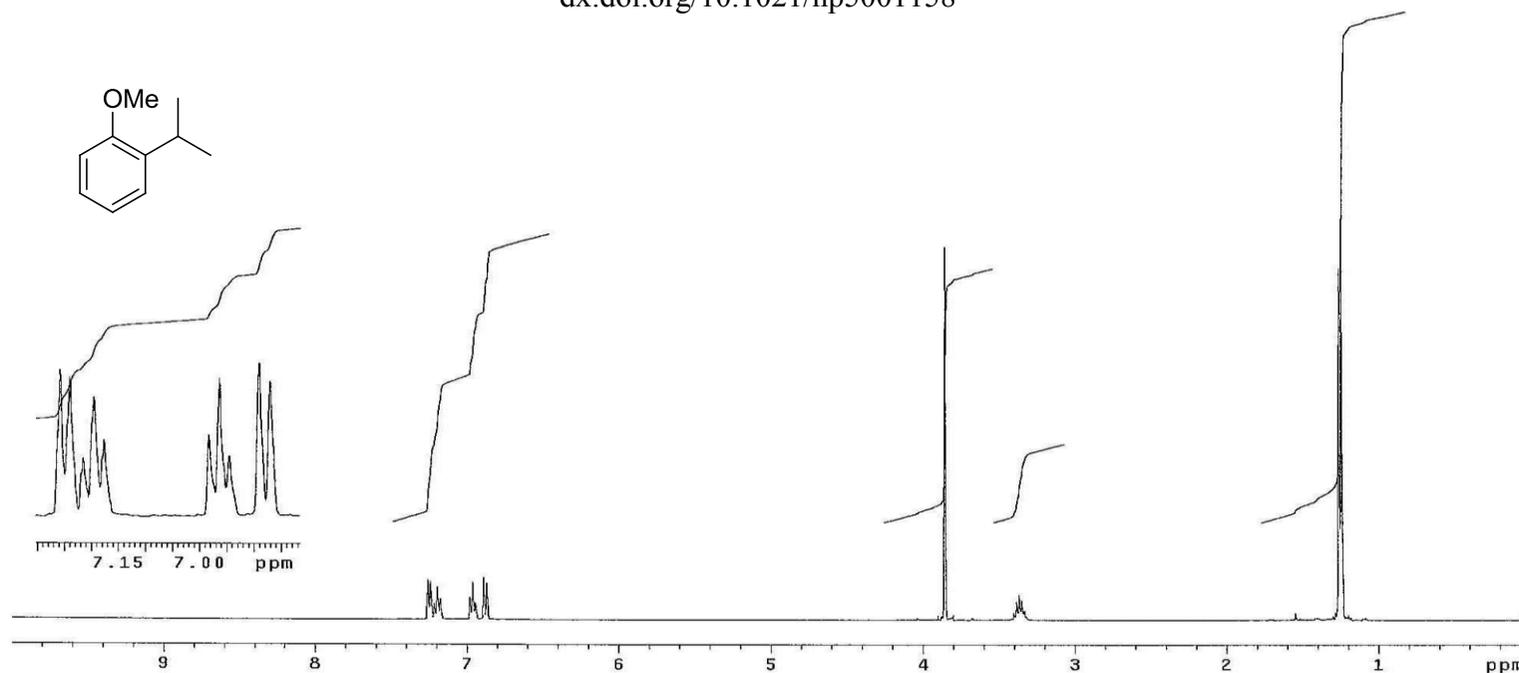


## Total Syntheses of Multicaulins *via* Oxidative Photocyclization of Stilbenes

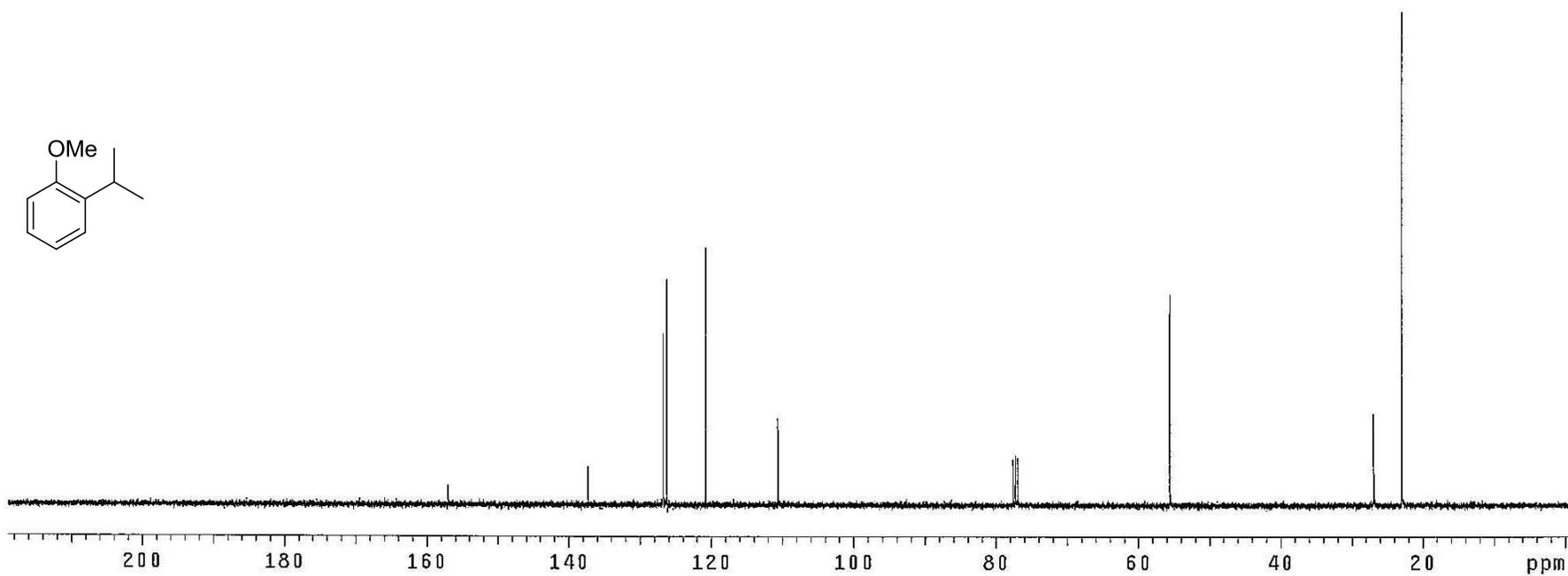
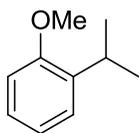
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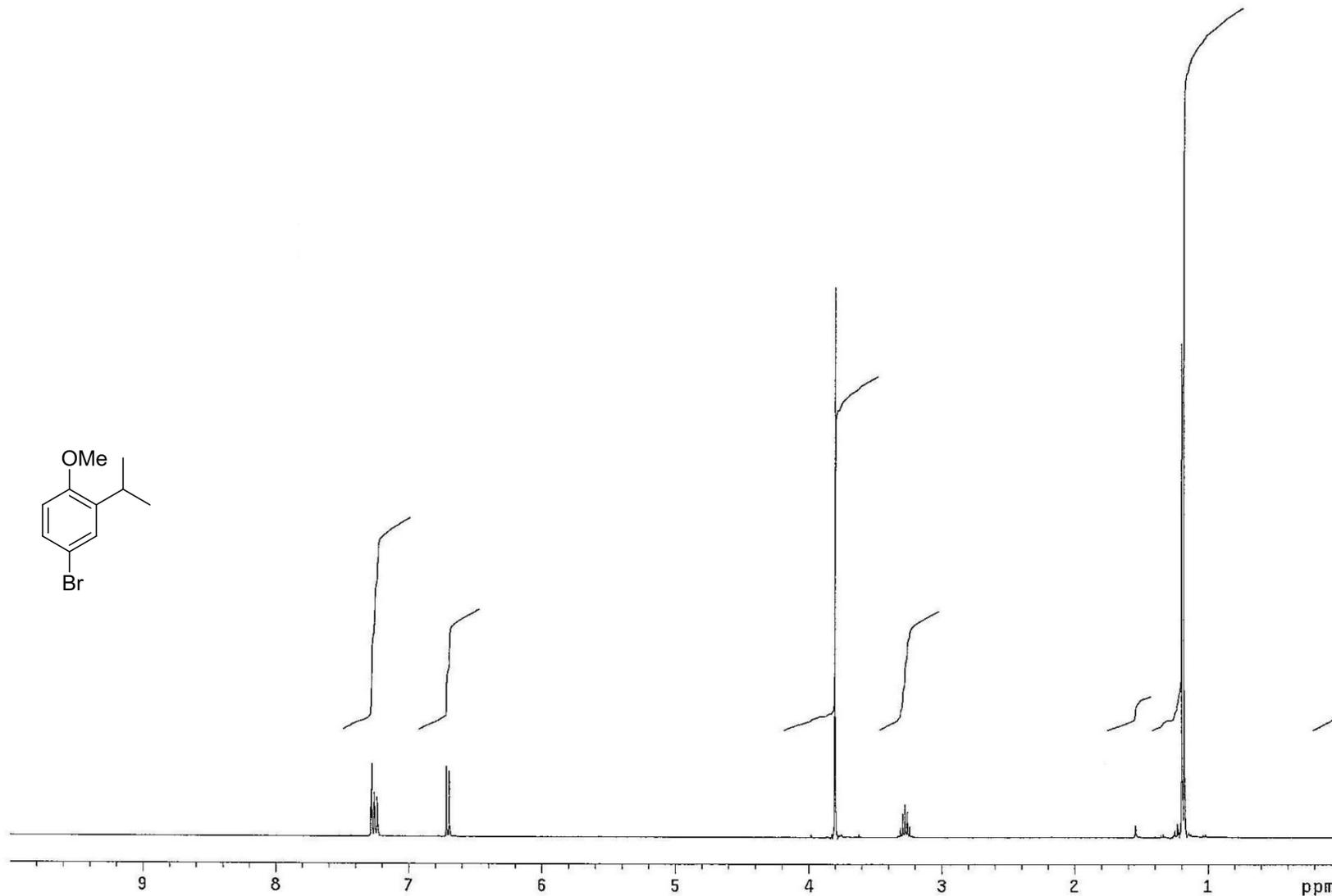
[dx.doi.org/10.1021/np5001158](https://doi.org/10.1021/np5001158)



