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

Supporting Information

A removable functional group strategy for regiodivergent Wittig rearrangement products

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Experimental Procedures

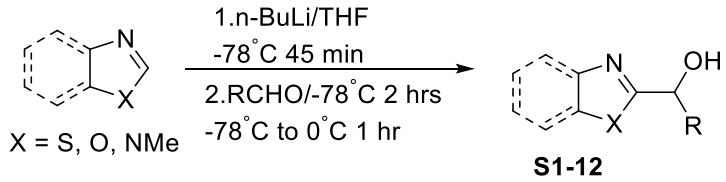
General Information

The regiodivergent rearrangement reactions and ether starting material synthesis were carried out with anhydrous and oxygen-free solvents in flame-dried glasswares under an inert atmosphere. All other reactions were carried out under anhydrous and argon atmosphere. THF was dried over sodium before use. All other solvents were purchased anhydrous and stored under argon over 4 Å molecular sieves. Commercially available reagents were purchased and used as obtained. Analytical thin-layer chromatography was performed on glass plates pre-coated with silica gel (Silica Gel 60 F_{254}; Merck). Plates were visualized using UV light (λ=254 nm) and then stained with either aqueous basic potassium permanganate ($KMnO_4$) or p-anisaldehyde and developed upon heating in Hitachi heat gun. Flash chromatography was performed using silica gel (Merck and Spectrochem, 230-400 mesh), eluting with solvents as indicated. Flash column was performed using Sebo aquarium air pump (SB-548A).

^{1}H and ^{13}C spectras were acquired in deuterated solvents at room temperature on Bruker: Ultrashield 400 MHz, Ultrashield 500 MHz spectrometer. Chemical shifts (δ) are reported for ^{1}HNMR in ppm from TMS as internal standard and ^{13}C from the residual solvent peak. ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reportedin terms of chemical shift (δ ppm).Melting points were checked in Buchi Melting Point B-540 instrument and reported in ºC. FT-IR were analyzed in Bruker ALPHA instrument and reported as cm^{-1}. High resolution (HRMS) mass spectral analyses were recordedon a Thermo Scientific Q-Exactive, Accela 1250 pump.

Preparation of Starting Materials:

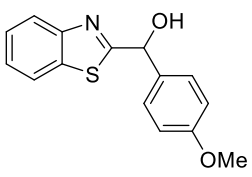
A: Preparation of FG-attached alcohols: The alcohols were prepared by modified literature procedure.[1]



S1-12

In an oven dried 100 ml round bottom flask with a magnetic bar, heterocycle (2.02 g, 15.0 mmol, 1.0 equiv.) was taken in dry THF (30 ml) and cooled to -78°C under argon atmosphere. To the solution, 1.25 equiv of n-BuLi (11.72 ml, 1.6 M in hexane) was added dropwise and stirred further 45 min at -78°C. A solution of aldehyde (18.75 mmol, 1.25 equiv) in THF (5 ml) was slowly added to it with continued stirring at -78°C for 2 additional hour, followed by warming to 0 °C over 1 h before quenching with 40 ml of Sat. NH_4Cl solution.The organic layer was extracted with EtOAc (3 times), and the combined organic layer was dried over anhydrous Na_2SO_4. The solvent removal under reduced pressure gave the crude product which was further purified by crystallization from EtOAc-Hexane (1:2) to obtain the pure product.

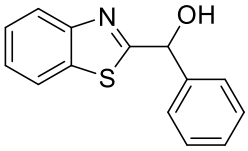
Benzo[d]thiazol-2-yl (4-methoxyphenyl)methanol (S1)



The titled compound was prepared by following the A, obtained as a light yellow solid (2.46 g ,72% yield). ***R*$_f$** (EtOAc/Pet ether = 20:80) = 0.2; **MP =** 100-102 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.78 (s, 3H), 4.11 (br s, 1H), 6.08 (s, 1H), 6.88 (d, *J* = 8.54 Hz, 2H), 7.31 - 7.38 (m, 1 H), 7.39 - 7.50 (m, 3H) 7.82 (d, *J* = 7.93 Hz, 1 H), 7.95 (d, *J* = 7.93 Hz, 1H); **^{13}C NMR (100**

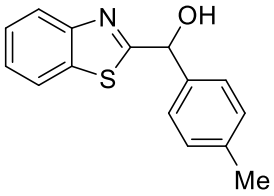
MHz, $CDCl_3$) δ 55.3, 74.0, 114.2, 121.7, 123.0, 125.1, 126.1, 128.2, 133.2, 135.2, 152.7, 159.8, 175.4. **FTIR (cm^{-1}):** 3591, 3020, 2841, 1608, 1216, 837. **HRMS:** Calculated for $C_{15}H_{14}O_2NS$ $[M+H]^+$: 272.0740, found: 272.0739.

Benzo[d]thiazol-2-yl(phenyl)methanol (S2)



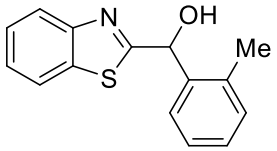
The titled compound was prepared by following A, obtained as a white solid (2.78 g ,77 % yield). The literature reported spectral data was compared favorably with our ^{1}H NMR spectra.[1]

Benzo[d]thiazol-2-yl(p-tolyl)methanol (S3)



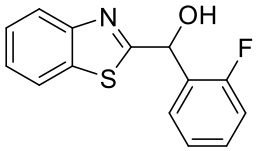
The titled compound was prepared by following A, obtained as a white solid (2.96 g, 77% yield). ***R*$_f$** (EtOAc/Pet ether = 20:80) = 0.2. **MP =** 165-169 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 2.33 (s, 3H), 4.14 (d, *J* = 3.21 Hz, 1H), 6.09 (d, *J* = 2.75 Hz, 1H), 7.17 (d, *J* = 7.79 Hz, 2H), 7.30 - 7.52 (m, 4H), 7.82 (d, *J* = 7.78 Hz, 1H), 7.95 (d, *J* = 7.78 Hz, 1H); **^{13}C NMR (100,$CDCl_3$)** δ 21.2, 74.2, 121.7, 123.0, 125.0, 126.0, 126.7, 129.5, 135.2, 138.0, 138.5, 152.6, 175.3. **FTIR (cm^{-1}):** 3376, 3021, 2835, 1593, 1217, 830. **HRMS:**Calculated for $C_{15}H_{14}ONS$ $[M+H]^+$: 256.0791, found: 256.0789.

Benzo[d]thiazol-2-yl(o-tolyl)methanol (S4)



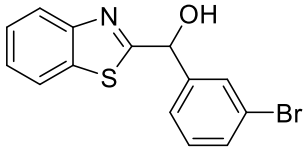
The titled compound was prepared by following A, obtained as a white solid (2.63 g, 69% yield). ***R*$_f$** (EtOAc/Pet ether = 20:80) = 0.2; **MP =** 110-113 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 2.42 (s, 3H), 4.03 (d, *J* = 3.66 Hz, 1H), 6.33 (d, *J* = 3.21 Hz, 1H), 7.17 - 7.21 (m, 1H), 7.22 - 7.27 (m, 2H), 7.33 - 7.39 (m, 1H), 7.43 – 7.47 (m, 1H), 7.50 - 7.54 (m, 1H), 7.76 - 7.88 (m, 1H), 7.98 (d, *J* = 8.24 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 19.4, 71.6, 121.7, 123.1, 125.1, 126.1, 126.4, 126.9, 128.6, 130.9, 135.4, 136.1, 139.0, 152.8, 174.8. **FTIR (cm^{-1}):** 3386, 3021, 1593, 1216, 767. **HRMS:** Calculated for $C_{15}H_{14}ONS$ $[M+H]^+$: 256.0791, found: 256.0787.

Benzo[d]thiazo-2-yl(2-fluorophenyl)methanol (S5)



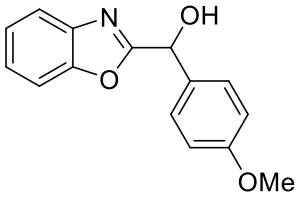
The titled compound was prepared by following A, obtained as a blackish solid (2.86 g, 74% yield). ***R*$_f$** (EtOAc/Pet ether = 20:80) = 0.2; **MP =** 119-121 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.53 (d, *J* = 3.66 Hz, 1H), 6.45 (d, *J* = 2.75 Hz, 1H), 7.04 - 7.11 (m, 1H), 7.16 (td, *J* = 7.56, 1.37 Hz, 1H), 7.28 - 7.39 (m, 2H), 7.42 - 7.48 (m, 1H), 7.55 (td, *J* = 7.56, 1.83 Hz, 1H), 7.79 - 7.86 (m, 1H), 7.97 (d, *J* = 8.24 Hz, 1H); **^{13}C NMR (100 MHz,$CDCl_3$)** δ 68.1, 68.2, 115.7 (d, *J* = 21.1 Hz), 121.7, 123.1, 124.6 (d, *J* = 3.8 Hz), 125.2, 126.2, 128.2, 128.3 (d, *J* = 2.9 Hz), 130.3 (d, *J* = 8.6 Hz), 135.2, 152.4, 160.1 (d, *J* = 248.2 Hz), 173.8. **FTIR (cm^{-1}):** 3389, 3021, 2930, 2860, 1741, 1591, 1495, 1447, 1371, 931. **HRMS:** Calculated for $C_{14}H_{11}ONFS$ $[M+H]^+$: 260.0540, found: 260.0540.

Benzo[d]thiazo-2-yl(3-bromophenyl)methanol (S6)



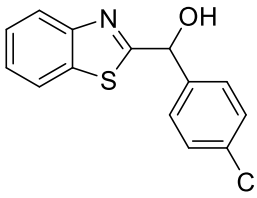
The titled compound was prepared by following A, obtained as a white solid (3.65 g, 76% yield). ***R*$_f$** (EtOAc/Pet ether = 20:80) = 0.2; **MP =** 78-81 °C. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 4.64 (s, 1H), 6.09 (s, 1H), 7.21 (t, *J* = 7.79 Hz, 1H), 7.33 - 7.38 (m, 1H), 7.40 - 7.48 (m, 3H), 7.69 (t, *J* = 1.60 Hz, 1H), 7.79 - 7.86 (m, 1H), 7.93 (d, *J* = 8.24 Hz, 1H); **^{13}C NMR (100 MHz,$CDCl_3$)** δ 73.5, 121.8, 122.8, 123.0, 125.3, 126.3,129.7, 130.3, 131.7, 135.1, 143.0, 152.3, 174.4. **FTIR (cm^{-1}):** 3284, 3068, 2871, 1651, 1578, 1507, 1470, 1427, 1155, 1058, 889. **HRMS:** Calculated for $C_{14}H_{11}ONBrS$ $[M+H]^+$: 319.9739, found: 319.9740.

Benzo[d]oxazol-2-yl(4-methoxyphenyl)methanol(S7)



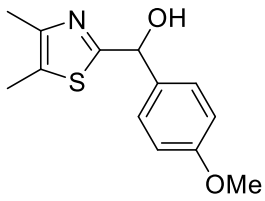
The titled compound was prepared by following A, obtained as a red solid (2.83 g ,74 % yield). The literature reported spectral data was compared favorably with our ^{1}H NMR spectra.[2]

4-(benzo[d]thiazol-2-yl(hydroxy)methyl)benzonitrile (S8)



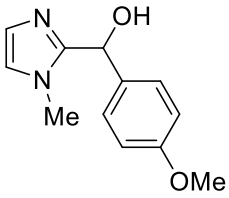
The titled compound was prepared by following A, at -85 °C, obtained as a red solid (3.32 g, 59% yield). ***R*$_f$**(EtOAc/Pet ether = 24:76) = 0.2. **MP =** 111-113 °C. **^{1}H NMR (200 MHz, CDCl$_3$)** δ 4.42 (br s, 1H), 6.21 (s, 1H), 7.32 - 7.54 (m, 2H), 7.66 (m, 4H), 7.83 (d, *J* = 6.87, 1H), 7.94 (d, *J* = 8.01 Hz, 1H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 73.4, 112.2, 118.5, 121.9, 123.1, 125.5, 126.4, 127.2, 132.5, 135.0, 145.7, 152.4, 173.7. **FTIR (cm^{-1}):** 3416, 3022, 2404, 2233, 1658, 1606, 1485, 1418, 1283, 1217, 1125, 1056, 938, 891. **HRMS:** Calculated for $C_{15}H_{11}N_2OS$ [M+H]$^+$: 267.0587, found: 267.0585.

(4, 5 dimethylthiazo-2-yl)(4-methoxyphenyl)methanol (S9)



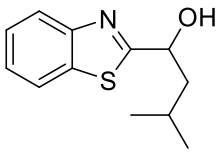
The titled compound was prepared by following A, obtained as a white solid (2.76 g, 74% yield). ***R*$_f$**(EtOAc/Pet ether = 20:80) = 0.2; **MP =** 120-122 °C. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 2.24 - 2.31 (m, 6H), 3.79 (s, 3H), 5.87 (s, 1H), 6.88 (dd, *J* = 8.58, 1.34 Hz, 2H), 7.37 (d, *J* = 8.39 Hz, 2H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 11.3, 14.5, 55.3, 73.2, 114.0, 127.0, 127.9, 134.0, 147.5, 159.6, 169.5. **FTIR (cm^{-1}):** 3375, 3016, 1611, 1512, 1457, 1249, 1218, 1171, 1036, 838. **HRMS:** Calculated for $C_{13}H_{16}NO_2S$ [M+H]$^+$: 272.0716, found: 272.0711.

(4-methoxyphenyl)(1-methyl-1H-imidazol-2-yl)methanol (S10)



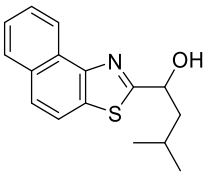
The titled compound was prepared by following A, obtained as a yellow solid (2.67 g, 81% yield). ***R*$_f$**(EtOAc/Pet ether = 45:55) = 0.2. **MP =** 102-104 °C. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 3.38 (s, 3H), 3.78 (s, 3H), 4.48 (br s, 1H), 5.85 (s, 1H), 6.74 (s, 1H), 6.80 - 6.90 (m, 3H), 7.22 (d, *J* = 8.55 Hz, 2H); **^{13}C NMR (100 MHz,CDCl$_3$)** δ 33.0, 55.2, 68.7, 113.8, 122.0, 126.2, 127.6, 133.0, 149.2, 159.0. **FTIR (cm^{-1}):** 3116, 3007, 2950, 2839, 1609, 1506, 1458, 1248, 1176, 1136, 1038, 935, 836. **HRMS:** Calculated for $C_{13}H_{16}NO_2S$ [M+H]$^+$: 219.1128, found: 219.1125.

1-(benzo[d]thiazol-2-yl)-3-methylbutan-1-ol (S11)



The titled compound was prepared by following A, obtained as a yellow solid (1.91 g, 87% yield). ***R*$_f$**(EtOAc/Pet ether = 90:10) = 0.2. **MP =** 57-59 °C. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 1.00 (d, *J* = 6.87 Hz, 3H), 1.10 (d, *J* = 7.63 Hz, 3H), 1.79 – 1.89 (m, 2H), 1.92 - 2.01 (m, 1H), 3.20 (br s, 1H), 5.15 (dd, *J* = 8.96, 4.39 Hz,1H), 7.37 (t, *J* = 7.63 Hz, 1H), 7.46 (t, *J* = 7.82 Hz, 1H), 7.88 (d, *J* = 8.01 Hz, 1H), 7.97 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR (125 MHz, CDCl$_3$)** δ 21.7, 23.3, 24.6, 47.1, 70.8, 121.8, 122.8, 125.0, 126.1, 134.8, 152.8, 176.7. **FTIR (cm^{-1}):** 3377, 3021, 2954, 2880, 1649, 1515, 1428, 1217, 1081, 1042, 928, 875. **HRMS:** Calculated for $C_{12}H_{16}NOS$ [M+H]$^+$: 222.0947, found: 222.0949.

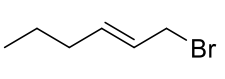
3-methyl-1-(naptho[2,1-d]thiazol-2-yl)butan-1-ol (S12)



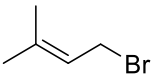
The titled compound was prepared by following A, obtained as a yellow solid (3.62 g, 89% yield). ***R*$_f$**(EtOAc/Pet ether; 90:10) = 0.4; **MP =** 63-65°C. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 1.02 (d, *J* = 6.60 Hz, 3H), 1.03 (d, *J* = 6.61 Hz, 3H), 1.87 – 1.91 (m, 2H), 1.95 - 2.03 (m, 1H), 3.39 (br s, 1H), 5.24 (dd, *J* = 8.39, 5.09 Hz, 1H), 7.55 (t, *J* = 8.12 Hz, 1H), 7.63 (t, *J* = 8.12 Hz, 1H), 7.76 (d, *J* = 8.53 Hz, 1H), 7.83 (d, *J* = 8.80 Hz, 1H), 7.92 (d, *J* = 7.98 Hz, 1H), 8.74 (d, *J* = 8.25

Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 21.9, 23.3, 24.7, 47.4, 70.8, 119.0, 123.7, 125.7, 126.0, 126.9, 128.0, 128.5, 131.5, 131.9, 148.9, 175.3. **FTIR (cm^{-1}):** 3413, 3020, 2960, 2873, 1596, 1512, 1466, 1426, 1373, 1064, 938, 892. **HRMS:** Calculated for $C_{16}H_8NOS$ $[M+H]^+$: 272.1104, found: 272.1102.

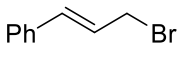
B: General scheme for the synthesis of substituted allyl bromide (3a-d):



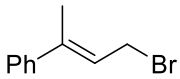
S13



S14



S15

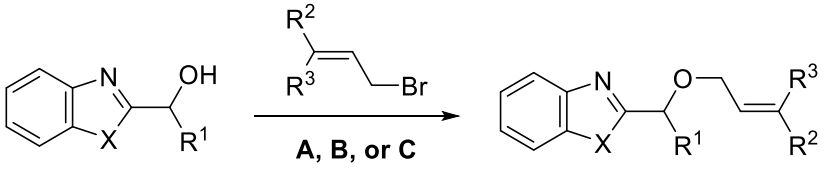


S16

Allyl bromides (**S13-16**) were synthesized following literature procedures.[3]

C: General procedure for the synthesis of ether (1):

The allylether substrates were synthesized from alcohol **S1-12** and allyl bromides **S13-16** via three different reaction conditions. For R^1 = Ar, the α C-H of alcohol is acidic enough for competitive C-alkylation as well as base mediated aerobic auto-oxidation. Hence, reactions with R^1 = Ar were carried out under oxygen-free condition at lower temperature.



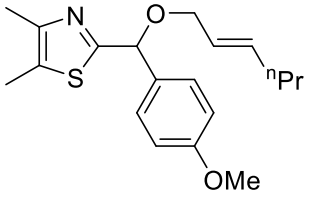
X = S, O
S-1

X = S, O
1

C1: In an oven dried 50 ml round bottom flask with a magnetic bar, alcohol (1 g, 3.69 mmol, 1.0 equiv) and NaOH (1.48 g, 36.88 mmol) were taken followed by sequential application of high vacuum for 5 min and argon back filling (4-5 times) to make the reaction container oxygen free. Dry acetone was purged through argon to make oxygen free and added to the reaction container, and cooled to -20 °C. A solution of allyl bromide (2.5 equiv) in oxygen-free acetone was added to the reaction mixture via cannula under positive argon pressure and sealed with electrical tape. The reaction mixture was stirred at that temperature for the completion, and quenched with saturated NH_4Cl solution.The organic layer was extracted with EtOAc (3 times) and combined organic layer dried over anhydrous Na_2SO_4. The solvent removal under reduced pressure gave the crude product which was further purified by column chromatography on silica gel using acetone-pet ether as eluent to obtain the desired product.

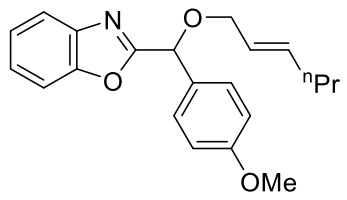
C2: In an oven dried 50 ml round bottom flask with a magnetic bar, alcohol (1 g, 3.69 mmol, 1.0 equiv.), NaOH (1.48 g, 36.88 mmol), and tetrabutylammonium iodide (258 mg, 0.80 mmol) were taken. The reaction container was made oxygen-free according to the previous method. Dry THF was purged with argon to make oxygen free and added to the reaction container, and cooled to 0 °C. A solution of allyl bromide (2.5 equiv) with oxygen-free THF was added to the reaction mixture via cannula under positive argon pressure and sealed with electrical tape. The reaction mixture was stirred at that temperature for 24 hours, and quenched with saturated NH_4Cl solution. The organic layer was extracted with EtOAc (3 times) and combined organic layer dried over anhydrous Na_2SO_4. The solvent removal under reduced pressure gave the crude product which was further purified by column chromatography on silica gel using acetone-pet ether as eluent to obtain the desired product.

