Supporting Information

"One-Pot Synthesis of Amides and Esters From 2,2,2-Trihaloethyl Esters Using Phosphorus (III) Reagents"

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General Procedures

Infrared spectra (IR) were recorded on a Mattson Polaris FT-IR equipped with a DTGS detector and are reported in wavenumbers (cm^{-1}) with broad signals denoted by (br). Mass spectra (MS) were obtained using a Kratos MS-80RFA mass spectrometer (DS-55/DS-90 peak matching option) and using electron impact (EI) at 70eV. Fast atom bombardment MS (FAB) were obtained on a VG Analytical ZAB-2F (Ion Tech FAB gun, 8 kV, Xe carrier gas).

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded in $CDCl_3$ on a Bruker AC-300 (300 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm, δ) relative to Me_4Si (δ 0.00). Proton NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quin), sextet (sex), septet (sep), multiplet (m), apparent (ap), and broad (br). Coupling constants are reported in hertz (Hz). Expanded sections shown on individual spectra are drawn on a scale of 20 Hz/cm. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AC-300 (75 MHz) spectrometer. Chemical shifts are reported in ppm (δ) relative to the central line of the 1:1:1 triplet of the internal deuterochloroform (δ 77.00). Carbon assignments, where indicated in parentheses, are based on Distortionless Enhancement by Polarization Transfer (DEPT) spectra obtained with phase angle Θ = 135°. The number of carbon resonances reported may

not match the actual number of carbons in some molecules due to magnetically and chemically equivalent carbons.

Tetrahydrofuran (THF),and benzene (PhH) were distilled from sodium/benzophenone ketyl immediately prior to use. Triethylamine (Et_3N), dichloromethane (CH_2Cl_2), butyl amine and diethyl amine were distilled from calcium hydride prior to use. Acetonitrile (CH_3CN) was distilled from calcium hydride and stored under 4 Å molecular sieves. *N*,*N*-dimethylformamide (DMF) was distilled under reduced pressure from magnesium sulfate, twice dried over 4 Å molecular sieves and stored over 4 Å molecular sieves. *N*,*N*,-dimethylaminopyriride (DMAP) was recrystallized from toluene. Tributylphosphine (PBu_3) was distilled under reduced pressure from calcium hydride or used as received from the Aldrich Chemical Company. Butanol, 2-pentanol, and *tert*-butanol were distilled from sodium metal. Menthol was dried by azeotropic removal of water by benzene and further dried in vacuo. 2-Methoxyethanol (anhydrous, 99.8%) used as received from Aldrich Chemical Company. Deuterochloroform (chloroform-*d*; $CDCl_3$), was stored over 4 Å molecular sieves. All other commercially obtained reagents and solvents were used as received without further purification unless otherwise indicated.

All moisture-sensitive reactions were performed in flame-dried or oven-dried glassware under a positive pressure of nitrogen. Bath temperatures were used to record the reaction temperature in all cases. All reactions were stirred magnetically unless otherwise indicated. Volatile solvents from reaction workups and chromatography solutions were concentrated using a Büchi rotary evaporator at reduced pressure. Residual solvents were removed by evacuation under high vacuum (*in vacuo*) at approximately 1 mm Hg. Analytical thin layer chromatography (TLC) was carried out on E. Merck (Darmstadt) TLC plates pre-coated with silica gel 60 F_{254} (250 μ layer thickness). TLC visualization was accomplished using either a UV lamp, iodine adsorbed on silica gel, or charring solution [*p*-anisaldehyde (PAA)]. Flash chromatography was performed on EM Science silica gel 60

(230-400 mesh). Solvent mixtures used for TLC and flash chromatography are reported in V/V_{total} x 100.

Experimental Procedures

2,2,2-Tribromoethyl benzoate (1a)

To a solution of 2,2,2-tribromoethanol (3.50 g, 12.4 mmol) and NEt_3 (3.80 mL, 27.3 mmol) in 75 mL of THF at 0 °C was added benzoyl chloride (1.60 mL, 13.8 mmol) dropwise over 10 min. The cold bath was removed and the reaction mixture stirred at ambient temperature for 6 h. The reaction mixture was filtered and diluted with diethyl ether (150 mL). This solution was washed with 2 M HCl (75 mL) and saturated $NaHCO_3$ (75 mL), dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (gradient elution, 1% to 2% EtOAc in hexanes) provided 4.1 g of **1a** (10.6 mmol, 86%) as a colorless oil.

Data for **1a**: R_f 0.43 (10% EtOAc in hexanes); **IR** (thin film) 3066, 2941, 1732, 1263, 1111, 731 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.17 (m, 2H), 7.62 (tt, 1H, J = 7.4, 1.3 Hz), 7.50 (m, 2H), 5.16 (s, 2H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 164.4 (C), 133.5 (CH), 129.8 (CH x 2), 128.6 (C), 128.4 (CH x 2), 76.3 (CH_2), 35.5 (C); **MS** (EI) *m/e* (relative intensity, assignment) 385.8 (7.7, M^+), 306.9 (23.8, M^+ -Br), 105.0 (100, M^+-OCH_2Br_3); experimental isotope pattern calculated for $C_9H_7Br_3O_2$ matches that observed.

2,2,2-Trichloroehtyl benzoate (1b)

To a solution of benzoyl chloride (0.60 mL, 5.2 mmol) and NEt_3 (1.10 mL, 0.79 mmol) in 20 mL of THF at 0 °C was added 2,2,2-trichloroethanol (0.40 mL, 4.2 mmol). The reaction mixture was stirred at 0 °C for 5 min and then at ambient temperature for 2 h. The reaction mixture was diluted with Et_2O (20 mL) and washed with 2 M HCl (40 mL).The aqueous phase was extracted with Et_2O (3 x 40 mL), and the combined organics were dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (2% EtOAc in hexanes) provided 925 mg of **1b** (3.65 mmol, 87%) as a white solid.

Data for **1b**: R_f 0.42 (10% EtOAc in hexanes); **IR** (thin film) 3064, 2953, 1736,1263, 1117, 719 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.14 (m, 2H), 7.62 (tt, 1H, J = 7.4, 1.3 Hz), 7.49 (m, 2H), 4.98 (s, 2H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 164.9 (C), 133.8 (CH), 130.0 (CH x 2), 128.6 (C), 128.5 (CH x 2), 95.0 (C), 74.4 (CH_2); **MS** (EI) *m/e* (relative

intensity, assignment) 252.0 (8.7, M^+), 105.0 (100, M^+-OCH_2Cl_3), 77.0 ($C_6H_5^+$); experimental isotope pattern calculated for $C_9H_7Cl_3O_2$ matches that observed.

_N_-Butylbenzamide (2) from 1a using HMPT

To a solution of **1a** (141 mg, 0.364 mmol), butylamine (37 μL, 0.37 mmol) and NEt_3 (0.13 mL, 0.93 mmol) in 3.6 mL of DMF at -55 °C was added HMPT (73 μL, 0.40 mmol) dropwise. The reaction mixture was stirred at -55 °C for 30 min. The reaction mixture was diluted with Et_2O (20 mL) and washed with 2 M HCl (20 mL).The aqueous phase was extracted with Et_2O (3 x 20 mL), and the combined organics were washed with sat NaCl (20 mL) and H_2O (20 mL), dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (30% EtOAc in hexanes) provided 53.9 mg of **2** (.304 mmol, 83%) as a colorless oil.

Data for **2**: R_f 0.43 (50% EtOAc in hexanes, PAA); **IR** (thin film) 3313, 2958, 2871, 1638, 1543, 1308, 695 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.77 (m, 2H), 7.46 (tt, *J*= 7.4, 1.3 Hz), 7.38 (m, 2H), 6.57 (br s, 1H), 3.42 (m, 2H), 1.57 (m, 2H), 1.38 (m, 2H), 0.93 (t, *J*=7.4 Hz); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 167.5 (C), 134.8 (C), 131.1 (CH), 128.3 (CH x 2), 126.8 (CH x 2), 39.7 (CH_2), 31.6 (CH_2), 20.0 (CH_2), 13.7 (CH_3); **MS** (EI) *m/e* (relative intensity, assignment) 177.1 (17.6, M^+), 105.0 (100, M^+-NHC_4H_9).

_N_-Butylbenzamide (2) from 1a using PBu_3

To a solution of **1a** (90 mg, 0.233 mmol), butylamine (23 μL, 0.23 mmol) and NEt_3 (0.08 mL, 0.57 mmol) in 2.3 mL of DMF at -55 °C was added PBu_3 (90 μL, 0.40 mmol) dropwise. The reaction mixture was allowed to warm to 0 °C over 75 min. The reaction mixture was diluted with Et_2O (20 mL) and washed with 2 M HCl (20 mL).The aqueous phase was extracted with Et_2O (3 x 20 mL), and the combined organics were washed with sat NaCl (20 mL) and H_2O (20 mL), dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (30% EtOAc in hexanes) provided 10.3 mg of **2** (.058 mmol, 25%) as a colorless oil.

_N_-Butylbenzamide (2) from 1a using PPh_3

To a solution of **1a** (121 mg, 0.313 mmol) and PPh_3 (410 mg, 1.56 mmol) in 3.0 mL of DMF was added butylamine (40 μL, 0.40 mmol) and NEt_3 (0.11 mL, 0.79 mmol). The reaction mixture was stirred at ambient temp for 48 h. The reaction mixture was diluted with Et_2O (20 mL) and washed with 2 M HCl (20 mL).The aqueous phase was extracted with Et_2O (3 x 20 mL), and the combined organics were washed with sat NaCl (20 mL) and H_2O

(20 mL), dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (30% EtOAc in hexanes) provided 13.3 mg of **2** (.075 mmol, 24%) as a colorless oil and 51 mg (0.13 mmol, 42%) of recoverd **1a**. All data for **2** match that of the previous procedure.

***N*-Butylbenzamide (2) from 1a in the absence of phosphine**

A solution of **1a** (57.5 mg, 0.150 mmol), butylamine (18 μL, 0.18 mmol) and NEt_3 (0.05 mL, 0.36 mmol) in 1.5 mL of DMFwas stirred at ambient temp for 48h. The reaction mixture was diluted with Et_2O (20 mL) and washed with 2 M HCl (20 mL).The aqueous phase was extracted with Et_2O (3 x 20 mL), and the combined organics were washed with sat NaCl (20 mL) and H_2O (20 mL), dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (30% EtOAc in hexanes) provided 4.5 mg of **2** (.025 mmol, 17%) as a colorless oil and 37.7 mg (0.087 mmol, 66%) of recoverd **1a**. All data for **2** match that of the previous procedures.

***N*-Butylbenzamide (2) from 1b using HMPT**

To a solution of **1b** (18.8 mg, 0.074 mmol) and butylamine (25 μL, 0.25 mmol) in 0.75 mL of DMF was added HMPT (16 μL, 0.088 mmol) dropwise. The reaction mixture was stirred at ambient temp for 4.5h. The reaction mixture was diluted with Et_2O (15 mL) and washed with 2 M HCl (15 mL).The aqueous phase was extracted with Et_2O (3 x 15 mL), and the combined organics were washed with sat NaCl (15 mL) and H_2O (15 mL), dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (30% EtOAc in hexanes) provided 2.3 mg of **2** (.013 mmol, 18%) as a colorless oil. All data for **2** match that of the previous procedures.

***N*-Butylbenzamide (2) from 1b using PBu_3**

To a solution of **1a** (121 mg, 0.477 mmol), butylamine (50 μL, 0.50 mmol) and NEt_3 (0.33 mL, 2.4 mmol) in 4.8 mL of DMF at room temp was added PBu_3 (0.35 mL, 1.4 mmol) dropwise. The reaction mixture was heated at 90 °C for 3.5 h. The reaction mixture was diluted with Et_2O (20 mL) and washed with 2 M HCl (20 mL).The aqueous phase was extracted with Et_2O (3 x 20 mL), and the combined organics were washed with sat NaCl (20 mL) and H_2O (20 mL), dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (30% EtOAc in hexanes) provided 34.4 mg of **2** (.194 mmol, 39%) as a colorless oil. All data for **2** match that of the previous procedures.

2,2,2-Tribomoethyl cyclohexanecarboxylate (3)

To a slurry of DMAP (0.93g, 7.6 mmol), DMAP•TFA (4-(*N*,*N*-dimethylamino)pyridinium trifluoroacetate, 1.8 g, 7.6 mmol), and diisopropylcarbodiimide (1.3 mL, 8.30 mmol) in 20 mL CH_2Cl_2 was added a solution of cyclohexanecarboxylic acid (1.1 g, 8.6 mmol) and 2,2,2-tribromoethanol (2.23 g 7.9 mmol) in 15 mL CH_2Cl_2 plus two 5 mL rinses via cannula. The reaction mixture was stirred at ambient temp for 6 h. The reaction mixture was then washed with 2 M HCl (50 mL).The aqueous phase was extracted with CH_2Cl_2 (30 mL), and the combined organics were dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (5% EtOAc in hexanes) provided 2.57 g of **3** (6.54 mmol, 83%) as a colorless oil.

Data for **3**: R_f 0.36 (5% EtOAc in hexanes); **IR** (thin film) 2931, 2854, 1747, 1153, 1124, 631 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 4.92 (s, 2H), 2.48 (tt, 1H, J = 11.0, 3.8 Hz), 2.02 (br d, 2HJ = 16.0 Hz), 1.78 (m, 2H), 1.67, (m, 1H), 1.51-1.45 (m, 2H), 1.40-1.20 (m, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 173.9, (C), 76.4, (CH_2), 42.8 (CH), 36.2 (C), 28.8 (CH_2 x 2), 25.6 (CH_2), 25.2 (CH_2 x 2); **MS** (EI) *m/e* (relative intensity, assignment) 392.8 (13.2, M^+), 306.9 (23.8, M^+ -Br), 264.8 (11.8, $CH_2Br_3^+$) 127.0 (58.2, M^+-CH_2Br_3), 111.1 (100, M^+-OCH_2Br_3) 83.1 (60.7, $C_6H_{11}^+$); experimental isotope pattern calculated for $C_9H_{13}Br_3O_2$ matches that observed.

***N*-(*tert*-Butoxycarbonyl)-L-alanine 2,2,2-tribromoethyl ester (4)**

To a slurry of DMAP (66 mg, 0.54 mmol), DMAP•TFA (125 mg, 0.529 mmol), and diisopropylcarbodiimide (90 μL, 0.57 mmol) in 2.4 mL CH_2Cl_2 was added a solution of *N*-(*tert*-butoxycarbonyl)-L-alanine (101 mg, 0.534 mmol) and 2,2,2-tribromoethanol (178 mg 0.629 mmol) in 1.0 mL CH_2Cl_2 plus two 0.5 mL rinses via cannula. The reaction mixture was stirred at ambient temp for 17.5 h. The reaction mixture was diluted with CH_2Cl_2 (15 mL) and washed with 2 M HCl (20 mL).The aqueous phase was extracted with CH_2Cl_2 (3 x 20 mL), and the combined organics were dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (20% EtOAc in hexanes) provided 209 mg of **4** (6.54 mmol, 86%) as a yellow oil.

Data for **4**: R_f 0.47 (20% EtOAc in hexanes); $[\alpha]^{22}_D$ -30.8 (c = 1.86, EtOH); **IR** (thin film) 3364, 2978, 1760, 1708, 1507, 1158 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 5.07 (br s, 1H,), 4.98 (ABq, 2H, J_{AB} = 12.2 Hz, $\Delta\nu_{AB}$ = 91.5 Hz), 4.48 (br quin, 1HJ = 7.2 Hz),

1.52 (d, 3H, J = 7.2 Hz), 1.46, (s, 9H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 171.6, (C), 155.0, (C), 80.1 (C), 77.0 (CH_2), 49.3 (CH) 35.0 (C), 28.3 (CH_3 x 3), 18.4 (CH_3).

General procedure for the synthesis of amides using HMPT

To a 0.1 M solution of tribromoethyl ester (1 equiv), amine or amine hydrochloride (1 equiv) and NEt_3 (2.5 - 3 equiv) in DMF at -55 °C was added HMPT (1.2 equiv) dropwise. The reaction mixture was stirred at -55 °C for 30 min. The reaction mixture was diluted with Et_2O (20 mL) and washed with 2 M HCl (20 mL).The aqueous phase was extracted with Et_2O (3 x 20 mL), and the combined organics were washed with sat NaCl (20 mL) and H_2O (20 mL), dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (EtOAc-hexanes) afforded the amide product.

***N,N*-Diethylbenzamide (5a)**

5a was obtained in 76% yield (38.5 mg) from **1a** and diethylamine as a colorless oil (flash chromatography 40% EtOAc in hexanes).

Data for **5a**: R_f 0.32 (50% EtOAc in hexanes); **IR** (thin film) 2986, 2942, 1655, 1427, 1287, 1096 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.39-7.31 (m, 5H), 3.53 (br s, 1H), 3.23 (br s, 2H), 1.23 (br s, 3H), 1.09 (br s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 171.1 (C), 137.1 (C), 128.9 (CH), 128.2 (CH x 2), 126.1 (CH x 2), 43.1 (CH_2), 39.0 (CH_2), 14.0 (CH_3), 12.8 (CH_3); **MS** (EI) *m/e* (relative intensity, assignment) 177.1 (31.5, M^+), 105.0 (100, $C_6H_5CO^+$).