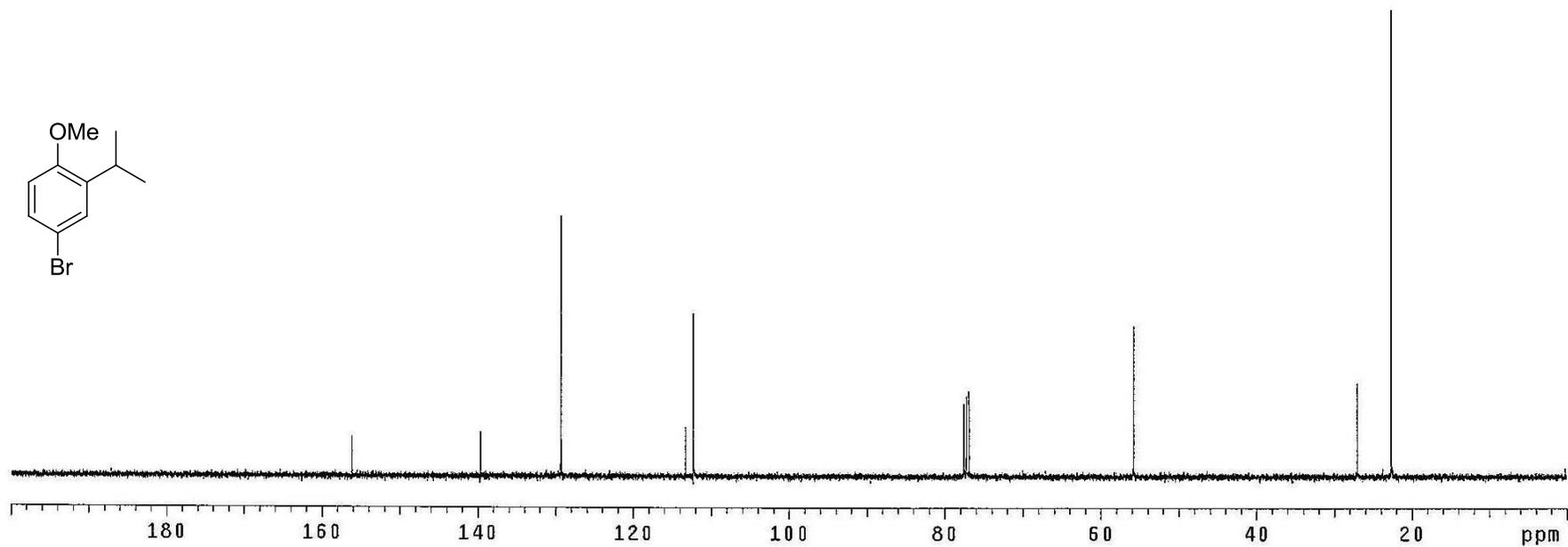
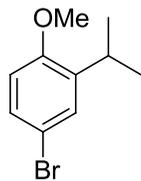
2-isopropylanisole (**10**) 400 MHz <sup>1</sup>H NMR Spectrum (CDCl<sub>3</sub>): δ 7.35 (dd, 1 H, H-3,  $J_{3,4} = 7.5$  Hz,  $J_{3,5} = 1.7$  Hz); 7.29 (dt, 1 H, H-5,  $J_{5,6} = J_{4,5} = 8.0$  Hz,  $J_{3,5} = 1.7$  Hz); 7.06 (dt, 1 H, H-4,  $J_{4,5} = J_{5,6} = 8.0$  Hz,  $J_{4,6} = 1.1$  Hz), 6.96 (dd, 1 H, H-6,  $J_{5,6} = 8.0$  Hz,  $J_{4,6} = 1.1$  Hz); 3.93 (s, 3H, OCH<sub>3</sub>); 3.50 (septet, 1H, CHMe<sub>2</sub>,  $J = 7.0$  Hz); 1.36 (d, 6H, CHMe<sub>2</sub>,  $J = 7.0$  Hz).



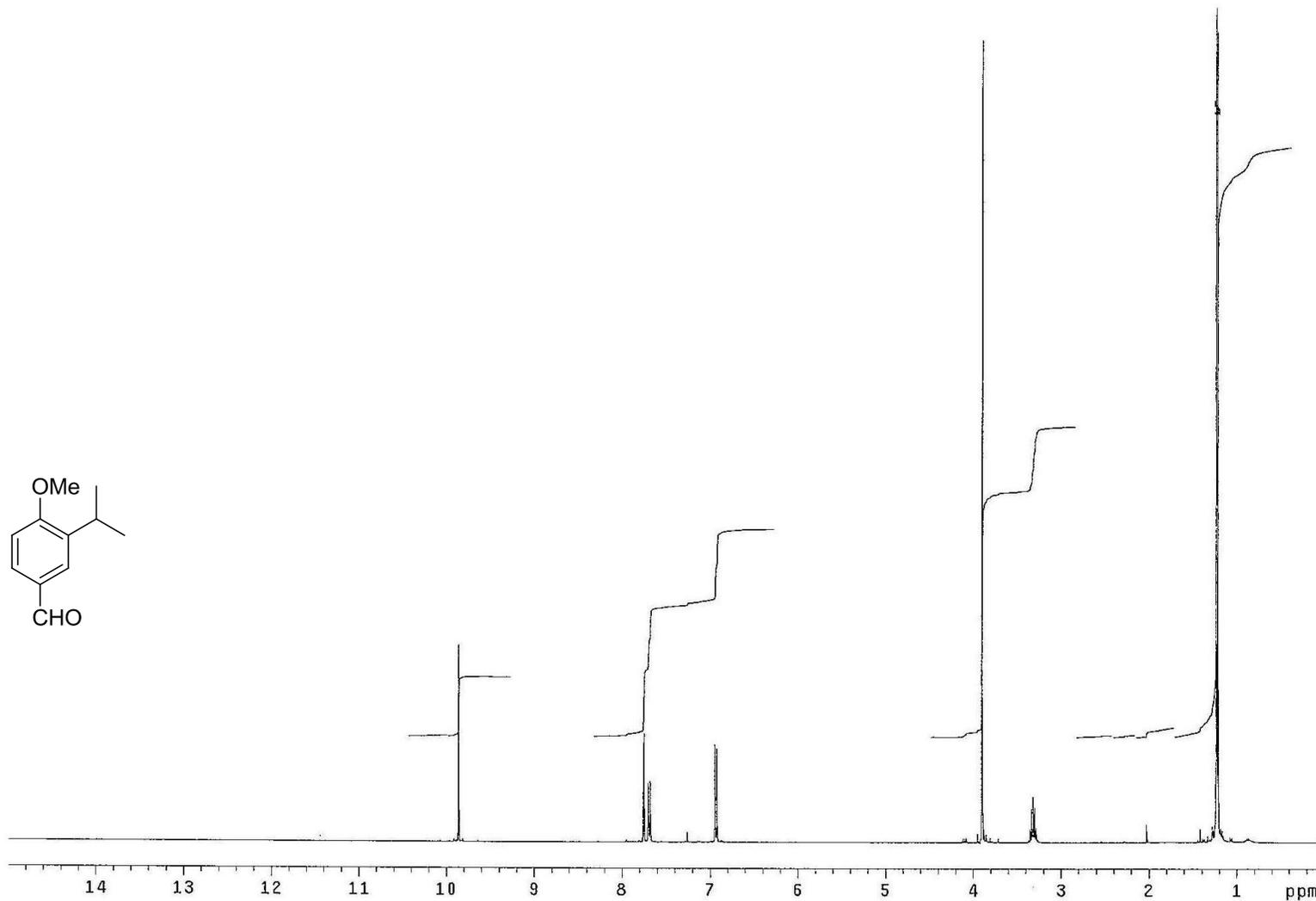
2-isopropylanisole (**10**) 100 MHz  $^{13}\text{C}$  NMR Spectrum ( $\text{CDCl}_3$ ):  $\delta$  156.7 (C-1); 136.9 (C-2); 126.5 (C-3); 125.9 (C-5); 120.5 (C-4); 110.2 (C-6); 55.2 (OMe); 26.6 ( $\underline{\text{C}}\text{HMe}_2$ ); 22.6 ( $\text{CH}\underline{\text{M}}\text{e}_2$ ).