(E)-2-((hex-2-ene-1-yloxy)(phenyl)methyl)-4,5-dimethylthiazole (1A-1)



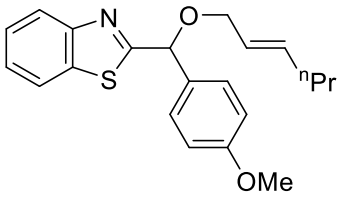
The titled compound was prepared by following the general procedure **C1** at 0 °C for 16 h, obtained as a yellowish liquid (1.12 g, 92% yield). R_f (Acetone/Pet ether = 4:96) = 0.2. **^{1}H NMR (200 MHz, $CDCl_3$)** δ 0.89 (t, *J* = 7.33 Hz, 3H), 1.33 - 1.50 (m, 2H), 1.95 - 2.09 (m, 2H), 2.27 (s, 3H), 2.29 (s, 3H), 3.79 (s, 3H), 4.02 (d, *J* = 5.18 Hz, 2H), 5.58 (s, 1H), 5.59 - 5.78 (m, 2H), 6.87 (d, *J* = 8.72 Hz, 2H), 7.37 (d, *J* = 8.59 Hz, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 11.3, 13.7, 14.7, 22.2, 34.4, 55.2, 69.8, 79.6, 113.9, 125.8, 126.7, 128.2, 132.3, 135.2, 147.6, 159.4, 168.4. **FTIR (cm^{-1}):** 3017, 2960, 2868, 1718, 1605, 1512, 1457, 1296, 1250, 1174, 1040, 973, 906, 837. **HRMS:** Calculated for $C_{20}H_{22}ONS$ $[M+H]^+$: 332.1679, found: 332.1675.

(E)-2-((hex-2-ene-1-yloxy)(4-methoxyphenyl)methyl)benzo[d]oxazole (1A-2)



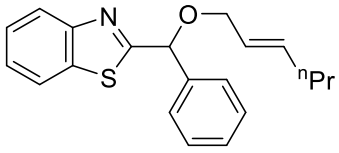
The titled compound was prepared by following the general procedure **C1** for 24 h, obtained as a yellowish liquid (970 mg, 78% yield). R_f (Acetone/Pet ether; 4:96) = 0.2; **^{1}H NMR (200 MHz, $CDCl_3$)** δ 0.88 - 0.93 (m, 3H), 1.33- 1.44 (m, 2H), 1.96-2.06 (m, 2H), 3.79 (s, 3H), 4.06 - 4.11 (m, 2H), 5.62 - 5.71 (m, 3H), 6.88 - 6.93 (m, 2H), 7.31 (m, 2H), 7.46 - 7.51 (m, 3H), 7.72 (m, 1H); **^{13}C NMR (50 MHz, $CDCl_3$)** δ 13.7, 22.1, 34.3, 55.3, 70.2, 75.7, 110.9, 114.1, 120.3, 124.3, 125.1, 125.3, 128.5, 128.7, 129.2, 136.2, 150.8, 159.9, 165.0. **FTIR (cm^{-1}):** 3061, 2957, 2926, 2866, 1720, 1606, 1511, 1455, 1249, 1169, 1042, 911. **HRMS:** m/z calculated for $C_{21}H_{24}O_3N$$[M+H]^+$: 338.1751, found: 338.1749.

(E)-2-((hex-2-ene-1-yloxy)(4-methoxyphenyl)methyl)benzo[d]thiazole (1A-3)



The titled compound was prepared by following the general procedure **C1** for 24 h, obtained as a yellowish liquid (977 mg, 75% yield). R_f (Acetone/Pet ether = 4:96) = 0.2. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 0.90 (t, *J* = 7.44 Hz, 3H), 1.40 (sex, *J* = 7.40 Hz, 2H), 2.03 (q, *J* = 6.87 Hz, 2H), 3.75 (s, 3H), 4.06 - 4.14 (m, 2H), 5.57 - 5.66 (m, 1H), 5.68 - 5.77 (m, 1H), 5.80 (s, 1H), 6.88 (d, *J* = 8.39 Hz, 2H), 7.28 - 7.34 (m, 1H), 7.38 - 7.47 (m, 3H), 7.83 (d, *J* = 8.01 Hz, 1H), 7.97 (d, *J* = 8.01 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 13.6, 22.1, 34.3, 55.1, 70.0, 79.8, 114.0, 121.6, 123.0, 124.8, 125.4, 125.7, 128.4, 131.3, 135.0, 135.6, 153.0, 159.5, 174.5**. FTIR (cm^{-1}):** 3065, 2957, 2868, 1604, 1511, 1452, 1252, 1708, 1168, 1106, 1042, 971, 910, 837. **HRMS:** Calculated for $C_{21}H_{24}O_2NS$ $[M+H]^+$: 354.1522, found: 354.1519.

(E)-2-((hex-2-ene-1-yloxy)(phenyl)methyl)benzo[d]thiazole (1A-4)

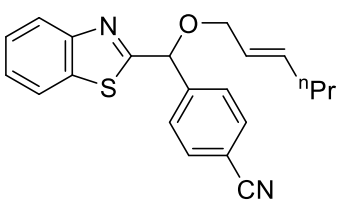


The titled compound was prepared by following the general procedure **C1** for 24 h, obtained as a yellowish liquid (1.03 g, 76% yield). R_f (Acetone/Pet ether = 4:96) = 0.2. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 0.90 (t, *J* = 7.25 Hz, 3H), 1.41 (sxt, *J* = 7.40 Hz, 2H), 2.04 (q, *J* = 6.99 Hz, 2H), 4.08 – 4.18 (m, 2H), 5.56 - 5.769 (m, 1H), 5.69 - 5.79 (m, 1H), 5.85 (s, 1H), 7.27 - 7.32 (m, 1H), 7.35 (q, *J* = 7.25 Hz, 3H), 7.43 (t, *J* = 7.63 Hz, 1H), 7.53 (d, *J* = 7.25 Hz, 2H), 7.86 (d, *J* = 8.01 Hz, 1H), 7.98 (d, *J* = 8.01 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 13.7, 22.2, 34.4, 70.3, 80.2, 121.7, 123.1, 125.0, 125.4, 125.8, 127.1, 128.3, 128.6, 135.1, 135.8, 139.3, 153.1, 174.3. **FTIR (cm^{-1}):** 3020, 2959, 2926 2864, 1721, 1597, 1504, 1446, 1216, 1066, 1017, 976, 914. **HRMS:**Calculated for $C_{20}H_{22}ONS$ $[M+H]^+$: 324.1417, found: 324.1413.

(E)-4-((benzo[d]thiazol-2-yl)(hex-2-ene-1-yloxy)methyl)benzonitrile (1A-5)

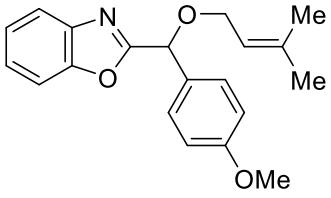
In an oven dried 50 ml round bottom flask with a magnetic bar, alcohol **S8** (300 mg, 1.13 mmol, 1.0 equiv), Ag_2O (1.47 g, 6.40 mmol) and allyl bromide (551 mg, 3.377 mmol) were taken followed by sequential application of high vacuum for 5 min and argon back filling (4-5 times) to make the reaction container oxygen free. Dry Diethyl ether was purged through argon to make oxygen free and added to the reaction container via cannula under positive argon pressure at room temperature and sealed with electrical tape. The reaction container was covered by aluminium foil and stirred at room temperature for 3 hours. The reaction mixture was

filtrate by passing through Celite-545 and washed with diethyl ether. The solvent removal under reduced pressure gave the crude product which was further purified by column chromatography on silica gel using acetone-pet ether as eluent to obtain the desired product (168 mg, 43% yield). R_f(Acetone/Pet ether = 4:96) =



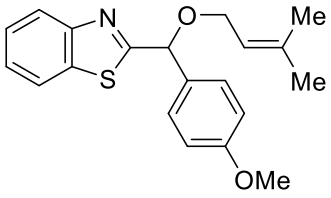
0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.90 (t, *J* = 7.63 Hz, 3H), 1.36 – 1.45 (m, 2H), 2.05 (q, *J* = 6.71 Hz, 2H), 4.15 (d, *J* = 5.49 Hz, 2H), 5.54 - 5.68 (m, 1H), 5.68 - 5.82 (m, 1H), 5.89 (s, 1H), 7.33 - 7.42 (m, 1H), 7.46 (t, *J* = 7.63 Hz, 1H), 7.66 (m, 4H), 7.87 (d, *J* = 7.93 Hz, 1H), 7.98 (d, *J* = 7.93 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 13.6, 22.1, 34.3, 70.8, 79.3, 112.1, 118.6, 121.8, 123.2,124.9, 125.3, 126.1, 127.6, 132.4, 135.0, 136.5, 144.5, 153.0, 172.8. **FTIR (cm^{-1}):** 3599, 3416, 2999, 2930, 1738, 1429, 1362, 1227, 1094, 1048, 905. **HRMS:** Calculated for $C_{21}H_{21}ON_2S$ $[M+H]^+$: 349.1369, found: 349.1369.

2-((4-methoxyphenyl)((3-methylbut-2-ene-1-yl)oxy)methyl)benzo[d]thiazole (1B-2)



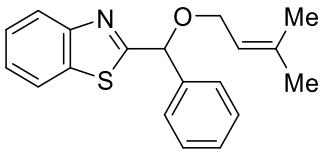
The titled compound was prepared by following the general procedure **C1** at 0 °C for 16 h, obtained as a yellowish liquid (911 mg, 72% yield). R_f(Acetone/pet ther = 04:96) = 0.2. **^{1}H NMR (200 MHz, $CDCl_3$)** δ 1.59 (s, 3H), 1.73 (s, 3H), 3.79 (s, 3H), 4.11(d, *J* = 6.595 Hz, 2H), 5.42 (t, *J* = 7.10 Hz, 1H), 5.67 (s, 1H), 6.91 (d, *J* = 8.84 Hz, 2H), 7.27 - 7.36 (m, 2H), 7.43 - 7.56 (m, 3H), 7.65 - 7.76 (m, 1H); **^{13}C NMR (50 MHz, $CDCl_3$)** δ 18.1, 25.8, 55.3, 65.9, 76.0, 110.9, 114.1, 120.19, 120.3, 124.3, 125.1, 128.7, 129.3, 138.5, 140.8, 150.9, 159.9, 165.1. **FTIR (cm^{-1}):** 2927, 1614, 1512, 1457, 1248, 1173, 1073. **HRMS:** Calculated for $C_{20}H_{22}O_3N$ $[M+H]^+$: 324.1594, found: 324.1593.

2-((4-methoxyphenyl)((3-methylbut-2-ene-1-yl)oxy)methyl)benzo[d]thiazole (1B-3)



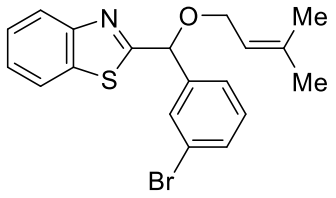
The titled compound was prepared by following the general procedure **C1** at 0 °C for 16 h, obtained as a yellowish liquid (959 mg, 76% yield). R_f(Acetone/pet ether = 04:96) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 1.61 (s, 3H), 1.76 (s, 3H), 3.78 (s, 3H), 4.14 (d, *J* = 7.32 Hz, 2H), 5.44 (t, *J* = 6.71 Hz, 1H), 5.77 (s, 1H), 6.91 (d, *J* = 8.54 Hz, 2H), 7.32 - 7.41 (m, 1H), 7.42 - 7.50 (m, 3H), 7.88 (d, *J* = 7.93 Hz, 1H), 7.99 (d, *J* = 8.55 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 18.2, 25.8, 55.2, 65.9, 80.0, 114.0, 120.3, 121.7, 123.1, 124.9, 125.8, 128.4, 131.6, 135.2, 138.2, 153.1, 159.6, 174.7. **FTIR (cm^{-1}):** 3064, 2925, 2860, 1709, 1602, 1510, 1449, 1251, 1168, 1118, 1069, 1032, 836. **HRMS**: Calculated for $C_{20}H_{22}O_2NS$ $[M+H]^+$: 340.1366, found: 340.1362.

2-(((3-methylbut-2-en-1-yl)oxy)(phenyl)methyl)benzo[d]thiazole (1B-4)



The titled compound was prepared by following the general procedure **C1** at 0 °C for 16 h, obtained as a yellowish liquid (1.11 g, 81% yield). R_f(Acetone/pet ether = 04:96) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 1.61 (s, 3H), 1.76 (s, 3H), 4.17 (d, *J* = 6.71 Hz, 2H), 5.45 (t, *J* = 6.71 Hz, 1H), 5.83 (s, 1H), 7.26 - 7.38 (m, 4H), 7.40 - 7.48 (m, 1H), 7.53 (d, *J* = 7.32 Hz, 2H), 7.85 (d, *J* = 7.93 Hz, 1H), 7.98 (d, *J* = 8.55 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 18.1, 25.8, 66.1, 80.4, 120.2, 121.7, 123.1, 125.0, 125.8, 127.0, 128.3, 128.6, 135.2, 138.3, 139.4, 153.1, 174.33. **FTIR (cm^{-1}):** 3018, 2977, 2927, 2869, 1719, 1672, 1597, 1509, 1445, 1382, 1216, 1161, 1065, 996, 941. **HRMS** :Calculated for $C_{20}H_{22}O_2NS$ $[M+H]^+$: 310.1260. found: 310.1254.

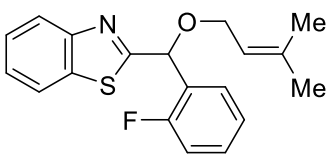
2-((3-bromophenyl)((3-methylbut-2-ene-1-yl)oxy)methyl)benzo[d]thiazole (1B-5)



The titled compound was prepared by following the general procedure **C1** at -40 °C for 16 h (1.5 mmol), obtained as a yellowish liquid (156 mg, 62% yield). R_f (Acetone/pet ether = 04:96) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 1.62 (s, 3H), 1.77 (s, 3H), 4.17 (d, *J* = 7.32 Hz, 2H), 5.43 (t, *J* = 6.71 Hz, 1H), 5.78 (s, 1H), 7.23 (t, *J* = 7.63 Hz, 1H), 7.37 (t, *J*=7.63 Hz, 1H), 7.40 - 7.50 (m, 3H), 7.70 (s, 1H), 7.88 (d, *J* = 7.93 Hz, 1H), 7.99 (d, *J* = 8.55 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 18.2, 25.9, 66.3, 79.6, 119.9, 121.8, 122.7, 123.2 , 125.2, 125.7, 126.0, 129.9, 130.1, 131.4, 135.1, 138.8, 141.7, 153.0, 173.6. **FTIR (cm^{-}**

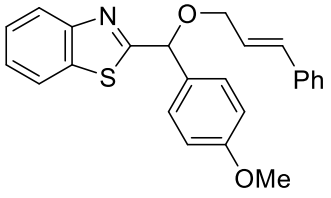
[1]): 3020, 2927, 2864, 1582, 1515, 1432, 1163, 1068, 930. **HRMS:** Calculated for $C_{19}H_{19}ONBrS$ $[M+H]^+$: 388.0365, found: 388.0367.

2-((2-fluorophenyl)((3-methylbut-2-ene-1-yl)oxy)methyl)benzo[d]thiazole (1B-6)



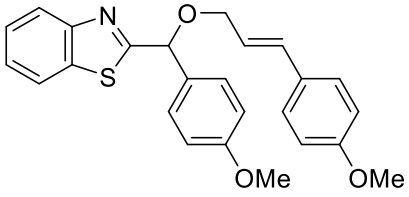
The titled compound was prepared by following the general procedure **C1** at -20 °C for 16 h (1.93 mmol), obtained as a yellowish liquid (245 mg, 74% yield; based on 50% starting material recovery). R_f (Acetone/pet ether = 04:96) = 0.2. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 1.62 (s, 3H), 1.76 (s, 3H), 4.19 (d, *J* = 6.87 Hz, 2H), 5.44 (t, *J* = 6.87 Hz, 1H), 6.17 (s, 1H), 7.07 (t, *J* = 9.16 Hz, 1H), 7.11 (t, *J* = 7.63 Hz, 1H), 7.26 - 7.32 (m, 1H), 7.35 (t, *J* = 7.63 Hz, 1H), 7.43 (t, *J* = 7.25 Hz, 1H), 7.54 (t, *J* = 7.44 Hz, 1H), 7.87 (d, *J* = 8.01 Hz, 1H), 7.99 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 18.1, 25.8, 66.3, 73.8, 73.8, 115.6 (d, *J* = 21.0 Hz), 120.0, 121.6, 123.3, 124.4 (d, *J* = 2.9 Hz), 125.0, 126.5 (d, *J* = 13.4 Hz), 128.7 (d, *J* = 2.86 Hz), 130.1 (d, *J* = 8.6 Hz), 135.1, 138.7, 153.2, 160.5 (d, *J* = 249.5 Hz), 172.9. **FTIR (cm^{-1}):** 3018, 2926, 2863, 1671, 1589, 1494, 1160, 1063, 938. **HRMS:** Calculated for $C_{19}H_{19}ONFS$ $[M+H]^+$: 328.1166, found: 328.1165.

2-((cinnamyloxy)((4-methoxyphenyl)methyl)benzo[d]thiazole (1C-1)



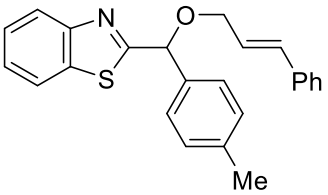
The titled compound was prepared by following the general procedure **C1** for 48h (1.84 mmol), obtained as a yellowish liquid (605 mg, 85% yield). R_f (Acetone/Pet ether = 05:95) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.77 (s, 3H), 4.30 – 4.32 (m, 2H), 5.86 (s,1H), 6.30 – 6.38 (m, 1H), 6.64 (d, *J* = 16.03 Hz, 1H), 6.89 - 6.96 (m, 2H), 7.22 - 7.28 (m, 1H), 7.30 - 7.38 (m, 3H), 7.36 - 7.40 (m, 2H), 7.40 - 7.42 (m, 1H), 7.44 - 7.49 (m, 2H), 7.85 (d, *J*=7.33 Hz, 1H), 7.98 (d, *J*= 8.24 Hz, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 55.2, 69.9, 80.3, 114.1, 121.7, 123.1, 125.0, 125.0, 125.9, 126.5, 127.8, 128.5, 128.5, 131.2, 133.2, 135.0, 136.5, 153.1, 159.7, 174.2. **FTIR (cm^{-1}):** 3016, 2849, 1605, 1510, 1450, 1250, 1219, 1167, 1110, 1041, 970, 836. **HRMS:** Calculated for $C_{24}H_{22}O_2NS$ $[M+H]^+$: 388.1366, found: 388.1365.

(E)-2-((4-methoxyphenyl)((3-(4-methoxyphenyl)allyl)oxy)methyl)benzo[d]thiazole (1C-2)



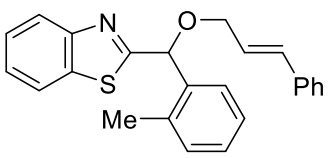
The titled compound was prepared by following the general procedure **C1** at -30 °C for 48h (1.84 mmol), obtained as a yellowish liquid (559 mg, 73% yield). R_f (Acetone/Pet ether = 05:95) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.79 (s, 3H), 3.81 (s, 3H), 4.27 - 4.32 (m, 2H), 5.86 (s, 1H), 6.18 - 6.25 (m, 1H), 6.58 (d, *J* = 16.05Hz 1H), 6.86 (d, *J* = 8.54 Hz, 2H), 6.91 (d, *J* = 8.55 Hz, 2H), 7.30 - 7.38 (m, 3H), 7.41 - 7.49 (m, 3H), 7.87 (d, *J* = 7.93 Hz, 1H), 7.98 (d, *J* = 7.93 Hz, 1H); **^{13}C NMR ($CDCl_3$, 50 MHz)** δ 55.3, 70.2, 80.2, 114.0, 114.2, 121.8, 122.8, 123.2, 125.0, 125.9, 127.9, 128.6, 129.3, 131.4, 133.1, 135.2, 153.2, 159.5, 159.8, 174.4. **FTIR (cm^{-1}):** 3014, 2926, 2847, 1715, 1606, 1511, 1454, 1250, 1171, 1110, 1037, 970, 838. **HRMS:** Calculated for $C_{25}H_{24}O_3NS$ $[M+H]^+$: 418.1471, found: 418.1469.