***N*,-Benzoylglycine ethyl ester (5b)**

5b was obtained in 77% yield (25.2 mg) from **1a** and glycine ethyl ester hydrochloride as a colorless oil (flash chromatography 40% EtOAc in hexanes).

Data for **5b**: R_f 0.36 (60% EtOAc in hexanes,); **IR** (thin film) 3336, 3063, 2981, 2937, 1751, 1642, 1533, 1200 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.82 (m, 2H), 7.48 (tt, 1H, J = 7.4, 1.3 Hz), 7.41 (m, 2H), 6.76 (br s, 1H), 4.26 (q, 2H, J = 7.2 Hz), 4.23 (d, 2H, J = 5.0 Hz), 1.31 (t, 3H, J = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 170.1 (C), 167.4 (C), 133.7 (C), 131.7 (CH), 128.6 (CH x 2), 127.0 (CH x 2), 61.6 (CH_2), 41.9 (CH_2), 14.1 (CH_3); **MS** (EI) *m/e* (relative intensity, assignment) 207.1 (14.8, M^+), 134.1 (25.2, M^+-$CO_2C_2H_5$) 105.0 (100, $C_6H_5CO^+$).

***N*,-Butylcyclohexanecarboxamide (6a)**

6a was obtained in 88% yield (41.9 mg) from **3** and butylamine as a white solid (flash chromatography gradient elution 30% to 40% EtOAc in hexanes).

Data for **6a**: R_f 0.33 (40% EtOAc in hexanes); **IR** (thin film) 3295, 3083, 2930, 2854, 1642, 1551, 1447 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 5.85 (br s, 1H), 3.27-3.20 (m, 2H), 2.08 (tt, 1H, J = 11.8, 3.5 Hz), 1.90-1.16 (m, 14H), 0.92 (t, 3H, J = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 176.0 (C), 45.5 (CH), 38.9 (CH_2), 31.7 (CH_2), 29.6 (CH_2 x 2), 25.7 (CH_2 x 3), 19.9 (CH_2), 13.6 (CH_3).

***N,N*-Diethylcyclohexanecarboxamide (6b)**

6b was obtained in 57% yield (29.6 mg) from **3** and diethylamine as a colorless oil (flash chromatography 40% EtOAc in hexanes).

Data for **6b**: R_f 0.22 (30% EtOAc in hexanes); **IR** (thin film) 2970, 2929, 2854, 1638, 1449, 1429 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 3.36 (q, 2H, J = 7.2 Hz), 3.32 (q, 2H, J = 7.2 Hz), 2.40 (tt, 1H, J = 11.4, 3.5 Hz), 2.08 (tt, 1H, J = 11.8, 3.5 Hz), 1.85-1.45 (m, 7H), 1.35-1.20 (m, 3H), 1.18 (t, 3H, J = 7.0 Hz), 1.09 (t, 3H, J = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 175.3 (C) 41.6 (CH_2), 40.7 (CH), 39.9 (CH_2), 29.5 (CH_2 x 2), 25.8 (CH_2 x 2), 25.7 (CH_2), 14.9 (CH_3), 13.0 (CH_3).

***N-tert*-Butoxycarbonyl-L-alanyl-L-alanine ethyl ester (7)**

7 was obtained in 70% yield (39.1 mg) from **4** and L-alanine ethyl ester hydrochloride as a white solid (flash chromatography 50% EtOAc in hexanes).

Data for **7**: R_f 0.38 (60% EtOAc in hexanes); $[\alpha]^{22}_D$ -48.1 (c = 1.0, EtOH); **IR** (thin film) 3332, 3261, 3075, 2948, 1752, 1688, 1656, 1540, 1521, 1269, 1167 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 6.73 (br s, 1H), 5.12 (br s, 1H), 4.55 (quin, 1H, J = 7.4 Hz), 4.23-4.16 (m, 3H), 1.45 (s, 9H), 1.40 (d, 3H, J = 7.2 Hz), 1.37 (d, 3H, J = 7.2 Hz), 1.28, (t, 3H, J = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 172.7 (C), 172.2 (C), 155.4 (C), 79.5 (C). 61.4 (CH_2), 49.9 (CH_2), 48.0 (CH), 28.3 (CH_3 x 3), 18.5 (CH_3), 18.3(CH_3), 14.1 (CH_3); **MS** (EI) *m/e* (relative intensity, assignment) 288.2 (2.4, M^+), 144.1 (100, $C_4H_9O_2CNHCHCH_3^+$) 116.1 (43.4, $C_4H_9O_2CNH^+$).

General procedure for the synthesis of esters

To a 0.1 M solution of tribromoethyl or trichloroethyl ester (1 equiv), alcohol (1 equiv) and DMAP (2 equiv) in DMF was added tributylphosphine (1.5 equiv) dropwise. The reaction mixture was stirred at ambient temperature for 1-5 h. The reaction mixture was diluted with Et_2O (20 mL) and washed with 2 M HCl (20 mL).The aqueous phase was extracted with Et_2O (3 x 20 mL), and the combined organics were washed with sat NaCl (20 mL) and H_2O (20 mL), dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (EtOAc-hexanes) and/or Kugelrohr distillation afforded the ester product.

2-Methoxyethyl benzoate (8a) from 2,2,2-tribromoethyl benzoate (1a)

8a was obtained in 69% yield (51.7 mg) from **1a** and 2-methoxyethanol as a colorless oil (flash chromatography 10% EtOAc in hexanes).

Data for **8a**: R_f 0.48 (40% EtOAc in hexanes); **IR** (thin film) 2986, 1736, 1704, 1515, 1246, 1167 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 6.81 (m, 2H), 6.28 (tt, 1H, J = 7.4, 1.3 Hz), 6.16 (m, 2H), 3.21 (m, 2H), 2.46 (m, 2H), 2.16 (s, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 166.4 (C), 132.8 (CH), 129.9 (C), 129.4 (CH x 2), 128.2 (CH x 2), 70.4 (CH_2), 63.9 (CH_2), 58.9 (CH_3).

Butyl benzoate (8b)

8b was obtained in 81% yield (51.8 mg) from **1a** and 1-butanol as a colorless oil after flash chromatography (1.5% EtOAc in hexanes) followed by Kugelrohr distillation.

Data for **8b**: R_f 0.42 (10% EtOAc in hexanes); **IR** (thin film) 2958, 1720, 1274, 709 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.05 (m, 2H), 7.55 (tt, 1H, J = 7.4, 1.3 Hz), 7.43 (m, 2H), 4.33 (t, 2H, J = 6.7 Hz), 1.81-1.70 (m, 2H), 1.55-1.41 (m, 2H), 0.98 (t, 3H, J = 7.3 Hz); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 166.7 (C), 132.7 (CH), 130.5 (C), 129.5 (CH x 2), 128.3 (CH x 2), 64.8 (CH_2), 30.8 (CH_2), 19.2 (CH_2), 13.7 (CH_3); **MS** (EI) *m/e* (relative intensity, assignment) 178.1 (3.2, M^+), 123.0 (85.4, $C_6H_5CO_2H_2^+$), 105.0 (100, $C_6H_5CO^+$).

Benzyl benzoate (8c)

8c was obtained in 77% yield (40.3 mg) from **1a** and benzyl alcohol as a colorless oil (flash chromatography 1.5% EtOAc in hexanes).

Data for **8c**: R_f 0.58 (20% EtOAc in hexanes); **IR** (thin film) 3063, 3033, 1719, 1271, 1109, 711 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.08 (m, 2H), 7.54 (tt, 1H, J = 7.3, 1.3 Hz), 7.47-7.30 (m, 7H), 5.36 (s, 2H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 166.4 (C), 136.0 (C),

133.0 (CH), 130.1 (C), 129.7 (CH x 2), 128.5 (CH x 2), 128.3 (CH x 2), 128.2 (CH), 128.1 (CH x 2), 66.6 (CH_2).

2-Pentyl benzoate (8d)

8d was obtained in 62% yield (31.4 mg) from **1a** and 2-pentanol as a colorless oil (flash chromatography 1.5% EtOAc in hexanes).

Data for **8d**: R_f 0.51 (10% EtOAc in hexanes); **IR** (thin film) 2960, 2925, 2854, 1718, 1278, 1118 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.05 (m, 2H), 7.55 (tt, 1H, *J* = 7.4, 1.3 Hz), 7.43 (m, 2H), 5.18 (m, 1H), 1.81-1.30 (m, 4H), 1.34 (d, 3H, *J* = 6.2 Hz), 0.94 (t, 3H, *J* = 7.4 Hz); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 166.2 (C), 132.7 (CH), 130.9 (C), 129.5 (CH x 2), 128.3 (CH x 2), 71.5 (CH), 38.2 (CH_2), 20.1 (CH_3), 18.7 (CH_2), 14.0 (CH_3); **MS** (EI) *m/e* (relative intensity, assignment) 192.1 (0.9, M^+), 123.0 (41.9, $C_6H_5CO_2H_2^+$), 105.0 (100, $C_6H_5CO^+$).

Menthyl benzoate (8e)

8e was obtained in 61% yield (39.6 mg) from **1a** and (-)-menthol as a colorless oil (flash chromatography 1.5% EtOAc in hexanes).

Data for **8e**: R_f 0.63 (10% EtOAc in hexanes); **IR** (thin film) 2954, 1714, 1274, 710 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.05 (m, 2H), 7.55 (tt, 1H, *J* = 7.3, 1.5 Hz), 7.44 (m, 2H), 4.94 (td, 1H, *J* = 10.9, 4.2 Hz), 2.13 (m, 1H), 1.97 (sep d, 1H, *J* = 8.8, 2.6 Hz), 1.78-1.68 (m, 2H), 1.63-1.47 (m, 2H), 1.2-0.9 (m, 3H), 0.94 (d, 3H, *J* = 3.1 Hz), 0.91 (d, 3H,*J* = 3.5 Hz), 0.79 (d, 3H, *J* = 6.8 Hz); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 166.1 (C), 132.6 (CH), 130.8 (C), 129.5 (CH x 2), 128.2 (CH x 2), 74.8 (CH), 47.3 (CH), 41.0 (CH_2), 34.3 (CH_2), 31.4 (CH), 28.2 (CH), 26.6 (CH_2), 23.6 (CH_3), 22.0 (CH_3), 16.5 (CH_3); **MS** (EI) *m/e* (relative intensity, assignment) 192.1 (0.9, M^+), 123.0 (41.9, $C_6H_5CO_2H_2^+$), 105.0 (100, $C_6H_5CO^+$).

2-Methoxyethyl cyclohexanecarboxylate (9a)

9a was obtained in 74% yield (33.8 mg) from **3** and 2-methoxyethanol as a colorless oil (flash chromatography 10% EtOAc in hexanes).

Data for **9a**: R_f 0.50 (20% EtOAc in hexanes); **IR** (thin film) 2932, 2855, 1734, 1171, 1129 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 4.22 (m, 2H), 3.59 (m, 2H), 3.39 (s, 3H), 2.35 (tt, 1H, *J* = 11.2, 3.6 Hz), 1.94-1.89 (m, 2H), 1.80-1.71 (m, 2H), 1.65 (m, 1H), 1.52-1.37 (m, 2H), 1.36-1.13 (m, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 176.0 (C), 70.5 (CH_2), 63.1 (CH_2), 58.9 (CH_3), 42.9 (CH), 28.9 (CH_2), 25.6 (CH_2), 25.3 (CH_2).

Butyl cyclohexanecarboxylate (9b)

9b was obtained in 65% yield (40.4 mg) from **3** and 1-butanol as a colorless oil (flash chromatography 1.5% EtOAc in hexanes).

Data for **9b**: R_f 0.55 (10% EtOAc in hexanes); **IR** (thin film) 2858, 2932, 2856, 1733, 1171 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 4.06 (t, 2H, *J* = 6.6 Hz), 2.28 (tt, 1H, *J* = 11.0, 3.5 Hz), 1.95-1.84 (m, 2H), 1.79-1.69 (m, 2H), 1.68-1.54 (m 3H), 1.50-1.13 (m, 7H), 0.93 (t, 3H, *J* = 7.4 Hz); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 176.2 (C), 63.9 (CH_2), 43.3 (CH), 30.7 (CH_2), 29.0 (CH_2 x 2), 25.8 (CH_2), 25.5 (CH_2 x 2), 19.1 (CH_2), 13.7 (CH_3).

Benzyl cyclohexanecarboxylate (9c)

9c was obtained in 70% yield (43 mg) from **3** and benzyl alcohol as a colorless oil (flash chromatography 1.5% EtOAc in hexanes).

Data for **9c**: R_f 0.22 (5% EtOAc in hexanes); **IR** (thin film) 2932, 2854, 1733, 1165 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 7.39-7.29 (m, 5H), 5.11, (s, 2H), 2.35 (tt, 1H, *J* = 11.2, 3.5 Hz), 1.98-1.87 (m, 2H), 1.80-1.70 (m, 2H), 1.68-1.59 (m, 1H), 1.54-1.38 (m, 2H), 1.36-1.13 (m, 3H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 175.9 (C), 136.3 (C), 128.5 (CH x 2), 128.0 (CH), 127.9 (CH x 2)65.8 (CH_2), 43.2 (CH), 29.0 (CH_2 x 2), 25.7 (CH_2), 25.4 (CH_2 x 2).

2-Pentyl cyclohexanecarboxylate (9d)

9d was obtained in 63% yield (34.9 mg) from **3** and 2-methoxyethanol as a colorless oil after flash chromatography (1.5% EtOAc in hexanes) followed by Kugelrohr distillation.

Data for **9d**: R_f 0.28 (5% EtOAc in hexanes); **IR** (thin film) 2933, 2856, 1729, 1173 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 4.90 (m, 1H), 2.25 (tt, 1H, *J* = 11.0, 3.5 Hz), 1.94-1.83 (m, 2H), 1.80-1.21 (m, 12H), 1.18 (d, 3H, *J* = 6.2 Hz), 0.90 (t, 3H, *J* = 7.2 Hz); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 175.8 (C), 71.1 (CH), 43.5 (CH), 38.1 (CH_2), 29.1 (CH_2), 29.0 (CH_2), 25.8 (CH_2), 25.5 (CH_2), 25.4 (CH_2), 20.0 (CH_3), 18.6 (CH_2), 13.9 (CH_3).

Menthyl cyclohexanecarboxylate (9e)

9e was obtained in 65% yield (34.4 mg) from **3** and (-)-menthol as a colorless oil (flash chromatography 1.5% EtOAc in hexanes).

Data for **9e**: R_f 0.65 (30% EtOAc in hexanes); **IR** (thin film) 2931, 2856, 1728, 1172 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 4.65 (tt, 1H, *J* = 10.8, 4.2 Hz), 2.26 (tt, 1H, *J* = 11.0, 3.7 Hz), 2.00-0.80 (m, 19H), 0.90, (d, 3H, *J* = 6.4 Hz), 0.89 (d, 3H, *J* = 7.0 Hz), 0.74 (d, 3H, *J* = 7.0 Hz); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 175.7 (C), 73.5 (CH), 47.1 (CH), 43.5 (CH), 40.9

(CH_2), 34.3 (CH_2), 31.3 (CH), 29.1 (CH_2), 29.0 (CH_2), 26.1 (CH), 25.8 (CH_2), 25.5 (CH_2), 25.4 (CH_2), 24.2 (CH_2), 23.3 (CH_3), 22.0 (CH_3), 16.1 (CH_3).

***tert*-Butyl benzoate (8f)**

To a solution of **1a** (101 mg, 0.261 mmol) and DMAP (60.5 mg, 0.52 mmol) in 2.6 mL of 1 : 1 v/v *tert*-butyl alcohol : DMF was added tributylphosphine (0.13 mL, 0.52 mmol) dropwise. The reaction mixture was stirred at ambient temperature for 6.2 h. The reaction mixture was diluted with Et_2O (20 mL) and washed with 2 M HCl (20 mL).The aqueous phase was extracted with Et_2O (3 x 20 mL), and the combined organics were washed with sat NaCl (20 mL) and H_2O (20 mL), dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (1.5% EtOAc in hexanes) followed by Kugelrohr distillation afforded 5.0 mg of **8f** (0.028 mmol, 11%) as a colorless oil.

Data for **8f**: R_f 0.59 (20% EtOAc in hexanes); **IR** (thin film) 2964, 2928, 2871, 1729, 1275 cm^{-1}; **^{1}H NMR** ($CDCl_3$, 300 MHz) δ 8.00, (m, 2H), 7.52 (tt, 1H, J = 7.4, 1.4 Hz), 7.41 (m, 2H), 1.60 (s, 9H); **^{13}C NMR** ($CDCl_3$, 75 MHz) δ 165.5 (C), 132.4 (CH), 132.0 (CH), 129.4 (CH x 2), 128.2 (CH x 2), 80.5 (C), 28.2 (CH_3 x 3); **MS** (EI) *m/e* (relative intensity, assignment) 178.1 (1.8, M^+), 123.0 (96.7, $C_6H_5CO_2H_2^+$), 105.0 (100, $C_6H_5CO^+$).

