Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Intramolecular Nucleophilic Addition of Carbanions Generated from *N*-Benzylamines to Cyclopropenes

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Supporting Information

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Syntheses of bromocyclopropanes **8a-m**

2-Bromo-1-methylcyclopropane-1-carbonyl chloride was synthesized according to our previously published procedure and had physical and spectral properties identical to those earlier reported.

N,N-Dibenzyl-2-bromo-1-methylcyclopropane-1-carboxamide (**8a**), Typical procedure I: 2-Bromo-1-methylcyclopropane-1-carbonyl chloride (494 mg, 2.50 mmol) in anhydrous DCM (7 mL) was added dropwise to a solution of dibenzyl-amine (493 mg, 2.50 mmol) and triethylamine (706 μL, 512 mg, 5.07 mmol) in anhydrous DCM (4 mL) stirred in a flame dried Schlenk flask under a nitrogen atmosphere. The reaction was stirred overnight at rt. The solvent was then evaporated in vacuum, and the residue was trituated with THF (7 mL). The precipitate was removed by suction filtration and the filter cake was rinsed with THF (2 x 4 mL). Then the precipitate was dissolved in H_2O (20 mL) and extracted with EtOAc (2 x 4 mL). The combined organic phases were washed with brine (20 mL, dried with $MgSO_4$, combined with the THF filtrate, and concentrated. The product was isolated by column chromatography eluting with a hexanes/EtOAc mixture (6:1) as a yellow oil (R_f 0.29). Yield 553.4 mg (1.54 mmol, 61%). ^{1}H NMR (500 MHz, $CDCl_3$) δ [7.51 – 7.48 (m), 7.42 – 7.27 (m), 7.25 – 7.06 (m), ∑10H], [5.25 (d, *J* = 14.5 Hz), 4.98 (d, *J* = 16.6 Hz), 4.73 – 7.46 (m), 4.37 (d, *J* = 16.7 Hz), 3.91 (d, *J* = 14.5 Hz), ∑4H], [3.24 (dd, *J* = 8.2, 4.9 Hz), 3.00 (dd, *J* = 7.5, 4.7 Hz), ∑1H], [1.81 (dd, *J* = 8.2, 6.7 Hz), 1.76 – 1.73 (m), ∑1H], [1.53 (s), 1.40 (s), ∑3H], [1.25 (t, *J* = 7.1 Hz), 0.95 (dd, *J* = 6.7, 4.9 Hz), ∑1H]; ^{13}C NMR (126 MHz, $CDCl_3$) δ (172.5, 171.3, 1C), (136.7, 136.1, 2C), (129.1, 128.9, 4C), (128.3, 127.1, 4C), (127.6, 127.4, 2C), (49.8, 47.5, 1C), [49.6 (br), 47.1 (br), 1C], 28.0 (1C), (27.3, 26.1, 1C), (22.7, 21.9, 1C), (22.1, 19.8, 1C); FT IR (NaCl, cm^{-1}): 3062, 3030, 2929, 1643, 1495, 1453, 1421, 1325, 1299, 1205, 1185, 1079, 1029, 1013, 749, 698; HRMS (TOF ES): found 358.0810, calculated for $C_{19}H_{21}BrNO$ (M + H) 358.0807 (0.8 ppm); EA found C 63.83, 63.58, H 5.43, 5.93, N 4.14, 3.90, calculated for $C_{19}H_{20}BrNO$: C 63.70, H 5.63; N 3.91.

2-Bromo-N-butyl-N-(4-(tert-butyl)benzyl)-1-methylcyclopropane-1-carbox-amide (**8b**). This compound was synthesized according to Typical procedure I employing 2-bromo-1-methylcyclopropane-1-carbonyl chloride (545 mg, 2.76 mmol), *N*-(4-(*tert*-butyl)benzyl)butan-1-amine (605 mg, 2.76 mmol), and triethylamine (1.40 mL, 1.02 g, 10.5 mmol). The reaction mixture was stirred at room temperature overnight. After standard aqueous workup and extraction, the material was filtered through a silica plug to give a pale-yellow glass, yield 882 mg (2.32 mmol, 84%). This material had purity by GC c.a. 98% and could be used in the cyclization step as is without additional purification. If desired, diastereomeric bromocyclopropanes can be additionaly purified and separated by preparative column chromatography on Silica gel eluting with a CH_2Cl_2/EtOAc mixture (40:1). Individual isomers were isolated as colorless crystals (*trans*-**8b**) and colorless glass

(*cis*-**8b**), respectively. NMR spectra of both diastereomers showed signals of two rotamers. Analysis of signals in proton spectra of *cis*-**8b** is complicated by severe broadening of the lines, which can be partially resolved by measuring ^{1}H NMR spectrum in benzene-d_6 at 75 ^{o}C. ***trans*-8b**: mp 93.3-93.8 ^{o}C; R_f 0.37 (CH_2Cl_2/EtOAc 40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ [7.38 (d, *J* = 8.2 Hz), 7.30 (d, *J* = 8.2 Hz), ∑2H], [7.21 (d, *J* = 8.2 Hz), 7.17 (d, *J* = 8.1 Hz), 7.09 (d, *J* = 8.2 Hz), ∑2H], [5.04 (d, *J* = 16.8 Hz), 4.81 (d, *J* = 15.0 Hz), 4.63 (br.m), 4.46 (d, *J* = 16.3 Hz) , ∑2H], [3.80 (ddd, *J* = 14.2, 10.8, 5.6 Hz), 3.53 (ddd, *J* = 13.9 11.5, 4.9 Hz), 3.25 (ddd, *J* = 14.1, 11.4, 4.9 Hz), 3.04 – 2.95 (m), 2.75 (ddd, *J* = 13.3, 10.0, 5.4 Hz) , ∑3H], [1.80 – 1.70 (m), 1.71 – 1.64 (m), 1.63 – 1.52 (m), 1.52 – 1.43 (m), 1.26 – 1.16 (m), ∑6H], [1.42 (s), 1.32 (s), ∑3H], [1.32 (s), 1.29 (s), ∑9H], [0.92 (t, *J* = 7.4 Hz), 0.86 (t, *J* = 7.3 Hz), ∑3H]; ^{13}C NMR (126 MHz, $CDCl_3$) δ (170.7, 170.6, 1C), (150.5, 150.1, 1C), (134.2, 133.8, 1C), (127.8, 126.5, 2C), (125.8, 125.3, 2C), (50.5, 47.3, 1C), (46.7, 45.4, 1C), (34.6, 34.6, 1C), 31.5 (3C), (30.5, 28.7, 1C), (28.2, 28.1, 1C), (26.3, 26.2, 1C), (22.7, 22.6, 1C), 22.1, 20.4, (14.0, 14.0 1C). ***cis*-8b**: R_f 0.27 (CH_2Cl_2/EtOAc 40:1); ^{1}H NMR (500 MHz, C_6D_6 at 75 ^{o}C) δ 7.26 (d, *J* = 8.3 Hz, 2H), 7.07 (br. s, 2H), 4.51 (br. s, 1H), 4.44 (d, *J* = 15.2 Hz, 1H), 3.29 – 3.04 (br. m, 3H), 1.70 (dd, *J* = 8.1, 6.5 Hz, 1H), [1.36 (s), 1.22 (s), ∑9H], 1.40 – 1.28 (m, 4H), 1.23 (br. s, 1H), 1.13 – 1.01 (m, 2H), 0.76 (t, *J* = 7.4 Hz, 3H), 0.65 (dd, *J* = 6.6, 4.9 Hz, 1H). ^{1}H NMR (500 MHz, $CDCl_3$ at RT) δ 7.38 – 7.30 (br. m, 2H), [7.28 – 7.25 (br.m), 7.13 – 7.05 (br. m), ∑2H], [4.65 (br.d, *J* = 16.3 Hz), 4.43 (br. d, *J* = 15.2 Hz), ∑2H], 3.35 – 3.14 (br.m, 3H), [1.76 (br.m), 1.68 (br.m), 1.57 (br.m), 1.50 (br.s), ∑6H], 1.32 (br.s, 11H), 1.00 – 0.78 (br.m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$ at RT) δ 172.1, (150.7, 150.3, 1C), (134.2, 133. 5, 1C), (127.5, 126.5, 2C), (125.9, 125.7, 2C), (50.3, 46.7, 1C), (46.3, 44.6, 1C), 34.6, 31.5 (3C), (30.2, 29.0, 1C), (27.8, 27.7, 1C), (26.3, 26.2, 1C), 21.9, (20.3, 20.2, 1C), (20.0, 19.9, 1C), 14.0. HRMS (TOF ES): found 402.1416, calculated for $C_{20}H_{30}BrNONa$ (M + Na) 402.1408 (2.0 ppm). EA found C 63.05, 63.27, H 7.78, 8.03, N 3.87, 3.59, calculated for $C_{20}H_{30}BrNO$: C 63.15, H 7.95; N 3.68.

2-Bromo-N-butyl-N-(4-methoxybenzyl)-1-methylcyclopropane-1-carboxamide (**8c**). This compound was synthesized according to Typical procedure I employing 2-bromo-1-methylcyclopropane-1-carbonyl chloride (584 mg, 2.96 mmol), *N*-(4-methoxybenzyl)butan-1-amine (572 mg, 2.96 mmol), and triethylamine (1.40 mL, 1.02 g, 10.5 mmol). The reaction mixture was stirred at room temperature overnight. After standard aqueous workup and extraction, the material was filtered through a silica plug to give a pale orange oil, yield 912 mg (2.58 mmol, 87%). This material had purity by GC c.a. 98% and could be used in the cyclization step as is without additional purification. If desired, it can be additionally purified by preparative column chromatography on Silica gel eluting with a CH_2Cl_2/EtOAc mixture (20:1) to isolated inseparable mixture of diastereomeric bromo-cyclopropanes **8c** as colorless oil, R_f 0.45 (CH_2Cl_2/EtOAc 20:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ [7.22 (d, *J* = 8.6 Hz), 7.17 (d, *J* = 8.5 Hz), 7.09 (br.m), ∑2H], [6.91 (d, *J* = 8.6 Hz), 6.95 – 6.79 (br.m), 6.82 (d, *J* = 8.6 Hz), ∑2H], [5.00 (d, *J* = 16.5 Hz), 4.86 (d, *J* = 14.7 Hz), 4.61 (br.m), 4.44 (d, *J* = 16.6 Hz), 4.40 (br.m), 4.34 (d, *J* = 14.8 Hz), ∑2H], [3.81 (s), 8.80 (br.s), 3.78 (s), ∑3H], [3.78 – 3.69 (m), 3.51 (ddd, *J* = 14.1, 11.6, 4.9 Hz), 3.27 (br.m), 3.22 – 3.15 (m), 3.00 (ddd, *J* = 7.3, 4.7, 2.5 Hz), 2.76 (ddd, *J* = 13.4,

10.0, 5.4 Hz), ∑2H], [1.80 – 1.70 (m), 1.70 – 1.64 (m), 1.62 – 1.49 (m), 1.46 – 1.41 (m), 1.33 – 1.15 (m), ∑7H], [1.48 (s), 1.40 (s), 1.33 (s), ∑3H], [0.93 (t, *J* = 7.4 Hz), 0.86 (t, *J* = 7.4 Hz), ∑3H]; ^{13}C NMR (126 MHz, $CDCl_3$) δ (172.0, 170.7, 1C), (159.1, 158.9, 1C), (129.7, 129.3, 128.1, 2C), (129.5, 128.7, 128.0, 1C), (114.4, 114.3, 114.1, 113.8, 2C), (55.4, 55.4, 55.3, 1C), (50.3, 50.1, 46.9, 46.5, 1C), (46.4, 46.1, 45.2, 44.5, 1C), (30.4, 30.2, 29.0, 28.7, 1C), (28.2, 28.2, 1C), (27.8, 27.6, 26.3, 26.2, 1C), (22.7, 22.6, 21.8, 1C), (22.0, 20.0, 19.8, 1C), (20.4, 20.3, 1C), (14.0, 14.0, 14.0, 1C); HRMS (TOF ES): found 376.0900, calculated for $C_{17}H_{24}BrNO_2Na$ (M + Na) 376.0888 (3.2 ppm). EA found C 57.83, 57.57, H 6.58, 6.96, N 3.94, 4.01, calculated for $C_{17}H_{24}BrNO_2$: C 57.63, H 6.83; N 3.95.

2-Bromo-N-butyl-1-methyl-N-(4-(trifluoromethyl)benzyl)cyclopropane-1-carboxamide (**8d**). This compound was synthesized according to Typical procedure I employing 2-bromo-1-methylcyclopropane-1-carbonyl chloride (1.00 g, 5.06 mmol), *N*-(4-(trifluoromethyl)benzyl)butan-1-amine (1.17 g, 5.06 mmol), and triethylamine (1.39 mL, 1.01 g, 10.0 mmol). The reaction mixture was stirred at room temperature overnight. The product was isolated by column chromatography eluting with a hexanes/EtOAc mixture (3:1) as a colorless oil (R_f 0.34). Yield: 1.73 g (4.40 mmol, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ [7.64 (d, *J* = 7.9 Hz), 7.54 (d, *J* = 7.9 Hz), ∑2H], 7.39 (m, 2H), [5.11 (d, *J* = 17.3 Hz), 4.90 (d, *J* = 15.3 Hz), 4.56 (d, *J* = 17.4 Hz), 4.47 (d, *J* = 15.3 Hz), ∑2H], [3.83 (ddd, *J* = 13.7, 10.2, 5.6 Hz), 3.60 (ddd, *J* = 14.3, 11.7, 4.9 Hz), 3.22 (ddd, *J* = 14.3, 11.5, 4.8 Hz), 3.02 (ddd, *J* = 15.6, 7.5, 4.7 Hz), 2.70 (ddd, *J* = 13.6, 10.1, 5.2 Hz), ∑3H], [1.76 – 1.70 (m), 1.67 (t, *J* = 5.8 Hz), 1.63 – 1.44 (m), 1.42 (s), 1.36 – 1.28 (m), 1.26 (s), 1.25 – 1.17 (m), ∑9H], [0.93 (t, *J* = 7.3 Hz), 0.86 (t, *J* = 7.3 Hz), ∑3H]; ^{13}C NMR (126 MHz, $CDCl_3$) δ (171.0, 170.8, 1C), (141.7, 141.3, 1C), [129.6 (q, $^2J_{CF}$ = 32.6 Hz), 129.4 (q, $^2J_{CF}$ = 32.4 Hz), 1C], (128.3, 127.1, 2C), [126.0 (q, $^3J_{CF}$ = 3.8 Hz), 125.4 (q, $^3J_{CF}$ = 3.8 Hz), 2C], [125.3 (q, $^1J_{CF}$ = 272.5 Hz), 124.2 (q, $^1J_{CF}$ = 271.4 Hz), 1C], (50.5, 47.7, 1C), (47.3, 45.7, 1C), (30.6, 28.6, 1C), (28.11, 28.05, 1C), (26.2, 26.0, 1C), (22.7, 22.6, 1C), (21.9, 21.8, 1C), 20.4 (1C), (13.98, 13.95, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.45, -62.51; FT IR (NaCl, cm^{-1}): 2962, 2935, 2874, 1644, 1416, 1326, 1164, 1125, 1067, 1018, 824; HRMS (TOF ES): found 414.0636, calculated for $C_{17}H_{21}BrF_3NONa$ $(M + Na)^+$ 414.0656 (4.8 ppm); EA found C 52.25, 51.88, H 5.64, 5.28, N 3.28, 3.70, calculated for $C_{17}H_{21}BrF_3NO$: C 52.05, H 5.40, N 3.57.

2-Bromo-N,1-dimethyl-N-(4-nitrobenzyl)cyclopropane-1-carboxamide (**8e**). This compound was synthesized according to Typical procedure I employing 2-bromo-1-methylcyclopropane-1-carbonyl chloride (494 mg, 2.50 mmol), *N*-methyl-1-(4-nitrophenyl)methanamine (415 mg, 2.50 mmol), and triethylamine (886 μL 642 mg, 6.35 mmol). The reaction mixture was stirred at room temperature overnight. The product was isolated by column chromatography eluting with a hexanes/EtOAc mixture (1:3) as a yellow oil (R_f 0.38). Yield: 458 mg (1.40 mmol, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 – 8.14 (m, 2H), [7.52 -7.44 (m), 7.37 (d, *J* = 8.7 Hz), ∑2H], [5.24 (d, *J* = 17.4 Hz), 4.93 (d, *J* = 14.7 Hz), 4.70 – 4.54 (m), 4.50 (d, *J* = 14.7 Hz), ∑2H], [3.24 – 3.18 (m), 3.14 (s), 3.09 – 3.02 (m), 2.92 (s), ∑4H], [1.78 (dd, *J* = 8.2, 6.8 Hz), 1.67 (dd, *J* = 6.8, 4.7 Hz), ∑1H], [1.52 (s), 1.45 (s), 1.32 (s), ∑3H], [1.25 (t, *J* = 7.2

Hz), 0.97 (t, *J* = 5.9 Hz), ∑1H]; ^{13}C NMR (126 MHz, $CDCl_3$) δ (172.2, 170.9, 1C), (147.4, 144.8, 1C), (128.9, 128.5, 2C), (127.4, 124.2, 1C), (124.1, 123.8, 2C), (51.1, 50.8, 1C), (35.5, 35.3, 1C), (27.7, 27.2, 1C), (26.0, 25.7, 1C), (22.4, 18.9, 1C), (21.8, 20.9, 1C); FT IR (NaCl, cm^{-1}): 2932, 2360, 1643, 1519, 1488, 1402, 1346, 1108, 935, 859, 737, 692. HRMS (TOF ES): found 349.0174, calculated for $C_{13}H_{15}BrN_2O_3Na$ (M + Na) 349.0164 (1.0 ppm); EA found C 47.43, 47.81, H 4.58, 4.90, N 8.57, 8.72, calculated for $C_{13}H_{15}BrN_2O_3$: C 47.72, H 4.62, N 8.56.

N-Benzyl-2-bromo-N-butyl-1-methylcyclopropane-1-carboxamide (**8f**). This compound was synthesized according to Typical procedure I employing 2-bromo-1-methylcyclopropane-1-carbonyl chloride (634 mg, 3.21 mmol), N-benzylbutyl-1-amine (524 mg, 3.21 mmol), and triethylamine (1.40 mL, 1.02 g, 10.5 mmol). The reaction mixture was stirred at room temperature overnight. After standard aqueous workup and extraction, the material was filtered through a silica plug to give a colorless oil, yield 895 mg (2.76 mmol, 86%). This material had purity by GC c.a. 95% and could be used in the cyclization step as is without additional purification. If desired, it can be additionally purified by preparative column chromatography on Silica gel eluting with a CH_2Cl_2/EtOAc mixture (40:1) to isolated inseparable mixture of diastereomeric bromocyclopropanes **8f** as colorless oil, R_f 0.45 (CH_2Cl_2/EtOAc 40:1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.22 (m, 4H), 7.16 (d, *J* = 7.2 Hz, 1H), [5.08 (d, *J* = 16.9 Hz), 4.88 (d, *J* = 14.9 Hz), 4.68 (br. m), 4.53 – 4.42 (m), ∑2H], [3.81 (dddd, *J* = 13.3, 10.1, 5.5, 1.5 Hz), 3.54 (ddd, *J* = 14.2, 11.8, 4.9 Hz), 3.36 – 3.14 (m), 3.04 – 2.97 (m), 2.75 (ddd, *J* = 13.4, 10.1, 5.4 Hz), ∑3H], [1.80 – 1.71 (m), 1.70 – 1.65 (m), 1.63 – 1.52 (m), 1.52 – 1.43 (br.m), 1.36 – 1.16 (m), ∑6H], [1.42 (s), 1.30 (s), ∑3H], [0.92 (t, *J* = 7.3 Hz), 0.86 (t, *J* = 7.4 Hz), ∑3H]; ^{13}C NMR (126 MHz, $CDCl_3$) δ (172.2, 170.7, 1C), (137.5, 137.4, 137.0, 136.7, 1C), (129.0, 128.9, 128.8, 128.5, 2C), (128.3, 127.9, 127.7, 127.6, 1C), (127.5, 127.3, 126.8, 126.7, 2C), (50.8, 50.6, 47.7, 47.2, 1C), (46.7, 46.4, 45.5, 44.8, 1C), (30.5, 30.2, 29.0, 28.7, 1C), (28.2, 28.1, 1C), (27.7, 27.5, 26.3, 26.2, 26.1, 1C), (22.7, 22.6, 21.8, 1C), (22.0, 22.0, 20.0, 19.8, 1C), (20.4, 20.3, 1C), (14.0, 14.0, 1C); HRMS (TOF ES): found 346.0797, calculated for $C_{16}H_{22}BrNONa$ (M + Na) 346.0782 (4.3 ppm). EA found C 59.34, 59.19, H 6.68, 6.91, N 4.14, 4.43, calculated for $C_{16}H_{22}BrNO$: C 59.27, H 6.84; N 4.32.

N-Benzyl-2-bromo-N-isopropyl-1-methylcyclopropane-1-carboxamide (**8g**). This compound was synthesized according to Typical procedure I employing 2-bromo-1-methylcyclopropane-1-carbonyl chloride (667 mg, 3.38 mmol), *N*-benzylpropan-2-amine (504 mg, 3.38 mmol), and triethylamine (1.40 mL, 1.02 g, 10.5 mmol). The reaction mixture was stirred at room temperature overnight. After standard aqueous workup and extraction, the material was filtered through a silica plug to give a yellow oil, yield 860 mg (2.77 mmol, 82%). This material had purity by GC c.a. 98% and could be used in the cyclization step as is without additional purification. If desired, it can be additionally purified by preparative column chromatography on Silica gel eluting with a CH_2Cl_2/EtOAc mixture (20:1) to isolated inseparable mixture of diastereomeric bromocyclopropanes **8g** as colorless oils, R_f 0.42 (CH_2Cl_2/EtOAc 20:1). It should be pointed out, that one of the diastereomers shows in NMR spectra two sets of signals due to restricted rotation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 –

7.10 (m, 5H), [5.09 (d, *J* = 17.4 Hz), 4.63 – 4.32 (m), 3.93 (sept, *J* = 6.7 Hz), ∑3H], [3.25 (br.dd, *J* = 8.3, 5.0 Hz), 3.07 (dd, *J* = 7.6, 4.8 Hz), 2.98 (dd, *J* = 7.5, 4.7 Hz), ∑1H], [1.77 (t, *J* = 7.5 Hz), 1.71 (dd, *J* = 6.5, 5.0 Hz), ∑1H], [1.68 (s), 1.54 (br.s), 1.45 (s), 1.40 (s), ∑3H], [1.38 – 1.24 (m), 1.25 – 1.11 (m), 1.25 – 1.11 (m), 0.96 – 0.90 (m), ∑7H]. ^{13}C NMR (126 MHz, $CDCl_3$) δ (172.1, 171.3, 170.5, 1C), (139.6, 139.3, 138.5, 1C), (128.7, 128.5, 128.3, 2C), (127.4, 126.8, 1C), (127.1, 126.8, 126.6, 2C), (50.4, 49.0, 48.9, 1C), (50.3, 44.7, 44.0, 1C), (29.0, 28.6, 1C), (27.4, 26.4, 26.1, 1C), (23.3, 22.8, 21.8, 1C), (22.9, 22.3, 1C), (22.2, 22.1, 21.4, 1C), (20.2, 19.9, 19.7, 1C); HRMS (TOF ES): found 332.0638, calculated for $C_{15}H_{20}BrNONa$ (M + Na) 332.0626 (3.6 ppm). EA found C 58.30, 58.03, H 6.63, 6.54, N 4.28, 4.60, calculated for $C_{15}H_{20}BrNO$: C 58.07, H 6.50; N 4.51.

N-Benzyl-2-bromo-N-cyclohexyl-1-methylcyclopropane-1-carboxamide (**8h**). This compound was synthesized according to Typical procedure I employing 2-bromo-1-methylcyclopropane-1-carbonyl chloride (592 mg, 3.00 mmol), *N*-benzylcyclohexylamine (568 mg, 3.0 mmol), and triethylamine (1.40 mL, 1.02 g, 10.5 mmol). The reaction mixture was stirred at room temperature overnight. After standard aqueous workup and extraction, the material was filtered through a silica plug to give a pale-yellow oil, yield 893 mg (2.55 mmol, 85%). This material had purity by GC c.a. 96% and could be used in the cyclization step as is without additional purification. If desired, it can be additionally purified by preparative column chromatography on Silica gel eluting with a CH_2Cl_2/EtOAc mixture (40:1) to isolated inseparable mixture of diastereomeric bromocyclopropanes **8h** as colorless oils, R_f 0.40 (CH_2Cl_2/EtOAc 40:1). It should be pointed out, that one of the diastereomers shows in NMR spectra two sets of signals due to restricted rotation. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.12 (m, 5H), [5.09 (d, *J* = 17.6 Hz), 4.61 (s), 4.57 (s), 4.44 (d, *J* = 17.6 Hz), 4.36 (d, *J* = 15.6 Hz), ∑2H], [3.95 (tt, *J* = 11.4, 3.1 Hz), 3.88 – 3.76 (m), ∑1H], [3.23 (dd, *J* = 8.1, 4.9 Hz), 3.08 (dd, *J* = 7.6, 4.8 Hz), 2.96 (dd, *J* = 7.5, 4.6 Hz), ∑1H], [2.02 (br.d, *J* = 11.8 Hz), 1.89 – 1.75 (m), 1.74 – 1.62 (m), 1.62 – 1.29 (m), 1.26 – 1.20 (m), 1.17 – 0.90 (m), ∑12H], [1.43 (s), 1.27 (s) ∑3H]; ^{13}C NMR (126 MHz, $CDCl_3$) δ (172.2, 171.3, 170.6, 1C), (139.6, 139.3, 138.9, 1C), (128.6, 128.4, 128.3, 2C), (127.3, 126.8, 1C), (127.2, 126.7, 126.6, 2C), (58.2, 58.2, 57.8, 1C), (49.7, 45.8, 45.1, 1C), (33.5, 32.5, 30.4, 1C), (32.8, 32.2, 30.0, 1C), (28.9, 28.7, 1C), (27.6, 26.3, 26.2, 1C), (26.3, 26.2, 26.2, 26.1, 26.1, 2C), (25.7, 25.5, 25.5, 1C), (23.5, 23.1, 21.6, 1C), (22.3, 22.2, 20.0, 1C); HRMS (TOF ES): found 372.0947, calculated for $C_{18}H_{24}BrNONa$ (M + Na) 372.0939 (2.1 ppm). EA found C 61.53, 61.91, H 7.03, 7.11, N 4.09, 4.15, calculated for $C_{18}H_{24}BrNO$: C 61.72, H 6.91; N 4.00.

N-Benzyl-2-bromo-N-(tert-butyl)-1-methylcyclopropane-1-carboxamide (**8i**). This compound was synthesized according to Typical procedure I employing 2-bromo-1-methylcyclopropane-1-carbonyl chloride (640 mg, 3.24 mmol), *N*-benzyl-2-methylpropan-2-amine (529 mg, 3.24 mmol), and triethylamine (1.40 mL, 1.02 g, 10.5 mmol). The reaction mixture was stirred at room temperature overnight. After standard aqueous workup and extraction, the material was filtered through a silica plug to afford a pale-yellow glass, yield 830 mg (2.56 mmol, 79%). This material had purity by GC c.a. 98% and could be used in the cyclization step as is without

additional purification. If desired, diastereomeric bromocyclopropanes can be additionaly purified and separated by preparative column chromatography on Silica gel eluting with a CH_2Cl_2/EtOAc mixture (40:1). HRMS (TOF ES): found 346.0786, calculated for $C_{16}H_{22}BrNONa$ (M + Na) 346.0782 (1.2 ppm). Individual isomers were isolated as colorless glass (*trans*-**8i**) and colorless crystalline solid (*cis*-**8i**), respectively. ***trans*-8i**: R_f 0.42 (CH_2Cl_2/EtOAc 40:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 4.78 (q, *J* = 17.8 Hz, 2H), 3.20 (dd, *J* = 8.2, 4.9 Hz, 1H), 1.71 (dd, *J* = 8.2, 6.7 Hz, 1H), 1.42 (s, 3H), 1.36 (s, 9H), 0.82 (dd, *J* = 6.7, 5.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.5, 140.0, 128.8 (2C), 127.1, 125.9 (2C), 58.3, 49.5, 28.6 (3C), 28.5, 27.9, 22.2, 20.3. ***cis*-8i**: mp 165.2-166.1 °C; R_f 0.35 (CH_2Cl_2/EtOAc 40:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.10 (m, 5H), 5.10 (d, *J* = 18.3 Hz, 1H), 4.61 (d, *J* = 18.3 Hz, 1H), 2.95 (dd, *J* = 7.5, 4.6 Hz, 1H), 1.67 (dd, *J* = 6.7, 4.6 Hz, 1H), 1.39 (s, 9H), 1.22 (s, 3H), 1.12 (dd, *J* = 7.5, 6.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.7, 140.8, 128.6 (2C), 126.9, 126.1 (2C), 59.0, 49.9, 30.4, 28.6 (3C), 26.9, 23.8, 22.4. EA found C 59.50, 59.03, H 7.01, 6.94, N 4.52, 4.19, calculated for $C_{16}H_{22}BrNO$: C 59.27, H 6.84; N 4.32.

2-Bromo-N-(4-fluorobenzyl)-N,1-dimethylcyclopropane-1-carboxamide (**8j**). This compound was synthesized according to Typical procedure I employing 2-bromo-1-methylcyclopropane-1-carbonyl chloride (340 mg, 1.72 mmol), 1-(4-fluorophenyl)-*N*-methylmethanamine (239 mg, 1.72 mmol), and triethylamine (988 μL 717 mg, 7.08 mmol). The reaction mixture was stirred at room temperature overnight. The product was isolated by column chromatography eluting with a hexanes/EtOAc mixture (1:1) as a yellow oil (R_f 0.37). Yield: 413 mg (1.37 mmol, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ [7.31 – 7.27 (m), 7.27 – 7.94 (m), ∑4H], 5.14 – 4.36 (m, 2H), [3.20 (dd, *J* = 8.2, 4.9 Hz), 3.10 – 2.85 (m), ∑4H], [1.82 – 1.73 (m), 1.69 – 1.63 (m), ∑1H], [1.49 (s), 1.42 (s), 1.35 (s), ∑3H], [1.22 (t, *J* = 7.1 Hz), 0.94 (dd, *J* = 6.7, 4.9 Hz), ∑1H]; ^{13}C NMR (126 MHz, $CDCl_3$) δ (171.2, 170.5, 1C), [162.23 (d, $^1J_{CF}$ = 246.1 Hz), 162.19 (d, $^1J_{CF}$ = 246.0 Hz), 1C], [132.9 (d, $^4J_{CF}$ = 3.5 Hz), 132.7 (br. s), 1C], [130.0 (d, $^3J_{CF}$ = 8.2 Hz), 128.3 (d, $^3J_{CF}$ = 7.9 Hz), 2C], [115.8 (d, $^2J_{CF}$ = 23.5 Hz), 115.3 (d, $^2J_{CF}$ = 21.7 Hz), 2C], (52.7, 50.7, 1C), (35.0, 33.5, 1C), (27.8, 25.8, 1C), [27.5 (br), 26.0, 1C], (25.8, 20.9, 1C), [21.8, 18.9 (br), 1C]; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.9, -115.3; FT IR (NaCl, cm^{-1}): 2930, 2360, 2342, 1700, 1684, 1645, 1540, 1508, 1403, 1222, 1106, 924, 817, 668, 650; HRMS (TOF ES): found 322.0217, calculated for $C_{13}H_{15}BrFNONa$ (M + Na) 322.0219 (0.6 ppm); EA found C 51.98, 52.10, H 5.24, 4.82, N 4.95, 4.69, calculated for $C_{13}H_{15}BrFNO$: C 52.02, H 5.04, N 4.67.

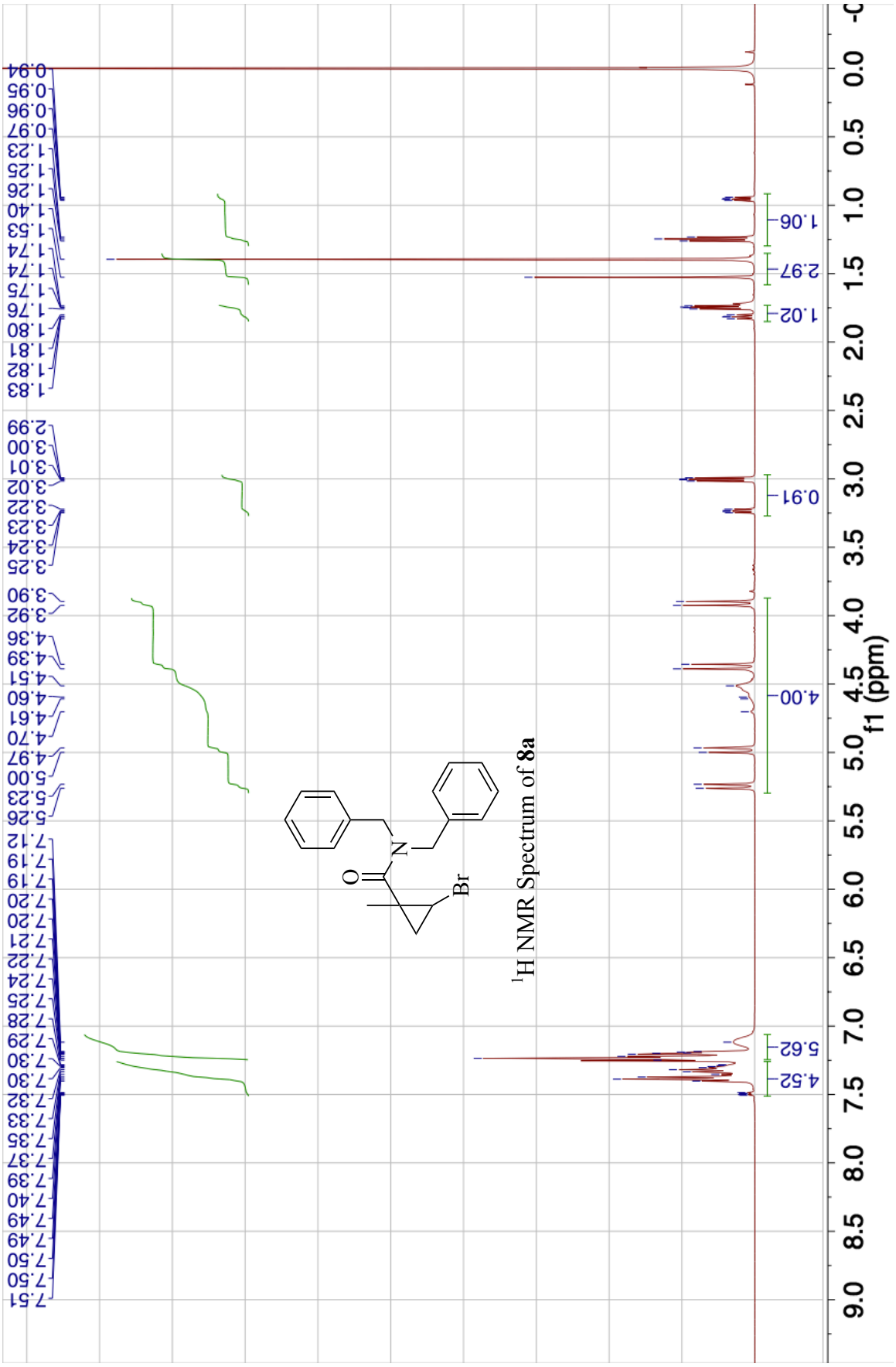
2-Bromo-N-(2,4-difluorobenzyl)-N,1-dimethylcyclopropane-1-carboxamide (**8k**). This compound was synthesized according to Typical procedure I employing 2-bromo-1-methylcyclopropane-1-carbonyl chloride (20) (400 mg, 2.03 mmol), 1-(2,4-difluorophenyl)-*N*-methylmethanamine (319 mg, 2.03 mmol), and triethyl-amine (710 μL, 515 mg, 5.09 mmol). The reaction mixture was stirred at room temperature overnight. The product was isolated by column chromatography eluting with a CH_2Cl_2/MeOH mixture (40:1) as a pale-yellow oil (R_f 0.43). Yield: 490 mg (1.54 mmol, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) δ [7.44 – 7.39 (m), 7.36 (s), 7.27 –

7.17 (m), ∑1 H], 6.95 – 6.75 (m, 2H), 5.08 – 4.45 (m, 2H), 3.23 – 2.83 (m, 4H), [1.75 (dd, J = 8.2, 6.6 Hz), 1.69 – 1.61 (m), ∑1H], [1.48 (s), 1.41 (s), 1.32 (s), ∑3 H], [1.21 (t, J = 7.2 Hz), 0.93 (dd, J = 6.7, 4.9 Hz), ∑1 H]; ^{13}C NMR (126 MHz, $CDCl_3$) δ (172.0, 170.7, 1C), [162.4 (dd, $^1J_{CF}$ = 249.0 Hz, $^3J_{CF}$ = 11.8 Hz), 162.2 (dd, $^1J_{CF}$ = 247.6 Hz, $^3J_{CF}$ = 11.9 Hz), 1C), [161.1 (dd, $^1J_{CF}$ = 248.2 Hz, $^3J_{CF}$ = 11.9 Hz), 1C], [131.8 (dd, $^3J_{CF}$ = 9.5 Hz, $^3J_{CF}$ = 5.7 Hz), 131.4 (br. s), 1C], [120.0 (dd, $^2J_{CF}$ = 15.0 Hz, $^4J_{CF}$ = 3.9 Hz), 119.9 (br. s), 1C], [111.7 (dd, $^2J_{CF}$ = 21.2 Hz, $^4J_{CF}$ = 3.9 Hz), 111.5 (dd, $^2J_{CF}$ = 20.8 Hz, $^4J_{CF}$ = 3.7 Hz), 1C], [104.3 (t, $^2J_{CF}$ = 25.2 Hz, $^4J_{CF}$ = 3.9 Hz), 103.5 (t, $^2J_{CF}$ = 25.5 Hz), 1C], [46.8 (d, $^3J_{CF}$ = 4.8 Hz), 44.2 (t, $^3J_{CF}$ = 3.6 Hz), 1C], (35.4, 35.1, 1C), (27.8, 27.4 (br), 1C), (25.9, 25.8, 1C), (21.80, 21.77, 1C), (20.9, 18.9, 1C); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.0 (d, $^4J_{FF}$ = 7.3 Hz), -111.1 (d, $^4J_{FF}$ = 7.4 Hz), -114.0 (d, $^4J_{FF}$ = 7.2 Hz), -115.1 (d, $^4J_{FF}$ = 7.4 Hz). FT IR (NaCl, cm^{-1}): 2933, 2360, 2341, 1645, 1505, 1487, 1430, 1403, 1269, 1139, 1106, 1091, 964, 850, 668, 621. HRMS (TOF ES): found 318.0309, calculated for $C_{13}H_{15}BrF_2NO$ (M + H) 318.0305 (1.3 ppm); EA found C 48.81, 49.33, H 4.64, 4.20, N 4.28, 4.32, calculated for $C_{13}H_{14}BrF_2NO$: C 49.08, H 4.44, N 4.40.

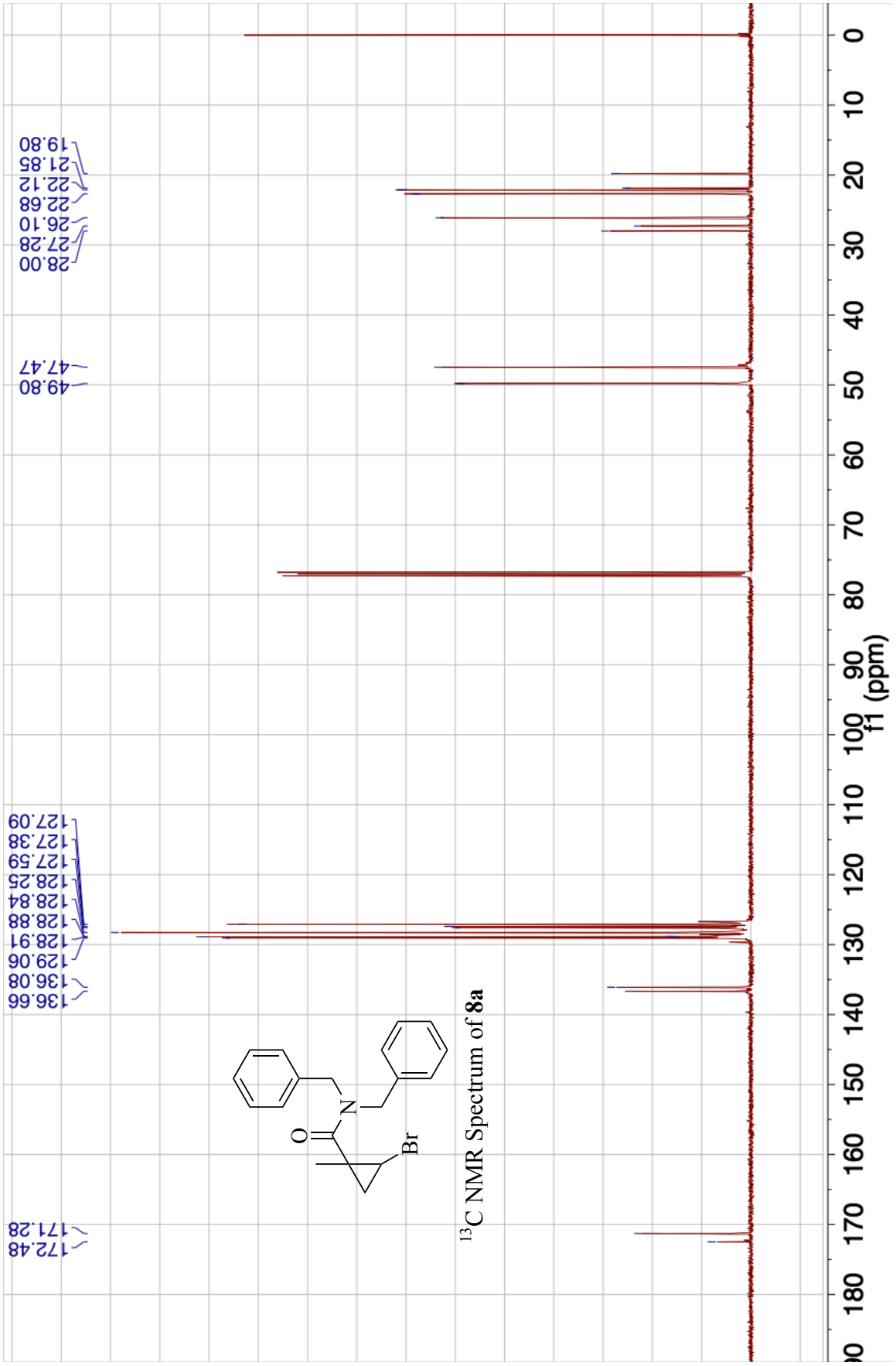
2-Bromo-N-(2-chlorobenzyl)-N,1-dimethylcyclopropane-1-carboxamide (**8l**). This compound was synthesized according to Typical procedure I employing 2-bromo-1-methylcyclopropane-1-carbonyl chloride (494 mg, 2.50 mmol), 1-(2-chlorophenyl)-*N*-methylmethanamine (389 mg, 2.50 mmol), and triethylamine (886 μL 642 mg, 6.35 mmol). The reaction mixture was stirred at room temperature overnight. The product was isolated by column chromatography eluting with a hexanes/EtOAc mixture (3:2) as a colorless glass (R_f 0.33). Yield: 586 mg (1.85 mmol, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ [7.45 – 7.28 (m), 7.24 – 7.19 (m), 7.12 (br. s), ∑4H], 5.12 – 4.52 (m, 2H), 3.26 – 2.88 (m, 4H), [1.77 (br. s), 1.69 – 1.65 (m), 1.52 (bs), 1.45 (s), 1.26 – 1.16 (m), 0.94 (br. s), ∑5H]; ^{13}C NMR (126 MHz, $CDCl_3$) δ (171.6, 170.7, 1C), (134.4, 134.2, 1C), (133.7, 132.8, 1C), (129.5, 128.8, 128.60, 128.56, 127.23, 127.18, 127.1, 127.0, 4C), (51.3, 48.7, 1C), (35.5, 34.5, 1C), (28.0, 26.0, 1C), (25.9, 25.6, 1C), (22.5, 21.8, 21.5, 21.0, 2C); FTIR (NaCl, cm^{-1}): 2932, 1644, 1486, 1443, 1402, 1093, 1050, 752; HRMS (TOF ES): found 322.0196, calculated for $C_{13}H_{15}BrClNOLi$ (M + Li) 322.0186 (3.1 ppm); EA found C 49.55, 49.04, H 4.64, 5.05, N 4.57, 4.30, calculated for $C_{13}H_{15}BrClNO$: C 49.32, H 4.78, N 4.42.

2-Bromo-N-(4-bromo-2-fluorobenzyl)-N,1-dimethylcyclopropane-1-carboxamide (**8m**). This compound was synthesized according to Typical procedure I employing 2-bromo-1-methylcyclopropane-1-carbonyl chloride (**20**) (494 mg, 2.50 mmol), 1-(4-bromo-2-fluorophenyl)-*N*-methylmethanamine (545 mg, 2.50 mmol), and triethylamine (886 μL 642 mg, 6.35 mmol). The reaction mixture was stirred at room temperature overnight. The product was isolated by column chromatography eluting with a hexanes/EtOAc mixture (3:2) as a pale-yellow oil (R_f 0.23). Yield: 853 mg (2.25 mmol, 90%). ^{1}H NMR (500 MHz, $CDCl_3$) δ [7.36 – 7.27 (m), 7.28 – 7.08 (m), ∑3H], 5.05 – 4.47 (m, 2H), 3.21 – 2.86 (m, 4H), [1.75 (dd, J = 8.2, 6.7 Hz), 1.64 (dd, J = 6.9, 4.7 Hz), ∑1H], [1.48 (s), 1.41 (s), 1.30 (s), ∑3H], [1.21 (t, J = 7.1 Hz), 0.93 (dd, J = 6.7, 4.9 Hz), ∑1H]; ^{13}C NMR (126 MHz, $CDCl_3$) δ [172.0, 170.8, 1C], 160.8 (d, $^1J_{CF}$ = 250.8 Hz, 1C), [131.9 (d, $^3J_{CF}$ = 4.6 Hz), 131.5 (br. s), 1C], [127.9 (d, $^4J_{CF}$ = 3.4 Hz),

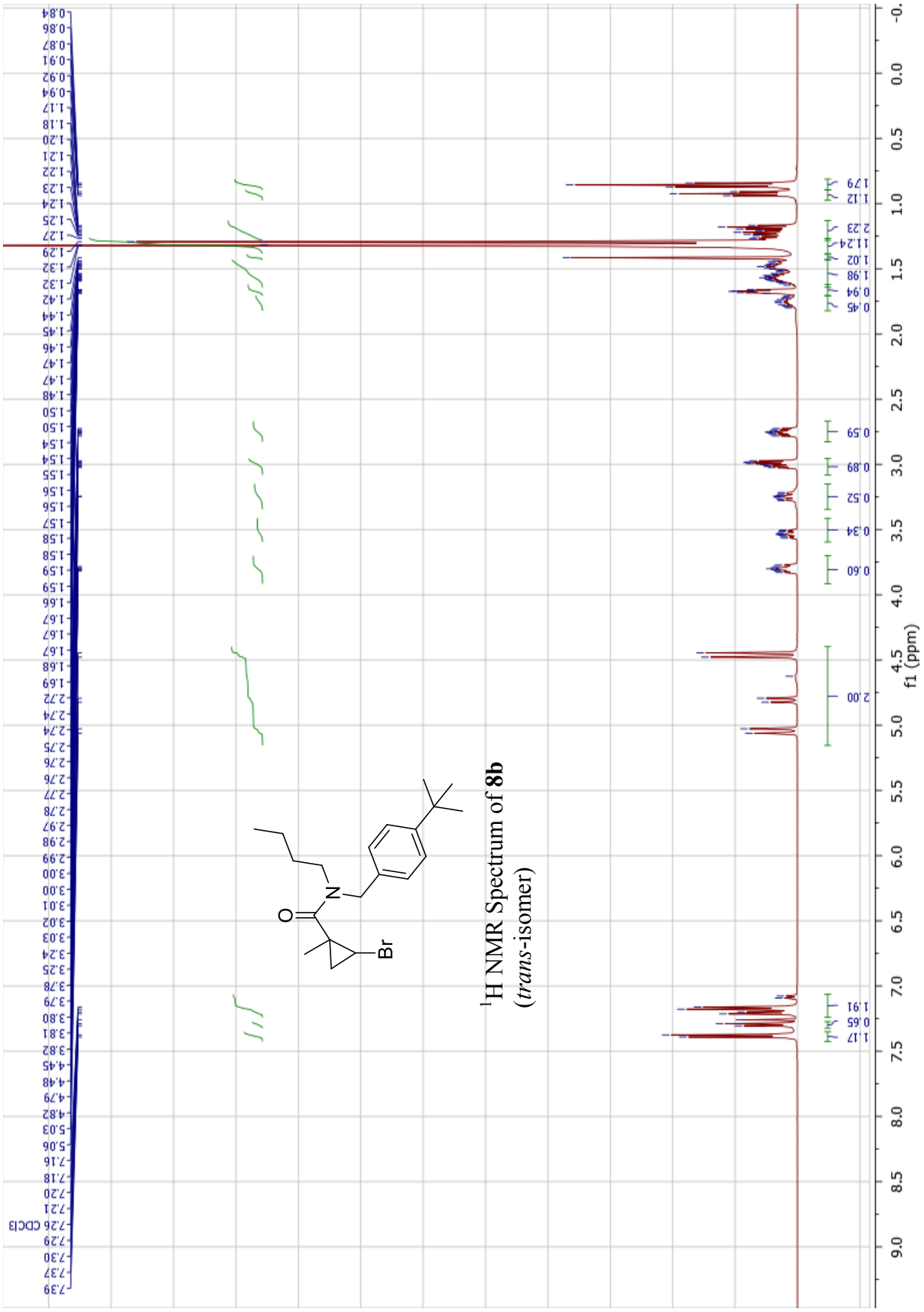
127.7 (d, $^{4}J_{CF}$ = 3.6 Hz), 1C], [123.3 (d, $^{2}J_{CF}$ = 15.2 Hz), 123.1 (br. s), 1C], [121.7 (br. s), 121.4 (d, $^{3}J_{CF}$ = 9.2 Hz), 1C], [119.2 (br. s), 118.8 (d, $^{2}J_{CF}$ = 22.4 Hz), 1C], [47.0 (br. s), 44.3 (d, $^{3}J_{CF}$ = 3.7 Hz), 1C], (35.5, 35.2, 1C), (27.8, 27.3, 1C), (25.9, 25.8, 1C), (21.79, 21.76, 1C), (20.9, 18.9, 1C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.3, -116.4; FT IR (NaCl, cm^{-1}): 2932, 1644, 1605, 1484, 1401, 1218, 1103, 875, 814, 611; HRMS (TOF ES): found 399.9341, calculated for $C_{13}H_{14}Br_2FNONa$ (M + Na) 399.9324 (4.3 ppm); EA found C 41.48, 41.39, H 3.52, 3.61, N 3.56, 3.76, calculated for $C_{13}H_{14}Br_2FNO$: C 41.19, H 3.72, N 3.70.