2-((cinnamyloxy)(4-tolyl)methyl)benzo[d]thiazole (1C-3)



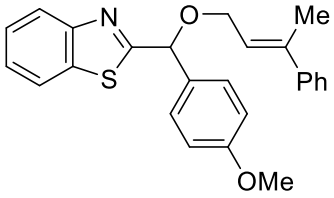
The titled compound was prepared by following the general procedure **C1** for 48 h (1 mmol), obtained as a yellowish liquid (258 mg, 71% yield). R_f (Acetone/Pet ether = 05:95) = 0.2. **^{1}H NMR (200 MHz, $CDCl_3$)** δ 2.33 (s, 3 H), 4.32 (d, *J* = 6.19 Hz, 2H), 5.88 (s, 1H), 6.28- 6.41 (m, 1H), 6.64 (d, *J* = 16.07 Hz, 1H), 7.15 - 7.25 (m, 3H), 7.32 - 7.47 (m, 8H), 7.85 (d, *J* = 8.72 Hz, 1H), 7.98 (d, *J* = 8.72 Hz, 1H); **^{13}C NMR ($CDCl_3$, 50 MHz)** δ 21.2, 70.0, 80.6, 121.7, 123.2, 125.0, 125.1, 125.8, 126.5, 127.0, 127.8, 128.5, 129.4, 133.2, 135.1, 136.1, 136.5, 138.3, 153.1, 174.1. **FTIR (cm^{-1}):** 3020, 2928, 2864, 1716, 1605, 1511, 1444, 1285, 1217, 1165, 1113, 1062, 970, 902. **HRMS:** Calculated for $C_{24}H_{22}ONS$ $[M+H]^+$: 372.1417, found: 372.1415.

2-((cinnamyloxy)(2-tolyl)methyl)benzo[d]thiazole (1C-4)



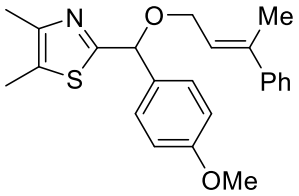
The titled compound was prepared by following the general procedure **C1** for 48 h (1 mmol), obtained as a yellowish liquid (145 mg, 40% yield). R_f (Acetone/Pet ether = 05:95) = 0.2. **^{1}H NMR (200 MHz, $CDCl_3$)** δ 2.42 (s, 3H), 4.27 – 4.32 (m, 2H), 6.07 (s, 1H), 6.25- 6.38 (m, 1H), 6.61 (d, *J* = 16.09 Hz, 1H), 7.09 - 7.24 (m, 5H), 7.26 - 7.38 (m, 5H), 7.59 - 7.66 (m, 1H), 7.78 (d, *J* = 8.72 Hz, 1H), 7.97 (d, *J* = 8.72 Hz, 1H); **^{13}C NMR ($CDCl_3$, 50 MHz)** δ 19.5, 69.9, 77.8, 121.6, 123.1, 124.9, 125.0, 125.7, 126.2, 126.4, 126.8, 127.7, 128.3, 128.4, 130.7, 133.0, 135.1, 136.3, 136.3, 137.3, 153.0, 173.2. **FTIR (cm^{-1}):** 3018, 2975, 2928, 1710, 1596, 1504, 1450, 1161, 1113, 1058, 970, 929. **HRMS:** Calculated for $C_{24}H_{22}ONS$ $[M+H]^+$: 372.1417, found: 372.1417.

(E)-2-((4-methoxyphenyl)((3-phenylbut-2-ene-1-yl)methyl)benzo[d]thiazole (1D-1)

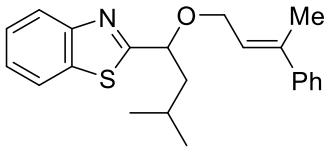


The titled compound was prepared by following the general procedure **C1** for 48 h (3.69 mmol), obtained as a yellowish liquid (1.05 g, 71% yield). R_f (Acetone/Pet ether = 05:95) = 0.2. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 2.01 (s, 3H), 3.79 (s, 3H), 4.37 (d, *J* = 6.69 Hz, 2H), 5.84 (s, 1H), 6.01 (t, *J* = 6.49 Hz, 1H), 6.83 - 6.97 (m, 2H), 7.25 - 7.53 (m, 9H), 7.81 - 7.92 (m, 1H), 7.92 - 8.05 (m, 1H); **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 16.3, 22.0, 23.2, 24.7, 46.5, 67.1, 78.2, 122.0, 123.0, 123.5, 125.1, 125.8, 126.0, 127.3, 128.2, 135.1, 139.3, 142.8, 153.2, 176.4. **FTIR (cm^{-1}):** 3065, 2937, 2847, 1693, 1603, 1507, 1450, 1377, 1251, 1169, 1041, 909, 837. **HRMS:** Calculated for $C_{25}H_{24}O_2NS$ $[M+H]^+$: 402.1522, found: 402.1523.

(E)-2-((4-methoxyphenyl)((3-phenylbut-2-ene-1-yl)oxy)methyl)-4,5-dimethylthiazole (1D-2)



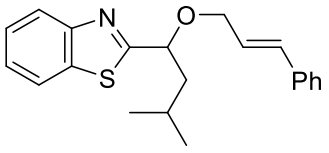
The titled compound was prepared by following the general procedure **C2** at 0 °C for 14 h (2 mmol), obtained as a yellowish liquid (633 mg, 83% yield). R_f (Acetone/Pet ether = 05:95) = 0.2. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 1.20 (s, 3H), 2.28 (s, 3H), 2.30 (s, 3H), 3.79 (s, 3H), 4.29 (d, *J* = 6.49 Hz, 2H), 5.63 (s, 1H), 5.98 (t, *J* = 6.10 Hz, 1H), 6.89 (d, *J* = 8.77 Hz, 2H), 7.25 (d, *J* = 7.25 Hz, 1H), 7.31 (t, *J* = 7.44 Hz, 2H), 7.37 - 7.44 (m, 4H); **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 11.3, 14.7, 16.2, 55.2, 66.2, 80.2, 113.9, 123.9, 125.8, 126.9, 127.2, 128.2, 128.2, 132.3, 138.7, 142.8, 147.6, 159.4, 168.2. **FTIR (cm^{-1}):** 3013, 2955, 2866, 1606, 1508, 1452, 1251, 1222, 1173, 1040, 838. **HRMS:** Calculated for $C_{23}H_{26}NO_2S$ $[M+H]^+$: 380.1679, found:380.1673.



(E)-2-((3-methyl-1-)((3-phenylbut-2-ene-1-yl)oxy)butyl)benzo[d]thiazole (1E-1)

The titled compound was prepared by following the general procedure **C1** at 0 °C for 16 h (4.52 mmol), obtained as a yellowish liquid (1.1 g, 69% yield). R_f (EtOAc/pet ether = 02:98) = 0.2. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 0.99 (d, *J* = 6.10 Hz, 6H), 1.67 - 1.74 (m, 1H), 1.89 - 1.97 (m, 2H), 2.01 (s, 3H), 4.24 (dd, *J* = 12.21, 6.87 Hz, 1H), 4.32 (dd, *J* = 12.21, 6.49 Hz, 1H), 4.88 – 8.91 (m, 1H), 5.98 - 6.05 (m, 1H), 7.21 - 7.26 (m, 1H), 7.30 (t, *J* = 7.44 Hz, 2H), 7.35 - 7.40 (m, 3H), 7.45 - 7.50 (m, 1H), 7.89 (d, *J* = 8.01 Hz, 1H), 8.01 (d, *J* =8 .01 Hz, 1H); **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 16.2, 21.9, 23.1, 24.6, 46.4, 67.0, 78.1, 121.9, 122.9, 123.4, 125.0, 125.7, 125.9, 127.2, 128.2, 135.0, 139.2, 142.7, 153.1, 176.3. **FTIR (cm^{-1}):** 3067, 2957, 2872, 1593, 1507, 1452, 1230, 1176, 1084, 1014, 910. **HRMS:** m/z calculated for $C_{22}H_{26}ONS[M+H]^+$: 352.1730, found: 352.1727.

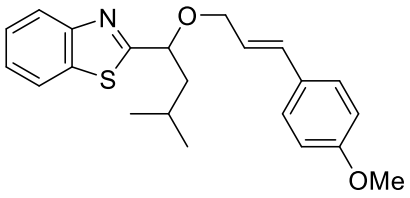
2-(1-(cinnamyloxy)-3-methybutyl)benzo[d]thiazole (1F-1)



The titled compound was prepared by following the general procedure **C2** at 0 °C for 16 h (1.53 mmol), obtained as a yellowish liquid (426 mg, 82% yield). R_f (EtOAc/pet etehr = 02:98) = 0.2. **^{1}HNMR (500 MHz, $CDCl_3$)** δ 0.98 (d, *J* = 4.96 Hz, 3H), 0.99 (d, *J* = 4.96 Hz, 3H), 1.68 - 1.75 (m, 1H), 1.86 - 1.95 (m, 2H), 4.1d (dd, *J* = 12.40, 7.44 Hz, 1H), 4.30 (dd, *J* = 12.59, 6.87 Hz, 1H), 4.86 - 4.94 (m, 1H), 6.31 (t, *J* = 6.10 Hz, 1H), 6.63 (d, *J* = 16.05 Hz, 1H), 7.26 - 7.29 (m, 1H), 7.30 (t, *J* = 7.44 Hz, 2H), 7.35 - 7.40 (m, 3H), 7.47 (t, *J* = 8.20 Hz, 1H), 7.90 (d, *J* = 8.01 Hz, 1H), 8.01 (d, *J* = 8.01 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 22.0, 23.2, 24.6,

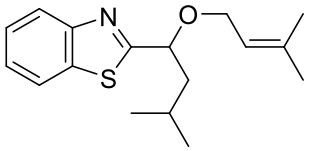
46.4, 70.7, 78.0, 121.9, 123.0, 125.0, 125.2, 125.9, 126.5, 127.8, 128.5, 133.2, 134.9, 136.5, 153.1 , 176.1**. FTIR (cm^{-1}):** 3022, 2963, 1721, 1596, 1517, 1432, 1087, 1019, 972, 927. **HRMS:** m/z calculated for $C_{21}H_{24}ONS[M+H]^+$: 338.1573, found: 338.1573.

(E)-2-(1-((3-(4-methoxyphenyl)allyl)oxy)-3-methylbutyl)benzo[d]thiazole (1F-2)



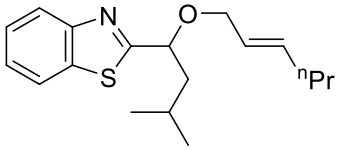
The titled compound was prepared by following the general procedure **C2** at 0 °C for 16 h (1.81 mmol), obtained as a yellowish liquid (476 mg, 71% yield). ***R$_f$*** (EtOAc/pet etehr = 02:98) = 0.2. **^{1}HNMR (500 MHz, CDCl$_3$)** δ 0.99 (d, *J* = 4.58 Hz, 3H), 0.98 (d, *J* = 4.96 Hz, 3H), 1.69 - 1.76 (m, 1H), 1.86 - 2.00 (m, 1H), 3.79 (s, 3H), 4.13 (dd, *J* = 12.21, 7.63 Hz, 1H), 4.29 (dd, *J* = 12.41, 7.24 Hz, 1H), 4.85 - 4.97 (m, 1H), 6.14- 6.19 (m, 1H), 6.57 (d, *J* = 16.03 Hz 1H), 6.84 (d, *J* = 8.77 Hz, 2H), 7.31 (d, *J* = 8.39 Hz, 2H), 7.38 (t, *J* = 8.01Hz, 1H), 7.47 (t, *J* = 8.20 Hz, 1H), 7.90 (d, *J* = 8.01 Hz, 1H), 8.00 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR (CDCl$_3$, 125 MHz)** δ 21.9, 23.1, 24.5, 46.4, 55.2, 70.9, 77.8, 113.9, 121.9, 122.8, 122.9, 125.0, 125.9, 127.7, 129.2, 133.0, 134.9, 153.1, 159.3, 176.3. **FTIR (cm^{-1}):** 2954, 1606, 1512, 1454, 1250, 1174, 1104, 1031, 969. **HRMS:** m/z calculated for $C_{22}H_{25}NNaO_2S[M+Na]^+$: 390.1498, found: 390.1492.

2-(3-methyl-1-((3-methylbut-2-ene-1-yl)oxy)butyl)benzo[d]thiazole (1G-1)



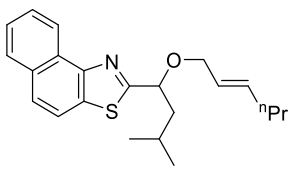
The titled compound was prepared by following the general procedure **C1** at 0 °C for 16 h (2.26 mmol), obtained as a yellowish liquid (580 mg, 88% yield). ***R$_f$*** (EtOAc/pet etehr = 02:98) = 0.2. **^{1}H NMR (400 MHz, CDCl$_3$)** δ 0.98 (d, *J* = 6.71 Hz, 6H), 1.63 (s, 3H), 1.64 - 1.70 (m, 1H), 1.75 (s, 3H), 1.85 - 1.95 (m, 2H), 3.97 - 4.05 (m, 1H), 4.05 - 4.16 (m, 1H), 4.81 – 4.85 (m, 1H), 5.40 (t, *J* = 7.02 Hz, 1H), 7.38 (t, *J* = 7.63 Hz, 1H), 7.47 (t, *J* = 7.63 Hz, 1H), 7.90 (d, *J* = 7.93 Hz,1H), 8.00 (d, *J* = 7.93 Hz, 1H); **^{13}C NMR (CDCl$_3$, 100 MHz)** δ 18.0, 21.8, 23.1, 24.5, 25.8, 46.5, 66.5, 77.7, 120.3, 121.9, 122.9, 124.9, 125.8, 134.9, 138.3, 153.1, 176.7. **FTIR (cm^{-1}):** 3064, 2957, 2848, 1719, 1515, 1449, 1314, 1220, 1173, 1077, 1010, 915, 860. **HRMS:** m/z calculated for $C_{17}H_{24}ONS[M+H]^+$: 290.1573, found: 290.1572.

(E)-2-(1-(hex-2-ene-1-yloxy)-3-methybutyl)benzo[d]thiazole (1H-1)



The titled compound was prepared by following the general procedure **C1** at 0 °C for 16 h (2.26 mmol), obtained as a yellowish (527 mg, 77% yield). ***R$_f$*** (EtOAc/pet etehr = 02:98) = 0.2. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 0.89 (t, *J* = 7.44 Hz, 3H), 0.98 (d, *J* = 6.48 Hz, 6H), 1.39 (sxt, *J* = 7.32 Hz, 1H), 1.62- 1.72 (m,1H), 1.83 - 1.96 (m, 2H), 2.00 – 2.04 (m, 2H), 3.94 (dd, *J* = 11.44, 6.87 Hz, 1H), 4.10 (dd, *J* = 11.44, 5.72 Hz, 1H), 4.82 – 4.85 (m, 1H), 5.53 - 5.63 (m, 1H), 5.64 - 5.76 (m, 1H), 7.32 - 7.39 (m, 1H), 7.41 - 7.52 (m, 1H), 7.88 (d, *J* = 7.63 Hz, 1H), 7.99 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR (CDCl$_3$, 125 MHz)** δ 13.6, 21.9, 22.0, 23.1, 24.5, 34.3, 46.3, 70.9, 77.4, 121.8, 122.8, 124.9, 125.6, 125.8, 134.9, 135.6, 153.1, 176.5. **FTIR (cm^{-1}):** 2957, 2869, 1589, 1515, 1455, 1313, 1177, 1086, 1011, 972, 911. **HRMS:** m/z calculated for $C_{18}H_{26}ONS[M+H]^+$: 304.1730, found: 304.1730.

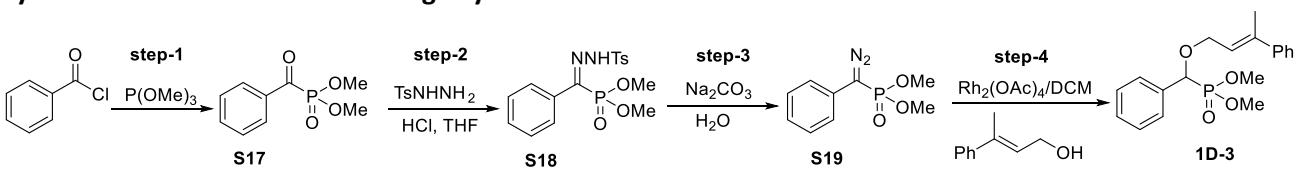
(E)-2-(1-(hex-2-en-1-yloxy)-3-methylbutyl)naphtho[1,2-d]thiazole (1H-2)



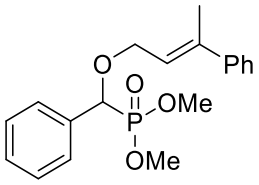
The titled compound was prepared by following the general procedure **C1** at 0 °C for 16 h (1.25 mmol), obtained as a yellowish liquid (380 mg, 86% yield). **^{1}H NMR (500 MHz, CDCl$_3$)** δ 0.89 (t, *J* = 7.43 Hz, 3H) 1.01 (d, *J* = 3.03 Hz, 3H) 1.02 (d, *J* = 2.75 Hz, 3H) 1.36 (sxt, *J* = 7.43 Hz, 2H) 1.75 - 1.79 (m, 1H) 1.89 – 1.98 (m, 2H) 2.03 (q, *J* = 6.97 Hz, 2H) 3.99 (dd, *J* = 11.83, 6.88 Hz, 1H) 4.12 (dd, *J* = 12.24, 6.19 Hz, 1H) 4.91 - 5.00 (m, 1H) 5.55 - 5.65 (m, 1H) 5.66 - 5.76 (m, 1H) 7.55 (t, *J* = 7.43 Hz, 1H) 7.65 (t, *J* = 7.57 Hz, 1H) 7.77 (d, *J* = 8.53 Hz, 1H) 7.89 (d, *J* = 8.80 Hz, 1H) 7.93 (d, *J* = 8.25 Hz, 1H) 8.79 (d, *J* = 8.25 Hz, 1H); **^{13}C NMR (CDCl$_3$, 125 MHz)** δ 13.7, 22.1, 22.1, 23.1, 24.6, 34.3, 46.7, 70.8, 77.7, 119.2, 123.8, 125.5, 125.8, 125.9,

126.8, 128.0, 128.7, 131.6, 131.8, 135.5, 149.3, 175.2. **FTIR (cm^{-1}):** 3067, 2958, 2866, 1583, 1508, 1466, 1378, 1102, 973, 811.

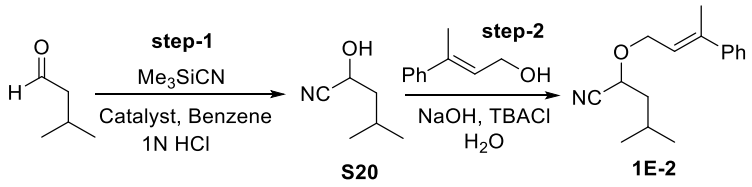
Synthesis of traceless FG containing allyl ethers:



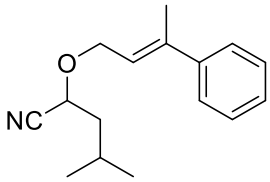
Dimethyl (E)-(phenyl((3-phenylbut-2-en-1-yl)oxy)methyl)phosphonate (1D-3)



The titled compound was prepared by following the literature procedure method[4] R_f (EtOAc/Pet ether = 45:55) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 1.93 (s, 3H), 3.66 - 3.75 (m, 6H), 4.19 (dd, *J* = 12.21, 7.32 Hz, 1H), 4.30 (dd, *J* = 12.21, 6.10 Hz, 1H), 4.80 (d, *J* = 15.87 Hz, 1H), 5.91 (t, *J* = 6.41 Hz, 1H), 7.29 - 7.42 (m, 8H), 7.49 (d, *J* = 7.32 Hz, 2 H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 16.1, 53.6, 53.7, 53.9 53.9, 66.9, 67.1, 76.2, 77.8, 123.0, 125.7, 127.3, 128.0, 128.1, 128.2, 128.5, 129.9, 134.4, 139.8, 142.6. **FTIR (cm^{-1}):** 3020, 2859, 2247, 1722, 1644, 1598, 1523, 1436, 1252, 1043, 928. **HRMS:** m/z calculated for $C_{19}H_{23}O_4NaP$ $[M+Na]^+$:369.1226, found:369.1216.



