Copper(I)-Catalyzed Regioselective Ullmann-Type Coupling of Primary Carbamates and 5-Substituted-1,2,3-triiodobenzenes: Facile Synthesis of 2,3-Diiodinated N-Arylcarbamates as Potential Antimicrobial Candidates

Supporting Information

Table of Contents

1. Experimental Details and Compound Data.

1.1 General Information

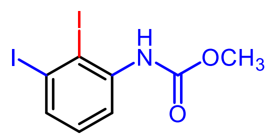
All commercial reagents and chromatography solvents were used as obtained unless otherwise stated. Ethanol, toluene, ethyl acetate, hexanes, anhydrous sodium sulfate (Na_2SO_4, BDH) were used as received. Anhydrous solvents were distilled over appropriate drying agents prior to use. Analytical thin layer chromatography (TLC) was performed on Merck silica gel 60 F_{254}. Merck Silica gel 60 (0.063 - 0.2 mm) was used for column chromatography. Visualization of TLC was accomplished with UV light (254 nm). NMR spectra were recorded on a Bruker-Avance 400 MHz spectrometer. The residual solvent protons (^{1}H) or the solvent carbon (^{13}C) were used as internal standards. ^{1}H-NMR data are presented as follows: chemical shift in ppm (δ) downfield from trimethylsilane (multiplicity, integration, coupling constant). The following abbreviations are used in reporting NMR data: s, singlet; bs, broad singlet; d, doublet; t, triplet; q, quartet; dq, doublet of quartets; dd, doublet of doublets; m, mutiplet. High resolution mass spectra were recorded using Chemical Ionization (CI) and Electrospray ionization (ESI) techniques.

1.2 General procedure for 2,3-diiodophenylcarbamate derivatives from 5-substituted-1,2,3-triiodobenzenes *via* Ullmann-type C-N cross-coupling reaction

In a flame-dried sealed tube, 1,2,3-triiodoarene (0.66 mmol), primary carbamate (0.79 mmol, 1.2 equiv.), copper iodide (10-mol%), DMEDA (20-mol %), potassium carbonate (4.0 equiv.) and 6.6 mL toluene (0.1M) were added under argon. The mixture was stirred at 110 ^oC for 12 h. The reaction was cooled down to room temperature and then

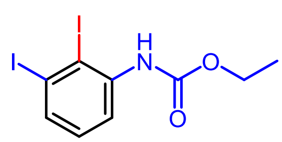
50 mL EtOAc was added. The mixture was filtrated over a pad of Celite 545®. Organic layers were combined, dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The crude product was purified by flash chromatography (5% EtOAc/hexane) to yield the pure desired product.

1.2.1 *Synthesis of methyl (2,3-diiodophenyl)carbamate (5A)*



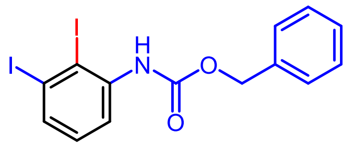
The title compound was prepared using the general procedure and isolated as white solid (**72%** yields). **M.p:** 125-126 °C. **IR** (cast film, cm^{-1}) 3324, 3007, 2994, 1701, 1624, 1251, 1027, 861. **δ_H** (400MHz, $CDCl_3$) δ: 8.00 (d, 1H, *J* = 8.1 Hz), 7.62 (dd, 1H, J^1 = 1.2 Hz, J^2 = 7.8 Hz), 7.16 (bs, 1H), 7.09 (dd, 1H, J^1 = 8.3 Hz, J^2 = 8.0 Hz), 3.80 (s, 3H). **δ_C** (100 MHz, $CDCl_3$) δ: 154.2, 140.4, 134.6, 130.5, 119.1, 108.7, 103.5, 52.8. **HRMS** (ESI) m/z for $C_8H_8I_2NO_2$ $[M+H]^+$: calcd. 403.8644; found, 403.8637.

1.2.2 *Synthesis of ethyl (2,3-diiodophenyl)carbamate (6A)*



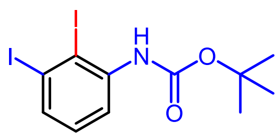
The title compound was prepared using the general procedure and isolated as white solid (**67%** yields). **M.p:** 116-118 °C. **IR** (cast film, cm^{-1}) 3327, 3004, 2995, 1697, 1627, 1263, 1042, 872. **δ_H** (400 MHz, $CDCl_3$) δ: 8.01 (d, 1H, *J* = 8.2 Hz), 7.62 (d, 1H, *J* = 7.7 Hz), 7.13 (bs, 1H), 7.08 (t, 1H, *J* = 8.04 Hz), 4.24 (q, 2H, *J* = 7.1 Hz), 1.34 (t, 3H, *J* = 7.1 Hz). **δ_C** (100 MHz, $CDCl_3$) δ: 153.7, 140.6, 134.5, 130.5, 119.1, 108.7, 103.4, 61.9, 14.6. **HRMS** (ESI) m/z for $C_9H_{10}I_2NO_2$ $[M+H]^+$: calcd. Exact 417.8801; found, 417.8798.

1.2.3 *Synthesis of N-(2,3-diiodophenyl)-2-phenoxyacetamide (7A)*



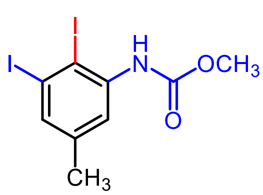
The title compound was prepared using the general procedure and isolated as white solid (**77%** yields). **M.p:** 131-132 °C. **IR** (cast film, cm^{-1}) 3361, 3014, 1689, 1614, 1527, 1271, 1107, 943, 764. **δH** (400 MHz, $CDCl_3$) δ: 8.03 (d, 1H, *J* = 8.2 Hz), 7.63 (d, 1H, *J* = 7.8 Hz), 7.34-7.44 (m, 5H), 7.23 (bs, 1H), 7.10 (t, 1H, J^1 = 8.0 Hz), 5.22 (s, 2H). **δC** (100 MHz, $CDCl_3$) δ: 153.6, 140.4, 135.9, 134.7, 130.5, 128.8, 128.7, 128.6, 119.2, 108.8, 103.6, 67.6. **HRMS** (ESI) m/z for $C_{14}H_{12}I_2NO_2$ $[M+H]^+$: calcd. Exact 479.8957; found, 479.8951.

1.2.4 Synthesis of tert-butyl (2,3-diiodophenyl)carbamate (8_A)



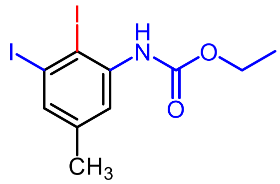
The title compound was prepared using the general procedure and isolated as colorless oil (**71%** yields). **IR** (cast film, cm^{-1}) 3351, 3012, 2994, 1694, 1644, 1276, 1043, 869. **δH** (400 MHz, $CDCl_3$) δ: 8.01 (d, 1H, *J* = 7.9 Hz), 7.59 (d, 1H, *J* = 7.8 Hz), 7.05 (dd, 1H, *J* = 7.9 Hz, *J* = 8.2 Hz), 7.02 (bs, 1H), 1.53 (s, 9H). **δC** (100 MHz, $CDCl_3$) δ: 152.8, 134.2, 130.4, 119.1, 108.7, 103.4, 81.5, 28.4. **HRMS** (ESI) m/z for $C_{11}H_{14}I_2NO_2$ $[M+H]^+$: calcd. 445.9114; found, 445.9106.

1.2.5 Synthesis of methyl (2,3-diiodo-5-methylphenyl)carbamate (10_A)



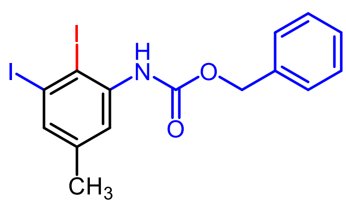
The title compound was prepared using the general procedure and isolated as white solid (**84%** yields). **M.p:** 123-124 °C. **IR** (cast film, cm^{-1}) 3341, 3007, 2992, 1692, 1627, 1273, 1136, 938, 626. **δH** (400MHz, $CDCl_3$) δ: 7.83 (s, 1H), 7.49 (s, 1H), 7.10 (bs, 1H), 3.79 (s, 3H), 2.26 (s, 3H). **δC** (100 MHz, $CDCl_3$) δ: 154.2, 141.1, 139.8, 135.5, 120.2, 108.5, 99.5, 52.8, 21.0. **HRMS** (ESI) m/z for $C_9H_{10}I_2NO_2$ $[M+H]^+$: calcd. 417.8801; found, 417.8798.

1.2.6 Synthesis of ethyl (2,3-diiodo-5-methylphenyl)carbamate (11A)



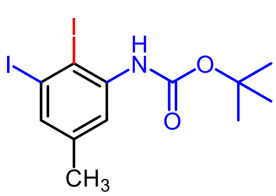
The title compound was prepared using the general procedure and isolated as white solid (**78%** yields). **M.p:** 101-102 °C. **IR** (cast film, cm^{-1}) 3361, 3002, 2988, 1701, 1637, 1267, 1109, 869. **δH** (400 MHz, CDCl3) δ: 7.84 (s, 1H), 7.48 (d, 1H, *J* = 0.9 Hz), 7.07 (bs, 1H), 4.23 (q, 2H, *J* = 7.1 Hz), 1.33 (t, 3H, *J* = 7.1 Hz). **δC** (100 MHz, CDCl3) δ: 153.8, 141.0, 140.0, 135.4, 120.1, 108.5, 99.4, 61.8, 21.0, 14.6. **HRMS** (ESI) m/z for $C_{10}H_{12}I_2NO_2$ $[M+H]^+$: calcd. Exact 431.8957; found, 431.8955.

1.2.7 Synthesis of N-(2,3-diiodo-5-methylphenyl)-2-phenoxyacetamide (12A)



The title compound was prepared using the general procedure and isolated as white solid (**77%** yields). **M.p:** 136-137 °C. **IR** (cast film, cm^{-1}) 3348, 3003, 2997, 1698, 1634, 1253, 1109, 933, 684. **δH** (400 MHz, CDCl3) δ: 7.86 (s, 1H), 7.50 (s, 1H), 7.36-7.51 (m, 5H), 7.17 (bs, 1H), 5.22 (s, 2H), 2.26 (s, 3H). **δC** (100 MHz, CDCl3) δ: 153.6, 141.0, 139.8, 135.9, 135.5, 128.8, 128.6, 128.5, 120.2, 108.5, 99.5, 67.5, 21.0. **HRMS** (ESI) m/z for $C_{15}H_{14}I_2NO_2$ $[M+H]^+$: calcd. Exact 493.9114; found, 493.9110.

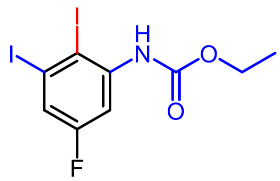
1.2.8 Synthesis of tert-butyl (2,3-diiodo-5-methylphenyl)carbamate (13A)



The title compound was prepared using the general procedure and isolated as colorless oil (**68%** yields). **IR** (cast film, cm^{-1}) 3348, 3008, 2989, 1695, 1637, 1286, 1112, 1031, 827. **δH** (400 MHz, CDCl3) δ: 7.85 (s, 1H), 7.47 (s, 1H), 6.99 (bs, 1H), 2.25 (s, 3H), 1.53 (s, 9H). **δC** (100

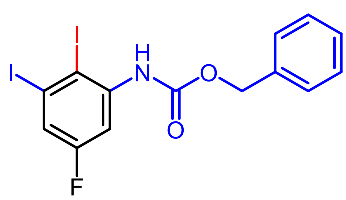
MHz, $CDCl_3$) δ: 152.9, 140.9, 140.4, 135.1, 119.9, 108.4, 99.3, 81.4, 28.5, 21.0. **HRMS** (ESI) m/z for $C_{12}H_{16}I_2NO_2$ $[M+H]^+$: calcd. 459.9270; found, 459.9262.

1.2.9 Synthesis of ethyl (5-fluoro-2,3-diiodophenyl)carbamate (15A)



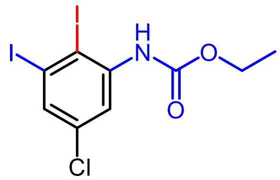
The title compound was prepared using the general procedure and isolated as white solid (**96%** yields). **M.p:** 93-94 °C. **IR** (cast film, cm^{-1}) 3376, 3014, 3001, 1689, 1612, 1283, 1032, 897, 784. **δ_H** (400 MHz, $CDCl_3$) δ: 7.96 (dd, 1H, J^1 = 2.7 Hz, J^2 = 10.9 Hz), 7.40 (dd, 1H, J^1 = 2.8 Hz, J^2 = 7.4 Hz), 7.24 (bs, 1H), 4.25 (q, 2H, J = 7.1 Hz), 1.33 (t, 3H, J = 7.1 Hz). **δ_C** (100 MHz, $CDCl_3$) δ: 164.3, 161.8, 153.4, 141.4, 141.3, 121.6, 121.3, 108.1, 108.0, 106.8, 106.5, 96.5, 96.4, 62.1, 14.6. **HRMS** (ESI) m/z for $C_9H_9FI_2NO_2$ $[M+H]^+$: calcd. Exact 435.8707; found, 435.8701.

1.2.10 Synthesis of benzyl (5-fluoro-2,3-diiodophenyl)carbamate (16A)



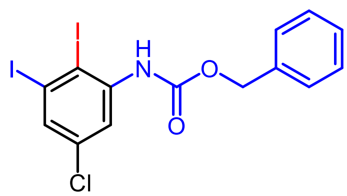
The title compound was prepared using the general procedure and isolated as white solid (**90%** yields). **M.p:** 133-134°C. **IR** (cast film, cm^{-1}) 3375, 3010, 2997, 1692, 1607, 1238, 1097, 1008, 914, 768. **δ_H** (400 MHz, $CDCl_3$) δ: 8.01 (dd, 1H, J^1 = 1.8 Hz, J^2 = 10.9 Hz), 7.36-7.43 (m, 6H), 7.32 (bs, 1H), 5.23 (s, 2H). **δ_C** (100 MHz, $CDCl_3$) δ: 164.3, 161.8, 153.2, 141.2, 141.1, 135.6, 128.9, 128.8, 128.7, 121.8, 121.5, 108.2, 108.1, 106.9, 106.6, 96.6, 96.5, 67.8. **HRMS** (ESI) m/z for $C_{14}H_{11}FI_2NO_2$ $[M+H]^+$: calcd. Exact 497.8863; found, 497.8861.

1.2.11 Synthesis of ethyl (5-chloro-2,3-diiodophenyl)carbamate (17A)



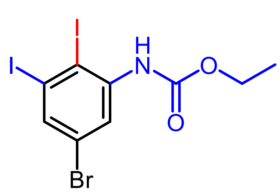
The title compound was prepared using the general procedure and isolated as white solid (**78%** yields). **M.p:** 91-93 °C. **IR** (cast film, cm^{-1}) 3347, 3016, 2984, 1688, 1627, 1283, 1009, 822, 631. **δ_H** (400 MHz, $CDCl_3$) δ: 8.14 (d, 1H, *J* = 1.8 Hz), 7.62 (d, 1H, *J* = 2.0 Hz), 7.18 (bs, 1H), 4.25 (q, 2H, *J* = 7.2 Hz), 1.34 (t, 3H, *J* = 7.2 Hz). **δ_C** (100 MHz, $CDCl_3$) δ: 153.4, 140.9, 136.3, 133.6, 118.9, 108.8, 100.5, 62.2, 14.6. **HRMS** (ESI) m/z for $C_9H_9ClI_2NO_2$ $[M+H]^+$: calcd. Exact 451.8411; found, 451.8407.

1.2.12 Synthesis of benzyl (5-chloro-2,3-diiodophenyl)carbamate (18$_A$)



The title compound was prepared using the general procedure and isolated as white solid (**63%** yields). **M.p:** 133-134 °C. **IR** (cast film, cm^{-1}) 3358, 3002, 2984, 1699, 1624, 1284, 1027, 912, 637. **δ_H** (400 MHz, $CDCl_3$) δ: 8.16 (d, 1H, *J* = 2.1 Hz), 7.63 (d, 1H, *J* = 2.3 Hz), 7.36-7.42 (m, 5H), 5.22 (s, 2H). **δ_C** (100 MHz, $CDCl_3$) δ: 153.3, 140.8, 136.3, 135.6, 133.7, 128.9, 128.8, 128.7, 118.9, 108.8, 100.6, 67.9. **HRMS** (ESI) m/z for $C_{14}H_{11}ClI_2NO_2$ $[M+H]^+$: calcd. Exact 513.8568; found, 513.8564.

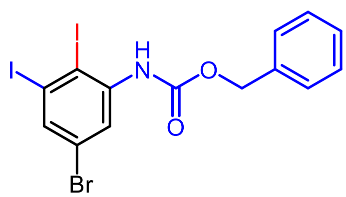
1.2.13 Synthesis of ethyl (5-bromo-2,3-diiodophenyl)carbamate (20$_A$)



The title compound was prepared using the general procedure and isolated as white solid (**69%** yields). **M.p:** 119-120 °C. **IR** (cast film, cm^{-1}) 3359, 3012, 2993, 1689, 1644, 1264, 1057, 961, 762. **δ_H** (400 MHz, $CDCl_3$) δ: 8.27 (d, 1H, *J* = 1.9 Hz), 7.76 (d, 1H, *J*

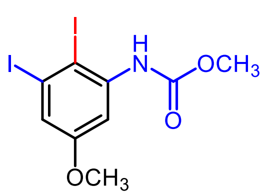
= 2.1 Hz), 7.16 (bs, 1H), 4.25 (q, 2H, *J* = 7.1 Hz), 1.33 (t, 3H, *J* = 7.1 Hz). **δ**$_C$ (100 MHz, $CDCl_3$) δ: 153.4, 141.2, 136.2, 124.1, 121.7, 109.2, 101.4, 62.2, 14.6. **HRMS** (ESI) m/z for $C_9H_9BrI_2NO_2$ $[M+H]^+$: calcd. Exact 495.7906; found, 495.7898.

1.2.14 Synthesis of benzyl (5-bromo-2,3-diiodophenyl)carbamate (21$_A$)



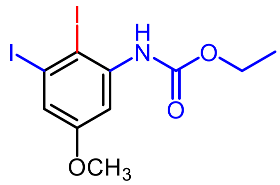
The title compound was prepared using the general procedure and isolated as white solid (**75%** yields). **M.p:** 145-146 °C. **IR** (cast film, cm^{-1}) 3352, 3019, 2987, 1685, 1598, 1239, 962, 664. **δ**$_H$ (400 MHz, $CDCl_3$) δ: 8.28 (s, 1H), 7.77 (d, 1H, *J* = 1.6 Hz), 7.26-7.44 (m, 5H), 7.24 (bs, 1H), 5.22 (s, 2H). **δ**$_C$ (100 MHz, $CDCl_3$) δ: 153.2, 140.9, 136.4, 135.6, 128.9, 128.8, 128.6, 124.1, 121.8, 109.2, 101.5, 67.9. **HRMS** (ESI) m/z for $C_{14}H_{11}BrI_2NO_2$ $[M+H]^+$: calcd. Exact 557.8063; found, 557.8058.

1.2.15 Synthesis of methyl (2,3-diiodo-5-methoxyphenyl)carbamate (22$_A$)



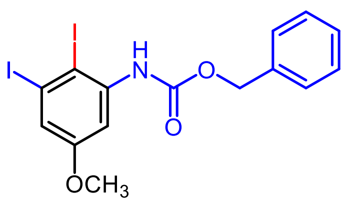
The title compound was prepared using the general procedure and isolated as white solid (**77%** yields). **M.p:** 125-126 °C. **IR** (cast film, cm^{-1}) 3482, 3082, 3005, 1687, 1628, 1352, 1278, 1083, 843, 622. **δ**$_H$ (400MHz, $CDCl_3$) δ: 7.75 (d, 1H, *J* = 2.8 Hz), 7.25 (d, 1H, *J* = 2.8 Hz), 7.17 (bs, 1H), 3.80 (s, 3H), 3.78 (s, 3H). **δ**$_C$ (100 MHz, $CDCl_3$) δ: 160.9, 154.1, 140.5, 121.3, 108.4, 105.1, 91.9, 55.8, 52.8. **HRMS** (ESI) m/z for $C_9H_{10}I_2NO_3$ $[M+H]^+$: calcd. 433.8750; found, 433.8746

1.2.16 Synthesis of ethyl (2,3-diiodo-5-methoxyphenyl)carbamate (23$_A$)



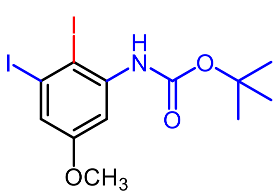
The title compound was prepared using the general procedure and isolated as white solid (**82%** yields). **M.p:** 89-90 °C**. IR** (cast film, cm^{-1}) 3351, 3022, 2981, 1691, 1622, 1299, 1285, 1012, 774. **δH** (400 MHz, $CDCl_3$) δ: 7.77 (d, 1H, *J* = 2.3 Hz), 7.25 (d, 1H, *J* = 2.7 Hz), 7.15 (bs, 1H), 4.24 (q, 2H, *J* = 7.1 Hz), 3.79 (s, 3H), 1.33 (t, 3H, *J* = 7.1 Hz). **δC** (100 MHz, $CDCl_3$) δ: 160.9, 153.7, 140.7, 121.3, 108.4, 105.0, 91.9, 61.9, 55.8, 14.6. **HRMS** (ESI) m/z for $C_{10}H_{12}I_2NO_3$ $[M+H]^+$: calcd. Exact 433.8750; found, 433.8744.

1.2.17 Synthesis of benzyl (2,3-diiodo-5-methoxyphenyl)carbamate (24A)



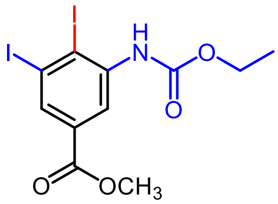
The title compound was prepared using the general procedure and isolated as white solid (**60%** yields). **M.p:** 105-106 °C. **IR** (cast film, cm^{-1}) 3354, 3002, 2978, 1697, 1627, 1277, 1251, 1057, 924, 643. **δH** (400 MHz, $CDCl_3$) δ: 7.77 (s, 1H), 7.38-7.42 (m, 5H), 7.25 (m, 2H), 5.22 (s, 2H), 3.78 (s, 3H). **δC** (100 MHz, $CDCl_3$) δ: 160.9, 153.5, 140.5, 135.8, 128.8, 128.7, 128.5, 121.4, 108.4, 105.2, 91.9, 67.6, 55.8. **HRMS** (ESI) m/z for $C_{15}H_{14}I_2NO_3$ $[M+H]^+$: calcd. Exact 509.9063; found, 509.9054.

1.2.18 Synthesis of tert-butyl (2,3-diiodo-5-methoxyphenyl)carbamate (26A)



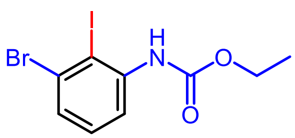
The title compound was prepared using the general procedure and isolated as colorless oil (**76%** yields). **IR** (cast film, cm^{-1}) 3359, 3017, 2995, 1675, 1642, 1274, 1245, 1063, 851. **δH** (400 MHz, $CDCl_3$) δ: 7.76 (d, 1H, *J* = 2.5 Hz), 7.23 (d, 1H, *J* = 2.7 Hz), 7.04 (bs, 1H), 3.78 (s, 3H), 1.53 (s, 9H). **δC** (100 MHz, $CDCl_3$) δ: 160.9, 152.7, 141.1, 120.9, 108.3, 104.9, 91.7, 81.5, 55.8, 28.4. **HRMS** (ESI) m/z for $C_{12}H_{16}I_2NO_3$ $[M+H]^+$: calcd. 475.9220; found, 475.9212.

1.2.19 Synthesis of methyl 3-((ethoxycarbonyl)amino)-4,5-diiodobenzoate (27_A)



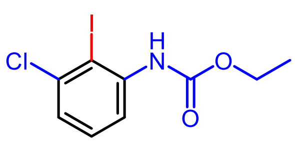
The title compound was prepared using the general procedure and isolated as white solid (**93%** yields). **M.p:** 107-108 °C. **IR** (cast film, cm^{-1}) 3412, 3022, 2985, 1749, 1684, 1638, 1299, 1246, 1003, 889. **δ_H** (400 MHz, $CDCl_3$) δ: 8.62 (s, 1H), 8.24 (d, 1H, *J* = 1.8 Hz), 7.18 (bs, 1H), 4.25 (q, 2H, *J* = 7.1 Hz), 3.91 (s, 3H), 1.33 (t, 3H, *J* = 7.1 Hz). **δ_C** (100 MHz, $CDCl_3$) δ: 165.4, 153.6, 140.7, 134.9, 132.4, 119.6, 109.2, 108.7, 62.1, 52.7, 14.6. **HRMS** (ESI) m/z for $C_{11}H_{12}I_2NO_4$ $[M+H]^+$: calcd. Exact 475.8856; found 475.8853.

1.2.20 Synthesis of ethyl (3-bromo-2-iodophenyl)carbamate (28_A)



The title compound was prepared using the general procedure and isolated as white solid (**84%** yields). **M.p:** 98-99 °C. **IR** (cast film, cm^{-1}) 3329, 3014, 2997, 1698, 1641, 1263, 1088, 827. **δ_H** (400 MHz, $CDCl_3$) δ: 8.00 (d, 1H, *J* = 8.2 Hz), 7.35 (d, 1H, *J* = 8.0 Hz), 7.20 (dd, 1H, *J* = 8.1 Hz, *J* = 8.0 Hz), 7.16 (bs, 1H), 4.23 (q, 2H, *J* = 7.1 Hz), 1.33 (t, 3H, *J* = 7.1 Hz). **δ_C** (100 MHz, $CDCl_3$) δ: 153.6, 141.1, 130.4, 130.2, 127.6, 118.3, 97.1, 61.9, 14.6. **HRMS** (ESI) m/z for $C_9H_{10}BrINO_2$ $[M+H]^+$: calcd. Exact 369.8940; found, 369.8935.

1.2.21 Synthesis of ethyl (3-chloro-2-iodophenyl)carbamate (29_A)

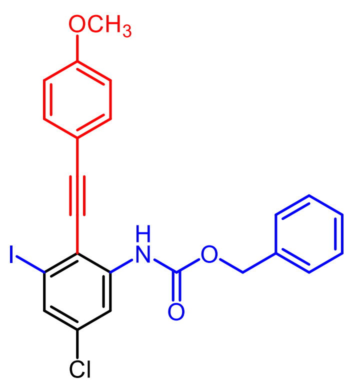


The title compound was prepared using the general procedure and isolated as white solid (**81%** yields). **M.p:** 83-84 °C. **IR** (cast film, cm^{-1}) 3321, 3006, 1701, 1653, 1275, 1097, 849. **δ_H** (400 MHz, $CDCl_3$) δ: 7.96 (d, 1H, *J* = 8.2 Hz), 7.16-7.29 (m, 3H), 4.25 (q, 2H, *J* = 7.1 Hz), 1.34 (t, 3H, *J* = 7.1 Hz). **δ_C** (100 MHz, $CDCl_3$) δ: 153.5, 140.9, 139.1, 129.9, 124.1, 117.8, 94.0, 61.9, 14.6. **HRMS** (ESI) m/z for $C_9H_{10}ClINO_2$ [M+H]$^+$: calcd. Exact 325.9445; found, 325.9442.

1.3 General procedure for Sonogashira cross-coupling reaction of benzyl (5-chloro-2,3-diiodophenyl)carbamate 24_A

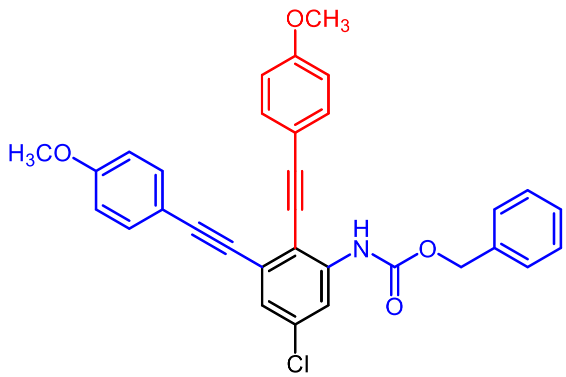
A flame-dried sealed tube was charged with benzyl (5-chloro-2,3-diiodophenyl)carbamate (0.60 mmol, 1.0 equiv.), 4-methoxyphenylacetylene (1.0 equiv.), copper iodide (20% mol) and potassium carbonate (7.0 equiv.) in 6.0 mL toluene (0.1M) under argon at room temperature for 24 h. The mixture was diluted with ethyl acetate (50 mL) and filtrated over a pad of Celite 545®. Organic layers were combined, dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The crude product was purified by flash chromatography (5% EtOAc/hexane) to yield the pure desired product.

1.3.1 Synthesis of benzyl (5-chloro-3-iodo-2-((4-methoxyphenyl)ethynyl)phenyl)-carbamate (34)



The title compound was prepared using the general procedure and isolated as white solid (**57%** yields). **M.p:** 107-109 °C**. IR** (cast film, cm^{-1}) 3328, 3025, 2215, 1691, 1617, 1264, 1198, 968, 662. **δ$_H$** (400 MHz, $CDCl_3$) δ: 8.27 (bs, 1H), 7.32-7.55 (m, 8H), 7.23 (d, 1H, *J* = 2.3 Hz), 6.89 (d, 2H, *J* = 8.7 Hz), 5.24 (s, 2H), 3.84 (s, 3H). **δ$_C$** (100 MHz, $CDCl_3$) δ:160.4, 152.8, 136.0, 135.6, 133.5, 133.2, 128.9, 128.8, 128.7, 126.7, 124.9, 121.5, 119.0, 114.5, 114.3, 96.3, 83.9, 67.8, 55.5. **HRMS** (ESI) m/z for $C_{23}H_{18}ClINO_3$ [M+H]$^+$: calcd. Exact 518.0020; found 518.0011.

Benzyl (5-chloro-2,3-bis((4-methoxyphenyl)ethynyl)phenyl)-carbamate

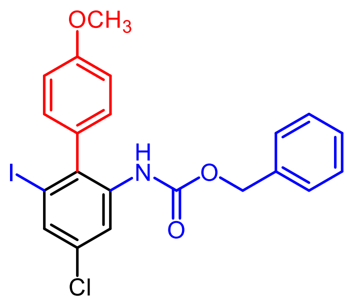


The title compound was isolated as white solid (**21%** yields). **M.p:** 116-118 °C. **δ_H** (400 MHz, $CDCl_3$) δ: 8.24 (bs, 1H), 7.58 (s, 1H), 7.36-7.51 (m, 9H), 7.20 (d, 1H, *J* = 2.0 Hz), 6.87 (dd, 4H, *J* = 9.2 Hz, *J* = 8.8 Hz), 5.25 (s, 2H), 3.84 (s, 3H), 3.82 (s, 3H). **δ_C** (100 MHz, $CDCl_3$) δ: 160.4, 160.2, 152.9, 139.7, 135.9, 134.7, 133.4, 133.3, 128.8, 128.6, 128.5, 127.4, 125.7, 117.4, 114.9, 114.5, 114.4, 114.3, 112.7, 101.4, 94.9, 86.1, 81.7, 67.5, 55.5, 55.4. **HRMS** (ESI) m/z for $C_{32}H_{25}ClNO_4$ $[M+H]^+$: calcd. Exact 522.1472; found, 522.1463.

1.4 General procedure for Suzuki-Miyaura cross-coupling reaction of benzyl (5-chloro-2,3-diiodophenyl)carbamate (24_A)

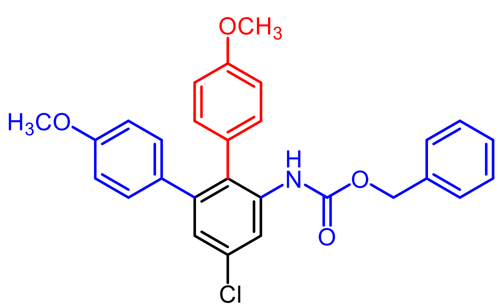
A flame-dried round-bottom flask was charged with benzyl(5-chloro-2,3-diiodophenyl)carbamate (0.6 mmol, 1.0 equiv.), an arylboronic acid (1.0 equiv.), tetrakis(triphenylphosphine)palladium(0) (16 mol-%), 6.0 mL toluene (0.1M), potassium carbonate (2 M solution, 1.4 mL), and ethanol (0.4 mL) under argon. The mixture was heated at 100 °C for 12 h. The reaction mixture was cooled down to room temperature and 50 mL EtOAc was added. The aqueous layer was extracted with ethyl acetate (2 X 50 mL). The combined organic layers were washed with brine, dried with anhyd. Na_2SO_4, filtered, and then concentrated under reduced pressure. The crude residue was purified by flash chromatography (5% EtOAc/hexane) to yield the pure desired product.

1.4.1 Synthesis of benzyl (4-chloro-6-iodo-4'-methoxy-[1,1'-biphenyl]-2-yl)carbamate (35)



The title compound was prepared using the general procedure and isolated as white solid (**79%** yields). **M.p:** 152-153 °C**. IR** (cast film, cm^{-1}) 3321, 3008, 1694, 1614, 1589, 1286, 1243, 1028, 937, 591. **δ_H** (400 MHz, $CDCl_3$) δ: 8.15 (bs, 1H), 7.29-7.45 (m, 6H), 7.17 (d, 2H, *J* = 8.5 Hz), 7.01 (d, 1H, *J* = 2.3 Hz), 6.94 (d, 2H, *J* = 8.5 Hz), 5.24 (s, 2H), 3.86 (s, 3H). **δ_C** (100 MHz, $CDCl_3$) δ: 159.6, 153.3, 148.8, 139.7, 136.7, 135.8, 135.2, 130.3, 128.8, 128.7, 128.6, 125.1, 118.4, 113.6, 92.5, 67.7, 55.5. **HRMS** (ESI) m/z for $C_{21}H_{18}ClINO_3$ $[M+H]^+$: calcd. Exact 494.0020; found, 494.0015.

