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

Reversal of Polarity by Catalytic SET Oxidation: Synthesis of Azabicyclo[m.n.0]alkanes *via* Chemoselective Reduction of Amidines

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Supporting Information

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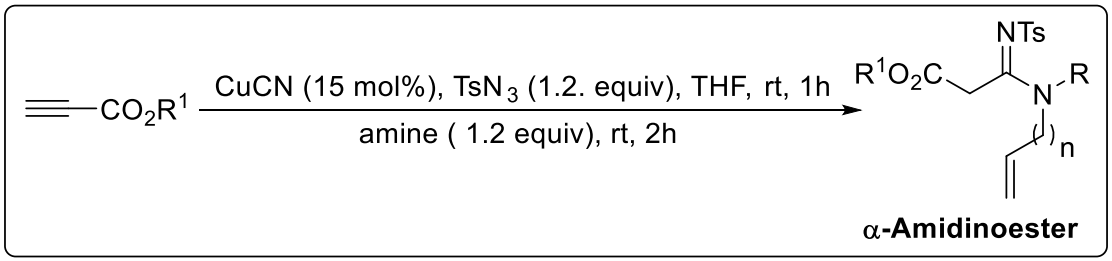
1. Experimental procedure for the preparation of *α*-amidinoesters

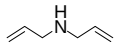
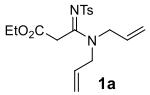
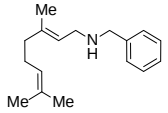
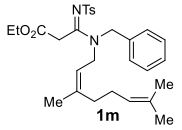
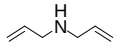
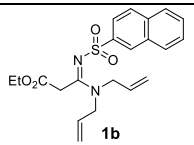
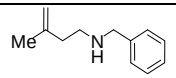
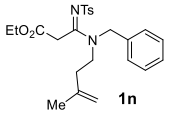
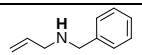
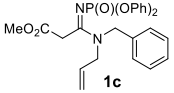
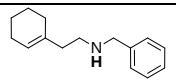
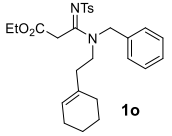
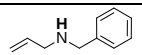
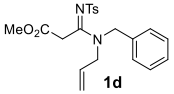
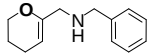
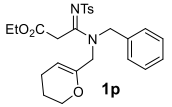
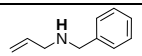
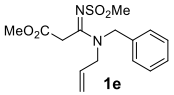
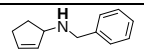
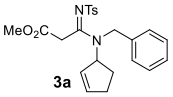
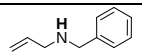
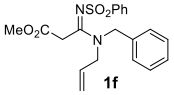
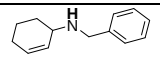
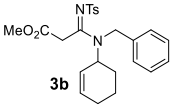
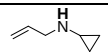
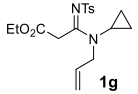
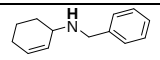
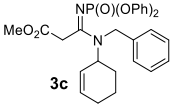
Preparation of starting materials: The amine derivatives **b**[1], **c**[2], **g**[3], **i**[4], **j**[5], **m**[6a] and **n**[6b] were prepared according to literature report. The sulfonyl and phosphoryl azides were prepared using the reported procedure.[7]

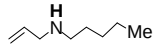
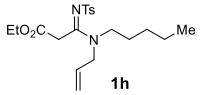
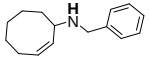
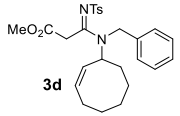
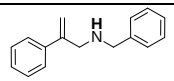
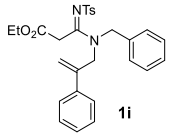
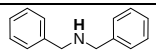
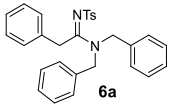
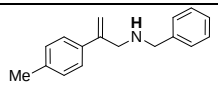
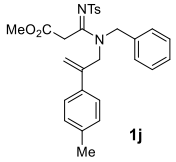
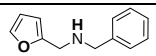
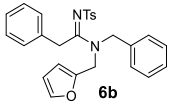
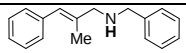
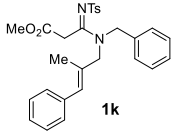
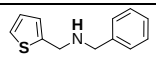
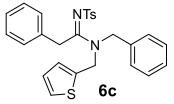
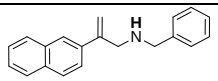
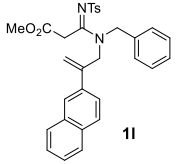
Procedure for the preparation of *α*-amidinoesters[8]



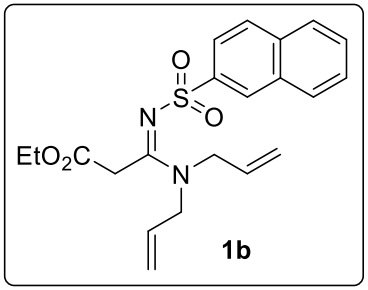
To a stirred solution of ethyl propiolate (1 equiv) in dry THF (3 mL/ mmol), was added CuCN (15 mol %) followed by TsN_3 (1.2 equiv) and the mixture was vigorously stirred at room temperature for 1h under N_2 atmosphere. To this reaction mixture, amine derivative (1.2 equiv) was added and the resultant mixture was stirred at room temperature until the completion of reaction as indicated by TLC. Then reaction mixture was diluted with saturated NH_4Cl (20 mL) and aqueous layer was extracted with dichloromethane (2 X 30 mL). The combined organic solvent was washed with brine solution (30 mL). Then organic layer was sepatarted, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product over silica gel using column chromatography yielded the α-amidinoester in quantitative yields.[8]

Table S1. Preparation of *α*-amidinoesters[8]

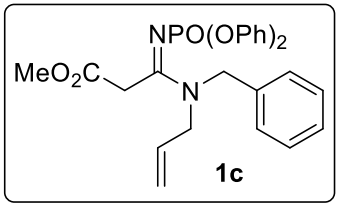
Entry	Amine	Time (h)	*α*-amidinoester	Isolated Yield (%)	Entry	Amine	Time (h)	*α*-amidinoester	Isolated Yield (%)
1		2	 **1a**	94	13		3	 **1m**	77
2		2	 **1b**	92	14		2	 **1n**	80
3		6	 **1c**	72	15		2	 **1o**	84
4		2	 **1d**	89	16		2	 **1p**	86
5		2	 **1e**	81	17		2	 **3a**	77
6		2	 **1f**	84	18		2	 **3b**	76
7		3	 **1g**	87	19		2	 **3c**	51

8		2	 **1h**	50	20		2	 **3d**	33
9		2	 **1i**	81	21		2	 **6a**	87
10		2	 **1j**	84	22		2	 **6b**	84
11		3	 **1k**	86	23		2	 **6c**	87
12		3	 **1l**	83					

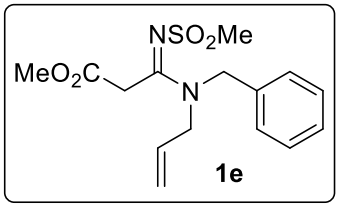
Note: The α-amidinoesters **1a**, **1d**, **1m** and **1n** were prepared according to literature report.[9]



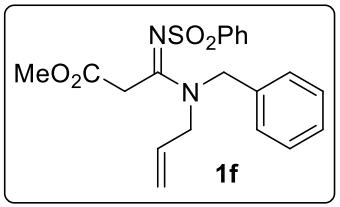
Preparation of *(Z)-ethyl 3-(diallylamino)-3-(naphthalen-2-ylsulfonylimino)propanoate* (1b): Following the general procedure, the reaction of ethyl propiolate (400 mg, 4.07 mmol) with naphthalenesulfonyl azide (1.14 g, 4.89 mmol) and diallylamine (475 mg, 4.89 mmol) was carried out and the product **1b** (1.51 g, 92%) was isolated as colourless oil (R_f = 0.3 in 30% EtOAc in hexane); **IR (neat):** 3065, 2987, 1736, 1642, 1552, 1478, 1423, 1323, 1286, 1244, 1192, 1118, 1029, 988, 927, 838, 771 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 8.76(d, *J* = 8.0 Hz, 1H), 8.25(dd, *J* = 7.2 Hz, 0.8 Hz, 1H), 7.97(d, *J* = 8.4 Hz, 1H), 7.86(d, *J* = 7.6 Hz, 1H), 7.60-7.45(m, 3H), 5.71-5.57(m, 2H), 5.23(d, *J* = 10.4 Hz, 1H), 5.15-5.03(m, 3H), 4.08(s, 3H), 4.07(s, 1H), 3.92(q, *J* = 7.2 Hz, 2H), 3.85-3.84(m, 2H), 1.09(t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 166.2, 161.1, 138.6, 134.1, 133.2, 131.1, 130.6, 128.7, 128.3, 127.4, 126.8, 126.6, 126.5, 124.0, 118.1, 118.0, 61.9, 51.1, 50.6, 36.3, 13.9; **HRMS(ESI):** m/z calcd for $C_{21}H_{24}N_2O_4NaS$ $[M+Na]^+$: 423.1354, found: 423.1349.



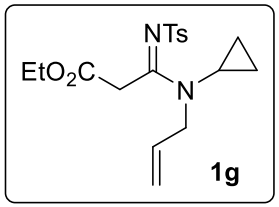
Preparation of *methyl 3-(allyl(benzyl)amino)-3-(diphenoxyphosphorylimino)propanoate* (1c): Under similar reaction conditions, methyl propiolate (500 mg, 5.95 mmol) was allowed to react with diphenylphosphoryl azide (1.96 g, 7.14 mmol) and *N*-allyl benzylamine (1.05 g, 7.14 mmol) and the resultant product **1c** (2 g, 72%) was obtained as colourless oil (R_f = 0.3 in 50% EtOAc in hexane); **IR (neat):** 3058, 2983, 2941, 2360, 2321, 1735, 1582, 1489, 1426, 1324, 1261, 1062, 994, 855, 732 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.37-7.20(m, 18.97H), 7.17-7.04(m, 10.51H), 5.74-5.65(m, 1.04H), 5.63-5.53(m, 0.50H), 5.23(d, *J* = 10.4 Hz, 1.05H), 5.11(d, *J* = 9.2 Hz, 1.36H), 5.08-5.06(m, 0.74H), 4.65(s, 2.01H), 4.51(s, 1.10H), 4.42(d, *J* = 5.6 Hz, 1.50H), 4.11(s, 2.08H), 4.06(s, 1.13H), 4.00(d, *J* = 5.6 Hz, 1.12H), 3.86-3.85(m, 2.10H), 3.66(s, 3.00H), 3.62(s, 1.80H), 2.01(s, 2.22H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.8, 151.7, 135.9, 135.1, 131.4, 131.0, 129.4, 129.4, 129.2, 128.8, 128.7, 128.1, 127.9, 127.6, 127.5, 126.3, 124.4, 124.4, 120.8, 120.8, 120.7, 120.7, 117.9, 52.7, 51.5, 50.8, 50.6, 43.8, 38.6, 38.4, 38.3, 23.3; **HRMS(ESI):** m/z calcd for $C_{26}H_{28}N_2O_5P$ $[M+H]^+$: 479.1730, found: 479.1745.



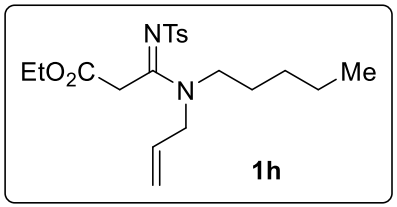
Preparation of *methyl 3-(allyl(benzyl)amino)-3-(methylsulfonylimino)propanoate* (1e): The three-component coupling reaction of methyl propiolate (500 mg, 5.95 mmol), mesyl azide (864 mg, 7.14 mmol) and *N*-allyl benzylamine (1.05 g, 7.14 mmol) was carried out using general procedure and the resultant product **1e** (1.56 g, 81%) was obtained as yellow oil (R_f = 0.3 in 30% EtOAc in hexane); **IR (neat):** 3058, 2982, 2950, 1742, 1643, 1609, 1558, 1492, 1427, 1340, 1279, 1268, 1252, 1206, 1175, 1127, 965, 848 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.39-7.28(m, 8.5H), 7.26-7.23(m, 1.14H), 7.19-7.12(m, 1.75H), 5.86-5.67(m, 2.19H), 5.34-5.13(m, 4.24H), 4.77(s, 2H), 4.65(s, 0.68H), 4.54(s, 1.14H), 4.45(s, 0.56H), 4.14(d, *J* = 5.2 Hz, 1.19H), 4.09(s, 2.07H), 4.05(s, 1.22H), 3.96(d, *J* = 6.0 Hz, 0.61H), 3.89(d, *J* = 4.0 Hz, 2.05H), 3.81(d, *J* = 6.0 Hz, 0.77H), 3.77(s,3H), 3.73(s, 1.78H), 3.01(s, 1.74H), 2.98(d, *J* = 3.2 Hz, 1.89H), 2.92(s, 3.03H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.5, 167.5, 161.2, 160.8, 159.4, 159.1, 135.5, 134.7, 134.7, 134.2, 131.3, 131.1, 130.5, 130.2, 129.3, 129.2, 128.9, 128.8, 128.8, 128.5, 128.3, 128.2, 128.0, 127.7, 127.5, 126.3, 120.7, 119.7, 118.2, 55.2, 53.8, 52.9, 51.4, 51.2, 50.5, 48.9, 47.8, 43.2, 43.1, 42.0, 36.6, 36.4; **HRMS(ESI):** m/z calcd for $C_{15}H_{21}N_2O_4S$ $[M+H]^+$: 325.1144, found: 325.1153.



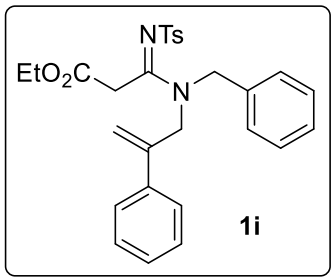
Preparation of *methyl 3-(allyl(benzyl)amino)-3-(phenylsulfonylimino)propanoate* (1f): Following the general procedure, the reaction of methyl propiolate (500 mg, 5.95 mmol) with benzenesulphonyl azide (1.3 g, 7.14 mmol) and *N*-allyl benzylamine (1.05 g, 7.14 mmol) was carried out and the product **1f** (1.93 g, 84%) was isolated as yellow oil (R_f = 0.25 in 30% EtOAc in hexane); **IR (neat):** 3080, 3023, 2953, 1861, 1742, 1552, 1484, 1444, 1338, 1286, 1158, 1088, 962, 844 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.92(d, *J* = 7.2 Hz, 1H), 7.80(d, *J* = 7.6 Hz, 2H), 7.51-7.43(m, 2.68H), 7.39-7.32(m, 3.65H), 7.27-7.19(m, 5.26H), 7.13(d, *J* = 7.2 Hz, 1H), 5.78-5.69(m, 1.55H), 5.28(d, *J* = 10.4 Hz, 1H), 5.21-5.15(m, 2H), 4.77(s, 2H), 4.55(s, 1H), 4.17-4.13(m, 4H), 3.90(d, *J* = 4.0 Hz, 2H), 3.69(s, 3H), 3.66(s, 1.62H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.2, 167.1, 161.2, 161.0, 143.3, 143.2, 135.4, 134.6, 131.7, 131.6, 131.0, 130.5, 129.3, 128.7, 128.5, 128.4, 128.3, 127.6, 127.6, 126.3, 126.3, 126.3, 118.2, 52.8, 51.6, 51.5, 51.4, 50.7, 36.4, 36.1; **HRMS(ESI):** m/z calcd for $C_{20}H_{23}N_2O_4S$ $[M+H]^+$: 387.1309, found: 387.1308.



Preparation of ethyl *3-(allyl(cyclopropyl)amino)-3-(tosylimino)propanoate* (1g): Under similar reaction conditions, ethyl propiolate (500 mg, 5.09 mmol) was allowed to react with tosyl azide (1.2 g, 6.11 mmol) and *N*-allylcyclopropanamine (593 mg, 6.11 mmol) and the resultant product **1g** (1.61 g, 87%) was obtained as pale yellow oil (R_f = 0.2 in 30% EtOAc in hexane); **IR (neat):** 3056, 2984, 2928, 2859, 2357, 2310, 1733, 1567, 1426, 1267, 1153, 1093, 1025, 899, 739 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.75(d, *J* = 8.0 Hz, 2H), 7.20(d, *J* = 7.6 Hz, 2H), 5.79-5.69(m, 1H), 5.12-5.05(m, 2H), 4.33(s, 2H), 4.15(q, *J* = 7.2 Hz, 2H), 4.15(q, *J* = 7.2 Hz, 2H), 2.78-2.72(m, 1H), 2.36(s, 3H), 1.23(t, *J* = 6.8 Hz, 3H), 0.91-0.87(m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 166.9, 163.4, 142.1, 140.6, 132.1, 129.0, 126.4, 117.2, 61.7, 52.8, 37.1, 32.0, 21.5, 14.1, 8.8; **HRMS(ESI):** m/z calcd for $C_{18}H_{24}N_2NaO_4S$ $[M+Na]^+$: 387.1349, found: 387.1348.

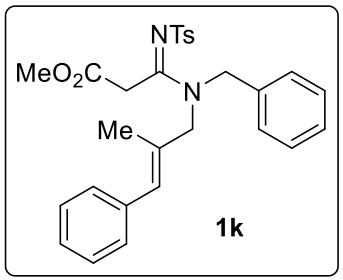


Preparation of *ethyl 3-(allyl(pentyl)amino)-3-(tosylimino)propanoate* (1h): The three-component coupling reaction of ethyl propiolate (374 mg, 3.81 mmol), tosyl azide (901 mg, 4.57 mmol) and *N*-allylpentan-1-amine (582 mg, 4.57 mmol) was carried out using general procedure and the resultant product **1h** (752 mg, 50%) was obtained as a yellow semisolid (R_f = 0.3 in 30% EtOAc in hexane); **IR (neat):** 3056, 2956, 2863, 2358, 1737, 1553, 1468, 1286, 1238, 1186, 1151, 1089, 1028, 959, 845 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.77-7.75(m, 2H), 7.22-7.18(m, 2H), 5.70-5.66(m, 1H), 5.23(d, *J* = 7.2 Hz, 1H), 5.19-5.10(m, 2H), 4.16-4.05(m, 5H), 4.01(s, 1H), 3.82(s, 1H), 3.75(s, 1H), 2.36(s, 3H), 2.03-1.90(m, 3H), 1.85(t, *J* = 8.0 Hz, 1H), 1.36-1.19(m, 3H), 0.91-0.86(m, 3H), 0.71(t, *J* = 7.2 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 166.8, 166.7, 161.2, 160.9, 142.0, 140.9, 140.8, 133.1, 132.0, 131.3, 131.0, 130.0, 129.0, 129.0, 127.2, 126.5, 126.4, 117.8, 61.8, 53.0, 52.9, 51.4, 49.1, 36.6, 36.2, 31.9, 31.8, 30.9, 29.9, 27.4, 27.2, 22.5, 21.7, 21.5, 14.1, 14.0, 14.0; **HRMS(ESI):** m/z calcd for $C_{20}H_{31}N_2O_4S$ $[M+H]^+$: 395.1931, found: 395.1923.

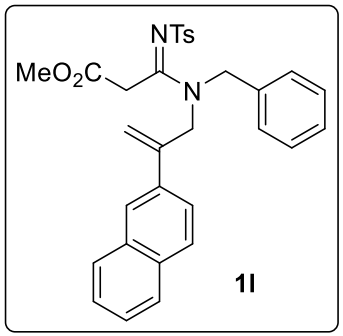


Preparation of *ethyl 3-(benzyl(2-phenylallyl)amino)-3-(tosylimino)propanoate* (1i): Following the general procedure, the reaction of ethyl propiolate (500 mg, 5.09 mmol) with tosyl azide (1.2 g, 6.11

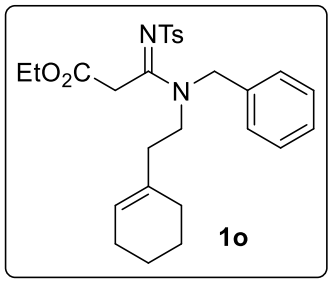
mmol) and *N*-benzyl-2-phenylprop-2-en-1-amine (1.36 g, 6.11 mmol) was carried out and the product **1i** (2 g, 81%) was isolated as pale yellow oil (R_f = 0.25 in 30% EtOAc in hexane); **IR (neat):** 3057, 2932, 2905, 2356, 2264, 1741, 1659, 1584, 1458, 1252, 1069, 1031, 861 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.80(d, *J* = 8.0 Hz, 1.42H), 7.70(d, *J* = 8.0 Hz,2H), 7.39-7.31(m, 5.61H), 7.28-7.25(m, 9.29H), 7.21-7.16(m, 4.06H), 7.12(d, *J* = 7.2 Hz, 1.55H), 5.55(s, 1.01H), 5.41(s, 0.7H), 5.27(s, 0.7H), 5.12(s, 1.02H), 4.82(s, 1.99H), 4.58(d, *J* = 4.8 Hz, 2.81H), 4.24(s, 2.02H), 4.16-4.13(m, 5.16H), 4.11-4.06(m, 1.93H), 2.37(s, 2.19H), 2.36(s, 3H), 1.22(t, *J* = 7.2 Hz, 3H), 1.18(t, *J* = 7.2 Hz, 2.37); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 166.8, 166.6, 161.8, 161.2, 142.2, 142.1, 141.5, 141.1, 140.7, 140.5, 138.8, 137.8, 135.6, 134.7, 129.3, 129.1, 128.8, 128.7, 128.5, 128.3, 128.1, 127.6, 126.5, 126.4, 126.2, 125.9, 114.0, 113.2, 62.0, 62.0, 52.0, 51.7, 51.5, 51.4, 36.6, 36.4, 21.5, 14.0; **HRMS(ESI):** m/z calcd for $C_{28}H_{30}N_2O_4NaS$ $[M+Na]^+$: 513.1819, found: 513.1816.



Preparation of *methyl 3-(benzyl((E)-2-methyl-3-phenylallyl)amino)-3-(tosylimino)propanoate* (1k): Under similar reaction conditions, methyl propiolate (1 g, 11.89 mmol) was allowed to react with tosyl azide (2.81 g, 14.27 mmol) and (*E*)-*N*-benzyl-2-methyl-3-phenylprop-2-en-1-amine (3.38 g, 14.27 mmol) and the resultant product **1k** (5 g, 86%) was obtained as a colourless solid (R_f = 0.25 in 30% EtOAc in hexane); m.p 99-100 ^oC; **IR (neat):** 3058, 3031, 2950, 2923, 2856, 1741, 1658, 1542, 1490, 1445, 1428, 1333, 1280, 1168, 1146, 1088, 1021, 962, 862, 809 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.78(d, *J* = 8.0 Hz, 1.84H), 7.70(d, *J* = 8.0 Hz, 2.17H), 7.41-7.32(m, 6.95H), 7.30-7.20(m, 11.44H), 7.18-7.14(m, 7.91H), 6.32(s, 0.90H), 6.27(s, 1.07H), 4.83(s, 2.09H), 4.59(s, 1.81H), 4.30(s, 1.74H), 4.23(s, 2.04H), 4.17(s, 1.75H), 3.95(s, 2.14H), 3.70(s, 3.00H), 3.68(s, 2.73H), 2.37(s, 3.10H), 2.35(s, 2.87H), 1.80(s, 3.17H), 1.78(s, 2.97H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.3, 167.3, 161.5, 161.3, 142.2, 140.5, 140.4, 137.1, 136.3, 135.6, 134.7, 132.1, 131.2, 129.4, 129.1, 128.9, 128.7, 128.4, 128.3, 128.2, 127.8, 127.7, 127.6, 127.2, 126.8, 126.7, 126.4, 126.2, 55.8, 55.4, 52.8, 51.8, 50.9, 36.4, 36.2, 21.5, 16.1, 15.7; **HRMS(ESI):** m/z calcd for $C_{28}H_{31}N_2O_4S$ $[M+H]^+$: 491.1929, found: 491.1935.

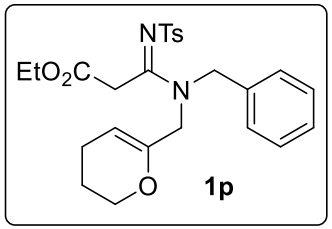


Preparation of *methyl 3-(benzyl(2-(naphthalen-2-yl)allyl)amino)-3-(tosylimino)propanoate* (1l): Following the general procedure, the reaction of methyl propiolate (500 mg, 5.95 mmol), tosyl azide (1.4 g, 7.14 mmol) and *N*-benzyl-2-(naphthalen-2-yl)prop-2-en-1-amine (1.95 g, 7.14 mmol) was carried out and the resultant product **1l** (2.59 g, 83%) was obtained as yellow oil (R_f = 0.25 in 30% EtOAc in hexane); **IR (neat):** 3075, 3028, 2951, 2853, 1740, 1647, 1554, 1447, 1362, 1292, 1213, 1153, 1089, 967, 911, 860, 811, 755 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.90-7.77(m, 3H), 7.72-7.64(m, 3H), 7.48-7.43(m, 3H), 7.38-7.24(m, 4H), 7.20-7.12(m, 3H), 5.71-5.21(m, 2H), 4.87-4.74(m, 2H), 4.58-4.39(m, 2H), 4.17(d, *J* = 10.8 Hz, 2H), 3.70-3.48(m, 3.14H), 2.36(s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 168.2, 167.1, 162.0, 161.5, 142.6, 141.5, 140.8, 140.4, 135.6, 135.5, 134.8, 134.6, 133.2, 133.2, 133.1, 133.0, 129.3, 129.1, 129.1, 128.8, 128.6, 128.4, 128.3, 128.2, 128.0, 127.7, 127.7, 127.6, 127.5, 126.8, 126.7, 126.5, 126.4, 126.3, 126.3, 126.2, 125.1, 124.6, 124.3, 123.8, 115.1, 113.5, 52.8, 52.6, 52.2, 51.8, 51.4, 51.3, 36.5, 36.2, 21.5; **HRMS(ESI):** m/z calcd for $C_{31}H_{31}N_2O_4S$ $[M+H]^+$: 527.1999, found: 527.1974.

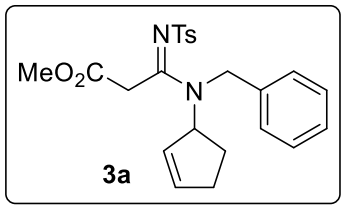


Preparation of *ethyl 3-(benzyl(2-cyclohexenylethyl)amino)-3-(tosylimino)propanoate* (1o): Under similar reaction conditions, ethyl propiolate (1.3 g, 13.25 mmol) was allowed to react with tosyl azide (3.1 g, 15.9 mmol) and *N*-benzyl-2-cyclohexenylethanamine (3.4 g, 15.9 mmol) and the resultant product **1o** (5.5 g, 84%) was obtained as a pale yellow solid (R_f = 0.3 in 30% EtOAc in hexane); m.p 59-60 ^oC; **IR (neat):** 3060, 3029, 2981, 2926, 2857, 1738, 1601, 1550, 1492, 1449, 1365, 1325, 1279, 1194, 1144, 1089, 1025, 965 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.84(d, *J* = 8.0 Hz, 1.49H), 7.79-7.74(m, 0.47H), 7.65(d, *J* = 8.0 Hz, 1.90H), 7.38-7.31(m, 2.62H), 7.25-7.20(m, 8.18H), 7.15-7.14(m, 3.86H), 5.42-5.25(m, 2.01H), 4.77(s, 1.91H), 4.63(s, 0.19H), 4.53(s, 1.42H), 4.44(s, 0.16H), 4.17-4.11(m, 5.55H), 4.08(s, 1.57H), 3.51(t, *J* = 7.6 Hz, 1.43H), 3.40(t, *J* = 7.2 Hz, 0.16H), 3.31(t, *J* = 7.6 Hz, 2.14H), 2.39(s, 2.97H), 2.35(s, 3.00H), 2.19-2.12(m, 3.80H), 1.95-1.86(m, 6.30H), 1.74(brs, 1.98H), 1.60-1.58(m, 2.42H), 1.52-1.50(m, 5.67H), 1.25-1.21(m, 5.83H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 166.7, 166.6, 160.6, 160.2, 142.1, 141.9, 140.9, 140.7, 135.8, 134.9, 134.2, 133.1, 129.2, 129.0, 129.0, 128.6, 128.2, 127.6, 127.5, 126.4, 126.4, 124.9, 123.7,

62.0, 61.9, 52.6, 51.4, 48.9, 47.5, 36.7, 36.6, 36.2, 34.7, 28.5, 28.1, 25.2, 25.2, 22.9, 22.7, 22.3, 22.1, 21.5, 21.5, 14.0; **HRMS(ESI):** m/z calcd for $C_{27}H_{35}N_2O_4S$ $[M+H]^+$: 483.2318, found: 483.2314.

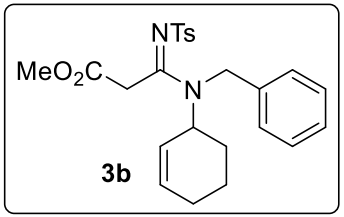


Preparation of *ethyl 3-(benzyl((3,4-dihydro-2H-pyran-6-yl)methyl)amino)-3-(tosylimino)propanoate* (1p): The three-component coupling reaction of ethyl propiolate (118 mg, 1.2 mmol), tosyl azide (262 mg, 1.33 mmol) and *N*-benzyl-1-(3,4-dihydro-2H-pyran-6-yl)methanamine (270 mg, 1.33 mmol) was carried out using general procedure and the resultant product **1p** (485 mg, 86%) was obtained as orange-yellow oil (R_f = 0.3 in 30% EtOAc in hexane); **IR (neat):** 3058, 2942, 2875, 2362, 2310, 1735, 1646, 1491, 1453, 1365, 1325, 1271, 1194, 1145, 1088, 1025, 970, 861, 813, 738 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.84(d, *J* = 7.6 Hz, 0.37H), 7.69(d, *J* = 7.6 Hz, 2.00H), 7.38-7.35(m, 0.52H), 7.27-7.23(m, 5.36H), 7.16(d, *J* = 7.6 Hz, 2.54H), 4.81(s, 1.95H), 4.68(s, 1.51H), 4.37(s, 1.88H), 4.16-4.09(m, 3.24H), 3.97(t, *J* = 4.4 Hz, 2.08H), 3.89(t, *J* = 4.8 Hz, 0.47H), 3.74(s, 1.99H), 2.40(s, 0.59H), 2.36(s, 3H), 2.04-2.01(m, 2.35H), 1.91(brs, 0.43H), 1.80-1.78(m, 2.02H), 1.74-1.71(m, 0.46H), 1.23(t, *J* = 7.2 Hz, 3.72H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 166.7, 166.4, 161.5, 161.0, 147.7, 147.5, 141.8, 141.8, 140.7, 140.5, 135.6, 134.8, 128.9, 128.8, 128.8, 128.4, 128.4, 127.9, 127.4, 127.2, 126.3, 126.1, 126.1, 126.1, 100.5, 98.9, 66.4, 66.0, 61.7, 52.1, 50.8, 50.6, 50.5, 36.4, 36.3, 21.9, 21.7, 21.3, 21.3, 19.8, 13.8; **HRMS(ESI):** m/z calcd for $C_{25}H_{31}N_2O_5S$ $[M+H]^+$: 471.1954, found: 471.1944.

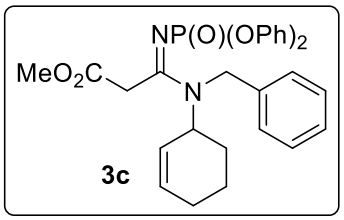


Preparation of *methyl 3-(benzyl(cyclopent-2-enyl)amino)-3-(tosylimino)propanoate* (3a): Following the general procedure, the reaction of methyl propiolate (1 g, 11.89 mmol) with tosyl azide (2.81 g, 14.27 mmol) and *N*-benzylcyclopent-2-enamine (2.67 g, 14.27 mmol) was carried out and the product **3a** (3.89 g, 77%) was isolated as an orange-yellow solid (R_f = 0.3 in 30% EtOAc in hexane); m.p 74-75 ^oC; **IR (neat):** 3060, 2953, 2854, 1741, 1595, 1540, 1486, 1426, 1335, 1289, 1279, 1206, 1147, 1088, 1012, 959, 910, 848 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.82(d, *J* = 6.4 Hz, 1.50H), 7.78(d, *J* = 6.8 Hz, 1.63H), 7.39(d, *J* = 6.4 Hz, 2.07H), 7.34(d, *J* = 6.0 Hz, 1.81H), 7.29-7.10(m, 12.2H), 7.03(d, *J* = 6.4 Hz, 2.07H), 5.99-5.95(m, 1.79H), 5.83-5.82(m, 0.78H), 5.56-5.53(m, 1.09H), 5.49-

5.47(m, 0.86H), 5.04(t, *J* = 6.4 Hz, 1.25H), 4.66(d, *J* = 12.4 Hz, 1.08H), 4.51-4.43(m, 3.89H), 4.23-4.17(m, 1.86H), 3.74(s, 3H), 3.71(d, *J* = 14.0 Hz, 1.01H), 3.63(s, 2.31H), 2.40(s, 6.35H), 2.32(s, 4.17H), 2.30-2.25(m, 2.44H), 1.74-1.69(m, 1.18H), 1.63-1.58(m, 0.91H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.4, 167.3, 161.5, 159.9, 143.2, 142.1, 141.8, 140.7, 140.3, 139.4, 137.4, 137.2, 137.0, 136.5, 129.6, 129.2, 129.1, 128.8, 128.8, 128.4, 128.3, 127.7, 126.6, 126.4, 126.3, 126.1, 125.4, 65.6, 64.9, 52.8, 52.7, 48.1, 47.7, 37.2, 36.5, 31.5, 31.3, 28.6, 28.6, 21.5, 21.4; **HRMS(ESI):** m/z calcd for $C_{23}H_{27}N_2O_4S$ $[M+H]^+$: 427.1619, found: 427.1621.

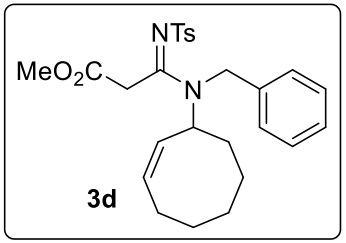


Preparation of *methyl 3-(benzyl(cyclohex-2-enyl)amino)-3-(tosylimino)propanoate* (3b): Under similar reaction conditions, methyl propiolate (500 mg, 5.94 mmol) was allowed to react with tosyl azide (1.4 g, 7.13 mmol) and *N*-benzylcyclohex-2-enamine (1.33 g, 7.13 mmol) and the resultant product **3b** (1.98 g, 76%) was obtained as a pale yellow solid (R_f = 0.3 in 30% EtOAc in hexane); m.p 102-103 ^oC; **IR (neat):** 3080, 3027, 2944, 2864, 1740, 1644, 1596, 1541, 1486, 1441, 1338, 1291, 1266, 1238, 1154, 1088, 991, 965, 876, 851, 805 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.73(d, *J* = 8.4 Hz, 2H), 7.25(d, *J* = 8.0 Hz, 4H), 7.21-7.03(m, 10H), 6.92(d, *J* = 8.0 Hz, 2H), 5.85-5.78(m, 2H), 5.42(d, *J* = 9.2 Hz, 2H), 5.36(d, *J* = 10.0 Hz, 1H), 4.67(d, *J* = 16.0 Hz, 1H), 4.55-4.40(m, 4H), 4.30(d, *J* = 16.2 Hz, 1H), 4.12(d, *J* = 17.6 Hz, 1H), 4.02(q, *J* = 6.0 Hz, 1H), 3.94-3.75(m, 2H), 3.66(s, 3H), 3.53(s, 3H), 2.31(s, 3H), 2.29(s, 3H), 1.94(s, 2H), 1.89-1.81(m, 6H), 1.69-1.61(m, 2H), 1.56-1.43(m, 3H), 1.41-1.32(m, 1H), 1.49(t, *J* = 8.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.3, 167.1, 161.8, 160.0, 142.0, 141.6, 140.6, 140.2, 137.2, 136.6, 133.4, 133.2, 129.0, 128.7, 128.2, 127.6, 126.3, 126.2, 126.1, 126.0, 125.9, 125.7, 125.3, 60.3, 56.6, 54.9, 52.7, 52.5, 48.8, 48.2, 37.0, 36.1, 28.4, 26.5, 24.4, 24.1, 21.4, 21.3, 21.1, 21.0, 20.8, 14.1; **HRMS(ESI):** m/z calcd for $C_{24}H_{29}N_2O_4S$ $[M+H]^+$: 441.1848, found: 441.1835.

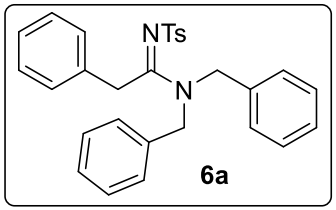


Preparation of *methyl 3-(benzyl(cyclohex-2-enyl)amino)-3-(diphenoxyphosphorylimino)propanoate* (3c): Following the general procedure, the reaction of methyl propiolate (509 mg, 6.05 mmol), diphenylphosphoryl azide (2 g, 7.26 mmol) and *N*-benzylcyclohex-2-enamine (1.35 g, 7.26 mmol) was carried out and the product **3c** (1.6 g, 51%) was isolated as yellow oil (R_f = 0.3 in 40% EtOAc in

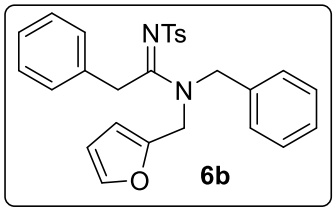
hexane); **IR (neat):** 3184, 3073, 3024, 2946, 2855, 2336, 2273, 1647, 1453, 1328, 1234, 1069, 917, 843, 761, 714 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.26(d, *J* = 8.1 Hz, 6.23H), 7.24-7.18(m, 19.43H), 7.11-7.06(m, 10.57H), 5.81-5.75(m, 2.23H), 5.37(d, *J* = 9.2 Hz, 2.17H), 5.31(d, *J* = 9.8 Hz, 1.31H), 4.63(d, *J* = 16.1 Hz, 1.15H), 4.57-4.38(m, 4.21H), 4.32(d, *J* = 16.0 Hz, 1.22H), 4.08(d, *J* = 17.8 Hz, 1.10H), 4.11(q, *J* = 6.0 Hz, 1.24H), 3.95-3.78(m, 2.31H), 3.77(s, 3.18H), 3.55(s, 3.15H),1.91(s, 2.32H), 1.90-1.86(m, 6.35H), 1.71-1.64(m, 2.17H), 1.57-1.43(m, 3.19H), 1.41-1.33(m, 1.11H), 1.52(t, *J* = 8.0 Hz, 1.15H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.5, 167.2, 163.0, 160.2, 142.5, 141.8, 140.9, 140.6, 137.6, 136.8, 133.4, 133.1, 129.8, 129.7, 129.4, 129.1, 128.8, 128.4, 128.3, 127.9, 126.7, 126.7, 126.5, 126.2, 126.1, 125.5, 125.2, 60.2, 56.8, 55.4, 52.8, 52.8, 49.0, 48.6, 37.2, 29.1, 26.9, 24.7, 24.3, 21.8, 21.7, 21.4, 21.3, 20.7, 19.2; **HRMS(ESI):** m/z calcd for $C_{29}H_{32}N_2O_5P$ $[M+H]^+$: 519.1981, found: 519.1979.



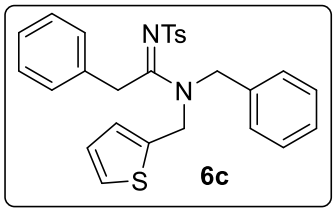
Preparation of *methyl 3-(benzyl((Z)-cyclooct-2-enyl)amino)-3-(tosylimino)propanoate* (3d): The three-component coupling reaction of methyl propiolate (814 mg, 9.68 mmol), tosyl azide (2.28 g, 11.6 mmol) and (*Z*)-*N*-benzylcyclooct-2-enamine (2.49 g, 11.6 mmol) was carried out using general procedure and the resultant product **3d** (1.47 g, 33%) was obtained as yellow oil (R_f = 0.25 in 30% EtOAc in hexane); **IR (neat):** 3074, 3027, 2932, 2857, 1741, 1603, 1541, 1438, 1337, 1288, 1208, 1152, 1089, 1013, 960, 861, 810 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** ppm 7.82(d, *J* = 9.2 Hz, 1.20H), 7.40(d, *J* = 6.4 Hz, 1.91H), 7.37-7.34(m, 1.18H), 7.30-7.27(m, 1.27H), 7.26-7.14(m, 4.19H), 7.15(d, *J* = 5.6 Hz, 3.31H), 7.03(d, *J* = 6.4 Hz, 2.01H), 5.78-5.64(m, 2.46H), 5.48-5.41(m, 1.77H), 4.89(d, *J* = 12.8 Hz, 1.13H), 4.74-4.70(m, 1.22H), 4.69-4.63(m, 2.28H), 4.55(d, *J* = 12.0 Hz, 1.16H), 4.08-4.00(m, 1.67H), 3.82(d, *J* = 14.0 Hz, 0.38H), 3.77(s, 0.31H), 3.75(s, 3.05H), 3.67(s, 1.96H), 2.41(s, 0.47H), 2.40(s, 2.06H), 2.32(s, 3H), 2.23-2.16(m, 1.24H), 2.18-1.98(m, 2.17H), 1.77-1.59(m, 7.39H), 1.53-1.50(m, 4.21H), 1.35-1.25(m, 4.33H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.5, 167.5, 161.1, 160.2, 142.0, 141.8, 141.0, 140.5, 137.2, 136.4, 132.1, 131.6, 129.7, 129.2, 129.0, 128.8, 128.4, 127.9, 127.4, 126.8, 126.6, 126.5, 126.3, 126.2, 125.8, 57.2, 56.1, 52.8, 52.7, 48.7, 48.6, 37.5, 36.5, 34.6, 33.1, 29.0, 28.8, 26.6, 26.6, 26.2, 26.1, 24.5, 24.5, 21.5, 21.5; **HRMS(ESI):** m/z calcd for $C_{26}H_{33}N_2O_4S$ $[M+H]^+$: 469.2140, found: 469.2151.



Preparation of *N,N-dibenzyl-2-phenyl-N'-tosylacetimidamide* (6a): Following the general procedure, the reaction of phenylacetylene (500 mg, 4.9 mmol) with tosyl azide (1.15 g, 5.8 mmol) and dibenzylamine (1.15 g, 5.8 mmol) was carried out and the product **6a** (1.99 g, 87%) was isolated as a pale yellow solid (R_f = 0.3 in 30% EtOAc in hexane); m.p 67-68 ^oC; **IR (neat):** 3073, 3030, 2929, 1593, 1541, 1487, 1455, 1358, 1287, 1250, 1145, 1086, 1034, 961, 910, 854, 793 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.75(d, *J* = 8.0 Hz, 2H), 7.34-7.28(m, 4H), 7.25-7.21(m, 6H), 7.19-7.13(m, 5H), 6.97(d, *J* = 7.2 Hz, 2H), 4.70(s, 2H), 4.48(s, 2H), 4.37(s, 2H), 2.36(s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 166.4, 142.0, 140.8, 140.1, 136.0, 134.9, 134.0, 129.2, 129.1, 129.0, 128.9, 128.7, 128.4, 128.3, 128.2, 128.1, 127.8, 127.0, 126.4, 126.0, 53.1, 51.2, 51.0, 37.0, 21.5; **HRMS(ESI):** m/z calcd for $C_{29}H_{29}N_2O_2S$ $[M+H]^+$: 469.1885, found: 469.1880.



Preparation of *N-benzyl-N-(furan-2-ylmethyl)-2-phenyl-N'-tosylacetimidamide* (6b): Under similar reaction conditions, phenylacetylene (500 mg, 4.9 mmol) was allowed to react with tosyl azide (1.15 g, 5.88 mmol) and *N*-benzyl-1-(furan-2-yl)methanamine (1.1 g, 5.88 mmol) and the resultant product **6b** (1.88 g, 84%) was obtained as yellow oil (R_f = 0.3 in 30% EtOAc in hexane); **IR (neat):** 3081, 3026, 2961, 1541, 1495, 1355, 1297, 1286, 1268, 1242, 1149, 1086, 1013, 954, 852, 801 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.80(d, *J* = 8.0 Hz, 2H), 7.73(d, *J* = 8.0 Hz, 2H), 7.38-7.16(m, 22H), 7.05(d, *J* = 7.2 Hz, 2H), 6.98(d, *J* = 6.8 Hz, 2H), 6.29(d, *J* = 10.8 Hz, 2H), 6.12-6.04(m, 2H), 4.73(s, 2H), 4.66(d, *J* = 9.6 Hz, 4H), 4.44(d, *J* = 6.0 Hz, 4H), 4.24(s, 2H), 2.38(s, 3H), 2.36(s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 166.1, 149.6, 148.5, 143.2, 142.3, 142.1, 142.0, 140.9, 136.0, 135.0, 134.2, 133.9, 129.1, 129.1, 129.0, 128.7, 128.3, 128.2, 128.1, 128.0, 127.8, 127.1, 127.0, 126.6, 126.6, 126.4, 110.6, 110.6, 109.6, 109.4, 51.6, 51.0, 44.2, 44.2, 37.1, 36.8, 21.5; **HRMS(ESI):** m/z calcd for $C_{27}H_{27}N_2O_3S$ $[M+H]^+$: 459.1677, found: 459.1672.



Preparation of *N-benzyl-2-phenyl-N-(thiophen-2-ylmethyl)-N'-tosylacetimidamide* (6c): The three-component coupling reaction of phenylacetylene (500 mg, 4.9 mmol), tosyl azide (1.15 g, 5.88 mmol) and

N-benzyl-1-(thiophen-2-yl)methanamine (1.19 g, 5.88 mmol) was carried out using general procedure and the resultant product **6c** (2 g, 87%) was obtained as yellow oil (R_f = 0.3 in 30% EtOAc in hexane); **IR (neat):** 3057, 2984, 2929, 1593, 1546, 1487, 1443, 1429, 1361, 1286, 1258, 1250, 1175, 1146, 1086, 1039, 961, 900, 854 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.87(d, *J* = 8.0 Hz, 2.00H), 7.74(d, *J* = 7.6 Hz, 0.90H), 7.35-7.30(m, 3.34H), 7.28-7.11(m, 14.42H), 6.99(d, *J* = 7.2 Hz, 2.09H), 6.94(t, *J* = 4.0 Hz, 0.57H), 6.88-6.76(m, 2.44H), 4.78(s, 2.06H), 4.74(s, 0.89H), 4.58(s, 0.90H), 4.48(s, 2.99H), 4.37(s, 2.07H), 2.38(t, 4.47H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 165.9, 165.9, 142.2, 140.8, 137.6, 136.0, 134.9, 133.9, 129.2, 129.2, 129.1, 129.0, 128.8, 128.4, 128.2, 128.1, 127.9, 127.2, 127.0, 126.7, 126.7, 126.5, 126.5, 126.3, 126.1, 50.7, 46.3, 46.0, 37.2, 37.0, 21.5; **HRMS(ESI):** m/z calcd for $C_{27}H_{27}N_2O_2S_2$ $[M+H]^+$: 475.1508, found: 475.1504.

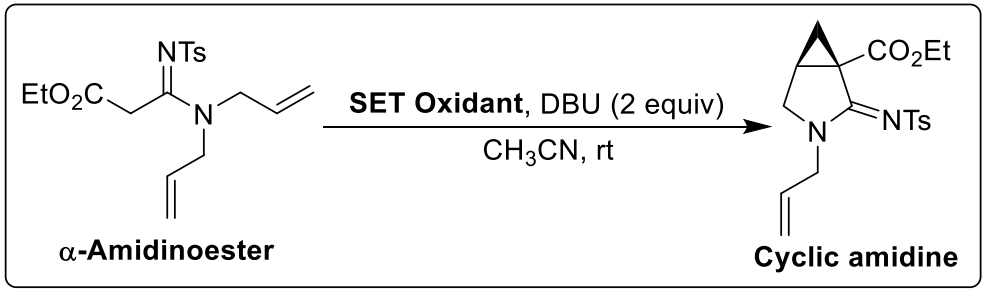
2. Optimization of reaction conditions

Procedure for the optimization of reaction conditions for catalytic SET oxidative cyclization of *α*-amidinoester 1: To a stirred solution of *α*-amidinoester (1 equiv) in dry acetonitrile (3 mL/ mmol), were added DBU, I_2, $CuBr_2$ and $K_2S_2O_8$ and reaction mixture was stirred at room temperature until the completion of reaction as indicated by TLC. The reaction mixture was diluted with saturated NH_4Cl (20 mL/ mmol) and extracted with DCM (2 X 30 mL/ mmol). The combined organic solvent was washed with brine solution (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product over silica gel using column chromatography (EtOAc/ Hexane as an eluent) yielded the cyclic amidine.

2A. Screening of SET oxidants

The screening of SET oxidants was performed using general procedure and the results are summarized in Table S2.

Table S2. Optimization of SET oxidant for the synthesis of cyclic amidine

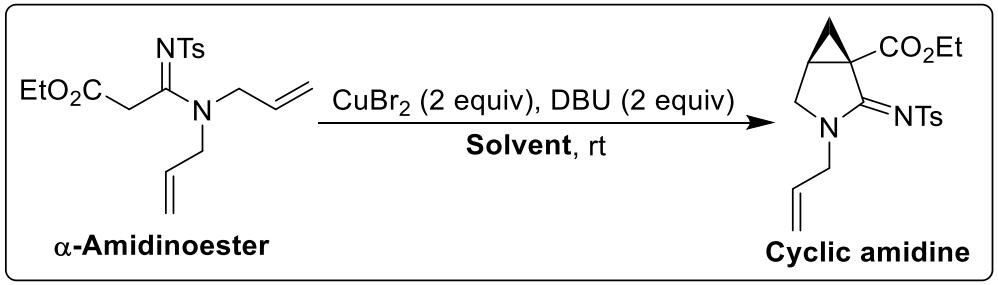


Entry	SET Oxidant (2 equiv)	Time (h)	Isolated yield (%)
1	CAN	24	-
2	$Mn(OAc)_3$	24	6
3	$Hg(OAc)_2$	24	5
4	$FeCl_3$	24	-
5	$Cu(OAc)_2$	24	11
6	$CuBr_2$	18	56
7	$AgNO_3$	24	-
8	Ag_2O	24	48
9	Ag_2CO_3	24	-
10	AgOAc	24	-
11	$AgBF_4$	24	-

2B. Screening of solvents

The screening of solvents was performed using general procedure and the results are summarized in Table S3.

Table S3. Optimization of solvent system for the synthesis of cyclic amidine

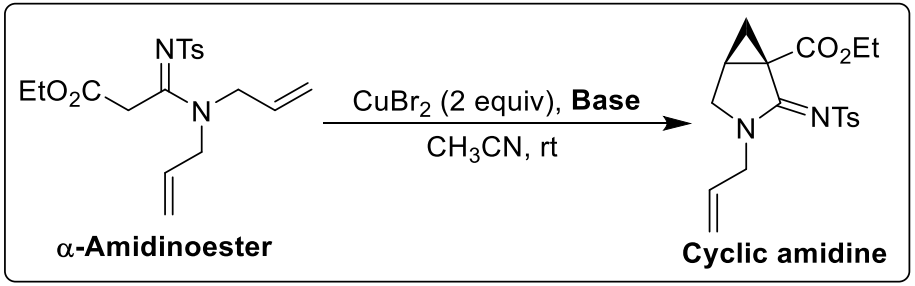


Entry	Solvent	Time (h)	Isolated yield (%)
1	DCM	24	8
2	DCE	24	12
3	Et_2O	24	18
4	THF	24	46
5	1,4-dioxane	24	14
6	Toluene	24	-
7	CH_3CN	18	56
8	DMSO	24	36
9	DMF	24	28

2C. Screening of bases

The screening of base was performed using general procedure and the results are summarized in Table S4.

Table S4. Optimization of base for the synthesis of cyclic amidine



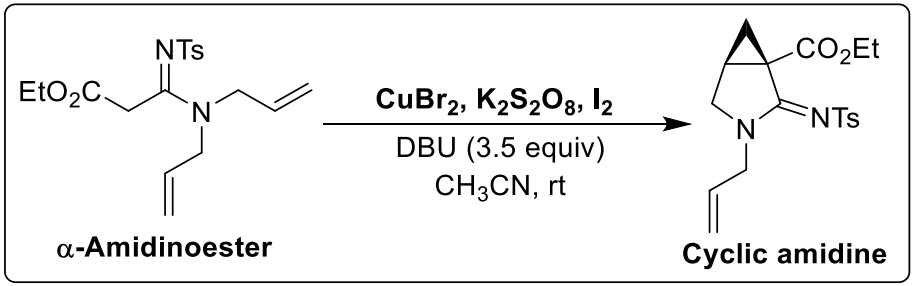
Entry	Base (equiv)	Time (h)	Isolated yield (%)
1	ethylenediamine (2)	24	21
2	triethylamine (2)	24	-
3	2,2'-bipyridine (2)	24	24
4	pyridine (2)	24	21
5	DABCO (2)	24	10
6	DMAP (2)	24	8
7	2,6-lutidine (2)	24	-
8	N^1,N^1,N^2,N^2-tetramethylethane-1,2-diamine (2)	24	32
9	4,4'-bipyridine (2)	24	26
10	potassium carbonate (2)	24	38
11	DBN (2)	24	21
12	DBU (2)	18	56

13	DBU (3)	14	58
14	DBU (3.5)	12	62
15	DBU (4)	18	53

2D. Screening of SET oxidant, Co-oxidant and additive

The screening of equivalents of $CuBr_2$, $K_2S_2O_8$ and I_2 were performed using general procedure and the results are summarized in Table S5.

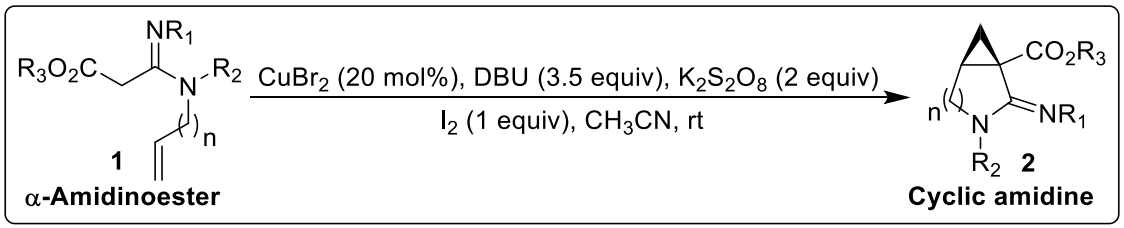
Table S5. Optimization of equivalents of $CuBr_2$, $K_2S_2O_8$ and I_2 for the synthesis of cyclic amidine



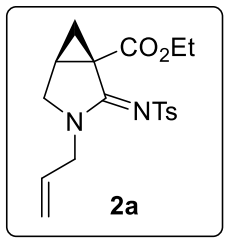
Entry	$CuBr_2$ (equiv)	$K_2S_2O_8$ (equiv)	I_2 (equiv)	Time (h)	Isolated yield (%)
1	2.0	-	-	18	62
2	0.1	2.0	-	8	69
3	0.2	2.0	-	4	78
4	0.2	3.0	-	4	73
5	0.2	2.0	0.5	2	86

6	0.2	2.0	1.0	1	93
7	0.2	2.0	1.5	1	82

Procedure for the catalytic SET oxidative cyclization of α-amidinoester

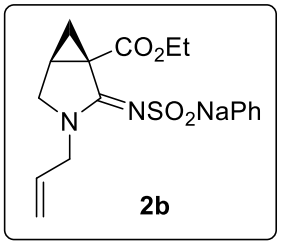


To a stirred solution of *α*-amidinoester **1** (1 equiv) in dry CH_3CN (3 mL/ mmol), DBU (3.5 equiv), $CuBr_2$ (20 mol%), $K_2S_2O_8$ (2 equiv) and I_2 (1 equiv) were added and the resultant mixture was stirred at room temperature. After completion of the reaction as indicated by TLC, the mixture was quenched with saturated $Na_2S_2O_3$ (30 mL) and extracted with DCM (3 X 30 mL). The combined organic layer was washed with brine solution (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography over silica gel using EtOAc-hexane as a solvent eluent to furnish pure cyclic amidine in good yield.



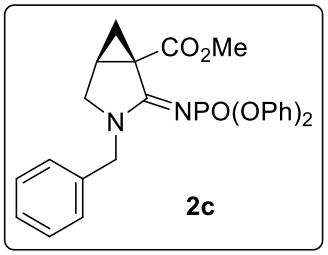
Preparation of *(1S,5S)-ethyl 3-allyl-2-(tosylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (2a): Following the general procedure, the SET oxidative cyclization of *α*-amidinoester **1a** (4.2 g, 11.53 mmol) using DBU (6.1 g, 40.36 mmol), I_2 (2.92 g, 11.53 mmol), $CuBr_2$ (515 mg, 2.3 mmol) and $K_2S_2O_8$ (6.23 g, 23.06 mmol) was carried

out and the resultant product **2a** (3.88 g, 93%) was obtained as a pale yellow crystals (R_f = 0.3 in 50% EtOAc in hexane); m.p 62-64 ^oC; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.77(d, *J* = 6.8 Hz, 2H), 7.21(d, *J* = 7.2 Hz, 2H), 5.59-5.52(m, 1H), 5.15-5.05(m, 2H), 4.31-4.17(m, 2H), 4.00-3.96(m, 1H), 3.85-3.81(m, 1H), 3.70(d, *J* = 10.8 Hz, 1H), 3.30(d, *J* = 11.6 Hz, 1H), 2.37(s, 3H), 2.24(brs, 2H), 1.29(t, *J* = 6.8 Hz, 3H), 0.93(s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.7, 164.3, 141.9, 141.3, 130.8, 129.1, 126.2, 119.5, 62.2, 49.6, 47.5, 35.0, 24.6, 21.5, 19.1, 13.9. The present data are in good agreement with the literature data.[9]

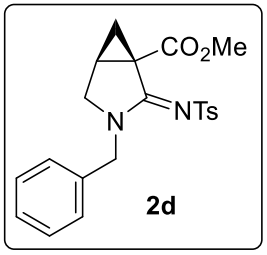


2b

Preparation of *(1S,5S,Z)-ethyl 3-allyl-2-(naphthalen-2-ylsulfonylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (2b): The reaction of *α*-amidinoester **1b** (412 mg, 1.02 mmol), DBU (548 mg, 3.6 mmol), I_2 (261 mg, 1.02 mmol), $CuBr_2$ (45 mg, 0.2 mmol) and $K_2S_2O_8$ (556 mg, 2.05 mmol) was carried out using general procedure and the corresponding product **2b** (324 mg, 79%) was isolated as a pale yellow solid (R_f = 0.3 in 50% EtOAc in hexane); m.p 88-89^{o}C; **IR (neat):** 3076, 3032, 2947, 2871, 1735, 1614, 1489, 1447, 1374, 1291, 1213, 1078, 1017, 966, 923, 767 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 8.88(d, *J* = 8.8 Hz, 1H), 8.24(d, *J* = 7.2 Hz, 1H), 7.96(d, *J* = 8.4 Hz, 1H), 7.86(d, *J* = 8.0 Hz, 1H), 7.58(t, *J* = 7.2 Hz, 1H), 7.54-7.45(m, 2H), 5.41-5.34(m, 1H), 4.98-4.89(m, 2H), 4.33-4.20(m, 2H), 3.85(dd, *J* = 15.2 Hz, 6.4 Hz, 1H), 3.71(dt, *J* = 15.2 Hz, 6.4 Hz, 2H), 3.26(d, *J* = 11.6 Hz, 1H), 2.30-2.23(m, 2H), 1.32(t, *J* = 6.8 Hz, 3H), 0.92(t, *J* = 4.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.7, 164.3, 139.2, 134.2, 132.9, 130.4, 128.6, 128.5, 127.3, 126.7, 126.4, 126.3, 124.2, 119.5, 62.3, 49.7, 47.5, 35.1, 24.7, 19.1, 14.0; **HRMS(ESI):** m/z calcd for $C_{21}H_{23}N_2O_4S$ $[M+H]^+$: 399.1373, found: 399.1363.

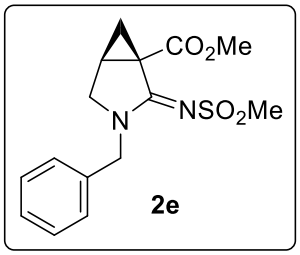


Preparation of *(1S,5S)-methyl 3-benzyl-2-(diphenoxyphosphorylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (2c): Under the similar reaction conditions, the reaction of *α*-amidinoester **1c** (1.5 g, 3.13 mmol), DBU (1.66 g, 10.97 mmol), I_2 (793 mg, 3.13 mmol), $CuBr_2$ (140mg, 0.62 mmol) and $K_2S_2O_8$ (1.69 g, 6.27 mmol) was carried out and resultant product **2c** (864 mg, 58%) was obtained as a pale yellow solid (R_f = 0.3 in 40% EtOAc in hexane); m.p 96-97 ^oC; **IR (neat):** 3064, 2982, 2931, 2875, 2367, 2238, 1732, 1625, 1581, 1442, 1261, 1184, 1019, 931, 855 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.35-7.29(m, 4H), 7.27-7.19(m, 7H), 7.13-7.06(m, 2H), 6.94-6.92(m, 2H), 4.63(d, *J* = 14.4 Hz, 1H), 4.19(d, *J* = 14.8 Hz, 1H), 3.71(s, 3H), 3.59-3.54(m, 1H), 3.15(d, *J* = 11.6 Hz, 1H), 2.21-2.14(m, 2H), 0.89-0.84(m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 168.3, 166.9, 166.7, 152.1, 152.0, 151.8, 151.7, 135.4, 129.4, 128.9, 128.2, 128.0, 124.2, 124.1, 120.7, 120.6, 120.5, 120.5, 52.6, 49.1, 47.9, 34.7, 24.3, 19.4; **HRMS(ESI):** m/z calcd for $C_{26}H_{26}N_2O_5P$ $[M+H]^+$: 477.1574, found: 477.1583.

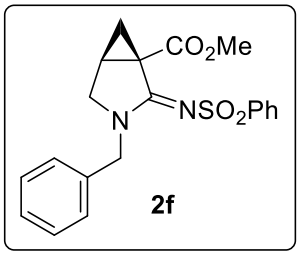


Preparation of *(1S,5S)-methyl 3-benzyl-2-(tosylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (2d): Following the general procedure, the SET oxidative cyclization of *α*-amidinoester **1d** (2.9 g, 7.2 mmol) using DBU (3.8 g, 25.3 mmol), I_2 (1.84 g, 7.2 mmol), $CuBr_2$ (323 mg, 1.4 mmol) and $K_2S_2O_8$ (3.9 g, 14.5 mmol) was carried out and the resultant product **2d** (2.42 g, 84%) was obtained as a pale yellow solid (R_f = 0.3 in 50% EtOAc in hexane); m.p 118-119^oC; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.80 (d, *J* = 7.2 Hz, 2H), 7.25-7.19 (m, 5H), 6.83 (d, *J* = 6.8 Hz, 2H), 4.74(d, *J* = 14.4 Hz, 1H), 4.22(d, *J* = 14.4 Hz, 1H), 3.76(s, 3H), 3.64(dd, *J* = 11.6 Hz, 4.0 Hz, 1H), 3.23 (d, *J* = 11.6 Hz, 1H),

2.40(s, 3H), 2.22(s, 2H), 0.87 (t, *J* = 9.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 168.1, 164.3, 142.0, 141.1, 134.9, 129.2, 128.9, 128.3, 128.2, 126.3, 52.6, 49.4, 48.6, 34.7, 24.6, 21.5, 18.8. The present data are in good agreement with the literature data.[9]

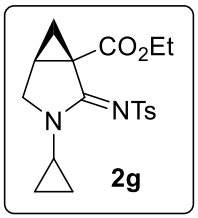


Preparation of *(1S,5S)-methyl 3-benzyl-2-(methylsulfonylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (2e): The reaction of *α*-amidinoester **1e** (3.99 g, 12.3 mmol), DBU (6.54 g, 43.08 mmol), I_2 (3.11 g, 12.3 mmol), $CuBr_2$ (549 mg, 2.46 mmol) and $K_2S_2O_8$ (6.64 g, 24.62 mmol) was carried out using general procedure and the corresponding product **2e** (2.61 g, 66%) was isolated as a pale yellow solid (R_f = 0.3 in 40% EtOAc in hexane); m.p 112-113 ^oC; **IR (neat):** 3065, 3035, 2951, 2878, 1737, 1581, 1490, 1446, 1383, 1289, 1277, 1270, 1206, 1163, 1130, 1060, 1008, 969, 904, 876, 768 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.35-7.27(m, 3H), 7.18(d, *J* = 6.8 Hz, 2H), 4.66(d, *J* = 14.8 Hz, 1H), 4.42(d, *J* = 14.8 Hz, 1H), 3.76(s, 3H), 3.63(dd, *J* = 11.2 Hz, 4.8 Hz, 1H), 3.25(d, *J* = 11.6 Hz, 1H), 3.01(s, 3H), 2.24-2.17(m, 2H), 0.97(t, *J* = 12.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 168.0, 164.8, 135.0, 129.1, 128.2, 128.2, 52.5, 49.4, 48.6, 42.2, 34.5, 24.5, 19.2; **HRMS(ESI):** m/z calcd for $C_{15}H_{19}N_2O_4S$ $[M+H]^+$: 323.1066, found: 323.1070.

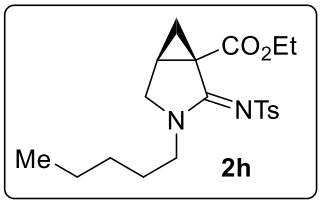


Preparation of *(1S,5S)-methyl 3-benzyl-2-(phenylsulfonylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (2f): Under the similar reaction conditions, the reaction of *α*-amidinoester **1f** (6.3 g, 16.3 mmol), DBU (8.68 g, 57.1 mmol), I_2 (4.12 g, 16.3 mmol), $CuBr_2$ (728 mg, 3.26 mmol) and $K_2S_2O_8$(8.8 g, 32.63 mmol) was carried out and the resultant product **2f** (4.63 g, 74%) was obtained as yellow oil (R_f = 0.3 in 40% EtOAc in hexane); **IR (neat):** 3060, 2996, 2949, 2878, 1738, 1578, 1487, 1444, 1382, 1296, 1271, 1252, 1205, 1152, 1090, 1021, 904, 846 cm^{-1};

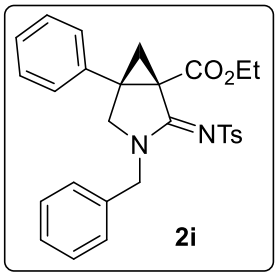
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 7.91(d, *J* = 8.0 Hz, 2H), 7.51-7.42(m, 3H), 7.24-7.16(m, 3H), 6.96(d, *J* = 7.2 Hz, 2H), 4.73(d, *J* = 14.4 Hz, 1H), 4.22(d, *J* = 14.8 Hz, 1H), 3.73(s, 3H), 3.65(dd, *J* = 11.6 Hz, 4.8 Hz, 1H), 3.24(d, *J* = 11.6 Hz, 1H), 2.25-2.19(m, 2H), 0.87(t, *J* = 10.8 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 168.0, 164.5, 143.8, 134.8, 131.5, 128.9, 128.6, 128.2, 128.1, 126.2, 52.6, 49.4, 48.6, 34.6, 24.6, 18.7; **HRMS(ESI):** m/z calcd for $C_{20}H_{21}N_2O_4S$ $[M+H]^+$: 385.1222, found: 385.1215.



Preparation of *(1S,5S)-ethyl 3-cyclopropyl-2-(tosylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (2g): Following the general procedure, the SET oxidative cyclization of *α*-amidinoester **1g** (298 mg, 0.81 mmol) using DBU (436 mg, 2.86 mmol), I_2 (207 mg, 0.81 mmol), $CuBr_2$ (36 mg, 0.16 mmol) and $K_2S_2O_8$ (442 mg, 1.63 mmol) was carried out and the resultant product **2g** (160 mg, 54%) was obtained as a yellow semisolid (R_f = 0.3 in 40% EtOAc in hexane); **IR (neat):** 3056, 2985, 2927, 2856, 2361, 2308, 1730, 1617, 1575, 1454, 1422, 1266, 1145, 1093, 1020, 902, 817, 744 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.76(d, *J* = 8.4 Hz, 2H), 7.18(d, *J* = 8.0 Hz, 2H), 4.25-4.08(m, 2H), 3.62(dd, *J* = 9.2 Hz, 6.0 Hz, 1H), 3.21(d, *J* = 11.6 Hz, 1H), 2.74-2.68(m, 1H), 2.34(s, 3H), 2.18-2.12(m, 2H), 1.23(t, *J* = 7.2 Hz, 3H), 0.86(t, *J* = 9.6 Hz, 1H), 0.80-0.70(m, 1H), 0.69-0.61(m, 2H), 0.48-0.39(m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.6, 165.7, 141.7, 141.3, 129.0, 126.0, 61.9, 49.8, 35.2, 27.5, 24.1, 21.4, 18.8, 13.8, 6.0, 5.5; **HRMS(ESI):** m/z calcd for $C_{18}H_{22}N_2O_4NaS$ $[M+Na]^+$: 385.1198, found: 385.1198.

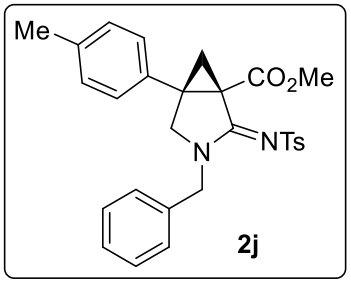


Preparation of *(1S,5S)-ethyl 3-pentyl-2-(tosylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (2h): The reaction of *α*-amidinoester **1h** (252 mg, 0.63 mmol), DBU (340 mg, 2.23 mmol), I_2 (162 mg, 0.63 mmol), $CuBr_2$ (28 mg, 0.12 mmol) and $K_2S_2O_8$ (345 mg, 1.27 mmol) was carried out using general procedure and the corresponding product **2h** (215 mg, 86%) was isolated as a yellow semisolid (R_f = 0.3 in 40% EtOAc in hexane); **IR (neat):** 3062, 2960, 2931, 2864, 1732, 1671, 1571, 1460, 1383, 1289, 1271, 1256, 1184, 1151, 1092, 1021, 945, 911, 902, 859, 819, 757 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.76(d, *J* = 8.0 Hz, 2H), 7.18(d, *J* = 7.6 Hz, 2H), 5.16(t, *J* = 7.2 Hz, 1H), 4.30-4.21(m, 1H), 4.20-4.14(m, 1H), 4.09(d, *J* = 14.4 Hz,1H), 3.60-3.52(m, 1H), 3.23(d, *J* = 11.6 Hz, 1H), 2.35(s, 3H), 1.91(d, *J* = 6.0 Hz, 2H), 1.81-1.74(m, 1H), 1.54-1.47(m, 1H), 1.26(t, *J* = 7.2 Hz, 3H), 1.14-1.03(m, 2H), 0.85(brs, 3H), 0.60(t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.8, 164.2, 141.7, 141.3, 132.7, 131.1, 129.0, 126.2, 62.0, 50.4, 49.0, 35.2, 31.8, 27.3, 24.4, 22.4, 21.1, 19.0, 14.0, 13.8; **HRMS(ESI):** m/z calcd for $C_{20}H_{29}N_2O_4S$ $[M+H]^+$: 393.1848, found: 393.1837.

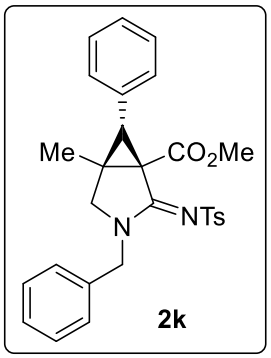


Preparation of *(1S,5R)-ethyl 3-benzyl-5-phenyl-2-(tosylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (2i): Under the similar reaction conditions, the reaction of *α*-amidinoester **1i** (540 mg, 1.1 mmol), DBU (587 mg, 3.85 mmol), I_2 (278 mg, 1.1 mmol), $CuBr_2$ (49 mg, 0.22 mmol) and $K_2S_2O_8$ (595 mg, 2.2 mmol) was carried out and the resultant product **2i** (397 mg, 74%) was obtained as pale-yellow oil (R_f = 0.3 in 50% EtOAc in hexane); **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.84(d, *J* = 8.0 Hz, 2H), 7.28-7.19(m, 10H), 7.02(d, *J* = 6.8 Hz, 2H), 4.94(d, *J* = 14.8 Hz, 1H), 4.23(d, *J* = 14.4 Hz, 1H), 4.09-4.01(m, 1H), 3.97-3.89(m, 1H), 3.75(d, *J* = 12.0 Hz, 1H), 3.53(d, *J* = 12.0 Hz, 1H), 2.71(d, *J* = 5.6 Hz, 1H), 2.41(s, 3H), 1.23(d, *J* = 5.6 Hz, 1H), 1.01(t, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 164.9,

164.4, 142.0, 141.0, 135.1, 135.1, 129.5, 129.2, 129.0, 128.8, 128.6, 128.3, 128.2, 126.5, 61.7, 56.6, 48.7, 41.3, 39.1, 22.0, 21.6, 13.9. The present data are in good agreement with the literature data.[9]

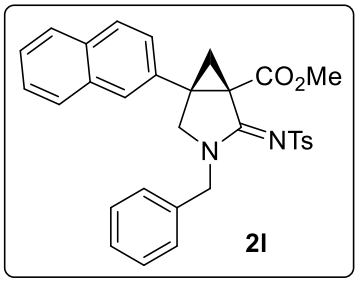


Preparation of *(1S,5R)-methyl 3-benzyl-5-p-tolyl-2-(tosylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (2j): Following the general procedure, the SET oxidative cyclization of *α*-amidinoester **1j** (850 mg, 1.73 mmol) using DBU (924 mg, 6.07 mmol), I_2 (438 mg, 1.73 mmol), $CuBr_2$ (77 mg, 0.34 mmol) and $K_2S_2O_8$ (936 mg, 3.46 mmol) was carried out and the resultant product **2j** (600 mg, 71%) was obtained as a pale yellow crystal (R_f = 0.3 in 50% EtOAc in hexane); m.p 115-116 ^oC ; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.85(d, *J* = 8.0 Hz, 2H), 7.27-7.21(m, 5H), 7.12(q, *J* = 8.4 Hz, 4H), 7.03(d, *J* = 6.8 Hz, 2H), 4.93(d, *J* = 14.4 Hz, 1H), 4.25(d, *J* = 14.4 Hz, 1H), 3.74(d, *J* = 12.0 Hz, 1H), 3.55(s, 3H), 3.52(s, 1H), 2.69(d, *J* = 5.6 Hz, 1H), 2.42(s, 3H), 2.31(s, 3H), 1.24(d, *J* = 5.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 165.4, 164.4, 142.0, 140.9, 138.5, 135.0, 131.9, 129.6, 129.1, 129.1, 129.0, 128.3, 128.2, 126.3, 56.6, 52.4, 48.6, 41.2, 39.1, 22.2, 21.5, 21.2. The present data are in good agreement with the literature data.[9]

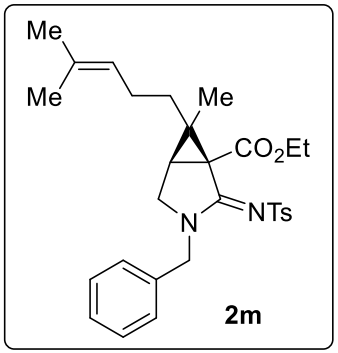


Preparation of *(1R,5R,6S)-methyl 3-benzyl-5-methyl-6-phenyl-2-(tosylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (2k): The reaction of *α*-amidinoester **1k** (2.8 g, 5.71 mmol), DBU (3.03 g, 19.99 mmol), I_2 (1.44 g, 5.71 mmol), $CuBr_2$ (255 mg, 1.14 mmol) and $K_2S_2O_8$ (3.08 g, 11.42 mmol) was carried out using general procedure and the corresponding product **2k** (2.32 g, 84%) was isolated as a pale yellow solid (R_f = 0.3 in 40% EtOAc in hexane); m.p 204-205 ^oC; **IR (neat):** 3057, 2989, 2949, 2874, 2307, 1963, 1908, 1746, 1738, 1599,

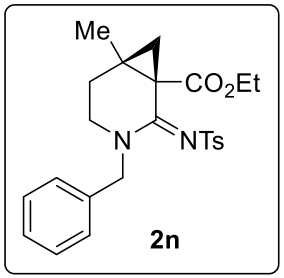
1587, 1558, 1485, 1470, 1453, 1357, 1268, 1209, 1141, 1089, 1029, 870, 814 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.87(d, *J* = 8.0 Hz, 2H), 7.26-7.22(m, 4H), 7.18-7.14(m, 1H), 7.13-7.09(m, 1H), 7.05-6.98(m, 4H), 6.42(d, *J* = 7.6 Hz, 2H), 4.35(d, *J* = 14.4 Hz, 1H), 3.95(d, *J* = 14.4 Hz, 1H), 3.86(s, 3H), 3.54(s, 1H), 3.29(s, 2H), 2.42(s, 3H), 1.47(s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 166.9, 162.8, 141.9, 141.3, 134.3, 132.0, 129.4, 129.1, 128.7, 128.7, 128.2, 127.8, 127.6, 126.3, 52.8, 51.9, 48.8, 45.5, 38.1, 36.1, 21.6, 17.5; **HRMS(ESI):** m/z calcd for $C_{28}H_{29}N_2O_4S$ $[M+H]^+$: 489.1818, found: 489.1838.



Preparation of *(1S,5R)-methyl 3-benzyl-5-(naphthalen-2-yl)-2-(tosylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (2l): Under the similar reaction conditions, the reaction of *α*-amidinoester **1l** (1 g, 1.9 mmol), DBU (1 g, 6.65 mmol), I_2 (480 mg, 1.9 mmol), $CuBr_2$ (84 mg, 0.38 mmol) and $K_2S_2O_8$(1 g, 3.8 mmol) was carried out and the resultant product **2l** (816 mg, 82%) was obtained as a pale yellow solid (R_f = 0.3 in 50% EtOAc in hexane); m.p 126-127 ^oC; **IR (neat):** 3070, 3031, 2951, 2873, 2324, 2288, 1740, 1640, 1586, 1488, 1437, 1356, 1287, 1265, 1243, 1210, 1146, 1088, 1024, 917, 819 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.85(d, *J* = 8.0 Hz, 2H), 7.79-7.73(m, 4H), 7.48-7.45(m,2H), 7.31-7.21(m, 6H), 7.05(d, *J* = 7.2 Hz, 2H), 4.96(d, *J* = 14.4 Hz, 1H), 4.26(d, *J* = 14.4 Hz, 1H), 3.84(d, *J* = 12 Hz, 1H), 3.59(d, *J* = 12 Hz, 1H), 3.49(s, 3H), 2.82(d, *J* = 5.6 Hz, 1H), 2.41(s, 3H), 1.34(d, *J* = 5.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 165.4, 164.4, 142.1, 140.9, 135.0, 133.2, 133.1, 132.3, 129.2, 129.1, 129.0, 128.9, 128.3, 128.2, 128.0, 127.8, 126.7, 126.7, 126.4, 126.2, 56.5, 52.5, 48.7, 41.3, 39.5, 22.4, 21.6; **HRMS(ESI):** m/z calcd for $C_{31}H_{29}N_2O_4S$ $[M+H]^+$: 525.1843, found: 525.1850.

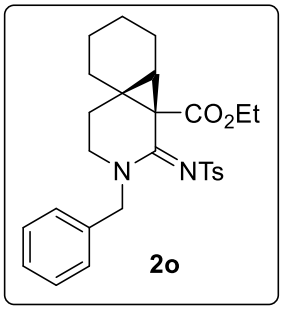


Preparation of *(1R,5S)-ethyl 3-benzyl-6-methyl-6-(4-methylpent-3-enyl)-2-(tosylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (2m): Following the general procedure, the SET oxidative cyclization of α-amidinoester **1m** (1.5 g, 2.93 mmol) using DBU (1.56 g, 10.28 mmol), I_2 (743 mg, 2.93 mmol), $CuBr_2$ (131 mg, 0.58 mmol) and $K_2S_2O_8$(1.58 g, 5.87 mmol) was carried out and the resultant product **2m** (1 g, 68%) was obtained as a brown semi solid (R_f = 0.3 in 40% EtOAc in hexane); **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.81(d, *J* = 8 Hz, 2H), 7.23(d, *J* = 8 Hz, 3H), 7.16(t, *J* = 7.6 Hz, 2H) 7.09(d, *J* = 7.2 Hz, 2H), 4.70(d, *J* = 14.4 Hz, 1H), 4.44 (t, *J* = 6.8 Hz, 1H), 4.31(d, *J* = 14.0 Hz,1H), 4.27-4.19(m, 1H), 4.12-4.06(m,1H), 3.64(dd, *J* = 12 Hz, 6.8 Hz, 1H), 3.15(d, *J* = 11.6 Hz, 1H), 2.41(s, 3H), 2.05(d, *J* = 6.4 Hz, 2H), 1.90-1.79 (m, 1H), 1.62(s, 3H), 1.57(s, 3H), 1.45(s, 3H), 1.23(t, *J* = 7.2 Hz, 3H), 1.19-1.15(m, 1H), 0.73-0.67(m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 168.7, 163.6, 142.0, 134.6, 131.8, 129.9, 129.1, 128.8, 128.1, 126.5, 126.4, 123.5, 61.5, 48.8, 47.1, 43.7, 35.6, 35.0, 30.1, 25.6, 24.3, 21.6, 19.3, 17.6, 13.8. The present data are in good agreement with the literature data.[9]



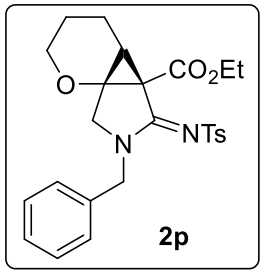
Preparation of *(1S,6R)-ethyl 3-benzyl-6-methyl-2-(tosylimino)-3-azabicyclo[4.1.0]heptane-1-carboxylate* (2n): The reaction of α-amidinoester **1n** (272 mg, 0.61 mmol), DBU (327 mg, 2.15 mmol), I_2 (156 mg, 0.61 mmol), $CuBr_2$ (27 mg, 0.12 mmol) and $K_2S_2O_8$ (332 mg, 1.23 mmol) was carried out using general procedure and the corresponding product **2n (**186 mg, 69%) was isolated as yellow oil (R_f = 0.3 in 40% EtOAc in hexane) and 12% recovered starting material; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.74(d, *J* = 7.6 Hz, 2H), 7.27-7.17(m, 7H), 5.19(d, *J* = 14.8 Hz, 1H), 4.44(d, *J* = 14.8 Hz, 1H), 4.24-4.12(m, 2H), 3.52(t, *J* = 12.8 Hz, 1H), 3.05(d, *J* = 12.8 Hz, 1H), 2.37(s, 3H), 2.01(s,

2H), 1.43(t, *J* = 12.8 Hz, 1H), 1.27-1.20(m, 7H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.6, 162.4, 141.8, 141.2, 135.7, 129.0, 128.8, 127.9, 126.3, 61.7, 53.8, 47.4, 36.4, 32.1, 31.2, 29.8, 21.5, 18.8, 14.1. The present data are in good agreement with the literature data.[9]

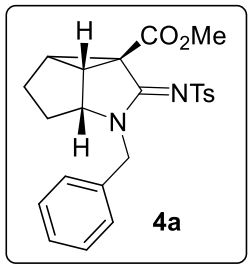


2o

Preparation of tricyclic amidine (2o): Under the similar reaction conditions, the reaction of *α*-amidinoester **1o** (454 mg, 0.94 mmol), DBU (501 mg, 3.29 mmol), I_2 (238 mg, 0.94 mmol), $CuBr_2$ (42 mg, 0.18 mmol) and $K_2S_2O_8$ (509 mg, 1.88 mmol) was carried out and the resultant product **2o** (253 mg, 56%) was obtained as orange-yellow oil (R_f = 0.25 in 40% EtOAc in hexane); **IR (neat):** 3056, 2985, 2932, 2861, 2360, 2337, 1724, 1605, 1548, 1442, 1266, 1200, 1151, 1091, 1021, 899 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.81-7.63(m, 4.75H), 7.38-7.30(m, 4.18H), 7.27-7.16(m, 6.17H), 7.11(d, *J* = 8.0 Hz, 1H), 5.47(s, 0.78H), 5.22(s, 0.59H), 5.15(s, 1.15H), 4.98(d, *J* = 14.4 Hz, 0.21H), 4.49-4.40(m, 0.46H), 4.30-4.20(m, 1.49H), 4.17-3.96(m, 1.42H), 3.51-3.39(m, 1.58H), 3.20-3.15(m, 0.45H), 3.05-3.01(m, 0.51H), 2.42(s, 1.27H), 2.40(s, 3H), 2.36(s, 0.75H), 2.31(s, 1.51H), 2.15-1.98(m, 3.30H), 1.87-1.72(m, 3.78H), 1.66-1.54(m, 3.86H), 1.45-1.44(m, 2.87H), 1.36-1.20(m, 4.36H), 1.16-1.10(m, 1.39H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 163.9, 161.0, 143.4, 142.8, 142.2, 141.7, 139.7, 139.4, 133.7, 132.8, 132.3, 130.9, 130.5, 130.1, 129.8, 129.7, 129.3, 129.0, 128.8, 128.7, 127.9, 127.7, 126.9, 126.8, 126.6, 126.4, 126.2, 125.6, 124.3, 61.9, 61.1, 47.8, 40.1, 37.2, 35.8, 27.5, 27.4, 25.2, 25.1, 22.8, 22.6, 22.6, 22.2, 22.1, 21.5, 21.4, 21.2, 20.6, 20.2, 14.1, 14.1, 13.7; **HRMS (ESI):** m/z calcd for $C_{27}H_{33}N_2O_4S$ $[M+H]^+$: 481.2161, found: 481.2179.

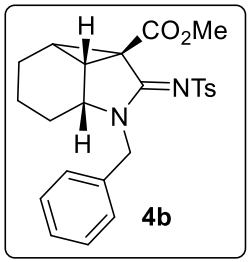


Preparation of tricyclic amidine (2p): Following the general procedure, the SET oxidative cyclization of *α*-amidinoester **1p** (224 mg, 0.47 mmol) using DBU (253 mg, 1.66 mmol), I_2 (120 mg, 0.47 mmol), $CuBr_2$ (21 mg, 0.09 mmol) and $K_2S_2O_8$ (257 mg, 0.95 mmol) was carried out and the resultant product **2p** (98 mg, 44%) was obtained as orange-yellow oil (R_f = 0.25 in 40% EtOAc in hexane); **IR (neat):** 3069, 2927, 2858, 2361, 1733, 1649, 1563, 1486, 1453, 1278, 1197, 1150, 1087, 1023, 905 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.67(d, *J* = 8.0 Hz, 2H), 7.16-7.02(m, 5H), 6.88(d, *J* = 6.8 Hz, 2H), 4.71(d, *J* = 14.4 Hz, 1H), 4.16-4.10(m, 2H), 4.05-3.97(m, 2H), 3.63(d, *J* = 10.8 Hz, 1H), 3.52(d, *J* = 11.6 Hz, 1H), 3.35(d, *J* = 11.6 Hz, 1H), 3.22(t, *J* = 10.4 Hz, 1H), 2.55(dd, *J* = 14.0 Hz, 5.6 Hz, 1H), 2.29(s, 3H), 1.93-1.78(m, 1H), 1.42-1.37(m, 1H), 1.29(d, *J* = 7.6 Hz, 1H), 1.13(t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 165.0, 164.3, 142.0, 140.9, 135.1, 129.1, 128.9, 128.1, 128.1, 126.3, 67.6, 65.8, 61.6, 52.4, 48.1, 39.7, 28.9, 21.8, 21.5, 15.5, 13.9; **HRMS (ESI):** m/z calcd for $C_{25}H_{29}N_2O_5S$ $[M+H]^+$: 469.1797, found: 469.1800.

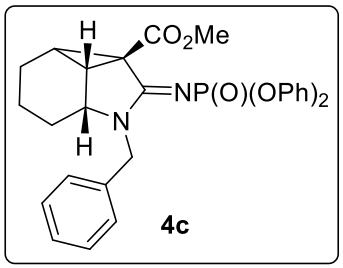


Preparation of tricyclic amidine (4a): The reaction of *α*-amidinoester **3a** (710 mg, 1.6 mmol), DBU (888 mg, 5.8 mmol), I_2 (421 mg, 1.6 mmol), $CuBr_2$ (74 mg, 0.33 mmol) and $K_2S_2O_8$ (900 mg, 3.3 mmol) was carried out using general procedure and the corresponding product **4a** (444 mg, 63%) was isolated as a pale yellow crystal (R_f = 0.3 in 50% EtOAc in hexane); m.p 117-118 ^oC and 12% recovered starting material; **IR (neat):** 3066, 3035, 2955, 2868, 1737, 1657, 1567, 1489, 1446, 1362, 1291, 1258, 1252, 1213, 1149, 1086, 1024, 935, 824 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.79(d, *J* = 8.0 Hz, 2H), 7.29-7.27(m, 3H), 7.25(d, *J* = 4.0 Hz, 2H), 7.23-7.19(m, 2H), 4.94(d, *J* = 15.2 Hz, 1H), 4.01-4.00(m, 1H), 3.80(d, *J* = 14.8 Hz, 1H), 3.70(s, 3H), 3.07(t, *J* = 6.8 Hz, 1H), 2.94(t, *J* = 5.6 Hz, 1H), 2.39(s, 3H), 2.21-2.14(m,

1H), 1.84-1.73(m, 2H), 1.37-1.30(m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 167.3, 162.3, 142.0, 141.2, 134.8, 129.1, 128.8, 128.5, 128.1, 126.2, 63.5, 52.4, 47.4, 43.2, 43.0, 38.4, 34.2, 23.0, 21.5; **HRMS(ESI):** m/z calcd for $C_{23}H_{25}N_2O_4S$ $[M+H]^+$: 425.1451, found: 425.1465.

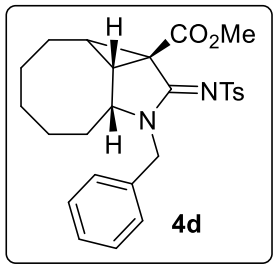


Preparation of tricyclic amidine (4b): Under the similar reaction conditions, the reaction of *α*-amidinoester **3b** (851 mg, 1.9 mmol), DBU (1.03 g, 6.7 mmol), I_2 (489 mg, 1.9 mmol), $CuBr_2$ (86 mg, 0.38 mmol) and $K_2S_2O_8$ (1.04 g, 3.8 mmol) was carried out and the resultant product **4b** (372 mg, 44%) was obtained as a pale yellow crystal (R_f = 0.3 in 50% EtOAc in hexane); m.p 84-85 ^oC and 35% recovered starting material; **IR (neat):** 3058, 2983, 2935, 2855, 2304, 1731, 1725, 1569, 1563, 1454, 1268, 1263, 1161, 1155, 1146, 1089, 893, 736, 708 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.71(d, *J* = 8.4 Hz, 2H), 7.28-7.21(m, 3H), 7.19-7.16(m, 4H), 5.11(d, *J* = 15.2 Hz, 1H), 3.81(d, *J* = 5.6 Hz, 1H), 3.60(s, 3H), 3.39(d, *J* = 15.2 Hz, 1H), 2.51-2.47(m, 1H), 2.40(t, *J* = 7.6 Hz, 1H), 2.32(s, 3H), 1.97-1.83(m, 2H), 1.69-1.65(m, 1H), 1.40-1.34(m, 2H), 0.86-0.75(m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 168.9, 164.3, 141.9, 141.3, 134.4, 129.2, 128.9, 128.4, 128.1, 126.1, 52.5, 52.2, 47.0, 39.6, 32.6, 25.1, 22.8, 21.5, 17.3, 13.9; **HRMS(ESI):**m/z calcd for $C_{24}H_{26}N_2NaO_4S$ $[M+Na]^+$: 461.1505, found: 461.1493.



Preparation of tricyclic amidine (4c): Following the general procedure, the SET oxidative cyclization of *α*-amidinoester **3c** (645 mg, 1.2 mmol) using DBU (663 mg, 4.3 mmol), I_2 (315 mg, 1.2 mmol), $CuBr_2$ (55 mg, 0.24 mmol) and $K_2S_2O_8$ (672 mg, 2.4 mmol) was carried out and the resultant product **4c** (231

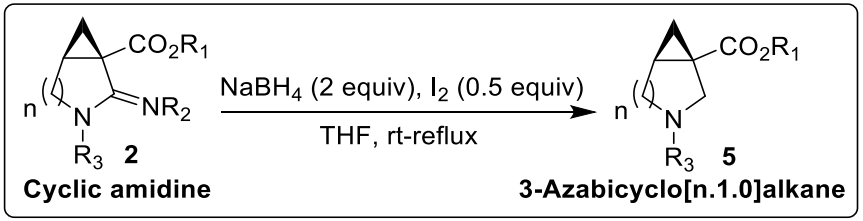
mg, 36%) was obtained as a pale yellow semisolid (R_f = 0.3 in 70% EtOAc in hexane) and 37% recovered starting material; **IR (neat):** 3077, 3031, 2935, 2859, 2285, 1735, 1622, 1570, 1485, 1456, 1361, 1305, 1278, 1274, 1263, 1240, 1204, 1175, 1159, 1087, 1033, 1019, 987, 928, 755 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.34-7.24(m, 11H), 7.18(d, *J* = 5.6 Hz, 2H), 7.12-7.07(m, 2H), 5.09(d, *J* = 12.0 Hz, 1H), 3.80-3.78(m, 1H), 3.70(s, 3H), 3.23(d, *J* = 12.0 Hz, 1H), 2.45-2.39(m, 2H), 1.90-1.82(m, 1H), 1.71-1.67(m, 1H), 1.60(dd, *J* = 12.4 Hz, 5.6 Hz, 1H), 1.40-1.34(m, 1H), 1.29-1.25(m, 1H), 0.61-0.51(m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 169.2, 166.3, 166.2, 152.2, 152.1, 151.7, 151.6, 134.9, 129.3, 129.2, 128.8, 128.4, 127.9, 124.3, 124.2, 121.1, 121.0, 120.9, 120.8, 52.5, 51.4, 46.0, 39.4, 32.2, 25.1, 22.6, 16.9, 13.6; **HRMS(ESI):** m/z calcd for $C_{29}H_{30}N_2O_5P$ $[M+H]^+$: 517.1892, found: 517.1875.



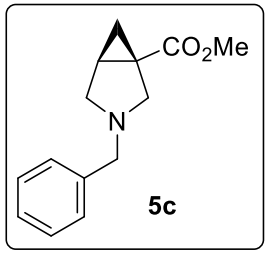
Preparation of tricyclic amidine (4d): The reaction of *α*-amidinoester **3d** (560 mg, 1.19 mmol), DBU (637 mg, 4.1 mmol), I_2 (302 mg, 1.19 mmol), $CuBr_2$ (53 mg, 0.23 mmol) and $K_2S_2O_8$ (646 mg, 2.39 mmol) was carried out using general procedure and the corresponding product **4d** (172 mg, 31%) was isolated as pale yellow oil (R_f = 0.3 in 50% EtOAc in hexane) and 30% recovered starting material; **IR (neat):** 3057, 2937, 2857, 2306, 1742, 1591, 1447, 1361, 1302, 1295, 1267, 1150, 1091, 1024, 916, 821 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.77(d, *J* = 8.0 Hz, 2H), 7.74(d, *J* = 8.0 Hz, 2H), 7.24-7.19(m, 10H), 7.17-7.12(m, 4H), 5.09(d, *J* = 14.8 Hz, 2H), 4.67-4.63(m, 1H), 4.56-4.53(m, 1H), 4.39(d, *J* = 5.2 Hz, 1H), 4.28(d, *J* = 5.2 Hz, 1H), 4.24(d, *J* = 5.2 Hz, 1H), 4.20(d, *J* = 5.2 Hz, 1H), 3.80(s, 6H), 3.78-3.70(m, 1H), 3.65-3.58(m, 1H), 2.55-2.52(m, 1H), 2.38(s, 6H), 2.27-2.18(m, 1H), 2.08-1.96(m, 6H), 1.66-1.54(m, 8H), 1.49-1.41(m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 170.8, 170.7, 162.8, 162.5, 142.1, 140.5, 134.4, 134.4, 129.1, 128.7, 128.6, 128.4, 128.0,

128.0, 127.9, 126.6, 126.4, 62.6, 59.9, 59.8, 57.6, 54.7, 53.0, 53.0, 47.6, 47.4, 47.1, 44.2, 36.1, 34.1, 32.8, 26.1, 26.0, 25.2, 22.7, 22.2, 22.1, 21.6; **HRMS(ESI):** m/z calcd for $C_{26}H_{31}N_2O_4S$ $[M+H]^+$: 467.1914, found: 467.1934.

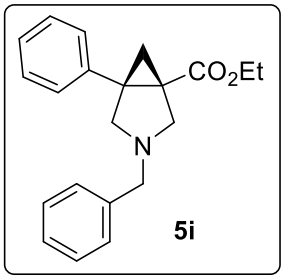
3. Procedure for chemoselective reduction of amidines



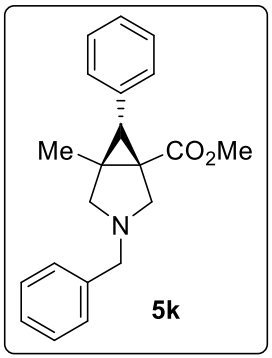
A round bottomed flask charged with amidine (1 equiv) and dry THF (3mL/mmol of amidine), sodiumborohydride (2 equiv) was added at room temperature. To this reaction mixture, iodine (0.5 equiv) in dry THF (3 mL) was added over 30 minutes[10] and the reaction mixture was stirred at reflux until the completion of reaction as indicated by TLC. Then the reaction mixture was cooled to 0 ^oC, methanol (15 mL) was added and the resultant mixture was allowed to stir for 30 minutes. The reaction mixture was evaporated under reduced pressure and the residue was diluted with H_2O_2 (3.1 equiv) followed by NaOMe/NaOEt (1 equiv) was added at 0 ^oC. The resultant mixture was allowed to stir for 30 minutes at room temperature, diluted with distilled water (15 mL) and extracted with EtOAc (2 X 30 mL). The combined EtOAc solvent was washed with brine solution (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude product was purified by column chromatography using EtOAc/ Hexane as an eluent.



Preparation of *(1S,5S)-methyl 3-benzyl-3-azabicyclo[3.1.0]hexane-1-carboxylate* (5c): a) The reaction of cyclic amidine **2c** (902 mg, 1.89 mmol) with $NaBH_4$ (143 mg, 3.78 mmol) and iodine (239 mg, 0.94 mmol), was carried out using general procedure and the resultant product **5c** (288 mg, 66%) was obtained as a yellow semisolid (R_f = 0.3 in 10% EtOAc in hexane); **IR (neat):** 3072, 3027, 2953, 2906, 2802, 1724, 1581, 1490, 1445, 1378, 1326, 1291, 1273, 1249, 1204, 1152, 1137, 1035, 970, 915 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.28-7.17(m, 5H), 3.62(s, 3H), 3.58(s, 2H), 3.04(d, *J* = 9.2 Hz, 1H), 2.91(d, *J*= 8.8 Hz, 1H), 2.70(d, *J* = 8.8 Hz, 1H), 2.38(dd, *J* = 8.8 Hz, 3.6 Hz, 1H), 1.92-1.88(m, 1H), 1.48(t, *J* = 4 Hz, 1H), 1.28(dd, *J* = 8.0 Hz, 3.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 173.8, 138.9, 128.4, 128.1, 126.9, 58.6, 53.7, 53.6, 51.5, 29.2, 27.5, 16.4; **HRMS(ESI):** m/z calcd for $C_{14}H_{18}NO_2[M+H]^+$: 232.1338, found: 232.1320; b) Under the similar reaction conditions, the reaction of cyclic amidine **2d** (422 mg, 1.06 mmol) with $NaBH_4$ (80 mg, 2.12 mmol) and iodine (134 mg, 0.53 mmol), was carried out and the resultant product **5c** (188 mg, 77%) was isolated as a yellow semisolid. The spectral data of the obtained product are in well agreement with the spectral data of compound **5c**; c) The reaction of cyclic amidine **2e** (735 mg, 2.28 mmol) with $NaBH_4$ (172 mg, 4.56 mmol) and iodine (288 mg, 1.14 mmol), was carried out using general procedure and the product **5c** (363 mg, 69%) was obtained as a yellow semisolid. The spectral data of the obtained product are in well agreement with the spectral data of compound **5c**; d) Under the similar reaction conditions, the reaction of cyclic amidine **2f** (741 mg, 1.92 mmol) with $NaBH_4$ (145 mg, 3.85 mmol) and iodine (244 mg, 0.96 mmol), was carried out and the resultant product **5c** (316 mg, 71%) was isolated as a yellow semisolid. The spectral data of the obtained product are in well agreement with the spectral data of compound **5c**.

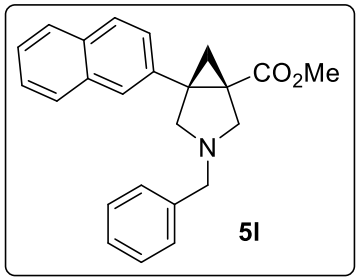


Preparation of *(1S,5R)-ethyl 3-benzyl-5-phenyl-3-azabicyclo[3.1.0]hexane-1-carboxylate* (5i): The chemoselective reduction of cyclic amidine **2i** (1 g, 2.04 mmol) using $NaBH_4$ (154 mg, 4.08 mmol) and iodine (259 mg, 1.02 mmol), was carried out using general procedure and the resultant product **5i** (400 mg, 61%) was obtained as pale yellow oil (R_f = 0.3 in 10% EtOAc in hexane); **IR (neat):** 3055, 2983, 2917, 2803, 1712, 1602, 1448, 1376, 1286, 1238, 1175, 1114, 1024, 872, 754 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.30-7.20(m, 19.96H), 3.89-3.76(m, 3.90H), 3.75-3.62(m, 4.09H), 3.20-3.14(m, 3.96H), 3.10(dd, *J* = 9.2 Hz, 4.4 Hz, 2.03H), 2.67(dd, *J* = 9.6 Hz, 3.6 Hz, 1.98H), 1.92(t, *J* = 4.0 Hz, 1.95H), 1.87(t, *J* = 3.6 Hz, 2H), 0.83-0.78(m, 5.94H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 171.0, 139.1, 138.2, 129.4, 128.6, 128.3, 128.2, 127.1, 127.1, 61.7, 60.1, 58.9, 55.4, 42.9, 35.9, 18.4, 13.9; **HRMS(ESI):** m/z calcd for $C_{21}H_{23}NO_2Na$ $[M+Na]^+$: 344.1621, found: 344.1619.



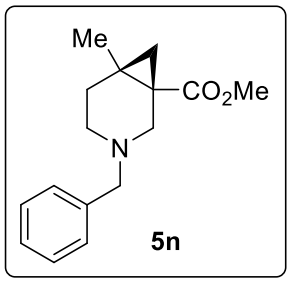
Preparation of *(1R,5R,6S)-methyl 3-benzyl-5-methyl-6-phenyl-3-azabicyclo[3.1.0]hexane-1-carboxylate* (5k): Following the general procedure, the reaction of cyclic amidine **2k** (1.26 g, 2.58 mmol) with $NaBH_4$ (195 mg, 5.16 mmol) and iodine (326 mg, 1.29 mmol), was carried out and the resultant product **5k** (554 mg, 67%) was obtained as colourless oil (R_f = 0.3 in 10% EtOAc in hexane); **IR (neat):** 3033, 2924, 2354, 1718, 1454, 1373, 1304, 1291, 1215, 1130, 954, 872, 810, 775, 728 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.28-7.16(m, 5H), 7.18-7.01(m, 5H), 4.61(d, *J* = 12.1 Hz, 1H), 4.41(d, *J* = 14.4 Hz, 1H), 4.23(d, *J* = 12.3 Hz, 1H),

4.03(d, *J* = 14.4 Hz, 1H), 3.89(s, 3H), 3.48-3.41(m, 1H), 3.31(s, 2H), 1.62(s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 172.4, 133.2, 132.6, 129.1, 128.8, 128.6, 127.9, 127.6, 126.5, 54.2, 53.9, 53.4, 49.2, 46.1, 39.2, 24.3, 16.4; **HRMS(ESI):** m/z calcd for $C_{21}H_{24}NO_2[M+H]^+$: 322.1740, found: 322.1737.



5l

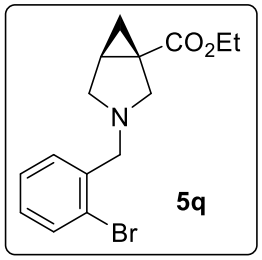
Preparation of *(1S,5R)-methyl 3-benzyl-5-(naphthalen-2-yl)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (5l): Under the similar reaction conditions, the reaction of cyclic amidine **2l** (1 g, 1.9 mmol) with $NaBH_4$ (144 mg, 3.81 mmol) and iodine (241 mg, 0.95 mmol), was carried out and the resultant product **5l** (463 mg, 68%) was isolated as yellow oil (R_f = 0.3 in 10% EtOAc in hexane); **IR (neat):** 3027, 2948, 2907, 2804, 1717, 1601, 1501, 1443, 1366, 1289, 1276, 1274, 1248, 1205, 1162, 1111, 970, 860, 820, 784 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.76-7.70(m, 4H), 7.42-7.37(m, 2H), 7.35-7.32(m, 1H), 7.30-7.25(m, 4H), 7.22-7.18(m, 1H), 3.68(q, *J* = 12.8 Hz, 2H), 3.30(s, 3H), 3.21(t, *J* = 9.2 Hz, 1H), 3.17-3.14(m, 2H), 2.74(d, *J* = 9.6 Hz, 1H), 2.01(d, *J* = 4.0 Hz, 1H), 1.96(d, *J* = 4.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 171.3, 138.9, 135.4, 133.3, 132.6, 128.6, 128.4, 128.3, 127.8, 127.7, 127.6, 127.1, 127.0, 126.0, 125.8, 61.5, 58.8, 55.4, 51.4, 43.1, 35.9, 18.9; **HRMS(ESI):** m/z calcd for $C_{24}H_{23}NO_2Na$ $[M+Na]^+$: 380.1621, found: 380.1621.



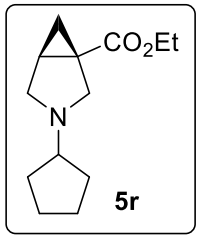
5n

Preparation of *(1S,6R)-ethyl 3-benzyl-6-methyl-3-azabicyclo[4.1.0]heptane-1-carboxylate* (5n): The chemoselective reduction of cyclic amidine **2n** (448 mg, 1.05 mmol) using $NaBH_4$ (80 mg, 2.1 mmol) and iodine (133 mg, 0.52 mmol), was carried out using general procedure and the resultant product **5n** (188 mg, 69%) was obtained as pale yellow oil (R_f = 0.2 in 10% EtOAc in hexane); **IR (neat):** 3027, 2929, 2345, 1717,

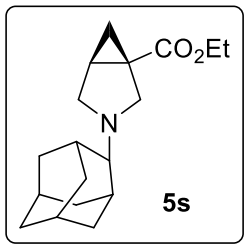
1451, 1365, 1299, 1286, 1238, 1211, 1123, 945, 872, 804, 781, 737 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.37-7.28(m, 4H), 7.24-7.22(m, 1H), 3.66(s, 3H), 3.48(q, *J* = 13.2 Hz, 2H), 3.19(d, *J* = 11.6 Hz, 1H), 2.62(d, *J* = 11.6 Hz, 1H), 2.30-2.22(m, 2H), 1.92-1.85(m, 1H), 1.78-1.72(m, 1H), 1.29(d, *J* = 4.4 Hz, 1H), 1.18(t, *J* = 7.6 Hz, 3H), 1.08(d, *J* = 4.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 173.8, 138.5, 129.0, 128.3, 127.1, 62.0, 54.5, 51.8, 49.1, 31.0, 30.4, 24.4, 24.0, 21.8; **HRMS(ESI):** m/z calcd for $C_{16}H_{22}NO_2$ $[M+H]^+$: 260. 1740, found: 260.1738.



Preparation of *(1S,5S)-methyl 3-(2-bromobenzyl)-3-azabicyclo[3.1.0]hexane-1-carboxylate* (5q): Following the general procedure, the reaction of cyclic amidine **2q** (741 mg, 1.51 mmol) with $NaBH_4$ (114 mg, 3.02 mmol) and iodine (191 mg, 0.75 mmol), was carried out and the resultant product **5q** (340 mg, 73%) was obtained as pale yellow oil (R_f = 0.3 in 10% EtOAc in hexane); **IR (neat):** 3056, 2986, 2907, 2807, 2307, 1715, 1575, 1469, 1432, 1376, 1287, 1276, 1274, 1216, 1154, 1033, 942, 892, 782, 775, 769 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.51(d, *J* = 8.0 Hz, 1H), 7.34(d, *J* = 7.6 Hz, 1H), 7.24(t, *J* = 7.6 Hz, 1H), 7.08(t, *J* = 7.2 Hz, 1H), 4.12(q, *J* = 6.8 Hz, 2H), 3.70(t, *J* = 15.2 Hz, 2H), 3.10(d, *J* = 8.8 Hz, 1H), 2.98(d, *J* = 8.8 Hz, 1H), 2.81(d, *J* = 8.8 Hz, 1H), 2.51(dd, *J* = 8.8 Hz, 3.6 Hz, 1H), 1.94-1.90(m, 1H), 1.47(t, *J* = 4.4 Hz, 1H), 1.30(dd, *J* = 8.0 Hz, 3.6 Hz, 1H), 1.23(t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 173.5, 138.3, 132.7, 130.3, 128.4, 127.2, 124.1, 60.5, 57.9, 53.8, 53.7, 29.4, 27.5, 16.4, 14.3. **HRMS(ESI):** m/z calcd for $C_{15}H_{19}BrNO_2[M+H]^+$: 324.0629, found: 324.0606.

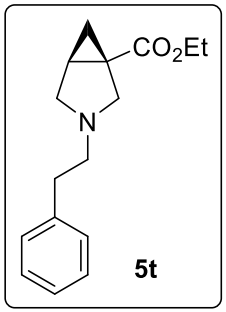


Preparation of *(1S,5S)-ethyl 3-cyclopentyl-3-azabicyclo[3.1.0]hexane-1-carboxylate* (5r): Under the similar reaction conditions, the reaction of cyclic amidine **2r** (460 mg, 1.04 mmol) with $NaBH_4$ (79 mg, 2.09 mmol) and iodine (132 mg, 0.52 mmol), was carried out and the resultant product **5r** (156 mg, 67%) was isolated as colourless oil (R_f = 0.25 in 10% EtOAc in hexane); **IR (neat):** 3056, 2987, 2917, 2801, 1715, 1599, 1448, 1371, 1268, 1232, 1147, 1033, 882, 775 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 4.20-4.15(m, 2.05H), 4.12-4.09(m, 1.15H), 4.03(d, *J* = 13.2 Hz, 0.38H), 3.57(q, *J* = 7.2 Hz, 0.78H), 3.51-3.42(m, 0.74H), 3.16-3.07(m, 1.20H), 3.02(dd, *J* = 13.2 Hz, 3.6 Hz, 0.43H), 2.54(d, *J* = 11.2 Hz, 0.80H), 2.50-2.44(m, 1.55H), 2.30-2.22(m, 0.38H), 2.00-1.84(m, 4.65H), 1.83-1.67(m, 4.87H), 1.59-1.48(m, 2.98H), 1.44(t, *J* = 4.8 Hz, 0.75H), 1.27-1.23(m, 4.28H), 1.05(t, *J* = 4.8 Hz, 0.82H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 171.9, 72.5, 70.6, 65.0, 64.5, 64.0, 61.4, 61.3, 34.2, 33.3, 31.3, 30.6, 28.2, 28.2, 28.1, 25.1, 25.0, 24.7, 14.4, 14.3, 14.3; **HRMS(ESI):** m/z calcd for $C_{13}H_{22}NO_2[M+H]^+$: 224.1829, found: 224.1835.



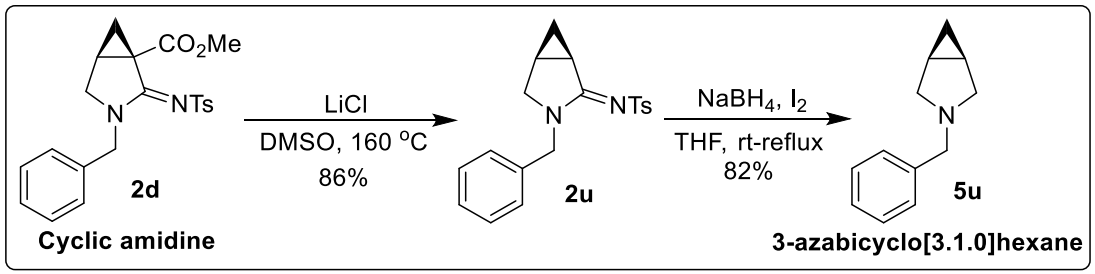
Preparation of *(1S,5S)-ethyl-3-adamantyl-3-azabicyclo[3.1.0]hexane-1-carboxylate* (5s): The chemoselective reduction of cyclic amidine **2s** (545 mg, 1.19 mmol) using $NaBH_4$ (90 mg, 2.3 mmol) and iodine (75 mg, 0.59 mmol), was carried out using general procedure and the resultant product **5s** (221 mg, 64%) was obtained as pale yellow oil (R_f = 0.25 in 10% EtOAc in hexane); **IR (neat):** 3055, 2991, 2924, 2792, 1712, 1610, 1451, 1367, 1269, 1228, 1154, 1031, 874, 761 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 4.10(q, *J* = 7.2 Hz, 2H), 3.11(d, *J* = 8.8 Hz, 1H), 2.99(d, *J* = 8.4 Hz, 1H), 2.52(d, *J* = 8.8 Hz, 1H), 2.23-2.19(m, 2H), 1.96-1.87(m, 4H), 1.78-1.74(m, 4H), 1.71(s, 1H), 1.66-1.62(m, 4H), 1.36-

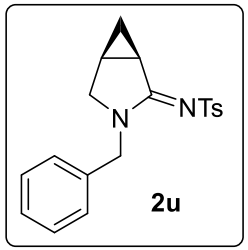
1.33(m, 3H), 1.25-1.20(m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 173.9, 67.9, 60.3, 51.4, 51.3, 37.9, 36.9, 31.3, 31.2, 31.1, 29.3, 27.6, 27.4, 16.7, 14.3; **HRMS(ESI):** m/z calcd for $C_{18}H_{28}NO_2[M+H]^+$: 290.2232, found: 290.2237.



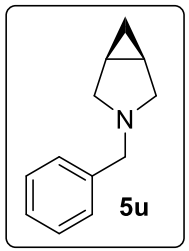
Preparation of *(1S,5S)-ethyl 3-phenethyl-3-azabicyclo[3.1.0]hexane-1-carboxylate* (5t): Following the general procedure, the reaction of cyclic amidine **2t** (602 mg, 1.41 mmol) with $NaBH_4$ (106 mg, 2.82 mmol) and iodine (178 mg, 0.7 mmol), was carried out and the resultant product **5t** (270 mg, 74%) was obtained as colourless oil (R_f = 0.3 in 10% EtOAc in hexane); **IR (neat):** 3058, 2994, 2926, 2792, 1714, 1608, 1454, 1373, 1278, 1231, 1169, 1030, 876, 758 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.32-7.27(m, 2H), 7.24-7.17(m, 3H), 4.18(q, *J* = 7.2 Hz, 2H), 4.13-4.10(m, 1H), 3.39-3.35(m, 1H), 3.24-3.15(m, 1H), 3.12-2.9(m, 5H), 2.37-2.31(m, 1H), 2.13-2.11(m, 1H), 1.43(t, *J* = 4.8 Hz, 1H), 1.24(t, *J* = 3.6 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 171.8, 138.3, 129.0, 128.8, 128.4, 126.7, 66.6, 63.3, 62.9, 61.6, 34.7, 33.0, 31.6, 31.4, 14.3; **HRMS(ESI):** m/z calcd for $C_{16}H_{22}NO_2$ $[M+H]^+$: 260.1586, found: 260.1591.

Synthesis of 3-azabicyclo[3.1.0]hexane 5u *via* chemoselective reduction of cyclic amidine



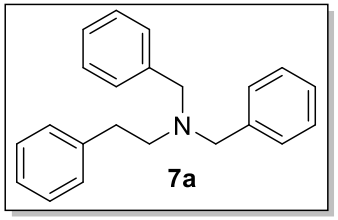


Preparation of *N*-((1R,5S,Z)-3-benzyl-3-azabicyclo [3.1.0]hexan-2-ylidene)-4-methylbenzenesulfonamide (2u): To a stirred solution of cyclic amidine **2d** (380 mg, 0.9 mmol) in DMSO (15 mL), distilled water (0.15 mL) and lithium chloride (101 mg, 2.3 mmol) were added. The resultant reaction mixture was allowed to stir at 160 ^{o}C for 18h. Then reaction mixture was diluted with water (45 mL) and extracted with diethyl ether (3 X 30 mL). The combined organic extracts were washed with brine solution, dried over anhy.Na_2SO_4, filtered and concentrated *in vacuo*. The resultant crude product was further purified over column chromatography to give the product **2u** (280 mg, 86%) as a pale yellow solid (R_f = 0.3 in 40% EtOAc in hexane); m.p 126-127 ^{o}C; **IR (neat):** 3028, 2939, 2871, 1677, 1569, 1485, 1300, 1229, 1152, 1086, 1020, 969, 878, 815 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.84(d, *J* = 8.0 Hz, 2H), 7.26-7.24(m, 5H), 7.09(brs, 2H), 4.53(d, *J* = 14.8 Hz, 1H), 4.38(d, *J* = 14.8 Hz, 1H), 3.49(dd, *J* = 11.2 Hz,6.0 Hz, 1H), 3.22(d, *J* = 11.6 Hz, 1H), 3.03(brs, 1H), 2.40(s, 3H), 1.91-1.87(m, 1H), 1.19-1.13(m, 1H), 0.33(d, *J* = 3.2 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 170.6, 142.0, 140.7, 135.3, 129.1, 128.7, 128.2, 127.9, 126.5, 51.0, 48.0, 21.5, 20.6, 14.1, 13.8; **HRMS(ESI):** m/z calcd for $C_{19}H_{21}N_2O_2S[M+H]^+$: 341.1263, found: 341.1254.

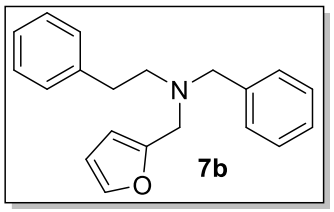


Preparation of *(1R,5S)-3-benzyl-3-azabicyclo[3.1.0]hexane* (5u): The chemoselective reduction of cyclic amidine **2u** (481 mg, 1.41 mmol) using $NaBH_4$ (106 mg, 2.82 mmol) and iodine (178 mg, 0.7 mmol), was carried out using general procedure and the resultant product **5u** (202 mg, 82%) was obtained as a colourless solid (R_f = 0.3 in 10% EtOAc in hexane); m.p 217-218 ^{o}C; **IR (neat):** 3055, 2928, 2856, 2685, 2306, 1428, 1265, 1154, 897, 727, 702 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.48-7.46(m, 2H), 7.37-7.35(m, 4H), 7.32-7.25(m, 1H), 4.02(s, 2H), 3.95(s, 1H), 3.41-3.36(m,

3H), 2.76(d, *J* = 13.2 Hz, 2H), 2.57(d, *J* = 10.8 Hz, 1H), 1.82(d, *J* = 2.8 Hz, 1H), 1.62(d, *J* = 3.6 Hz, 3H), 1.28-1.25(m, 0.6H), 1.16(q, *J* = 7.6 Hz, 1H), 1.07(q, *J* = 7.2 Hz, 0.45H), 0.73(q, *J* = 4 Hz, 1H), 0.19(q, *J* = 4.4 Hz, 0.39H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 132.9, 132.6, 132.5, 131.9, 128.9, 128.8, 128.3, 128.2, 65.1, 64.9, 63.7, 25.0, 24.6, 20.5, 19.2; **HRMS(ESI):** m/z calcd for $C_{12}H_{16}N[M+H]^+$: 174.1228, found: 174.1212.

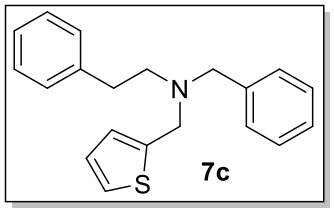


Preparation of *N,N-dibenzyl-2-phenylethanamine* (7a): Following the general procedure, the reaction of amidine **6a** (1.38 g, 2.95 mmol) with $NaBH_4$ (223 mg, 5.91 mmol) and iodine (372 mg, 1.47 mmol), was carried out and the resultant product **7a** (762 mg, 86%) was obtained as colourless oil (R_f = 0.35 in 10% EtOAc in hexane); **IR (neat):** 3056, 3031, 2934, 2801, 2715, 1602, 1545, 1493, 1449, 1369, 1264, 1252, 1122, 1075, 1025, 974, 914, 903, 754 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.35-7.25(m, 6H), 7.22-7.13(m, 7H), 7.06(d, *J* = 7.6 Hz, 2H), 3.63(s, 4H), 2.82-2.78(m, 2H), 2.71-2.68(m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 140.6, 139.8, 128.9, 128.8, 128.5, 128.4, 128.2, 127.2, 126.9, 125.9, 58.3, 55.2, 33.6; **HRMS(ESI):** m/z calcd for $C_{22}H_{24}N$ $[M+H]^+$: 302.1842, found: 302.1838.

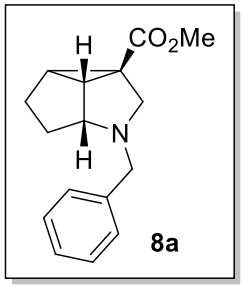


Preparation of *N-benzyl-N-(furan-2-ylmethyl)-2-phenylethanamine* (7b): Under the similar reaction conditions, the reaction of amidine **6b** (1.03 g, 2.24 mmol) with $NaBH_4$ (169 mg, 4.49 mmol) and iodine (284 mg, 1.12 mmol), was carried out and the resultant product **7b** (549 mg, 84%) was isolated as a colourless semisolid (R_f = 0.3 in 10% EtOAc in hexane); **IR (neat):** 3079, 3027, 2934, 2812, 1668, 1602, 1496, 1453, 1373, 1286, 1238, 1138, 1072, 1012, 919, 870, 808 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.38(s, 1H), 7.33-7.29(m,

4H), 7.27(s, 1H), 7.25-7.21(m, 2H), 7.18(d, *J* = 7.2 Hz, 1H), 7.14(d, *J* = 7.2 Hz, 2H), 6.32(t, *J* = 2.4 Hz, 1H), 6.17(d, *J* = 3.2 Hz, 1H), 3.71(s, 2H), 3.67(s, 2H), 2.84-2.79(m, 2H), 2.76-2.70(m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 152.7, 142.0, 140.6, 139.3, 129.0, 128.9, 128.3, 128.3, 127.0, 126.0, 110.1, 108.6, 58.1, 55.3, 49.6, 33.9; **HRMS(ESI):** m/z calcd for $C_{20}H_{22}NO$ $[M+H]^+$: 292.1696, found: 292.1691.

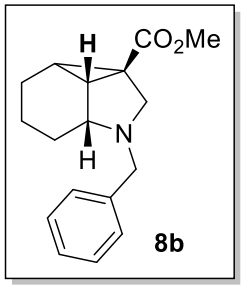


Preparation of *N-benzyl-2-phenyl-N-(thiophen-2-ylmethyl)ethanamine* (7c): The chemoselective reduction of amidine **6c** (1.01 g, 2.13 mmol) using $NaBH_4$ (161 mg, 4.26 mmol) and iodine (269 mg, 1.06 mmol), was carried out using general procedure and the resultant product **7c** (568 mg, 87%) was obtained as a colourless semisolid (R_f = 0.3 in 10% EtOAc in hexane); **IR (neat):** 3064, 3030, 2933, 2805, 1644, 1601, 1492, 1449, 1366, 1245, 1210, 1115, 1026, 974, 909, 816, 791 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.31-7.14(m, 9H), 7.09(d, *J* = 6.0 Hz, 2H), 6.90-6.86(m, 2H), 3.84(s, 2H), 3.65(s, 2H), 2.79-2.72(m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 143.1, 140.5, 139.4, 128.9, 128.7, 128.3, 128.3, 126.9, 126.4, 125.9, 125.5, 124.7, 57.9, 55.0, 52.5, 33.8; **HRMS(ESI):** m/z calcd for $C_{20}H_{22}NS$ $[M+H]^+$: 308.1467, found: 308.1465.

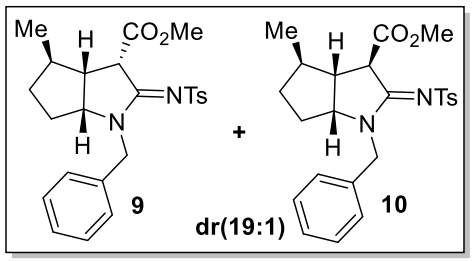


Preparation of *2-azabicyclo[3.3.0]octane* derivative (8a): Following the general procedure, the reaction of tricyclic amidine **4a** (800 mg, 1.88 mmol) with $NaBH_4$ (142 mg, 3.77 mmol) and iodine (238 mg, 0.94 mmol), was carried out and the resultant product **8a** (305 mg, 63%) was obtained as colourless oil (R_f = 0.4 in 10% EtOAc in hexane); **IR (neat):** 3058, 2961, 2935, 2865, 2310, 1736, 1564, 1485, 1427, 1269, 1154, 1088, 1030,

961, 891 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.51(d, *J* = 6.0 Hz, 2H), 7.36-7.35(brm, 3H), 4.12(d, *J* = 12.4 Hz, 1H), 3.99(d, *J* = 12.4 Hz, 1H), 3.93(d, *J* = 13.6 Hz, 1H), 3.71(brs, 1H), 3.69(s, 3H), 3.20(d, *J* = 13.6 Hz, 1H), 2.74-2.66(m, 2H), 2.49(t, *J* = 6.0 Hz, 1H), 2.20-2.13(m, 1H), 1.83-1.76(m, 1H), 1.73-1.62(m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 170.9, 132.9, 132.4, 129.1, 128.1, 74.1, 67.6, 58.9, 52.4, 43.4, 39.5, 38.3, 33.7, 24.1; **HRMS (ESI):** m/z calcd for $C_{16}H_{20}NO_2$ $[M+H]^+$: 258.1426, found: 258.1424.

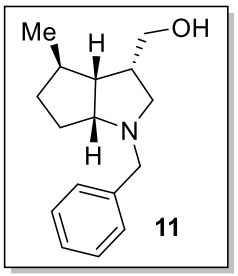


Preparation of octahydroindole derivative (8b): Under the similar reaction conditions, the reaction of tricyclic amidine **4b** (500 mg, 1.14 mmol) with $NaBH_4$ (86 mg, 2.28 mmol) and iodine (144 mg, 0.57 mmol), was carried out and the resultant product **8b** (179 mg, 58%) was isolated as colourless oil (R_f = 0.4 in 10% EtOAc in hexane); **IR (neat):** 3056, 2958, 2934, 2864, 2306, 1738, 1577, 1447, 1337, 1268, 1158, 1091, 1021, 962, 889, 823 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.30-7.23(brm, 5H), 3.78(d, *J* = 13.2 Hz, 1H), 3.64(d, *J* = 7.6 Hz, 1H), 3.62(s, 3H), 3.42-3.36(m, 2H), 2.99(d, *J* = 10.4 Hz, 1H), 2.35(t, *J* = 6.8 Hz, 1H), 1.94-1.90(m, 2H), 1.72-1.66(m, 2H), 1.50-1.47(m, 1H). 1.33-1.26(m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 174.4, 139.9, 128.5, 128.3, 126.9, 56.7, 56.2, 52.6, 51.9, 35.2, 32.6, 27.1, 24.8, 17.9, 17.4; **HRMS (ESI):** m/z calcd for $C_{17}H_{22}NO_2$ $[M+H]^+$: 272.1584, found: 272.1580.



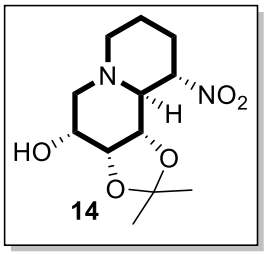
Preparation of *(3S,3aR,4R,6aR)-methyl 1-benzyl-4-methyl-2-(tosylimino)octahydrocyclopenta[b]pyrrole-3-carboxylate* (9) and *(3R,3aR,4R,6aR)-methyl 1-benzyl-4-methyl-2-(tosylimino)octahydrocyclopenta[b]pyrrole-3-carboxylate* (10): To a stirred solution of MeMgBr (1 mL, 3 mmol) and CuCN (140 mg, 1.56 mmol) in dry THF (10 mL) at 0

^{o}C for about 30 minutes under N_2 atmosphere was added tricyclic amidine **4a** (604 mg, 1.42 mmol) in dry THF (3 mL). The reaction mixture was stirred at room temperature until the completion of reaction as indicated by TLC. Then reaction mixture was cooled to 0 ^{o}C, diluted with saturated Na_2SO_4 (20 mL) and extracted with EtOAc (2 X 30 mL). The combined EtOAc solvent was washed with brine solution (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude product using column chromatography yielded the product **9** and **10** (525 mg, 84%) as a colorless oil, as an inseparable (19:1) mixture of diastereomers (R_f = 0.3 in 50% EtOAc in hexane); **IR (neat):** 3055, 2983, 2933, 2862, 2300, 1739, 1643, 1576, 1428, 1266, 1153, 1092, 1025, 895, 744 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.75(d, *J* = 8.4 Hz, 2H), 7.28-7.21(m, 7H), 5.31(d, *J* = 14.8 Hz, 1H), 4.29(s, 1H), 4.03-3.98(m, 1H), 3.96(s, 1H), 3.67(s, 3H), 2.38(s, 3H), 2.15(t, *J* = 8.4 Hz, 1H), 1.96-1.87(m, 1H), 1.86-1.80(m, 1H), 1.79-1.60(m, 2H), 1.25-1.20(m, 1H), 1.09(d, *J* = 6.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 170.4, 163.8, 142.1, 140.4, 134.5, 129.1, 128.8, 128.2, 127.9, 126.4, 63.8, 53.5, 52.6, 51.3, 46.7, 40.9, 33.5, 29.7, 21.5, 18.1; **HRMS(ESI):** m/z calcd for $C_{24}H_{29}N_2O_4S$ $[M+H]^+$: 441.1779, found: 441.1778.



Preparation of *((3S,3aR,4R,6aR)-1-benzyl-4-methyloctahydrocyclopenta[b]pyrrol-3-yl)methanol* (11): A round bottomed flask charged with dry THF (10 mL) and lithium aluminium hydride (332 mg, 8.74 mmol) was allowed to reflux for 15 minutes. To this reaction mixture, cyclic amidines **9** and **10** (481 mg, 1.09 mmol) in dry THF (3 mL) was added over five minutes and the reaction mixture was stirred at reflux until the completion of reaction as indicated by TLC. The reaction mixture was quenched by the addition of moist Na_2SO_4 and extracted with EtOAc (2 X 30 mL). The combined EtOAc solvent was washed with brine solution (30 mL), dried over anhydrous Na_2SO_4, filtered and concentrated under

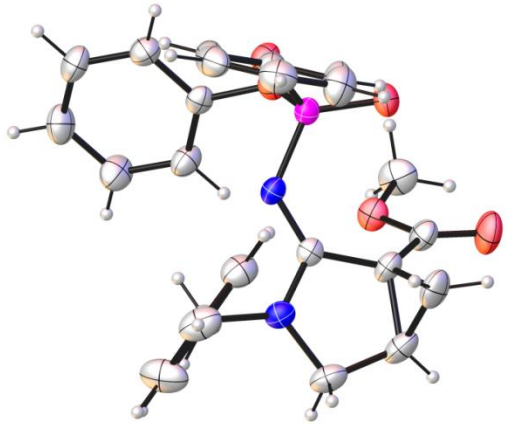
reduced pressure. Purification of the crude product using column chromatography yielded the product **11** (219 mg, 82%) as colorless oil (R_f = 0.3 in 50% EtOAc in hexane); **IR (neat):** 3426, 3081, 3033, 2954, 2918, 2884, 2781, 1656, 1501, 1454, 1362, 1290, 1252, 1161,1031, 1024, 791 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 7.31-7.23(m, 5H), 3.75-3.68(m, 2H), 3.54(dd, *J* = 10.0 Hz, 5.2 Hz, 1H), 3.45(d, *J* = 12.8 Hz, 1H), 3.30(q, *J* = 6.8 Hz, 1H), 2.92(dd, *J* = 9.2 Hz, 6.0 Hz, 1H), 2.69(s, 1H), 2.35(dd, *J* = 9.2 Hz, 5.6 Hz, 1H), 1.92(q, *J* = 4.8 Hz, 1H), 1.88-1.81(m, 2H), 1.76-1.63(m, 1H), 1.62-1.48(m, 2H), 1.19-1.10(m, 1H), 0.97(d, *J* = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 139.1, 128.9, 128.3, 127.0, 68.3, 67.4, 56.9, 56.7, 54.5, 46.1, 41.4, 34.4, 28.0, 19.6; **HRMS(ESI):** m/z calcd for $C_{16}H_{24}NO$ $[M+H]^+$: 246.1863, found: 246.1860.



Preparation of *(3aR,4R,10S,10aS,10bS)-2,2-dimethyl-10-nitrooctahydro-3aH-[1,3]dioxolo[4,5-a]quinolizin-4-ol* (14): The chemoselective reduction of cyclic amidine **13**[11] (421 mg, 0.95 mmol) using $NaBH_4$ (72 mg, 1.91 mmol) and iodine (121 mg, 0.47 mmol), was carried out using general procedure and the resultant product **14** (166 mg, 64%) was obtained as orange-brown semisolid (R_f = 0.3 in 70% EtOAc in hexane); **$[\alpha]^{30}_D$** +8.21 (c 1.0, $CHCl_3$); **IR (neat):** 3570, 3056, 2942, 1709, 1656, 1555, 1455, 1377, 1280, 1227, 1155, 1092, 1041, 861, 785 cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$): δ** ppm 4.35-4.32(m, 1H), 4.30-4.27(m, 1H), 4.06(dd, *J* = 7.6 Hz, 5.2 Hz, 1H), 3.98-3.94(m, 1H), 2.85-2.77(m, 2H), 2.45(t, *J* = 8.4 Hz, 1H), 2.34(t, *J* = 11.2 Hz, 1H), 2.24-2.19(m, 2H), 2.01-1.91(m, 1H), 1.77(d, *J* = 14.0 Hz, 1H), 1.59-1.50(m, 1H), 1.44(s, 3H), 1.31(s, 3H), 1.12(s, 1H); **^{13}C NMR (100 MHz, $CDCl_3$): δ** ppm 110.5, 88.1, 77.9, 75.0, 65.3, 64.9, 56.7, 54.4, 30.0, 27.5, 26.5, 22.5; **HRMS(ESI):** m/z calcd for $C_{12}H_{20}N_2O_5Na$ $[M+Na]^+$: 295.1264, found: 295.1265.

4. Crystal data and structure refinement for compound 2c, 2k, 2u, 4a and 4b

Single crystal X-ray analysis of methyl (1*S*,5*S*,*E*)-3-benzyl-2-((diphenoxyphosphoryl)imino)-3-azabicyclo[3.1.0]hexane-1-carboxylate 2c



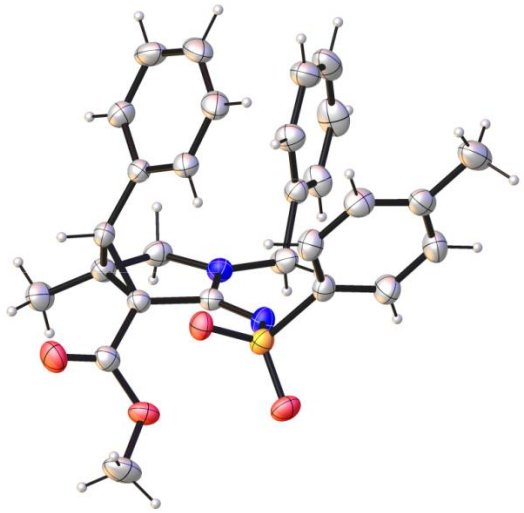
X-ray structure of cyclic amidine 2c

Table S6. Crystal data and structure refinement for compound 2c

CCDC	1911213
Empirical formula	$C_{26}H_{25}N_2O_5P$
Formula weight	476.45 g/mol
Temperature	296 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/n

Unit cell dimensions	a = 14.0275(5) Å alpha = 90 deg.
	b = 9.3309(3) Å beta = 101.9190(14) deg.
	c = 18.6042(7) Å gamma = 90 deg.
Volume	2382.59(15) Å^3
Z, Calculated density	4, 1.328 g/cm^3
Absorption coefficient	0.9760 mm^-1
F(000)	1000
Crystal size	0.160 x 0.220 x 0.250 mm^3
Theta range for data collection	4.832 to 53.03 deg.
Reflections collected / unique	17571 / 4194 [R(int) = 2.06%]
Completeness to theta =25.00	100.0 %
Absorption correction	Multi scans
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4194 / 0 / 308
Goodness-of-fit on F^2	1.048
R indices (all data)	R1 = 3.65%, wR2 = 10.29%
Absolute structure parameter	0.04
Extinction coefficient	n/a
Largest diff. peak and hole	0.242 and -0.345 eÅ^-3

Single crystal X-ray analysis of methyl (6*S*,*Z*)-3-benzyl-5-methyl-6-phenyl-2-(tosylimino)-3-azabicyclo[3.1.0]hexane-1-carboxylate 2k



X-ray structure of cyclic amidine 2k

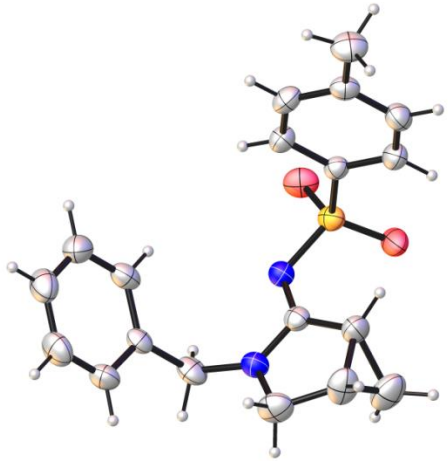
Table S7. Crystal data and structure refinement for compound 2k

CCDC	1976700
Empirical formula	$C_{28}H_{28}N_2O_4S$
Formula weight	488.58 g/mol
Temperature	296 K

Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 10.9256(6) Å alpha = 90 deg.
	b = 19.2120(12) Å beta = 108.176(4) deg.
	c = 12.4670(8) Å gamma = 90 deg.
Volume	2486.3(3) Å^3
Z, Calculated density	4, 1.305 g/cm^3
Absorption coefficient	0.9830 mm^-1
F(000)	1032
Crystal size	0.100 x 0.120 x 0.180 mm^3
Theta range for data collection	4.827 to 40.57 deg.
Reflections collected / unique	27394 / 3861[R(int) = 5.81%]
Completeness to theta =25.00	98.9 %
Absorption correction	Multi-scan method (SADABS)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3861 / 0 / 320
Goodness-of-fit on F^2	1.026
R indices (all data)	R1 = 4.39%, wR2 = 11.58%
Absolute structure parameter	0.04
Extinction coefficient	n/a

Largest diff. peak and hole	0.174 and-0.282 eÅ^-3

Single crystal X-ray analysis of *N*-((1R,5S,Z)-3-benzyl-3-azabicyclo[3.1.0]hexan-2-ylidene)-4-methylbenzenesulfonamide 2u



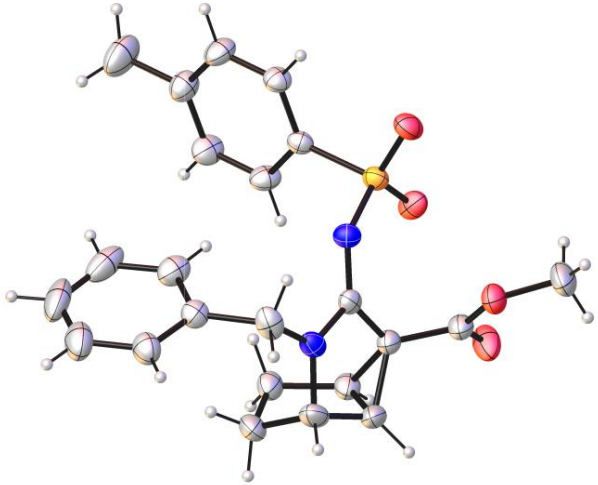
X-ray structure of cyclic amidine 2u

Table S8. Crystal data and structure refinement for compound 2u

CCDC	1982272
Empirical formula	$C_{19}H_{20}N_2O_2S$
Formula weight	340.43 g/mol
Temperature	296 K
Wavelength	0.71073 Å

Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 10.5135(9) Å alpha = 90 deg.
	b = 19.3340(17) Å beta = 114.646(3) deg.
	c = 9.3500(8) Å gamma = 90 deg.
Volume	1727.4(3) Å^3
Z, Calculated density	4, 1.309 g/cm^3
Absorption coefficient	0.9520 mm^-1
F(000)	720
Crystal size	0.100 x 0.220 x 0.250 mm^3
Theta range for data collection	4.755 to 41.18 deg.
Reflections collected / unique	8924 / 2798 [R(int) = 3.58%]
Completeness to theta =25.00	97.6 %
Absorption correction	Multi-scan method (SADABS)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2798 / 0 / 218
Goodness-of-fit on F^2	0.981
R indices (all data)	R1 = 4.85%, wR2 = 11.31%
Absolute structure parameter	0.05
Extinction coefficient	n/a
Largest diff. peak and hole	0.312 and -0.252 eÅ^-3

Single crystal X-ray analysis of (Z)-N-(1-benzyl-2a-((methylperoxy)-l2-methyl)hexahydro-1-azacyclopropa[cd]pentalen-2(1H)-ylidene)-4-methylbenzenesulfonamide 4a



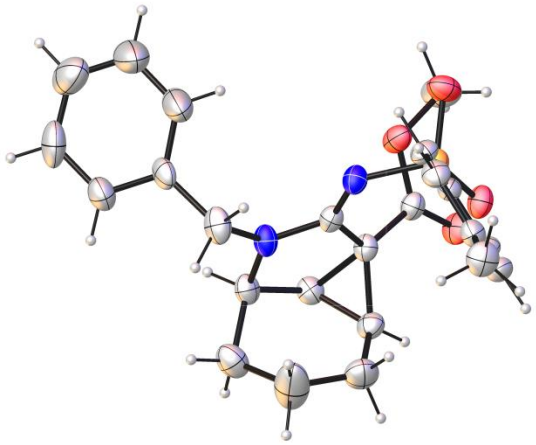
X-ray structure of cyclic amidine 4a

Table S9. Crystal data and structure refinement for compound 4a

CCDC	1983751
Empirical formula	$C_{23}H_{24}N_2O_4S$
Formula weight	424.50 g/mol
Temperature	296 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/n

Unit cell dimensions	a = 10.7975(4) Å alpha = 90 deg.
	b = 15.5298(5) Å beta = 111.2414(13) deg.
	c = 13.5300(5) Å gamma = 90 deg.
Volume	2114.62(13) Å^3
Z, Calculated density	4, 1.333 g/cm^3
Absorption coefficient	0.946 mm^-1
F(000)	896
Crystal size	0.100 x 0.220 x 0.250 mm^3
Theta range for data collection	4.823 to 53.79 deg.
Reflections collected / unique	16761 / 3725 [R(int) = 2.30%]
Completeness to theta =25.00	100.0 %
Absorption correction	Multi-scan method (SADABS)
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3725 / 0 / 274
Goodness-of-fit on F^2	1.020
R indices (all data)	R1 = 3.73%, wR2 = 10.31%
Absolute structure parameter	0.04
Extinction coefficient	n/a
Largest diff. peak and hole	0.188 and -0.300 eÅ^-3

Single crystal X-ray analysis of *N*-((2aS,2a^{1}S,2b*R*,*Z*)-1-benzyl-2a-((ethylperoxy)-λ^2-methyl)octahydro-2*H*-cyclopropa[*cd*]indol-2-ylidene)-4-methylbenzenesulfonamide 4b



X-ray structure of tricyclic amidine 4b

Table S10. Crystal data and structure refinement for compound 4b

CCDC	1911212
Empirical formula	$C_{24}H_{26}N_2O_4S$
Formula weight	438.53 g/mol
Temperature	296 K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P 21/n
Unit cell dimensions	a = 20.7942(7) Å alpha = 90 deg.

	b = 11.5133(3) Å beta = 117.4001(11) deg.
	c = 21.0097(7) Å gamma = 90 deg.
Volume	4465.6(2) Å^3
Z, Calculated density	4, 1.305 g/cm^3
Absorption coefficient	0.9790 mm^-1
F(000)	1856 e^-
Crystal size	0.120 x 0.220 x 0.250 mm^3
Theta range for data collection	4.412 to 42.90 deg.
Reflections collected / unique	24678 / 7862[R(int) = 3.86%]
Completeness to theta =25.00	100.0 %
Absorption correction	Multi-scan method (SADABS)
Refinement method	Full-matrix least-squares on F^2
Data	7862
Goodness-of-fit on F^2	1.038
R indices (all data)	R1 = 5.82%, wR2 = 16.77%
Extinction coefficient	n/a
Largest diff. peak and hole	0.388 and -0.321 eÅ^-3

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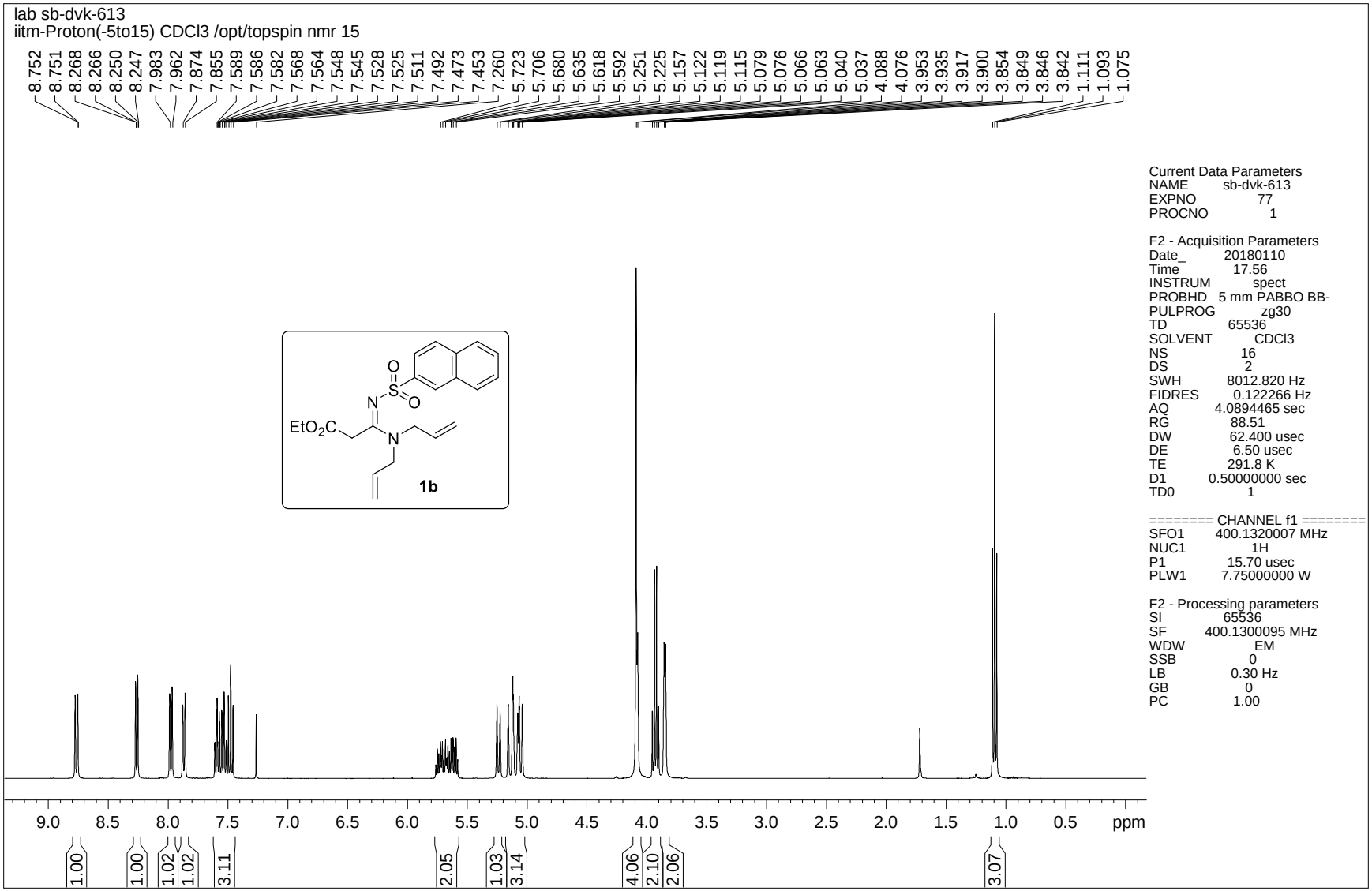
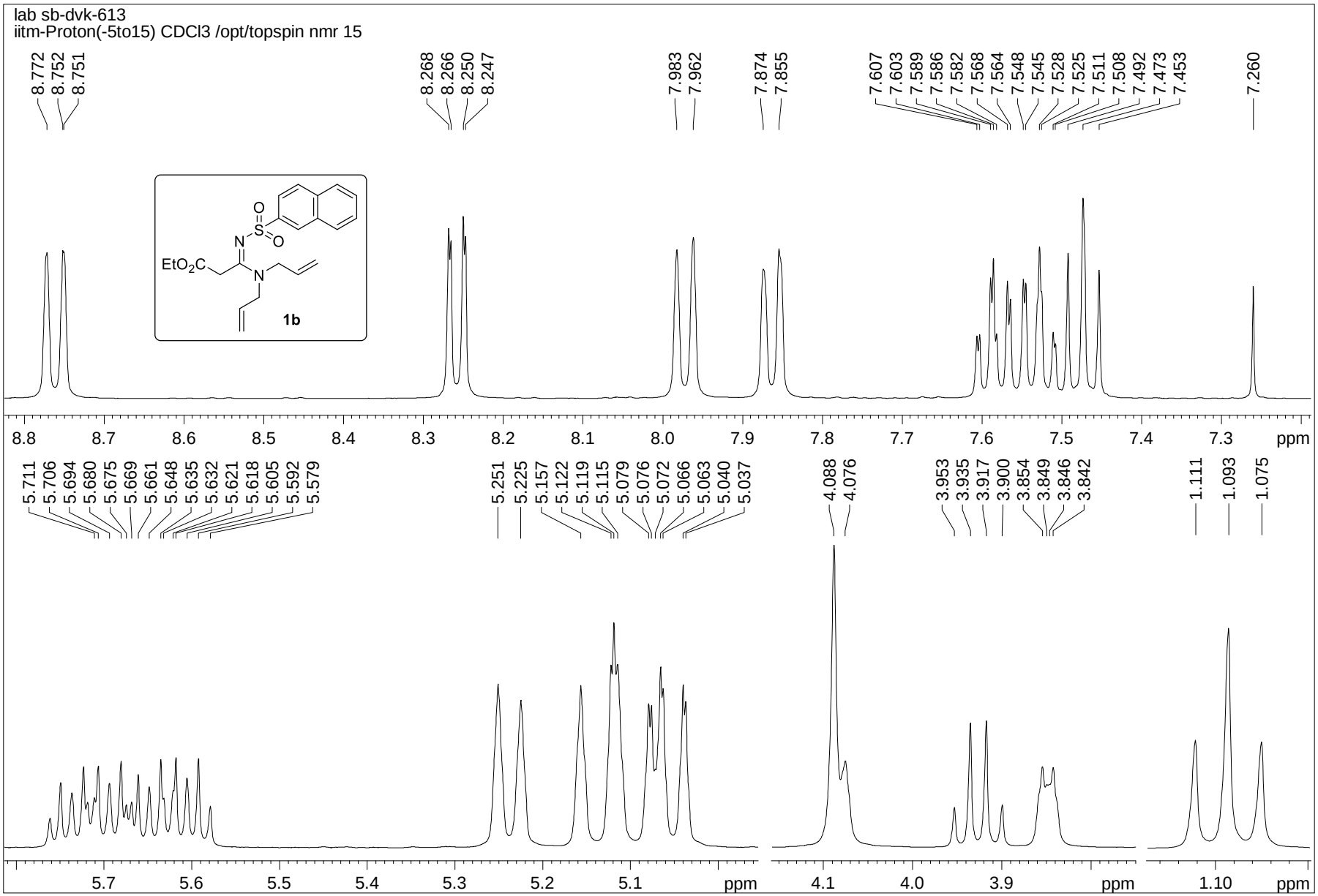
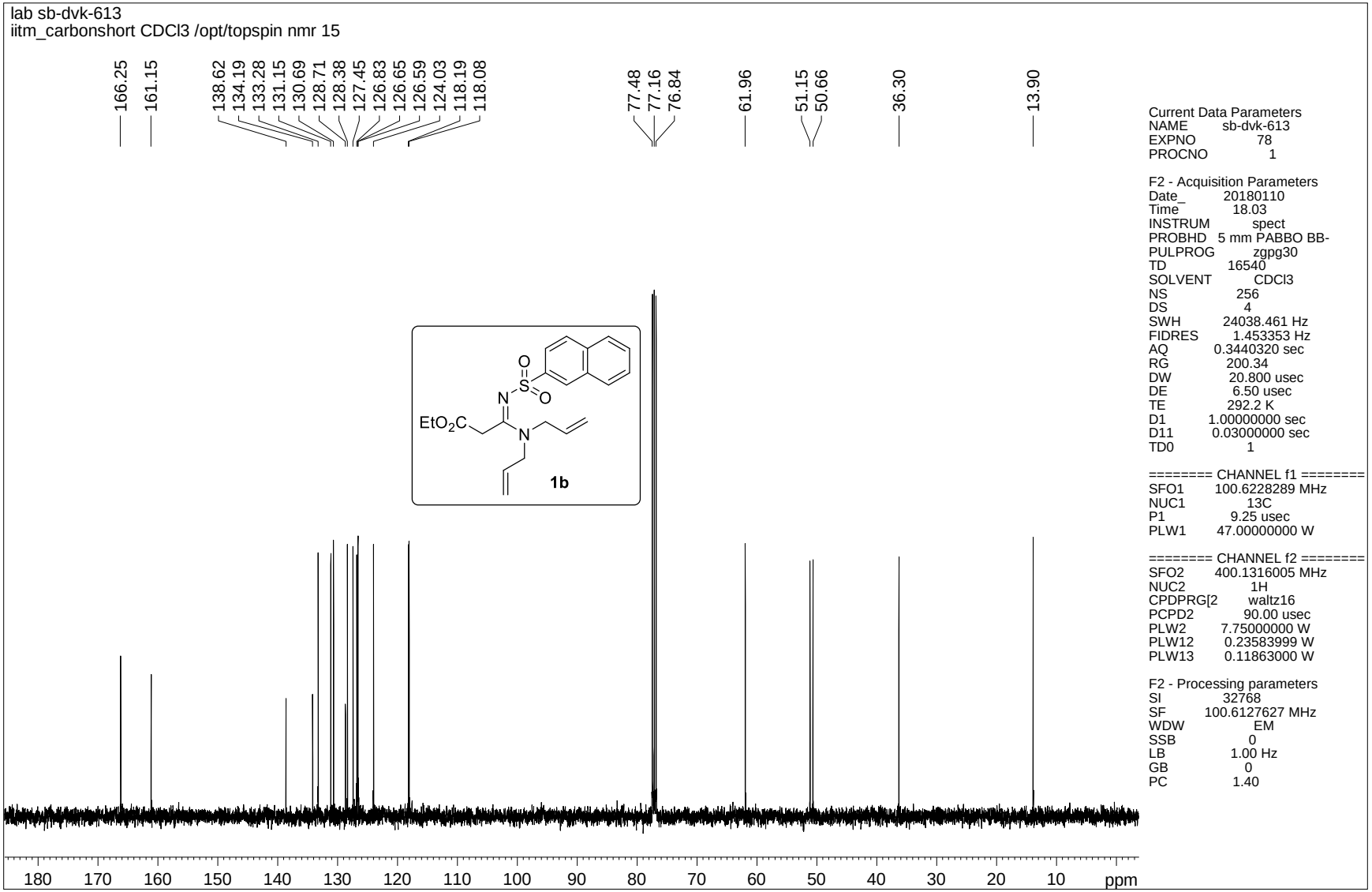