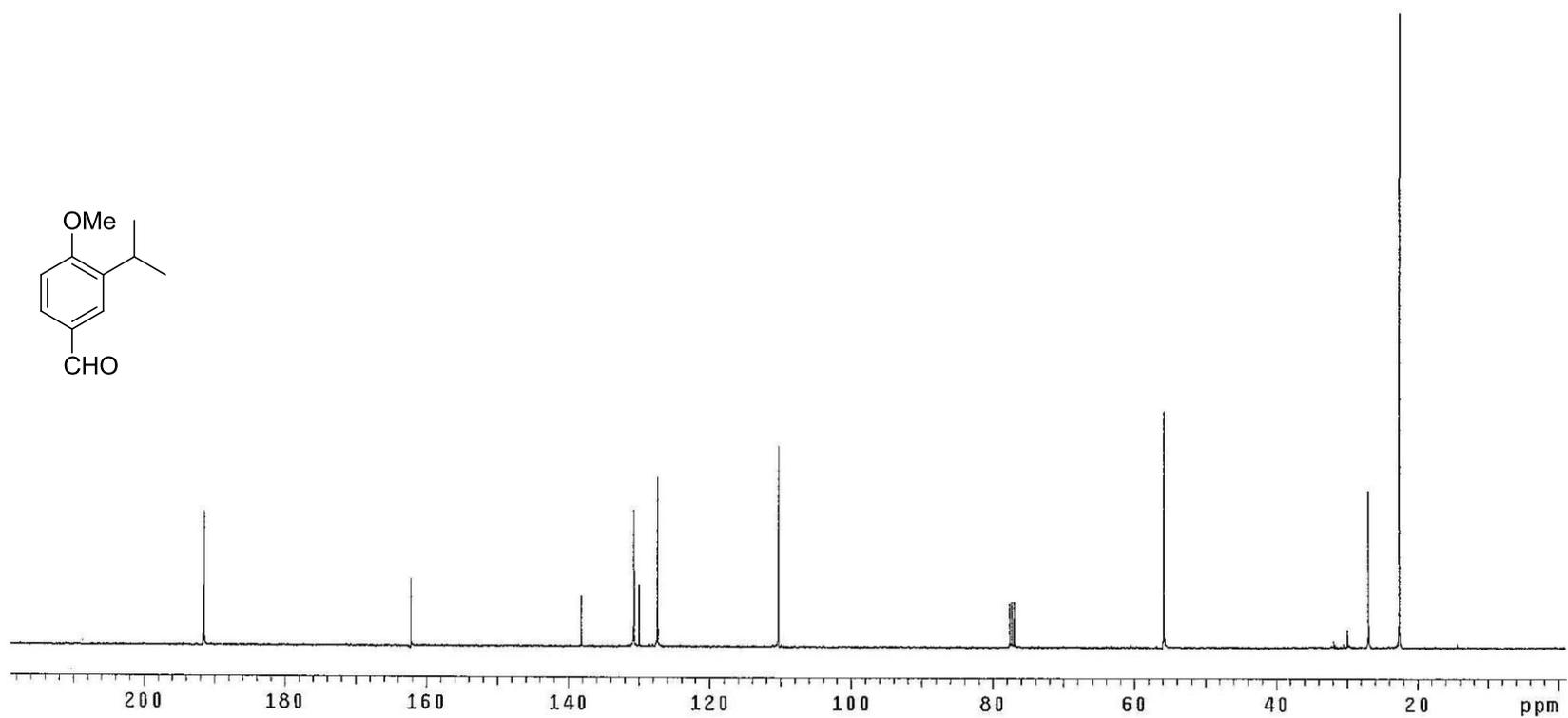
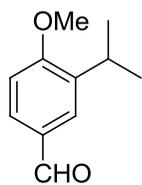
4-bromo-2-isopropylanisole (**11**) 400 MHz <sup>1</sup>H-NMR Spectrum (CDCl<sub>3</sub>): δ 7.34 (d, 1 H, H-3,  $J_{3,5} = 2.4$  Hz); 7.29 (dd, 1H, H-5,  $J_{5,6} = 8.5$  Hz,  $J_{3,5} = 2.4$  Hz); 6.73 (d, 1H, H-6,  $J_{5,6} = 8.5$  Hz); 3.83 (s, 3H, OCH<sub>3</sub>); 3.33 (septet, 1H, CHMe<sub>2</sub>,  $J = 6.9$  Hz); 1.24 (d, 6H, CHMe<sub>2</sub>,  $J = 6.9$  Hz).



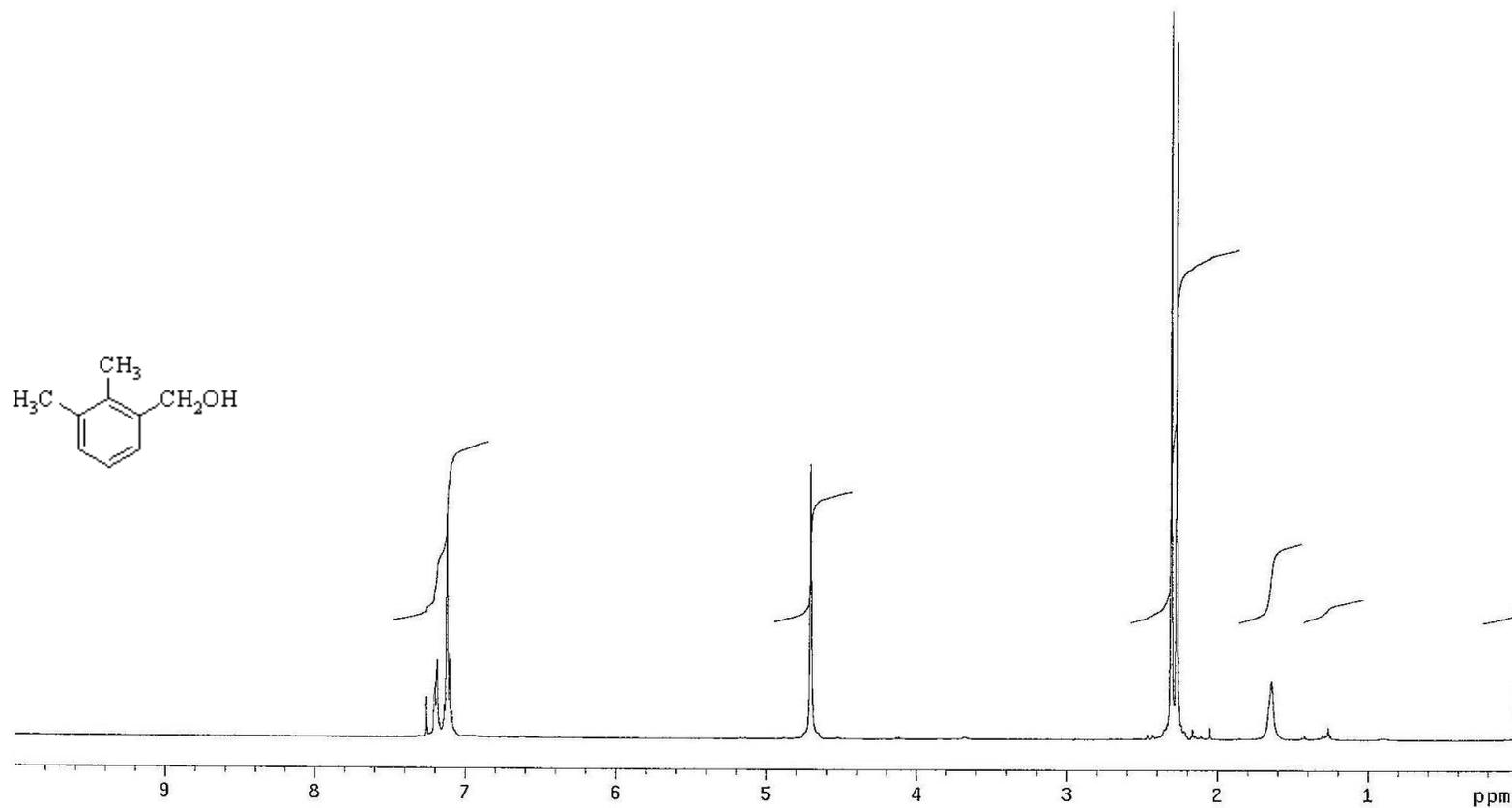
4-bromo-2-isopropylanisole (**11**) 100 MHz  $^{13}\text{C-NMR}$  Spectrum ( $\text{CDCl}_3$ ):  $\delta$  155.9 (C-1); 139.4 (C-2); 129.1 (C-3); 129.0 (C-5); 113.0 (C-4); 112.0 (C-6); 55.4 ( $\text{OCH}_3$ ); 26.8 ( $\text{CHMe}_2$ ); 22.4 ( $\text{CHMe}_2$ ).



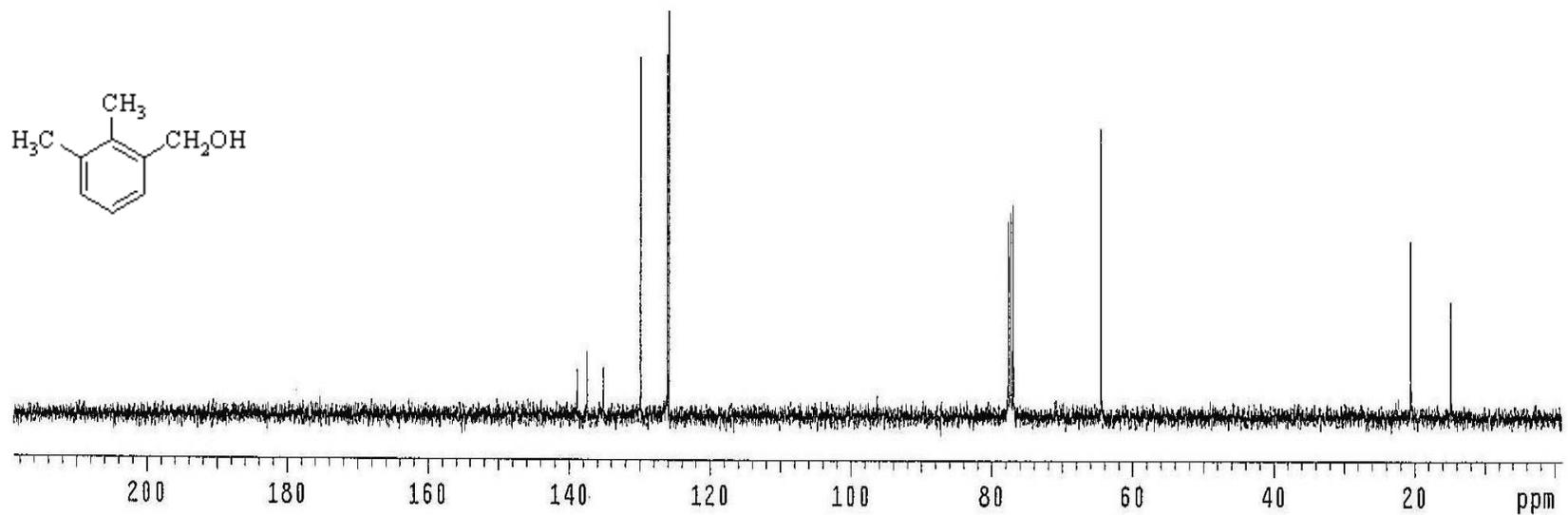
**3-isopropyl-4-methoxybenzaldehyde (12)** 400 MHz  $^1\text{H}$ -NMR Spectrum ( $\text{CDCl}_3$ ):  $\delta$  9.87 (s, 1 H, CHO); 7.75 (s, 1 H, H-2); 7.69 (d, 1 H, H-6,  $J = 8.2$  Hz); 6.94 (d, 1 H, H-5,  $J = 8.2$  Hz); 3.86 (s, 3 H,  $\text{OCH}_3$ ); 3.32 (septet, 1 H,  $\text{CHMe}_2$ ,  $J = 6.9$  Hz); 1.22 (d, 6 H,  $\text{CHMe}_2$ ,  $J = 6.9$  Hz).



