SUPPORTING INFORMATION

Total synthesis of 1α,25-dihydroxyvitamin D_3 analogs modified at the side chain and D-ring

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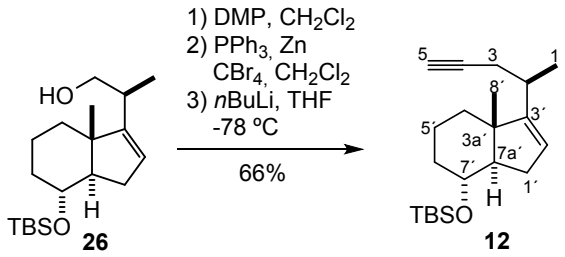
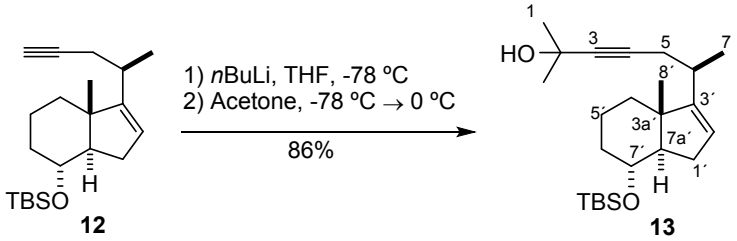
1. Synthesis of 1α,25-dihydroxy-16-en-23-in-vitamin D_3 (3).



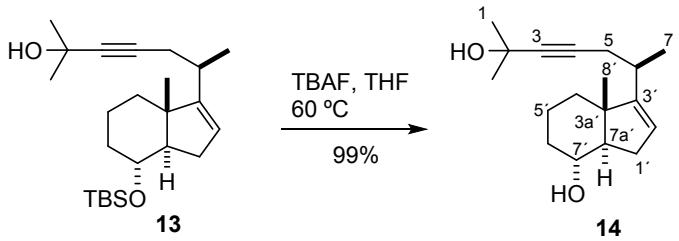
***tert*-Butyldimethyl[(3a*S*,7*R*,7a*R*)-3a-methyl-3-((*R*)-pent-4-yn-2-yl)-3a,4,5,6,7,7a-hexahydro-1H-inden-7-yl)oxy]silane (12)**.

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 5.37 (m, 1H, H-2´), 3.75 (td, J_1 = 10.2, J_2 = 6.2, 1H, H-7´), 1.94 (m, 1H, H-5), 1.12 (d, J = 6.8, 3H, H-1), 0.88 (s, 9H, Me_3C-Si), 0.79 (s, 3H, H-8´), 0.04 (s, 6H, 2xMe-Si). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 159.8 (C, C-3´), 121.6 (CH, C-2´), 84.0 (CH, C-5), 70.2 (CH, C-7´), 69.0 (C, C-4), 58.2 (CH, C-7a´), 49.0 (C, C-3a´), 37.1 (CH_2), 34.4 (CH_2), 34.3 (CH_2), 31.9 (CH, C-2), 31.6 (CH_2), 26.2 (CH_2), 26.0 (3xCH_3, Me_3CSi), 21.9 (CH_2), 21.1 (CH_3, C-1), 18.3 (C, CSi), 16.0 (CH_3, C-8´), -4.1 (CH_3, Me-Si), -4.5 (CH_3, Me-Si). **IR** (film, cm^{-1}): 2865 (ν_{C-H}). **HRMS** (ESI-TOF$^+$, m/z): calcd for $[M+Na]^+$, $[C_{21}H_{36}ONaSi]^+$, 355.2427; found 355.2434.



(*R*)-6-[(3a*S*,7*R*,7a*R*)-7-((*tert*-Butyldimethylsilyl)oxy)-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-3-yl]-2-methylhept-3-yn-2-ol (13).

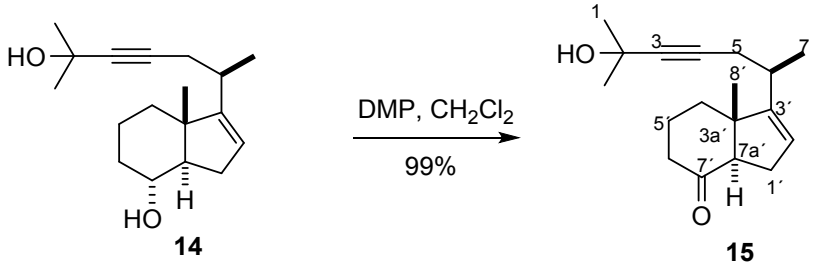
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 5.35 (m, 1H, H-2´), 3.74 (td, J_1 = 10.2, J_2 = 6.2, 1H, H-7´), 1.48 (s, 6H, 2xH-1), 1.08 (d, J = 6.7, 3H, H-7), 0.87 (s, 9H, Me_3C-Si), 0.79 (s, 3H, H-8´), 0.04 (s, 6H, 2xMe-Si). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 158.9 (C, C-3´), 121.5 (CH, C-2´), 86.0 (C, C-3), 82.0 (C, C-4), 70.2 (CH, C-7´), 65.4 (C, C-2), 58.2 (CH, C-7a´), 49.0 (C, C-3a´), 37.1 (CH_2), 34.3 (CH_2), 32.1 (CH, C-6), 31.9 (2xCH_3, C-1), 31.6 (CH_2), 26.3 (CH_2), 26.0 (3xCH_3, Me_3CSi), 21.9 (CH_2), 21.3 (CH_3, C-7), 18.3 (C, CSi), 16.1 (CH_3, C-8´), -4.1 (CH_3, Me-Si), -4.5 (CH_3, Me-Si). **IR** (film, cm^{-1}): 2869 (ν_{C-H}). **HRMS** (EI$^+$, m/z): calcd for $[M]^+$, $[C_{24}H_{42}O_2Si]^+$, 390.2954; found 390.2939.



(3a*S*,7*R*,7a*R*)-3-[(*R*)-6-Hydroxy-6-methylhept-4-yn-2-yl]-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-7-ol (14).

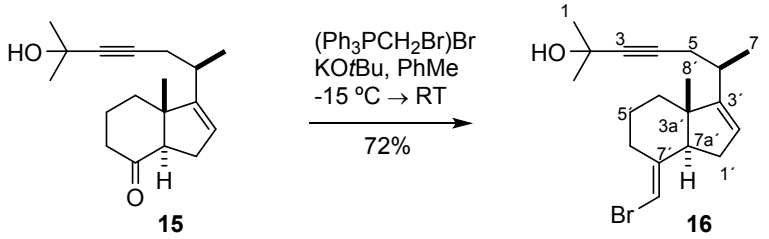
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 5.36 (m, 1H, H-2´), 3.77 (td, J_1 = 10.6, J_2 = 6.1, 1H, H-7´), 1.46 (s, 6H, 2xH-1), 1.08 (3d, J = 6.7, H, H-7), 0.78 (s, 3H, H-8´). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 158.9 (C, C-3´), 121.3 (CH, C-2´), 86.1 (C, C-3), 81.8 (C, C-4), 69.7 (CH, C-7´), 65.3 (C, C-2), 58.2 (CH, C-7a´), 49.3 (C, C-3a´), 36.6 (CH_2), 34.2 (CH_2), 32.1 (CH, C-6), 31.8 (2xCH_3, C-1), 30.7 (CH_2), 26.3 (CH_2), 21.9 (CH_2), 21.3 (CH_3, C-7), 16.2 (CH_3, C-8´). **IR** (film, cm^{-1}): 3357 (ν_{O-H}), 2853 (ν_{C-H}). **HRMS** (EI$^+$, m/z):

calcd for $[M]^+$, $[C_{18}H_{28}O_2]^+$, 276.2089; found 276.2080.



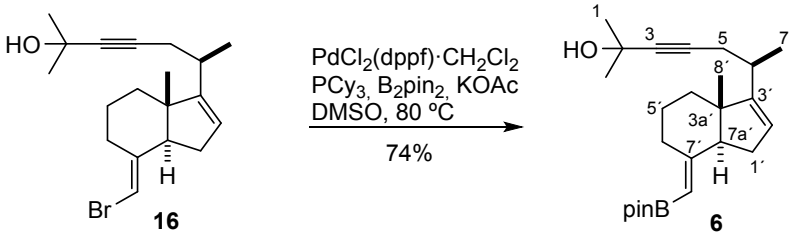
(3a*R*,7a*S*)-1-[(*R*)-6-Hydroxy-6-methylhept-4-yn-2-yl]-7a-methyl-3,3a,5,6,7,7a-hexahydro-4H-inden-4-one (15).

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 5.36 (m, 1H, H-2´), 2.83 (dd, J_1 = 10.6, J_2 = 6.6, 1H, H-7a´), 1.45 (s, 6H, 2xH-1), 1.13 (d, J = 6.7, 3H, H-7), 0.82 (s, 3H, H-8´). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 211.1 (C, C-7´), 156.6 (C, C-3´), 121.4 (CH, C-2´), 86.3 (C, C-3), 81.3 (C, C-4), 65.4 (C, C-2), 63.1 (CH, C-7a´), 53.9 (C, C-3a´), 40.6 (CH_2), 34.4 (CH_2), 32.4 (CH, C-6), 31.8 (2xCH_3, C-1), 27.3 (CH_2), 26.2 (CH_2), 24.1 (CH_2), 21.1 (CH_3, C-7), 17.3 (CH_3, C-8´).



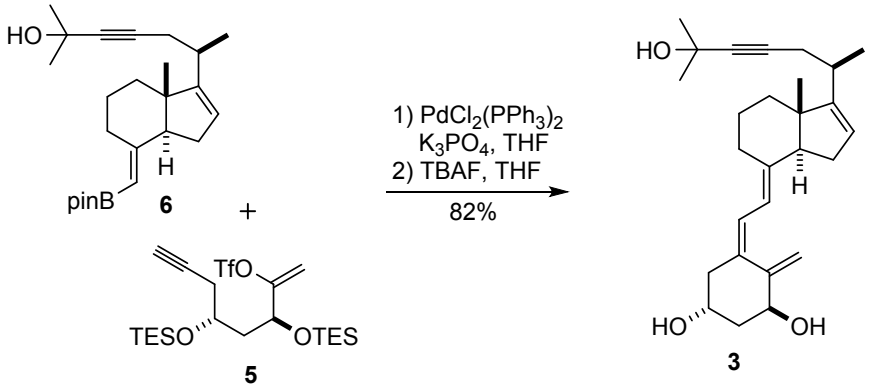
(*R*)-6-[(3a*S*,7a*R*,*E*)-7-(Bromomethylene)-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-3-yl]-2-methylhept-3-yn-2-ol (16).

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 5.75 (m, 1H, HCBr), 5.38 (m, 1H, H-2´), 2.83 (m, 1H, H-6'), 1.47 (s, 6H, H-1), 1.12 (d, J = 6.7, 3H, H-7), 0.73 (s, 3H, H-8´). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 158.4 (C, C-3´), 144.6 (C, C-7´), 121.3 (CH, C-2´), 97.2 (CH, HCBr), 86.2 (C, C-3), 81.7 (C, C-4), 65.4 (C, C-2), 57.6 (CH, C-7a´), 49.8 (C, C-3a´), 34.8 (CH_2), 32.4 (CH, C-6), 31.9 (2xCH_3, C-1), 30.9 (CH_2), 29.4 (CH_2), 26.2 (CH_2), 22.7 (CH_2), 20.9 (CH_3, C-7), 16.9 (CH_3, C-8´). **IR** (film, cm^{-1}): 3373 (ν_{O-H}), 2851 (ν_{C-H}). **HRMS** (ESI-TOF$^+$, m/z): calcd for $[M+Na]^+$, $[C_{19}H_{27}ONaBr]^+$, 373.1137; found 373.1137.



(*R*)-2-Methyl-6-[(3a*S*,7a*S*,*E*)-3a-methyl-7-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)-3a,4,5,6,7,7a-hexahydro-1H-inden-3-yl]hept-3-yn-2-ol (6).

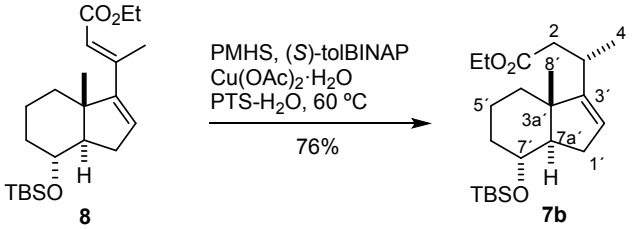
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 5.36 (m, 1H, H-2´), 5.00 (s, 1H, HCB), 3.14 (m, 1H, H-6´), 1.47 (s, 6H, 2xH-1), 1.27 (s, 12H, 4xCH_3-pinacol), 1.11 (d, J = 5.9, 3H, H-7), 0.71 (s, 3H, H-8´). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 165.5 (C, C-3´), 158.4 (C, C-7´), 121.2 (CH, C-2´), 86.1 (C, C-3), 82.8 (C, C-pinacol), 81.9 (C, C-4), 65.5 (C, C-2), 60.3 (CH, C-7a´), 50.4 (C, C-3a´), 35.4 (CH_2), 32.9 (CH_2), 32.4 (CH, C-6), 31.9 (2xCH_3, C-1), 29.7 (CH_2), 26.2 (CH_2), 26.2 (CH_2), 25.1 (2xCH_3, CH_3-pinacol), 25.0 (2xCH_3, CH_3-pinacol), 24.5 (CH_2), 21.0 (CH_3, C-7), 17.2 (CH_3, C-8´). **IR** (film, cm^{-1}): 3446 (ν_{O-H}), 2852 (ν_{C-H}). **HRMS** (EI$^+$, m/z): calcd for $[M]^+$, $[C_{25}H_{39}O_3B]^+$, 398.2992; found 398.2977.



1α,25-Dihydroxy-16-en-23-yne-vitamin D_3 (3).

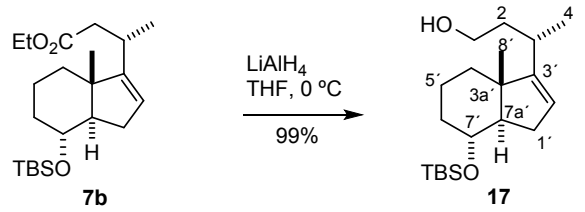
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 6.37 (d, *J* = 11.2, 1H, H-6), 6.10 (d, *J* = 11.5, 1H, H-7), 5.38 (m, 1H, H-16), 5.33 (s, 1H, H-19), 5.01 (s, 1H, H-19), 4.44 (m, 1H, H-1), 4.23 (m, 1H, H-3), 2.82 (m, 1H), 2.60 (m, 1H), 2.35 (m, 3H), 2.23 (m, 2H), 2.01 (m, 2H), 1.92 (m, 1H), 1.79 (m, 3H), 1.48 (s, 6H, H-26 and H-27), 1.12 (d, *J* = 6.9, 3H, H-21), 0.71 (s, 3H, H-18). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 158.6 (C, C-17), 147.8 (C, C-10), 142.5 (C, C-8), 133.2 (C, C-5), 125.1 (CH, C-6), 121.4 (CH, C-16), 117.2 (CH; C-7), 111.9 (CH_2, C-19), 86.2 (C, C-24), 81.9 (C, C-23), 70.9 (CH, C-1), 67.0 (CH, C-3), 65.5 (C, C-25), 58.5 (CH, C-14), 50.1 (C, C-13), 45.4 (CH_2), 43.0 (CH_2), 35.4 (CH_2), 32.4 (CH, C-20), 31.9 (2xCH_3, C-26 and C-27), 29.9 (CH_2), 29.6 (CH_2), 28.9 (CH_2), 26.3 (CH_2), 23.7 (CH_2), 20.9 (CH_3, C-21), 17.1 (CH_3, C-18). **HRMS** (ESI-TOF$^+$, m/z): calcd for $[M+Na]^+$, $[C_{27}H_{38}O_3Na]^+$, 433.2719; found 433.2705.

2. Synthesis of 1α,25-dihydroxy-20-epi-24a-homo-26,27-dimethyl-vitamin D_3 (4).



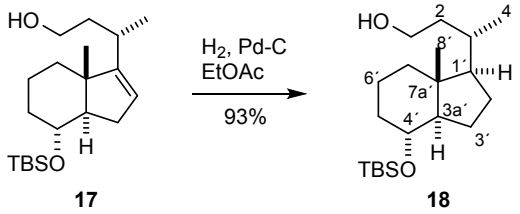
Ethyl (*S*)-3-[(3a*S*,7*R*,7a*R*)-7-((*tert*-butyldimethylsilyl)oxy)-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-3-yl] butanoate (7b).

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 5.37 (m, 1H, H-2´), 4.09 (q, *J* = 7.2, 2H, O$\underline{CH_2}$$CH_3$), 3.73 (td, J_1 = 10.6, J_2 = 4.6, 1H, H-7´), 1.23 (t, *J* = 7.1, 3H, O$CH_2\underline{CH_3}$), 1.09 (d, *J* = 6.9, 3H, H-4), 0.86 (s, 9H, Me_3C-Si), 0.79 (s, 3H, H-8´), 0.03 (s, 6H, 2xCH_3-Si). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 172.8 (C, C-1), 159.0 (C, C-3´), 122.0 (CH, C-2´), 70.1 (CH, C-7´), 60.2 (CH_2, O$\underline{C}H_2CH_3$), 58.1 (CH, C-7a´), 49.0 (C, C-3a´), 42.0 (CH_2), 37.0 (CH_2), 34.1 (CH_2), 31.5 (CH_2), 29.0 (CH_3, O$CH_2\underline{C}H_3$), 26.0 (3xCH_3, Me_3C-Si), 21.8 (CH_2), 21.2 (CH, C-3), 18.3 (C, CSi), 16.4 (CH_3, C-8´), 14.4 (CH_3, C-4), -4.1 (CH_3, Me-Si), -4.6 (CH_3, Me-Si). **IR** (film, cm^{-1}): 2933 (ν_{C-H}), 1721 ($\nu_{C=O}$). **HRMS** (ESI-TOF$^+$, m/z): calcd for $[M+H]^+$, $[C_{22}H_{41}O_3Si]^+$, 381.2819; found 381.2825.



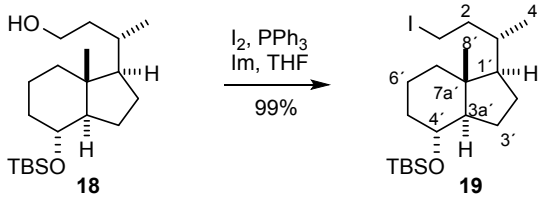
(*S*)-3-[(3a*S*,7*R*,7a*R*)-7-((*tert*-Butyldimethylsilyl)oxy)-3a-methyl-3a,4,5,6,7,7a-hexahydro-1H-inden-3-yl]butan-1-ol (17).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.39 (m, 1H, H-2´), 3.75 (td, J_1 = 10.4, J_2 = 4.8, 1H, H-7´), 3.63 (m, 2H, H-1), 1.10 (d, J = 6.9, 3H, H-4), 0.88 (s, 9H, Me_3C-Si), 0.79 (s, 3H, H-8´), 0.05 (s, 6H, 2xMe-Si). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 160.5 (C, C-3´), 121.7 (CH, C-2´), 70.2 (CH, C-7´), 61.5 (CH_2, C-1), 58.1 (CH, C-7a´), 49.3 (C, C-3a´), 40.1 (CH_2), 37.1 (CH_2), 34.3 (CH_2), 31.6 (CH_2), 28.5 (CH, C-3), 26.0 (3xCH_3, Me_3CSi), 21.9 (CH_3, C-4), 21.9 (CH_2), 18.3 (C, CSi), 16.4 (CH_3, C-8´), -4.1 (CH_3, Me-Si), -4.5 (CH_3, Me-Si). **IR** (film, cm^{-1}): 3331 (ν_{O-H}), 2851 (ν_{C-H}). **HRMS** (ESI-TOF$^+$, m/z): calcd for $[M+H]^+$, $[C_{20}H_{39}O_2Si]^+$, 339.2713; found 339.2707.