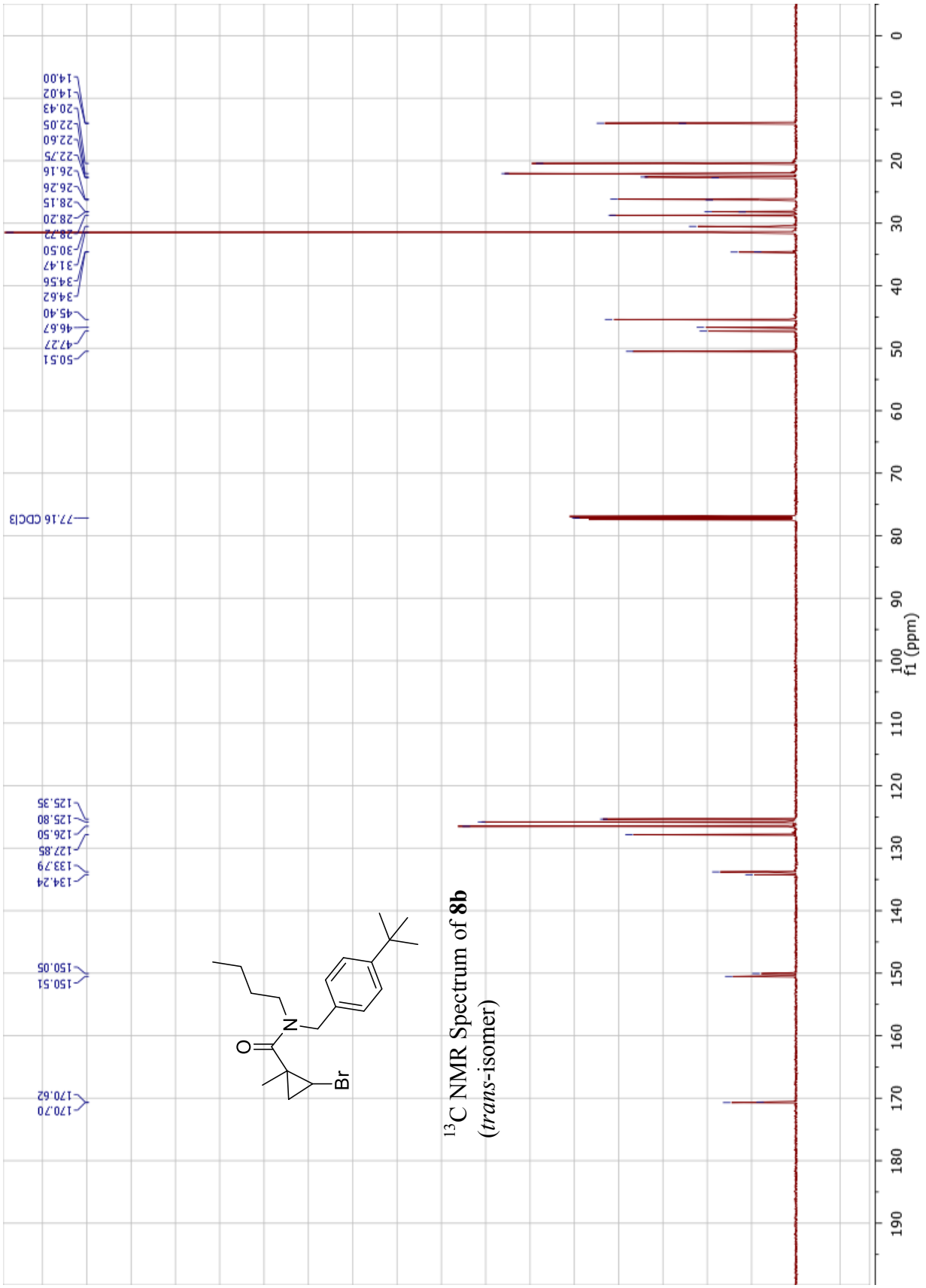
^{1}H NMR Spectrum of **8a**



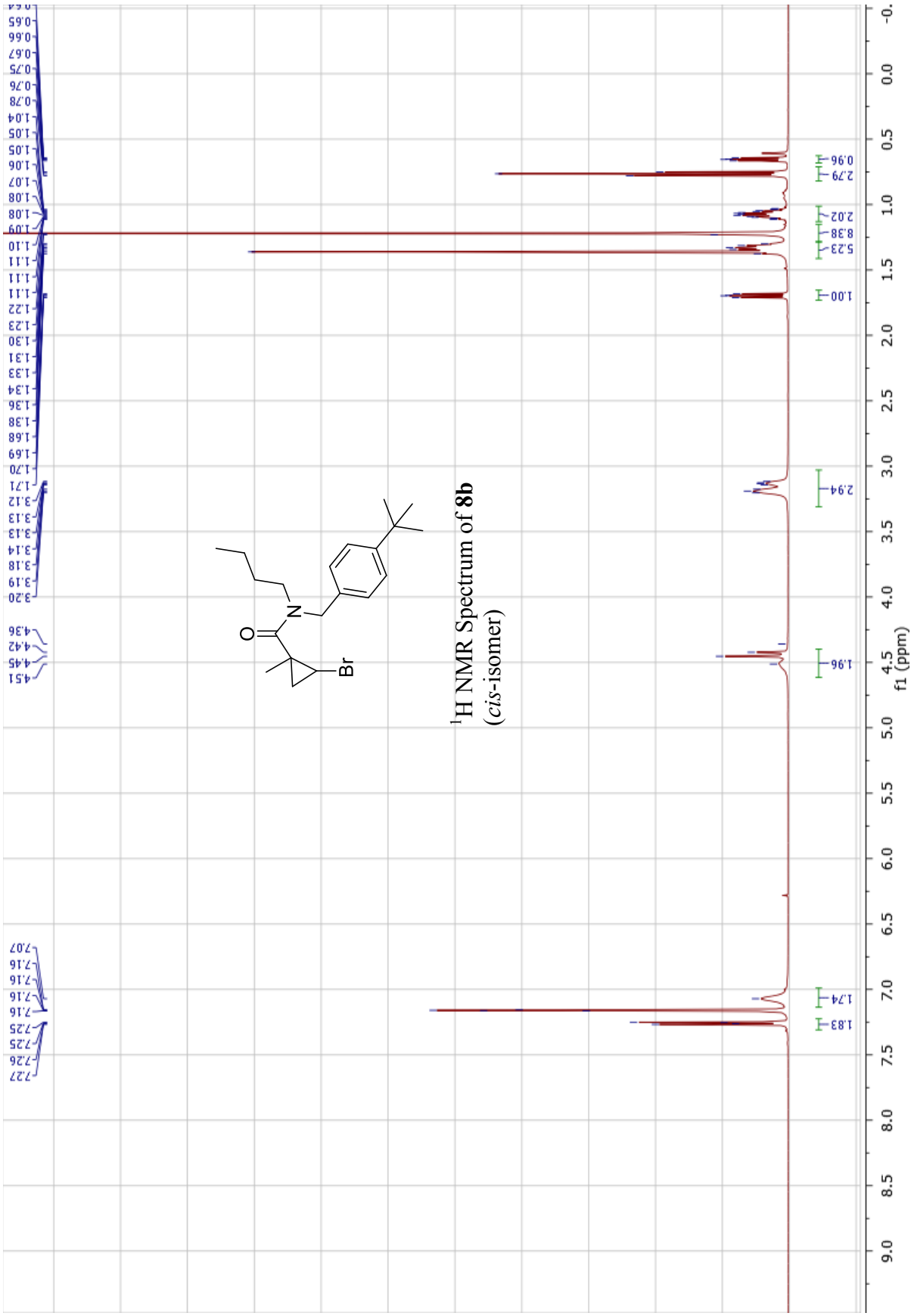
^{13}C NMR Spectrum of **8a**



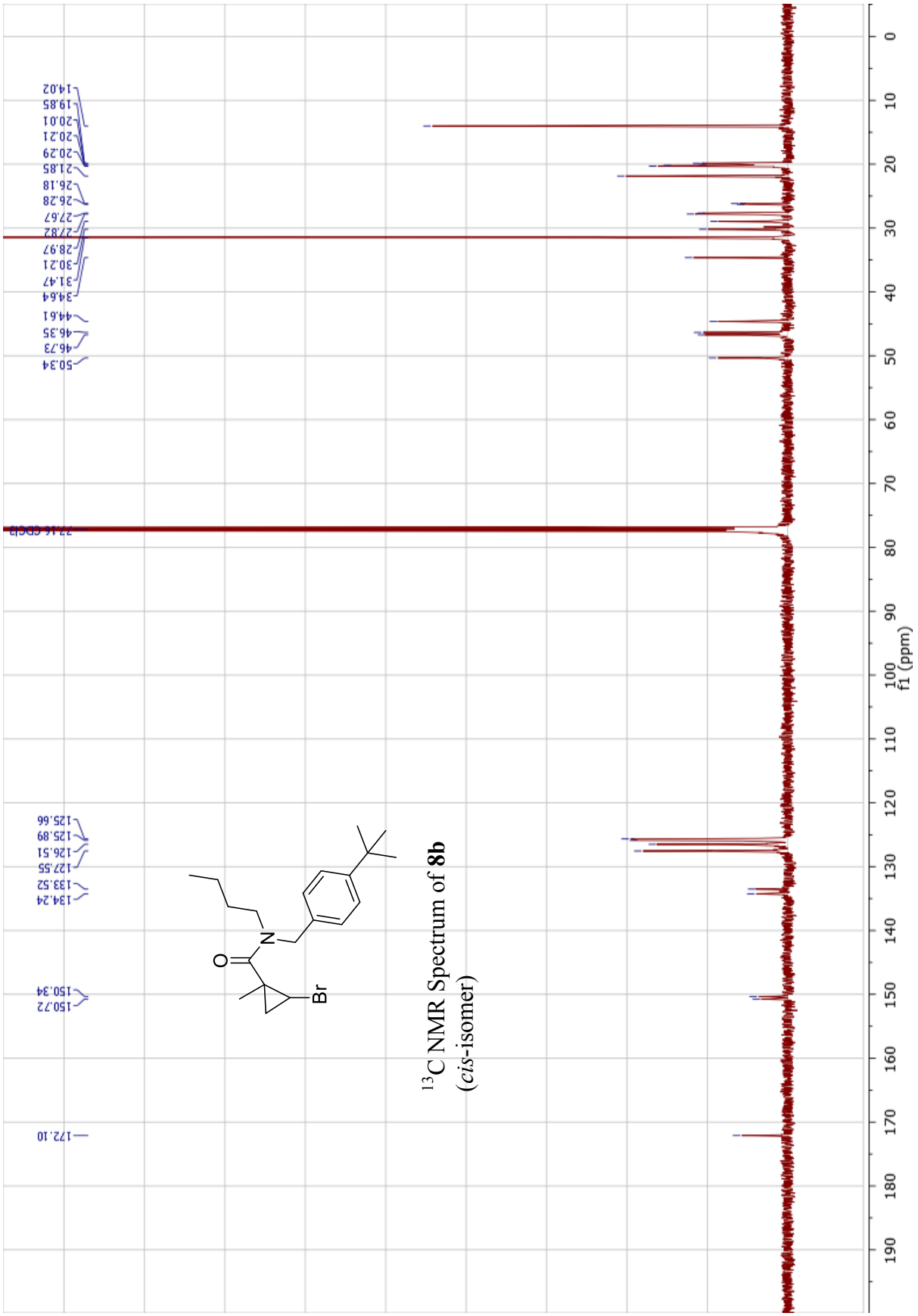
^{1}H NMR Spectrum of **8b**
(*trans*-isomer)



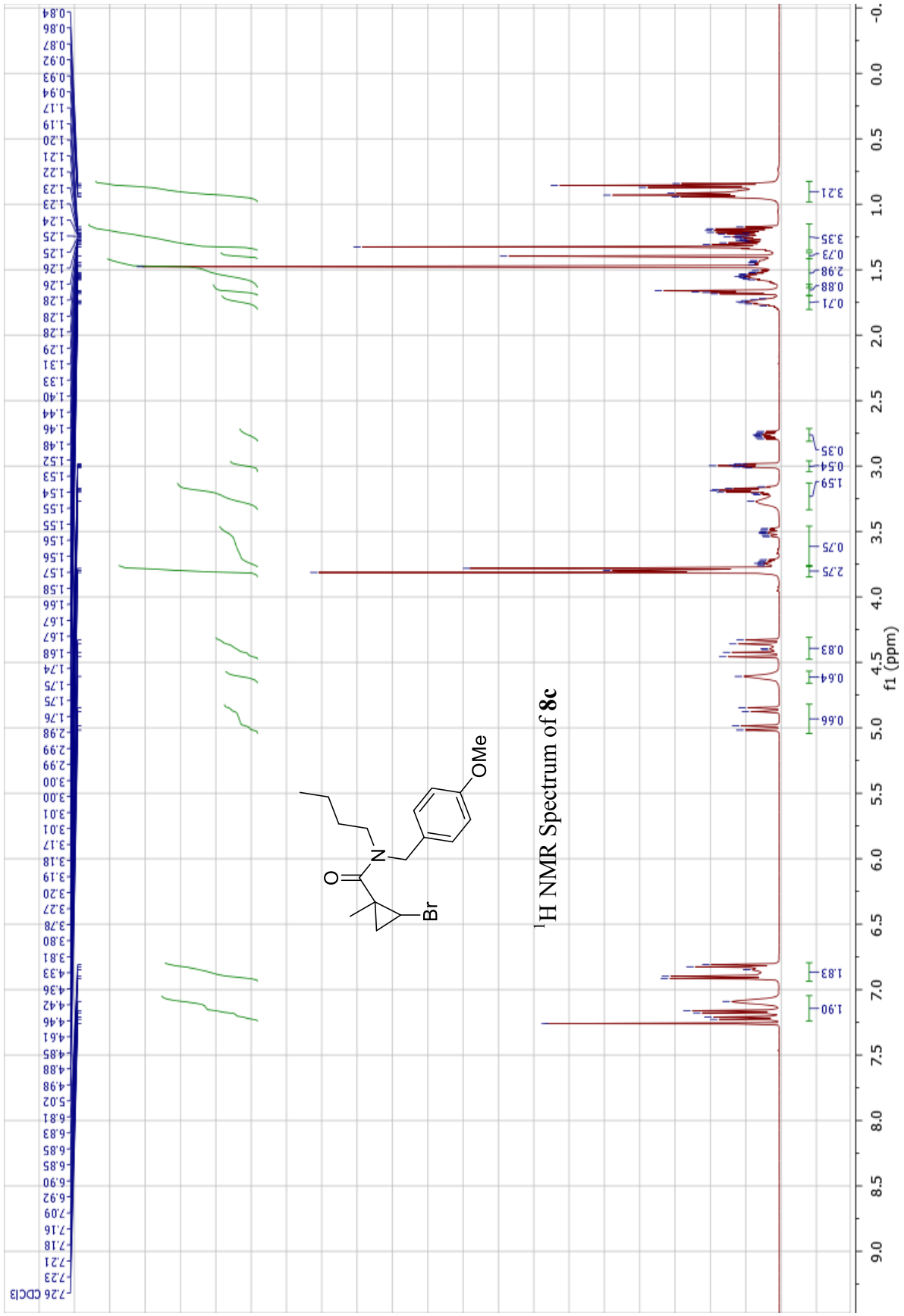
^{13}C NMR Spectrum of **8b**
(*trans*-isomer)



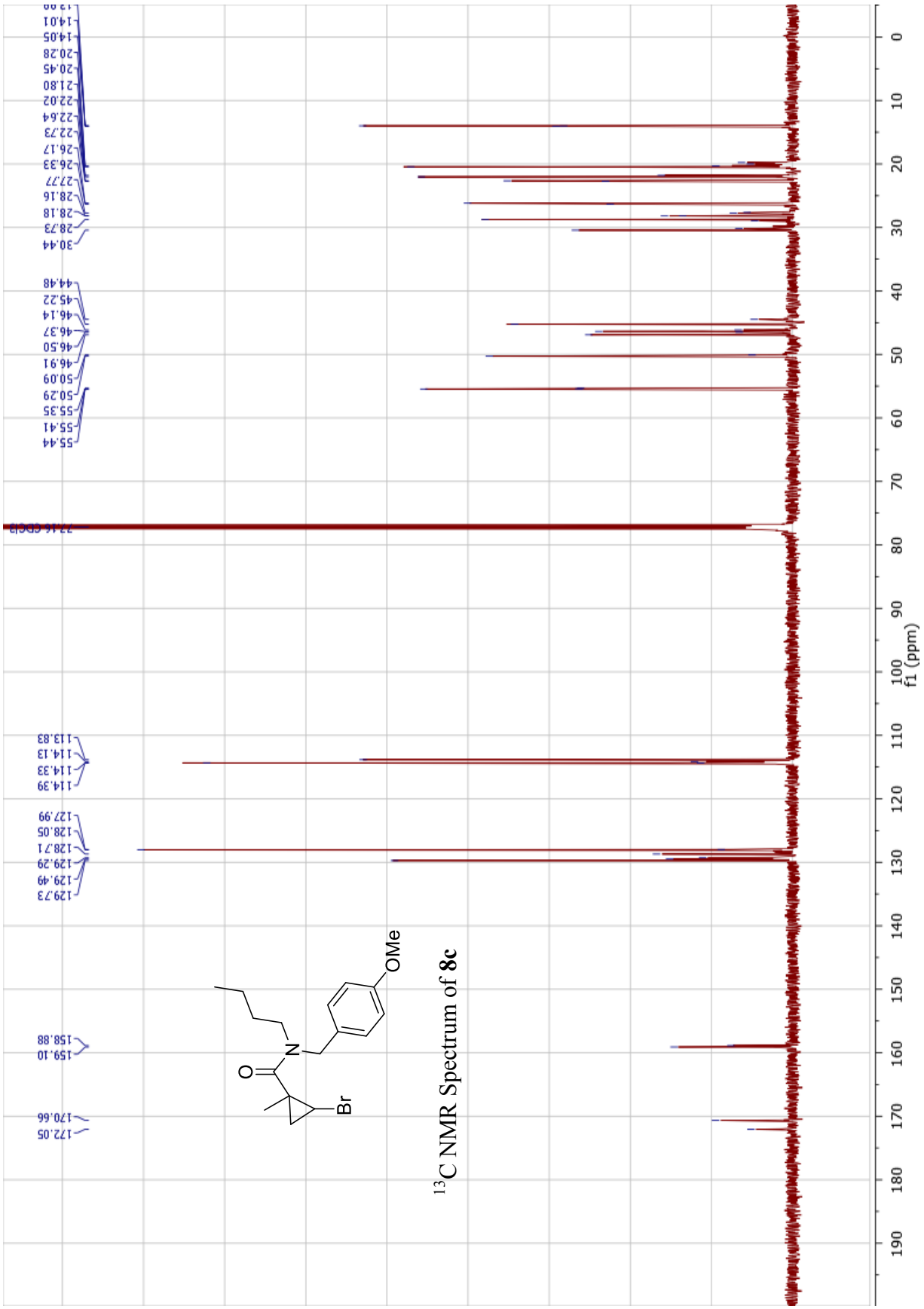
^{1}H NMR Spectrum of **8b**
(*cis*-isomer)



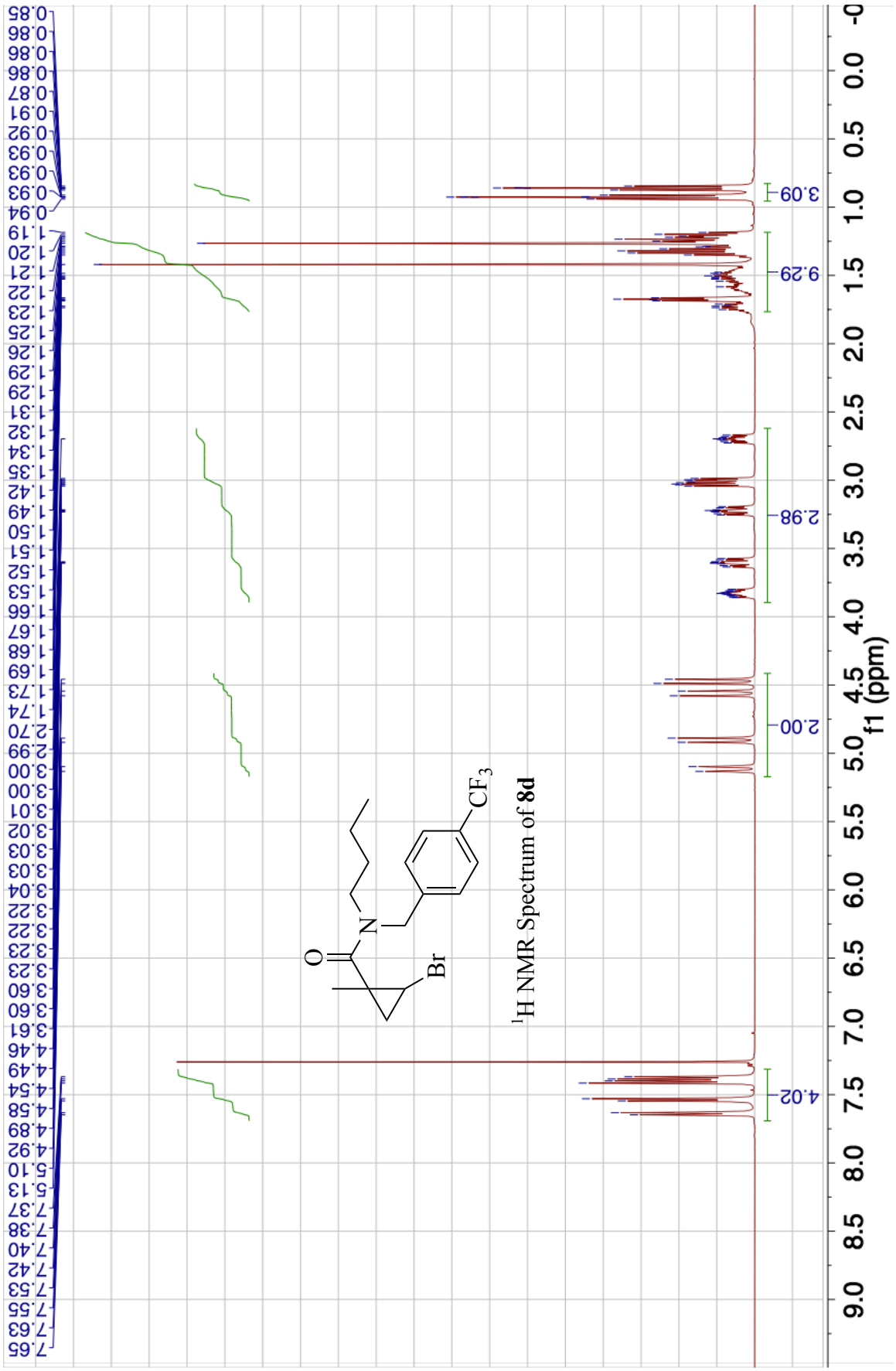
^{13}C NMR Spectrum of **8b**
(*cis*-isomer)



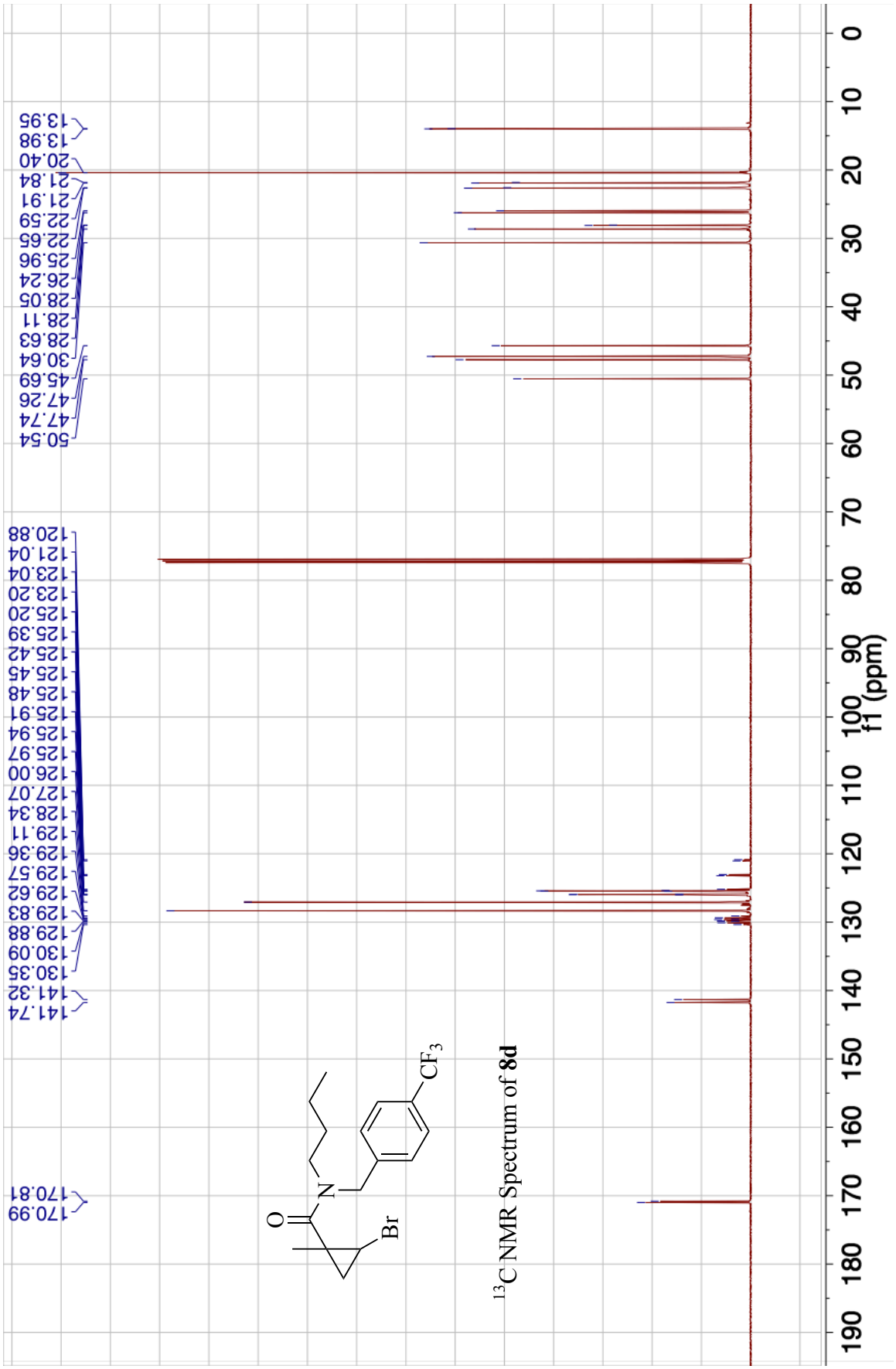
^{1}H NMR Spectrum of **8c**



^{13}C NMR Spectrum of **8c**



^{1}H NMR Spectrum of **8d**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129.88
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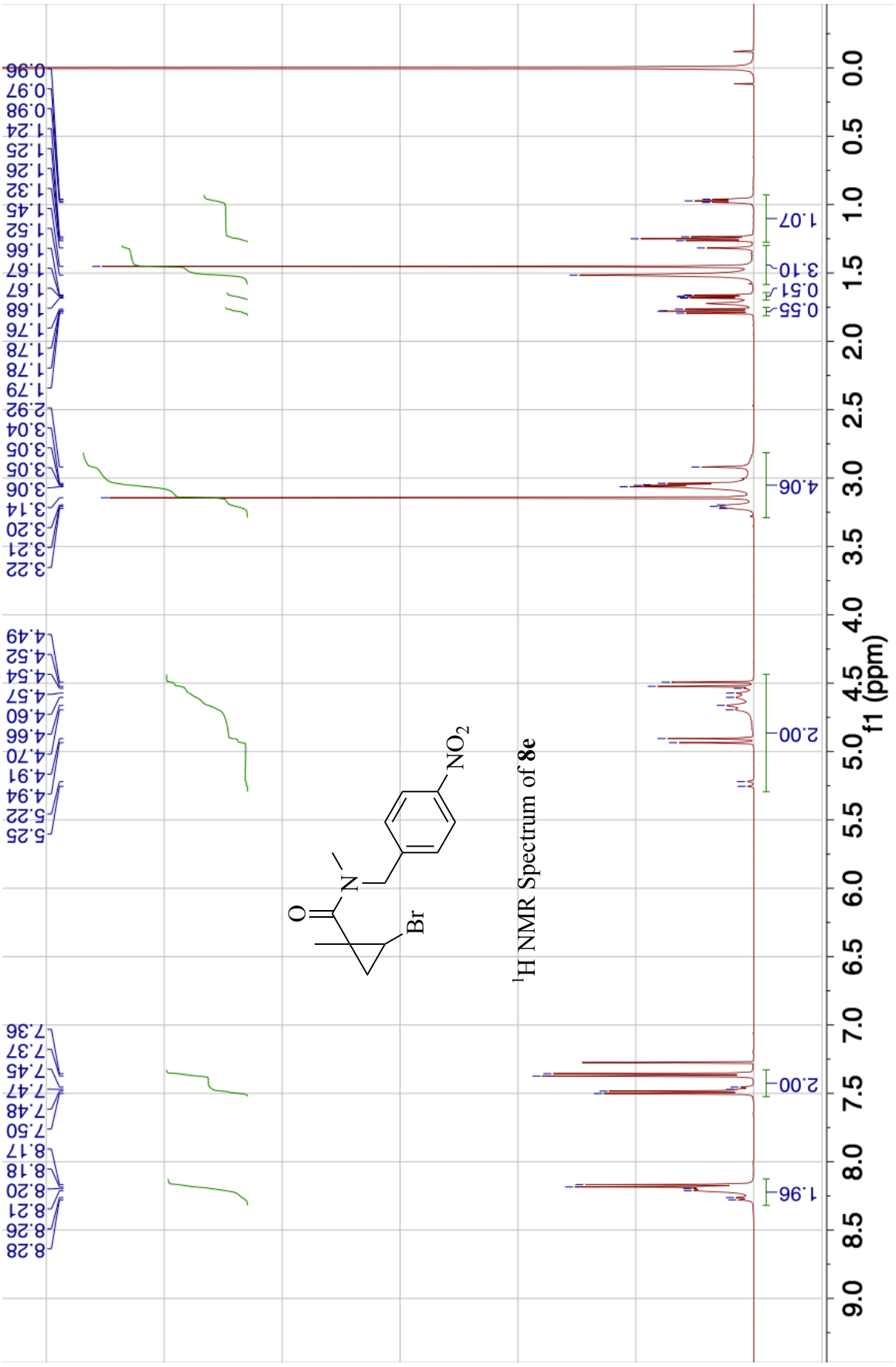
N
Br
CF3
13C NMR Spectrum of 8d
f1 (ppm)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8.28
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3.10
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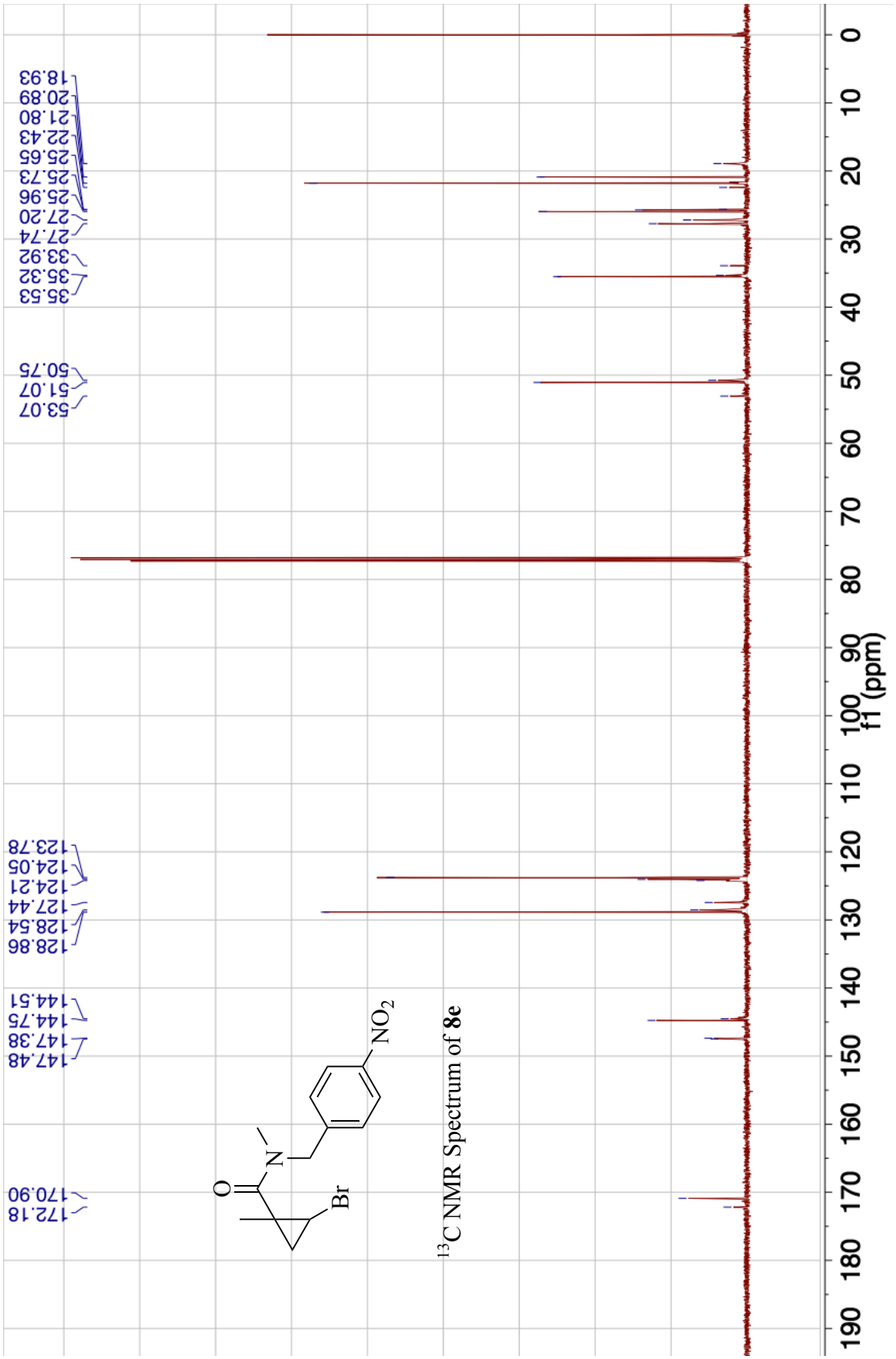
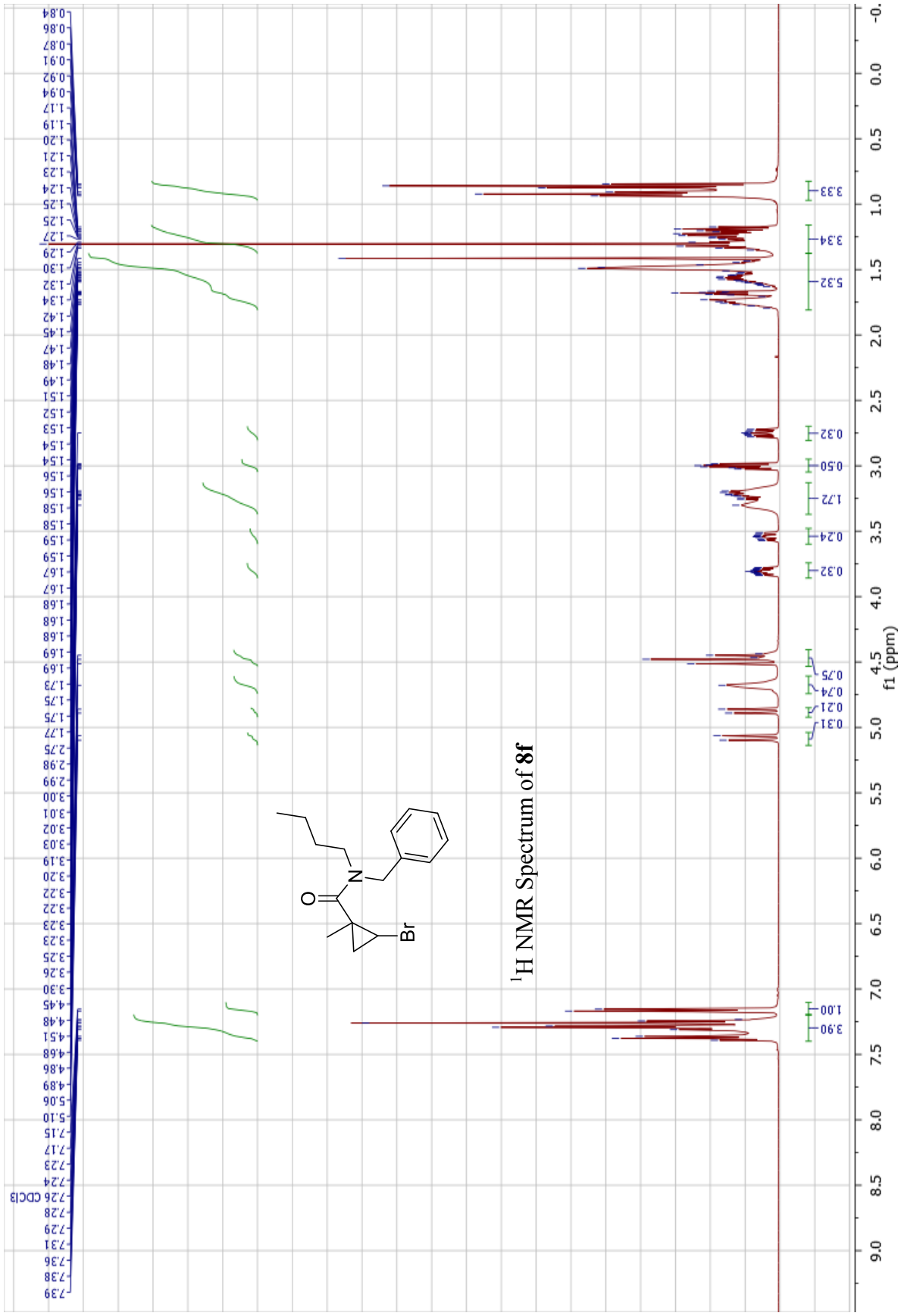
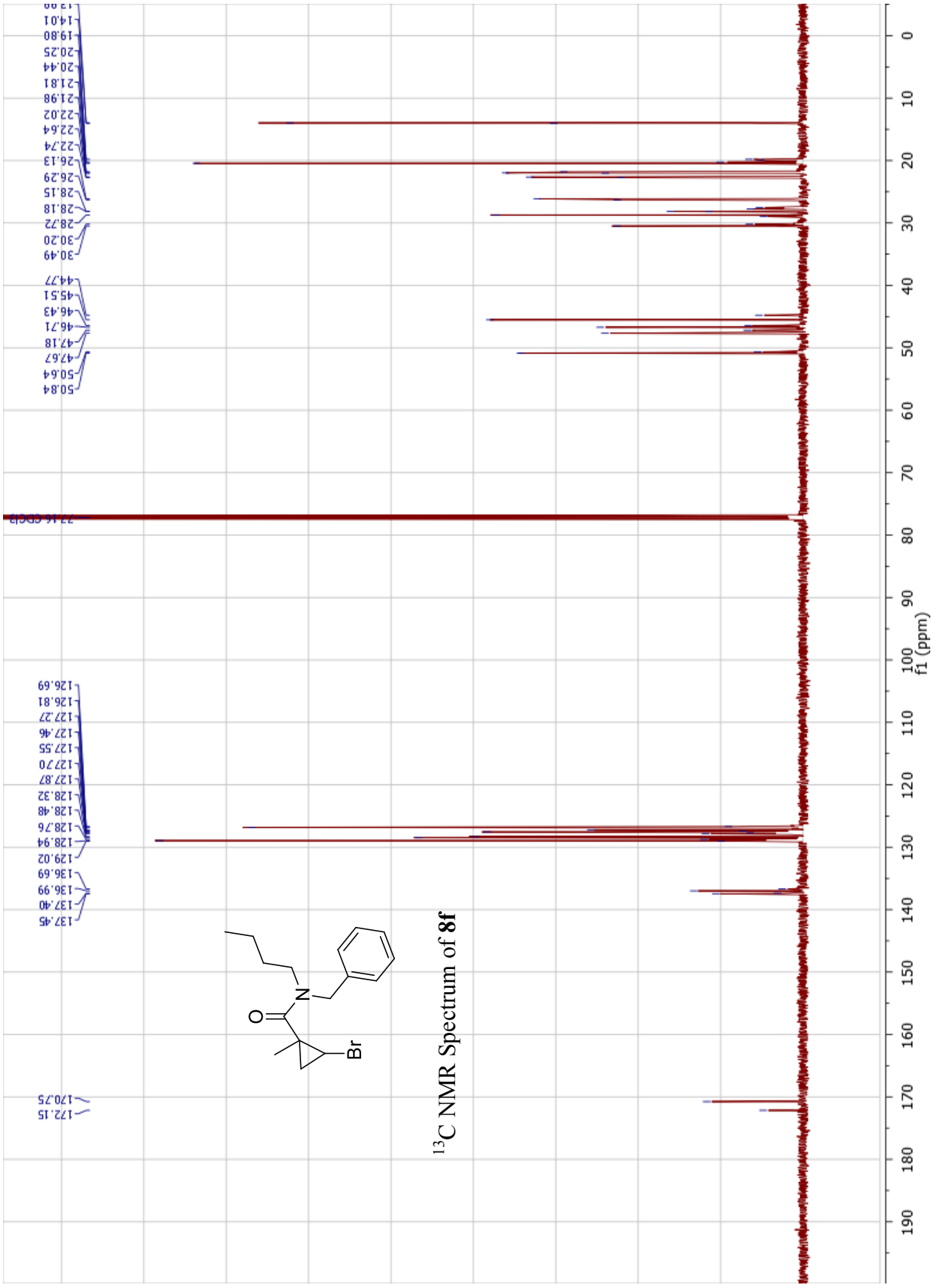
2.00
2.00
1.96
O
N
Br
NO2
1H NMR Spectrum of 8e
f1 (ppm)