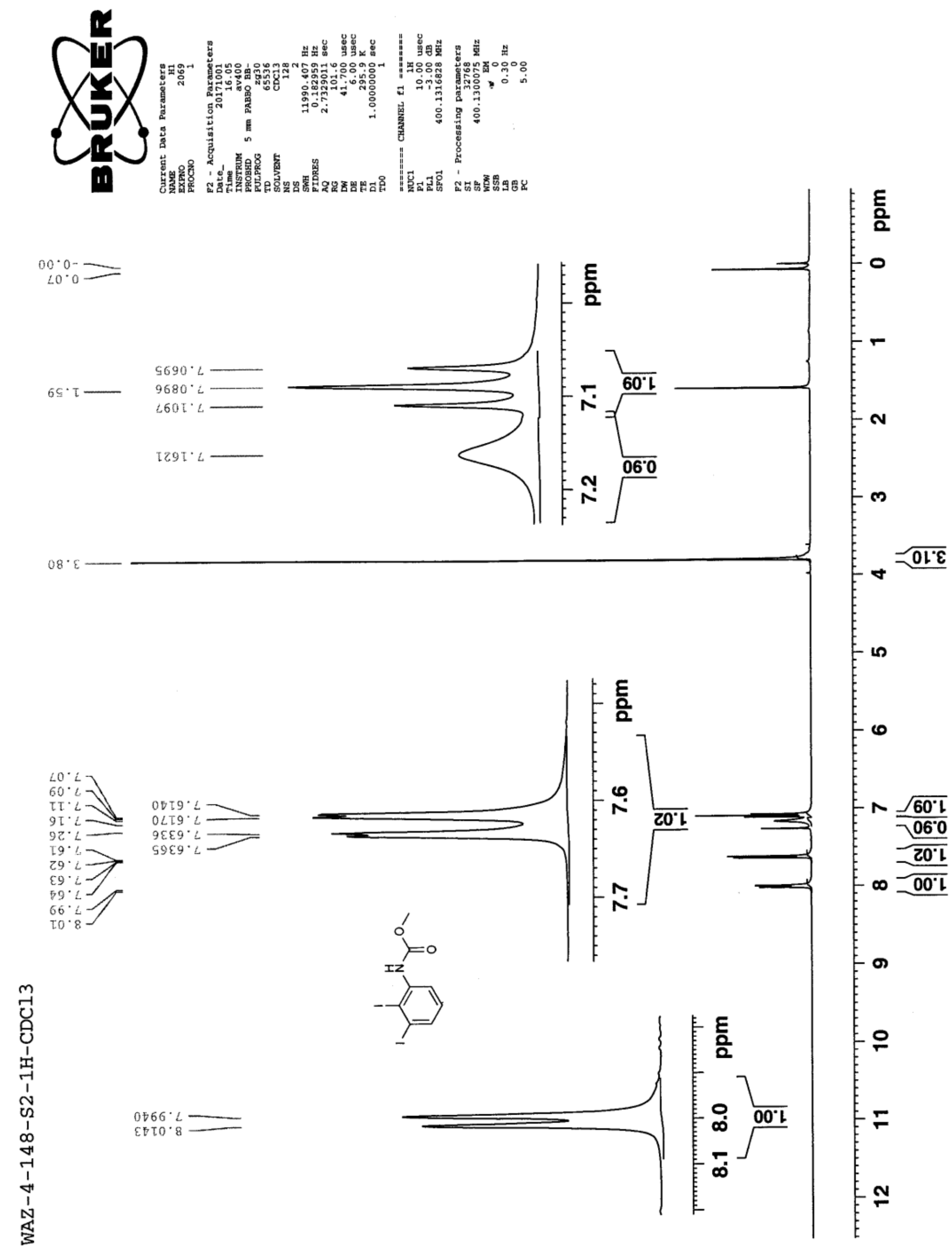
Benzyl (5'-chloro-4,4''-dimethoxy-[1,1':2',1''-terphenyl]-3'-yl)carbamate



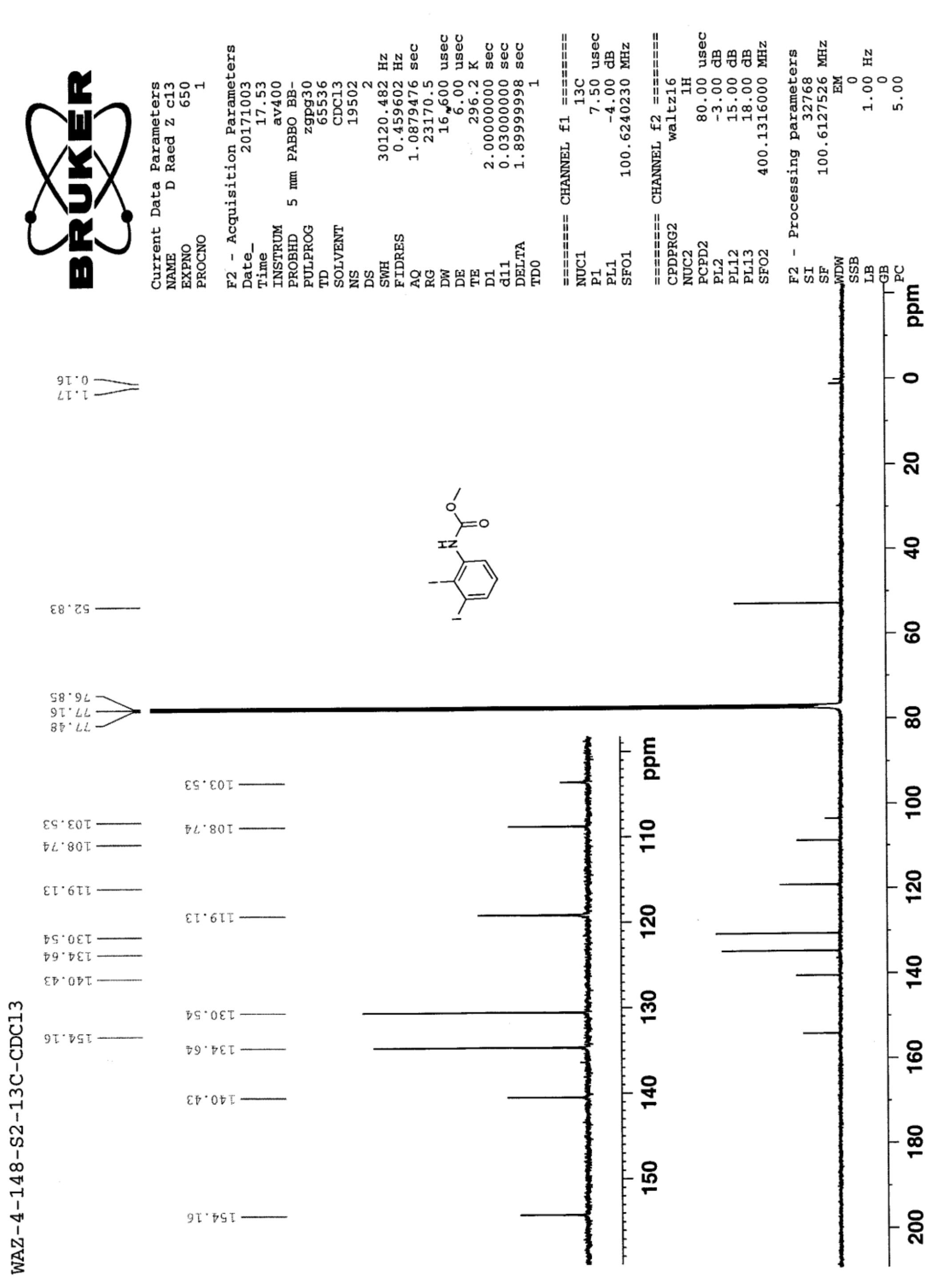
The title compound was isolated as colorless oil (**8%** yields). **δ_H** (400 MHz, $CDCl_3$) δ: 8.27 (bs, 1H), 7.35 (m, 5H), 7.10 (d, 1H, *J* = 1.9 Hz), 6.89-6.96 (m, 4H), 6.81 (d, 2H, *J* = 8.6 Hz), 6.67 (d, 2H, *J* = 8.6 Hz), 6.60 (s, 1H), 5.14 (s, 2H), 3.79 (s, 3H), 3.74 (s, 3H). **δ_C** (100 MHz, $CDCl_3$) δ: 159.2, 158.5, 153.2, 143.3, 137.1, 136.1, 133.8, 132.8, 132.1, 130.7, 128.8, 128.5, 127.8, 127.3, 124.9, 117.7, 114.7, 113.4, 67.3, 55.3, 55.2 (missing one peak due to overlapping)**. HRMS** (ESI) m/z for $C_{28}H_{25}ClNO_4$ $[M+H]^+$: calcd. Exact 474.1472; found, 474.1465.

1.5 NMR Spectra for New Compound

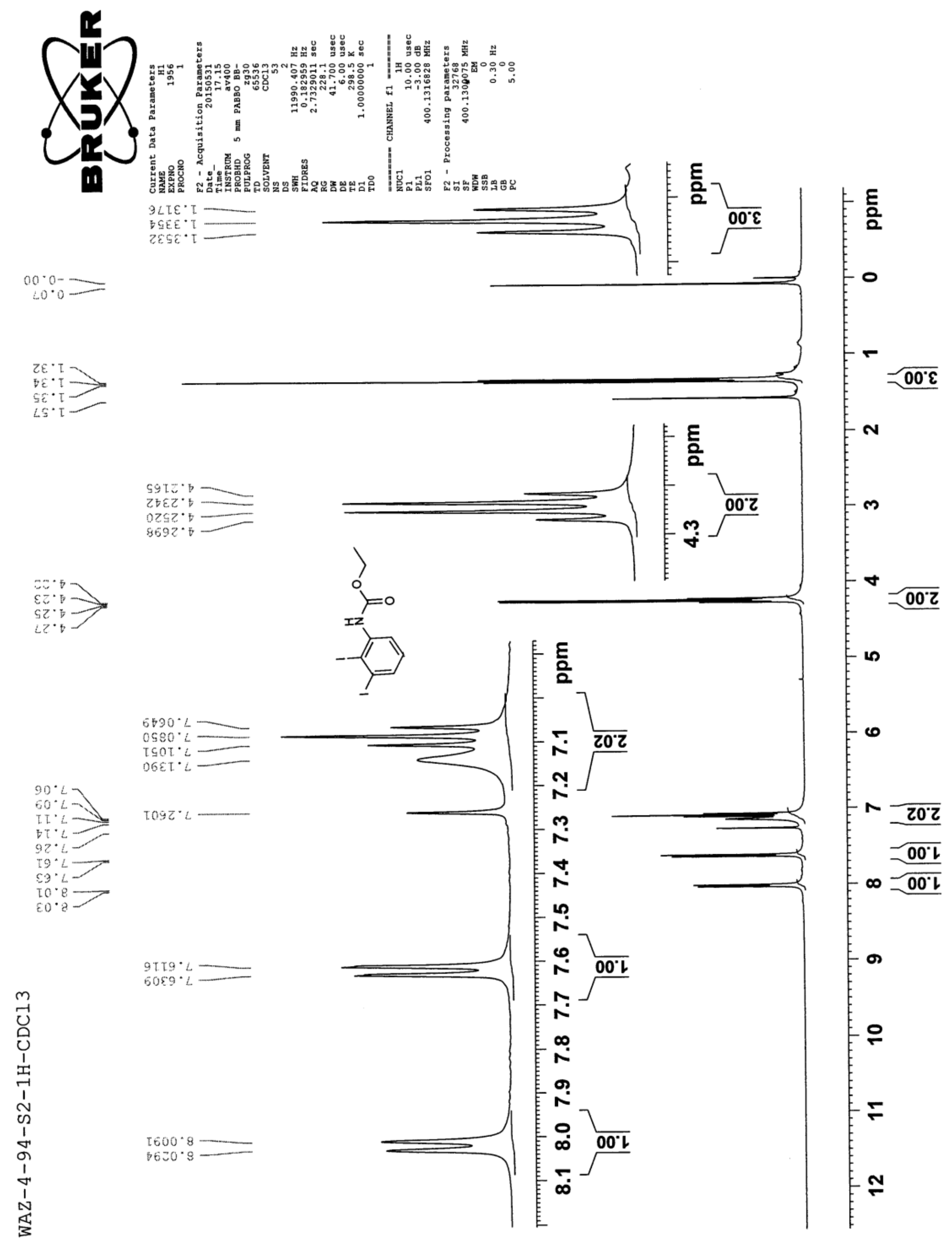
1.5.1 [1]H-NMR of methyl (2,3-diiodophenyl)carbamate (5_A) in $CDCl_3$ at 25 °C.



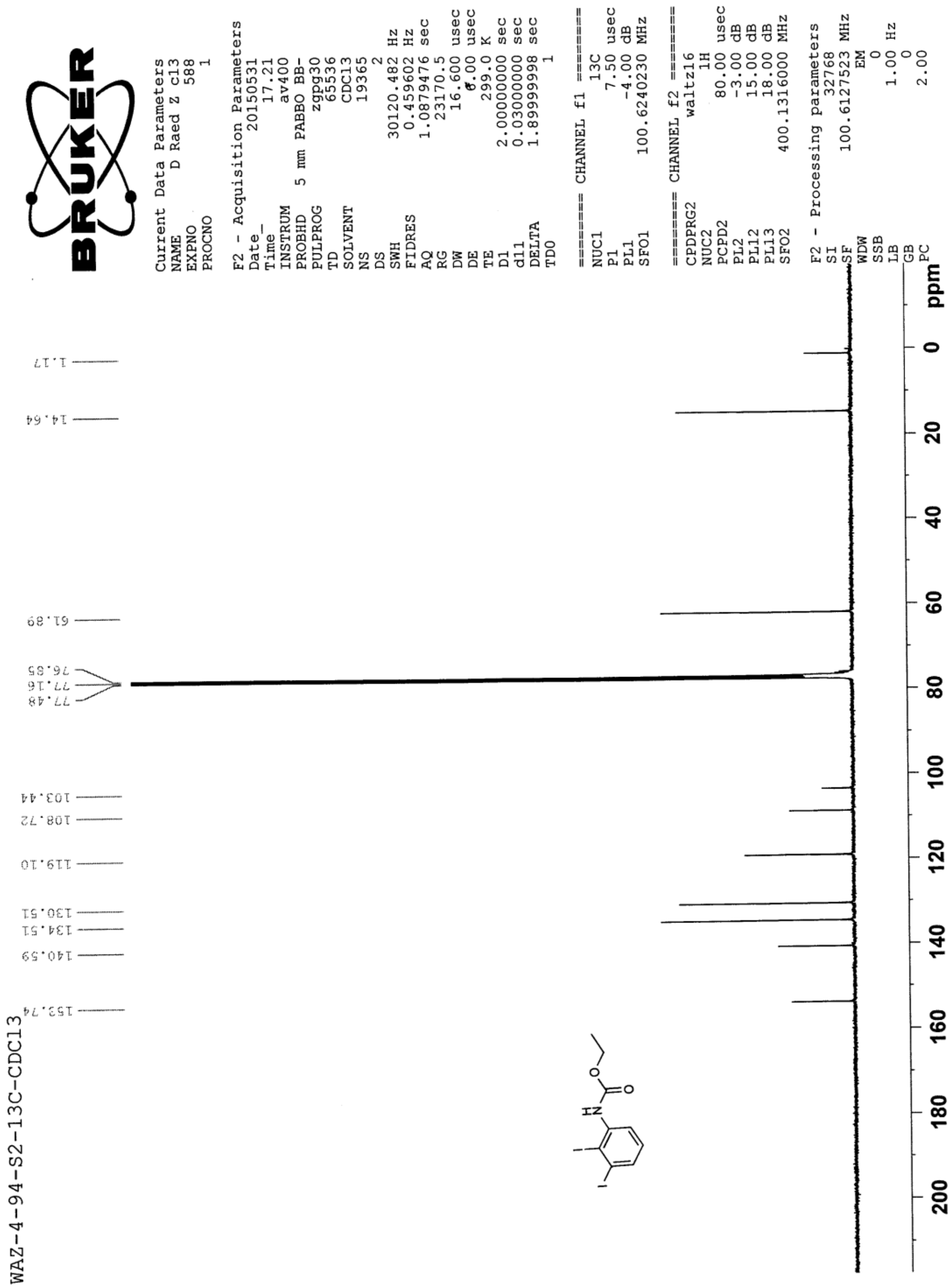
1.5.2 ^{13}C-NMR of methyl (2,3-diiodophenyl)carbamate (5_A) in $CDCl_3$ at 25 °C.



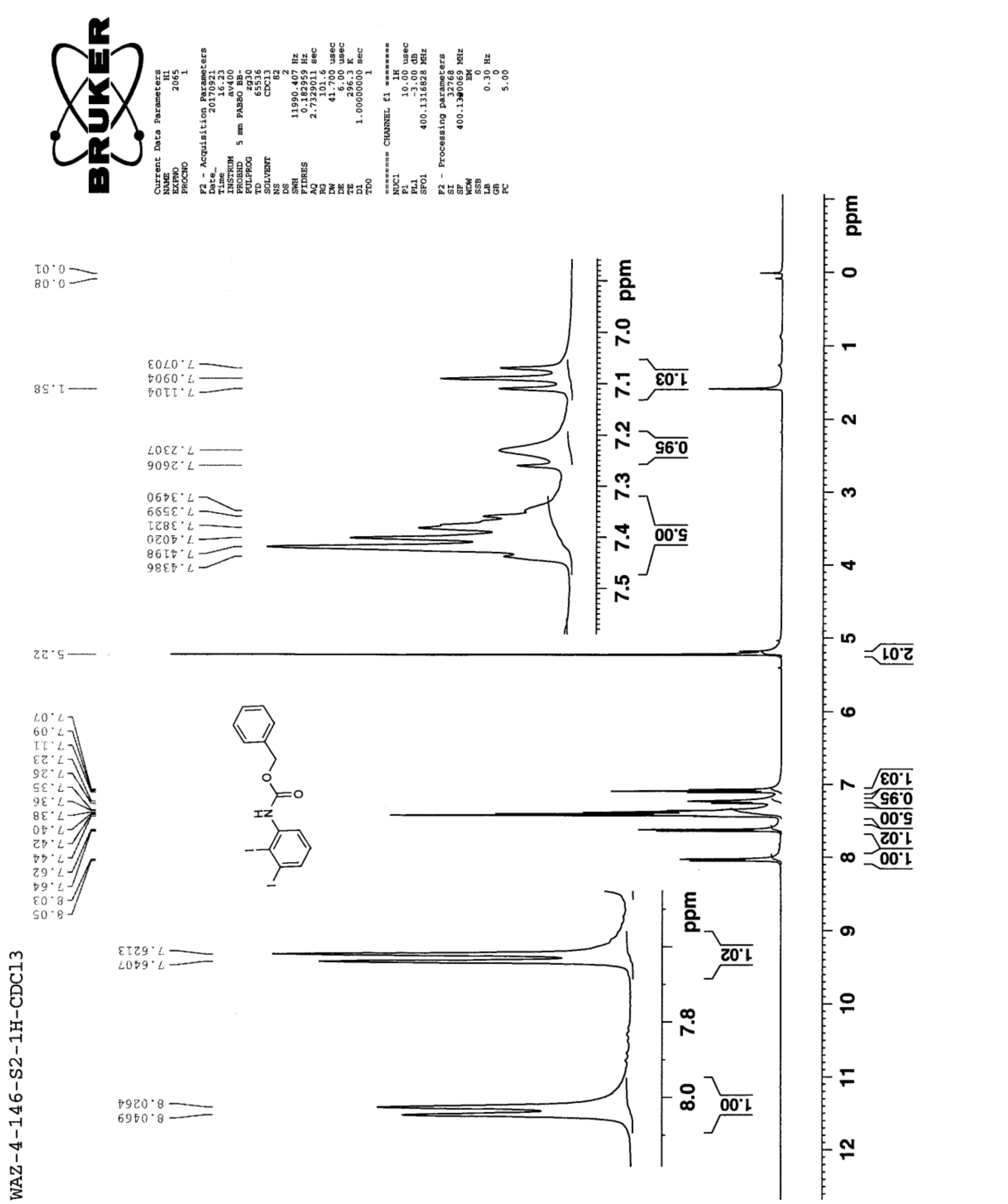
1.5.3 ^{1}H-NMR of ethyl (2,3-diiodophenyl)carbamate (6_A) in $CDCl_3$ at 25 ^{o}C.



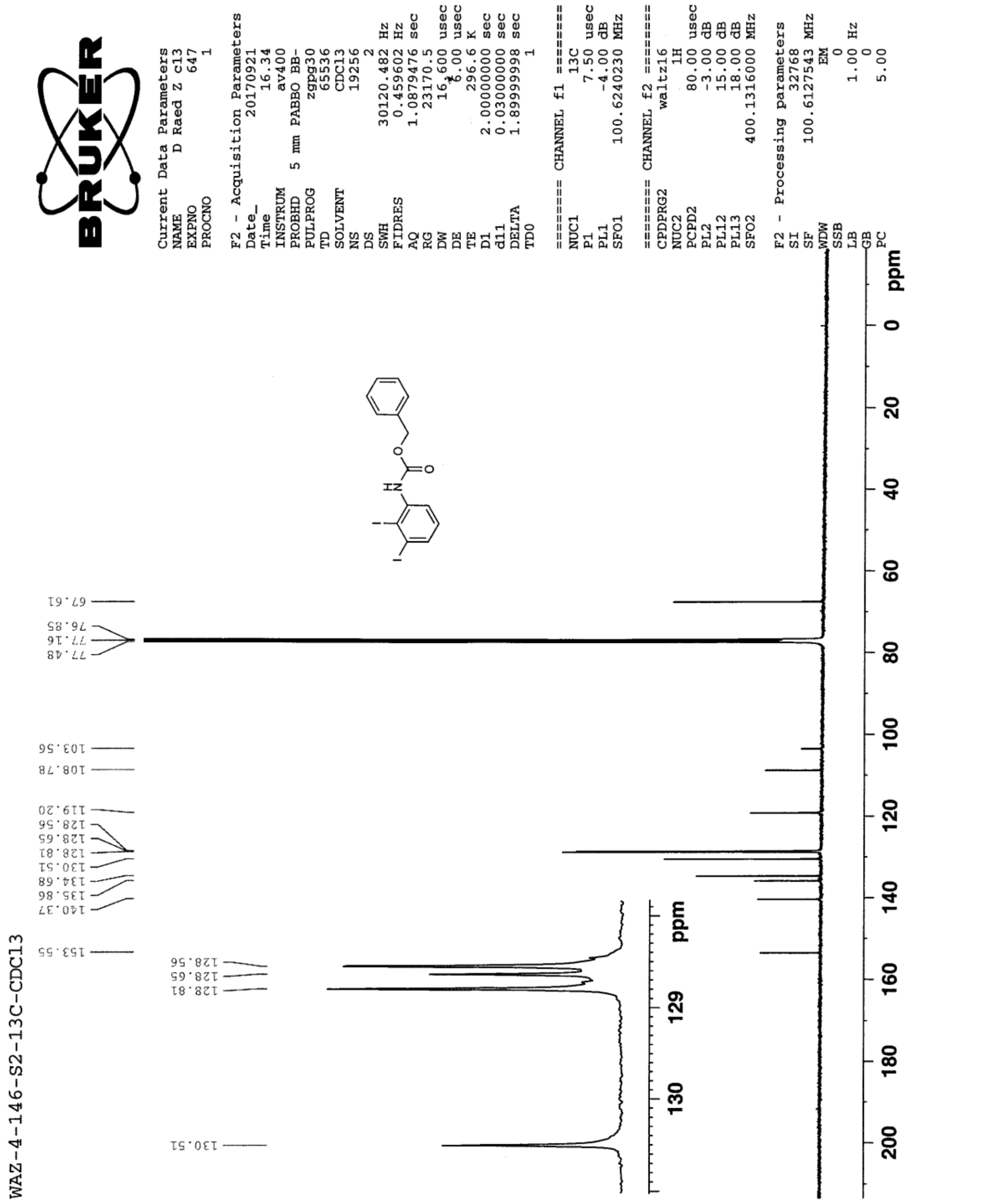
1.5.4 ^{13}C-NMR of ethyl (2,3-diiodophenyl)carbamate (6_A) in $CDCl_3$ at 25 ^{o}C.



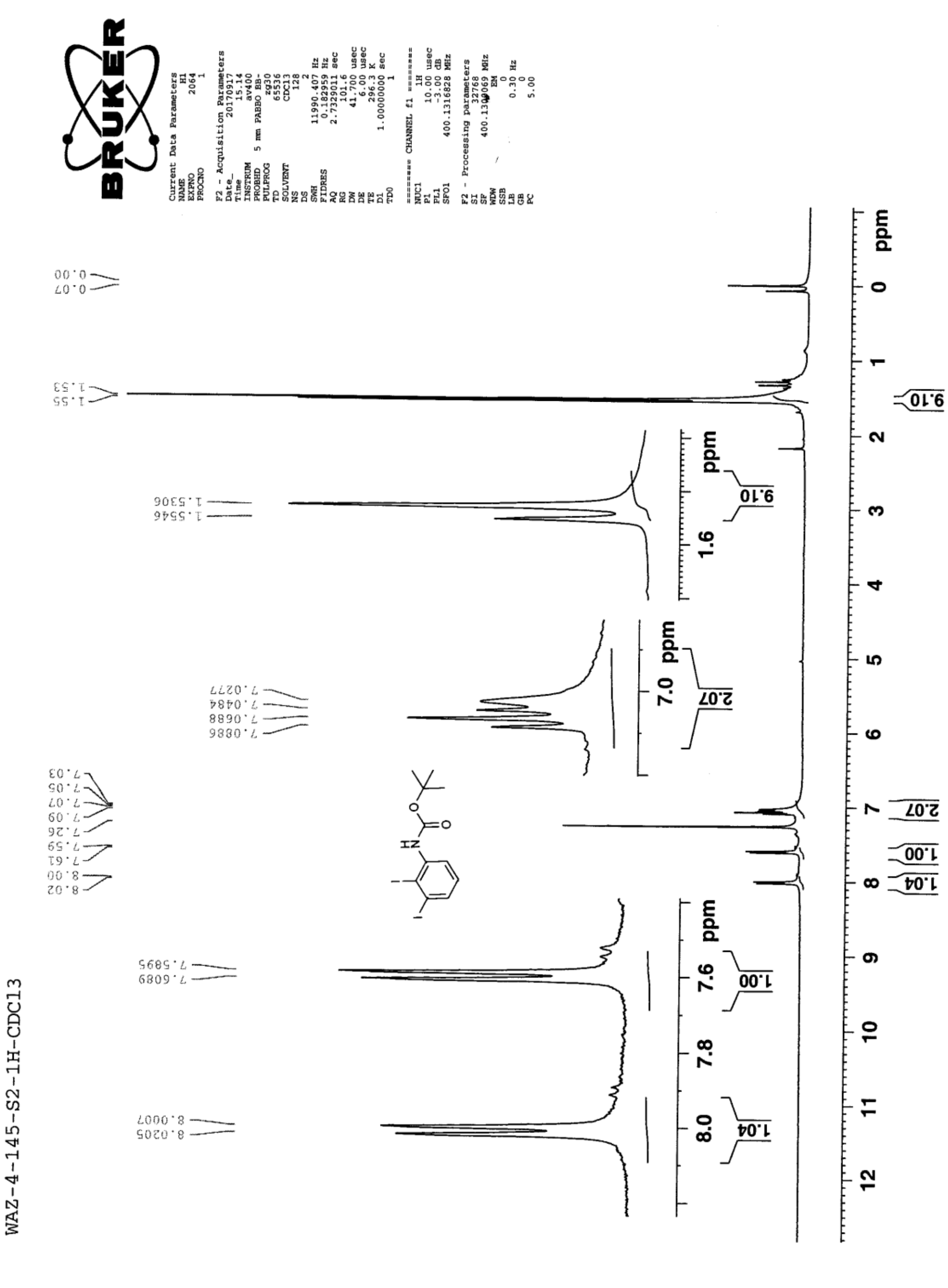
1.5.5 [1]H-NMR of N-(2,3-diiodophenyl)-2-phenoxyacetamide (7_A) in $CDCl_3$ at 25 °C.



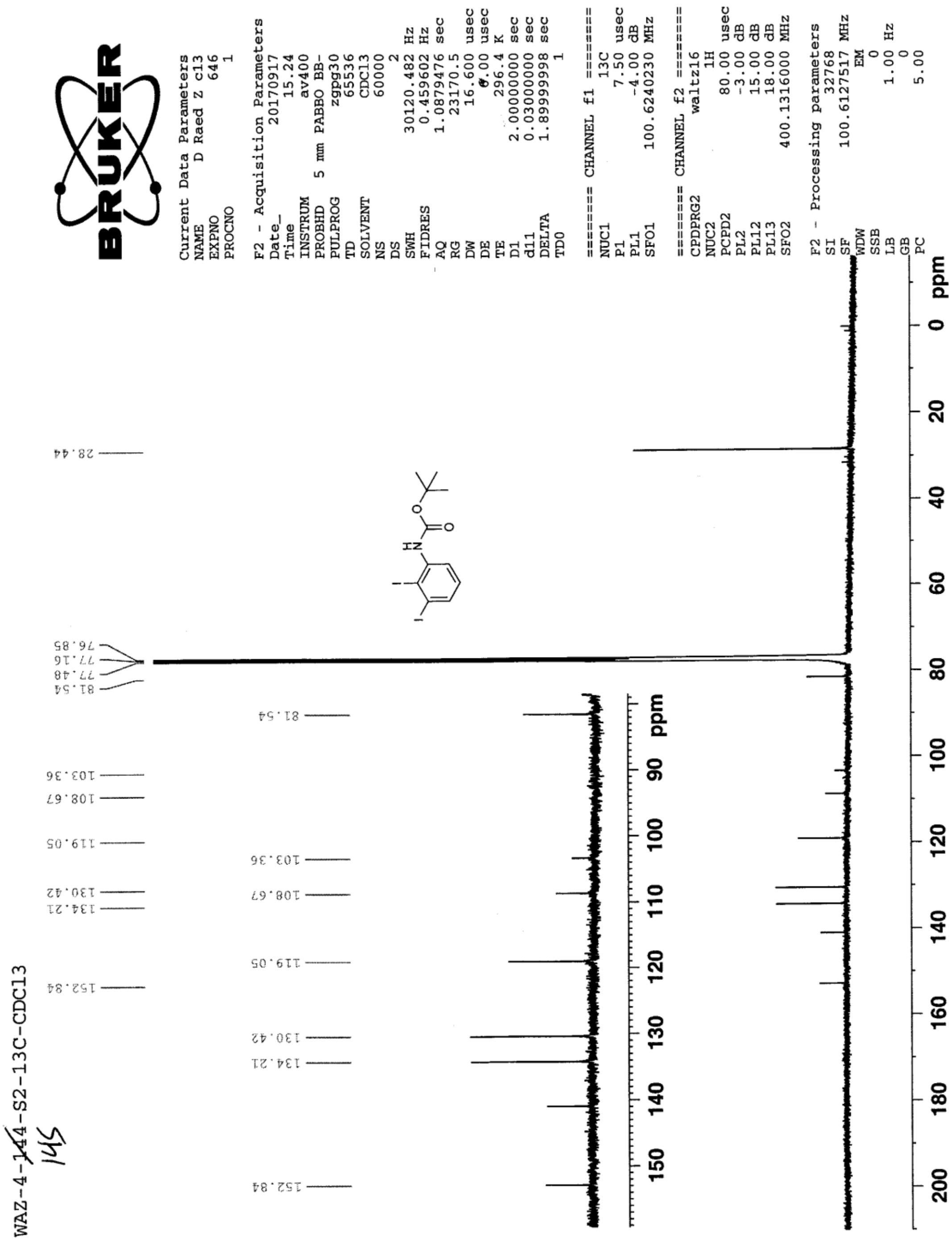
1.5.6 ^{13}C-NMR of N-(2,3-diiodophenyl)-2-phenoxyacetamide (7$_A$) in $CDCl_3$ at 25 ^oC.



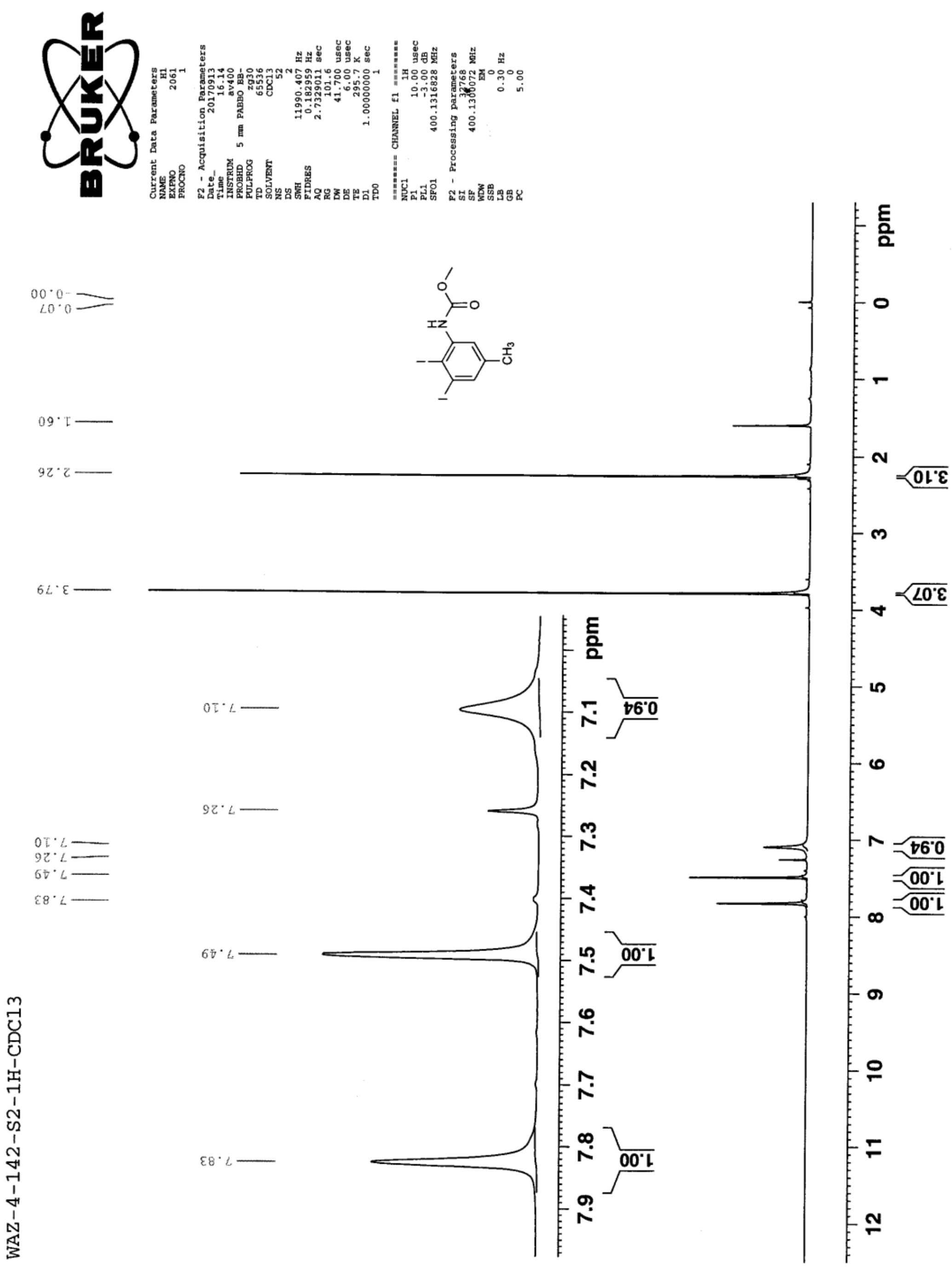
1.5.7 [1]H-NMR of tert-butyl (2,3-diiodophenyl)carbamate (8_A) in $CDCl_3$ at 25 °C.