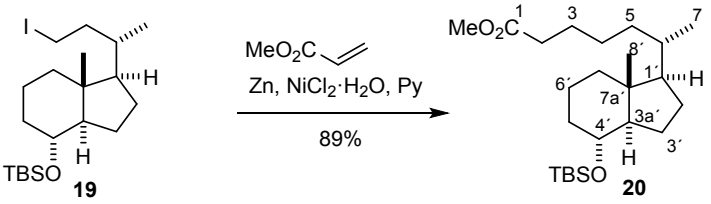
(*S*)-3-[(1*R*,3a*R*,4*R*,7a*R*)-4-((*tert*-Butyldimethylsilyl)oxy)-7a-methyloctahydro-1H-inden-1-yl]butan-1-ol (18).

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 3.59 (m, 3H, H-4´, 2xH-1), 0.85 (s, 9H, Me_3C-Si), 0.82 (d, J = 6.9, 3H, H-4), 0.67 (s, 3H, H-8´), 0.01 (s, 6H, 2xMe-Si). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 71.8 (CH, C-4´), 60.9 (CH_2, C-1), 57.3 (CH), 56.7 (CH), 44.6 (C, C-7a´), 39.4 (CH_2), 38.4 (CH_2), 36.6 (CH_2), 32.1 (CH), 27.6 (CH_2), 26.0 (3xCH_3, Me_3C-Si), 24.4 (CH_2), 22.0 (CH_2), 18.8 (CH_3, C-4), 18.3 (C, CSi), 12.4 (CH_3, C-8´), -4.1 (CH_3, Me-Si), -4.5 (CH_3, Me-Si). **IR** (film, cm^{-1}): 3337 (ν_{O-H}), 2857 (ν_{C-H}). **HRMS** (ESI-TOF$^+$, m/z): calcd for $[M+Na]^+$, $[C_{20}H_{40}O_2NaSi]^+$, 363.2689; found 363.2706.



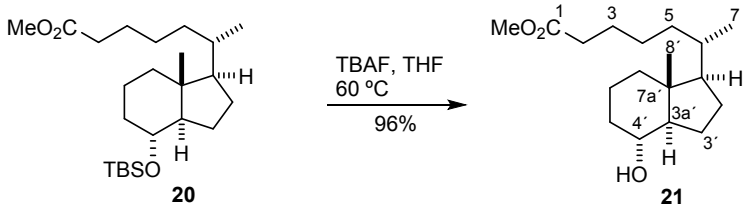
***tert*-Butyl[(1*R*,3a*R*,4*R*,7a*R*)-1-((*S*)-4-iodobutan-2-yl)-7a-methyloctahydro-1H-inden-4-yl)oxy]dimethylsilane (19)**.

^{1}H-NMR (250 MHz): δ = 3.52 (td, J_1 = 9.7, J_2 = 4.4, 1H, H-4´), 3.27 (td, J_1 = 9.2, J_2 = 3.4, 1H, H-1), 3.08 (m, 1H, H-1), 0.86 (s, 9H, Me_3C-Si), 0.81 (d, J = 5.9, 3H, H-4), 0.68 (s, 3H, H-8´), 0.02 (s, 6H, 2xCH_3Si). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 71.6 (CH, C-4´), 57.3 (CH), 56.0 (CH), 44.5 (C, C-7a´), 39.5 (CH_2), 39.2 (CH_2), 36.6 (CH_2), 36.0 (CH), 27.6 (CH_2), 26.0 (3xCH_3, Me_3C-Si), 24.3 (CH_2), 21.2 (CH_2), 18.2 (C, CSi), 17.7 (CH_3, C-4), 12.4 (CH_3, C-8´), 5.2 (CH_2, C-1), -4.0 (CH_3, Me-Si), -4.5 (CH_3, Me-Si). **IR** (film, cm^{-1}): 2856 (ν_{C-H}). **HRMS** (ESI-TOF$^+$, m/z): calcd for $[M+Na]^+$, $[C_{20}H_{39}ONaSiI]^+$, 473.1707; found 473.1716.



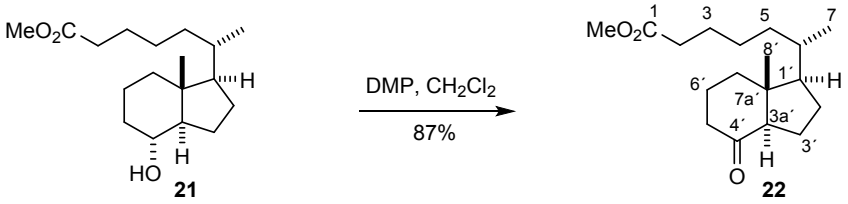
Methyl (*S*)-6-[(1*R*,3a*R*,4*R*,7a*R*)-4-((*tert*-butyldimethylsilyl)oxy)-7a-methyloctahydro-1H-inden-1-yl]heptanoate (20).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.66 (s, 3H, CH_3O), 3.53 (td, J_1 = 10.1, J_2 = 4.4, 1H, H-4´), 2.30 (t, J = 7.3, 2H, H-2), 0.87 (s, 9H, Me_3C-Si), 0.81 (d, J = 6.5, 3H, H-7), 0.66 (s, 3H, H-8´), 0.03 (s, 6H, 2xMe-Si). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 173.3 (C, C-1), 71.7 (CH, C-4´), 57.2 (CH), 56.2 (CH), 51.4 (CH_3, OCH_3), 44.5 (C, C-7a´), 39.2 (CH_2), 36.6 (CH_2), 34.9 (CH_2), 34.8 (CH), 27.5 (CH_2), 25.9 (3xCH_3, Me_3C-Si), 25.8 (CH_2), 25.3 (CH_2), 24.4 (CH_2), 21.9 (CH_2), 18.6 (CH_3, C-7), 18.2 (C, CSi), 12.3 (CH_3, C-8´), -4.2 (CH_3, Me-Si), -4.6 (CH_3, Me-Si). **IR** (film, cm^{-1}): 2856 (ν_{C-H}), 1742 ($\nu_{C=O}$). **HRMS** (ESI-TOF$^+$, m/z): calcd for [M+Na]$^+$, [$C_{24}H_{46}O_3NaSi$]$^+$, 433.3108; found 433.3121.



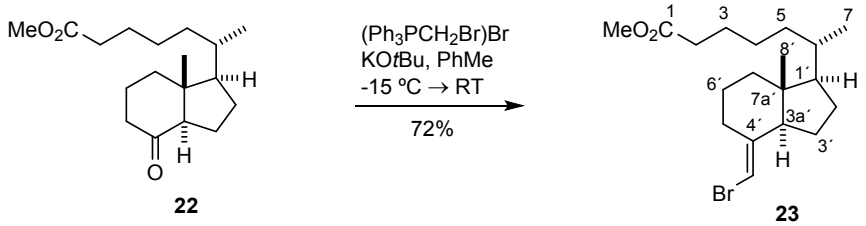
Methyl (*S*)-6-[(1*R*,3a*R*,4*R*,7a*R*)-4-hydroxy-7a-methyloctahydro-1H-inden-1-yl]heptanoate (21).

^{1}H-NMR (250 MHz, $CDCl_3$): δ = 3.59 (s, 3H, CH_3O), 3.49 (m, 1H, H-4´), 2.23 (td, J_1 = 7.5, J_2 = 2.4, 2H, H-2), 0.75 (d, J = 6.5, 3H, H-7), 0.60 (s, 3H, H-8´). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 174.1 (C, C-1), 70.8 (CH, C-4´), 57.0 (CH), 55.9 (CH), 51.3 (CH_3, OCH_3), 44.5 (C, C-7a´), 39.0 (CH_2), 38.9 (CH_2), 35.7 (CH_2), 34.7 (CH_2), 34.5 (CH), 34.0 (CH_2), 27.5 (CH_2), 25.6 (CH_2), 25.1 (CH_2), 23.2 (CH_2), 21.7 (CH_2), 18.5 (CH_3, C-7), 12.1 (CH_3, C-8´). **IR** (film, cm^{-1}): 3389 (ν_{O-H}), 2865 (ν_{C-H}), 1739 ($\nu_{C=O}$). **HRMS** (ESI-TOF$^+$, m/z): calcd for [M+Na]$^+$, [$C_{18}H_{32}O_3Na$]$^+$, 319.2243; found 319.2254.



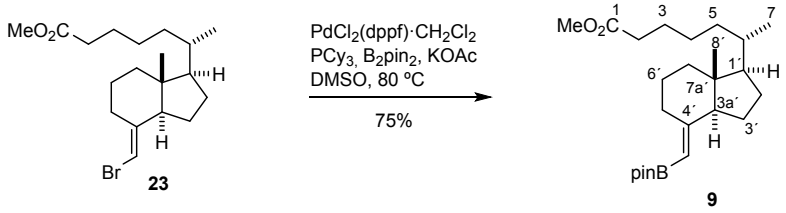
Methyl (*S*)-6-[(1*R*,3a*R*,7a*R*)-7a-methyl-4-oxooctahydro-1H-inden-1-yl]heptanoate (22).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 3.60 (s, 3H, CH_3O), 2.37 (dd, J_1 = 11.3, J_2 = 7.6, 1H, H-3a´), 2.25 (t, J = 7.4, 2H, H-2), 0.77 (d, J = 6.1, 3H, H-7), 0.56 (s, 3H, H-8´). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 212.1 (C, C-4´), 174.2 (C, C-1), 62.0 (CH), 56.2 (CH), 51.5 (CH_3, OCH_3), 50.0 (C, C-7a´), 41.0 (CH_2), 38.9 (CH_2), 35.4 (CH), 35.2 (CH_2), 34.8 (CH_2), 34.2 (CH_2), 27.2 (CH_2), 25.8 (CH_2), 25.3 (CH_2), 24.1 (CH_2), 19.0 (CH_2), 18.5 (CH_3, C-7), 12.8 (CH_3, C-8´). **IR** (film, cm^{-1}): 2872 (ν_{C-H}), 1737 ($\nu_{C=O}$), 1712 ($\nu_{C=O}$). **HRMS** (EI$^+$, m/z): calcd for [M]$^+$, [$C_{18}H_{30}O_3$]$^+$, 294.2195; found 294.2182.



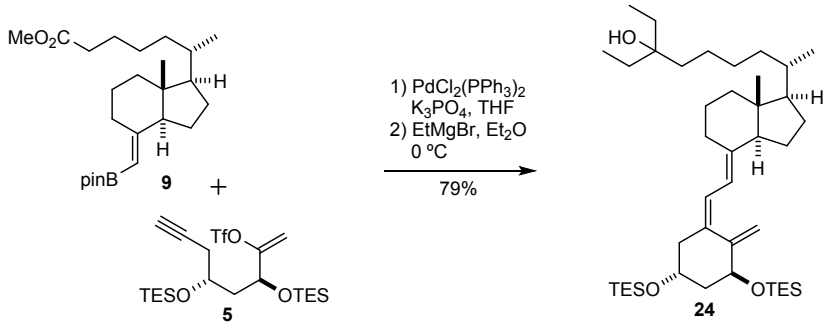
Methyl (*S*)-6-[(1*R*,3a*R*,7a*R*,*E*)-4-(bromomethylene)-7a-methyloctahydro-1H-inden-1-yl]heptanoate (23).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 5.63 (s, 1H, HCBr), 3.66 (s, 3H, CH_3O), 2.86 (m, 1H, H-5´), 2.30 (t, *J* = 7.5, 2H, H-2), 0.82 (d, *J* = 5.8, 3H, H-7), 0.54 (s, 3H, H-8´). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 174.4 (C, C-1), 145.2 (C, C-4´), 97.5 (CH, HCBr), 56.0 (CH), 55.5 (CH), 51.6 (CH_3, OCH_3), 45.6 (C, C-7a´), 39.9 (CH_2), 35.4 (CH), 35.3 (CH_2), 34.3 (CH_2), 31.2 (CH_2), 27.4 (CH_2), 25.9 (CH_2), 25.5 (CH_2), 25.4 (CH_2), 22.7 (CH_2), 22.0 (CH_2), 18.6 (CH_3, C-7), 12.2 (CH_3, C-8´). **IR** (film, cm^{-1}): 2868 (ν_{C-H}), 1739 ($\nu_{C=O}$). **HRMS** (ESI-TOF$^+$, m/z): calcd for $[M+Na]^+$, $[C_{19}H_{31}BrO_2Na]^+$, 393.1405; found 393.1398.



Methyl (*S*)-6-[(1*R*,3a*S*,7a*R*,*E*)-7a-methyl-4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methylene)octahydro-1H-inden-1-yl]heptanoate (9).

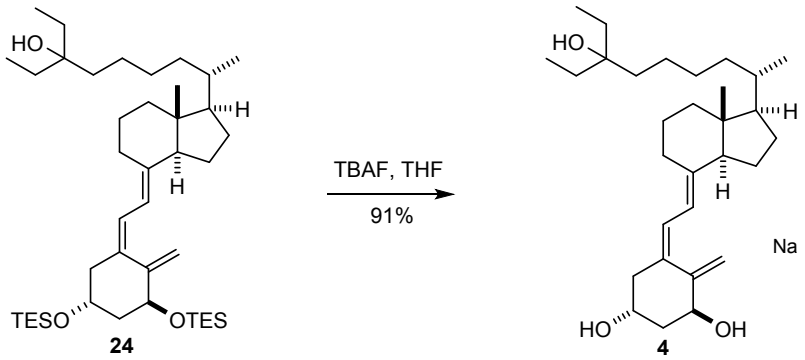
^{1}H-NMR (250 MHz, $CDCl_3$): δ = 4.89 (s, 1H, HCB), 3.65 (s, 3H, CH_3O), 3.16 (m, 1H, H-5´), 2.29 (t, *J* = 7.5, 2H, H-2), 1.25 (s, 12H, 4xCH_3-pinacol), 0.81 (d, *J* = 5.7, 3H, H-7), 0.52 (s, 3H, H-8´). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 174.4 (C, C-1), 166.3 (C, C-4´), 82.7 (C, C-pinacol), 58.1 (CH), 56.5 (CH), 51.6 (CH_3, OCH_3), 46.4 (C, C-7a´), 40.5 (CH_2), 35.4 (CH), 35.3 (CH_2), 34.3 (CH_2), 34.3 (CH_2), 33.4 (CH_2), 27.3 (CH_2), 25.9 (CH_2), 25.5 (CH_2), 25.0 (2xCH_3, CH_3-pinacol), 24.9 (2xCH_3, CH_3-pinacol), 24.5 (CH_2), 22.3 (CH_2), 18.7 (CH_3, C-7), 12.5 (CH_3, C-8´). **IR** (film, cm^{-1}): 2855 (ν_{C-H}), 1726 ($\nu_{C=O}$). **HRMS** (ESI-TOF$^+$, m/z): calcd for $[M+H]^+$, $[C_{25}H_{44}BO_4]^+$, 419.3327; found 419.3329.



1α-[(Triethylsilyl)oxy]-25-hydroxy-20-epi-24a-homo-26,27-dimethyl vitamin D_3 triethylsilyl ether (24).

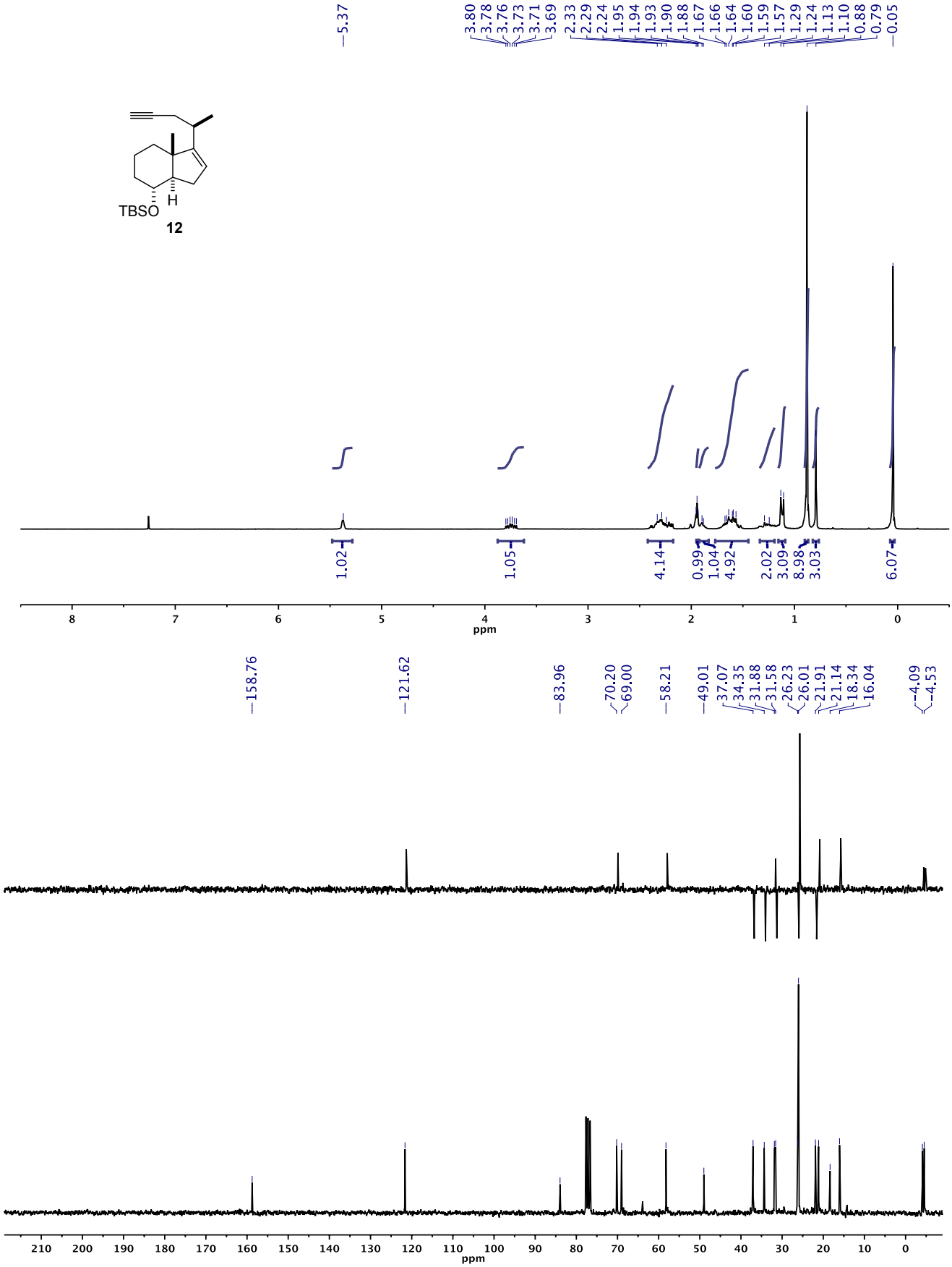
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.24 (d, *J* = 11.2, 1H, H-6), 6.04 (d, *J* = 11.1, 1H, H-7), 5.21 (s, 1H, H-19), 4.88 (s, 1H, H-19), 4.39 (m, 1H, H-1), 4.20 (m, 1H, H-3), 2.84 (m, 1H), 2.46 (m, 1H), 2.23 (m, 1H), 1.81 (m, 11H), 1.46 (q, *J* = 7.6, 4H, C-27 and C-29), 1.23 (m, 10H), 0.95 (t, *J* = 7.9, 18H, CH_3-TES), 0.86 (t, *J* = 7.6, 6H, C-28 and C-30), 0.59 (q, *J* = 7.9, 12H, CH_2-TES), 0.54 (s, 3H, H-18). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 148.5 (C, C-10), 141.3 (C, C-8), 135.1 (C, C-5), 123.4 (CH, C-6), 118.0 (CH, C-7), 111.4 (CH_2, C-19), 77.4 (CH, C-1), 71.8 (CH, C-3), 56.5 (CH), 56.4 (CH), 46.2 (CH_2), 46.0 (C), 45.2 (CH_2), 40.7 (CH_2), 38.5 (CH_2), 35.8 (CH), 35.7 (CH_2), 31.2 (2xCH_2, C-27 and C-29), 29.1 (CH_2), 27.5 (CH_2), 27.2 (CH_2), 23.7 (CH_2), 22.1 (CH_2), 18.8 (CH_3, C-21), 12.4 (CH_3, C-18), 7.9

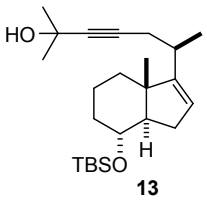
(2xCH_3, C-28 and C-30), 7.0 (3xCH_3, TES), 5.0 (6xCH_2, TES). **IR** (film, cm^{-1}): 3418 (ν_{O-H}), 2875 (ν_{C-H}). **HRMS** (EI$^+$, m/z): calcd for $[M+H]^+$, $[C_{42}H_{78}O_3Si_2]^+$, 686.5489; found 686.5477.



