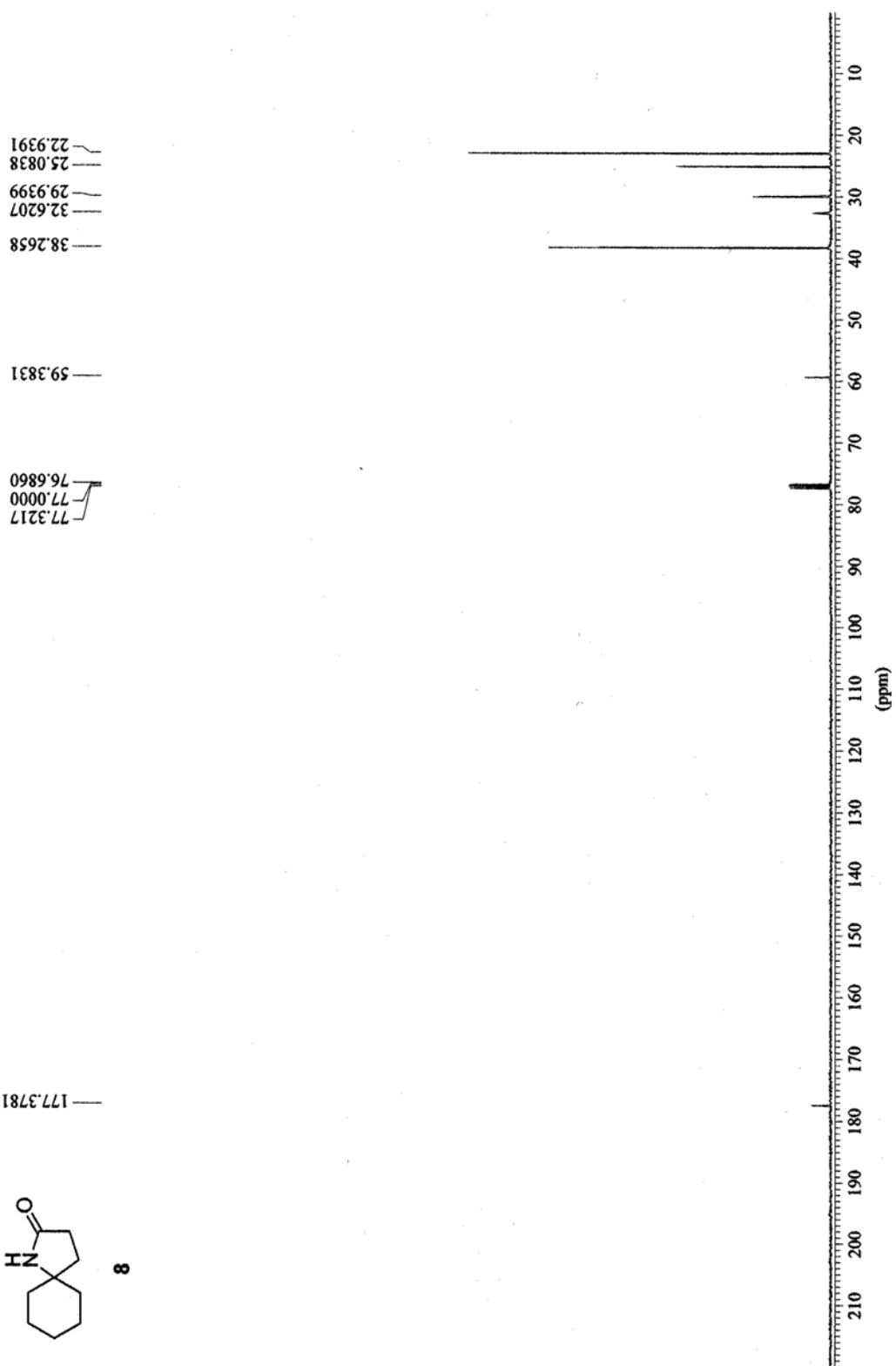


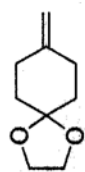




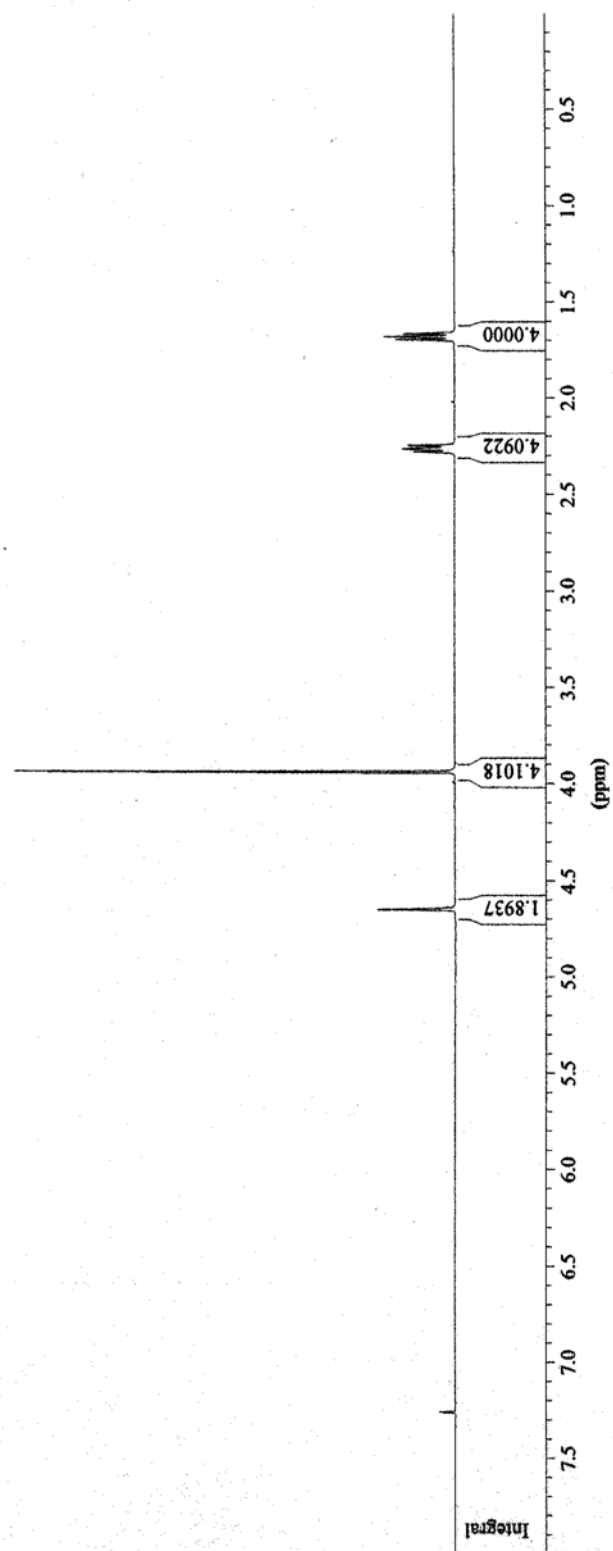
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