2-Methoxyethyl benzoate (8a) from 2,2,2-trichloroethyl benzoate (1b)

To a solution of **1b** (73 mg, 0.288 mmol), DMAP (67 mg, 0.54 mmol) and 2-methoxyethanol (25 μL, 0.317 mmol) in 2.8 mL of DMF was added tributylphosphine (0.36 mL, 1.44 mmol) dropwise. The reaction mixture was heated at 100 °C for 4.5 h. The reaction mixture was diluted with Et_2O (20 mL) and washed with 2 M HCl (20 mL).The aqueous phase was extracted with Et_2O (3 x 20 mL), and the combined organics were washed with sat NaCl (20 mL) and H_2O (20 mL), dried (MgSO4), filtered, and concentrated. Purification by flash chromatography (10% EtOAc in hexanes) afforded 23.7 mg of **8a** (0..131 mmol, 11%) as a colorless oil. All data for **8a** match that of the previous procedure.

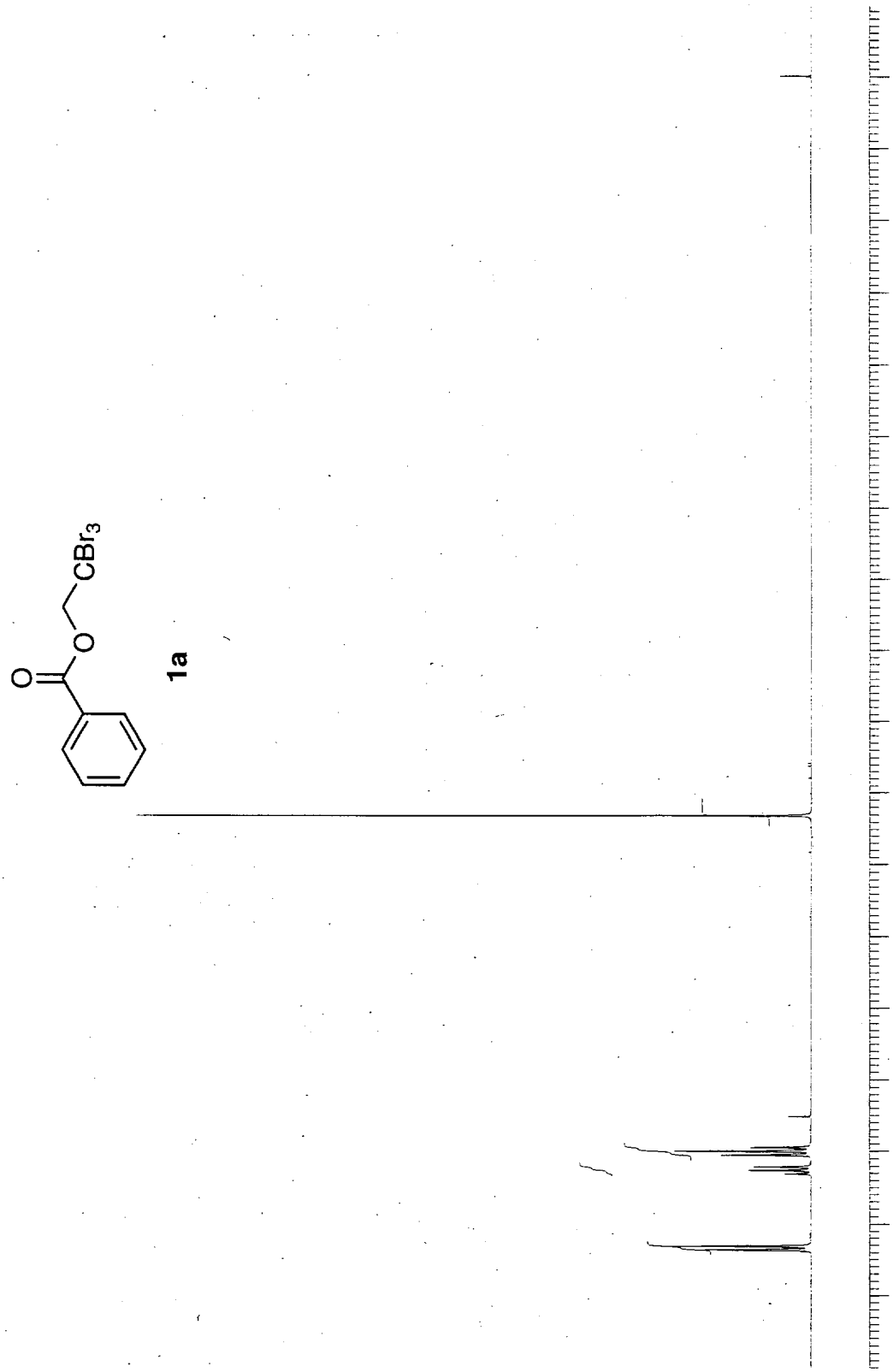


Figure 1: ^{1}H NMR ($CDCl_3$, 300 MHz) of **1a**.

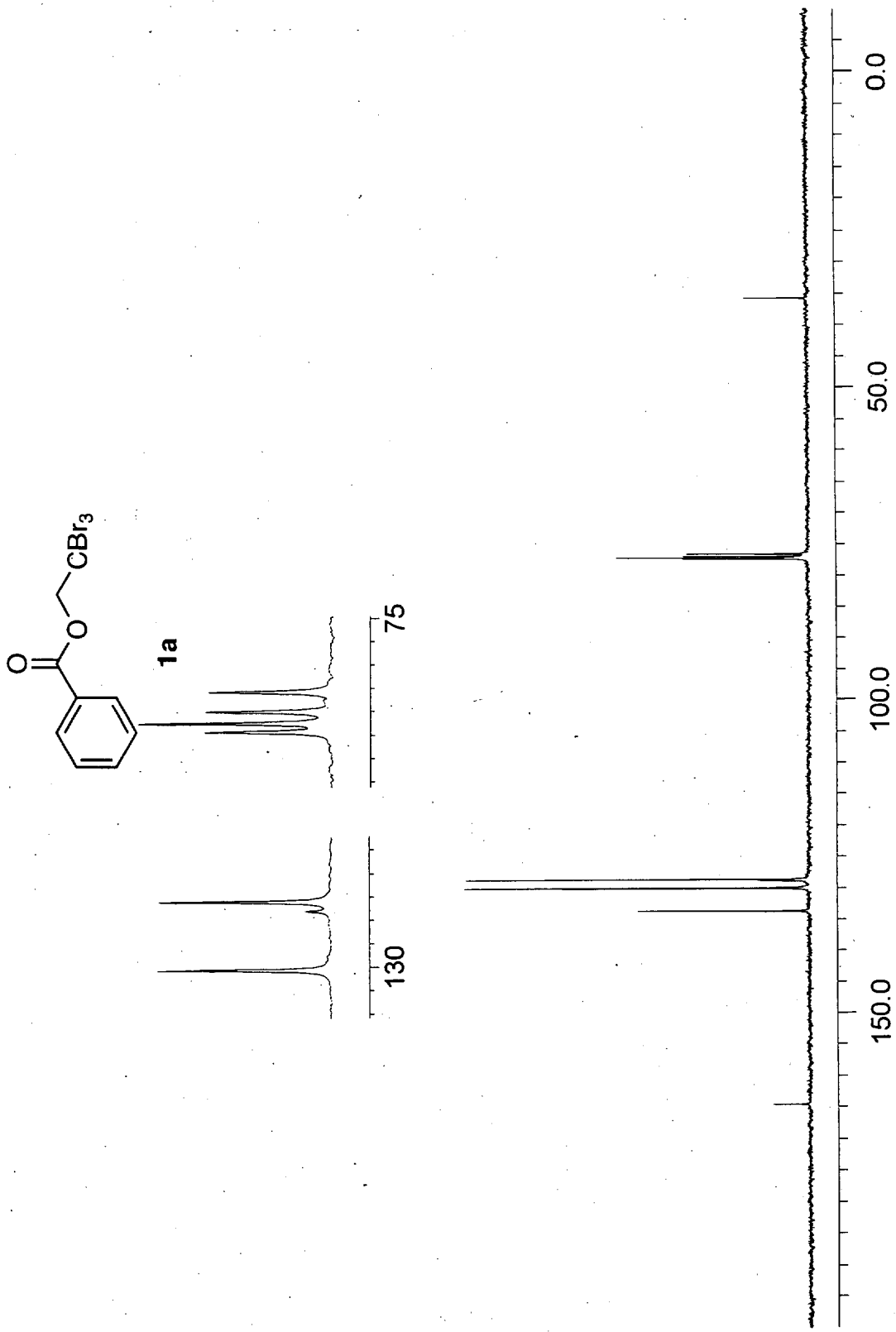


Figure 2: ^{13}C NMR ($CDCl_3$, 300 MHz) of **1a**.

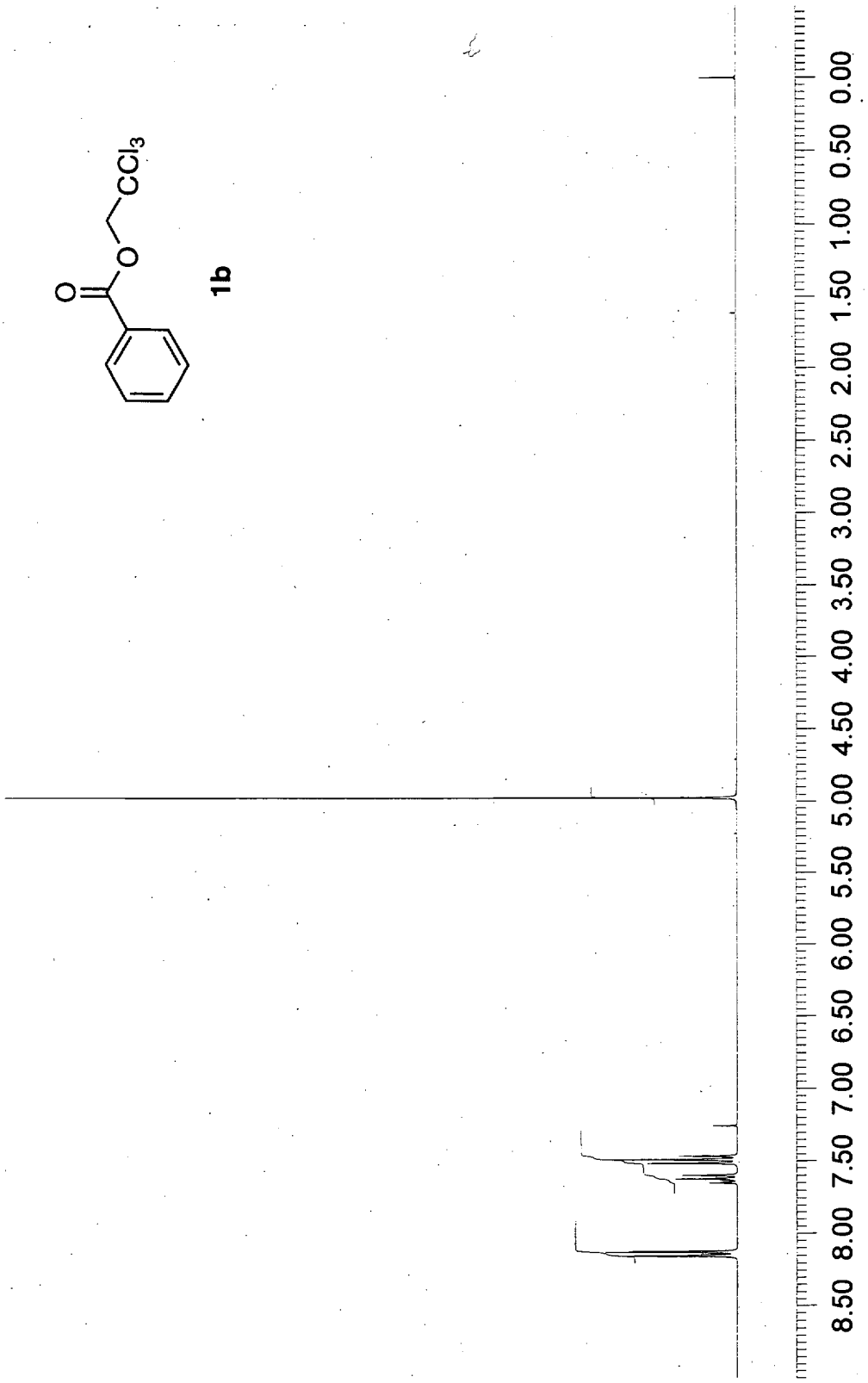


Figure 3: ^{1}H NMR ($CDCl_3$, 300 MHz) of **1b**.

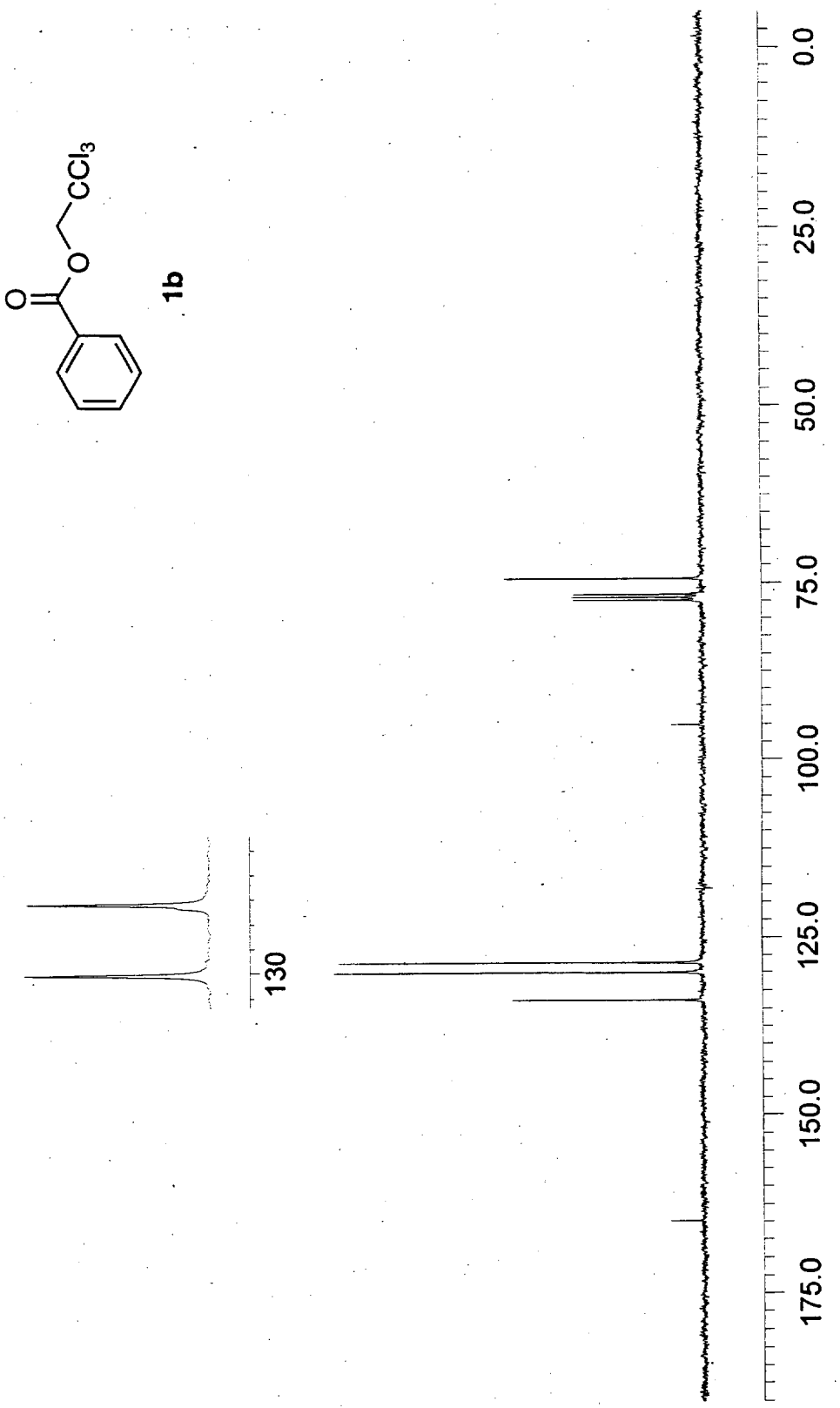


Figure 4: ^{13}C NMR ($CDCl_3$, 300 MHz) of **1b**.

