Supporting Information

for

Gram-scale, Stereoselective Synthesis and Biological Evaluation of (+)-Armillariol C

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1-(5-Bromofuran-2-yl)ethan-1-one (**3**): mp = 88-89 °C; IR (neat) ν_{max} 3142, 3088, 2943, 1654, 1562, 1451, 1354, 1298, 1004, 798, 661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, J = 3.6 Hz, 1H), 6.49 (d, J = 3.6 Hz, 1H), 2.46 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 185.5, 154.5, 128.2, 118.9, 114.4, 25.8.

(*E*)-Trifluoro(hept-1-en-1-yl)borate (**4b**): mp = > 300 °C; IR (neat) ν_{max} 3281, 2955, 2921, 2887, 1644, 1466, 1308, 1098, 922, 758 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 5.46 (dt, J = 17.4, 6.2 Hz, 1H), 5.19 (dd, J = 17.4, 3.5 Hz, 1H), 1.91-1.82 (m, 2H), 1.32-1.17 (m, 6H), 0.85 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, DMSO-d_6): δ 134.1, 134.0, 35.8, 31.5, 29.4, 22.6, 14.5; ESIMS *m/z* 165 $[M]^-$.

(*E*)-1-(5-(Hept-1-en-1-yl)furan-2-yl)ethan-1-one (2): R_f = 0.3 (hexanes/EtOAc 90:10); IR (neat) ν_{max} 3133, 2929, 2860, 1727, 1673, 1515, 1258, 1019, 811, 627 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.14 (d, J = 3.6 Hz, 1H), 6.50 (dt, J = 15.9, 7.1 Hz, 1H), 6.27 (d, J = 3.6 Hz, 1H), 6.24 (dt, J = 15.9, 1.5 Hz, 1H), 2.46 (s, 3H), 2.21 (qd, J = 7.3, 1.5 Hz, 2H), 1.52-1.43 (m, 2H), 1.36-1.28 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 186.2, 157.3, 151.0, 136.2, 119.6, 117.8, 108.2, 32.9, 31.4, 28.5, 25.8, 22.5, 14.0; ESIMS *m/z* 207 $(M+H)^+$; HRESIMS *m/z* 207.1376 (calcd for $C_{13}H_{19}O_2$, 207.1380).

(*E*)-1-(5-(Hept-1-en-1-yl)thiophen-2-yl)ethan-1-one (6): mp = 49-50 °C; R_f = 0.4 (hexanes/EtOAc 90:10); IR (neat) ν_{max} 3089, 2928, 2869, 1648, 1442, 1358, 1276, 1116, 891, 714, 672, 604 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (d, J = 3.9 Hz, 1H), 6.87 (d, J = 3.8 Hz, 1H), 6.47 (d, J = 15.7 Hz, 1H), 6.29 (dt, J = 15.7, 6.9 Hz, 1H), 2.51 (s, 3H), 2.20 (q, J = 6.8 Hz, 2H), 1.51-1.42 (m, 2H), 1.37-1.27 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 190.5, 151.6, 141.3, 135.7, 133.2, 124.9, 122.7, 32.9, 31.4, 28.6, 26.5, 22.5, 14.0; ESIMS *m/z* 223 $(M+H)^+$; HRESIMS *m/z* 223.1158 (calcd for $C_{13}H_{19}OS$, 223.1151).

(*E*)-1-(5-Styrylfuran-2-yl)ethan-1-one (8): mp = 58-60 °C; R_f = 0.3 (hexanes/EtOAc 90:10); IR (neat) ν_{max} 3047, 3022, 1668, 1500, 1278, 1022, 947, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, J = 7.1 Hz, 2H), 7.40-7.28 (m, 4H), 7.20 (d, J = 3.6 Hz, 1H), 6.92 (d, J = 16.3 Hz, 1H), 6.48 (d, J = 3.6 Hz, 1H), 2.51 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 186.2, 157.1, 151.5, 136.0, 132.0, 128.9, 128.7, 126.9, 119.7, 115.4, 110.4, 26.0; ESIMS *m/z* 213 $(M+H)^+$; HRESIMS *m/z* 213.0908 (calcd for $C_{14}H_{13}O_2$, 213.0910).

1,1'-([2,2'-Bifuran]-5,5'-diyl)bis(ethan-1-one) (2a): mp = 206-207 °C; R_f = 0.2 (hexanes/EtOAc 80:20); IR (neat) ν_{max} 3141, 2918, 1659, 1545, 1423, 1281, 1036, 967, 802, 619 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (d, J = 3.7 Hz, 2H), 6.87 (d, J = 3.7 Hz, 2H), 2.46 (s, 3H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 185.2, 151.5, 147.1, 118.5, 109.1, 25.1; ESIMS *m/z* 219 $(M+H)^+$; HRESIMS *m/z* 219.0652 (calcd for $C_{12}H_{11}O_4$, 219.0652).

(+)-Armillariol C (1a): R_f = 0.20 (hexanes/EtOAc 60:40); $[\alpha]_D^{20}$ = + 23.0 (c = 0.20, $CHCl_3$); IR (neat) ν_{max} 3400, 2955, 2930, 2861, 1662, 1515, 1359, 1298, 1024, 925, 811 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, J = 3.5 Hz, 1H), 6.49 (d, J = 3.6 Hz, 1H), 4.57 (d, J = 4.4 Hz, 1H), 3.96-3.90 (m, 1H), 3.49 (bs, 1H), 2.87 (bs, 1H), 2.44 (s, 3H), 1.59-1.41 (m, 3H), 1.38-1.20 (m, 5H), 0.87 (t, J = 6.8 Hz, 3H);

$^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ 186.7, 160.0, 151.8, 119.1, 109.8, 73.2, 71.0, 33.0, 31.7, 25.9, 25.3, 22.5, 14.0; ESIMS *m/z* 263 $(M+H)^+$; HRESIMS *m/z* 263.1255 (calcd for $C_{13}H_{20}NaO_4$, 263.1254).

(-)-Armillariol C (1b): R_f = 0.20 (hexanes/EtOAc 60:40); $[\alpha]_D^{20}$ -24.4 (*c* = 1.00, $CHCl_3$); IR (neat) ν_{max} 3400, 2955, 2929, 2859, 1662, 1515, 1359, 1295, 1023, 925, 811, 629 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 3.5 Hz, 1H), 6.49 (d, *J* = 3.6 Hz, 1H), 4.57 (d, *J* = 4.4 Hz, 1H), 3.96-3.90 (m, 1H), 3.65 (d, *J* = 4.3 Hz, 1H), 3.03 (bs, 1H), 2.44 (s, 3H), 1.59-1.41 (m, 3H), 1.38-1.20 (m, 5H), 0.87 (t, *J* = 6.8 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ 186.7, 160.0, 151.8, 119.1, 109.8, 73.2, 71.0, 33.0, 31.7, 25.9, 25.3, 22.5, 14.0; ESIMS *m/z* 263 $(M+Na)^+$; HRESIMS *m/z* 263.1255 (calcd for $C_{13}H_{20}NaO_4$, 263.1254).

(-)-1-(5-((1*R*,2*S*)-1,2-Dihydroxyheptyl)thiophen-2-yl)ethan-1-one (7a): mp = 62-64 °C; R_f = 0.2 (hexanes/EtOAc 60:40); $[\alpha]_D^{25}$ -24.65 (*c* = 2.00, $CHCl_3$); IR (neat) ν_{max} 3338, 2925, 2855, 1655, 1627, 1454, 1361, 1291, 1062, 804, 766 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 3.8 Hz, 1H), 7.03 (d, *J* = 3.8 Hz, 1H), 4.70 (t, *J* = 5.1 Hz, 1H), 3.71 (d, *J* = 2.8 Hz, 1H), 3.52 (d, *J* = 4.2 Hz, 1H), 2.79 (bs, 1H), 2.52 (s, 3H), 1.47-1.39 (m, 3H), 1.30-1.19 (m, 5H), 0.86 (t, *J* = 6.9 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ 192.1, 154.6, 143.5, 132.5, 125.8, 75.8, 73.5, 32.8, 31.7, 26.6, 25.3, 22.6, 14.0; ESIMS *m/z* 257 $(M+H)^+$; HRESIMS *m/z* 257.1204 (calcd for $C_{13}H_{20}NaO_4$, 257.1206).

(+)-1-(5-((1*S*,2*R*)-1,2-Dihydroxyheptyl)thiophen-2-yl)ethan-1-one (7b): mp = 62-64 °C; R_f = 0.20 (hexanes/EtOAc 60:40); $[\alpha]_D^{25}$ +25.8 (*c* = 0.50, $CHCl_3$); IR (neat) ν_{max} 3338, 2925, 2855, 1655, 1627, 1454, 1361, 1291, 1062, 804, 766 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 3.8 Hz, 1H), 7.03 (d, *J* = 3.8 Hz, 1H), 4.70 (t, *J* = 5.1 Hz, 1H), 3.71 (d, *J* = 2.8 Hz, 1H), 3.52 (d, *J* = 4.2 Hz, 1H), 2.79 (bs, 1H), 2.52 (s, 3H), 1.47-1.39 (m, 3H), 1.30-1.19 (m, 5H), 0.86 (t, *J* = 6.9 Hz, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ 192.1, 154.6, 143.5, 132.5, 125.8, 75.8, 73.5, 32.8, 31.7, 26.6, 25.3, 22.6, 14.0; ESIMS *m/z* 257 $(M+H)^+$; HRESIMS *m/z* 257.1204 (calcd for $C_{13}H_{20}NaO_4$, 257.1206).

(-)-1-(5-((1*R*,2*S*)-1,2-Dihydroxy-2-phenylethyl)furan-2-yl)ethan-1-one (9a): R_f = 0.25 (hexanes/EtOAc 50:50); $[\alpha]_D^{25}$ -85.6 (*c* = 0.33, $CHCl_3$); IR (neat) ν_{max} 3374, 3122, 2955, 2924, 1655, 1514, 1359, 1299, 1199, 1025, 925, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.20 (m, 5H), 7.02 (d, *J* = 3.5 Hz, 1H), 6.27 (d, *J* = 3.6 Hz, 1H), 4.98 (d, *J* = 6.6 Hz, 1H), 4.78 (d, *J* = 4.8 Hz, 1H), 3.97 (bs, 1H), 3.78 (bs, 1H), 2.32 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ 186.9, 158.3, 151.7, 139.5, 128.4, 128.2, 126.5, 118.7, 110.5, 76.0, 72.7, 25.8; ESIMS *m/z* 247 $(M+H)^+$; HRESIMS *m/z* 247.0963 (calcd for $C_{14}H_{15}O_4$, 247.0965) and *m/z* 229.0860 (calcd for $C_{14}H_{13}O_3$, 229.0859).

(+)-1-(5-((1*S*,2*R*)-1,2-Dihydroxy-2-phenylethyl)furan-2-yl)ethan-1-one (9b): R_f = 0.25 (hexanes/EtOAc 50:50); $[\alpha]_D^{25}$ +86.7 (*c* = 0.33, $CHCl_3$); IR (neat) ν_{max} 3382, 3124, 3064, 2911, 1655, 1514, 1388, 1299, 1199, 1025, 925, 762, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.20 (m, 5H), 7.02 (d, *J* = 3.5 Hz, 1H), 6.27 (d, *J* = 3.6 Hz, 1H), 4.98 (d, *J* = 6.6 Hz, 1H), 4.78 (d, *J* = 4.8 Hz, 1H), 3.89 (bs, 1H), 3.70 (bs, 1H), 2.32 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$): δ 186.9, 158.3, 151.7, 139.5, 128.4, 128.2, 126.5, 118.7, 110.5, 76.0, 72.7, 25.8; ESIMS *m/z* 247 $(M+H)^+$; HRESIMS *m/z* 247.0963 (calcd for $C_{14}H_{15}O_4$, 247.0965) and *m/z* 229.0860 (calcd for $C_{14}H_{13}O_3$, 229.0859).

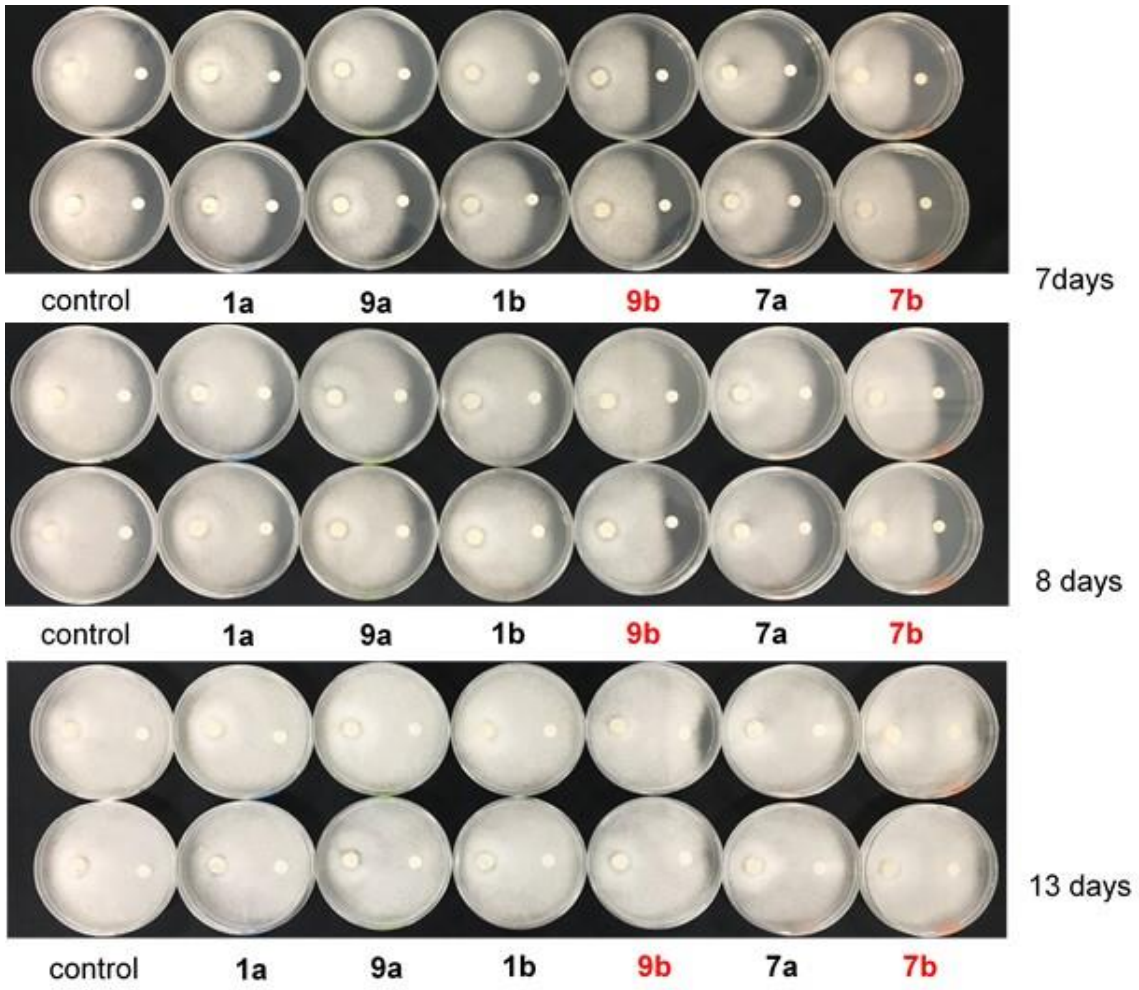
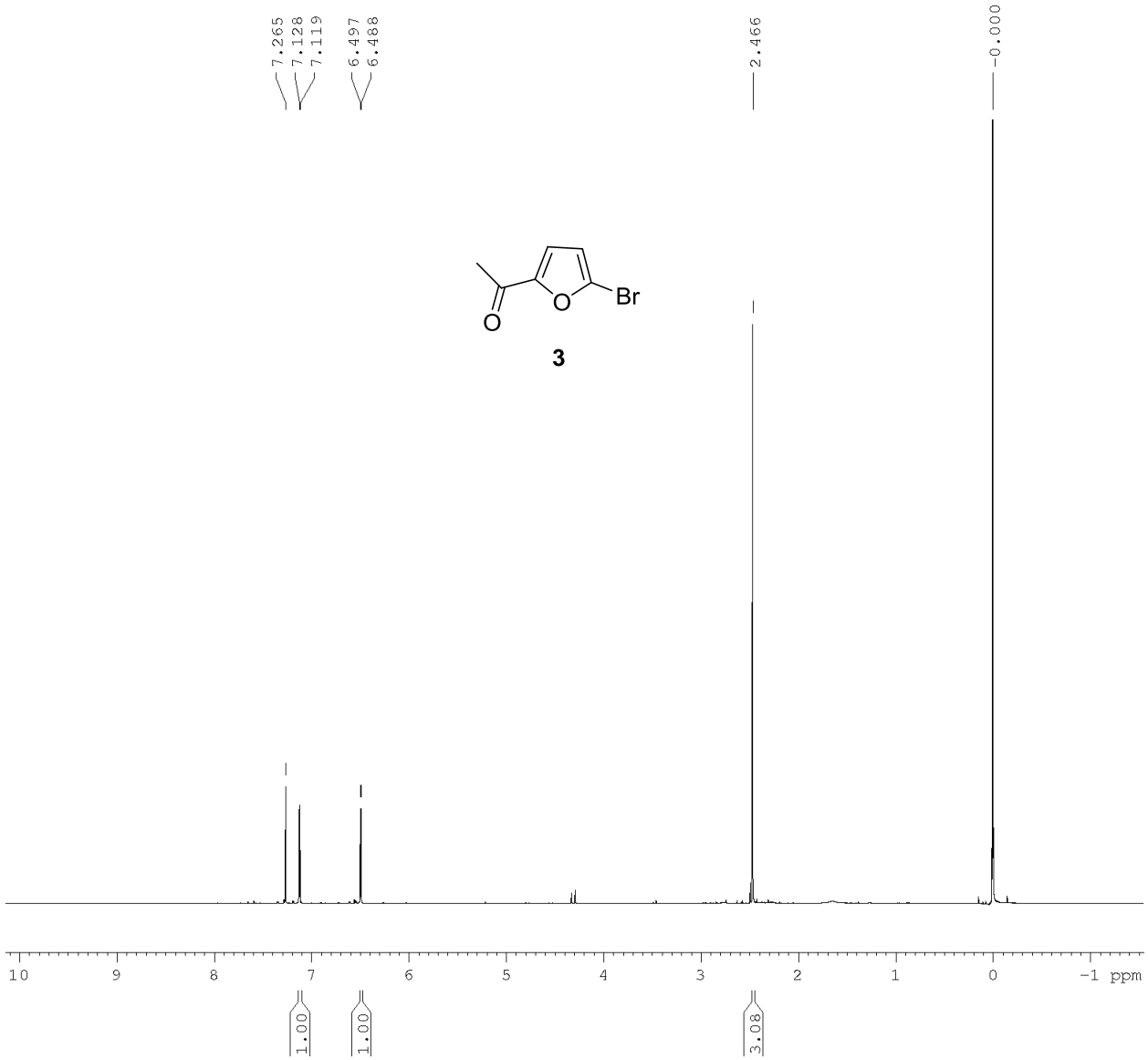
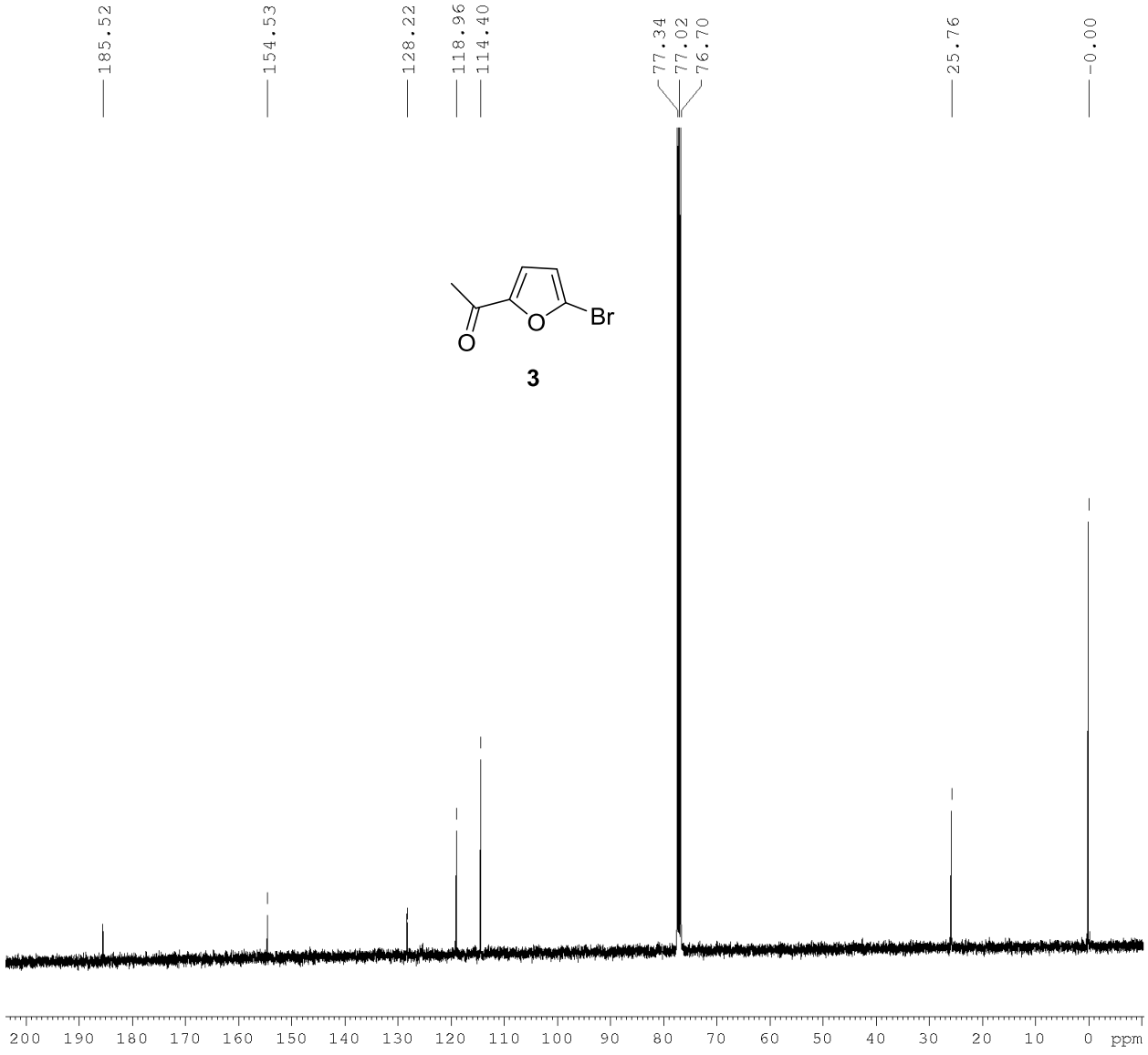


Figure 1. Mycelial growth-regulating activity of (+)-armillariol C (**1a**) and analogues against *Flammulina velutipes*. Each disk contained 1 μmol of test compound.