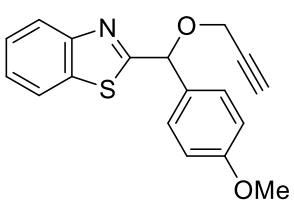
(E)-4-methyl-2-((3-phenylbut-2-ene-1-yl)oxy)pentanenitrile (1E-2)



The titled compound was prepared by following the literature procedure[5] R_f (EtOAc/Pet ether = 2:98) = 0.2. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 0.99 (d, *J* = 5.34 Hz, 3H), 1.00 (d, *J* = 5.34 Hz, 3H), 1.67 – 1.73 (m, 1H), 1.84 - 1.91 (m, 1H), 1.92 - 1.99 (m, 1H), 2.17 (s, 3H), 4.25 - 4.35 (m, 2H), 4.51 (dd, *J* = 11.83, 6.10 Hz, 1H), 5.87 - 5.95 (m, 1H), 7.30 - 7.34 (m, 1H), 7.35 - 7.39 (m, 2H), 7.43 - 7.47 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 16.3, 22.0, 22.5, 24.4, 42.2, 66.4, 67.0, 118.8, 121.8, 125.8, 127.6, 128.3, 140.9, 142.5. **FTIR (cm^{-1}):** 3029, 2958, 2873, 2254, 1641, 1605, 1457, 1380, 1271, 1091, 1027, 909. **HRMS:** m/z calculated for $C_{16}H_{21}NNaO$ $[M+Na]^+$: 266.1515, found: 266.1511.

2-((4-methoxyphenyl)(prop-2-yn-1-yloxy)methyl)benzo[d]thiazole (S21)

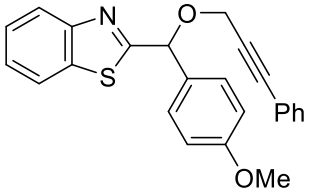
The titled compound was prepared by following the general procedure **C1** at -20 °C for 24 h (1.62 mmol), obtained as a yellowish liquid (381 mg, 76 % yield). R_f (Acetone/Pet ether; 4:96) = 0.2. **^{1}H NMR (200 MHz, $CDCl_3$)**



δ 2.50 (t, *J* = 2.40 Hz, 1H), 3.76 (s, 3H), 4.15 - 4.43 (m, 2H), 6.05 (s, 1H), 6.89 (d, *J* = 8.72 Hz, 2H), 7.26 - 7.42 (m, 2H), 7.48 (d, *J* = 8.72 Hz, 2H), 7.84 (d, *J* = 8.59 Hz, 1H), 7.99 (d, *J* = 8.08 Hz, 1H); **^{13}C NMR (50 MHz, $CDCl_3$)** δ 55.2, 56.2, 75.5, 78.7, 79.5, 114.2, 121.7, 123.2, 125.0, 125.9, 128.9, 130.1, 135.0, 153.1, 159.9, 172.9. **FTIR (cm^{-1}):** 3017, 2972, 2912, 2847, 2120, 1607, 1512, 1449, 1218, 1170, 1075, 1027, 924. **HRMS:** m/z calculated for $C_{18}H_{15}NNaO_2S$ $[M+Na]^+$: 332.0716, found: 332.0712.

2-((4-methoxyphenyl)((3-phenylprop-2-yn-1-yl)oxy)methyl)benzo[d]thiazole (1F-1)

In an oven dried 25 ml round bottom flask with a magnetic bar, terminal alkyne (250 mg, 0.81 mmol) in dry THF (5 ml) was added iodobenzene (330 mg, 1.62 mmol) and triethylamine (1.01 ml, 10 mmol). To that, $Pd(PPh_3)_4$



(46 mg, 5 mol%) and CuI (15 mg, 0.1 mmol) catalysts were added and purged with argon for 5 min. The reaction mixture was allowed to stir at rt for 5 h and upon completion (judged by TLC), passed through celite. The solvent was removed under reduced pressure to obtain crude product which was further purified by column chromatography on silica gel using Acetone-pet ether as eluent to give the desired product (45 mg, 15 % yield). $\mathbf{R_f}$(Acetone/Pet ether = 3.5:96.5) = 0.2. **^{1}H NMR (200 MHz, $CDCl_3$)** δ 3.79 (s, 3H), 4.39 - 4.66 (m, 2H), 6.13 (s, 1H), 6.91 (d, *J* = 8.72 Hz, 2H), 7.27 - 7.34 (m, 3H), 7.38 - 7.55 (m, 6H), 7.87 (d, *J* = 8.72 Hz, 1H), 7.99 (d, *J* = 7.45 Hz, 1H); **^{13}C NMR (50 MHz, $CDCl_3$)** δ 55.3, 57.1, 79.7, 84.1, 87.3, 114.2, 121.7, 122.4, 123.2, 125.0, 125.9, 128.3, 128.6, 128.9, 130.4, 131.80, 135.1, 153.1, 159.9, 173.3. **FTIR (cm^{-1}):** 3297, 3064, 3009, 2966, 2909, 2846, 2288, 2119, 2044, 1605, 1511, 1450, 1250, 1167, 1075, 1025, 836. **HRMS:** m/z calculated for $C_{24}H_{19}NNaO_2S$ $[M+Na]^+$:408.1029, found: 408.1021.

D. General procedure for Wittig rearrangement reactions

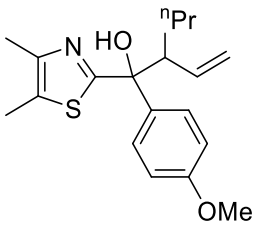
[2,3] for substrate class 1A (R^1 = Ar, R^2 = Alk, R^3 = H):

In a flame dried 25 ml round bottom flask with a magnetic bar, KO^{t}Bu (2.5 equiv) and dry MeCN was taken and made oxygen-free via the freeze-thaw method. In another flame dried pear shaped 10 ml flask, ether **1A** (0.2 mmol, 1.0 equiv) was taken with 1 ml of MeCN and made oxygen-free via the same method. After cooling both the solution to -40 °C, the ether solution was transferred to the base container via a cannula under positive argon pressure and sealed with insulating tape. The reaction mixture was stirred at that temperature for 4 h and quenched with saturated NH_4Cl solution. The organic layer was extracted with EtOAc (3 times) and combined organic layer dried over anhydrous Na_2SO_4. The solvent removal under reduced pressure gave the crude product which was further purified by column chromatography on silica gel using acetone-pet ether as eluent to obtain the desired product.

[1,2] for substrate class 1A (R^1 = Ar, R^2 = Alk, R^3 = H):

In a flame dried 25 ml round bottom flask with a magnetic bar, KO^{t}Bu (2.5 equiv) and dry MeCN was taken and made oxygen-free via freeze-thaw method. In another flame dried pear shaped 10 ml flask, ether **1A** (0.2 mmol, 1.0 equiv) was taken with 1 ml of MeCN and made oxygen-free via the same method. After cooling both the solution to 0 °C, the ether solution was transferred to the base container via a cannula under positive argon pressure and sealed with insulating tape. The reaction mixture was slowly brought to room temperature and stirred (~26 °C). The eaction was monitored via crude NMR analysis of aliquots, and quenched with saturated NH_4Cl solution. The organic layer was extracted with EtOAc (3 times) and combined organic layer dried over anhydrous Na_2SO_4. The solvent removal under reduced pressure gave the crude product which was further purified by column chromatography on silica gel using acetone-pet ether as eluent to obtain the desired product.

1-(4,5-dimethylthiazol-2-yl)-1-(4-methoxyphenyl)-2-vinylpentan-1-ol (2A-1)



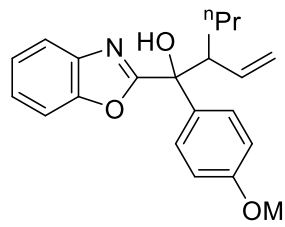
The titled compound was prepared by following the general procedure for [2,3] (0.2 mmol), obtained as a yellowish liquid (59 mg, 90% yield). $\boldsymbol{R_f}$ (Acetone/pet ether = 04:96) = 0.2. **dr ratio**: 58:42. **^{1}H NMR (400 MHz, $CDCl_3$) Major isomer:** δ 0.83 (t, *J* = 7.32 Hz, 3H), 1.05 - 1.18 (m, 1H), 1.22 - 1.29 (m, 1H), 1.30 - 1.42 (m, 1H), 1.45 - 1.56 (m, 1H), 2.27 (s, 6H), 2.95 (t, *J* = 9.77 Hz, 1H), 3.76 (s, 3H), 4.10 (s, 1H), 4.91 - 5.02 (m, 2H), 5.49 - 5.63 (m, 1H), 6.83 (d, *J* = 8.54 Hz, 2H), 7.51 (d, *J* = 8.54 Hz, 2H); **Minor isomer:** δ 0.78 (t, *J* = 7.02 Hz, 3H), 1.05 - 1.18 (m, 1H), 1.22 - 1.29 (m, 1H), 1.30 - 1.42 (m, 1H), 1.45 - 1.56 (m, 1H), 2.24 (s, 6H), 3.04 (t, *J* = 9.77 Hz, 1H), 3.78 (s, 3H), 4.25 (s, 1H), 5.02 - 5.10 (m, 2H), 5.67 - 5.79 (m, 1H), 6.87 (d, *J* = 8.55 Hz, 2H), 7.58 (d, *J* = 8.55 Hz, 2H); **^{13}C NMR (100MHz, $CDCl_3$)** δ 11.3, 13.9, 13.9, 14.6, 14.6, 20.5, 20.6, 29.8, 30.5, 53.7, 54.8, 55.1, 55.1, 80.0, 80.1, 113.2, 113.5, 118.1, 118.1, 126.7, 126.8, 126.9, 127.1, 136.4, 136.0,

137.3, 137.5, 146.0, 146.6, 158.4, 158.5, 171.8, 172.4. **FTIR (cm^{-1}):** 3443, 2956, 2870, 1609, 1510, 1460, 1302, 1250, 1176, 1039, 909, 831. **HRMS:** m/z calculated for $C_{19}H_{26}O_2NS[M+H]^+$: 332.1679, found: 332.1672.

No [1,2] with this substrate.

1-(benzo[d]oxazol-2-yl)-1-(4-methoxyphenyl)-2-vinylpentan-1-ol (2A-2)

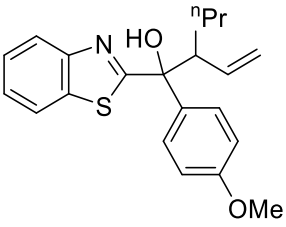
The titled compound was prepared by following the general procedure for [2,3] (0.18 mmol), obtained as a yellowish liquid (46 mg, 74% yield); **dr ratio**: 78:22. **^{1}H NMR (400 MHz, $CDCl_3$) Major isomer:** δ 0.81 (t, *J* = 6.86 Hz, 3H), 1.07 - 1.15 (m, 2H), 1.30 - 1.47 (m, 2H), 3.08 - 3.16 (m, 1H), 3.77 (s, 3H), 3.86 (s, 1H), 4.89 - 4.95 (m, 1H), 4.99 - 5.03 (m, 1H), 5.56 - 5.67 (m, 1H), 6.84 - 6.87 (m, 2H), 7.32 - 7.35 (m, 2H), 7.53 - 7.56 (m, 1H), 7.56 - 7.59 (m, 2H), 7.67 - 7.71 (m, 1H); **Minor isomer:** δ 0.81 (t, *J* = 6.86 Hz, 3H), 1.07 - 1.15 (m, 2H), 1.30 - 1.47 (m, 2H), 3.08 - 3.16 (m, 1H), 3.77 (s, 3H), 3.86 (s, 1H), 4.89 - 4.95 (m, 1H), 4.99 - 5.03 (m, 1H), 5.56 - 5.67 (m, 1H), 6.84 - 6.87 (m, 2H), 7.32 - 7.35 (m, 2H), 7.53 - 7.56 (m, 1H), 7.56 - 7.59 (m, 2H), 7.67 - 7.71 (m, 2H)**; ^{13}C NMR (100MHz, $CDCl_3$)** δ 13.8, 13.9, 20.4, 20.5, 29.3, 29.7, 30.9, 31.3, 53.2, 55.2, 78.2, 78.3, 110.7, 110.9, 113.4, 113.7, 118.2, 118.7, 119.9, 120.0, 124.6, 125.0, 127.0, 127.1, 133.8, 136.3, 137.3, 140.2, 151.3, 158.8, 168.9. **FTIR (cm^{-1}):** 3526, 3074, 2954, 2869, 1609, 1562, 1510, 1459, 1249, 1176, 1096, 1037, 910, 823. **HRMS:** m/z calculated for $C_{21}H_{24}O_3N[M+H]^+$: 338.1751, found: 338.1749.



No [1,2] with this substrate.

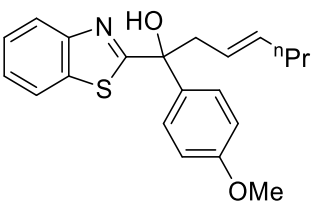
1-(benzo[d]thiazol-2-yl)-1-(4-methoxyphenyl)-2-vinylpentan-1-ol (2A-3)

The titled compound was prepared by following the general procedure for [2,3] (0.22 mmol), obtained as a yellowish liquid (68 mg, 89% yield). ***R$_f$*** (Acetone/pet etehr = 4.5:95.5) = 0.2. **dr ratio**: 69:29. **^{1}H NMR (400 MHz, $CDCl_3$) Major isomer:** δ 0.80 (t, *J* = 7.43 Hz, 3H), 1.10 - 1.20 (m, 2H), 1.36 - 1.46 (m, 2H), 3.18 (ddd, *J* = 11.11, 9.04, 2.29 Hz, 1H), 3.76 (s, 3H), 3.91 (s, 1H), 5.05 - 5.11 (m, 2H), 5.61 (ddd, *J* = 17.40, 10.53, 9.16 Hz, 1H), 6.83 - 6.86 (m, 2H), 7.28 - 7.37 (m, 2H), 7.57 - 7.61 (m, 2H), 7.67 (d, *J* = 9.16 Hz, 1H), 8.00 (d, *J* = 8.24 Hz, 1H); **Minor isomer:** δ 0.81 (t, *J* = 7.43 Hz, 3H), 1.28 – 1.35 (m, 2H), 1.57 - 1.65 (m, 2H), 3.29 (ddd, *J* = 11.11, 9.04, 2.29 Hz, 1H), 3.78 (s, 3H), 4.08 (s, 1H), 5.01 - 5.05 (m, 2H), 5.78 (ddd, *J* = 17.06, 10.65, 8.47 Hz, 1H), 6.89 (d, *J* = 9.16 Hz, 2H), 7.44 - 7.49 (m, 2H), 7.64 - 7.68 (m, 2H), 7.76 - 7.80 (m, 1H), 7.96 (d, *J* = 8.24 Hz, 1 H); **^{13}C NMR (100MHz, $CDCl_3$)** δ 13.9, 14.0, 20.5, 20.7, 29.5,29.7, 53.1, 54.6, 55.2, 55.2, 80.7, 80.9, 113.4, 113.7, 118.7, 118.8, 121.7, 123.0, 123.1, 124.8, 124.9, 125.8, 125.9, 126.9, 127.3, 134.8, 135.3, 135.6, 135.8, 136.8, 137.0, 152.3, 152.7, 158.7, 158.8, 178.0, 178.8. **FTIR (cm^{-1}):** 3518, 3070, 3017, 2958, 2871, 1609, 1508, 1452, 1248, 1218, 1042, 918. **HRMS:** m/z calculated for $C_{21}H_{24}O_2NS[M+H]^+$: 354.1522, found: 354.1518.

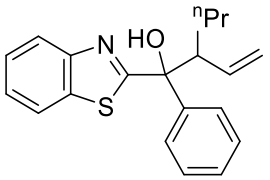


(E)-1-(benzo[d]thiazol-2-yl)-1-(4-methoxyphenyl)hept-3-en-1-ol(3A-3)

The titled compound was prepared by following the general [1,2] procedure for 116 h (0.1 mmol), obtained as a yellowish liquid (16 mg, 44% yield; 77% with 23% unidentified isomeric compound). ***R$_f$*** (Acetone/pet ether = 4.5:95.5) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.82 (t, *J* = 7.33 Hz, 3H), 1.30 - 1.35 (m, 2H), 1.95 (m, 2H), 2.96 (dd, *J* = 13.73, 8.24 Hz, 1H), 3.38 (dd, *J* = 13.73, 6.41 Hz, 1H), 3.56 (s, 1H), 3.78 (s, 3H), 5.26 - 5.38 (m, 1H), 5.63 - 5.77 (m, 1H), 6.87 (d, *J* = 8.55 Hz, 2H), 7.34 (t, *J* = 7.63 Hz, 1H), 7.45 (t, *J* = 7.63 Hz, 1H), 7.61 (d, *J* = 9.16 Hz, 2H), 7.83 (d, *J* = 7.93 Hz, 1H), 8.01 (d, *J* = 7.93 Hz, 1H); **^{13}C NMR (100MHz, $CDCl_3$)** δ 13.5, 22.4, 34.7, 46.2, 55.2, 77.3, 113.6, 121.7, 123.1, 123.7, 124.8, 125.8, 126.7, 135.6, 135.8, 138.1, 153.4, 158.9, 178.6. **FTIR (cm^{-1}):** 3522, 3156, 2958, 2926, 2859, 1602, 1509, 1466, 1380, 1250, 1174, 1093, 909, **HRMS:** Calculated for $C_{21}H_{24}O_2NS[M]^+$: 354.1522, found: 354.1513.

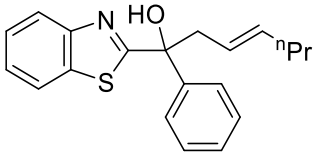


1-(benzo[d]thiazol-2-yl)-1-phenyl-2-vinylpentan-1-ol (2A-4)



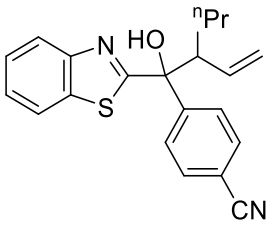
The titled compound was prepared by following the general procedure for [2,3] (0.2 mmol), obtained as a yellowish liquid (54 mg, 85% yield); **dr ratio:** 70:30. **^{1}H NMR (500 MHz, $CDCl_3$) Major isomer:** δ 0.81 (t, *J* = 6.87 Hz, 3H),, 3H), 1.12 - 1.23 (m, 1H), 1.27 - 1.33 (m, 1H), 1.37 - 1.44 (m, 1H), 1.59 - 1.68 (m, 1H), 3.23 (t, *J* = 9.92 Hz 1H), 3.97 - 4.01 (m, 1H), 5.00 - 5.07 (m, 2H), 5.55 - 5.65 (m, 1H), 7.17 - 7.25 (m, 1H), 7.28 - 7.38 (m, 3H), 7.39 - 7.46 (m, 1H), 7.70 (d, *J* = 8.01 Hz, 2H), 7.81 (d, *J* = 8.01 Hz, 1H), 8.00 (d, *J* = 8.01 Hz, 1H); **Minor isomer:** δ 0.78 - 0.84 (m, 3H), 1.13 - 1.23 (m, 1H), 1.28 - 1.35 (m, 1H), 1.37 - 1.44 (m, 1H), 1.69 - 1.79 (m, 1H), 3.35 (t, *J* = 9.54 Hz, 1H), 4.11 - 4.33 (m, 1H), 5.07 - 5.16 (m, 2H), 5.75 - 5.89 (m, 1H), 7.18 - 7.24 (m, 1H), 7.28 - 7.38 (m, 3H), 7.40 - 7.46 (m, 1H), 7.75- 7.79 (m, 3H), 7.96 (d, *J* = 8.01 Hz, 1H); **^{13}C NMR (125MHz, $CDCl_3$)** δ 13.9, 20.4, 20.6, 29.5, 30.5, 53.1254.5, 81.0, 81.2, 118.8, 121.6, 123.0, 123.1, 124.8, 124.9, 125.7, 125.8, 125.9, 126.0, 127.3, 127.4, 128.1, 128.4, 135.6, 135.8, 136.7, 136.8, 142.7, 143.1, 152.2, 152.6, 177.6, 178.4. **FTIR (cm^{-1}):** 3520, 3069, 3018, 2960, 2871, 1596, 1501, 1447, 1217, 1123, 1056, 919. **HRMS:** m/z calculated for $C_{20}H_{22}ONS[M+H]^+$: 324.1417, found: 324.1414.