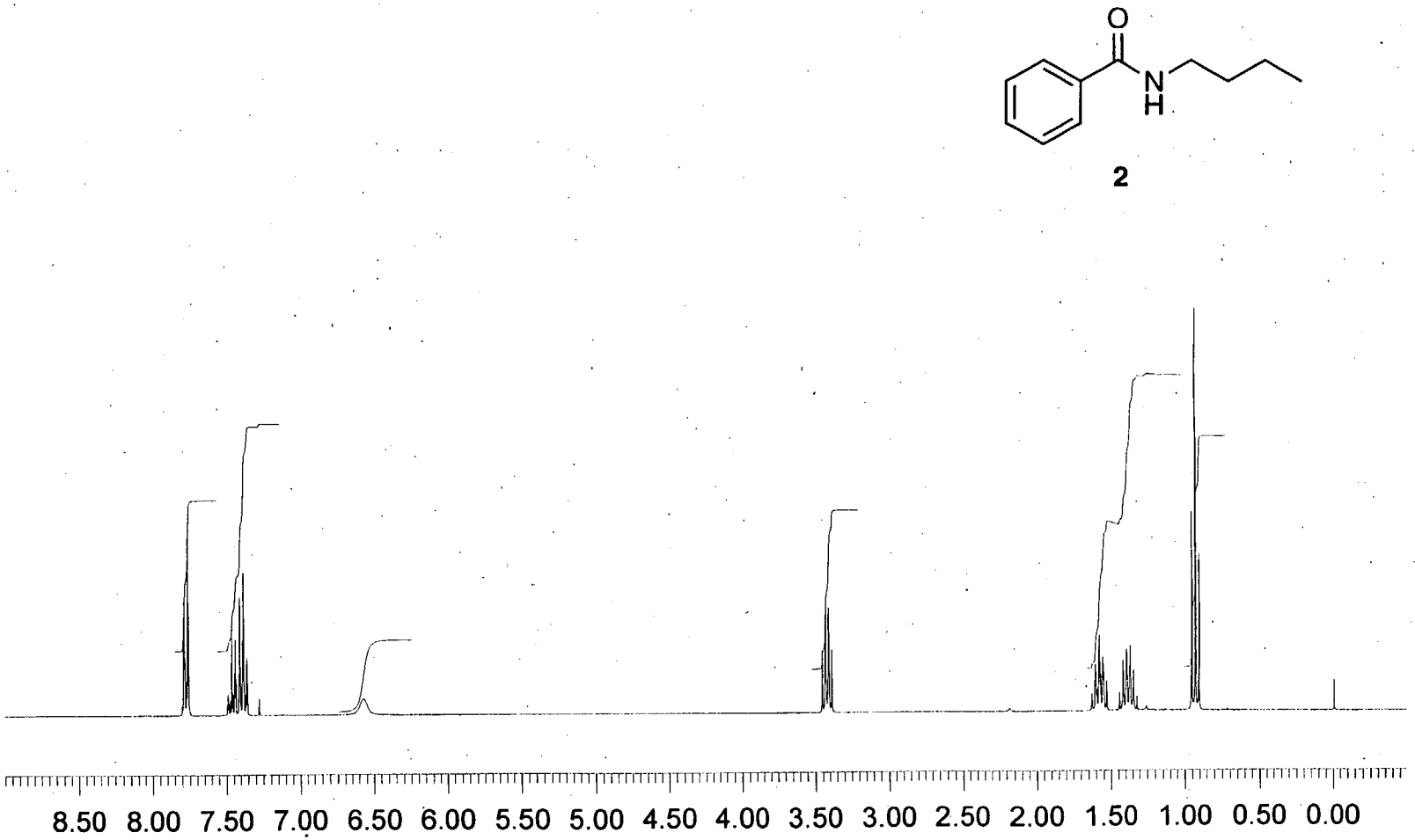


Figure 5: ^{1}H NMR ($CDCl_3$, 300 MHz) of **2**.

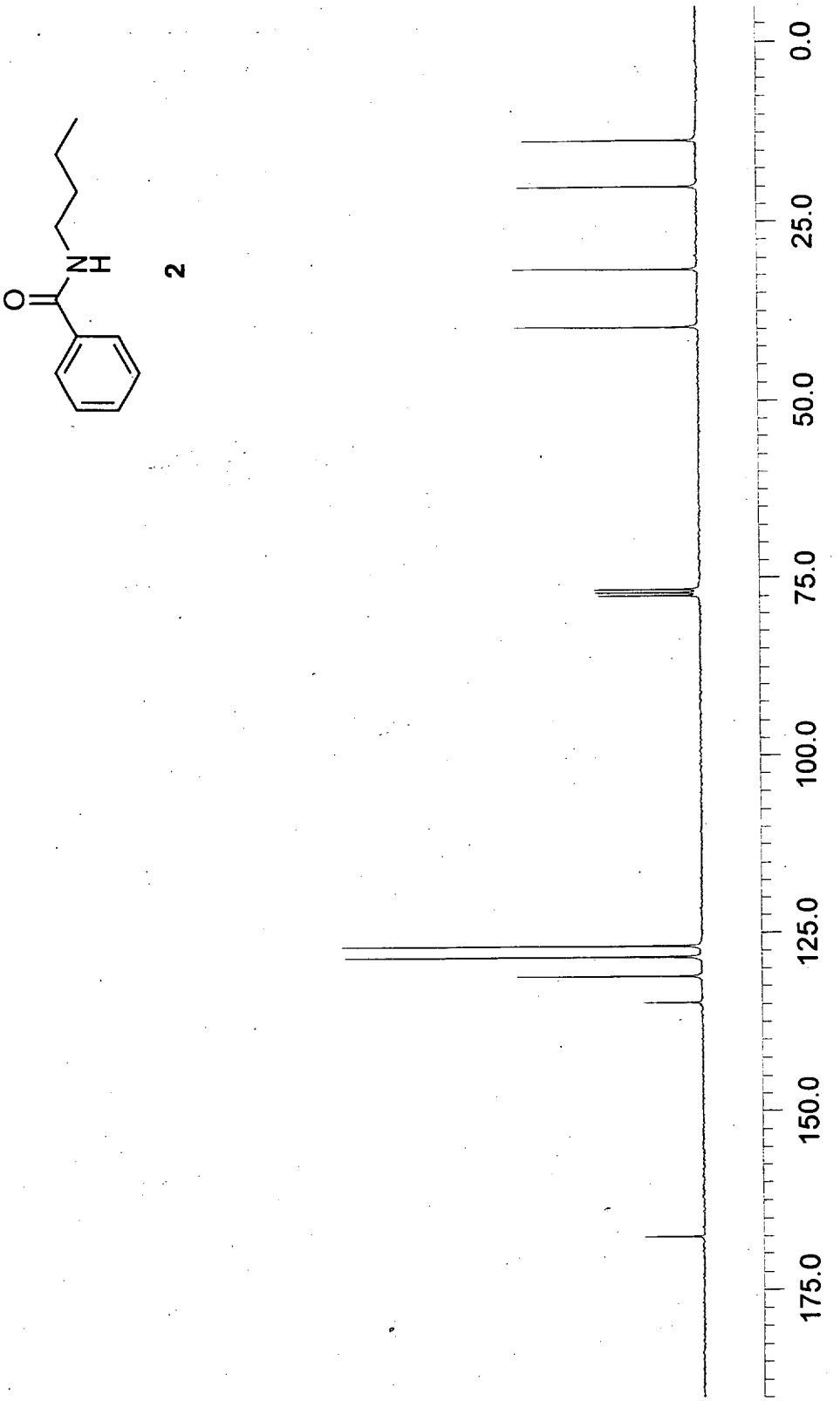


Figure 6: ^{13}C NMR ($CDCl_3$, 300 MHz) of **2**.

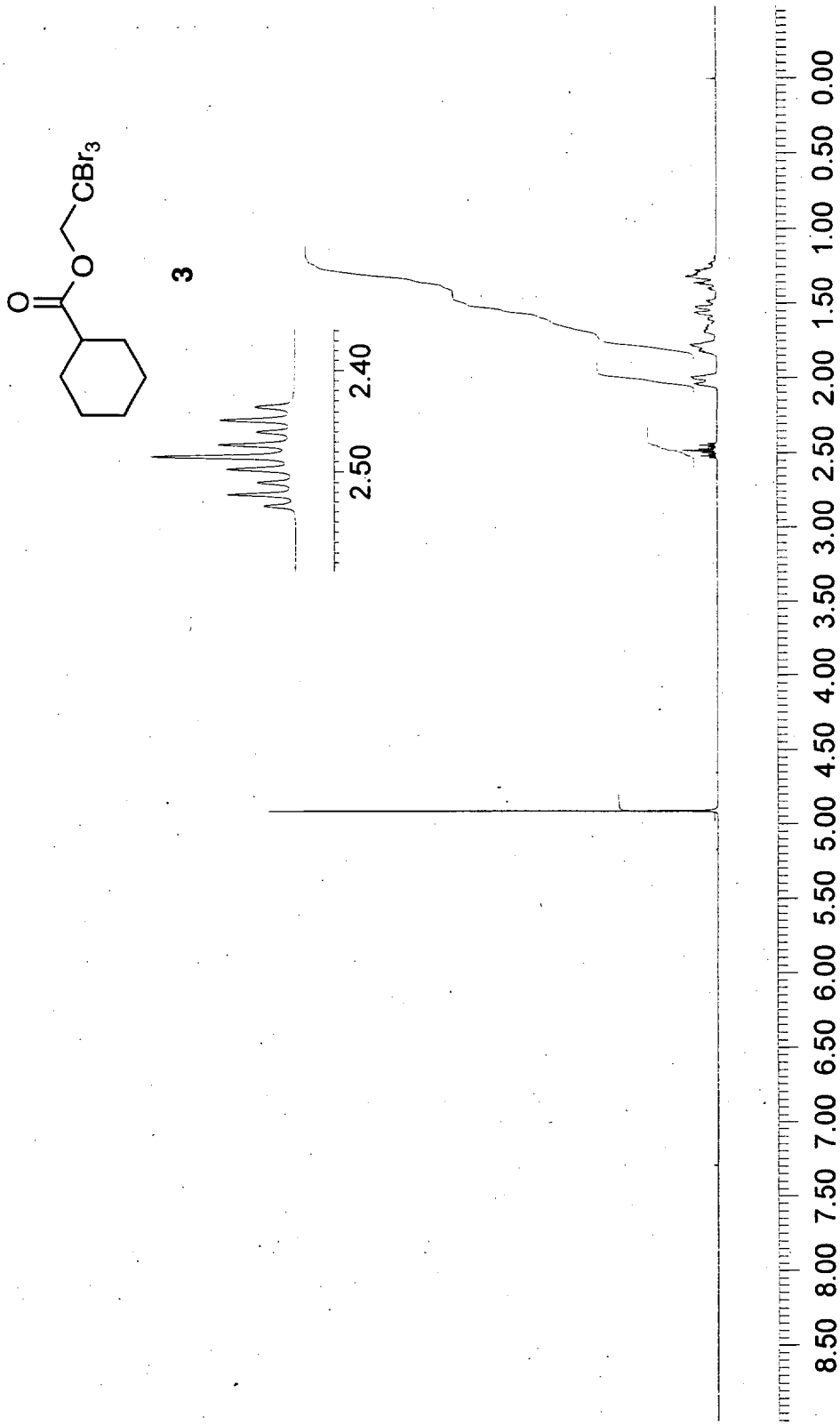


Figure 7: ^{1}H NMR ($CDCl_3$, 300 MHz) of **3**.

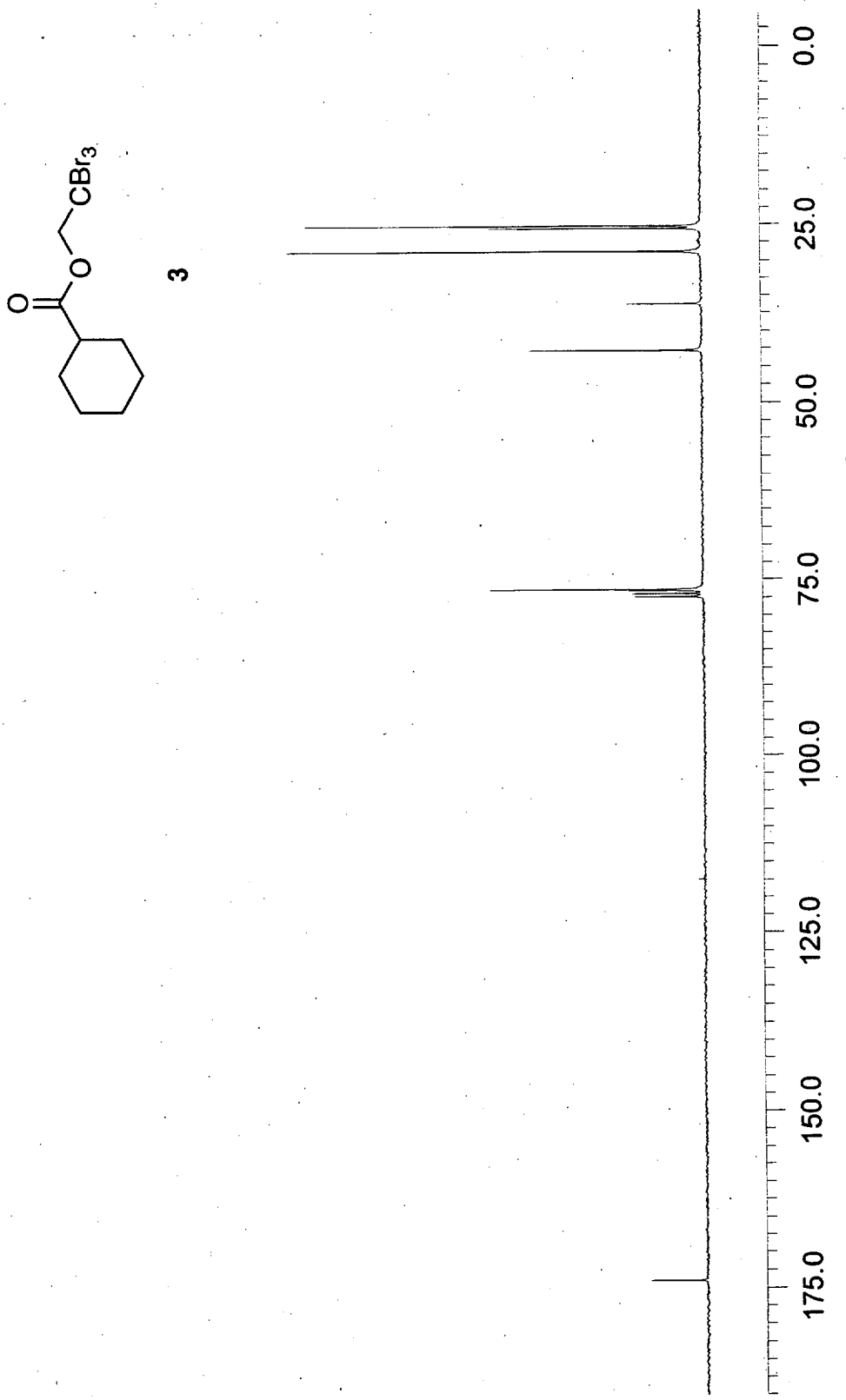


Figure 8: ^{13}C NMR ($CDCl_3$, 300 MHz) of **3**.

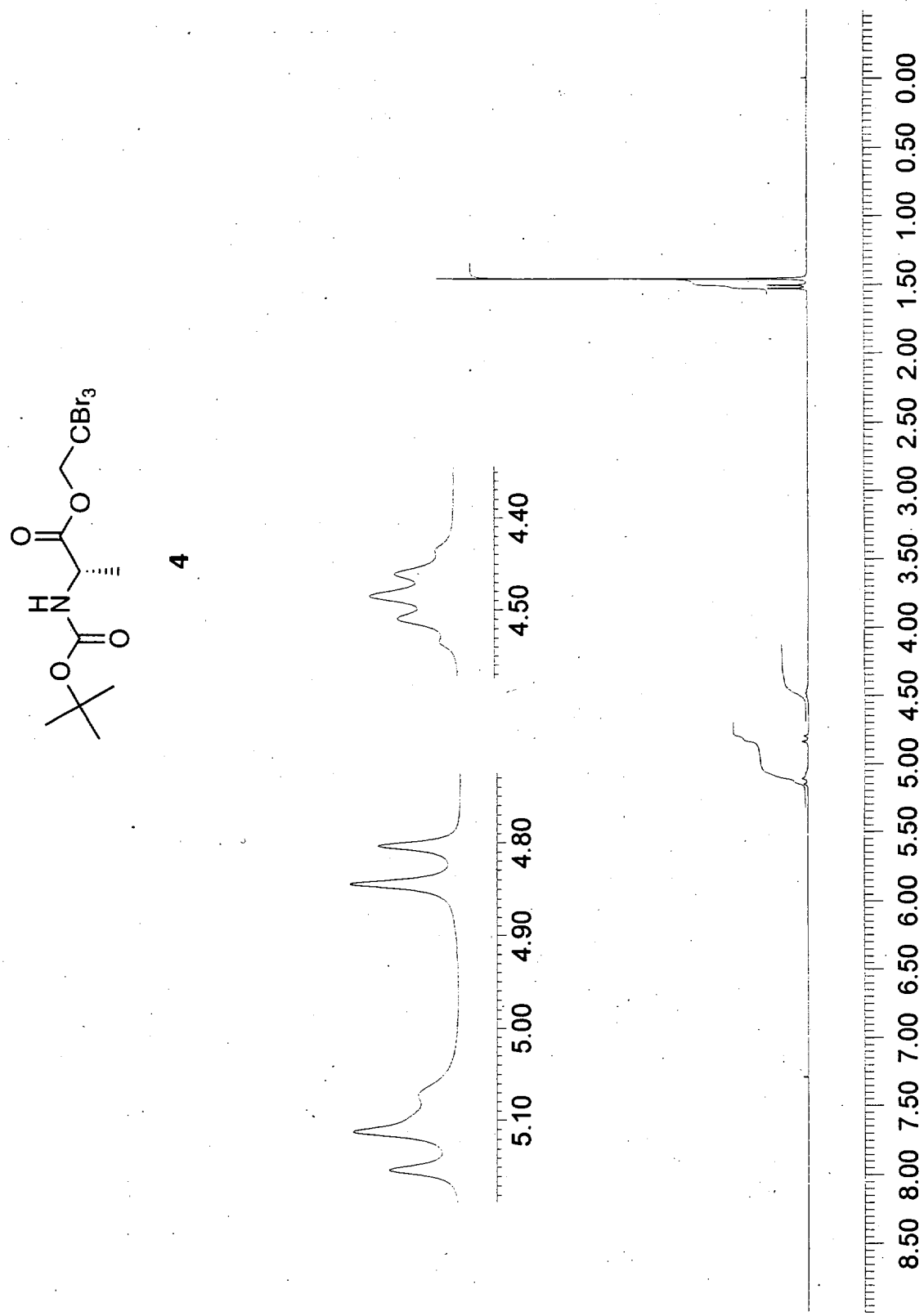


Figure 9: ^{1}H NMR ($CDCl_3$, 300 MHz) of **4**.