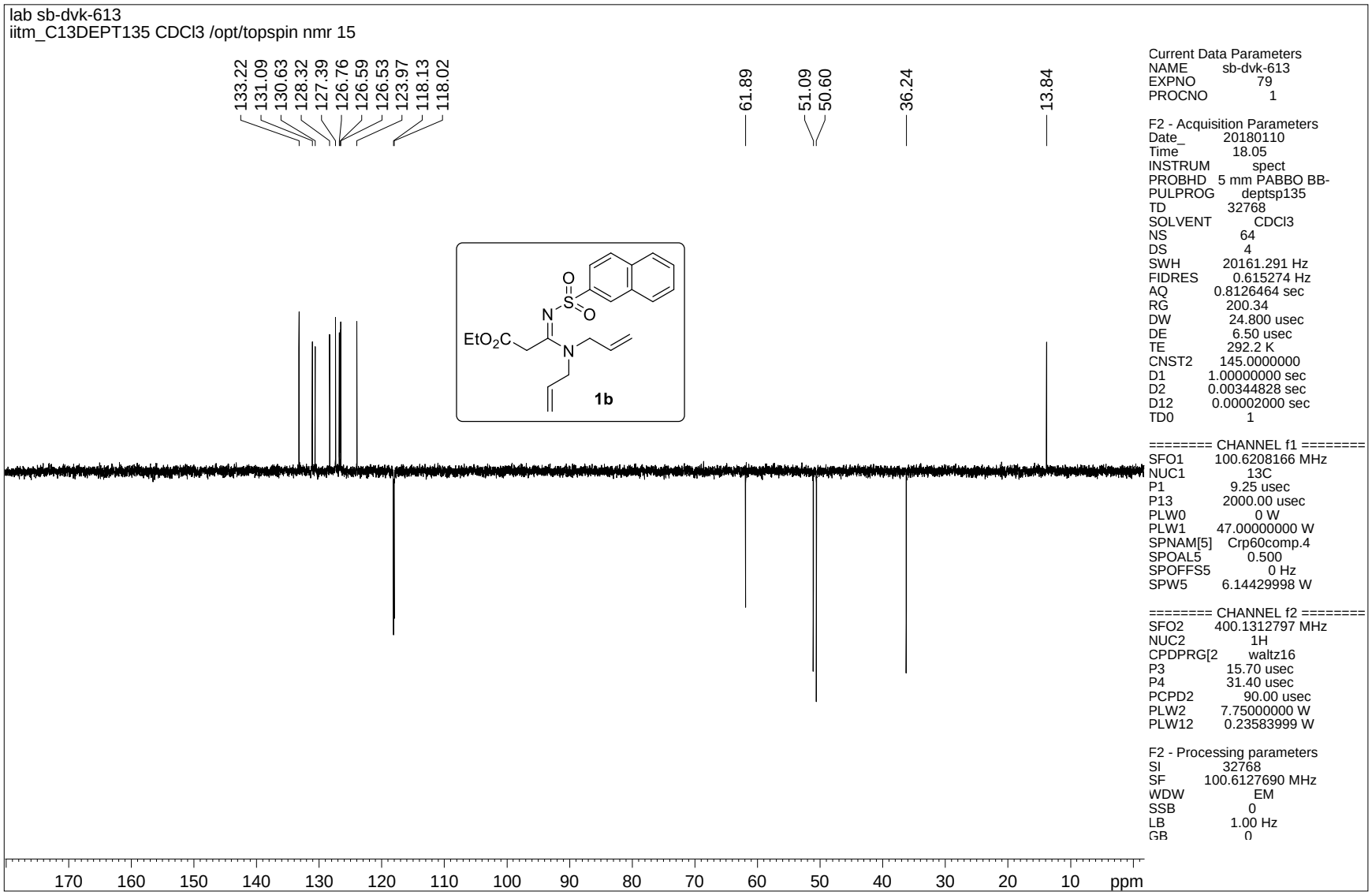
^{1}H NMR spectrum of compound 1b



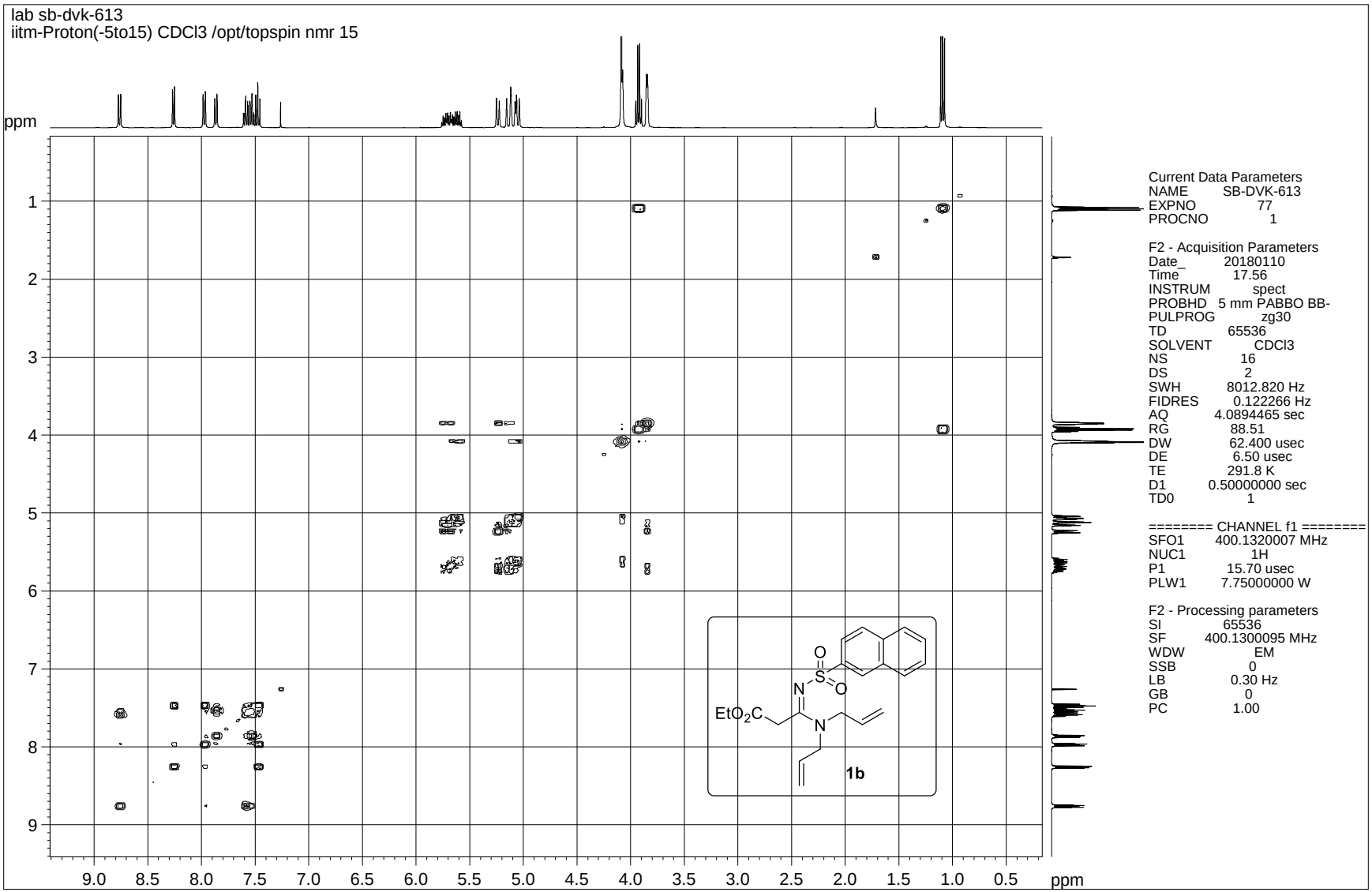
^{1}H NMR spectrum of compound 1b



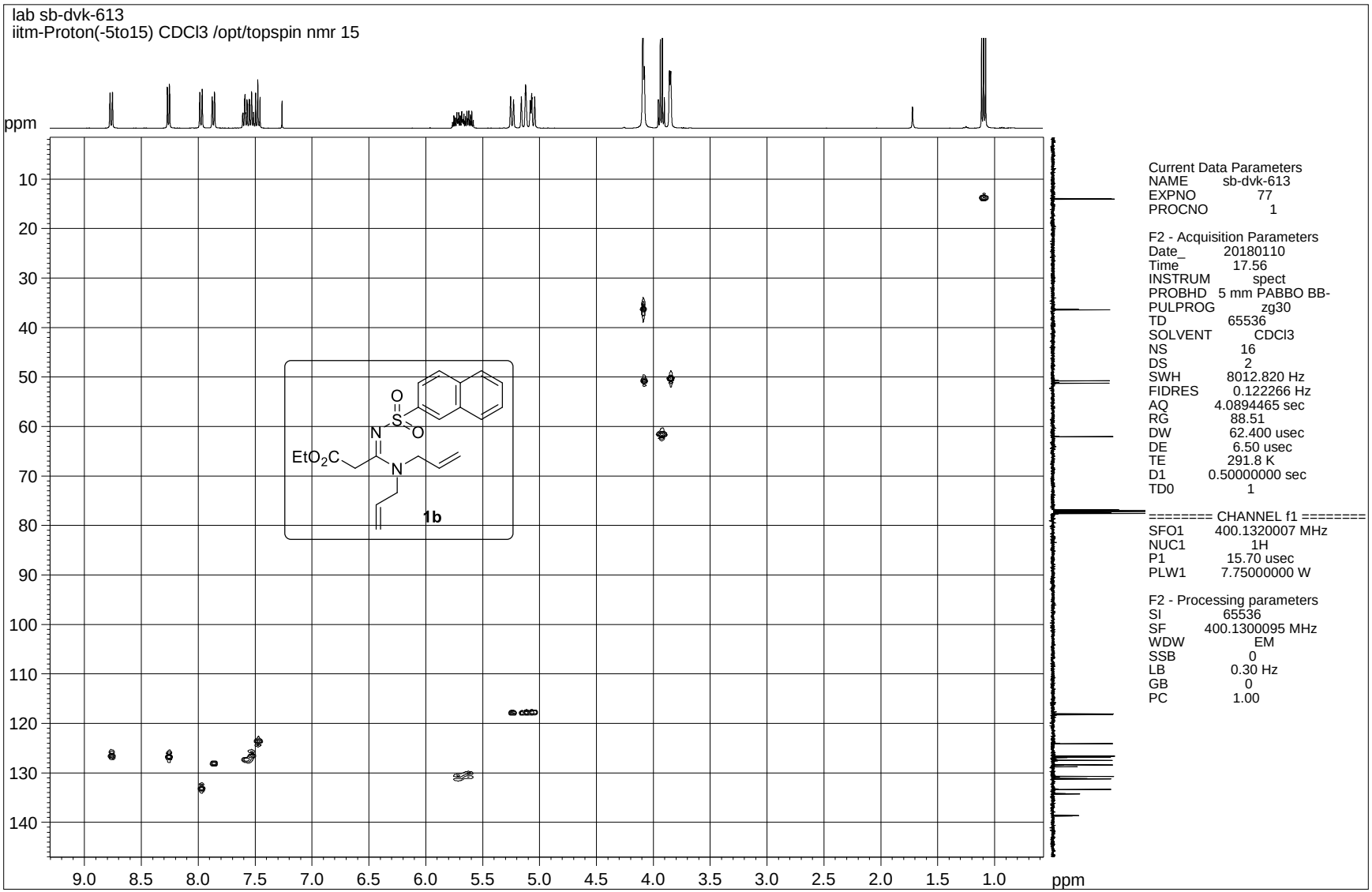
^{13}C NMR spectrum of compound 1b



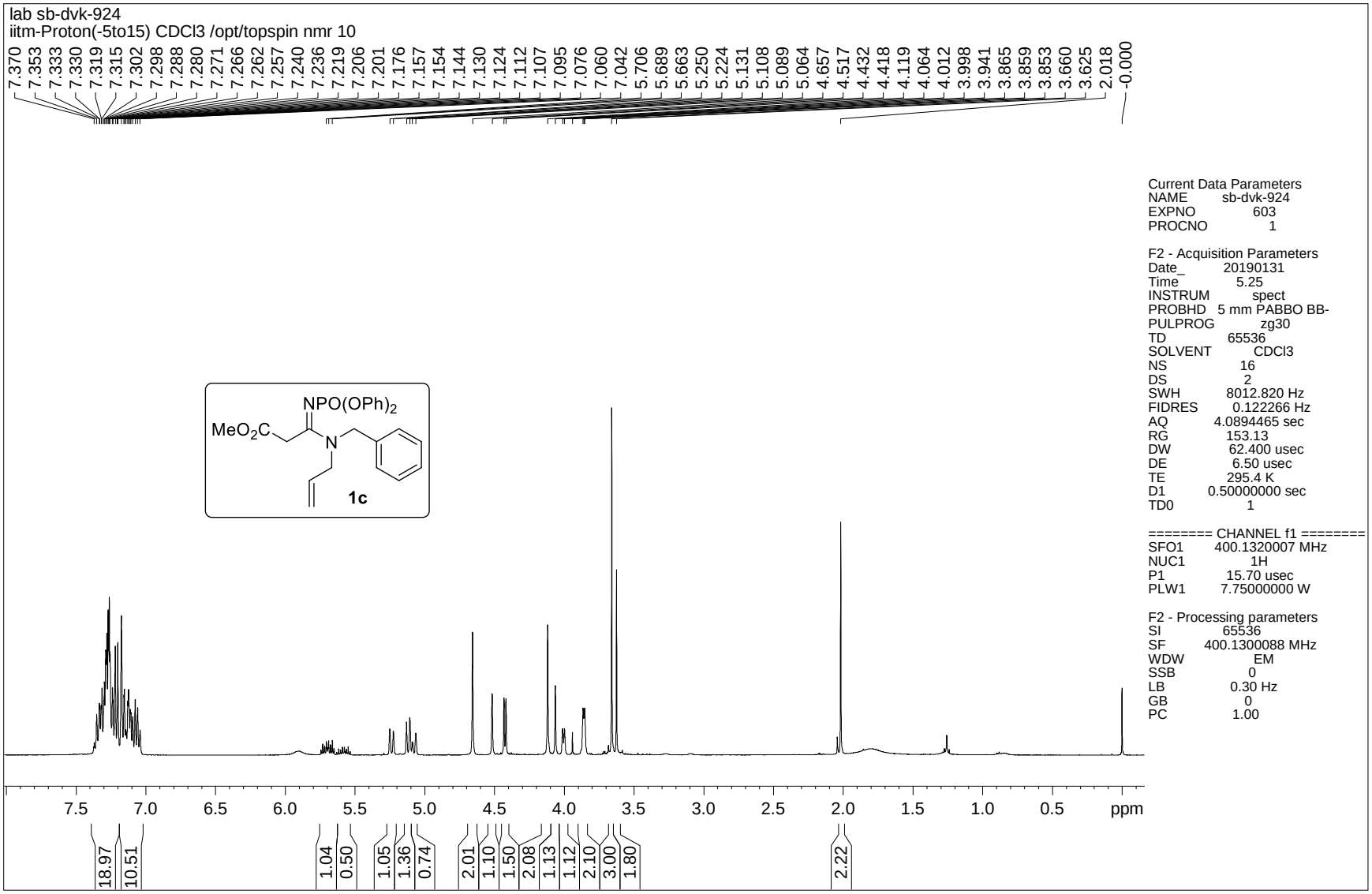
DEPT-135 NMR spectrum of compound 1b



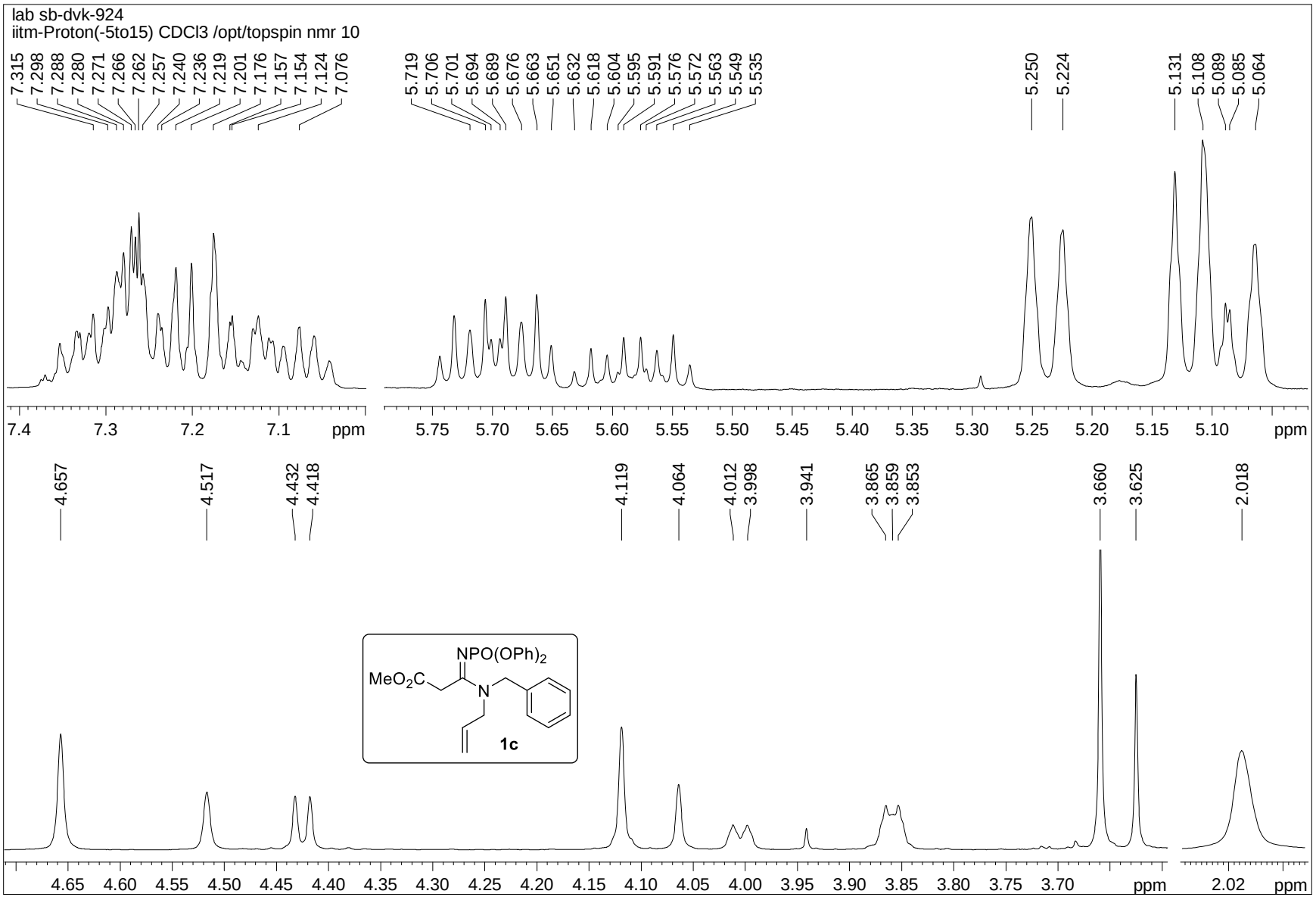
^{1}H-^{1}H COSY NMR spectrum of compound 1b



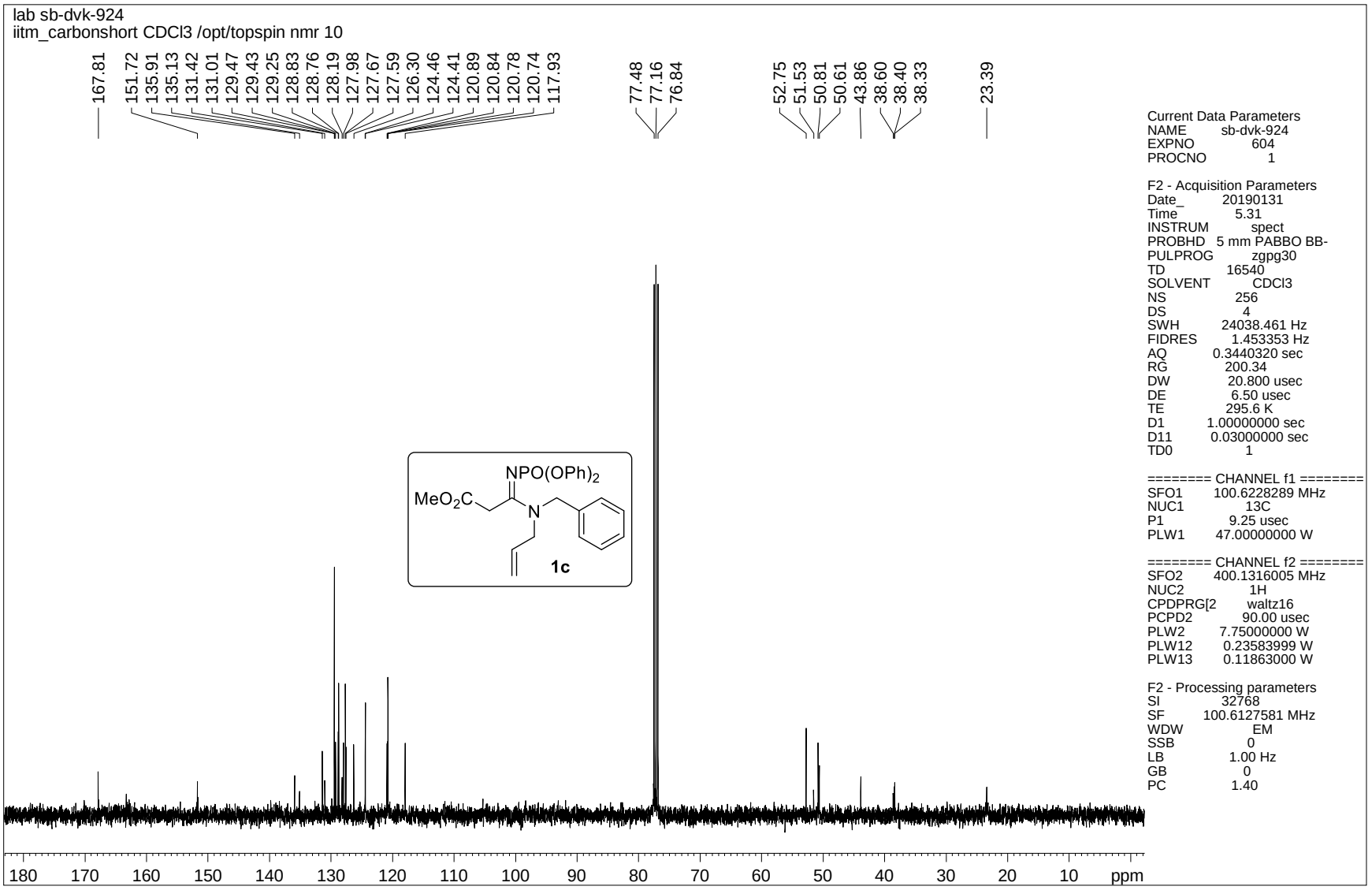
^{1}H-^{13}C HSQC NMR spectrum of compound 1b



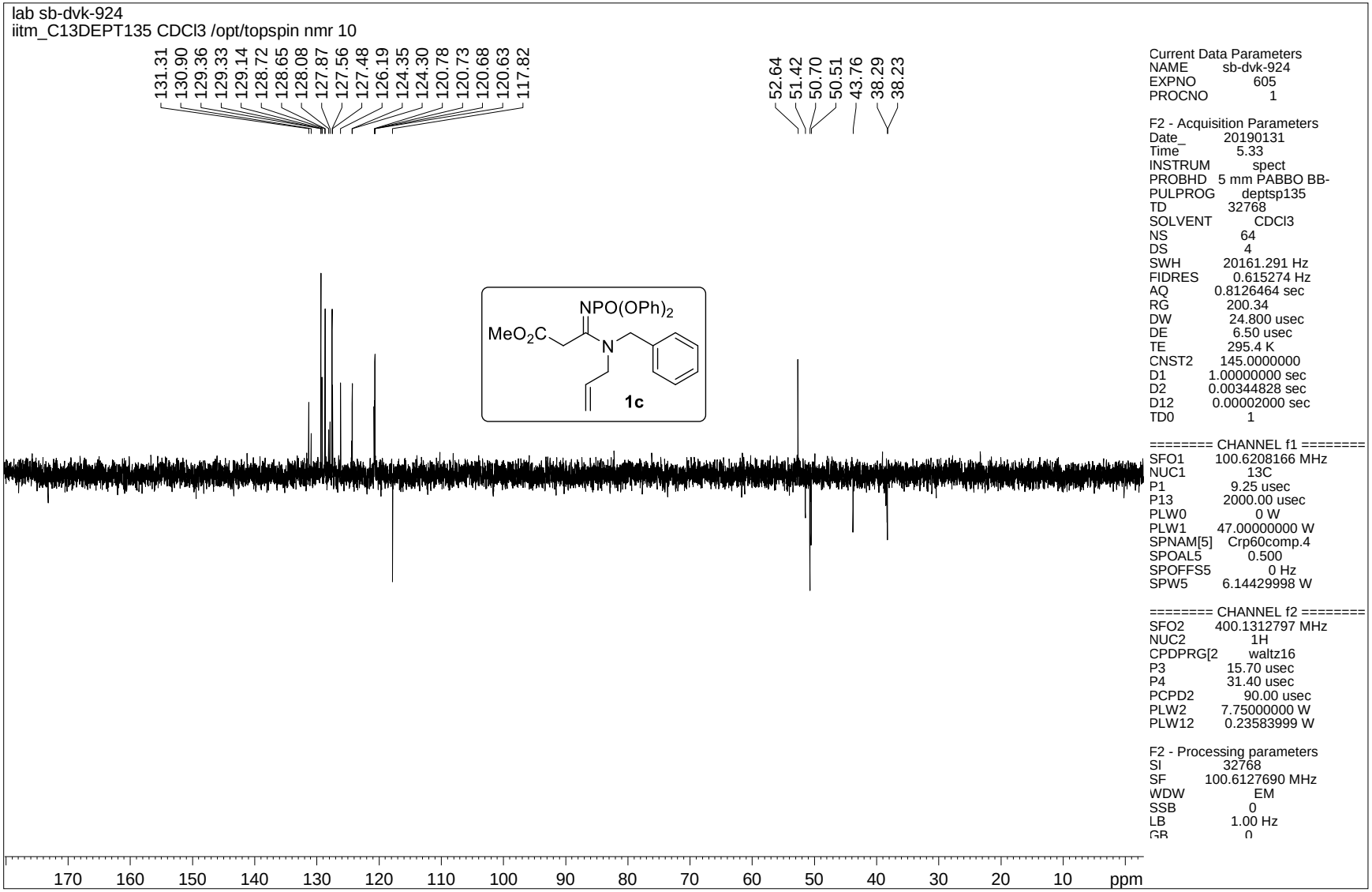
^{1}H NMR spectrum of compound 1c



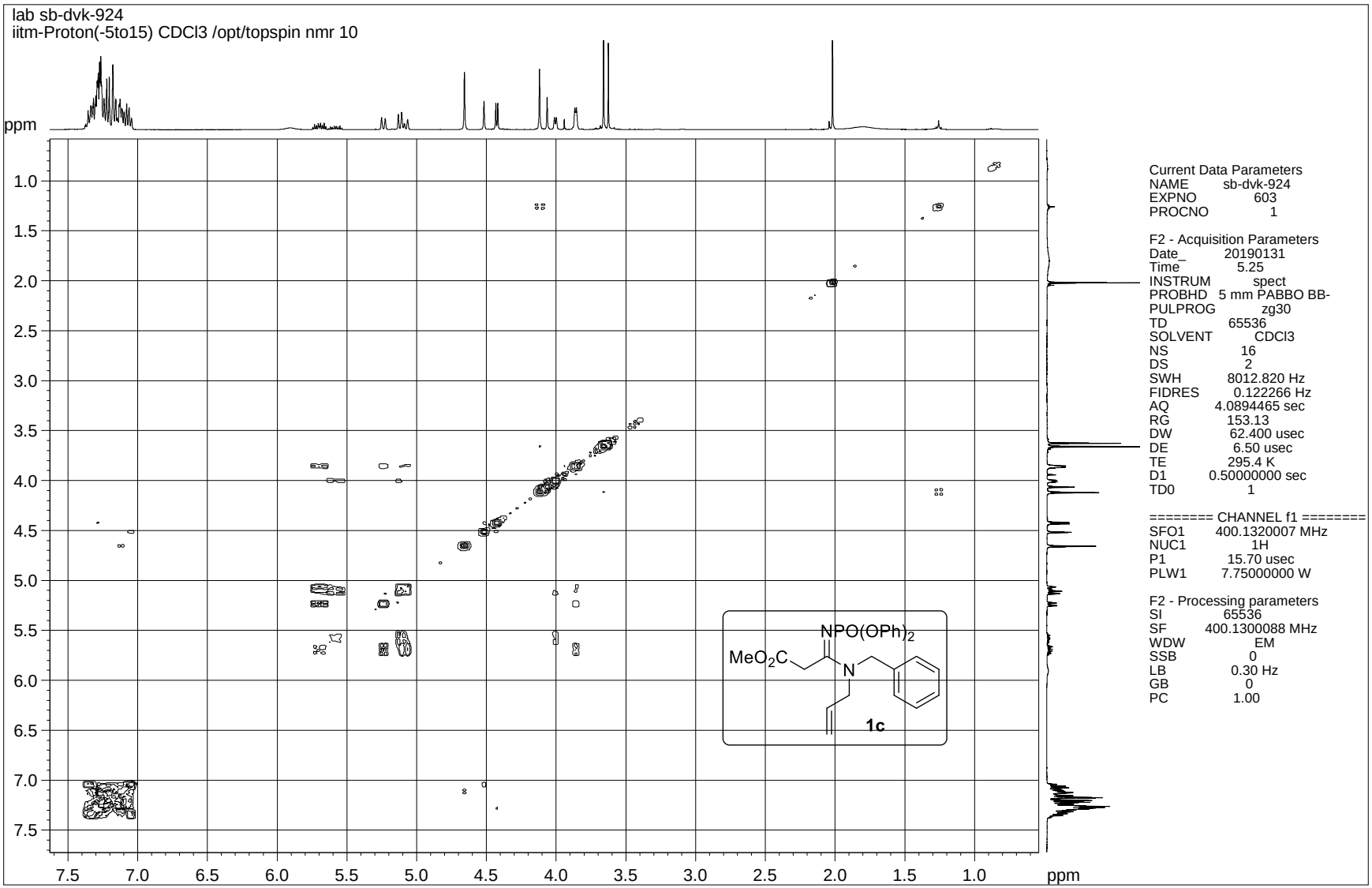
^{1}H NMR spectrum of compound 1c



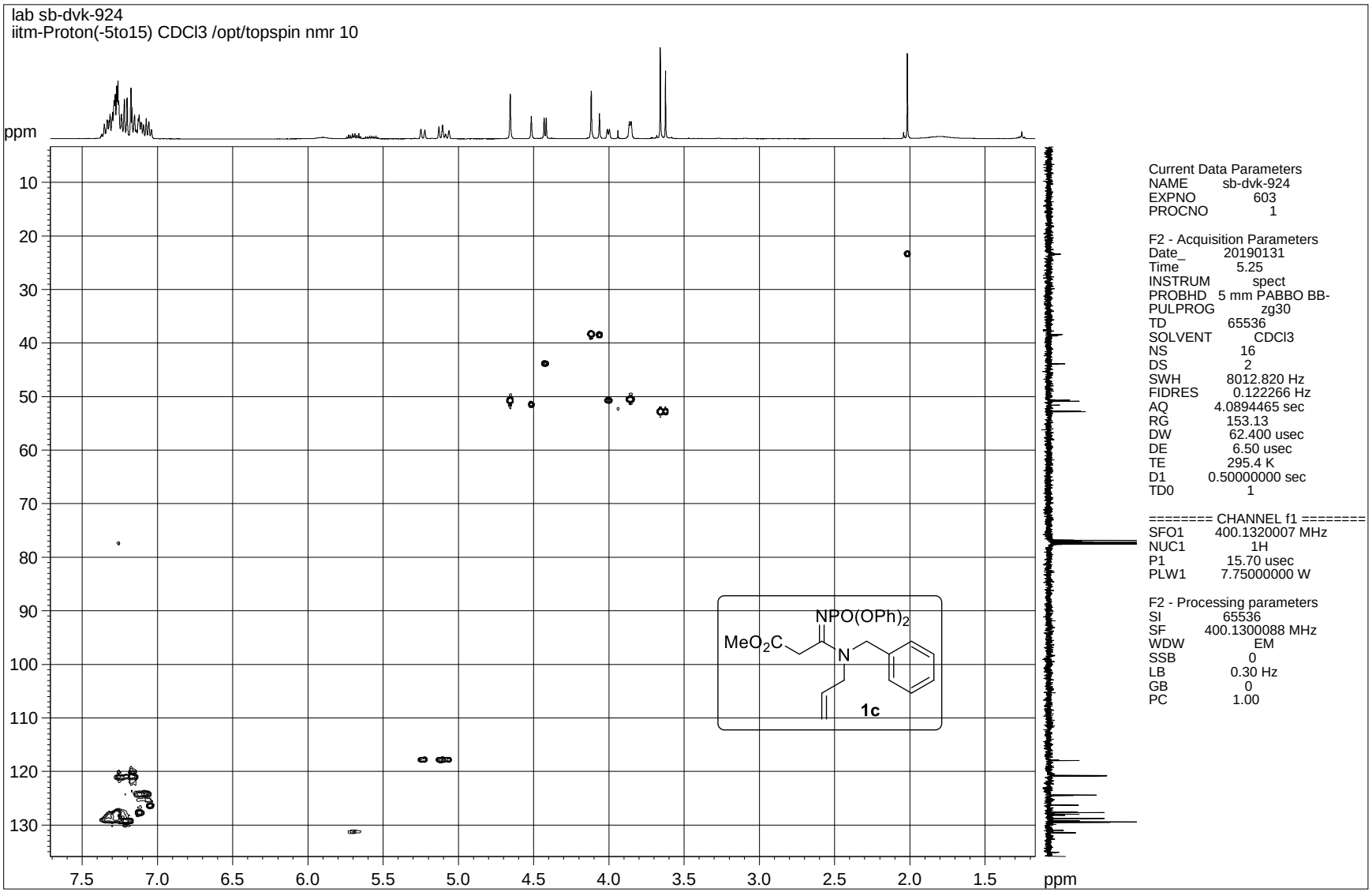
^{13}C NMR spectrum of compound 1c



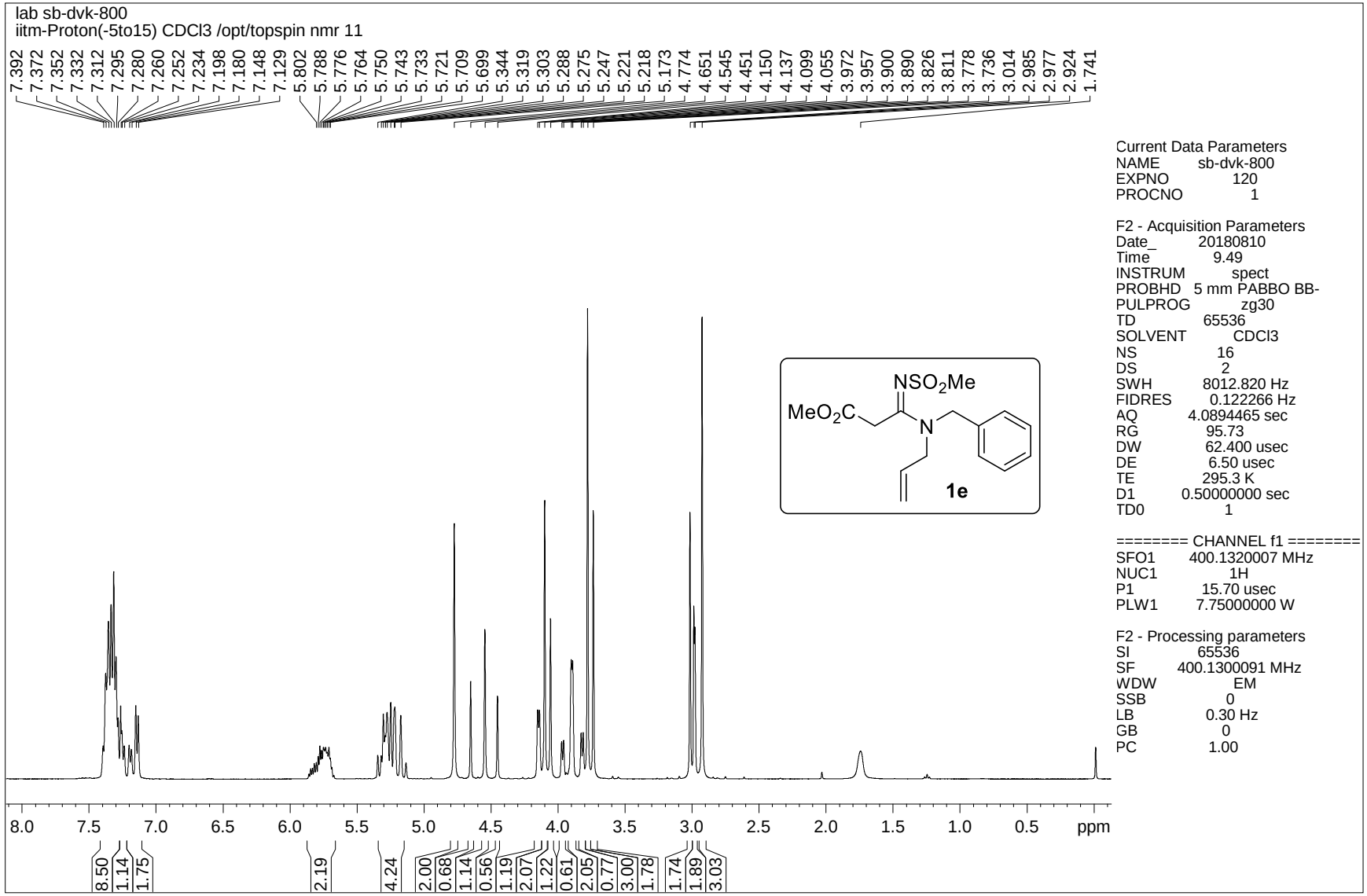
DEPT-135 NMR spectrum of compound 1c



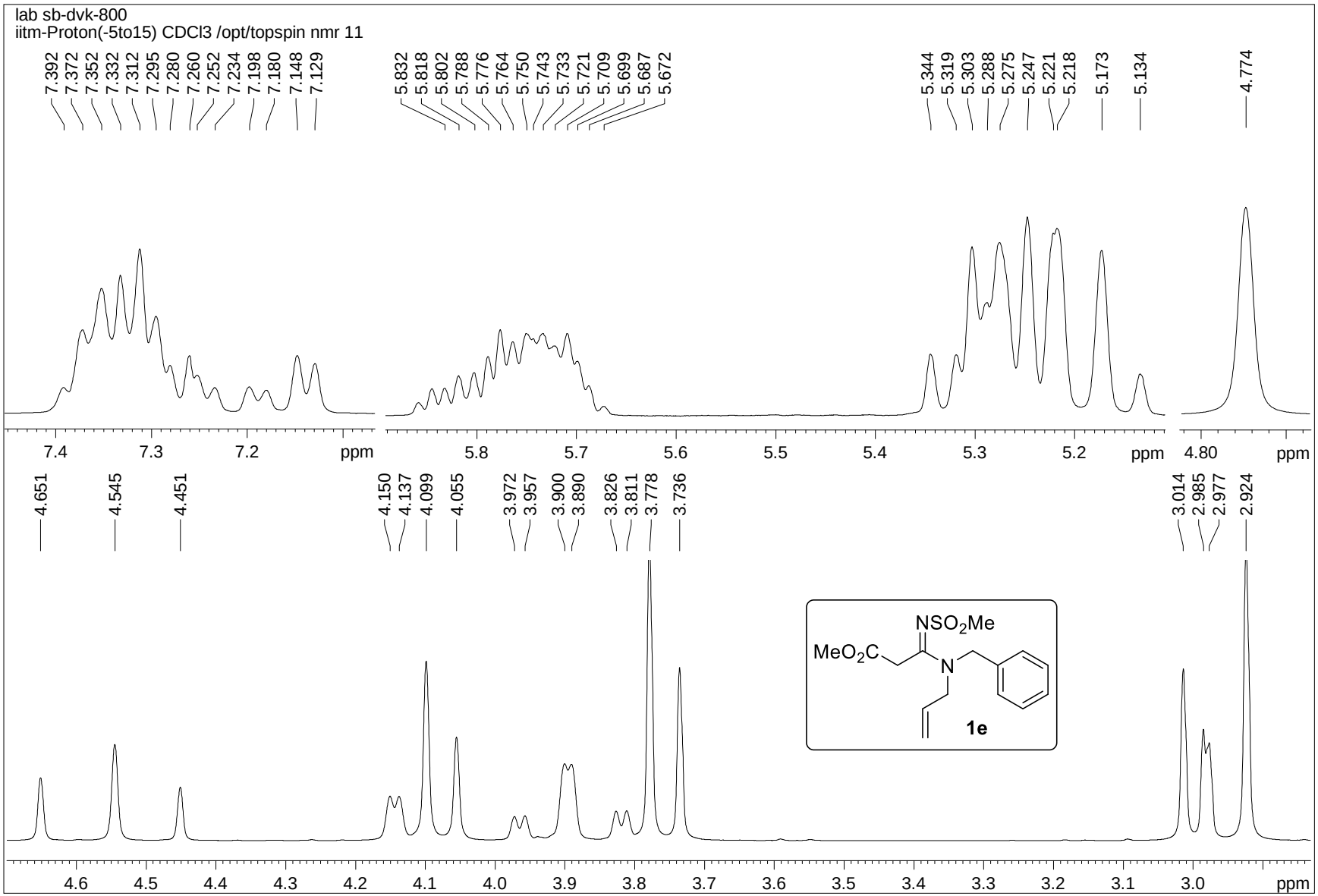
^{1}H-^{1}H COSY NMR spectrum of compound 1c



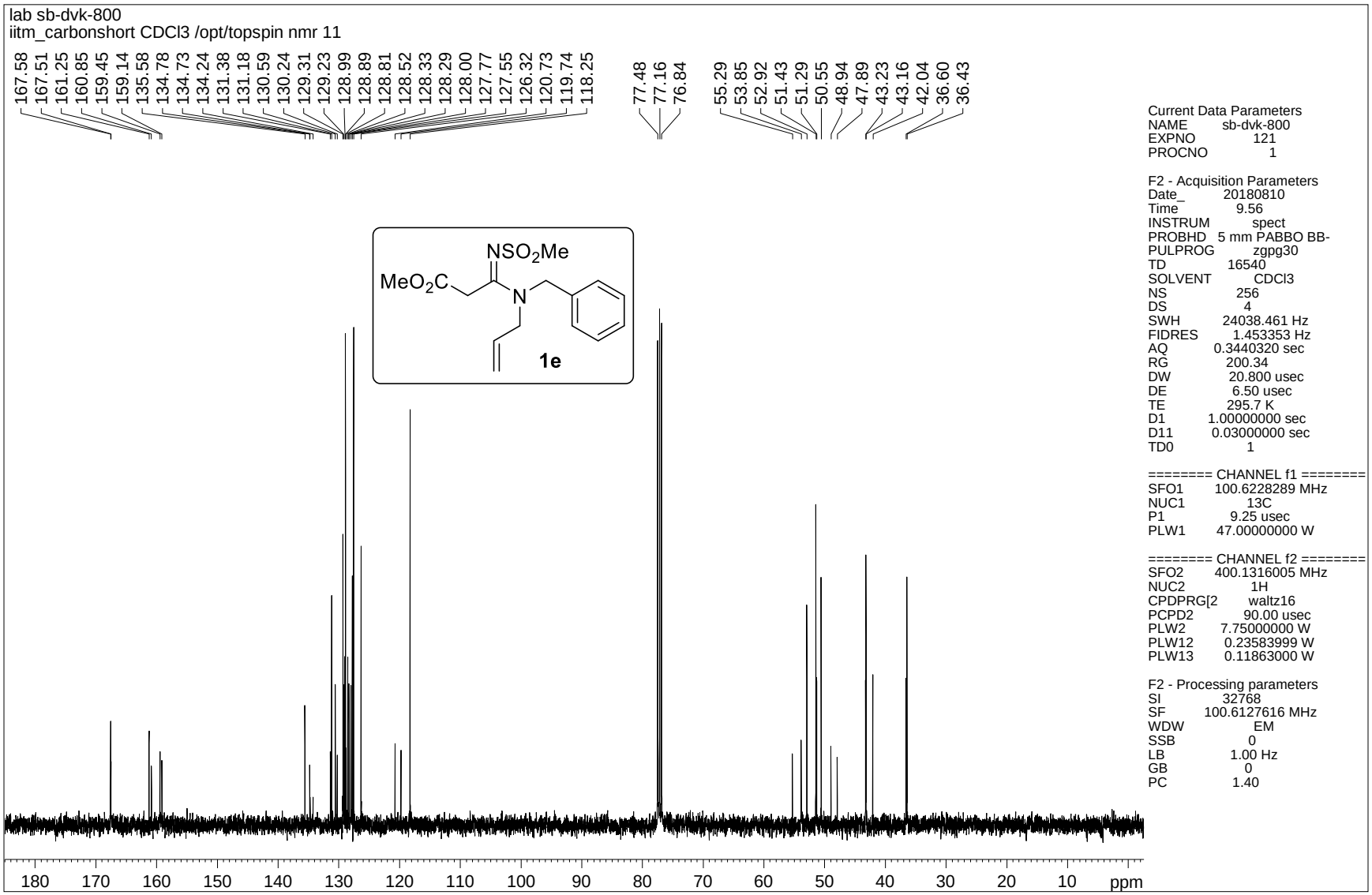
^{1}H-^{13}C HSQC NMR spectrum of compound 1c



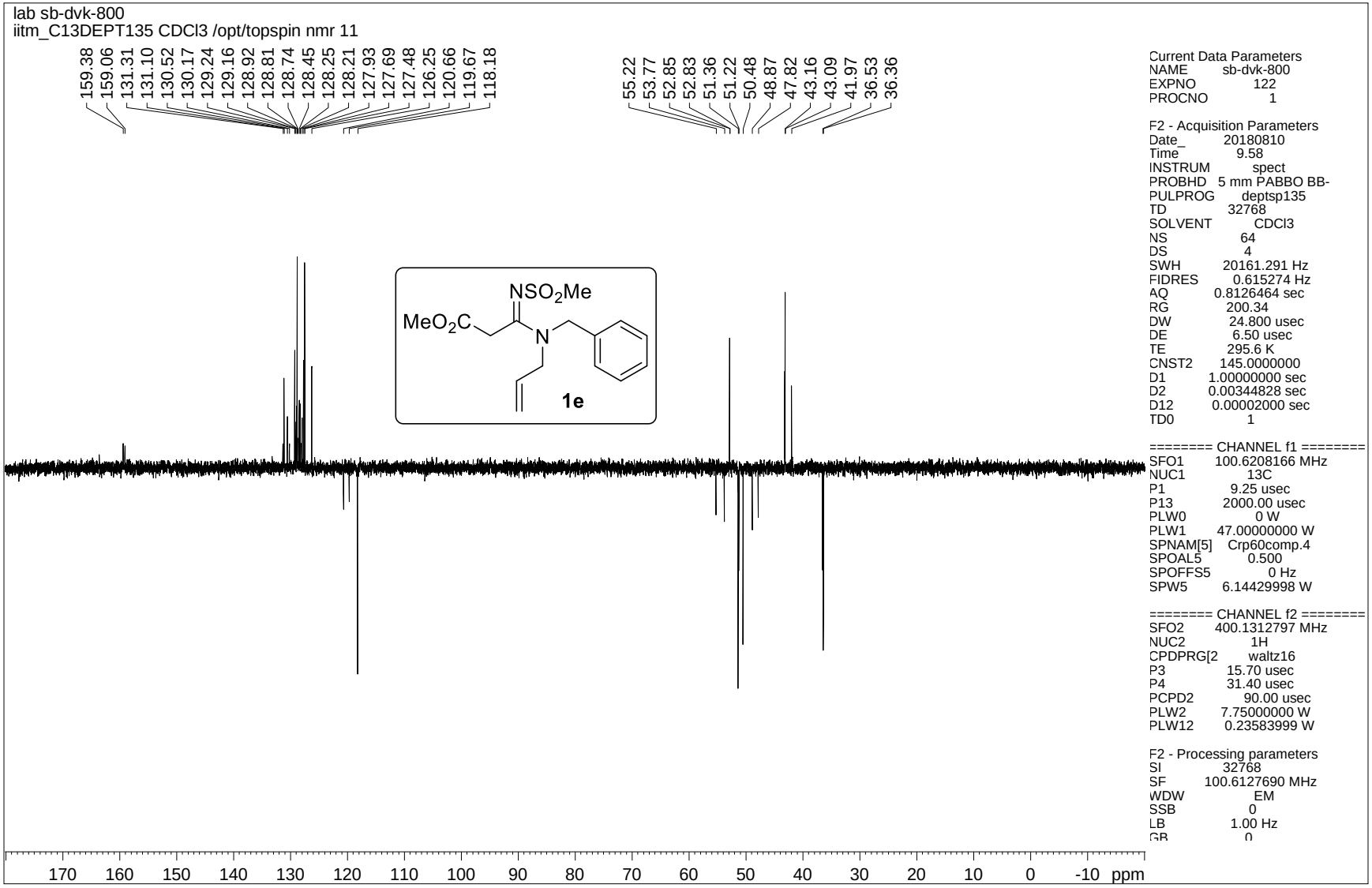
^{1}H NMR spectrum of compound 1e



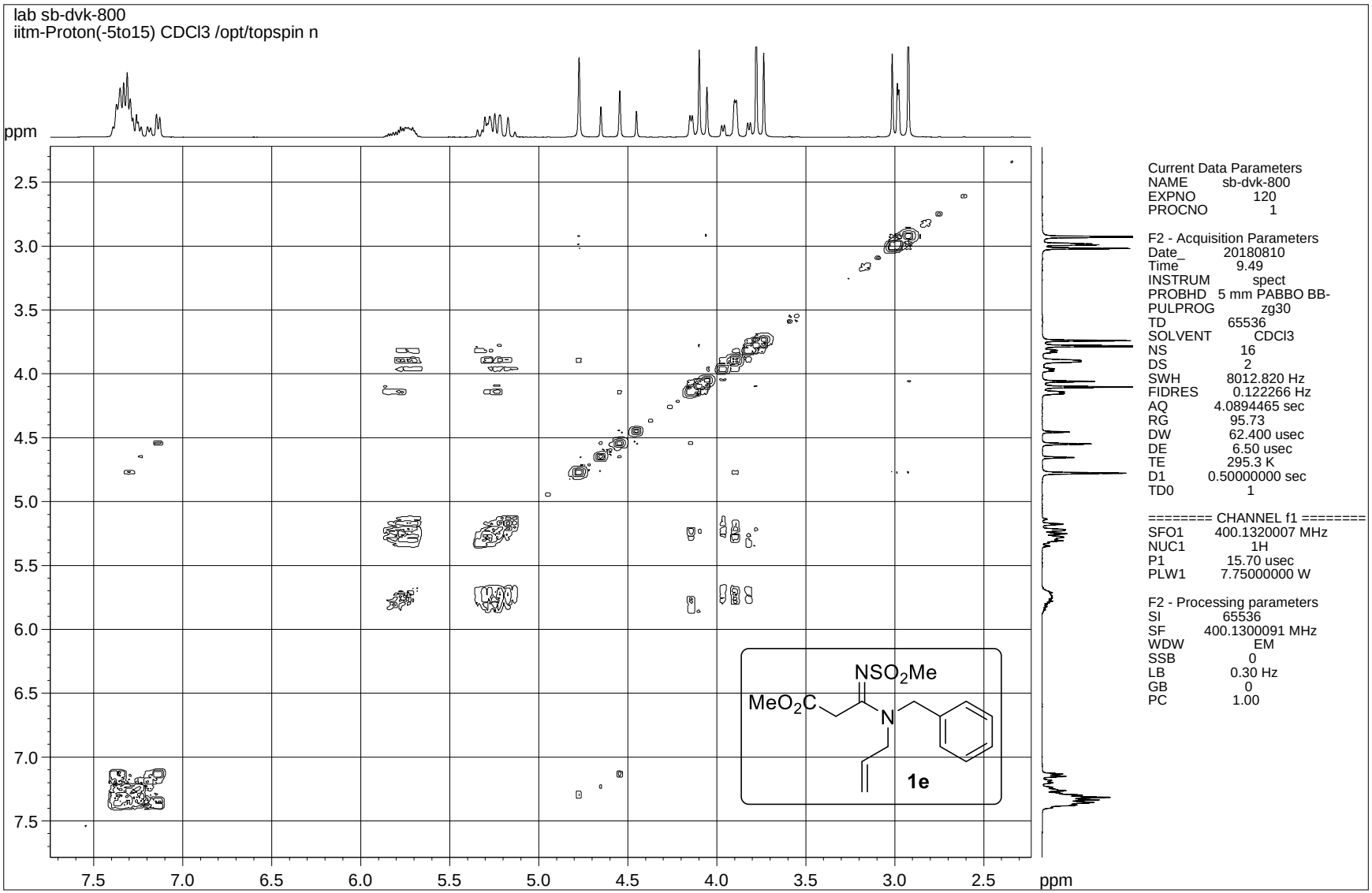
^{1}H NMR spectrum of compound 1e



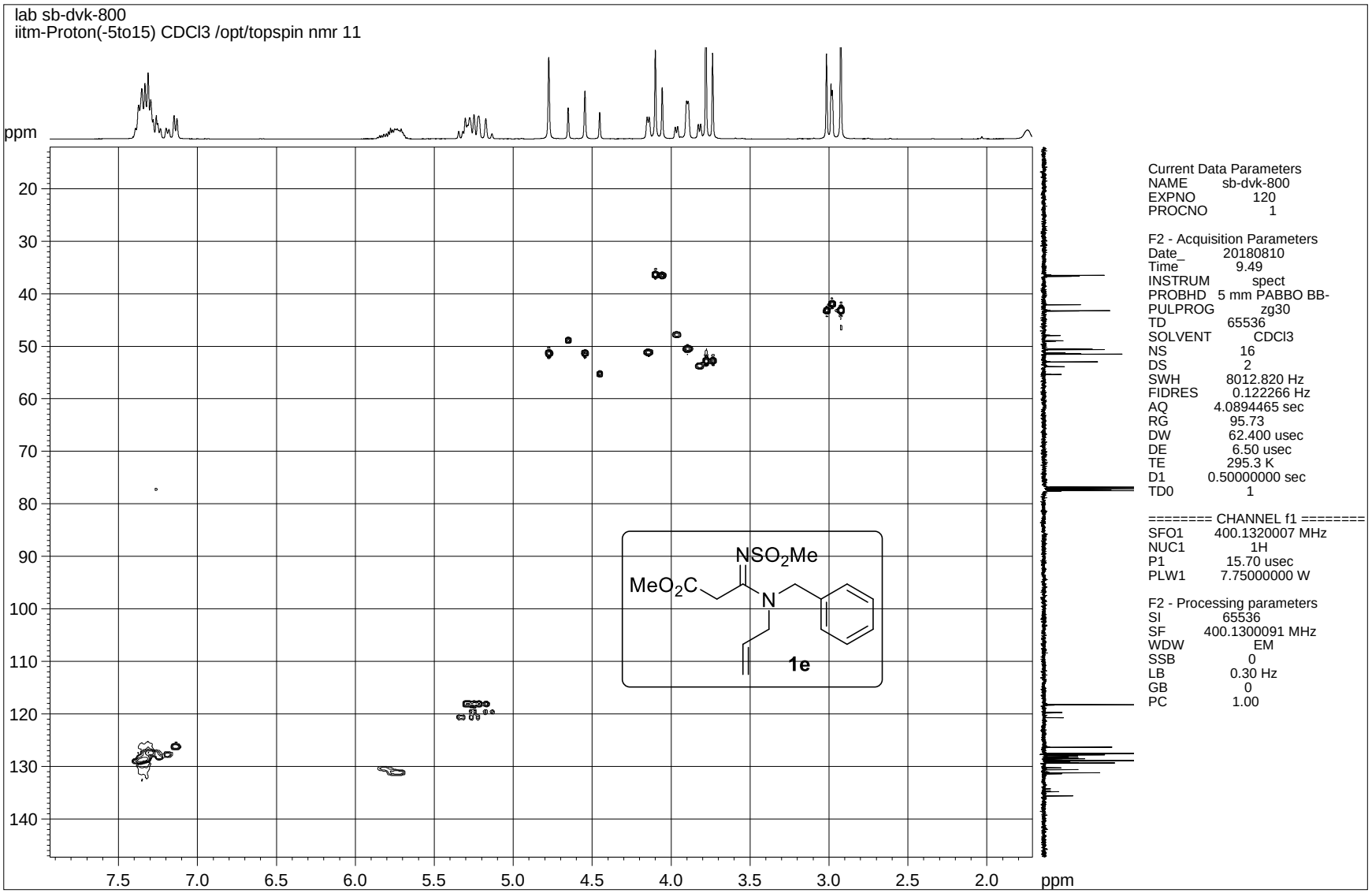
^{13}C NMR spectrum of compound 1e



DEPT-135 NMR spectrum of compound 1e

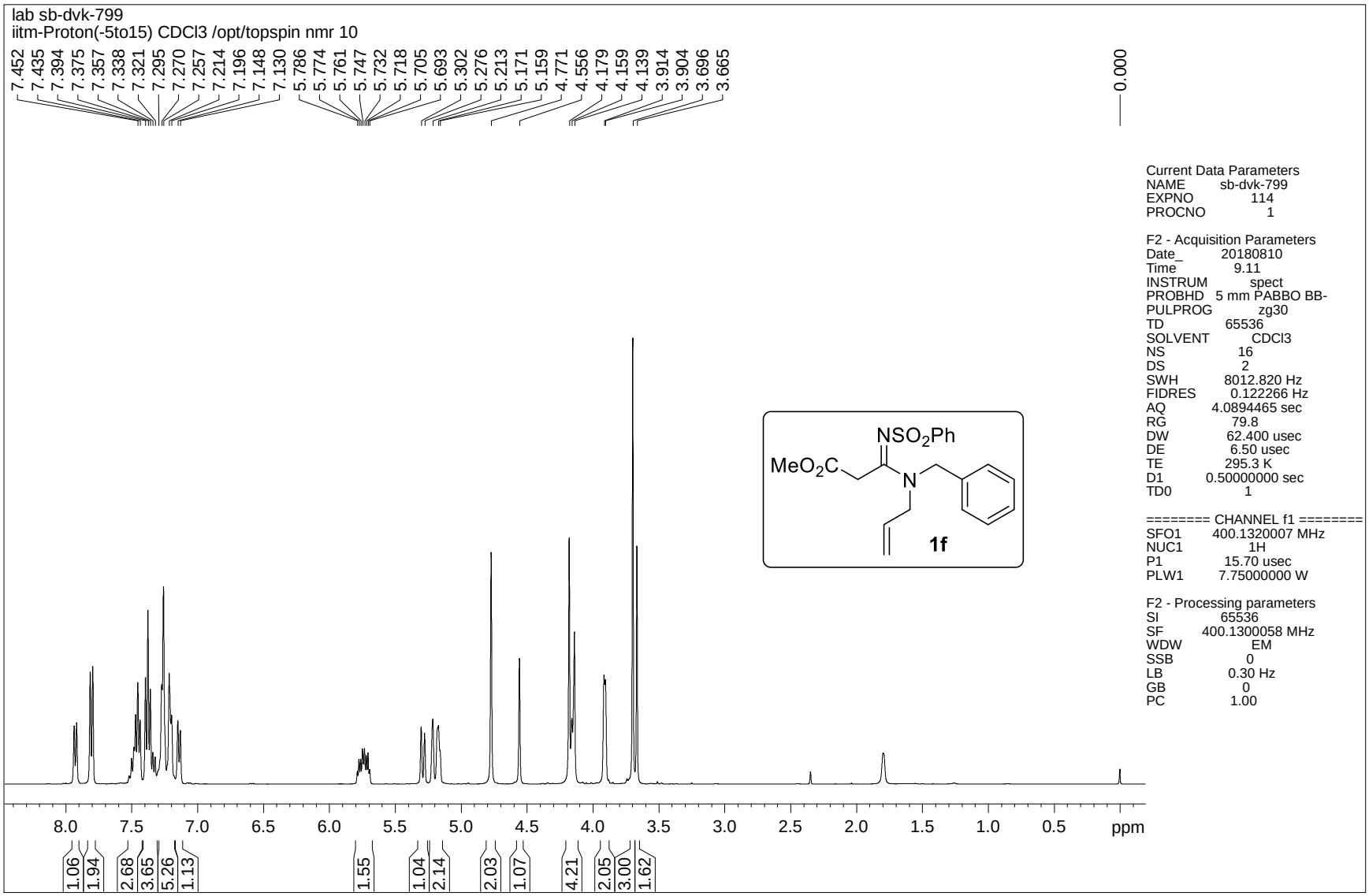


^{1}H-^{1}H COSY NMR spectrum of compound 1e

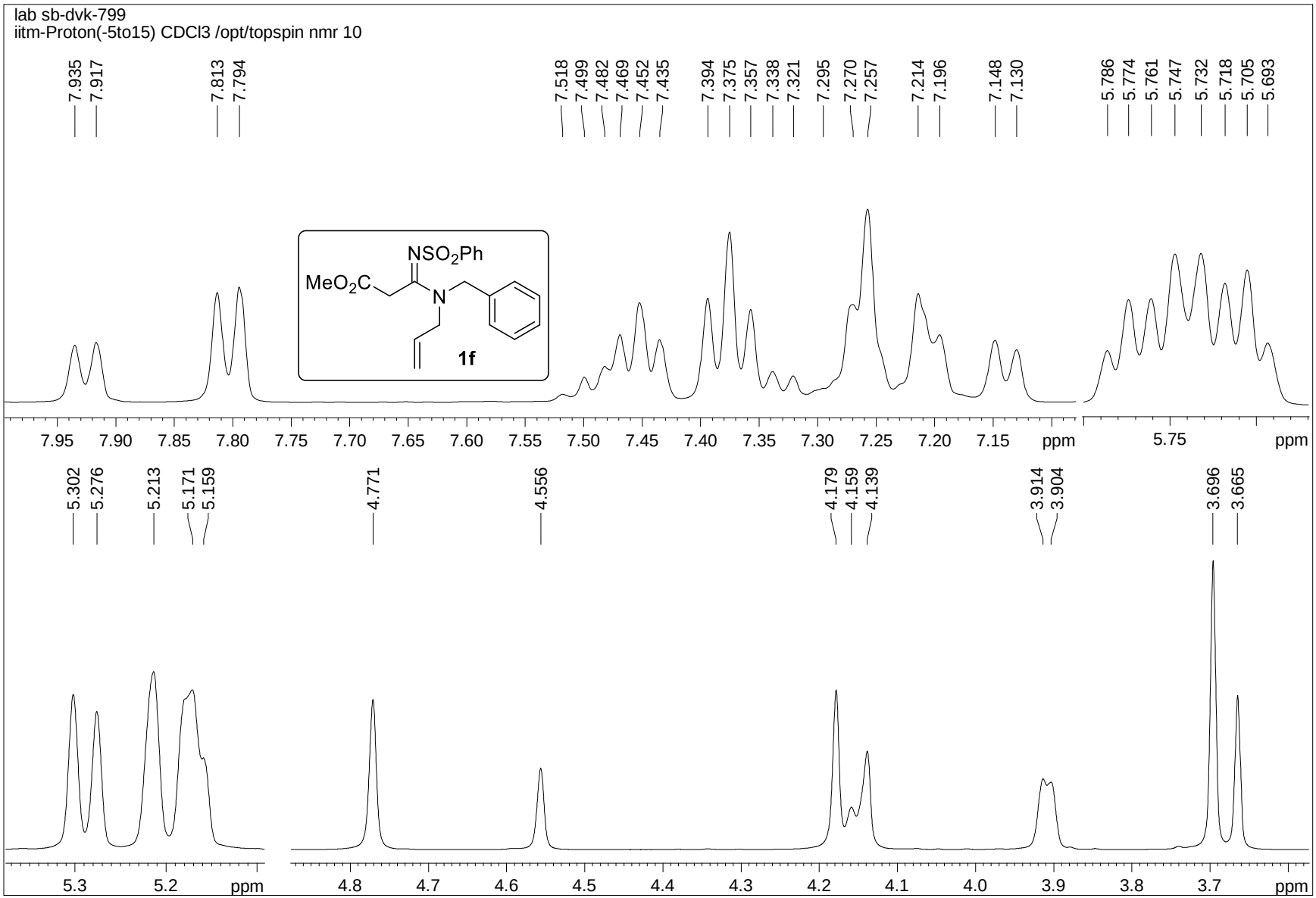


V

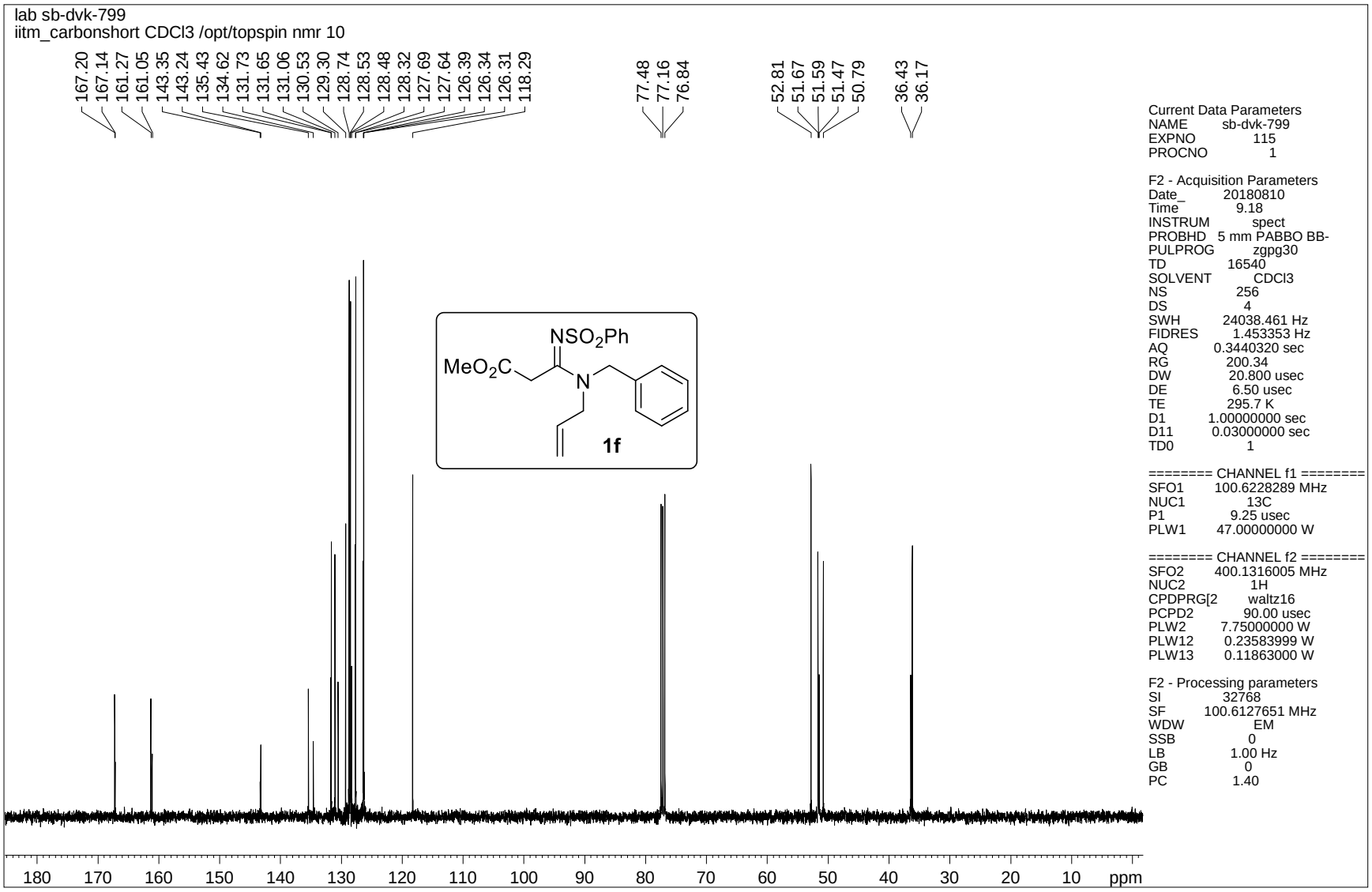
^{1}H-^{13}C HSQC NMR spectrum of compound 1e



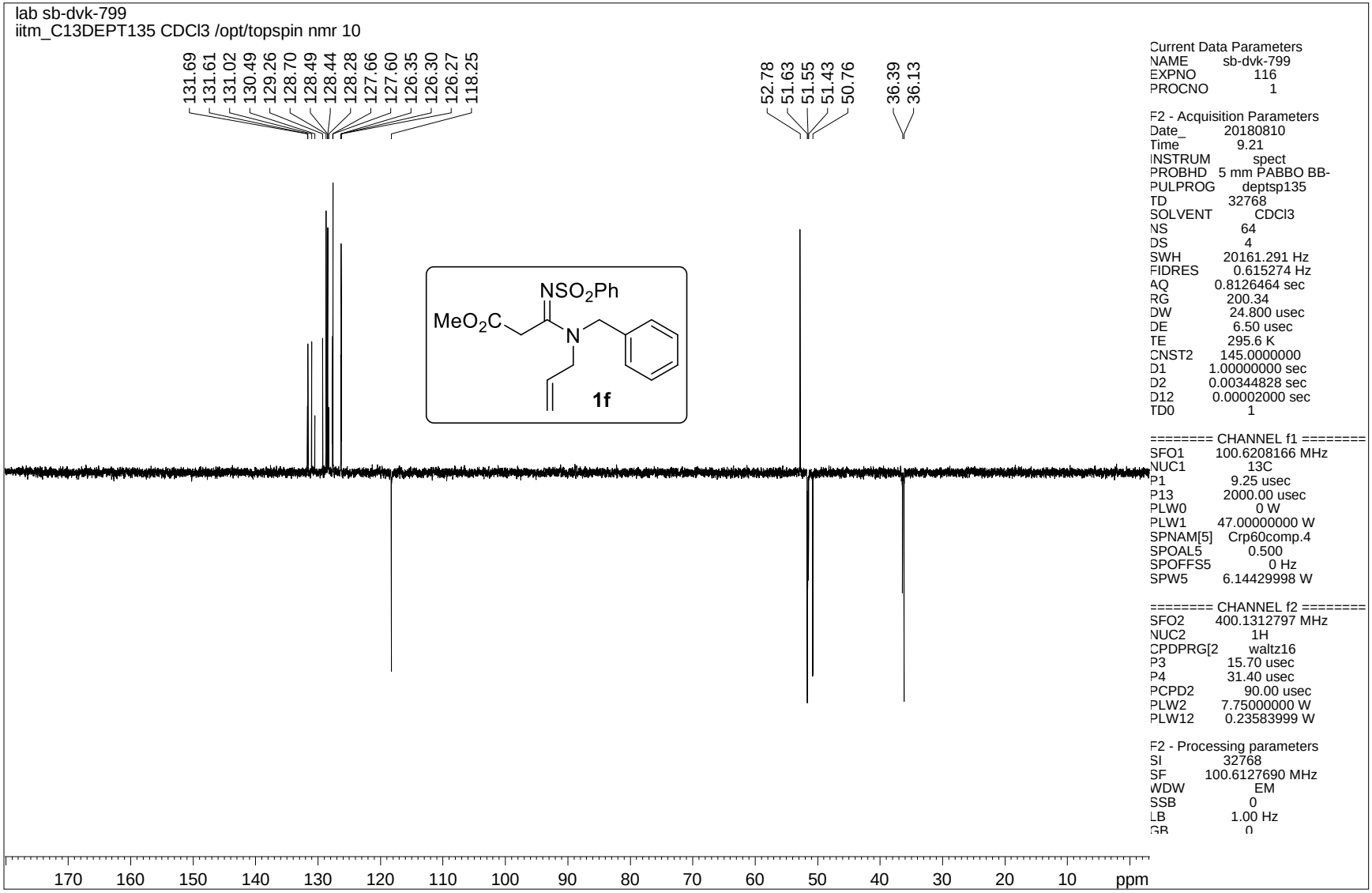
^{1}H NMR spectrum of compound 1f



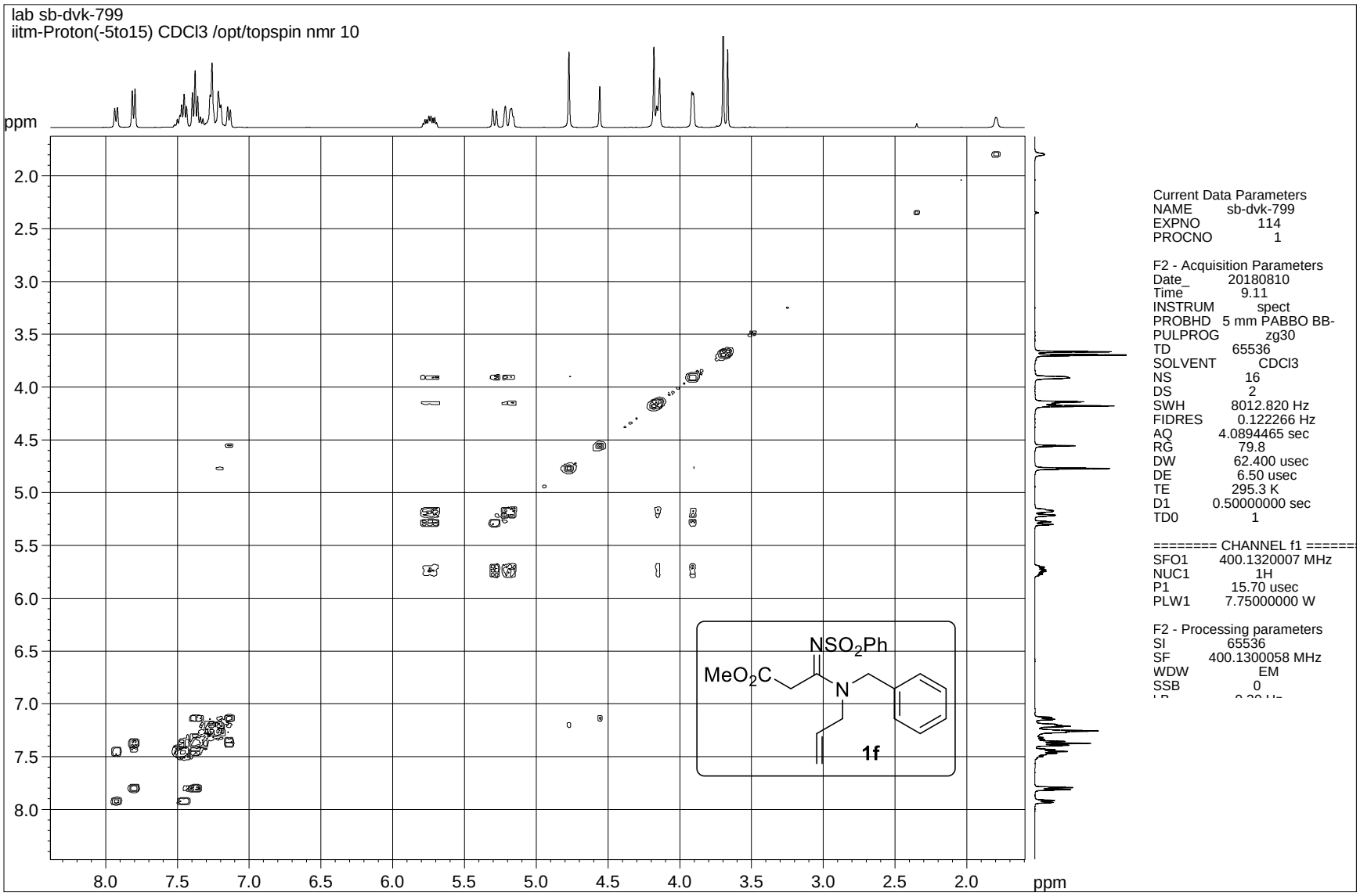
^{1}H NMR spectrum of compound 1f



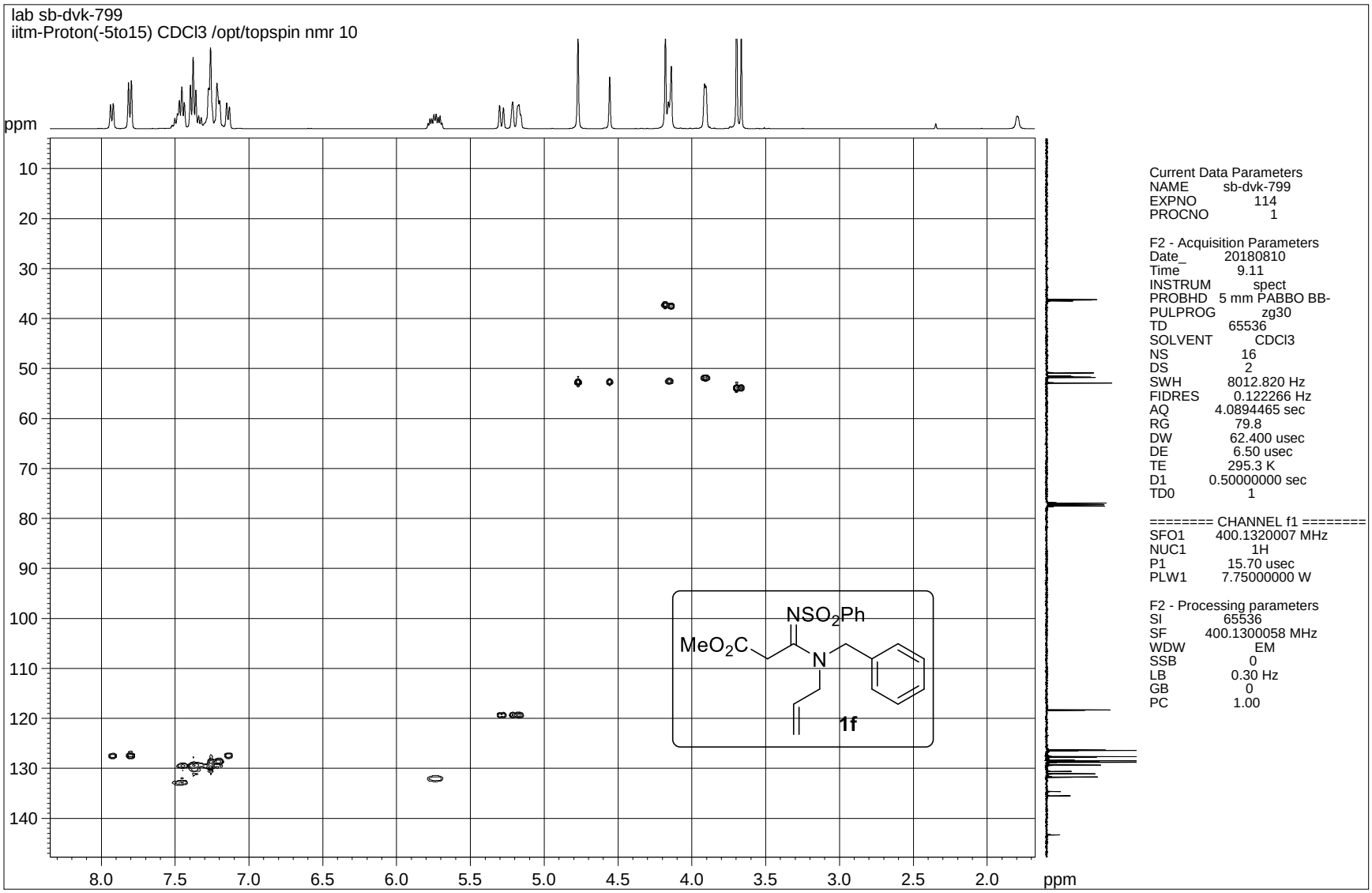
^{13}C NMR spectrum of compound 1f



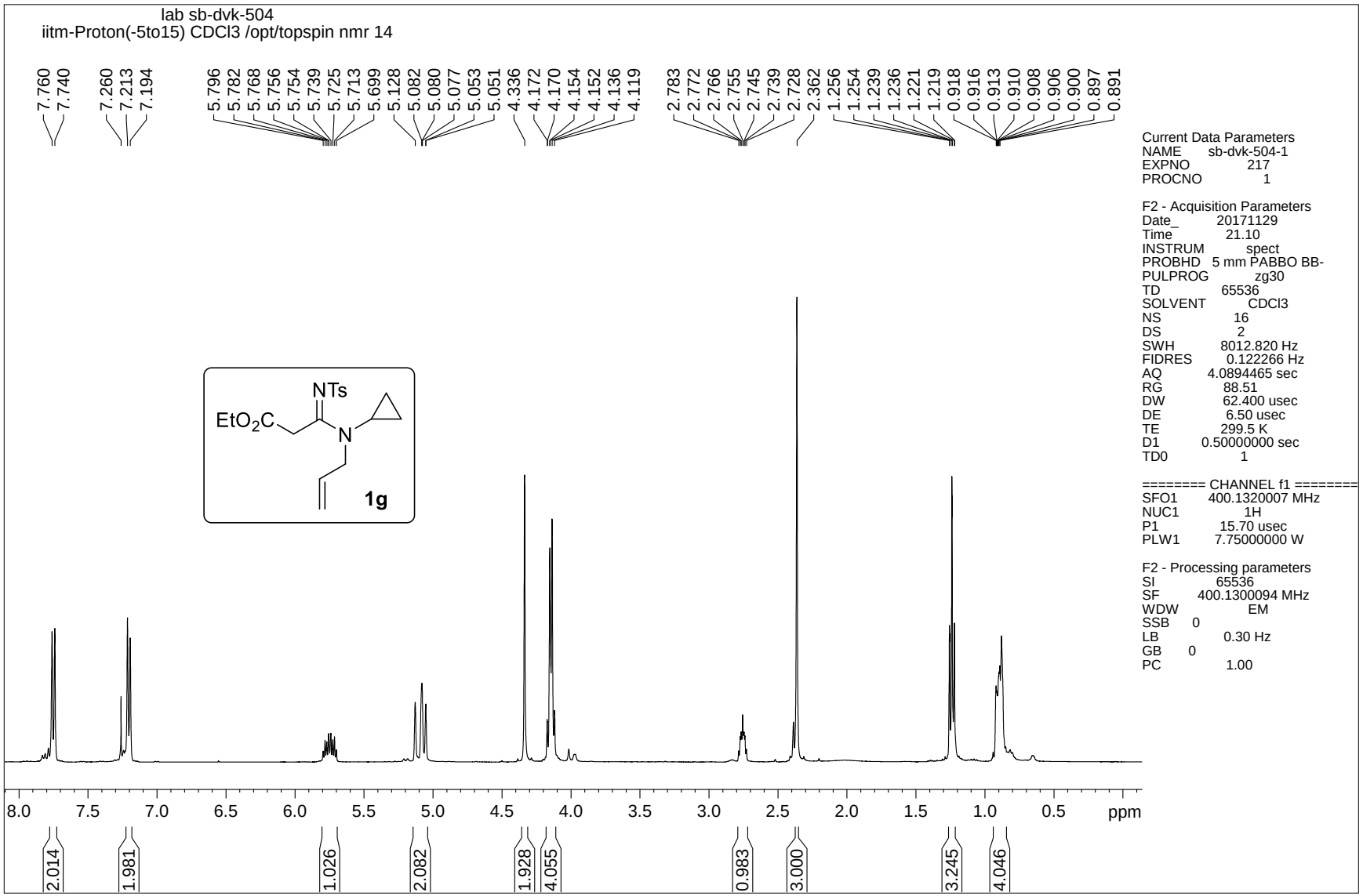
DEPT-135 NMR spectrum of compound 1f



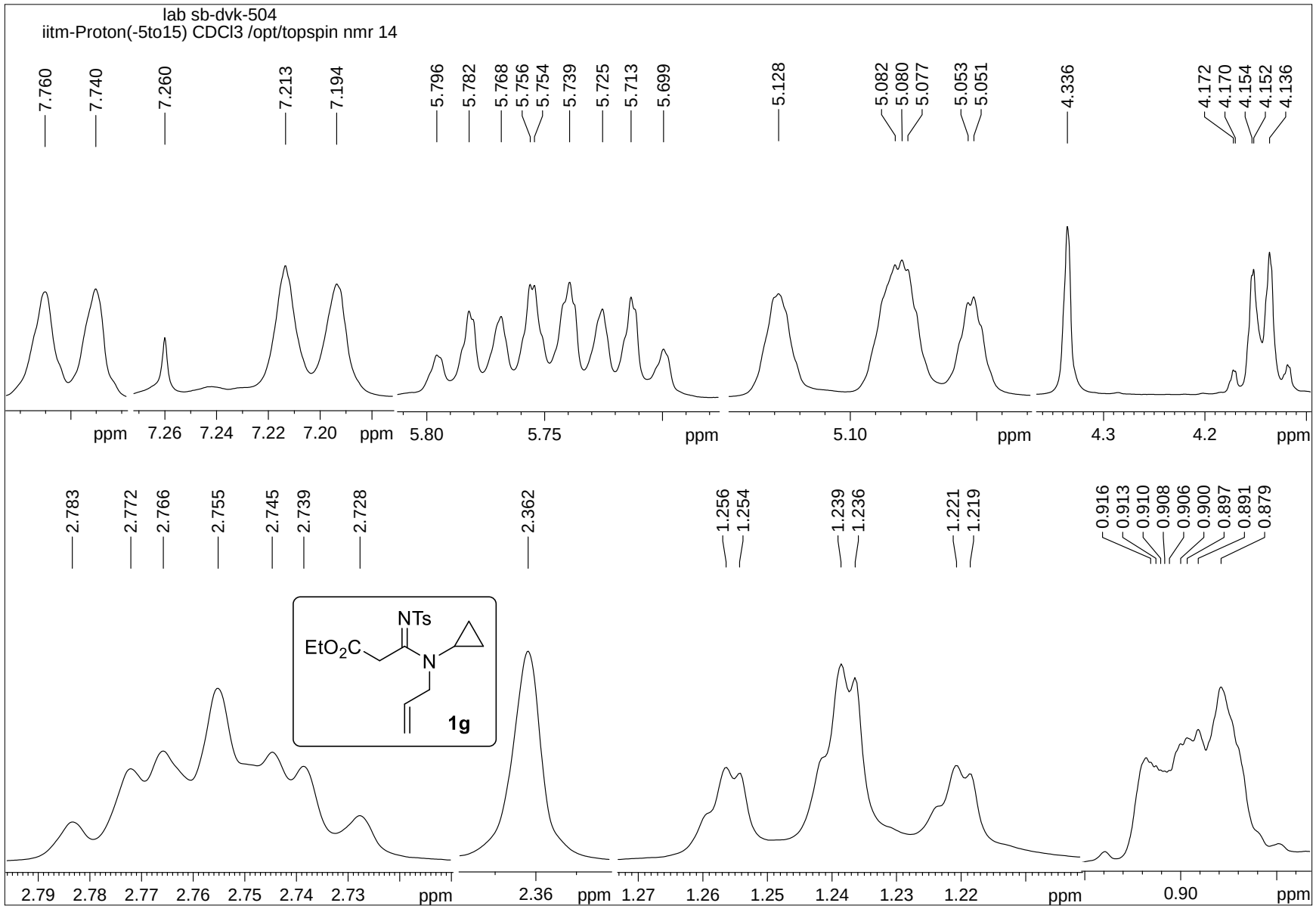
^{1}H-^{1}H COSY NMR spectrum of compound 1f



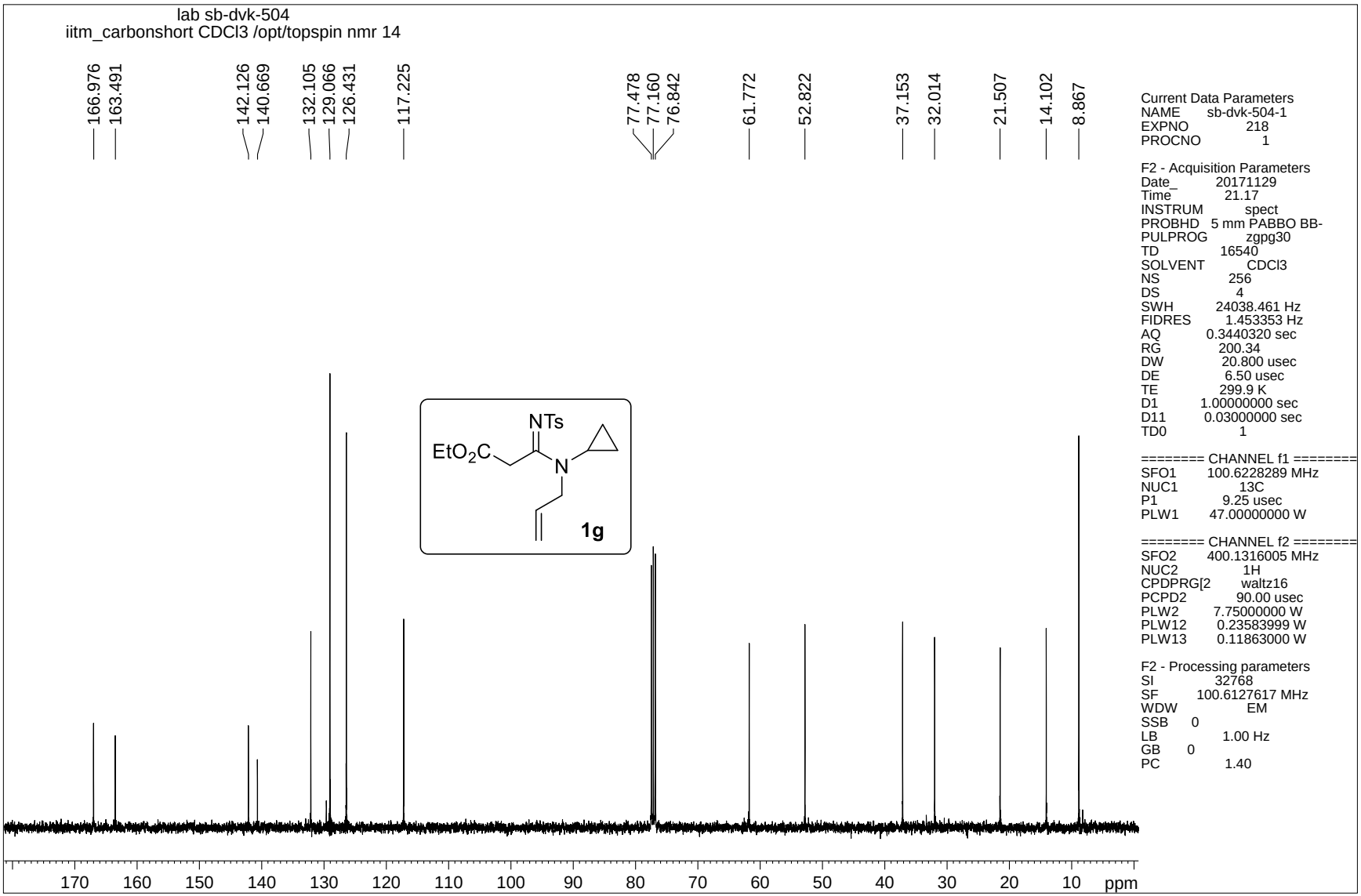
^{1}H-^{13}C HSQC NMR spectrum of compound 1f



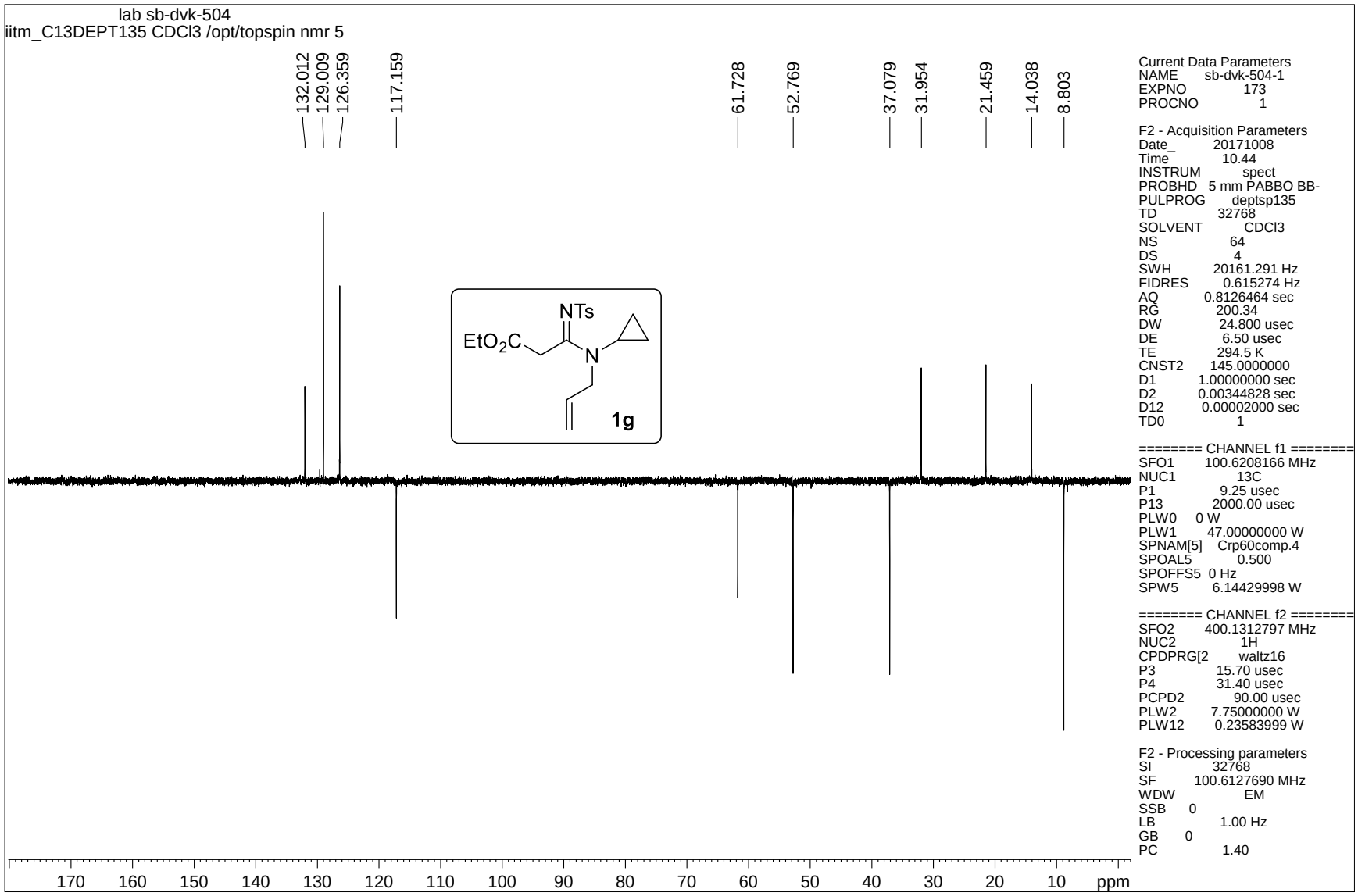
^{1}H NMR spectrum of compound 1g



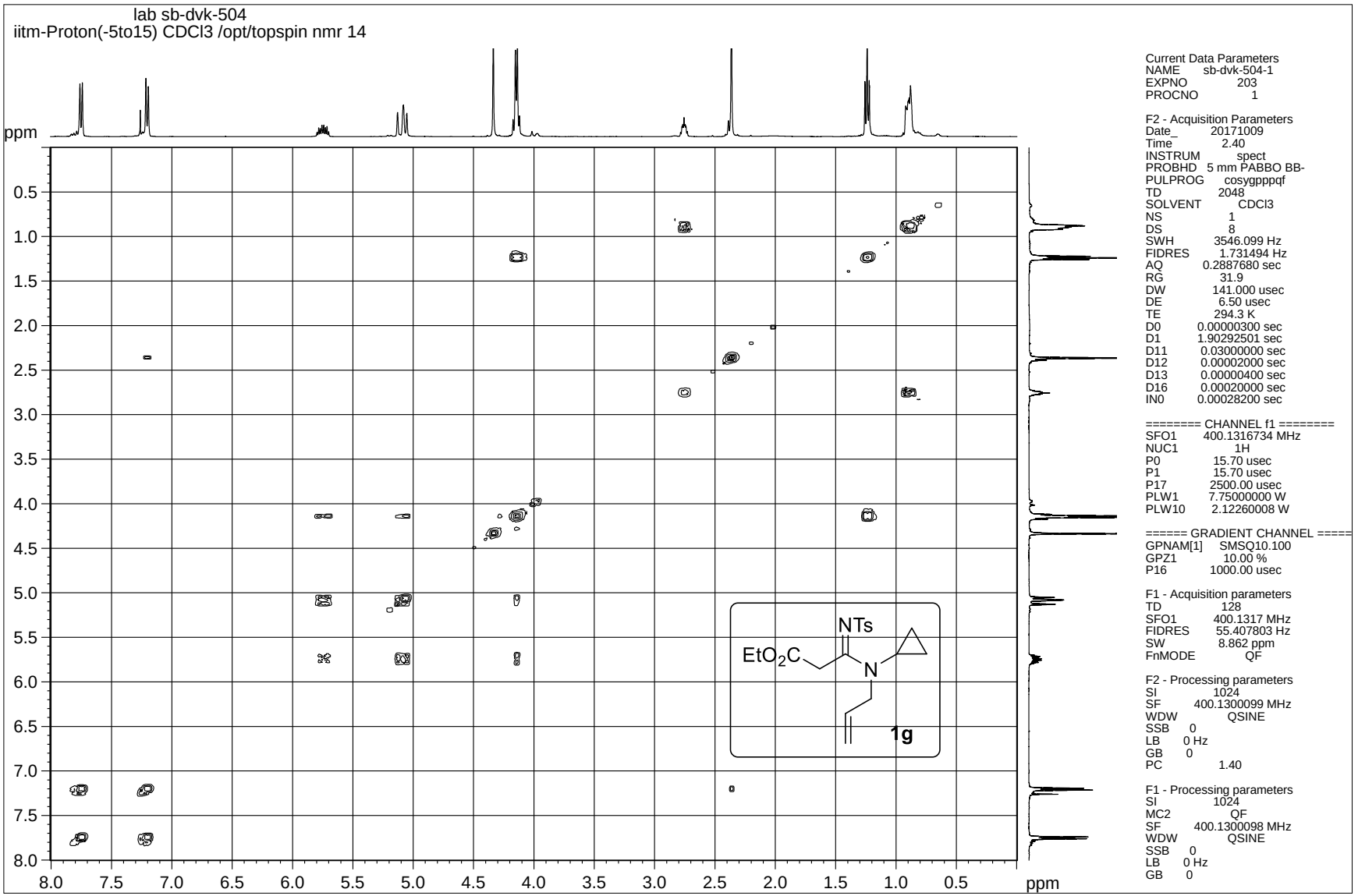
^{1}H NMR spectrum of compound 1g



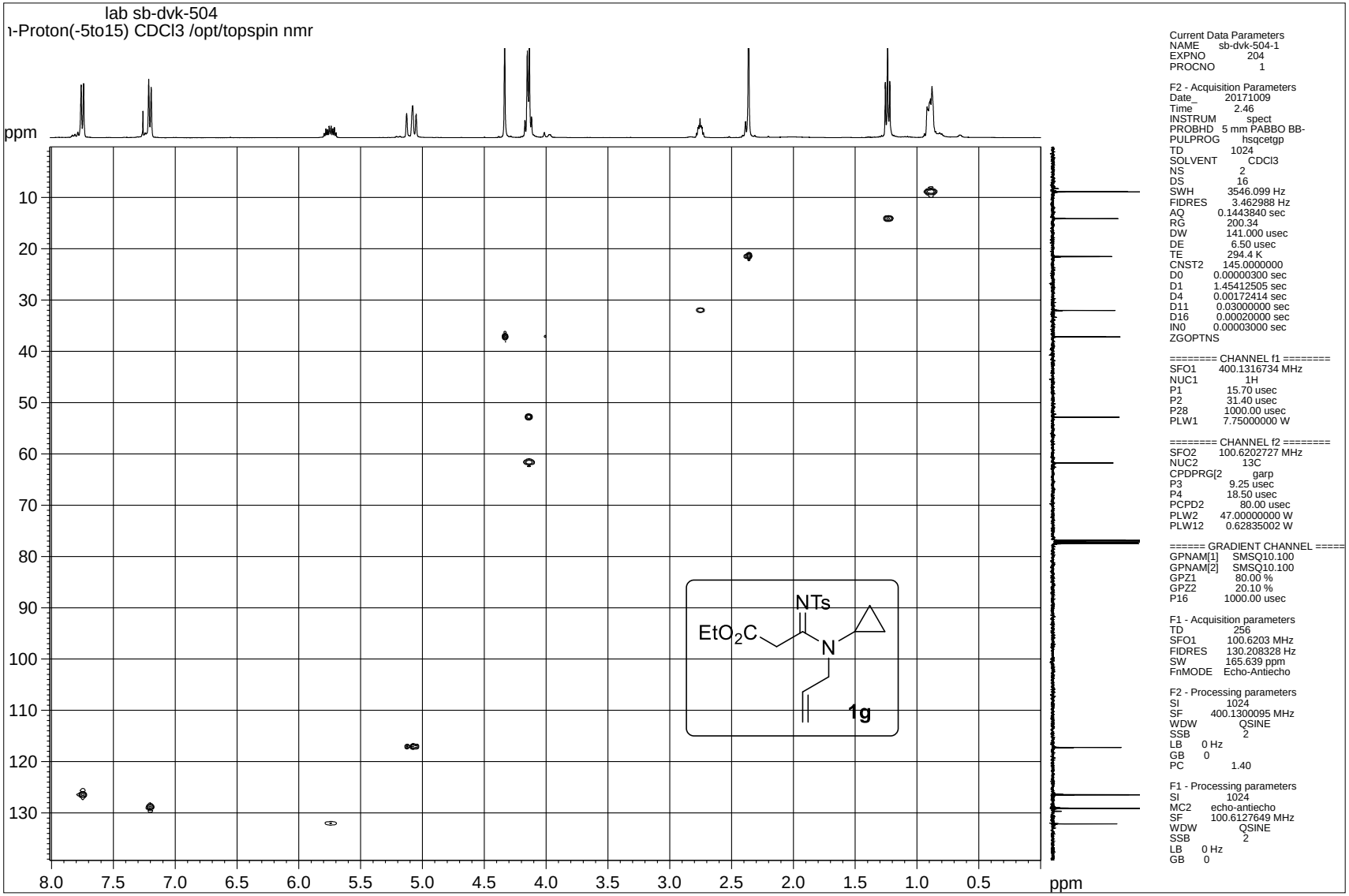
^{13}C NMR spectrum of compound 1g



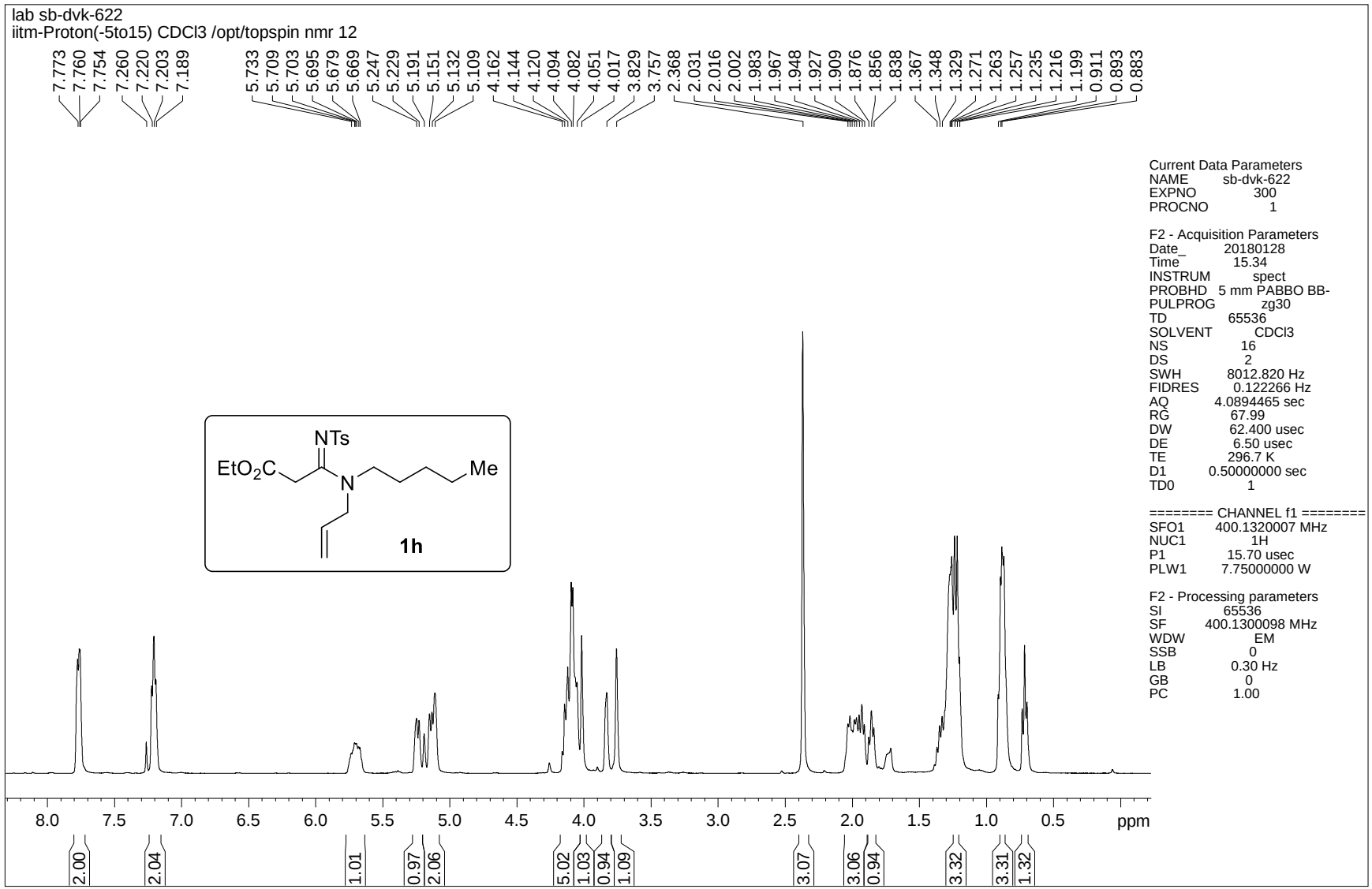
DEPT-135 NMR spectrum of compound 1g



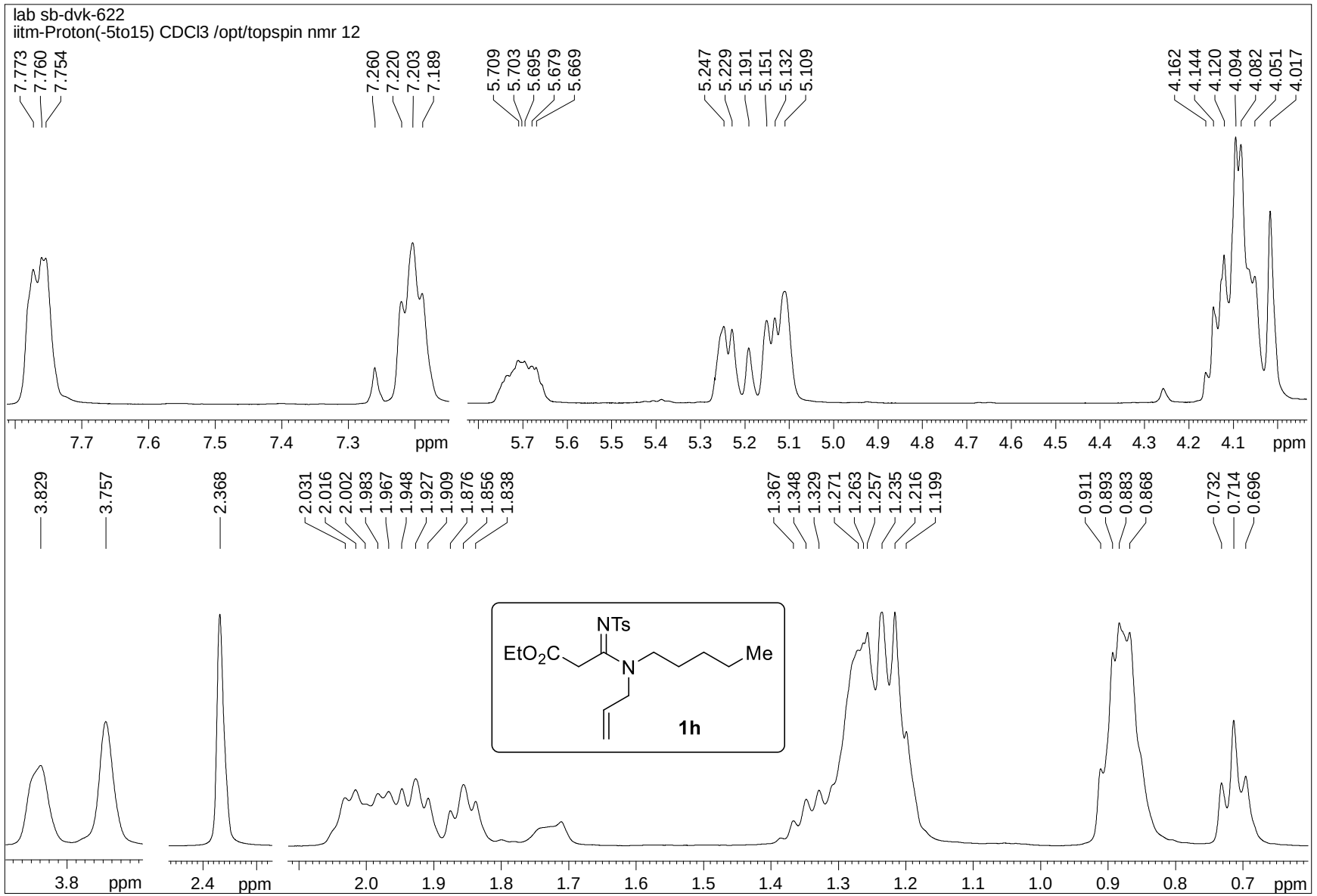
^{1}H-^{1}H COSY NMR spectrum of compound 1g



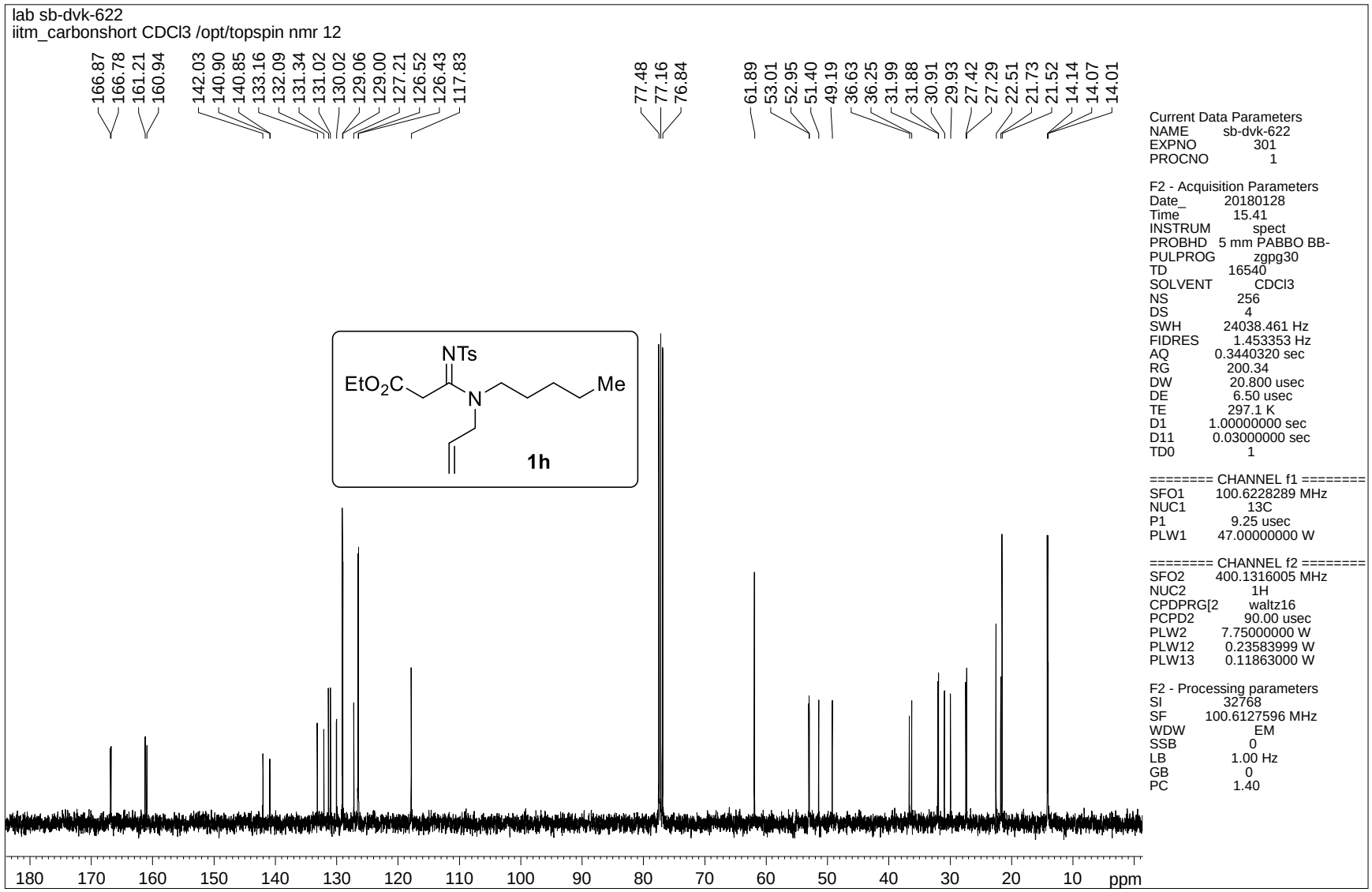
^{1}H-^{13}C HSQC NMR spectrum of compound 1g



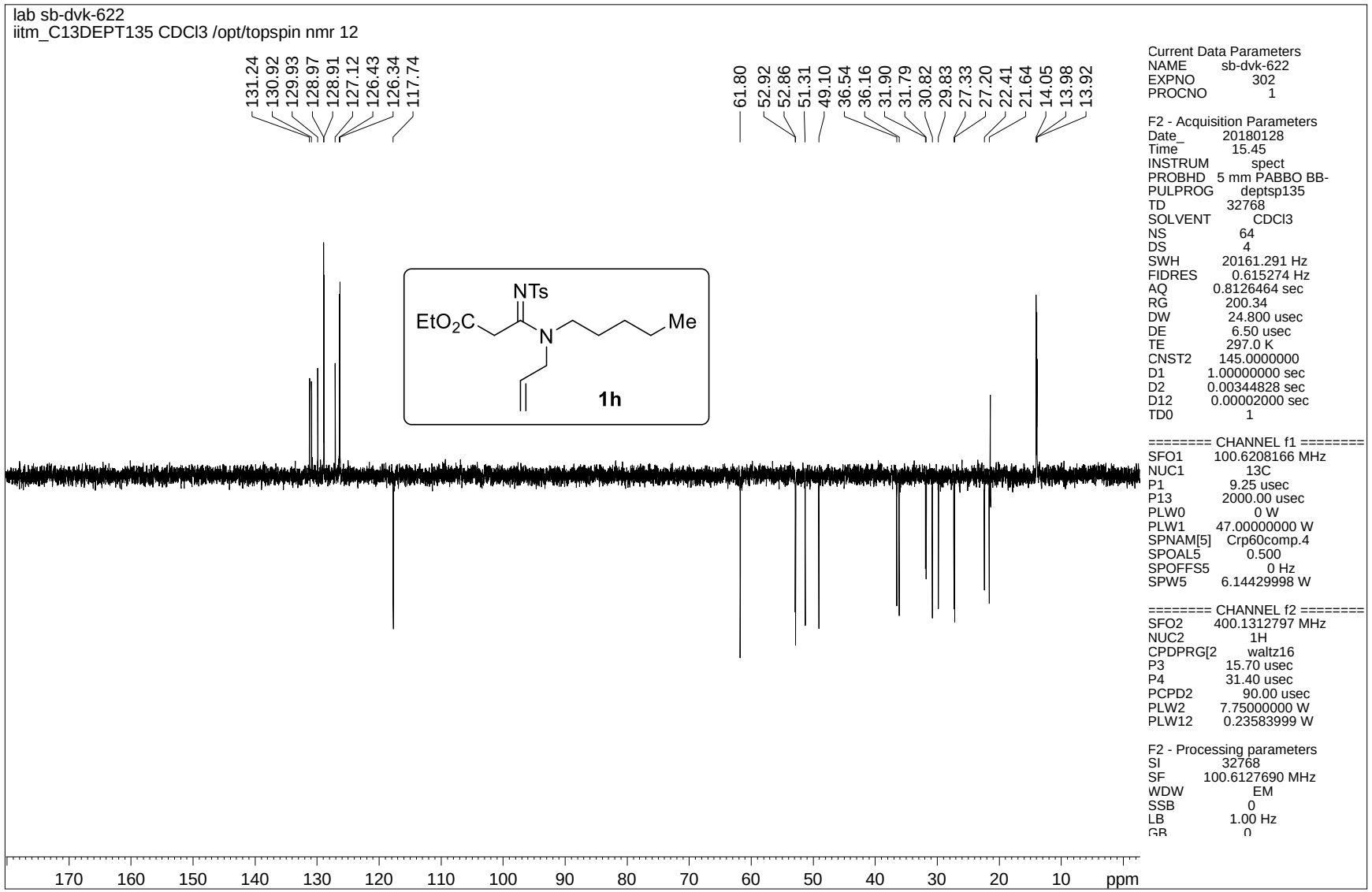
^{1}H NMR spectrum of compound 1h



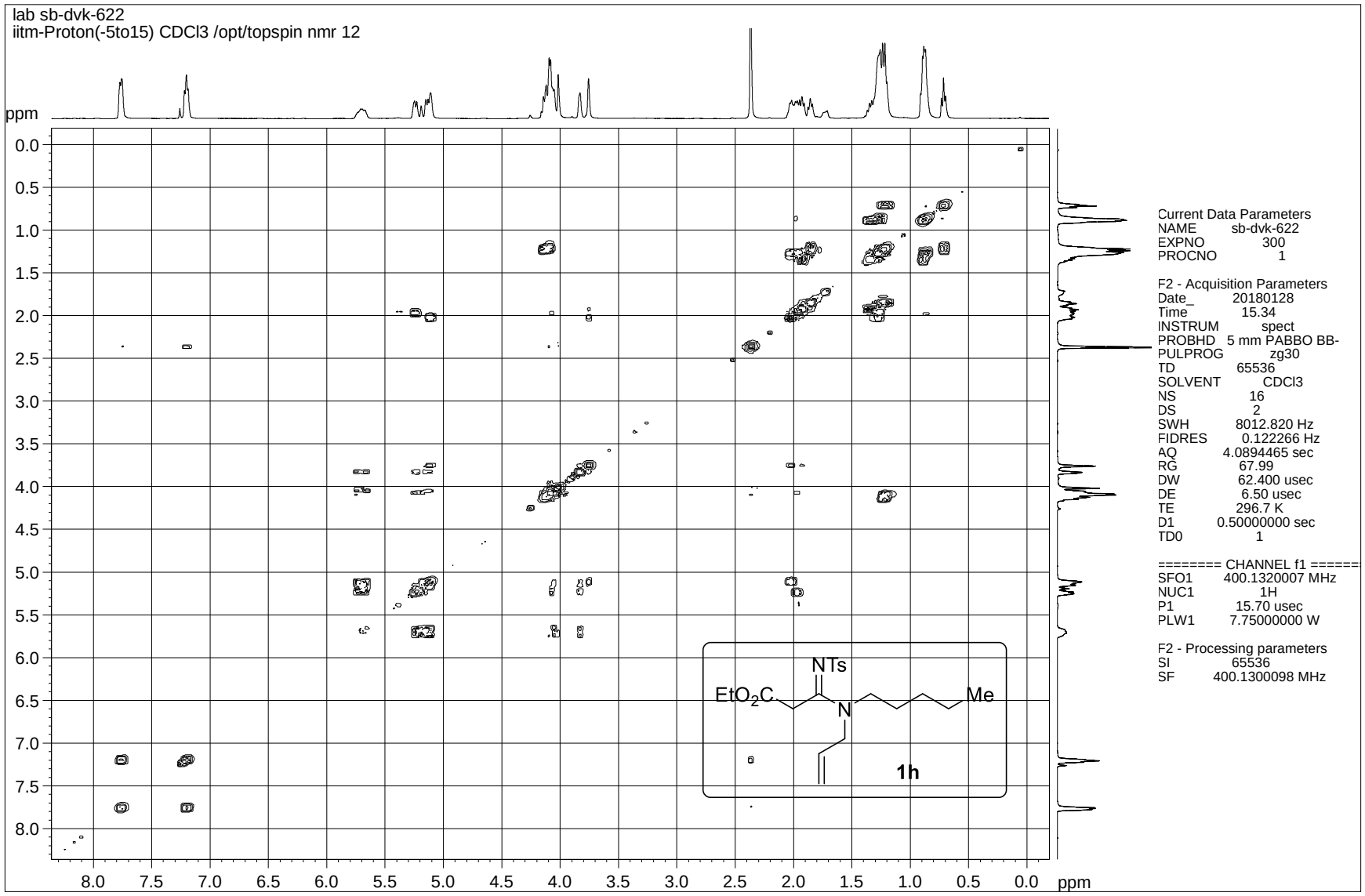
^{1}H NMR spectrum of compound 1h



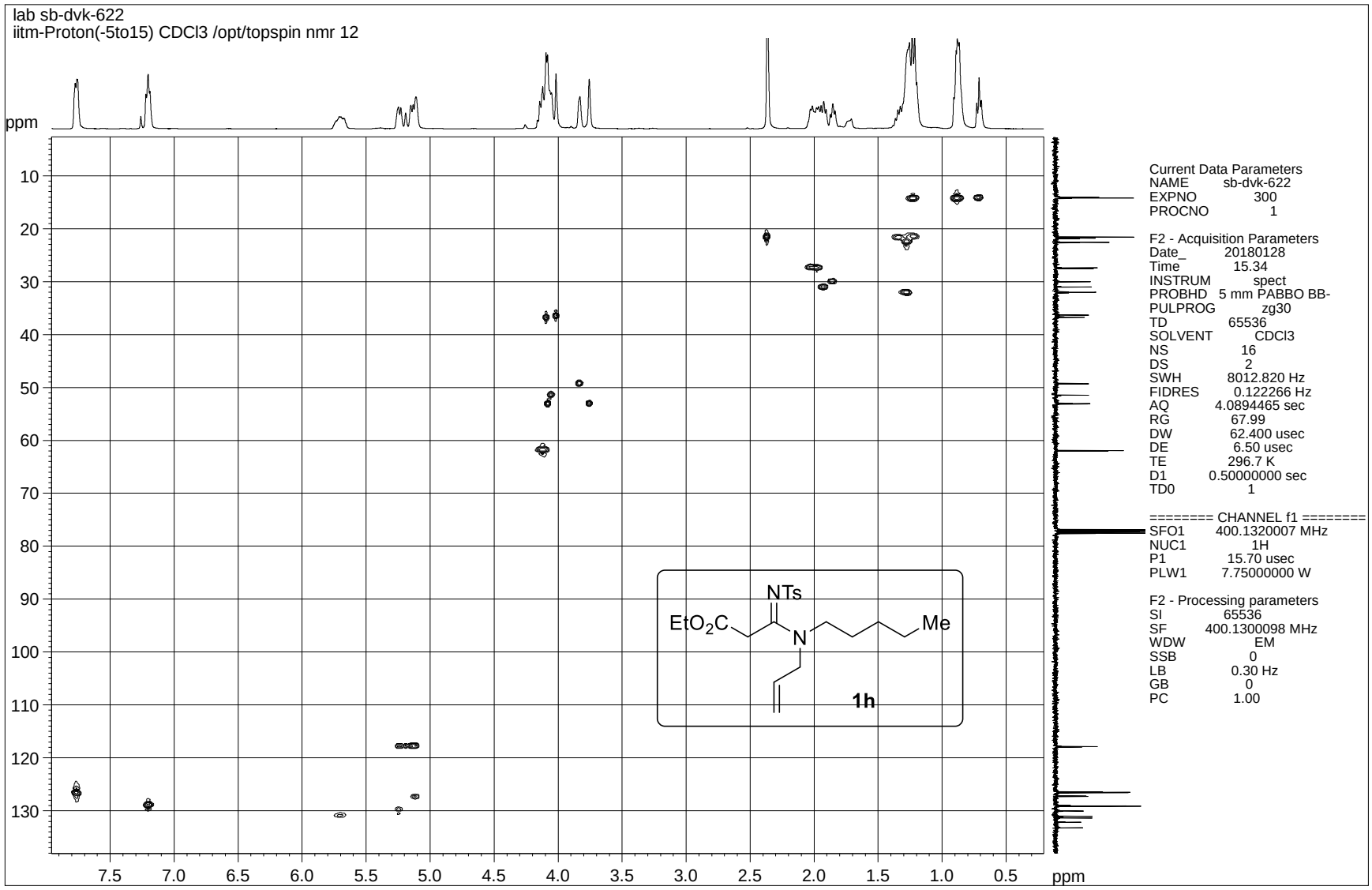
^{13}C NMR spectrum of compound 1h



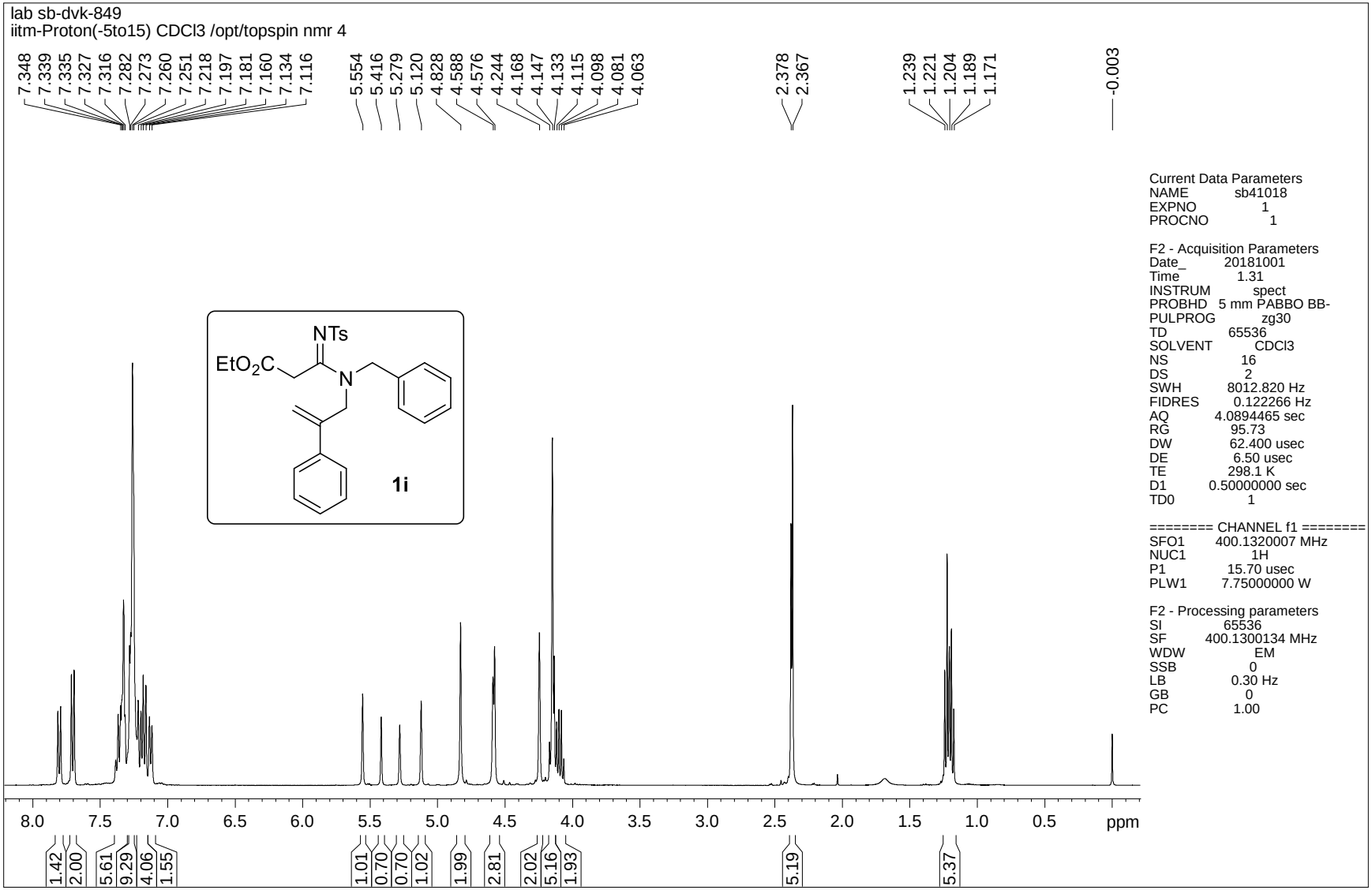
DEPT-135 NMR spectrum of compound 1h



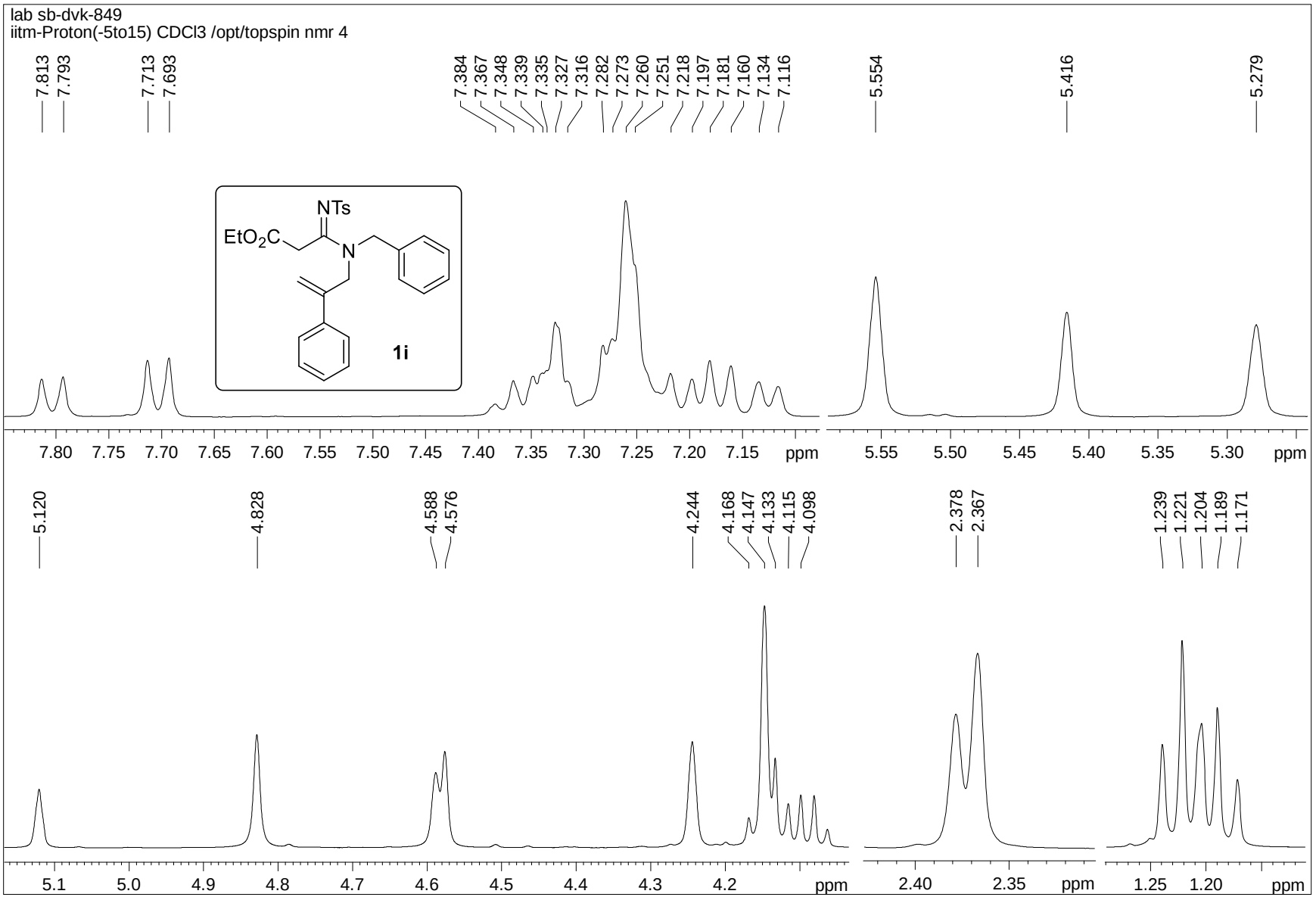
^{1}H-^{1}H COSY NMR spectrum of compound 1h



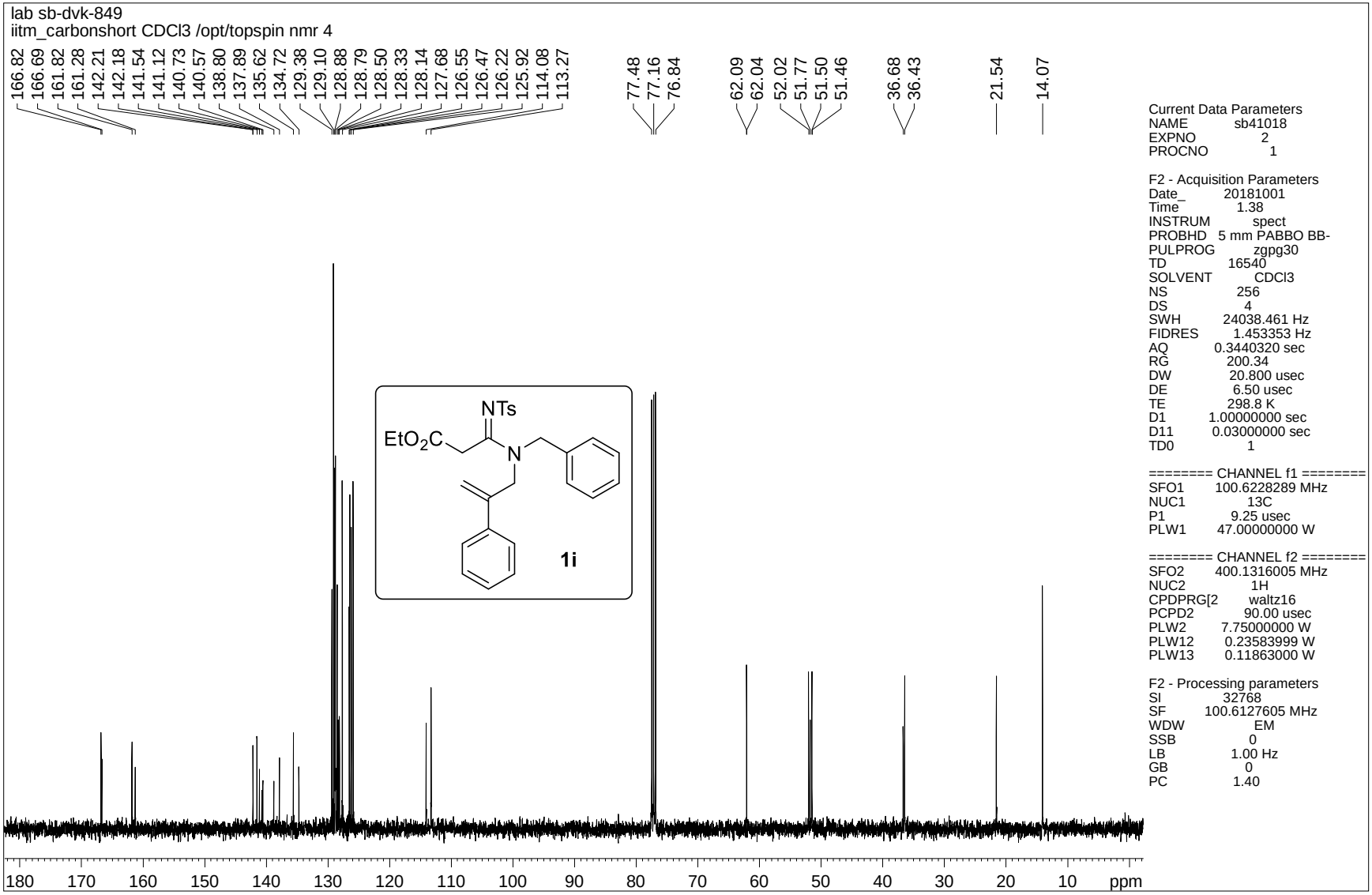
^{1}H-^{13}C HSQC NMR spectrum of compound 1h



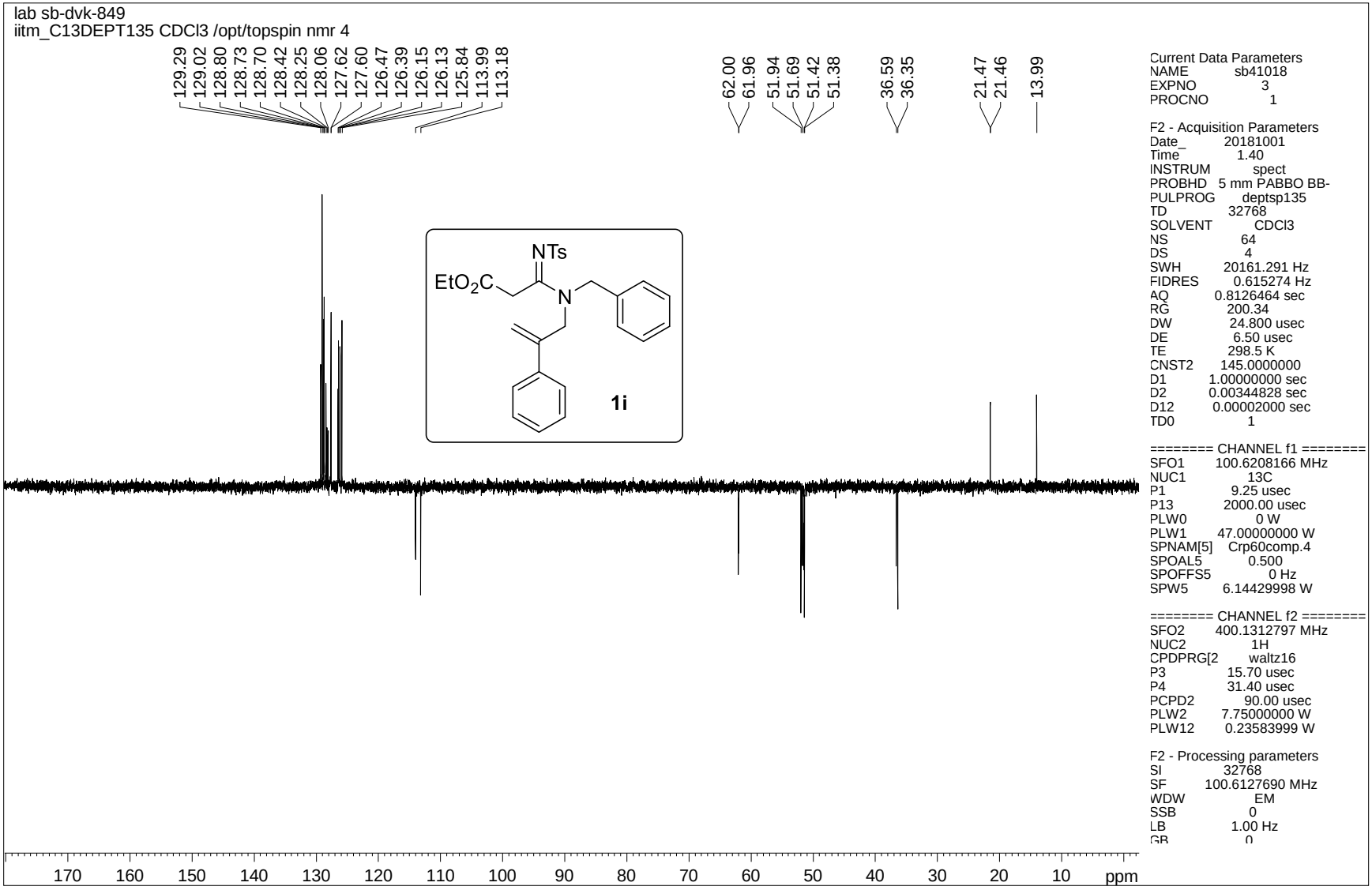
^{1}H NMR spectrum of compound 1i



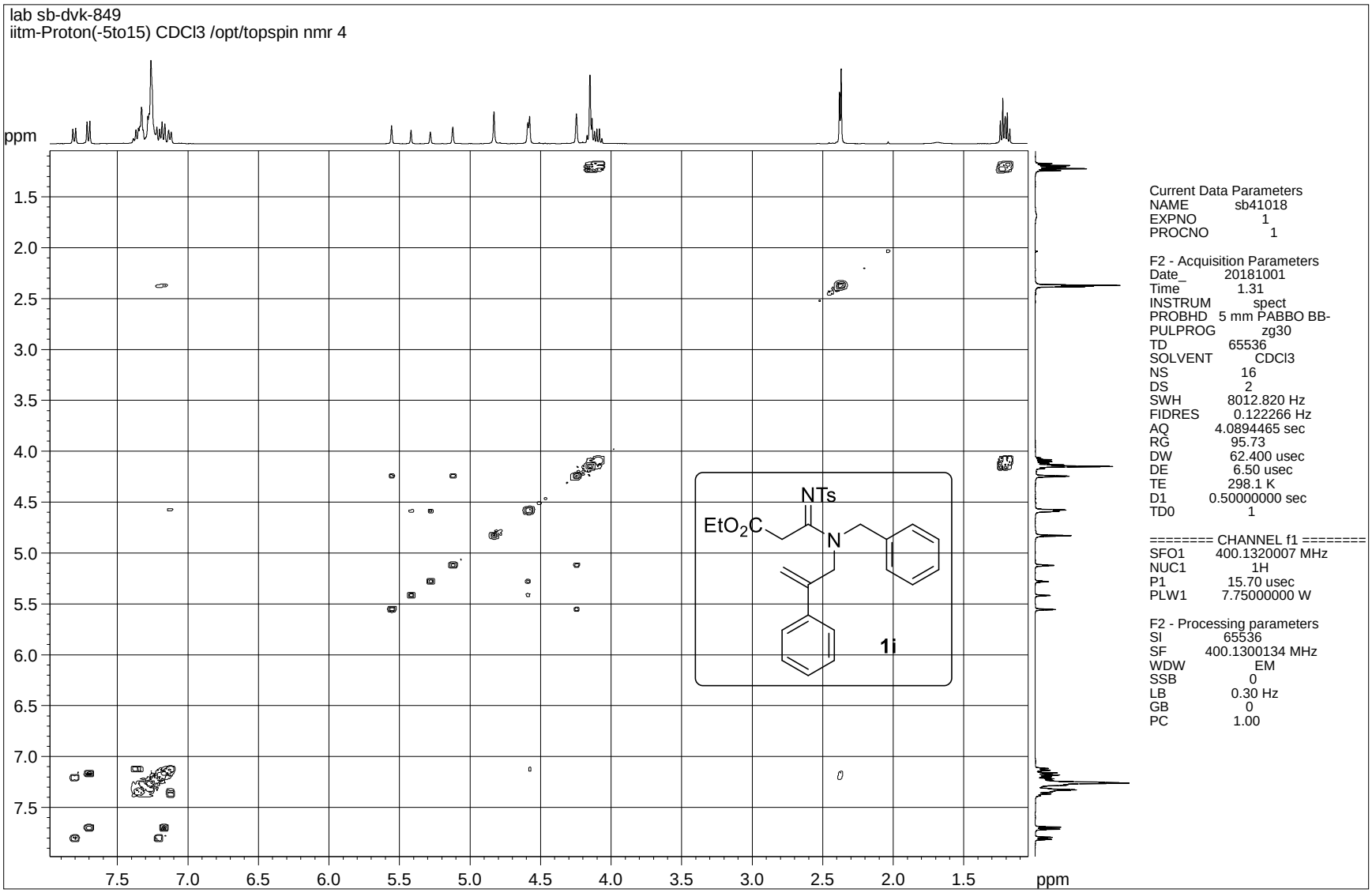
^{1}H NMR spectrum of compound 1i



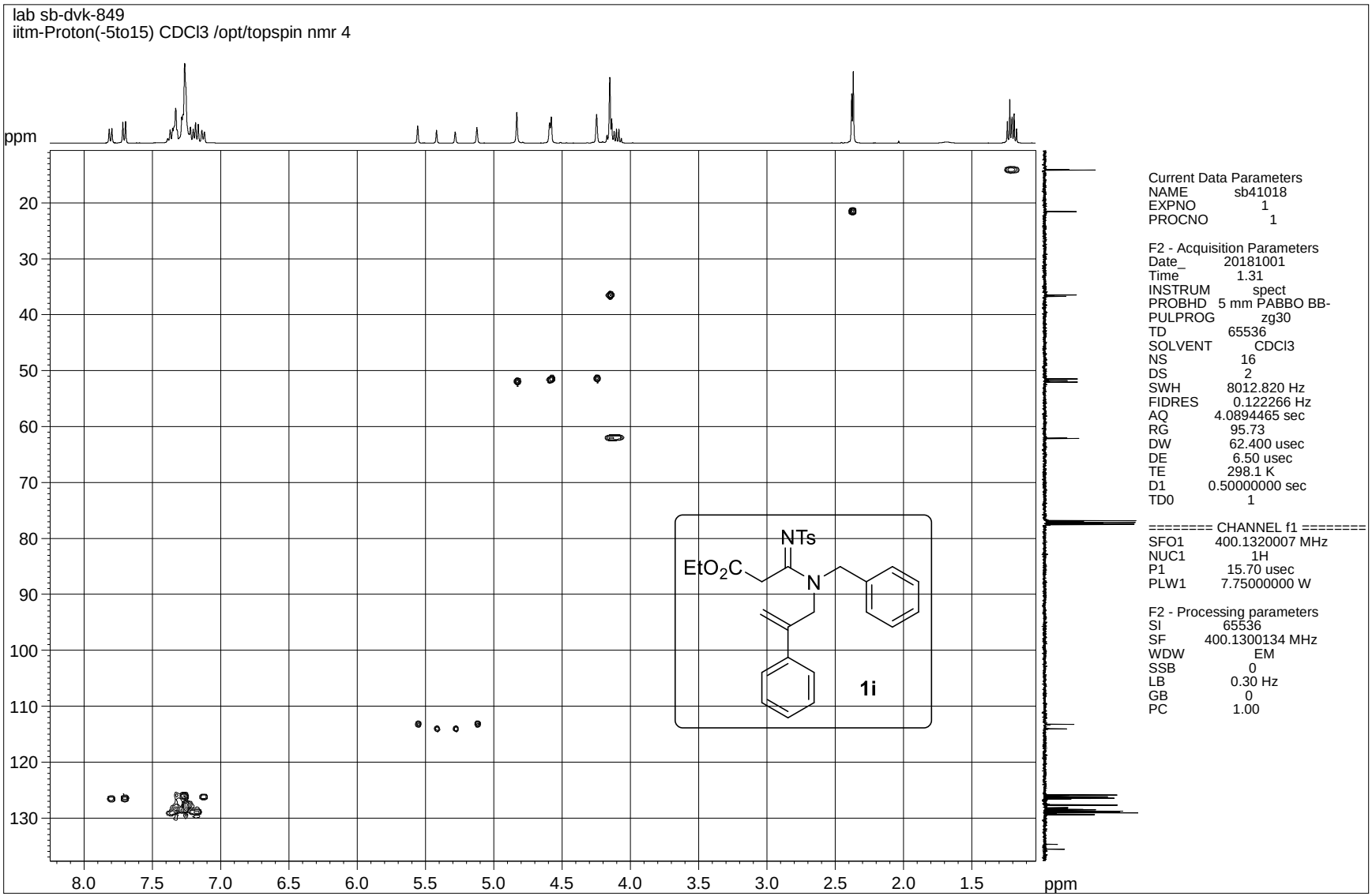
^{13}C NMR spectrum of compound 1i



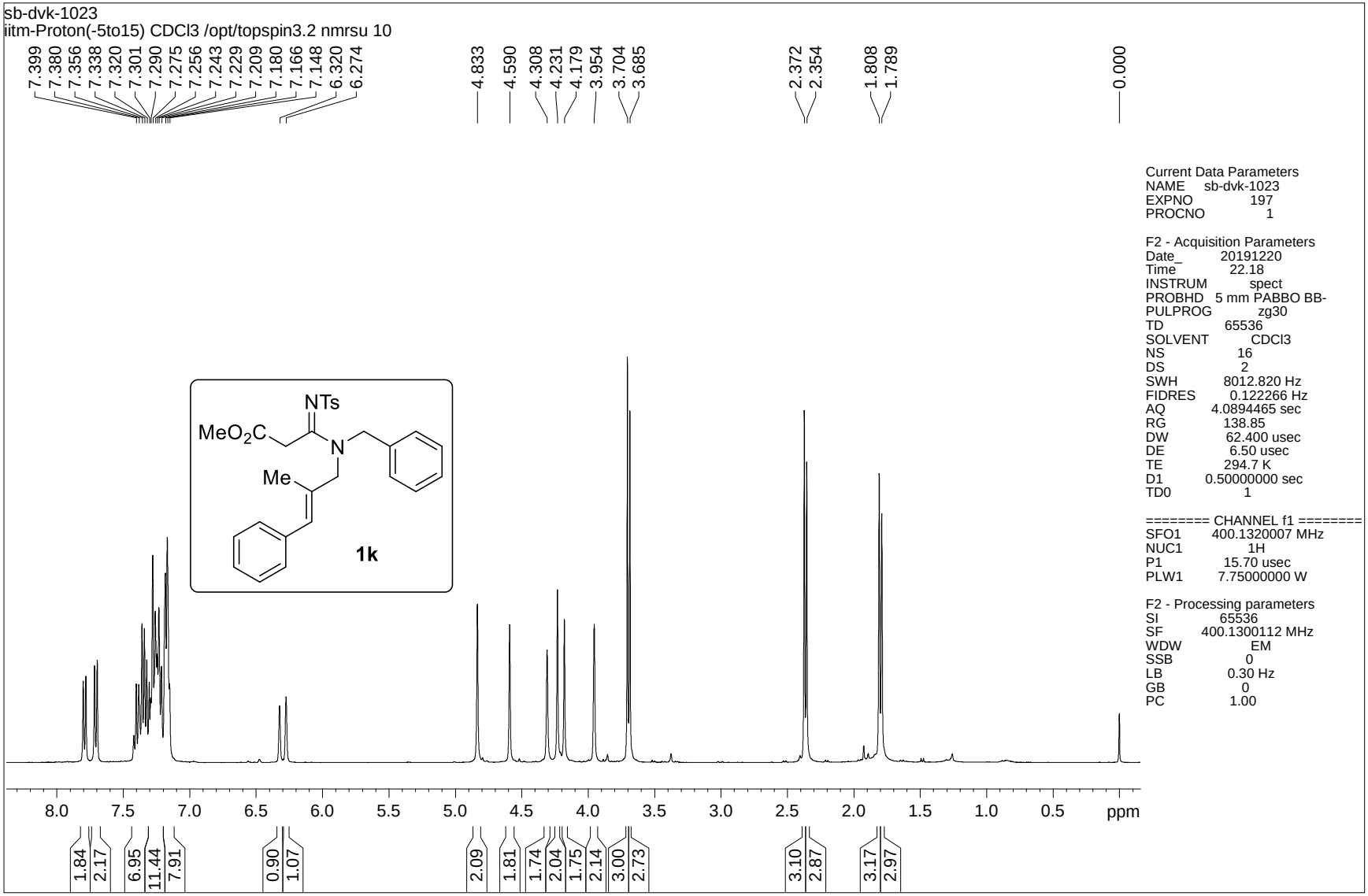
DEPT-135 NMR spectrum of compound 1i



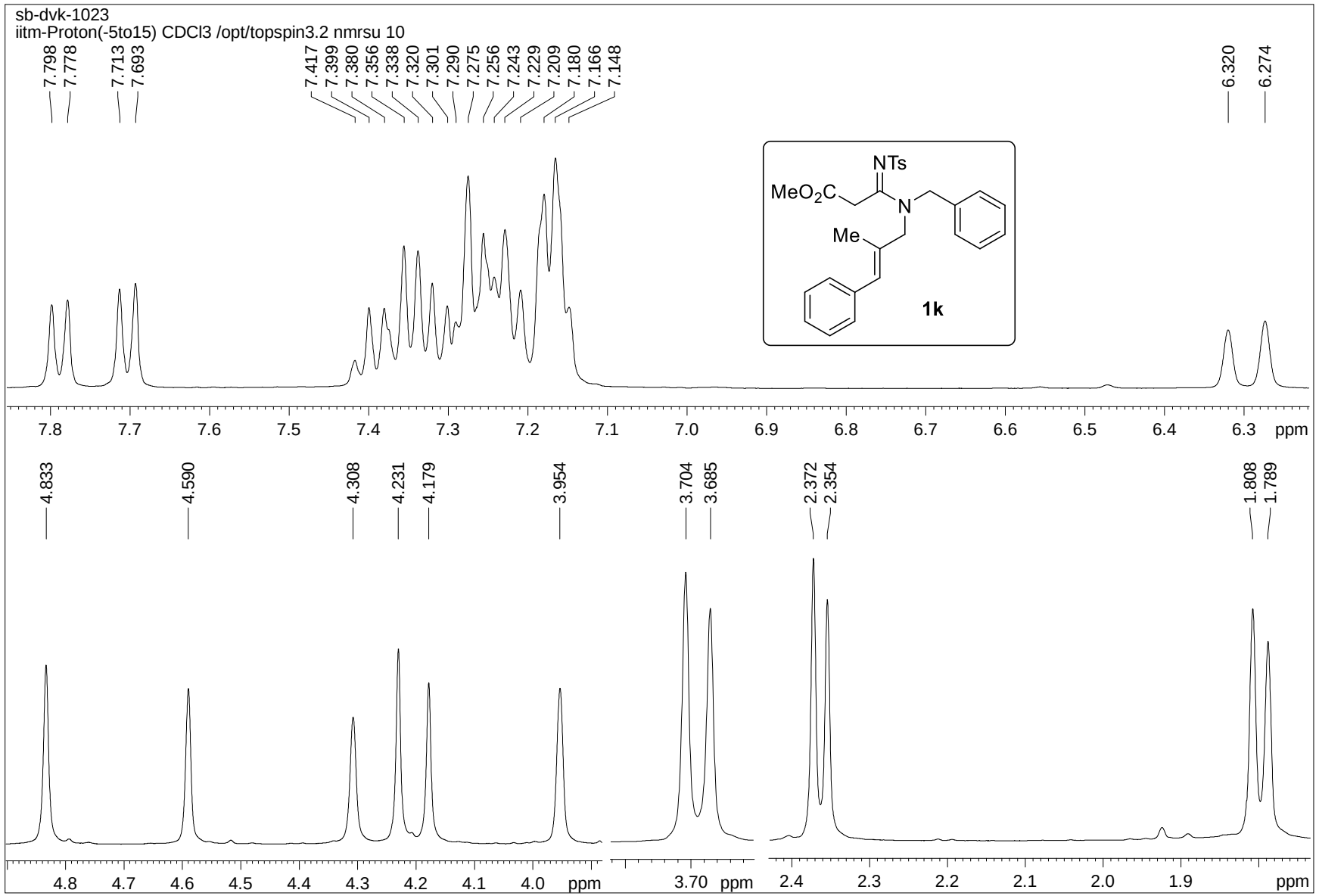
^{1}H-^{1}H COSY NMR spectrum of compound 1i



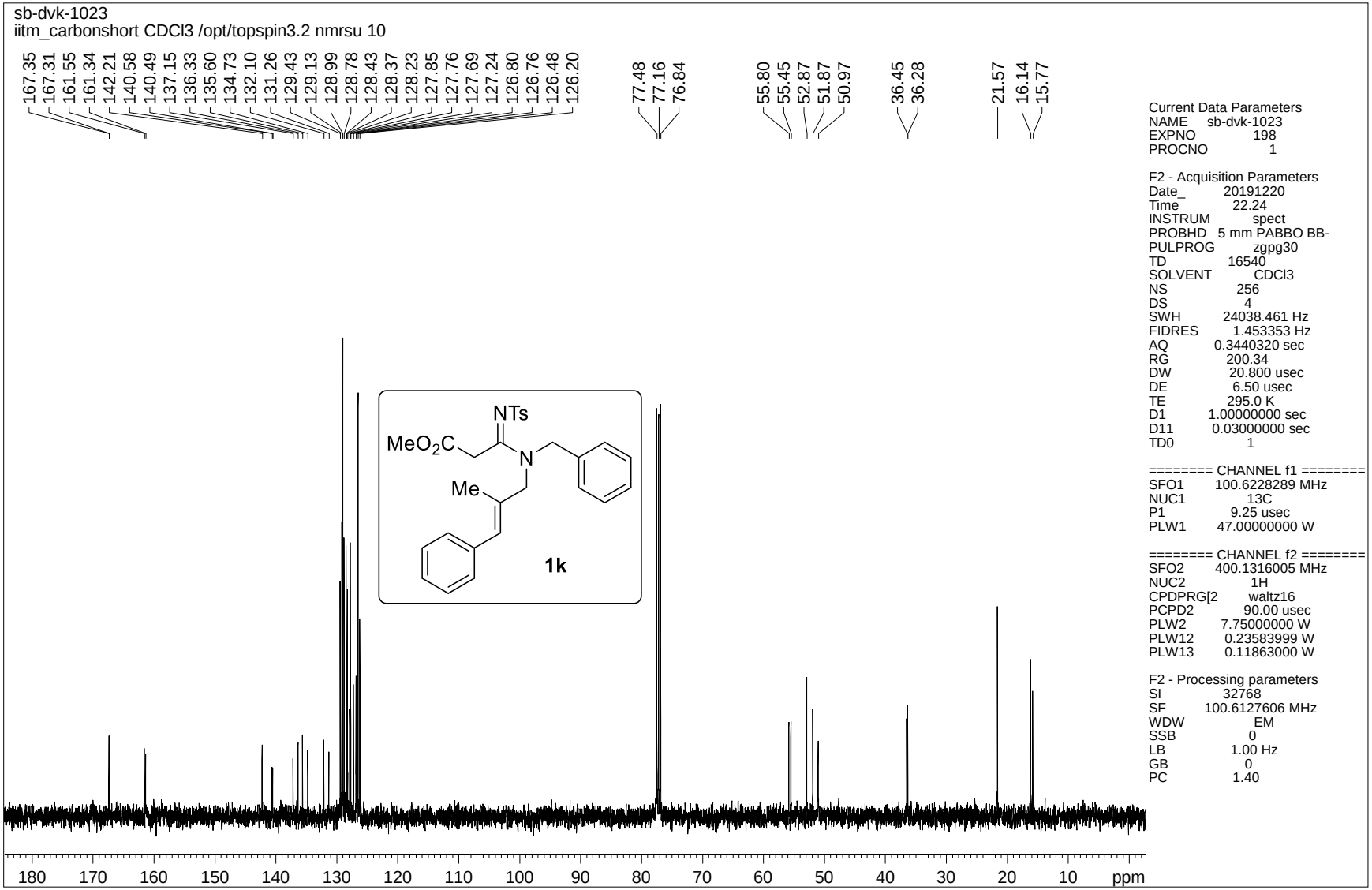
^{1}H-^{13}C HSQC NMR spectrum of compound 1i