(E)-1-(benzo[d]thiazol-2-yl)-1-phenylhept-3-en-1-ol (3A-4)



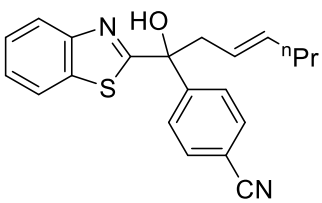
The titled compound was prepared by following the general [1,2] procedure for 120h (0.16 mmol), obtained as a yellowish liquid (32 mg, 62% yield; ~16% [2,3] remains & 22% unidentified isomeric compound). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.81 (t, *J* = 7.32 Hz, 3H), 1.28 - 1.36 (m, 2H), 1.95 (m, 2H), 2.98 (dd, *J* = 13.73, 8.24 Hz, 1H), 3.42 (dd, *J* = 14.04, 6.71 Hz, 1H), 3.62 (s, 1H), 5.28 - 5.37 (m, 1H), 5.64 - 5.76 (m, 1H), 7.24 - 7.28 (m, 1H), 7.33 (t, *J* = 6.71 Hz, 3H), 7.45 (t, *J* = 7.63 Hz, 1H), 7.71 (d, *J* = 7.32 Hz, 2H), 7.83 (d, *J* = 7.93 Hz, 1H), 8.02 (d, *J* = 7.93 Hz, 1H), **^{13}C NMR (100MHz, $CDCl_3$)** δ 13.5, 22.4, 34.6, 46.2, 77.7, 121.7, 123.1, 123.6, 124.8, 125.4, 125.8, 127.5, 128.3, 135.6, 138.3, 143.5, 153.3, 178.3. **FTIR (cm^{-1}):** 3528, 3067, 3026, 2960, 2869, 1803, 1594, 1502, 1447, 1349, 1245, 1139, 1062, 978, 910. **HRMS:**Calculated for $C_{20}H_{21}ONNaS[M+Na]^+$: 346.1236, found: 346.1228.

4-(1-(benzo[d]thiazol-2-yl)-1-hydroxy-2-vinylpentyl)benzonitrile (2A-5)



The titled compound was prepared by following the general procedure for [2,3] (0.2 mmol), obtained as a yellowish liquid (55 mg, 79% yield). R_f (Acetone/pet etehr = 05:95) = 0.2. **dr ratio:** 55:45. **^{1}H NMR (400 MHz, $CDCl_3$) Major isomer:** δ 0.81 (t, *J* = 7.43 Hz, 3H), 1.08 - 1.16 (m, 2H), 1.34 - 1.50 (m, 2H), 3.22 (t, *J* = 9.77 Hz, 1H), 4.07 (s, 1H), 4.93 - 5.09 (m, 2H), 5.49 – 5.58 (m, 1H), 7.31 - 7.40 (m, 2H), 7.60 (d, *J* = 7.93 Hz, 2H), 7.81 (d, *J* = 7.93 Hz, 1H), 7.86 (d, *J* = 7.93 Hz, 2H), 7.99 (d, *J* = 7.93 Hz, 1H); **Minor isomer:** δ 0.83 (t, *J* = 7.43 Hz, 3H), 1.10 - 1.18 (m, 2H), 1.52 - 1.64 (m, 2H), 3.39 (t, *J* = 9.46 Hz, 1H), 4.14 (s, 1H), 5.09 - 5.21 (m, 2H), 5.72 – 5.81 (m, 1H), 7.42 - 7.51 (m, 2H), 7.65 (d, *J* = 7.93 Hz, 2H), 7.86 (d, *J* = 7.93 Hz, 1H), 7.95 (d, *J* = 8.55 Hz, 2H), 8.02 (d, *J* = 7.93 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 13.8, 13.8, 20.3, 20.5, 29.2, 30.5, 52.9, 54.6, 80.7, 81.1, 111.1, 111.2, 118.7, 118.7, 119.5, 119.7, 121.7, 121.7, 123.1, 123.2, 125.1, 125.2, 126.1, 126.2, 126.7, 126.9, 131.9, 132.1, 135.4, 135.5, 135.8, 135.9, 147.8, 148.3, 152.5, 152.6, 176.2, 177.0. **FTIR (cm^{-1}):** 3456, 3071, 3019, 2961, 2869, 2232, 1707, 1607, 1504, 1218, 1138, 1071, 915, 842. **HRMS:** m/z calculated for $C_{21}H_{21}ON_2S[M+H]^+$: 349.1369 found: 349.1370.

(E)-4-(1-(benzo[d]thiazol-2-yl)-1-hydroxyhept-3-en-1-yl)benzonitrile (3A-5)



The titled compound was prepared by following the general [1,2] procedure for 7h (0.16 mmol), obtained as a yellowish liquid (32 mg, 63% yield; with ~23% unidentified isomeric compound). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.83 (t, *J* = 7.25 Hz, 3H), 1.30 - 1.37 (m, 2H), 1.96 (q, *J* = 7.25 Hz, 2H), 2.90 (dd, *J* = 13.73, 8.39 Hz, 1H), 3.43 (dd, *J* = 14.11, 6.10 Hz, 1H), 3.64 (s, 1H), 5.22 - 5.31 (m, 1H), 5.69 - 5.77 (m, 1H), 7.35 - 7.40 (m, 1H), 7.46 - 7.51 (m, 1H), 7.61 - 7.66 (m, 2H), 7.84 - 7.91 (m, 3H), 8.03 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 13.5, 22.3, 34.6, 46.5, 77.4,

111.4, 118.7, 121.8, 122.8, 123.3, 125.2, 126.1, 126.4, 132.1, 135.5, 139.2, 148.6, 153.4, 176.8. **FTIR (cm^{-1}):** 3527, 3021, 2927, 2860, 2248, 1607, 1504, 1466, 1145, 1089, 979. **HRMS:** m/z calculated for $C_{21}H_{21}ON_2S[M+H]^+$: 349.1369, found: 349.1370.

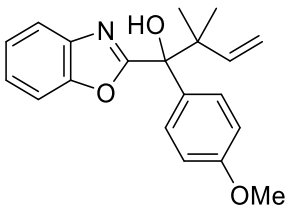
[2,3] for substrate class 1B (R^1 = Ar, R^2 = Me, R^3 = Me):

The procedure for substrate class **1B** is exactly same as class **1A**.

[1,2] for substrate class 1B (R^1 = Ar, R^2 = Me, R^3 = Me):

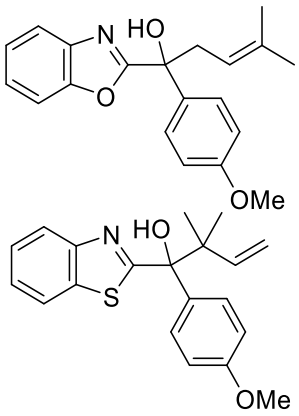
The procedure for class **1B** is similar to class **1A** except stirring the reaction at 0 °C.

1-(benzo[d]oxazol-2-yl)-1-(4-methoxyphenyl)-2,2-dimethylbut-3-en-1-ol (2B-2)



The titled compound was prepared by following the general procedure for [2,3] (0.2 mmol), obtained as a yellowish liquid (58 mg, 90% yield). R_f (Acetone/Pet ether = 4.5:95.5) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 1.15 (s, 3H), 1.23 (s, 3H), 3.78 (s, 3H), 4.07 (s, 1H), 4.97 - 5.07 (m, 2H), 6.09 - 6.20 (m, 1H), 6.84 (d, *J* = 8.54 Hz, 2H), 7.29 - 7.37 (m, 2H), 7.54 - 7.62 (m, 1H), 7.67 (d, *J* = 8.54 Hz, 2H), 7.69 - 7.74 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 22.6, 22.6, 45.9, 55.2, 79.9, 110.8, 112.6, 114.1, 120.1, 124.5, 125.0, 128.7, 131.7, 139.8, 143.8, 151.0, 158.9, 168.8. **FTIR (cm^{-1}):** 3414, 3065, 2925, 2860, 1716, 1648, 1590, 1485, 1448, 1283, 1223, 1223, 1122, 1065, 887. **HRMS:** m/z calculated for $C_{20}H_{21}O_3NNa[M+Na]^+$: 346.1414, found: 346.1407.

1-(benzo[d]oxazol-2-yl)-1-(4-methoxyphenyl)-4-methylpent-3-ene-1-ol (3B-2)

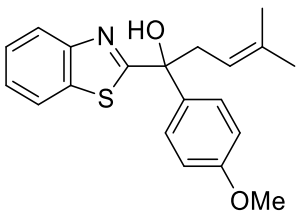


The titled compound was prepared by following the general procedure for [1,2] for 8 h (0.2 mmol), obtained as a yellowish liquid (50 mg, 78% yield). R_f (Acetone/pet ether = 4.5:95.5) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 1.64 (s, 3H), 1.67 (s, 3H), 3.01 (dd, *J* = 14.69, 7.82 Hz, 1H), 3.24 (dd, *J* = 14.50, 6.87 Hz, 1H), 3.50 (br s, 1H), 3.78 (s, 3H), 5.13 (t, *J* = 7.25 Hz, 1H), 6.88 (d, *J* = 8.77 Hz, 2H), 7.28 - 7.36 (m, 2H), 7.45 - 7.50 (m, 1H), 7.54 (d, *J* = 8.77 Hz, 2H), 7.69 - 7.77 (m, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 18.2, 26.0, 40.1, 55.3, 75.5, 110.8, 113.7, 117.2, 120.2, 124.4, 125.0, 126.7, 134.6, 137.9, 140.6, 151.2, 159.2, 168.8. **FTIR (cm^{-1}):** 3415, 3063, 2924, 2851, 1665, 1607, 1511, 1454, 1247, 1172, 1092, 910. **HRMS:** m/z calculated for $C_{20}H_{21}O_3NNa[M+Na]^+$: 346.1414, found: 346.1407.

1-(benzo[d]thiazol-2-yl)-1-(4-methoxyphenyl)-2,2-dimethylbut-3-en-1-ol (2B-3)

The titled compound was prepared by following the general procedure for [2,3] (0.2 mmol), obtained as a yellowish liquid (61 mg, 91% yield). R_f (Acetone/Pet ether = 4.5:95.5) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 1.18 (s, 3H), 1.34 (s, 3H), 3.71 (s, 1H), 3.77 (s, 3H), 5.12 - 5.24 (m, 2H), 5.96 (dd, *J* = 17.70, 10.99 Hz, 1H), 6.84 (d, *J* = 9.16 Hz, 2H), 7.34 (t, *J* = 7.32 Hz, 1H), 7.46 (t, *J* = 7.63 Hz, 1H), 7.81 (d, *J* = 9.16 Hz, 2H), 7.84 (d, *J* = 7.93 Hz, 1H), 8.05 (d, *J* = 7.93 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 22.1, 23.0, 46.9, 55.2, 81.6, 112.5, 115.6, 121.3, 123.2, 124.7, 125.6, 129.1, 131.7, 135.1, 144.2, 153.4, 158.8, 178.0. **FTIR (cm^{-1}):** 3526, 3071, 3017, 2972, 2843, 1602, 1508, 1218, 1127, 1031, 935, 833. **HRMS:** m/z calculated for $C_{20}H_{22}O_2NS[M+H]^+$: 340.1366, found: 340.1361.

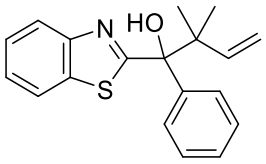
1-(benzo[d]thiazol-2-yl)-1-(4-methoxyphenyl)-4-methylpent-3-en-1-ol (3B-3)



The titled compound was prepared by following the general procedure for [1,2] for 4 h (0.2 mmol), obtained as a yellowish liquid (61 mg, 91% yield). R_f (Acetone/pet ether = 4.5:95.5) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 1.69 (s, 6H), 3.07 (dd, *J* = 14.20, 8.24 Hz, 1H), 3.34 (dd, *J* = 14.43, 6.64 Hz, 1H), 3.54 (s, 1H), 3.77 (s, 3H), 5.07 – 5.11 (m, 1H), 6.87 (d, *J*= 9.16 Hz, 2H), 7.31 - 7.37 (m, 1H), 7.42 - 7.49 (m, 1H), 7.60 - 7.66

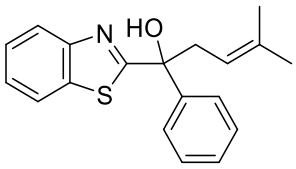
(m, 2H), 7.83 (d, *J* = 8.70 Hz, 1H), 8.01 (d, *J* = 10.07 Hz, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 18.3, 26.1, 41.5, 55.2, 78.1, 113.6, 117.5, 121.7, 123.1, 124.8, 125.8, 126.7, 135.6, 136.0, 138.8, 153.3, 158.9, 178.9. **FTIR (cm^{-1}):** 3522, 3018, 2973, 2844, 1610, 1510, 1447, 1217, 1176, 1080, 1031. **HRMS:** m/z calculated for $C_{20}H_{22}O_2NS[M+H]^+$: 340.1366, found: 340.1367.

1-(benzo[d]thiazol-2-yl)-2,2-dimethyl-1-phenylbut-3-ene-1-ol (2B-4)



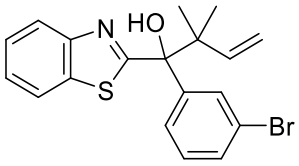
The titled compound was prepared by following the general procedure for [2,3] (0.2 mmol), obtained as a yellowish liquid (51 mg, 83% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 1.19 (s, 3H), 1.36 (s, 3H), 3.78 (s, 1H), 5.16 - 5.24 (m, 2H), 5.92 - 6.01 (m, 1H), 7.24 - 7.27 (m, 1H), 7.29 - 7.37 (m, 3H), 7.44 - 7.48 (m, 1H), 7.84 (d, *J* = 7.63 Hz, 1H), 7.89 (d, *J* = 8.01 Hz, 2H), 8.06 (d, *J* = 8.01 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 22.1, 23.0, 46.8, 81.8, 115.8, 121.4, 123.3, 124.8, 125.7, 127.2, 127.9, 131.3, 135.1, 139.6, 144.1, 153.4, 177.7. **FTIR (cm^{-1}):** 3525, 3068, 2976, 2928, 1648, 1593, 1485, 1128, 1020, 908. **HRMS:** m/z calculated for $C_{19}H_{20}ONS[M+H]^+$:310.1260, found: 310.1256.

1-(benzo[d]thiazol-2-yl)-4-methyl-1-phenylpent-3-ene-1-ol (3B-4)



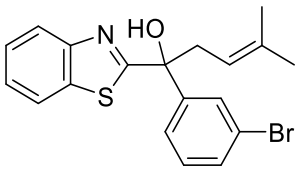
The titled compound was prepared by following the general procedure for [1,2] (0.2 mmol), obtained as a yellowish liquid (57 mg, 87% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 1.69 (s, 6H), 3.09 (dd, *J* = 14.50, 8.39 Hz, 1H), 3.38 (dd, *J* = 14.50, 6.49 Hz, 1H), 3.57 (br s, 1H), 5.10 (t, *J* = 7.44 Hz, 1H), 7.24 - 7.28 (m, 1H), 7.31 - 7.37 (m, 3H), 7.45 (t, *J* = 7.44 Hz, 1H), 7.71 (d, *J* = 7.63 Hz, 2H), 7.83 (d, *J* = 8.01 Hz, 1H), 8.02 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 18.3, 26.1, 41.5, 78.4, 117.5, 121.7, 123.2, 124.8, 125.4, 125.8, 127.5, 128.3, 135.7, 139.0, 143.8, 153.3, 178.5. **FTIR (cm^{-1}):** 3512, 3063, 2974, 2923, 1669, 1596, 1501, 1442, 1372, 1316, 1221, 889. **HRMS:** m/z calculated for $C_{19}H_{20}ONS[M+H]^+$: 310.1260, found: 310.1256.

1-(benzo[d]thiazol-2-yl)-1-(3-bromophenyl)-2,2-dimethylbut-3-en-1-ol (2B-5)



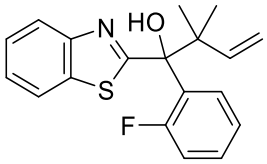
The titled compound was prepared by following the general procedure for [2,3] (0.2 mmol), obtained as a yellowish liquid (63 mg, 82% yield). ***R_f*** (Acetone/Pet ether = 4.5:95.5) = 0.2. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 1.18 (s, 3H), 1.35 (s, 3H), 3.80 (br s, 1H), 5.17 - 5.32 (m, 2H), 5.91 (dd, *J* = 17.17, 11.06 Hz, 1H), 7.17 (t, *J* = 7.63 Hz, 1H), 7.32 - 7.44 (m, 2H), 7.48 (t, *J* = 7.44 Hz, 1H), 7.86 (d, *J* = 6.10 Hz, 2H), 8.07 (m, 2H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 22.0, 22.9, 46.9, 81.2, 116.3, 121.4, 121.6, 123.4, 125.0, 125.8, 126.8, 128.6, 130.5, 130.8, 135.0, 142.0, 143.6, 153.3, 176.9. **FTIR (cm^{-1}):** 3523, 3070, 3016, 2971, 2927, 2862, 1706, 1653, 1575, 1470, 1270, 1173, 1134, 1068, 1013, 921. **HRMS:** m/z calculated for $C_{19}H_{19}ONBrS[M+H]^+$: 388.0365, found: 388.0367.

1-(benzo[d]thiazol-2-yl)-1-(3-bromophenyl)-4-methylpent-3-ene-1-ol (3B-5)



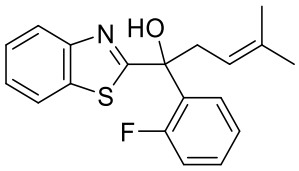
The titled compound was prepared by following the general procedure for [1,2] (0.12 mmol), obtained as a yellowish liquid (40 mg, 88% yield). ***R_f*** (Acetone/pet ether = 4.5:95.5) = 0.2. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 1.69 (s, 6H), 3.04 (dd, *J* = 14.20, 8.24 Hz, 1H), 3.34 (dd, *J* = 14.43, 6.64 Hz, 1H), 3.58 (s, 1H), 5.06 (t, *J* = 7.44 Hz, 1H), 7.20 (t, *J* = 8.01 Hz, 1H), 7.32 - 7.41 (m, 2H), 7.46 (t, *J* = 7.63 Hz, 1H), 7.65 (d, *J* = 8.01 Hz, 1H), 7.84 (d, *J* = 8.01 Hz, 1H), 7.91 (s, 1H), 8.03 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 18.3, 26.1, 41.6, 78.0, 117.0, 121.7, 122.5, 123.2, 124.3, 125.0, 125.9, 128.6, 129.8, 130.6, 135.6, 139.6, 146.0, 153.3, 177.7. **FTIR (cm^{-1}):** 3515, 3065, 2976, 2923, 1664, 1577, 1507, 1428, 1214, 1112, 1074, 987. **HRMS:** m/z calculated for $C_{19}H_{19}ONBrS[M+H]^+$: 388.0365, found: 388.0367.

1-(benzo[d]thiazol-2-yl)-1-(2-fluorophenyl)-2,2-dimethylbut-3-en-1-ol (2B-6)



The titled compound was prepared by following the general procedure for [2,3] (0.2 mmol), obtained as a yellowish liquid (52 mg, 79% yield). ***R_f*** (Acetone/pet ether = 4.5:95.5) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 1.26 (s, 3H), 1.32 (s, 3H), 4.34(d, *J* = 7.63 Hz, 1H), 5.08 - 5.23 (m, 2H), 6.12 - 6.27 (m, 1H,) 6.96 - 7.12 (m, 2H), 7.21 - 7.28 (m, 1H), 7.37 (t, *J* = 7.63 Hz, 1H), 7.48 (t, *J* = 7.63 Hz, 1H), 7.87 (d, *J* = 7.93 Hz, 1H), 8.03 - 8.13 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 22.0, 23.2, 47.5, 82.9, 115.2, 116.5 (d, *J* = 26.2 Hz), 121.4, 123.2 (d, *J* = 3.1 Hz), 123.4, 124.9, 125.6, 126.8 (d, *J* = 6.2 Hz), 129.5 (d, *J* = 9.2 Hz), 131.6 (d, *J* = 2.3 Hz), 135.3, 143.8, 153.0, 160.5 (d, *J* = 245.1 Hz), 176.1. **FTIR (cm^{-1}):** 3628, 3073, 3020, 2977, 2931, 1714, 1579, 1482, 1446, 1320, 1273, 1215, 1113, 1087, 1023, 926. **HRMS:** m/z calculated for $C_{19}H_{19}ONFS[M+H]^+$: 328.1166, found: 328.1164.