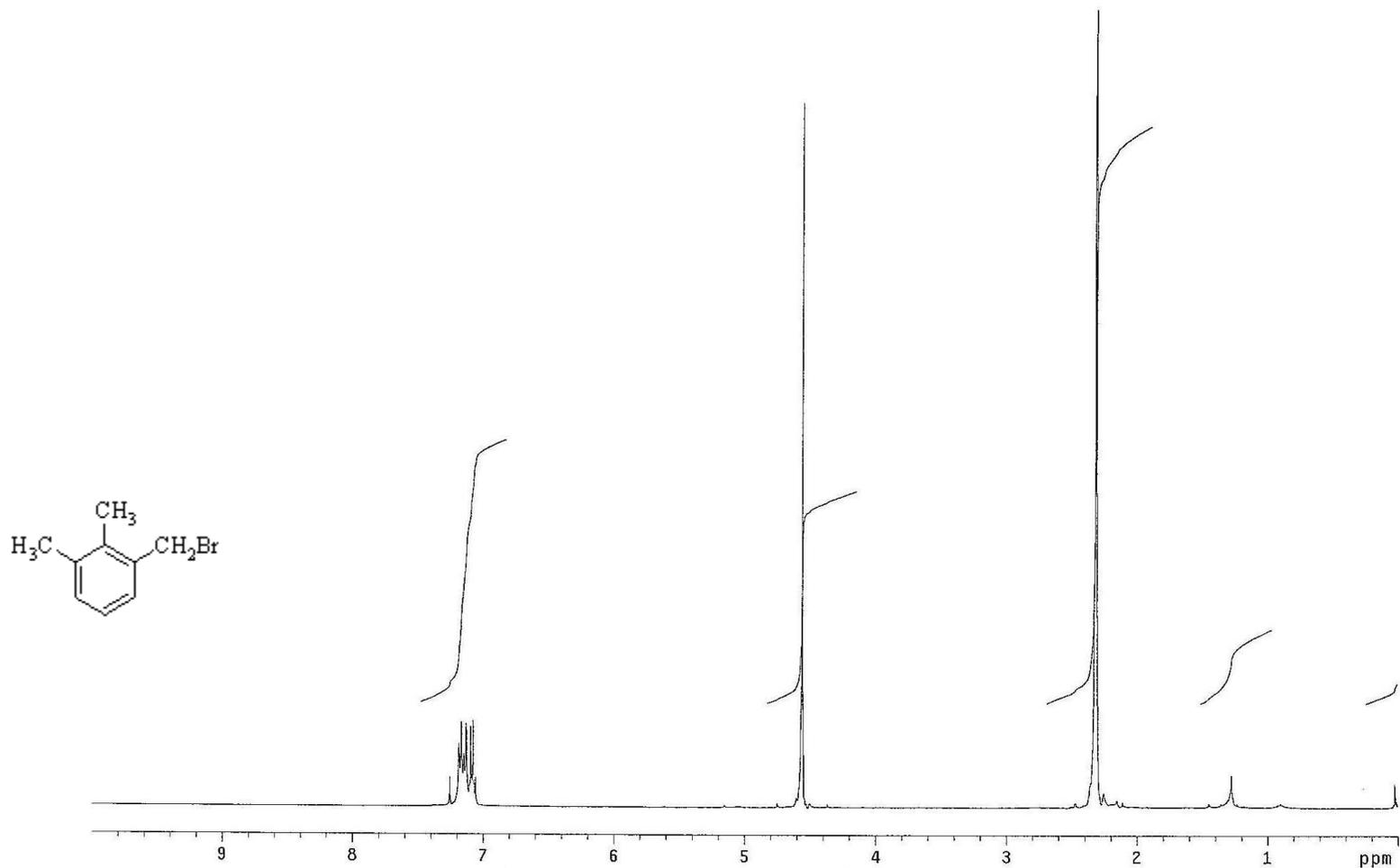
**3-isopropyl-4-methoxybenzaldehyde (12)** 100 MHz <sup>13</sup>C-NMR Spectrum (CDCl<sub>3</sub>): δ 191.5 (CHO); 162.2 (C-4); 138.2 (C-1); 130.7 (C-2<sup>a</sup>); 129.9 (C-3); 127.4 (C-6<sup>a</sup>); 110.0 (C-5); 55.8 (OCH<sub>3</sub>); 26.9 (CHMe<sub>2</sub>); 22.6 (CHMe<sub>2</sub>).



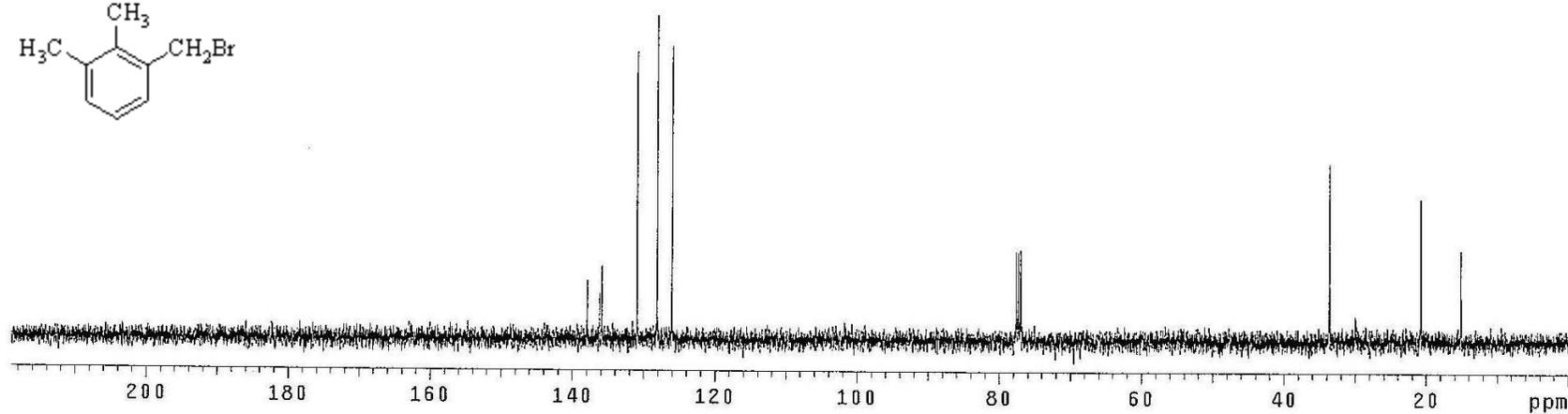
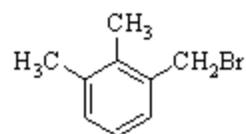
**2,3-dimethylbenzyl alcohol (14)** 400 MHz <sup>1</sup>H-NMR Spectrum (CDCl<sub>3</sub>): δ 7.21 ( dd, 1 H, *J* = 6.4 Hz, *J* = 2.4 Hz); 7.18-7.10 (m, 2 H); 4.64 (s, CH<sub>2</sub>OH); 2.34 (s, 3 H, CH<sub>3</sub>); 2.27 (s, 3 H, CH<sub>3</sub>).