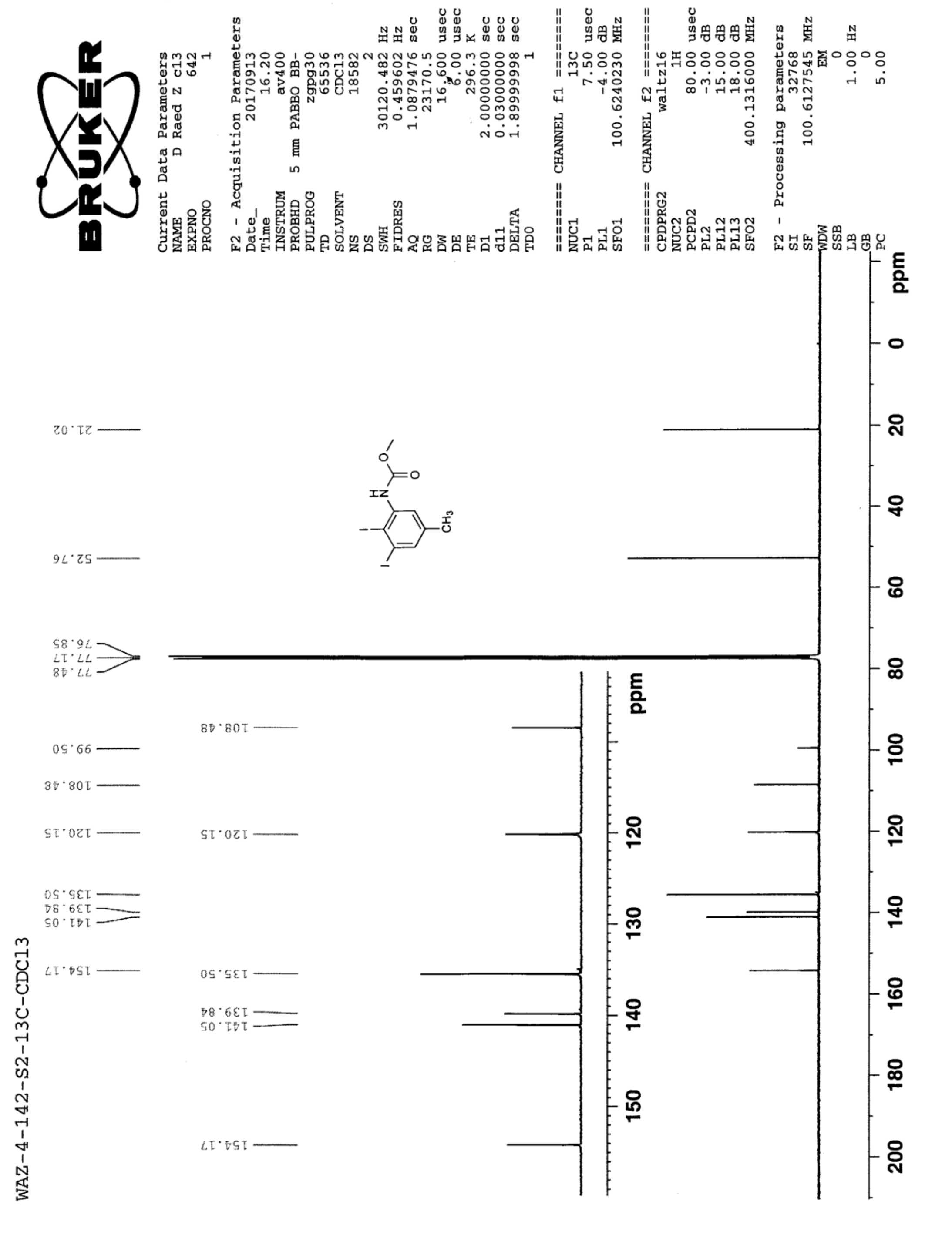
1.5.8 ¹³C-NMR of tert-butyl (2,3-diiodophenyl)carbamate (8A) in CDCl₃ at 25 °C.



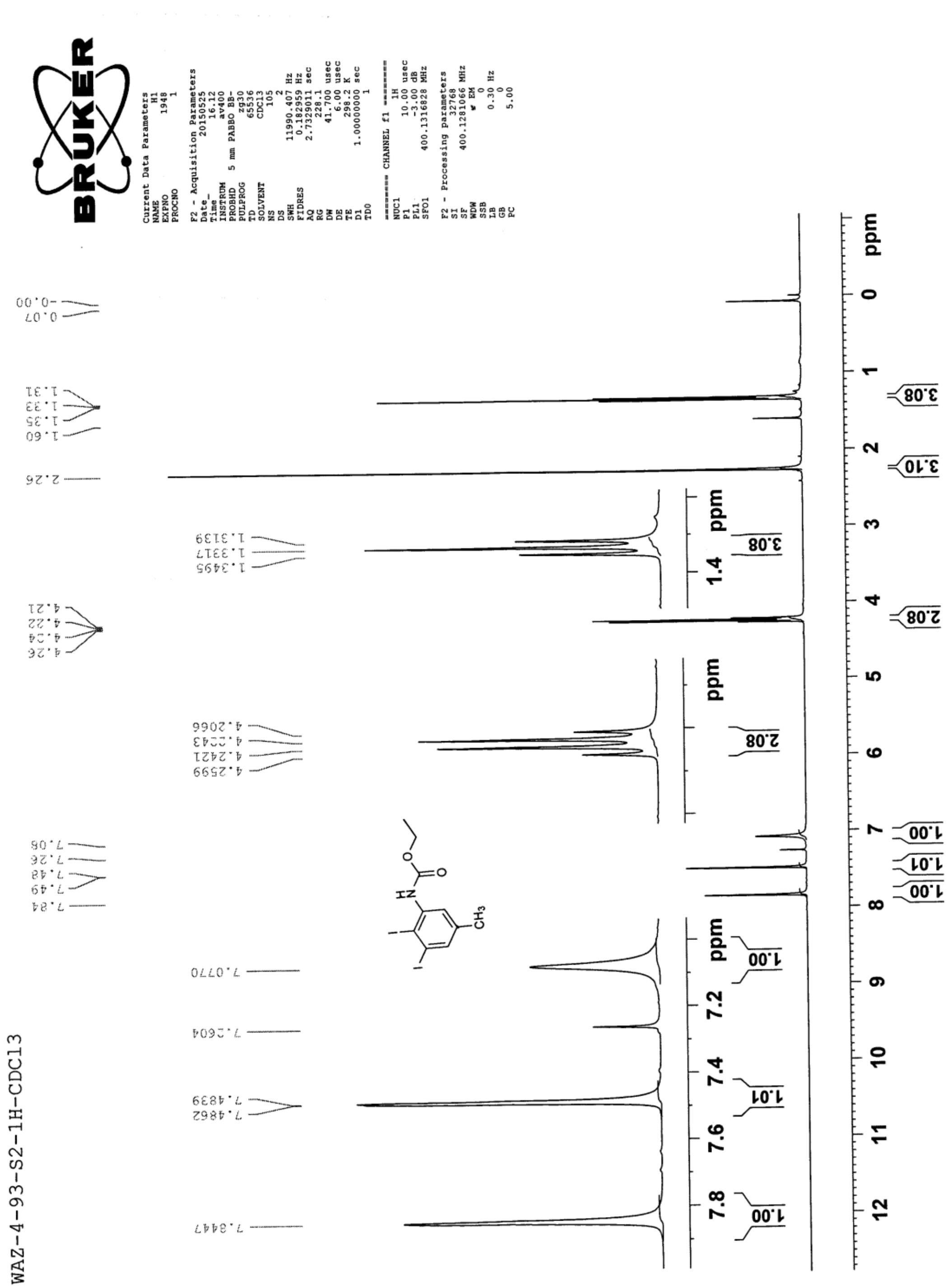
1.5.9 ^{1}H-NMR of (2,3-diiodo-5-methylphenyl)carbamate (10_A) in $CDCl_3$ at 25 °C.



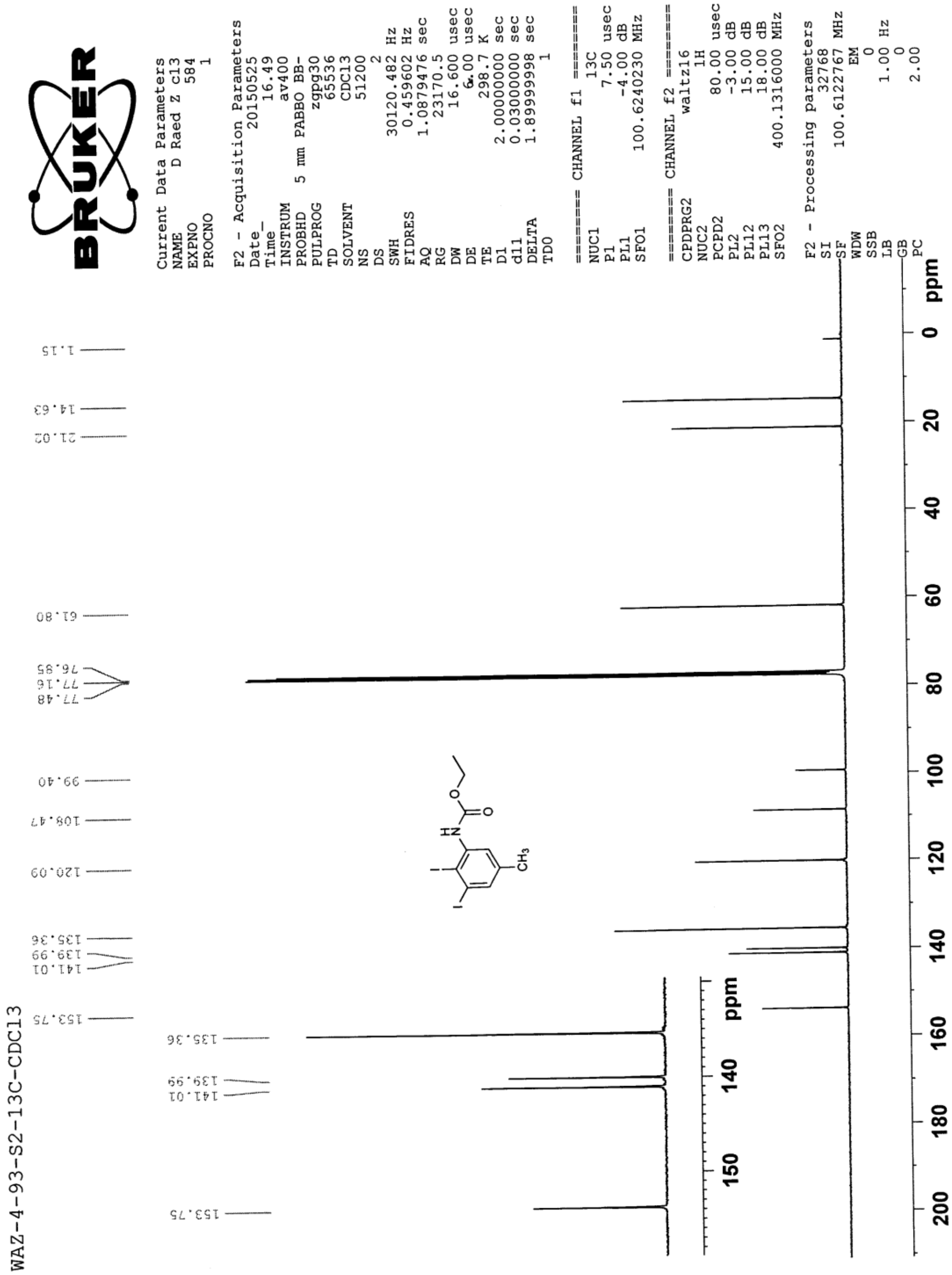
1.5.10 ^{13}C-NMR of (2,3-diiodo-5-methylphenyl)carbamate (10_A) in $CDCl_3$ at 25 °C.



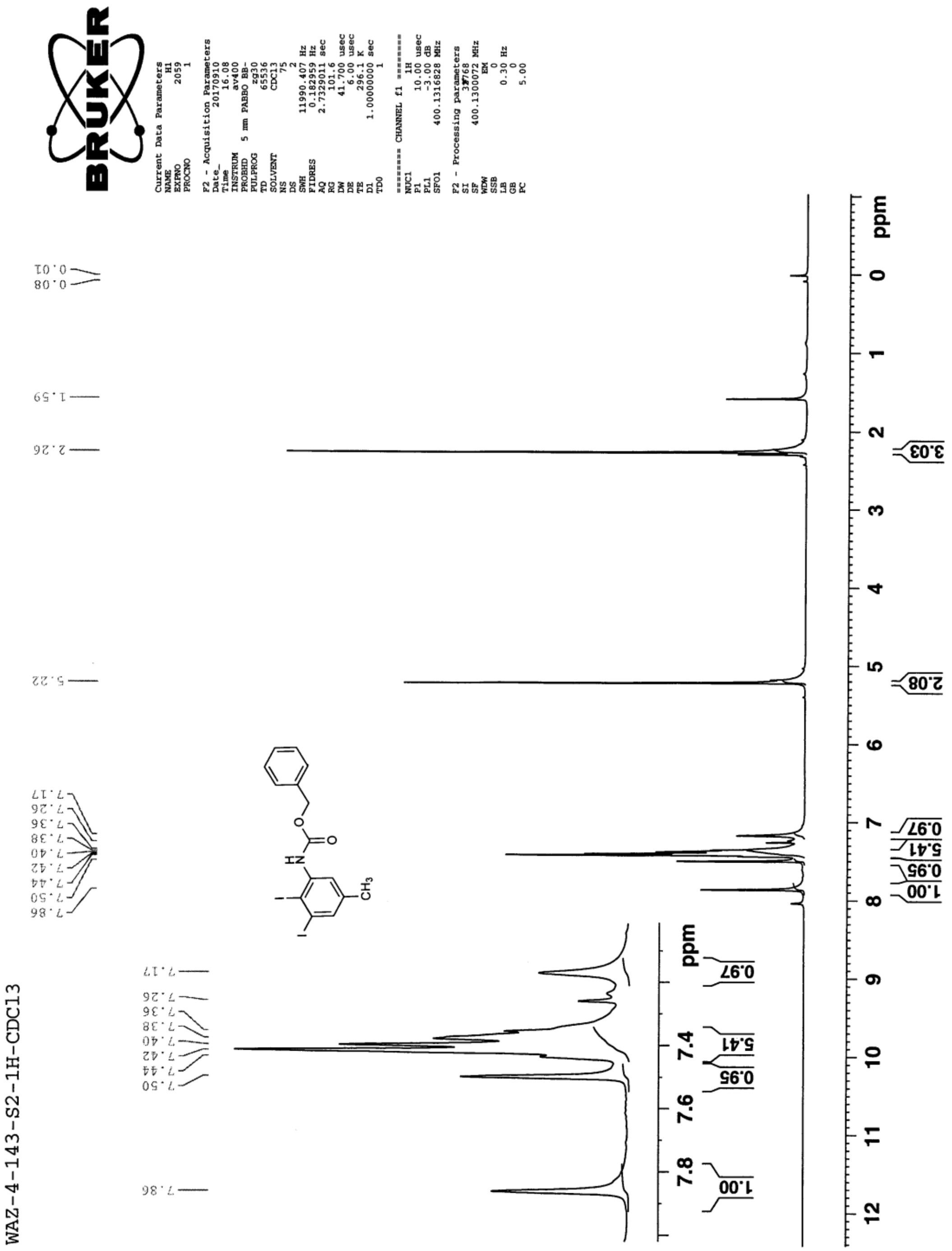
1.5.11 [1]H-NMR of ethyl (2,3-diiodo-5-methylphenyl)carbamate (11_A) in $CDCl_3$ at 25 °C.



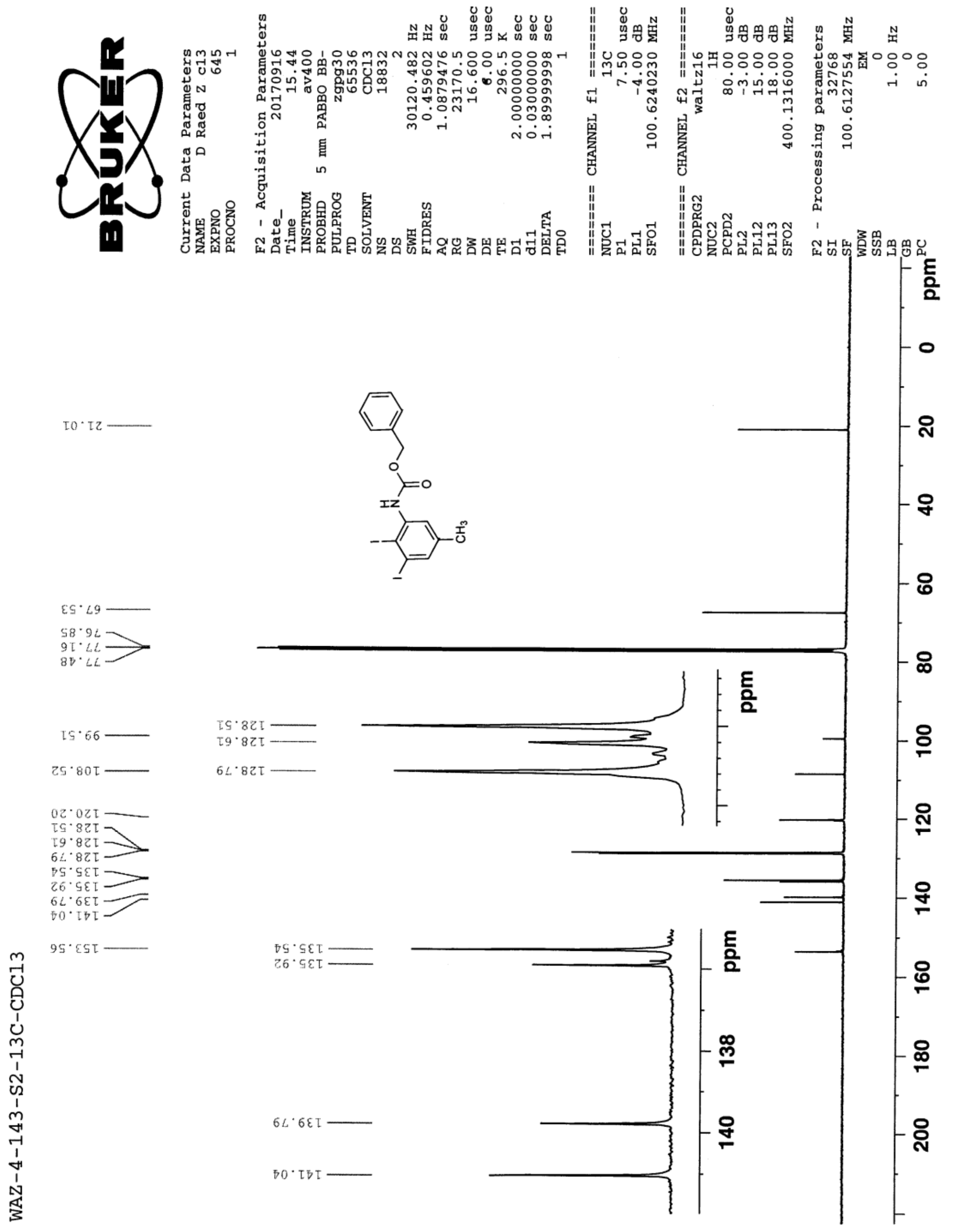
1.5.12 ^{13}C-NMR of ethyl (2,3-diiodo-5-methylphenyl)carbamate (11_A) in $CDCl_3$ at 25 ^oC.



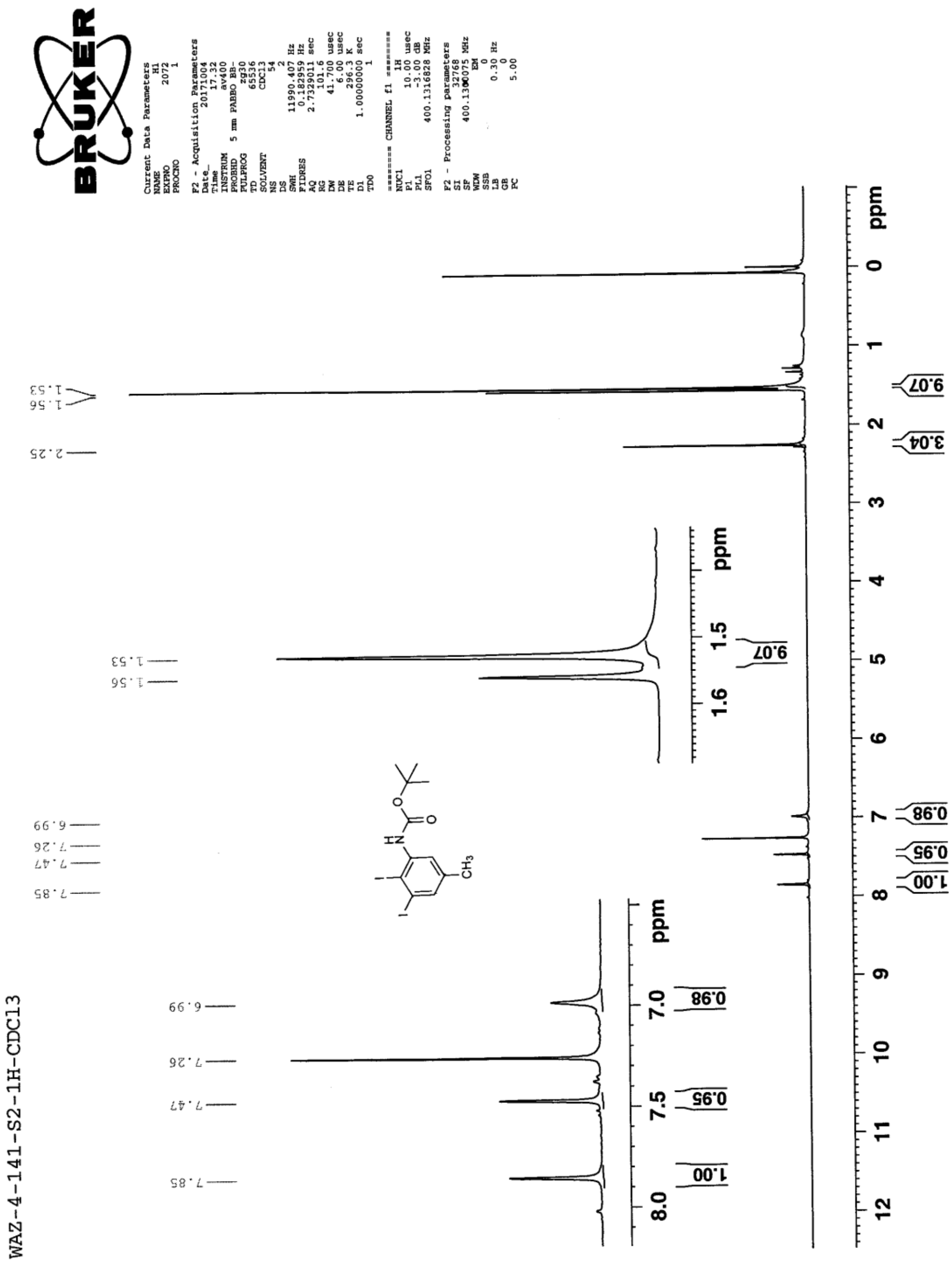
1.5.13 ¹H-NMR of benzyl (2,3-diiodo-5-methylphenyl)carbamate (12_A) in $CDCl_3$ at 25 °C.



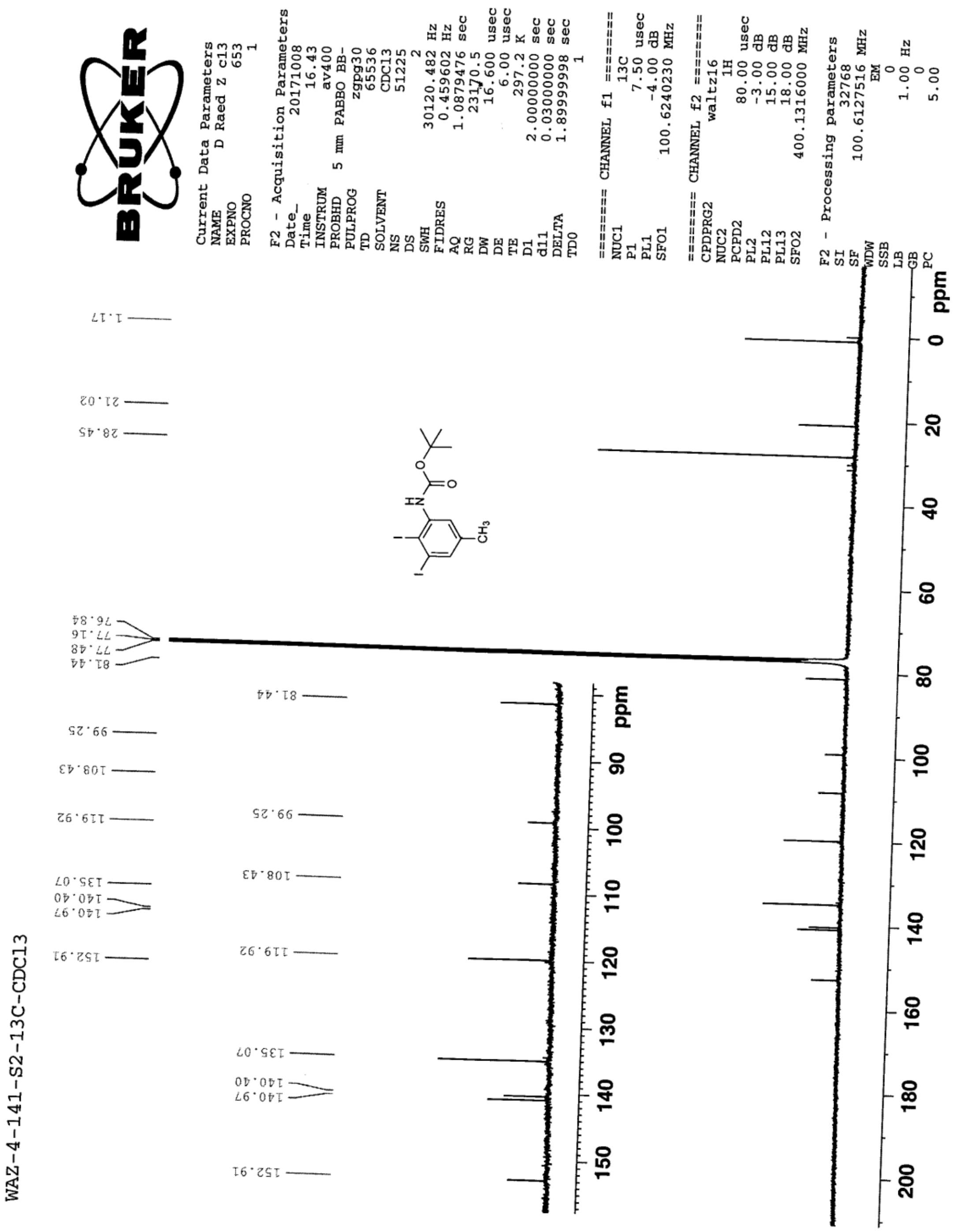
1.5.14 ^{13}C-NMR of benzyl (2,3-diiodo-5-methylphenyl)carbamate (12_A) in $CDCl_3$ at 25 ^{o}C.



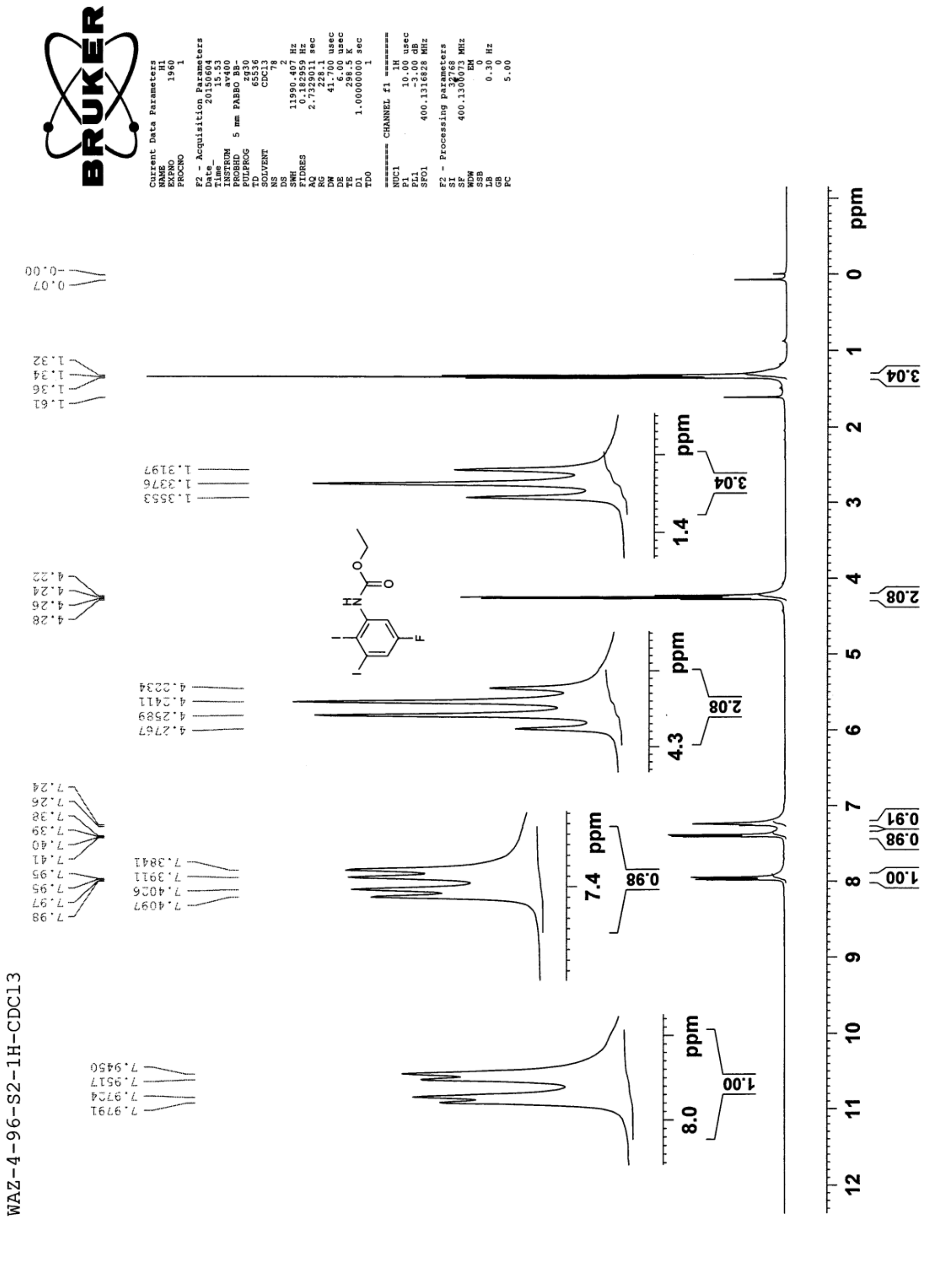
1.5.15 [1]H-NMR of tert-butyl (2,3-diiodo-5-methylphenyl)carbamate (13_A) in $CDCl_3$ at 25 °C.



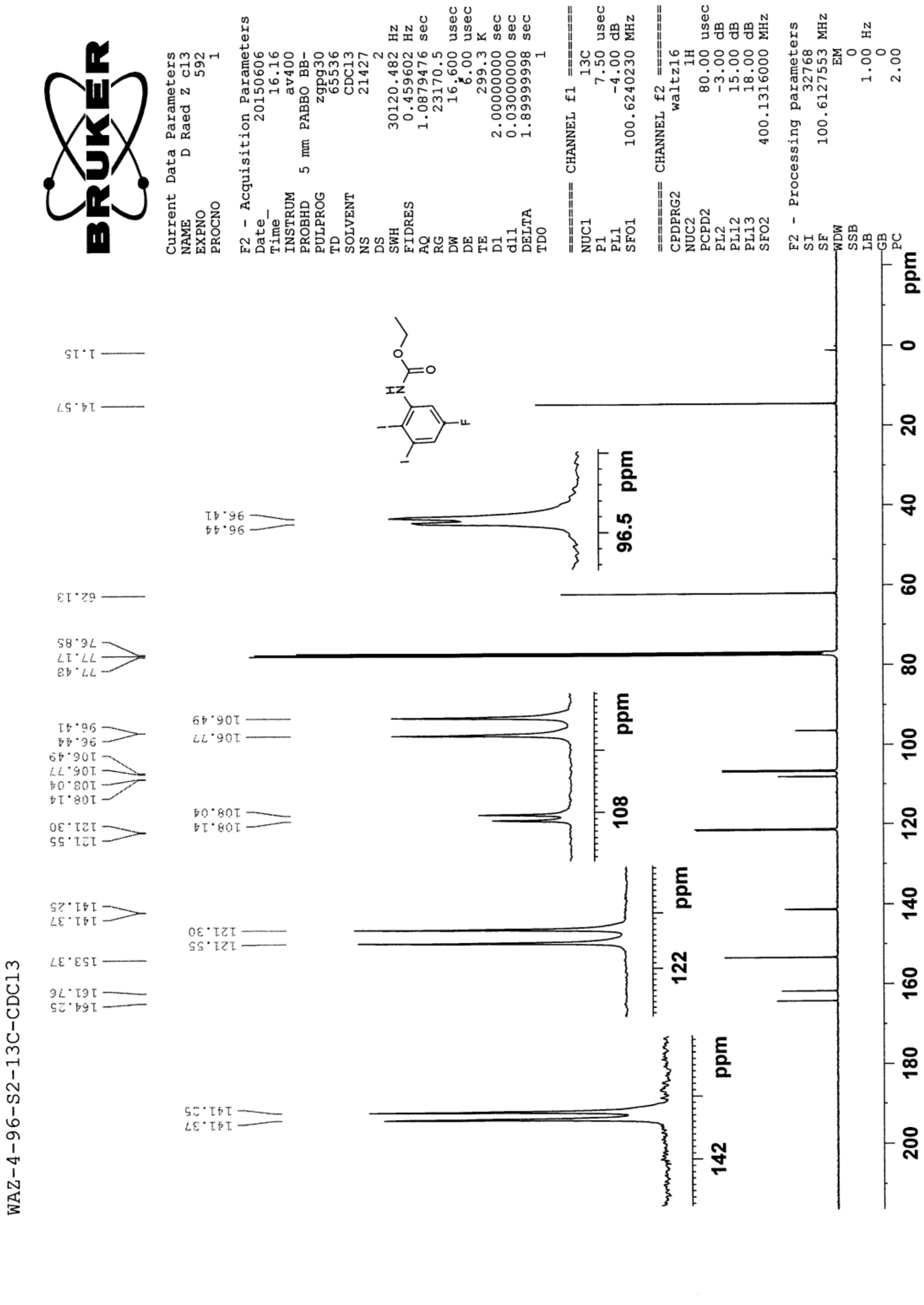
1.5.16 ^{13}C-NMR of tert-butyl (2,3-diiodo-5-methylphenyl)carbamate (13$_A$) in $CDCl_3$ at 25 ^{o}C.