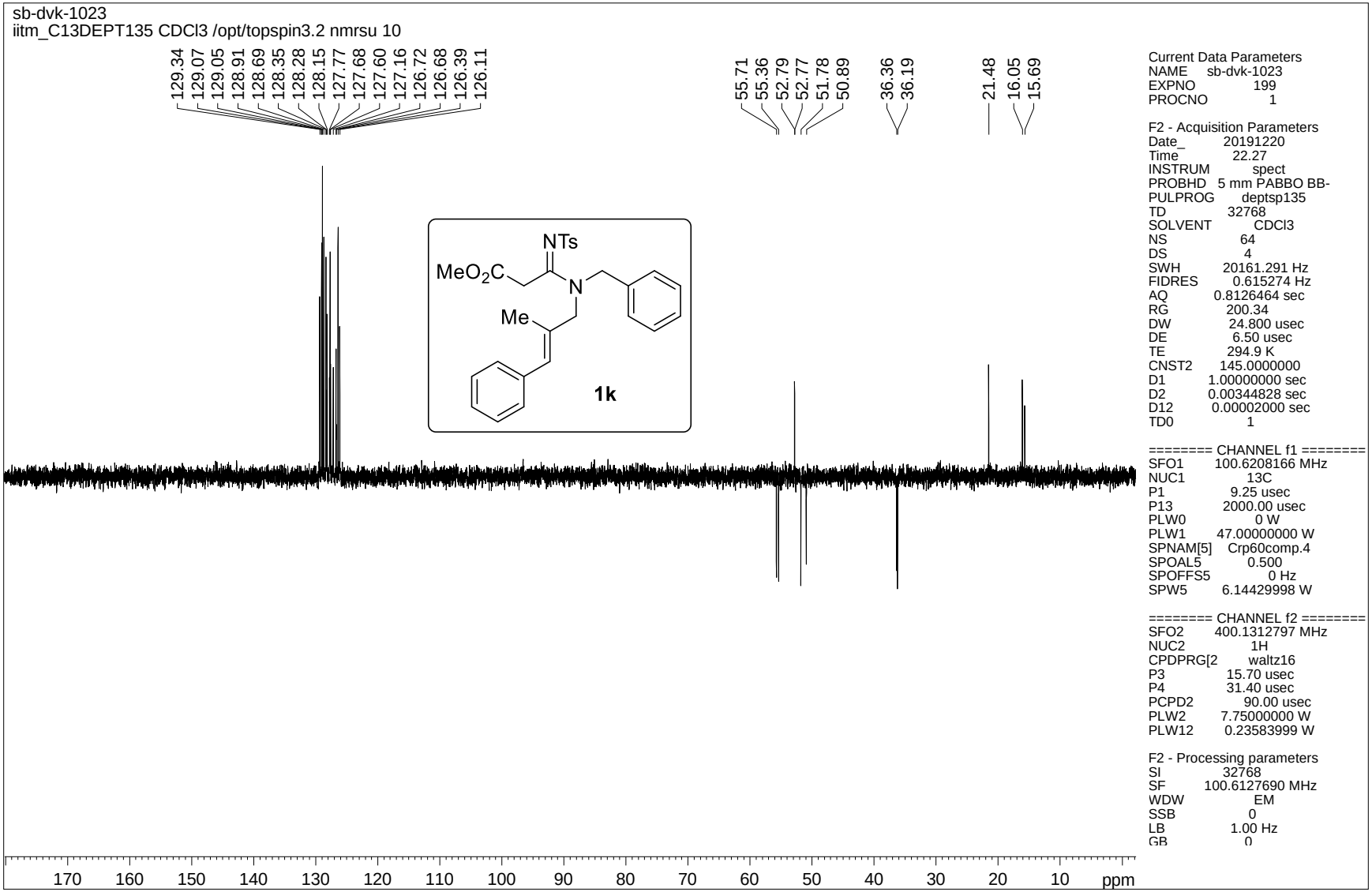
^{1}H NMR spectrum of compound 1k



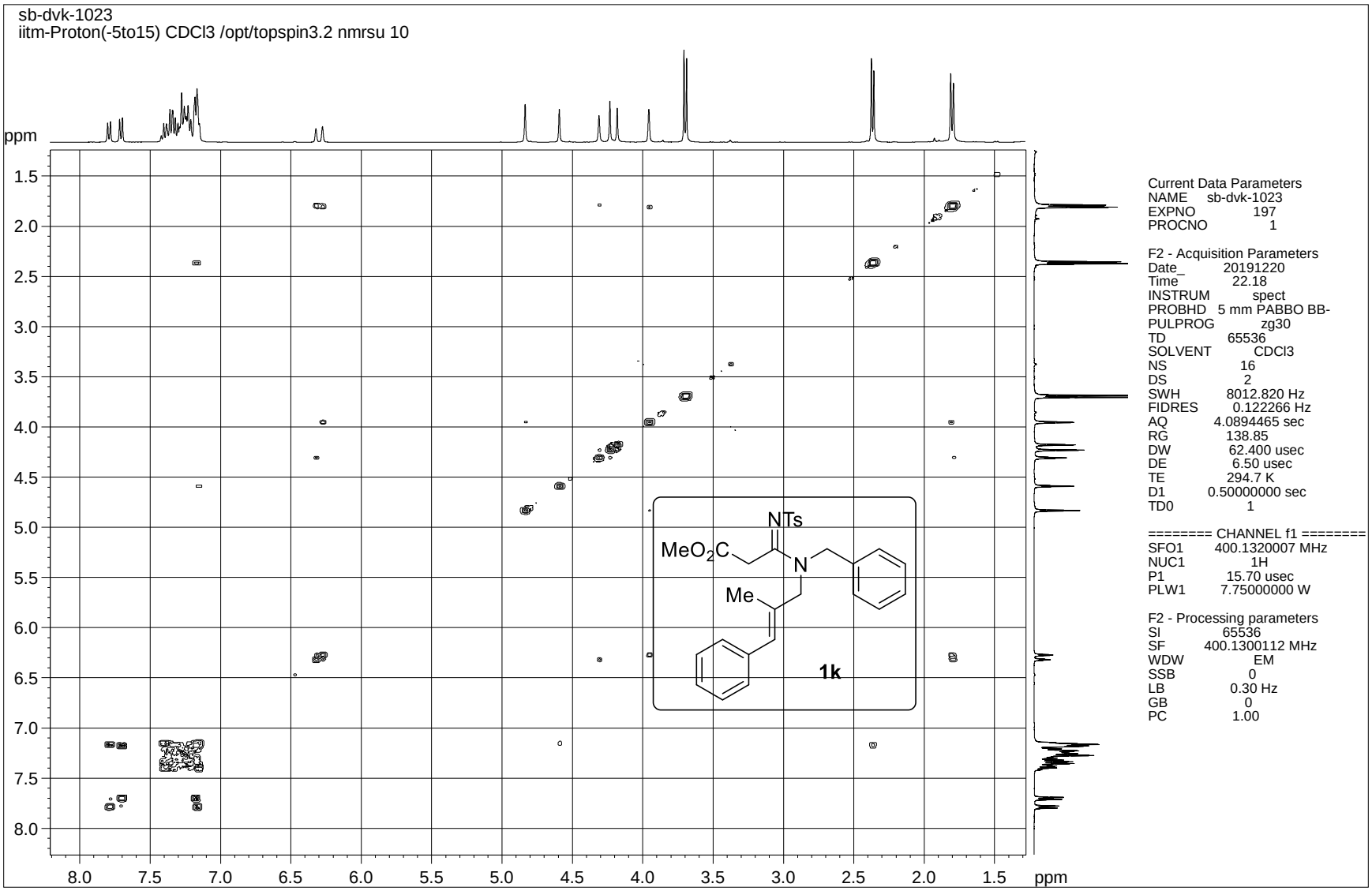
^{1}H NMR spectrum of compound 1k



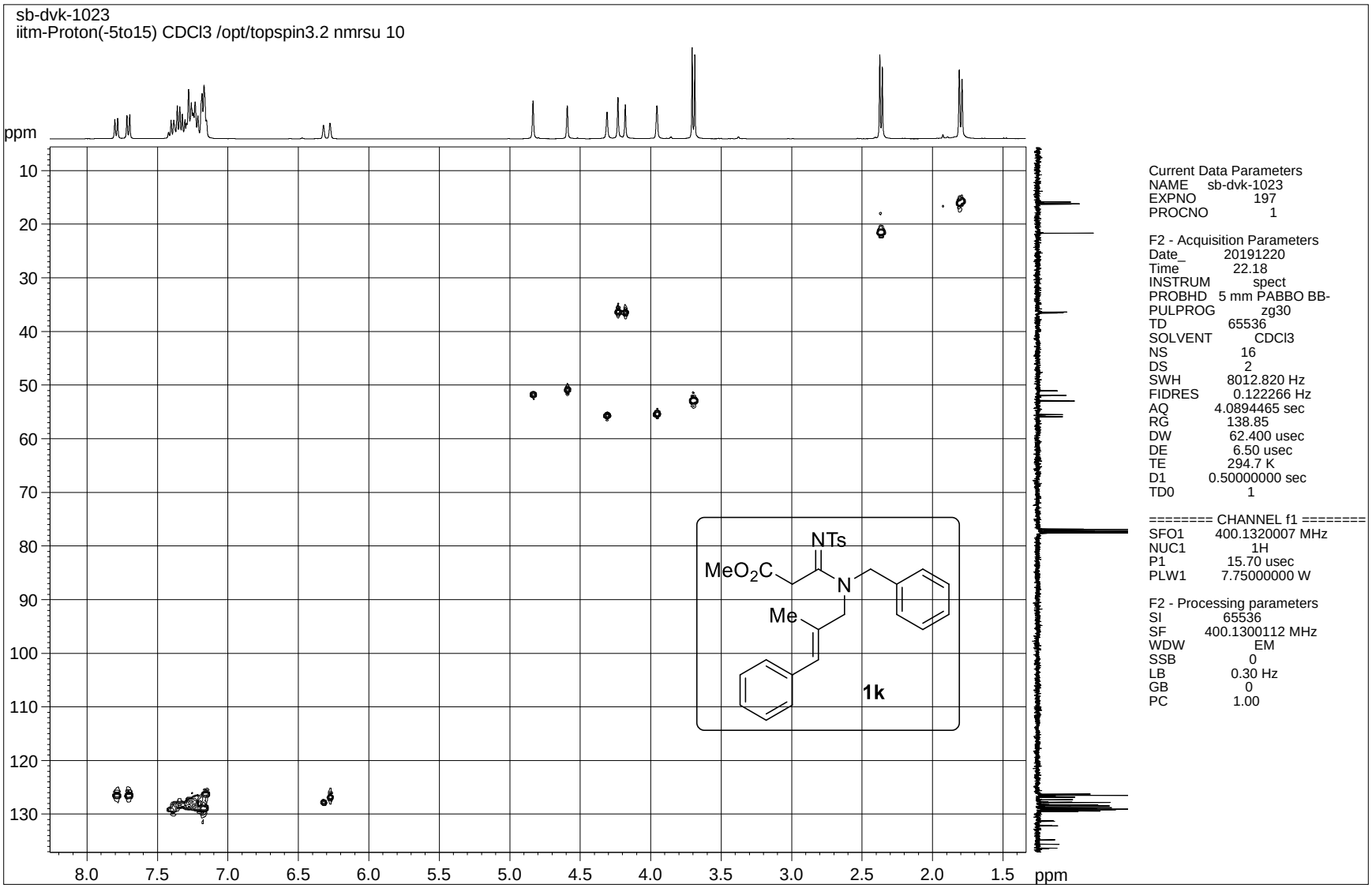
^{13}C NMR spectrum of compound 1k



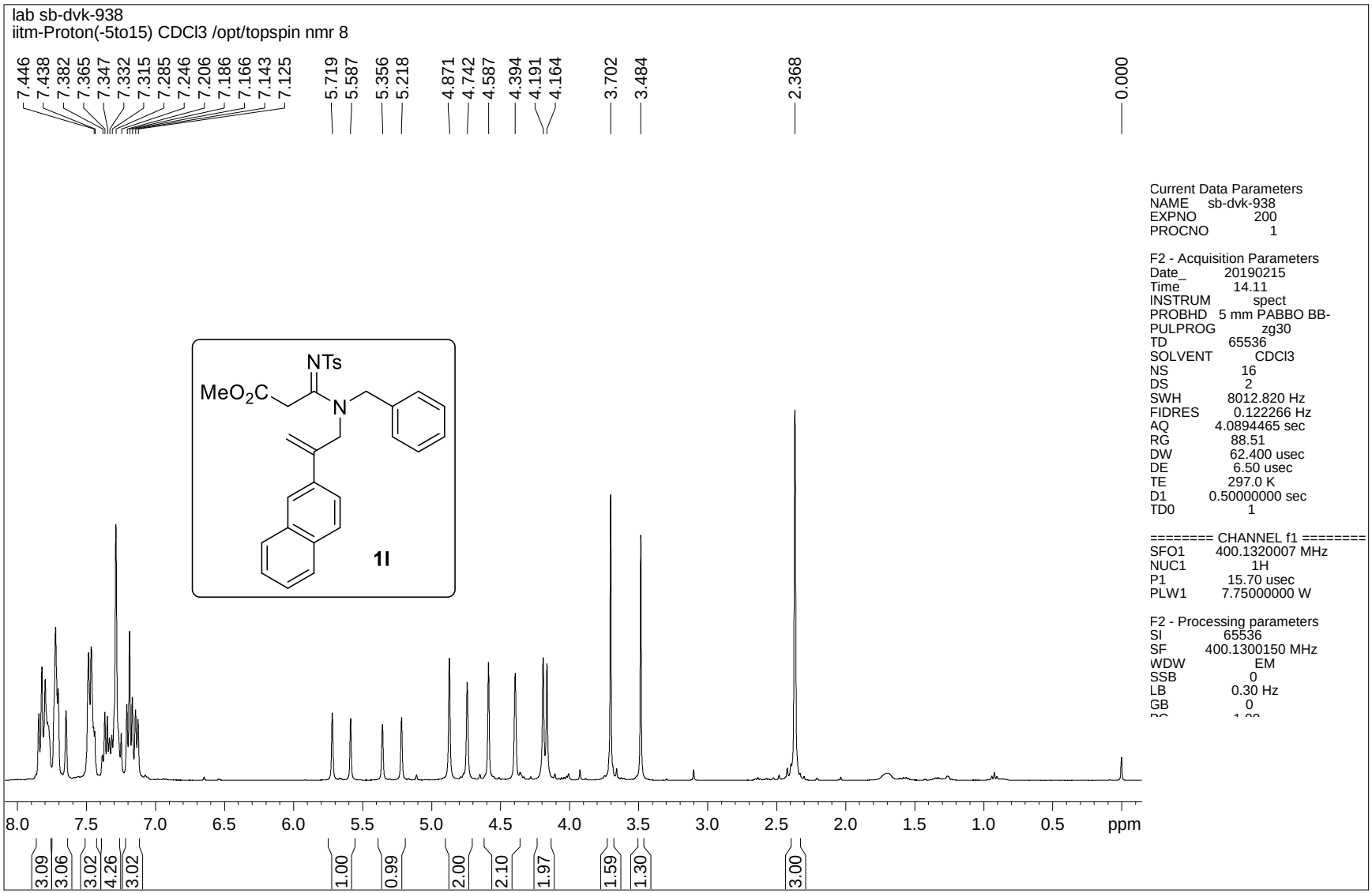
DEPT-135 NMR spectrum of compound 1k



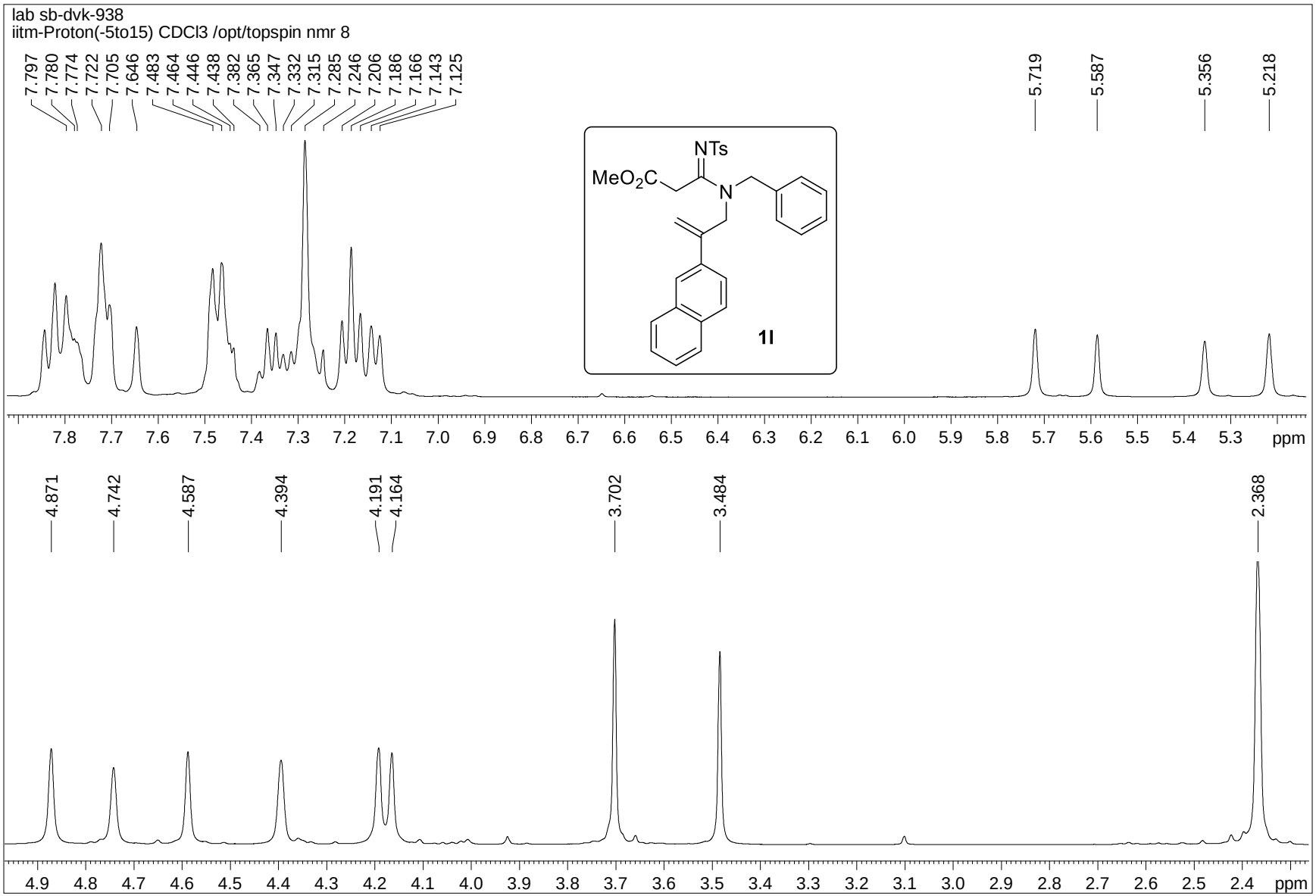
^{1}H-^{1}H COSY NMR spectrum of compound 1k



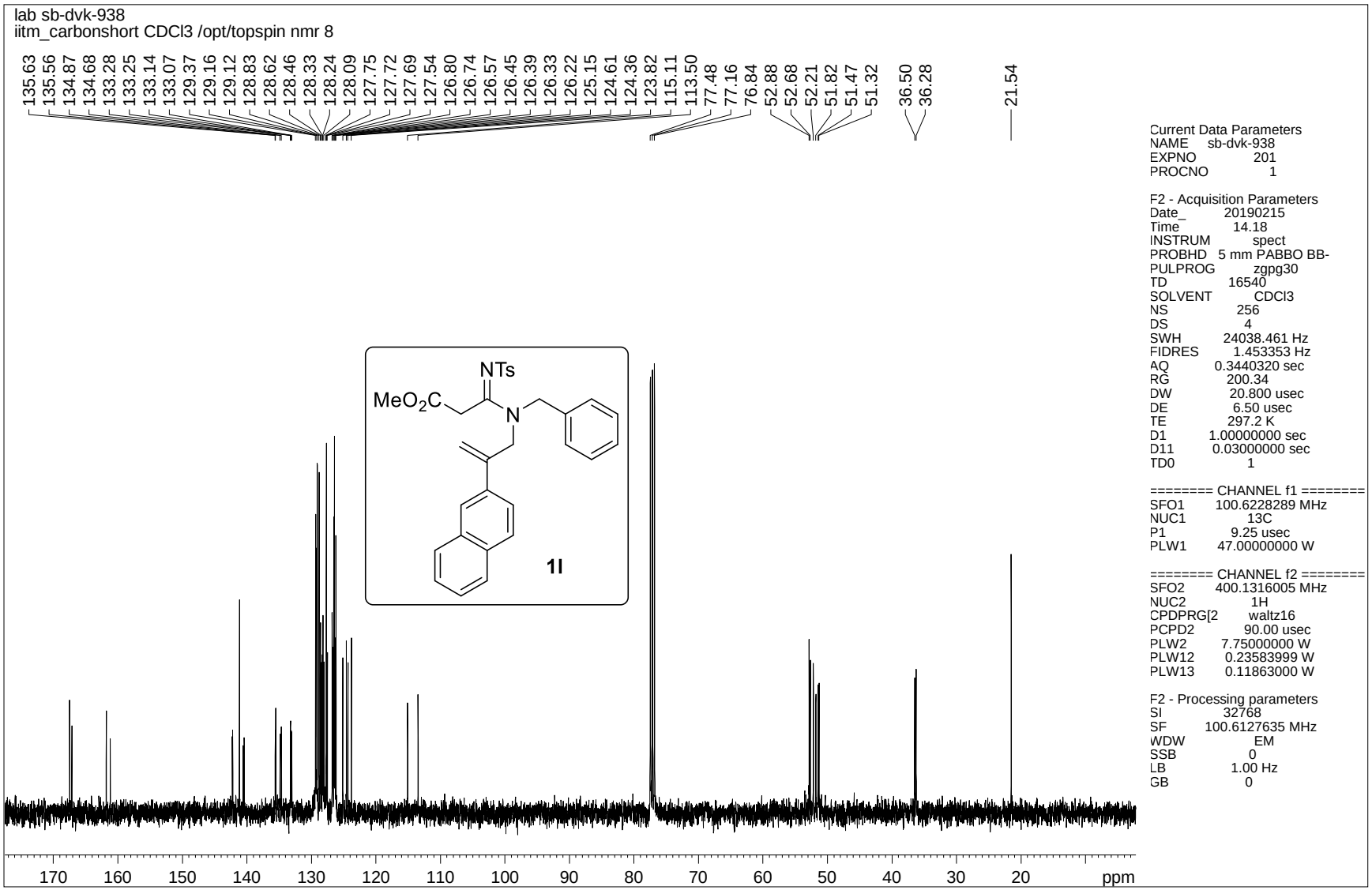
^{1}H-^{13}C HSQC NMR spectrum of compound 1k



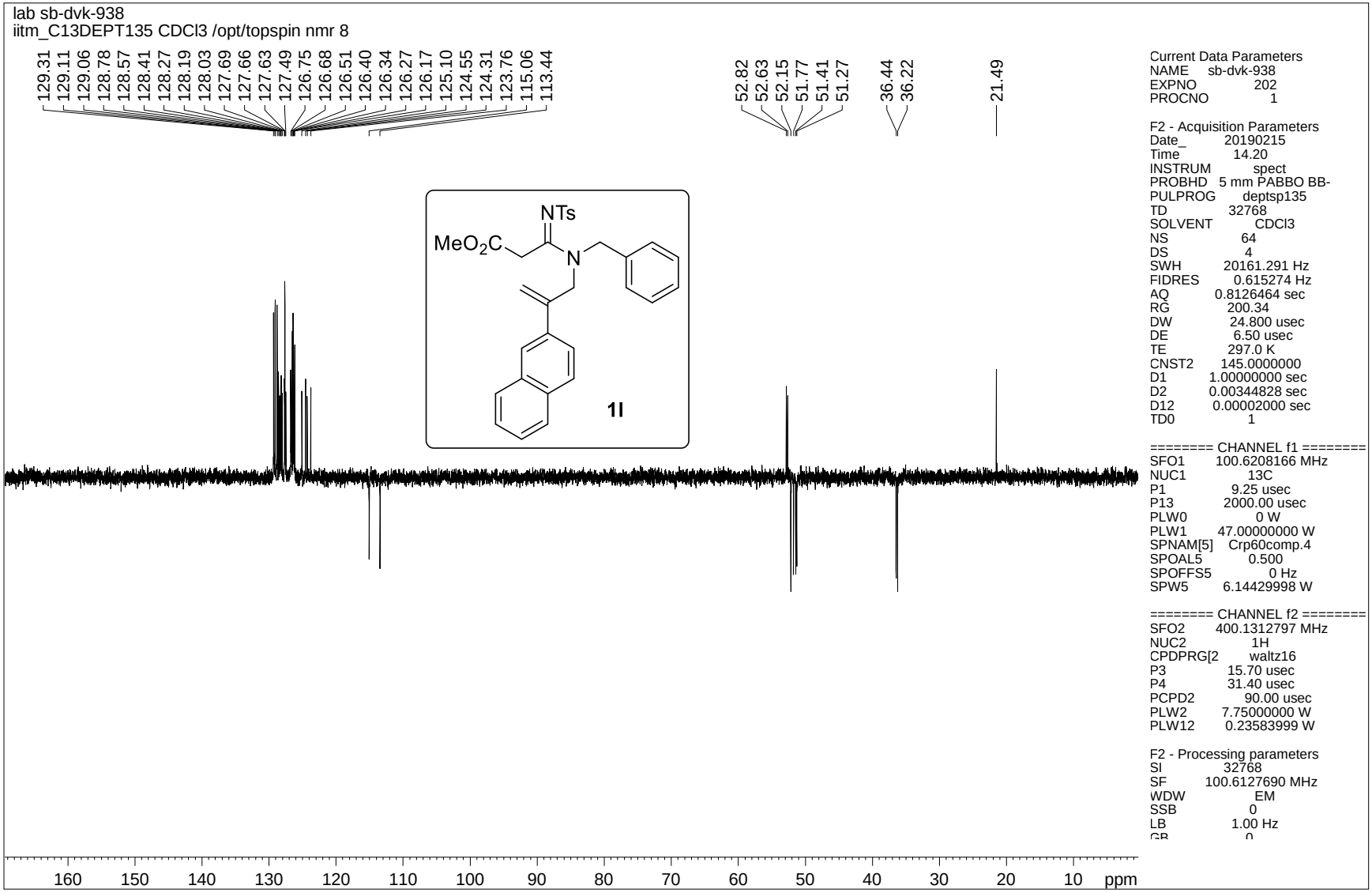
^{1}H NMR spectrum of compound 1l



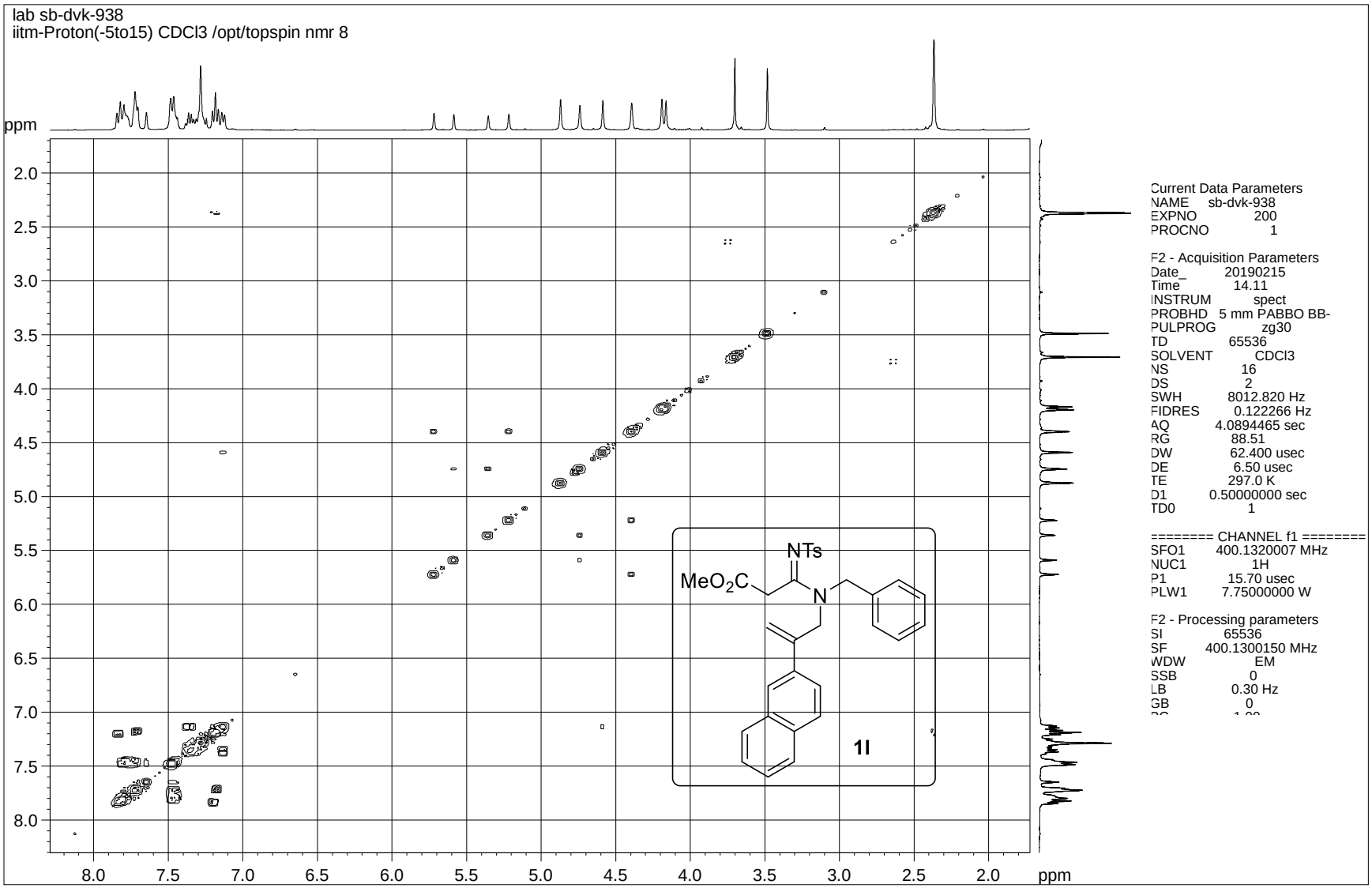
^{1}H NMR spectrum of compound 1l



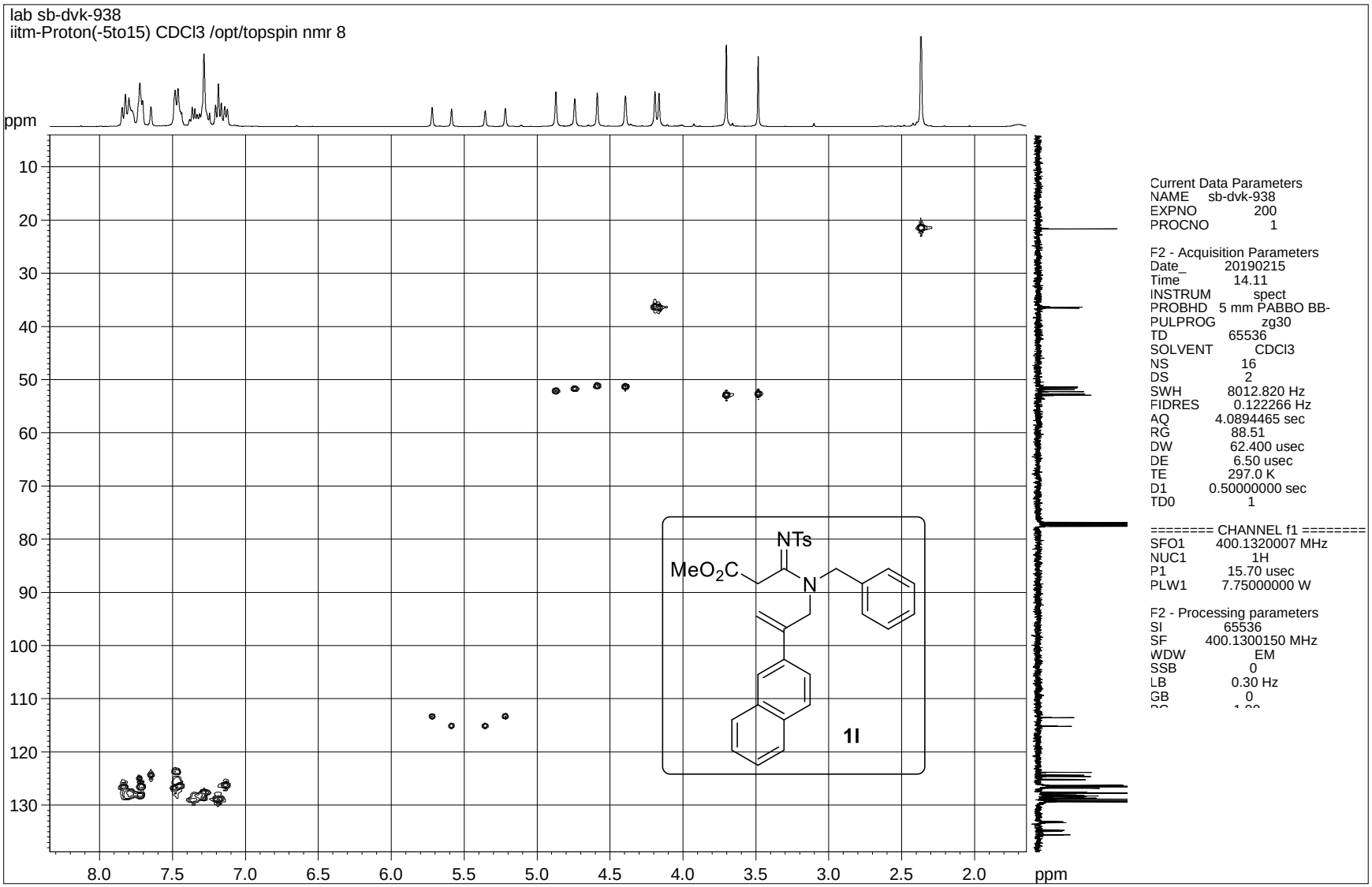
^{13}C NMR spectrum of compound 1l



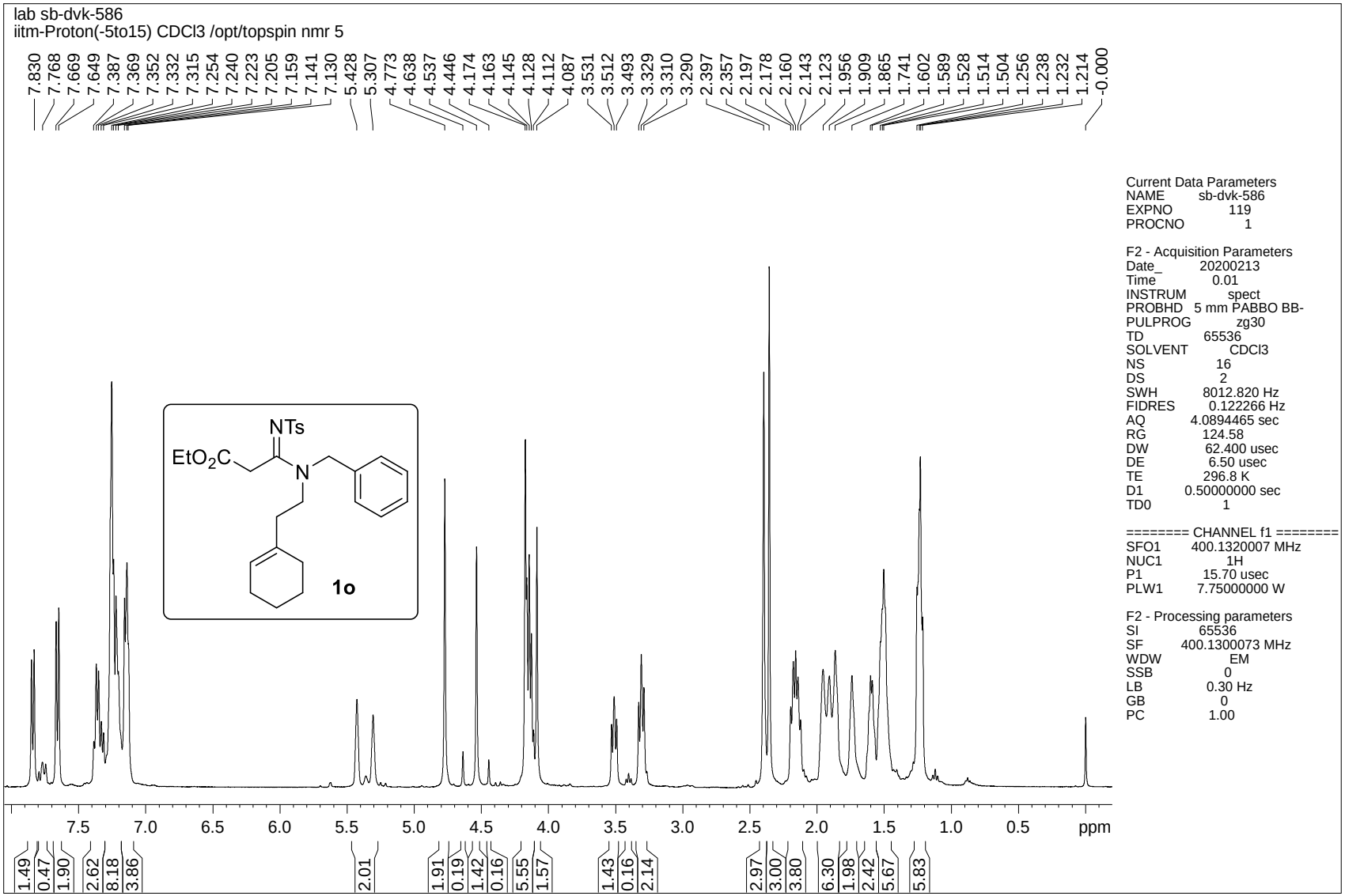
DEPT-135 NMR spectrum of compound 1l



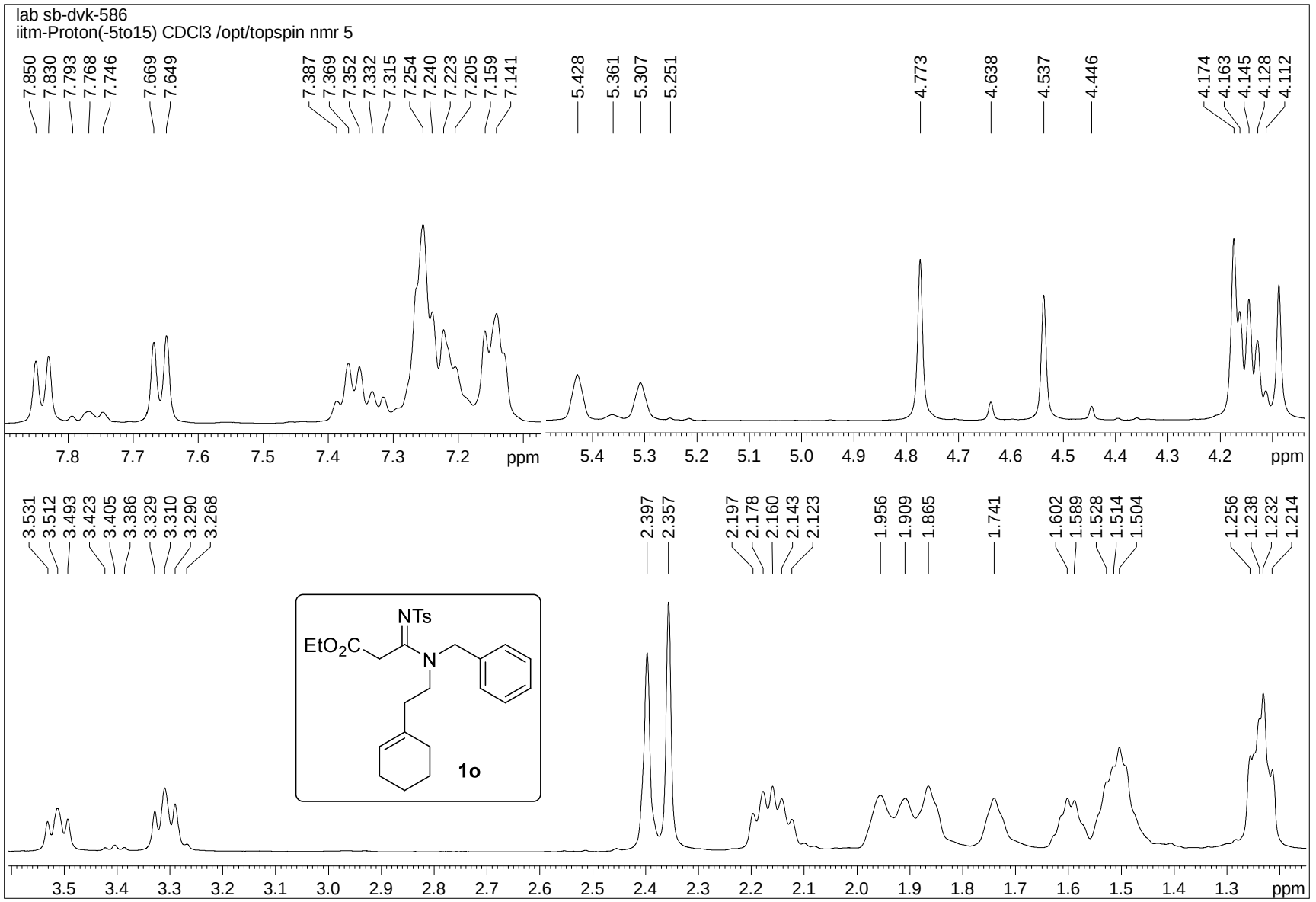
^{1}H-^{1}H COSY NMR spectrum of compound 1l



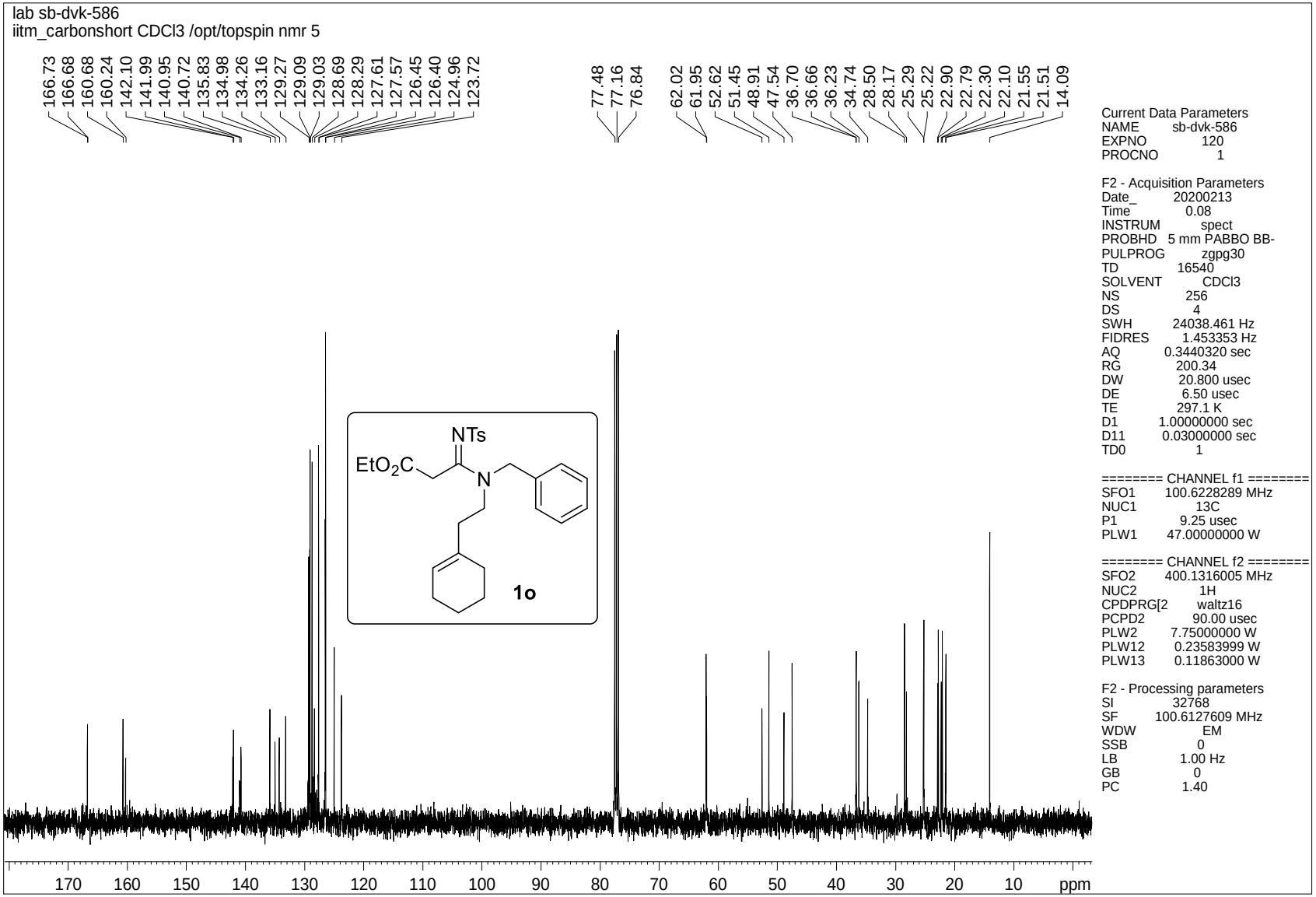
^{1}H-^{13}C HSQC NMR spectrum of compound 1l



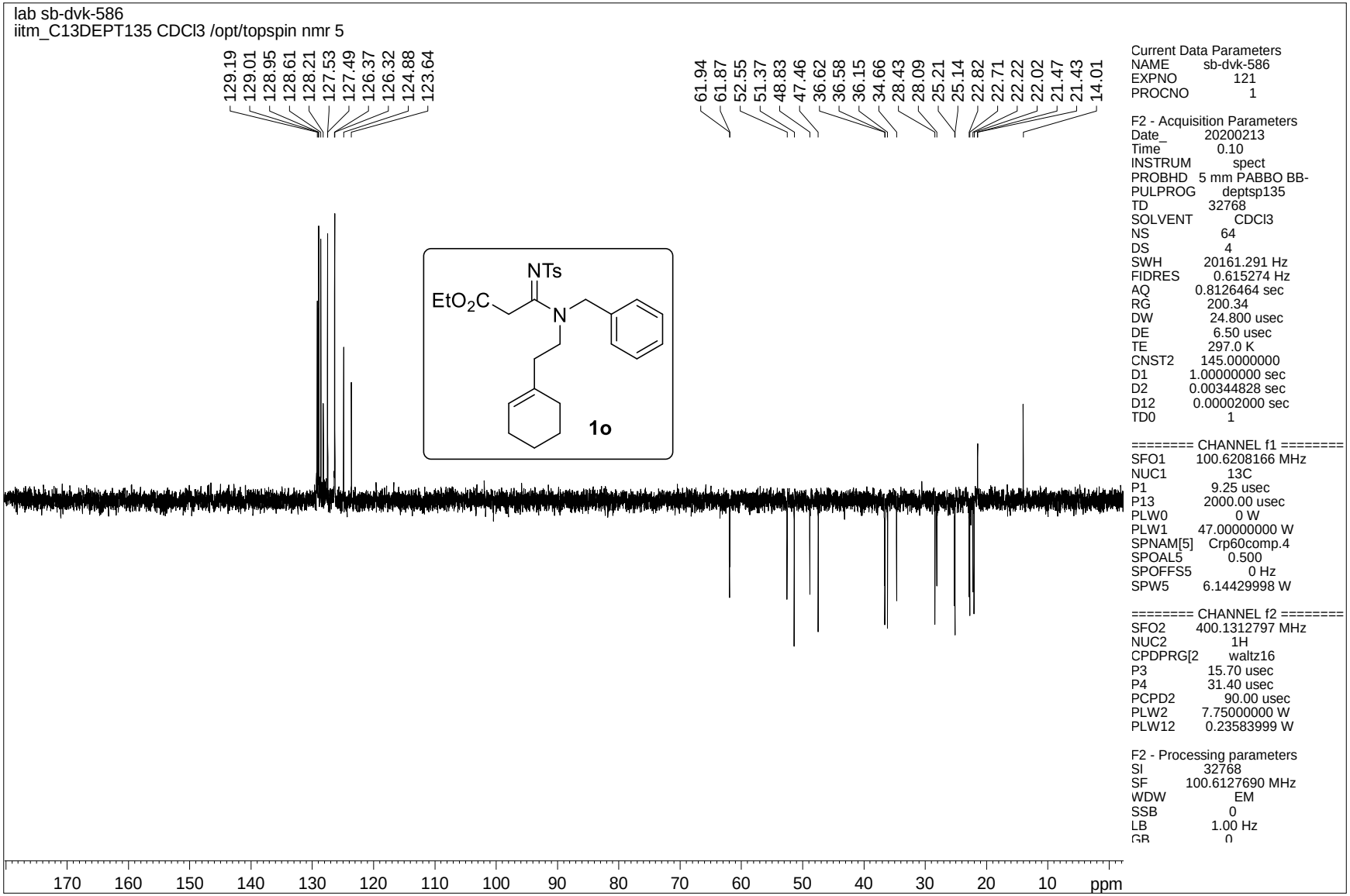
^{1}H NMR spectrum of compound 1o



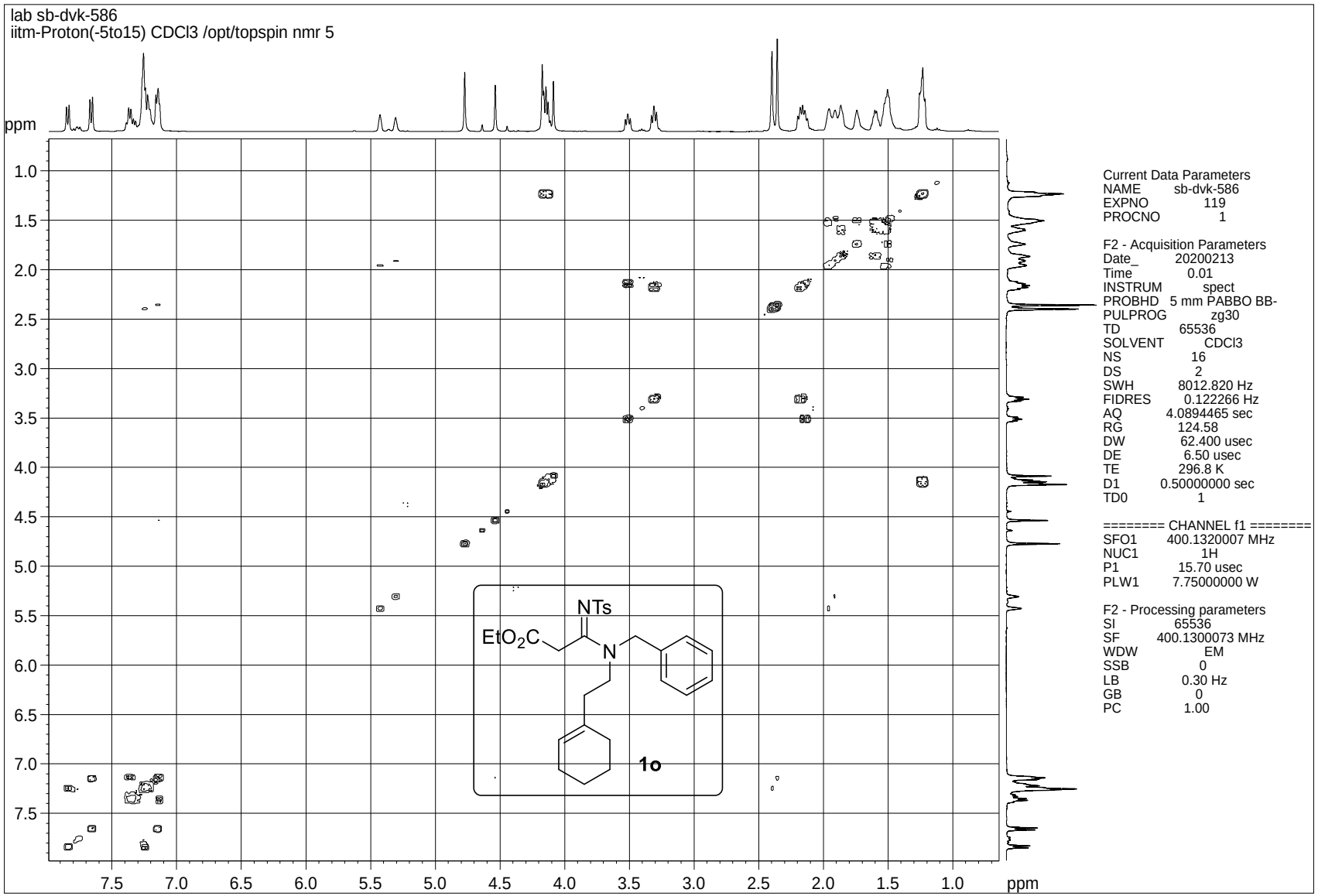
^{1}H NMR spectrum of compound 1o



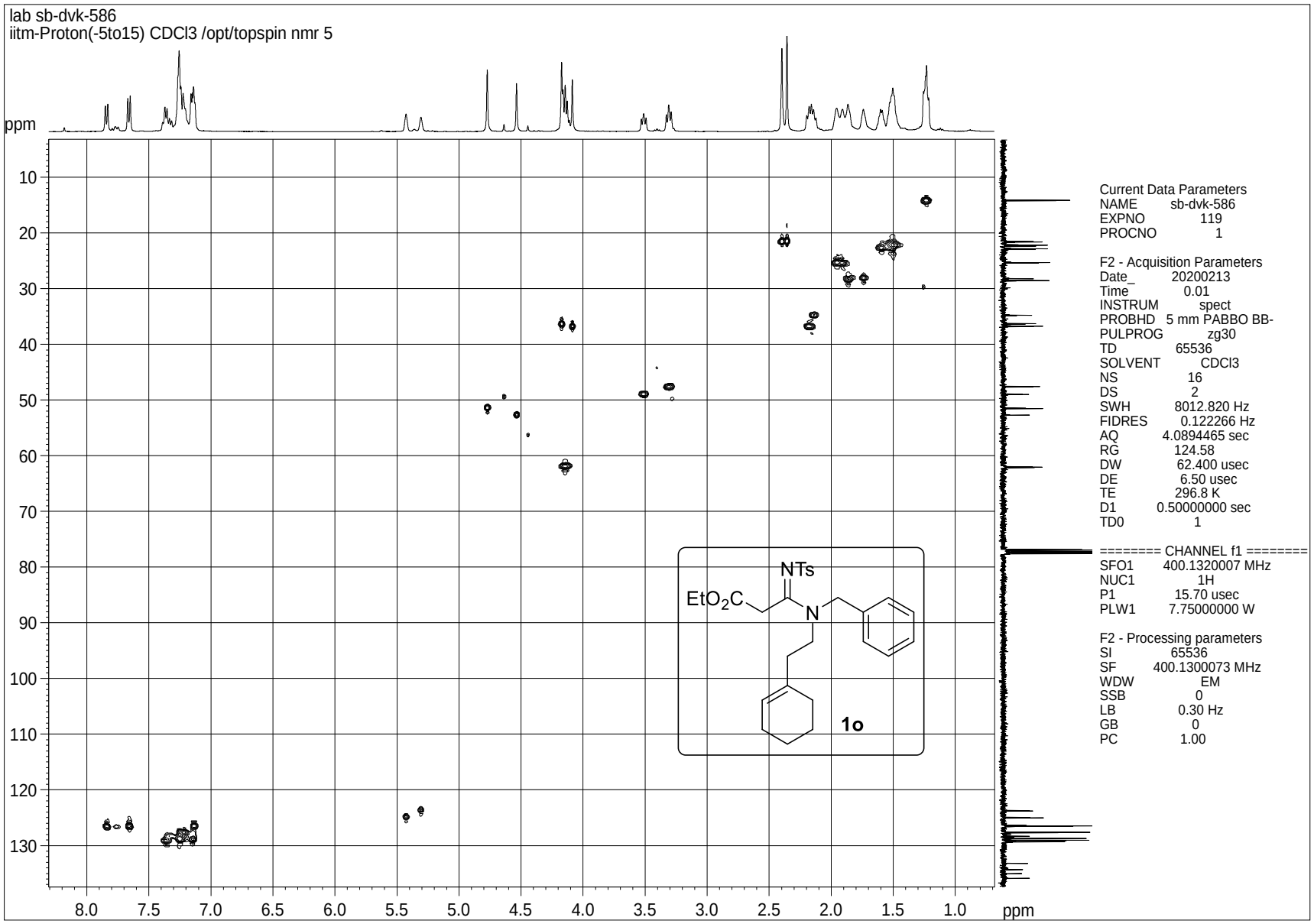
^{13}C NMR spectrum of compound 1o



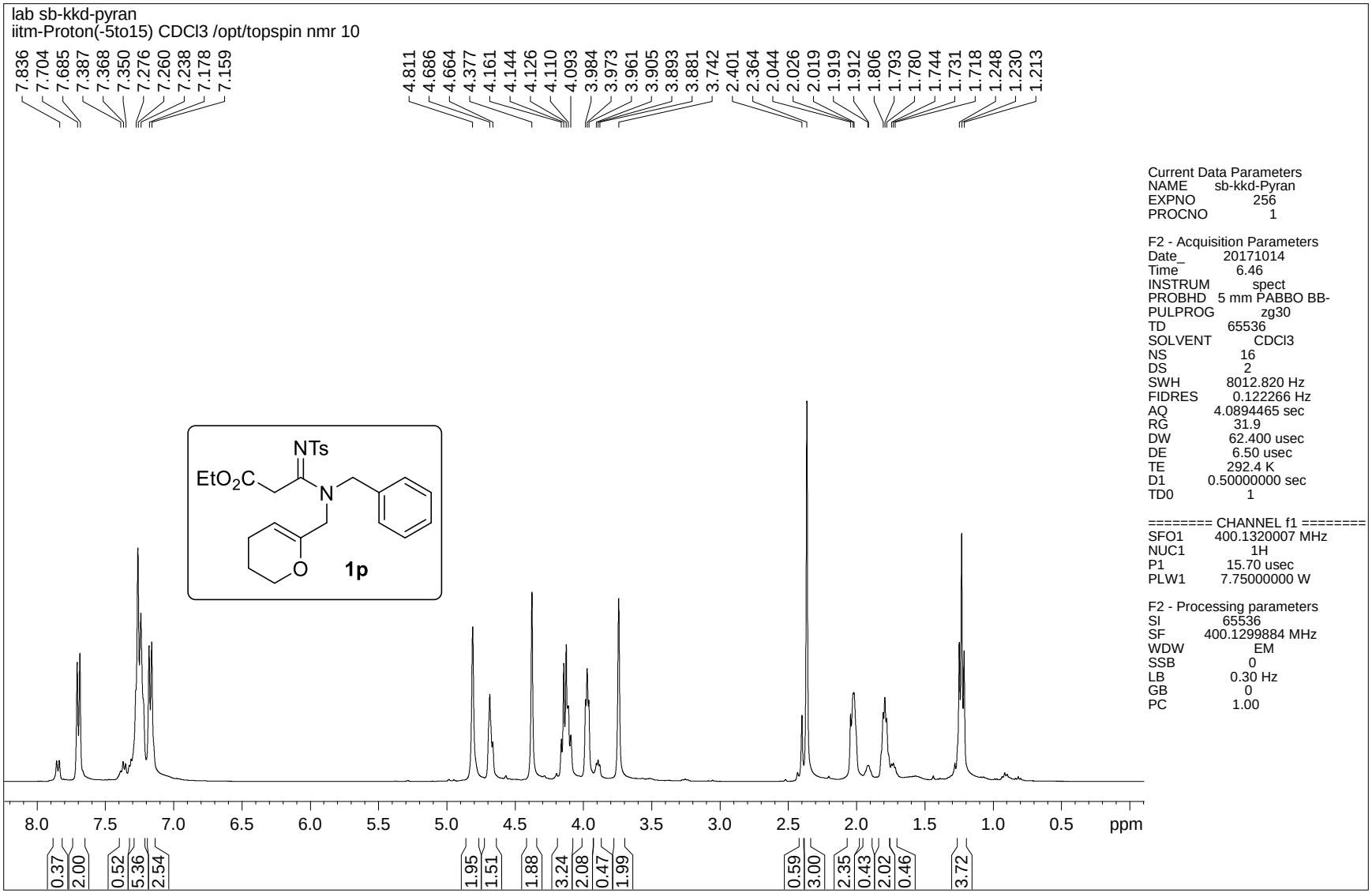
DEPT-135 NMR spectrum of compound 1o



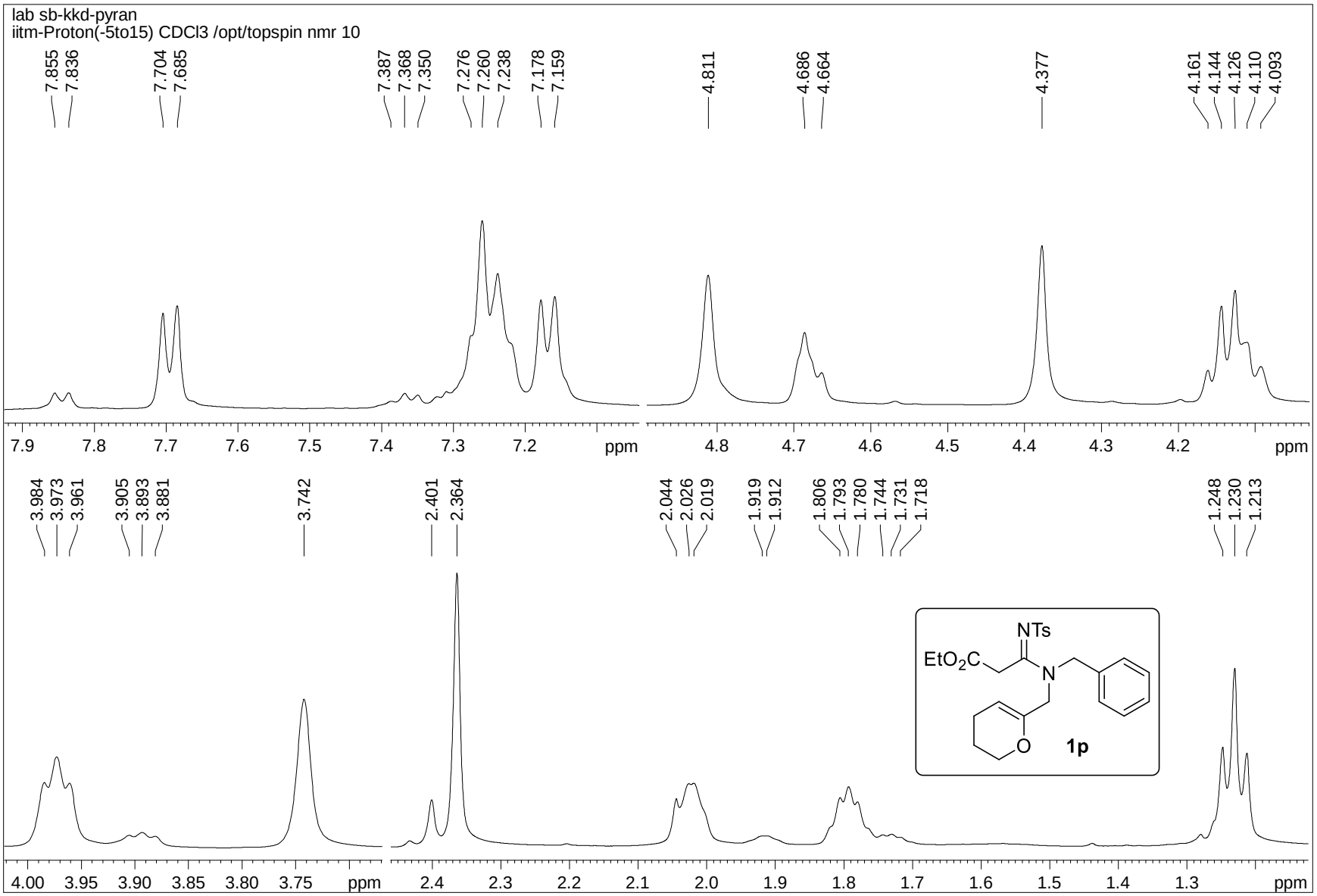
^{1}H-^{1}H COSY NMR spectrum of compound 1o



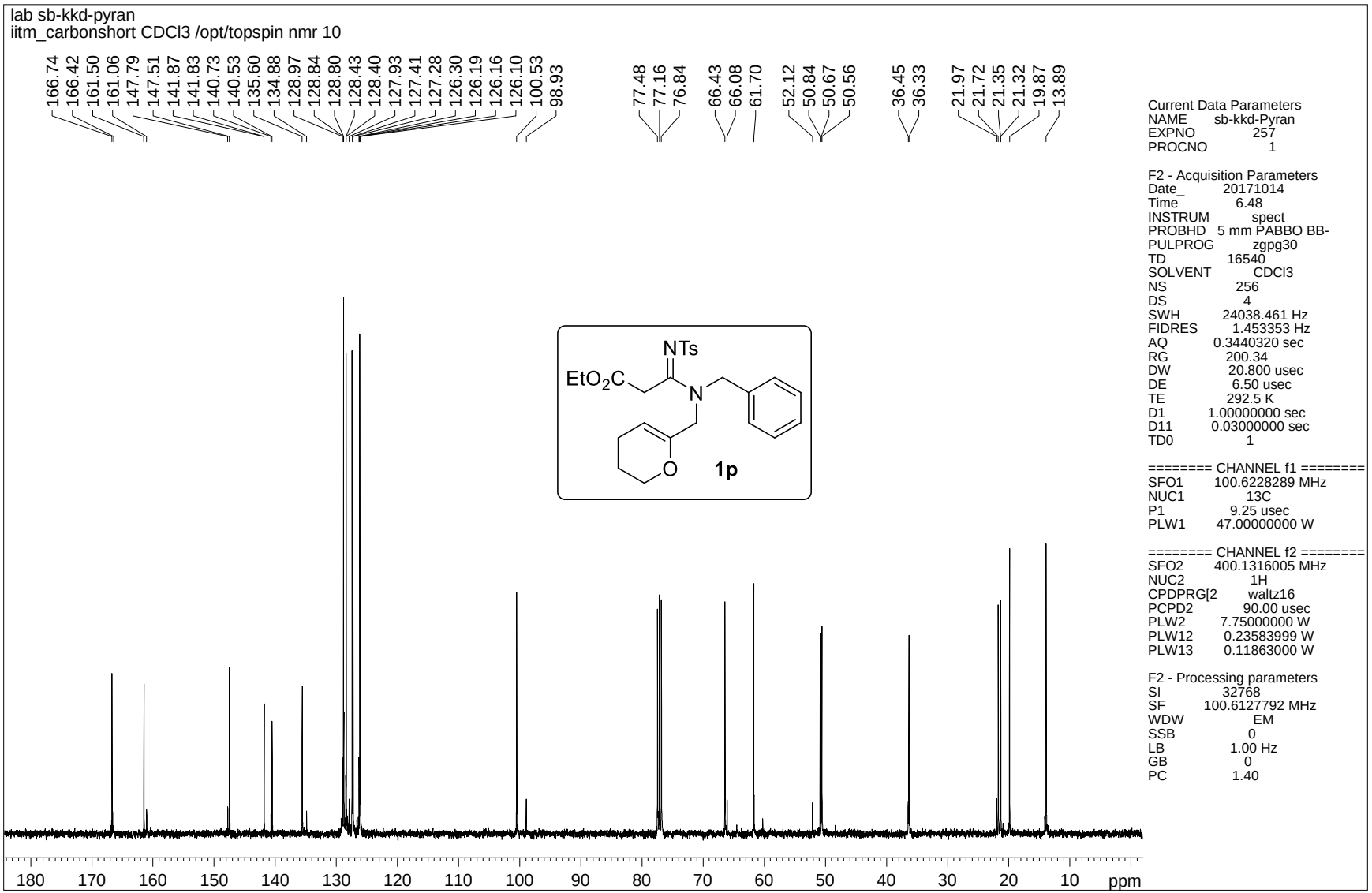
^{1}H-^{13}C HSQC NMR spectrum of compound 1o



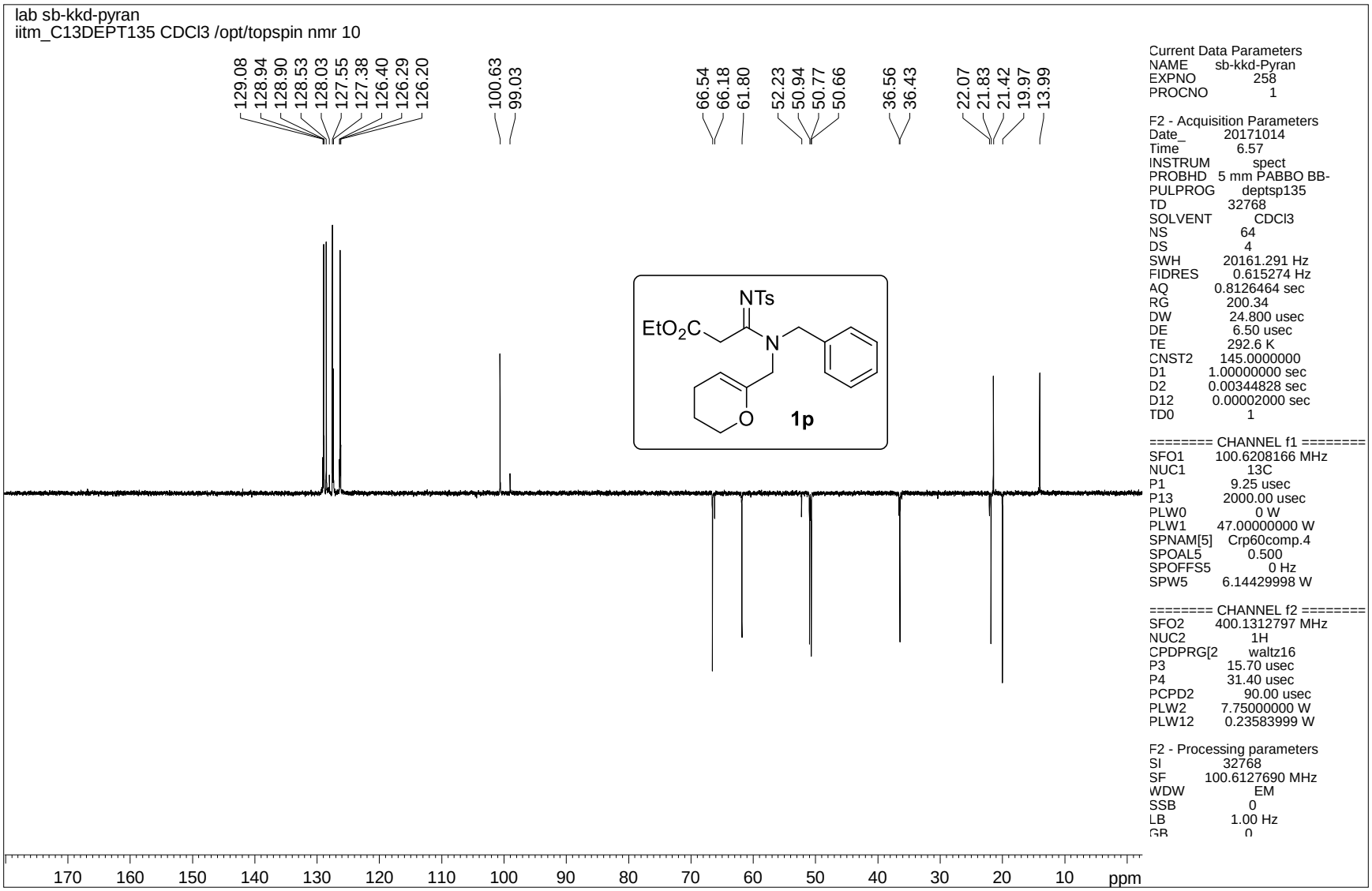
^{1}H NMR spectrum of compound 1p



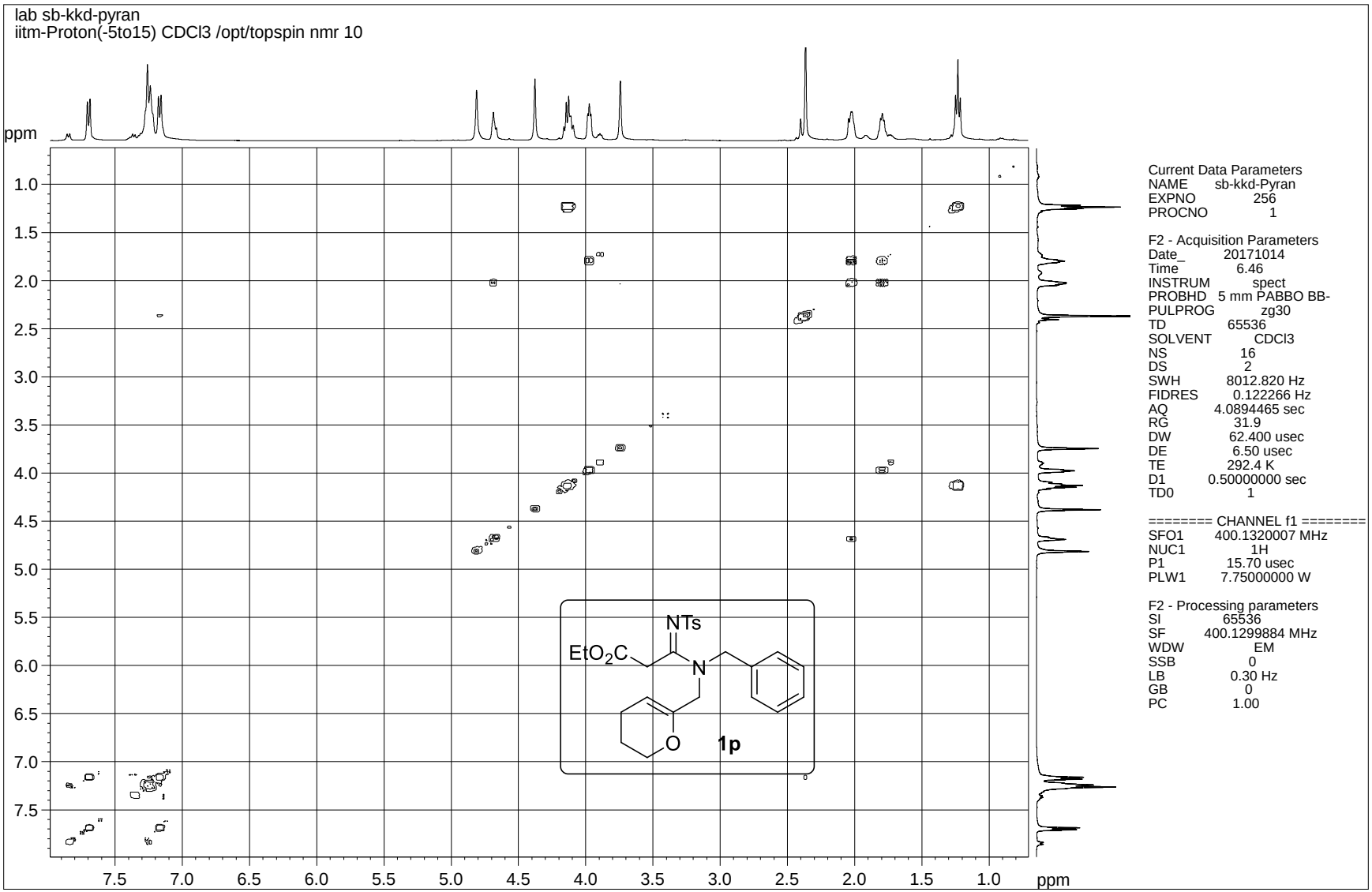
^{1}H NMR spectrum of compound 1p



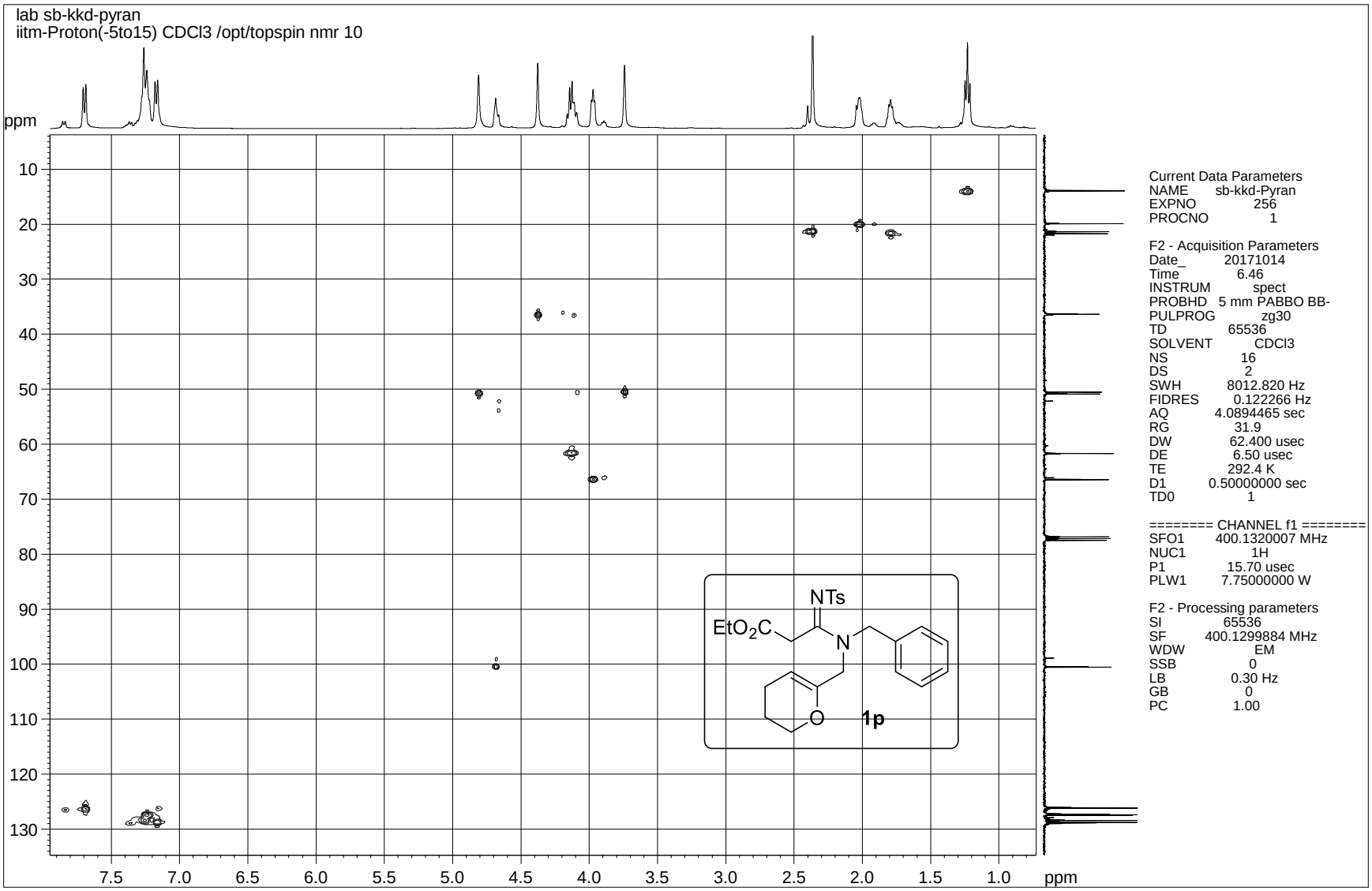
^{13}C NMR spectrum of compound 1p



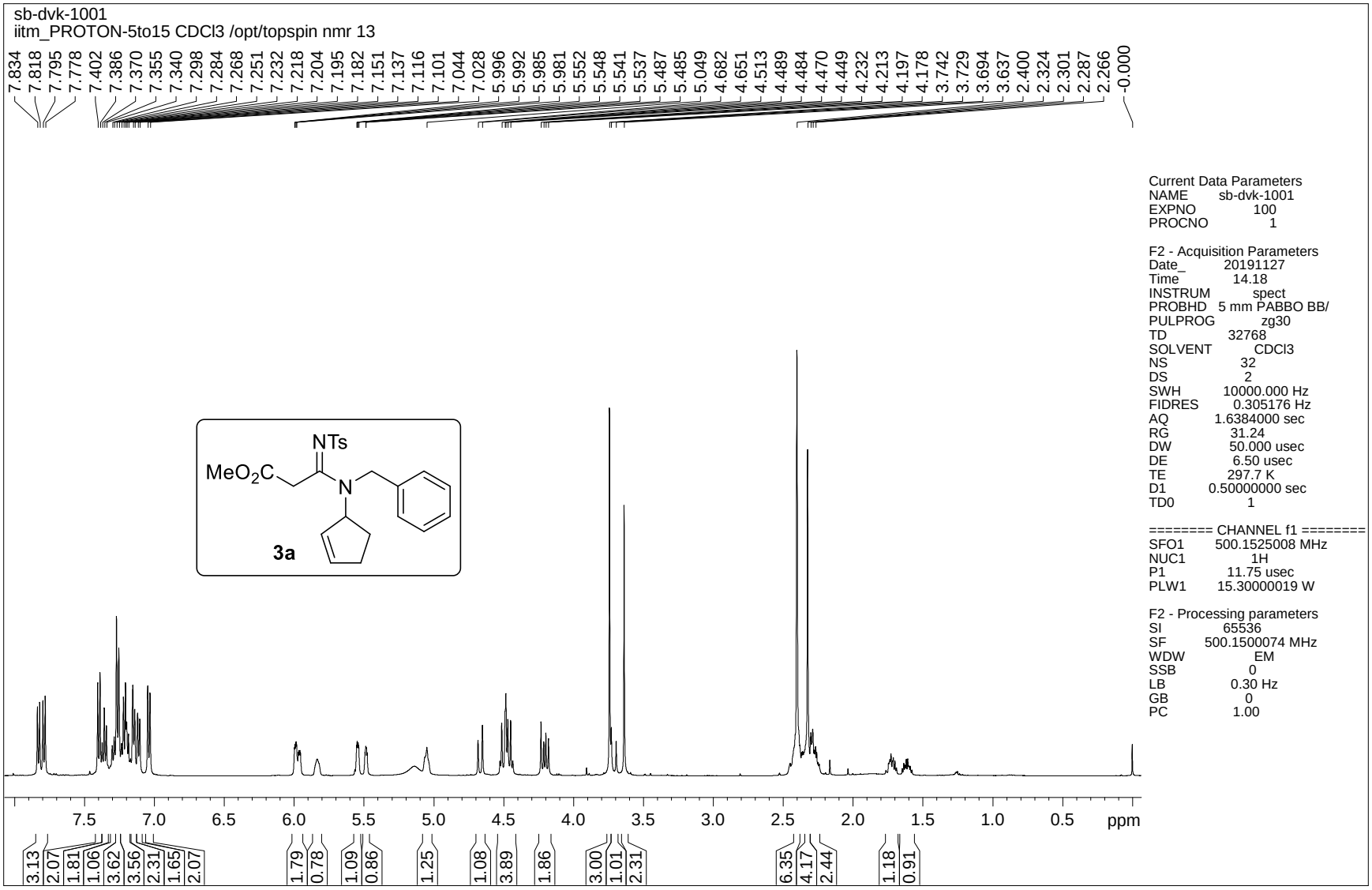
DEPT-135 NMR spectrum of compound 1p



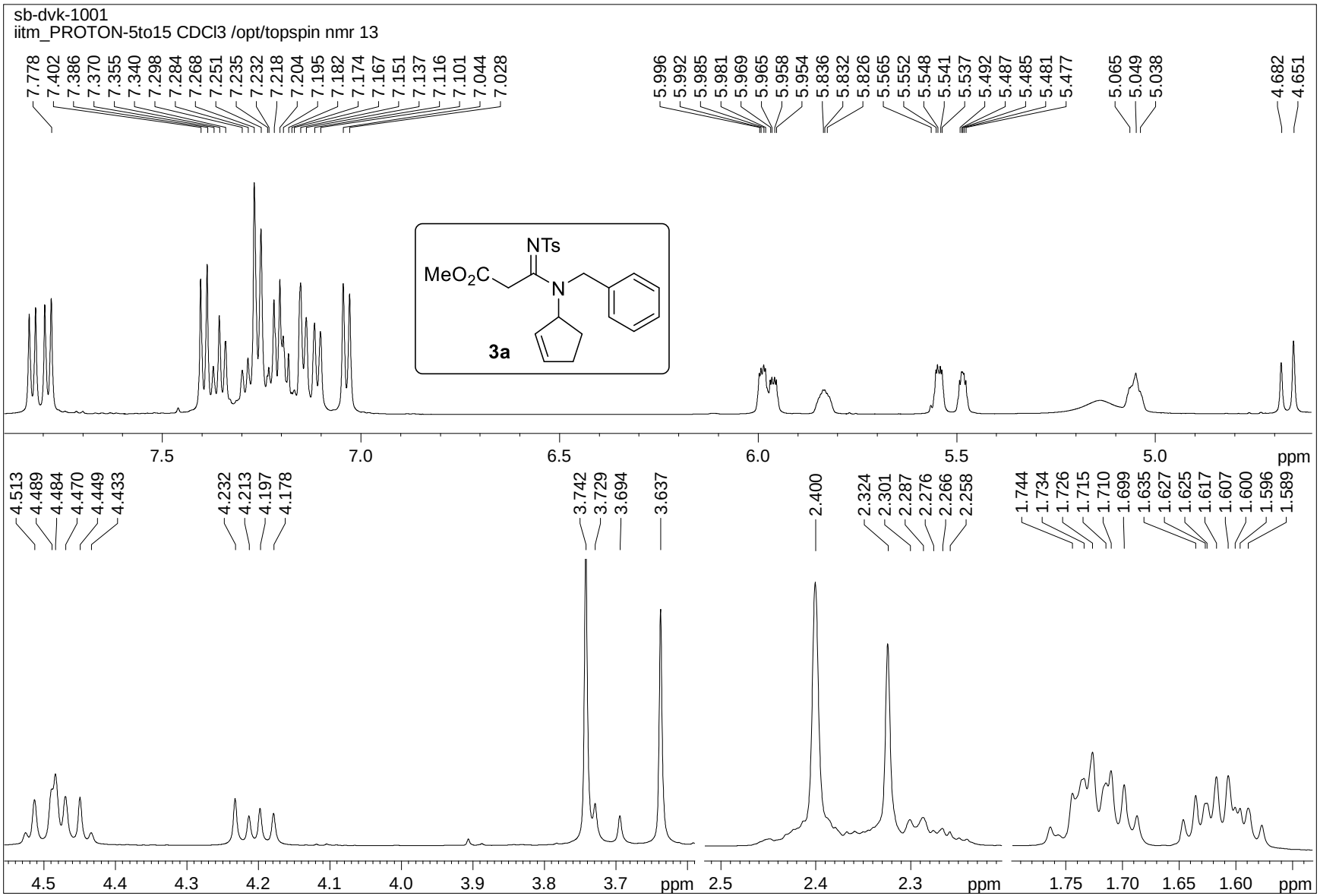
^{1}H-^{1}H COSY NMR spectrum of compound 1p



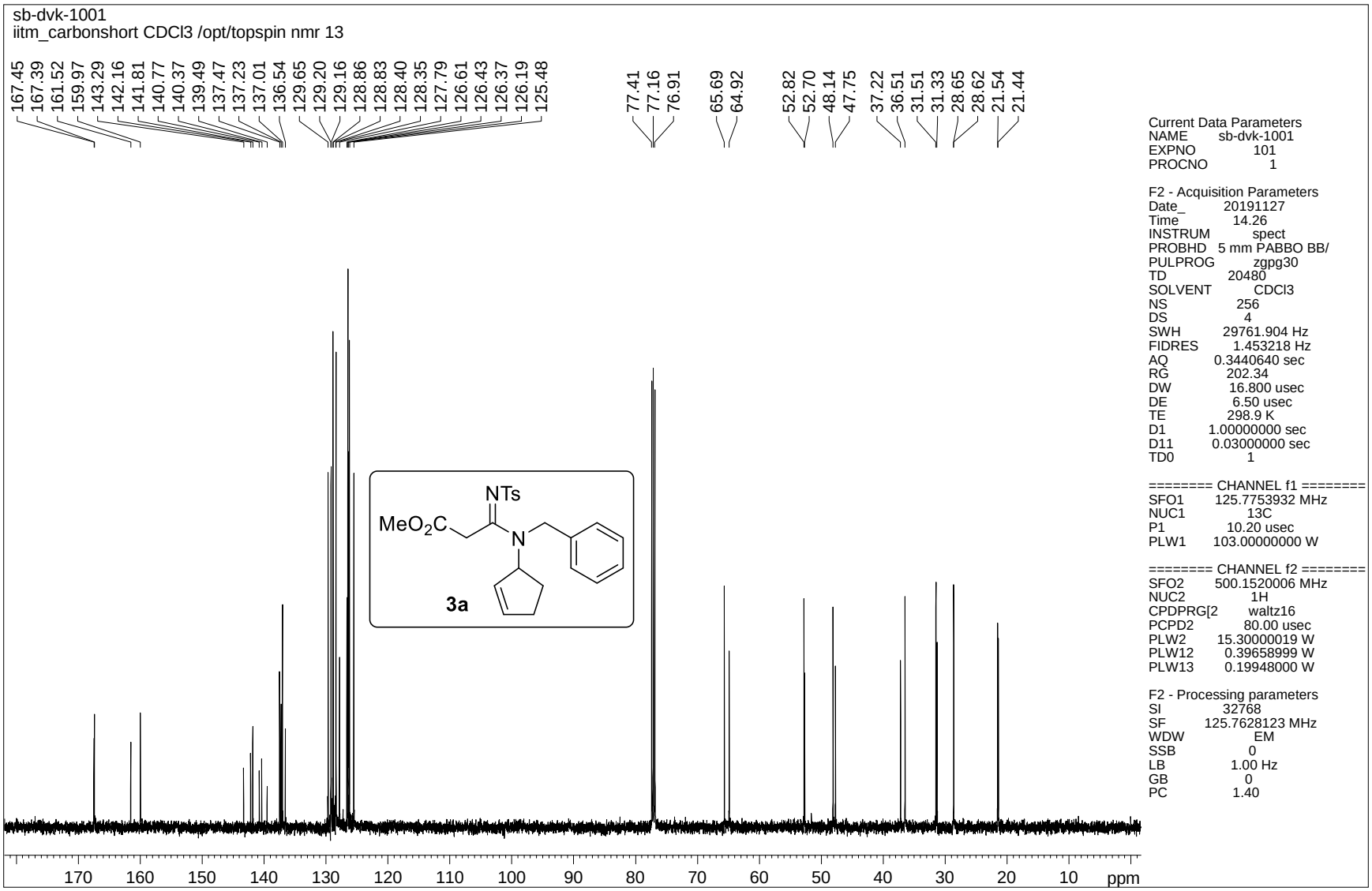
^{1}H-^{13}C HSQC NMR spectrum of compound 1p



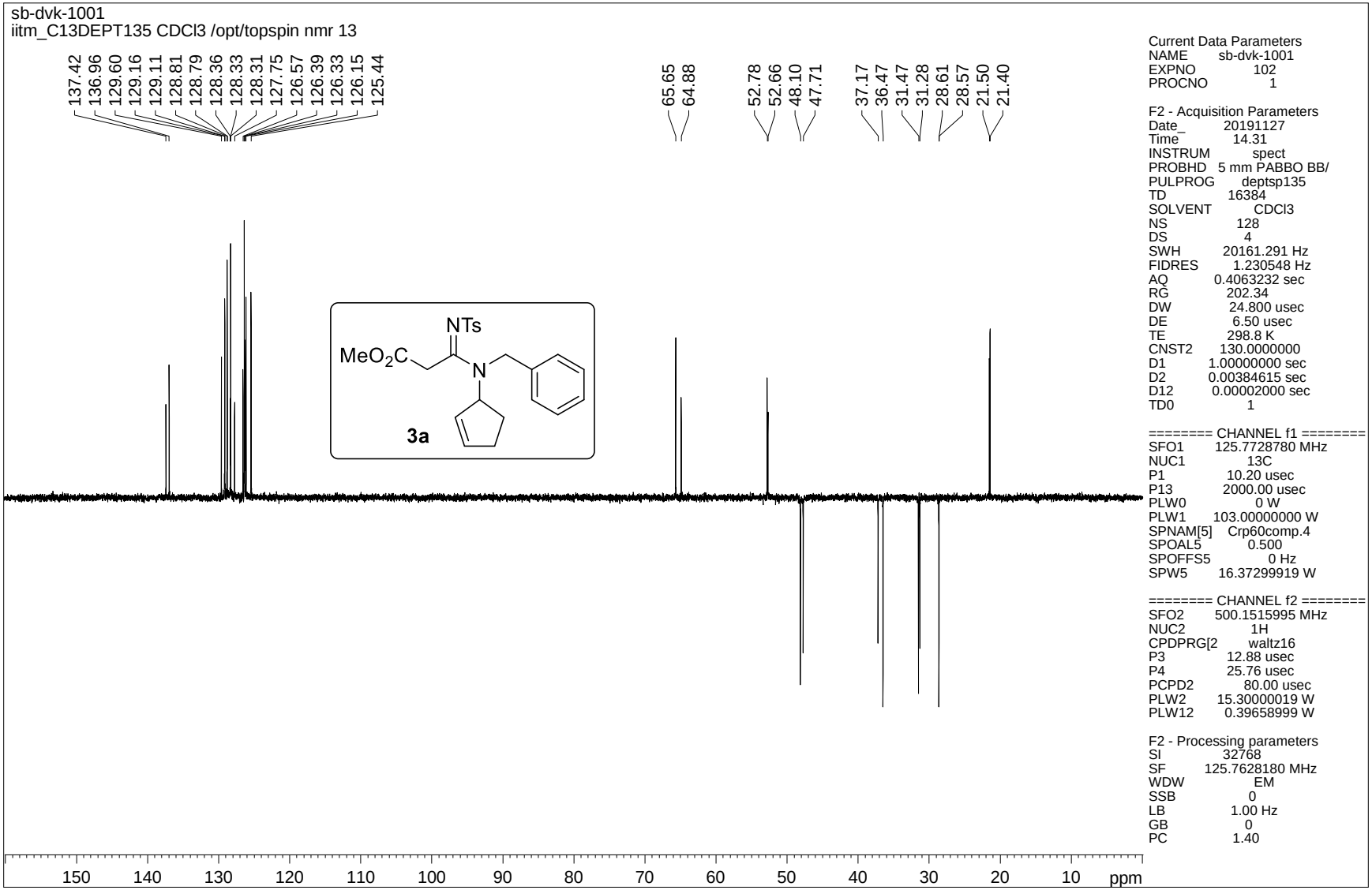
^{1}H NMR spectrum of compound 3a



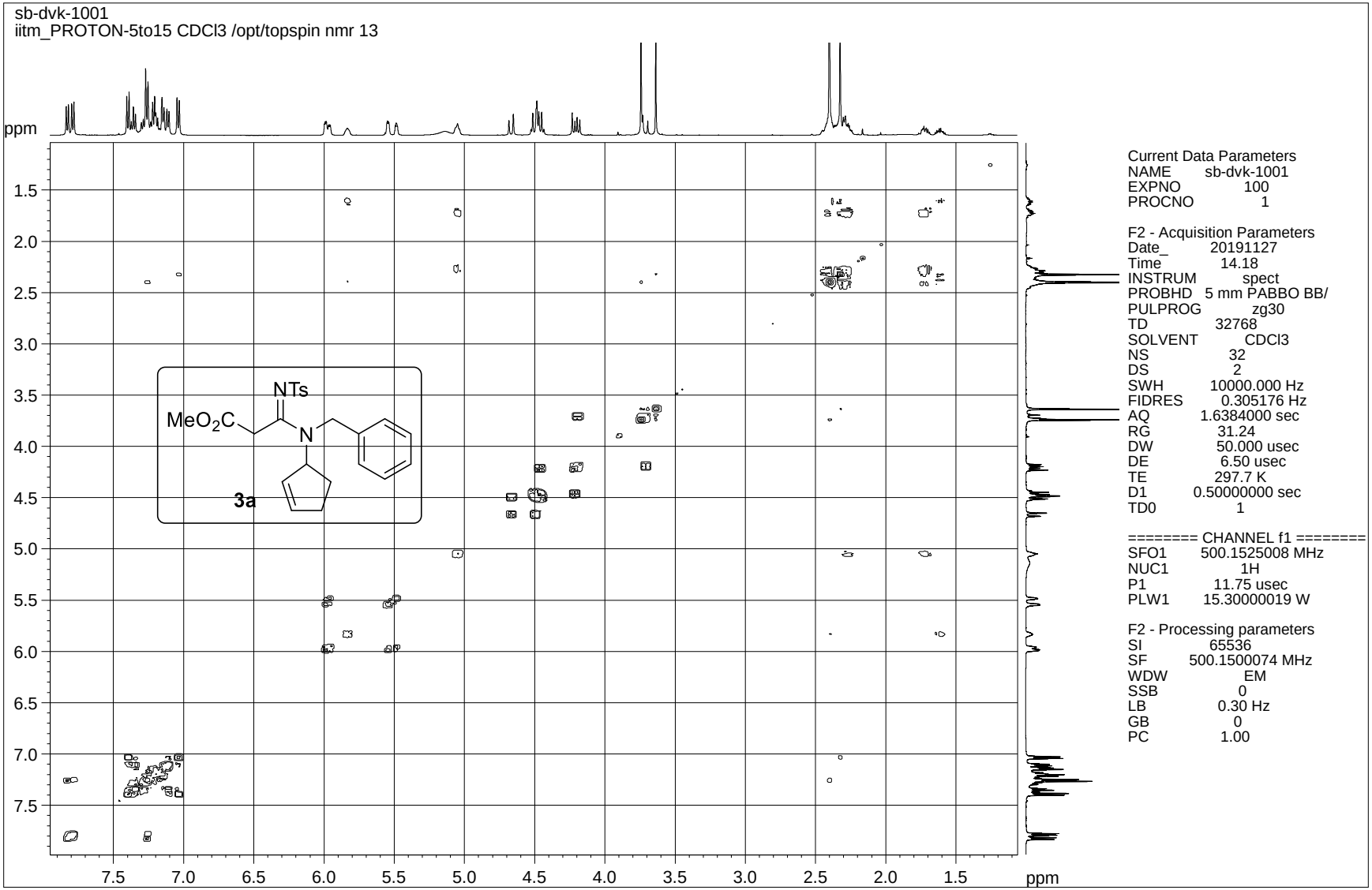
^{1}H NMR spectrum of compound 3a



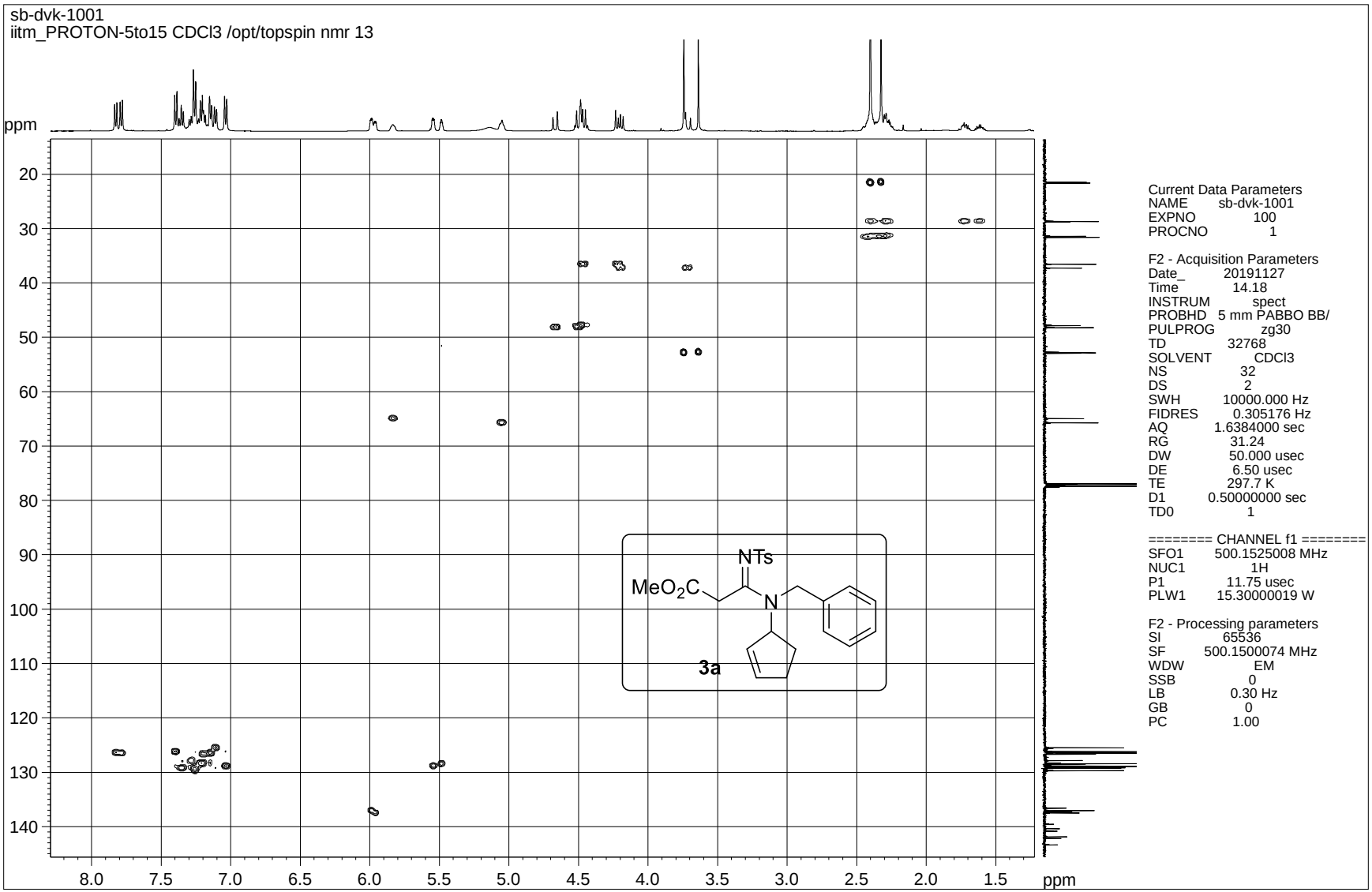
^{13}C NMR spectrum of compound 3a



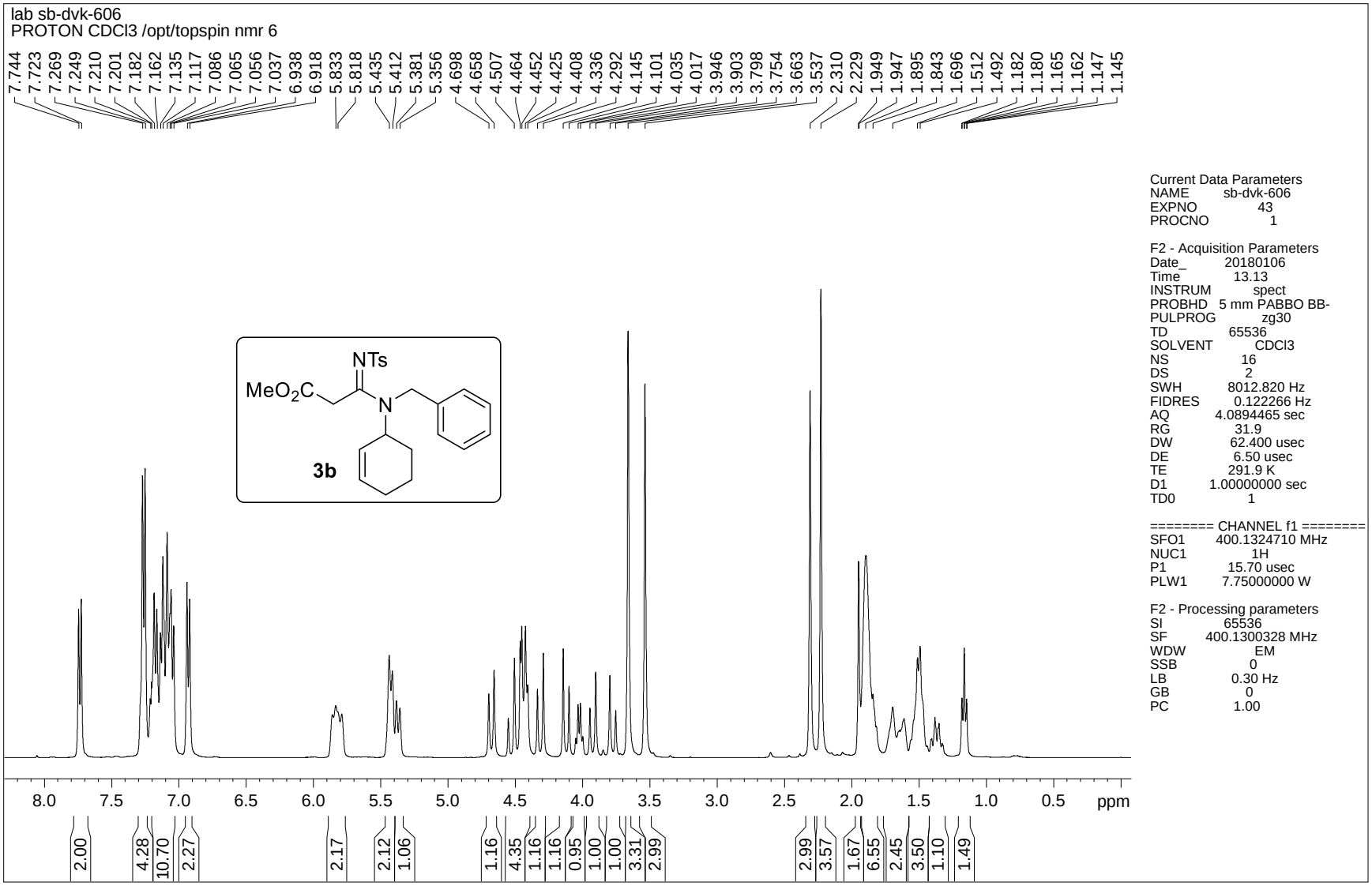
DEPT-135 NMR spectrum of compound 3a



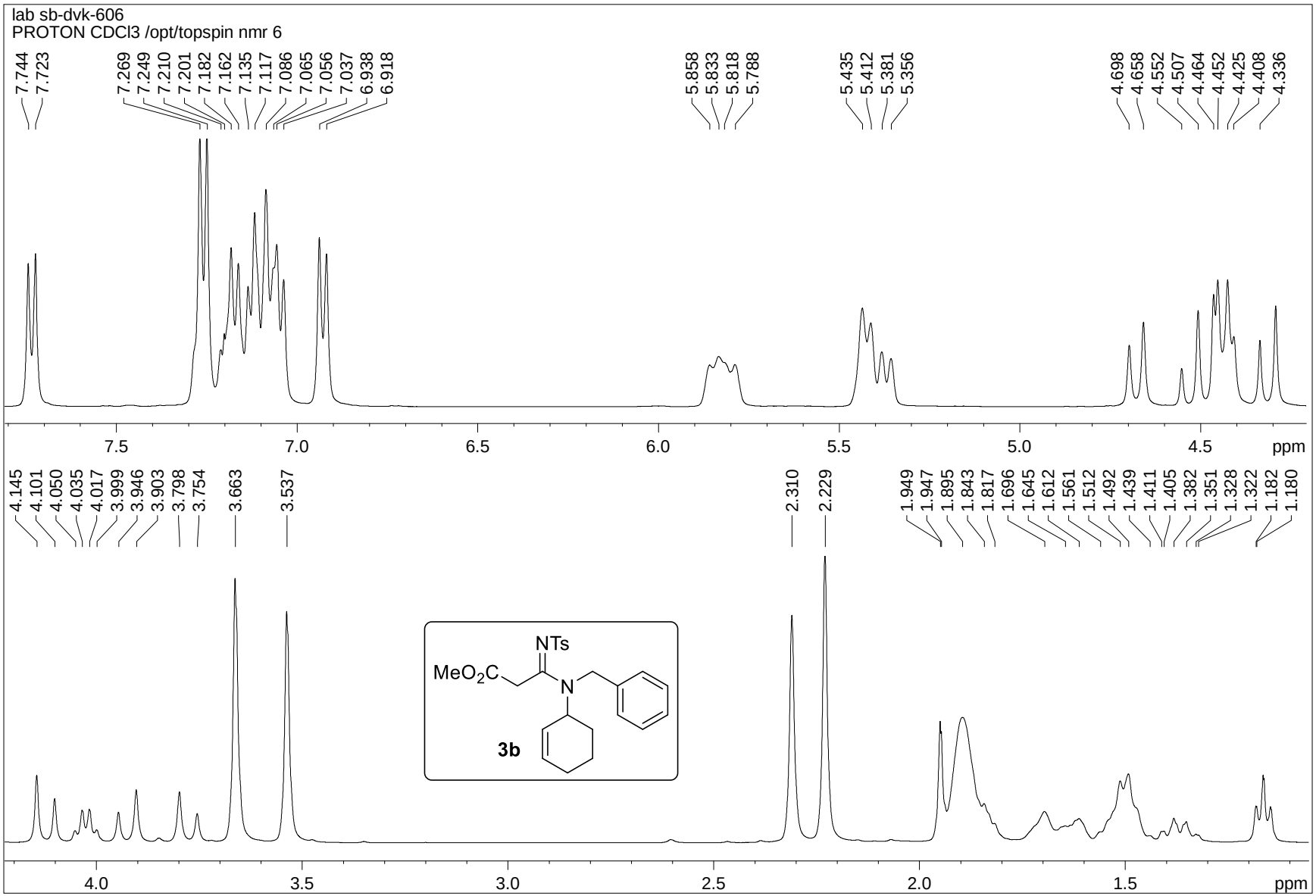
^{1}H-^{1}H COSY NMR spectrum of compound 3a



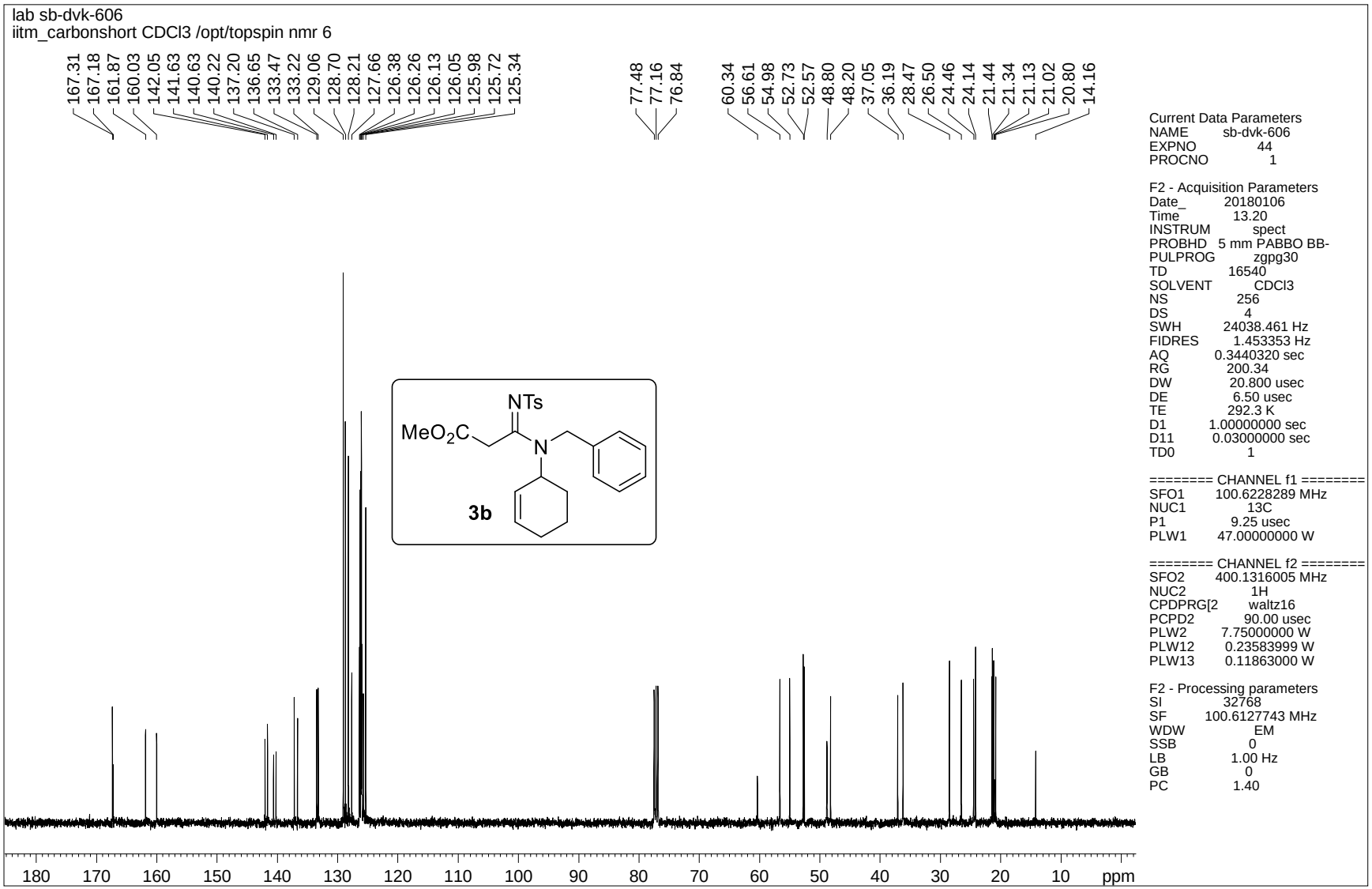
^{1}H-^{13}C HSQC NMR spectrum of compound 3a



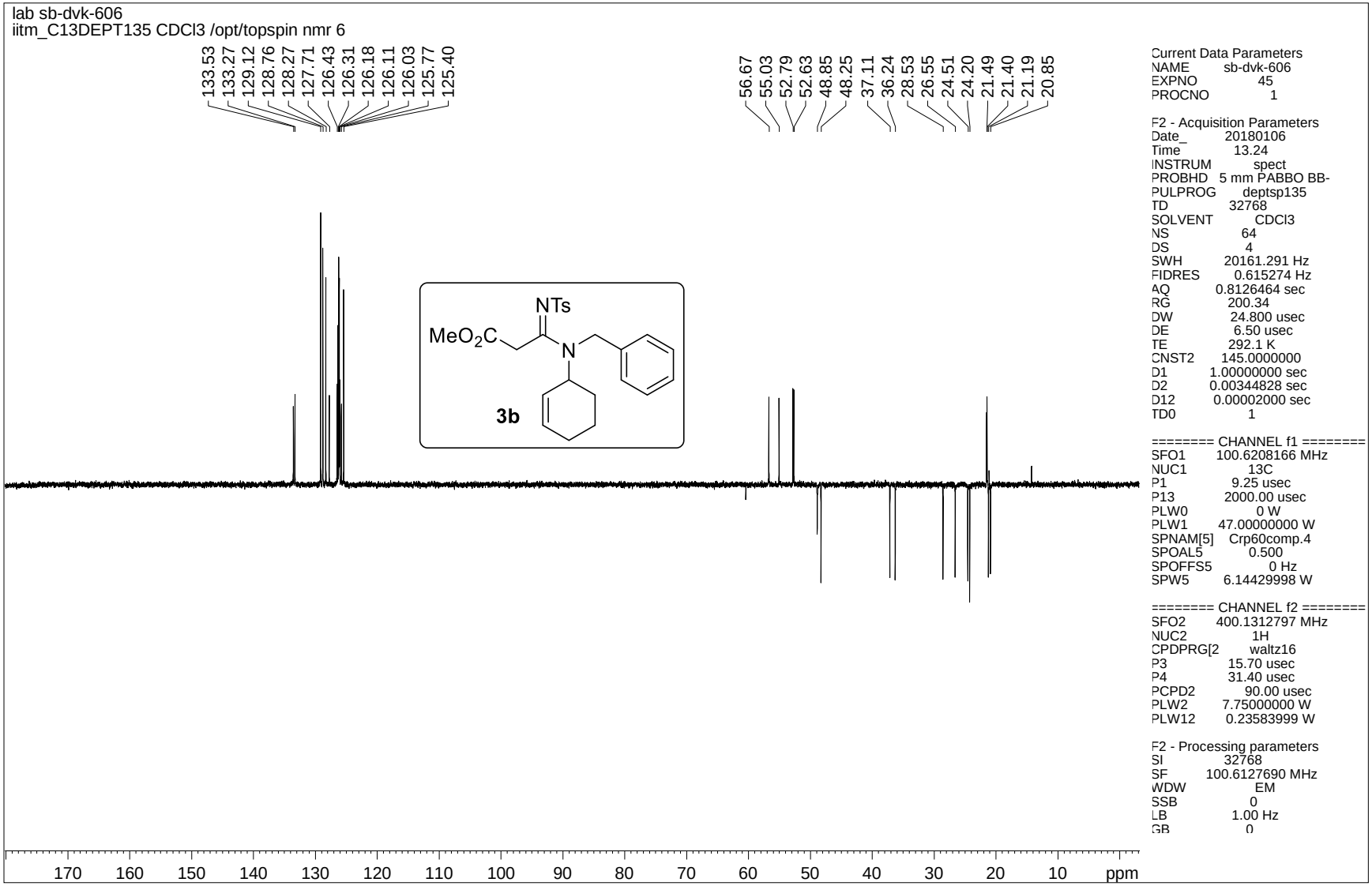
^{1}H NMR spectrum of compound 3b



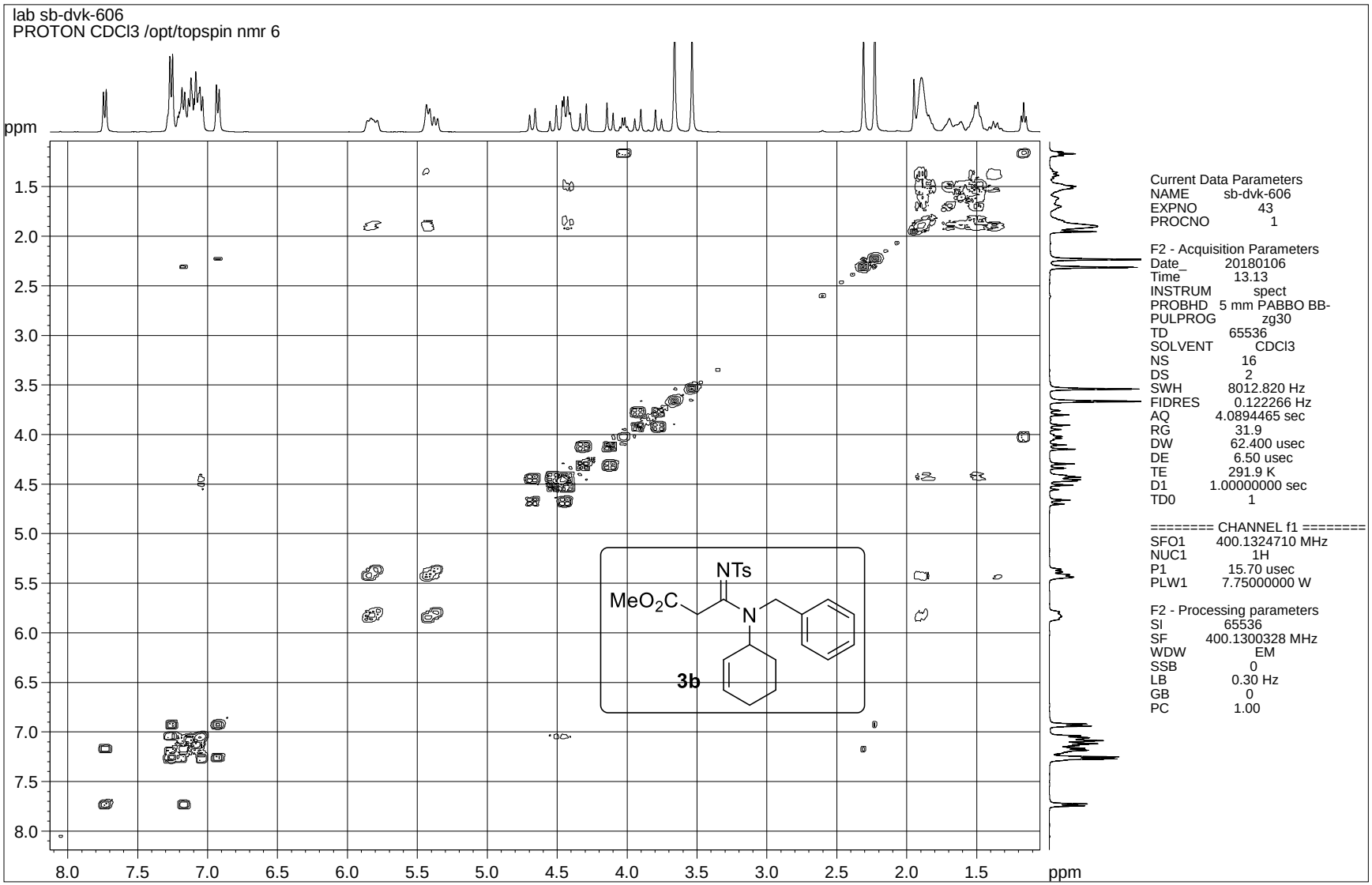
^{1}H NMR spectrum of compound 3b



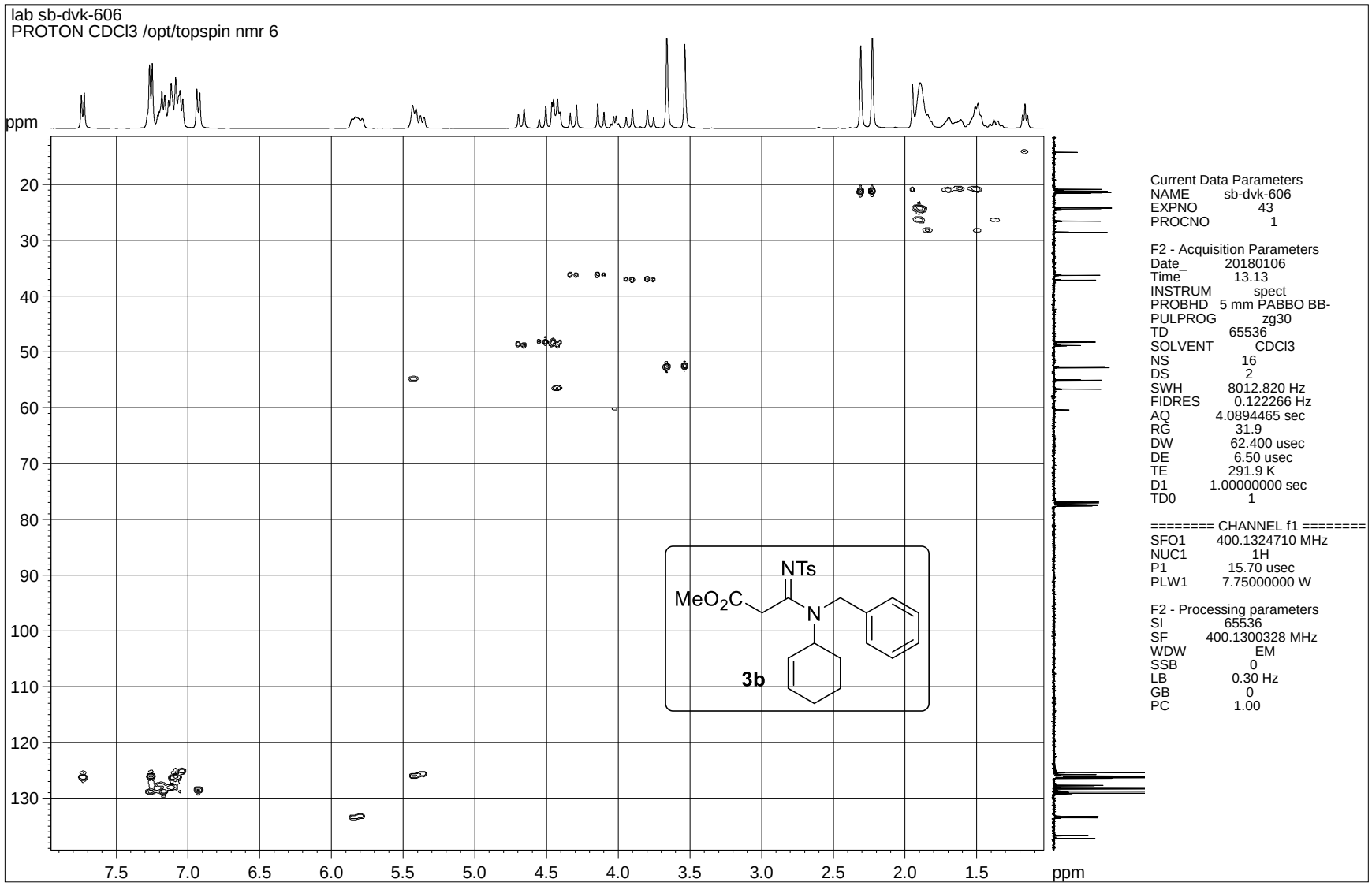
^{13}C NMR spectrum of compound 3b



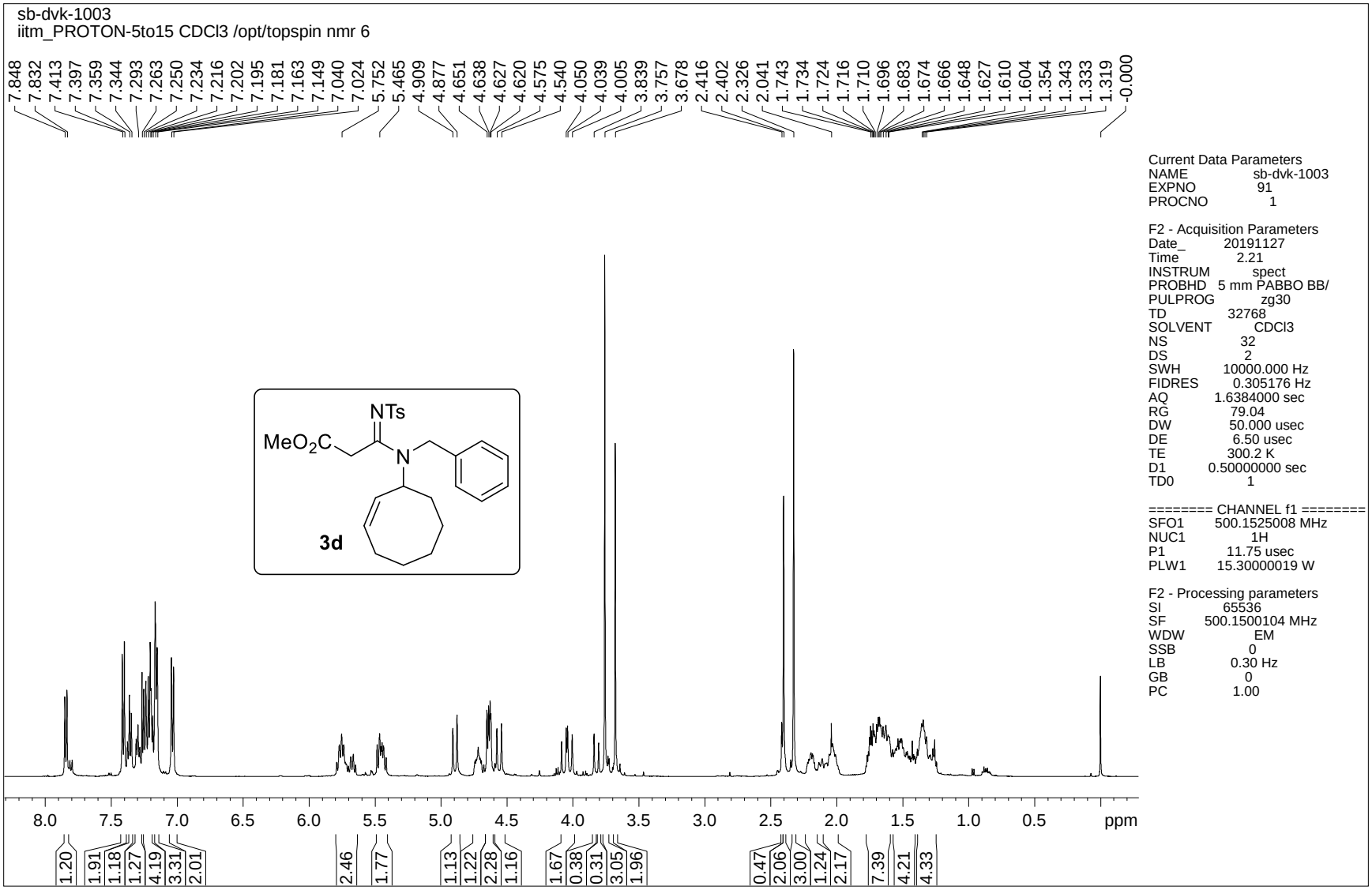
DEPT-135 NMR spectrum of compound 3b



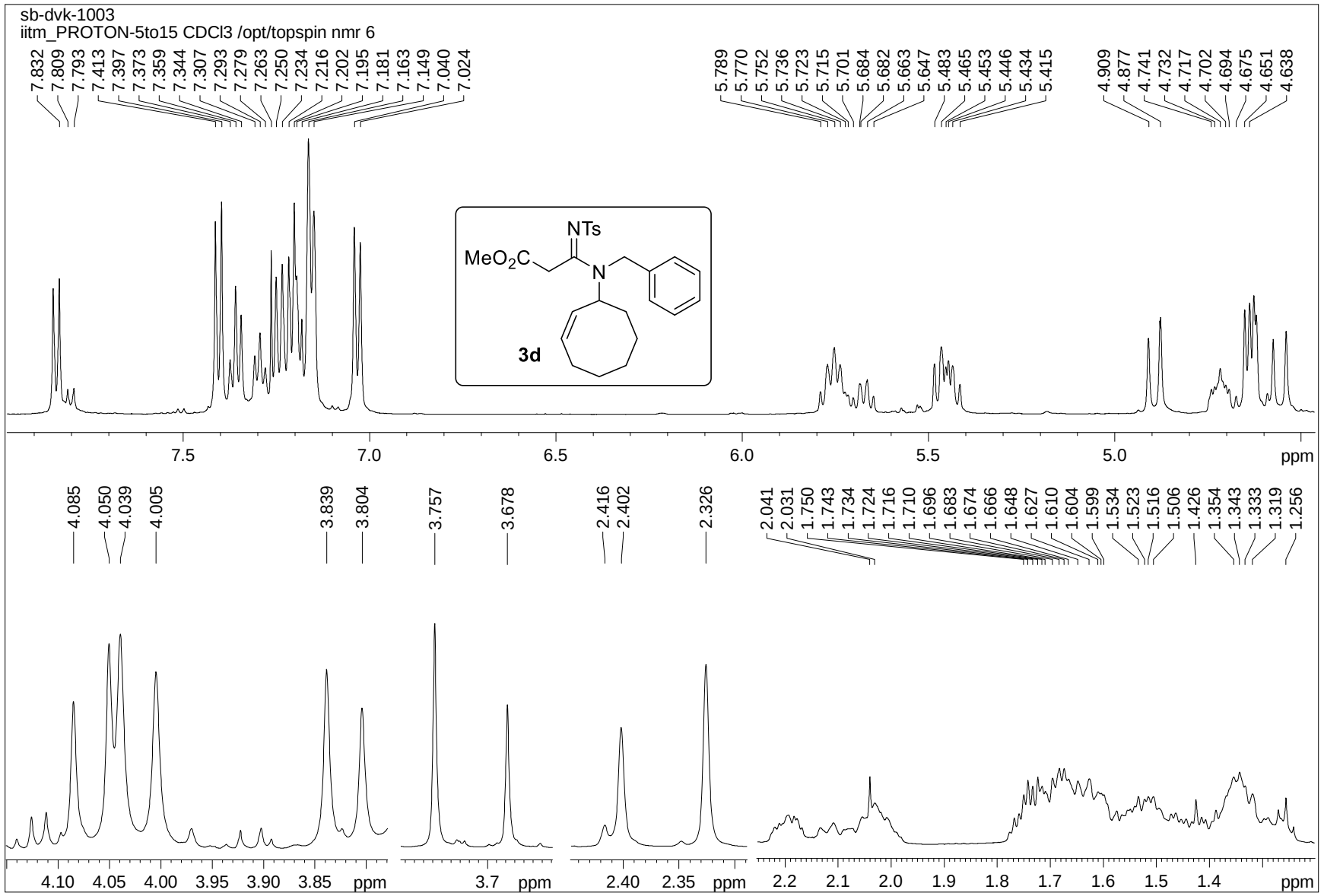
^{1}H-^{1}H COSY NMR spectrum of compound 3b



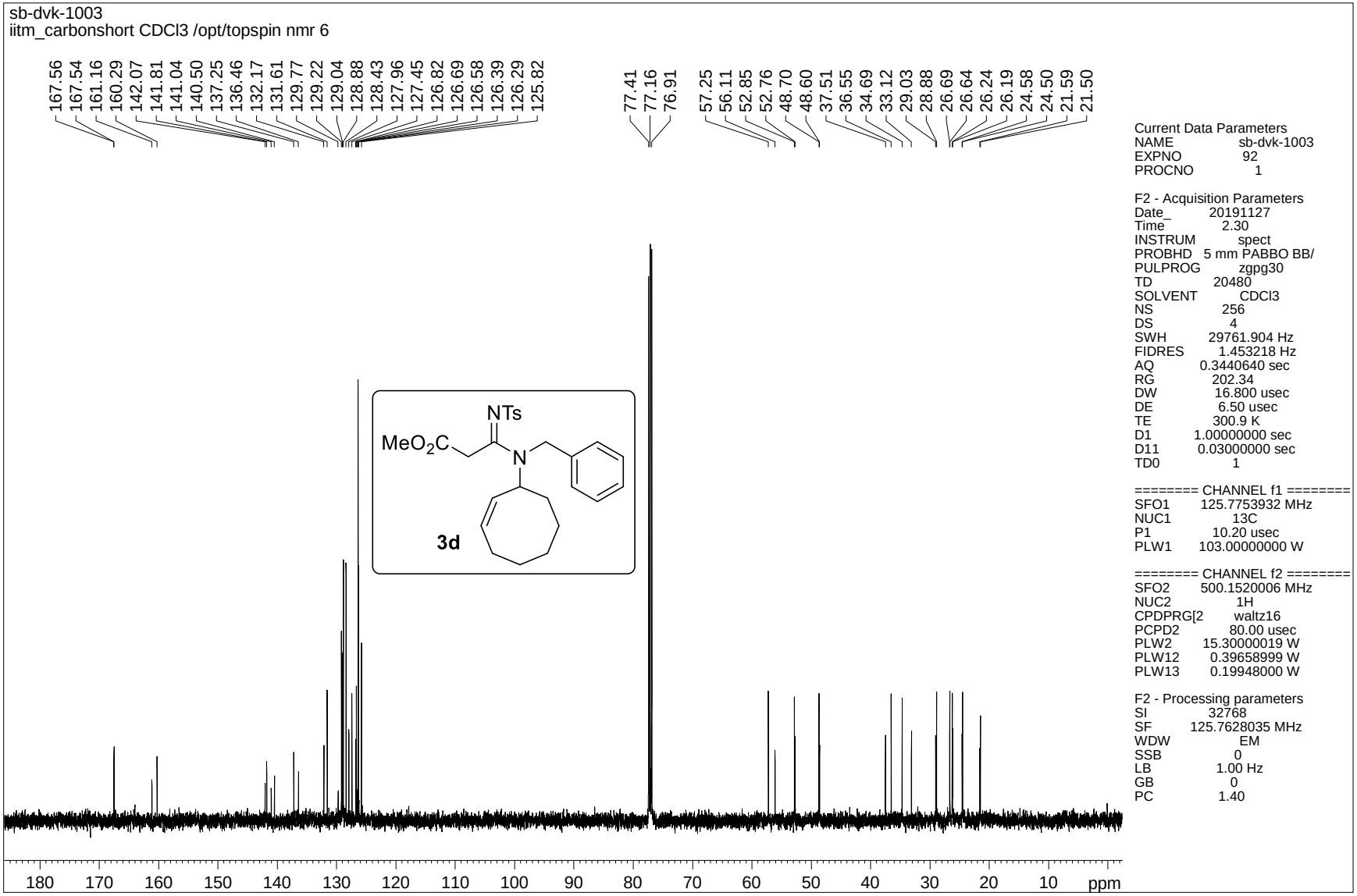
^{1}H-^{13}C HSQC NMR spectrum of compound 3b



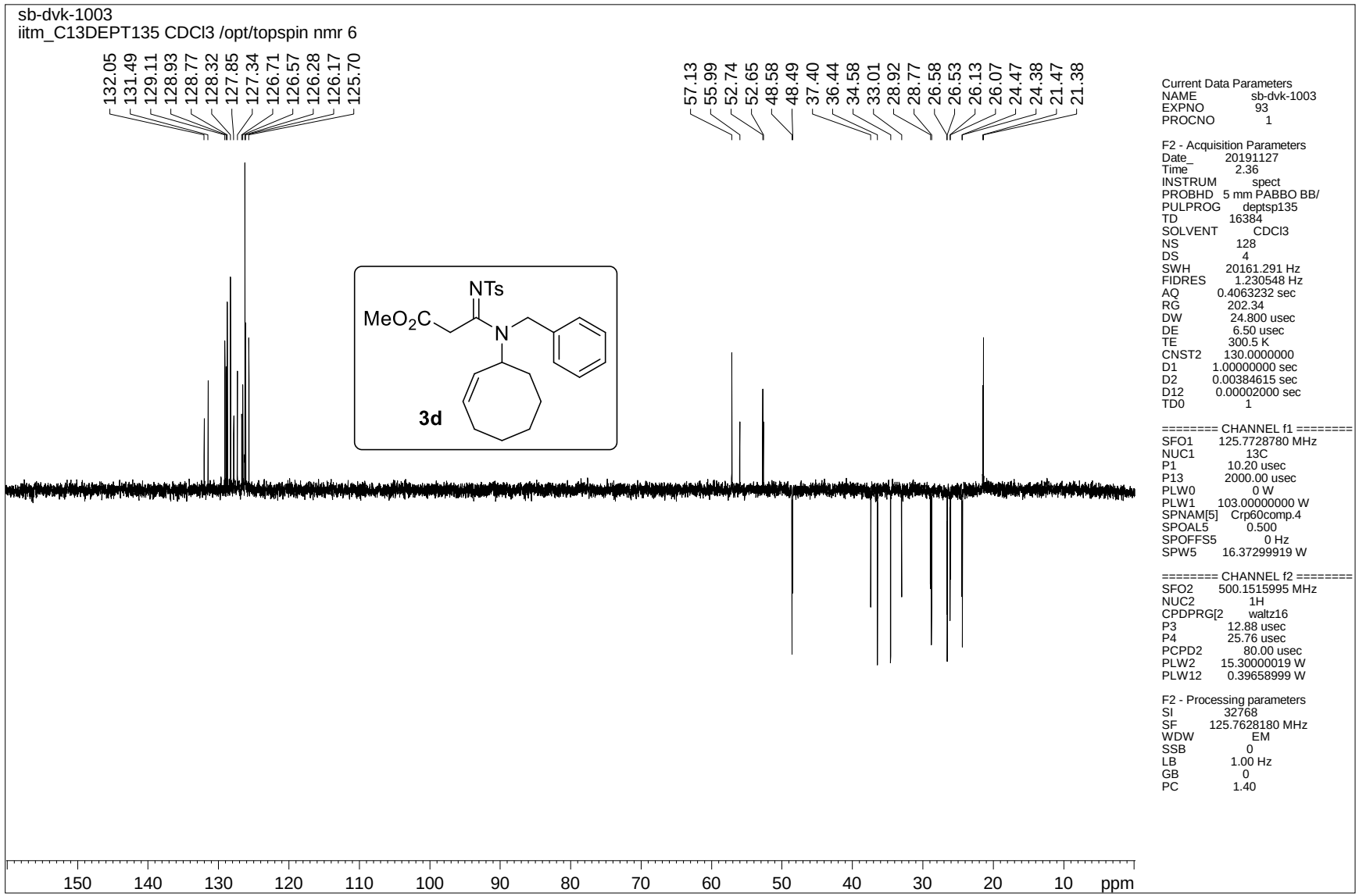
^{1}H NMR spectrum of compound 3d



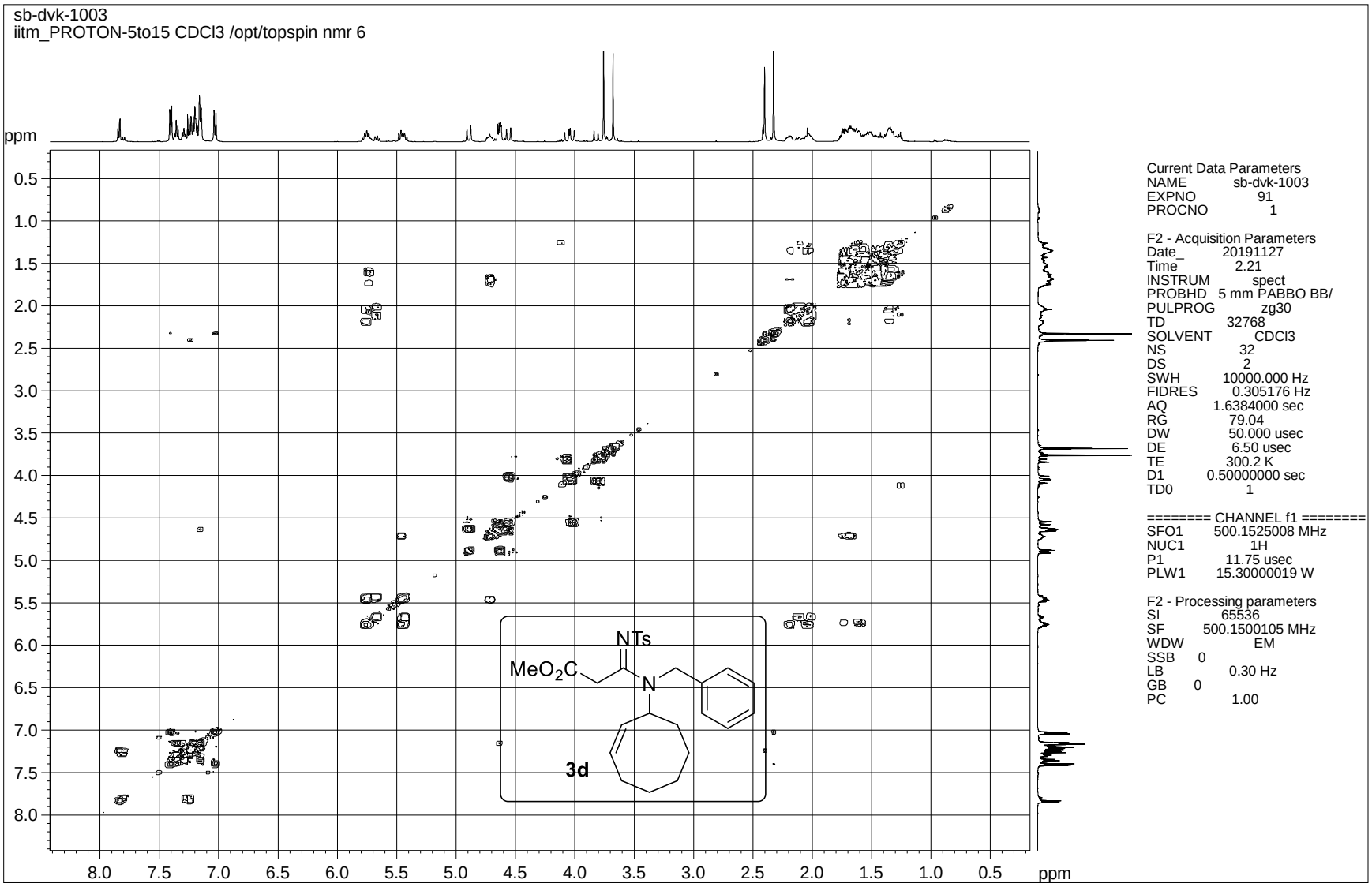
^{1}H NMR spectrum of compound 3d



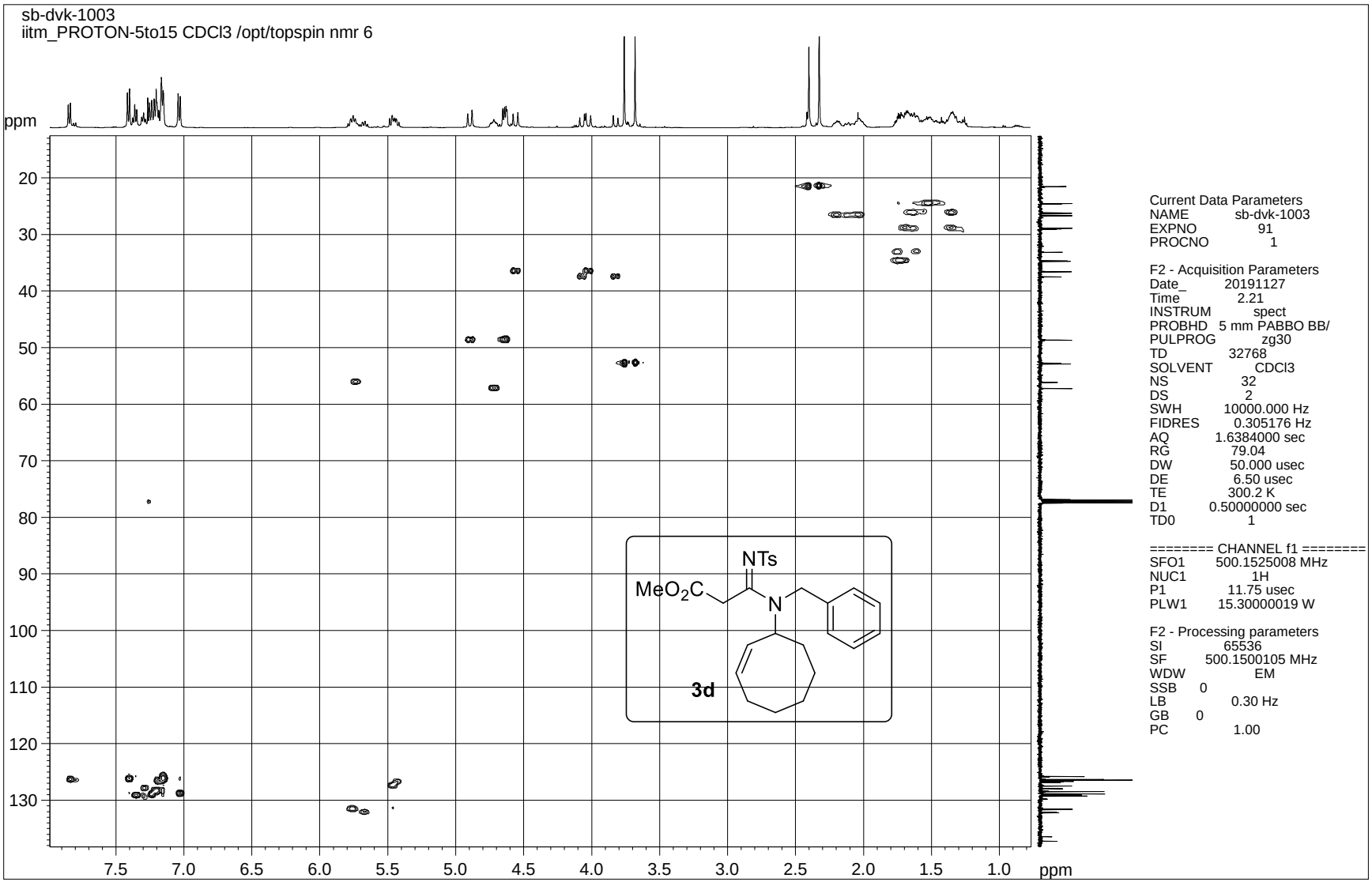
^{13}C NMR spectrum of compound 3d



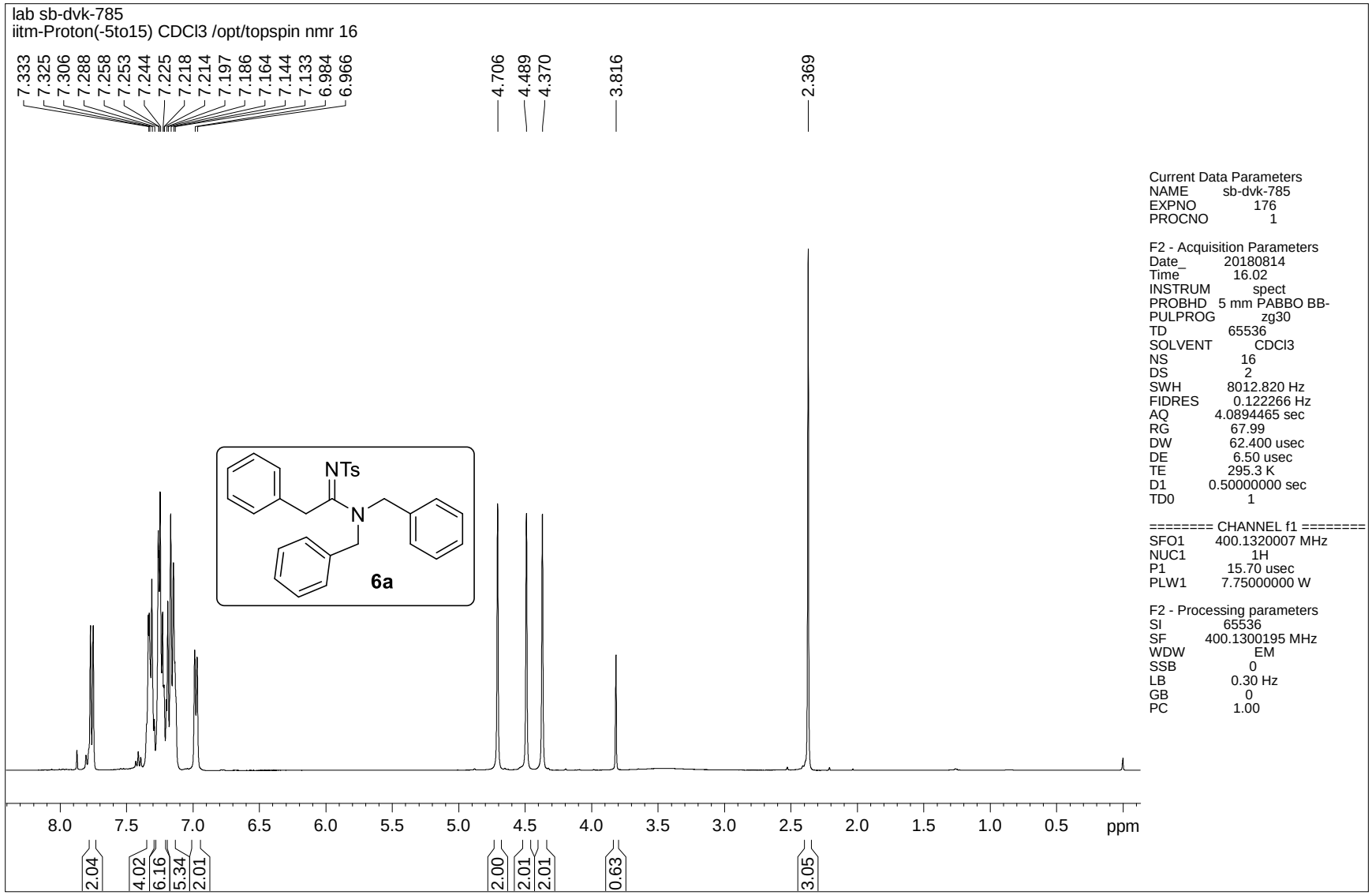
DEPT-135 NMR spectrum of compound 3d



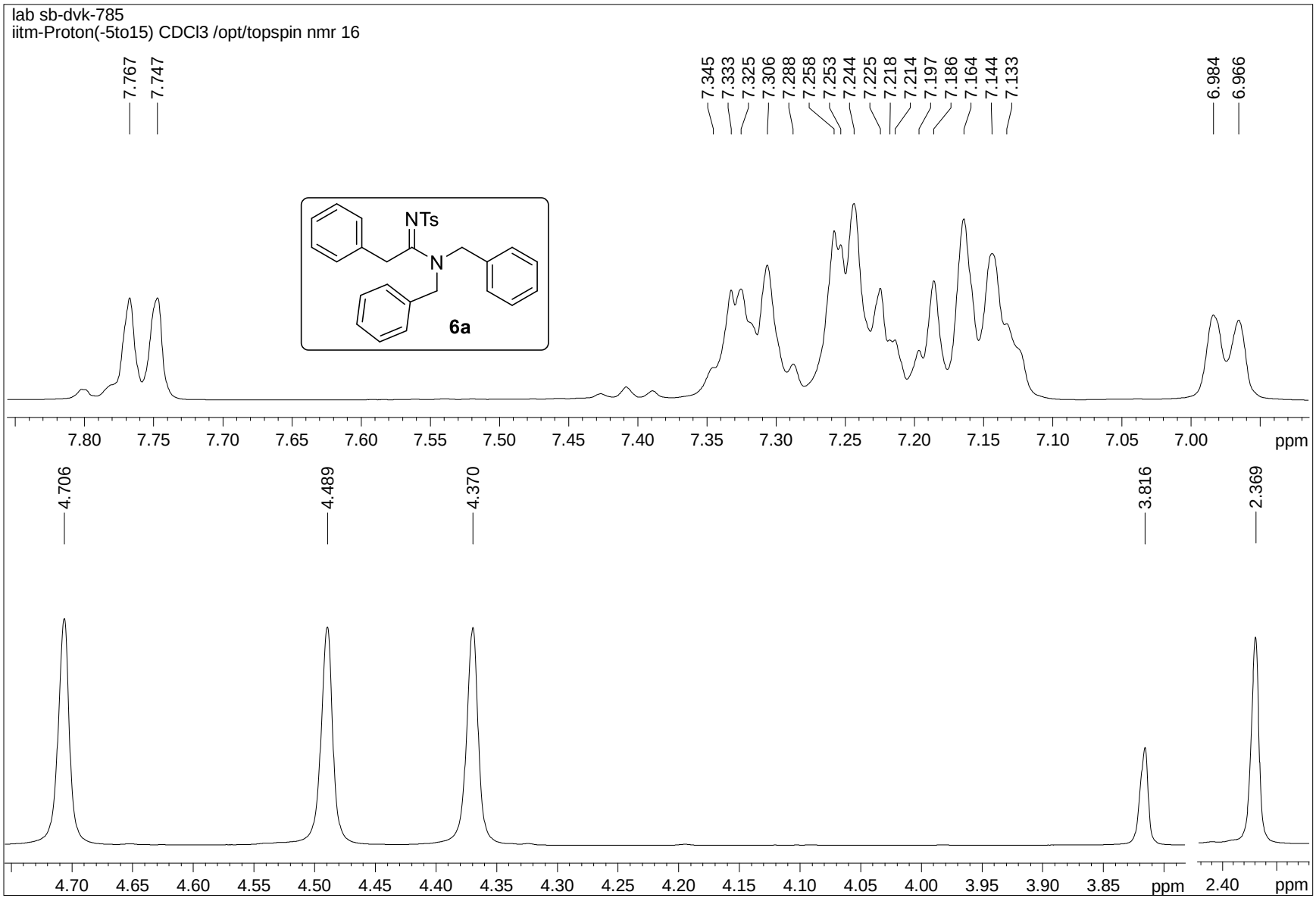
^{1}H-^{1}H COSY NMR spectrum of compound 3d



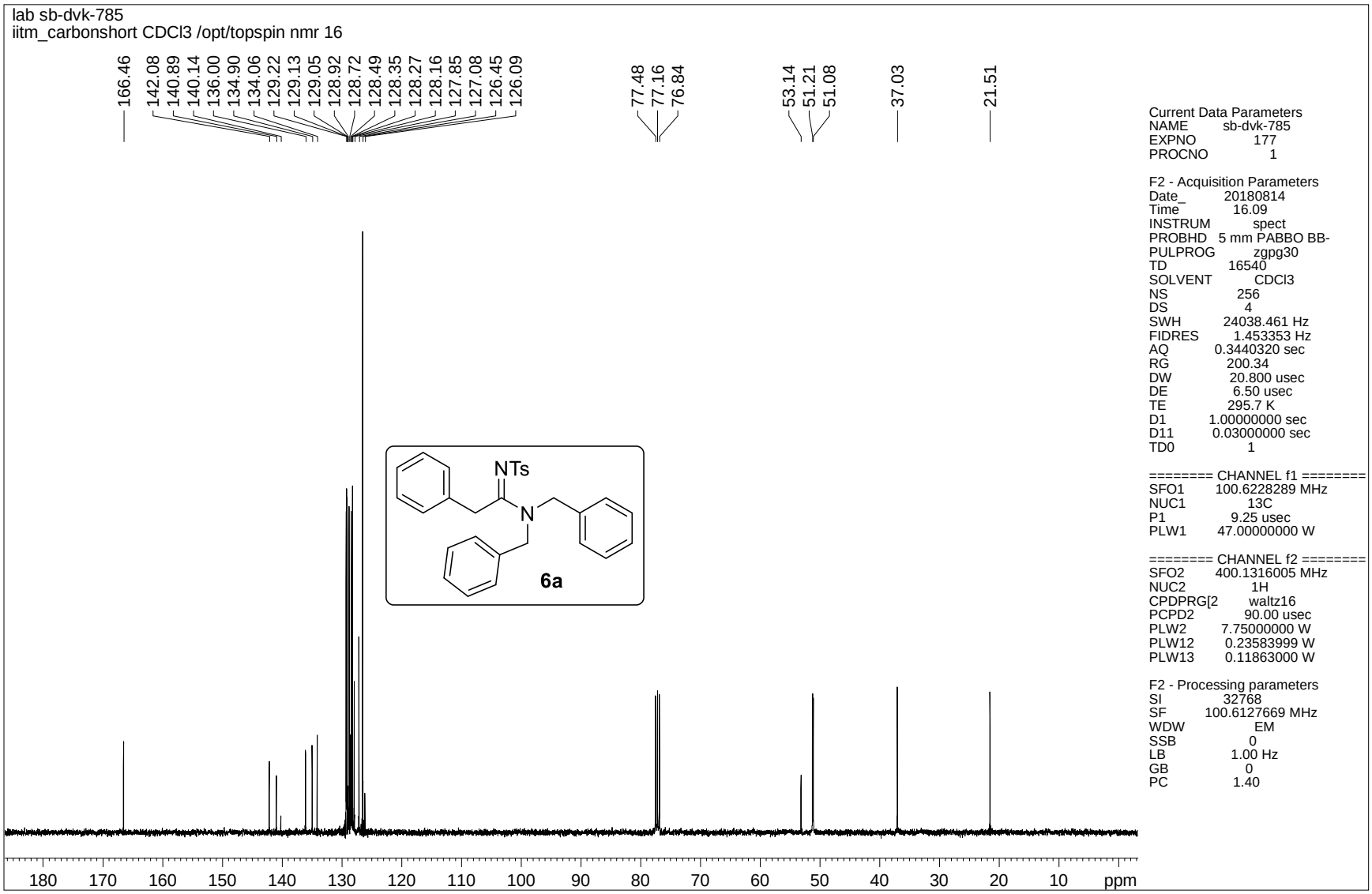
^{1}H-^{13}C HSQC NMR spectrum of compound 3d