1-(benzo[d]thiazol-2-yl)-1-(2-fluorophenyl)-4-methylpent-3-ene-1-ol (3B-6)



The titled compound was prepared by following the general procedure for [1,2] (0.2 mmol), obtained as a yellowish liquid (57 mg, 87% yield). ***R_f*** (Acetone/pet ether = 4.5:95.5) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 1.67 (s, 6H), 3.27 - 3.42 (m, 2H), 3.92 (d, *J* = 2.44 Hz, 1H), 5.16 (t, *J* = 7.02 Hz, 1H), 7.01(dd, *J* = 7.93 Hz, 1H), 7.14 (t, *J* = 7.93 Hz, 1H), 7.24 - 7.32 (m, 1H), 7.35 (t, *J* = 7.63 Hz, 1H), 7.45 (t, *J* = 7.63 Hz, 1H), 7.67 (t, *J* = 7.93 Hz, 1H), 7.84 (d, *J* = 7.93 Hz, 1H), 8.01 (d, *J* = 8.55 Hz, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 18.2, 26.0, 39.4, 39.4, 116.3 (d, *J* = 23.1 Hz), 117.4, 121.6, 123.3, 124.1 (d, *J* = 3.1 Hz), 125.0, 125.9, 128.1 (d, *J* = 3.9 Hz), 129.9 (d, *J* = 9.2 Hz), 130.9 (d, *J* = 11.6 Hz), 135.7, 137.7, 152.5, 160.0 (d, *J* = 248.2 Hz), 176.8. **FTIR (cm^{-1}):** 3513, 3019, 2980, 2925, 2863, 1667, 1581, 1491, 1446, 1217, 1114, 1072 **HRMS:** m/z calculated for $C_{19}H_{19}ONFS[M+H]^+$: 328.1165, found: 328.1165.

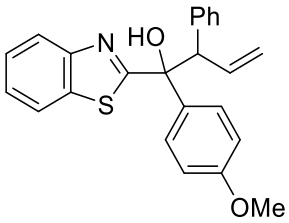
[2,3] for substrate class 1C (R^1 = Ar, R^2 = Ph, R^3 = H):

In a flame dried 25 ml round bottom flask with a magnetic bar, ether **1C** (0.2 mmol, 1.0 equiv) was taken with 1 ml of dry and oxygen free THF. After cooling the solution to -78 °C, n-BuLi (1.6M in Hexane, 1 mmol) was added dropwise. The reaction mixture was allowed to stir for 4 h and then quenched with saturated NH_4Cl solution. The organic layer was extracted with EtOAc (3 times) and combined organic layer dried over anhydrous Na_2SO_4. The solvent removal under reduced pressure gave the crude product which was further purified by column chromatography on silica gel using acetone-pet ether as eluent to obtain the desired product.

[1,2] for substrate class 1C (R^1 = Ar, R^2 = Ph, R^3 = H):

The procedure for substrate class **1C** is exactly same as class **1B**.

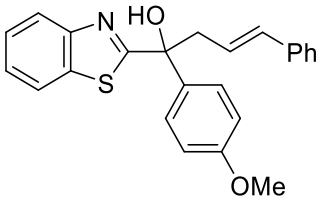
1-(benzo[d]thiazol-2-yl)-1-(4-methoxyphenyl)-2-phenylbut-3-en-1-ol (2C-1)



The titled compound was prepared by following the general procedure for [2,3] (0.2 mmol), obtained as a yellowish liquid (68 mg, 88% yield). ***R_f*** (Acetone/Pet etehr = 5.5:94.5) = 0.2. **dr ratio:** 55:45. **^{1}H NMR (500 MHz, $CDCl_3$) Major isomer:** δ 3.82 (s, 3H), 4.00 (s, 1H), 4.84 (d, *J* = 8.39 Hz, 1H), 5.12 (dd, *J* = 16.98, 10.49 Hz, 2H), 6.19 - 6.22 (m, 1H), 6.74 (d, *J* = 8.77 Hz, 2H), 7.12 - 7.20 (m, 5H), 7.32 (t, *J* = 7.63 Hz, 1H), 7.38 (t, *J* = 7.63 Hz, 1H), 7.74 (d, *J* = 8.01 Hz, 1H), 7.81 (d, *J* = 8.77 Hz, 2H), 7.95 (d, *J* = 8.39 Hz, 1H); **Minor isomer:** δ 3.72 (s, 3H), 3.91 (s, 1H), 4.75 (d, *J* = 7.63 Hz, 1H), 5.05 (d, *J* = 17.17 Hz, 2H), 6.28 - 6.38 (m, 1H), 6.93 (d, *J* = 8.77 Hz, 2H), 7.26 - 7.35 (m, 5H), 7.43 (t, *J* = 7.44 Hz, 1H), 7.51 (t, *J* = 7.63 Hz, 1H), 7.56 (d, *J* = 8.77 Hz, 2H), 7.87 (d, *J* = 8.01 Hz, 1H), 8.08 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 55.1, 55.2, 59.1, 60.0, 80.6, 81.1, 113.2, 113.6, 118.6, 119.5, 121.6, 121.8, 123.0, 123.2, 124.7, 124.9, 125.8, 125.9, 126.7, 127.0, 127.1, 127.5, 128.0, 128.3, 129.8, 129.9, 134.3, 134.4, 135.5, 135.7, 136.4,

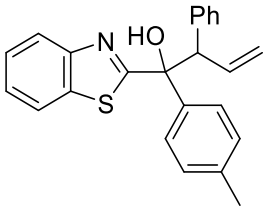
136.6, 138.8, 139.3, 152.6, 152.9, 158.6, 158.9, 177.9, 178.4**. FTIR (cm^{-1}):** 3538, 3018, 2968, 2843, 1601, 1506, 1451, 1217, 1177, 1126, 1033. **HRMS:** m/z calculated for $C_{24}H_{22}O_2NS[M+H]^+$: 388.1366, found: 388.1364.

(E)-1-(benzo[d]thiazol-2-yl)-1-((4-methoxyphenyl)-4-phenylbut-3-ene-1-ol (3C-1)



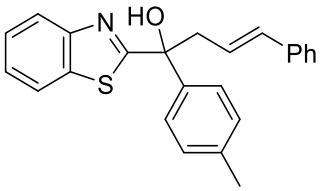
The titled compound was prepared by following the general procedure for [1,2] for 12 h (0.3 mmol), obtained as a yellowish liquid (105 mg, 91% yield). R_f (Acetone/pet ether = 5.5:94.5) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.22 (dd, *J* = 14.04, 7.93 Hz, 1H), 3.52 - 3.59 (dd, *J* = 14.04, 6.41 Hz, 1H), 3.60 (s, 1H), 3.79 (s, 3H), 6.01 - 6.19 (m, 1H), 6.62 (d, *J* = 16.03 Hz, 1H), 6.89 (d, *J* = 8.54 Hz, 2H), 7.21 (d, *J* = 6.71 Hz, 1H), 7.24- 7.30 (m, 4H), 7.36 (t, *J* = 7.63 Hz, 1H), 7.47 (t, *J* =7.63 Hz, 1H), 7.64 (d, *J* = 8.55 Hz, 2H), 7.84 (d, *J* = 7.93 Hz, 1H), 8.04 (d, *J* = 8.55 Hz, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 46.6, 55.2, 77.9, 113.7, 121.7, 123.2, 123.6, 124.9, 125.9, 126.3, 126.7, 127.7, 128.5, 135.7, 136.0, 136.6, 153.2, 159.0, 178.2. **FTIR (cm^{-1}):** 3441**,** 3014, 2968, 2928, 1721, 1607, 1508, 1173, 1091, 828. **HRMS:** m/z calculated for $C_{24}H_{22}O_2NS[M+H]^+$: 388.1366, found: 388.1363.

1-(benzo[d]thiazol-2-yl)-2-phenyl-1-(p-tolyl)but-3-en-1-ol (2C-2)



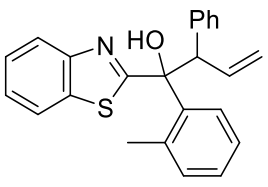
The titled compound was prepared by following the general procedure for [2,3] (0.25 mmol), obtained as a yellowish liquid (69 mg, 75% yield). R_f (Acetone/Pet ether = 5.5:94.5) = 0.2. **dr ratio**: 70:30. **^{1}H NMR (400 MHz, $CDCl_3$) Major isomer:** δ 2.31 (s, 3H), 3.93 (s, 1H), 4.83 (d, *J* = 8.54 Hz, 1H), 5.02 - 5.12 (m, 2H), 6.11 - 6.22 (m, 1H), 7.07 - 7.21 (m, 5H), 7.22 - 7.28 (m, 1H), 7.28 - 7.33 (m, 2H), 7.35 - 7.40 (m, 1H), 7.69 (d, *J* = 7 .93 Hz, 1H), 7.75 (d, *J* = 8.54 Hz, 2H), 7.90 (d, *J* = 8.54 Hz, 1H); **Minor isomer:** δ 2.19 (s, 3H), 4.03 (s, 1H), 4.75 (d, *J* = 7.32 Hz, 3H), 4.99 (m, 2H), 6.24 - 6.36 (m, 1H), 6.98 (d, *J* = 7.93 Hz, 2H), 7.07 - 7.21 (m, 3H), 7.22 - 7.28 (m, 1H), 7.28 - 7.33 (m, 2H), 7.45 (t, *J* = 7.63 Hz, 1H), 7.50 (d, *J* = 7.93 Hz, 2H), 7.82 (d, *J* = 7.93 Hz, 1H), 8.04 (d, *J* = 7.93 Hz, 1H); **^{13}C NMR (100MHz, $CDCl_3$)** δ 20.9, 21.0, 58.9, 59.8, 80.8, 81.2, 118.6, 119.5, 121.5, 121.7, 123.0, 123.1, 124.7, 124.9, 125.7, 125.7, 125.9, 126.0, 126.6, 128.0, 128.2, 128.6, 128.9, 129.7, 129.9, 135.5, 135.7, 136.4, 136.7, 136.8, 137.1, 138.8, 139.2, 139.2, 139.4, 152.5, 152.8, 177.7, 178.2. **FTIR (cm^{-1}):** 3414, 3022, 2927, 1664, 1604, 1521, 1485, 1216, 1123, 892. **HRMS:** m/z calculated for $C_{24}H_{22}ONS[M+H]^+$: 372.1417, found: 372.1416.

(E)-1-(benzo[d]thiazol-2-yl)-4-phenyl-1-(4-tolyl)but-3-ene-1-ol (3C-2)



The titled compound was prepared by following the general procedure for [1,2] for 12 h (0.13 mmol), obtained as a yellowish liquid (44 mg, 88% yield). R_f (Acetone/pet ether = 5.5:94.5) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 2.31 (s, 3H), 3.23 (dd, *J* = 13.73, 8.24 Hz, 1H), 3.58 (dd, *J* = 14.04, 6.71 Hz, 1H), 3.65 (br s, 1H), 6.05 - 6.19 (m, 1H), 6.61 (d, *J* = 16.06 Hz, 1H), 7.12 - 7.21 (m, 3H), 7.21 - 7.29 (m, 4H), 7.33 (t, *J* = 7.32 Hz, 1H), 7.45 (t, *J* = 7.63 Hz, 1H), 7.60 (d, *J* = 7.93 Hz, 2H), 7.81 (d, *J* = 7.93 Hz, 1H), 8.03 (d, *J* =7 .93 Hz, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 21.0, 46.5, 78.1, 121.7, 123.1, 123.6, 124.9, 125.3, 125.9, 126.3, 127.6, 128.5, 129.1, 135.7, 136.0, 136.6, 137.4, 140.6, 153.2, 178.1. **FTIR (cm^{-1}):** 3490, 3015, 2974, 2928, 1703, 1604, 1507, 1219, 1178, 1140, 970, 916. **HRMS:** m/z calculated for $C_{24}H_{22}ONS[M+H]^+$: 372.1417, found: 372.1417.

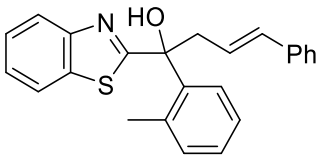
1-(benzo[d]thiazol-2-yl)-2-phenyl-1-(o-tolyl)but-3-en-1-ol (2C-3)



The titled compound was prepared by following the general procedure for [2,3] (0.25 mmol), obtained as a yellowish liquid (58 mg, 63% yield). R_f (Acetone/Pet ether = 5.5:94.5) = 0.2. **dr ratio:** 91:09. **^{1}H NMR (400 MHz, $CDCl_3$) Major isomer:** δ 2.41 (s, 3H), 4.02 (s, 1H), 4.90 (d, *J* = 8.54 Hz, 1H), 5.17 - 5.24 (m, 2H), 6.35 - 6.47 (m, 1H), 7.09 (m, 4H), 7.15 - 7.22 (m, 3H), 7.23 - 7.31 (m, 2H), 7.32 - 7.41 (m, 1H), 7.70 (d, *J* = 7.93 Hz, 1H), 7.81 (d, *J* = 7.93 Hz, 1H), 7.88 (d, *J* = 7.93 Hz, 1H); **Minor isomer:** δ 2.52 (s, 3H), 4.19 (s, 1H), 4.91 (d, *J* = 8.54 Hz, 1H), 5.11 – 5.17 (m, 2H), 6.28 - 6.35 (m, 1H), 6.95 (d, *J* = 4.88 Hz, 1H), 7.02 - 7.05 (m, 2H), 7.14 – 7.20 (m, 1H),

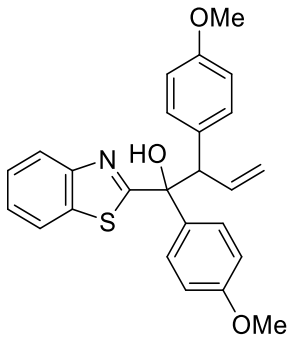
7.32 - 7.42 (m, 1H), 7.45 - 7.50 (m, 2H), 7.52 - 7.60 (m, 2H), 7.98 - 8.08 (m, 3H), 8.19 (d, *J* = 7.32 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$)** δ 22.4, 57.8, 81.3, 118.4, 121.5, 123.0, 124.8, 125.6, 125.8, 126.9, 127.9, 128.0, 128.1, 130.0, 132.9, 137.5, 139.8, 139.9, 151.7, 176.6. **FTIR (cm^{-1}):** 3412, 3022, 2935, 2966, 1593, 1433, 1502, 1159, 1042, 927. **HRMS:** m/z calculated for $C_{24}H_{22}ONS[M+H]^+$: 372.1417, found: 372.1415.

(E)-1-(benzo[d]thiazol-2-yl)-4-phenyl-1-(2-tolyl)but-3-ene-1-ol (3C-3)



The titled compound was prepared by following the general procedure for [1,2] for 12 h (0.25 mmol), obtained as a yellowish liquid (65 mg, 71% yield). ***R_f*** (Acetone/pet ether = 5.5:94.5) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 2.30 (s, 3H), 3.42 (dd, *J* = 14.04, 7.93 Hz, 1H), 3.49 (dd, *J* = 14.04, 6.71 Hz, 1H), 3.76 (s, 1H), 6.11 - 625 (m, 1H), 6.58 (d, *J* = 16.06 Hz, 1H), 7.16 (d, *J* = 3.66 Hz, 1H), 7.20 (d, *J* = 6.71 Hz, 1H), 7.22 - 7.29 (m, 6H), 7.36 (t, *J* = 7.32 Hz, 1H), 7.47 (t, *J* = 7.63 Hz, 1H), 7.60 - 7.70 (m, 1H), 7.81 (d, *J* = 7.93 Hz, 1H), 8.02 (d, *J* = 7.93 Hz, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 21.7, 45.4, 78.5, 121.7, 123.3, 123.8, 125.1, 125.7, 126.0, 126.3, 126.5, 127.5, 128.4, 128.5, 132.7, 135.5, 135.9, 136.9, 137.6, 140.8, 152.4, 177.8. **FTIR (cm^{-1}):** 3523, 3019, 2926, 2860, 1704, 1595, 1498, 1449, 1176, 974, 922. **HRMS:** m/z calculated for $C_{24}H_{22}ONS[M+H]^+$: 372.1417, found: 372.1415.

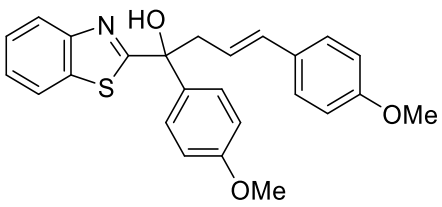
1-(benzo[d]thiazol-2-yl)-1,2-bis(4-methoxyphenyl)but-3-en-1-ol (2C-4)



The titled compound was prepared by following the general procedure for [2,3] (0.2 mmol), obtained as a yellowish liquid (73 mg, 88% yield). ***R_f*** (Acetone/Pet ether = 5.5:94.5) = 0.2. **dr ratio:** 67:33. **^{1}H NMR (500 MHz, $CDCl_3$) Major isomer:** δ 3.68 (s, 3H), 3.77 (s, 3H), 3.83 (s, 1H), 4.78 (d, *J* = 8.39 Hz, 1H), 5.00 - 5.12 (m, 2H), 6.08 - 6.19 (m, 1H), 6.68 (d, *J* = 8.39 Hz, 2H), 6.88 (d, *J* = 8.77 Hz, 2H), 7.20 (d, *J* = 8.77 Hz, 2H), 7.29 (t, *J* = 7.63 Hz, 1H), 7.39 (t, *J* = 7.63 Hz, 1H), 7.71 (d, *J* = 7.63 Hz, 1H), 7.76 (d, *J* = 8.77 Hz, 2H), 7.93 (d, *J* = 8.39 Hz, 1H); **Minor isomer:** δ 3.69 (s, 3H), 3.71 (s, 3H), 3.80 (s, 1H), 4.66 (d, *J* = 7.25 Hz, 1H), 4.98 – 5.04 (m, 2H), 6.22 - 6.32 (m, 1H), 6.69 - 6.73 (m, 4H), 7.15 (d, *J* = 8.77 Hz, 2H), 7.34 (t, *J* = 7.63 Hz, 1H), 7.46 (t, *J* = 7.63 Hz, 1H), 7.53 (d, *J* = 8.77 Hz, 2H), 7.83 (d, *J* = 8.01 Hz, 1H), 8.04 (d, *J* = 8.01 Hz, 1H); **^{13}C NMR (125MHz, $CDCl_3$)** δ 55.1, 55.1, 55.2, 55.3, 58.2, 59.2, 80.7, 81.1, 113.2, 113.4, 113.5, 113.7, 118.3, 119.2, 121.6, 121.7, 123.0, 123.1, 124.7, 124.9, 125.7, 125.9, 127.1, 127.4, 130.7, 130.8, 130.9, 131.2, 134.4, 135.5, 135.6, 136.6, 136.9, 152.7, 152.9, 158.2, 158.4, 158.5, 158.8, 178.2, 178.4. **FTIR (cm^{-1}):** 3533, 3016, 2951, 2841, 1602, 1506, 1454, 1175, 1123, 1032. **HRMS:** m/z calculated for $C_{25}H_{23}O_3NNaS[M+Na]^+$: 440.1291, found: 440.1283.

(E)-1-(benzo[d]thiazol-2-yl)-1,4-bis(4-methoxyphenyl)but-3-ene-1-ol (3C-4)

The titled compound was prepared by following the general procedure for [1,2] for 4 h (0.2 mmol), obtained as a yellowish liquid (76 mg, 91% yield). ***R_f*** (Acetone/pet ether = 5.5:94.5) 0.2. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 3.18 (dd, *J* = 14.11, 8.01 Hz, 1H), 3.55 (dd, *J* = 13.73, 6.87 Hz, 1H), 3.60 (s, 1H), 3.77 (s, 3H), 3.78 (s, 3H), 5.90 - 6.02 (m, 1H), 6.56 (d, *J* = 15.06 Hz, 1H), 6.79 (d, *J* = 8.39 Hz, 2H), 6.88 (d, *J* = 8.39 Hz, 2H), 7.21 (d, *J* = 8.39 Hz, 2H), 7.35 (t, *J* = 7.32 Hz, 1H), 7.46 (t, *J* = 8.39 Hz, 1H), 7.64 (d, *J* = 9.16 Hz, 2H), 7.83 (d, *J* = 7.63 Hz, 1H), 8.03 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 46.7, 55.2, 55.3, 77.9, 113.7, 113.9, 121.2, 121.7, 123.2, 124.9, 125.9, 126.7, 127.6, 129.5, 135.6, 135.7, 135.7, 153.3, 159.0, 159.3, 178.4. **FTIR (cm^{-1}):** 3535, 3020, 2962, 2841, 1608, 1511, 1452, 1248, 1178, 1127, 1034, 978, 936, 890. **HRMS:** m/z calculated for $C_{25}H_{23}O_3NNaS[M+Na]^+$: 440.1291, found: 440.1283.