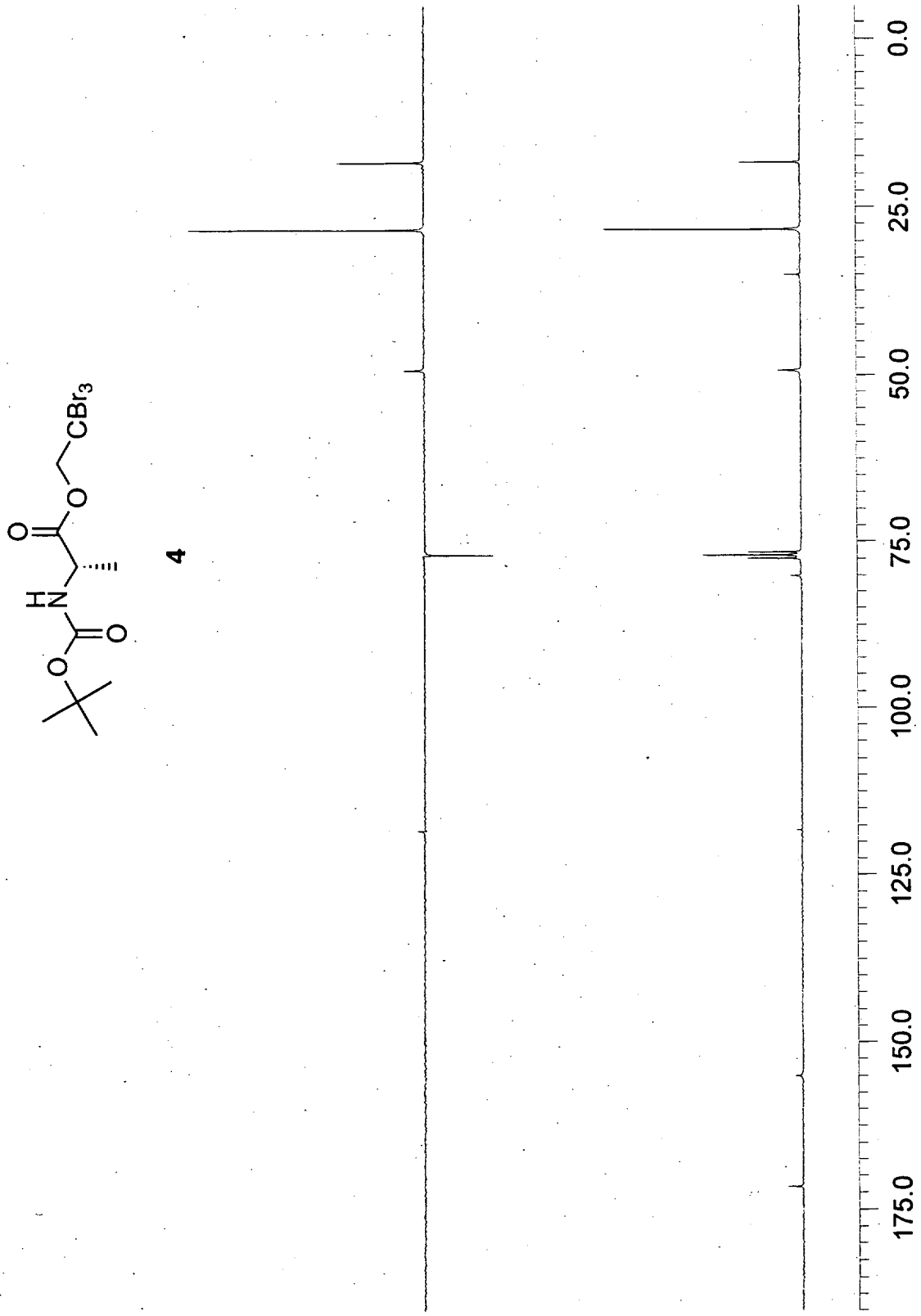
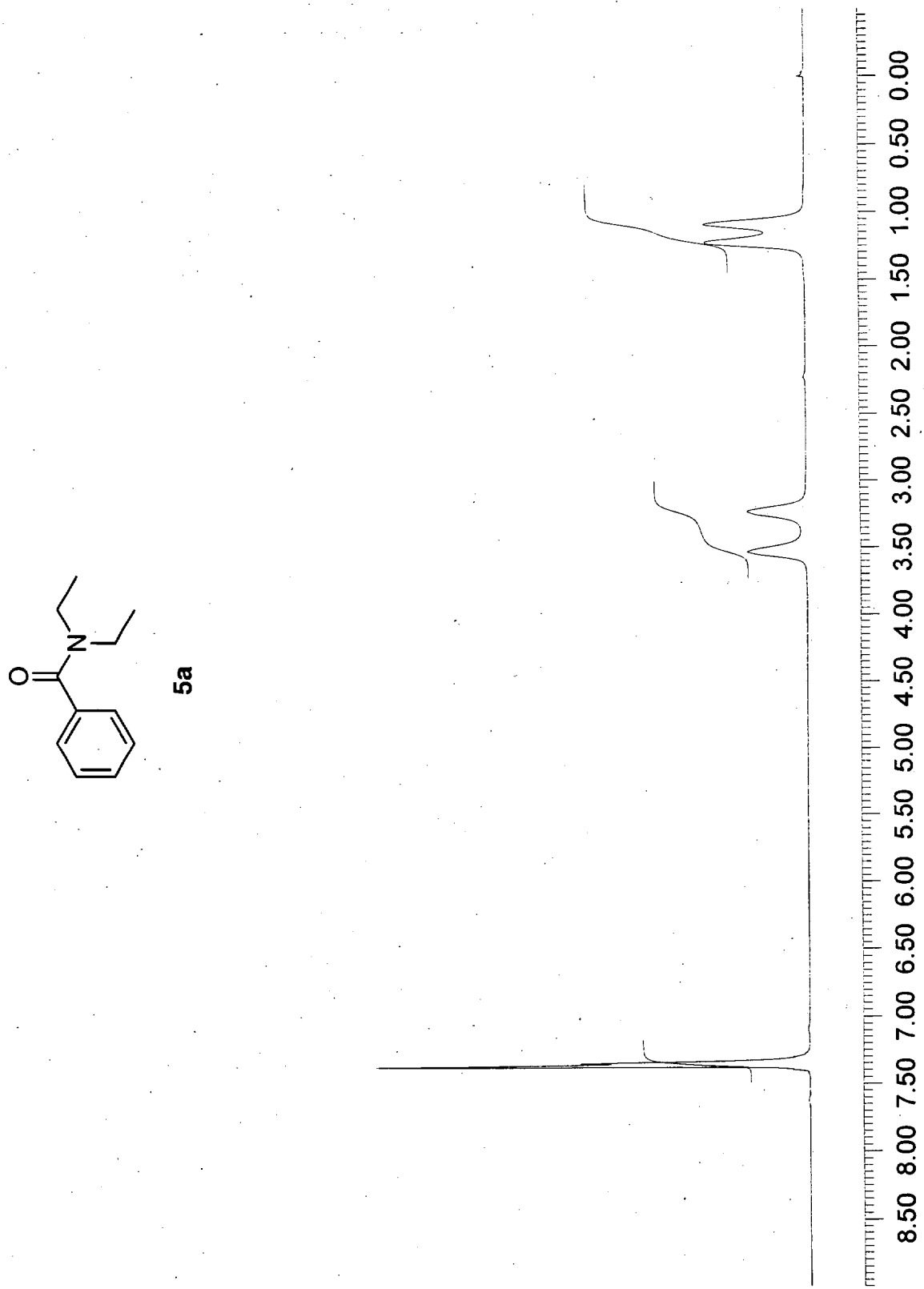


Figure 10: ^{13}C NMR ($CDCl_3$, 300 MHz) of **4**.



5a

Figure 11: ^{1}H NMR ($CDCl_3$, 300 MHz) of **5a**.

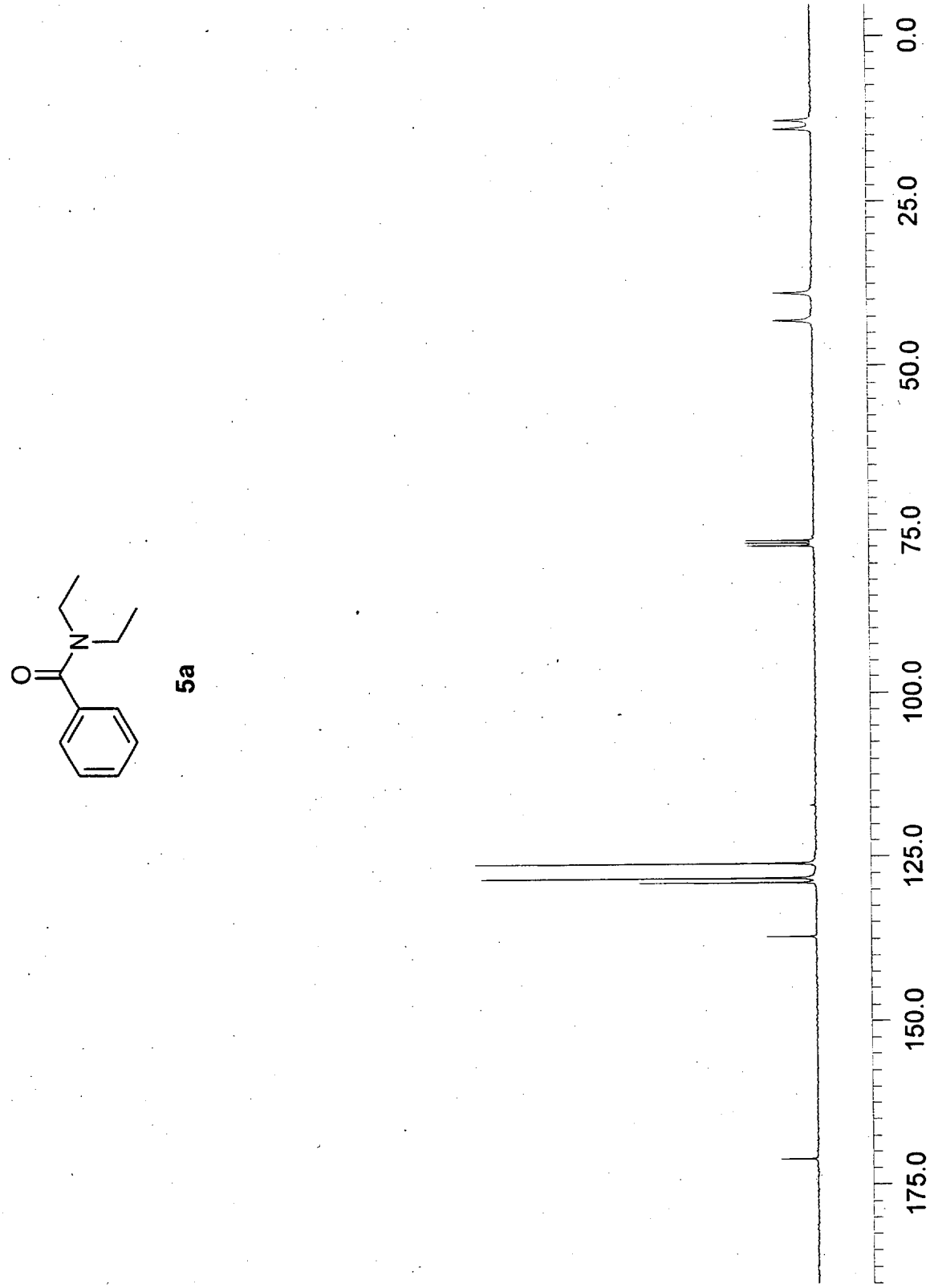


Figure 12: ^{13}C NMR ($CDCl_3$, 300 MHz) of **5a**.

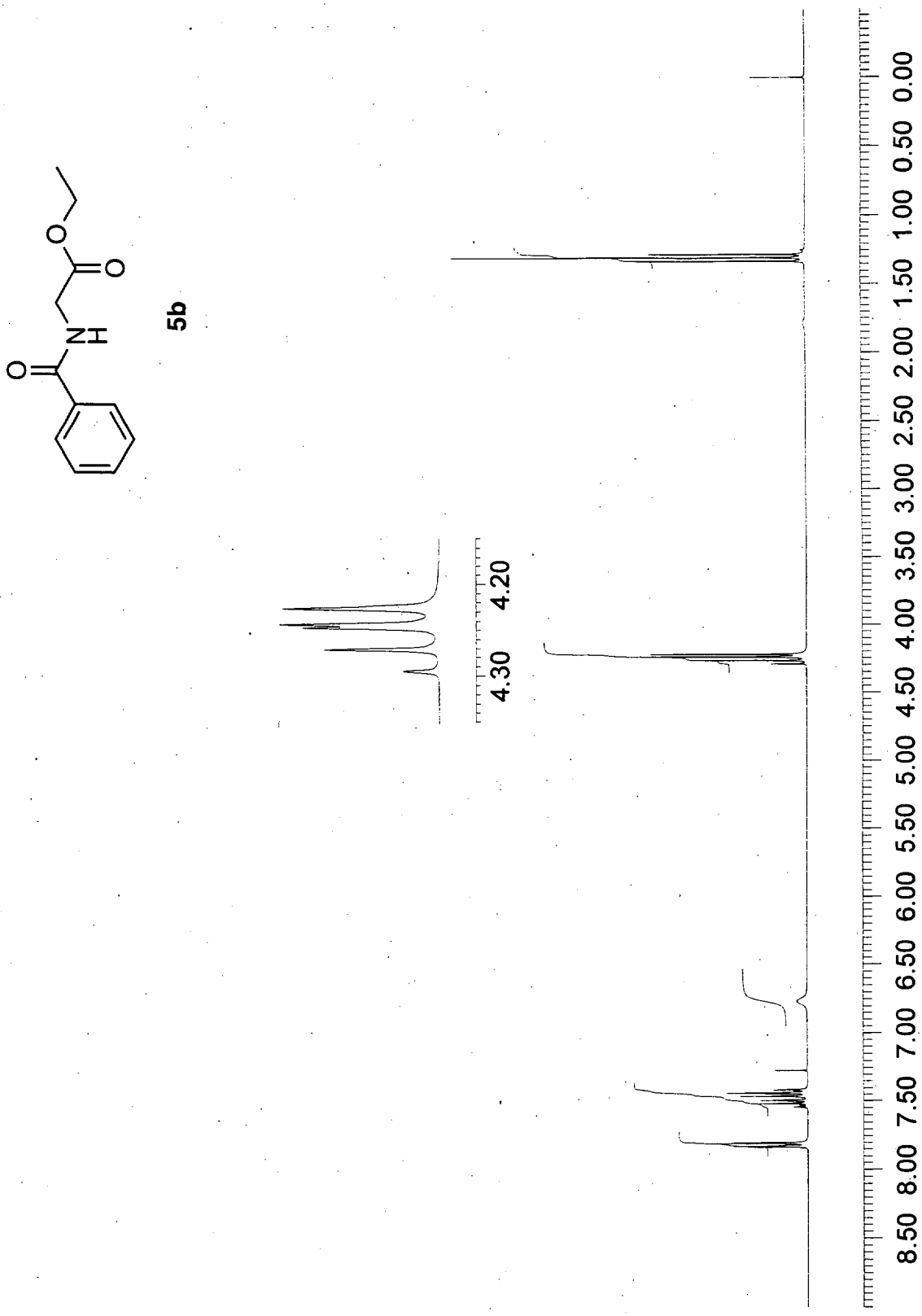
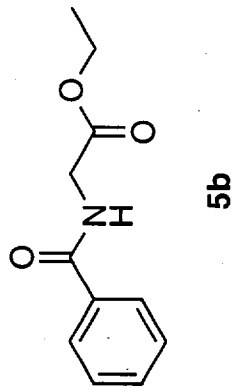


Figure 13: ^{1}H NMR ($CDCl_3$, 300 MHz) of **5b**.