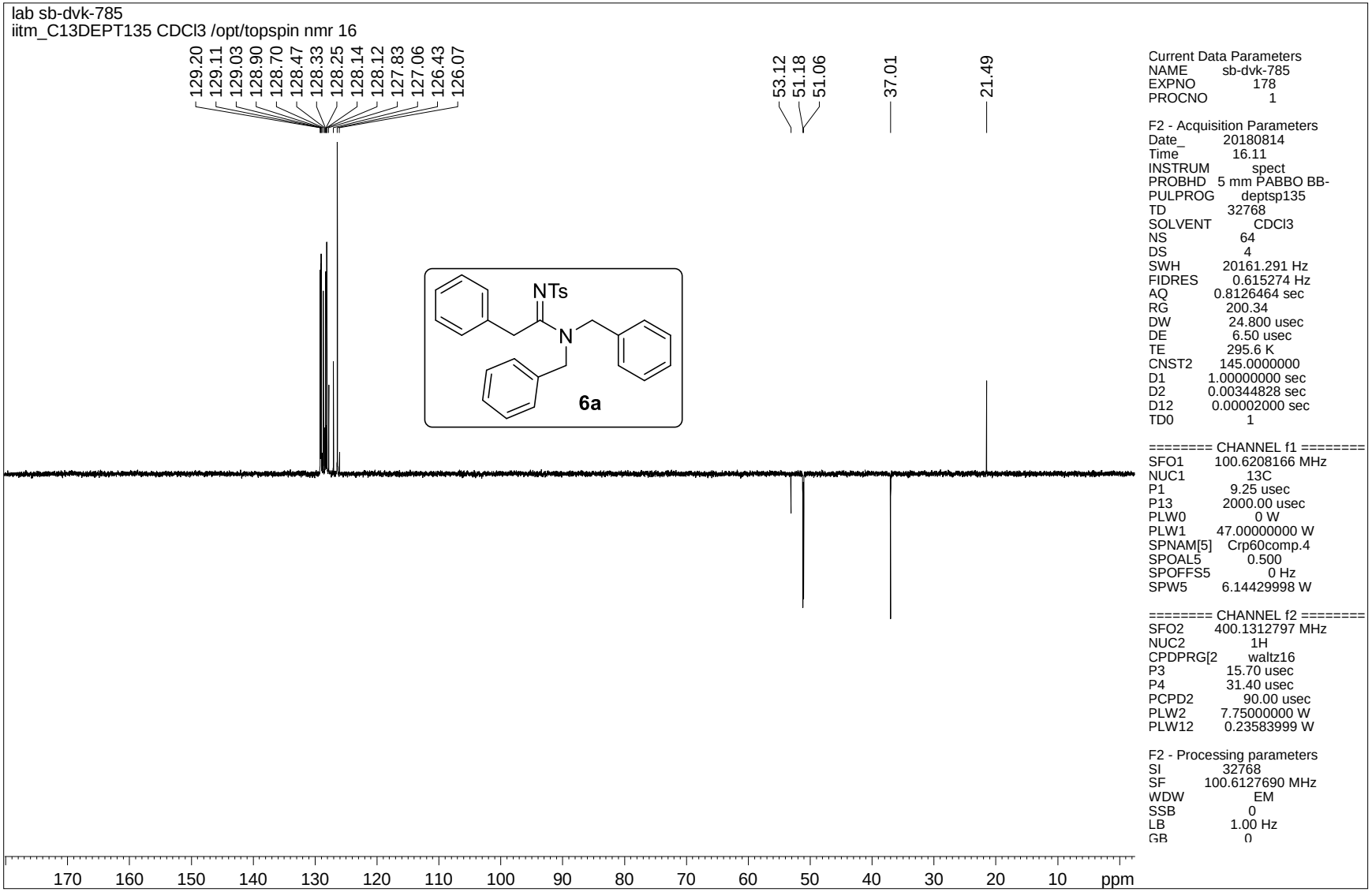
^{1}H NMR spectrum of compound 6a



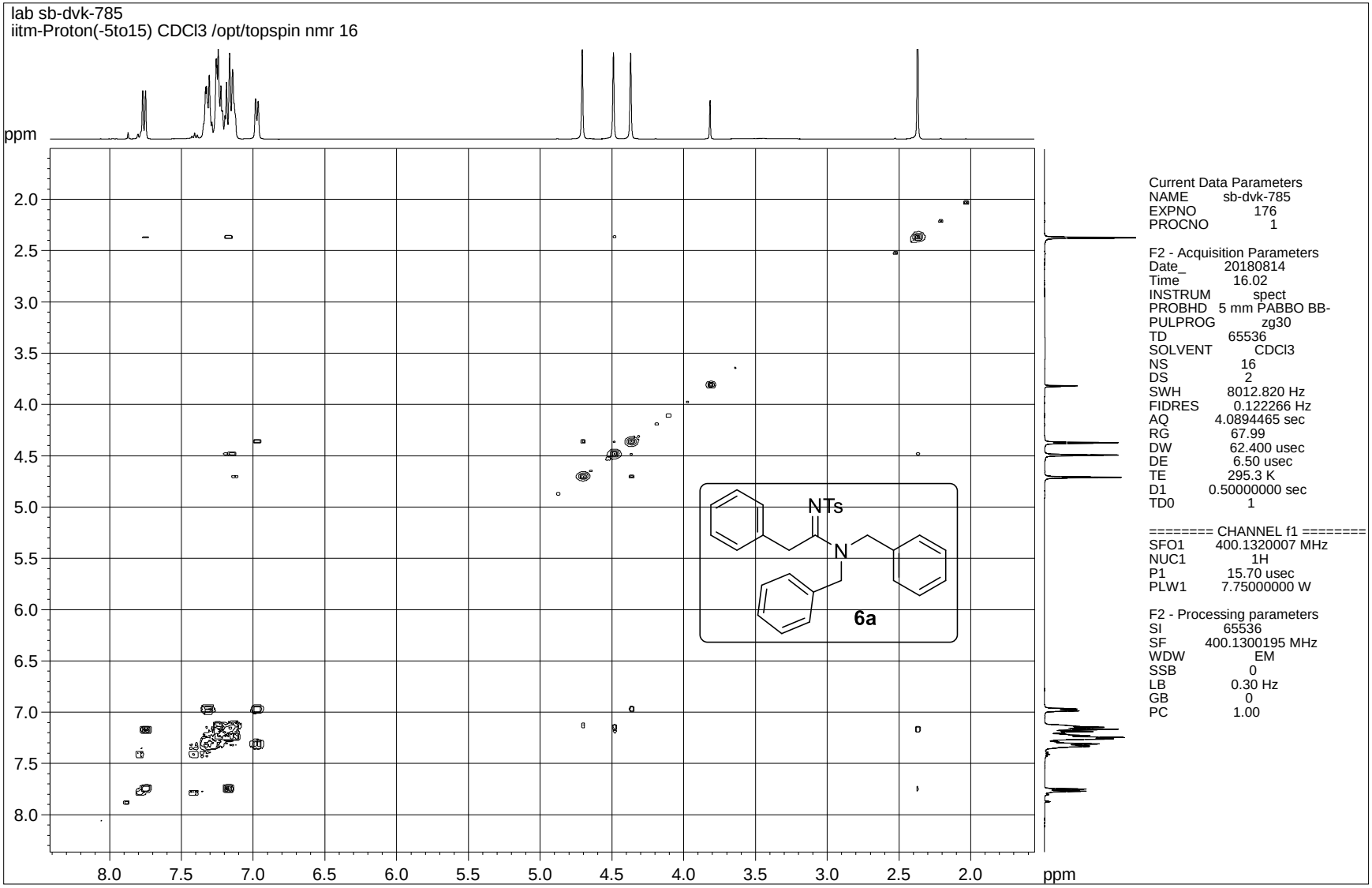
^{1}H NMR spectrum of compound 6a



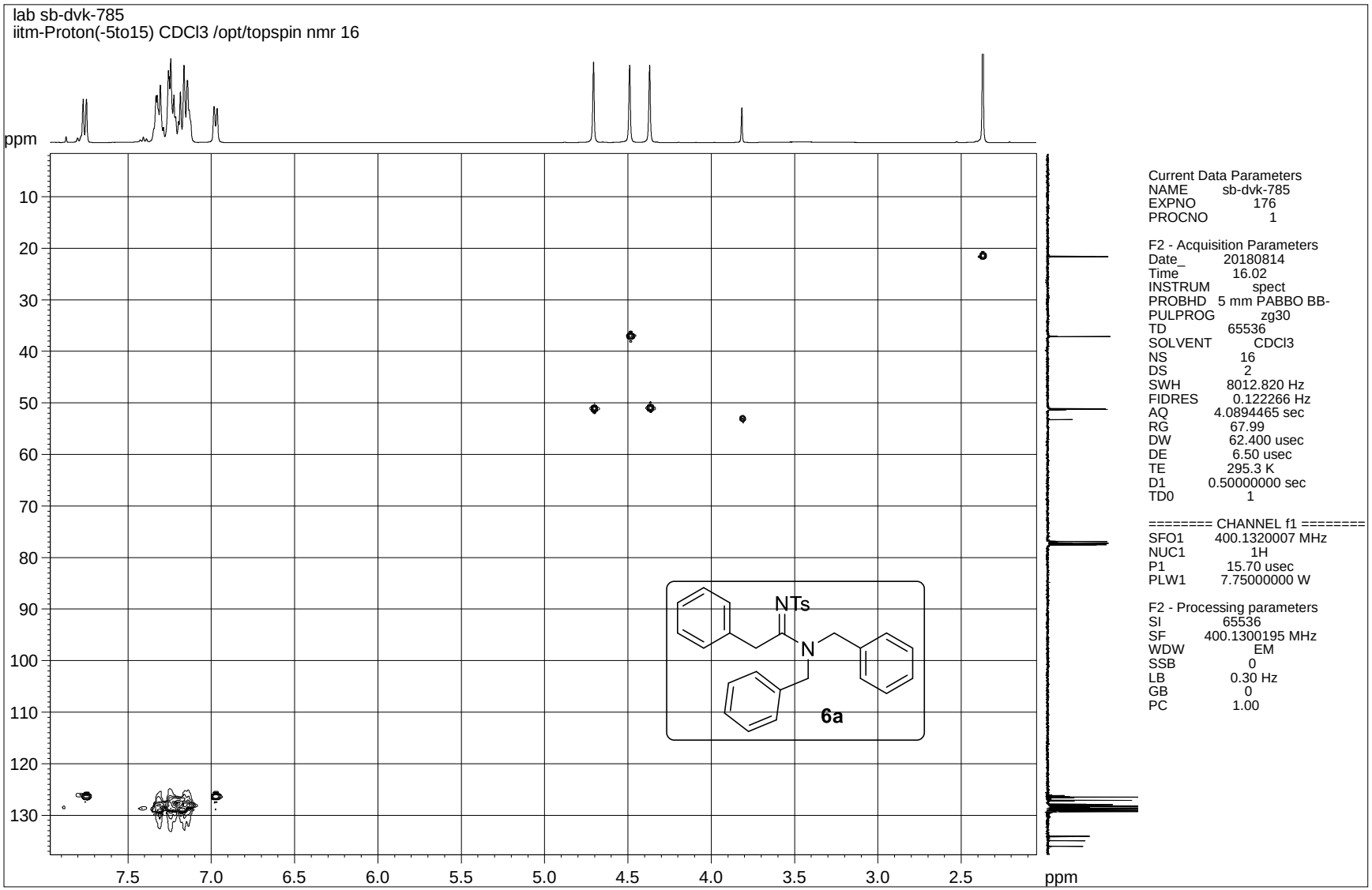
^{13}C NMR spectrum of compound 6a



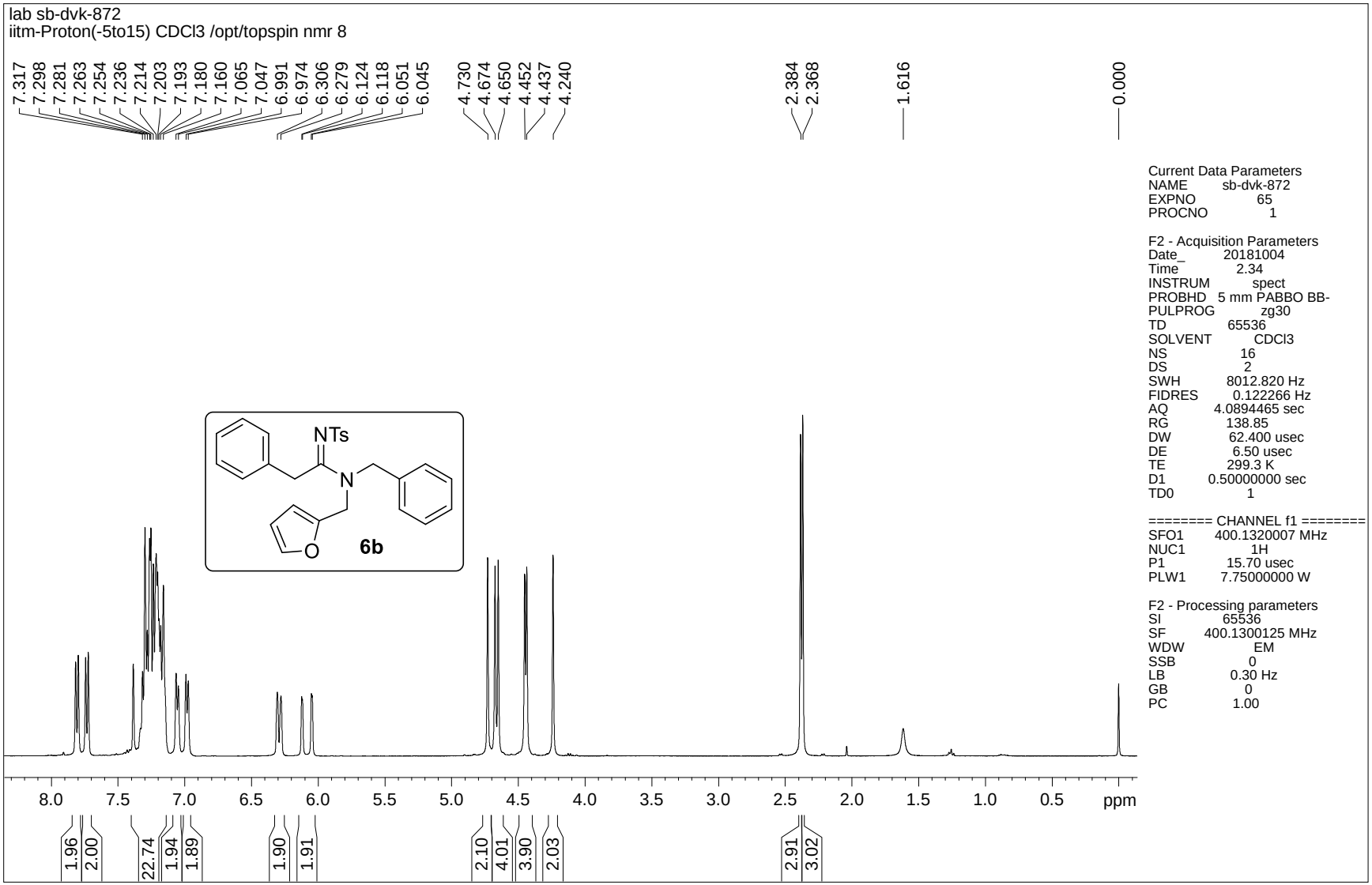
DEPT-135 NMR spectrum of compound 6a



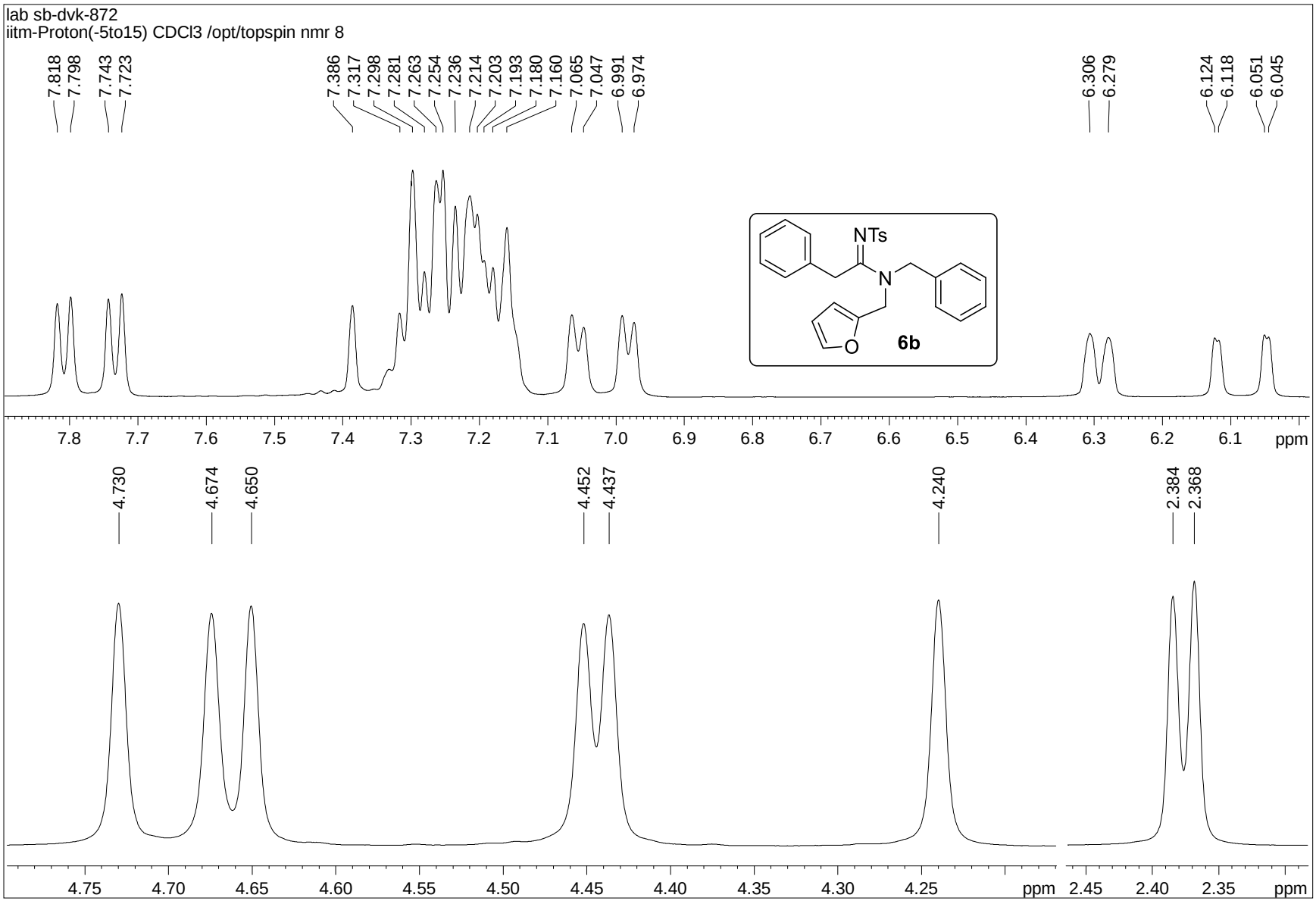
^{1}H-^{1}H COSY NMR spectrum of compound 6a



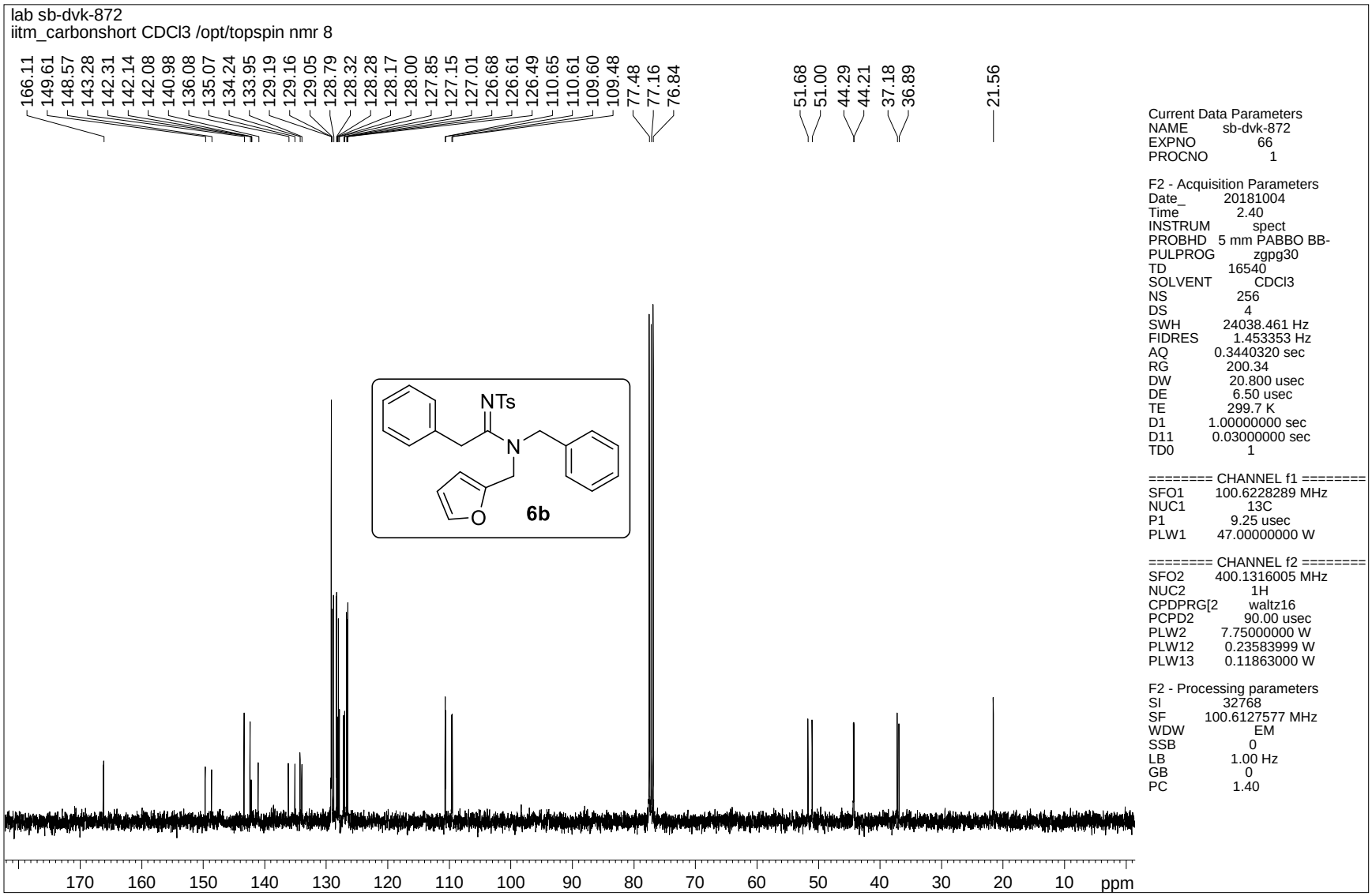
^{1}H-^{13}C HSQC NMR spectrum of compound 6a



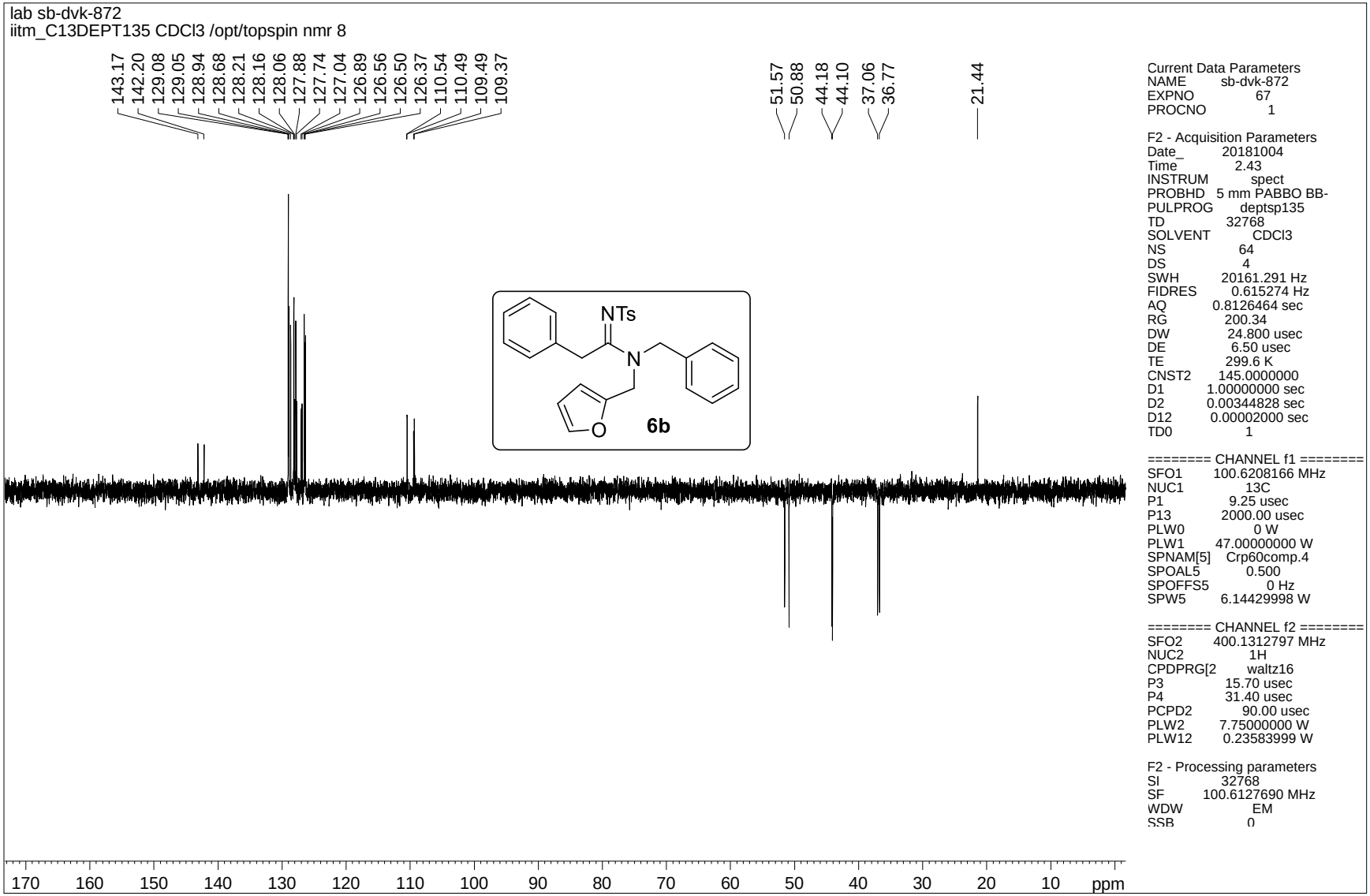
^{1}H NMR spectrum of compound 6b



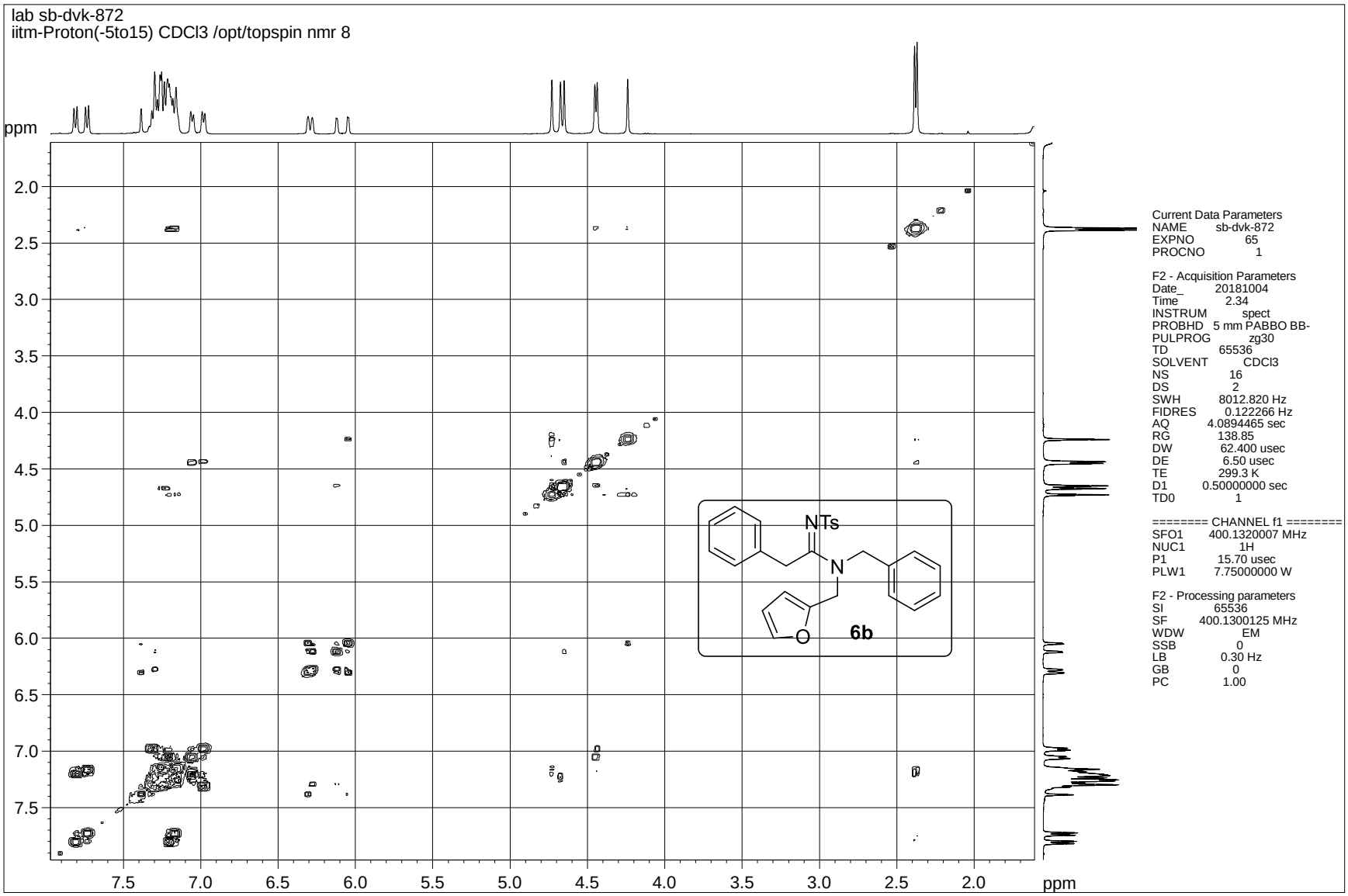
^{1}H NMR spectrum of compound 6b



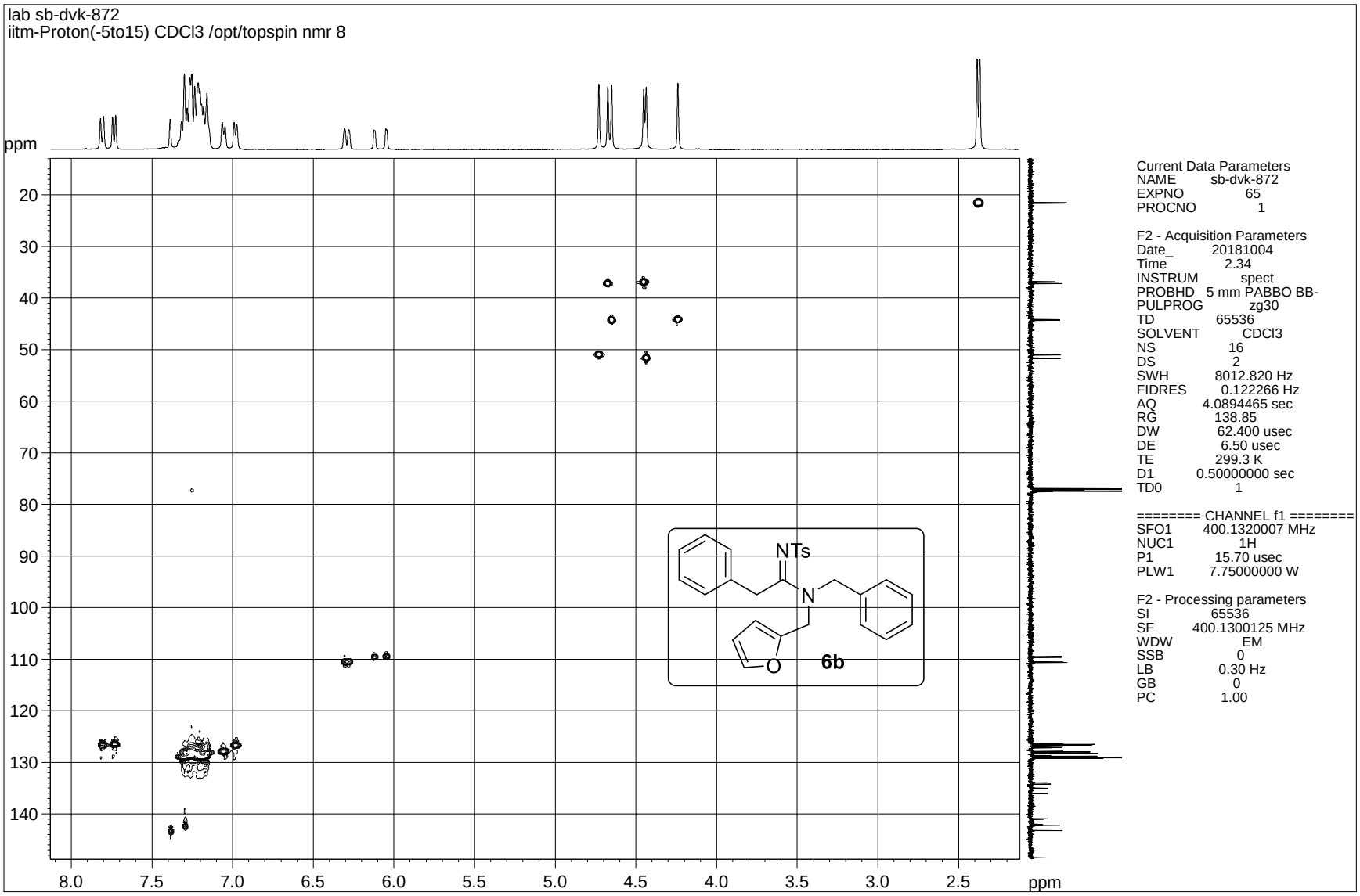
^{13}C NMR spectrum of compound 6b



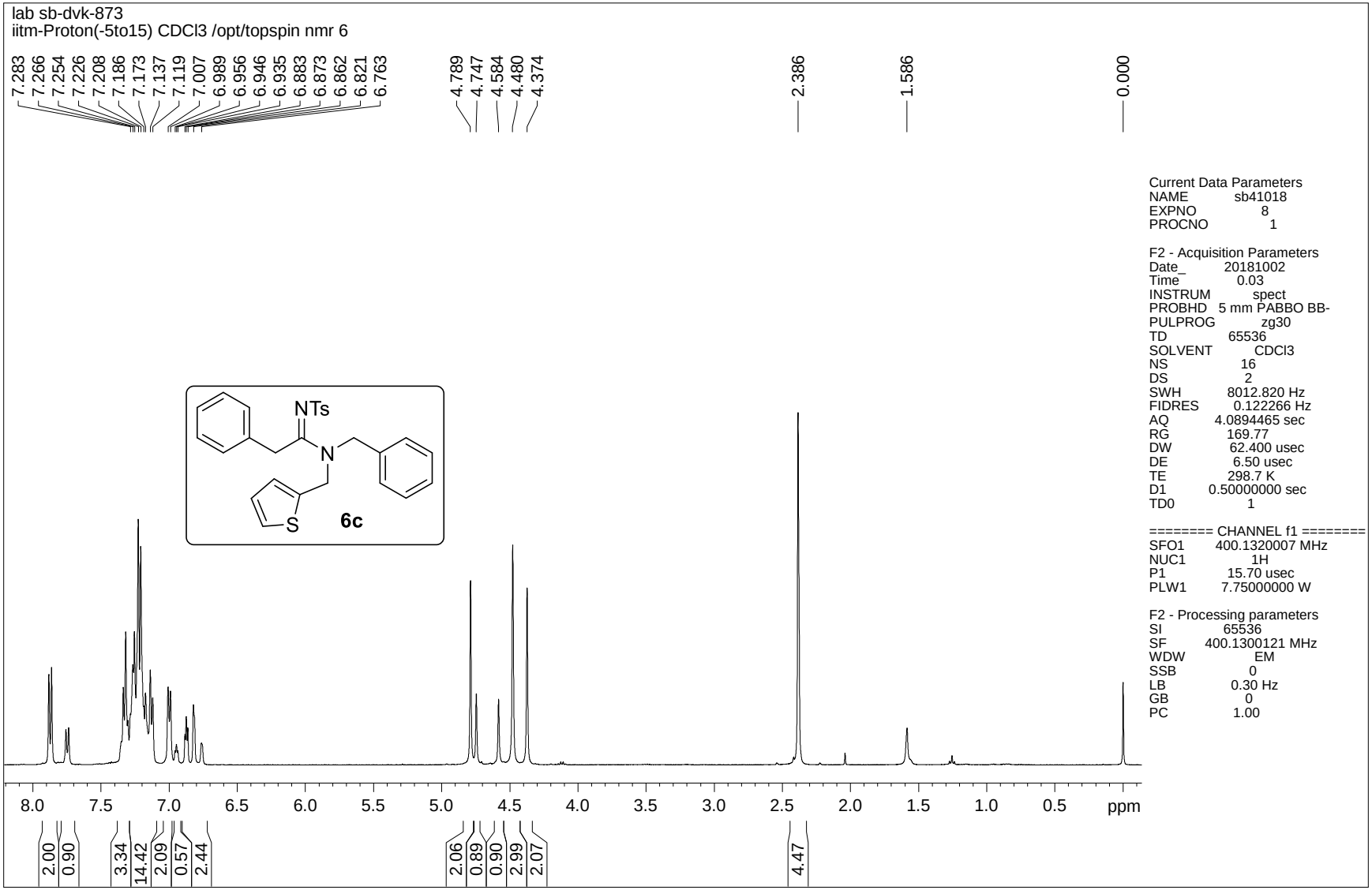
DEPT-135 NMR spectrum of compound 6b



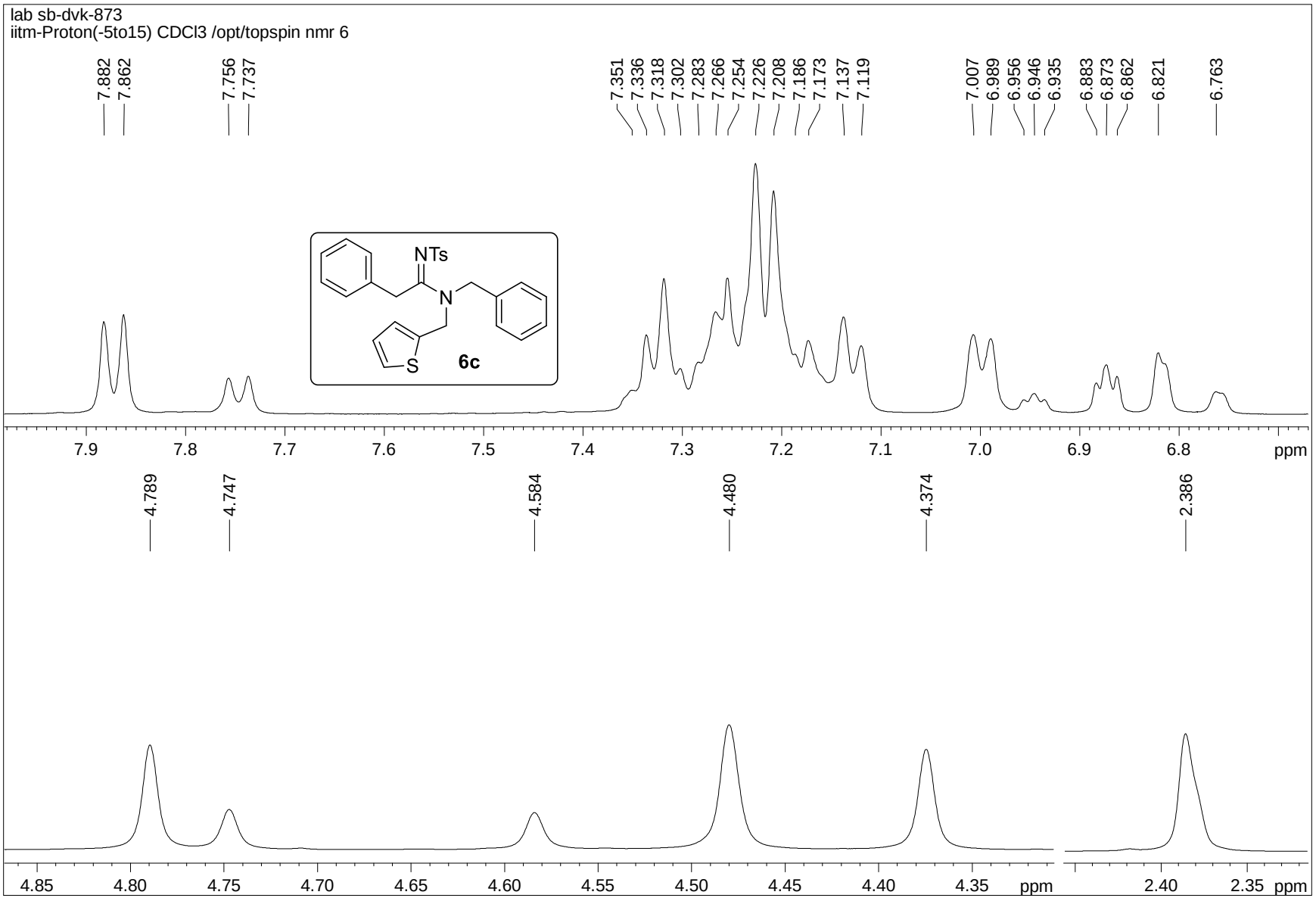
^{1}H-^{1}H COSY NMR spectrum of compound 6b



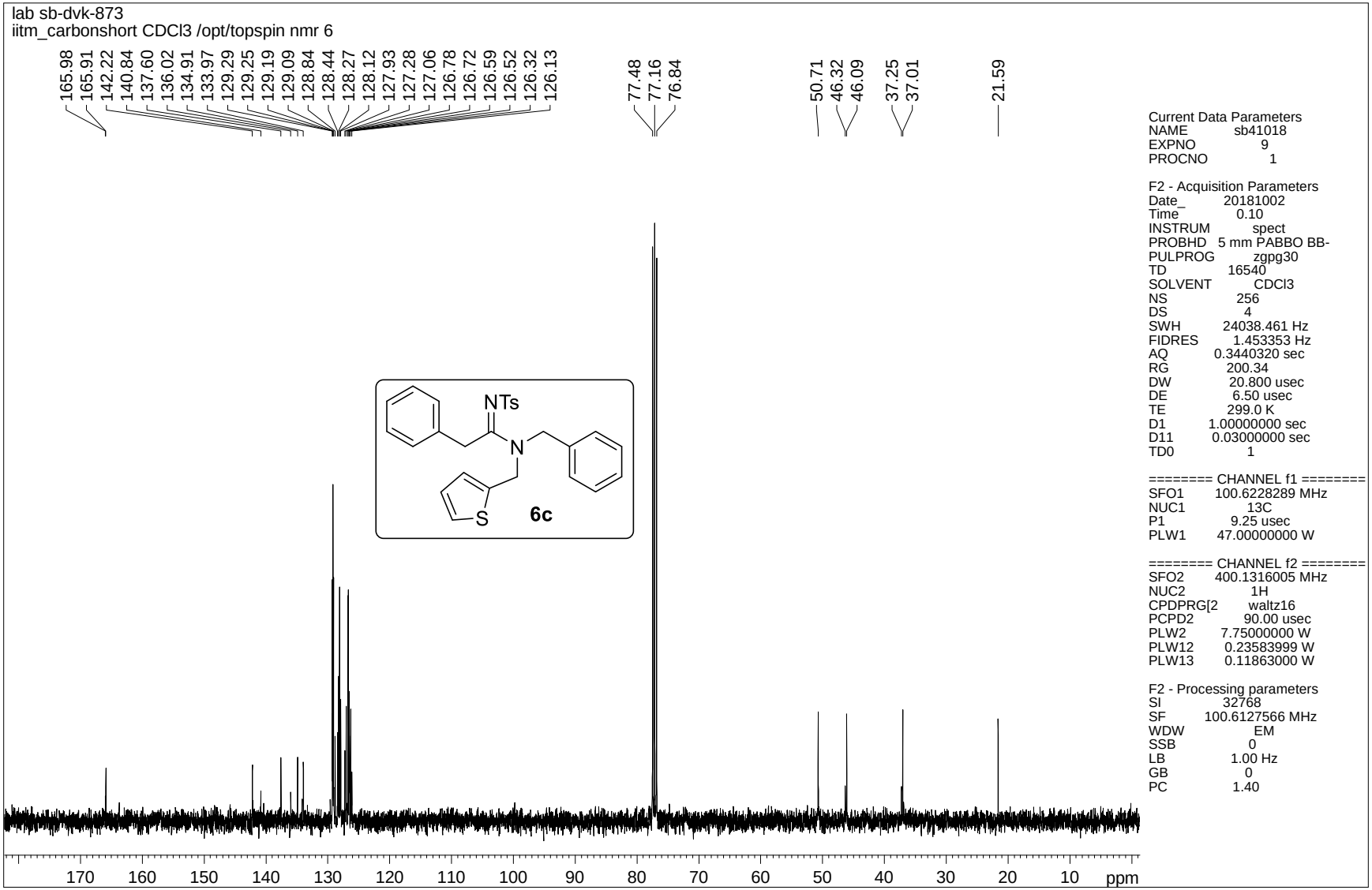
^{1}H-^{13}C HSQC NMR spectrum of compound 6b



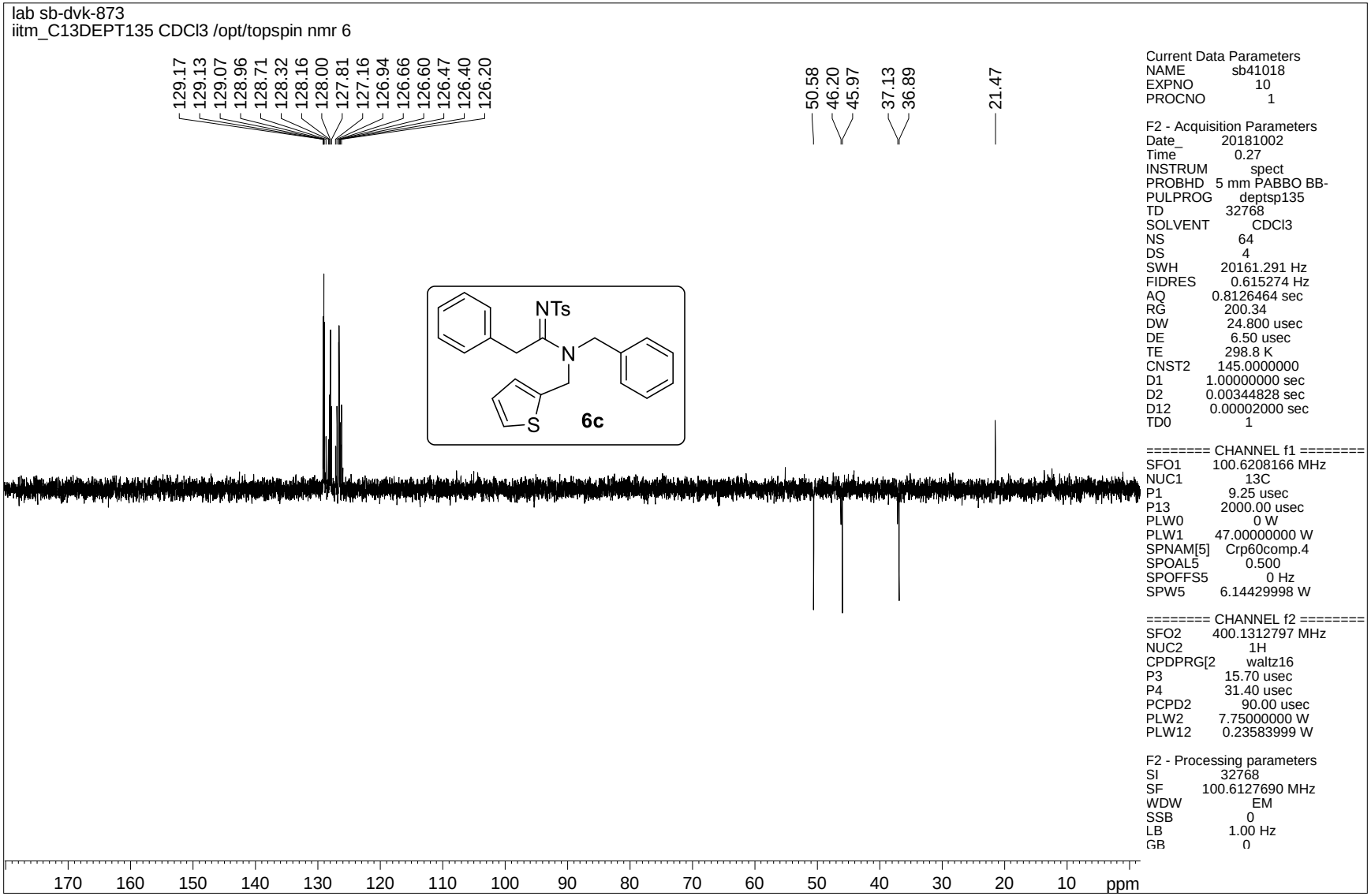
^{1}H NMR spectrum of compound 6c



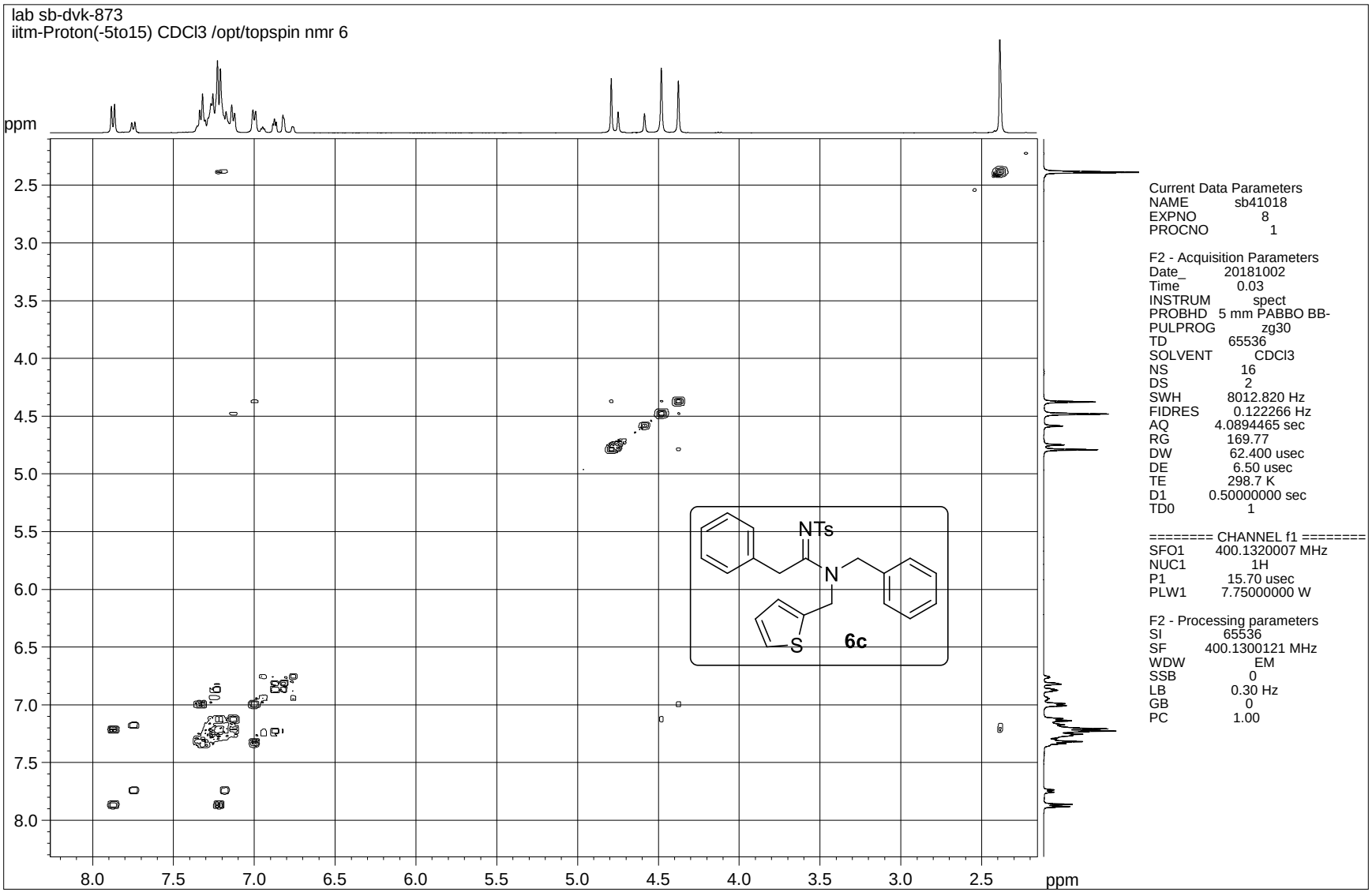
^{1}H NMR spectrum of compound 6c



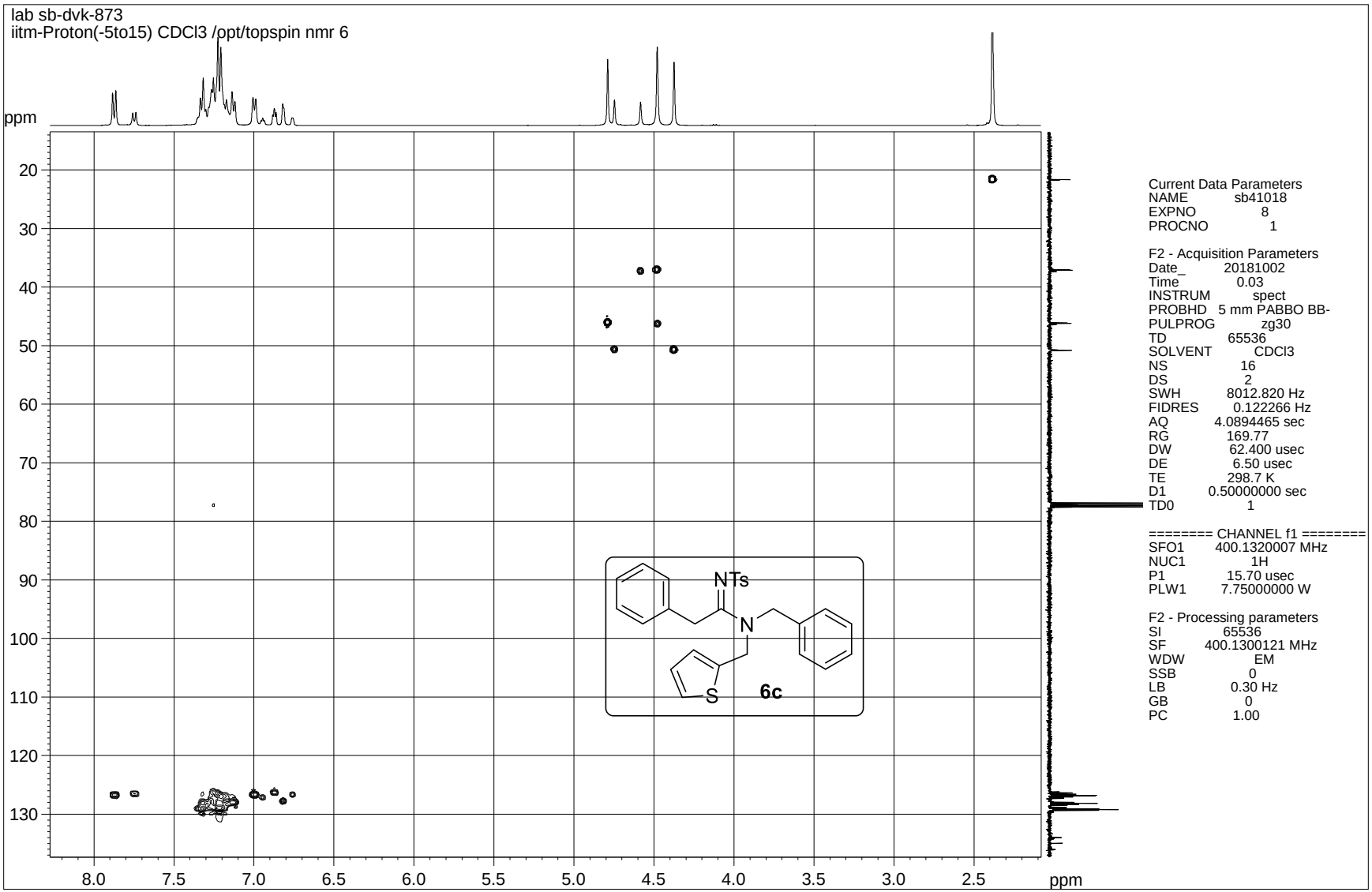
^{13}C NMR spectrum of compound 6c



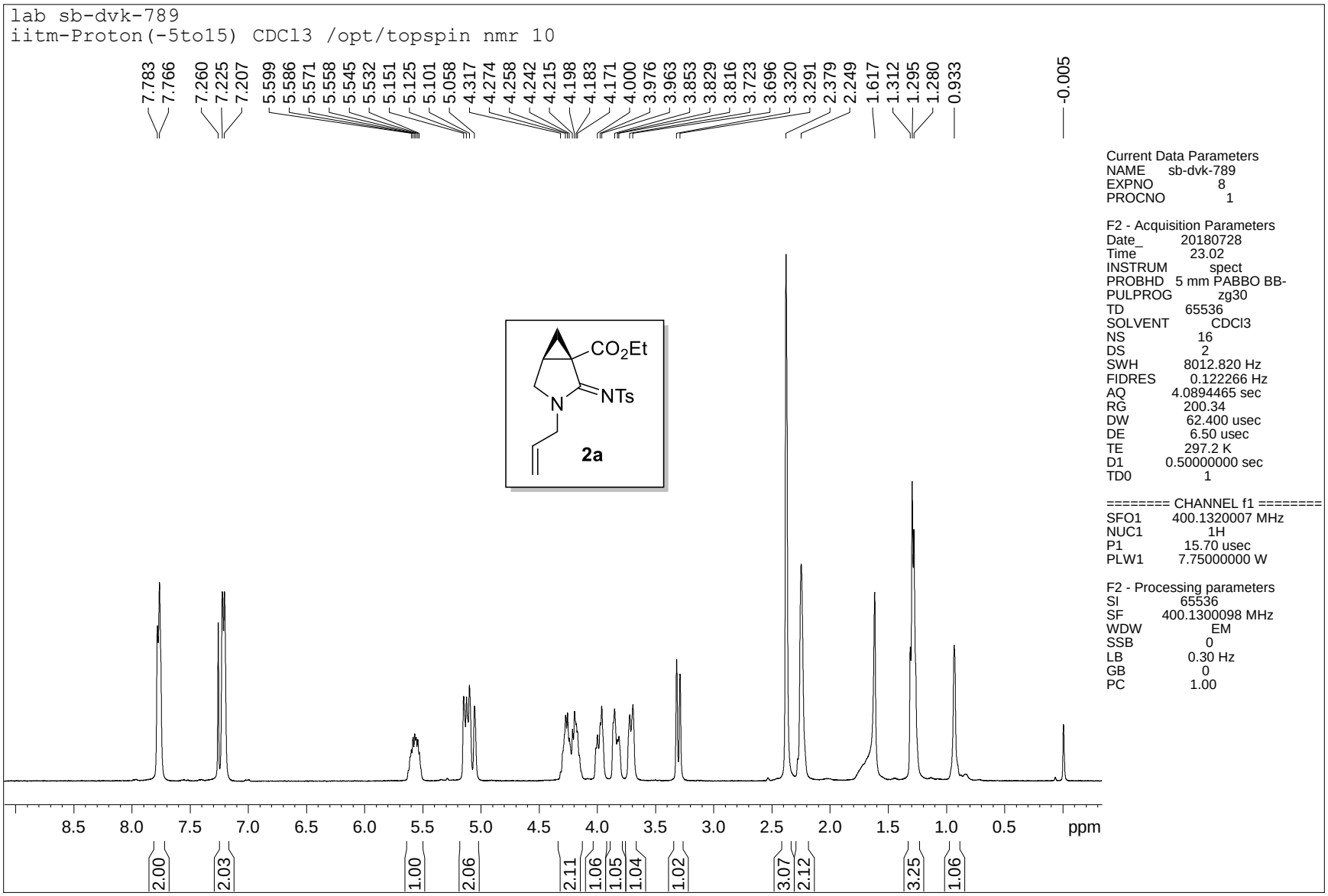
DEPT-135 NMR spectrum of compound 6c



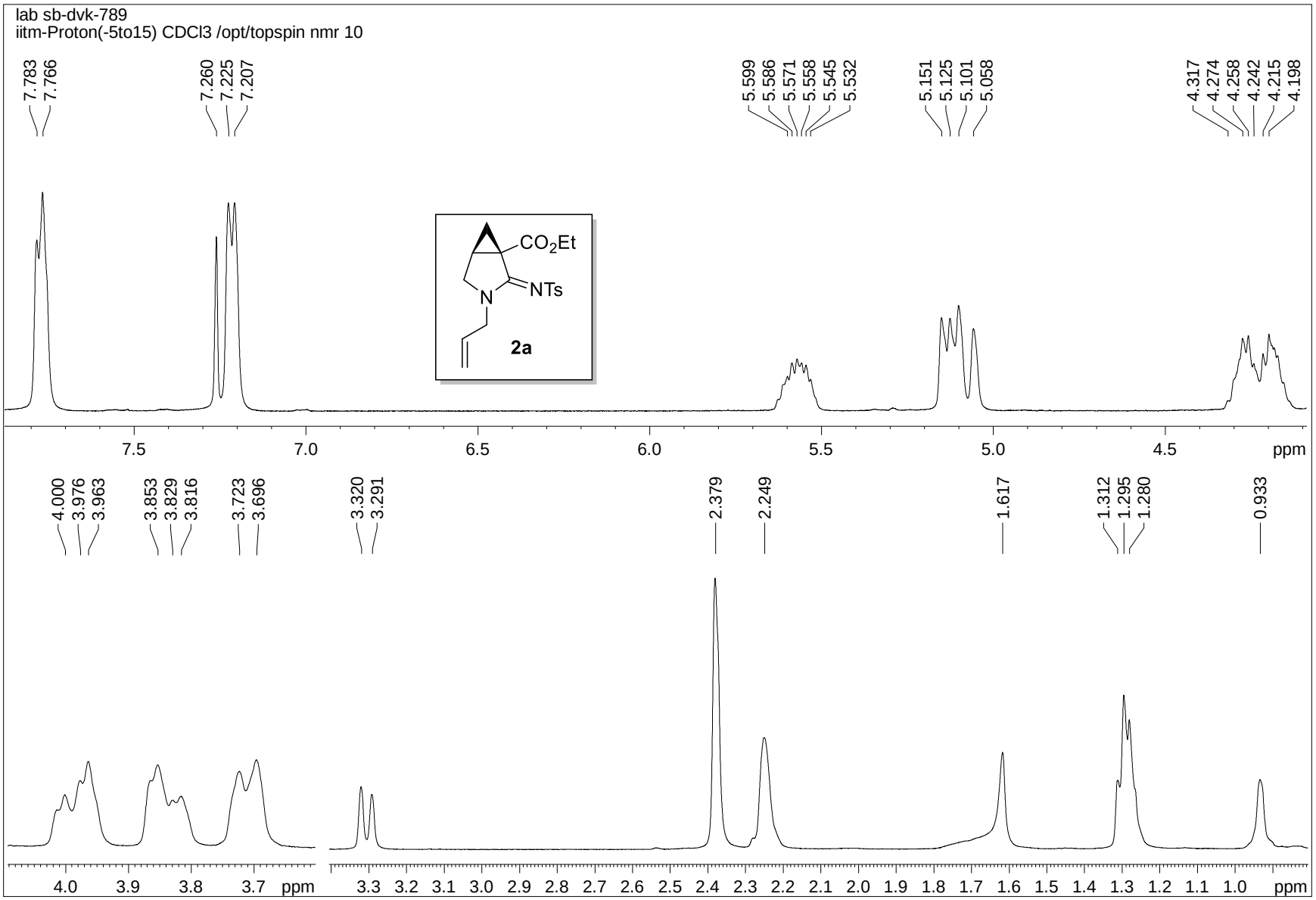
^{1}H-^{1}H COSY NMR spectrum of compound 6c



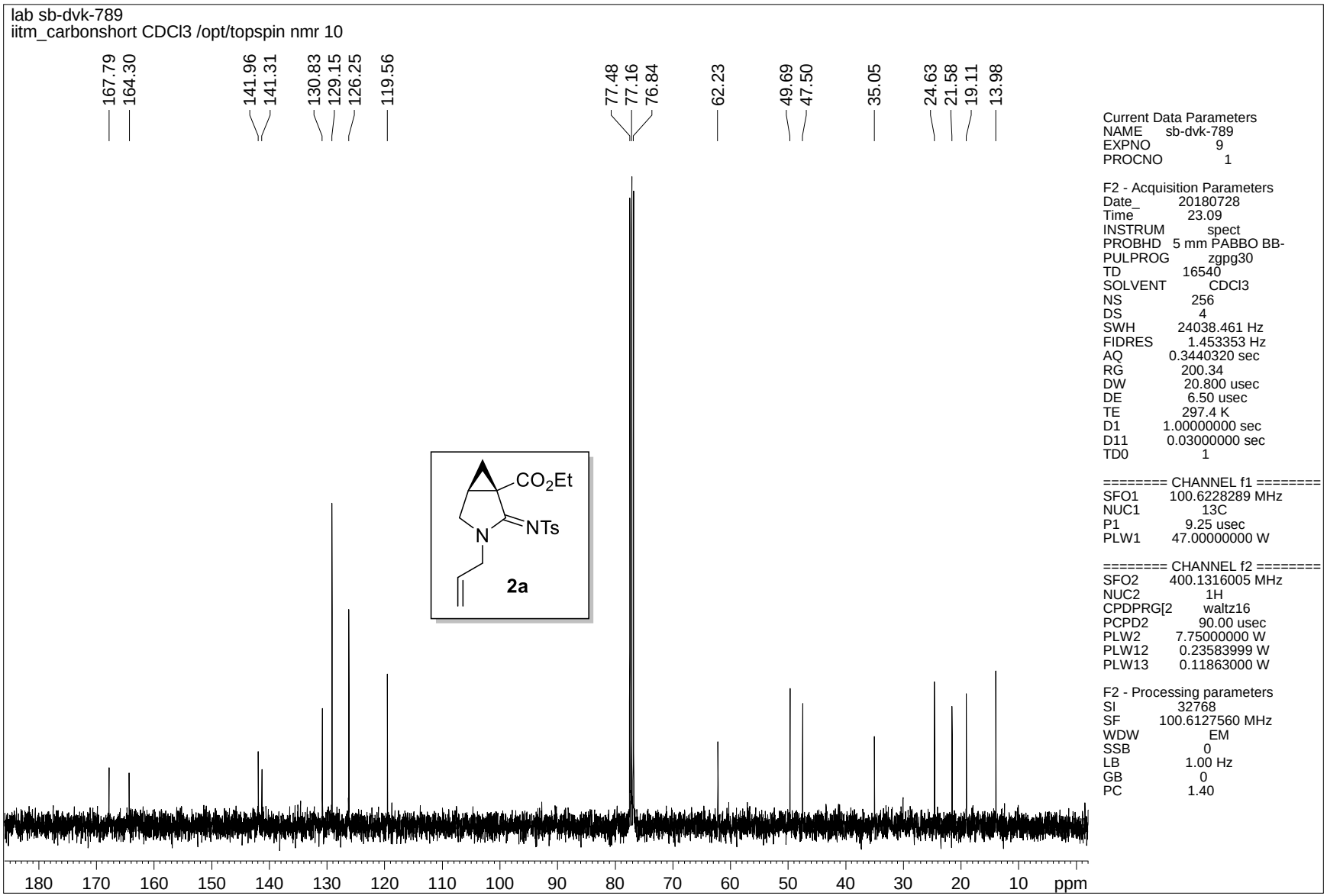
^{1}H-^{13}C HSQC NMR spectrum of compound 6c



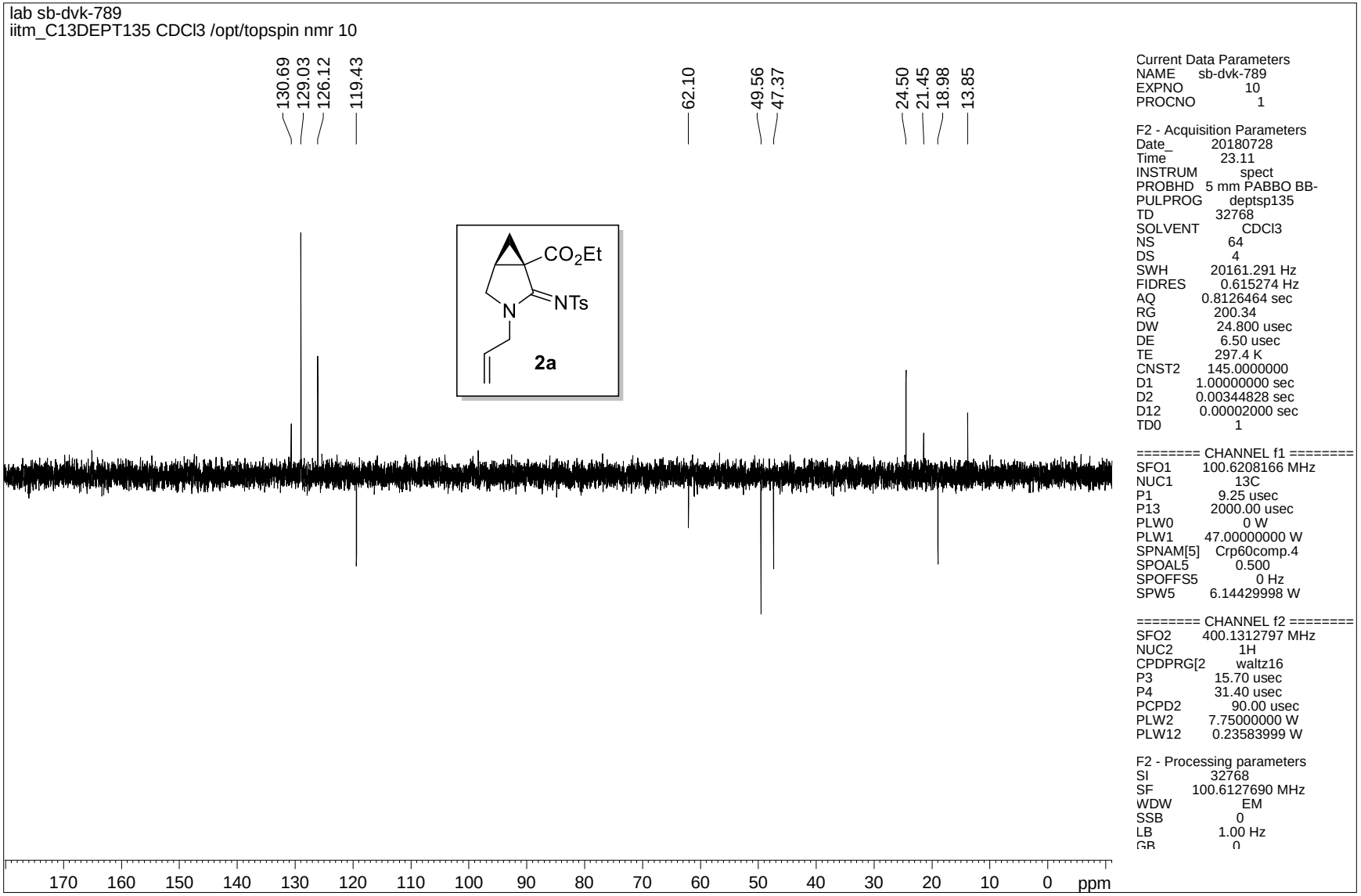
^{1}H NMR spectrum of compound 2a



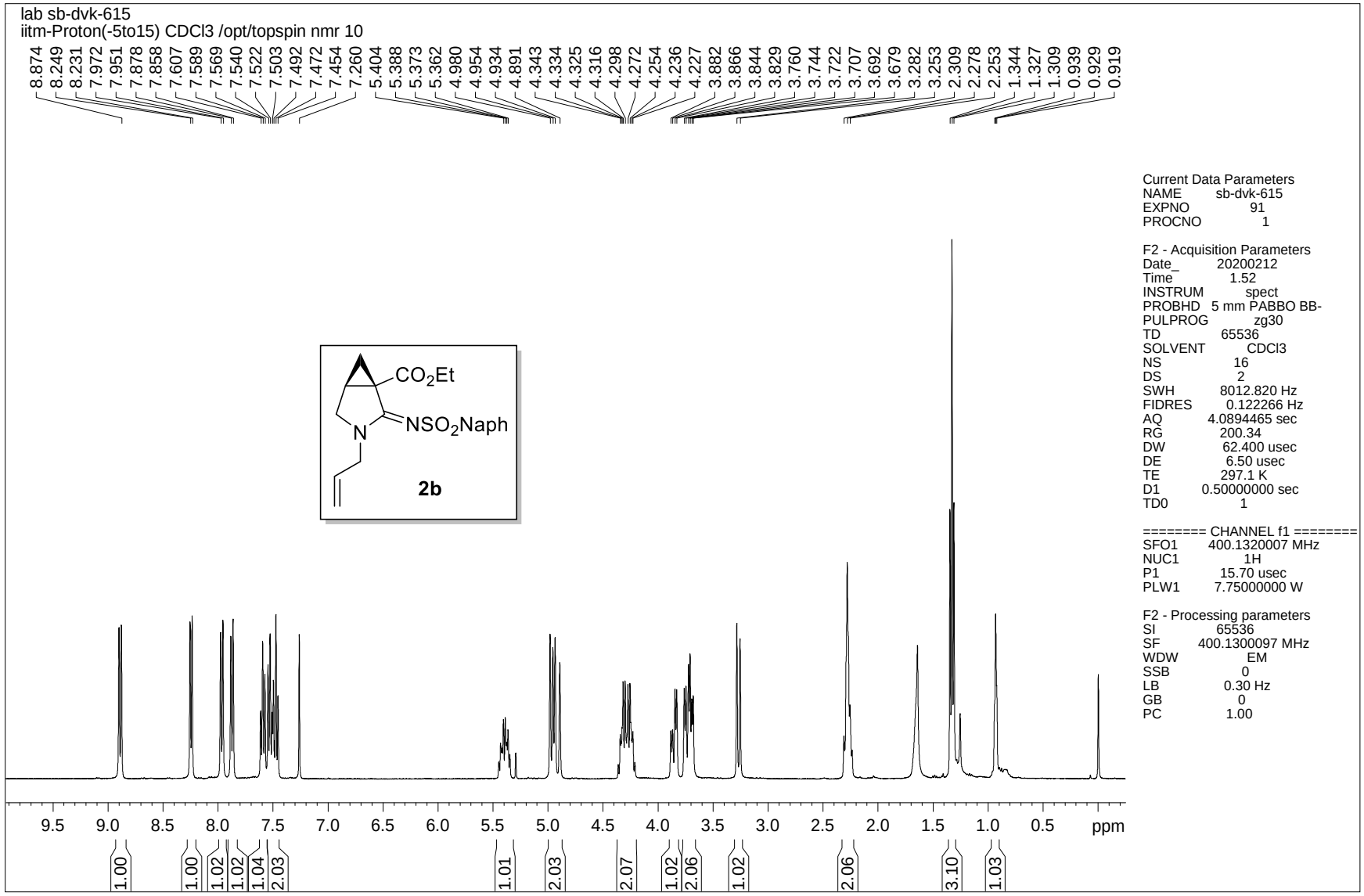
^{1}H NMR spectrum of compound 2a



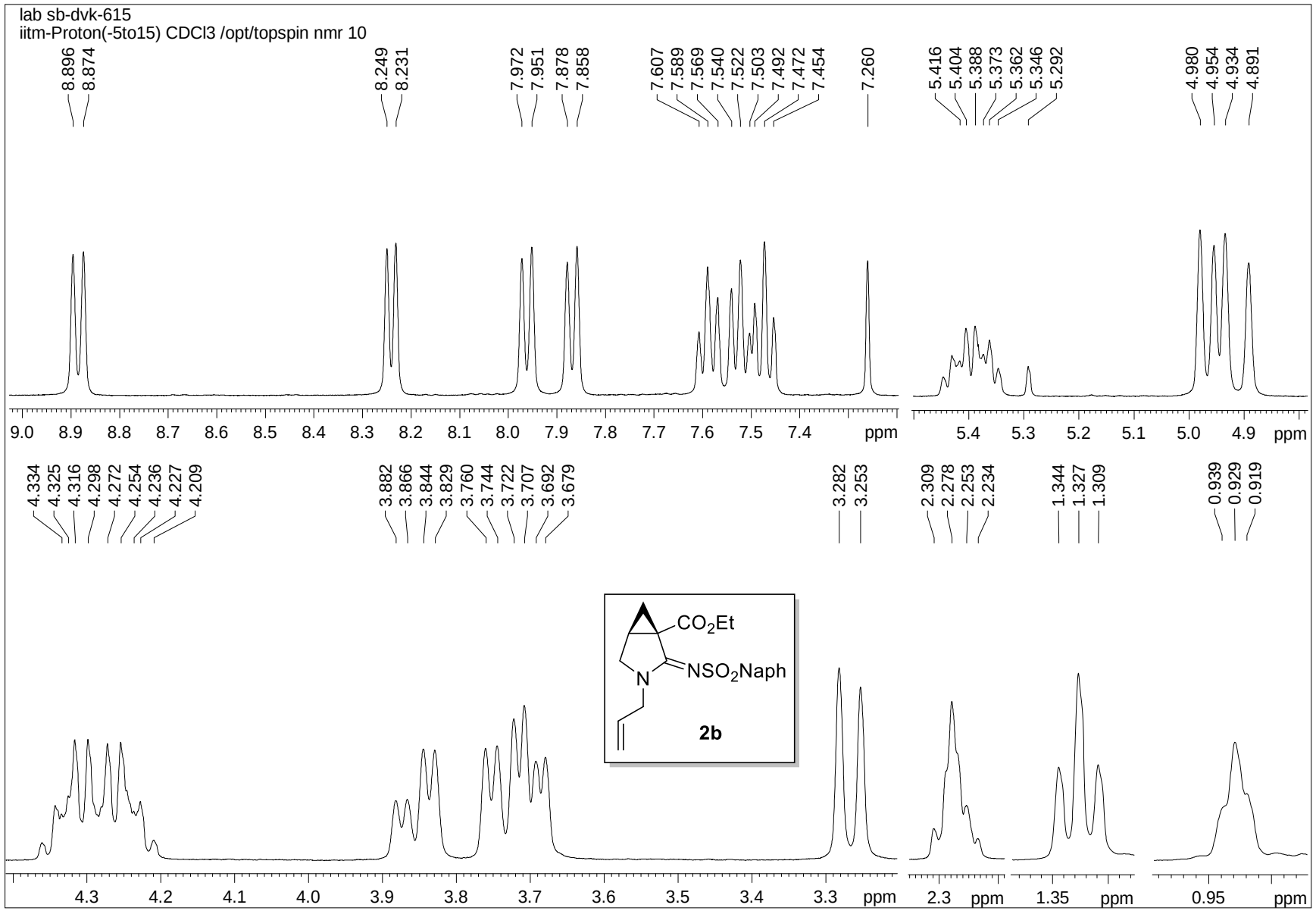
^{13}C NMR spectrum of compound 2a



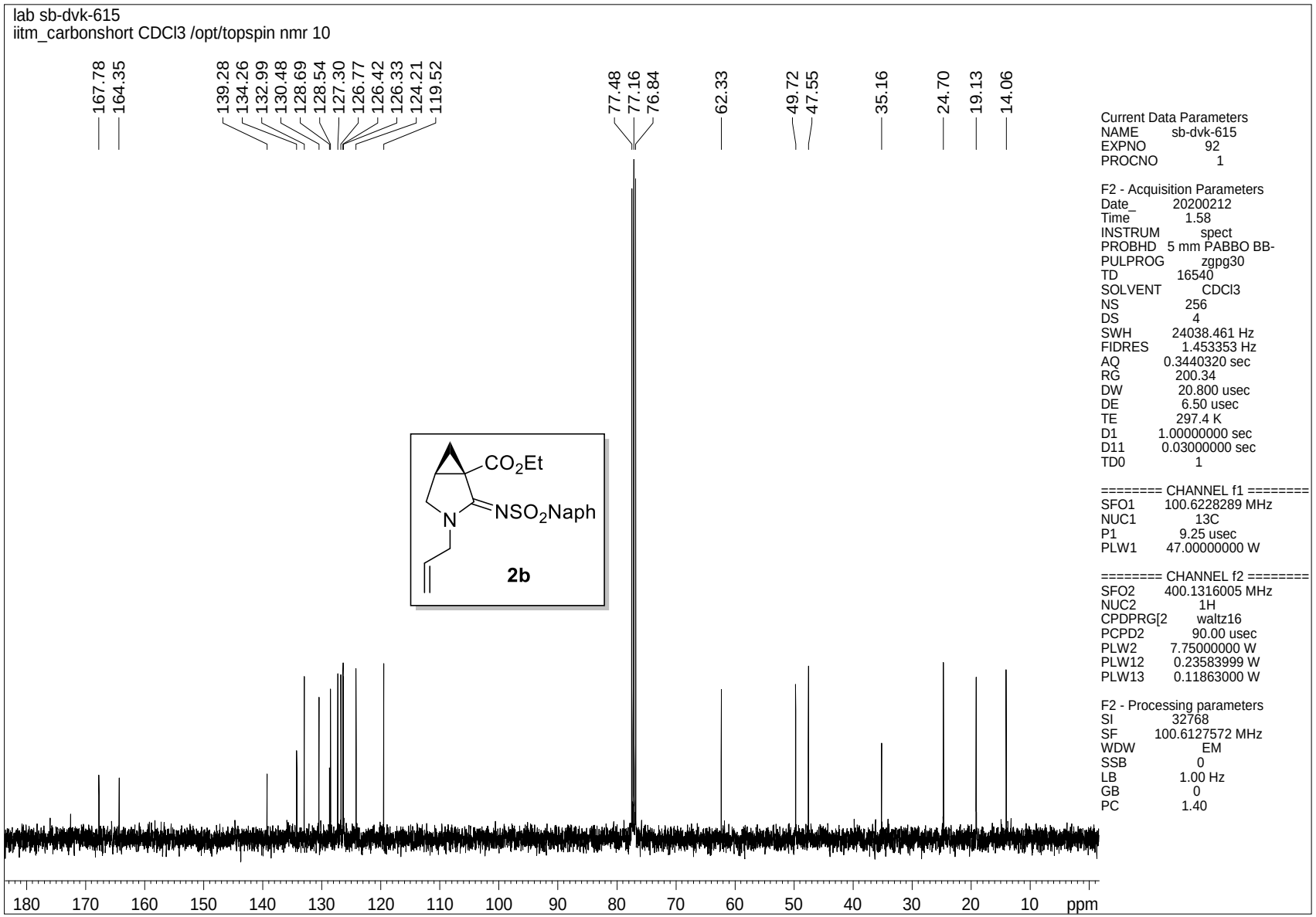
DEPT-135 NMR spectrum of compound 2a



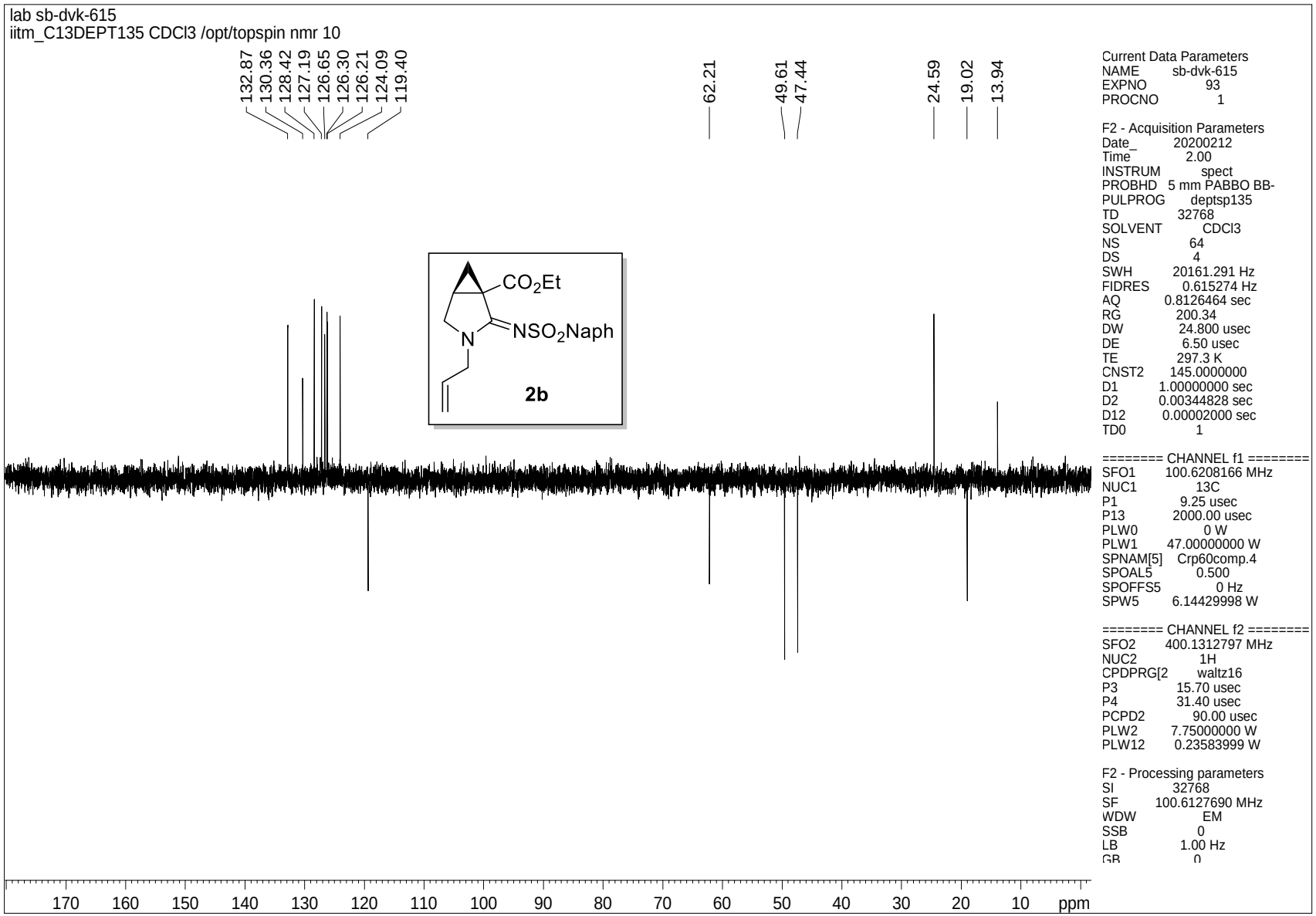
^{1}H NMR spectrum of compound 2b



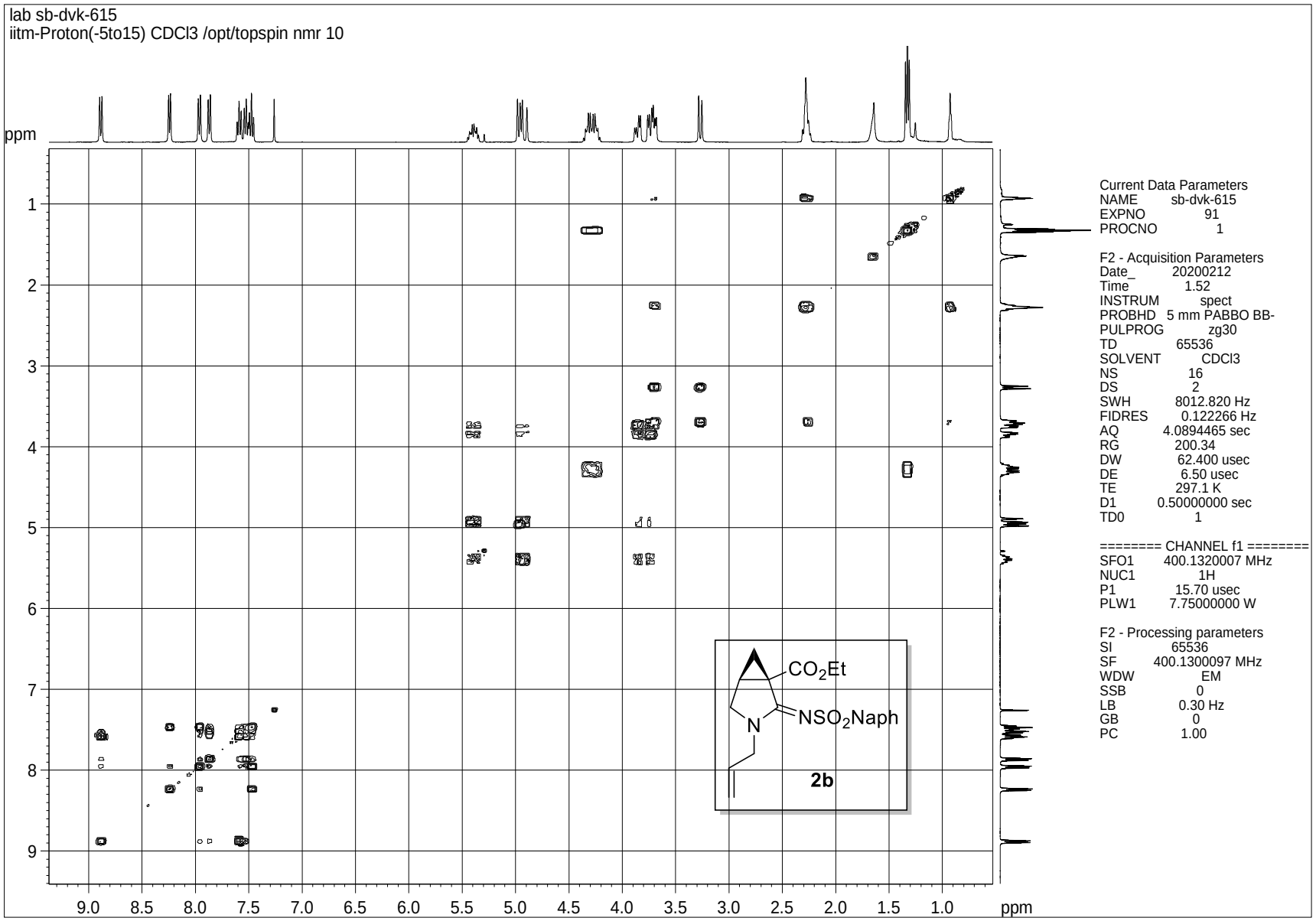
[1]H NMR spectrum of compound 2b



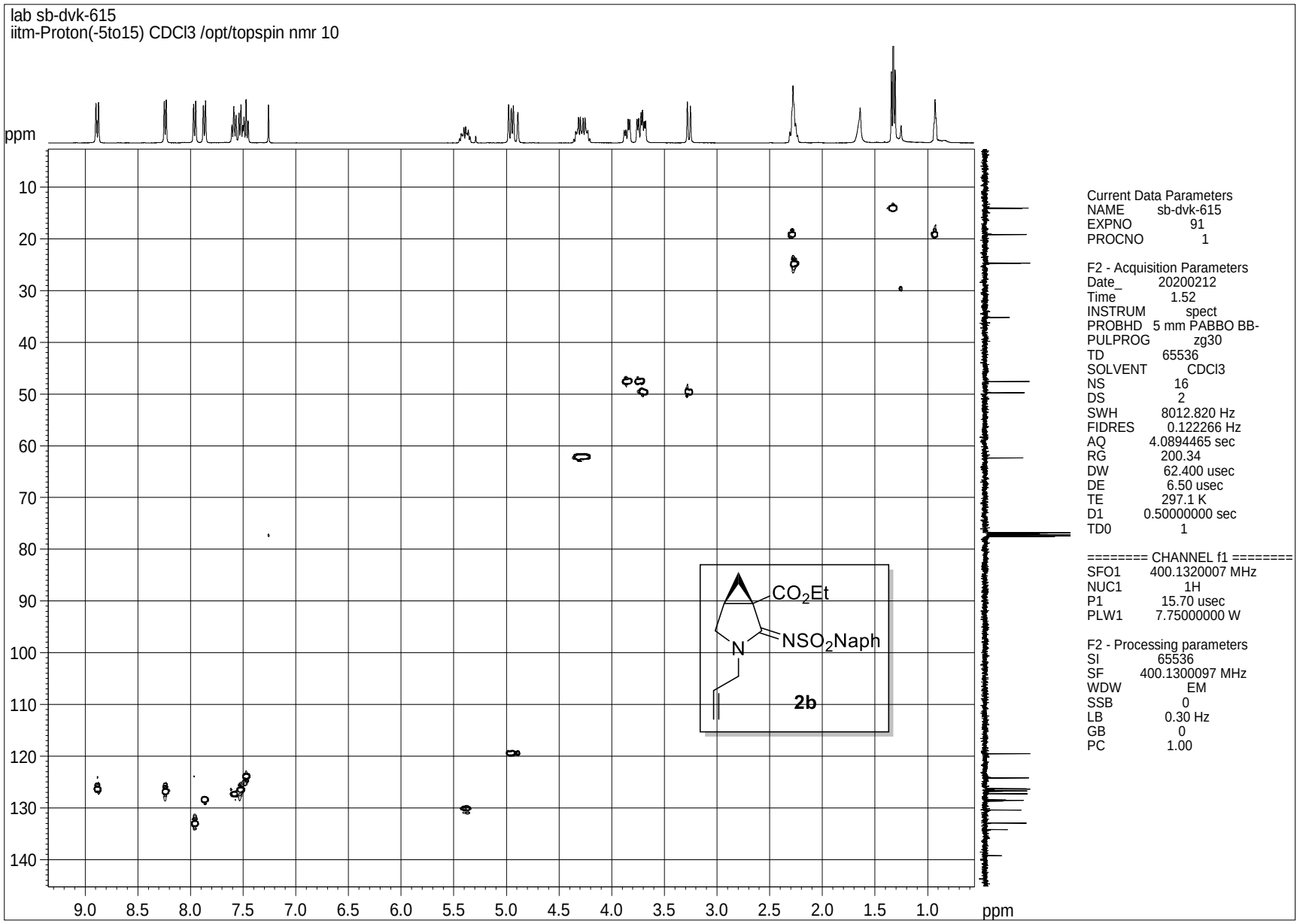
^{13}C NMR spectrum of compound 2b



DEPT-135 NMR spectrum of compound 2b

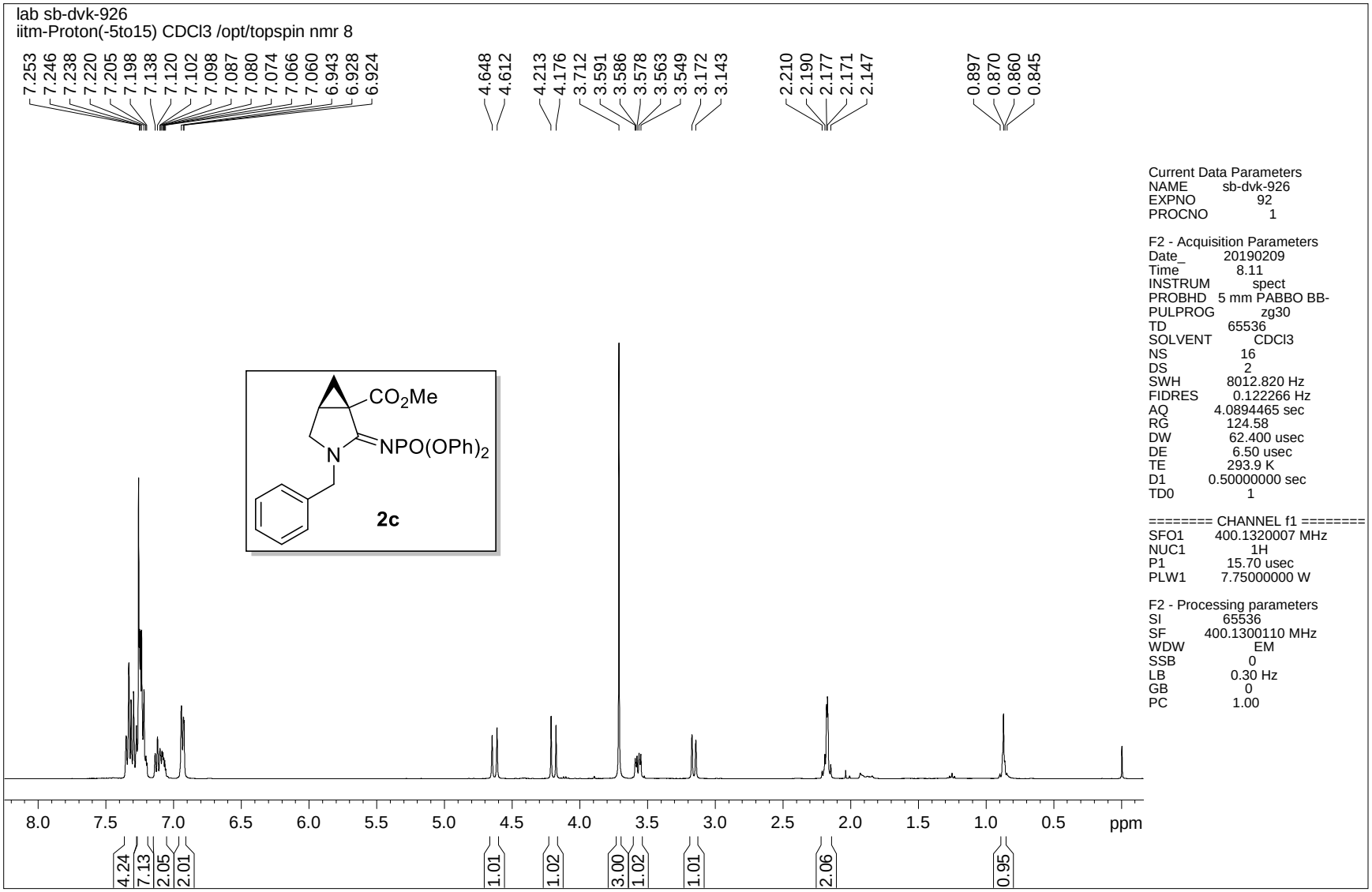


^{1}H-^{1}H COSY NMR spectrum of compound 2b

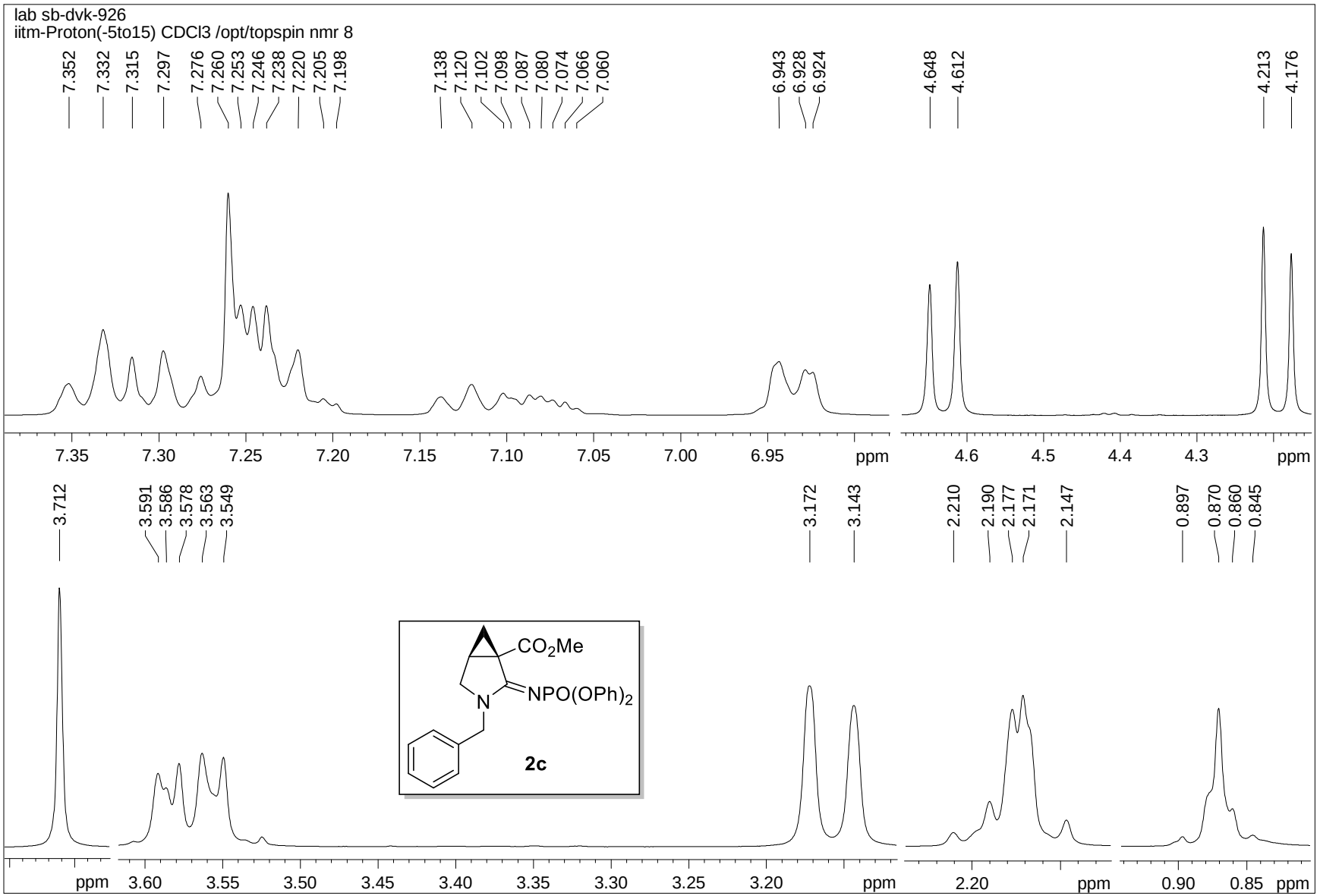


S

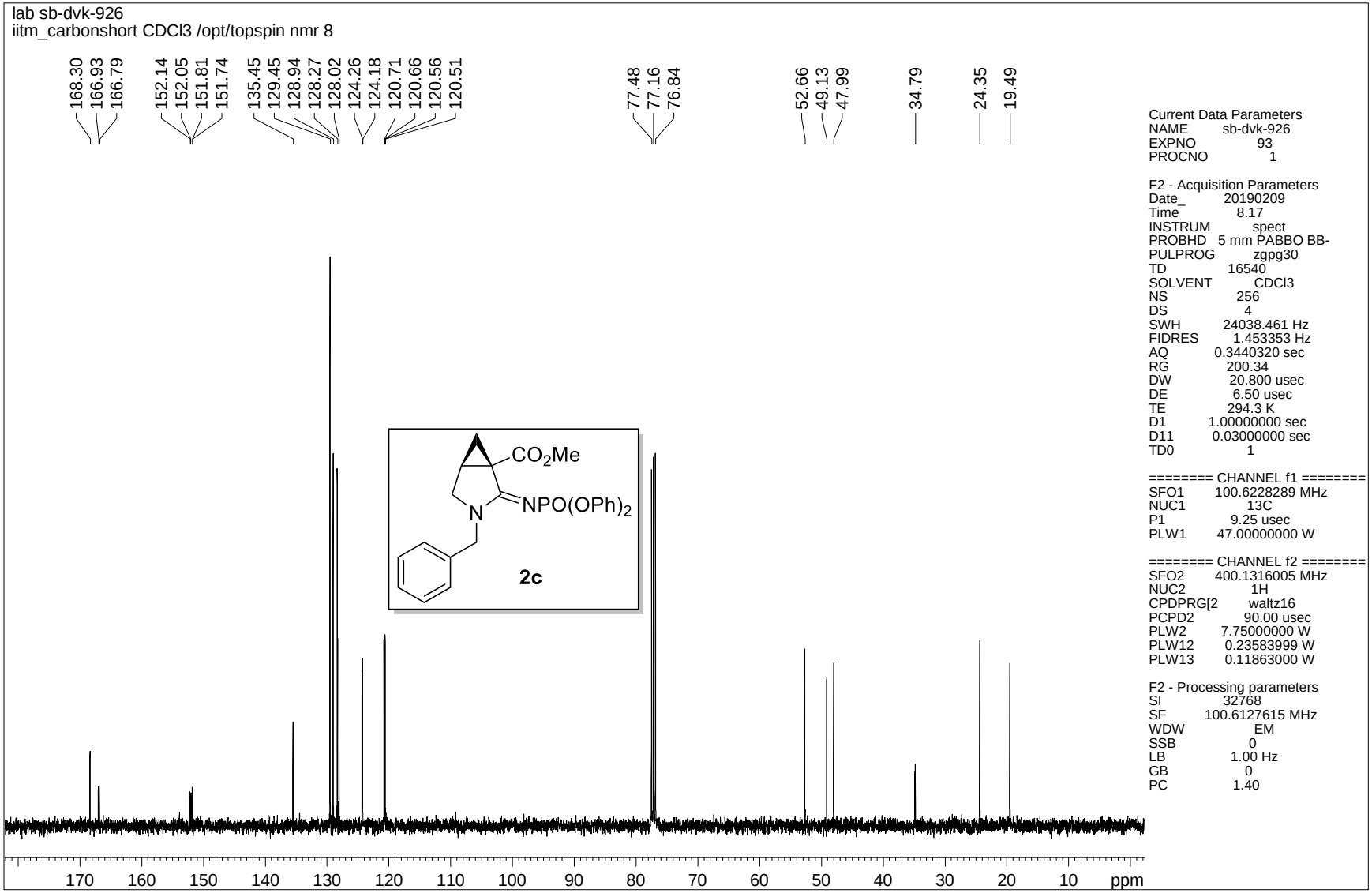
^{1}H-^{13}C HSQC NMR spectrum of compound 2b



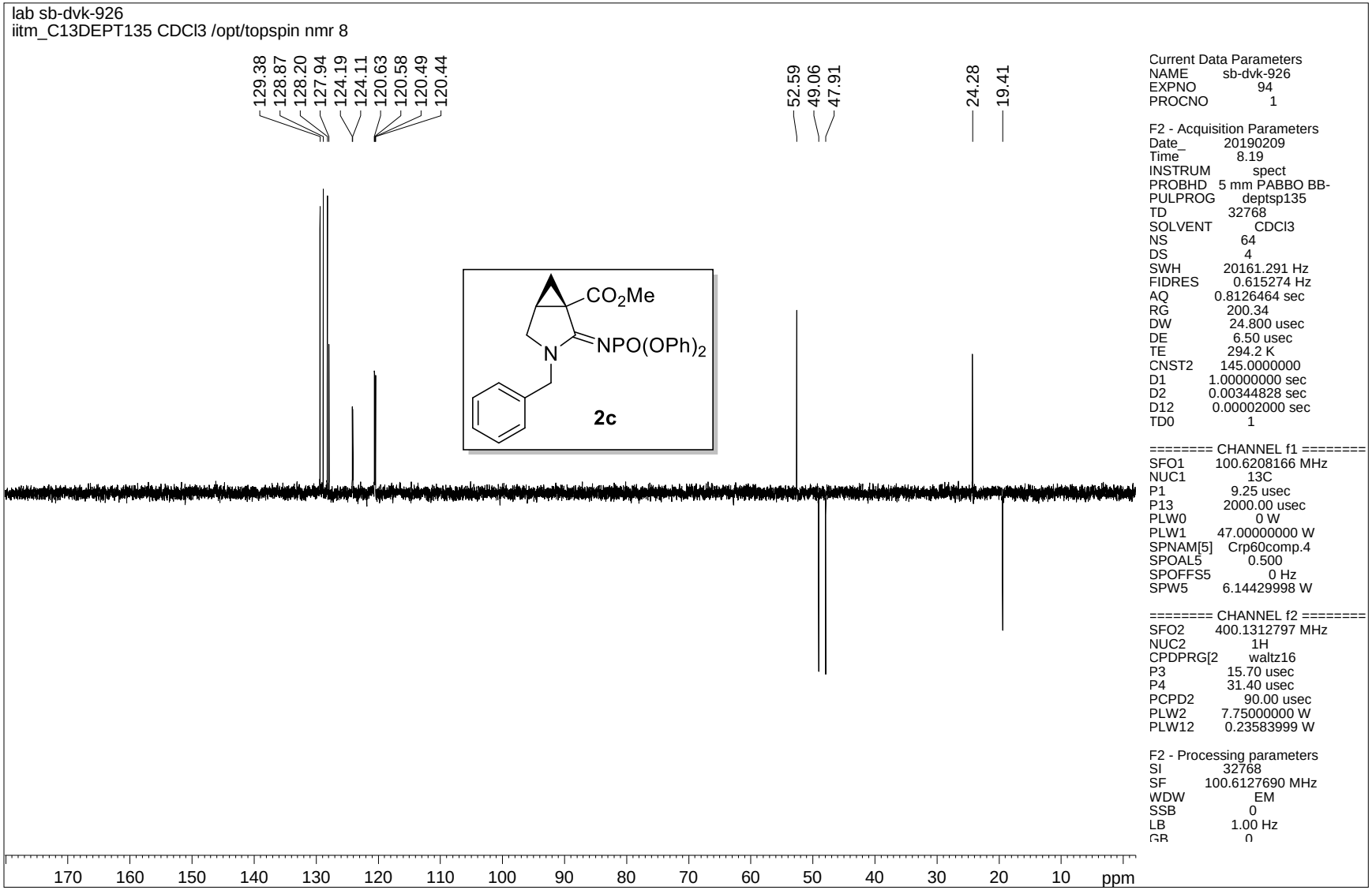
^{1}H NMR spectrum of compound 2c



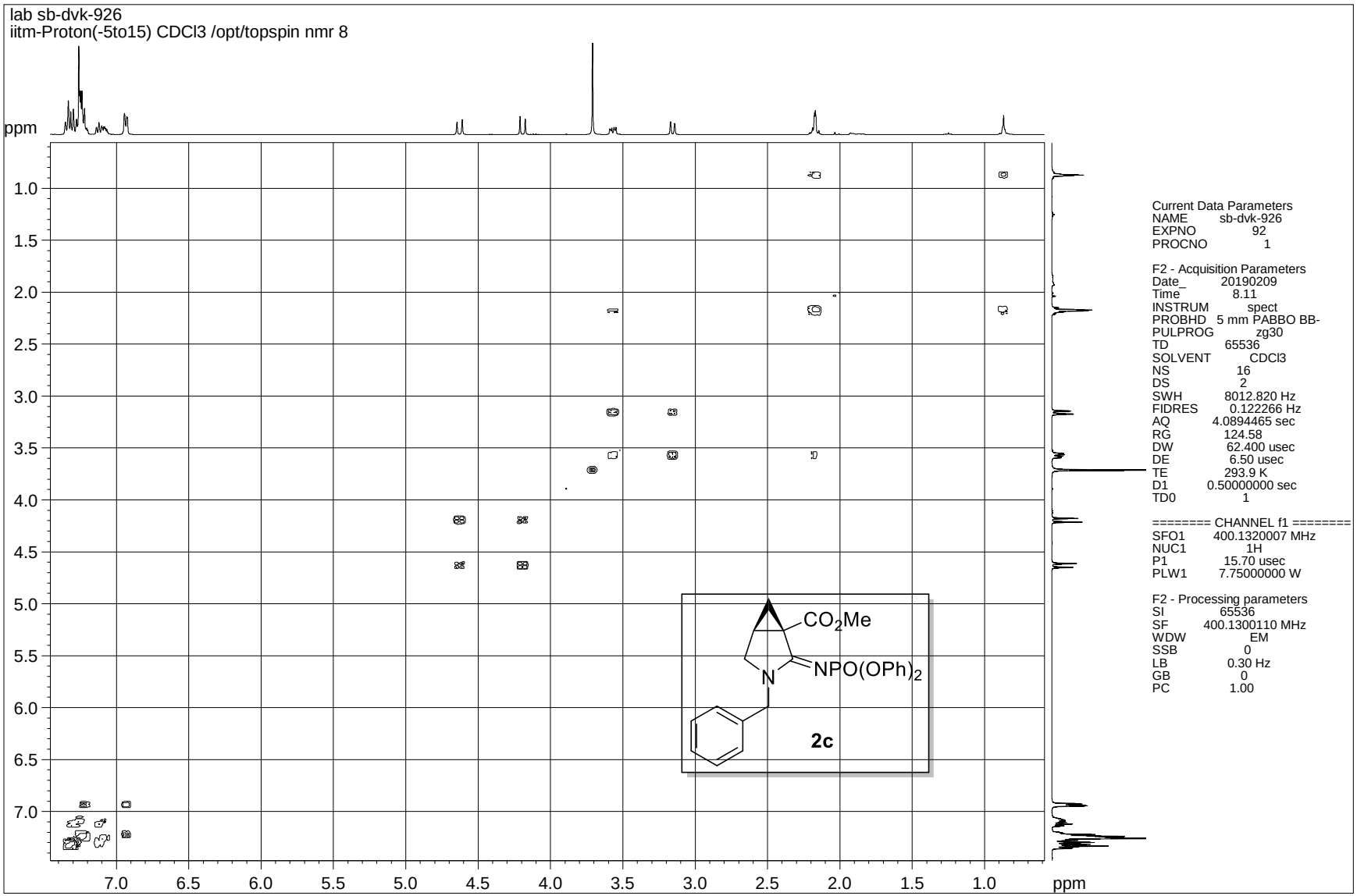
^{1}H NMR spectrum of compound 2c



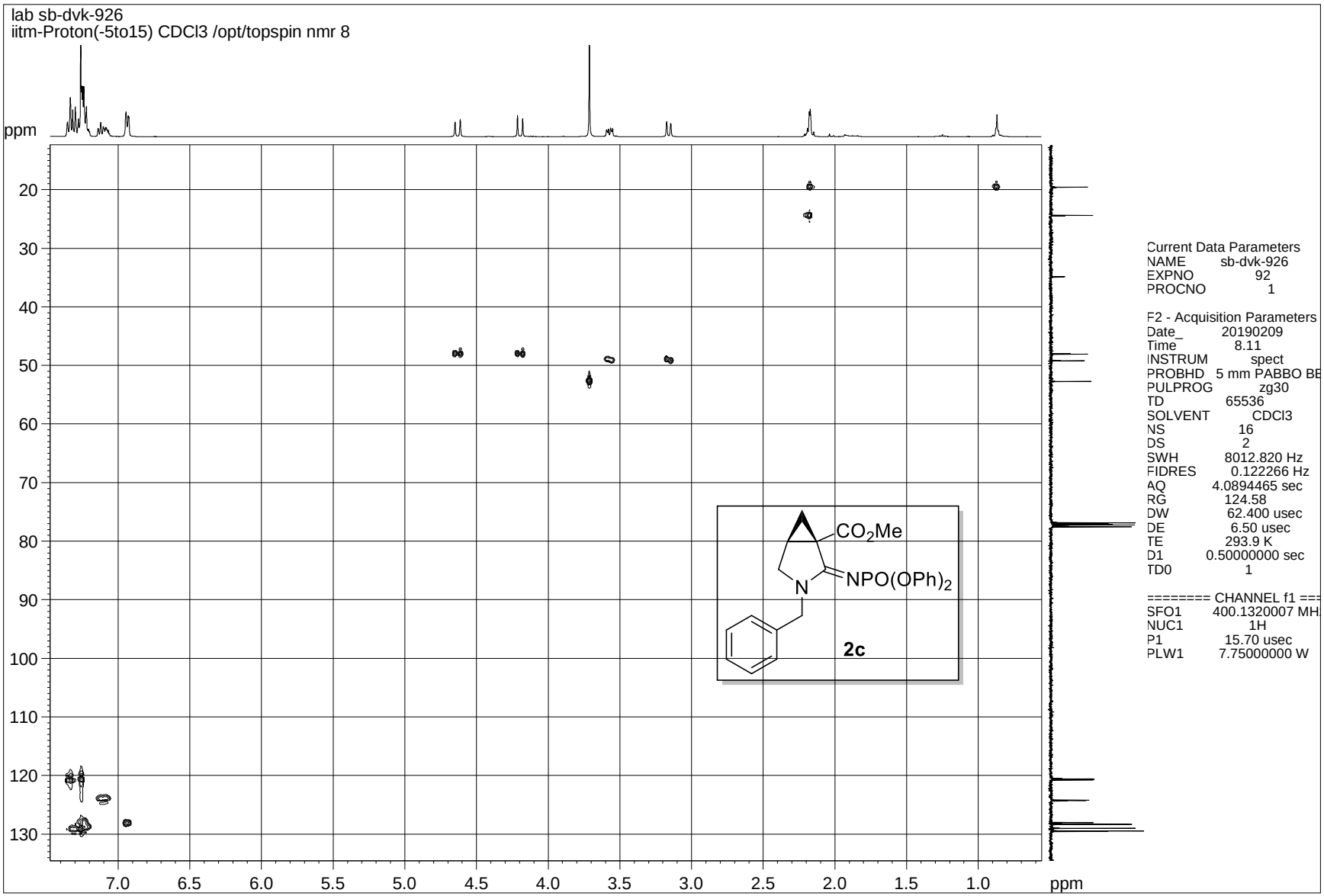
^{13}C NMR spectrum of compound 2c



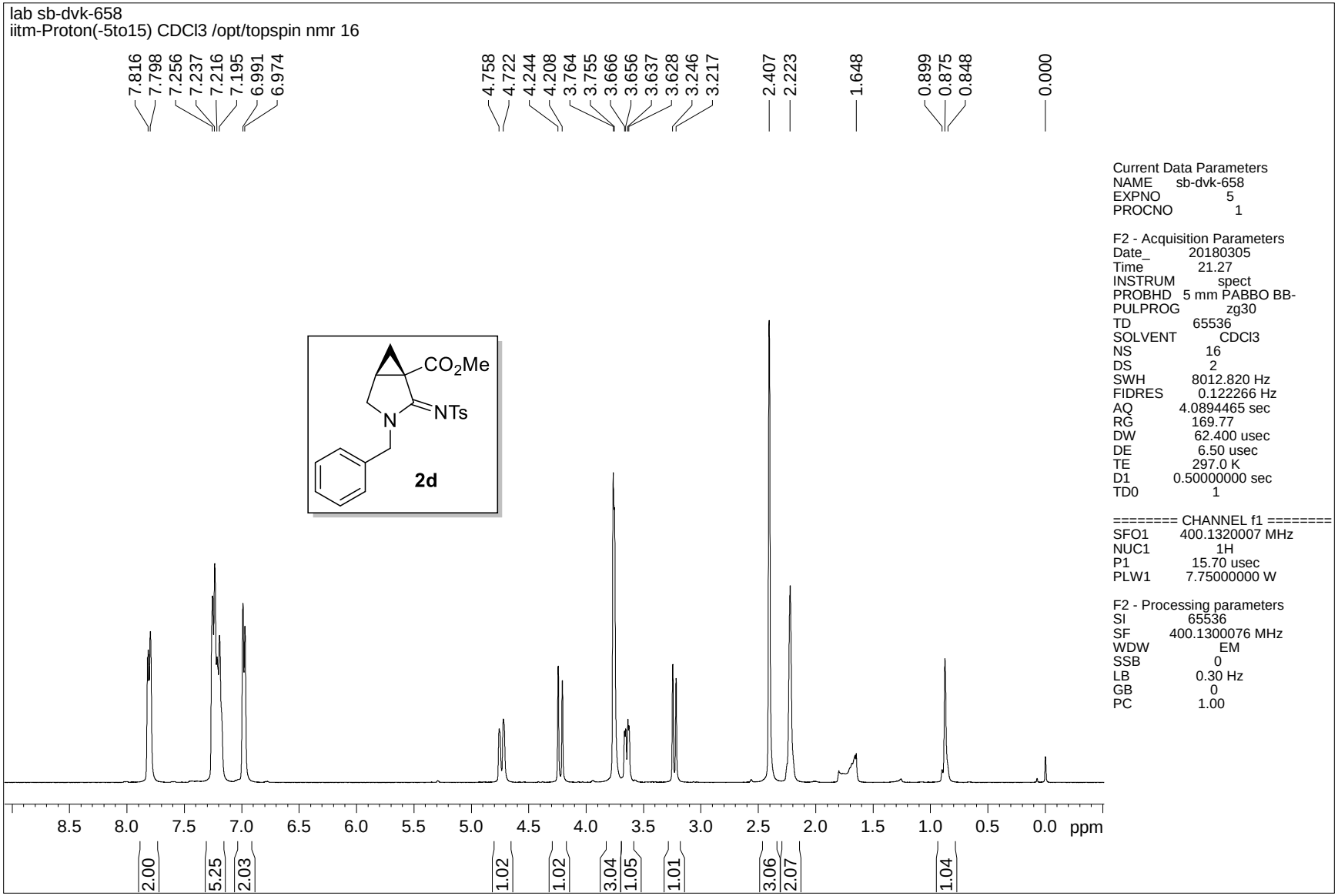
DEPT-135 NMR spectrum of compound 2c



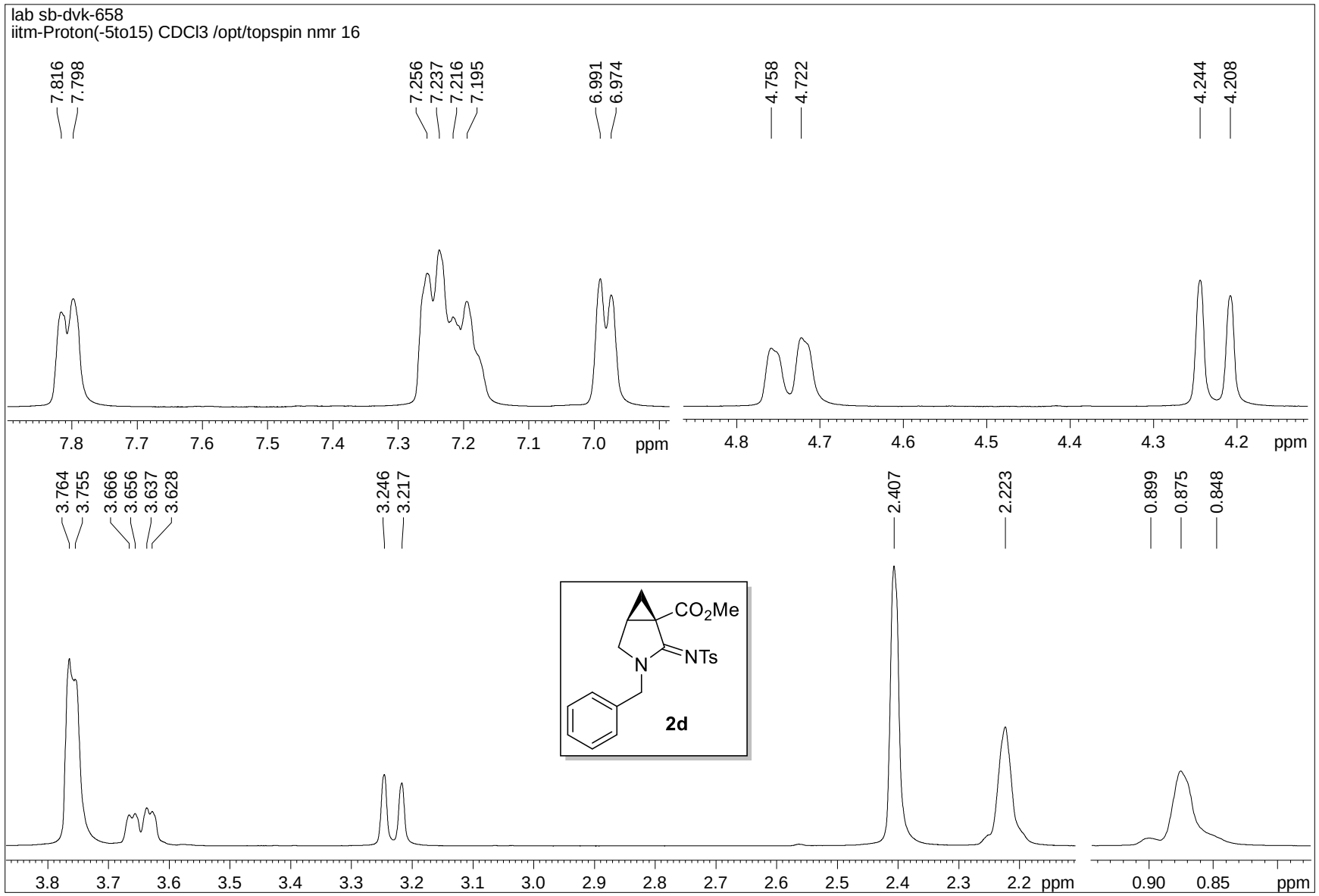
^{1}H-^{1}H COSY NMR spectrum of compound 2c



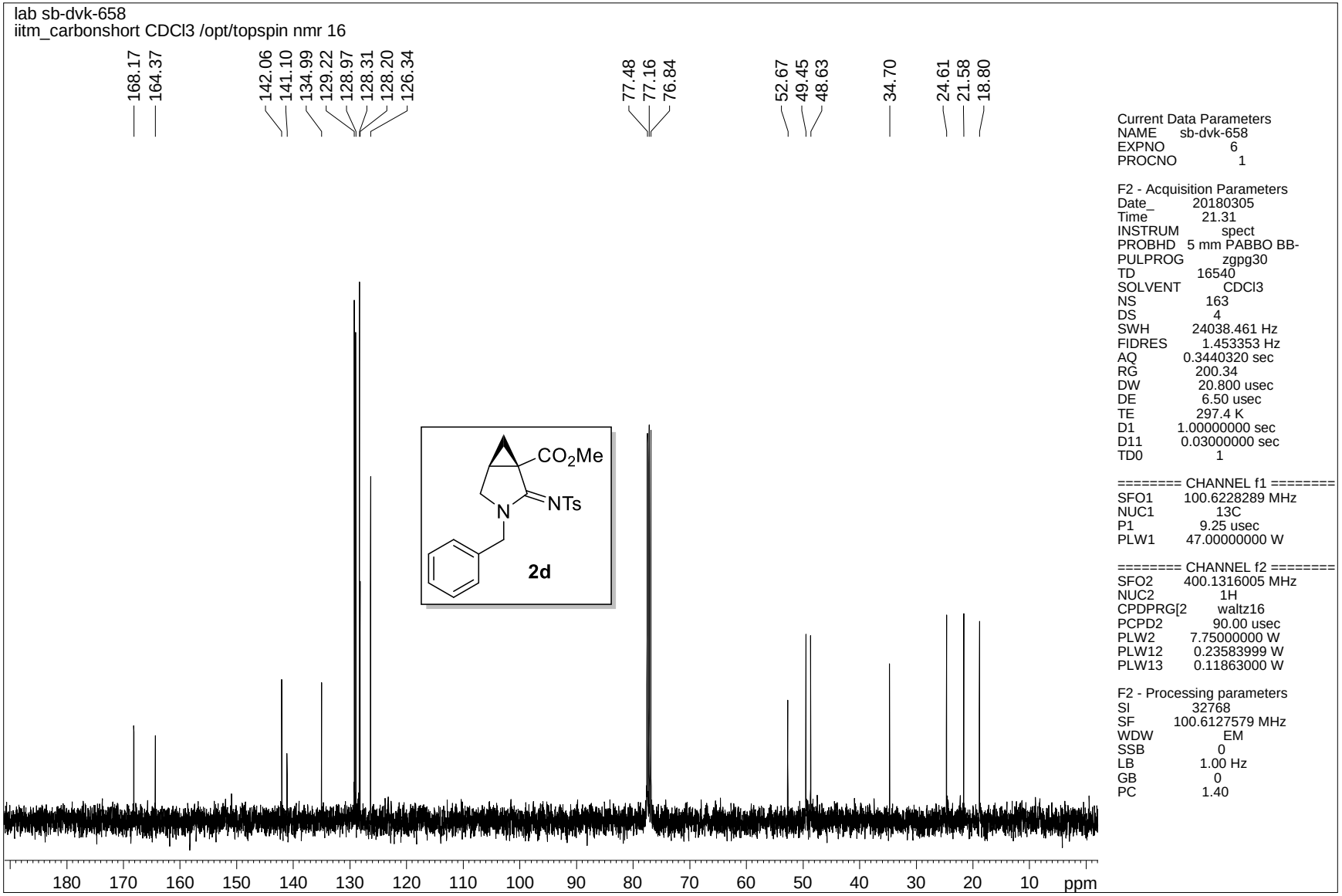
^{1}H-^{13}C HSQC NMR spectrum of compound 2c



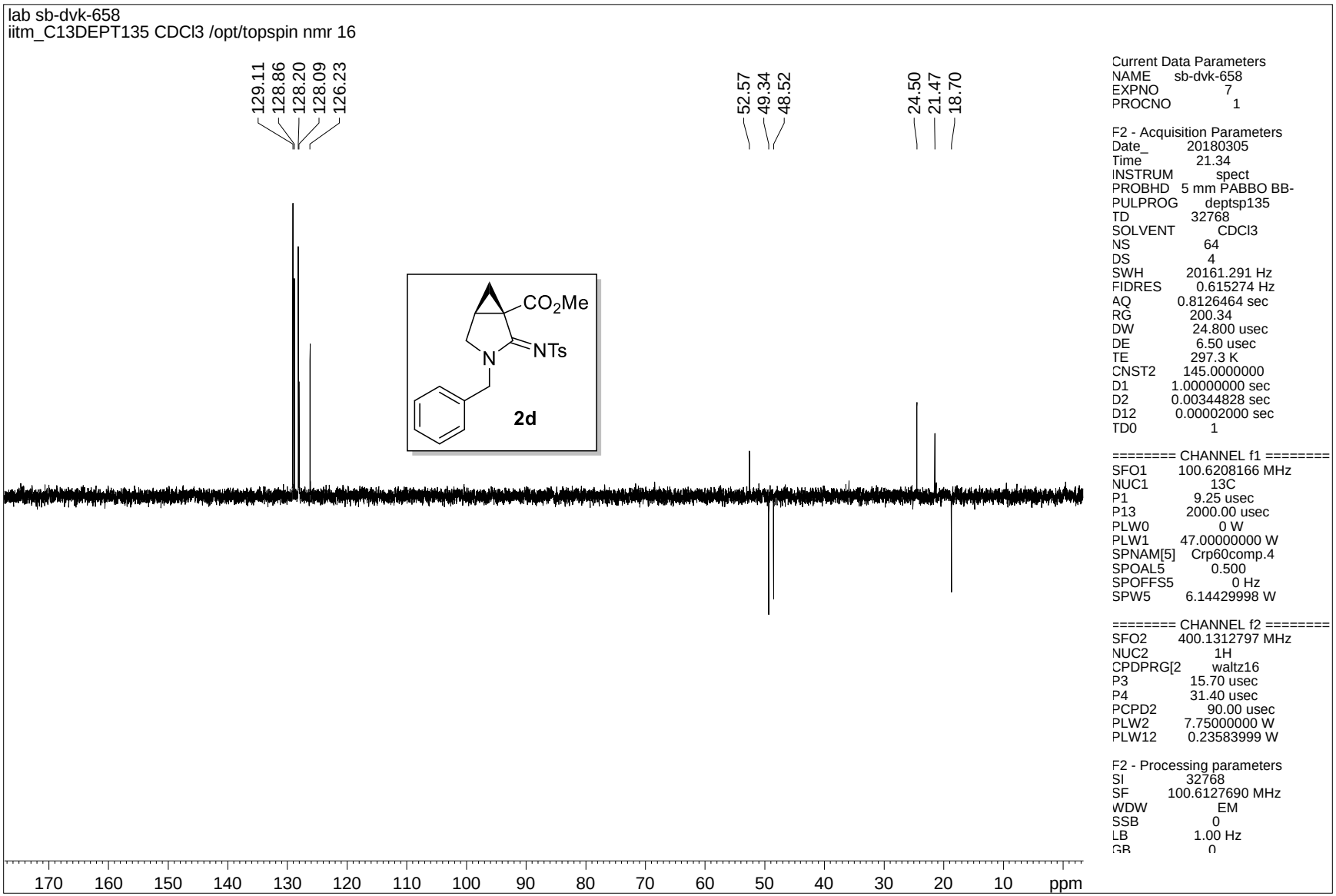
^{1}H NMR spectrum of compound 2d



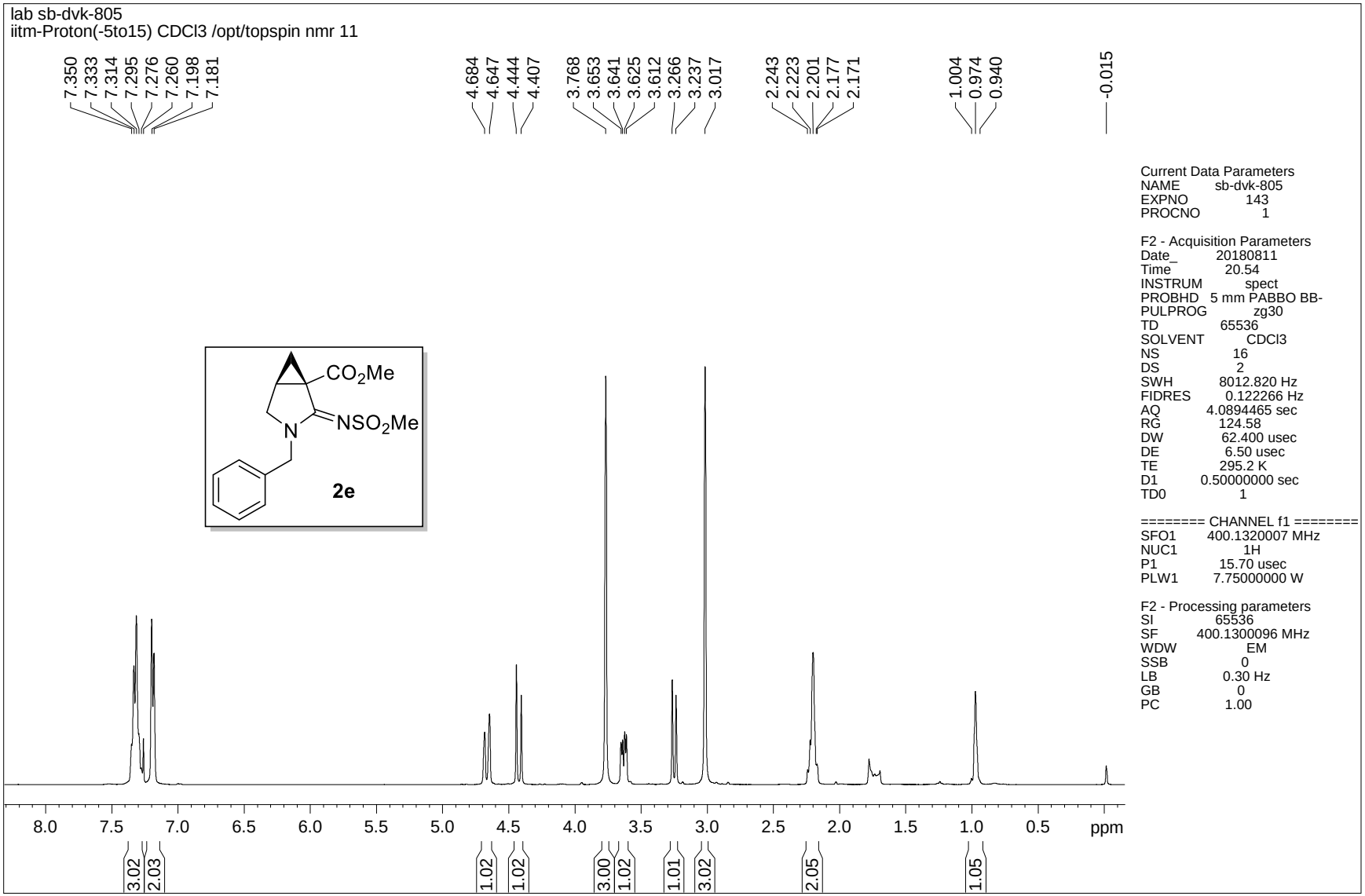
[1]H NMR spectrum of compound 2d



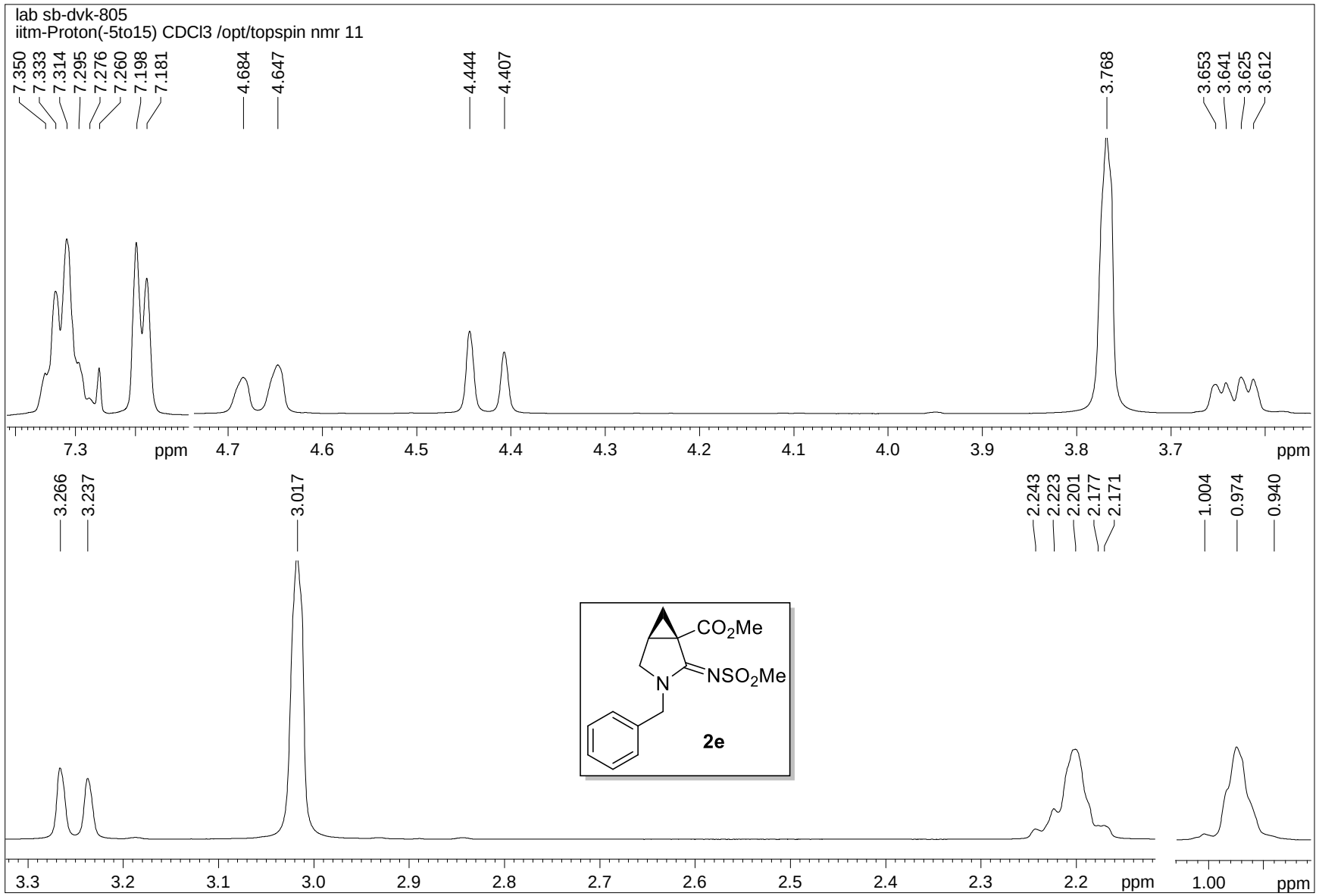
^{13}C NMR spectrum of compound 2d



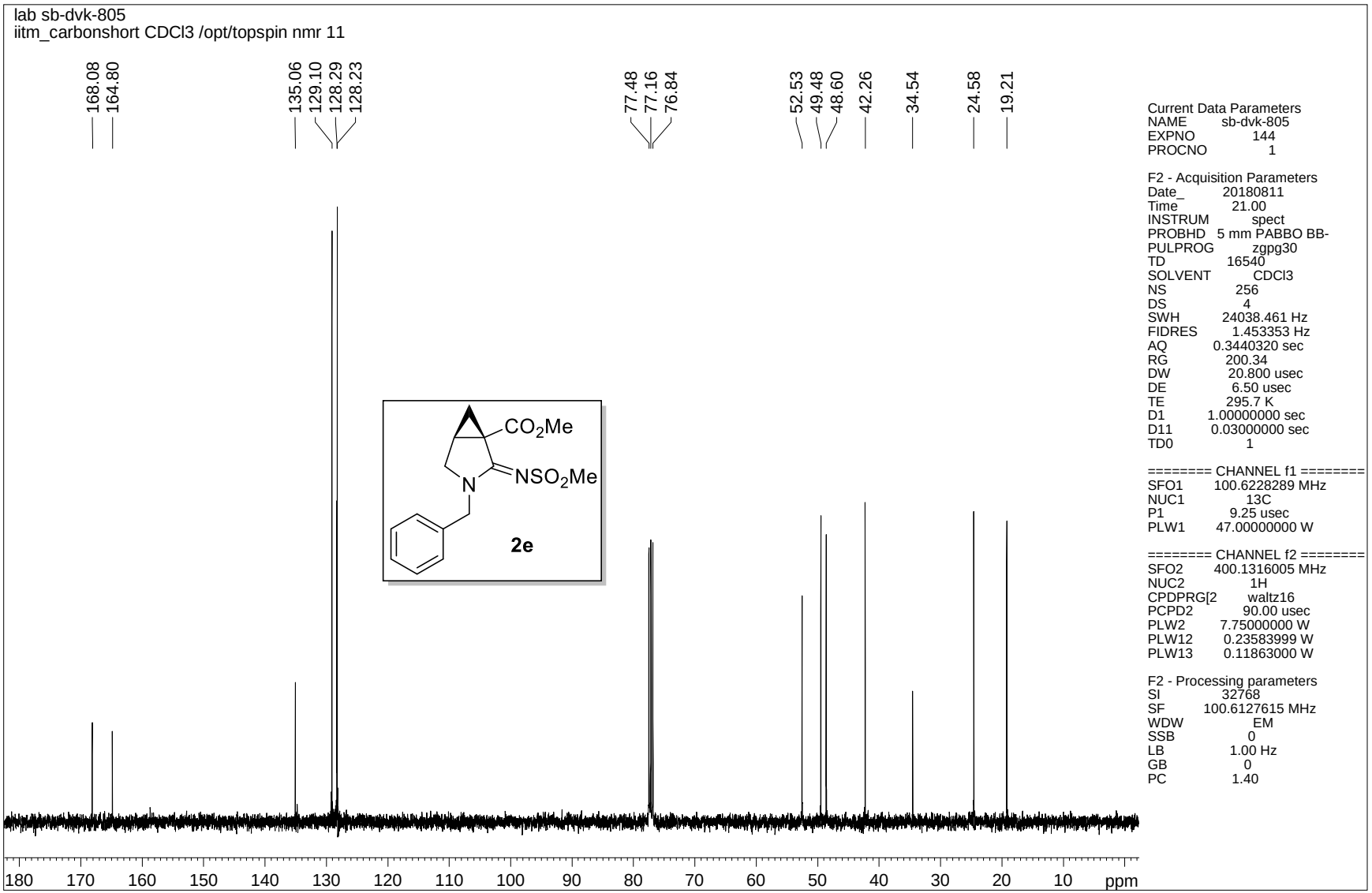
DEPT-135 NMR spectrum of compound 2d



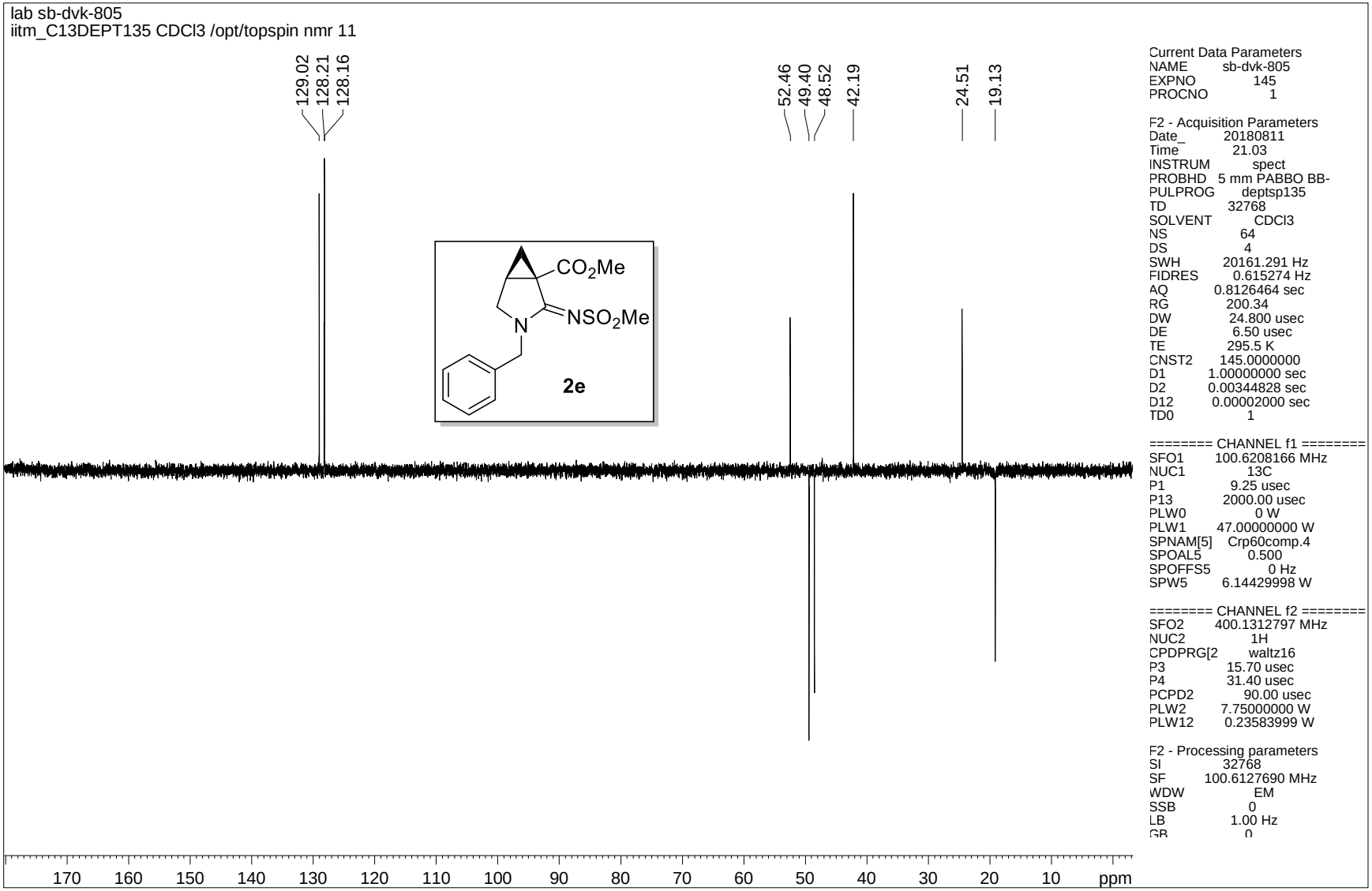
^{1}H NMR spectrum of compound 2e



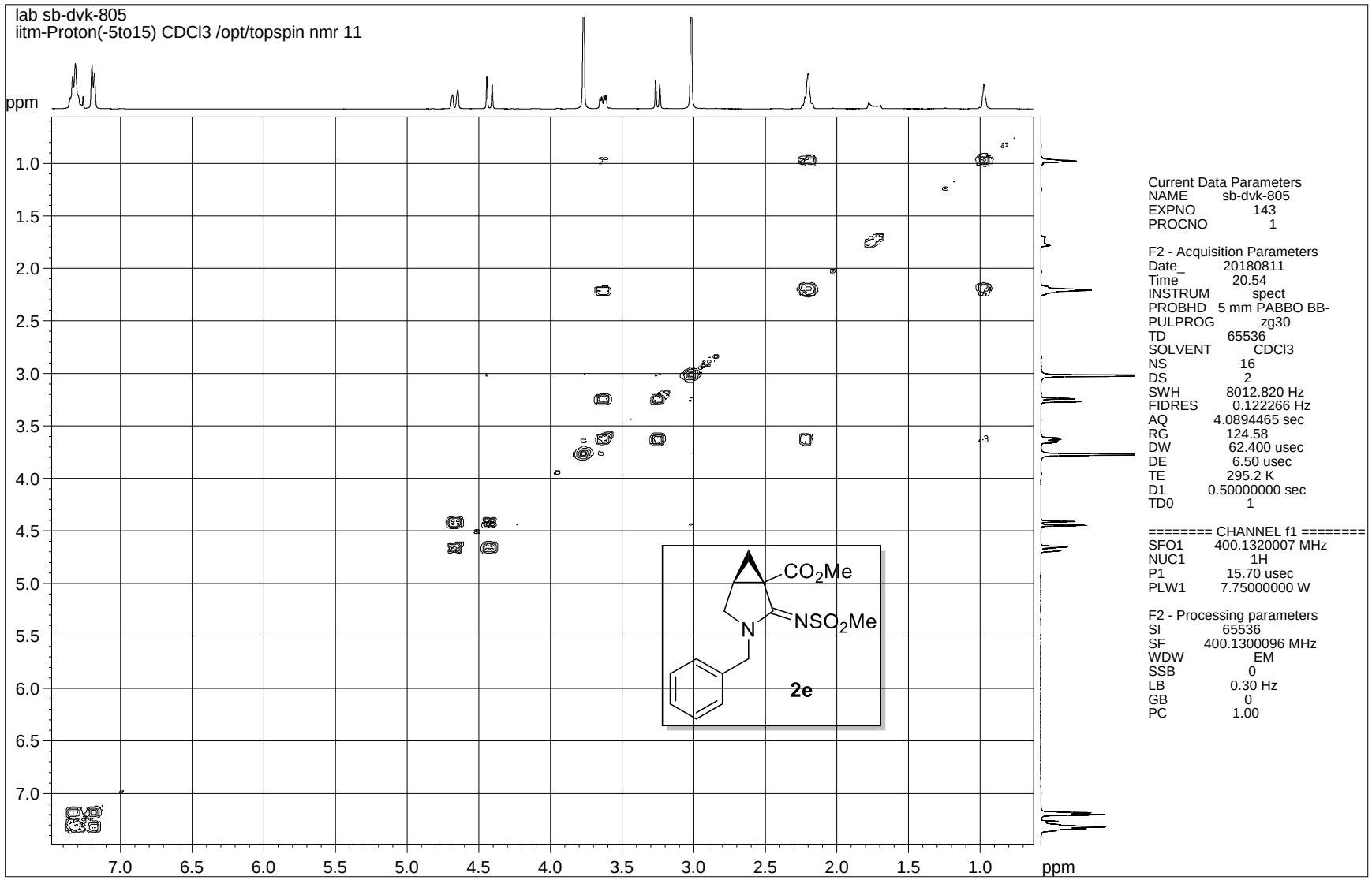
[1]H NMR spectrum of compound 2e



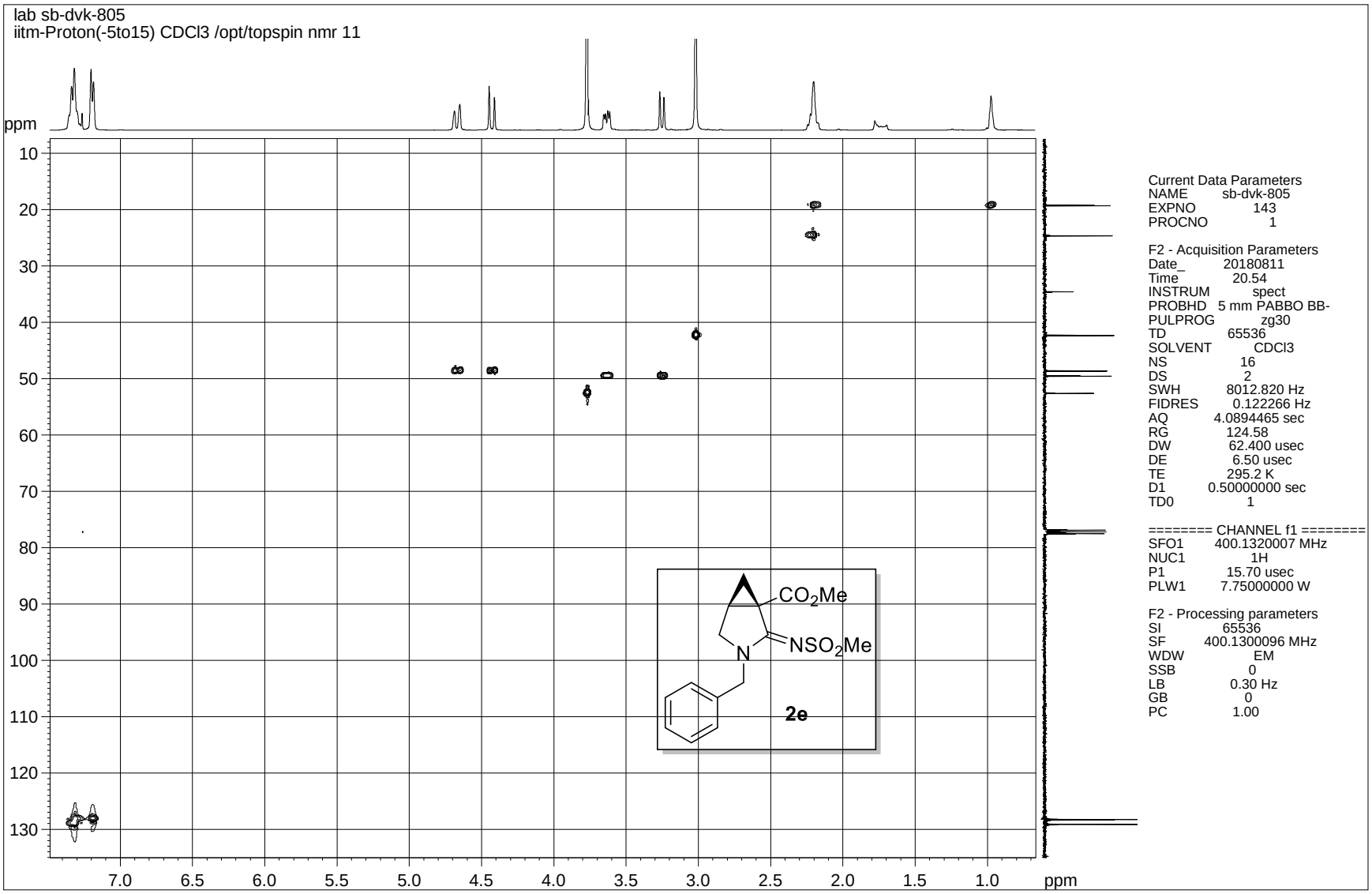
^{13}C NMR spectrum of compound 2e



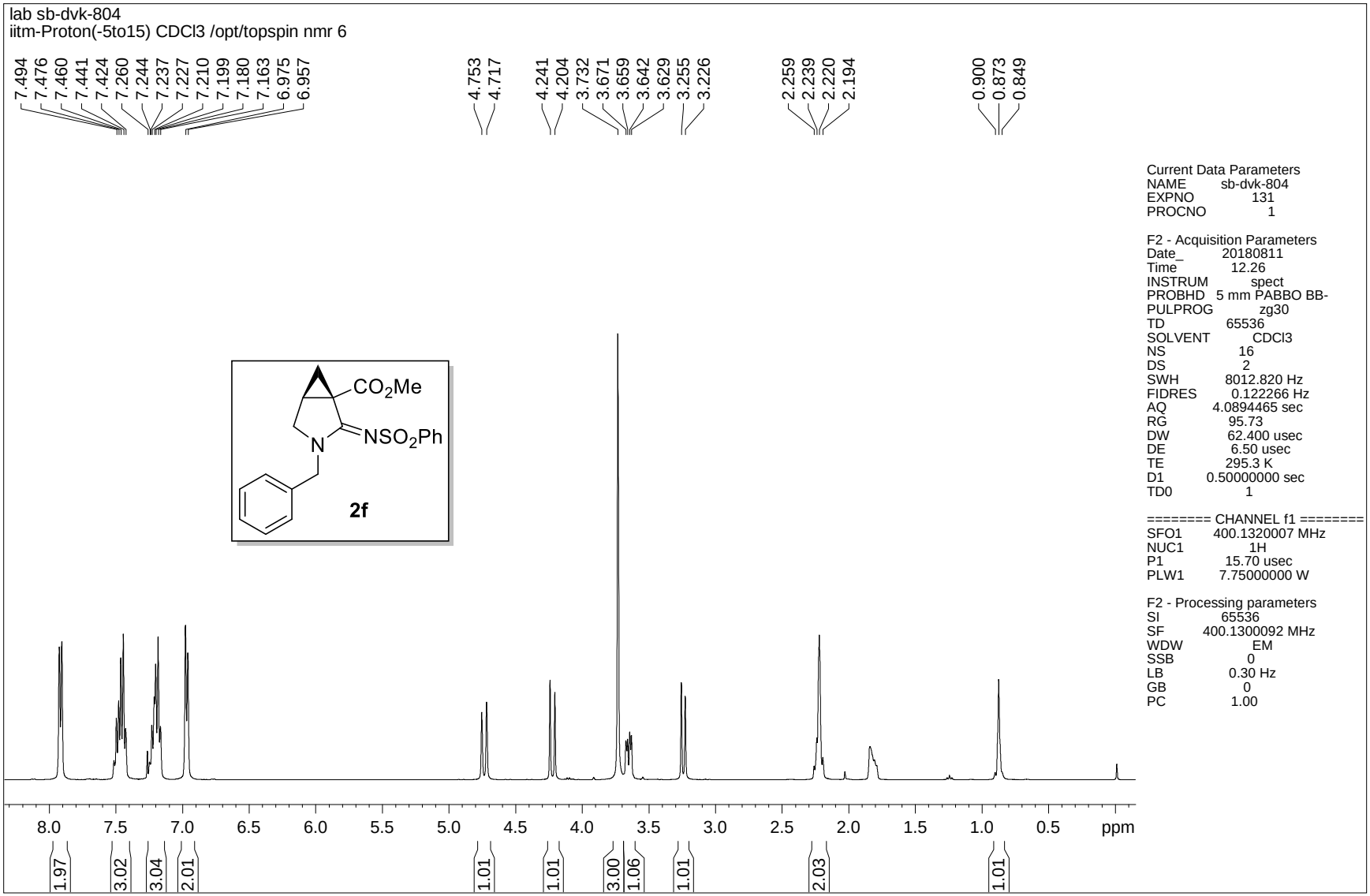
DEPT-135 NMR spectrum of compound 2e



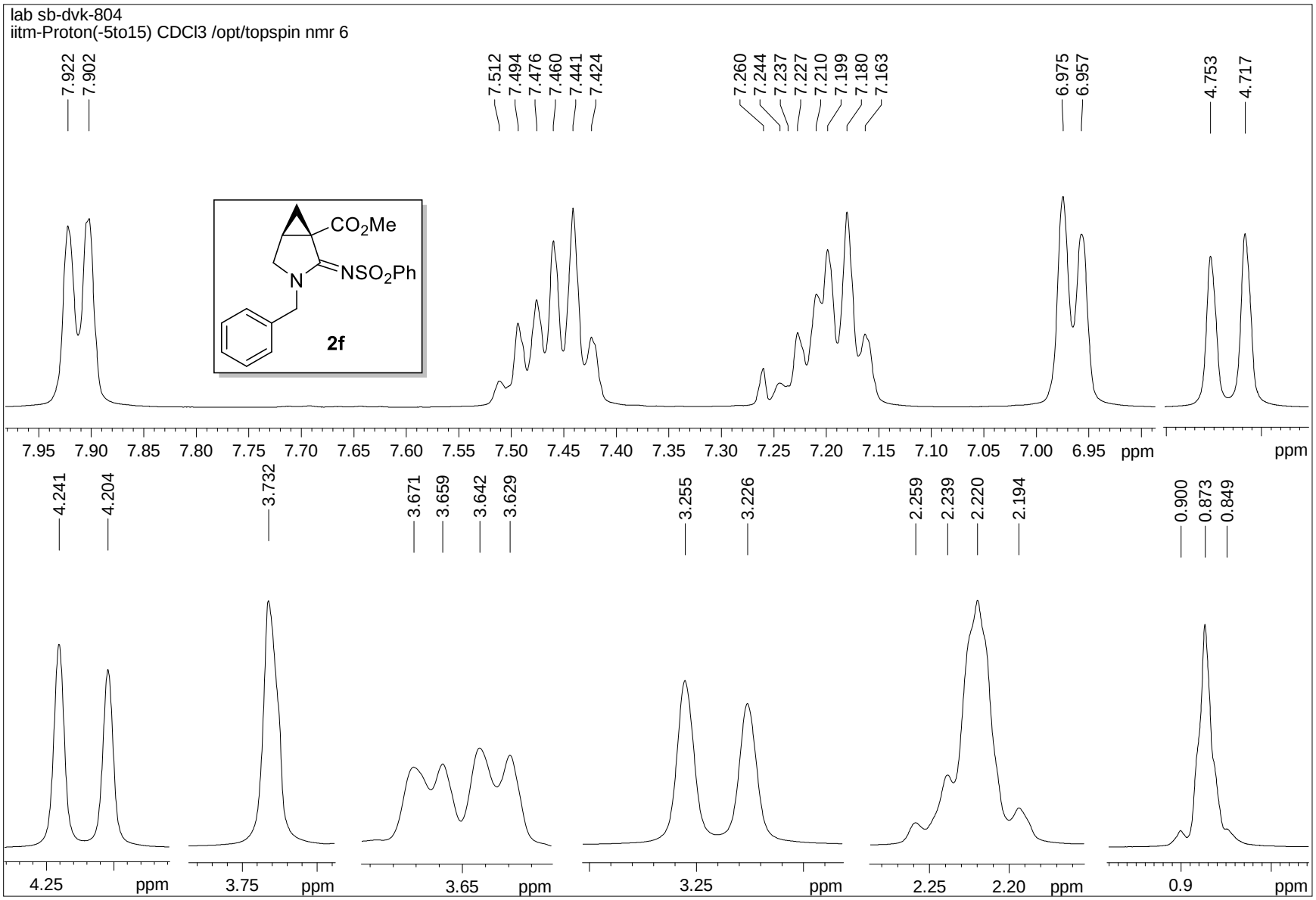
^{1}H-^{1}H COSY NMR spectrum of compound 2e



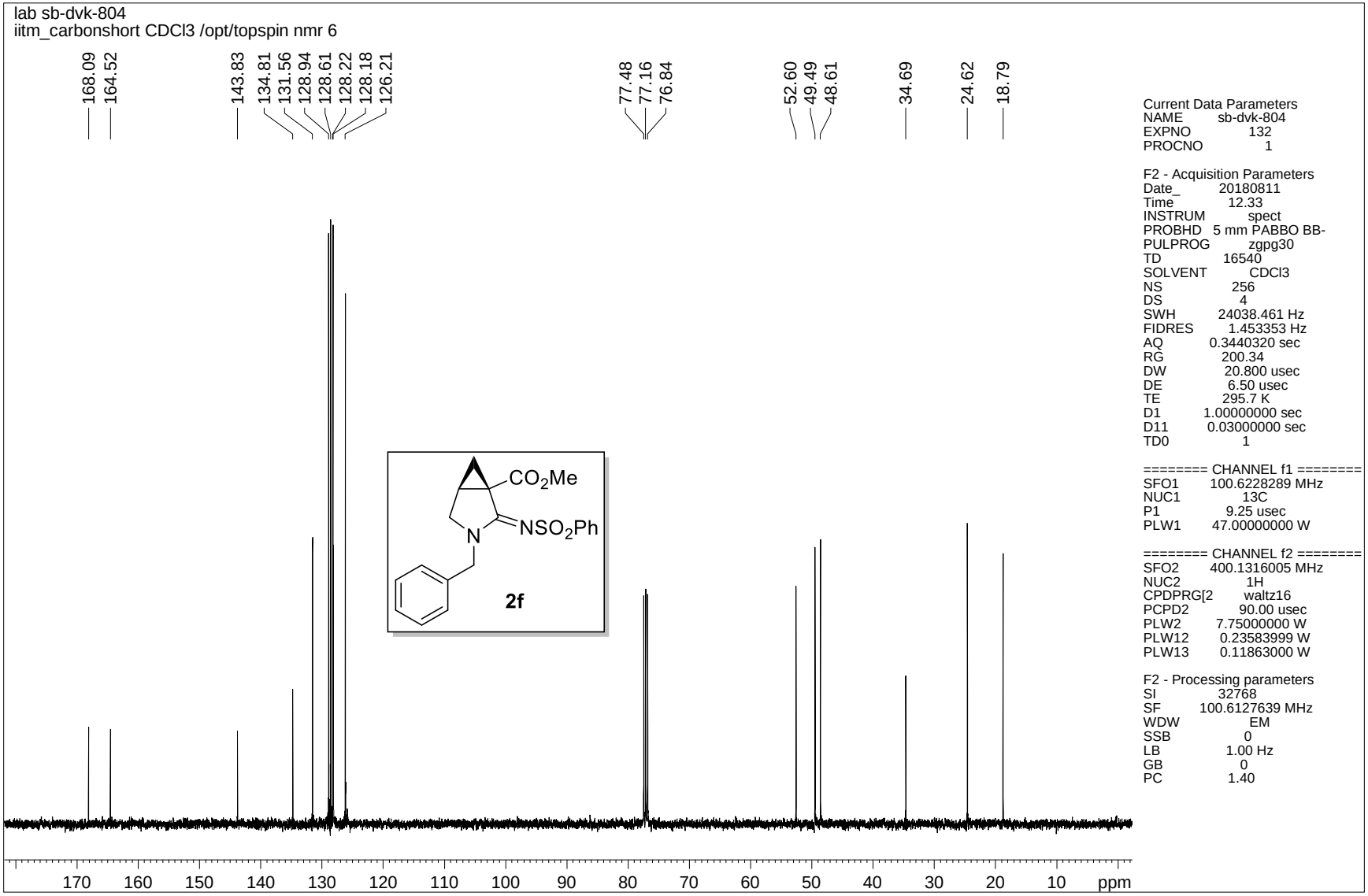
^{1}H-^{13}C HSQC NMR spectrum of compound 2e



