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Supporting Information

Cu-Catalyzed Asymmetric Borylative Cyclization of Cyclohexadienone-Containing 1,6-Enynes**

Ping Liu, Yuki Fukui, Ping Tian, Zhi-Tao He, Cai-Yun Sun, Nuo-Yi Wu, and Guo-Qiang Lin

tianping@sioc.ac.cn
lingq@sioc.ac.cn

Key Laboratory of Synthetic Chemistry of Natural Substances,
Shanghai Institute of Organic Chemistry,
Chinese Academy of Sciences,
345 Lingling Road, Shanghai 200032, China.

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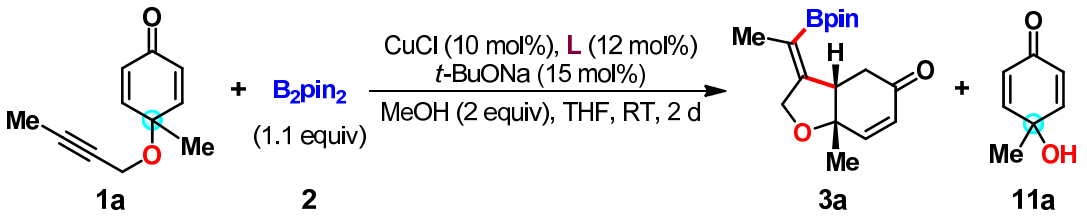
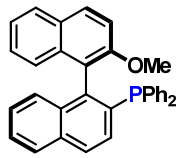
1. General Information

All solvents were dried before use following the standard procedures. Unless otherwise indicated, all starting materials purchased from commercial suppliers were used without further purification. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-400 MHz in the indicated solvents. Chemical shifts are reported in δ (ppm) referenced to an internal TMS standard for ^{1}H NMR and $CDCl_3$ (δ = 77.10 ppm) for ^{13}C NMR. Coupling constants (*J*) are quoted in Hz. Optical rotations were measured on a JASCO P-1030 polarimeter. IR spectra were recorded on Nicolet iN 10 MX. ESI mass spectra were recorded on Agilent1200/G6100A. HRMS of boron-containing compounds is based on ^{10}B.

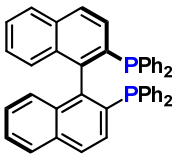
2. Preliminary Reaction Investigation

Initially, various ligands were investigated in Cu-catalyzed tandem borylative cyclization of the model substrate **1a**.

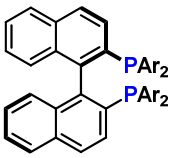




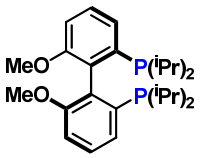
(*R*)-MOP, **L1**



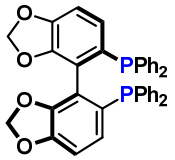
(*R*)-Binap, **L2**



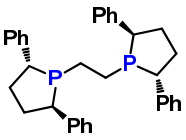
(Ar = 3,5-Me_2-Ph-)
(*R*)-Xyl-BINAP, **L7**



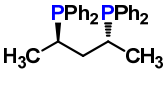
(*R*)-^{i}Pr-MeOBIPHEP, **L8**



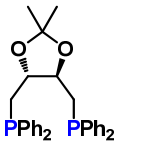
(*R*)-Segphos, **L9**



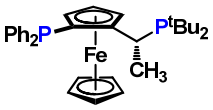
(*R,R*)-Ph-BPE, **L10**



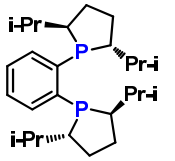
(R,R)-BDPP, **L11**



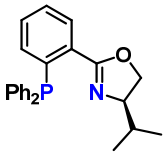
(R,R)-DIOP, **L12**



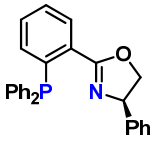
(*R*,S_p)-Josiphos, **L3**



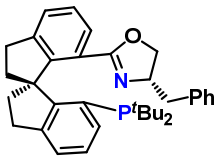
(*R,R*)-*i*Pr-Duphos, **L4**



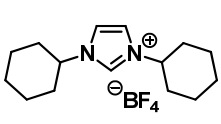
(*R*)-*i*Pr-PHOX, **L5**



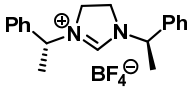
(*R*)-Ph-PHOX, **L13**



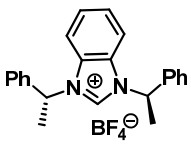
L14



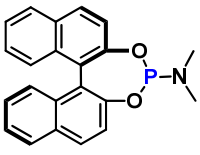
ICy•HBF_4, **L15**



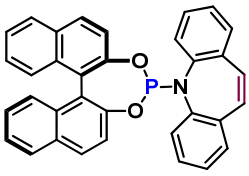
L16



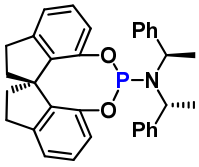
L17



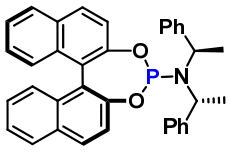
(*R*)-MonoPhos, **L18**



L19



(*R*)-SIPHOS-PE, **L20**



(*S,R,R*)-**L6**

Table 3. Evaluation of Various Ligands for Cu-Catalyzed Tandem Borylative Cyclization of **1a**.[a]

Entry	Ligand	Yield of Recovered 1a (%)[b]	Conversion (%)[c]	Yield of 11a (%)[b]	Yield of 3a (%)[b]	*ee* of 3a (%)[d]
1	Ph_3P	25	75	0	49	--
2[e, g]	**L15**, ICy·HBF_4	14	86	33	27	--
3	**L1**, (*R*)-MOP	16	84	0	47	-2
4	**L2**, (*R*)-Binap	45	55	0	15	56
5[f]	**L2**, (*R*)-Binap	43	57	0	10	47
6	**L7**, (*R*)-Xyl-Binap	57	43	0	12	49
7	**L8**, (*R*)-*i*Pr-MeO-Biphep	57	43	0	18	52
8	**L9**, (*R*)-Segphos	61	39	0	20	48
9	**L10**, (*R*,*R*)-Ph-BPE	62	38	0	10	-1
10	**L11**, (*R*,*R*)-BDPP	49	51	0	3	39
11	**L12**, (*R*,*R*)-DIOP	47	53	0	10	40
12	**L3**, (*R*,*S*p)-Josiphos	60	40	0	12	-21
13	**L4**, (*R*,*R*)-*i*Pr-Duphos	57	43	0	7	-65
14	**L5**, (*R*)-*i*Pr-PHOX	35	65	0	33	-10
15	**L13**, (*R*)-Ph-PHOX	52	48	0	45	1
16	**L14**	61	39	0	37	-4
17[e]	**L16**	24	76	0	47	-35
18[e]	**L17**	66	34	0	7	-2
19	**L18**, (*R*)-MonoPhos	24	76	0	64	-45
20	**L19**	59	41	0	26	-78
21	**L20**, (*R*)-SIPHOS-PE	42	58	0	54	88
22	**L6**	24	76	0	70	94
23[h,j]	**L6**	27	73	0	58	90
24[i,j]	**L6**	33	67	0	51	87

[a] The reaction was carried out with **1a** (0.1 mmol), **2** (0.11 mmol), CuCl (10 mol%), **L** (12 mol%), *t*-BuONa (15 mol%), and MeOH (2 equiv) in THF (2 mL) at room temperature under N_2 atmosphere.

[b] Yield of isolated yield.

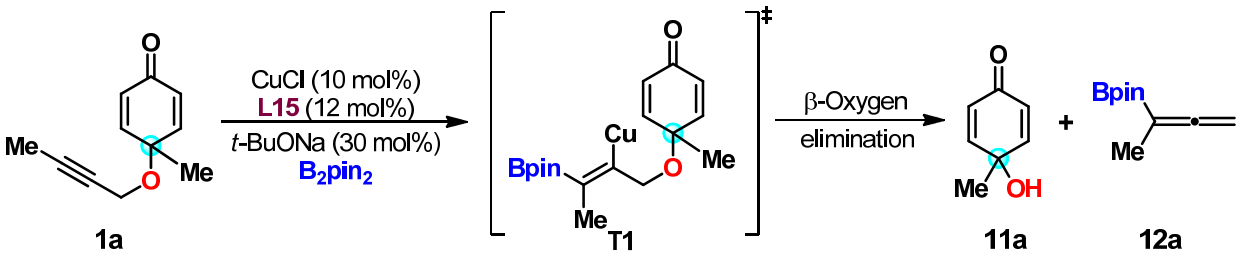
[c] Conversion was determined by the recovered **1a**.

[d] Determined by HPLC analysis using a chiral stationary phase.

[e] *t*-BuONa (30 mol%) was used.

[f] At 60°C.

[g] Using ICy·HBF$_4$ (**L15**) as ligand, a side product **11a** was observed, which might be caused by the β-oxygen elimination of intermediate **T1**. (Scheme 4)

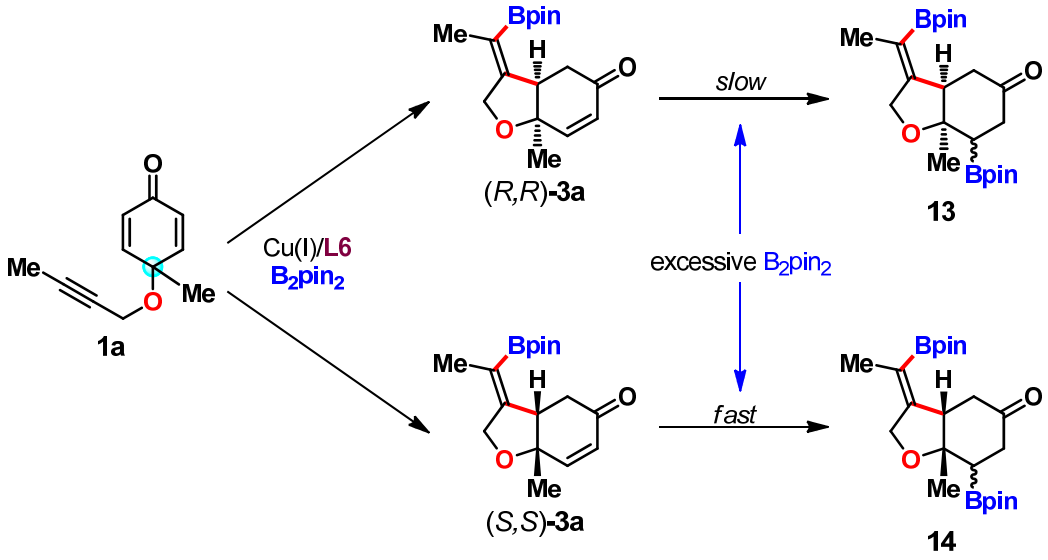


Scheme 4

[h] B_2pin_2 (**2**, 1.2 equiv) was used.

[i] B_2pin_2 (**2**, 1.3 equiv) was used.

[j] Increasing B_2pin_2 (**2**) loading led to different levels of erosion in both yields and enantioselectivities (Table 3, entries 23-24), which might be caused by the further conjugate borylation of the excessive B_2pin_2 to **3a**. (Scheme 5)

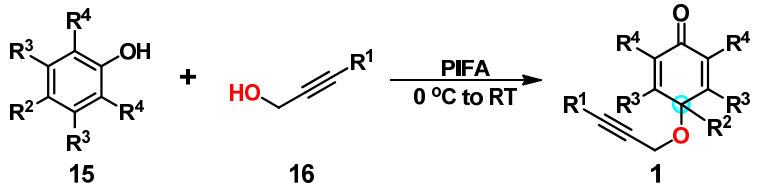


Scheme 5

Optimal Reaction Conditions: The reaction was carried out with **1a** (0.1 mmol), **2** (0.11 mmol), CuCl (10 mol%), **L6** (12 mol%), *t*-BuONa (15 mol%), and MeOH (2 equiv) in THF (2 mL) at room temperature under N_2 atmosphere.

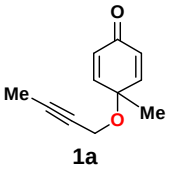
3. SUBSTRATE PREPARATION

3.1 General Procedure for Preparation of Substrates 1a-1c and 1g-1r.[1]



A well-stirred solution of substituted phenol **15** (1.0 mmol) in 1 mL of 3-substituted propargyl alcohol **16** was cooled to 0 °C and treated with phenyliodine(III)bis(trifluoroacetate) (PIFA, 516 mg, 1.2 mmol, 1.2 equiv, for substrates **1a**, **1b**, **1c**, **1g**, **1i**, **1j**, **1m**, **1n**, **1o**) or phenyliodine (III) diacetate (PIDA, 387 mg, 1.2 mmol, 1.2 equiv, for substrates **1h**, **1k**, **1l**, **1p**, **1q**, **1r**) in several portions. The resulting mixture was warmed to room temperature and stirred overnight. Then it was diluted with water (30 mL) and extracted with ethyl acetate (30 mL ×3). The combined organic phases were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent to afford the desired product **1**.

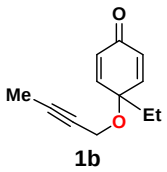
4-(But-2-yn-1-yloxy)-4-methylcyclohexa-2,5-dienone (1a)[1]



1a

White solid. 76 mg, 43% yield. mp 81 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.83 (d, J = 10.4 Hz, 2H), 6.30 (d, J = 10.4 Hz, 2H), 3.96 (q, J = 2.4 Hz, 2H), 1.84 (t, J = 2.0 Hz, 3H), 1.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.05, 151.09, 130.38, 83.33, 75.58, 72.97, 54.37, 26.43, 3.73; ESI-MS: $[M+Na]^{\oplus}$ 199.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{11}H_{12}O_2Na^{\oplus}$ 199.0730, found 199.0732; IR (KBr) ν (cm^{-1}) 2975, 2928, 1665, 1630, 1380, 1309, 1081, 1033, 900, 865.

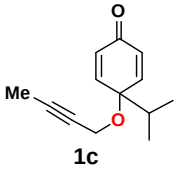
4-(But-2-yn-1-yloxy)-4-ethylcyclohexa-2,5-dienone (1b)[1c]



1b

Yellow solid. 57 mg, 30% yield. mp 61-62 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.77 (d, J = 10.4 Hz, 2H), 6.36 (d, J = 10.4 Hz, 2H), 3.98 (q, J = 2.4 Hz, 2H), 1.85-1.80 (m, 5H), 0.83 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.41, 150.29, 131.60, 83.17, 75.74, 54.22, 32.24, 7.83, 3.71; ESI-MS: $[M+Na]^{\oplus}$ 213.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{12}H_{14}O_2Na^{\oplus}$ 213.0886, found 213.0891; IR (KBr) ν (cm^{-1}) 3035, 2974, 2928, 1670, 1604, 1390, 1051, 924, 876, 809.

4-(But-2-yn-1-yloxy)-4-isopropylcyclohexa-2,5-dienone (1c) [1c]



1c

Yellow solid. 37 mg, 18% yield. mp 56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.78 (d, J = 10.4 Hz, 2H), 6.39 (d, J = 10.4 Hz, 2H), 3.96 (q, J = 2.4 Hz, 2H), 2.06-2.03 (m, 1H), 1.84 (t, J = 2.4 Hz, 3H), 0.94 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.59, 149.51, 132.19, 82.97, 78.75, 76.00, 54.18, 36.59, 17.13, 3.76; ESI-MS: $[M+Na]^{\oplus}$ 227.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{13}H_{16}O_2Na^{\oplus}$ 227.1043, found 227.1049; IR (KBr) ν (cm^{-1}) 3045, 2997, 2968, 1661, 1622, 1388, 1276, 1066, 924, 862, 802.

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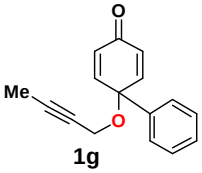
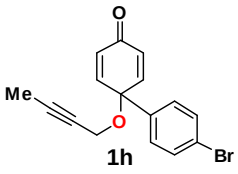
[1] (a) Tello-Aburto, R.; Harned, A. M. *Org. Lett.* **2009**, *11*, 3998. (b) Keilitz, J.; Newman, S. G.; Lautens, M. *Org. Lett.* **2013**, *15*, 1148. (c) He, Z.-T.; Tian, B.; Fukui, Y.; Tong, X.; Tian, P.; Lin, G.-Q. *Angew. Chem. Int. Ed.* **2013**, *52*, 5314.

1-(But-2-yn-1-yloxy)-[1,1'-biphenyl]-4(1H)-one (1g)[1c,2]



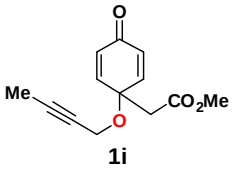
Red solid. 52 mg, 22% yield. mp 97 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.48 (d, J = 7.2 Hz, 2H), 7.38-7.30 (m, 3H), 6.88 (d, J = 10.4 Hz, 2H), 6.38 (d, J = 10.4 Hz, 2H), 4.20 (q, J = 2.4 Hz, 2H), 1.86 (t, J = 2.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.58, 149.96, 137.86, 129.88, 128.90, 128.53, 125.88, 83.47, 76.79, 75.86, 54.13, 3.78; ESI-MS: $[M+Na]^{\oplus}$ 261.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{14}O_2Na^{\oplus}$ 261.0886, found 261.0890; IR (KBr) ν (cm^{-1}) 3065, 3039, 2925, 2863, 1668, 1489, 1448, 1279, 1051, 927, 753, 697.

4'-Bromo-1-(but-2-yn-1-yloxy)-[1,1'-biphenyl]-4(1H)-one (1h)



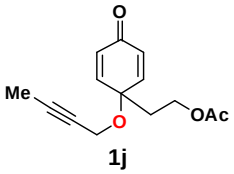
Light yellow solid. 30 mg, 10% yield. mp 126-127 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.48 (d, J = 8.8 Hz, 2H), 7.35 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 10.0 Hz, 2H), 6.39 (d, J = 10.0 Hz, 2H), 4.19 (q, J = 2.4 Hz, 2H), 1.86 (t, J = 2.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.29, 149.38, 137.02, 132.01, 130.15, 127.67, 122.68, 83.73, 76.48, 75.67, 54.24, 3.79; ESI-MS: $[M(C_{16}H_{13}{}^{79}BrO_2)+Na]^{\oplus}$ 339.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{13}{}^{79}BrO_2Na^{\oplus}$ 338.9997, found 338.9991; IR (KBr) ν (cm^{-1}) 3037, 2977, 2932, 2869, 2240, 1667, 1630, 1455, 1384, 1118, 1095, 1082, 867.

Methyl 2-(1-(but-2-yn-1-yloxy)-4-oxocyclohexa-2,5-dien-1-yl)acetate (1i)



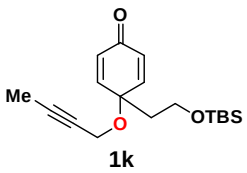
White solid. 9 mg, 4% yield. mp 59-60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.97 (d, J = 10.4 Hz, 2H), 6.37 (d, J = 10.4 Hz, 2H), 3.98 (q, J = 2.4 Hz, 2H), 3.66 (s, 3H), 2.78 (s, 2H), 1.83 (t, J = 2.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.88, 168.59, 148.37, 131.47, 83.70, 75.48, 73.12, 54.20, 52.07, 44.55, 3.73; ESI-MS: $[M+Na]^{\oplus}$ 257.0; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{13}H_{14}O_4Na^{\oplus}$ 257.0790, found 257.0784; IR (KBr) ν (cm^{-1}) 3084, 2988, 2919, 2954, 2868, 2320, 2239, 1732, 1704, 1666, 1625, 1460, 1440, 1390, 1371, 1357, 1290, 1244, 1185, 1166, 1095, 1062, 997, 873.

2-(1-(But-2-yn-1-yloxy)-4-oxocyclohexa-2,5-dien-1-yl)ethyl acetate (1j)[1c]



Yellow oil. 62 mg, 25% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.83 (d, J = 10.0 Hz, 2H), 6.36 (d, J = 10.0 Hz, 2H), 4.15 (t, J = 6.4 Hz, 2H), 3.97 (q, J = 2.4 Hz, 2H), 2.12 (t, J = 6.8 Hz, 2H), 2.01 (s, 3H), 1.84 (t, J = 2.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.94, 170.69, 149.46, 131.33, 83.52, 75.55, 74.31, 59.40, 54.10, 38.62, 20.88, 3.70; ESI-MS: $[M+Na]^{\oplus}$ 271.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{14}H_{16}O_4Na^{\oplus}$ 271.0941, found 271.0946; IR (KBr) ν (cm^{-1}) 2983, 2930, 1690, 1671, 1630, 1525, 1368, 1254, 1166, 1053, 863, 779.

4-(But-2-yn-1-yloxy)-4-(2-((tert-butyldimethylsilyl)oxy)ethyl)cyclohexa-2,5-dienone (1k)

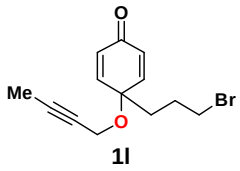


Light yellow solid. 44 mg, 14% yield. mp 70-72 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.86 (d, J = 10.0 Hz, 2H), 6.31 (d, J = 10.0 Hz, 2H), 3.95 (q, J = 2.0 Hz, 2H), 3.68 (t, J = 6.0 Hz, 2H), 1.99 (t, J = 6.0 Hz, 2H), 1.82 (t, J = 2.0 Hz, 3H), 0.85 (s, 9H), 0.00 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.40, 150.45, 130.60,

[2] J. K. Hexum, R. Tello-Aburto, N. B. Struntz, A. M. Harned, D. A. Harki, *ACS Med. Chem. Lett.* **2012**, *3*, 459.

83.15, 75.70, 74.76, 57.84, 53.85, 42.86, 25.77, 18.07, 3.70, -5.50; ESI-MS: $[M+Na]^{\oplus}$ 343.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{28}O_3SiNa^{\oplus}$ 343.1705, found 343.1700; IR (KBr) ν (cm^{-1}) 3080, 3035, 2954, 2929, 2896, 2859, 2323, 2242, 1740, 1664, 1625, 1604, 1472, 1461, 1437, 1401, 1390, 1277, 1255, 1185, 1155, 1084, 1084, 1038, 1005, 924, 880.

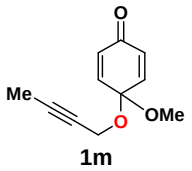
4-(3-Bromopropyl)-4-(but-2-yn-1-yloxy)cyclohexa-2,5-dienone (1l)



1l

Light yellow solid. 42 mg, 15% yield. mp 71-73 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.80 (d, J = 10.4 Hz, 2H), 6.37 (d, J = 10.4 Hz, 2H), 3.98 (q, J = 2.4 Hz, 2H), 3.37 (t, J = 12.8 Hz, 2H), 1.91-1.96 (m, 2H), 1.84-1.89 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.09, 149.83, 131.69, 83.49, 75.65, 75.47, 54.29, 38.21, 33.06, 26.94, 3.78; ESI-MS: $[M+Na]^{\oplus}$ 305.1/307.1 (1:1); HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{13}H_{15}{}^{79}BrO_2Na^{\oplus}$ 305.0153, found 305.0148; IR (KBr) ν (cm^{-1}) 3038, 2968, 2943, 2919, 2890, 2857, 2241, 1694, 1672, 1629, 1604, 1450, 1385, 1285, 1176, 1062, 865.

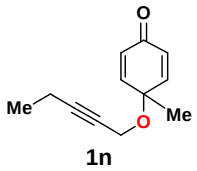
4-(But-2-yn-1-yloxy)-4-methoxycyclohexa-2,5-dienone (1m)



1m

Light yellow Oil. 8 mg, 4% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.87 (d, J = 10.0 Hz, 2H), 6.26 (d, J = 10.0 Hz, 2H), 4.27 (q, J = 2.0 Hz, 2H), 3.40 (s, 3H), 1.85 (t, 3H, J = 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.15, 142.83, 129.76, 92.66, 83.22, 75.11, 51.49, 50.70, 3.72. ESI-MS: $[M+Na]^{\oplus}$ 215.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{11}H_{12}O_3Na^{\oplus}$ 215.0684, found 215.0679; IR (KBr) ν (cm^{-1}) 3055, 2942, 2922, 2834, 2305, 2239, 1670, 1640, 1617, 1459, 1386, 1317, 1247, 1181, 1155, 1104, 1063, 1027, 967, 952, 915, 857.

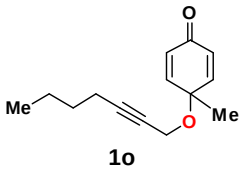
4-Methyl-4-(pent-2-yn-1-yloxy)cyclohexa-2,5-dienone (1n)



1n

White Solid. 80 mg, 42% yield. mp 53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.84 (d, J = 10.0 Hz, 2H), 6.30 (d, J = 10.0 Hz, 2H), 3.98 (t, J = 2.0 Hz, 2H), 2.19-2.25 (m, 2H), 1.13 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.14, 151.21, 130.38, 89.13, 75.84, 73.03, 54.44, 26.48, 13.61, 12.58; ESI-MS: $[M+Na]^{\oplus}$ 213.0; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{12}H_{14}O_2Na^{\oplus}$ 213.0891, found 213.0886; IR (KBr) ν (cm^{-1}) 3068, 3041, 2926, 2866, 2241, 1670, 1627, 1487, 1389, 1052, 1023, 1005, 869.

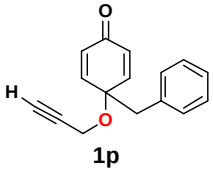
4-(Hept-2-yn-1-yloxy)-4-methylcyclohexa-2,5-dienone (1o)



1o

Yellow solid. 46 mg, 21% yield. mp 43-44 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.84 (d, J = 10.0 Hz, 2H), 6.29 (d, J = 10.0 Hz, 2H), 3.99 (t, J = 2.0 Hz, 2H), 2.22-2.18 (m, 2H), 1.50-1.36 (m, 7H), 0.90 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.16, 151.27, 130.35, 87.91, 76.55, 73.07, 54.48, 30.57, 26.50, 22.01, 18.59, 13.61; ESI-MS: $[M+Na]^{\oplus}$ 241.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{14}H_{18}O_2Na^{\oplus}$ 241.1199, found 241.1203; IR (KBr) ν (cm^{-1}) 3036, 2960, 2930, 1709, 1664, 1626, 1456, 1398, 1195, 1083, 878.

4-Benzyl-4-(prop-2-yn-1-yloxy)cyclohexa-2,5-dienone (1p)

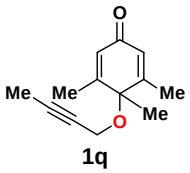


1p

Light yellow solid. 76 mg, 32% yield. mp 94-95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.23-7.28 (m, 2H), 7.14-7.17 (m, 2H), 6.79 (d, J = 10.0 Hz, 2H), 6.28 (d, J = 10.0 Hz, 2H), 4.00 (d, J = 2.8 Hz, 2H), 3.06 (s, 2H), 2.45 (t, J = 2.4 Hz, 1H). ^{13}C

NMR (100 MHz, $CDCl_3$) δ (ppm) 185.01, 149.54, 134.44, 131.55, 130.78, 128.12, 127.26, 80.45, 76.37, 75.01, 53.80, 46.31; ESI-MS: $[M+Na]^{\oplus}$ 261.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{16}H_{14}O_2Na^{\oplus}$ 261.0886, found 261.0876; IR (KBr) ν (cm^{-1}) 3259, 3026, 2946, 2922, 2903, 2860, 2126, 1699, 1668, 1629, 1609, 1494, 1453, 1398, 1386, 1374, 1256, 1085, 1050, 959, 871.

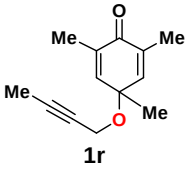
4-(But-2-yn-1-yloxy)-3,4,5-trimethylcyclohexa-2,5-dienone (1q)



1q

White solid. 64 mg, 31% yield. mp 60-61 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.17 (s, 2H), 3.65 (q, J = 2.0 Hz, 2H), 2.05 (s, 6H), 1.85 (t, J = 2.0 Hz, 3H), 1.45 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.12, 160.23, 129.35, 82.99, 77.04, 74.62, 53.58, 25.11, 18.01, 3.76; ESI-MS: $[M+Na]^{\oplus}$ 227.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{13}H_{16}O_2Na^{\oplus}$ 227.1048, found 227.1043; IR (KBr) ν (cm^{-1}) 3252, 3049, 2998, 2980, 2955, 2918, 2902, 2863, 2233, 1675, 1638, 1623, 1444, 1386, 1307, 1173, 1083, 1036, 902, 890.

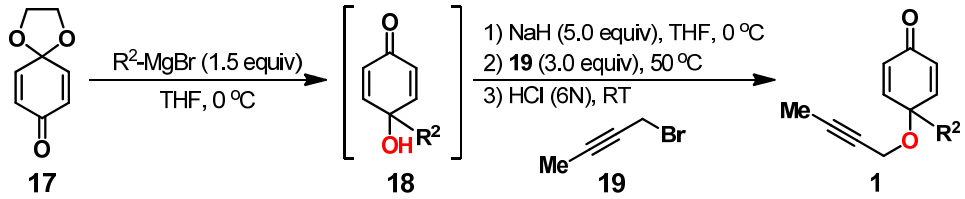
4-(But-2-yn-1-yloxy)-2,4,6-trimethylcyclohexa-2,5-dienone (1r)



1r

Colorless Oil. 87 mg, 43% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.55 (s, 2H), 3.91 (q, J = 2.4 Hz, 2H), 1.91 (s, 6H), 1.84 (t, J = 2.4 Hz, 3H), 1.42 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 186.57, 146.19, 136.77, 82.89, 76.02, 72.89, 53.79, 26.70, 16.02, 3.81; ESI-MS: $[M+Na]^{\oplus}$ 227.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{13}H_{16}O_2Na^{\oplus}$ 227.1048, found 227.1043; IR (KBr) ν (cm^{-1}) 3272, 2978, 2923, 2857, 2242, 1675, 1644, 1447, 1372, 1074, 1037, 905.

3.2 General Procedure for Preparation of Substrates 1d-1f.

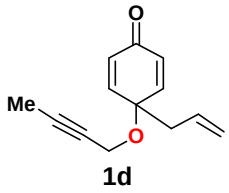


To a well-stirred solution of 1,4-dioxaspiro[4.5]deca-6,9-dien-8-one **17**[3] (1.0 mmol) in THF (1 mL) was added Grignard reagent (1.5 mmol, 1.5 equiv) dropwise at 0 °C under argon atmosphere. The resulting mixture was stirred for 15 min, then quenched by water (50 mL) and extracted with DCM (50 mL ×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to give a crude product **18**, which was used in next step without further purification.

To a solution of the above crude product **18** in THF (10 mL) was added NaH (60% in Mineral oil, 5.0 mmol, 5.0 equiv) in several portions at 0 °C under argon atmosphere, followed by the addition of 1-bromo-2-butyne (**19**, 3.0 mmol, 3.0 equiv). The resulting mixture was heated at 50 °C overnight. The mixture was quenched by water (10 mL) at 0 °C and subsequently acidified with 6*N* HCl (0.9 mL). The resulting mixture was stirred at room temperature for 2 h to hydrolyze the ketal. Then it was extracted with DCM (50 mL ×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent to afford the pure substrates **1**.

[3] J. Wegner, S. V. Ley, A. Kirschning, A.-L. Hansen, J. M. Garcia, I. R. Baxendale, *Org. Lett.* **2012**, *14*, 696.

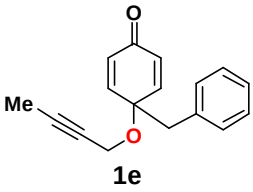
4-Allyl-4-(but-2-yn-1-yloxy)cyclohexa-2,5-dienone (1d)



1d

Colorless oil, 54.7 mg, 27% yield (3 steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.79 (d, J = 10.4 Hz, 2H), (6.34 d, J = 10.4 Hz, 2H), 5.62-5.73 (m, 1H), 5.04-5.12 (m, 2H), 3.99 (q, J = 2.0 Hz, 2H), 2.53 (d, J = 7.2 Hz, 2H), 1.84 (t, J = 2.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.25, 149.96, 131.39, 130.84, 119.80, 83.39, 75.68, 75.60, 54.31, 43.92, 3.72; ESI-MS: $[M+Na]^{\oplus}$ 225.0; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{13}H_{14}O_2Na^{\oplus}$ 225.0891, found 225.0886; IR (KBr) ν (cm^{-1}) 3078, 2979, 2920, 2859, 2230, 1670, 1630, 1507, 1440, 1381, 1254, 1198, 1173, 1157, 1142, 1051, 997, 942, 861.

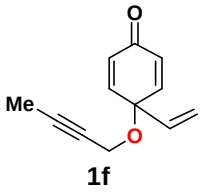
4-Benzyl-4-(but-2-yn-1-yloxy)cyclohexa-2, 5-dienone (1e)



1e

White solid, 47.9 mg, 19% yield (3 steps). mp 59-60 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.27-7.12 (m, 5H), 6.79 (d, J = 10.0 Hz, 2H), 6.25 (d, J = 10.0 Hz, 2H), 3.97 (q, J = 2.0 Hz, 2H), 3.06 (s, 2H), 1.84 (t, J = 2.0 Hz, 3H), ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.09, 149.92, 134.52, 131.28, 130.73, 128.04, 127.17, 83.32, 76.15, 75.81, 54.41, 46.34, 3.75; ESI-MS: $[M+Na]^{\oplus}$ 275.0; HRMS (FTMS-ESI): $[M+H]^{\oplus}$ calcd for $C_{17}H_{17}O_2^{\oplus}$ 253.1223, found 253.1228; IR (KBr) ν (cm^{-1}) 3062, 3030, 2920, 2858, 1670, 1629, 1495, 1455, 1382, 1049, 860, 770, 704.

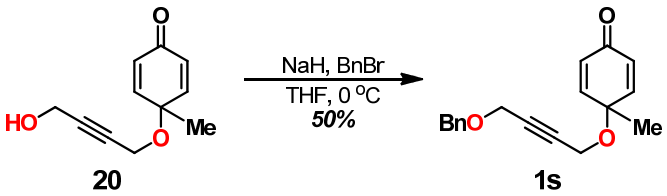
4-(But-2-yn-1-yloxy)-4-vinylcyclohexa-2, 5-dienone (1f)



1f

Pale yellow solid, 65.9 mg, 35% yield (3 steps). mp 52-54 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.81 (d, J = 10.0 Hz, 2H), 6.34 (d, J = 10.0 Hz, 2H), 5.76 (dd, J=10.4, 17.6 Hz, 1H), 5.44 (d, J = 17.6 Hz, 1H), 5.27 (d, J = 10.4 Hz, 1H), 4.07 (q, J = 2.4 Hz, 2H), 1.84 (t, J = 2.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.20, 148.71, 135.92, 130.43, 117.44, 83.53, 75.77, 75.65, 54.03, 3.74; ESI-MS: $[M+Na]^{\oplus}$ 211.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{12}H_{12}O_2Na^{\oplus}$ 211.0730, found 211.0733; IR (KBr) ν (cm^{-1}) 3042, 2975, 2923, 2865, 1670, 1627, 1507, 1387, 1283, 1050, 926, 878, 691.

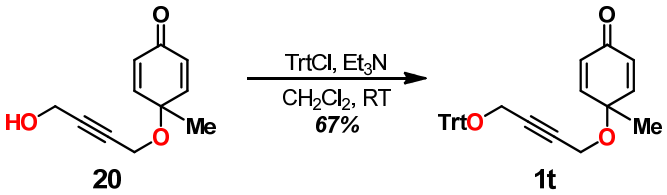
3.3 Preparation of Substrates 1s and 1t.



4-((4-(Benzyloxy)but-2-yn-1-yl)oxy)-4-methylcyclohexa-2,5-dienone (1s) To a well-stirred solution of alcohol **20**[4] (1.5 g, 7.8 mmol) in dry THF (30 mL) was added NaH (60% in mineral oil, 1.6 g, 39.0 mmol, 5.0 equiv) in several portions at 0 ^{o}C under argon atmosphere. Then benzyl bromide (2.7 g, 15.6 mmol, 2 equiv) was added. The resulting mixture was warmed to room temperature and stirred for 2 h. Then it was diluted with water (30 mL) and extracted with ether (30 mL ×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent to afford the desired product **1s** (1.1 g, 50% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.36-7.25 (m, 5H), 6.82 (d, J = 10.0 Hz, 2H),

[4] S.-Y. Cai, Z. Liu, W.-B. Zhang, X.-Y. Zhao, D. Z. Wang, *Angew. Chem. Int. Ed.* **2011**, *50*, 11133.

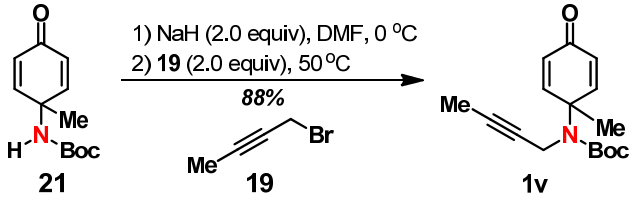
6.30 (d, J = 10.0 Hz, 2H), 4.56 (s, 2H), 4.19 (s, 2H), 4.05 (s, 2H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.84, 150.70, 137.28, 130.43, 128.39, 127.93, 127.84, 83.01, 82.89, 73.12, 71.63, 57.38, 53.94, 26.29; ESI-MS: $[M+Na]^{\oplus}$ 305.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{18}O_3Na^{\oplus}$ 305.1148, found 305.1136; IR (KBr) ν (cm^{-1}) 3032, 2981, 2930, 2856, 1671, 1630, 1497, 1454, 1383, 1352, 1300, 1242, 1180, 1125, 1076, 1032, 861, 738, 698.



20 1t

4-Methyl-4-((4-(trityloxy)but-2-yn-1-yl)oxy)cyclohexa-2,5-dienone (1t) A solution of alcohol **20**[4] (100 mg, 0.52 mmol), trityl chloride (189 mg, 0.68 mmol, 1.3 equiv.) and Et_3N (79 mg, 0.78 mmol, 1.5 equiv.) in DCM (30 mL) was stirred for 2 d at room temperature. Then it was diluted with water (30 mL) and extracted with DCM (30 mL ×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent to afford the desired product **1t** (151 mg, 67% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.47-7.42 (m, 6H), 7.33-7.21 (m, 9H), 6.83 (d, J = 10.0 Hz, 2H), 6.30 (d, J = 10.0 Hz, 2H), 4.02 (s, 2H), 3.78 (s, 2H), 1.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.09, 150.97, 143.45, 130.12, 128.67, 128.02, 127.28, 87.51, 83.73, 81.99, 73.24, 54.23, 53.15, 26.45; ESI-MS: $[M+Na]^{\oplus}$ 457.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{30}H_{26}O_3Na^{\oplus}$ 457.1774, found 457.1762; IR (KBr) ν (cm^{-1}) 3084, 3063, 2983, 2912, 2856, 1673, 1630, 1489, 1448, 1383, 1368, 1184, 1164, 1058, 1029, 900, 864, 746, 704, 632.

3.4 Preparation of Substrates 1u, 1v and 1w.



21 19 1v

***tert*-Butyl but-2-yn-1-yl(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)carbamate (1v)** To a well-stirred solution of substrate **21**[5] (3.3 g, 14.8 mmol) in DMF (30 ml) was added NaH (60% in mineral oil, 1182 mg, 29.6 mmol, 2 equiv.) in several portions at 0 °C under argon atmosphere. Then 1-bromo-2-butyne (**19**, 3931 mg, 29.6 mmol, 2 equiv.) was added and the resulting mixture was stirred at 0 °C for another 1 min. The reaction was quenched by sat. NH_4Cl aq. (50 mL) and extracted with AcOEt (100 mL ×3). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent to afford the pure **1v** (3.575 g, 88% yield) as pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.07 (d, J = 10.0 Hz, 2H), 6.16 (d, J = 10.4 Hz, 2H), 4.16 (d, J = 2.4 Hz, 2H), 1.83 (t, J = 2.4 Hz, 3H), 1.69 (s, 3H), 1.38 (s,9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm)185.30, 154.96, 153.92, 126.63, 81.71, 79.58, 76.07, 57.48, 34.39, 28.13, 26.19, 3.56; ESI-MS: $[M+Na]^{\oplus}$ 298.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$calcd for $C_{16}H_{21}NO_3Na^{\oplus}$ 298.1414, found 298.1425; IR (KBr) ν (cm^{-1}) 3042, 2979, 2923, 1698, 1668, 1629, 1605,1456, 1432, 1390, 1367, 1281, 1246, 1162, 1127, 1088, 1031, 874, 854.

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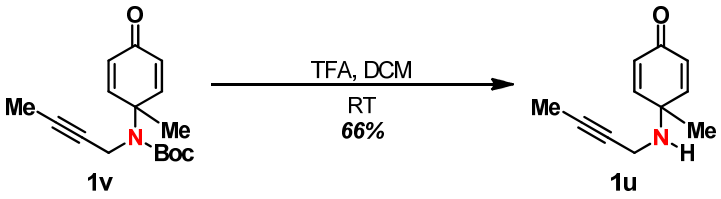
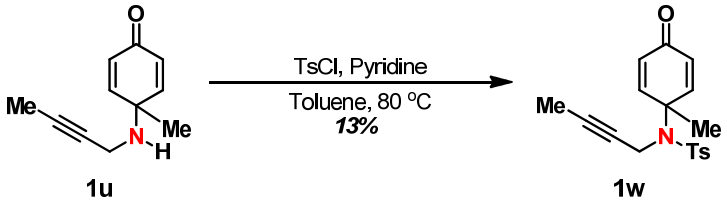
[5] Carreño, M. C.; Luzón, C. G.; Ribagorda, M. *Chem. Eur. J.* **2002**, *8*, 208.

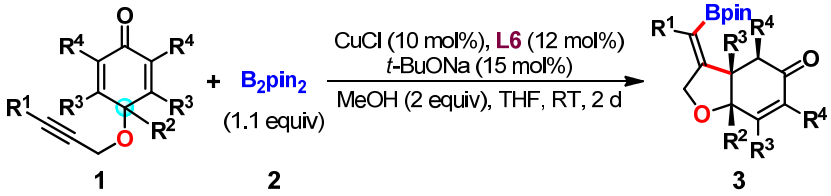


4-(But-2-ynylamino)-4-methylcyclohexa-2,5-dienone (**1u**). To a well-stirred solution of **1v** (2.5 g, 9.1 mmol) in DCM (45 mL) was added TFA (4.5 mL). The resulting mixture was stirred for 5h at room temperature, and then concentrated under reduced pressure. The residue was diluted with sat. Na_2CO_3 aq. (30 mL) and extracted with AcOEt (30 mL×4). The combined organic phases were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent to afford the pure **1u** (1.045 g, 66% yield) as pale yellow solid. mp 58-59 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.78 (d, J = 10.0 Hz, 2H), 6.27 (d, J = 10.0 Hz, 2H), 3.20-3.15 (m, 2H), 1.81-1.78 (m, 3H), 1.67 (br, 1H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 185.49, 153.99, 129.48, 79.91, 77.19, 55.27, 34.21, 26.67, 3.47; ESI-MS: $[M+Na]^{\oplus}$ 198.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{11}H_{13}NONa^{\oplus}$ 198.0889, found 198.0880; IR (KBr) ν (cm^{-1}) 3279, 2976, 2804, 1663, 1621, 1497, 1397, 1383, 1293, 1182, 1110, 1092, 861, 827, 789, 704, 469.



***N*-(But-2-ynyl)-4-methyl-*N*-(1-methyl-4-oxocyclohexa-2,5-dienyl)benzenesulfonamide (1w)** To a well-stirred solution of pyridine (911 mg, 11.41 mmol, 4 equiv.) and **1u** (500 mg, 2.85 mmol) in toluene (30 mL) was added TsCl (1632 mg, 8.56 mmol, 3 equiv) at room temperture. The resulting mixture was heated to 80 ^oC overnight. Then the mixture was quenched by HCl (2*N*, 20 mL) at room temperture and subsequently extracted with AcOEt (30 mL ×2). The combined organic phases were washed with sat. $NaHCO_3$, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent to afford the pure **1w** (121.3 mg, 13% yield) as pale yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.79 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 10.0 Hz, 2H), 6.13 (d, J = 10.0 Hz, 2H), 4.25-4.24 (m, 2H), 2.43 (s, 3H), 1.78-1.76 (m, 3H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 184.54, 151.72, 143.78, 138.38, 129.36, 127.82, 127.48, 81.70, 75.43, 36.77, 26.08, 21.48, 3.43; ESI-MS: $[M+Na]^{\oplus}$ 352.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{19}NO_3SNa^{\oplus}$ 352.0978, found 352.09736; IR (KBr) ν (cm^{-1}) 2921, 1670, 1629, 1598, 1448, 1393, 1334, 1247, 1189, 1160, 1091, 891, 862, 812, 812, 706, 688, 591, 574, 549.

4. SCOPE OF THE SUBSTRATES



1 **2** **3**

For **1a** to **1m**: R^1 = Me-, R^3 = R^4 = H

1a: R^2 = Me- **1b**: R^2 = Et- **1c**: R^2 = i-Pr- **1d**: R^2 = CH_2=CH-CH_2- **1e**: R^2 = $PhCH_2$-

1f: R^2 = CH_2=CH- **1g**: R^2 = Ph- **1h**: R^2 = 4-Br-Ph- **1i**: R^2 = MeOC(O)-CH_2- **1j**: R^2 = AcO-$(CH_2)_2$-

1k: R^2 = TBSO-$(CH_2)_2$- **1l**: R^2 = Br-$(CH_2)_3$- **1m**: R^2 = MeO-

For **1n** to **1p**: R^3 = R^4 = H

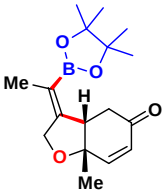
1n: R^1 = Et-, R^2 = Me- **1o**: R^1 = *n*-Bu-, R^2 = Me- **1p**: R^1 = H-, R^2 = $PhCH_2$-

For **1q** to **1r**: R^1 = R^2 = Me-

1q: R^3 = Me-, R^4 = H- **1r**: R^3 = H-, R^4 = Me-

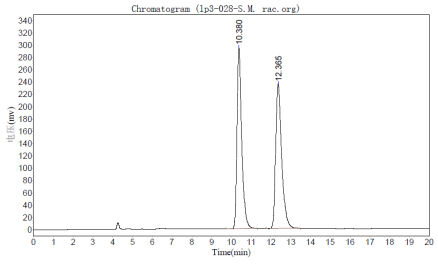
GENERAL PROCEDURE: A dried Schlenk flask was charged with CuCl (1.5 mg, 0.015 mmol, 10 mol%), ligand **L6** (9.7 mg, 0.018 mmol, 12 mol%), B_2pin_2 (**2**, 41.9 mg, 0.165 mmol, 1.1 equiv; except for substrate **1j**, 1.2 equiv of **2**; for substrates **1l**, **1m and 1o**, 1.3 equiv of **2**), *t*-BuONa (2.2 mg, 0.0225 mmol, 15 mol%) and anhydrous THF (2 mL) under nitrogen atmosphere. After the mixture was stirred at room temperature for 30 min, a solution of cyclohexadienone-containing 1,6-enyne substrate **1** (0.15 mmol) in anhydrous THF (1.5 mL) was added, followed by anhydrous MeOH (12.2 μL, 0.30 mmol, 2.0 equiv). The resulting mixture was stirred at room temperature for 2 days. The reaction mixture was quenched with 1 N $NaHCO_3$ (5 mL), and extracted with EtOAc (15 mL × 3). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel (300-400 mesh) column chromatography to afford the desired product **3**.

(3a*S*,7a*S*,*Z*)-7a-Methyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3a)



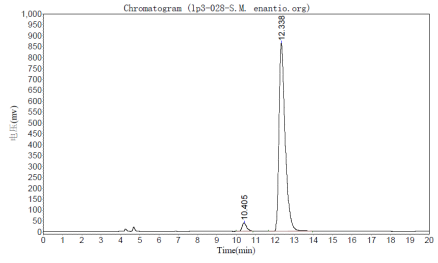
3a

White solid. 32.0 mg, 70% yield; mp 73-75 °C; $[\alpha]_D^{25}$ -91.2 (*c* 0.50, $CHCl_3$) for 94% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.63 (d, *J* = 10.4 Hz, 1H), 6.00 (d, *J* = 10.4 Hz, 1H), 4.49 (s, 2H), 3.36 (t, *J* = 7.6 Hz, 1H), 2.55-2.67 (m, 2H), 1.63 (s, 3H), 1.38 (s, 3H), 1.28 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.04, 157.23, 149.01, 129.72, 83.47, 79.04, 69.83, 47.57, 39.75, 25.03, 24.88, 24.87, 16.95; ESI-MS: $[M+Na]^{\oplus}$ 327.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{25}{}^{10}BO_4Na^{\oplus}$ 326.1780, found 326.1774; IR (KBr) ν (cm^{-1}) 2975, 2929, 2862, 1682, 1656, 1367, 1306, 1218, 1148, 1018, 890; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7 mL/min; Retention time: 10.4 min (*R*, *R*-isomer), 12.3 min (*S*,*S*-isomer).



Results

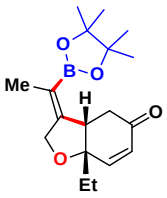
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.380	294853.906	4947239.000	49.8314
2		12.365	234990.703	4980714.500	50.1686
Total			529844.609	9927953.500	100.0000



Results

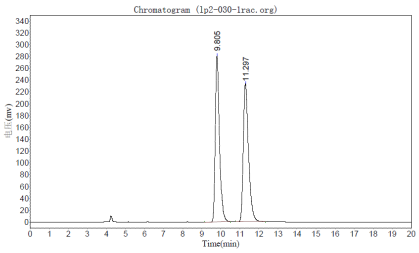
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.405	37951.035	614142.250	3.1176
2		12.338	863158.875	19085218.000	96.8824
Total			901109.910	19699360.250	100.0000

(3a*S*,7a*S*,*Z*)-7a-Ethyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3b)



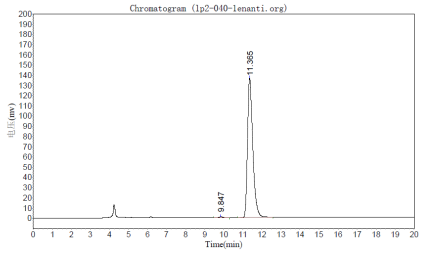
3b

White solid. 33.6 mg, 70% yield; mp 74-75 °C; $[\alpha]_D^{25}$ -94.8 (*c* 0.29, $CHCl_3$) for 99% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.66 (d, *J* = 10.4 Hz, 1H), 6.07 (d, *J* = 10.4 Hz, 1H), 4.47 (AB, J_{AB} = 14.8 Hz, 2H), 3.46 (t, *J* = 7.6 Hz, 1H), 2.60 (t, *J* = 7.6 Hz, 2H), 1.65-1.71 (m, 2H), 1.62 (s, 3H), 1.28 (s, 6H), 1.26 (s, 6H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.21, 157.66, 147.80, 130.72, 83.45, 81.64, 69.69, 45.13, 40.04, 30.29, 24.98, 24.94, 16.93, 8.35; ESI-MS: $[M+Na]^{\oplus}$ 341.0; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{27}{}^{10}BO_4Na^{\oplus}$ 340.1936, found 340.1931; IR (KBr) *v* (cm^{-1}) 2970, 2927, 2857, 1690, 1653, 1460, 1364, 1313, 1208, 1144, 1023, 848; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7 mL/min; Retention time: 9.8 min (*R*, *R*-isomer), 11.4 min (*S*,*S*-isomer).



Results

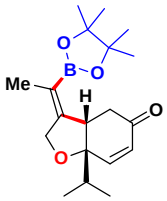
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.805	281324.813	4308706.500	49.2042
2		11.297	233794.516	4448080.000	50.7958
Total			515119.328	8756786.500	100.0000



Results

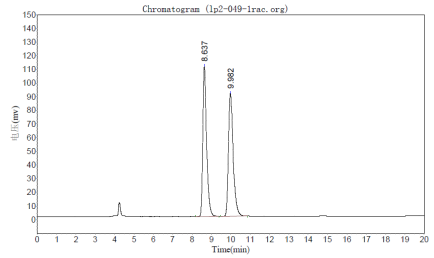
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.847	909.089	14255.102	0.5423
2		11.365	136688.750	2614560.750	99.4577
Total			137597.839	2628815.852	100.0000

(3a*S*,7a*S*,*Z*)-7a-Isopropyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3c)



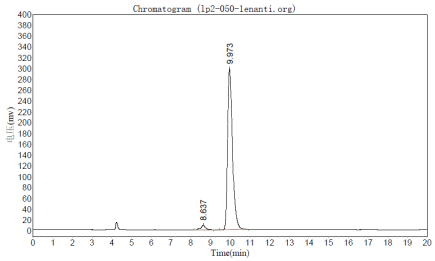
3c

White solid. 32.6 mg, 65% yield; mp 104-106 °C; $[\alpha]_D^{25}$ -111.0 (*c* 0.50, $CHCl_3$) for 95% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.67 (d, *J* = 10.4 Hz, 1H), 6.12 (d, *J* = 10.4 Hz, 1H), 4.40-4.48 (m, 2H), 3.60 (t, *J* = 7.6 Hz, 1H), 2.54-2.66 (m, 2H), 1.89-2.00 (m, 1H), 1.62 (s, 3H), 1.28 (s, 6H), 1.26 (s, 6H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.34, 158.38, 145.93, 131.48, 83.82, 83.42, 69.35, 43.91, 40.89, 33.72, 24.97, 24.94, 17.81, 16.92, 16.55; ESI-MS: $[M+Na]^{\oplus}$ 355.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{19}H_{29}{}^{10}BO_4Na^{\oplus}$ 354.2093, found 354.2087; IR (KBr) *v* (cm^{-1}) 2961, 2930, 2874, 2856, 1730, 1690, 1652, 1468, 1363, 1305, 1210, 1144, 1027, 965, 849; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7 mL/min; Retention time: 8.6 min (*R*, *R*-isomer), 10.0 min (*S*,*S*-isomer).



Results

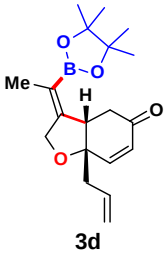
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.637	109802.844	1481303.875	49.4667
2		9.982	89955.102	1513241.250	50.5333
Total			199757.945	2994545.125	100.0000



Results

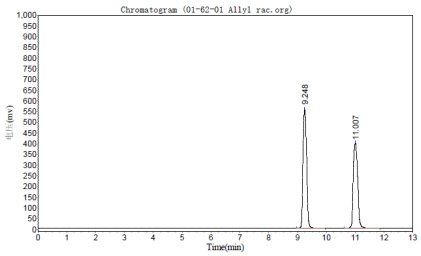
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		8.637	8451.410	143471.906	2.7453
2		9.973	296869.750	5082527.000	97.2546
Total			305321.160	5225998.906	100.0000

(3a*S*,7a*S*,*Z*)-7a-allyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3d)



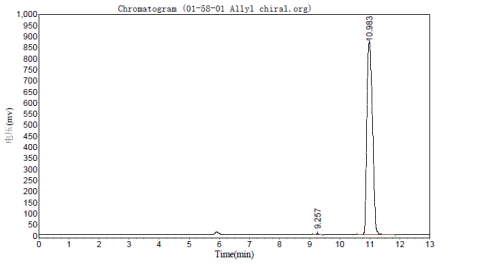
3d

Colorless oil. 29.7 mg, 60% yield; $[\alpha]_D^{25}$ -85.1 (*c* 0.52, $CHCl_3$) for >99% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.68 (d, *J* = 10.0 Hz, 1H), 6.05 (d, *J* = 10.0 Hz, 1H), 5.84-5.70 (m, 1H), 5.17-5.08 (m, 2H), 4.51 (AB, J_{AB} = 14.8 Hz, 2H), 3.51 (t, *J* = 8.0 Hz, 1H), 2.65-2.52 (m, 2H), 2.50-2.43 (m, 1H), 2.38-2.30 (m, 1H), 1.63 (s, 3H), 1.28 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.97, 157.12, 147.35, 132.50, 130.62, 119.19, 83.44, 80.71, 69.83, 45.54, 42.25, 39.80, 24.92, 24.90, 16.88; ESI-MS: $[M+H]^{\oplus}$ 331.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{19}H_{27}BO_4Na^{\oplus}$ 352.1931, found 352.1934; IR (KBr) *v* (cm^{-1}) 2978, 2967, 2853, 1691, 165.4, 1364, 1307, 1274, 1212, 1145, 1094, 1022, 968, 928, 849, 786, 685; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7 mL/min; Retention time: 9.3 min (*R*, *R*-isomer), 11.0min (*S*,*S*-isomer).



Results

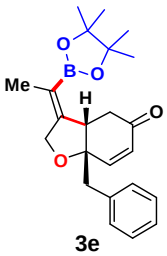
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.248	556105.188	4912343.000	53.8064
2		11.007	400742.844	4217326.000	46.1936
Total			956848.031	9129669.000	100.0000



Results

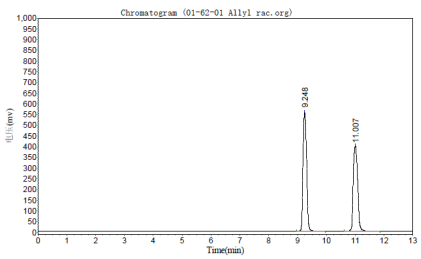
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.257	2371.714	24207.100	0.2140
2		10.983	870780.625	11287487.000	99.7860
Total			873152.339	11311694.100	100.0000

(3a*S*,7a*S*,*Z*)-7a-Benzyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3e)



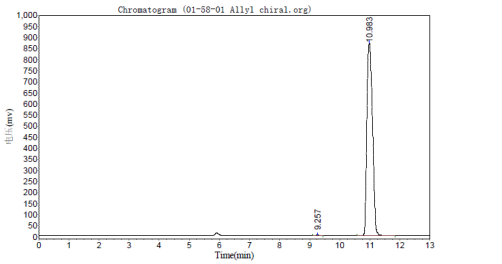
3e

White solid, 32.2 mg, 58% yield; mp 92-94 ^oC; $[\alpha]_D^{25}$ -126.1 (*c* 0.64, $CHCl_3$) for >99% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.30-7.16 (m, 5H), 6.65 (d, *J* = 10.0 Hz, 1H), 5.99 (d, *J* = 10.0 Hz, 1H), 4.57 (AB, J_{AB} = 14.8 Hz, 2H), 3.61 (t, *J* = 7.6 Hz, 1H), 3.01 (d, *J* = 13.6 Hz, 1H), 2.87 (d, *J* = 13.6 Hz, 1H), 2.59-2.42 (m, 2H), 1.63 (s, 3H), 1.28 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.91, 157.08, 147.36, 135.91, 130.56, 130.50, 128.29, 126.90, 83.44, 81.58, 69.93, 45.47, 44.08, 39.73, 24.04, 16.91; ESI-MS: $[M+H]^{\oplus}$ 381.2; HRMS (FTMS-ESI): $[M+H]^{\oplus}$ calcd for $C_{23}H_{30}BO_4^{\oplus}$ 380.2268, found 380.2278; IR (KBr) *v* (cm^{-1}) 3028, 2976, 2922, 2857, 1683, 1496, 1455, 1366, 1224, 1146, 1112, 1089, 1013, 938, 849, 700, 687; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7 mL/min; Retention time: 11.2 min (*R*, *R*-isomer), 13.3min (*S*,*S*-isomer).



Results

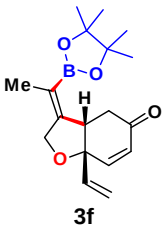
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.248	556105.188	4912343.000	53.8064
2		11.007	400742.844	4217326.000	46.1936
Total			956848.031	9129669.000	100.0000



Results

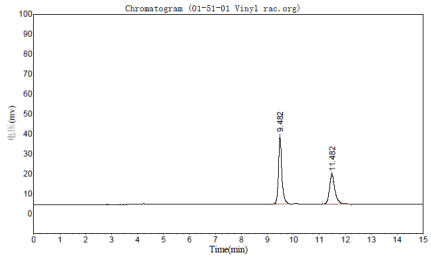
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.257	2371.714	24207.100	0.2140
2		10.983	870780.625	11287487.000	99.7860
Total			873152.339	11311694.100	100.0000

(3a*S*,7a*S*,*Z*)-3-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-7a-vinyl-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3f)



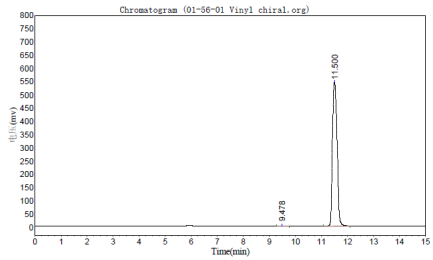
3f

White solid. 29.9 mg, 63% yield; mp 75-77 °C; $[\alpha]_D^{25}$ -142.4 (*c* 0.78, $CHCl_3$) for >99% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.56 (d, *J* = 10.0 Hz, 1H), 6.07 (d, *J* = 10.0 Hz, 1H), 5.85 (dd, *J* = 10.8, 17.4 Hz, 1H), 5.36 (d, *J* = 17.6 Hz, 1H), 5.27 (d, *J* = 10.8 Hz, 1H), 4.50 (AB, J_{AB} = 14.8 Hz, 2H), 3.55 (t, *J* = 7.6 Hz, 1H), 2.70-2.57 (m, 2H), 1.61 (s, 3H), 1.28 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.88, 156.54, 146.59, 139.07, 130.49, 116.38, 83.46, 81.49, 70.32, 46.39, 39.32, 24.98, 24.87, 16.90; ESI-MS: $[M+H]^{\oplus}$ 317.3; HRMS (FTMS-ESI): $[M+H]^{\oplus}$ calcd for $C_{18}H_{26}BO_4^{\oplus}$ 316.1955, found 316.1966; IR (KBr) ν (cm^{-1}) 2980, 2945, 2846, 1678, 1657, 1401, 1370, 1326, 1308, 1268, 1215, 1168, 1149, 1114, 1021, 932, 848, 782, 684; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7 mL/min; Retention time: 9.5 min (*R*, *R*-isomer), 11.5min (*S*,*S*-isomer).



Results

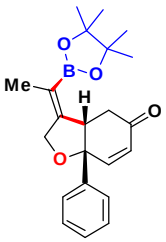
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.482	33770.172	296600.500	57.7150
2		11.482	15125.902	217305.109	42.2850
Total			48896.074	513905.609	100.0000



Results

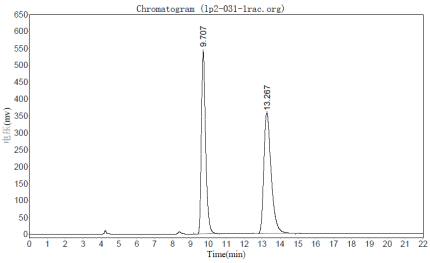
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.478	922.498	11507.348	0.1720
2		11.500	542222.500	6678938.000	99.8280
Total			543144.998	6690445.348	100.0000

(3a*S*,7a*S*,*Z*)-7a-Phenyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3g)



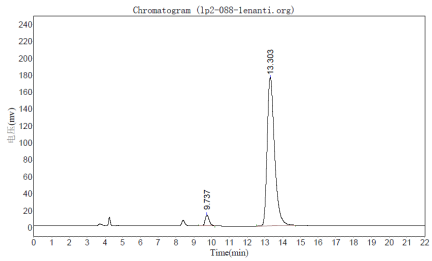
3g

Colorless oil. 35.7 mg, 65% yield; $[\alpha]_D^{25}$ -143.6 (*c* 1.00, $CHCl_3$) for 92% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 10.4 Hz, 1H), 6.10 (d, *J* = 10.4 Hz, 1H), 4.59 (AB, J_{AB} = 14.8 Hz, 2H), 3.88 (t, *J* = 7.2 Hz, 1H), 2.68-2.81 (m, 2H), 1.57 (s, 3H), 1.26 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.04, 156.28, 147.92, 142.48, 129.39, 128.79, 127.90, 125.59, 83.45, 83.30, 70.47, 48.61, 39.79, 24.94, 24.87, 16.96; ESI-MS: $[M+Na]^{\oplus}$ 389.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{27}{}^{10}BO_4Na^{\oplus}$ 388.1936, found 388.1931; IR (KBr) ν (cm^{-1}) 3029, 2979, 2923, 2858, 1684, 1654, 1449, 1402, 1365, 1314, 1266, 1214, 1146, 1106, 1017, 971, 851; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7 mL/min; Retention time: 9.7 min (*R*, *R*-isomer), 13.3 min (*S*,*S*-isomer).



Results

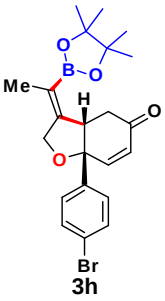
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.707	538782.375	8701880.000	46.1425
2		13.267	356791.719	10156837.000	53.8575
Total			895574.094	18858717.000	100.0000



Results

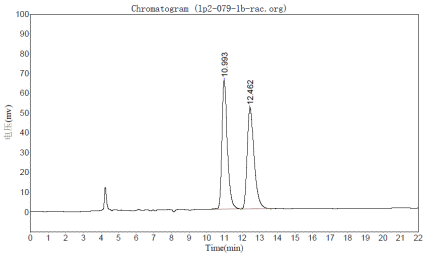
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.737	13185.913	205913.594	3.9764
2		13.303	175222.031	4972531.000	96.0236
Total			188407.944	5178444.594	100.0000

(3a*S*,7a*S*,*Z*)-7a-(4-Bromophenyl)-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3h)



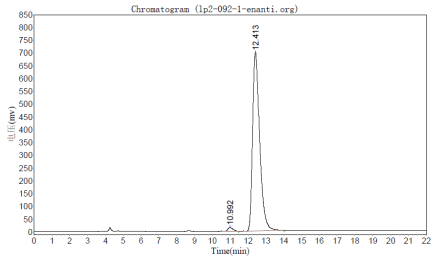
3h

Colorless oil. 42.8 mg, 64% yield; $[\alpha]_D^{25}$ -137.4 (*c* 1.04, $CHCl_3$) for 97% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.50 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 10.4 Hz, 1H), 6.10 (d, *J* = 10.4 Hz, 1H), 4.57 (AB, J_{AB} = 14.8 Hz, 2H), 3.85 (t, *J* = 7.2 Hz, 1H), 2.66-2.77 (m, 2H), 1.57 (s, 3H), 1.26 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.71, 155.72, 147.14, 141.75, 131.93, 129.61, 127.42, 122.02, 83.49, 82.92, 70.44, 48.56, 39.74, 24.92, 24.88, 16.93; ESI-MS: $[M+Na]^{\oplus}$ 467.1/469.1 (1:1); HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{26}{}^{10}B^{79}BrO_4Na^{\oplus}$ 466.1036, found 466.1053; IR (KBr) *v* (cm^{-1}) 2978, 2929, 2852, 1690, 1655, 1589, 1485, 1451, 1363, 1310, 1265, 1213, 1144, 1095, 1073, 1009, 968, 849; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7 mL/min; Retention time: 11.0 min (*R*, *R*-isomer), 12.4 min (*S*,*S*-isomer).



Results

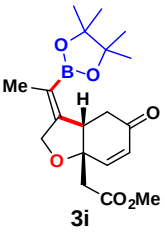
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.993	65333.145	1387081.250	49.8301
2		12.462	51156.801	1396542.375	50.1699
Total			116489.945	2783623.625	100.0000



Results

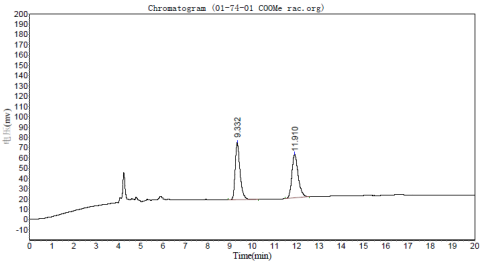
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.992	14229.114	279739.781	1.4303
2		12.413	697066.313	19277728.000	98.5696
Total			711295.427	19557467.781	100.0000

Methyl 2-((3a*S*,7a*S*,*Z*)-5-oxo-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4,5,7a-hexahydrobenzofuran-7a-yl)acetate (3i)



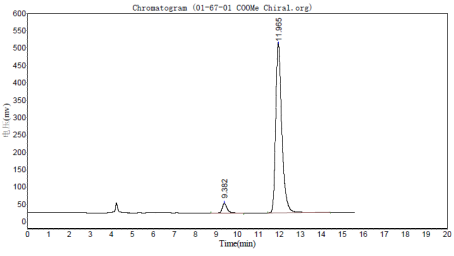
3i

White solid. 27.5 mg, 51% yield; mp 86-87 ^oC; $[\alpha]_D^{25}$ -72.2 (*c* 0.62, $CHCl_3$) for 91% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.98 (d, *J* = 10.0 Hz, 1H), 6.08 (d, *J* = 10.0 Hz, 1H), 4.55 (AB, J_{AB} = 14.8 Hz, 2H), 3.69 (s, 3H), 3.67-3.60 (m, 1H), 2.79-2.48 (m, 4H), 1.64 (s, 3H), 1.28 (s, 6H), 1.26 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.45, 169.97, 156.00, 145.80, 130.51, 83.56, 79.23, 70.12, 51.98, 46.57, 42.78, 39.56, 24.96, 24.91, 16.93 ; ESI-MS: $[M+Na]^{\oplus}$ 385.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{19}H_{27}BO_6Na^{\oplus}$ 384.1829, found 384.1832; IR (KBr) *v* (cm^{-1}) 2978, 2851, 1739, 1691, 1655, 1438, 1364, 1307, 1273, 1214, 1145, 1019, 968, 849, 685; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 80/20; flow rate = 0.7 mL/min; Retention time: 9.3 min (*R*, *R*-isomer), 11.9min (*S*,*S*-isomer).



Results

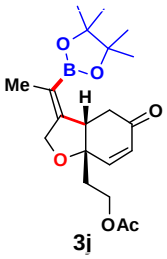
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.332	55686.215	838556.938	50.3118
2		11.910	42394.301	828163.250	49.6882
Total			98080.516	1666720.188	100.0000



Results

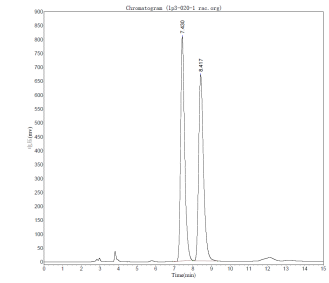
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.382	28314.559	435198.594	4.2577
2		11.965	488818.438	9786368.000	95.7423
Total			517132.996	10221566.594	100.0000

2-((3a*S*,7a*S*,*Z*)-5-oxo-3-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4,5,7a-hexahydrobenzofuran-7a-yl)ethyl acetate (3j)



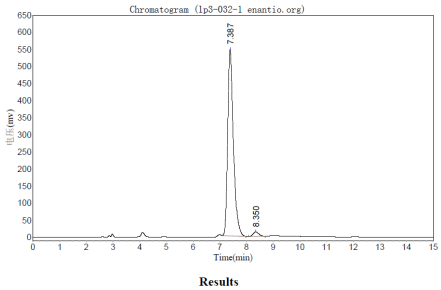
3j

Colorless oil. 33.6 mg, 60% yield; $[\alpha]_D^{25}$ -100.6 (*c* 0.94, $CHCl_3$) for 95% *ee* (1.2 equiv. of B_2pin_2 was used); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.72 (d, *J* = 10.4 Hz, 1H), 6.06 (d, *J* = 10.4 Hz, 1H), 4.47 (AB, J_{AB} = 14.8 Hz, 2H), 4.15-4.29 (m, 2H), 3.50 (t, *J* = 7.2 Hz, 1H), 2.57-2.68 (m, 2H), 1.95-2.11 (m, 5H), 1.63 (s, 3H), 1.28 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.54, 170.86, 156.63, 146.80, 130.53, 83.52, 80.03, 69.77, 60.19, 46.22, 39.79, 36.12, 25.02, 24.84, 21.02, 17.00; ESI-MS: $[M+Na]^{\oplus}$ 399.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{20}H_{29}{}^{10}BO_6Na^{\oplus}$ 398.1991, found 398.1986; IR (KBr) ν (cm^{-1}) 2978, 2933, 1740, 1687, 1608, 1474, 1455, 1368, 1238, 1145, 1095, 1040, 983, 966, 871, 850; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 70/30; flow rate = 1.0 mL/min; Retention time: 7.4 min (*R*, *R*-isomer), 8.4 min (*S*,*S*-isomer).



Results

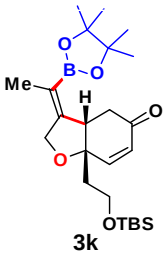
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.430	806825.313	12232237.000	50.4137
2		8.417	668869.438	12031486.000	49.5863
Total			1475694.750	24263723.000	100.0000



Results

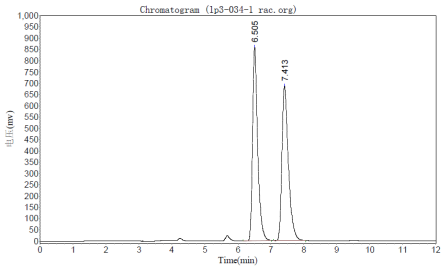
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.387	545290.500	8120843.500	97.5096
2		8.350	13361.660	207406.281	2.4904
Total			558652.160	8328249.781	100.0000

(3a*S*,7a*S*,*Z*)-7a-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3k)



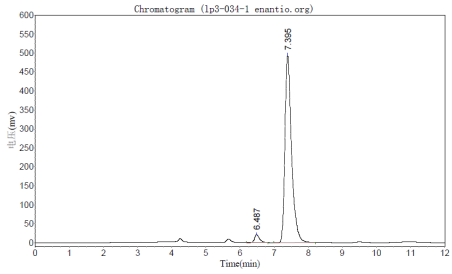
3k

Colorless oil. 37.3 mg, 55% yield; $[\alpha]_D^{25}$ -80.6 (*c* 0.98, $CHCl_3$) for 94% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.75 (d, *J* = 10.4 Hz, 1H), 6.02 (d, *J* = 10.4 Hz, 1H), 4.44 (s, 2H), 3.71-3.81 (m, 2H), 3.52 (t, *J* = 6.8 Hz, 1H), 2.61-2.72 (m, 2H), 1.92 (t, *J* = 6.4 Hz, 2H), 1.62 (s, 3H), 1.28 (s, 6H), 1.27 (s, 6H), 0.89 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.05, 157.30, 148.40, 129.99, 83.44, 80.71, 69.63, 58.86, 45.98, 40.26, 39.79, 26.00, 25.01, 24.85, 18.30, 17.03, -5.34, -5.37; ESI-MS: $[M+Na]^{\oplus}$ 471.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{24}H_{41}{}^{10}BO_5SiNa^{\oplus}$ 470.2750, found 470.2745; IR (KBr) ν (cm^{-1}) 2955, 2930, 2857, 1721, 1687, 1607, 1472, 1450, 1363, 1312, 1255, 1214, 1145, 1097, 1008, 984, 966, 938, 837; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7 mL/min; Retention time: 6.5 min (*R*, *R*-isomer), 7.4 min (*S*,*S*-isomer).



Results

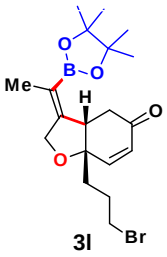
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.505	857385.125	9316013.000	50.0154
2		7.413	684924.125	9310281.000	49.9846
Total			1542309.250	18626294.000	100.0000



Results

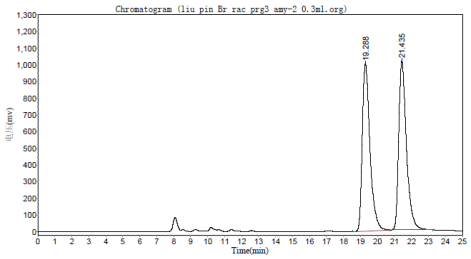
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.487	20077.881	209476.594	3.0504
2		7.395	493566.313	6657657.000	96.9496
Total			513644.193	6867133.594	100.0000

(3a*S*,7a*S*,*Z*)-7a-(3-bromopropyl)-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3l)



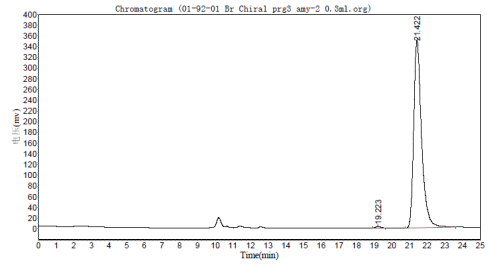
3l

White solid. 178 mg, 72% yield (0.6 mmol of **1l** and 1.3 equiv. of B_2pin_2 were used); mp 96-98 °C; $[\alpha]_D^{25}$ -77.4 (*c* 0.89, $CHCl_3$) for 99% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.65 (d, *J* = 10.0 Hz, 1H), 6.06 (d, *J* = 10.0 Hz, 1H), 4.47 (s, 2H), 3.47-3.40 (m, 3H), 2.69-2.55 (m, 2H), 2.05-1.72 (m, 4H), 1.63 (s, 3H), 1.29 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.72, 156.86, 147.05, 130.75, 83.51, 80.79, 69.78, 45.88, 39.82, 35.98, 33.69, 27.36, 24.98, 24.90, 16.99; ESI-MS: $[M+Na]^{\oplus}$ 433.2/434.9 (1:1); HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{19}H_{28}{}^{10}B^{79}BrO_4Na^{\oplus}$ 432.1193, found 432.1193; IR (KBr) ν (cm^{-1}) 3390, 2977, 2931, 1755, 1688, 1473, 1453, 1361, 1214, 1143, 1010, 983, 966, 8551, 674 ; HPLC: Phenomenex Lux 5u Amylose-2 (PA-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow rate = 0.3 mL/min; Retention time: 19.3 min (*R*, *R*-isomer), 21.4 min (*S*,*S*-isomer)



Results

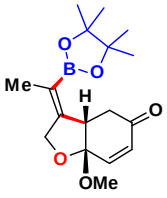
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.288	1005998.250	31453262.000	49.6281
2		21.435	1014658.625	31924626.000	50.3719
Total			2020656.875	63377888.000	100.0000



Results

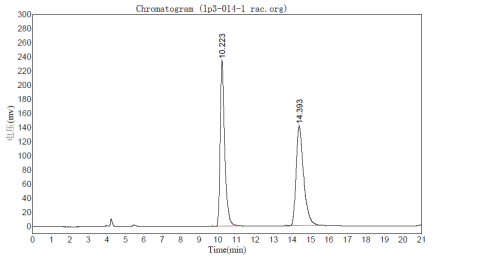
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.223	1820.068	39867.750	0.3685
2		21.422	349268.906	10778526.000	99.6315
Total			351088.974	10818393.750	100.0000

(3a*S*,7a*S*,*Z*)-7a-Methoxy-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3m)



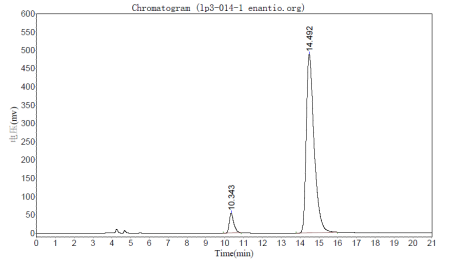
3m

White solid. 23.4 mg, 49% yield; mp 74-76 °C; $[\alpha]_D^{25}$ -128.3 (*c* 0.51, $CHCl_3$) for 88% *ee* (1.3 equiv. of B_2pin_2 was used); ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.94 (d, *J* = 10.4 Hz, 1H), 6.08 (d, *J* = 10.4 Hz, 1H), 4.63 (AB, J_{AB} = 14.8 Hz, 2H), 3.68 (dd, *J* = 12.4 Hz, *J* = 6.0 Hz, 1H), 3.38 (s, 3H), 2.77 (dd, *J* = 16.0 Hz, *J* = 6.0 Hz, 1H), 2.29 (dd, *J* = 16.0 Hz, *J* = 12.4 Hz, 1H), 1.65 (s, 3H), 1.26 (s, 6H), 1.25 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.40, 155.59, 139.70, 130.62, 103.63, 83.46, 70.94, 48.91, 41.49, 25.10, 24.80, 16.61; ESI-MS: $[M+Na]^{\oplus}$ 343.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{25}{}^{10}BO_5Na^{\oplus}$ 342.1729, found 342.1724; IR (KBr) ν (cm^{-1}) 2978, 2929, 2854, 1693, 1659, 1454, 1366, 1308, 1273, 1216, 1146, 1130, 1102, 1071, 1011, 927, 849; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7 mL/min; Retention time: 10.3 min (*R*, *R*-isomer), 14.5 min (*S*,*S*-isomer).



Results

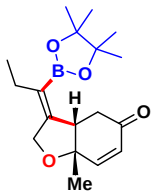
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.223	233194.094	3974547.500	50.1321
2		14.393	140039.672	3953609.000	49.8679
Total			373233.766	7928156.500	100.0000



Results

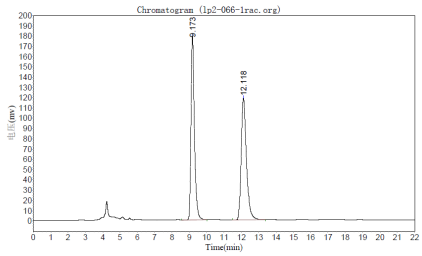
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.343	54305.719	907745.063	5.9938
2		14.492	488614.188	14236909.000	94.0062
Total			542919.906	15144654.063	100.0000

(3a*S*,7a*S*,*Z*)-7a-Methyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3n)



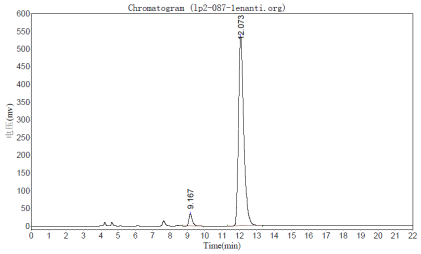
3n

White solid. 26.4 mg, 55% yield; mp 108-110 °C; $[\alpha]_D^{25}$ -109.4 (*c* 0.98, $CHCl_3$) for 92% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.62 (d, *J* = 10.0 Hz, 1H), 6.00 (d, *J* = 10.0 Hz, 1H), 4.53 (s, 2H), 3.35 (t, *J* = 7.2 Hz, 1H), 2.55-2.66 (m, 2H), 1.93-2.07 (m, 2H), 1.39 (s, 3H), 1.29 (s, 6H), 1.27 (s, 6H), 0.94 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.95, 155.86, 149.04, 129.71, 83.33, 78.77, 69.02, 47.45, 39.87, 25.37, 25.02, 24.77, 24.67, 14.00; ESI-MS: $[M+Na]^{\oplus}$ 341.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{27}{}^{10}BO_4Na^{\oplus}$ 340.1936, found 340.1931; IR (KBr) *v* (cm^{-1}) 2977, 2931, 1720, 1686, 1604, 1474, 1456, 1373, 1273, 1215, 1143, 1067, 1010, 983, 852; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7 mL/min; Retention time: 9.2 min (*R*, *R*-isomer), 12.1 min (*S*,*S*-isomer).



Results

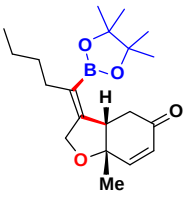
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.173	178811.891	2490468.250	49.8499
2		12.118	118526.555	2505462.500	50.1501
Total			297338.445	4995930.750	100.0000



Results

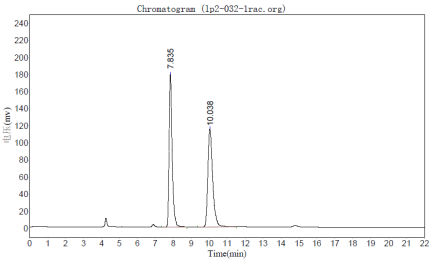
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		9.167	34275.395	468796.063	3.9694
2		12.073	535091.813	11341326.000	96.0306
Total			569367.207	11810122.062	100.0000

(3a*S*,7a*S*,*Z*)-7a-Methyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3o)



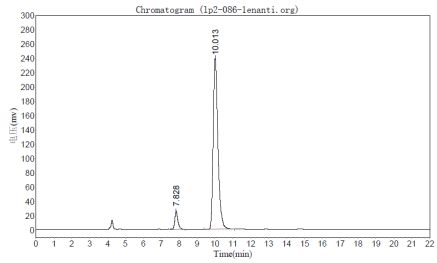
3o

Colorless oil. 24.8 mg, 47% yield; $[\alpha]_D^{25}$ -100.7 (*c* 0.49, $CHCl_3$) for 87% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.62 (d, *J* = 10.0 Hz, 1H), 6.00 (d, *J* = 10.0 Hz, 1H), 4.53 (s, 2H), 3.36 (t, *J* = 7.6 Hz, 1H), 2.59 (d, *J* = 7.6 Hz, 2H), 1.92-2.05 (m, 2H), 1.38 (s, 3H), 1.26-1.32 (m, 16H), 0.89 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.02, 156.10, 149.02, 129.72, 83.33, 78.71, 69.30, 47.55, 39.95, 31.91, 31.83, 25.01, 24.79, 24.74, 22.70, 14.19; ESI-MS: $[M+Na]^{\oplus}$ 369.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{20}H_{31}{}^{10}BO_4Na^{\oplus}$ 368.2249, found 368.2244; IR (KBr) *v* (cm^{-1}) 2959,, 2930, 2871, 1690, 1516, 1456, 1371,1307, 1276, 1218, 1143, 1116, 1056, 1009, 982, 852; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7 mL/min; Retention time: 7.8 min (*R*, *R*-isomer), 10.0 min (*S*,*S*-isomer).



Results

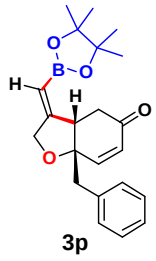
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.835	178756.094	2157449.000	49.9053
2		10.038	114732.672	2165632.500	50.0947
Total			293488.766	4323081.500	100.0000



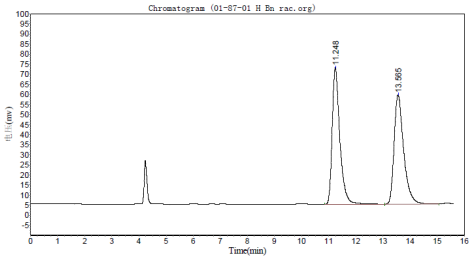
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.828	25233.064	307244.125	6.4824
2		10.013	239584.688	4432458.000	93.5177
Total			264817.752	4739702.125	100.0000

(3a*S*,7a*S*,*E*)-7a-benzyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3p)

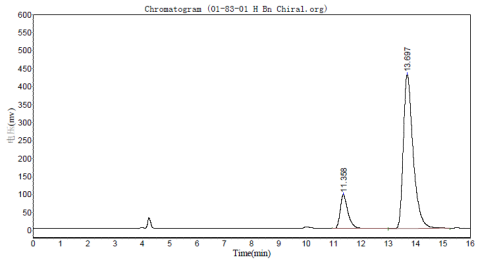


White solid. 34.4 mg, 63% yield; mp 80-82 °C; $[\alpha]_D^{25}$ -51.9 (*c* 0.85, $CHCl_3$) for 70% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31-7.19 (m, 5H), 6.57 (d, *J*= 10.0 Hz, 1H), 5.99 Hz (d, *J*= 10.0 Hz, 1H), 5.31-5.28 (m, 1H), 4.45 (s, 2H), 3.43 (t, *J*= 6.0 Hz, 1H), 3.09-2.87 (m, 3H), 2.42 (dd, *J*= 6.0 and 16.8 Hz, 1H), 1.29 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.23, 165.45, 148.22, 135.67, 130.69, 130.47, 128.36, 127.02, 83.51, 82.29, 72.14, 45.83, 44.05, 38.45, 24.91, 24.89; ESI-MS: $[M+Na]^{\oplus}$ 389.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{22}H_{27}{}^{10}BO_4Na^{\oplus}$ 388.1931, found 388.1943; IR (KBr) *v* (cm^{-1}) 2977, 2926, 2852, 1690, 1660, 1496, 1455, 1373, 1332, 1262, 1143, 1043, 969, 850, 763, 701; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow rate = 0.5mL/min; Retention time: 11.3 min (*R, R*-isomer), 13.6 min (*S,S*-isomer).