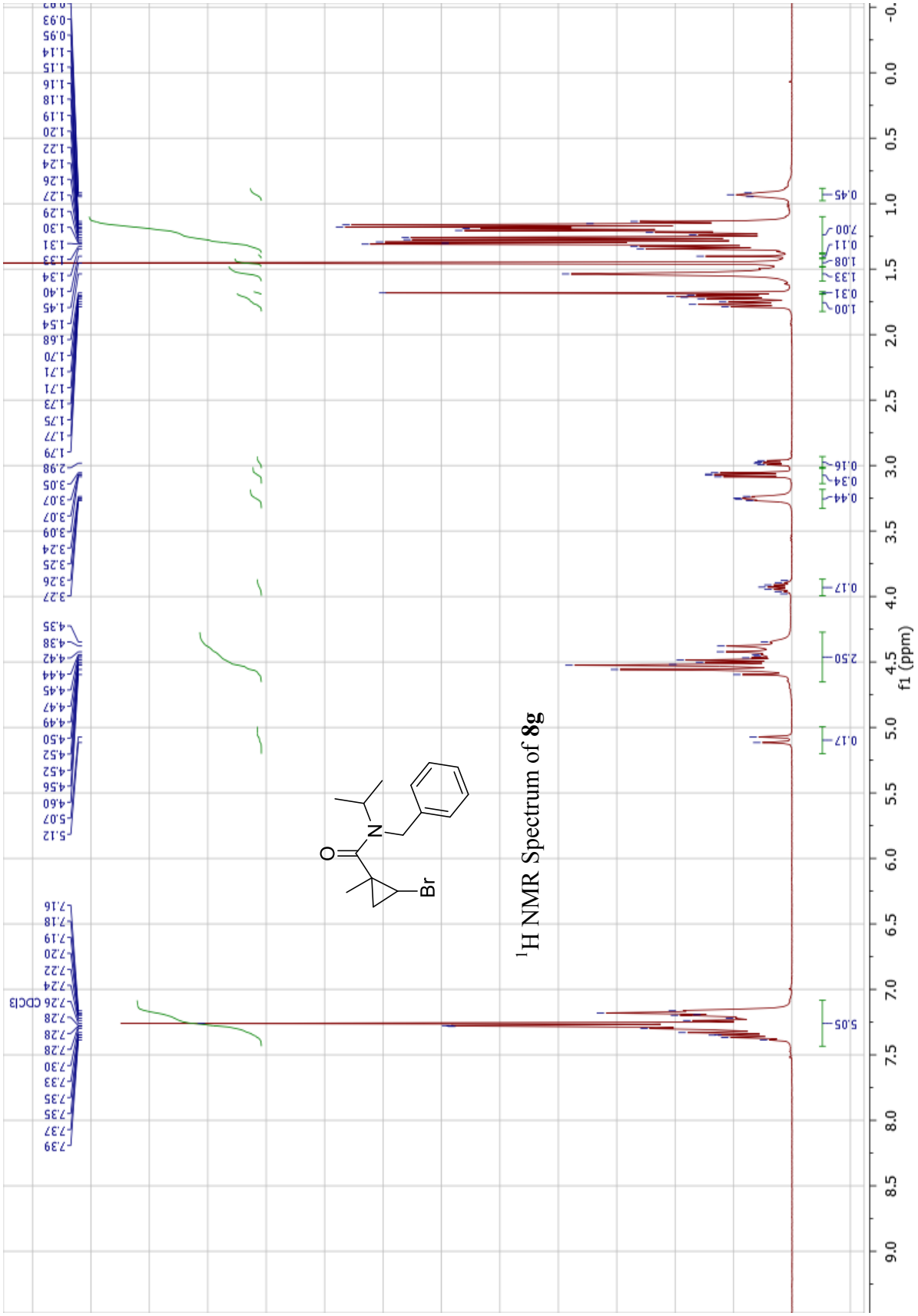
^{13}C NMR Spectrum of **8e**



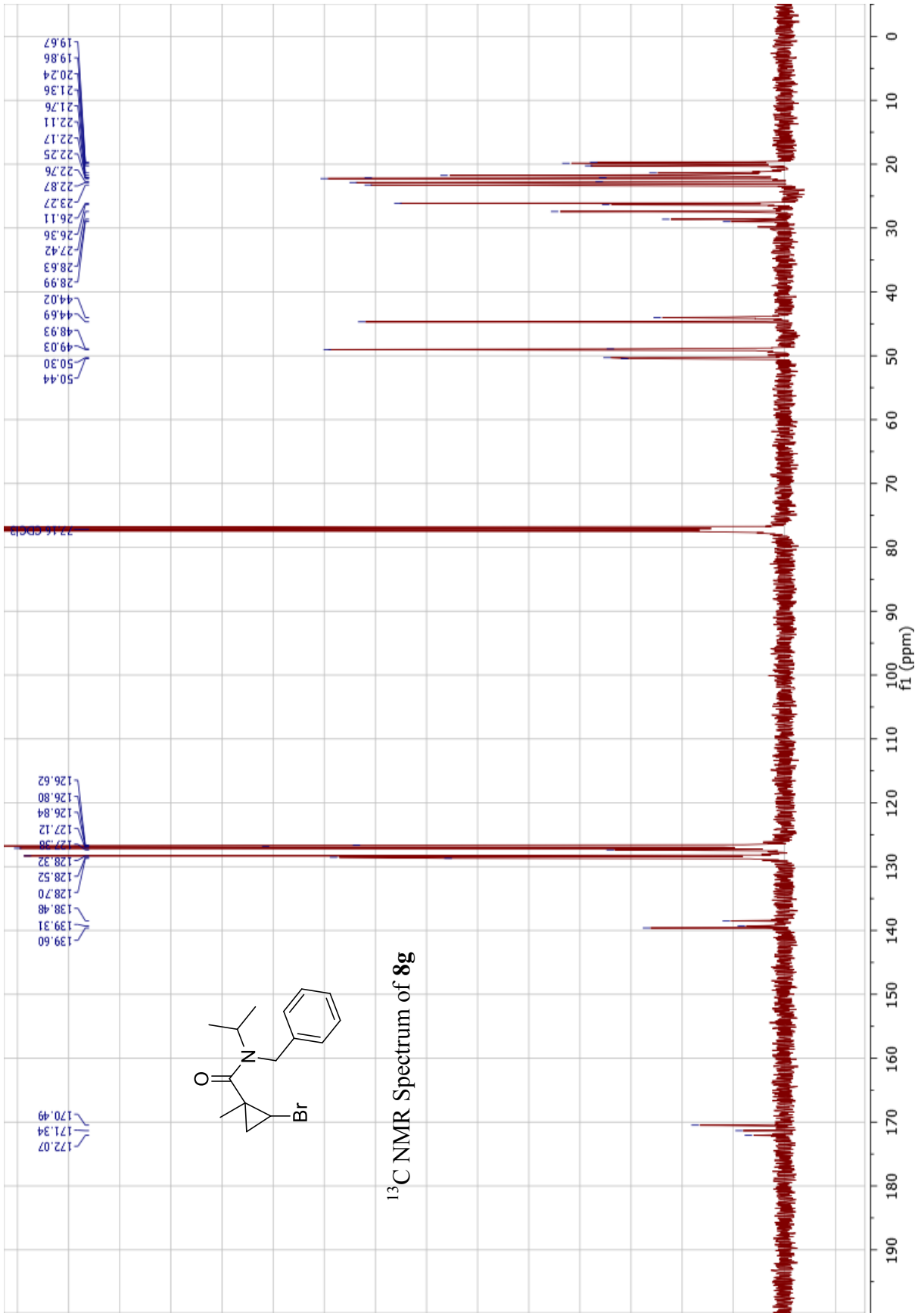
^{1}H NMR Spectrum of **8f**



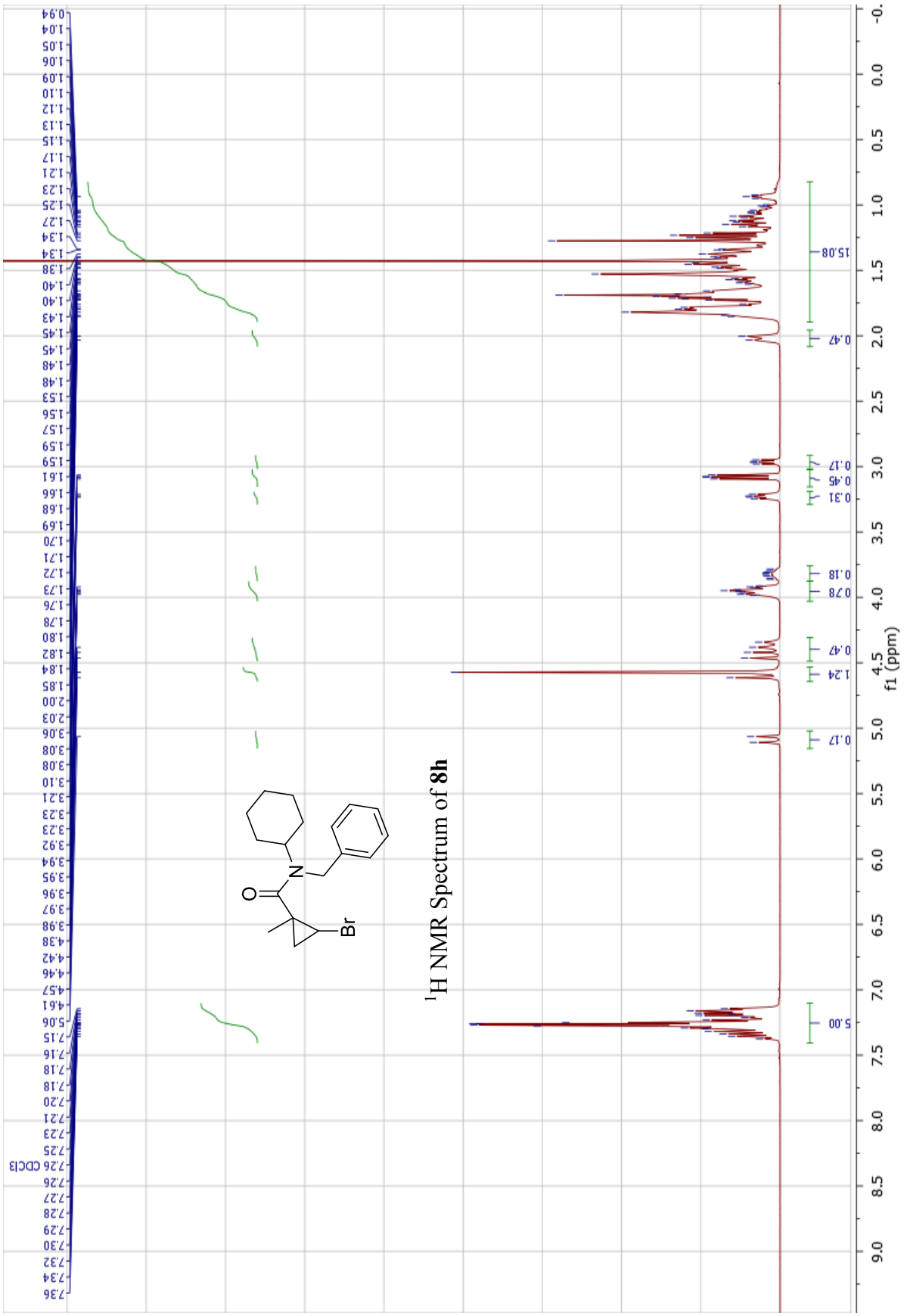
^{13}C NMR Spectrum of **8f**



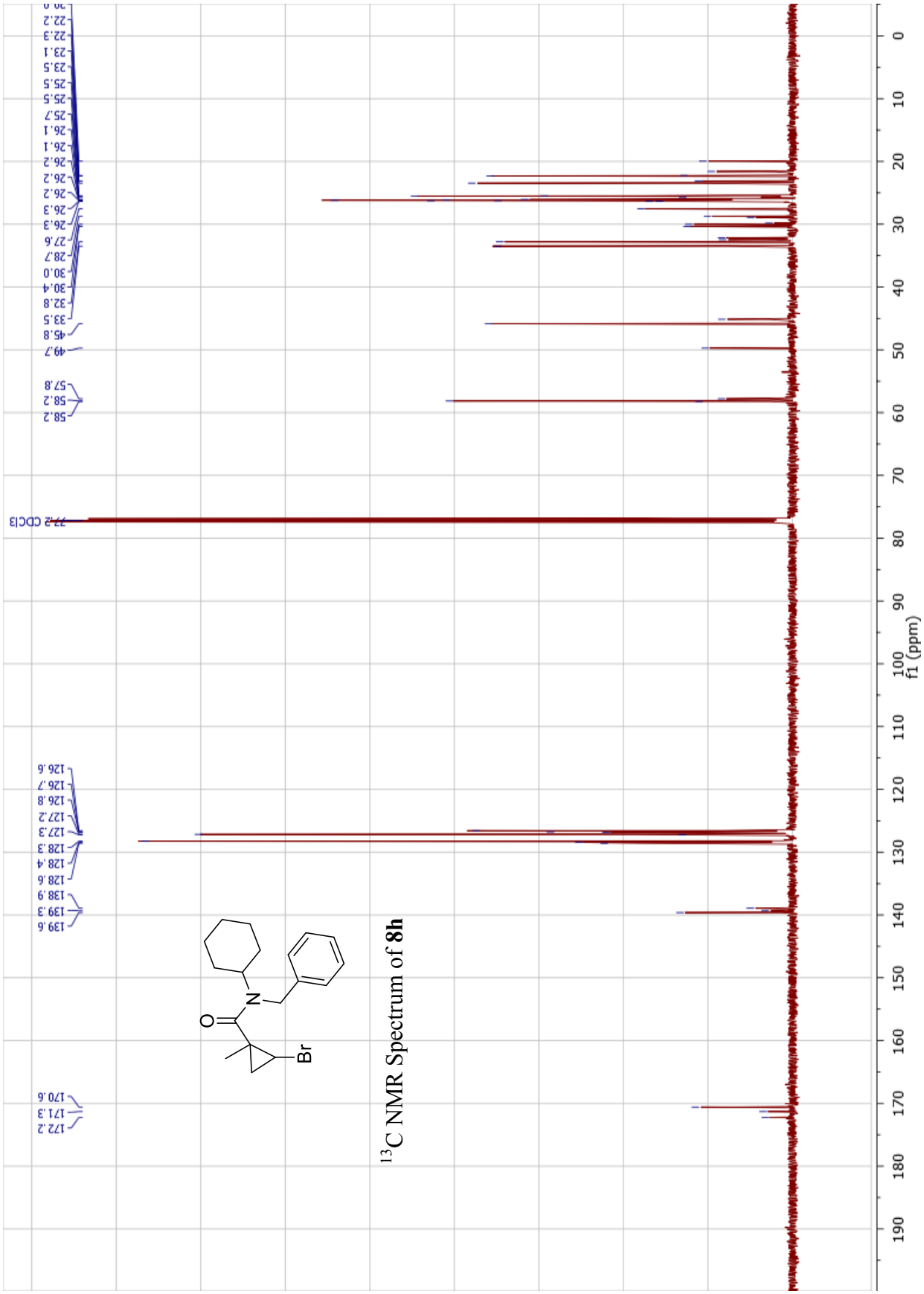
^{1}H NMR Spectrum of **8g**



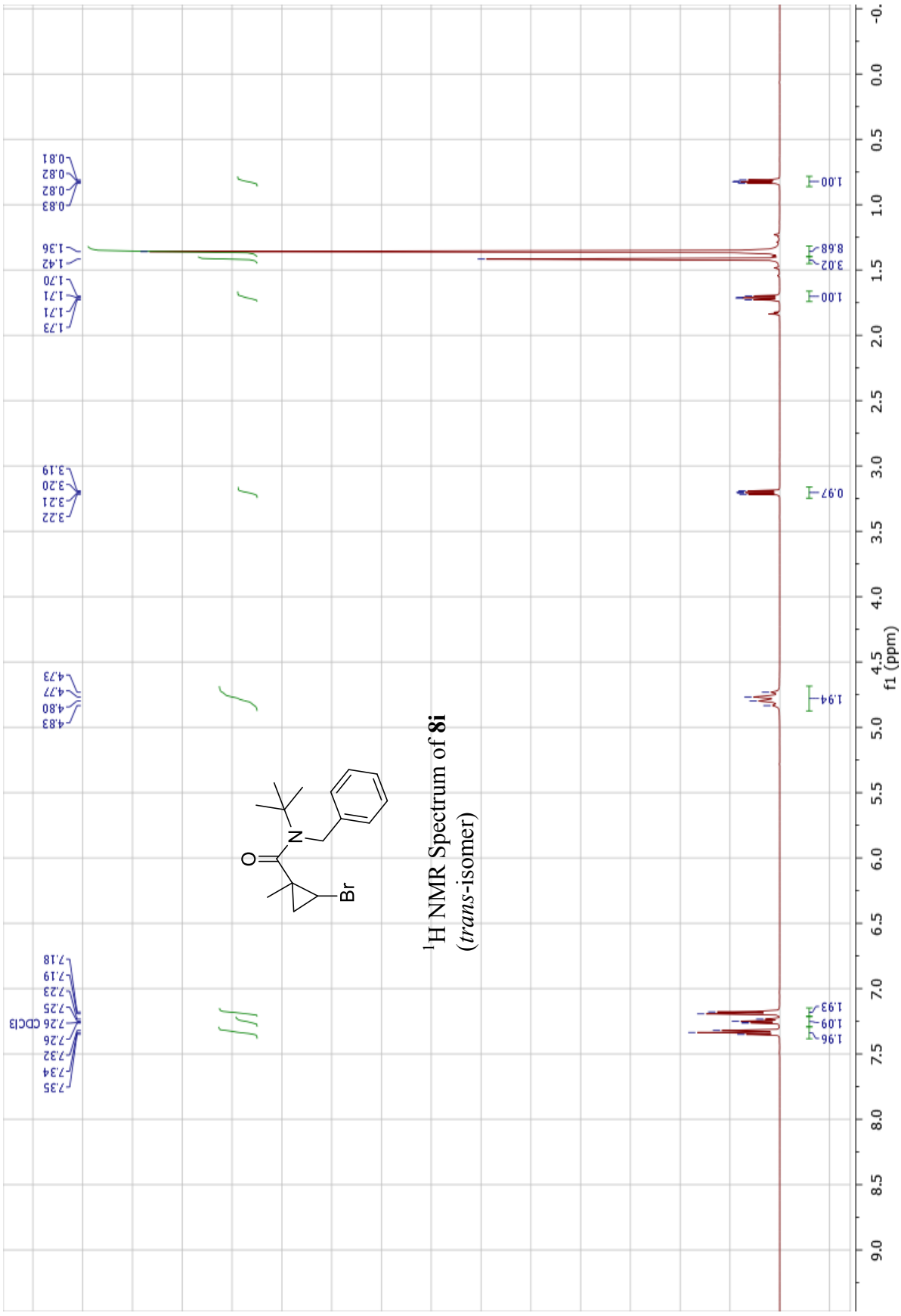
^{13}C NMR Spectrum of **8g**



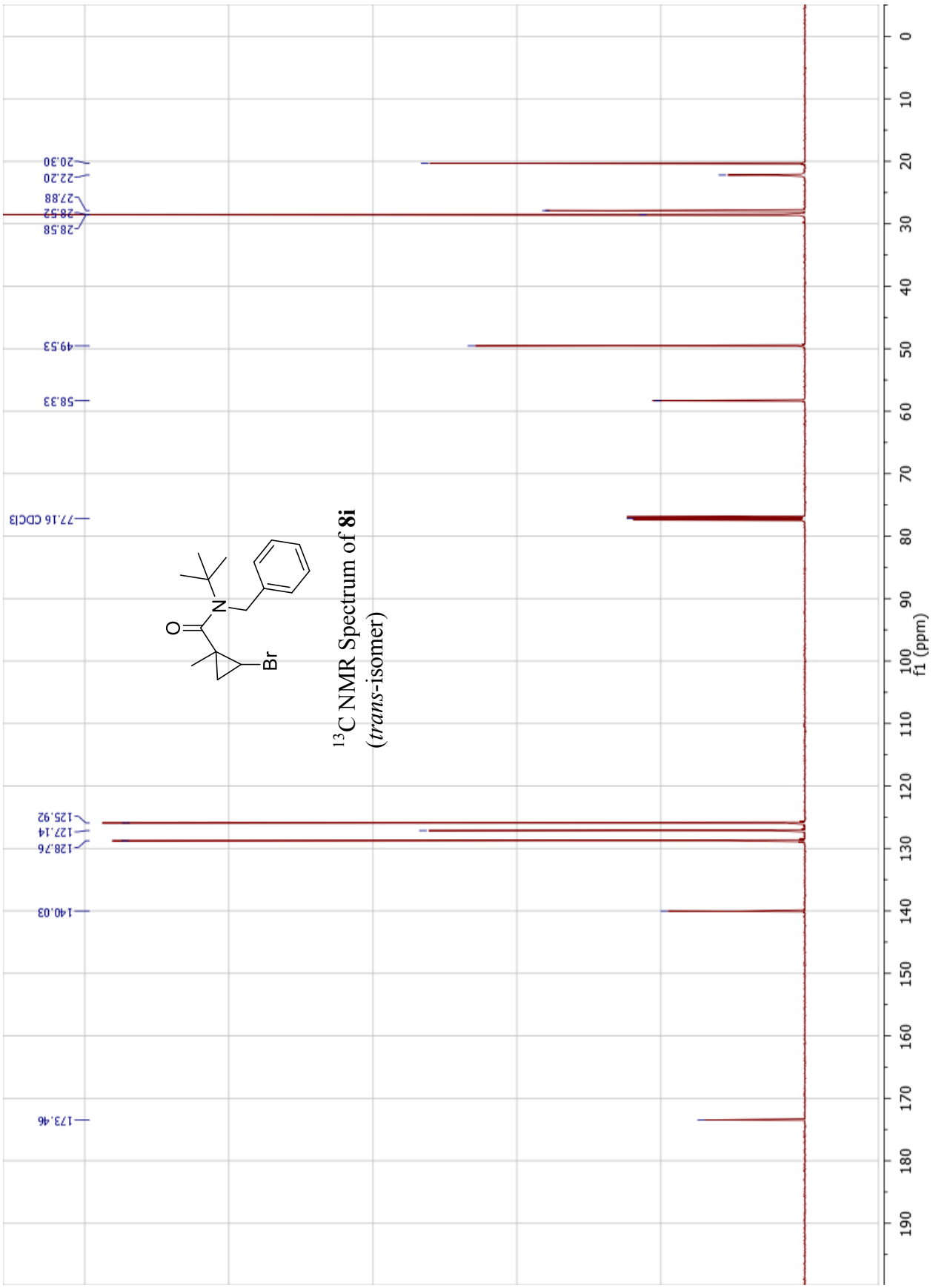
^{1}H NMR Spectrum of **8h**



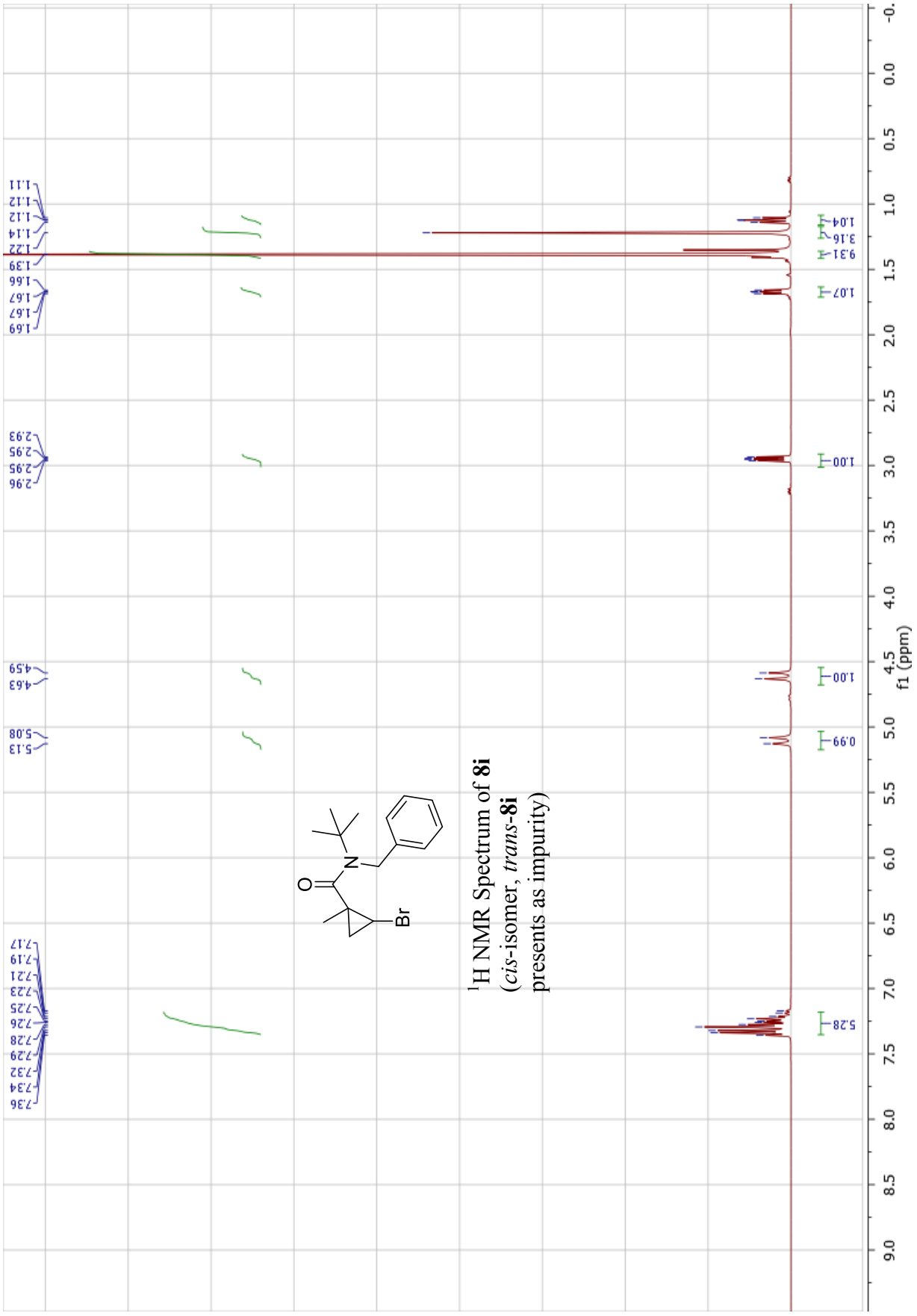
^{13}C NMR Spectrum of **8h**



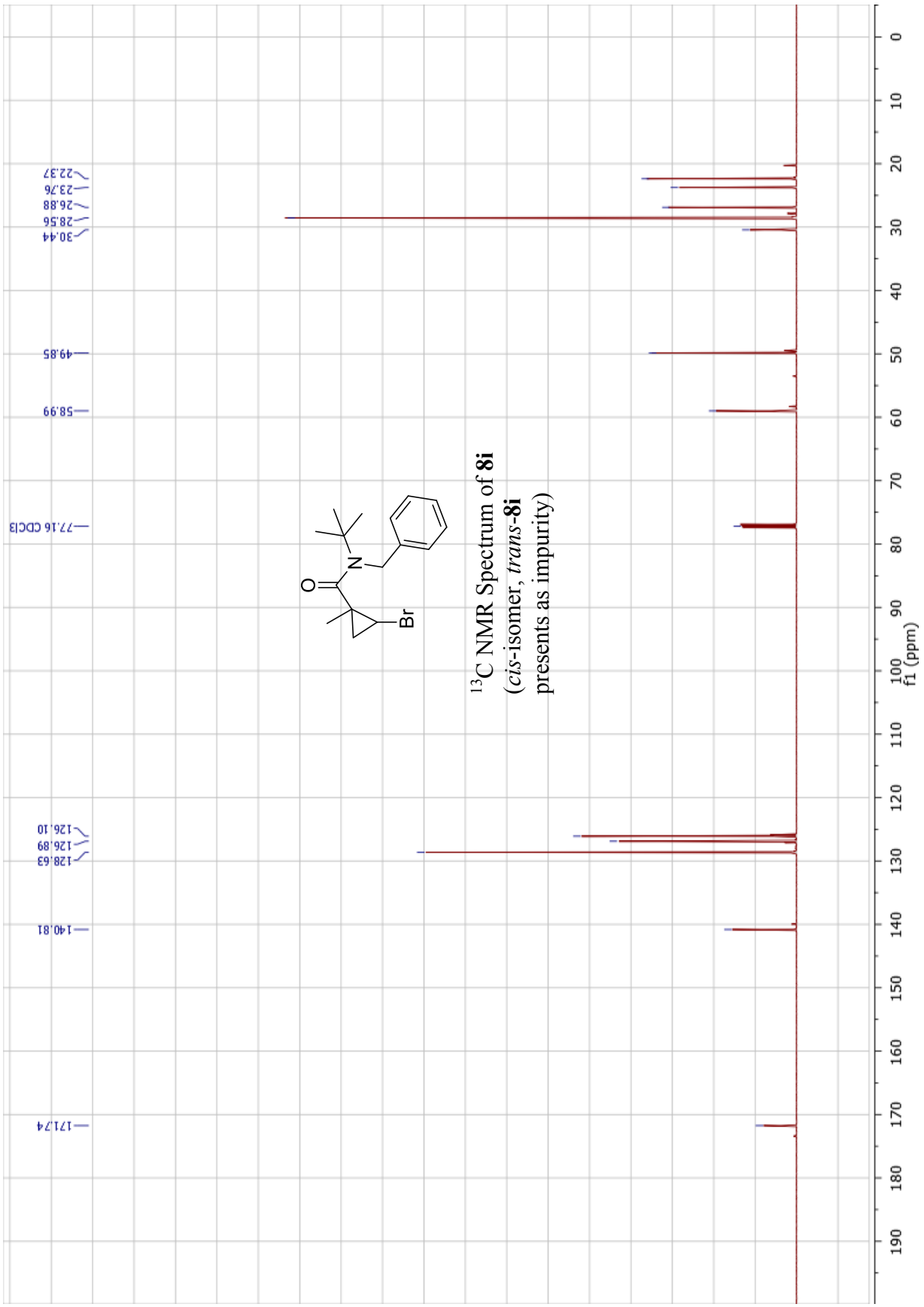
^{1}H NMR Spectrum of **8i**
(*trans*-isomer)



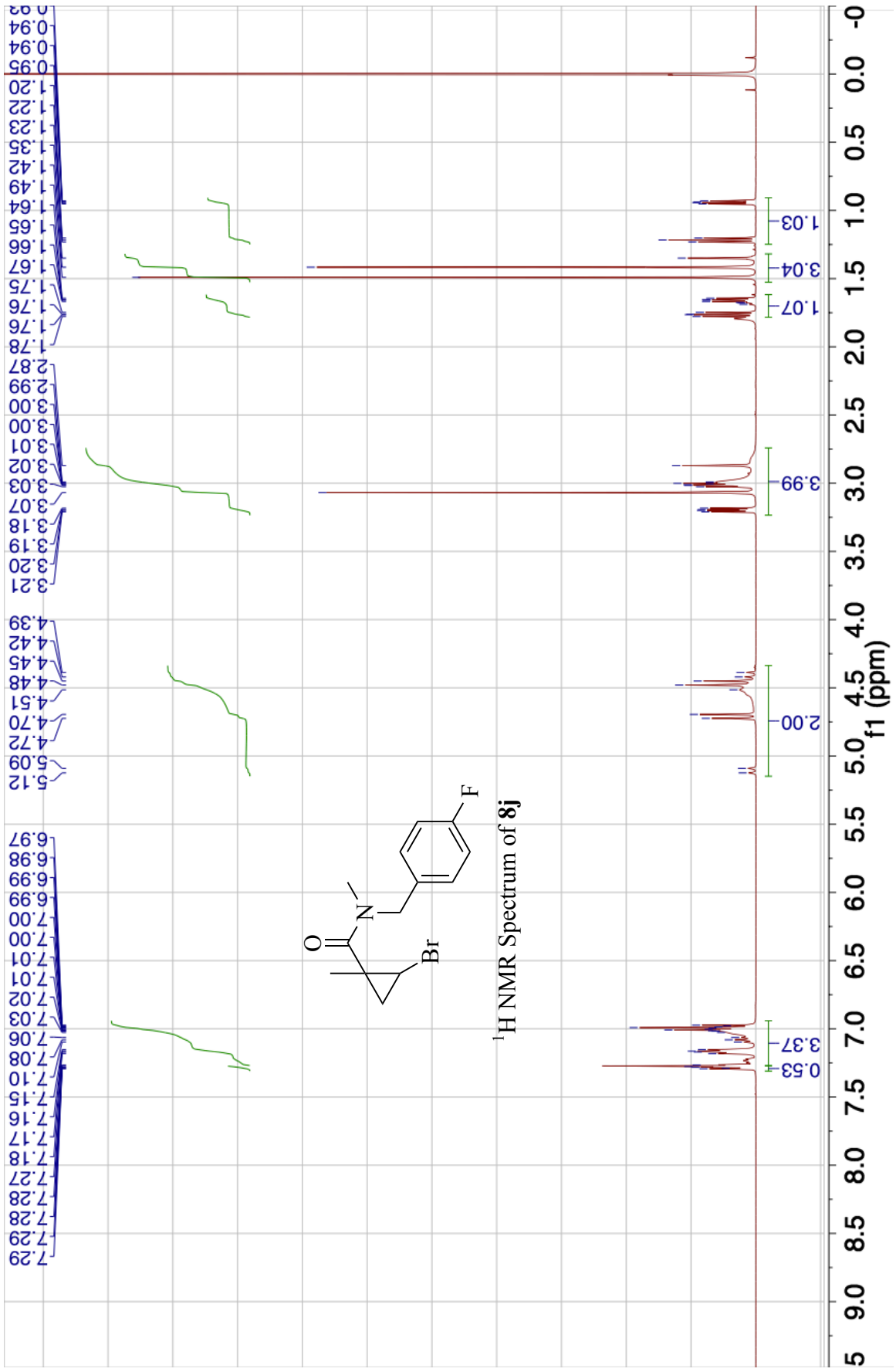
^{13}C NMR Spectrum of **8i**
(*trans*-isomer)



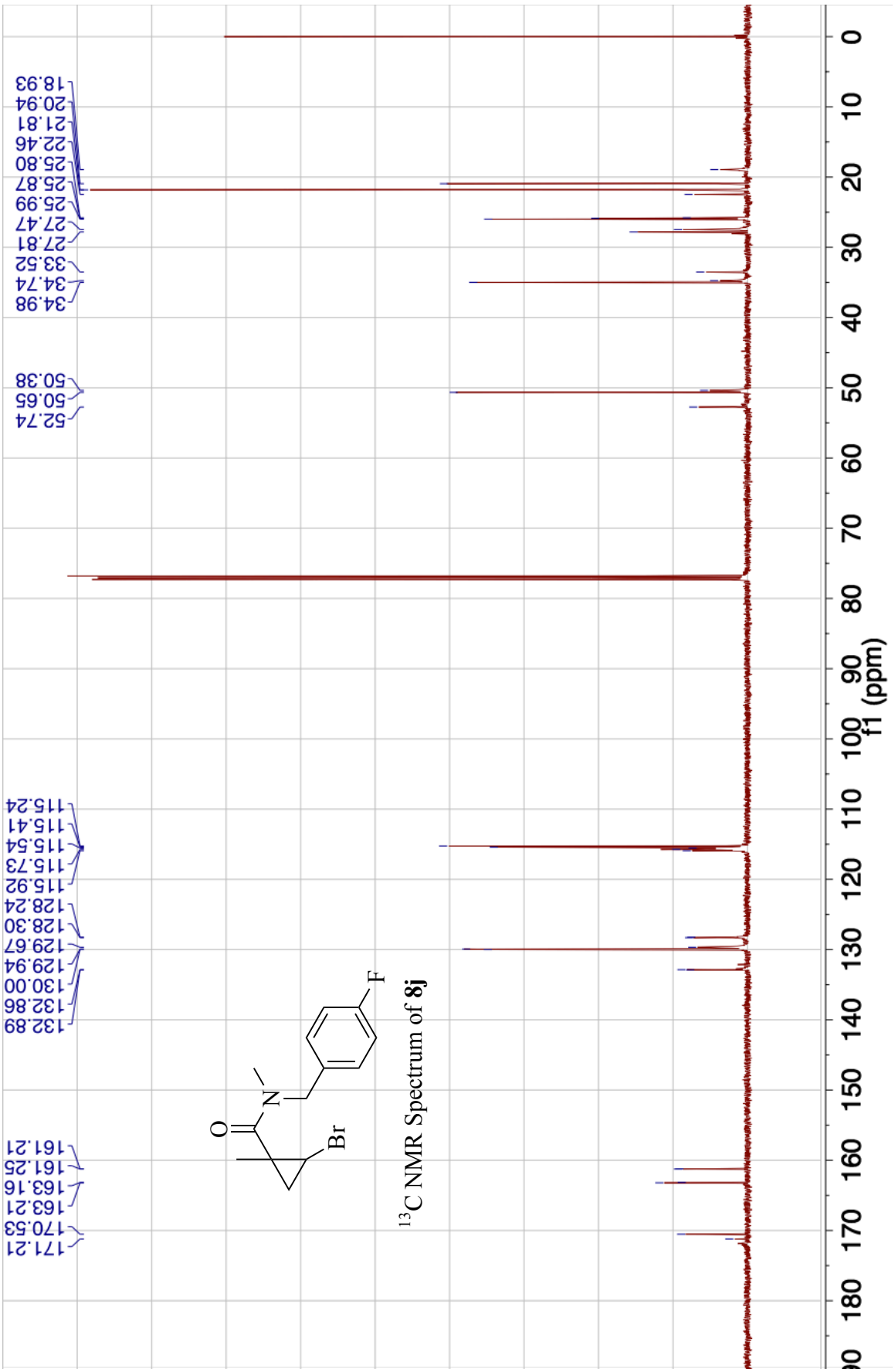
^{1}H NMR Spectrum of **8i**
(*cis*-isomer, *trans*-**8i**
presents as impurity)



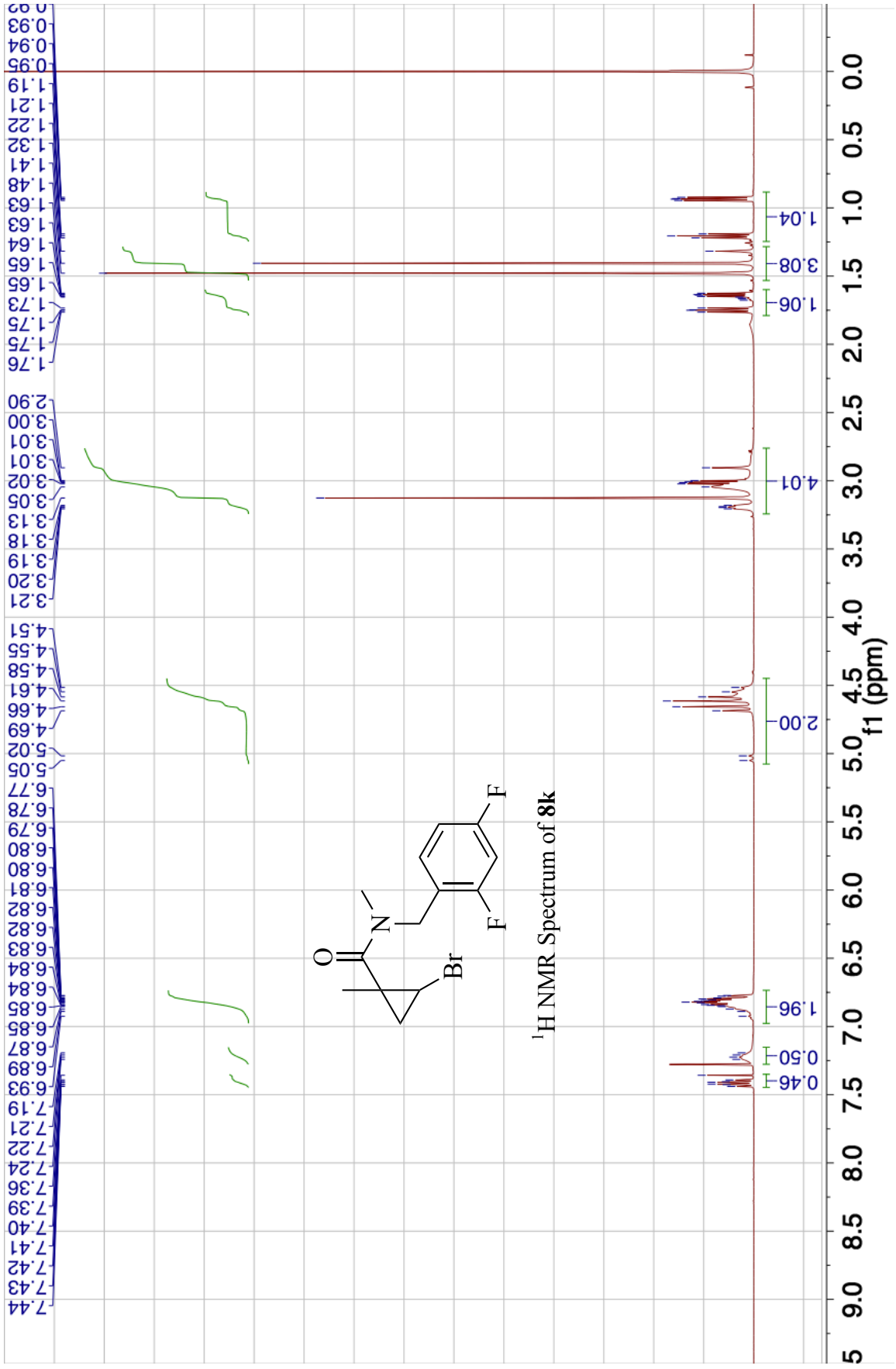
^{13}C NMR Spectrum of **8i**
(*cis*-isomer, *trans*-**8i**
presents as impurity)