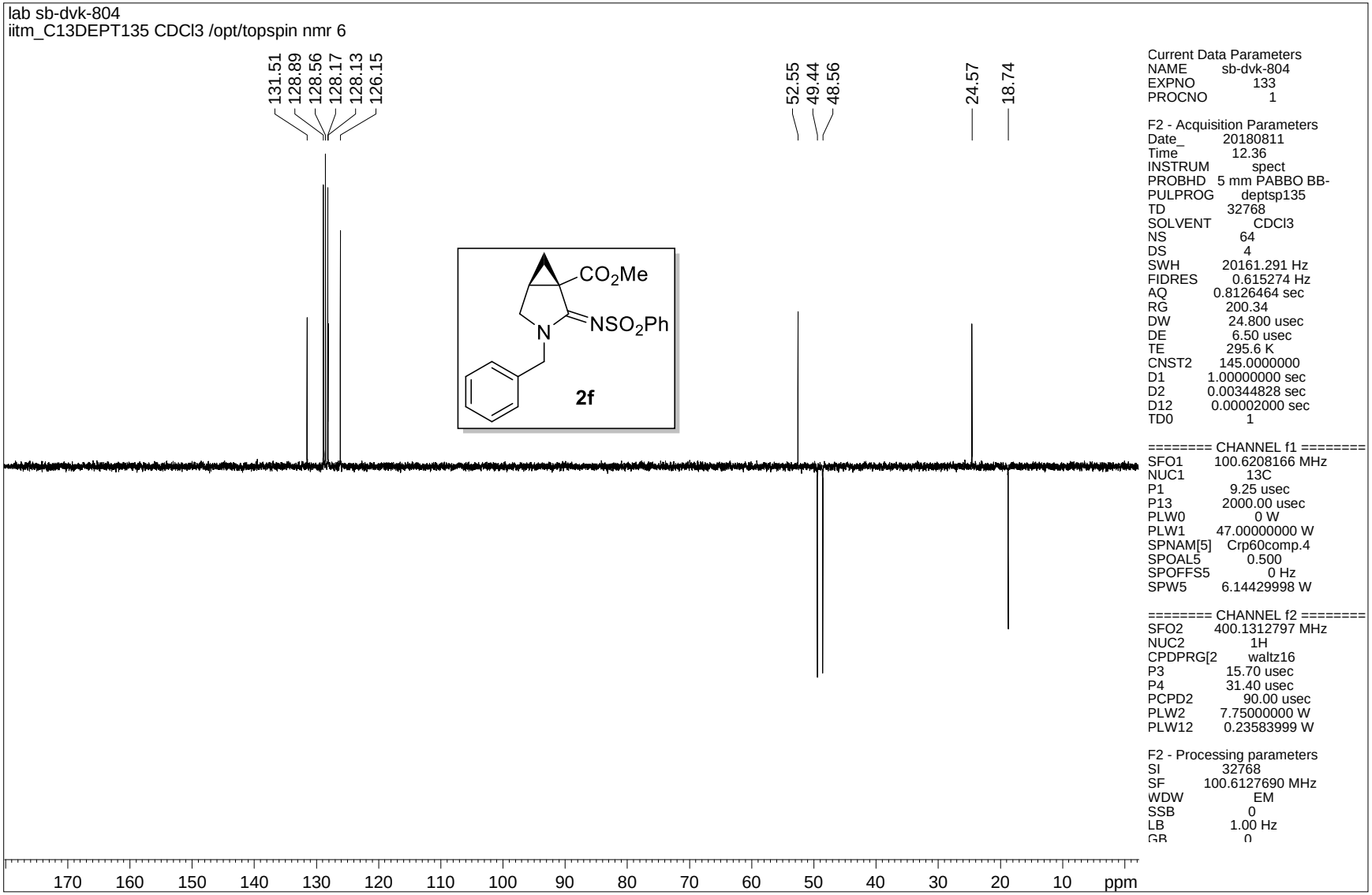
^{1}H NMR spectrum of compound 2f



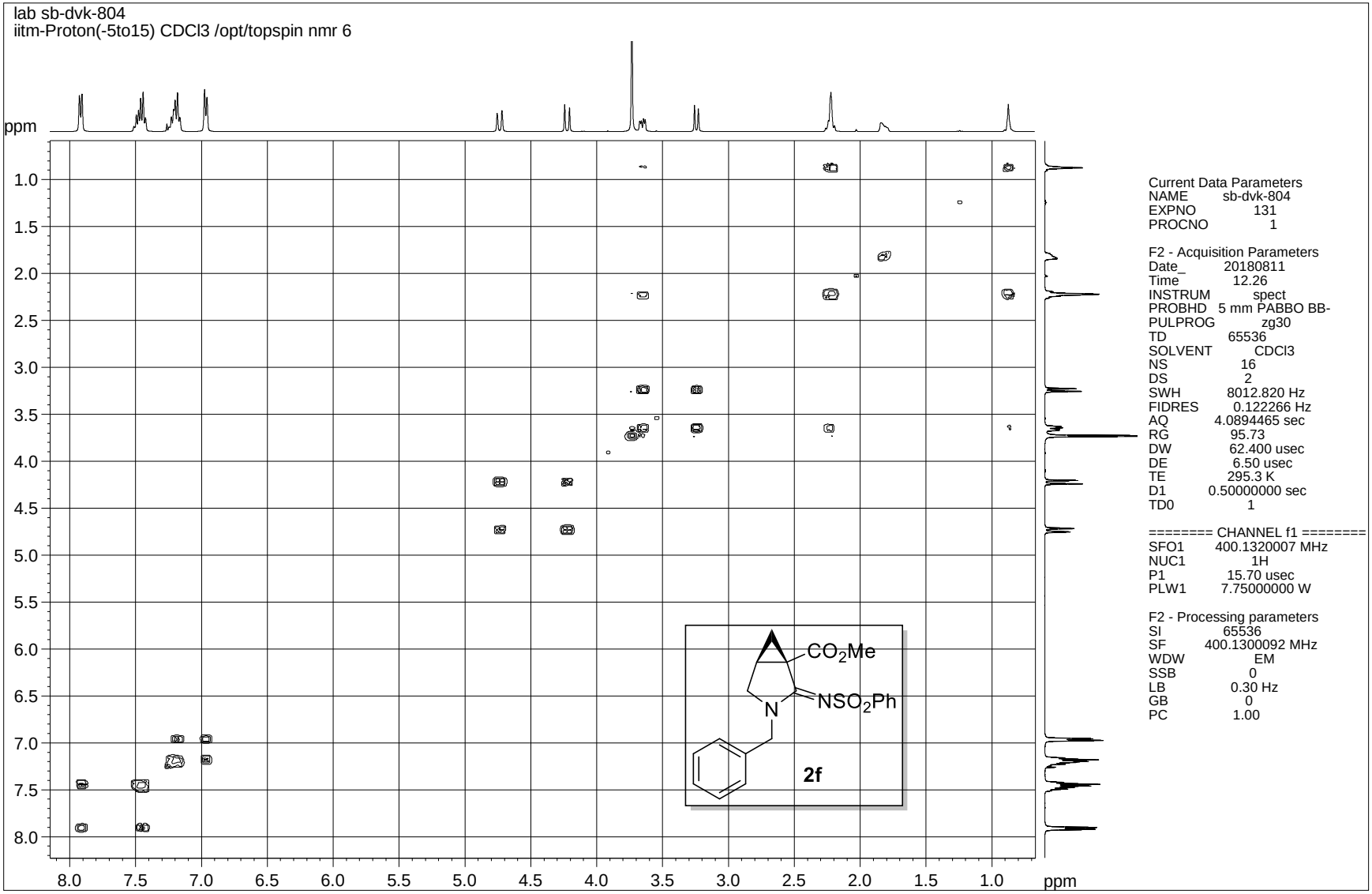
^{1}H NMR spectrum of compound 2f



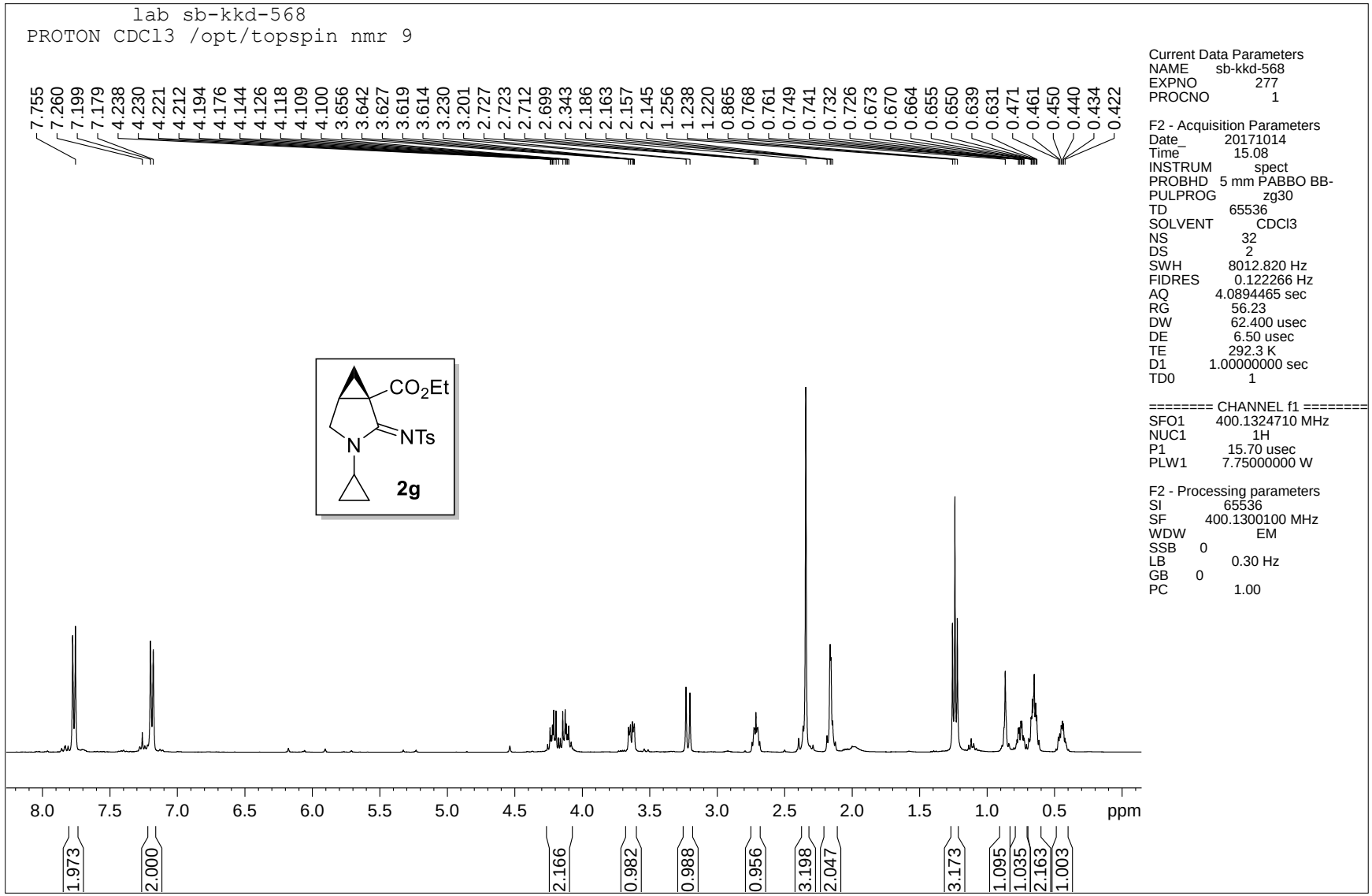
^{13}C NMR spectrum of compound 2f



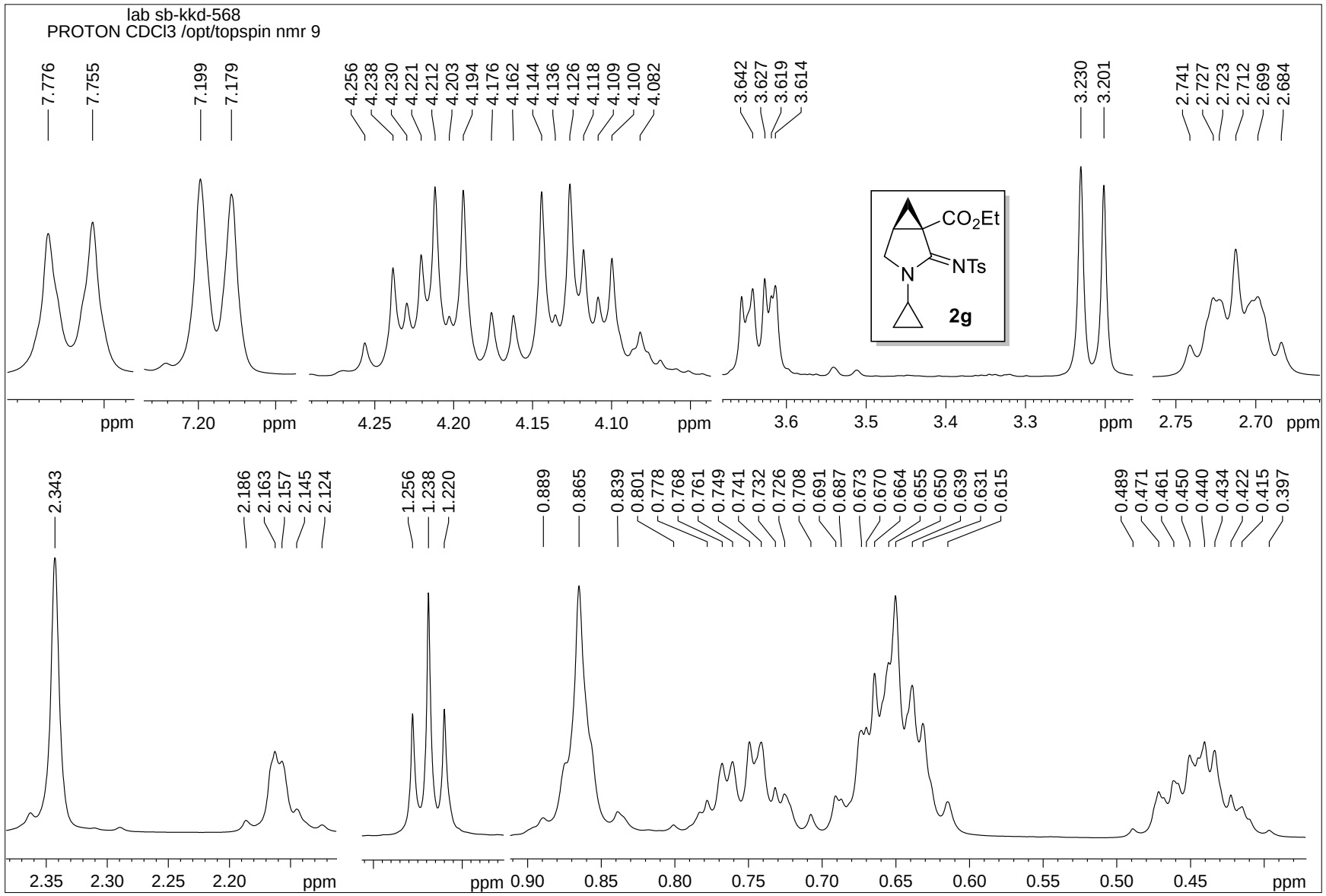
DEPT-135 NMR spectrum of compound 2f



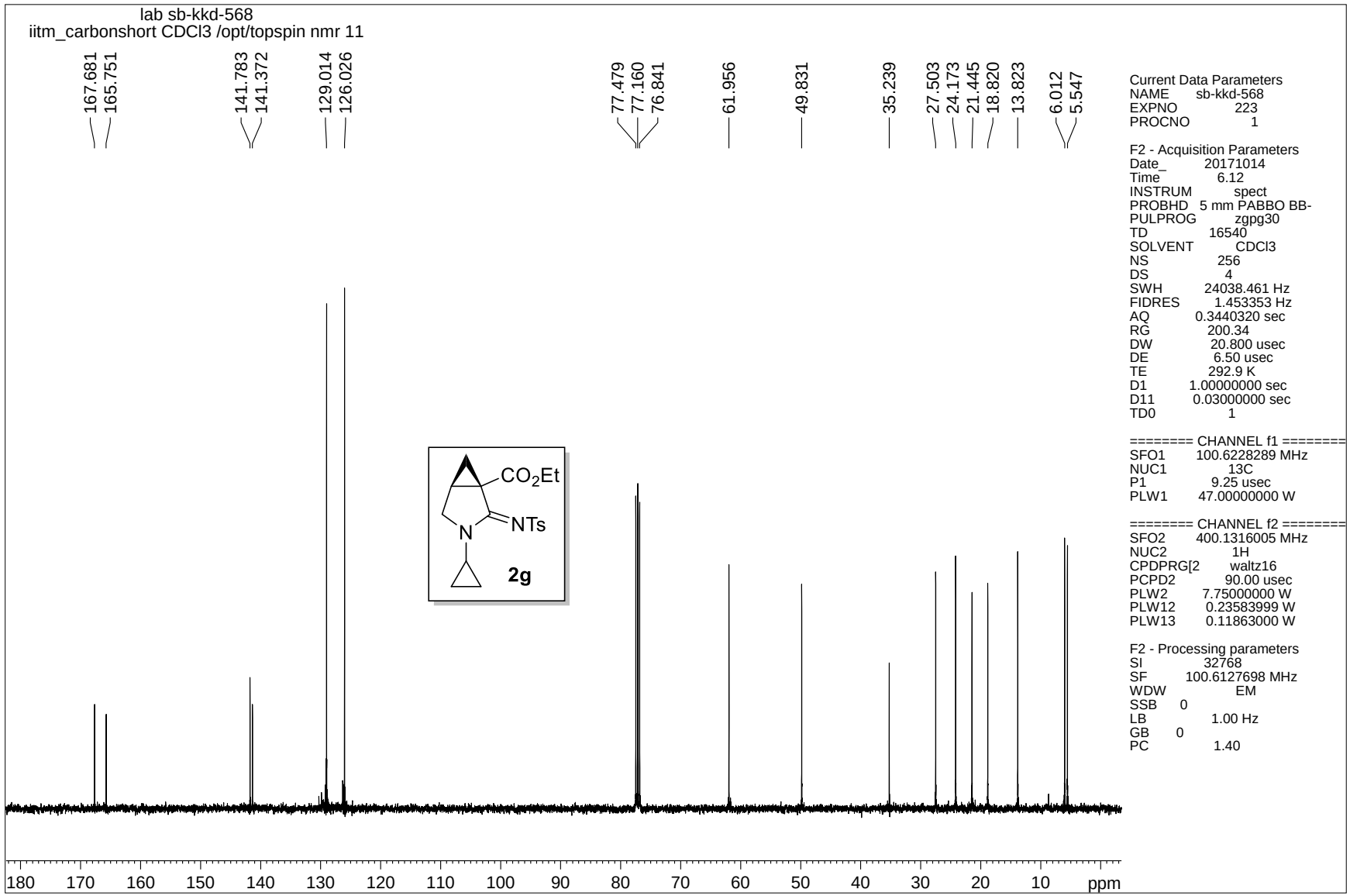
^{1}H-^{1}H COSY NMR spectrum of compound 2f



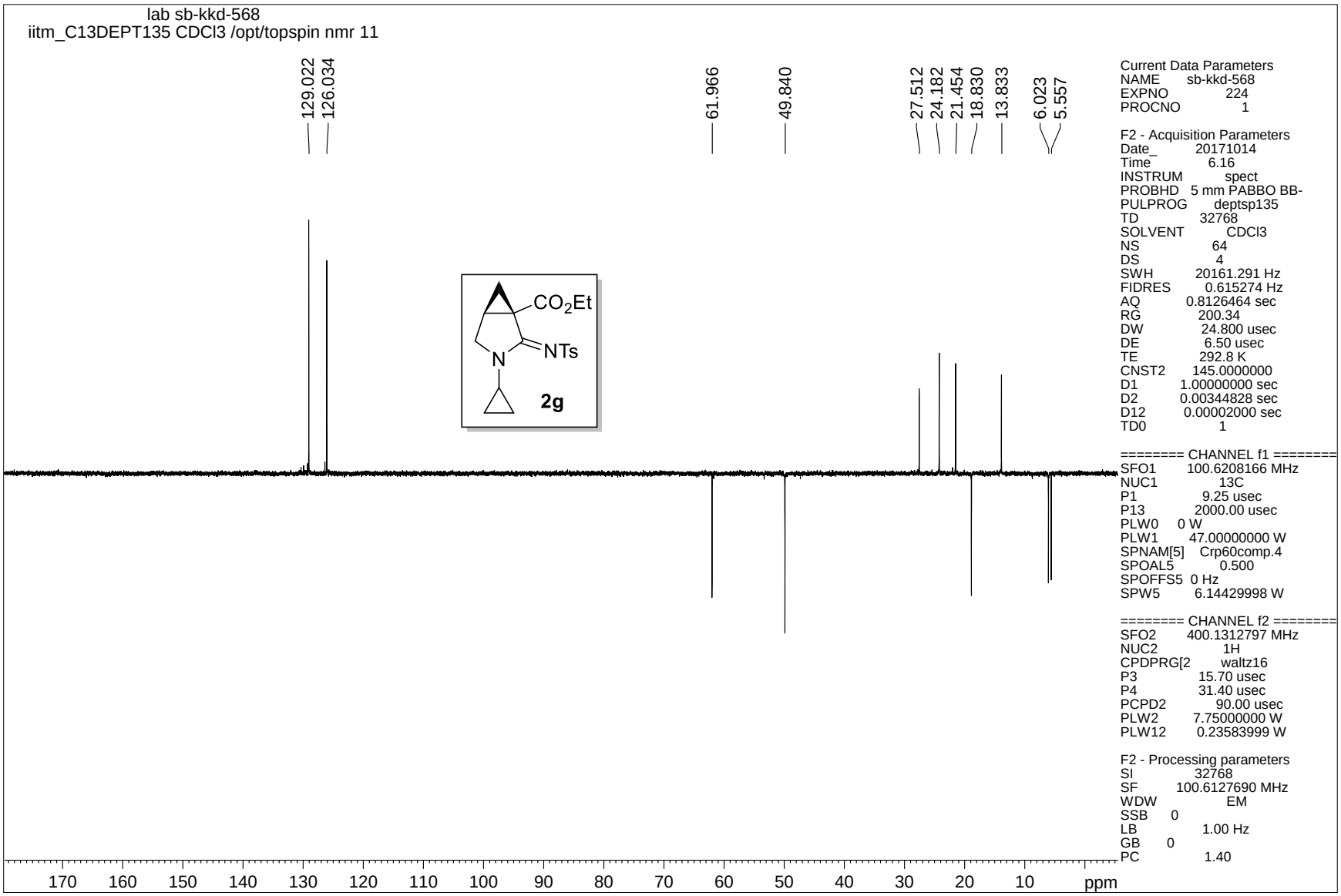
^{1}H NMR spectrum of compound 2g



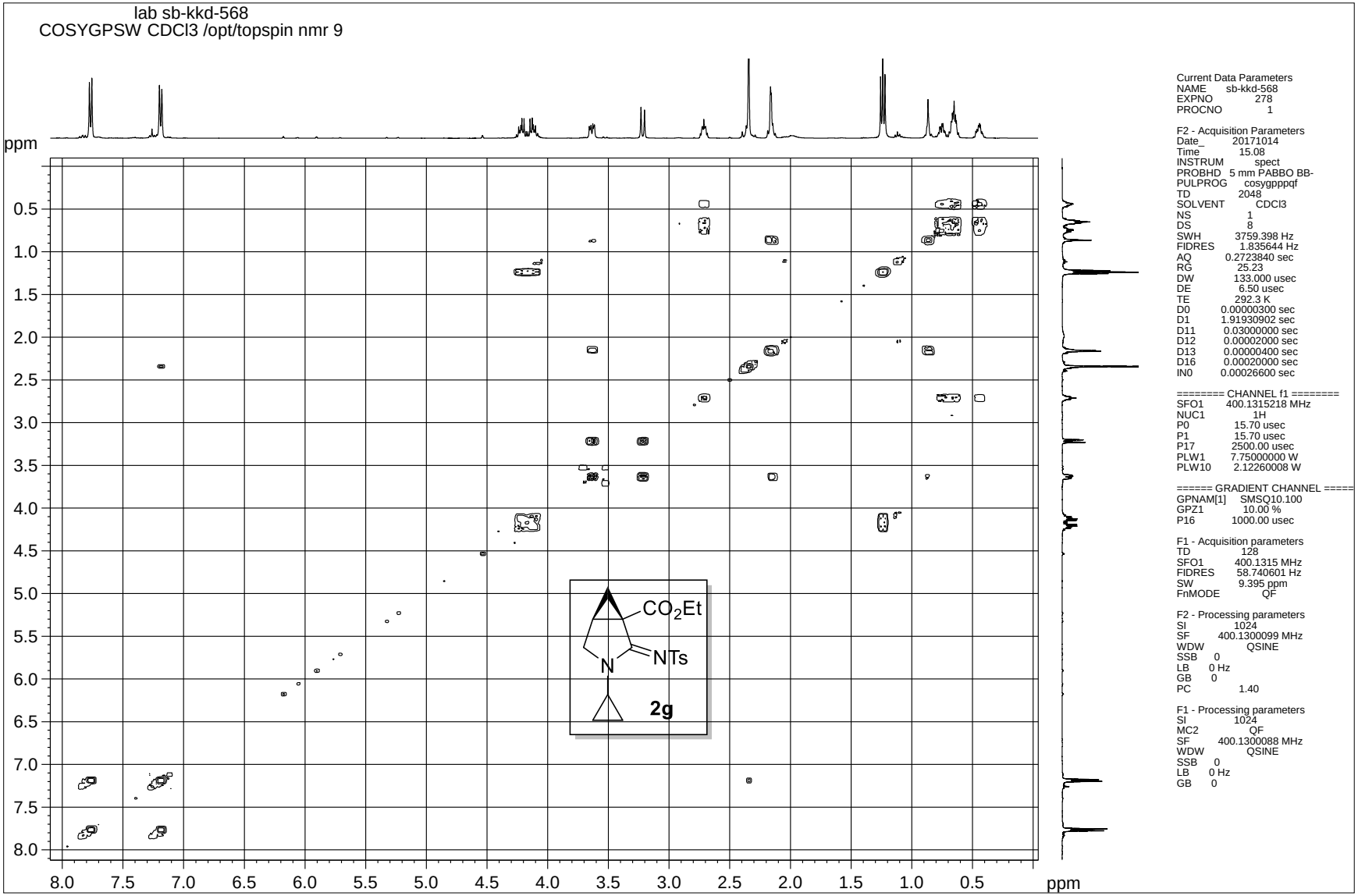
^{1}H NMR spectrum of compound 2g



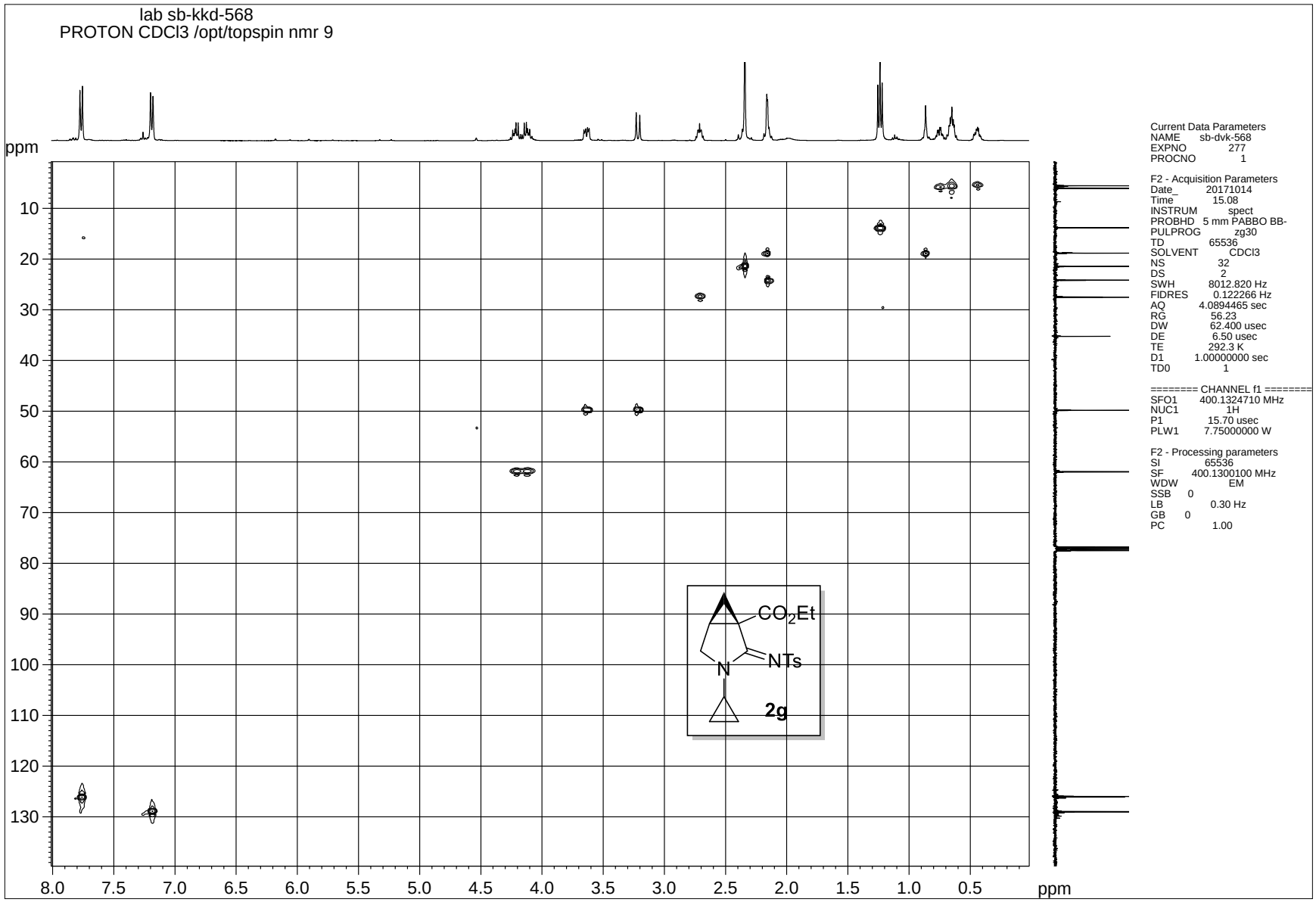
^{13}C NMR spectrum of compound 2g



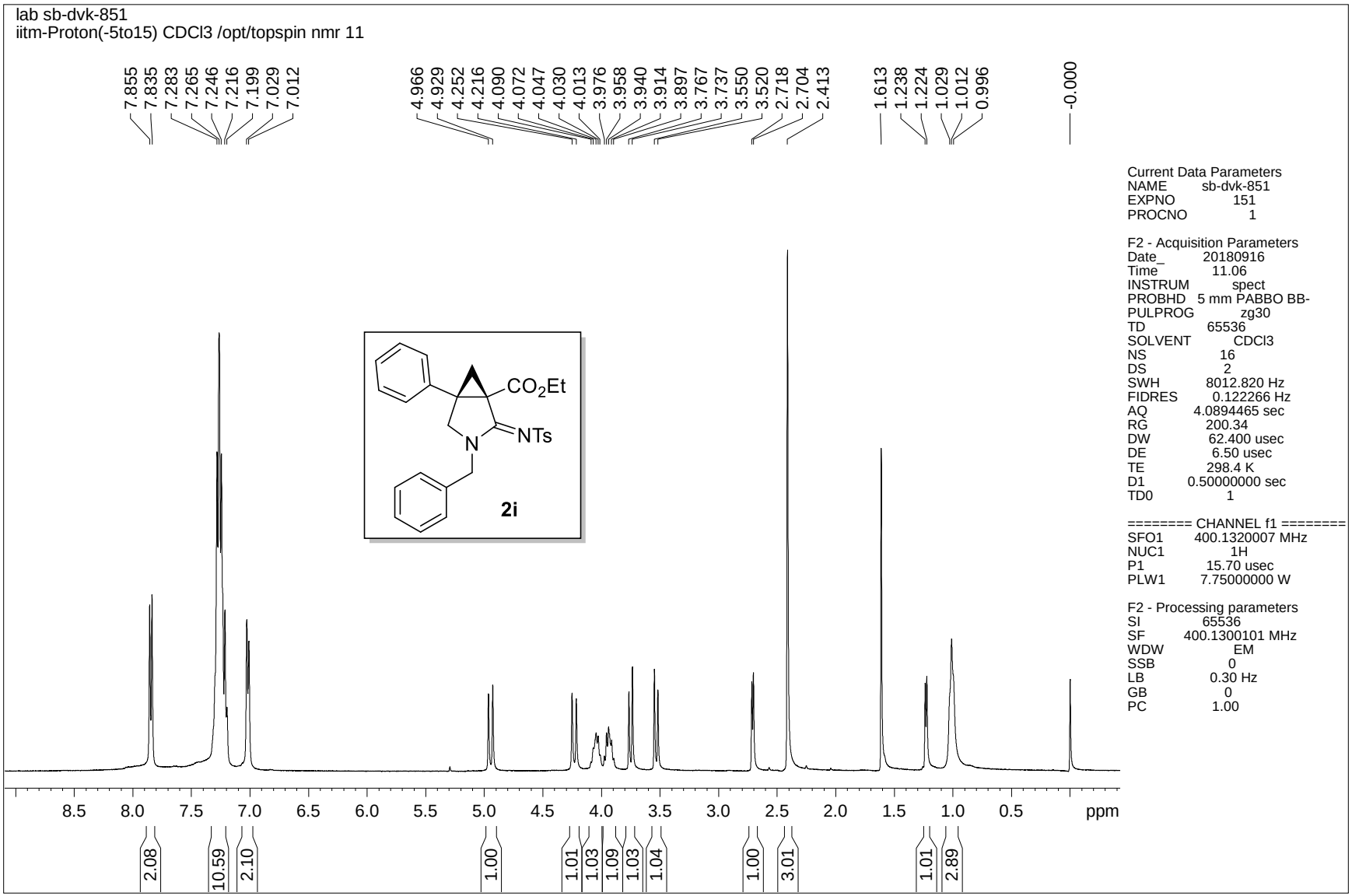
DEPT-135 NMR spectrum of compound 2g



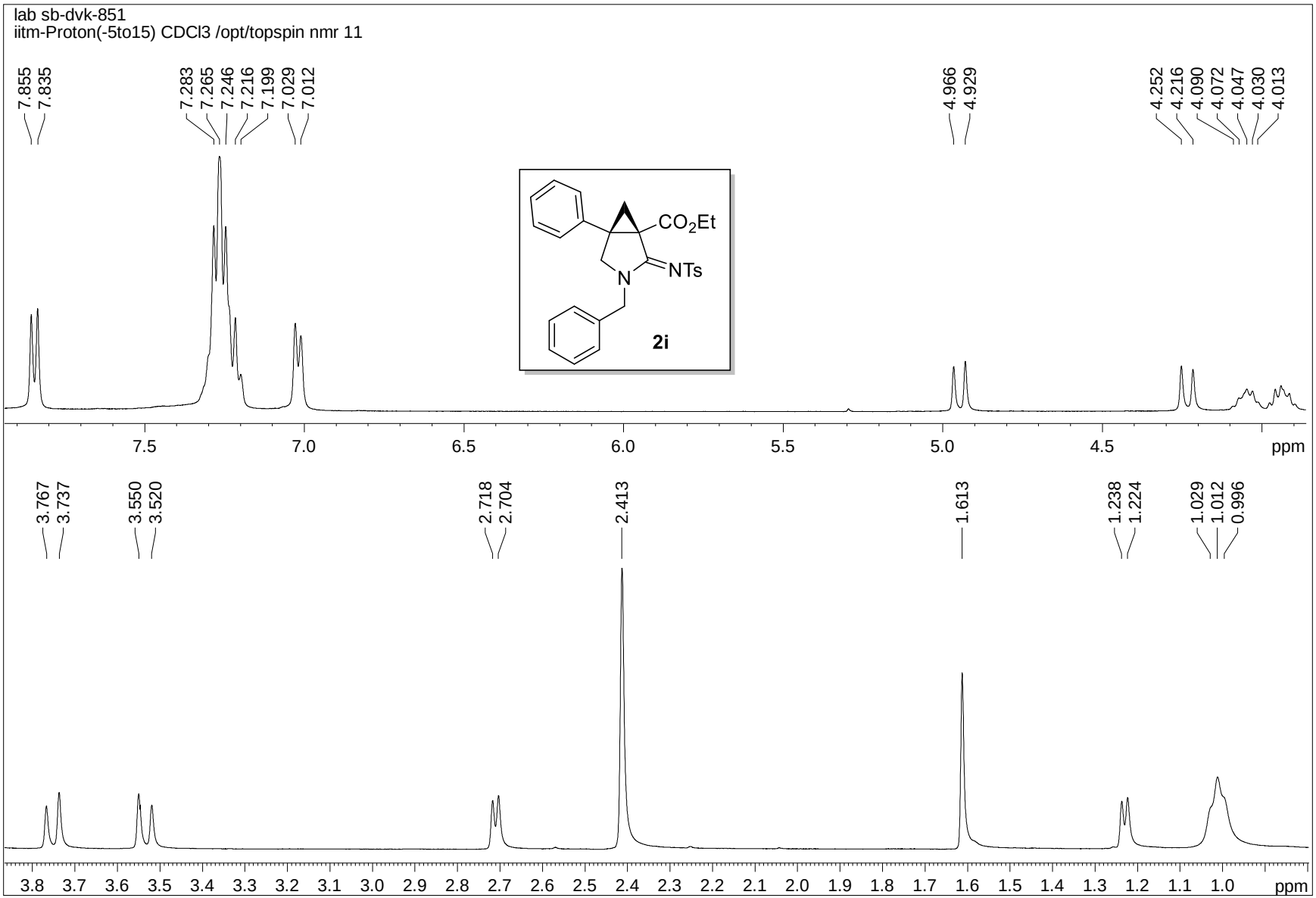
^{1}H-^{1}H COSY NMR spectrum of compound 2g



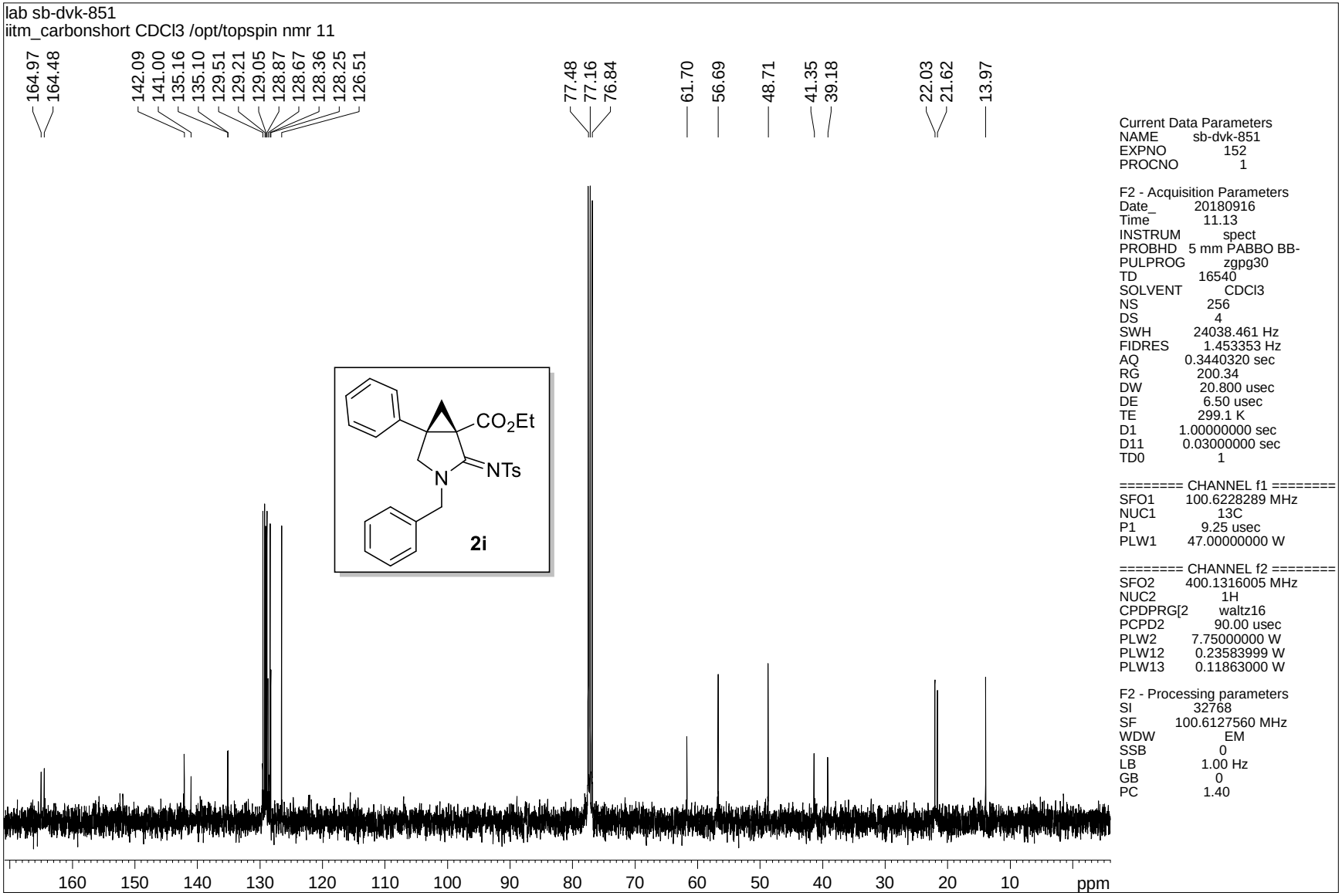
^{1}H-^{13}C HSQC NMR spectrum of compound 2g



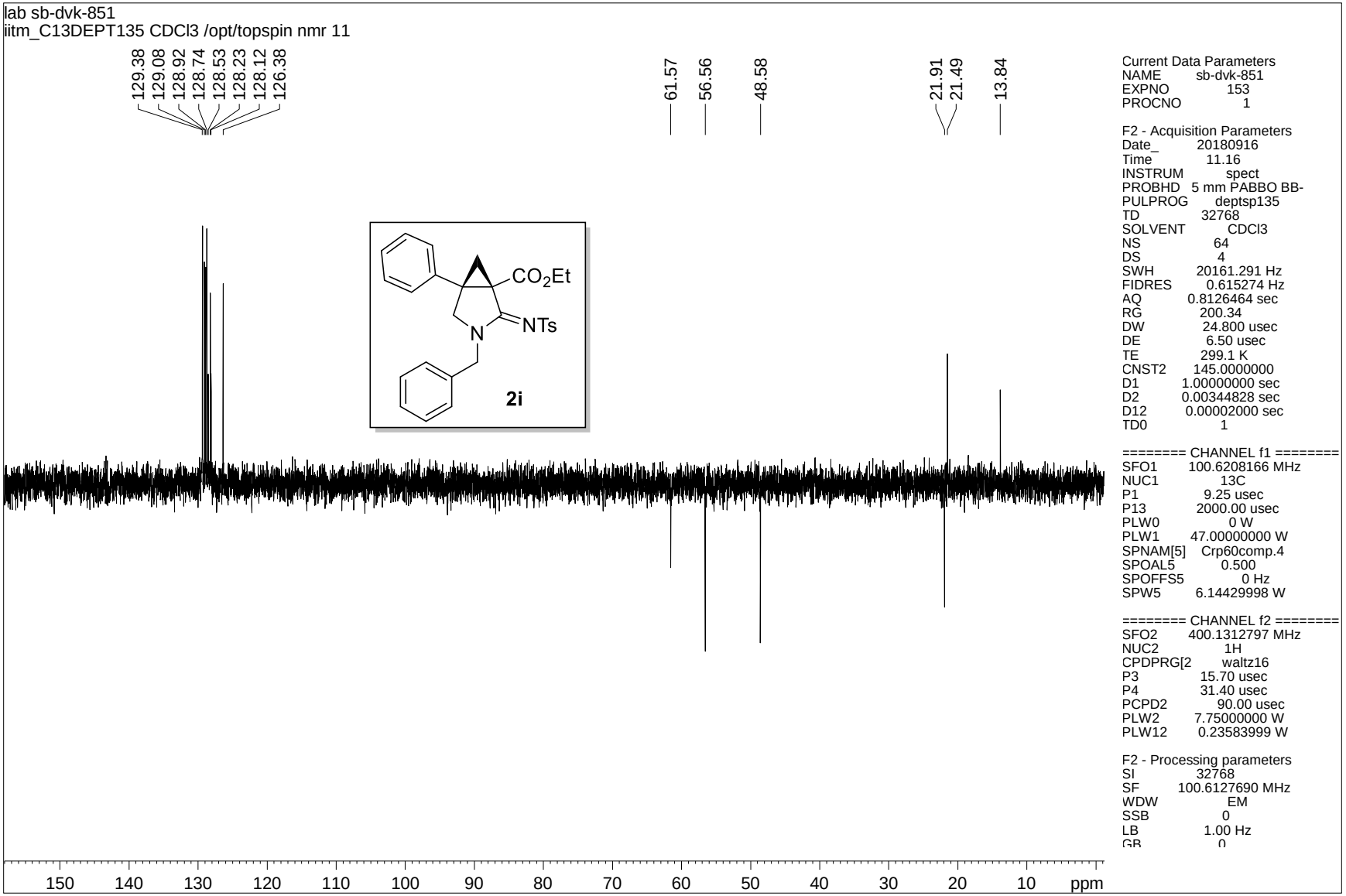
^{1}H NMR spectrum of compound 2i



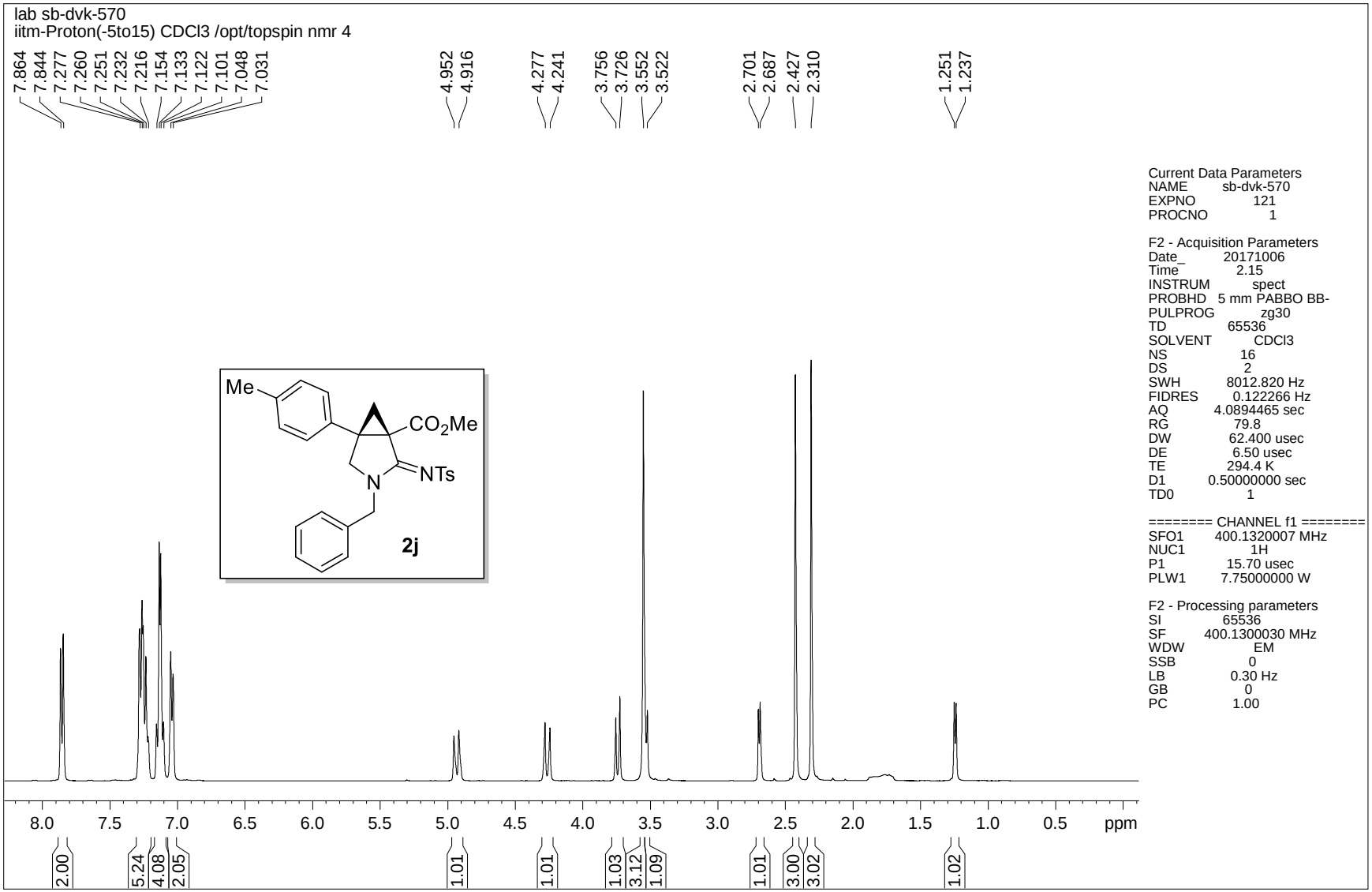
^{1}H NMR spectrum of compound 2i



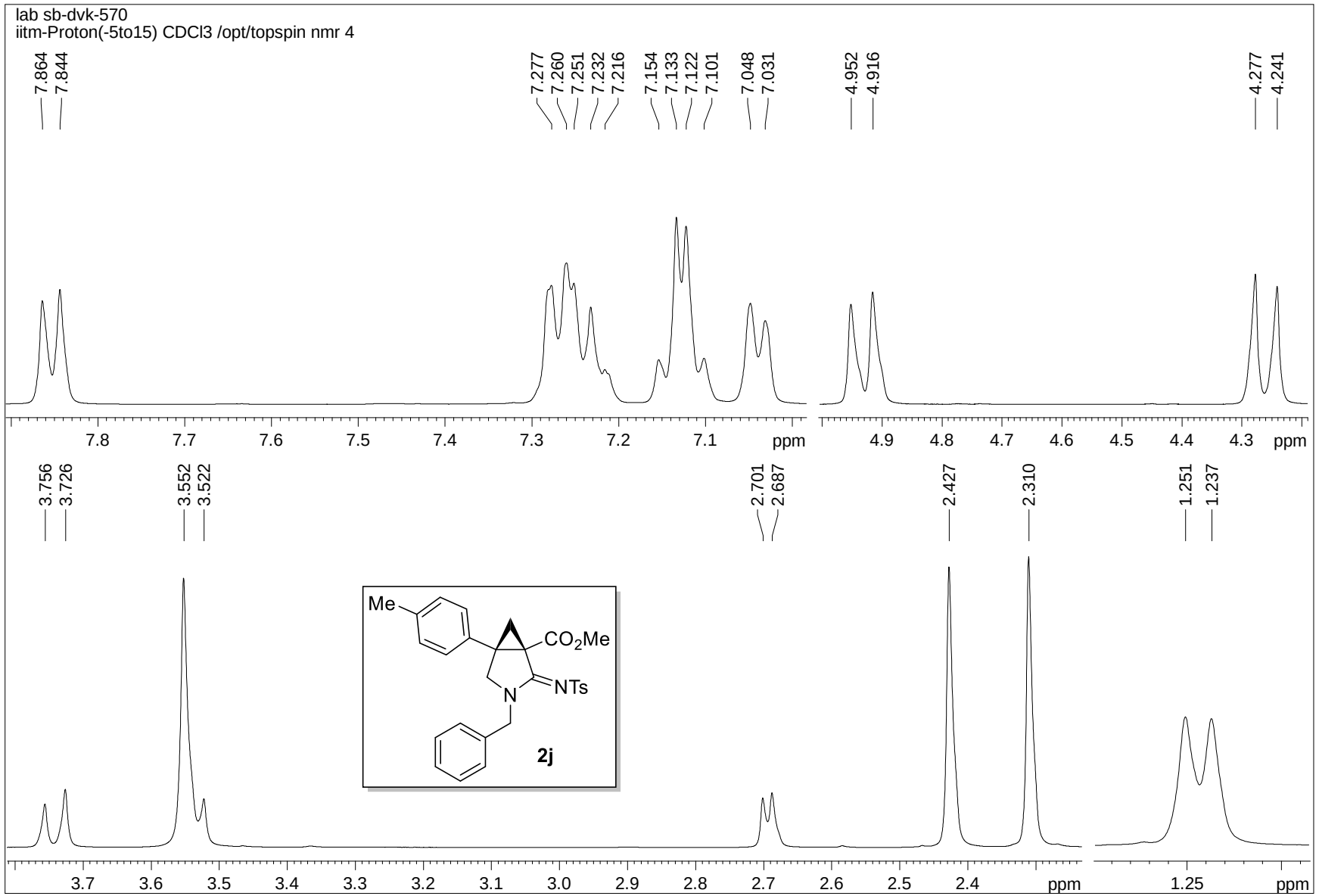
^{13}C NMR spectrum of compound 2i



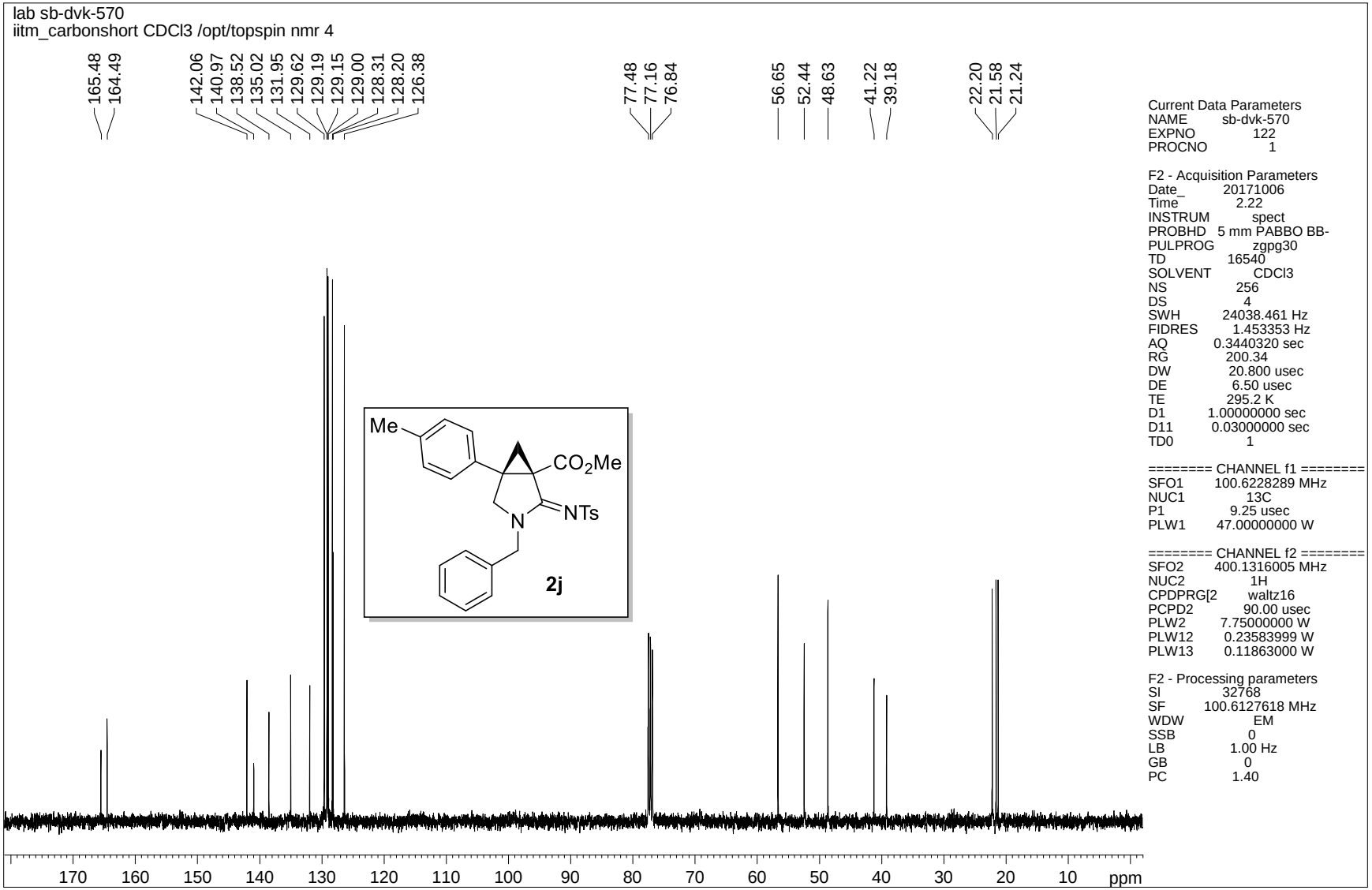
DEPT-135 NMR spectrum of compound 2i



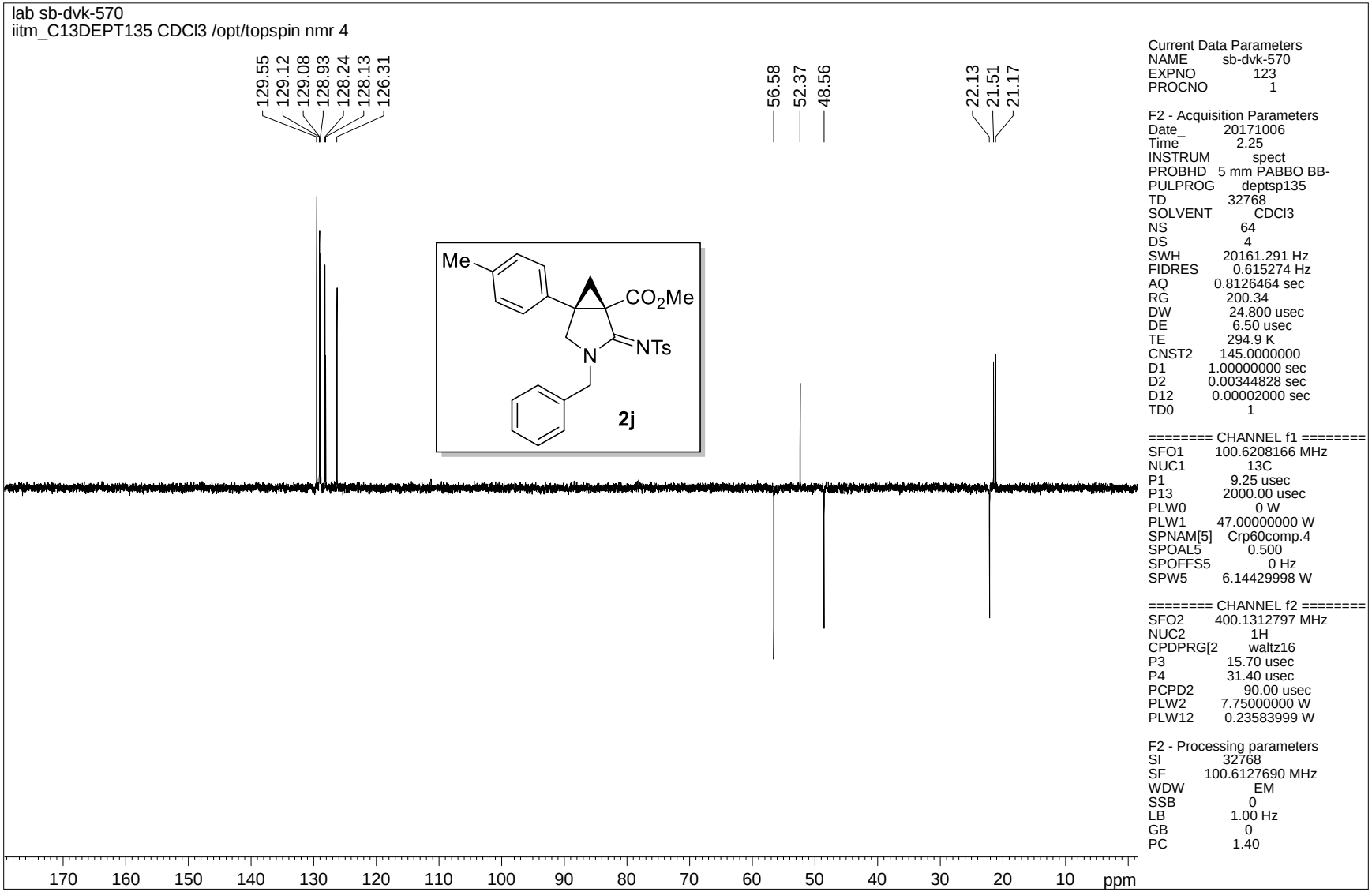
^{1}H NMR spectrum of compound 2j



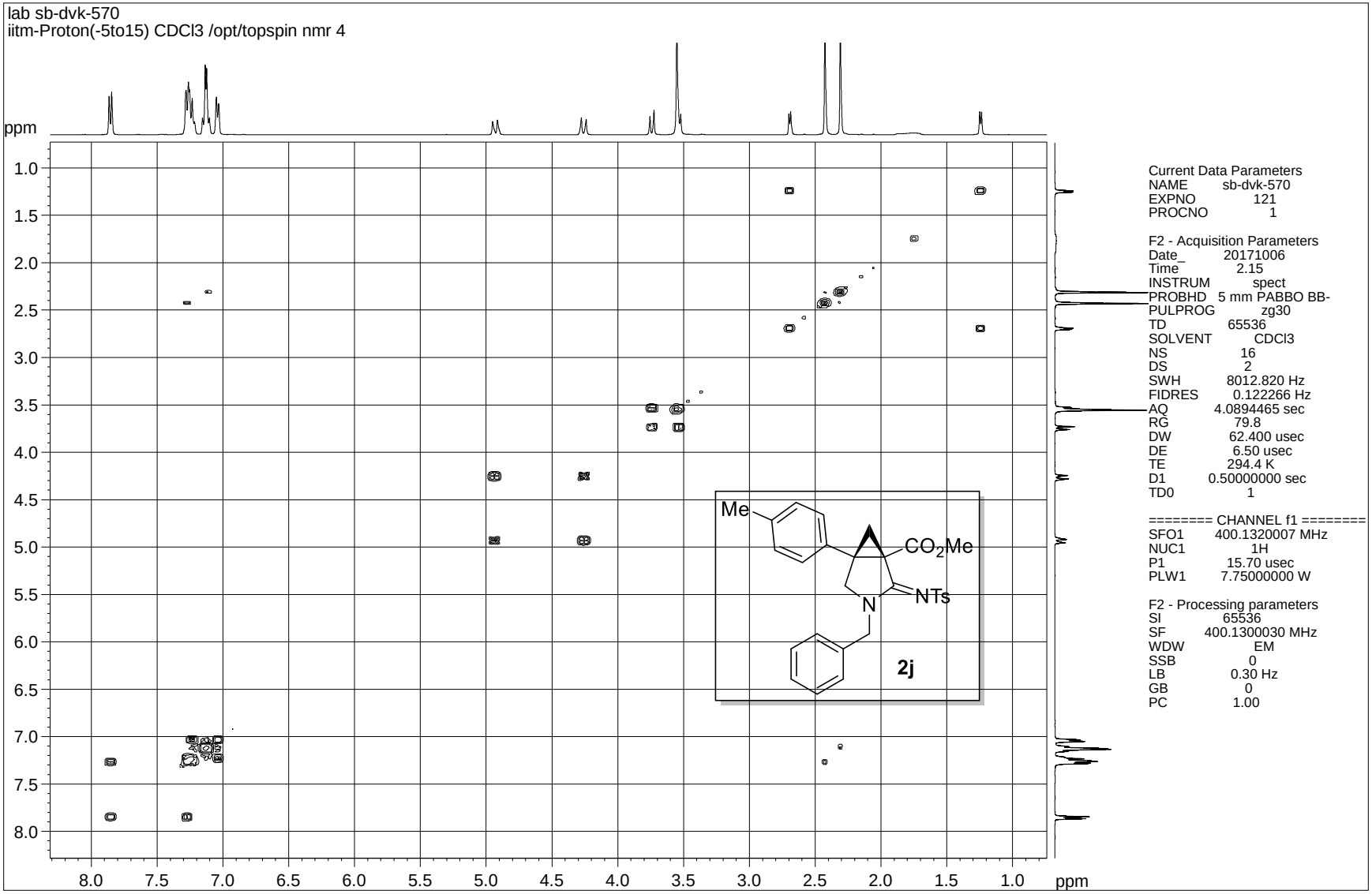
[1]H NMR spectrum of compound 2j



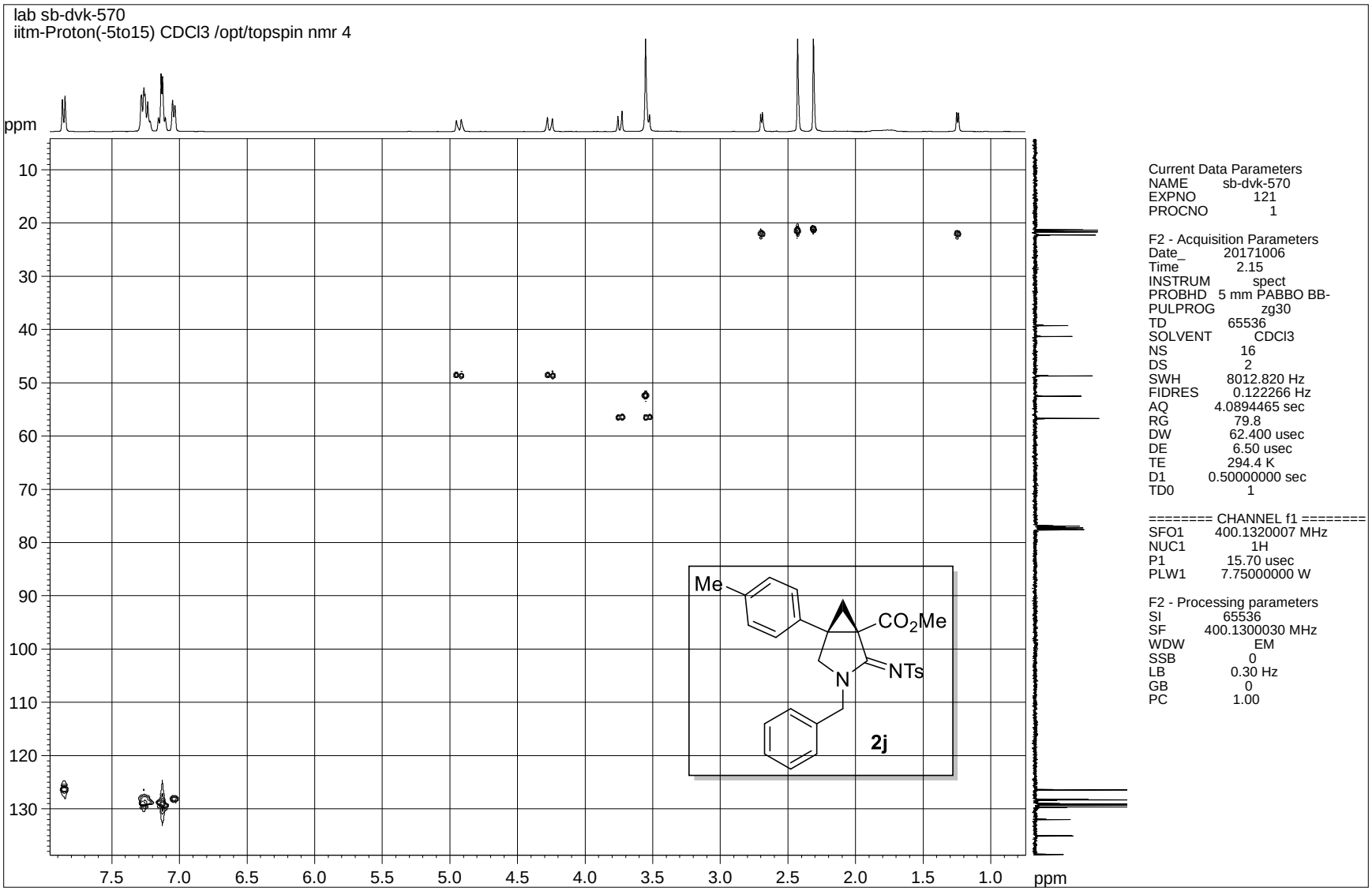
^{13}C NMR spectrum of compound 2j



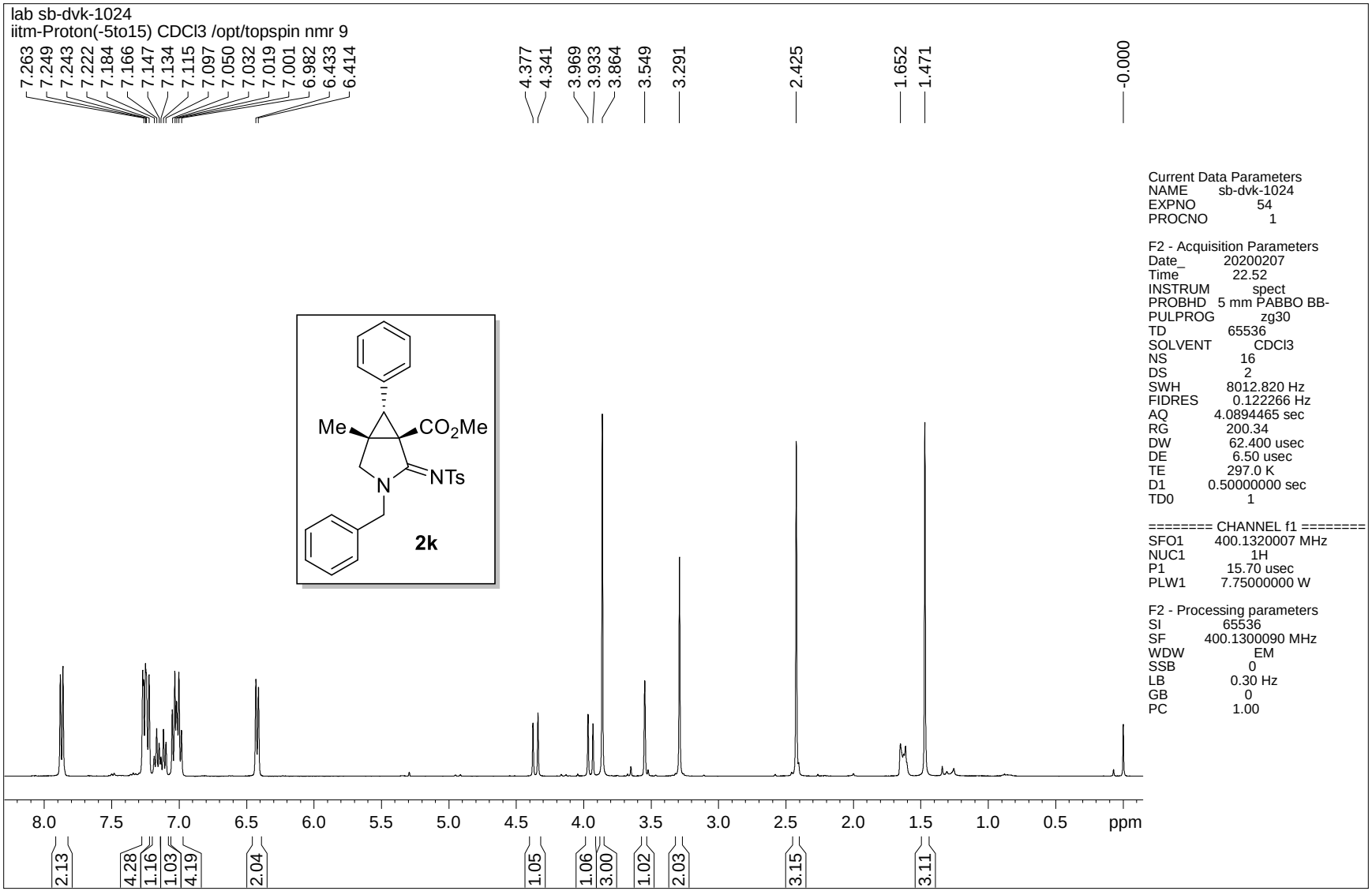
DEPT-135 NMR spectrum of compound 2j



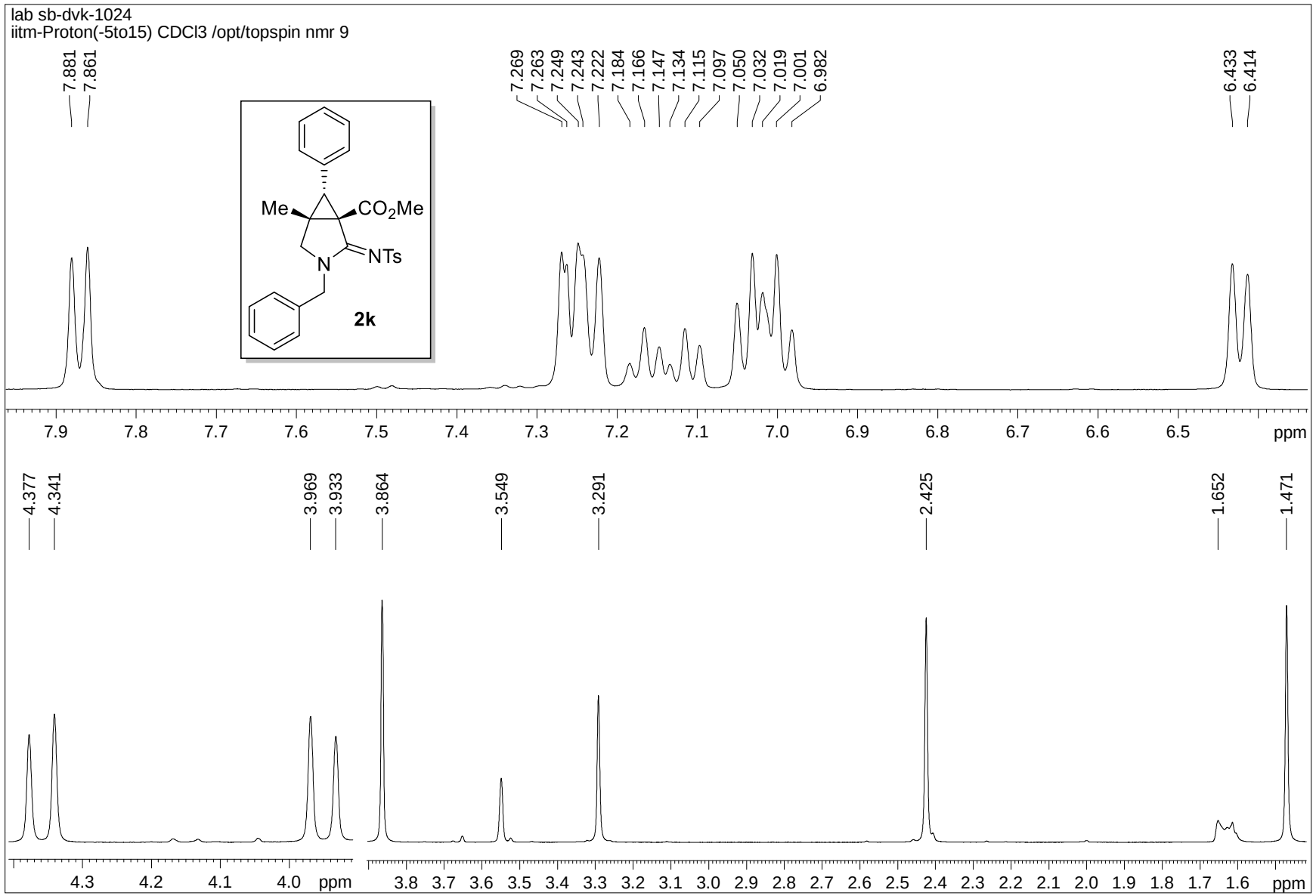
^{1}H-^{1}H COSY NMR spectrum of compound 2j



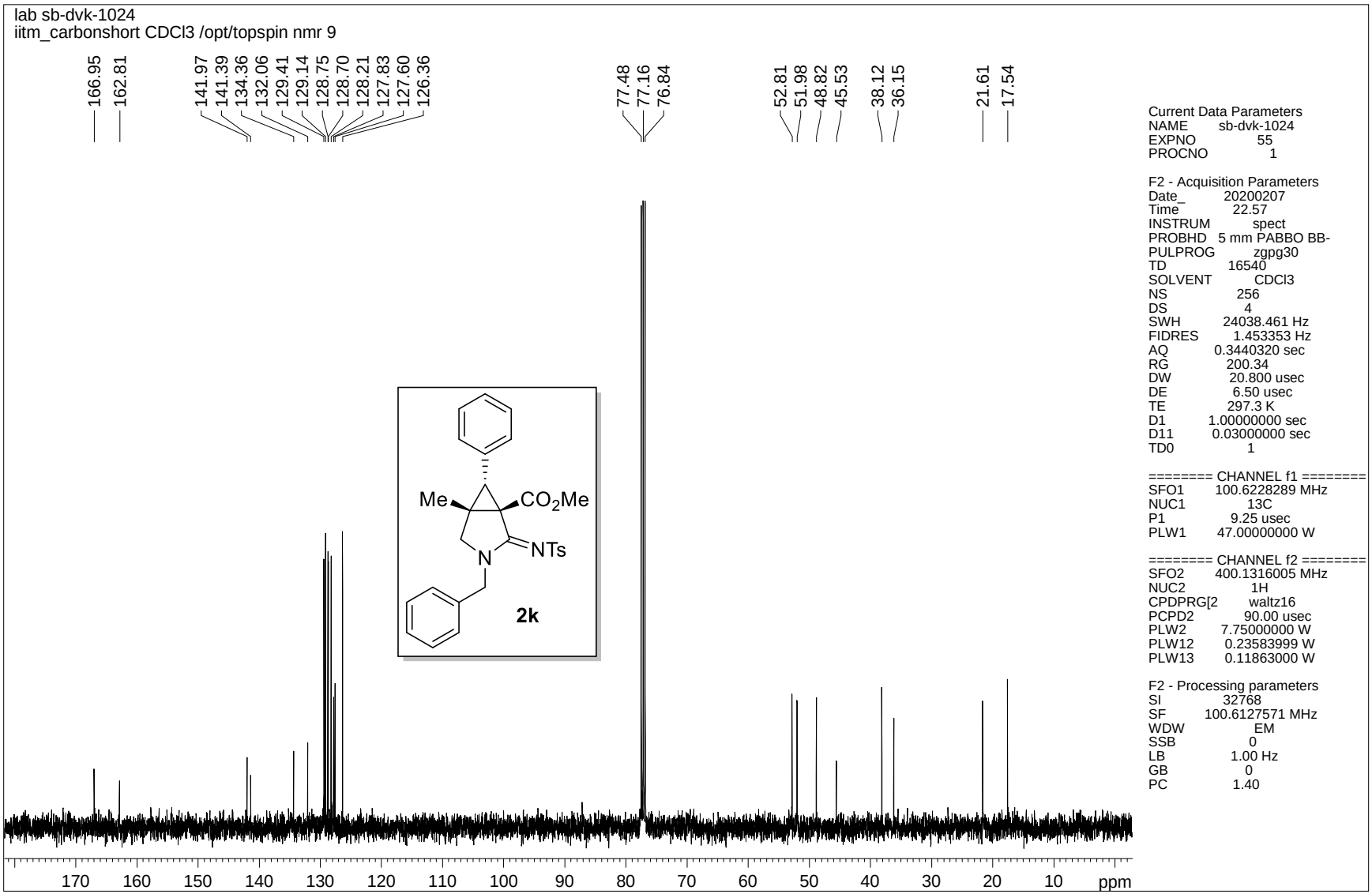
^{1}H-^{13}C HSQC NMR spectrum of compound 2j



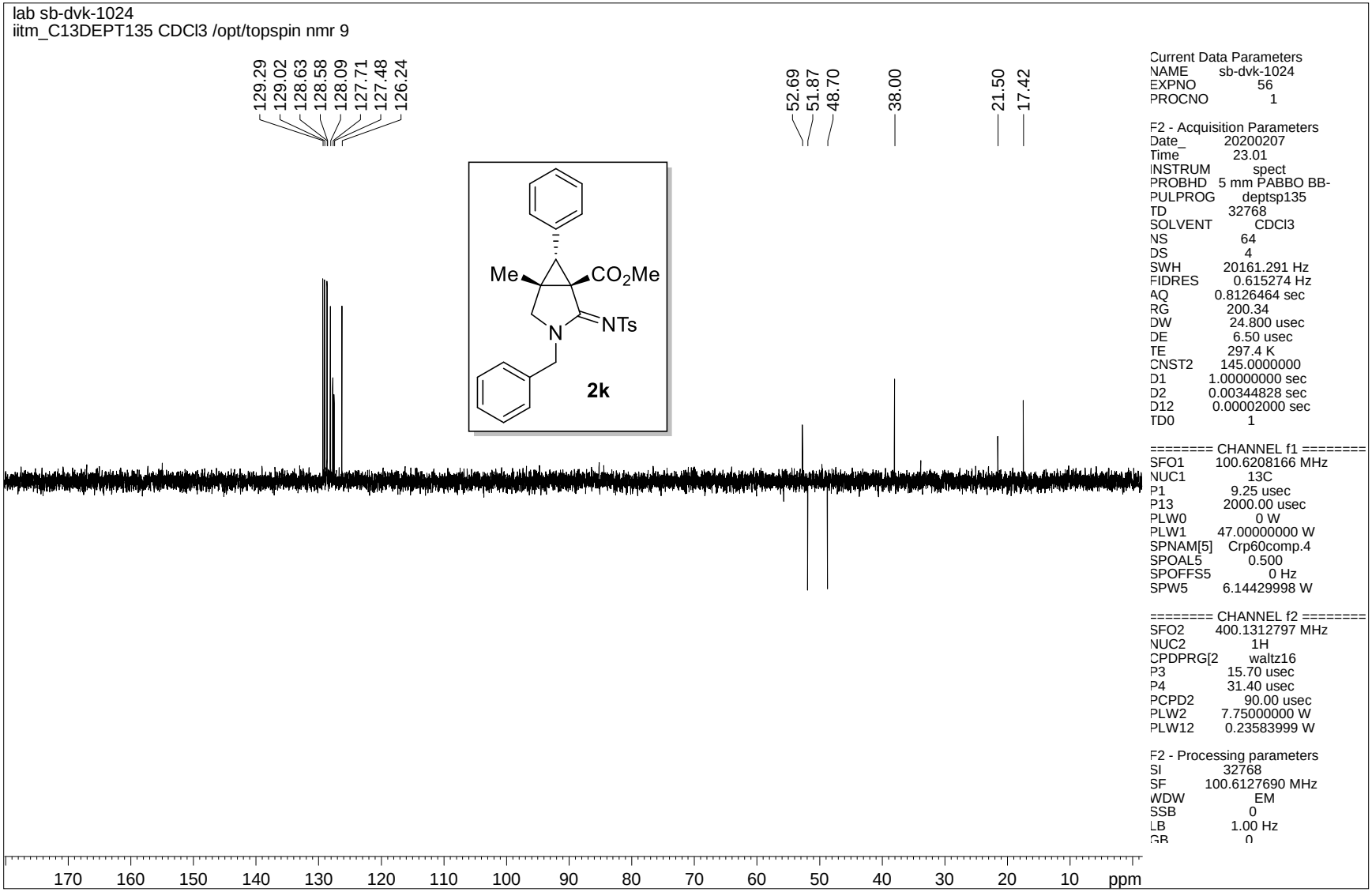
^{1}H NMR spectrum of compound 2k



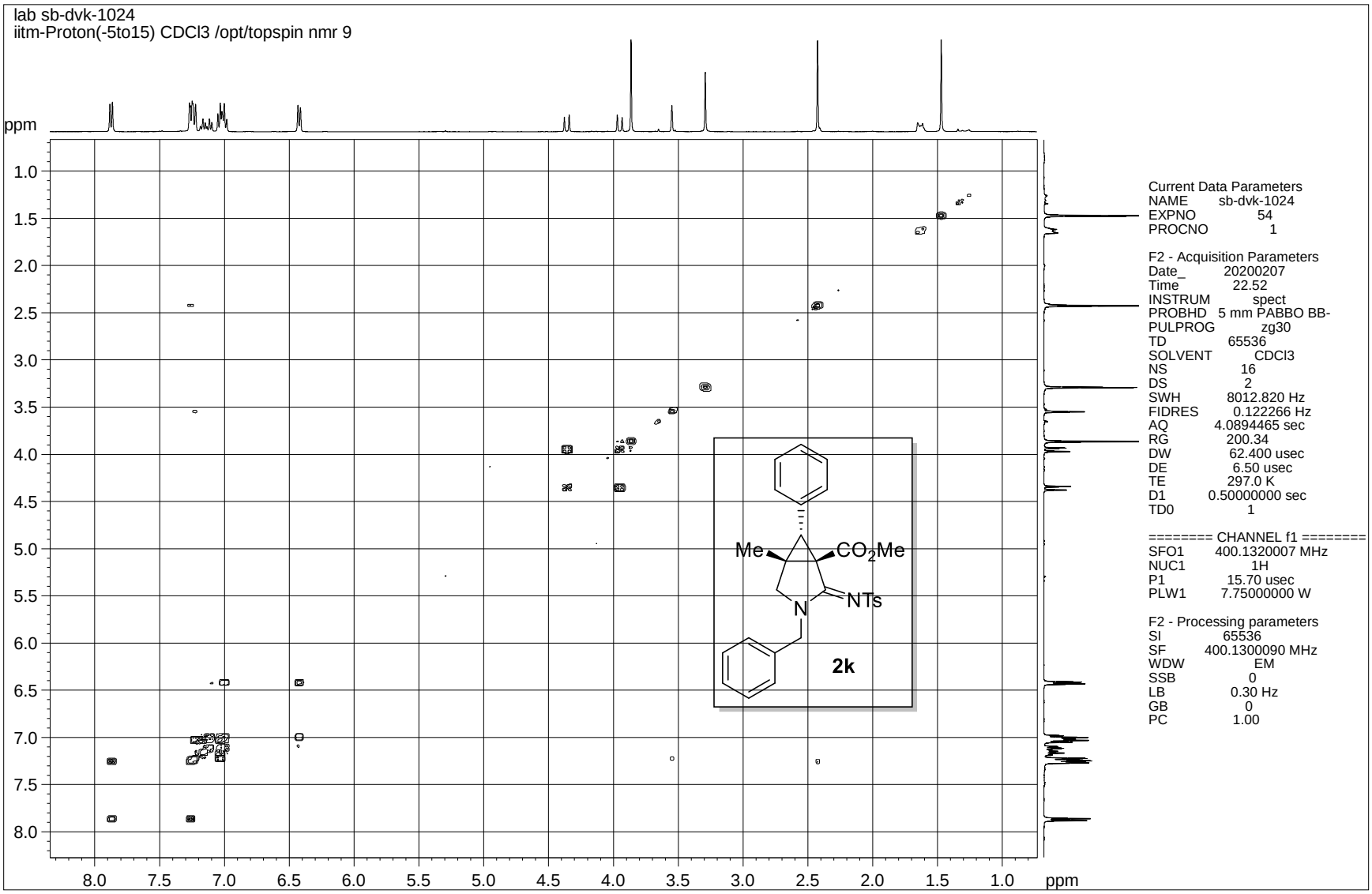
^{1}H NMR spectrum of compound 2k



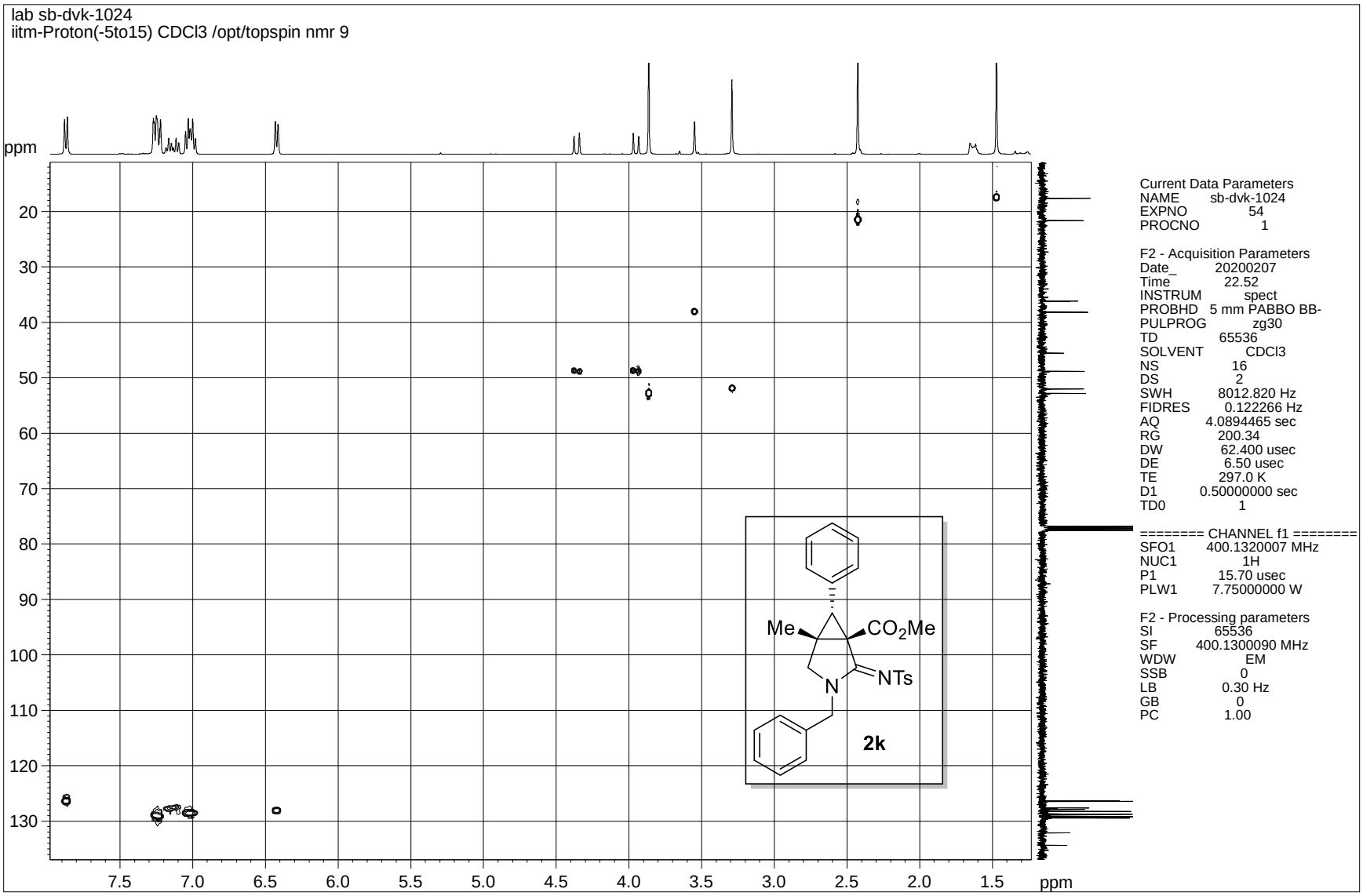
^{13}C NMR spectrum of compound 2k



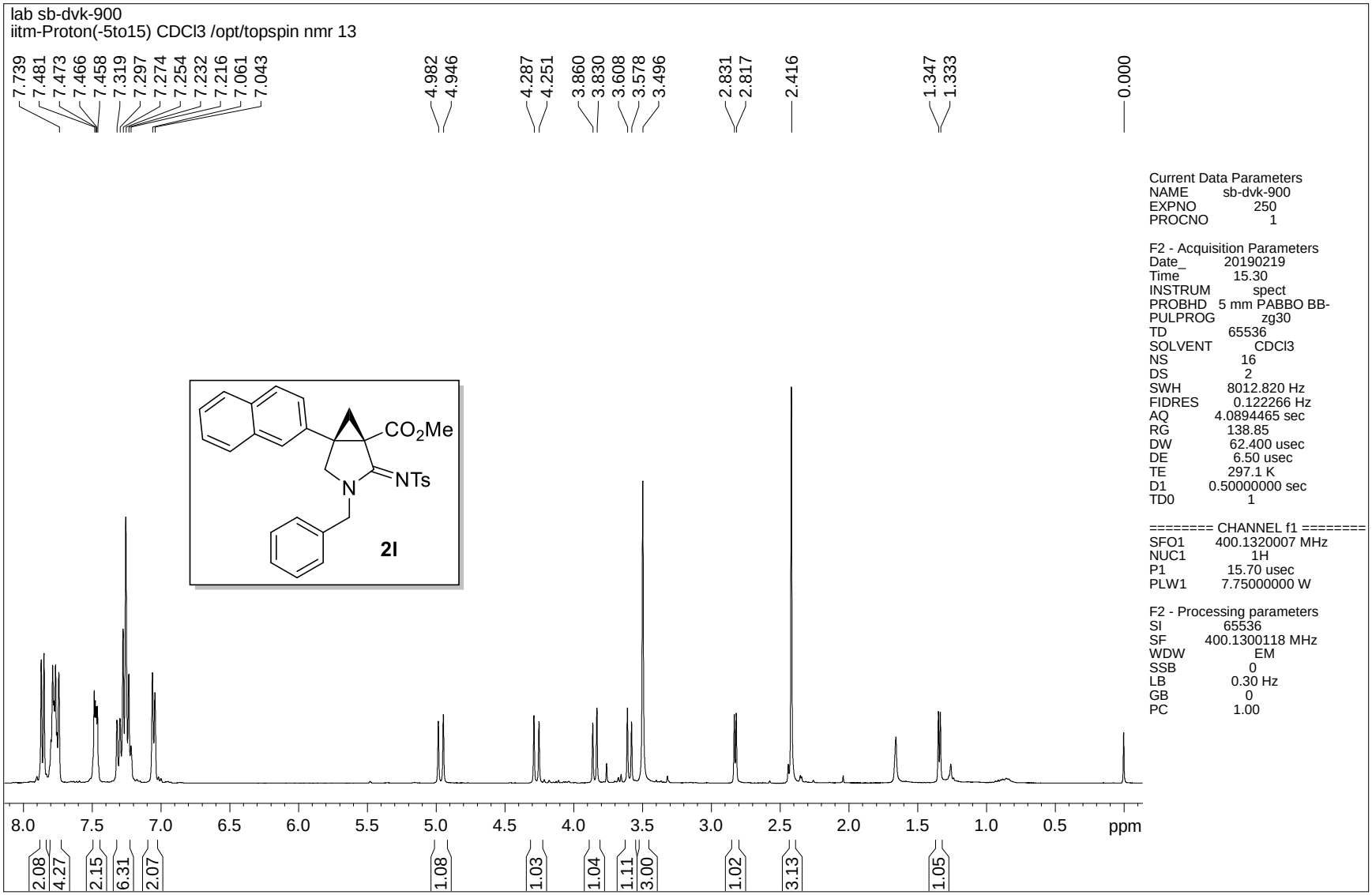
DEPT-135 NMR spectrum of compound 2k



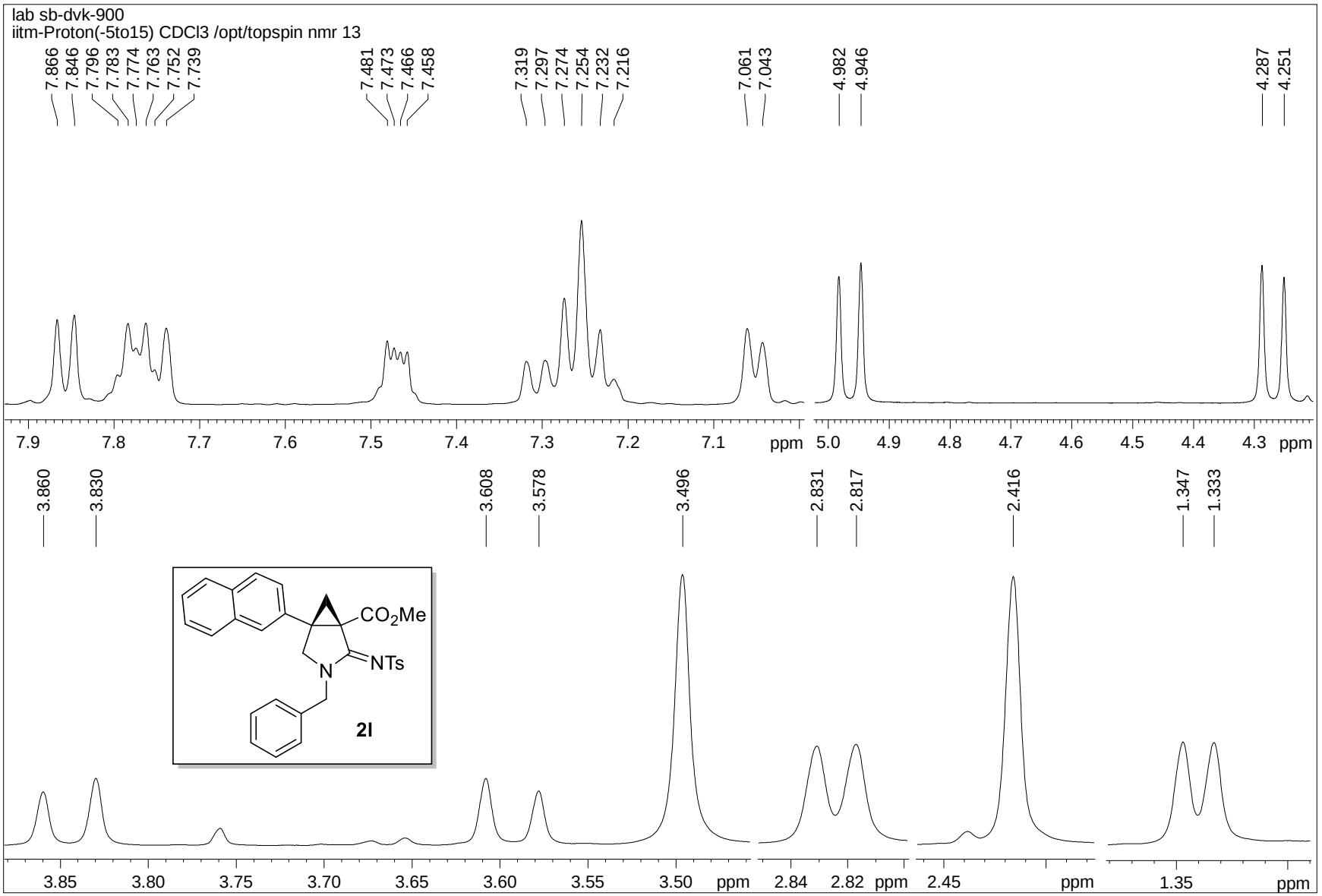
^{1}H-^{1}H COSY NMR spectrum of compound 2k



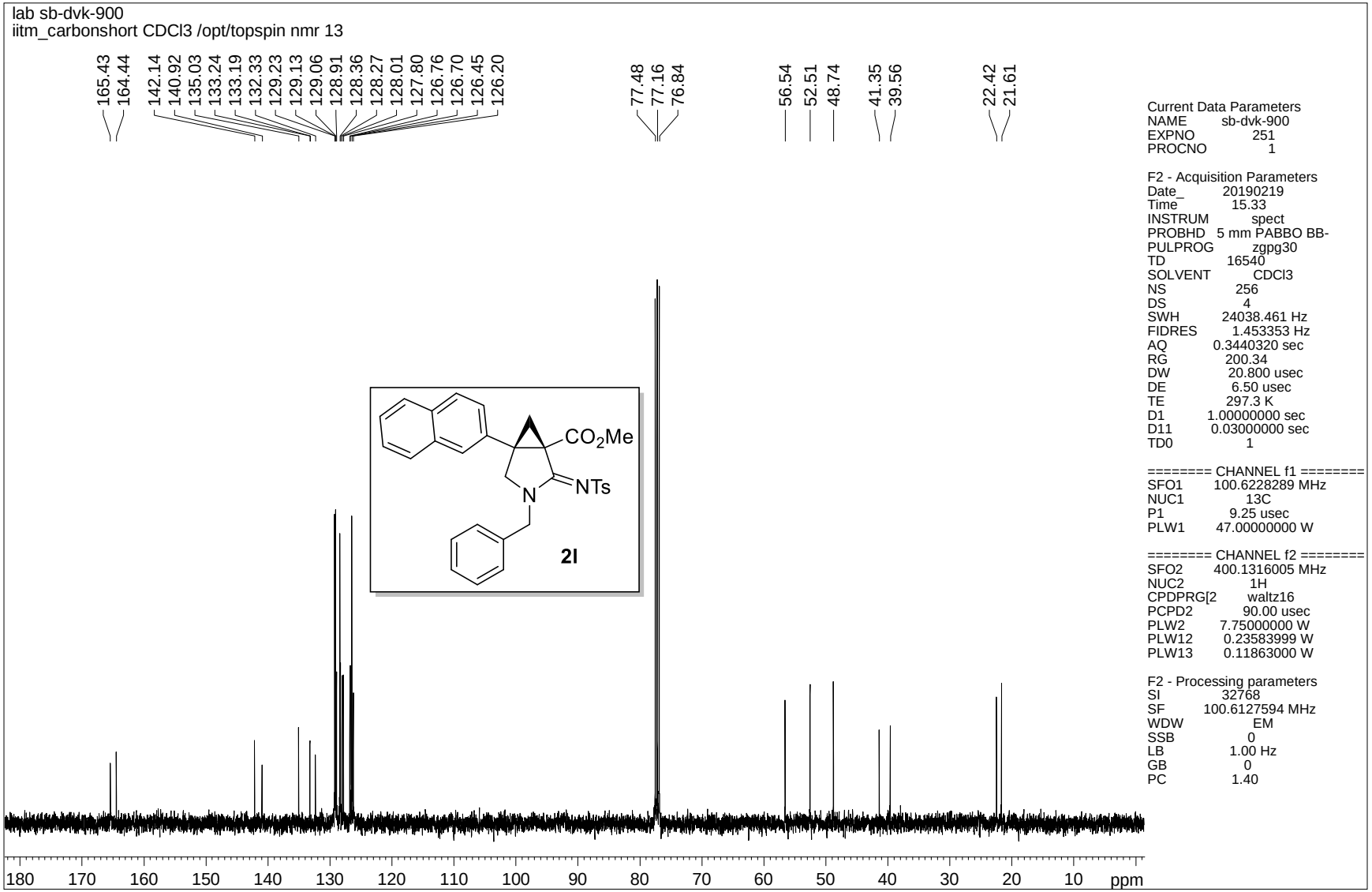
^{1}H-^{13}C HSQC NMR spectrum of compound 2k



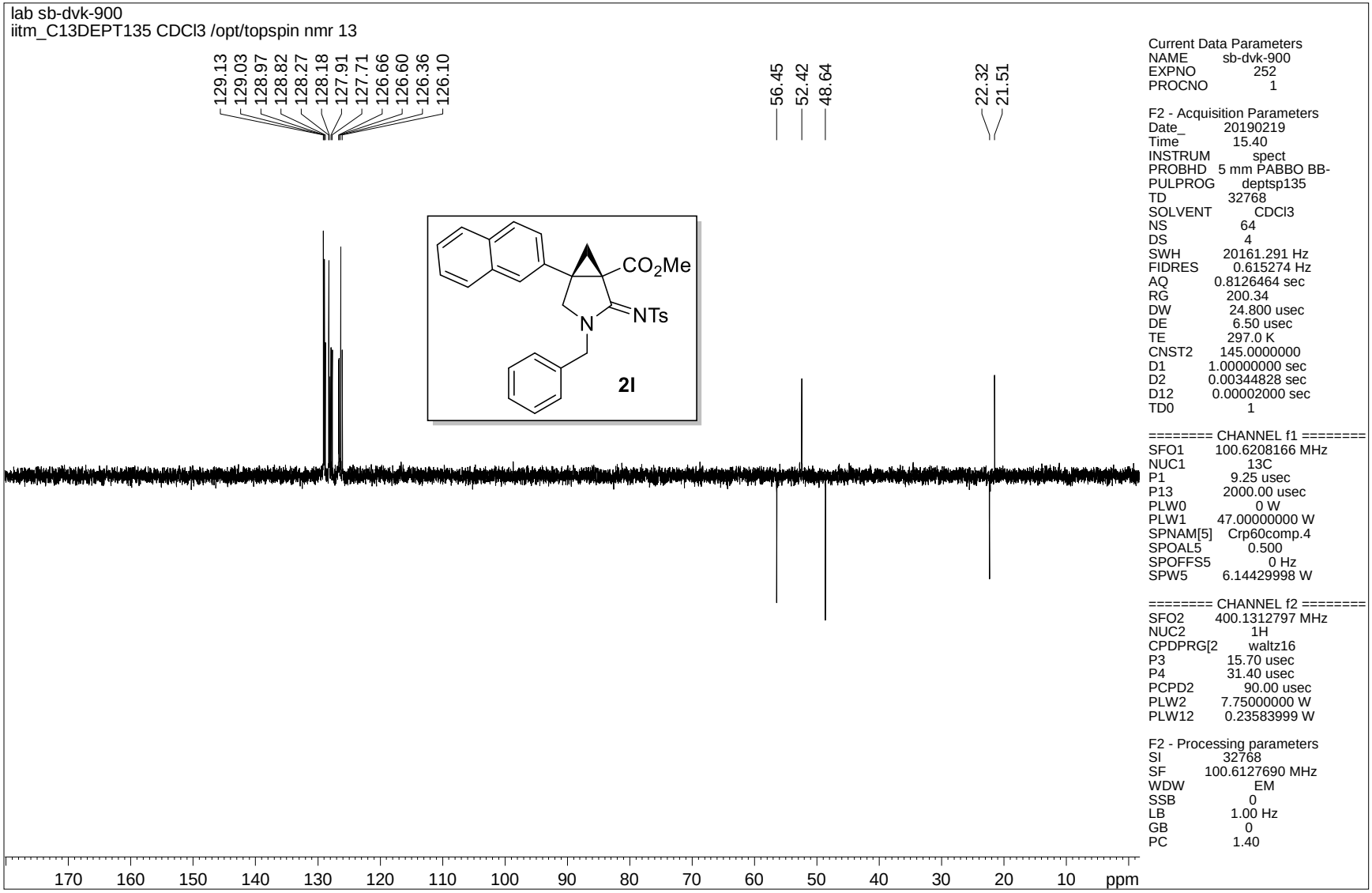
^{1}H NMR spectrum of compound 2l



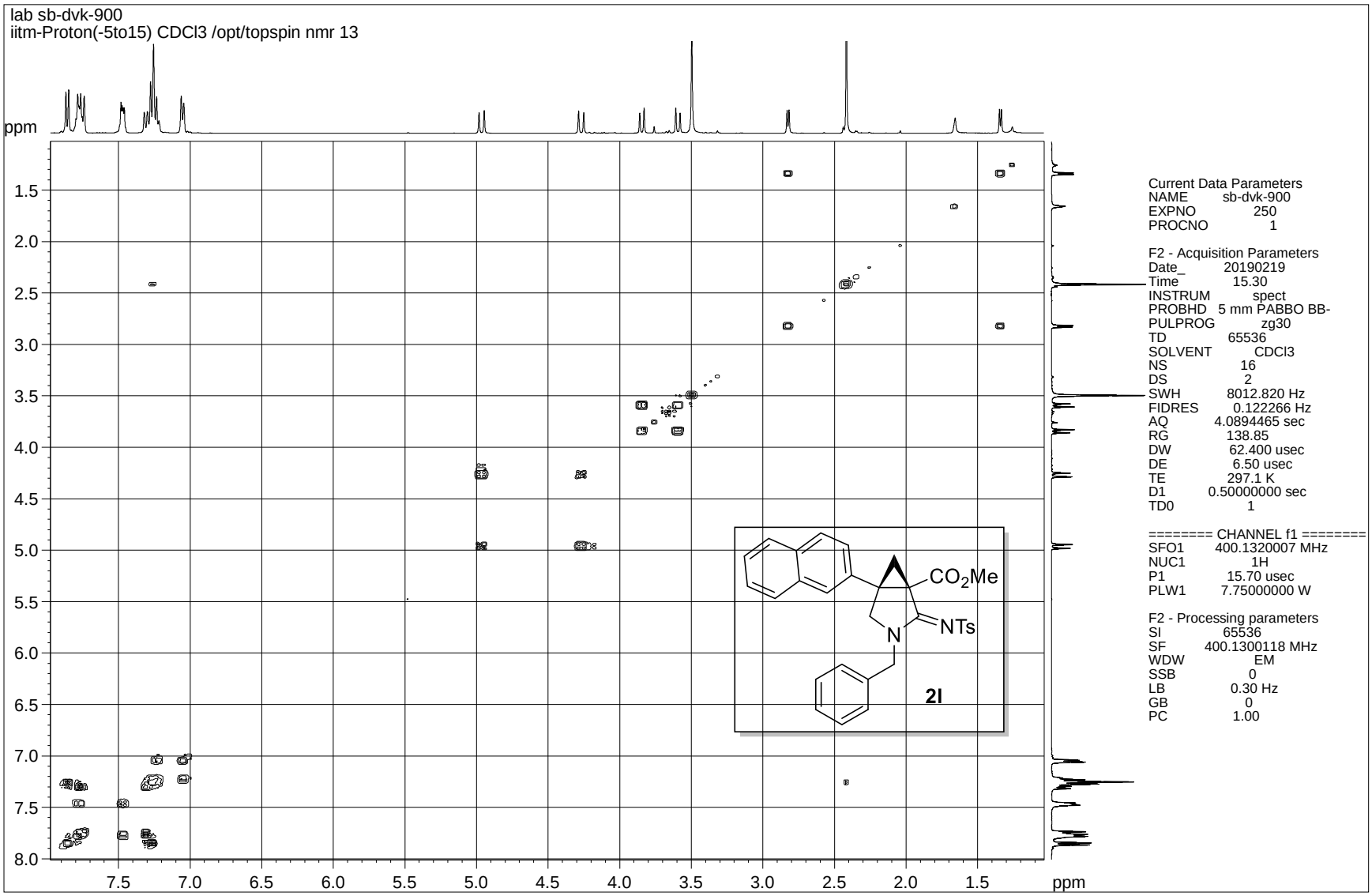
[1]H NMR spectrum of compound 2l



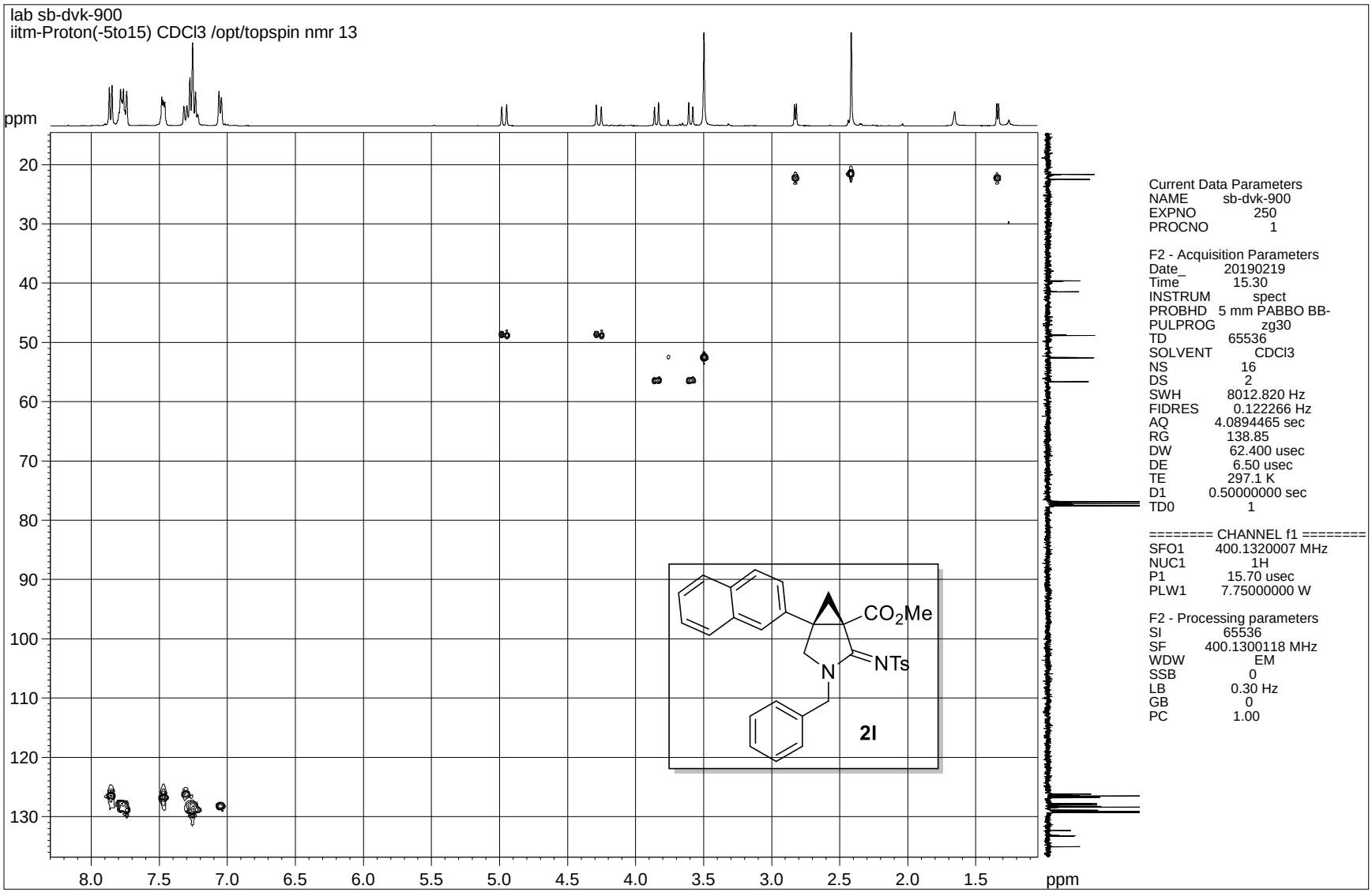
^{13}C NMR spectrum of compound 2l



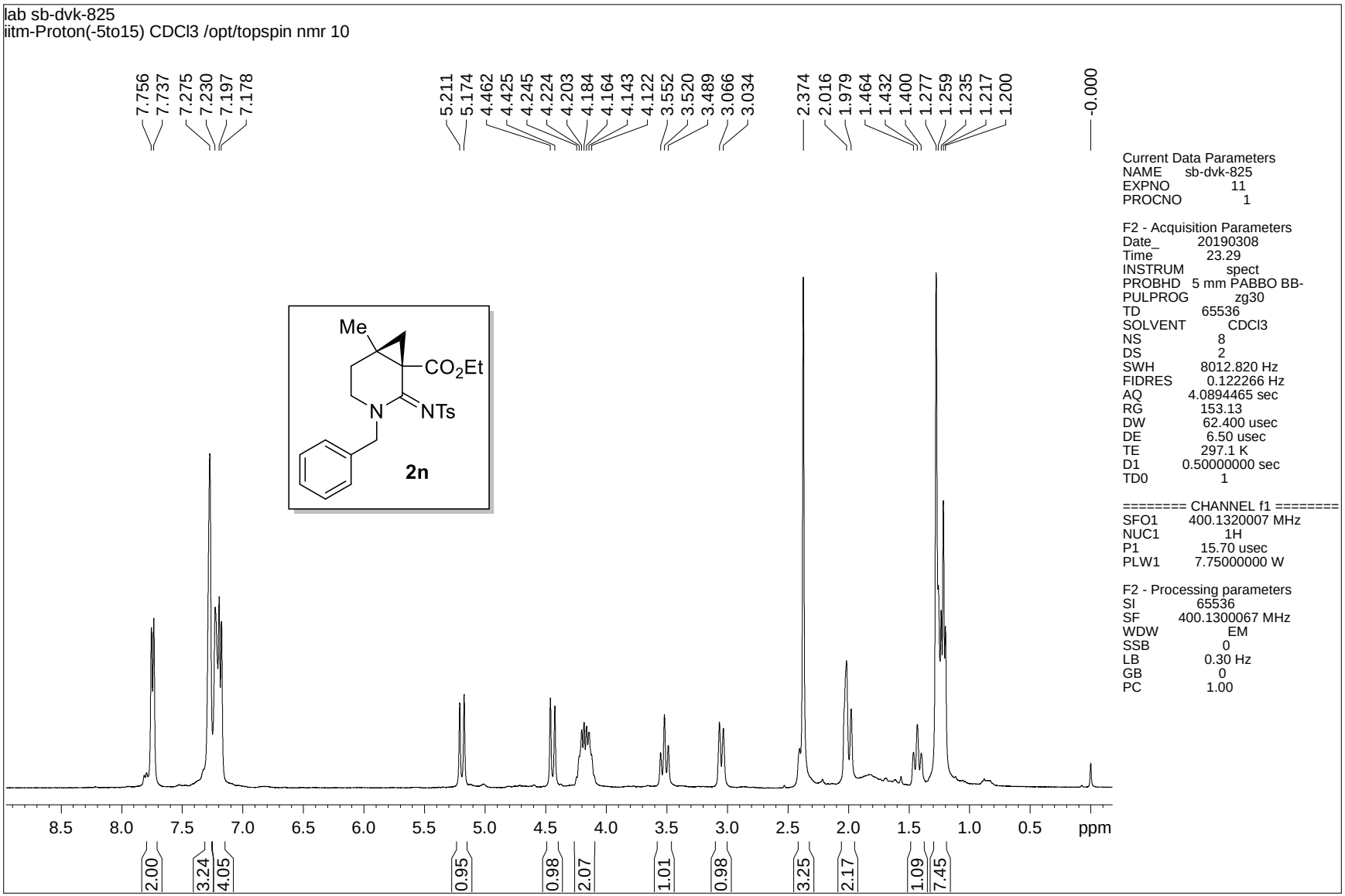
DEPT-135 NMR spectrum of compound 2l



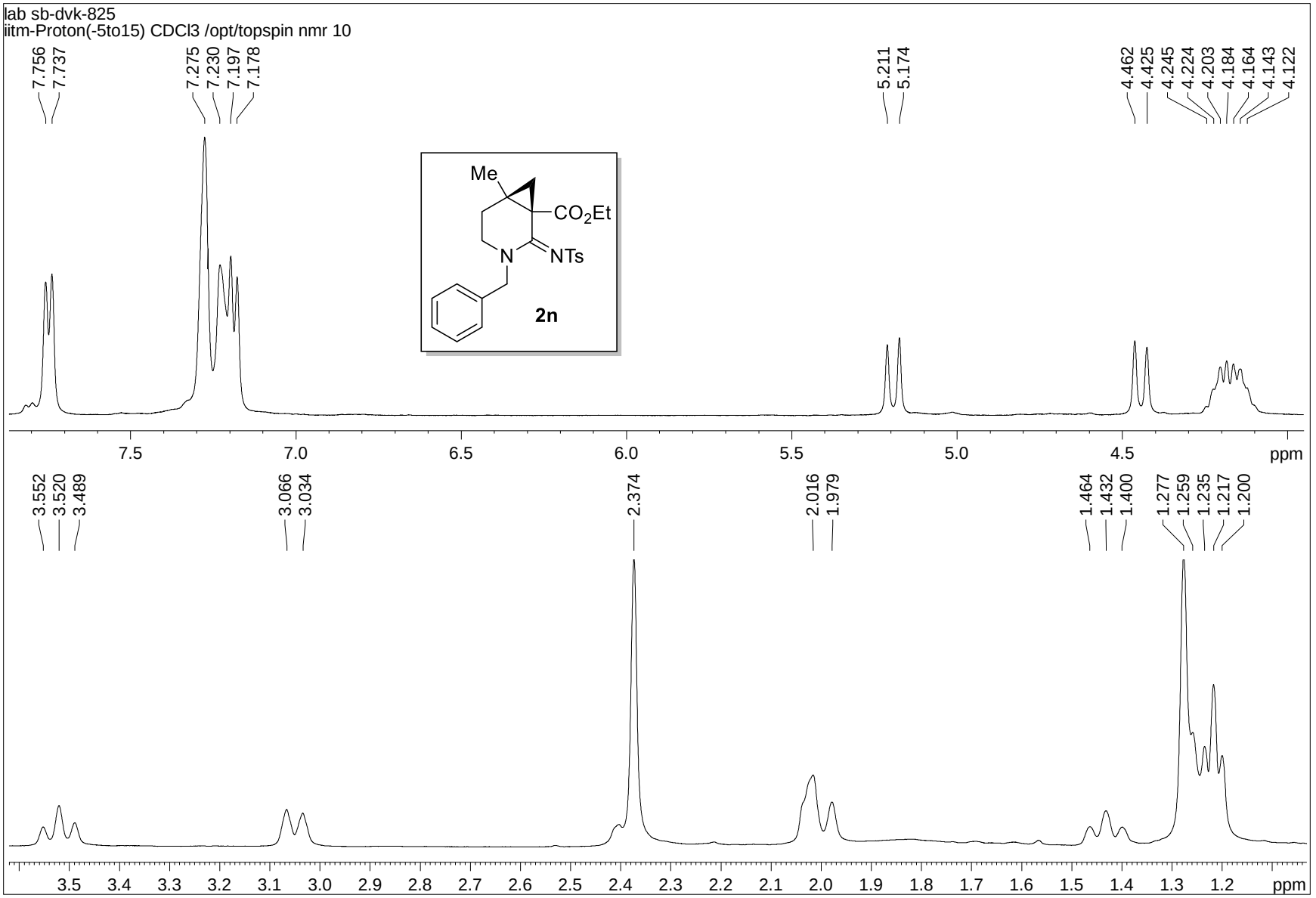
^{1}H-^{1}H COSY NMR spectrum of compound 2l



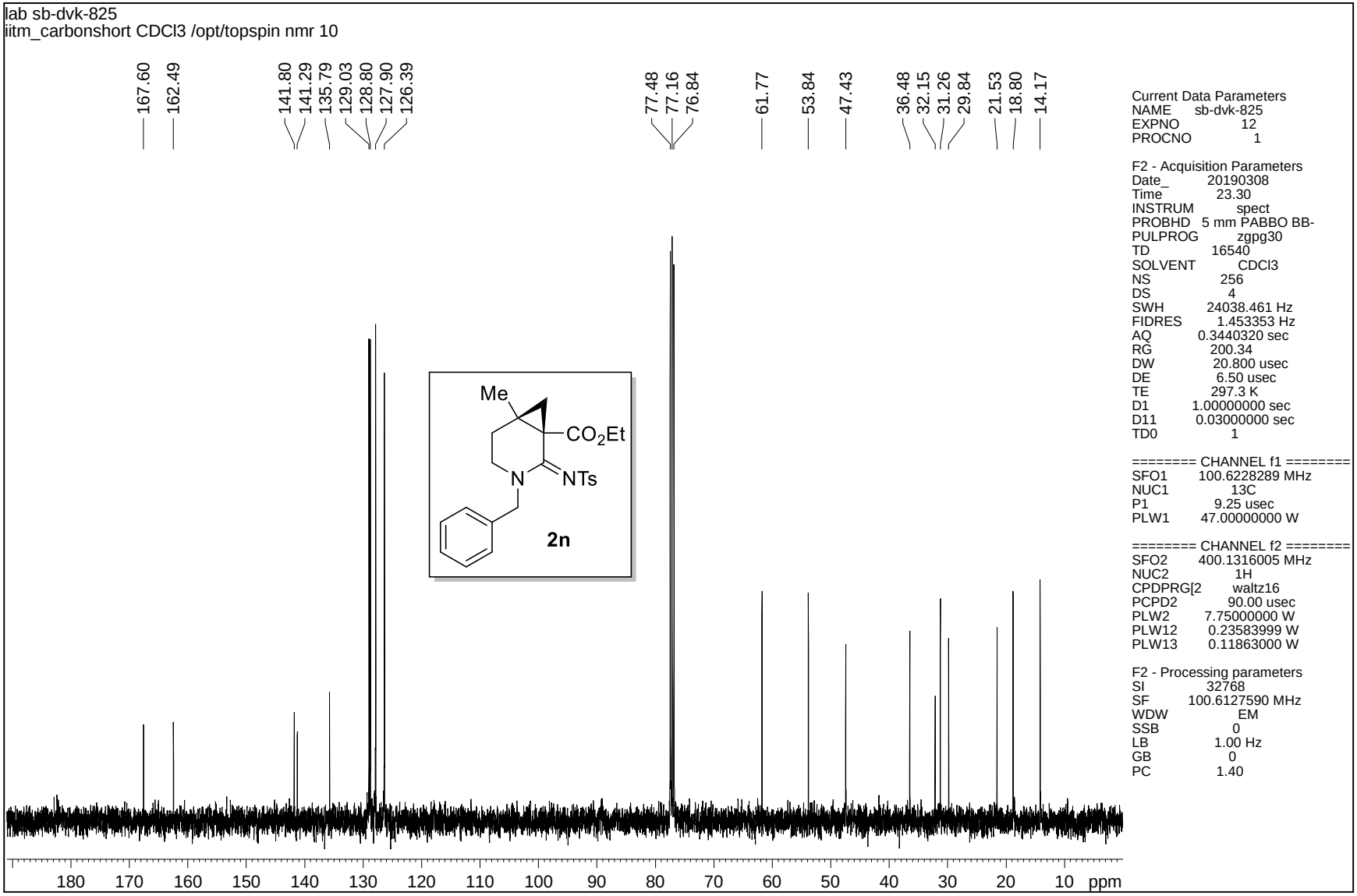
^{1}H-^{13}C HSQC NMR spectrum of compound 2l



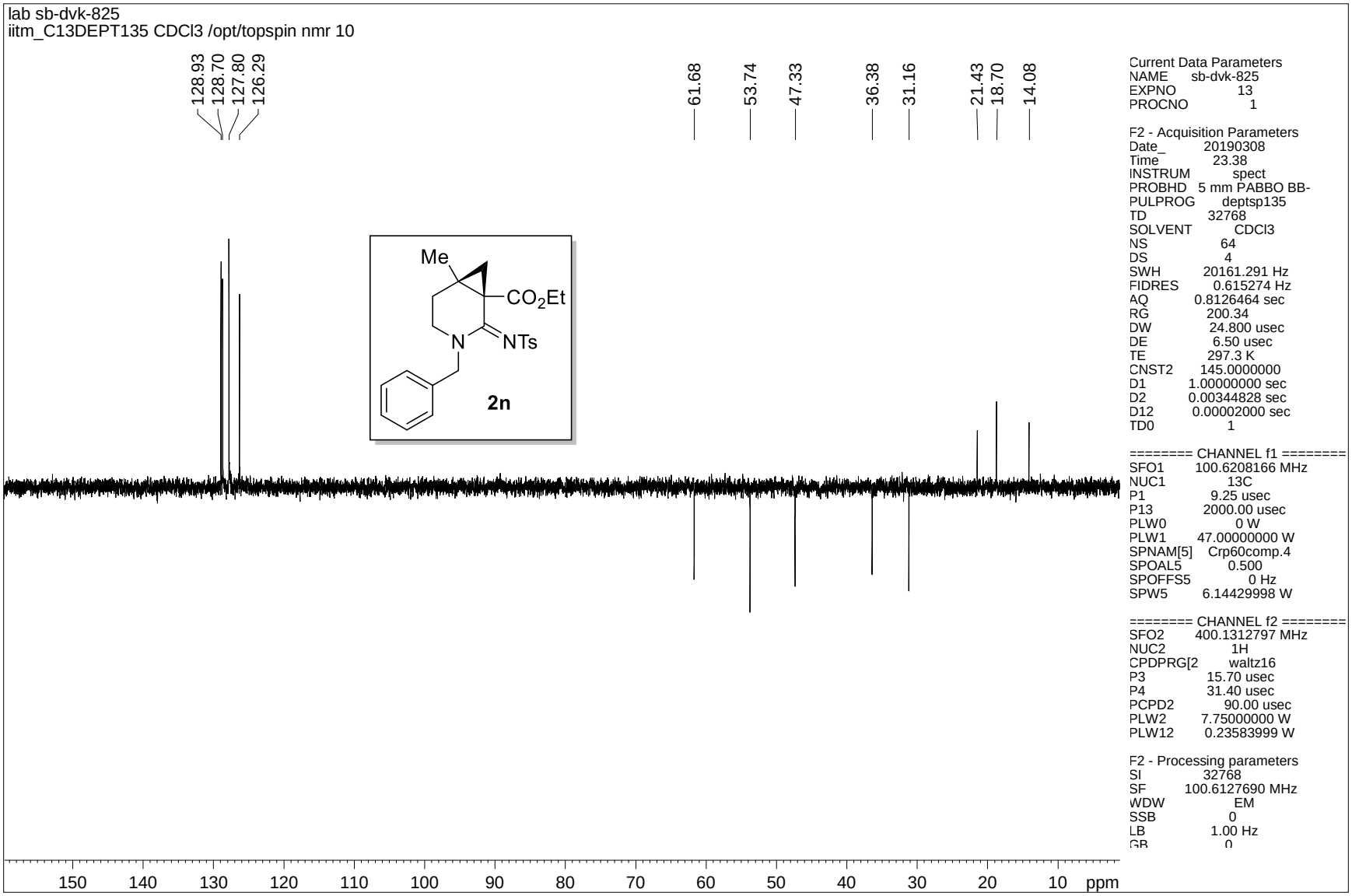
^{1}H NMR spectrum of compound 2n



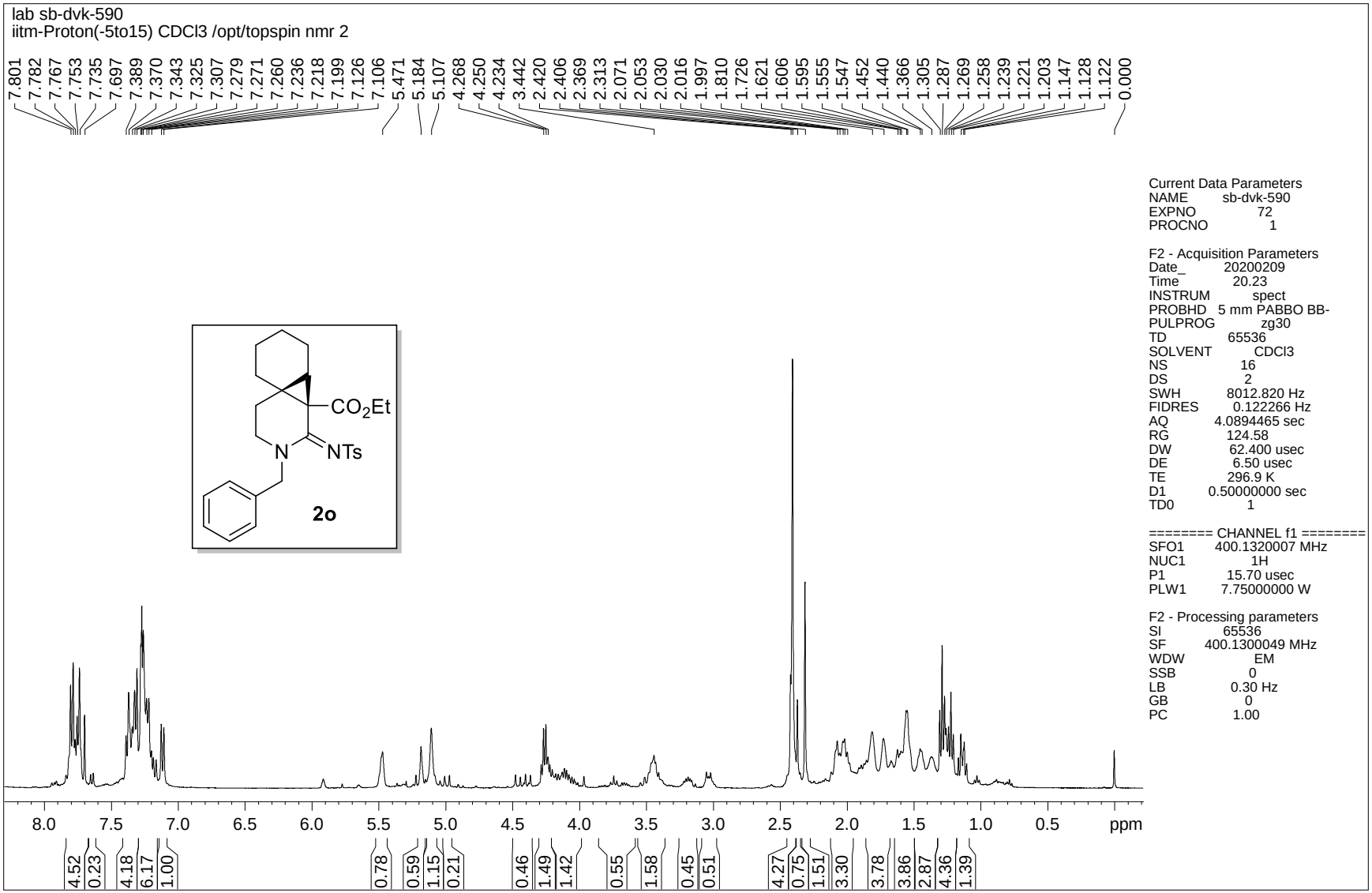
^{1}H NMR spectrum of compound 2n



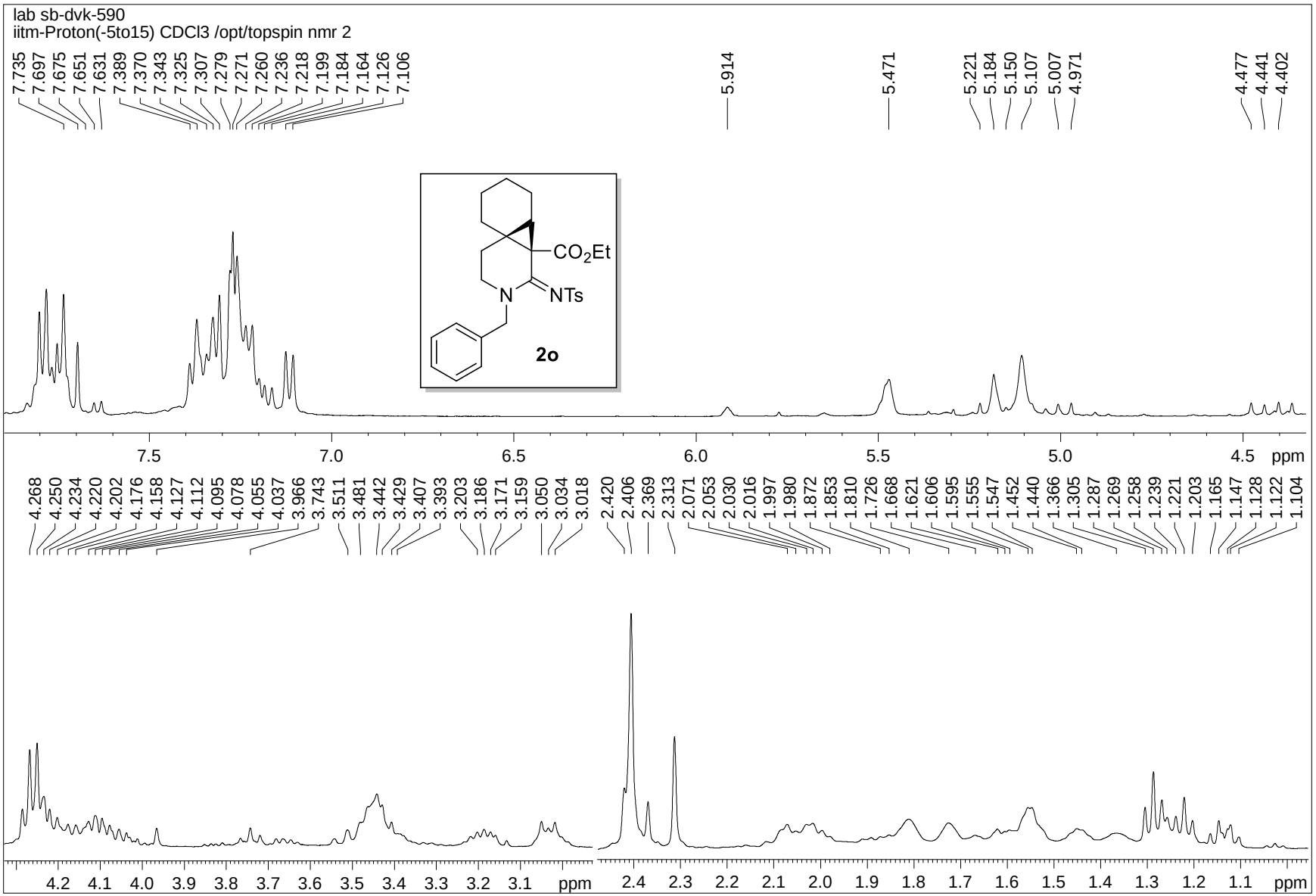
^{13}C NMR spectrum of compound 2n



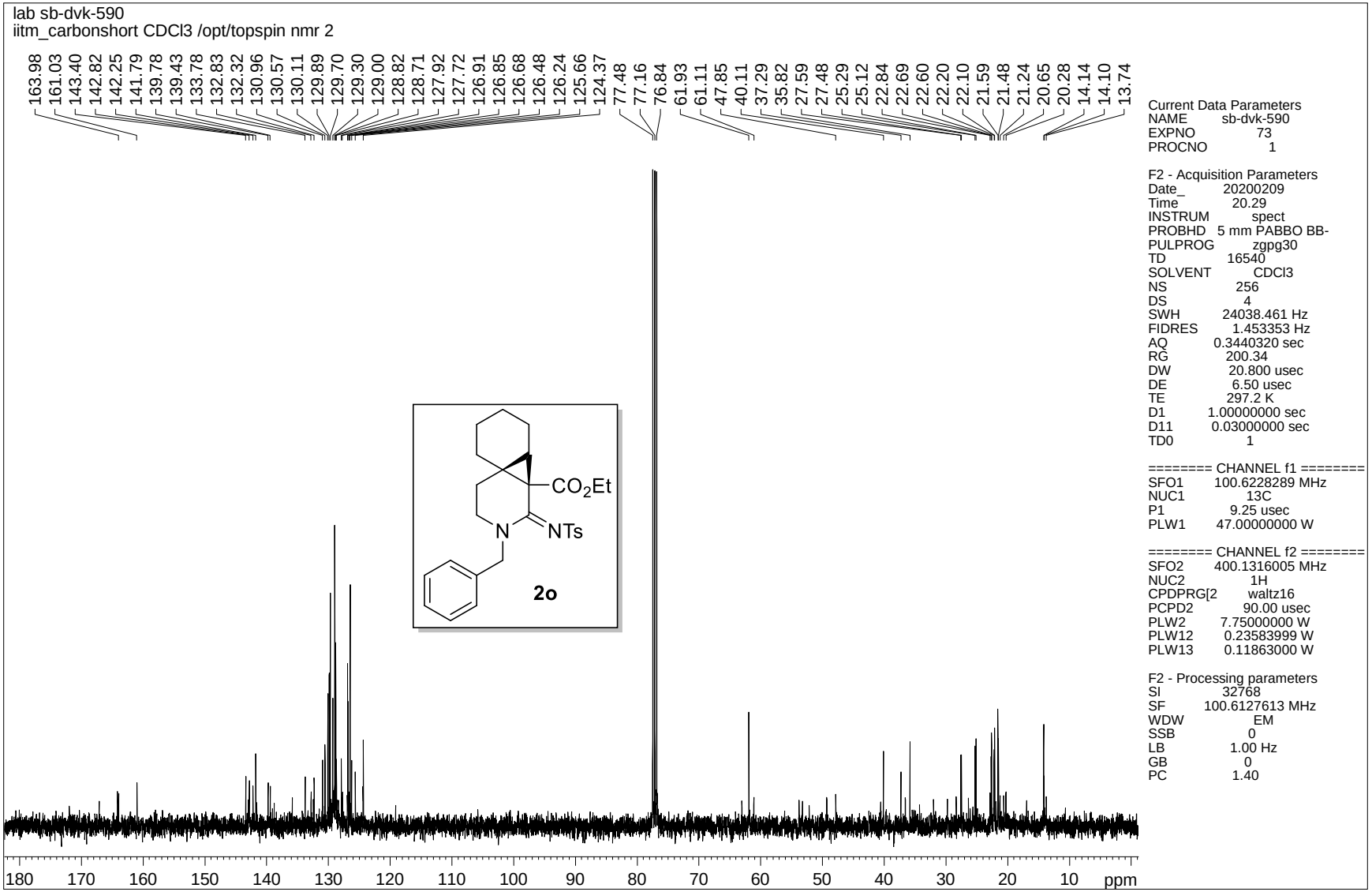
DEPT-135 NMR spectrum of compound 2n



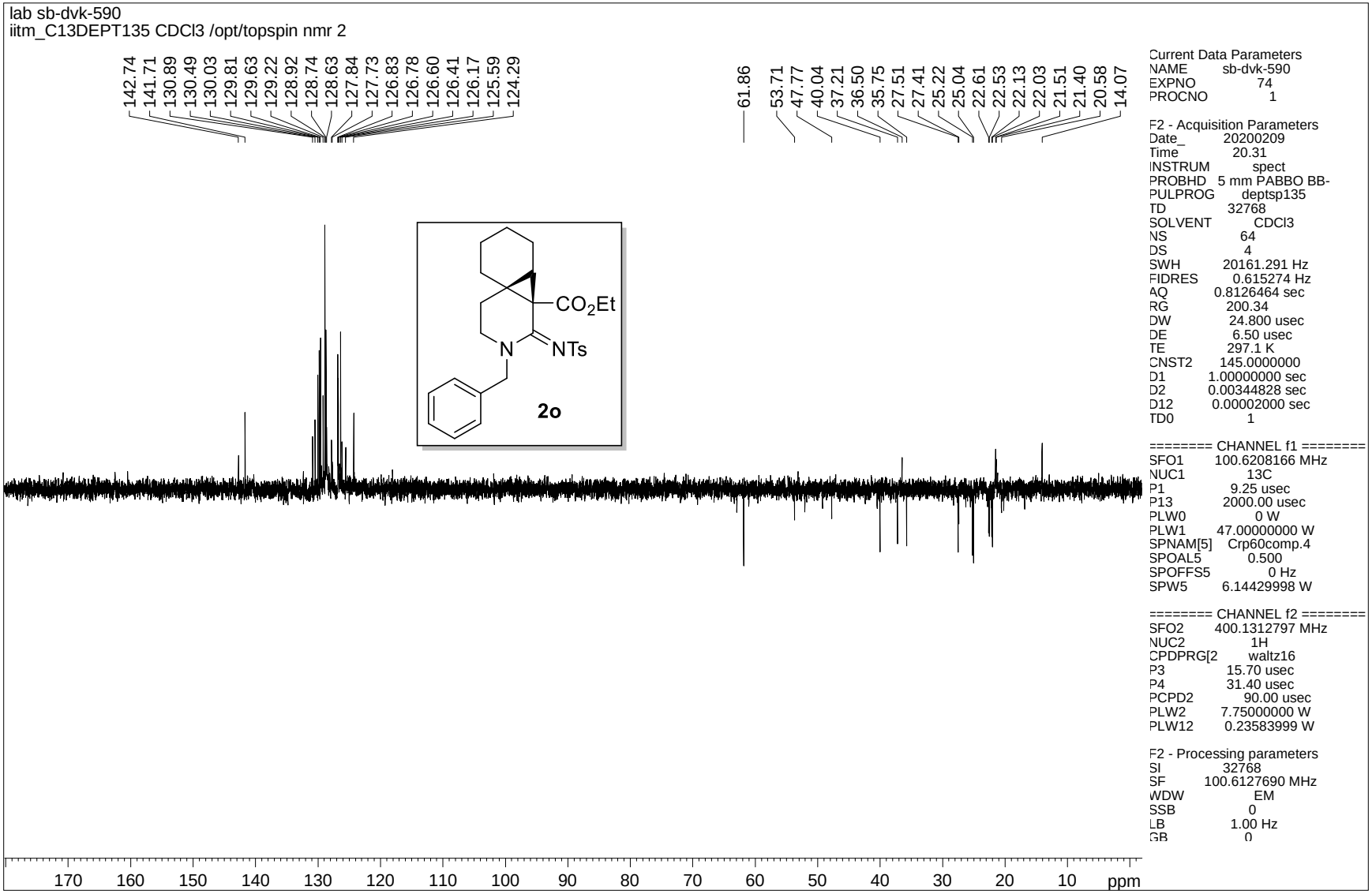
^{1}H NMR spectrum of compound 2o



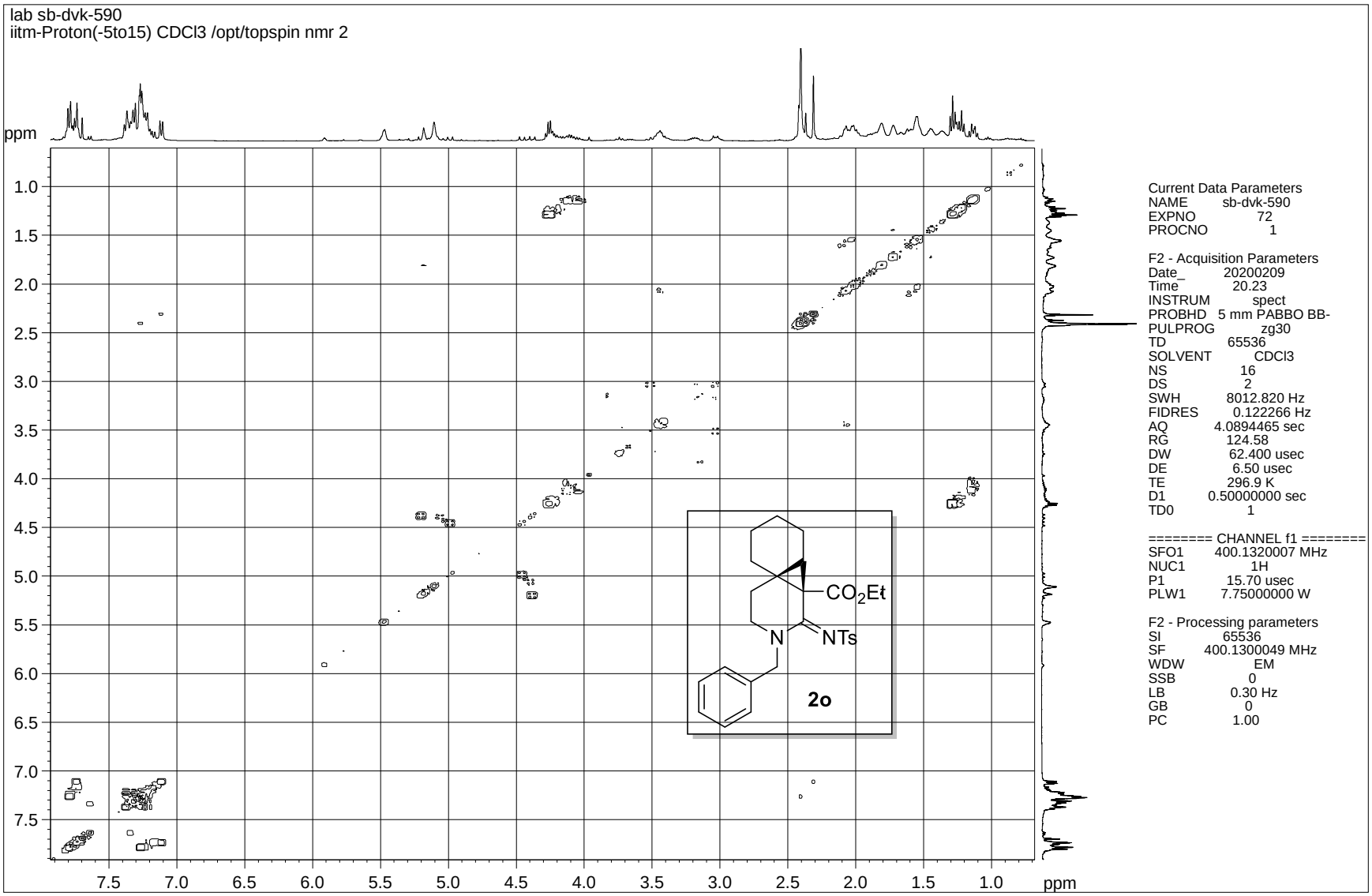
^{1}H NMR spectrum of compound 2o



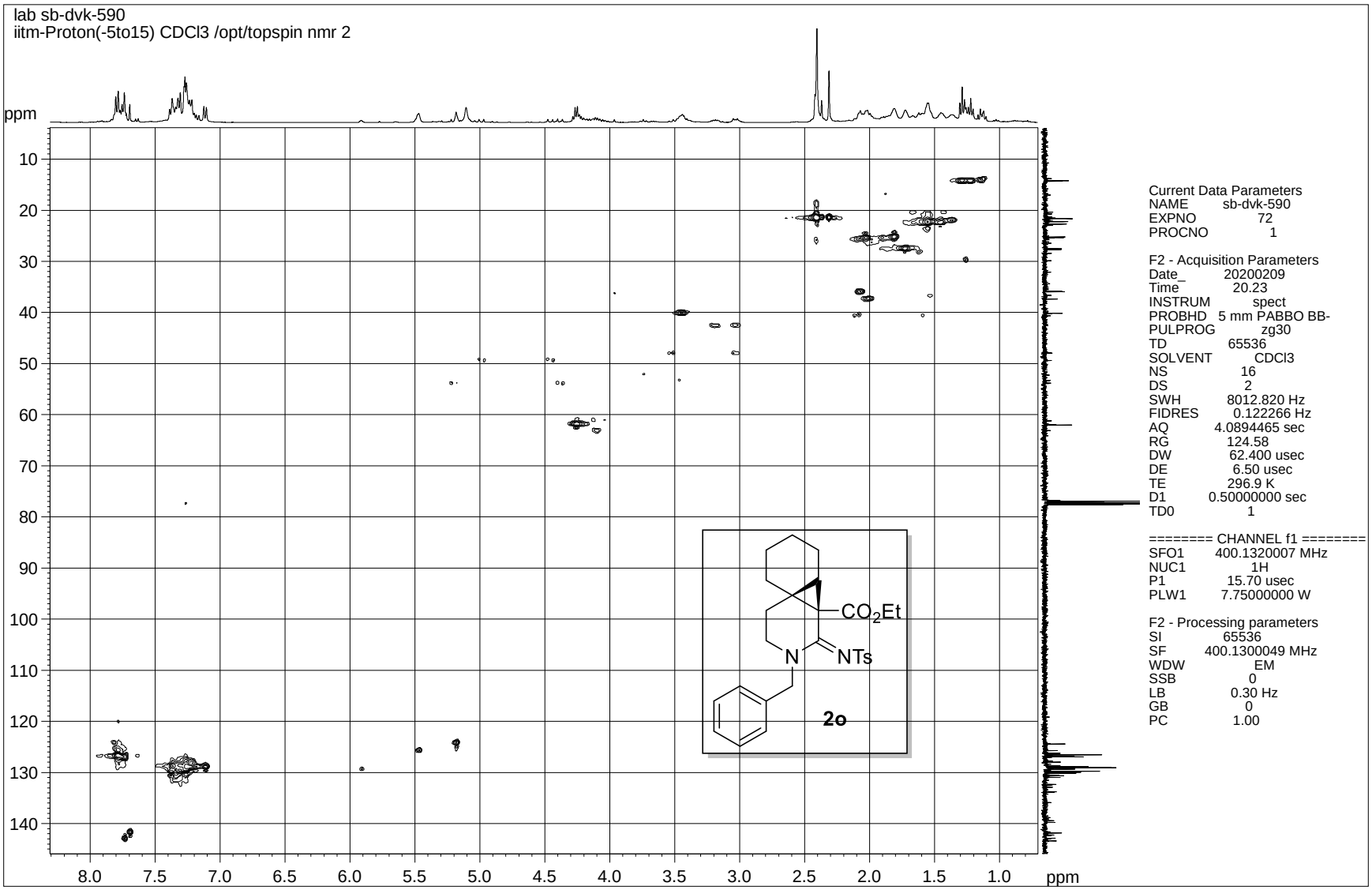
^{13}C NMR spectrum of compound 2o



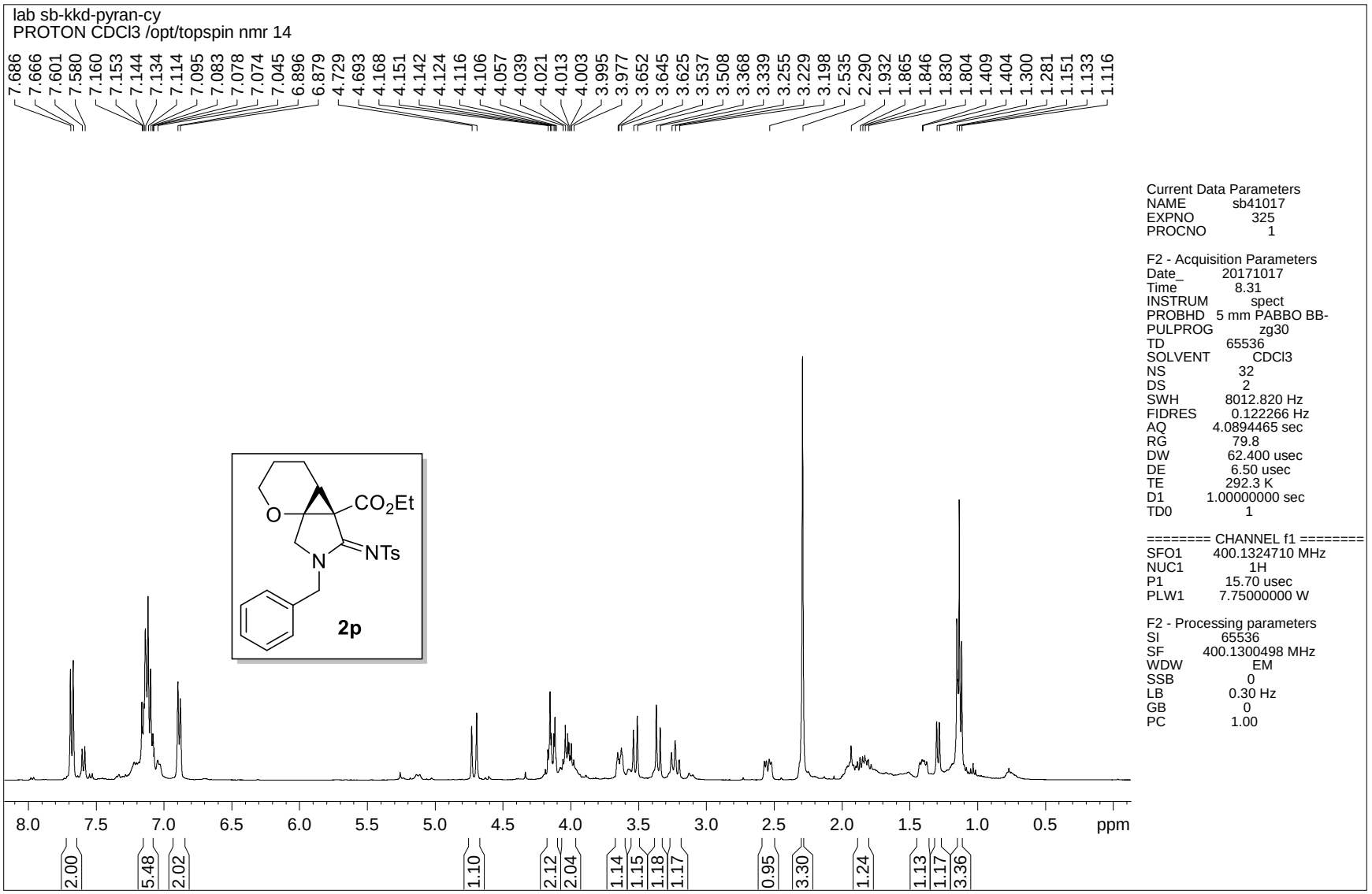
DEPT-135 NMR spectrum of compound 2o



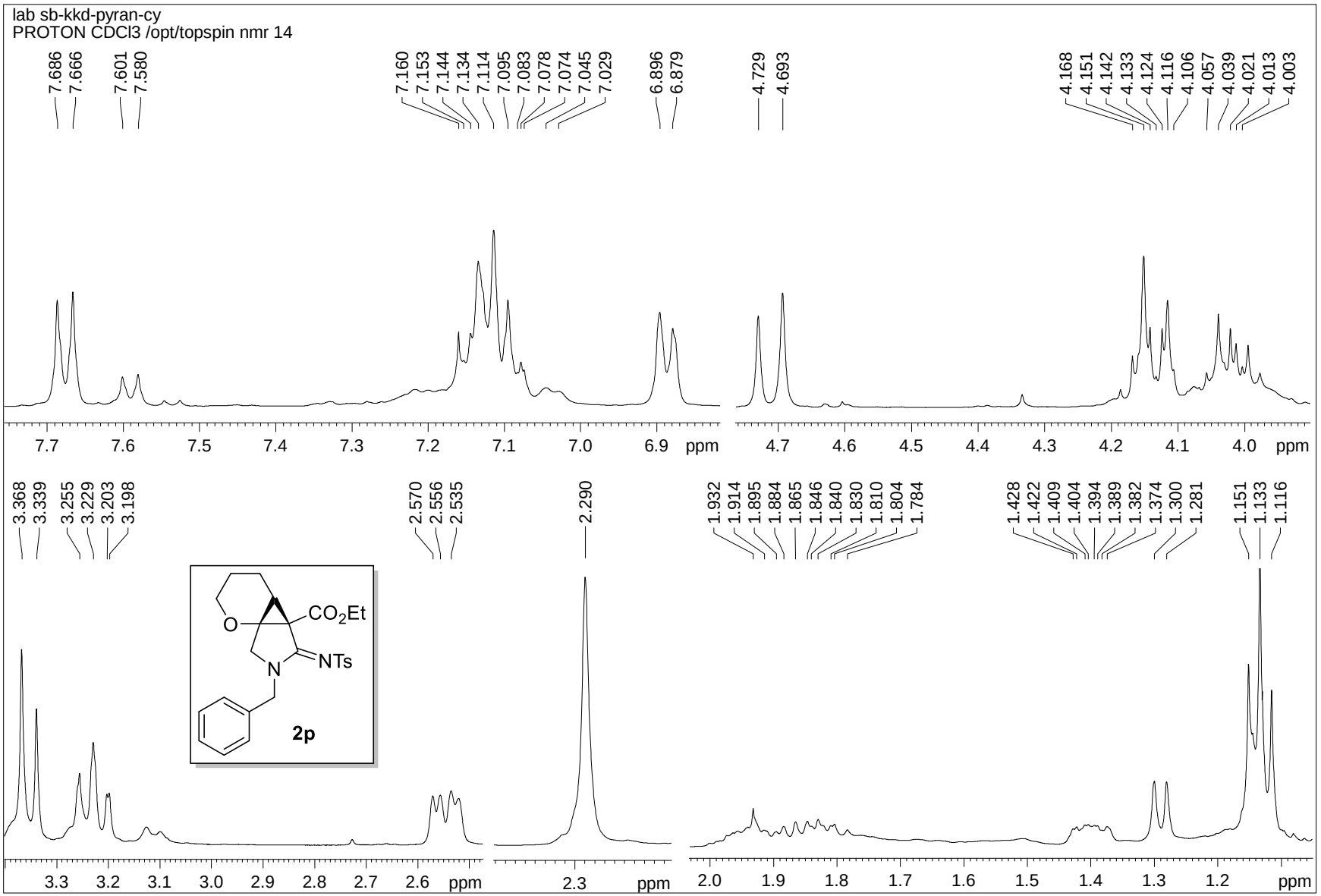
^{1}H-^{1}H COSY NMR spectrum of compound 2o



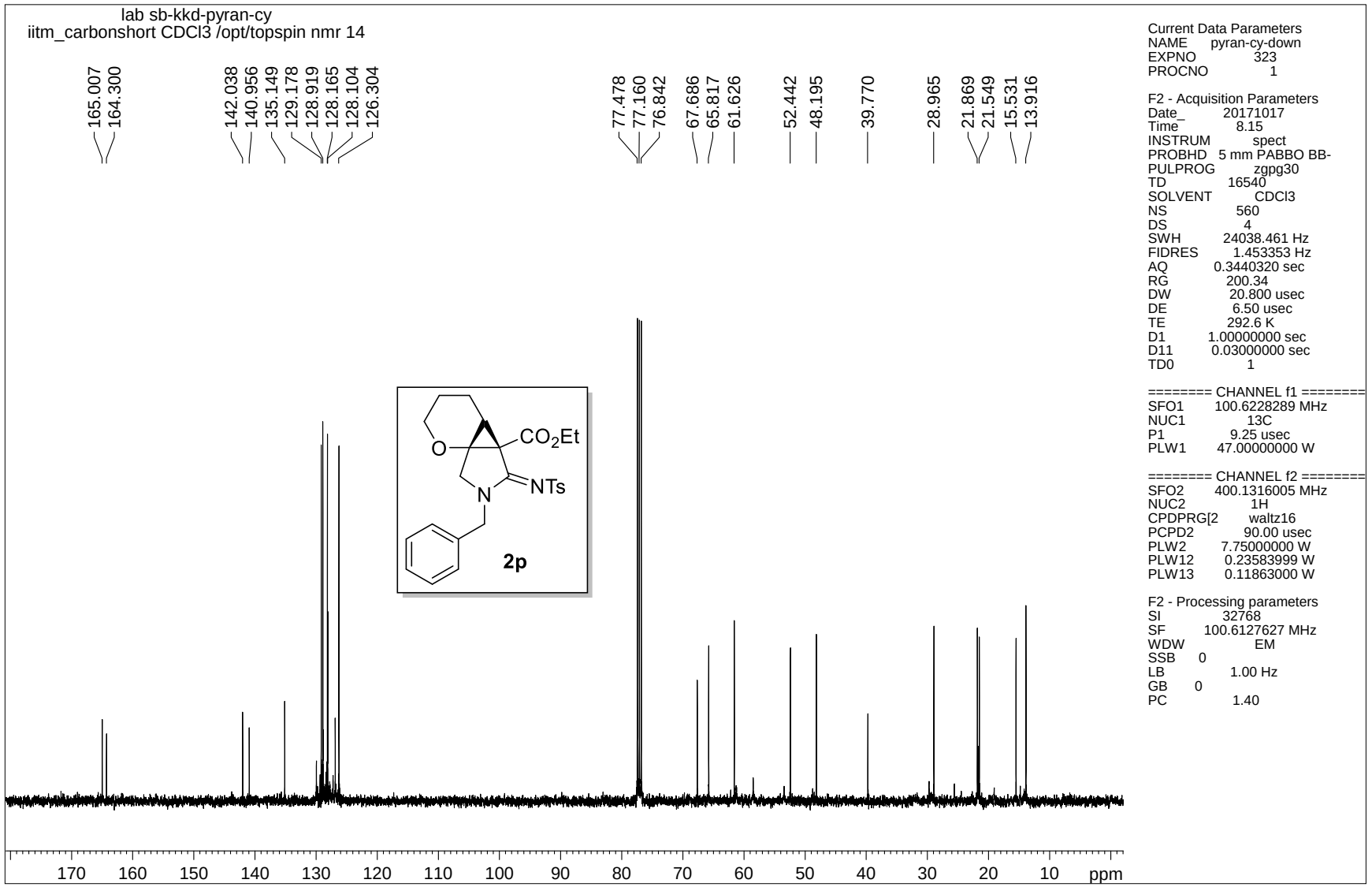
^{1}H-^{13}C HSQC NMR spectrum of compound 2o