1α,25-Dihydroxy-20-epi-24a-homo-26,27-dimethyl-vitamin D_3 (4).
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 6.37 (d, *J* = 11.2, 1H, H-6), 6.01 (d, *J* = 11.1, 1H, H-7), 5.32 (s, 1H, H-19), 4.99 (s, 1H, H-19), 4.42 (m, 1H, H-1), 4.21 (m, 1H, H-3), 2.84 (m, 1H), 2.58 (m, 1H), 2.30 (m, 1H), 1.98 (m, 4H), 1.68 (m, 8H), 1.45 (q, *J* = 7.5, 4H, C-26 and C-28), 1.25 (m, 9H), 0.85 (t, *J* = 7.5, 6H, C-28 and C-30), 0.53 (s, 3H, H-18). **^{13}C-NMR** (63 MHz, $CDCl_3$): δ = 147.8 (C, C-10), 143.3 (C, C-8), 133.0 (C, C-5), 125.1 (CH, C-6), 117.2 (CH, C-7), 111.9 (CH_2, C-19), 74.8 (C), 70.9 (CH, C-1), 67.0 (CH, C-3), 56.5 (CH), 56.4 (CH), 46.1 (CH_2), 45.4 (C), 43.0 (CH_2), 40.5 (CH_2), 38.5 (CH_2), 35.8 (CH_2), 35.6 (CH), 31.2 (2xCH_2, C-26 and C-28), 29.2 (CH_2), 27.4 (CH_2), 27.2 (CH_2), 24.0 (CH_2), 24.0 (CH_2), 23.7 (CH_2), 22.3 (CH_2), 18.7 (CH_3, C-21), 12.4 (CH_3, C-18), 7.9 (2xCH_3, C-28 and C-30). **HRMS** (ESI-TOF$^+$, m/z): calcd for $[M+Na]^+$, $[C_{30}H_{50}O_3Na]^+$, 481.3658; found 481.33671.