Results

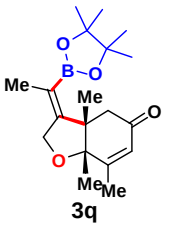
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.248	67731.797	1331678.125	50.1518
2		13.565	54315.250	1323617.750	49.8482
Total			122047.047	2655295.875	100.0000

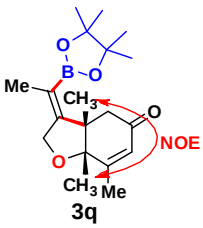


Results

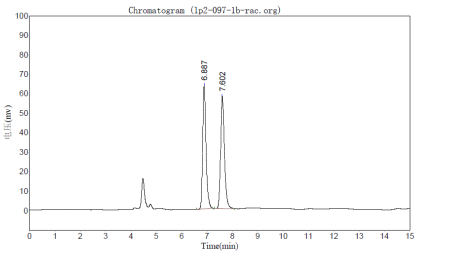
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.358	94183.813	1852301.750	14.8834
2		13.697	428040.531	10593118.000	85.1166
Total			522224.344	12445419.750	100.0000

(3a*S*,7a*S*,*Z*)-3a,7,7a-trimethyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3q)



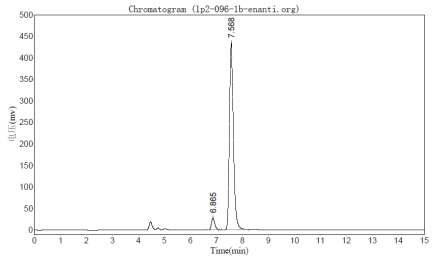


White solid. 32.2 mg, 65% yield; mp 92-94 °C; $[\alpha]_D^{25}$ +20.1 (*c* 0.96, $CHCl_3$) for 90% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 5.80 (s, 1H), 4.18 (AB, J_{AB} = 14.8 Hz, 2H), 3.58 (d, *J* = 17.2 Hz, 1H), 2.21 (d, *J* = 17.2 Hz, 1H), 1.94 (s, 3H), 1.55 (s, 3H), 1.36 (s, 3H), 1.34 (s, 6H), 1.30 (s, 6H), 1.23 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.34, 162.76, 157.68, 129.05, 85.69, 83.61, 69.33, 49.41, 43.31, 25.04, 24.97, 23.06, 17.93, 17.84, 17.31; ESI-MS: $[M+Na]^{\oplus}$ 355.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{19}H_{29}{}^{10}BO_4Na^{\oplus}$ 354.2093, found 354.2087; IR (KBr) *v* (cm^{-1}) 2978, 2930, 2829, 1674, 1450, 1373, 1347, 1299, 1214, 1172, 1140, 1119, 1042, 967, 882, 845; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / *i*-propanol = 97/03; flow = 0.7 mL/min; Retention time: 6.9 min (*R, R*-isomer), 7.6 min (*S,S*-isomer). The relative configuration was determined by the NOSEY (See Page S114).



Results

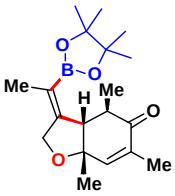
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.887	63436.336	591200.563	49.6524
2		7.602	57728.906	599477.688	50.3476
Total			121165.242	1190678.250	100.0000



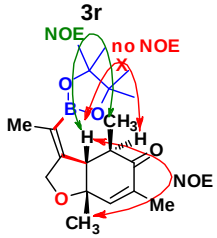
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.865	27131.273	237277.813	4.9851
2		7.568	434355.438	4522500.500	95.0149
Total			461486.711	4759778.313	100.0000

(3a*S*,4*R*,7a*S*,*Z*)-4,6,7a-Trimethyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3r)

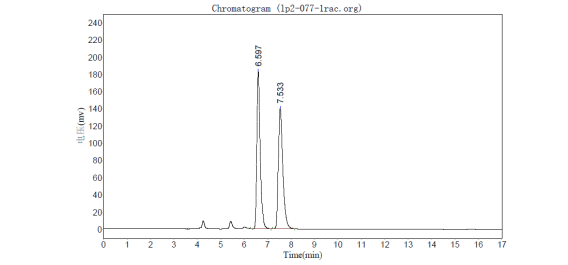


3r



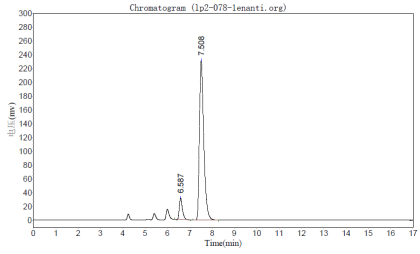
3r

White solid. 30.6 mg, 61% yield; mp 127-129 °C; $[\alpha]_D^{25}$ -79.3 (*c* 0.51, $CHCl_3$) for 82% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.37 (d, *J* = 1.6 Hz, 1H), 4.46 (AB, J_{AB} = 14.8 Hz, 2H), 3.26 (d, *J* = 9.2 Hz, 1H), 2.55-2.63 (m, 1H), 1.81 (d, *J* = 1.2 Hz, 3H), 1.66 (s, 3H), 1.33 (s, 3H), 1.26 (s, 6H), 1.24 (s, 6H), 1.13 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 202.10, 156.44, 142.79, 135.57, 83.35, 78.88, 69.17, 54.01, 43.35, 26.24, 25.09, 24.85, 17.02, 16.08, 13.64; ESI-MS: $[M+Na]^{\oplus}$ 355.2; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{19}H_{29}{}^{10}BO_4Na^{\oplus}$ 354.2093, found 354.2087; IR (KBr) ν (cm^{-1}) 2985, 2942, 2924, 2900, 2851, 1679, 1652, 1449, 1398, 1373, 1360, 1303, 1290, 1220, 1151, 1114, 1088, 1013, 968, 861; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7 mL/min; Retention time: 6.6 min (minor), 7.5 min (major). The relative configurations were determined by the NOSEY (See Page S117).



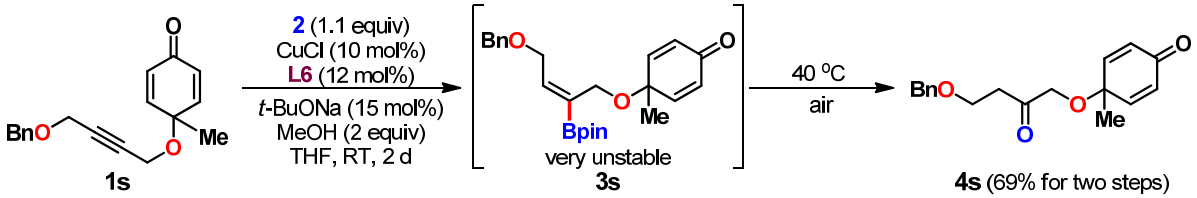
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.597	182590.844	1837876.750	49.9994
2		7.533	139477.500	1837918.500	50.0006
Total			322068.344	3675795.250	100.0000

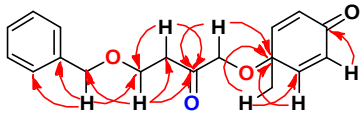


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.587	30896.674	299400.719	8.8714
2		7.508	230826.844	3075502.500	91.1286
Total			261723.518	3374903.219	100.0000

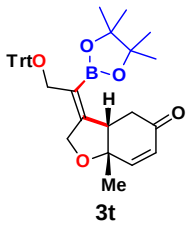


4-(4-(Benzyloxy)-2-oxobutoxy)-4-methylcyclohexa-2,5-dienone (4s) After the general procedure for-Cu-catalyzed asymmetric borylative cyclization, the reaction mixture was passed through silica gel (300-400 mesh) and washed with EtOAc. Then silica gel (500 mg) was added to the solution. The mixture was concentrated in vacuo. The resulting residue was stirred at 40 °C for 7 d under air atmosphere. The residue was purified by silica gel (300-400 mesh) column chromatography to afford **4s** (31.0 mg, 69% yield) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.37-7.25 (m, 5H), 6.73 (d, *J*= 10.0 Hz, 2H), 6.26 (d, *J*= 10.0 Hz, 2H), 4.78 (s, 2H), 3.97 (s, 2H), 3.73 (t, *J*= 6.0 Hz, 2H), 2.67 (t, *J*= 6.0 Hz, 2H), 1.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 205.93, 184.86, 150.40, 137.96, 130.69, 128.52, 127.87, 127.82, 73.41, 73.14, 71.38, 65.15, 39.58, 26.15; ESI-MS: $[M+Na]^{\oplus}$ 323.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{18}H_{20}O_4Na^{\oplus}$ 323.1254, found 323.1252; IR (KBr) ν (cm^{-1}), 3032, 2962, 2919, 2850, 1724, 1674, 1632, 1454, 1384, 1365, 1261, 1091, 1027, 863, 801, 740, 700. The positon of carbonyl group (**blue**) in **4s** was determined by HMBC (See Page S120-122).



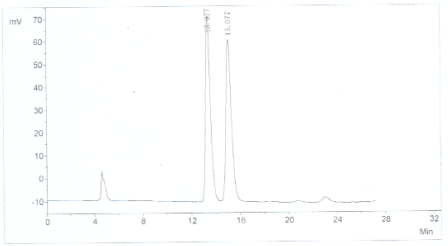
4s (HMBC correlations)
Solvent: $CDCl_3$

(3a*S*,7a*S*,*Z*)-7a-methyl-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(trityloxy)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (3t)

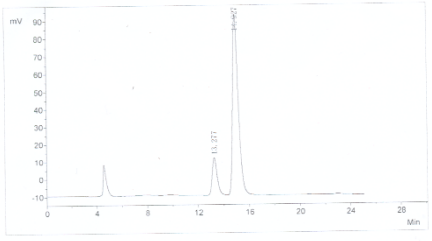


3t

Colorless oil. 44.5 mg, 53%; $[\alpha]_D^{25}$ -80.3 (*c* 1.02, $CHCl_3$) for 70% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) . 7.50-7.45 (m, 6H), 7.31-7.18 (m, 9H), 6.56 (d, *J*= 10.0 Hz, 1H), 5.97 (m, *J* = 10.0 Hz, 1H), 4.21 (s, 2H), 3.59 (d, *J* = 9.6 Hz, 1H), 3.48 (d, *J* = 9.6 Hz, 1H), 3.37 (t, *J* = 7.2 Hz, 1H), 2.71-2.55 (m, 2H), 1.37 (s, 3H), 1.33 (s, 6H), 1.32 (s, 6H). ^{13}C NMR (100 MHz, acetone-d_6) δ (ppm) 197.74, 162.41, 150.27, 145.35, 130.26, 129.69, 128.68, 127.93, 87.51, 84.50, 79.85, 69.51, 63.56, 48.92, 40.14, 25.52, 25.41, 24.51; ESI-MS: $[M+Na]^{\oplus}$ 585.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{36}H_{39}{}^{10}BO_5Na^{\oplus}$ 584.2819, found 584.2792; IR (KBr) *v* (cm^{-1}) 2968, 2924, 2852, 1689, 1597, 1490, 1449, 1372, 1308, 1277, 1218, 1142, 1113, 1048, 953, 898, 850, 799, 746, 705, 632; HPLC: DAICEL CHIRALCEL IC-H Column; detected at 214 nm; *n*-hexane / *i*-propanol = 95/05; flow rate = 0.7mL/min; Retention time: 13.4min (*R*, *R*-isomer), 15.1 min (*S*,*S*-isomer).



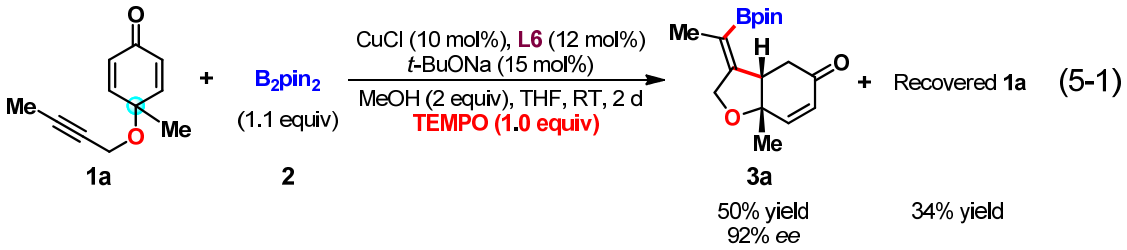
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		13.377	81617.9	2259405.4	49.5620
2	2		15.077	71165.9	2299340.6	50.4380
Total				152813.7	4558746.1	100.0000



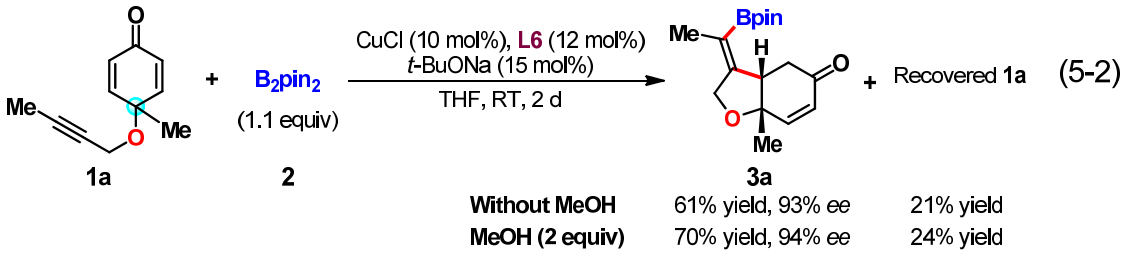
No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		13.277	21214.0	582744.5	15.2389
2	2		14.927	101829.3	3241302.1	84.7611
Total				123043.3	3824046.6	100.0000

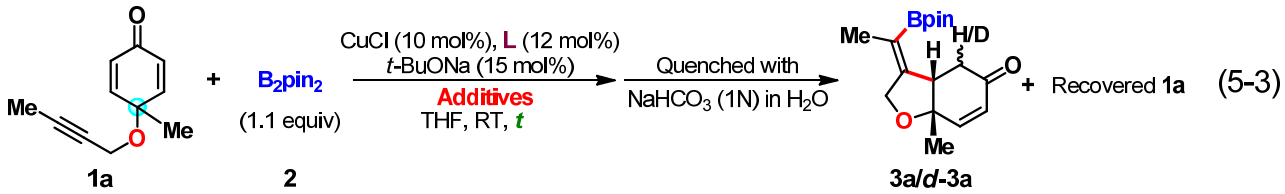
5. MECHANISM INVESTIGATION

To probe the reaction mechanism, several controlled experiments were designed and investigated.



PROCEDURE: A dried Schlenk flask was charged with CuCl (1.0 mg, 0.01 mmol, 10 mol%), ligand **L6** (6.5 mg, 0.012 mmol, 12 mol%), B_2pin_2(27.9 mg, 0.11 mmol, 1.1 equiv), *t*-BuONa (1.4 mg, 0.015mmol, 15 mol%) and anhydrous THF (1.0 mL) under nitrogen atmosphere. After the mixture was stirred at room temperature for 30 min, a solution of substrate **1a** (17.6 mg, 0.1 mmol) and TEMPO (15.6 mg, 0.1 mmol) in anhydrous THF (1.0 mL) was added, followed by anhydrous MeOH (8.1 μL, 0.20 mmol, 2.0 equiv) was added. The resulting mixture was stirred at room temperature for 2 days. The reaction mixture was quenched with $NaHCO_3$ (1 N, 5 mL), and extracted with EtOAc (15 mL × 3). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel (300-400 mesh) column chromatography to afford the desired product **3a**.



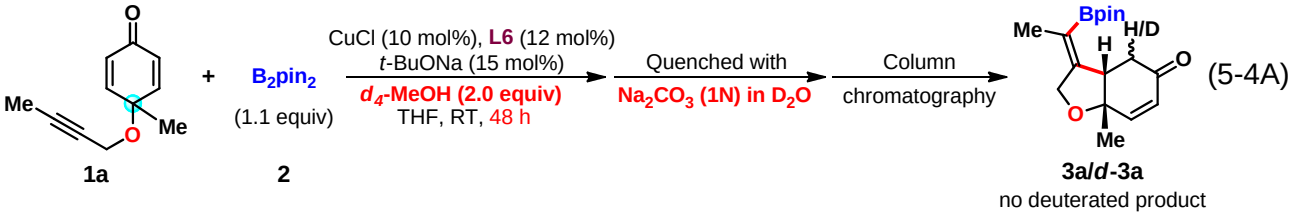


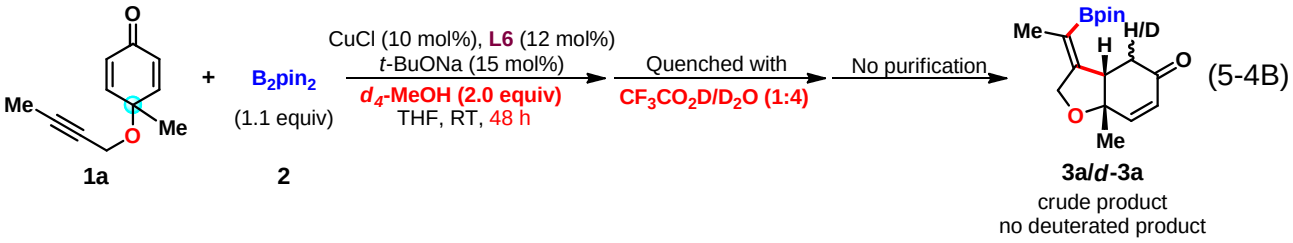
1a (0.1 mmol), THF (2.0 mL), **L** = **L6**, ***d*****$_4$-MeOH (2.0 equiv), 48 h** — 64% yield (no deuterated product); 22% yield — (5-3A)

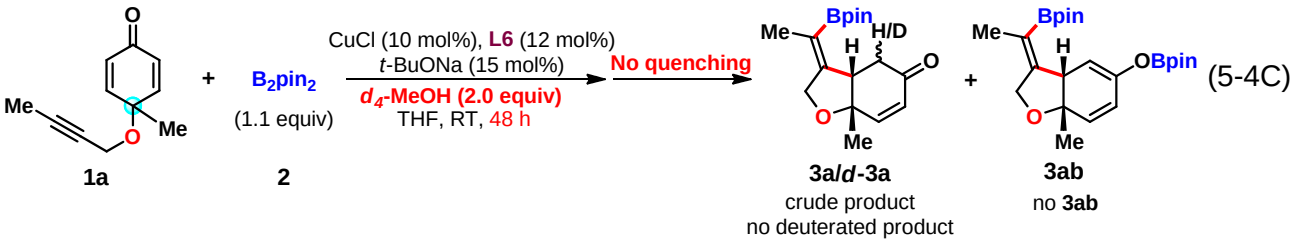
1a (0.1 mmol), THF (2.0 mL), **L** = **L6**, **D_2O (2.0 equiv), 48 h** — 13% yield (no deuterated product); 68% yield — (5-3B)

1a (0.3 mmol), THF (2.0 mL), **L** = **L6**, ***d*****$_4$-MeOH (2.0 equiv), 48 h** **Operated in glove box.** — 65% yield (17% deuterated product); 25% yield — (5-3C)

1a (0.3 mmol), THF (2.0 mL), **L** = **Ph_3P**, ***d*****$_4$-MeOH (2.0 equiv), 18 h** **Operated in glove box.** — 43% yield (60% deuterated product); 34% yield — (5-3D)





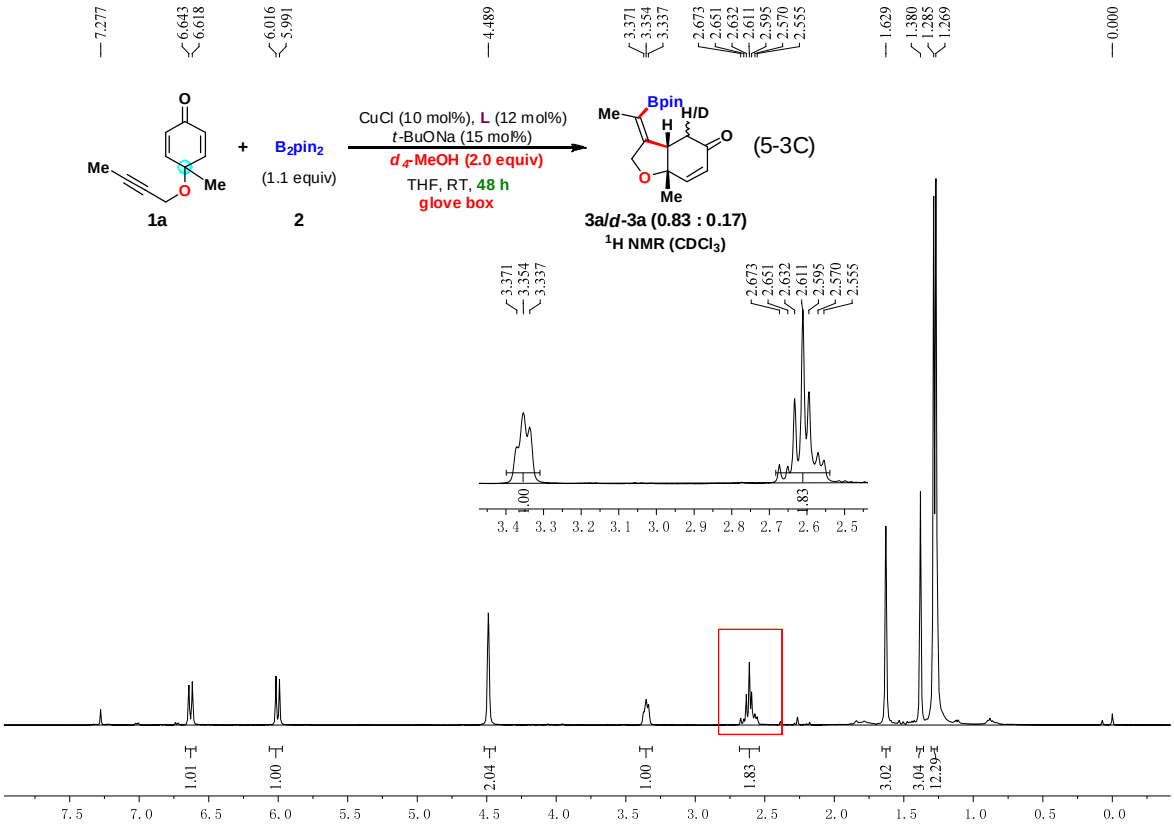


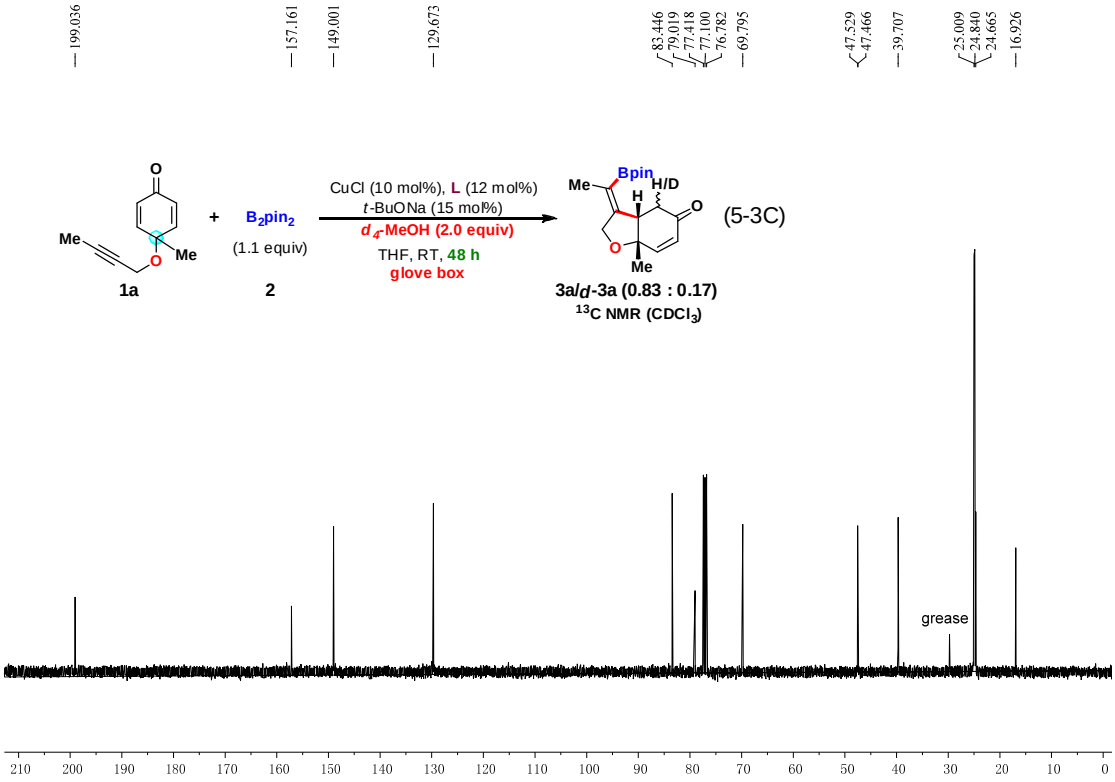
PROCEDURE for 5-3A and 5-3B: A dried Schlenk flask was charged with CuCl (1.0 mg, 0.01 mmol, 10 mol%), ligand **L6** (6.5 mg, 0.012 mmol, 12 mol%), B_2pin_2 (27.9 mg, 0.11 mmol, 1.1 equiv), *t*-BuONa (1.4 mg, 0.015mmol, 15 mol%) and anhydrous THF (1.0 mL) under nitrogen atmosphere. After the mixture was stirred at room temperature for 30 min, a solution of substrate **1a** (17.6 mg, 0.1 mmol) in anhydrous THF (1.0 mL) was added, followed by anhydrous d_4-MeOH (8.1 μL, 0.20 mmol, 2.0 equiv, for

eq 5-3A) or D_2O (3.6 μL, 0.20 mmol, 2.0 equiv, for eq 5-3B) was added. The resulting mixture was stirred at room temperature for 2 days. The reaction mixture was quenched with $NaHCO_3$ (1 N, 5 mL), and extracted with EtOAc (15 mL × 3). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel (300-400 mesh) column chromatography to afford the desired product **3a**.

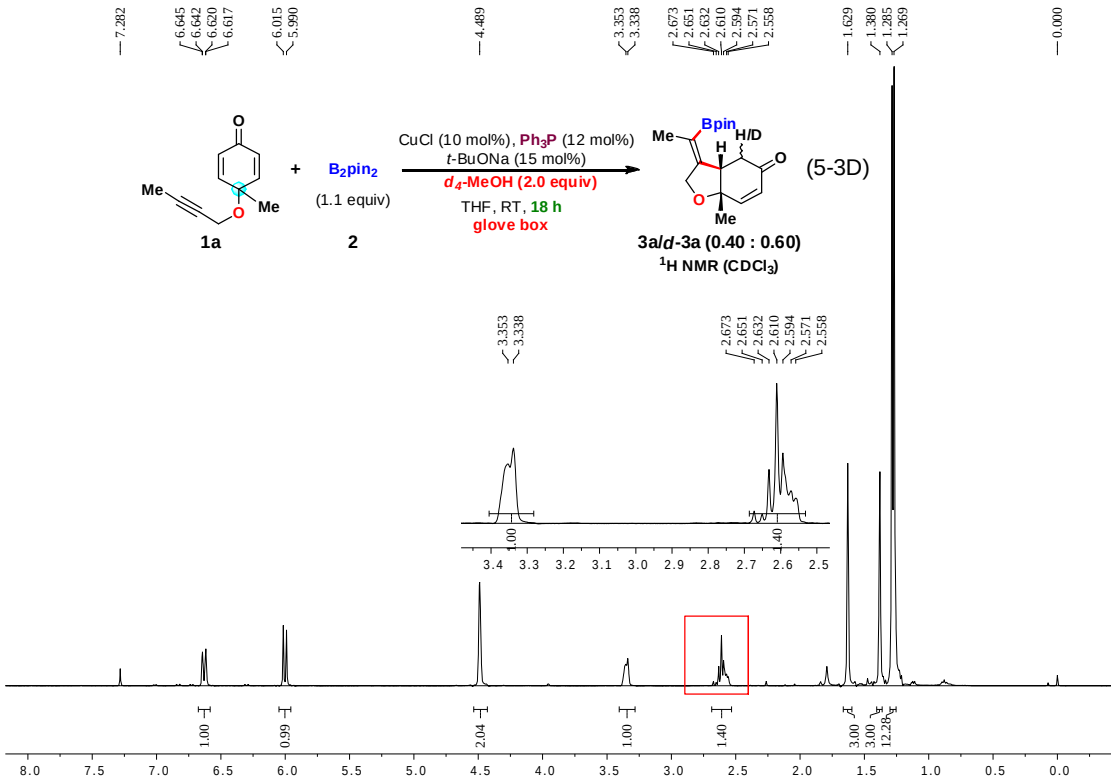
PROCEDURE for 5-3C and 5-3D: In a glove box, a dried Schlenk flask was charged with CuCl (3.0 mg, 0.03 mmol, 10 mol%), ligand **L6** (19.5 mg, 0.036 mmol, 12 mol%, for eq 5-3C) or Ph_3P (9.4 mg, 0.036 mmol, 12 mol%, for eq 5-3D), B_2pin_2(83.7 mg, 0.33 mmol, 1.1 equiv), *t*-BuONa (4.2 mg, 0.045mmol, 15 mol%) and anhydrous THF (1.0 mL). After the mixture was stirred at room temperature for 30 min, a solution of substrate **1a** (52.8 mg, 0.3 mmol) in anhydrous THF (1.0 mL) was added, followed by anhydrous d_4-MeOH (24.3 μL, 0.60 mmol, 2.0 equiv) was added. The resulting mixture was stirred at room temperature for 2 days (for eq 5-3C) or 18 h (for eq 5-3D). The reaction mixture was quenched with $NaHCO_3$ (1 N, 15 mL), and extracted with EtOAc (45 mL × 3). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel (300-400 mesh) column chromatography to afford a mixture of the desired products **3a** and ***d*-3a.**

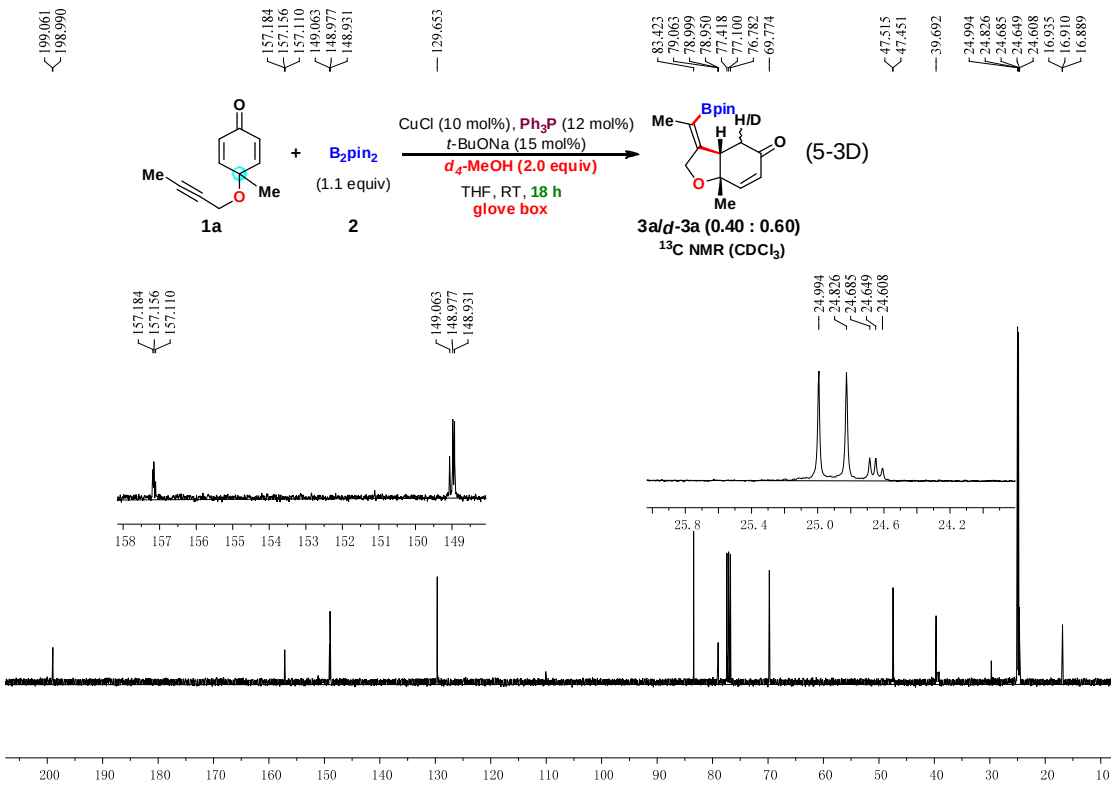
Spectral data for eq 5-3C: Colorless Oil. **3a** and ***d*-3a** (0.83 : 0.17, determined by ^{1}H NMR; 59.7 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.63 (d, J = 10.0 Hz, 1H), 6.00 (d, J = 10.0 Hz, 1H), 4.49 (s, 2H), 3.37-3.34 (m,1H), 2.67-2.56 (m, 1.83 H), 1.63 (s, 3H), 1.38 (s, 3H), 1.29 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.04, 157.16, 149.00, 129.67, 83.45, 79.02, 69.79, 47.53, 47.47, 39.71, 25.01, 24.84, 24.67, 16.93; ESI-MS: $[M+Na]^{\oplus}$ 327.2 (100%, **3a**), 328.1(39%, ***d*-3a**); HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{25}{}^{10}BO_4Na^{\oplus}$ 326.1774 (**3a**), found 326.1777 (**3a**); $[M+Na]^{\oplus}$ calcd for $C_{17}H_{24}D^{10}BO_4Na^{\oplus}$ 327.1837 (***d*-3a**), found 327.1842 (***d*-3a**).



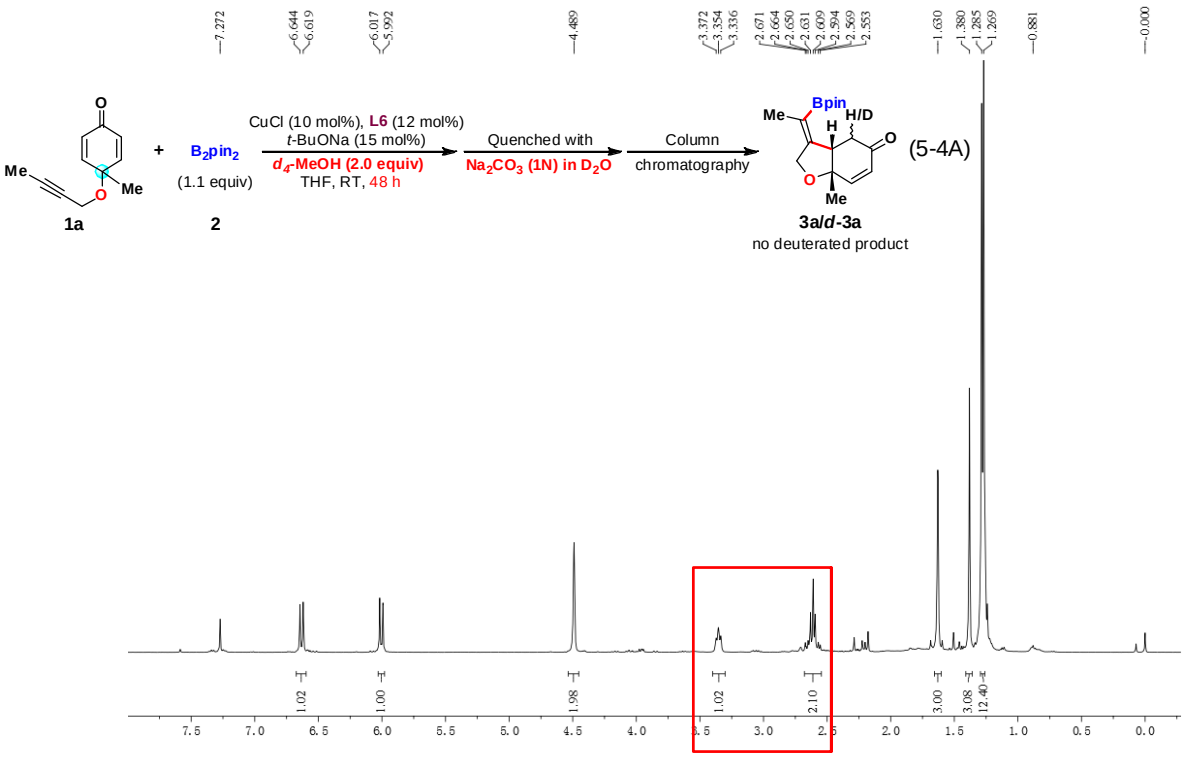


Spectral data for eq 5-3D: Colorless Oil. **3a** and ***d*-3a** (0.40 : 0.60, determined by ^{1}H-NMR; 43.2 mg, 43% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.65-6.62 (m, 1H), 6.00 (d, J = 10.0 Hz, 1H), 4.49 (s, 2H), 3.35-3.34 (m,1H), 2.67-2.56 (m, 1.40 H), 1.63 (s, 3H), 1.38 (s, 3H), 1.29 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 199.06, 198.99, 157.18, 157.16, 157.11, 149.06, 148.98, 148.93, 83.42, 79.06, 79.00, 78.95, 69.77, 47.51, 47.45, 39.69, 24.99, 24.83, 24.69, 24.65, 24.61, 16.93, 16.91, 16.89; ESI-MS: $[M+Na]^{\oplus}$ 327.2 (57%, **3a**); 328.1 (100%, ***d*-3a**); HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{25}{}^{10}BO_4Na^{\oplus}$ 326.1774 (**3a**), found 326.1775 (**3a**); $[M+Na]^{\oplus}$ calcd for $C_{17}H_{24}D^{10}BO_4Na^{\oplus}$ 327.1837 (***d*-3a**), found 327.1839 (***d*-3a**).

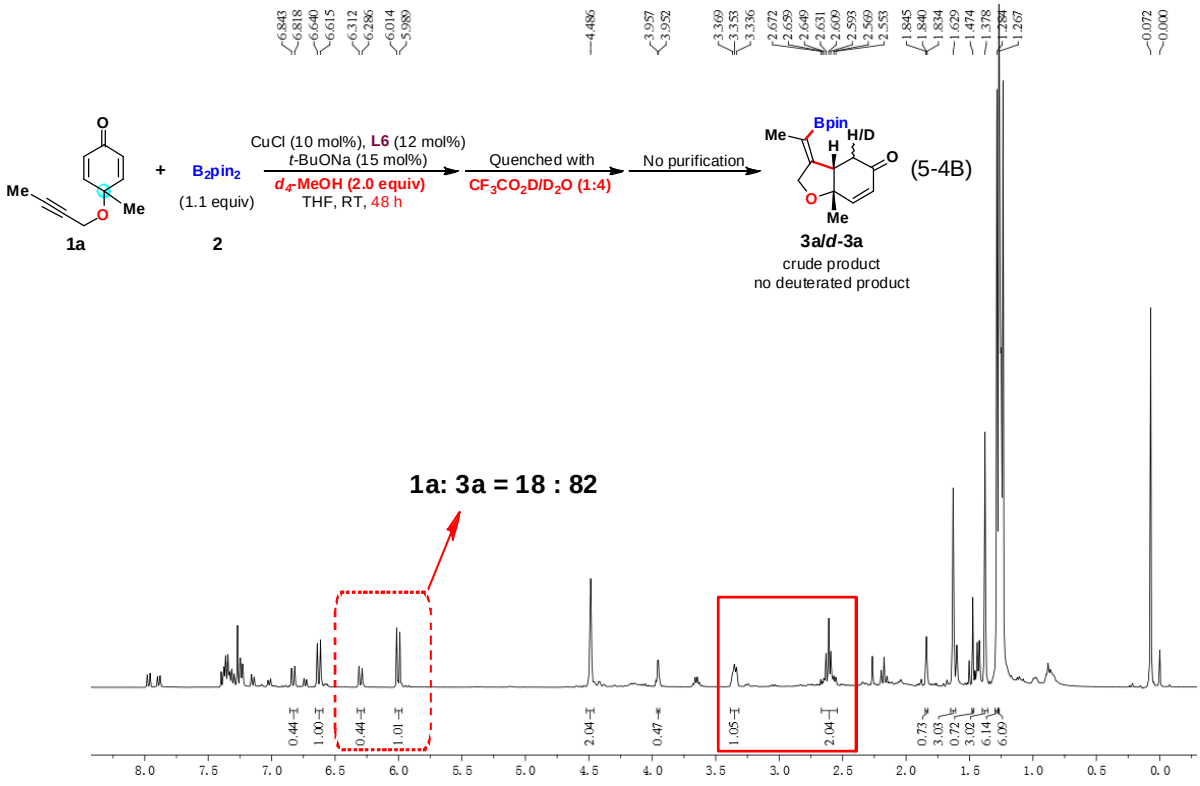




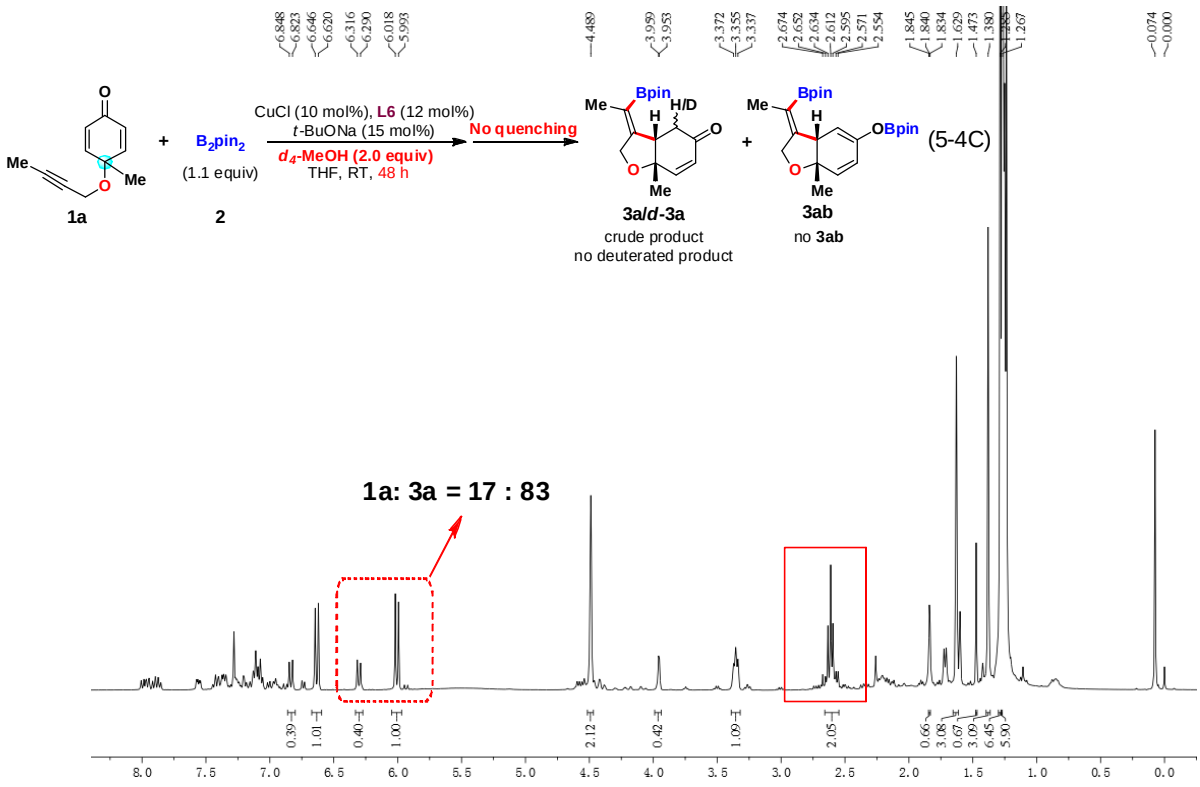
PROCEDURE for 5-4A: A dried Schlenk flask was charged with CuCl (1.0 mg, 0.01 mmol, 10 mol%), ligand **L6** (6.5 mg, 0.012 mmol, 12 mol%), B_2pin_2 (27.9 mg, 0.11 mmol, 1.1 equiv), *t*-BuONa (1.4 mg, 0.015mmol, 15 mol%) and anhydrous THF (1.0 mL) under nitrogen atmosphere. After the mixture was stirred at room temperature for 30 min, a solution of substrate **1a** (17.6 mg, 0.1 mmol) in anhydrous THF (1.0 mL) was added, followed by anhydrous d_4-MeOH (8.1 μL, 0.20 mmol, 2.0 equiv) was added. The resulting mixture was stirred at room temperature for 2 days. The reaction mixture was quenched with a solution of Na_2CO_3 in D_2O (1 N, 2 mL), and extracted with EtOAc (15 mL × 3). The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel column chromatography to afford the product **3a** (no ***d*-3a**).



PROCEDURE for 5-4B: A dried Schlenk flask was charged with CuCl (1.0 mg, 0.01 mmol, 10 mol%), ligand **L6** (6.5 mg, 0.012 mmol, 12 mol%), B_2pin_2 (27.9 mg, 0.11 mmol, 1.1 equiv), *t*-BuONa (1.4 mg, 0.015mmol, 15 mol%) and anhydrous THF (1.0 mL) under nitrogen atmosphere. After the mixture was stirred at room temperature for 30 min, a solution of substrate **1a** (17.6 mg, 0.1 mmol) in anhydrous THF (1.0 mL) was added, followed by anhydrous d_4-MeOH (8.1 μL, 0.20 mmol, 2.0 equiv) was added. The resulting mixture was stirred at room temperature for 2 days. The reaction mixture was quenched with a solution of CF_3CO_2D (0.5 mL) in D_2O (2 mL) and concentrated in vacuo to give the crude product **3a** (No ***d*-3a** was observed in the ^{1}H NMR spectrum.)



PROCEDURE for 5-4C: A dried Schlenk flask was charged with CuCl (1.0 mg, 0.01 mmol, 10 mol%), ligand **L6** (6.5 mg, 0.012 mmol, 12 mol%), B_2pin_2 (27.9 mg, 0.11 mmol, 1.1 equiv), *t*-BuONa (1.4 mg, 0.015mmol, 15 mol%) and anhydrous THF (1.0 mL) under nitrogen atmosphere. After the mixture was stirred at room temperature for 30 min, a solution of substrate **1a** (17.6 mg, 0.1 mmol) in anhydrous THF (1.0 mL) was added, followed by anhydrous d_4-MeOH (8.1 μL, 0.20 mmol, 2.0 equiv) was added. After the resulting mixture was stirred at room temperature for 2 days, it was concentrated in vacuo to give the crude product **3a** (No **3ab** was observed in the ^{1}H NMR and ESI-MS spectrums.)



Conclusions:

[1] The reaction performed well in the presence of TEMPO (1 equiv) affording the desired product **3a** in 50% yield and 92% *ee* (eq 5-1), which may exclude a radical process in this tandem reaction.

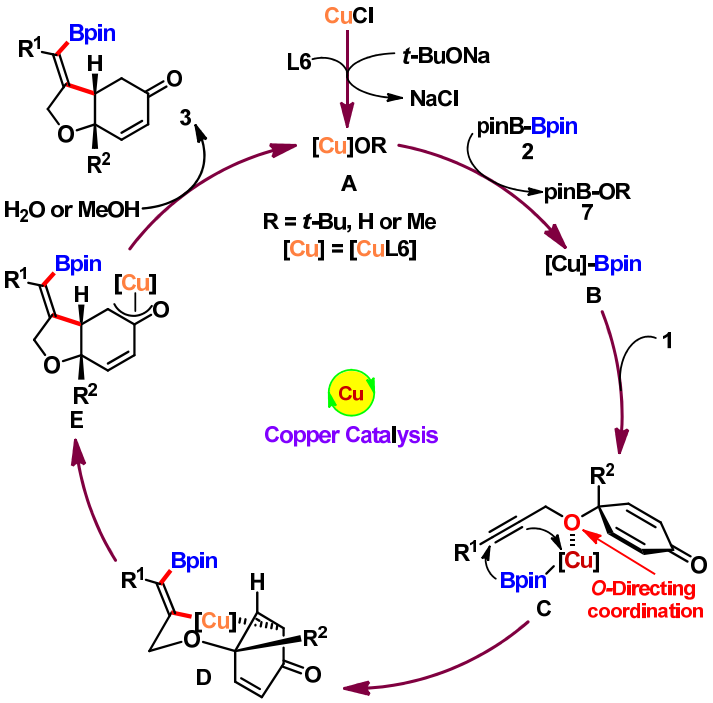
[2] Without methanol under standard condition, the reaction still worked well, albeit in a little lower yield (eq 5-2). The reaction system including dry THF solvent (distilled under Na, 0.8‰ water content, determined by Karl Fischer titration), still contained trace water, which could be acted as the proton source to promote the dissociation of copper. However, the reaction was remarkably inhibited in the presence of the excessive water (eq 5-3B).

[3] In a 0.1 mmol reaction scale, no deuterated product was observed with d_4-MeOH (2 equiv) or D_2O (2 equiv) as additive (eq 5-3A, 3B). The trace water in reaction system should provide the protons. In a 0.3 mmol reaction scale under glove box, 17% deuterated product was observed in the presence of d_4-MeOH (2 equiv, eq 5-3C). Using PPh_3 as ligand, the deuterated product was increased to 60% (eq 5-3D). The protons should come from the trace water and d_4-MeOH.

[4] Owing to the low deuteration rates in the product **3a**, we suspected that the enol boronate **3ab** was a stable intermediate, resulting from the direct transmetallation between enolate copper **E** (Scheme 5-1) and bis(pinacolato)diboron (B_2pin_2, **2**). However, no deuterated product (***d*-3a**) or **3ab** was observed in the ^1H NMR spectrums, after the reaction mixture was quenched with a solution of Na_2CO_3 (1 N) in D_2O (eq 5-4A) or CF_3CO_2D in D_2O (eq 5-4B). Without quenching procedure (eq 5-4C), **3ab** was still not observed in the ^1H NMR and ESI-MS spectrums. Thus we supposed that **3ab** was not involved in the transmetallation step.

On the basis of the above results, a plausible mechanism was proposed in scheme 5-1. Initiation of the reaction through the transmetallation of a (pinacolato)boron group (Bpin) from boron to copper species **A** generated the borylated copper **B**, which was coordinated with substrate **1** and subsequently un-

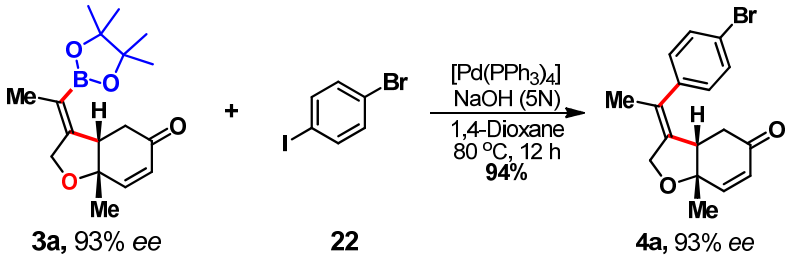
derwent *syn*-addition to carbon-carbon triple bond in the substrate **1** to afford borylated alkenyl-copper intermediate **D**. The favorable six-membered chair form with axial H atom and equatorial R^2 group in **D** enabled *syn*-migratory insertion of alkenyl-copper across the carbon-carbon double bond in cyclohex-adienone, forming the oxa-π-allylcopper intermediate **E**, which was readily protonated by trace water or methanol to regenerate **A** and liberate the product **3**.



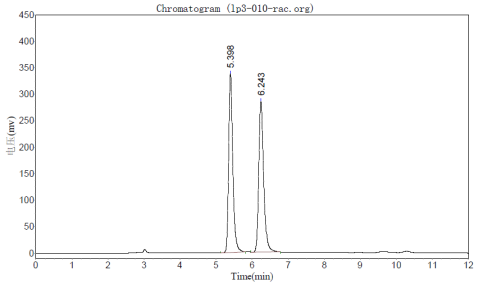
Scheme 5-1 Proposed mechanism

6. TRANSFORMATION OF THE CYCLIZATION PRODUCTS

4.1 The Transformation of Cyclization Product 3a.

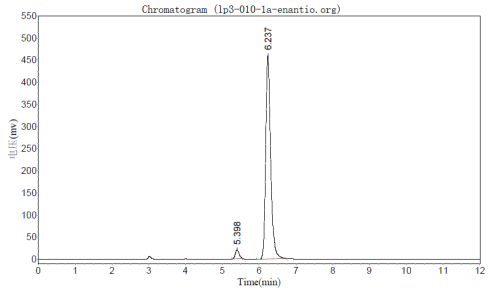


(3a*S*,7a*S*,*E*)-3-(1-(4-bromophenyl)ethylidene)-7a-methyl-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (4a)[1c] A mixture of **3a** (30.4 mg, 0.1 mmol), 1-bromo-4-iodobenzene (**22**, 42.4 mg, 0.15 mmol), $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol), aq. NaOH (5N, 30 μL, 0.15 mmol) in dioxane (2 mL) was stirred at 80 ^oC under N_2 atmosphere overnight. After cooled to room temperature, the reaction mixture was filtered and washed with CH_2Cl_2. The filtrate was concentrated under reduced pressure and purified by flash column chromatography using hexane/ethyl acetate as eluent (20:1) to afford the desired product **4a**. White solid. 31.2 mg, 94% yield; mp 162-164 ^oC; $[\alpha]_D^{25}$ +38.4 (*c* 0.50, $CHCl_3$) for 93% *ee*; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.48 (d, *J* = 8.4 Hz, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 10.4 Hz, 1H), 5.92 (d, *J* = 10.4 Hz, 1H), 4.39 (AB, J_{AB} = 13.6 Hz, 2H), 3.09 (s, 1H), 2.16 (dd, *J* = 16.4 Hz, *J* = 5.6 Hz, 1H), 2.01 (dd, *J* = 16.8 Hz, *J* = 4.0 Hz, 1H), 1.84 (s, 3H), 1.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 197.41, 150.28, 141.17, 136.68, 131.86, 129.93, 129.20, 129.01, 121.22, 80.70, 69.73, 46.70, 36.91, 23.33, 21.92; ESI-MS: $[M+Na]^{\oplus}$ 355.0/357.0 (1:1); HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{17}H_{17}{}^{79}BrO_2Na^{\oplus}$ 355.0304, found 355.0300; IR (KBr) ν (cm^{-1}) 3029, 2977, 2968, 1676, 1482, 1450, 1395, 1229, 1040, 873, 822; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / i-propanol = 90/10; flow = 1.0 mL/min; Retention time: 5.4 min (*R*, *R*-isomer), 6.2 min (*S*,*S*-isomer).



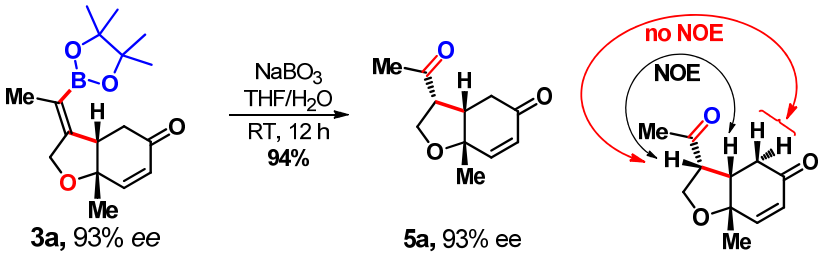
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.398	338402.656	2726331.500	50.1638
2		6.243	285770.219	2708528.500	49.8362
Total			624172.875	5434860.000	100.0000

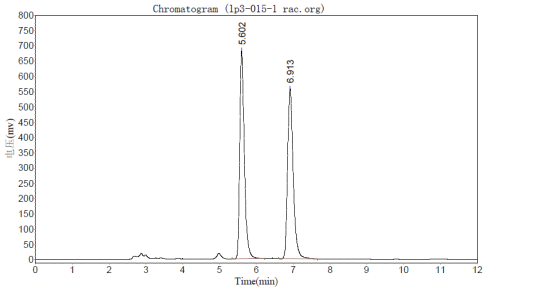


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.398	20148.514	153971.500	3.4228
2		6.237	459436.844	4344393.000	96.5772
Total			479585.357	4498364.500	100.0000

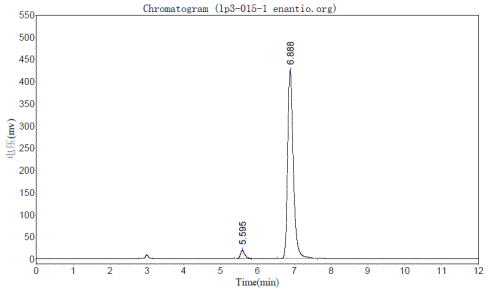


(3*R*,3a*S*,7a*S*)-3-acetyl-7a-methyl-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (5a) To a solution of **3a** (25 mg, 0.08 mmol) in THF/H_2O (1:1, 4 mL) was added $NaBO_3$•$4H_2O$ (124 mg, 0.8 mmol, 10.0 equiv.) and the reaction mixture was stirred at room temperature overnight. Then it was diluted with H_2O (10 mL) and extracted with ethyl acetate (15 mL ×3). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent (6:1) to afford the desired product **5a**. Colorless oil. 14.7 mg, 94% yield; $[\alpha]_D^{25}$ +28.5 (*c* 0.51, $CHCl_3$) for 93% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.60 (d, *J* = 10.4 Hz, 1H), 5.99 (d, *J* = 10.4 Hz, 1H), 4.00-3.92 (m, 2H), 3.02-3.08 (m, 1H), 2.74-2.79 (m, 1H), 2.60-2.71 (m, 2H), 2.18 (s, 3H), 1.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 205.91, 196.87, 152.62, 129.07, 80.60, 67.57, 56.97, 45.75, 37.76, 29.79, 23.38; ESI-MS: $[M+Na]^{\oplus}$ 217.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{11}H_{14}O_3Na^{\oplus}$ 217.0841, found 217.0835; IR (KBr) *v* (cm^{-1}) 2973, 2930, 2884, 1712, 1681, 1420, 1374, 1358, 1286, 1234, 1174, 1155, 1119, 1053, 1024, 876; HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; n-hexane / *i*-propanol = 70/30; flow = 1.0 mL/min; Retention time: 5.6 min (minor), 6.9 min (major). The relative configuration of acetyl substitution was determined by the NOSEY (See Page S132).



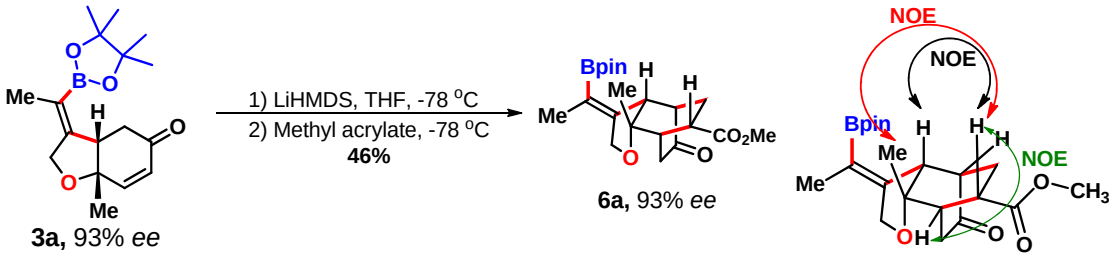
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.602	680854.750	5821362.500	49.8891
2		6.913	556886.563	5847248.000	50.1109
Total			1237741.313	11668610.500	100.0000



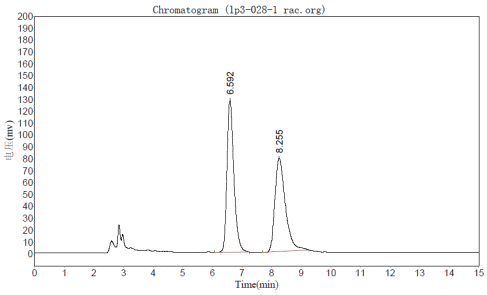
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		5.595	18343.594	150452.203	3.2697
2		6.888	423764.688	4450891.000	96.7303
Total			442108.281	4601343.203	100.0000



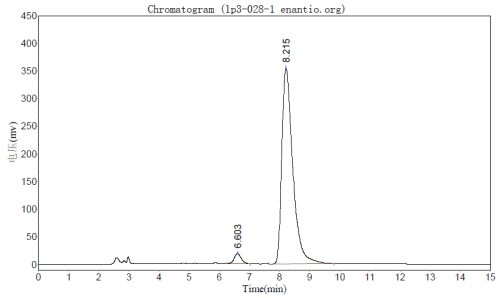
(3a*S*,4*R*,6*S*,7*S*,7a*S*,*Z*)-methyl-7a-methyl-9-oxo-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)octahydro-4,7-ethanobenzofuran-6-carboxylate (6a) To a solution of LiHMDS (120 μL, 1.0 N in THF, 0.12 mmol) in THF (1 mL) was added a solution of **3a** (30.4 mg, 0.1 mmol) in THF (1.5 mL) dropwise at -5 °C. After the reaction mixture was stirred for 30 min, methyl acrylate (12.9 mg, 0.15 mmol)

was added and the resulting reaction mixture was still stirred overnight at the same temperature. Then the reaction was quenched with aqueous saturated NH_4Cl (10 mL) and extracted with EtOAc (15 mL × 3). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash column chromatography using hexane/ethyl acetate eluent (10:1) to afford the recovered **3a** (5.2 mg, 17% yield) and the desired product **6a** (17.9 mg, 46% yield) as colorless oil. $[\alpha]_D^{25}$ -60.4 (*c* 0.99, $CHCl_3$) for 94% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.39 (s, 2H), 3.74 (s, 3H), 3.08 (s, 1H), 2.88(t, *J* = 9.2Hz, 1H), 2.62-2.67 (m, 2H), 2.51-2.52 (m, 1H), 2.08-2.21 (m, 3H),1.61 (s, 3H), 1.36 (s, 3H), 1.26 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 215.06, 174.92, 156.57, 84.25, 83.28, 70.49, 54.79, 52.28, 50.91, 41.93, 37.58, 36.32, 25.64, 25.15, 24.94, 22.63, 17.02; ESI-MS: $[M+Na]^{\oplus}$ 413.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{21}H_{31}{}^{10}BO_6Na^{\oplus}$ 412.2148, found 412.2142; IR (KBr) *v* (cm^{-1}) 2976, 1731, 1649, 1438, 1402, 1364, 1310, 1282, 1213, 1177, 1145, 1099, 1058, 1029, 967, 856; HPLC: Phenomenex Lux 5u Cellulose-2 (PC-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 70/30; flow rate = 1.0 mL/min; Retention time: 6.6 min (minor), 8.2 min (major). The relative configurations were determined by the NOSEY (See Page S140-141).



Results

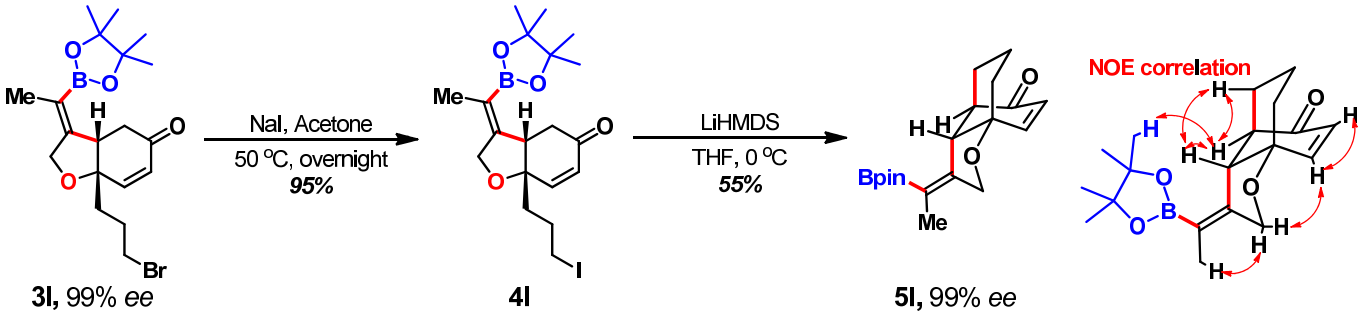
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.592	127600.398	2035743.000	51.4219
2		8.255	78372.586	1923162.375	48.5781
Total			205972.984	3958905.375	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		6.603	18255.059	298599.906	3.2287
2		8.215	353955.719	8949618.000	96.7713
Total			372210.777	9248217.906	100.0000

4.2 The Transformation of Cyclization Product 3l

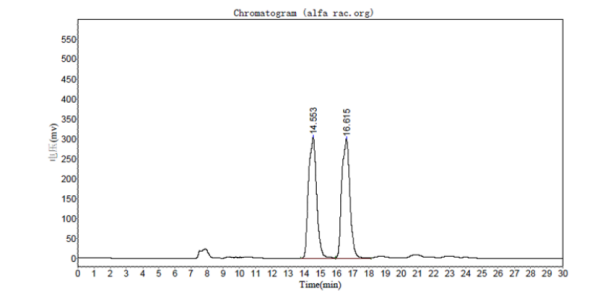


3l, 99% *ee* **4l** **5l,** 99% *ee*

(3a*S*,7a*S*,*Z*)-7a-(3-Iodopropyl)-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-2,3,3a,4-tetrahydrobenzofuran-5(7a*H*)-one (4l) A mixture of **3l** (50 mg, 0.122 mmol) and NaI (182 mg, 1.22 mmol, 10 equiv) in acetone (10 mL) was stirred for overnight at 50 °C. The resulting mixture was concentrated in vacuo and the residue was purified by silica gel (300-400 mesh) column chromatography to afford **4l** (53.2 mg, 95%) as white solid. mp 101-103 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.64 (d, *J* = 10.4 Hz, 1H), 6.06 (d, *J* = 10.4 Hz, 1H), 4.47 (s, 2H), 3.43 (t, J = 7.2 Hz, 1H), 3.21 (t, *J* = 6.4 Hz, 2H),

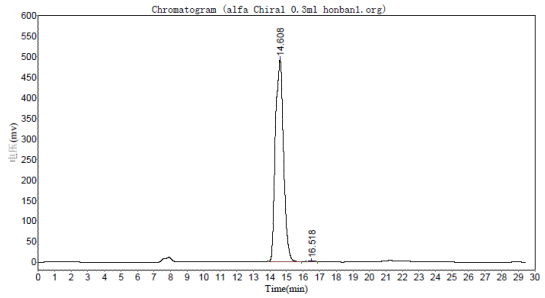
2.68-2.55 (m, 2H), 2.01-1.69 (m, 4H), 1.63 (s, 3H), 1.29 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 198.73, 156.86, 147.12, 130.78, 83.54, 80.74, 69.83, 45.91, 39.84, 38.30, 28.14, 25.01, 24.94, 17.01, 6.55; ESI-MS: $[M+Na]^{\oplus}$ 481.1; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{19}H_{28}{}^{10}BIO_4Na^{\oplus}$ 480.1054, found 480.1064; IR (KBr) ν (cm^{-1}) 2976, 2925, 2853, 1687, 1624, 1451, 1363, 1307, 1273, 1213, 1144, 1094, 1022, 966, 850, 685.

(3a*S*,4*R*,7a*S*,*Z*)-3-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)-3a,4-dihydro-2H-4,7a-propanobenzofuran-5(3H)-one (5l) To a solution of **4l** (30.6 mg, 0.067 mmol) in dry THF (1 mL) was added to a solution of LiHMDS (1 M THF solution, 0.344 ml, 5 equiv) in dry THF (1 mL) at 0 °C. The resulting mixture was warmed to room temperature and stirred for overnight. The reaction mixture was quenched by aqueous saturated NH_4Cl (10 mL) and extracted with AcOEt (20 mLx3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by silica gel (300-400 mesh) column chromatography to afford **5l** (12.1 mg, 55%) as white solid. mp 102-104 °C; $[\alpha]_D^{25}$ -69.8 (*c* 0.32, $CHCl_3$) for 99% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.53 (dd, *J* = 10.0, 2.0 Hz, 1H), 6.09 (d, *J* = 10.0 Hz, 1H), 4.35 (AB, J_{AB} = 14.4 Hz, 2H), 3.81-3.77 (m, 1H), 2.65 (m, 1H), 1.95-1.88 (m, 1H), 1.85-1.62 (m, 4H), 1.59 (s, 3H), 1.55-1.42 (m, 1H), 1.31 (s, 6H)1.28 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 200.62, 152.15, 151.75, 133.15, 83.68, 82.23, 71.24, 54.07, 45.98, 31.18, 28.31, 25.06, 24.97, 19.78, 17.50; ESI-MS: $[M+H]^{\oplus}$ 331.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{19}H_{27}{}^{10}BO_4Na^{\oplus}$ 352.1931, found 352.1925; IR (KBr) ν (cm^{-1}) 2976, 2933, 2862, 1716, 1683, 1540, 1456, 1358, 1305, 1212, 1180, 1134, 1084, 1005, 965, 925, 849, 820, 690.; HPLC: Phenomenex Lux 5u Amylose-2 (PA-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow rate = 0.3 mL/min; Retention time: 14.6 min (major), 16.6 min (minor). The relative configurations were determined by the NOSEY (See Page S154-155).



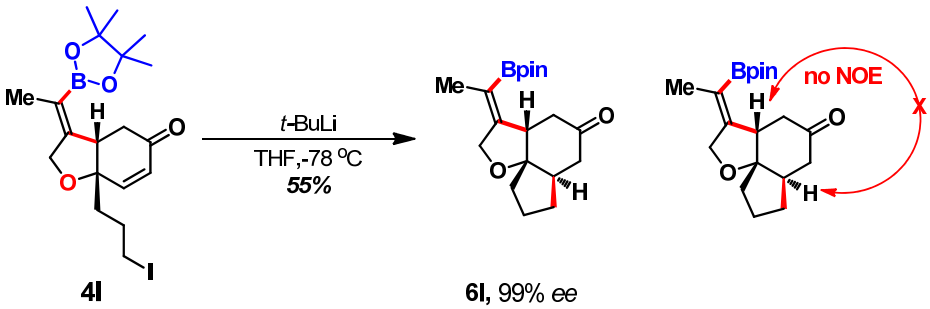
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.553	303796.031	10564501.000	50.3617
2		16.615	299556.500	10412732.000	49.6383
Total			603352.531	20977233.000	100.0000



Results

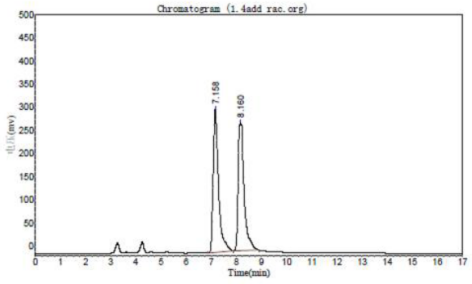
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.608	493670.156	16845688.000	99.7114
2		16.518	2314.115	48757.297	0.2886
Total			495984.271	16894445.297	100.0000



4l **6l**, 99% *ee*

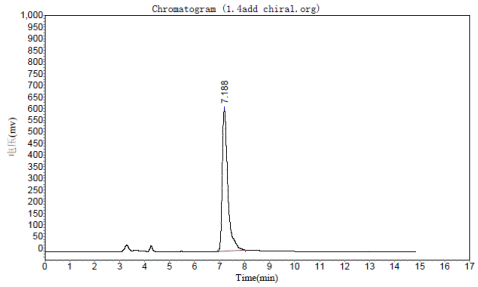
(3a*S*,6a*R*,91*S*,*Z*)-3-(1-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)ethylidene)octahydroindeno[4-b]furan-5(6*H*)-one (6l) To a solution of **4l** (34 mg, 0.074 mmol) in dry THF (2 mL) was added *t*-BuLi (1.5M in THF, 0.148 mL, 0.223 mmol, 3 equiv.) dropwise at -78 °C. After the resulting mixture was

stirred for 2 min, it was quenched by MeOH (0.5 mL). The mixture was passed through silica gel (300-400 mesh), washed with EtOAc and concentrated in vacuo. The residue was purified by silica gel (300-400 mesh) column chromatography to afford **6l** (13.2 mg, 55%) as white solid. mp 111-112 ^{o}C; $[\alpha]_D^{25}$ -70.9 (*c* 0.34, $CHCl_3$) for 99% *ee*; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 4.42 (AB, J_{AB} = 15.2 Hz, 2H), 3.19 (dd, *J* = 12.8, 4.4 Hz, 1H), 2.48-2.32 (m, 3H), 2.23-2.09 (m, 2H), 2.09-1.99 (m, 1H), 1.92-1.84 (m, 1H), 1.83-1.66 (m, 2H), 1.63 (s, 3H), 1.48-1.39 (m, 1H), 1.32-1.23 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 213.10, 158.26, 93.11, 83.31, 68.57, 45.98, 44.04, 43.00, 42.00, 36.06, 31.86, 25.10, 24.76, 23.50, 16.59; ESI-MS: $[M+Na]^{\oplus}$ 355.3; HRMS (FTMS-ESI): $[M+Na]^{\oplus}$ calcd for $C_{19}H_{29}{}^{10}BO_4Na^{\oplus}$ 354.2087, found 354.2079; IR (KBr) ν (cm^{-1}) 2954, 2868, 1716, 1652, 1456, 1403, 1364, 1306, 1212, 1145, 1112, 1029, 966, 850, 686.; HPLC: Phenomenex Lux 5u Amylose-2 (PA-2) Column; detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow rate = 0.7 mL/min; Retention time: 7.2 min (major), 8.2 min (minor). The relative configuration was determined by the NOSEY (See Page S163).