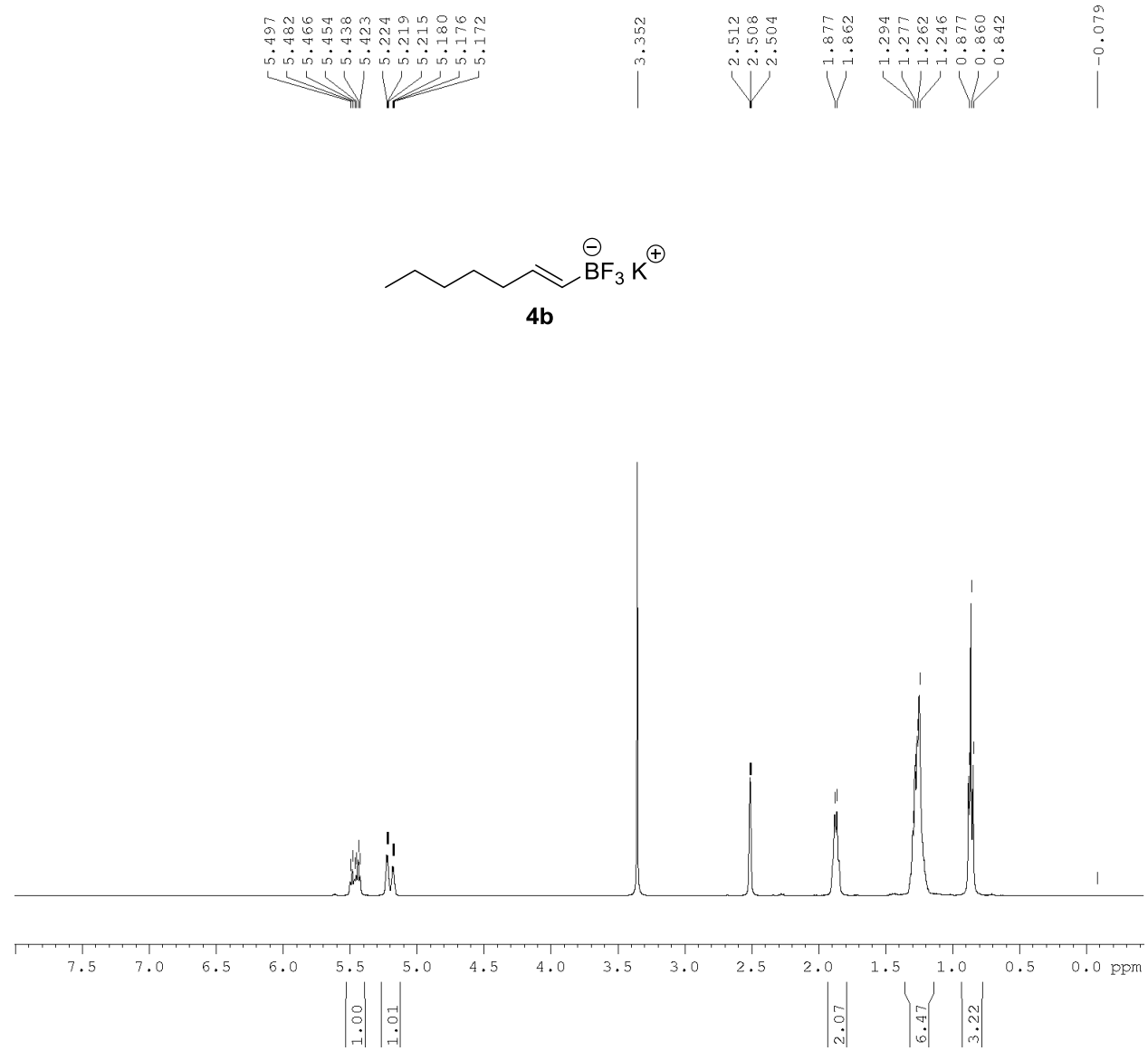
^{1}H NMR spectra of compound **3** ($CDCl_3$, 400 MHz):



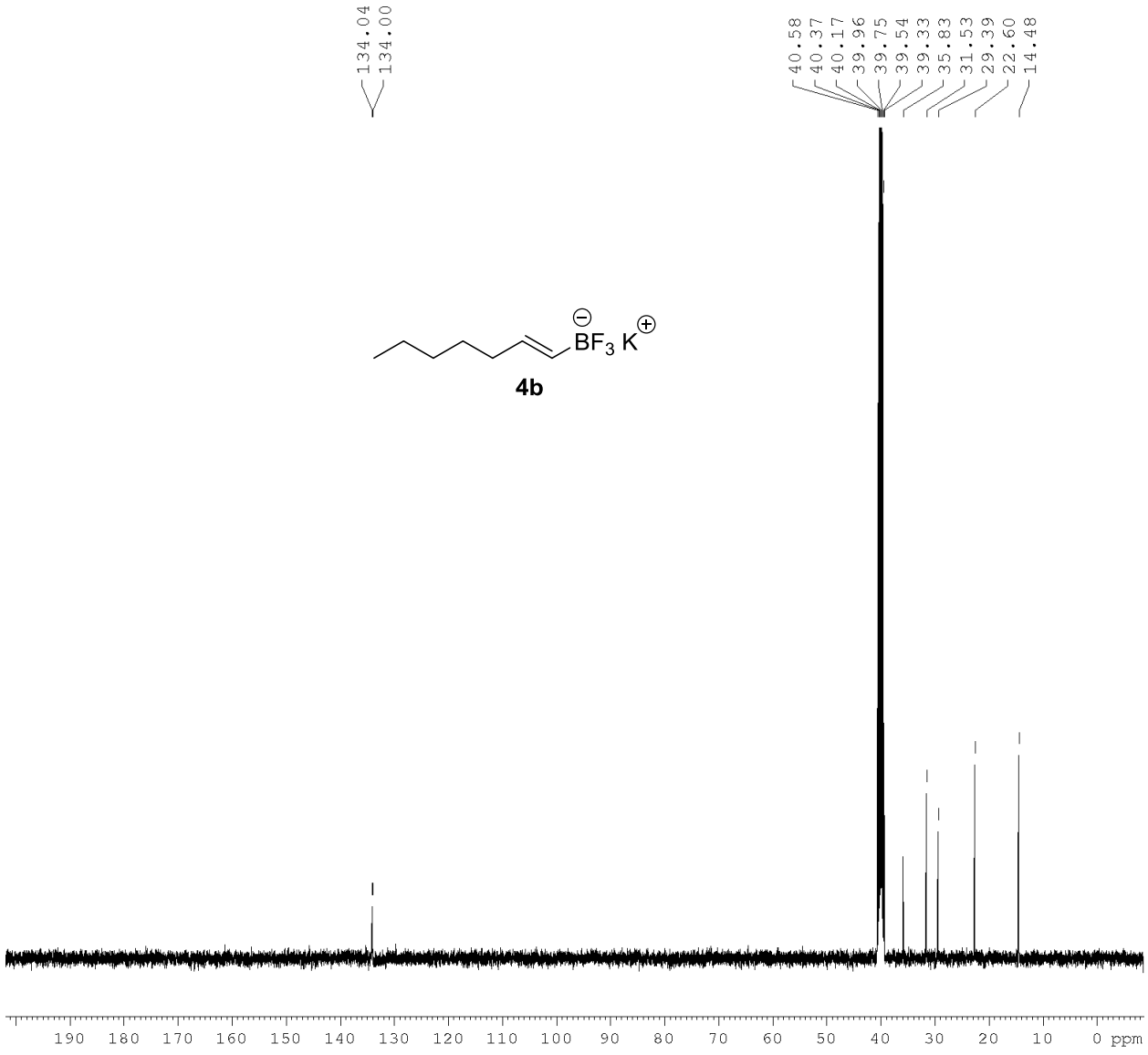
^{13}C NMR spectra of compound **3** ($CDCl_3$, 100 MHz):



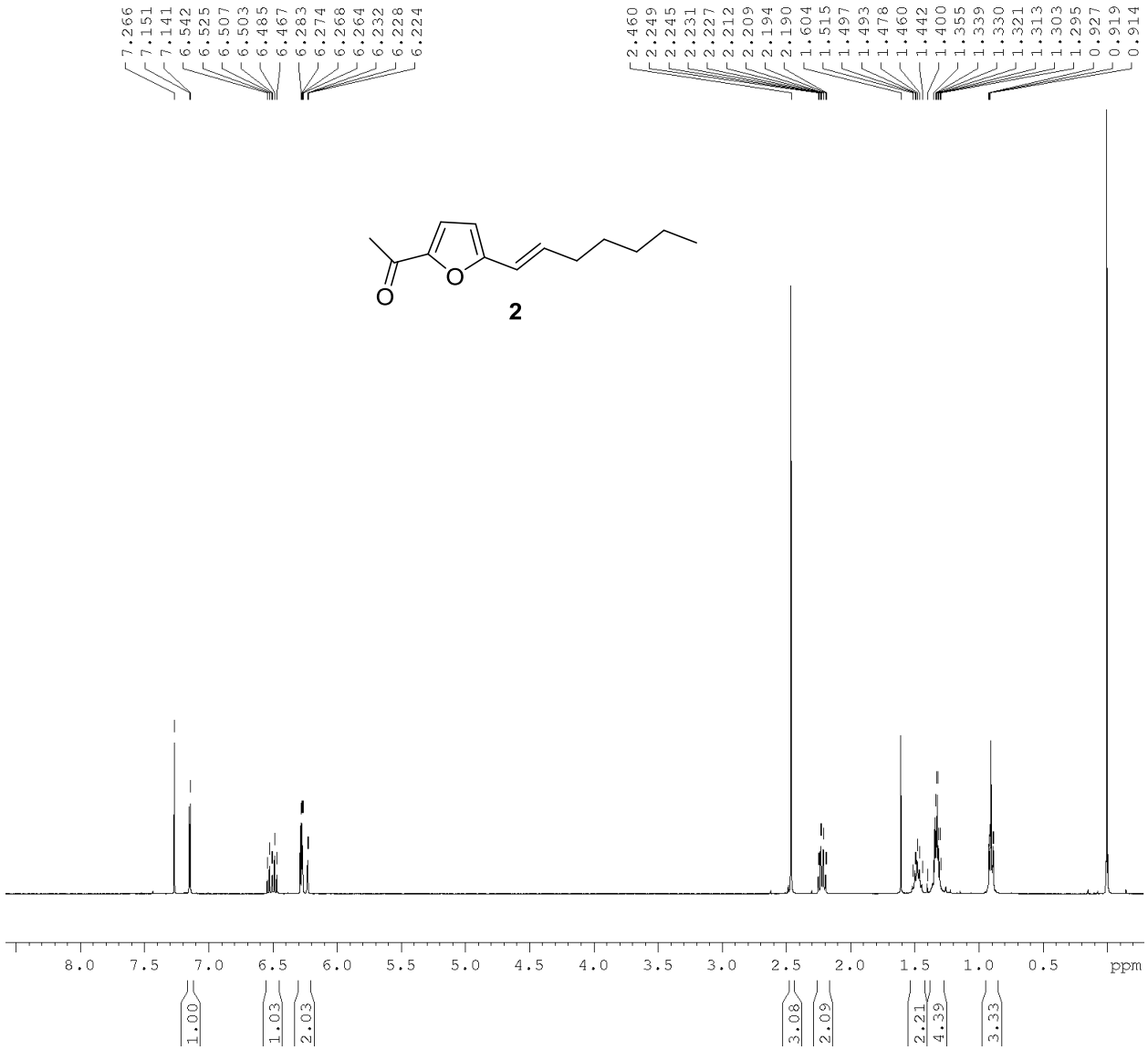
^{1}H NMR spectra of compound **4b** (DMSO-d_6, 400 MHz):



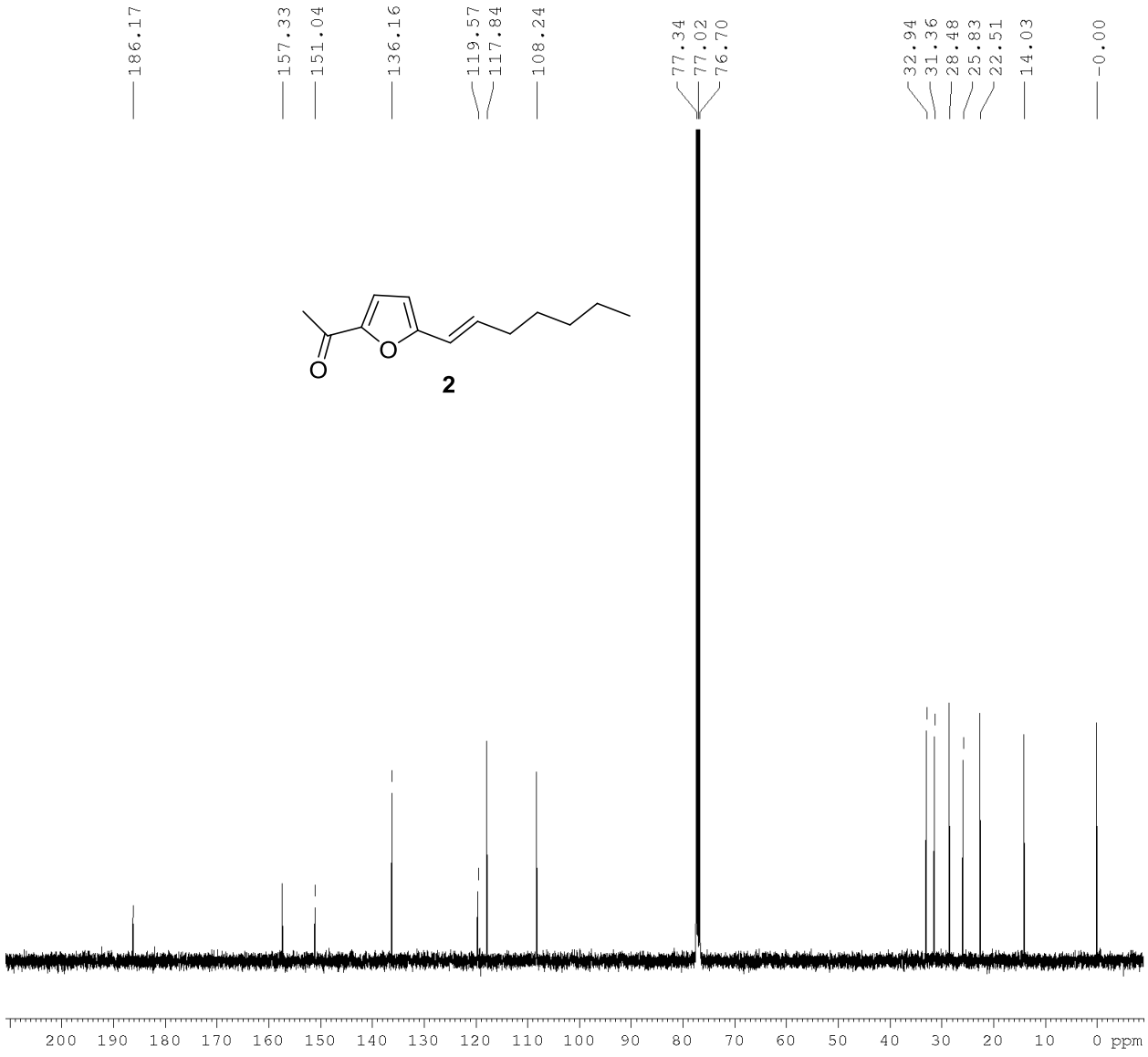
^{13}C NMR spectra of compound **4b** (DMSO-d_6, 100 MHz):



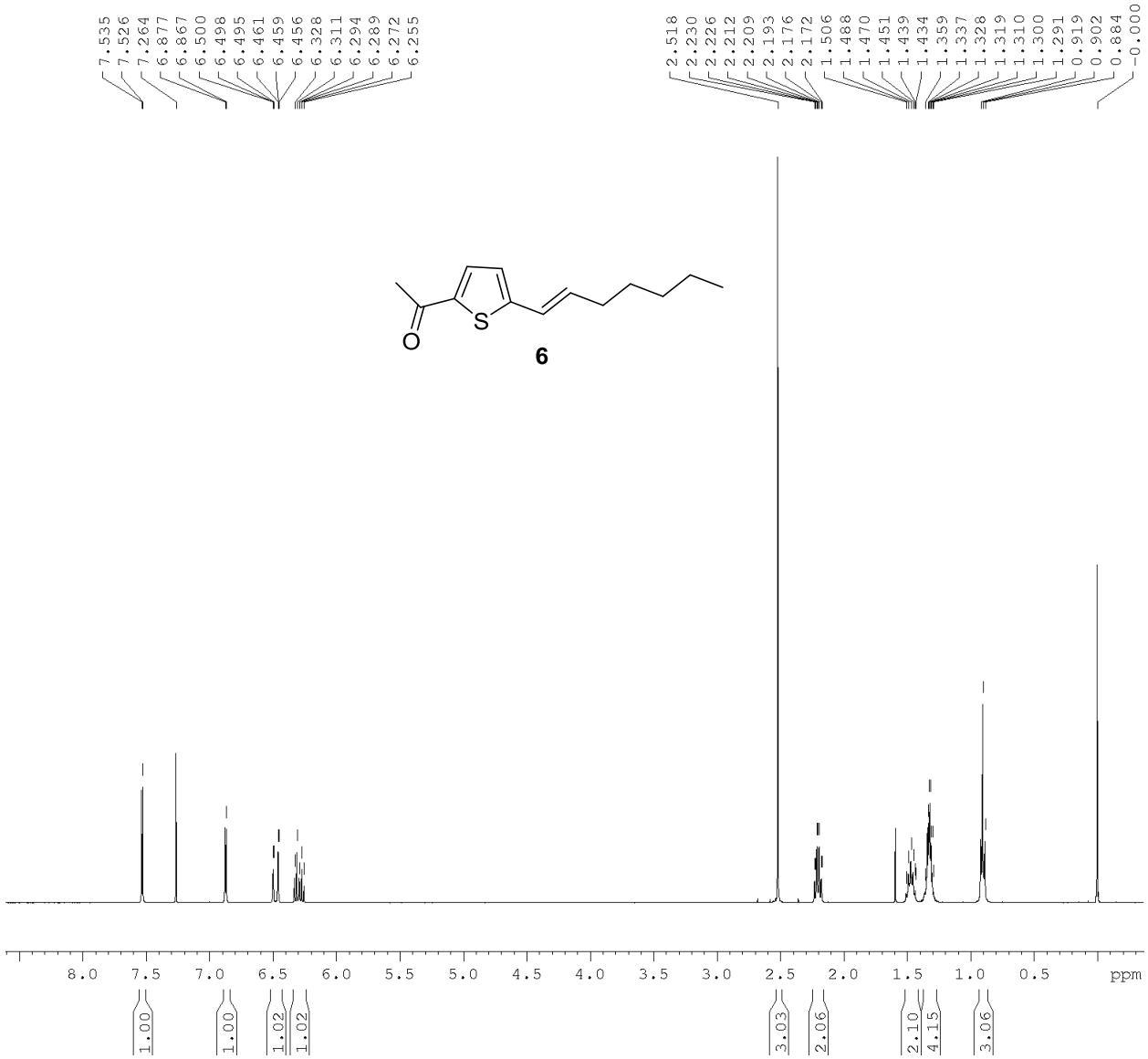
^{1}H NMR spectra of compound **2** ($CDCl_3$, 400 MHz):



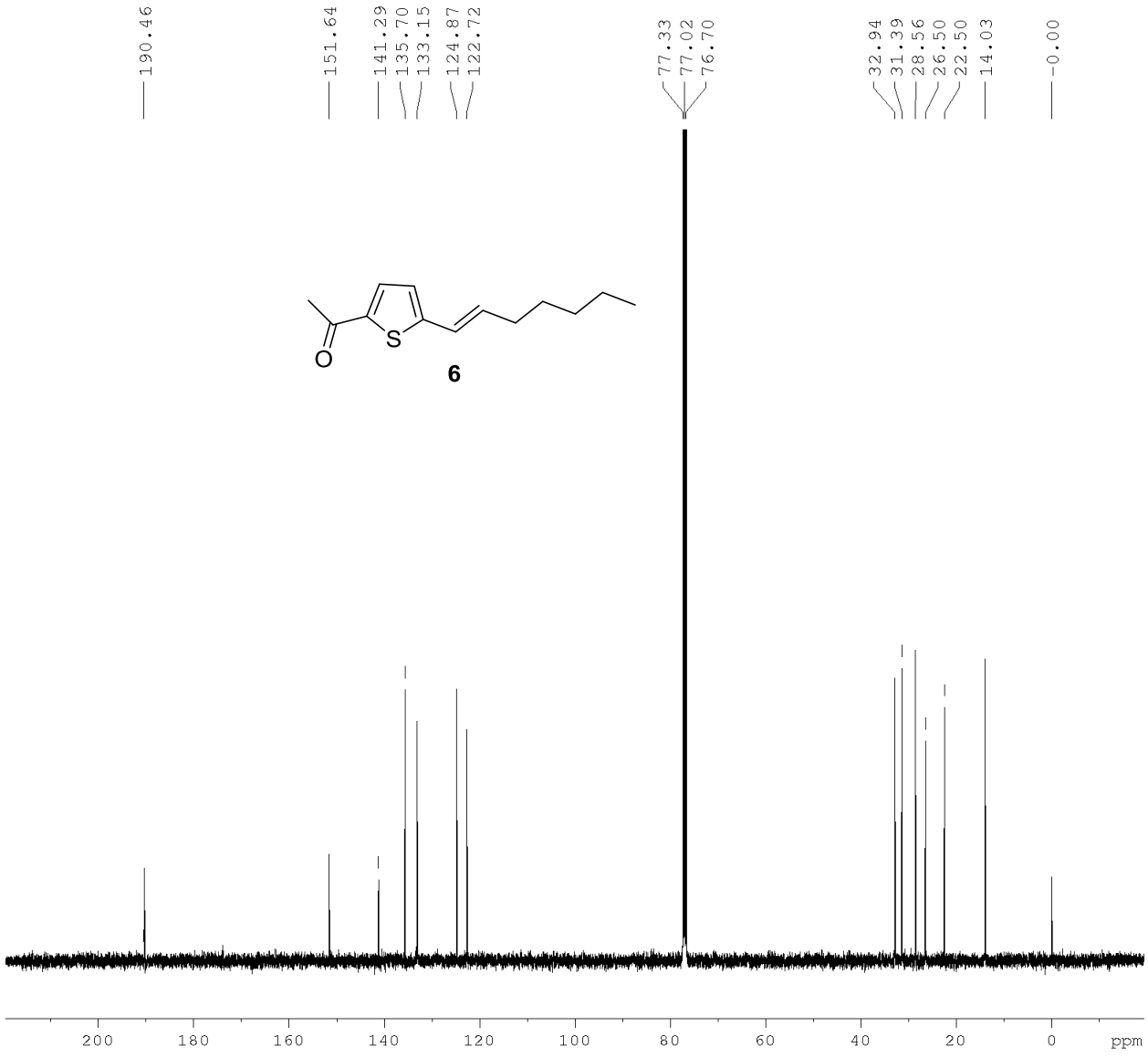
^{13}C NMR spectra of compound **2** ($CDCl_3$, 100 MHz):



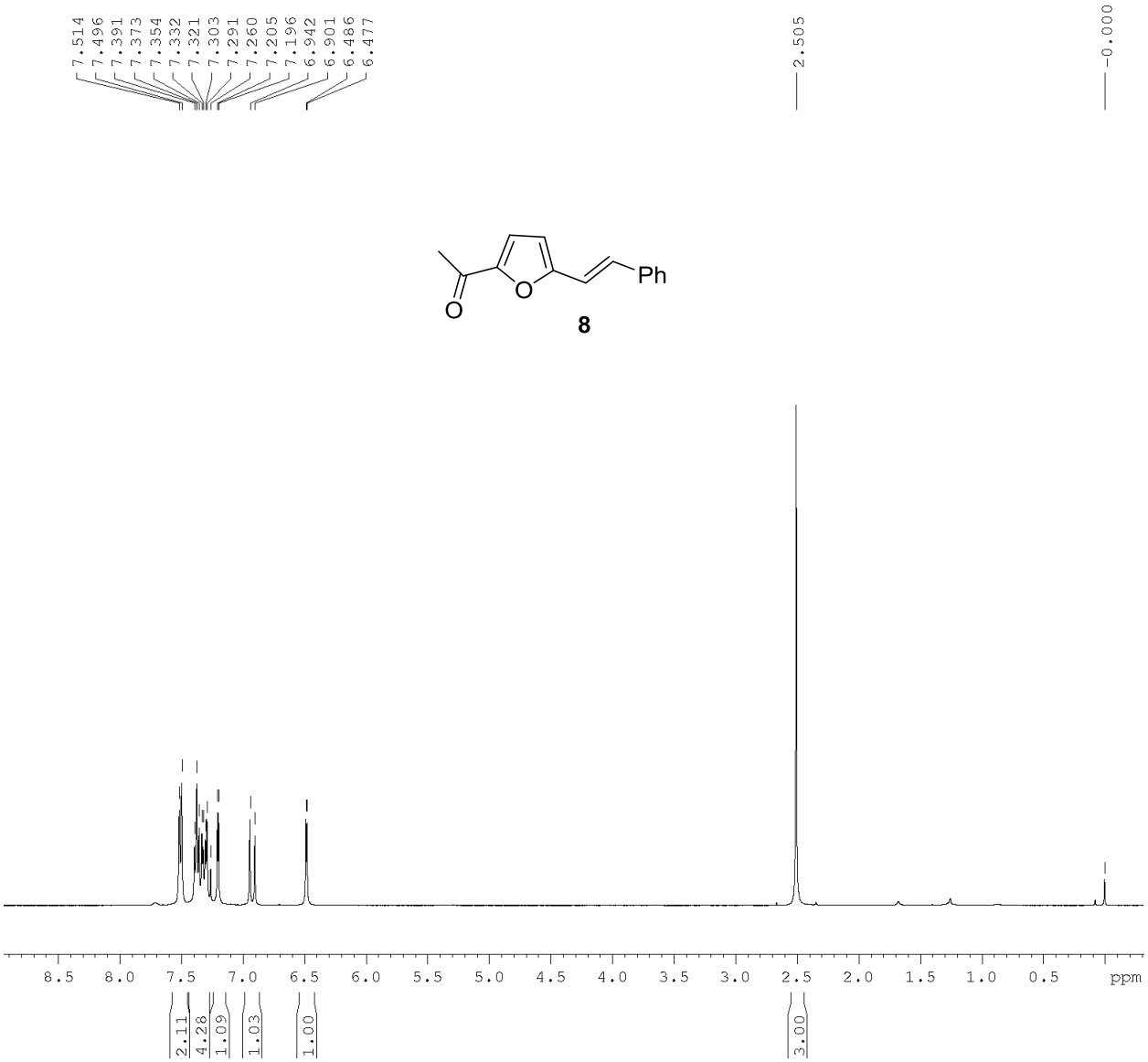
^{1}H NMR spectra of compound **6** ($CDCl_3$, 400 MHz):