5b

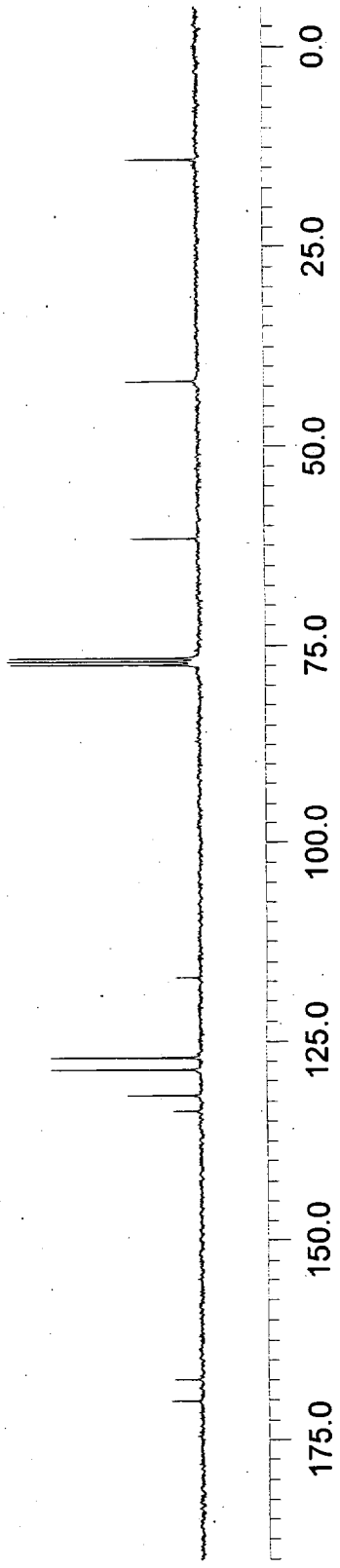


Figure 14: ^{13}C NMR ($CDCl_3$, 300 MHz) of **5b**.

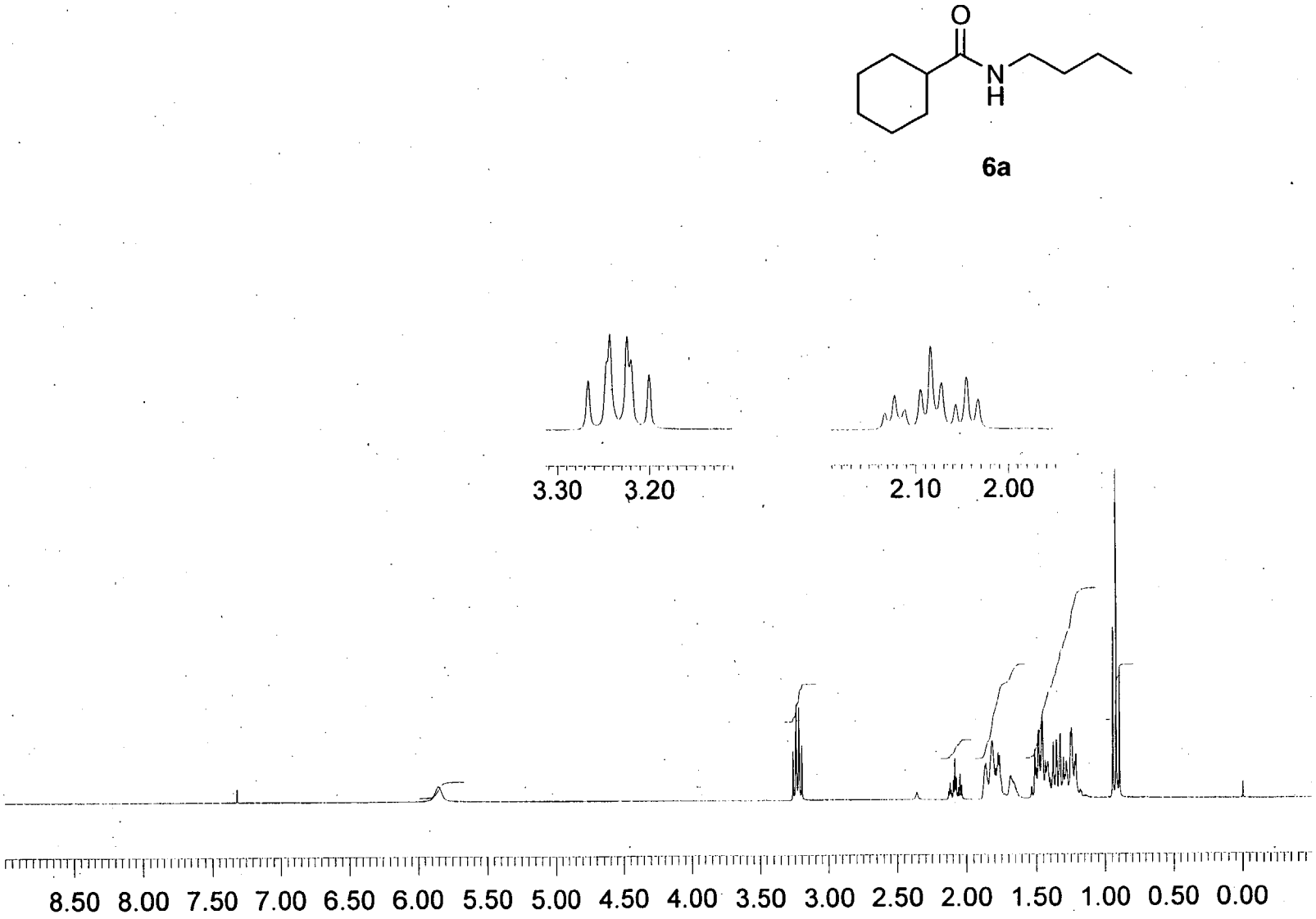


Figure 15: ^{1}H NMR ($CDCl_3$, 300 MHz) of **6a**.

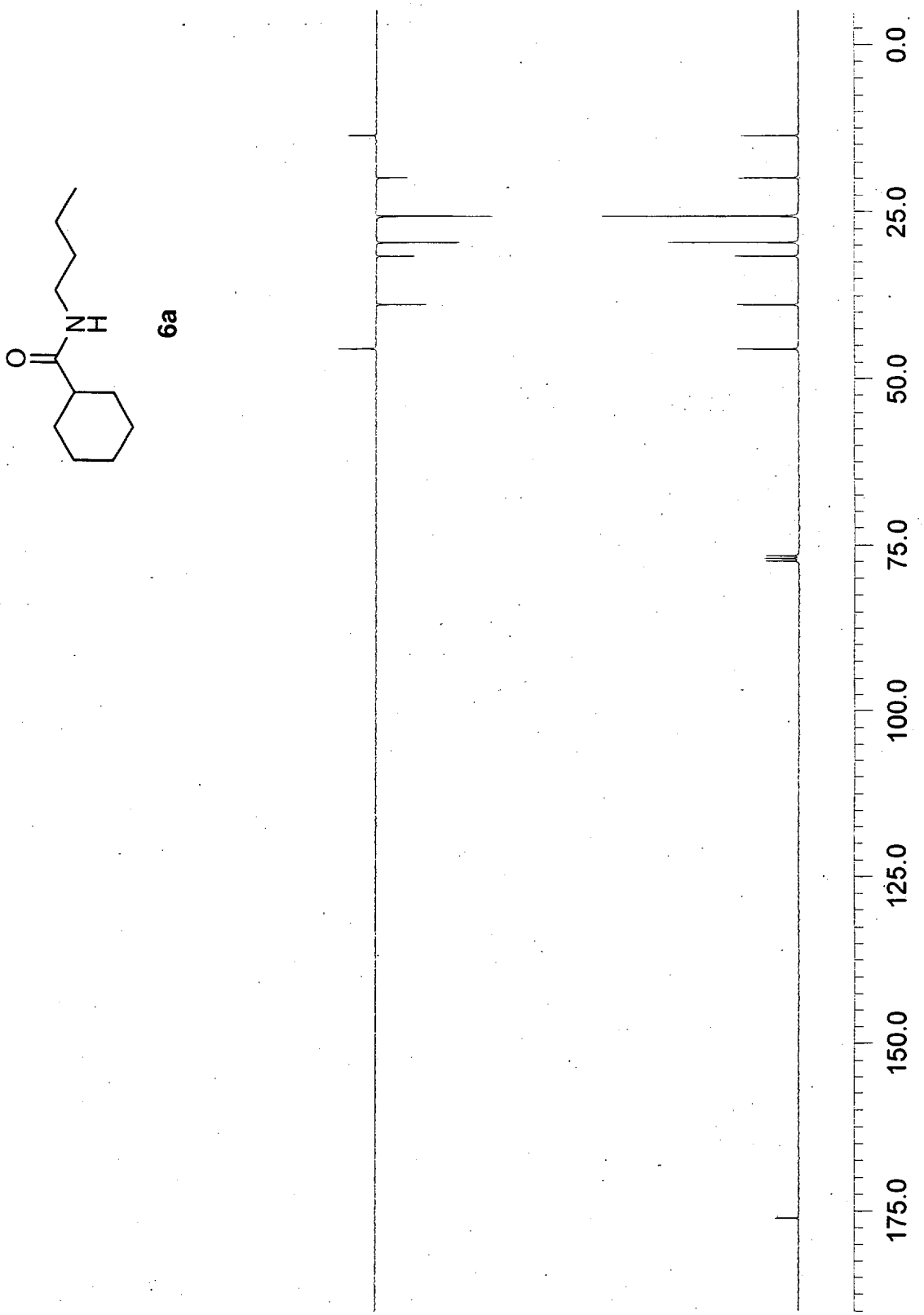
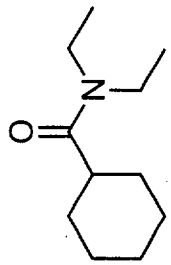


Figure 16: ^{13}C NMR ($CDCl_3$, 300 MHz) of **6a**.



6b

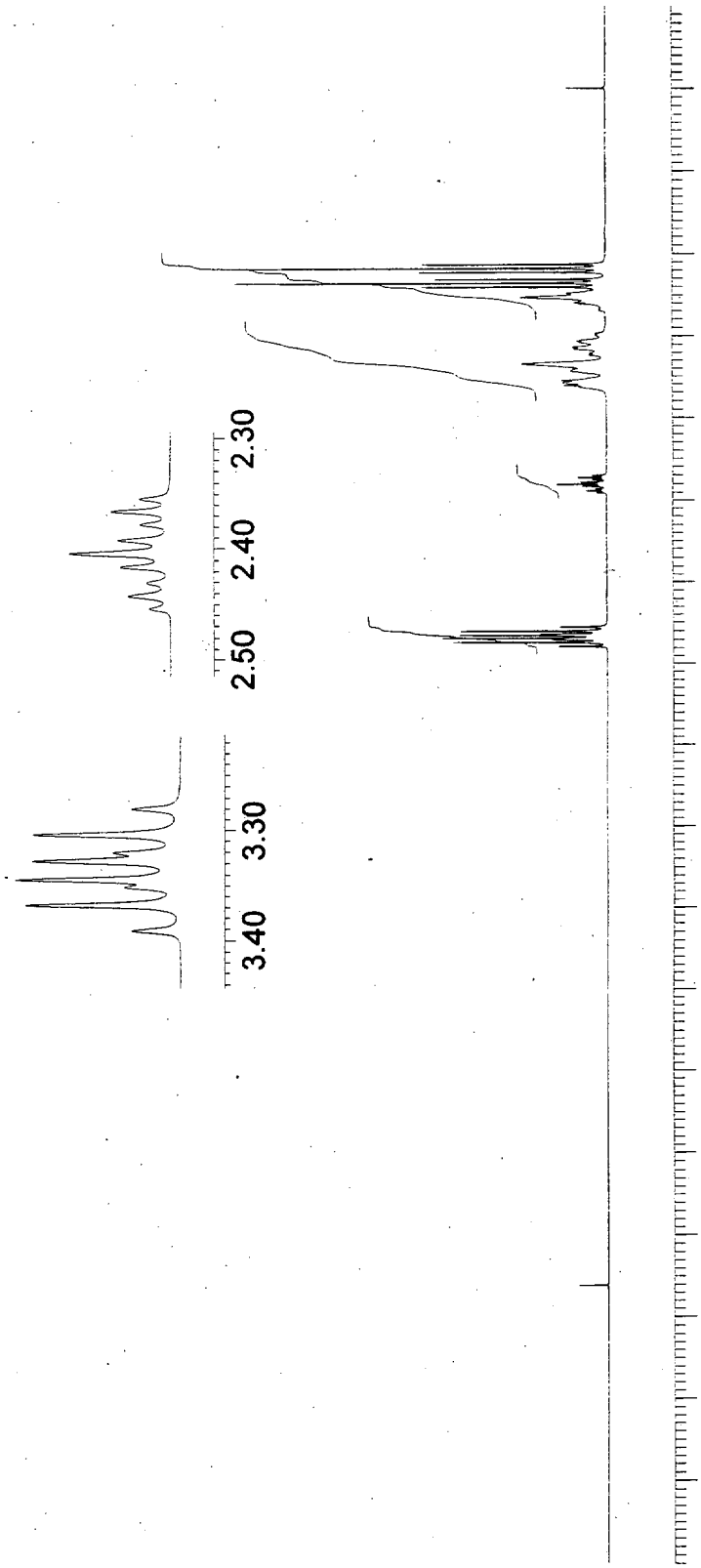


Figure 17: ^{1}H NMR ($CDCl_3$, 300 MHz) of **6b**.

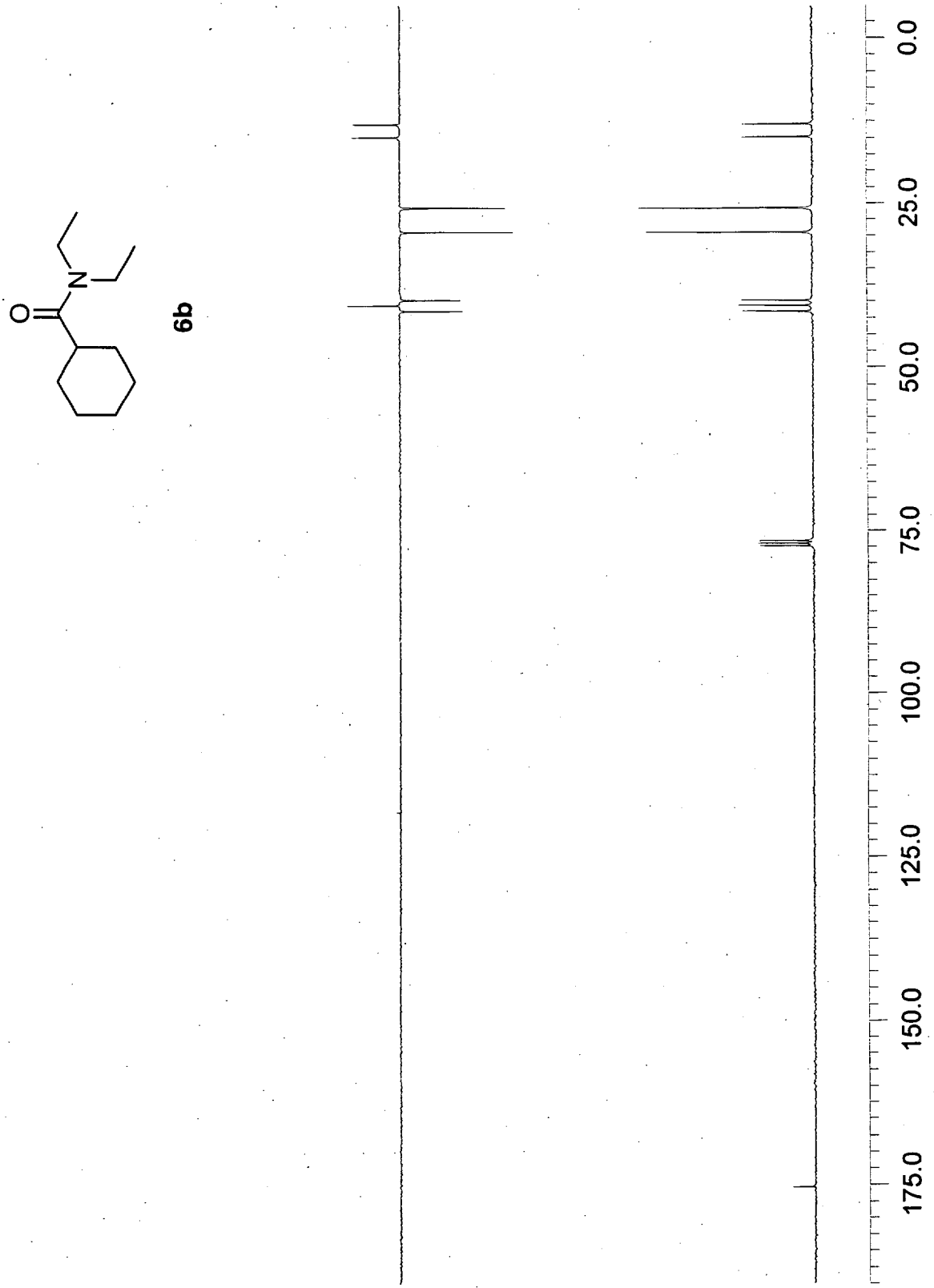


Figure 18: ^{13}C NMR ($CDCl_3$, 300 MHz) of **6b**.