Results

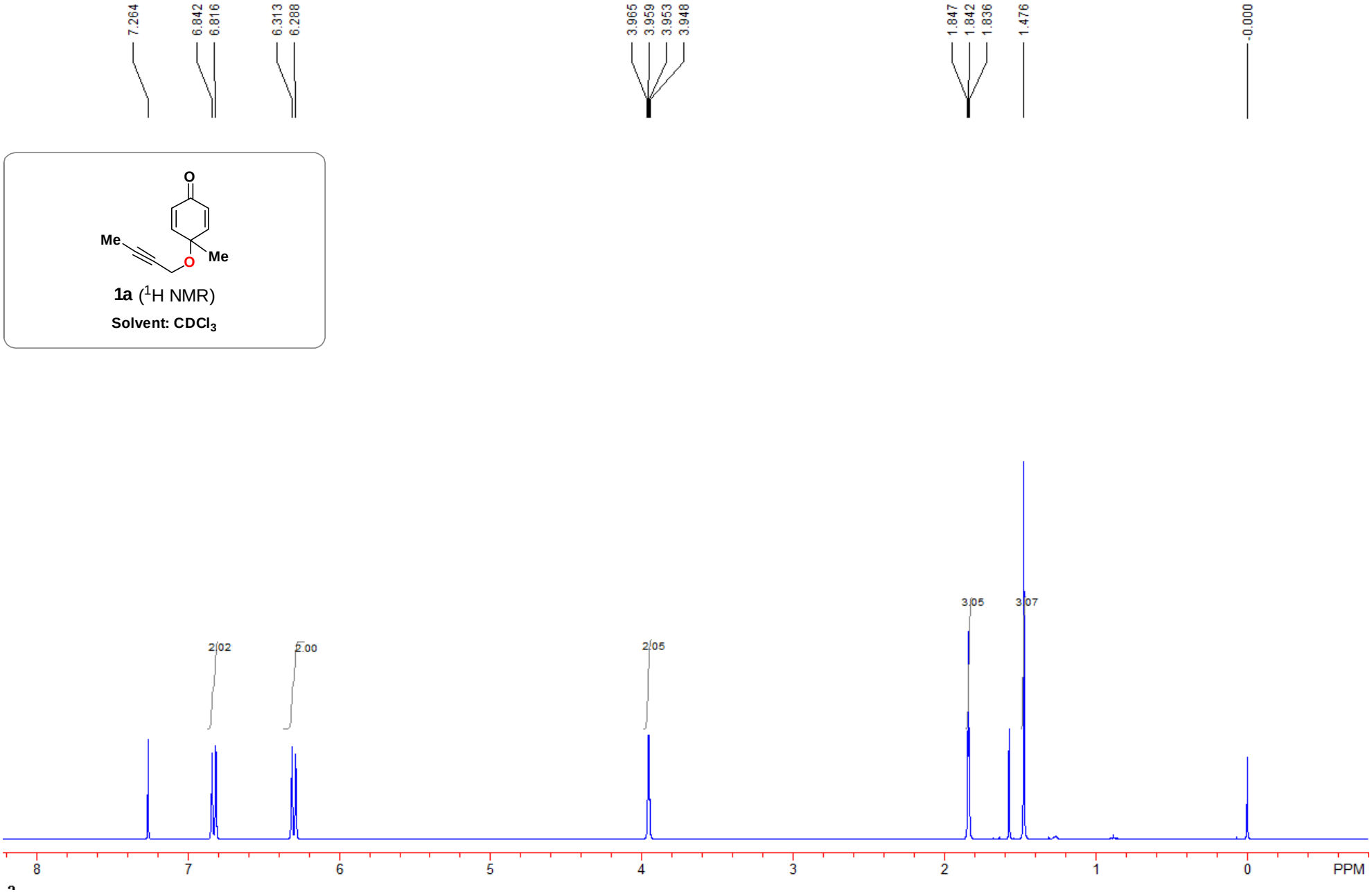
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.158	309135.344	4564355.500	48.9742
2		8.160	318772.125	4755568.000	51.0258
Total			627907.469	9319923.500	100.0000

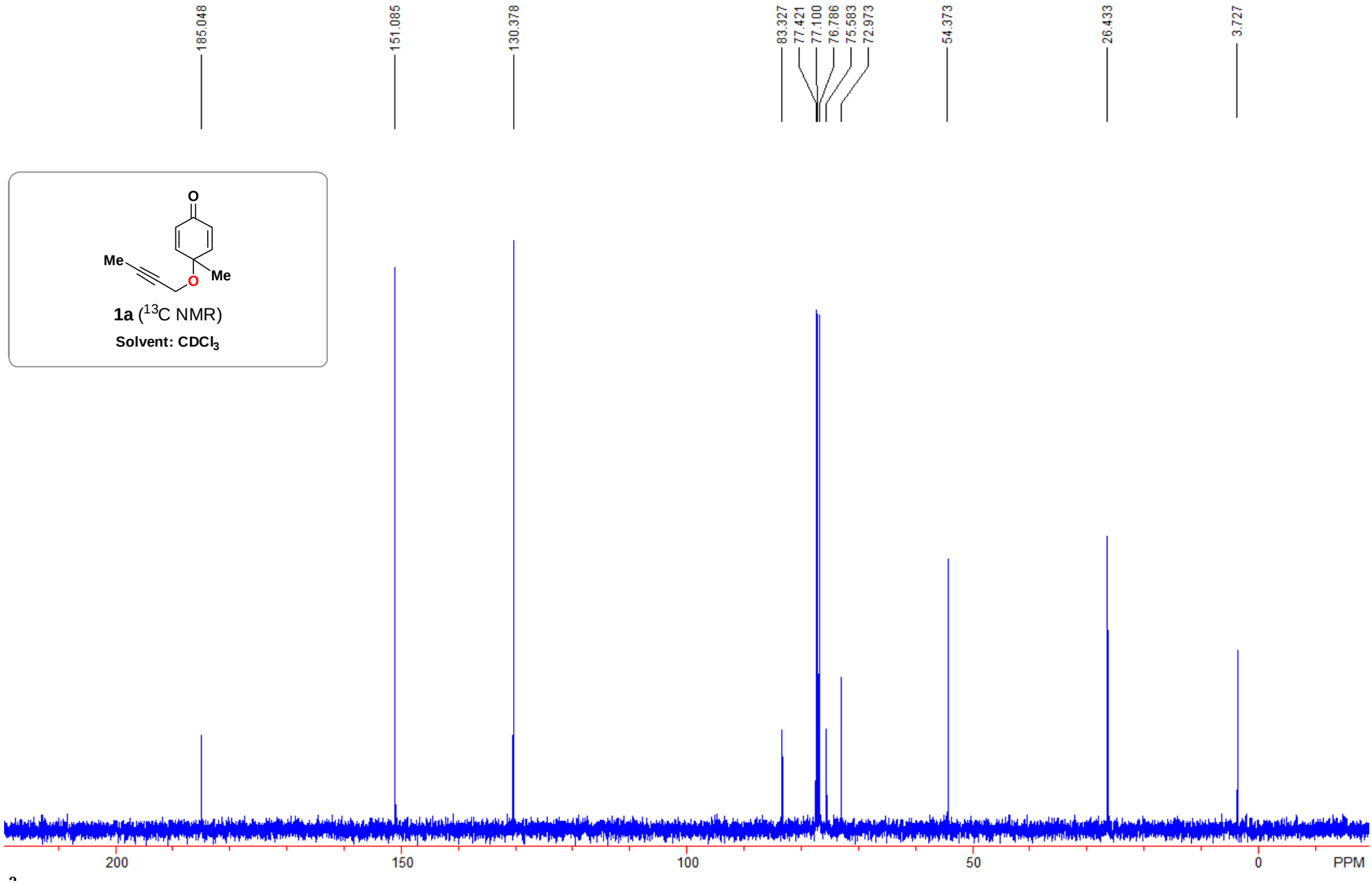


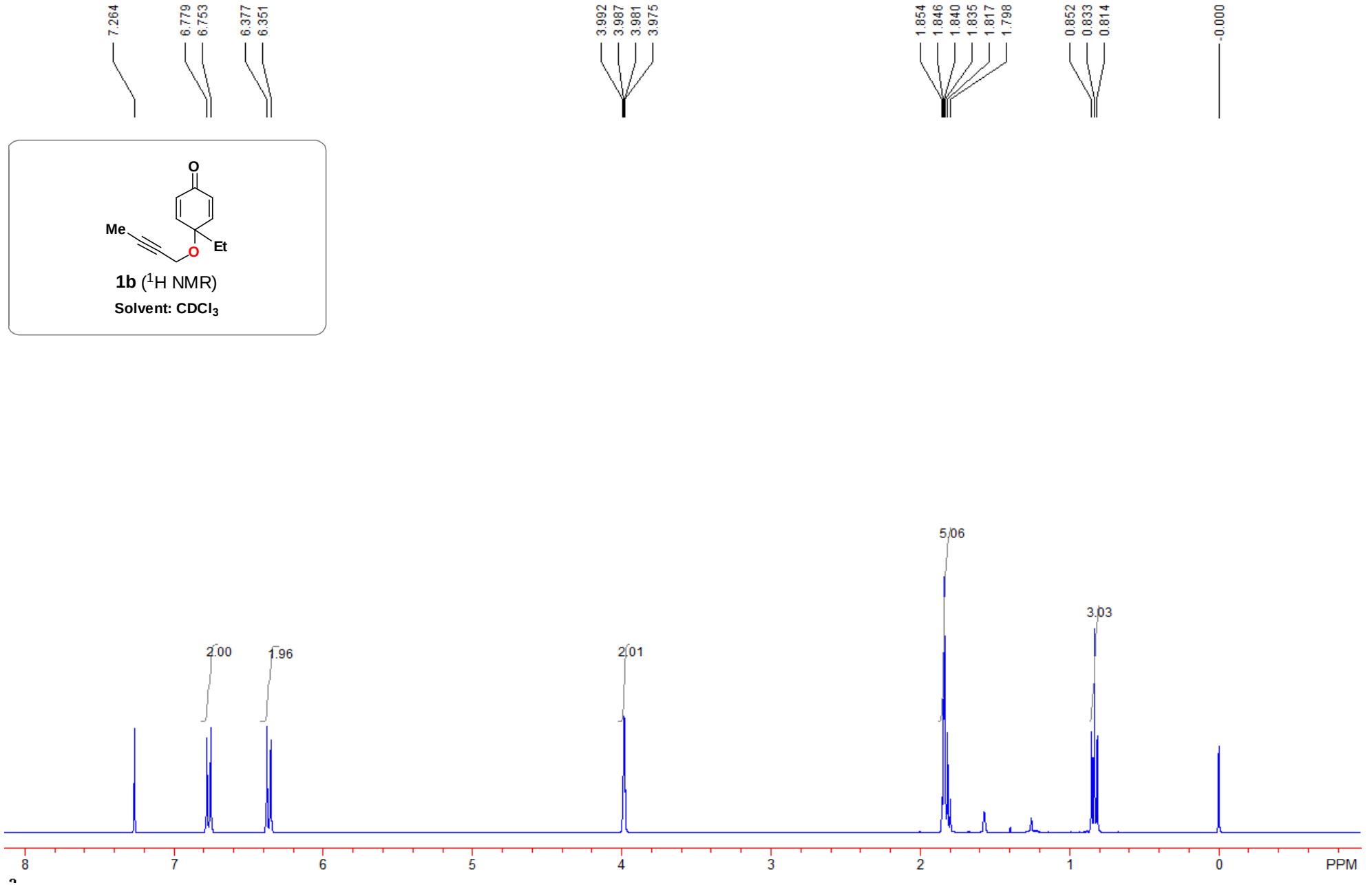
Results

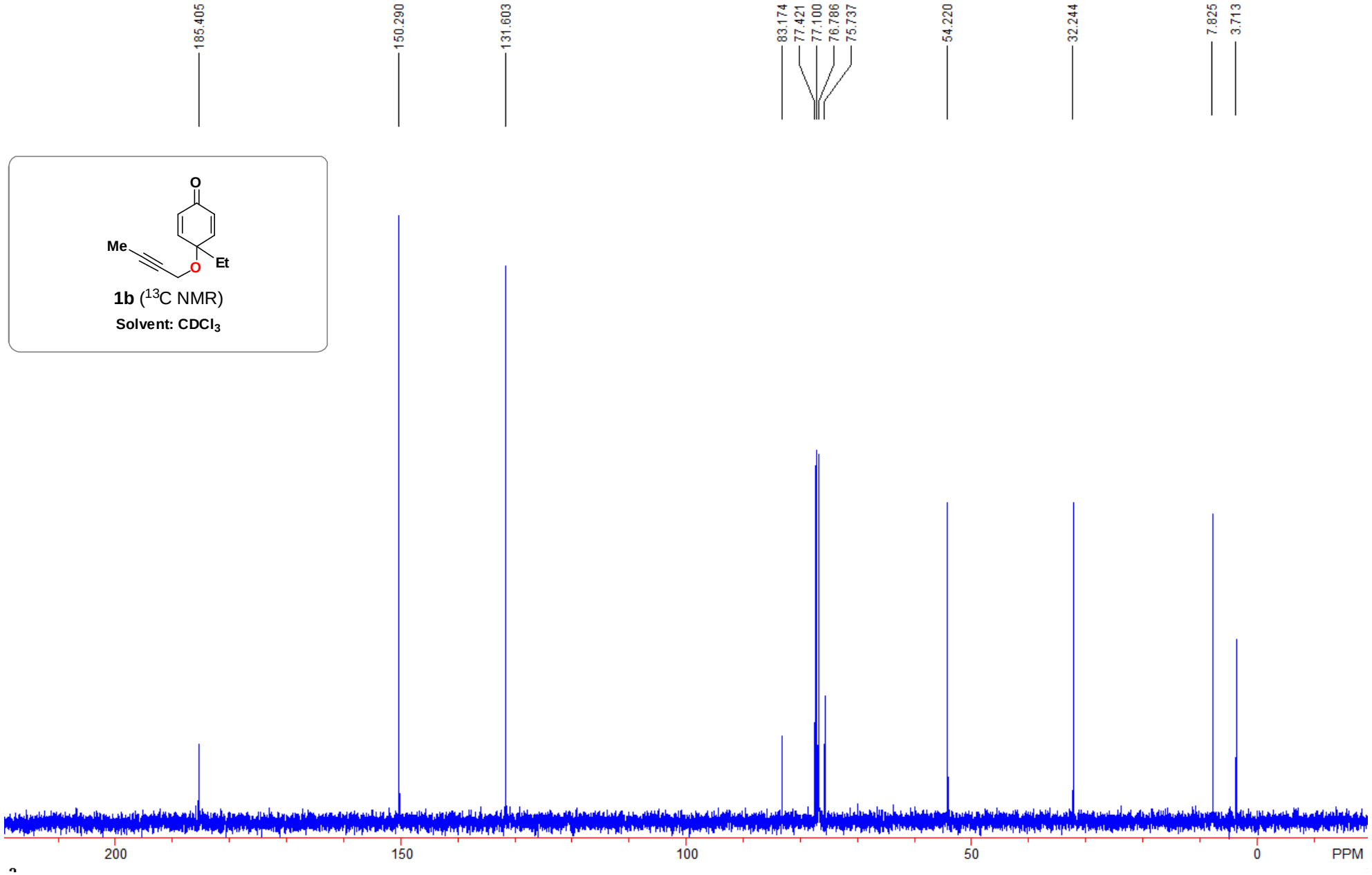
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.188	611045.313	9337060.000	100.0000
Total			611045.313	9337060.000	100.0000

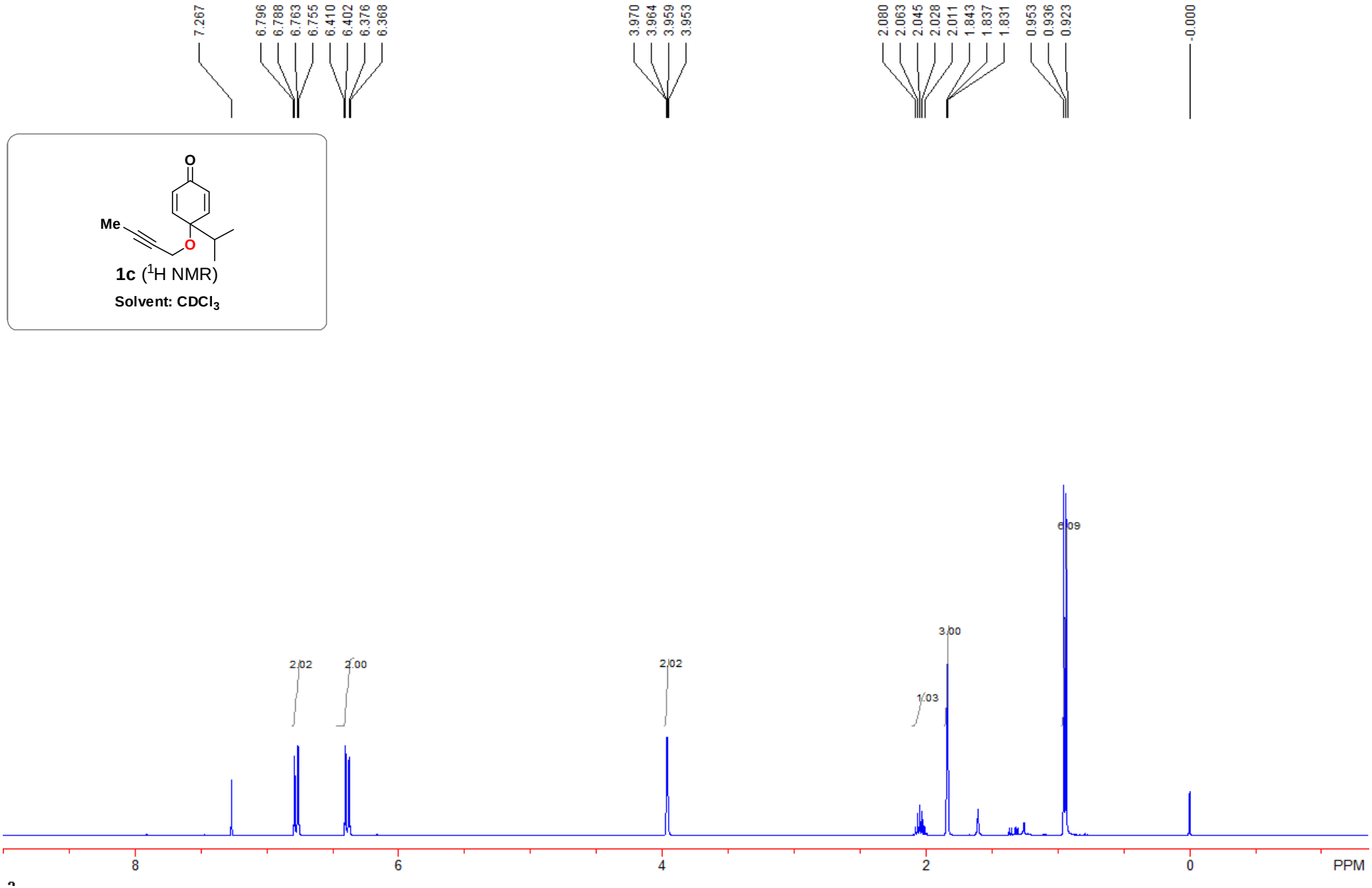
7. ^{1}H NMR, ^{13}C NMR, HSQC, HMBC, DEPT, H-H COSY & NOSEY COPIES

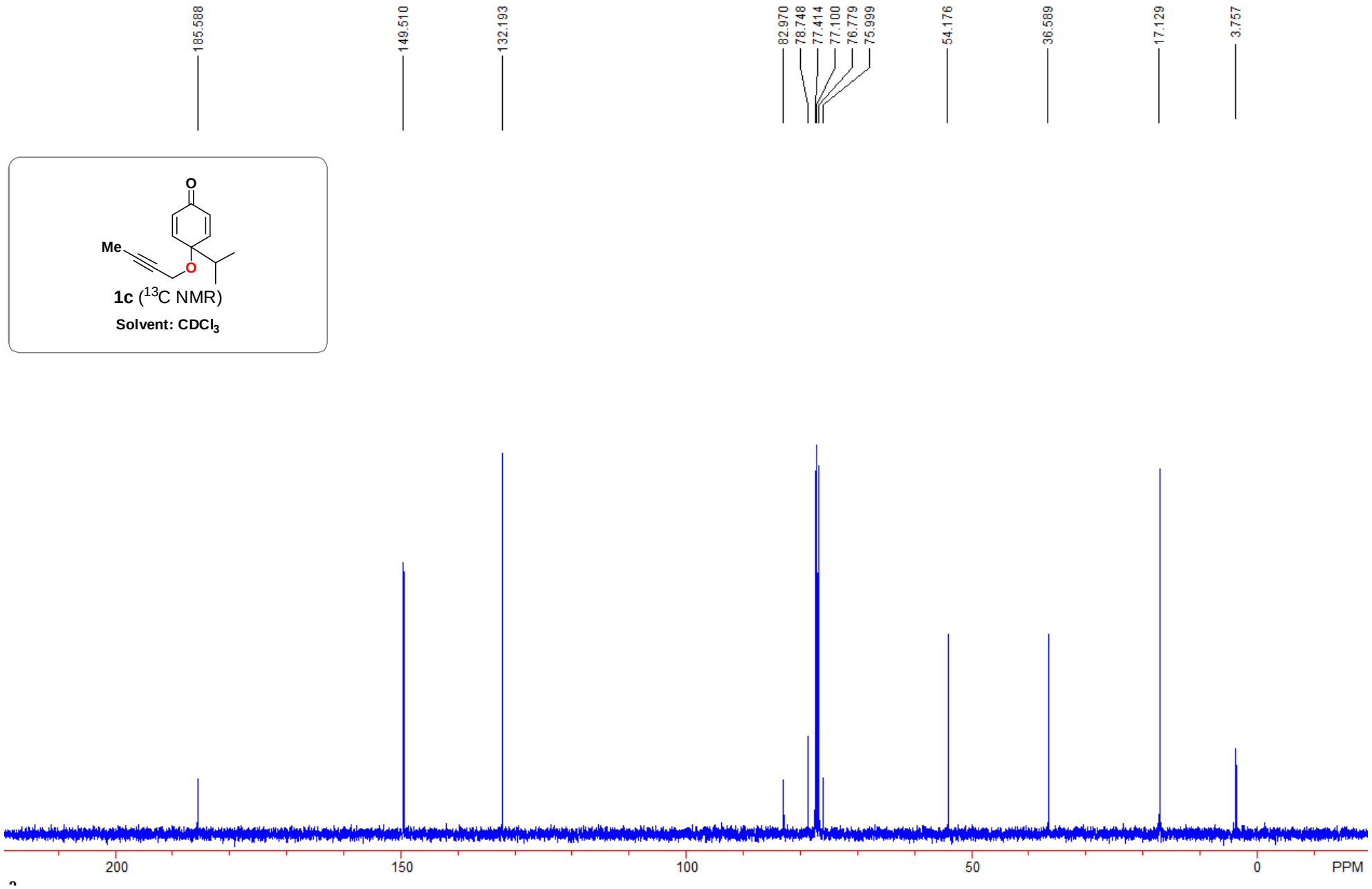

7.264
6.842
6.816
6.313
6.288
3.965
3.959
3.953
3.948
1.847
1.842
1.836
1.476
-0.000
O
Me
Me
O
1a (1H NMR)
Solvent: CDCl3
2.02
2.00
2.05
3.05
3.07
8
7
6
5
4
3
2
1
0
PPM

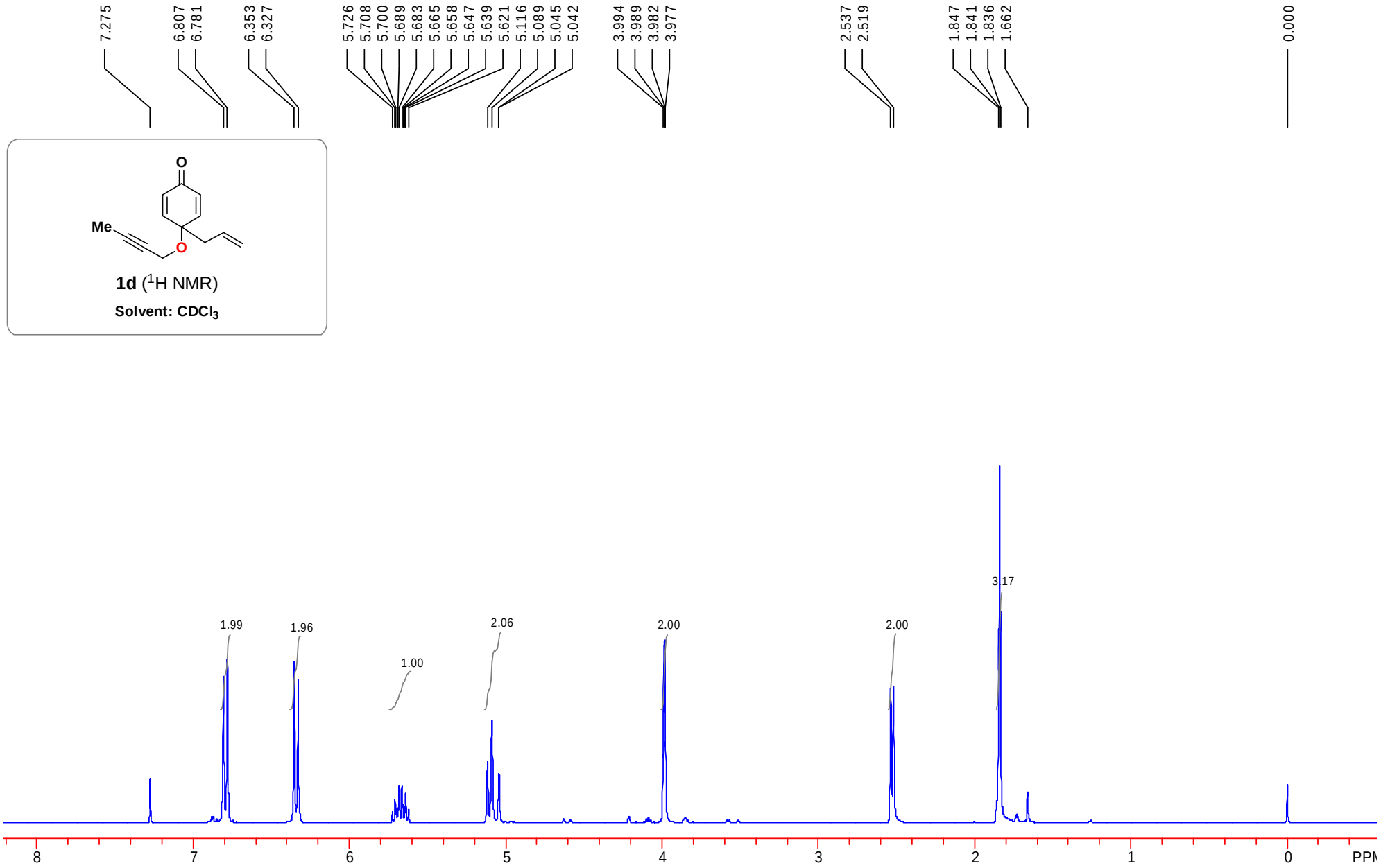

185.048
151.085
130.378
83.327
77.421
77.100
76.786
75.583
72.973
54.373
26.433
3.727
O
Me
O
Me
1a (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM

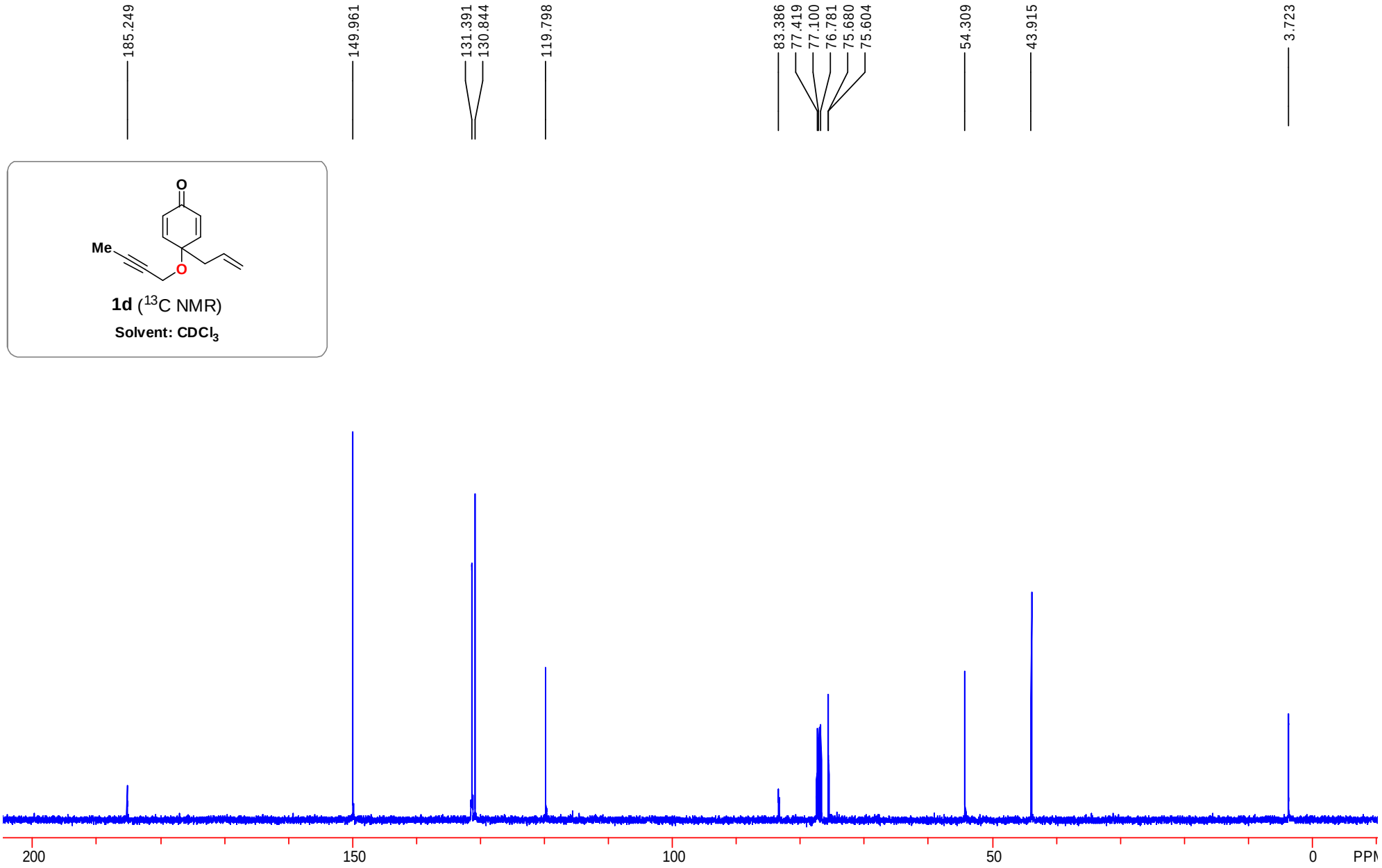

7.264
6.779
6.753
6.377
6.351
3.992
3.987
3.981
3.975
1.854
1.846
1.840
1.835
1.817
1.798
0.852
0.833
0.814
-0.000
O
Me
O
Et
1b (1H NMR)
Solvent: CDCl3
5.06
3.03
2.00
1.96
2.01
8
7
6
5
4
3
2
1
0
PPM

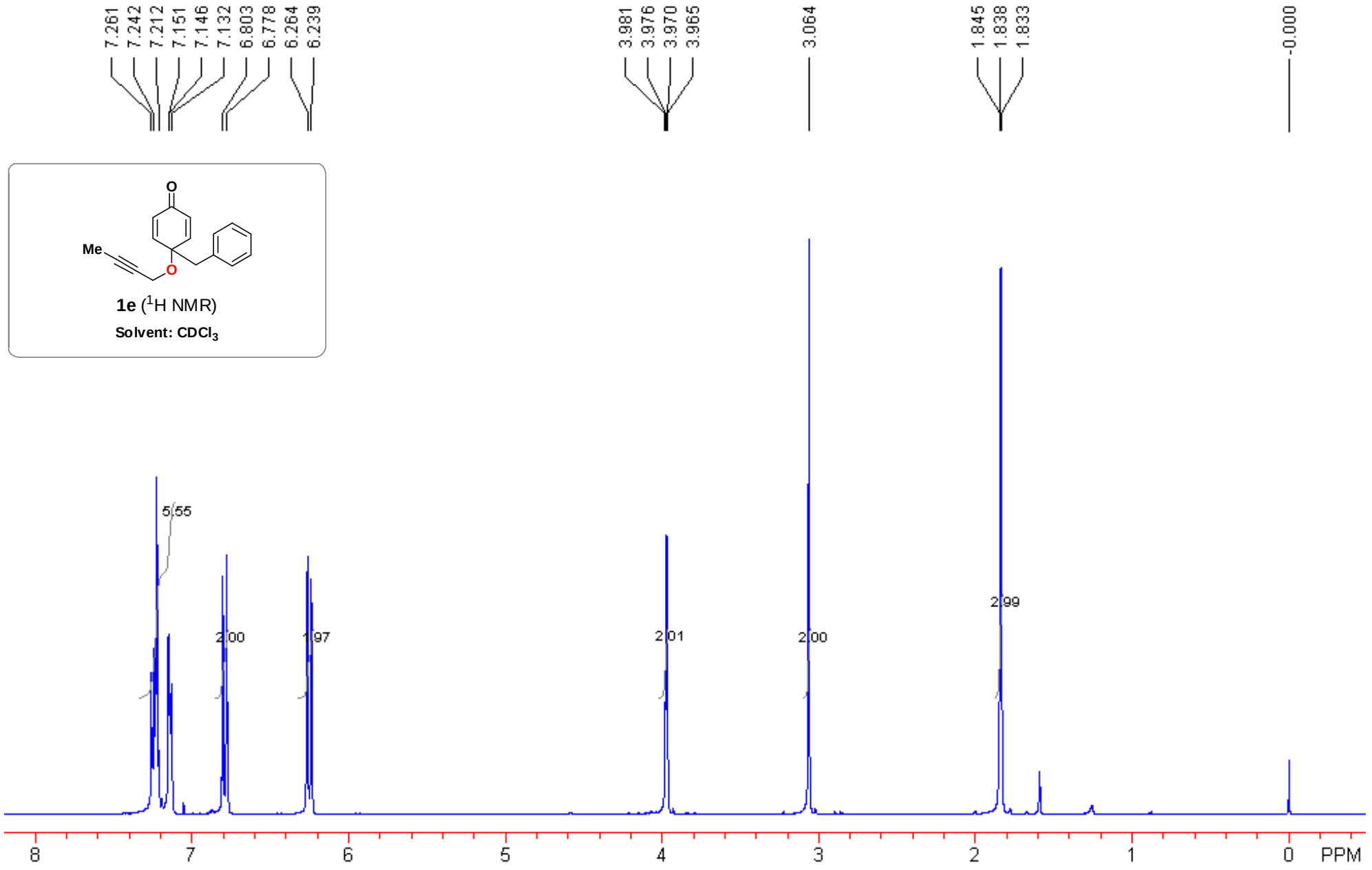

185.405
150.290
131.603
83.174
77.421
77.100
76.786
75.737
54.220
32.244
7.825
3.713
O
Me
O
Et
1b (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM

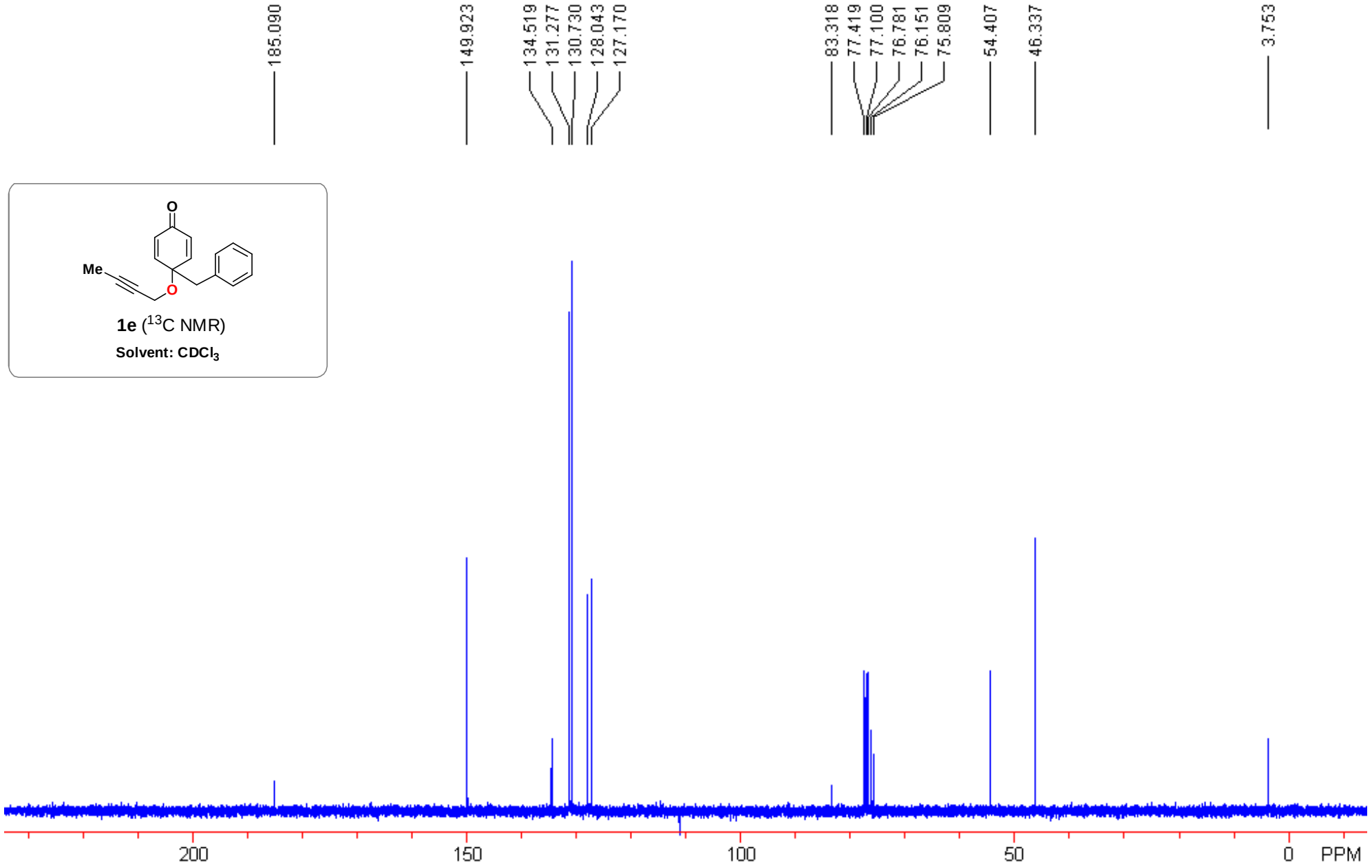

7.267
6.796
6.788
6.763
6.755
6.410
6.402
6.376
6.368
3.970
3.964
3.959
3.953
2.080
2.063
2.045
2.028
2.011
1.843
1.837
1.831
0.953
0.936
0.923
-0.000
O
Me
O
1c (1H NMR)
Solvent: CDCl3
2.02
2.00
2.02
1.03
3.00
6.09
8
6
4
2
0
PPM

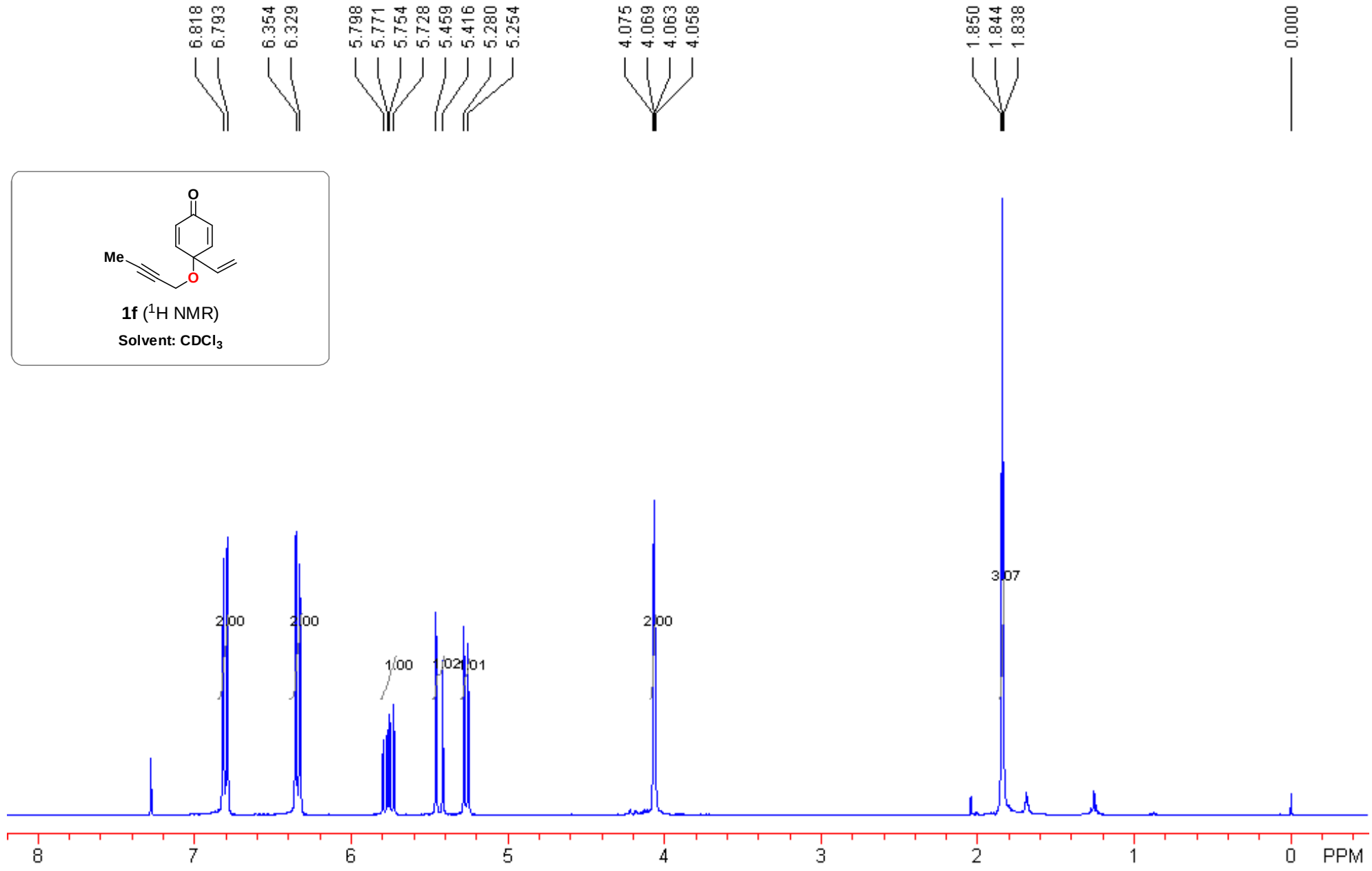

185.588
149.510
132.193
82.970
78.748
77.414
77.100
76.779
75.999
54.176
36.589
17.129
3.757
O
Me
O
1c (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM

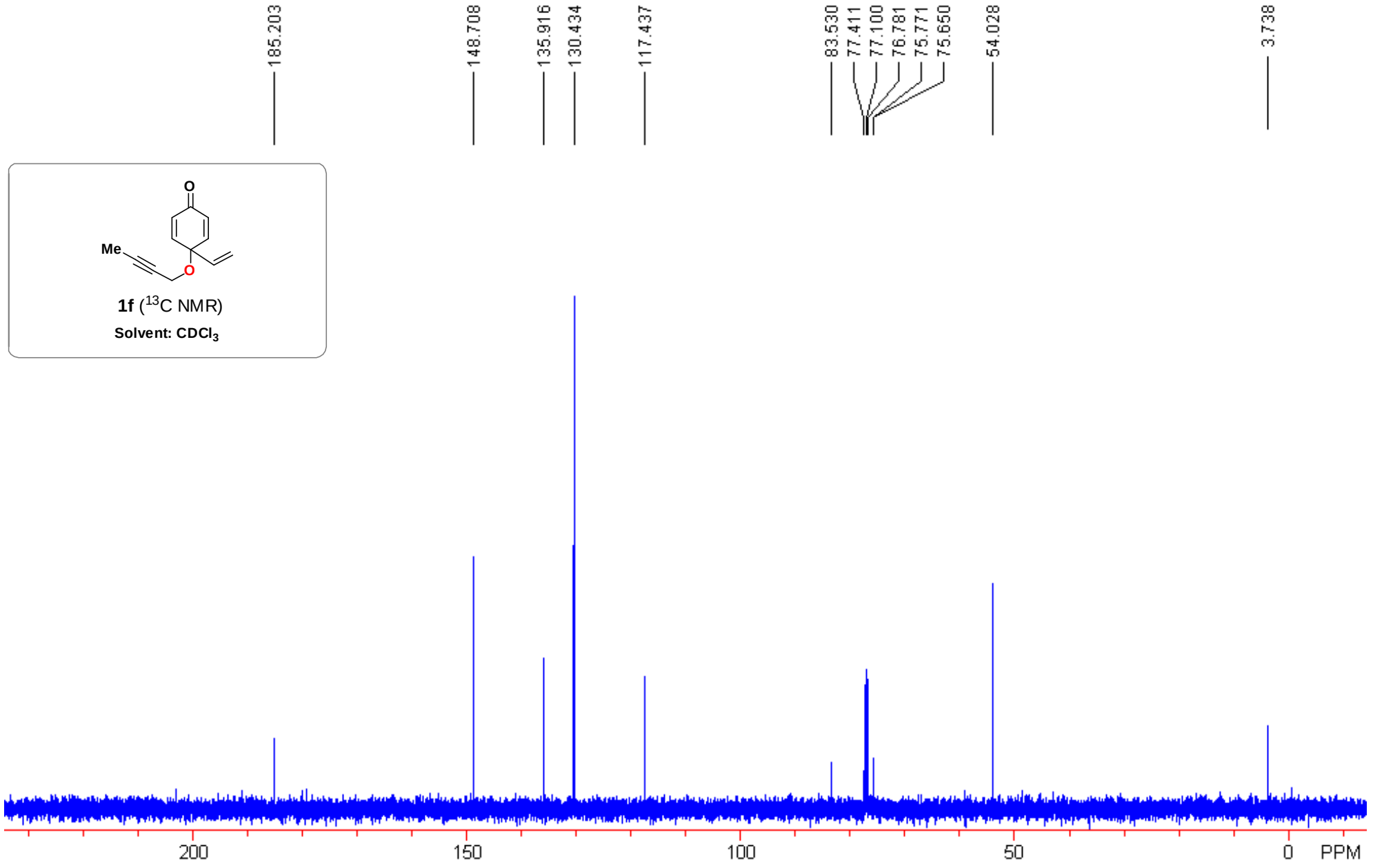

7.275
6.807
6.781
6.353
6.327
5.726
5.708
5.700
5.689
5.683
5.665
5.658
5.647
5.639
5.621
5.116
5.089
5.045
5.042
3.994
3.989
3.982
3.977
2.537
2.519
1.847
1.841
1.836
1.662
0.000
O
Me
O
1d (1H NMR)
Solvent: CDCl3
1.99
1.96
1.00
2.06
2.00
2.00
3.17
8
7
6
5
4
3
2
1
0
PPM

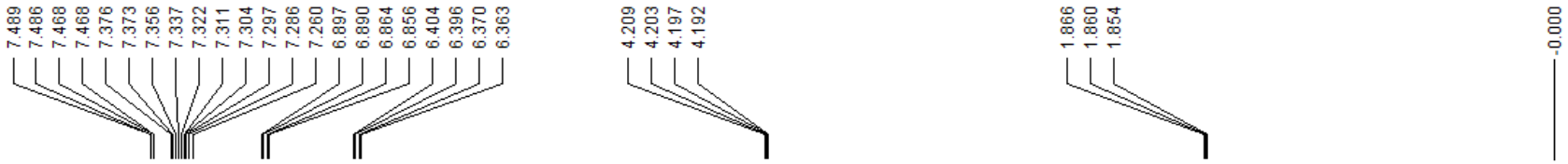

185.249
149.961
131.391
130.844
119.798
83.386
77.419
77.100
76.781
75.680
75.604
54.309
43.915
3.723
O
Me
O
1d (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM

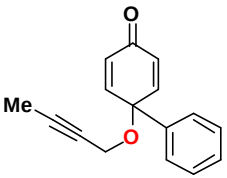

7.261
7.242
7.212
7.151
7.146
7.132
6.803
6.778
6.264
6.239
3.981
3.976
3.970
3.965
3.064
1.845
1.838
1.833
-0.000
O
Me
O
1e (1H NMR)
Solvent: CDCl3
5.55
2.00
1.97
2.01
2.00
2.99
8
7
6
5
4
3
2
1
0
PPM


185.090
149.923
134.519
131.277
130.730
128.043
127.170
83.318
77.419
77.100
76.781
76.151
75.809
54.407
46.337
3.753
O
Me
O
1e (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM


6.818
6.793
6.354
6.329
5.798
5.771
5.754
5.728
5.459
5.416
5.280
5.254
4.075
4.069
4.063
4.058
1.850
1.844
1.838
0.000
O
Me
O
1f (1H NMR)
Solvent: CDCl3
2.00
2.00
1.00
1.02
1.01
2.00
3.07
8
7
6
5
4
3
2
1
0
PPM

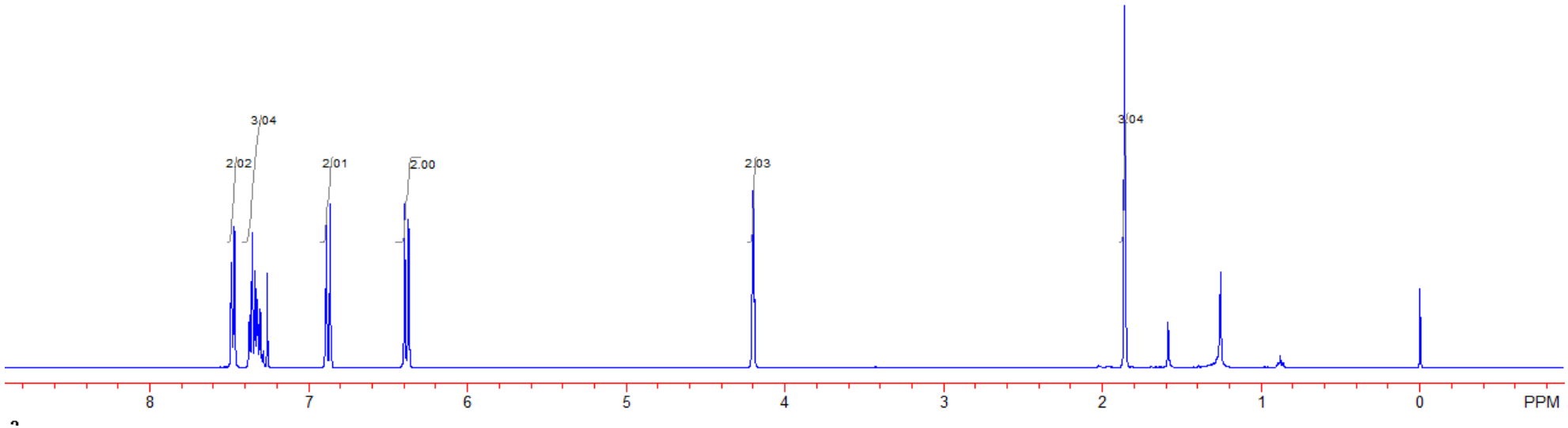

185.203
148.708
135.916
130.434
117.437
83.530
77.411
77.100
76.781
75.771
75.650
54.028
3.738
O
Me
O
1f (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM

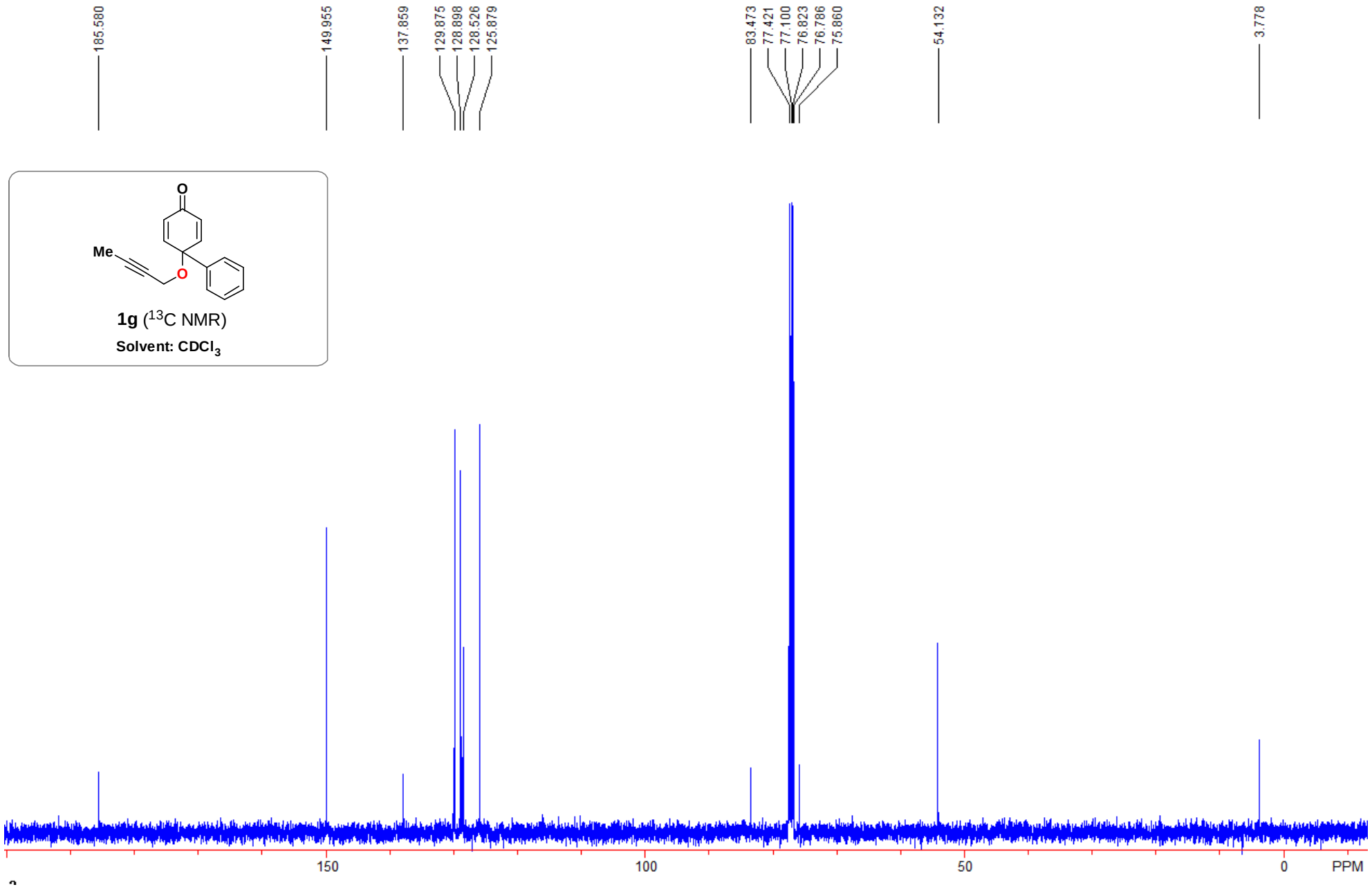


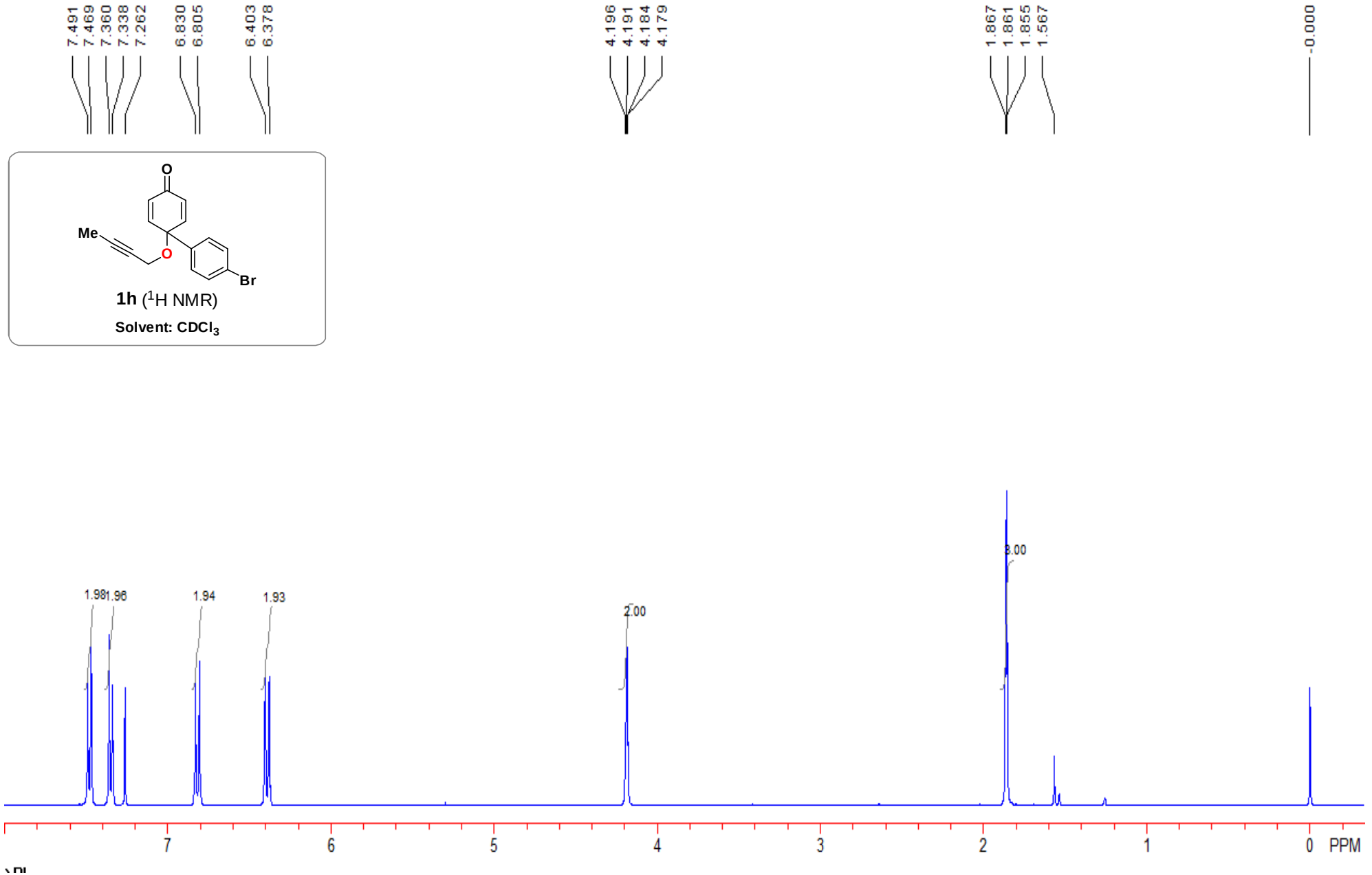


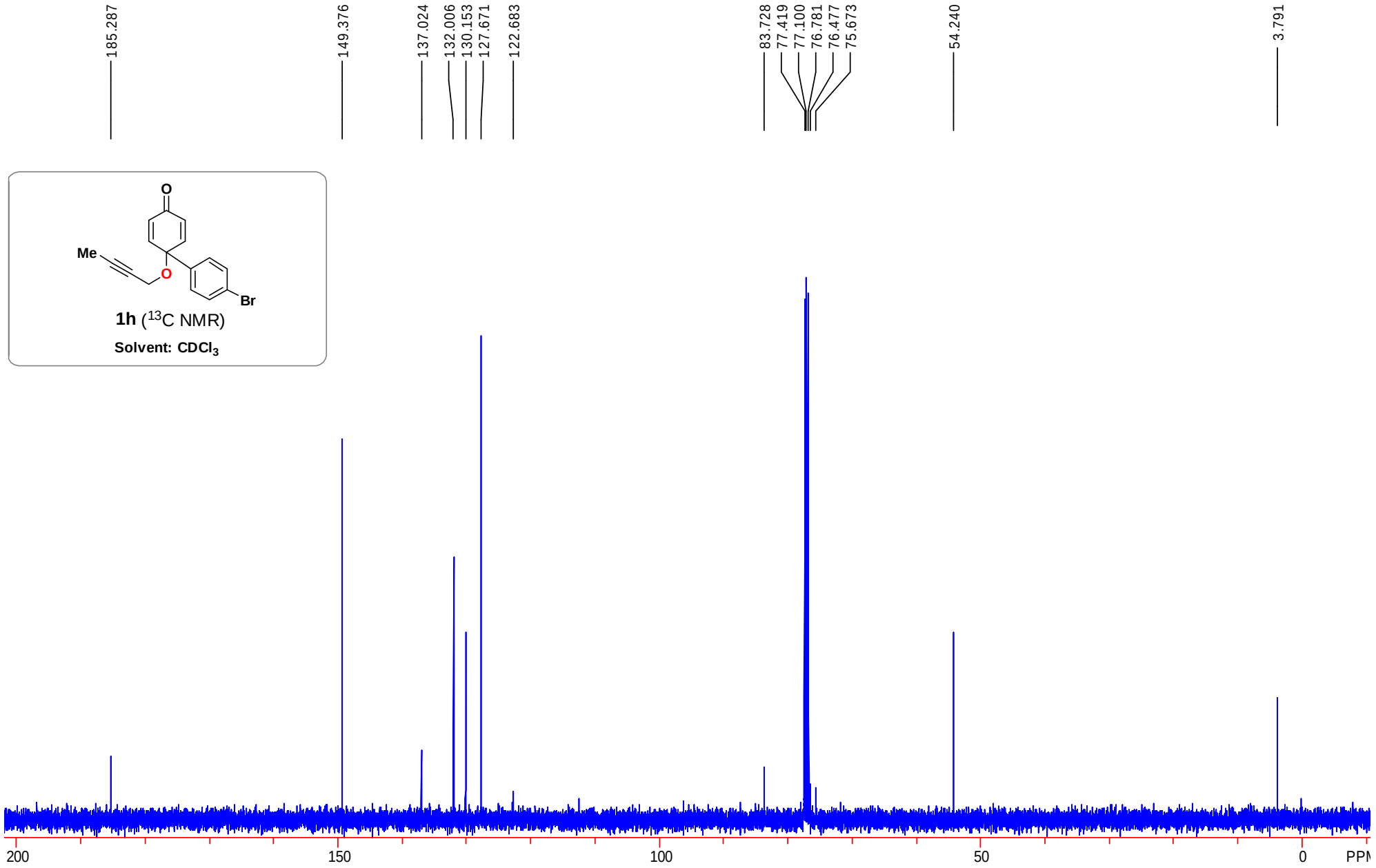
1g (^{1}H NMR)

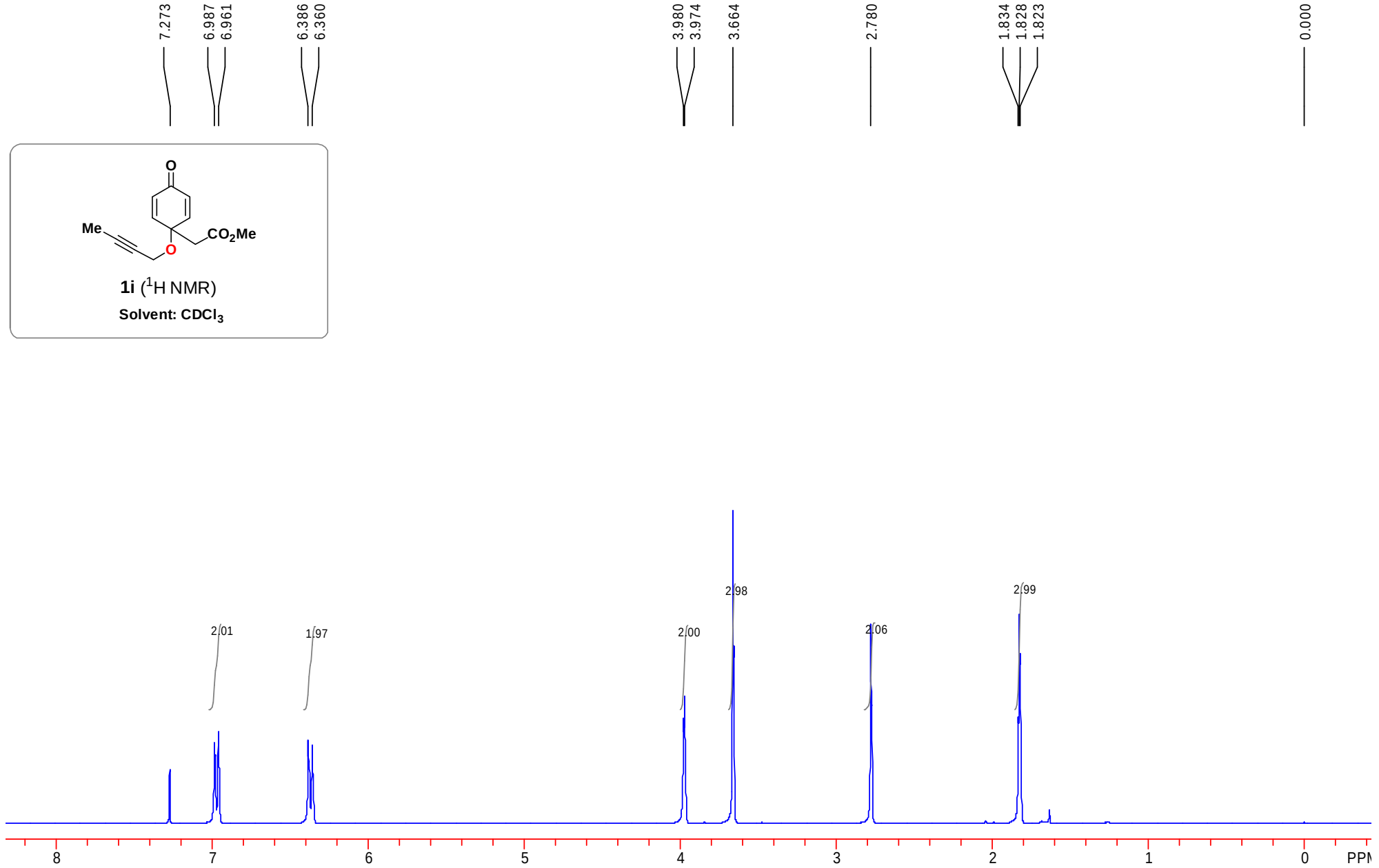
Solvent: $CDCl_3$

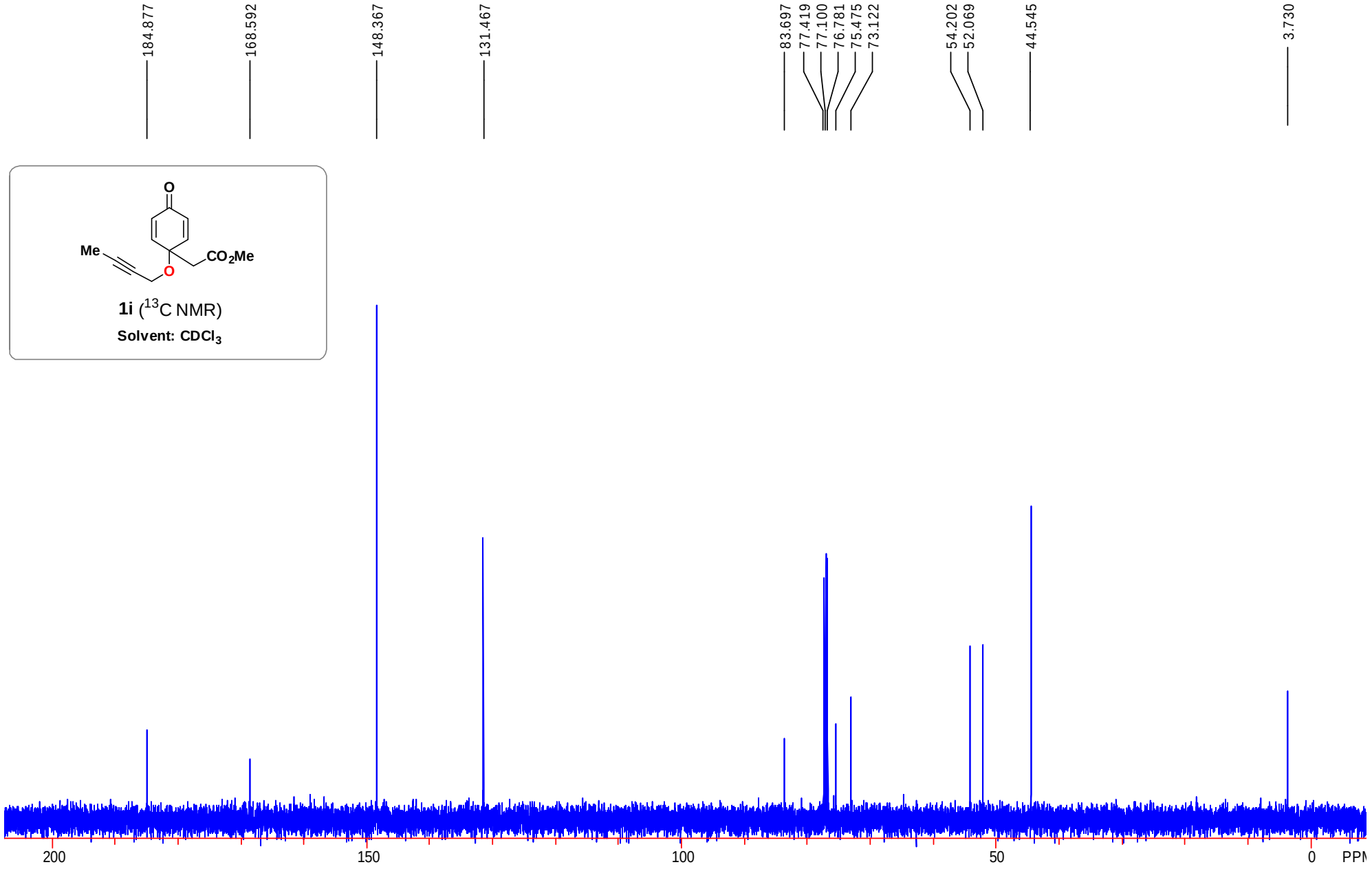



185.580
149.955
137.859
129.875
128.898
128.526
125.879
83.473
77.421
77.100
76.823
76.786
75.860
54.132
3.778
O
Me
O
1g (13C NMR)
Solvent: CDCl3
150
100
50
0
PPM


7.491
7.469
7.360
7.338
7.262
6.830
6.805
6.403
6.378
4.196
4.191
4.184
4.179
1.867
1.861
1.855
1.567
0.000
O
Me
O
Br
1h (1H NMR)
Solvent: CDCl3
1.98
1.96
1.94
1.93
2.00
3.00
7
6
5
4
3
2
1
0
PPM


185.287
149.376
137.024
132.006
130.153
127.671
122.683
83.728
77.419
77.100
76.781
76.477
75.673
54.240
3.791
O
Me
O
Br
1h (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM


7.273
6.987
6.961
6.386
6.360
3.980
3.974
3.664
2.780
1.834
1.828
1.823
0.000
O
Me
CO2Me
O
1i (1H NMR)
Solvent: CDCl3
2.01
1.97
2.00
2.98
2.06
2.99
8
7
6
5
4
3
2
1
0
PPM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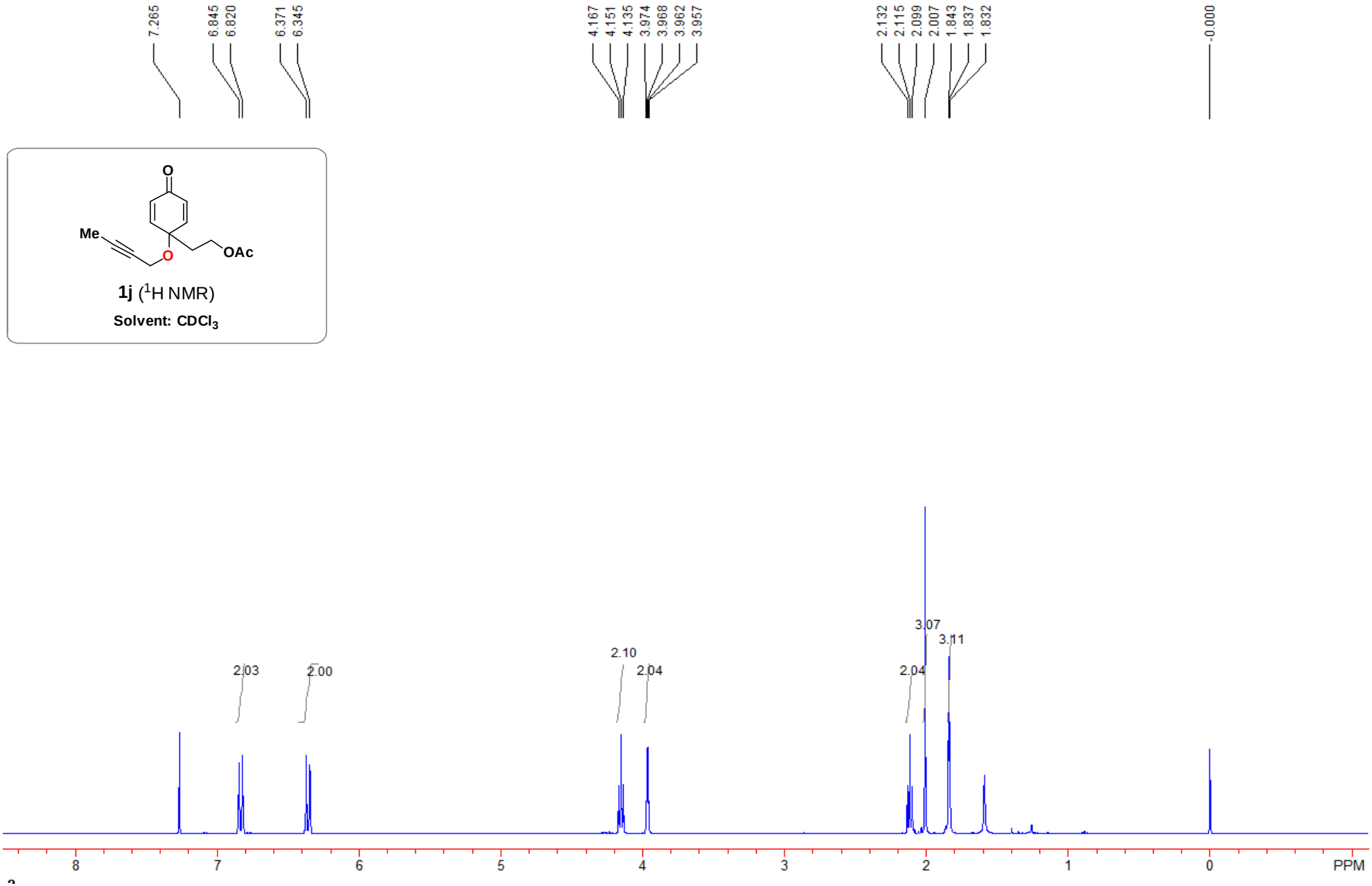
168.592
148.367
131.467
83.697
77.419
77.100
76.781
75.475
73.122
54.202
52.069
44.545
3.730
O
Me
CO2Me
O
1i (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM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6.845
6.820
6.371
6.345
4.167
4.151
4.135
3.974
3.968
3.962
3.957
2.132
2.115
2.099
2.007
1.843
1.837
1.832
-0.000
O
Me
O
OAc
1j (1H NMR)
Solvent: CDCl3
2.03
2.00
2.10
2.04
2.04
3.07
3.11
8
7
6
5
4
3
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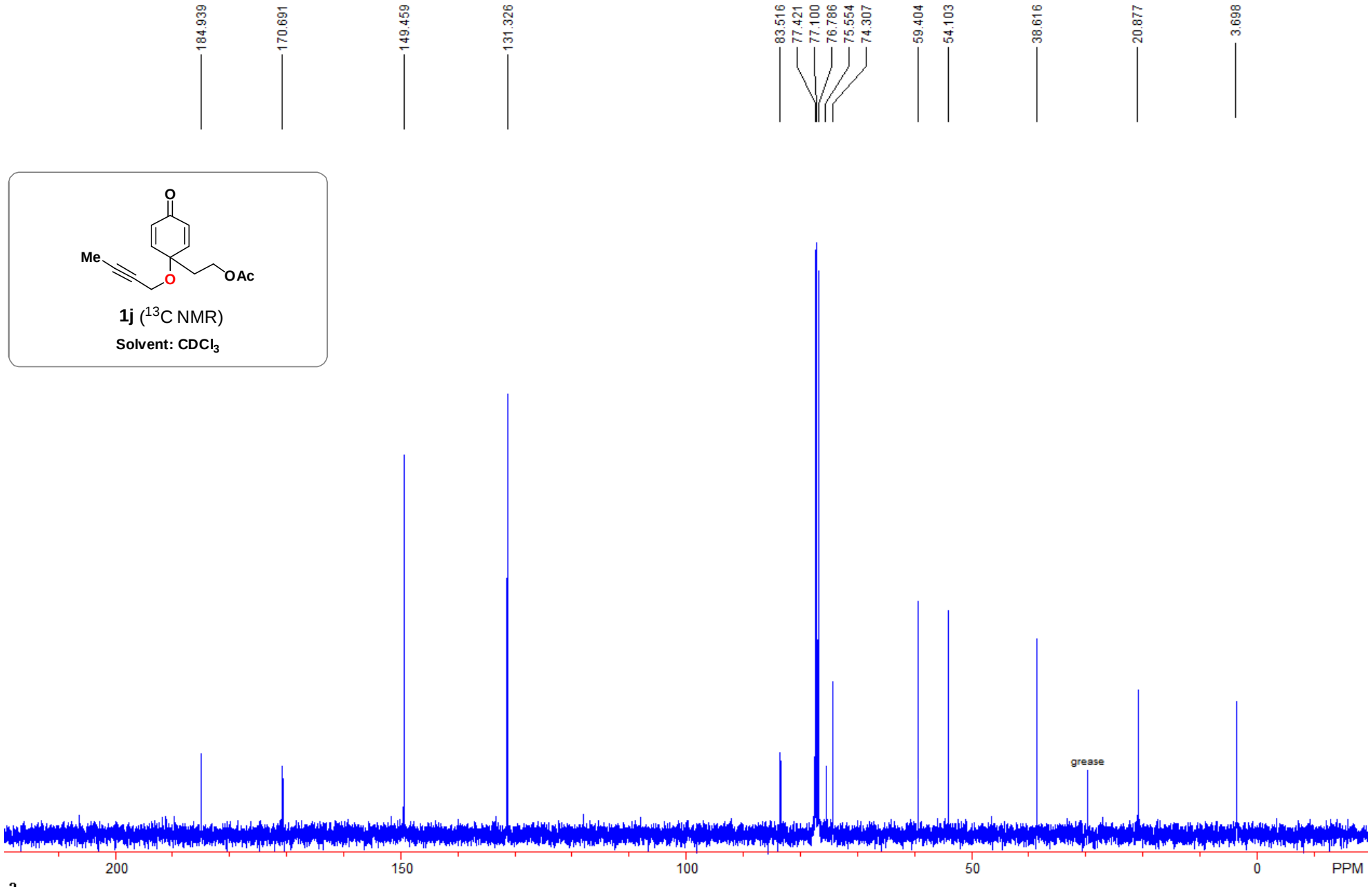
PPM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149.459
131.326
83.516
77.421
77.100
76.786
75.554
74.307
59.404
54.103
38.616
20.877
3.698
O
Me
O
OAc
1j (13C NMR)
Solvent: CDCl3
grease
200
150
100
50
0
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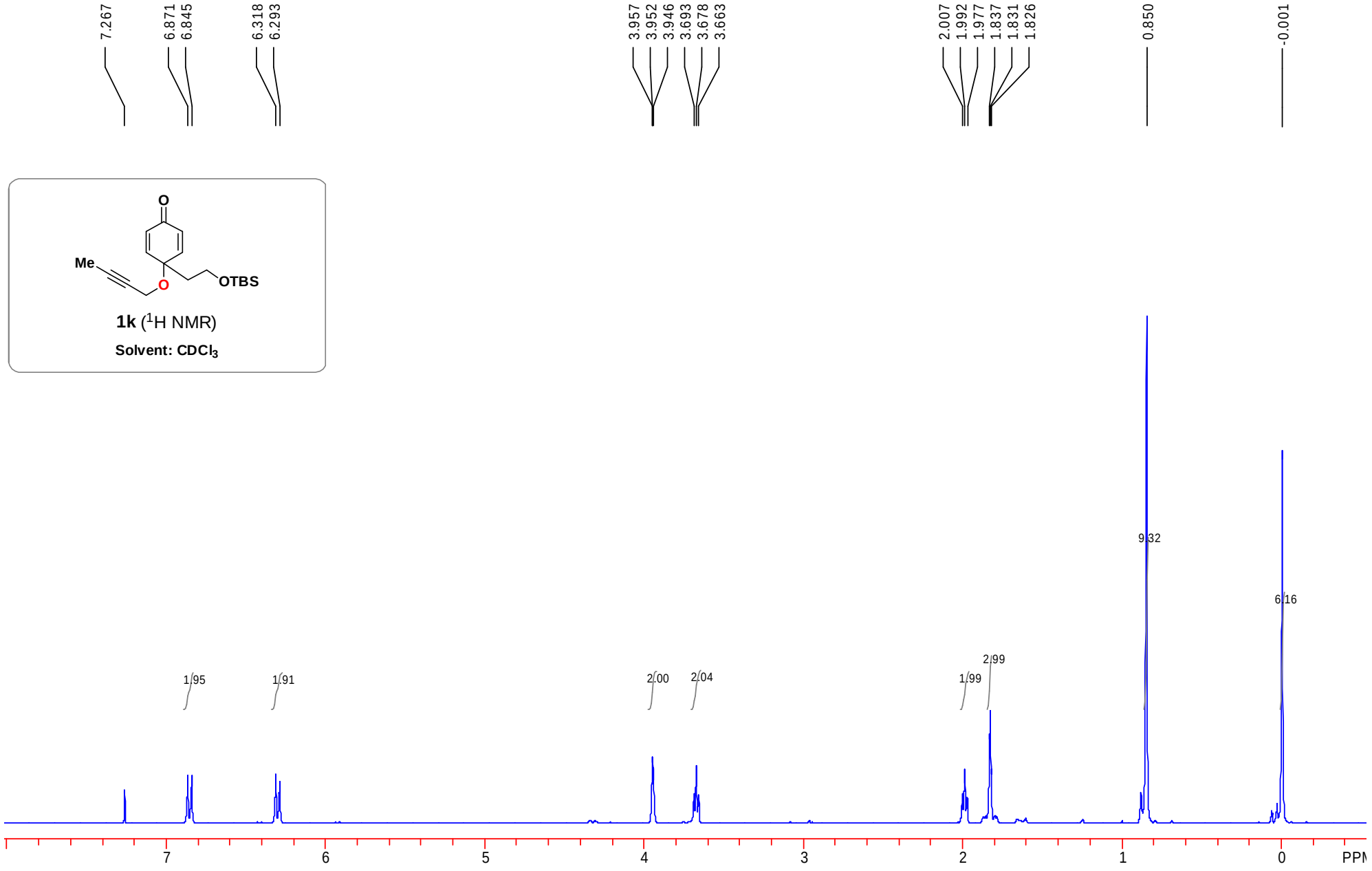
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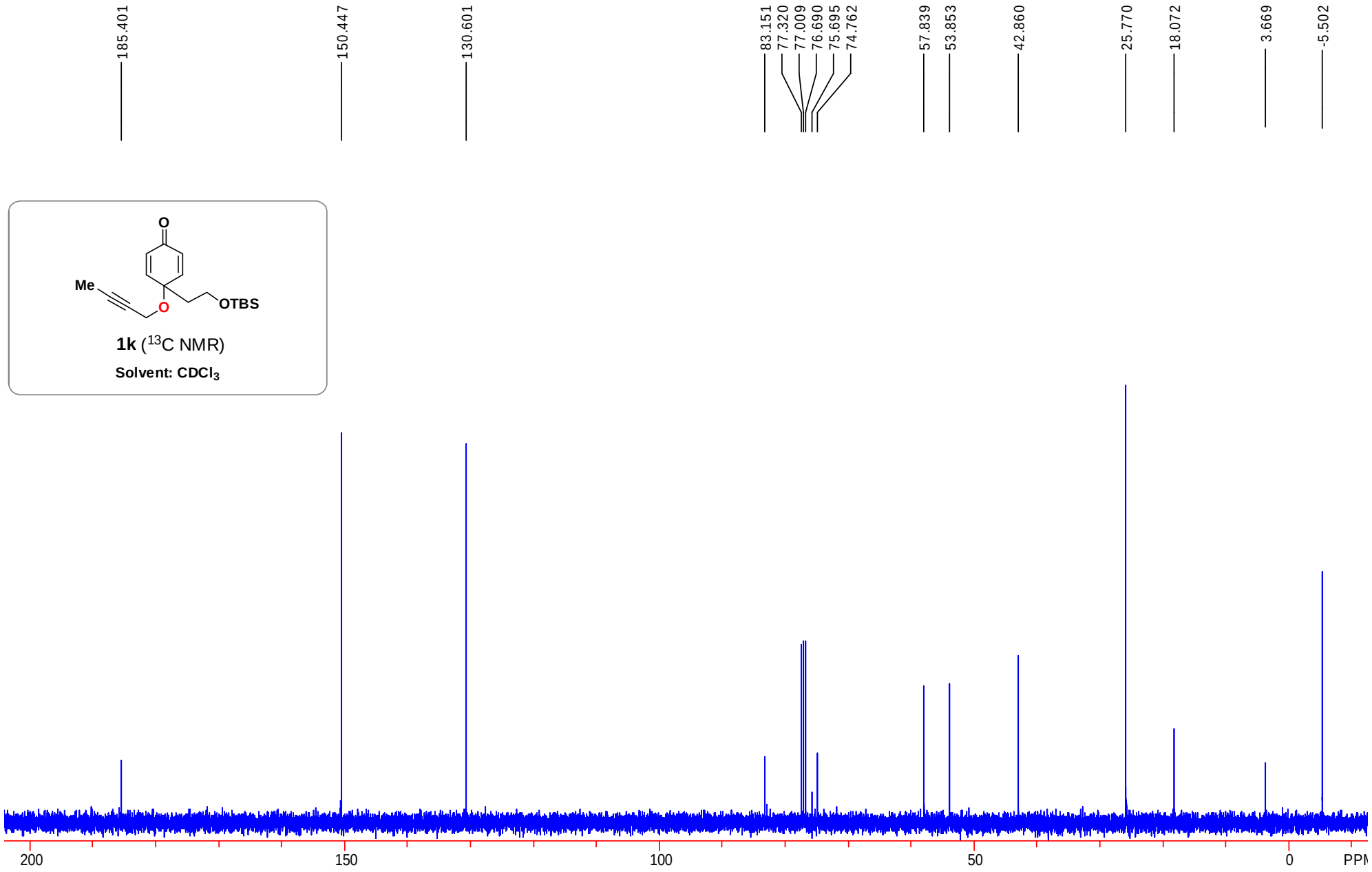
6.871
6.845
6.318
6.293
3.957
3.952
3.946
3.693
3.678
3.663
2.007
1.992
1.977
1.837
1.831
1.826
0.850
-0.001
O
Me
O
OTBS
1k (1H NMR)
Solvent: CDCl3
1.95
1.91
2.00
2.04
1.99
2.99
9.32
6.16
7
6
5
4
3
2
1
0
PPM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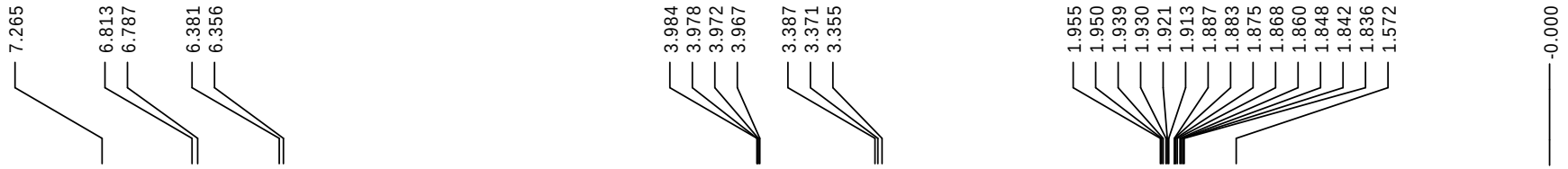
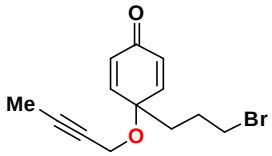
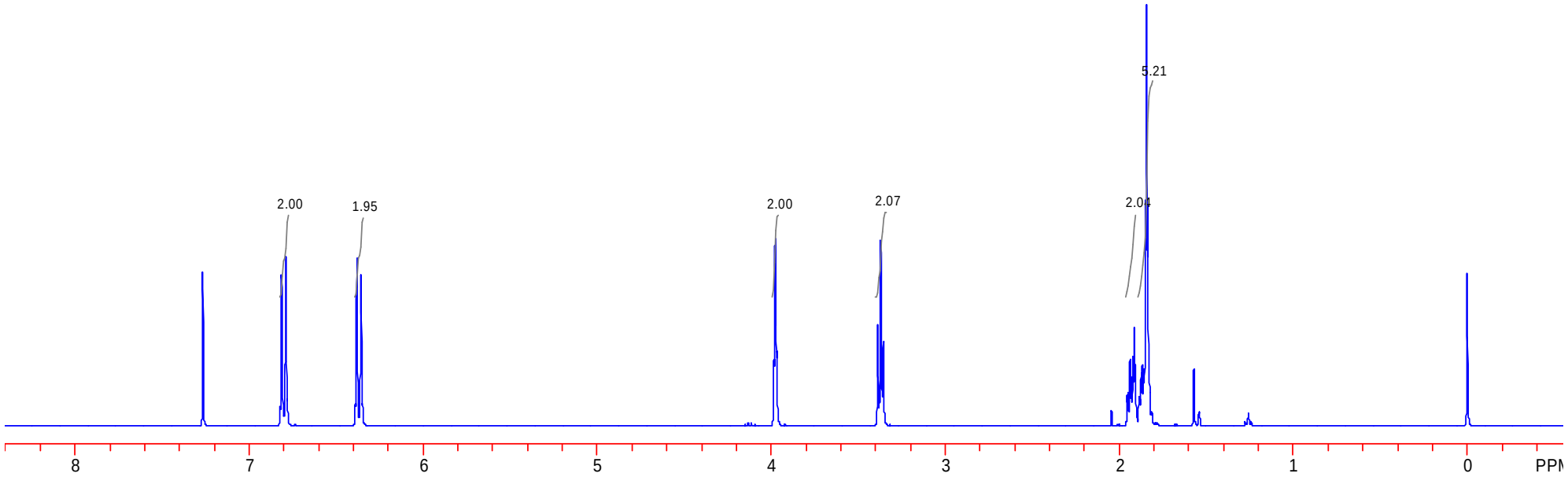
130.601
83.151
77.320
77.009
76.690
75.695
74.762
57.839
53.853
42.860
25.770
18.072
3.669
-5.502
O
Me
O
OTBS
1k (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM

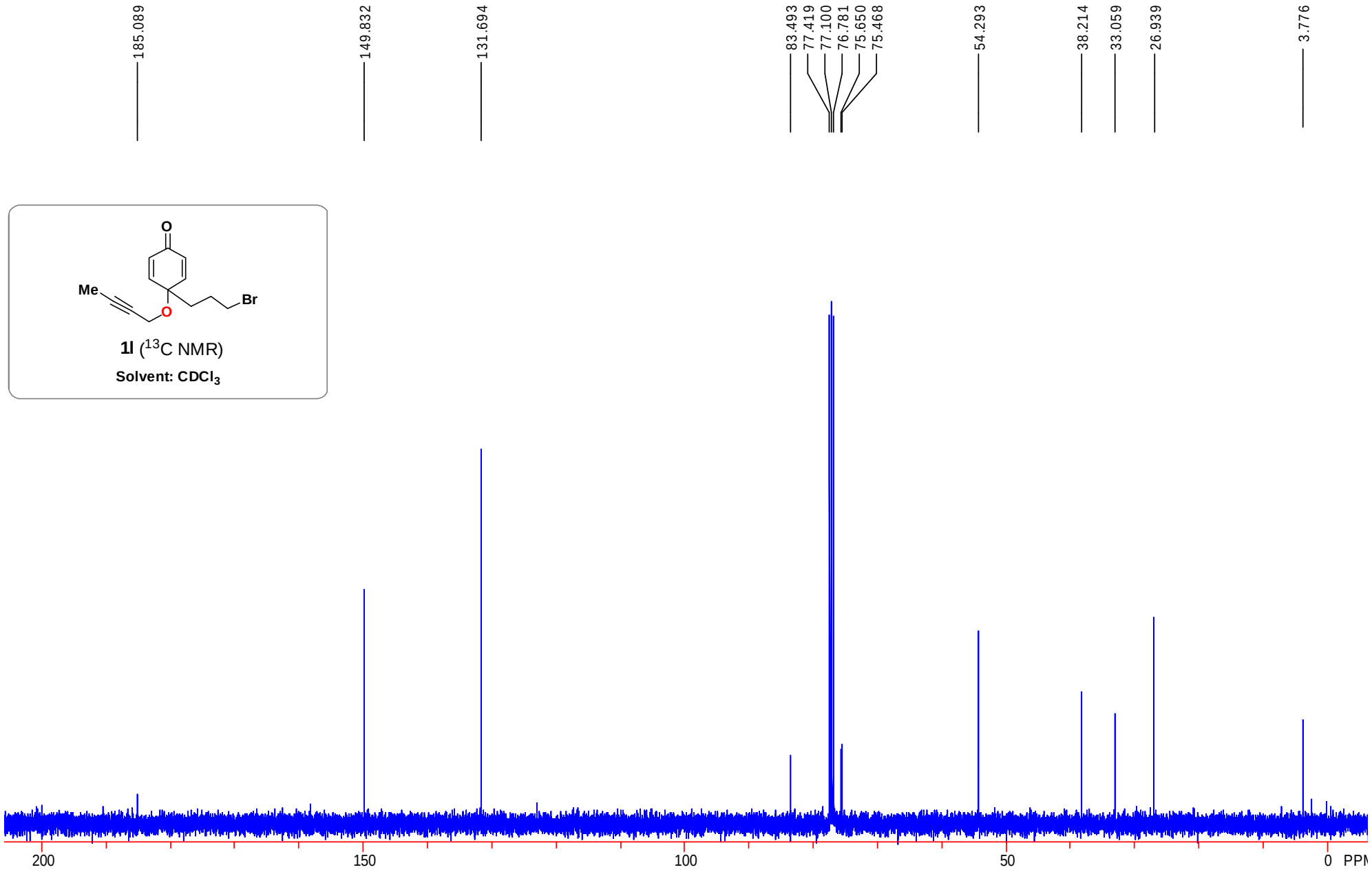




1l (^{1}H NMR)