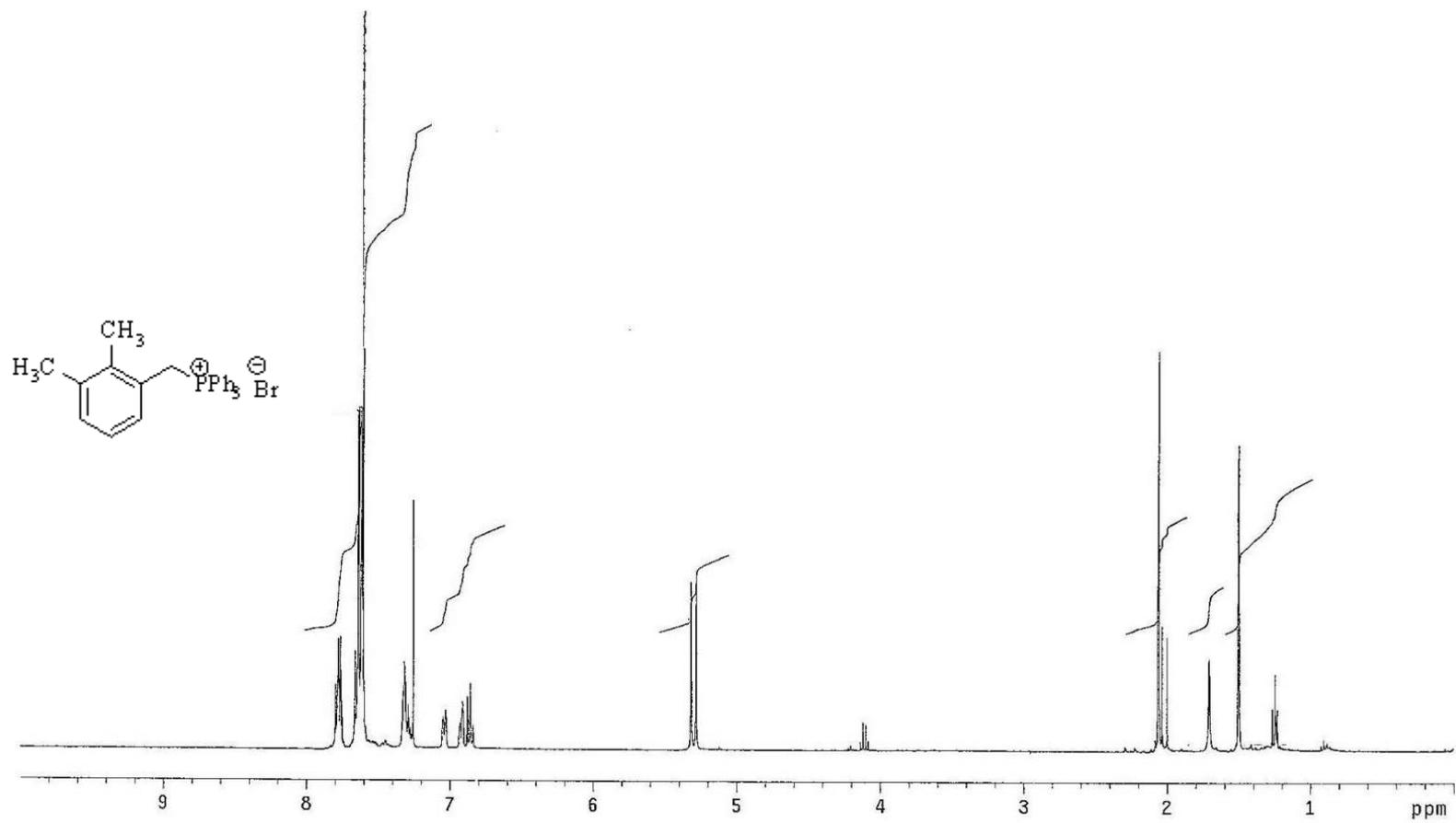
**2,3-dimethylbenzyl alcohol (14)** 100 MHz <sup>13</sup>C-NMR Spectrum (CDCl<sub>3</sub>): <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 138.9; 137.3; 135.1; 129.8; 126.0; 125.8; 64.2 (CH<sub>2</sub>OH); 20.6 (CH<sub>3</sub>); 14.8 (CH<sub>3</sub>).



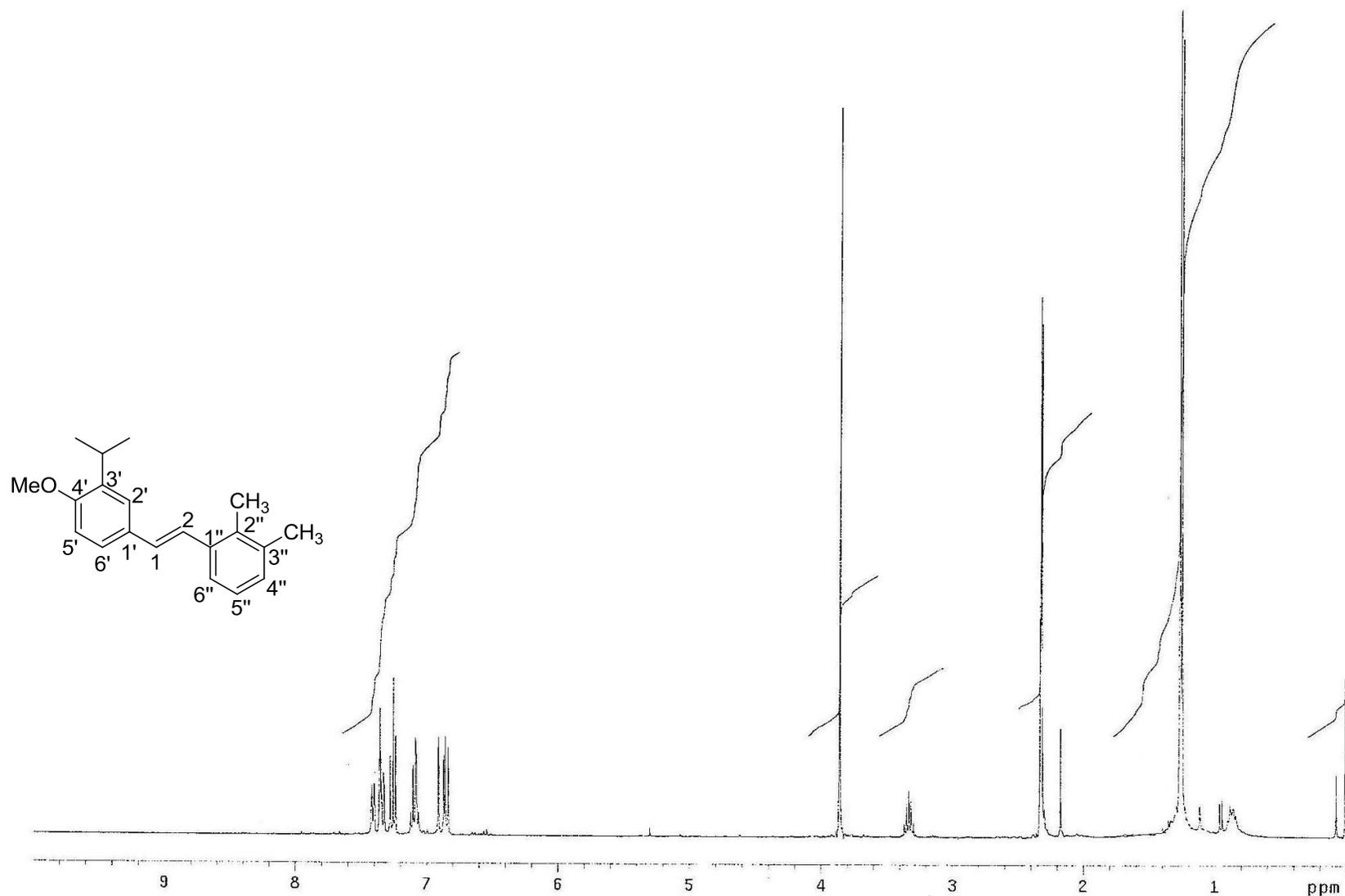
**2,3-dimethylbenzyl bromide (15)** 400 MHz  $^1\text{H-NMR}$  Spectrum ( $\text{CDCl}_3$ ):  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.16 (bd, 1 H,  $J=7.5$  Hz); 7.13 (bd, 1 H,  $J=6.6$  Hz); 7.07 (quasi t, 1 H,  $J=7.7$  Hz); 4.55 (s, 2 H,  $\text{CH}_2\text{Br}$ ); 2.30 (s, 6 H,  $2 \times \text{CH}_3$ ).



**2,3-dimethylbenzyl bromide (15)** 100 MHz <sup>13</sup>C-NMR Spectrum (CDCl<sub>3</sub>): <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 137.9; 136.1; 135.9; 130.9; 128.1; 126.0; 33.6 (CH<sub>2</sub>Br); 20.7 (CH<sub>3</sub>); 15.1 (CH<sub>3</sub>).

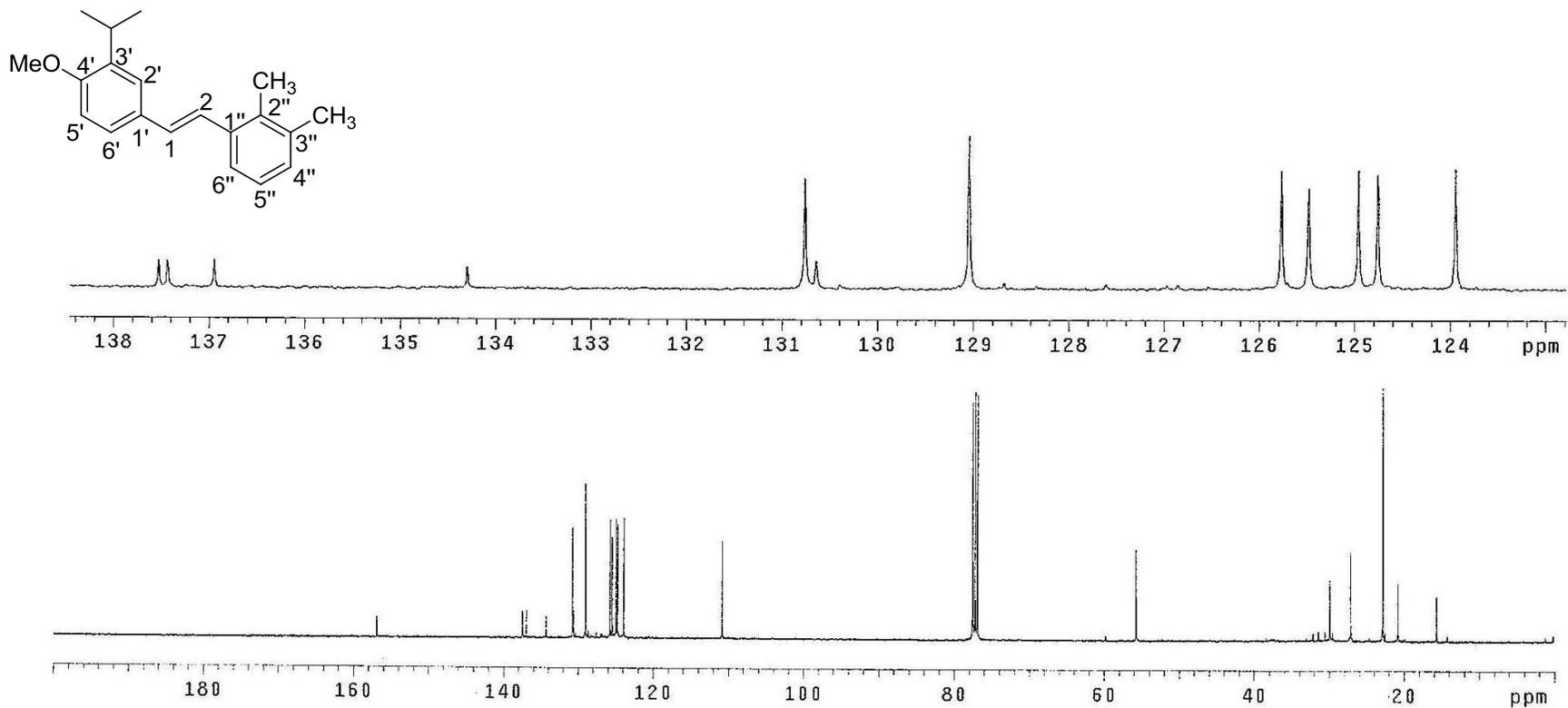


(2,3-dimethyl)triphenylphosphonium bromide. 400 MHz  $^1\text{H-NMR}$  Spectrum ( $\text{CDCl}_3$ )