^{1}H and ^{13}C NMR spectra

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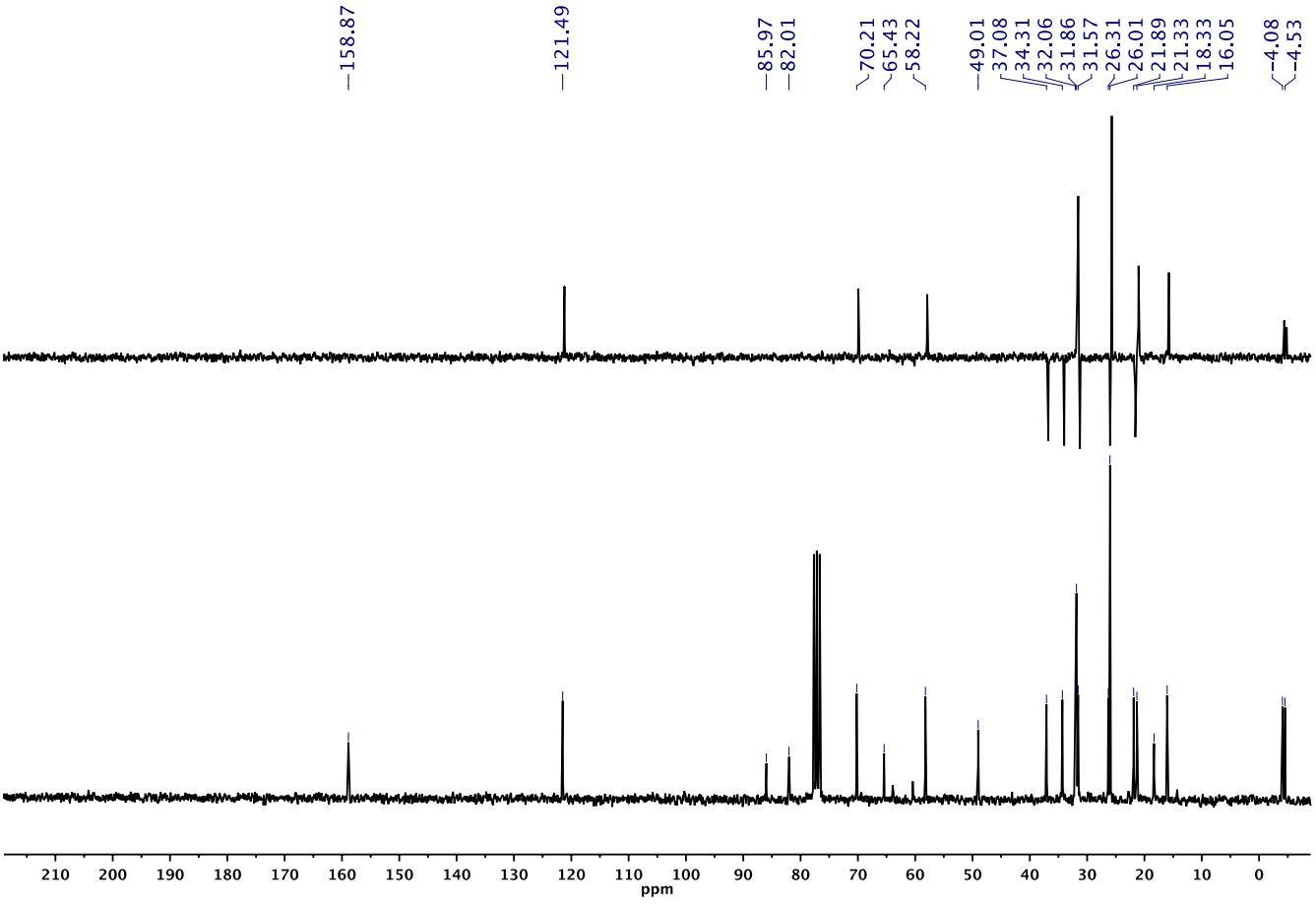
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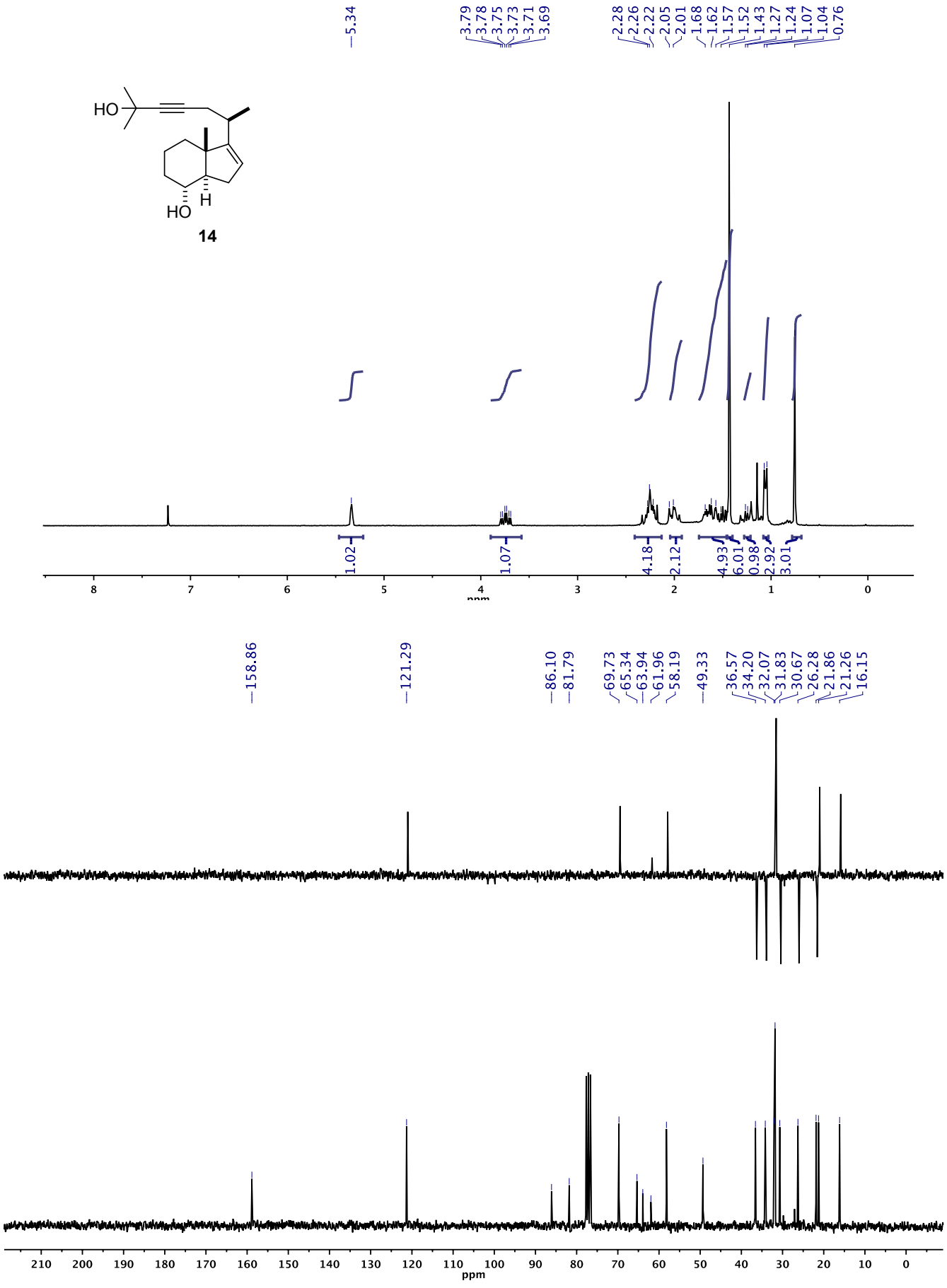
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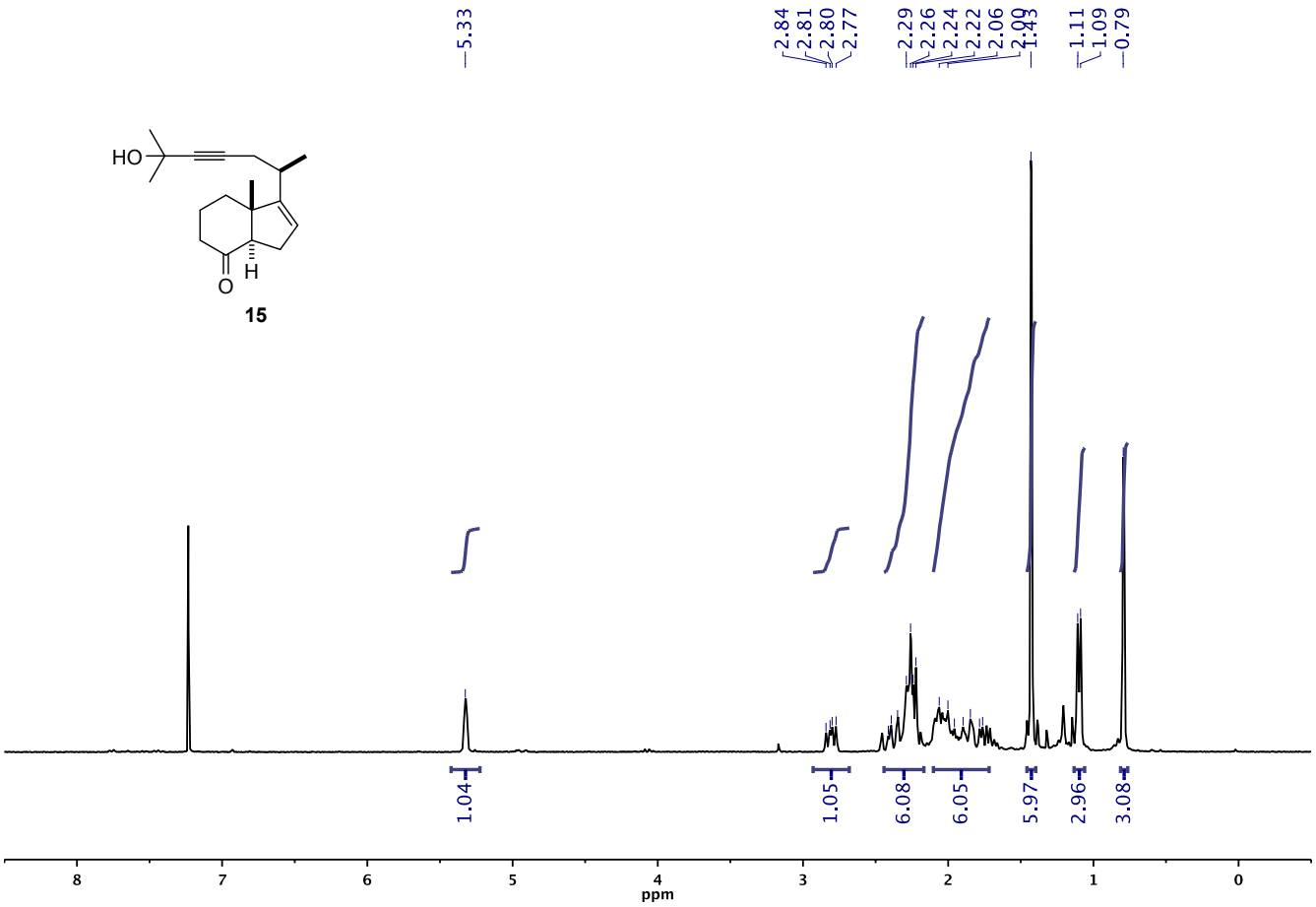
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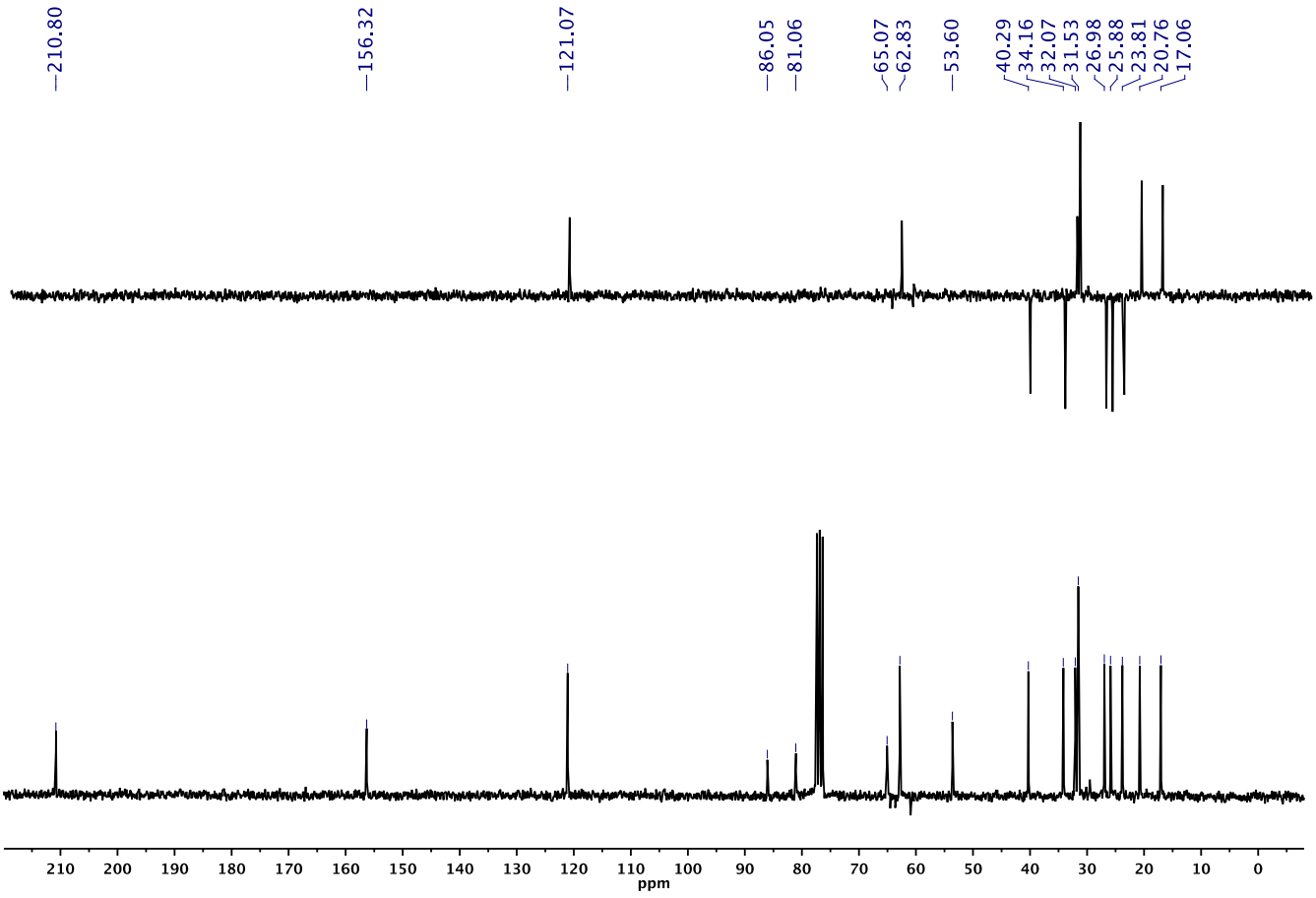
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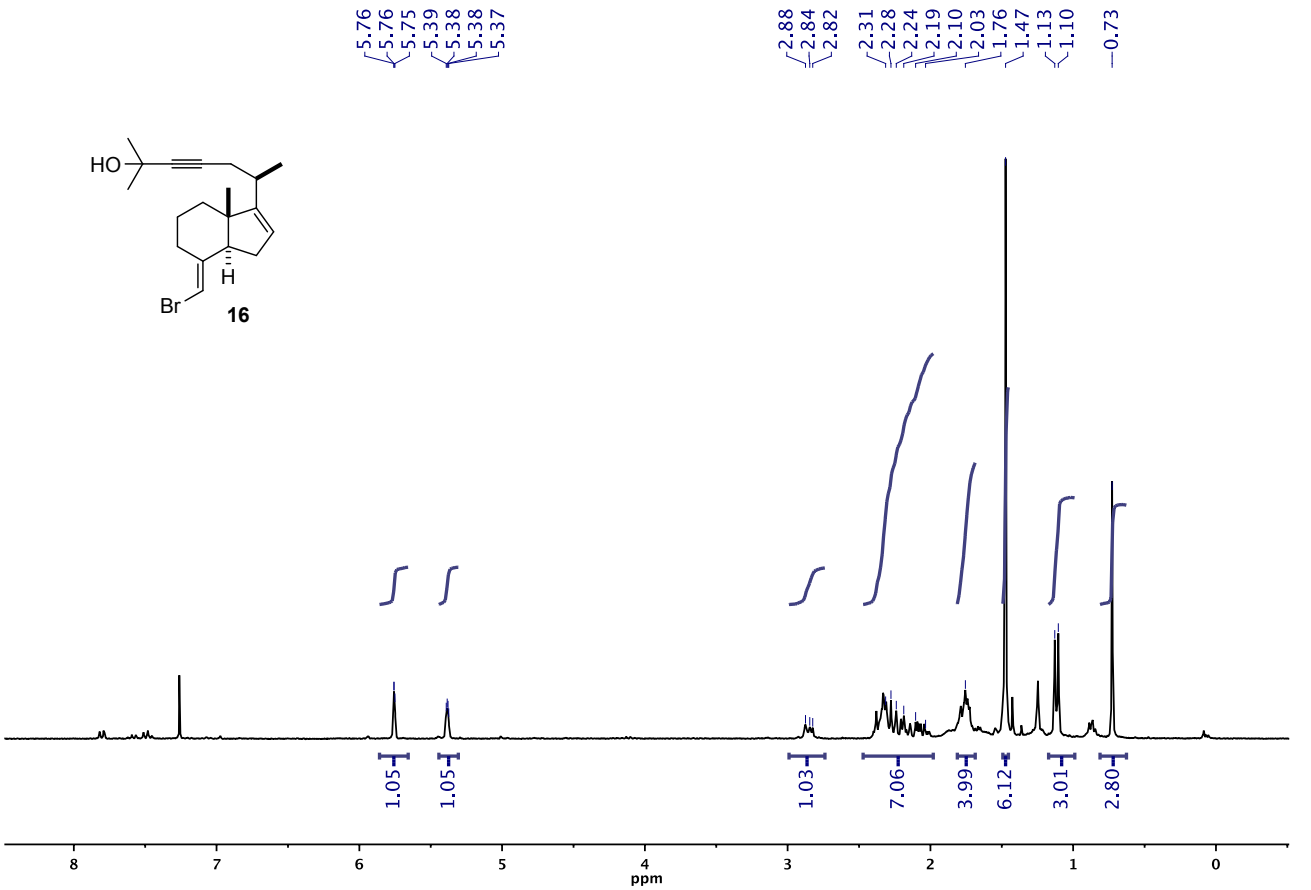
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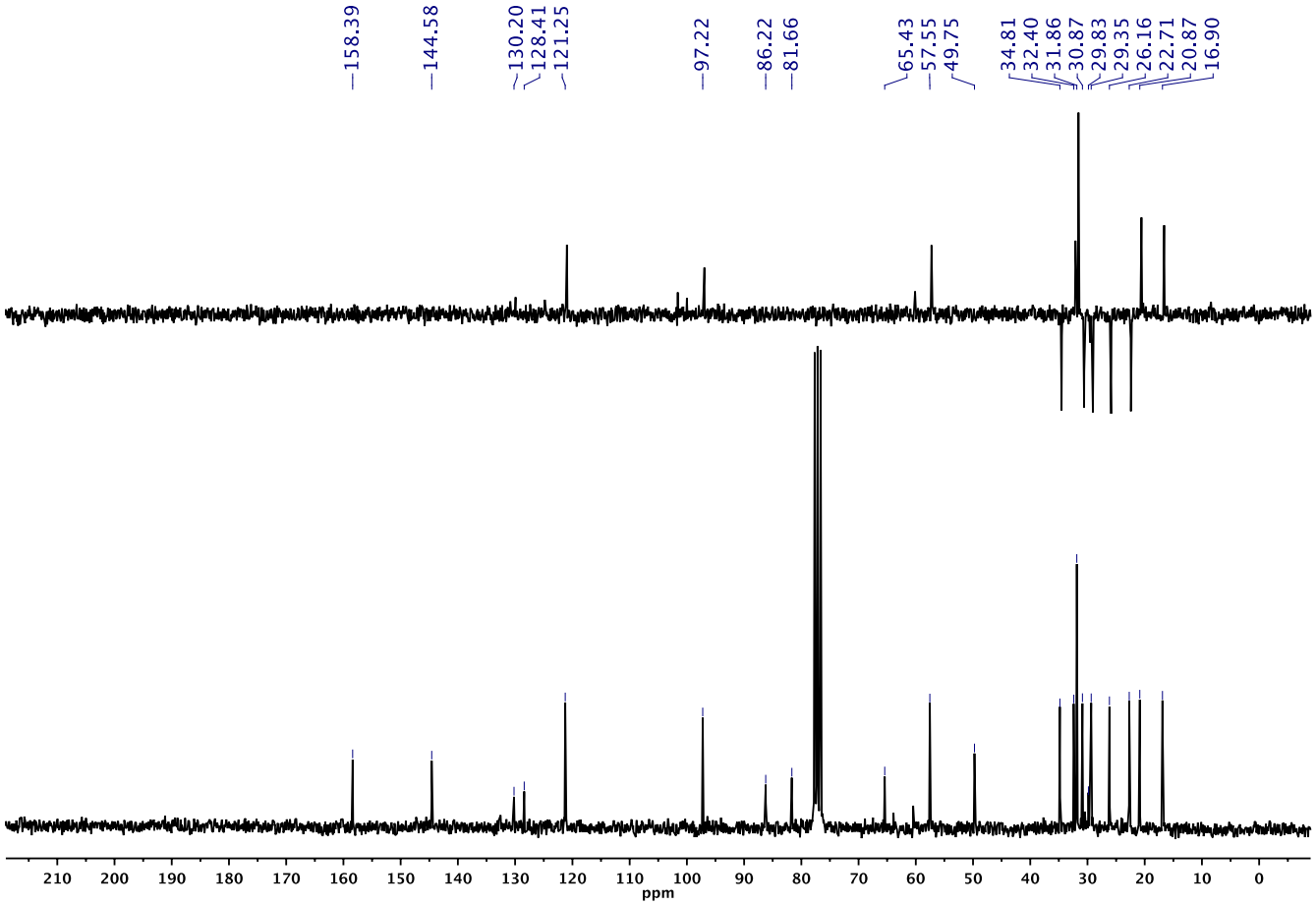
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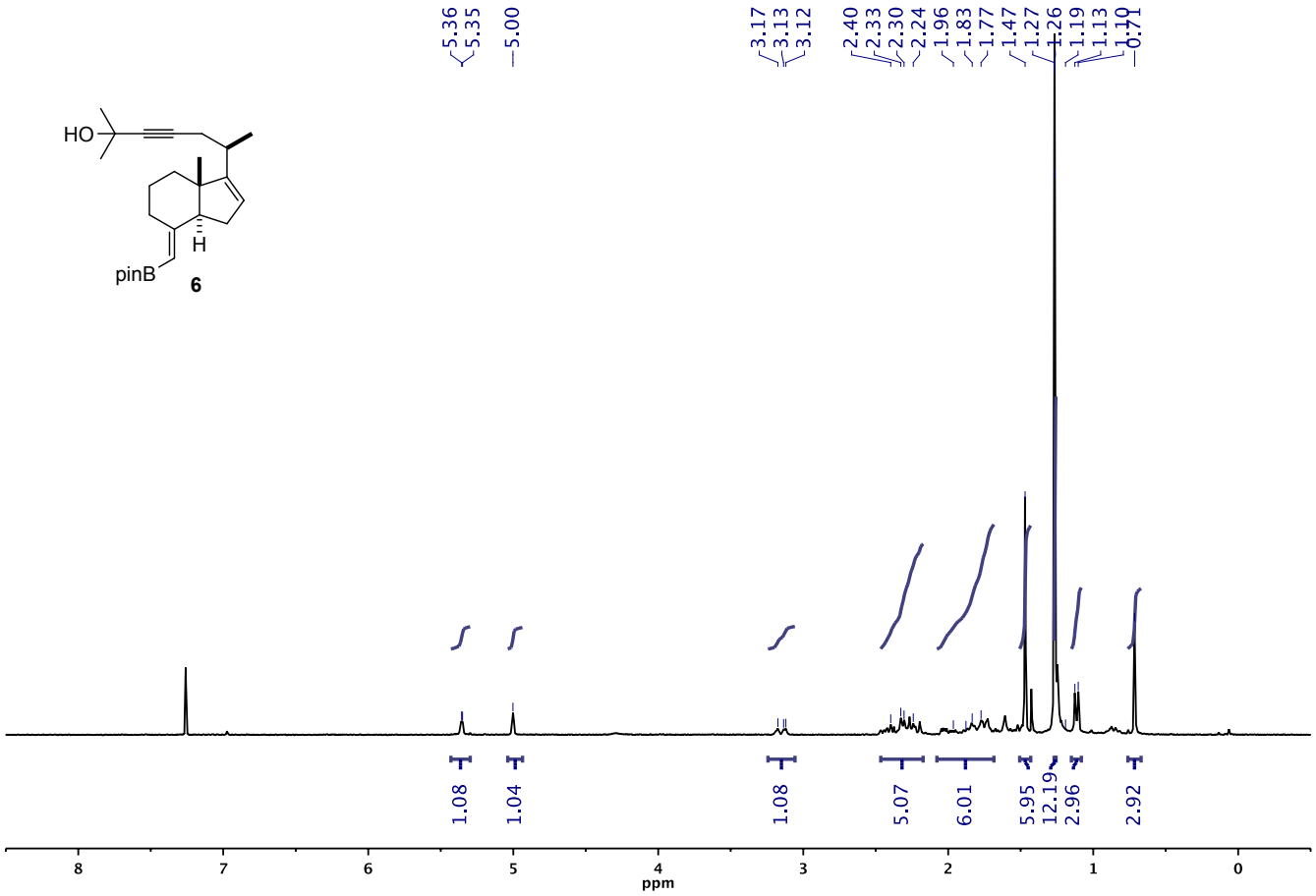
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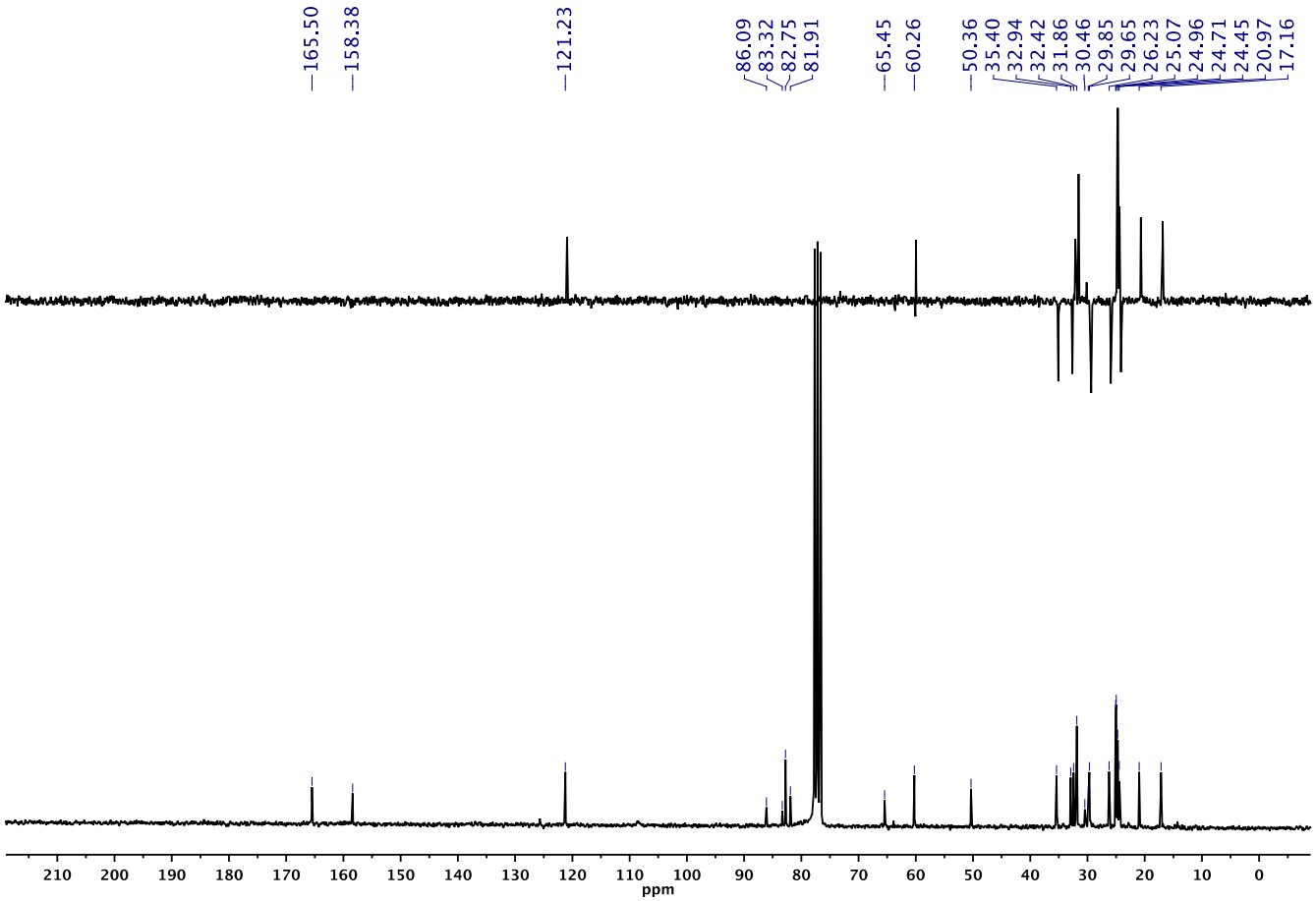
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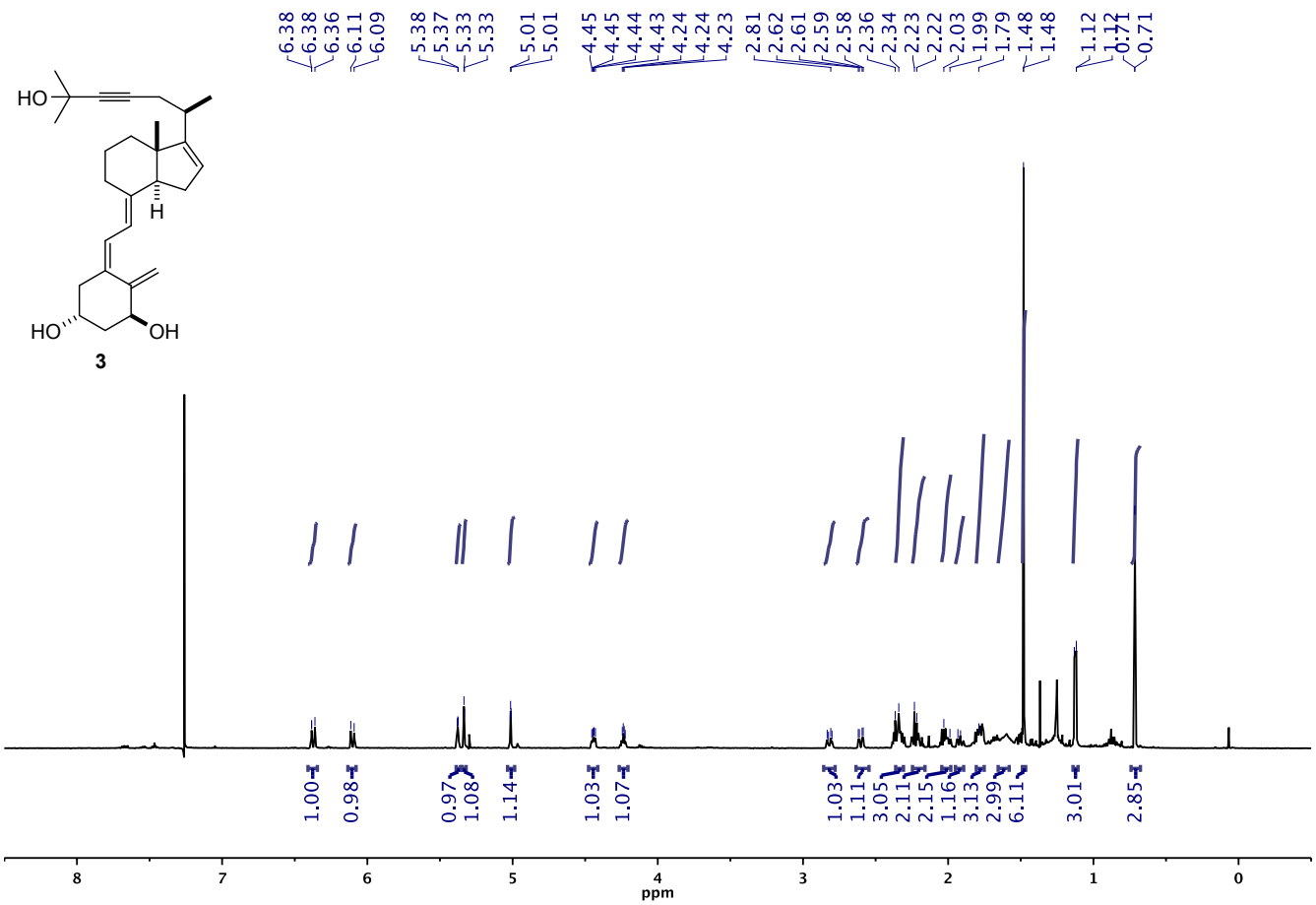
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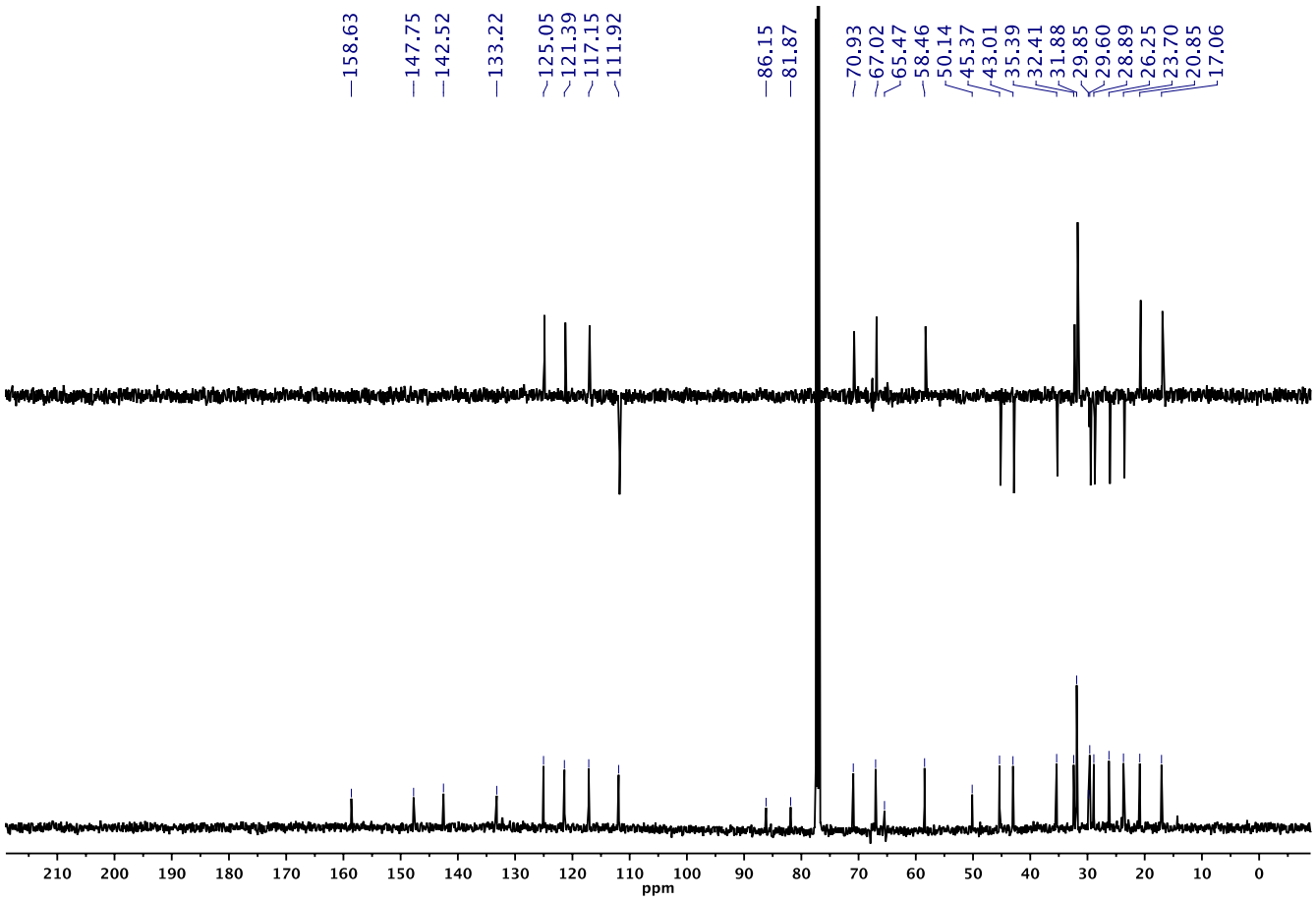
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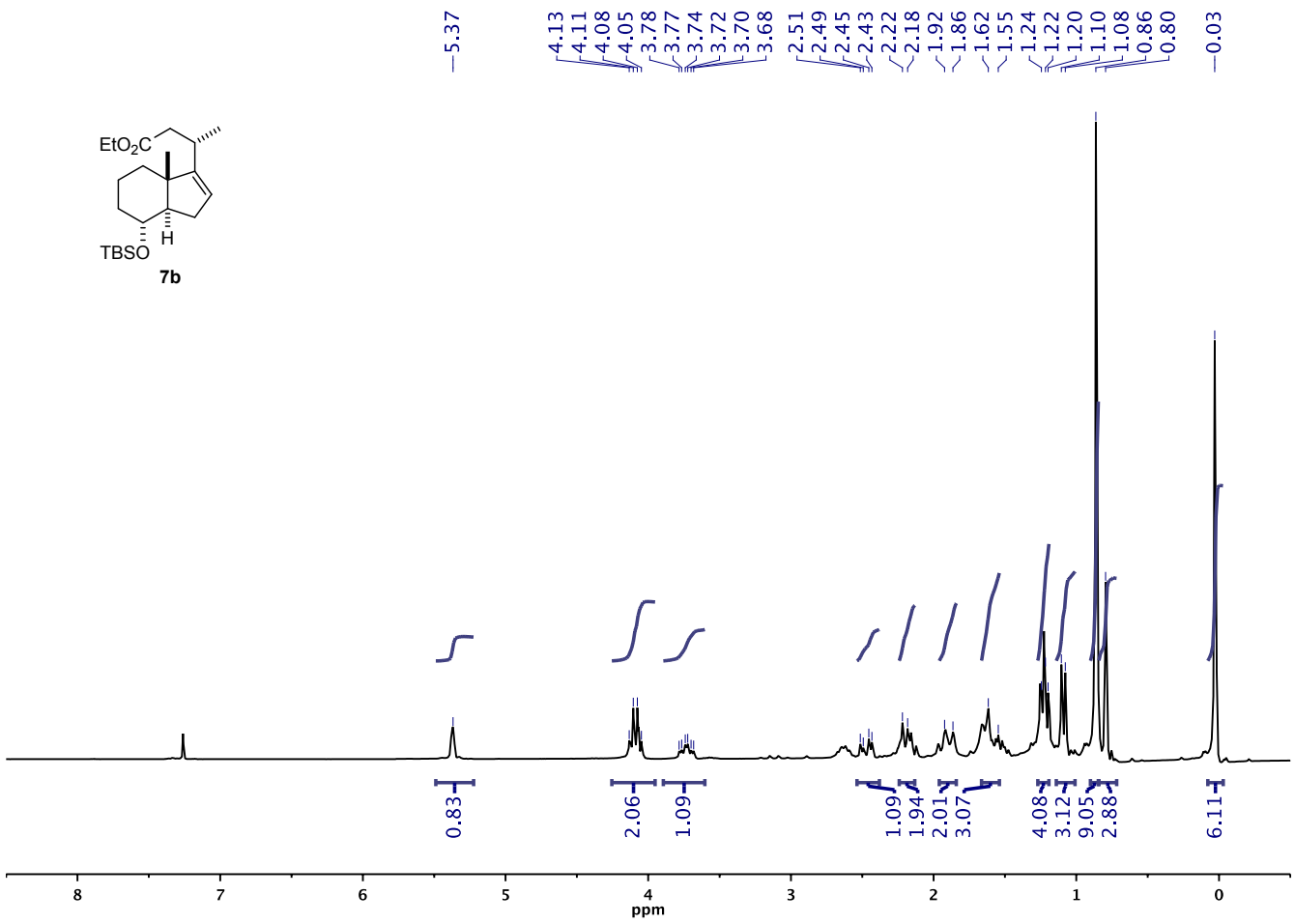
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4.11
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3.68
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2.49
2.45
2.43
2.22
2.18
1.92
1.86
1.62
1.55
1.24
1.22
1.20
1.10
1.08
0.86
0.80
0.03
EtO2C
TBSO
H
7b
0.83
2.06
1.09
1.09
1.94
2.01
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3.12
9.05
2.88
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6
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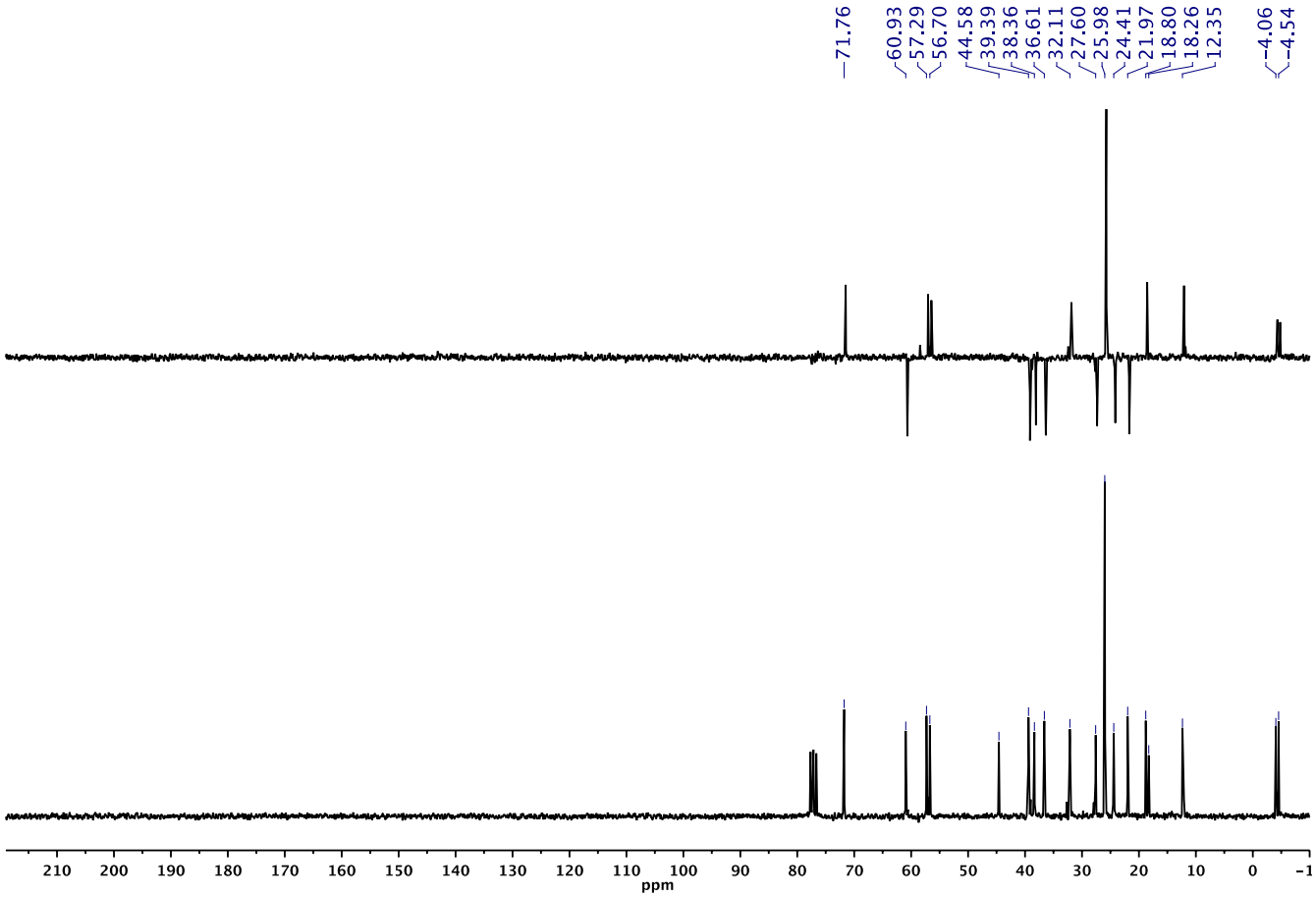