Solvent: $CDCl_3$

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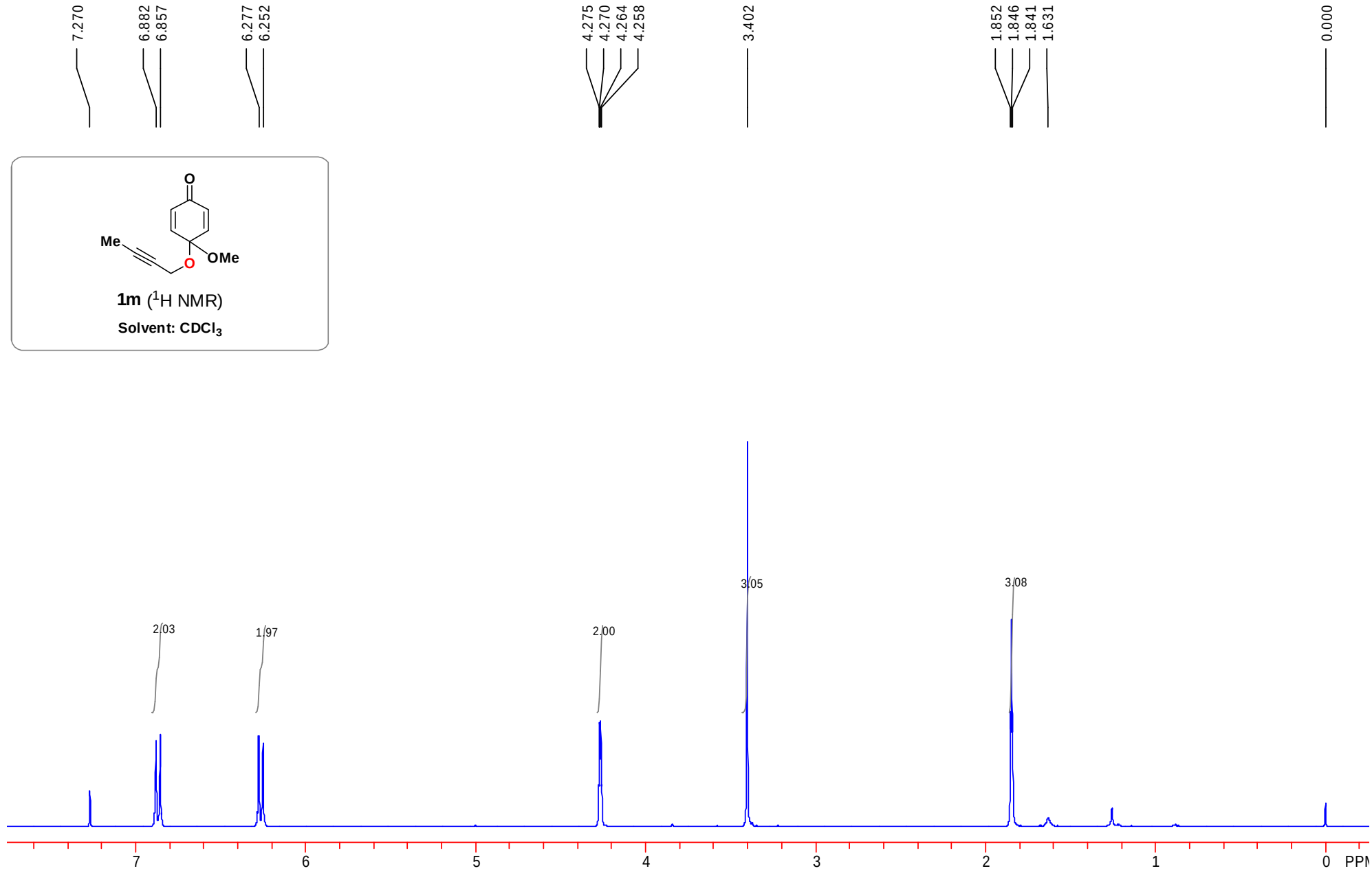
149.832
131.694
83.493
77.419
77.100
76.781
75.650
75.468
54.293
38.214
33.059
26.939
3.776
O
Me
O
Br
1l (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM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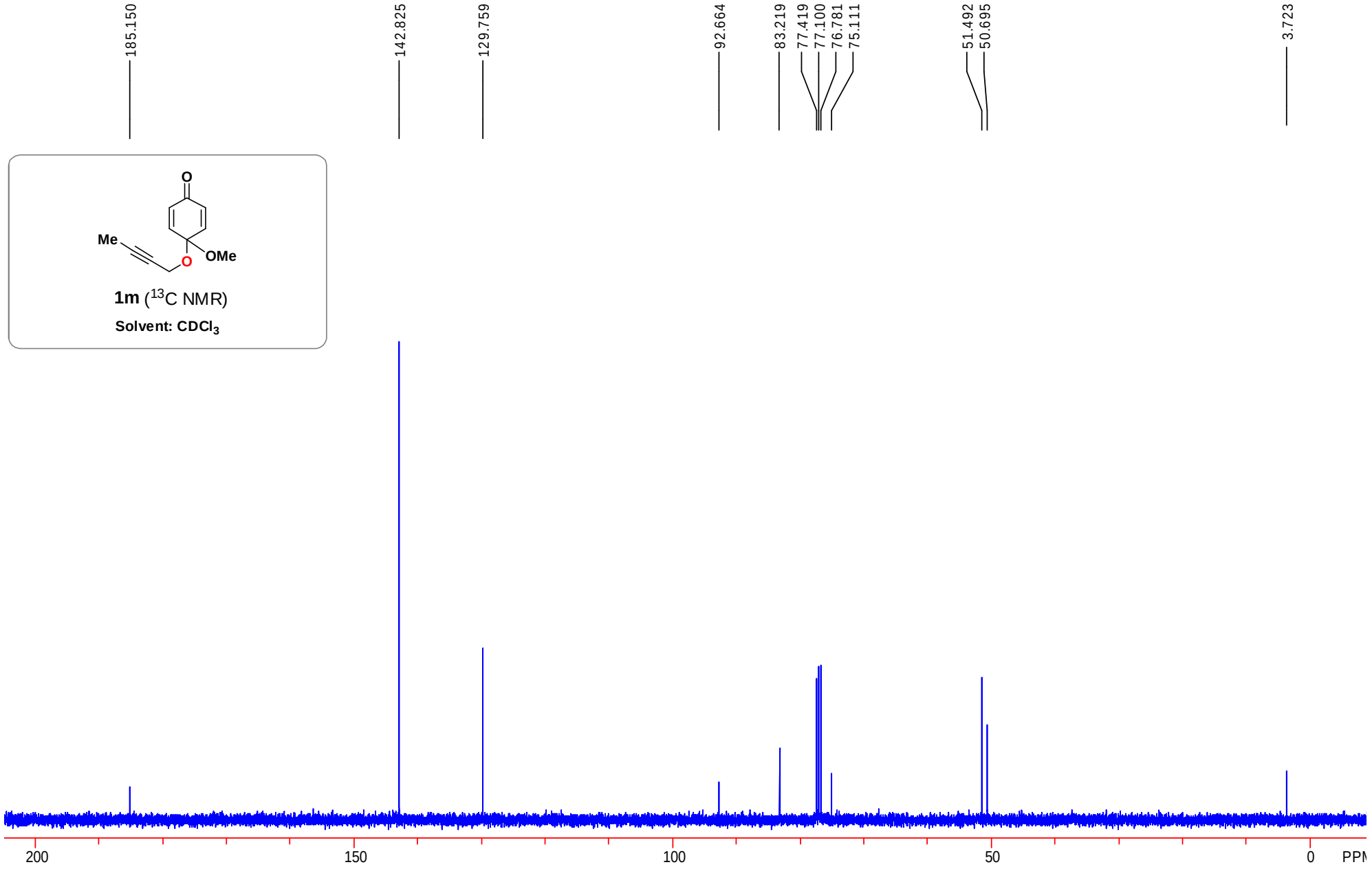
6.882
6.857
6.277
6.252
4.275
4.270
4.264
4.258
3.402
1.852
1.846
1.841
1.631
0.000
O
Me
O
OMe
1m (1H NMR)
Solvent: CDCl3
2.03
1.97
2.00
3.05
3.08
7
6
5
4
3
2
1
0
PPM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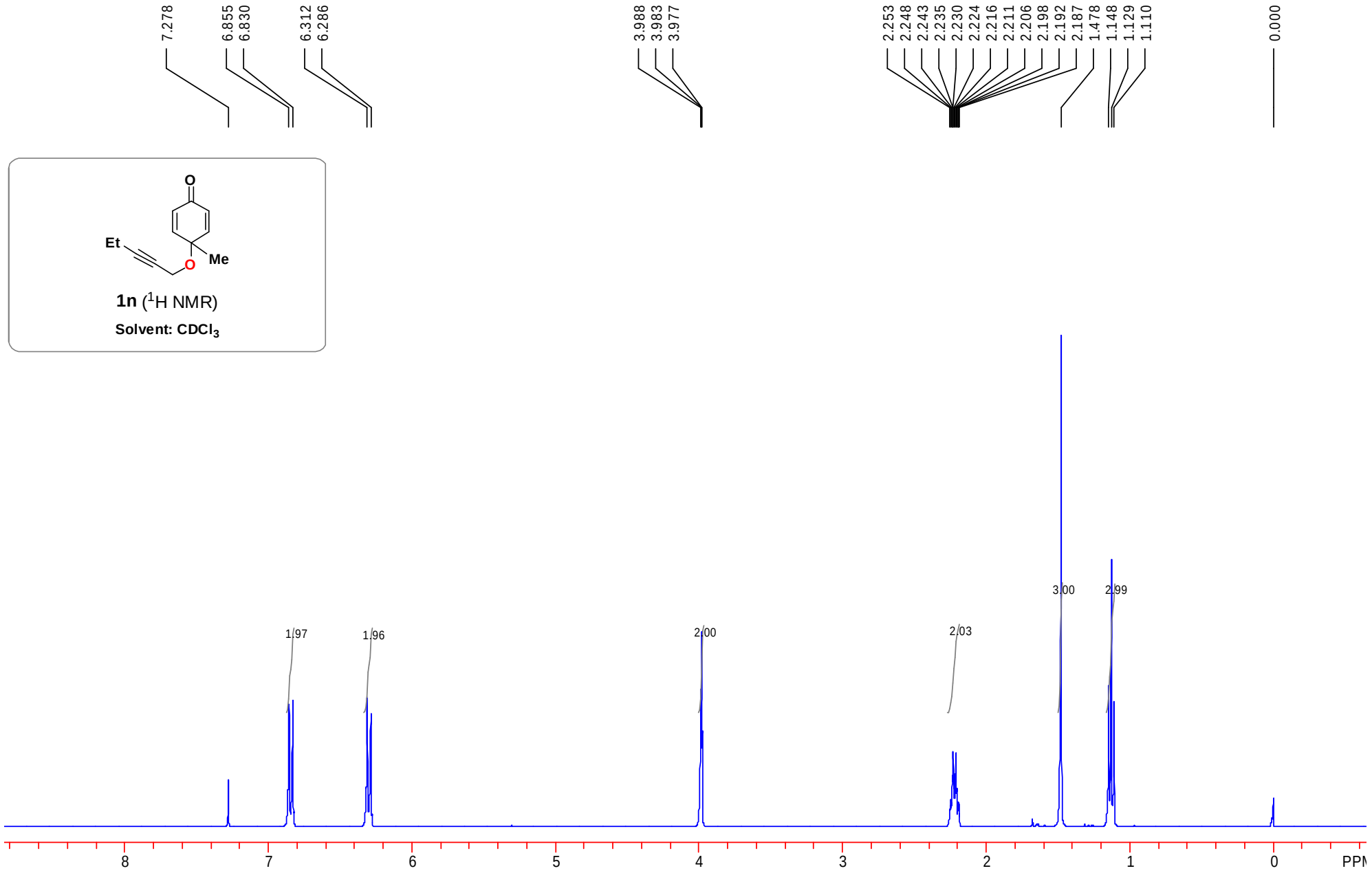
142.825
129.759
92.664
83.219
77.419
77.100
76.781
75.111
51.492
50.695
3.723
O
Me
O
OMe
1m (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM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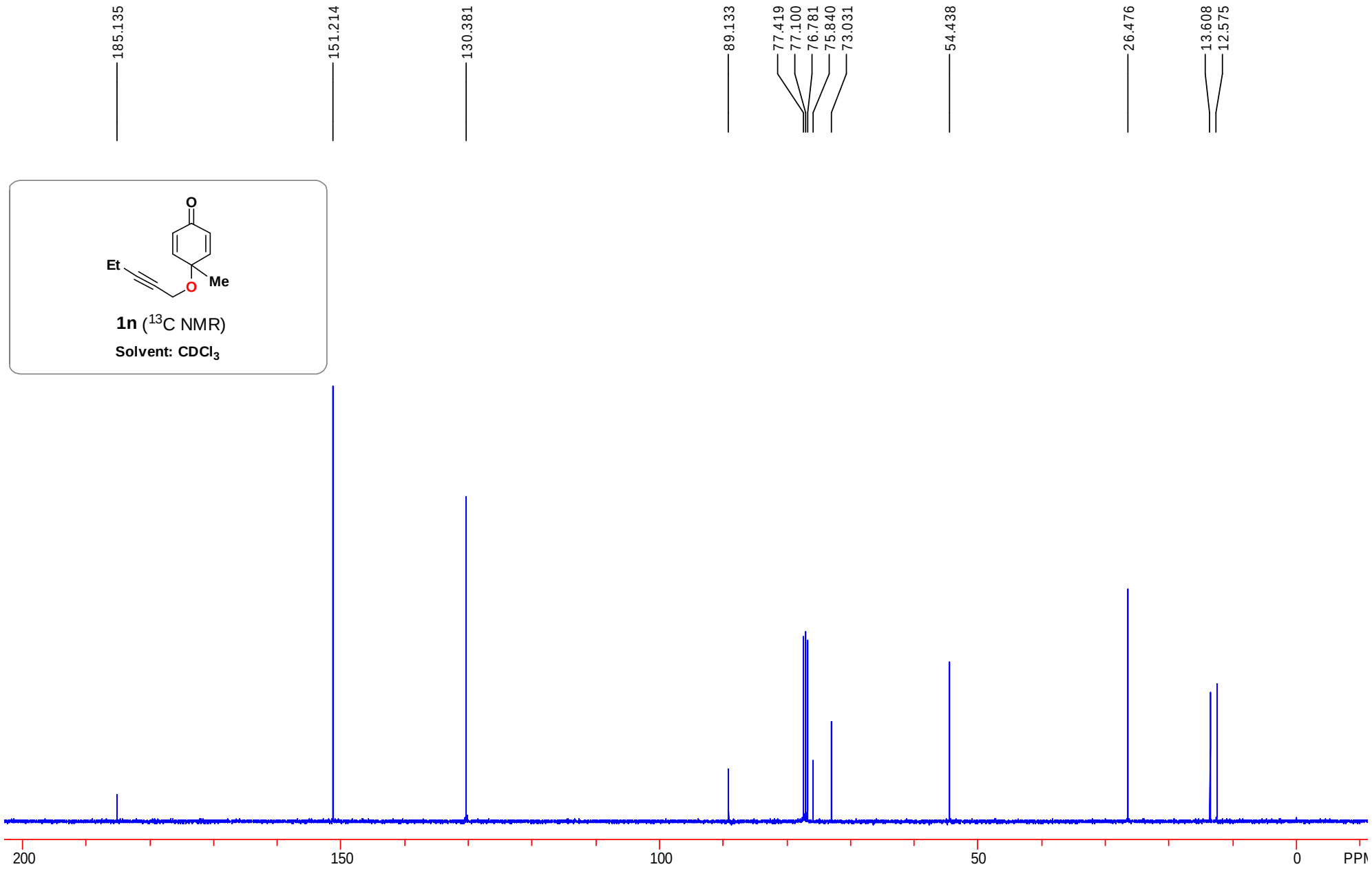
6.855
6.830
6.312
6.286
3.988
3.983
3.977
2.253
2.248
2.243
2.235
2.230
2.224
2.216
2.211
2.206
2.198
2.192
2.187
1.478
1.148
1.129
1.110
0.000
O
Et
Me
O
1n (1H NMR)
Solvent: CDCl3
1.97
1.96
2.00
2.03
3.00
2.99
8
7
6
5
4
3
2
1
0
PPM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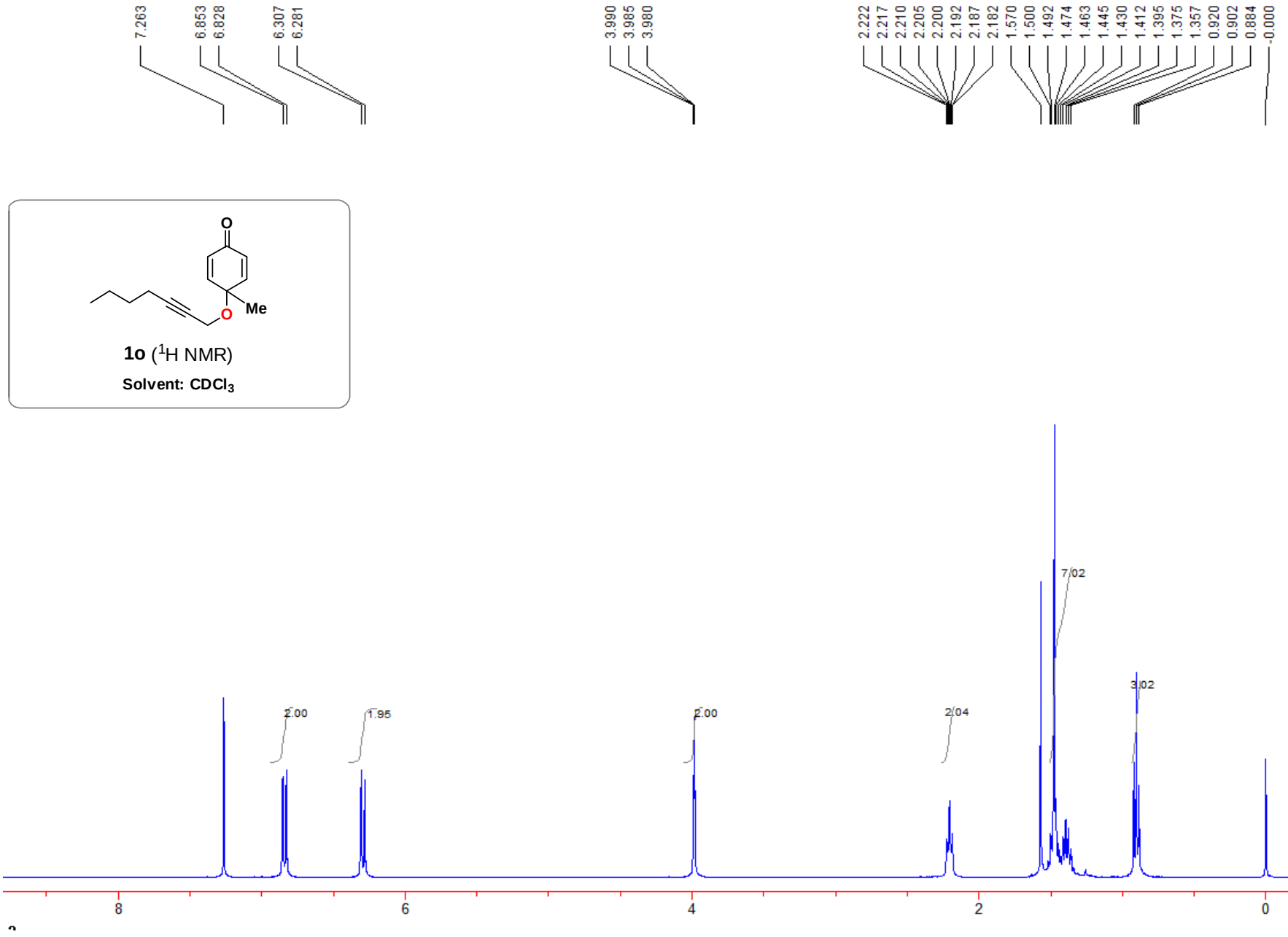
151.214
130.381
89.133
77.419
77.100
76.781
75.840
73.031
54.438
26.476
13.608
12.575
O
Et
Me
O
1n (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM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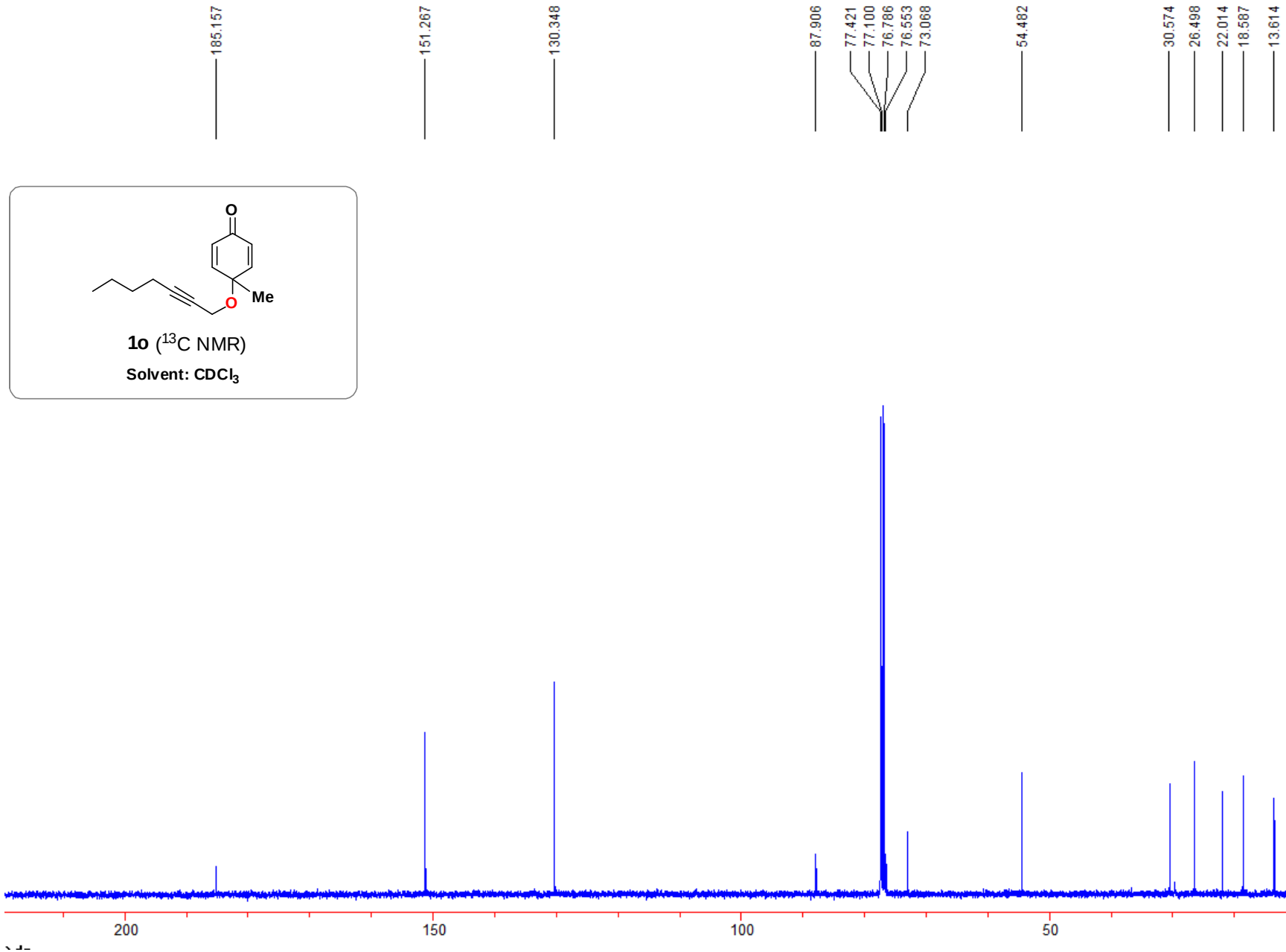
6.853
6.828
6.307
6.281
3.990
3.985
3.980
2.222
2.217
2.210
2.205
2.200
2.192
2.187
2.182
1.570
1.500
1.492
1.474
1.463
1.445
1.430
1.412
1.395
1.375
1.357
0.920
0.902
0.884
-0.000
O
Me
O
1o (1H NMR)
Solvent: CDCl3
2.00
1.95
2.00
2.04
7.02
3.02
8
6
4
2
0
PPM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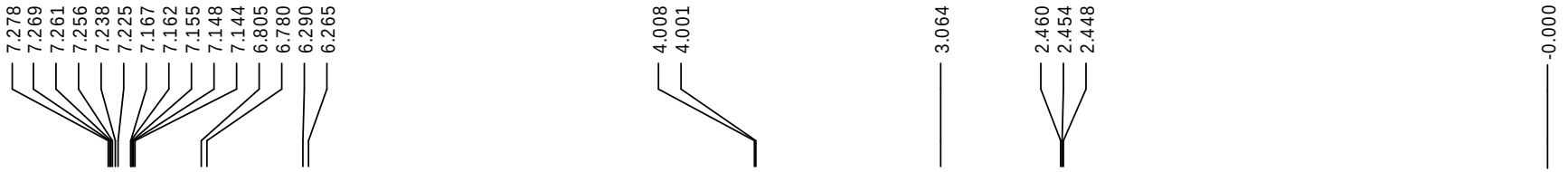
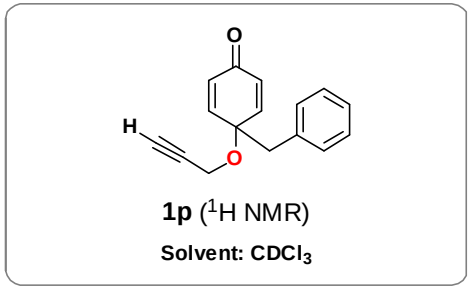
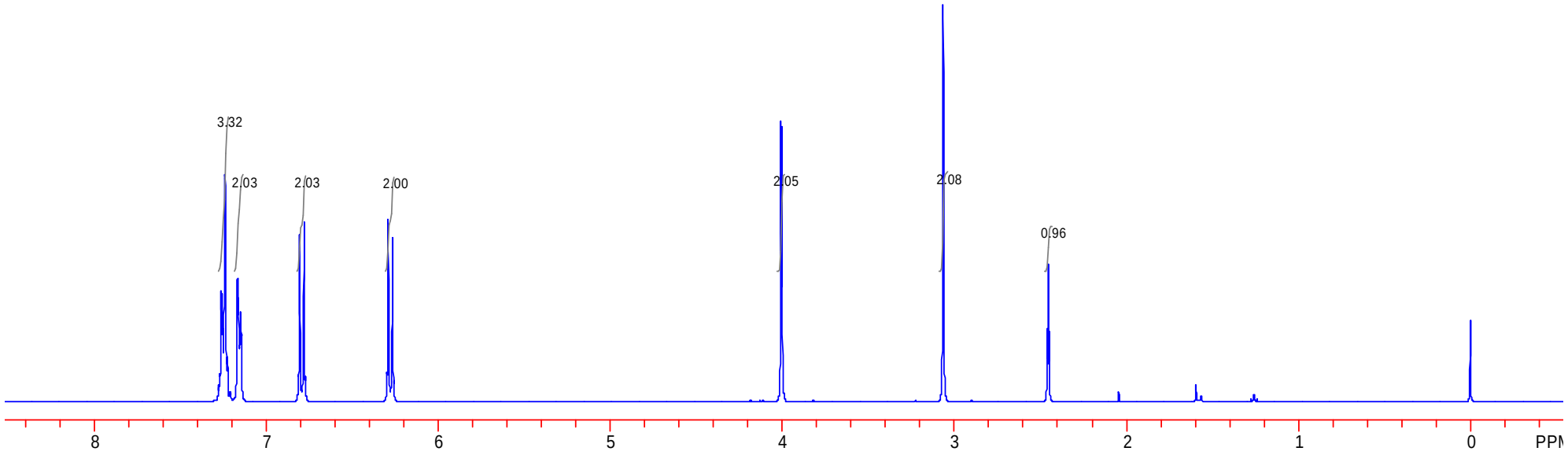
130.348
87.906
77.421
77.100
76.786
76.553
73.068
54.482
30.574
26.498
22.014
18.587
13.614
O
O
Me
1o (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM

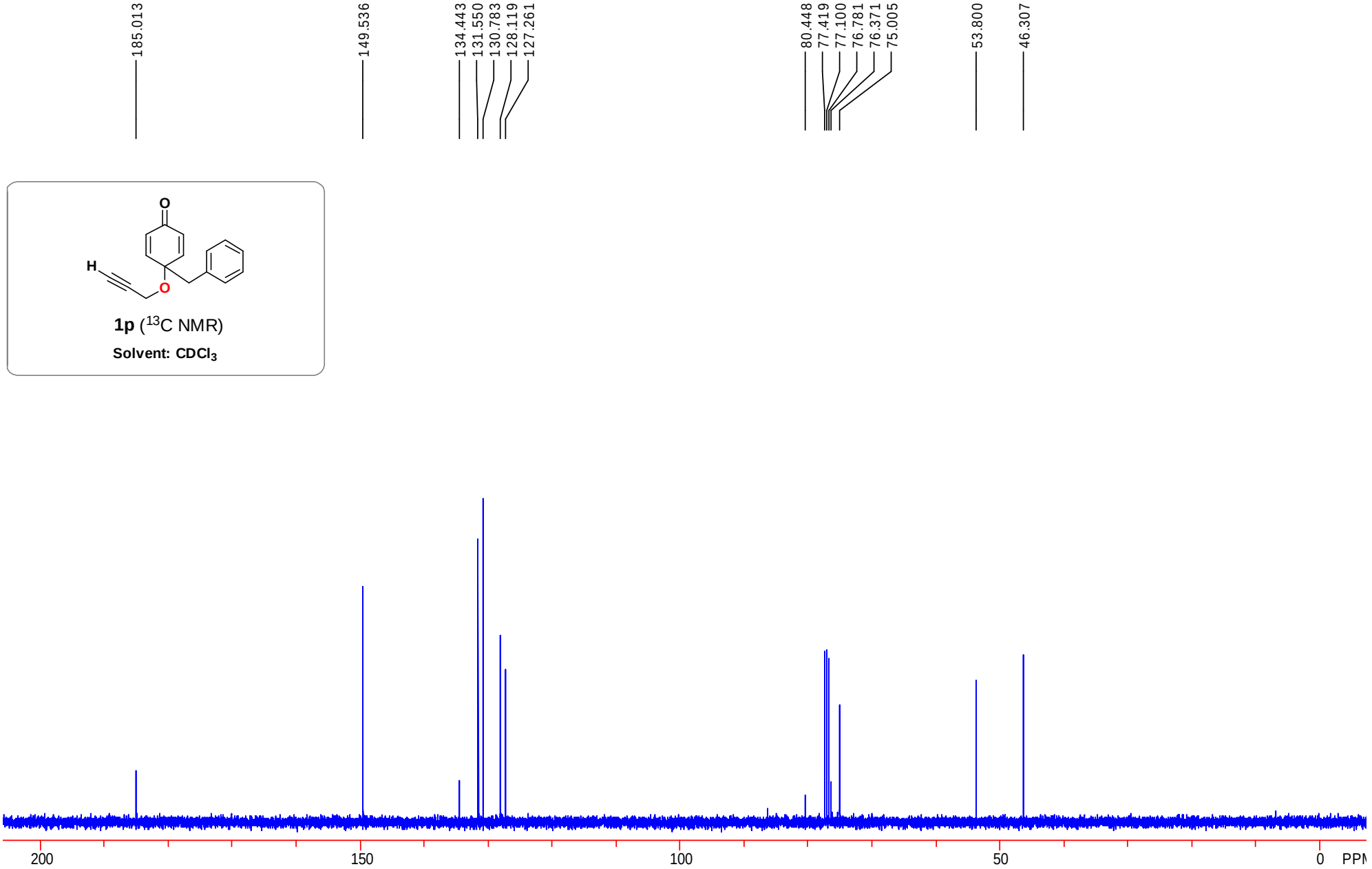




1p (^{1}H NMR)

Solvent: $CDCl_3$

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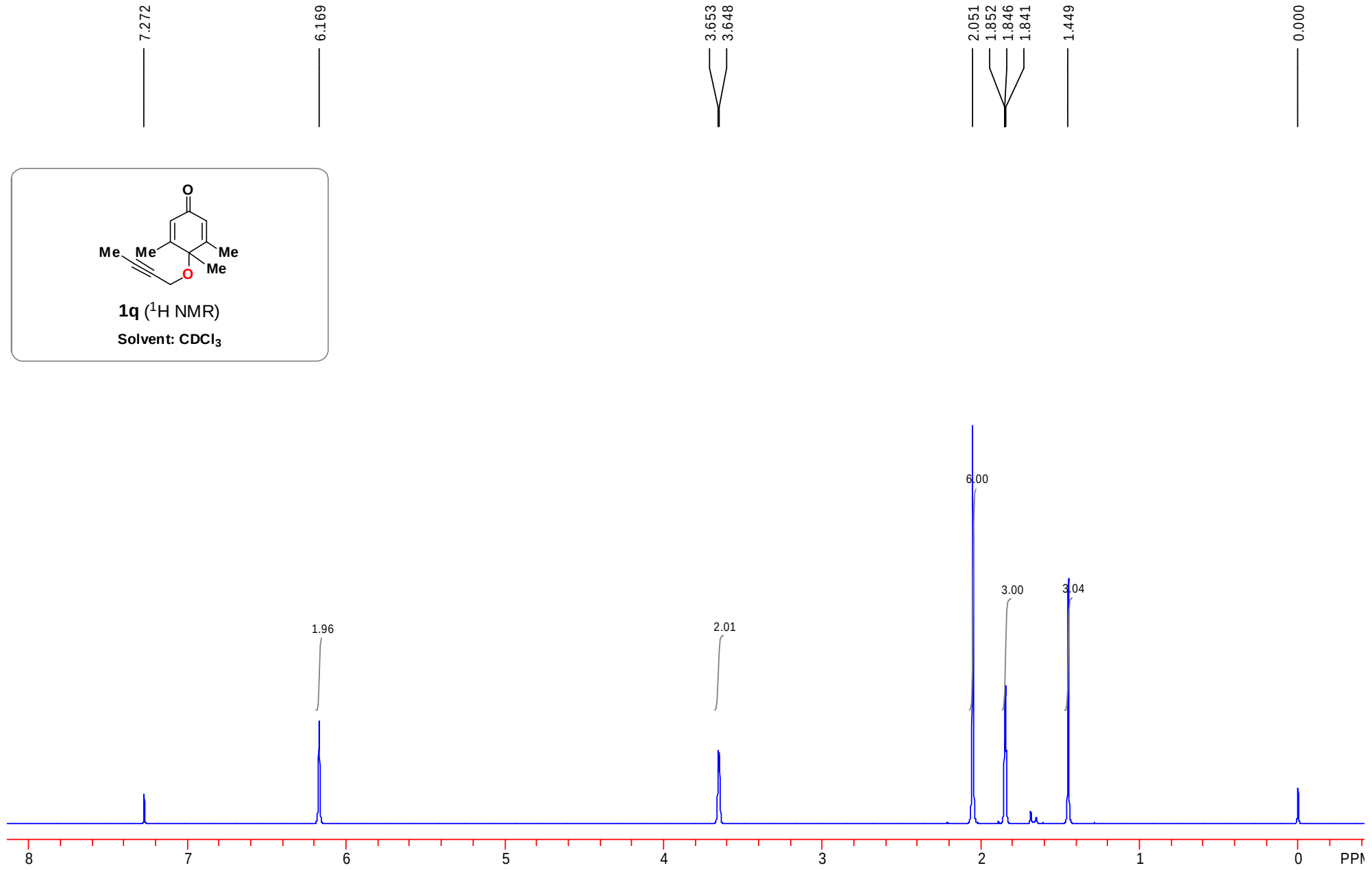
134.443
131.550
130.783
128.119
127.261
80.448
77.419
77.100
76.781
76.371
75.005
53.800
46.307
O
H
O
1p (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM


7.272
6.169
3.653
3.648
2.051
1.852
1.846
1.841
1.449
0.000
O
Me
Me
Me
Me
O
1q (1H NMR)
Solvent: CDCl3
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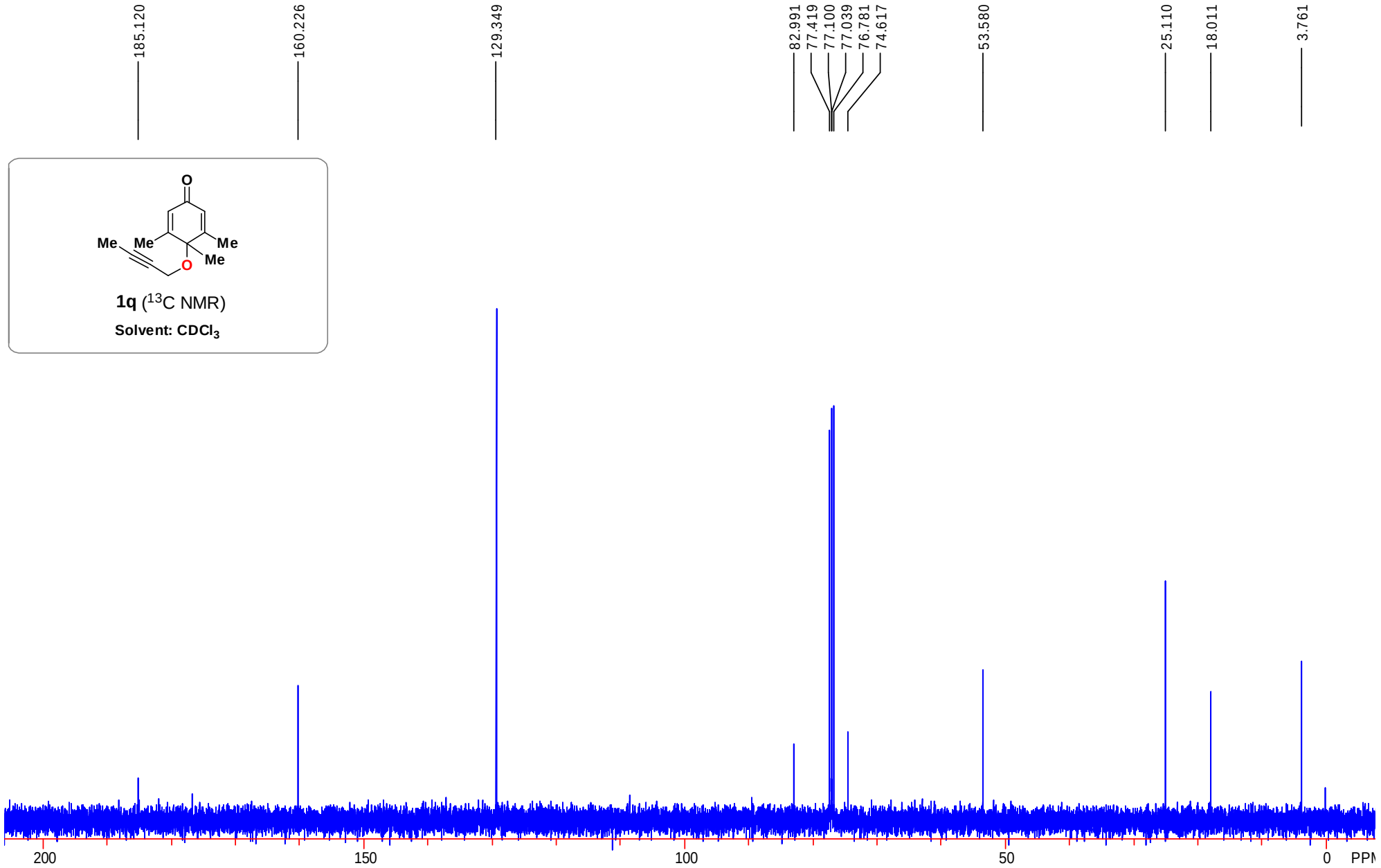
6.00
3.00
3.04
8
7
6
5
4
3
2
1
0
PPM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77.100
77.039
76.781
74.617
53.580
25.110
18.011
3.761
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Me
Me
Me
O
1q (13C NMR)
Solvent: CDCl3
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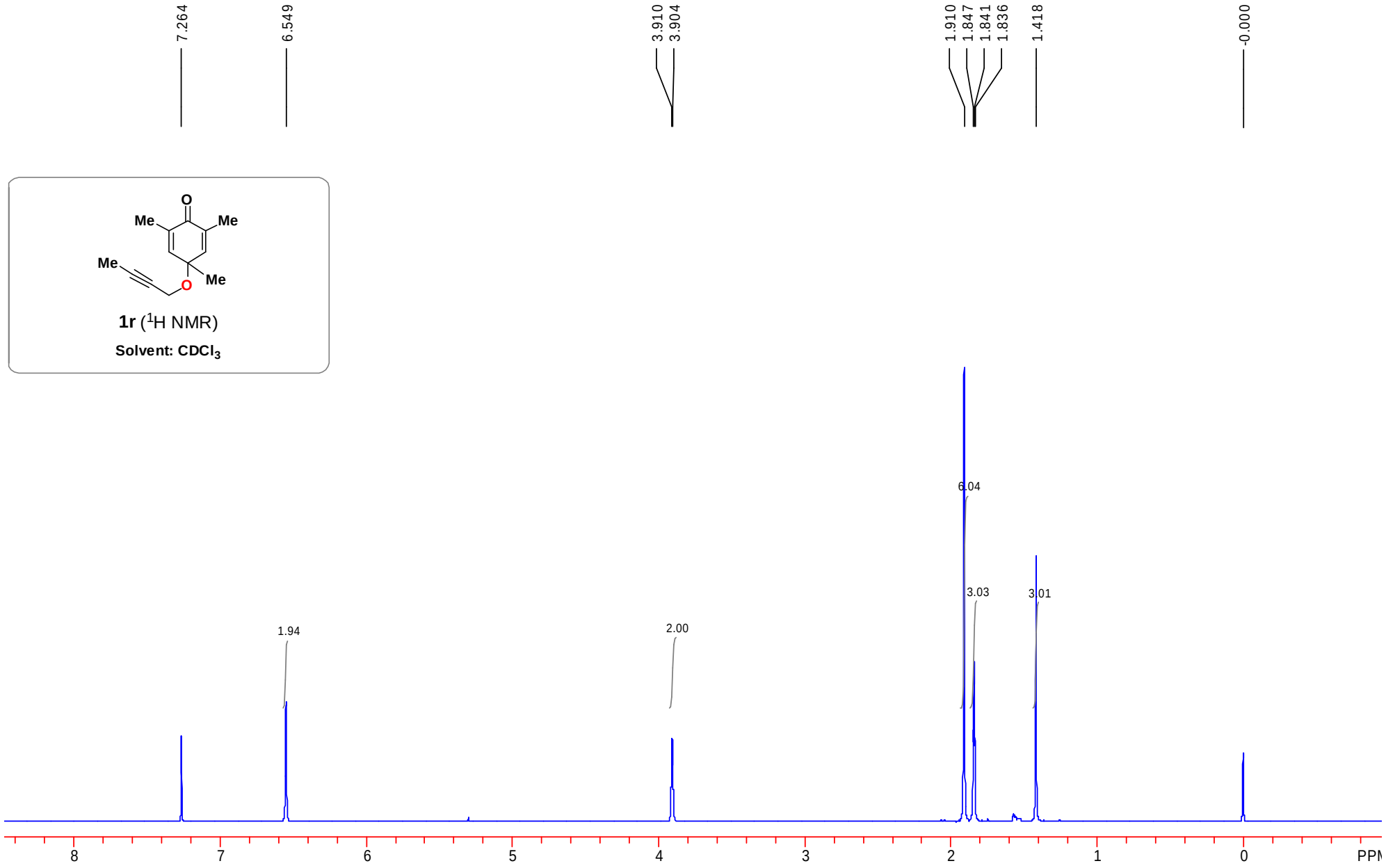
150
100
50
0
PPM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3.904
1.910
1.847
1.841
1.836
1.418
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Me
Me
Me
Me
O
O
1r (1H NMR)
Solvent: CDCl3
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3.01
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8
7
6
5
4
3
2
1
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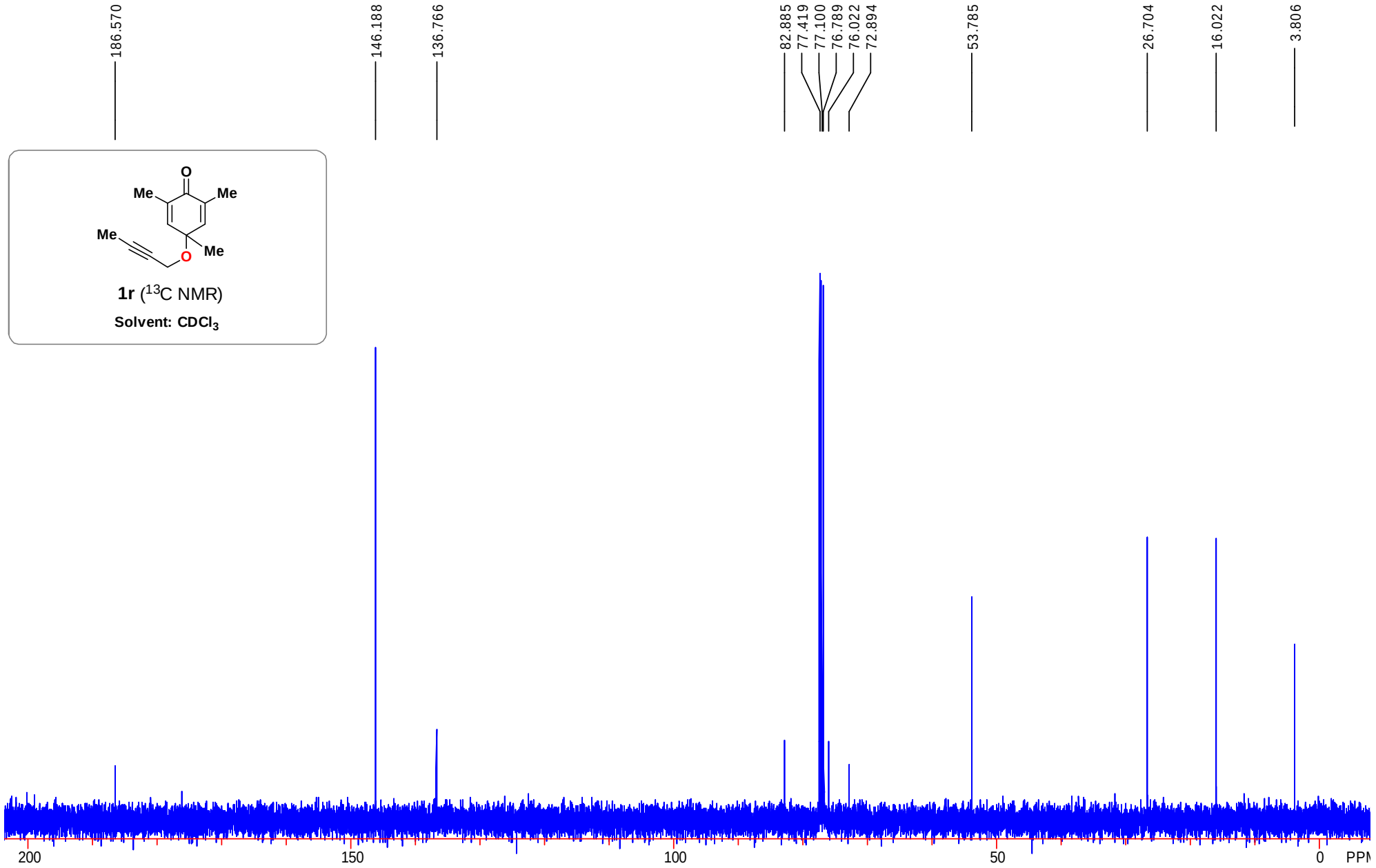
PPM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76.789
76.022
72.894
53.785
26.704
16.022
3.806
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Me
Me
Me
O
Me
1r (13C NMR)
Solvent: CDCl3
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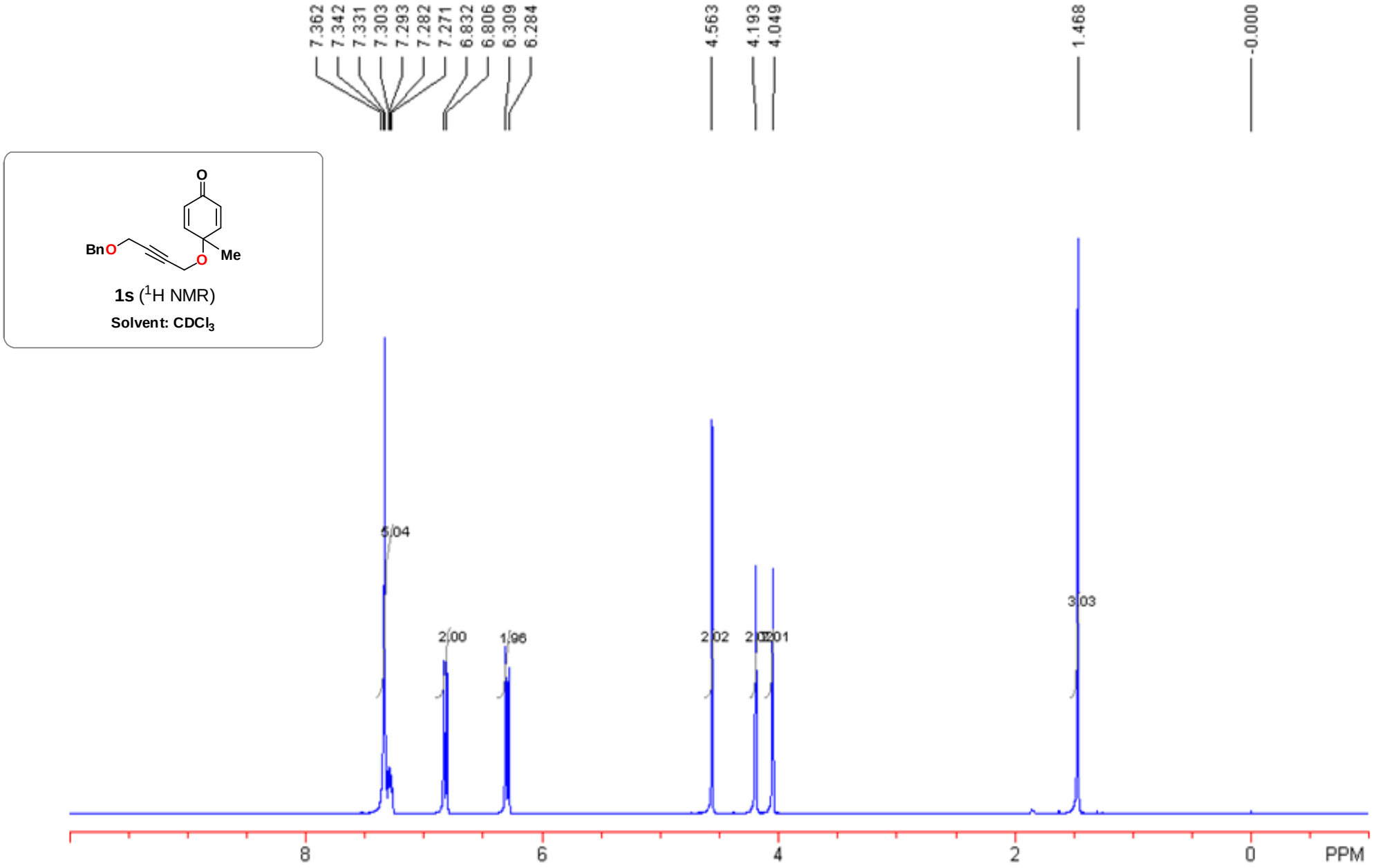
150
100
50
0
PPM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7.293
7.282
7.271
6.832
6.806
6.309
6.284
4.563
4.193
4.049
1.468
-0.000
BnO
O
Me
1s (1H NMR)
Solvent: CDCl3
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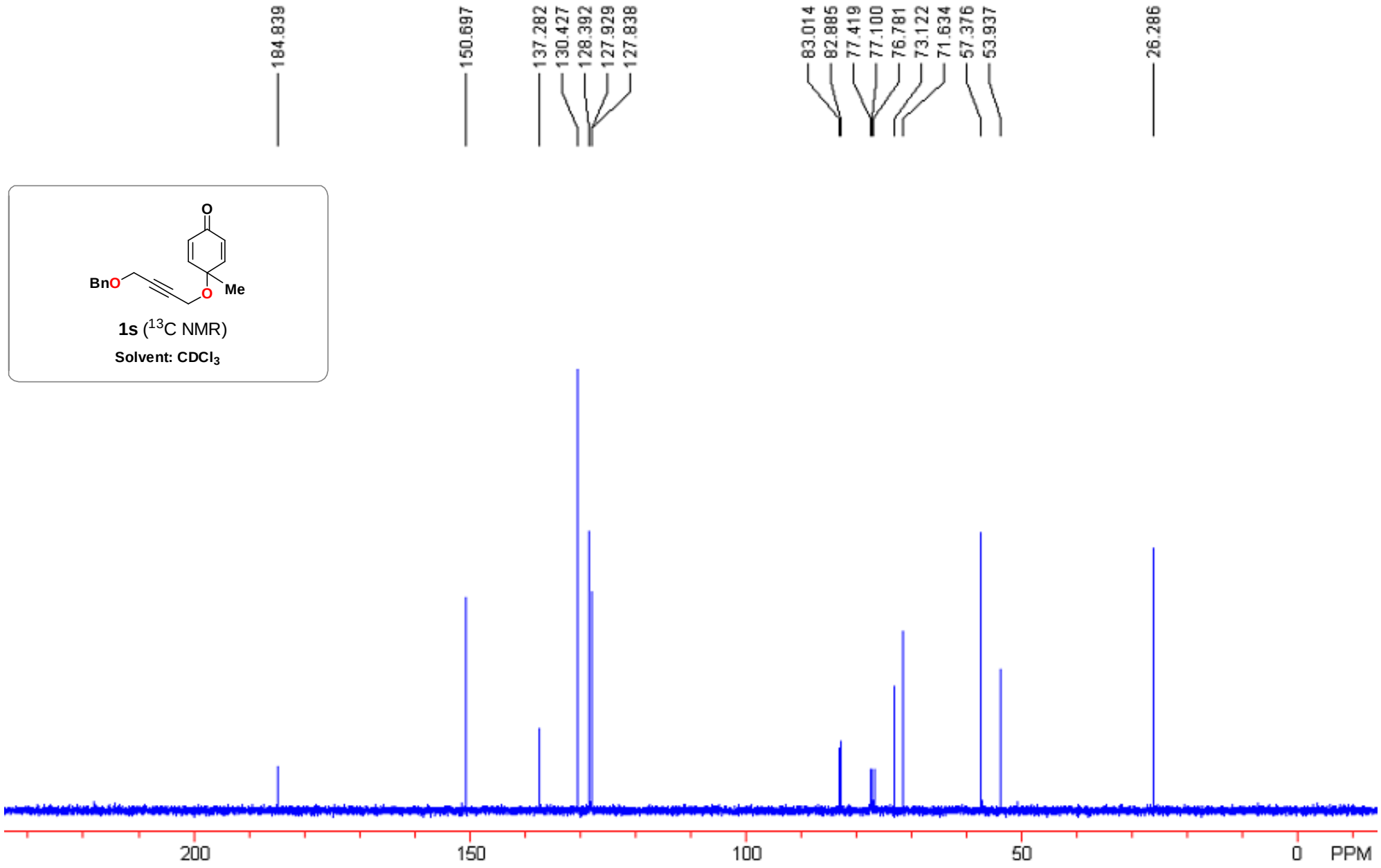
1.96
2.02
2.01
3.03
8
6
4
2
0
PPM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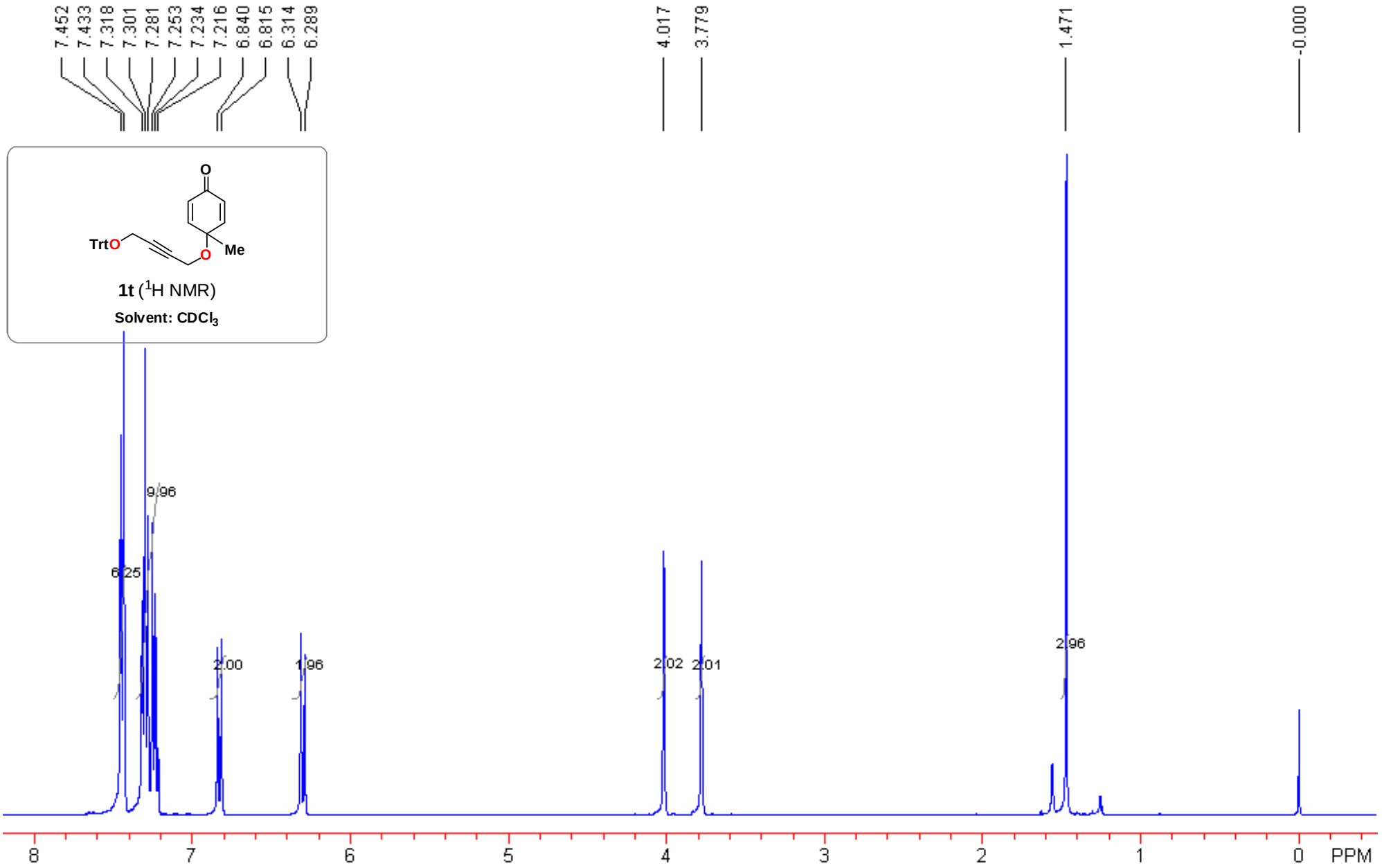
137.282
130.427
128.392
127.929
127.838
83.014
82.885
77.419
77.100
76.781
73.122
71.634
57.376
53.937
26.286
BnO
O
Me
1s (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM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7.318
7.301
7.281
7.253
7.234
7.216
6.840
6.815
6.314
6.289
4.017
3.779
1.471
-0.000
O
TrtO
O
Me
1t (1H NMR)
Solvent: CDCl3
9.96
6.25
2.00
1.96
2.02
2.01
2.96
8
7
6
5
4
3
2
1
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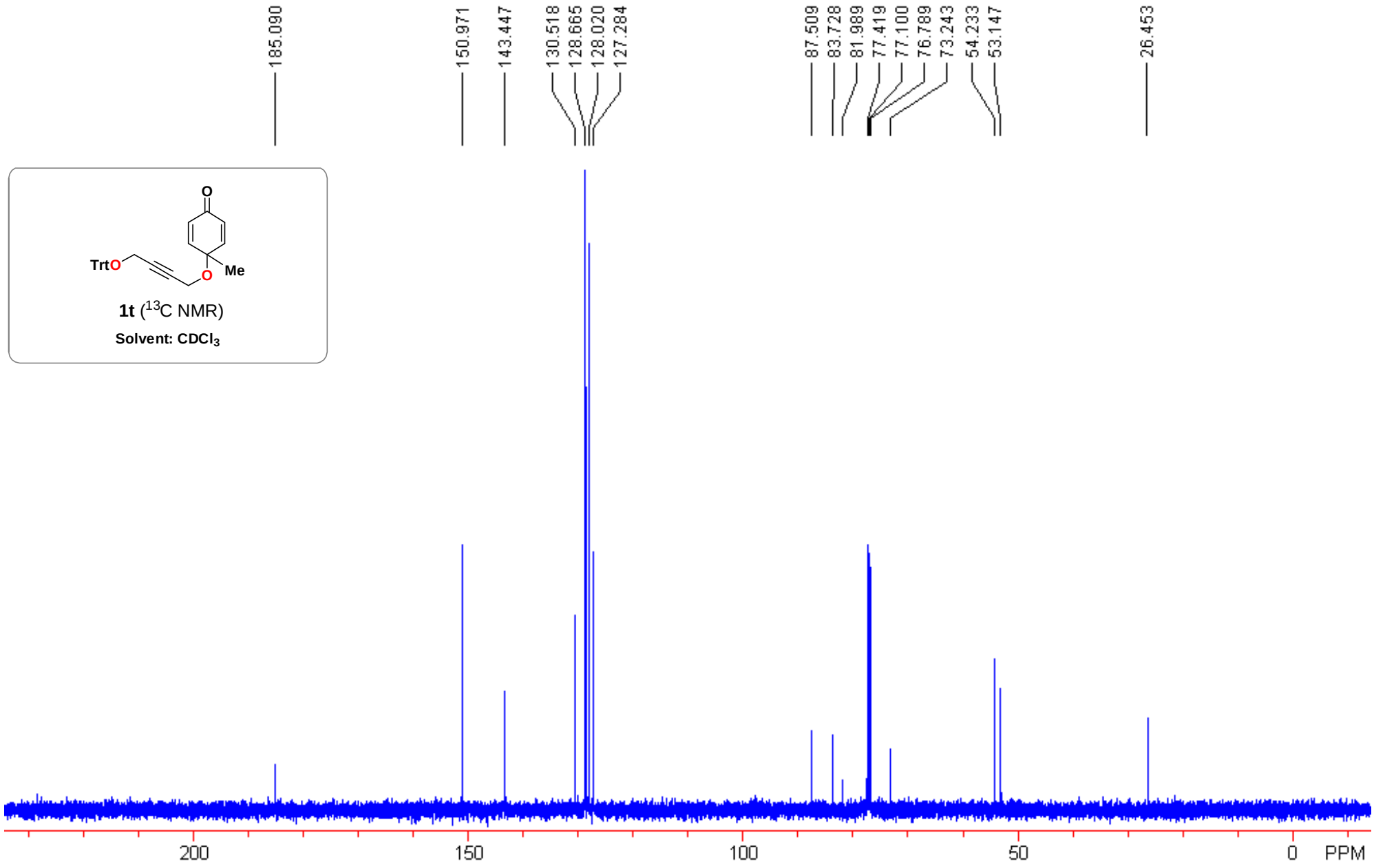
PPM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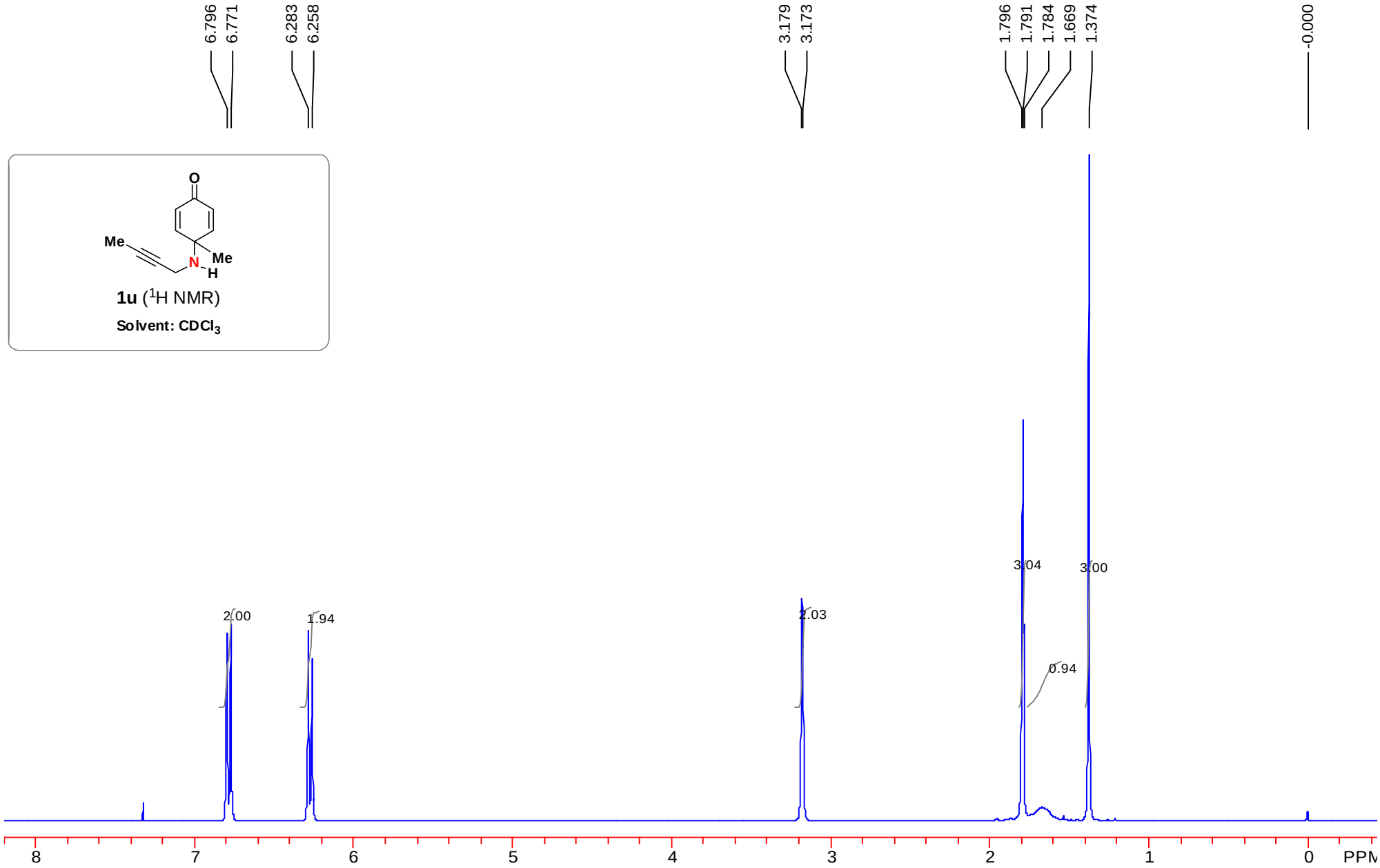
128.020
127.284
87.509
83.728
81.989
77.419
77.100
76.789
73.243
54.233
53.147
26.453
O
TrtO
O
Me
1t (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM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6.283
6.258
3.179
3.173
1.796
1.791
1.784
1.669
1.374
-0.000
O
Me
N
H
Me
1u (1H NMR)
Solvent: CDCl3
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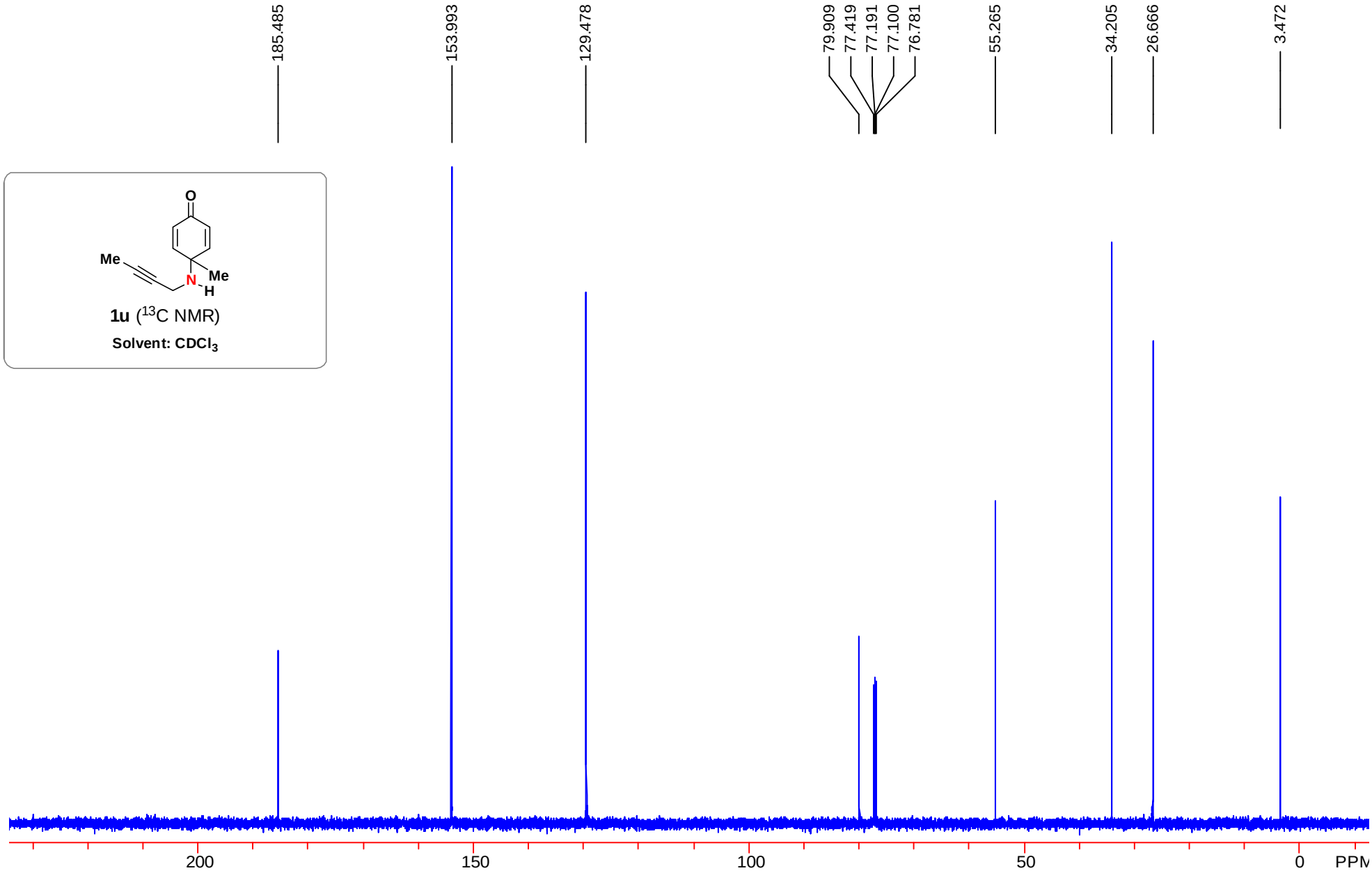
2.03
3.04
0.94
3.00
8
7
6
5
4
3
2
1
0
PPM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79.909
77.419
77.191
77.100
76.781
55.265
34.205
26.666
3.472
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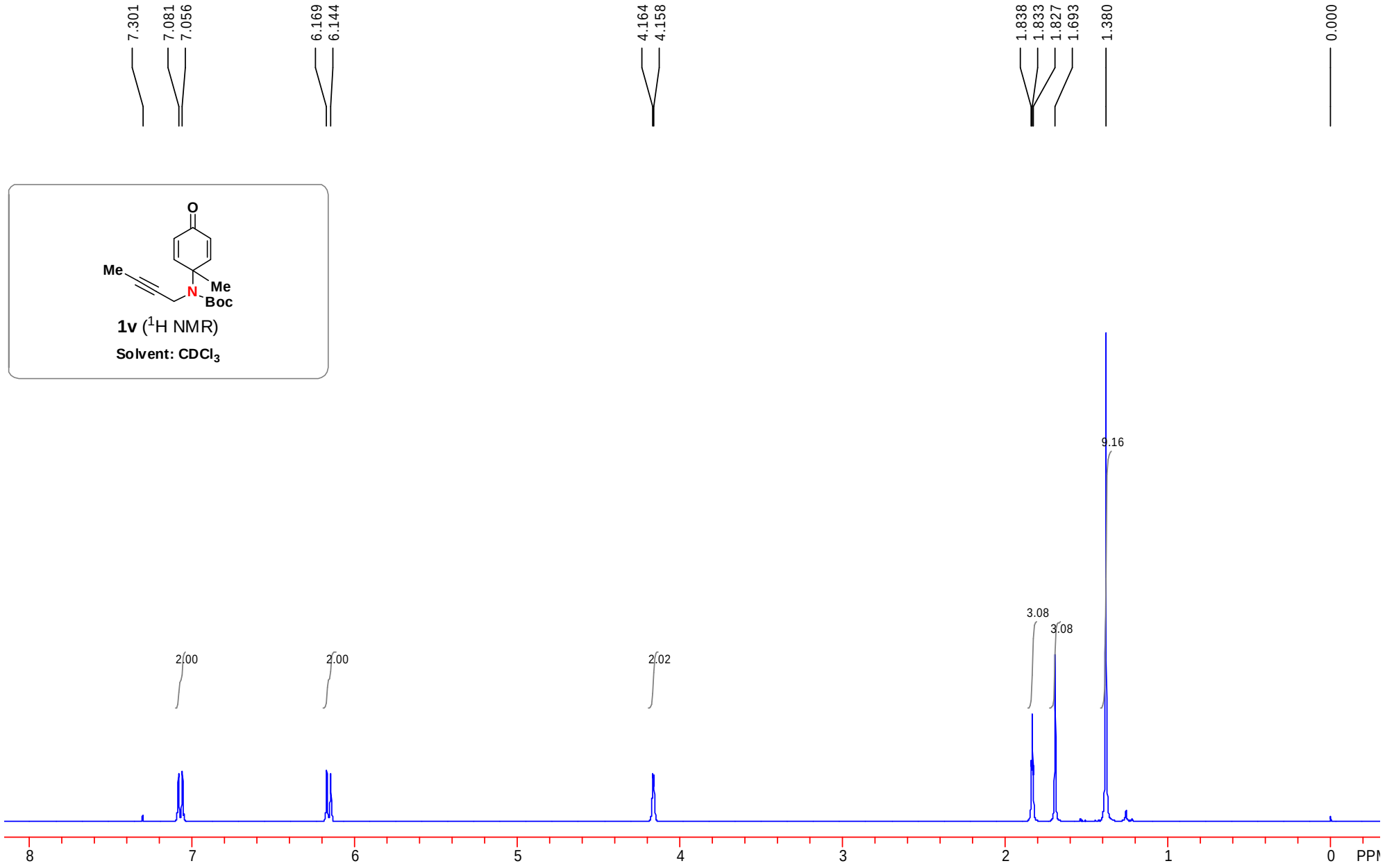
Me
N
Me
H
1u (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM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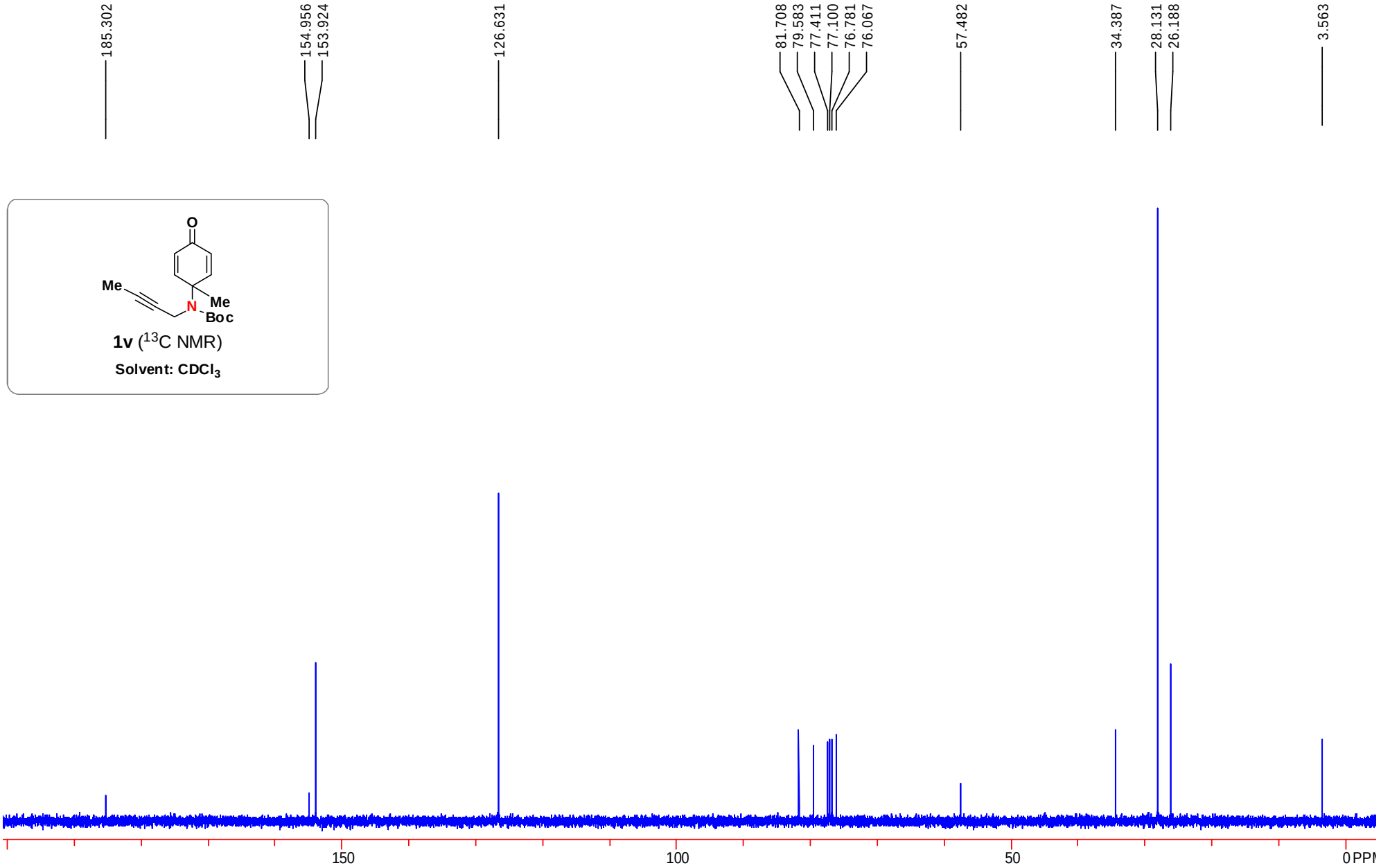
7.056
6.169
6.144
4.164
4.158
1.838
1.833
1.827
1.693
1.380
0.000
O
Me
N
Me
Boc
1v (1H NMR)
Solvent: CDCl3
9.16
3.08
3.08
2.00
2.00
2.02
8
7
6
5
4
3
2
1
0
PPM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126.631
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77.411
77.100
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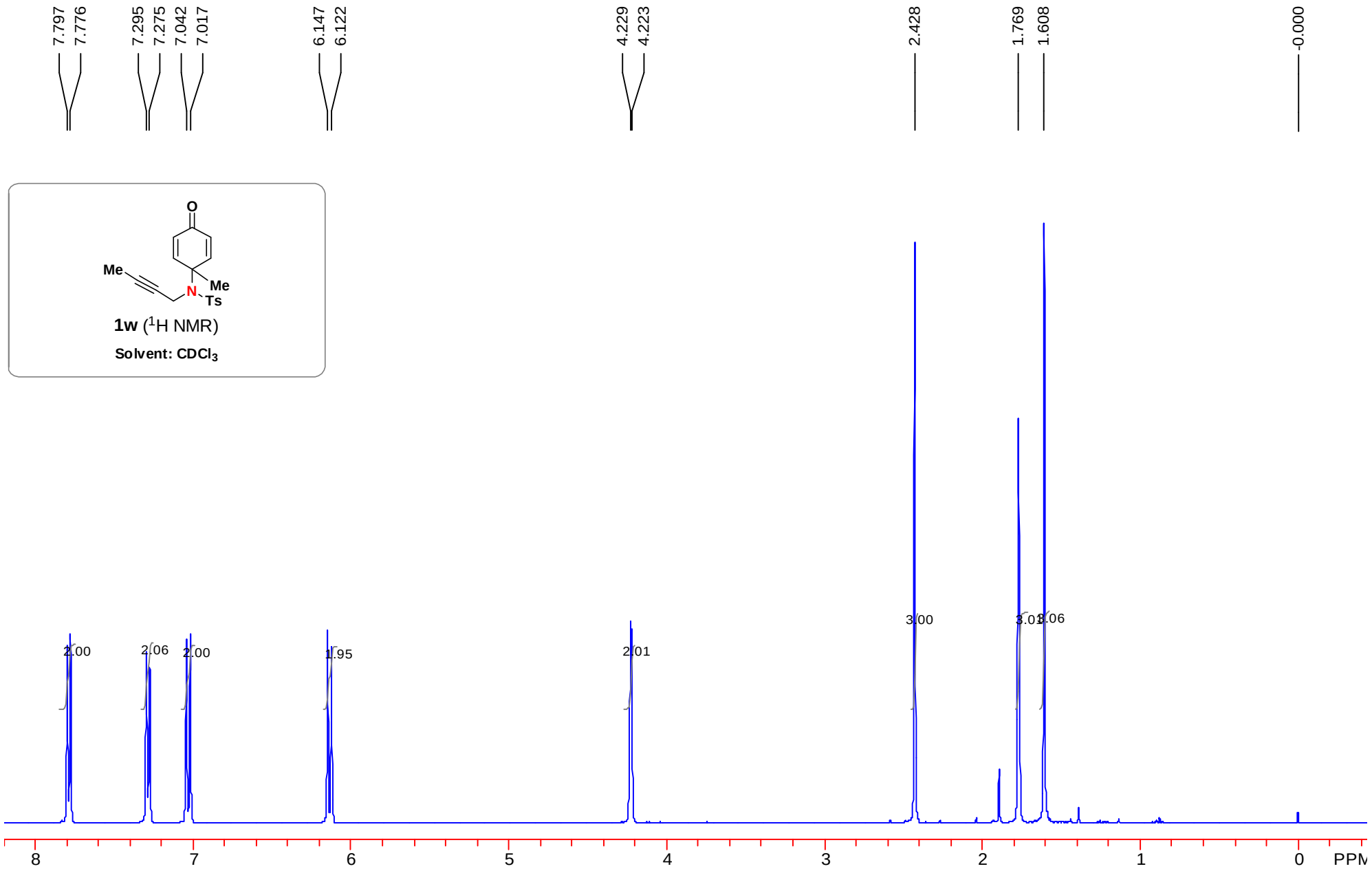
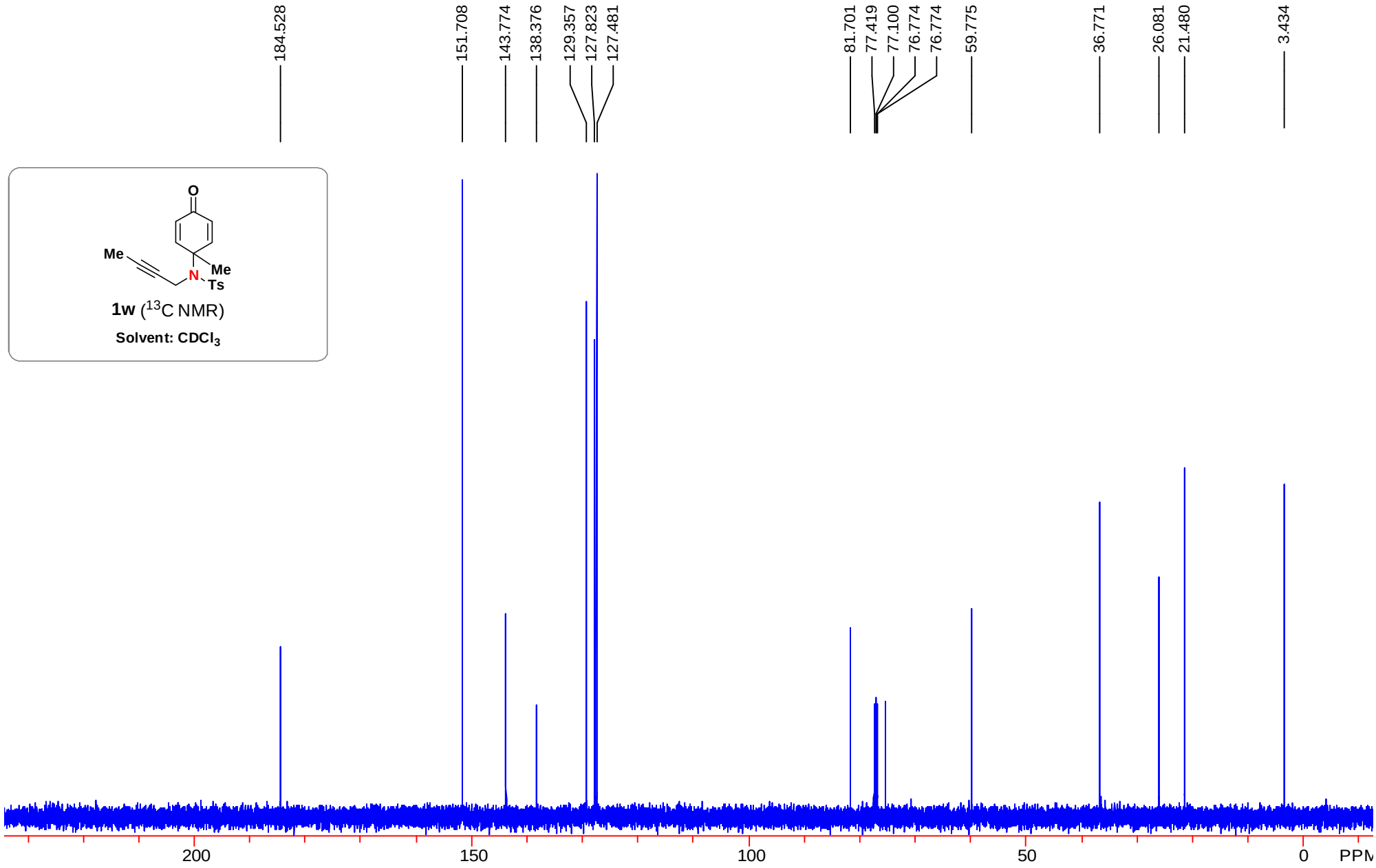
76.067
57.482
34.387
28.131
26.188
3.563
O
Me
N
Me
Boc
1v (13C NMR)
Solvent: CDCl3
150
100
50
0 PPM


7.797
7.776
7.295
7.275
7.042
7.017
6.147
6.122
4.229
4.223
2.428
1.769
1.608
-0.000
O
Me
N
Me
Ts
1w (1H NMR)
Solvent: CDCl3
2.00
2.06
2.00
1.95
2.01
3.00
3.03
3.06
8
7
6
5
4
3
2
1
0
PPM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143.774
138.376
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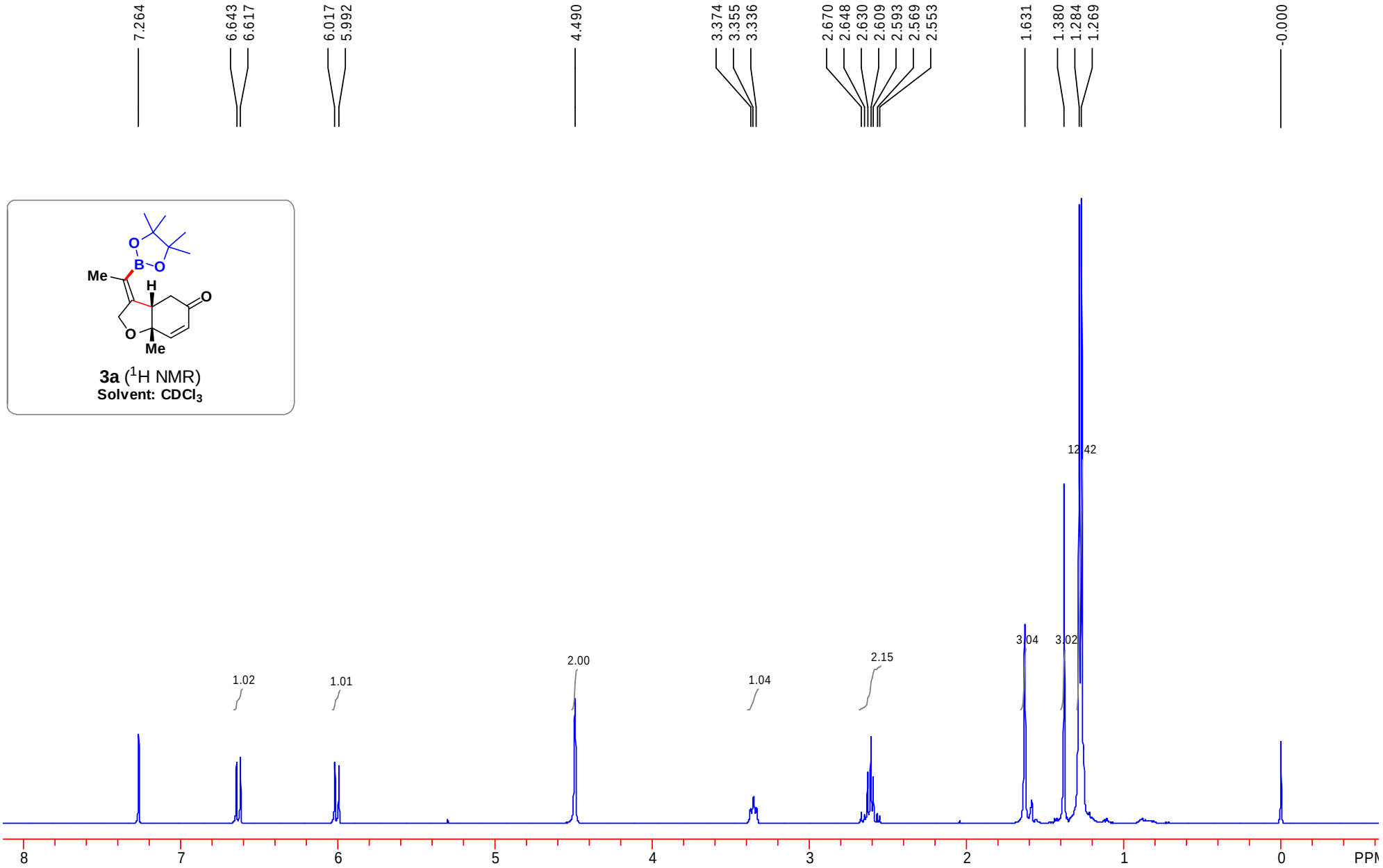
127.481
81.701
77.419
77.100
76.774
76.774
59.775
36.771
26.081
21.480
3.434
O
Me
N
Me
Ts
1w (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM


7.264
6.643
6.617
6.017
5.992
4.490
3.374
3.355
3.336
2.670
2.648
2.630
2.609
2.593
2.569
2.553
1.631
1.380
1.284
1.269
-0.000
Me
O
B
O
H
O
O
Me
3a (1H NMR)
Solvent: CDCl3
1.02
1.01
2.00
1.04
2.15
3.04
3.02
12.42
8
7
6
5
4
3
2
1
0
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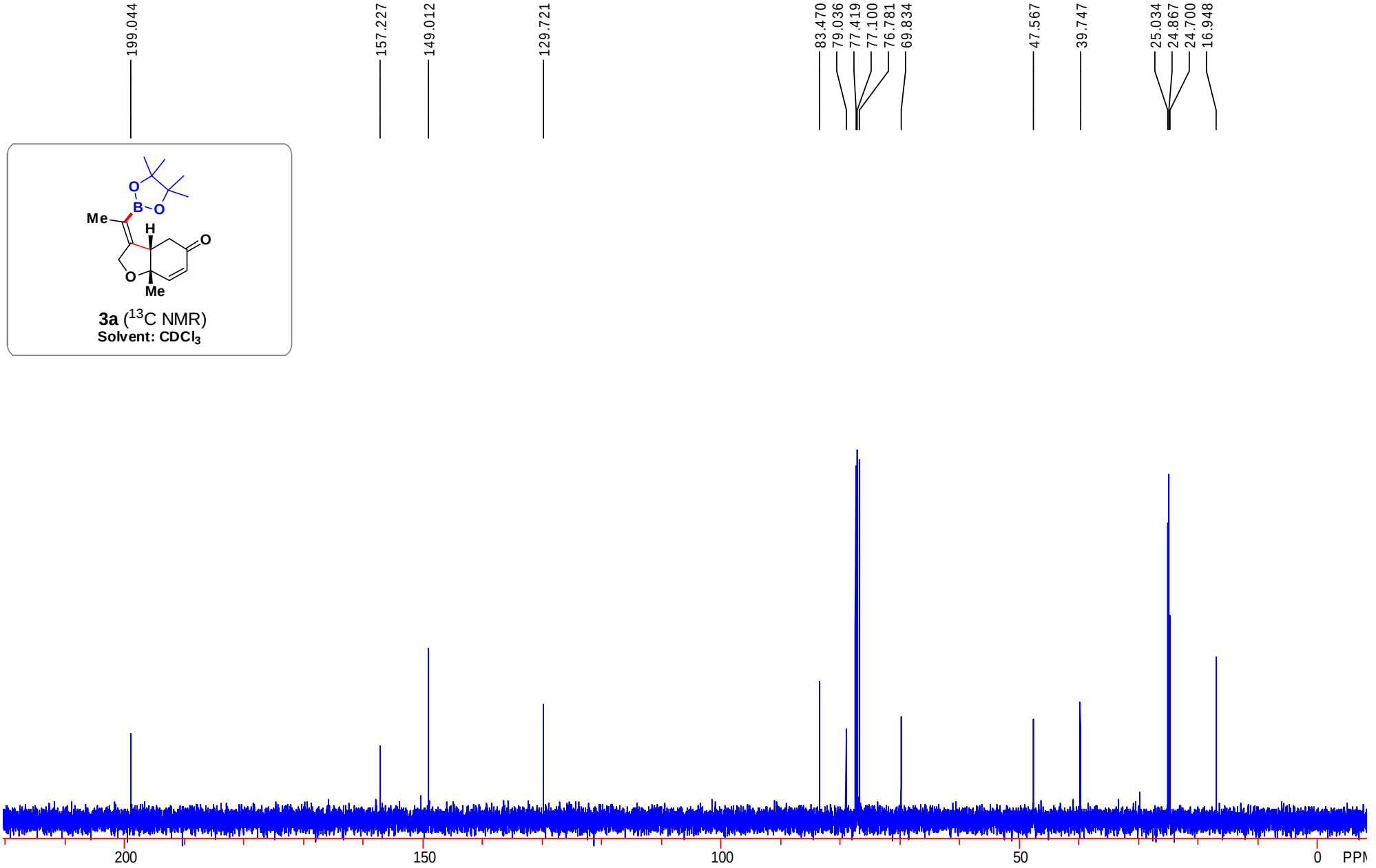
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129.721
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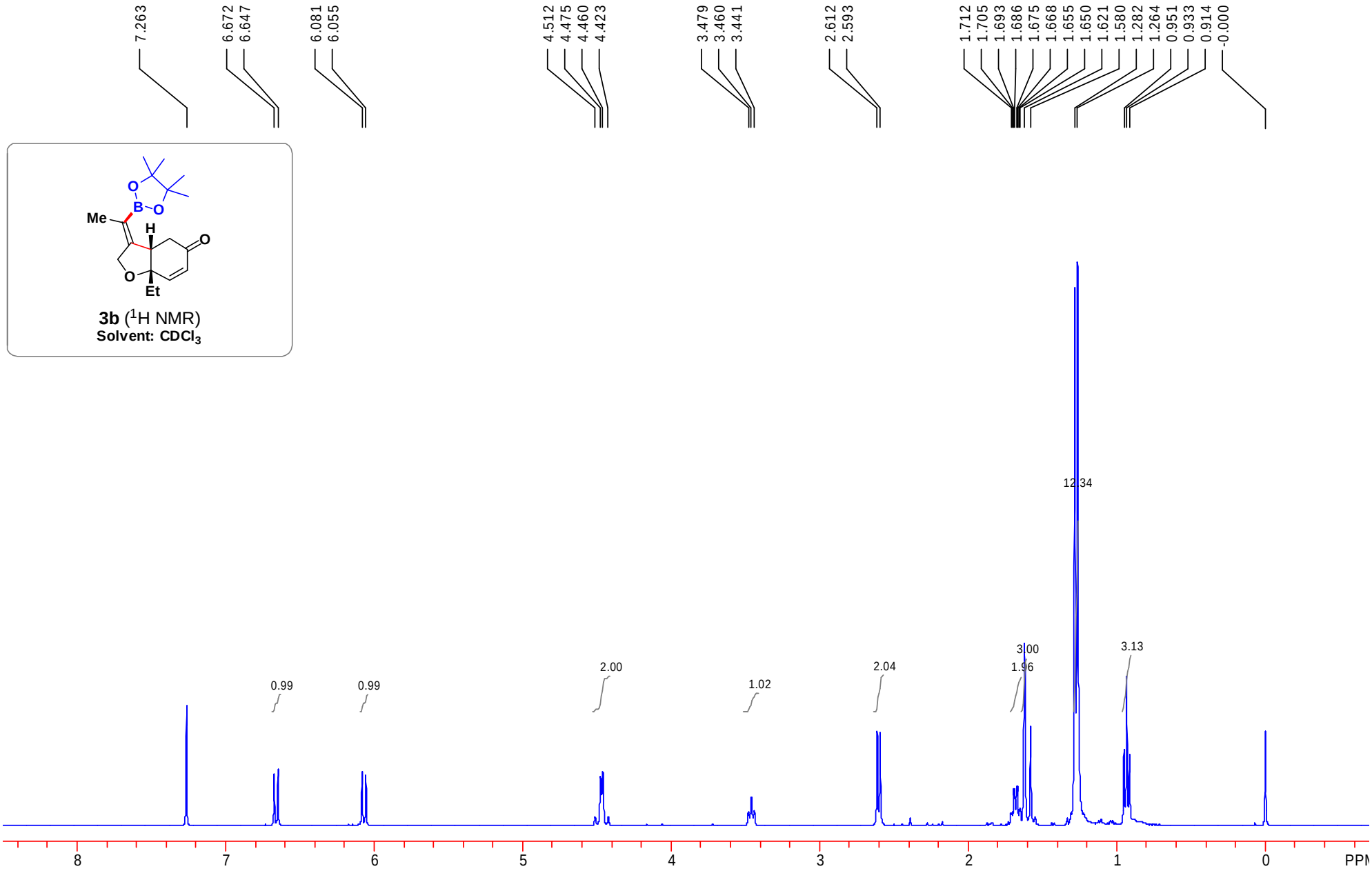
79.036
77.419
77.100
76.781
69.834
47.567
39.747
25.034
24.867
24.700
16.948
Me
H
O
O
B
O
O
Me
3a (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM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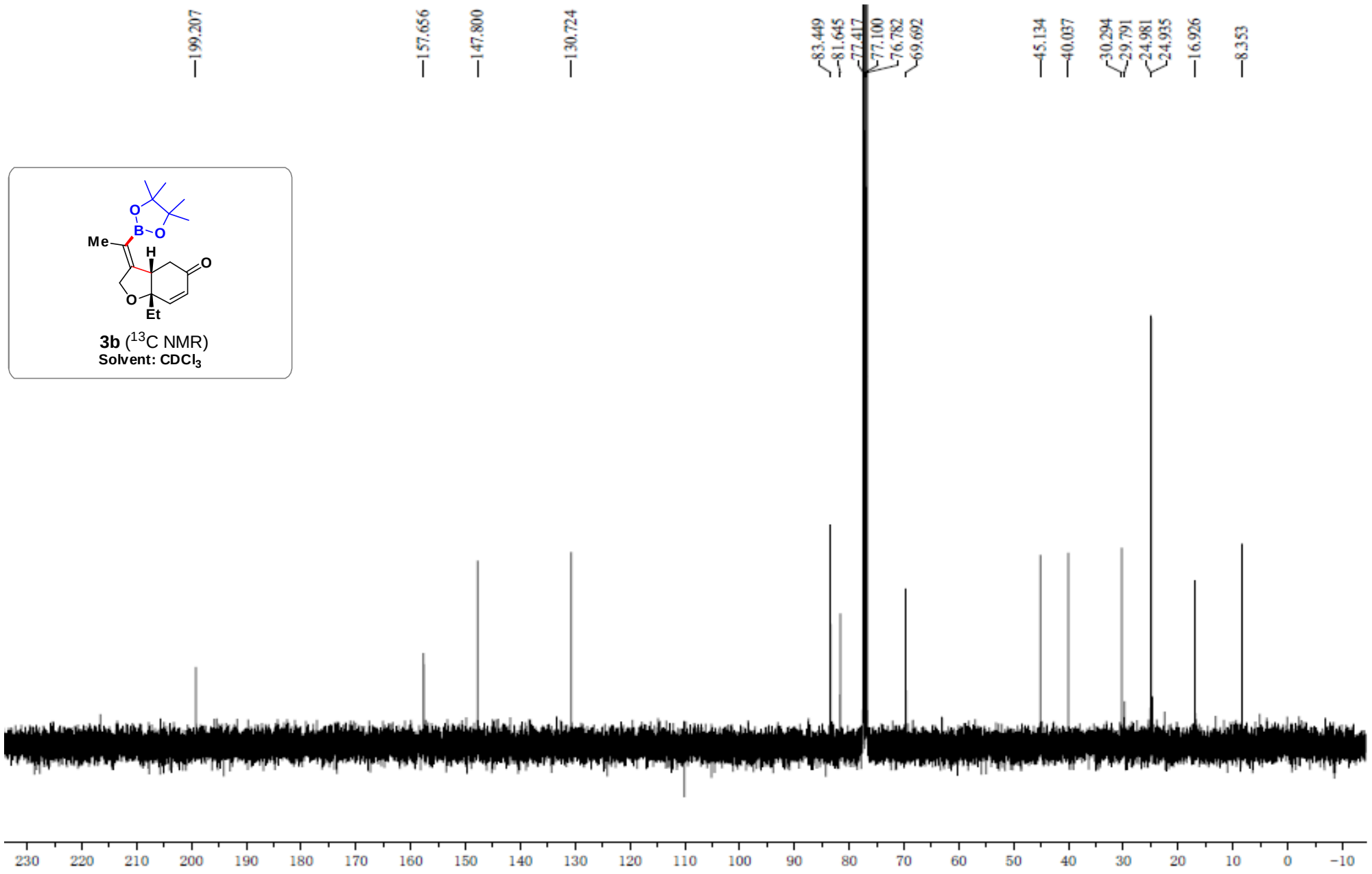
6.672
6.647
6.081
6.055
4.512
4.475
4.460
4.423
3.479
3.460
3.441
2.612
2.593
1.712
1.705
1.693
1.686
1.675
1.668
1.655
1.650
1.621
1.580
1.282
1.264
0.951
0.933
0.914
-0.000
Me
H
O
O
B
O
O
Et
3b (1H NMR)
Solvent: CDCl3
0.99
0.99
2.00
1.02
2.04
1.96
3.00
12.34
3.13
8
7
6
5
4
3
2
1
0
PPM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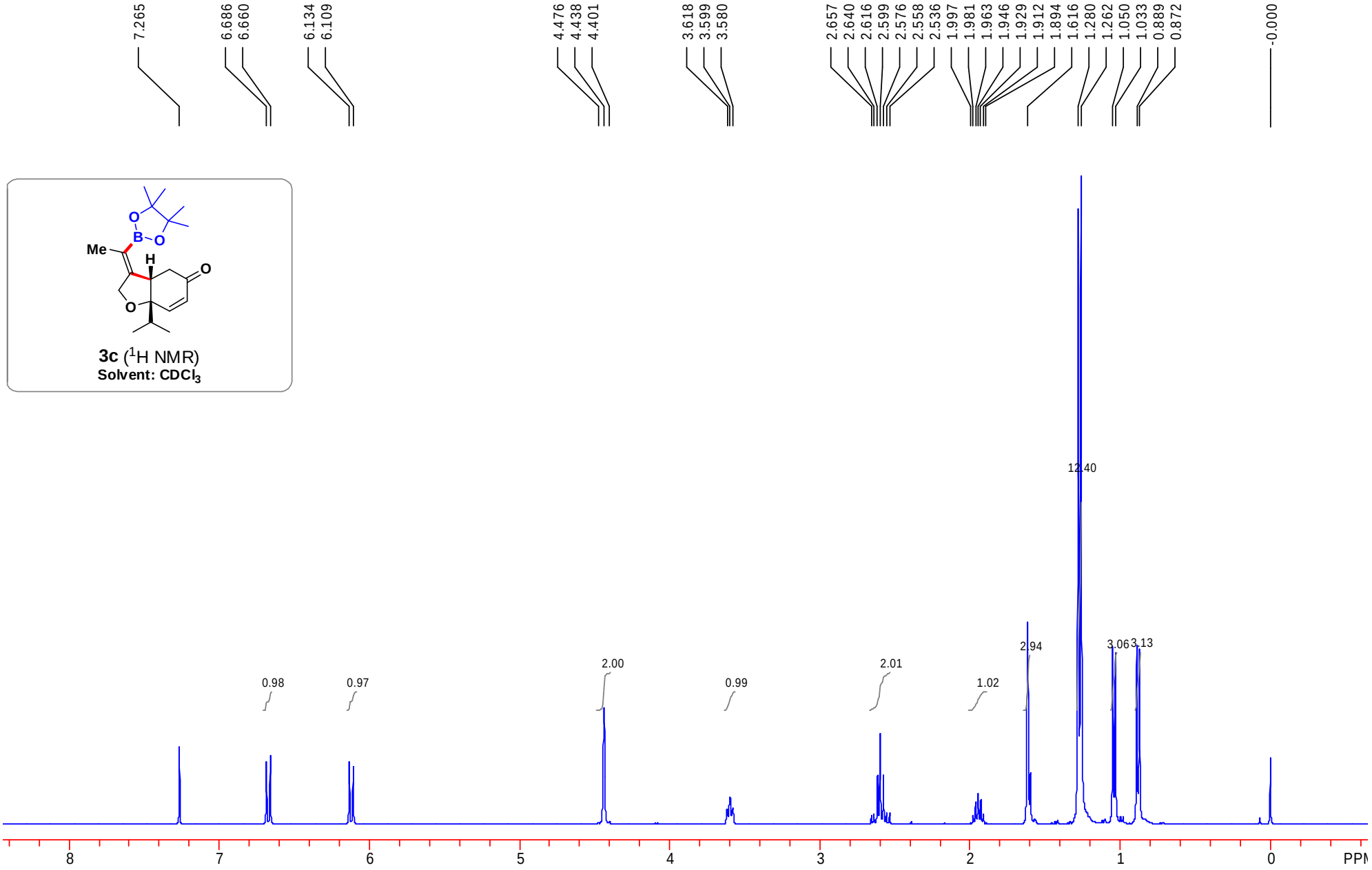
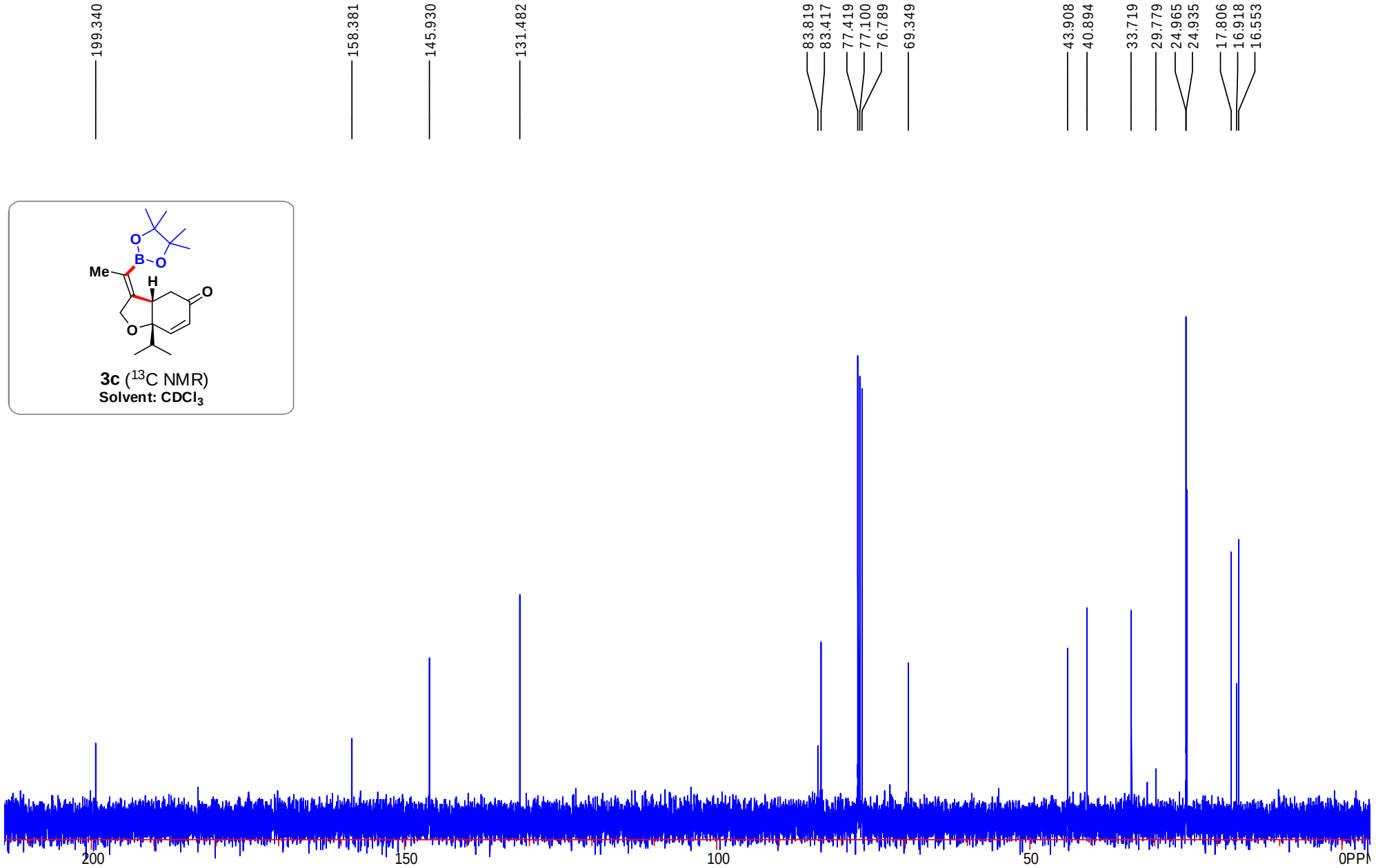
157.656
147.800
130.724
83.449
81.645
77.417
77.100
76.782
69.692
45.134
40.037
30.294
29.791
24.981
24.935
16.926
8.353
Me
H
O
O
B
O
O
Et
3b (13C NMR)
Solvent: CDCl3
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10


7.265
6.686
6.660
6.134
6.109
4.476
4.438
4.401
3.618
3.599
3.580
2.657
2.640
2.616
2.599
2.576
2.558
2.536
1.997
1.981
1.963
1.946
1.929
1.912
1.894
1.616
1.280
1.262
1.050
1.033
0.889
0.872
-0.000
Me
H
O
O
B
O
O
3c (1H NMR)
Solvent: CDCl3
0.98
0.97
2.00
0.99
2.01
1.02
2.94
12.40
3.06
3.13
8
7
6
5
4
3
2
1
0
PPM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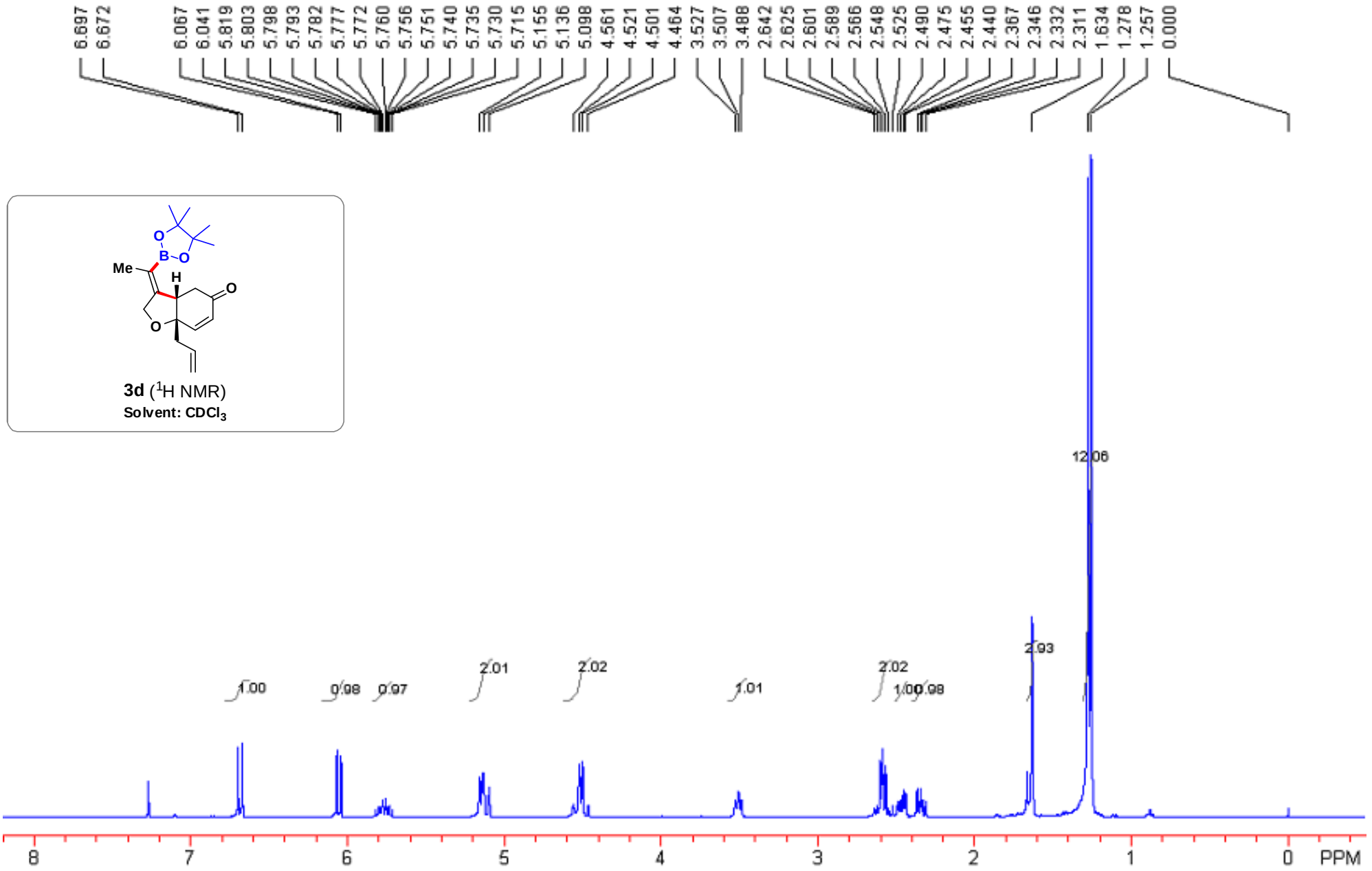
158.381
145.930
131.482
83.819
83.417
77.419
77.100
76.789
69.349
43.908
40.894
33.719
29.779
24.965
24.935
17.806
16.918
16.553
Me
H
O
B
O
O
O
3c (13C NMR)
Solvent: CDCl3
200
150
100
50
0PPM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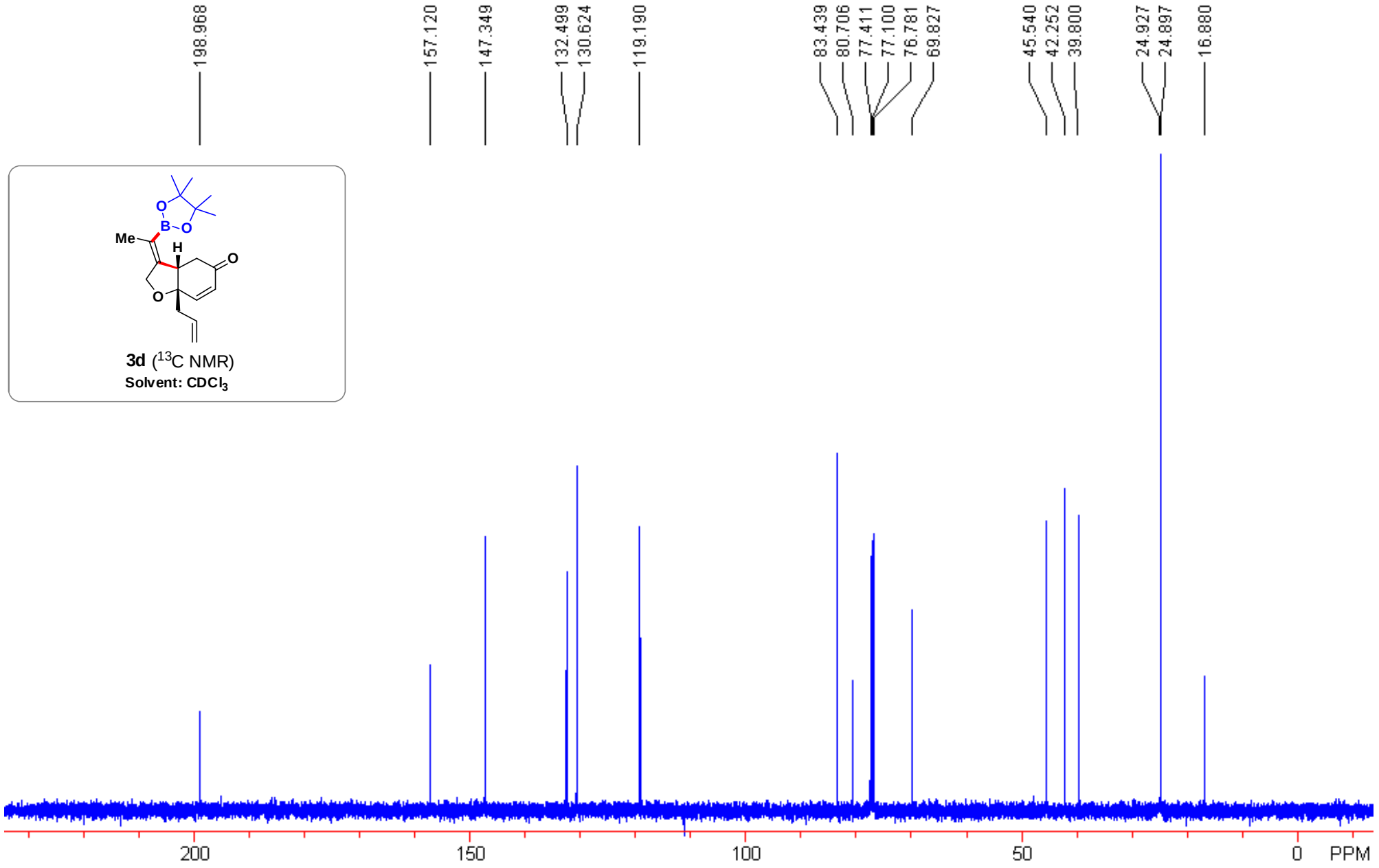
6.672
6.067
6.041
5.819
5.803
5.798
5.793
5.782
5.777
5.772
5.760
5.756
5.751
5.740
5.735
5.730
5.715
5.155
5.136
5.098
4.561
4.521
4.501
4.464
3.527
3.507
3.488
2.642
2.625
2.601
2.589
2.566
2.548
2.525
2.490
2.475
2.455
2.440
2.367
2.346
2.332
2.311
1.634
1.278
1.257
0.000
Me
H
O
O
B
O
3d (1H NMR)
Solvent: CDCl3
12.06
2.93
2.02
2.02
2.01
1.01
1.00
0.98
0.97
1.00
0.98
8
7
6
5
4
3
2
1
0
PPM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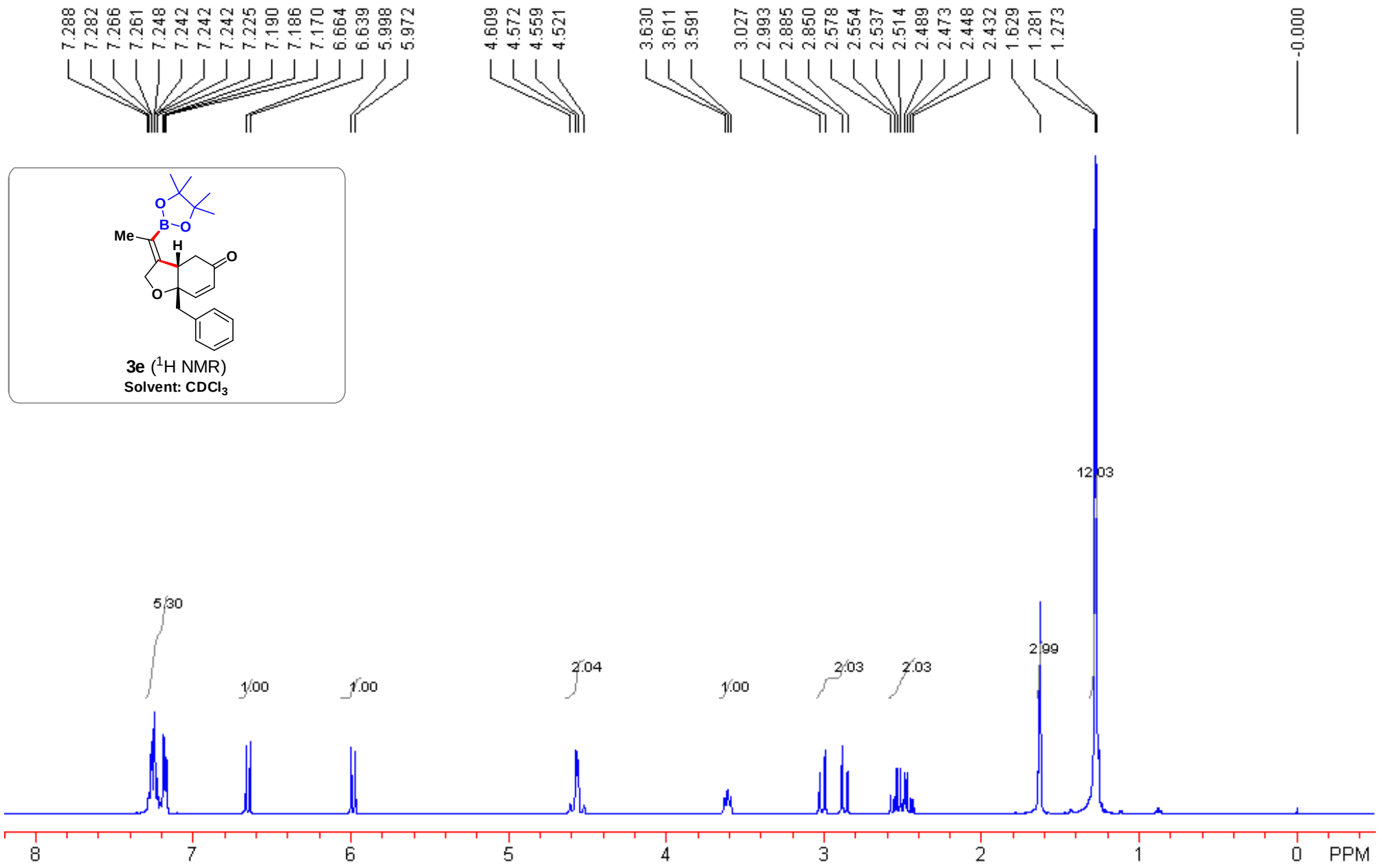
157.120
147.349
132.499
130.624
119.190
83.439
80.706
77.411
77.100
76.781
69.827
45.540
42.252
39.800
24.927
24.897
16.880
Me
H
O
O
B
O
O
3d (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM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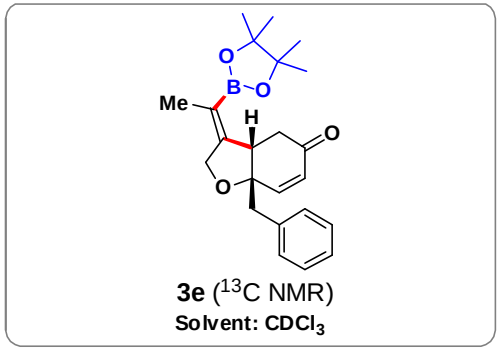
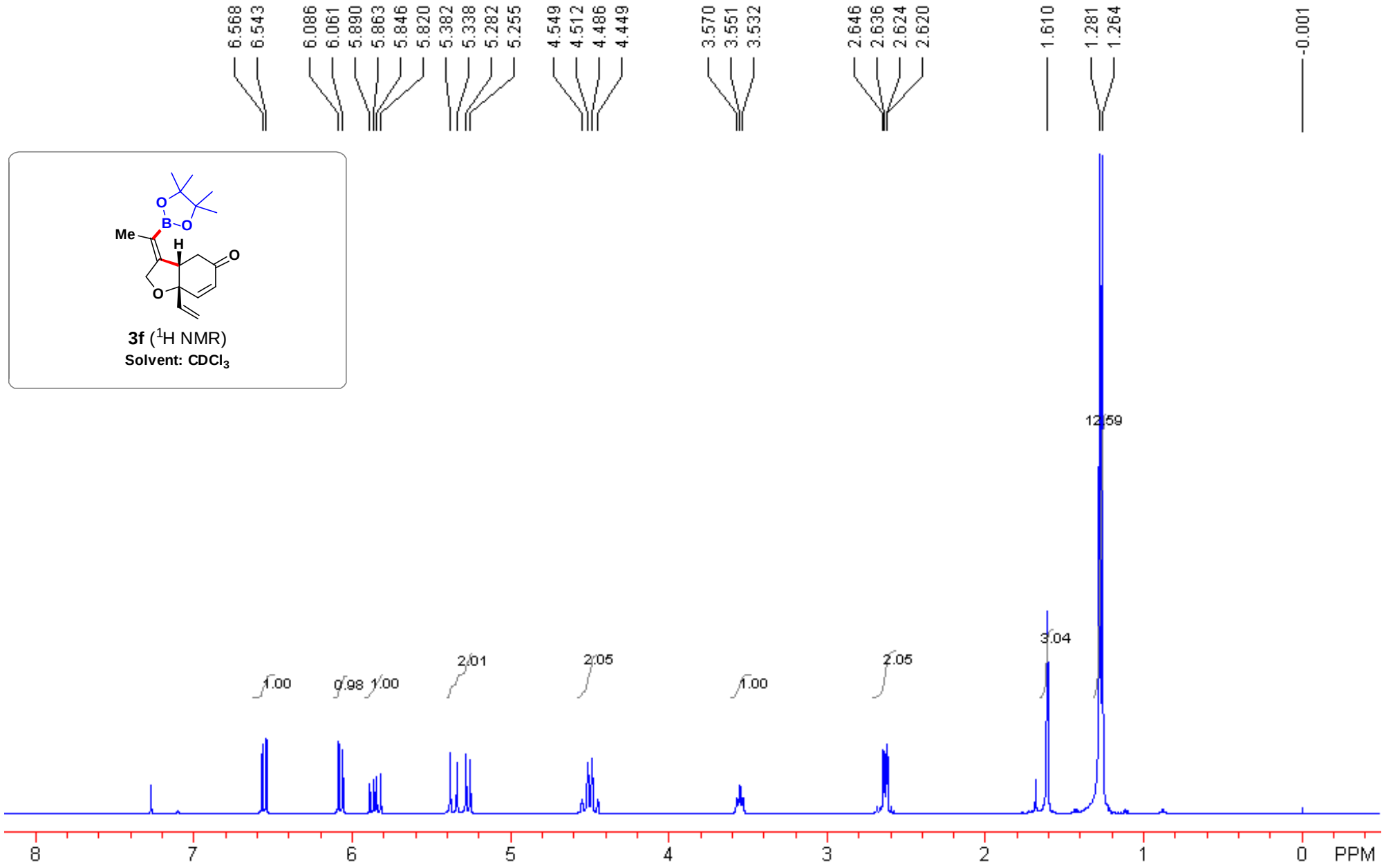
7.282
7.266
7.261
7.248
7.242
7.242
7.242
7.225
7.190
7.186
7.170
6.664
6.639
5.998
5.972
4.609
4.572
4.559
4.521
3.630
3.611
3.591
3.027
2.993
2.885
2.850
2.578
2.554
2.537
2.514
2.489
2.473
2.448
2.432
1.629
1.281
1.273
-0.000
Me
H
O
O
B
O
O
3e (1H NMR)
Solvent: CDCl3
5.30
1.00
1.00
2.04
1.00
2.03
2.03
2.99
12.03
8
7
6
5
4
3
2
1
0
PPM



3e (^{13}C NMR)

Solvent: $CDCl_3$

198.907
157.082
147.357
135.908
130.556
130.495
128.293
126.904
83.439
81.579
77.411
77.100
76.781
69.933
45.471
44.075
39.732
24.935
16.910
200
150
100
50
0
PPM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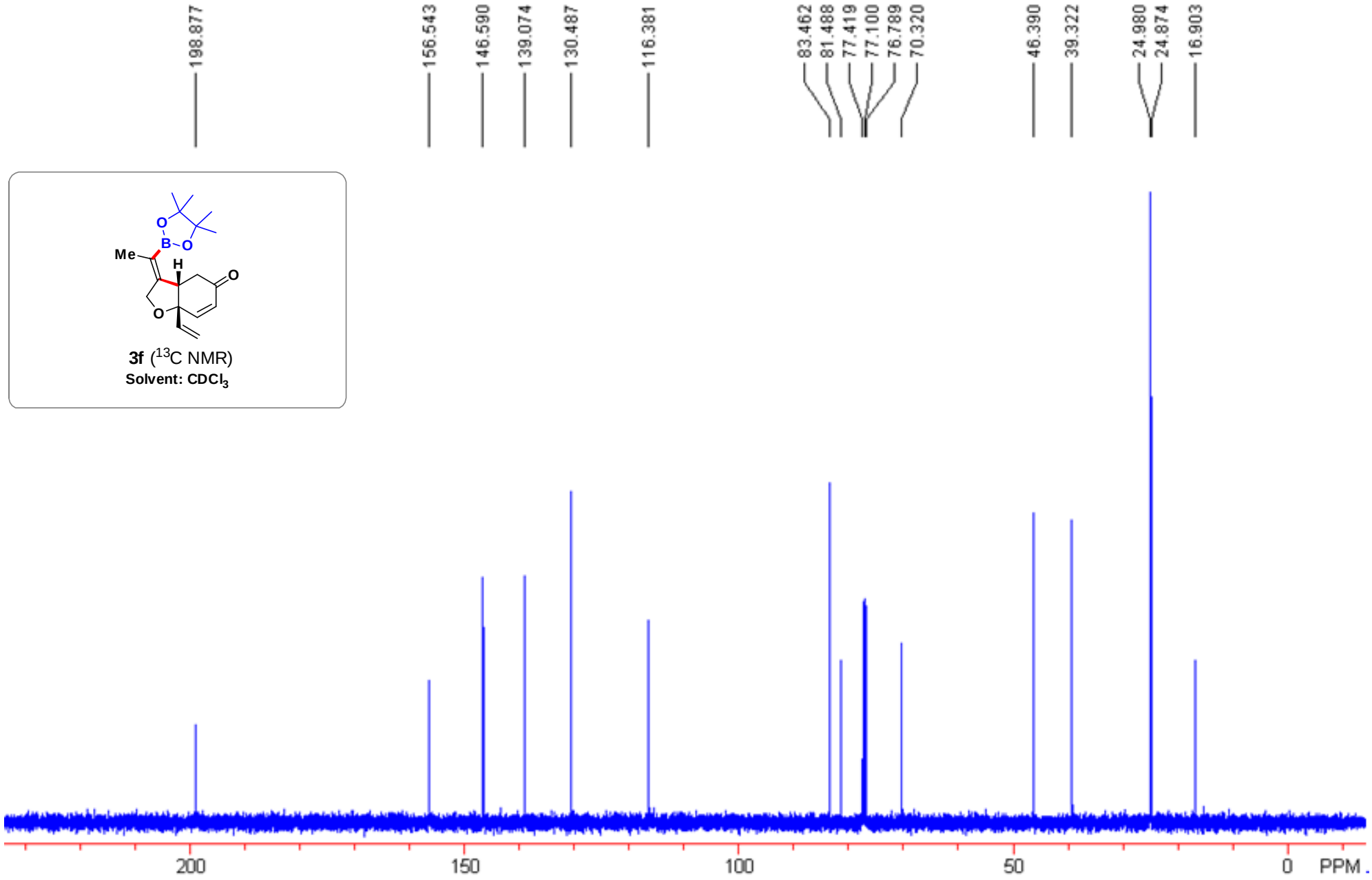
6.543
6.086
6.061
5.890
5.863
5.846
5.820
5.382
5.338
5.282
5.255
4.549
4.512
4.486
4.449
3.570
3.551
3.532
2.646
2.636
2.624
2.620
1.610
1.281
1.264
-0.001
Me
H
O
O
B
O
O
3f (1H NMR)
Solvent: CDCl3
1.00
0.98
1.00
2.01
2.05
1.00
2.05
3.04
12.59
8
7
6
5
4
3
2
1
0
PPM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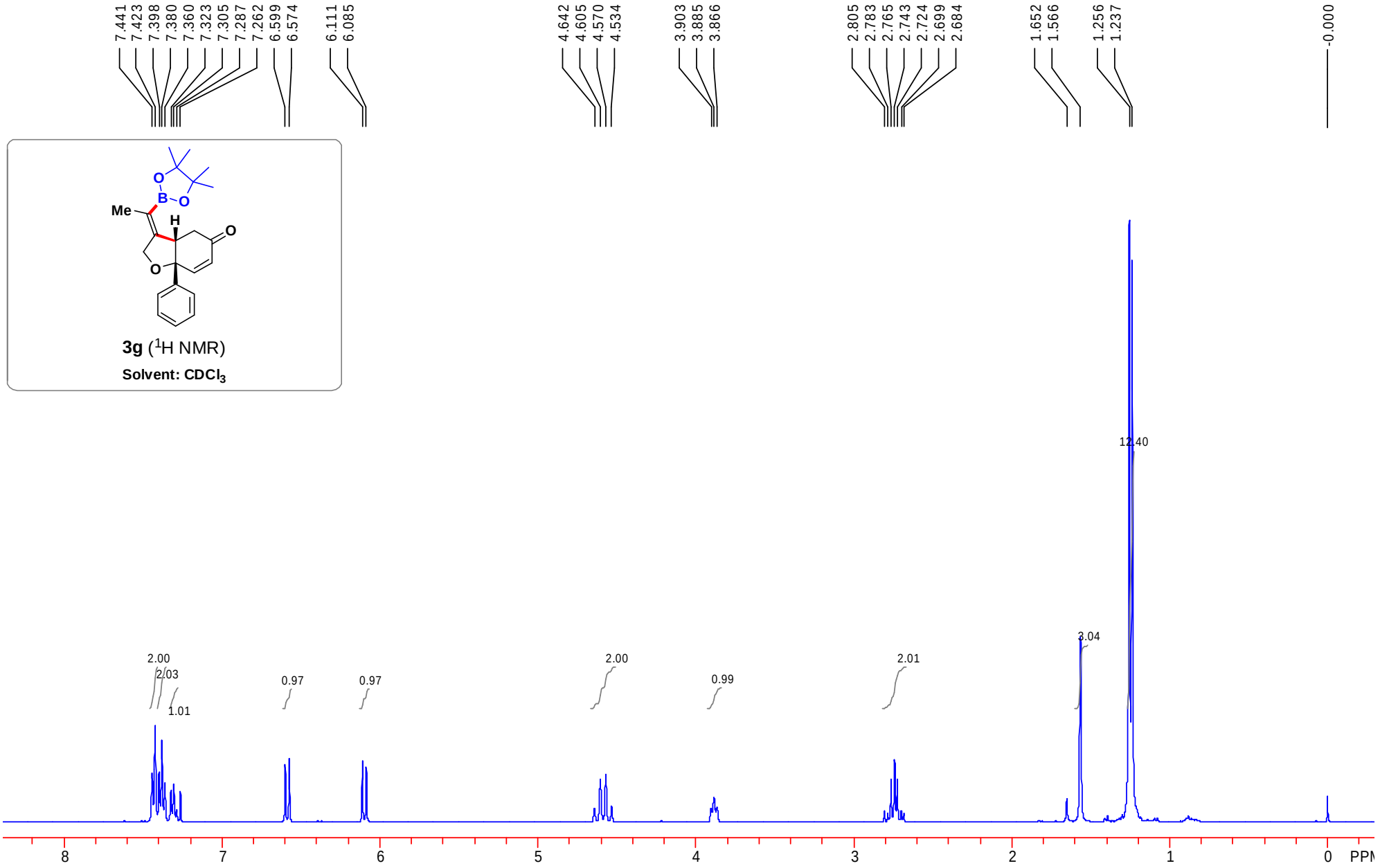
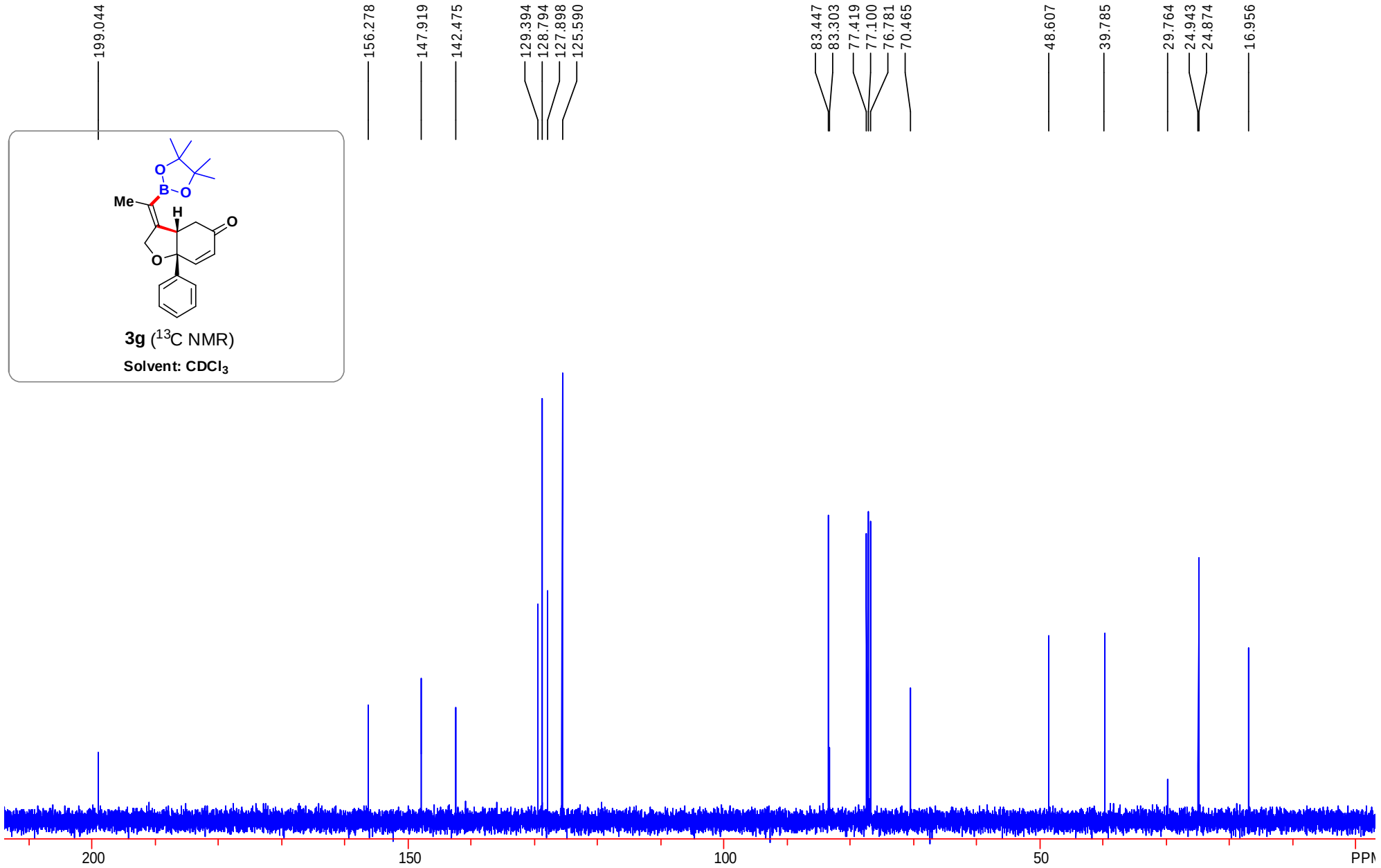
146.590
139.074
130.487
116.381
83.462
81.488
77.419
77.100
76.789
70.320
46.390
39.322
24.980
24.874
16.903
Me
H
O
B
O
O
O
3f (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM


7.441
7.423
7.398
7.380
7.360
7.323
7.305
7.287
7.262
6.599
6.574
6.111
6.085
4.642
4.605
4.570
4.534
3.903
3.885
3.866
2.805
2.783
2.765
2.743
2.724
2.699
2.684
1.652
1.566
1.256
1.237
-0.000
Me
H
O
B
O
O
O
3g (1H NMR)
Solvent: CDCl3
2.00
2.03
1.01
0.97
0.97
2.00
0.99
2.01
3.04
12.40
8
7
6
5
4
3
2
1
0
PPM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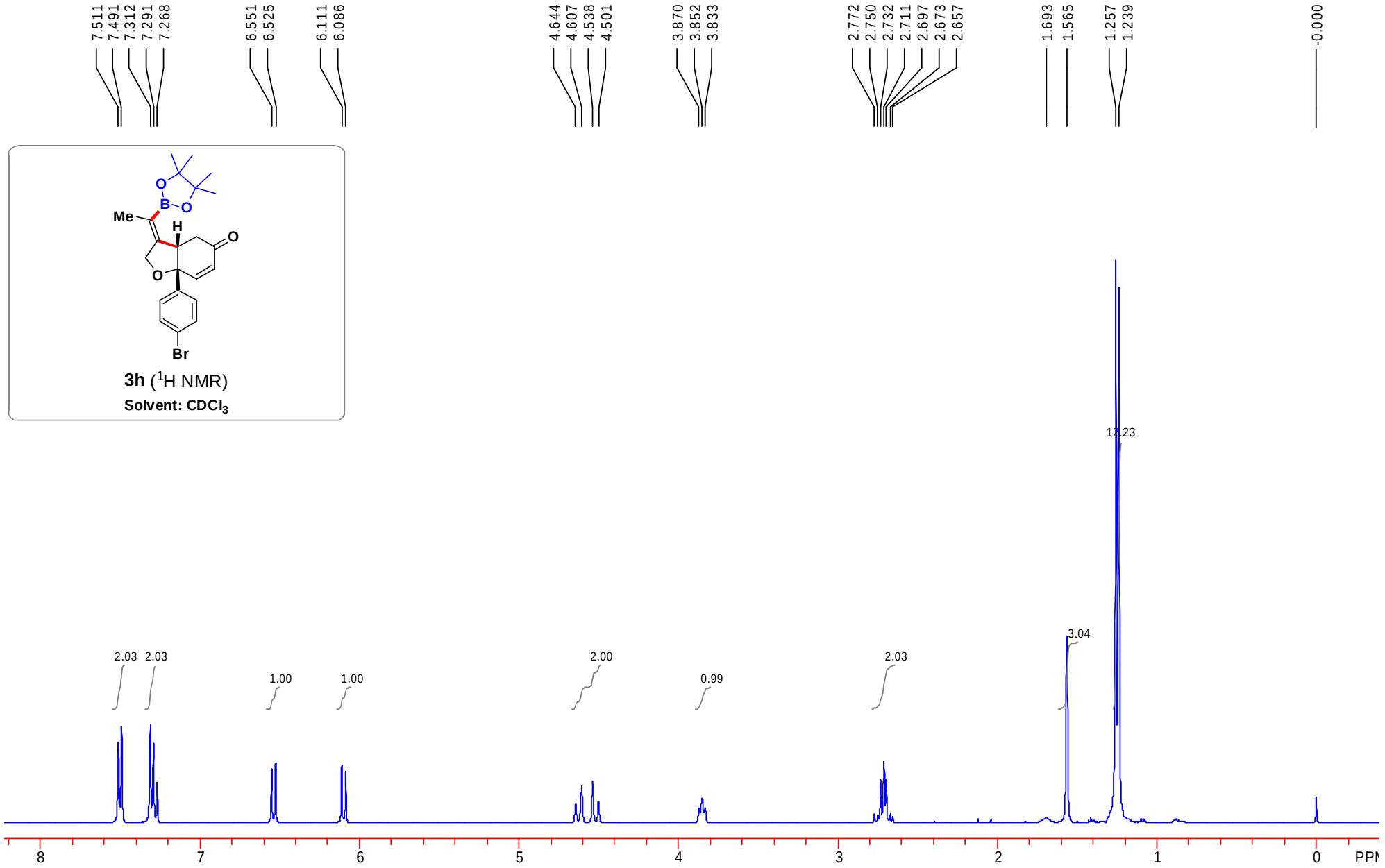
128.794
127.898
125.590
83.447
83.303
77.419
77.100
76.781
70.465
48.607
39.785
29.764
24.943
24.874
16.956
Me
H
O
O
B
O
O
3g (13C NMR)
Solvent: CDCl3
200
150
100
50
PPM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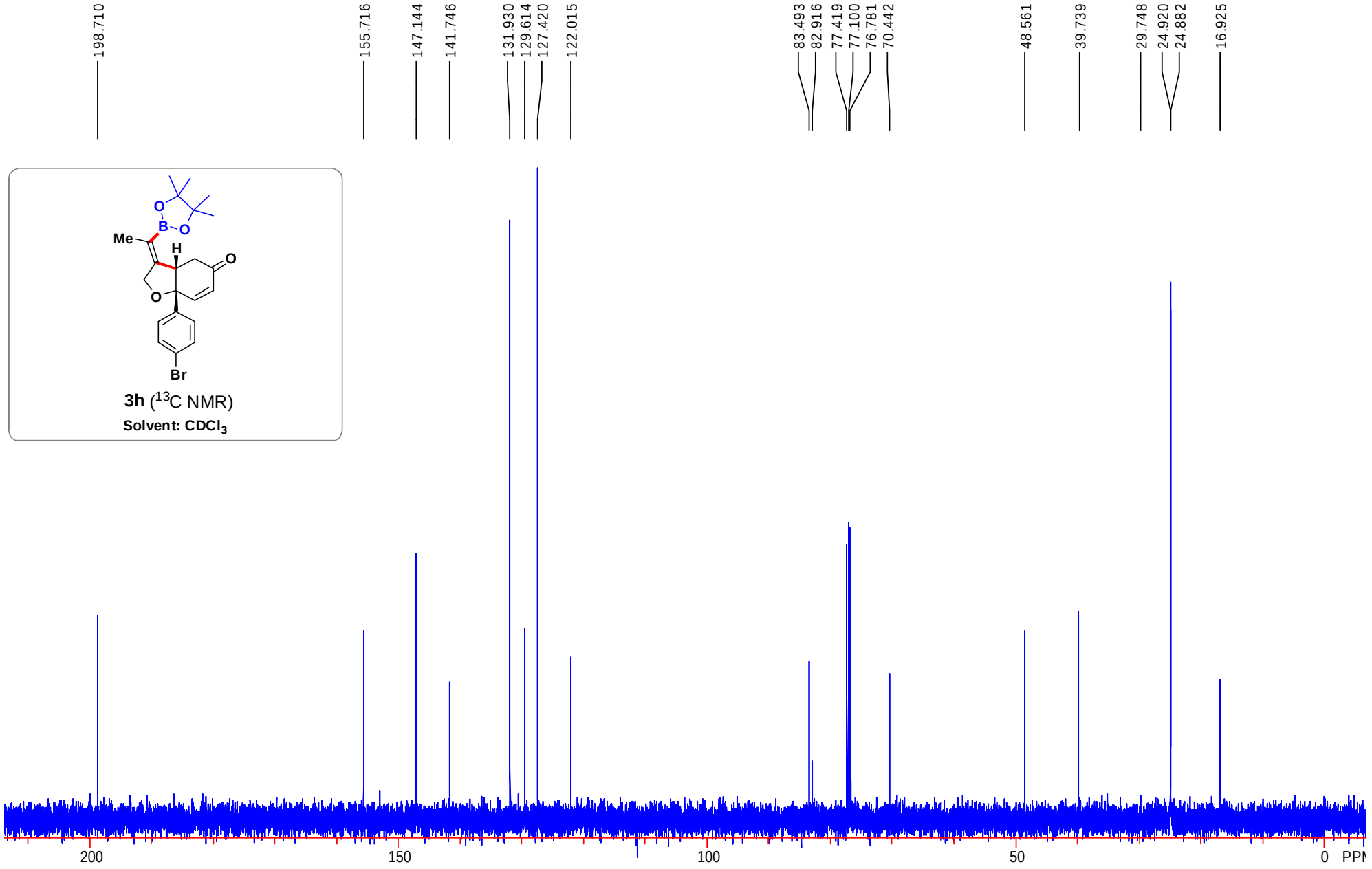
7.491
7.312
7.291
7.268
6.551
6.525
6.111
6.086
4.644
4.607
4.538
4.501
3.870
3.852
3.833
2.772
2.750
2.732
2.711
2.697
2.673
2.657
1.693
1.565
1.257
1.239
-0.000
Me
H
O
O
B
O
O
Br
3h (1H NMR)
Solvent: CDCl3
2.03
2.03
1.00
1.00
2.00
0.99
2.03
3.04
12.23
8
7
6
5
4
3
2
1
0
PPM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131.930
129.614
127.420
122.015
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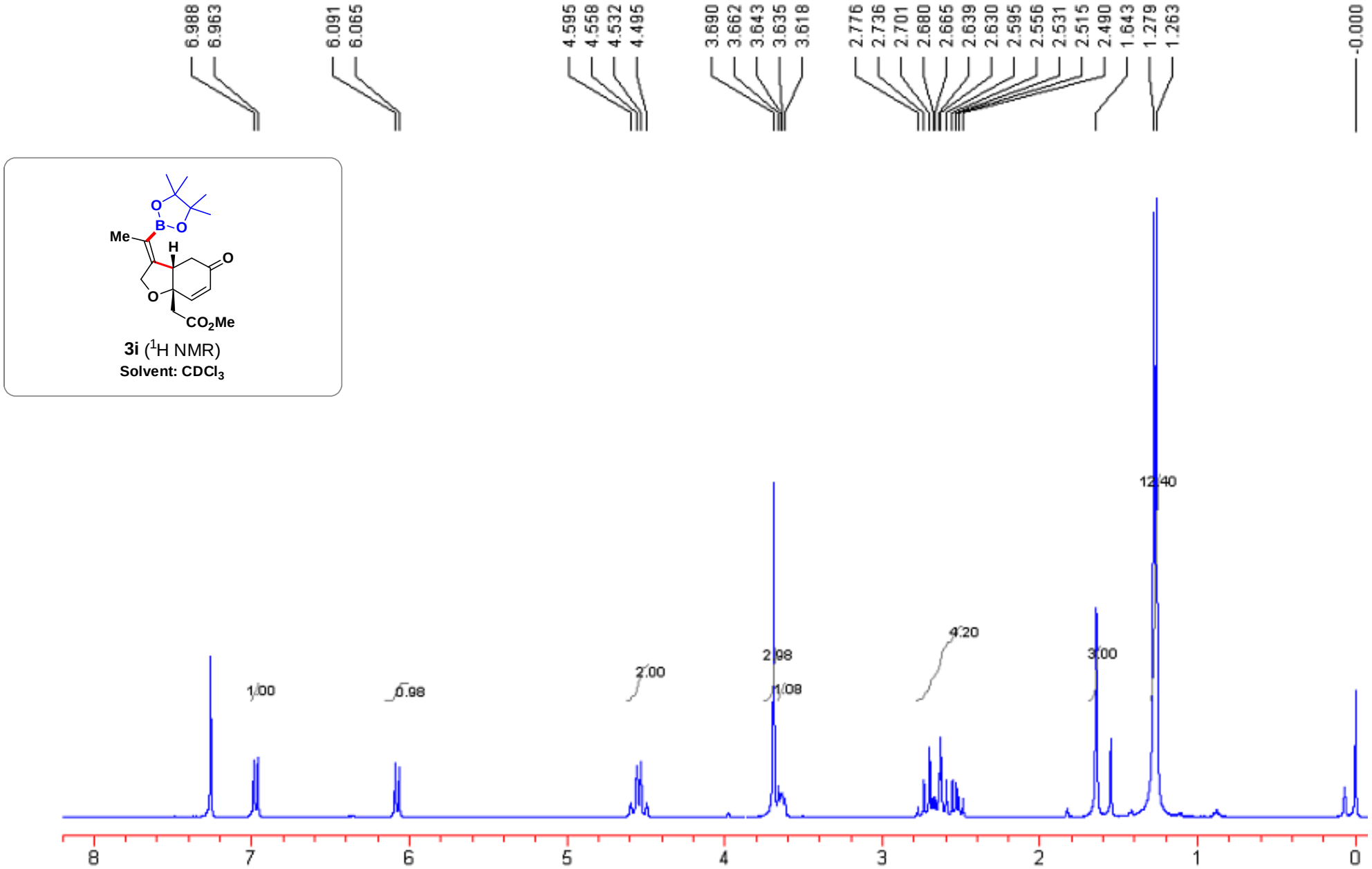
82.916
77.419
77.100
76.781
70.442
48.561
39.739
29.748
24.920
24.882
16.925
Me
H
O
B
O
O
O
Br
3h (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM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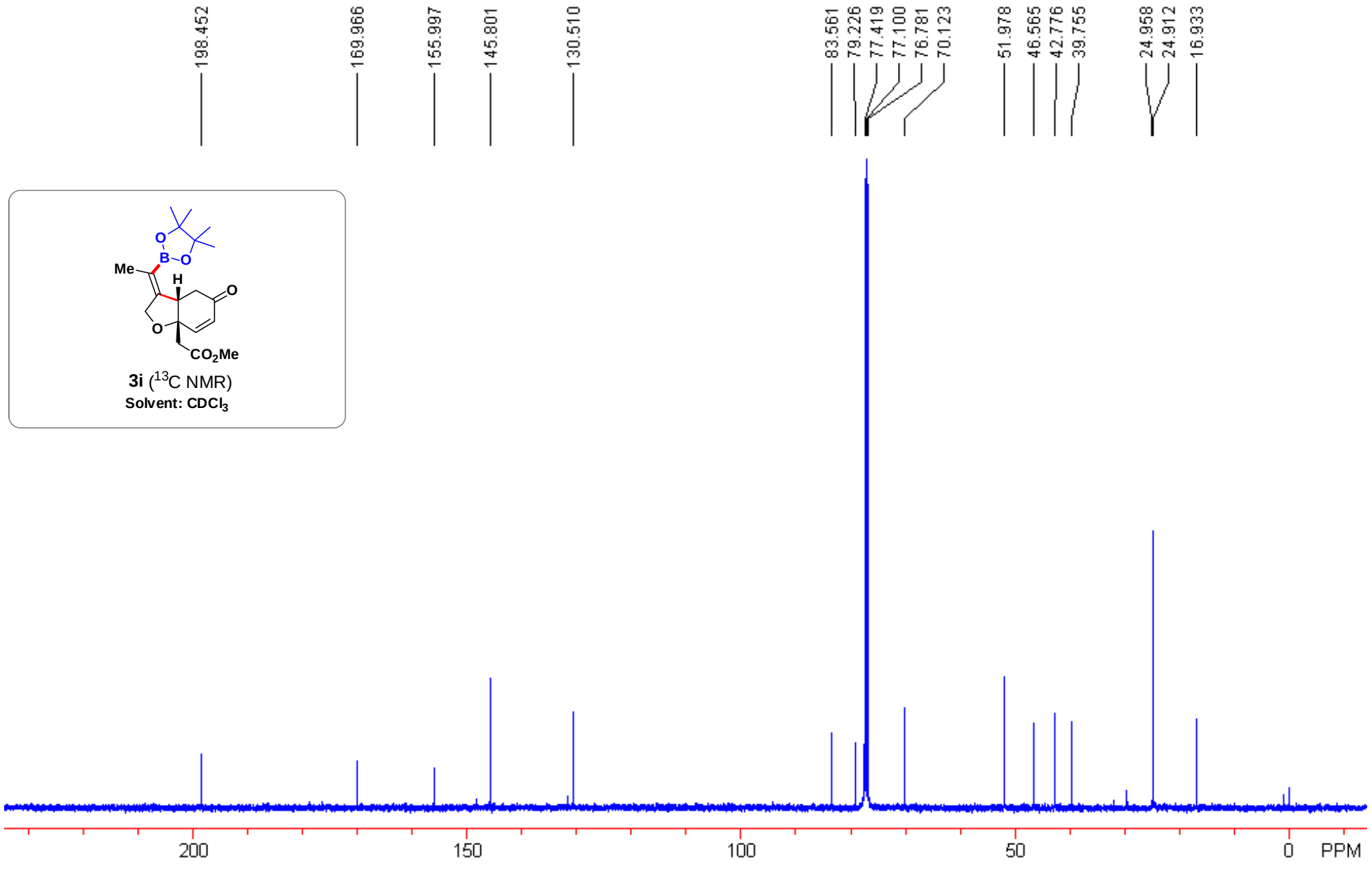
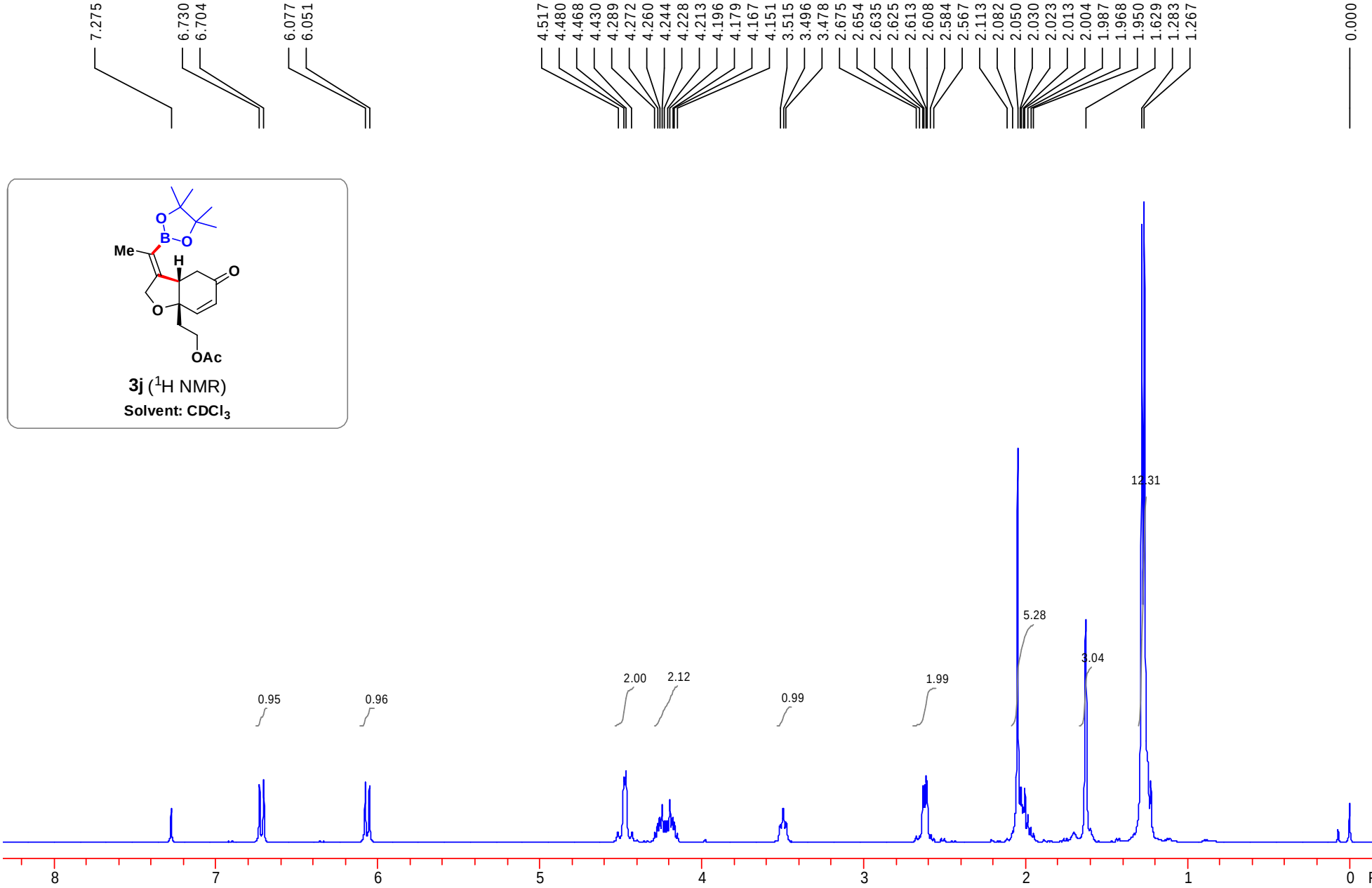
6.963
6.091
6.065
4.595
4.558
4.532
4.495
3.690
3.662
3.643
3.635
3.618
2.776
2.736
2.701
2.680
2.665
2.639
2.630
2.595
2.556
2.531
2.515
2.490
1.643
1.279
1.263
-0.000
Me
H
O
O
B
O
O
CO2Me
3i (1H NMR)
Solvent: CDCl3
1.00
0.98
2.00
2.98
1.08
4.20
3.00
12.40
8
7
6
5
4
3
2
1
0


198.452
169.966
155.997
145.801
130.510
83.561
79.226
77.419
77.100
76.781
70.123
51.978
46.565
42.776
39.755
24.958
24.912
16.933
Me
H
O
O
B
O
O
CO2Me
3i (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM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6.730
6.704
6.077
6.051
4.517
4.480
4.468
4.430
4.289
4.272
4.260
4.244
4.228
4.213
4.196
4.179
4.167
4.151
3.515
3.496
3.478
2.675
2.654
2.635
2.625
2.613
2.608
2.584
2.567
2.113
2.082
2.050
2.030
2.023
2.013
2.004
1.987
1.968
1.950
1.629
1.283
1.267
0.000
Me
H
O
B
O
O
O
OAc
3j (1H NMR)
Solvent: CDCl3
0.95
0.96
2.00
2.12
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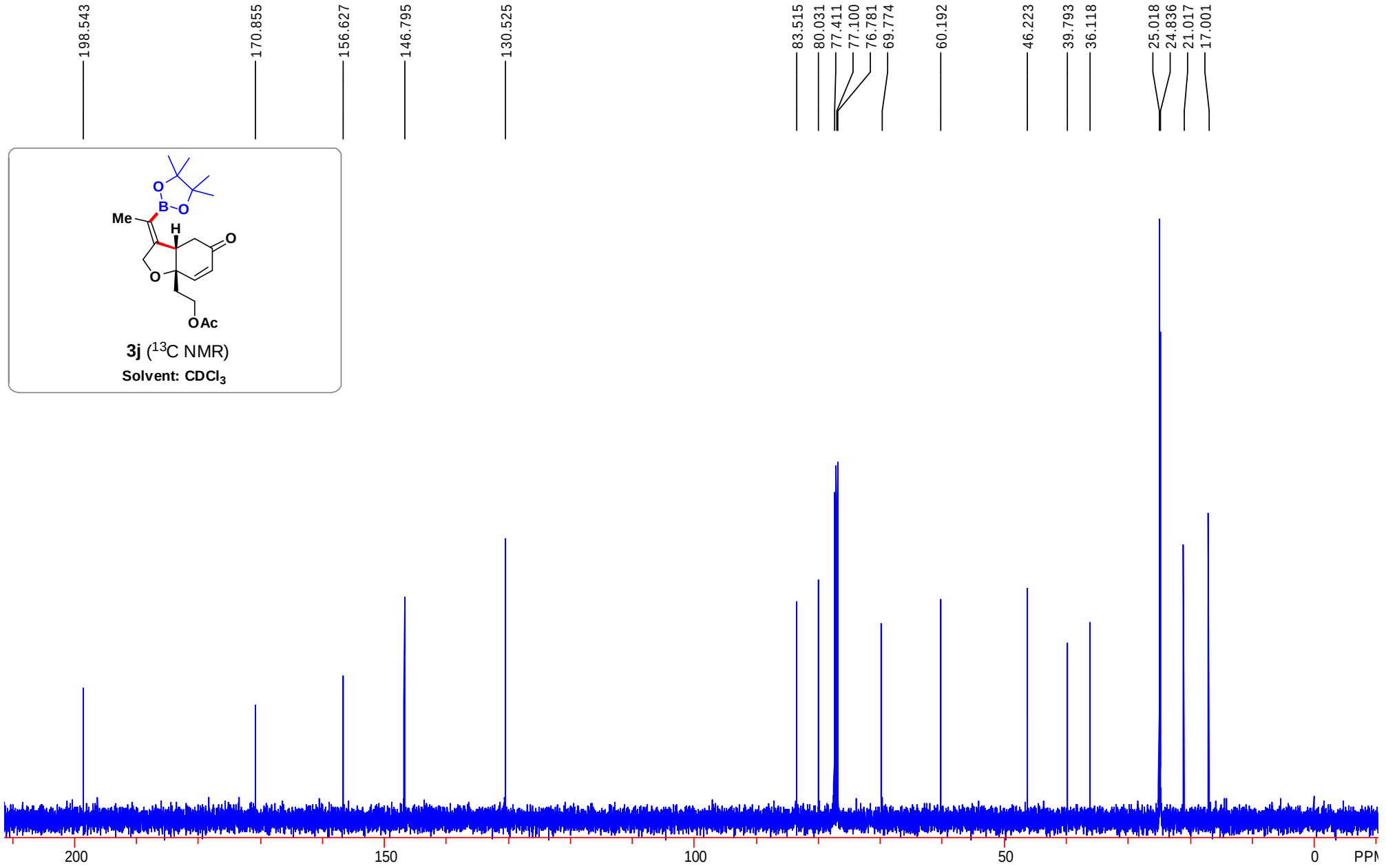
1.99
5.28
3.04
12.31
8
7
6
5
4
3
2
1
0
PPM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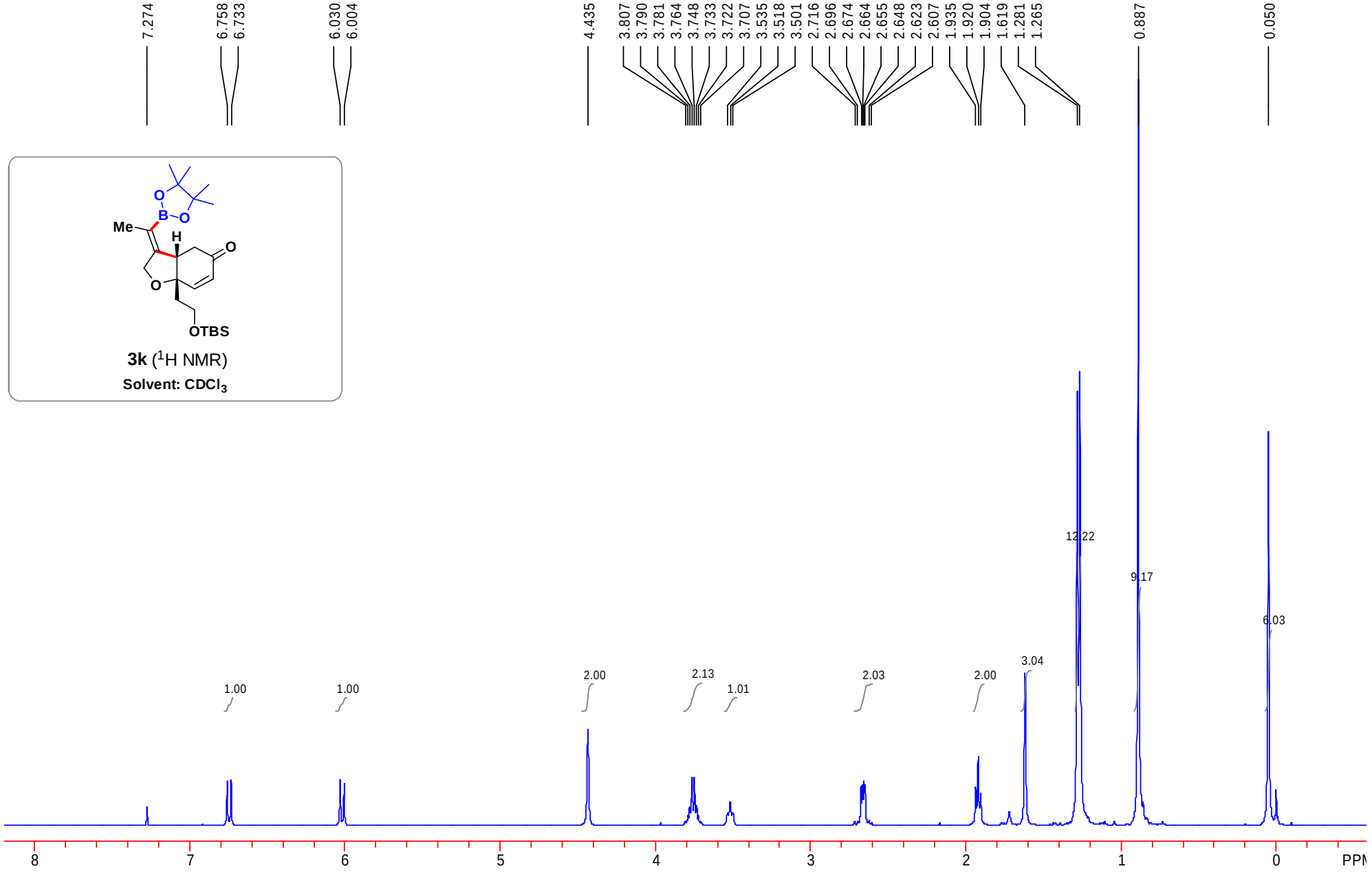
170.855
156.627
146.795
130.525
83.515
80.031
77.411
77.100
76.781
69.774
60.192
46.223
39.793
36.118
25.018
24.836
21.017
17.001
Me
H
O
B
O
O
O
OAc
3j (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM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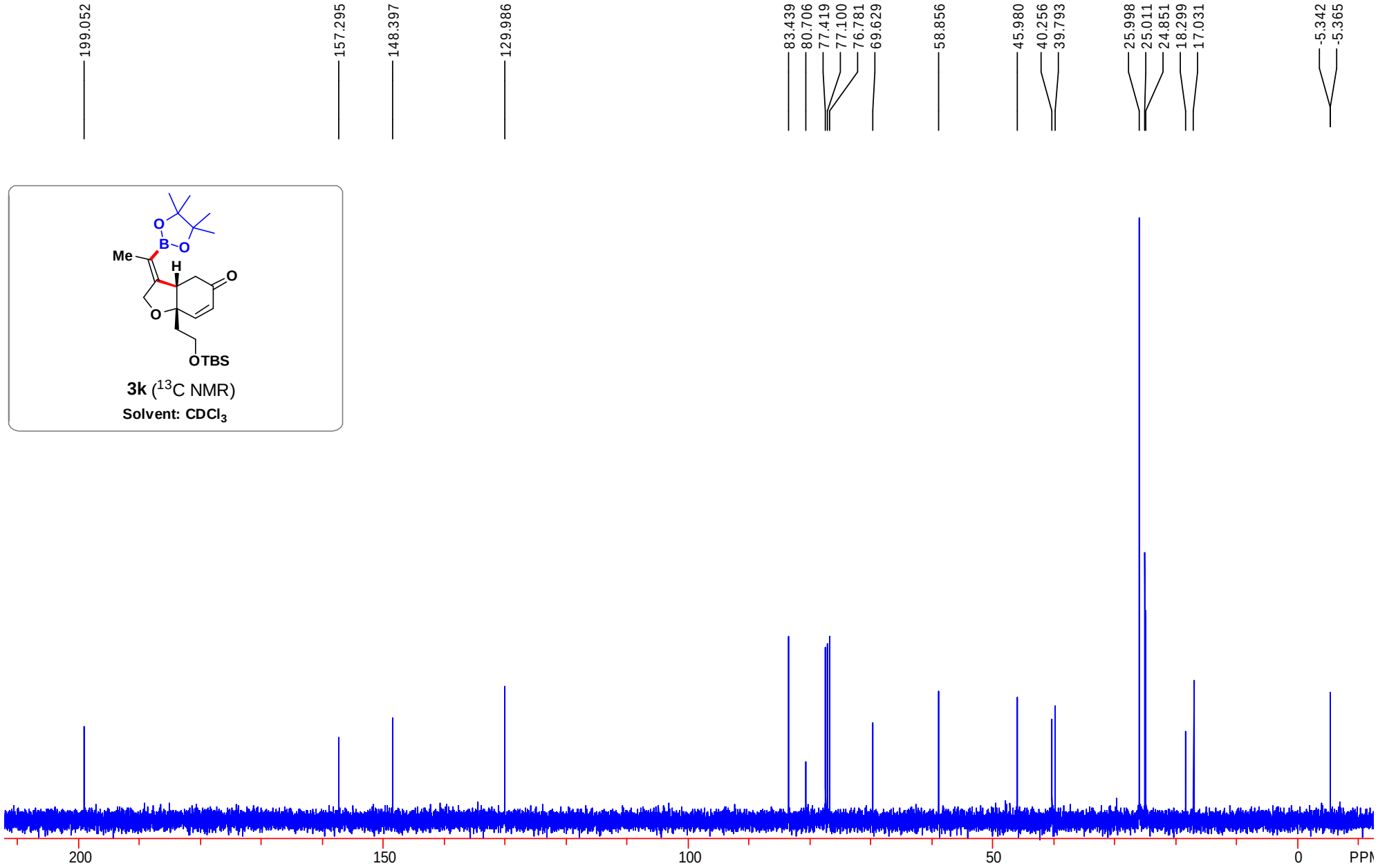
6.733
6.030
6.004
4.435
3.807
3.790
3.781
3.764
3.748
3.733
3.722
3.707
3.535
3.518
3.501
2.716
2.696
2.674
2.664
2.655
2.648
2.623
2.607
1.935
1.920
1.904
1.619
1.281
1.265
0.887
0.050
Me
H
O
O
B
O
O
OTBS
3k (1H NMR)
Solvent: CDCl3
1.00
1.00
2.00
2.13
1.01
2.03
2.00
3.04
12.22
9.17
6.03
8
7
6
5
4
3
2
1
0
PPM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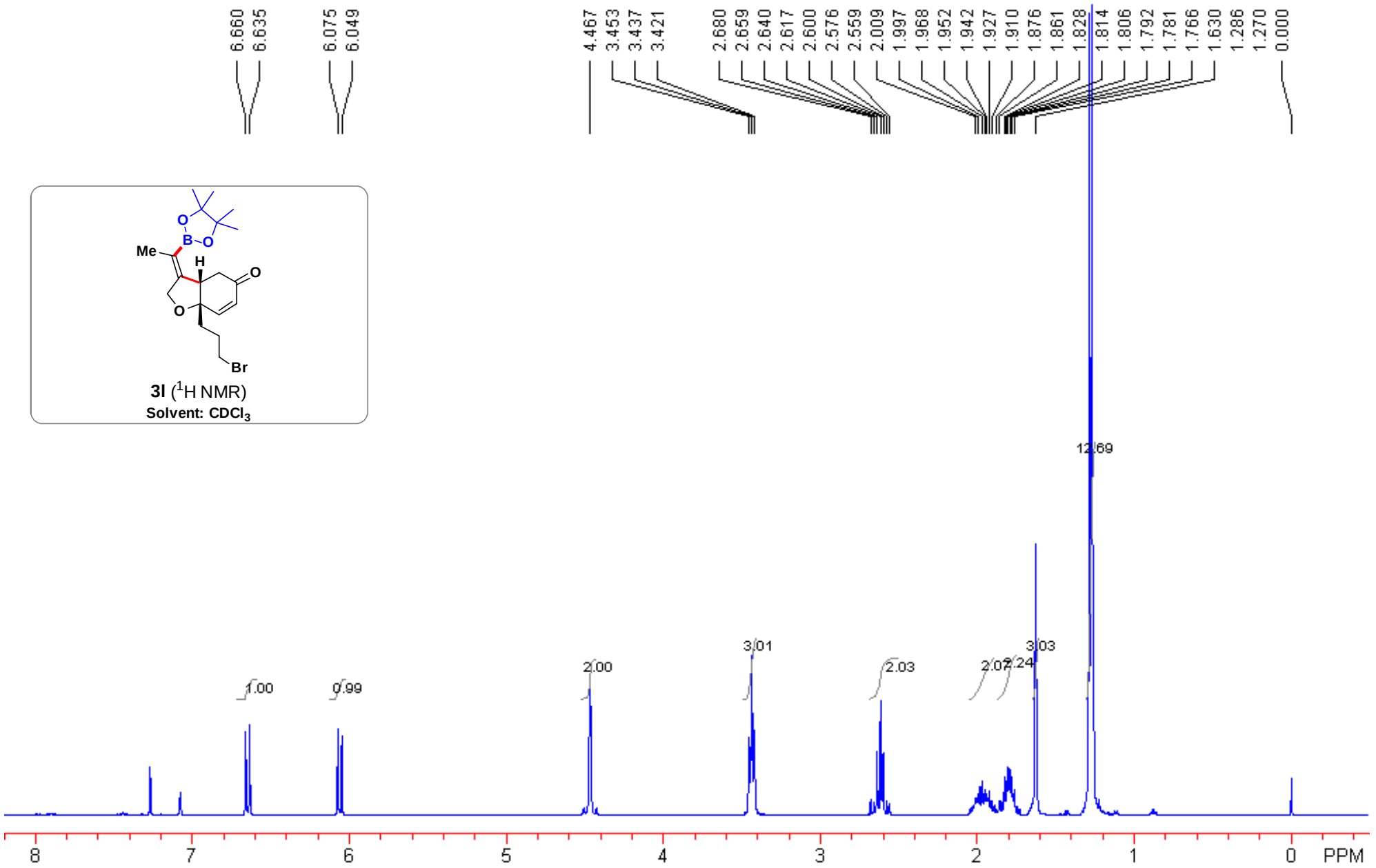
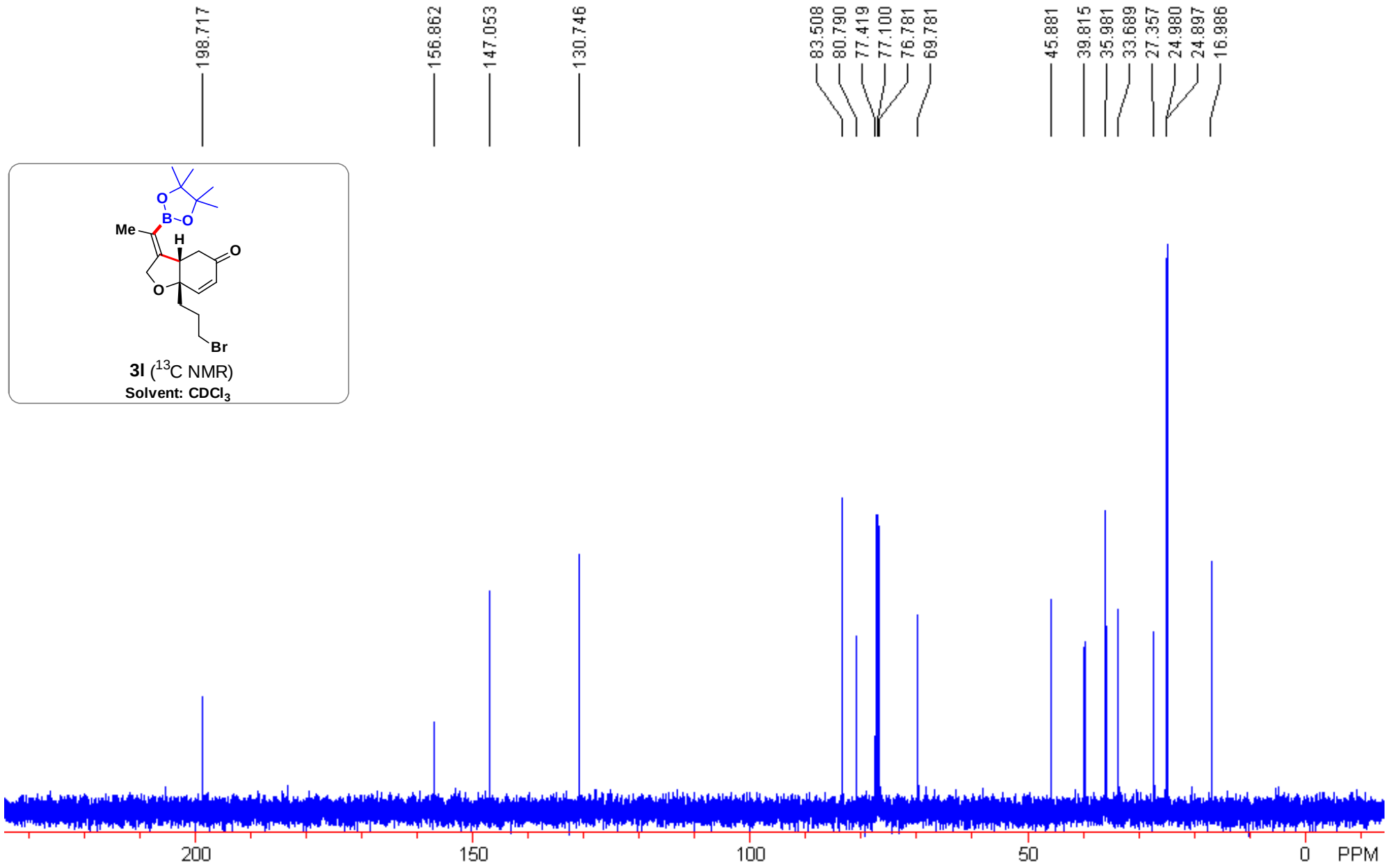
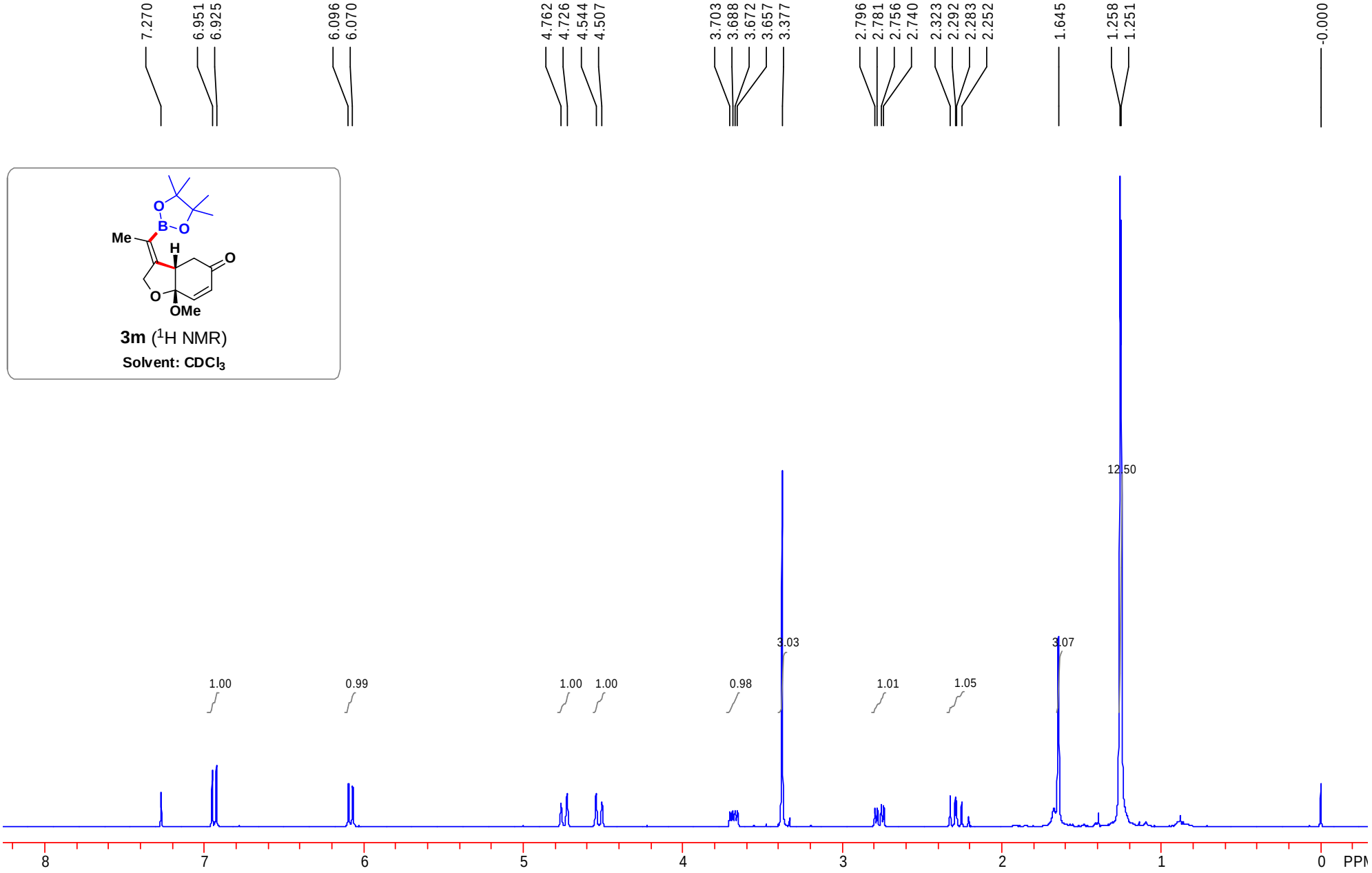
148.397
129.986
83.439
80.706
77.419
77.100
76.781
69.629
58.856
45.980
40.256
39.793
25.998
25.011
24.851
18.299
17.031
-5.342
-5.365
Me
H
O
O
B
O
O
OTBS
3k (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM

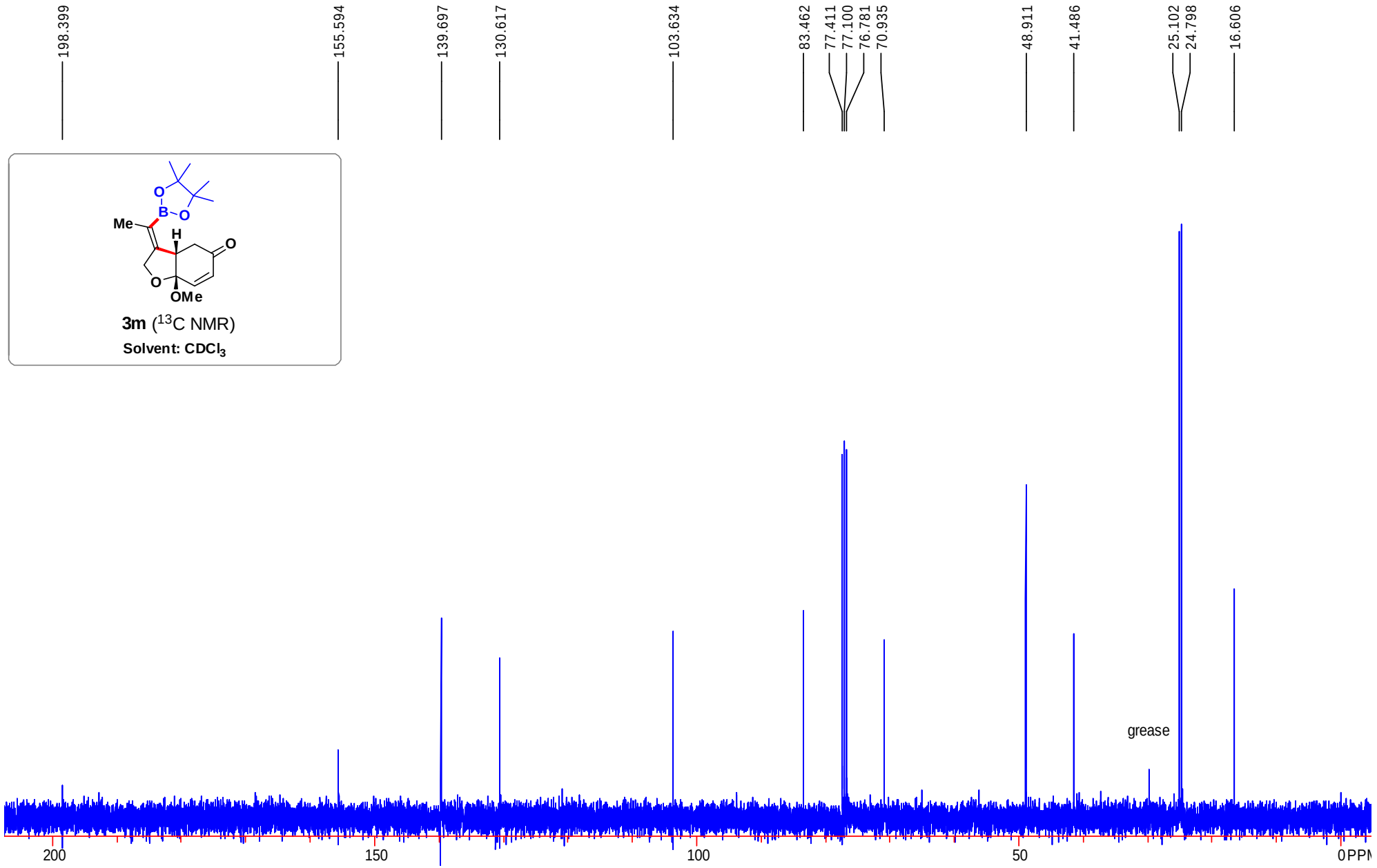

6.660
6.635
6.075
6.049
4.467
3.453
3.437
3.421
2.680
2.659
2.640
2.617
2.600
2.576
2.559
2.009
1.997
1.968
1.952
1.942
1.927
1.910
1.876
1.861
1.828
1.814
1.806
1.792
1.781
1.766
1.630
1.286
1.270
0.000
Me
H
O
O
B
O
O
Br
3l (1H NMR)
Solvent: CDCl3
12.69
3.03
3.01
2.24
2.07
2.03
2.00
1.00
0.99
8
7
6
5
4
3
2
1
0
PPM

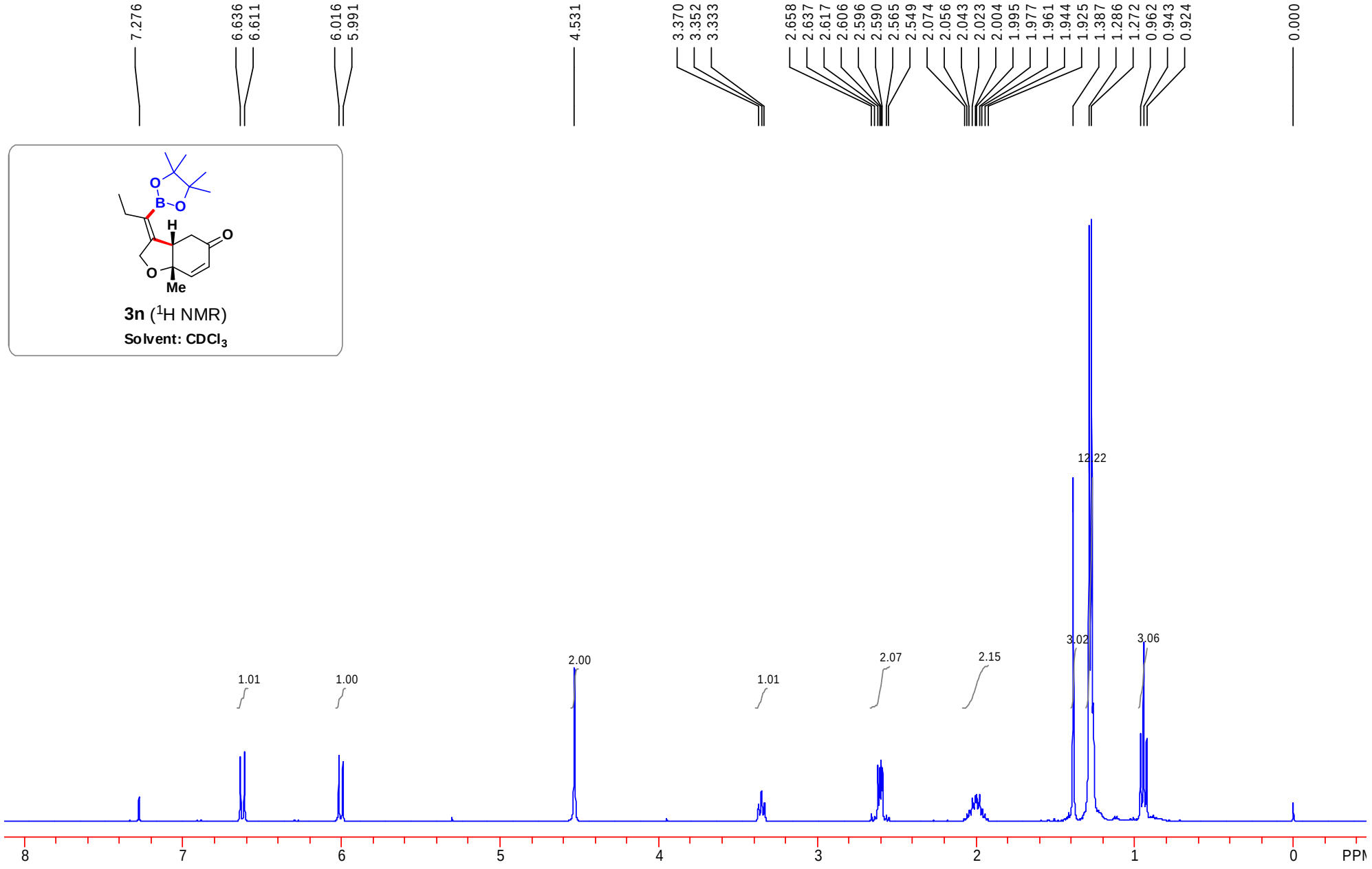


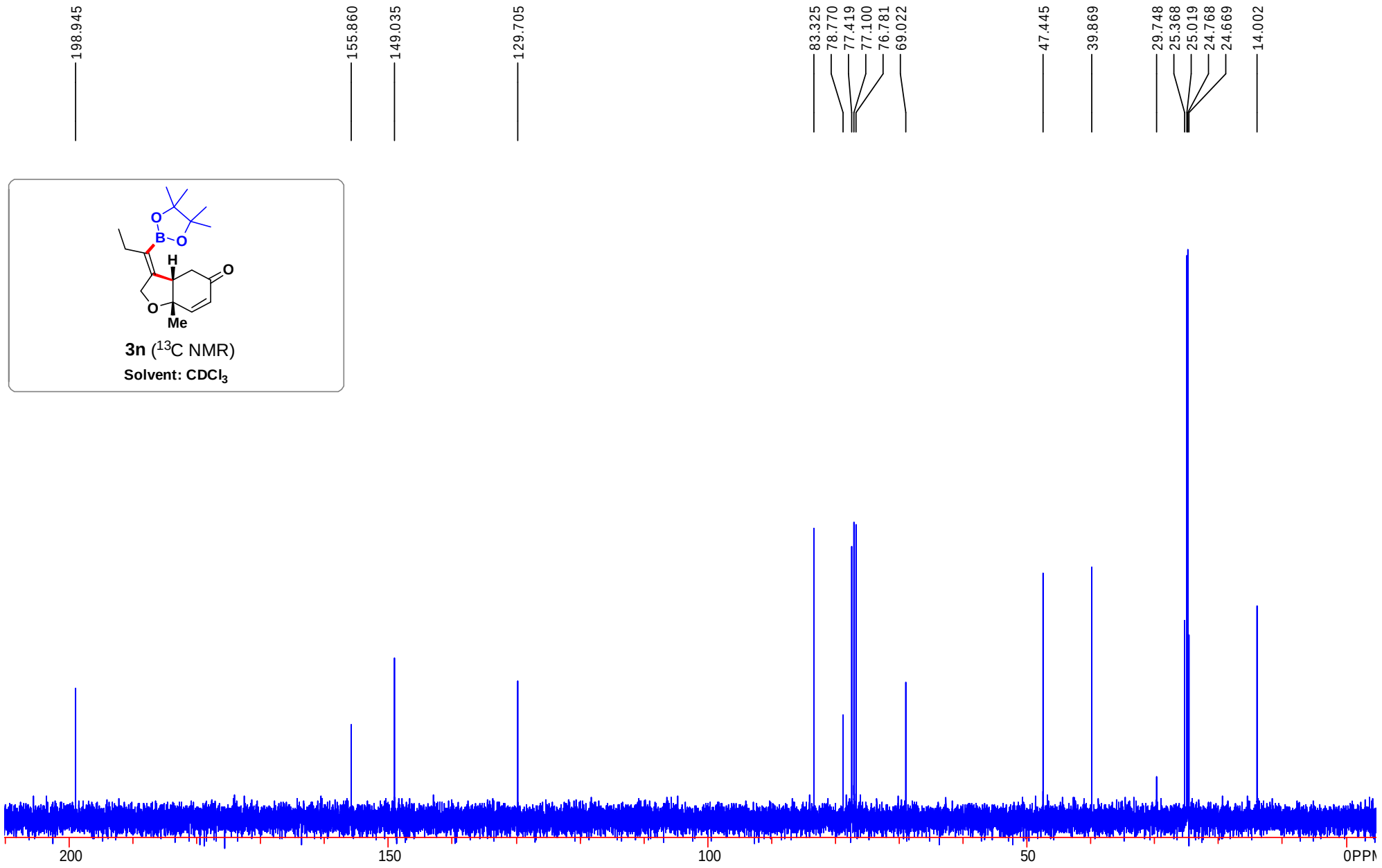
3l (^{13}C NMR)

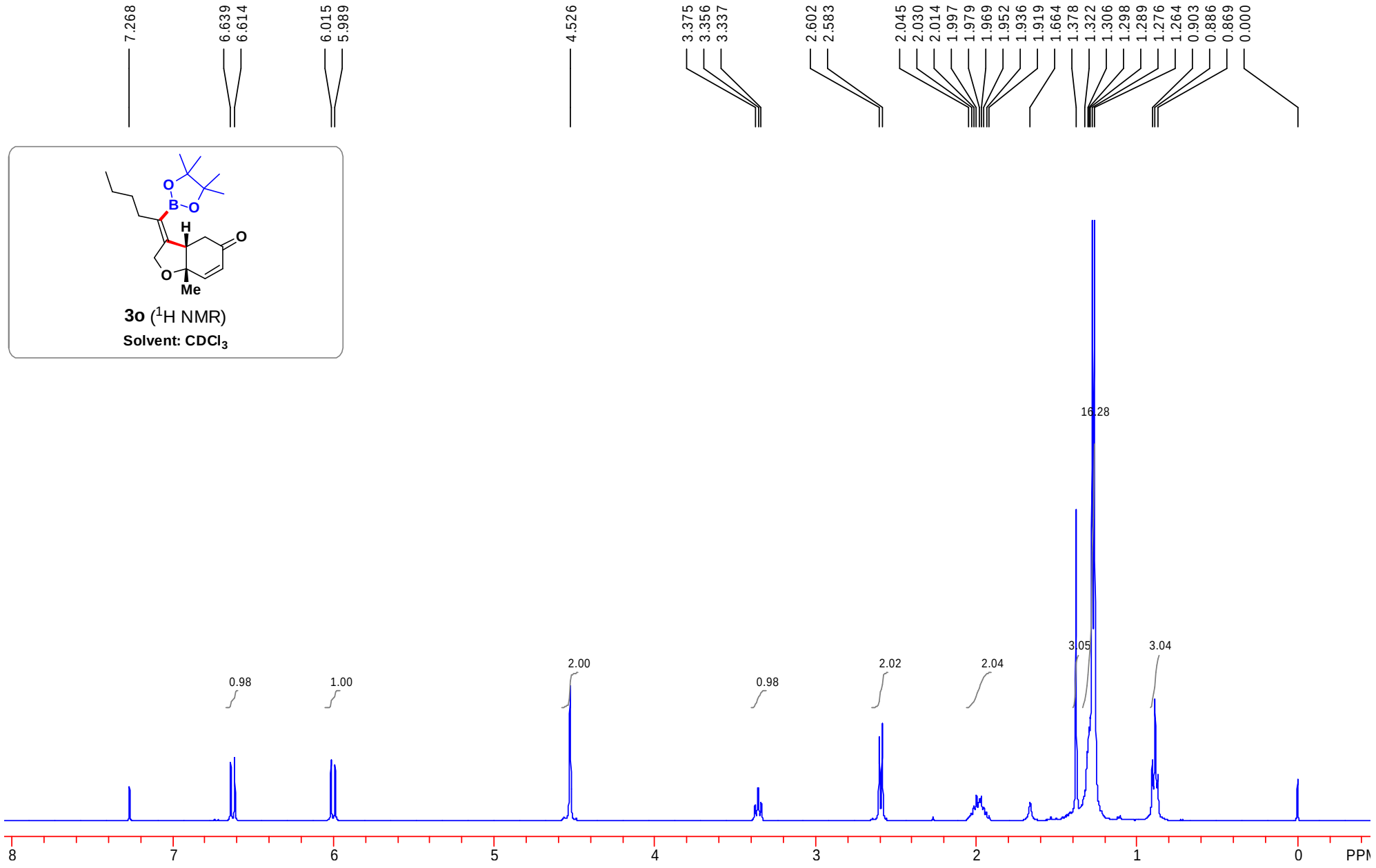
Solvent: $CDCl_3$

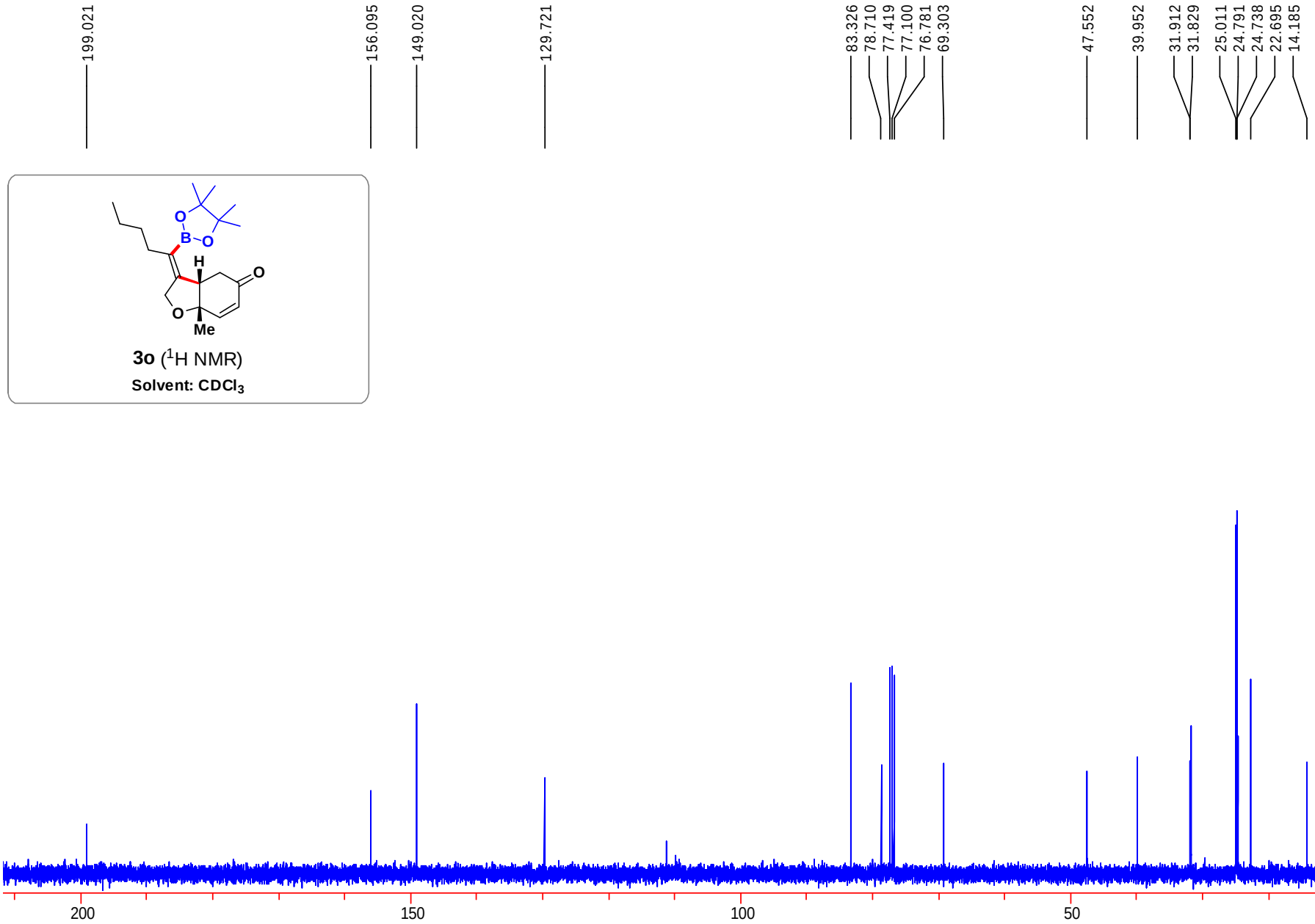

7.270
6.951
6.925
6.096
6.070
4.762
4.726
4.544
4.507
3.703
3.688
3.672
3.657
3.377
2.796
2.781
2.756
2.740
2.323
2.292
2.283
2.252
1.645
1.258
1.251
-0.000
Me
H
O
O
B
O
O
OMe
3m (1H NMR)
Solvent: CDCl3
12.50
3.03
3.07
1.00
0.99
1.00
1.00
0.98
1.01
1.05
8
7
6
5
4
3
2
1
0
PPM

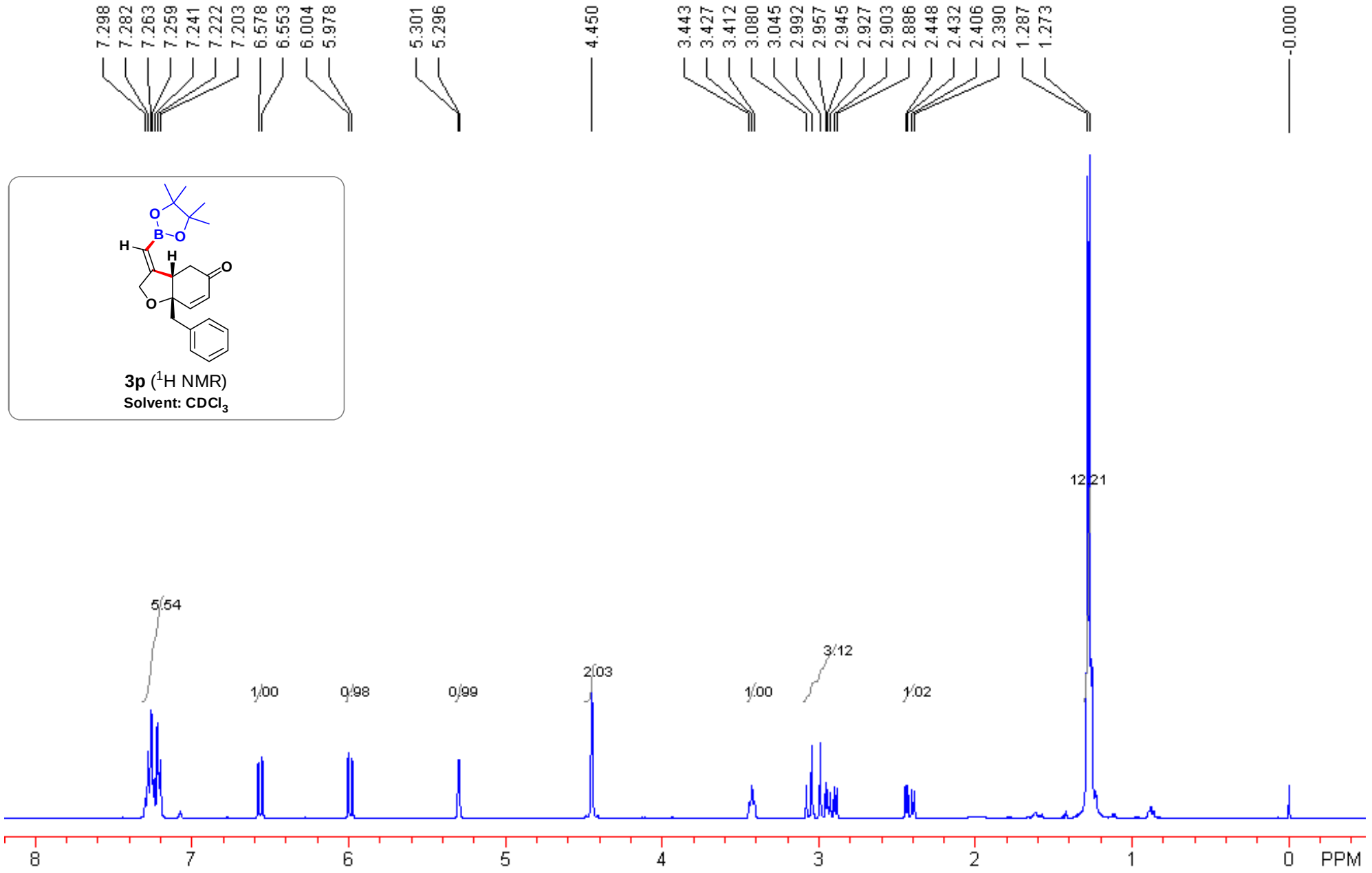

198.399
155.594
139.697
130.617
103.634
83.462
77.411
77.100
76.781
70.935
48.911
41.486
25.102
24.798
16.606
Me
H
O
O
B
O
O
OMe
3m (13C NMR)
Solvent: CDCl3
grease
200
150
100
50
0 PPM

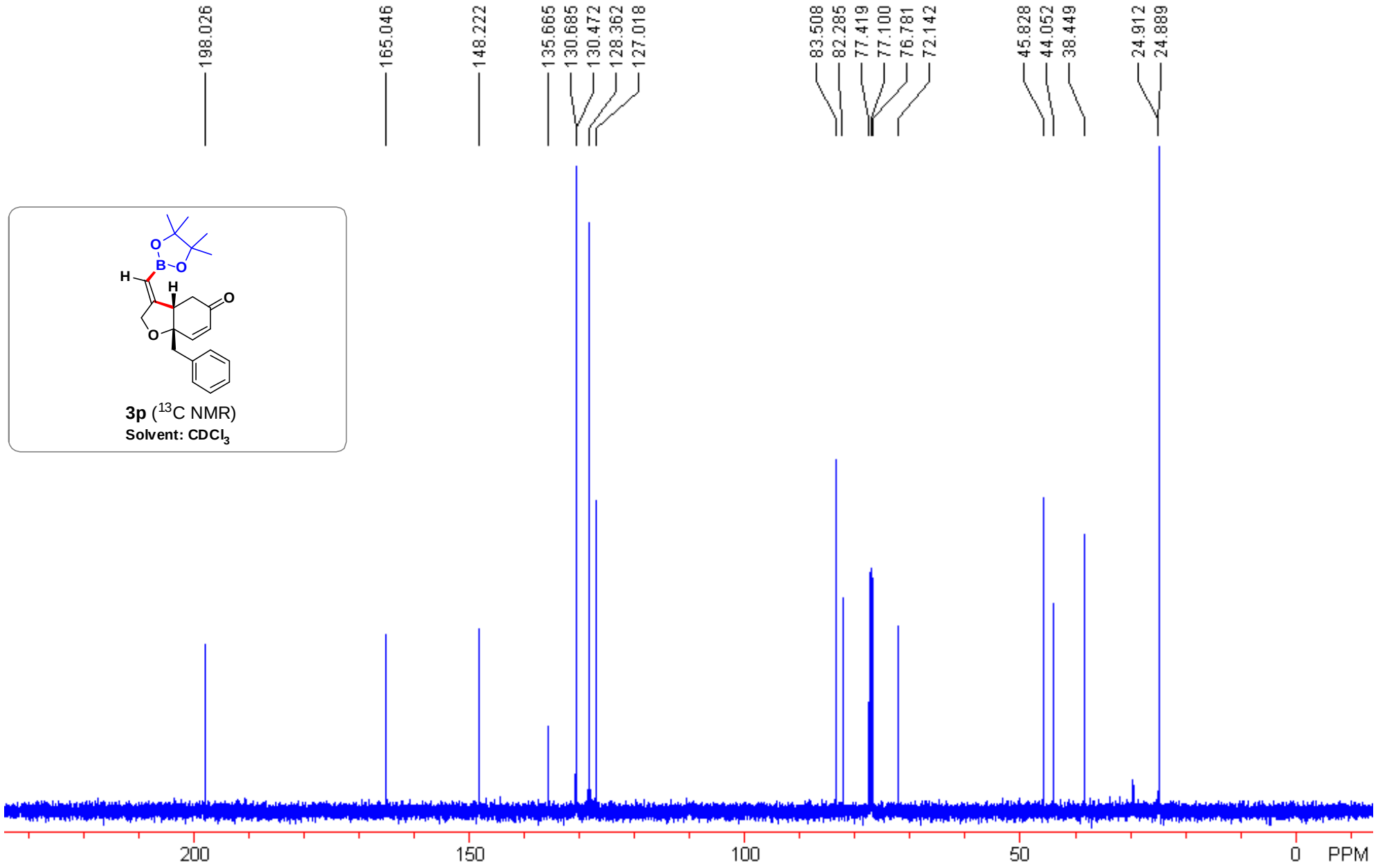

7.276
6.636
6.611
6.016
5.991
4.531
3.370
3.352
3.333
2.658
2.637
2.617
2.606
2.596
2.590
2.565
2.549
2.074
2.056
2.043
2.023
2.004
1.995
1.977
1.961
1.944
1.925
1.387
1.286
1.272
0.962
0.943
0.924
0.000
O
B
O
H
O
O
Me
3n (1H NMR)
Solvent: CDCl3
1.01
1.00
2.00
1.01
2.07
2.15
12.22
3.02
3.06
8
7
6
5
4
3
2
1
0
PPM

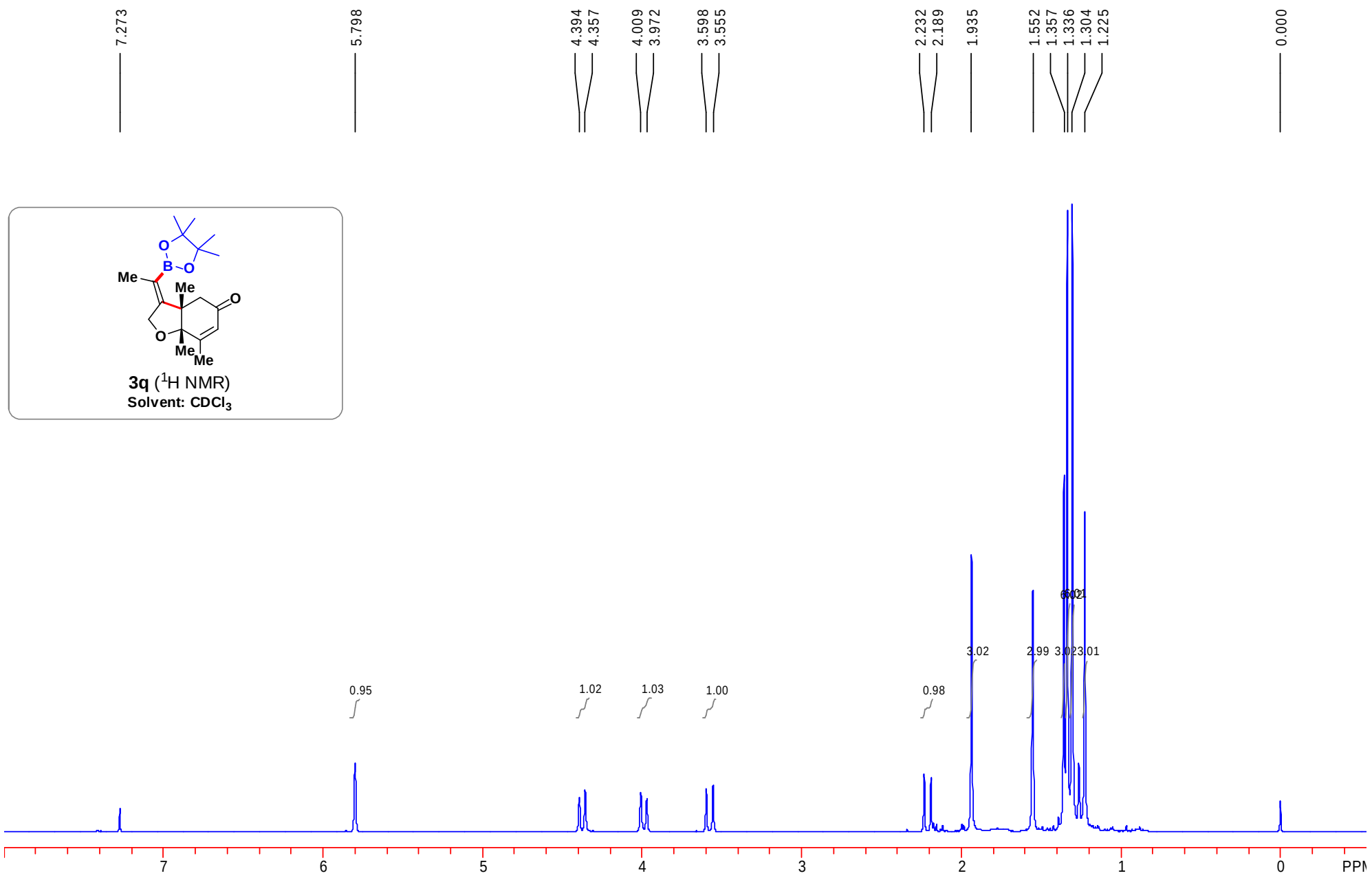

198.945
155.860
149.035
129.705
83.325
78.770
77.419
77.100
76.781
69.022
47.445
39.869
29.748
25.368
25.019
24.768
24.669
14.002
O
B
O
H
O
O
Me
3n (13C NMR)
Solvent: CDCl3
200
150
100
50
0PPM

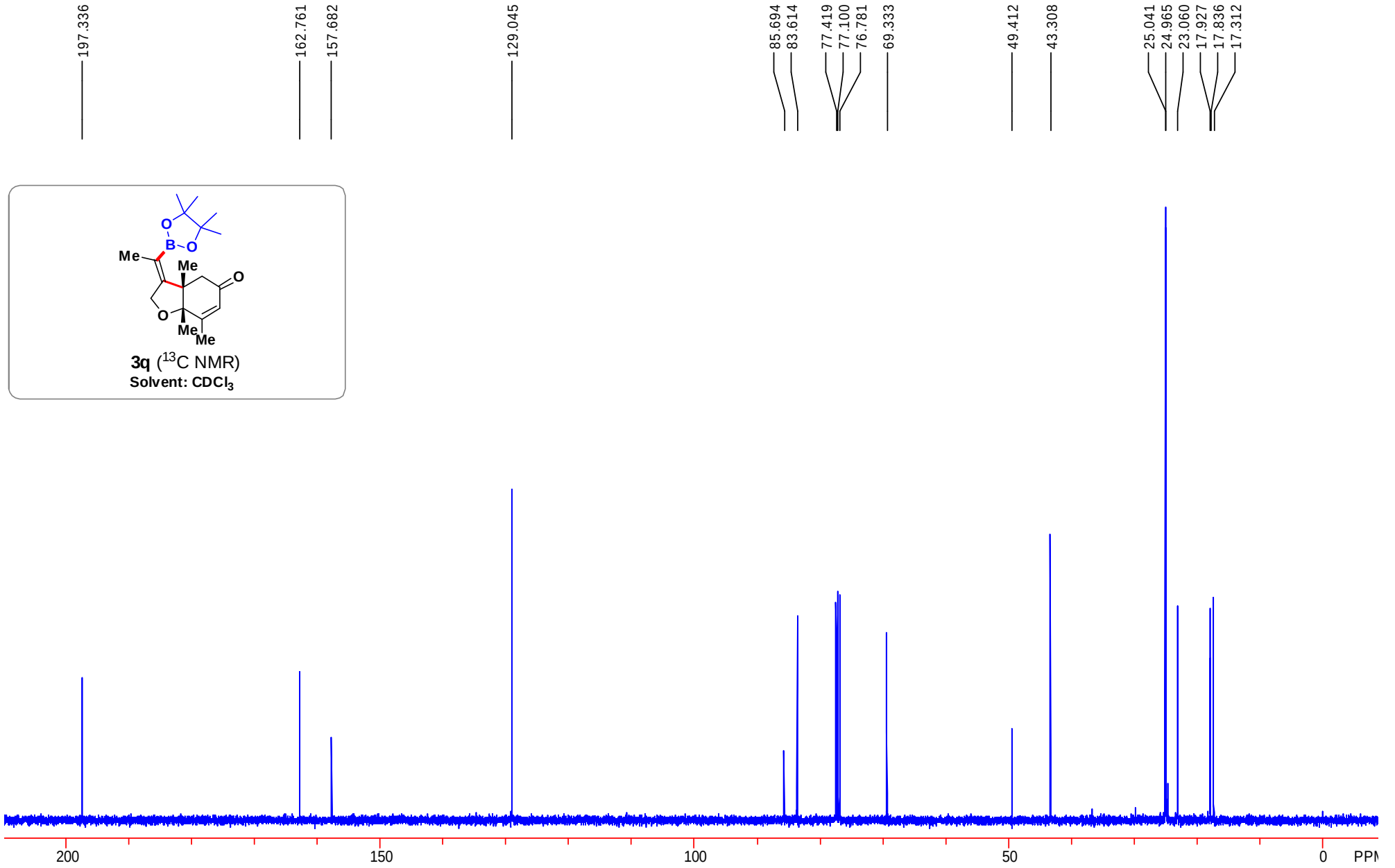

7.268
6.639
6.614
6.015
5.989
4.526
3.375
3.356
3.337
2.602
2.583
2.045
2.030
2.014
1.997
1.979
1.969
1.952
1.936
1.919
1.664
1.378
1.322
1.306
1.298
1.289
1.276
1.264
0.903
0.886
0.869
0.000
O
B
O
H
O
O
Me
3o (1H NMR)
Solvent: CDCl3
16.28
3.05
3.04
2.00
2.02
2.04
0.98
1.00
0.98
8
7
6
5
4
3
2
1
0
PPM


199.021
156.095
149.020
129.721
83.326
78.710
77.419
77.100
76.781
69.303
47.552
39.952
31.912
31.829
25.011
24.791
24.738
22.695
14.185
O
B
O
H
O
O
Me
3o (1H NMR)
Solvent: CDCl3
200
150
100
50
0
PPM


7.298
7.282
7.263
7.259
7.241
7.222
7.203
6.578
6.553
6.004
5.978
5.301
5.296
4.450
3.443
3.427
3.412
3.080
3.045
2.992
2.957
2.945
2.927
2.903
2.886
2.448
2.432
2.406
2.390
1.287
1.273
-0.000
O
B
O
H
H
O
O
3p (1H NMR)
Solvent: CDCl3
12.21
5.54
1.00
0.98
0.99
2.03
1.00
3.12
1.02
8
7
6
5
4
3
2
1
0
PPM


198.026
165.046
148.222
135.665
130.685
130.472
128.362
127.018
83.508
82.285
77.419
77.100
76.781
72.142
45.828
44.052
38.449
24.912
24.889
O
B
O
H
H
O
O
3p (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM


7.273
5.798
4.394
4.357
4.009
3.972
3.598
3.555
2.232
2.189
1.935
1.552
1.357
1.336
1.304
1.225
0.000
3q (1H NMR)
Solvent: CDCl3
0.95
1.02
1.03
1.00
0.98
3.02
2.99
3.01
7
6
5
4
3
2
1
0
PPM


197.336
162.761
157.682
129.045
85.694
83.614
77.419
77.100
76.781
69.333
49.412
43.308
25.041
24.965
23.060
17.927
17.836
17.312
Me
Me
Me
Me
O
O
B
O
O
3q (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM

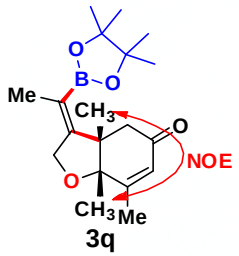
20120531p2-096-1b

Sample Name:
20120531p2-096-1b
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
20120531p2-096-1b_20130228_01
FidFile: NOESY_01

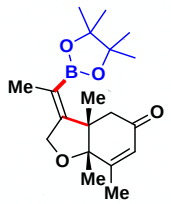
Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Feb 28 2013

Temp. 25.0 C / 298.1 K
Operator: sioc

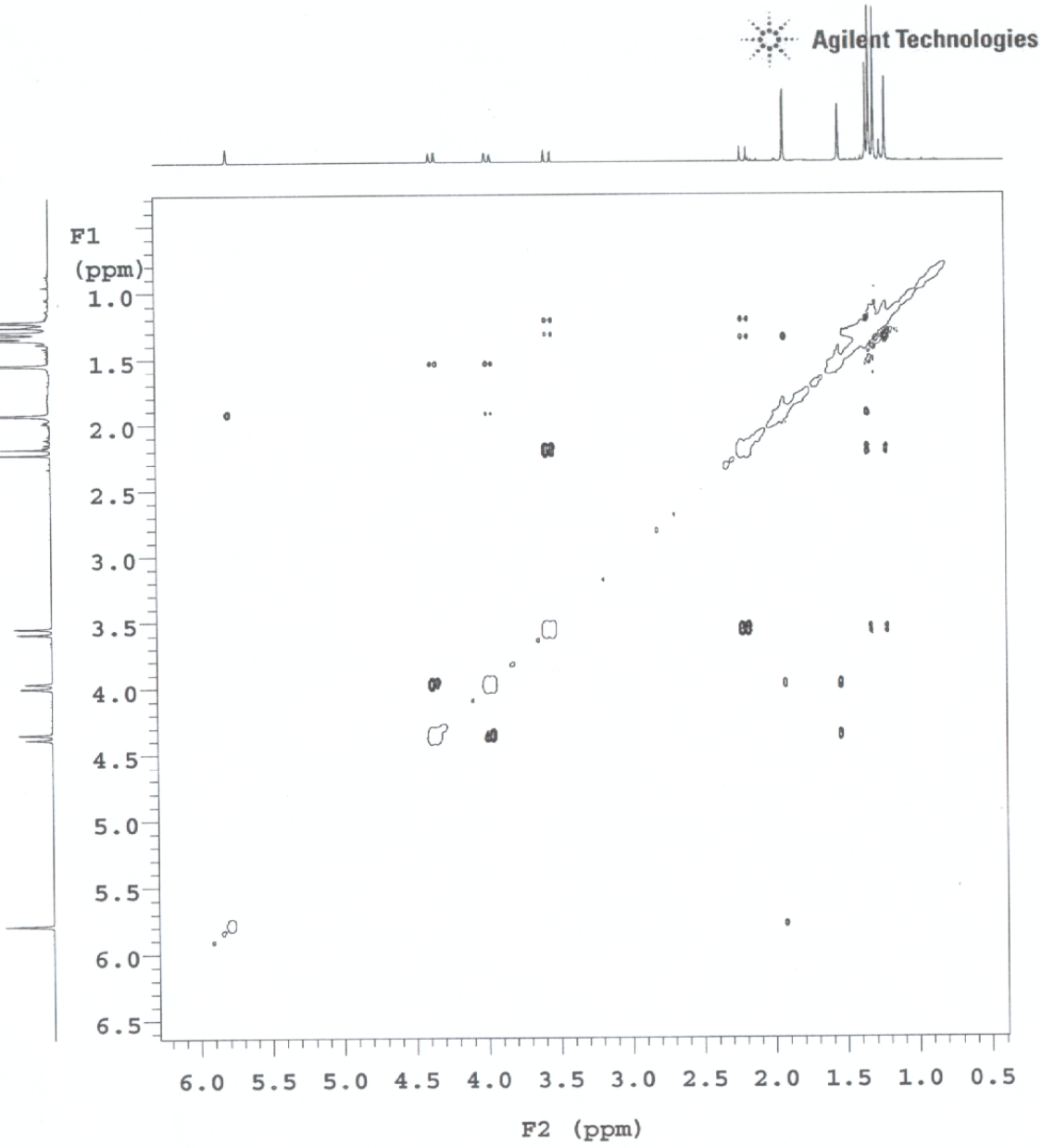
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3811.0 Hz
2D Width 3811.0 Hz
32 repetitions
2 x 256 increments
OBSERVE H1, 399.6607443 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.037 sec
FT size 2048 x 2048
Total time 8 hr, 36 min

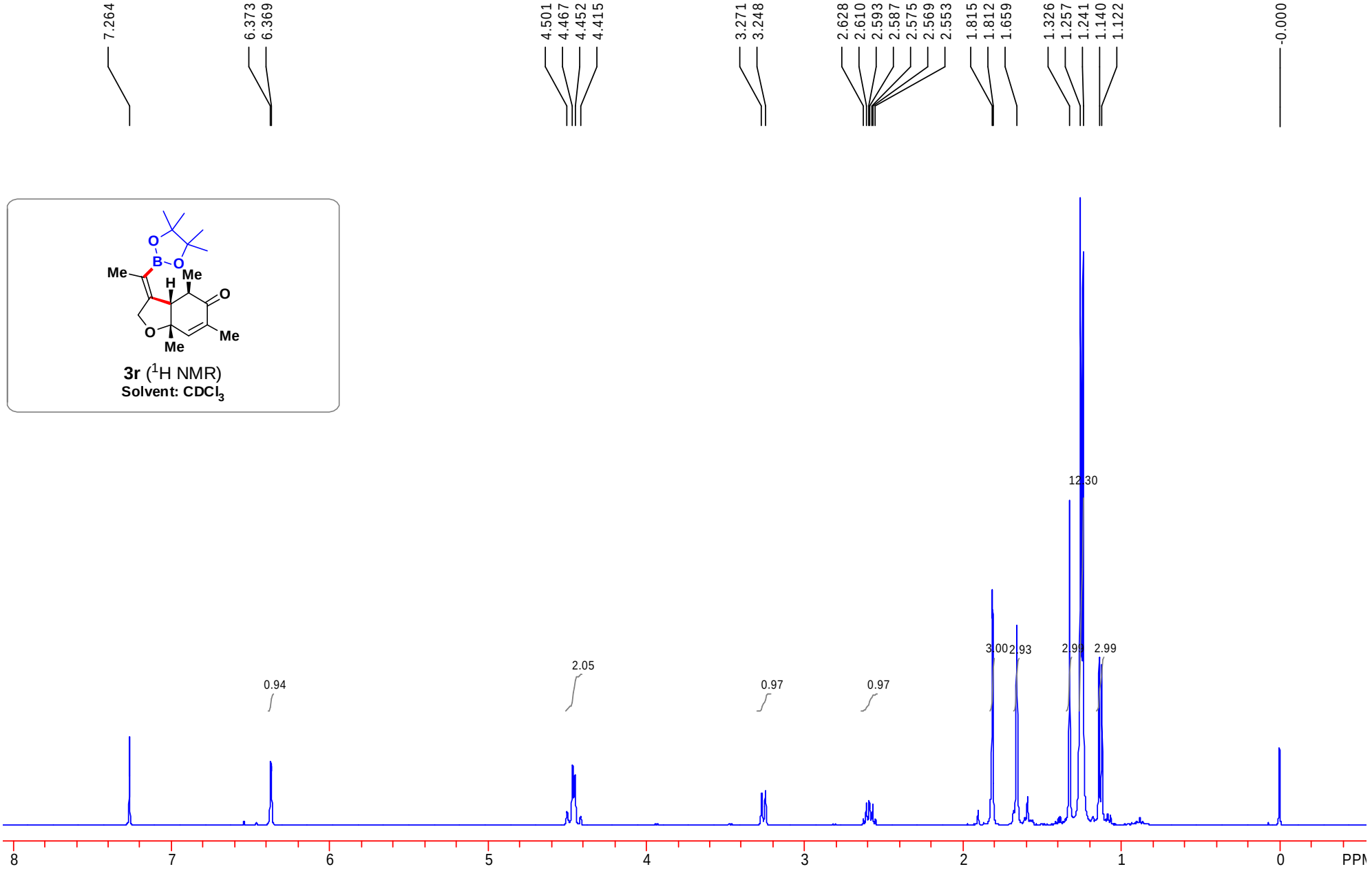


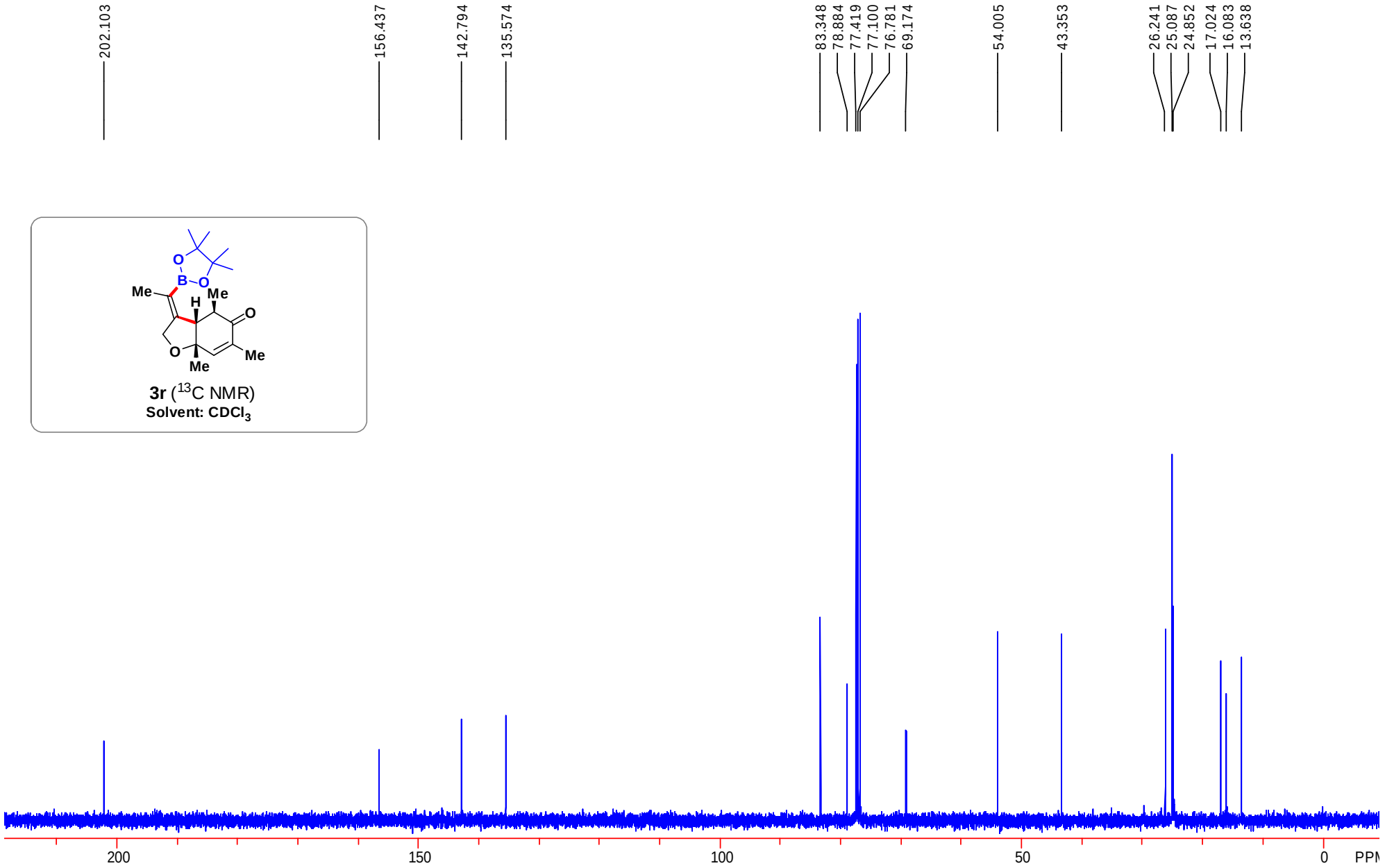
3q



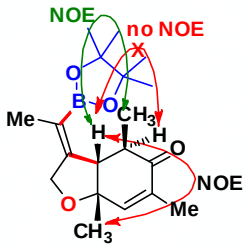
3q (NOSEY)
Solvent: $CDCl_3$



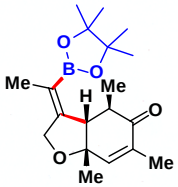

7.264
6.373
6.369
4.501
4.467
4.452
4.415
3.271
3.248
2.628
2.610
2.593
2.587
2.575
2.569
2.553
1.815
1.812
1.659
1.326
1.257
1.241
1.140
1.122
-0.000
Me
O
B
O
Me
H
Me
O
O
Me
Me
3r (1H NMR)
Solvent: CDCl3
0.94
2.05
0.97
0.97
12.30
3.00
2.93
2.99
2.99
8
7
6
5
4
3
2
1
0
PPM


202.103
156.437
142.794
135.574
83.348
78.884
77.419
77.100
76.781
69.174
54.005
43.353
26.241
25.087
24.852
17.024
16.083
13.638
O
B
O
Me
H
Me
O
O
Me
Me
3r (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM

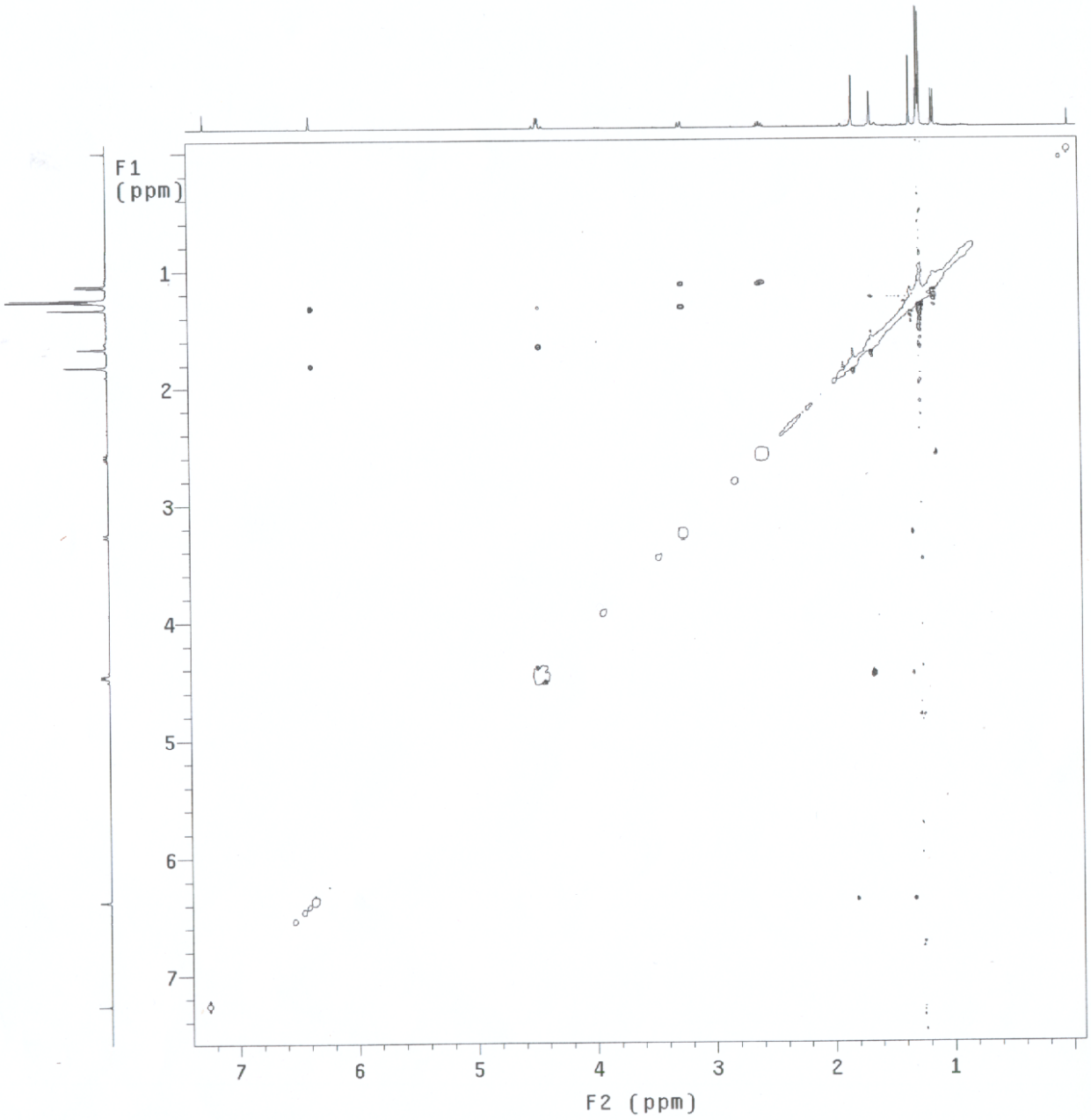
```
20120531p2-078-1a

 Sample Name:
   20120531p2-078-1a
 Data Collected on:
   Agilent-NMR-vnmrs400
 Archive directory:
   /home/sioc/date
 Sample directory:
   20120531p2-078-1a_20130128_01
 FidFile: NOESY

Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Jan 28 2013

 Temp. 25.0 C / 298.1 K
Operator: sioc

 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width    4401.4 Hz
 2D Width 4401.4 Hz
 8 repetitions
 2 x 256 increments
OBSERVE   H1, 399.6613957 MHz
DATA PROCESSING
 Gauss apodization 0.069 sec
F1 DATA PROCESSING
 Gauss apodization 0.048 sec
FT size 2048 x 2048
Total time 2 hr, 2 min
```

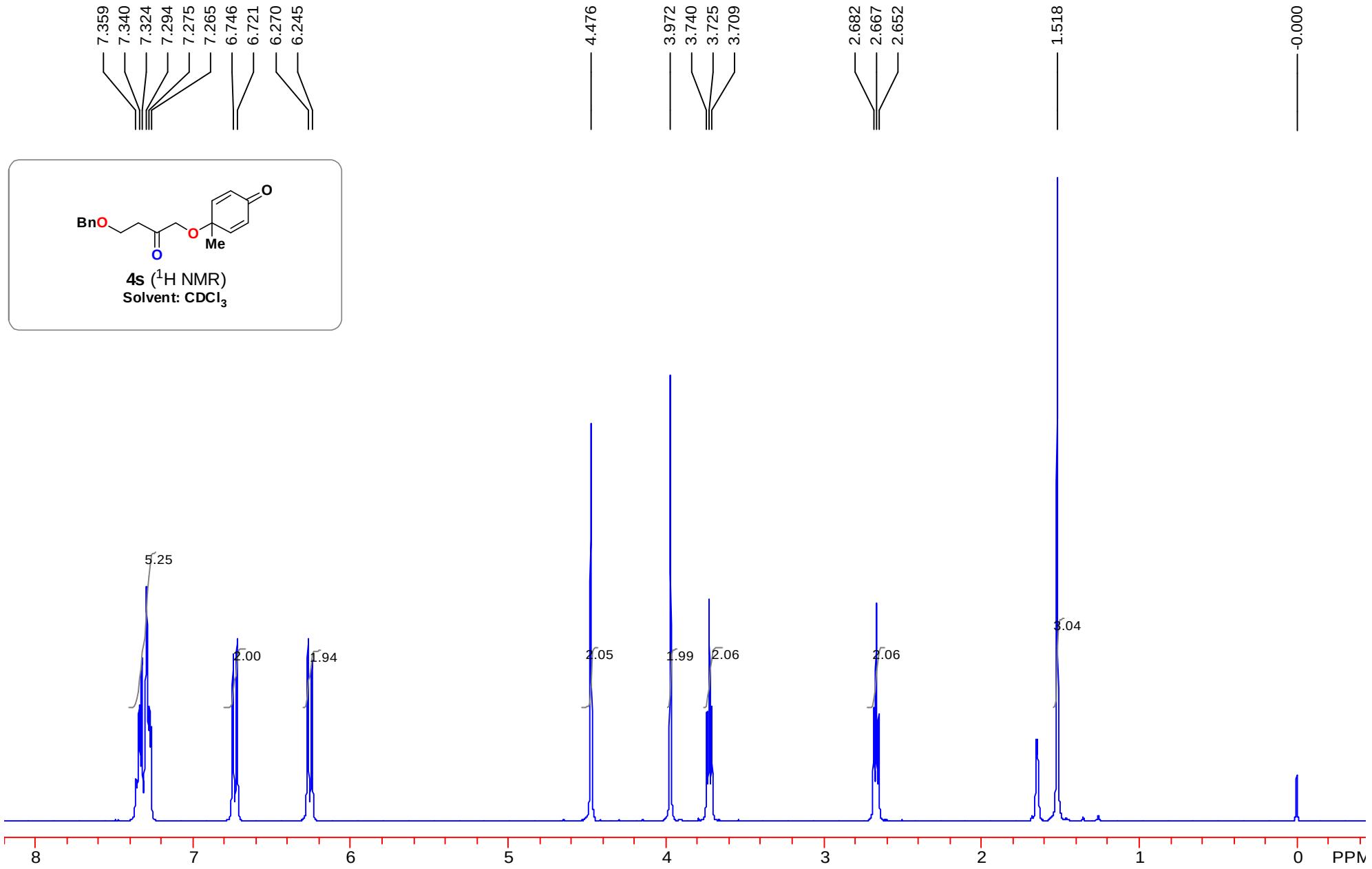


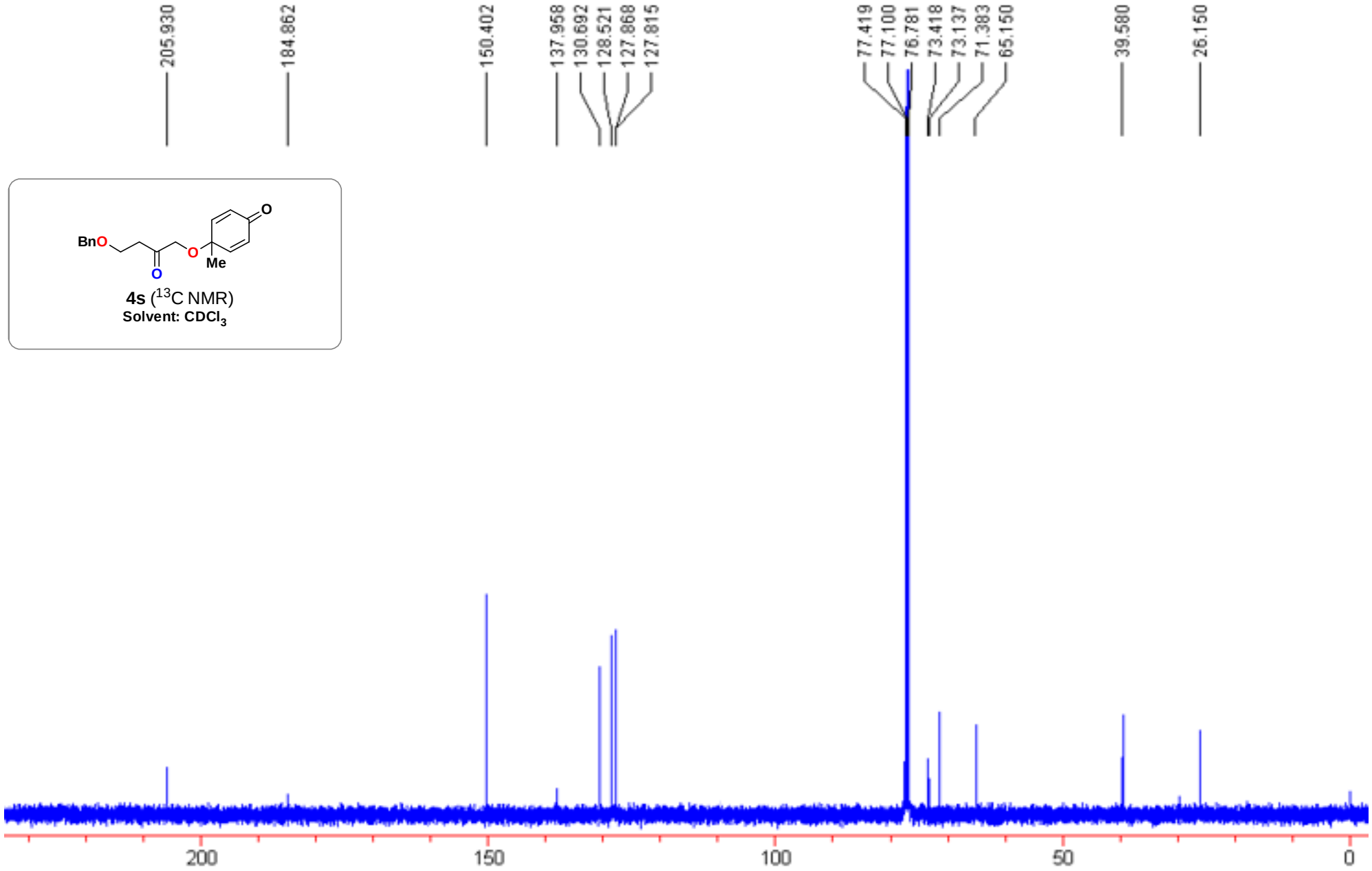
3r

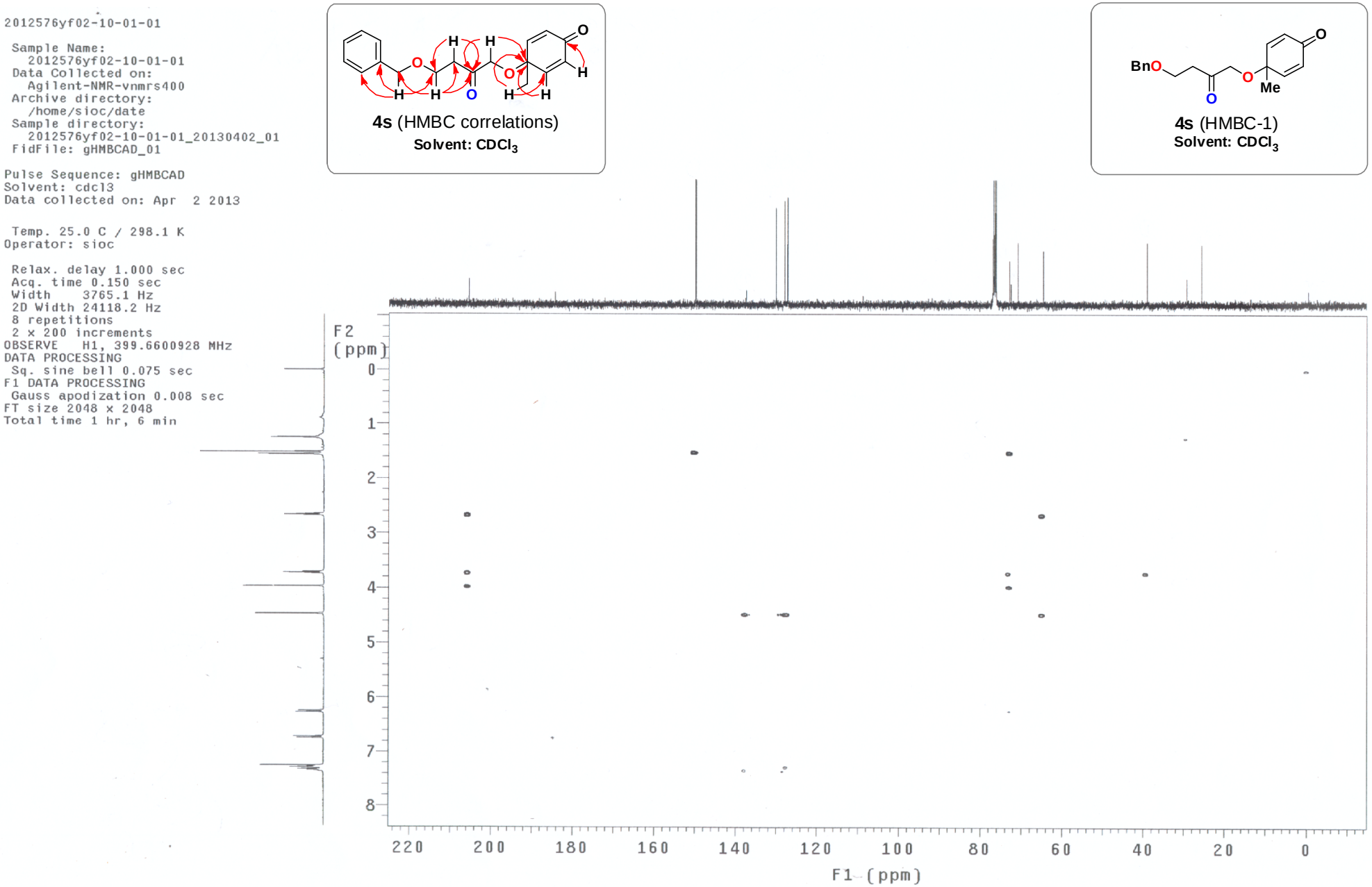


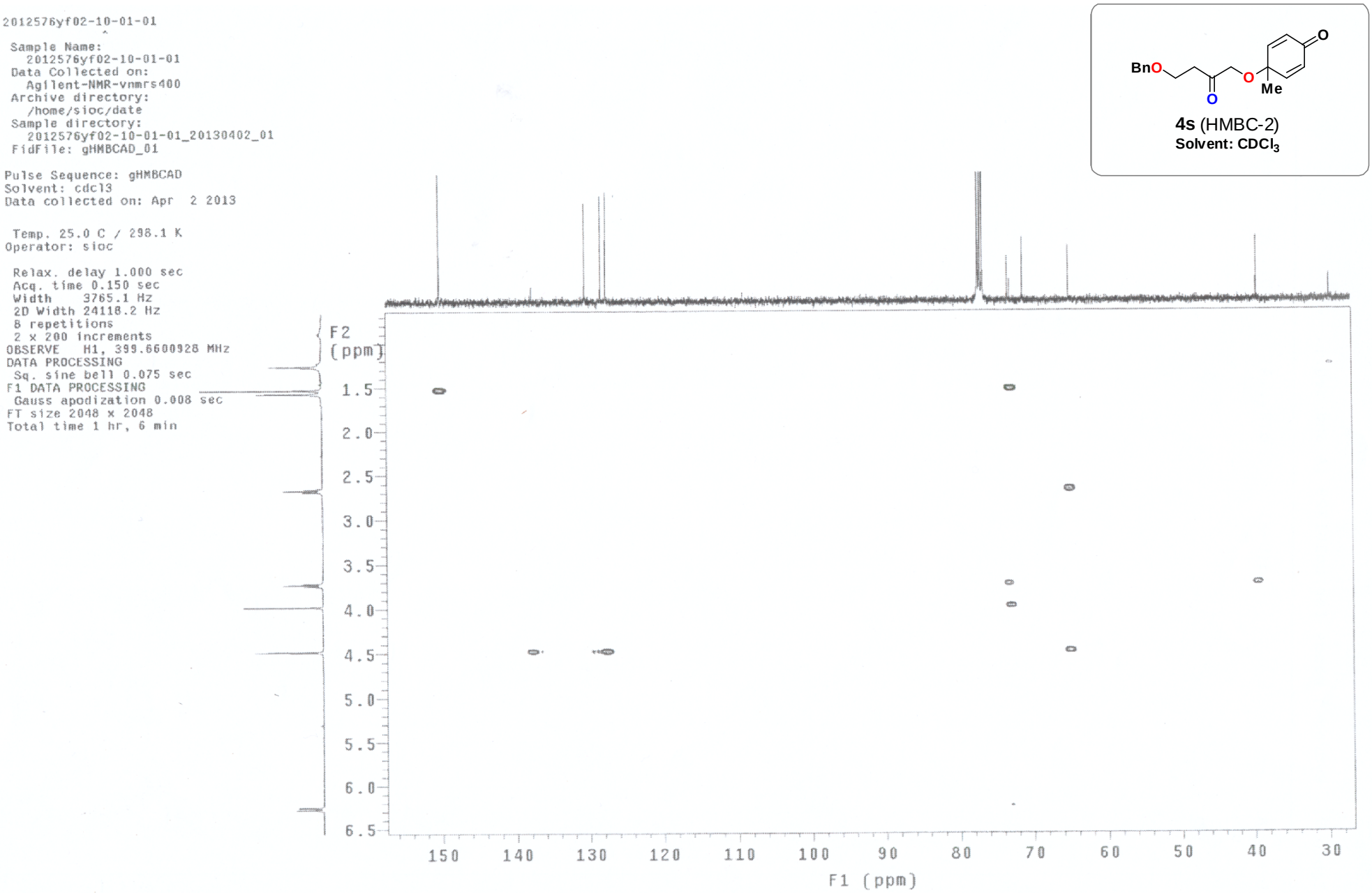
3r (NOSEY)
Solvent: $CDCl_3$

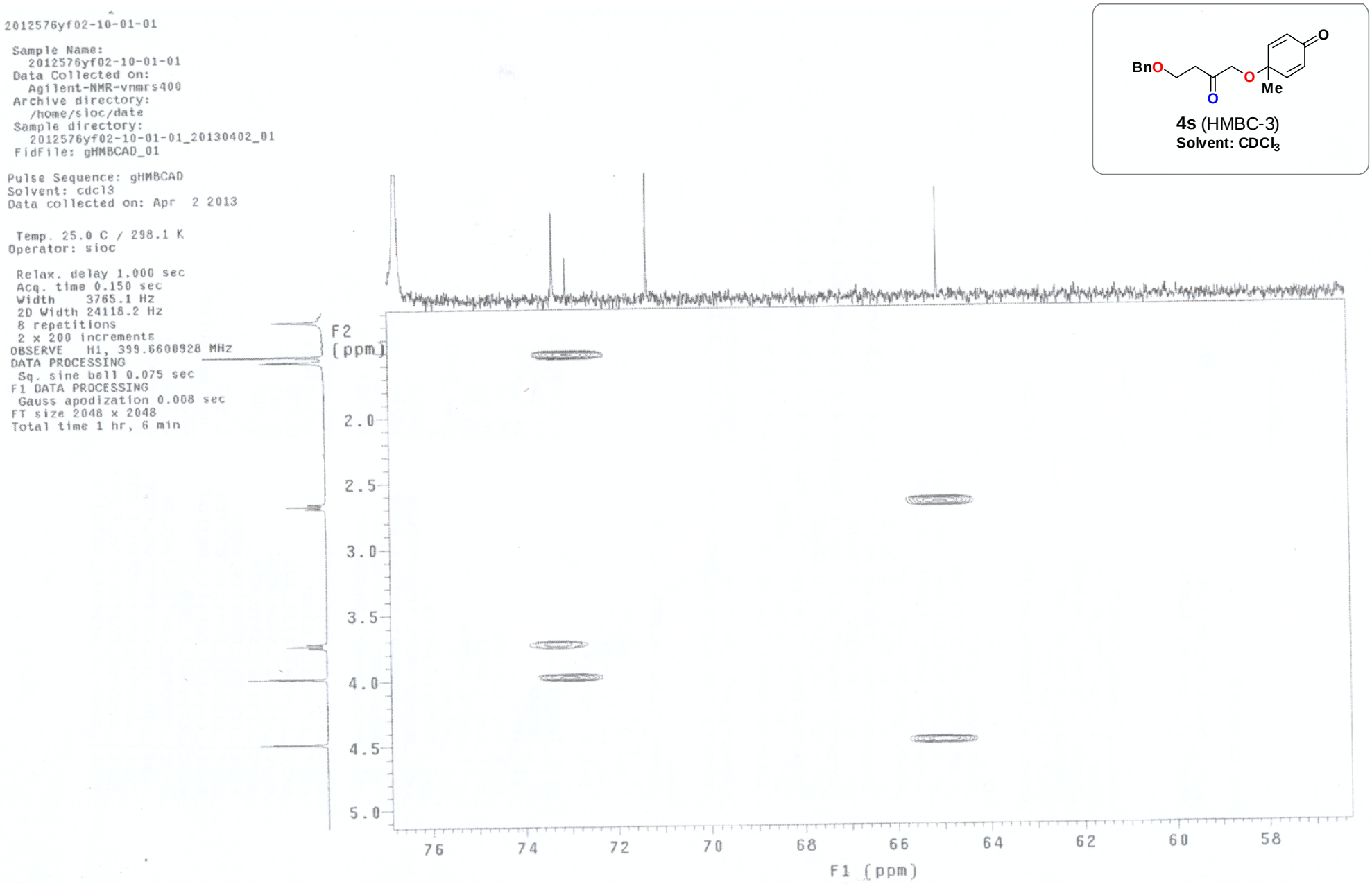


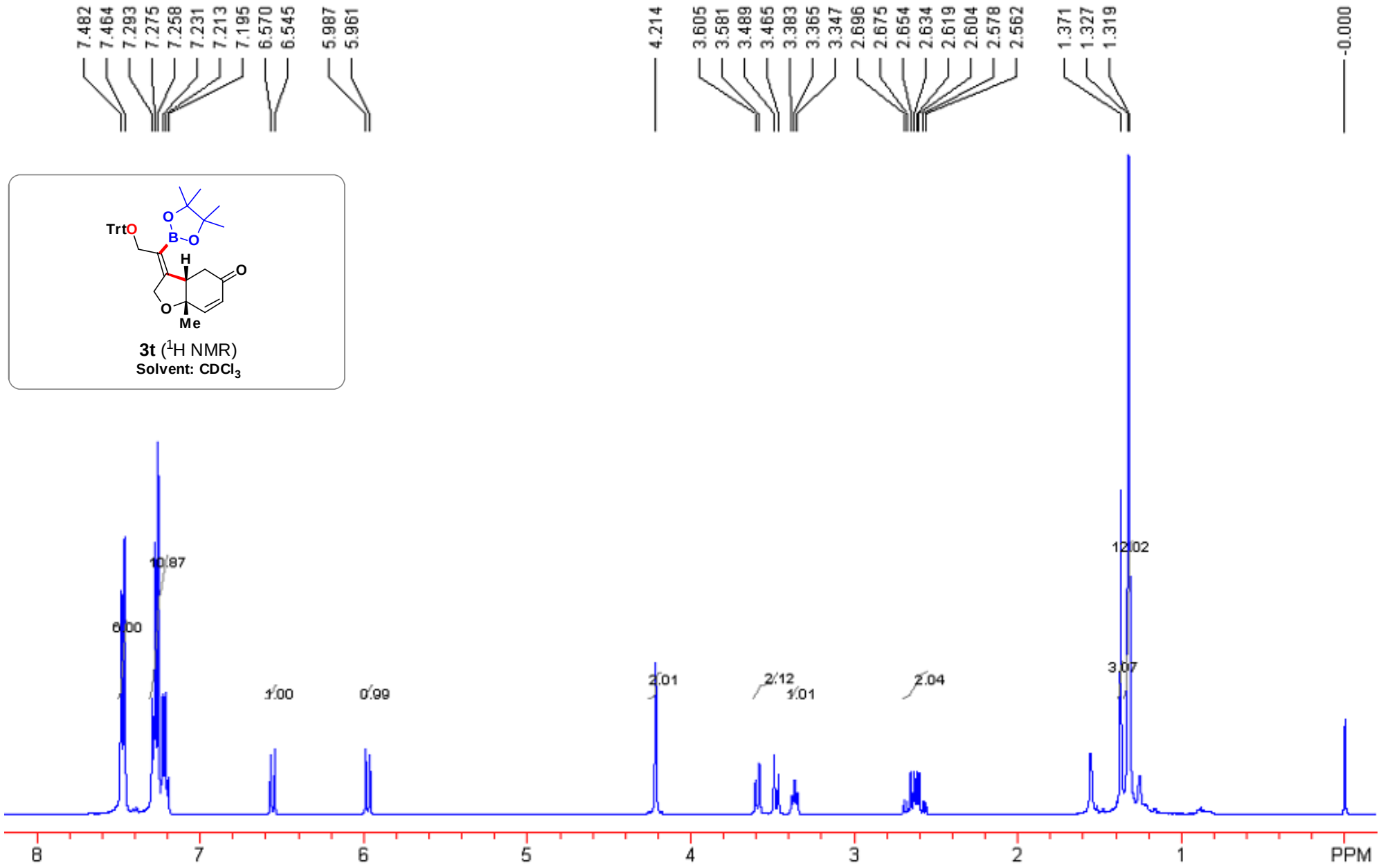

7.359
7.340
7.324
7.294
7.275
7.265
6.746
6.721
6.270
6.245
4.476
3.972
3.740
3.725
3.709
2.682
2.667
2.652
1.518
-0.000
BnO
O
O
Me
O
4s (1H NMR)
Solvent: CDCl3
5.25
2.00
1.94
2.05
1.99
2.06
2.06
3.04
8
7
6
5
4
3
2
1
0
PPM