**(E)-1-(3-isopropyl-4-methoxyphenyl)-2-(2,3-dimethylphenyl)ethene (16)** 400 MHz <sup>1</sup>H-NMR Spectrum (CDCl<sub>3</sub>): δ 7.41

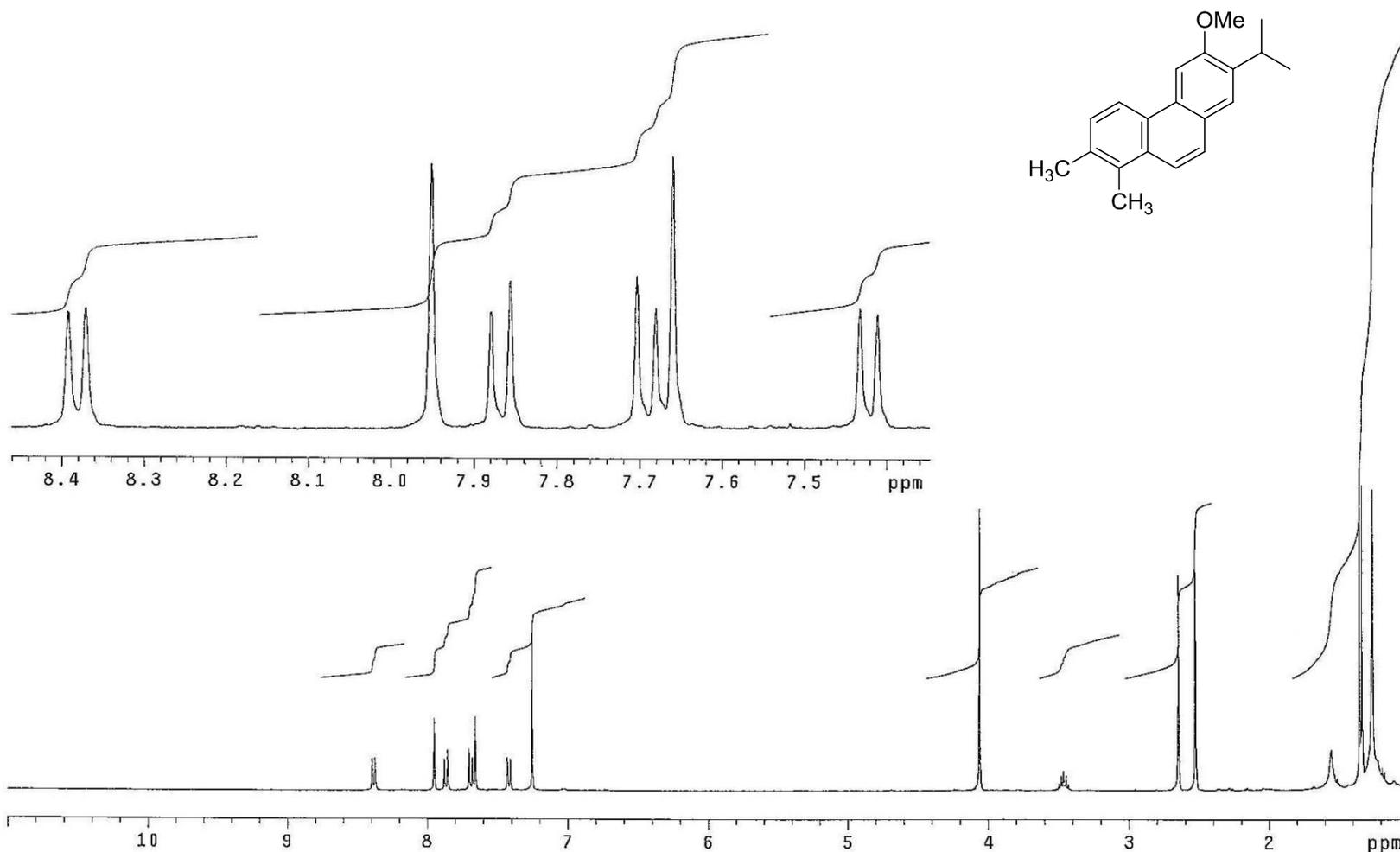
(bd, 1 H, H-6'', J<sub>5'',6''</sub> = 7.0 Hz); 7.36-7.32 (m, 2 H, H-2', H-5''); 7.26 (d, 1 H, H-2, J<sub>1,2</sub> = 16.1 Hz); 7.11 (d, 1 H, H-5', J<sub>5',6'</sub> = 7.3 Hz); 7.07 (bd, 1 H, H-6'); 6.89 (d, 1 H, H-1, J<sub>1,2</sub> = 16.1 Hz); 6.85 (d, 1 H, H-4'', J<sub>4'',5''</sub> = 8.1 Hz); 3.86 (s, 3 H, OCH<sub>3</sub>); 3.33 (septet, 1 H, CHMe<sub>2</sub>, J = 7.0 Hz); 2.33 (s, 3 H, CH<sub>3</sub>); 2.32 (s, 3 H, CH<sub>3</sub>); 1.25 (d, 6 H, CHMe<sub>2</sub>, J = 7.0 Hz).



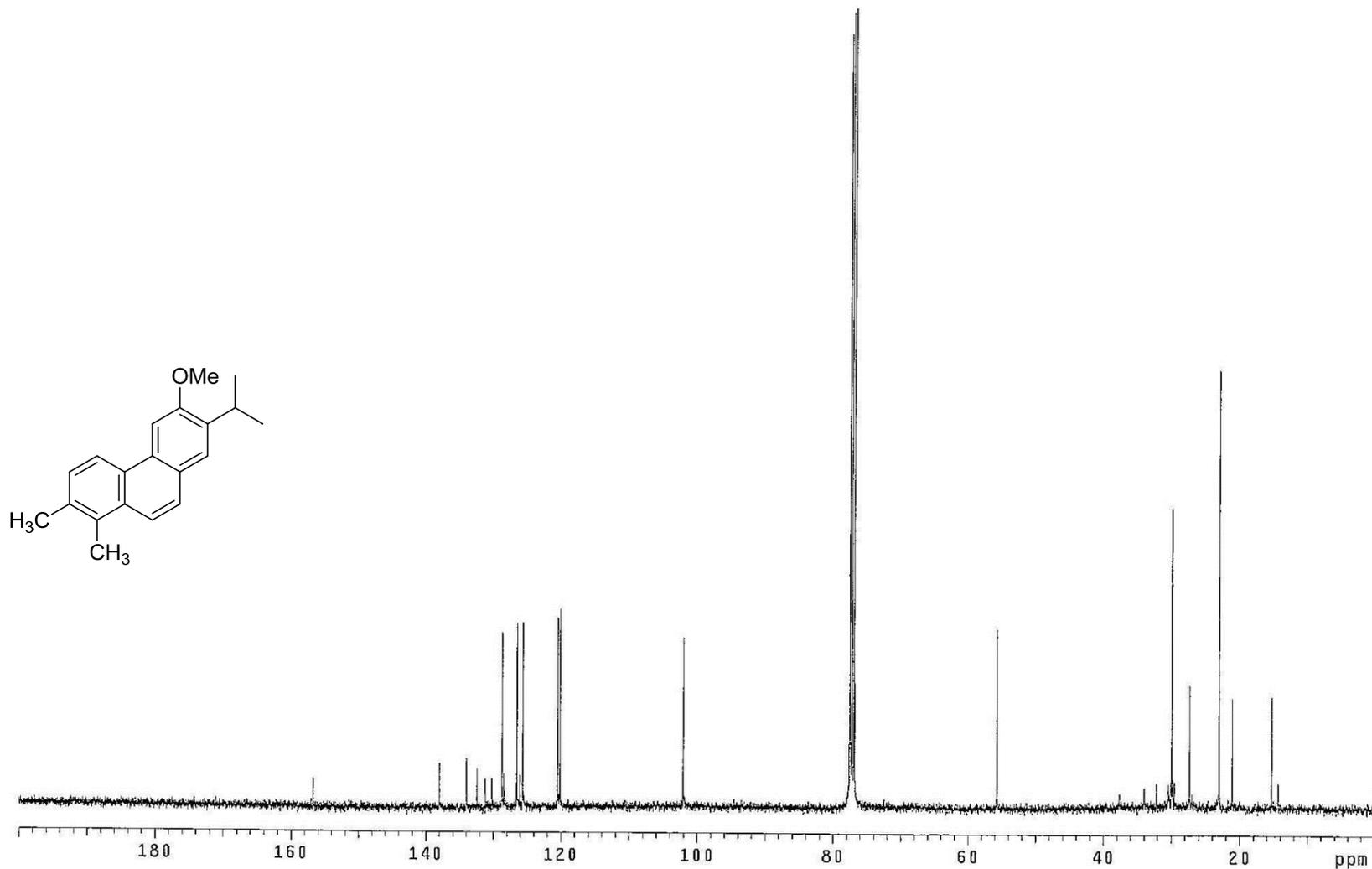
**(E)-1-(3-isopropyl-4-methoxyphenyl)-2-(2,3-dimethylphenyl)ethene (16)** 100 MHz <sup>13</sup>C-NMR Spectrum (CDCl<sub>3</sub>): δ 156.9