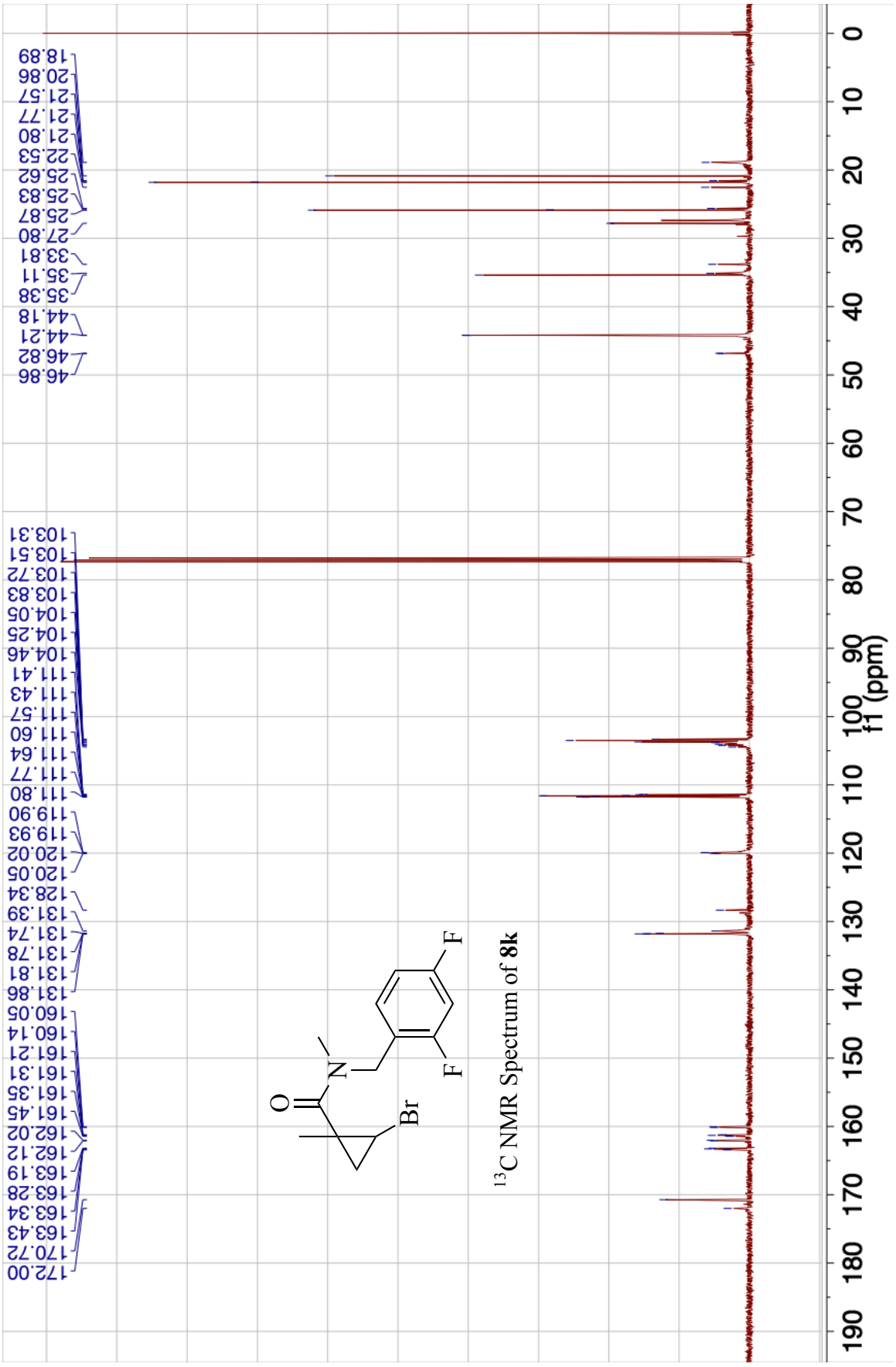
^{1}H NMR Spectrum of **8j**



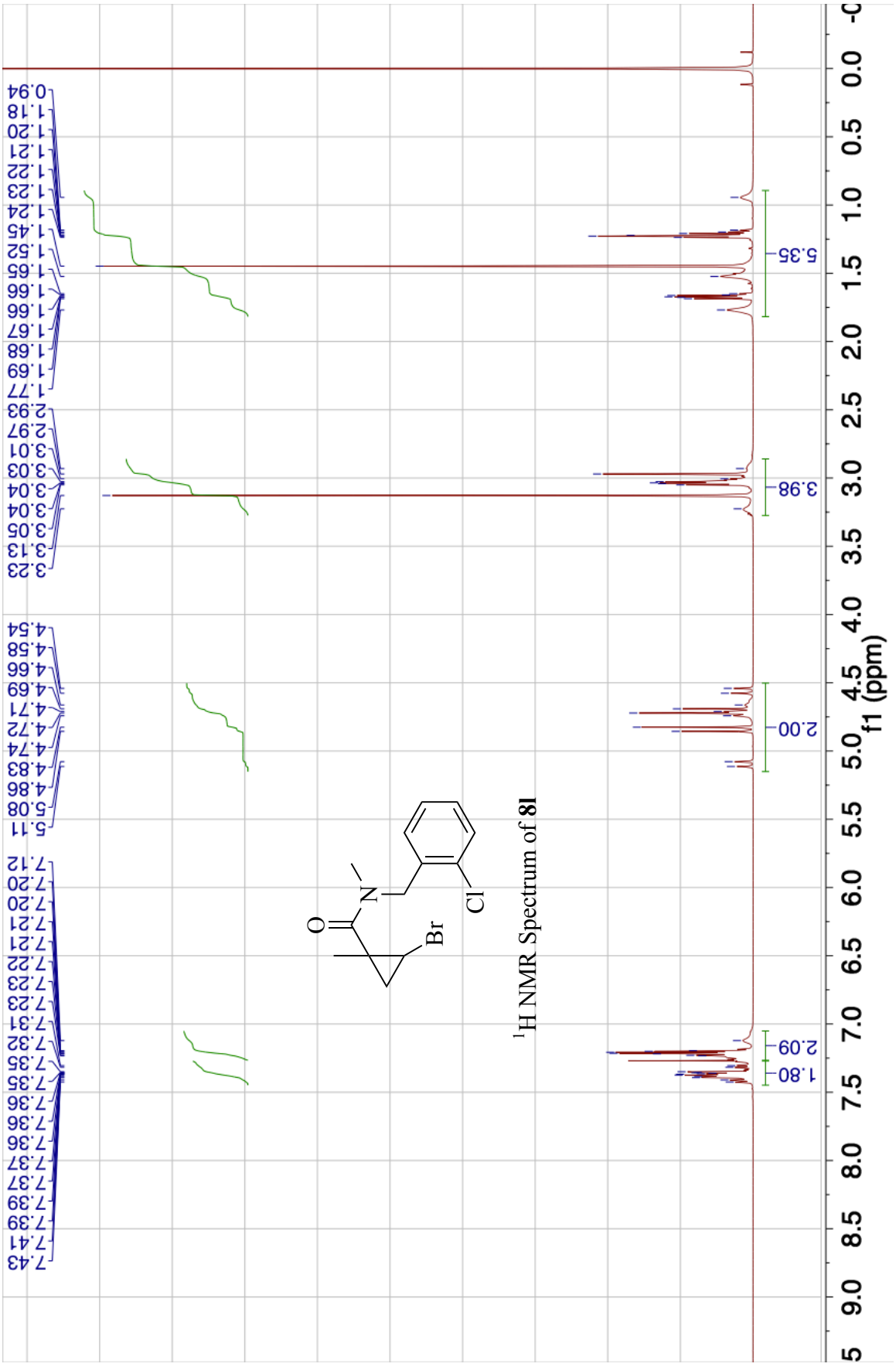
^{13}C NMR Spectrum of **8j**



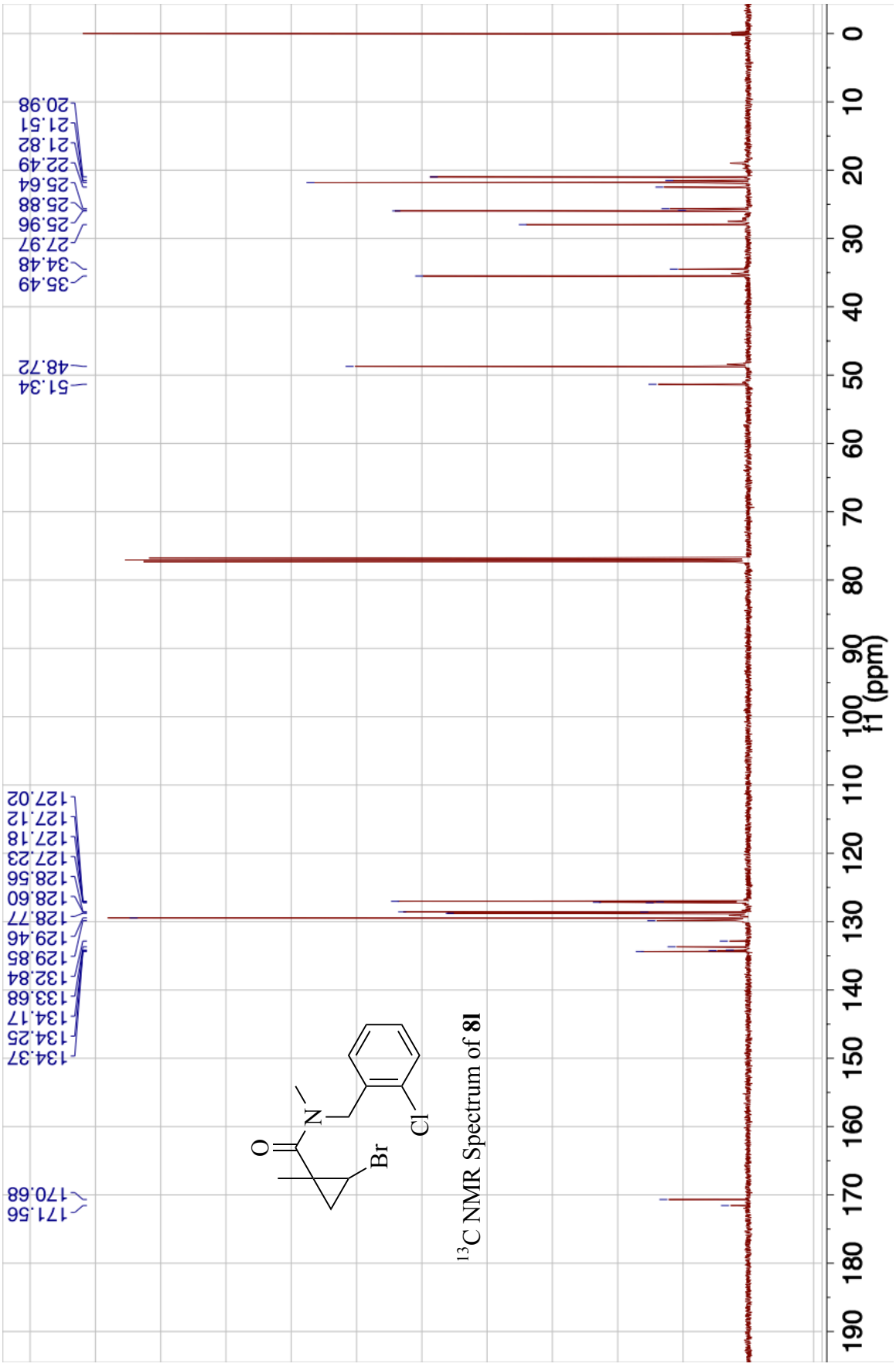
^{1}H NMR Spectrum of **8k**



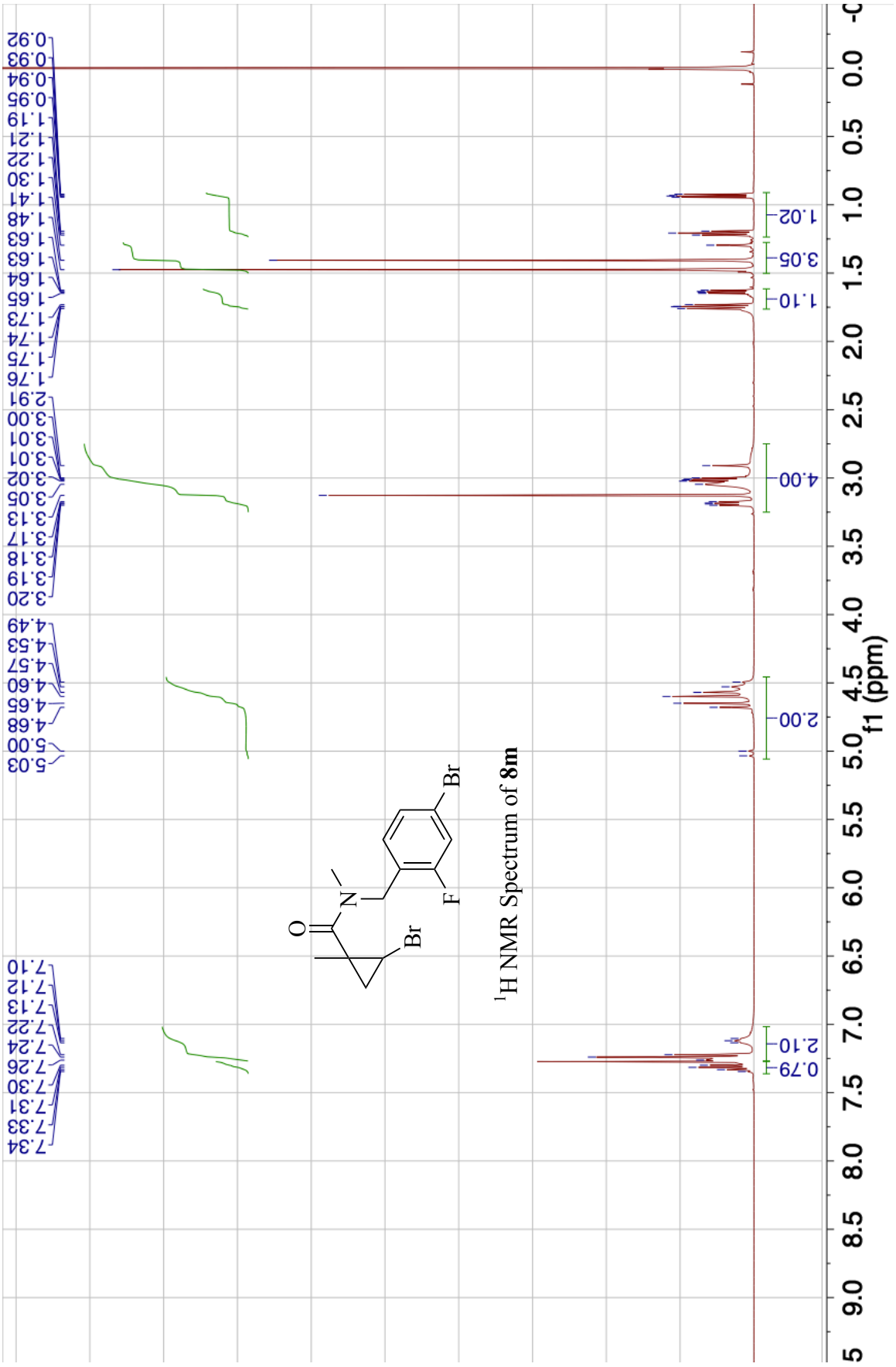
^{13}C NMR Spectrum of **8k**



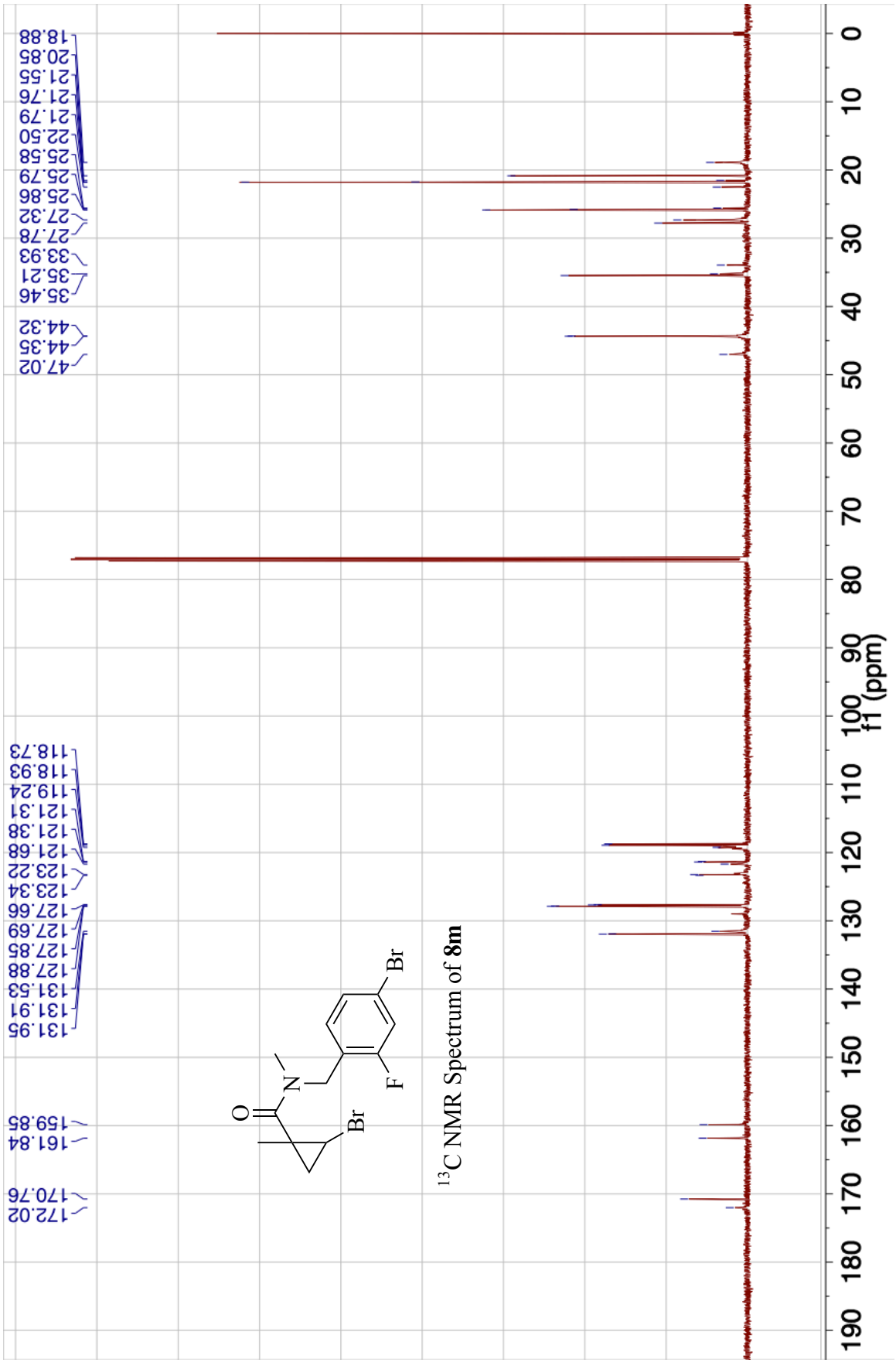
^{1}H NMR Spectrum of **8l**



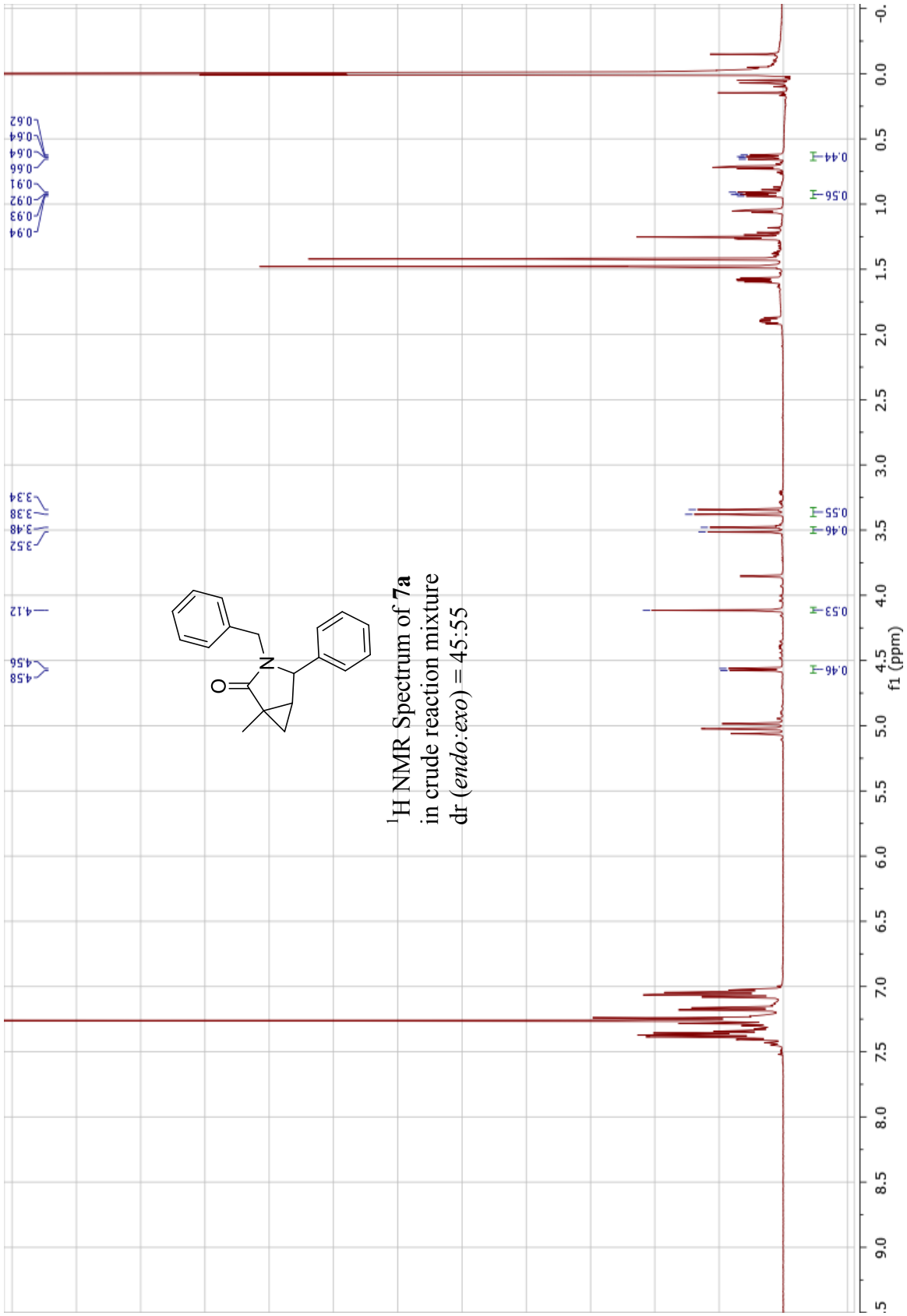
^{13}C NMR Spectrum of **8l**



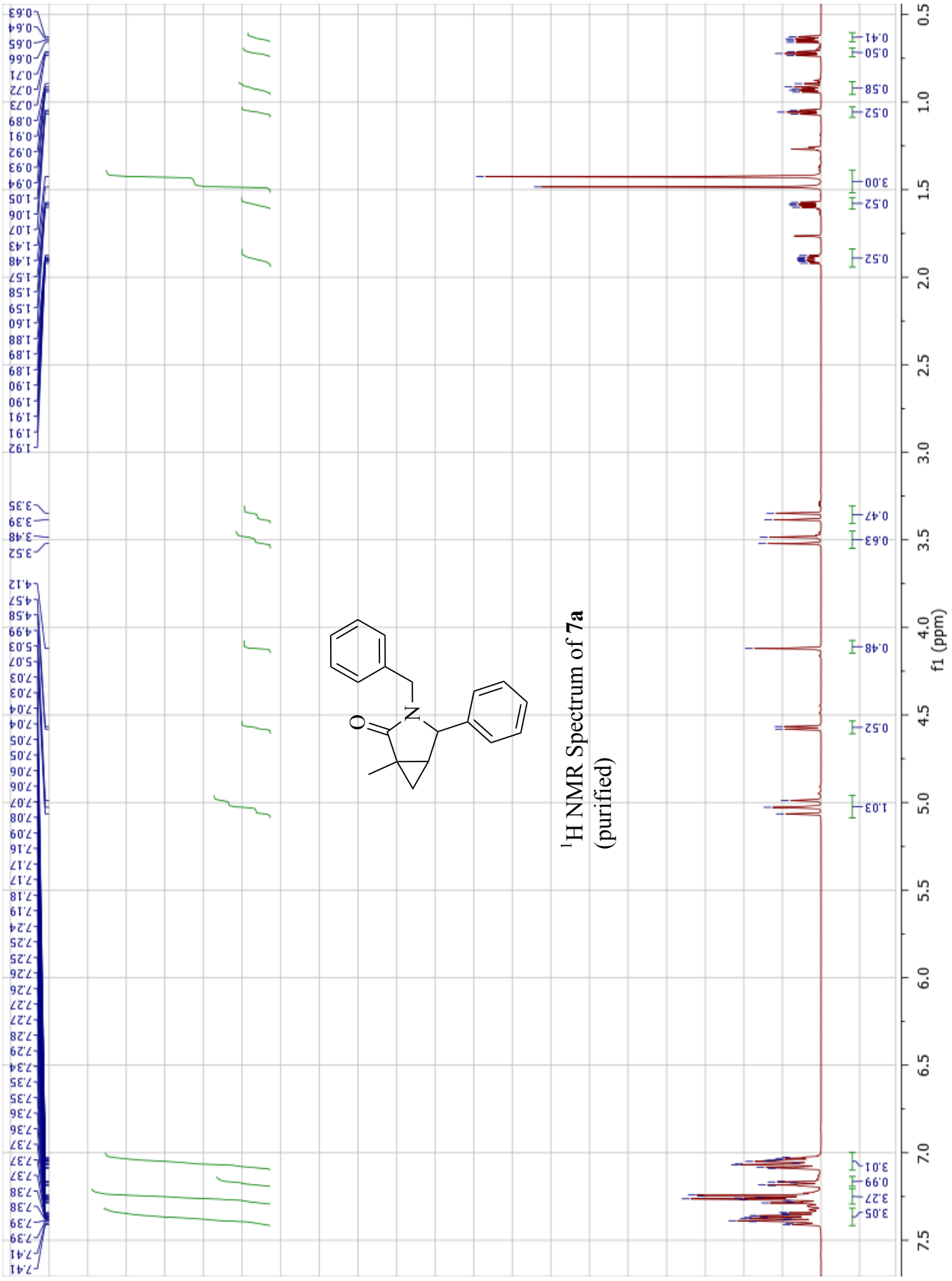
^{1}H NMR Spectrum of **8m**



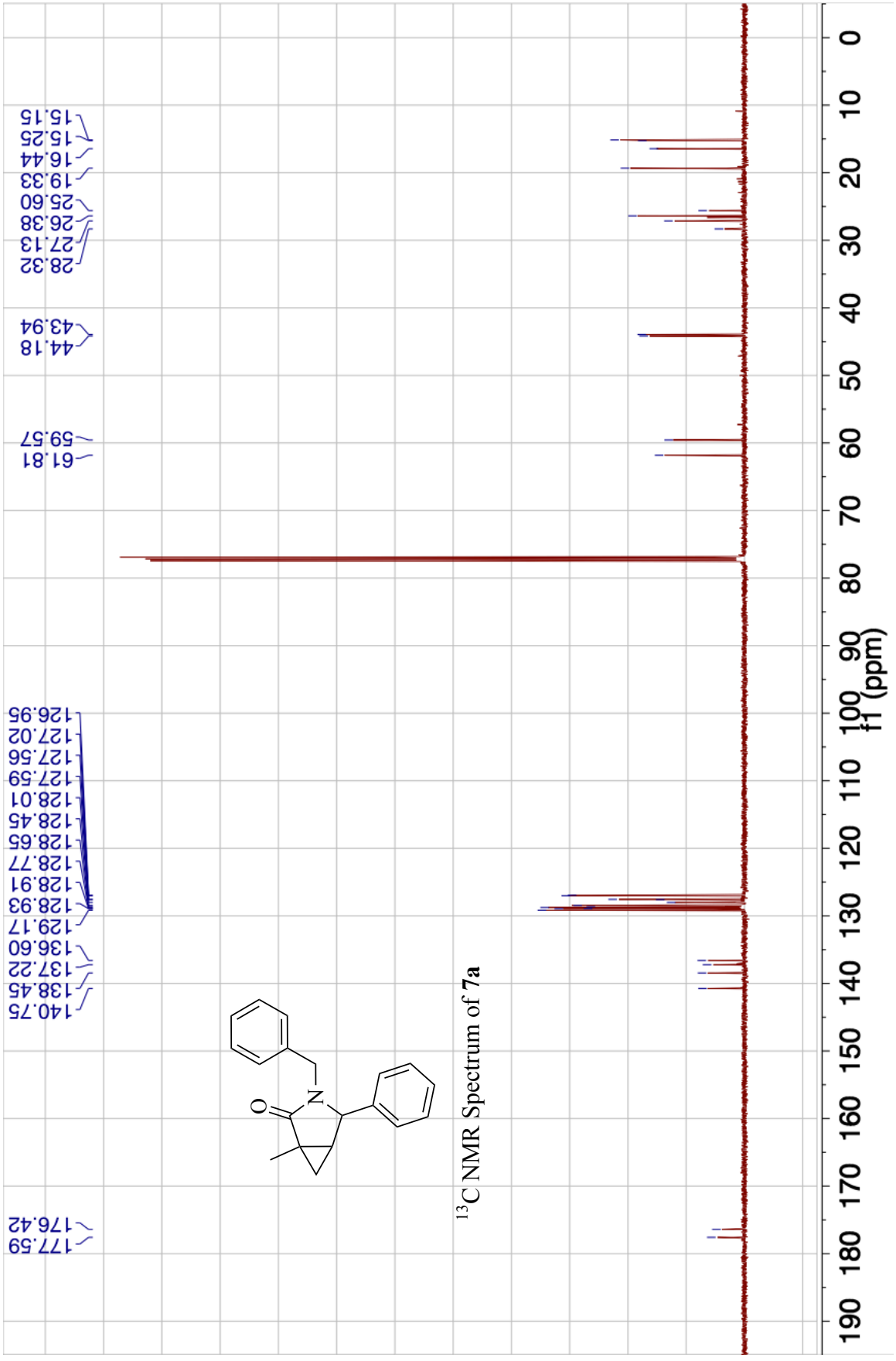
^{13}C NMR Spectrum of **8m**



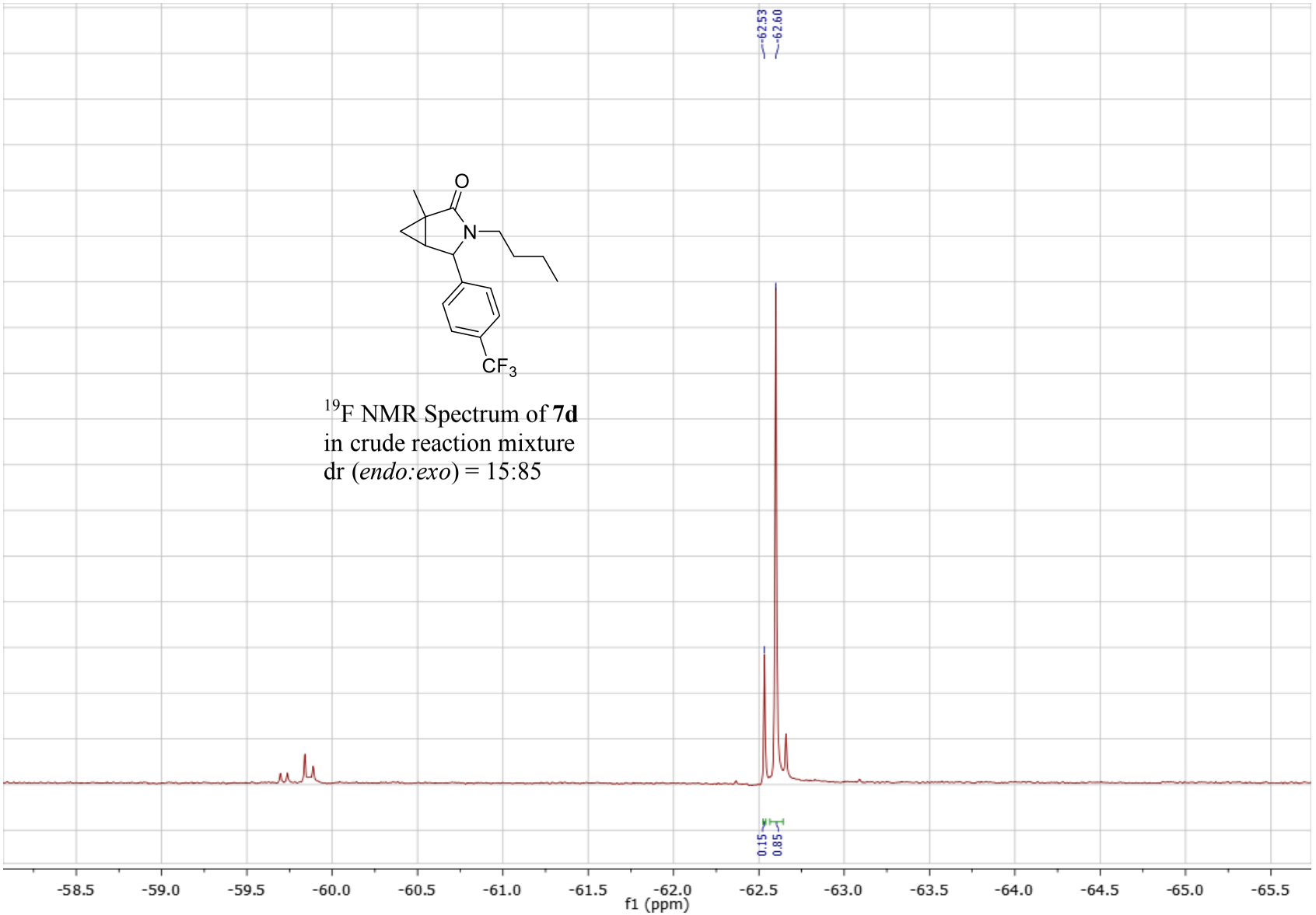
^{1}H NMR Spectrum of **7a**
in crude reaction mixture
dr (*endo*:*exo*) = 45:55



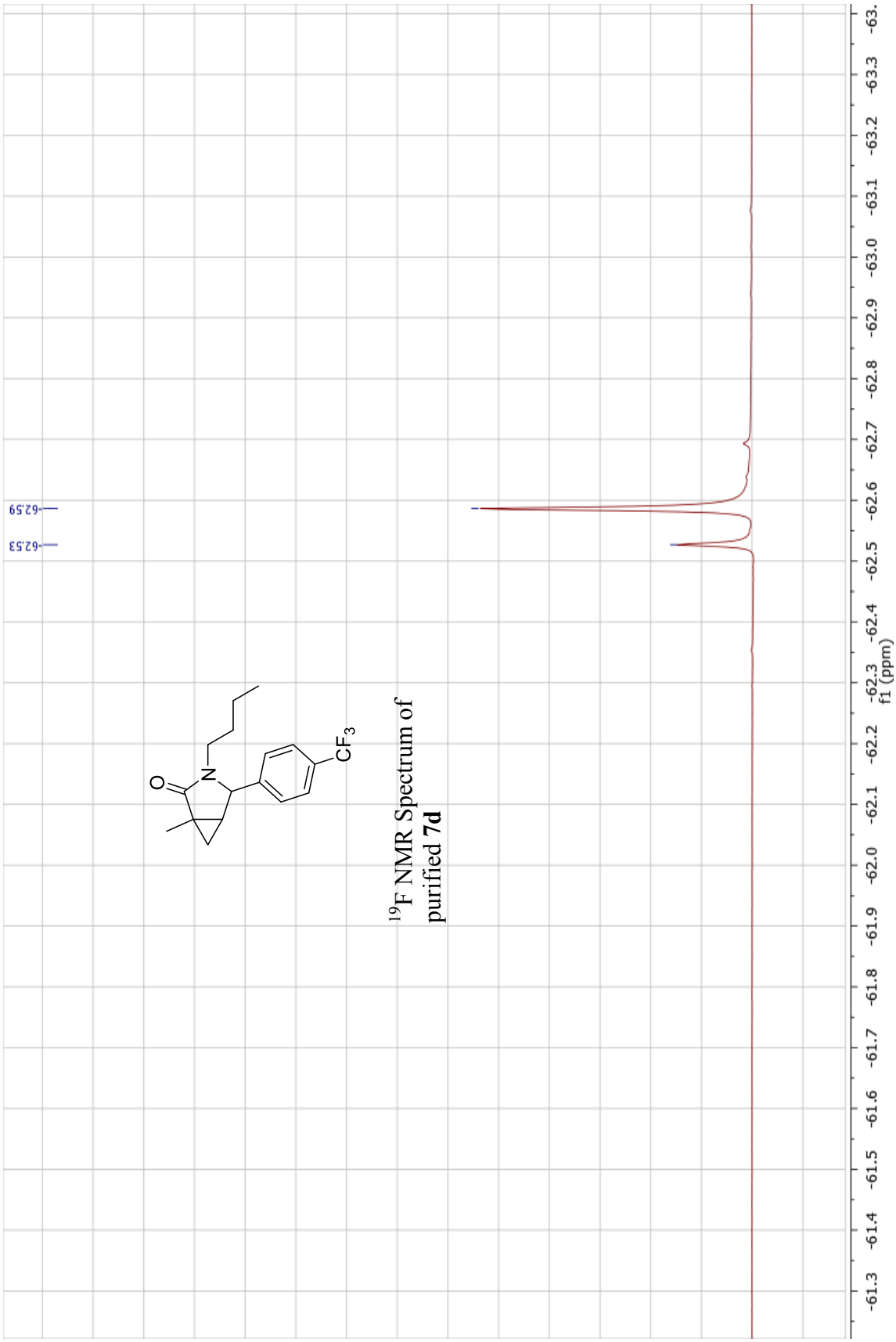
^{1}H NMR Spectrum of **7a**
(purified)



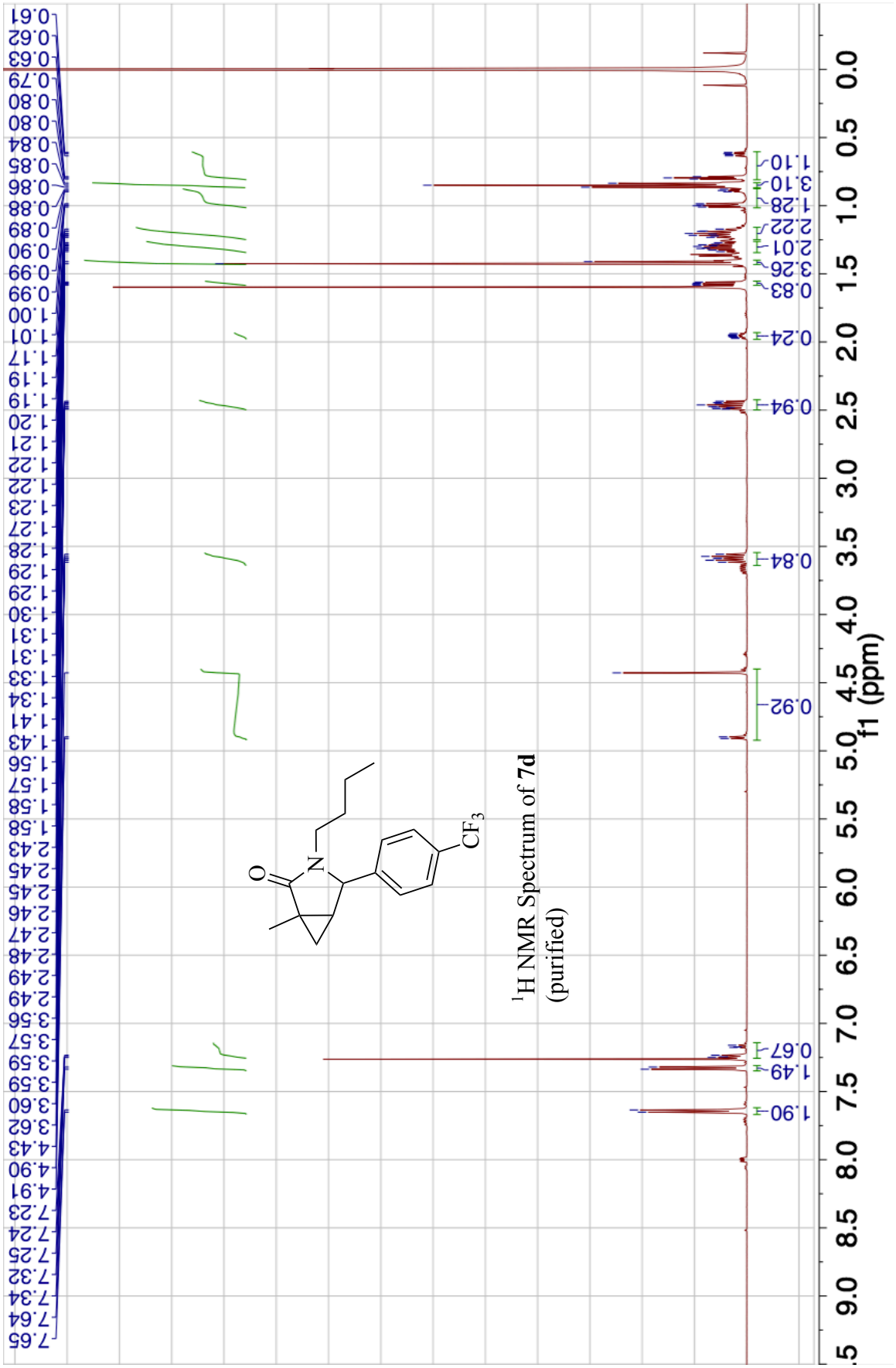
^{13}C NMR Spectrum of **7a**

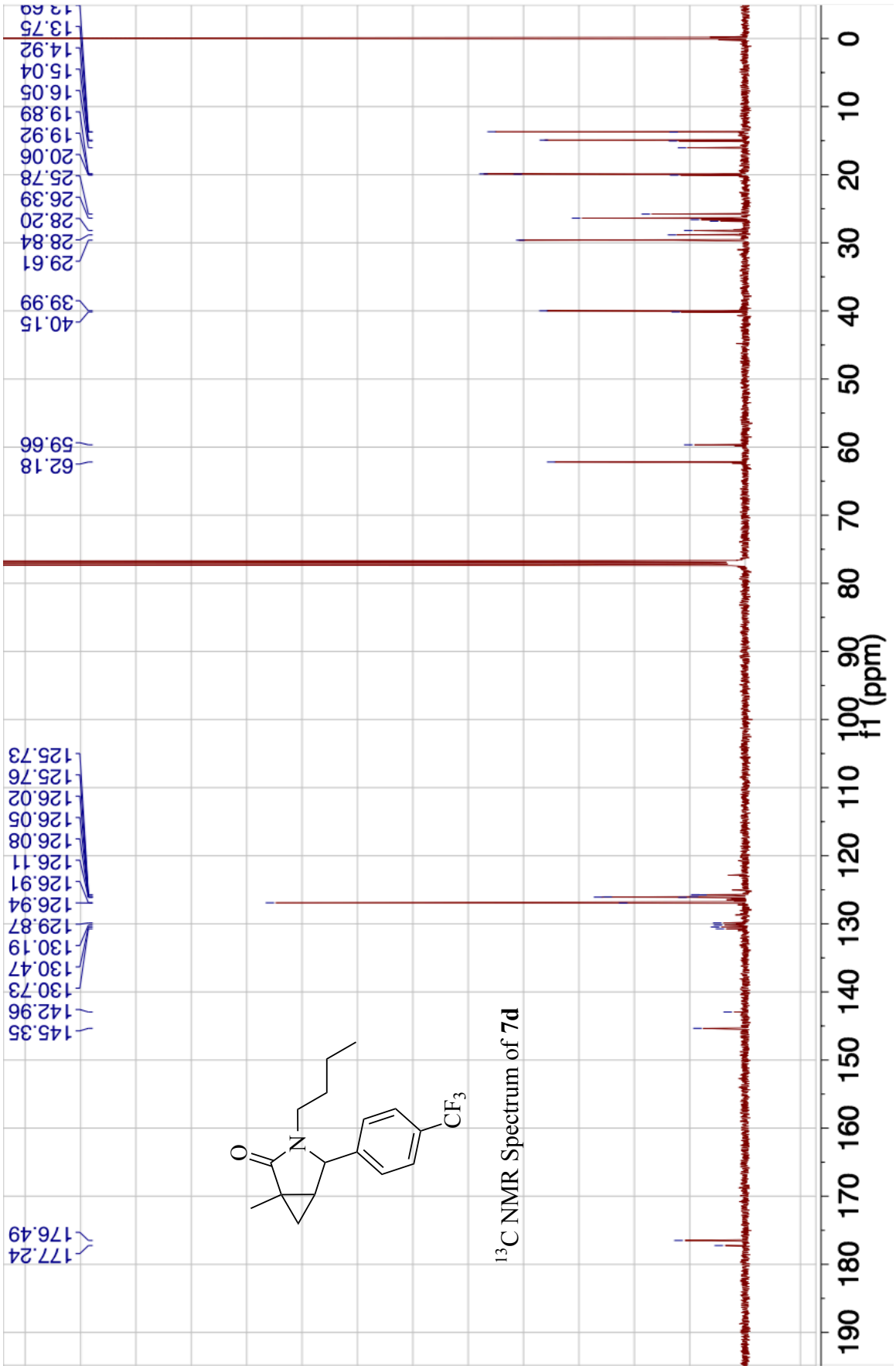


^{19}F NMR Spectrum of **7d**
in crude reaction mixture
dr (*endo:exo*) = 15:85

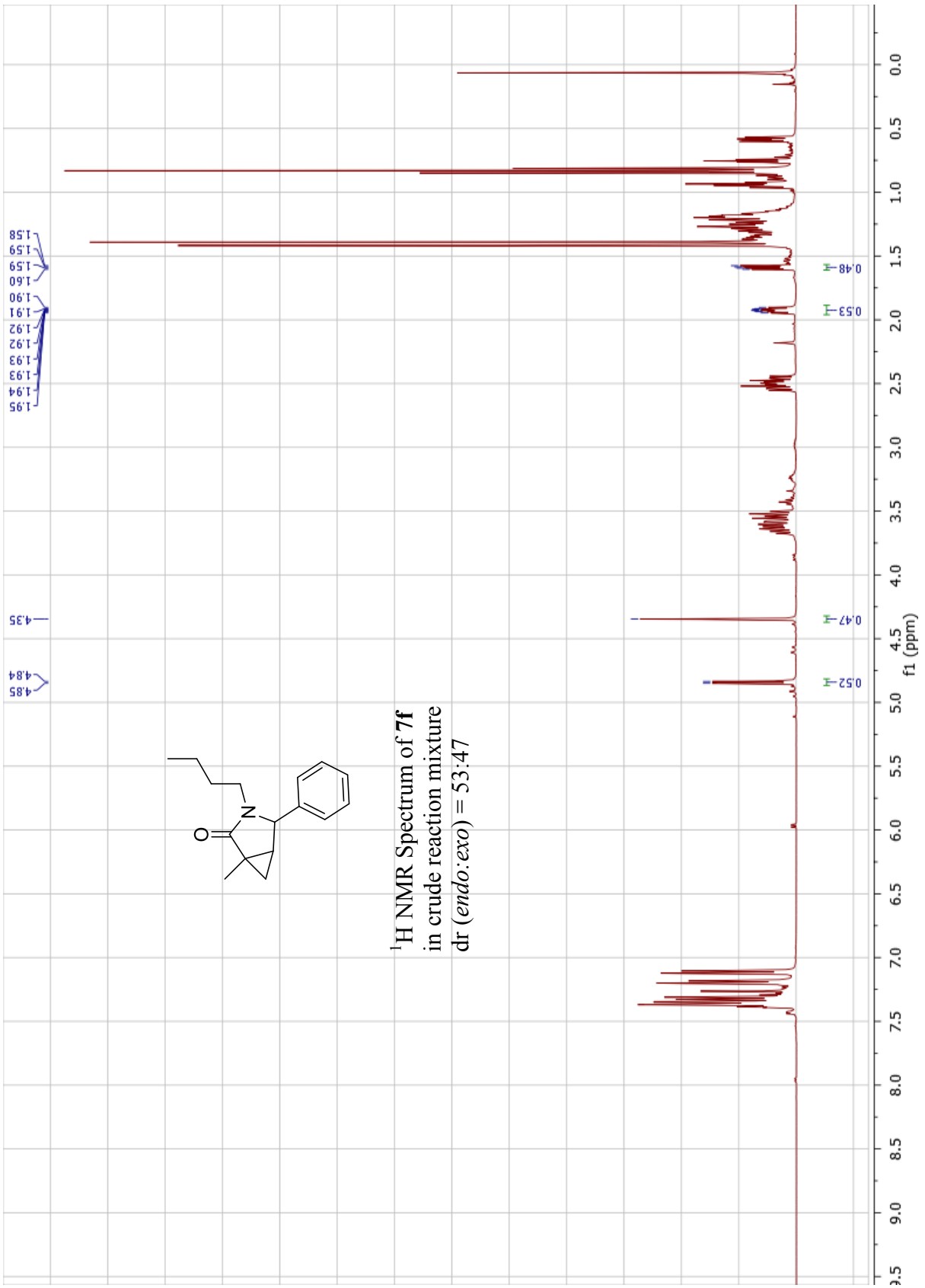


^{19}F NMR Spectrum of purified **7d**

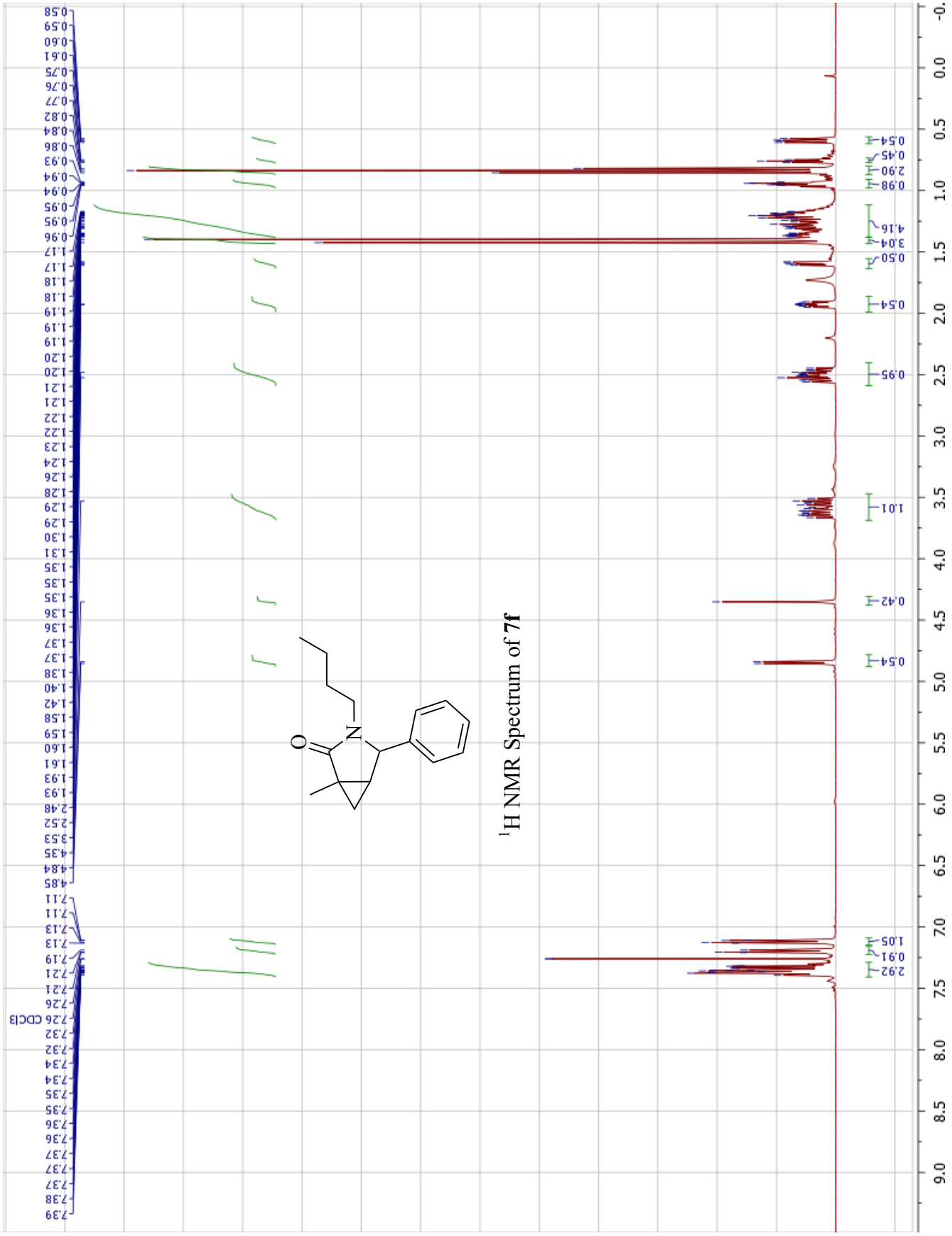

O
N
CF3
1H NMR Spectrum of 7d
(purified)
f1 (ppm)



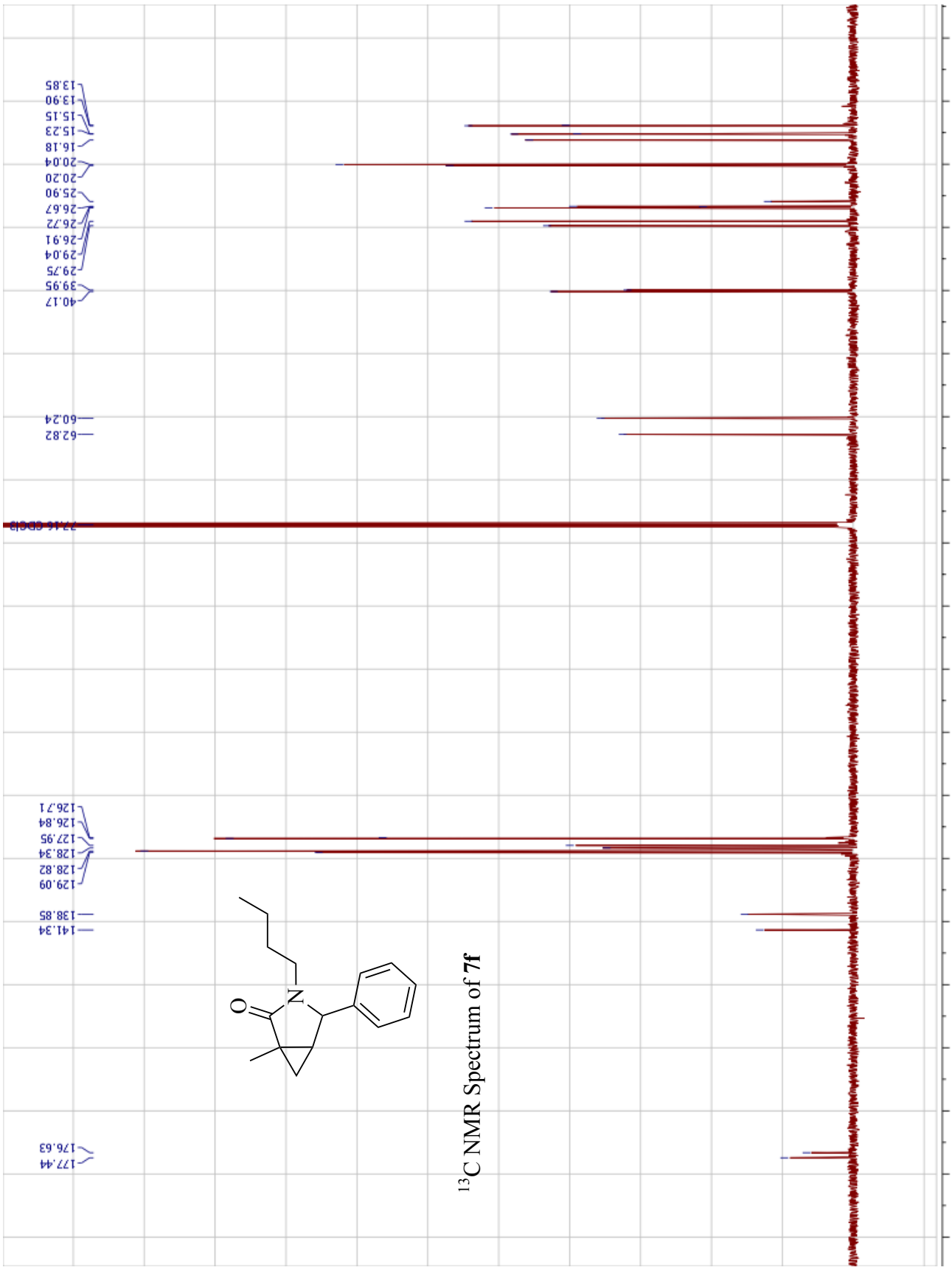
^{13}C NMR Spectrum of **7d**



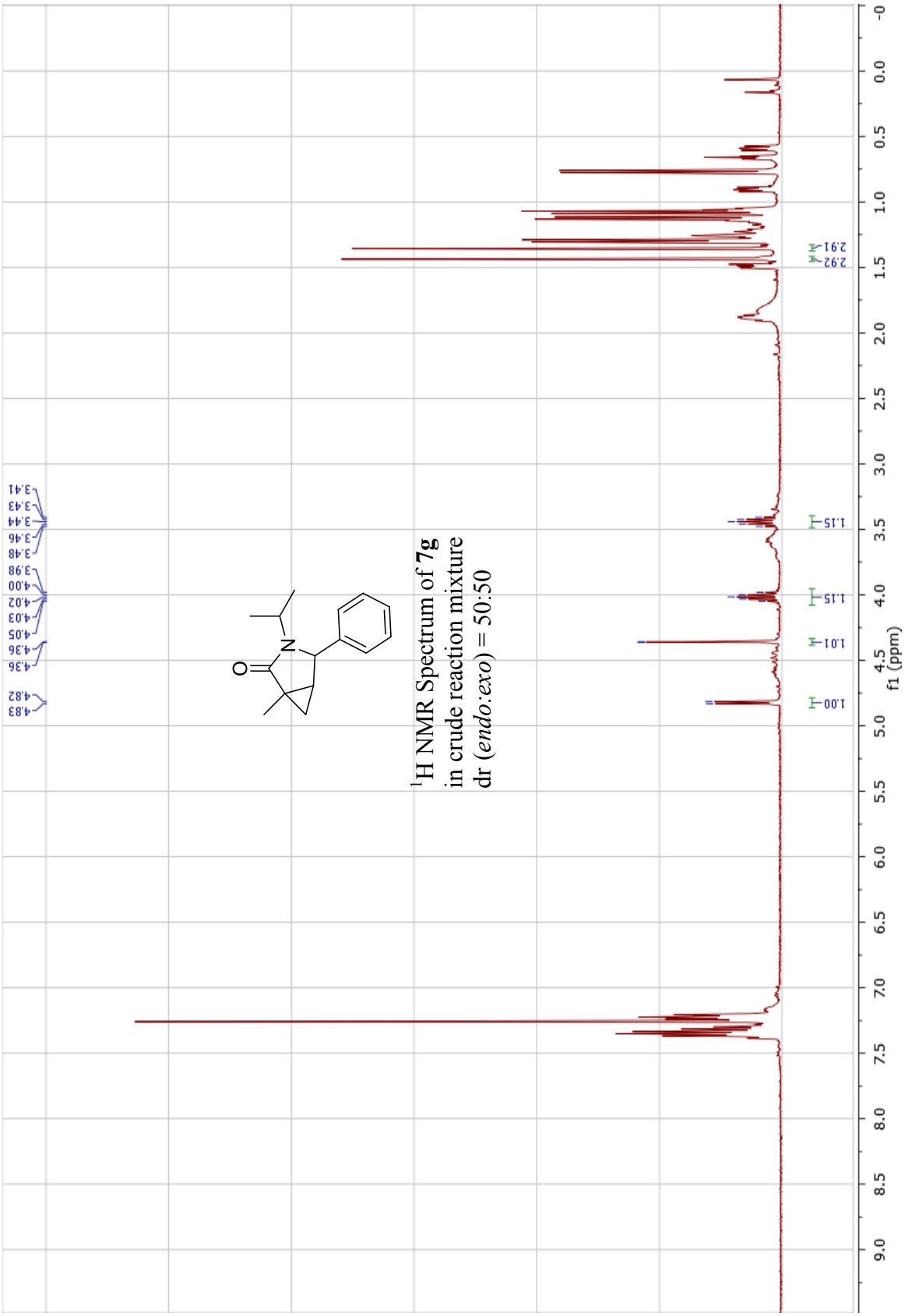
^{1}H NMR Spectrum of **7f**
in crude reaction mixture
dr (*endo:exo*) = 53:47