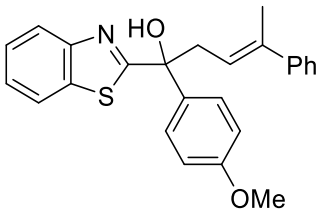
[2,3] for substrate class 1D and 1E (R^1 = Ar/Alkyl, R^2 = Ph, R^3 = Me):

The procedure is similar to class **1C** with different solvents (THF, diethyl ether, and DCM) and temperature from -78 °C to -90 °C. No [2.3] obtained in any cases.

[1,2] for substrate class 1D and 1E (R^1 = Ar, R^2 = Ph, R^3 = Me):

The procedure for class **1D** substrate is similar to class **1A** with different base and reaction temperature.

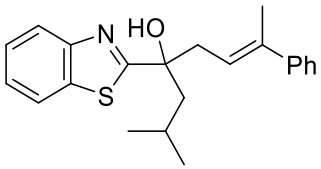
(E)-1-(benzo[d]thiazol-2-yl)-1-((4-methoxyphenyl)-4-phenylpen-3-ene-1-ol (3D-1)



The titled compound was prepared by following the general procedure for [1,2] with 30 mol% KO^{t}Bu in acetonitrile at 0 °C for 12 h (0.12 mmol), obtained as a yellowish liquid (45 mg, 90% yield). ***R*$_f$** (Acetone/pet ether = 4.5:95.5) = 0.2. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 2.10 (s, 3H,) 3.32 (dd, *J* = 14.88, 8.01 Hz, 1H), 3.51 (dd, *J* = 14.88, 6.87 Hz, 1H), 3.62 (br s, 1H), 3.78 (s, 3H), 5.75 (t, *J* = 7.25 Hz, 1H), 6.88 (d, *J* = 8.77 Hz, 2H), 7.17 - 7.22 (m, 1H), 7.23 - 7.329 (m, 4H), 7.31 - 7.37 (m, 1H), 7.45 (t, *J* = 7.63 Hz, 1H), 7.63 (d, *J* = 8.77 Hz, 2H), 7.83 (d, *J* = 8.01 Hz, 1H), 8.02 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR (CDCl$_3$, 125MHz)** δ 16.5, 42.1, 55.2, 78.5, 113.7, 121.3, 121.7, 123.2, 124.9, 125.8, 125.9, 126.8, 127.1, 128.2, 135.7, 135.9, 140.4, 143.3, 153.1, 159.1, 178.4. **FTIR (cm^{-1}):** 3522, 2929, 2838, 1601, 1508, 1451, 1178, 1033, 908. **HRMS:** m/z calculated for $C_{25}H_{24}O_2NS[M+H]^+$: 424.1342, found: 424.1337.

No [2,3] for this substrate.

(E)-4-(benzo[d]thiazol-2-yl)-2-methyl-7-phenyloct-6-ene-4-ol (3E-1)



The titled compound was prepared by following the general procedure for [1,2] with LiHMDS (2 equiv) in THF at 0 °C for 1 h (0.2 mmol), obtained as a yellowish liquid (61 mg, 88% yield). ***R*$_f$** (EtOAc/pet ether = 2:98) = 0.2. **^{1}H NMR (500 MHz, CDCl$_3$)** δ 0.77 (d, *J* = 6.48 Hz, 3H), 1.01 (d, *J* = 6.87 Hz, 3H), 1.77 - 1.89 (m, 1H), 1.93 - 2.00 (m, 1H), 2.04 (s, 3H), 2.06 - 2.12 (m, 1H), 2.91 (dd, *J* = 14.50, 8.39 Hz, 1H), 2.98 (dd, *J* = 14.50, 6.87 Hz, 1H), 3.25 (s, 1H), 5.69 (t, *J* = 7.44 Hz, 1H), 7.16 - 7.23 (m, 1H), 7.24 – 7.28 (m, 4H), 7.37 (t, *J* = 7.63 Hz, 1H), 7.47 (t, *J* = 7.63 Hz, 1H), 7.88 (d, *J* = 8.01 Hz, 1H), 8.00 (d, *J* = 8.01 Hz, 1H); **^{13}C NMR (CDCl$_3$, 125 MHz)** δ 16.4, 24.1, 24.3, 24.4, 42.8, 50.6, 78.7, 121.1, 121.8, 122.9, 124.7, 125.8, 125.9, 127.0, 128.2, 135.5, 139.9, 143.4, 153.2, 179.2. **FTIR (cm^{-1}):** 3455, 3018, 2965, 2843, 1670, 1606, 1512, 1455, 1173, 1036, 974. **HRMS:** m/z calculated for $C_{22}H_{25}ONNaS[M+Na]^+$: 374.1549, found: 374.1544.

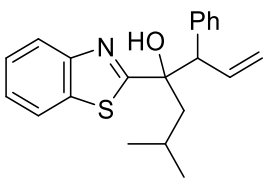
[2,3] for substrate class 1F (R^1 = Alk, R^2 = Ar, R^3 = H):

The procedure for substrate class **1F** is exactly same as class **1C**.

[1,2] for substrate class 1F (R^1 = Alk, R^2 = Ar, R^3 = H):

The procedure for substrate class **1F** is similar to class **1B** with KHMDS base (3 equiv) for 2h.

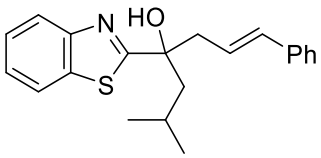
4-(benzo[d]thiazol-2-yl)-6-methyl-3-phenylhept-1-en-4-ol (2F-1)



The titled compound was prepared by following the general procedure for [2,3] (0.3 mmol), obtained as a yellow solid (77 mg, 77 % yield). ***R*$_f$** (EtOAc/pet ether = 02:98) = 0.2; **dr ratio:** 64:36. **^{1}H NMR (500 MHz, CDCl$_3$) Major isomer:** δ 0.61 (d, *J* = 6.10 Hz, 3H), 0.86 (d, *J* = 5.72 Hz, 3H), 1.53 – 1.60 (m, 2H), 1.99 - 2.06 (m, 1H), 3.27 (s, 1 H) 3.85 (d, *J*=8.77 Hz, 1 H) 4.86 - 4.97 (m, 2 H) 6.19 - 6.28 (m, 1 H) 7.06 (s, 2H), 7.30 – 7.35 (m, 3H), 7.38 (t, *J* = 7.63 Hz, 1H), 7.47 - 7.51 (t, *J* = 7.63 Hz, 1H), 7.89 (d, *J* = 8.01 Hz, 1H), 8.03 (d, *J* = 8.01 Hz, 1H); **Minor isomer:** δ 0.70 (d, *J* = 6.49 Hz, 3H), 0.98 (d, *J* = 6.87 Hz, 3H), 1.55 – 1.62 (m, 2H), 1.99 - 2.06 (m, 1H), 3.31 (s, 1H), 3.89 (d, *J* = 9.92 Hz, 1H), 5.23 - 5.30 (m, 2H), 6.38 - 6.47 (m, 1H), 7.24 - 7.29 (m, 3H),

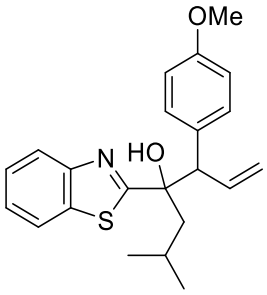
7.31 (m, 3H), 7.43 (t, *J* = 7.63 Hz, 1H), 7.77 (d, *J* = 8.01 Hz, 1H), 7.92 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 24.0, 24.2, 24.4, 24.3, 24.5, 48.9, 49.3, 61.9, 62.1, 80.4, 80.8, 118.1, 118.5, 121.6, 121.7, 122.8, 122.9, 124.6, 124.7, 125.8, 125.9, 126.7, 127.1, 128.1, 128.4, 128.8, 129.6, 135.4, 135.5, 136.4, 136.5, 139.4, 139.6, 152.7, 152.9, 178.3, 178.4. **FTIR (CM^{-1}):** 3469, 3022, 2959, 2868, 1690, 1597, 1510, 1431, 1070, 1022, 927. **HRMS:** m/z calculated for $C_{21}H_{24}ONS[M+H]^+$:338.1573, found:338.1574.

(E)-4-(benzo[d]thiazol-2-yl)-6-methyl-1-phenylhept-1-ene-4-ol (3F-1)



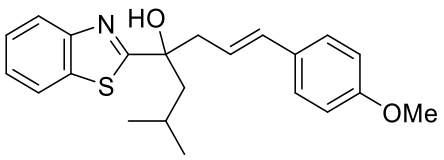
The titled compound was prepared by following the general procedure for [1,2] (0.2 mmol), obtained as a yellow liquid (52 mg, 88% yield). ***R_f*** (EtOAc/pet ether = 2:98) = 0.2. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 0.76 (d, *J* = 6.87 Hz, 3H), 0.09 (d, *J* = 6.48 Hz, 3H), 1.75 - 1.83 (m, 1H), 1.92 (dd, *J* = 14.11, 6.49 Hz, 1H), 2.07 (dd, *J* = 14.31, 5.91 Hz, 1H), 2.79 (dd, *J* = 13.73, 8.77 Hz, 1H), 3.06 (dd, *J* = 14.31, 5.53 Hz, 1H), 3.27 (s, 1H), 6.00 - 6.11 (m, 1H), 6.53 (d, *J* = 15.86 Hz, 1H), 7.14 - 7.23 (m, 1H), 7.23 - 7.32 (m, 4H), 7.38 (t, *J* = 7.25 Hz, 1H),) 7.48 (t, *J* = 7.25 Hz, 1H), 7.89 (d, *J* = 8.01 Hz, 1H), 8.01 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 24.2, 24.3, 24.3, 47.2, 50.6, 78.1, 121.8, 122.9, 123.5, 124.8, 125.9, 126.3, 127.5, 128.5, 135.4, 135.5, 136.8, 153.3, 179.1. **FTIR (cm^{-1}):** 3436, 3065, 3027, 2953, 2863, 1594, 1505, 1442, 1247, 1135, 1060, 971, 917. **HRMS:** m/z calculated for $C_{21}H_{24}ONS[M+H]^+$:338.1573 found:338.1573.

4-(benzo[d]thiazol-2-yl)-3-(4-methoxyphenyl)-6-methylhept-1-en-4-ol (2F-2)



The titled compound was prepared by following the general procedure for [2,3] (0.2 mmol), obtained as a yellow liquid (55 mg, 75 % yield). ***R_f*** (EtOAc/pet ether = 02:98) = 0.2: **dr ratio**: 70:30. **^{1}H NMR (500 MHz, $CDCl_3$) Major isomer:** δ 0.61 (d, *J* = 6.10 Hz, 3H), 0.87 (d, *J* = 6.10 Hz, 3H), 1.53 - 1.59 (m, 2H), 1.96 - 2.07 (m, 1H), 3.23 (s, 1H), 3.66 (s, 3H), 3.81 (d, *J* = 9.54 Hz, 1H), 4.85 - 4.98 (m, 2H), 6.18 – 6.23 (m, 1H), 6.61 (d, *J* = 8.39 Hz, 2H), 6.98 (d, *J* = 8.77 Hz, 2H), 7.32 (t, *J* = 7.63 Hz, 1H), 7.43 (t, *J* = 7.63 Hz, 1H), 7.78 (d, *J* = 8.01 Hz, 1H), 7.94 (d, *J* = 8.39 Hz, 1H); **Minor isomer:** δ 0.69 (d, *J* = 6.48 Hz, 3H), 0.97 (d, *J* = 6.87 Hz, 3H), 1.53 - 1.59 (m, 2H), 1.96 - 2.07 (m, 1H), 3.28 (s, 1H), 3.80 (s, 3H), 3.86 (d, *J* = 9.54 Hz, 1H), 5.20 - 5.29 (m, 2H), 6.34 – 6.42 (m, 1H), 6.85 (d, *J* = 8.77 Hz, 2H), 7.21 (d, *J* = 8.39 Hz, 2H), 7.38 (t, *J* = 7.44 Hz, 1H), 7.48 (t, *J* = 7.63 Hz, 1H), 7.88 (d, *J* = 7.63 Hz, 1H), 8.02 (d, *J* = 8.01 Hz, 1H); **^{13}C NMR ($CDCl_3$, 125 MHz):** δ 24.0, 24.1, 24.2, 24.3, 24.4, 24.5, 48.9, 49.3, 55.0, 55.2, 61.0, 61.3, 80.4, 80.9, 113.6, 113.8, 117.8, 118.2, 121.6, 171.7, 122.8, 122.9, 124.6, 124.7, 125.8, 125.9, 129.8, 130.5, 130.6, 131.5, 135.4, 135.5, 136.6, 136.8, 152.7, 152.9, 158.2, 158.6, 178.4, 178.5**. FTIR (CM^{-1}):** 3425, 2955, 2863, 1675, 1608, 1509, 1175, 1127, 1035, 909. **HRMS:** m/z calculated for $C_{22}H_{25}O_2NNaS[M+Na]^+$: 390.1498, found: 390.1490.

E)-4-(benzo[d]thiazol-2-yl)-1-(4-methoxyphenyl)-6-methyl-1-phenylhept-1-ene-4-ol (3F-2)



The titled compound was prepared by following the general procedure for [1,2] (0.2 mmol), Obtained as a yellow liquid (65 mg, 89% yield). ***R_f*** (EtOAc/pet ether = 2:98) = 0.2. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 0.76 (d, *J* = 6.49 Hz, 3H), 0.98 (d, *J* = 6.49 Hz, 3H), 1.75 – 1.82 (m, 1H), 1.91 (dd, *J* = 14.31, 6.29 Hz, 1H), 2.07 (dd, *J* = 14.50, 5.72 Hz, 1H), 2.75 (dd, *J* = 13.73, 8.77 Hz, 1H), 3.06 (dd, *J* = 13.92, 5.53 Hz, 1H), 3.26 (s, 1H), 3.77 (s, 3H), 5.85 – 5.91 (m, 1H), 6.45 (d, *J* = 16.06 Hz, 1H), 6.79 (d, *J* = 8.77 Hz, 2H), 7.21 (d, *J* = 8.77 Hz, 2H), 7.38 (t, *J* = 7.25 Hz, 1H), 7.48 (t, *J* = 7.63 Hz,1H), 7.89 (d, *J* = 8.01 Hz, 1H), 8.01 (d, *J* = 8.01 Hz, 1H); **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 24.2, 24.3, 24.3, 47.2, 50.5, 55.2, 78.1, 113.9, 121.1, 121.8, 122.9, 124.7, 125.9, 127.5, 129.6, 135.0, 135.5, 153.3, 159.2, 179.4. **FTIR (cm^{-1}):** 3685, 3022, 2928, 2861, 1710, 1598, 1509, 1434, 1131, 1060, 916. **HRMS:** m/z calculated for $C_{22}H_{25}O_2NNaS[M+Na]^+$: 390.1498, found: 390.1492.

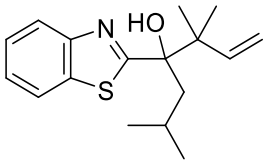
[2,3] for substrate class 1G (R^1 = Alk, R^2 = Me, R^3 = Me):

The procedure for substrate class **1G** is exactly same as class **1C** for 2h.

[1,2] for substrate class 1G (R^1 = Alk, R^2 = Me, R^3 = Me):

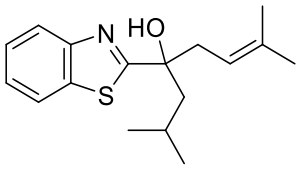
The procedure for substrate class **1G** is similar to class **1F** at 0 °C – room temperature for 12 h.

4-(benzo[d]thiazol-2-yl)-3,3,6-trimethylhept-1-en-4-ol (2G-1)



The titled compound was prepared by following the general procedure for [2,3] (0.2 mmol), obtained as a yellowish liquid (44 mg, 76 % yield). R_f(EtOAc/pet ether = 01:99) = 0.2. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.63 (d, *J* = 6.71 Hz, 3H), 0.96 (d, *J* = 6.71 Hz, 3H), 1.10 (s, 3H), 1.19 (s, 3H), 1.53 – 1.59 (m, 1H), 1.83 (dd, *J* = 14.04, 6.71 Hz, 1H), 2.15 (dd, *J* = 14.04, 4.88 Hz, 1H), 3.39 (br s, 1H), 5.07 - 5.22 (m, 2H), 6.01 - 6.18 (m, 1H), 7.36 (t, *J* = 7.32 Hz, 1H), 7.46 (t, *J* = 7.32 Hz, 1H), 7.87 (d, *J* = 7.93 Hz, 1H), 8.01 (d, *J* = 7.93 Hz, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 22.2, 22.5, 24.1, 24.4, 24.5, 44.9, 45.7, 81.8, 115.0, 121.4, 122.9, 124.7, 125.7, 135.6, 144.2, 152.4, 177.5. **FTIR (cm^{-1}):** 3463, 3071, 2959, 2874, 1630, 1502, 1453, 1127, 1090, 1005, 918. **HRMS:** m/z calculated for $C_{17}H_{24}ONS[M+H]^+$: 312.1393, found: 312.1386.

4-(benzo[d]thiazol-2-yl)-2,7-dimethyloct-6-ene-4-ol (3G-1)



The titled compound was prepared by following the general procedure for [1,2] (0.2 mmol), obtained as a yellowish liquid (49 mg, 86% yield). R_f(EtOAc/pet ether = 2:98) = 0.2. **NMR (500 MHz, $CDCl_3$)** δ 0.74 (d, *J* = 6.49 Hz, 3H), 0.98 (d, *J* = 6.48 Hz, 3H), 1.64 (s, 3H), 1.68 (s, 3H), 1.73 – 1.80 (m, 1H), 1.88 (dd, *J* = 14.31, 6.29 Hz, 1H), 2.03 (dd, *J* = 14.31, 5.91 Hz, 1H), 2.70 (dd, *J* = 14.11, 8.77 Hz, 1H), 2.79 (dd, *J* = 14.31, 6.29 Hz, 1H), 3.12 (s, 1H), 5.02 (t, *J* = 7.63 Hz, 1H), 7.37 (t, *J* = 8.20 Hz, 1H), 7.47 (t, *J* = 8.20 Hz, 1H), 7.88 (d, *J* = 8.01 Hz, 1H), 8.00 (d, *J* = 8.01 Hz, 1H); **^{13}C NMR (125 MHz, $CDCl_3$)** δ 18.2, 24.1, 24.3, 24.3, 26.0, 42.0, 50.4, 78.4, 117.3, 121.7, 122.8, 124.6, 125.8, 135.5, 138.0, 153.4, 180.0. **FTIR (cm^{-1}):** 3518, 3064, 2961, 2872, 1512, 1447, 1174, 1075, 1014. **HRMS:** Calculated for $C_{17}H_{24}ONS$ $[M+H]^+$: 312.1393, found:312.1387.

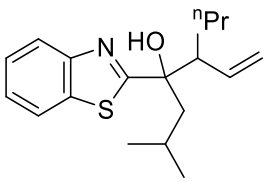
[2,3] for substrate class 1H (R^1 = Alk, R^2 = Alk, R^3 = H):

The procedure for substrate class **1H** is similar to class **1C**.

[1,2] for substrate class 1H (R^1 = Alk, R^2 = Alk, R^3 = H):

The procedure for substrate class **1H** is similar to class **1G** at 55 °C for 6 h.

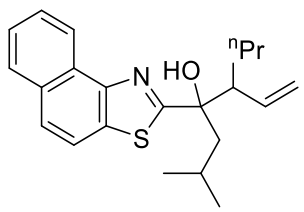
4-(benzo[d]thiazol-2-yl)-2-methyl-5-vinyloctan-4-ol (2H-1)



The titled compound was prepared by following the general procedure for [2,3] (0.478 mmol), obtained as a yellowish liquid (123 mg, 86% yield). R_f(EtOAc/pet ether = 01:99) = 0.2 **dr ratio**: 89:11. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.64 - 0.70 (m, 3H), 0.76 (t, *J* = 7.32 Hz, 3H), 0.96 (d, *J* = 6.71 Hz, 3H), 1.04 - 1.19 (m, 2H), 1.25 - 1.34 (m, 1H), 1.39 - 1.48 (m, 1H), 1.56 - 1.66 (m, 1H), 1.88 - 1.97 (m, 2H), 2.44 (t, *J* = 10.38 Hz, 1H), 3.36 (s, 1H), 5.14 - 5.29 (m, 1H), 5.65 (dt, *J* = 17.24, 9.99 Hz, 1H), 7.37 (t, *J* = 7.32 Hz, 1H), 7.48 (t, *J* = 7.32 Hz, 1H), 7.88 (d, *J* = 7.93 Hz, 1H), 8.01 (d, *J* = 8.55 Hz, 1H); **^{13}C NMR (100MHz, $CDCl_3$)** δ 13.8, 20.5, 24.2, 24.3, 30.3, 49.6, 56.4, 80.0, 118.9, 121.7, 122.9, 124.7, 125.9, 135.5, 137.6, 152.7, 178.7. **FTIR (cm^{-1}):** 3499, 3070, 2956, 2872, 1693, 1636, 1508, 1453, 1140, 1057, 916. **HRMS:** Calculated for $C_{18}H_{25}ONNaS$ $[M+H]^+$: 326.1549, found: 326.1545.