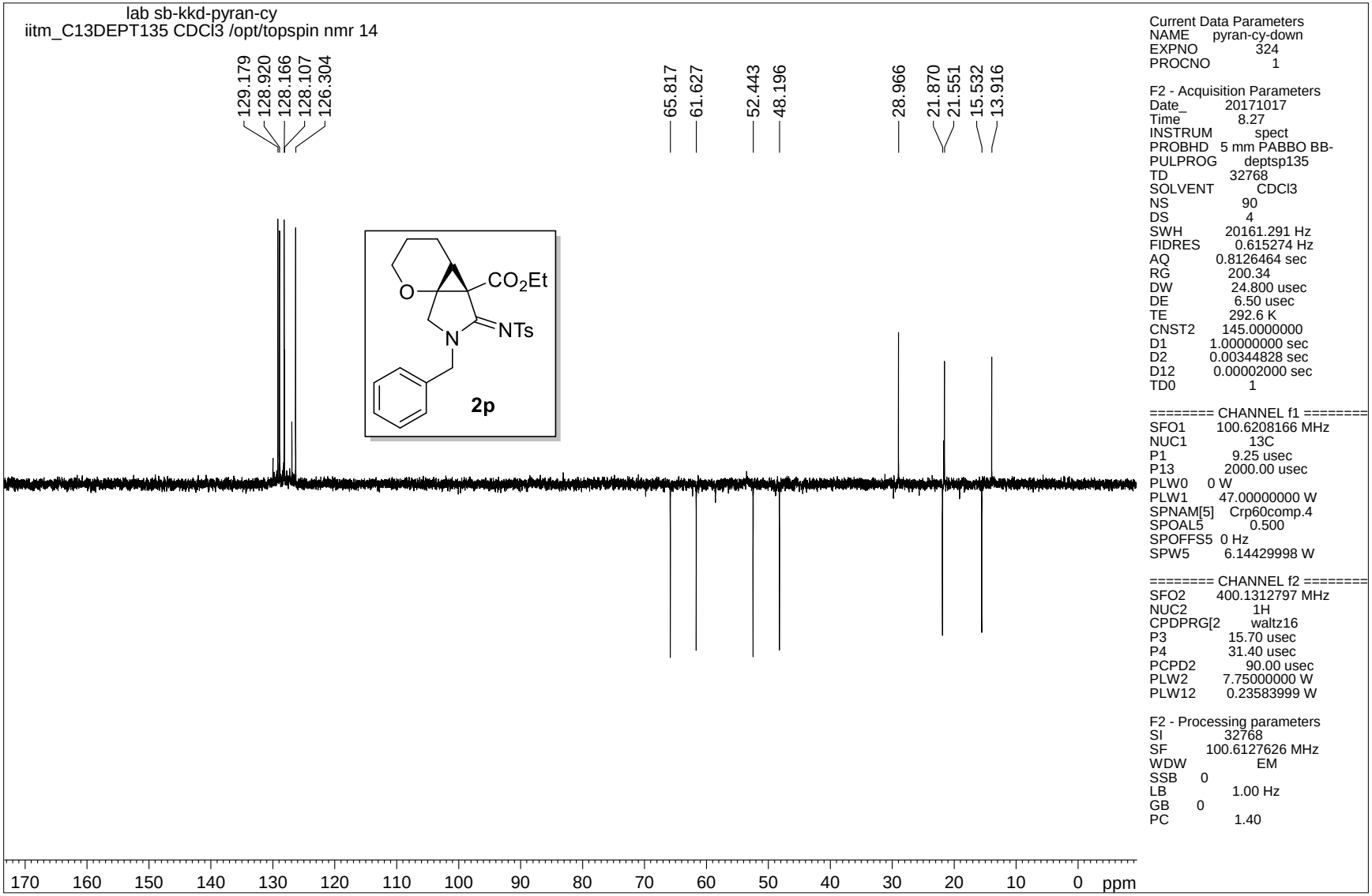
^{1}H NMR spectrum of compound 2p



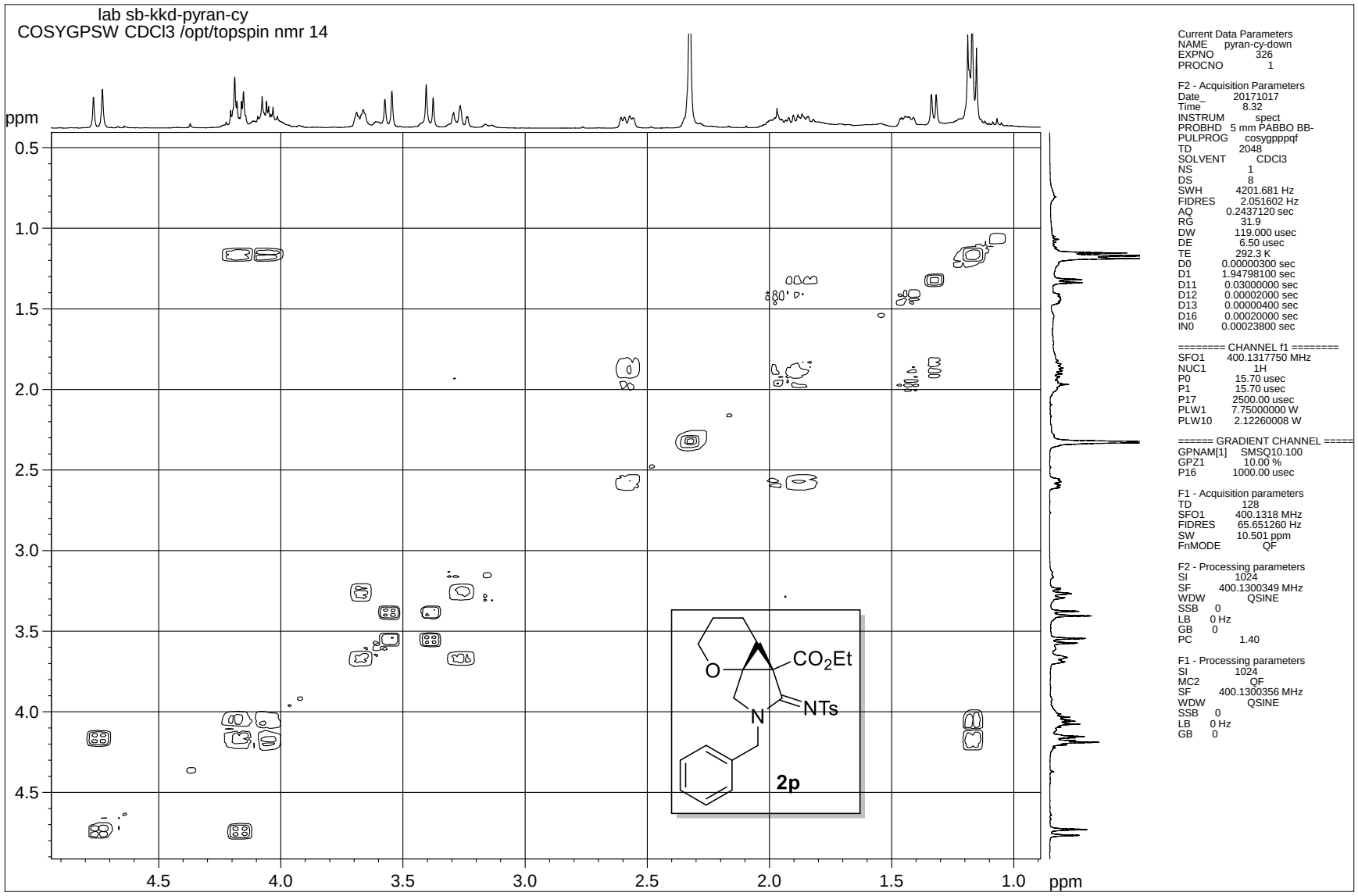
^{1}H NMR spectrum of compound 2p



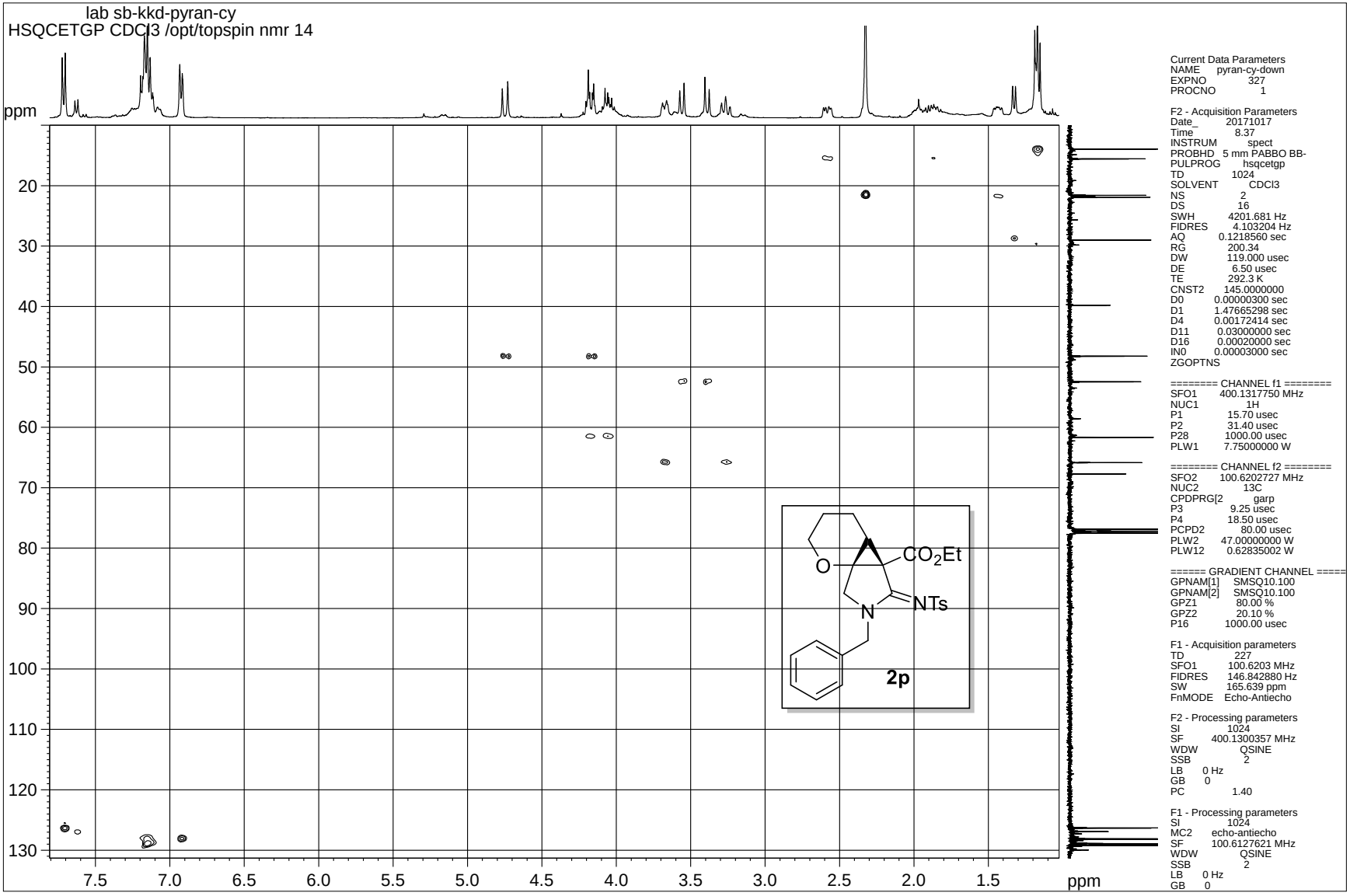
^{13}C NMR spectrum of compound 2p



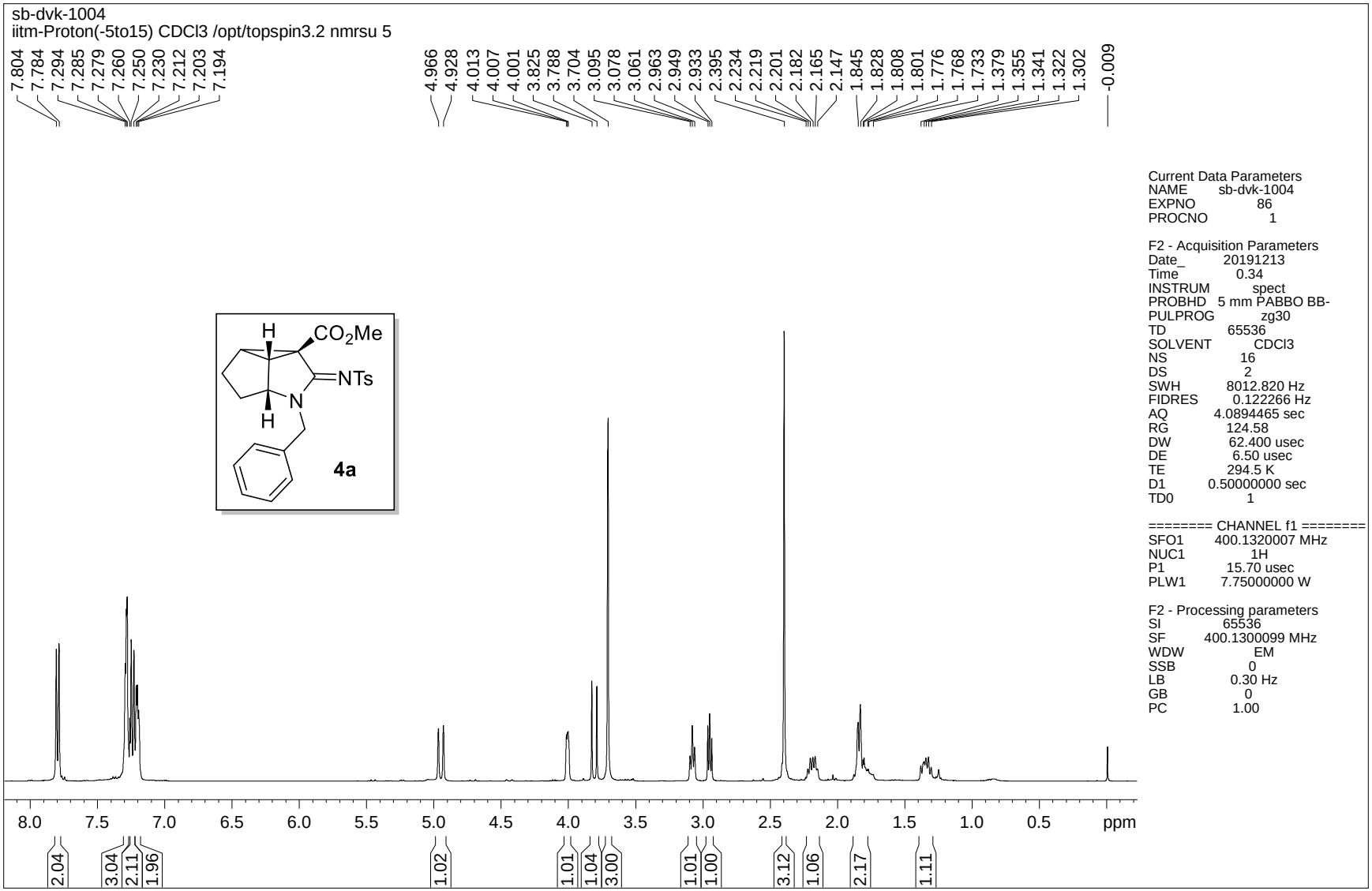
DEPT-135 NMR spectrum of compound 2p



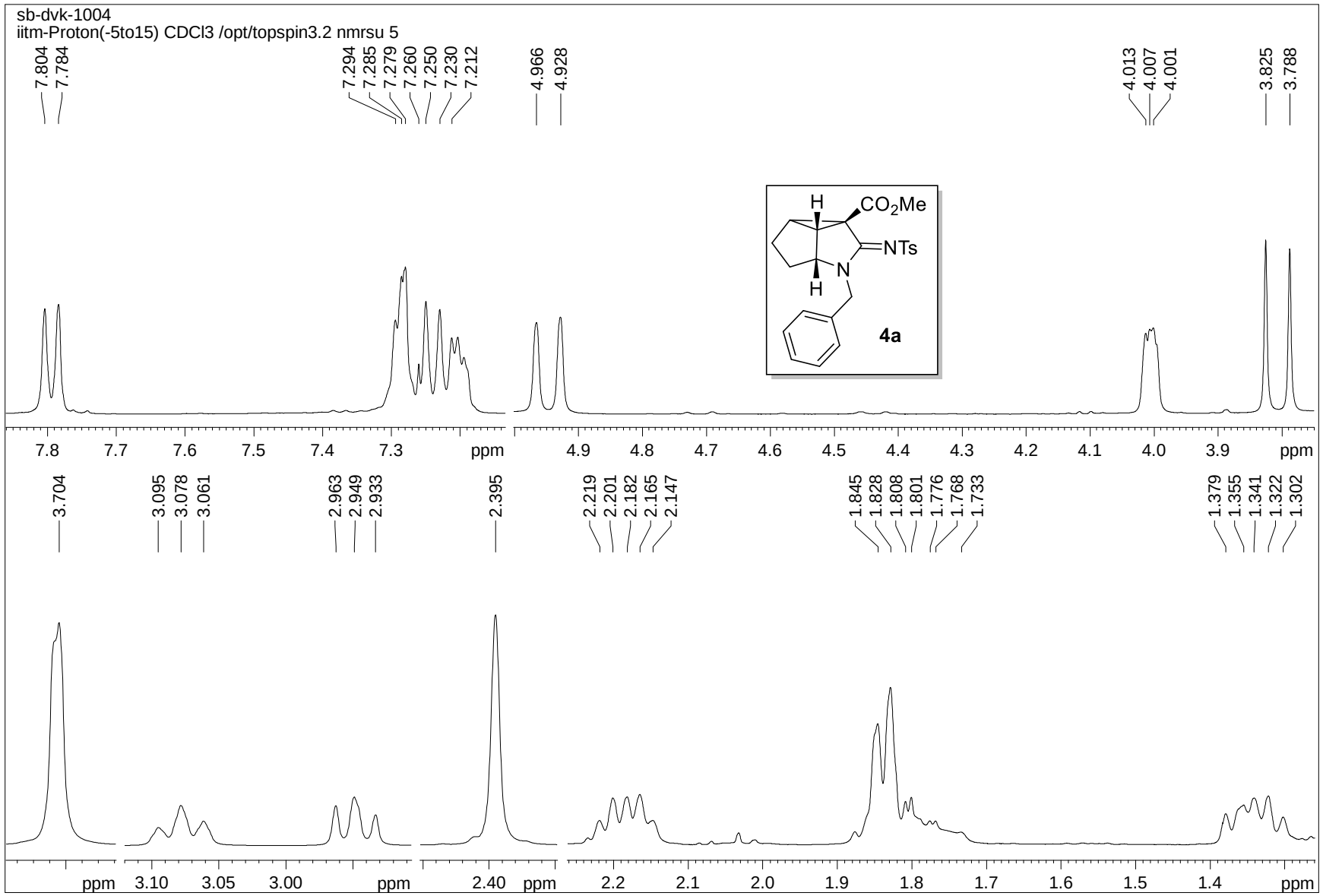
^{1}H-^{1}H COSY NMR spectrum of compound 2p



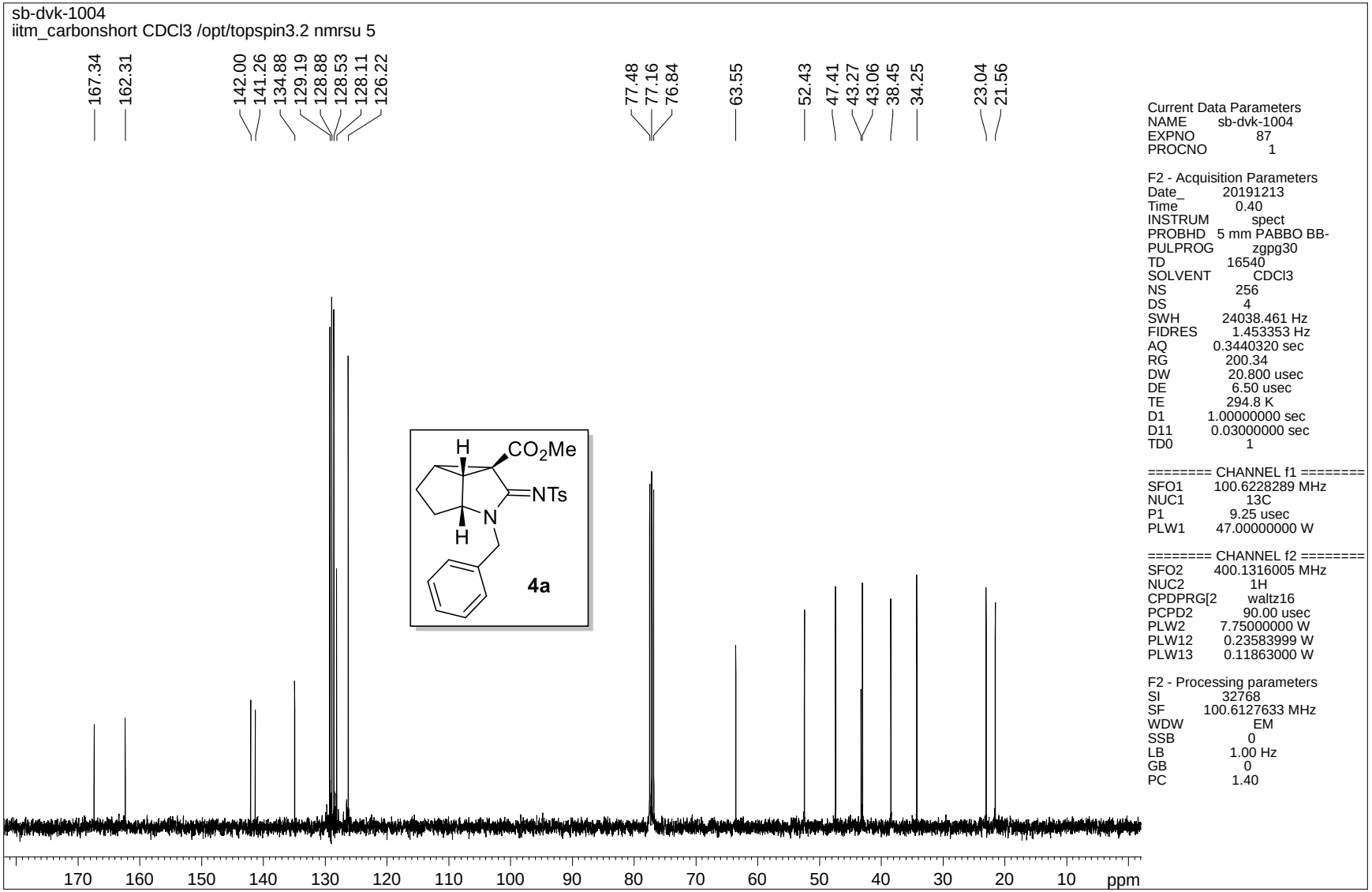
^{1}H-^{13}C HSQC NMR spectrum of compound 2p



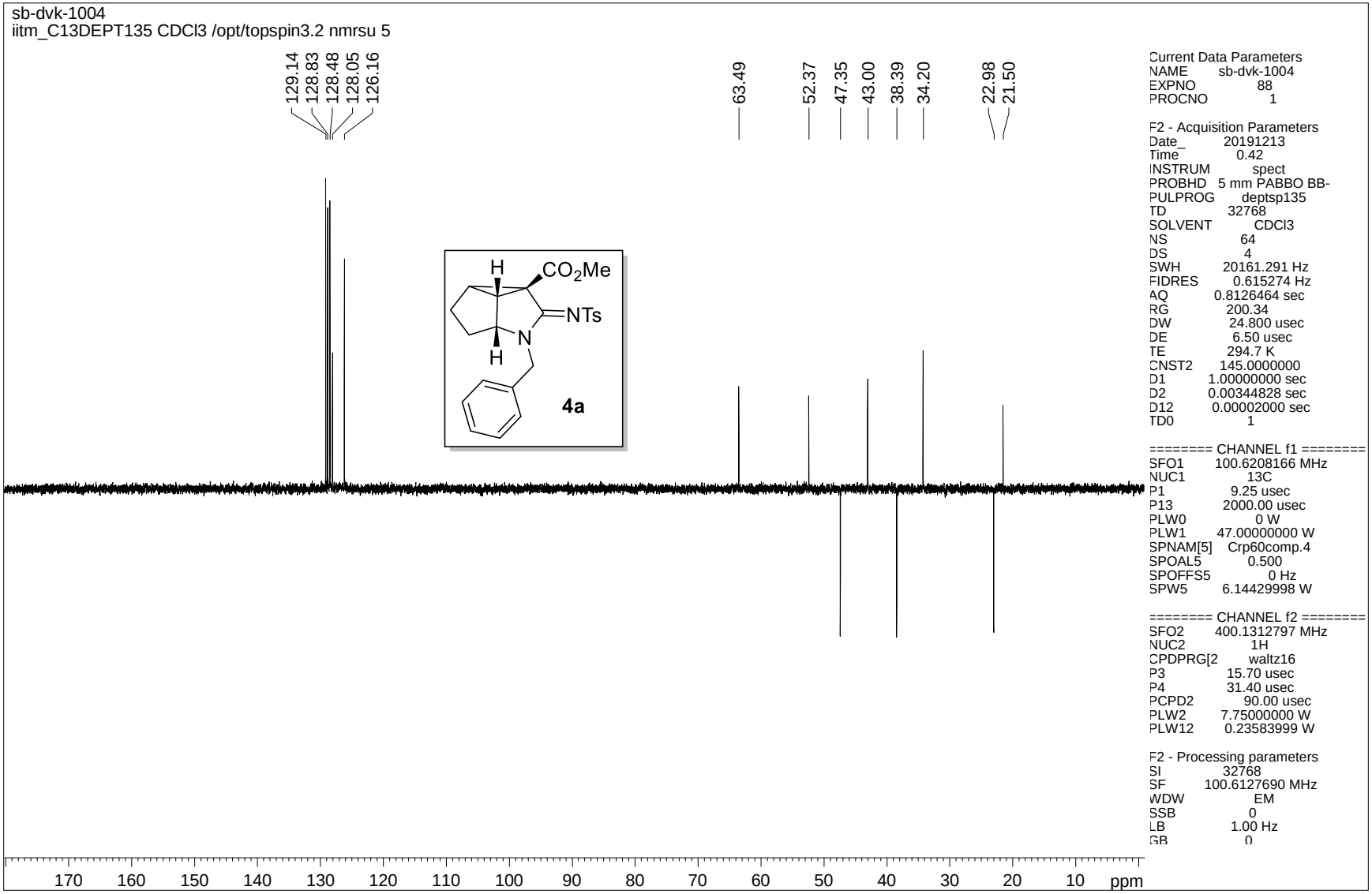
^{1}H NMR spectrum of compound 4a



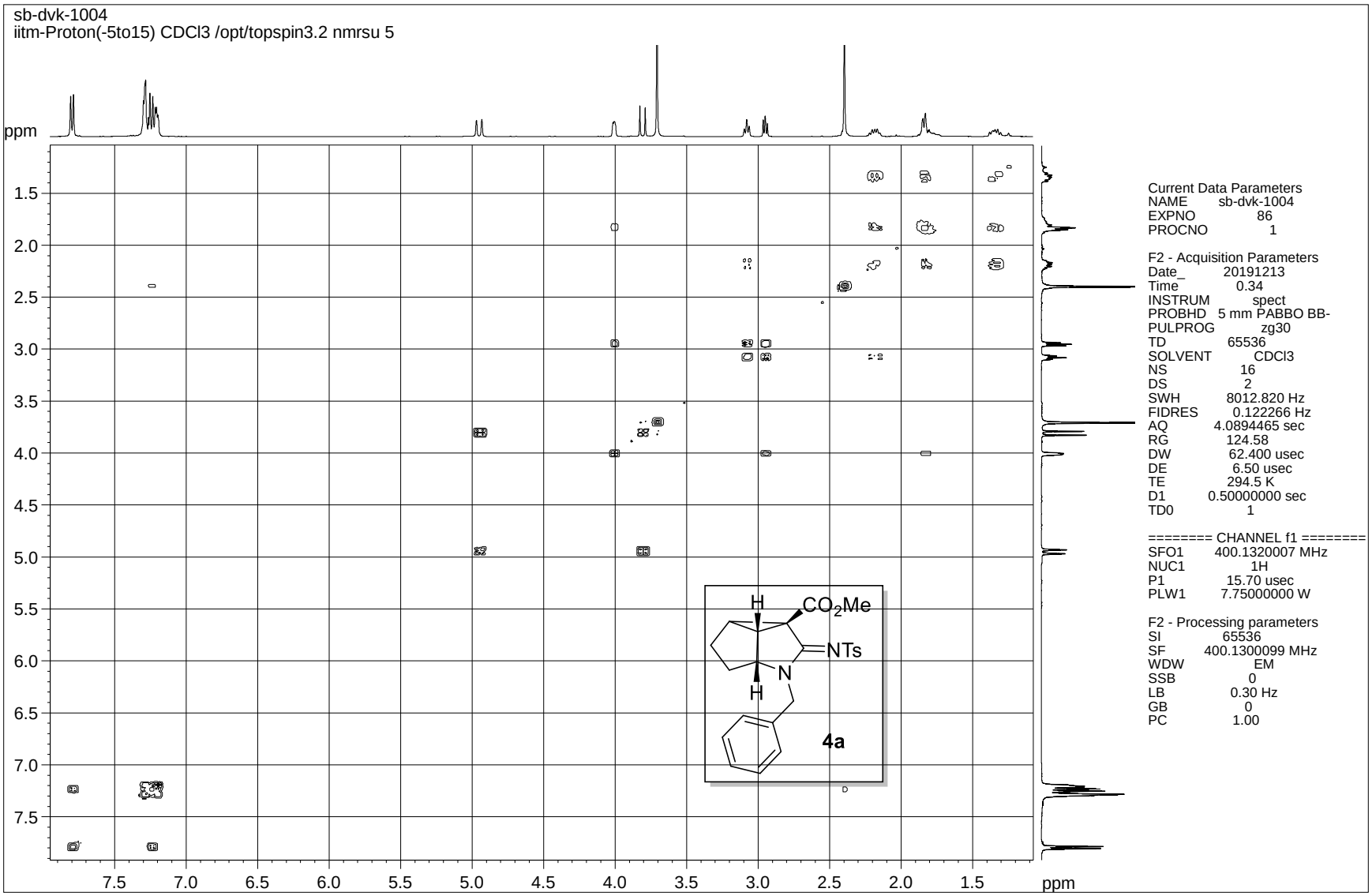
^{1}H NMR spectrum of compound 4a



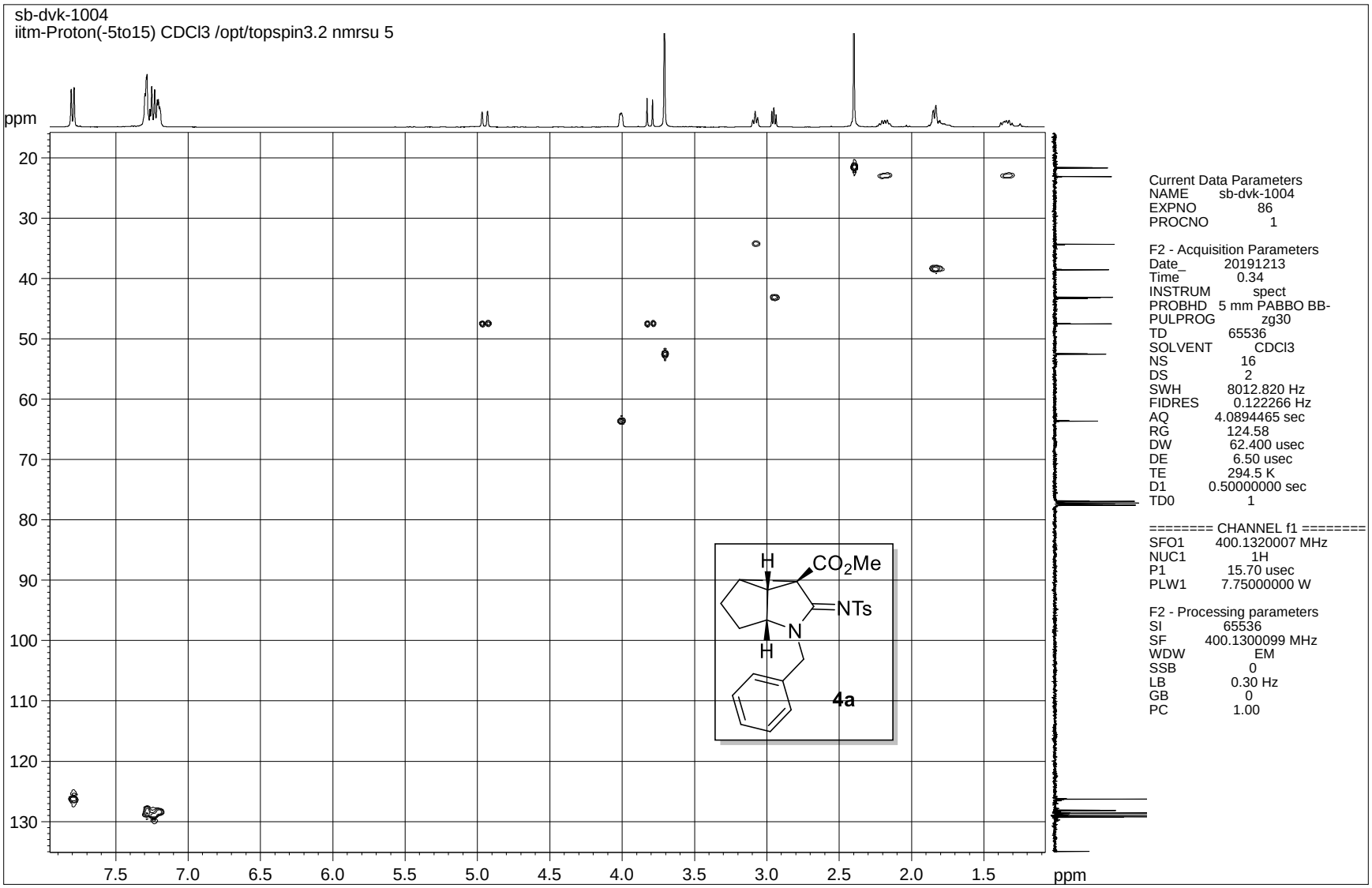
^{13}C NMR spectrum of compound 4a



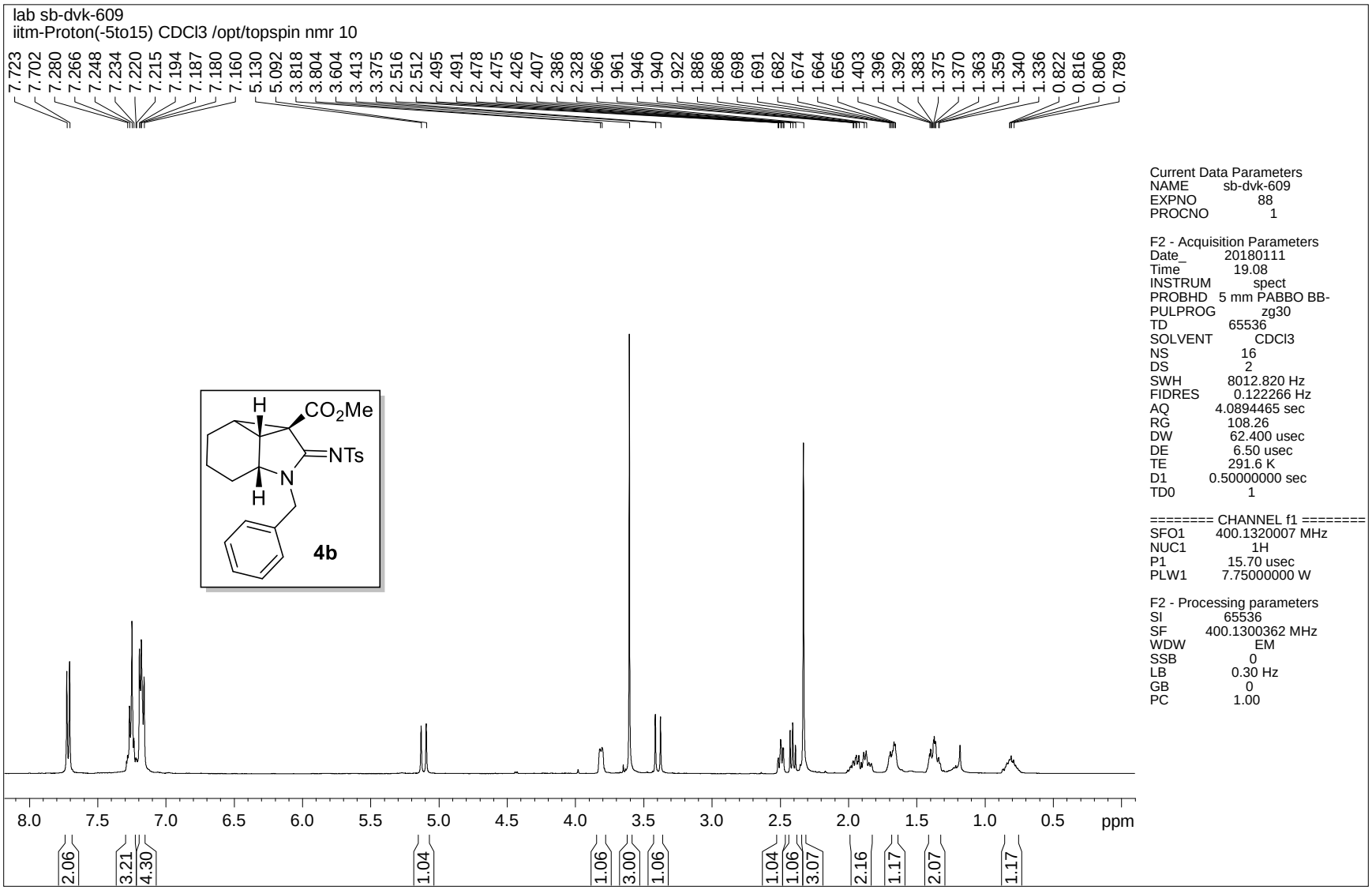
DEPT-135 NMR spectrum of compound 4a



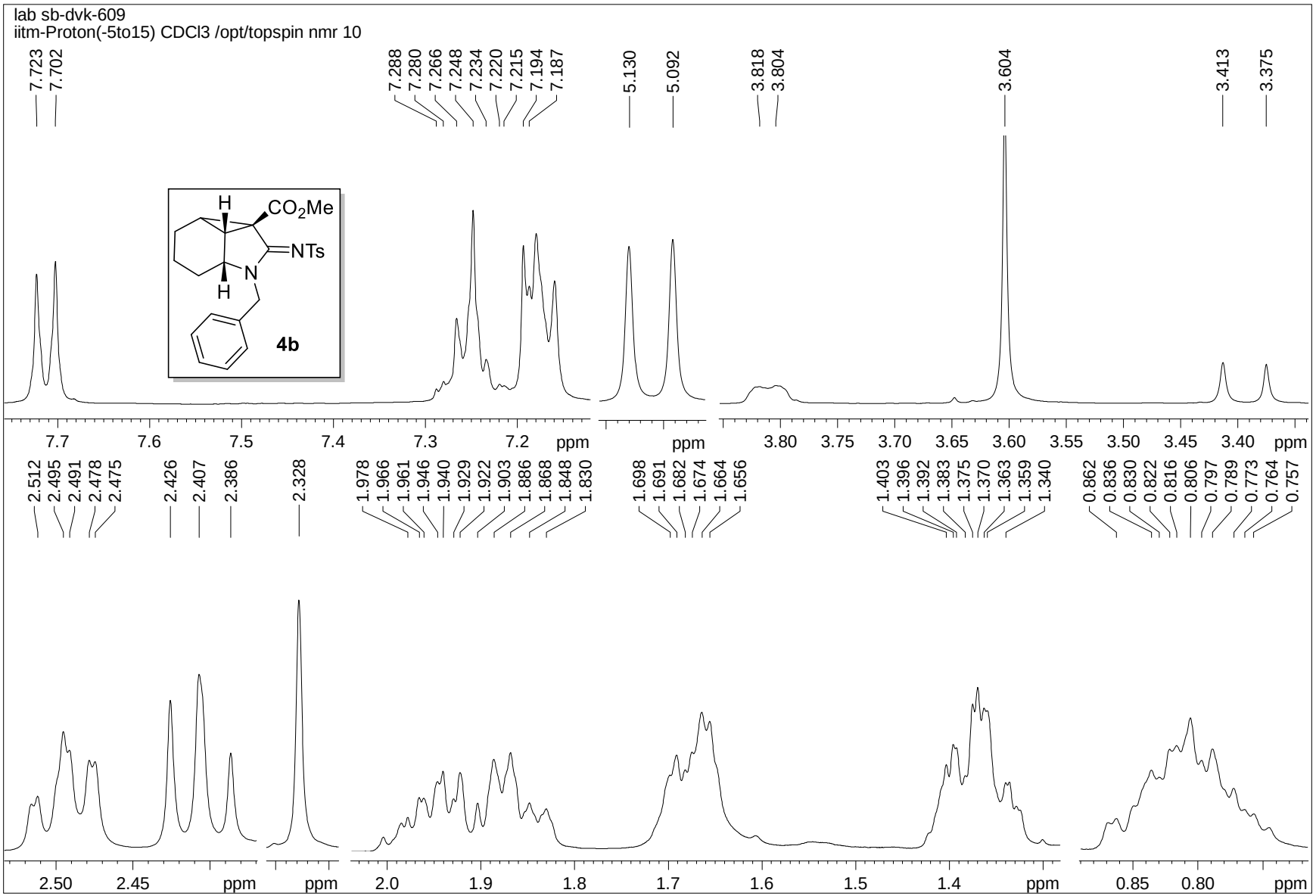
^{1}H-^{1}H COSY NMR spectrum of compound 4a



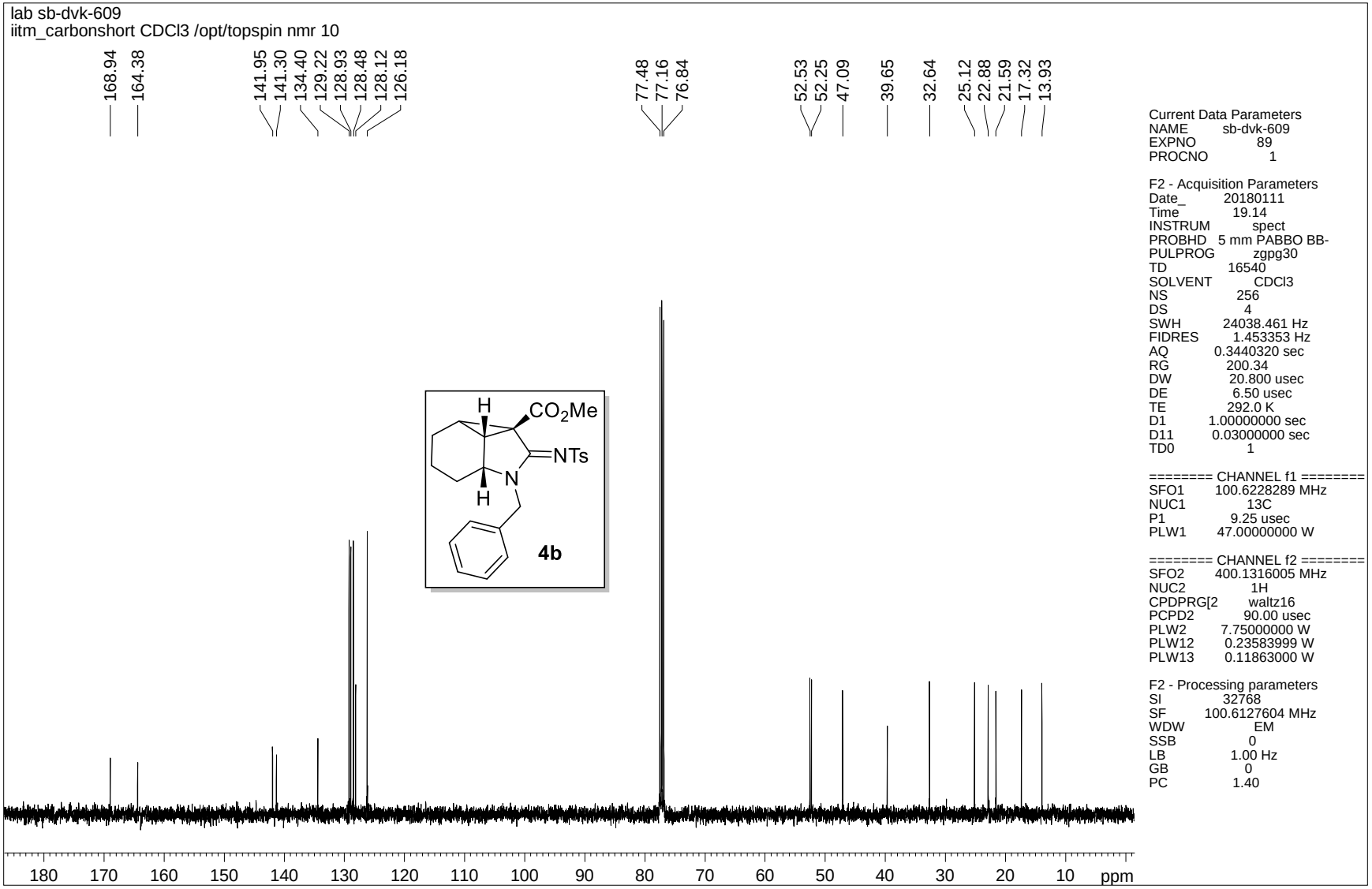
^{1}H-^{13}C HSQC NMR spectrum of compound 4a



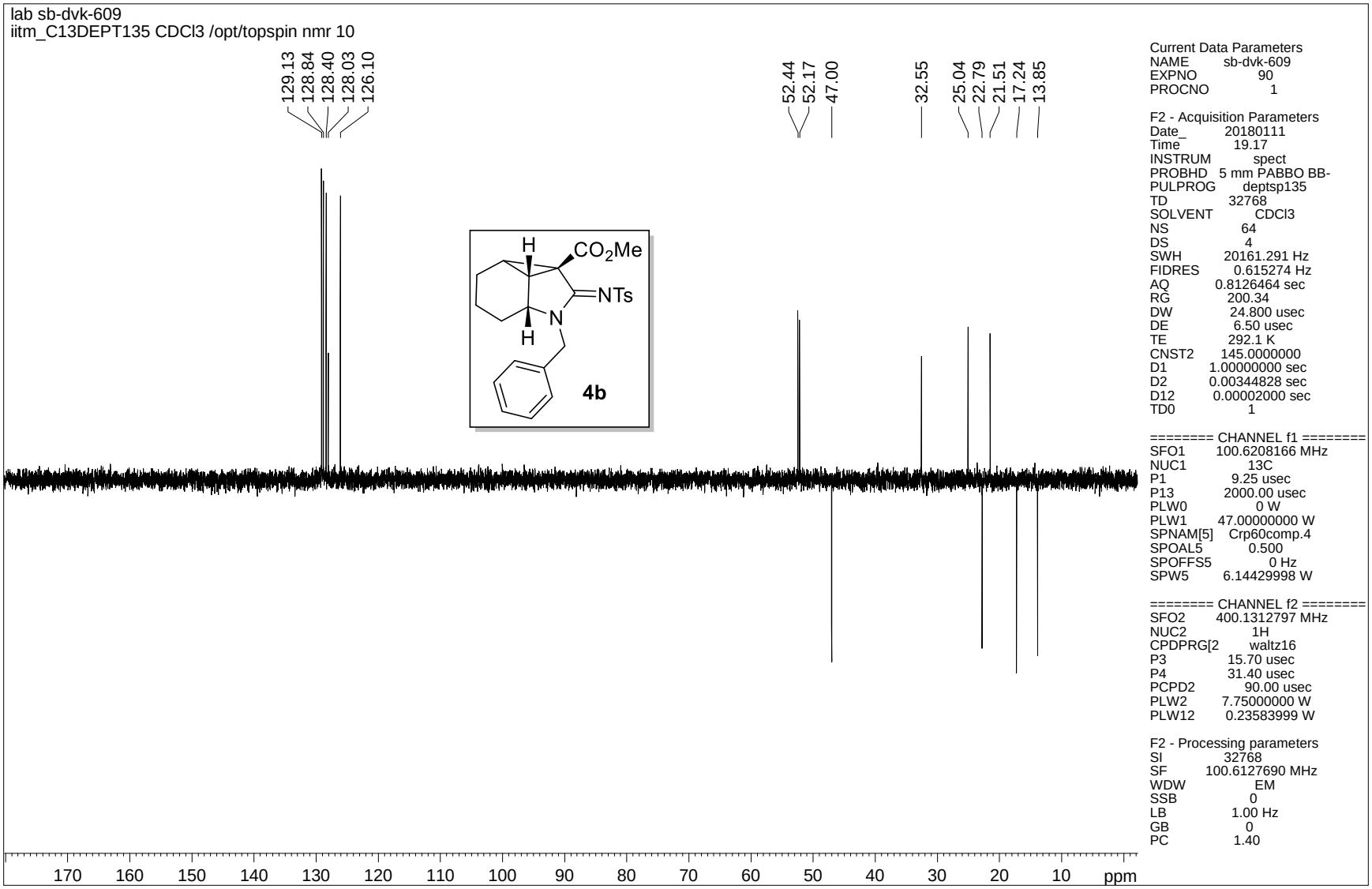
^{1}H NMR spectrum of compound 4b



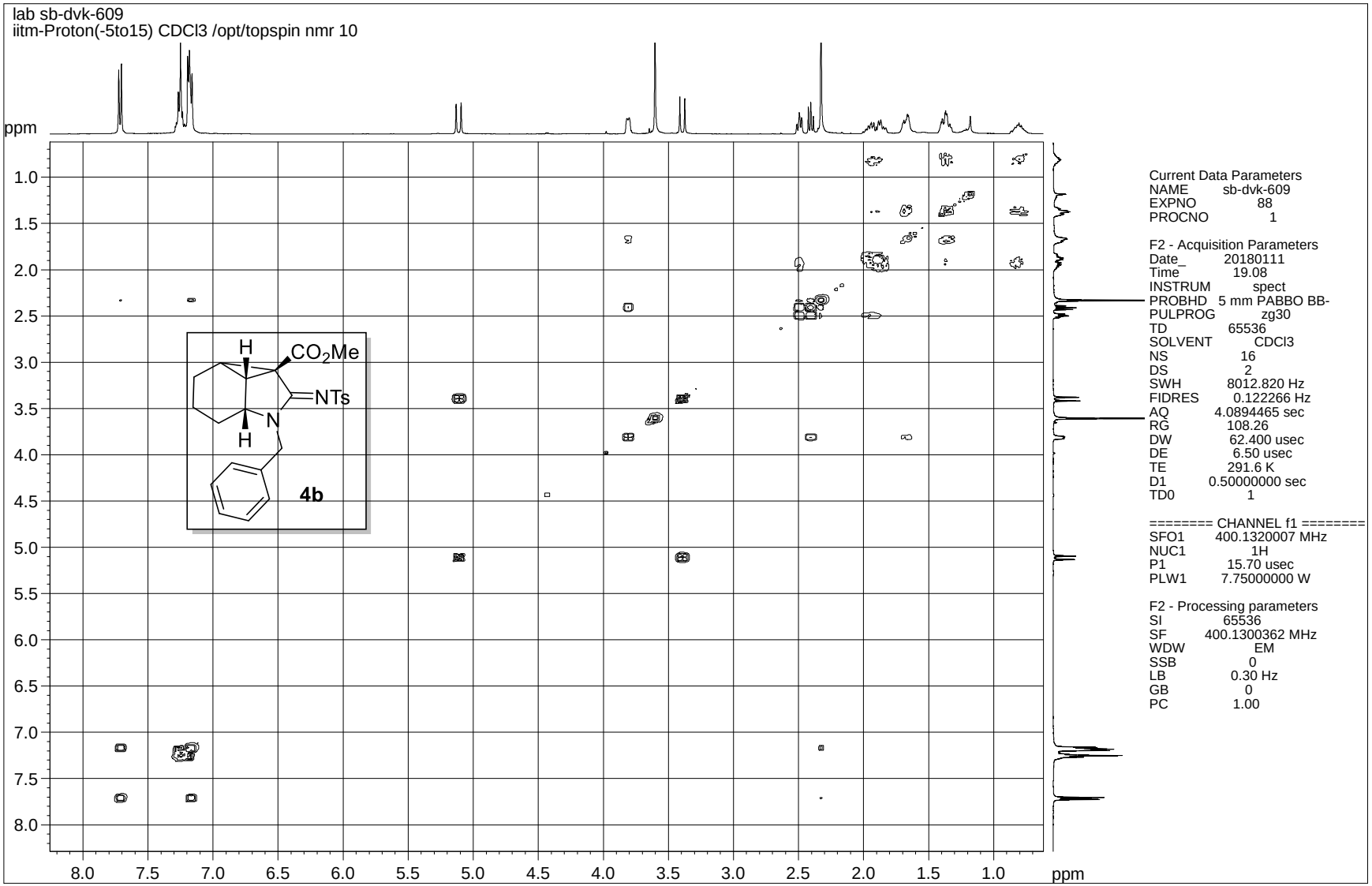
^{1}H NMR spectrum of compound 4b



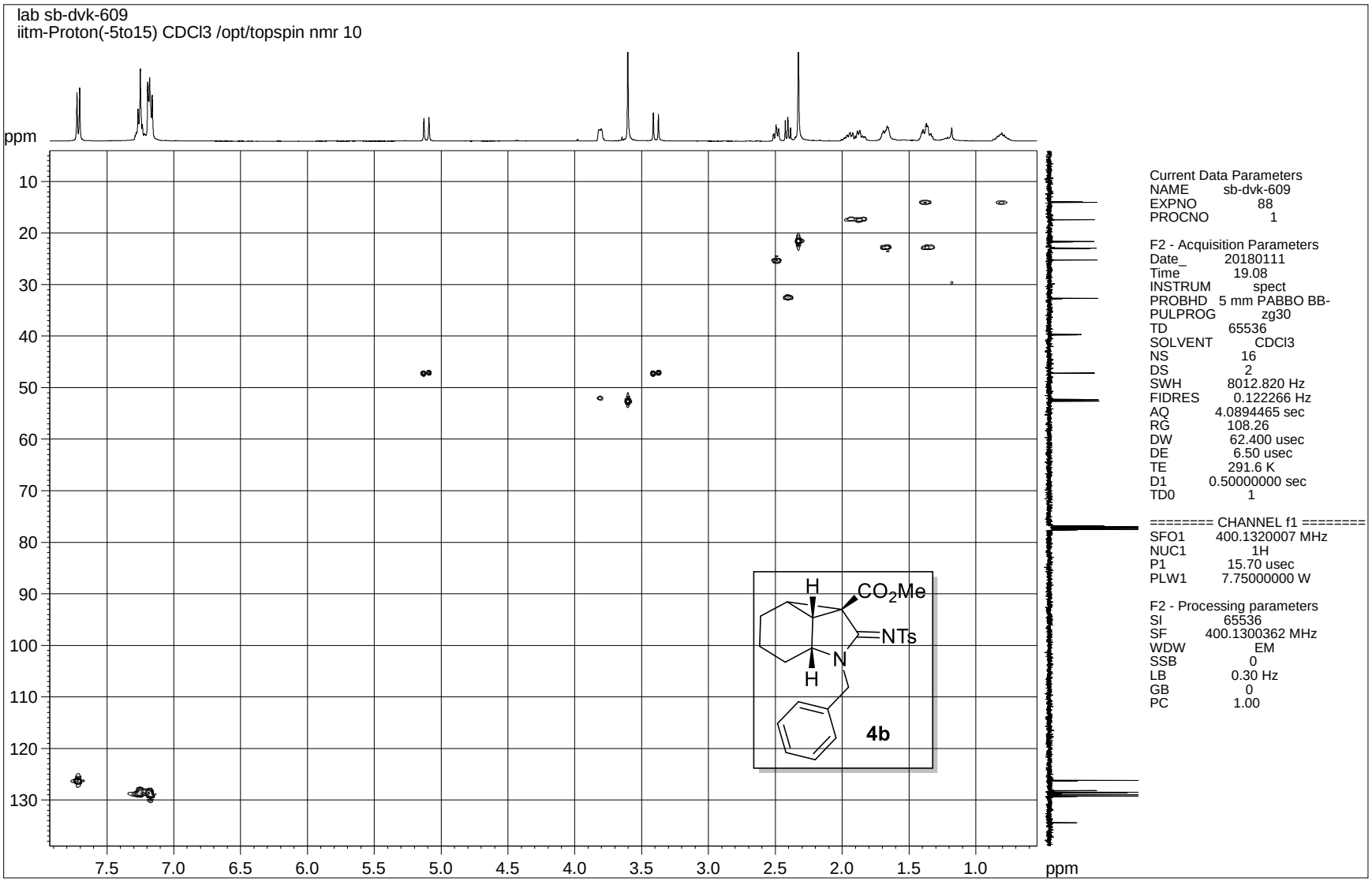
^{13}C NMR spectrum of compound 4b



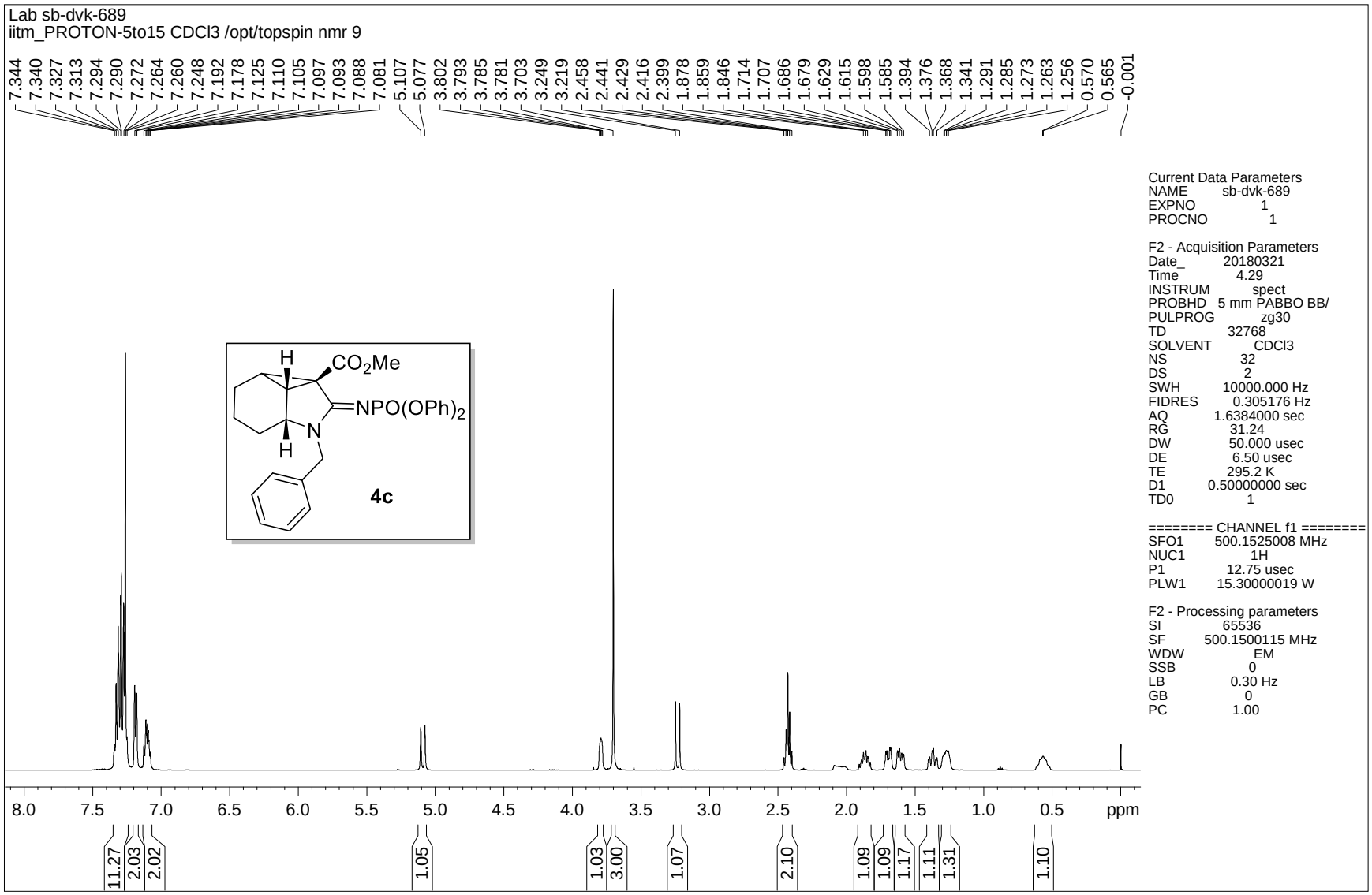
DEPT-135 NMR spectrum of compound 4b



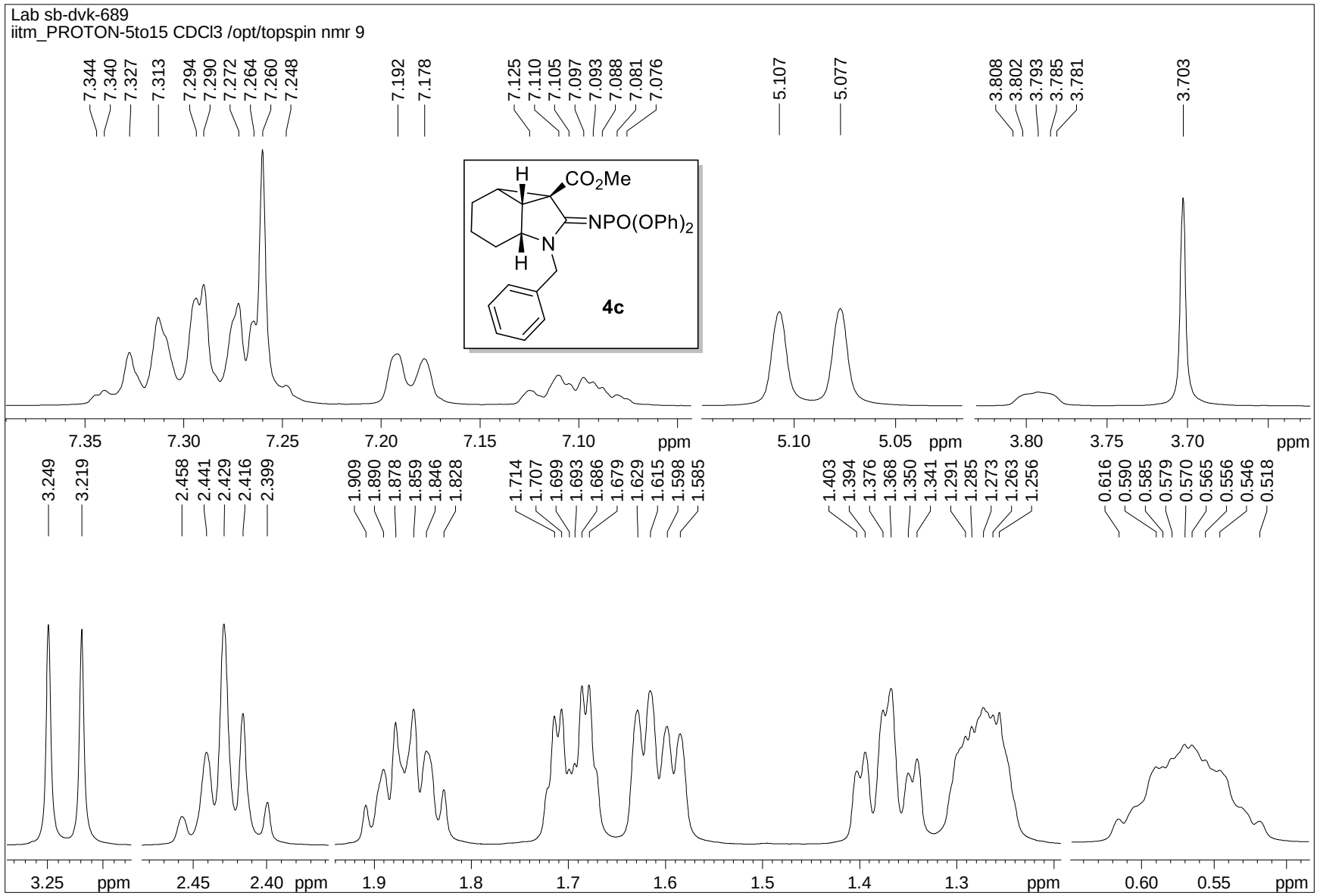
^{1}H-^{1}H COSY NMR spectrum of compound 4b



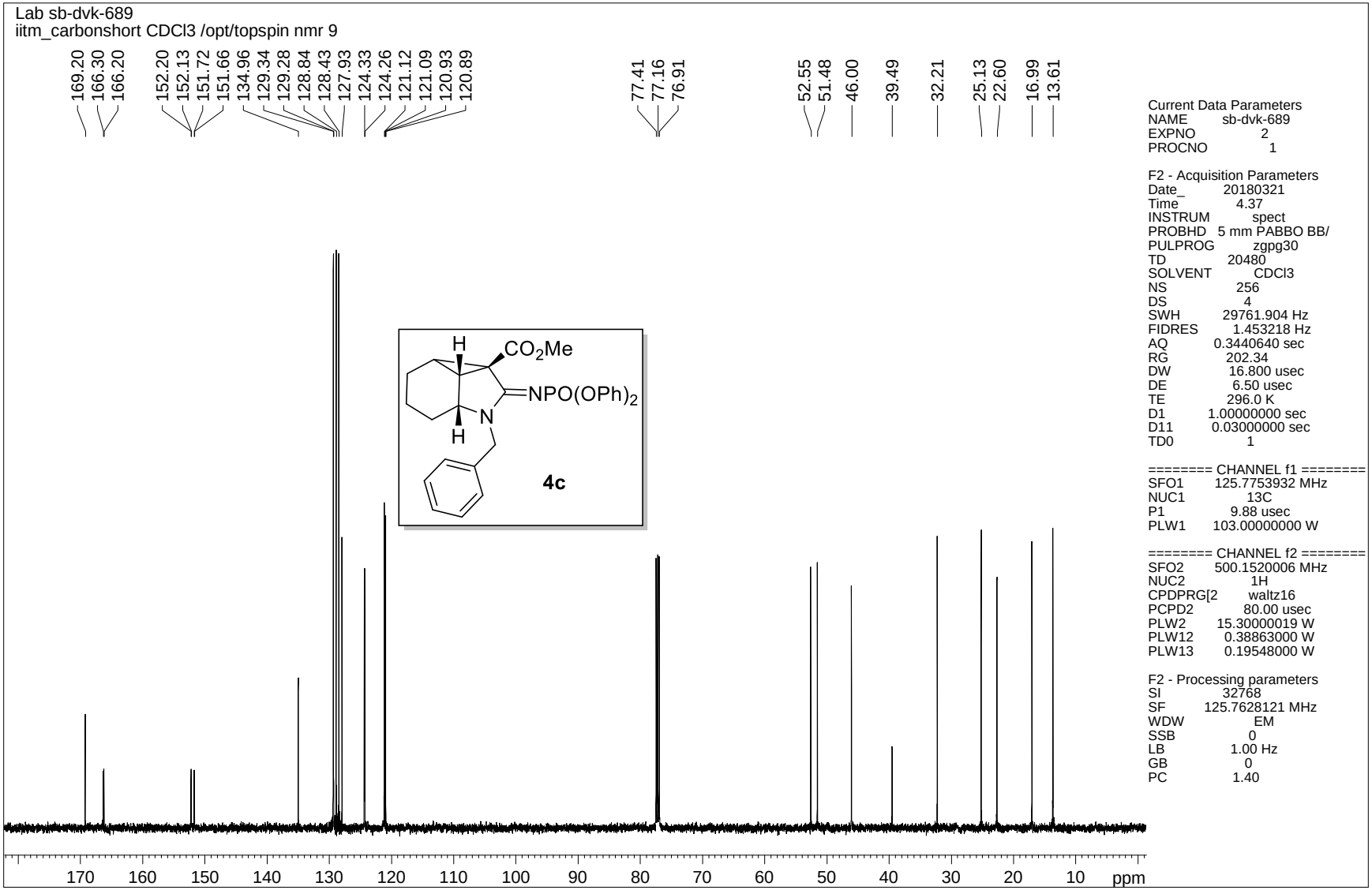
^{1}H-^{13}C HSQC NMR spectrum of compound 4b



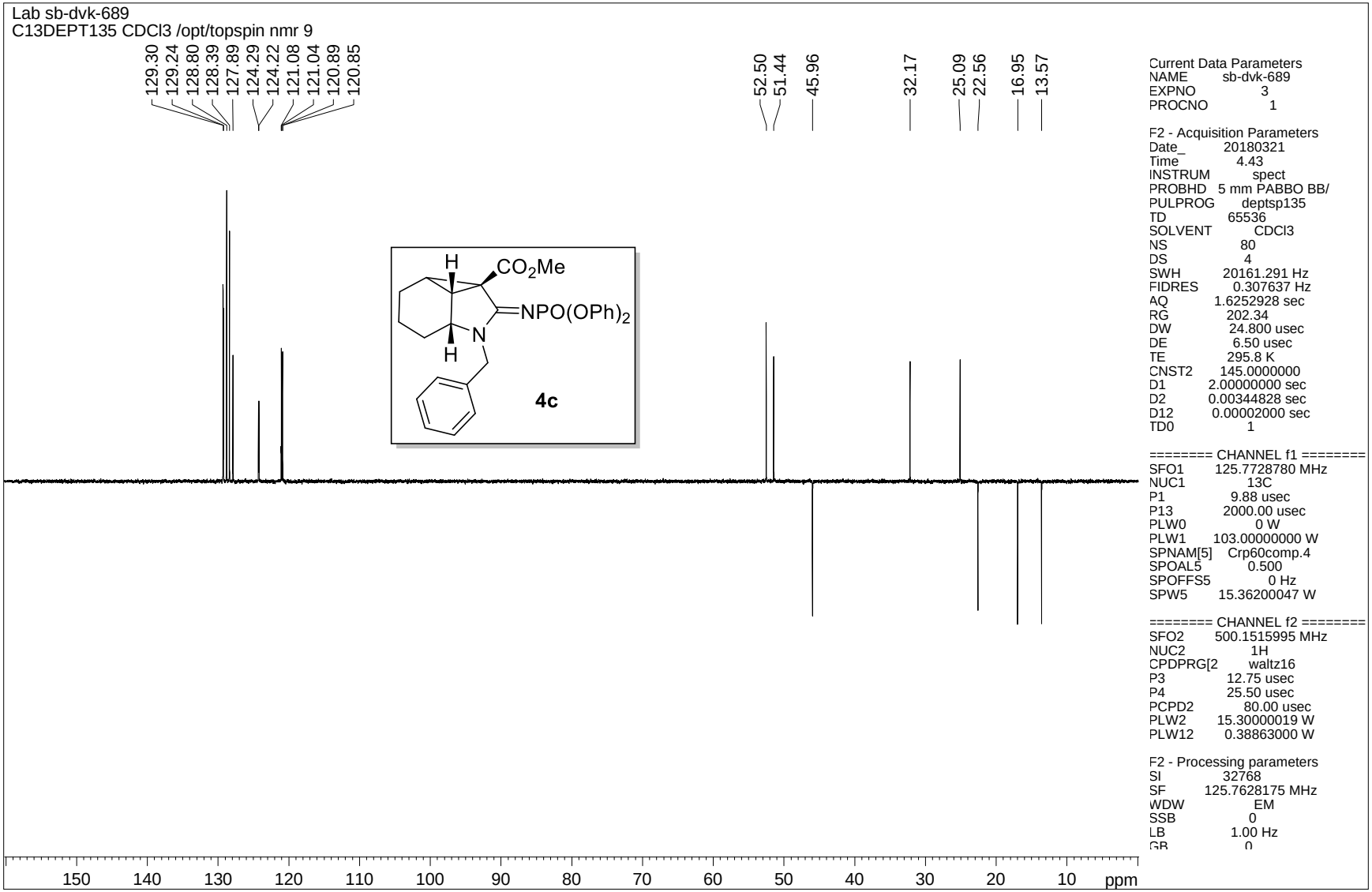
^{1}H NMR spectrum of compound 4c



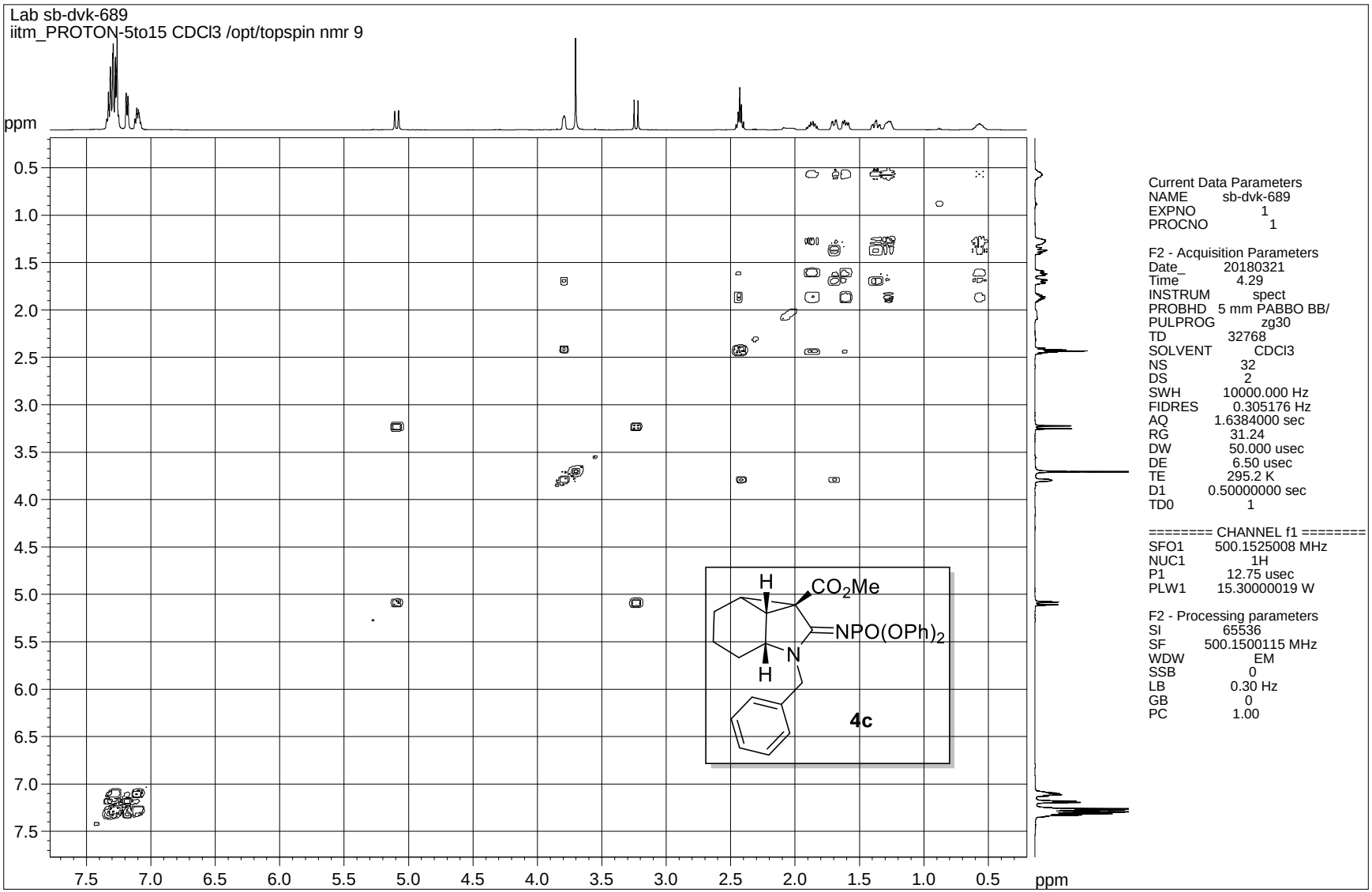
^{1}H NMR spectrum of compound 4c



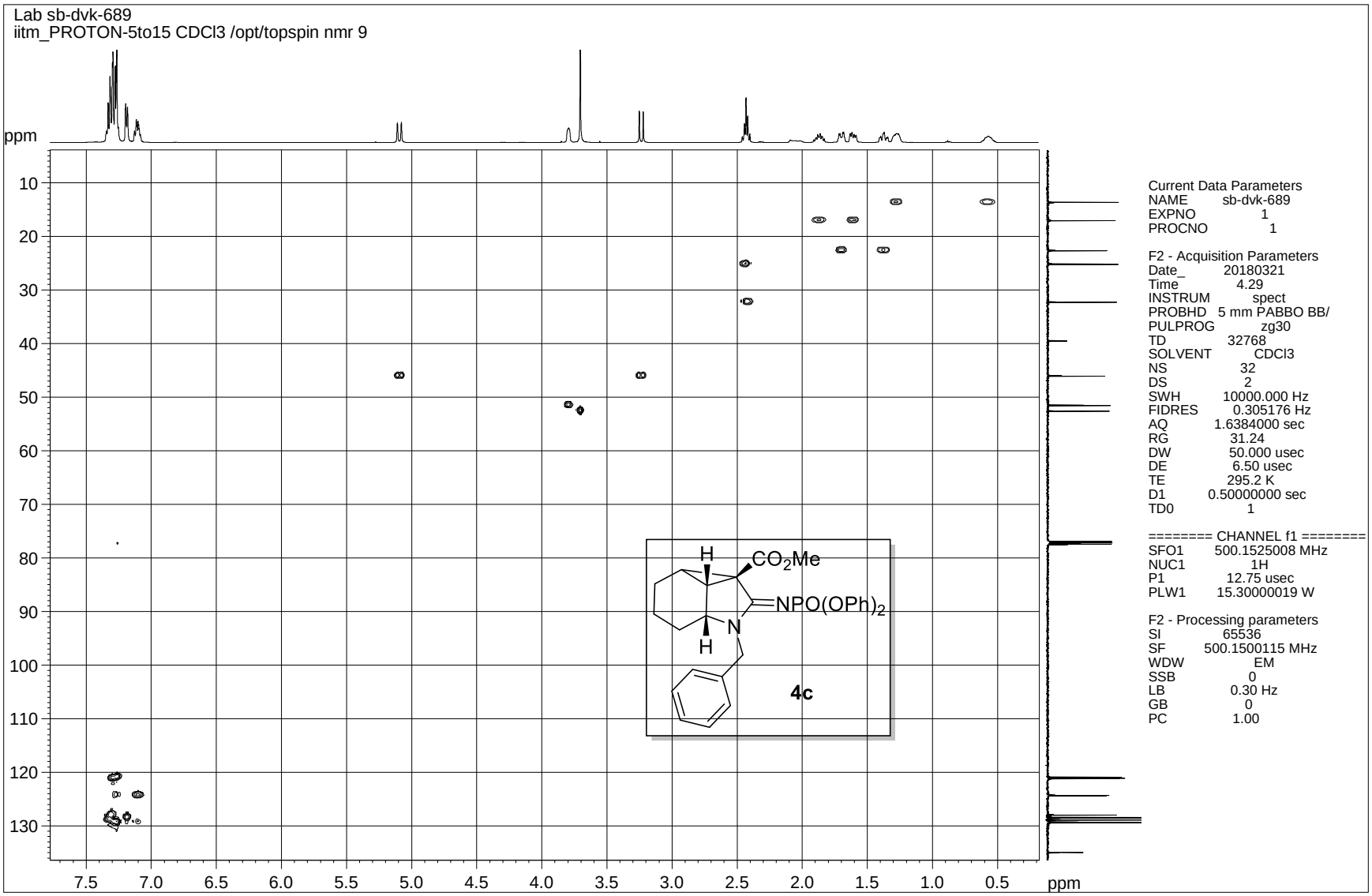
^{13}C NMR spectrum of compound 4c



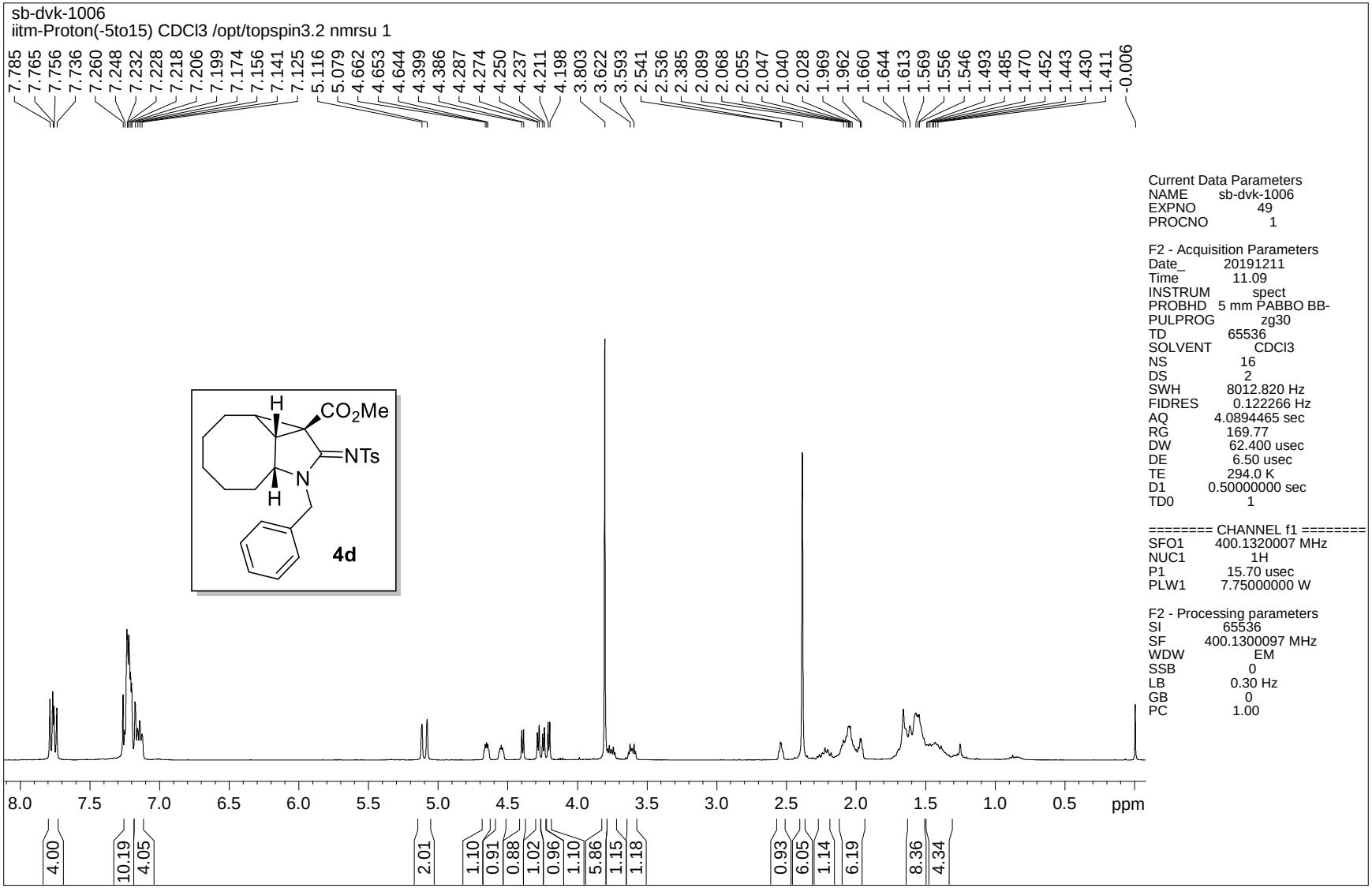
DEPT-135 NMR spectrum of compound 4c



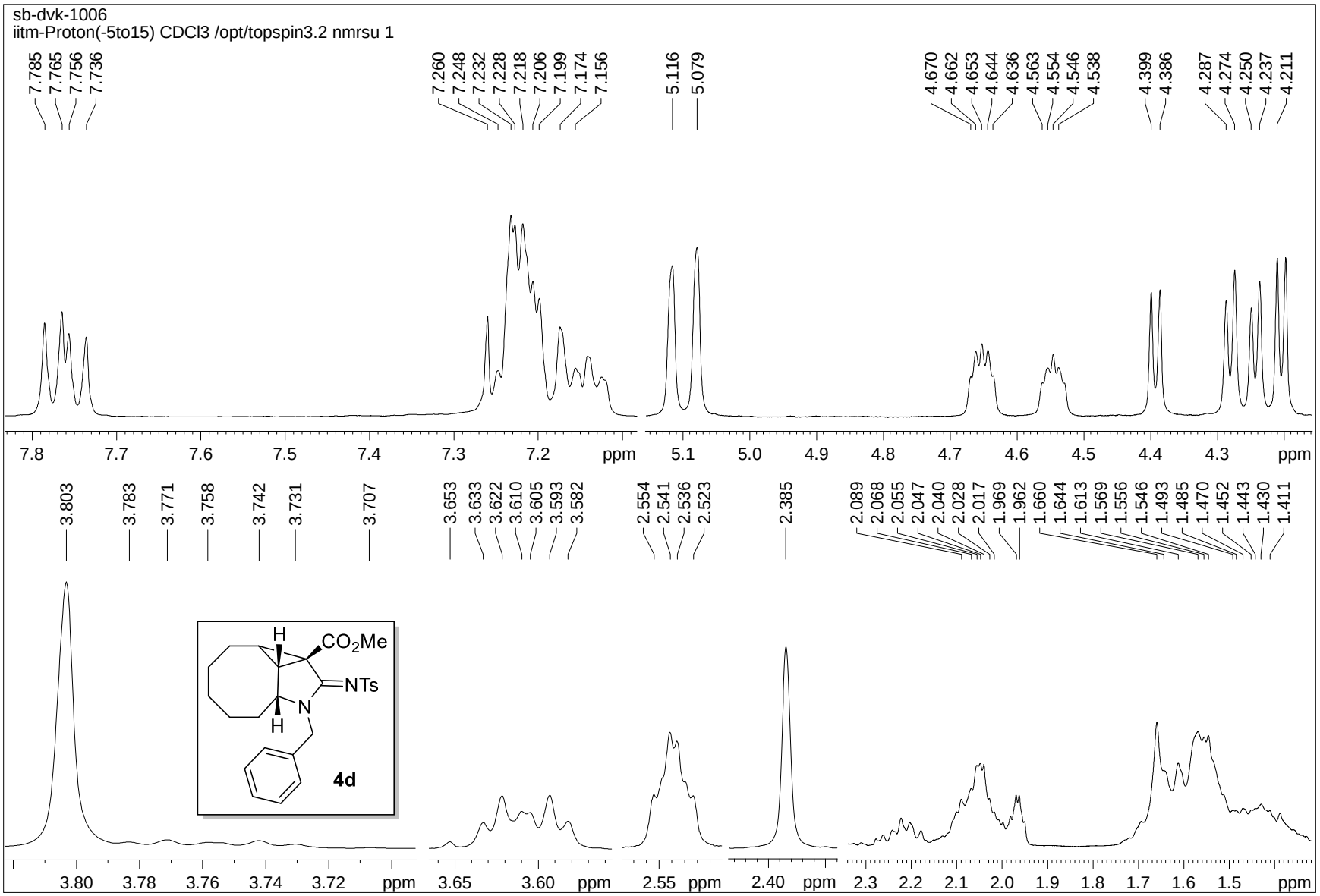
^{1}H-^{1}H COSY NMR spectrum of compound 4c



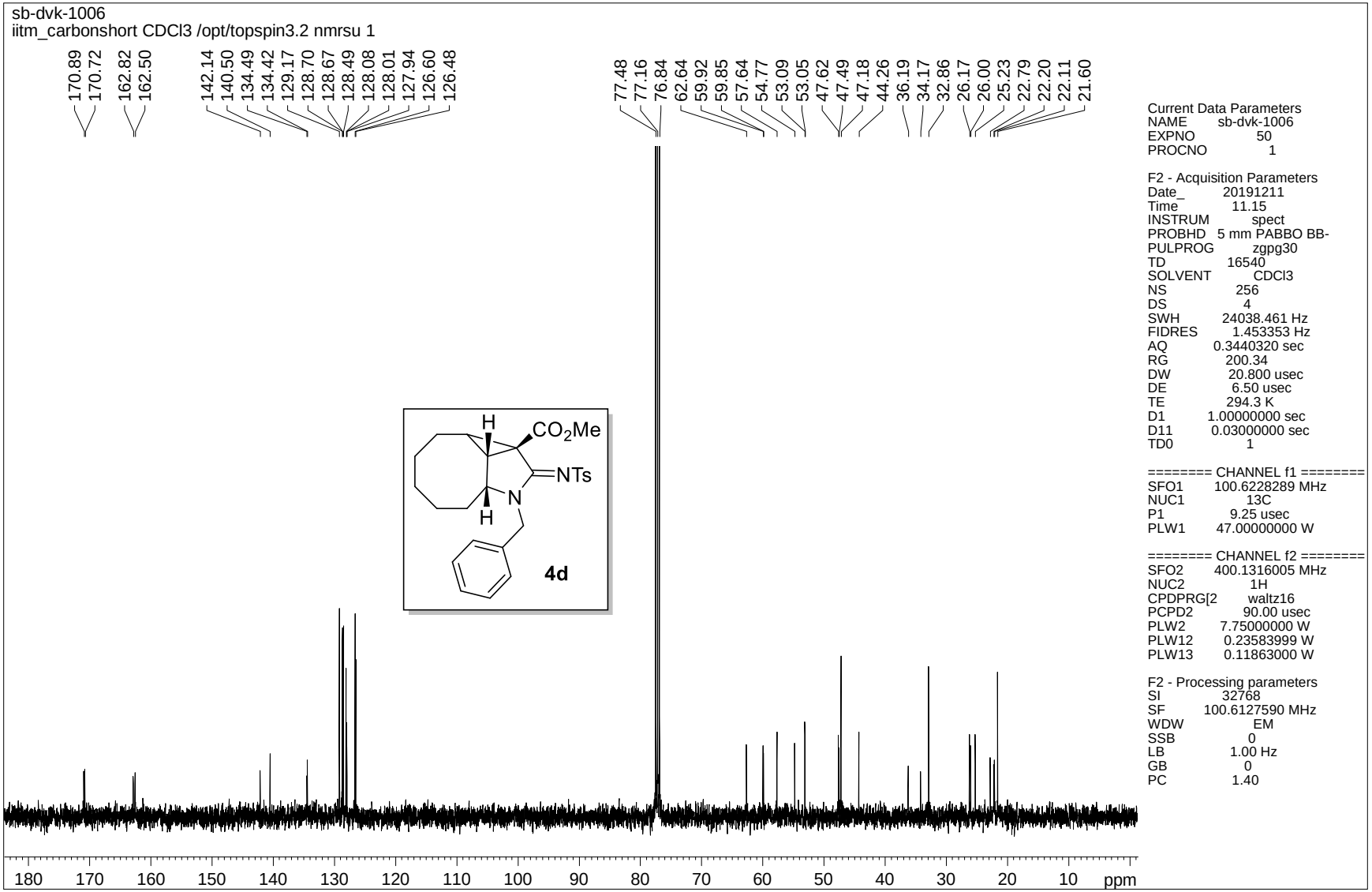
^{1}H-^{13}C HSQC NMR spectrum of compound 4c



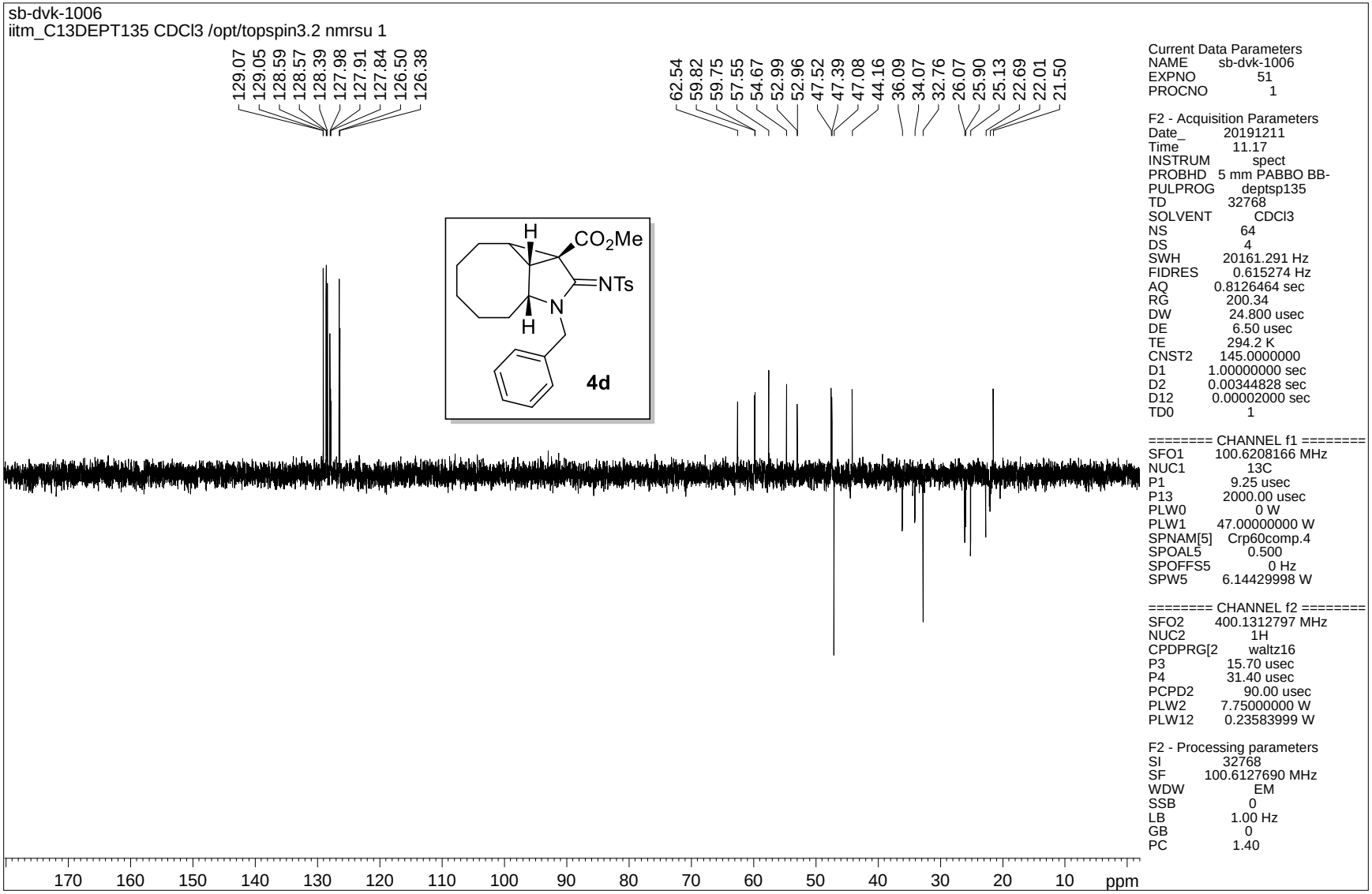
^{1}H NMR spectrum of compound 4d



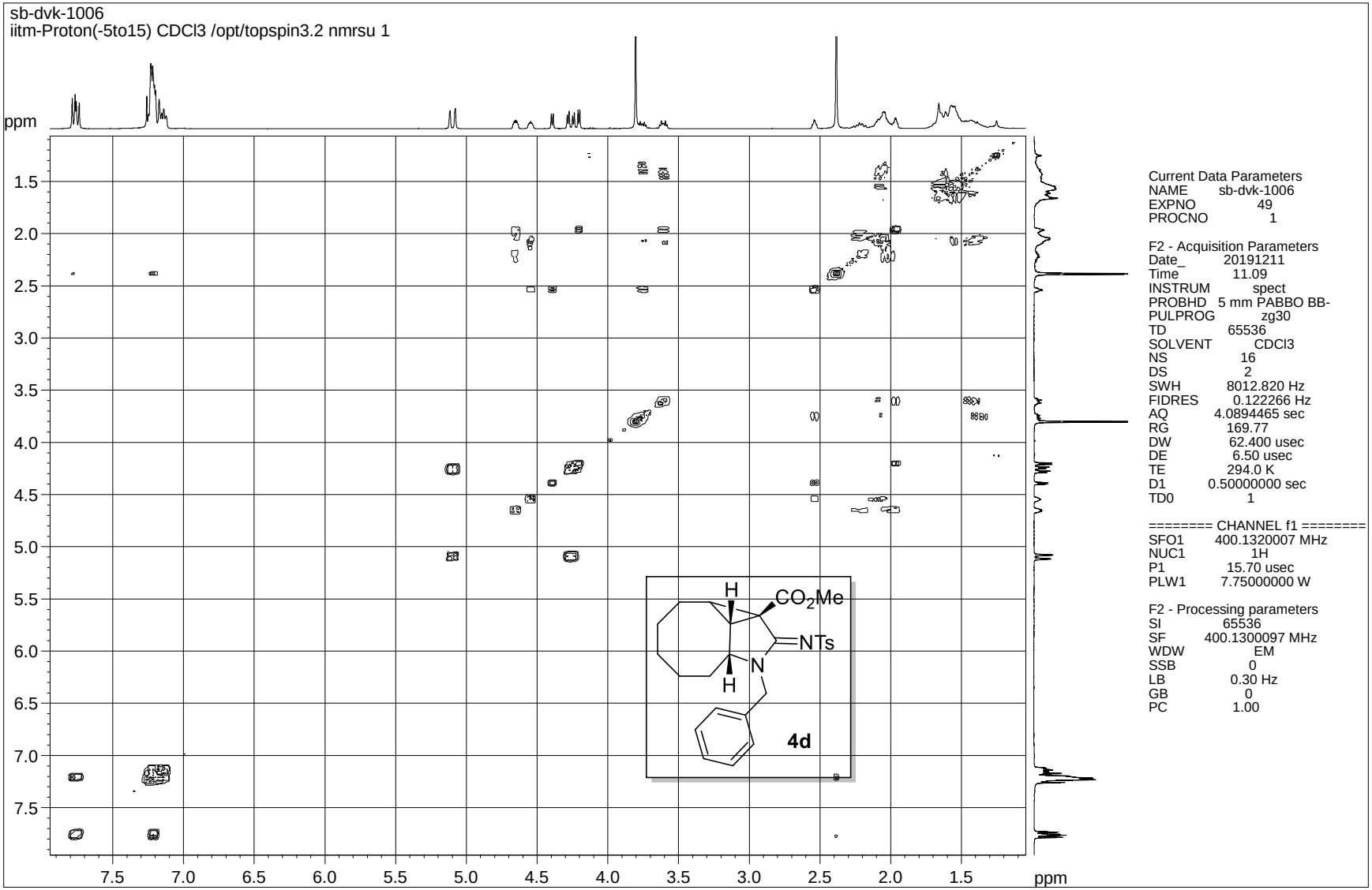
^{1}H NMR spectrum of compound 4d



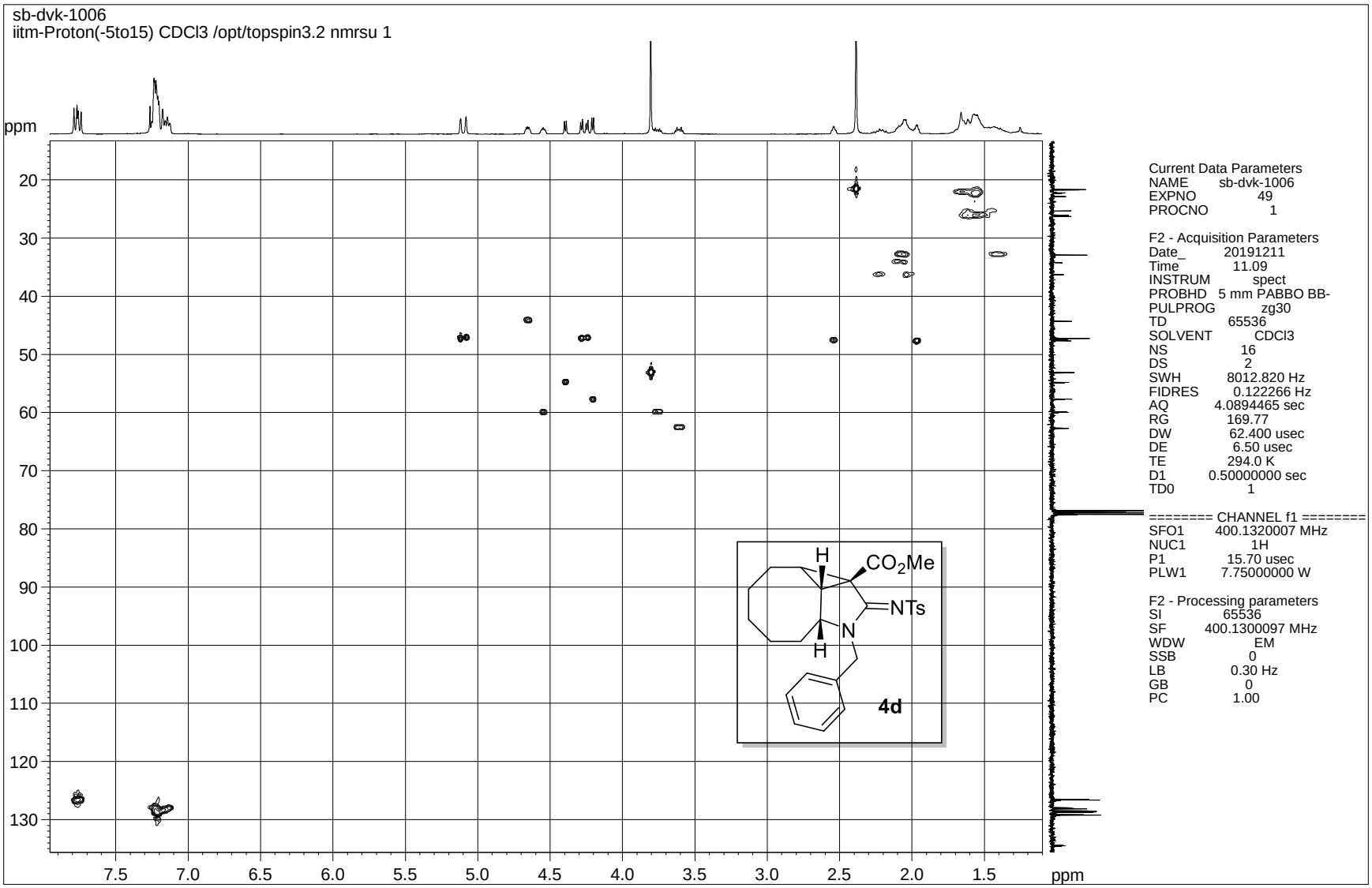
^{13}C NMR spectrum of compound 4d



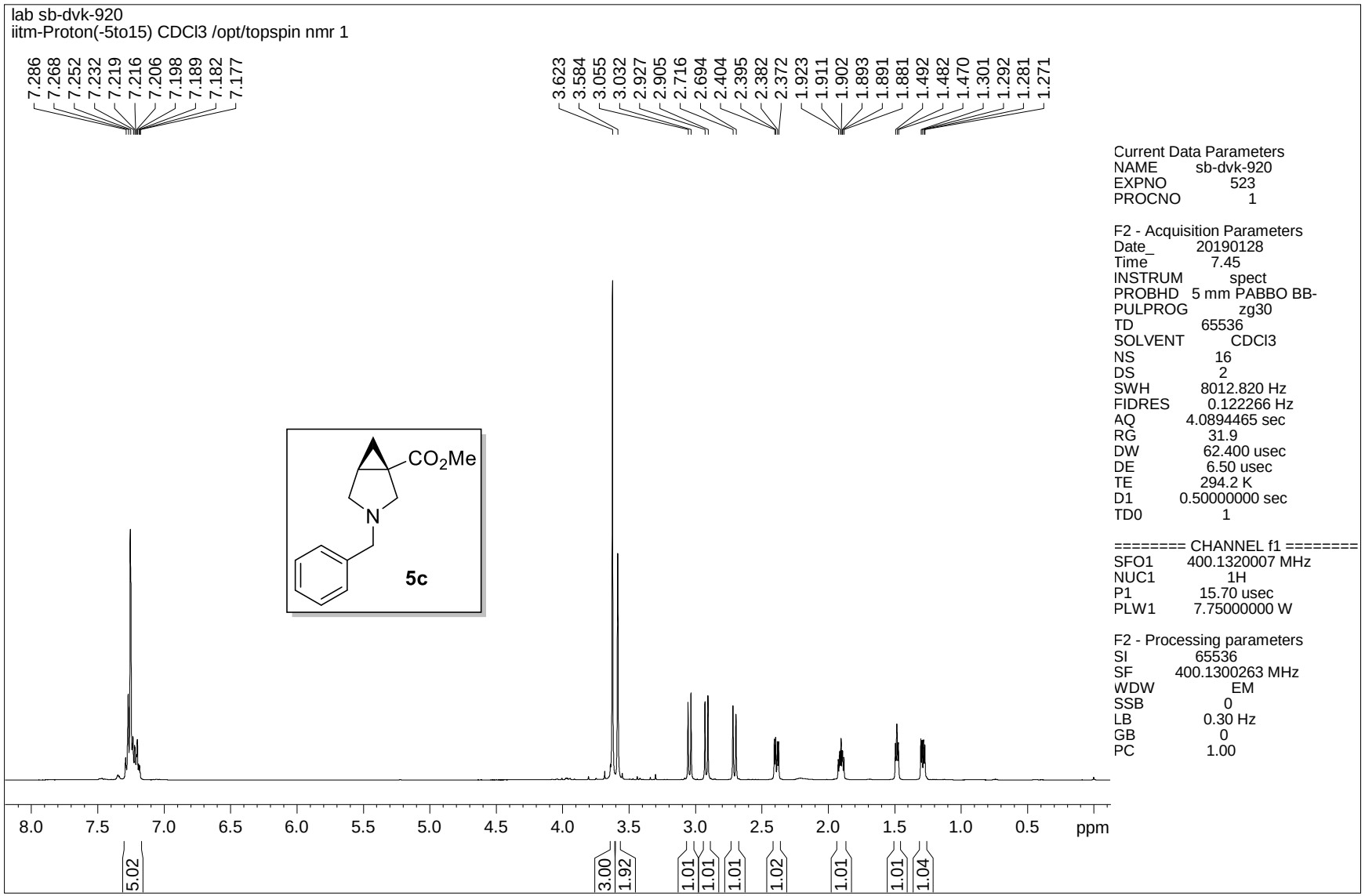
DEPT-135 NMR spectrum of compound 4d



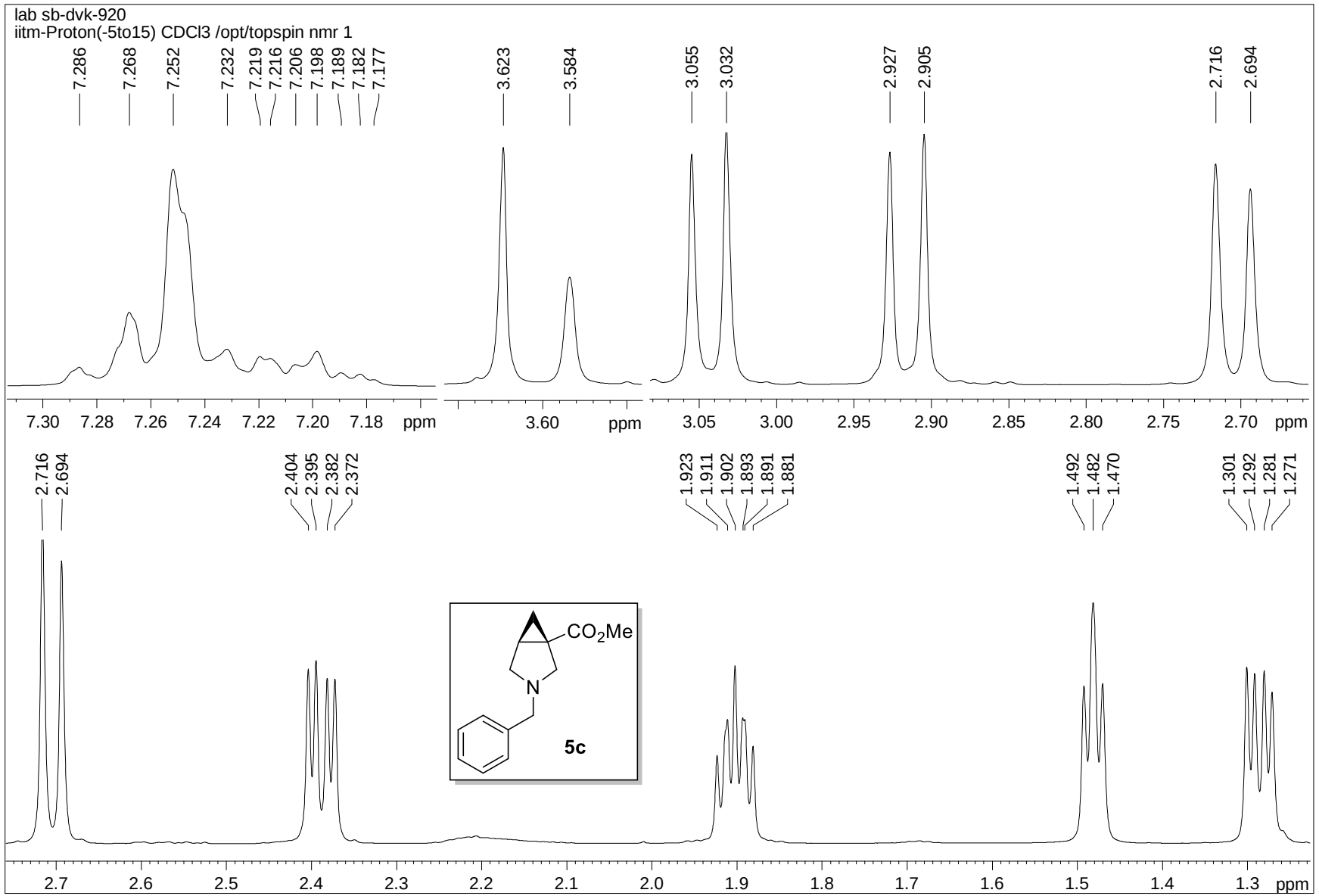
^{1}H-^{1}H COSY NMR spectrum of compound 4d



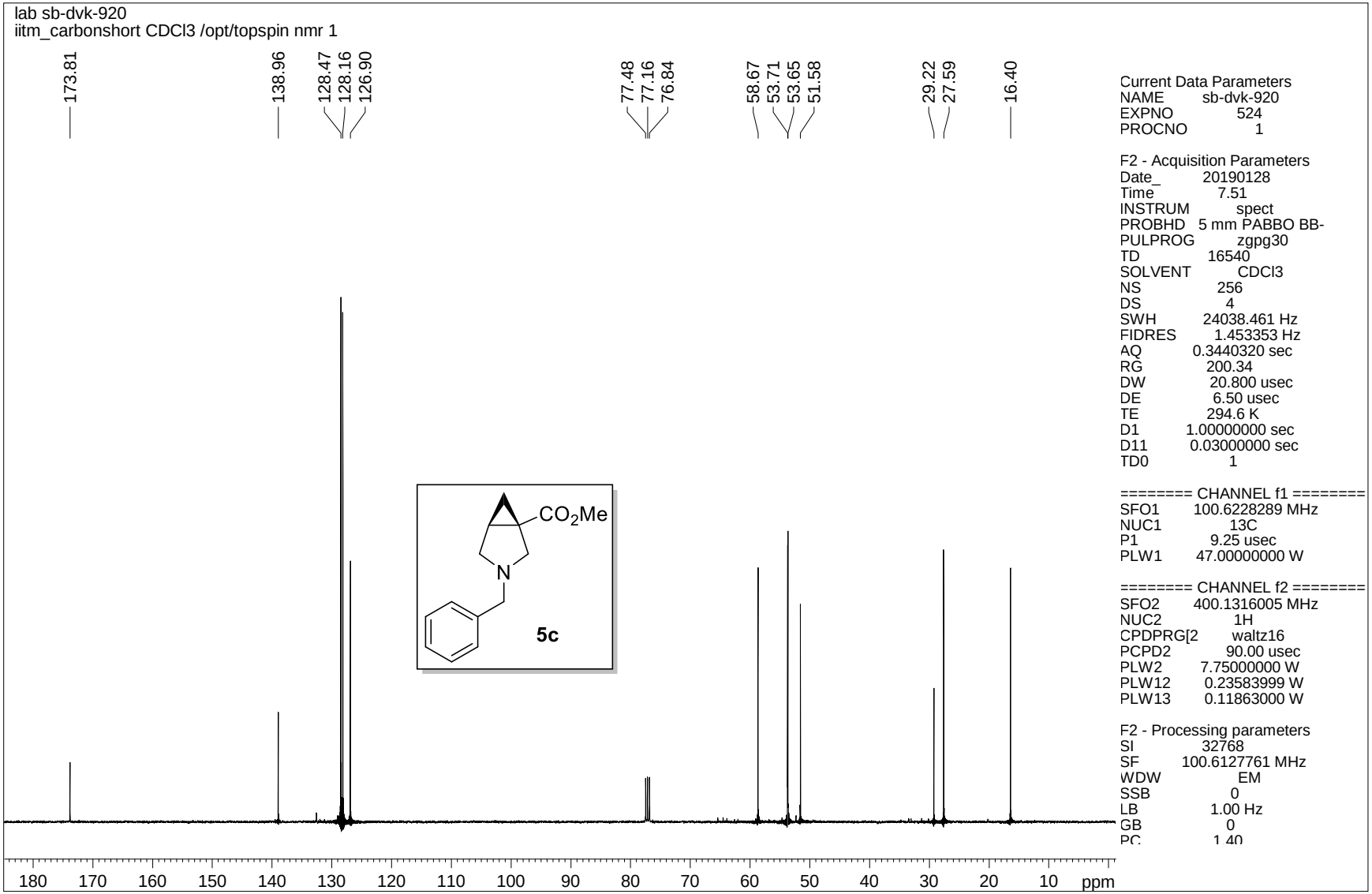
^{1}H-^{13}C HSQC NMR spectrum of compound 4d



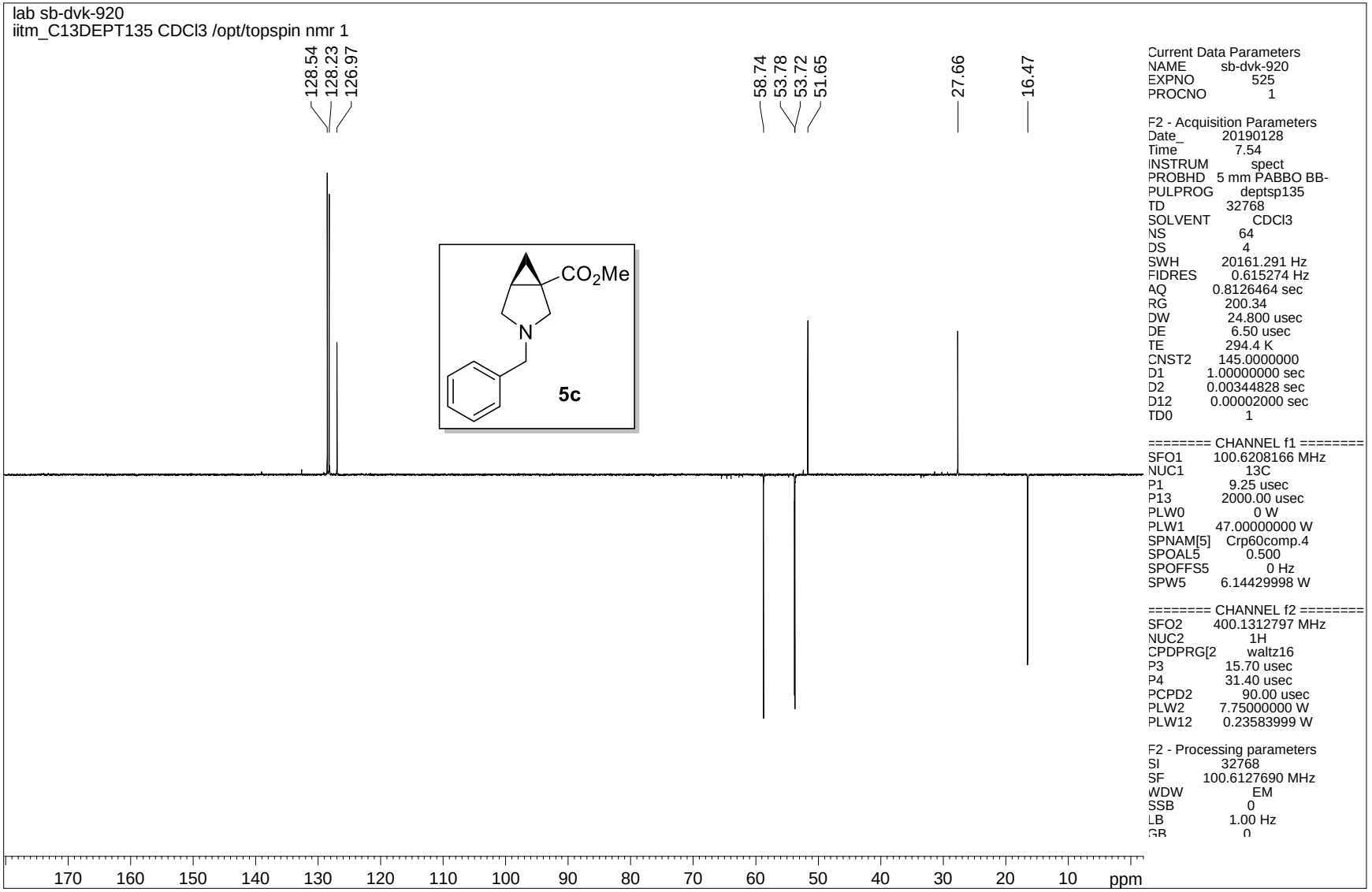
^{1}H NMR spectrum of compound 5c



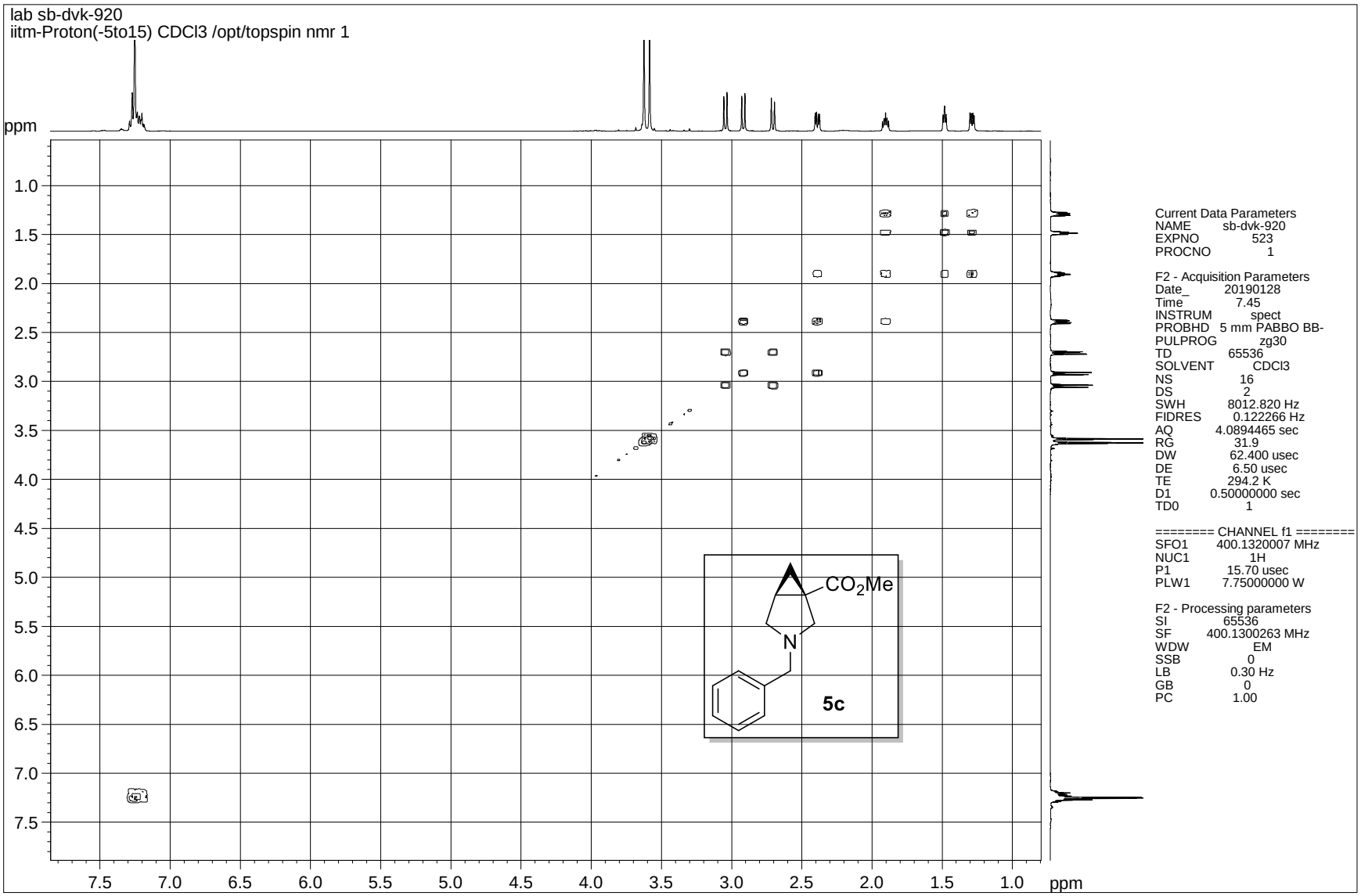
^{1}H NMR spectrum of compound 5c



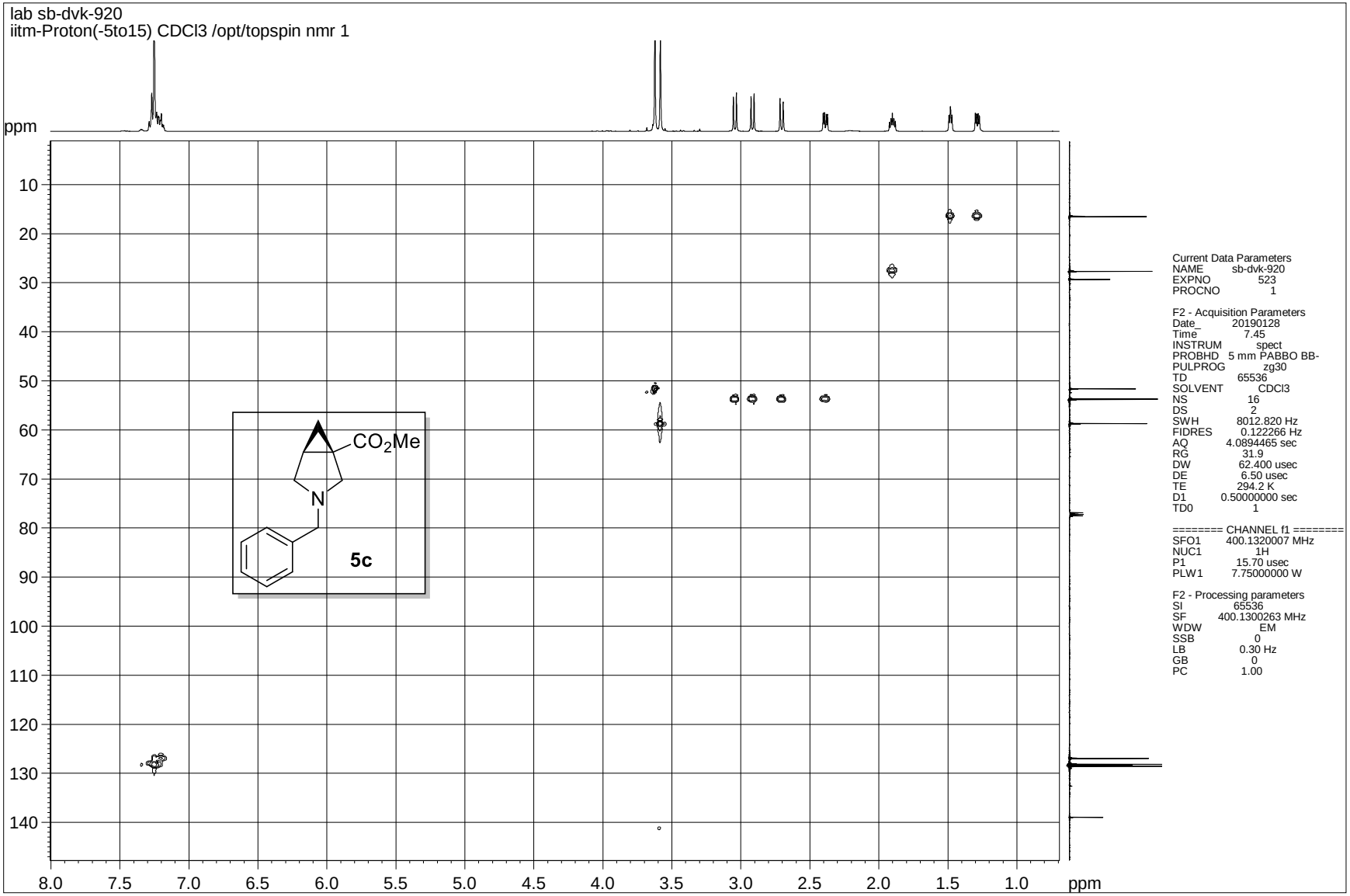
^{13}C NMR spectrum of compound 5c



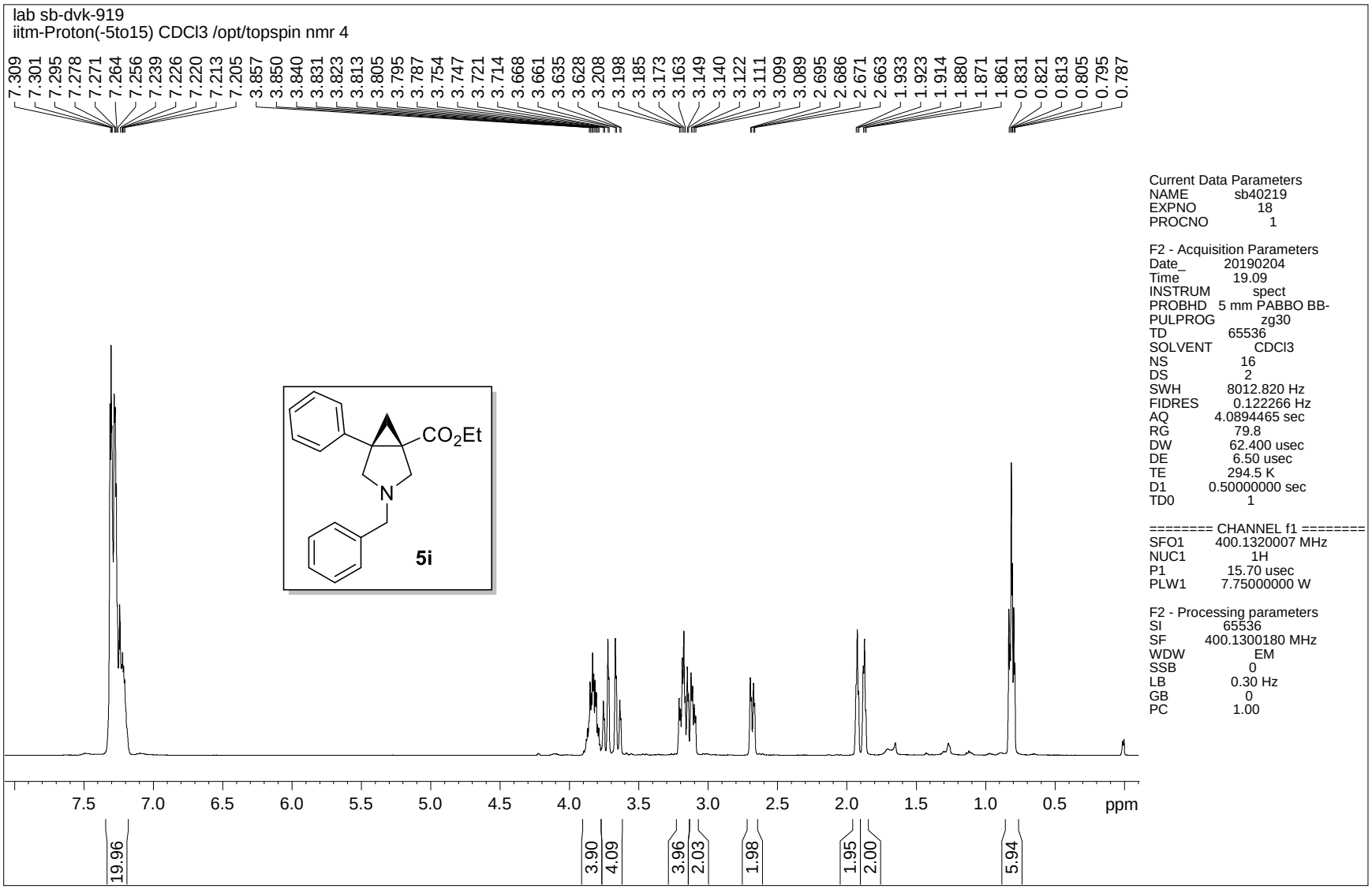
DEPT-135 NMR spectrum of compound 5c



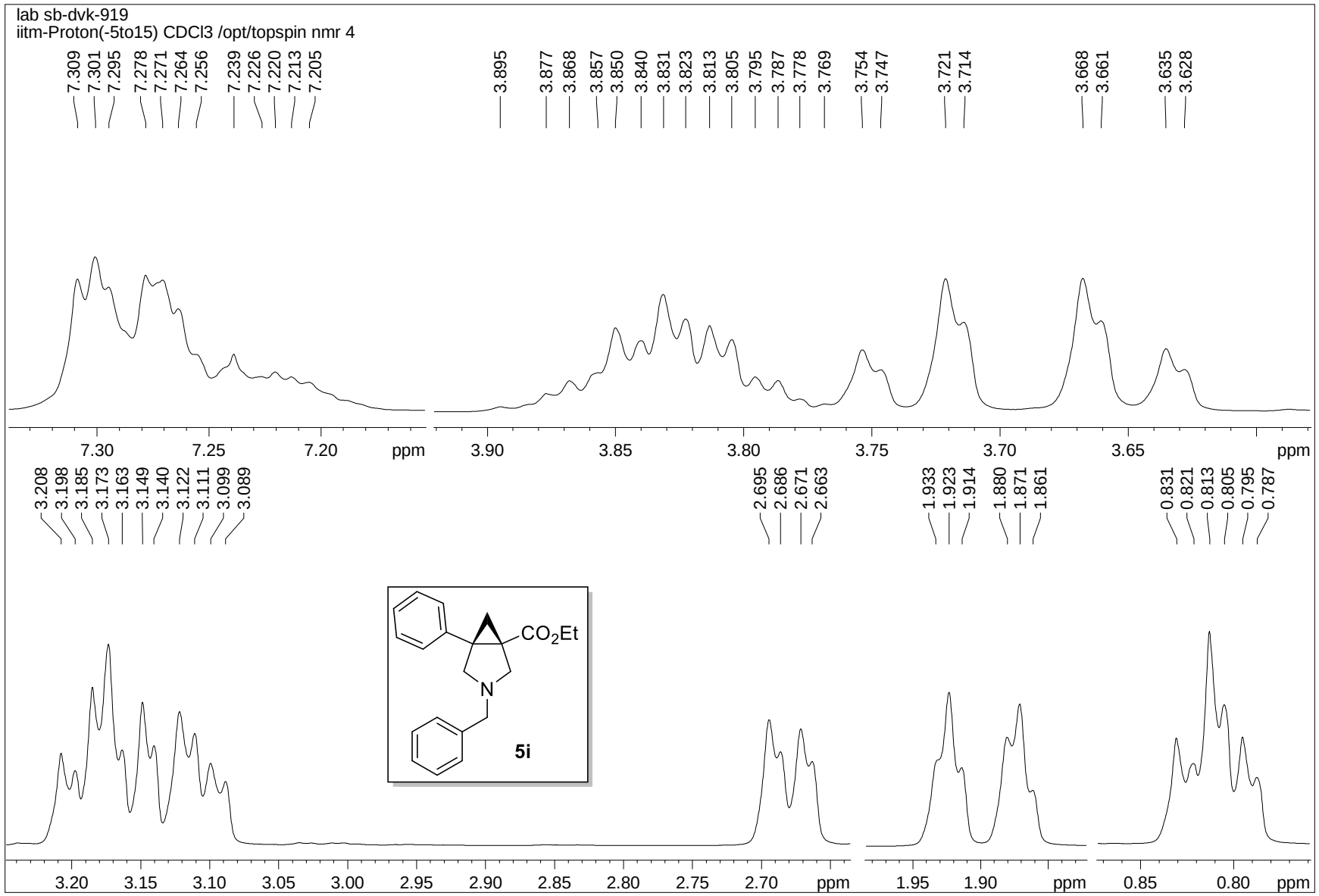
^{1}H-^{1}H COSY NMR spectrum of compound 5c



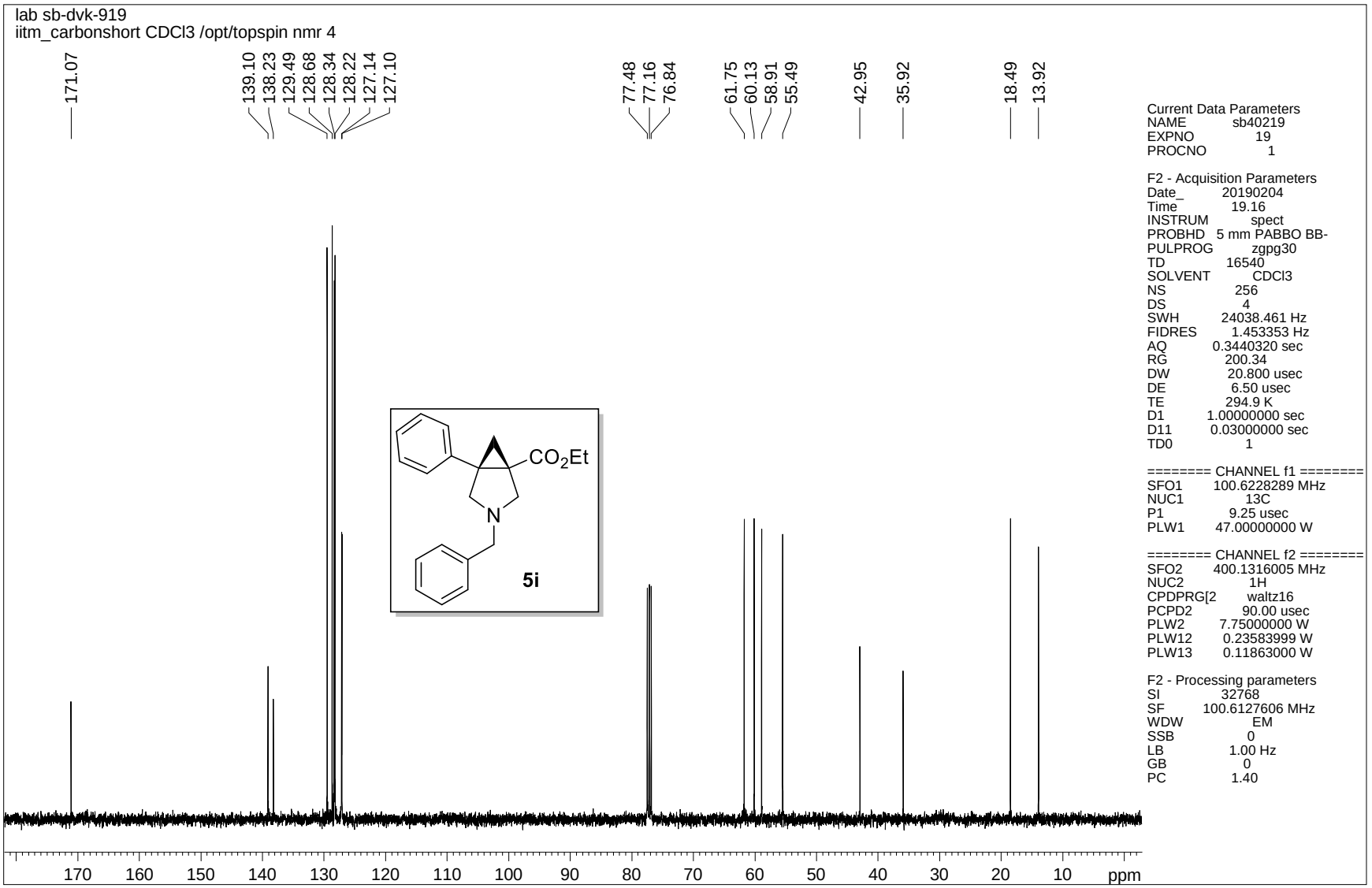
^{1}H-^{13}C HSQC NMR spectrum of compound 5c



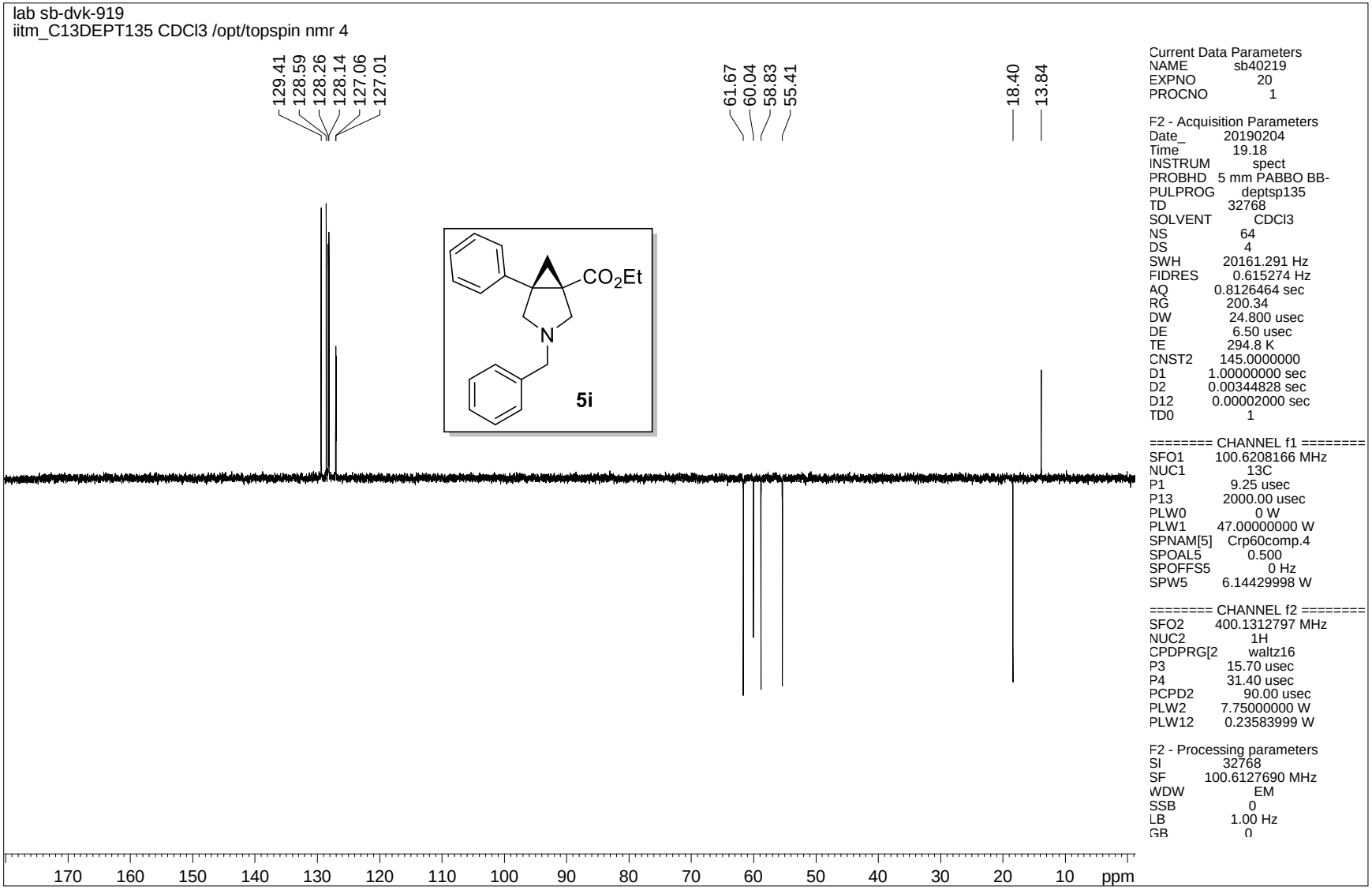
^{1}H NMR spectrum of compound 5i



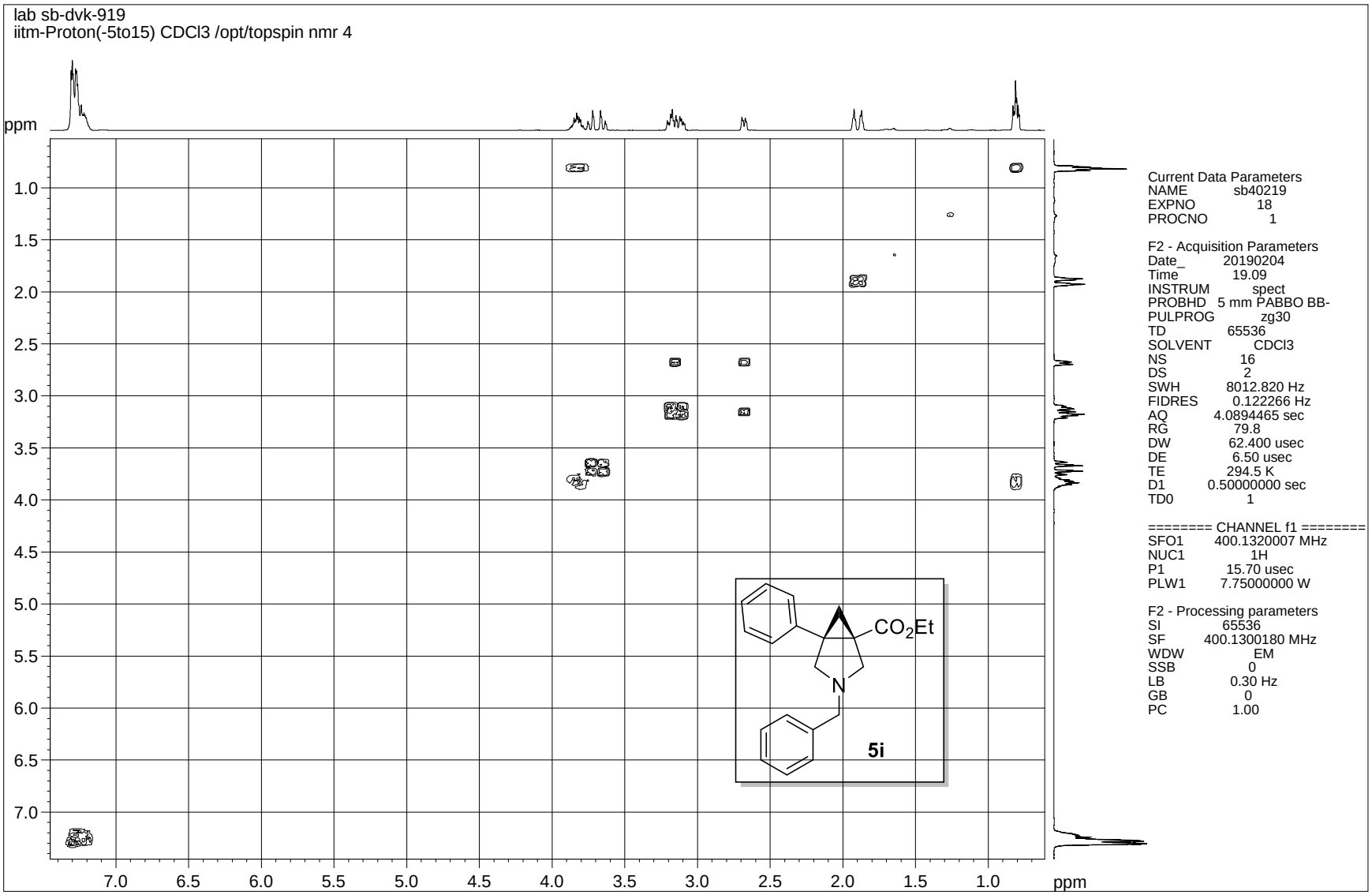
^{1}H NMR spectrum of compound 5i



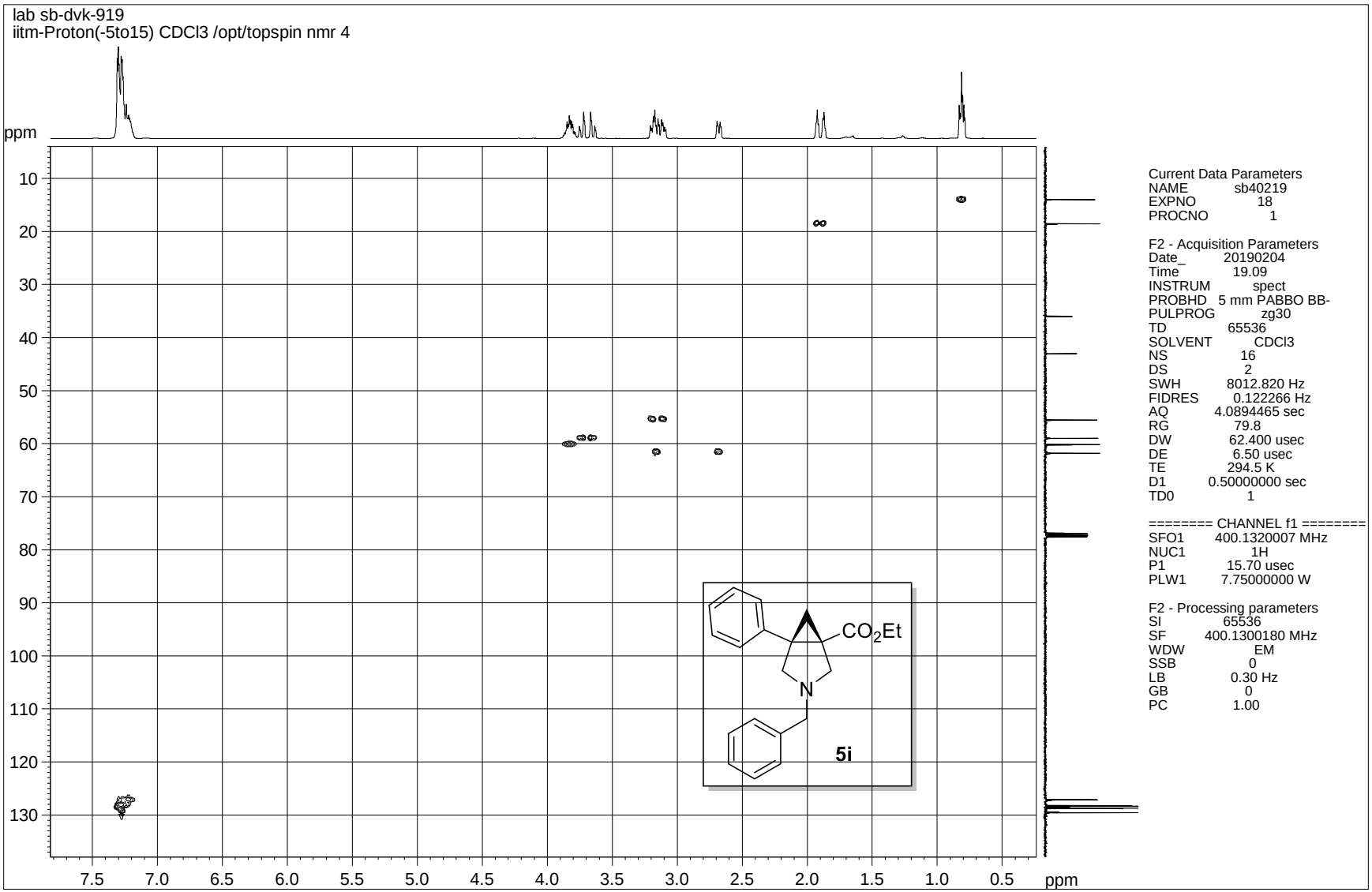
^{13}C NMR spectrum of compound 5i



DEPT-135 NMR spectrum of compound 5i

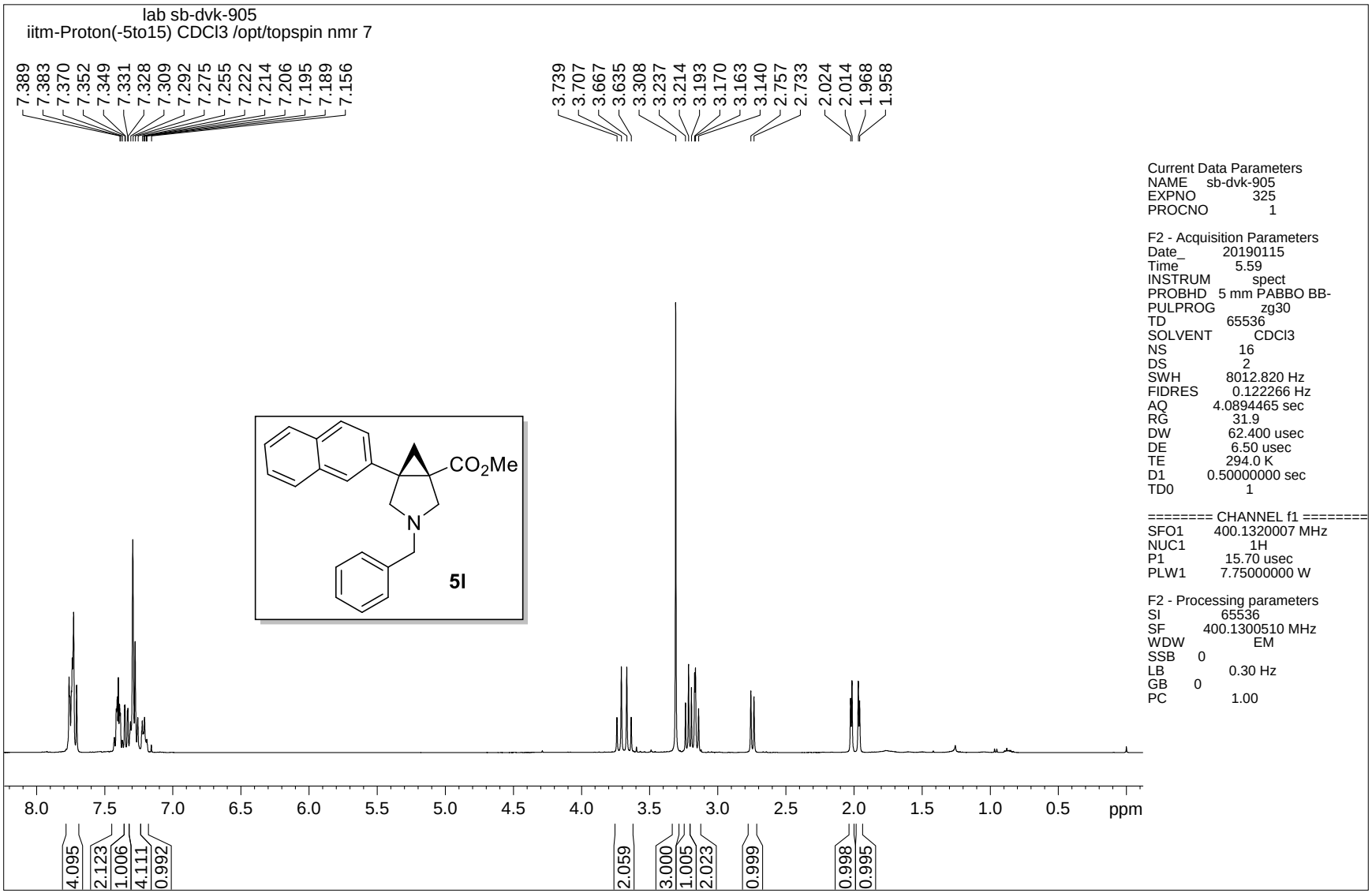


^{1}H-^{1}H COSY NMR spectrum of compound 5i

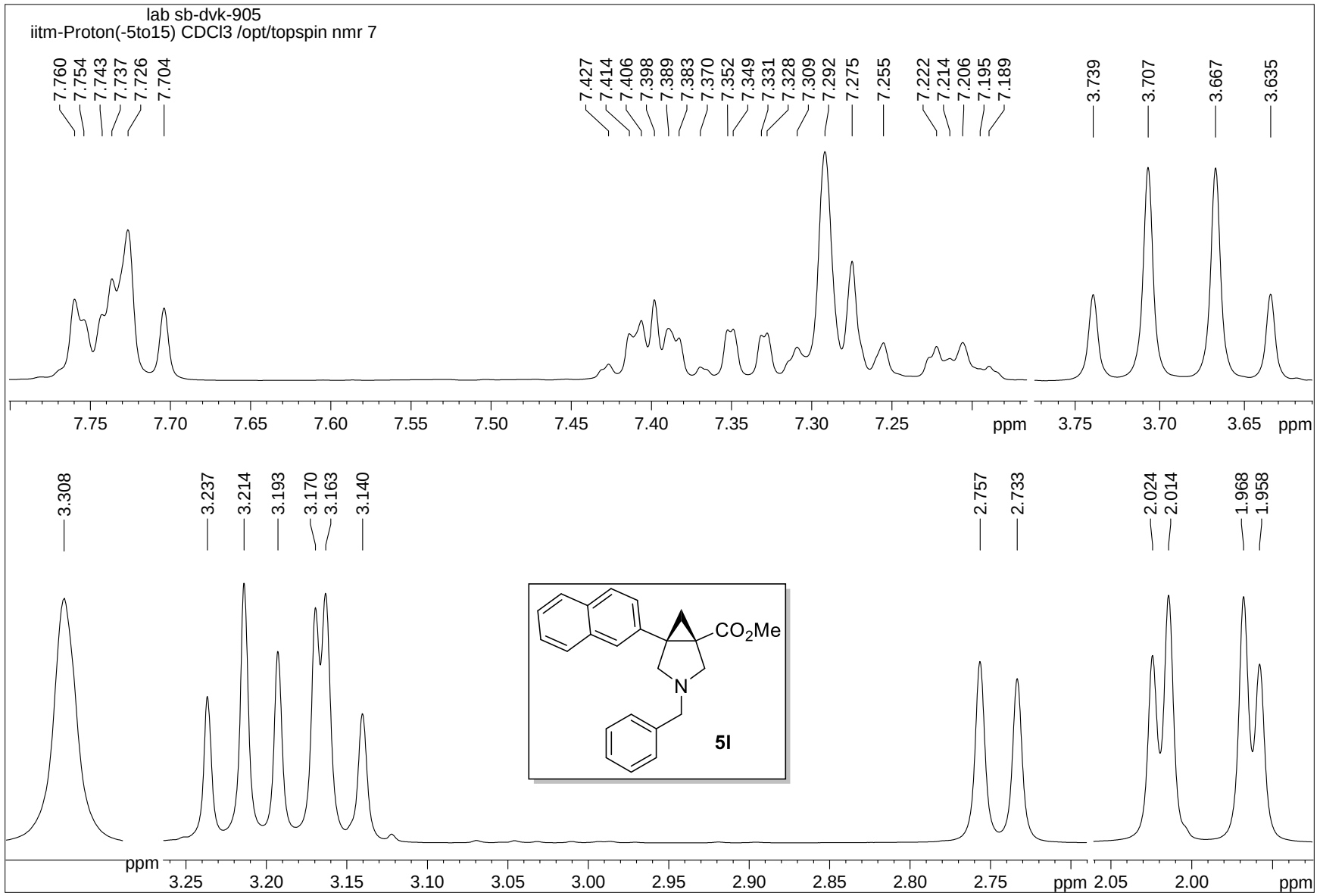


S

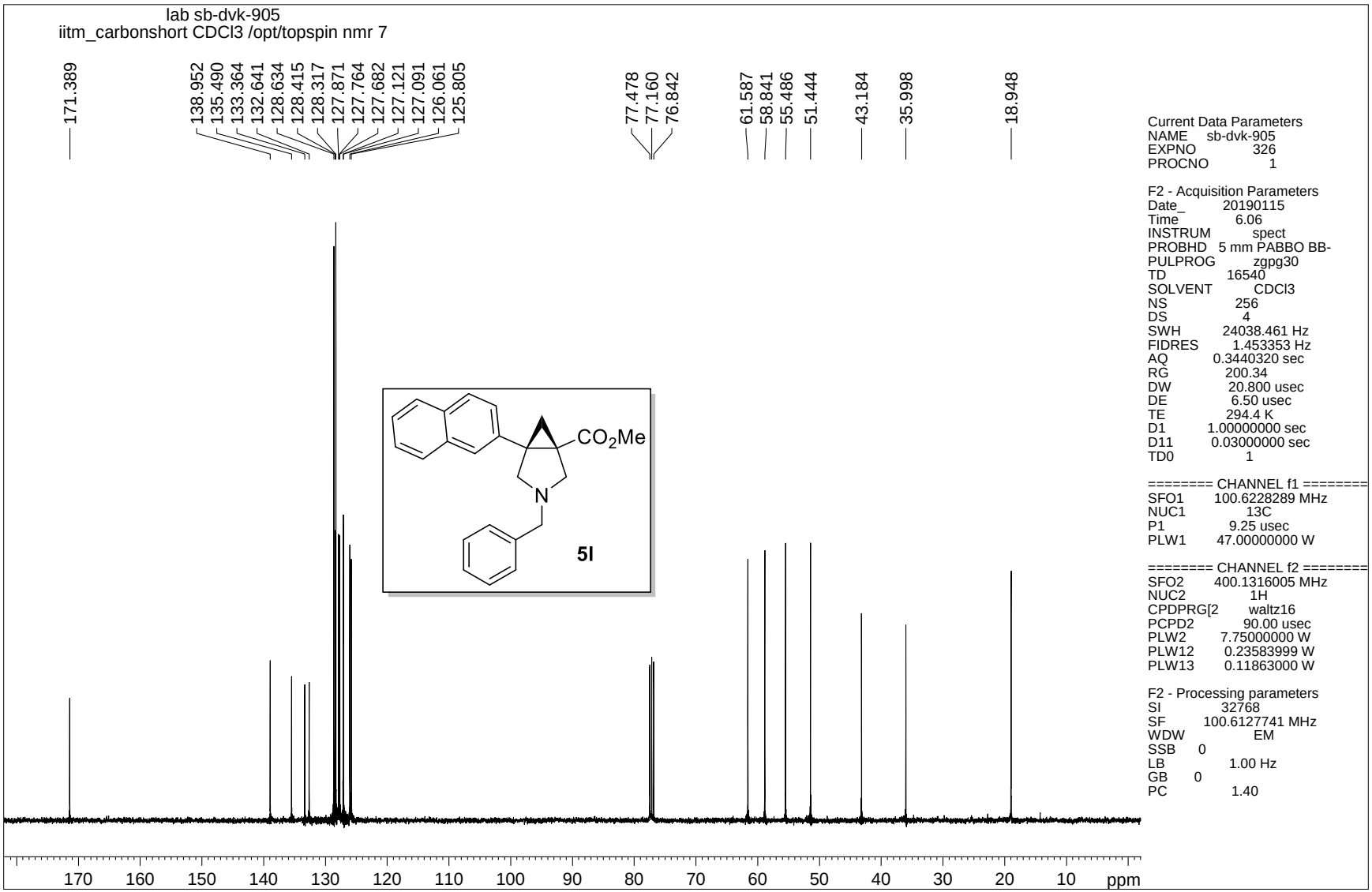
^{1}H-^{13}C HSQC NMR spectrum of compound 5i