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38.36
36.61
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27.60
25.98
24.41
21.97
18.80
18.26
12.35
4.06
4.54
210
200
190
180
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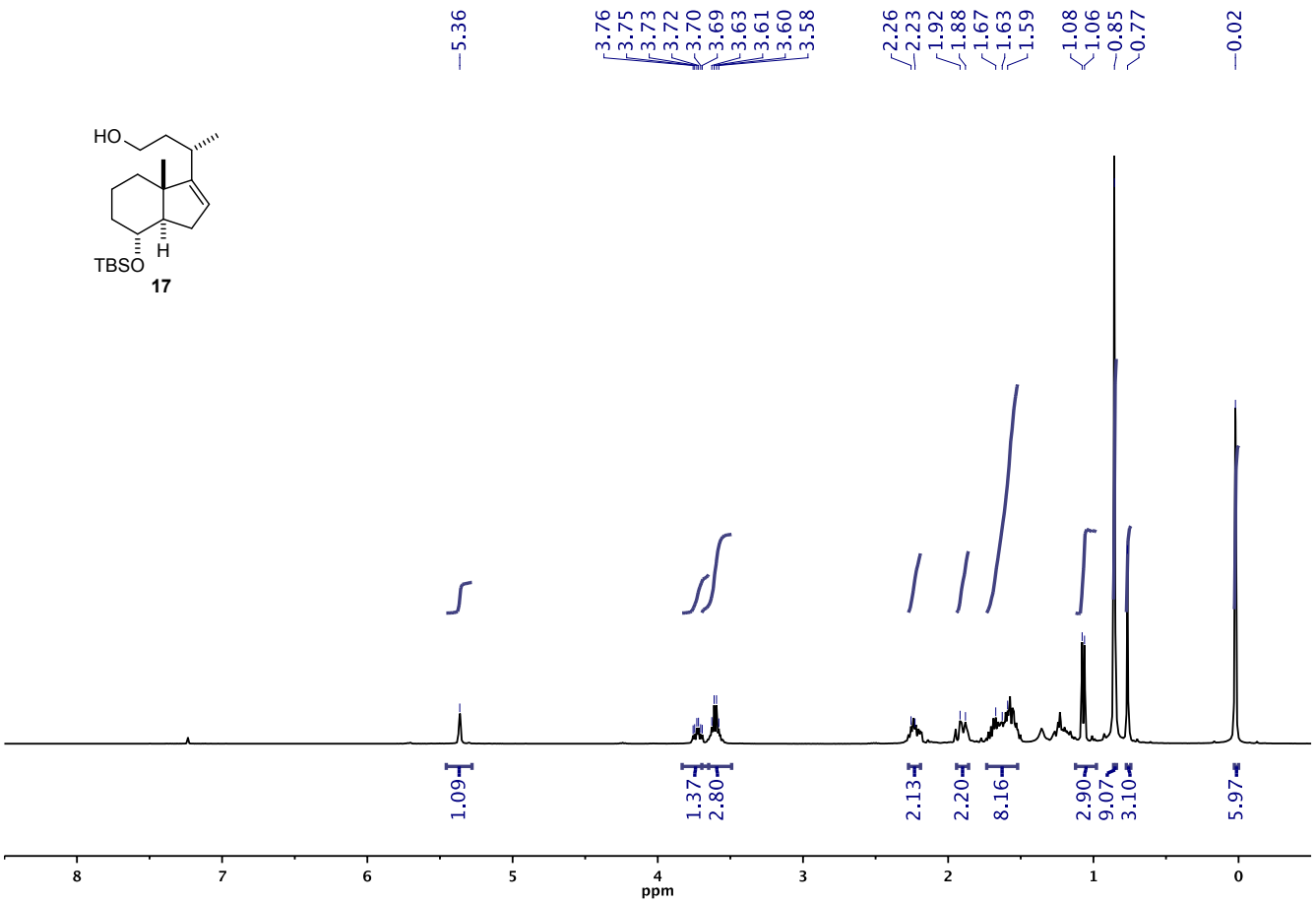
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3.63
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3.60
3.58
2.26
2.23
1.92
1.88
1.67
1.63
1.59
1.08
1.06
0.85
0.77
0.02
HO
TBSO
H
17
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1.37
2.80
2.13
2.20
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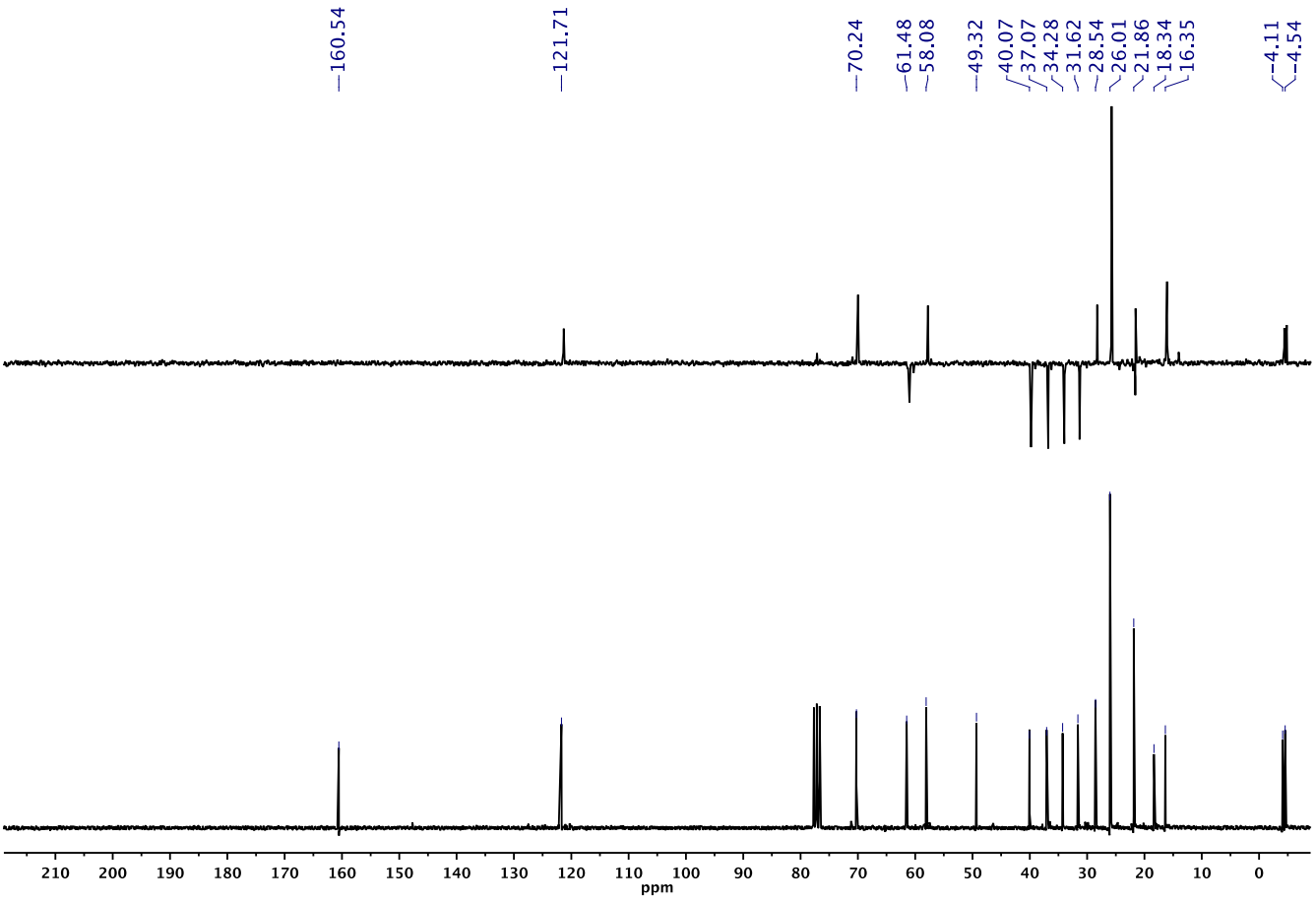
2.90
9.07
3.10
5.97
ppm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28.54
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18.34
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4.11
4.54
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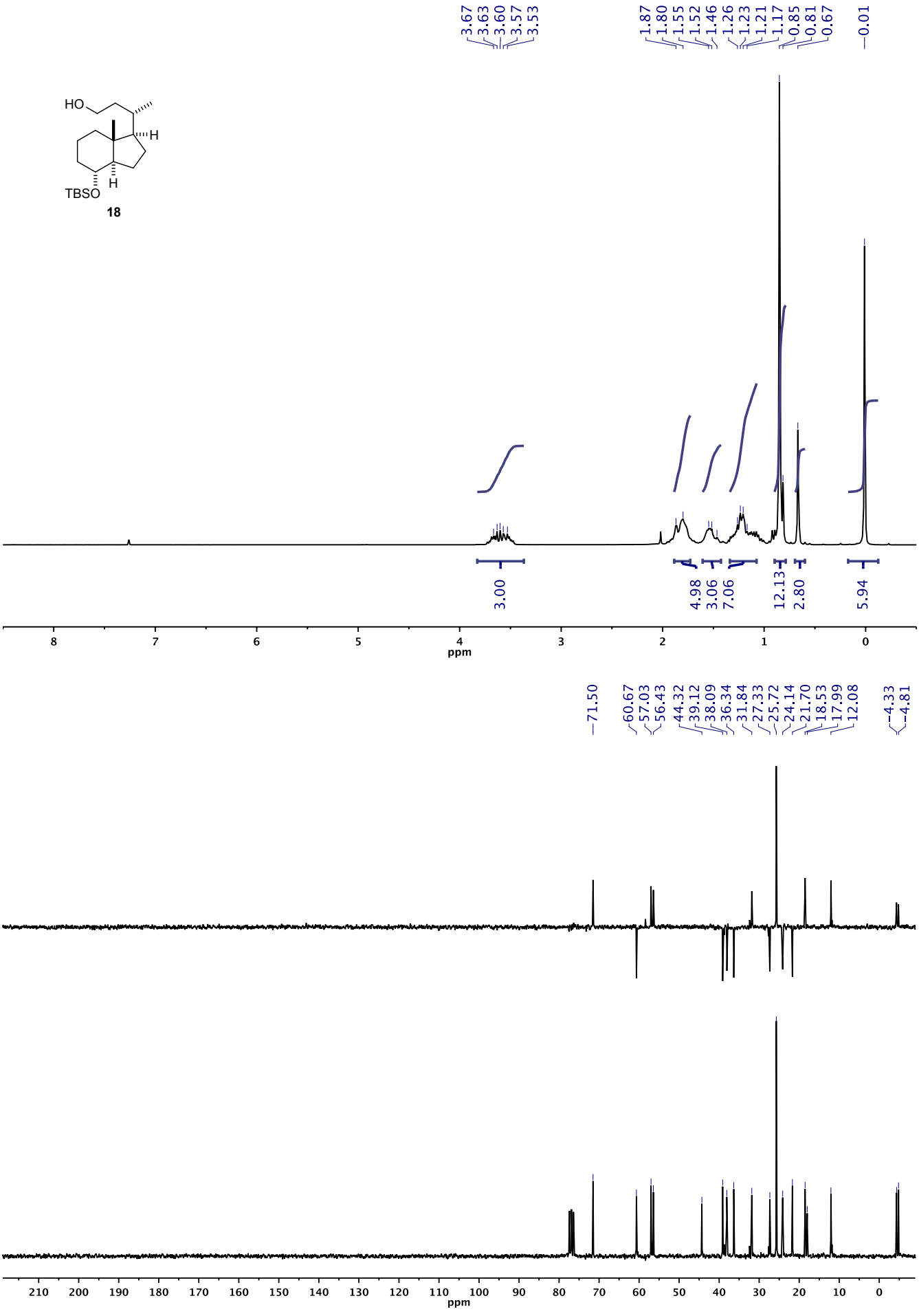
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H
H
TBSO
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1.80
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1.52
1.46
1.26
1.23
1.21
1.17
0.85
0.81
0.67
0.01
3.00
4.98
3.06
7.06
12.13
2.80
5.94
ppm
71.50
60.67
57.03
56.43
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38.09
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27.33
25.72
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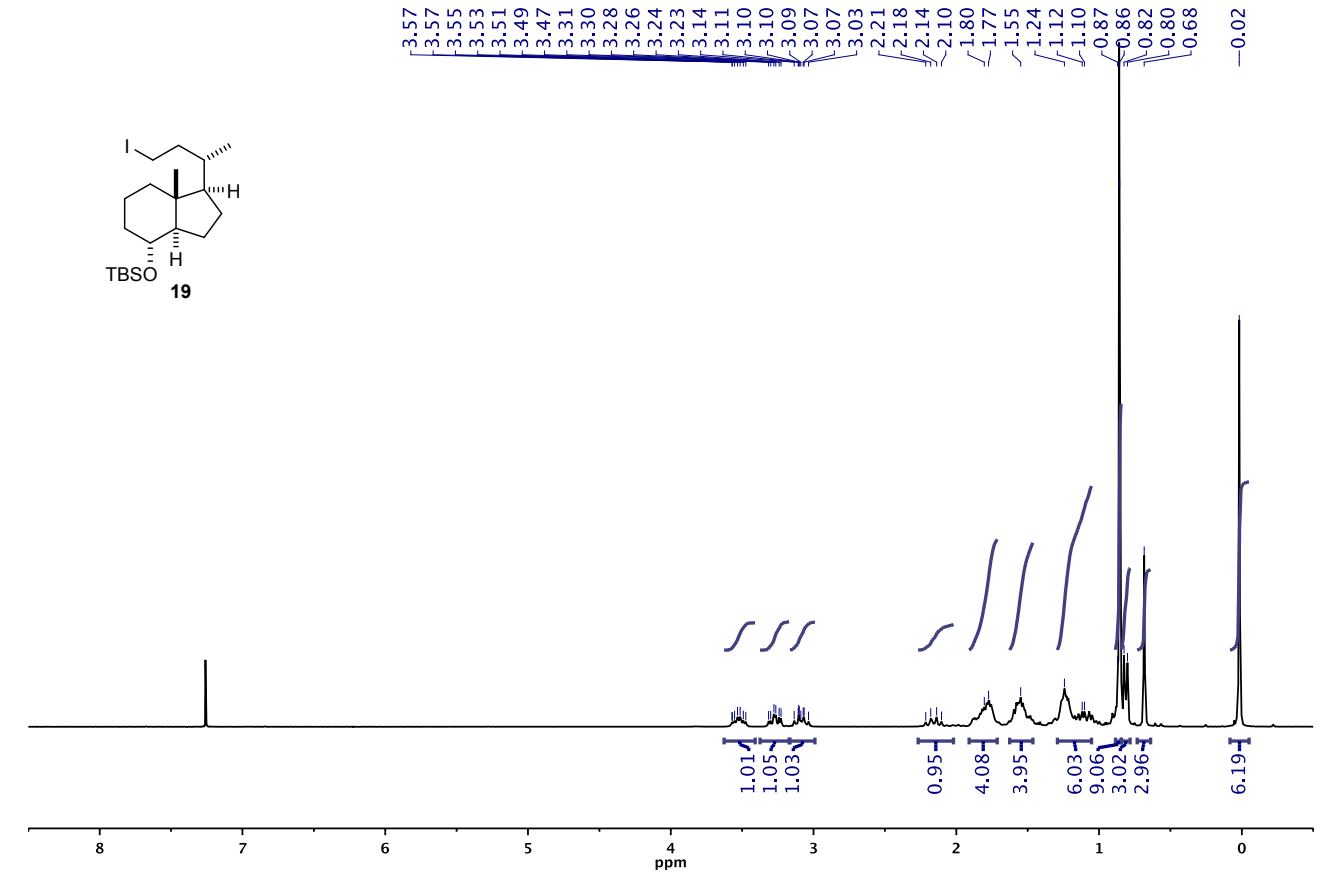
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3.23
3.14
3.11
3.10
3.10
3.09
3.07
3.07