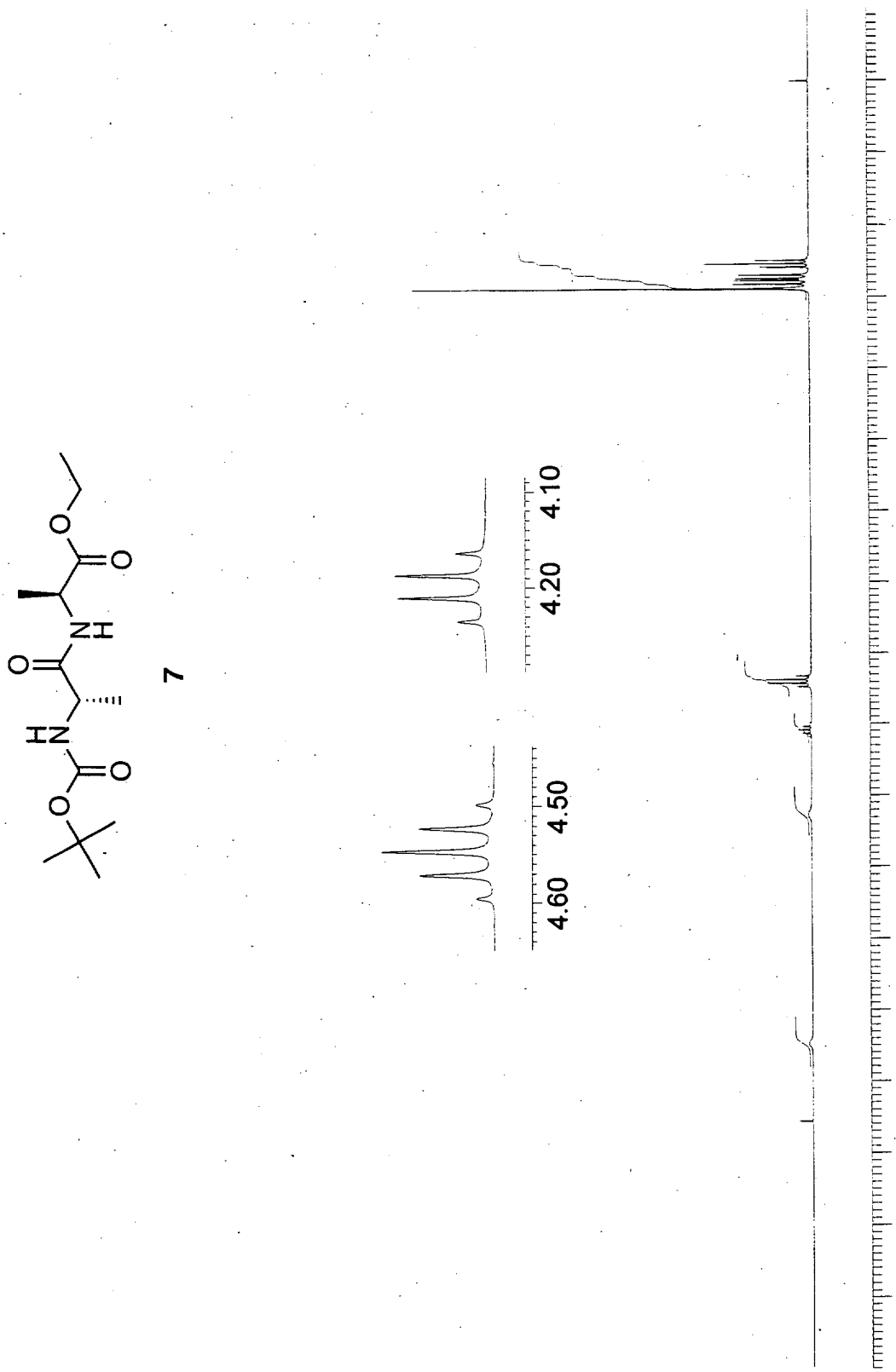
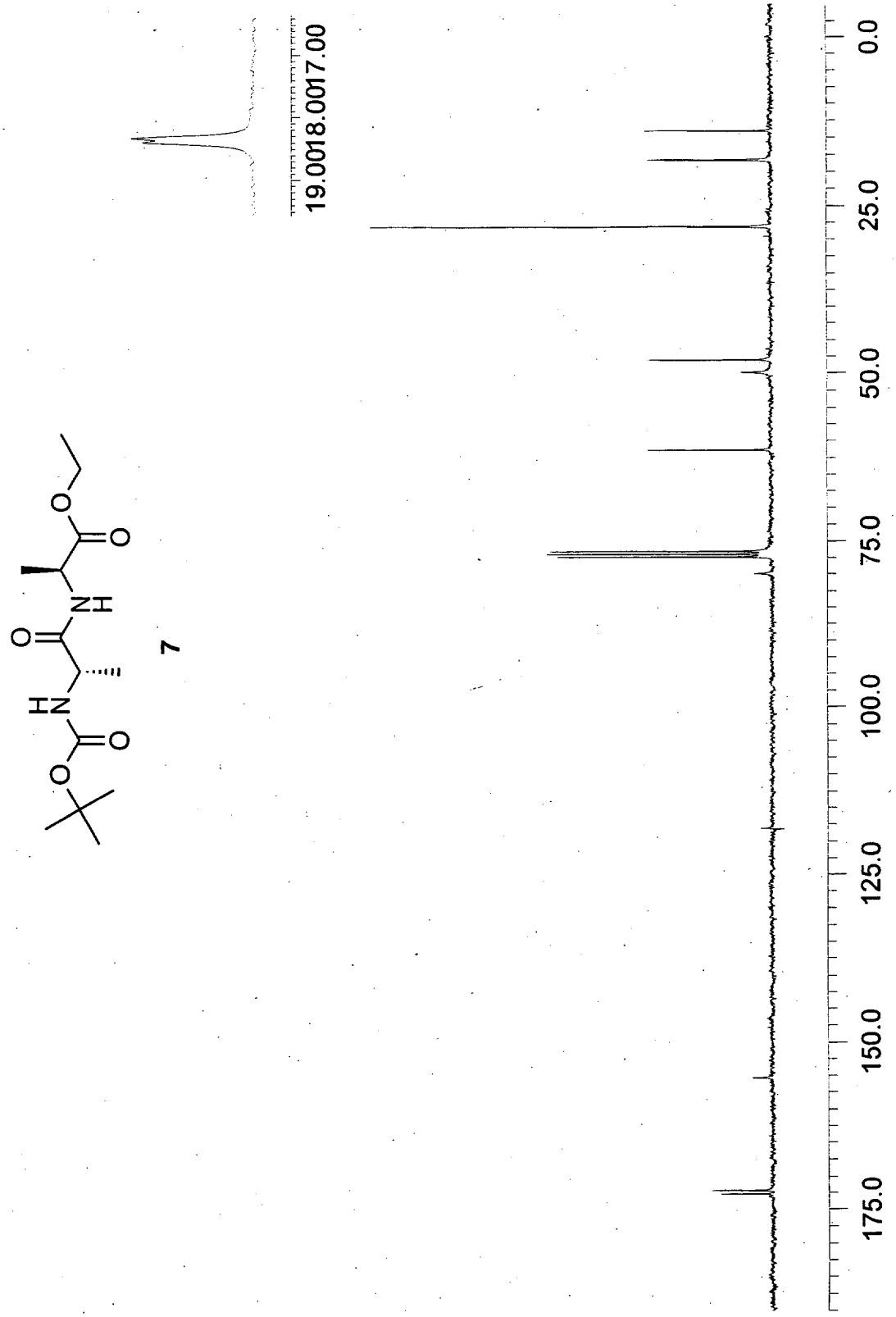
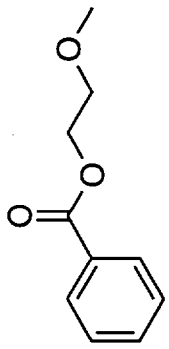


Figure 19: ^{1}H NMR ($CDCl_3$, 300 MHz) of **7**.



7

Figure 20: ^{13}C NMR ($CDCl_3$, 300 MHz) of **7**.



8a

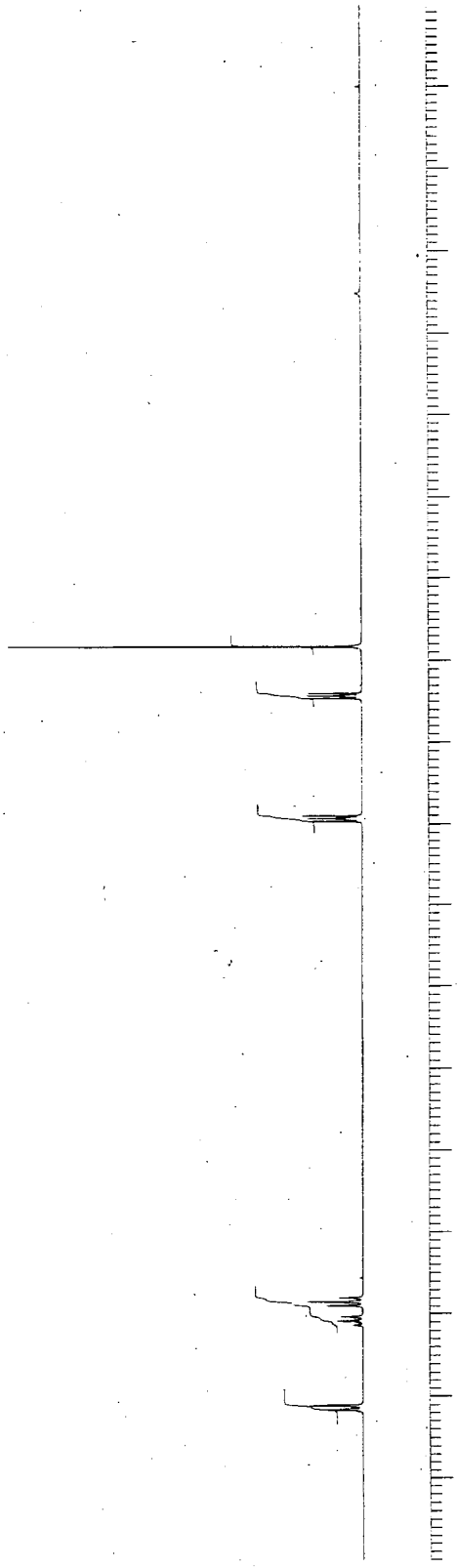
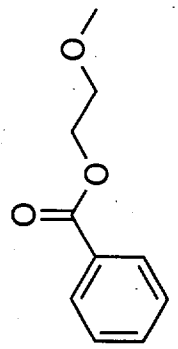


Figure 21: ^{1}H NMR ($CDCl_3$, 300 MHz) of **8a**.



8a

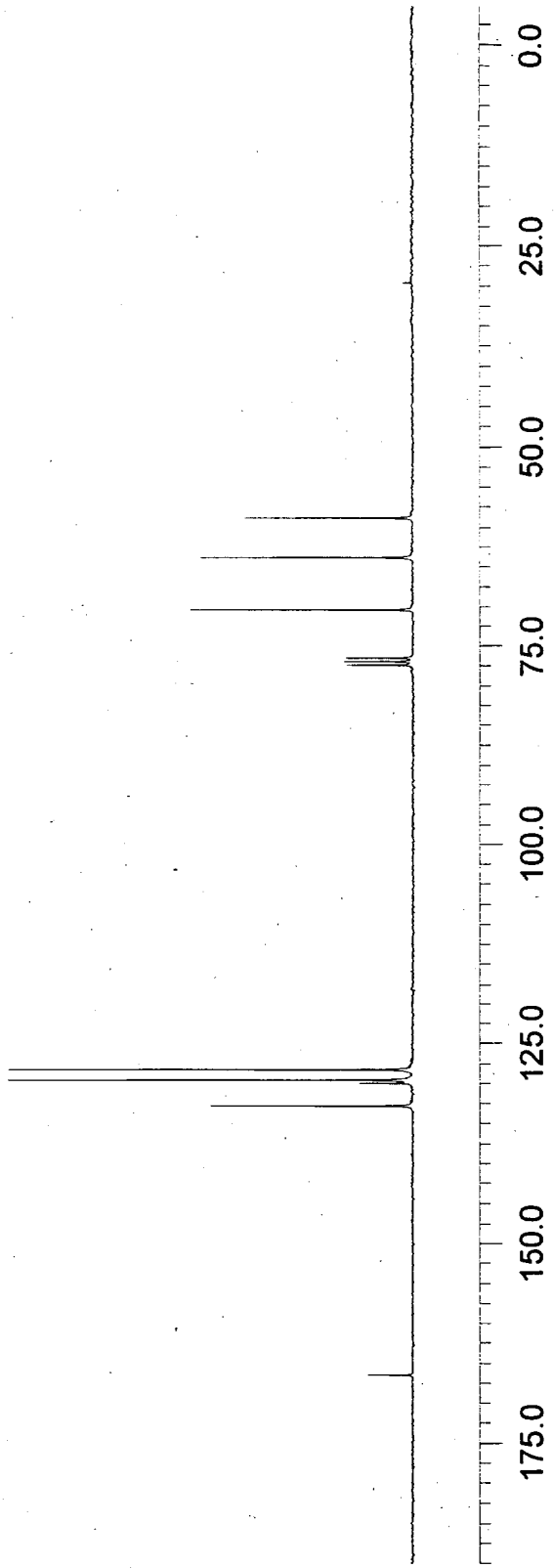
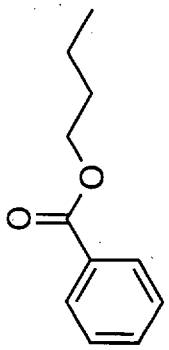


Figure 22: ^{13}C NMR ($CDCl_3$, 300 MHz) of **8a**.



8b

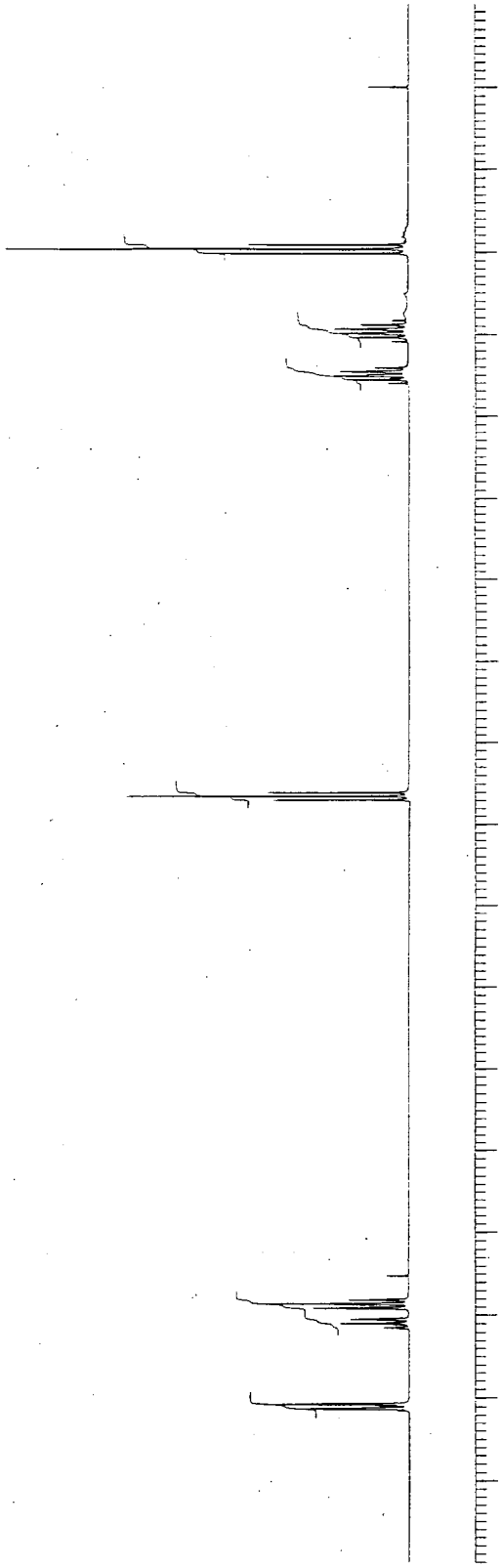
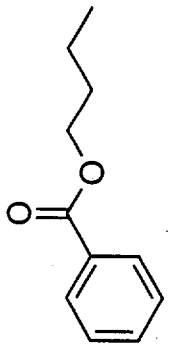


Figure 23: ^{1}H NMR ($CDCl_3$, 300 MHz) of **8b**.