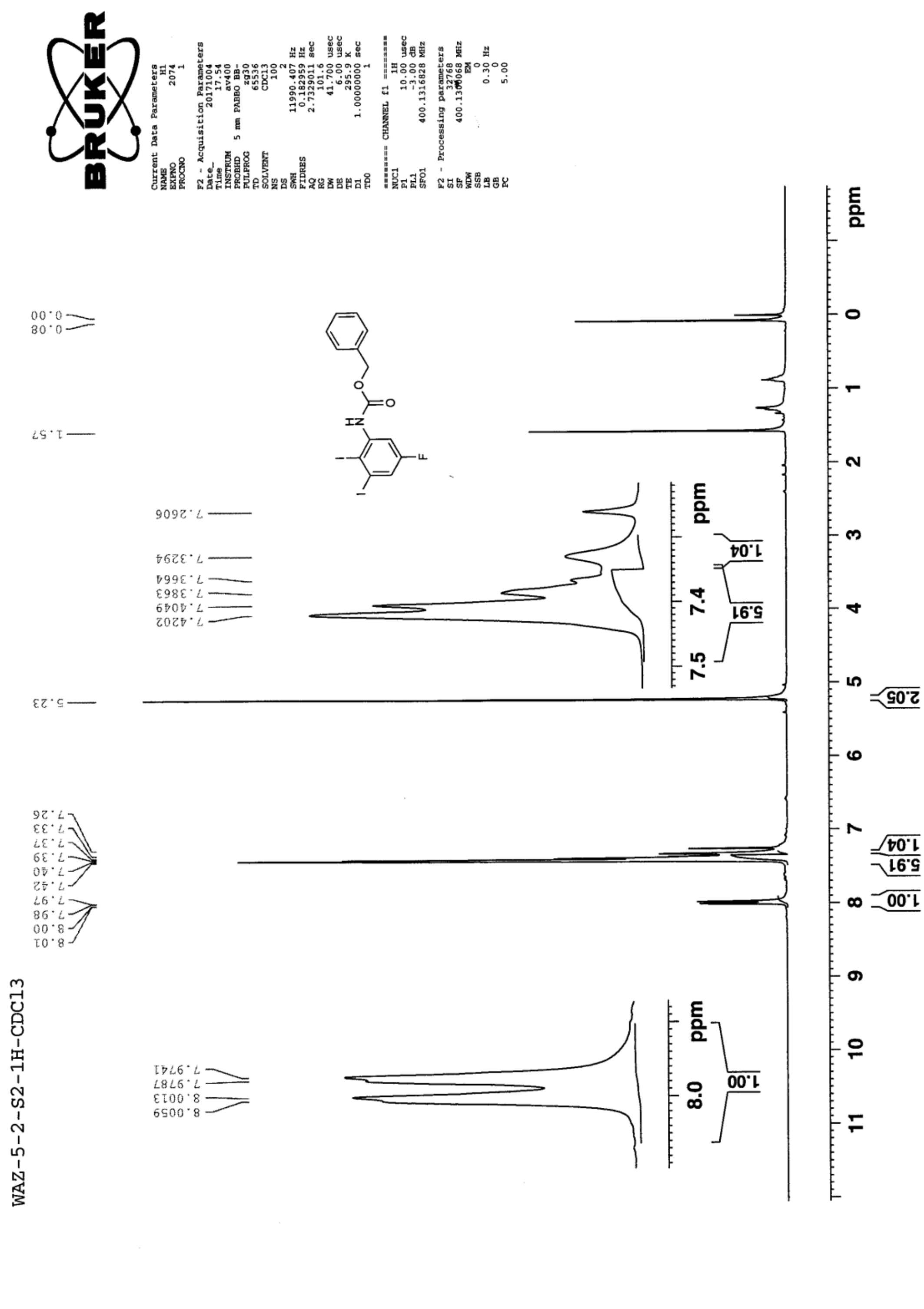
1.5.17 ^{1}H-NMR of ethyl (5-fluoro-2,3-diiodophenyl)carbamate (15_A) in $CDCl_3$ at 25 ^{o}C.



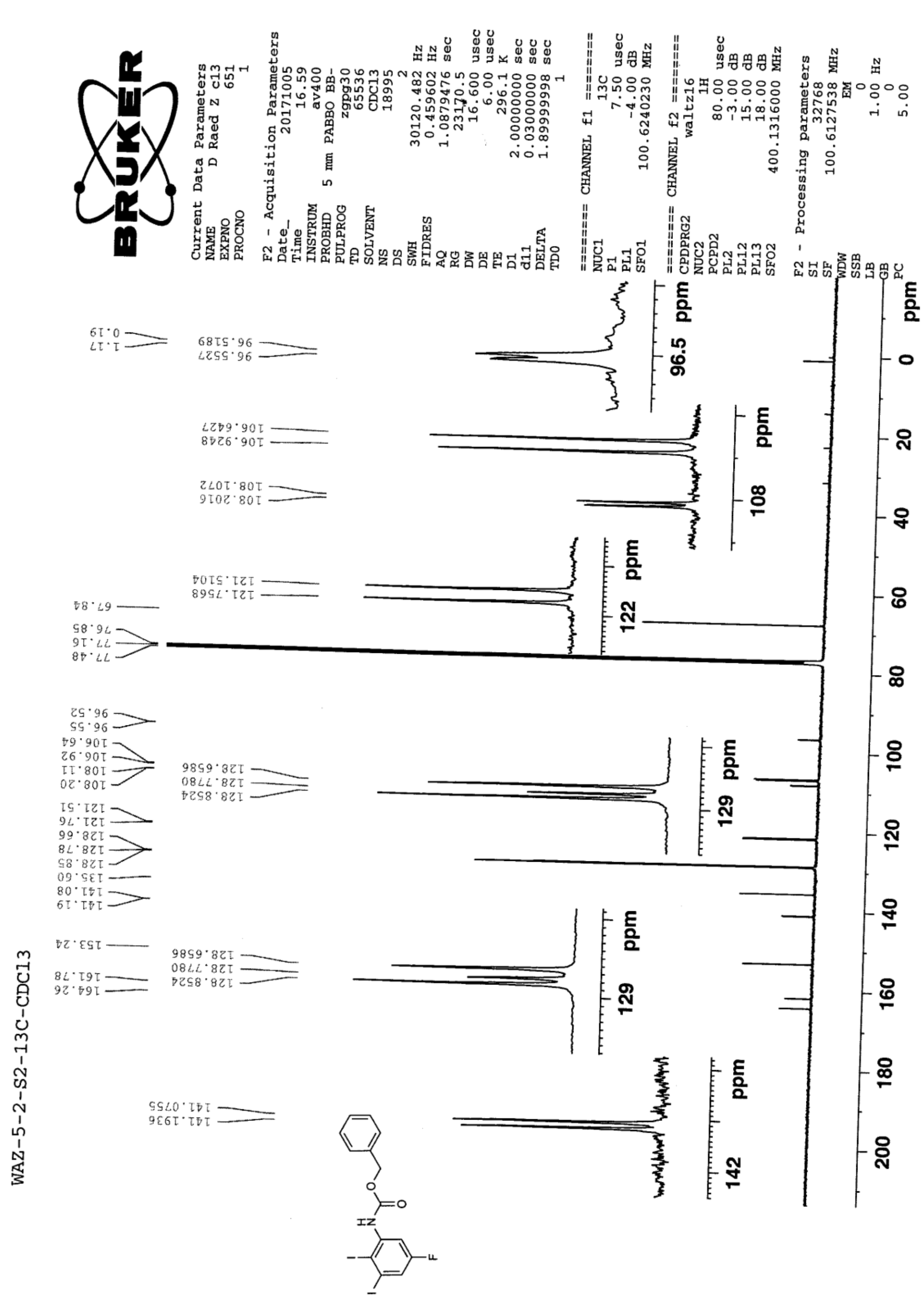
1.5.18 ^{13}C-NMR of ethyl (5-fluoro-2,3-diiodophenyl)carbamate (15_A) in $CDCl_3$ at 25 °C.



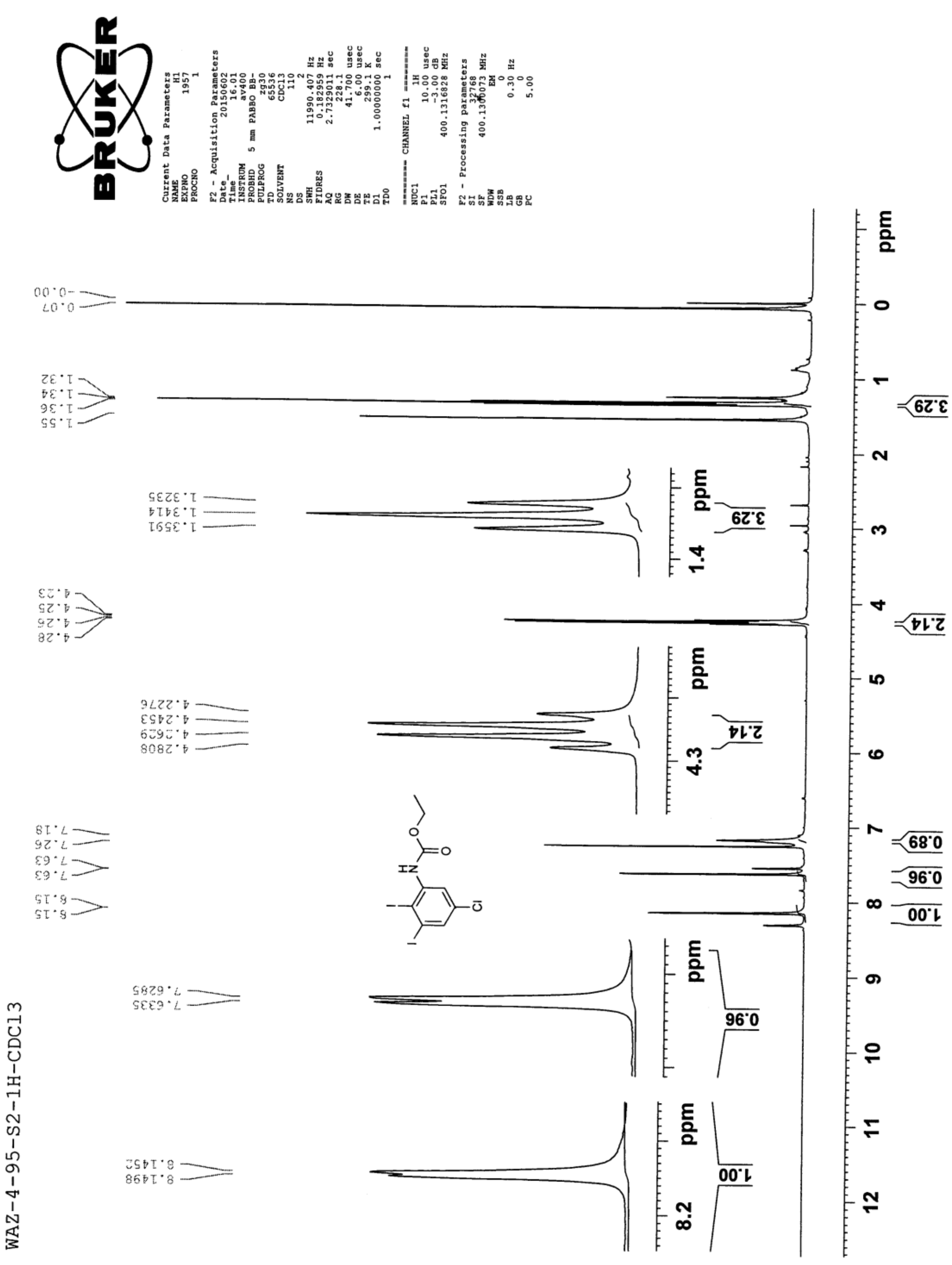
1.5.19 ¹H-NMR of benzyl (5-fluoro-2,3-diiodophenyl)carbamate (16A) in $CDCl_3$ at 25 °C.



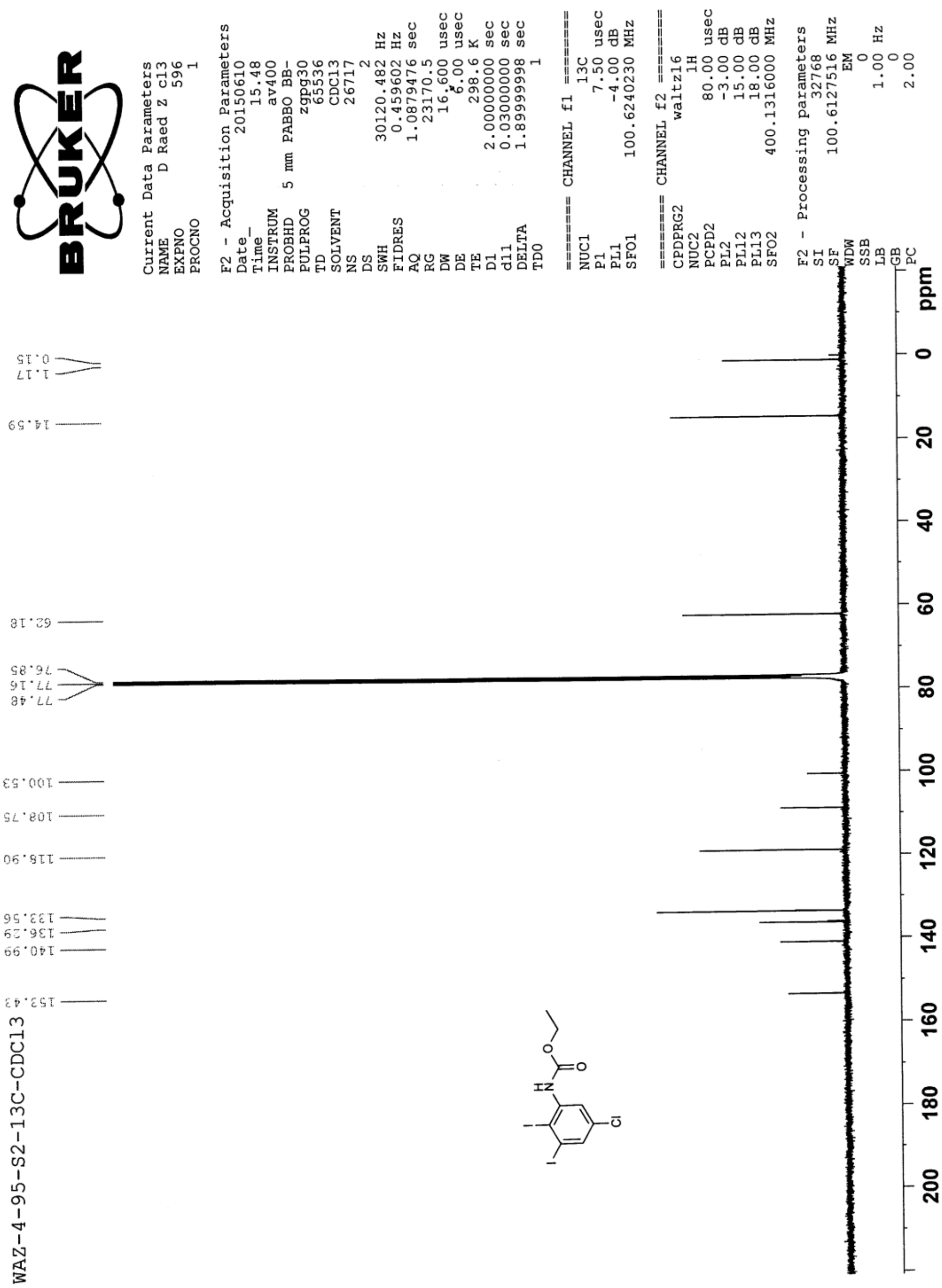
1.5.20 ^{13}C-NMR of benzyl (5-fluoro-2,3-diiodophenyl)carbamate (16_A) in $CDCl_3$ at 25 ^{o}C.



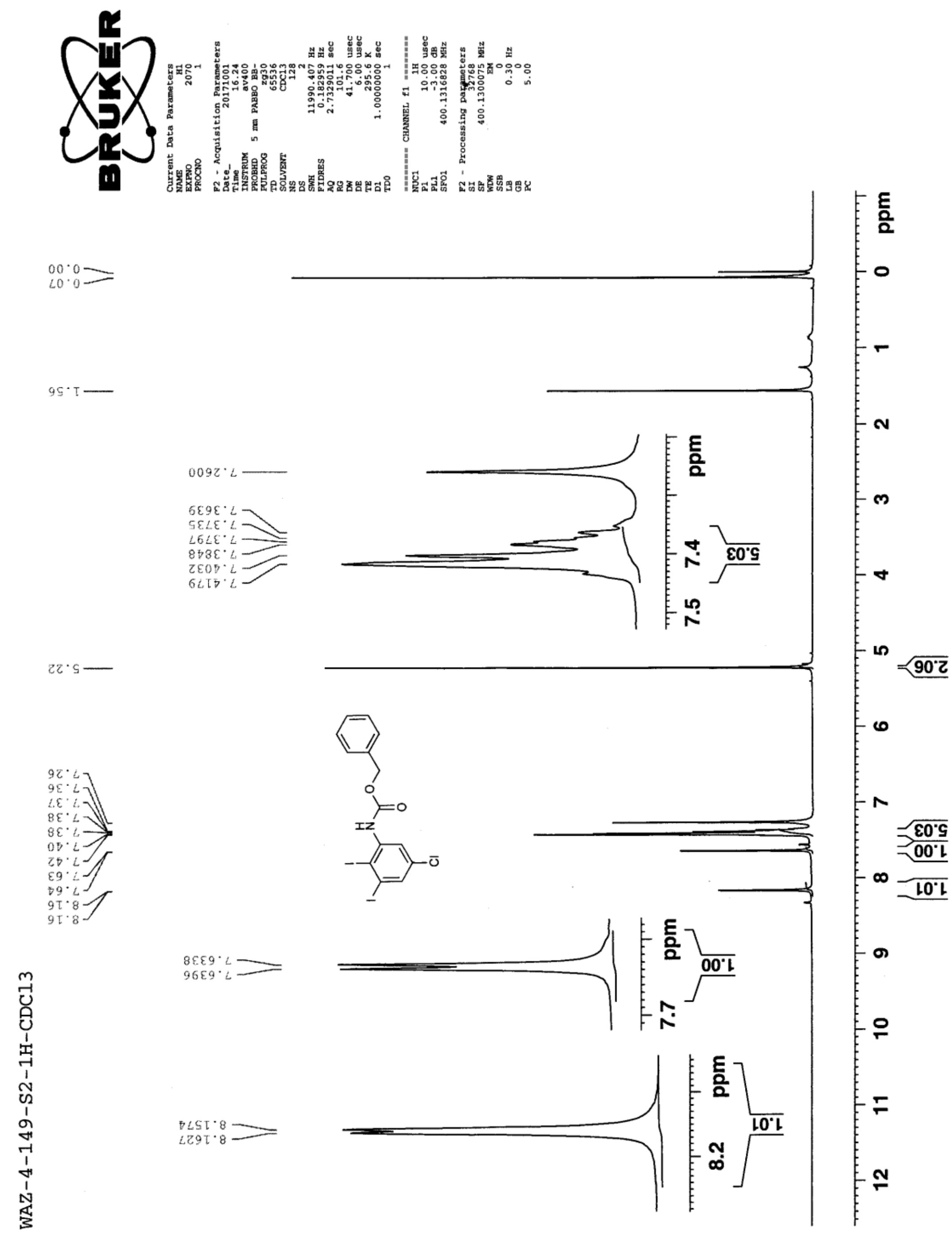
1.5.21 [1]H-NMR of ethyl (5-chloro-2,3-diiodophenyl)carbamate (17A) in $CDCl_3$ at 25 °C.



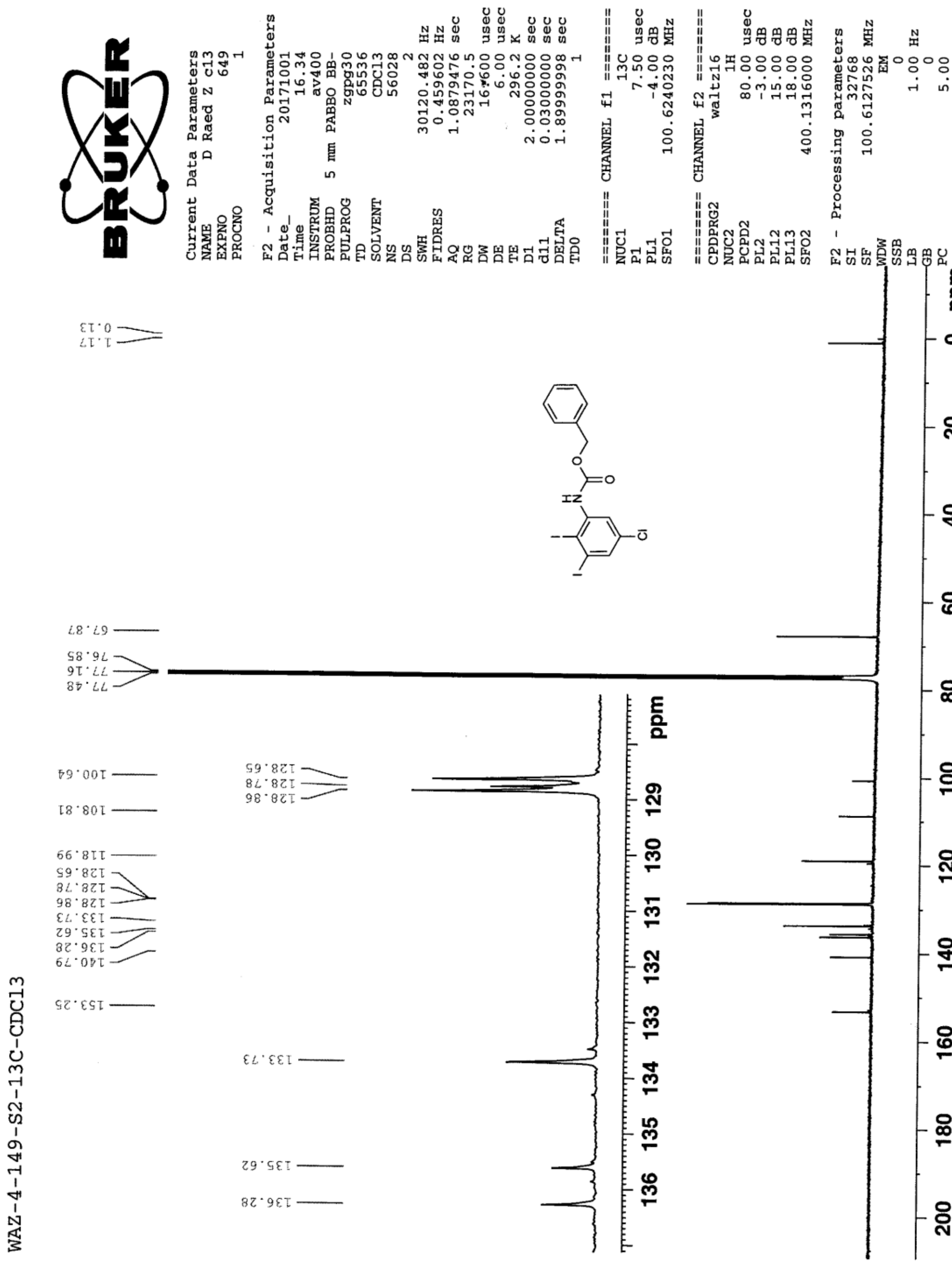
1.5.22 ^{13}C-NMR of ethyl (5-chloro-2,3-diiodophenyl)carbamate (17$_A$) in $CDCl_3$ at 25 ^{o}C.



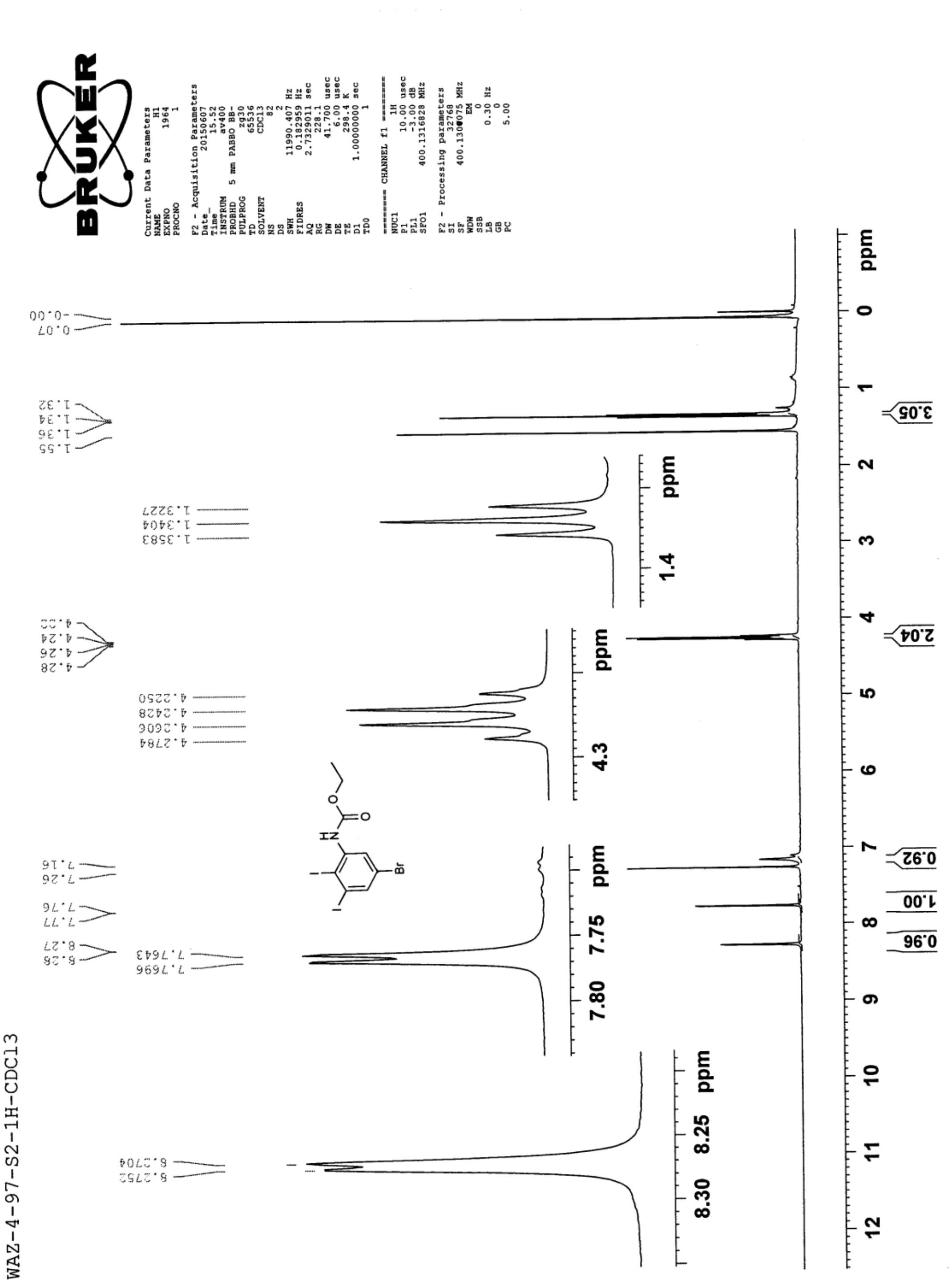
1.5.23 [1]H-NMR of benzyl (5-chloro-2,3-diiodophenyl)carbamate (18_A) in $CDCl_3$ at 25 °C.



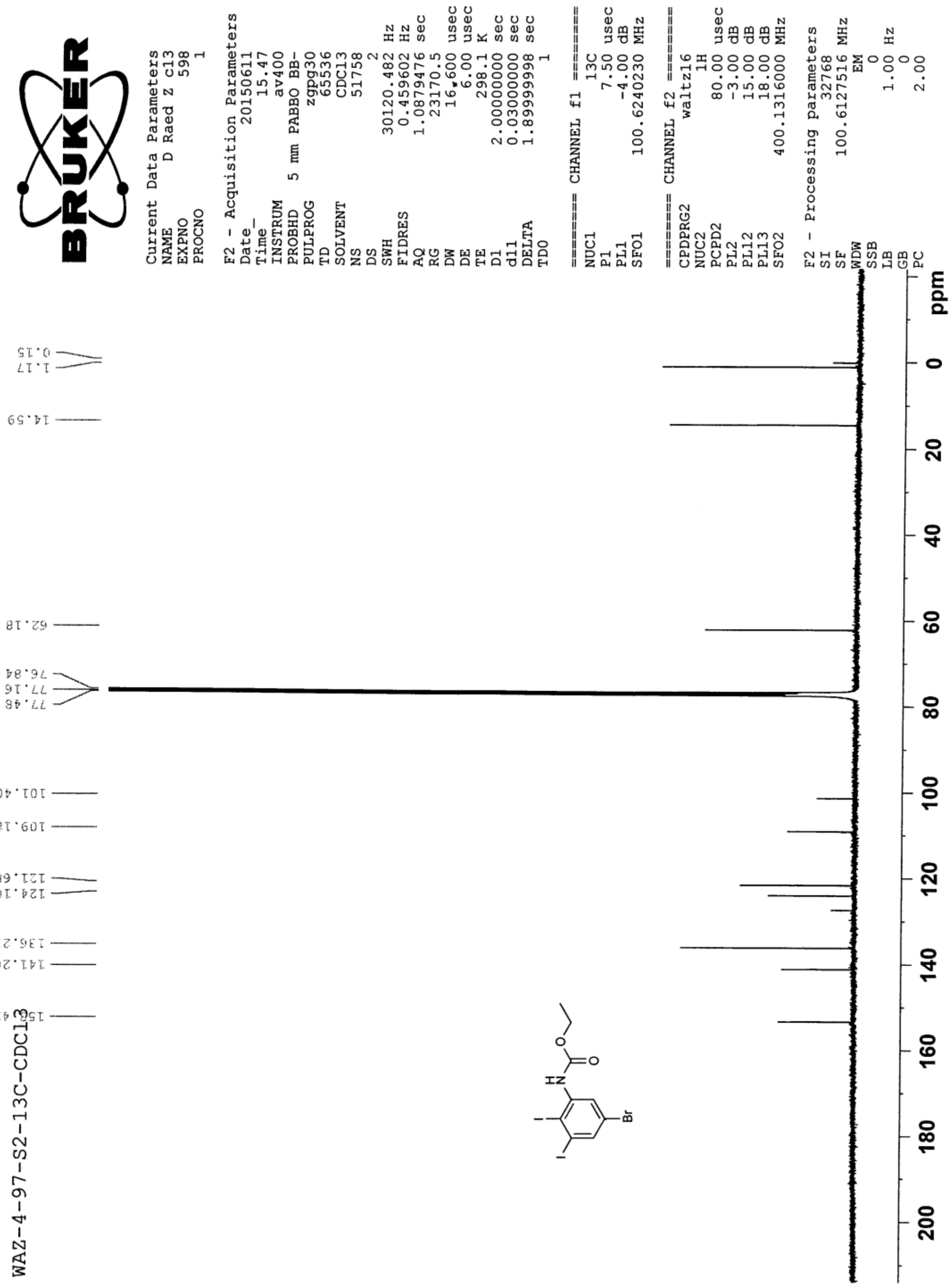
1.5.24 ^{13}C-NMR of benzyl (5-chloro-2,3-diiodophenyl)carbamate (18$_A$) in $CDCl_3$ at 25 ^{o}C.



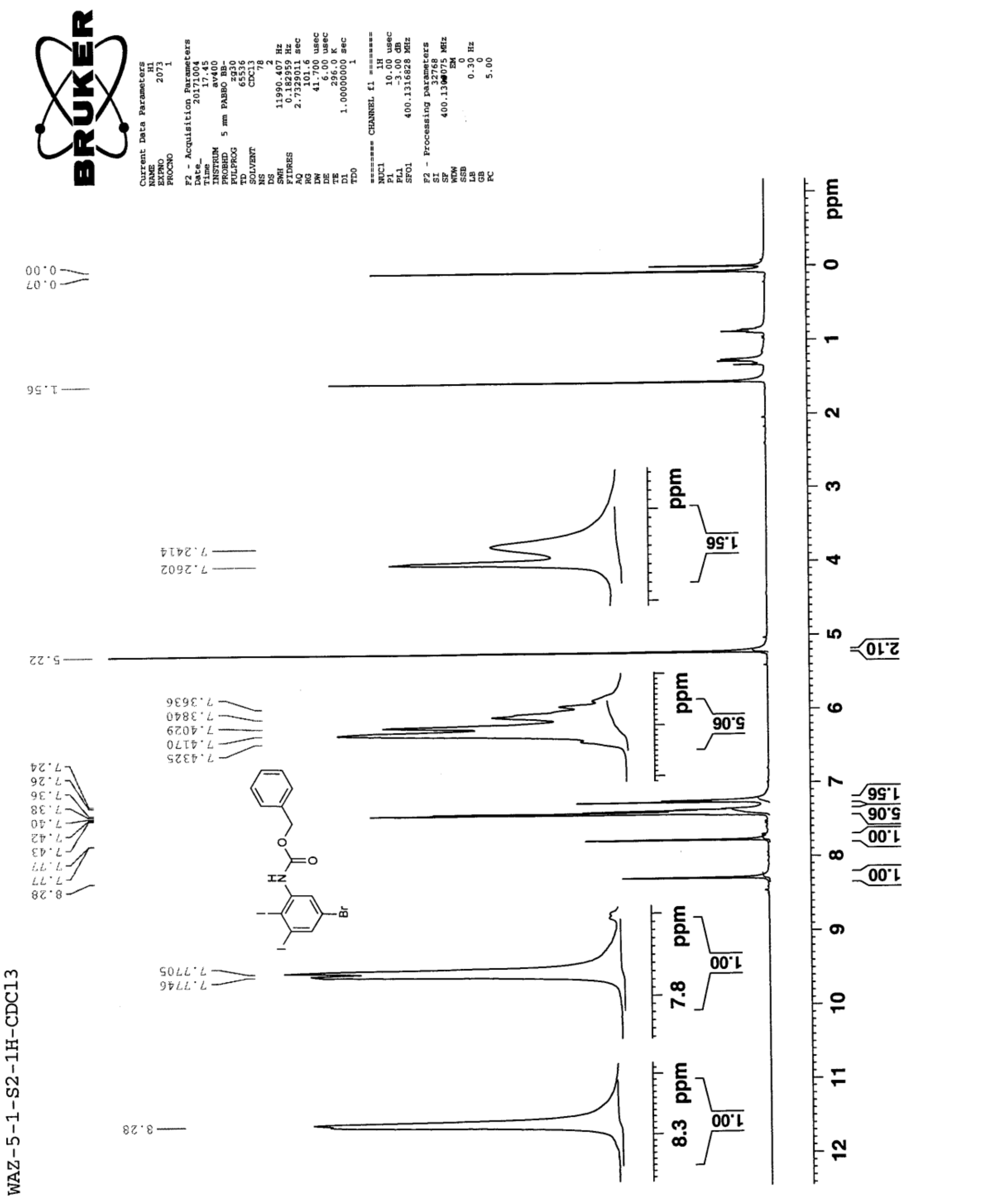
1.5.25 ¹H-NMR of ethyl (5-bromo-2,3-diiodophenyl)carbamate (20_A) in $CDCl_3$ at 25 °C.