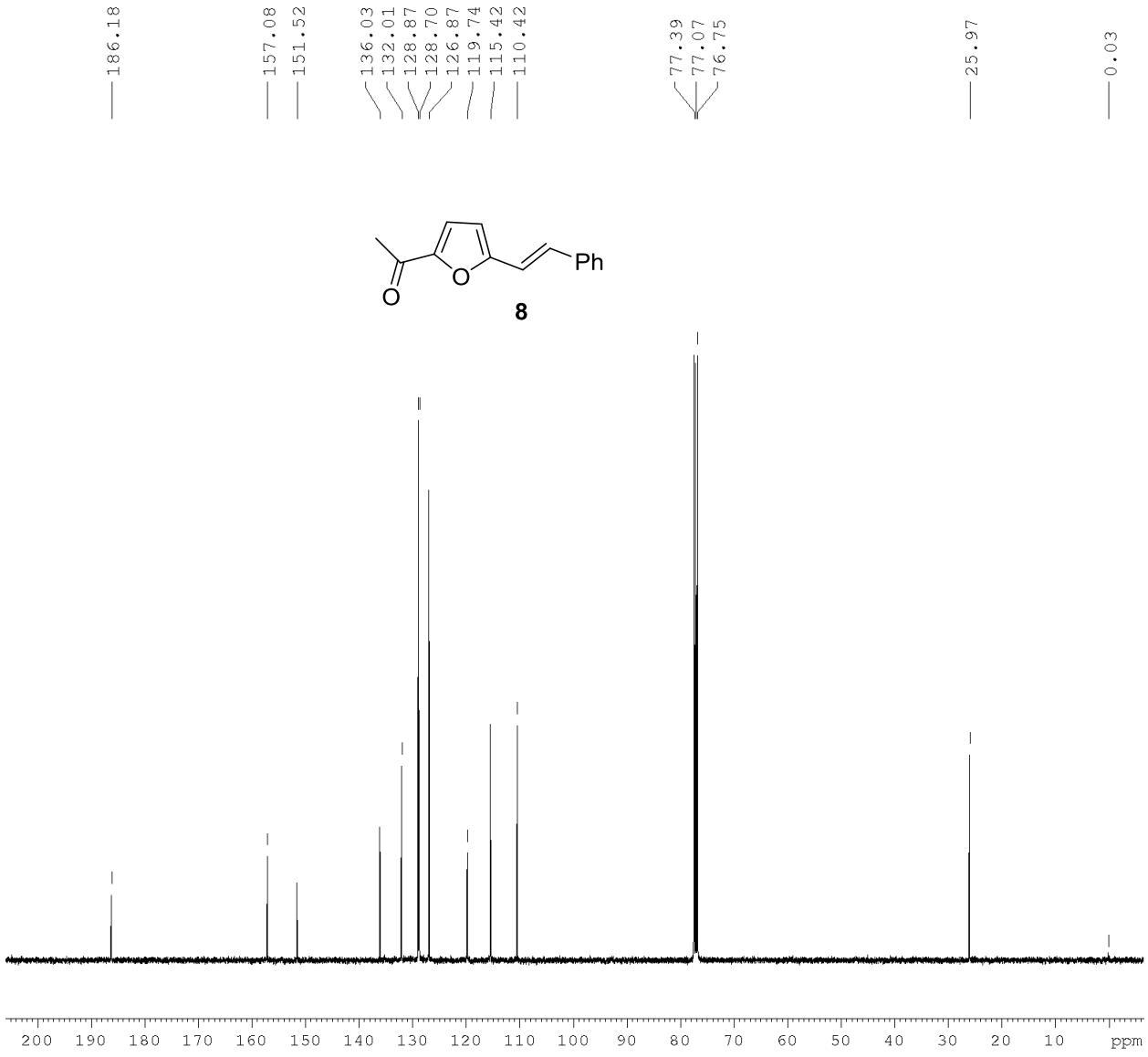
^{13}C NMR spectra of compound **6** ($CDCl_3$, 100 MHz):



^{1}H NMR spectra of compound **8** ($CDCl_3$, 400 MHz):

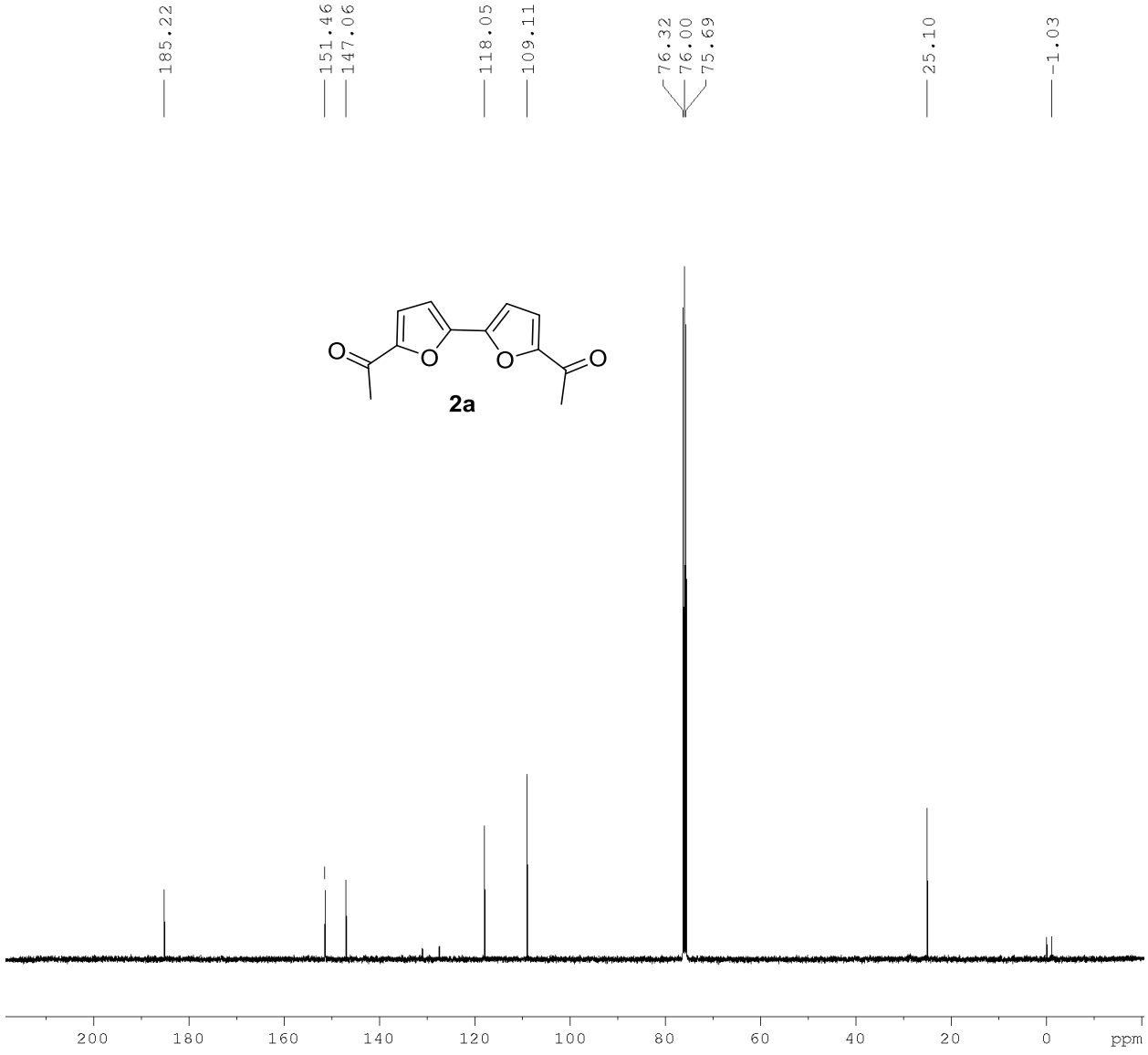


^{13}C NMR spectra of compound **8** ($CDCl_3$, 100 MHz):

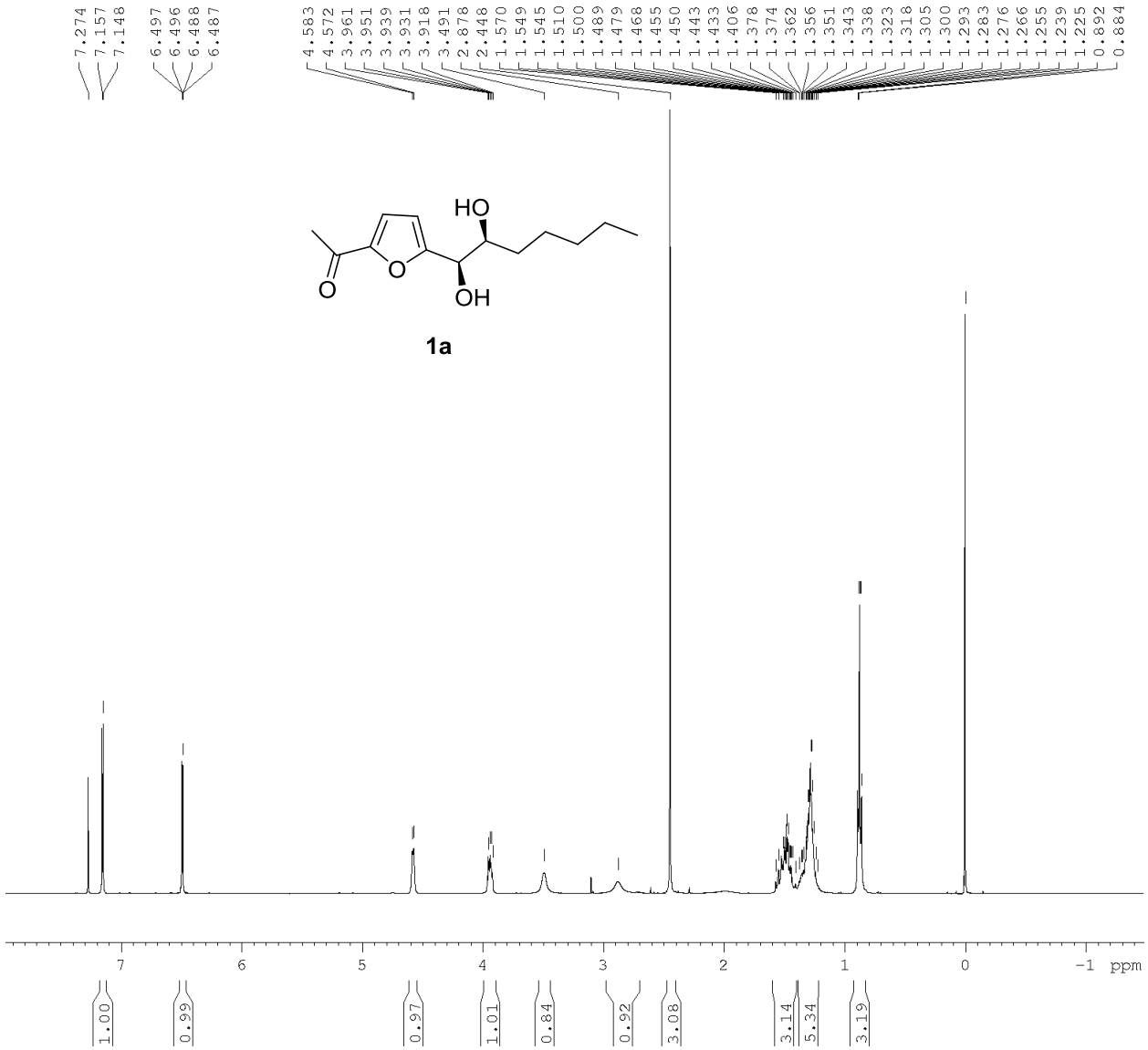


^{1}H NMR spectra of compound **2a** ($CDCl_3$, 400 MHz):

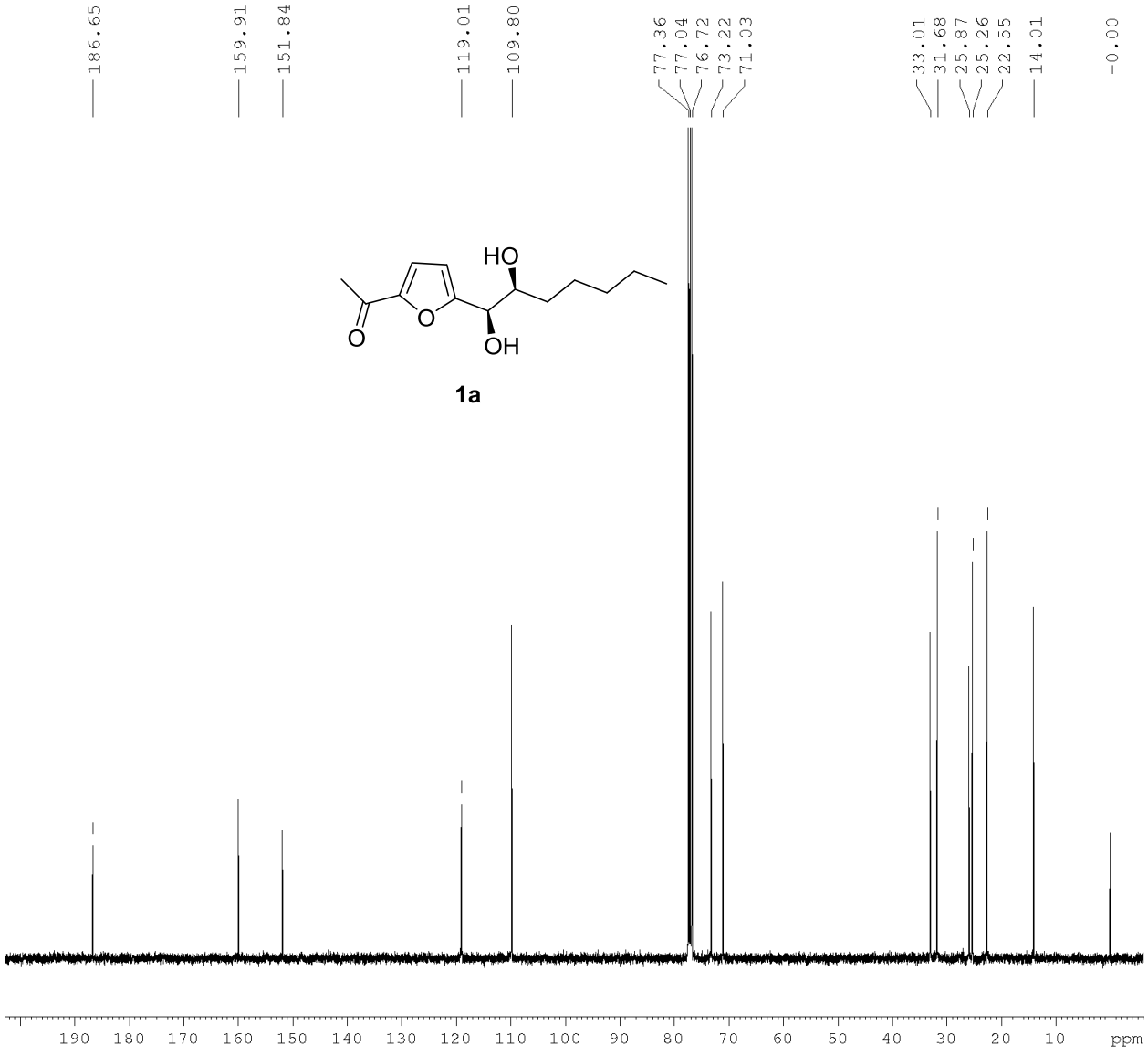
^{13}C NMR spectra of compound **2a** ($CDCl_3$, 100 MHz):



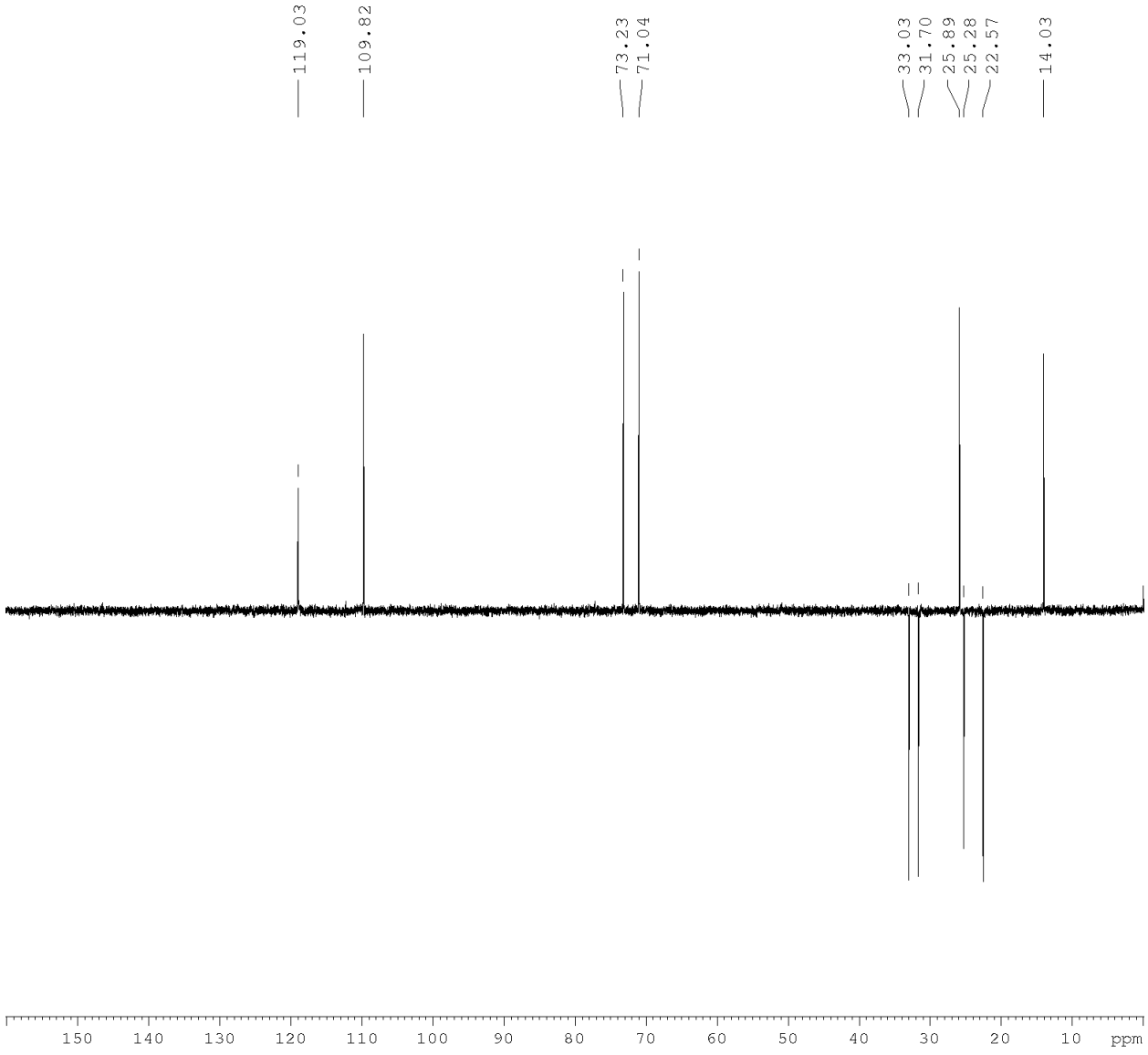
^{1}H NMR spectra of compound **1a** ($CDCl_3$, 400 MHz):



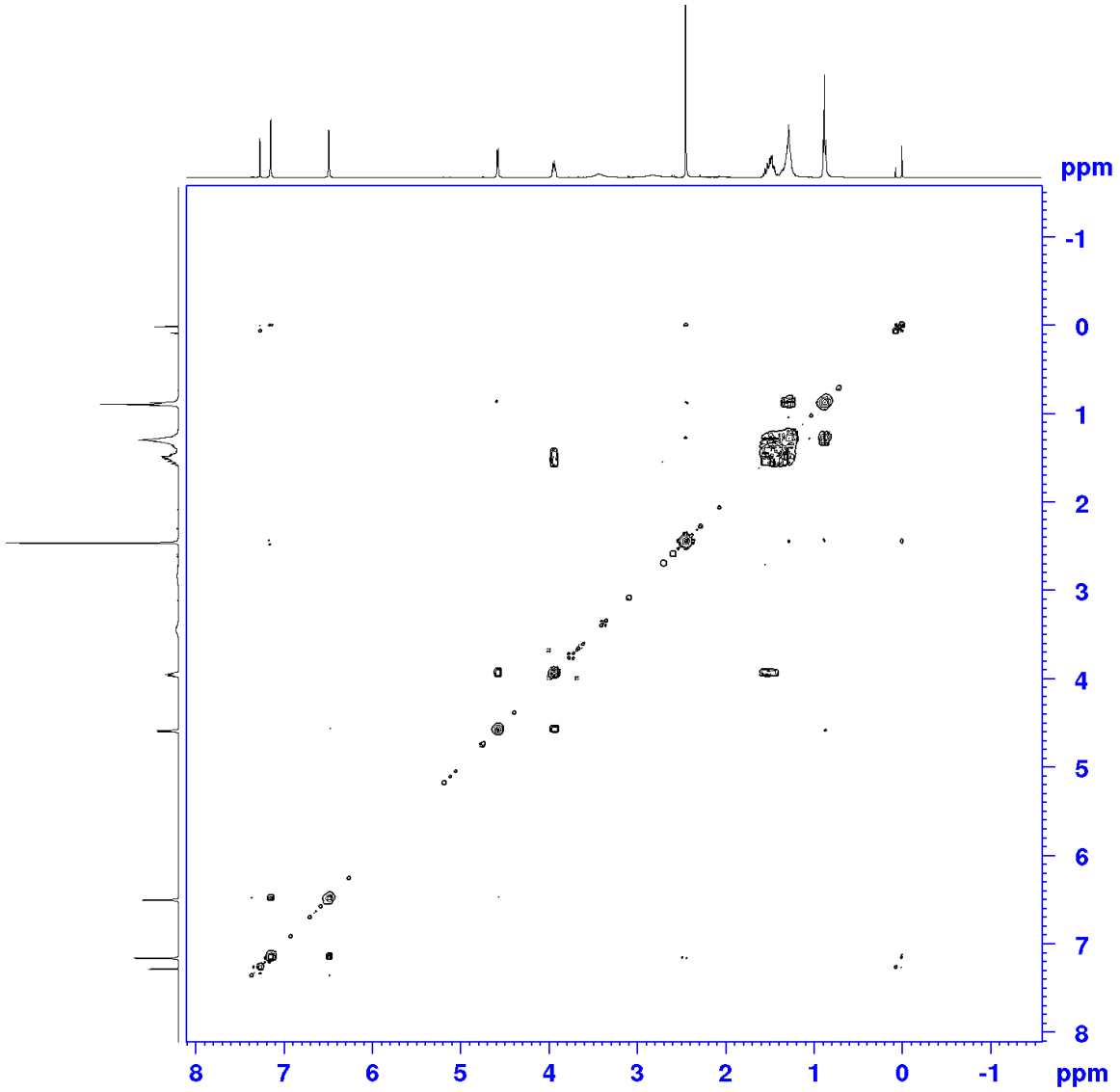
^{13}C NMR spectra of compound **1a** ($CDCl_3$, 100 MHz):