(C-4'); 137.5 (s); 137.4 (s); 136.9 (s); 134.3 (s); 130.8(d); 130.6 (s); 129.0 (d); 125.8 (d); 125.5 (d); 125.0 (d); 124.0 (d);

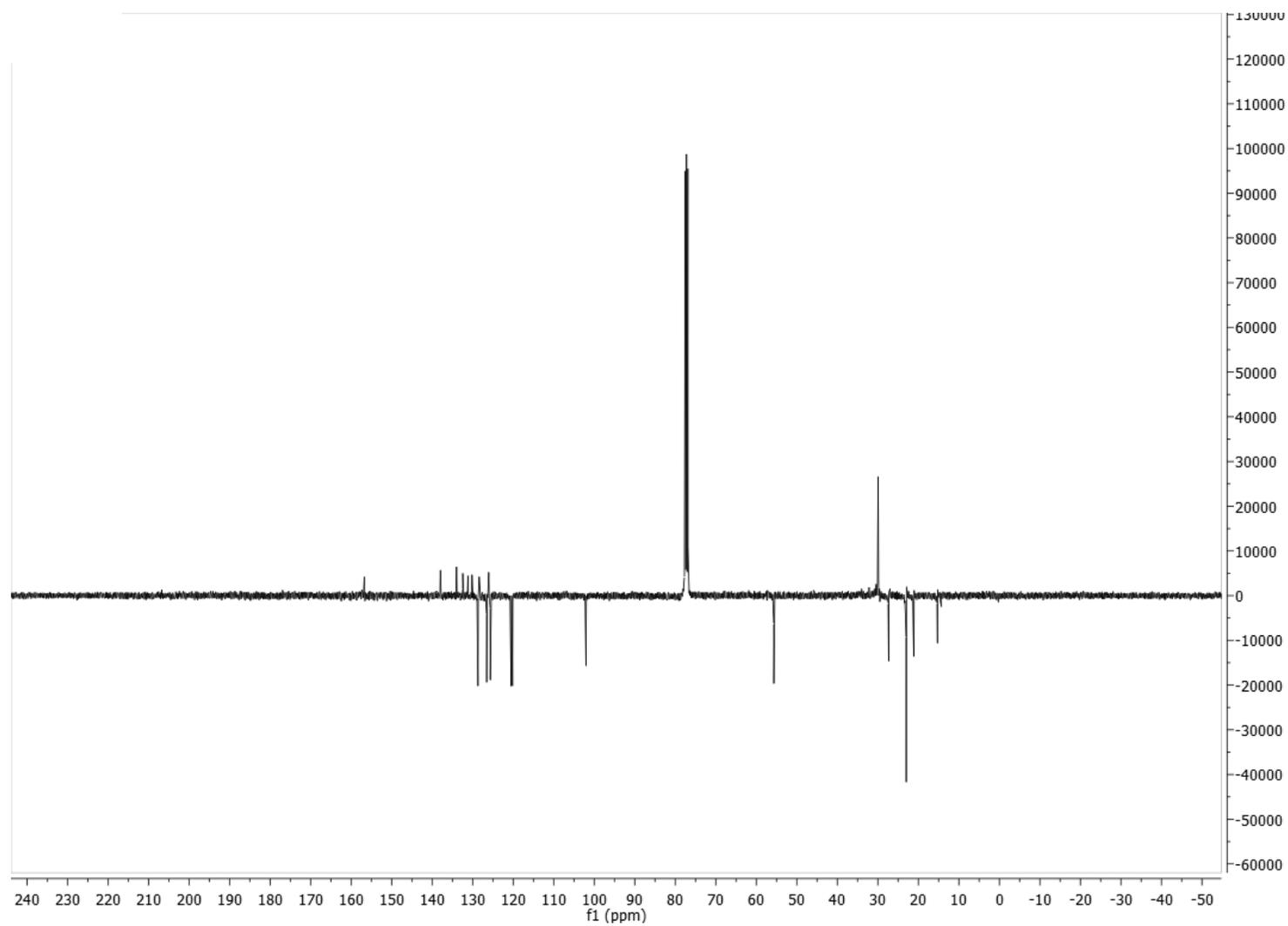
110.9 (d); 55.7 (OCH<sub>3</sub>); 27.1 (CHMe<sub>2</sub>); 22.8 (CHMe<sub>2</sub>); 20.9 (CH<sub>3</sub>); 15.7 (CH<sub>3</sub>).



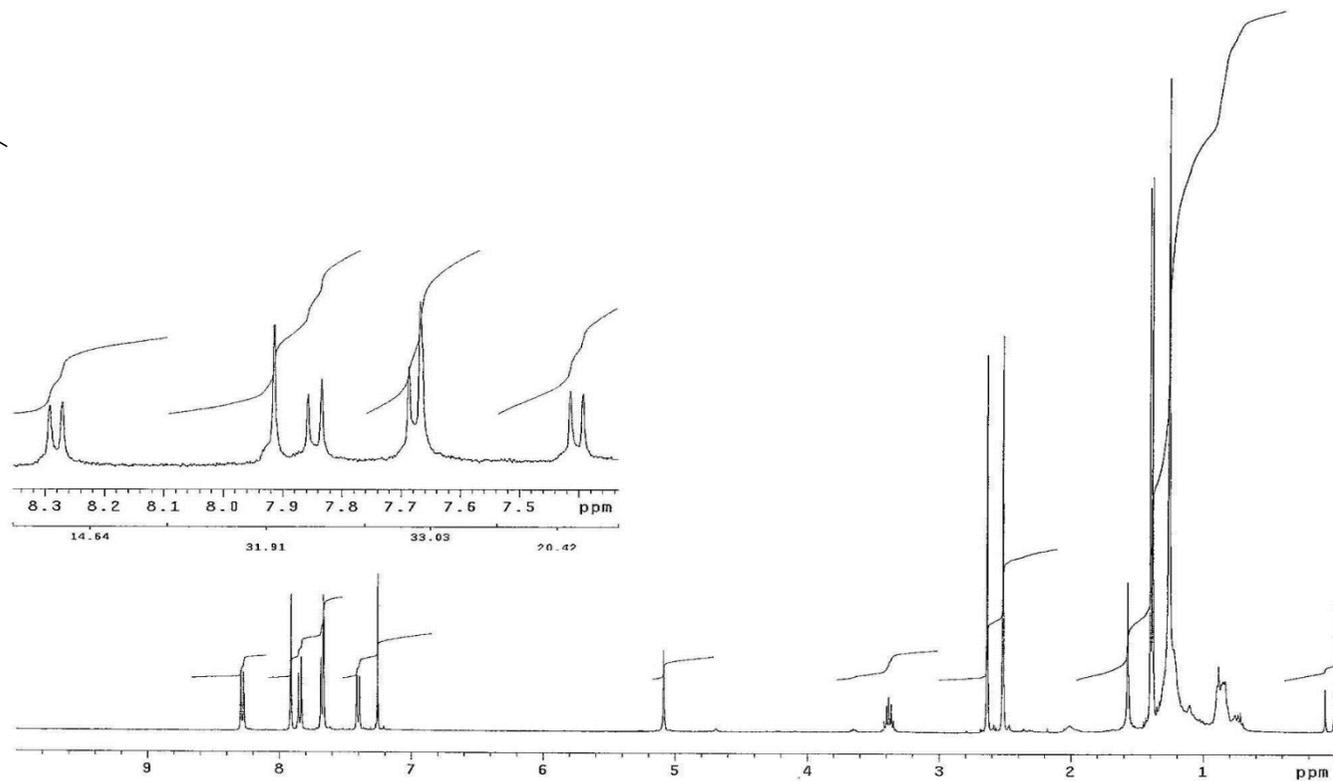
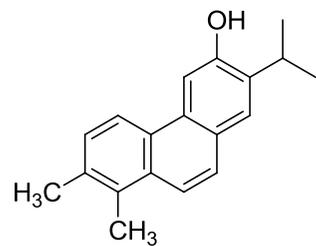
**7-Isopropyl-6-methoxy-1,2-dimethylphenanthrene (Multicaulin) (1)** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.38 (d, 1 H, H-4, J = 8.8 Hz); 7.95 (s, 1 H, H-5); 7.86 (d, 1 H, H-10, J = 9.2 Hz); 7.69 (d, 1 H, H-9, J = 9.2 Hz); 7.66 (s, 1 H, H-8); 7.42 (d, 1 H, H-3, J = 8.8 Hz); 4.06 (s, 3 H, OCH<sub>3</sub>); 3.46 (septet, 1 H, CHMe<sub>2</sub>, J = 7.0 Hz); 2.65 (s, 3H, CH<sub>3</sub>); 2.53 (s, 3 H, CH<sub>3</sub>); 1.33 (d, 6 H, CHMe<sub>2</sub>, J = 7.0 Hz).