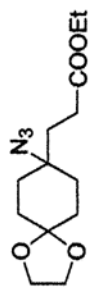




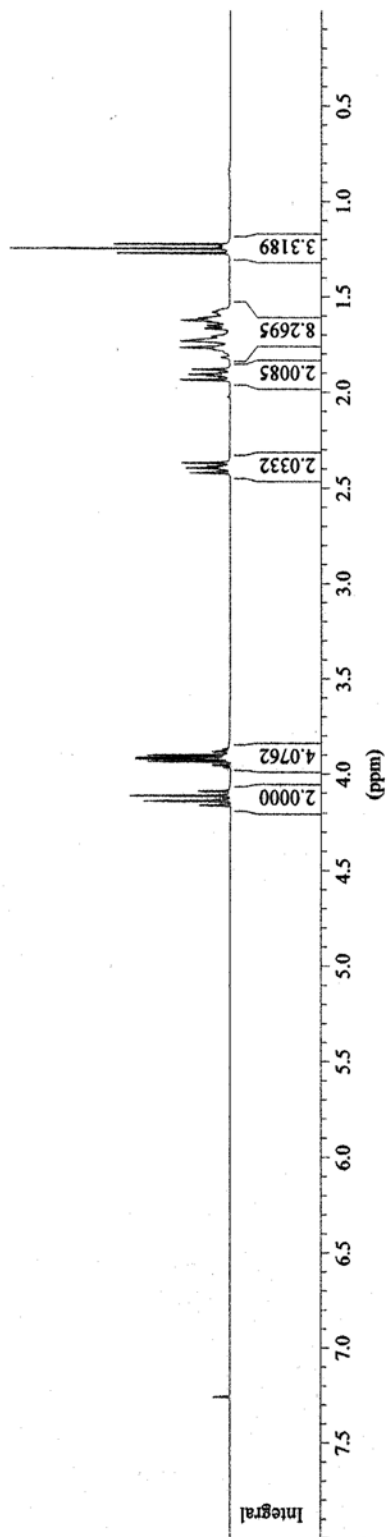


10





11



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