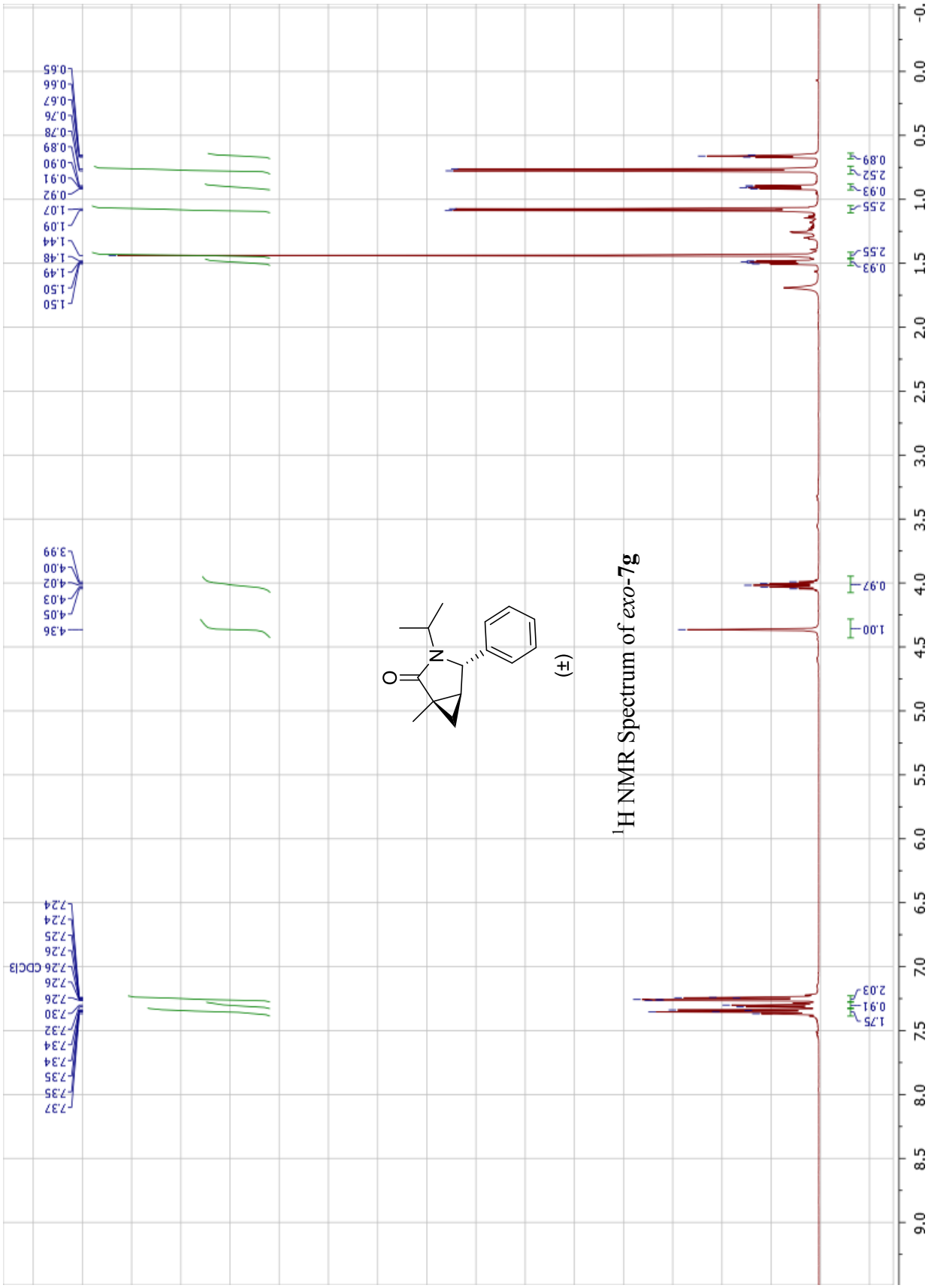


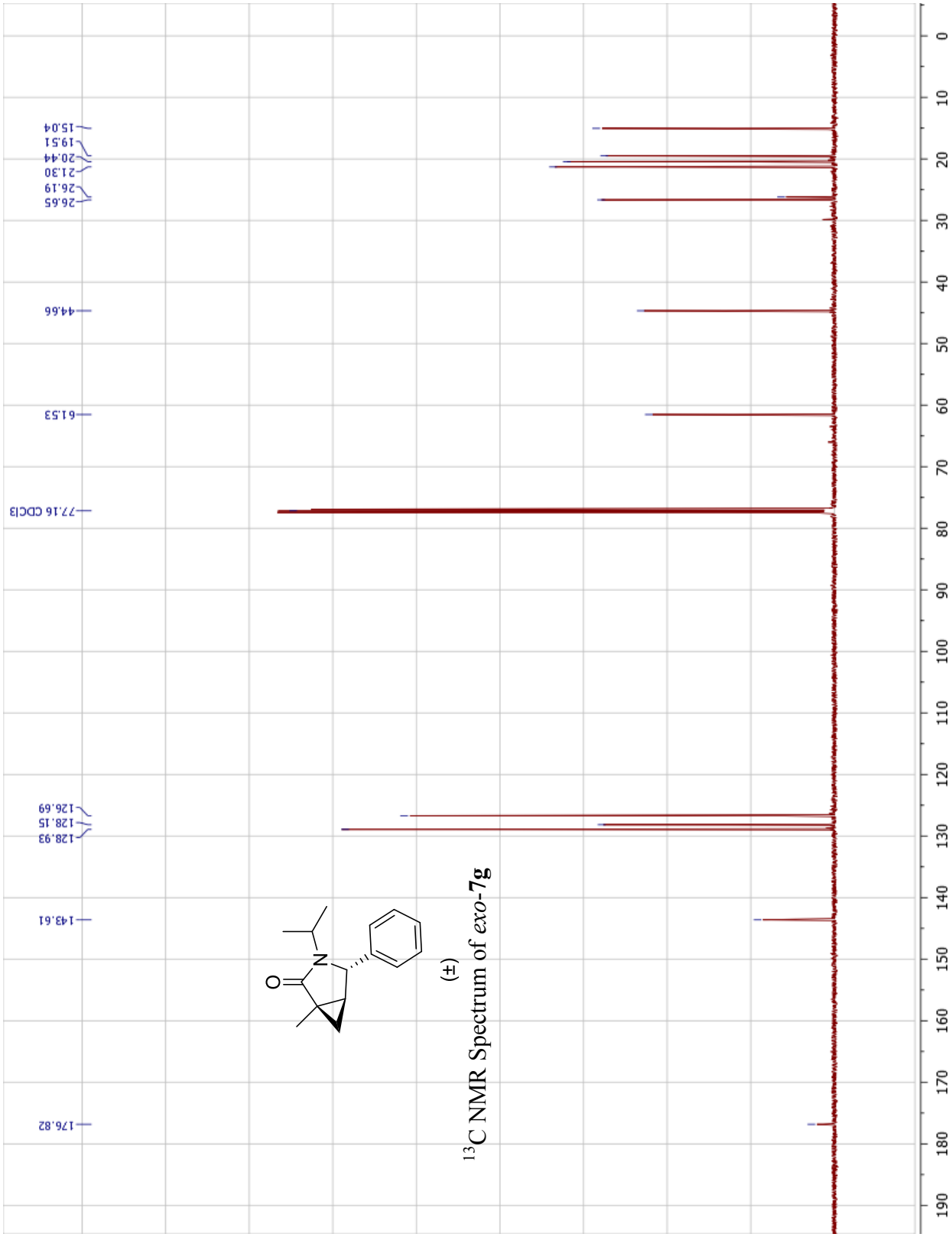
^{1}H NMR Spectrum of **7f**



^{13}C NMR Spectrum of **7f**

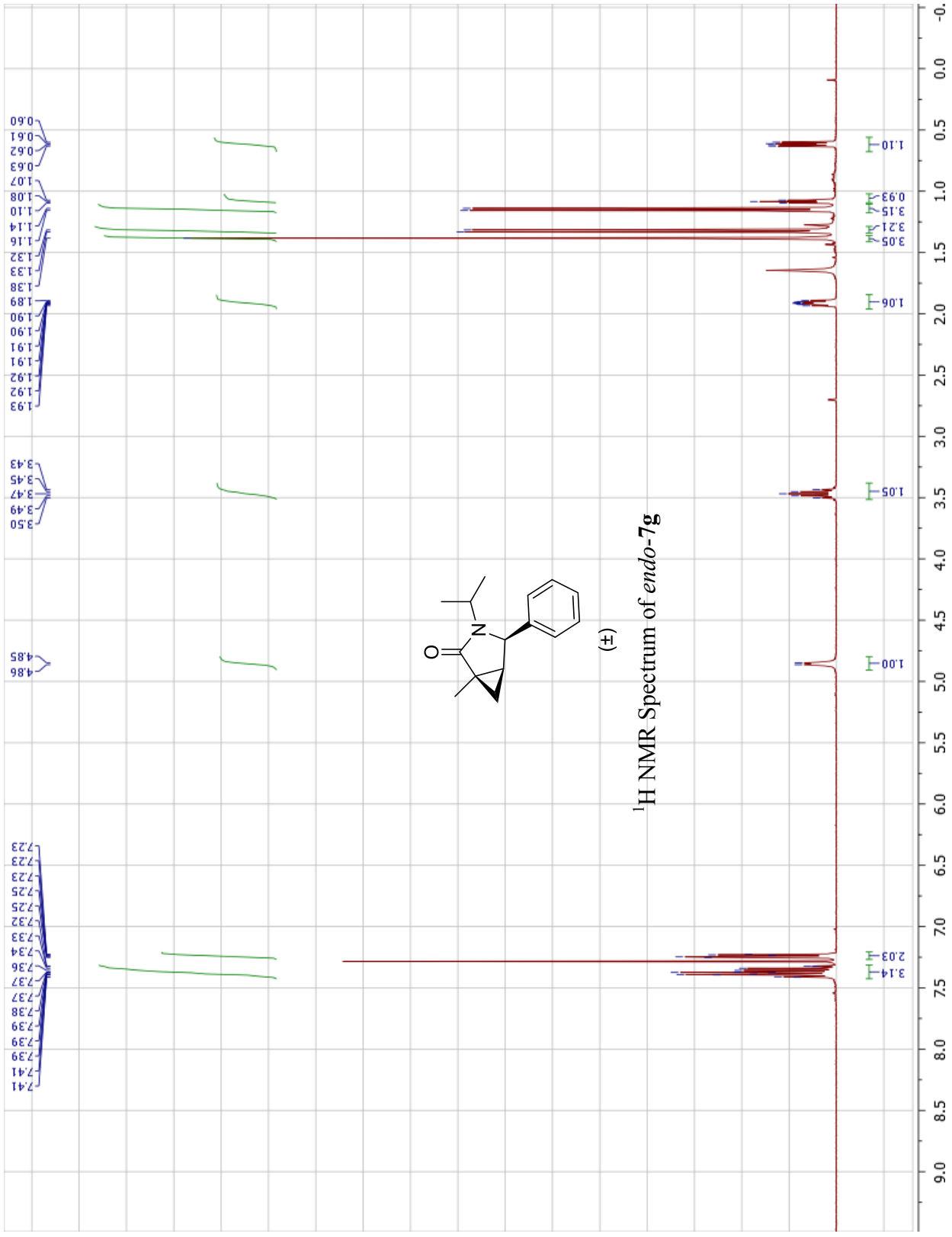

^{1}H NMR Spectrum of **7g**
in crude reaction mixture
dr (*endo:exo*) = 50:50
O
N
4.83
4.82
4.36
4.36
4.05
4.03
4.02
4.00
3.98
3.48
3.46
3.44
3.43
3.41
2.92
2.91
1.15
1.15
1.01
1.00
f1 (ppm)


(±)
^{1}H NMR Spectrum of *exo*-**7g**

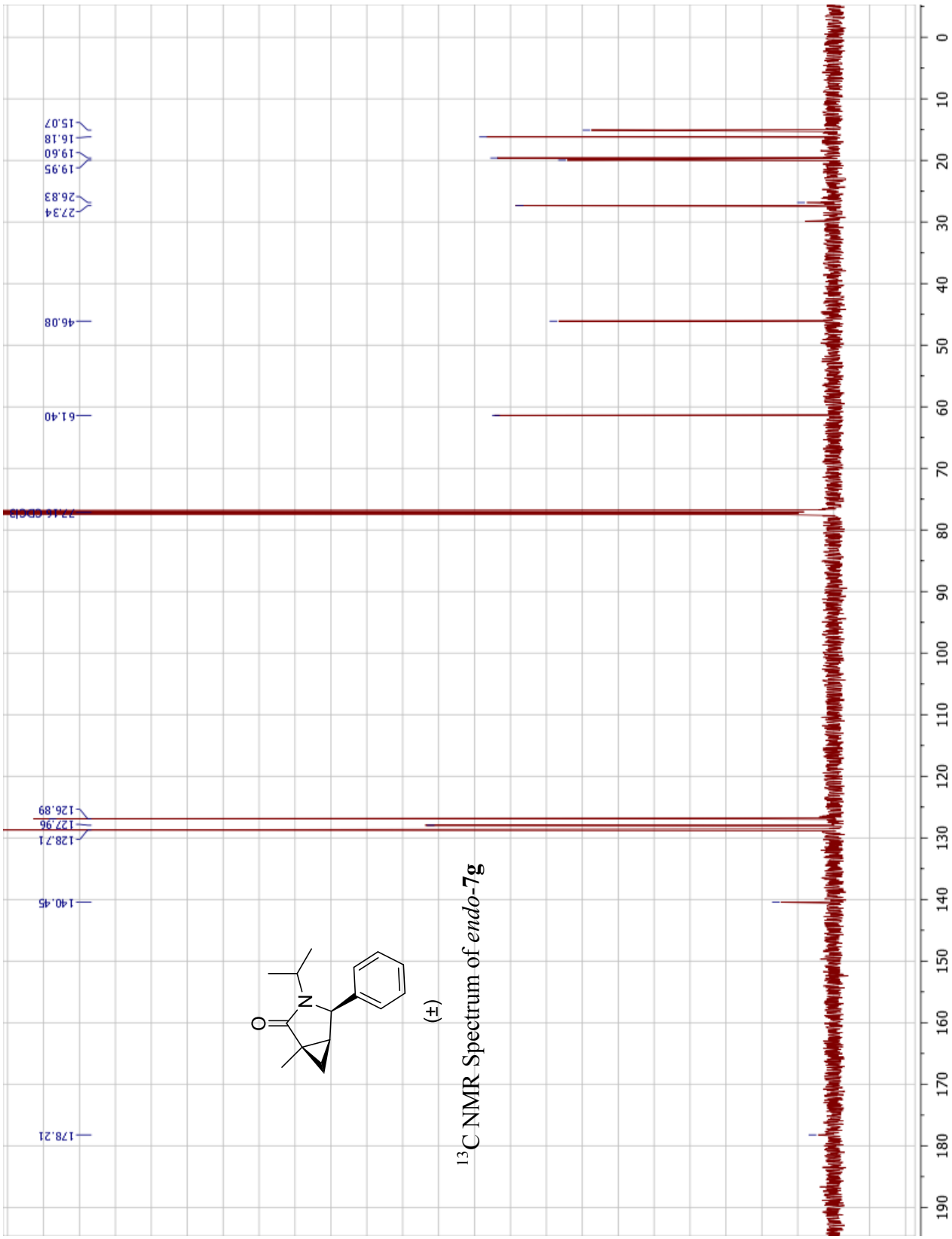


(±)

^{13}C NMR Spectrum of *exo*-**7g**

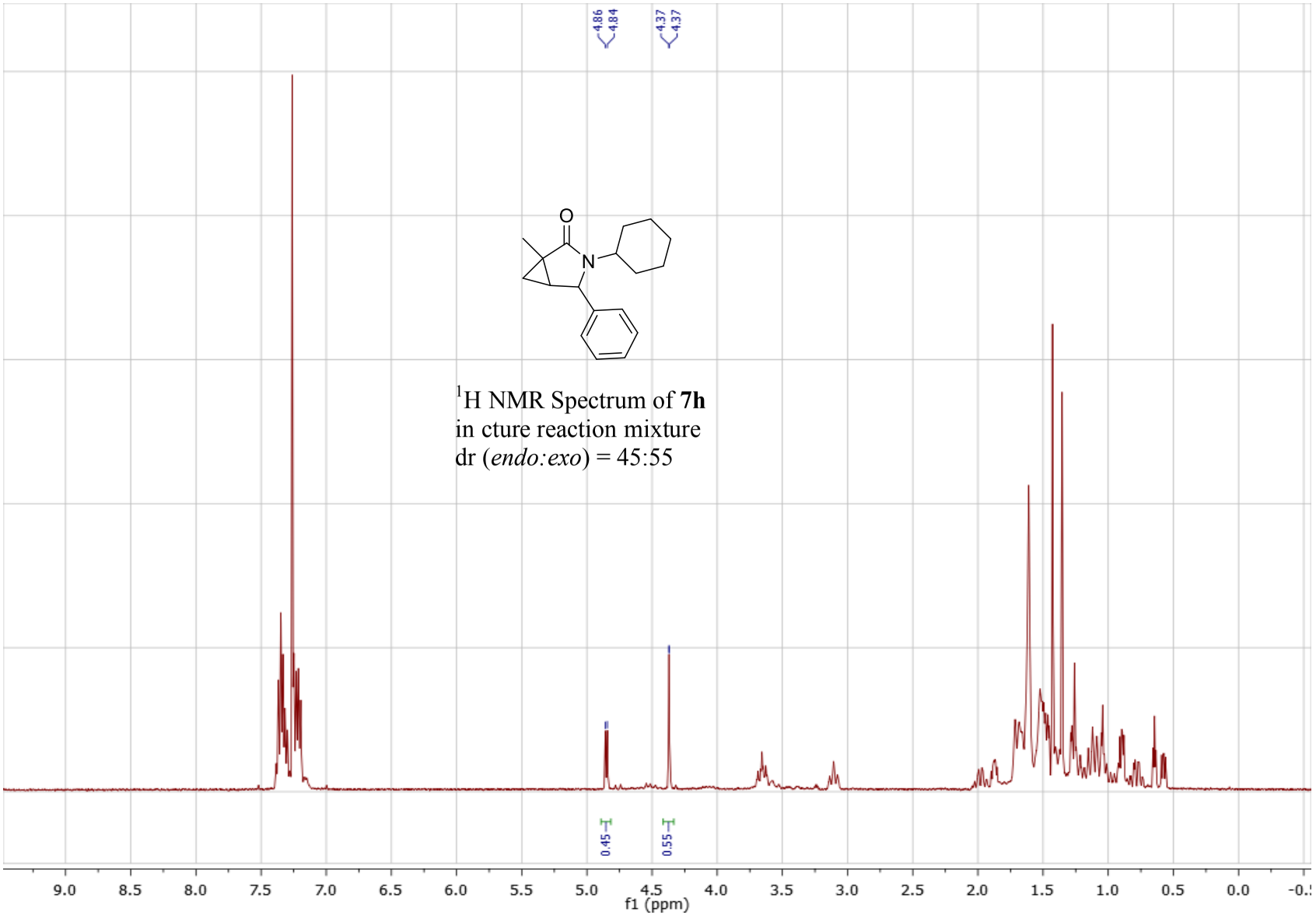


^{1}H NMR Spectrum of *endo*-**7g**

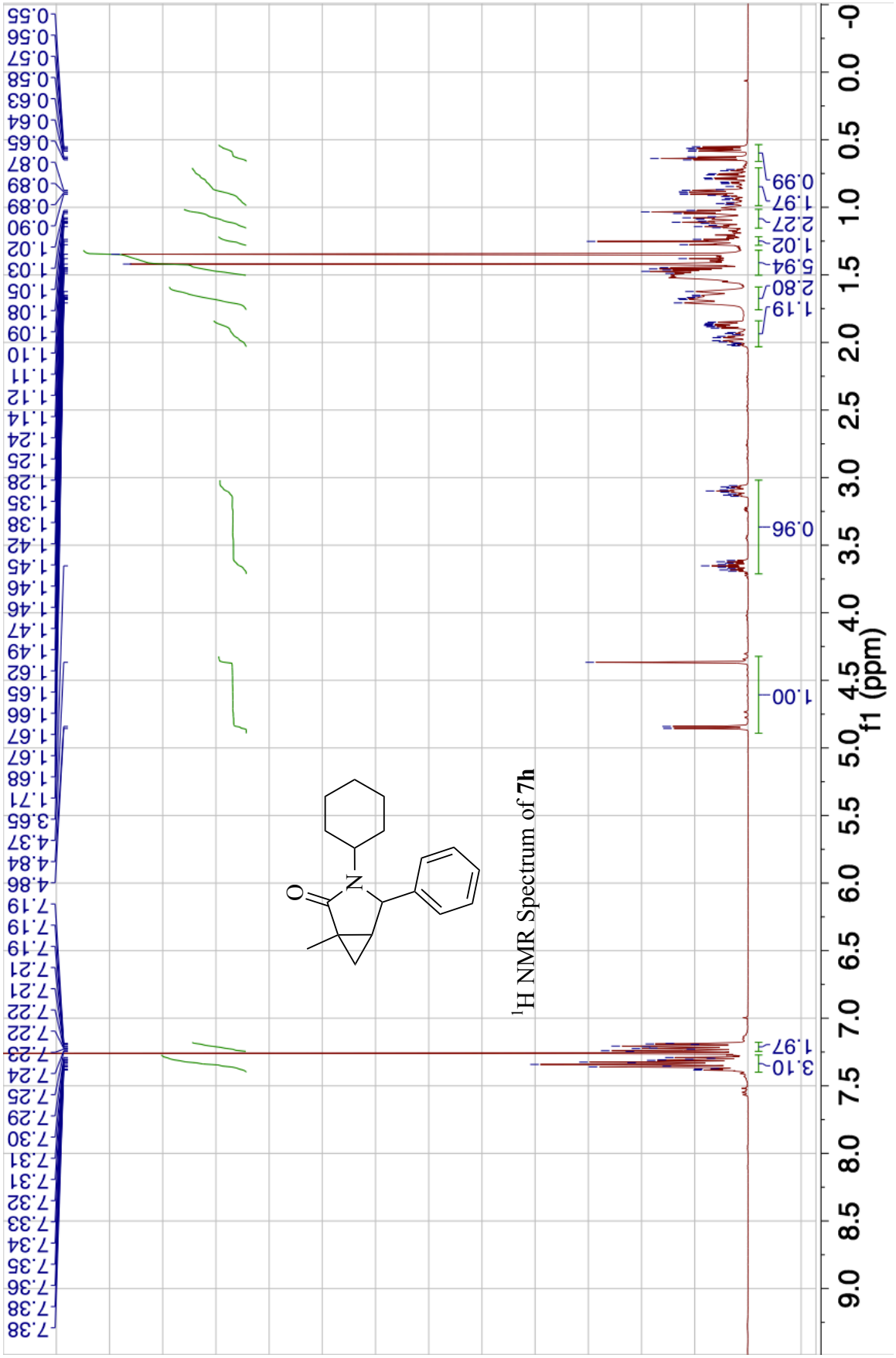


(±)

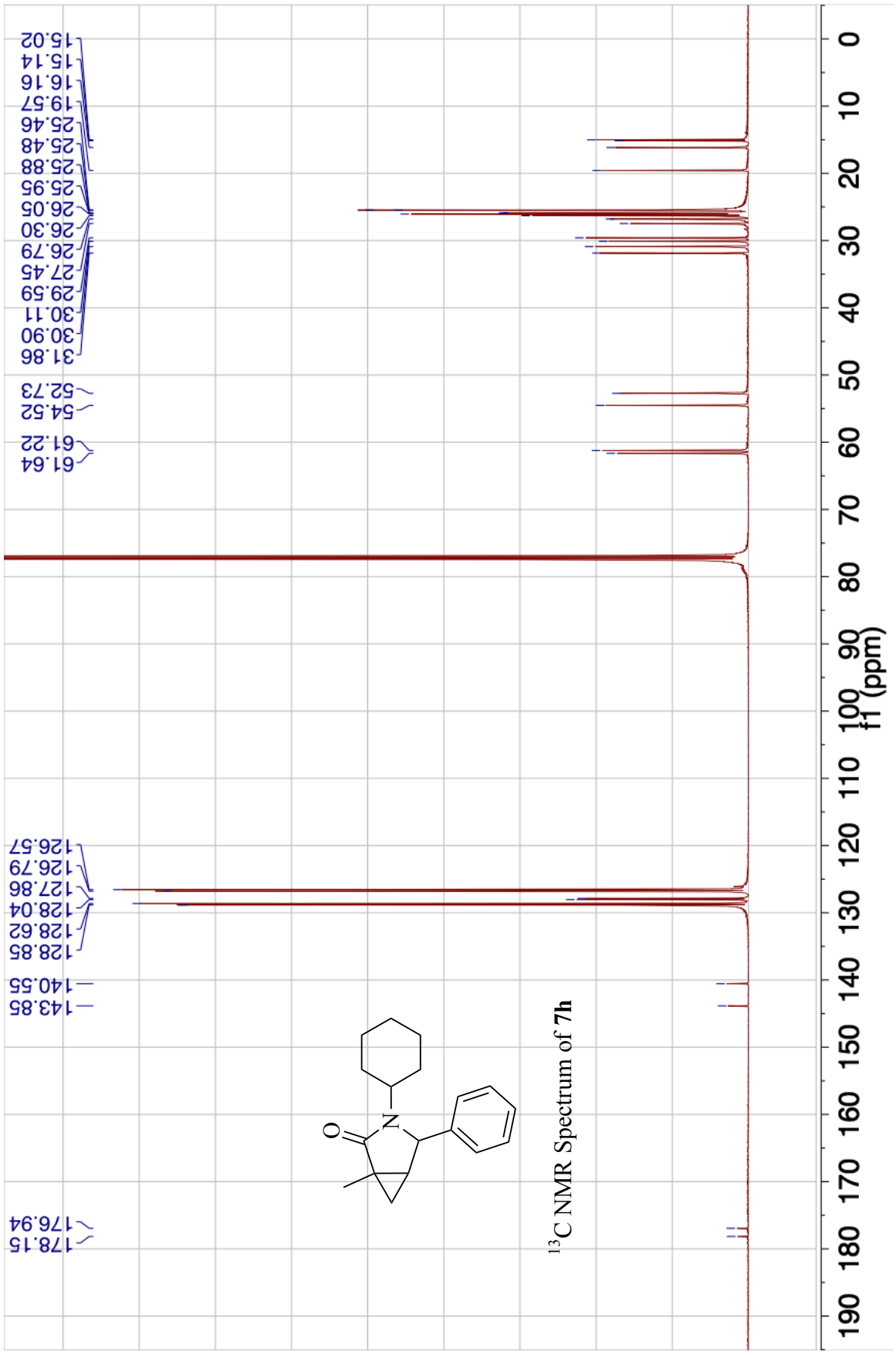
^{13}C NMR Spectrum of *endo*-**7g**

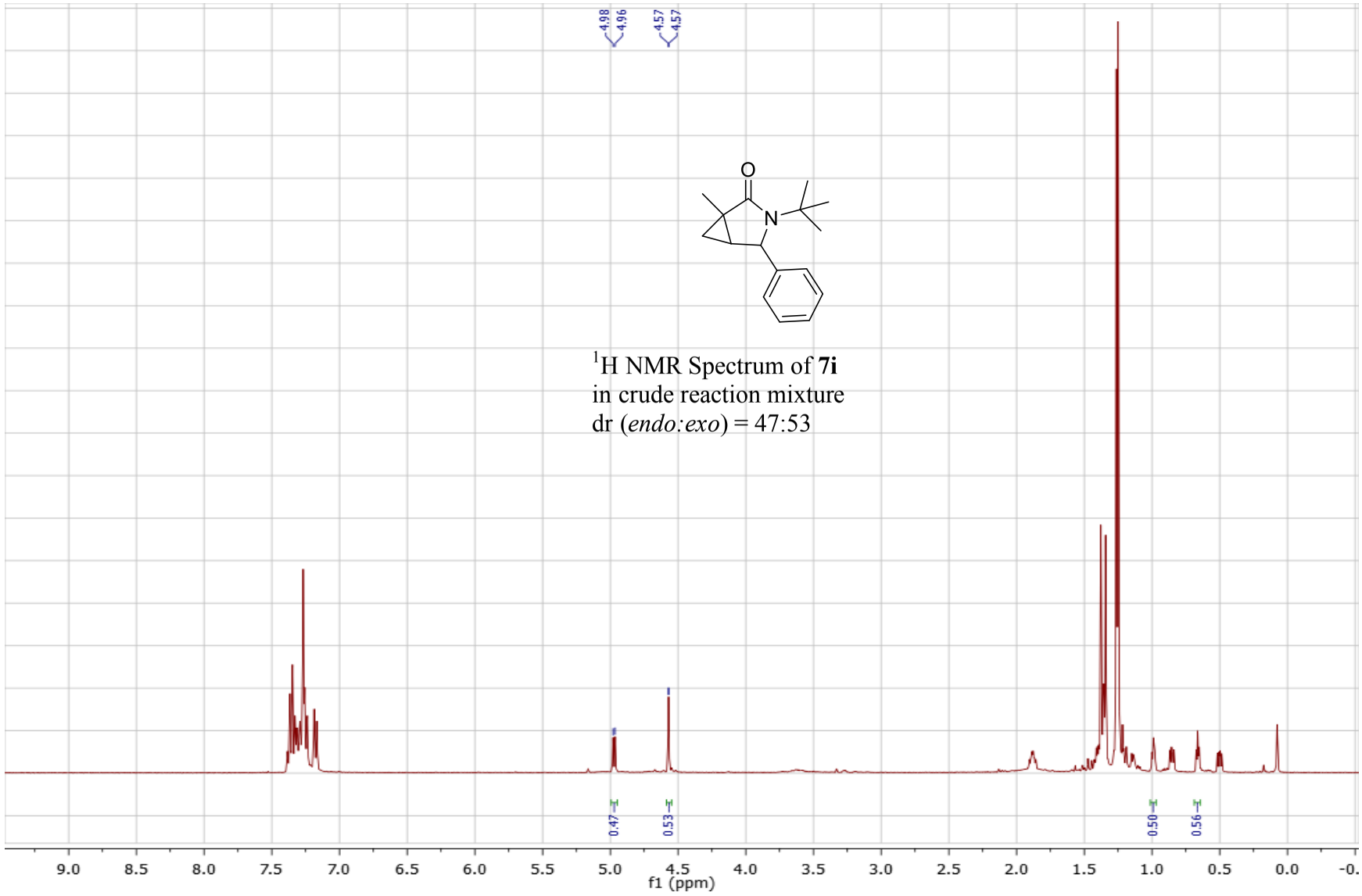


^{1}H NMR Spectrum of **7h**
in cture reaction mixture
dr (*endo:exo*) = 45:55

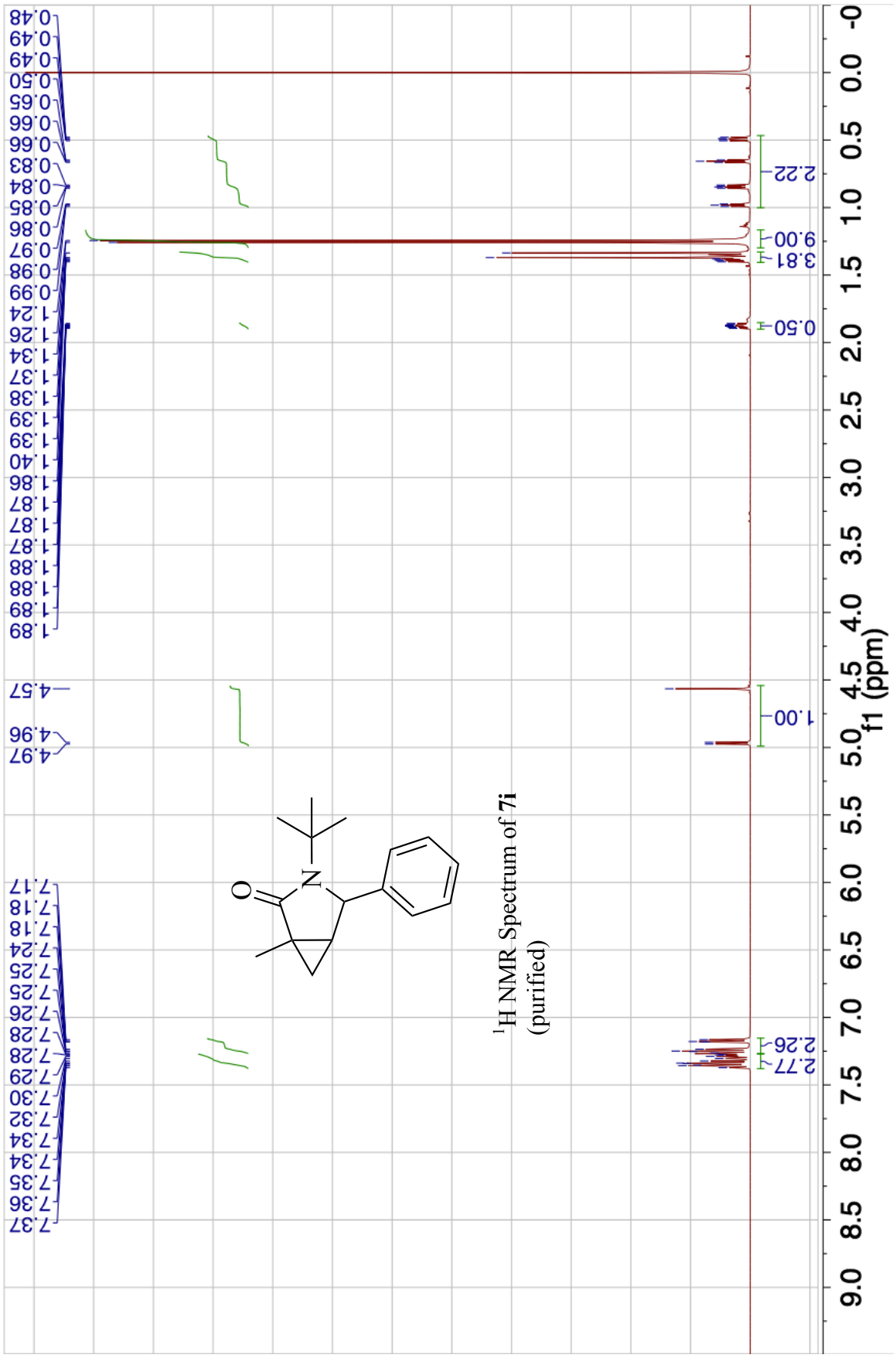


^{1}H NMR Spectrum of **7h**

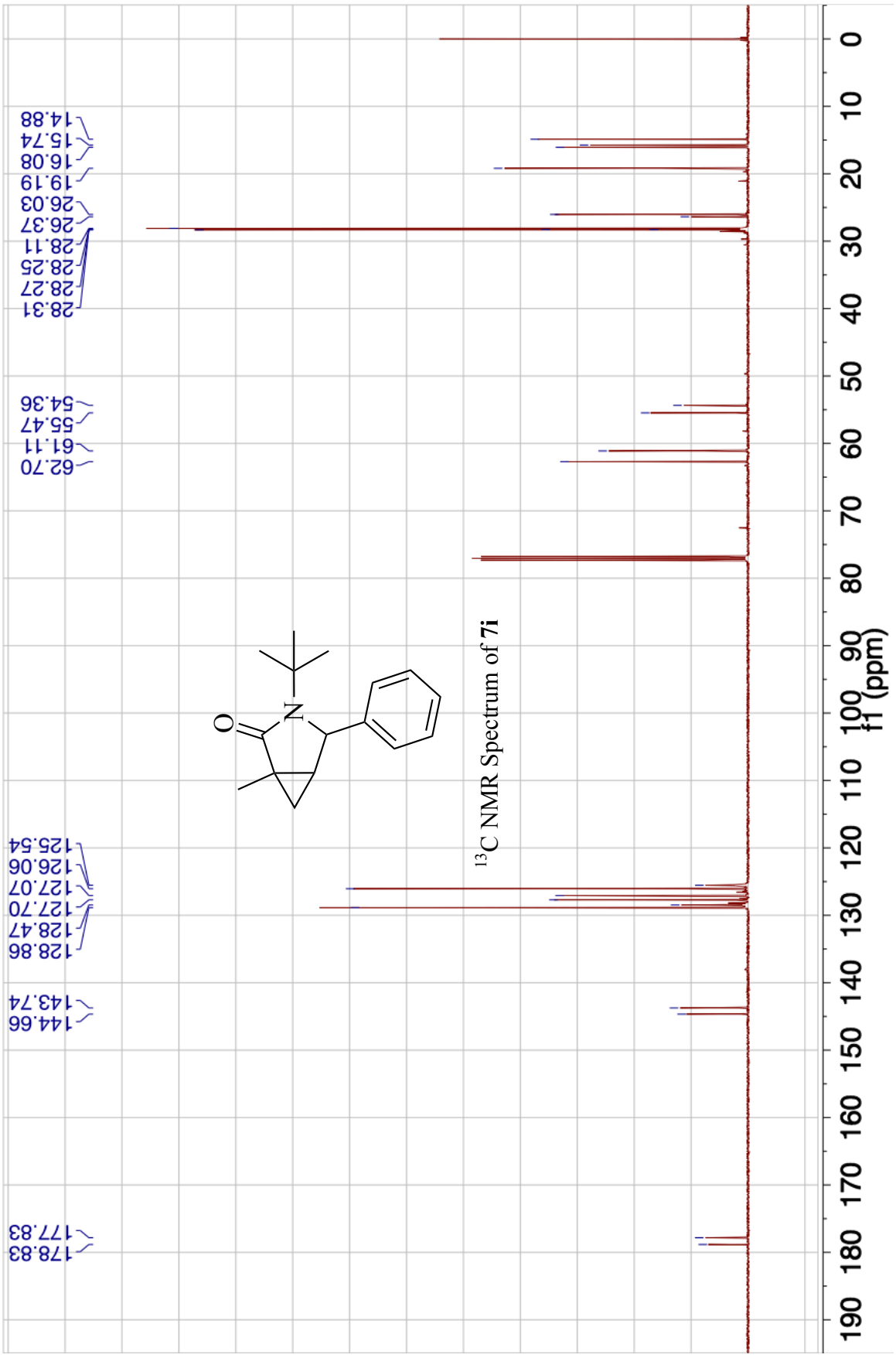

15.02
15.14
16.16
19.57
25.46
25.48
25.88
25.95
26.05
26.30
26.79
27.45
29.59
30.11
30.90
31.86
52.73
54.52
61.22
61.64
126.57
126.79
127.86
128.04
128.62
128.85
140.55
143.85
176.94
178.15
O
N
^{13}C NMR Spectrum of **7h**
f1 (ppm)

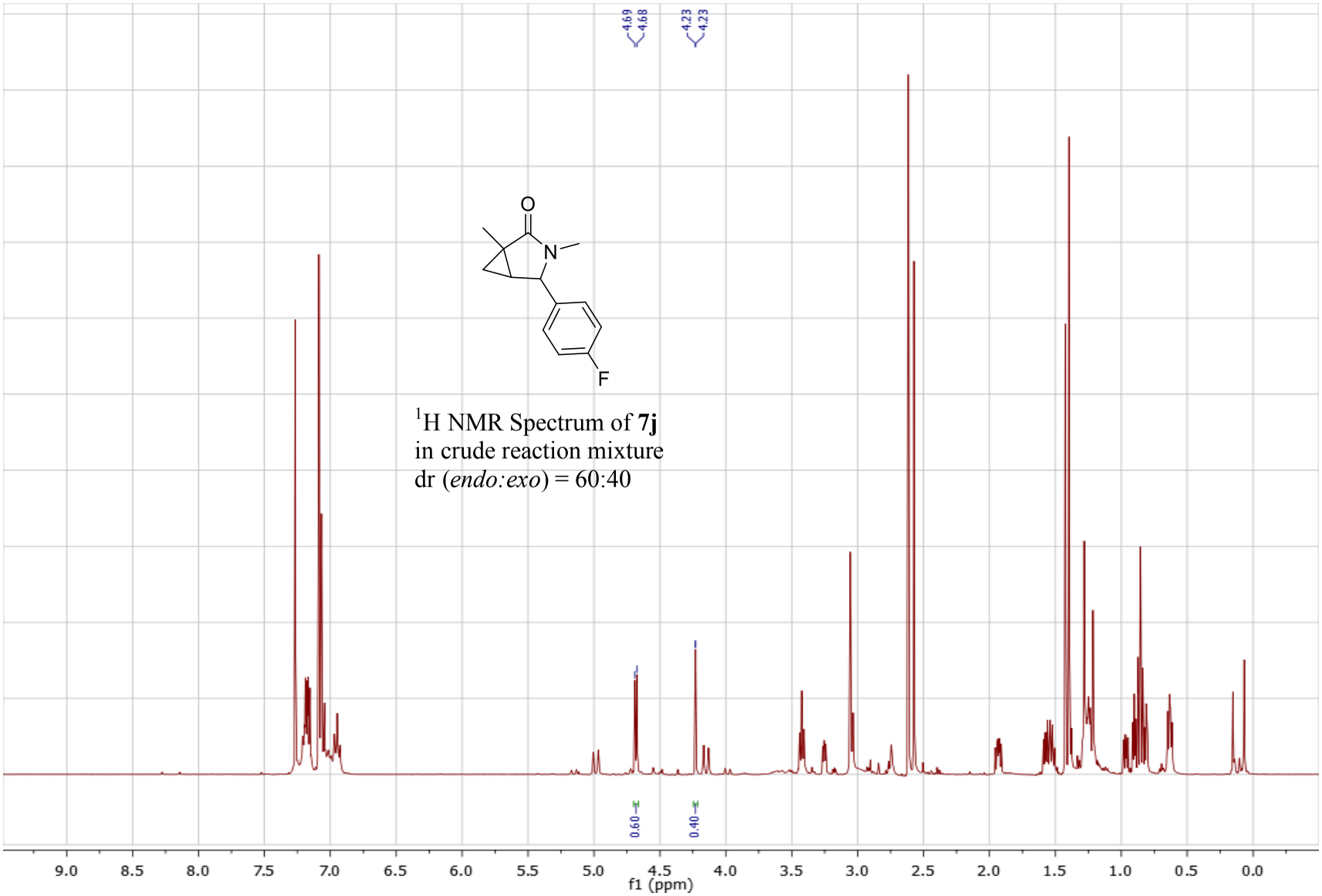


^{1}H NMR Spectrum of **7i**
in crude reaction mixture
dr (*endo:exo*) = 47:53

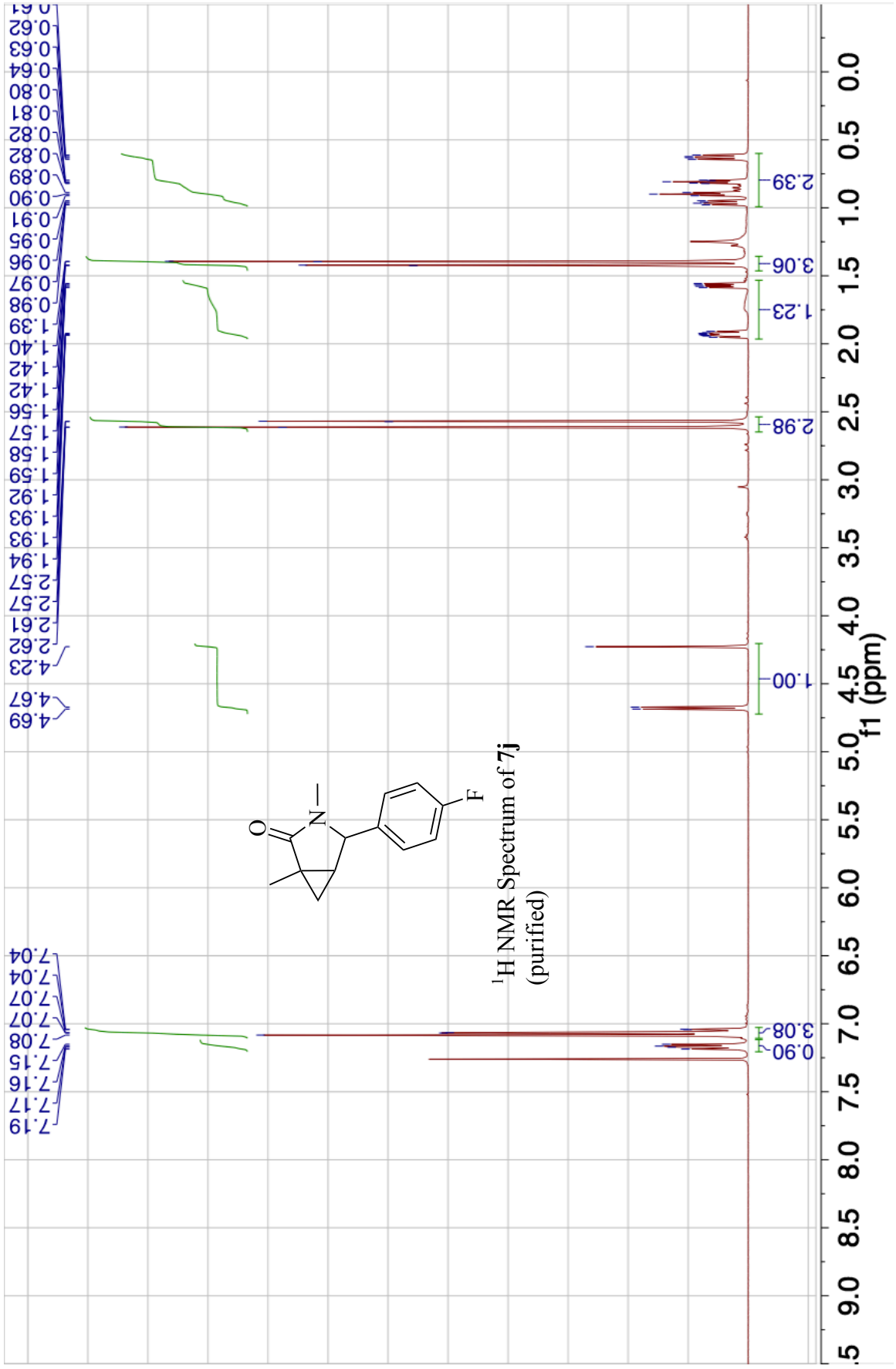


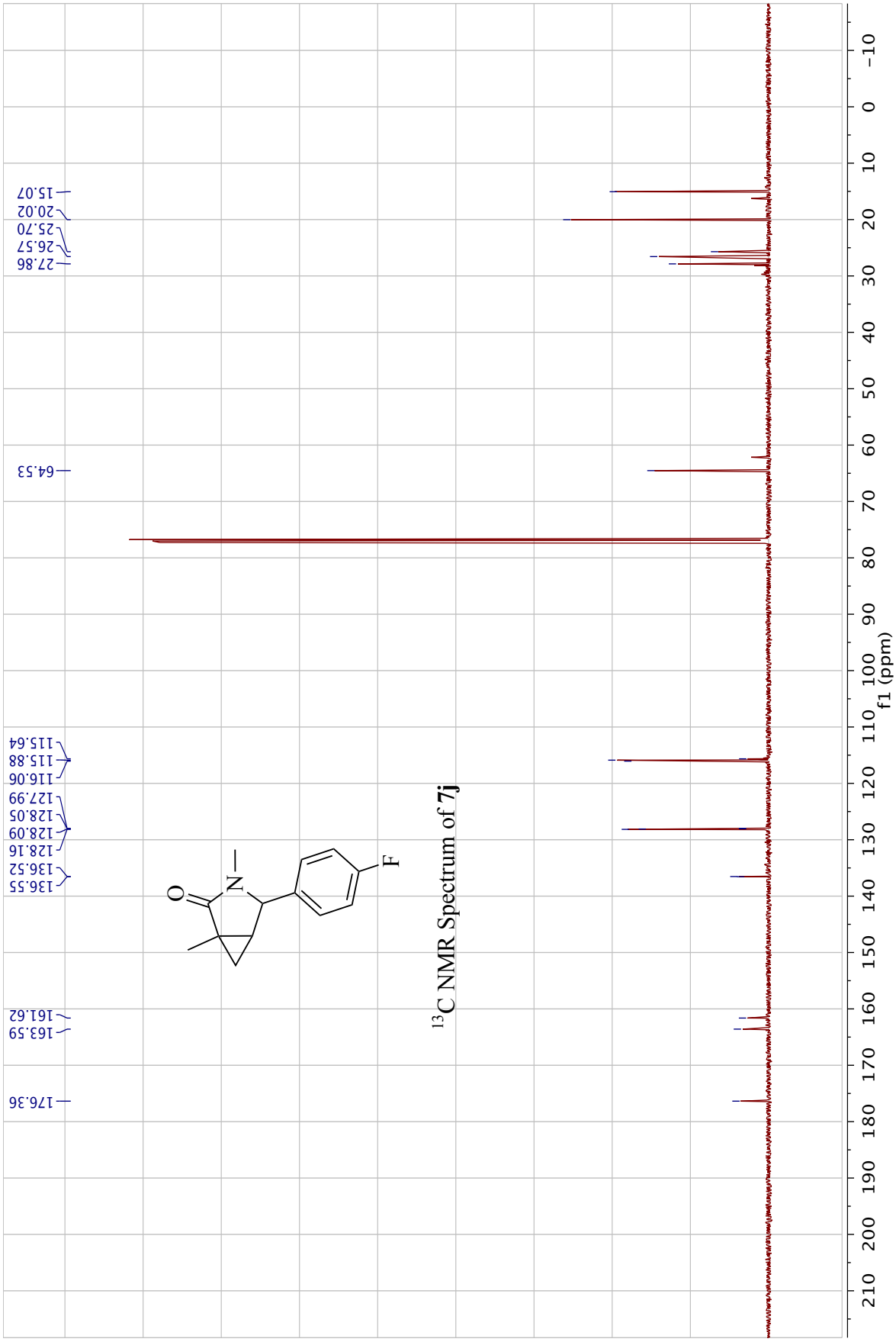
^{1}H NMR Spectrum of **7i**
(purified)


14.88
15.74
16.08
19.19
26.03
26.37
28.11
28.25
28.27
28.31
54.36
55.47
61.11
62.70
125.54
126.06
127.07
127.70
128.47
128.86
143.74
144.66
177.83
178.83
O
N
^{13}C NMR Spectrum of **7i**
f1 (ppm)

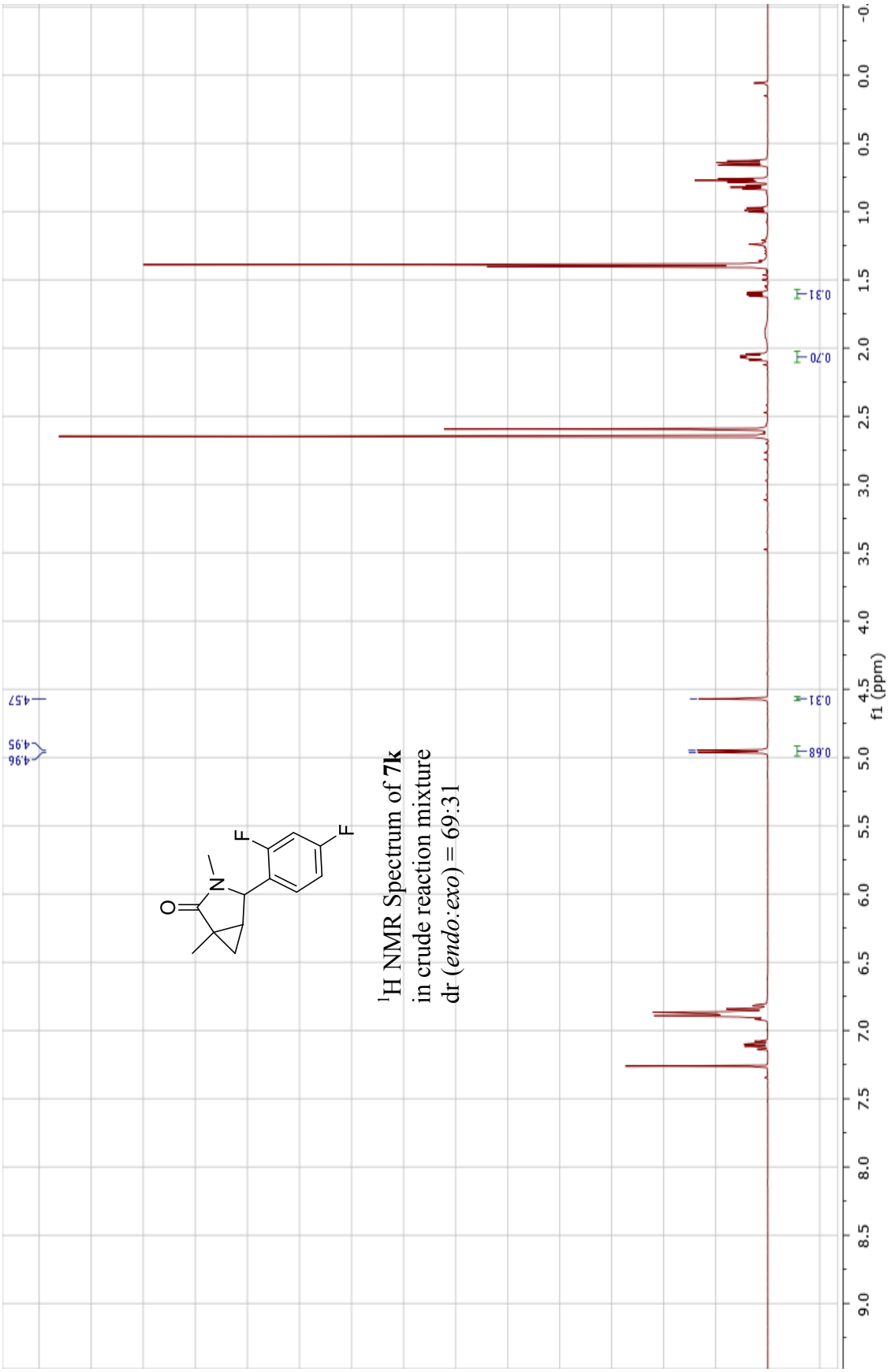


^{1}H NMR Spectrum of **7j**
in crude reaction mixture
dr (*endo:exo*) = 60:40

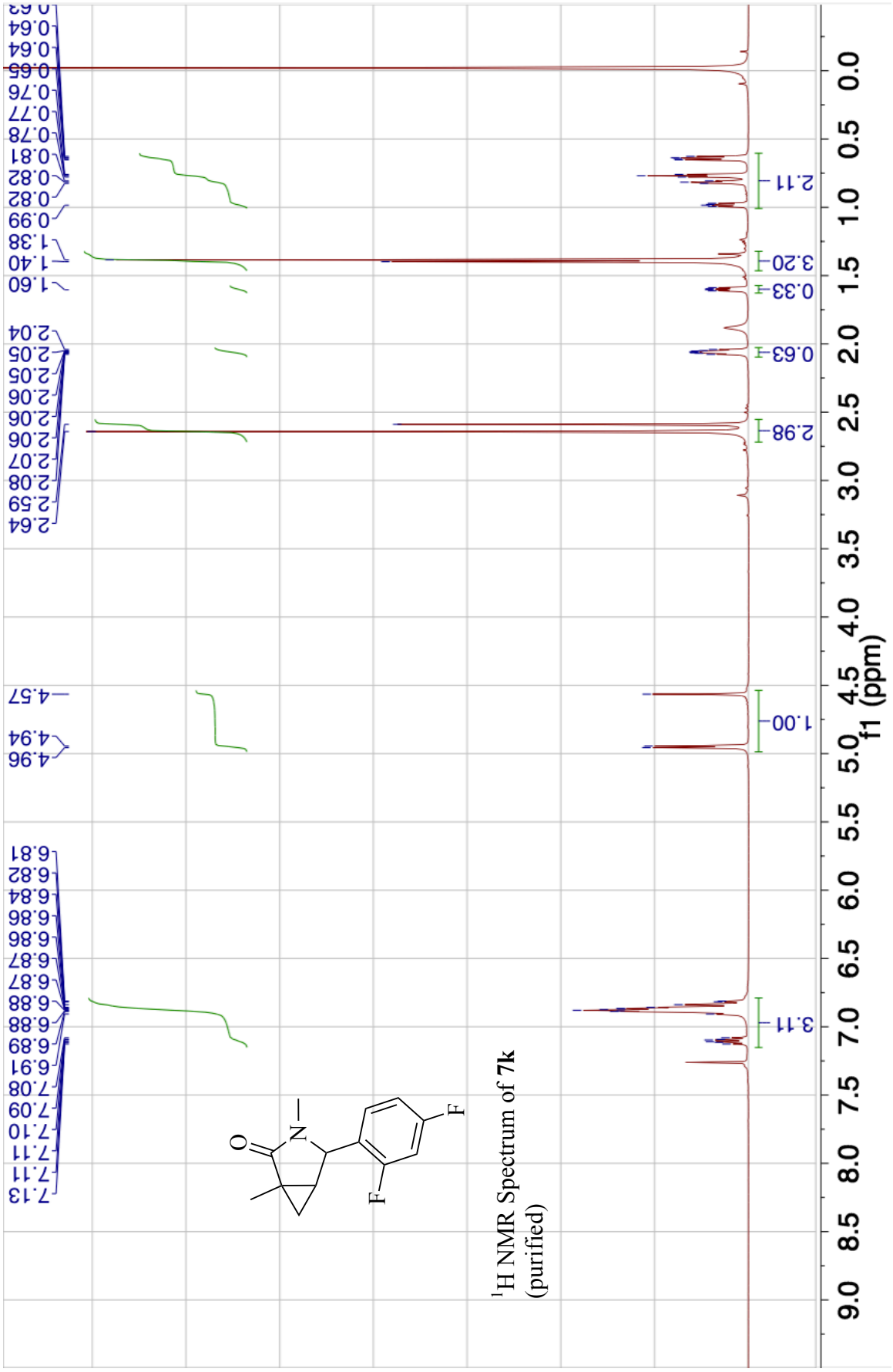

0.61
0.62
0.63
0.64
0.80
0.81
0.82
0.82
0.89
0.90
0.91
0.95
0.96
0.97
0.98
1.39
1.40
1.42
1.42
1.56
1.57
1.58
1.59
1.92
1.93
1.93
1.94
2.57
2.57
2.61
2.62
4.23
4.67
4.69
7.04
7.04
7.07
7.07
7.08
7.15
7.16
7.17
7.19
2.39
3.06
1.23
2.98
1.00
0.90
3.08
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
f1 (ppm)
O
N
F
^{1}H NMR Spectrum of 7j
(purified)