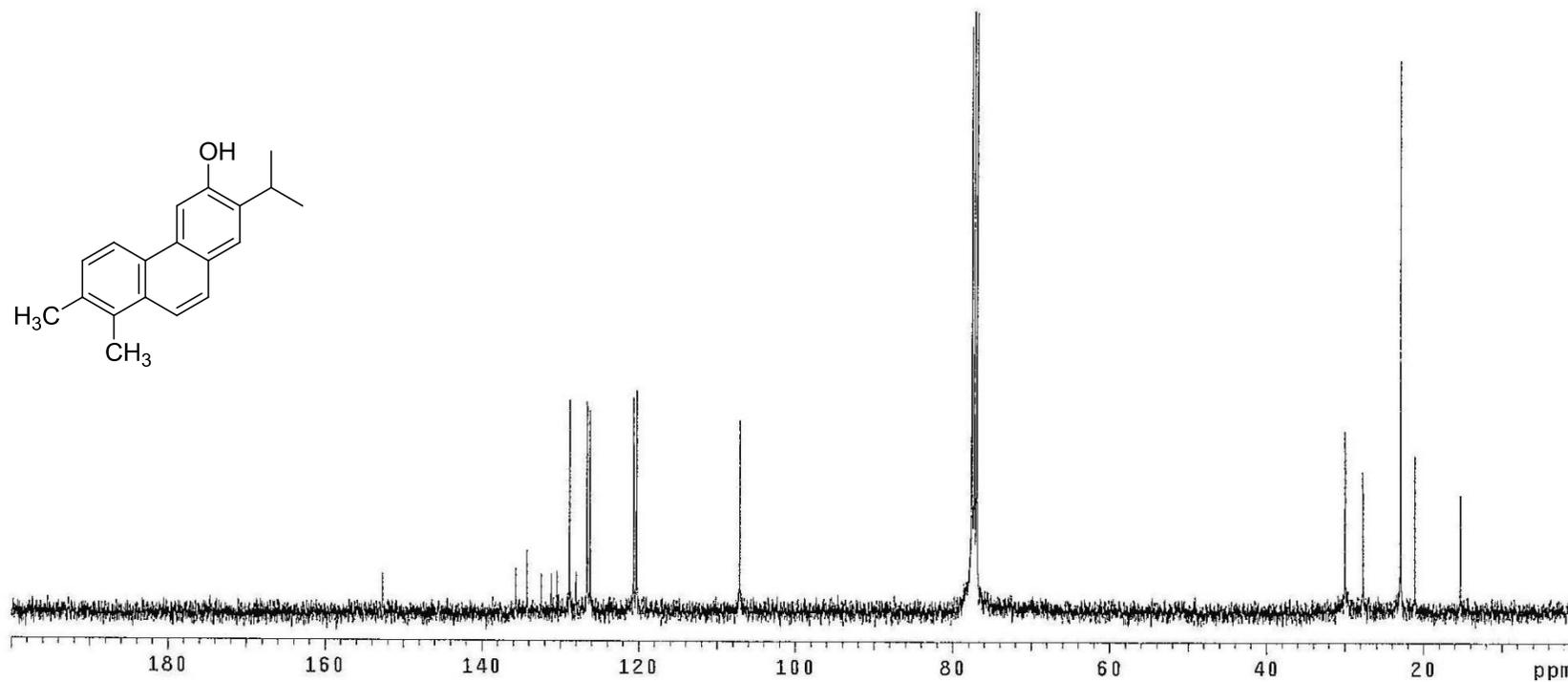
**7-Isopropyl-6-methoxy-1,2-dimethylphenanthrene (Multicaulin) (1)** 100 MHz  $^{13}\text{C}$ -NMR Spectrum ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.8 (C-6); 138.0 (s); 134.0 (s); 132.4 (s); 131.1 (s); 130.2 (s); 128.7 (d); 128.4 (s); 126.5 (d); 126.0 (s); 125.6 (d); 120.5 (d); 120.2 (d); 102.0 (d); 55.6 ( $\text{OCH}_3$ ); 27.3 ( $\underline{\text{CHMe}}_2$ ); 23.0 ( $\text{CHMe}_2$ ); 21.1 ( $\text{CH}_3$ ); 15.3 ( $\text{CH}_3$ ).



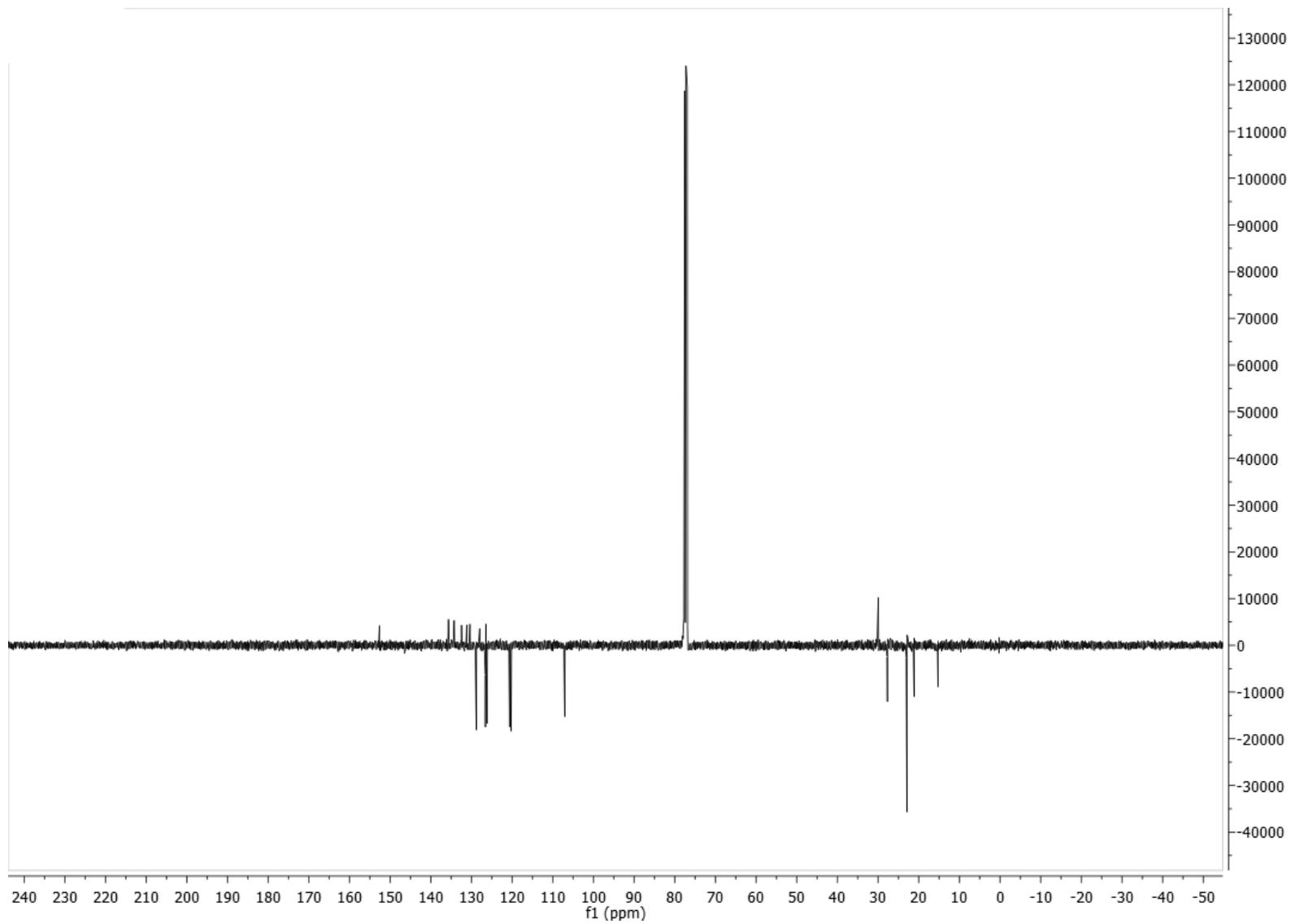
**7-Isopropyl-6-methoxy-1,2-dimethylphenanthrene (Multicaulin) (1) 100 MHz APT Spectrum (CDCl<sub>3</sub>)**



**7-Isopropyl-1,2-dimethylphenanthren-6-ol (*O*-demethylmulticaulin) (2)** 400 MHz  $^1\text{H-NMR}$  Spectrum ( $\text{CDCl}_3$ ):  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.28 (d, 1 H, H-4,  $J = 8.4$  Hz); 7.91 (s, 1 H, H-5); 7.84 (d, 1 H, H-10,  $J = 9.1$  Hz); 7.68 (d, 1 H, H-9,  $J = 9.1$  Hz); 7.67 (s, 1 H, H-8); 7.40 (d, 1 H, H-3,  $J = 8.4$  Hz); 3.38 (septet, 1 H,  $\underline{\text{CH}}\text{Me}_2$ ,  $J = 7.0$  Hz); 2.64 (s, 3 H,  $\text{CH}_3$ ); 2.52 (s, 3 H,  $\text{CH}_3$ ); 1.39 (d, 6 H,  $\text{CH}\underline{\text{Me}}_2$ ,  $J = 7.0$  Hz).



**7-Isopropyl-1,2-dimethylphenanthren-6-ol (*O*-demethylmulticaulin) (2)**  $^{13}\text{C}$ -NMR Spectrum ( $\text{CDCl}_3$ ):  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.6 (s); 135.6 (s); 134.2 (s); 132.4 (s); 131.1 (s); 130.4 (s); 128.8 (d); 128.0 (s); 126.5 (d); 126.5 (s); 126.2 (d); 120.6 (d); 120.2 (d); 107.1 (d); 27.7 ( $\text{CHMe}_2$ ); 22.7 ( $\text{CHMe}_2$ ); 21.1 ( $\text{CH}_3$ ); 15.2 ( $\text{CH}_3$ ).



**7-Isopropyl-1,2-dimethylphenanthren-6-ol (*O*-demethylmulticaulin) (2) APT Spectrum (CDCl<sub>3</sub>)**