3.03
2.21
2.18
2.14
2.10
1.80
1.77
1.55
1.24
1.12
1.10
0.87
0.86
0.82
0.80
0.68
0.02
I
H
H
TBSO
19
1.01
1.05
1.03
0.95
4.08
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9.06
3.02
2.96
6.19
8
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6
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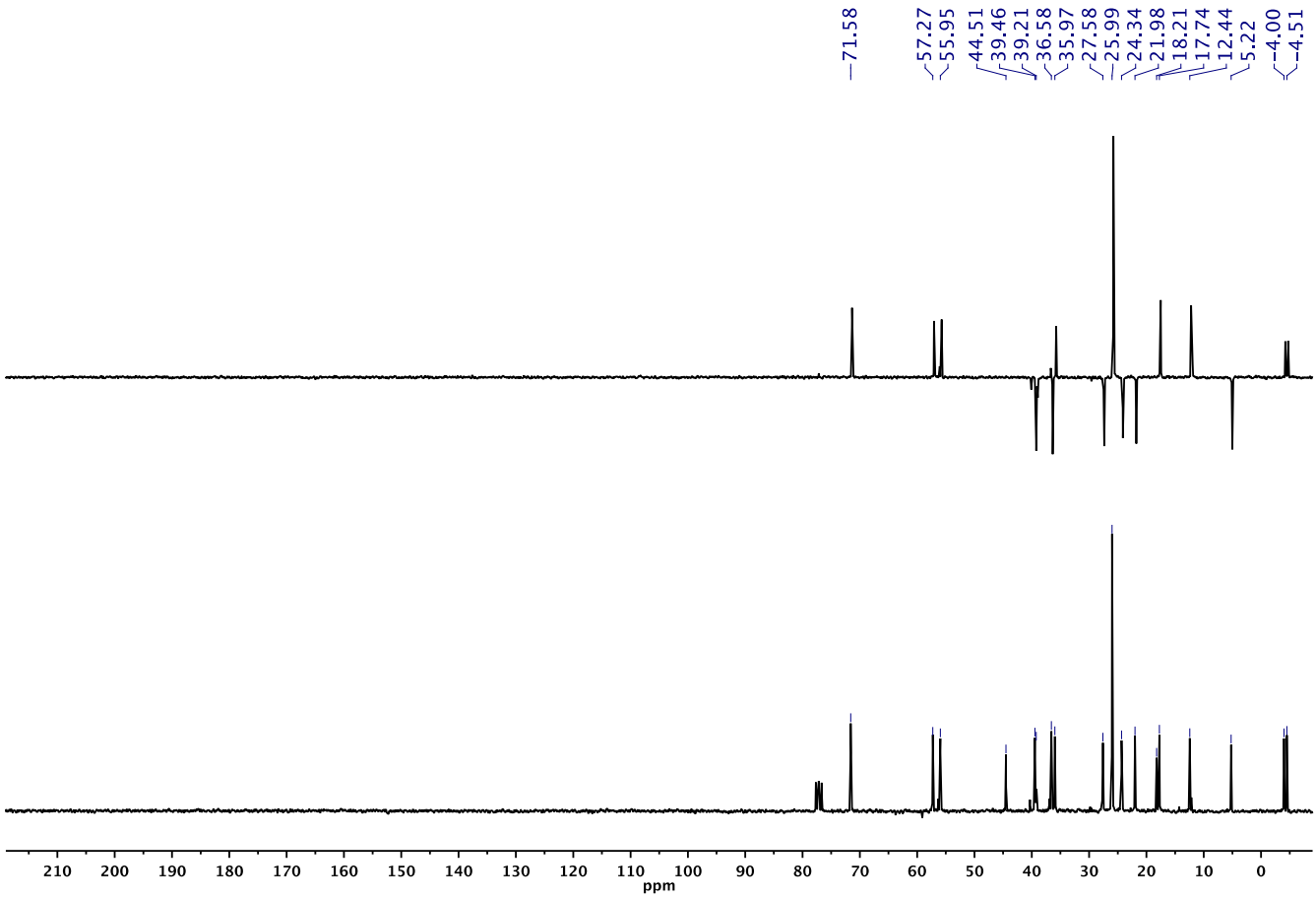
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39.21
36.58
35.97
27.58
25.99
24.34
21.98
18.21
17.74
12.44
5.22
-4.00
-4.51
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200
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140
130
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110
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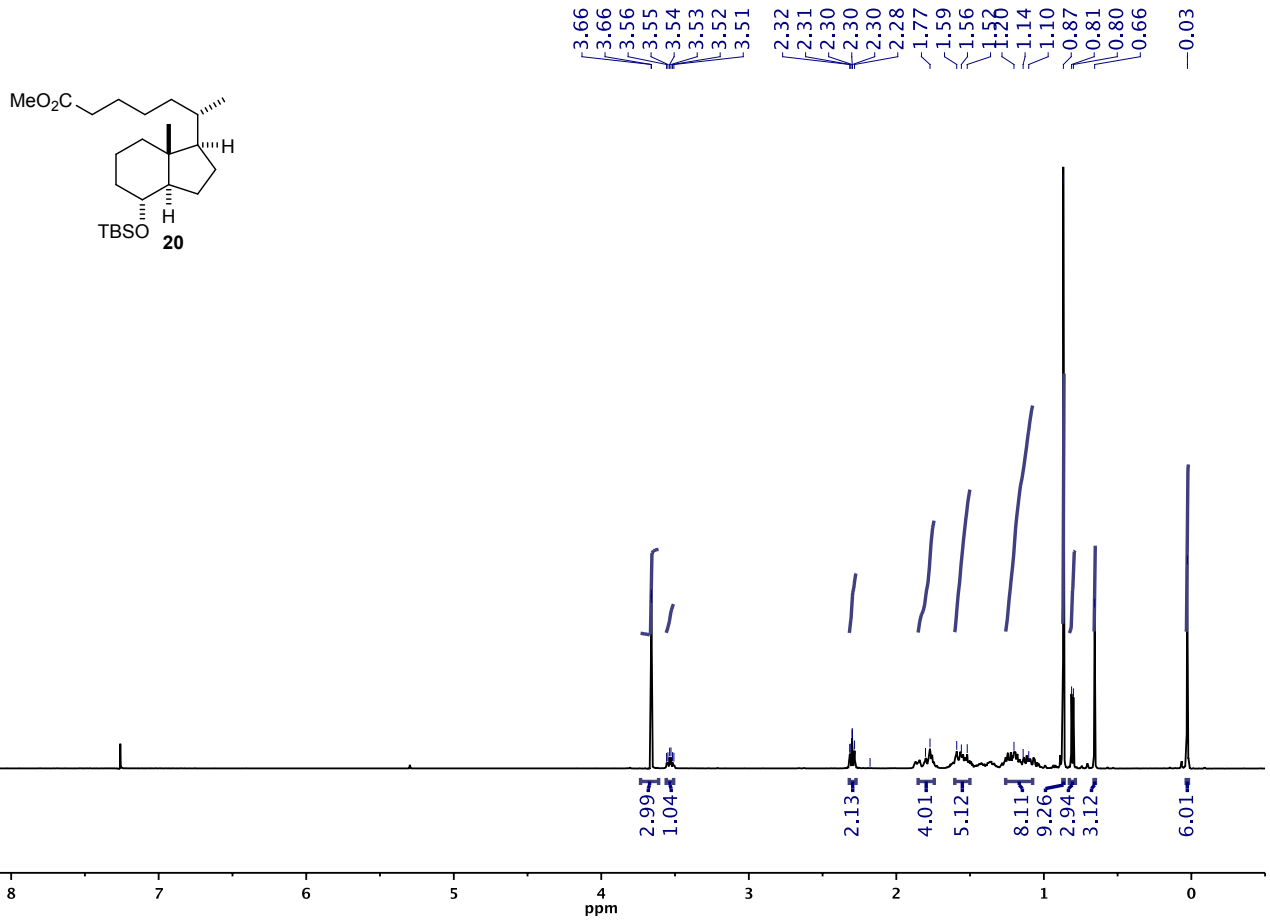
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3.56
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3.54
3.53
3.52
3.51
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2.31
2.30
2.30
2.28
1.77
1.59
1.56
1.20
1.14
1.10
0.87
0.81
0.80
0.66
0.03
MeO2C
H
TBSO
H
20
2.99
1.04
2.13
4.01
5.12
8.11
9.26
2.94
3.12
6.01
8
7
6
5
4
3
2
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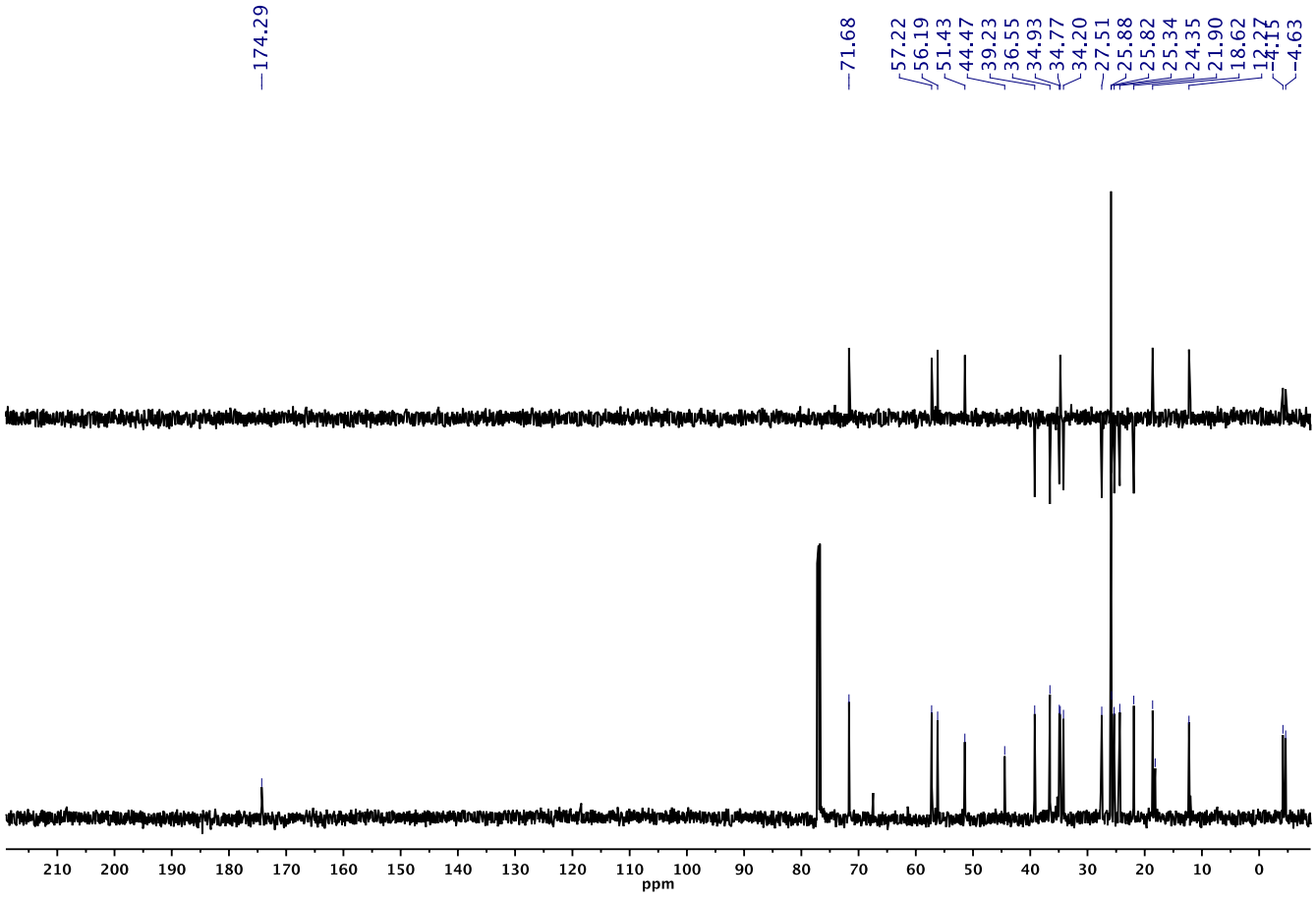
0
ppm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71.68
57.22
56.19
51.43
44.47
39.23
36.55
34.93
34.77
34.20
27.51
25.88
25.82
25.34
24.35
21.90
18.62
-4.15
-4.63
210
200
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140
130
120
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100
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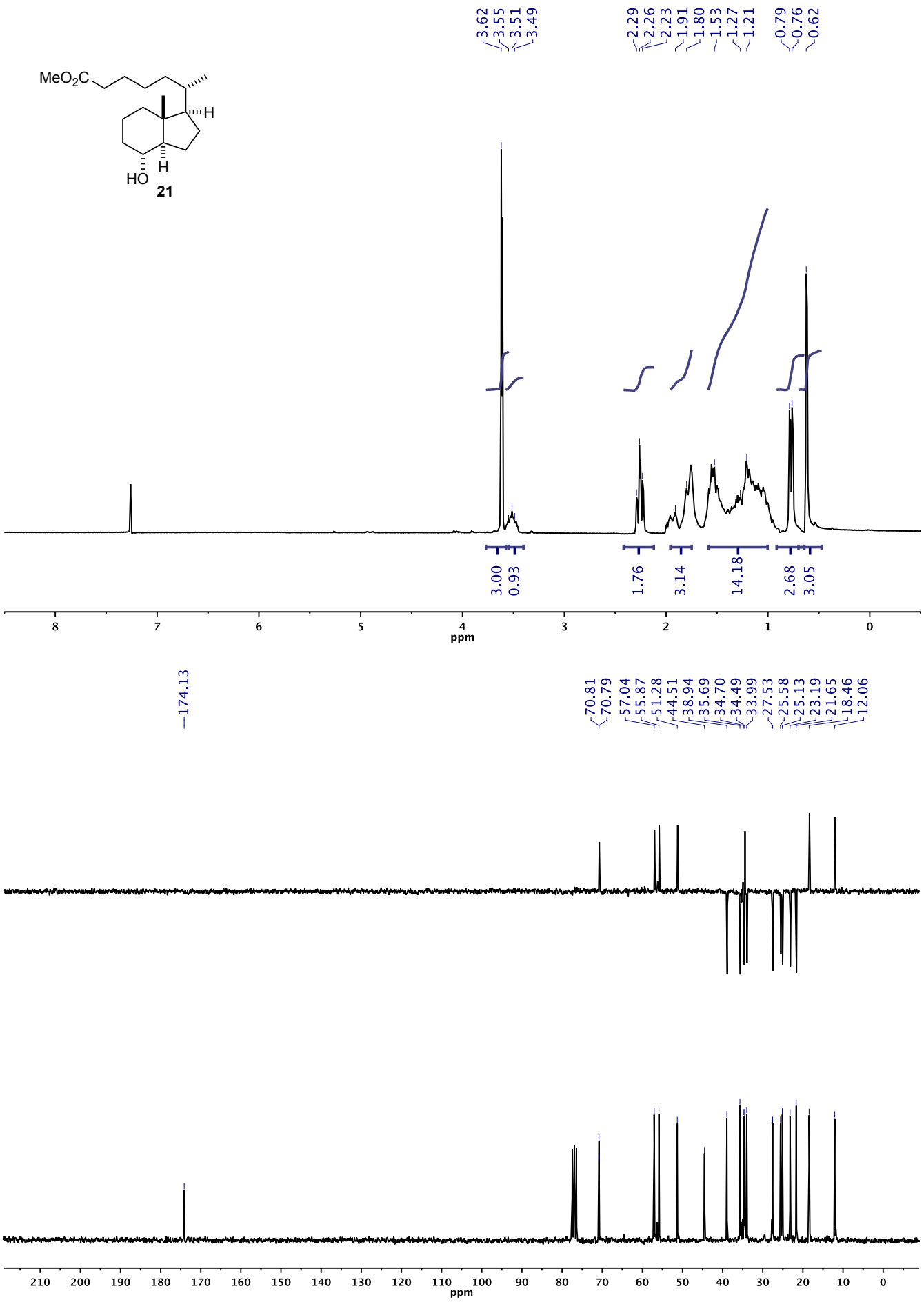