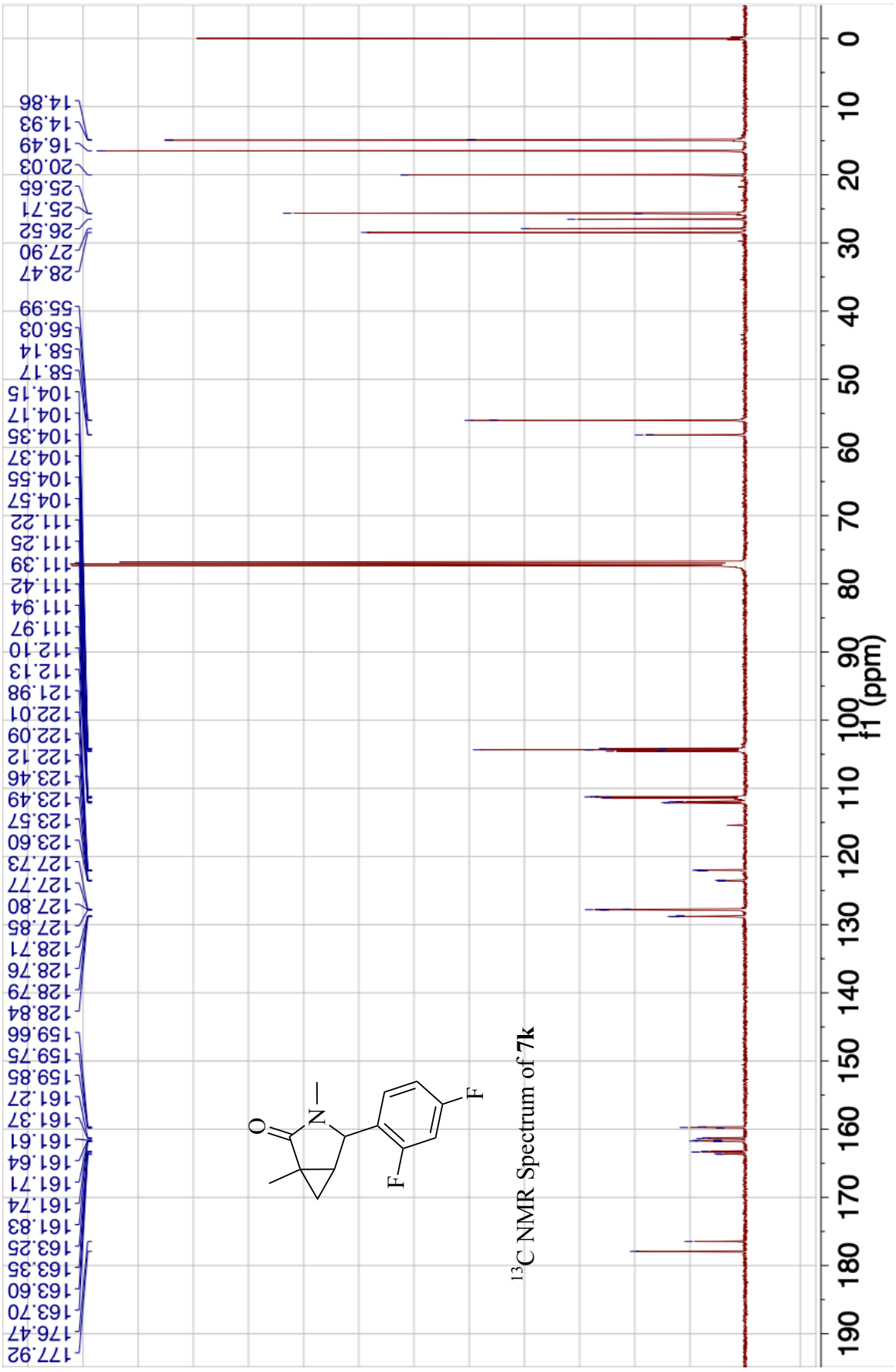
^{13}C NMR Spectrum of **7j**



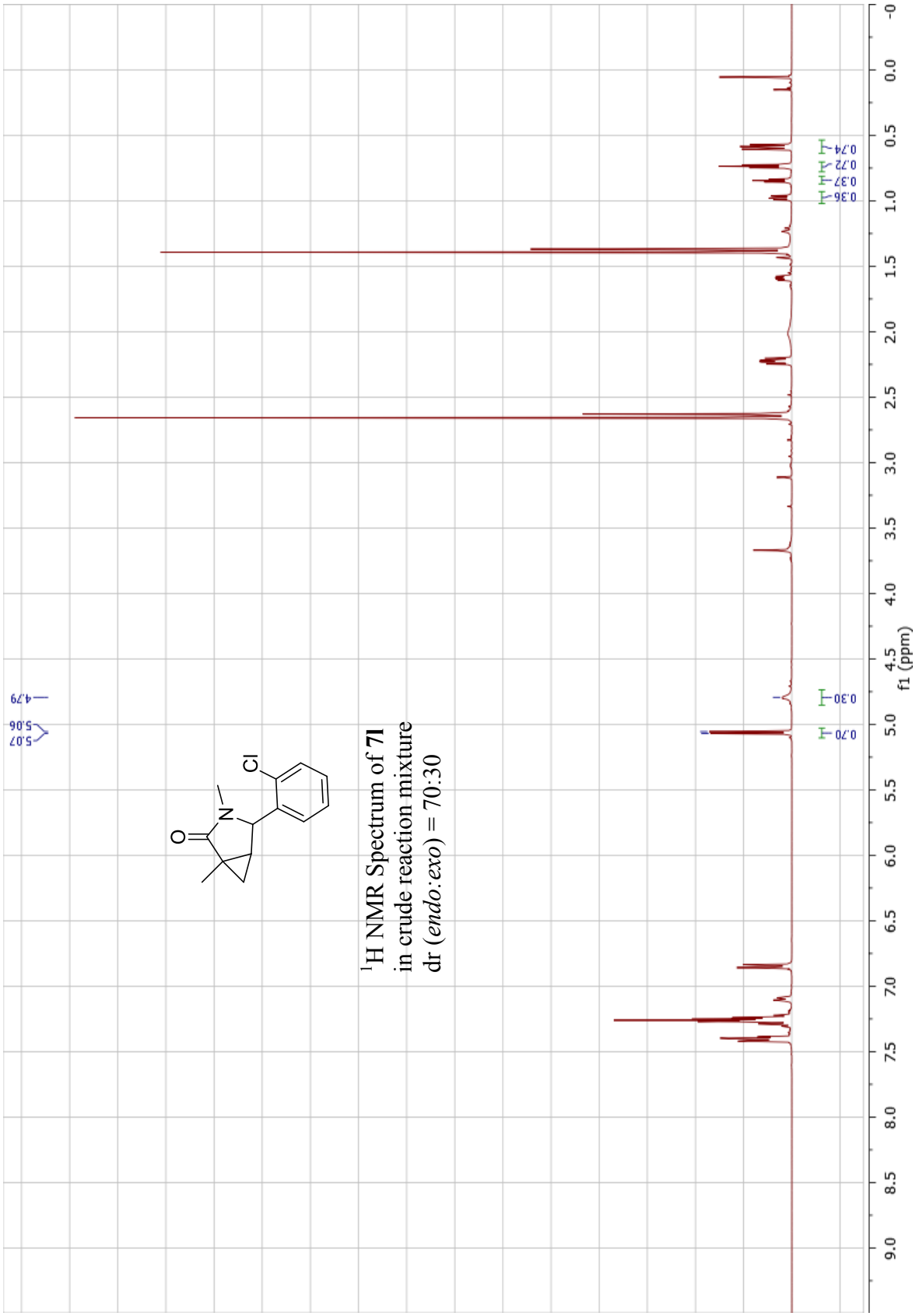
^{1}H NMR Spectrum of **7k**
in crude reaction mixture
dr (*endo*:*exo*) = 69:31



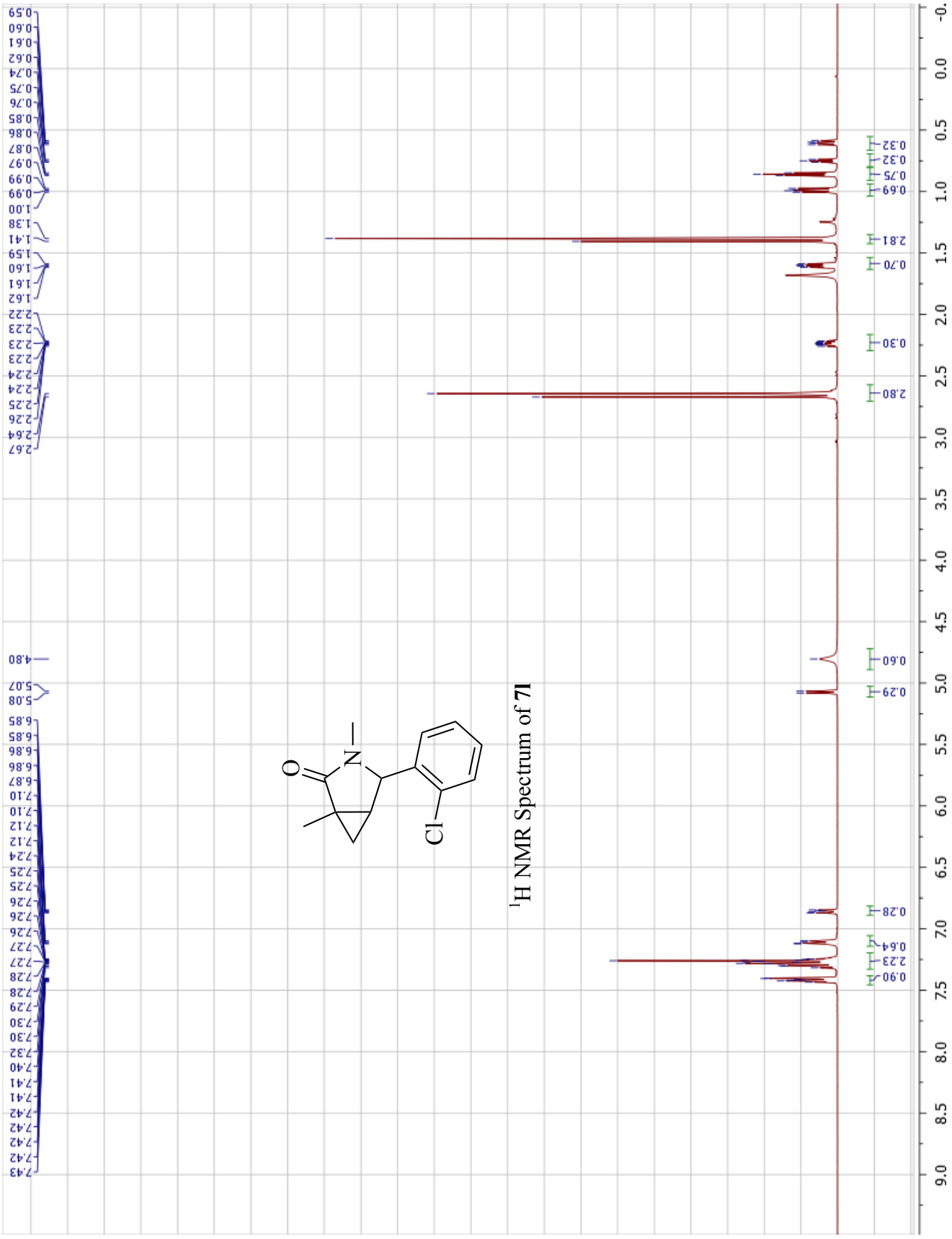
^{1}H NMR Spectrum of **7k** (purified)



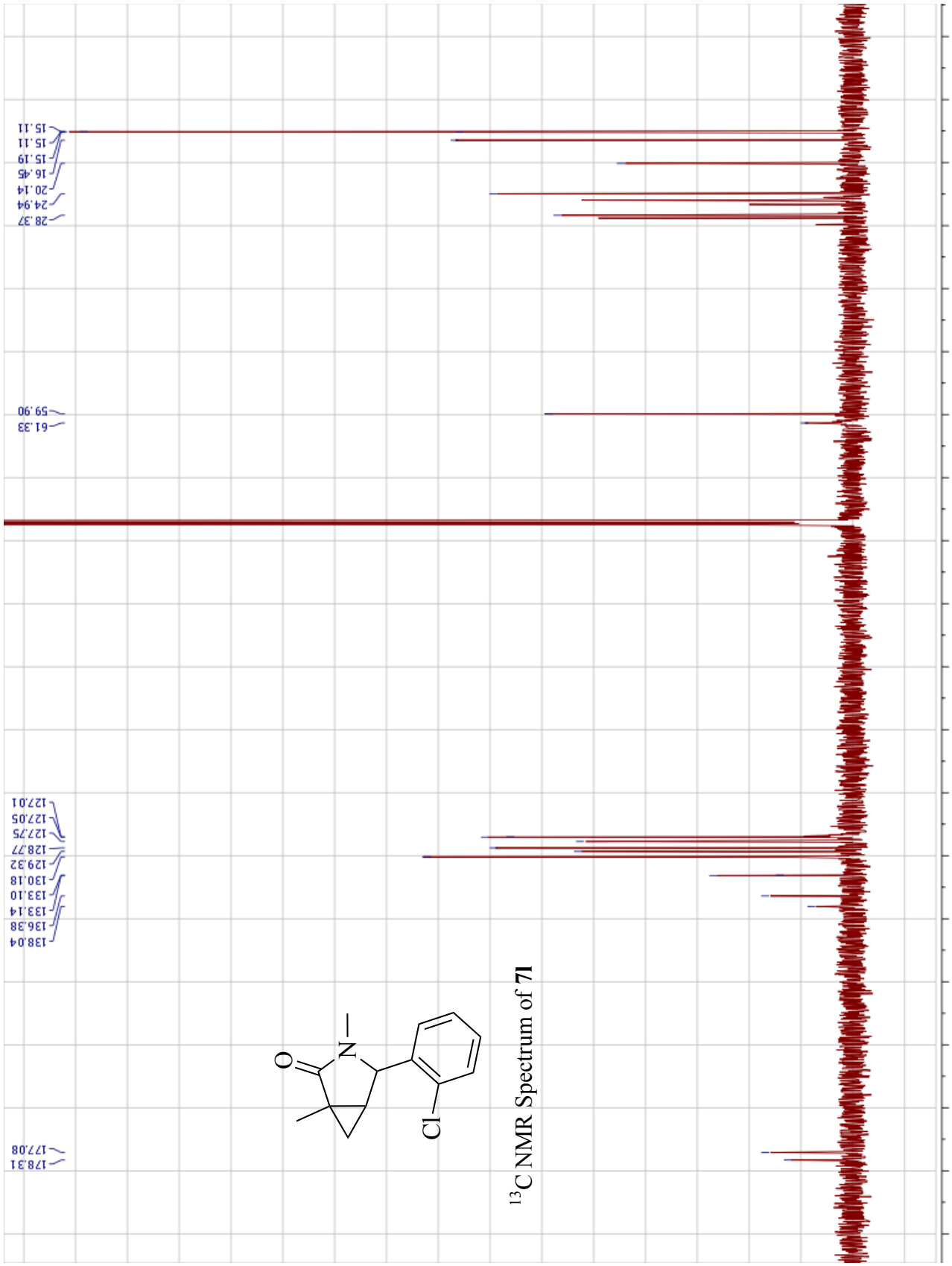
^{13}C NMR Spectrum of **7k**



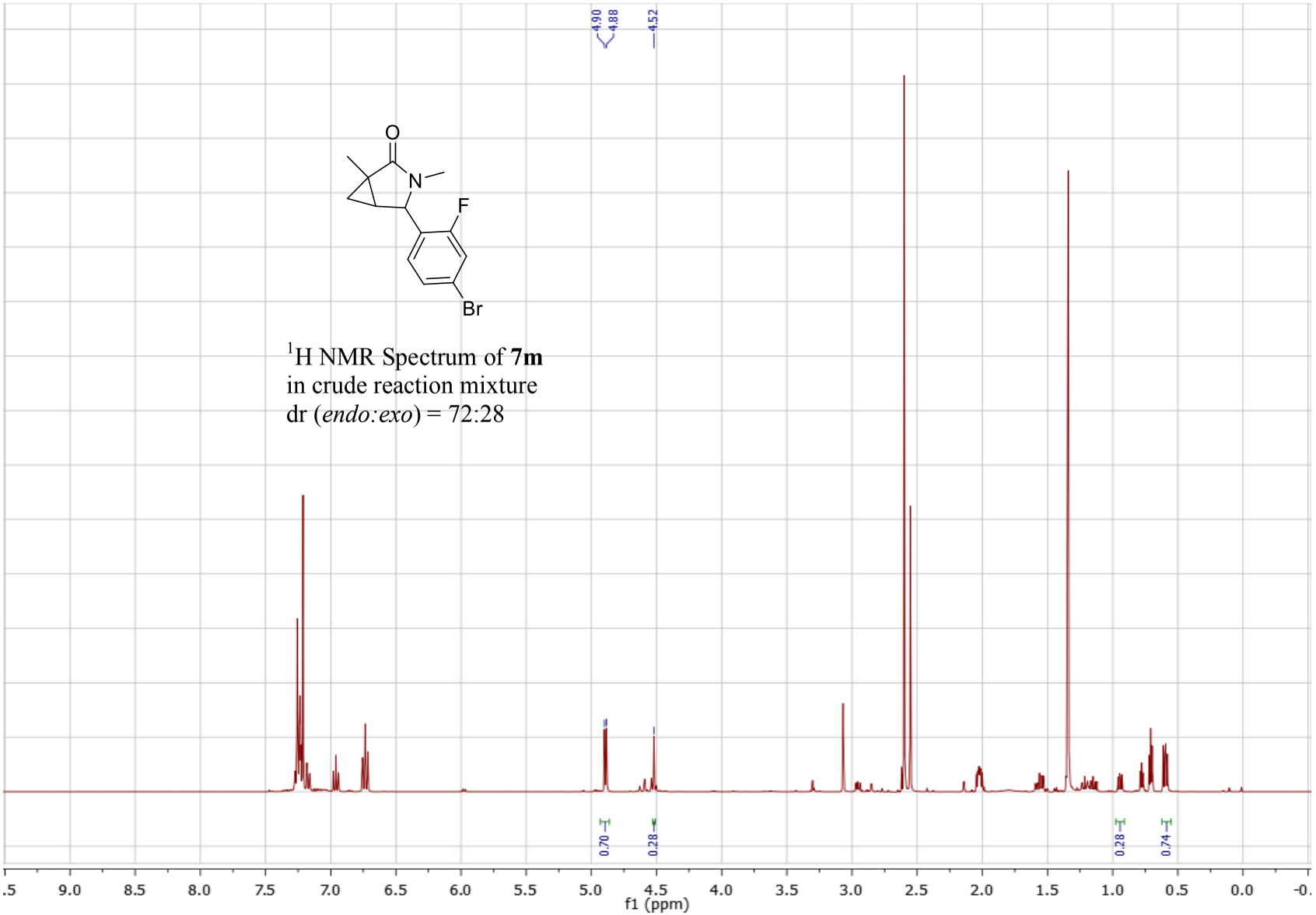
^{1}H NMR Spectrum of **7l**
in crude reaction mixture
dr (*endo:exo*) = 70:30



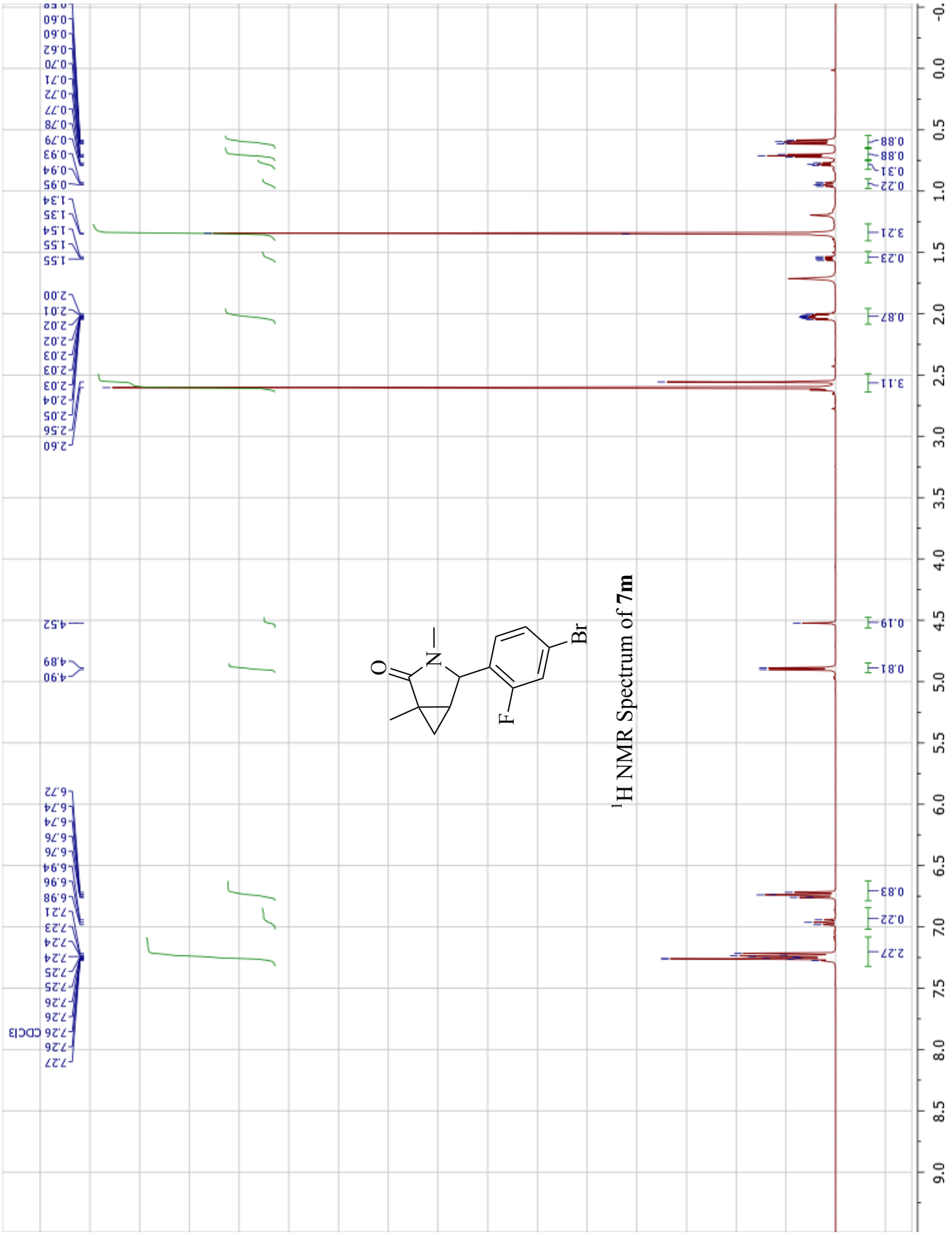
^{1}H NMR Spectrum of **7l**



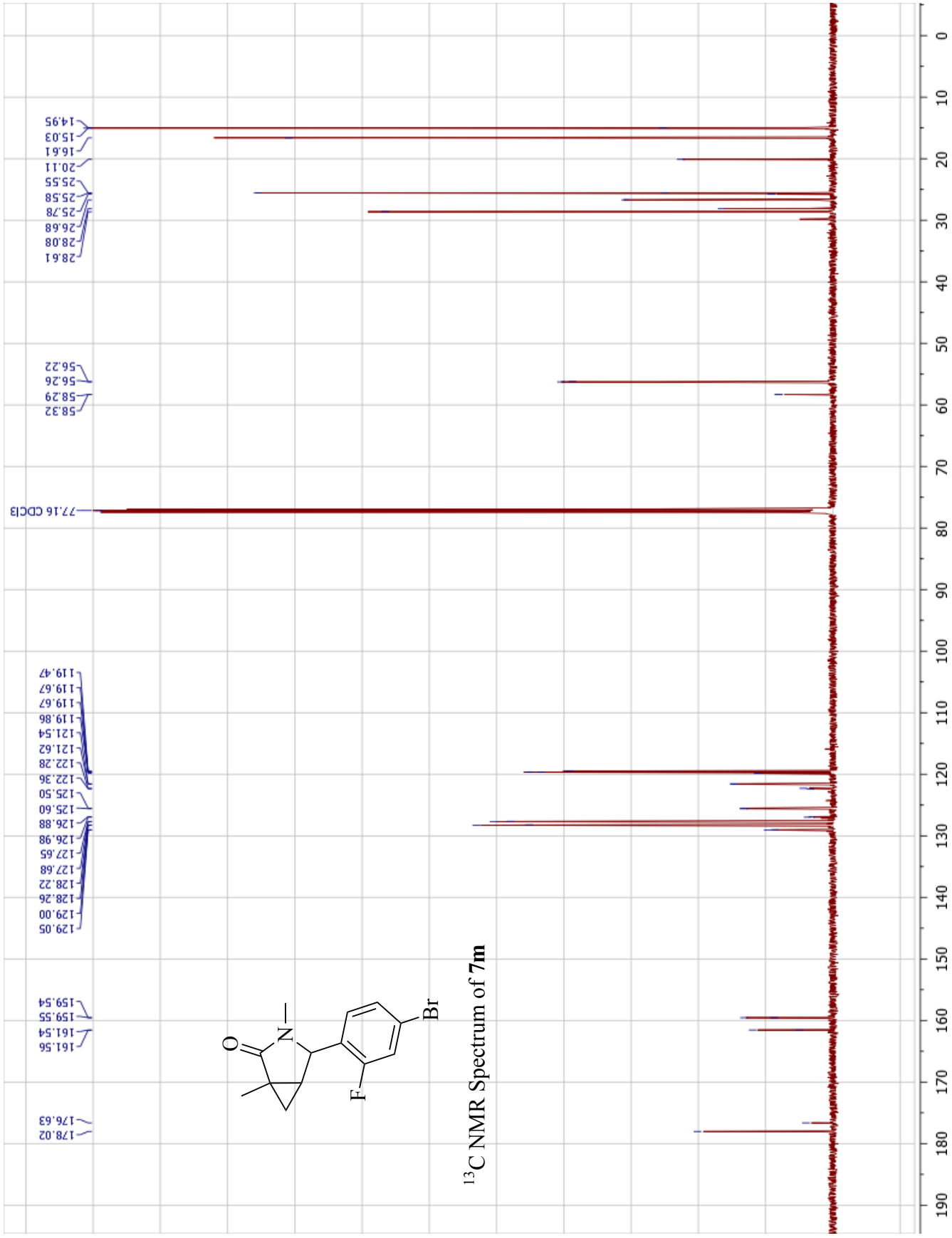
^{13}C NMR Spectrum of **71**



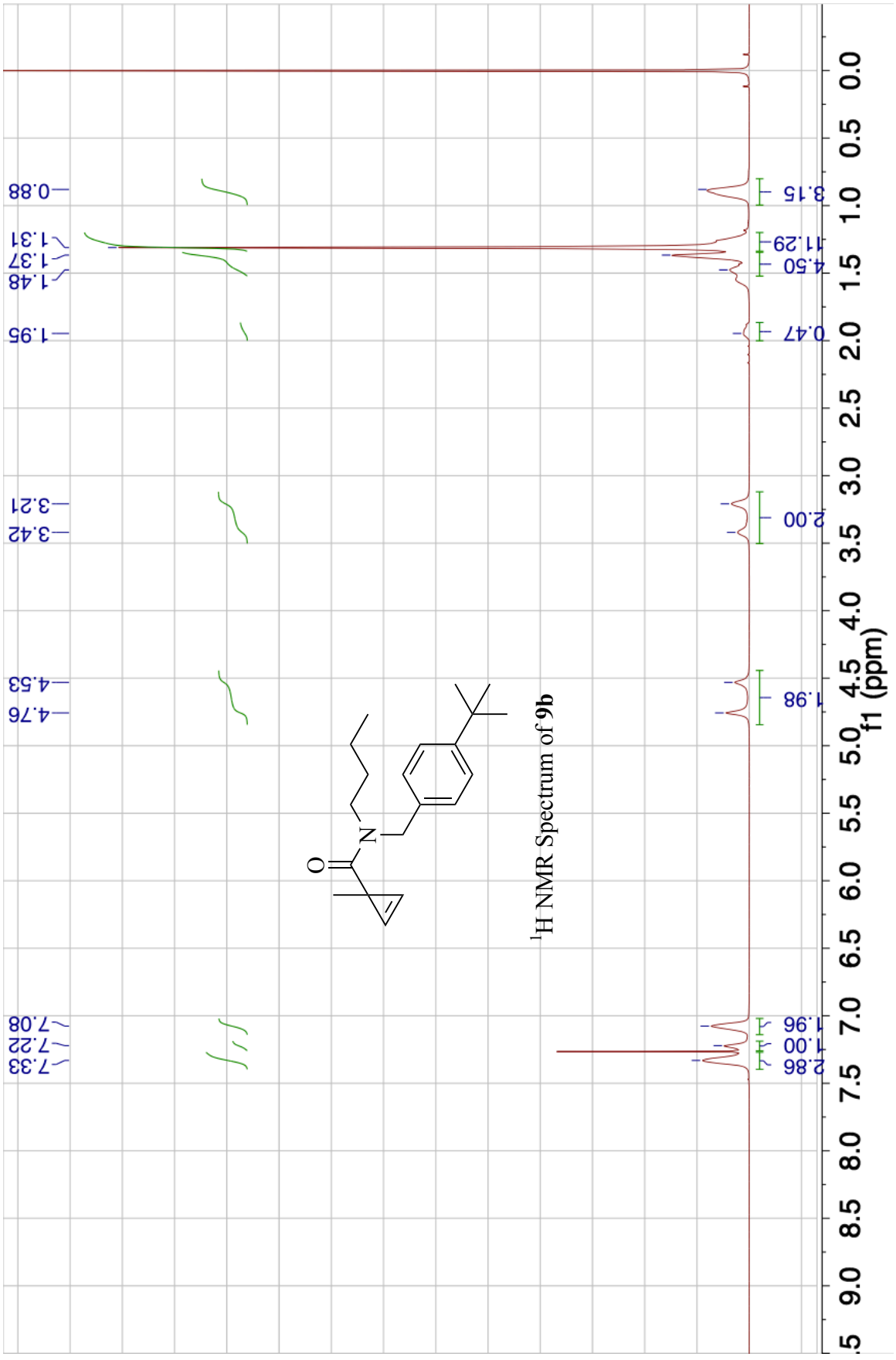
^{1}H NMR Spectrum of **7m**
in crude reaction mixture
dr (*endo:exo*) = 72:28



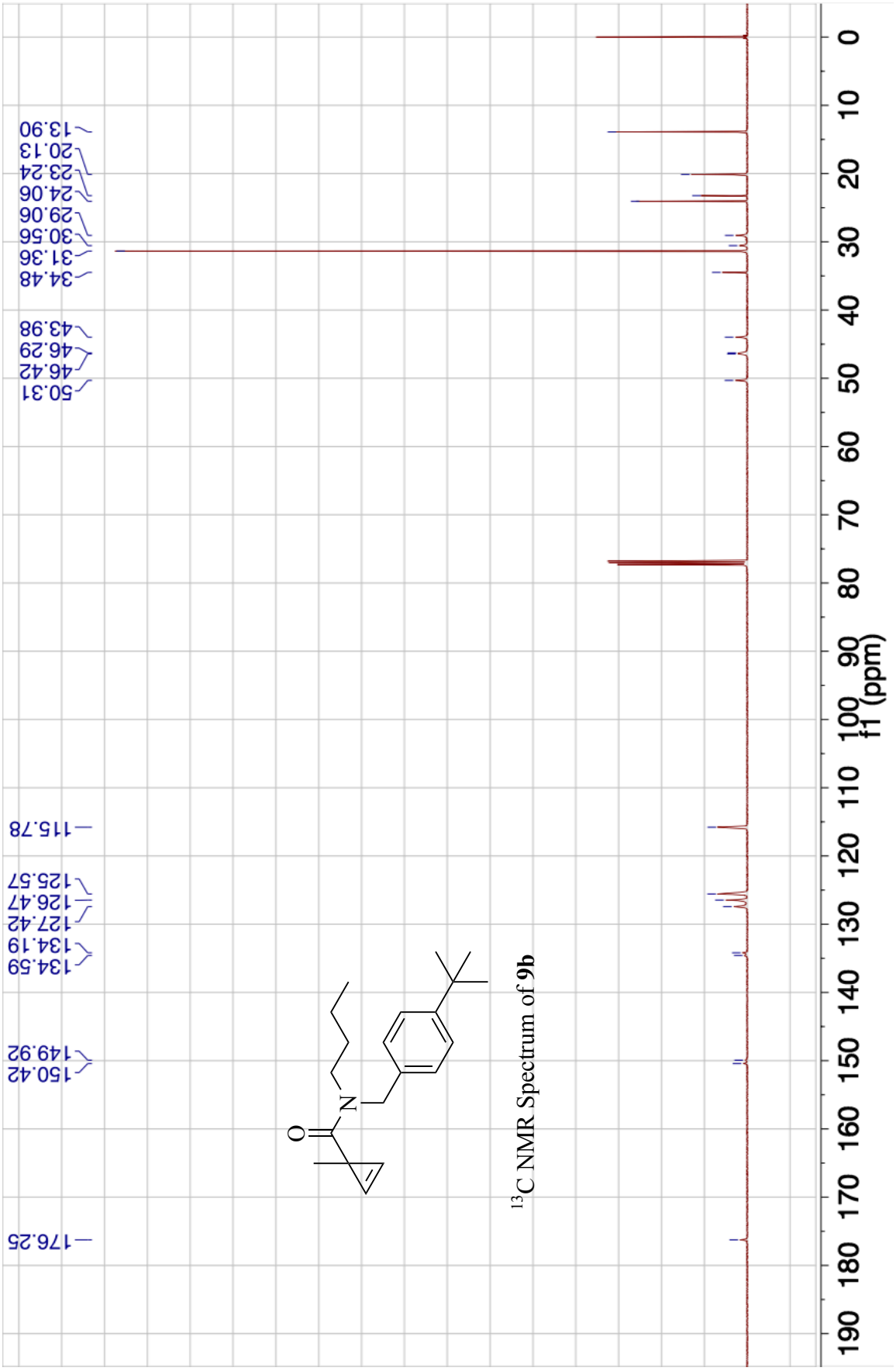
^{1}H NMR Spectrum of **7m**



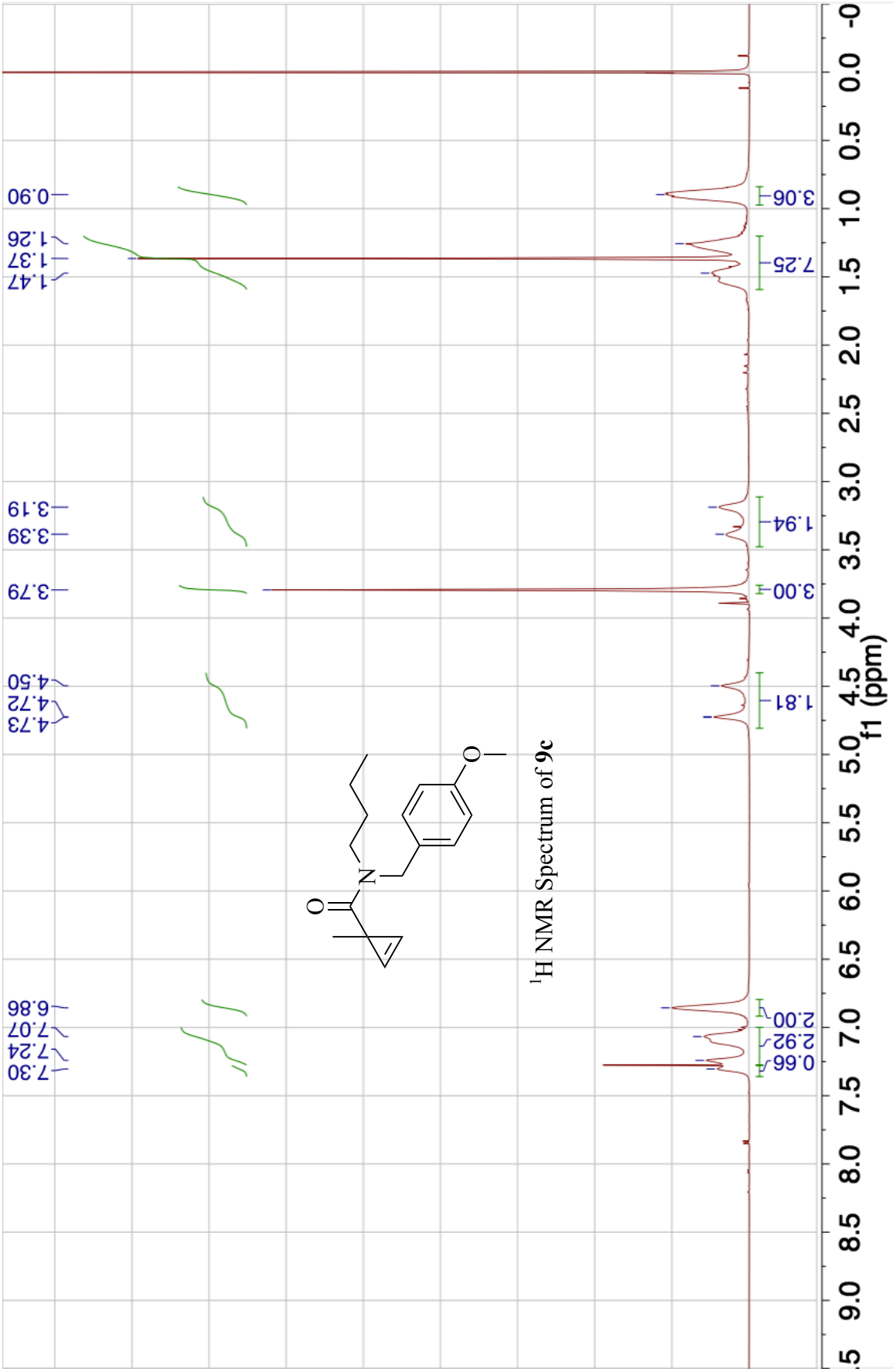
^{13}C NMR Spectrum of **7m**



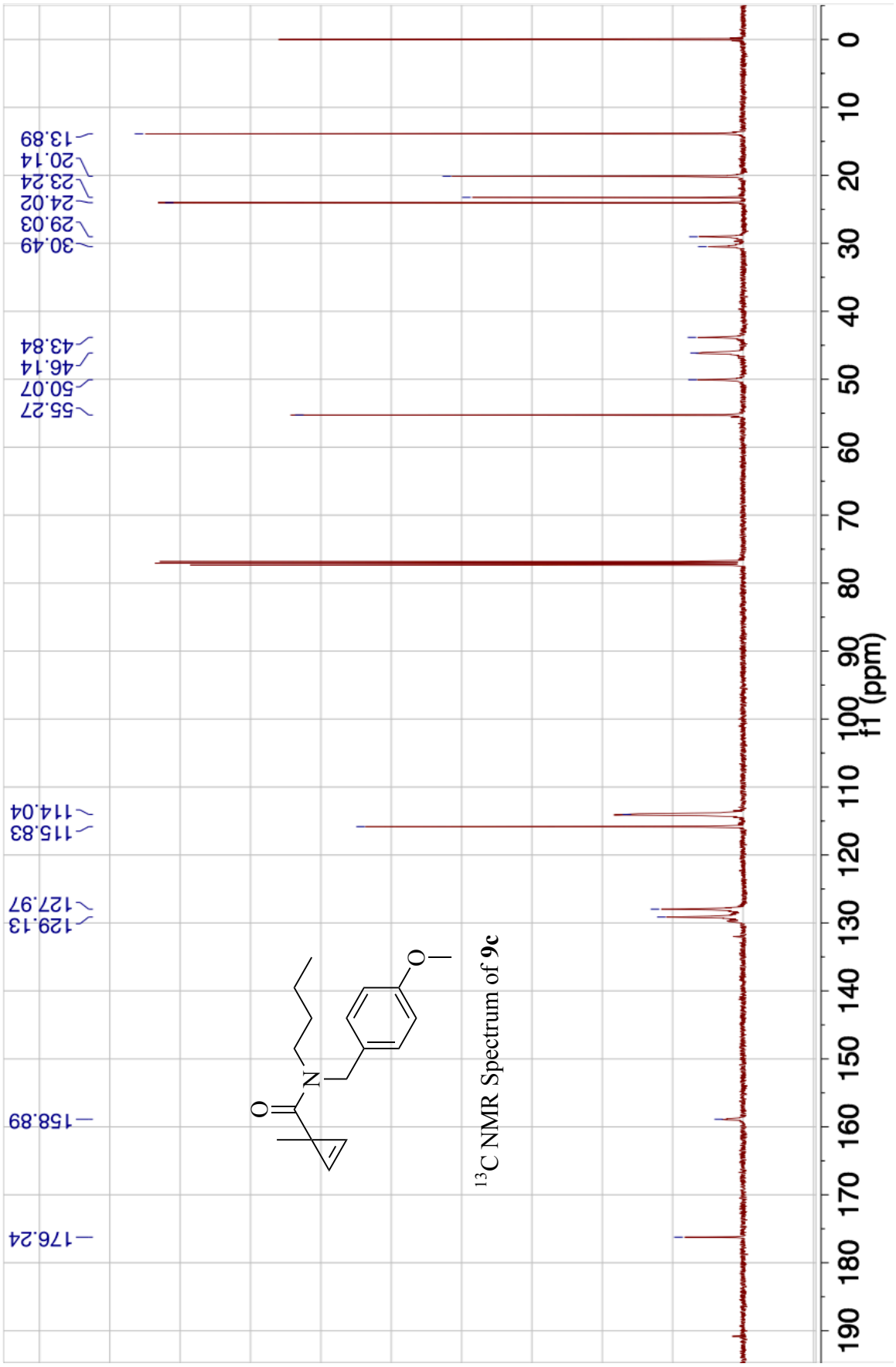
^{1}H NMR Spectrum of **9b**



^{13}C NMR Spectrum of **9b**



^{1}H NMR Spectrum of **9c**



^{13}C NMR Spectrum of **9c**

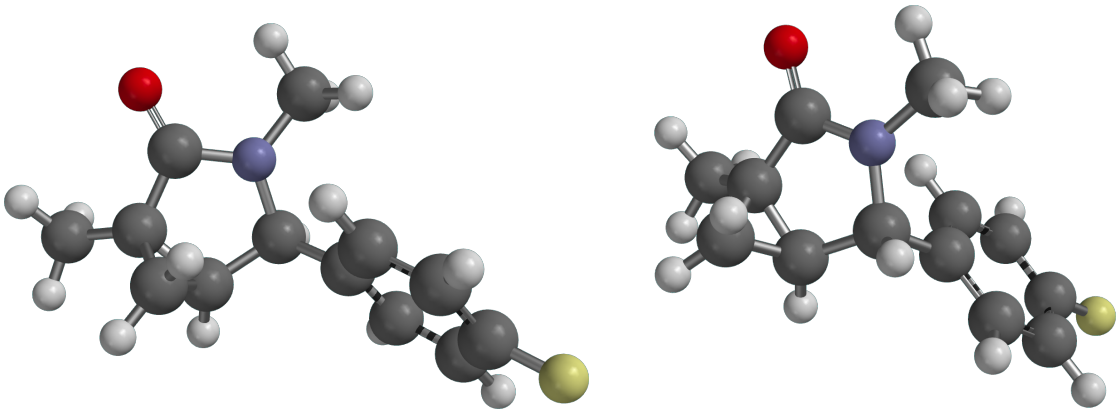


Figure 1. Geometries of *endo*-**7j** (left) and *exo*-**7j** (right) optimized by DFT (b3lyp 6-311+G**) in THF.

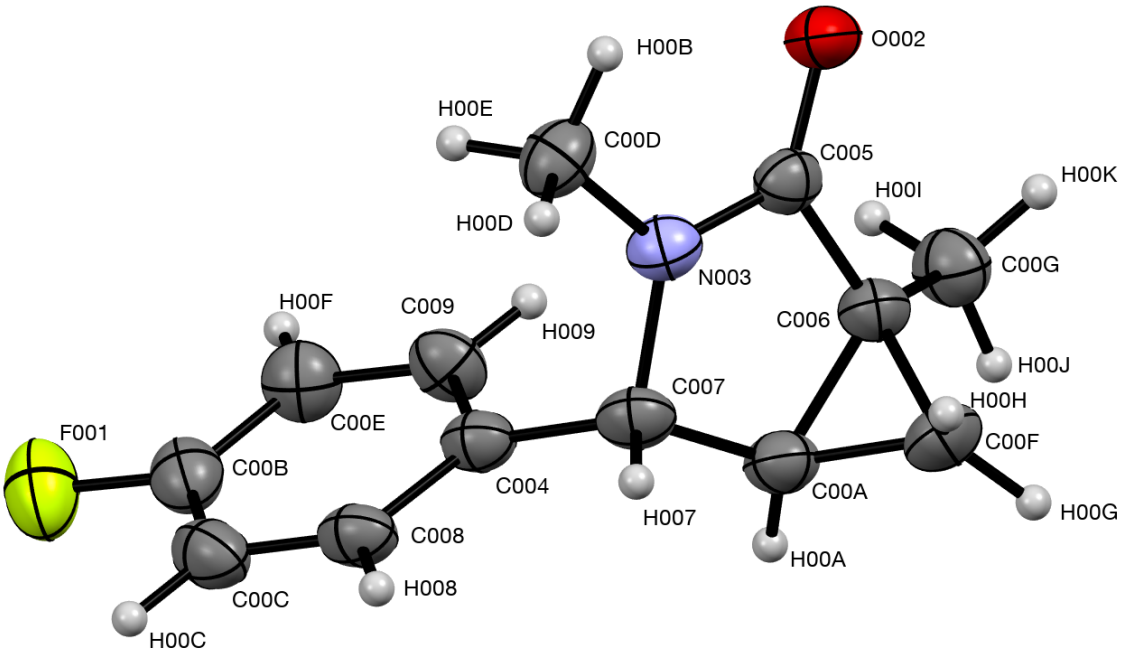
Table 1. Cartesian coordinates of atomic centers and calculated thermodynamic parameters of the optimized structure of *endo*-**7j.**

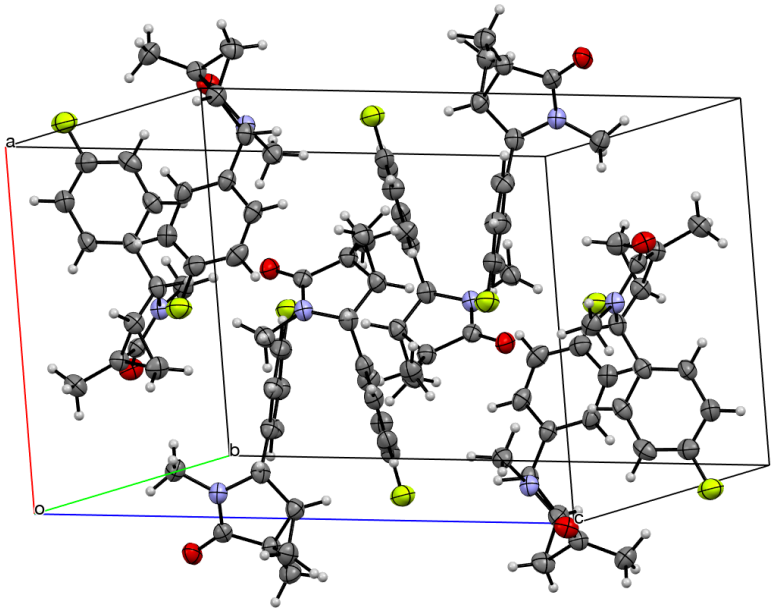
Atom	X	Y	Z	Thermodynamics
H	-1.184794	-2.163768	-1.017460	ZPE
C	-1.265710	-1.289130	-0.384014	639.15 kJ/mol
C	-2.592485	-0.857311	0.200052	
N	-1.310126	1.056018	-0.252156	H°
C	-2.553920	0.652222	0.189908	-733.564217 au
C	-0.511583	-0.027882	-0.826723	
C	-1.524845	-1.475998	1.084284	S°
H	-1.010494	-0.854626	1.807295	494.09 J/(mol*K)
H	-0.563451	0.034406	-1.924099	
H	-1.713478	-2.489911	1.419282	G°
O	-3.466053	1.396086	0.501466	-733.615783 au
C	-3.924354	-1.524496	-0.034819	
H	-3.822816	-2.612188	-0.006579	Cv
H	-4.342966	-1.243177	-1.005110	232.10 J/(mol*K)
H	-4.639304	-1.223901	0.734918	
C	0.957731	-0.010150	-0.438146	
C	3.648023	-0.121049	0.246786	
C	1.397021	0.455662	0.804838	
C	1.904510	-0.519337	-1.332352	
C	3.255031	-0.585195	-0.998043	
C	2.744494	0.404568	1.156174	
H	0.683357	0.876430	1.502886	
H	1.585283	-0.871343	-2.308260	
H	3.993801	-0.977946	-1.685562	
H	3.095405	0.768872	2.113846	
F	4.961089	-0.171127	0.581112	
C	-1.024819	2.449181	-0.543642	
H	-0.062856	2.752222	-0.124416	
H	-1.818851	3.051102	-0.103160	
H	-1.003888	2.626657	-1.626044	

Table 2. Cartesian coordinates of atomic centers and calculated thermodynamic parameters of the optimized structure of *exo*-**7j.**

Atom	X	Y	Z	Thermodynamics
H	-0.729529	-2.028550	0.903651	ZPE
C	-1.296578	-1.106674	0.879808	638.64 kJ/mol
C	-2.419492	-0.898457	-0.113391	
N	-1.326720	1.142116	0.214810	H°
C	-2.357934	0.562888	-0.487444	-733.566579 au
C	-0.519334	0.209601	1.001296	
C	-2.721087	-1.101487	1.360573	S°
H	-3.078354	-0.259253	1.944319	454.31 J/(mol*K)
H	-3.154654	-2.057110	1.633517	
O	-3.092835	1.138820	-1.270825	G°
C	-2.870228	-1.881232	-1.163548	-733.618169 au
H	-2.870127	-2.900226	-0.768763	
H	-2.215454	-1.854463	-2.039129	Cv
H	-3.882340	-1.639543	-1.497295	232.36 J/(mol*K)
C	0.916821	0.091151	0.509511	
C	3.535984	-0.219868	-0.356257	
C	1.964353	-0.012177	1.427672	
C	1.214526	0.039989	-0.856220	
C	2.525214	-0.113612	-1.299594	
C	3.283054	-0.172280	1.004563	
H	1.753576	0.033122	2.491414	
H	0.416165	0.133714	-1.583769	
H	2.767887	-0.147908	-2.354532	
H	4.102025	-0.250906	1.708737	
F	4.814905	-0.365639	-0.781429	
H	-0.494100	0.543226	2.047307	
C	-1.069635	2.568788	0.199842	
H	-1.786609	3.029956	-0.478842	
H	-0.055739	2.782715	-0.151334	
H	-1.191164	3.000824	1.199639	

X-Ray Crystallography Data for *exo*-7j





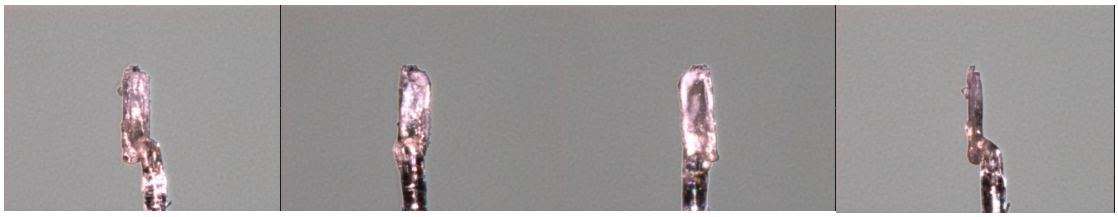


Table 1 Crystal data and structure refinement for *exo*-7j.