8b

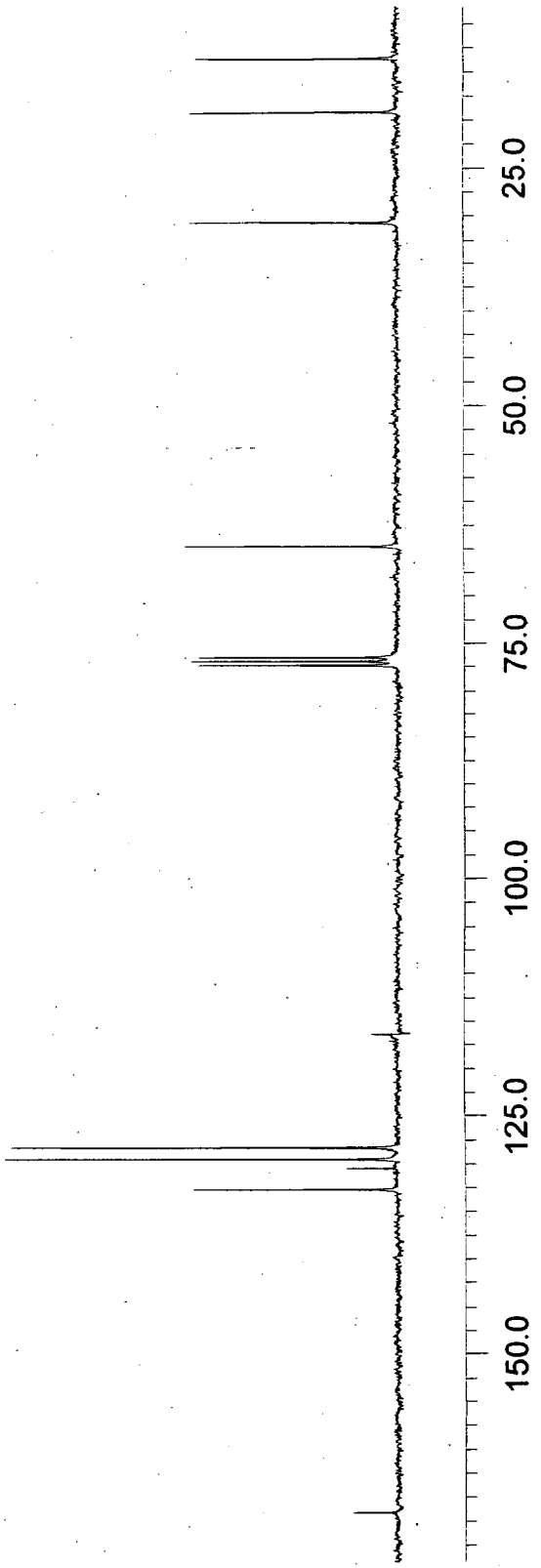
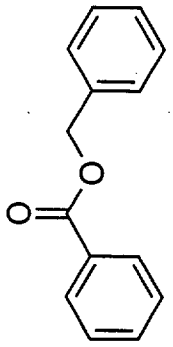


Figure 24: ^{13}C NMR ($CDCl_3$, 300 MHz) of **8b**.



8c

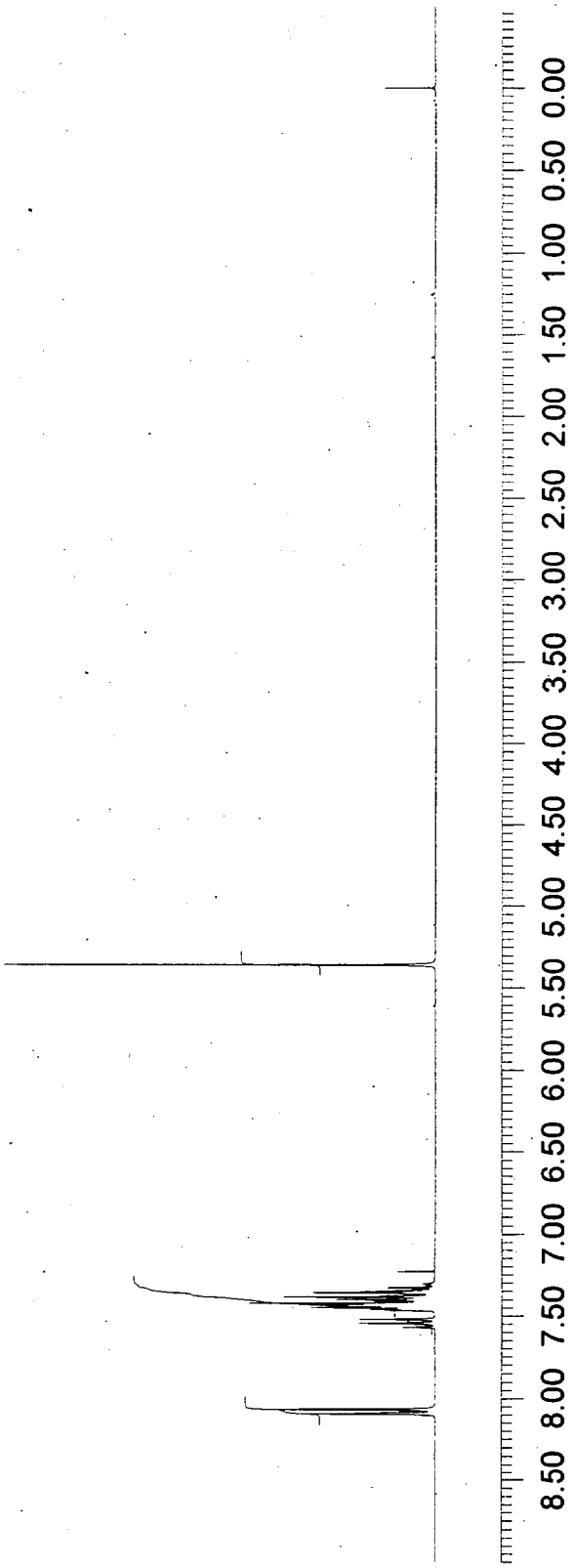


Figure 25: ^{1}H NMR ($CDCl_3$, 300 MHz) of **8c**.

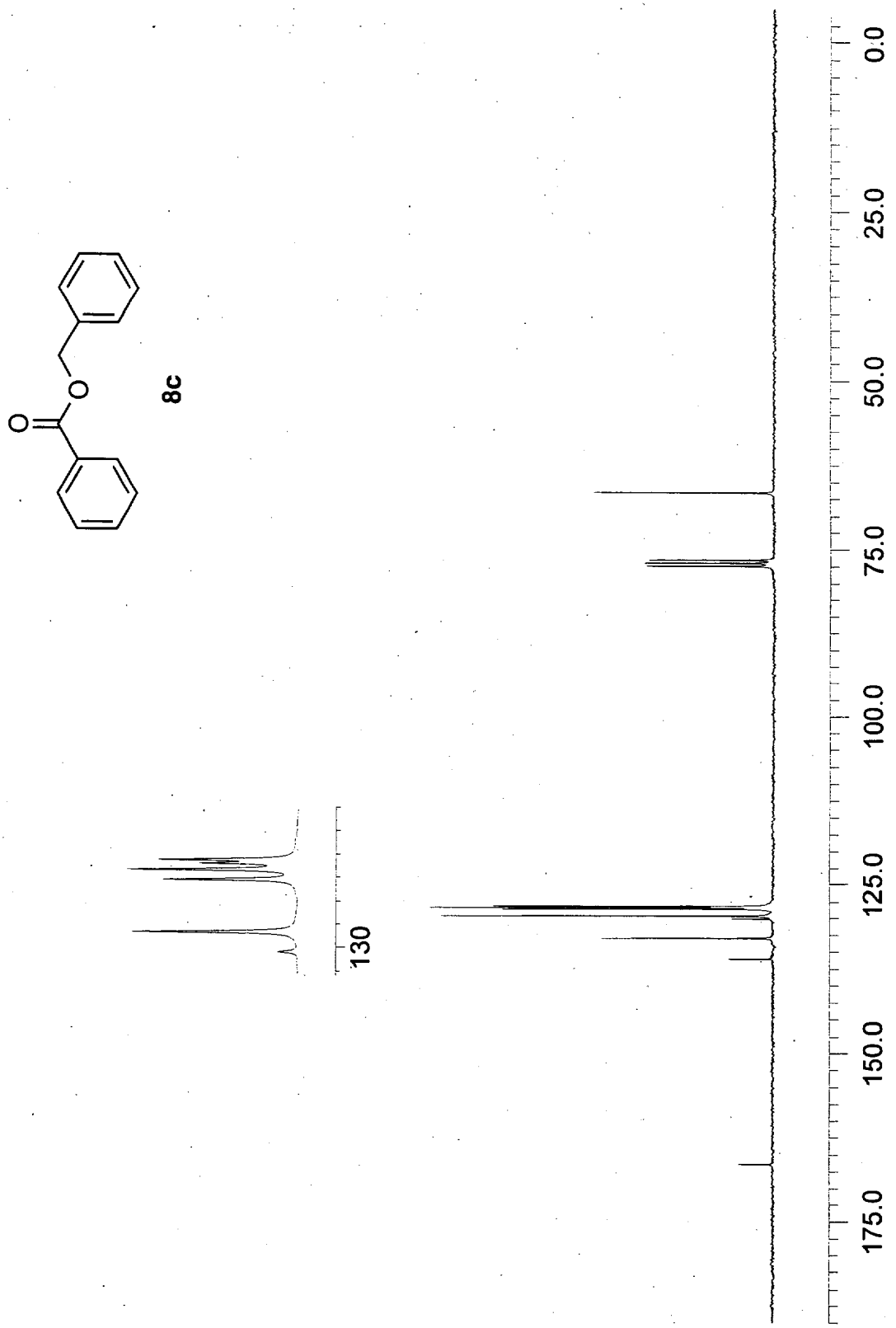
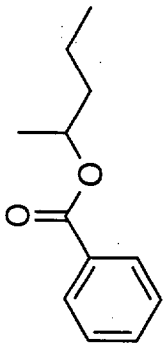


Figure 26: ^{13}C NMR ($CDCl_3$, 300 MHz) of **8c**.



8d

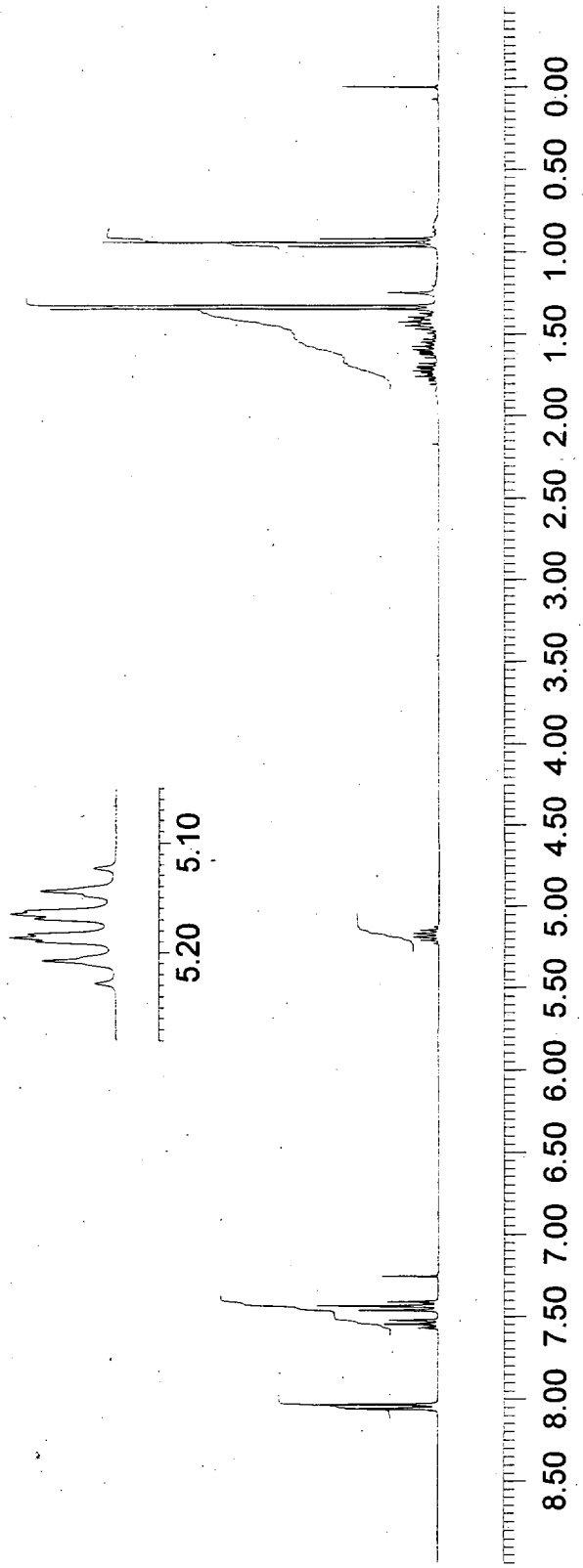


Figure 27: ^{1}H NMR ($CDCl_3$, 300 MHz) of **8d**.

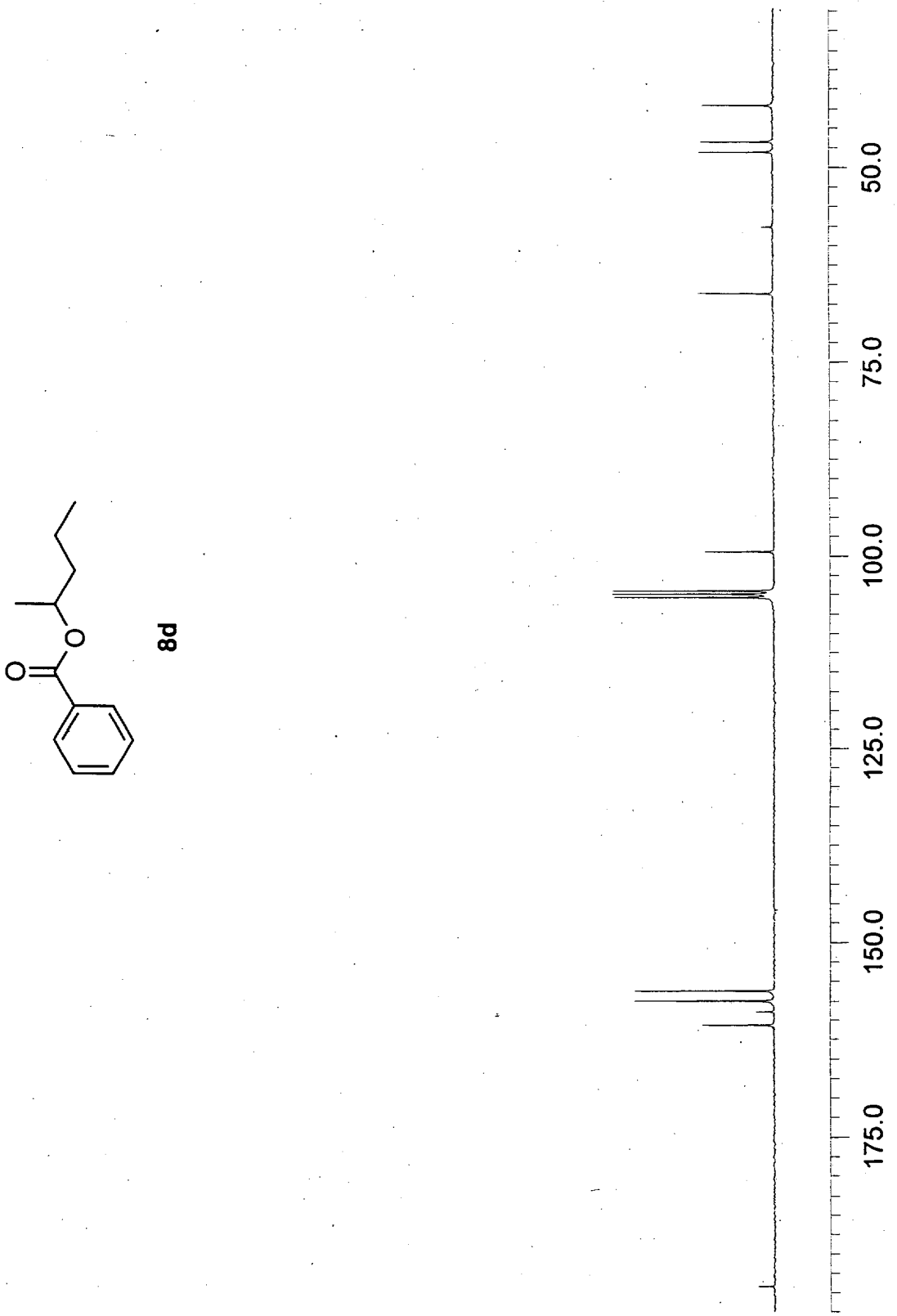


Figure 28: ^{13}C NMR ($CDCl_3$, 300 MHz) of **8d**.