0
ppm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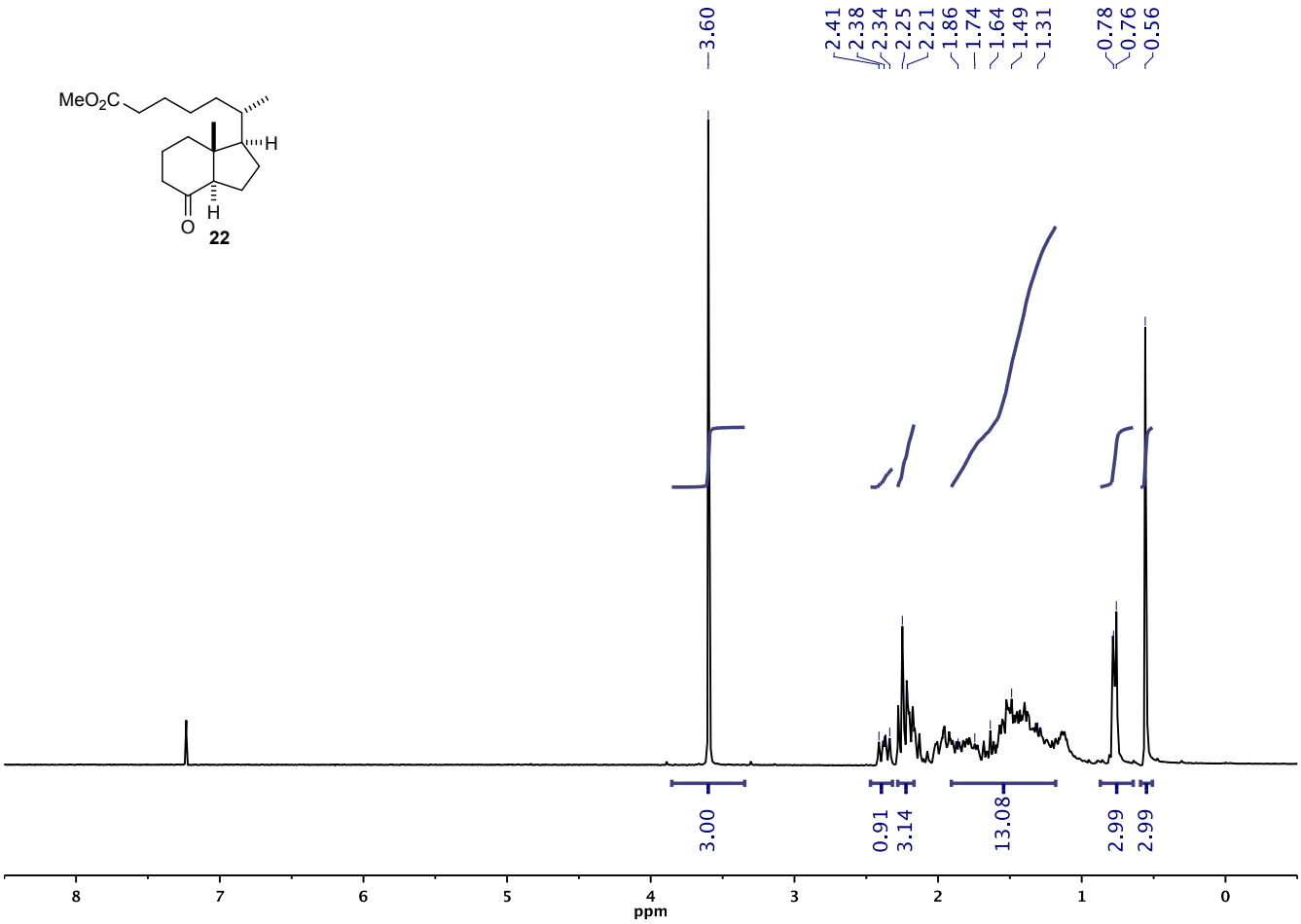
H
HO
H
21
3.62
3.55
3.51
3.49
2.29
2.26
2.23
1.91
1.80
1.53
1.27
1.21
0.79
0.76
0.62
3.00
0.93
1.76
3.14
14.18
2.68
3.05
ppm
174.13
70.81
70.79
57.04
55.87
51.28
44.51
38.94
35.69
34.70
34.49
33.99
27.53
25.58
25.13
23.19
21.65
18.46
12.06
ppm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H
O
22
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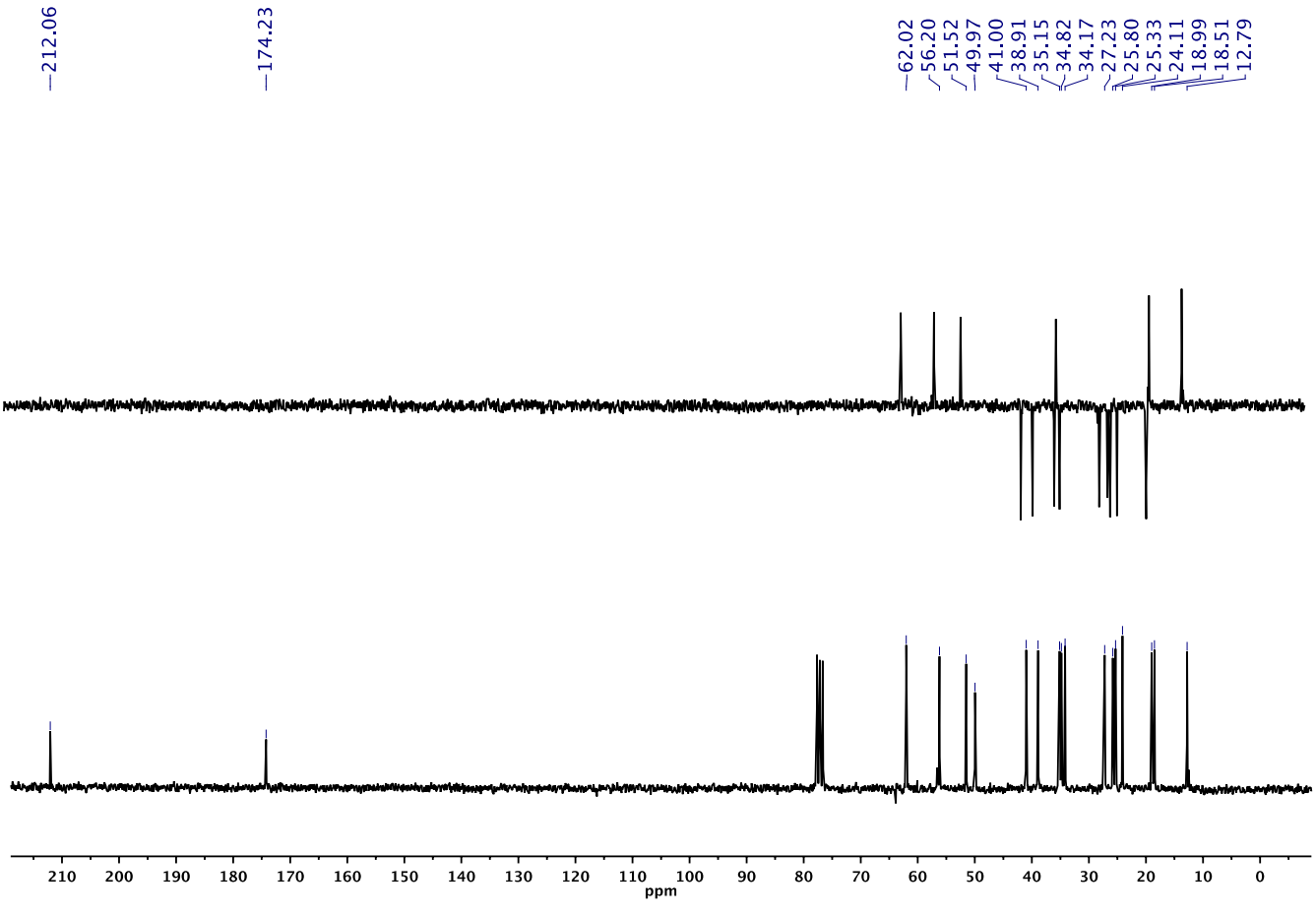
2.34
2.25
2.21
1.86
1.74
1.64
1.49
1.31
0.78
0.76
0.56
3.00
0.91
3.14
13.08
2.99
2.99
8
7
6
5
4
3
2
1
0
ppm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174.23
62.02
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51.52
49.97
41.00
38.91
35.15
34.82
34.17
27.23
25.80
25.33
24.11
18.99
18.51
12.79
210
200
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180
170
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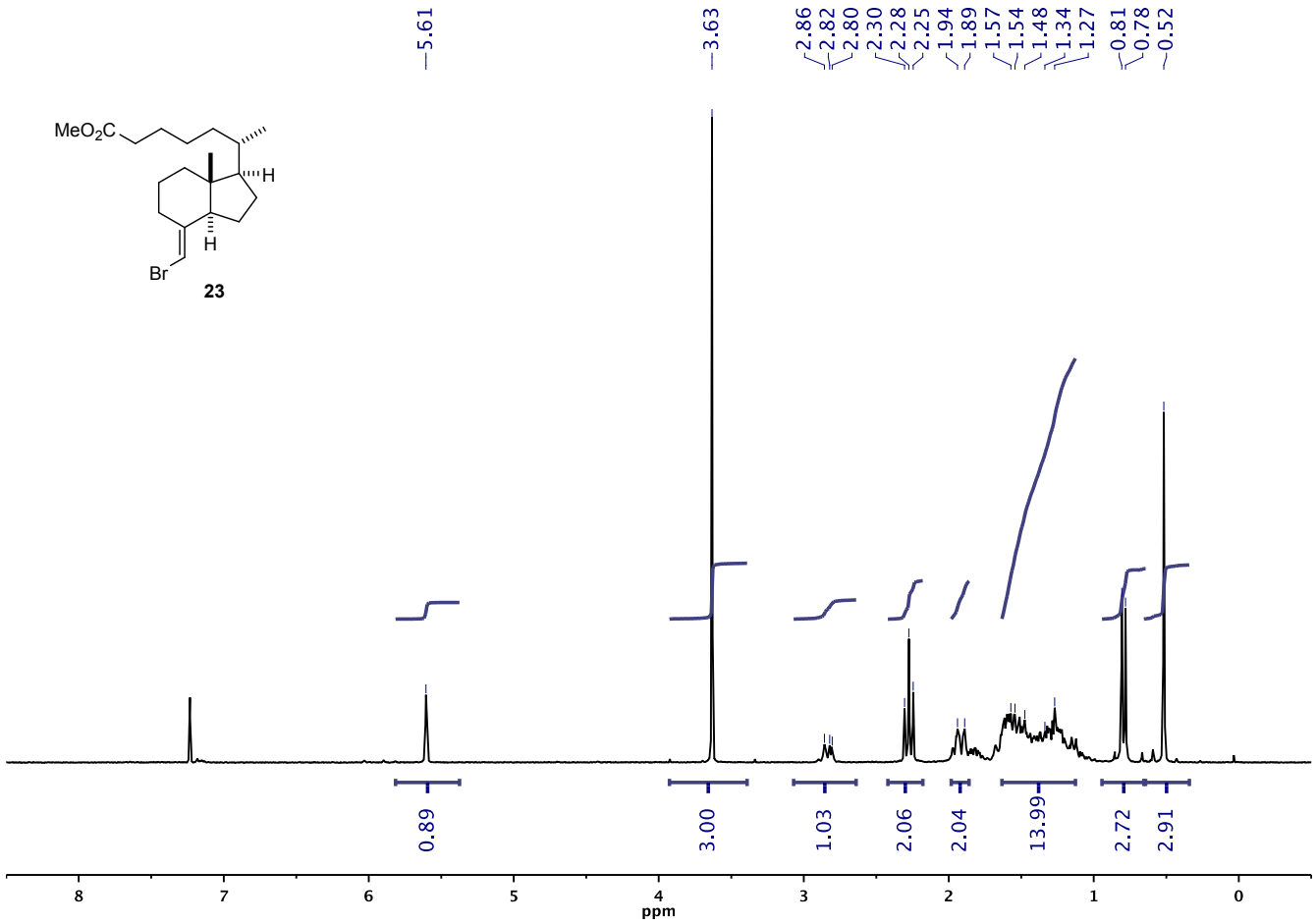
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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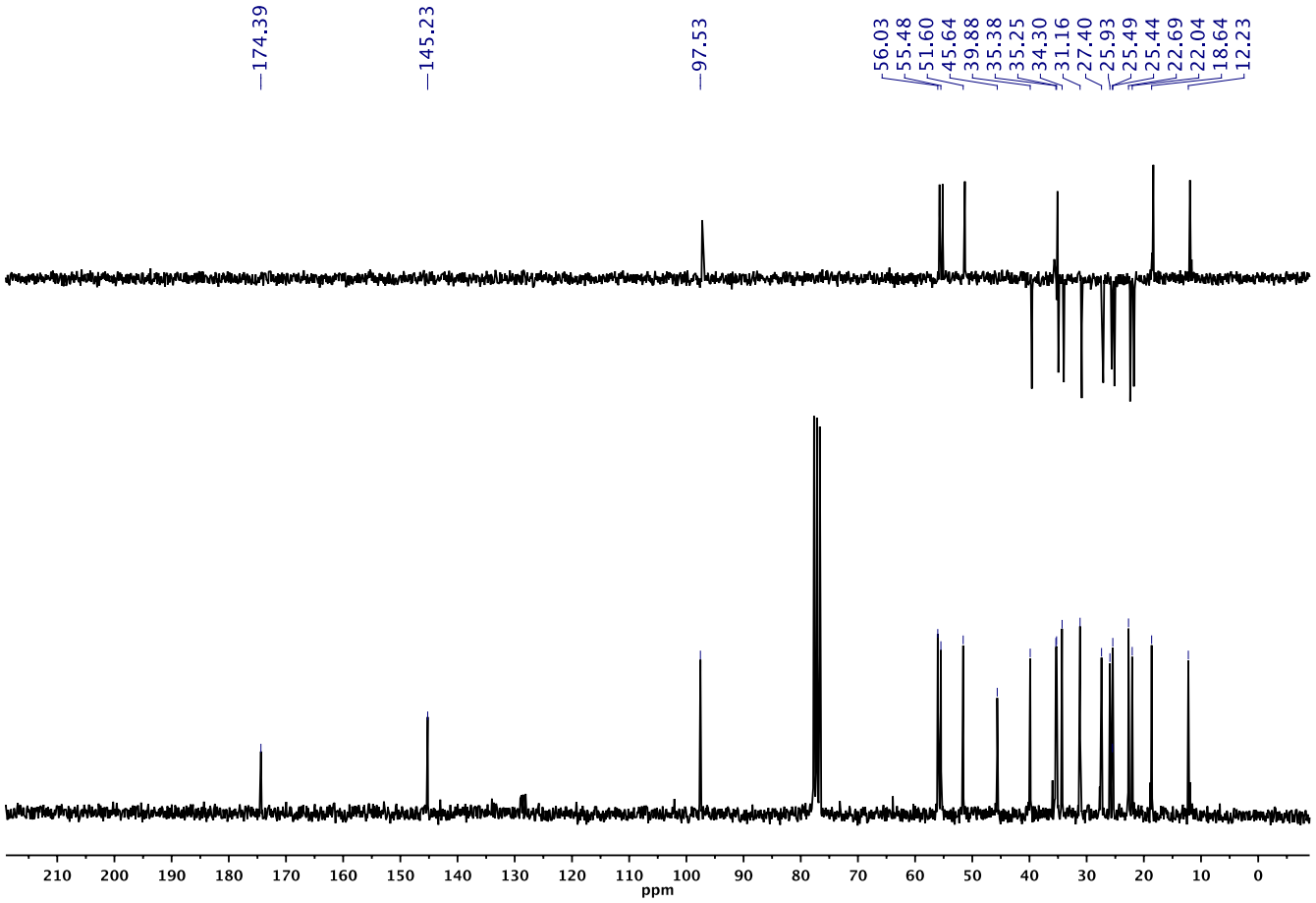
2.82
2.80
2.30
2.28
2.25
1.94
1.89
1.57
1.54
1.48
1.34
1.27
0.81
0.78
0.52
MeO2C
H
H
Br
23
0.89
3.00
1.03
2.06
2.04
13.99
2.72
2.91
ppm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51.60
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39.88
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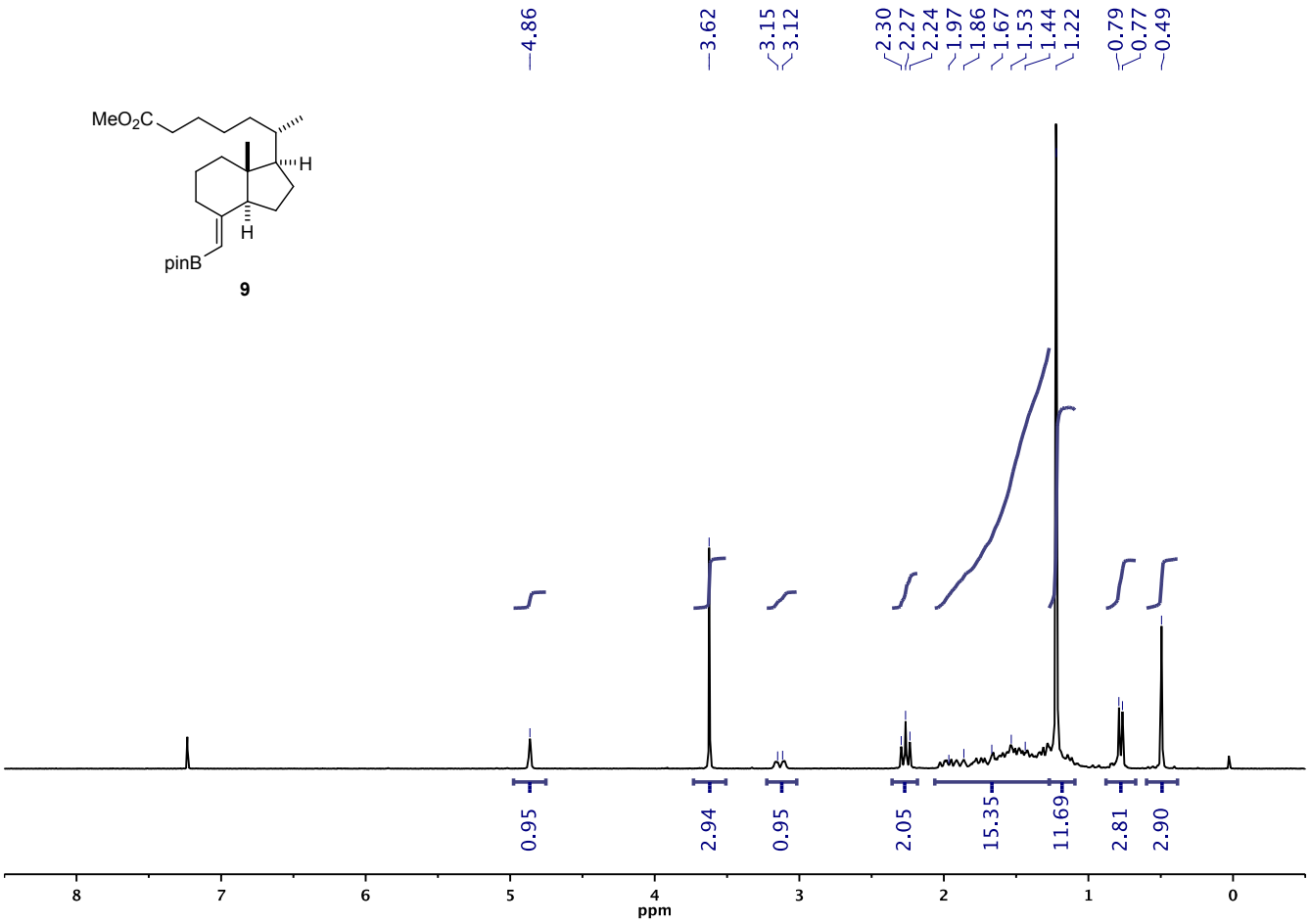
31.16
27.40
25.93
25.49
25.44
22.69
22.04
18.64
12.23