Identification code	ANNA_01092017_Cl_f2631_23
Empirical formula	$C_{13}H_{14}FNO$
Formula weight	219.25
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	Pbca
a/Å	11.0397(5)
b/Å	10.6042(3)
c/Å	19.2081(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2248.64(16)
Z	8
ρ_{calc}g/cm^3	1.295
μ/mm^{-1}	0.766
F(000)	928.0
Crystal size/mm^3	0.393 × 0.123 × 0.052
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.208 to 152.184
Index ranges	$-13 \leq h \leq 13$, $-13 \leq k \leq 8$, $-24 \leq l \leq 22$
Reflections collected	15534
Independent reflections	2317 [R_{int} = 0.0633, R_{sigma} = 0.0299]
Data/restraints/parameters	2317/0/147
Goodness-of-fit on F^2	1.054
Final R indexes [I>=2σ (I)]	R_1 = 0.0652, wR_2 = 0.1715
Final R indexes [all data]	R_1 = 0.0736, wR_2 = 0.1812
Largest diff. peak/hole / e Å^{-3}	0.32/-0.26

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for *exo*-7j. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
F001	-426.0(13)	6524.0(16)	4438.9(7)	59.0(4)
O002	5979.8(14)	4831.1(13)	2931.1(8)	42.6(4)
N003	4591.2(16)	6439.0(15)	2903.5(8)	36.1(4)
C004	2957.0(19)	7277.1(16)	3638.6(10)	34.6(4)
C005	5560.7(18)	5827.1(16)	3161.4(10)	33.5(4)
C006	6040.4(18)	6544.5(16)	3772.1(10)	35.4(4)
C007	4184(2)	7525.3(17)	3319.8(10)	36.5(5)
C008	1973(2)	8049.3(17)	3484.5(11)	39.2(5)
C009	2767.4(19)	6248.4(18)	4080.9(10)	39.9(5)
C00A	5196(2)	7658.9(16)	3854.6(11)	38.5(5)
C00B	693(2)	6783(2)	4180.4(11)	42.5(5)
C00C	834(2)	7812(2)	3754.4(11)	45.0(5)
C00D	3920(2)	6033(2)	2292.1(11)	43.3(5)
C00E	1635(2)	5992(2)	4353.3(11)	43.8(5)
C00F	6449(2)	7863.0(18)	3576.0(12)	44.5(5)
C00G	6620(2)	5822(2)	4353.8(11)	45.7(5)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for *exo*-7j. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F001	40.2(8)	86.3(10)	50.4(8)	-4.0(7)	2.1(6)	-0.7(7)
O002	43.7(9)	31.6(7)	52.6(8)	-9.5(6)	4.6(6)	-1.6(6)
N003	41.6(9)	33.7(8)	32.9(8)	-1.9(6)	-1.0(7)	-1.0(6)
C004	41.7(11)	27.6(8)	34.3(9)	-0.6(6)	-4.2(8)	2.8(7)
C005	35.5(10)	29.0(8)	35.9(9)	0.6(7)	3.8(7)	-4.9(7)
C006	37.6(10)	29.0(8)	39.6(10)	-1.8(7)	-0.4(8)	-0.5(7)
C007	46.2(11)	25.6(8)	37.8(9)	1.9(7)	-1.1(8)	1.8(7)
C008	47.9(12)	28.4(8)	41.4(10)	-1.1(7)	-9.1(9)	6.5(8)
C009	43.4(11)	34.8(9)	41.4(10)	8.3(7)	-1.6(9)	7.1(8)
C00A	43.9(11)	28.6(8)	42.9(10)	-3.7(7)	-1.7(8)	0.1(7)
C00B	39.8(11)	52.2(11)	35.6(9)	-7.5(8)	-1.5(8)	1.1(9)
C00C	45.7(12)	42.9(10)	46.5(11)	-7.1(8)	-9.7(9)	12.2(8)
C00D	46.5(12)	47.0(11)	36.4(10)	-1.5(8)	-3.1(9)	-7.3(9)
C00E	46.7(12)	44.4(10)	40.3(10)	6.6(8)	-1.1(9)	0.6(9)
C00F	46.6(12)	30.6(9)	56.2(12)	-3.5(8)	-0.2(10)	-7.9(8)
C00G	46.8(12)	44.3(10)	46.0(11)	0.5(8)	-8.6(9)	6.1(9)

Table 4 Bond Lengths for *exo*-7j.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F001	C00B	1.359(3)	C006	C00A	1.514(3)
O002	C005	1.235(2)	C006	C00F	1.516(3)
N003	C005	1.346(3)	C006	C00G	1.498(3)
N003	C007	1.473(2)	C007	C00A	1.524(3)
N003	C00D	1.454(3)	C008	C00C	1.383(3)
C004	C007	1.509(3)	C009	C00E	1.383(3)
C004	C008	1.392(3)	C00A	C00F	1.499(3)
C004	C009	1.398(3)	C00B	C00C	1.373(3)
C005	C006	1.495(3)	C00B	C00E	1.376(3)

Table 5 Bond Angles for *exo*-7j.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C005	N003	C007	114.84(16)	N003	C007	C004	110.97(15)
C005	N003	C00D	124.04(17)	N003	C007	C00A	102.40(16)
C00D	N003	C007	120.97(17)	C004	C007	C00A	113.61(16)
C008	C004	C007	120.76(17)	C00C	C008	C004	121.51(19)
C008	C004	C009	118.11(19)	C00E	C009	C004	121.24(18)
C009	C004	C007	121.11(17)	C006	C00A	C007	107.96(15)
O002	C005	N003	125.33(18)	C00F	C00A	C006	60.45(13)
O002	C005	C006	125.70(18)	C00F	C00A	C007	116.69(18)
N003	C005	C006	108.97(16)	F001	C00B	C00C	118.8(2)
C005	C006	C00A	105.15(16)	F001	C00B	C00E	118.4(2)
C005	C006	C00F	112.31(16)	C00C	C00B	C00E	122.8(2)
C005	C006	C00G	118.45(16)	C00B	C00C	C008	118.11(19)
C00A	C006	C00F	59.29(13)	C00B	C00E	C009	118.18(19)
C00G	C006	C00A	125.73(18)	C00A	C00F	C006	60.26(12)
C00G	C006	C00F	121.97(18)				

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for *exo*-7j.

Atom	*x*	*y*	*z*	U(eq)
H007	4148	8296	3021	44
H008	2086	8755	3187	47
H009	3429	5716	4196	48
H00A	4994	7965	4333	46
H00C	169	8346	3648	54
H00B	4395	5403	2037	65
H00D	3767	6761	1990	65
H00E	3147	5662	2437	65
H00F	1510	5290	4652	53
H00G	7044	8284	3883	53
H00H	6534	8061	3075	53
H00I	6058	5175	4522	69
H00J	6818	6400	4735	69
H00K	7363	5420	4185	69

Experimental

Single crystals of $C_{13}H_{14}FNO$ [*exo*-**7j**] were recrystallized from EtOAc. A suitable crystal was selected and mounted by acrylic glue on the glass stick on a SuperNova, Dual, Cu at zero, AtlasS2 diffractometer. The crystal was kept at 150.00(10) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of *exo*-7j

Crystal Data for $C_{13}H_{14}FNO$ (M =219.25 g/mol): orthorhombic, space group Pbca (no. 61), a = 11.0397(5) Å, b = 10.6042(3) Å, c = 19.2081(9) Å, V = 2248.64(16) Å^3, Z = 8, T = 150.00(10) K, μ(CuKα) = 0.766 mm^{-1}, *Dcalc* = 1.295 g/cm^3, 15534 reflections measured (9.208° ≤ 2Θ ≤ 152.184°), 2317 unique (R_{int} = 0.0633, R_{sigma} = 0.0299) which were used in all calculations. The final R_1 was 0.0652 (I > 2σ(I)) and wR_2 was 0.1812 (all data).