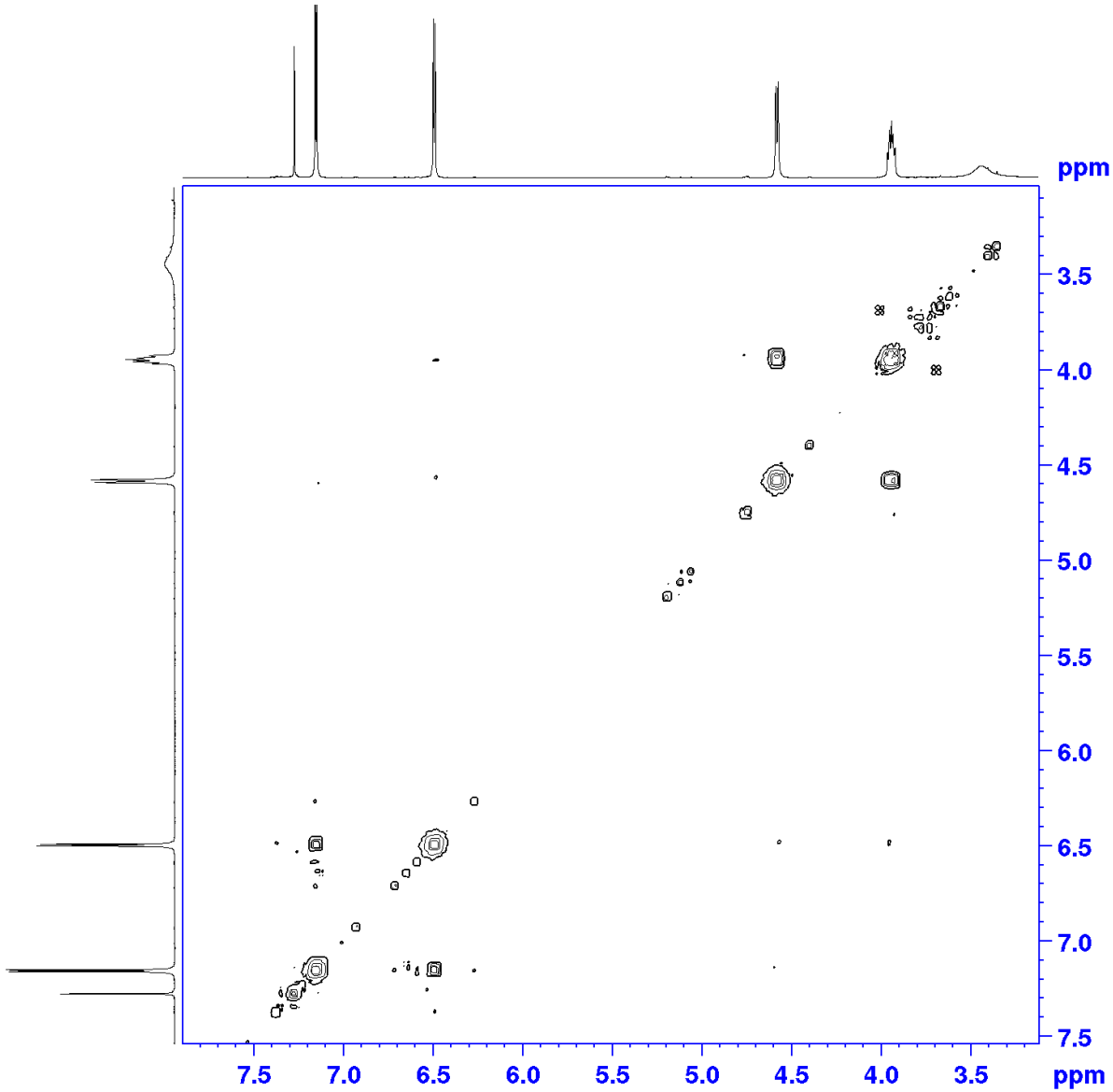
DEPT135 spectra of compound **1a** ($CDCl_3$, 400 MHz):



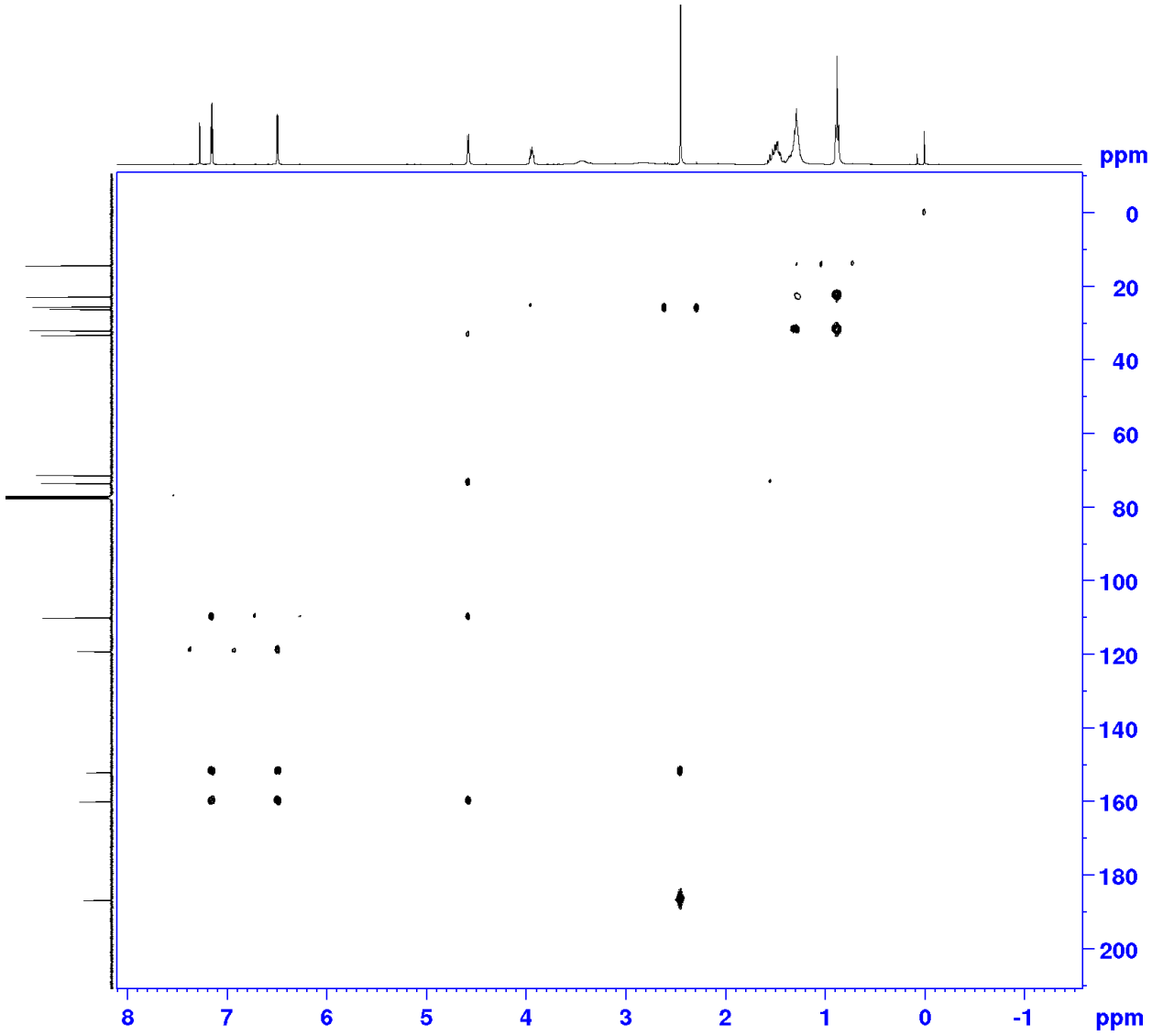
COSY spectra of compound **1a** ($CDCl_3$, 400 MHz):



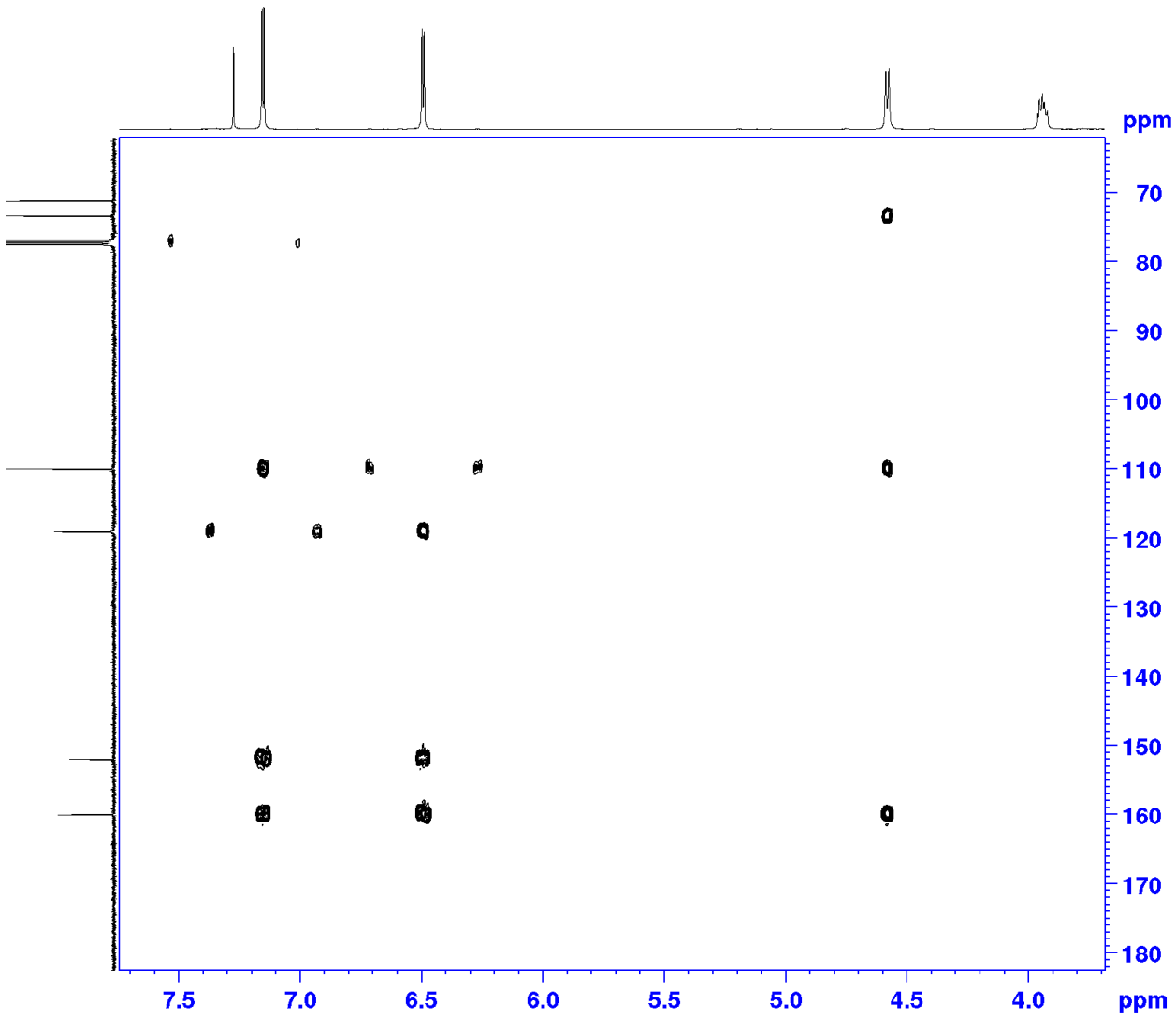
COSY spectra of compound **1a** ($CDCl_3$, 400 MHz):



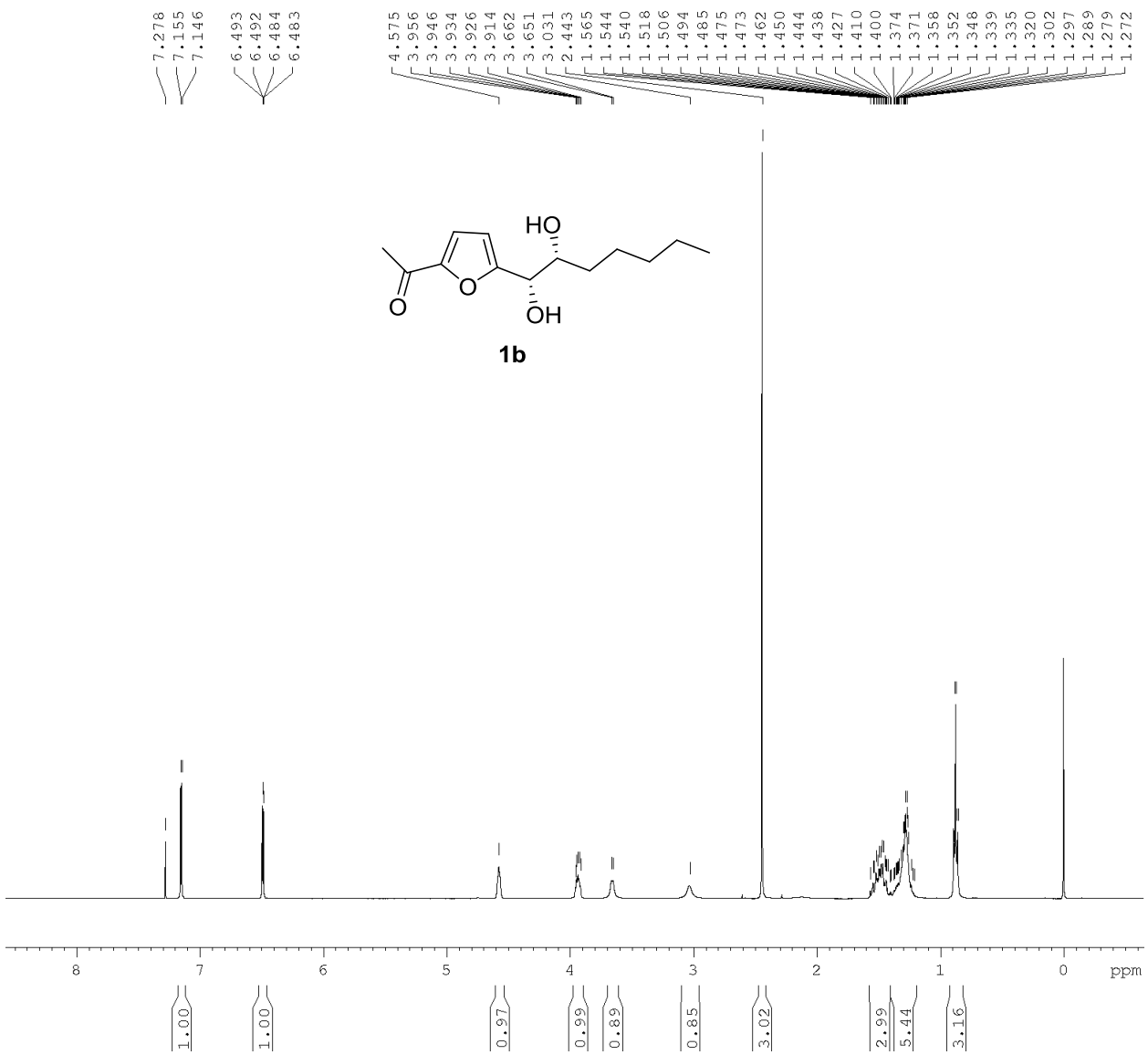
HMBC spectra of compound **1a** ($CDCl_3$, 400 MHz):



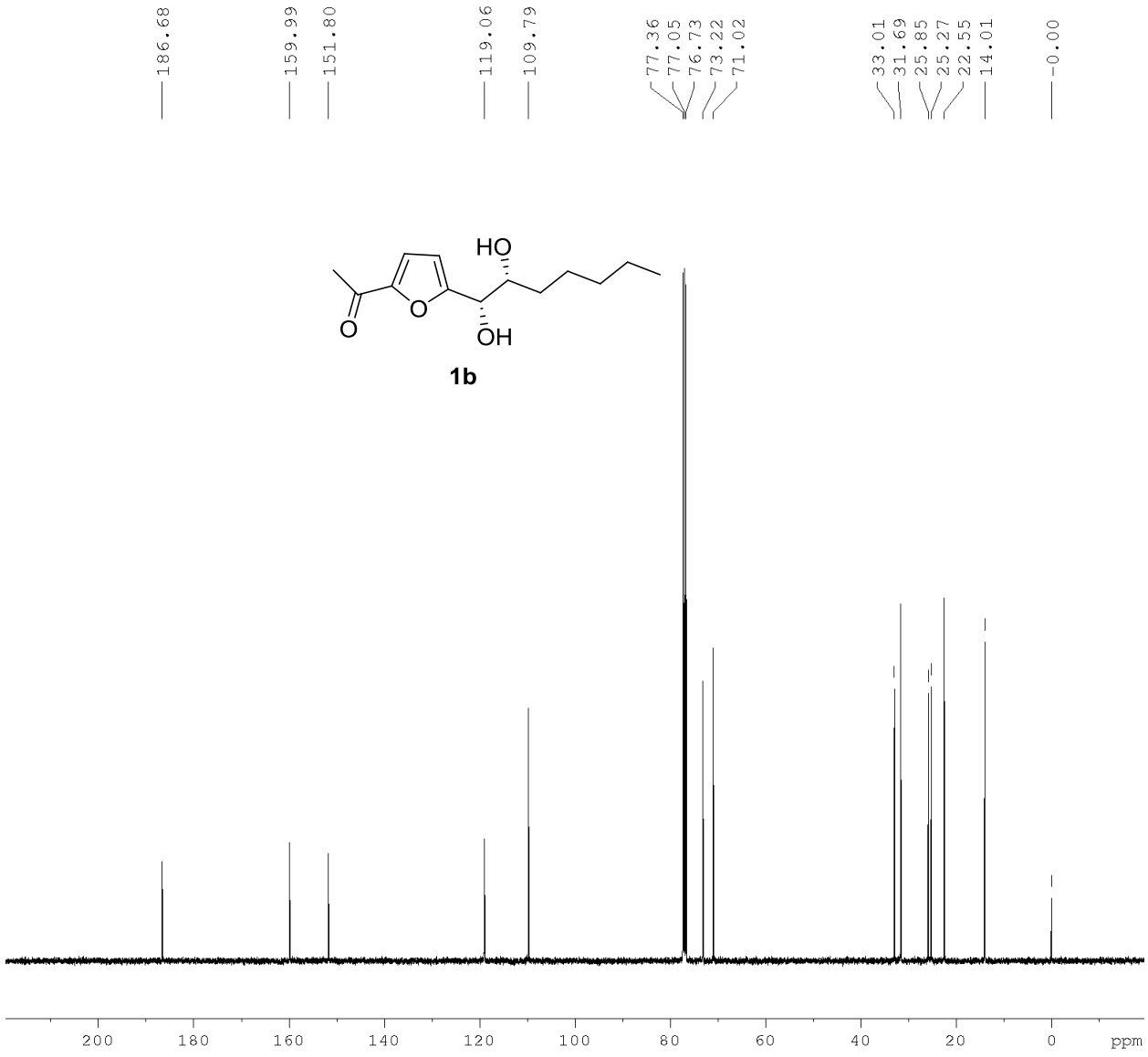
HMBC spectra of compound **1a** ($CDCl_3$, 400 MHz):



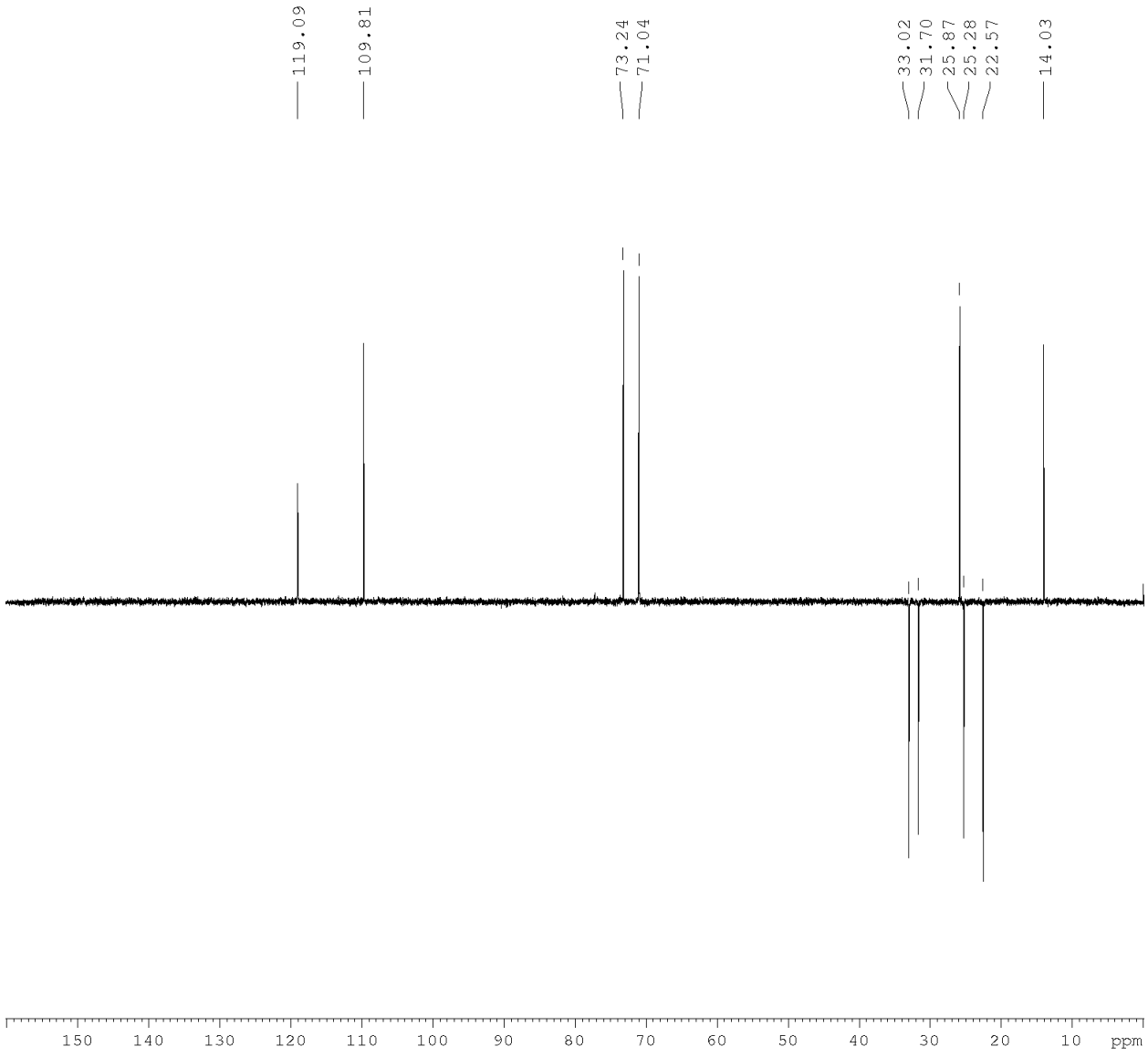
^{1}H NMR spectra of compound **1b** ($CDCl_3$, 400 MHz):