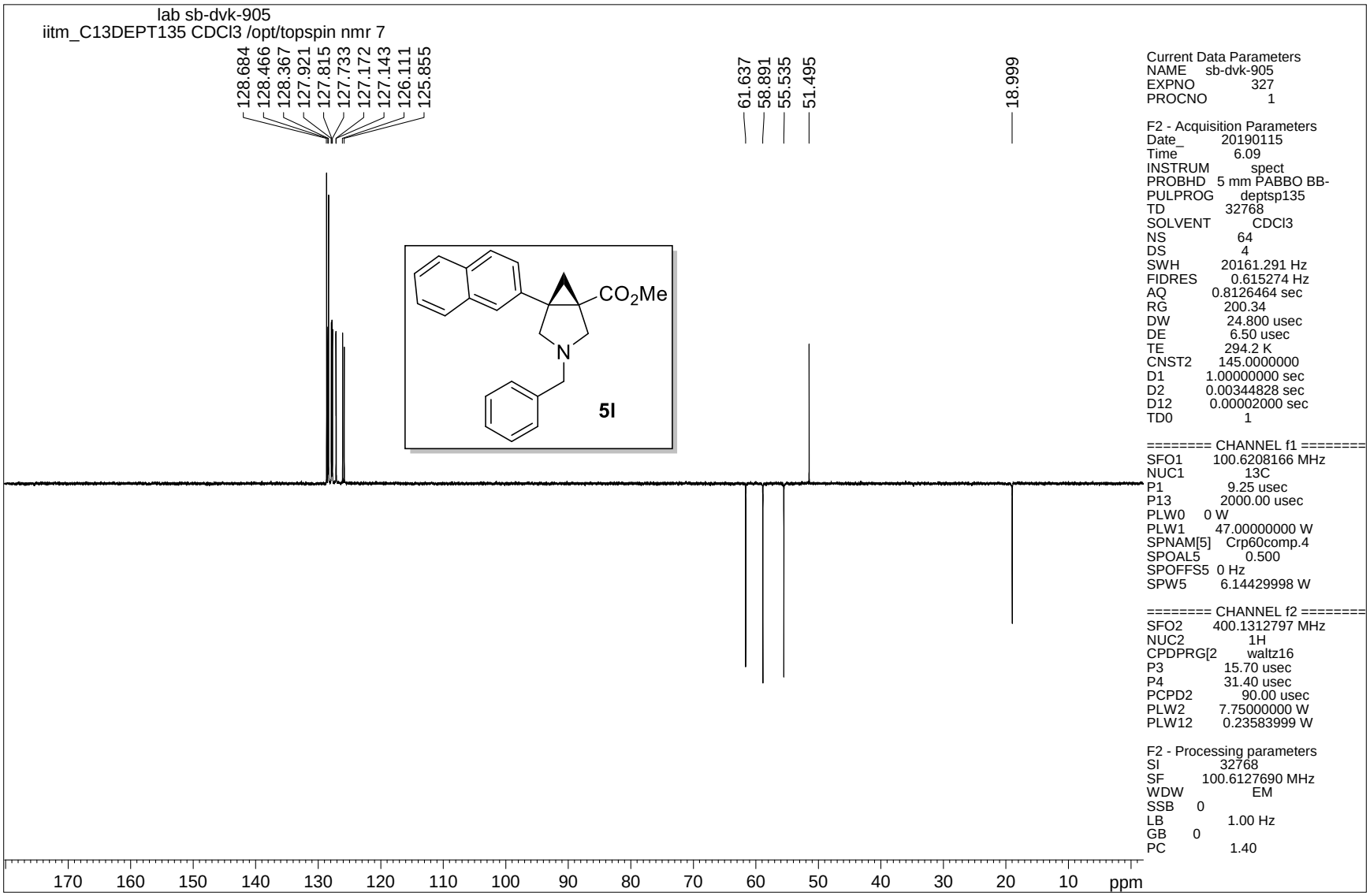
^{1}H NMR spectrum of compound 5l



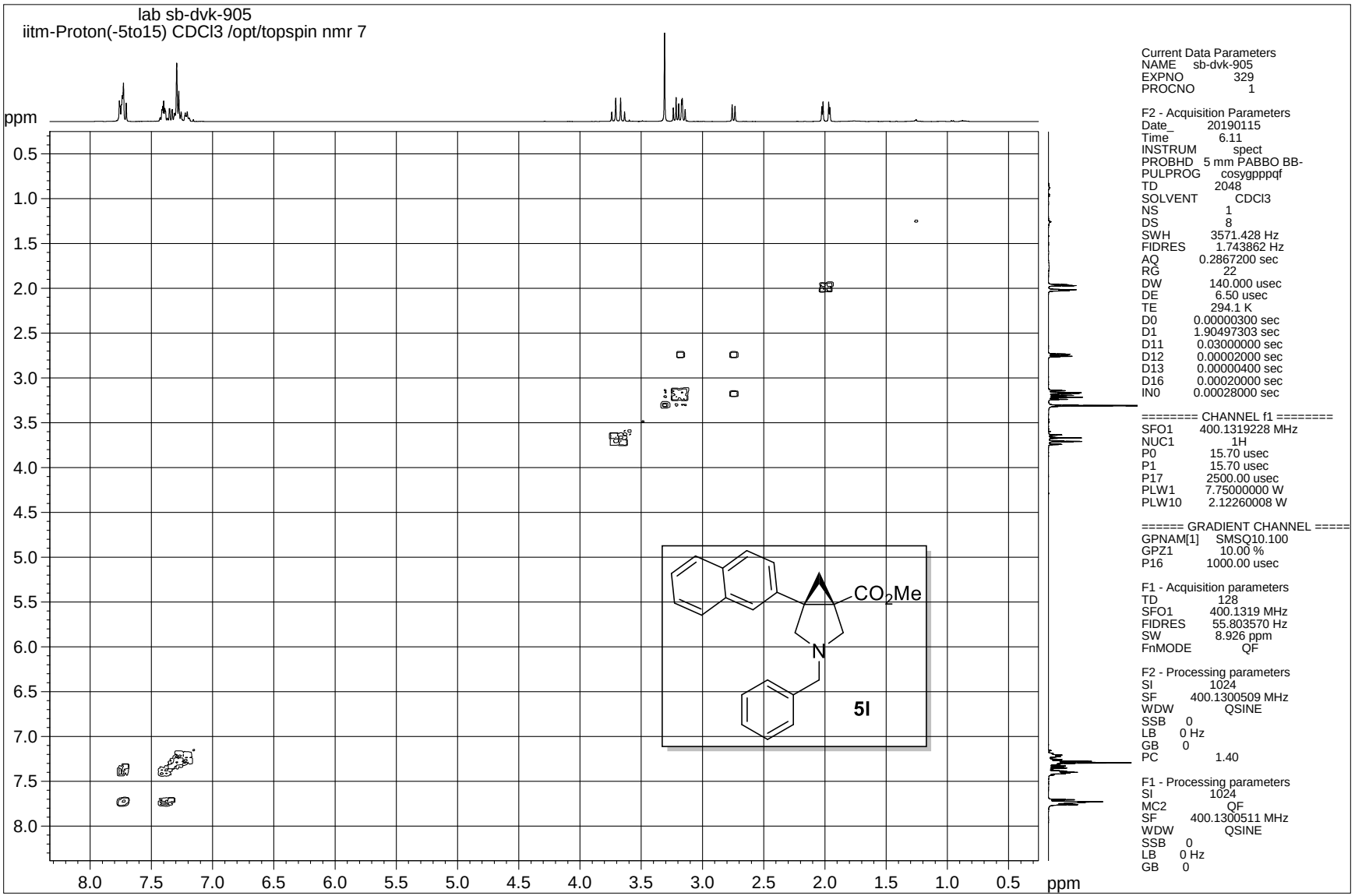
^{1}H NMR spectrum of compound 5l



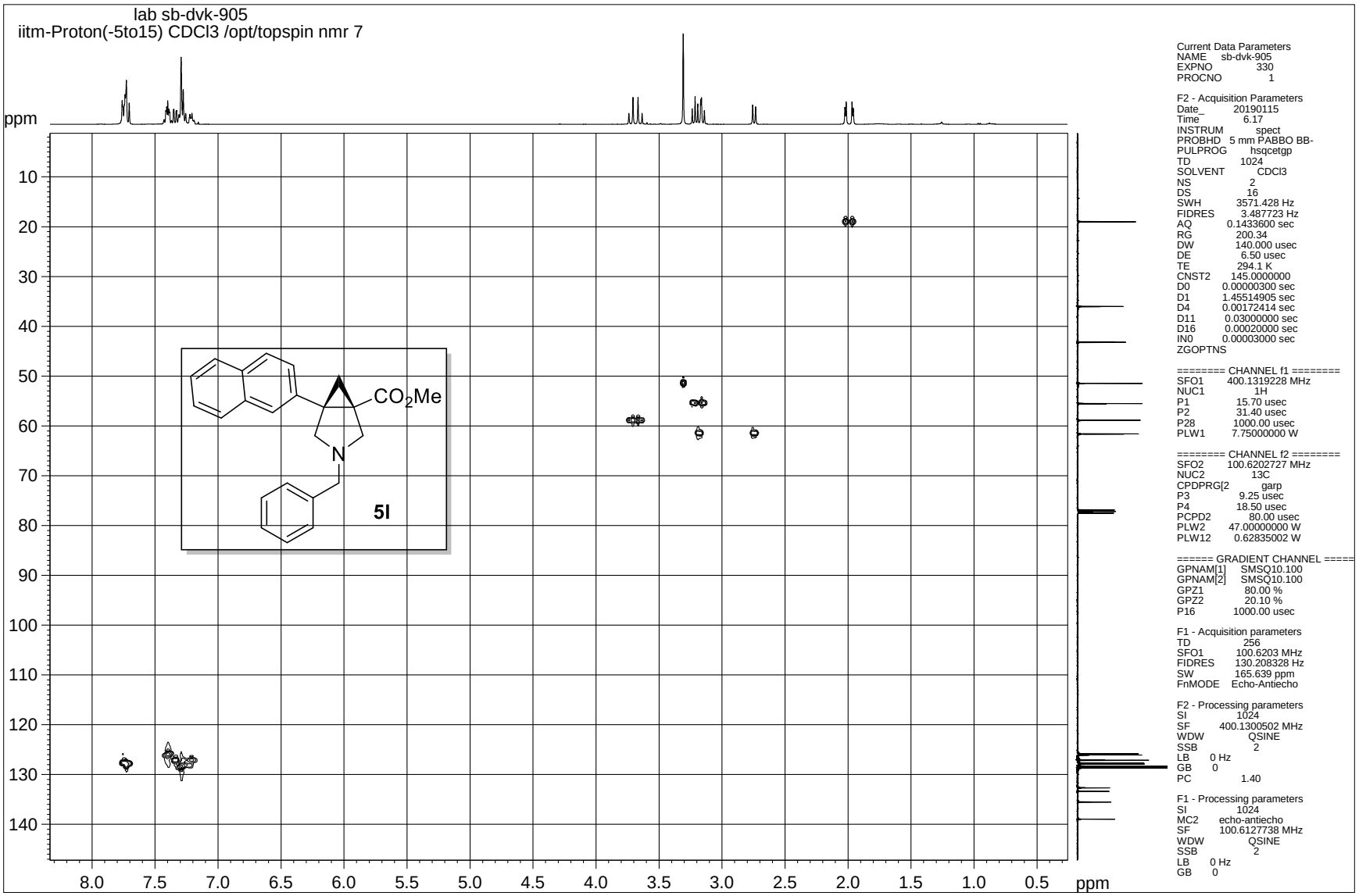
^{13}C NMR spectrum of compound 5l



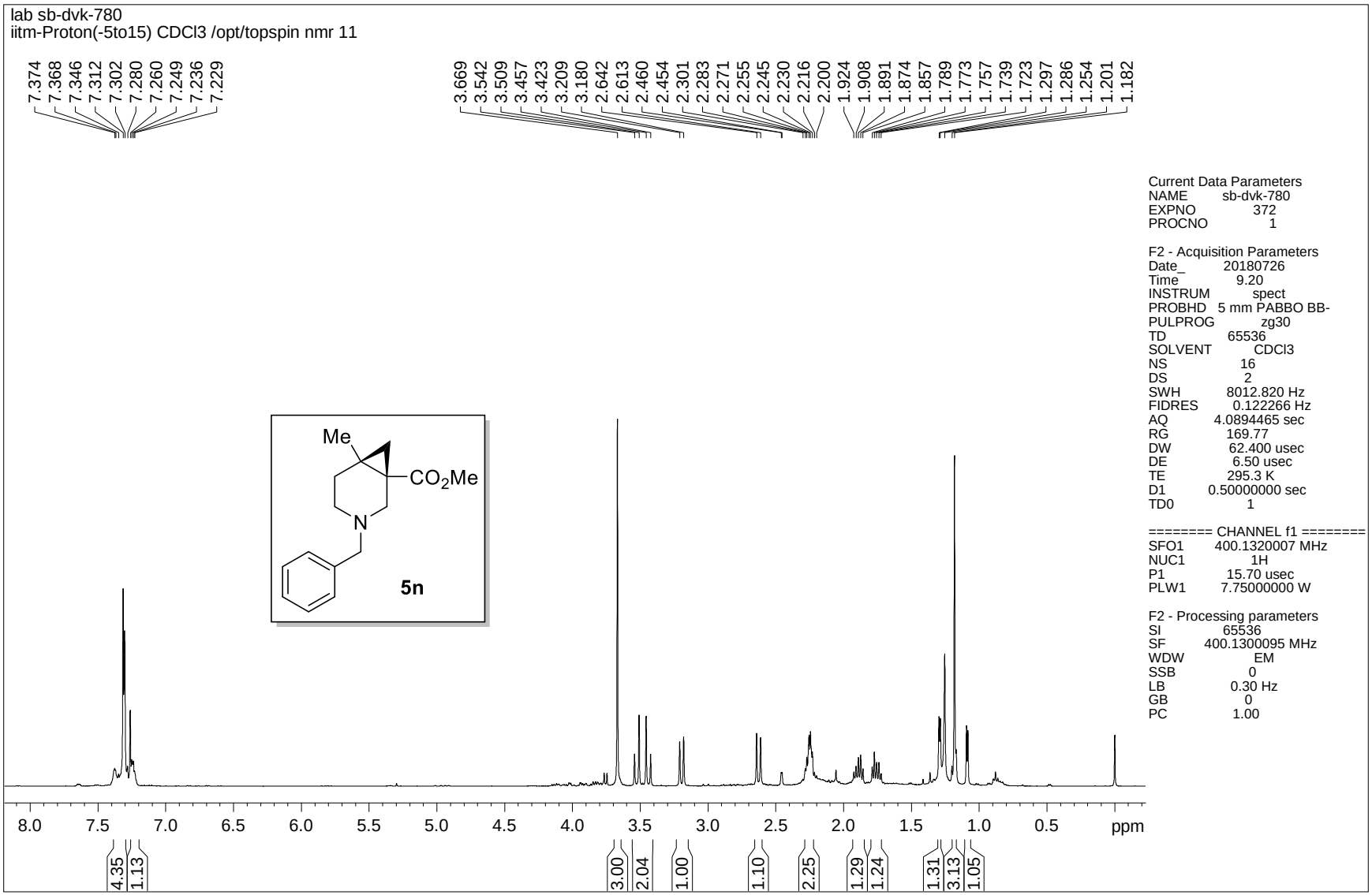
DEPT-135 NMR spectrum of compound 5l



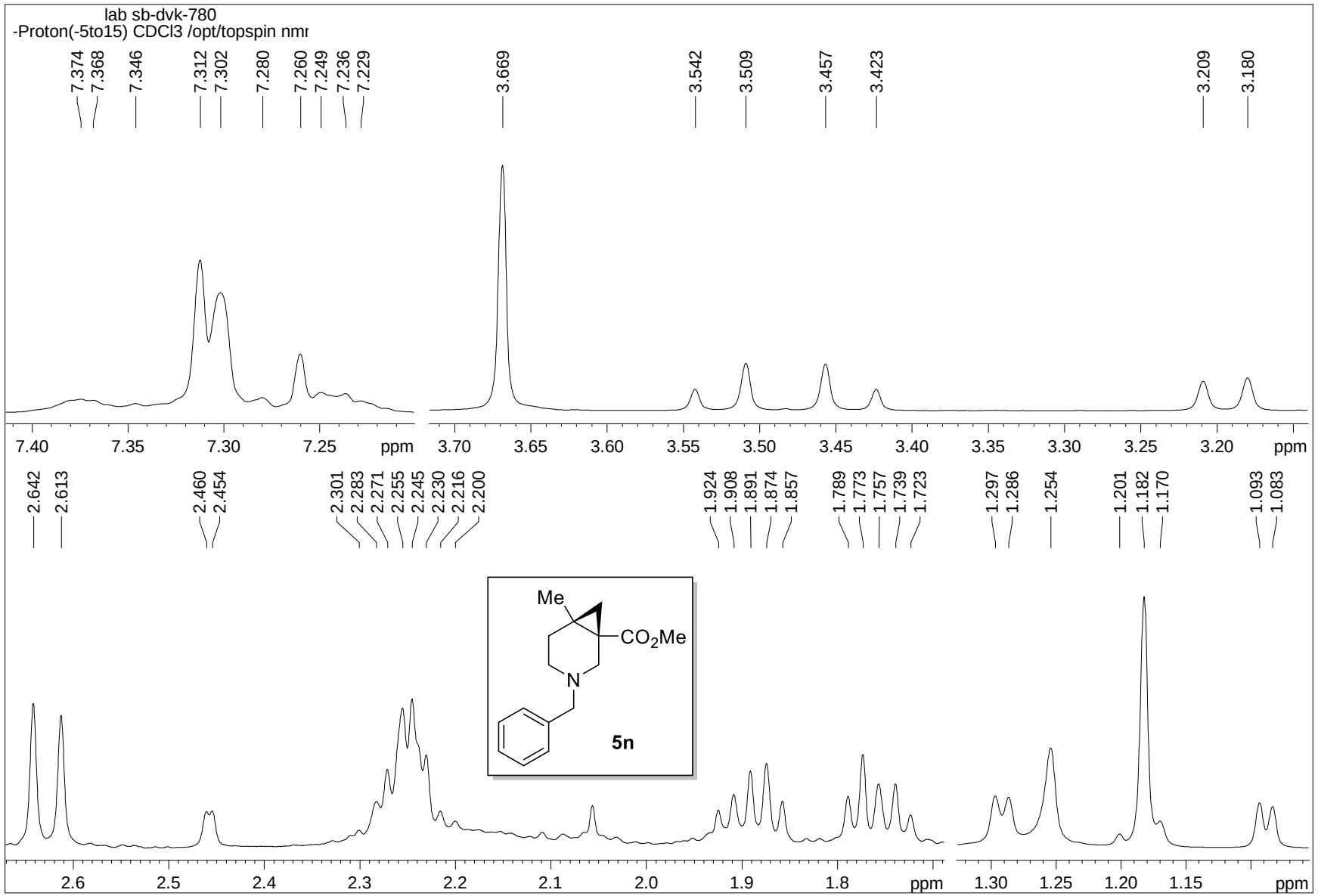
^{1}H-^{1}H COSY NMR spectrum of compound 5l



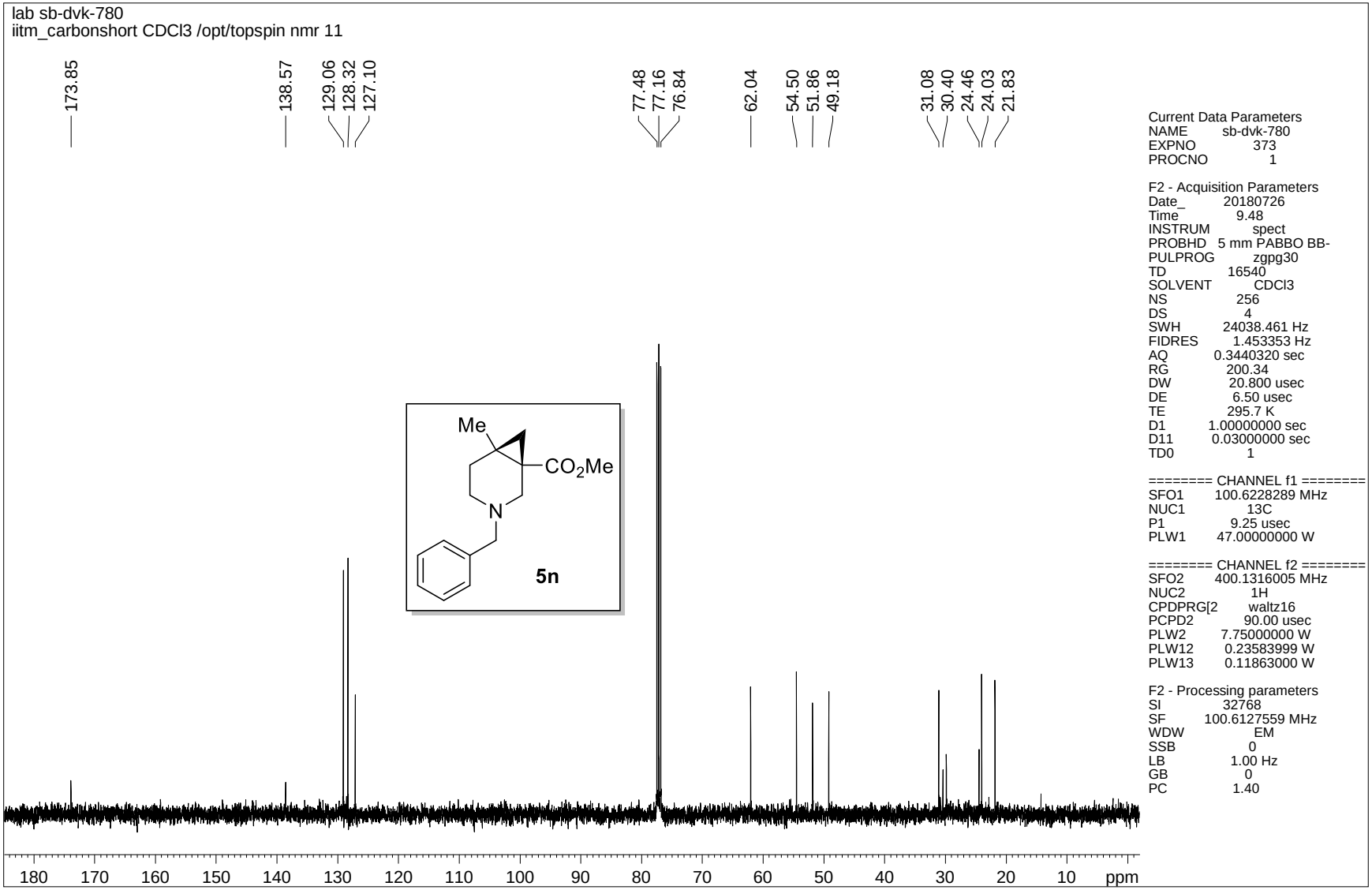
^{1}H-^{13}C HSQC NMR spectrum of compound 5l



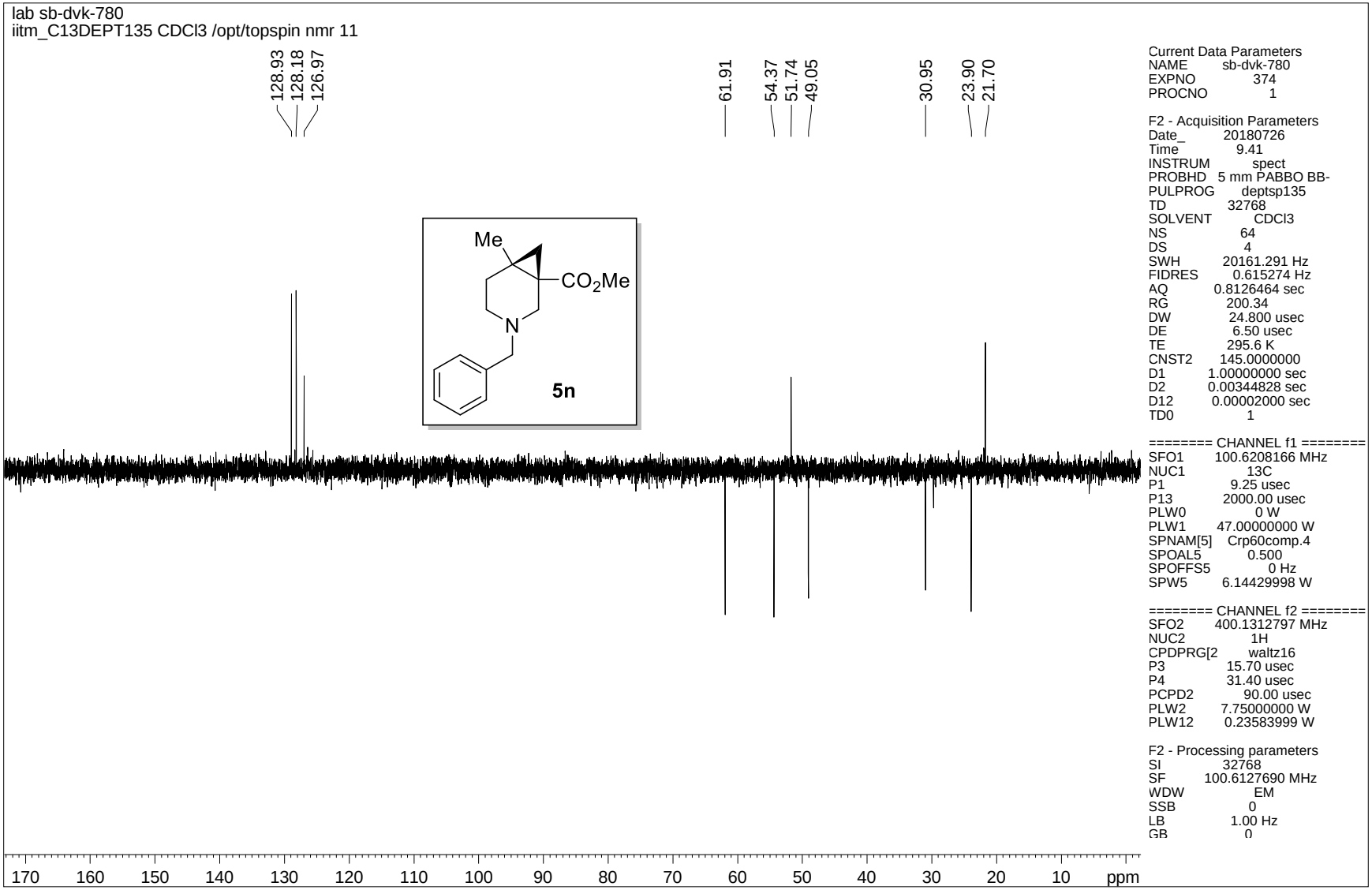
^{1}H NMR spectrum of compound 5n



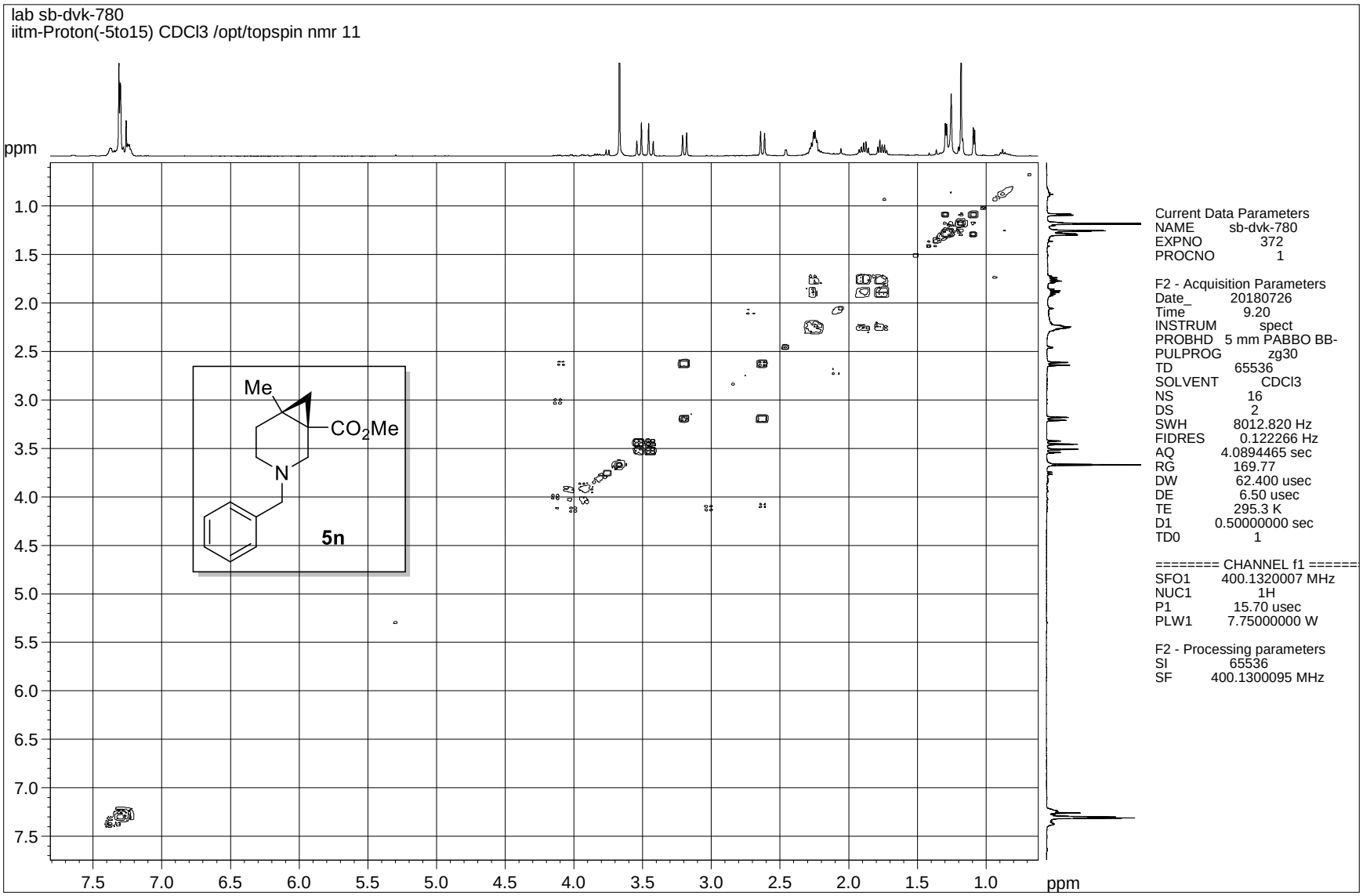
^{1}H NMR spectrum of compound 5n



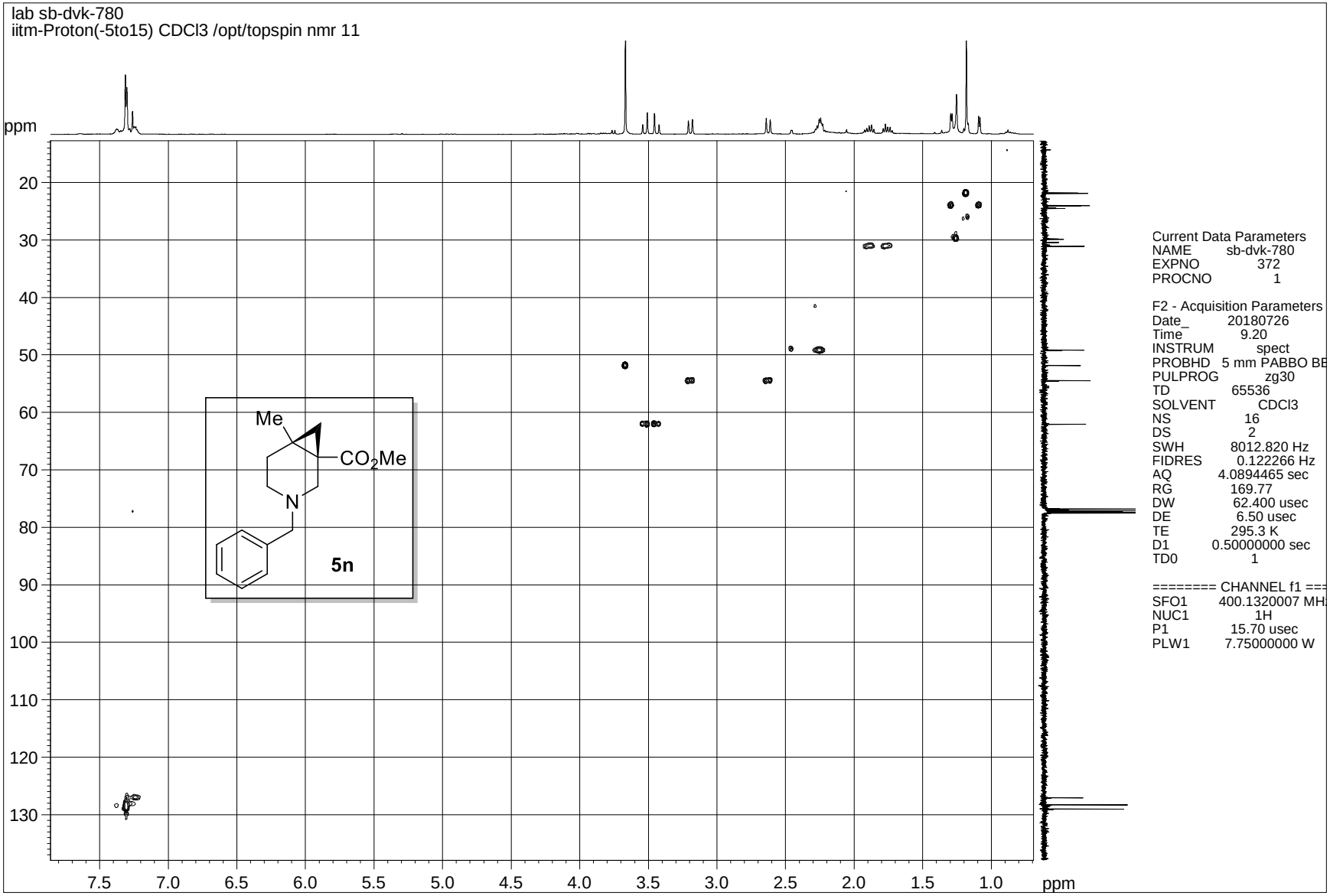
^{13}C NMR spectrum of compound 5n



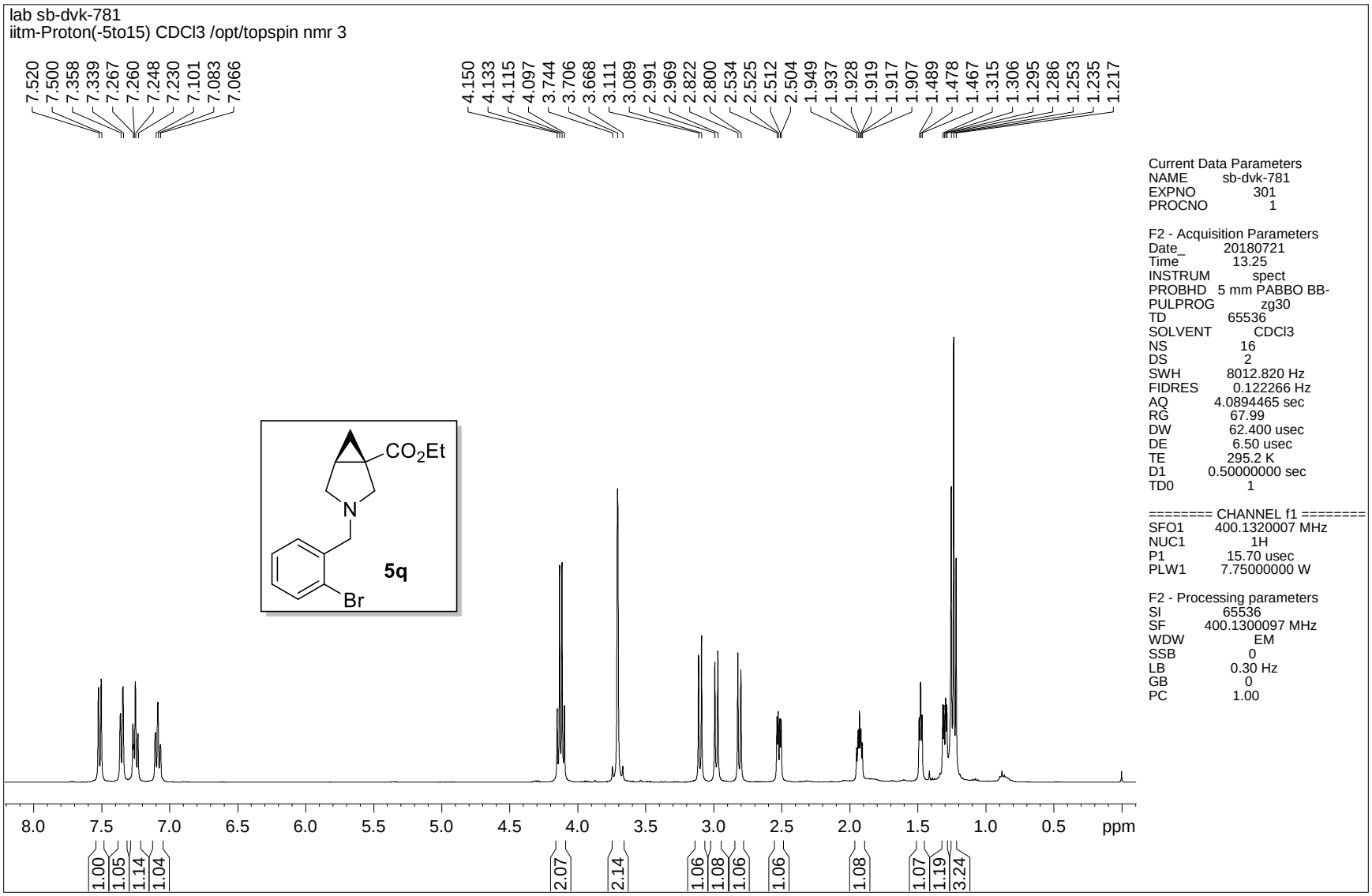
DEPT-135 NMR spectrum of compound 5n



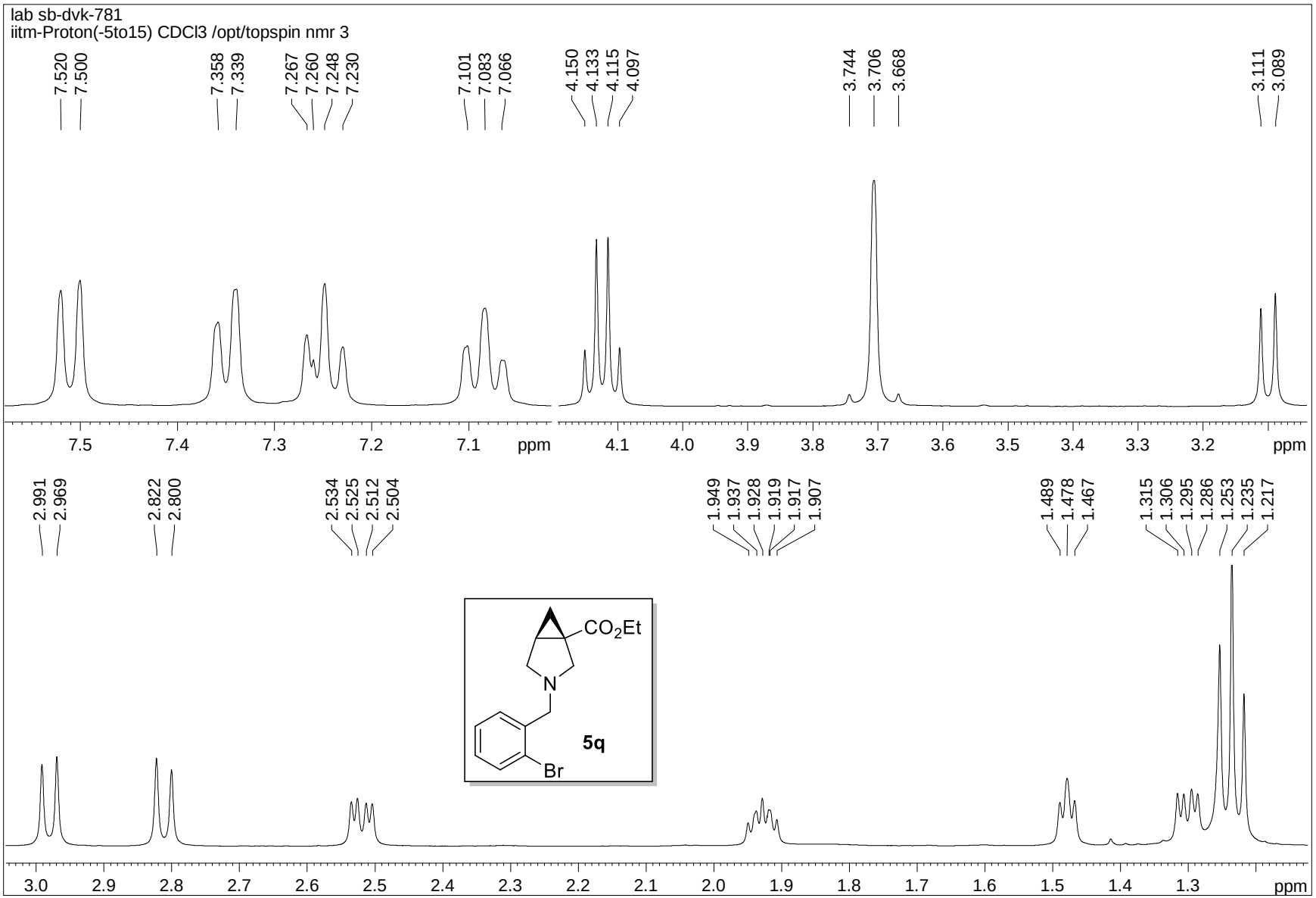
^{1}H-^{1}H COSY NMR spectrum of compound 5n



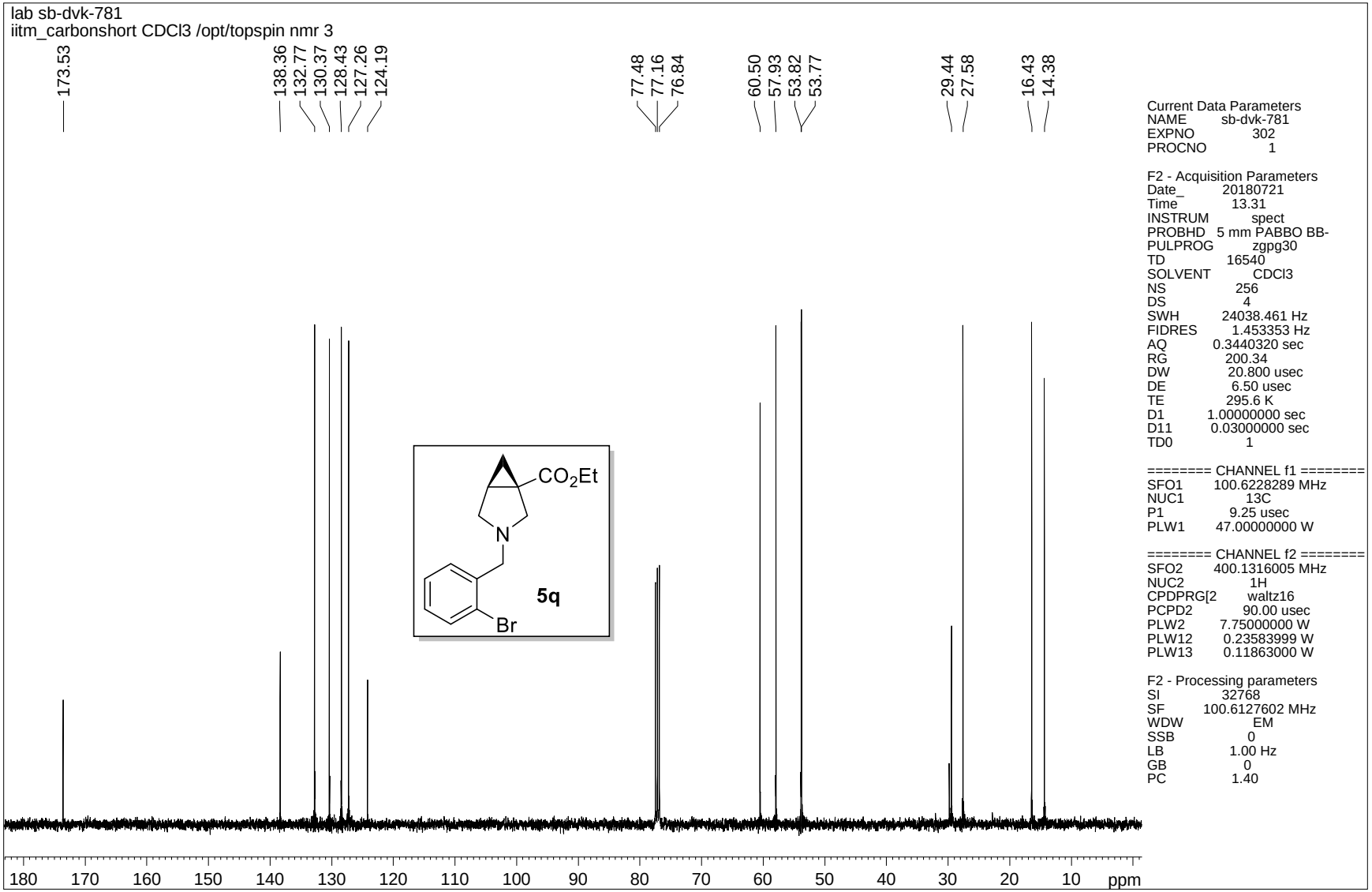
^{1}H-^{13}C HSQC NMR spectrum of compound 5n



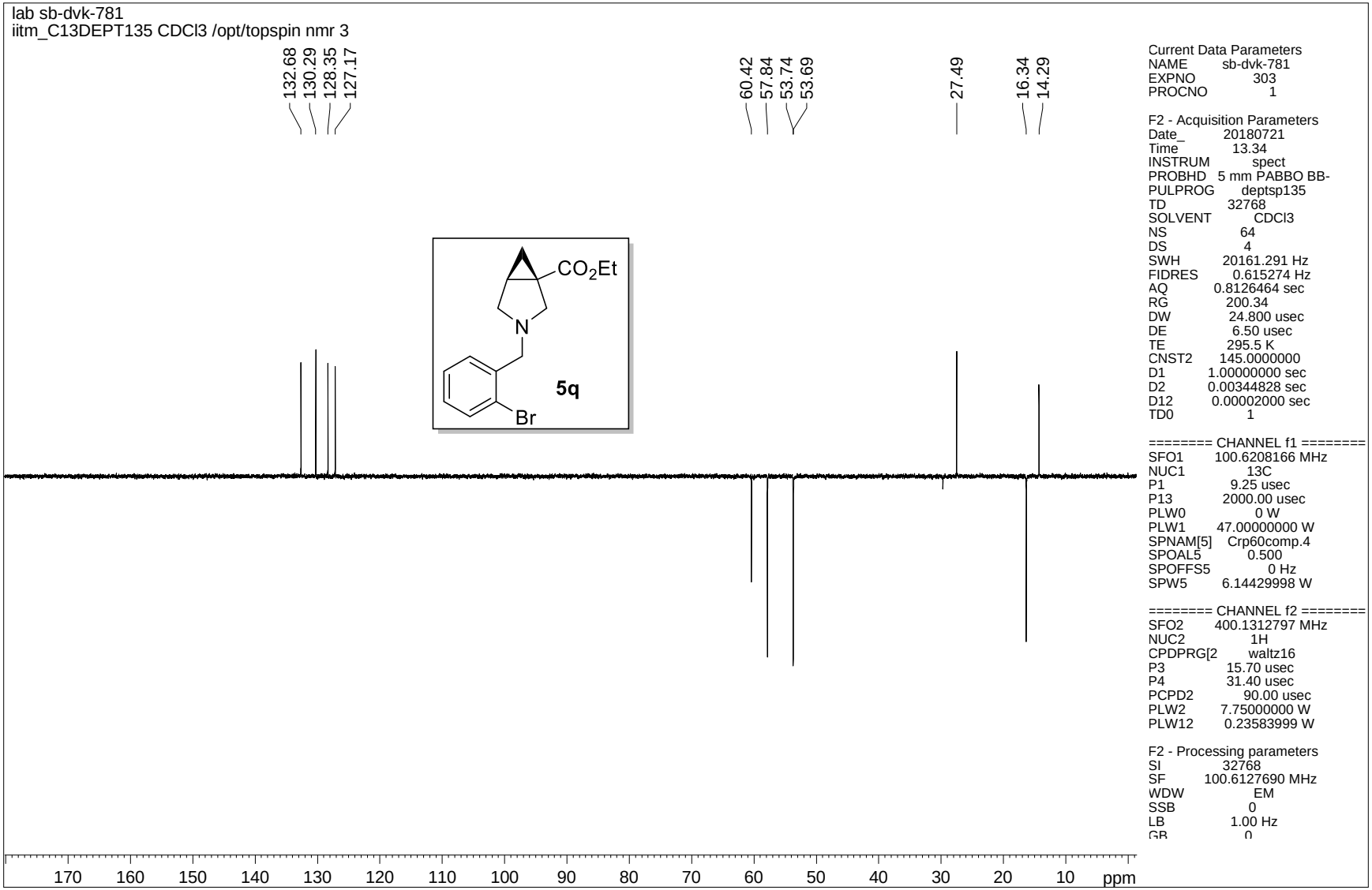
^{1}H NMR spectrum of compound 5q



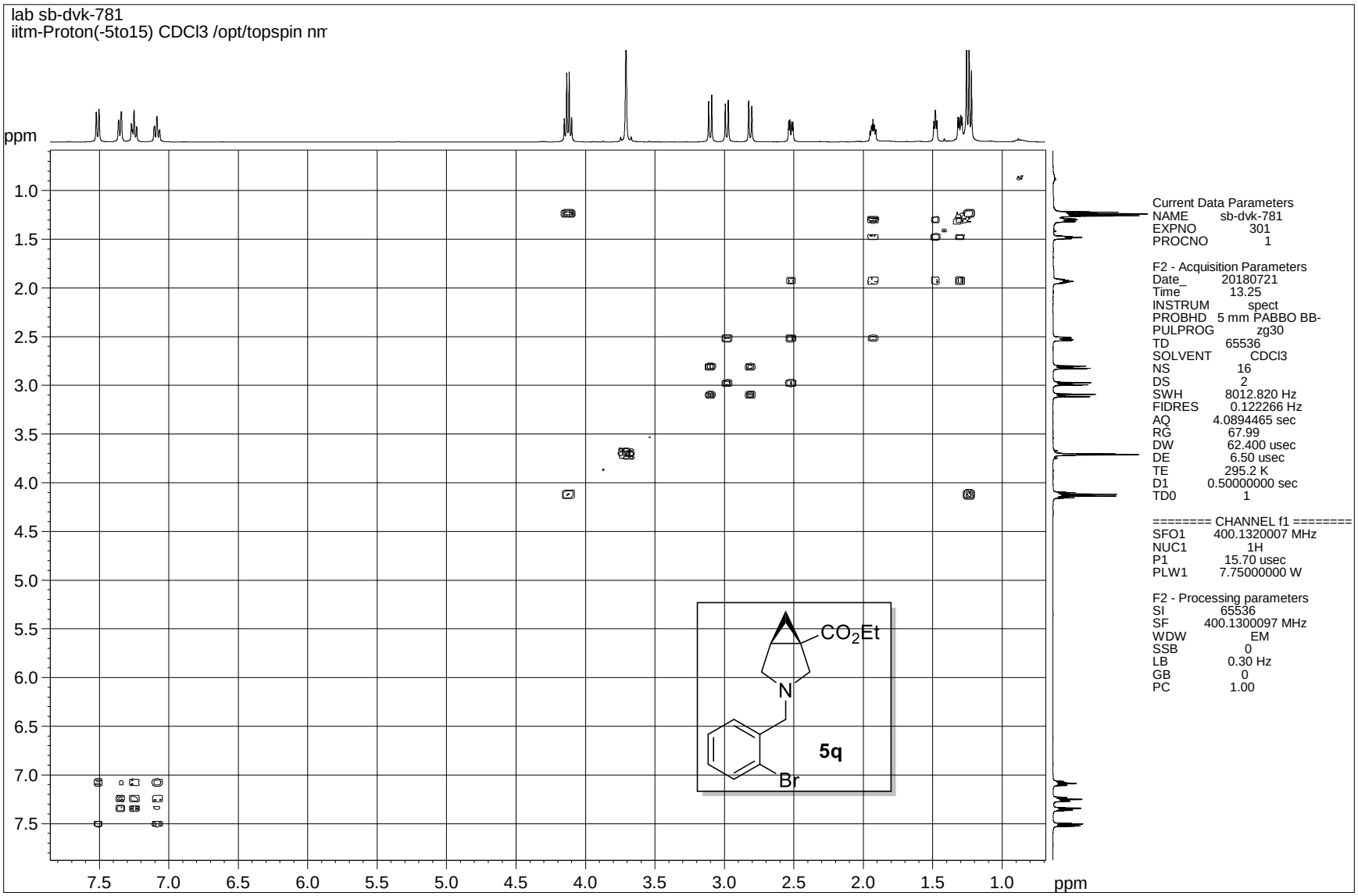
^{1}H NMR spectrum of compound 5q



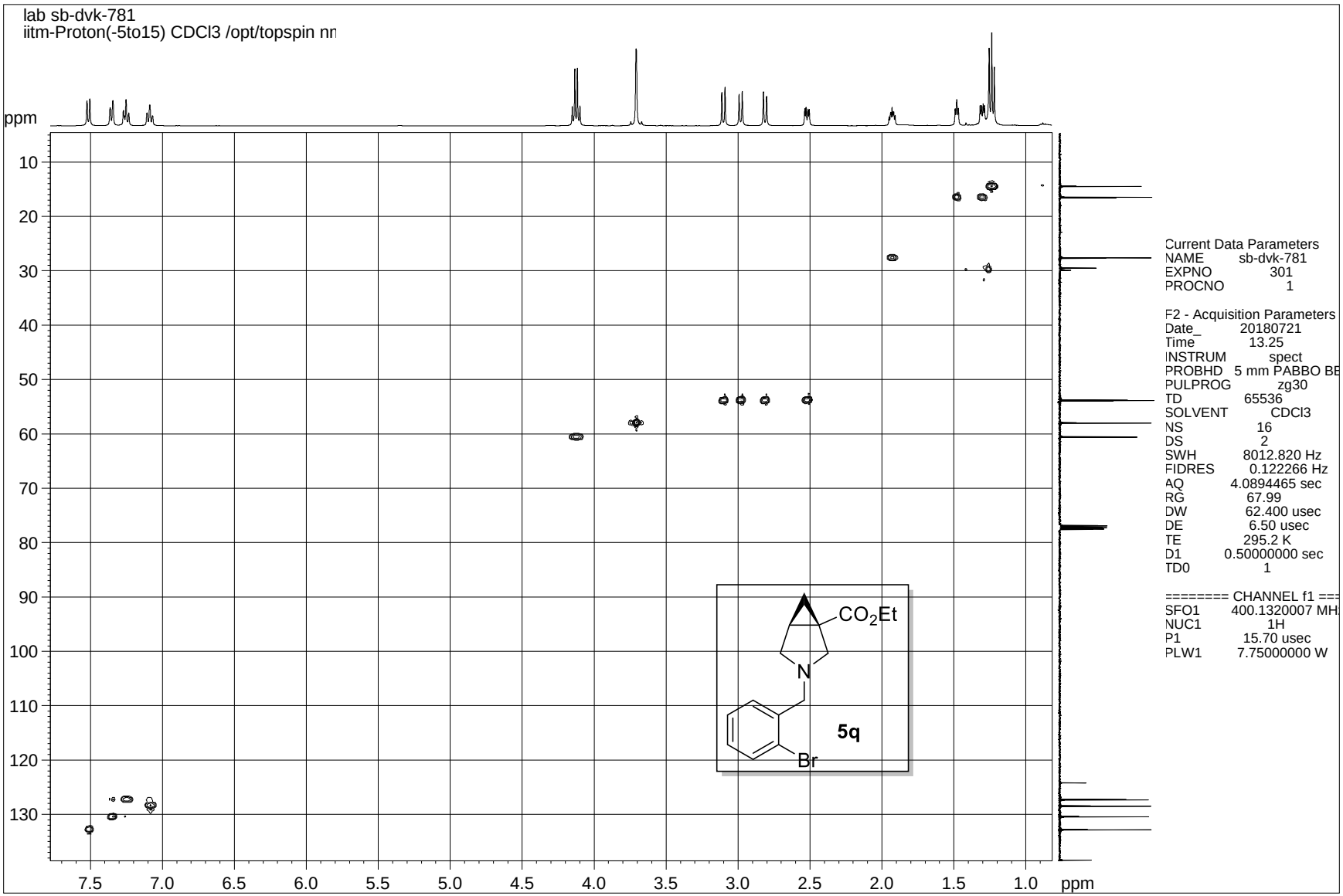
^{13}C NMR spectrum of compound 5q



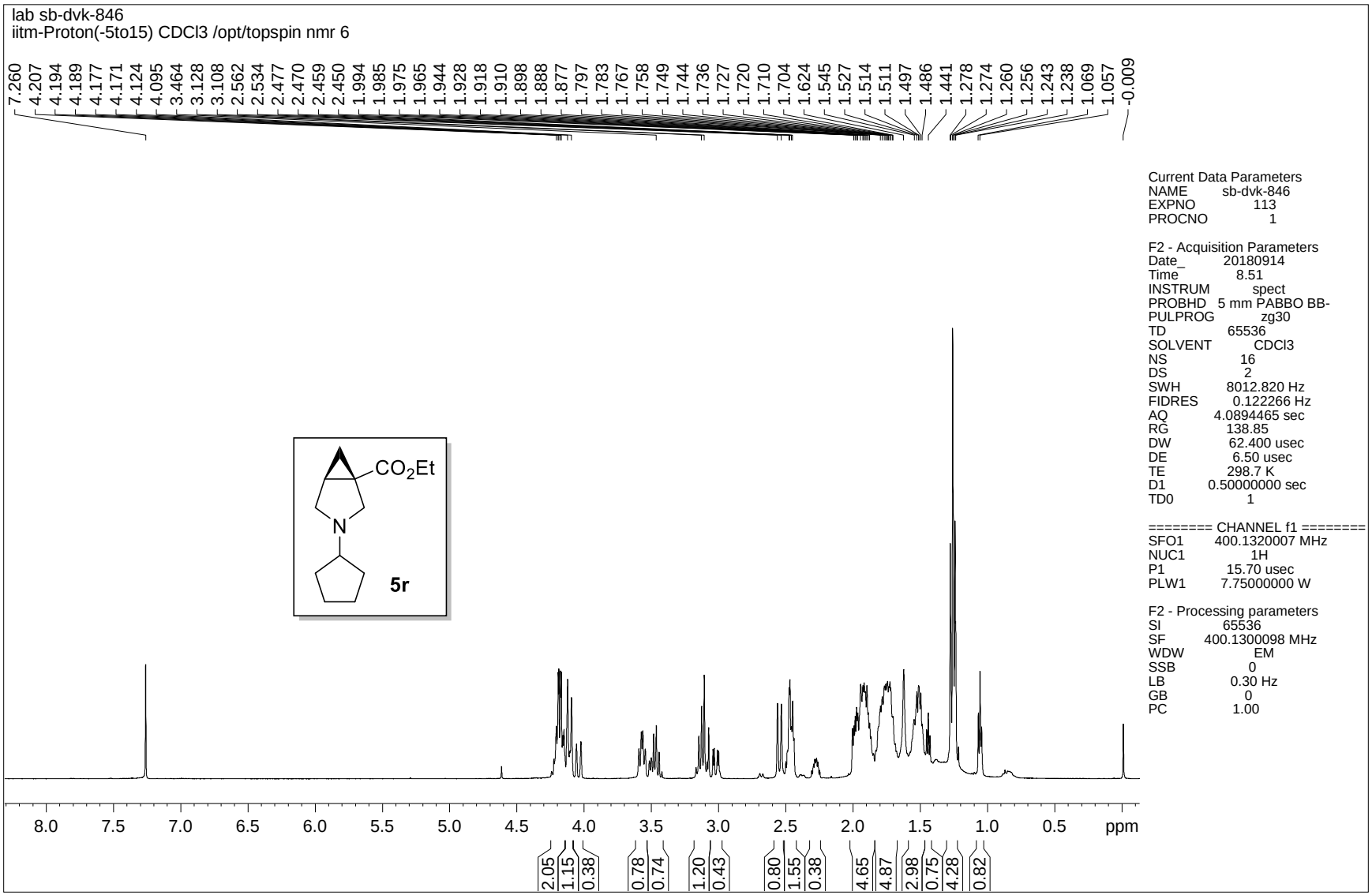
DEPT-135 NMR spectrum of compound 5q



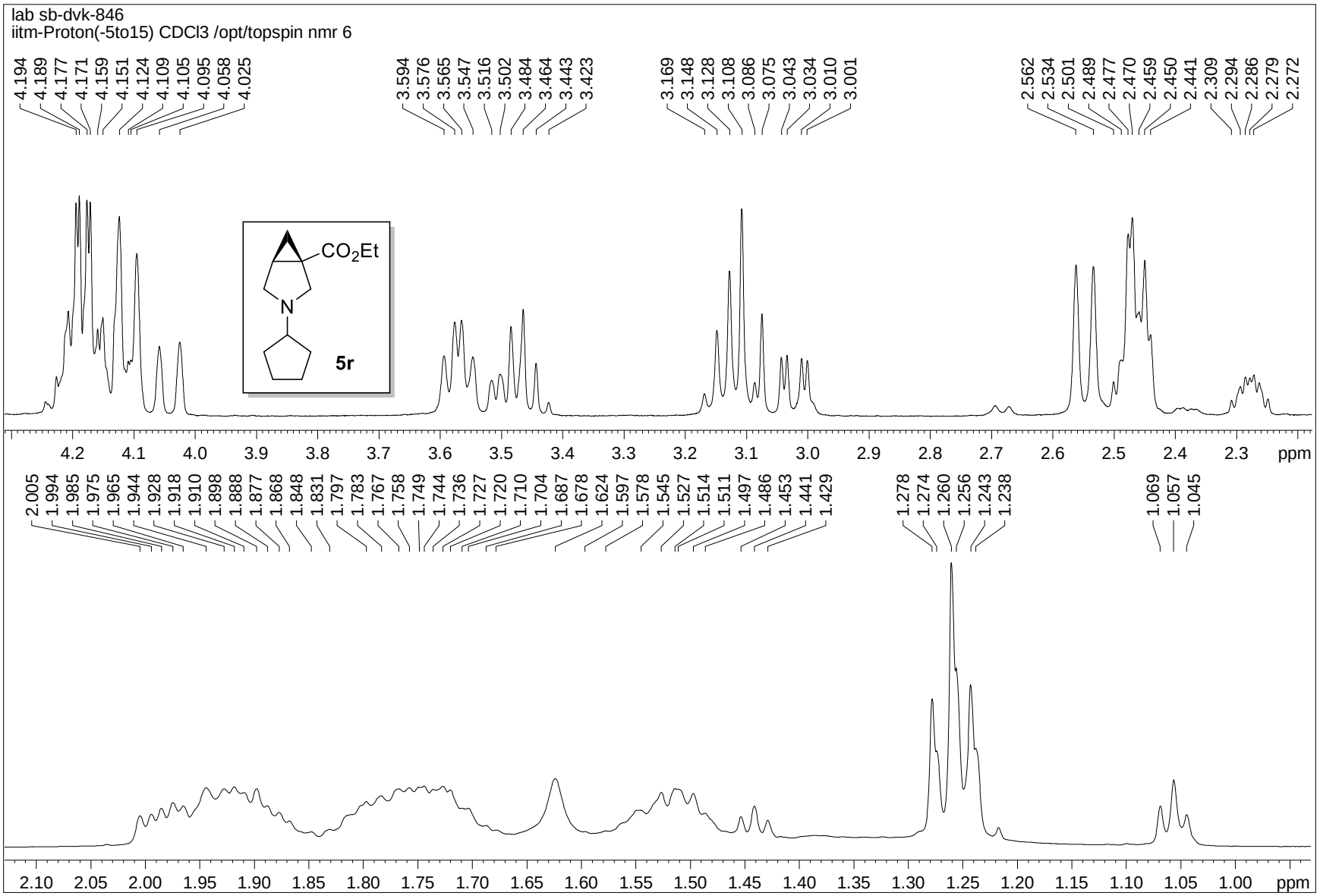
^{1}H-^{1}H COSY NMR spectrum of compound 5q



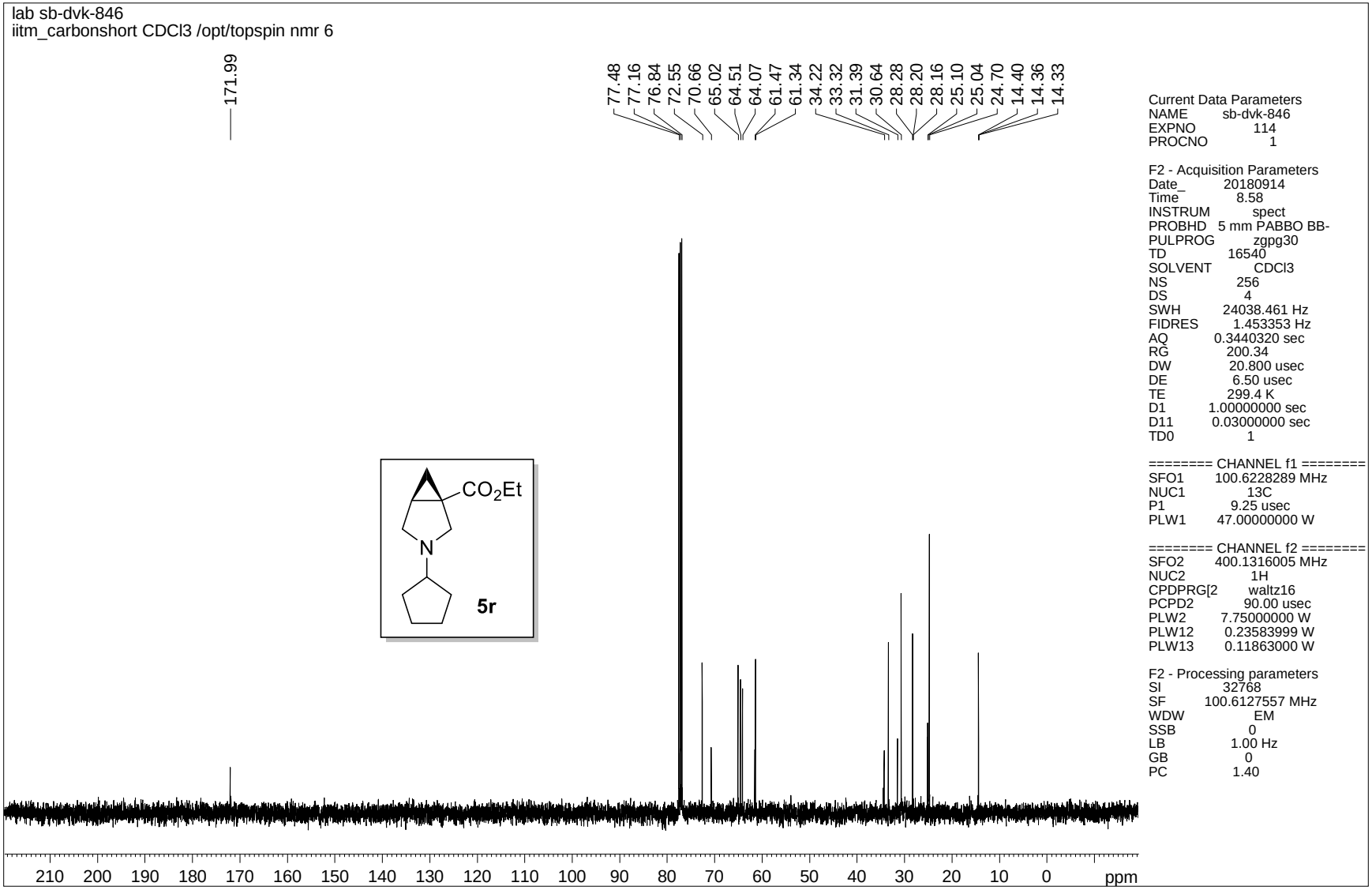
^{1}H-^{13}C HSQC NMR spectrum of compound 5q



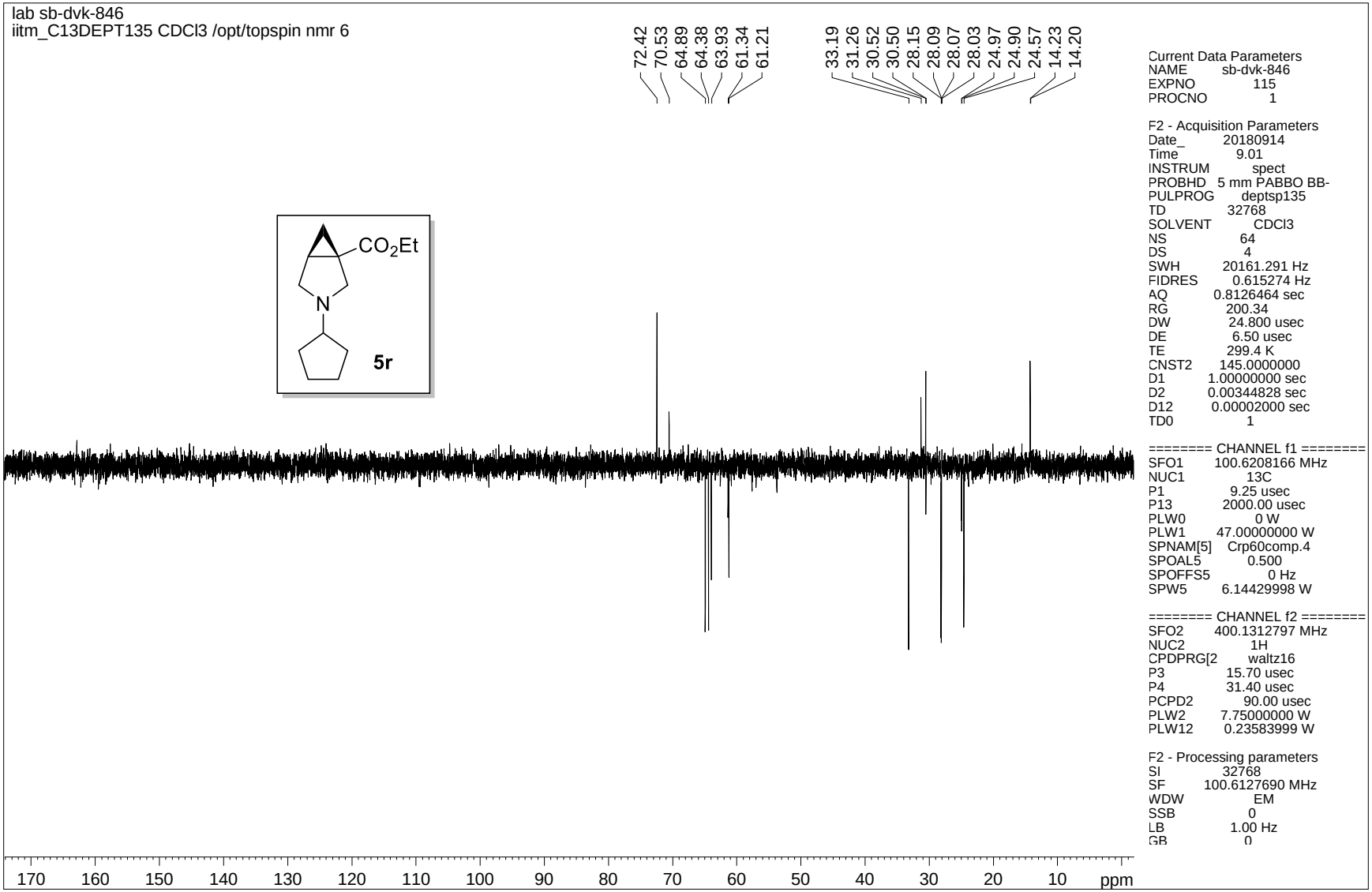
^{1}H NMR spectrum of compound 5r



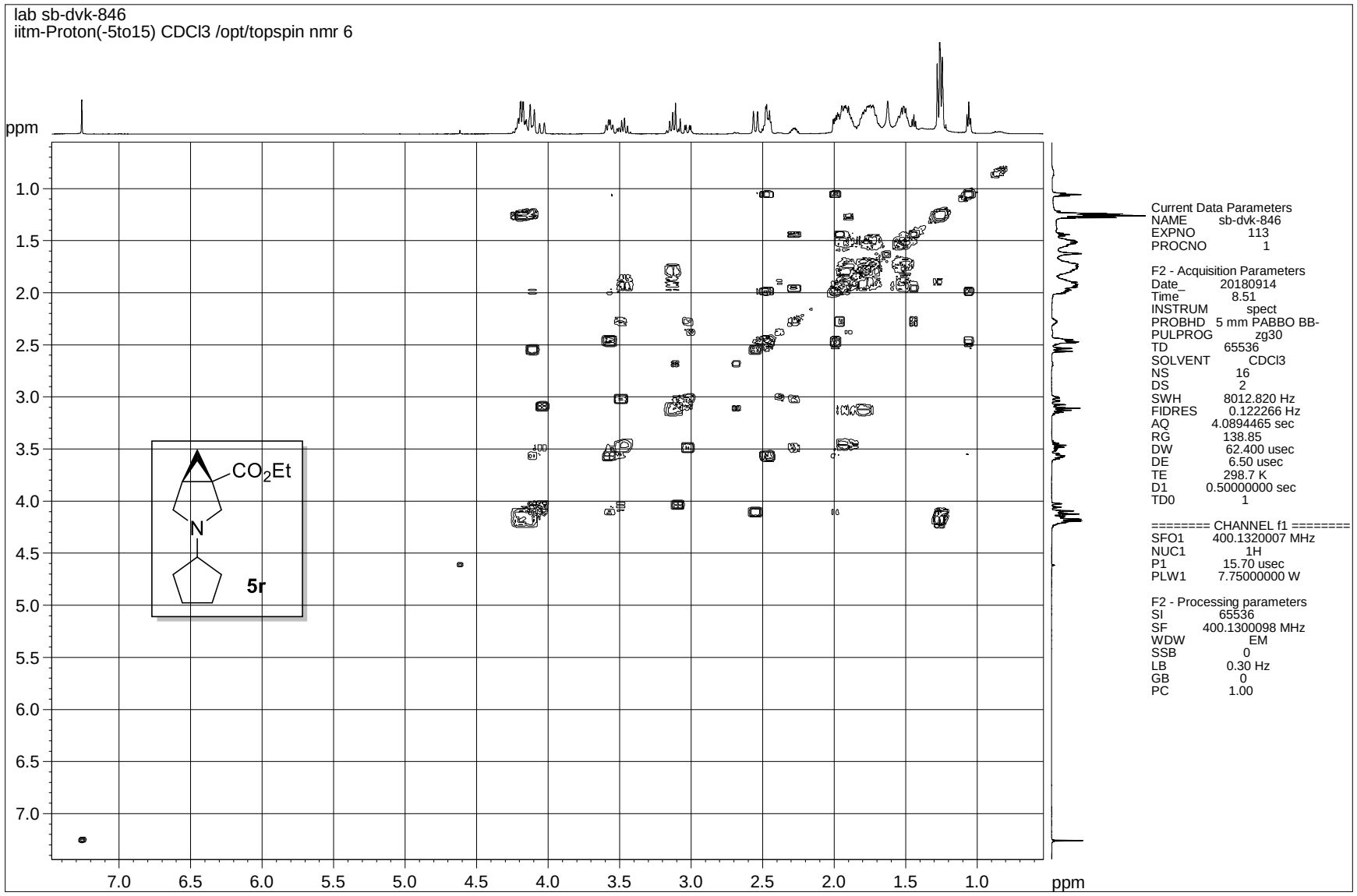
^{1}H NMR spectrum of compound 5r



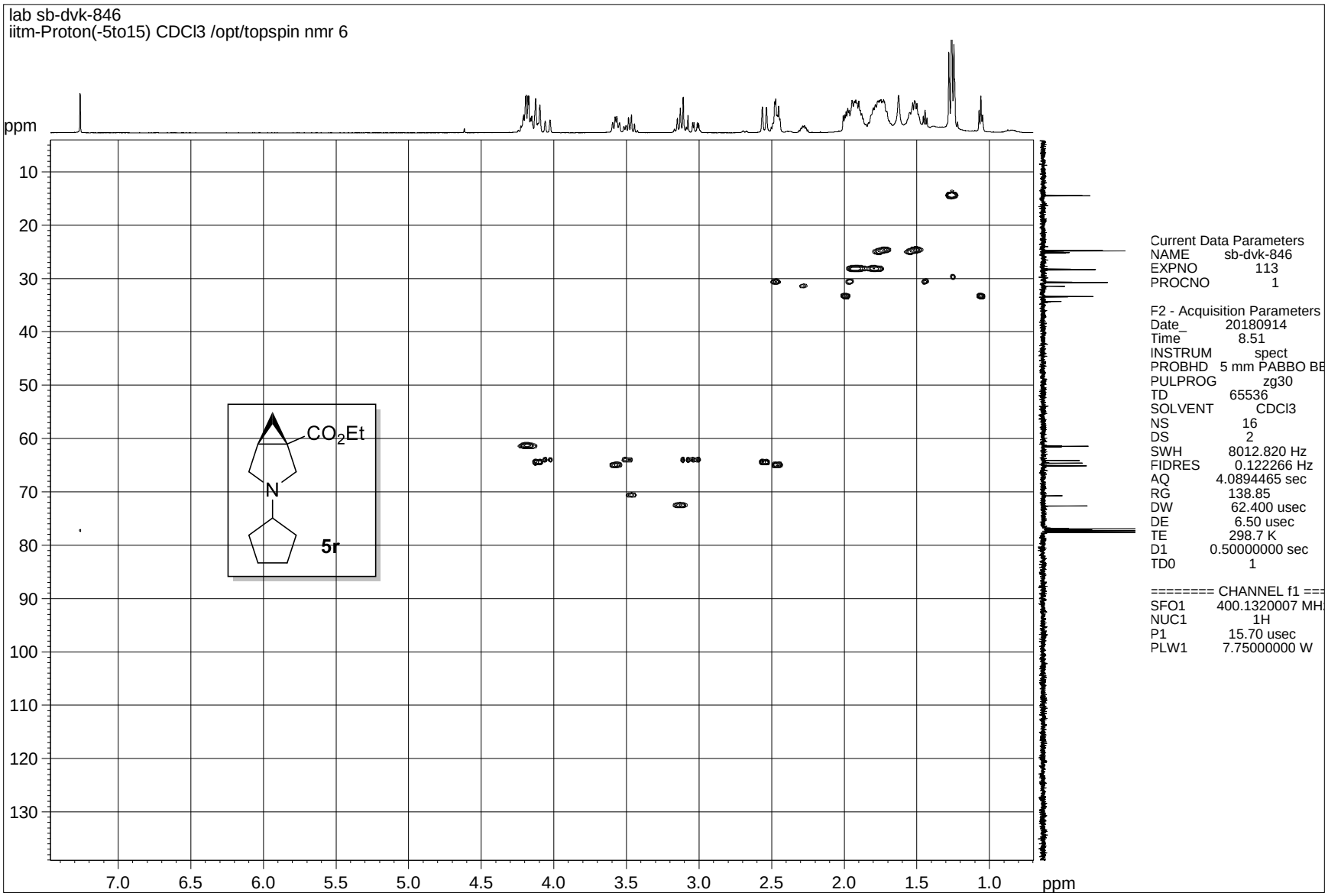
^{13}C NMR spectrum of compound 5r



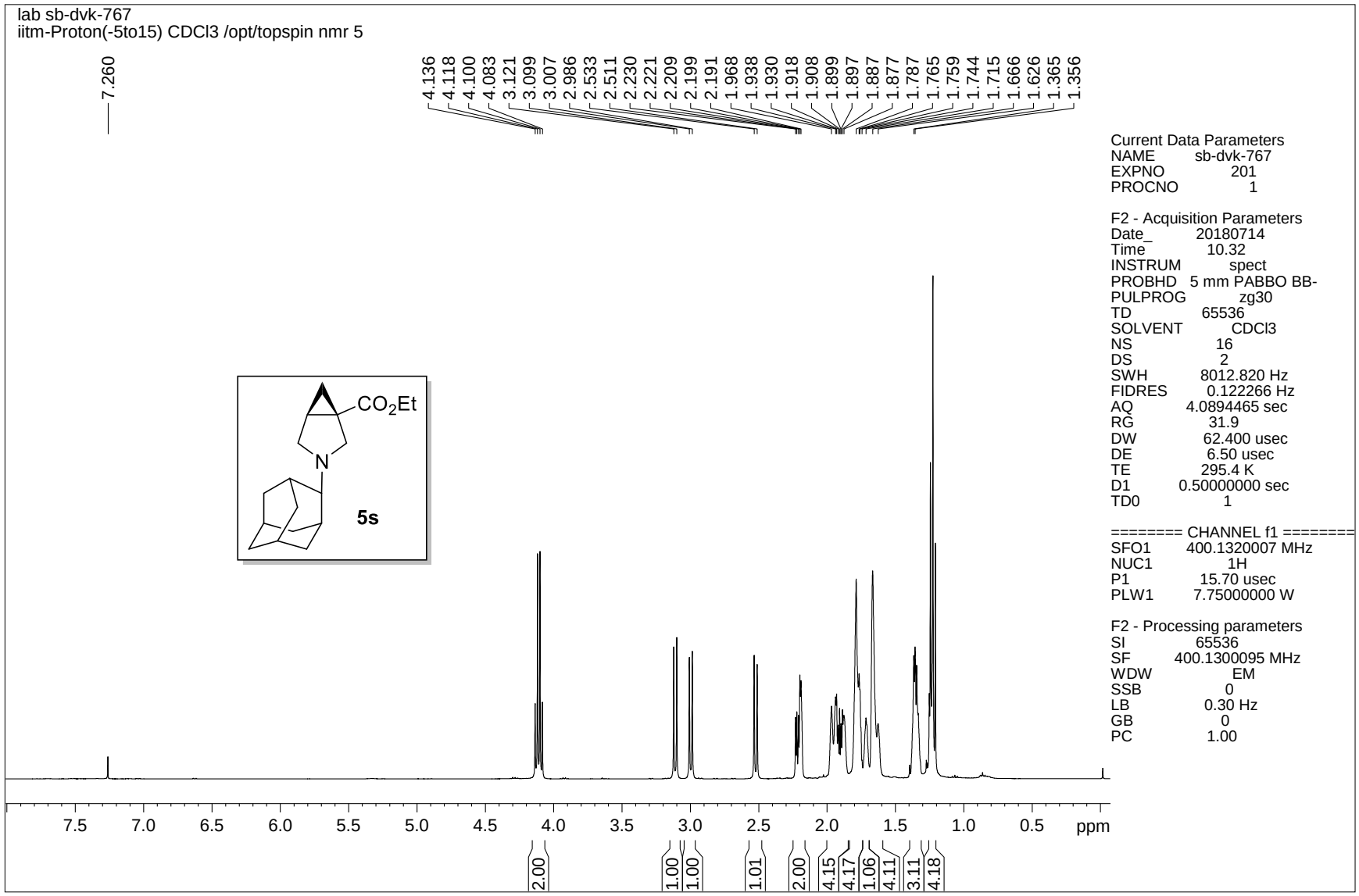
DEPT-135 NMR spectrum of compound 5r



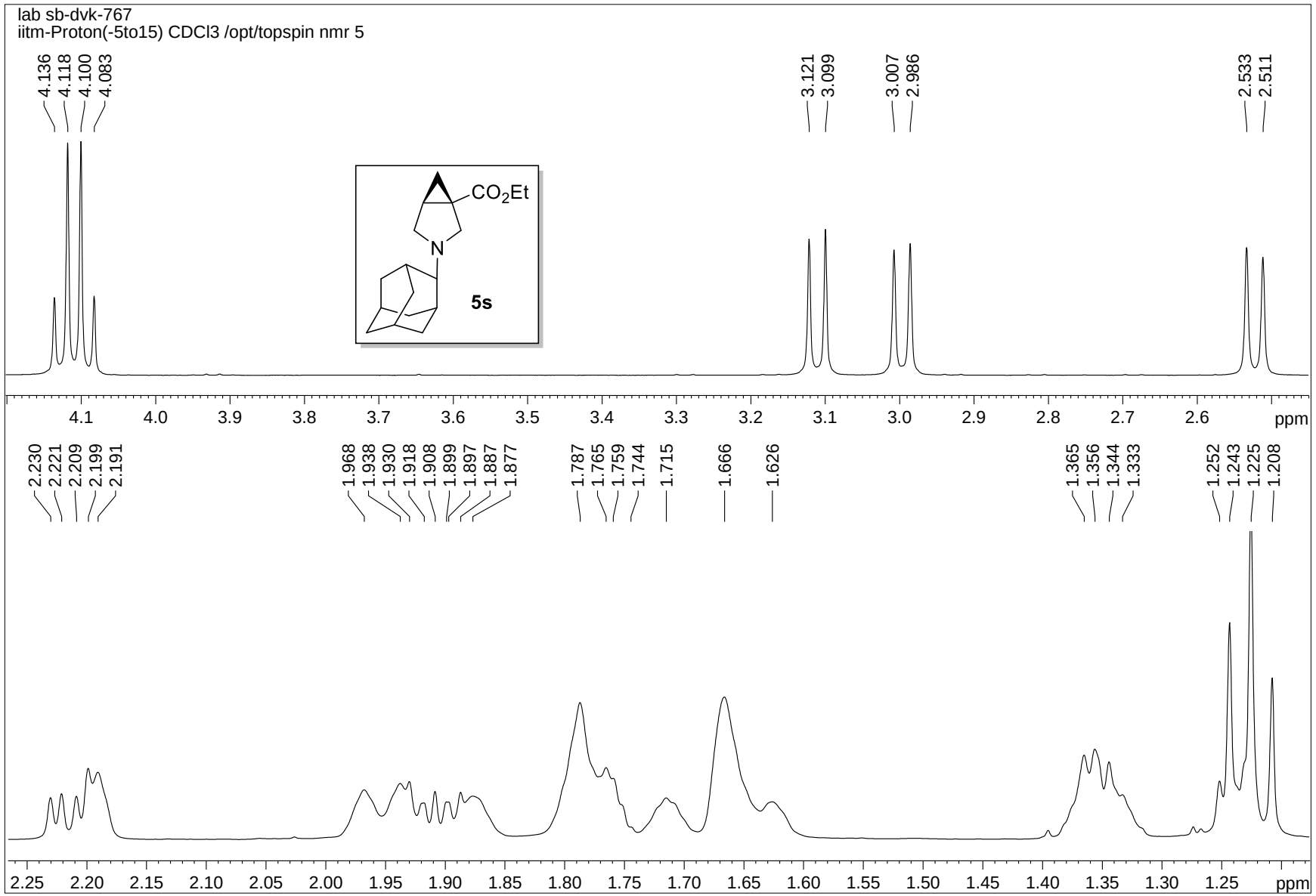
^{1}H-^{1}H COSY NMR spectrum of compound 5r



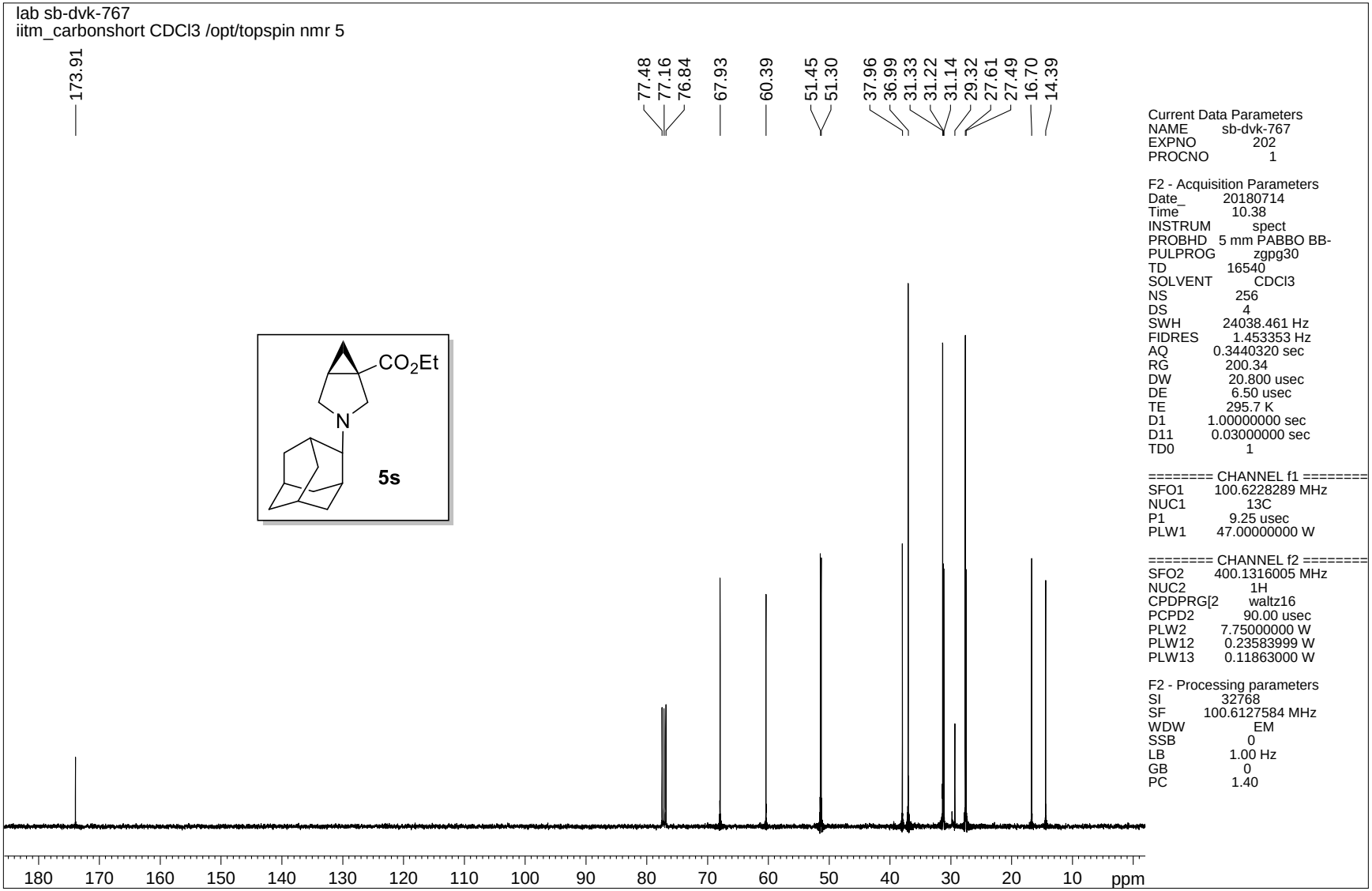
^{1}H-^{13}C HSQC NMR spectrum of compound 5r



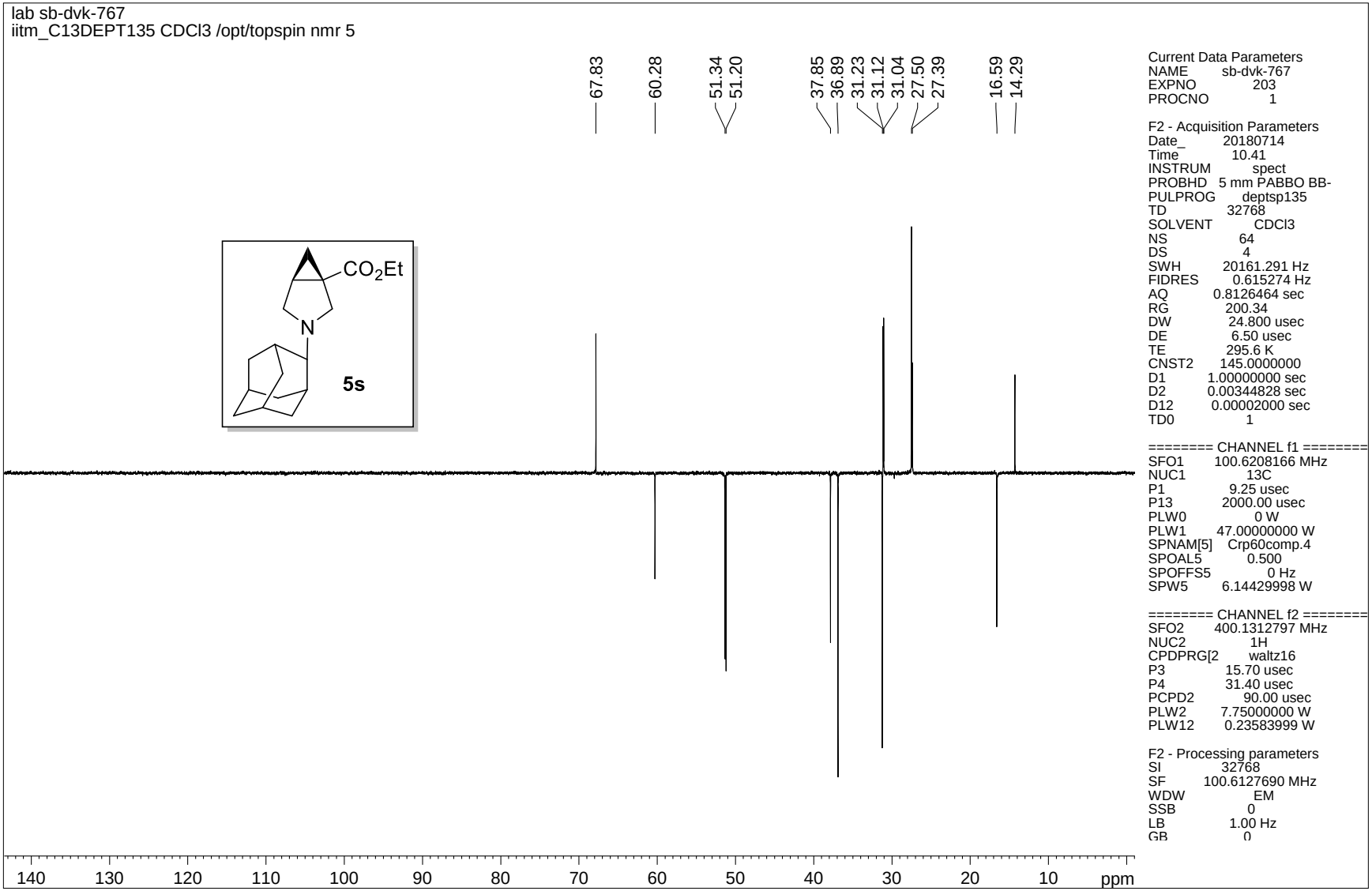
^{1}H NMR spectrum of compound 5s



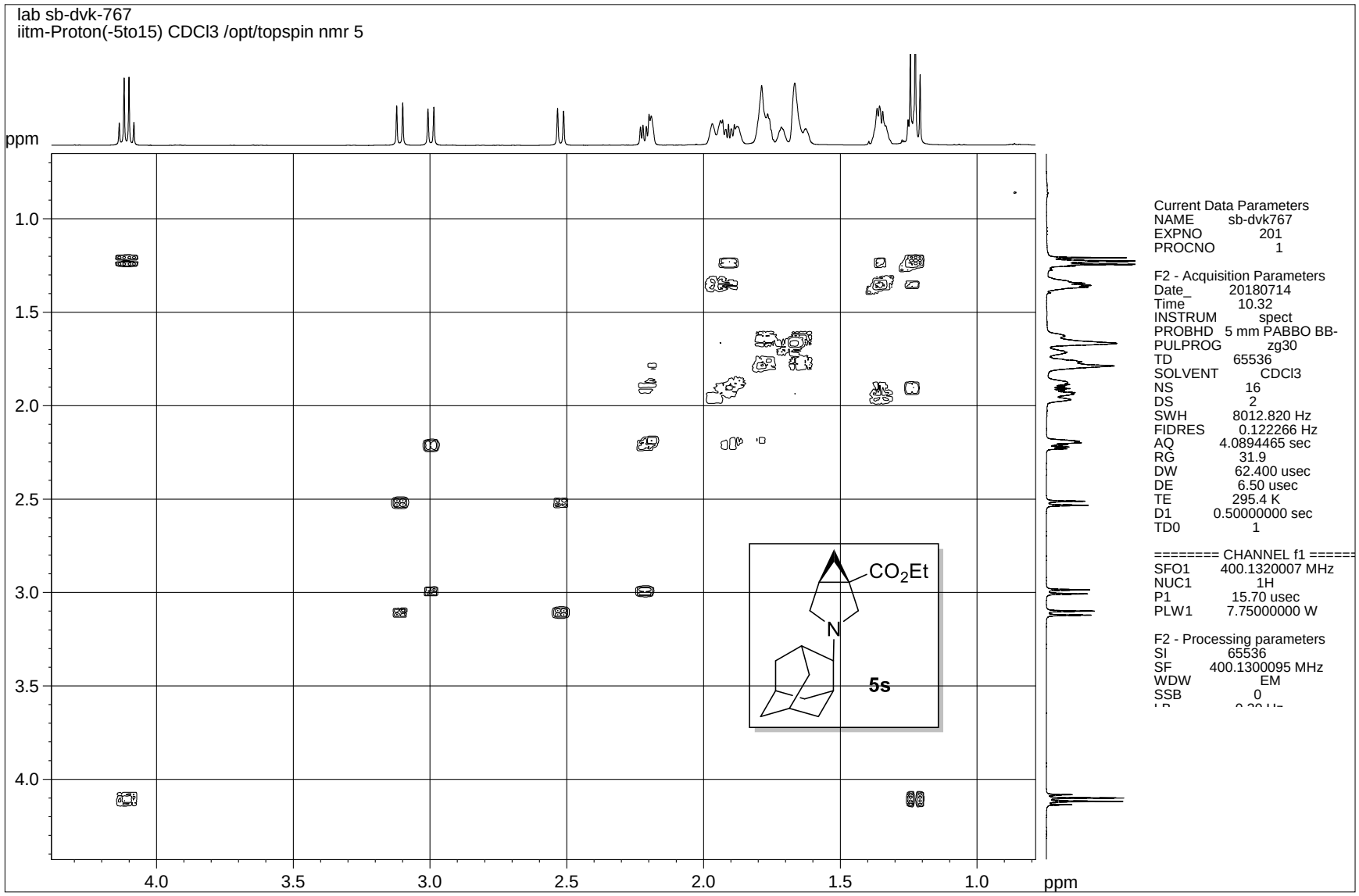
^{1}H NMR spectrum of compound 5s



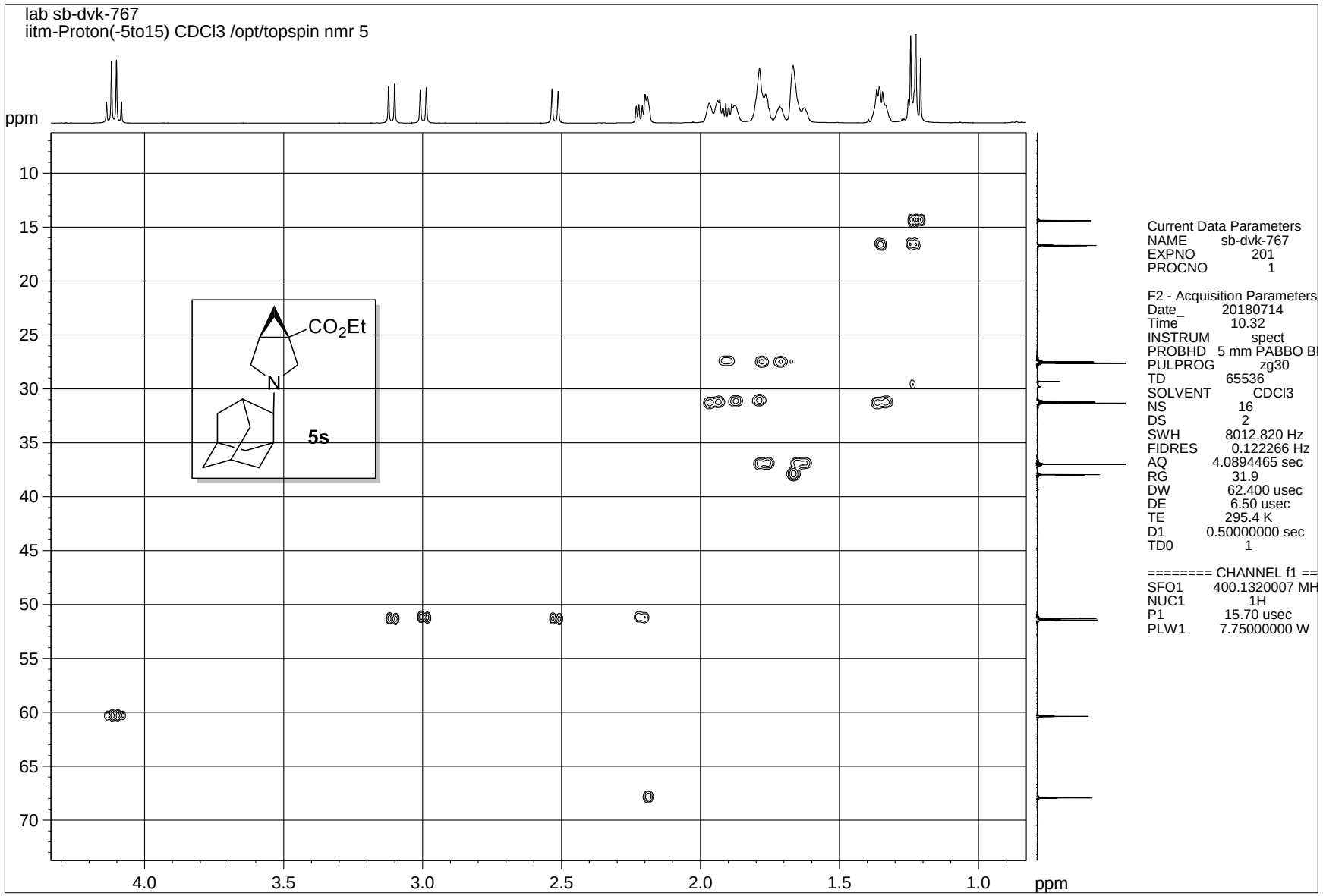
^{13}C NMR spectrum of compound 5s



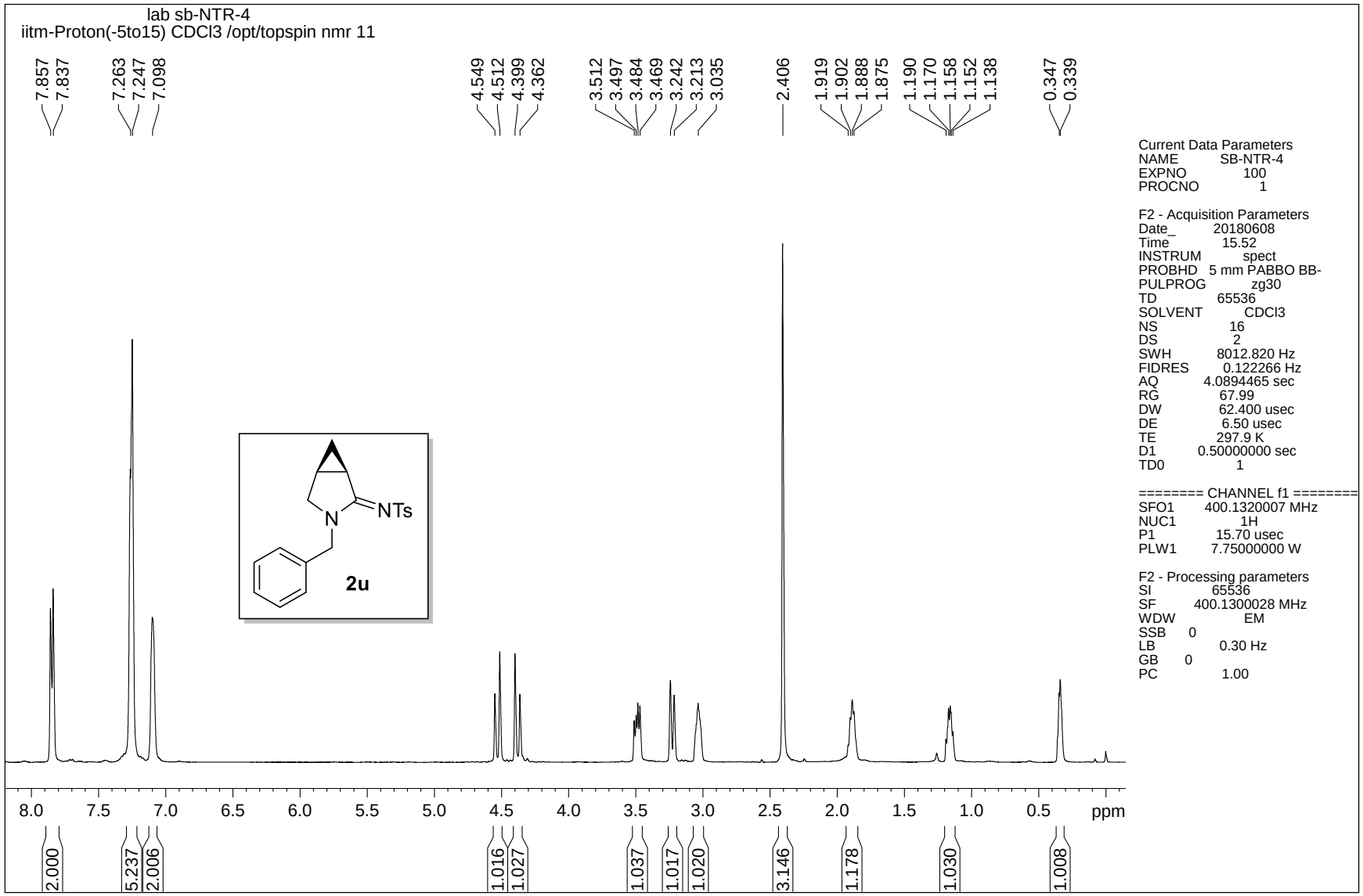
DEPT-135 NMR spectrum of compound 5s



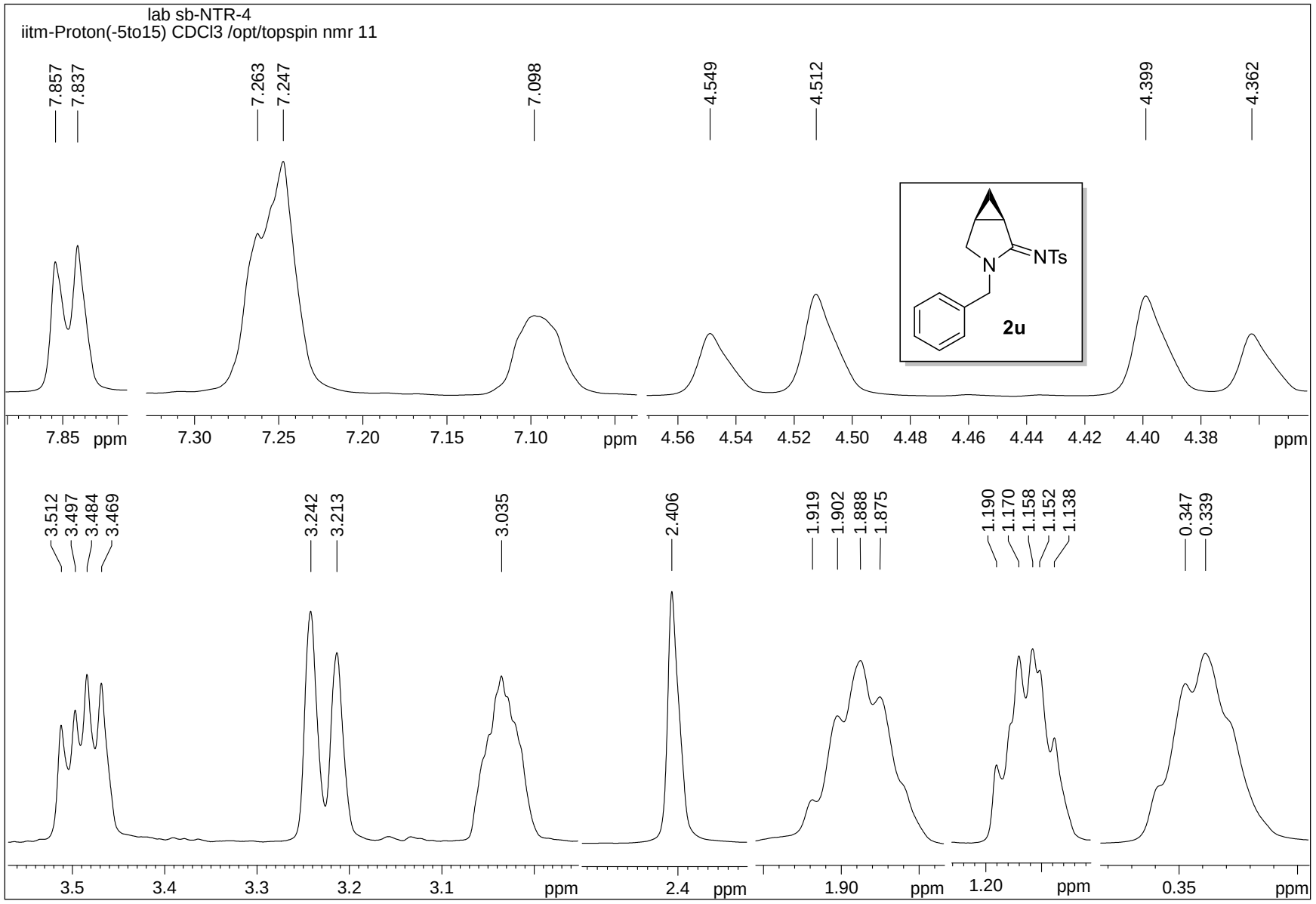
^{1}H-^{1}H COSY NMR spectrum of compound 5s



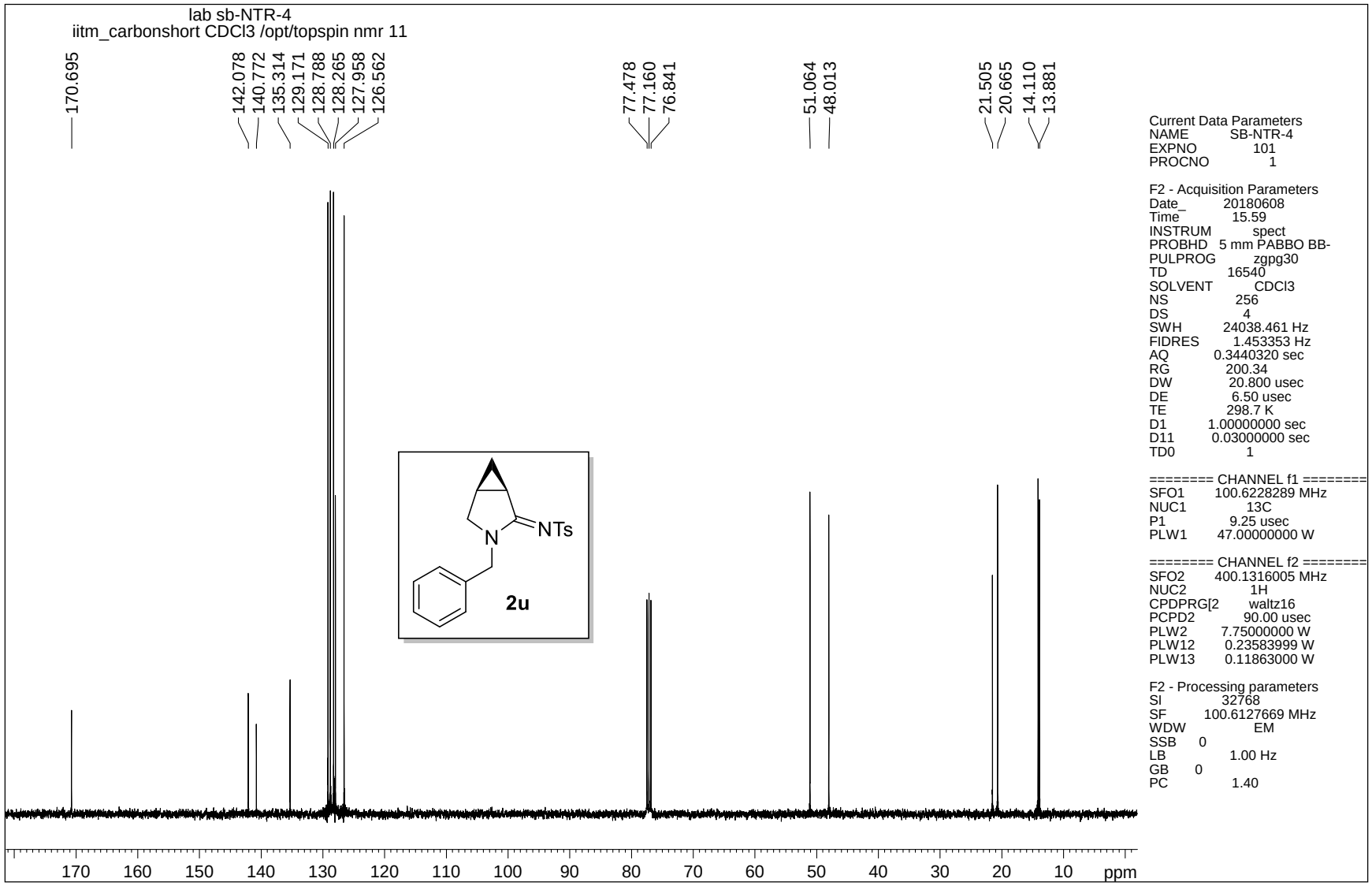
^{1}H-^{13}C HSQC NMR spectrum of compound 5s



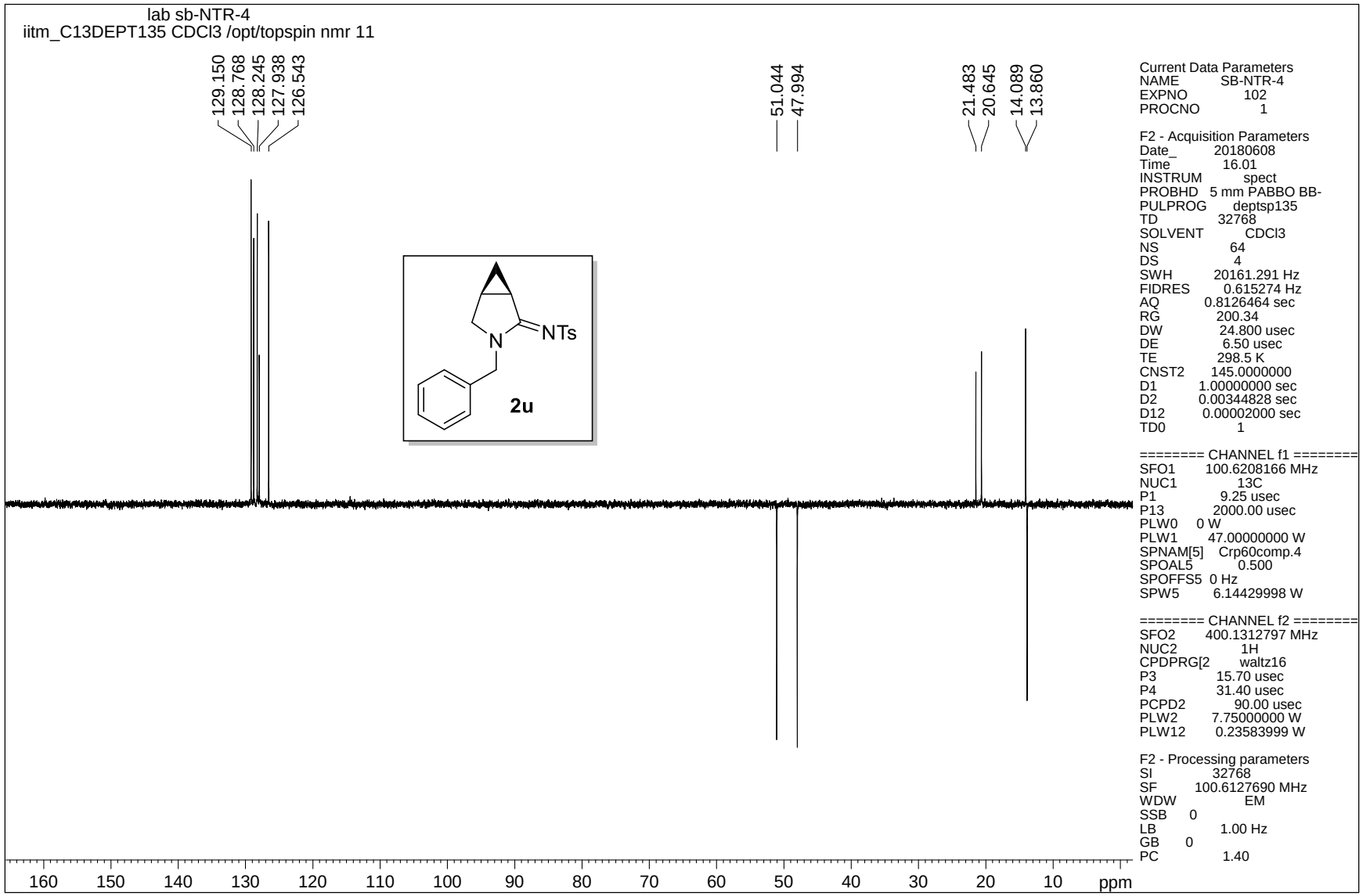
^{1}H NMR spectrum of compound 2u



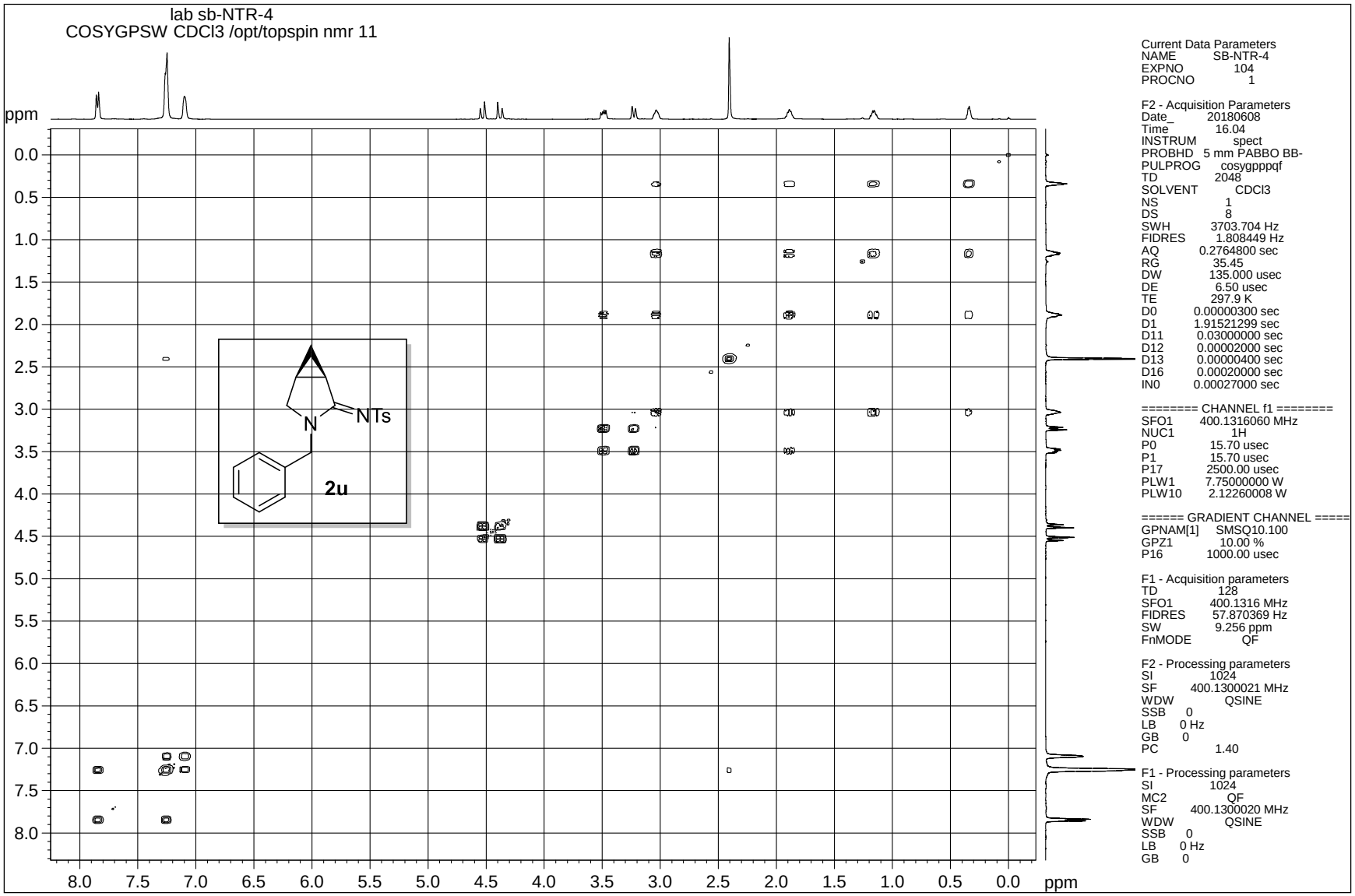
^{1}H NMR spectrum of compound 2u



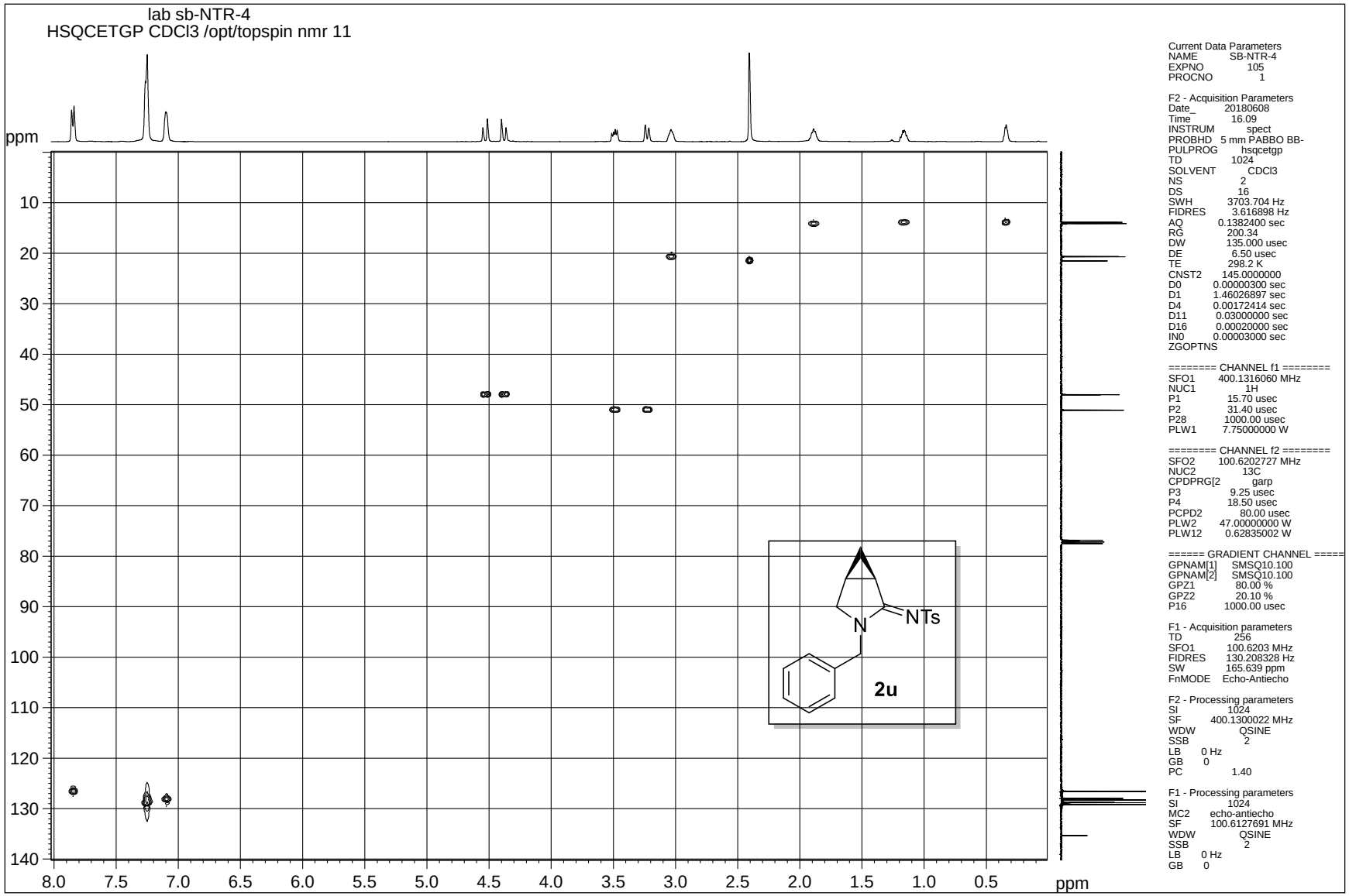
^{13}C NMR spectrum of compound 2u



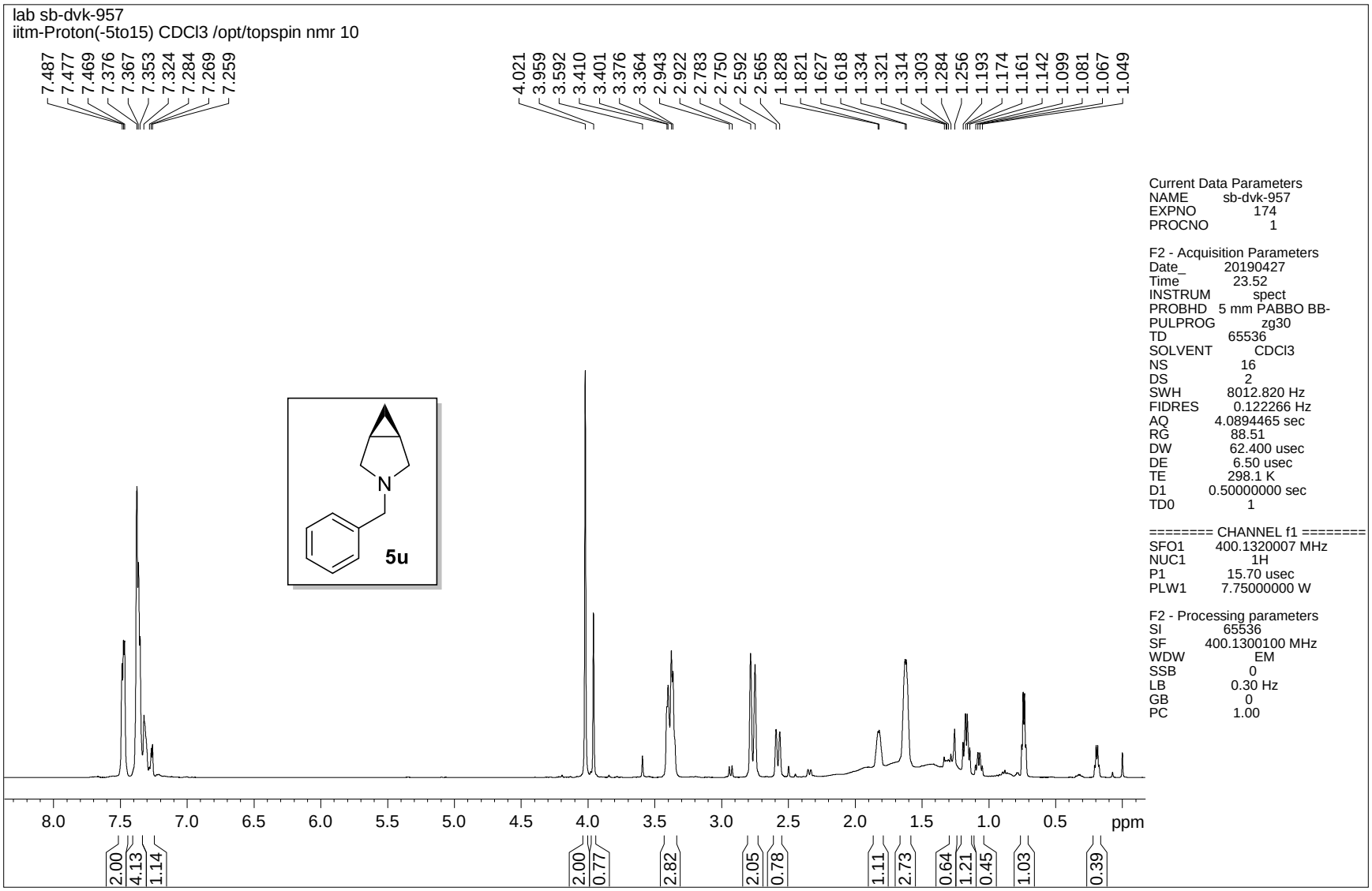
DEPT-135 NMR spectrum of compound 2u



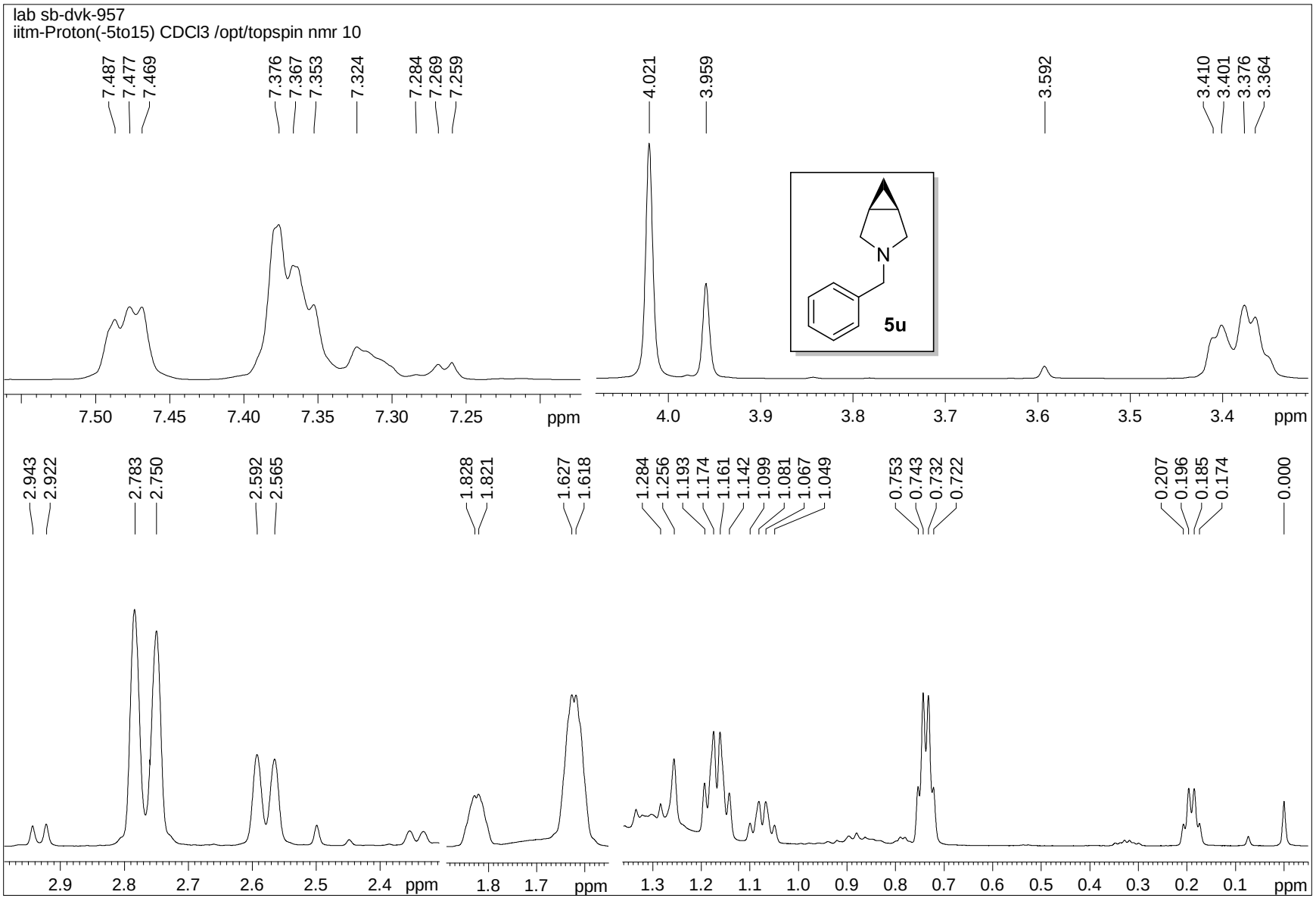
^{1}H-^{1}H COSY NMR spectrum of compound 2u



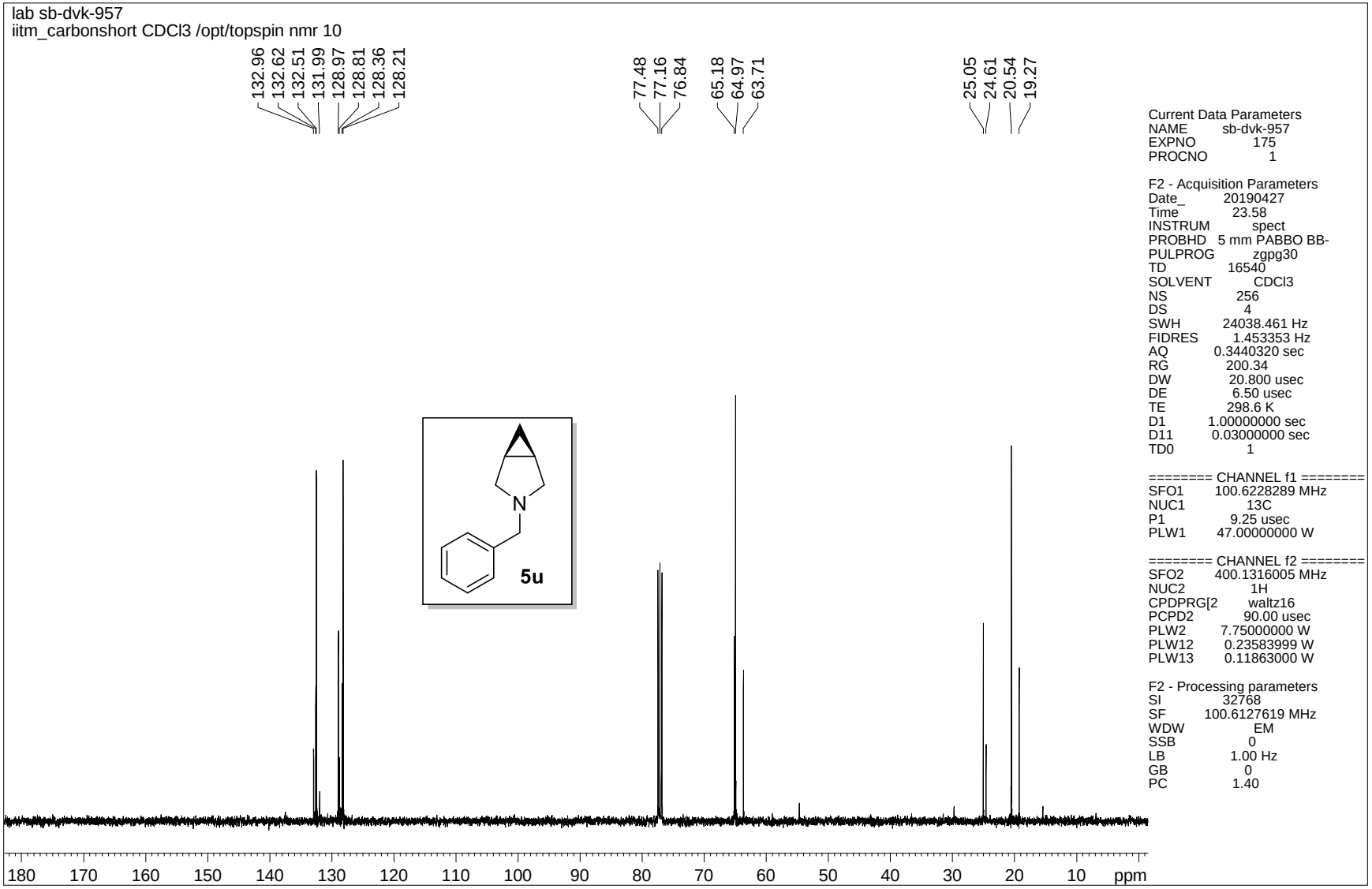
^{1}H-^{13}C HSQC NMR spectrum of compound 2u



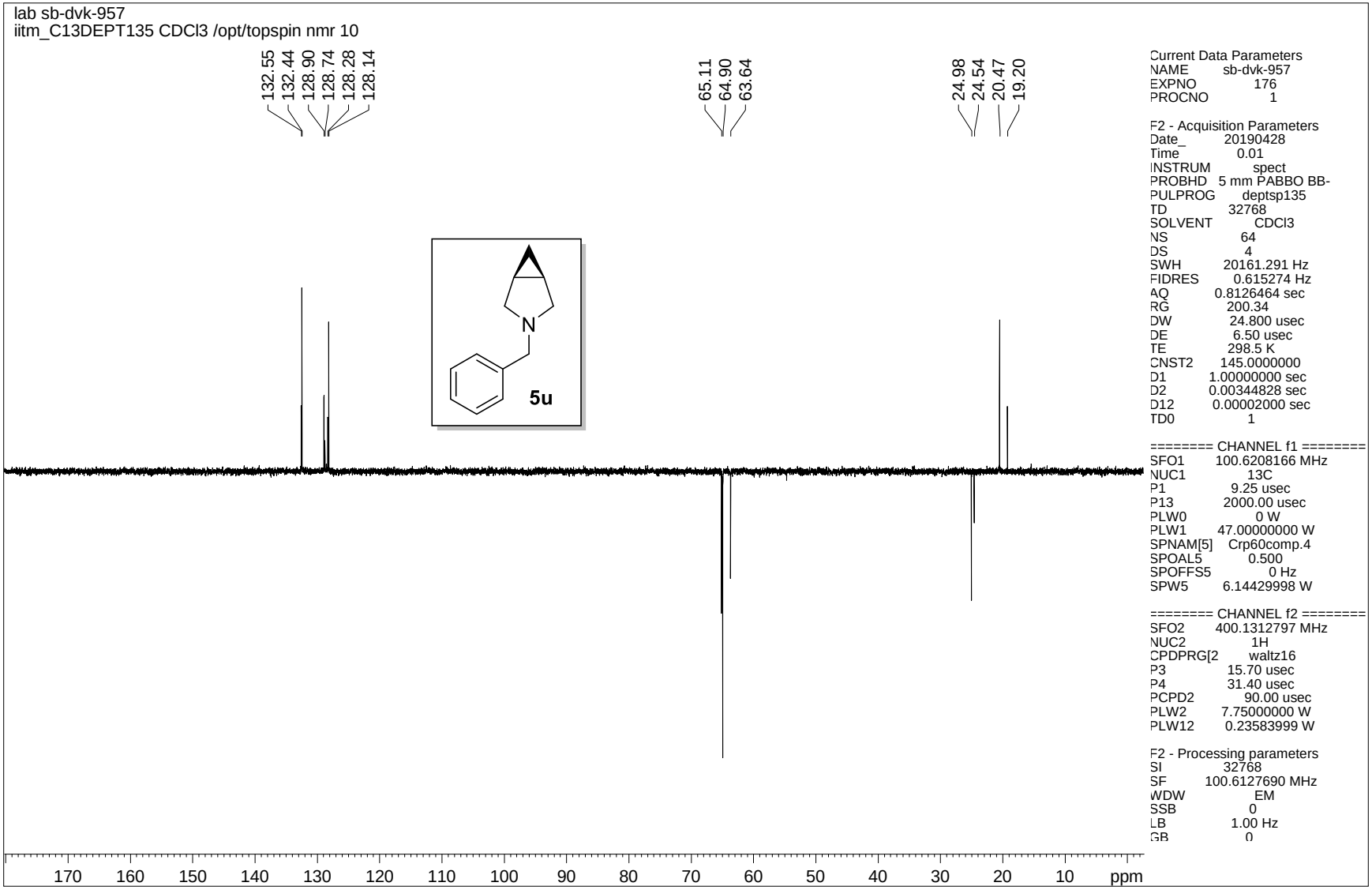
^{1}H NMR spectrum of compound 5u



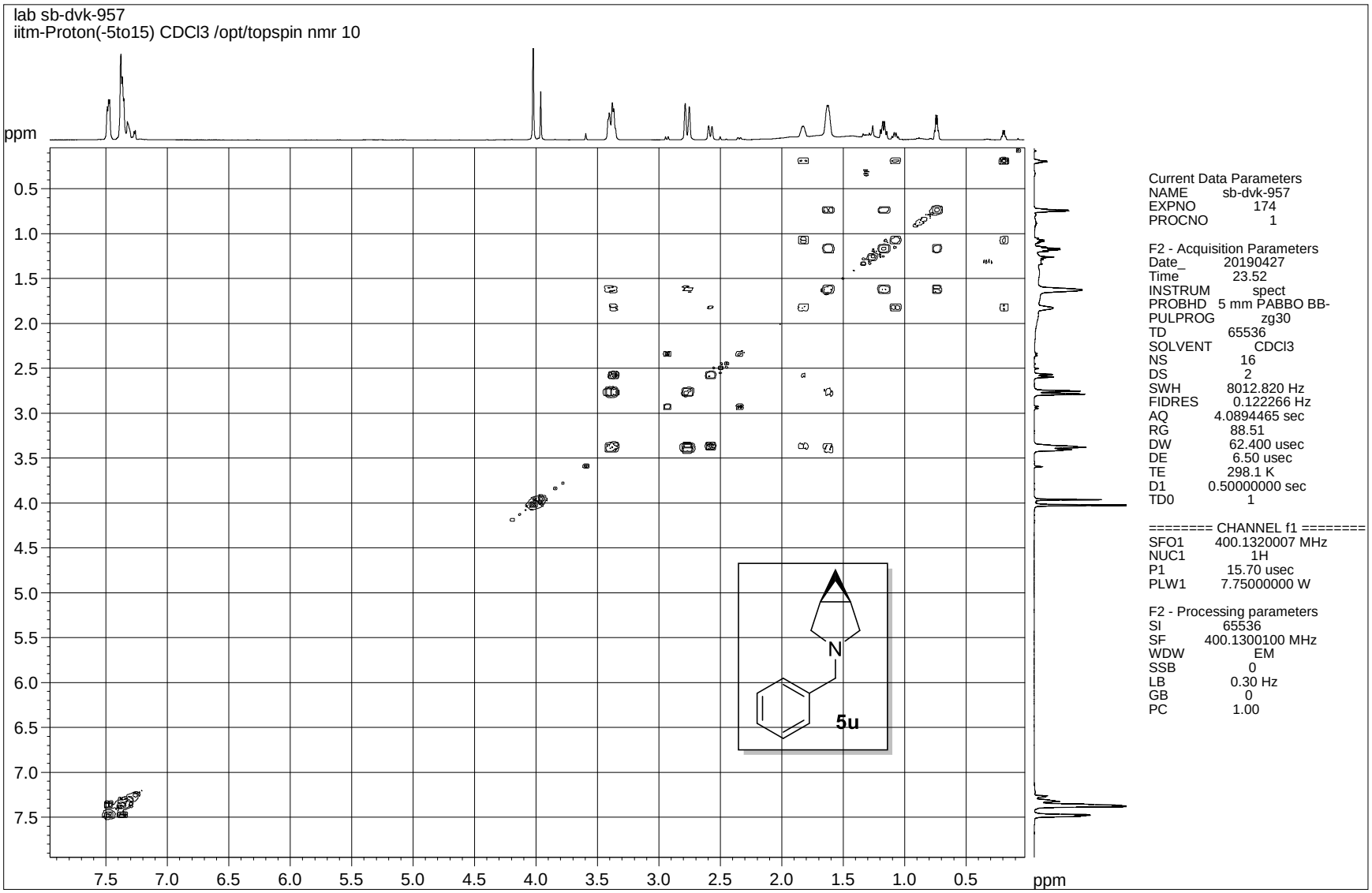
^{1}H NMR spectrum of compound 5u



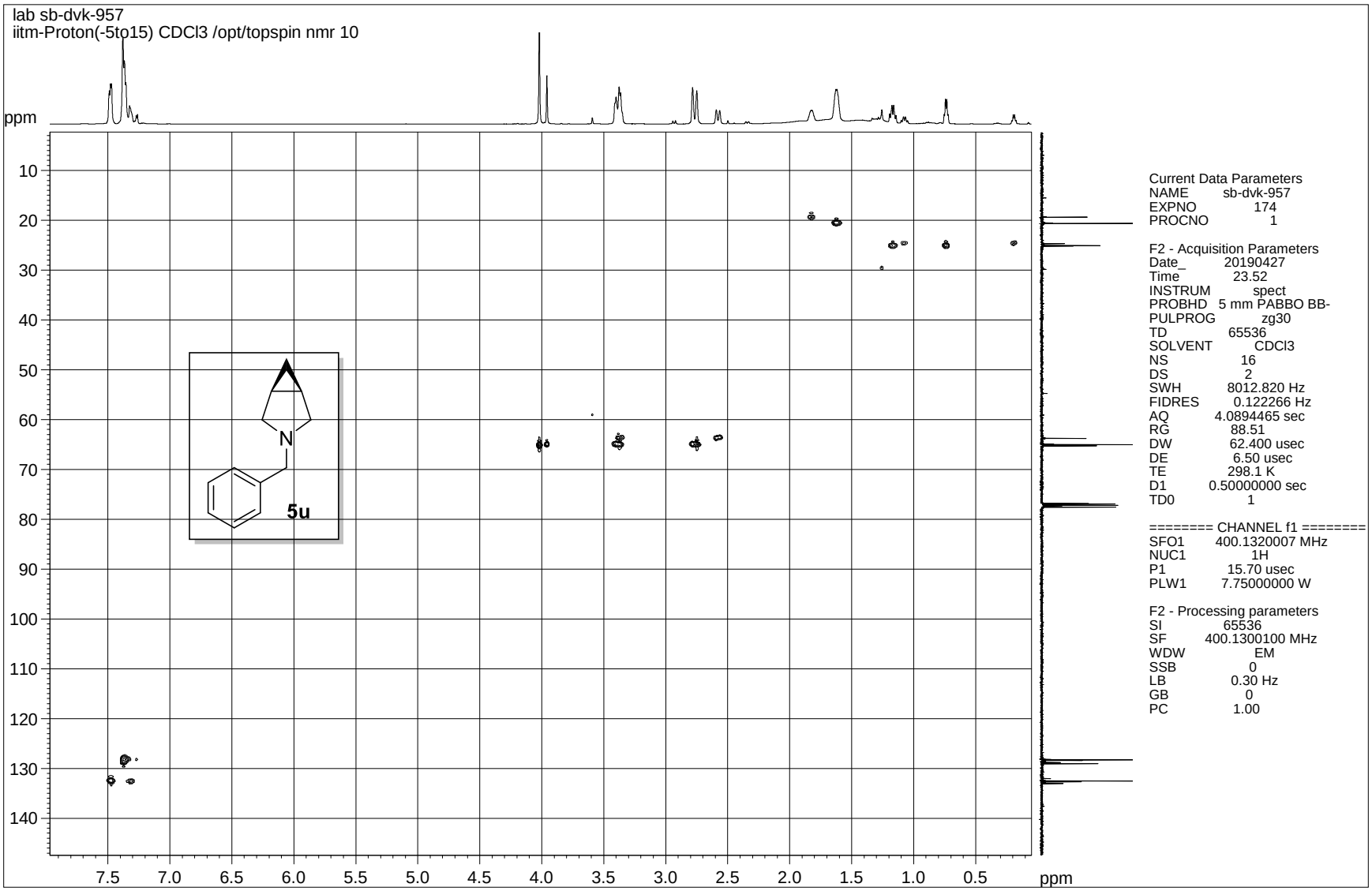
^{13}C NMR spectrum of compound 5u



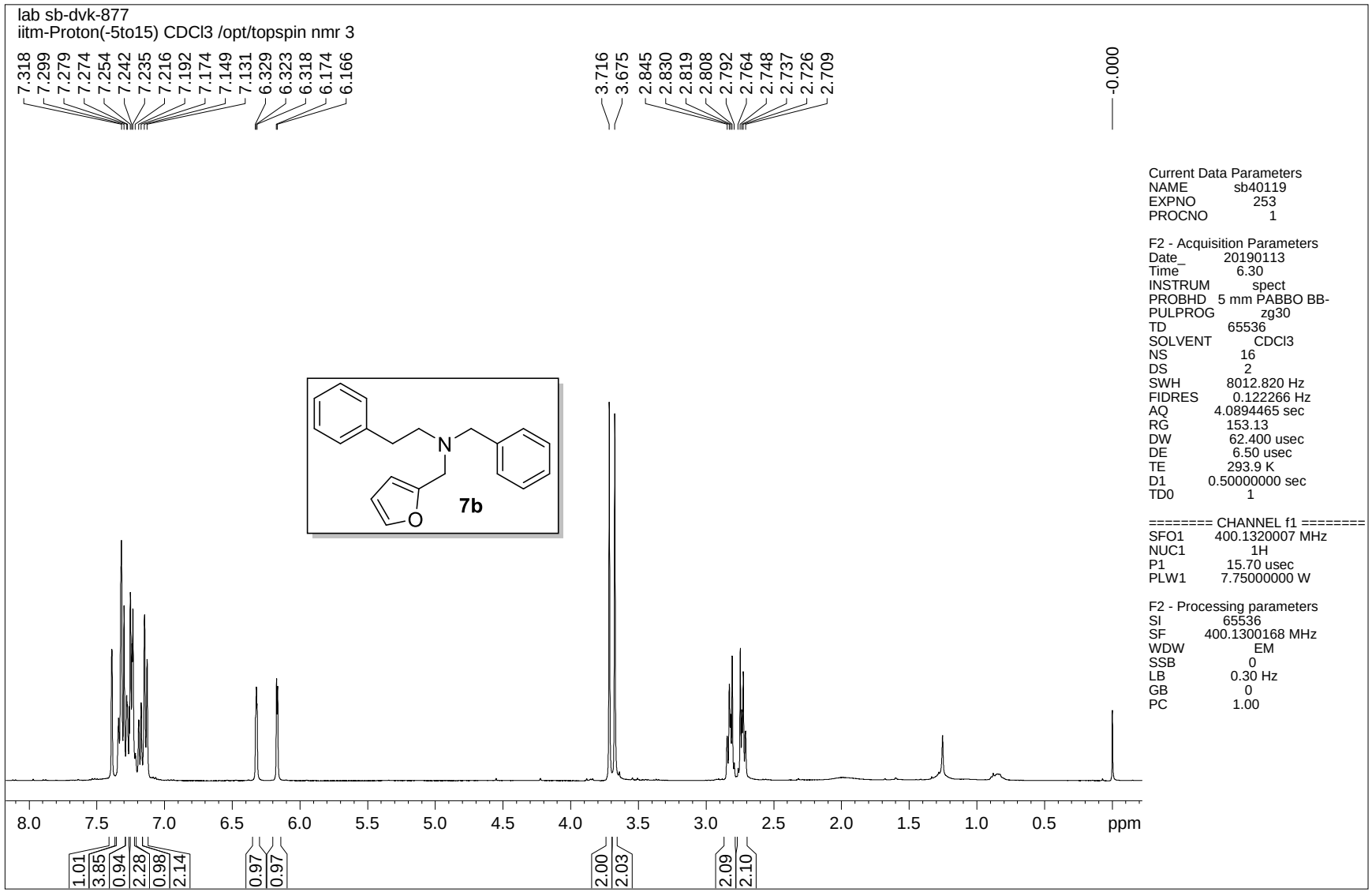
DEPT-135 NMR spectrum of compound 5u



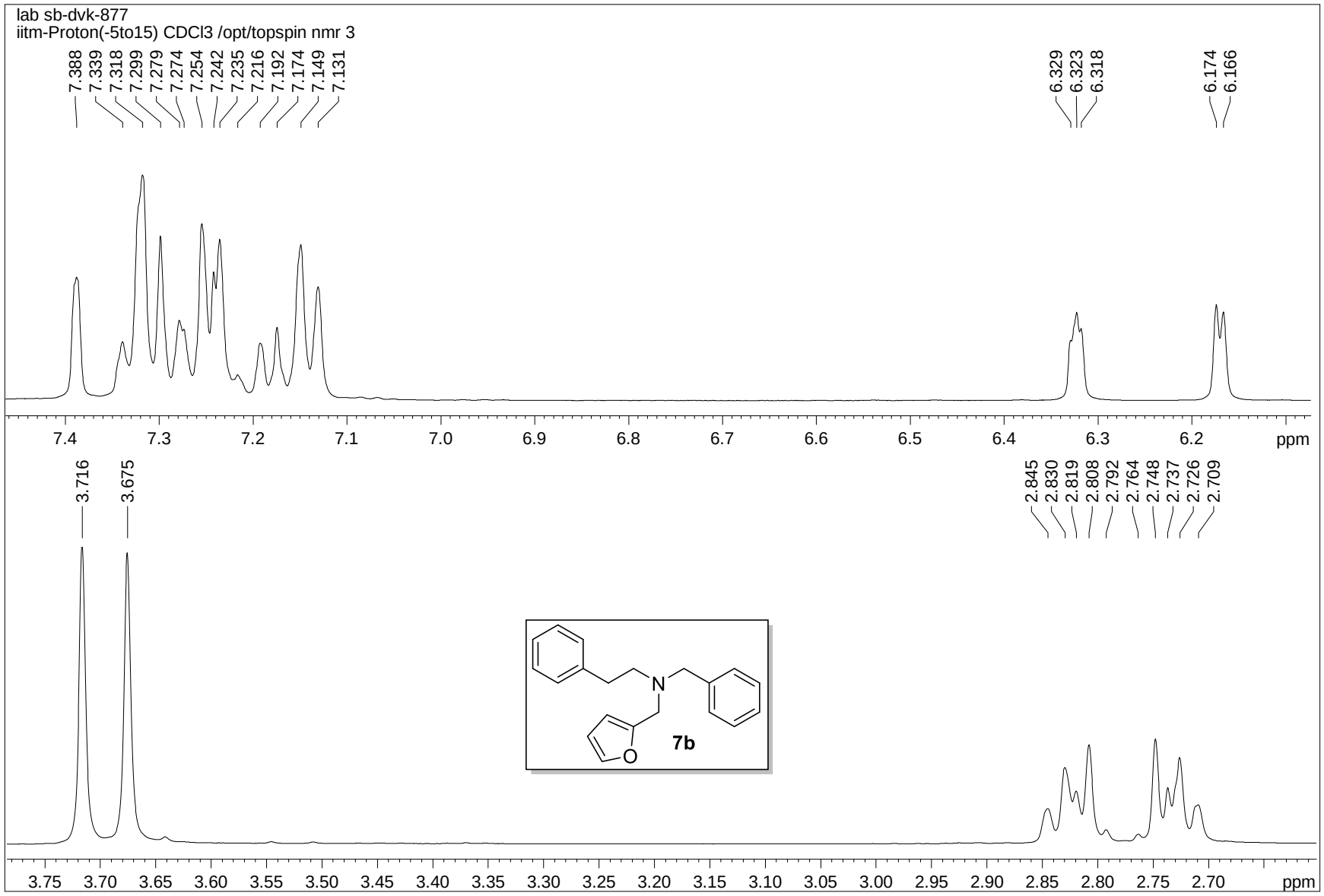
^{1}H-^{1}H COSY NMR spectrum of compound 5u



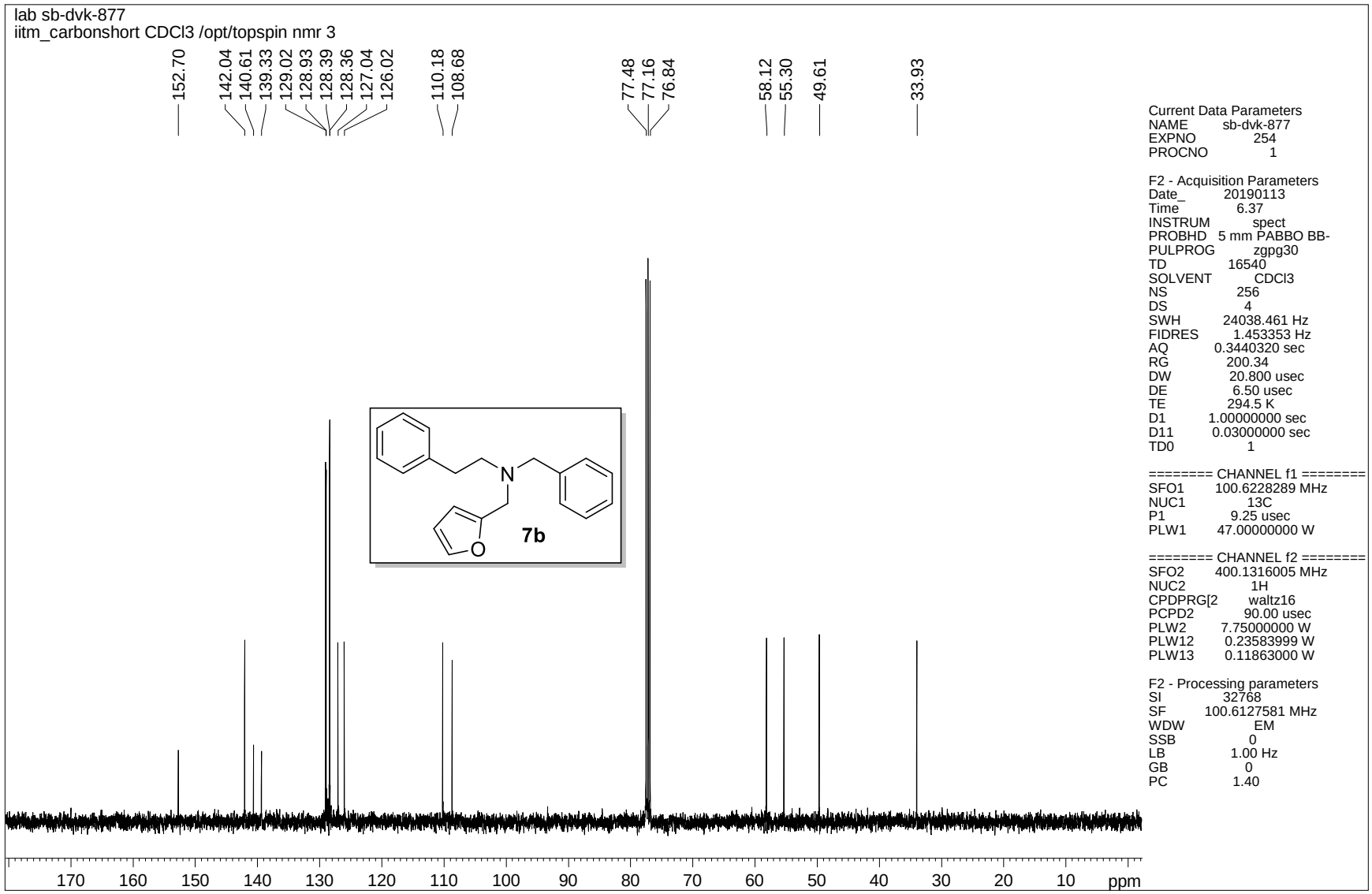
^{1}H-^{13}C HSQC NMR spectrum of compound 5u