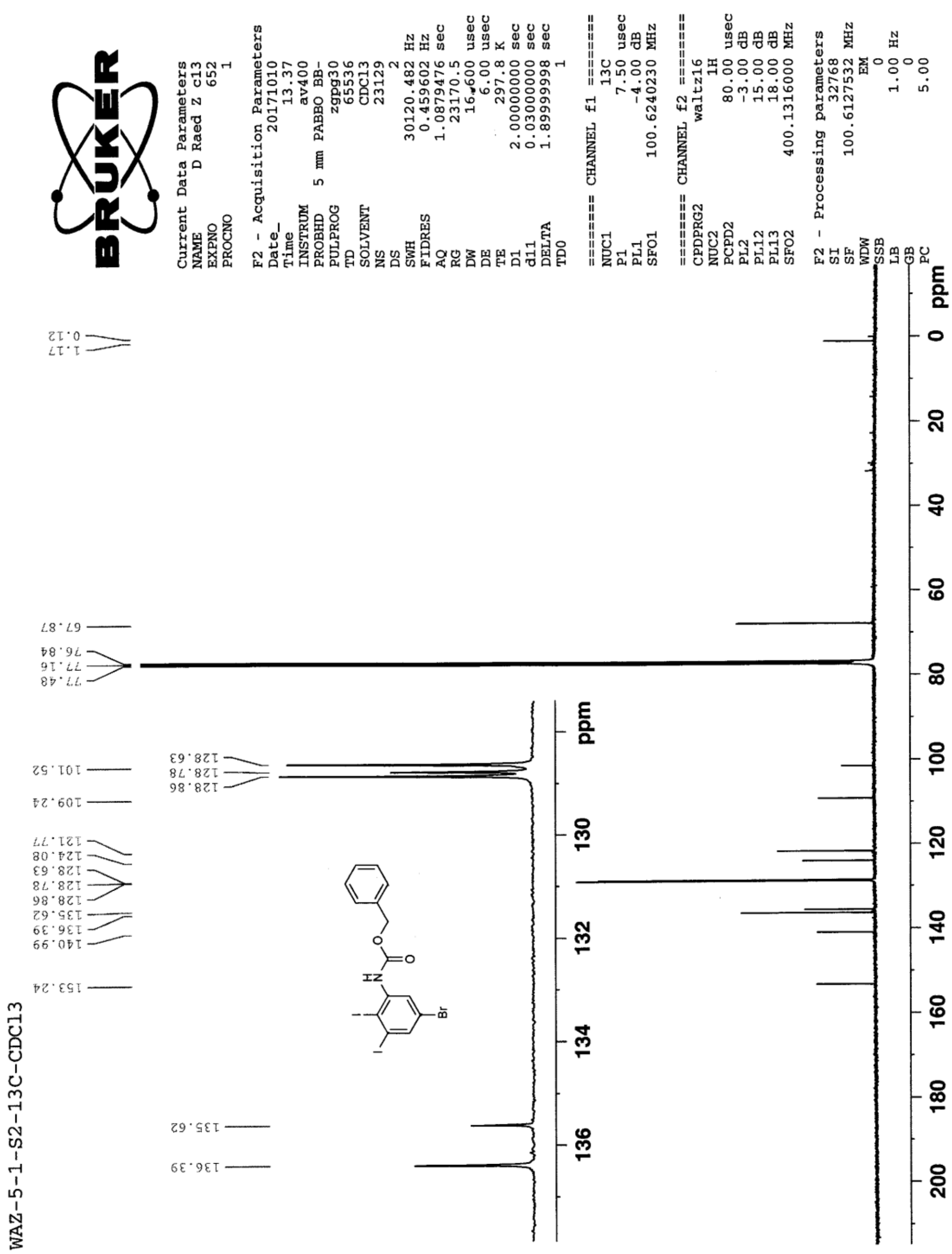
1.5.26 ^{13}C-NMR of ethyl (5-bromo-2,3-diiodophenyl)carbamate (20_A) in $CDCl_3$ at 25 °C.



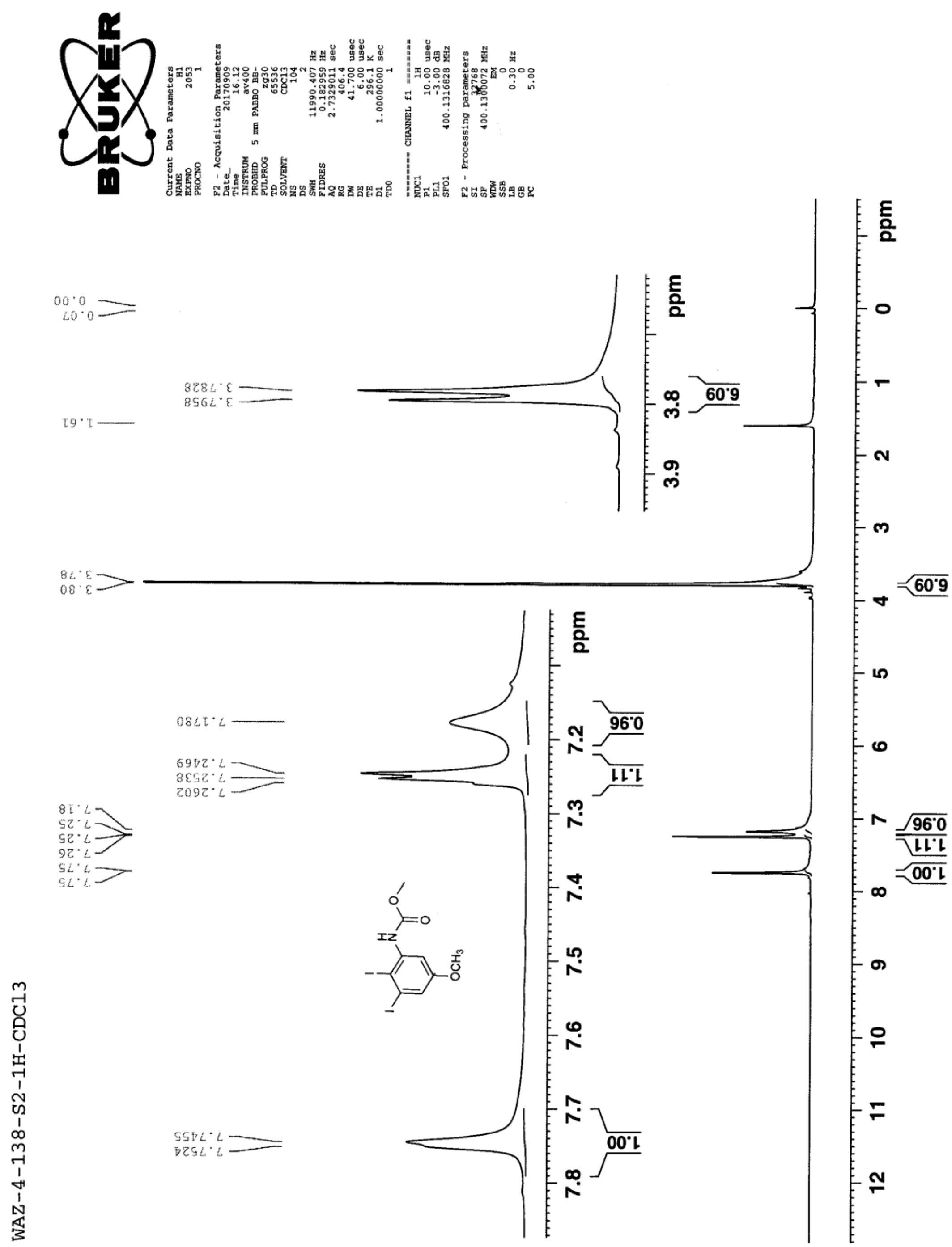
1.5.27 [1]H-NMR of benzyl (5-bromo-2,3-diiodophenyl)carbamate (21A) in $CDCl_3$ at 25 °C.



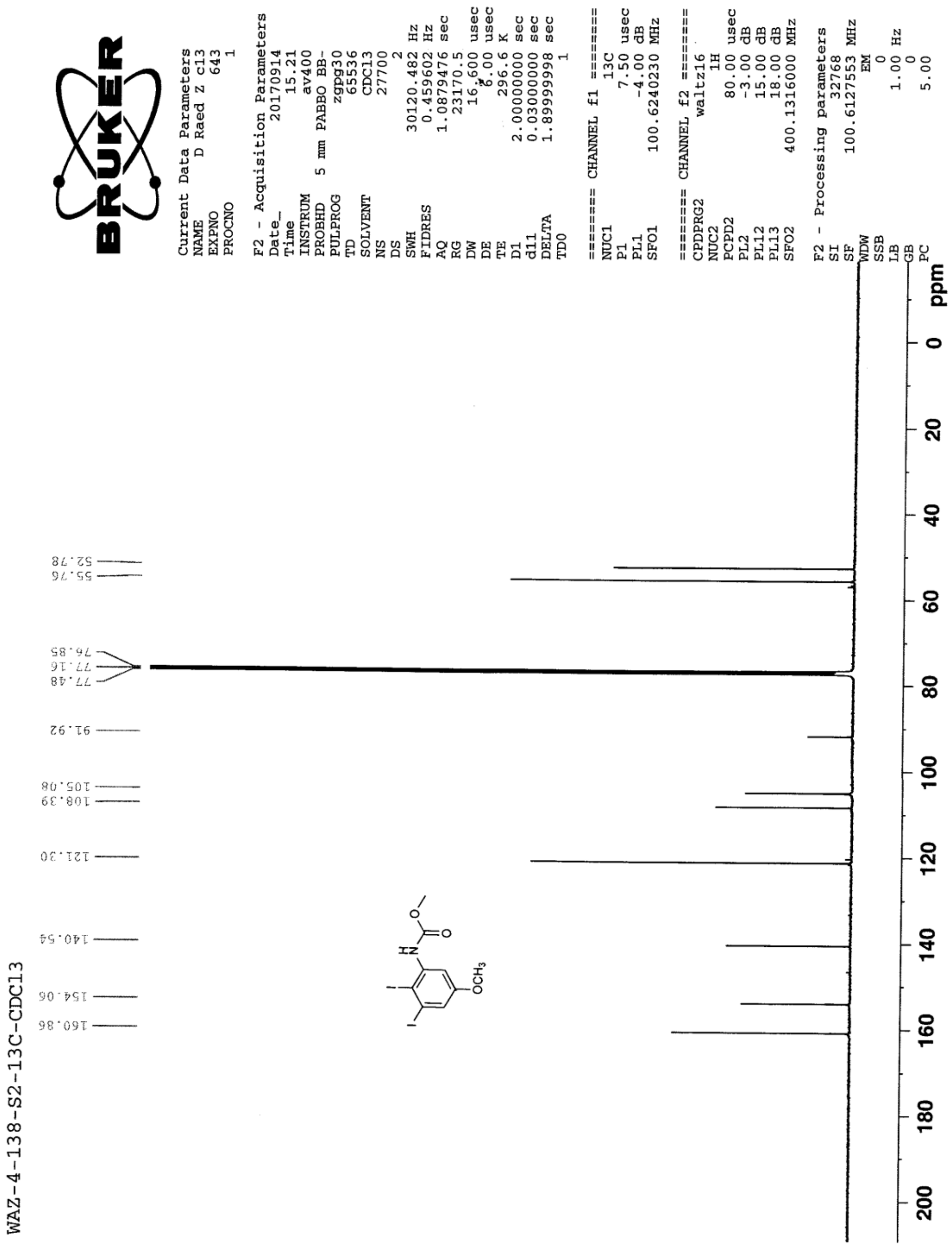
1.5.28 ^{13}C-NMR of benzyl (5-bromo-2,3-diiodophenyl)carbamate (21_A) in $CDCl_3$ at 25 ^{o}C.



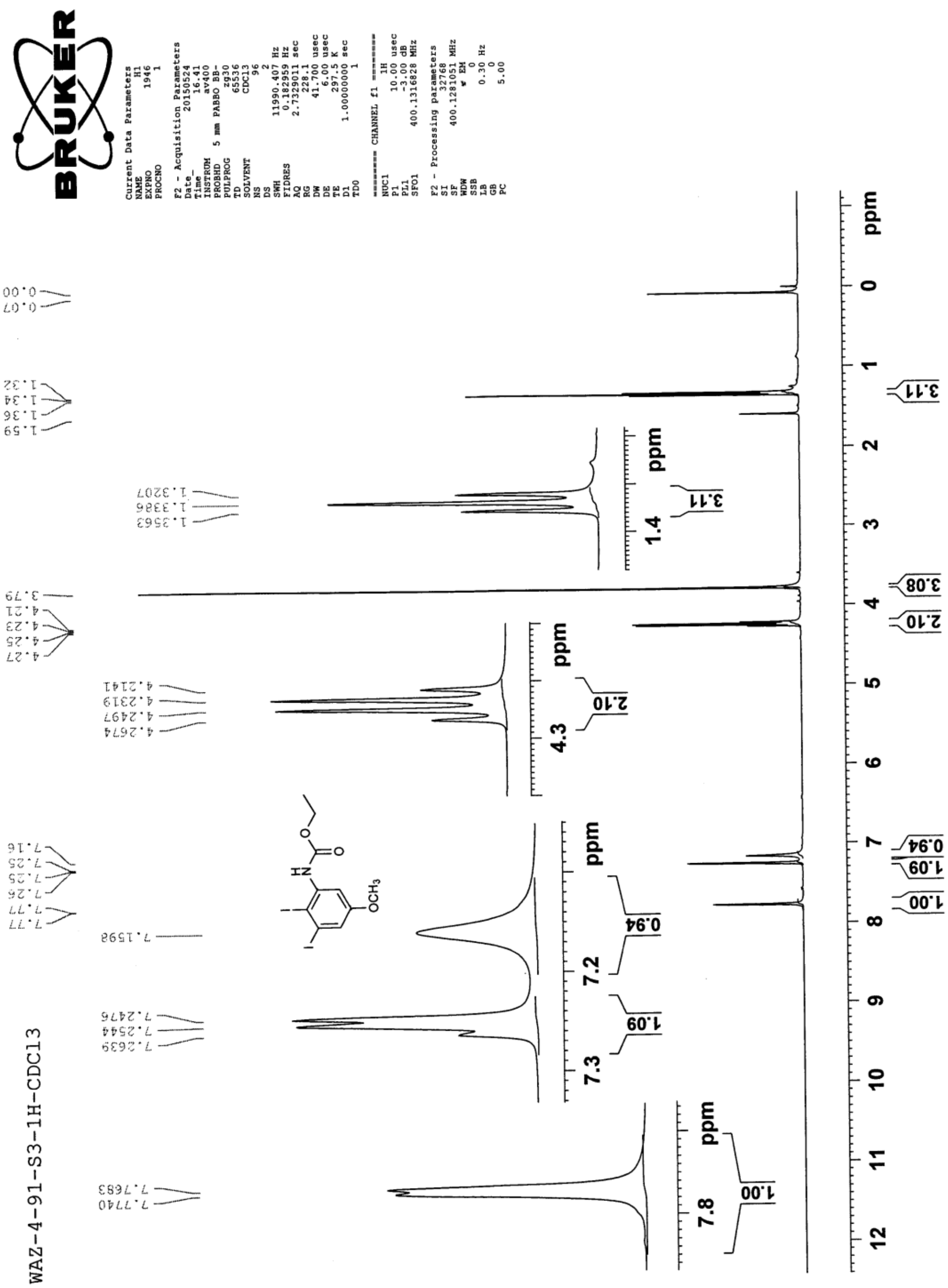
1.5.29 ^{1}H-NMR of methyl (2,3-diiodo-5-methoxyphenyl)carbamate (22_A) in $CDCl_3$ at 25 ^oC.



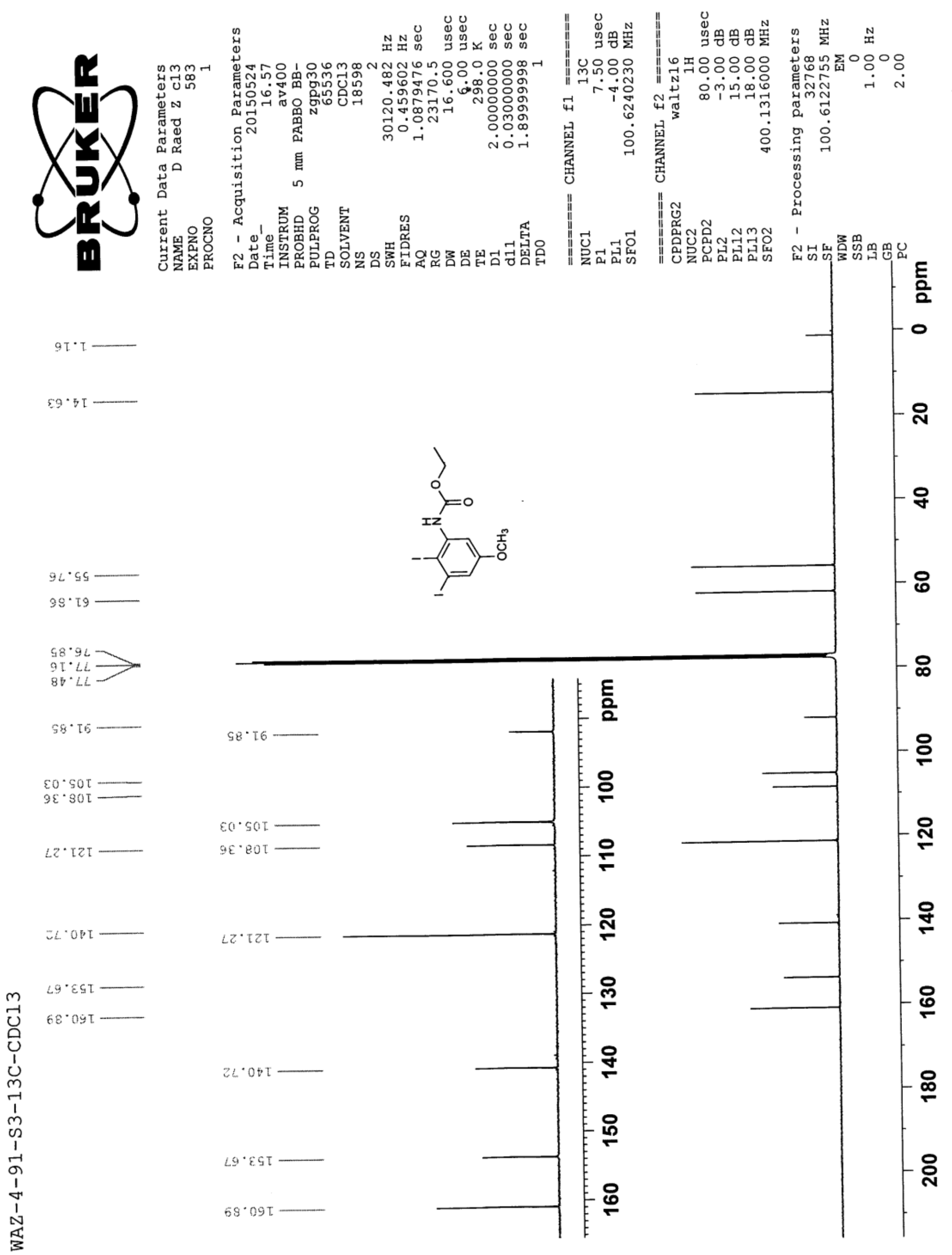
1.5.30 ^{13}C-NMR of methyl (2,3-diiodo-5-methoxyphenyl)carbamate (22$_A$) in $CDCl_3$ at 25 ^{o}C.



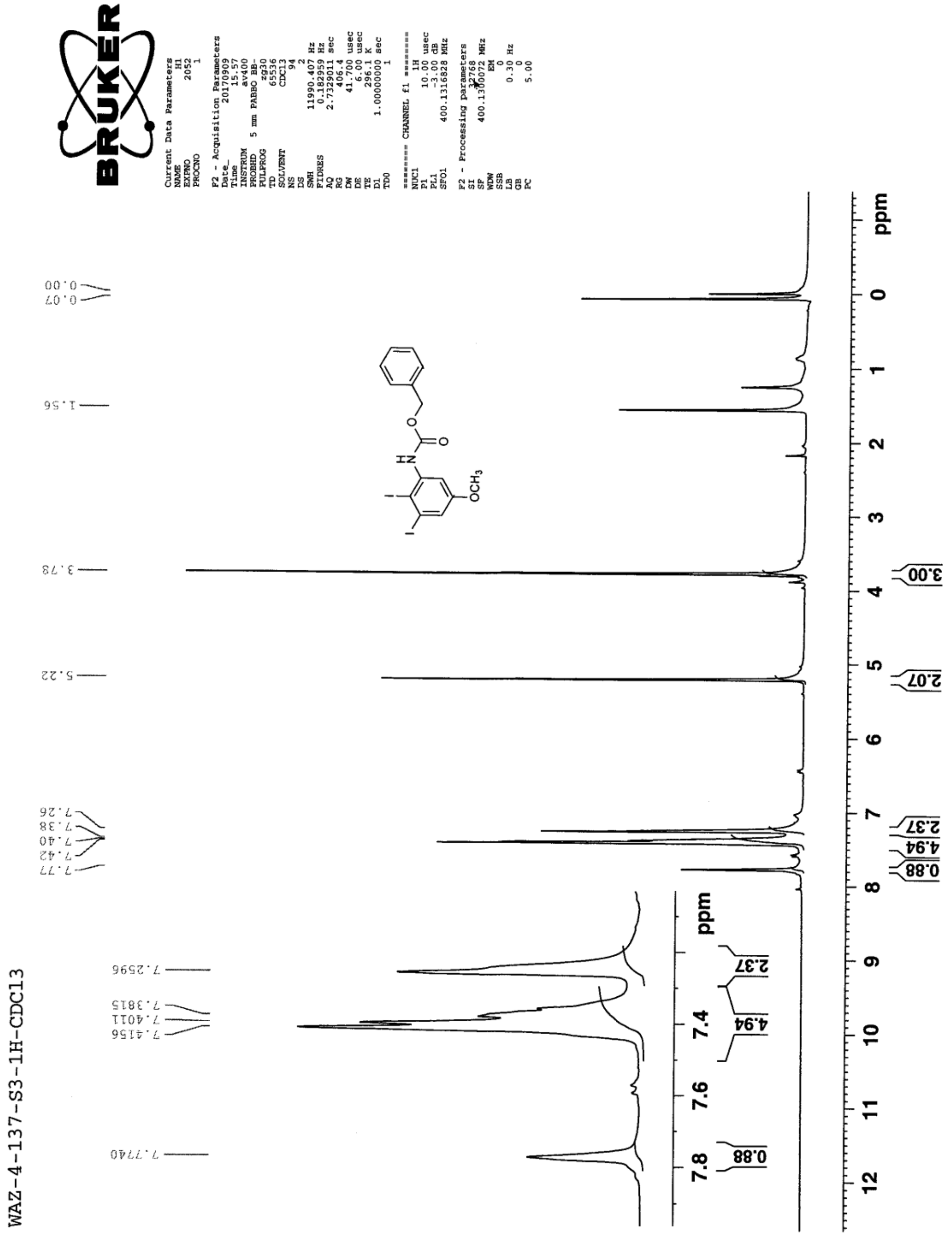
1.5.31 ^{1}H-NMR of ethyl (2,3-diiodo-5-methoxyphenyl)carbamate (23_A) in $CDCl_3$ at 25 ^{o}C.



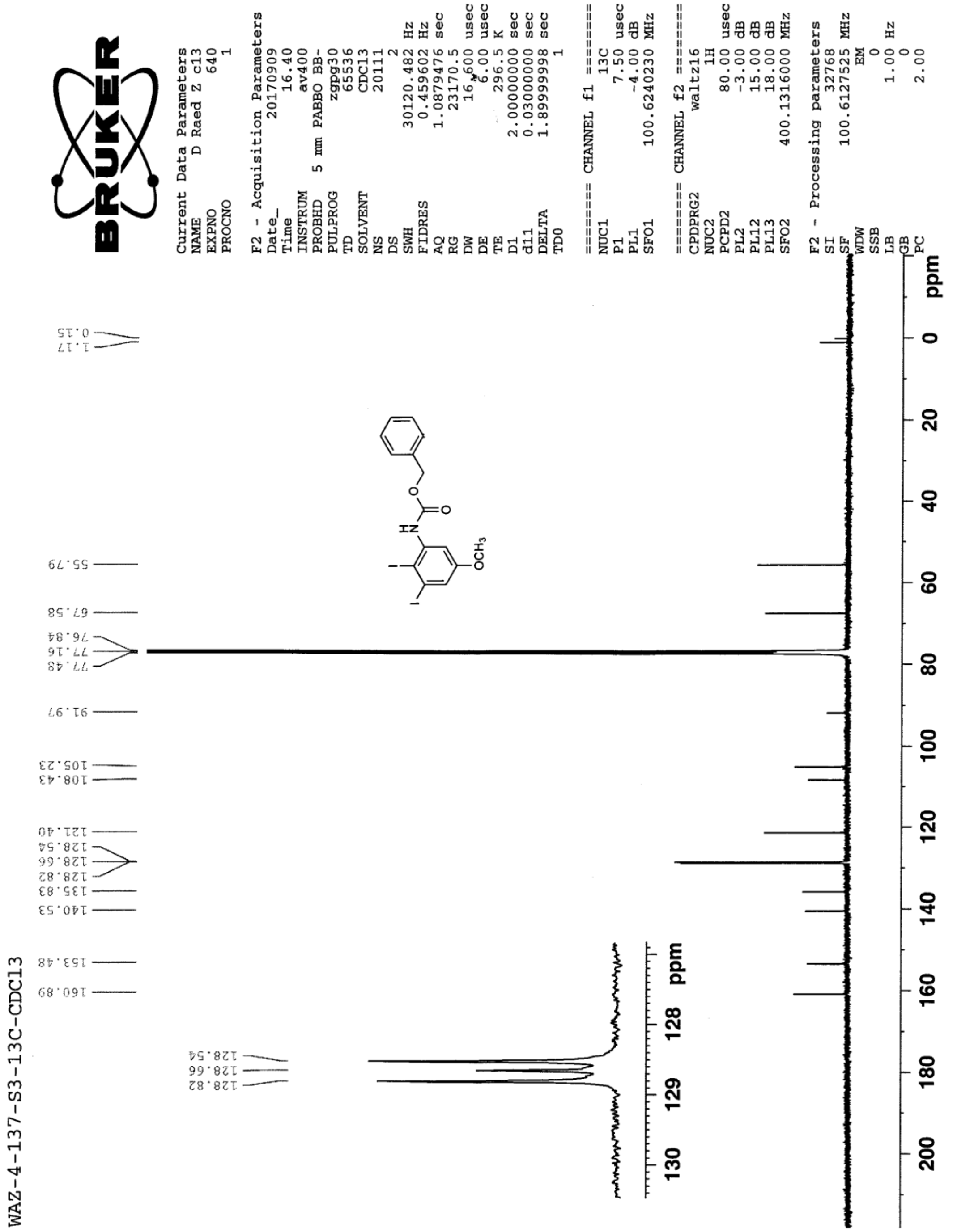
1.5.32 ^{13}C-NMR of ethyl (2,3-diiodo-5-methoxyphenyl)carbamate (23_A) in $CDCl_3$ at 25 ^{o}C.



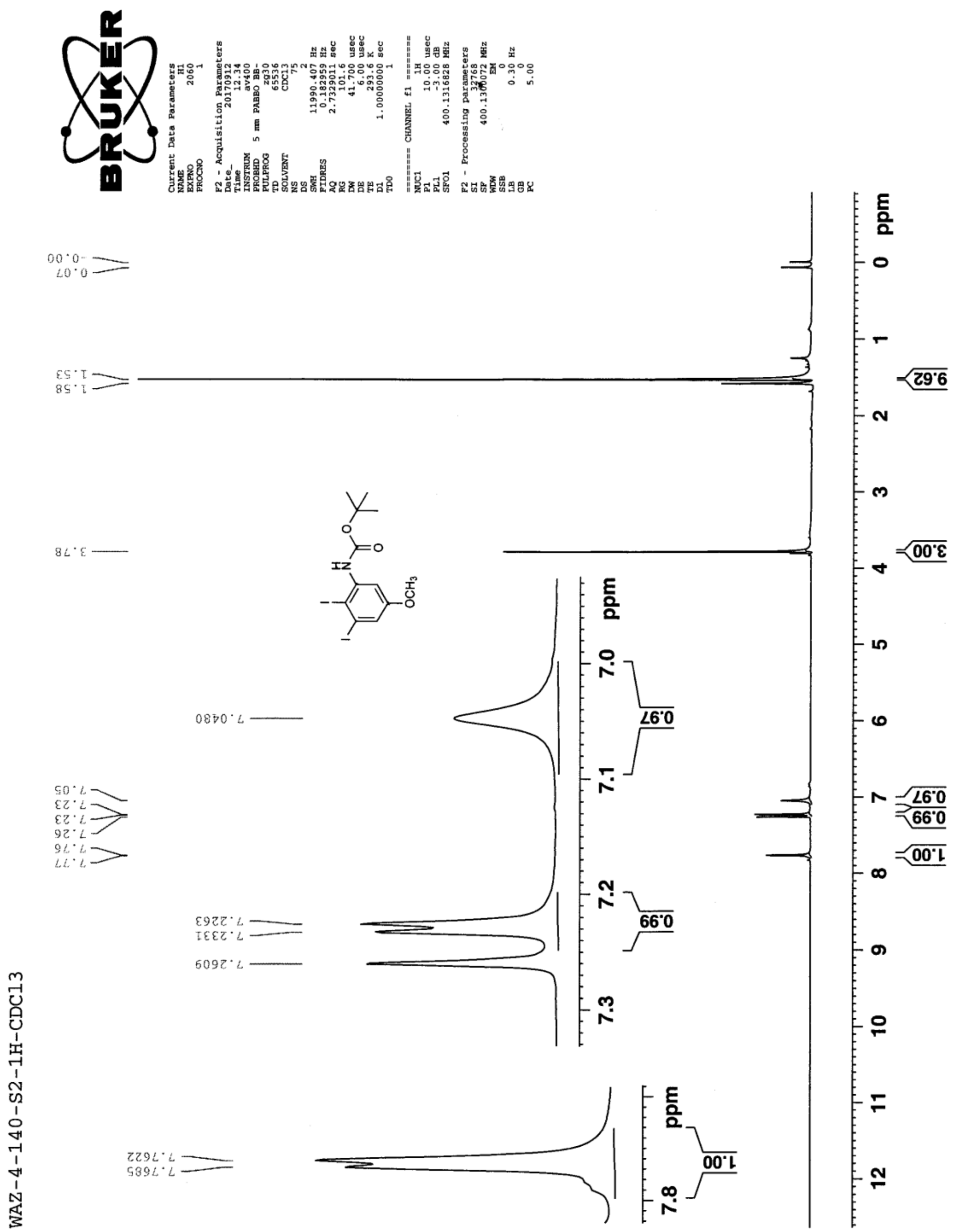
1.5.33 [1]H-NMR of benzyl (2,3-diiodo-5-methoxyphenyl)carbamate (24_A) in $CDCl_3$ at 25 °C.



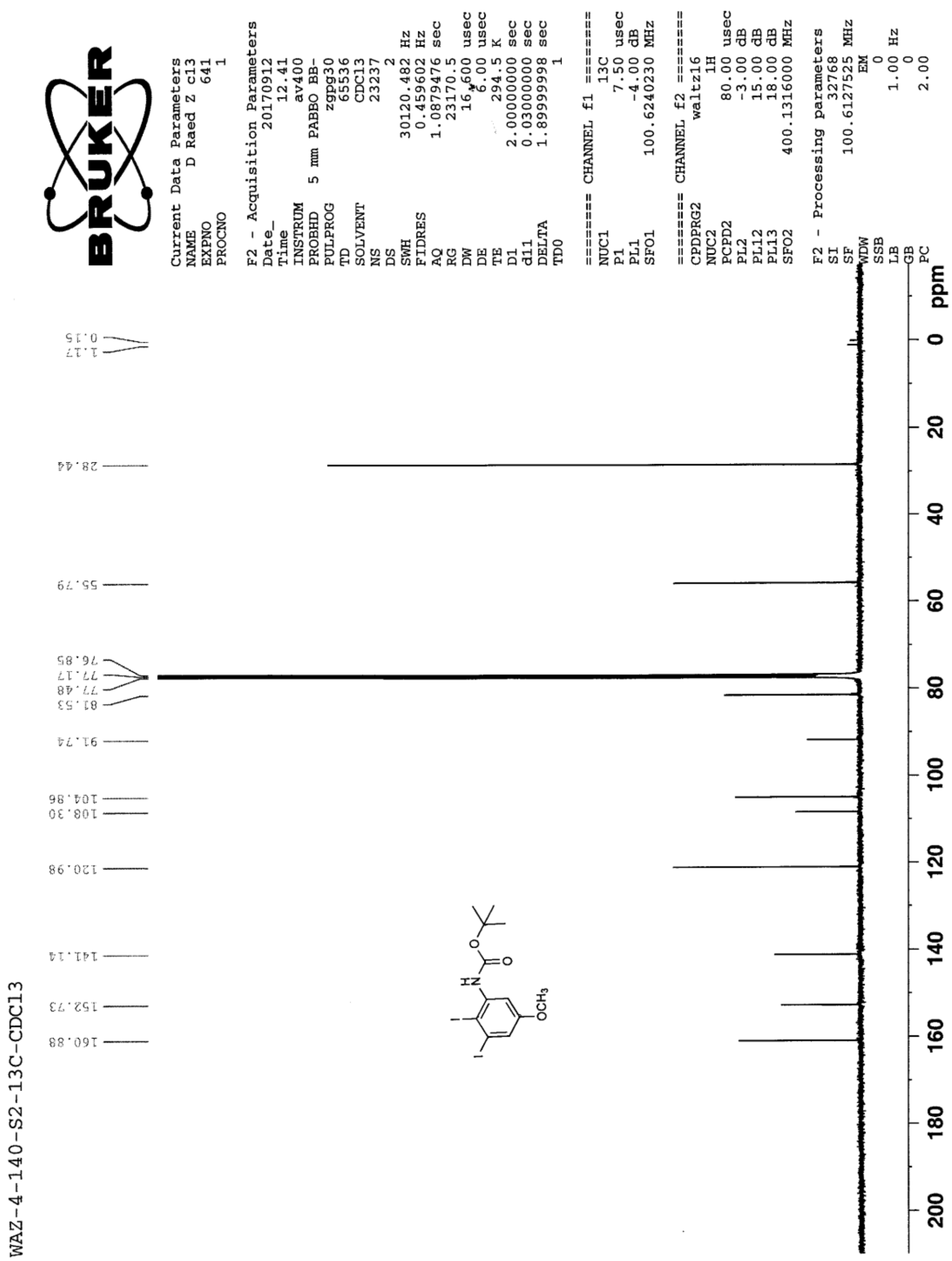
1.5.34 ^{13}C-NMR of benzyl (2,3-diiodo-5-methoxyphenyl)carbamate (24_A) in $CDCl_3$ at 25 ^oC.



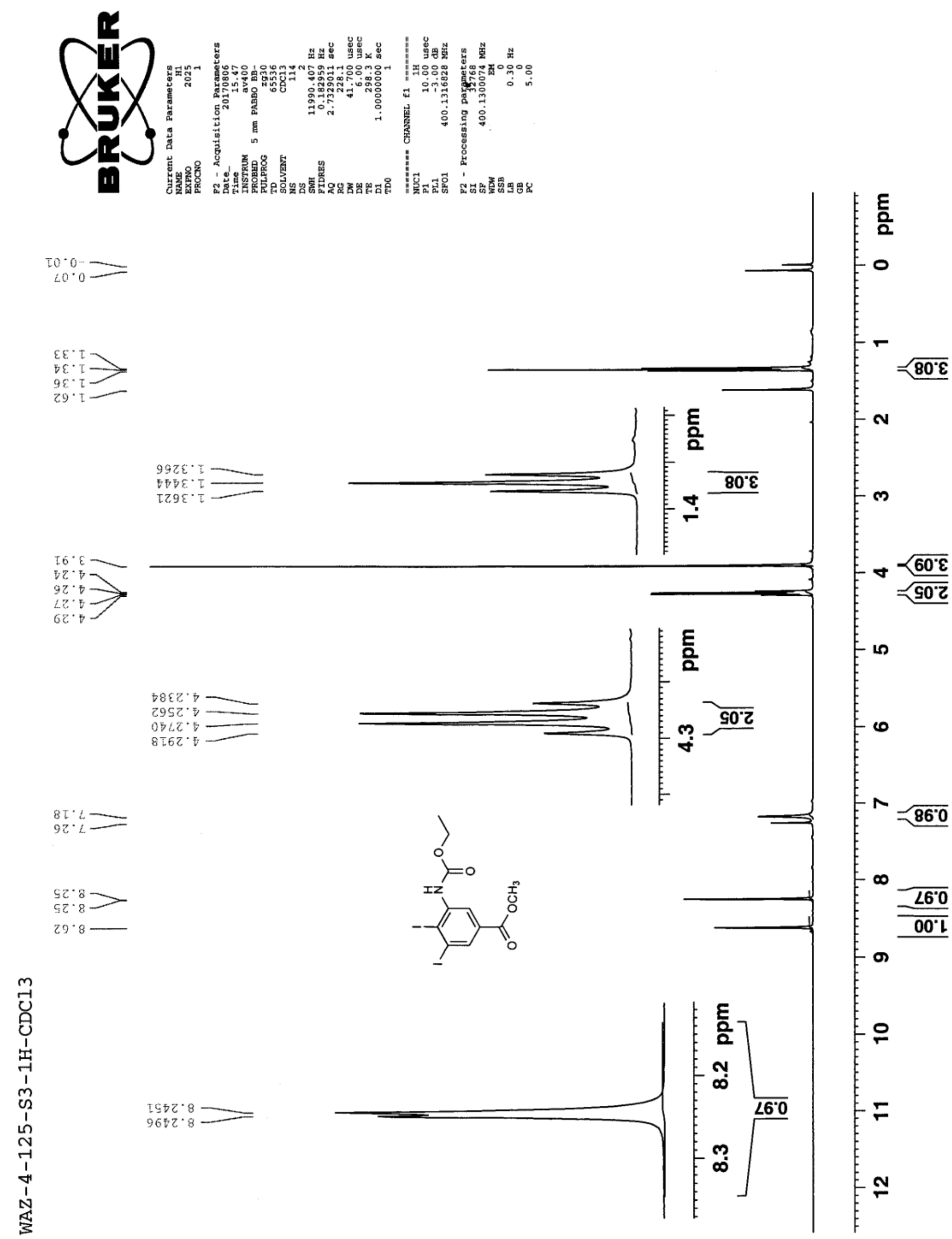
1.5.35 ^{1}H-NMR of tert-butyl (2,3-diiodo-5-methoxyphenyl)carbamate (26_A) in $CDCl_3$ at 25 ^{o}C.