ppm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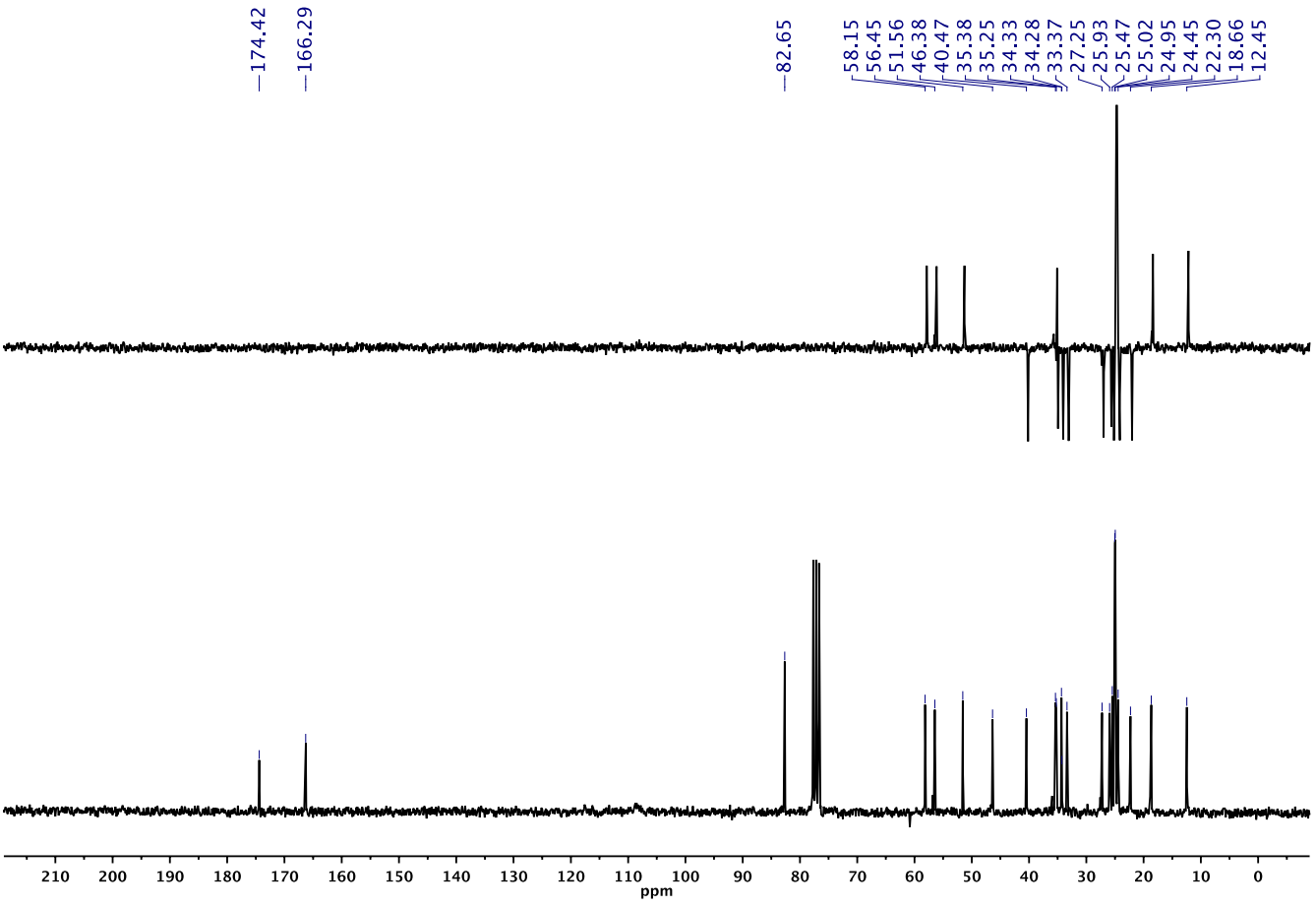
3.12
2.30
2.27
2.24
1.97
1.86
1.67
1.53
1.44
1.22
0.79
0.77
0.49
MeO2C
H
H
pinB
9
0.95
2.94
0.95
2.05
15.35
11.69
2.81
2.90
ppm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35.38
35.25
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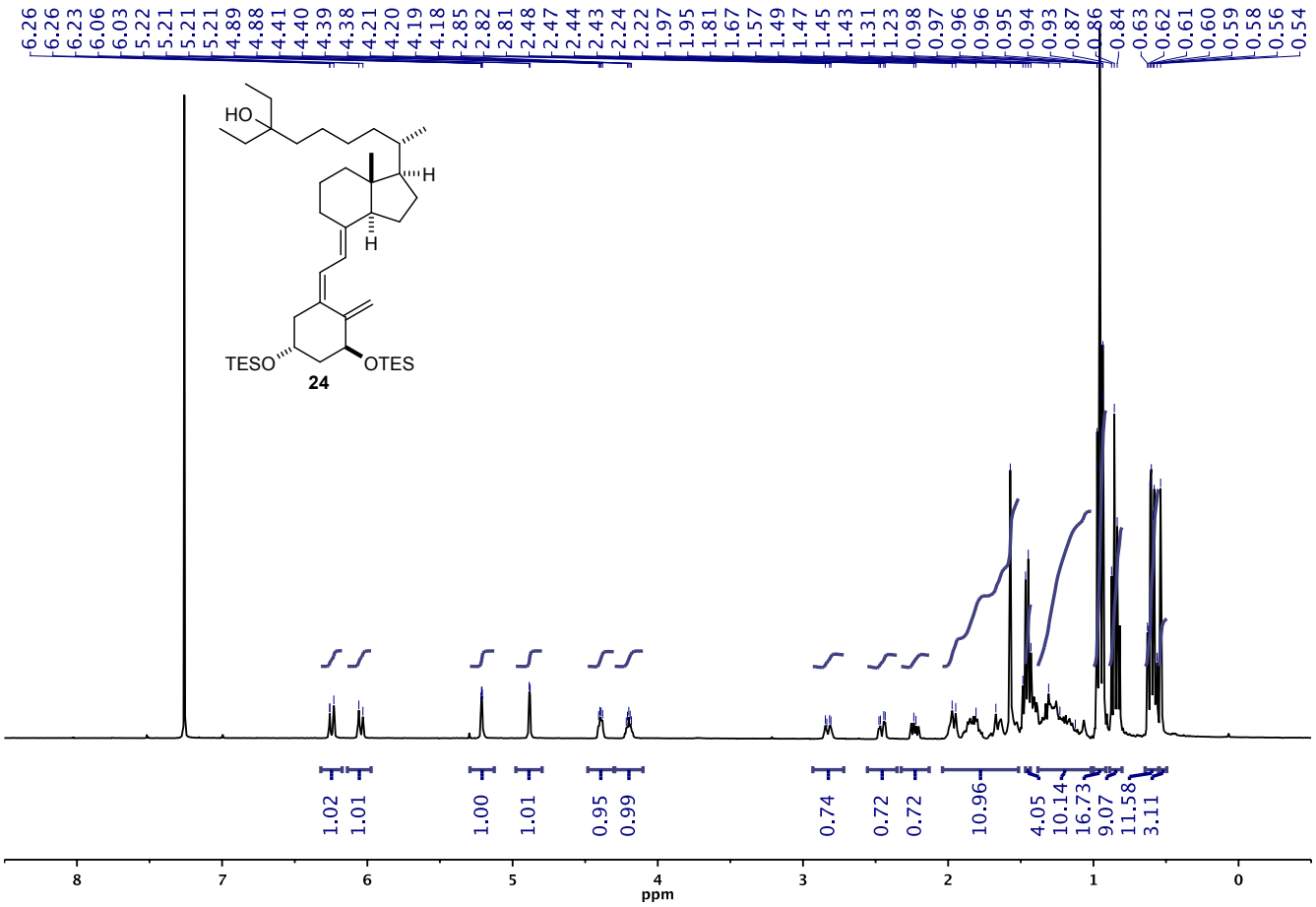
27.25
25.93
25.47
25.02
24.95
24.45
22.30
18.66
12.45
ppm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H
TESO
OTES
24
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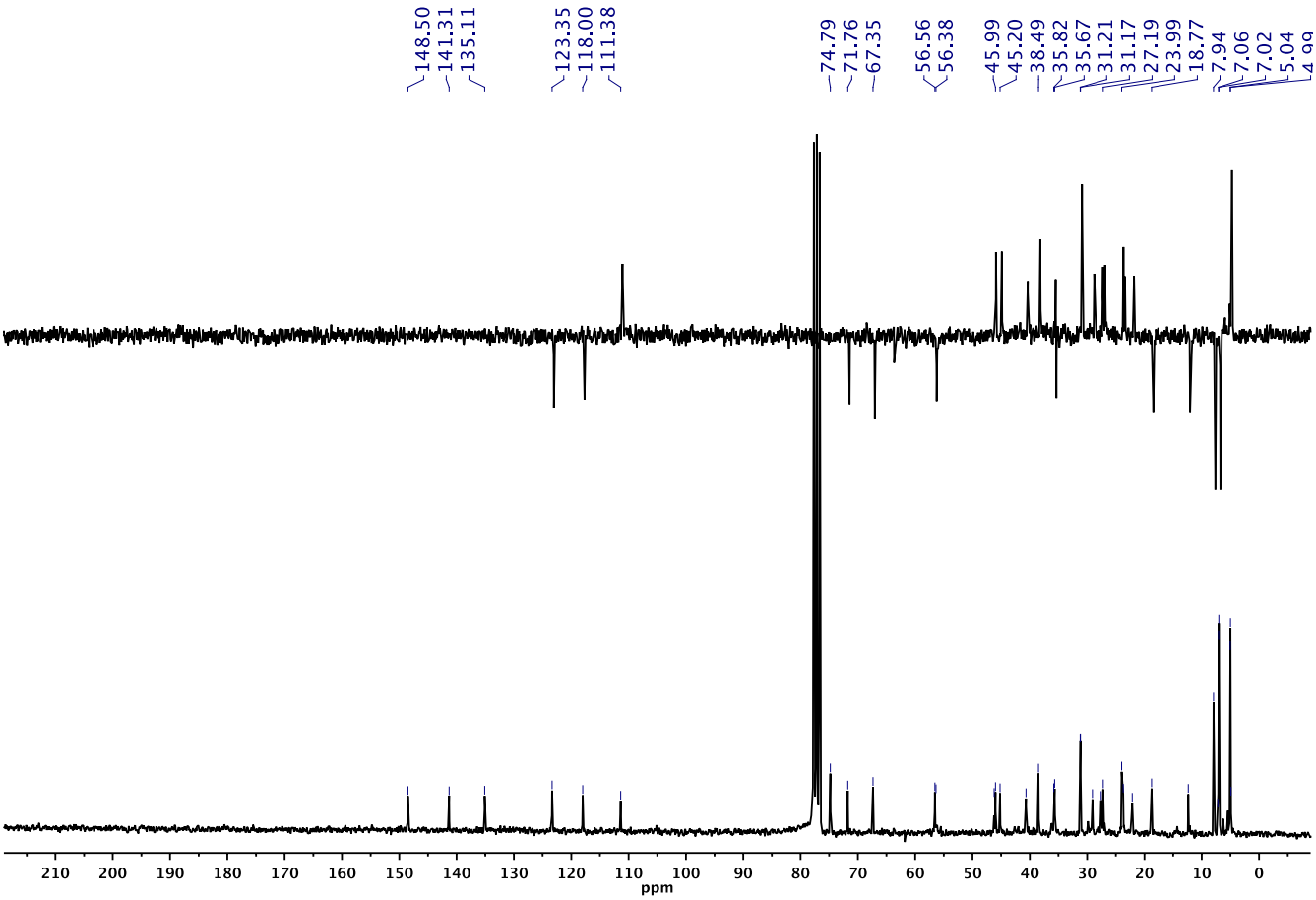
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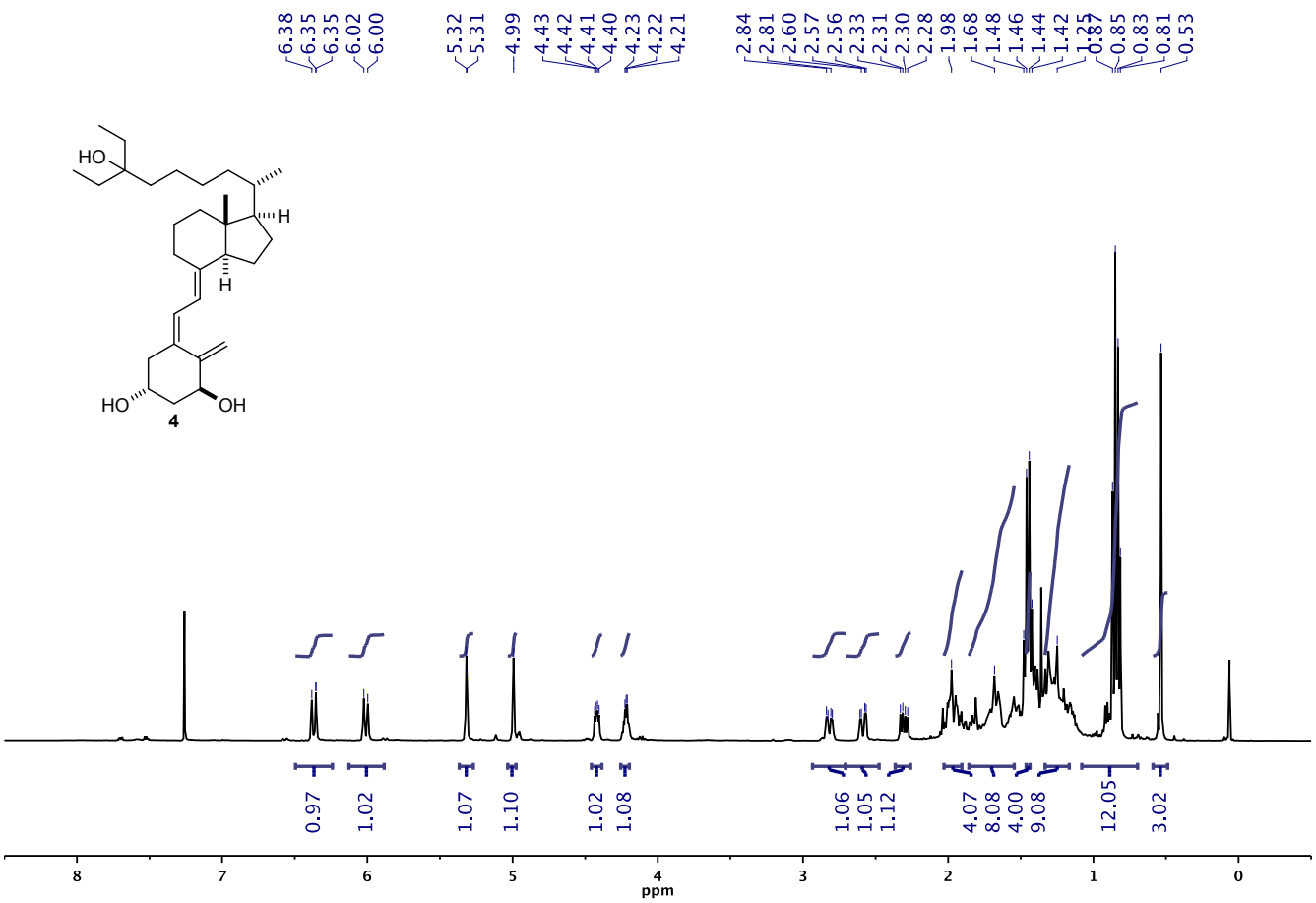
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6.35
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5.31
4.99
4.43
4.42
4.41
4.40
4.23
4.22
4.21
2.84
2.81
2.60
2.57
2.56
2.33
2.31
2.30
2.28
1.98
1.68
1.48
1.46
1.44
1.42
1.25
0.87
0.85
0.83
0.81
0.53
HO
H
H
HO
OH
4
0.97
1.02
1.07
1.10
1.02
1.08
1.06
1.05
1.12
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9.08
12.05
3.02
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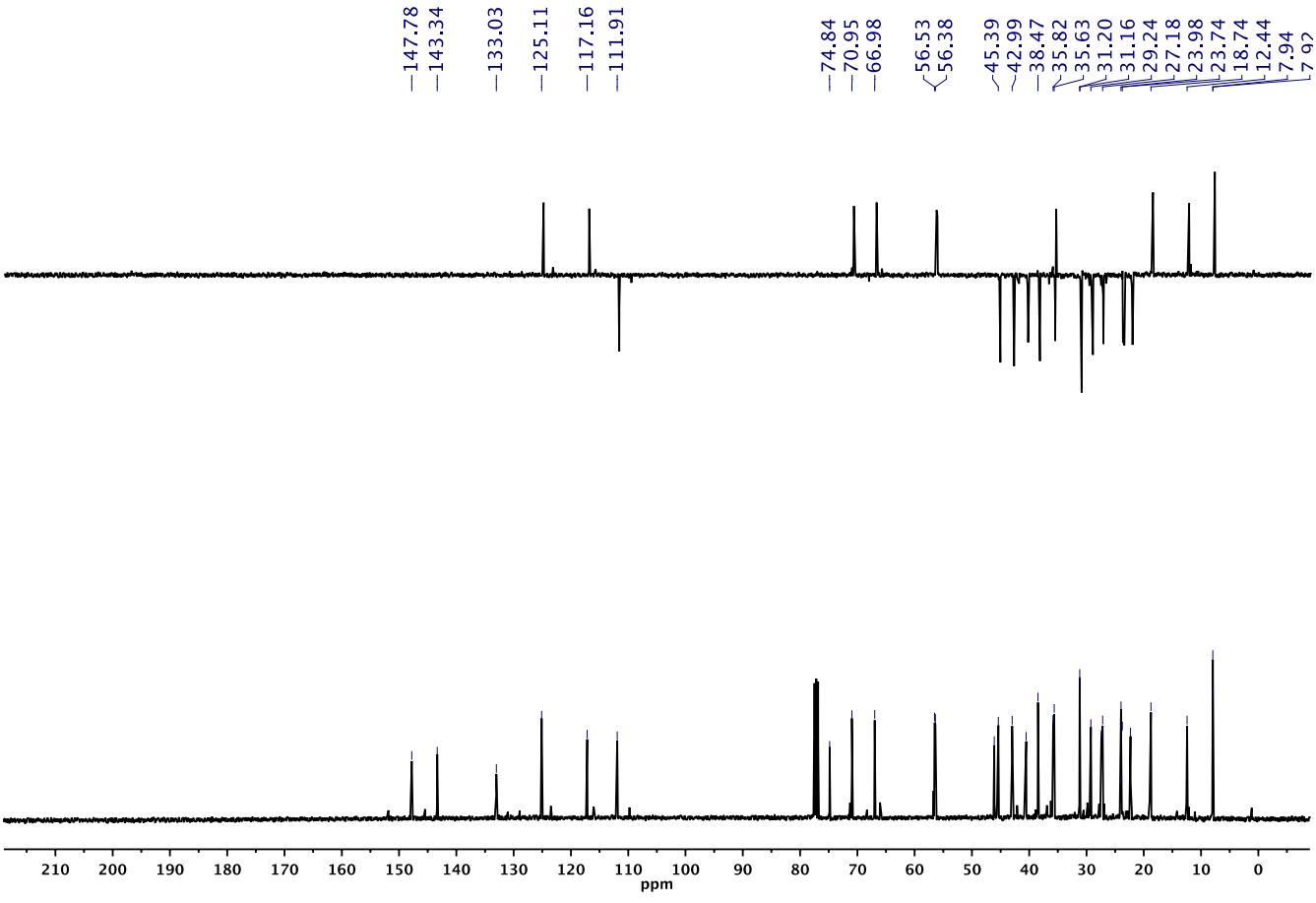
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111.91
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70.95
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56.53
56.38
45.39
42.99
38.47
35.82
35.63
31.20
31.16
29.24
27.18
23.98
23.74
18.74
12.44
7.94
210
200
190
180
170
160
150
140
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120
110
100
90
80
70
60
50
40
30
20
10
0
ppm