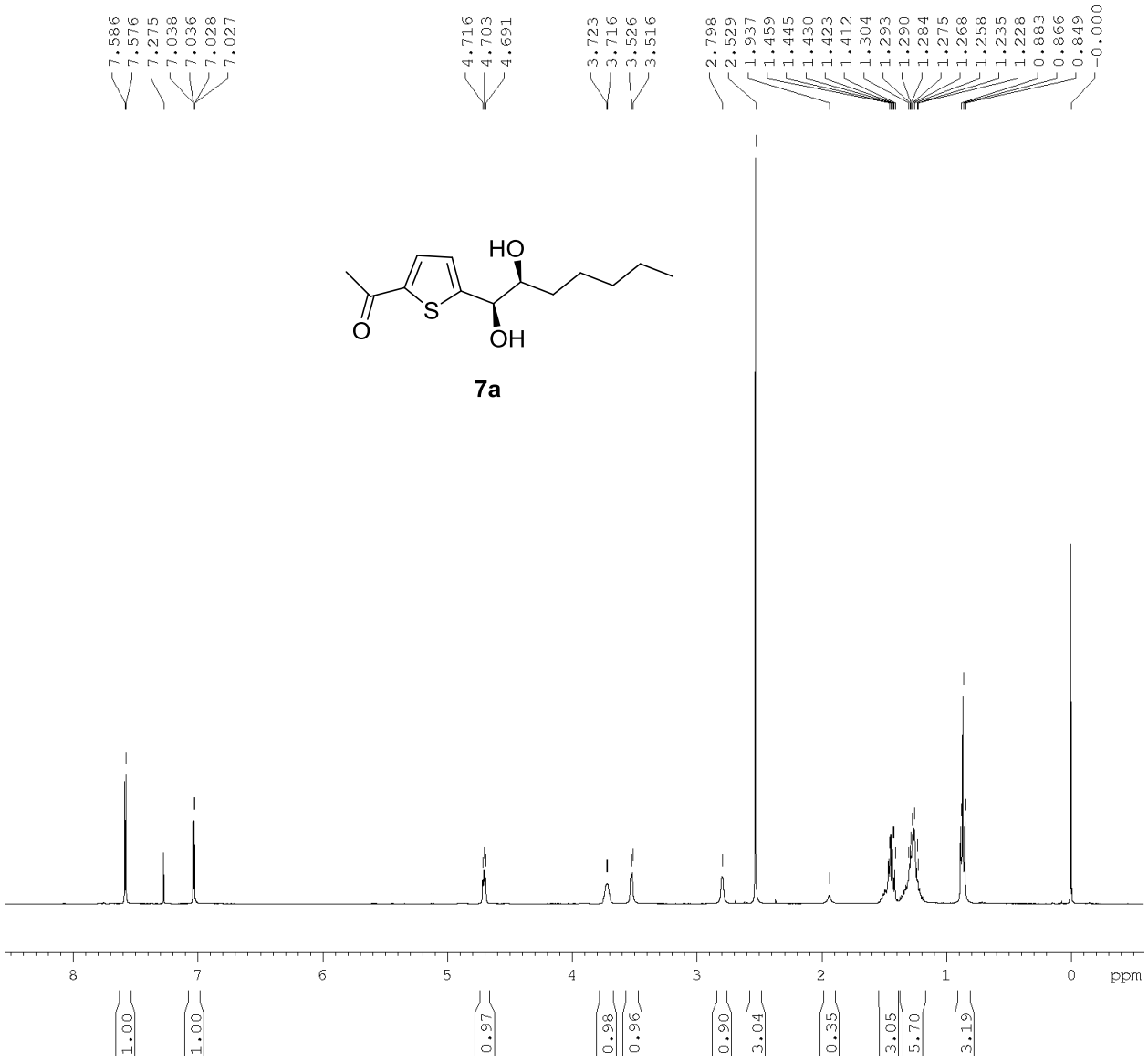
^{13}C NMR spectra of compound **1b** ($CDCl_3$, 100 MHz):



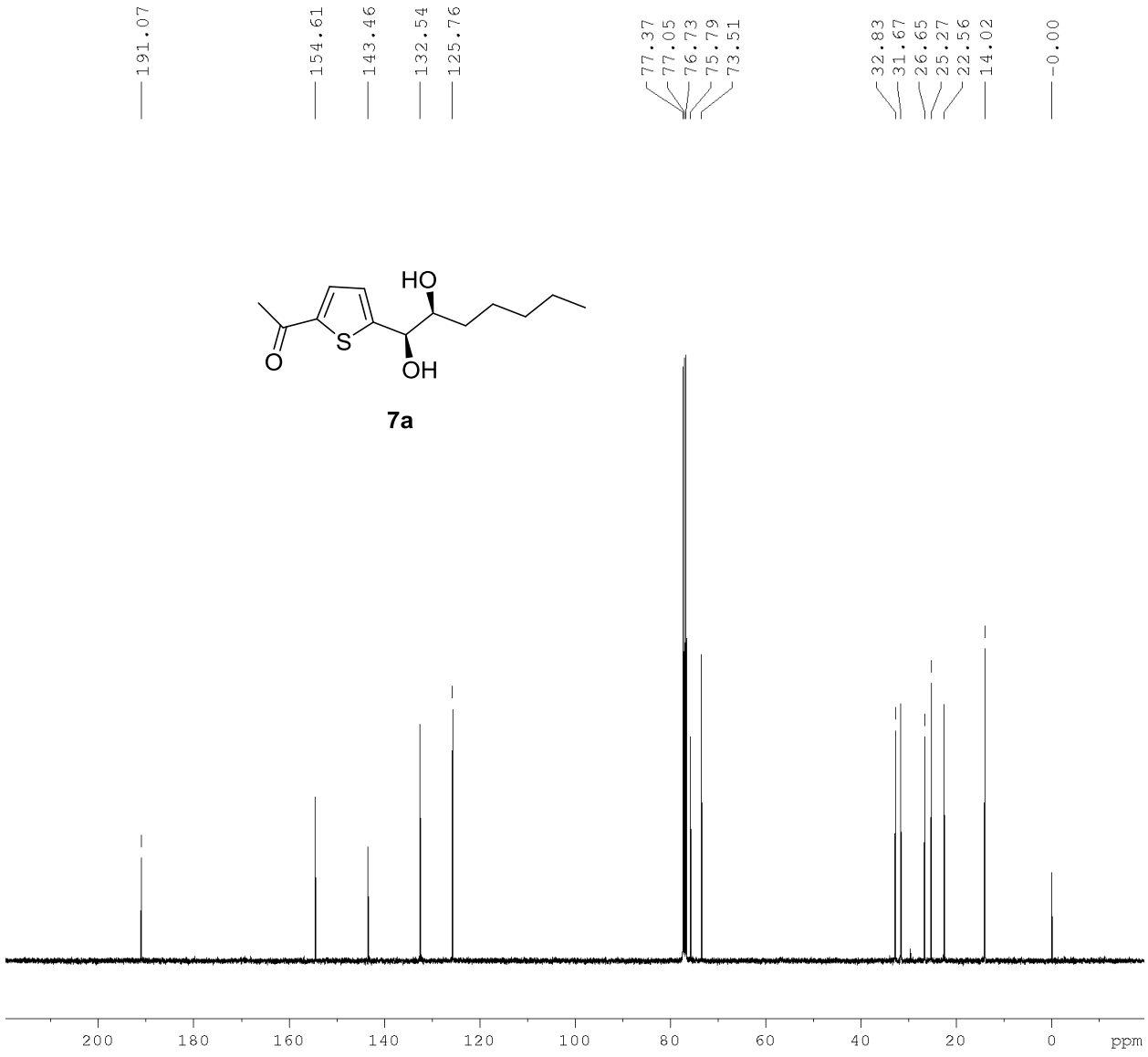
DEPT135 spectra of compound **1b** ($CDCl_3$, 400 MHz):



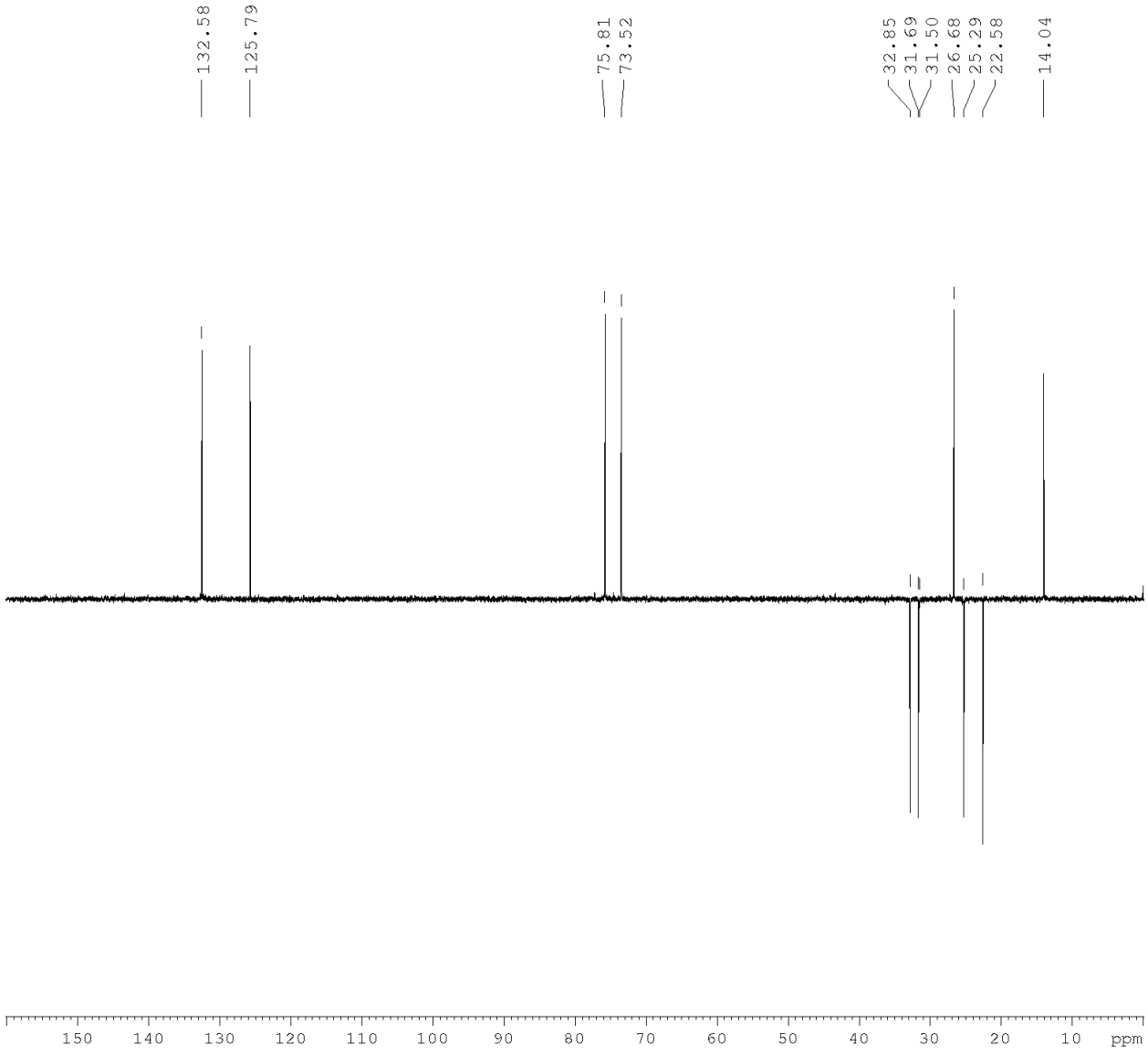
^{1}H NMR spectra of compound **7a** ($CDCl_3$, 400 MHz):



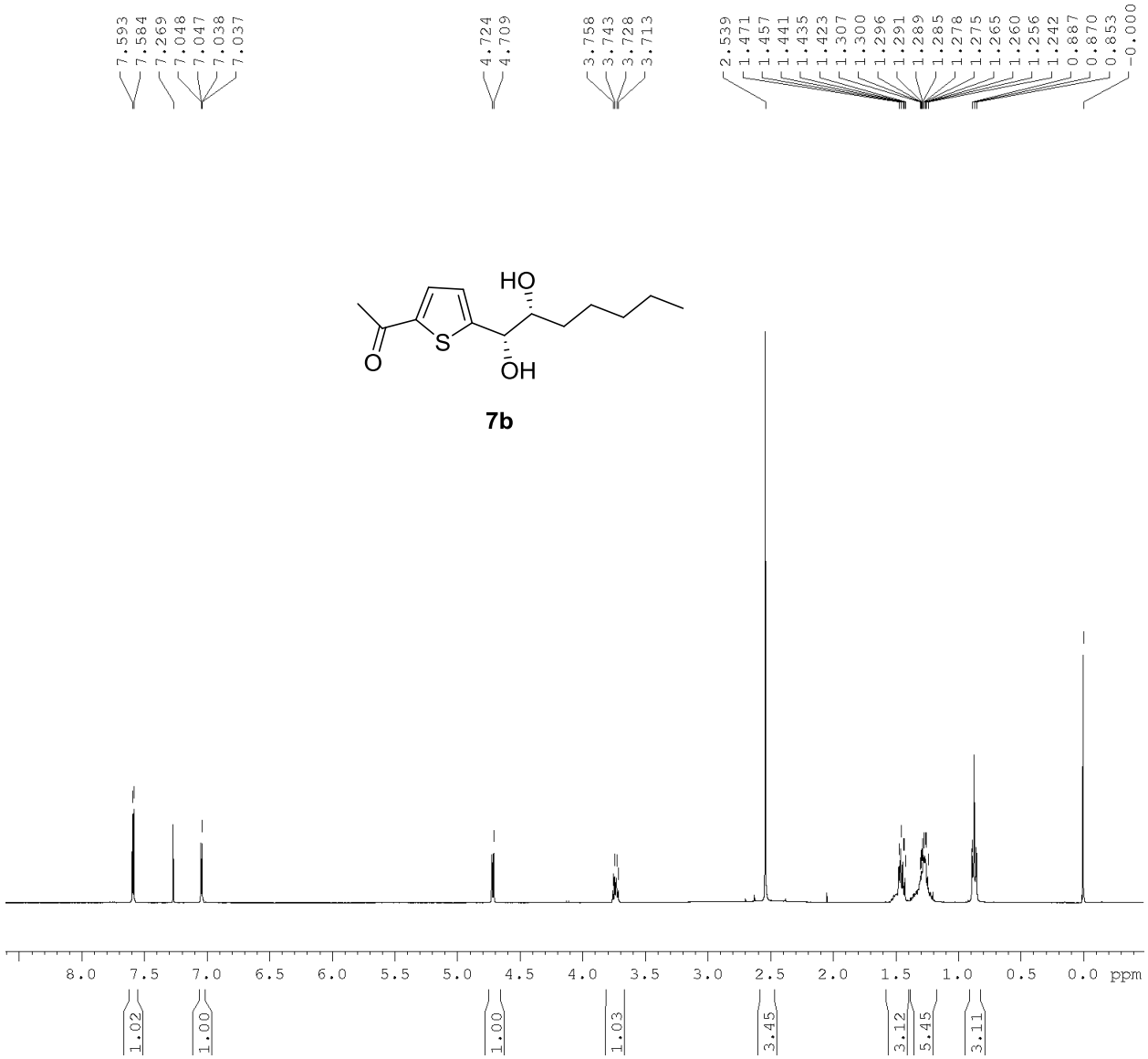
^{13}C NMR spectra of compound **7a** ($CDCl_3$, 100 MHz):



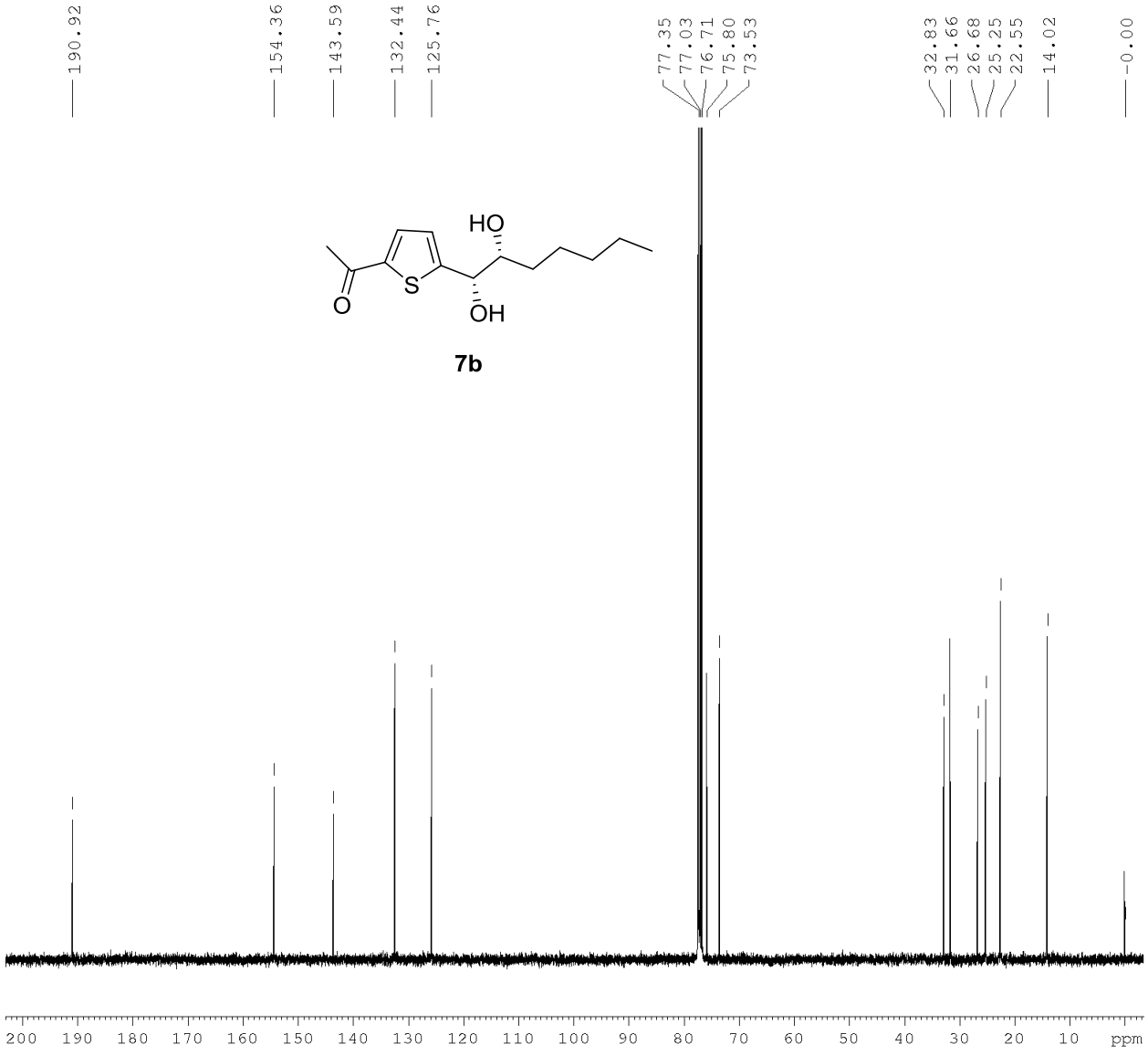
DEPT135 NMR spectra of compound **7a** ($CDCl_3$, 400 MHz):



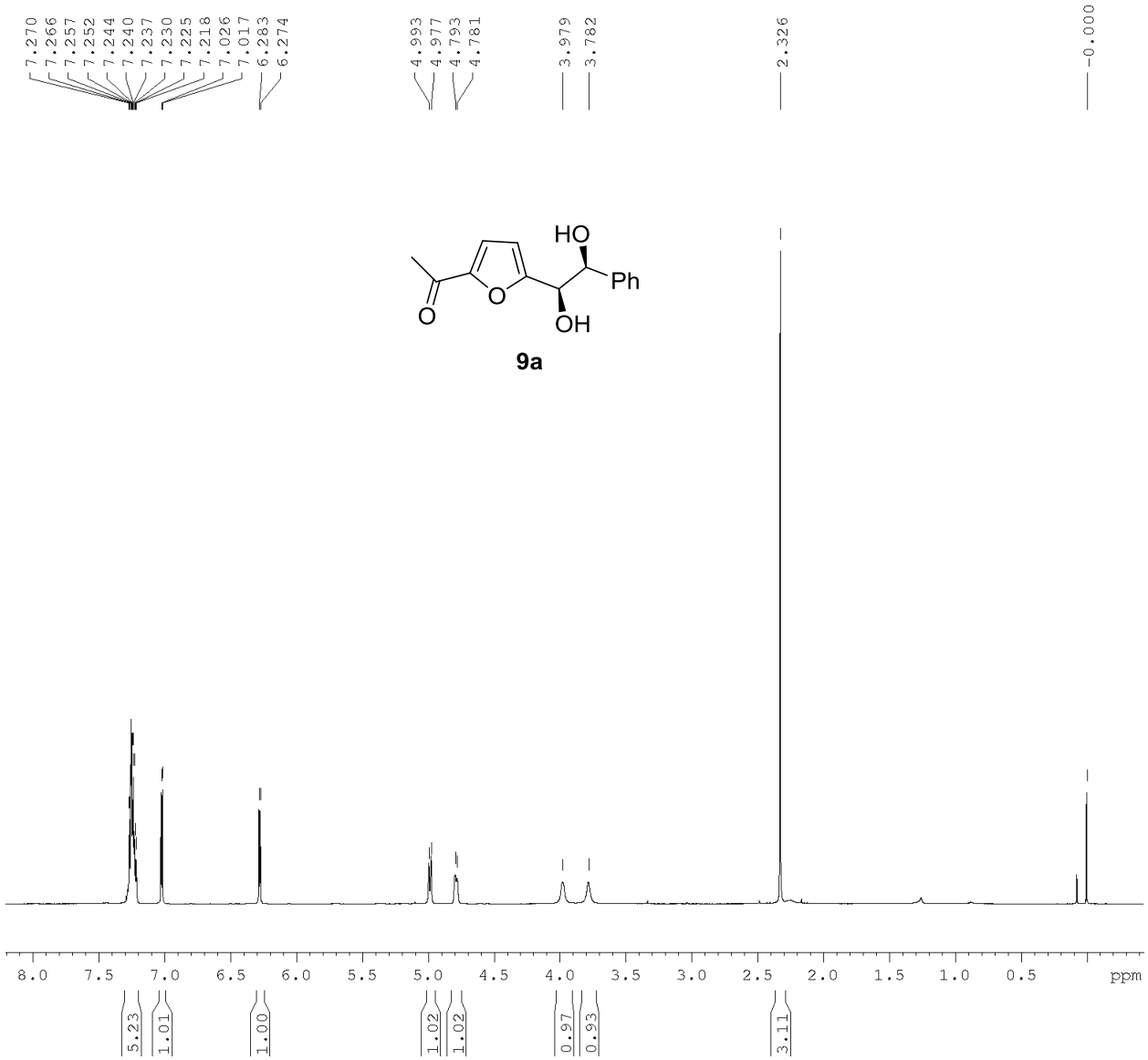
^{1}H NMR spectra of compound **7b** ($CDCl_3$, 400 MHz):