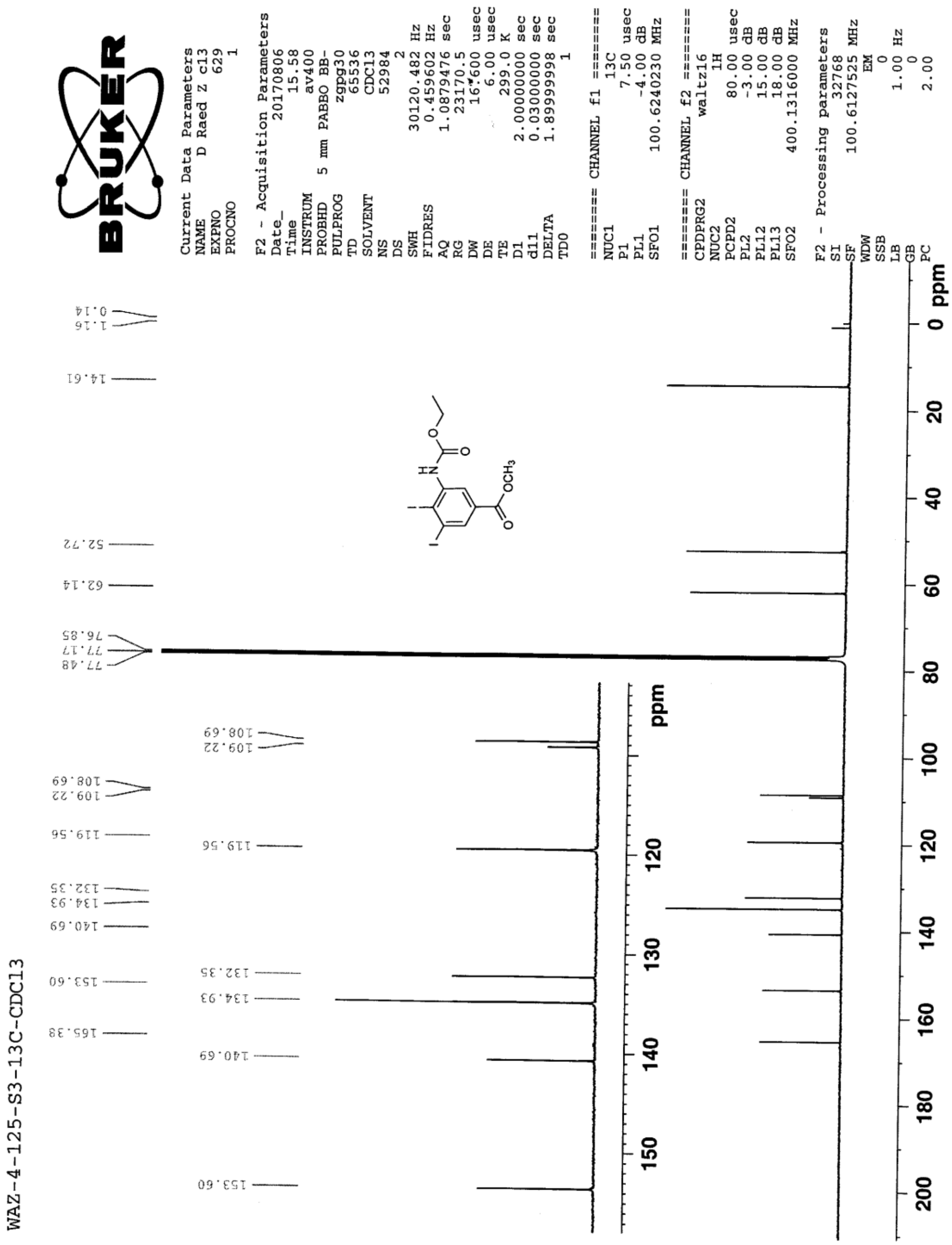
1.5.36 ¹³C-NMR of tert-butyl (2,3-diiodo-5-methoxyphenyl)carbamate (26A) in $CDCl_3$ at 25 °C.



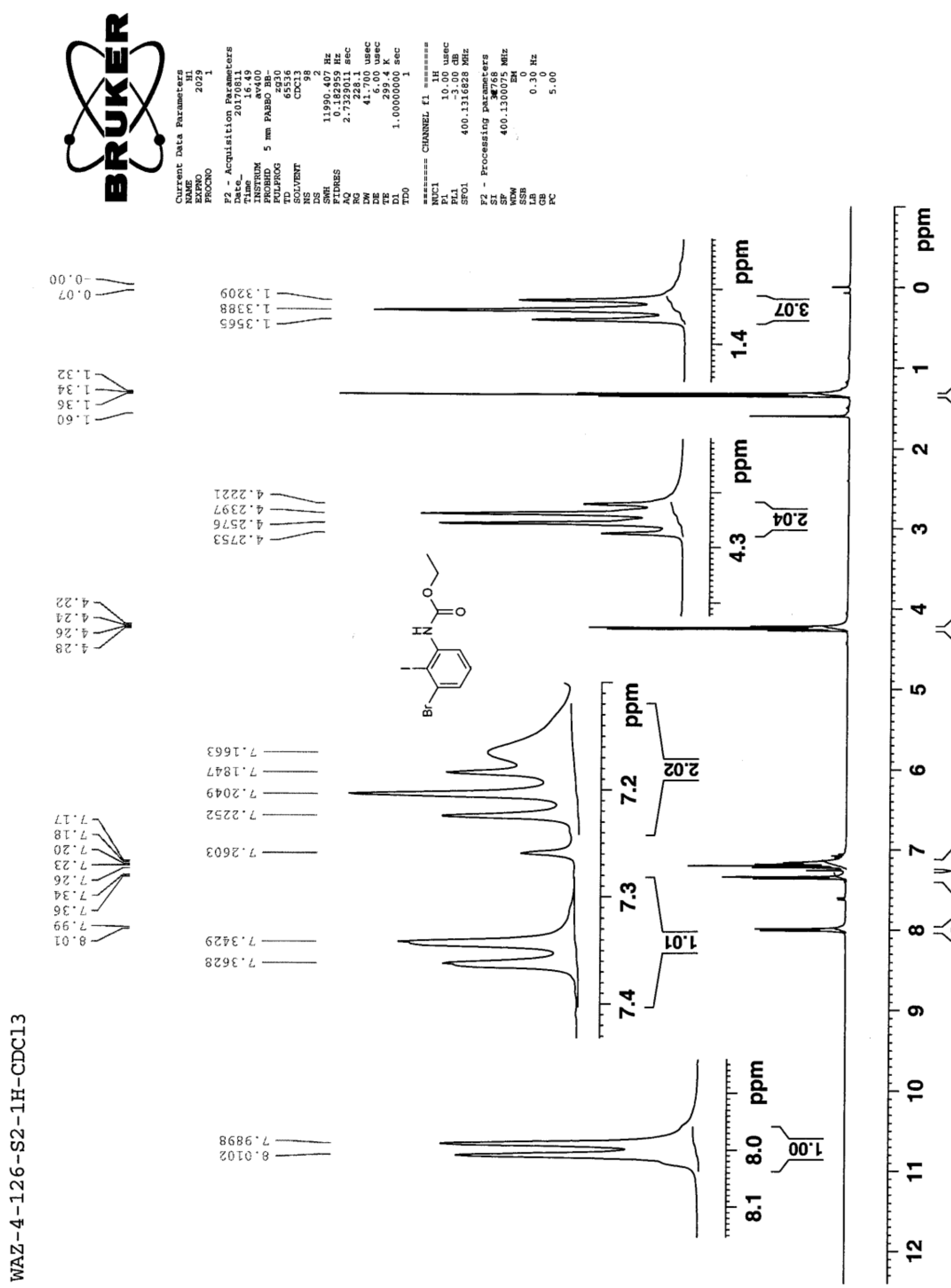
1.5.37 ^{1}H-NMR of methyl 3-((ethoxycarbonyl)amino)-4,5-diiodobenzoate (27$_A$) in $CDCl_3$ at 25 ^{o}C.



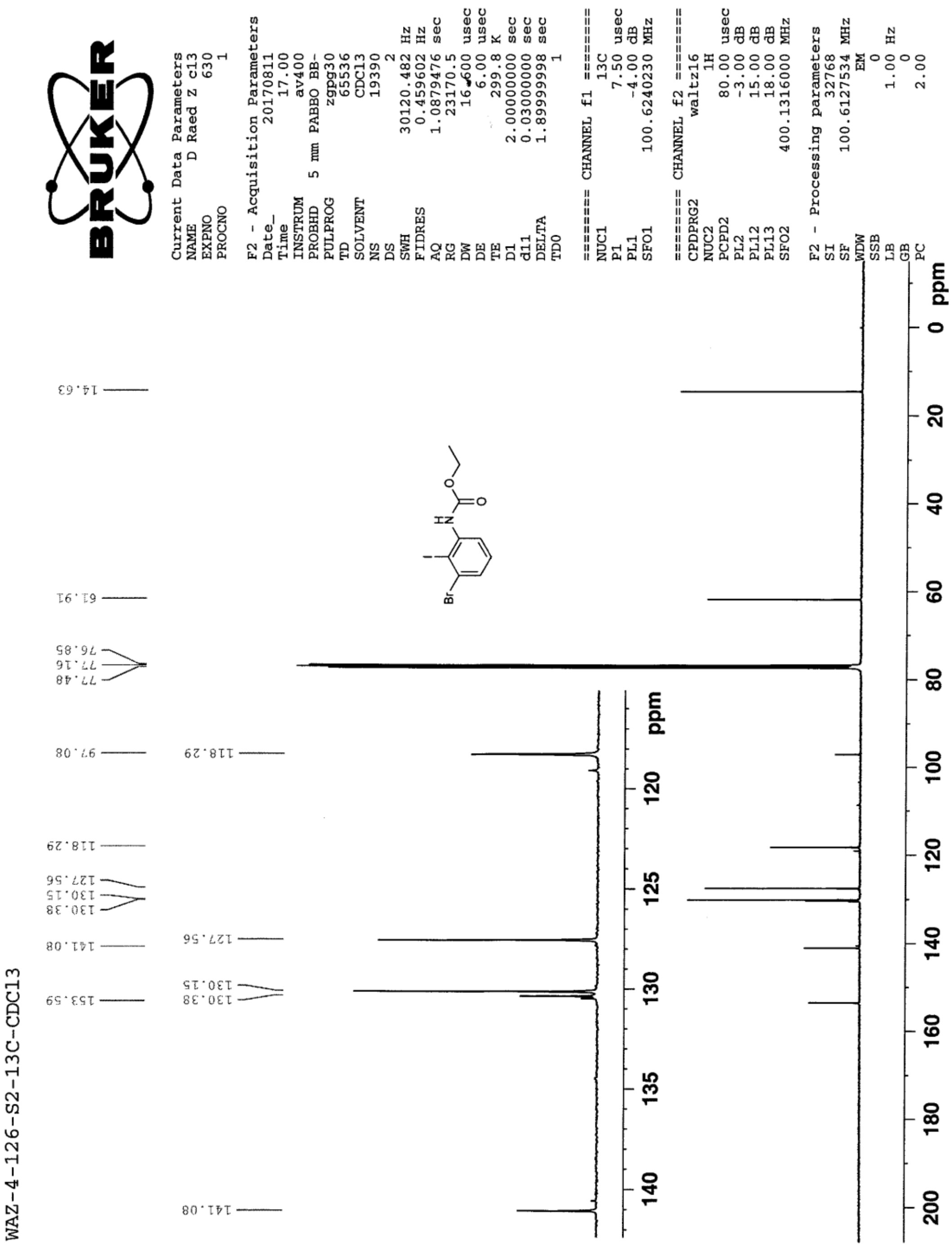
1.5.38 ^13C-NMR of methyl 3-((ethoxycarbonyl)amino)-4,5-diiodobenzoate (27A) in CDCl3 at 25 °C.



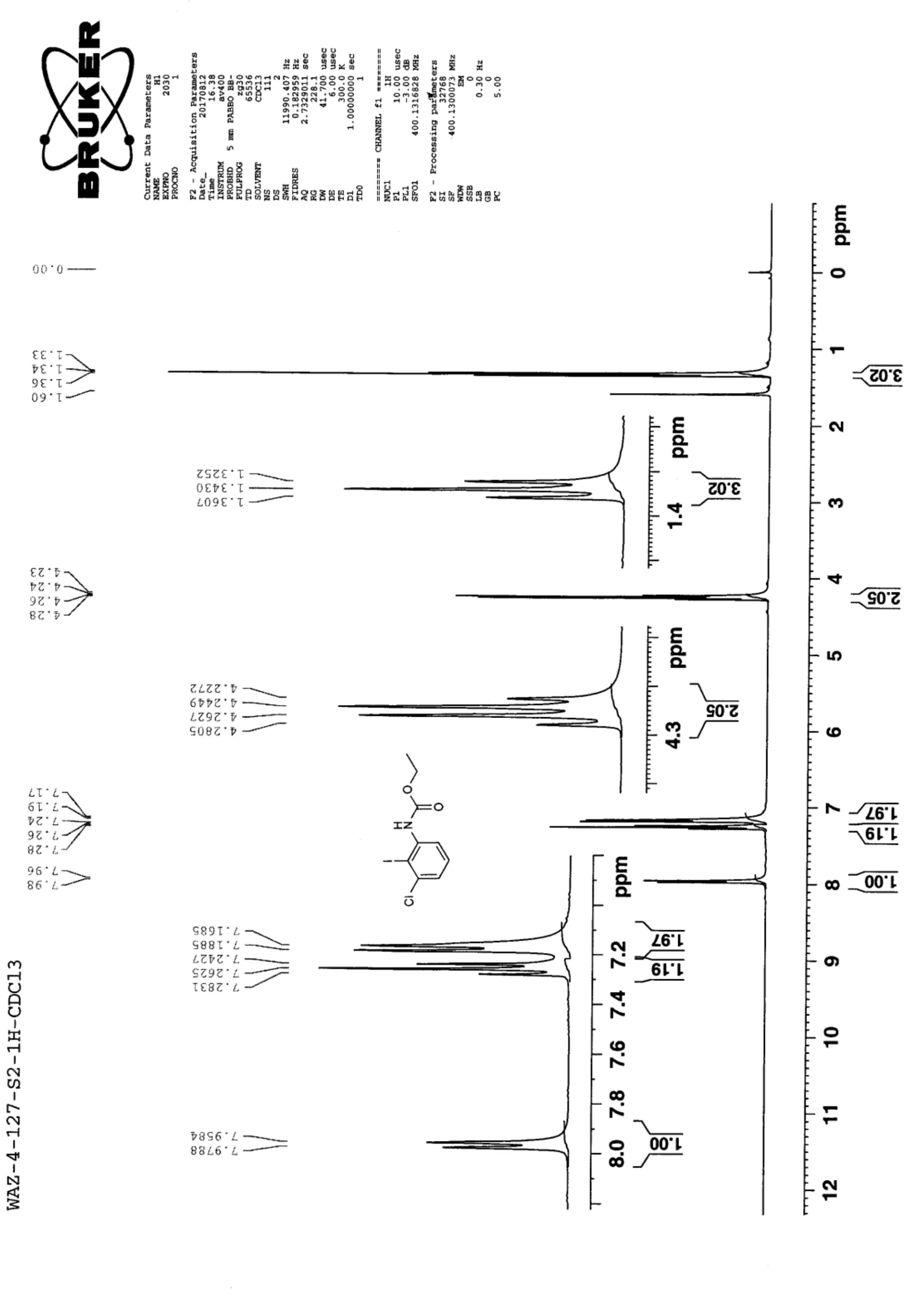
1.5.39 ^{1}H-NMR of ethyl (3-bromo-2-iodophenyl)carbamate (28_A) in $CDCl_3$ at 25 ^{o}C.



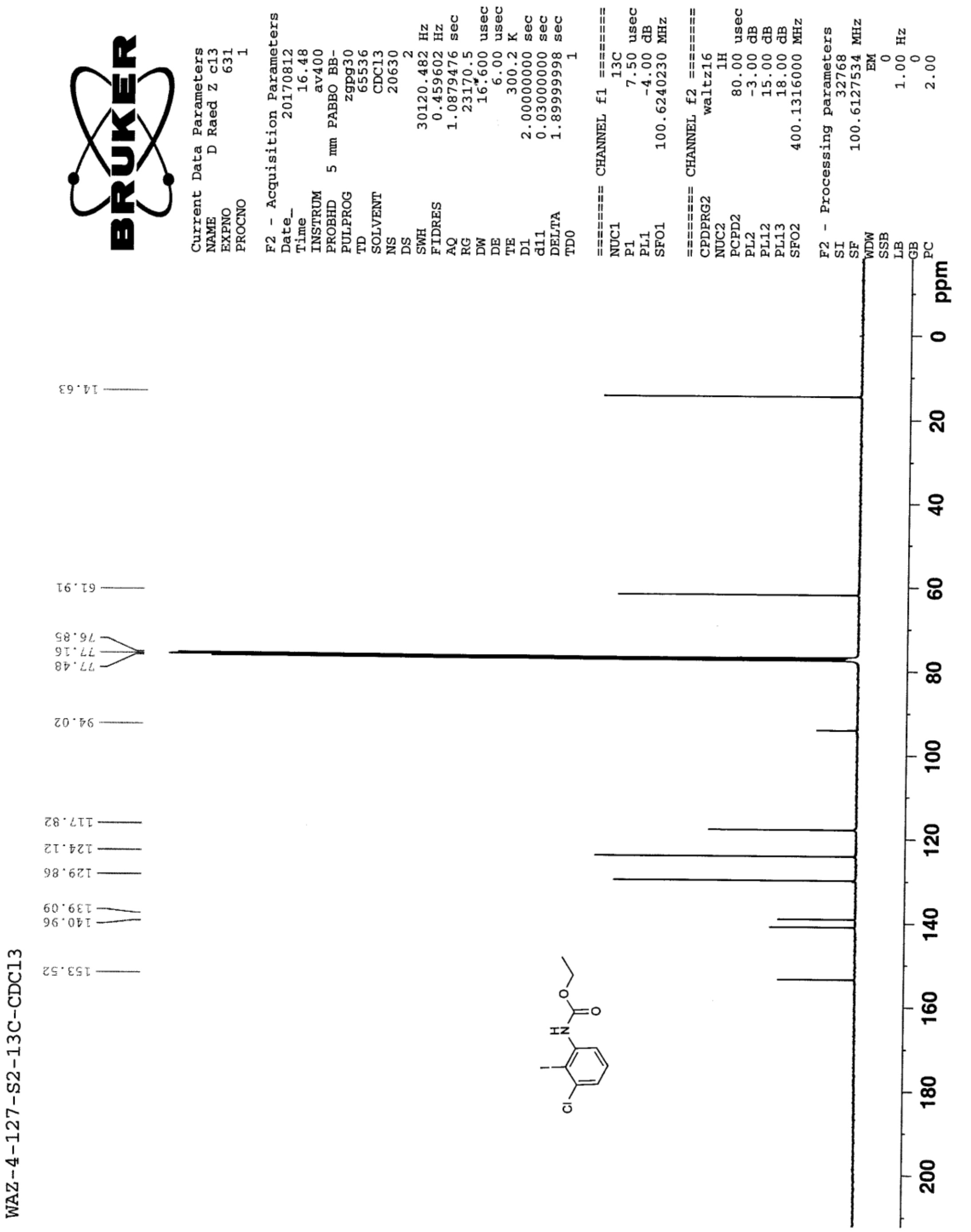
1.5.40 ^{13}C-NMR of ethyl (3-bromo-2-iodophenyl)carbamate (28_A) in $CDCl_3$ at 25 °C.



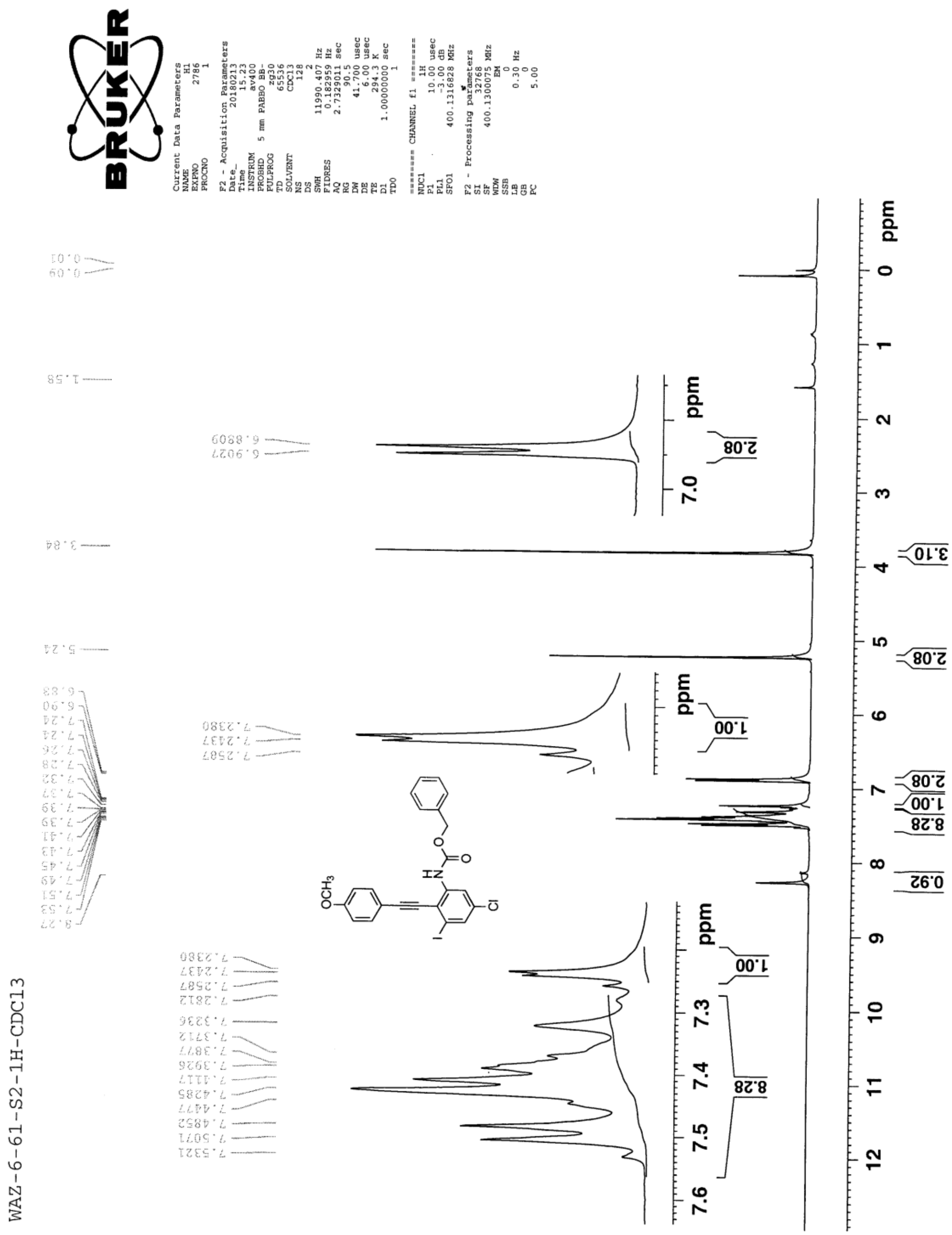
1.5.41 [1]H-NMR of ethyl (3-chloro-2-iodophenyl)carbamate (29_A) in $CDCl_3$ at 25 °C.



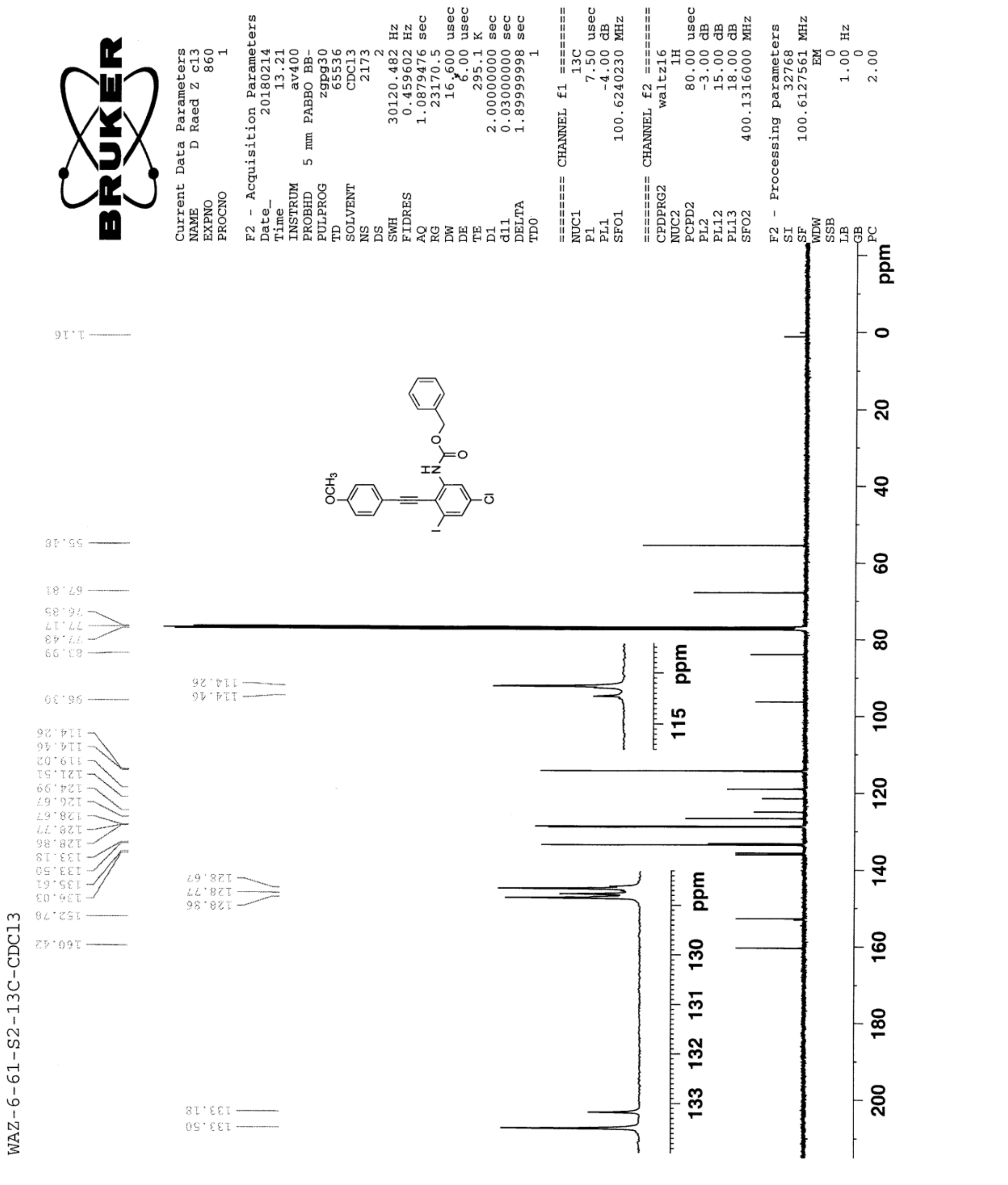
1.5.42 ^{13}C-NMR of ethyl (3-chloro-2-iodophenyl)carbamate (29$_A$) in $CDCl_3$ at 25 ^{o}C.



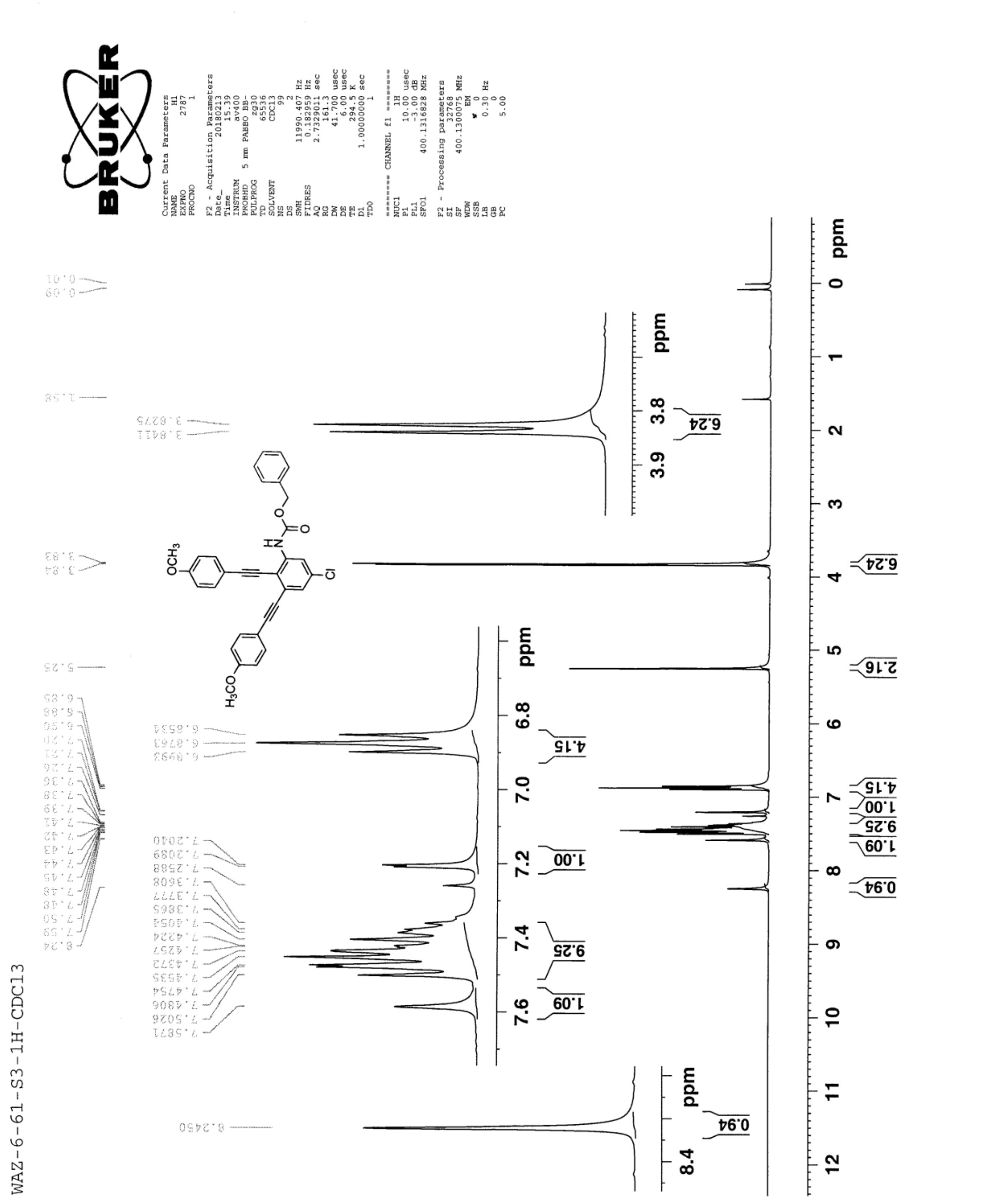
1.5.43 ¹H-NMR of benzyl (5-chloro-3-iodo-2-((4-methoxyphenyl)ethynyl)phenyl)-carbamate (34) in $CDCl_3$ at 25 °C.



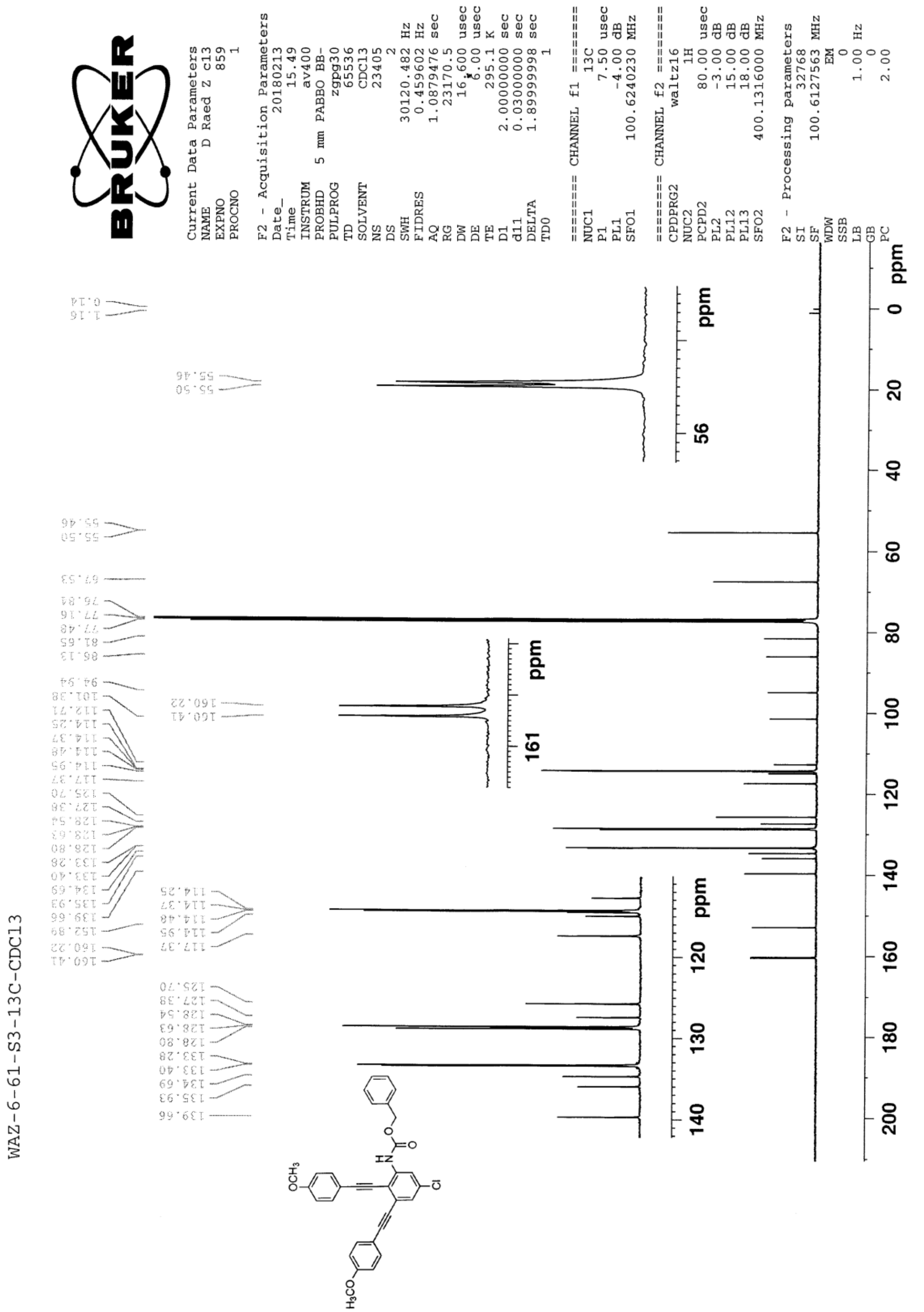
1.5.44 ^{13}C-NMR of benzyl (5-chloro-3-iodo-2-((4-methoxyphenyl)ethynyl)phenyl)-carbamate (34) in $CDCl_3$ at 25 ^{o}C.