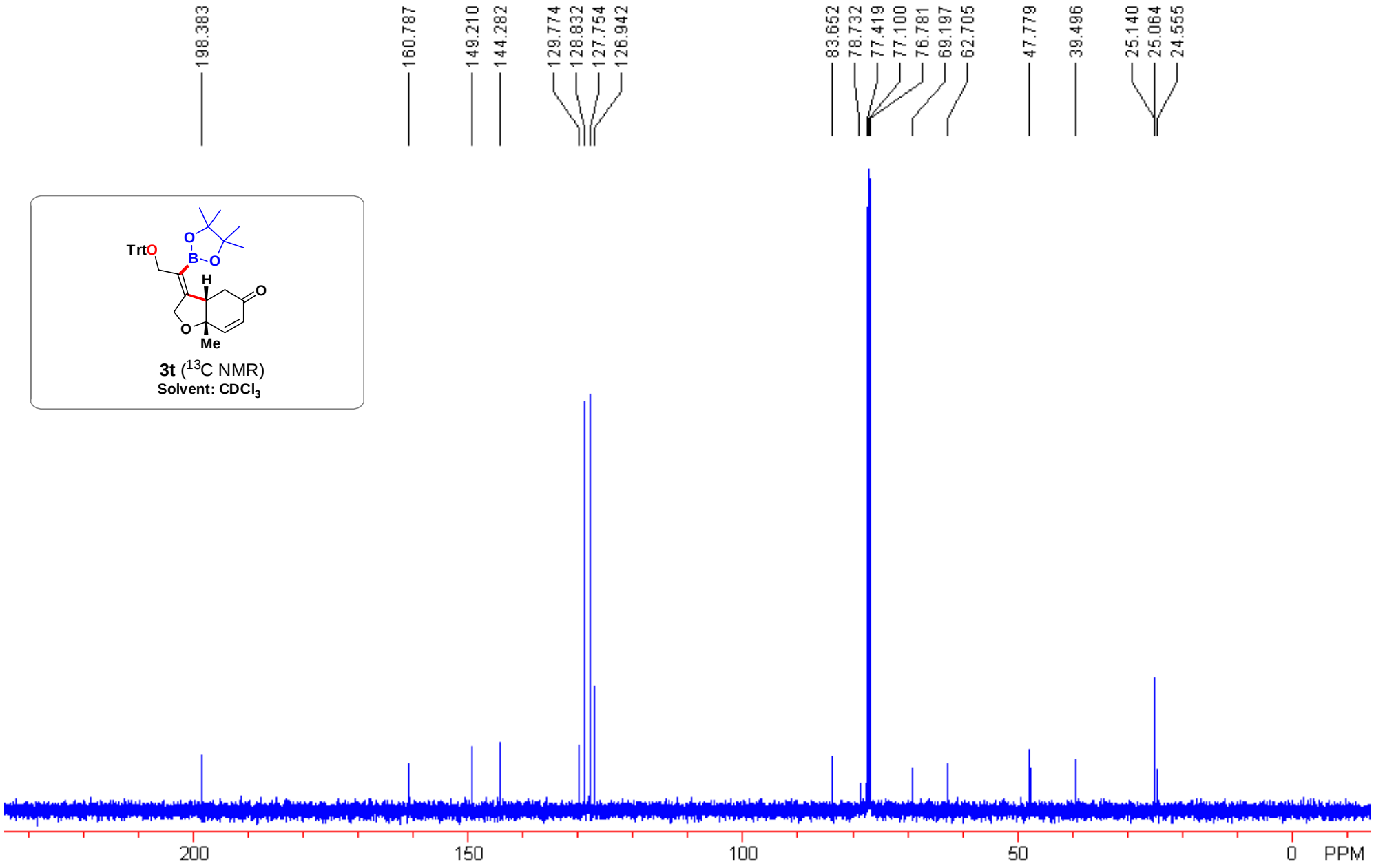

205.930
184.862
150.402
137.958
130.692
128.521
127.868
127.815
77.419
77.100
76.781
73.418
73.137
71.383
65.150
39.580
26.150
BnO
O
O
O
Me
4s (13C NMR)
Solvent: CDCl3
200
150
100
50
0

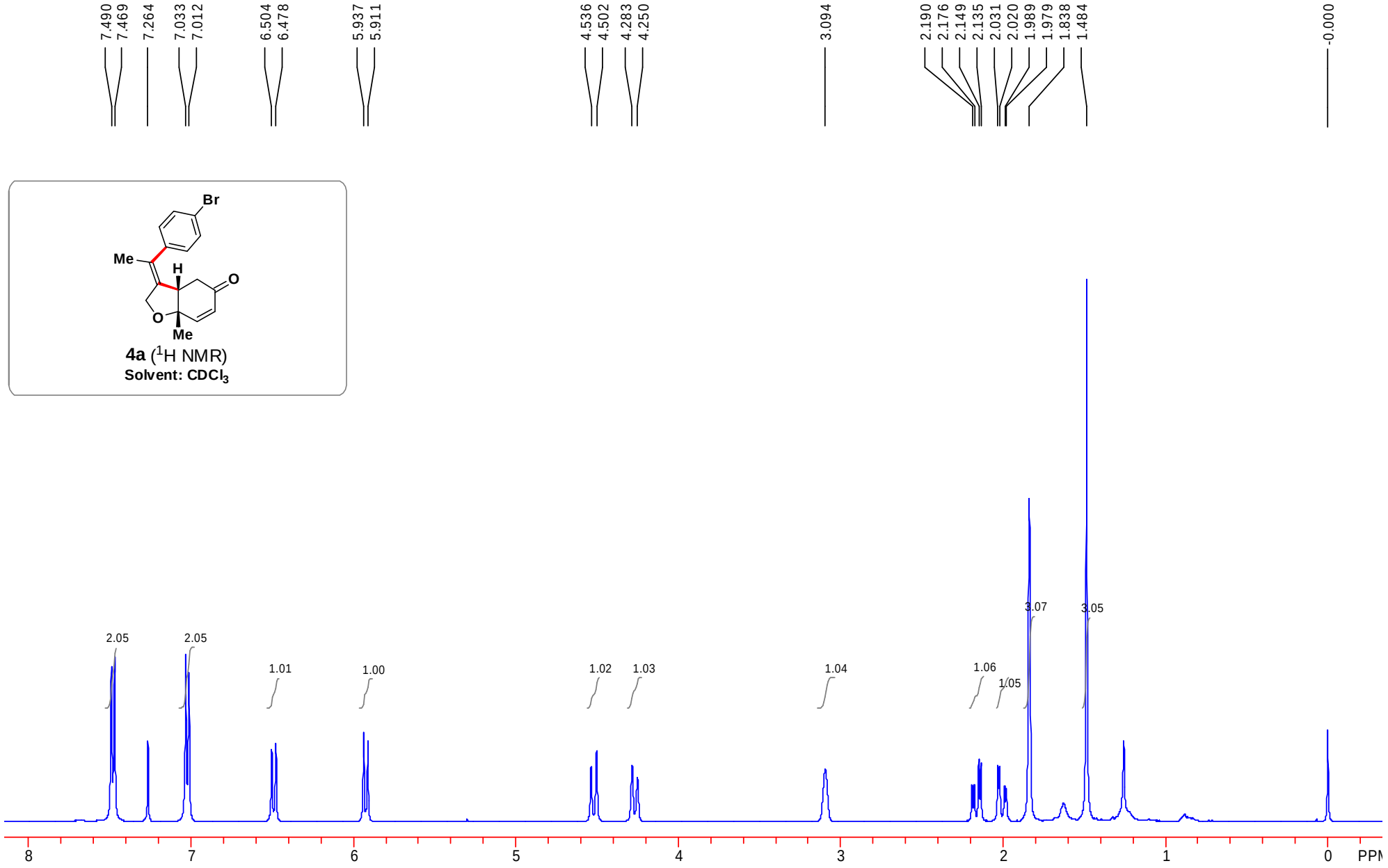

2012576yf02-10-01-01
Sample Name:
2012576yf02-10-01-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-10-01-01_20130402_01
FidFile: gHMBCAD_01
Pulse Sequence: gHMBCAD
Solvent: cdcl3
Data collected on: Apr 2 2013
Temp. 25.0 C / 298.1 K
Operator: sioc
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3765.1 Hz
2D Width 24118.2 Hz
8 repetitions
2 x 200 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Gauss apodization 0.008 sec
FT size 2048 x 2048
Total time 1 hr, 6 min
4s (HMBC correlations)
Solvent: CDCl3
4s (HMBC-1)
Solvent: CDCl3
F2 (ppm)
F1 (ppm)

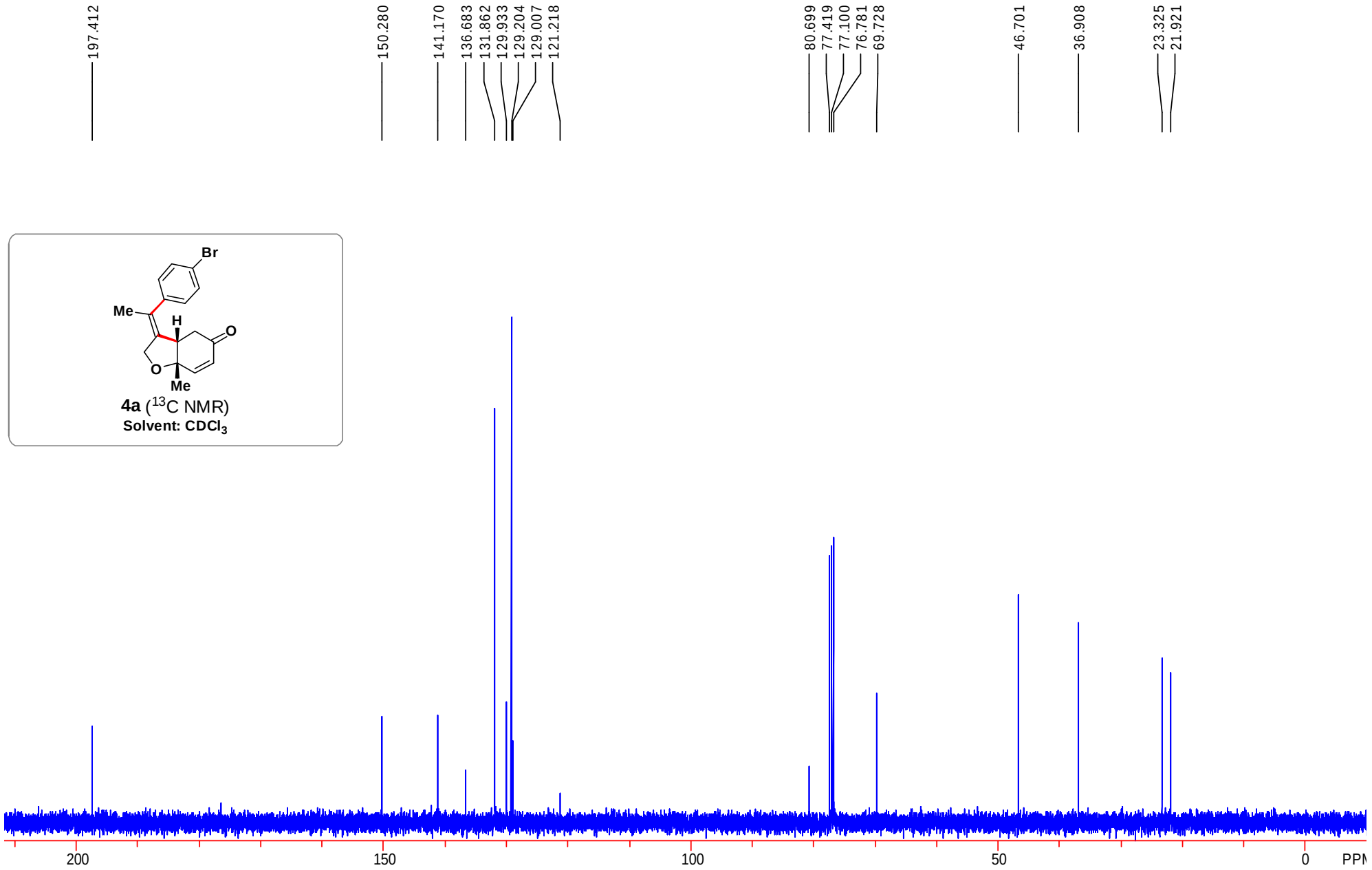

2012576yf02-10-01-01
Sample Name:
2012576yf02-10-01-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-10-01-01_20130402_01
FidFile: gHMBCAD_01
Pulse Sequence: gHMBCAD
Solvent: cdcl3
Data collected on: Apr 2 2013
Temp. 25.0 C / 298.1 K
Operator: sioc
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3765.1 Hz
2D Width 24118.2 Hz
8 repetitions
2 x 200 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Gauss apodization 0.008 sec
FT size 2048 x 2048
Total time 1 hr, 6 min
BnO
O
O
O
Me
4s (HMBC-2)
Solvent: CDCl3
F2 (ppm)
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
150
140
130
120
110
100
90
80
70
60
50
40
30
F1 (ppm)

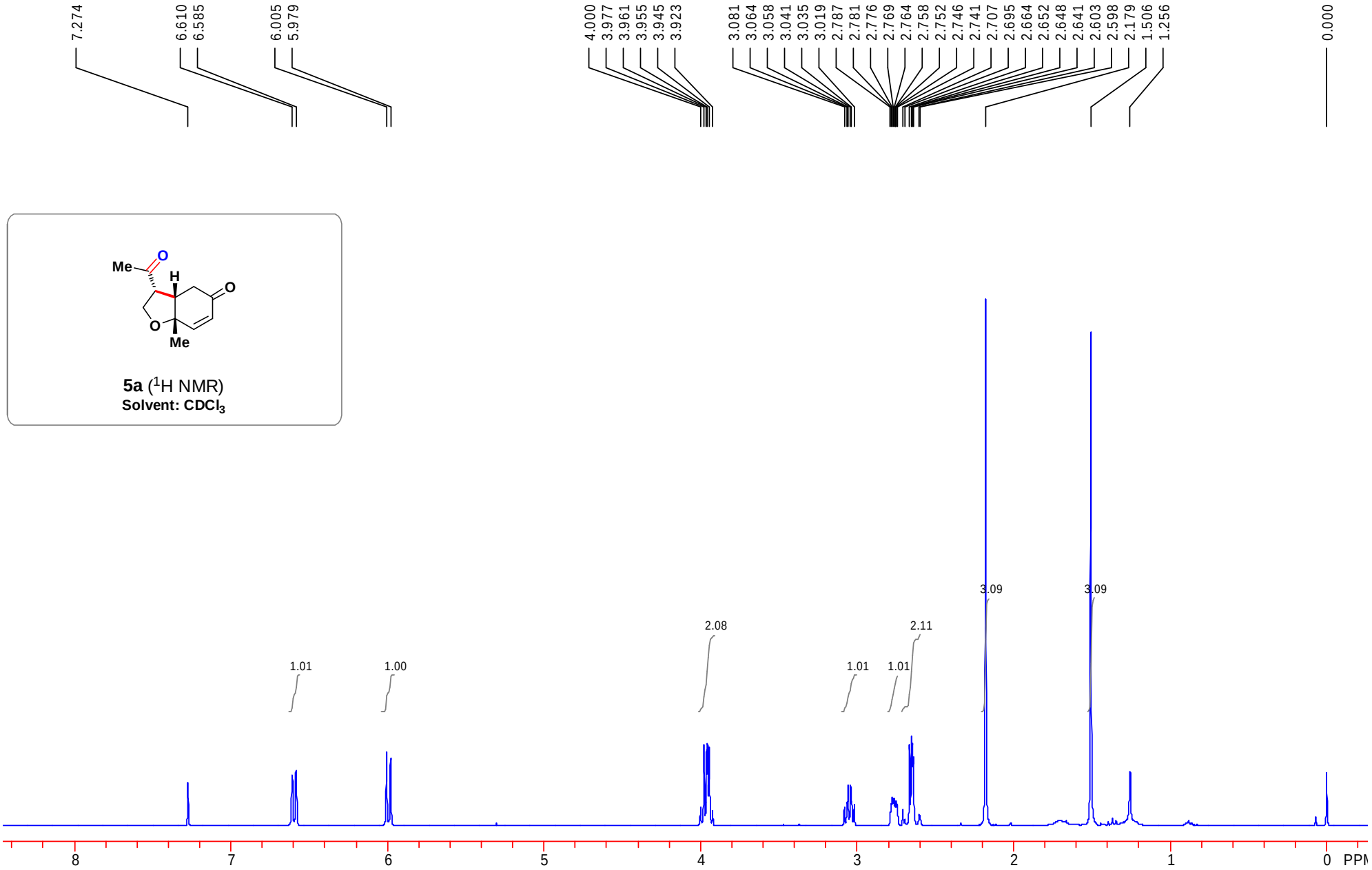

2012576yf02-10-01-01
Sample Name:
2012576yf02-10-01-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-10-01-01_20130402_01
FidFile: gHMBCAD_01
Pulse Sequence: gHMBCAD
Solvent: cdcl3
Data collected on: Apr 2 2013
Temp. 25.0 C / 298.1 K
Operator: sioc
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3765.1 Hz
2D Width 24118.2 Hz
8 repetitions
2 x 200 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Gauss apodization 0.008 sec
FT size 2048 x 2048
Total time 1 hr, 6 min
BnO
O
O
O
Me
4s (HMBC-3)
Solvent: CDCl3
F2 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
76
74
72
70
68
66
64
62
60
58
F1 (ppm)

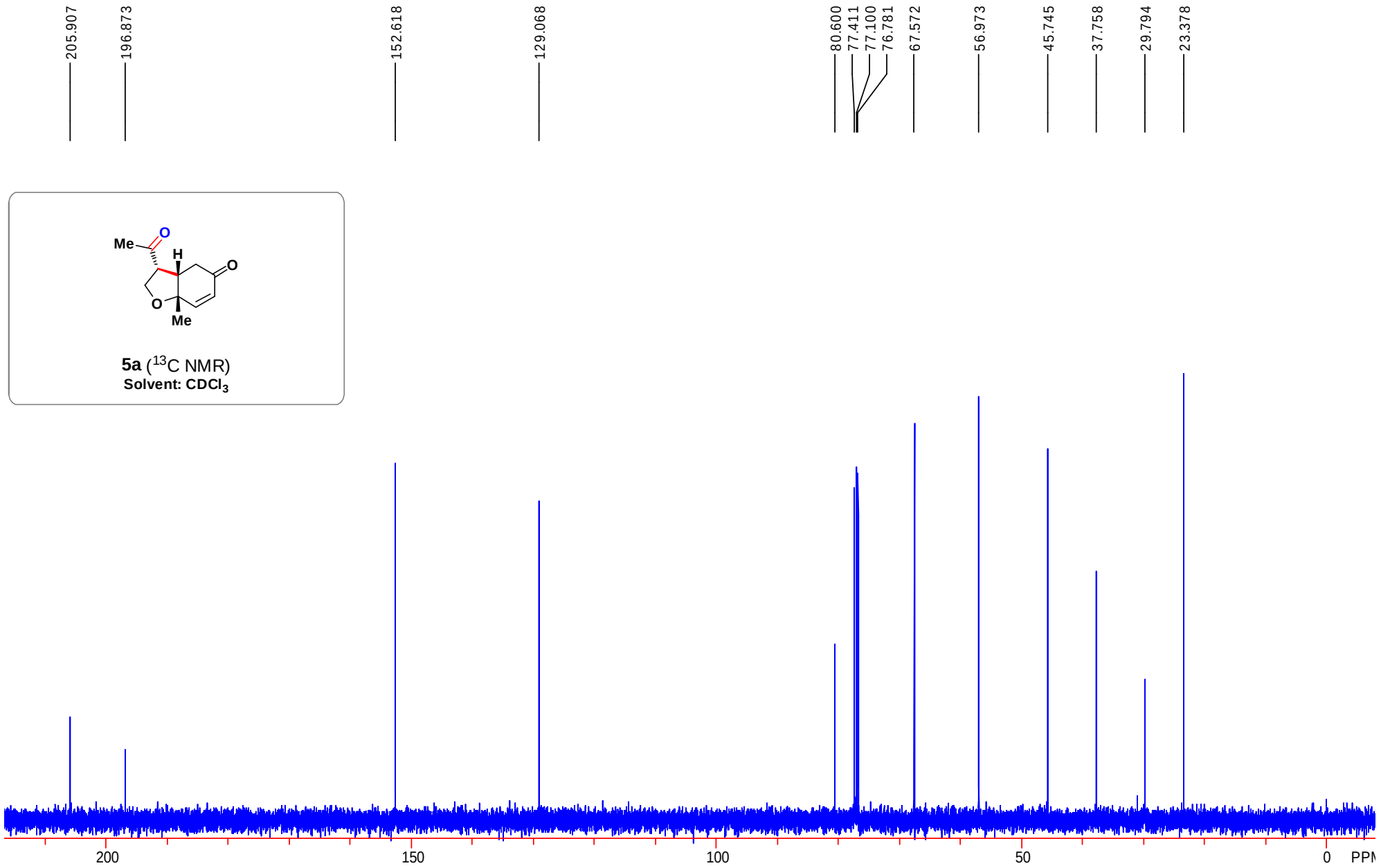

7.482
7.464
7.293
7.275
7.258
7.231
7.213
7.195
6.570
6.545
5.987
5.961
4.214
3.605
3.581
3.489
3.465
3.383
3.365
3.347
2.696
2.675
2.654
2.634
2.619
2.604
2.578
2.562
1.371
1.327
1.319
-0.000
TrtO
O
B
O
H
O
O
Me
3t (1H NMR)
Solvent: CDCl3
6.00
10.87
1.00
0.99
2.01
2.12
1.01
2.04
12.02
3.07
8
7
6
5
4
3
2
1
PPM


198.383
160.787
149.210
144.282
129.774
128.832
127.754
126.942
83.652
78.732
77.419
77.100
76.781
69.197
62.705
47.779
39.496
25.140
25.064
24.555
TrtO
O
B
O
H
O
O
Me
3t (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM

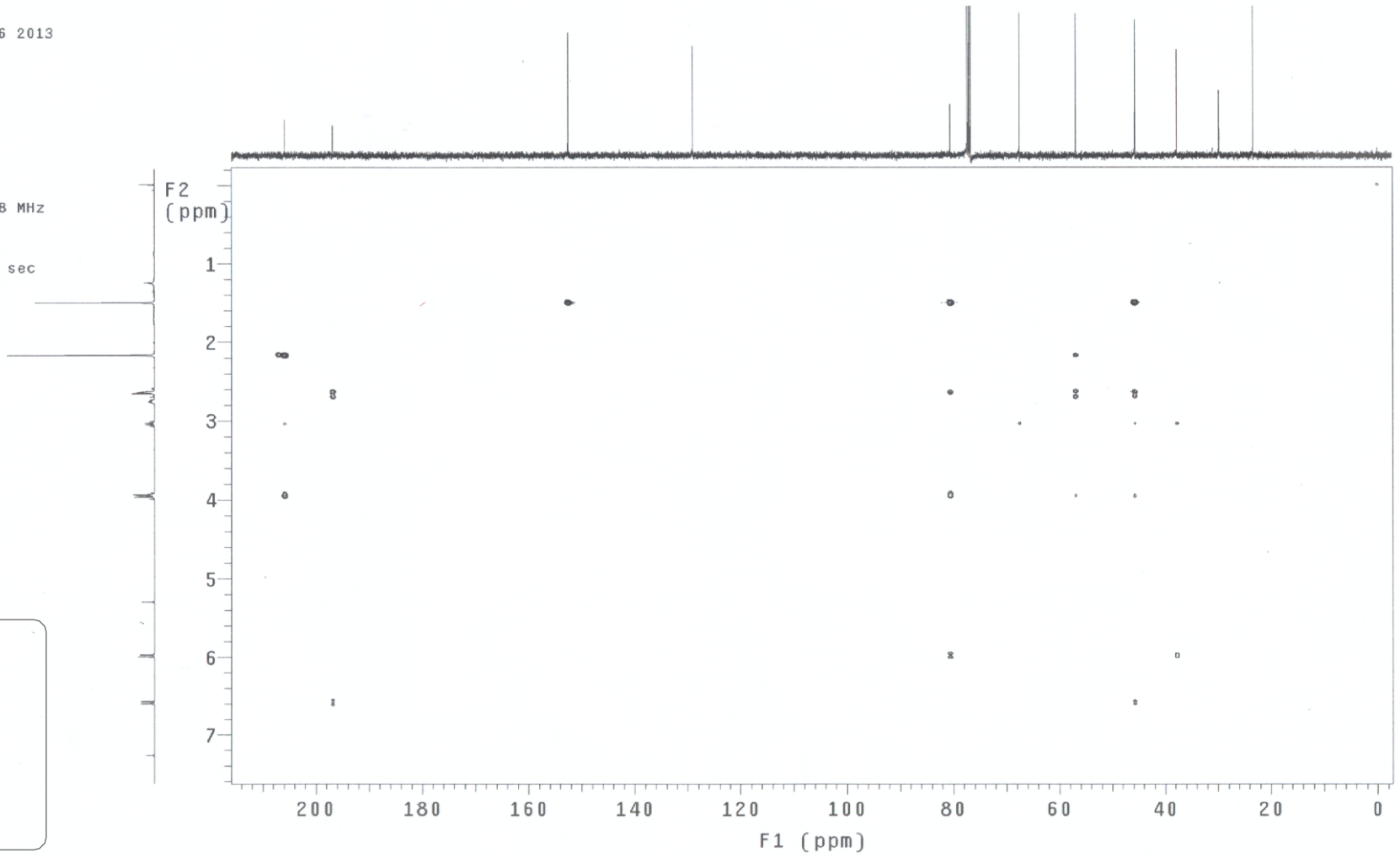

7.490
7.469
7.264
7.033
7.012
6.504
6.478
5.937
5.911
4.536
4.502
4.283
4.250
3.094
2.190
2.176
2.149
2.135
2.031
2.020
1.989
1.979
1.838
1.484
-0.000
Br
Me
H
O
O
Me
4a (1H NMR)
Solvent: CDCl3
2.05
2.05
1.01
1.00
1.02
1.03
1.04
1.06
1.05
3.07
3.05
8
7
6
5
4
3
2
1
0
PPM

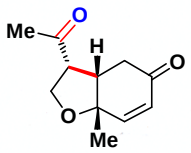

197.412
150.280
141.170
136.683
131.862
129.933
129.204
129.007
121.218
80.699
77.419
77.100
76.781
69.728
46.701
36.908
23.325
21.921
Br
Me
H
O
O
Me
4a (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM


7.274
6.610
6.585
6.005
5.979
4.000
3.977
3.961
3.955
3.945
3.923
3.081
3.064
3.058
3.041
3.035
3.019
2.787
2.781
2.776
2.769
2.764
2.758
2.752
2.746
2.741
2.707
2.695
2.664
2.652
2.648
2.641
2.603
2.598
2.179
1.506
1.256
0.000
Me
O
H
O
O
Me
5a (1H NMR)
Solvent: CDCl3
1.01
1.00
2.08
1.01
1.01
2.11
3.09
3.09
8
7
6
5
4
3
2
1
0
PPM

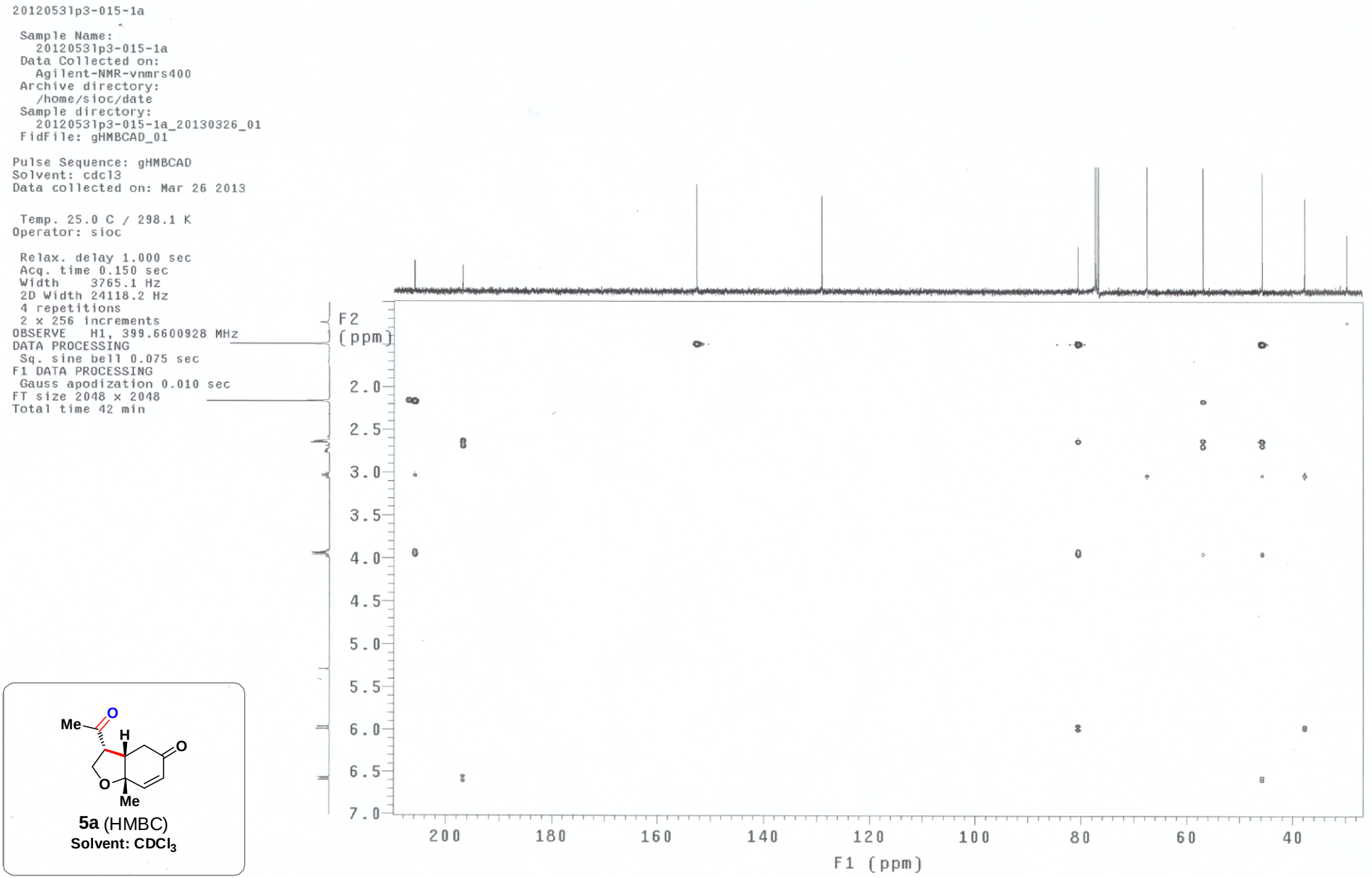

205.907
196.873
152.618
129.068
80.600
77.411
77.100
76.781
67.572
56.973
45.745
37.758
29.794
23.378
Me
O
H
O
O
Me
5a (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM

```
20120531p3-015-1a

 Sample Name:
   20120531p3-015-1a
 Data Collected on:
   Agilent-NMR-vnmrs400
 Archive directory:
   /home/sioc/date
 Sample directory:
   20120531p3-015-1a_20130326_01
 FidFile: gHMBCAD_01

Pulse Sequence: gHMBCAD
Solvent: cdcl3
Data collected on: Mar 26 2013

 Temp. 25.0 C / 298.1 K
Operator: sioc

 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width     3765.1 Hz
 2D Width 24118.2 Hz
 4 repetitions
 2 x 256 increments
OBSERVE   H1, 399.6600928 MHz
DATA PROCESSING
 Sq. sine bell 0.075 sec
F1 DATA PROCESSING
 Gauss apodization 0.010 sec
FT size 2048 x 2048
Total time 42 min
```

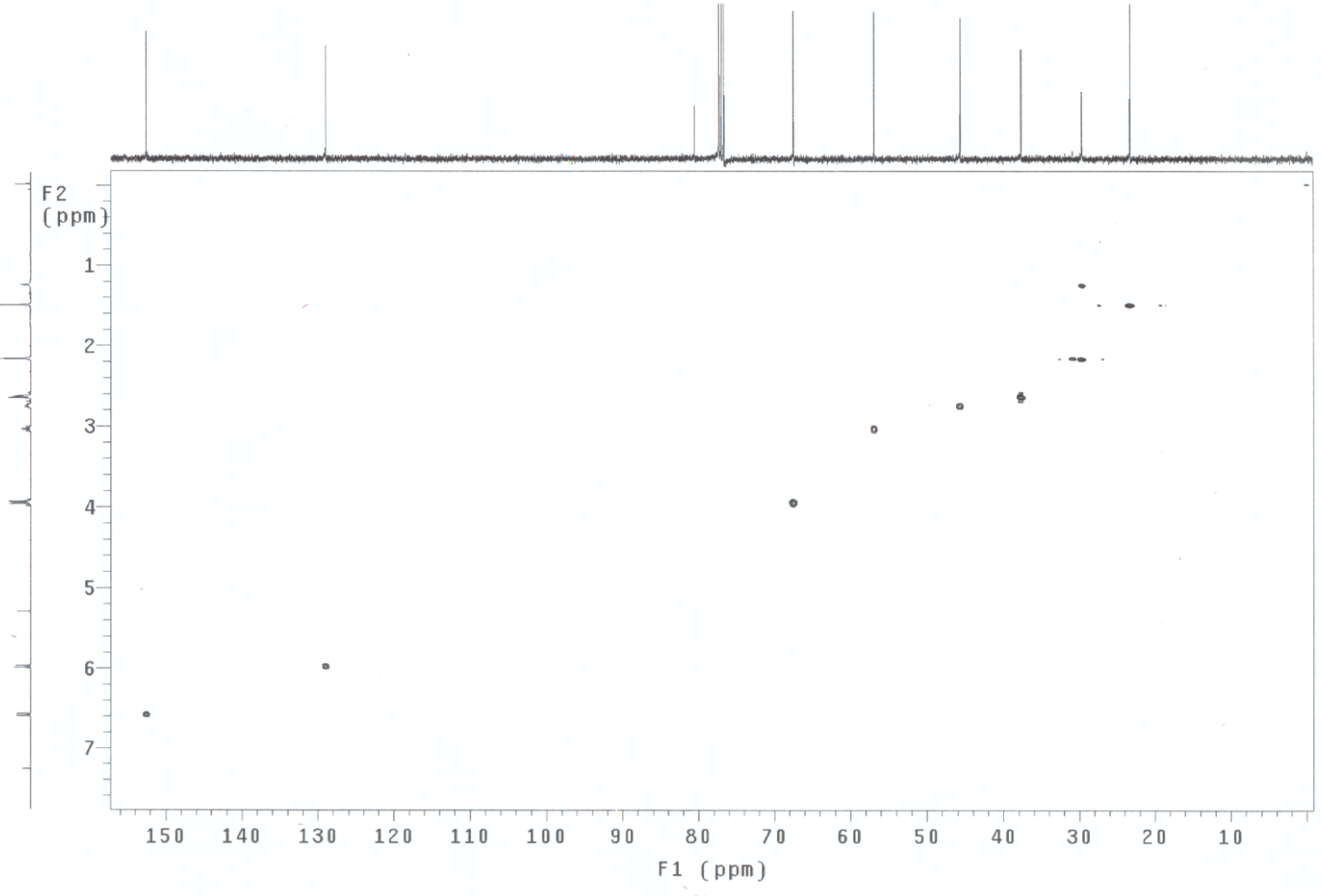


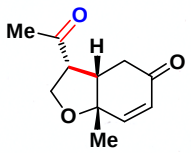


5a (HMBC)
Solvent: $CDCl_3$


20120531p3-015-1a
Sample Name:
20120531p3-015-1a
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
20120531p3-015-1a_20130326_01
FidFile: gHMBCAD_01
Pulse Sequence: gHMBCAD
Solvent: cdcl3
Data collected on: Mar 26 2013
Temp. 25.0 C / 298.1 K
Operator: sioc
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3765.1 Hz
2D Width 24118.2 Hz
4 repetitions
2 x 256 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Gauss apodization 0.010 sec
FT size 2048 x 2048
Total time 42 min
F2 (ppm)
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
200
180
160
140
120
100
80
60
40
F1 (ppm)
Me
O
H
O
O
Me
5a (HMBC)
Solvent: CDCl3

```
20120531p3-015-1a

 Sample Name:
   20120531p3-015-1a
 Data Collected on:
   Agilent-NMR-vnmrs400
 Archive directory:
   /home/sioc/date
 Sample directory:
   20120531p3-015-1a_20130326_01
 FidFile: gHSQCAD_01

Pulse Sequence: gHSQCAD
Solvent: cdcl3
Data collected on: Mar 26 2013

 Temp. 25.0 C / 298.1 K
Operator: sioc

 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width    3765.1 Hz
 2D Width 20100.5 Hz
 4 repetitions
 2 x 256 increments
OBSERVE   H1, 399.6600928 MHz
DECOUPLE C13, 100.5036547 MHz
 Power 37 dB
 on during acquisition
 off during delay
 W40_ATB3 modulated
DATA PROCESSING
 Gauss apodization 0.069 sec
F1 DATA PROCESSING
 Gauss apodization 0.012 sec
FT size 2048 x 2048
Total time 41 min
```





5a (HSQC)
Solvent: $CDCl_3$

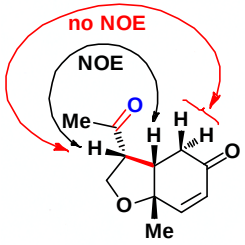
20120531p3-015-1a

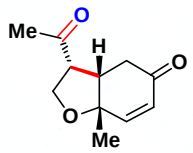
Sample Name:
20120531p3-015-1a
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
20120531p3-015-1a_20130322_01
FidFile: NOESY_01

Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Mar 22 2013

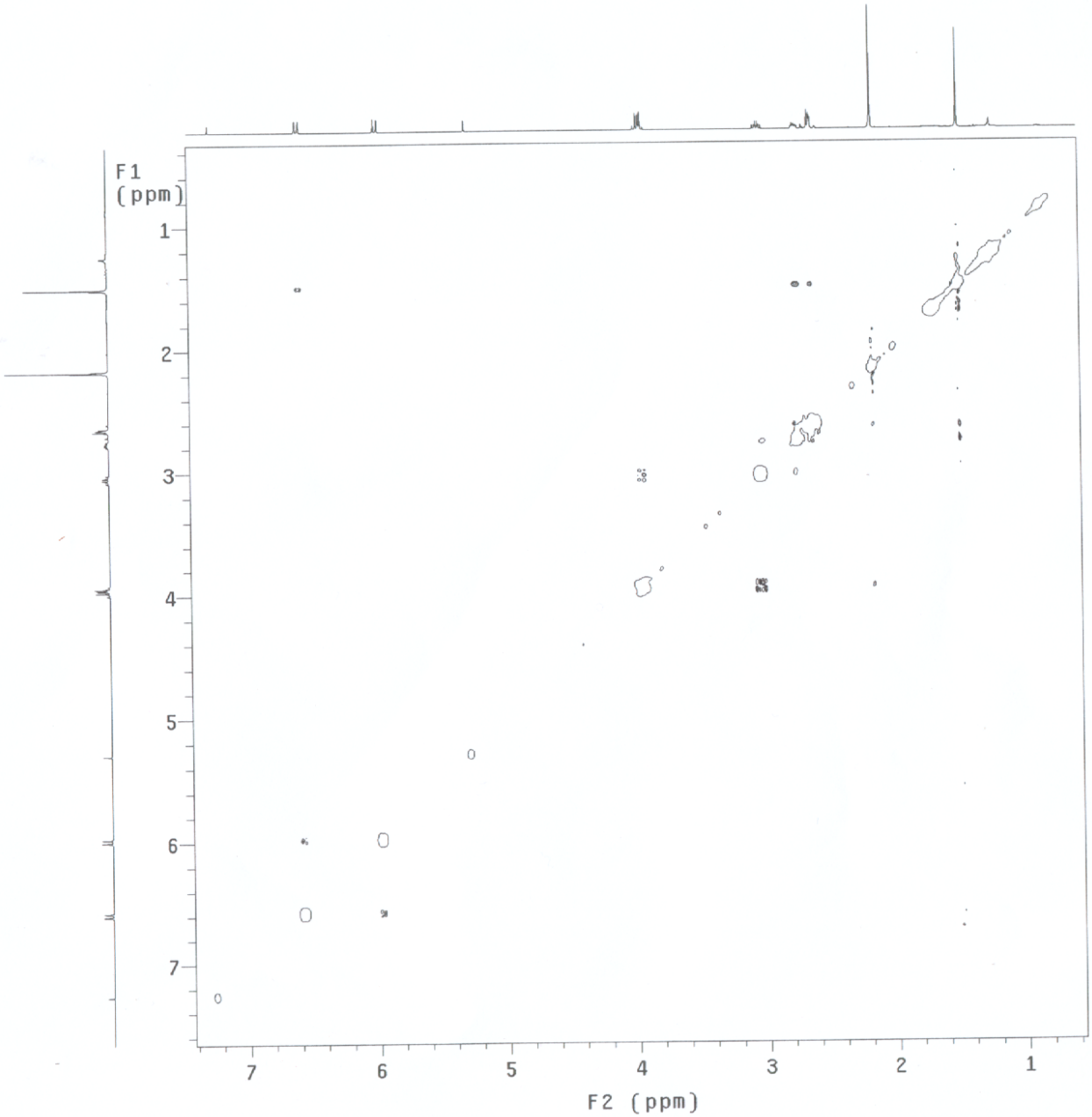
Temp. 25.0 C / 298.1 K
Operator: sioc

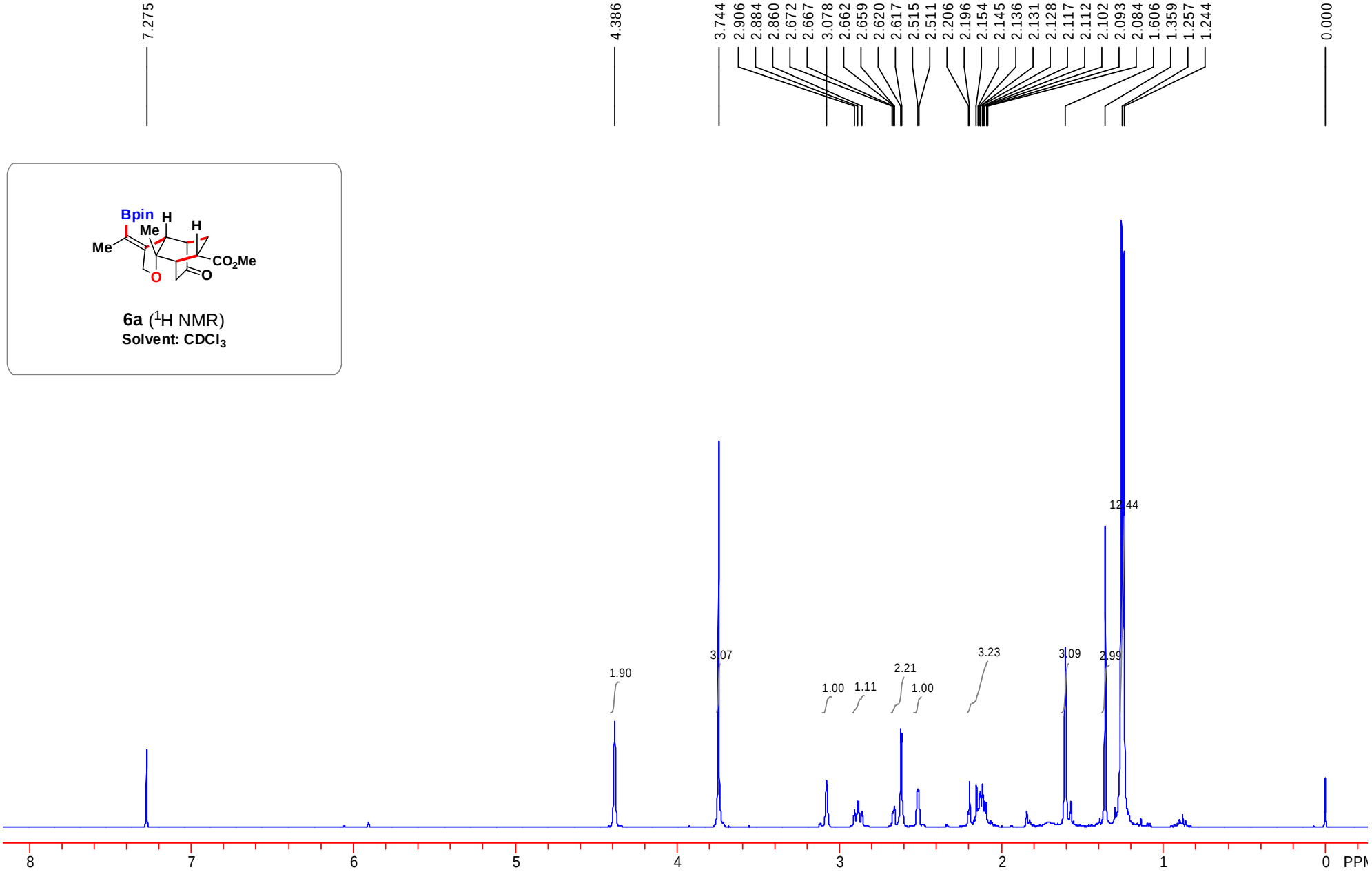
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3720.2 Hz
2D Width 3720.2 Hz
8 repetitions
2 x 256 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.037 sec
FT size 2048 x 2048
Total time 2 hr, 9 min

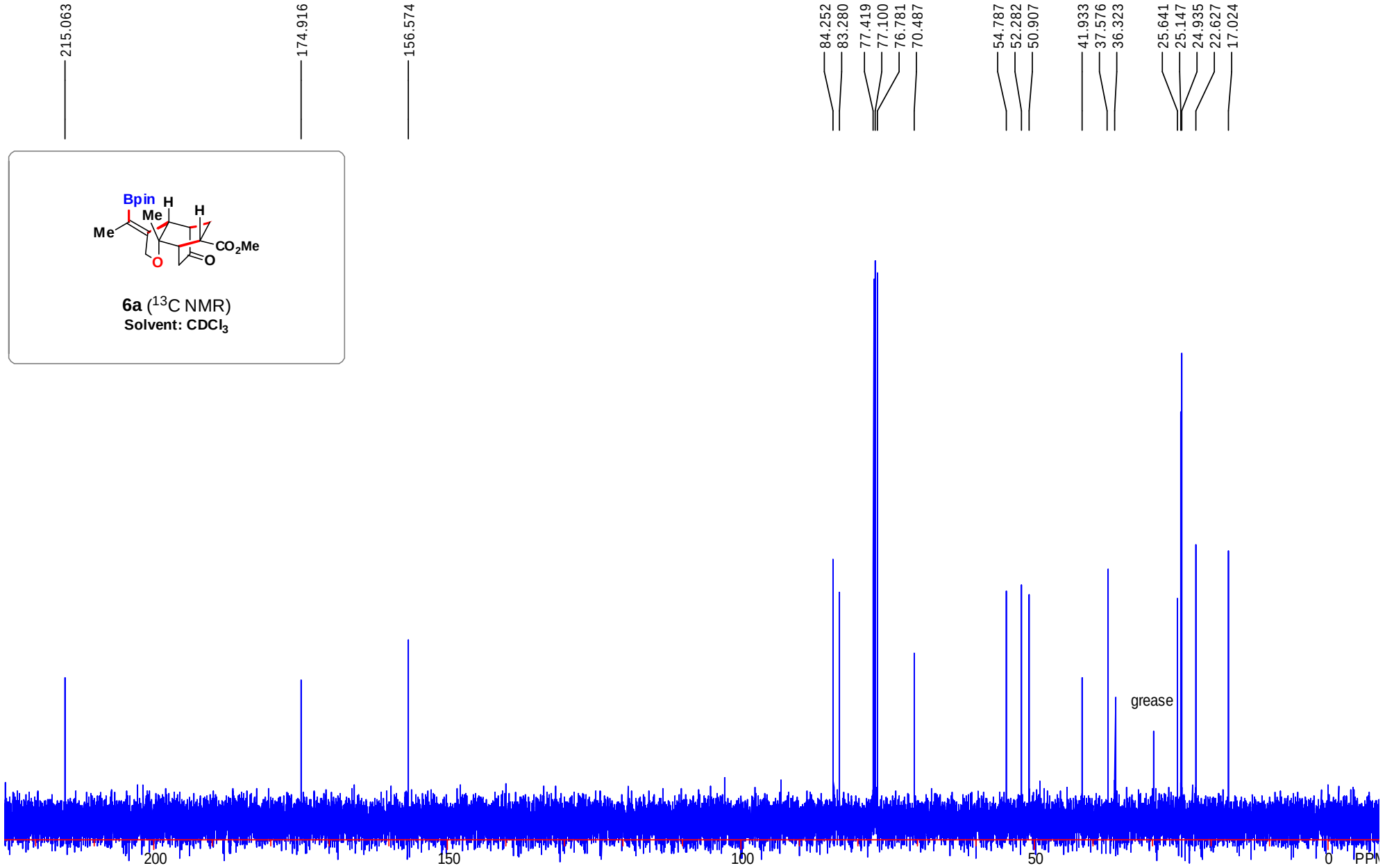




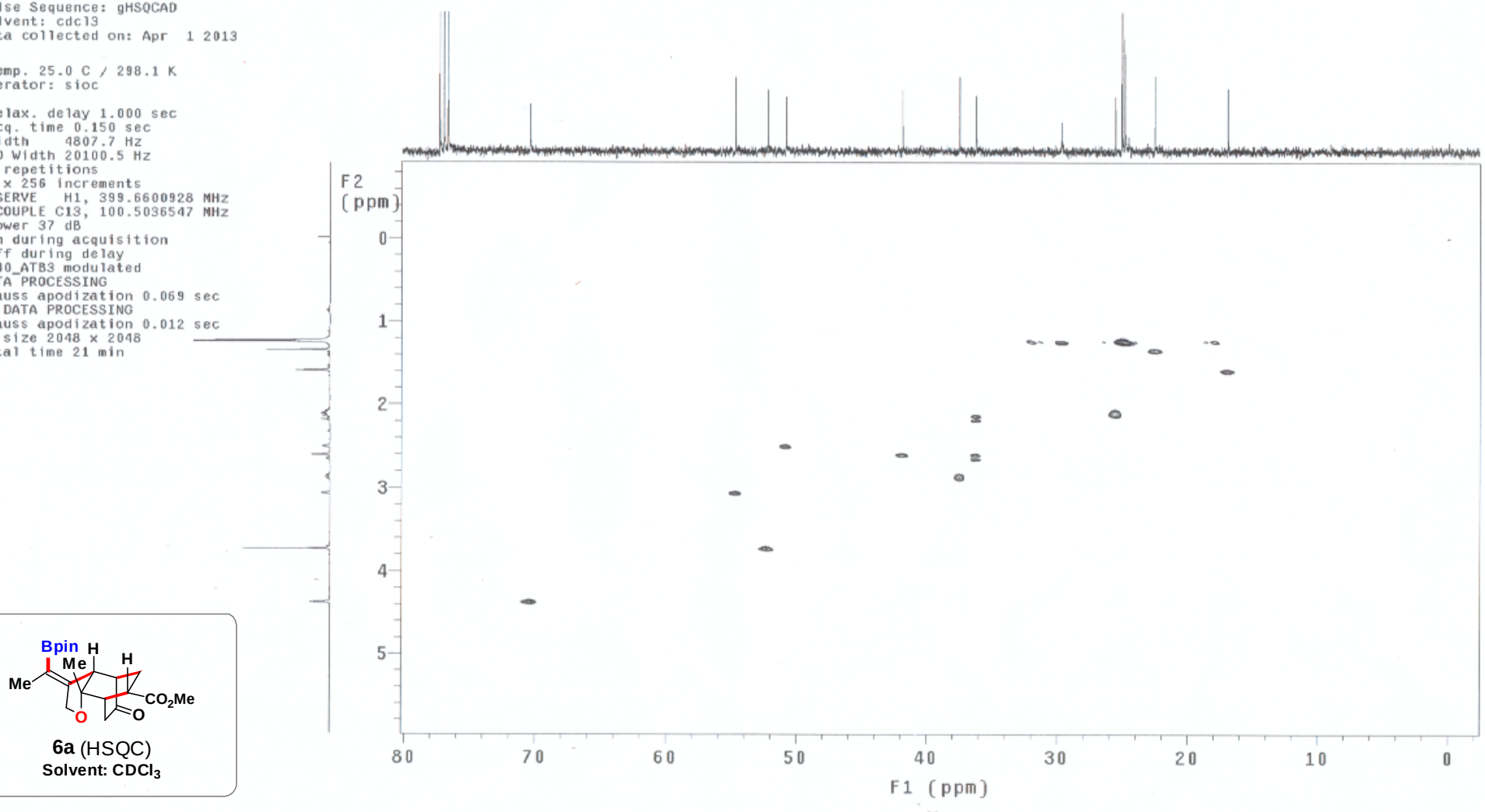
5a (NOSEY)
Solvent: $CDCl_3$



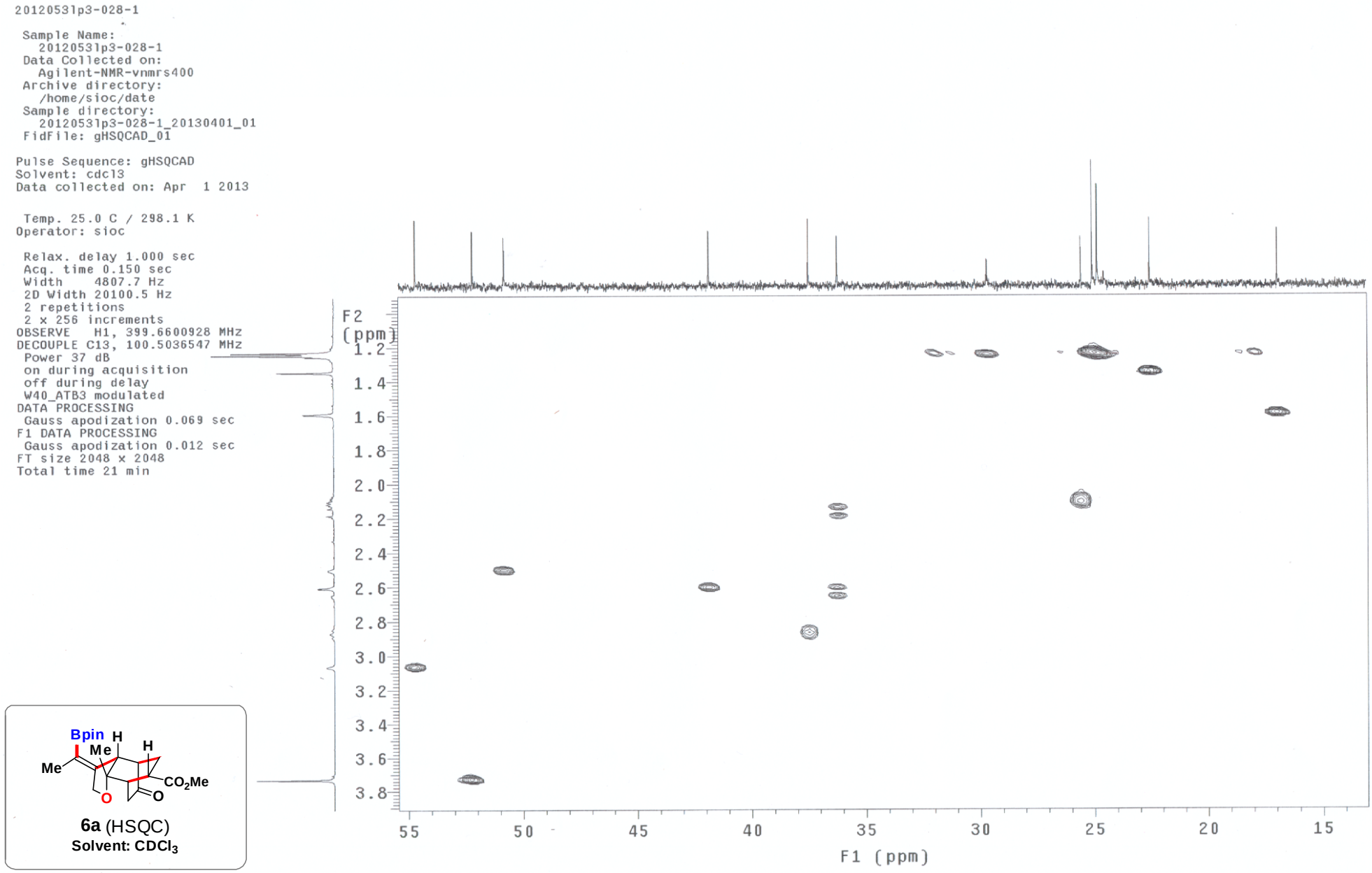

7.275
4.386
3.744
2.906
2.884
2.860
2.672
2.667
3.078
2.662
2.659
2.620
2.617
2.515
2.511
2.206
2.196
2.154
2.145
2.136
2.131
2.128
2.117
2.112
2.102
2.093
2.084
1.606
1.359
1.257
1.244
0.000
Bpin
H
Me
H
Me
CO2Me
O
O
6a (1H NMR)
Solvent: CDCl3
1.90
3.07
1.00
1.11
2.21
1.00
3.23
3.09
2.99
12.44
8
7
6
5
4
3
2
1
0
PPM

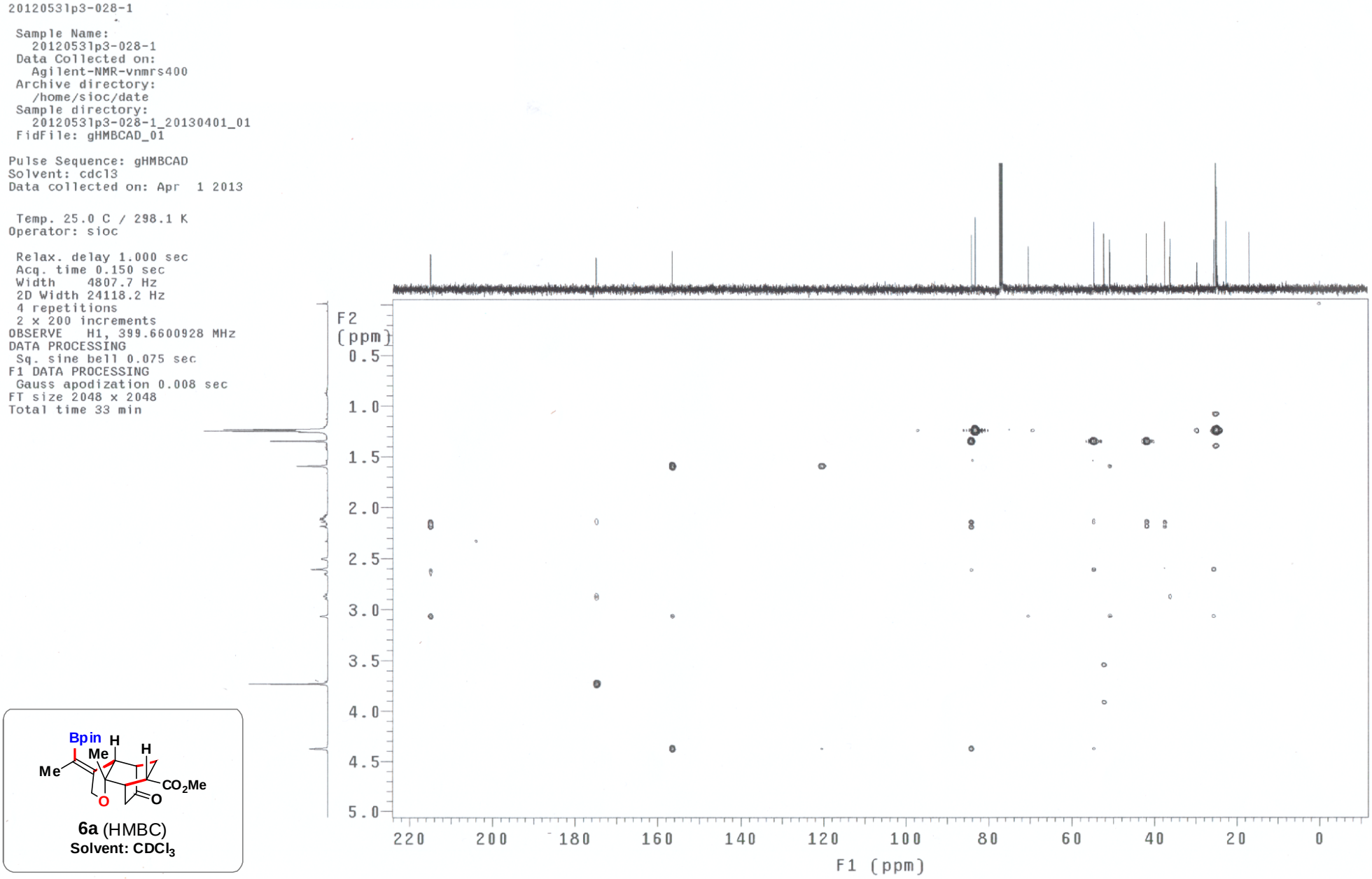

215.063
174.916
156.574
84.252
83.280
77.419
77.100
76.781
70.487
54.787
52.282
50.907
41.933
37.576
36.323
25.641
25.147
24.935
22.627
17.024
Bpin
H
Me
H
Me
CO2Me
O
O
6a (13C NMR)
Solvent: CDCl3
grease
200
150
100
50
0
PPM

```
20120531p3-028-1

 Sample Name:
   20120531p3-028-1
 Data Collected on:
   Agilent-NMR-vnmrs400
 Archive directory:
   /home/sioc/date
 Sample directory:
   20120531p3-028-1_20130401_01
 FidFile: gHSQCAD_01

Pulse Sequence: gHSQCAD
Solvent: cdcl3
Data collected on: Apr  1 2013

 Temp. 25.0 C / 298.1 K
Operator: sioc

 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width    4807.7 Hz
 2D Width 20100.5 Hz
 2 repetitions
 2 x 256 increments
OBSERVE   H1, 399.6600928 MHz
DECOUPLE C13, 100.5036547 MHz
 Power 37 dB
 on during acquisition
 off during delay
 W40_ATB3 modulated
DATA PROCESSING
 Gauss apodization 0.069 sec
F1 DATA PROCESSING
 Gauss apodization 0.012 sec
FT size 2048 x 2048
Total time 21 min
```

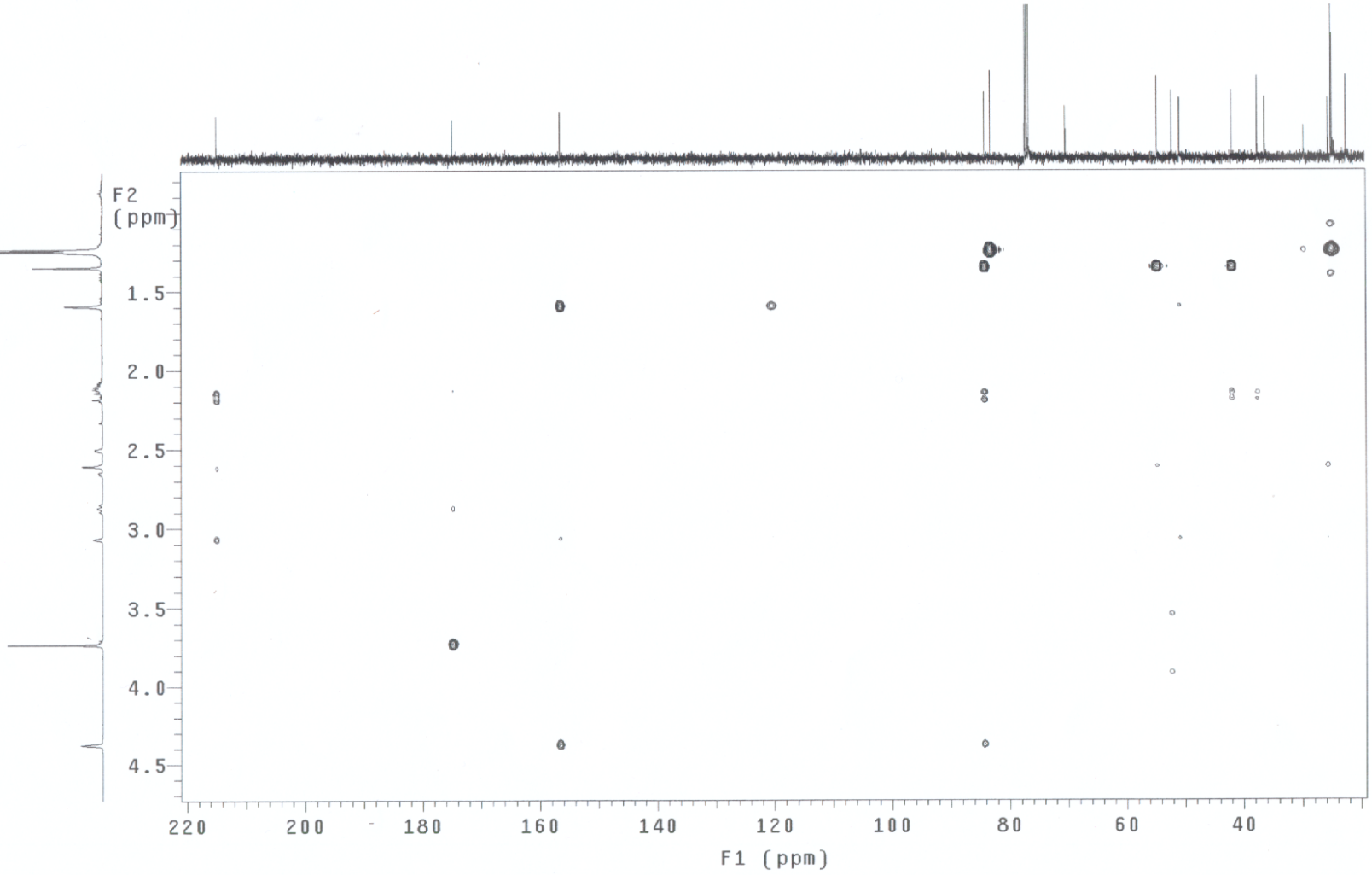


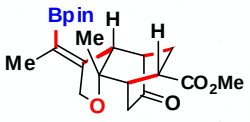
6a (HSQC)
Solvent: $CDCl_3$


20120531p3-028-1
Sample Name:
20120531p3-028-1
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
20120531p3-028-1_20130401_01
FidFile: gHSQCAD_01
Pulse Sequence: gHSQCAD
Solvent: cdcl3
Data collected on: Apr 1 2013
Temp. 25.0 C / 298.1 K
Operator: sioc
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4807.7 Hz
2D Width 20100.5 Hz
2 repetitions
2 x 256 increments
OBSERVE H1, 399.6600928 MHz
DECOUPLE C13, 100.5036547 MHz
Power 37 dB
on during acquisition
off during delay
W40_ATB3 modulated
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.012 sec
FT size 2048 x 2048
Total time 21 min
F2 (ppm)
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
3.4
3.6
3.8
55
50
45
40
35
30
25
20
15
F1 (ppm)
Bpin
H
Me
H
Me
CO2Me
O
O
6a (HSQC)
Solvent: CDCl3

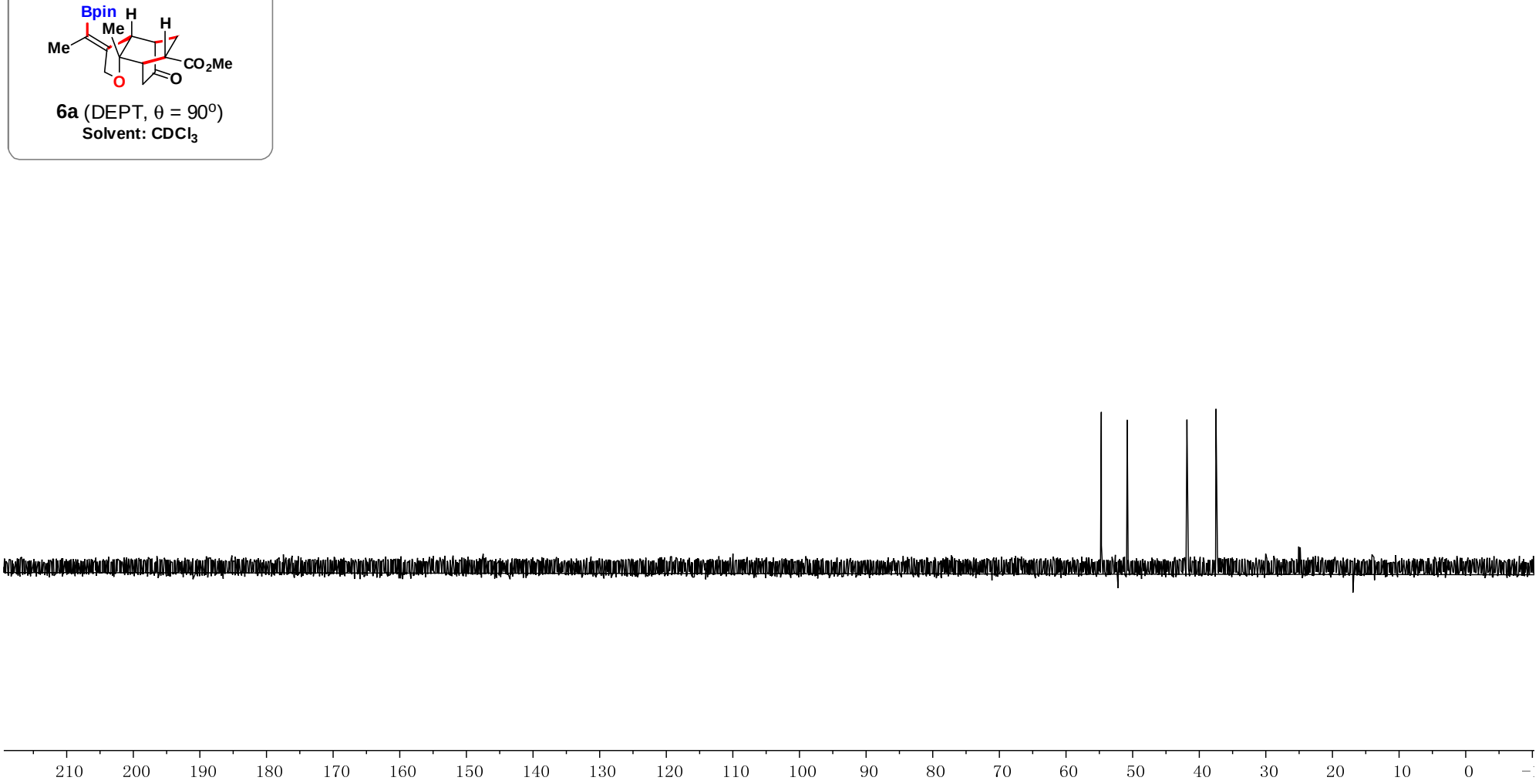

20120531p3-028-1
Sample Name:
20120531p3-028-1
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
20120531p3-028-1_20130401_01
FidFile: gHMBCAD_01
Pulse Sequence: gHMBCAD
Solvent: cdcl3
Data collected on: Apr 1 2013
Temp. 25.0 C / 298.1 K
Operator: sioc
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4807.7 Hz
2D Width 24118.2 Hz
4 repetitions
2 x 200 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Gauss apodization 0.008 sec
FT size 2048 x 2048
Total time 33 min
F2 (ppm)
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
220
200
180
160
140
120
100
80
60
40
20
0
F1 (ppm)
Bpin
H
Me
H
Me
CO2Me
O
O
6a (HMBC)
Solvent: CDCl3

```
20120531p3-028-1

 Sample Name:
   20120531p3-028-1
 Data Collected on:
   Agilent-NMR-vnmrs400
 Archive directory:
   /home/sioc/date
 Sample directory:
   20120531p3-028-1_20130401_01
 FidFile: gHMBCAD_01

Pulse Sequence: gHMBCAD
Solvent: cdcl3
Data collected on: Apr  1 2013

 Temp. 25.0 C / 298.1 K
Operator: sioc

 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width     4807.7 Hz
 2D Width 24118.2 Hz
 4 repetitions
 2 x 200 increments
OBSERVE   H1, 399.6600928 MHz
DATA PROCESSING
 Sq. sine bell 0.075 sec
F1 DATA PROCESSING
 Gauss apodization 0.008 sec
FT size 2048 x 2048
Total time 33 min
```

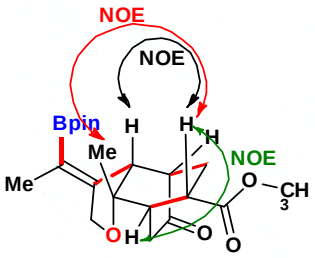


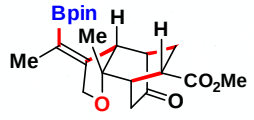


6a (HMBC)
Solvent: $CDCl_3$

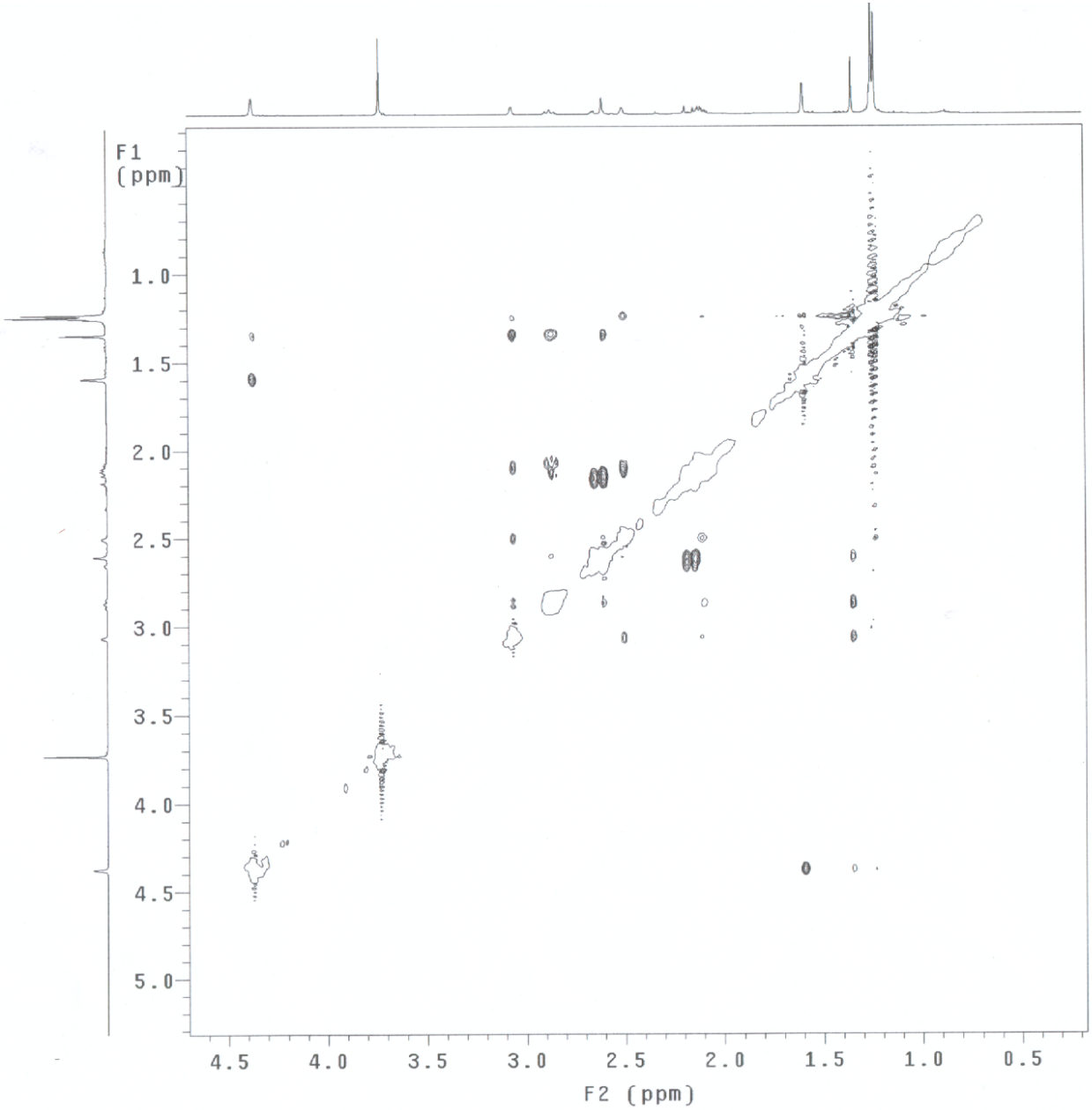

54.695
50.813
41.846
37.485
Bpin
H
Me
H
Me
CO2Me
O
O
6a (DEPT, θ = 90°)
Solvent: CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

```
20120531p3-028-1

 Sample Name:
   20120531p3-028-1
 Data Collected on:
   Agilent-NMR-vnmrs400
 Archive directory:
   /home/sioc/date
 Sample directory:
   20120531p3-028-1_20130401_0_
 FidFile: NOESY_01

Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Apr  1 2013

 Temp. 25.0 C / 298.1 K
Operator: sioc

 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width     4807.7 Hz
 2D Width 4807.7 Hz
 8 repetitions
 2 x 200 increments
OBSERVE   H1, 399.6600928 MHz
DATA PROCESSING
 Gauss apodization 0.069 sec
F1 DATA PROCESSING
 Gauss apodization 0.038 sec
FT size 2048 x 2048
Total time 1 hr, 41 min
```





6a (NOSEY)
Solvent: $CDCl_3$



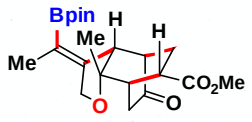
20120531p3-028-1

Sample Name:
20120531p3-028-1
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
20120531p3-028-1_20130401_01
FidFile: NOESY_01

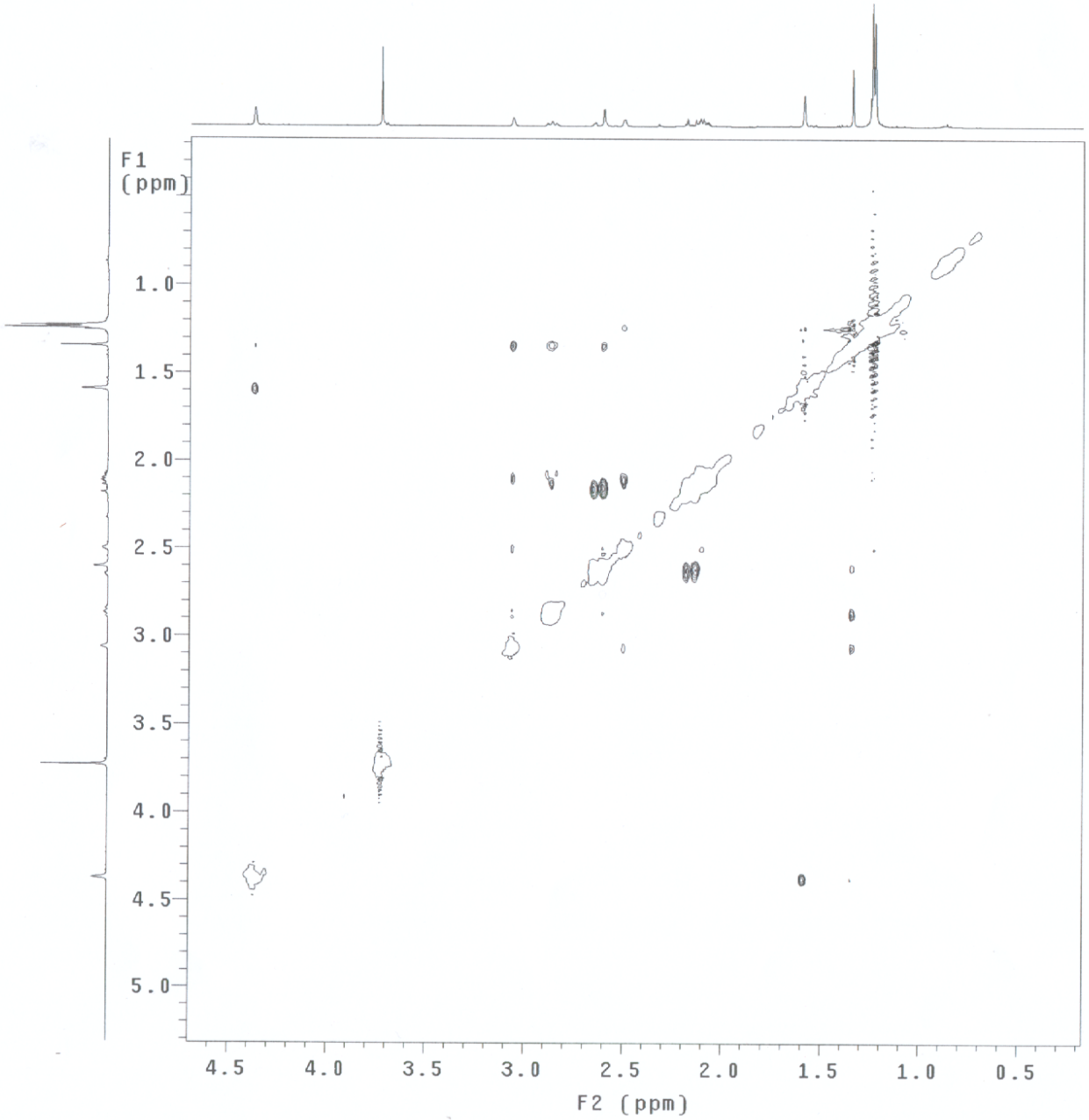
Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Apr 1 2013

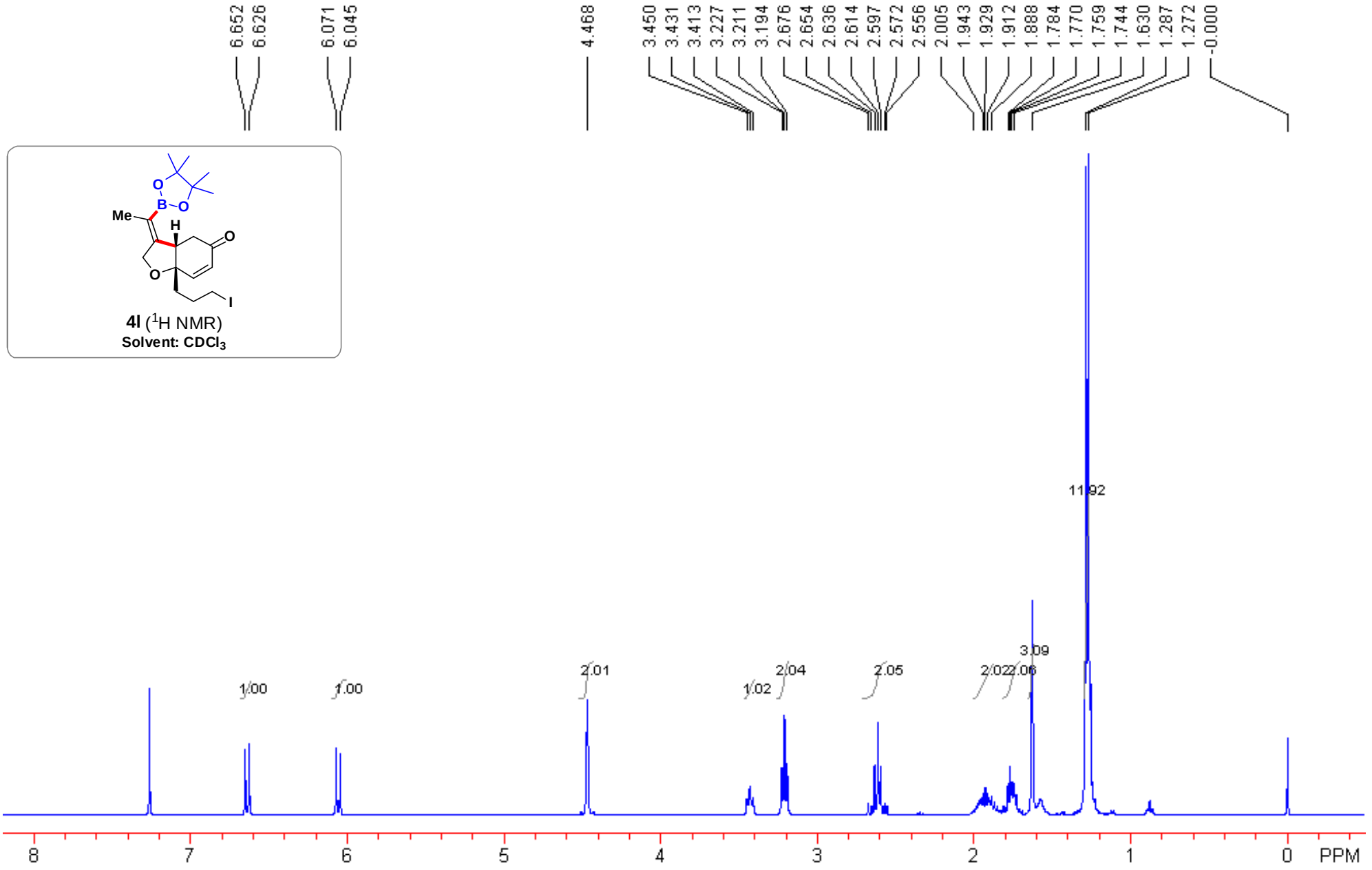
Temp. 25.0 C / 298.1 K
Operator: sioc

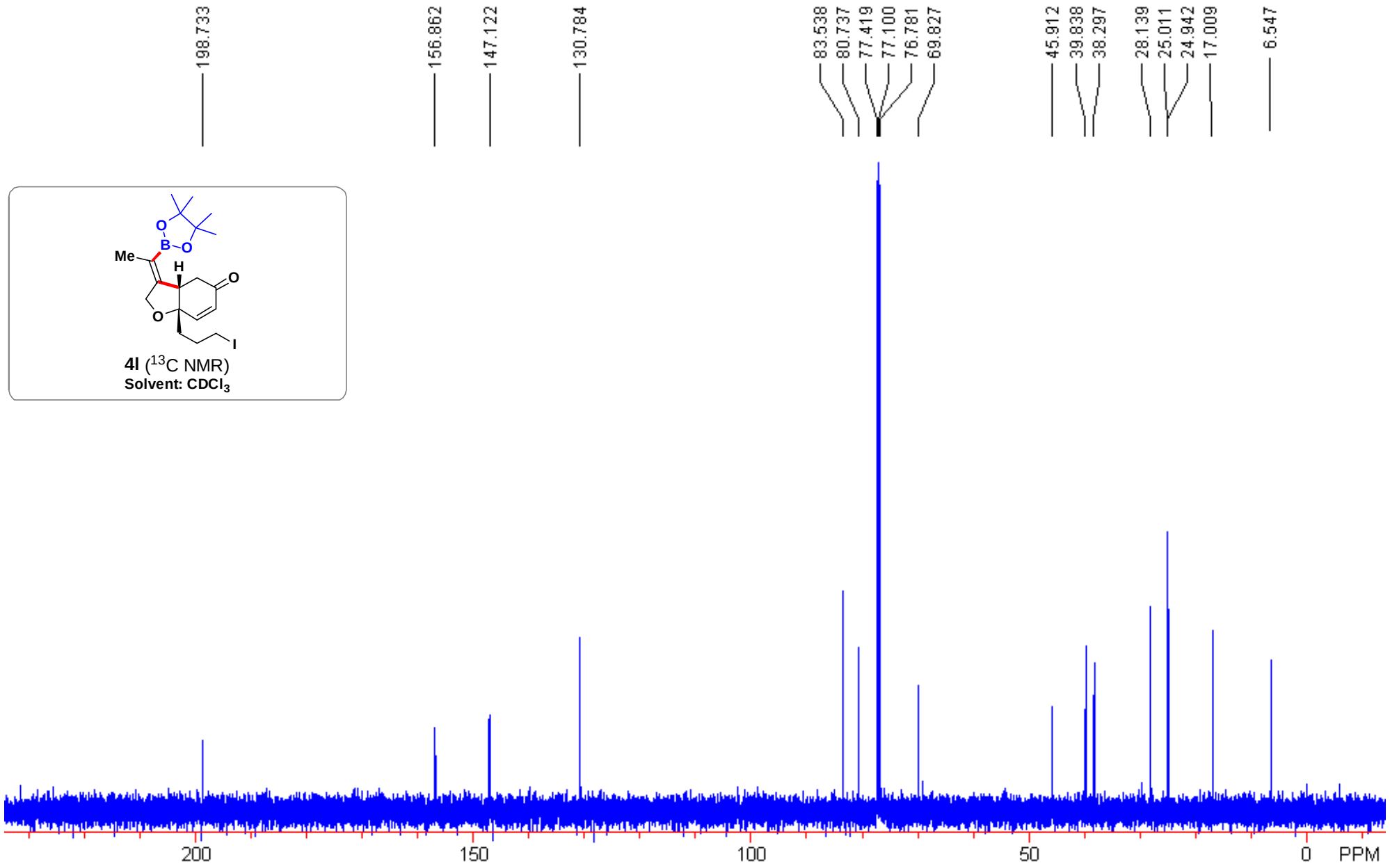
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4807.7 Hz
2D Width 4807.7 Hz
8 repetitions
2 x 200 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.038 sec
FT size 2048 x 2048
Total time 1 hr, 41 min