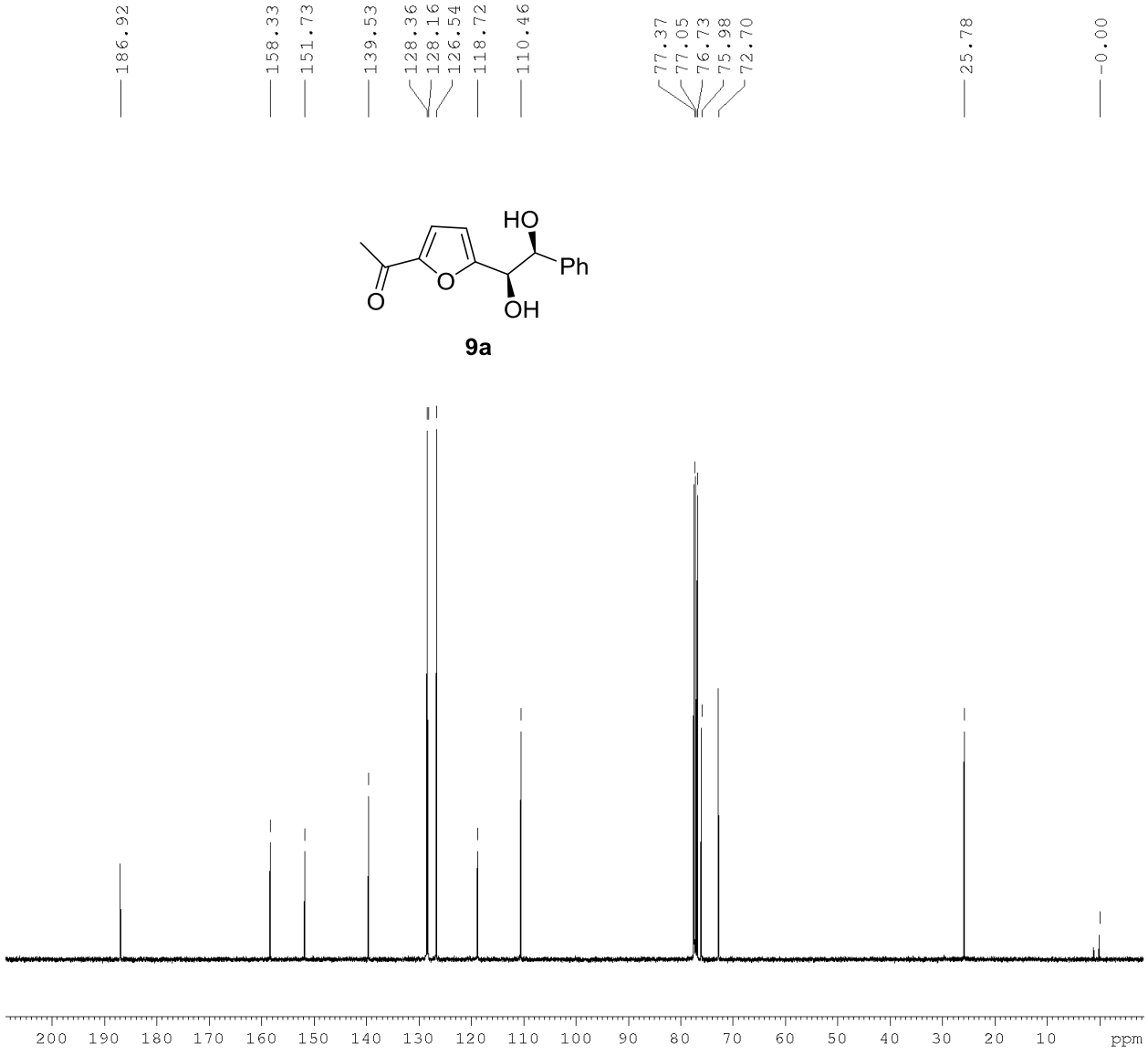
^{13}C NMR spectra of compound **7b** ($CDCl_3$, 100 MHz):



^{1}H NMR spectra of compound **9a** ($CDCl_3$, 400 MHz):

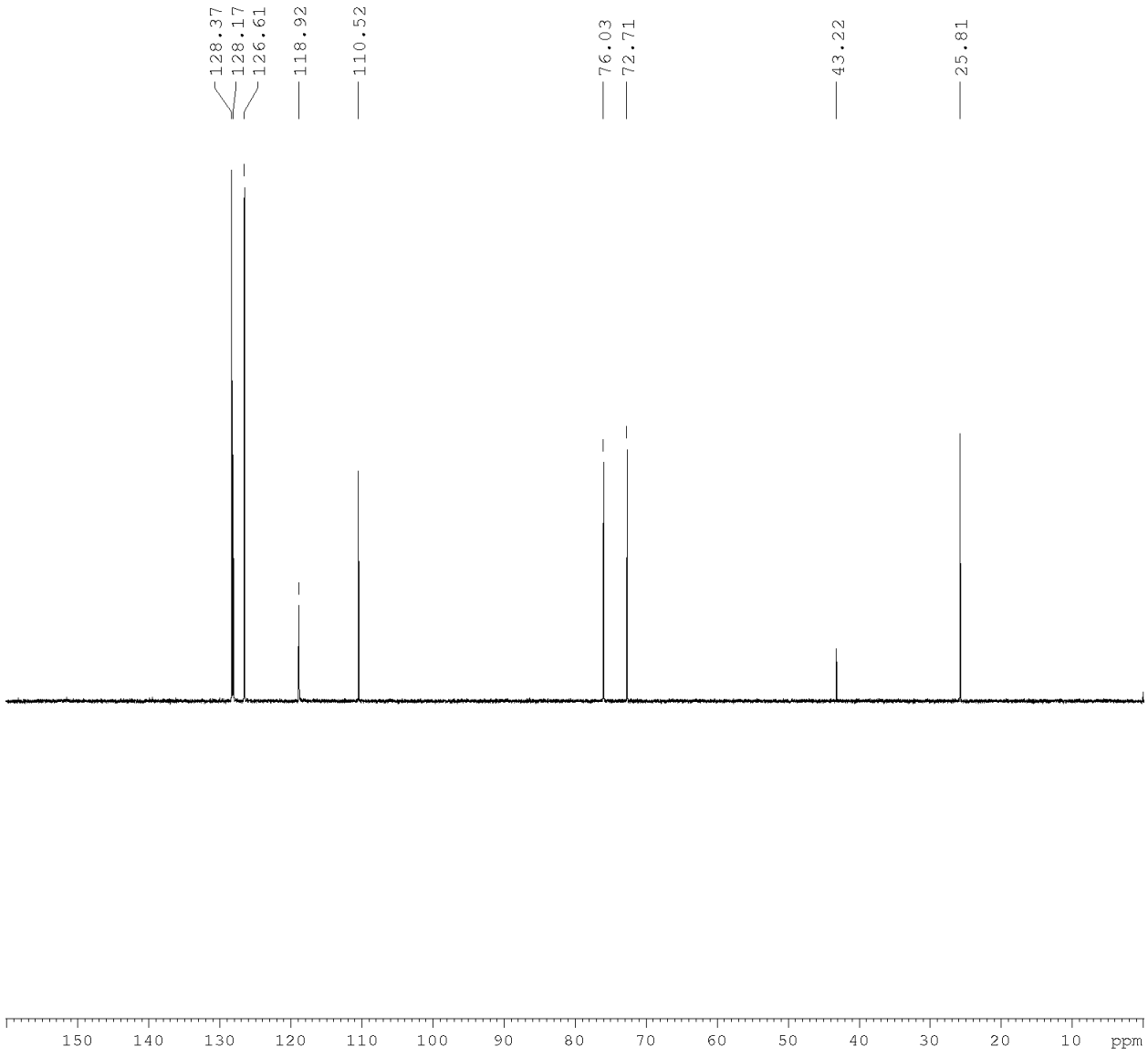


^{13}C NMR spectra of compound **9a** ($CDCl_3$, 100 MHz):

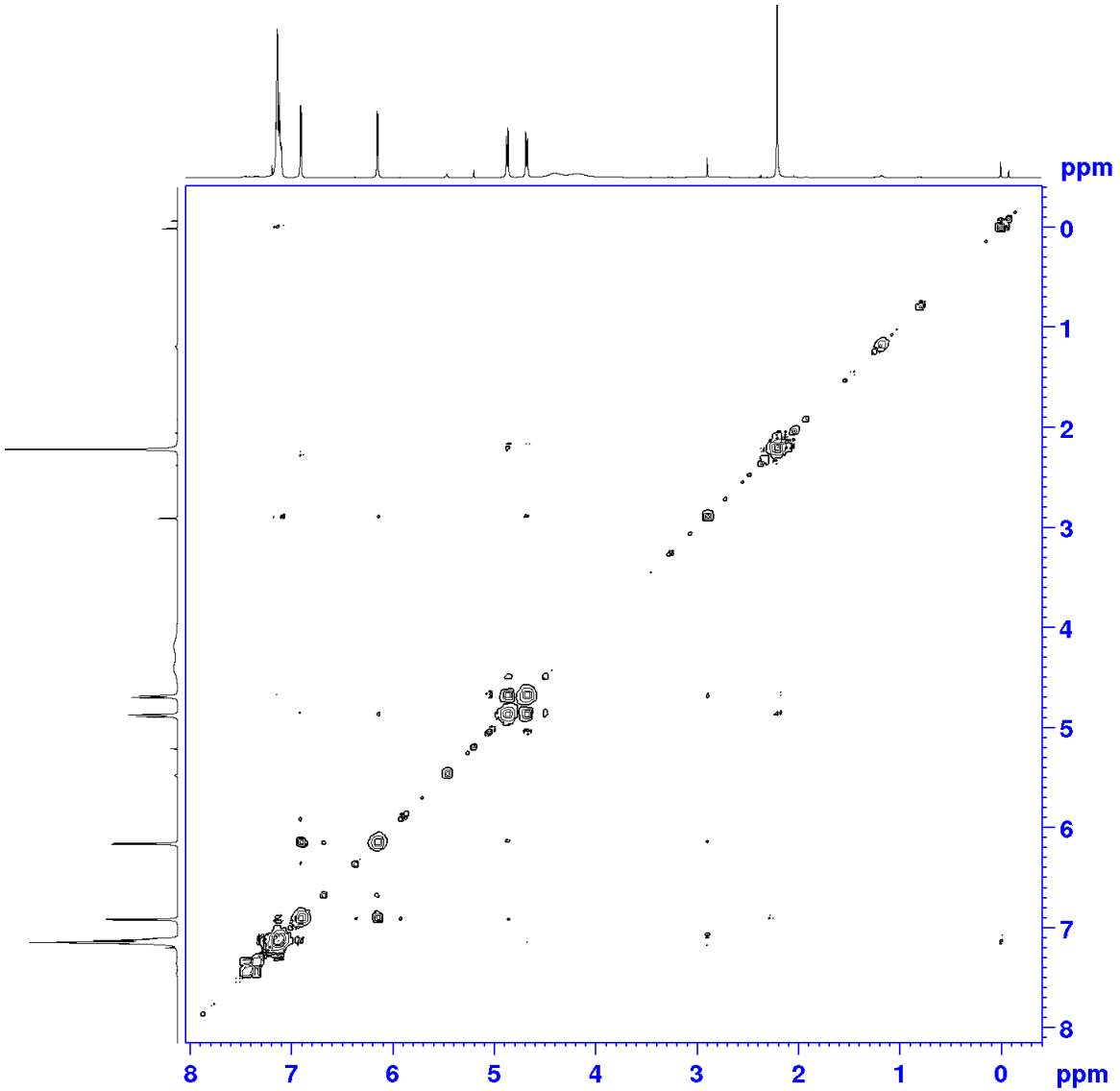


9a

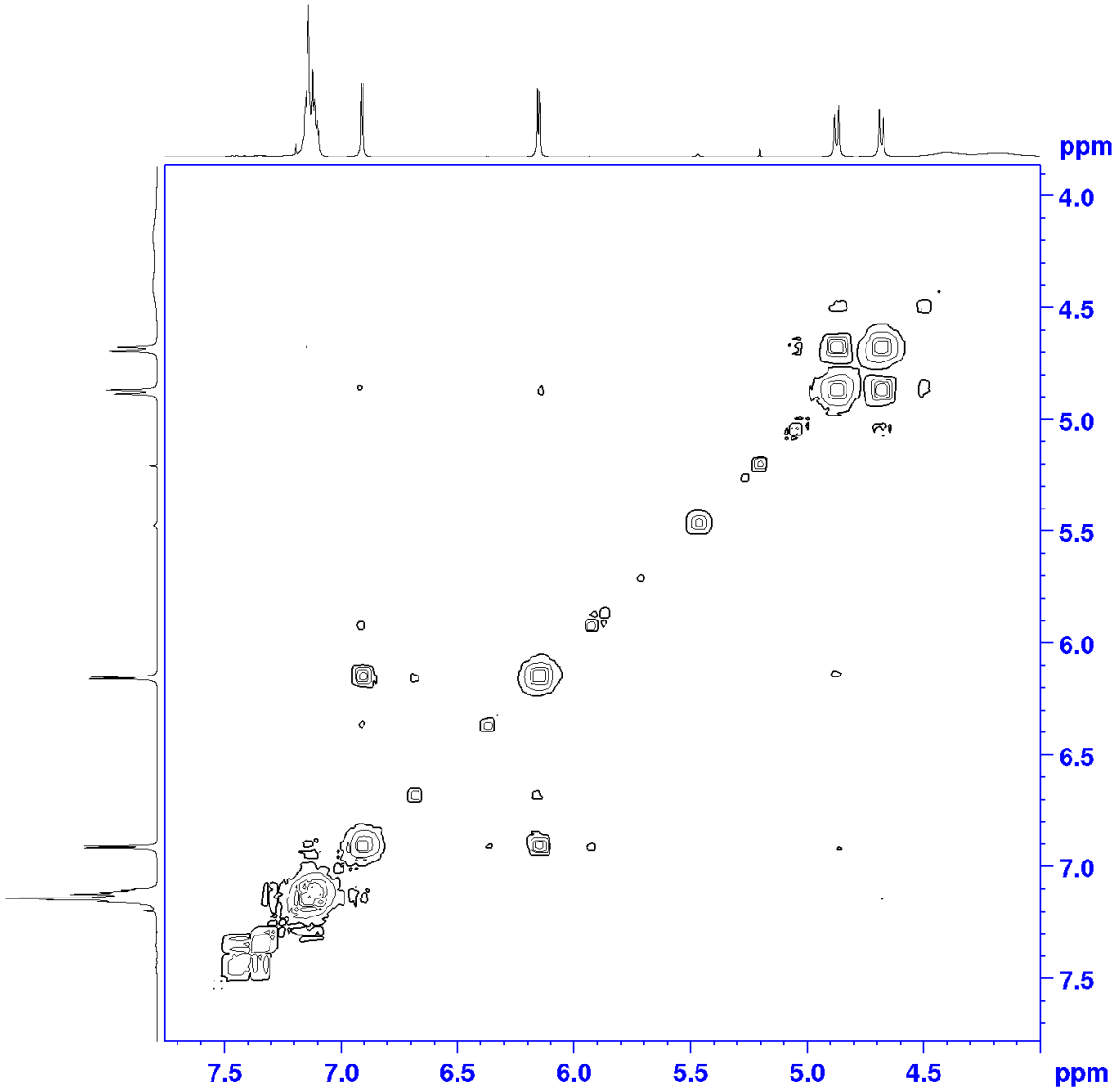
DEPT135 NMR spectra of compound **9a** ($CDCl_3$, 400 MHz):



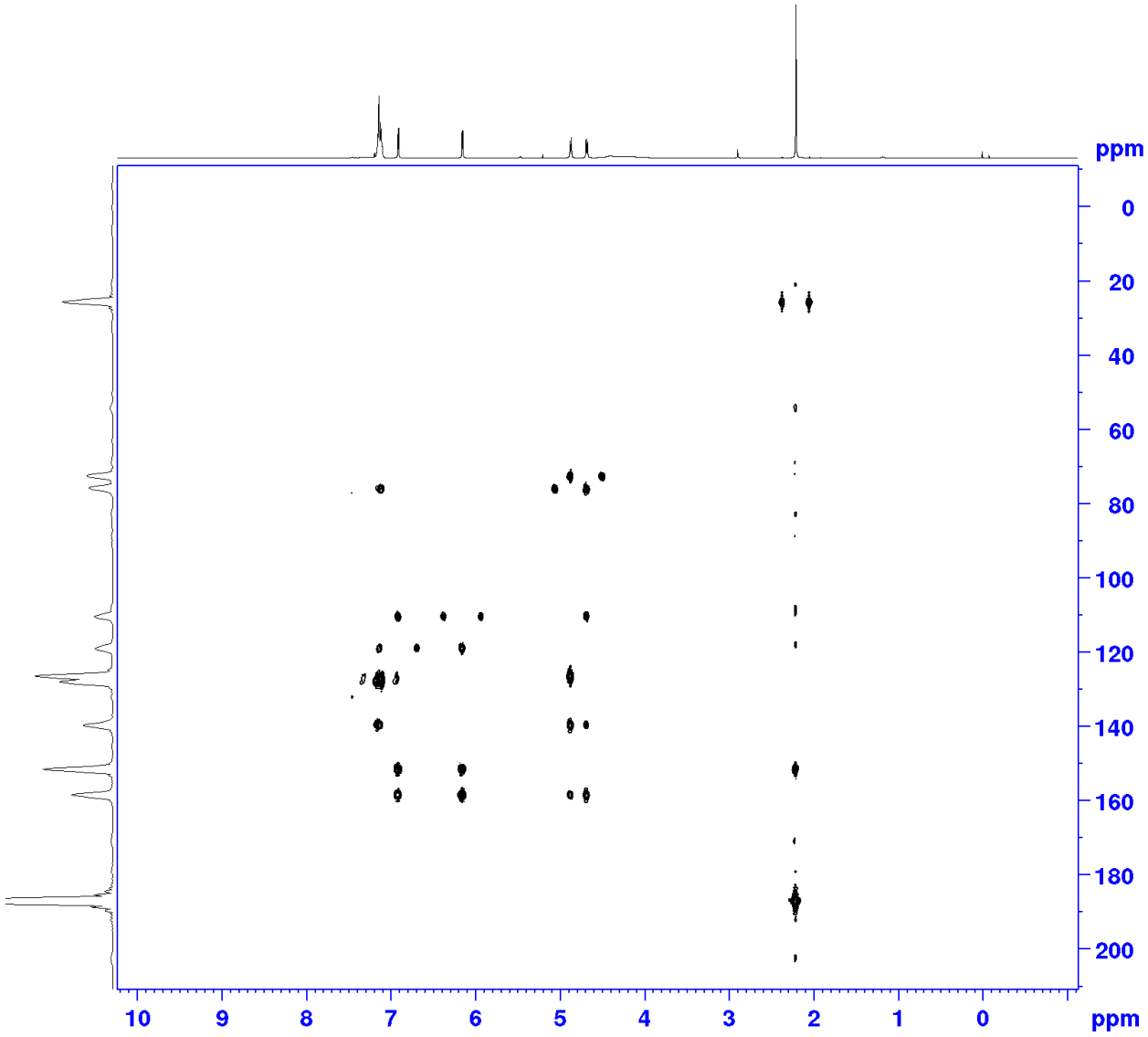
COSY NMR spectra of compound **9a** ($CDCl_3$, 400 MHz):



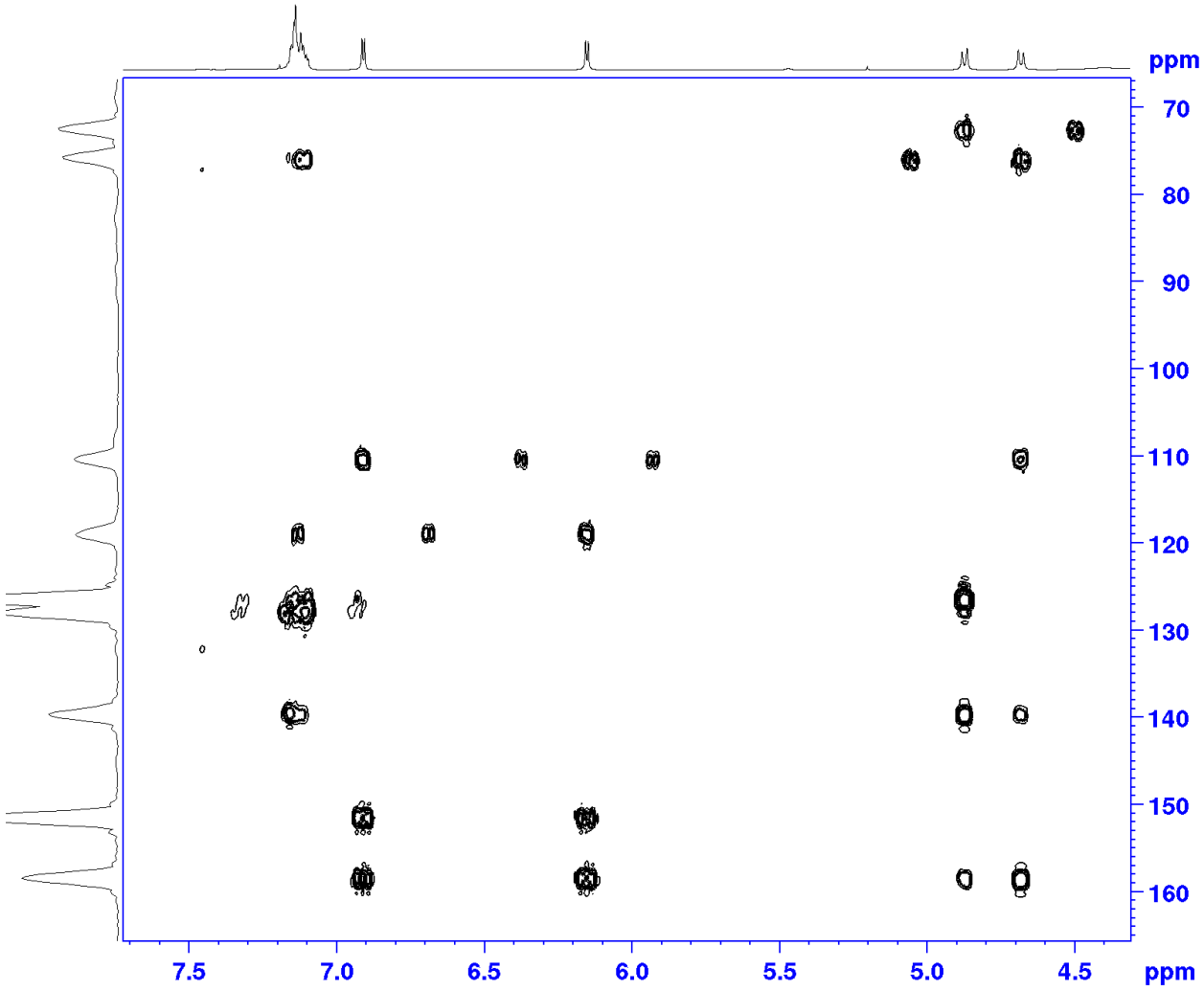
COSY NMR spectra of compound **9a** ($CDCl_3$, 400 MHz):



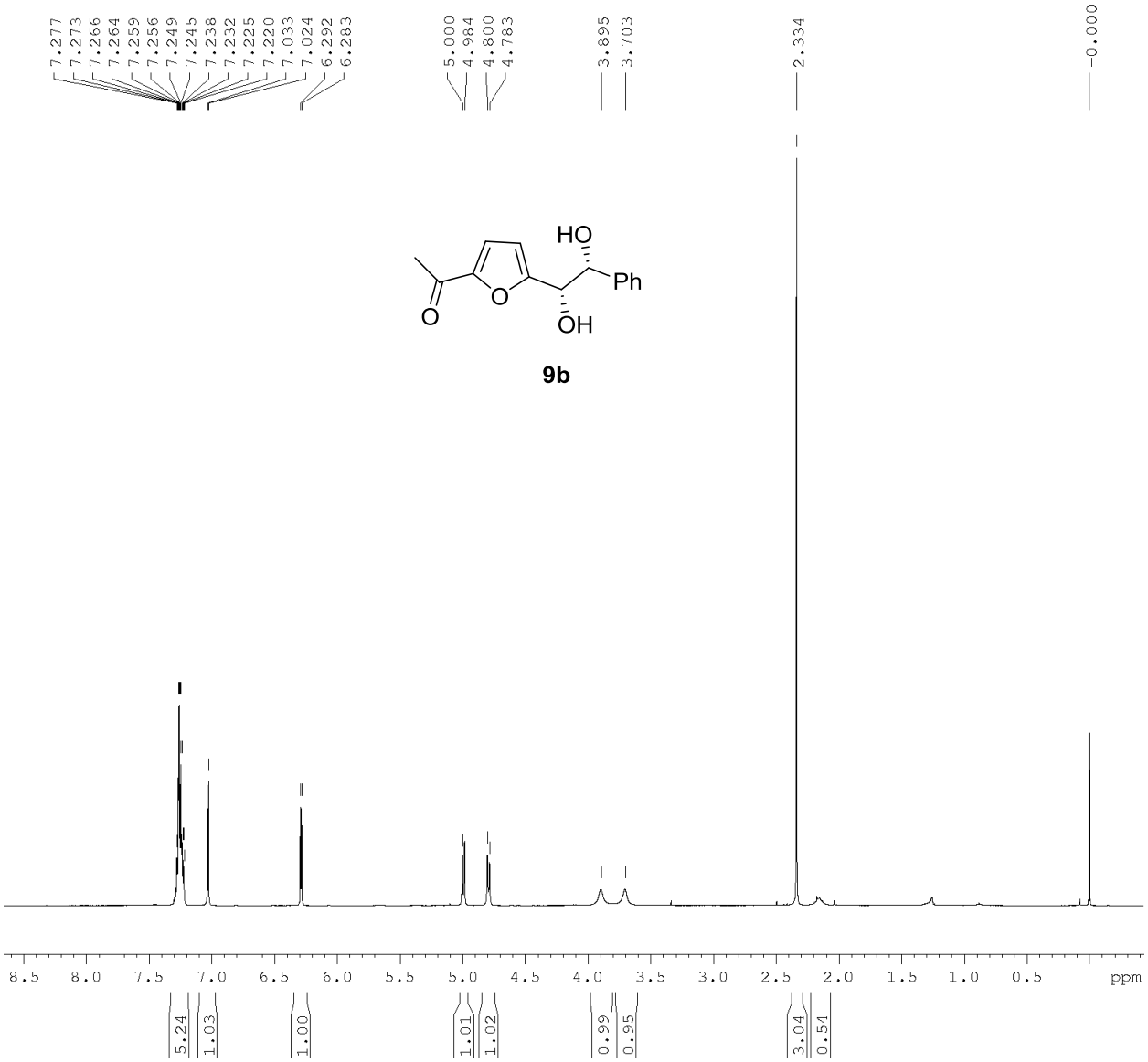
HMBC NMR spectra of compound **9a** ($CDCl_3$, 400 MHz):