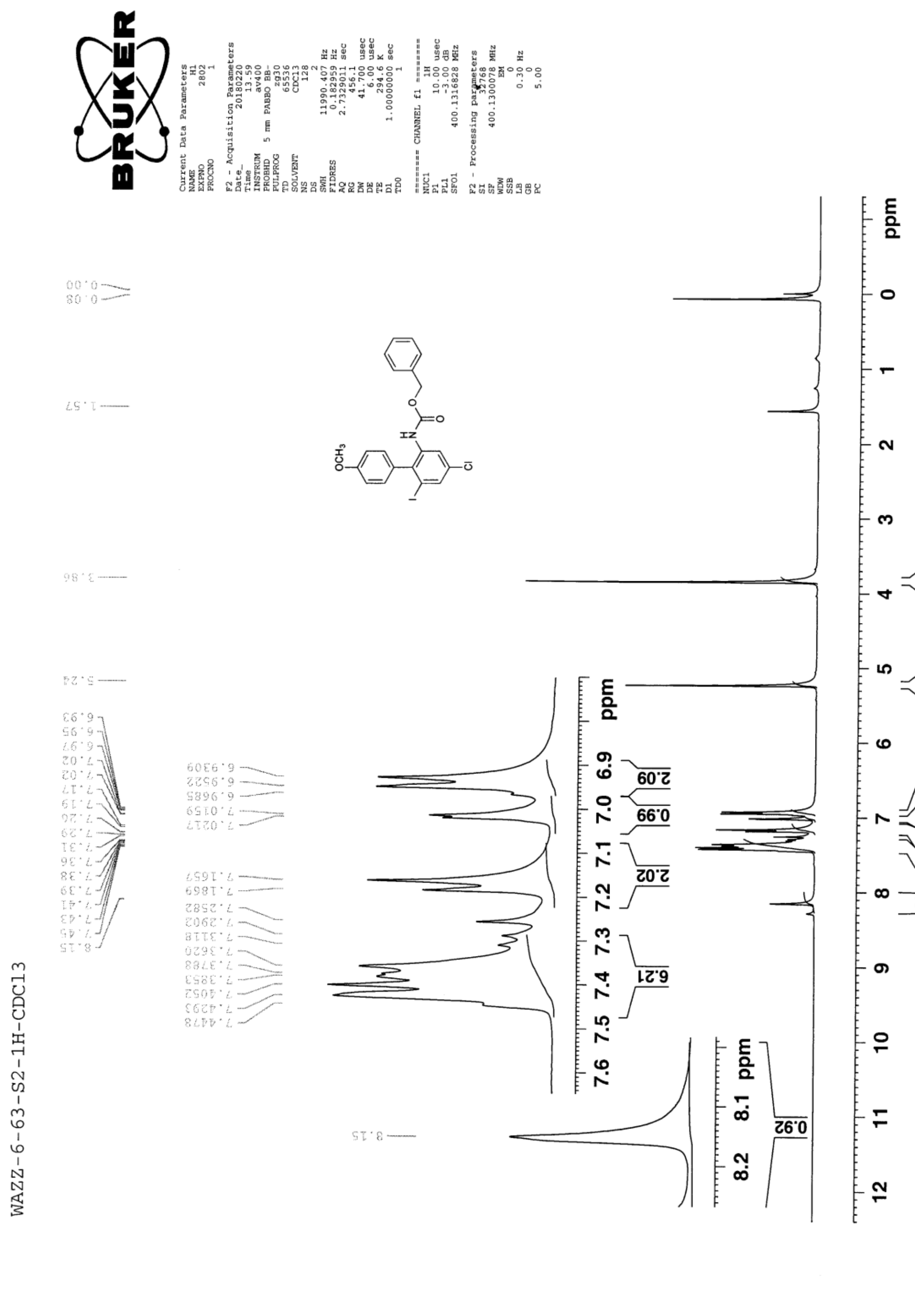
1.5.45 ^{1}H-NMR of benzyl (5-chloro-2,3-bis((4-methoxyphenyl)ethynyl)phenyl)-carbamate (bis-coupling pdt) in $CDCl_3$ at 25 ^oC.



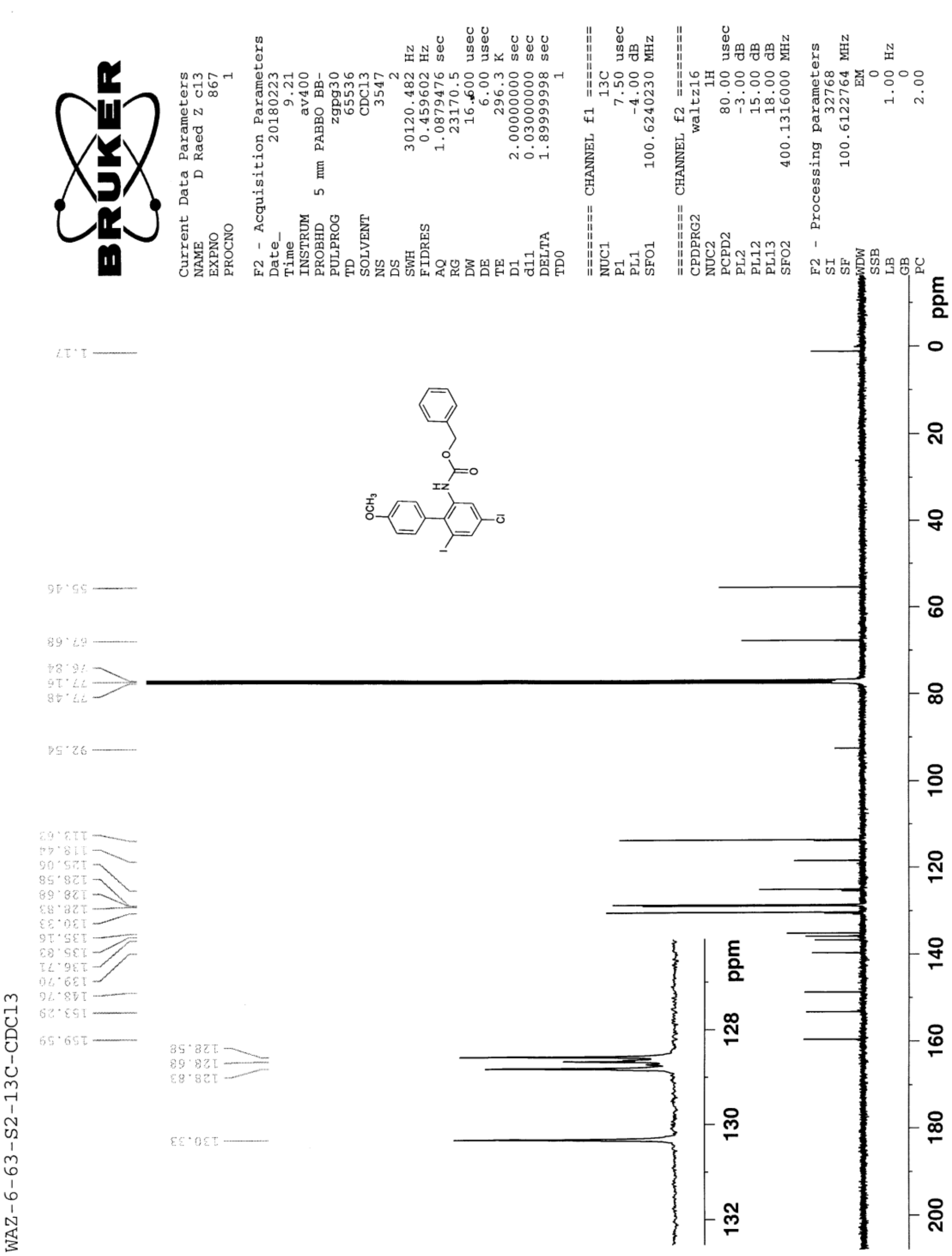
1.5.46 [13]C-NMR of benzyl (5-chloro-2,3-bis((4-methoxyphenyl)ethynyl)phenyl)-carbamate (bis-coupling pdt) in $CDCl_3$ at 25 °C.



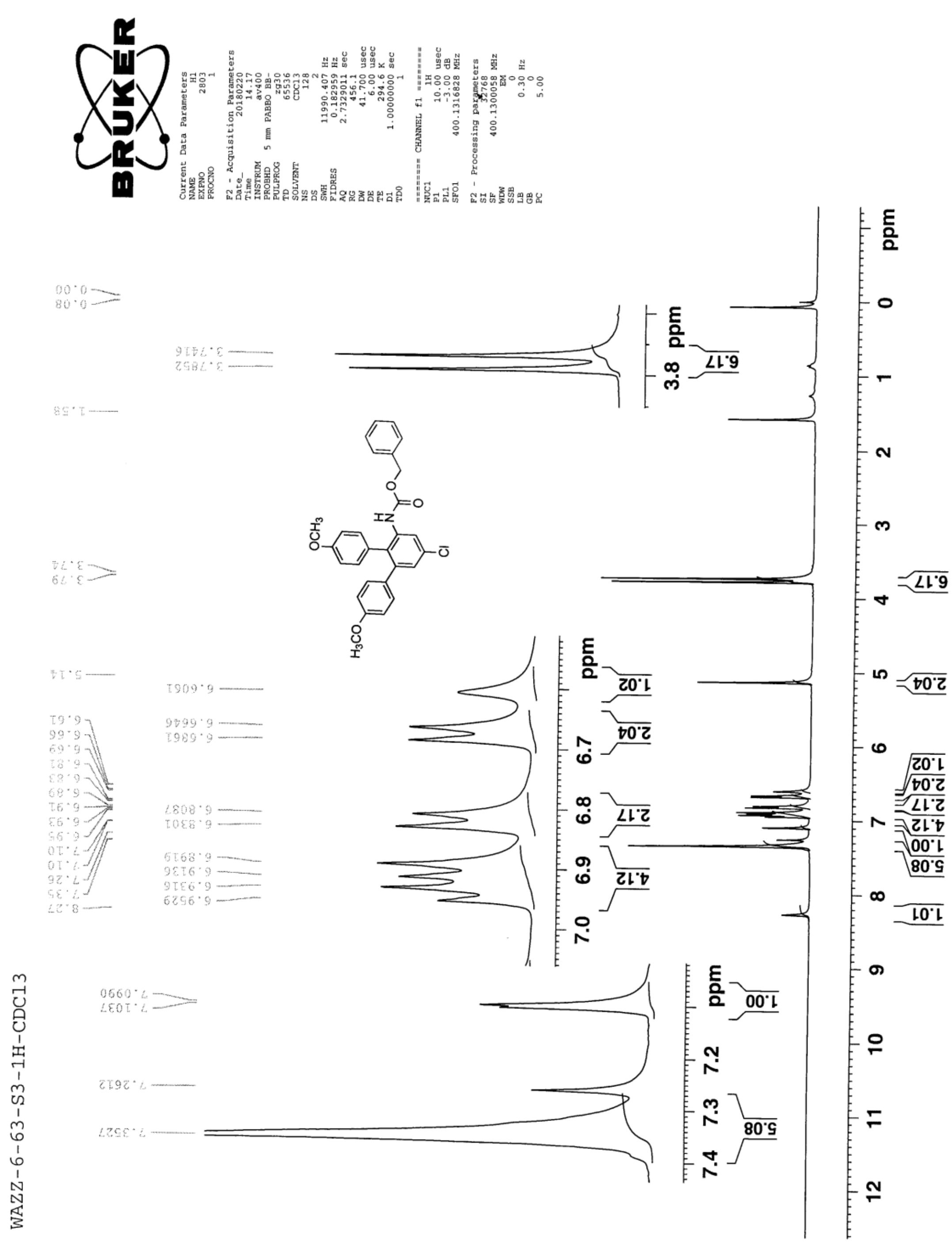
1.5.47 ^{1}H-NMR of benzyl (4-chloro-6-iodo-4'-methoxy-[1,1'-biphenyl]-2-yl)carbamate (35) in $CDCl_3$ at 25 ^{o}C.



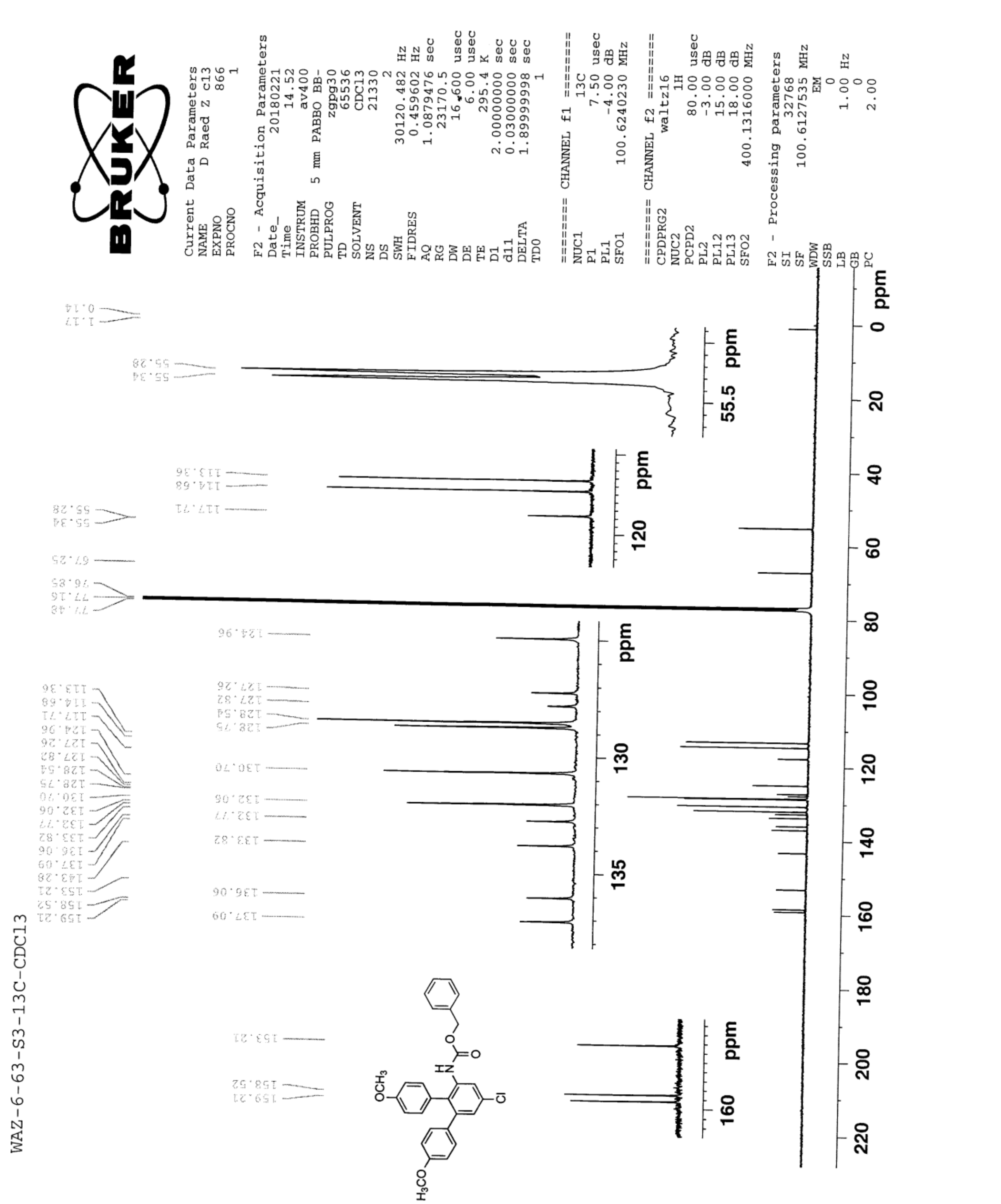
1.5.48 [13]C-NMR of benzyl (4-chloro-6-iodo-4'-methoxy-[1,1'-biphenyl]-2-yl)carbamate (35) in $CDCl_3$ at 25 °C.



1.5.49 ^{1}H-NMR of benzyl (5'-chloro-4,4''-dimethoxy-[1,1':2',1''-terphenyl]-3'-yl)carbamate (bis-coupling pdt) in $CDCl_3$ at 25 °C.



1.5.50 ^{13}C-NMR of benzyl (5'-chloro-4,4''-dimethoxy-[1,1':2',1''-terphenyl]-3'-yl)carbamate (bis-coupling pdt) in $CDCl_3$ at 25 ^{o}C.



1.6.2 X-ray data of ethyl (2,3-diiodophenyl)carbamate (**6A**)

STRUCTURE REPORT

XCL Code: JUS1711 **Date:** 20 October 2017

Compound: Ethyl (2,3-diiodophenyl)carbamate
Formula: $C_9H_9I_2NO_2$

Supervisor: R. M. Al-Zoubi, Jordan University of Science and Technology
Crystallographer: R. McDonald

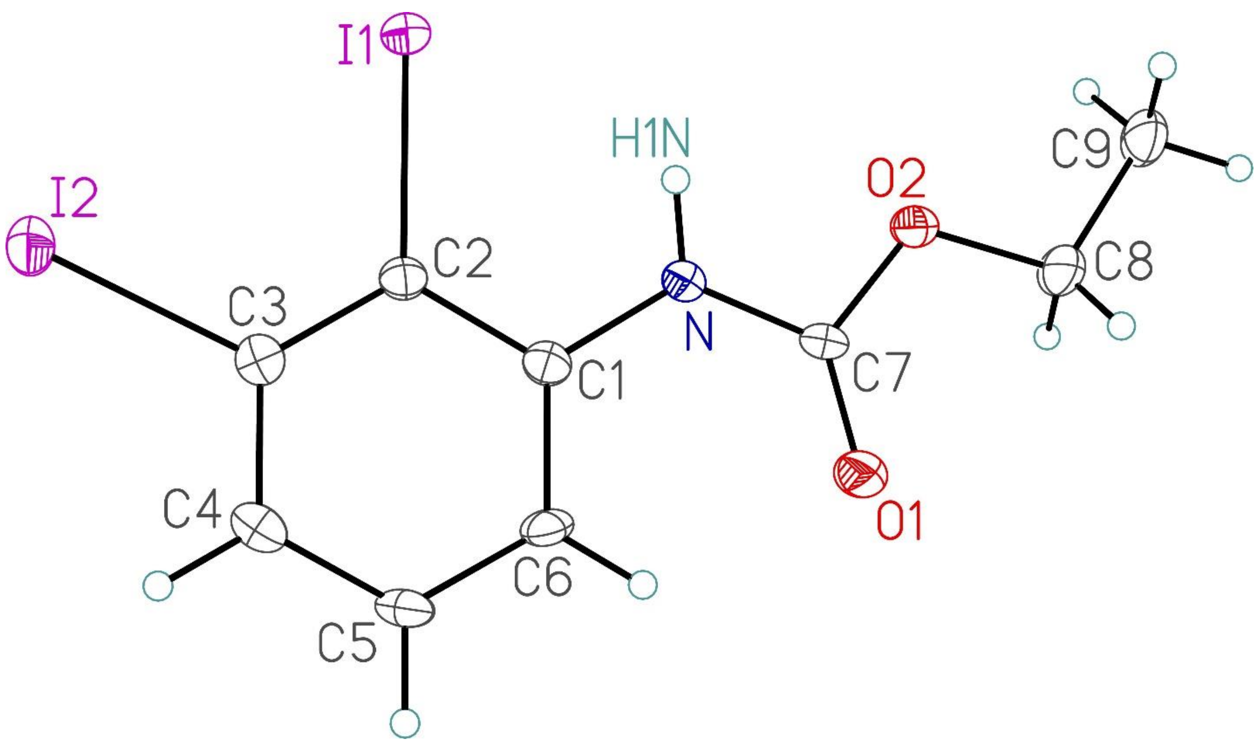
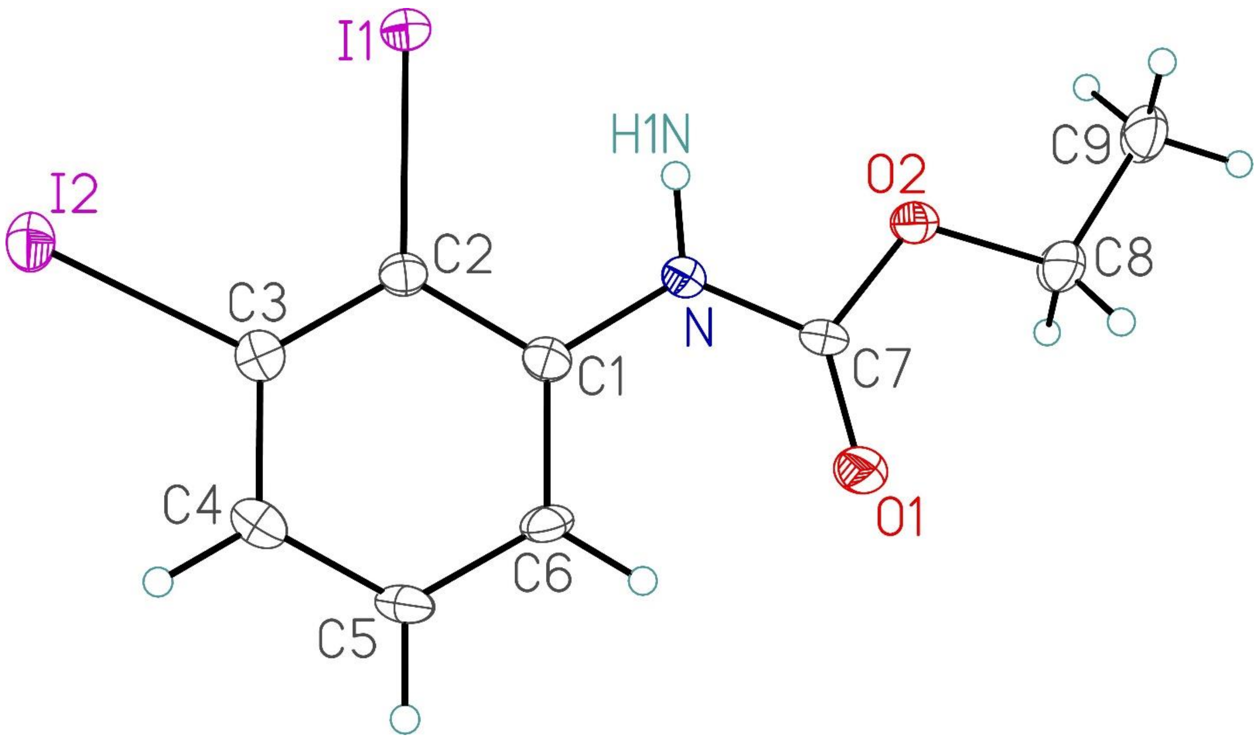


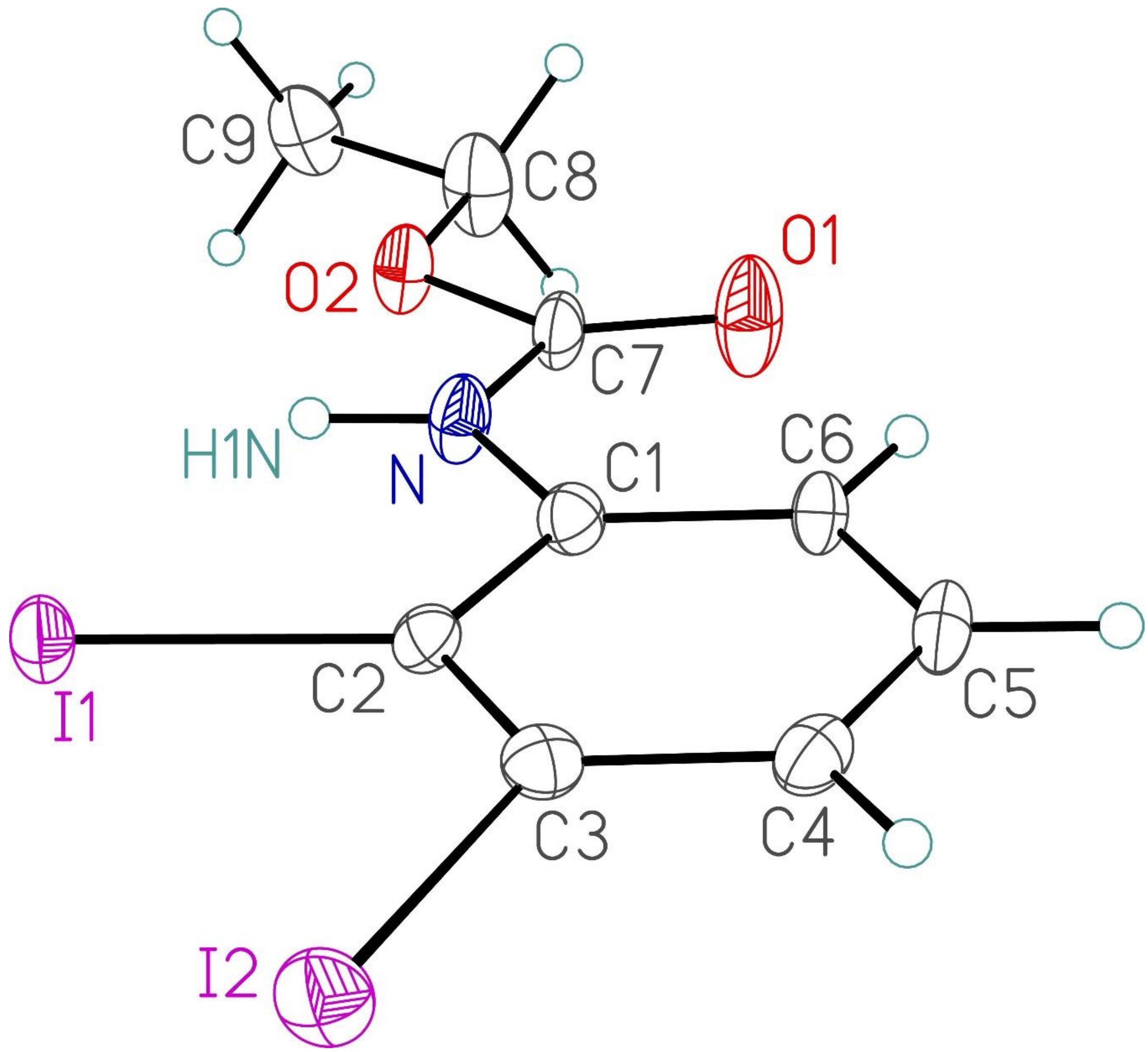
Figure Legends

Figure 1. Perspective view of the ethyl (2,3-diiodophenyl)carbamate molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 30% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

Figure 2. Alternate view of the molecule.



I1
I2
H1N
O2
C9
C2
C3
N
C8
C1
C7
C4
O1
C6
C5


C9
C8
O2
O1
C7
H1N
N
C1
C6
I1
C2
C5
C3
C4
I2

List of Tables

Table 1. Crystallographic Experimental Details

A. Crystal Data	
formula	$C_9H_9I_2NO_2$
formula weight	416.97
crystal dimensions (mm)	0.40 × 0.18 × 0.13
crystal system	monoclinic
space group	$P2_1/c$ (No. 14)
unit cell parameters[a]	
a (Å)	12.230 (3)
b (Å)	13.783 (4)
c (Å)	7.0214 (18)
β (deg)	99.948 (3)
V (Å^3)	1165.8 (5)
Z	4
ρ_{calcd} (g cm^{-3})	2.376
μ (mm^{-1})	5.371
B. Data Collection and Refinement Conditions	
diffractometer	Bruker PLATFORM/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–80
scan type	ω scans (0.3°) (15 s exposures)
data collection 2θ limit (deg)	56.54
total data collected	9415 ($-16 \le h \le 16$, $-18 \le k \le 18$, $-9 \le l \le 9$)
independent reflections	2585 (R_{int} = 0.0452)
number of observed reflections (*NO*)	2403 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	Patterson/structure expansion (*DIRDIF–2008*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d])
absorption correction method	multi-scan (*TWINABS*)
range of transmission factors	0.3742–0.2287
data/restraints/parameters	2585 / 0 / 128
goodness-of-fit (S)[e] [all data]	1.120
final R indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0385
wR_2 [all data]	0.1126
largest difference peak and hole	1.058 and –1.218 e Å^{-3}

[a]Obtained from least-squares refinement of 4513 reflections with 4.50° < 2θ < 56.44°.

(continued)

Table 1. Crystallographic Experimental Details (continued)

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. The crystal used for data collection was found to display non-merohedral twinning. Both components of the twin were indexed with the program *CELL_NOW* (Bruker AXS Inc., Madison, WI, 2004). The second twin component can be related to the first component by 180º rotation about the [1 0 0] axis in both real and reciprocal space. Integrated intensities for the reflections from the two components were written into a *SHELXL-2014* HKLF 5 reflection file with the data integration program *SAINT* (version 8.38A), using all reflection data (exactly overlapped, partially overlapped and non-overlapped). The refined value of the twin fraction (*SHELXL-2014* BASF parameter) was 0.1855(14).

[c]Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Smits, J. M. M.; Garcia-Granda, S.; Gould, R. O. (2008). The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen, The Netherlands.

[d]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0631P)^2 + 3.7884P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

Atom	*x*	*y*	*z*	U_{eq}, Å^2
I1	0.33053(4)	0.00919(3)	0.13582(7)	0.03223(14)*
I2	0.06847(4)	0.13694(4)	0.01482(8)	0.03922(16)*
O1	0.6467(5)	0.2903(4)	0.3380(12)	0.0575(19)*
O2	0.6969(4)	0.1331(3)	0.3480(9)	0.0369(12)*
N	0.5216(5)	0.1666(4)	0.2407(10)	0.0344(13)*
C1	0.4204(5)	0.2164(5)	0.1846(9)	0.0272(13)*
C2	0.3217(5)	0.1617(4)	0.1341(9)	0.0249(11)*
C3	0.2209(5)	0.2097(5)	0.0822(9)	0.0276(13)*
C4	0.2164(6)	0.3110(5)	0.0764(10)	0.0304(13)*
C5	0.3135(6)	0.3630(4)	0.1274(10)	0.0302(14)*
C6	0.4148(6)	0.3177(4)	0.1792(10)	0.0294(14)*
C7	0.6237(6)	0.2059(5)	0.3105(11)	0.0316(15)*
C8	0.8099(6)	0.1622(6)	0.4241(17)	0.050(2)*
C9	0.8813(6)	0.0755(6)	0.4564(16)	0.048(2)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$.