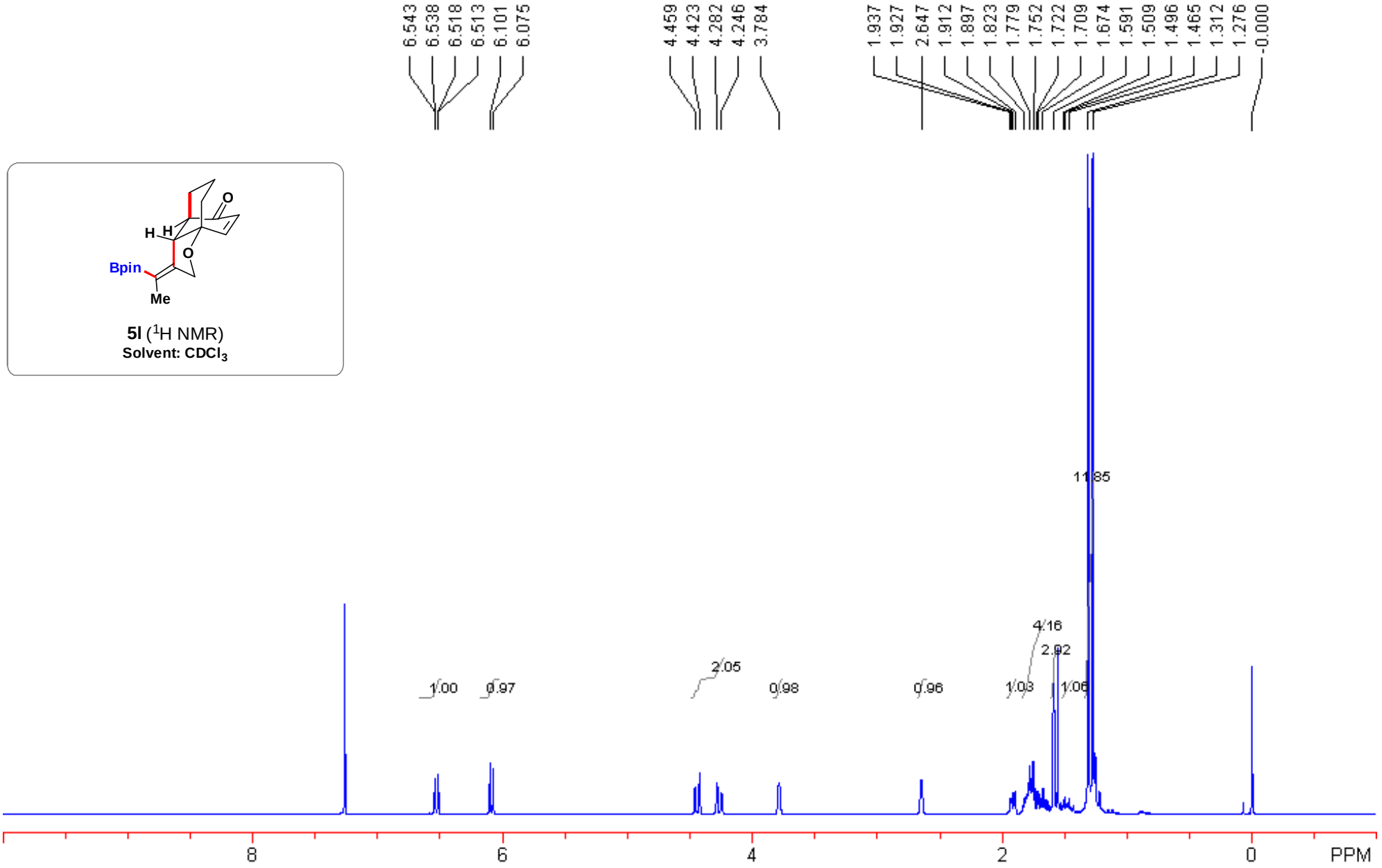


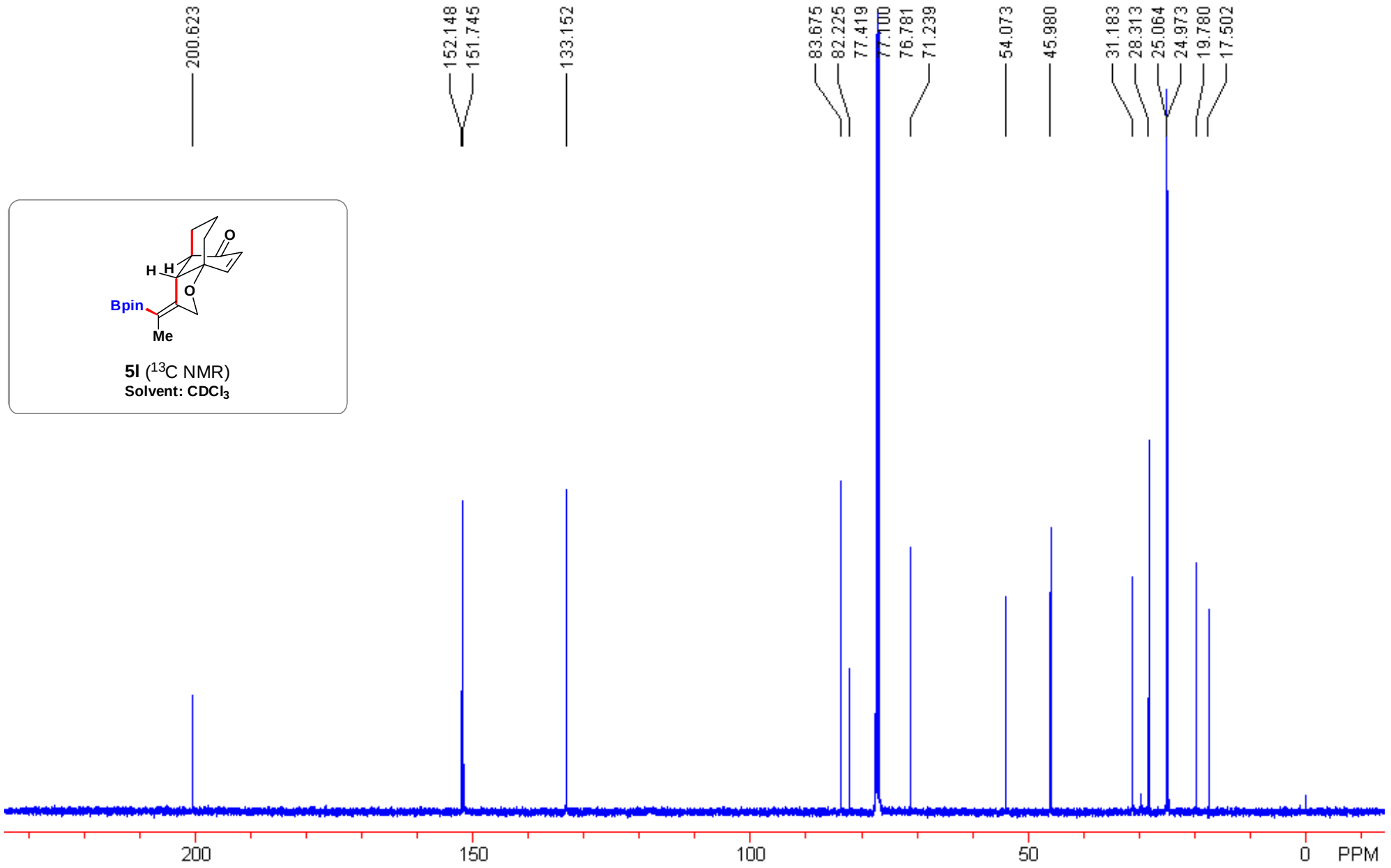
6a (NOESY)
Solvent: $CDCl_3$

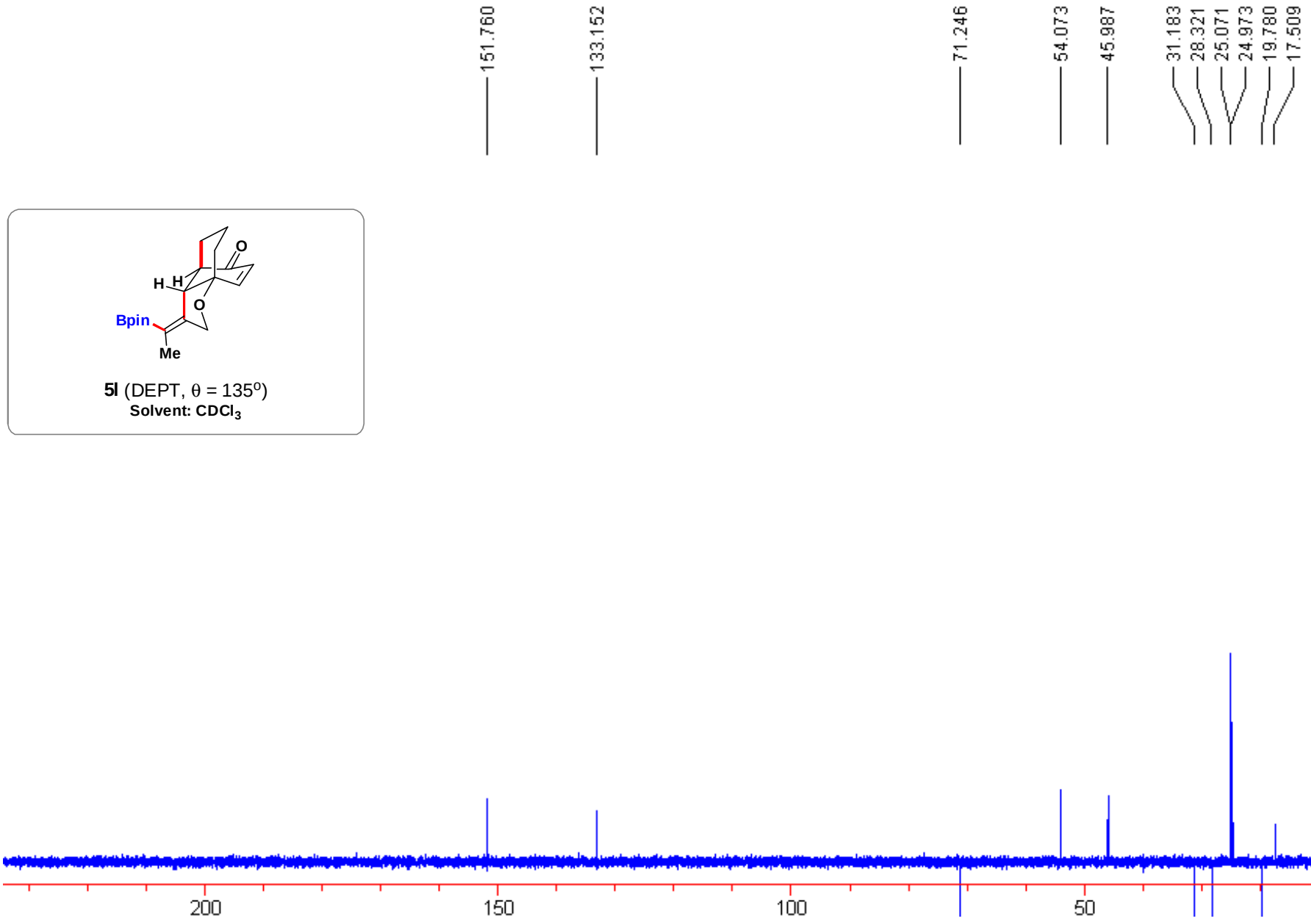



6.652
6.626
6.071
6.045
4.468
3.450
3.431
3.413
3.227
3.211
3.194
2.676
2.654
2.636
2.614
2.597
2.572
2.556
2.005
1.943
1.929
1.912
1.888
1.784
1.770
1.759
1.744
1.630
1.287
1.272
-0.000
Me
H
O
B
O
O
O
I
4l (1H NMR)
Solvent: CDCl3
1.00
1.00
2.01
1.02
2.04
2.05
2.02
2.06
3.09
11.92
8
7
6
5
4
3
2
1
0
PPM


198.733
156.862
147.122
130.784
83.538
80.737
77.419
77.100
76.781
69.827
45.912
39.838
38.297
28.139
25.011
24.942
17.009
6.547
Me
H
O
B
O
O
O
I
4l (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM


6.543
6.538
6.518
6.513
6.101
6.075
4.459
4.423
4.282
4.246
3.784
1.937
1.927
2.647
1.912
1.897
1.823
1.779
1.752
1.722
1.709
1.674
1.591
1.509
1.496
1.465
1.312
1.276
0.000
O
H
H
O
Bpin
Me
5l (1H NMR)
Solvent: CDCl3
11.85
4.16
2.92
2.05
1.00
0.97
0.98
0.96
1.03
1.06
8
6
4
2
0
PPM


200.623
152.148
151.745
133.152
83.675
82.225
77.419
77.100
76.781
71.239
54.073
45.980
31.183
28.313
25.064
24.973
19.780
17.502
O
H
H
O
Bpin
Me
5l (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM


151.760
133.152
71.246
54.073
45.987
31.183
28.321
25.071
24.973
19.780
17.509
O
H
H
O
Bpin
Me
5l (DEPT, θ = 135°)
Solvent: CDCl3
200
150
100
50
0
PPM

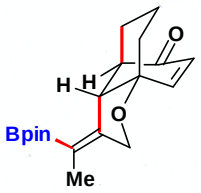
2012576yf02-16-01

Sample Name:
2012576yf02-16-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-16-01_20130408_01
FidFile: gCOSY_01

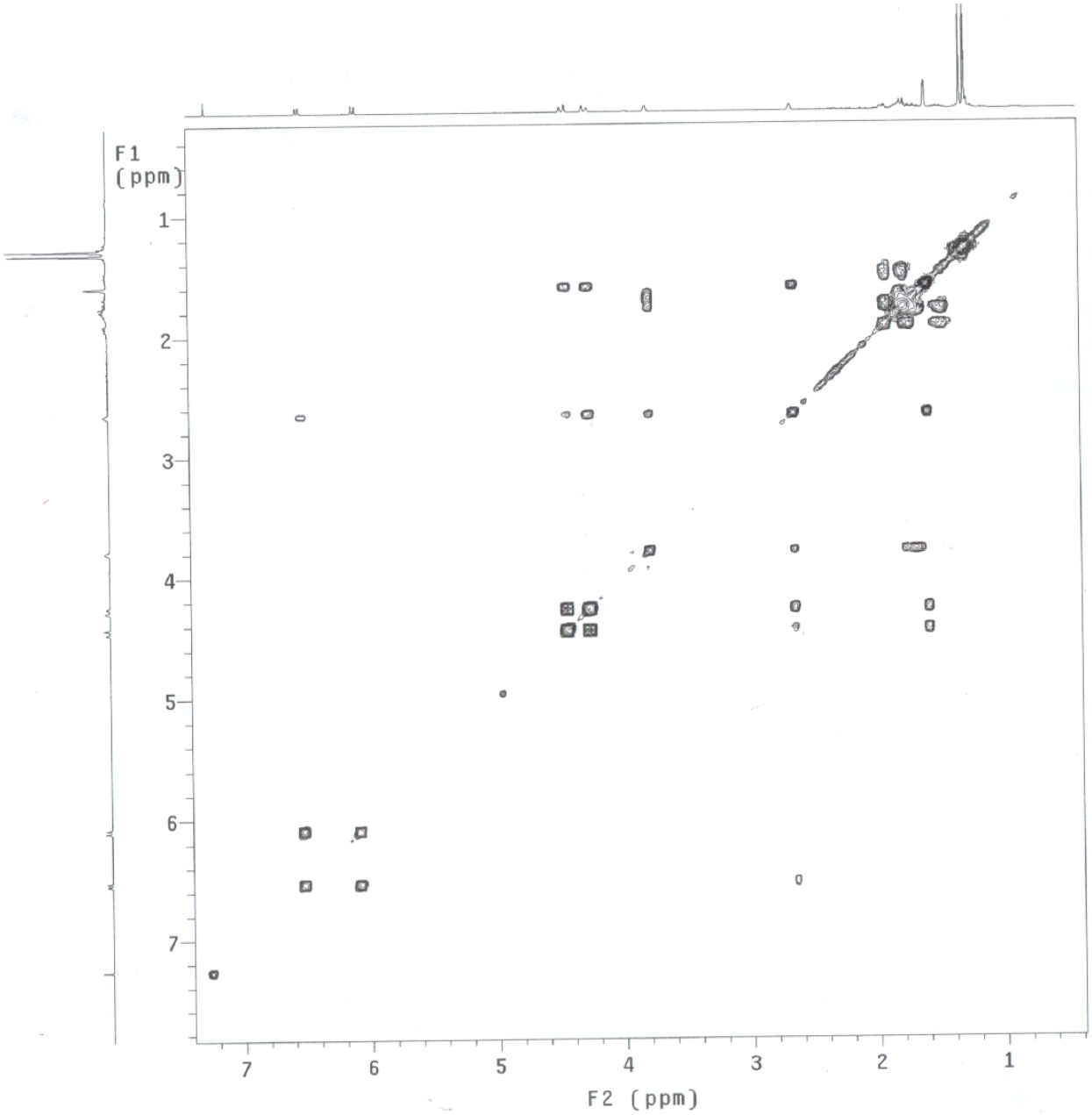
Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Apr 8 2013

Temp. 25.0 C / 298.1 K
Operator: sioc

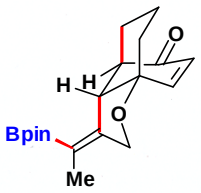
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4058.4 Hz
2D Width 4058.4 Hz
8 repetitions
256 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Sq. sine bell 0.040 sec
FT size 2048 x 2048
Total time 41 min



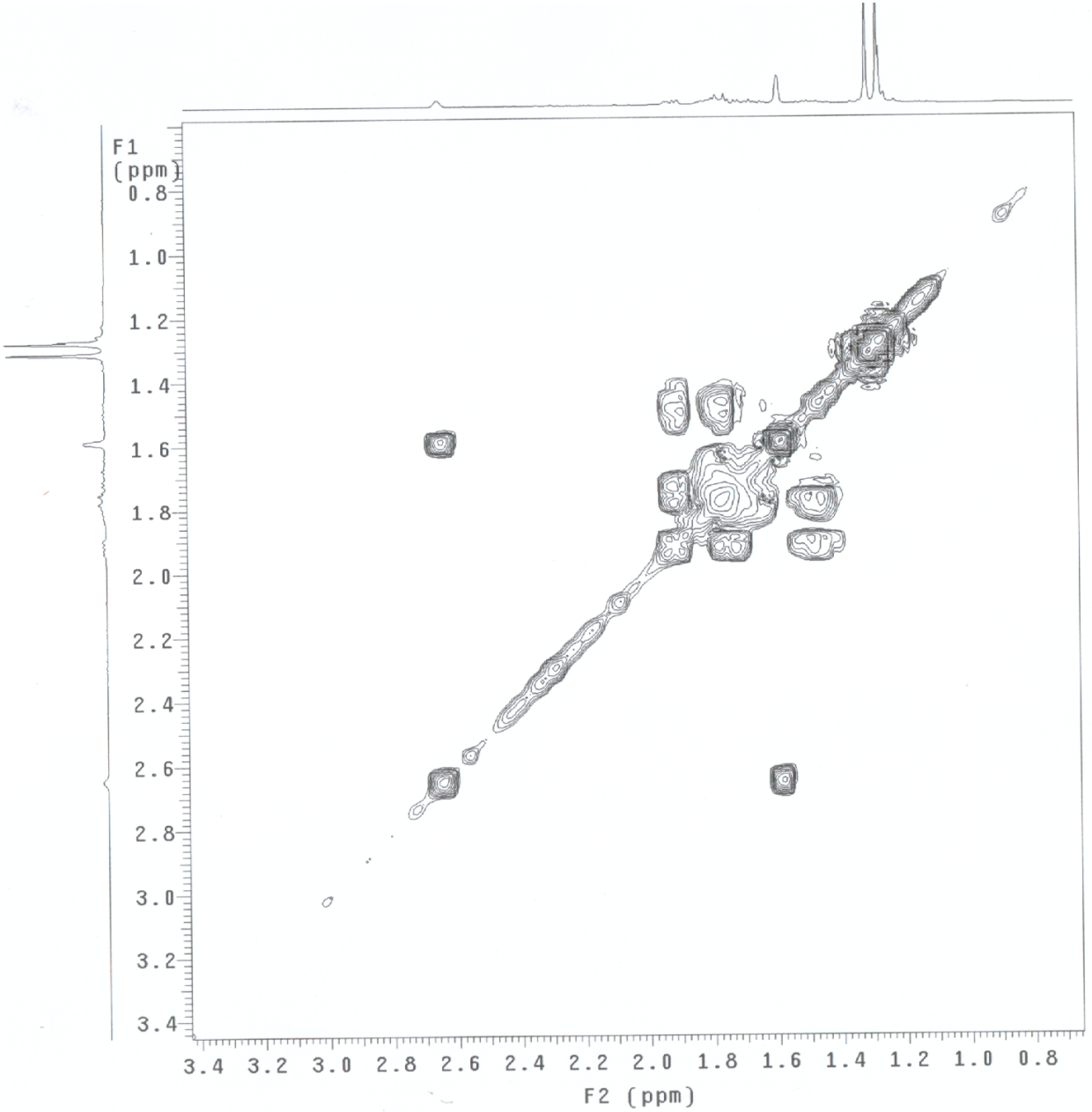
5l (H-H COSY)
Solvent: $CDCl_3$

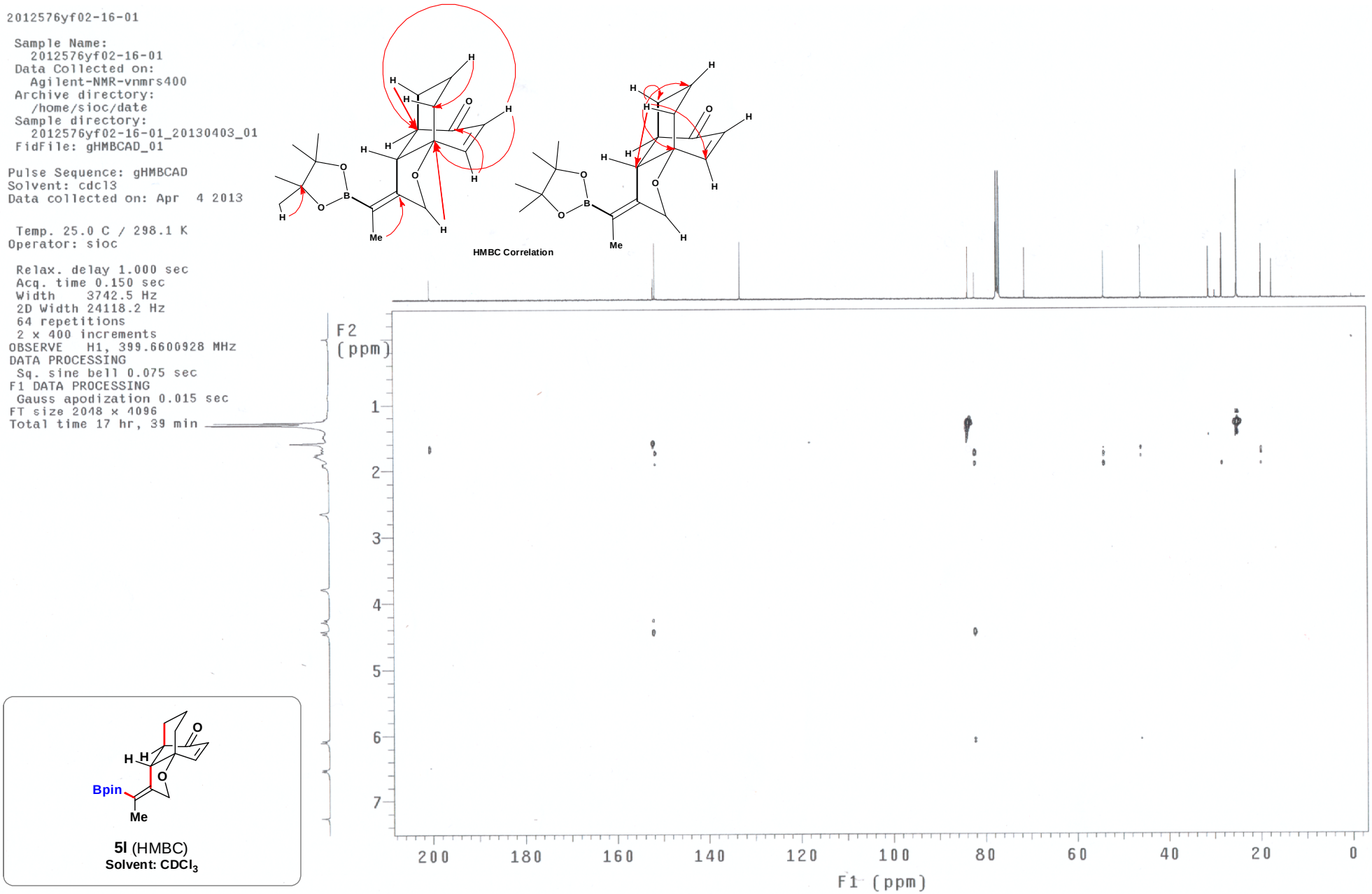


```
2012576yf02-16-01

 Sample Name:
   2012576yf02-16-01
 Data Collected on:
   Agilent-NMR-vnmrs400
 Archive directory:
   /home/sioc/date
 Sample directory:
   2012576yf02-16-01_20130408_01
 FidFile: gCOSY_01

Pulse Sequence: gCOSY
Solvent: cdcl3
Data collected on: Apr  8 2013

 Temp. 25.0 C / 298.1 K
Operator: sioc

 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width    4058.4 Hz
 2D Width 4058.4 Hz
 8 repetitions
 256 increments
OBSERVE   H1, 399.6600928 MHz
DATA PROCESSING
 Sq. sine bell 0.075 sec
F1 DATA PROCESSING
 Sq. sine bell 0.040 sec
FT size 2048 x 2048
Total time 41 min
```



5l (H-H COSY)
Solvent: $CDCl_3$




2012576yf02-16-01
Sample Name:
2012576yf02-16-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-16-01_20130403_01
FidFile: gHMBCAD_01
Pulse Sequence: gHMBCAD
Solvent: cdcl3
Data collected on: Apr 4 2013
Temp. 25.0 C / 298.1 K
Operator: sioc
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3742.5 Hz
2D Width 24118.2 Hz
64 repetitions
2 x 400 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Gauss apodization 0.015 sec
FT size 2048 x 4096
Total time 17 hr, 39 min
HMBC Correlation
F2 (ppm)
F1 (ppm)
Bpin
Me
5l (HMBC)
Solvent: CDCl3

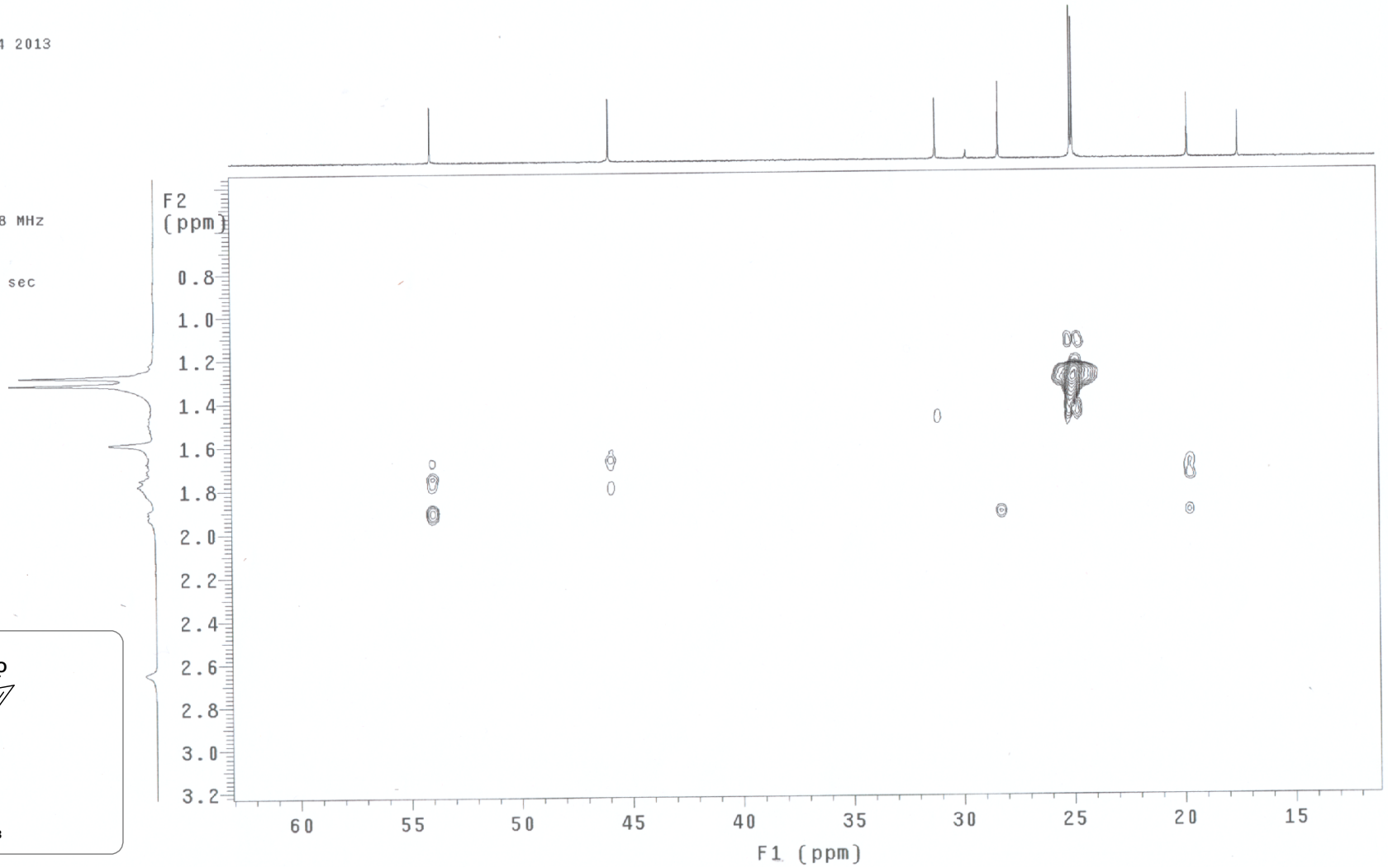
2012576yf02-16-01

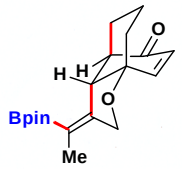
Sample Name:
2012576yf02-16-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-16-01_20130403_01
FidFile: gHMBCAD_01

Pulse Sequence: gHMBCAD
Solvent: cdcl3
Data collected on: Apr 4 2013

Temp. 25.0 C / 298.1 K
Operator: sioc

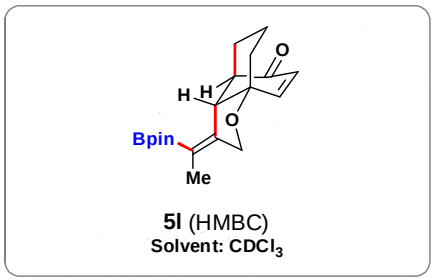
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3742.5 Hz
2D Width 24118.2 Hz
64 repetitions
2 x 400 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Gauss apodization 0.015 sec
FT size 2048 x 4096
Total time 17 hr, 39 min



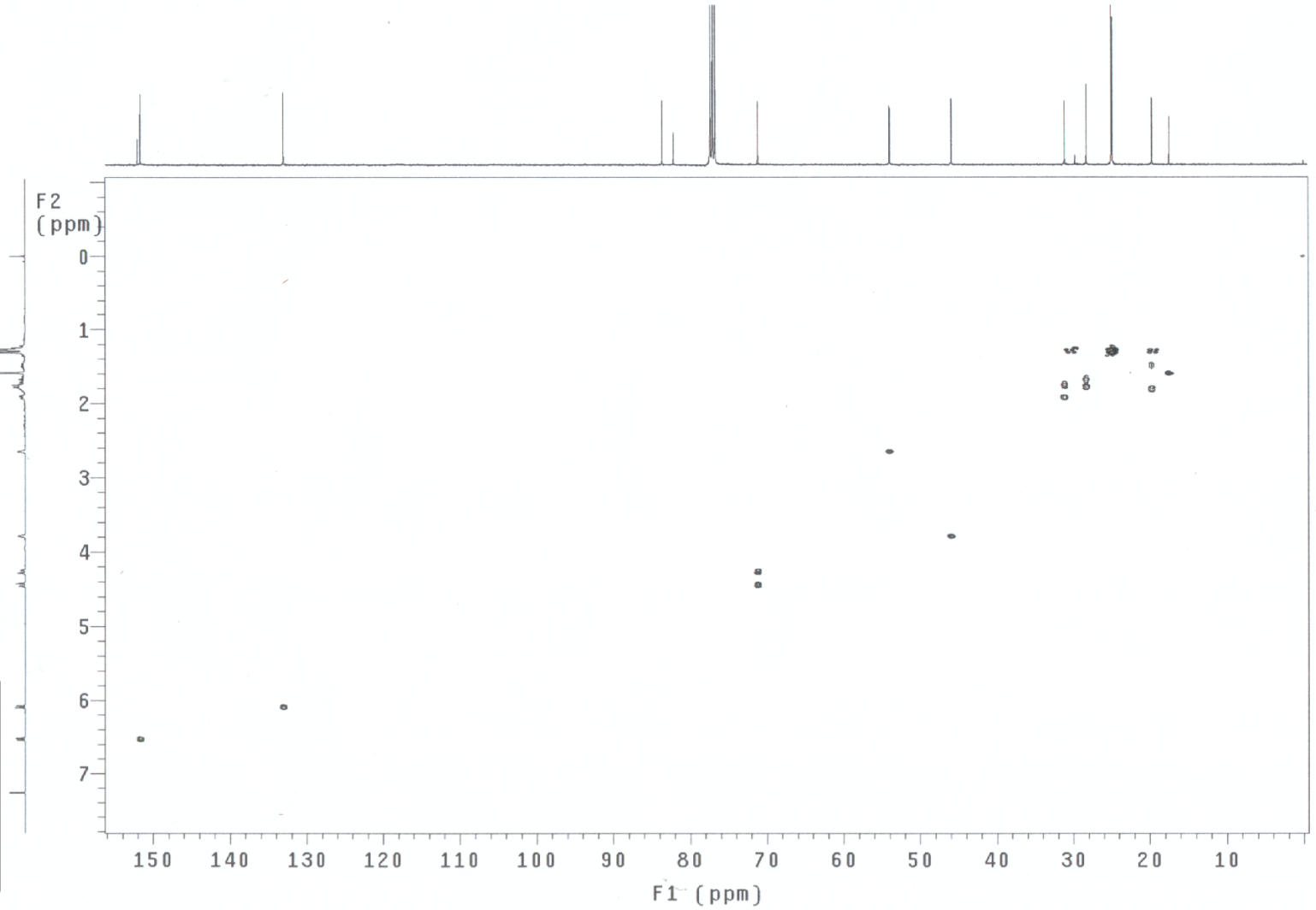


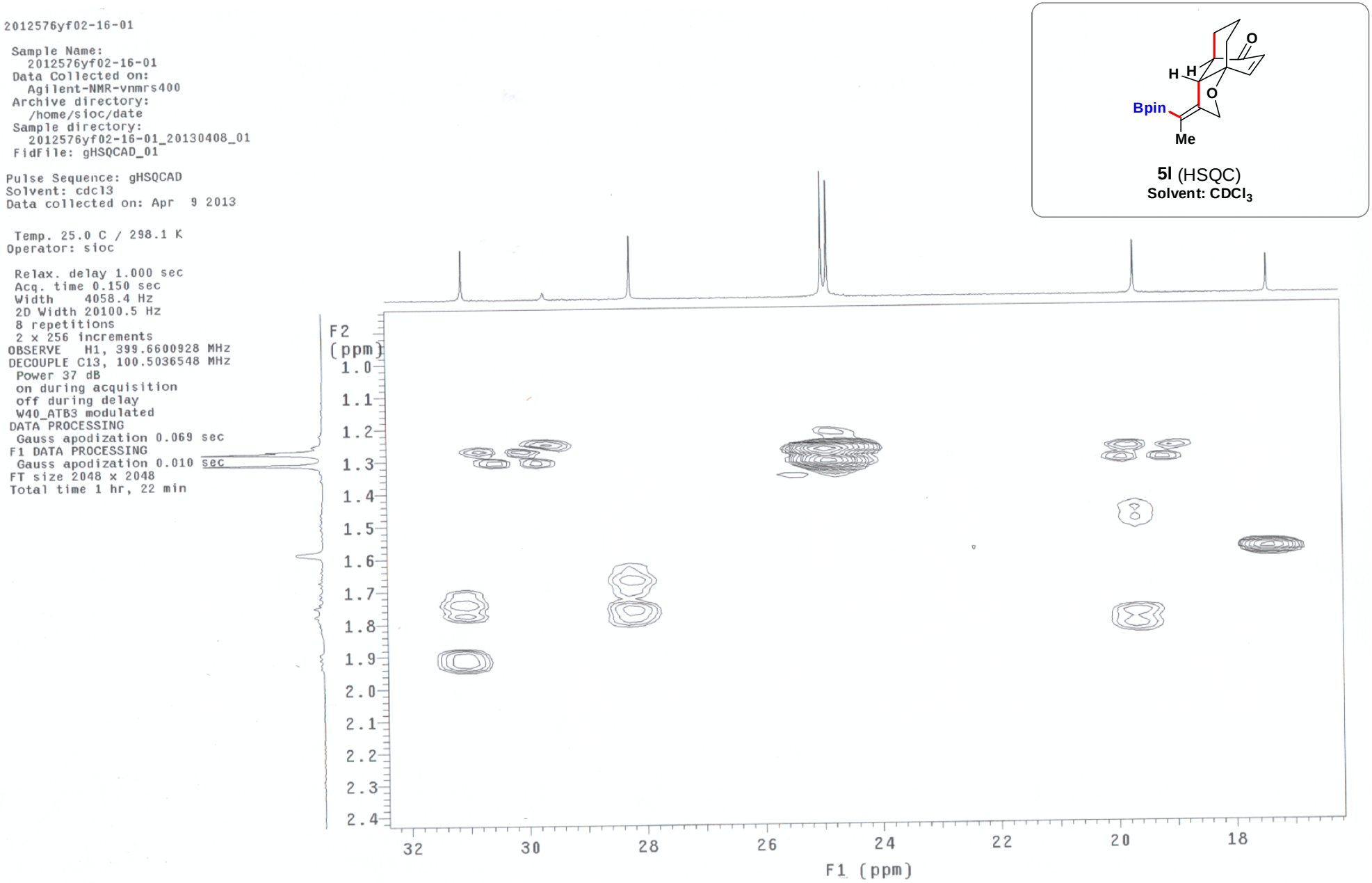
5l (HMBC)
Solvent: $CDCl_3$

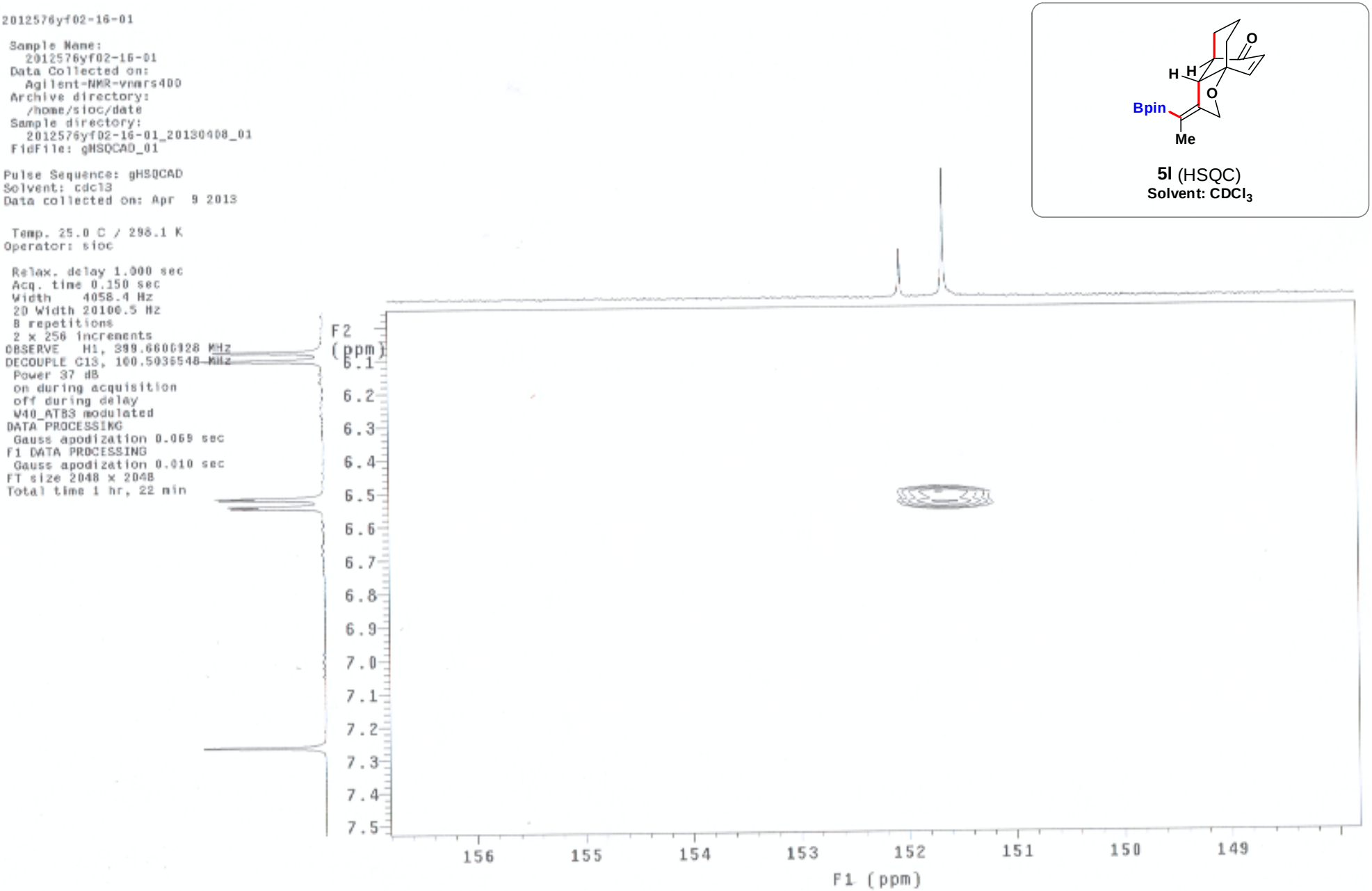
```
 Sample Name:
   2012576yf02-16-01
 Data Collected on:
   Agilent-NMR-vnmrs400
 Archive directory:
   /home/sioc/date
 Sample directory:
   2012576yf02-16-01_20130408_01
 FidFile: gHSQCAD_01

Pulse Sequence: gHSQCAD
Solvent: cdcl3
Data collected on: Apr  9 2013

 Temp. 25.0 C / 298.1 K
Operator: sioc

 Relax. delay 1.000 sec
 Acq. time 0.150 sec
 Width     4058.4 Hz
 2D Width 20100.5 Hz
 8 repetitions
 2 x 256 increments
OBSERVE   H1, 399.6600928 MHz
DECOUPLE C13, 100.5036548 MHz
 Power 37 dB
 on during acquisition
 off during delay
 W40_ATB3 modulated
DATA PROCESSING
 Gauss apodization 0.069 sec
F1 DATA PROCESSING
 Gauss apodization 0.010 sec
FT size 2048 x 2048
Total time 1 hr, 22 min
```



5l (HMBC)
Solvent: $CDCl_3$




2012576yf02-16-01
Sample Name:
2012576yf02-16-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-16-01_20130408_01
FidFile: gHSQCAD_01
Pulse Sequence: gHSQCAD
Solvent: cdcl3
Data collected on: Apr 9 2013
Temp. 25.0 C / 298.1 K
Operator: sioc
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4058.4 Hz
2D Width 20100.5 Hz
8 repetitions
2 x 256 increments
OBSERVE H1, 399.6600928 MHz
DECOUPLE C13, 100.5036548 MHz
Power 37 dB
on during acquisition
off during delay
W40_ATB3 modulated
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.010 sec
FT size 2048 x 2048
Total time 1 hr, 22 min
O
H
H
O
Bpin
Me
5l (HSQC)
Solvent: CDCl3
F2 (ppm)
1.0
1.1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
2.0
2.1
2.2
2.3
2.4
32
30
28
26
24
22
20
18
F1 (ppm)


2012576yf02-16-01
Sample Name:
2012576yf02-16-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-16-01_20130408_01
FidFile: gHSQCAD_01
Pulse Sequence: gHSQCAD
Solvent: cdcl3
Data collected on: Apr 9 2013
Temp. 25.0 C / 298.1 K
Operator: sioc
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4058.4 Hz
20 Width 20100.5 Hz
8 repetitions
2 x 256 increments
OBSERVE H1, 399.6600328 MHz
DECOUPLE C13, 100.5036548 MHz
Power 37 dB
on during acquisition
off during delay
W40_ATB3 modulated
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.010 sec
FT size 2048 x 2048
Total time 1 hr, 22 min
F2 (ppm)
6.1
6.2
6.3
6.4
6.5
6.6
6.7
6.8
6.9
7.0
7.1
7.2
7.3
7.4
7.5
156
155
154
153
152
151
150
149
F1 (ppm)
O
H
H
O
Bpin
Me
5l (HSQC)
Solvent: CDCl3

2012576yf02-16-01

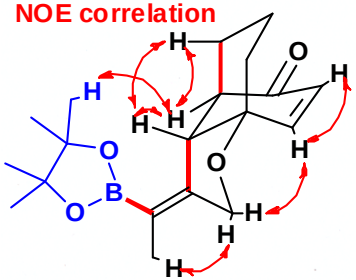
Sample Name:
2012576yf02-16-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-16-01_20130408_01
FidFile: NOESY_01

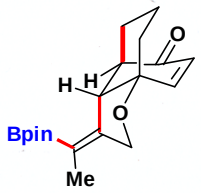
Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Apr 8 2013

Temp. 25.0 C / 298.1 K
Operator: sioc

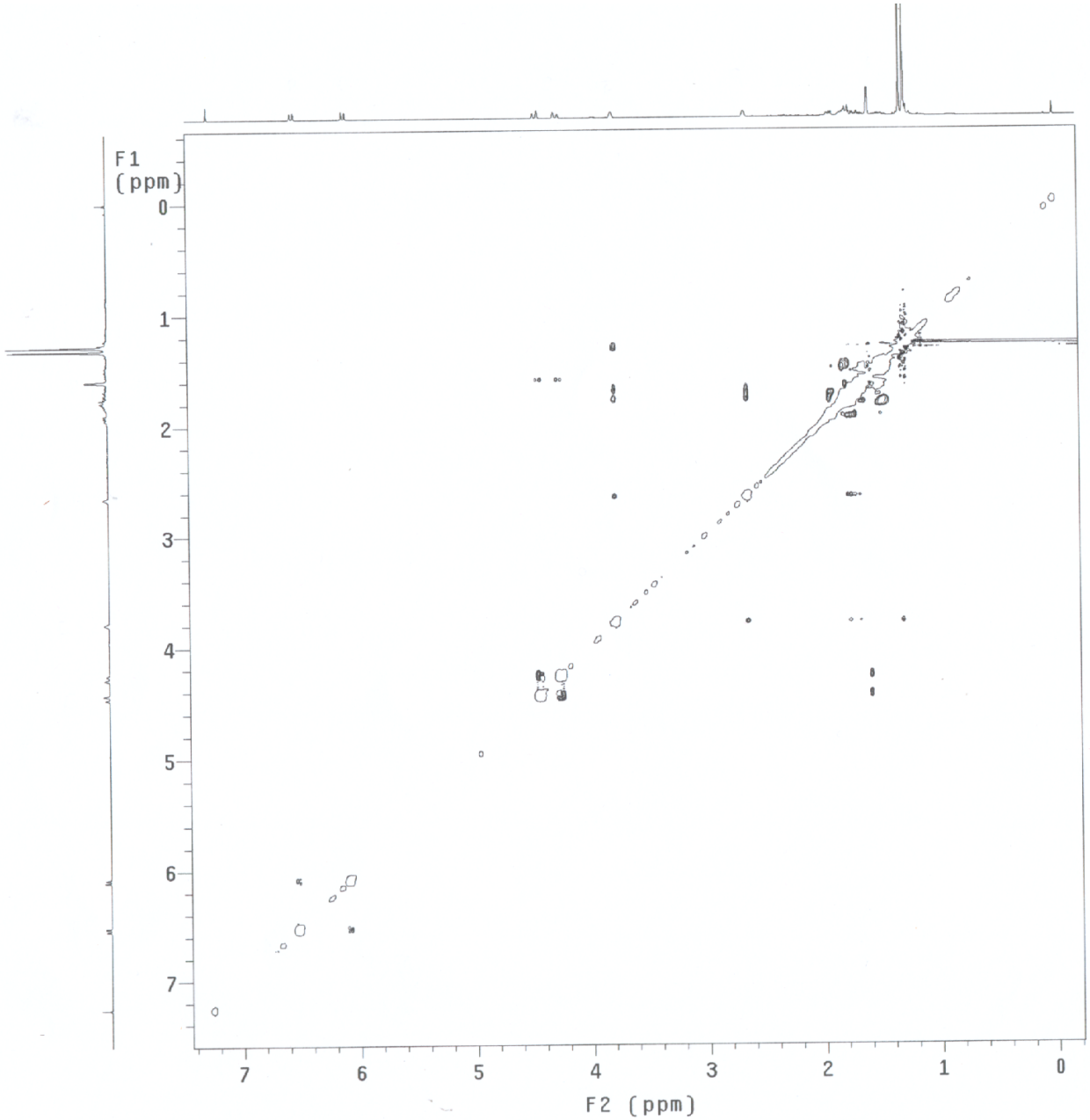
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4058.4 Hz
2D Width 4058.4 Hz
64 repetitions
2 x 200 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.045 sec
FT size 4096 x 4096
Total time 13 hr, 22 min

NOE correlation





5l (NOSEY)
Solvent: $CDCl_3$



2012576yf02-16-01

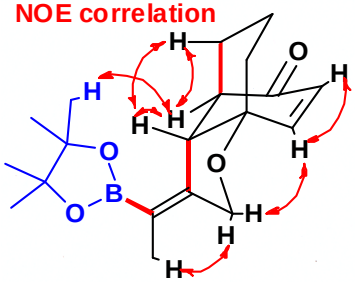
Sample Name:
2012576yf02-16-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-16-01_20130408_01
FidFile: NOESY_01

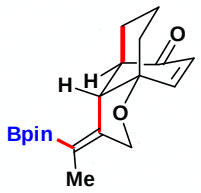
Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Apr 8 2013

Temp. 25.0 C / 298.1 K
Operator: sioc

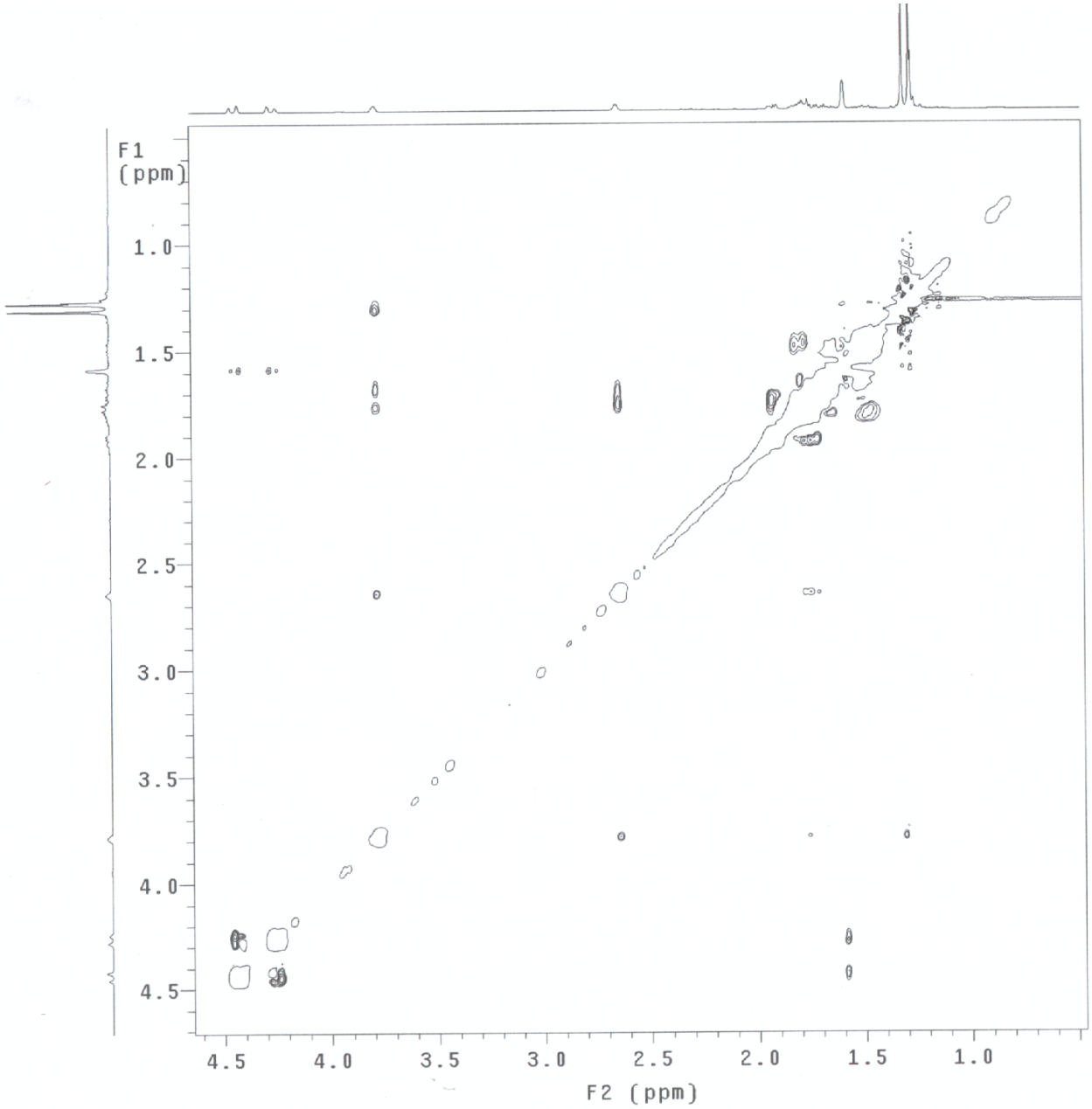
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 4058.4 Hz
2D Width 4058.4 Hz
64 repetitions
2 x 200 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.045 sec
FT size 4096 x 4096
Total time 13 hr, 22 min

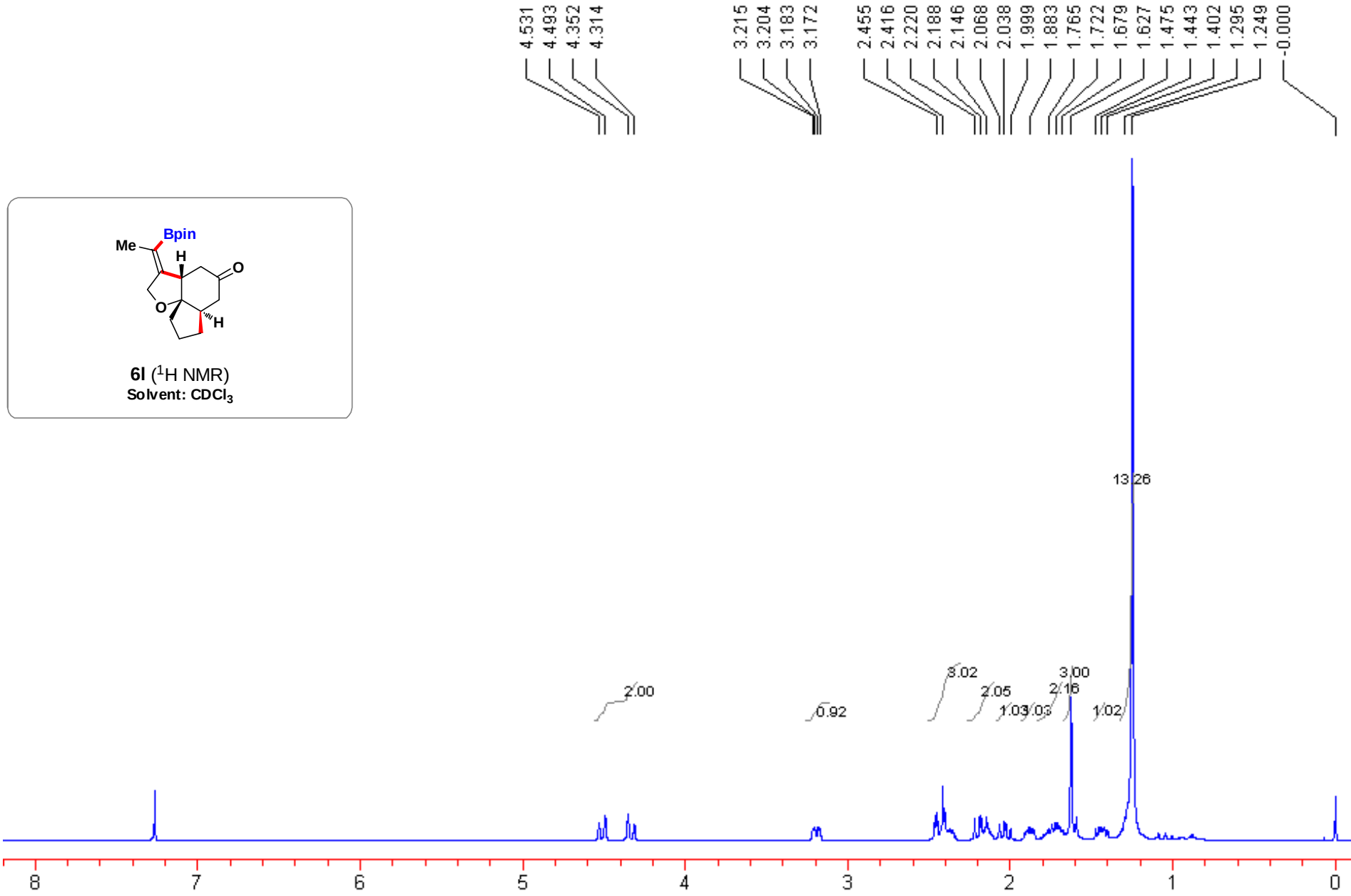
NOE correlation

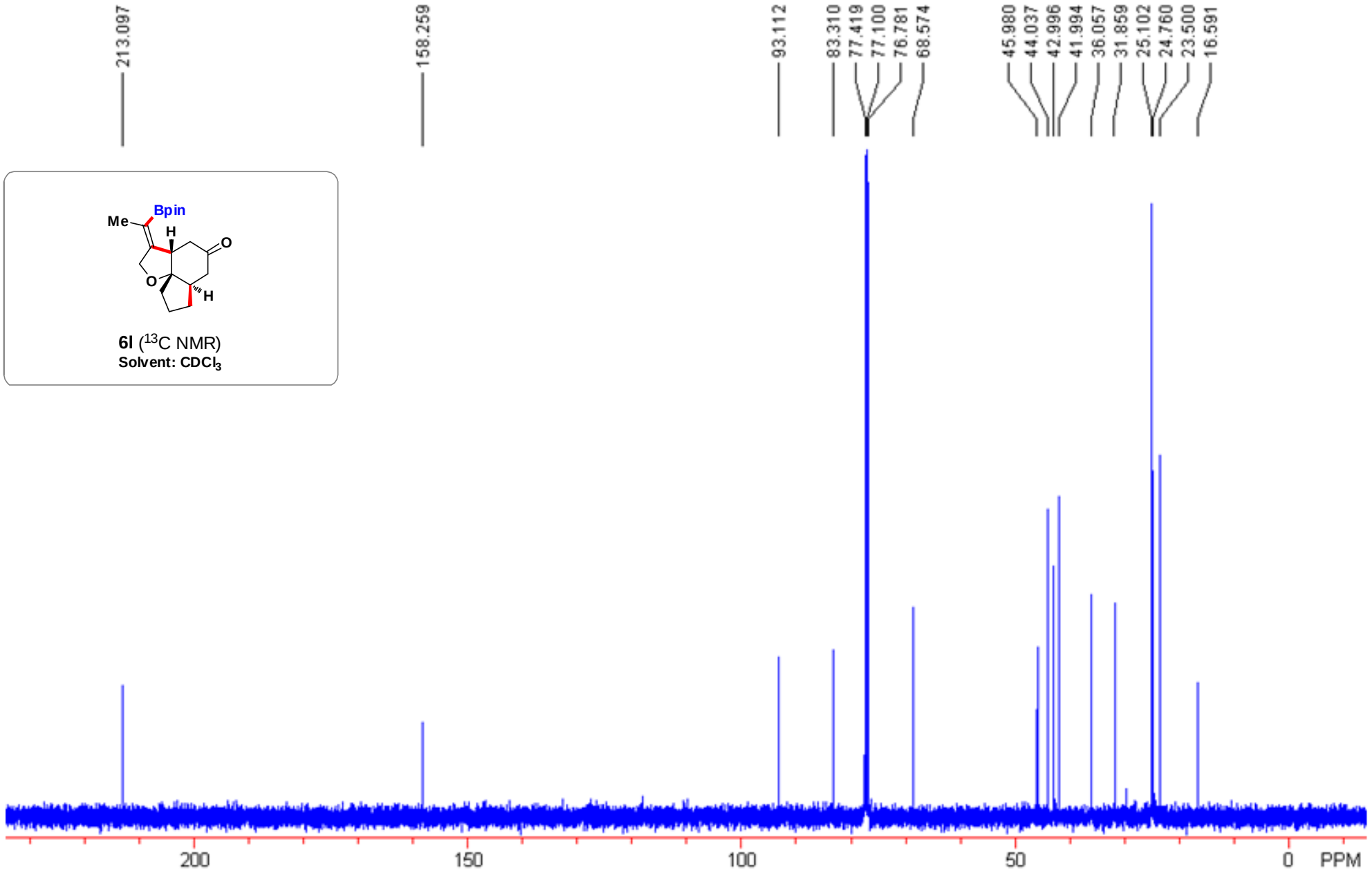


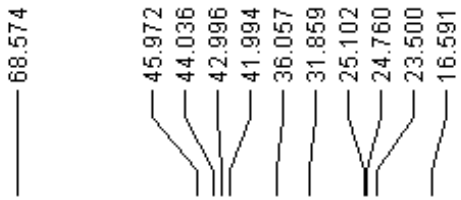


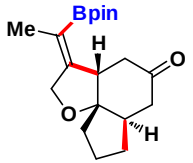
5l (NOSEY)
Solvent: $CDCl_3$



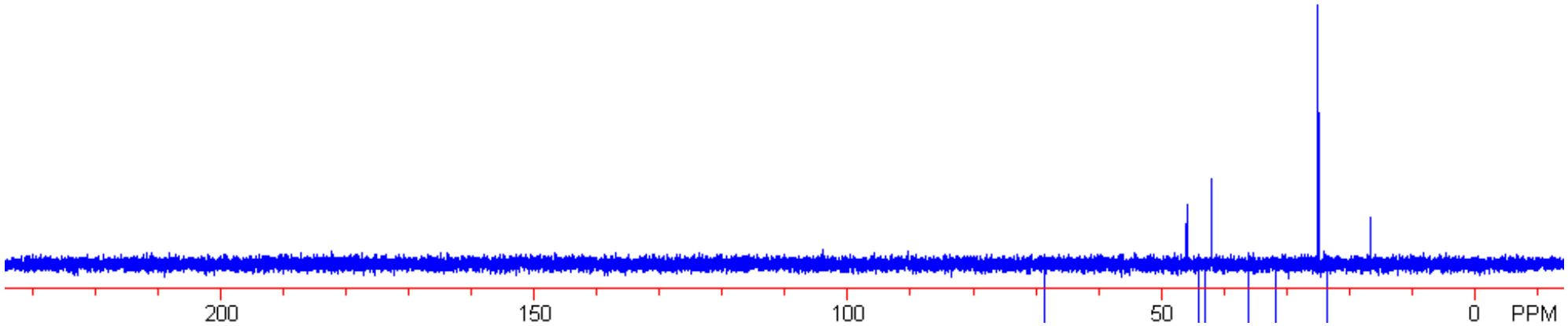

4.531
4.493
4.352
4.314
3.215
3.204
3.183
3.172
2.455
2.416
2.220
2.188
2.146
2.068
2.038
1.999
1.883
1.765
1.722
1.679
1.627
1.475
1.443
1.402
1.295
1.249
-0.000
Bpin
Me
H
O
O
H
6l (1H NMR)
Solvent: CDCl3
13.26
3.02
3.00
2.16
2.05
2.00
1.03
1.03
1.02
0.92
8
7
6
5
4
3
2
1
0
PPM

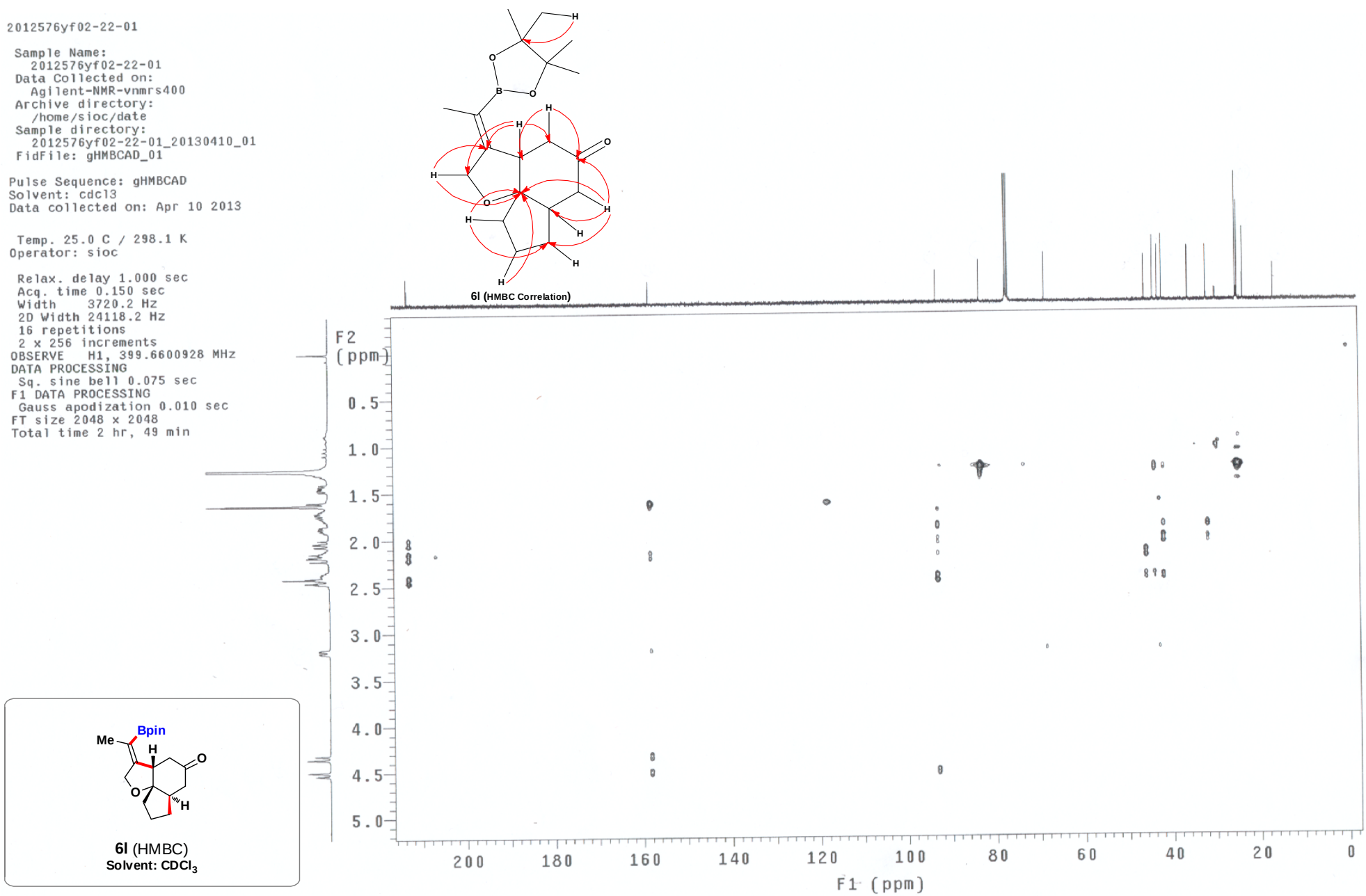

213.097
158.259
93.112
83.310
77.419
77.100
76.781
68.574
45.980
44.037
42.996
41.994
36.057
31.859
25.102
24.760
23.500
16.591
Bpin
Me
H
O
O
H
6l (13C NMR)
Solvent: CDCl3
200
150
100
50
0
PPM





6l (DEPT, θ = 135°)
Solvent: $CDCl_3$




2012576yf02-22-01
Sample Name:
2012576yf02-22-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-22-01_20130410_01
FidFile: gHMBCAD_01
Pulse Sequence: gHMBCAD
Solvent: cdcl3
Data collected on: Apr 10 2013
Temp. 25.0 C / 298.1 K
Operator: sioc
Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3720.2 Hz
2D Width 24118.2 Hz
16 repetitions
2 x 256 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Gauss apodization 0.010 sec
FT size 2048 x 2048
Total time 2 hr, 49 min
6l (HMBC Correlation)
F2 (ppm)
F1 (ppm)
Me
Bpin
6l (HMBC)
Solvent: CDCl3

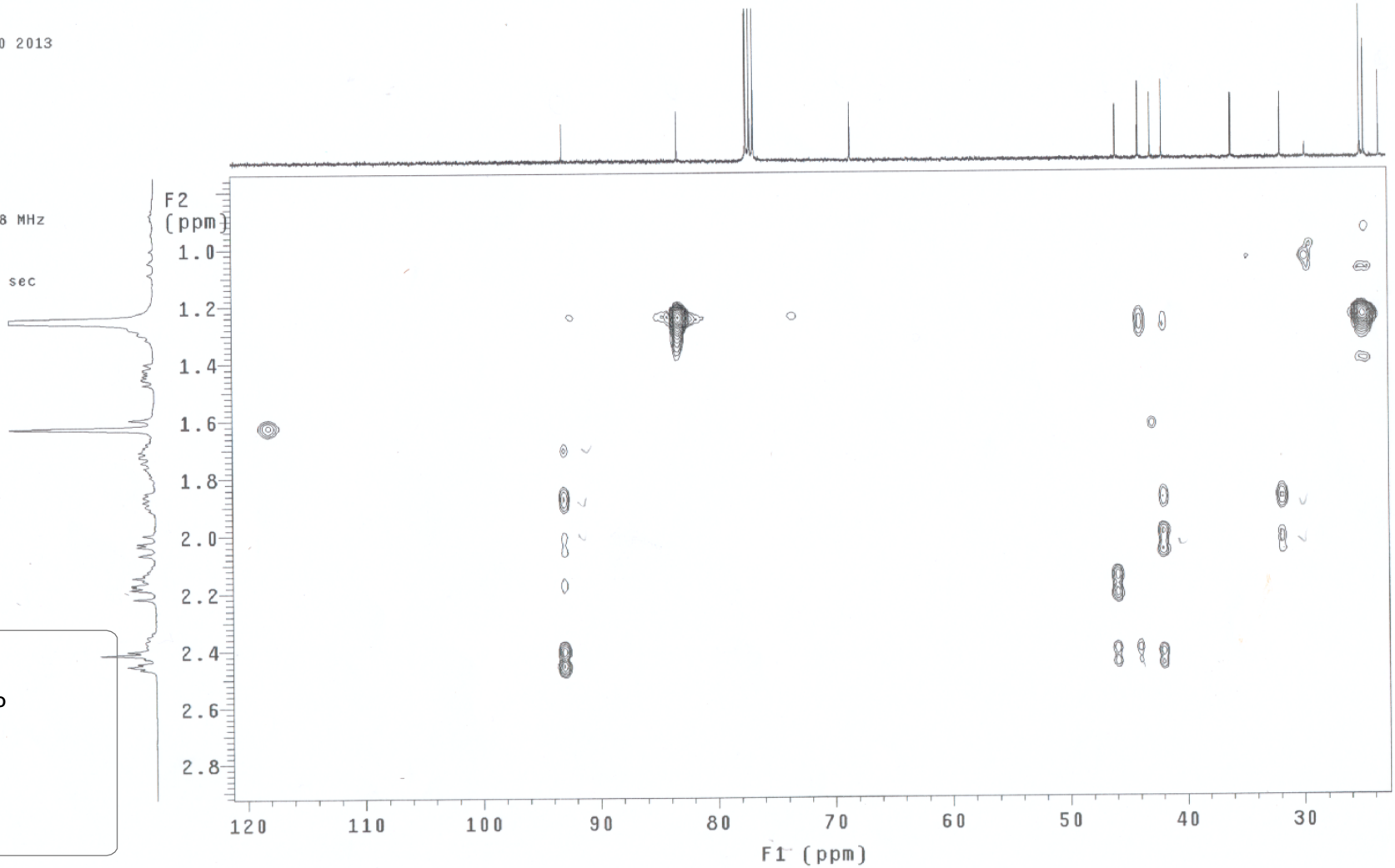
2012576yf02-22-01

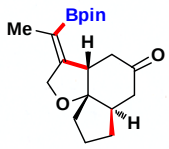
Sample Name:
2012576yf02-22-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-22-01_20130410_01
FidFile: gHMBCAD_01

Pulse Sequence: gHMBCAD
Solvent: cdcl3
Data collected on: Apr 10 2013

Temp. 25.0 C / 298.1 K
Operator: sioc

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3720.2 Hz
2D Width 24118.2 Hz
16 repetitions
2 x 256 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Sq. sine bell 0.075 sec
F1 DATA PROCESSING
Gauss apodization 0.010 sec
FT size 2048 x 2048
Total time 2 hr, 49 min





6l (HMBC)
Solvent: $CDCl_3$

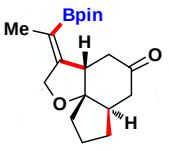
2012576yf02-22-01

Sample Name:
2012576yf02-22-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-22-01_20130410_01
FidFile: gHSQCAD_01

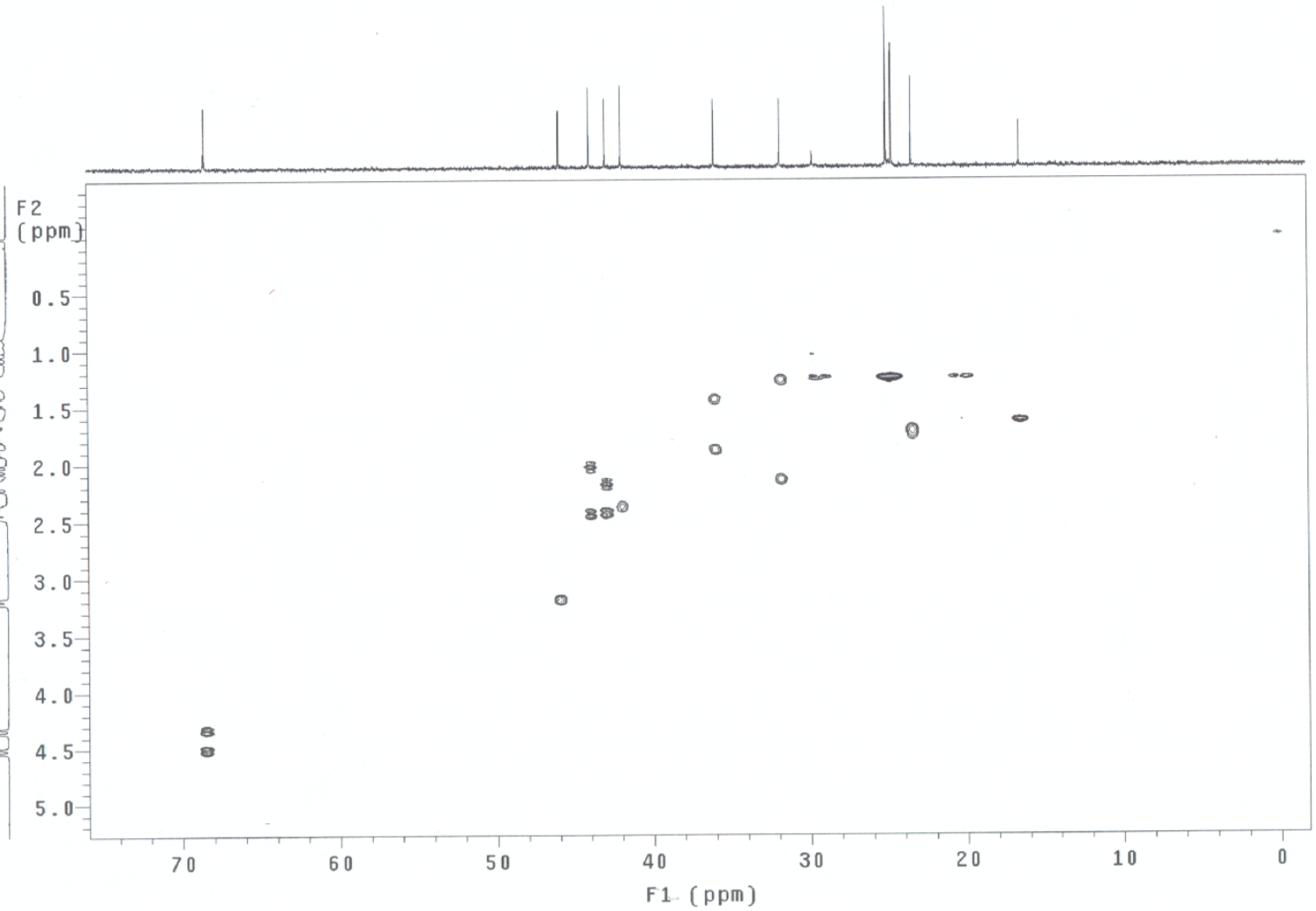
Pulse Sequence: gHSQCAD
Solvent: cdcl3
Data collected on: Apr 10 2013

Temp. 25.0 C / 298.1 K
Operator: sioc

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3720.2 Hz
2D Width 20100.5 Hz
8 repetitions
2 x 256 increments
OBSERVE H1, 399.6600928 MHz
DECOUPLE C13, 100.5036548 MHz
Power 37 dB
on during acquisition
off during delay
W40_ATB3 modulated
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.012 sec
FT size 2048 x 2048
Total time 1 hr, 22 min



6l (HSQC)
Solvent: $CDCl_3$



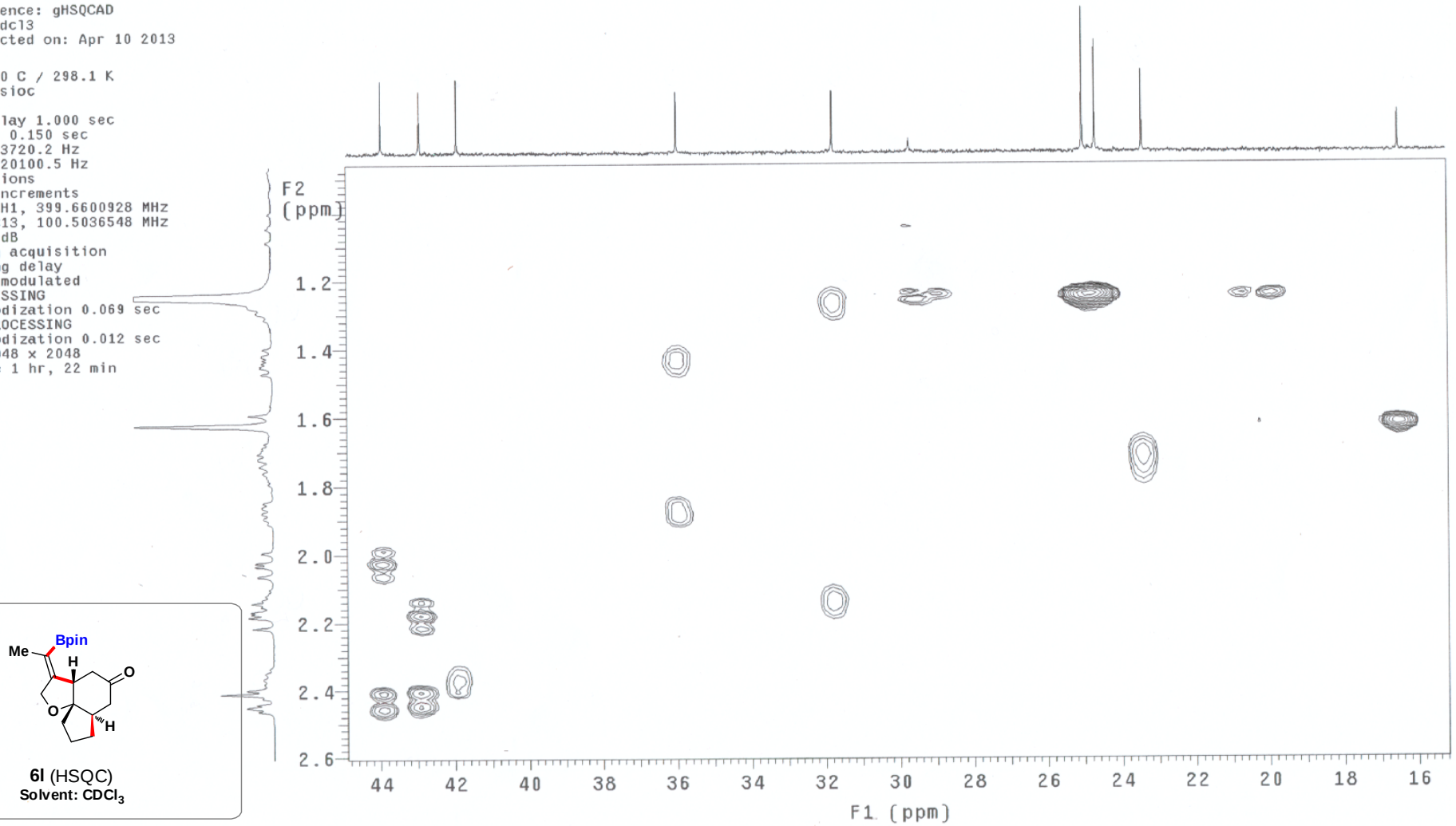
2012576yf02-22-01

Sample Name:
2012576yf02-22-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-22-01_20130410_01
FidFile: gHSQCAD_01

Pulse Sequence: gHSQCAD
Solvent: cdcl3
Data collected on: Apr 10 2013

Temp. 25.0 C / 298.1 K
Operator: sioc

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3720.2 Hz
2D Width 20100.5 Hz
8 repetitions
2 x 256 increments
OBSERVE H1, 399.6600928 MHz
DECOUPLE C13, 100.5036548 MHz
Power 37 dB
on during acquisition
off during delay
W40_ATB3 modulated
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.012 sec
FT size 2048 x 2048
Total time 1 hr, 22 min



6l (HSQC)
Solvent: $CDCl_3$

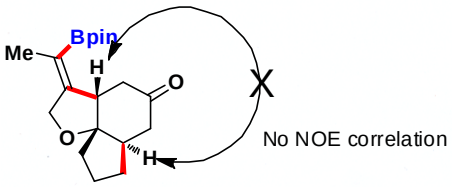
2012576yf02-22-01

Sample Name:
2012576yf02-22-01
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/sioc/date
Sample directory:
2012576yf02-22-01_20130410_01
FidFile: NOESY_01

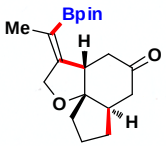
Pulse Sequence: NOESY
Solvent: cdcl3
Data collected on: Apr 10 2013

Temp. 25.0 C / 298.1 K
Operator: sioc

Relax. delay 1.000 sec
Acq. time 0.150 sec
Width 3720.2 Hz
2D Width 3720.2 Hz
32 repetitions
2 x 256 increments
OBSERVE H1, 399.6600928 MHz
DATA PROCESSING
Gauss apodization 0.069 sec
F1 DATA PROCESSING
Gauss apodization 0.037 sec
FT size 2048 x 2048
Total time 8 hr, 36 min



No NOE correlation



6l (NOESY)
Solvent: $CDCl_3$