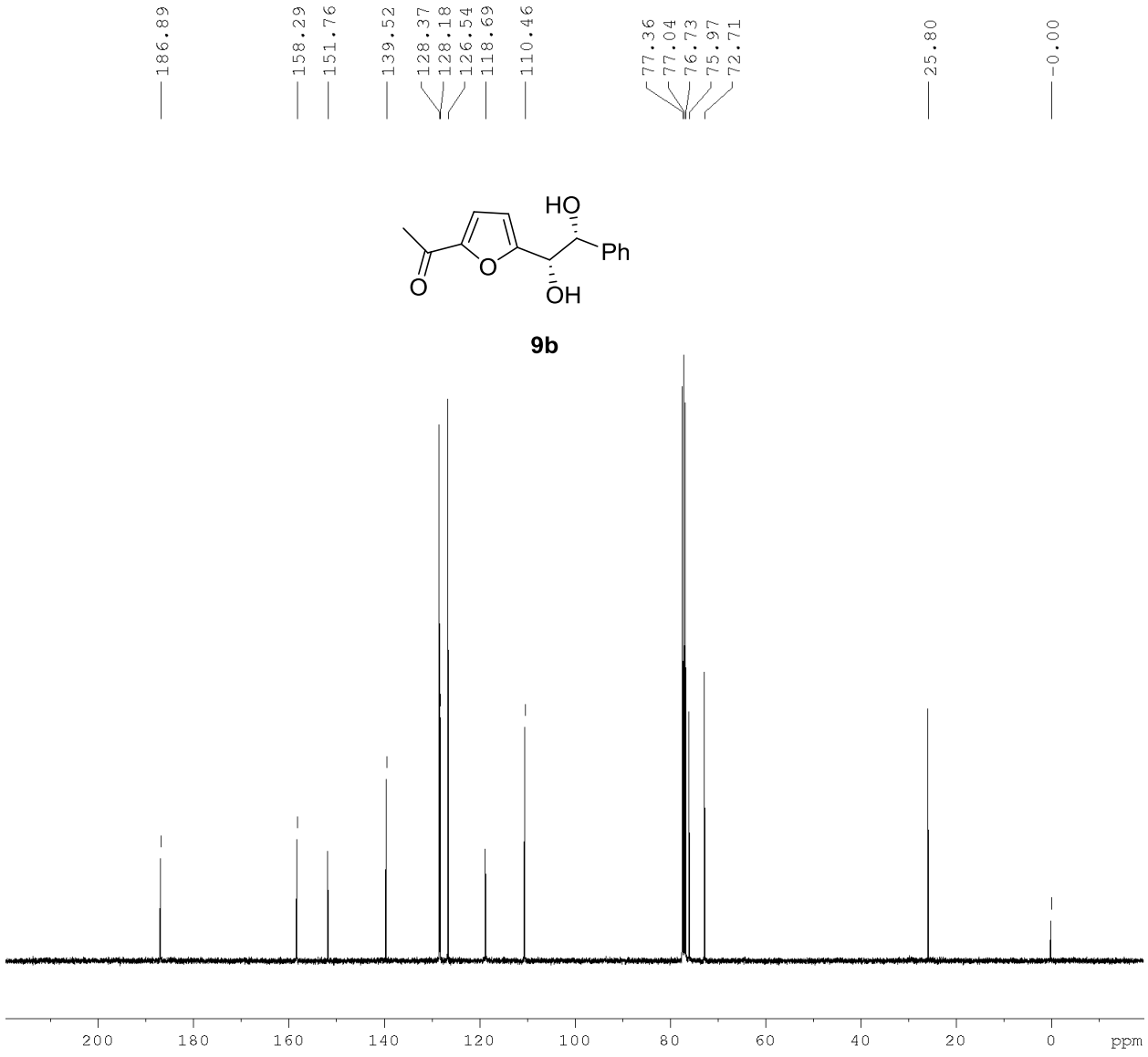
HMBC NMR spectra of compound **9a** ($CDCl_3$, 400 MHz):



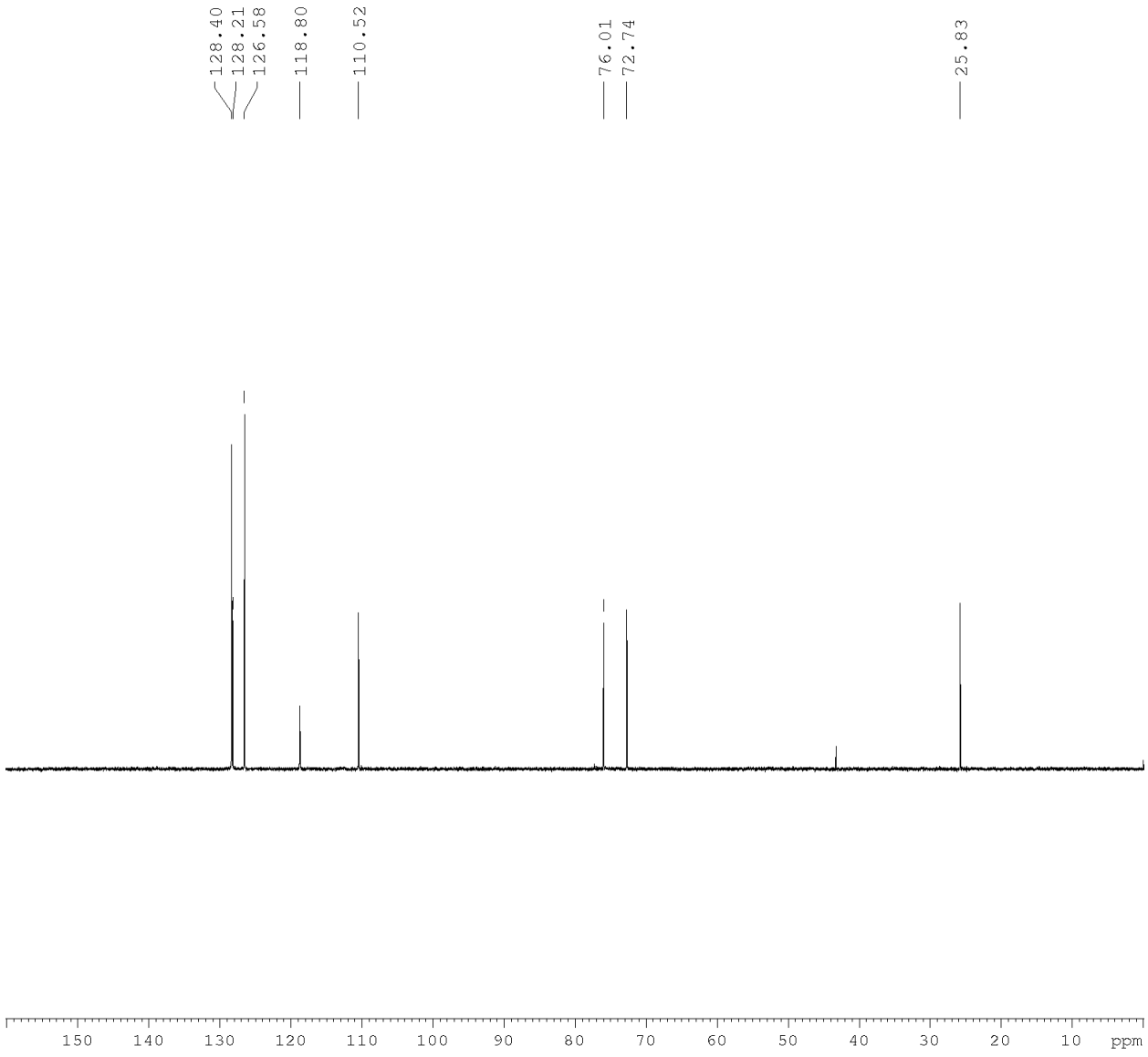
^{1}H NMR spectra of compound **9b** ($CDCl_3$, 400 MHz):



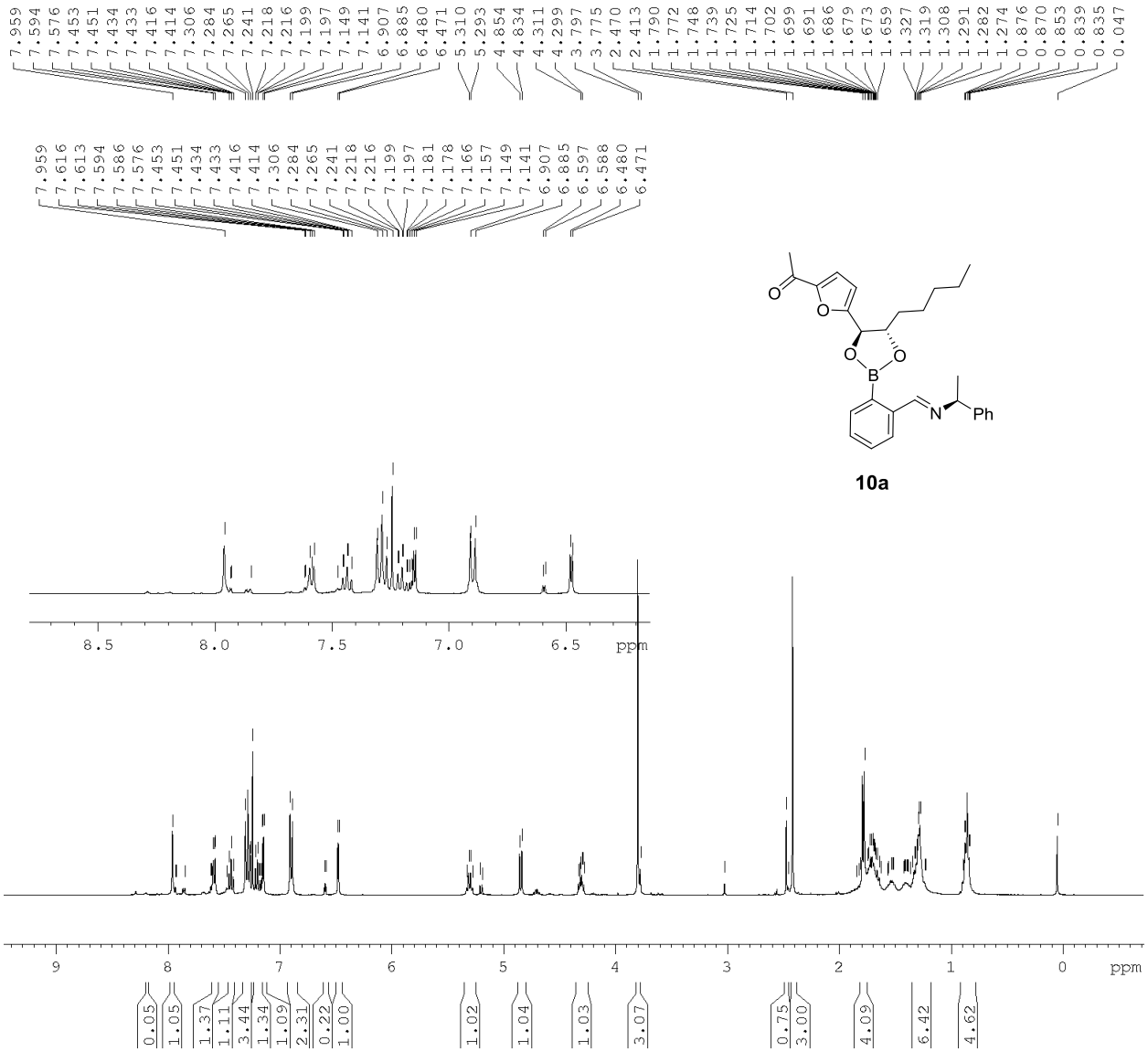
^{13}C NMR spectra of compound **9b** ($CDCl_3$, 100 MHz):



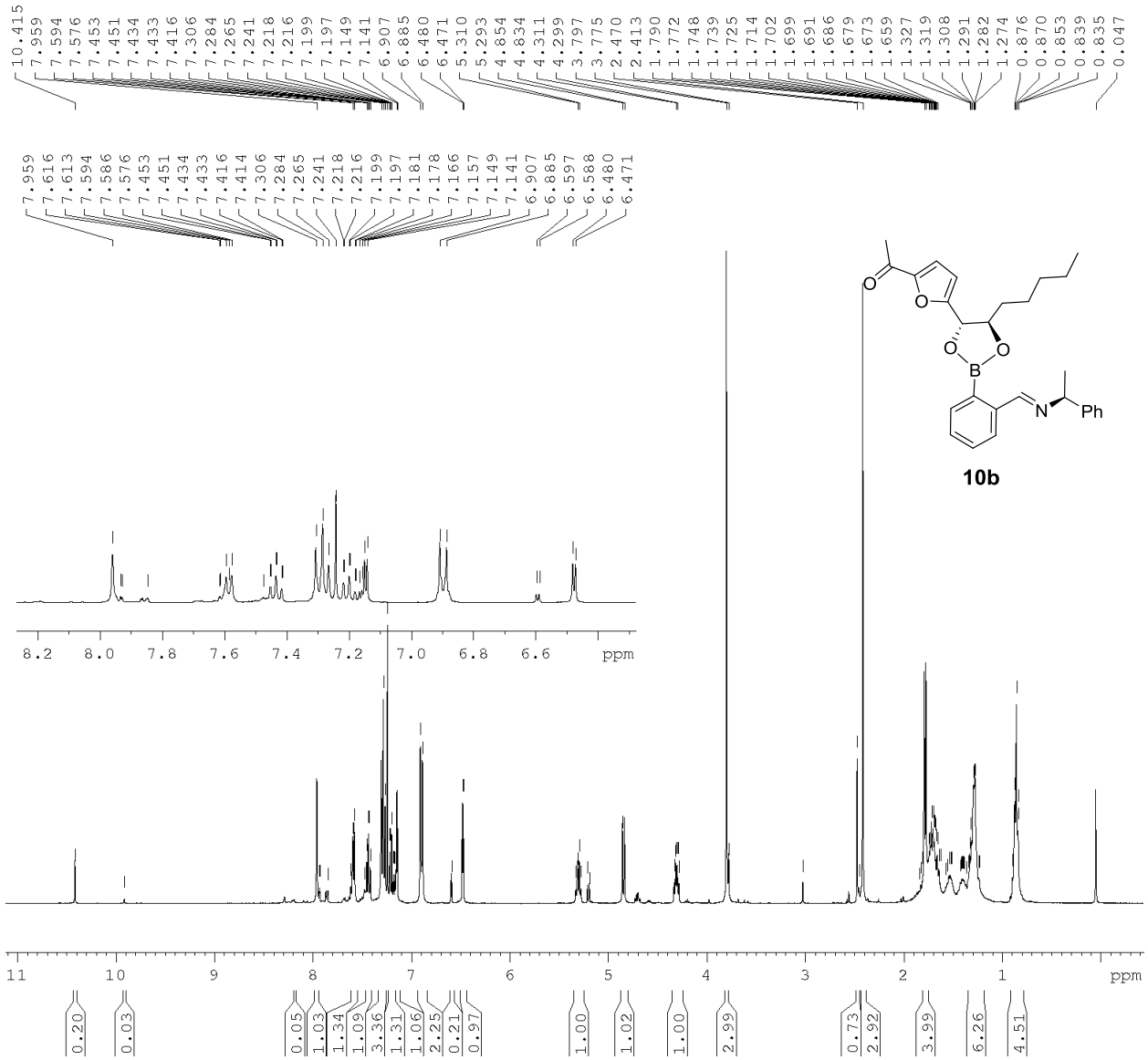
DEPT135 NMR spectra of compound **9b** ($CDCl_3$, 100 MHz):



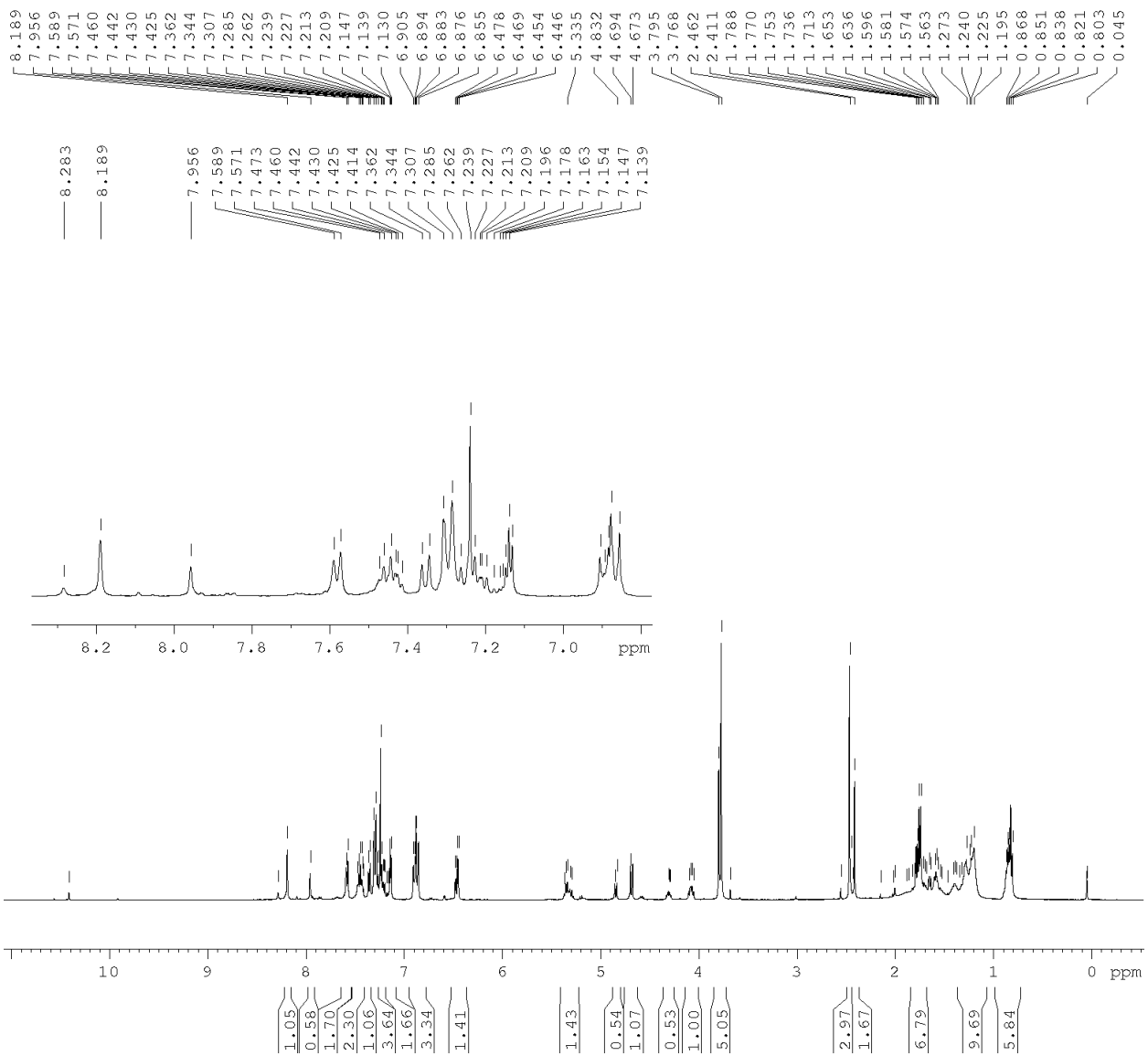
^{1}H NMR spectra of compound **10a** ($CDCl_3$, 400 MHz):



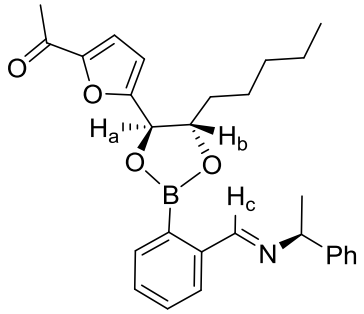
^{1}H NMR spectra of compound **10b** ($CDCl_3$, 400 MHz):



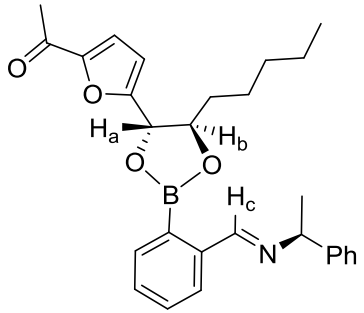
^{1}H NMR spectra of compound **10a+10b** (mixture, $CDCl_3$, 400 MHz):



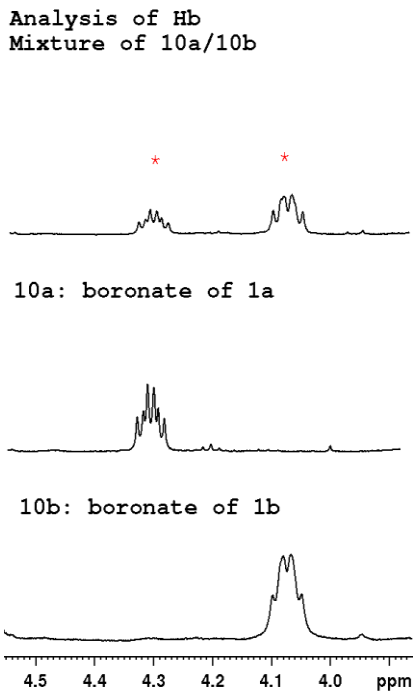
Determination of enantiomeric excess of **1a** and **1b** via boronates **10a** and **10b**.