Table 3. Selected Interatomic Distances (Å)

Atom1	Atom2	Distance	Atom1	Atom2	Distance
I1	C2	2.105(6)	C1	C2	1.415(9)
I2	C3	2.098(7)	C1	C6	1.398(9)
O1	C7	1.205(9)	C2	C3	1.391(9)
O2	C7	1.340(8)	C3	C4	1.398(9)
O2	C8	1.450(9)	C4	C5	1.381(10)
N	C1	1.412(9)	C5	C6	1.379(10)
N	C7	1.371(9)	C8	C9	1.475(11)

Table 4. Selected Interatomic Angles (deg)

Atom1	Atom2	Atom3	Angle	Atom1	Atom2	Atom3	Angle
C7	O2	C8	115.3(5)	I2	C3	C4	116.2(5)
C1	N	C7	127.5(6)	C2	C3	C4	120.8(6)
N	C1	C2	118.6(6)	C3	C4	C5	118.9(6)
N	C1	C6	122.0(6)	C4	C5	C6	121.8(6)
C2	C1	C6	119.4(6)	C1	C6	C5	119.8(6)
I1	C2	C1	119.4(5)	O1	C7	O2	124.2(7)
I1	C2	C3	121.2(5)	O1	C7	N	127.7(6)
C1	C2	C3	119.4(6)	O2	C7	N	108.1(5)
I2	C3	C2	123.0(5)	O2	C8	C9	109.5(6)

Table 5. Torsional Angles (deg)

Atom1	Atom2	Atom3	Atom4	Angle	Atom1	Atom2	Atom3	Atom4	Angle
C8	O2	C7	O1	-0.8(12)	N	C1	C6	C5	-178.6(7)
C8	O2	C7	N	-179.8(8)	C2	C1	C6	C5	0.8(10)
C7	O2	C8	C9	-179.4(8)	I1	C2	C3	I2	3.2(7)
C7	N	C1	C2	-173.8(7)	I1	C2	C3	C4	-178.2(5)
C7	N	C1	C6	5.6(12)	C1	C2	C3	I2	-177.6(5)
C1	N	C7	O1	0.3(14)	C1	C2	C3	C4	1.0(10)
C1	N	C7	O2	179.3(7)	I2	C3	C4	C5	177.3(5)
N	C1	C2	I1	-2.0(8)	C2	C3	C4	C5	-1.4(10)
N	C1	C2	C3	178.7(6)	C3	C4	C5	C6	1.6(11)
C6	C1	C2	I1	178.6(5)	C4	C5	C6	C1	-1.3(11)
C6	C1	C2	C3	-0.7(9)					

Table 6. Anisotropic Displacement Parameters (U_{ij}, Å^2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	0.0314(2)	0.0209(2)	0.0438(3)	-0.00102(16)	0.0048(2)	-0.00065(15)
I2	0.0273(2)	0.0406(3)	0.0487(3)	0.0020(2)	0.0039(2)	-0.00115(17)
O1	0.032(3)	0.029(3)	0.104(6)	-0.002(3)	-0.008(3)	0.005(2)
O2	0.029(2)	0.024(2)	0.055(3)	-0.006(2)	-0.002(2)	0.0011(17)
N	0.024(3)	0.023(3)	0.055(4)	-0.005(3)	0.001(3)	0.003(2)
C1	0.029(3)	0.025(3)	0.027(3)	0.002(2)	0.004(2)	0.002(2)
C2	0.029(3)	0.024(3)	0.022(3)	-0.004(2)	0.005(2)	0.000(2)
C3	0.030(3)	0.031(3)	0.022(3)	0.002(2)	0.004(2)	0.001(2)
C4	0.037(3)	0.030(3)	0.025(3)	0.001(3)	0.006(3)	0.010(3)
C5	0.043(4)	0.018(3)	0.027(3)	-0.001(2)	-0.001(3)	0.005(2)
C6	0.036(3)	0.017(3)	0.034(3)	-0.007(2)	0.004(3)	-0.004(2)
C7	0.032(3)	0.017(3)	0.046(4)	-0.001(3)	0.007(3)	0.004(2)
C8	0.025(3)	0.036(4)	0.084(7)	-0.004(5)	-0.007(4)	-0.004(3)
C9	0.027(3)	0.042(4)	0.070(6)	0.008(4)	-0.001(4)	-0.003(3)

The form of the anisotropic displacement parameter is:
$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$

Table7. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H1N	0.518943	0.103033	0.229669	0.041
H4	0.147611	0.343564	0.038111	0.036
H5	0.310489	0.431916	0.126790	0.036
H6	0.480596	0.355214	0.211150	0.035
H8A	0.812049	0.197518	0.547454	0.060
H8B	0.837428	0.206220	0.331462	0.060
H9A	0.957723	0.095215	0.507901	0.057
H9B	0.854241	0.032449	0.549213	0.057
H9C	0.879559	0.041130	0.333736	0.057

1.6.2 X-ray data of ethyl (2,3-diiodo-5-methoxyphenyl)carbamate (**23A**)

STRUCTURE REPORT

XCL Code: JUS1710 **Date:** 20 October 2017

Compound: Ethyl (2,3-diiodo-5-methoxyphenyl)carbamate
Formula: $C_{10}H_{11}I_2NO_3$

Supervisor: R. M. Al-Zoubi, Jordan University of Science and Technology
Crystallographer: R. McDonald

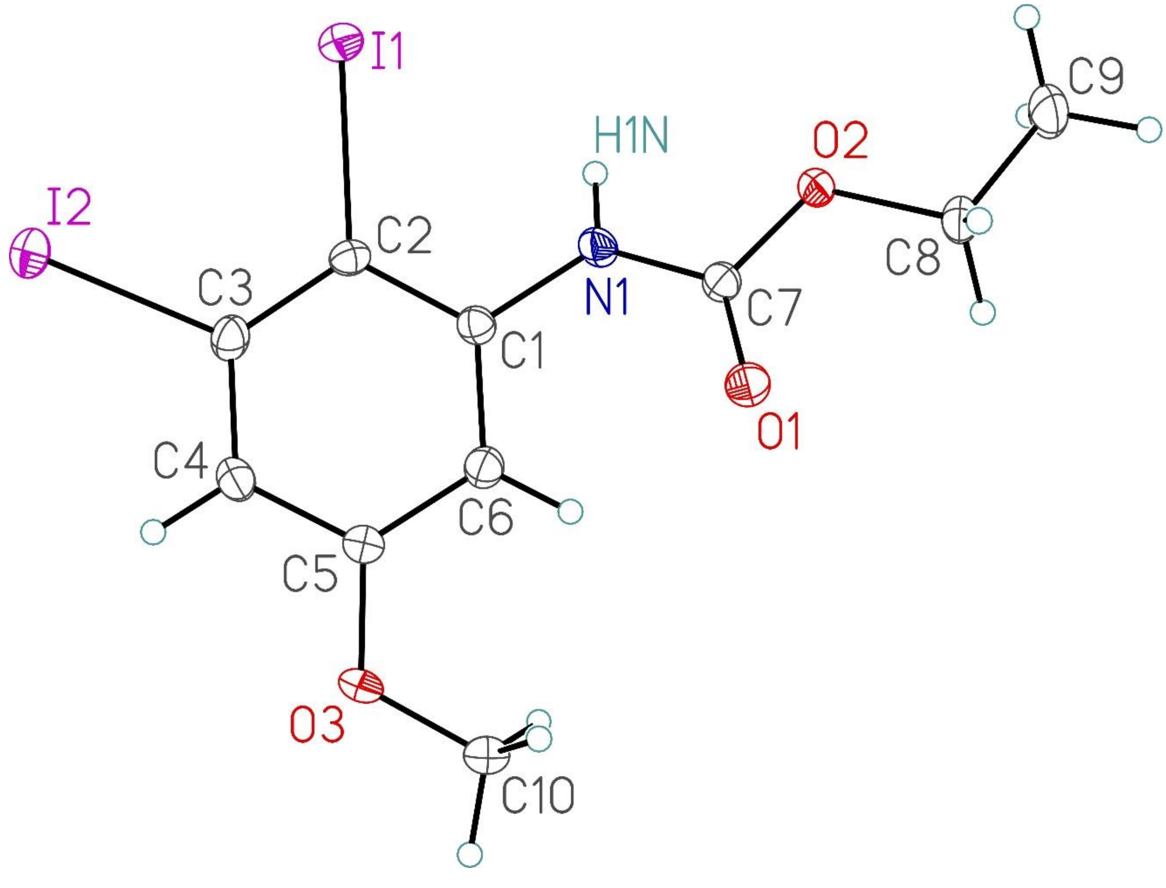


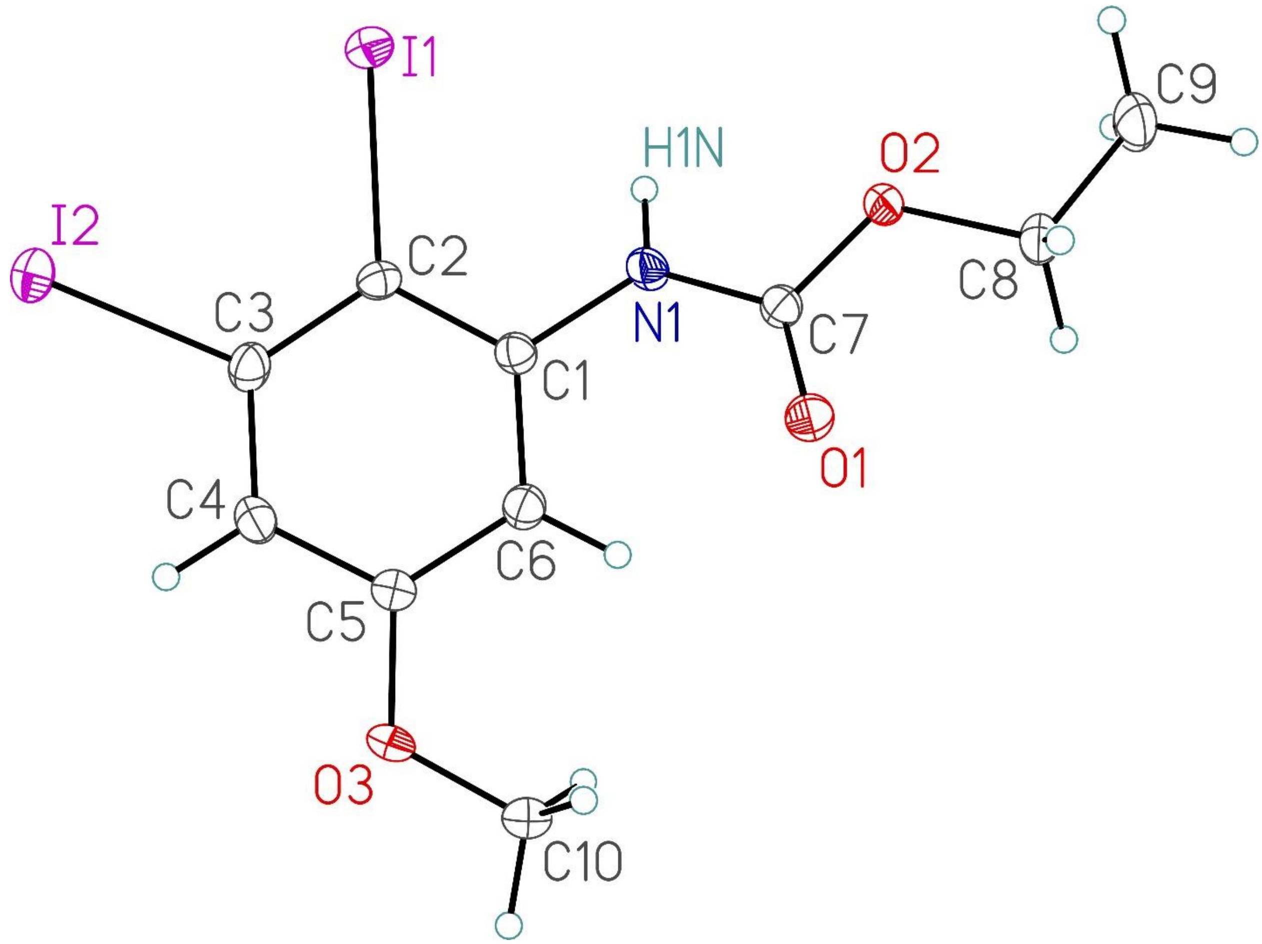
Figure Legends

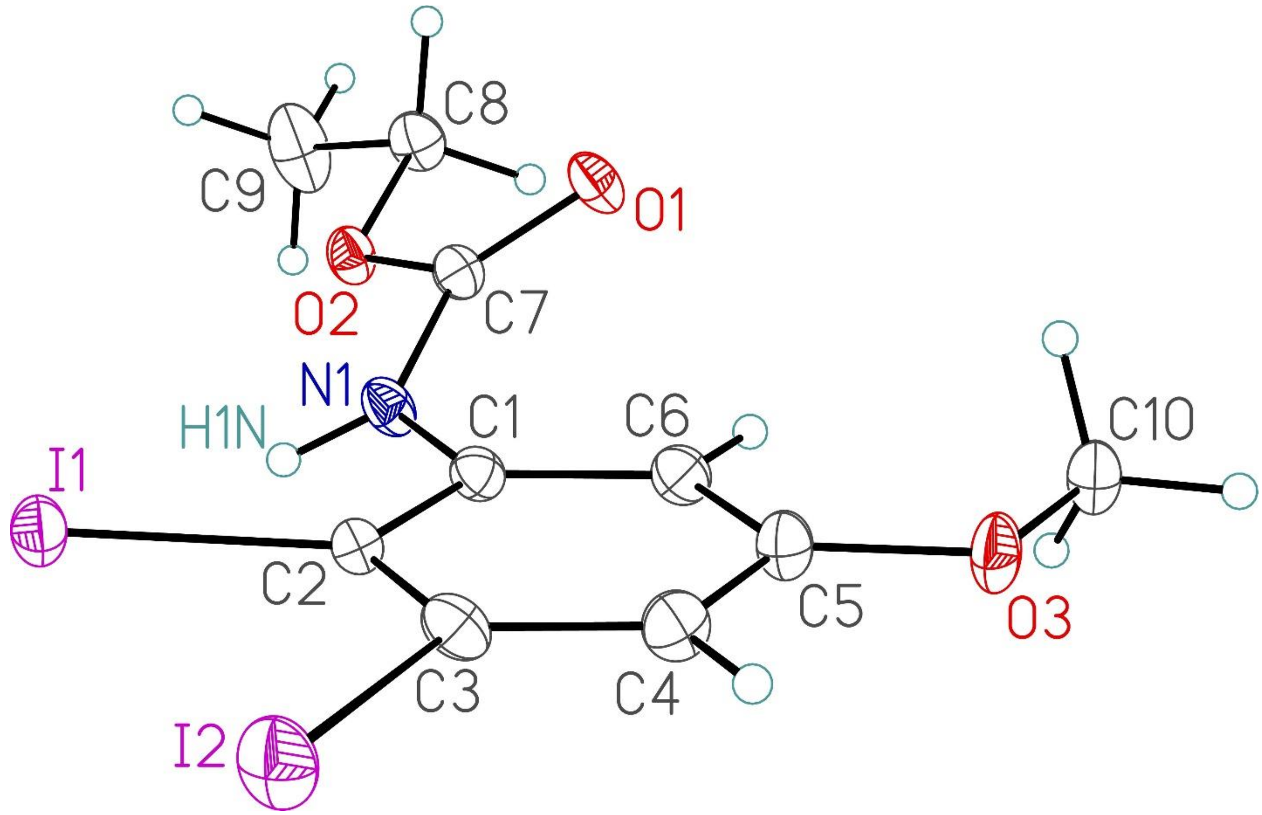
Figure 1. Perspective view of one of the two crystallographically-independent molecules of ethyl (2,3-diiodo-5-methoxyphenyl)carbamate (molecule A) showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 30% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters.

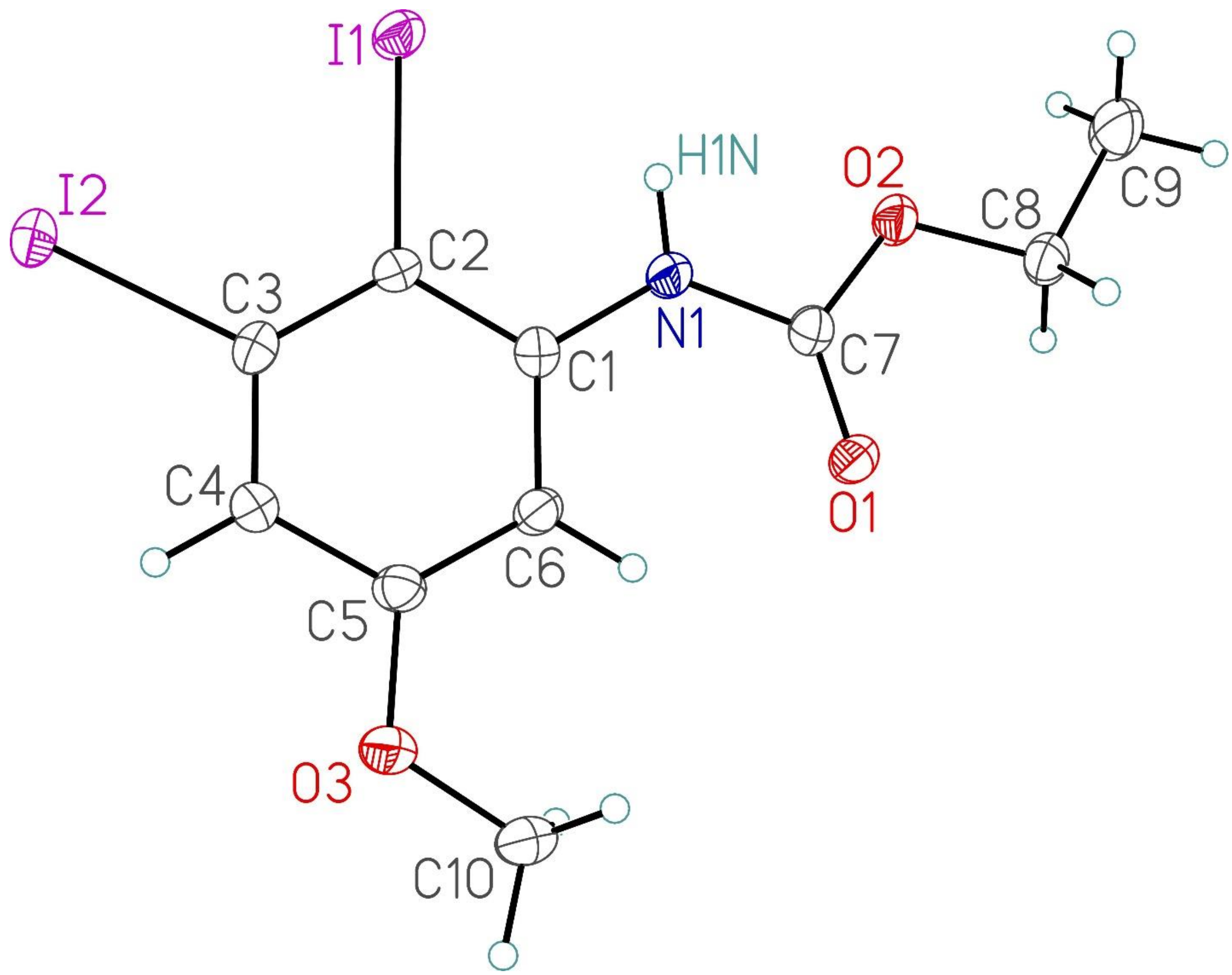
Figure 2. Alternate view of molecule A.

Figure 3. View of the second crystallographically-independent molecule of ethyl (2,3-diiodo-5-methoxyphenyl)carbamate (molecule B).

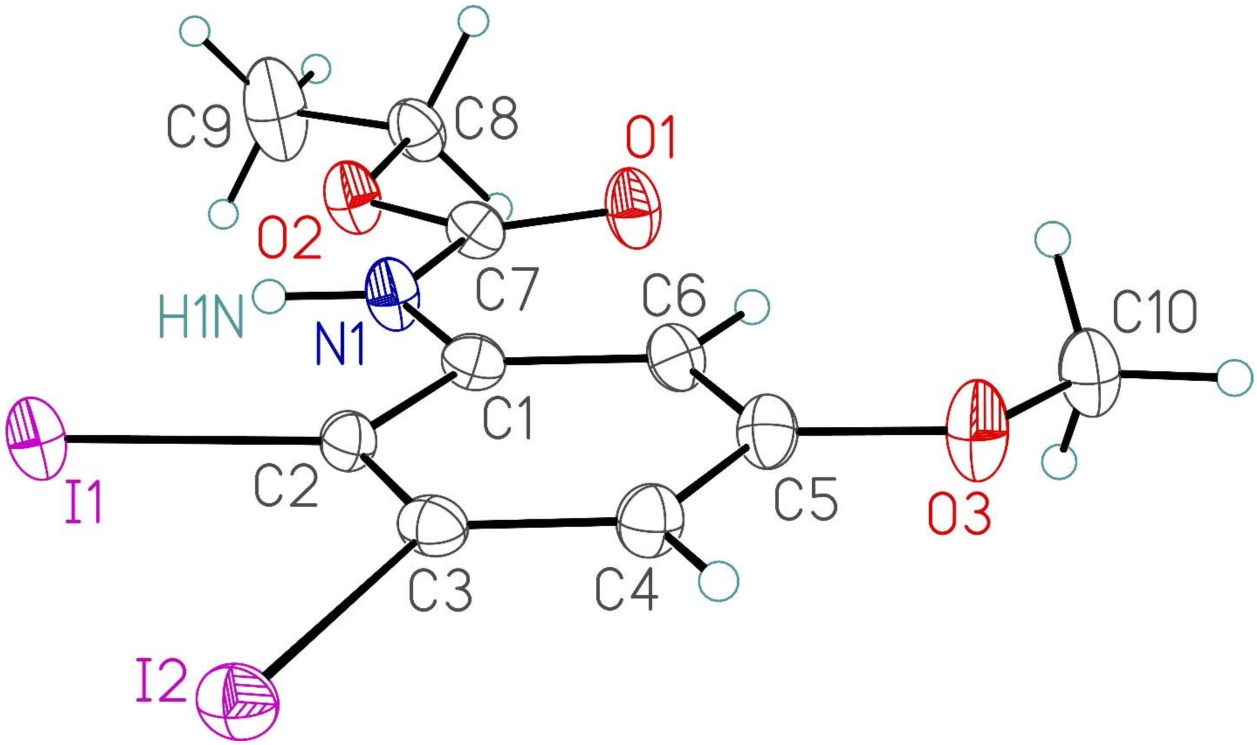
Figure 4. Alternate view of molecule B.


I1
I2
H1N
O2
C9
C2
C3
N1
C7
C8
C1
O1
C4
C6
C5
O3
C10


C8
C9
O1
O2
C7
N1
H1N
C1
C6
C10
I1
C2
C5
O3
C3
C4
I2



I1
I2
C2
C3
C1
N1
H1N
O2
C8
C9
C7
O1
C4
C6
C5
O3
C10


C9
C8
O1
O2
C7
H1N
N1
C6
C10
C1
I1
C2
C5
O3
C3
C4
I2

List of Tables

Table 1. Crystallographic Experimental Details

A. Crystal Data	
formula	$C_{10}H_{11}I_2NO_3$
formula weight	447.00
crystal dimensions (mm)	0.73 × 0.06 x 0.03
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters[a]	
a (Å)	4.7279 (3)
b (Å)	14.6599 (10)
c (Å)	19.2246 (13)
α (deg)	102.2361 (8)
β (deg)	95.5377 (8)
γ (deg)	92.5611 (9)
V (Å^3)	1293.21 (15)
Z	4
ρ_{calcd} (g cm^{-3})	2.296
μ (mm^{-1})	4.856
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (15 s exposures)
data collection 2θ limit (deg)	56.86
total data collected	11890 ($-6 \le h \le 6$, $-19 \le k \le 19$, $-25 \le l \le 25$)
independent reflections	6233 (R_{int} = 0.0181)
number of observed reflections (*NO*)	5308 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	Patterson/structure expansion (*DIRDIF–2008*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–2014*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.9049–0.2738
data/restraints/parameters	6233 / 0 / 289
goodness-of-fit (S)[e] [all data]	1.060
final R indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0272
wR_2 [all data]	0.0665
largest difference peak and hole	0.872 and –0.617 e Å^{-3}

[a]Obtained from least-squares refinement of 8313 reflections with 4.36° < 2θ < 56.18°.

(continued)

Table 1. Crystallographic Experimental Details (continued)

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Smits, J. M. M.; Garcia-Granda, S.; Gould, R. O. (2008). The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen, The Netherlands.

[d]Sheldrick, G. M. *Acta Crystallogr.* **2015**, *C71*, 3–8.

[e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0289P)^2 + 1.1161P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

[f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

(a) Molecule A

Atom	x	y	z	U_{eq}, Å^2
I1	0.53912(5)	0.12949(2)	0.57118(2)	0.03236(7)*
I2	0.44327(6)	0.35142(2)	0.69200(2)	0.04231(8)*
O1	-0.2919(5)	0.09634(17)	0.36437(13)	0.0323(5)*
O2	0.0619(5)	0.00146(16)	0.33413(12)	0.0280(5)*
O3	-0.2792(5)	0.42087(17)	0.48486(13)	0.0347(6)*
N1	0.1614(6)	0.1247(2)	0.42307(15)	0.0276(6)*
C1	0.1228(6)	0.2091(2)	0.47219(17)	0.0245(6)*
C2	0.2758(6)	0.2281(2)	0.54024(17)	0.0245(6)*
C3	0.2363(7)	0.3127(3)	0.58741(18)	0.0302(7)*
C4	0.0500(7)	0.3749(2)	0.56829(18)	0.0313(7)*
C5	-0.1009(7)	0.3545(2)	0.50035(18)	0.0298(7)*
C6	-0.0621(7)	0.2721(2)	0.45164(18)	0.0283(7)*
C7	-0.0468(6)	0.0767(2)	0.37323(17)	0.0248(6)*
C8	-0.1323(7)	-0.0504(3)	0.27465(18)	0.0334(8)*
C9	0.0226(10)	-0.1279(3)	0.2350(2)	0.0577(13)*
C10	-0.4380(8)	0.4027(3)	0.41750(19)	0.0346(8)*

(b) Molecule B

Atom	x	y	z	U_{eq}, Å^2
I1	1.10616(5)	0.39252(2)	0.25632(2)	0.03874(7)*
I2	1.35192(5)	0.15891(2)	0.23177(2)	0.03606(7)*
O1	0.3171(6)	0.39057(19)	0.02905(14)	0.0429(6)*
O2	0.3920(6)	0.51727(18)	0.12029(13)	0.0400(6)*
O3	0.7127(6)	0.0844(2)	-0.01808(15)	0.0481(7)*
N1	0.6481(6)	0.3967(2)	0.12614(16)	0.0348(7)*
C1	0.7574(7)	0.3090(2)	0.11395(18)	0.0287(7)*
C2	0.9634(7)	0.2888(2)	0.16493(17)	0.0274(7)*
C3	1.0734(7)	0.2001(3)	0.15385(18)	0.0298(7)*
C4	0.9868(7)	0.1334(3)	0.09263(19)	0.0329(7)*
C5	0.7835(7)	0.1547(3)	0.04166(19)	0.0331(7)*
C6	0.6687(7)	0.2408(3)	0.05189(18)	0.0319(7)*
C7	0.4398(7)	0.4308(3)	0.08610(18)	0.0309(7)*
C8	0.1818(9)	0.5648(3)	0.0829(2)	0.0403(9)*
C9	0.1530(13)	0.6587(3)	0.1289(3)	0.0745(17)*
C10	0.4825(9)	0.0965(3)	-0.0676(2)	0.0469(10)*

Anisotropically-refined atoms are marked with an asterisk (*). The form of the anisotropic displacement parameter is: $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23}$

$+ 2hla^{*}c^{*}U_{13} + 2hka^{*}b^{*}U_{12})]$.

Table 3. Selected Interatomic Distances (Å)

(a) Molecule A

Atom1	Atom2	Distance
I1	C2	2.092(3)
I2	C3	2.100(3)
O1	C7	1.212(4)
O2	C7	1.349(4)
O2	C8	1.448(4)
O3	C5	1.376(4)
O3	C10	1.400(4)
N1	C1	1.419(4)
N1	C7	1.361(4)
C1	C2	1.399(4)
C1	C6	1.391(4)
C2	C3	1.404(5)
C3	C4	1.377(5)
C4	C5	1.393(5)
C5	C6	1.395(5)
C8	C9	1.491(5)

(b) Molecule B

Atom1	Atom2	Distance
I1	C2	2.098(3)
I2	C3	2.102(3)
O1	C7	1.208(4)
O2	C7	1.339(4)
O2	C8	1.458(4)
O3	C5	1.374(4)
O3	C10	1.418(5)
N1	C1	1.389(4)
N1	C7	1.368(4)
C1	C2	1.400(5)
C1	C6	1.400(5)
C2	C3	1.404(5)
C3	C4	1.376(5)
C4	C5	1.399(5)
C5	C6	1.379(5)
C8	C9	1.489(6)

Table 4. Selected Interatomic Angles (deg)

(a) Molecule A

Atom1	Atom2	Atom3	Angle
C7	O2	C8	114.2(2)
C5	O3	C10	118.0(3)
C1	N1	C7	124.1(3)
N1	C1	C2	119.2(3)
N1	C1	C6	119.6(3)
C2	C1	C6	121.1(3)
I1	C2	C1	120.2(2)
I1	C2	C3	121.7(2)
C1	C2	C3	118.0(3)
I2	C3	C2	123.1(2)
I2	C3	C4	115.4(2)
C2	C3	C4	121.5(3)
C3	C4	C5	119.6(3)
O3	C5	C4	116.1(3)
O3	C5	C6	123.5(3)
C4	C5	C6	120.4(3)
C1	C6	C5	119.4(3)
O1	C7	O2	124.2(3)
O1	C7	N1	126.8(3)
O2	C7	N1	109.0(3)
O2	C8	C9	107.7(3)

(b) Molecule B

Atom1	Atom2	Atom3	Angle
C7	O2	C8	115.6(3)
C5	O3	C10	117.9(3)
C1	N1	C7	129.4(3)
N1	C1	C2	119.0(3)
N1	C1	C6	121.7(3)
C2	C1	C6	119.3(3)
I1	C2	C1	119.3(2)
I1	C2	C3	121.0(2)
C1	C2	C3	119.7(3)
I2	C3	C2	122.4(2)
I2	C3	C4	116.6(3)
C2	C3	C4	120.9(3)
C3	C4	C5	119.0(3)
O3	C5	C4	114.9(3)
O3	C5	C6	123.8(3)
C4	C5	C6	121.3(3)
C1	C6	C5	119.9(3)
O1	C7	O2	124.7(3)
O1	C7	N1	126.4(3)
O2	C7	N1	108.9(3)
O2	C8	C9	108.2(3)

Table 5. Torsional Angles (deg)

(a) Molecule A

Atom1	Atom2	Atom3	Atom4	Angle
C8	O2	C7	O1	6.0(4)
C8	O2	C7	N1	-174.3(3)
C7	O2	C8	C9	177.3(3)
C10	O3	C5	C4	-179.2(3)
C10	O3	C5	C6	2.6(5)
C7	N1	C1	C2	147.7(3)
C7	N1	C1	C6	-33.4(5)
C1	N1	C7	O1	-2.0(5)
C1	N1	C7	O2	178.3(3)
N1	C1	C2	I1	-3.7(4)
N1	C1	C2	C3	179.2(3)
C6	C1	C2	I1	177.4(2)
C6	C1	C2	C3	0.2(5)
N1	C1	C6	C5	179.5(3)
C2	C1	C6	C5	-1.6(5)
I1	C2	C3	I2	1.9(4)
I1	C2	C3	C4	-176.1(3)
C1	C2	C3	I2	179.0(2)
C1	C2	C3	C4	1.0(5)
I2	C3	C4	C5	-178.9(3)
C2	C3	C4	C5	-0.8(5)
C3	C4	C5	O3	-178.9(3)
C3	C4	C5	C6	-0.6(5)
O3	C5	C6	C1	180.0(3)
C4	C5	C6	C1	1.8(5)

(b) Molecule B

Atom1	Atom2	Atom3	Atom4	Angle
C8	O2	C7	O1	-2.1(5)
C8	O2	C7	N1	177.7(3)
C7	O2	C8	C9	179.1(4)
C10	O3	C5	C4	172.1(3)
C10	O3	C5	C6	-8.5(6)
C7	N1	C1	C2	-177.0(3)
C7	N1	C1	C6	3.5(6)
C1	N1	C7	O1	-3.6(6)
C1	N1	C7	O2	176.5(3)
N1	C1	C2	I1	-1.5(4)
N1	C1	C2	C3	179.2(3)
C6	C1	C2	I1	178.0(2)
C6	C1	C2	C3	-1.3(5)
N1	C1	C6	C5	179.7(3)
C2	C1	C6	C5	0.2(5)
I1	C2	C3	I2	6.9(4)
I1	C2	C3	C4	-177.6(3)
C1	C2	C3	I2	-173.8(2)
C1	C2	C3	C4	1.7(5)
I2	C3	C4	C5	174.8(3)
C2	C3	C4	C5	-0.9(5)
C3	C4	C5	O3	179.2(3)
C3	C4	C5	C6	-0.2(5)
O3	C5	C6	C1	-178.8(3)
C4	C5	C6	C1	0.6(5)

Table 6. Anisotropic Displacement Parameters (U_{ij}, Å^2)

(a) Molecule A

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	0.03298(12)	0.03113(13)	0.03262(12)	0.00822(9)	-0.00309(9)	0.00664(9)
I2	0.04820(15)	0.04178(15)	0.03004(13)	-0.00189(10)	-0.00965(10)	0.00530(11)
O1	0.0196(11)	0.0366(14)	0.0372(13)	0.0003(11)	-0.0001(9)	0.0063(10)
O2	0.0267(11)	0.0252(12)	0.0286(12)	-0.0005(9)	-0.0029(9)	0.0058(9)
O3	0.0392(13)	0.0256(13)	0.0378(14)	0.0026(10)	-0.0004(11)	0.0154(11)
N1	0.0204(12)	0.0283(15)	0.0310(14)	-0.0010(12)	0.0023(11)	0.0065(11)
C1	0.0220(14)	0.0253(16)	0.0258(15)	0.0040(13)	0.0037(12)	0.0025(12)
C2	0.0208(14)	0.0254(16)	0.0278(16)	0.0083(13)	0.0002(12)	0.0021(12)
C3	0.0245(15)	0.0367(19)	0.0261(16)	0.0016(14)	-0.0009(13)	0.0007(14)
C4	0.0339(17)	0.0276(18)	0.0294(17)	-0.0006(14)	0.0031(14)	0.0041(14)
C5	0.0309(17)	0.0285(18)	0.0295(17)	0.0047(14)	0.0013(13)	0.0078(14)
C6	0.0272(16)	0.0305(18)	0.0264(16)	0.0046(13)	0.0017(13)	0.0017(13)
C7	0.0236(15)	0.0278(17)	0.0227(15)	0.0035(13)	0.0042(12)	0.0044(13)
C8	0.0334(18)	0.0321(19)	0.0293(17)	-0.0022(14)	-0.0034(14)	0.0016(15)
C9	0.058(3)	0.050(3)	0.048(3)	-0.021(2)	-0.016(2)	0.022(2)
C10	0.0366(19)	0.0318(19)	0.0356(19)	0.0078(15)	0.0001(15)	0.0111(15)

(b) Molecule B

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	0.04131(14)	0.04106(15)	0.02931(12)	0.00028(10)	-0.00483(10)	0.00784(11)
I2	0.03280(12)	0.03950(14)	0.03841(13)	0.01488(11)	0.00004(9)	0.00719(10)
O1	0.0486(15)	0.0396(15)	0.0349(14)	0.0001(12)	-0.0100(12)	0.0134(12)
O2	0.0493(15)	0.0352(14)	0.0331(13)	0.0038(11)	-0.0046(11)	0.0146(12)
O3	0.0521(17)	0.0392(16)	0.0433(16)	-0.0074(12)	-0.0103(13)	0.0120(13)
N1	0.0410(16)	0.0317(16)	0.0282(15)	0.0011(12)	-0.0051(12)	0.0089(13)
C1	0.0289(16)	0.0305(18)	0.0287(17)	0.0091(14)	0.0063(13)	0.0049(14)
C2	0.0257(15)	0.0301(18)	0.0253(16)	0.0051(13)	0.0010(12)	-0.0011(13)
C3	0.0257(16)	0.0361(19)	0.0301(17)	0.0133(15)	0.0019(13)	0.0021(14)
C4	0.0337(18)	0.0293(18)	0.0345(18)	0.0049(15)	0.0014(14)	0.0049(14)
C5	0.0305(17)	0.0336(19)	0.0320(18)	0.0000(15)	0.0025(14)	0.0036(14)
C6	0.0311(17)	0.0361(19)	0.0268(16)	0.0047(14)	-0.0009(13)	0.0040(14)
C7	0.0304(17)	0.0336(19)	0.0299(17)	0.0084(15)	0.0038(14)	0.0057(14)
C8	0.052(2)	0.038(2)	0.0312(19)	0.0098(16)	-0.0006(16)	0.0100(18)
C9	0.104(4)	0.050(3)	0.058(3)	-0.004(2)	-0.026(3)	0.037(3)
C10	0.052(2)	0.046(2)	0.036(2)	-0.0021(18)	-0.0065(18)	0.0037(19)

The form of the anisotropic displacement parameter is:
$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2klb^*c^*U_{23} + 2hla^*c^*U_{13} + 2hka^*b^*U_{12})]$

Table 7. Derived Atomic Coordinates and Displacement Parameters for Hydrogen Atoms

Atom	*x*	*y*	*z*	U_{eq}, Å^2
H1NA	0.330437	0.101959	0.424953	0.033
H4A	0.024492	0.431387	0.601218	0.038
H6A	-0.161099	0.259045	0.404849	0.034
H8A	-0.196534	-0.008898	0.242665	0.040
H8B	-0.301585	-0.076151	0.292416	0.040
H9A	-0.104193	-0.164274	0.194286	0.069
H9B	0.189310	-0.101629	0.217515	0.069
H9C	0.084669	-0.168621	0.267072	0.069
H10A	-0.554847	0.455358	0.413676	0.041
H10B	-0.308535	0.394547	0.380119	0.041
H10C	-0.561748	0.345555	0.411556	0.041
H1NB	0.723868	0.436108	0.165334	0.042
H4B	1.063896	0.073778	0.085092	0.039
H6B	0.529541	0.253741	0.016853	0.038
H8C	-0.003805	0.527964	0.073510	0.048
H8D	0.244254	0.571566	0.036449	0.048
H9D	0.012327	0.691805	0.104635	0.089
H9E	0.090168	0.651255	0.174603	0.089
H9F	0.337363	0.694705	0.137670	0.089
H10D	0.454851	0.041595	-0.107371	0.056
H10E	0.308633	0.103802	-0.043541	0.056
H10F	0.524755	0.152433	-0.085998	0.056