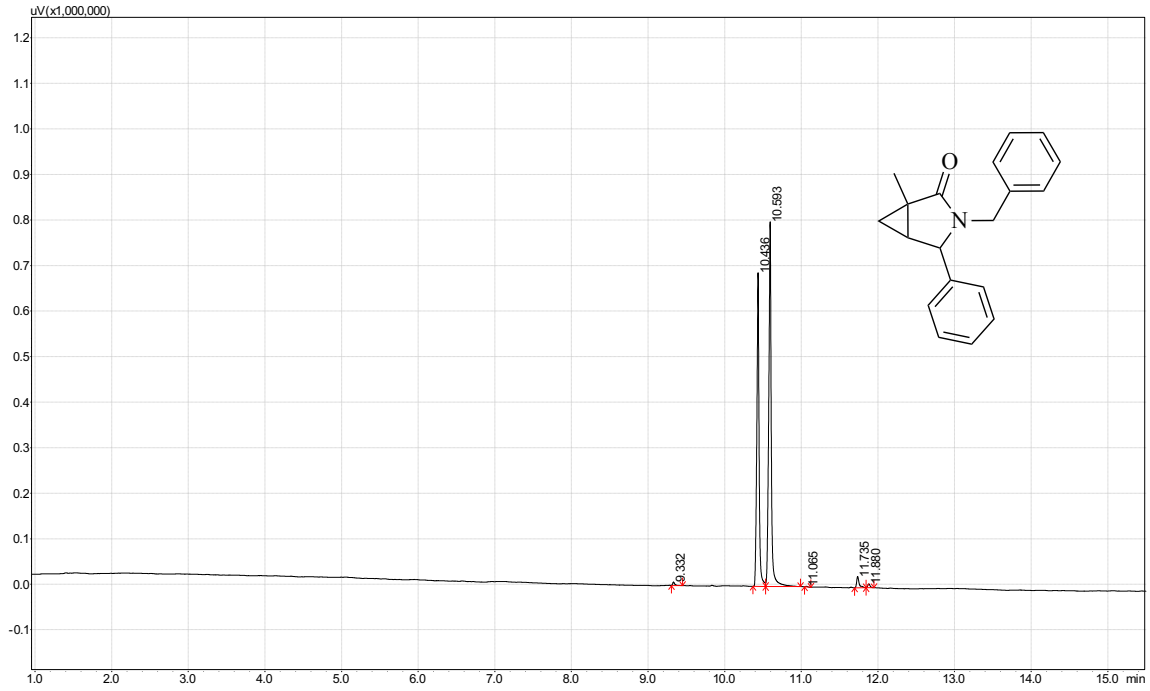
Refinement model description

Number of restraints - 0, number of constraints - unknown.
Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2.a Ternary CH refined with riding coordinates:
 C007(H007), C00A(H00A)
2.b Secondary CH2 refined with riding coordinates:
 C00F(H00G,H00H)
2.c Aromatic/amide H refined with riding coordinates:
 C008(H008), C009(H009), C00C(H00C), C00E(H00F)
2.d Idealised Me refined as rotating group:
 C00D(H00B,H00D,H00E), C00G(H00I,H00J,H00K)
```

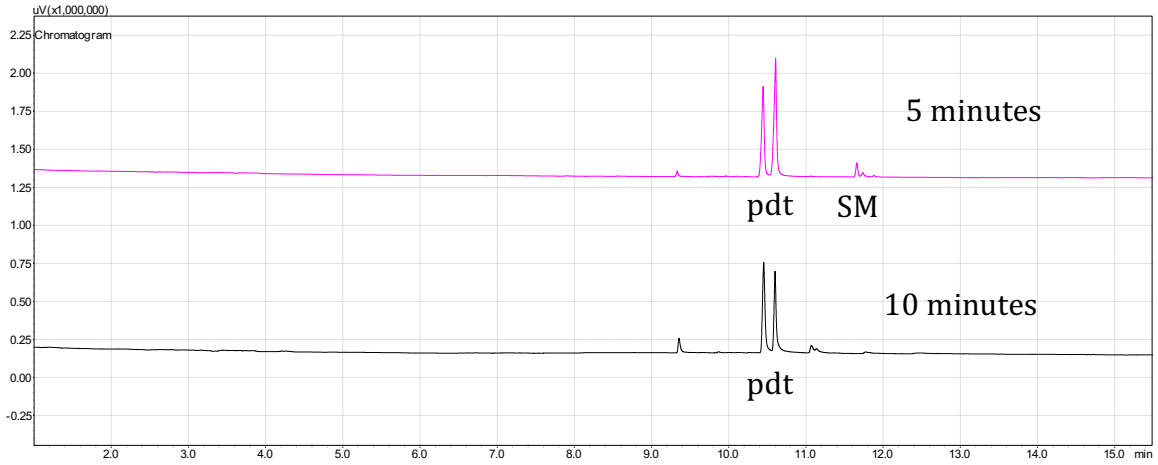
This report has been created with Olex2, compiled on 2017.03.28 svn.r3405 for OlexSys.

GC of **7a**

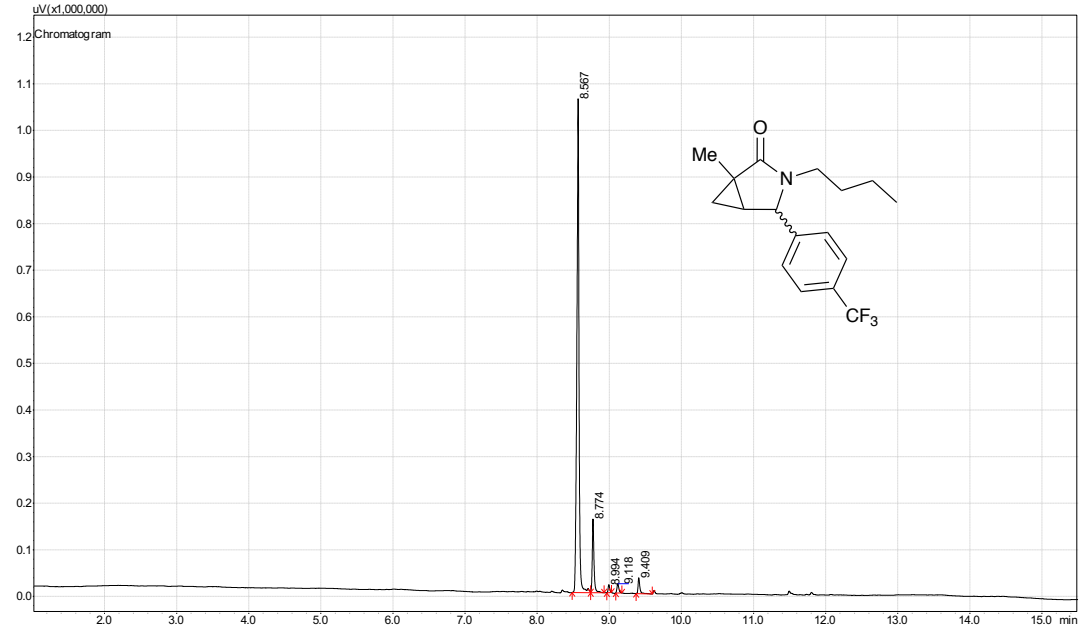


Peak#	Ret.Time	Area	Height	Conc.
1	9.332	16807.2	8285.4	0.55690
2	10.436	1397102.4	666254.8	44.78205
3	10.593	1817771.4	778658.9	52.33725
4	11.065	2157.5	1237.8	0.08320
5	11.735	58170.3	25284.1	1.69946
6	11.880	17610.8	8050.9	0.54114

Time profile of the analytical run for **7a** (preparative run was quenched after 10 minutes)

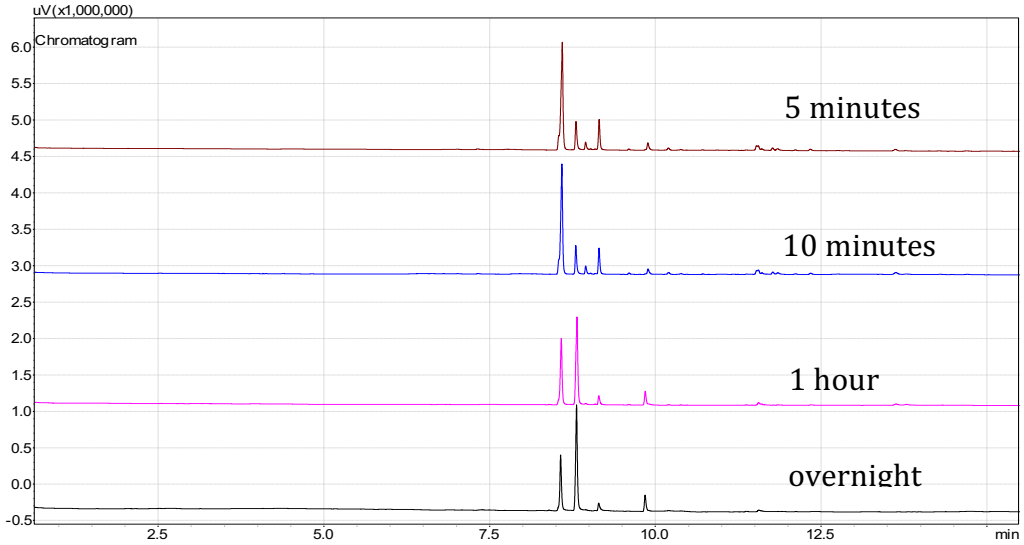


GC of **7d**

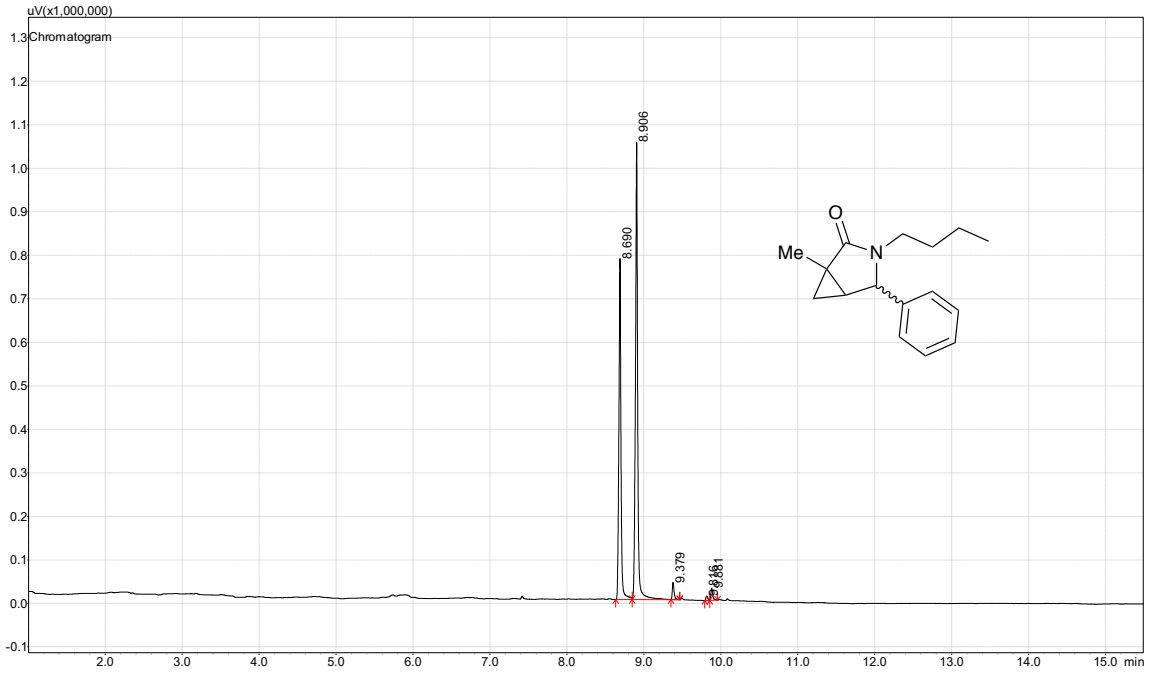


Peak#	Ret.Time	Area	Height	Conc.
1	8.567	2177559.3	970308.1	81.66344
2	8.774	263619.0	149718.9	12.60070
3	8.994	26296.4	16713.8	1.40667
4	9.118	36327.8	18547.8	1.56102
5	9.409	62571.4	32890.8	2.76817

Time profile of the analytical run for **7d** (preparative run was quenched after 5 minutes)

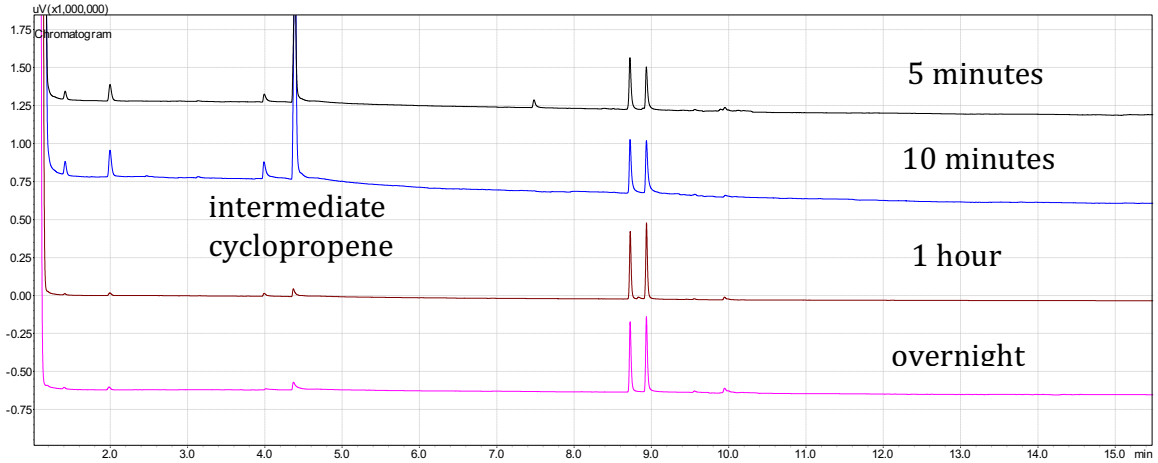


GC of **7f**

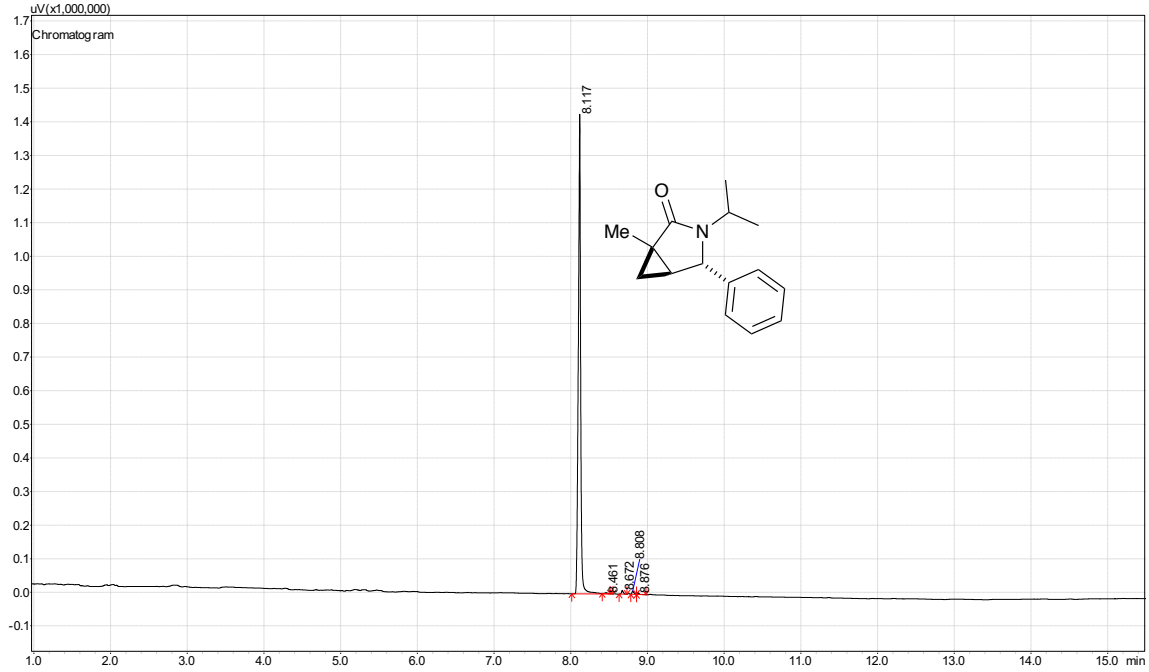


Peak#	Ret.Time	Area	Height	Conc.
1	8.690	1479834.7	752954.4	40.35928
2	8.906	2117155.4	1036677.8	55.56720
3	9.379	64009.9	38201.0	2.04762
4	9.816	17499.1	10154.8	0.54431
5	9.881	48043.2	27641.0	1.48159

Time profile of the analytical run for **7f** (preparative run was quenched after running the reaction overnight)

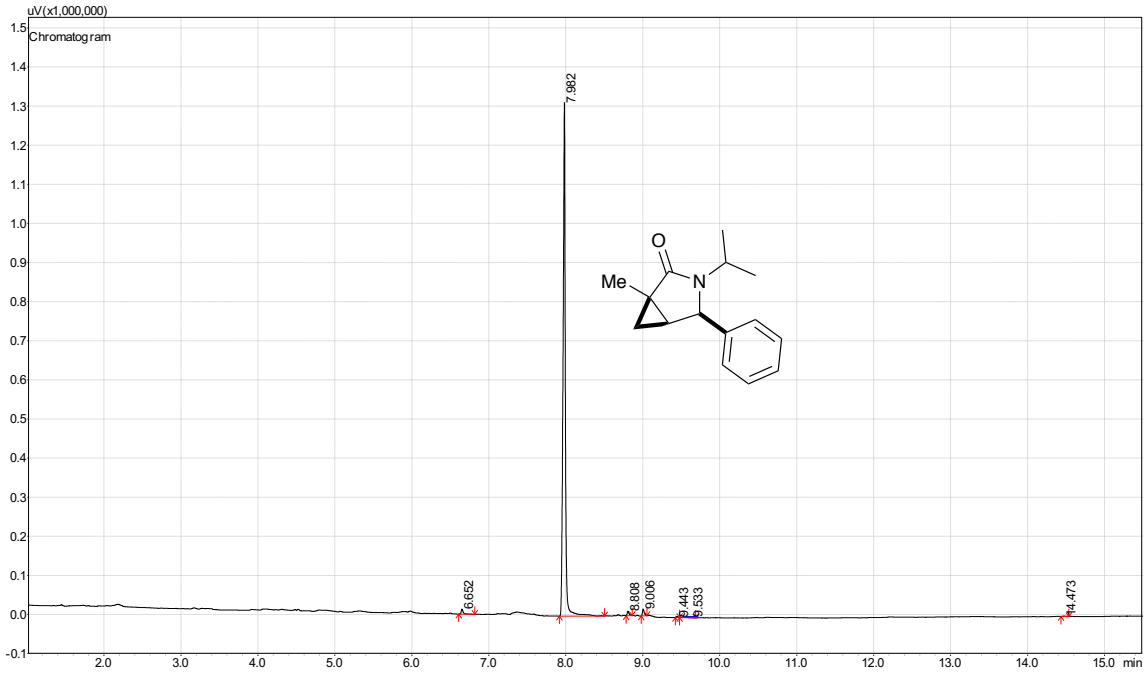


GC **7g** (exo)



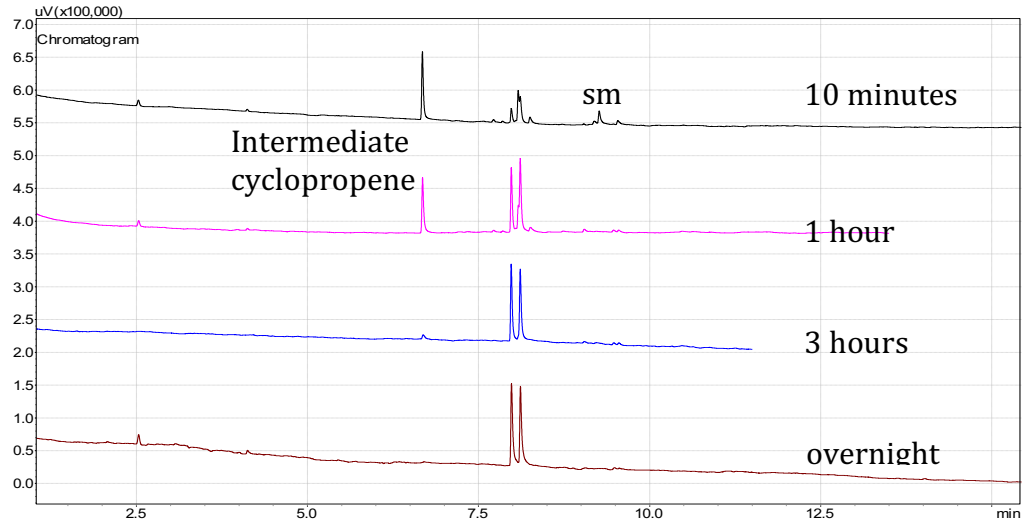
Peak#	Ret.Time	Area	Height	Conc.
1	0.035	3928.3	1297.1	0.09157
2	8.117	3014048.4	1386820.6	97.90870
3	8.461	6357.1	2903.4	0.20498
4	8.672	18741.1	11329.0	0.79982
5	8.808	18026.2	9723.3	0.68646
6	8.876	8448.1	4369.4	0.30847

GC **7g** (endo)

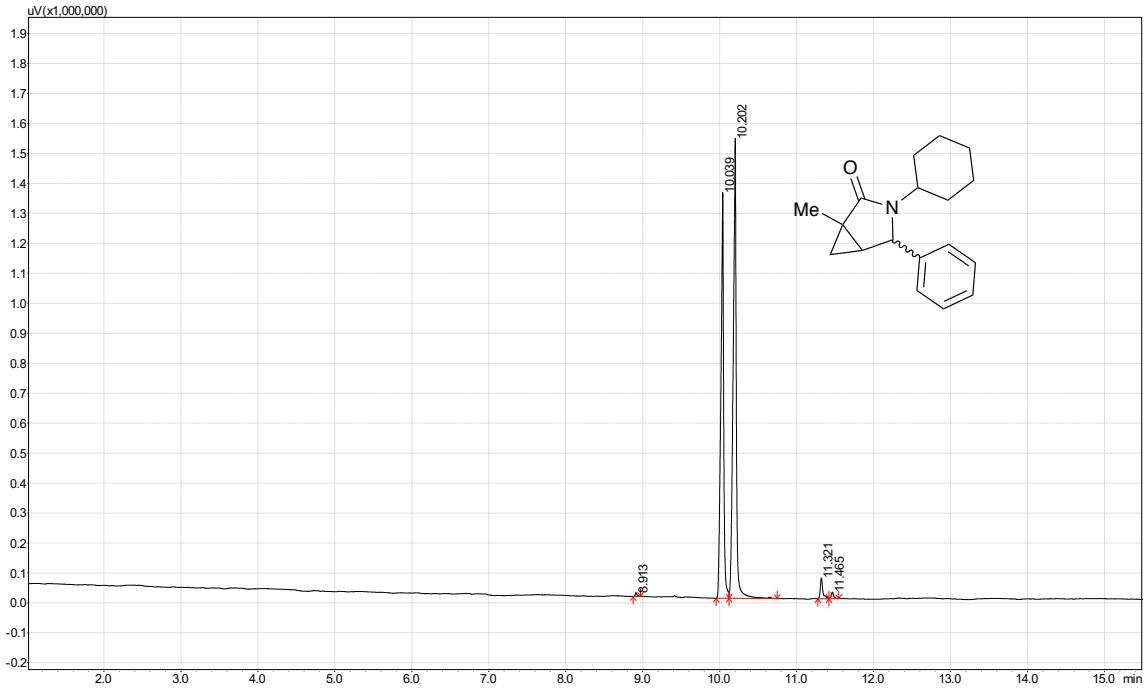


Peak#	Ret.Time	Area	Height	Conc.
1	6.652	24564.6	12723.7	0.95680
2	7.982	2721244.3	1282749.1	96.46021
3	8.808	20417.8	11802.7	0.88754
4	9.006	29208.2	16177.6	1.21653
5	9.443	4047.3	2391.9	0.17986
6	9.533	8840.5	2594.0	0.19506
7	14.473	6318.5	1383.1	0.10401

Time profile of the analytical run for **7g** (preparative run was quenched after 3 hrs)

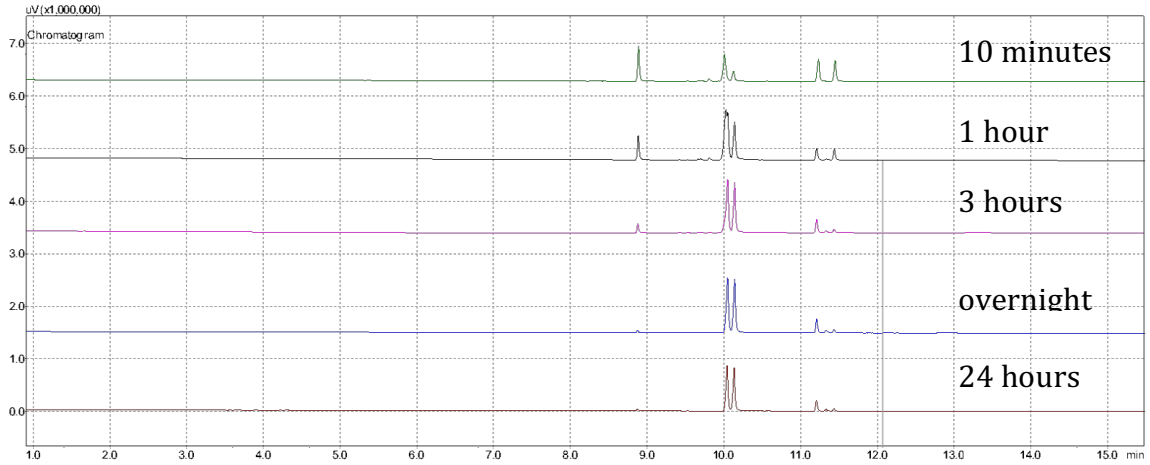


GC of **7h**

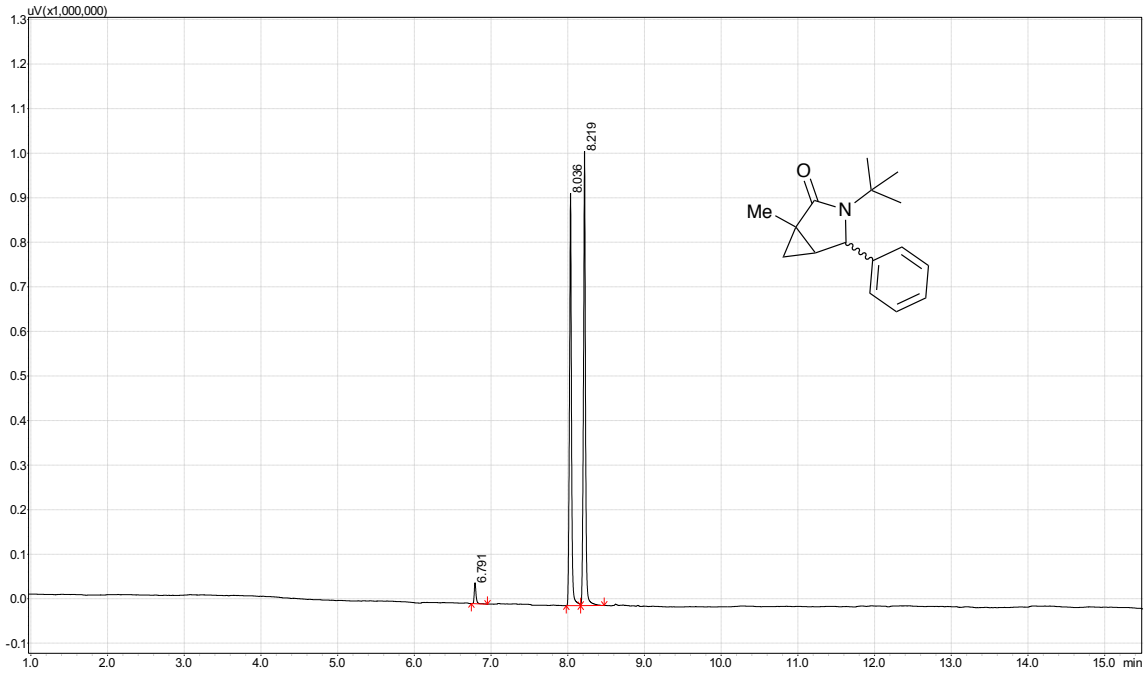


Peak#	Ret.Time	Area	Height	Conc.
1	8.913	18482.1	11316.6	0.39244
2	10.039	3404166.7	1309495.3	45.41159
3	10.202	4321507.0	1473928.4	51.11392
4	11.321	160962.5	66814.8	2.31705
5	11.465	49775.5	22059.5	0.76499

Time profile of the analytical run for **7h** (preparative run was quenched after running the reaction overnight)

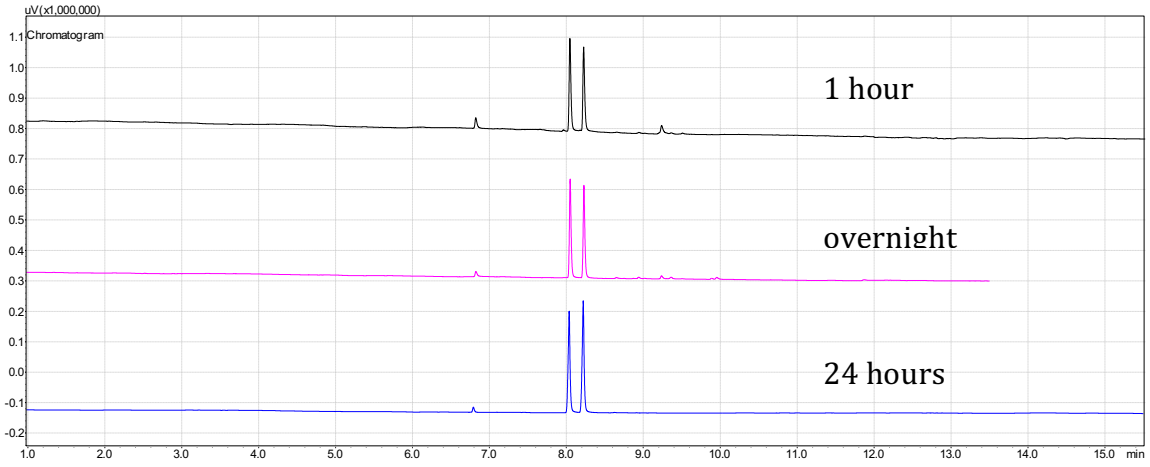


GC of **7i**

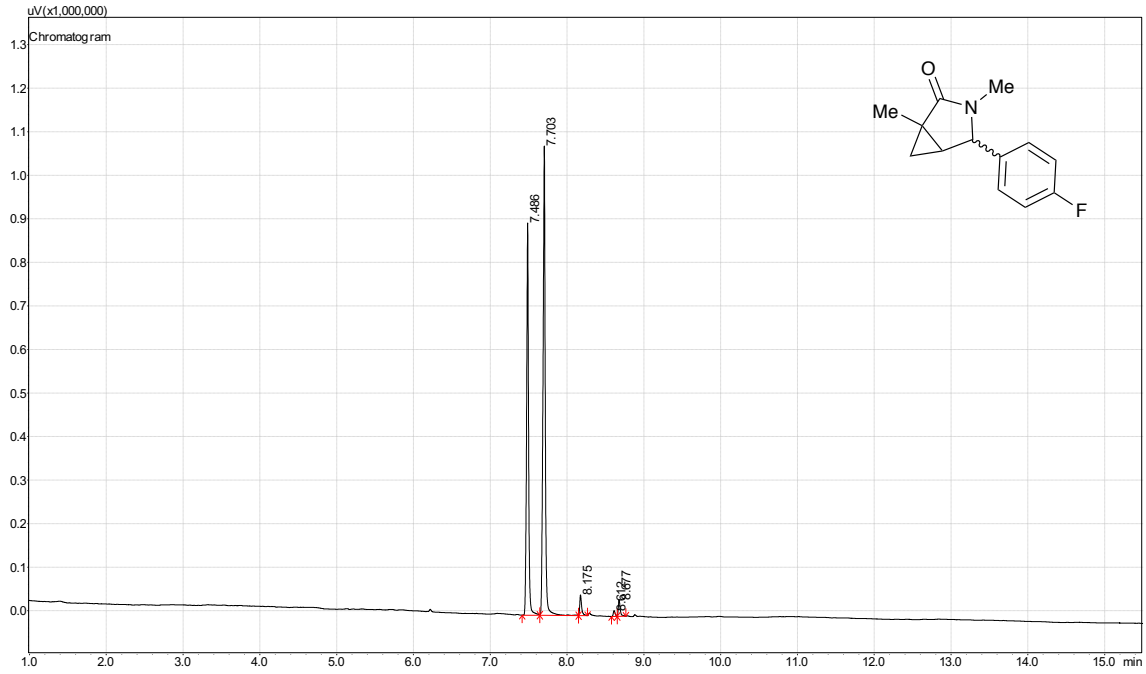


Peak#	Ret.Time	Area	Height	Conc.
1	6.791	77040.2	45676.5	2.41556
2	8.036	1670496.8	869434.7	45.97927
3	8.219	1865151.8	975816.5	51.60517

Time profile of the analytical run for **7i** (preparative run was quenched after running the reaction overnight)

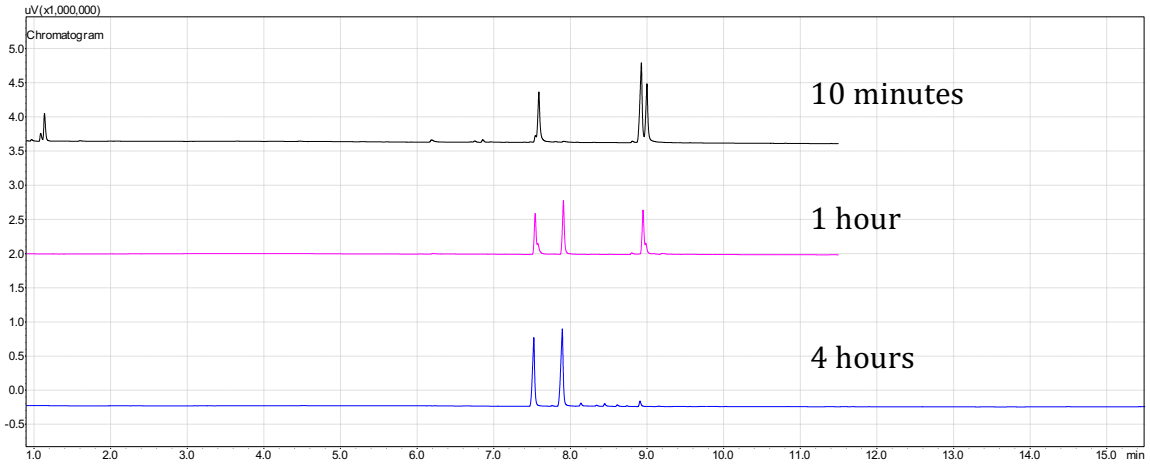


GC of **7j**

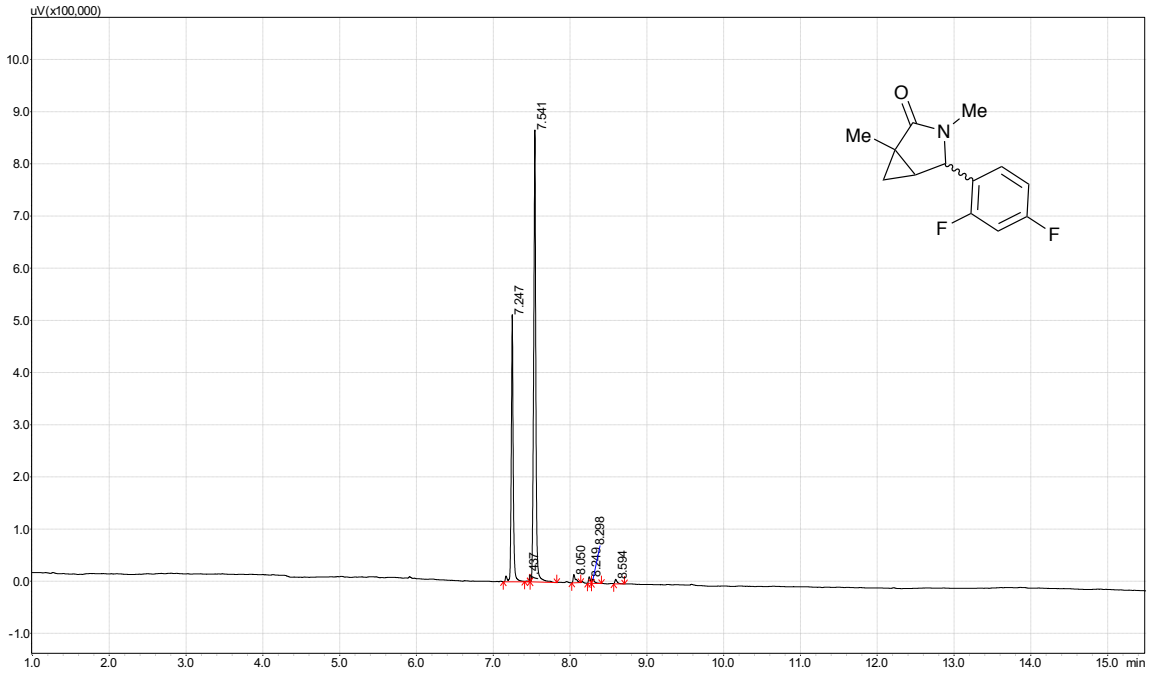


Peak#	Ret.Time	Area	Height	Conc.
1	7.486	1594262.4	863170.5	42.58879
2	7.703	2181284.7	1064589.1	52.52678
3	8.175	82979.3	47607.0	2.34893
4	8.612	22394.6	13118.4	0.64726
5	8.677	66519.2	38270.0	1.88824

Time profile of the analytical run for **7j** (preparative run was quenched after 4 hours)

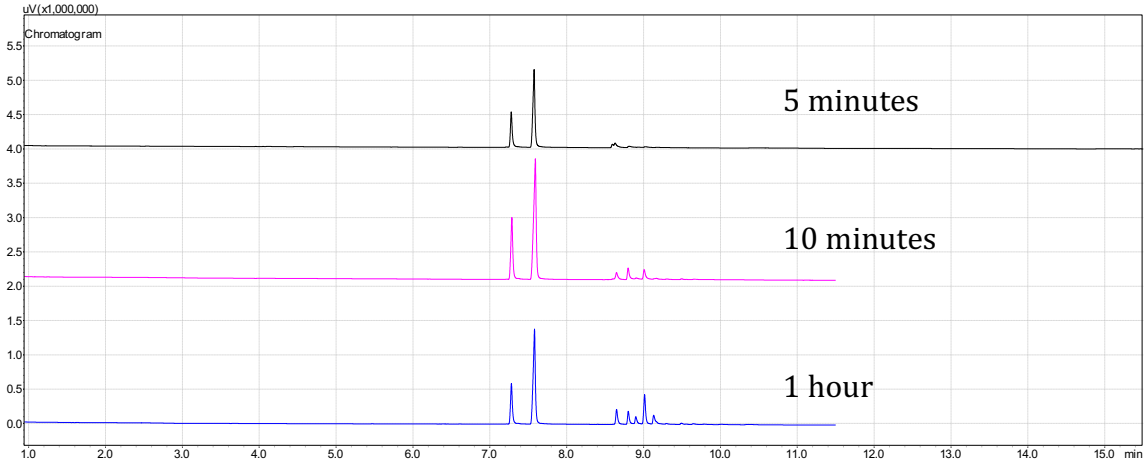


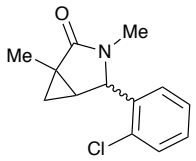
GC of **7k**



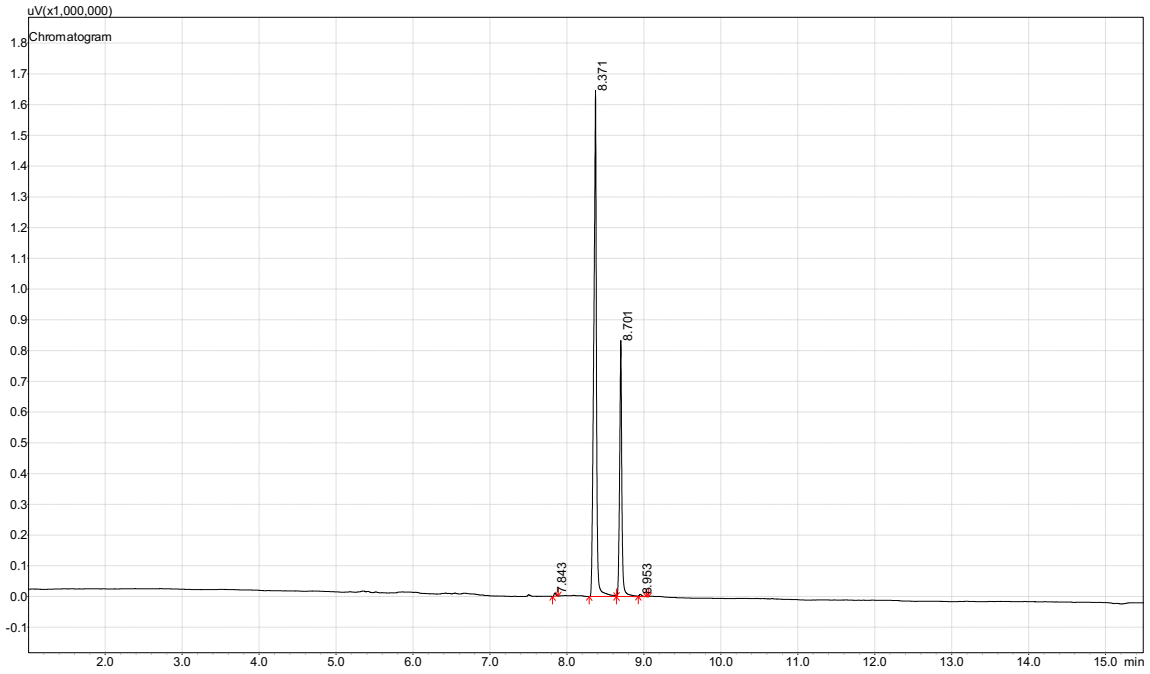
Peak#	Ret.Time	Area	Height	Conc.
1	7.247	901056.9	476269.3	35.30059
2	7.437	2490.4	1466.6	0.10870
3	7.541	1687628.2	825419.7	61.17926
4	8.050	36874.2	15616.9	1.15751
5	8.249	21354.2	12908.6	0.95678
6	8.298	19015.8	8461.6	0.62716
7	8.594	19205.9	9039.4	0.66999

Time profile of the analytical run for **7k** (preparative run was quenched after 5 minutes)





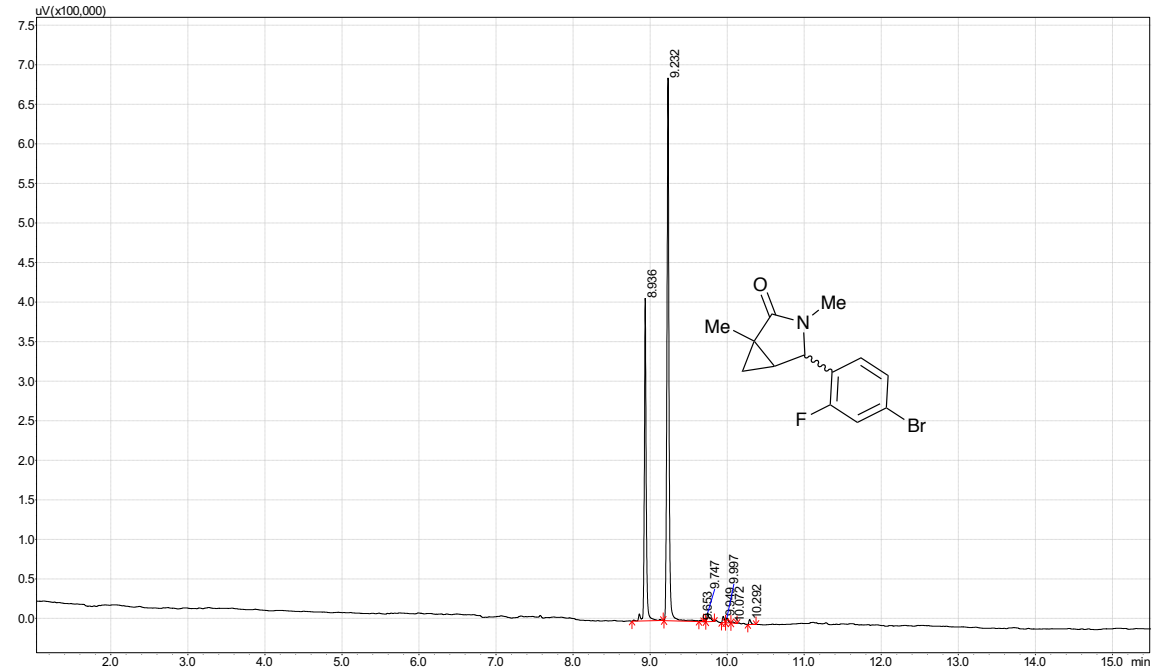
GC of **7l**



Peak#	Ret.Time	Area	Height	Conc.
1	0.035	5331.8	1974.6	0.08061
2	7.843	17591.9	10232.2	0.41768
3	8.371	3947924.9	1616903.6	66.00226
4	8.701	1670731.6	814221.4	33.23665
5	8.953	13539.0	6438.1	0.26281

Time profile of the analytical run for **7l** is provided in the main text of this paper (see Figure 2).

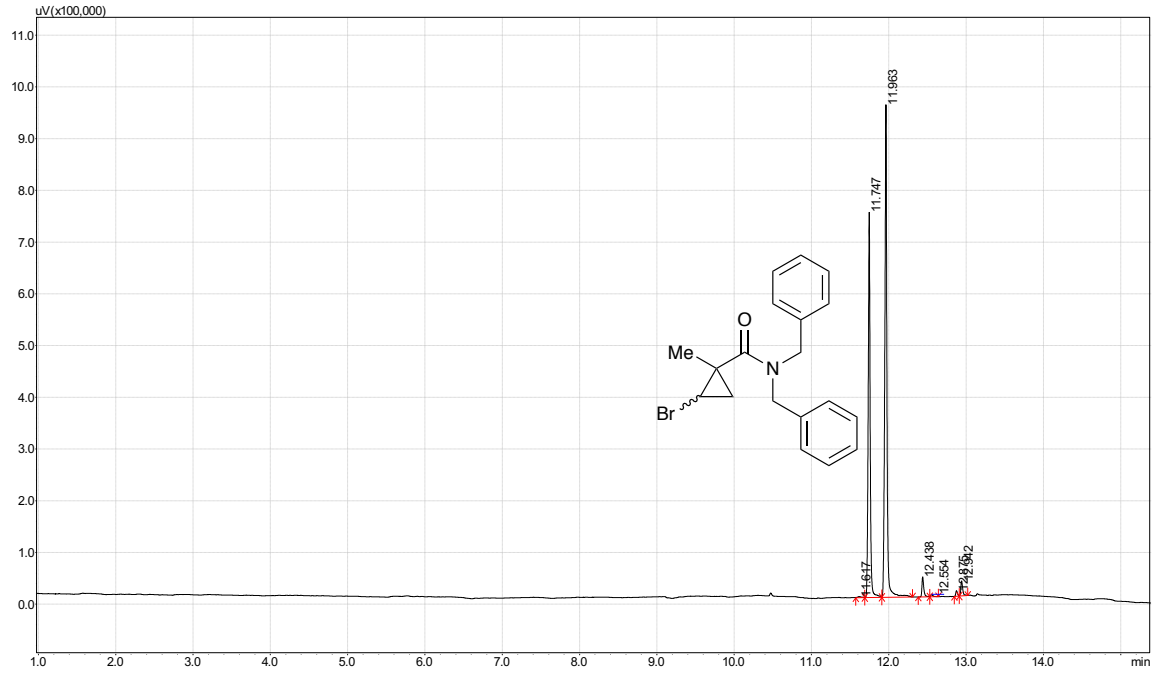
GC of **7m**



Peak#	Ret.Time	Area	Height	Conc.
1	8.936	680871.8	366803.9	34.35746
2	9.232	1263883.2	666138.7	62.39529
3	9.653	2750.9	1509.1	0.14135
4	9.747	26984.1	11268.1	1.05545
5	9.949	14234.2	8223.6	0.77028
6	9.997	11389.6	6164.4	0.57740
7	10.072	3010.3	1301.2	0.12188
8	10.292	11406.5	6201.5	0.58088

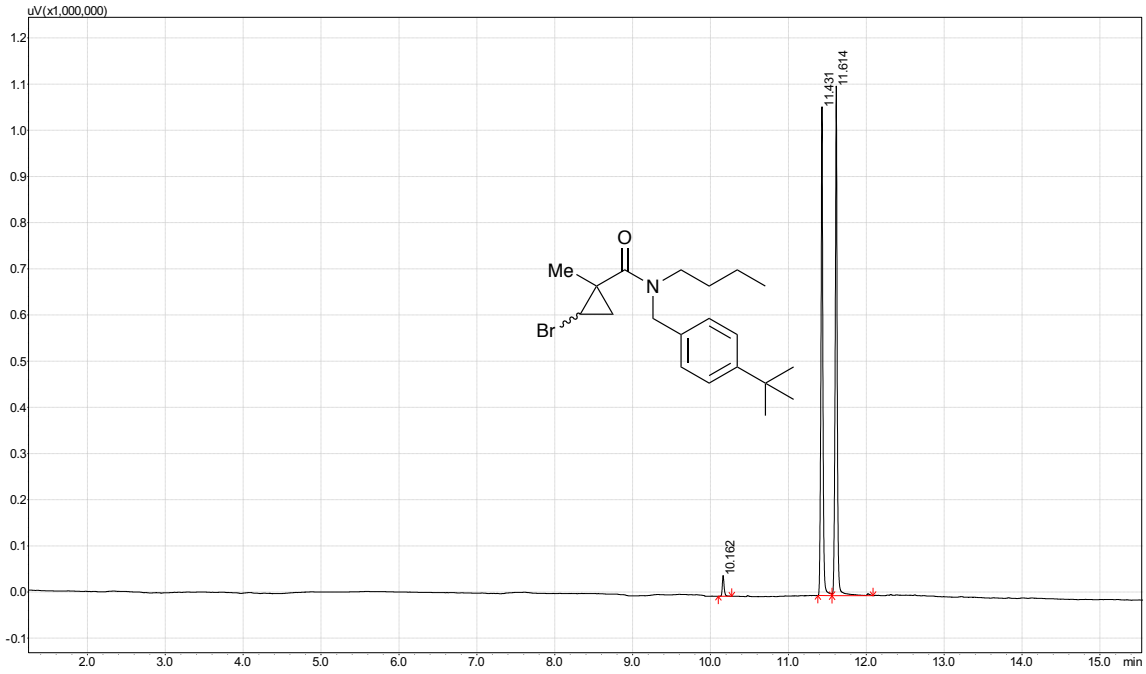
Time profile of the analytical run for **7m** is provided in the main text of this paper (see Figure 1).

GC of **8a**



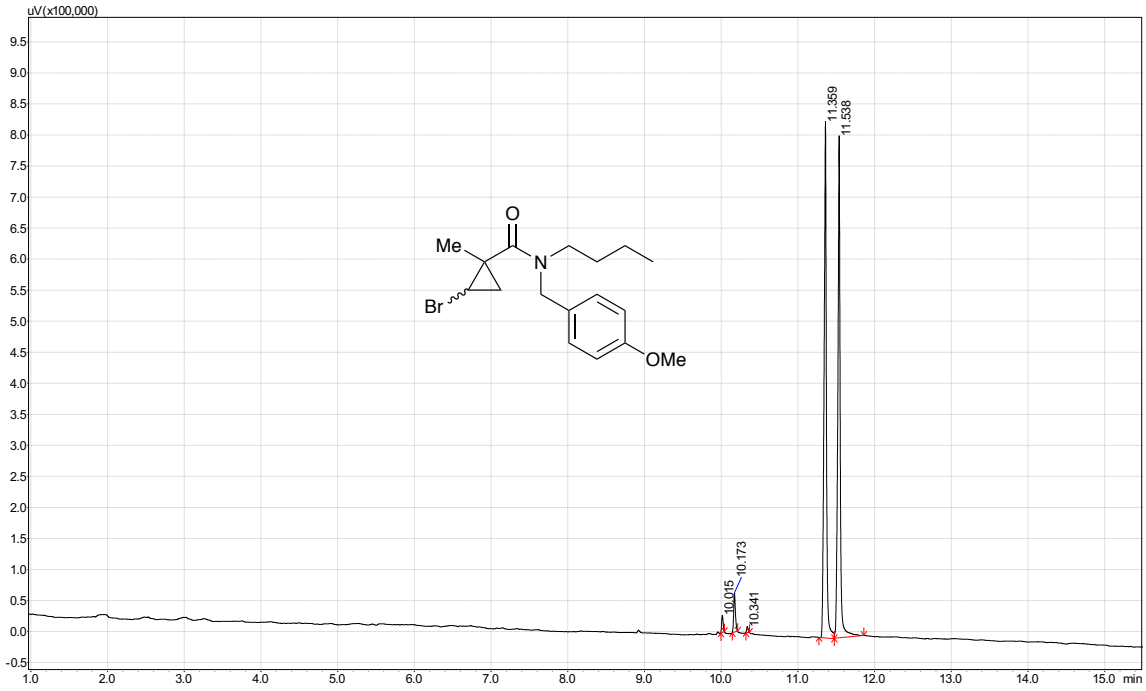
Peak#	Ret.Time	Area	Height	Conc.
1	11.617	7422.0	1953.0	0.11225
2	11.747	1295355.6	716860.8	41.19972
3	11.963	1807786.1	939498.6	53.99525
4	12.438	65312.4	38289.8	2.20061
5	12.554	9548.9	4615.7	0.26528
6	12.875	17194.9	10324.4	0.59337
7	12.942	49914.3	28422.8	1.63353

GC of **8b**



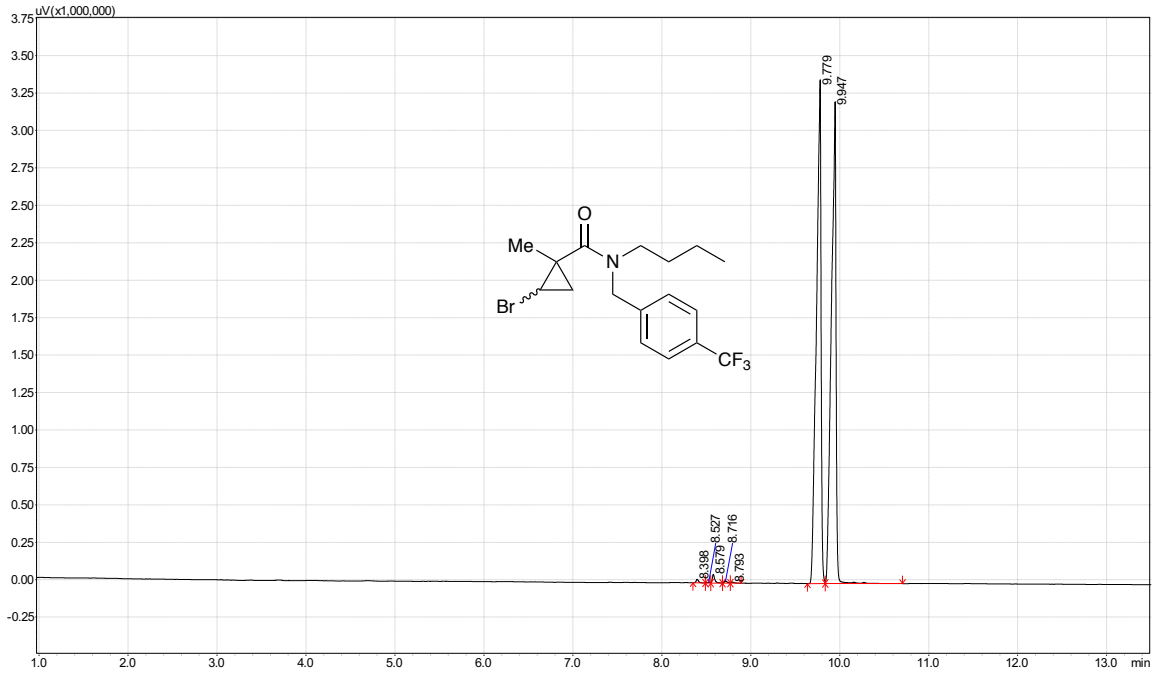
Peak#	Ret.Time	Area	Height	Conc.
1	10.162	74207.6	44897.5	2.06991
2	11.431	1821445.4	1035409.6	47.73551
3	11.614	1987139.5	1088748.2	50.19458

GC of **8c**



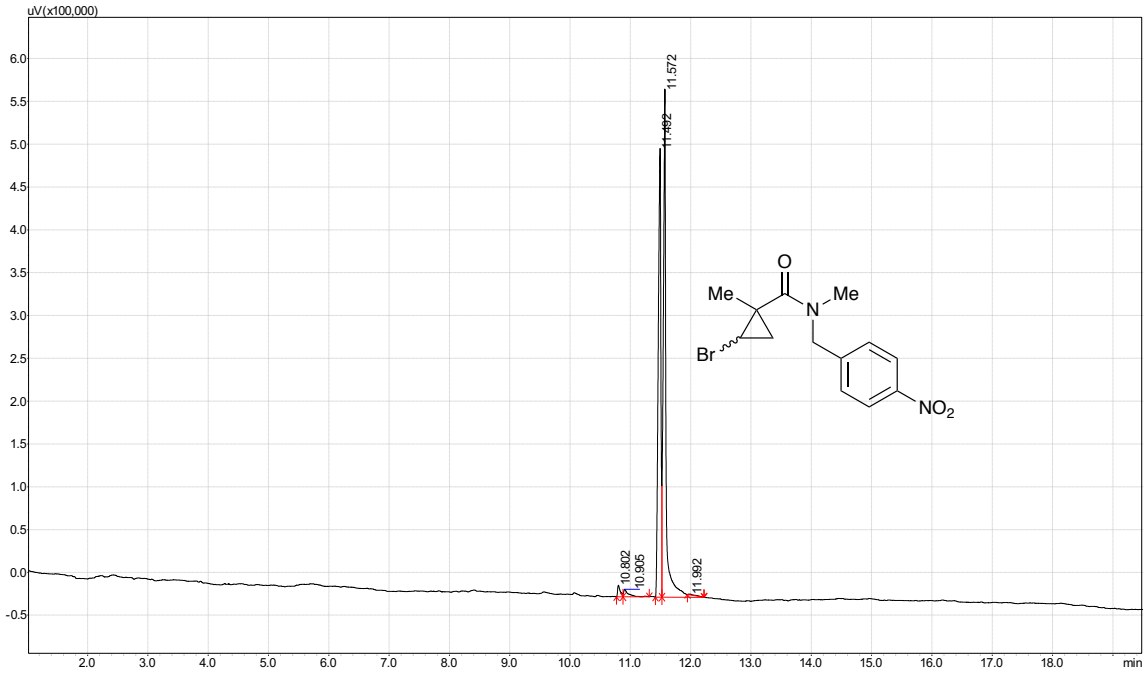
Peak#	Ret.Time	Area	Height	Conc.
1	10.015	37582.4	26132.0	1.57253
2	10.173	74353.9	50833.2	3.05896
3	10.341	14547.1	9209.9	0.55422
4	11.359	1759485.3	785205.4	47.25092
5	11.538	1701170.2	790397.4	47.56336

GC of **8d**



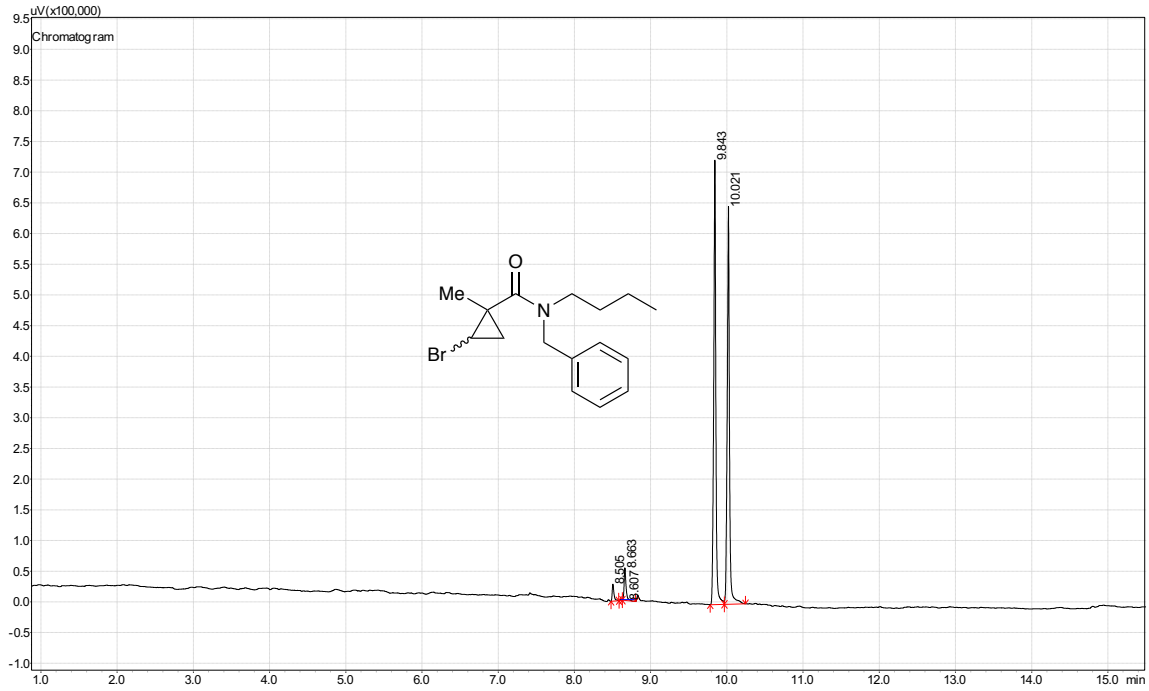
Peak#	Ret.Time	Area	Height	Conc.
1	8.398	47667.3	24329.6	0.36693
2	8.527	9954.6	4243.6	0.06400
3	8.579	116097.8	58677.9	0.88497
4	8.716	31642.1	14460.6	0.21809
5	8.793	16414.2	7283.4	0.10985
6	9.779	12077544.7	3336961.5	50.32732
7	9.947	11630985.1	3184560.5	48.02884

GC of **8e**



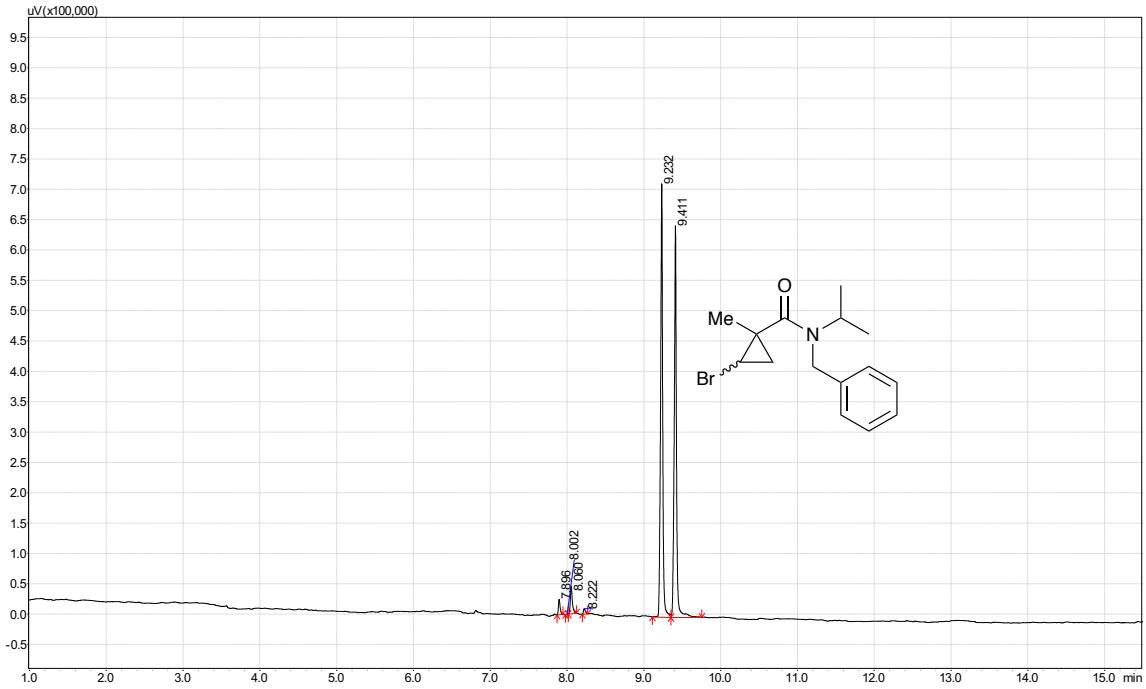
Peak#	Ret.Time	Area	Height	Conc.
1	10.802	42408.1	13390.4	1.18215
2	10.905	44894.0	8657.8	0.76434
3	11.492	1585406.5	521545.0	46.04400
4	11.572	1873705.6	588114.9	51.92105
5	11.992	7995.4	1001.9	0.08846

GC of **8f**



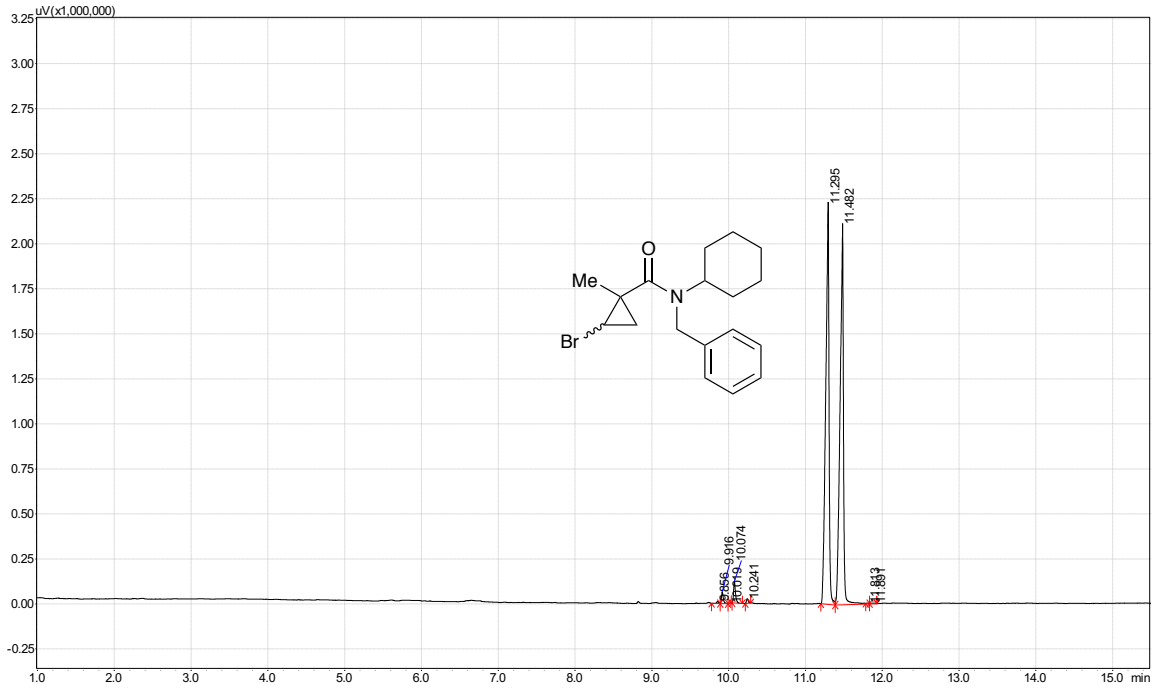
Peak#	Ret.Time	Area	Height	Conc.
1	8.505	45430.1	27268.3	1.91727
2	8.607	1845.1	1478.6	0.10396
3	8.663	94428.5	51467.4	3.61875
4	9.843	1399540.2	703479.5	49.46269
5	10.021	1319650.5	638548.9	44.89732

GC of **8g**



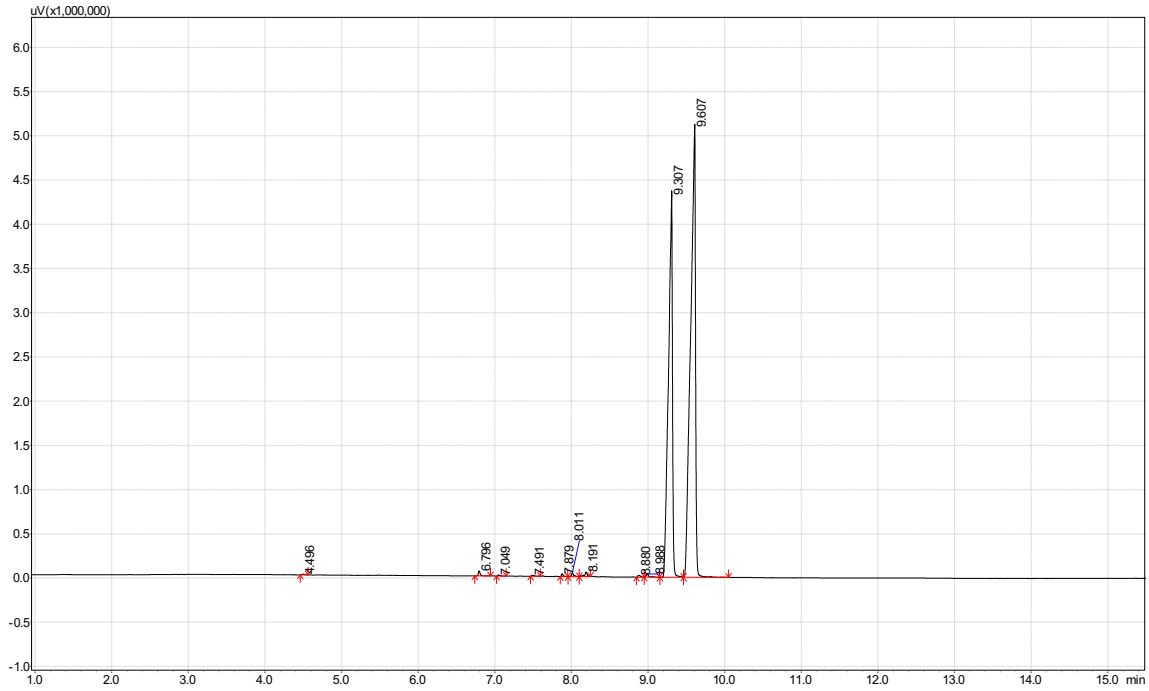
Peak#	Ret.Time	Area	Height	Conc.
1	7.896	41253.9	24848.7	1.76551
2	8.002	681.5	448.4	0.03186
3	8.060	83053.6	32668.5	2.32110
4	8.222	16736.1	8853.0	0.62901
5	9.232	1375266.7	702619.6	49.92135
6	9.411	1313624.5	638015.1	45.33118

GC of **8h**



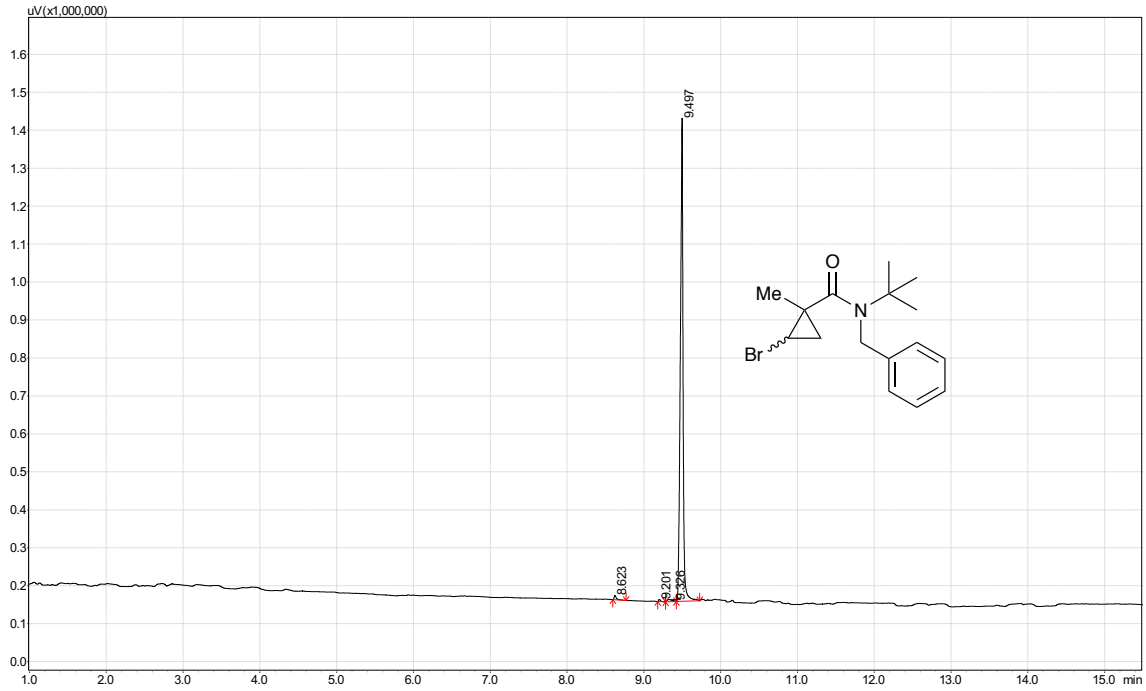
Peak#	Ret.Time	Area	Height	Conc.
1	9.856	20537.8	10778.3	0.23921
2	9.916	106765.5	60035.2	1.33242
3	10.019	2482.8	1974.7	0.04383
4	10.074	208751.5	110113.4	2.44386
5	10.241	40970.0	25587.8	0.56789
6	11.295	6582384.9	2200599.2	48.84009
7	11.482	6464216.5	2092439.5	46.43959
8	11.813	3892.6	1933.0	0.04290
9	11.891	8138.7	2262.4	0.05021

GC of **8i**



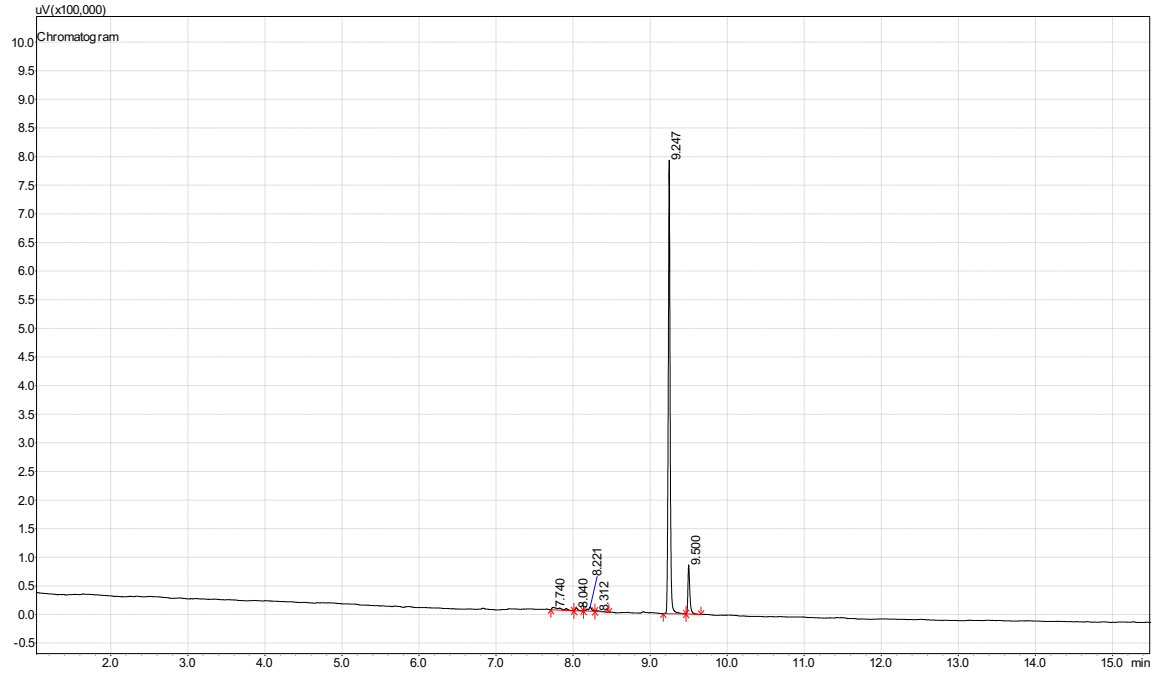
Peak#	Ret.Time	Area	Height	Conc.
1	4.496	20326.6	9473.7	0.09933
2	6.796	94409.3	56234.8	0.58961
3	7.049	22661.1	12516.4	0.13123
4	7.491	30494.2	12133.2	0.12721
5	7.879	48337.3	27963.1	0.29319
6	8.011	83217.1	39487.1	0.41401
7	8.191	124108.9	51054.6	0.53530
8	8.880	48580.5	21017.6	0.22036
9	8.988	88382.5	34419.1	0.36088
10	9.307	15692983.0	4320112.0	45.29549
11	9.607	22515184.7	4953209.3	51.93338

GC of *trans*-**8i**



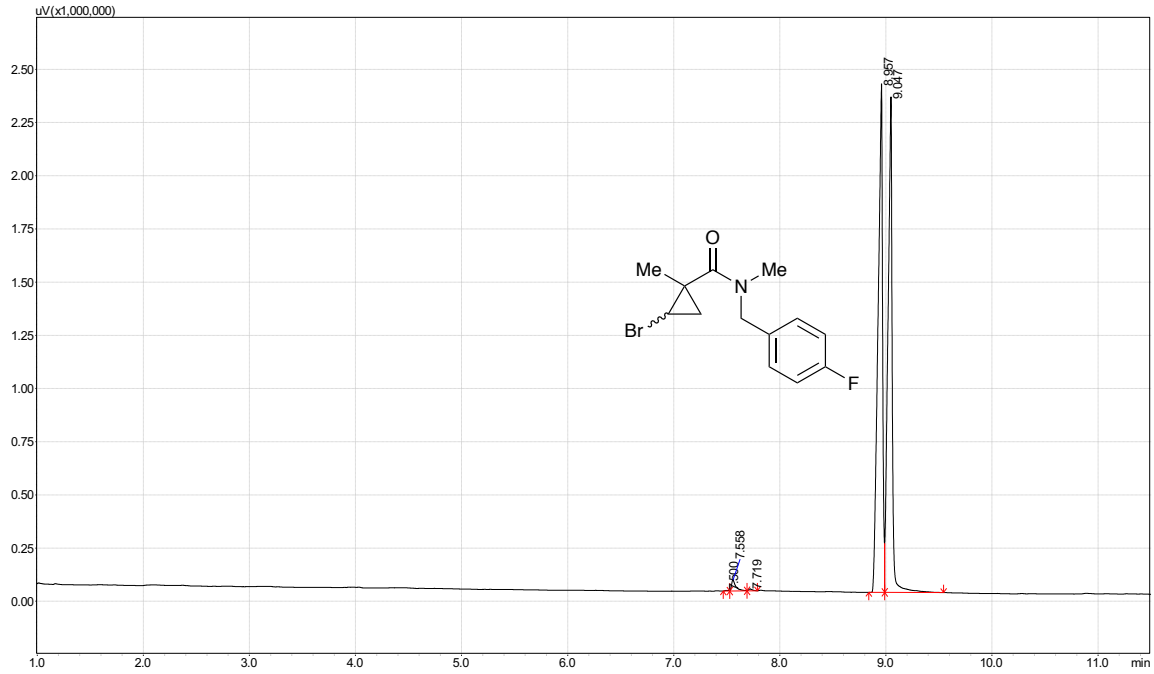
Peak#	Ret.Time	Area	Height	Conc.
1	8.623	24559.3	11558.8	0.93082
2	9.201	9508.9	5718.7	0.46052
3	9.326	28295.6	5710.2	0.45983
4	9.497	3088292.0	1218799.1	98.14882

GC of *cis*-**8i**



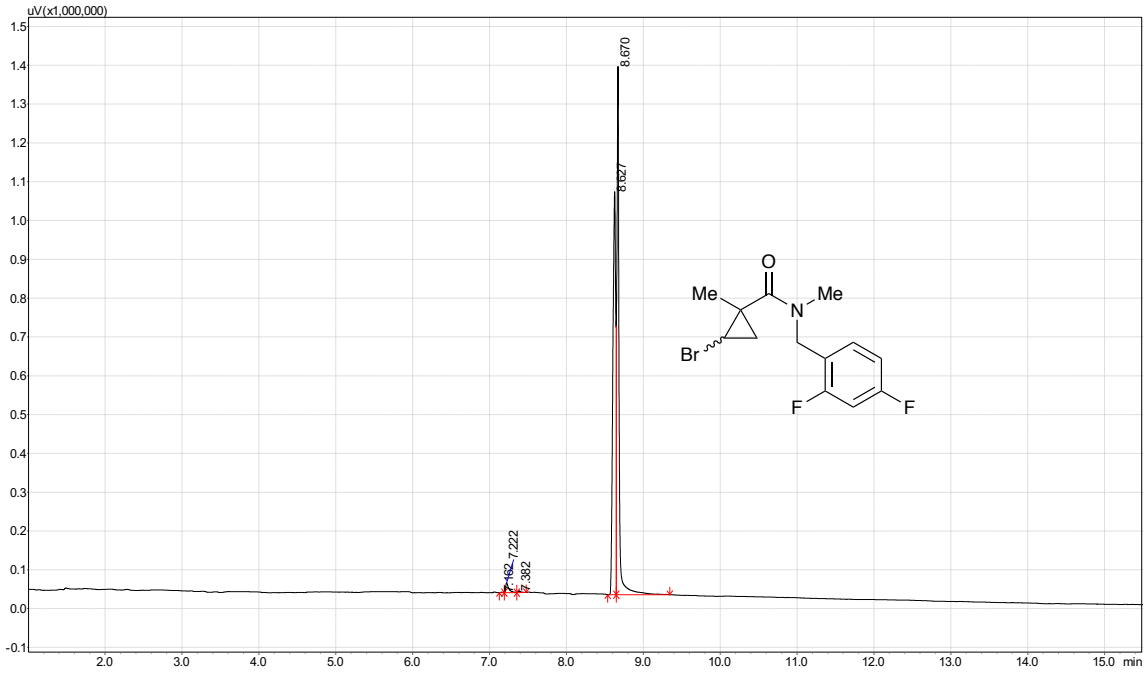
Peak#	Ret.Time	Area	Height	Conc.
1	7.740	37990.2	4190.7	0.47326
2	8.040	12014.0	5738.7	0.64807
3	8.221	24531.3	7249.0	0.81863
4	8.312	7056.0	1340.5	0.15138
5	9.247	1322956.1	782000.9	88.31139
6	9.500	147487.8	84984.3	9.59728

GC of **8j**



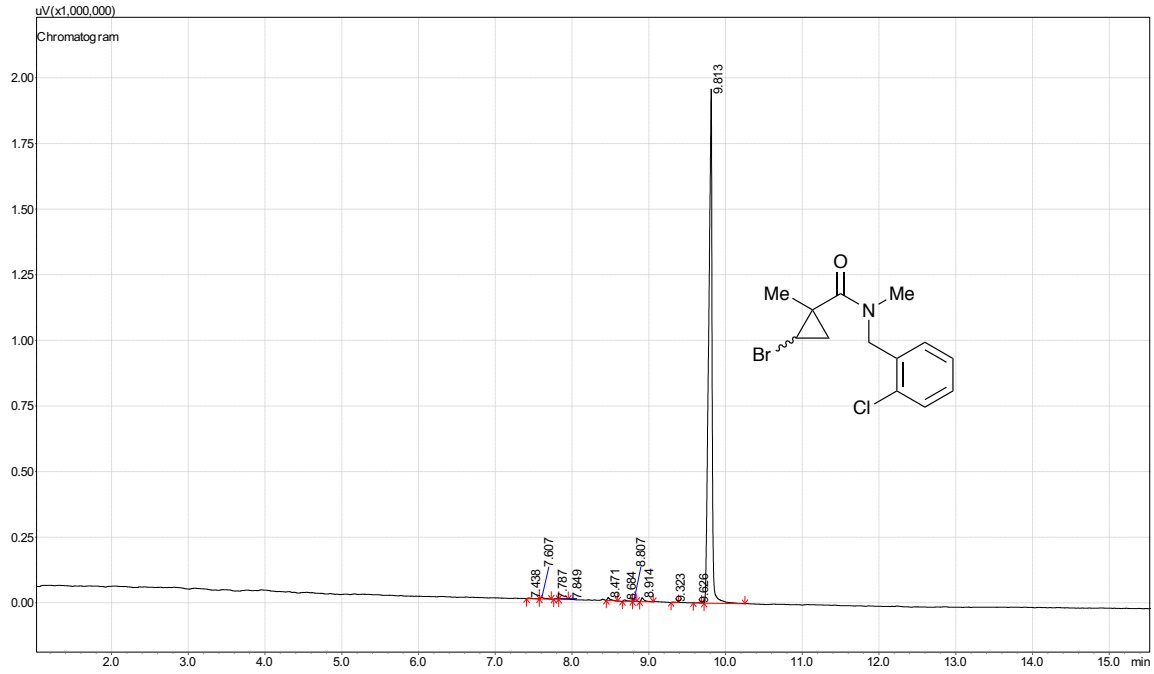
Peak#	Ret.Time	Area	Height	Conc.
1	7.500	7723.1	2887.8	0.06097
2	7.558	143708.5	50909.5	1.07486
3	7.719	21658.6	8787.7	0.18554
4	8.957	7066063.2	2370123.5	50.04096
5	9.047	6450796.1	2303658.8	48.63767

GC of **8k**



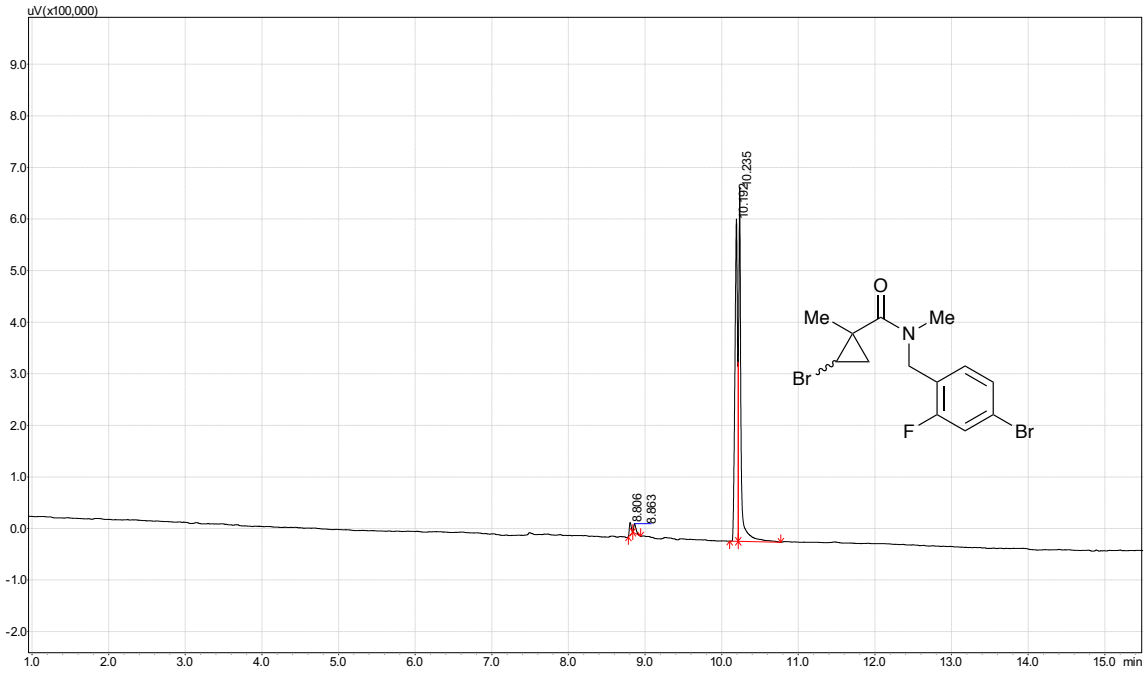
Peak#	Ret.Time	Area	Height	Conc.
1	7.162	3444.1	1336.5	0.05589
2	7.222	69320.8	24946.0	1.04323
3	7.382	10844.7	4248.9	0.17769
4	8.627	2716262.0	1034776.1	43.27395
5	8.670	2740754.7	1325914.3	55.44924

GC of **8l**



Peak#	Ret.Time	Area	Height	Conc.
1	7.438	9253.9	2449.4	0.12374
2	7.607	19411.0	5367.9	0.27118
3	7.787	5470.5	2250.4	0.11369
4	7.849	7411.4	2158.8	0.10906
5	8.471	30551.1	10663.8	0.53873
6	8.684	19342.6	5604.5	0.28313
7	8.807	2536.5	1105.4	0.05584
8	8.914	38712.2	14256.9	0.72024
9	9.323	3177.5	1309.0	0.06613
10	9.626	2937.2	1002.8	0.05066
11	9.813	5991022.4	1933280.6	97.66758

GC of **8m**



Peak#	Ret.Time	Area	Height	Conc.
1	8.806	42579.5	23767.5	1.79752
2	8.863	37720.2	18148.3	1.37255
3	10.192	1491860.5	615102.2	46.51976
4	10.235	1417870.5	665220.6	50.31018