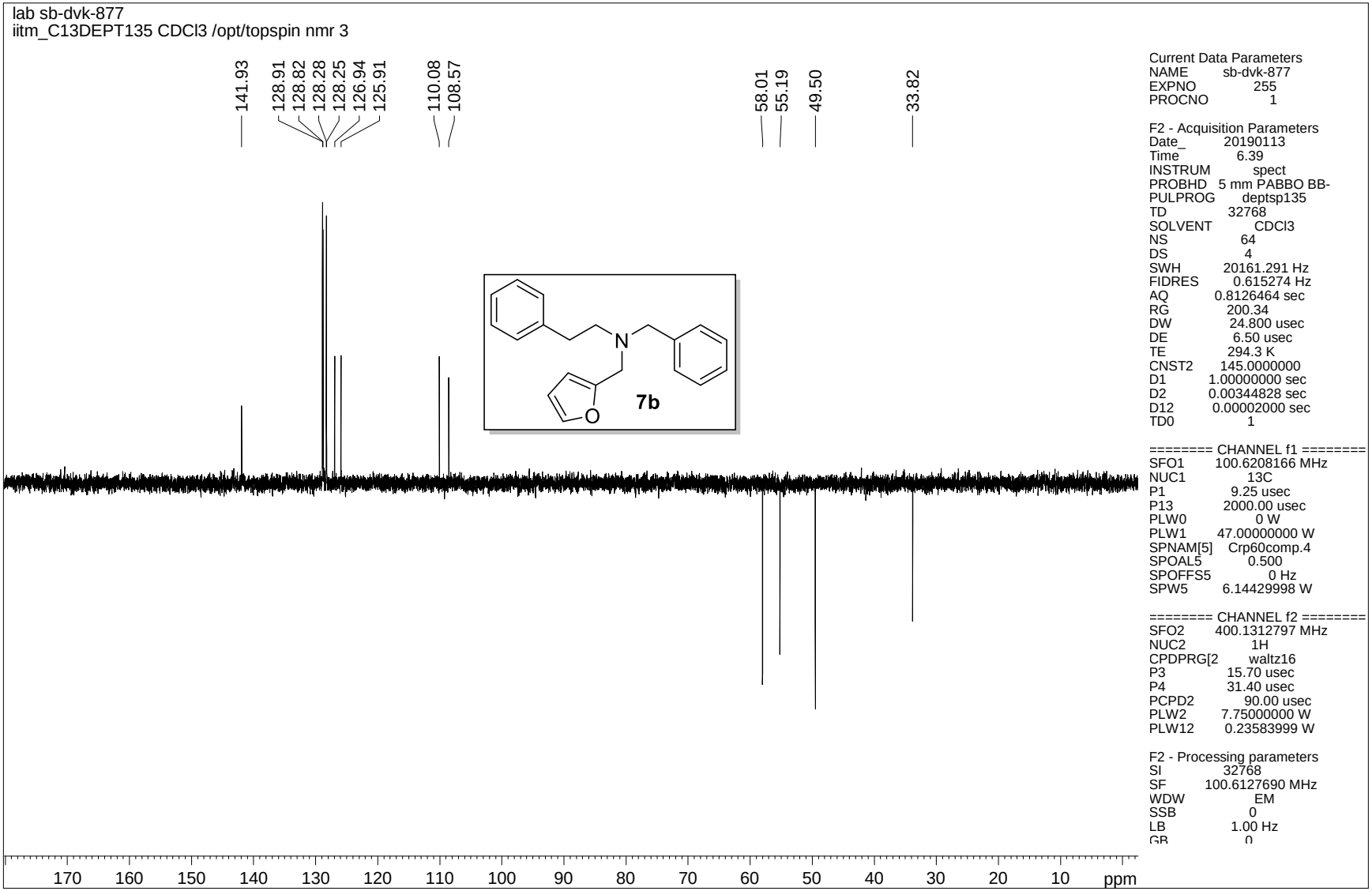
^{1}H NMR spectrum of compound 7b



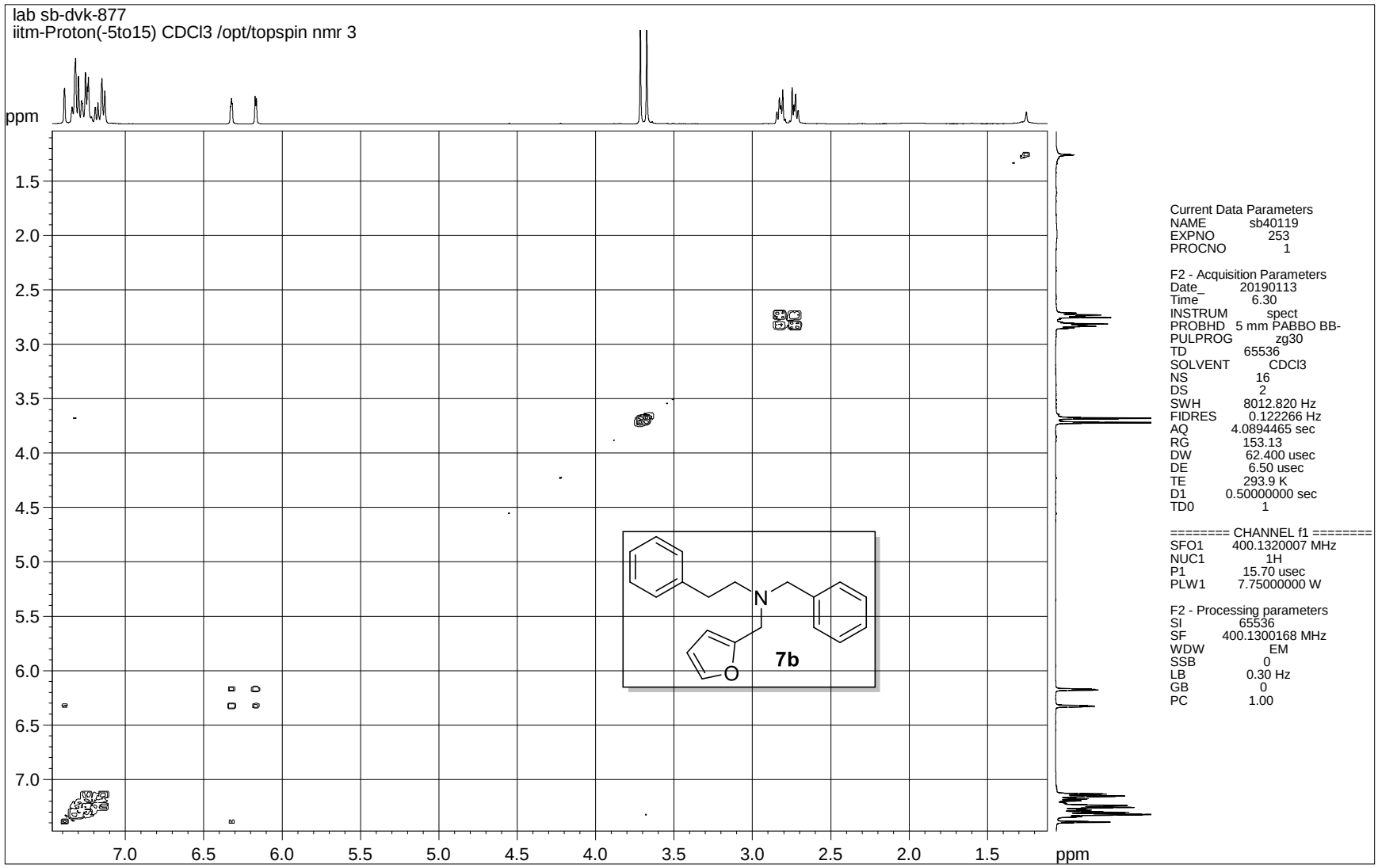
^{1}H NMR spectrum of compound 7b



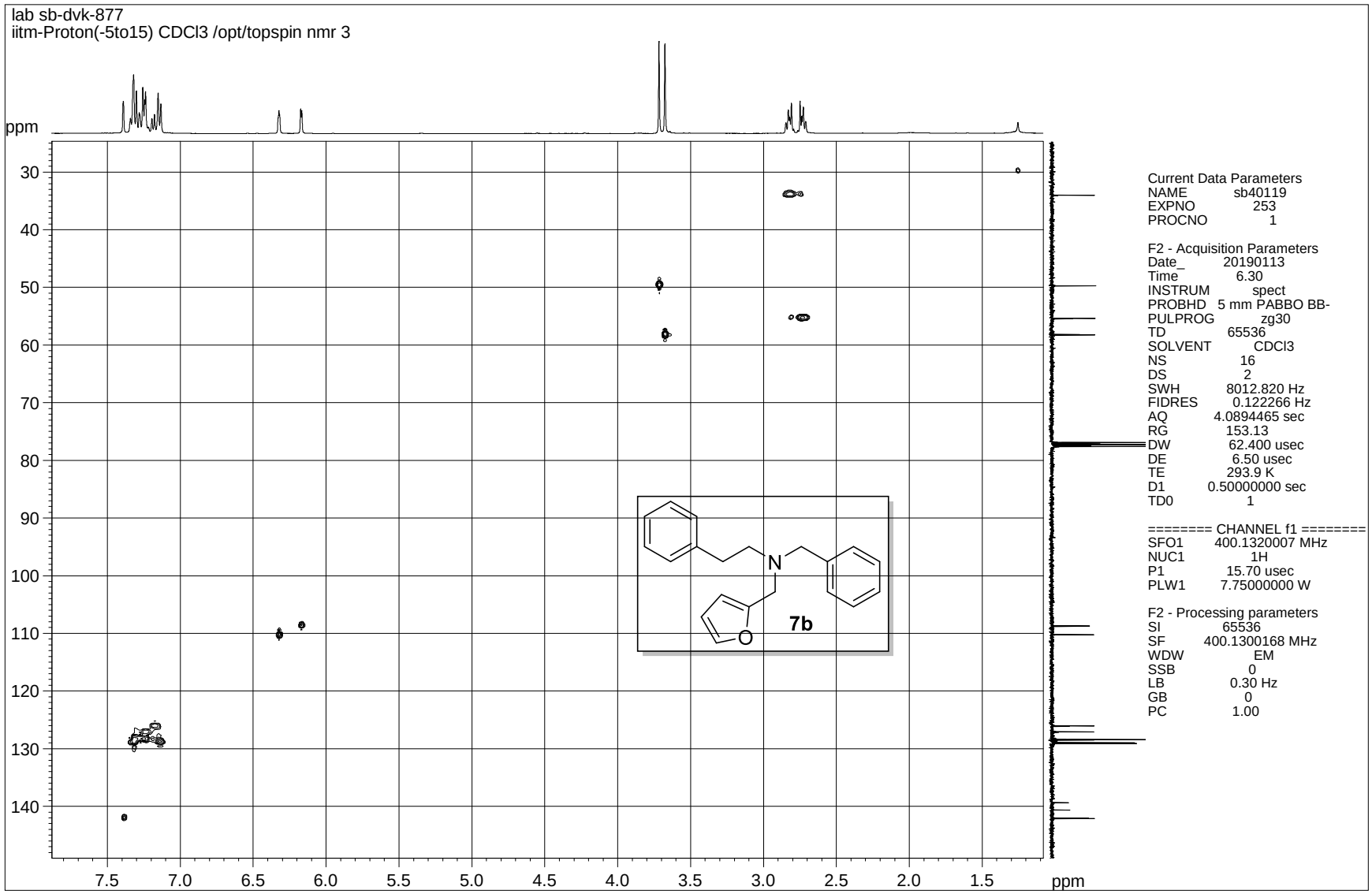
^{13}C NMR spectrum of compound 7b



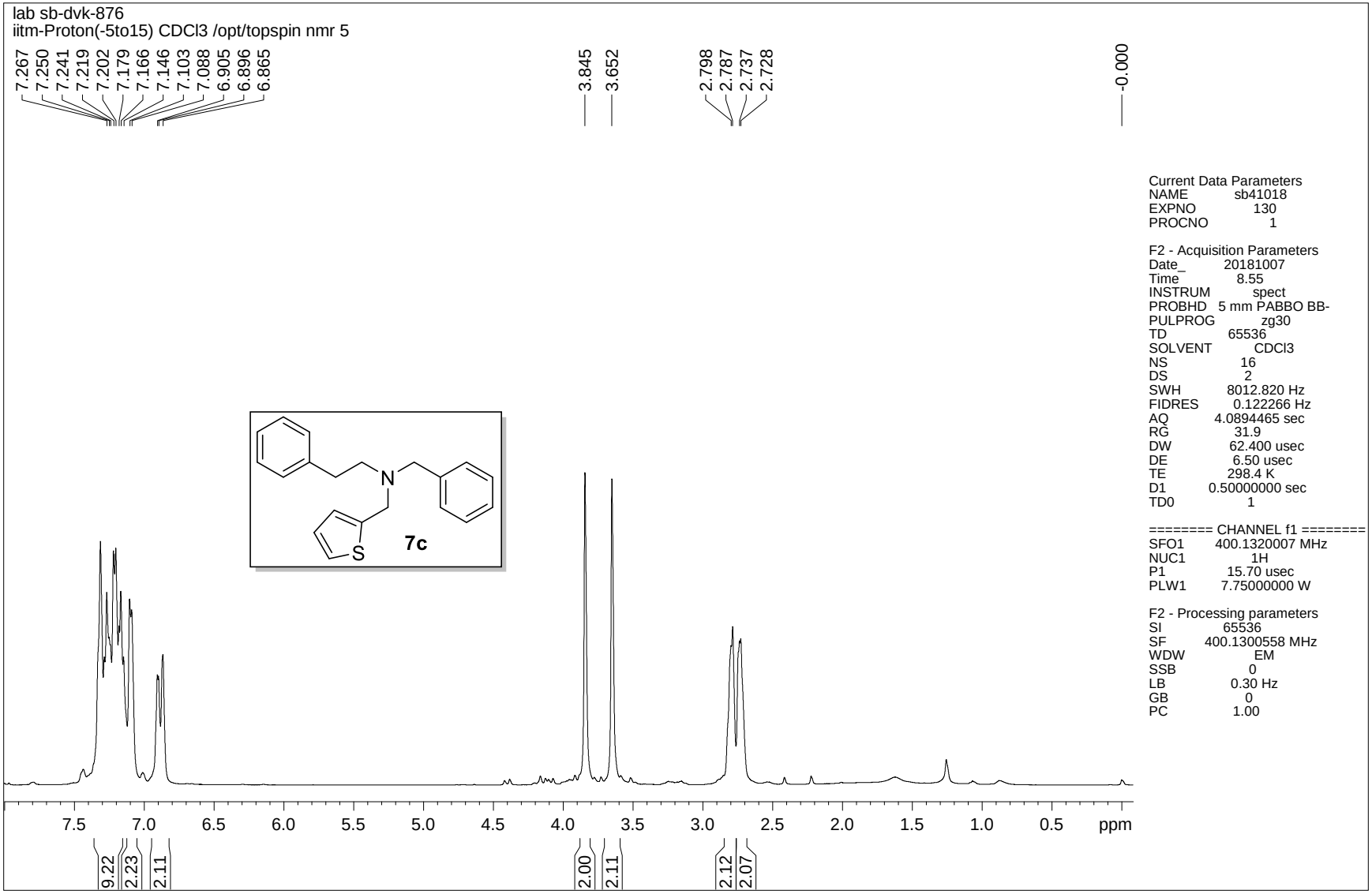
DEPT-135 NMR spectrum of compound 7b



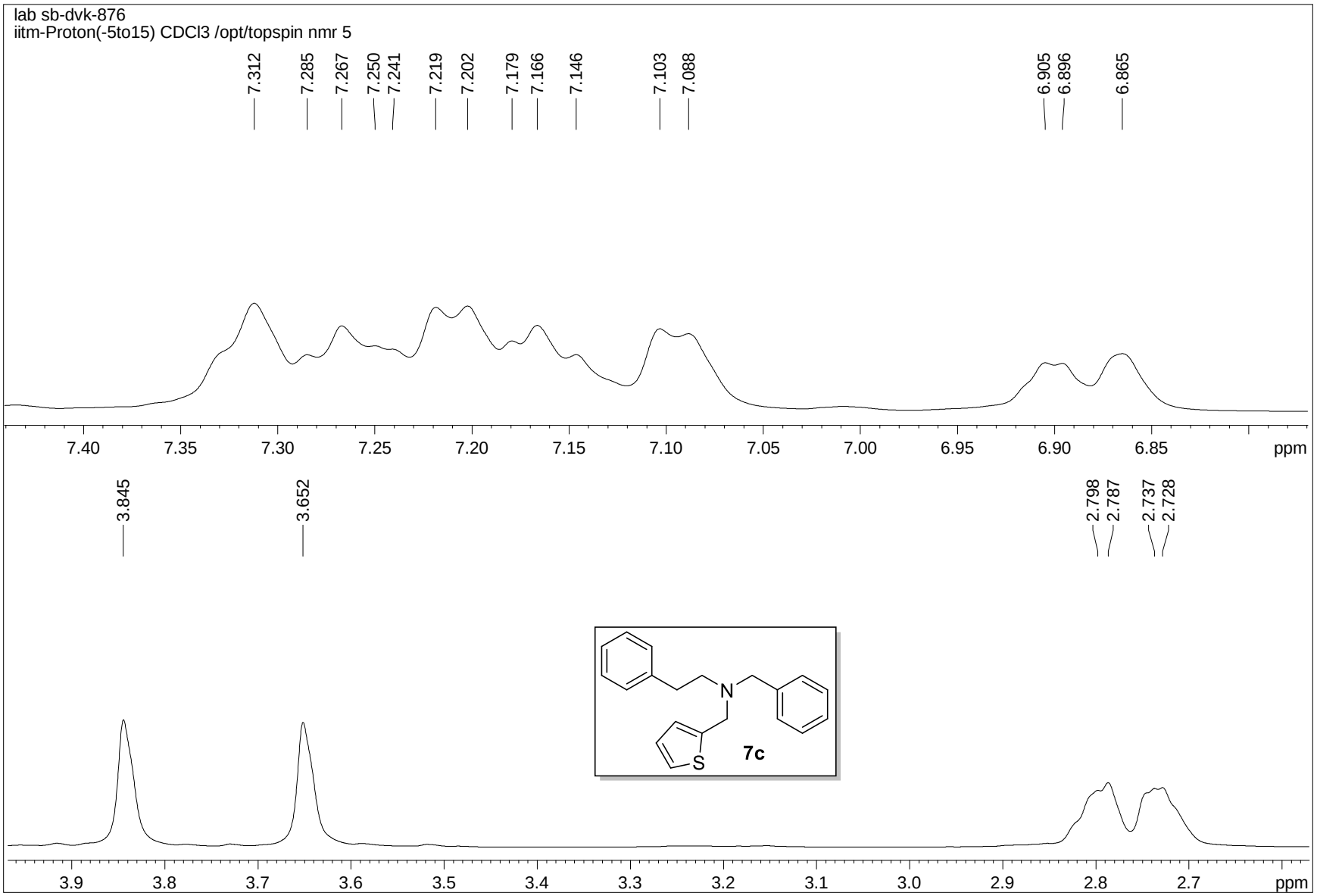
^{1}H-^{1}H COSY NMR spectrum of compound 7b



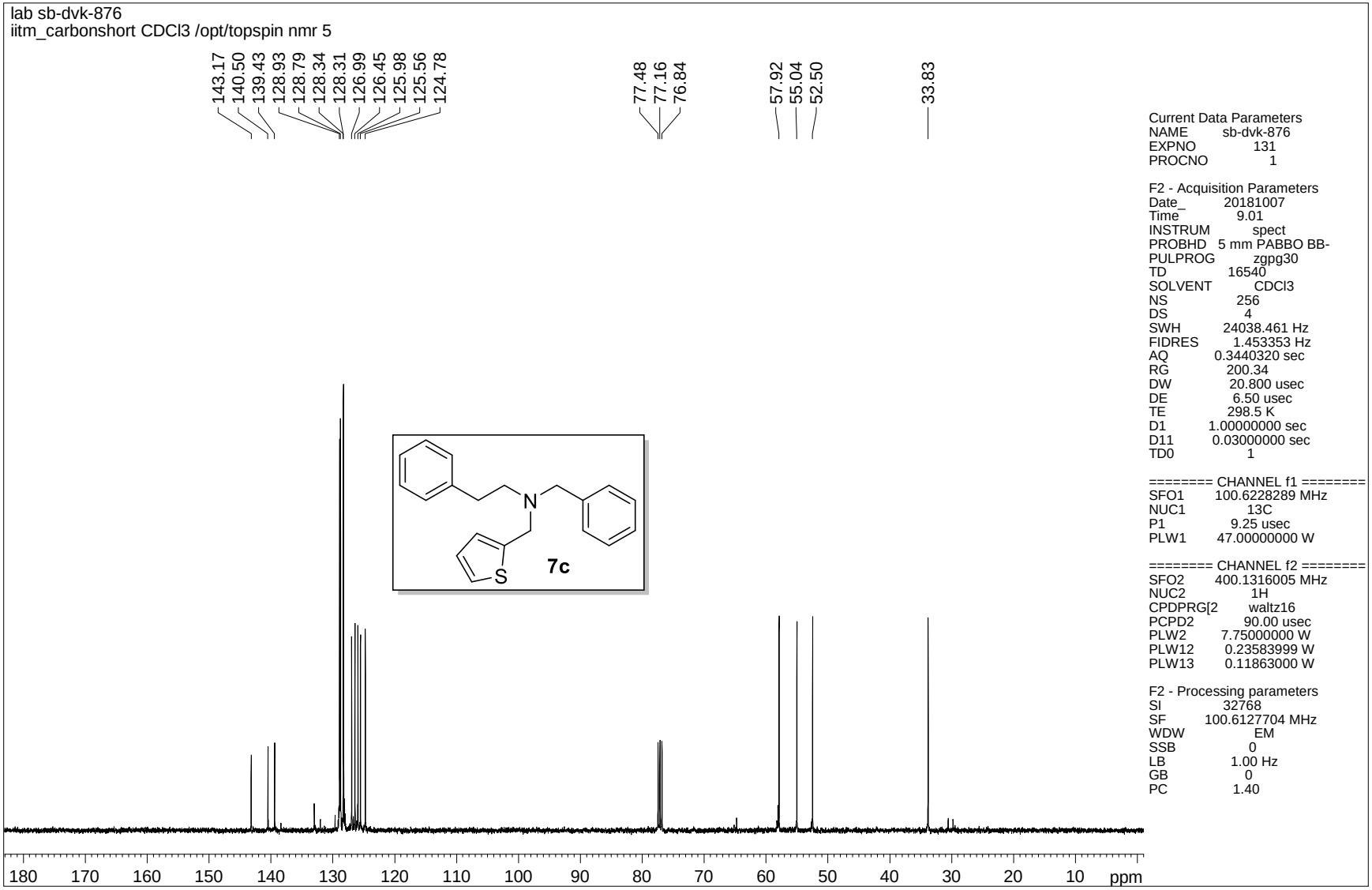
^{1}H-^{13}C HSQC NMR spectrum of compound 7b



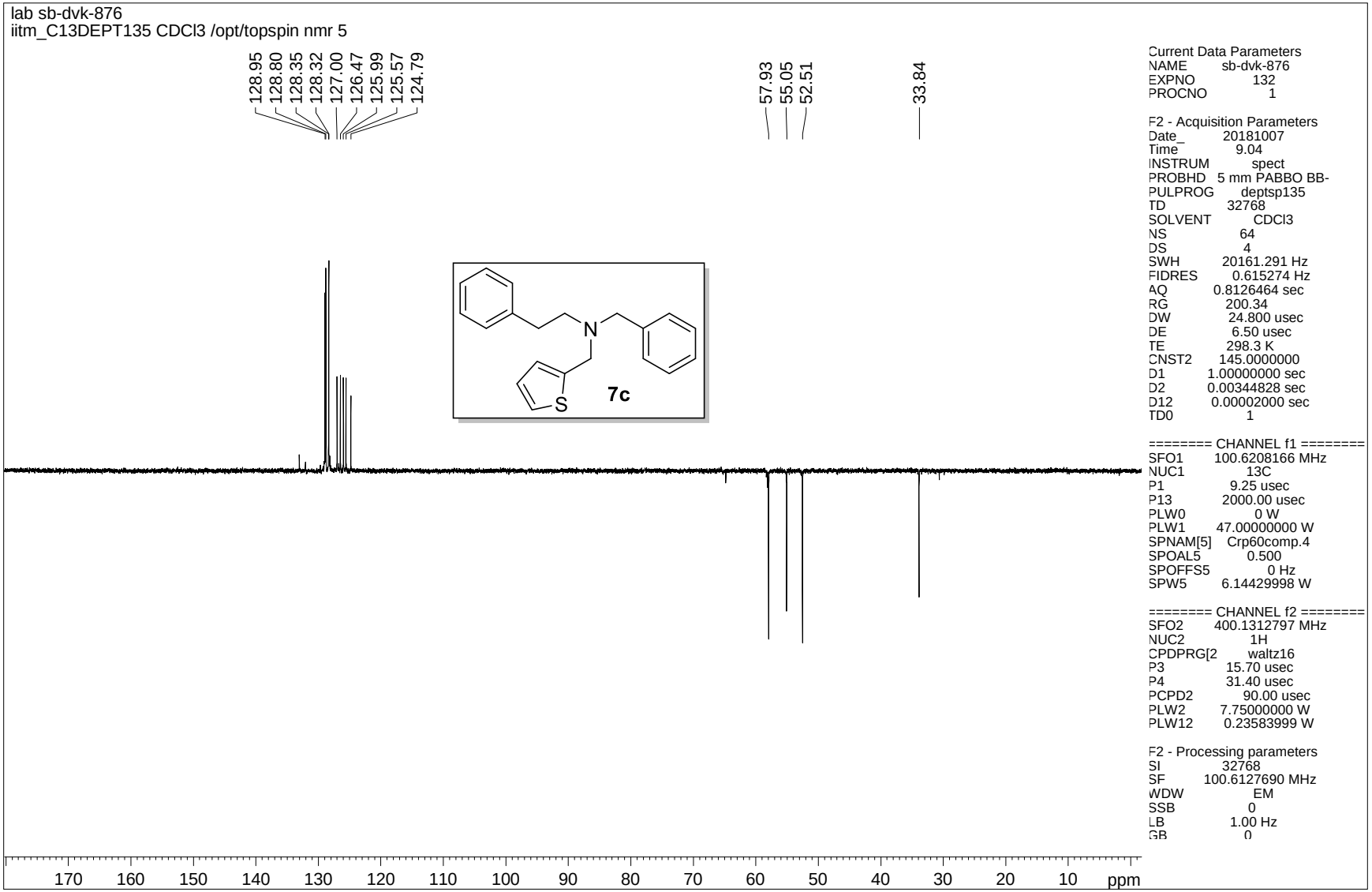
^{1}H NMR spectrum of compound 7c



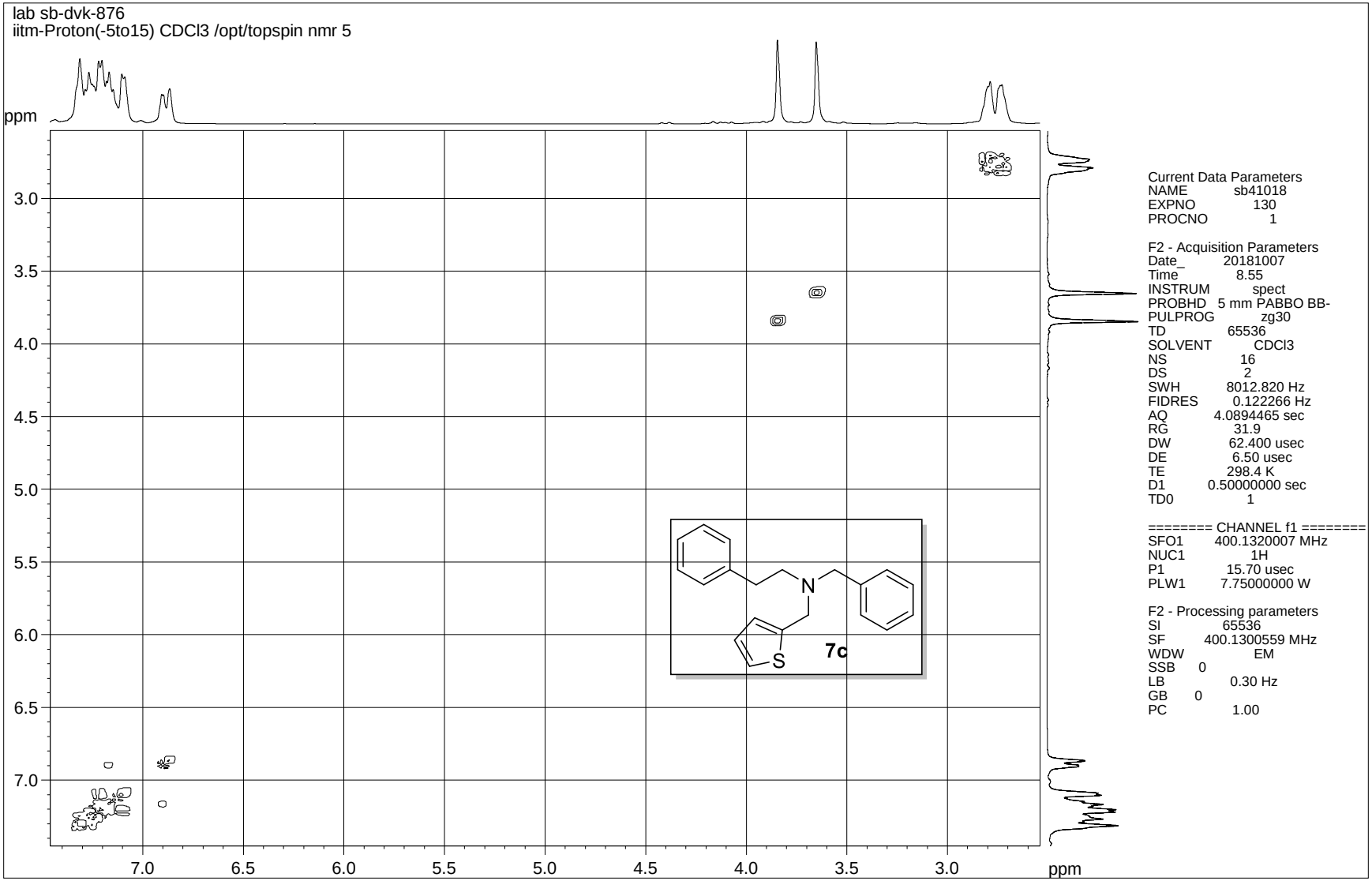
^{1}H NMR spectrum of compound 7c



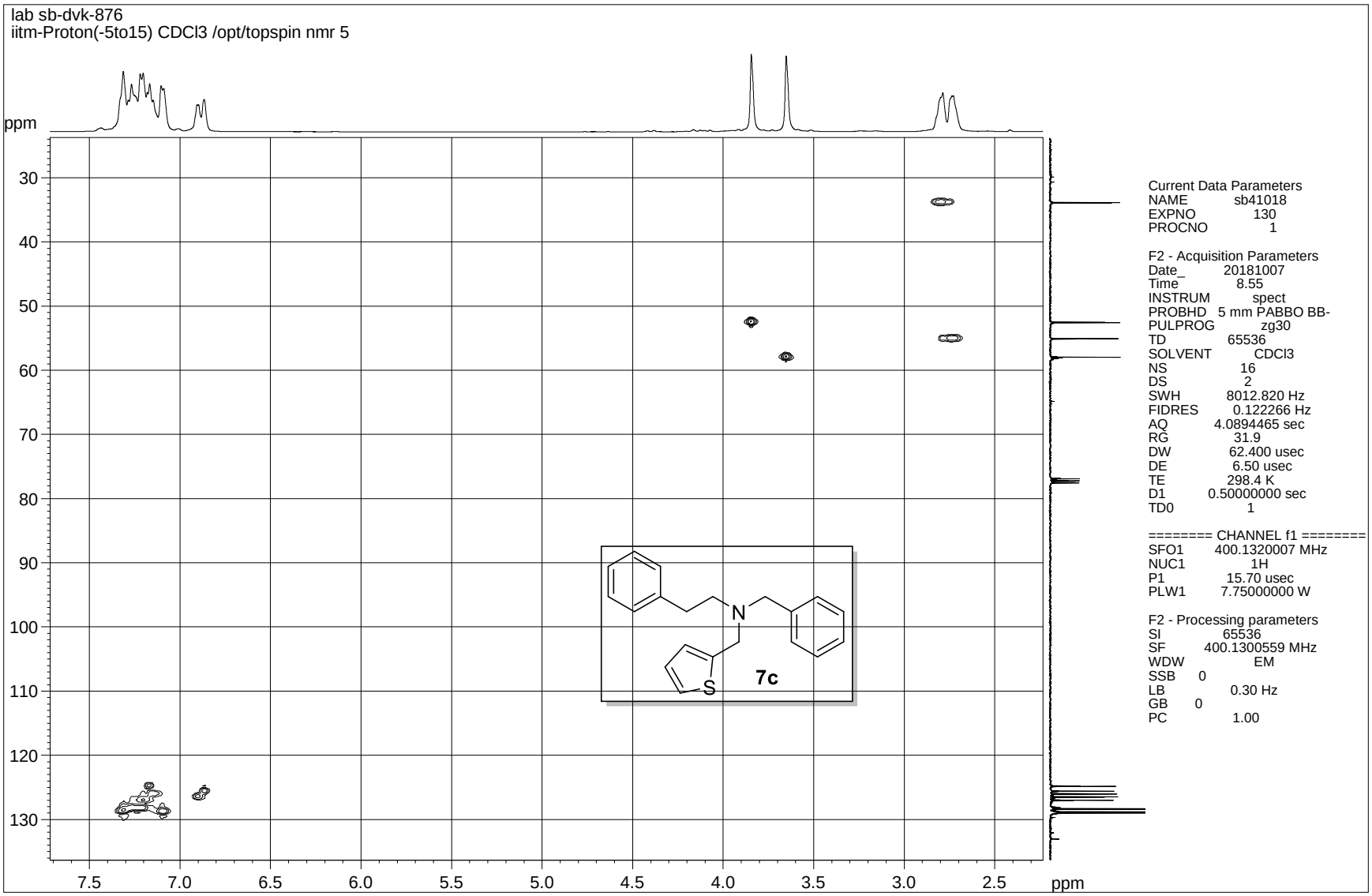
^{13}C NMR spectrum of compound 7c



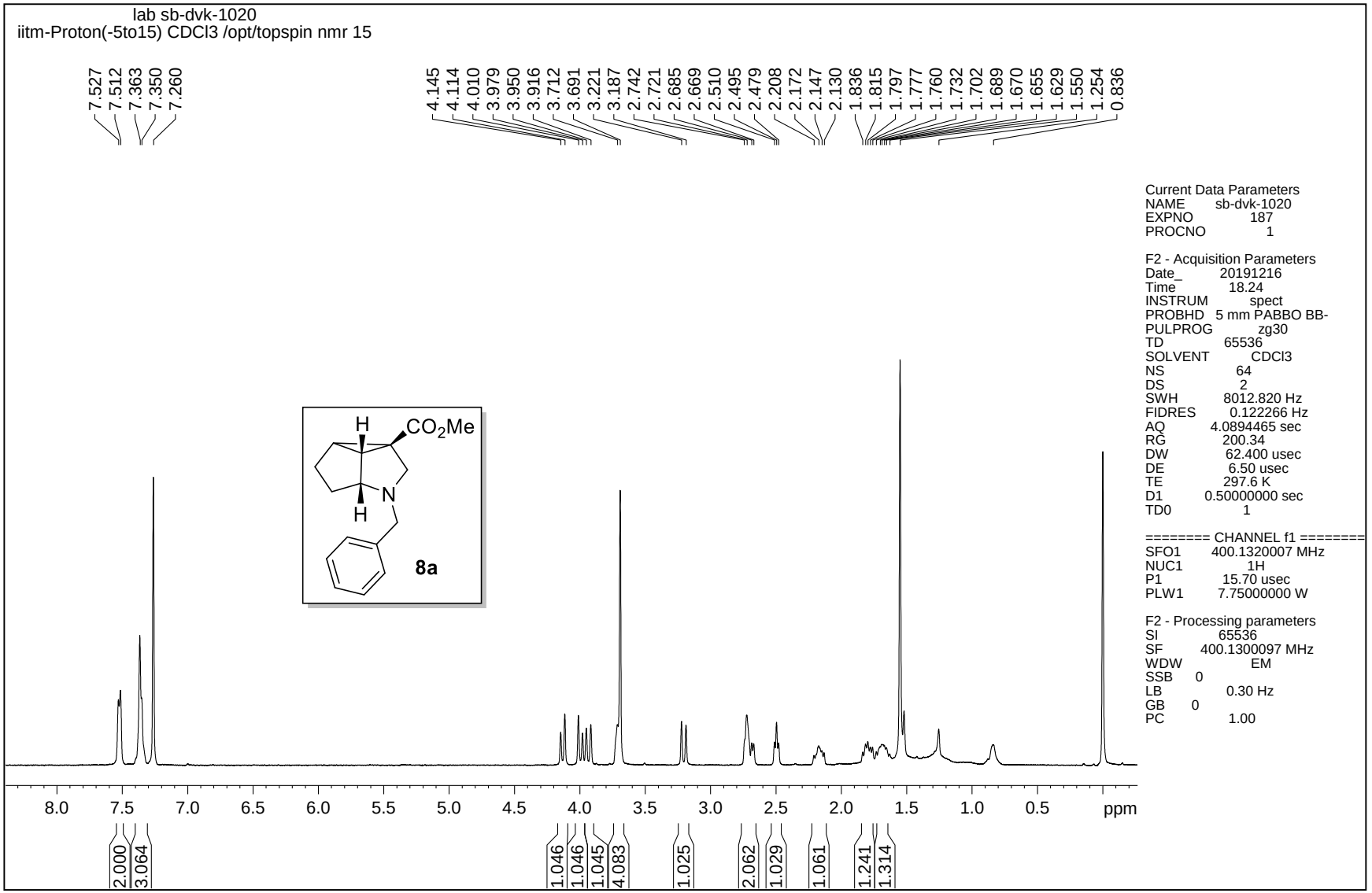
DEPT-135 NMR spectrum of compound 7c



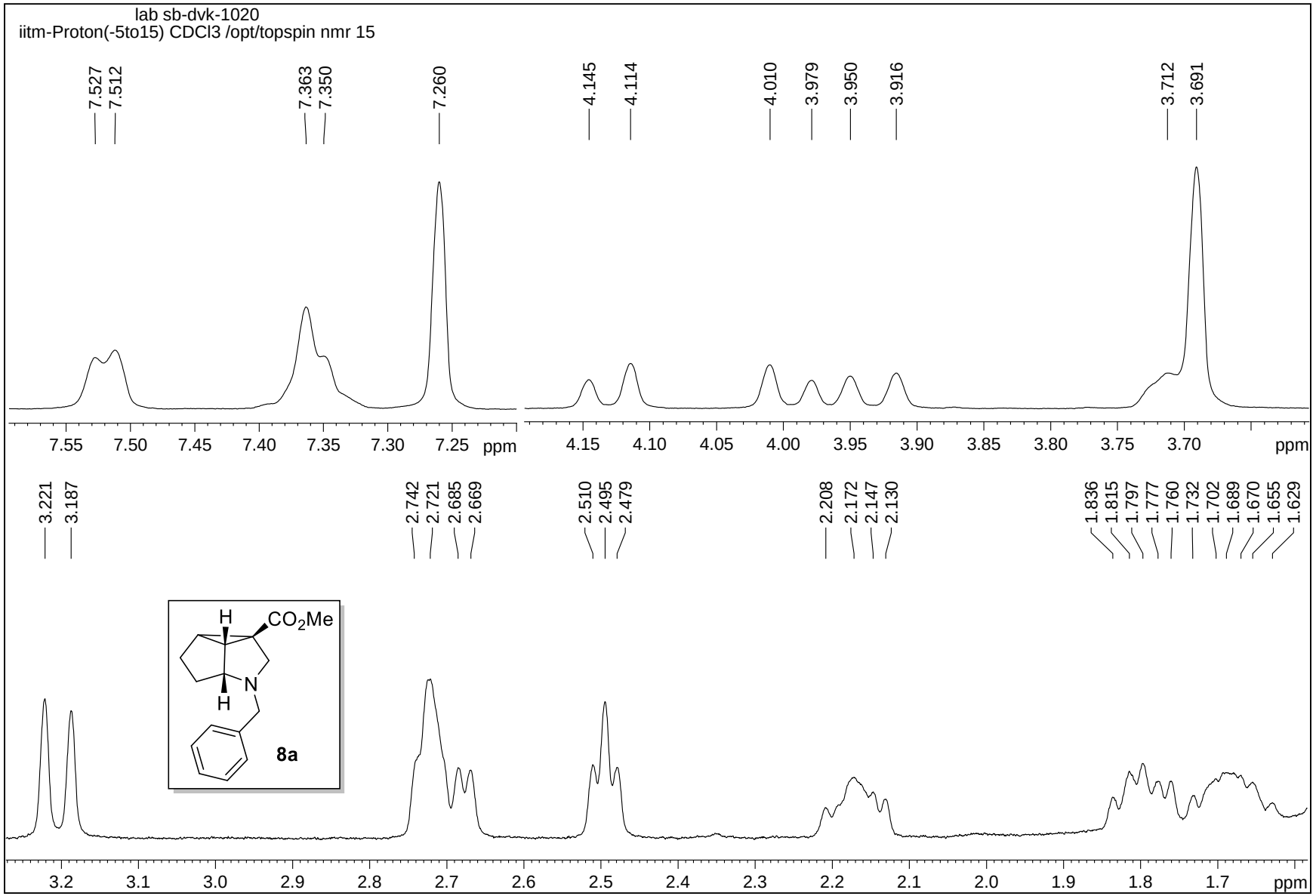
^{1}H-^{1}H COSY NMR spectrum of compound 7c



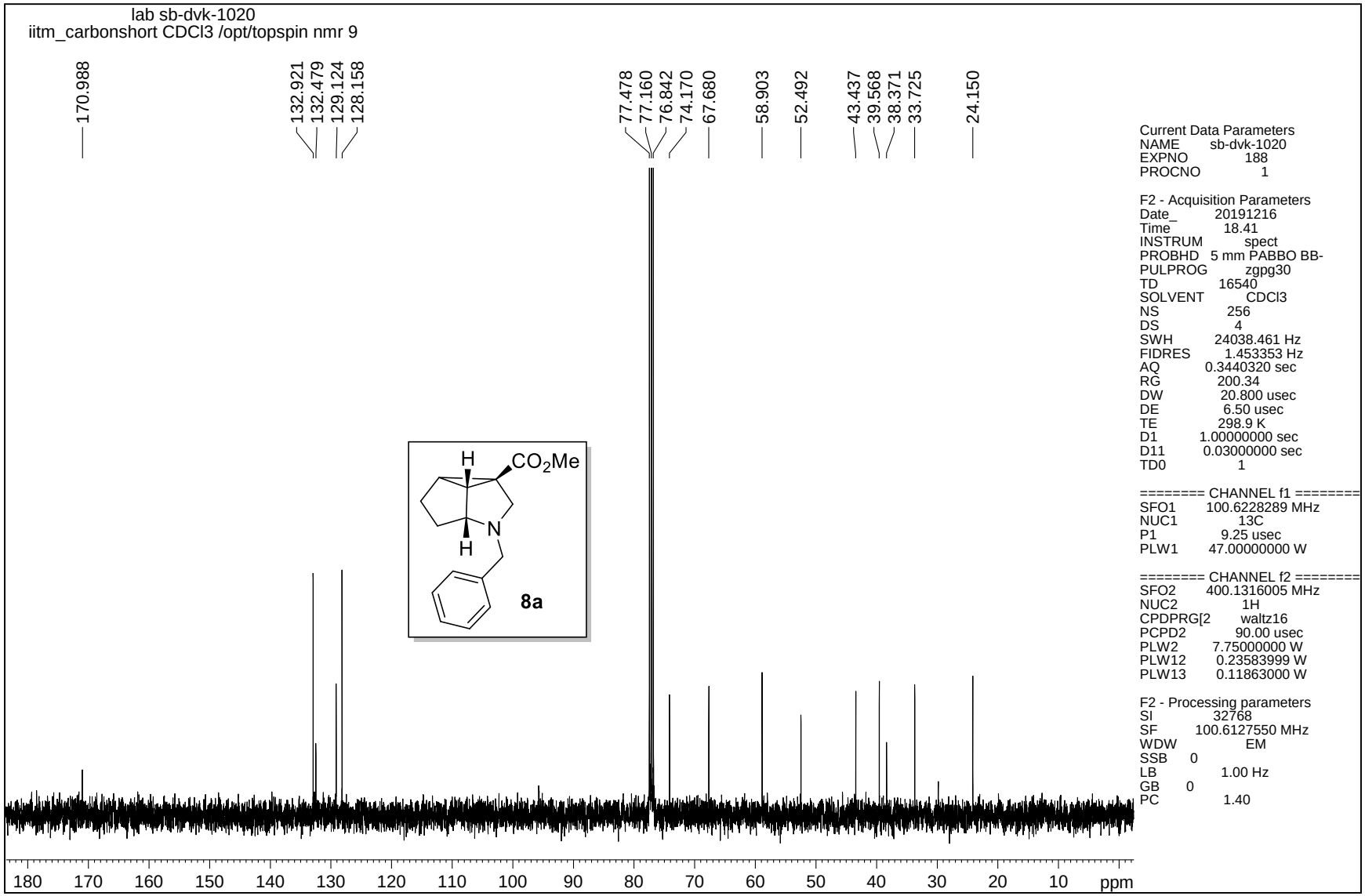
^{1}H-^{13}C HSQC NMR spectrum of compound 7c



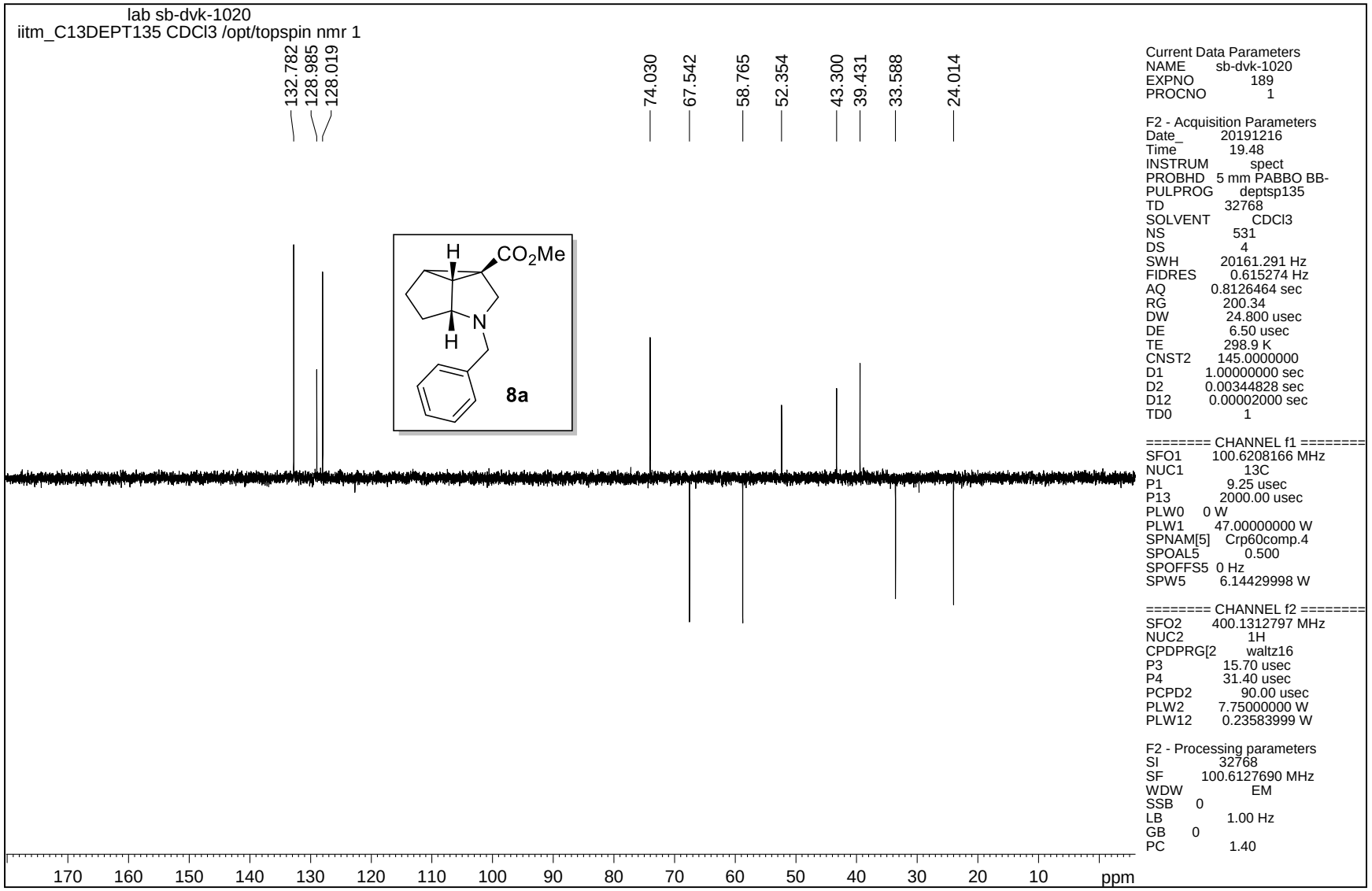
^{1}H NMR spectrum of compound 8a



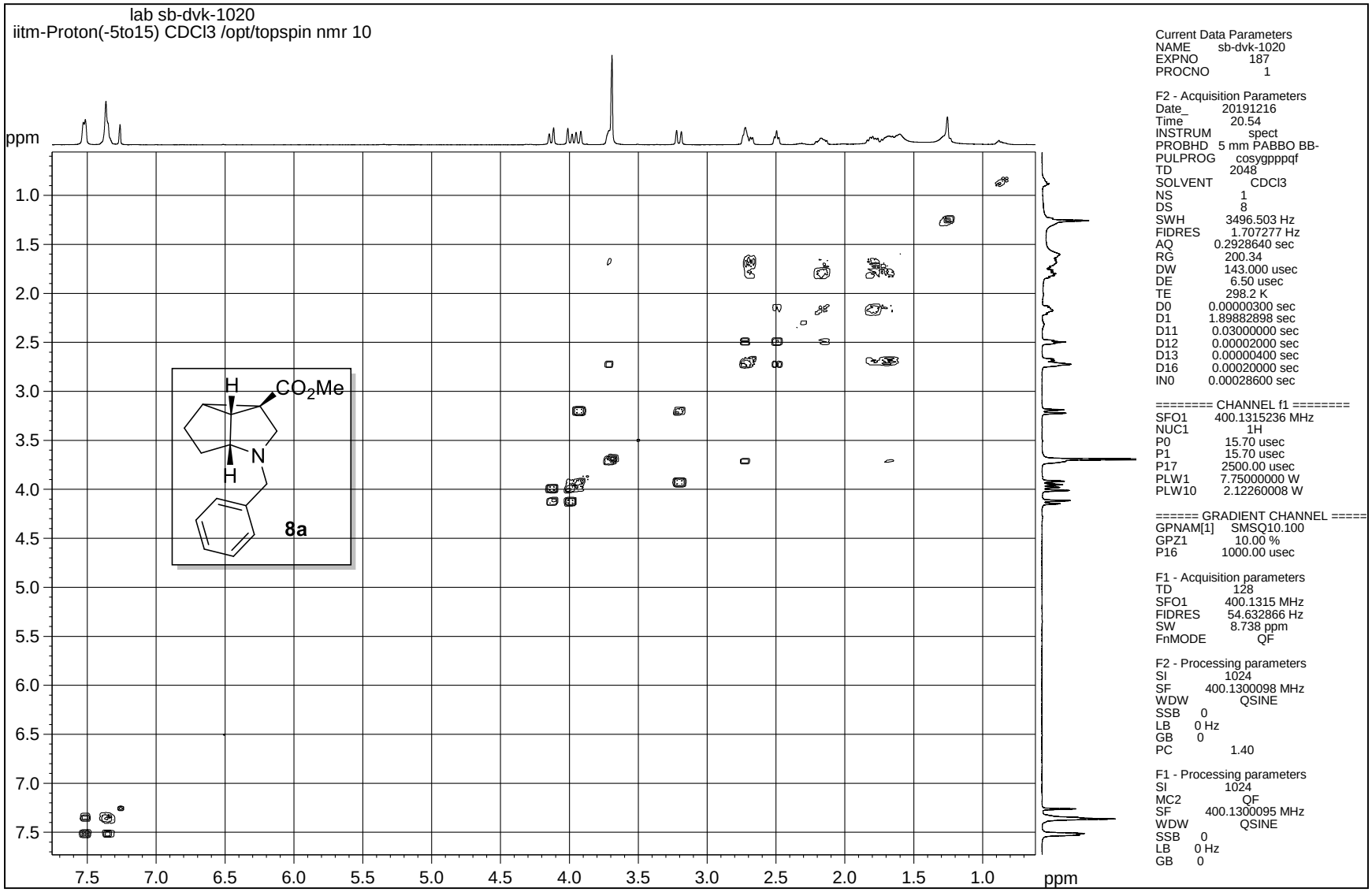
^{1}H NMR spectrum of compound 8a



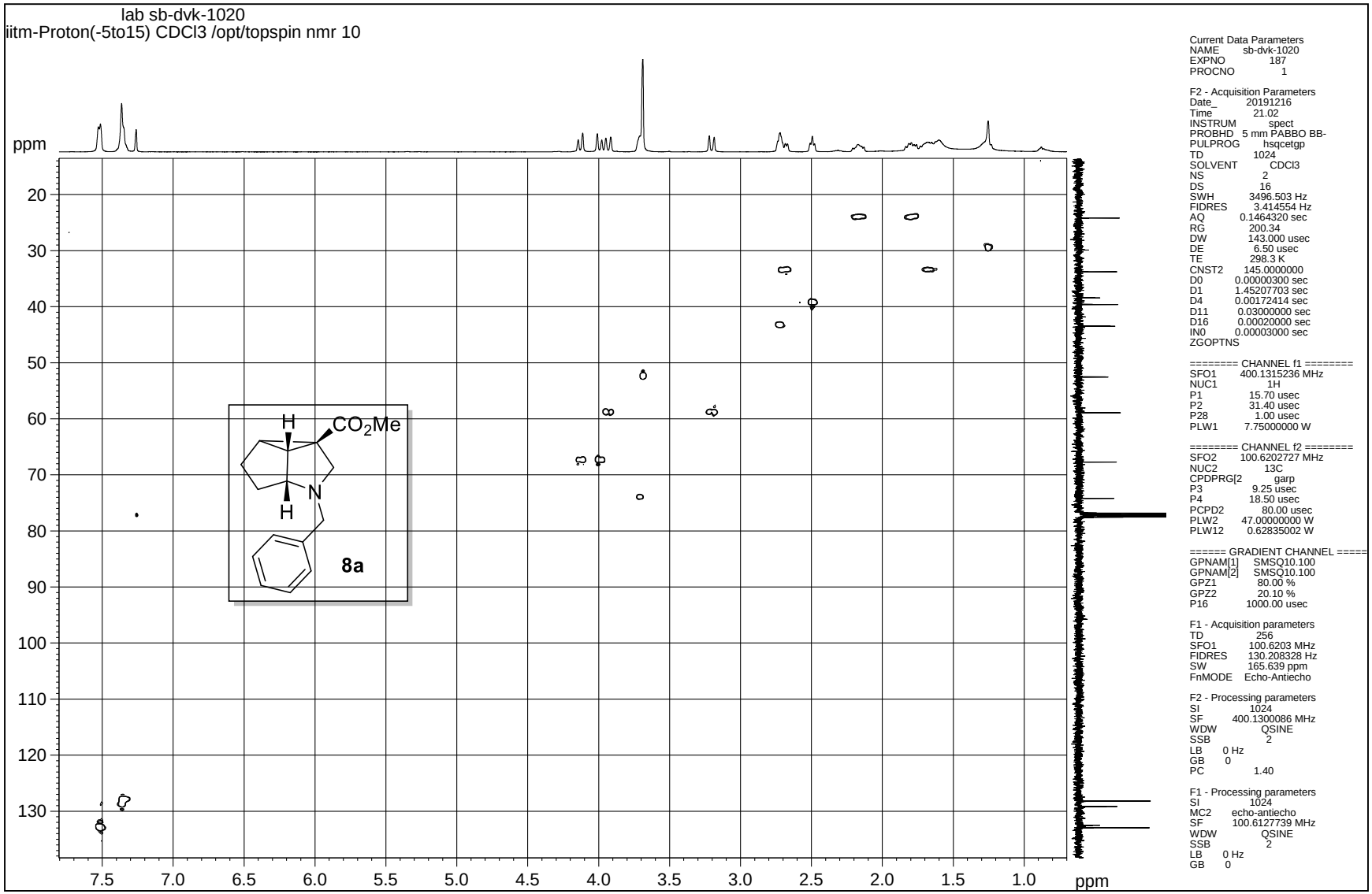
^{13}C NMR spectrum of compound 8a



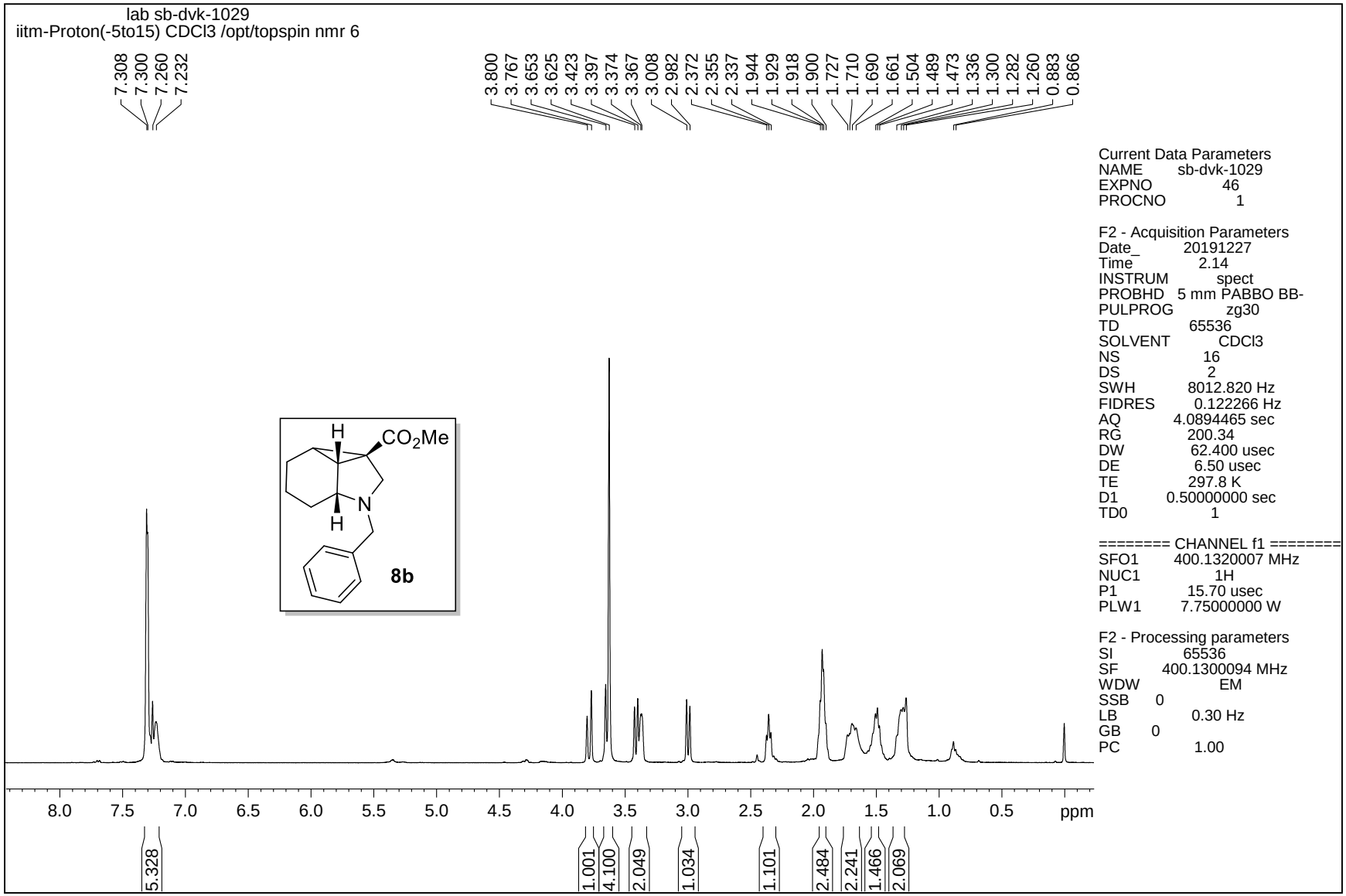
DEPT-135 NMR spectrum of compound 8a



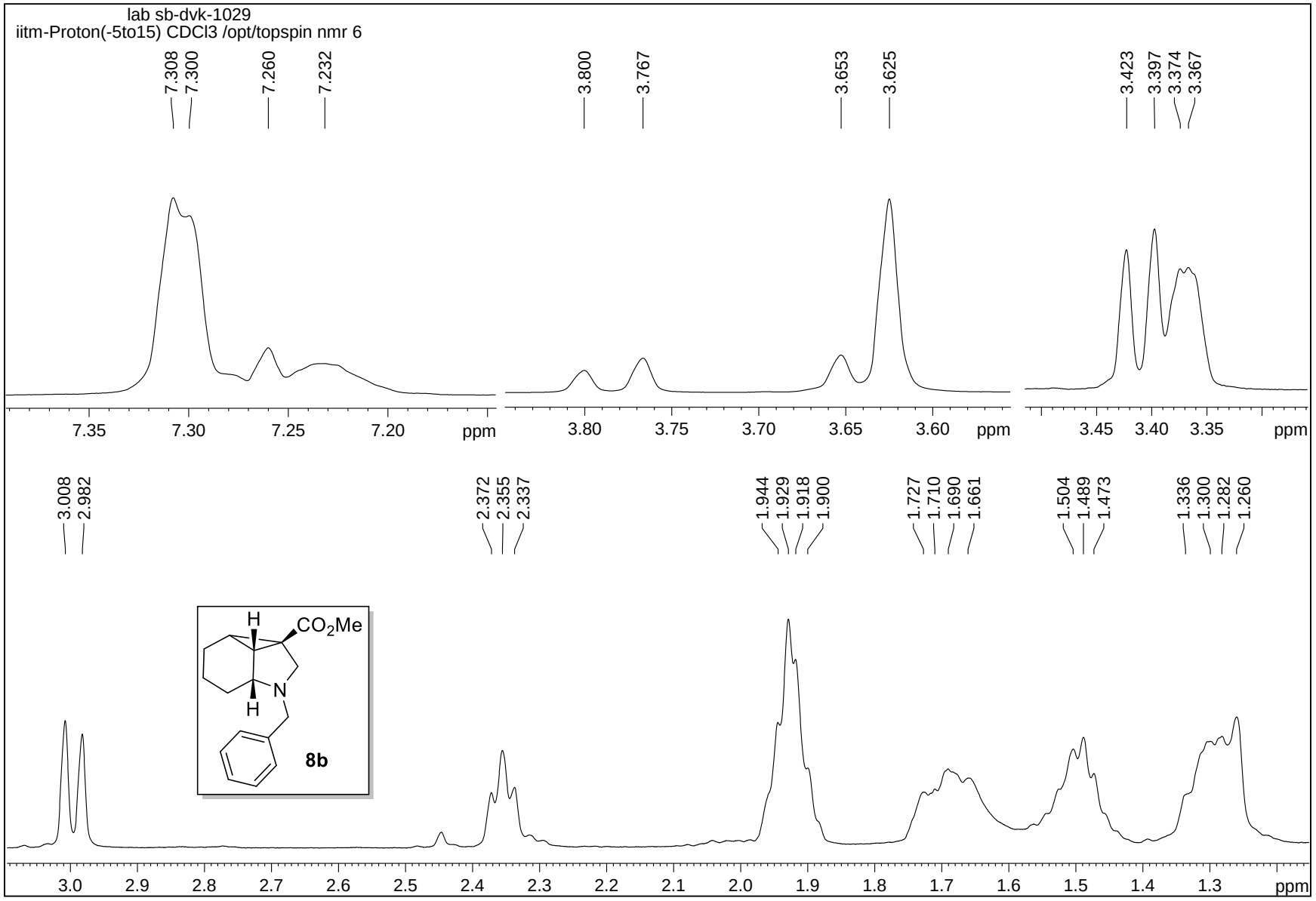
^{1}H-^{1}H COSY NMR spectrum of compound 8a



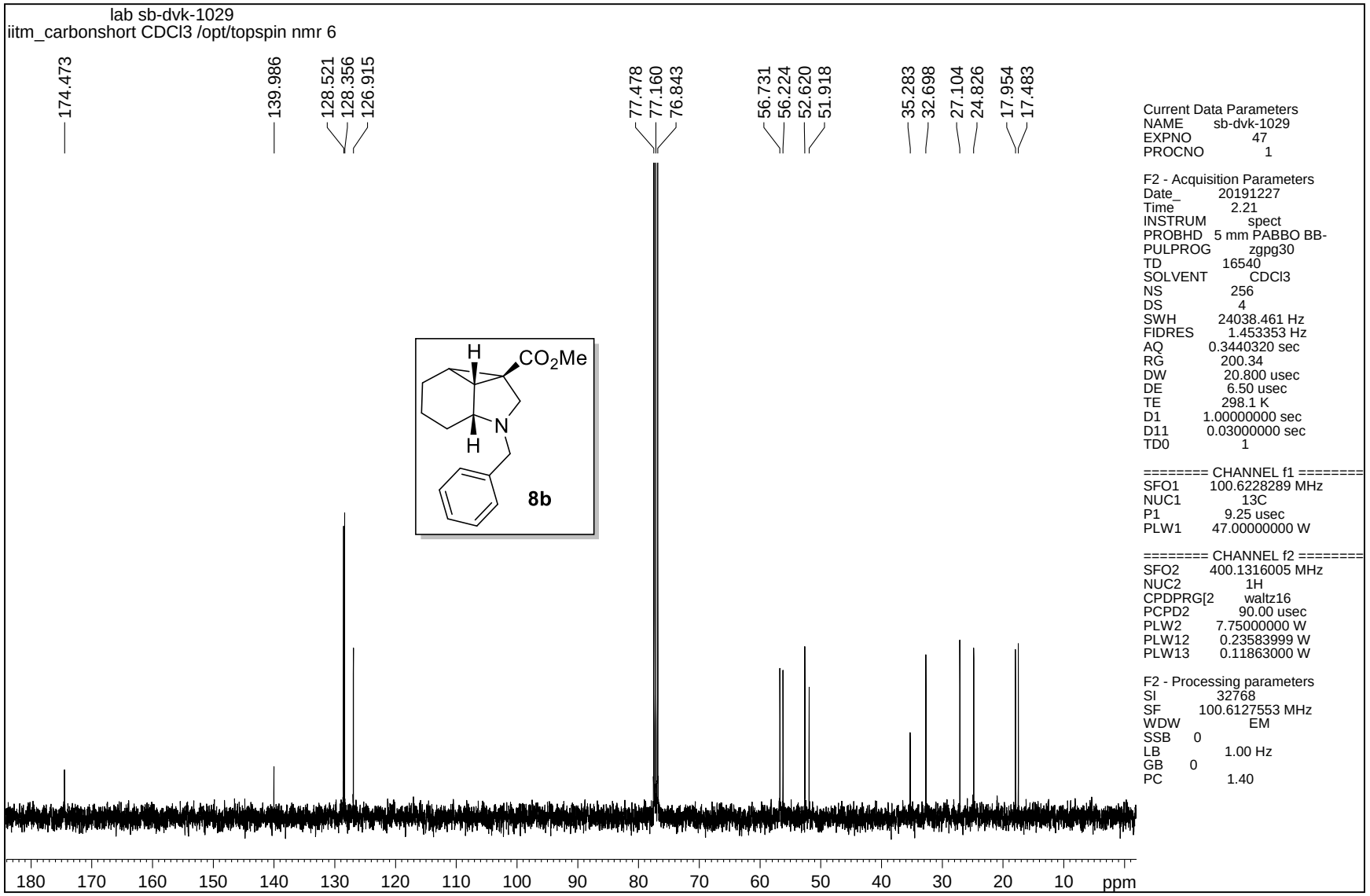
^{1}H-^{13}C HSQC NMR spectrum of compound 8a



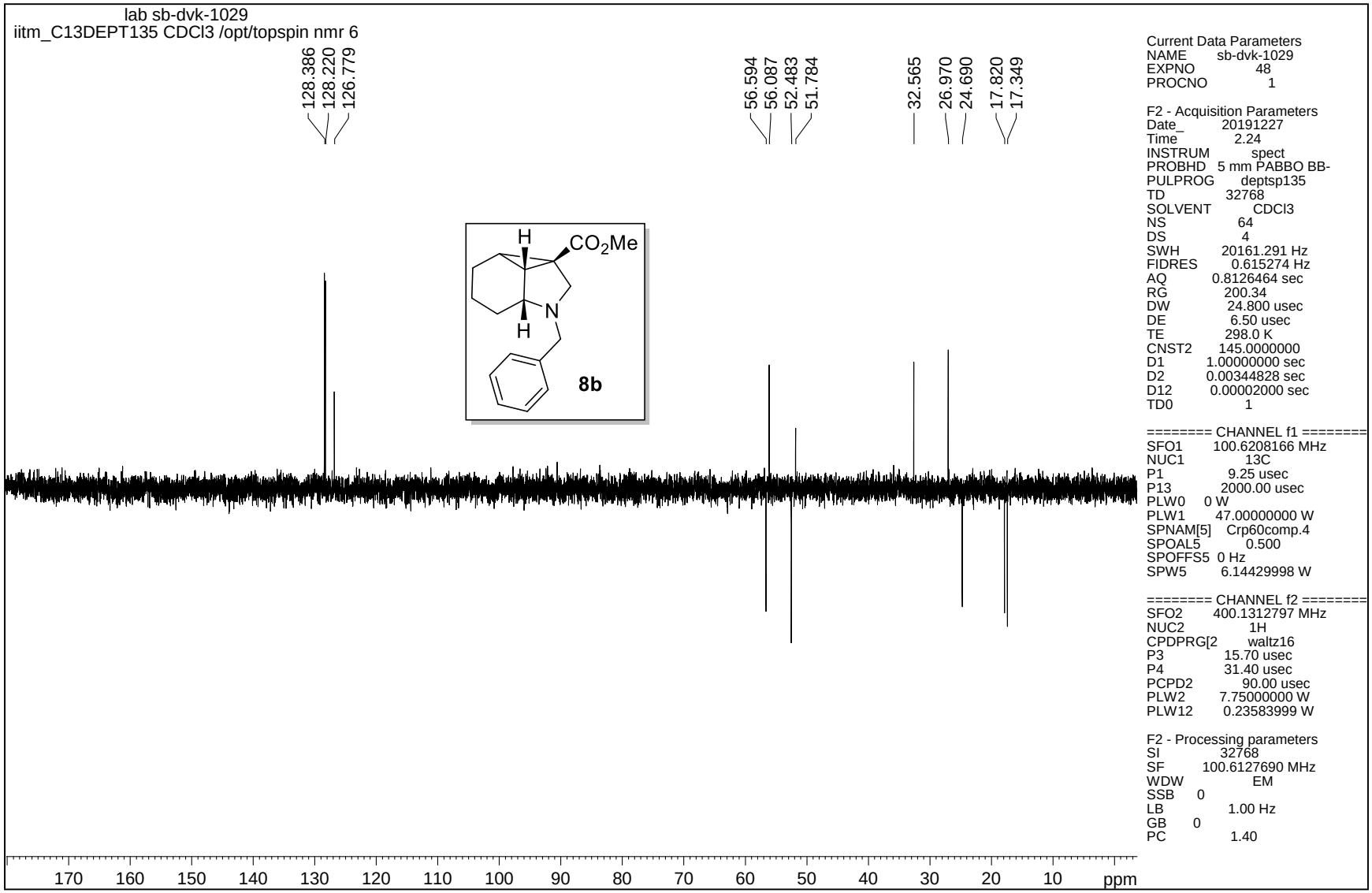
^{1}H NMR spectrum of compound 8b



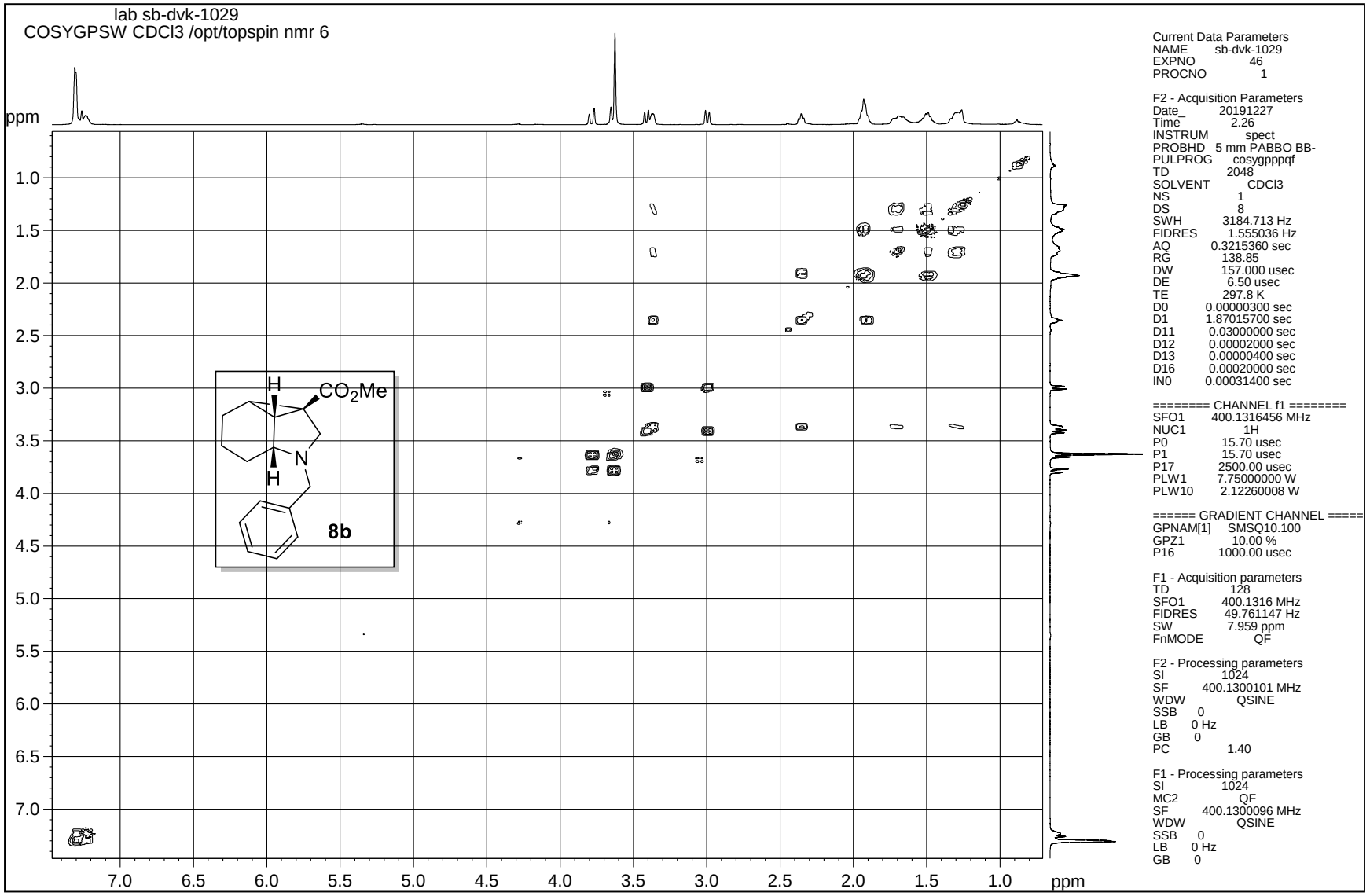
^{1}H NMR spectrum of compound 8b



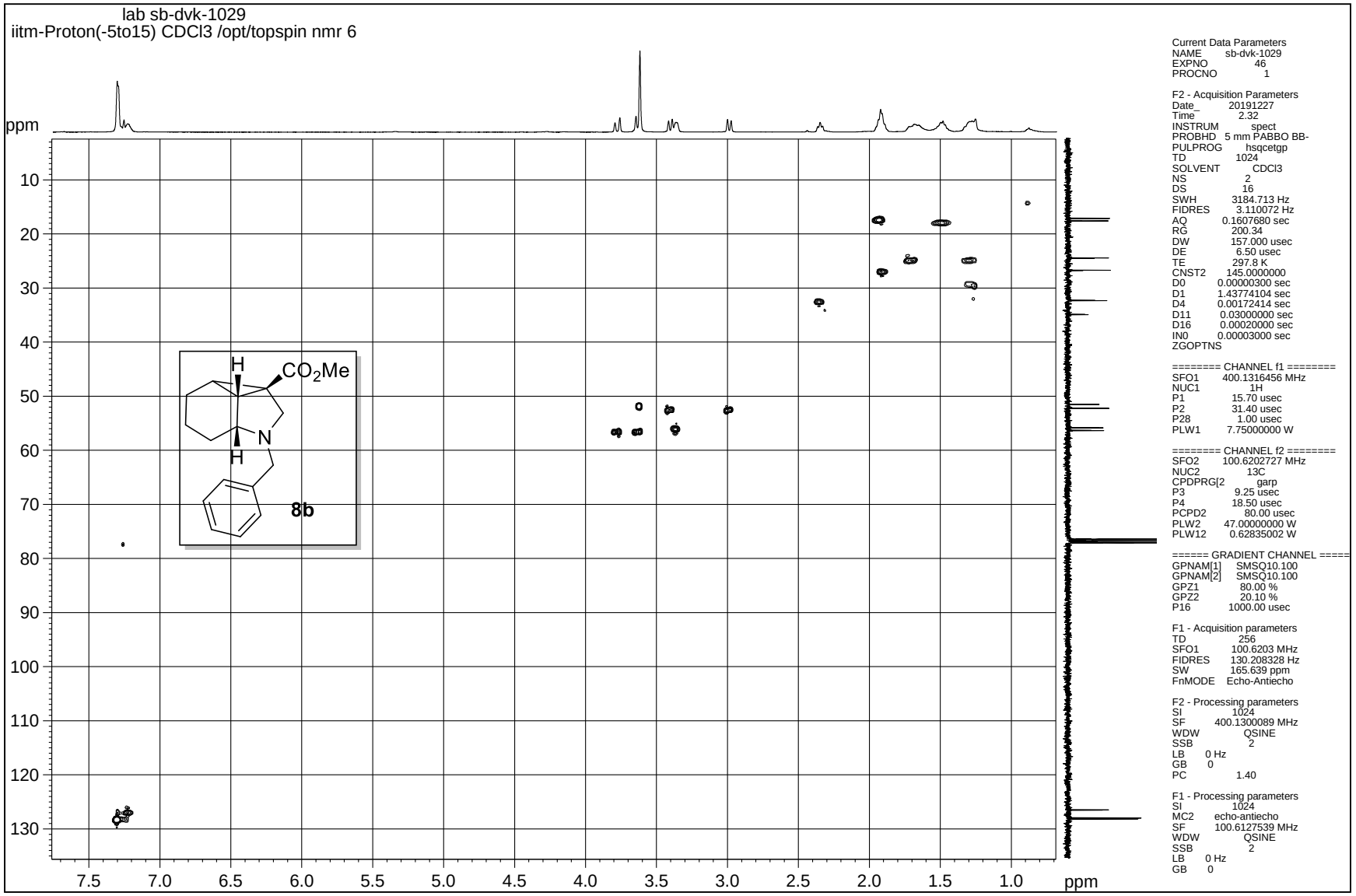
^{13}C NMR spectrum of compound 8b



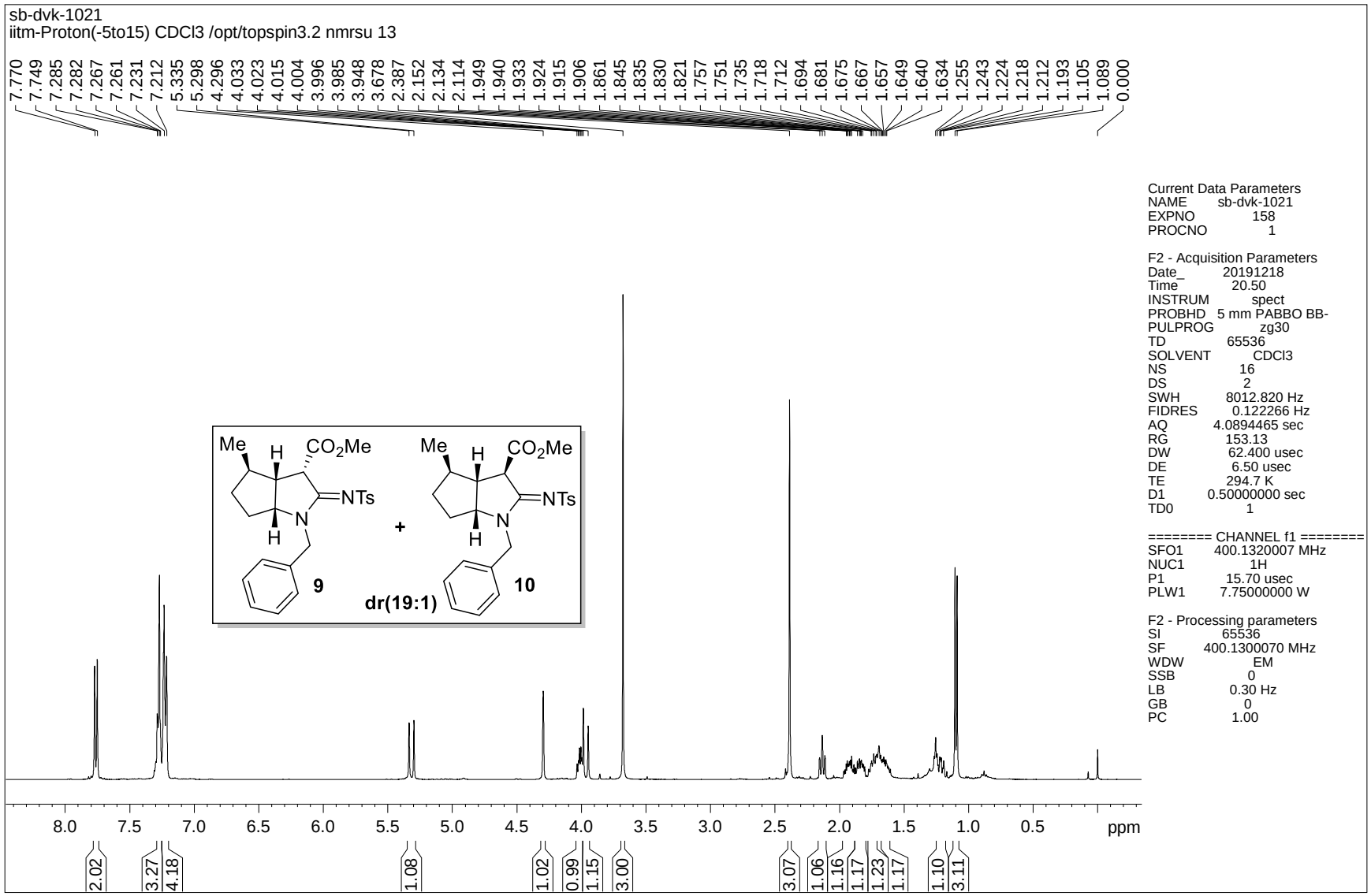
DEPT-135 NMR spectrum of compound 8b



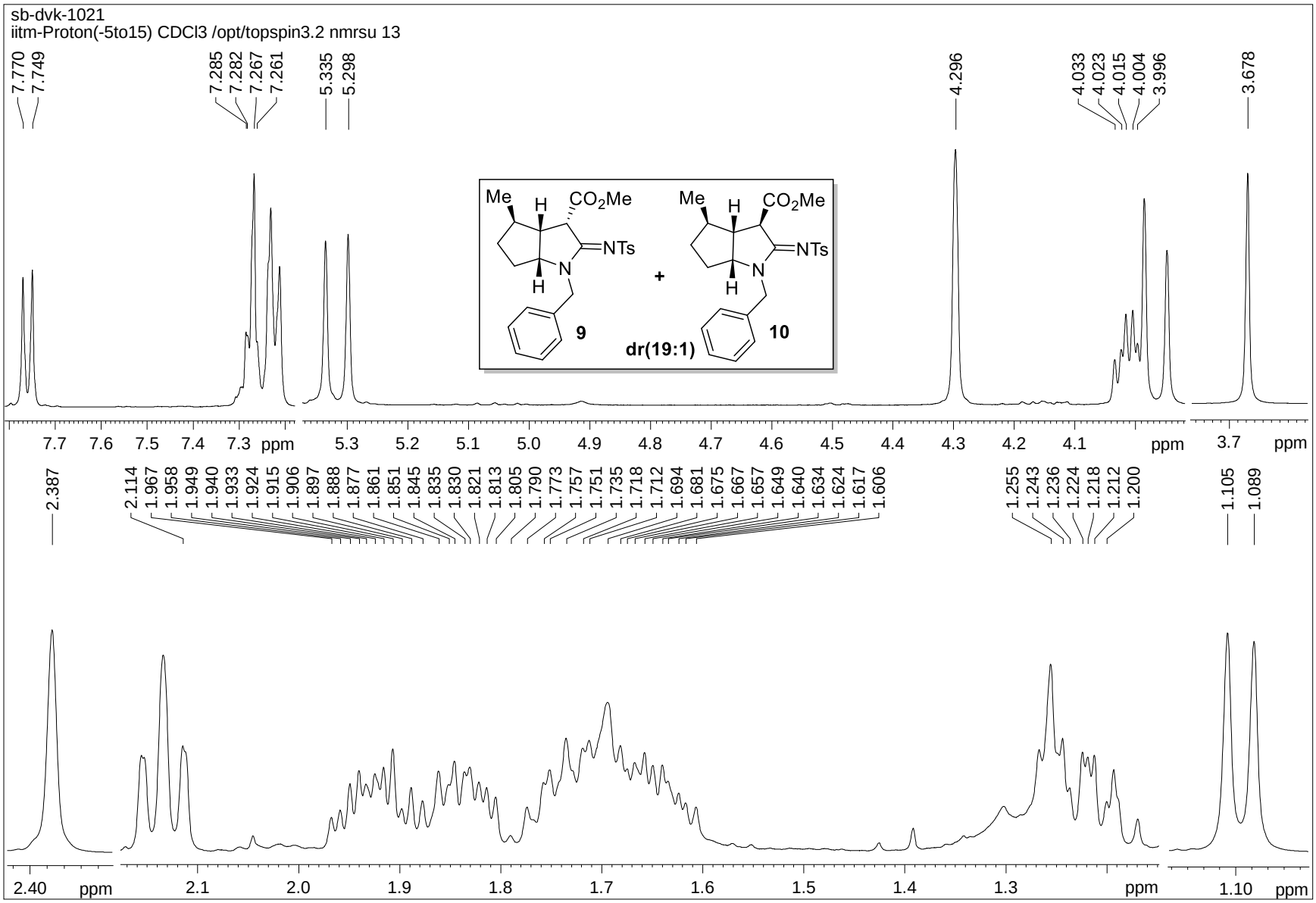
^{1}H-^{1}H COSY NMR spectrum of compound 8b



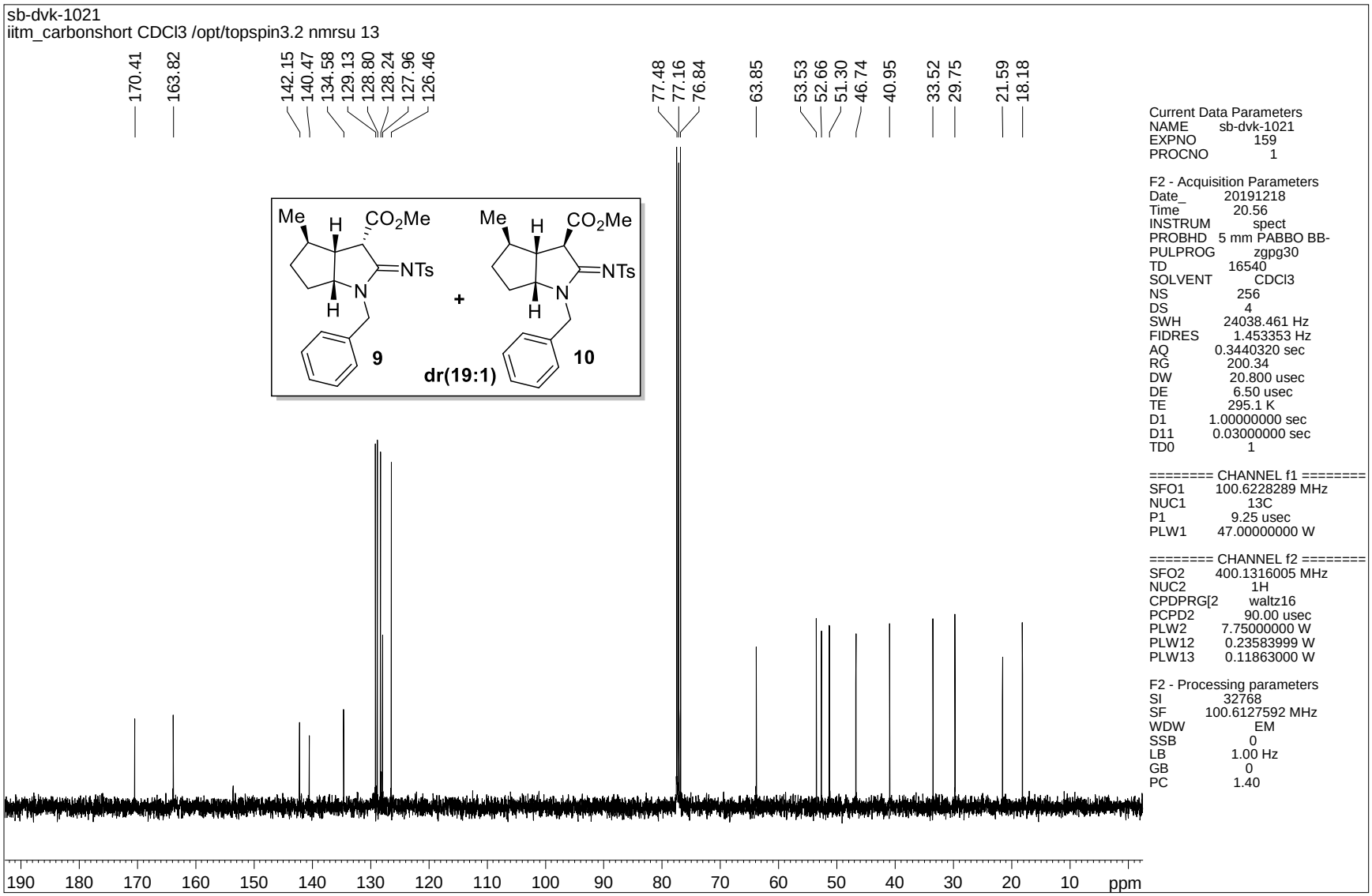
^{1}H-^{13}C HSQC NMR spectrum of compound 8b



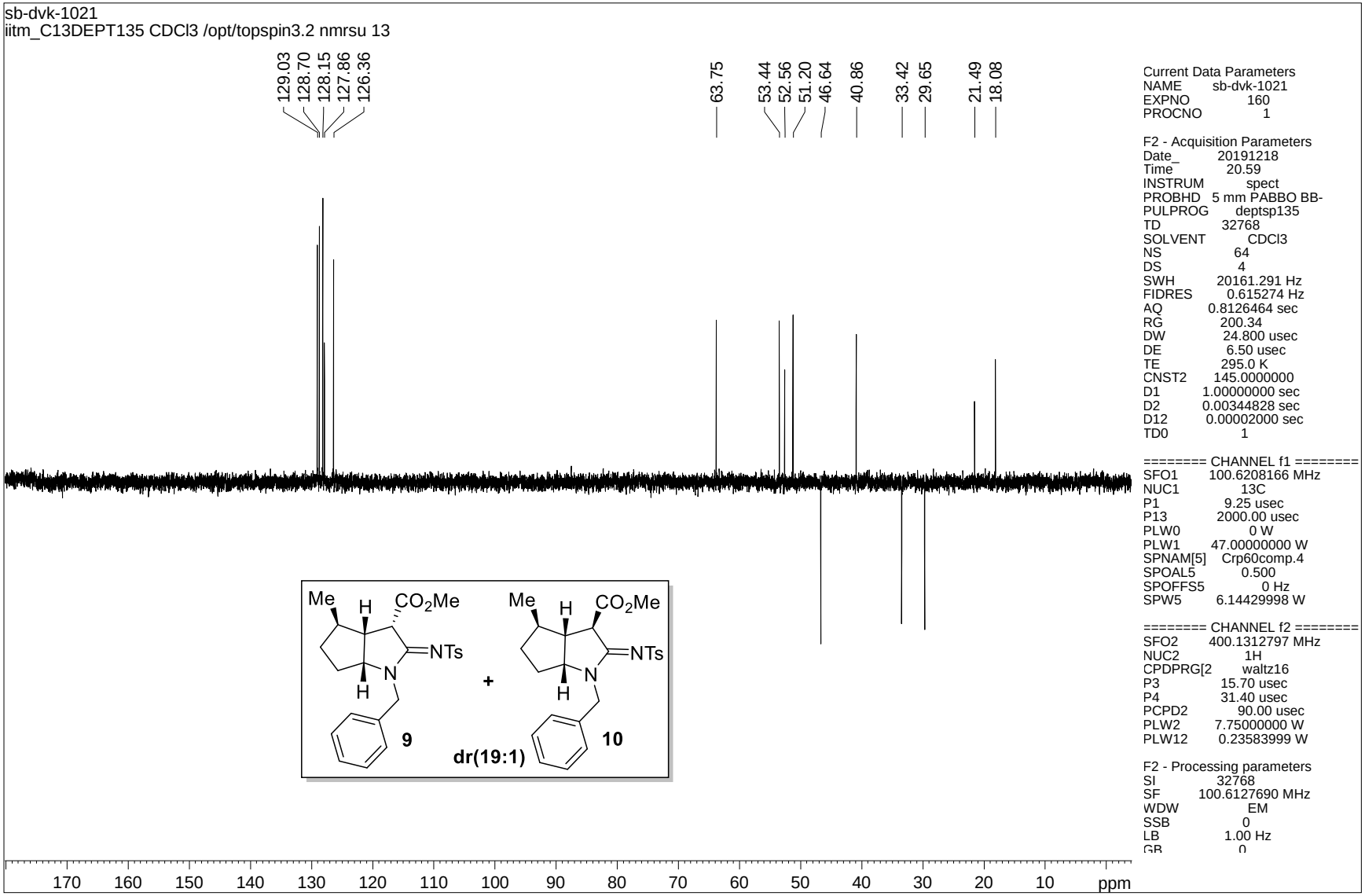
^{1}H NMR spectrum of diastereomers 9 and 10



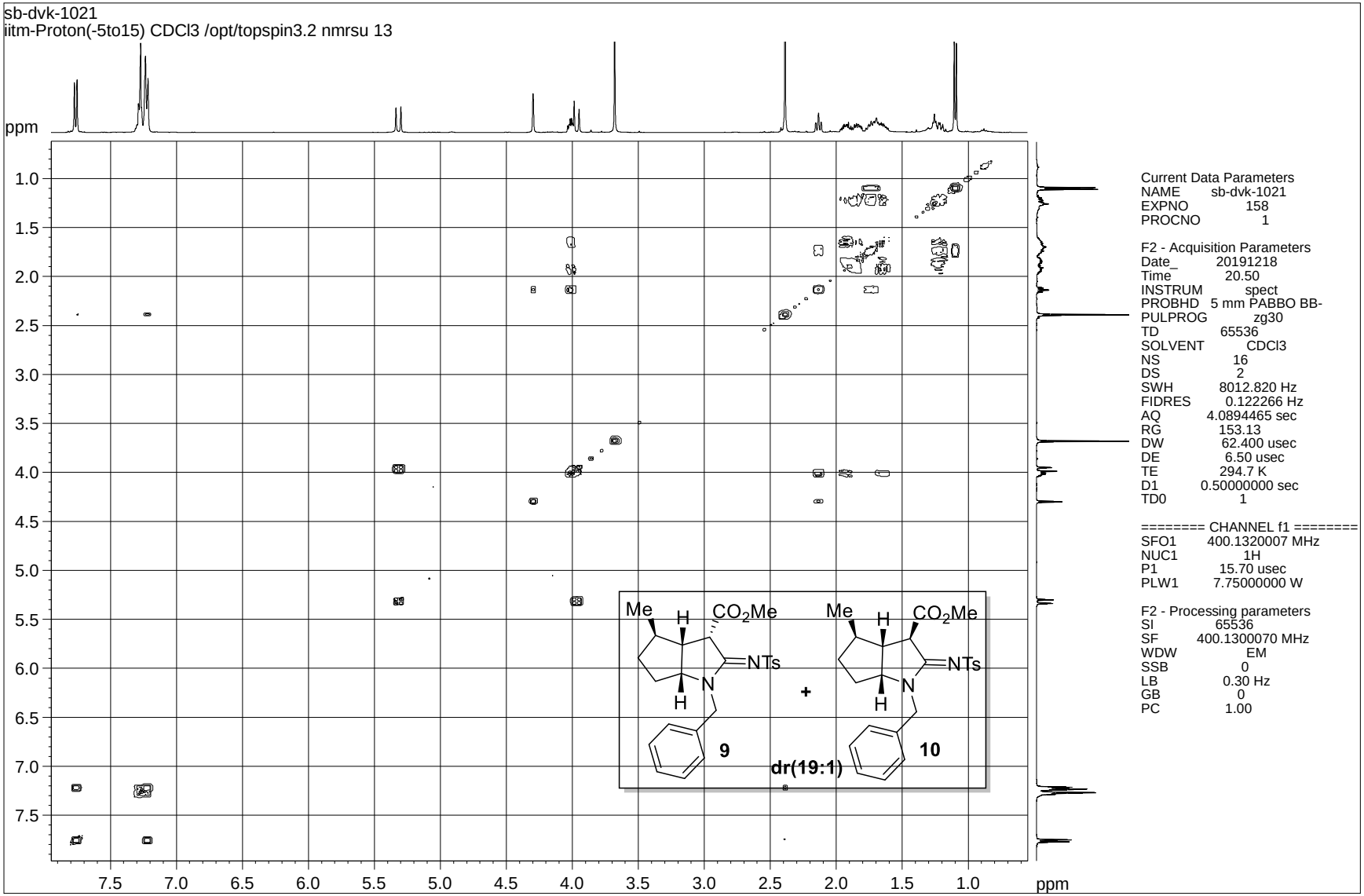
[1]H NMR spectrum of diastereomers 9 and 10



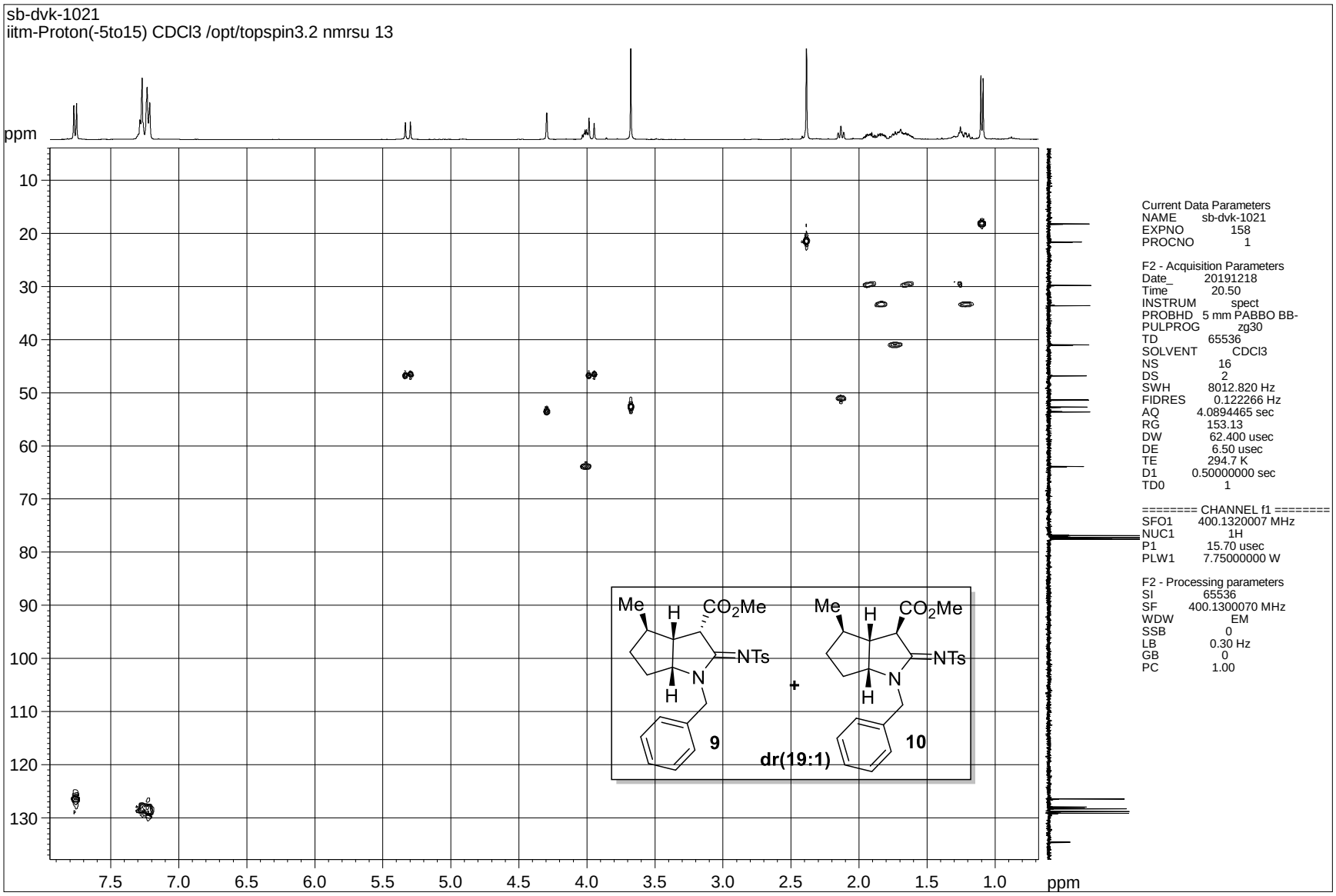
^{13}C NMR spectrum of diastereomer 9 and 10



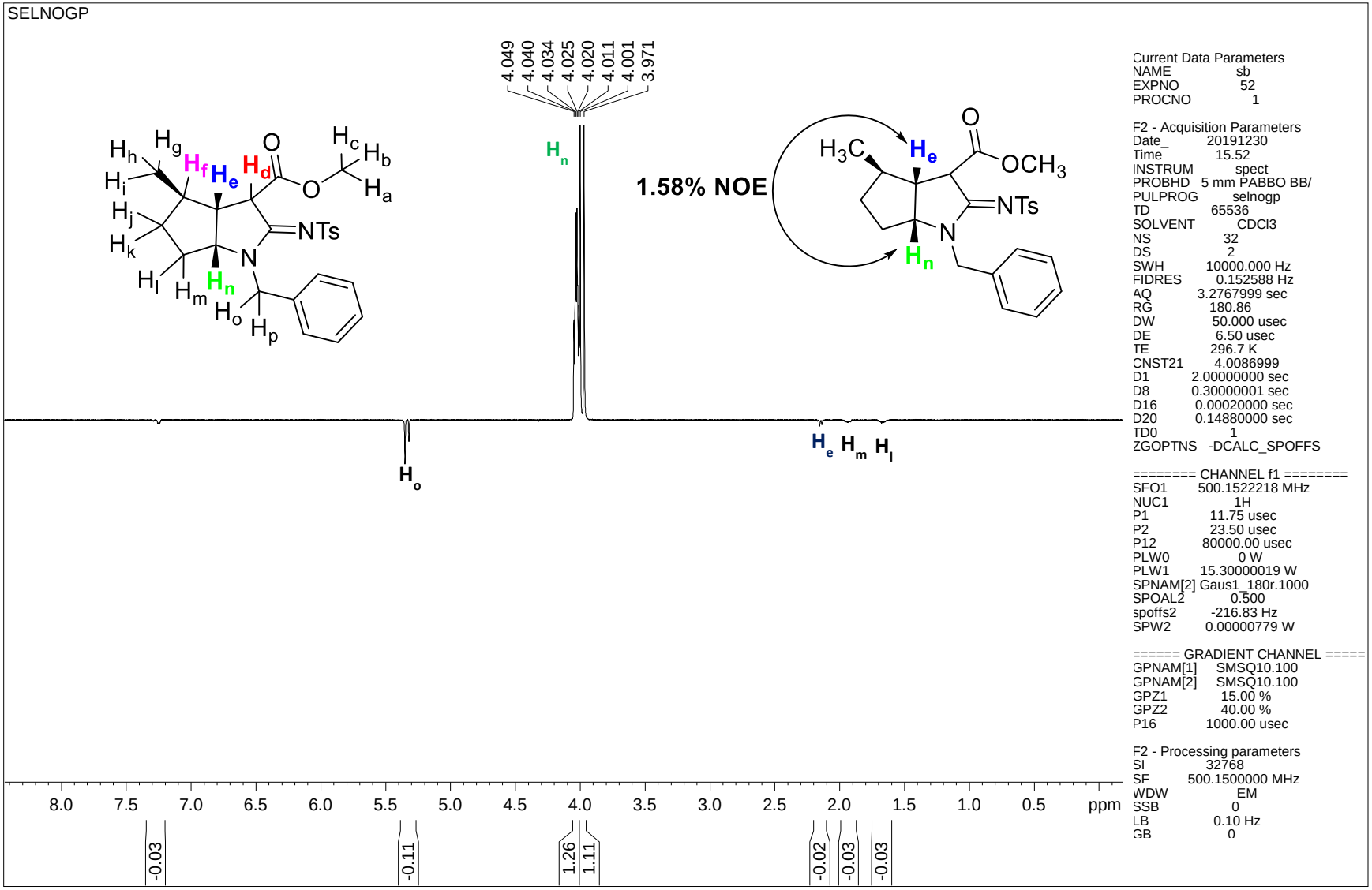
DEPT-135 NMR spectrum of diastereomers 9 and 10



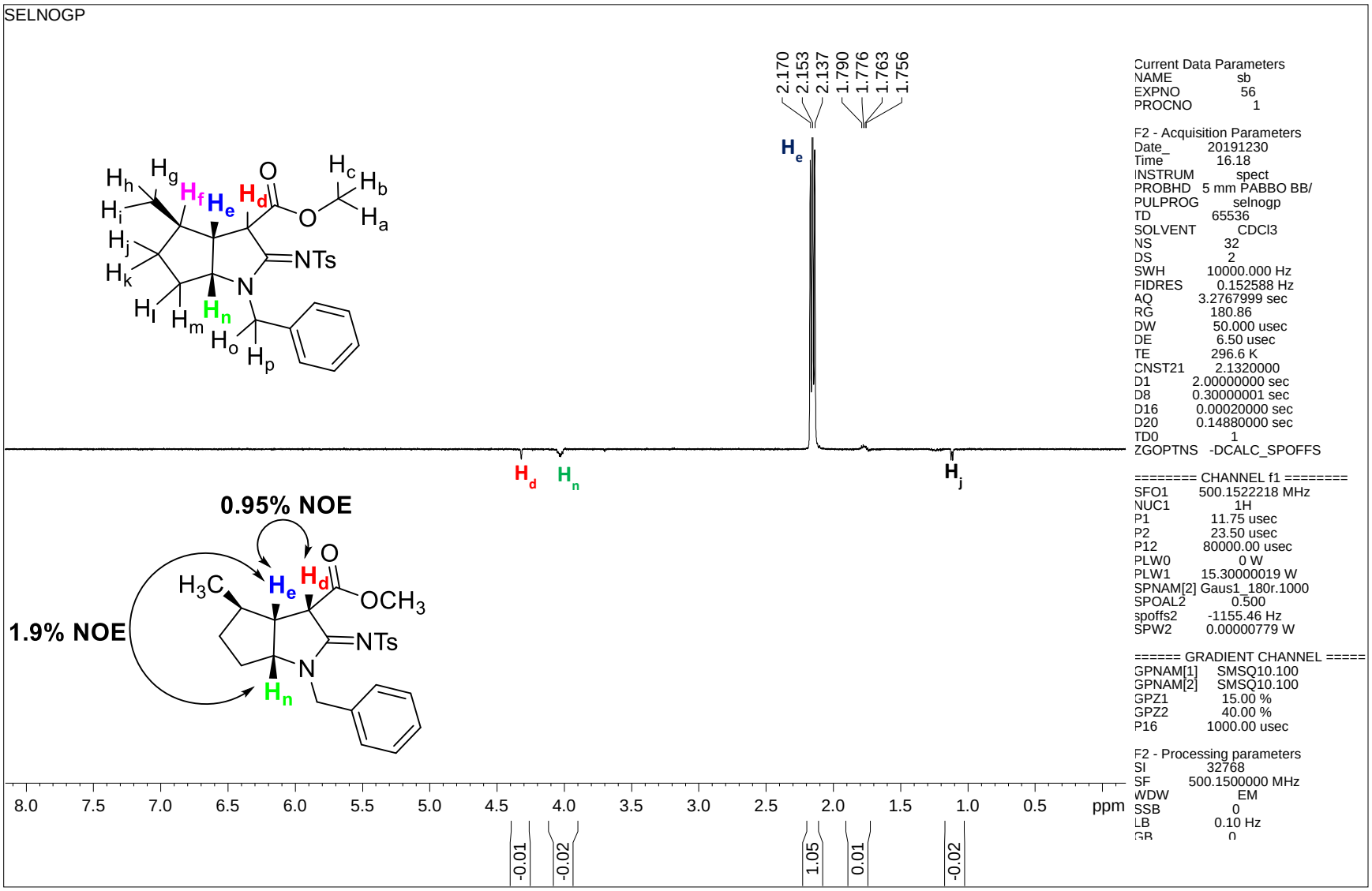
^{1}H-^{1}H COSY NMR spectrum of diastereomers 9 and 10



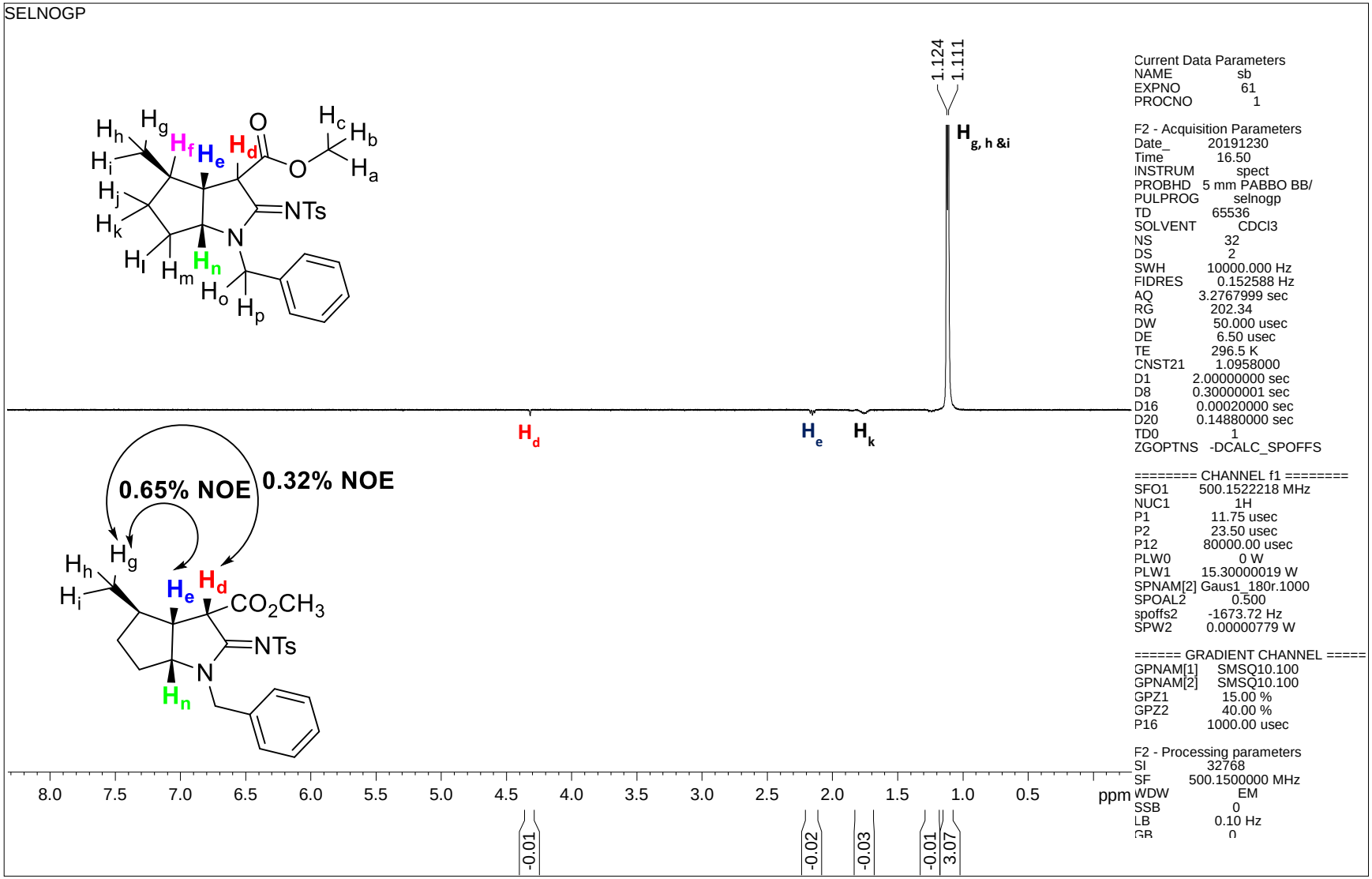
^{1}H-^{13}C HSQC NMR spectrum of diastereomers 9 and 10



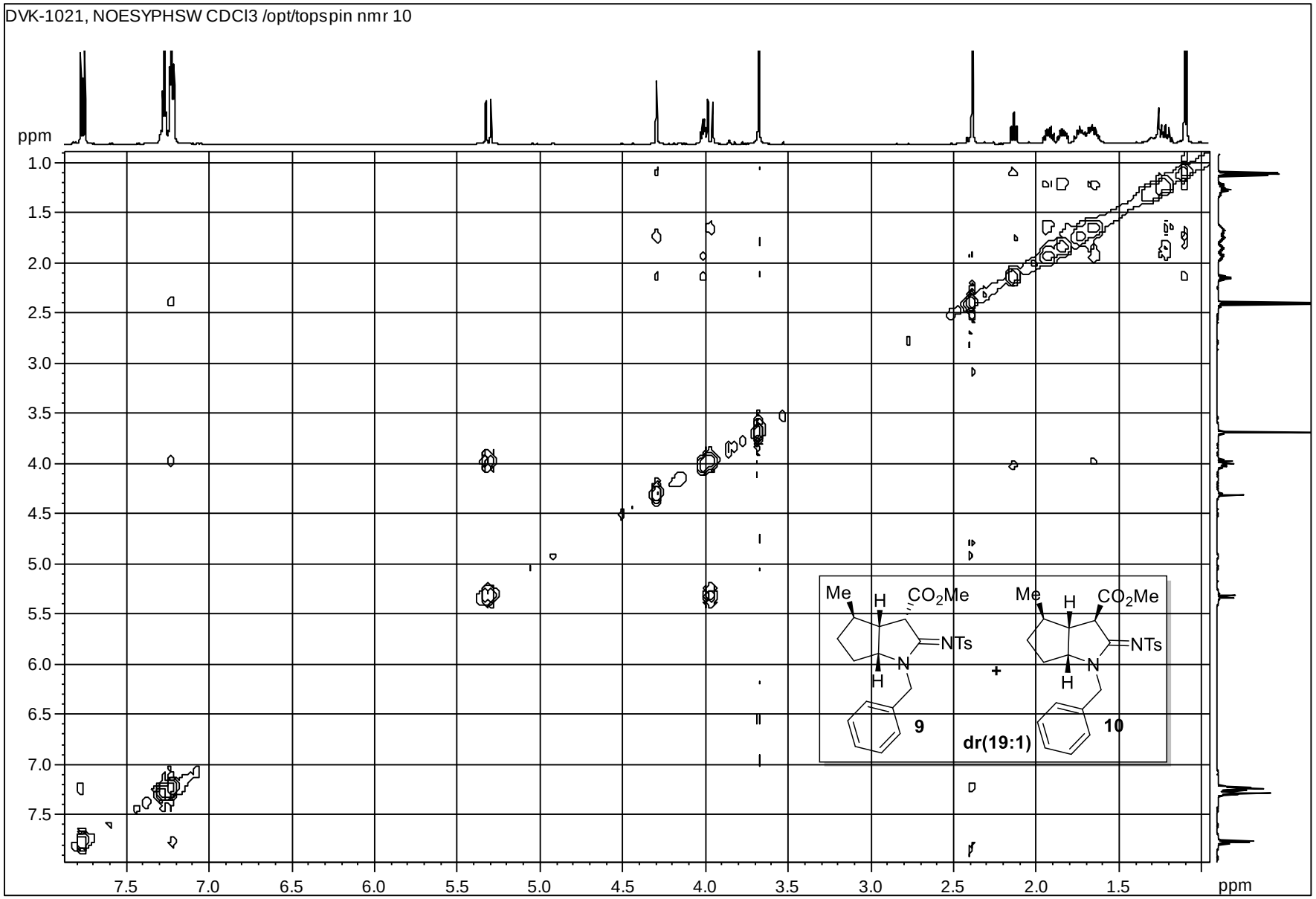
1D-NOE spectrum of diastereomers 9 and 10



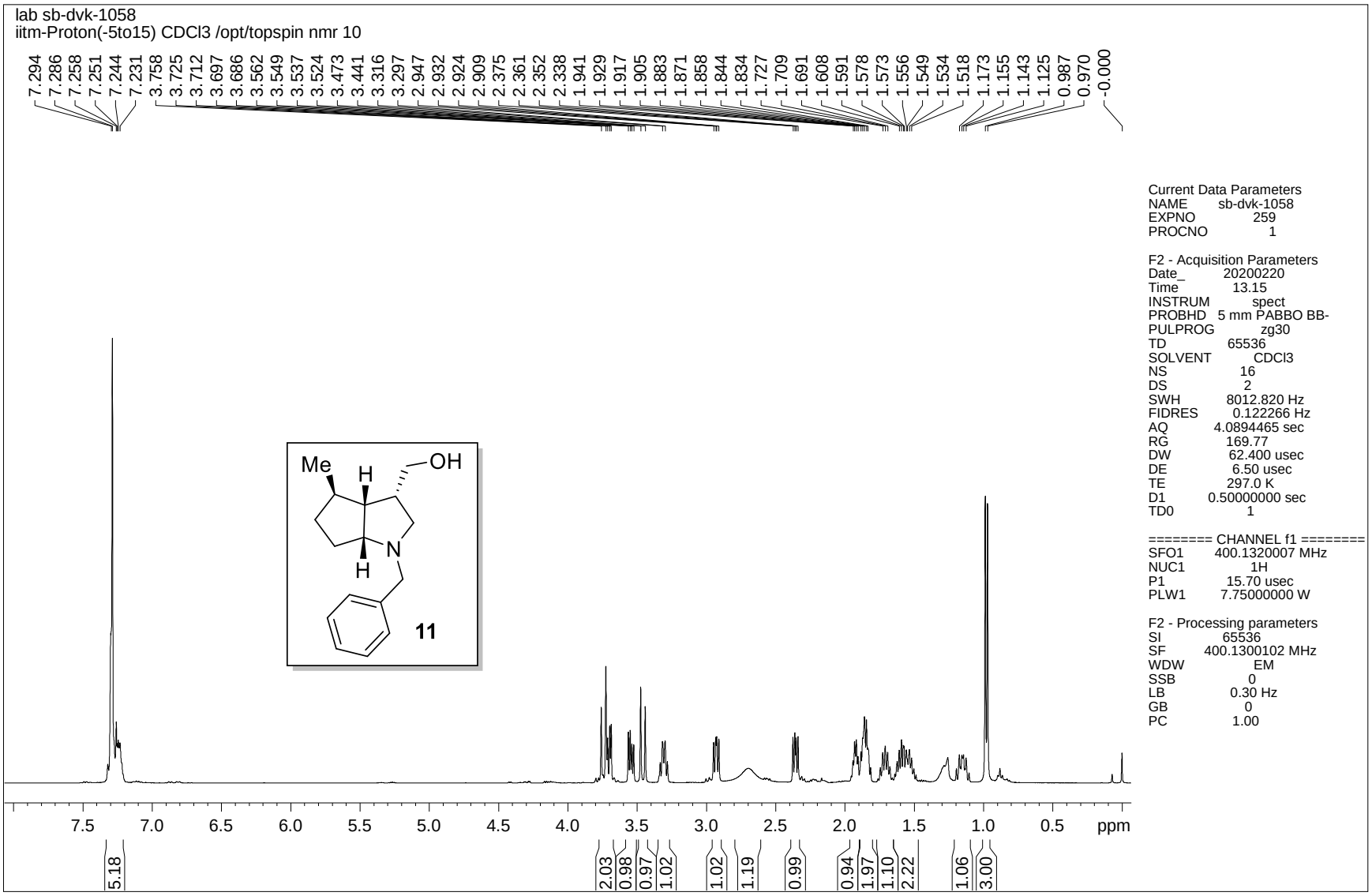
1D-NOE spectrum of diastereomers 9 and 10



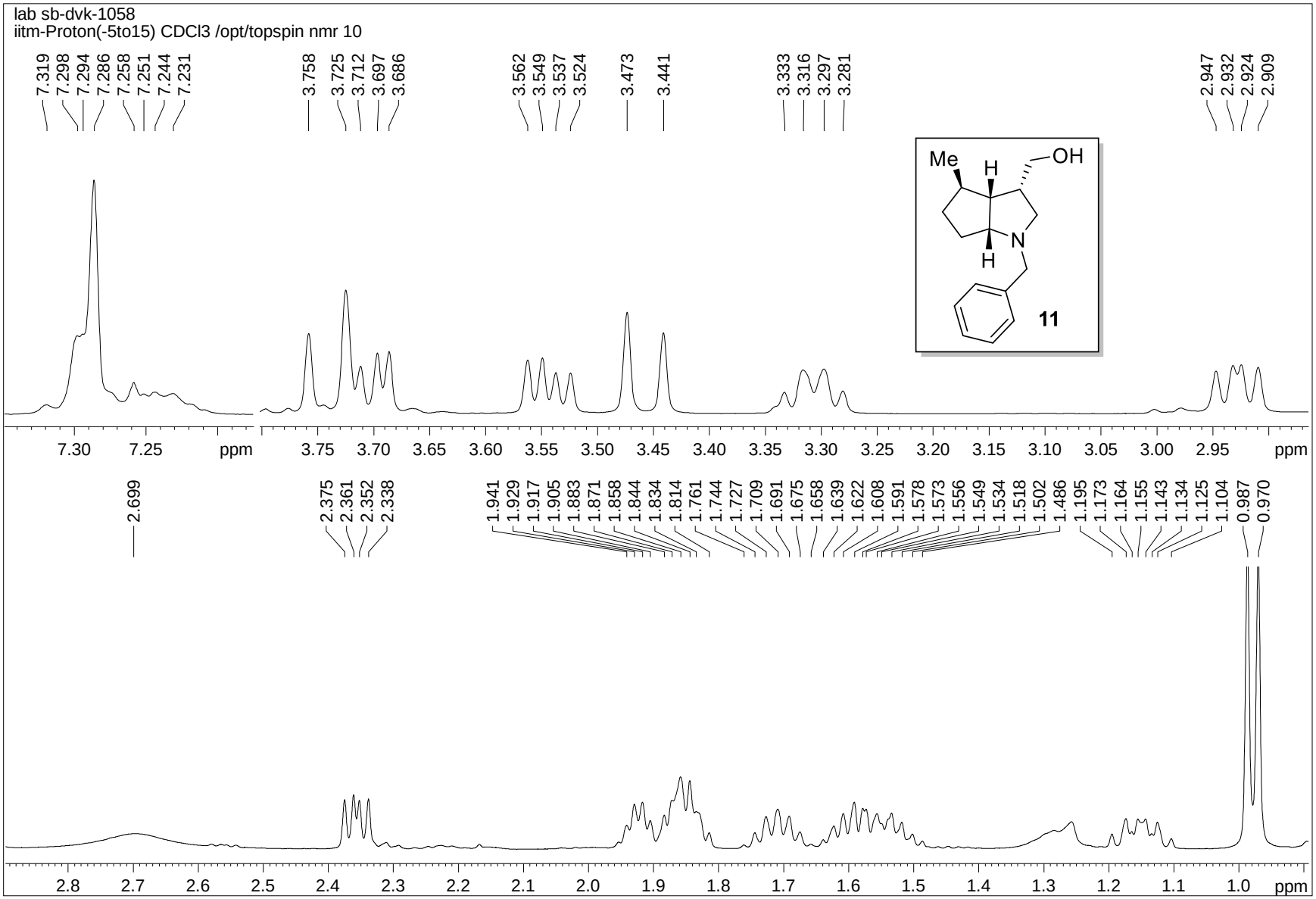
1D-NOE spectrum of diastereomers 9 and 10



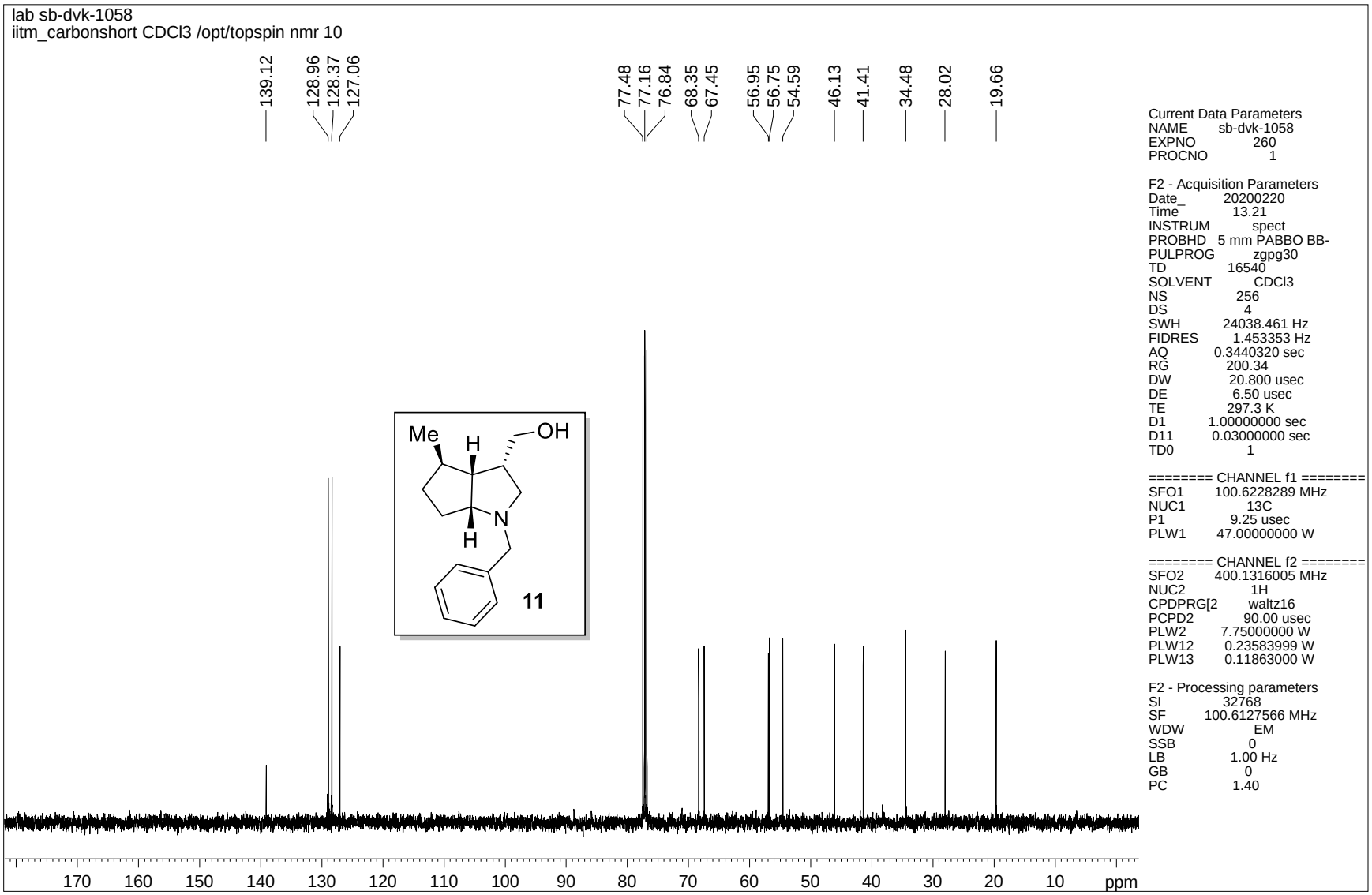
2D-NOE spectrum of diastereomers 9 and 10



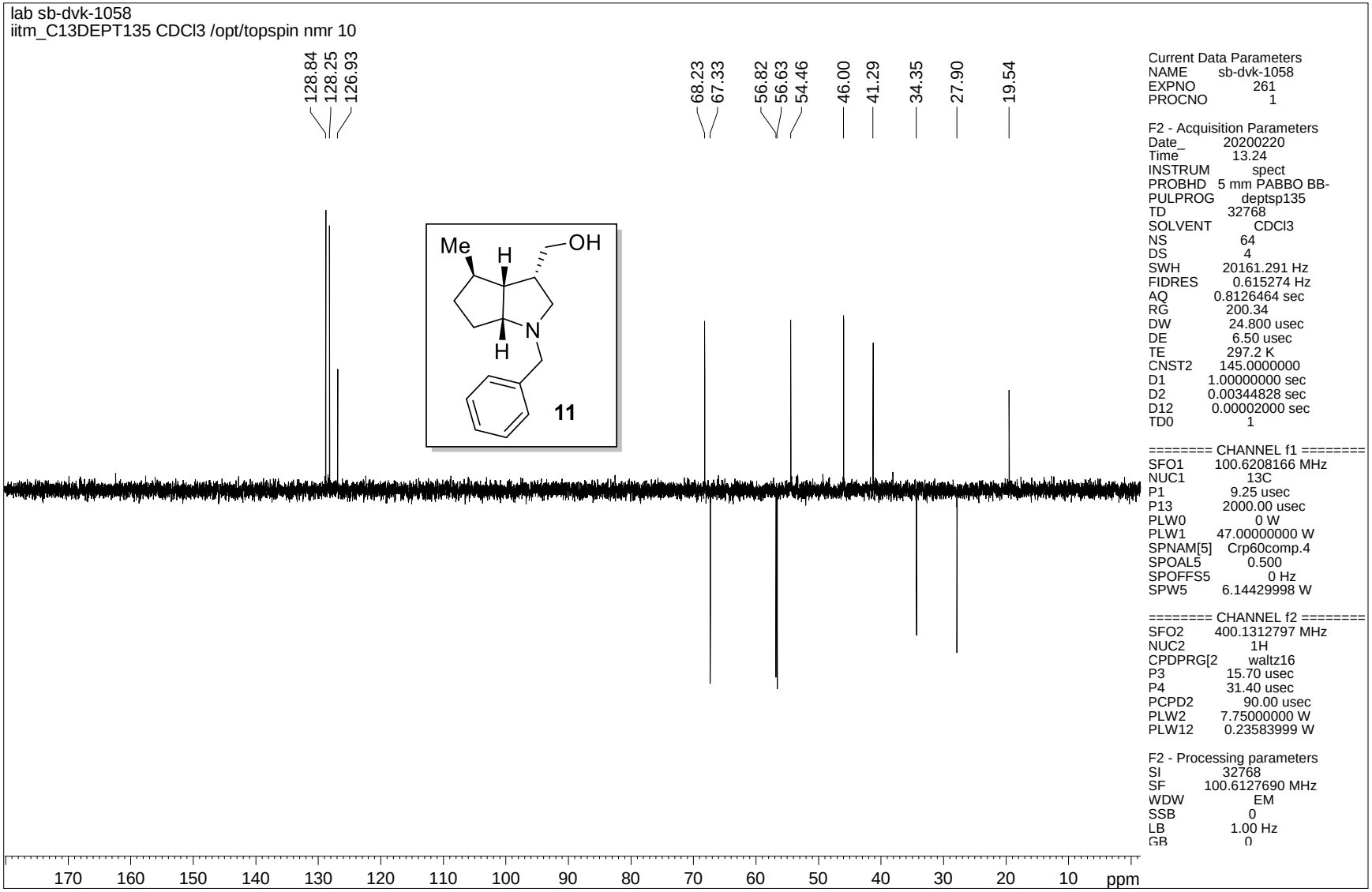
^{1}H NMR spectrum of compound 11



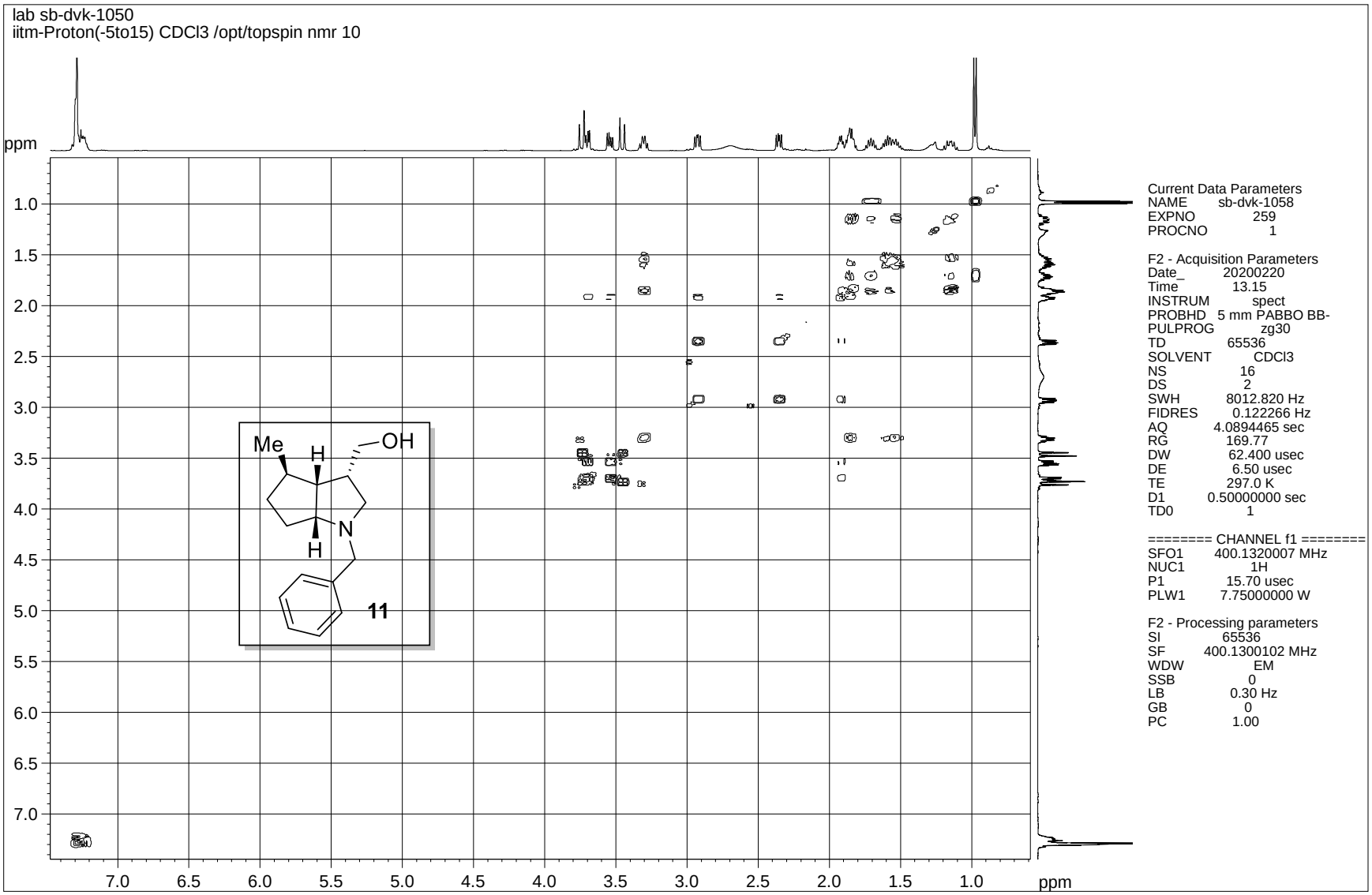
^{1}H NMR spectrum of compound 11



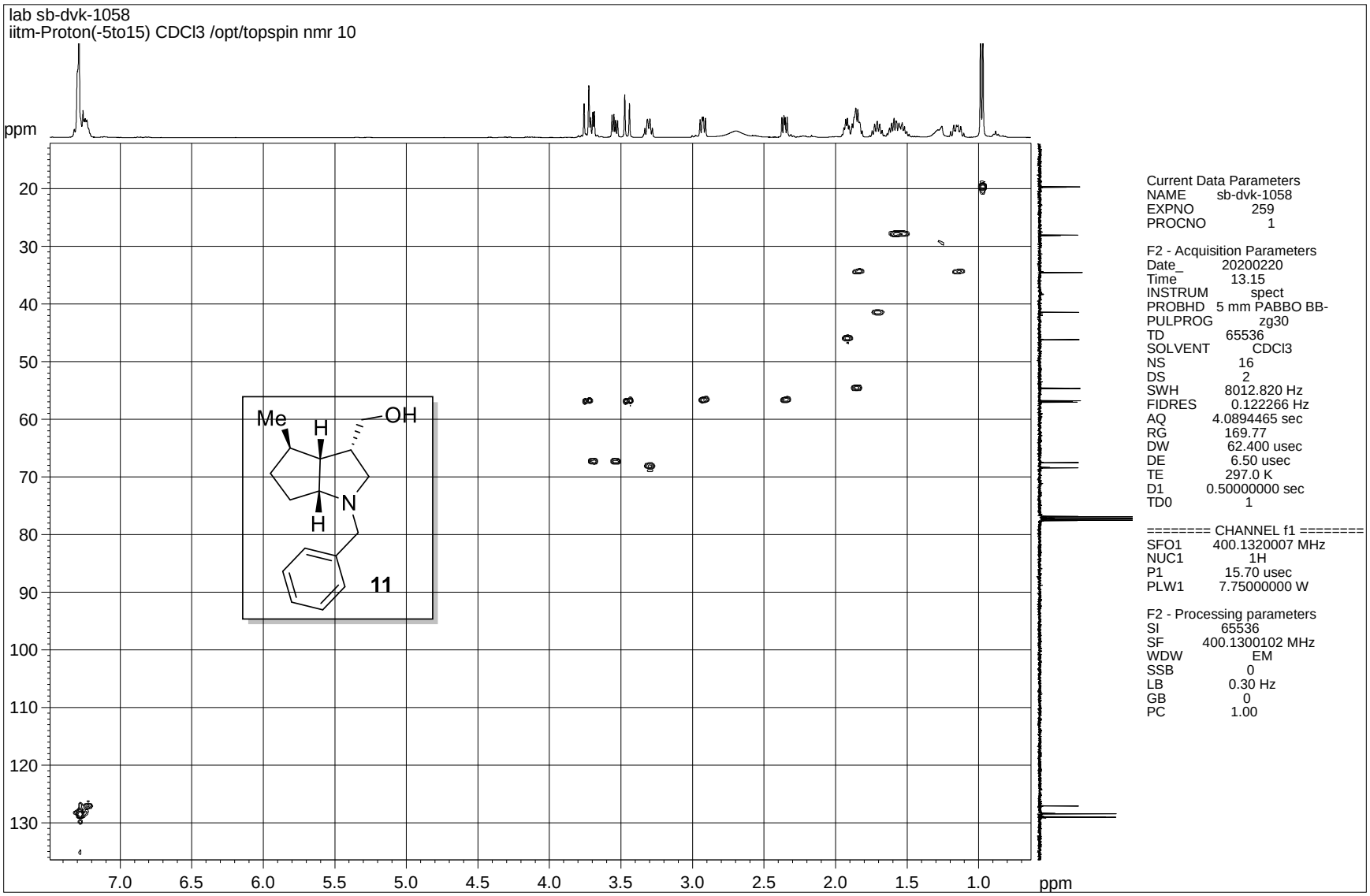
^{13}C NMR spectrum of compound 11



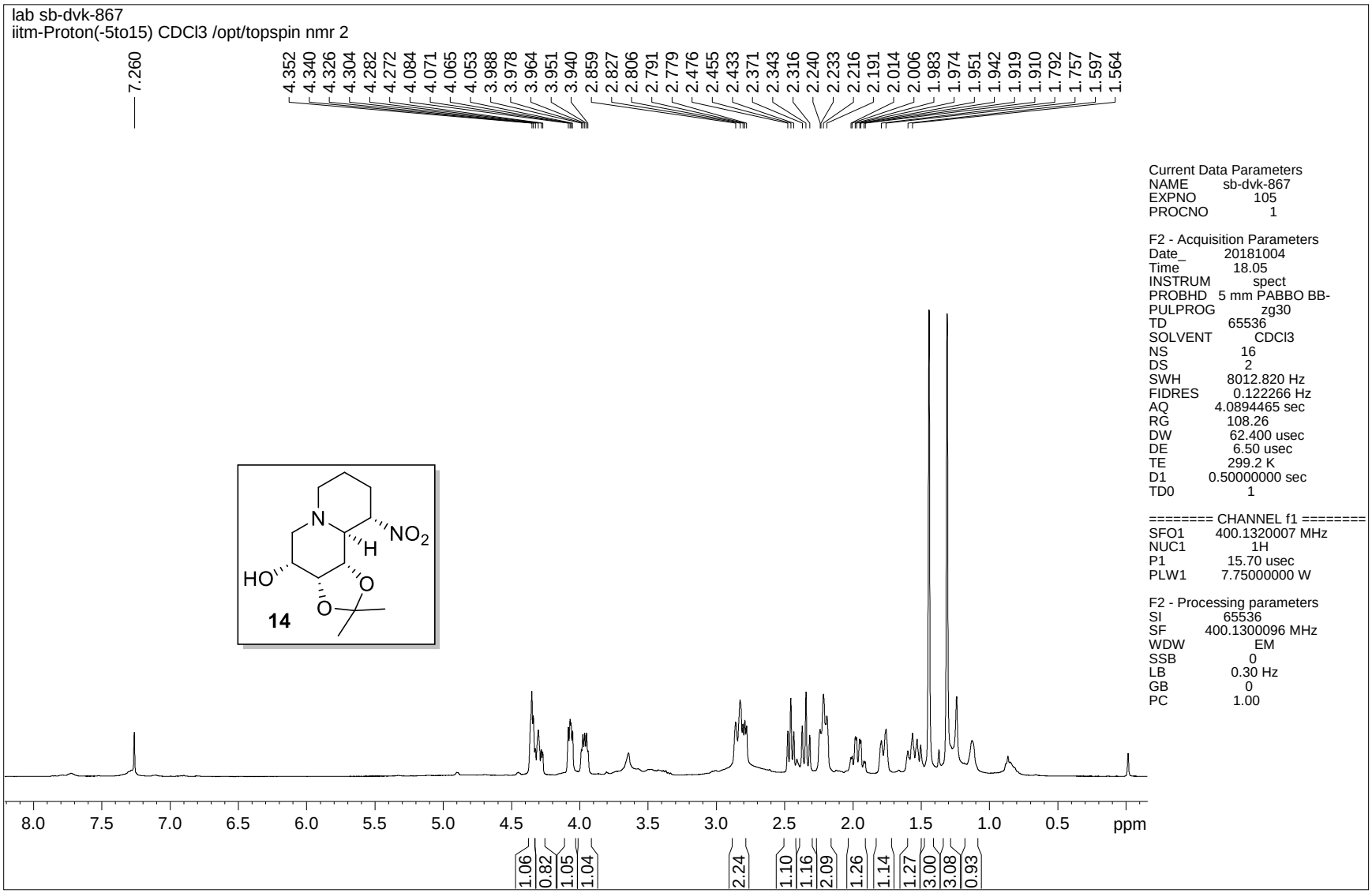
DEPT-135 NMR spectrum of compound 11



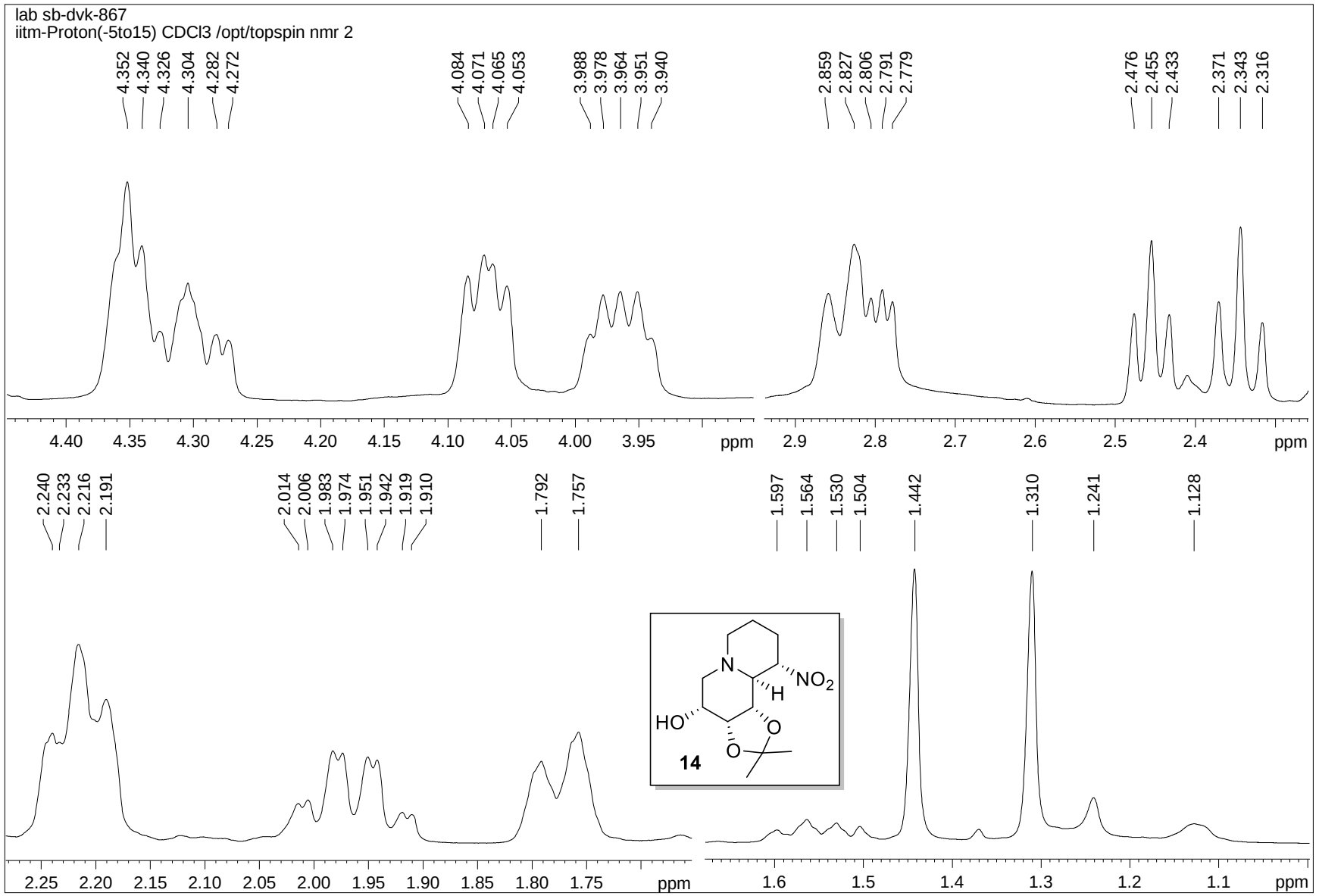
^{1}H-^{1}H COSY NMR spectrum of compound 11



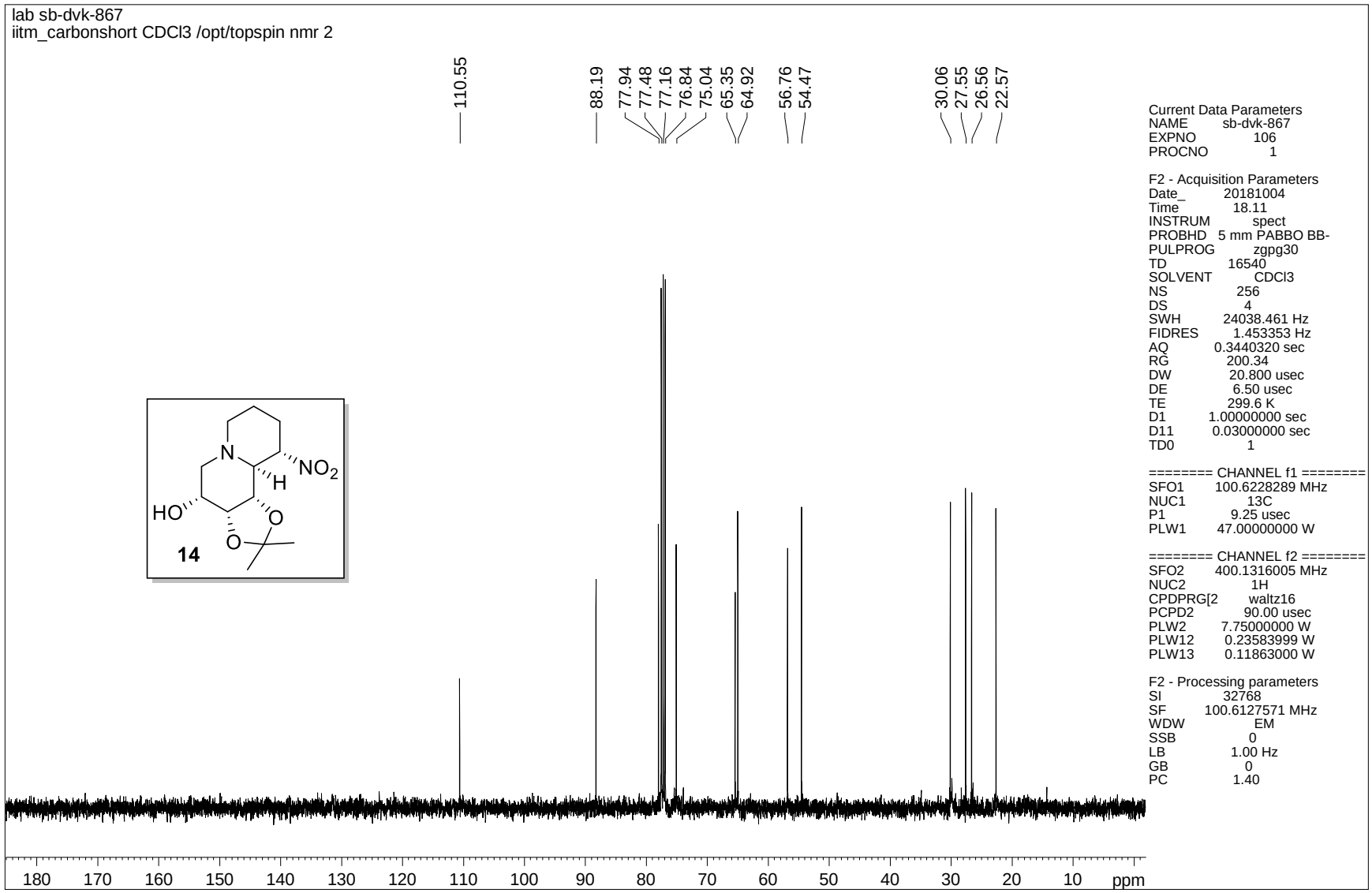
^{1}H-^{13}C HSQC NMR spectrum of compound 11



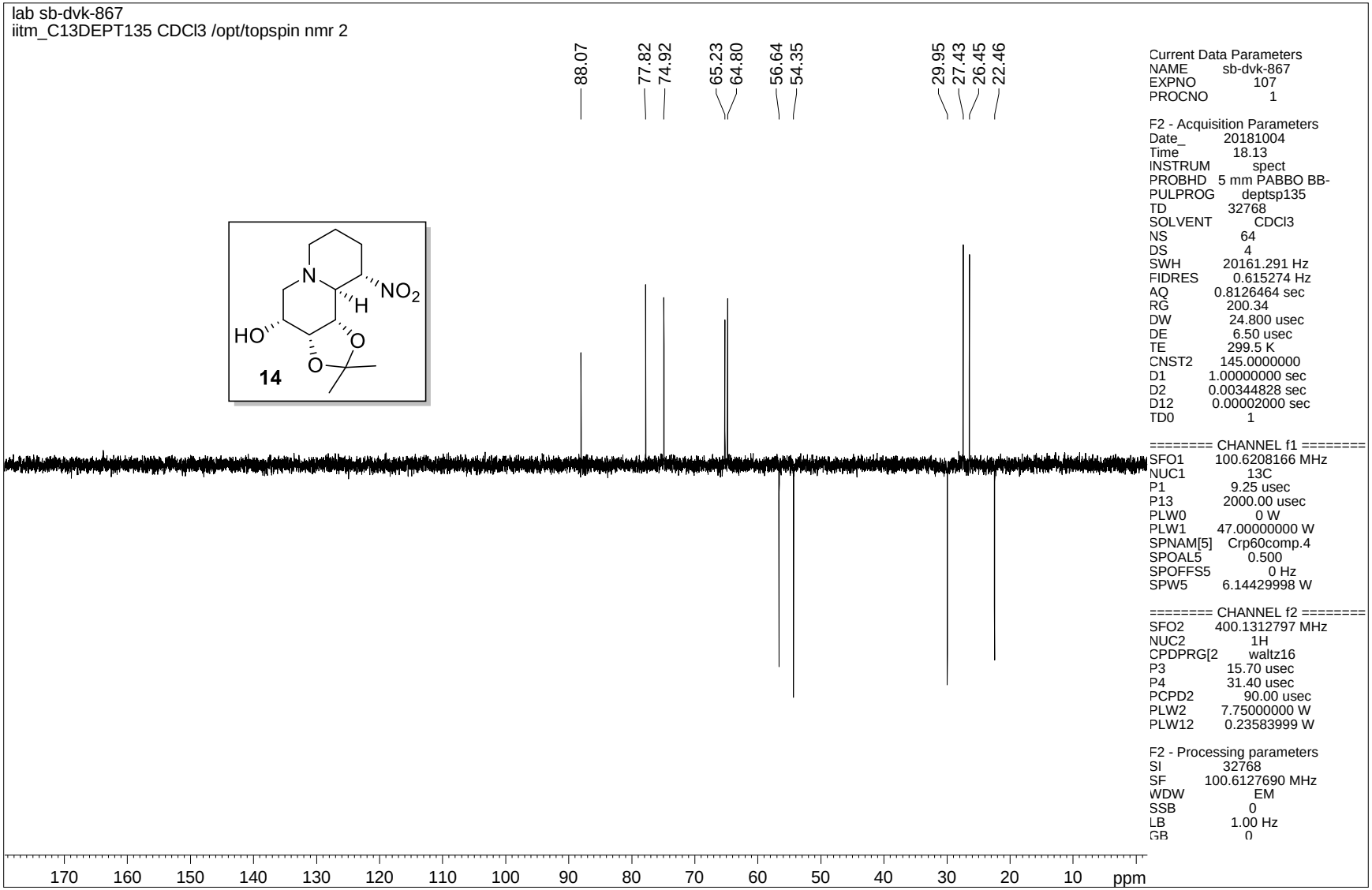
^{1}H NMR spectrum of compound 14



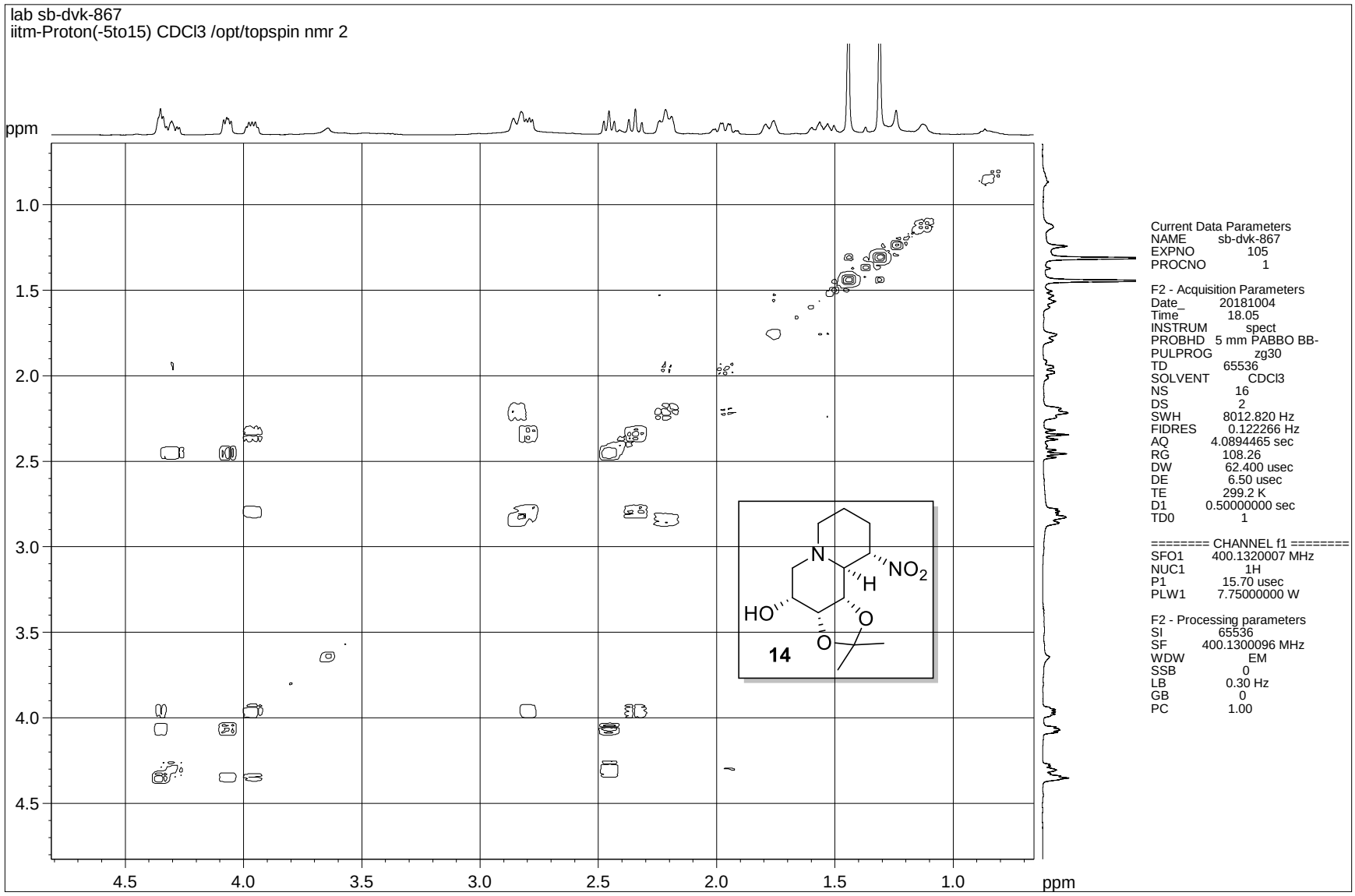
^{1}H NMR spectrum of compound 14



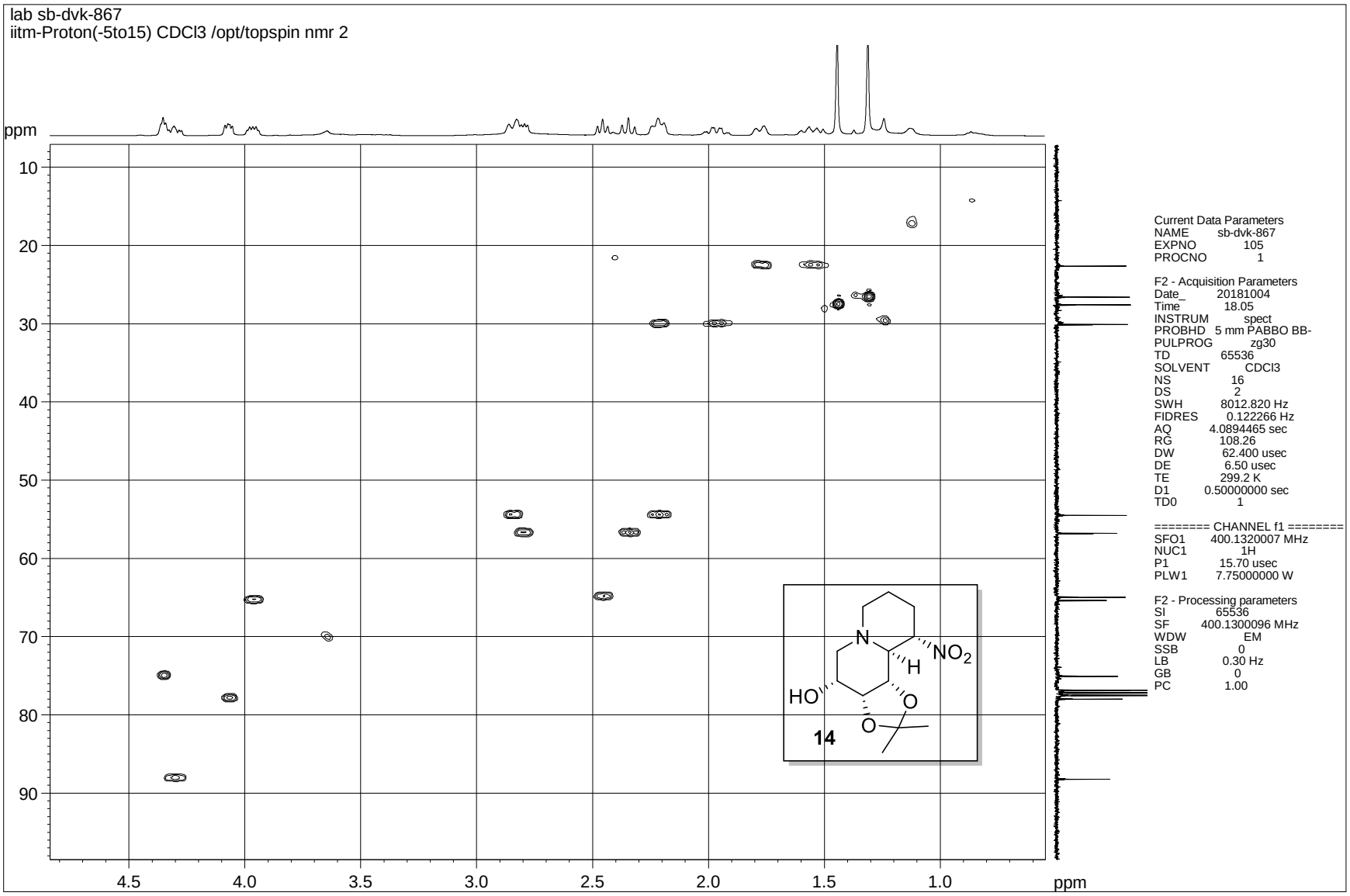
^{13}C NMR spectrum of compound 14



DEPT-135 NMR spectrum of compound 14



^{1}H-^{1}H COSY NMR spectrum of compound 14



^{1}H-^{13}C HSQC NMR spectrum of compound 14