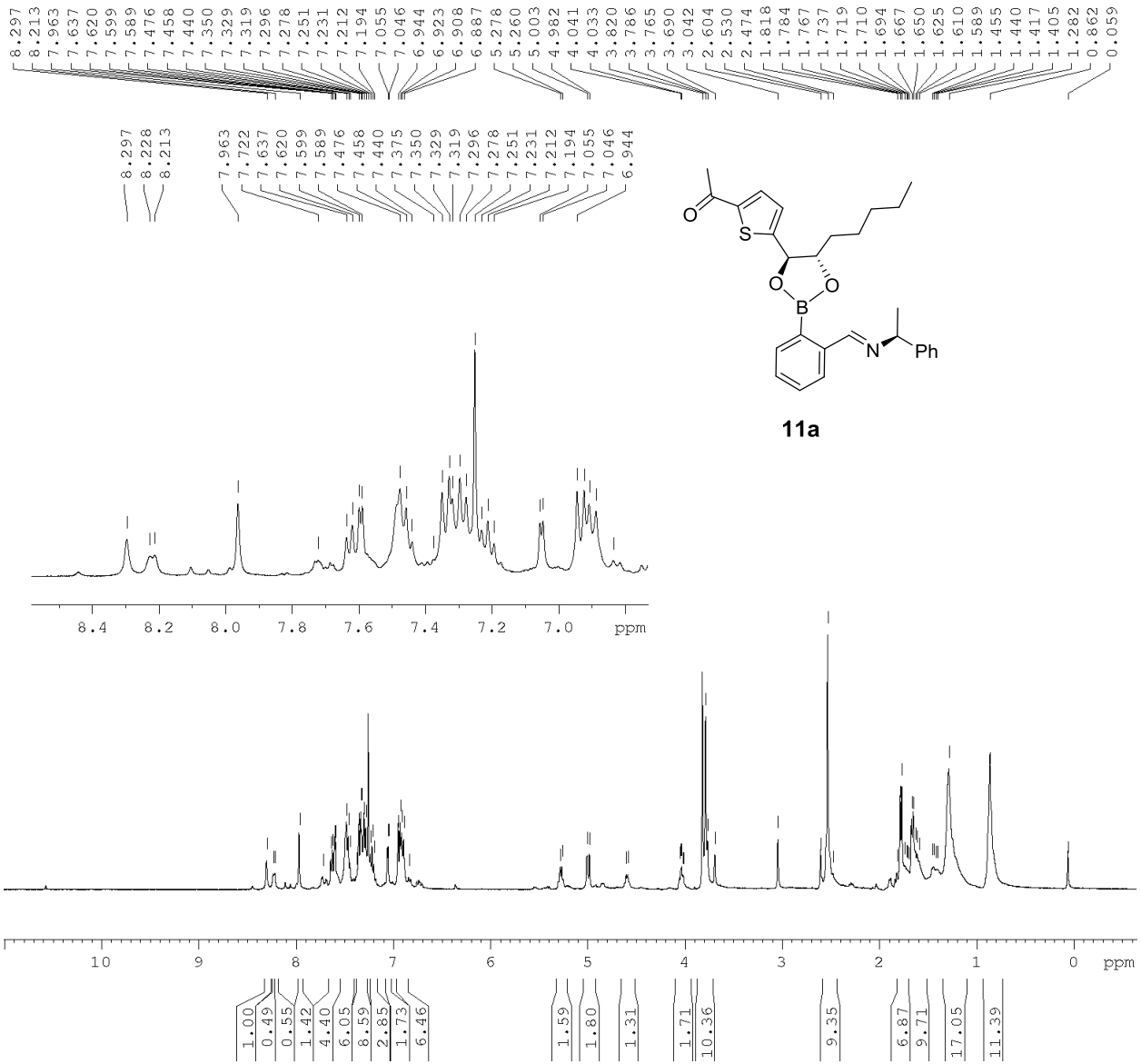
10a



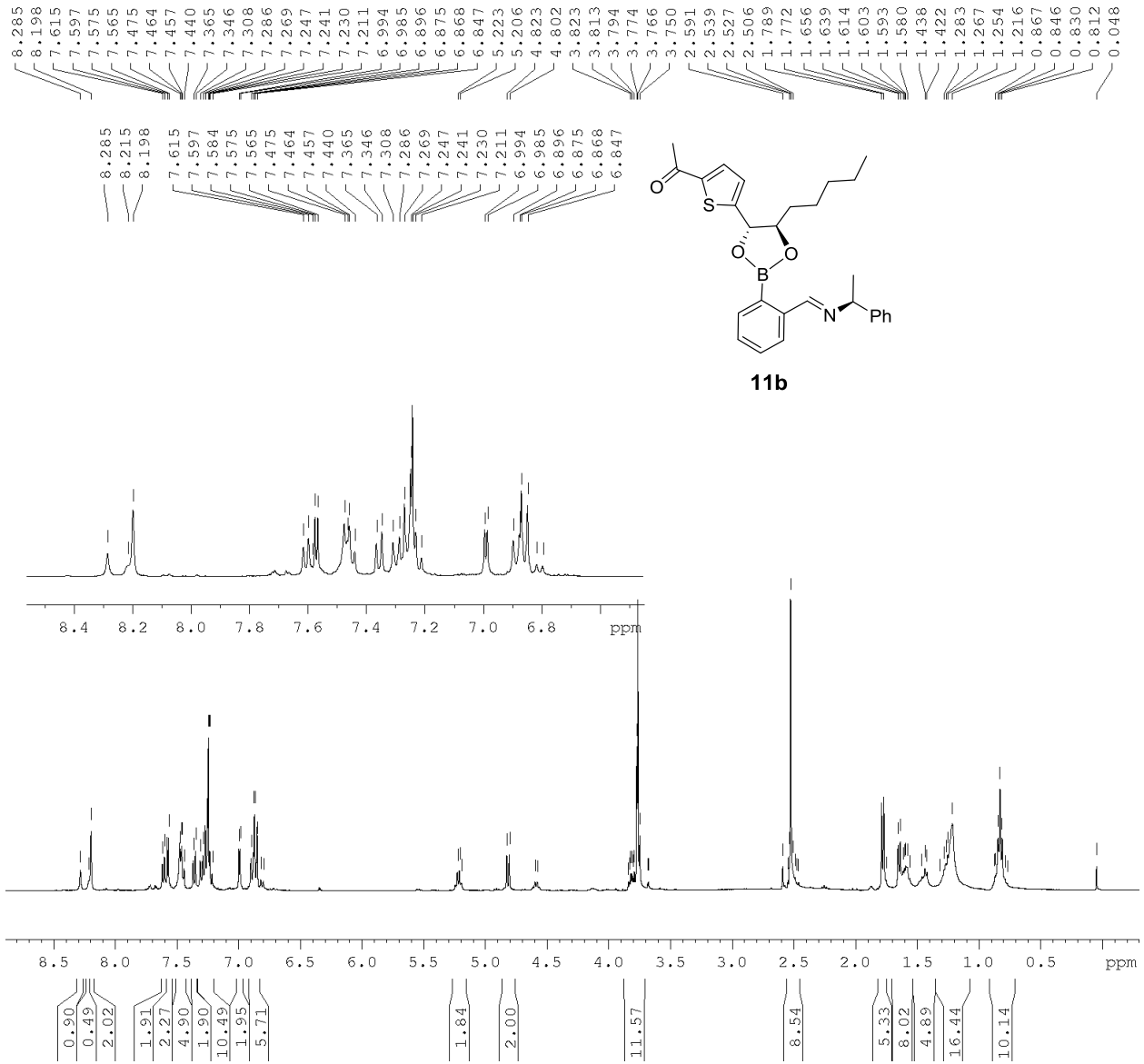
10b



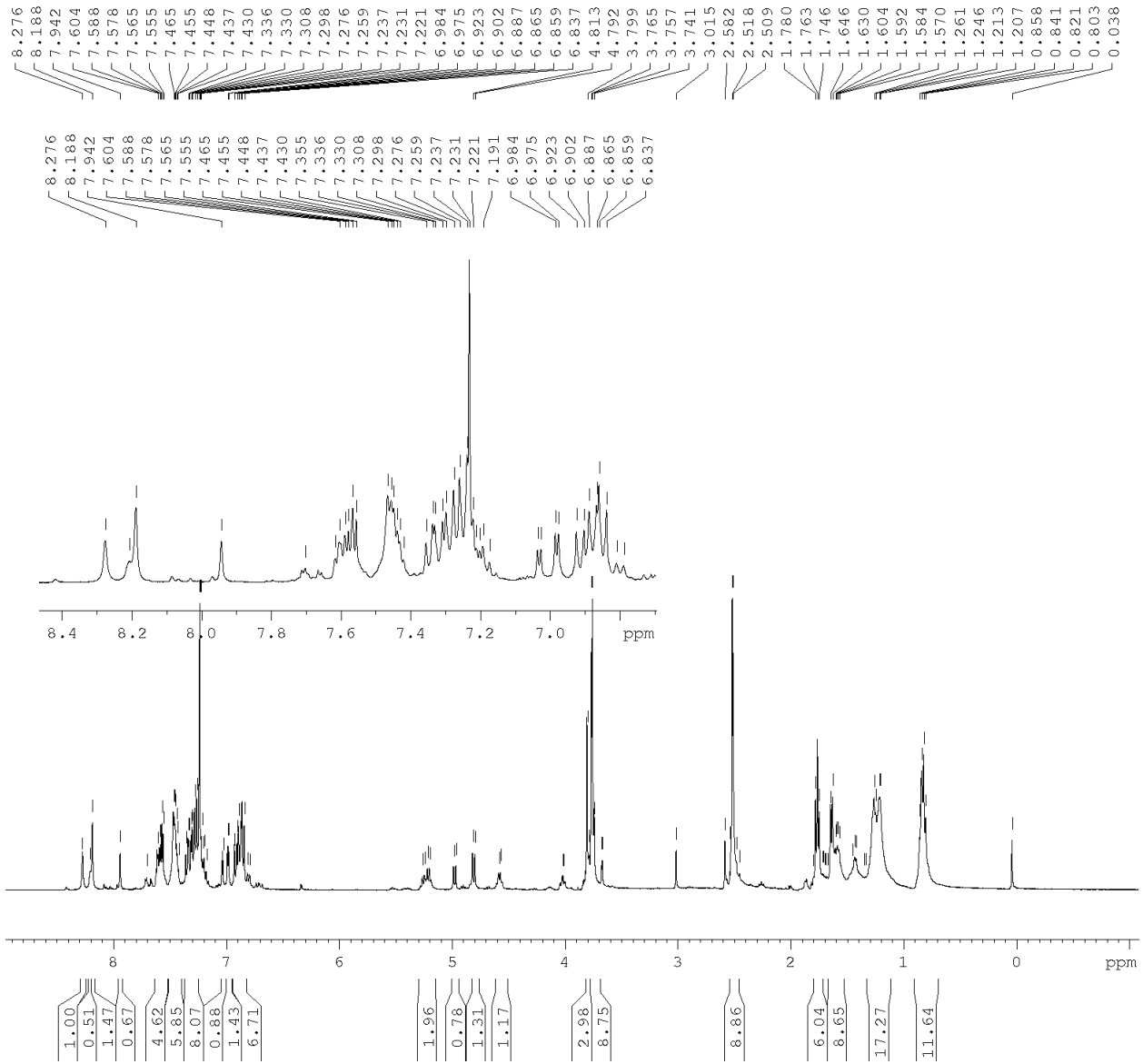
^{1}H NMR spectra of compound **11a** ($CDCl_3$, 400 MHz):



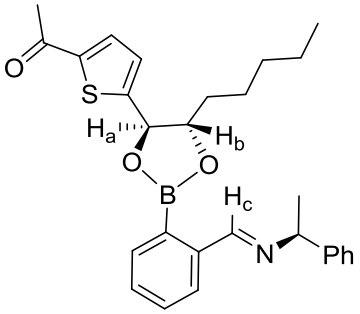
^{1}H NMR spectra of compound **11b** ($CDCl_3$, 400 MHz):



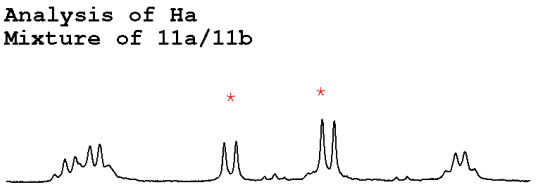
^{1}H NMR spectra of compound **11a+11b** (mixture, $CDCl_3$, 400 MHz):



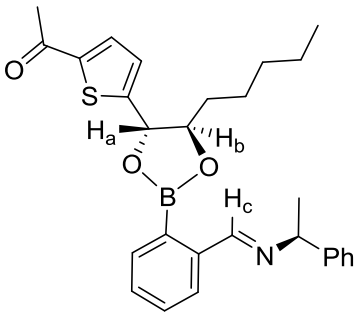
Determination of enantiomeric excess of **7a** and **7b** via boronates **11a** and **11b**



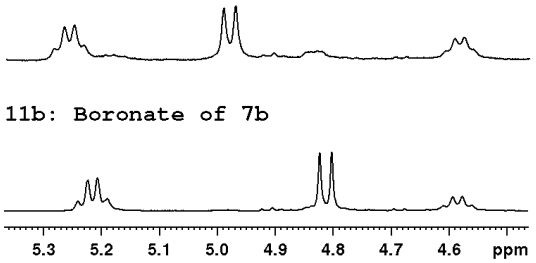
11a



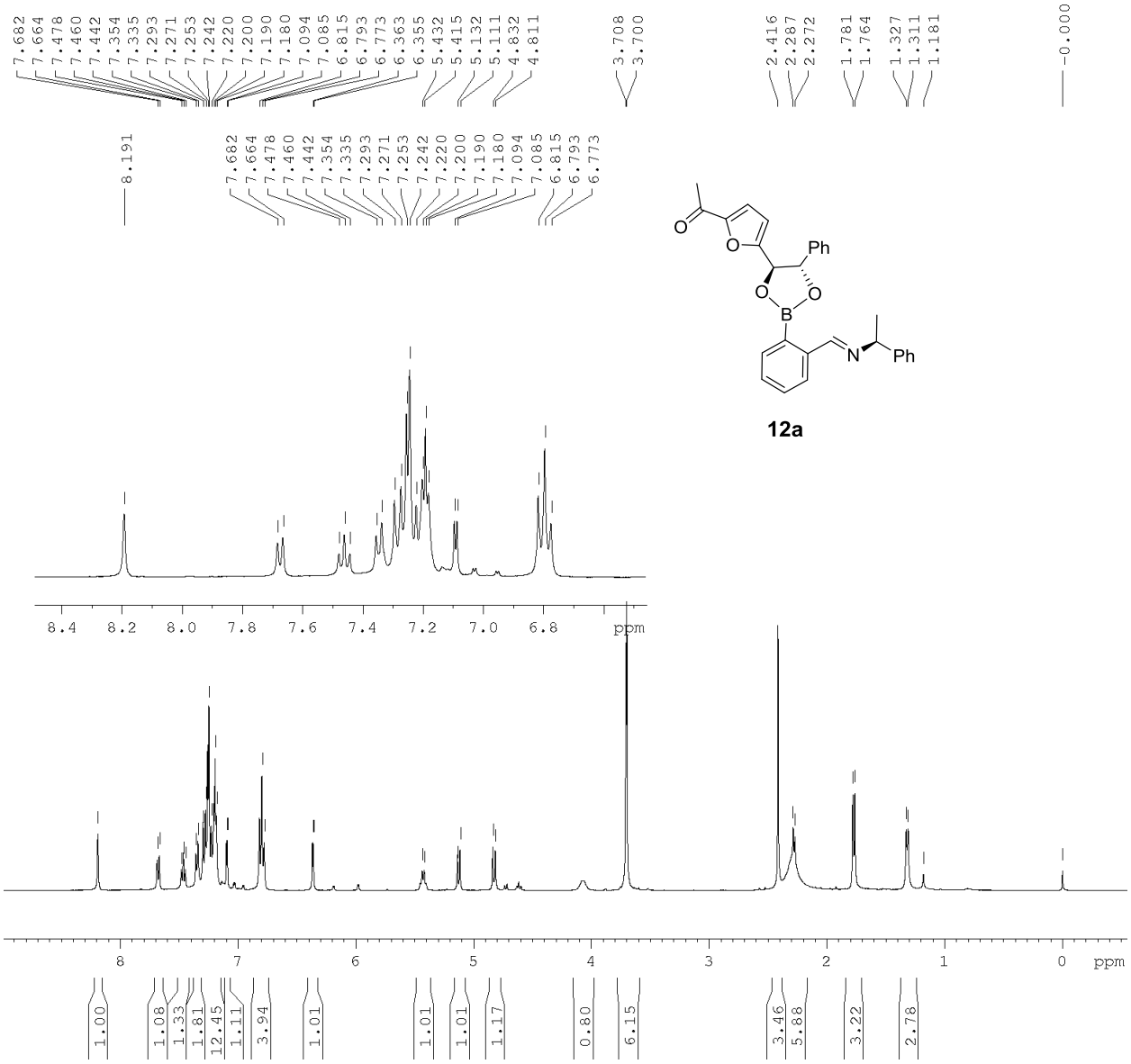
11a: Boronate of 7a



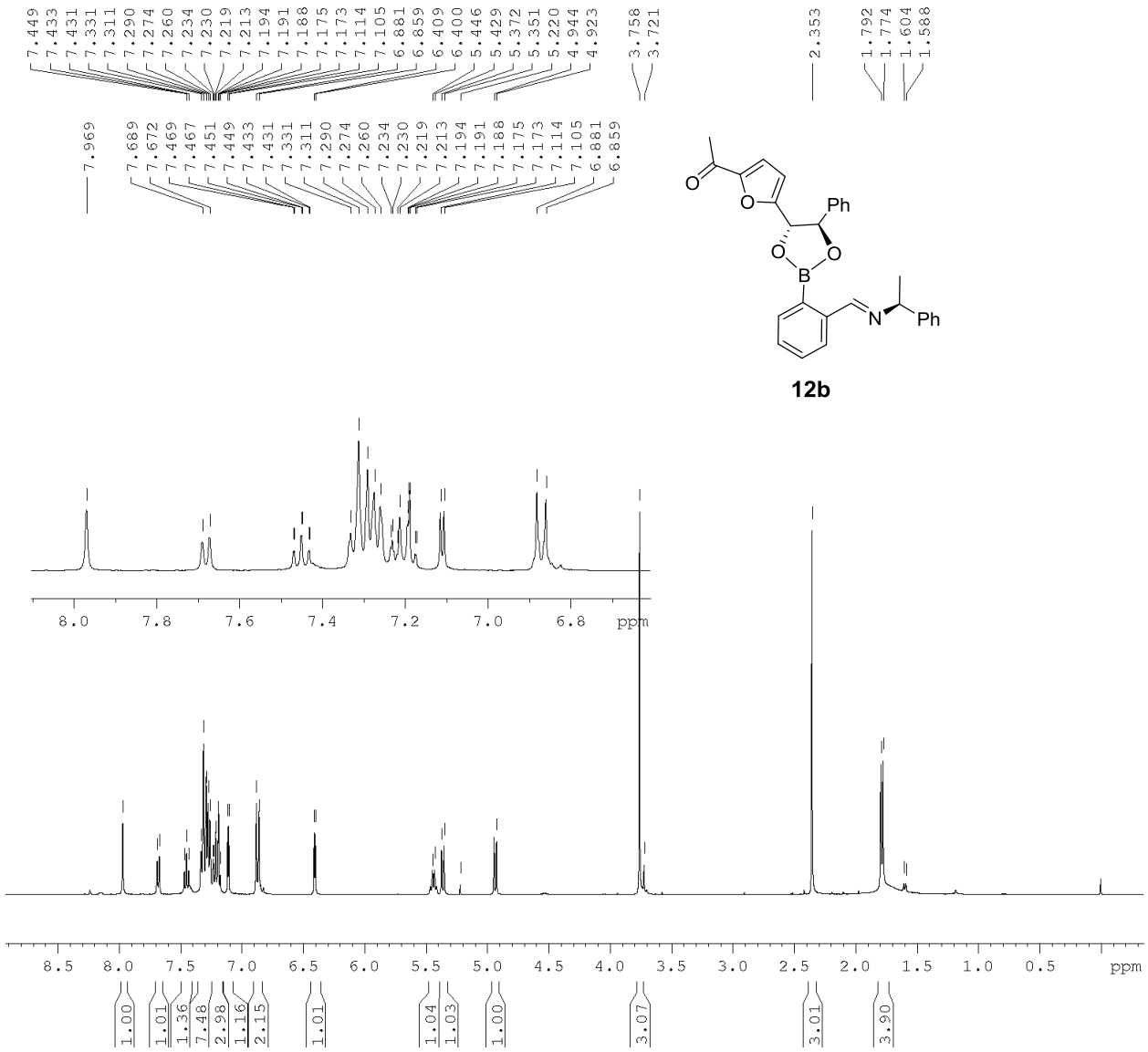
11b



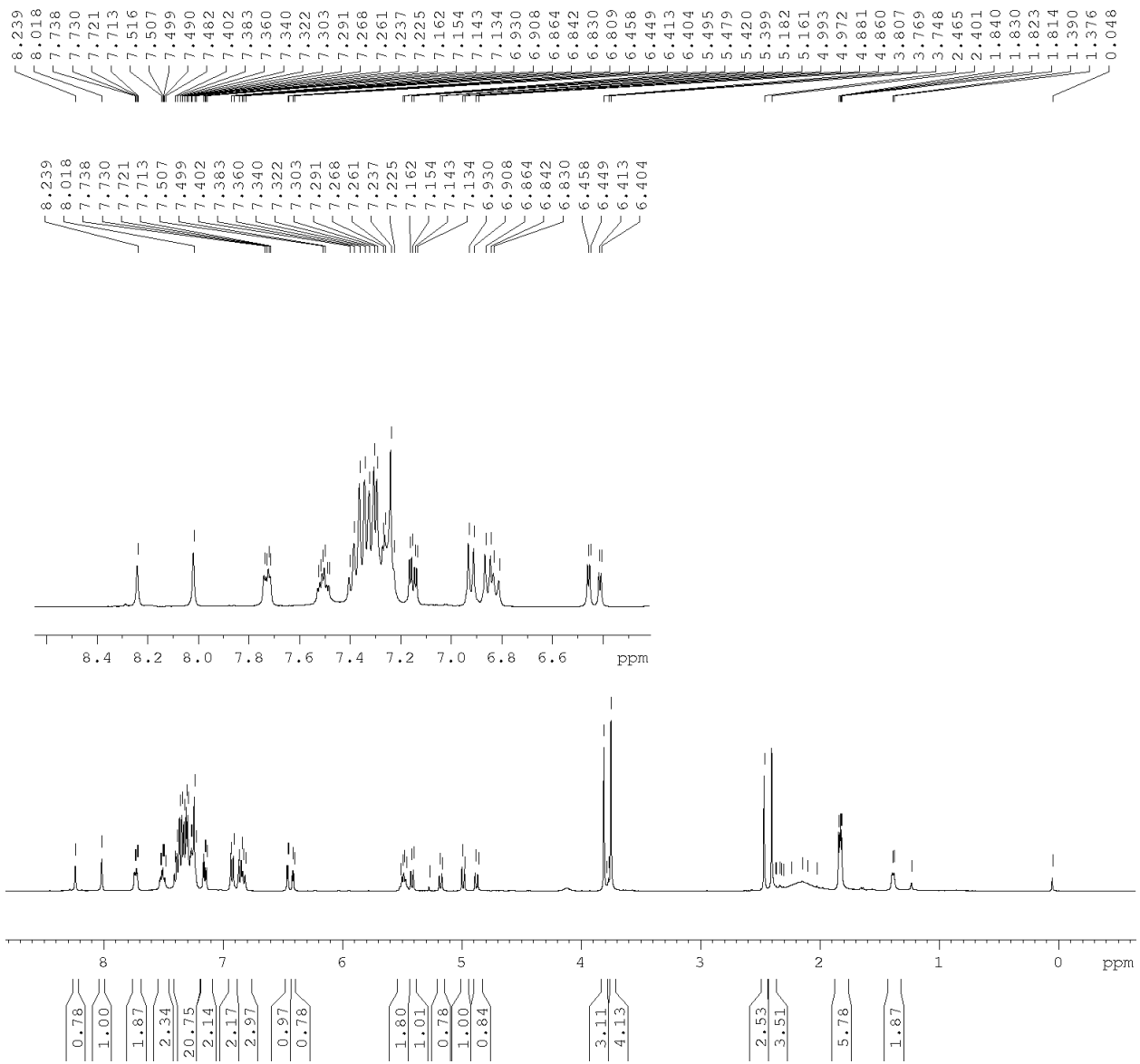
^{1}H NMR spectra of compound **12a** ($CDCl_3$, 400 MHz):



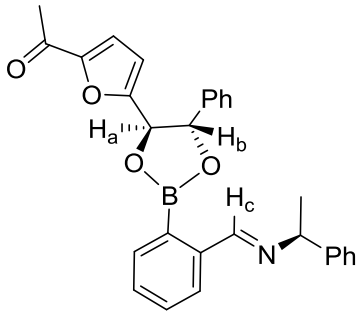
^{1}H NMR spectra of compound **12b** ($CDCl_3$, 400 MHz):



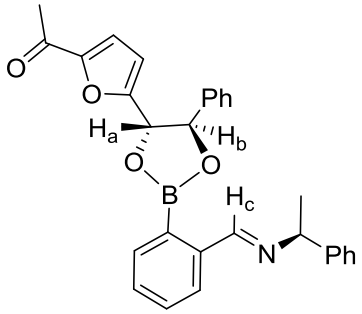
^{1}H NMR spectra of compound **12a+12b** (mixture, $CDCl_3$, 400 MHz):



Determination of enantiomeric excess of **9a** and **9b** via boronates **12a** and **12b**.



12a



12b