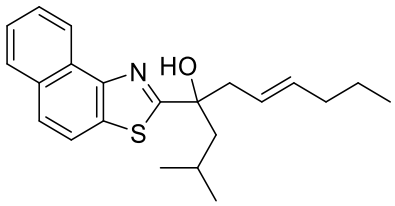
No [1,2] for this substrate.

2-methyl-4-(naphtho[1,2-d]thiazol-2-yl)-5-vinyloctan-4-ol (2H-2)



The titled compound was prepared by following the general procedure for [2,3] (0.3 mmol), obtained as a yellowish liquid (76 mg, 72% yield). **dr ratio:** 61:39 **^{1}H NMR (500 MHz, $CDCl_3$) Major isomer:** δ 0.66 (d, *J* = 6.49 Hz, 3H), 0.77 (t, *J* = 7.25 Hz, 3H), 0.98(d, *J* = 6.86 Hz, 3H), 1.06 - 1.13 (m, 2H), 1.28 - 1.36 (m, 2H), 1.62 – 1.67 (m, 1H), 1.88 - 1.96 (m, 2H), 2.40 - 2.50 (m, 1H), 3.67 (s, 1H), 5.22 - 5.27 (m, 2H), 5.64 – 5.71 (m, 1H), 7.55 - 7.60 (m, 1H), 7.65 - 7.69 (m, 1H), 7.79 (m, 1H), 7.89 (m, 1H), 7.95 (m, 1H), 8.82 (d, *J* = 8.39 Hz, 1H); **Minor isomer:** δ 0.70 (d, *J* = 6.87 Hz, 3H), 0.83 (t, *J* = 7.06 Hz, 3H), 0.96 - 1.00 (m, 3H), 1.18 - 1.27 (m, 2H), 1.45 - 1.50 (m, 1H), 1.68 - 1.75 (m, 1H), 1.79 – 1.85 (m, 1H), 1.98 - 2.05 (m, 1H), 2.09 (dd, *J* = 14.31, 5.53 Hz, 1H), 2.40 - 2.50 (m, 1H), 3.70 (s, 1H), 5.02 - 5.13 (m, 2H), 5.64 – 5.71 (m, 1H), 5.82 (dt, *J* = 16.98, 9.82 Hz, 1H), 7.55 - 7.60 (m, 1H), 7.65 - 7.69 (m, 1H), 7.79 (m, 1H), 7.89 (m, 1H), 7.95 (m, 1H), 8.82 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 13.8, 13.9, 20.5, 20.7, 24.2, 24.3, 24.4, 24.5, 30.1, 30.4, 48.6, 49.8, 56.7, 80.0, 80.0, 118.6, 118.8, 119.1, 124.0, 125.4, 125.4, 125.9, 126.0, 126.8, 128.0, 128.6, 131.8, 132.1, 137.8, 137.9, 148.4, 148.7, 176.5, 177.3. **HRMS:** Calculated for $C_{22}H_{28}ONS[M+H]^+$: 354.1886 found: 354.1882.

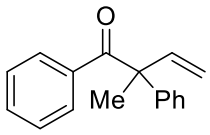
(E)-2-methyl-4-(naphtho[1,2-d]thiazol-2-yl)dec-6-en-4-ol (3H-2)



The titled compound was prepared by following the general procedure for [1,2] (0.06 mmol), obtained as a yellowish liquid (8 mg, 40% yield; with ~25% [2,3]).**^{1}H NMR (400 MHz, $CDCl_3$)** δ 0.74 (d, *J* = 6.10 Hz, 3H), 0.79 (t, *J* = 7.32 Hz, 3H), 0.98 (d, *J* = 6.10 Hz, 3H), 1.76 - 1.83 (m, 1H), 1.88 - 1.96 (m, 3H), 2.01 - 2.11 (m, 3H), 2.60 (dd, *J* = 13.73, 8.85 Hz, 1H), 2.95 (dd, *J* = 13.73, 5.80 Hz, 1H), 3.38 (s, 1H), 5.22 – 5.30 (m, 1H), 5.54 - 5.64 (m, 1H), 7.54 - 7.60 (m, 1H), 7.66 (t, *J* = 7.02 Hz, 1H), 7.79 (d, *J* = 8.55 Hz, 1H), 7.90 (d, *J* = 9.16 Hz, 1H), 7.95 (d, *J* = 7.93 Hz, 1H), 8.81 (d, *J* = 8.55 Hz, 1H). **HRMS:** Calculated for $C_{22}H_{28}ONS$ $[M+H]^+$: 354.1886, found: 354.1883.

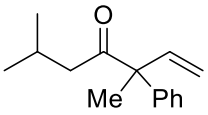
[2,3] for substrate class 1D and 1E (R^1 = Alk, R^2 = Ph, R^3 = Me) with phosphate and cyano as traceless LG:

2-methyl-1,2-diphenylbut-3-en-1-one (4D-3)

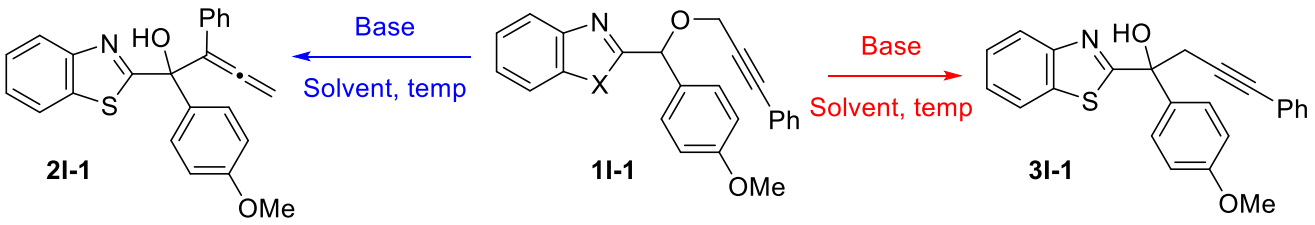


The titled compound was prepared with LiHMDS (3 equiv) in diethyl ether at 0 °C for 2 h (0.16 mmol), obtained as a colorless liquid (28 mg, 74%). Spectral data matches with literature.[6]

3,6-dimethyl-3-phenylhept-1-en-4-one(4E-2)



The titled compound was with LDA (3 equiv) in THF at -78 °C for 1 h (0.12 mmol), obtained as a colorless liquid (19 mg,73% yield). **^{1}H NMR (200 MHz, $CDCl_3$)** δ 0.72 (d, *J* = 5.94 Hz, 6H), 1.47 (s, 3H), 2.00 - 2.09 (m, 1H), 2.10 - 2.17 (m, 2H), 5.04 (dd, *J* = 17.43, 0.76 Hz, 1H), 5.25 (dd, *J* = 17.43, 0.76 Hz, 1H), 6.30 - 6.49 (m, 1H), 7.10 - 7.16 (m, 2H), 7.22 - 7.31 (m, 3H); **^{13}C NMR ($CDCl_3$, 50 MHz)** δ 22.4, 22.5, 22.5, 24.1, 47.6, 59.5, 116.1, 127.0, 128.2, 128.6, 140.3, 143.0, 209.8. **FTIR (cm^{-1}):** 2958, 2847, 1709, 1600, 1458, 1370, 1162, 109, 1022. **HRMS:** m/z calculated for $C_{15}H_{21}O[M+H]^+$: 217.1587, found: 217.1586.



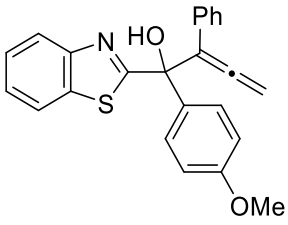
[2,3] for substrate class 1I:

The procedure for substrate class 1I is same as substrate class **1A.**

[1,2] for class 9 substrates:

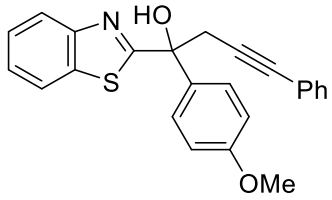
The procedure for substrate class **1I** is exactly same as class **1B** at 0 °C – room temperature.

1-(benzo[d]thiazol-2-yl)-1-(4-methoxyphenyl)-2-phenylbuta-2,3-dien-1-ol (2I-1)



The titled compound was prepared by following the general procedure for [2,3] (0.10mmol), obtained as a yellowish liquid (28 mg, 72% yield). R_f(Acetone/pet ether = 05:95) = 0.2. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 3.79 (s, 3H), 4.47 (d, 1H), 4.59 (d, 1H), 6.13 (s, 1H), 6.88 - 6.95 (m, 2H), 7.29 - 7.32 (m, 3H), 7.33 - 7.37 (m, 1H), 7.39 - 7.45 (m, 3H), 7.48 (d, *J* = 8.77 Hz, 2H), 7.87 (d, *J* = 8.01 Hz, 1H), 7.99 (d, *J* = 8.39 Hz, 1H); **^{13}C NMR ($CDCl_3$, 125 MHz)** δ 55.3, 79.8, 84.2, 87.3, 114.2, 121.7, 122.4, 123.3, 125.0, 125.9, 128.3, 128.6, 128.9, 130.5, 131.8, 135.1, 153.2, 160.0, 173.3, 198.3. **FTIR (cm^{-1}):** 3533, 3017, 2928, 1966, 1607, 1509, 1452, 1251, 1071. **HRMS:** m/z calculated for $C_{24}H_{19}O_2NNaS$ $[M+Na]^+$: 408.1029, found: 408.1022.

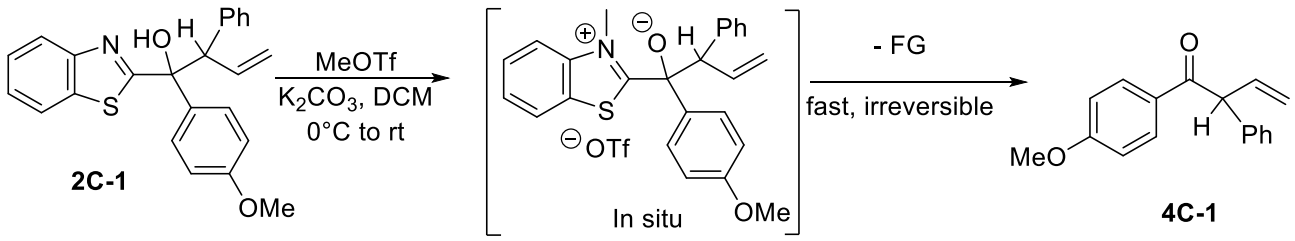
1-(benzo[d]thiazol-2-yl)-1-(4-methoxyphenyl)-4-phenylbut-3-yn-1-ol (3I-1)



The titled compound was prepared by following the general procedure for [1,2] (0.10 mmol), obtained as a yellowish liquid(19 mg, 52% yield). R_f(Acetone/pet ether = 05:95) = 0.2 **^{1}H NMR (400 MHz, $CDCl_3$)** δ 3.47 (d, 1H) 3.72 - 3.84 (m, 4H) 4.00 (br s, 1H) 6.89 (d, *J* = 9.16 Hz, 2H) 7.19 - 7.27 (m, 5H) 7.36 (t, *J* = 7.32 Hz, 1H) 7.46 (t, *J* = 7.32 Hz, 1H) 7.64 (d, *J* = 9.16 Hz, 2H) 7.85 (d, *J* = 7.93 Hz, 1H) 8.04 (d, *J* = 7.93 Hz, 1H); **^{13}C NMR ($CDCl_3$, 100 MHz)** δ 34.7, 55.3, 77.5, 84.3, 85.0, 113.7, 121.7, 122.7, 123.3, 125.0, 125.9, 126.8, 128.2, 131.7, 134.6, 135.7, 153.2, 159.3, 177.1 .**FTIR (cm^{-1}):** 3526, 3067, 2925, 2854, 2250, 1966, 1603, 1506, 1452, 1250, 1177, 1083, 1032, 910. **HRMS:** m/z calculated for $C_{24}H_{19}O_2NNaS$ $[M+Na]^+$: 408.1029, found: 408.1021.

Removal of benzothiazole group from rearranged product:

The alcohol (0.13 mmol) was taken in DCM with 7 equiv K_2CO_3, and cooled to 0 ºC under argon atmosphere. MeOTf (1.5 equiv) was added dropwise and slowly brought to room temperature. The progress was monitored by TLC, and upon completion (2h), quenched with saturated ammonium chloride solution. The organic layer was extracted with DCM, and solvent removal gave crude which was prtified by silica column to obtain 19 mg (60%) product. Spectral data matches with literature.[7]



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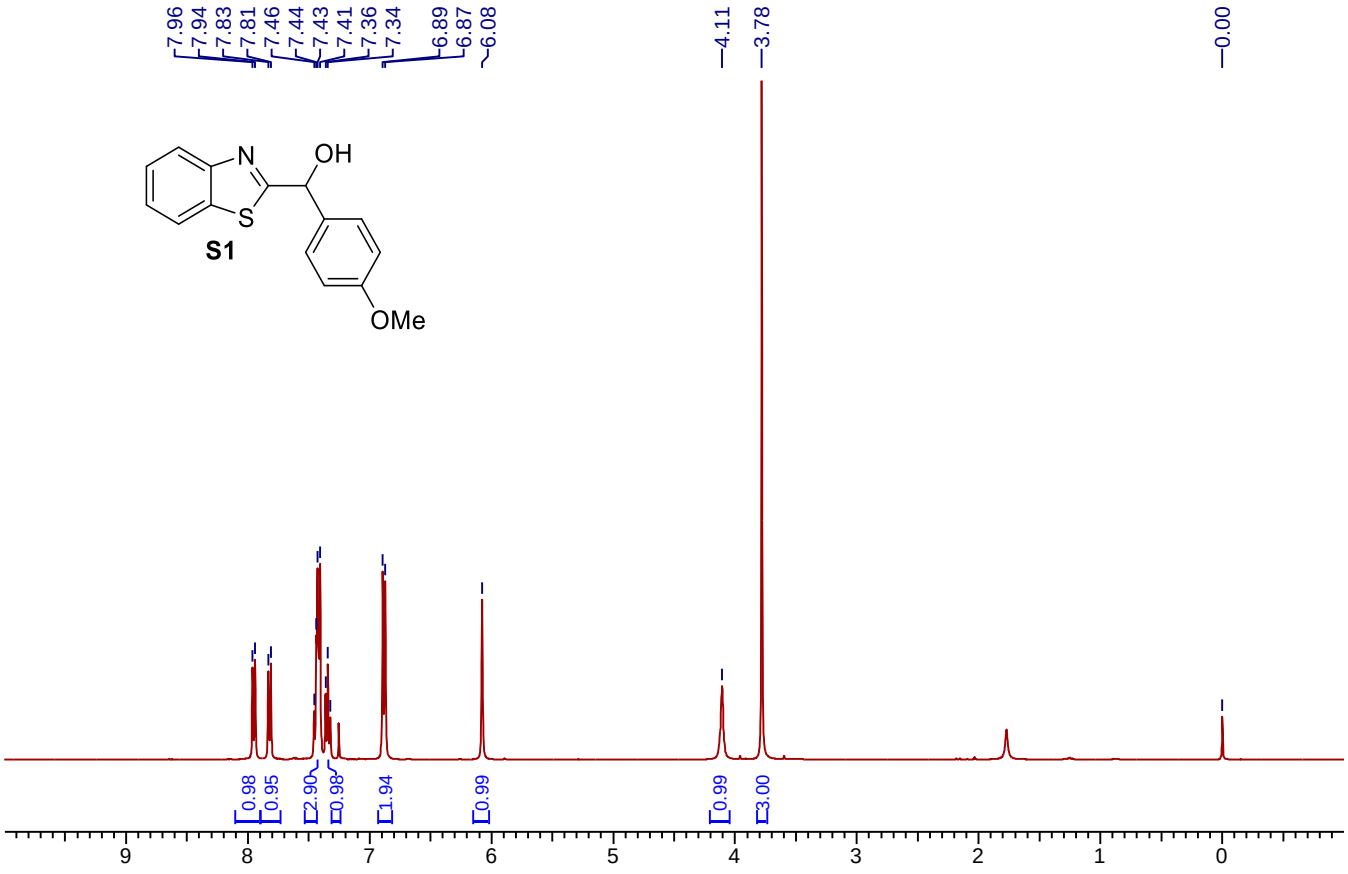
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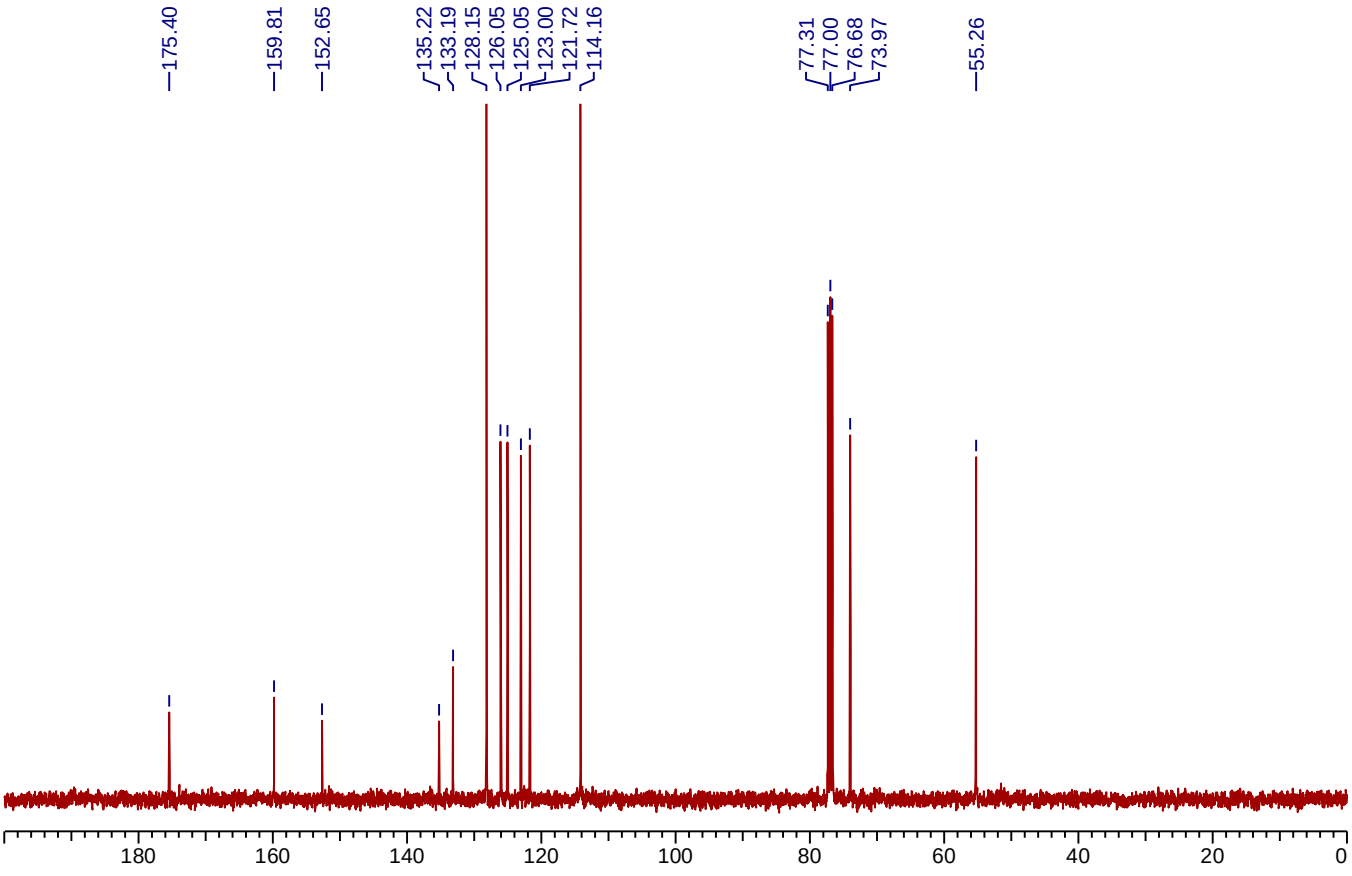
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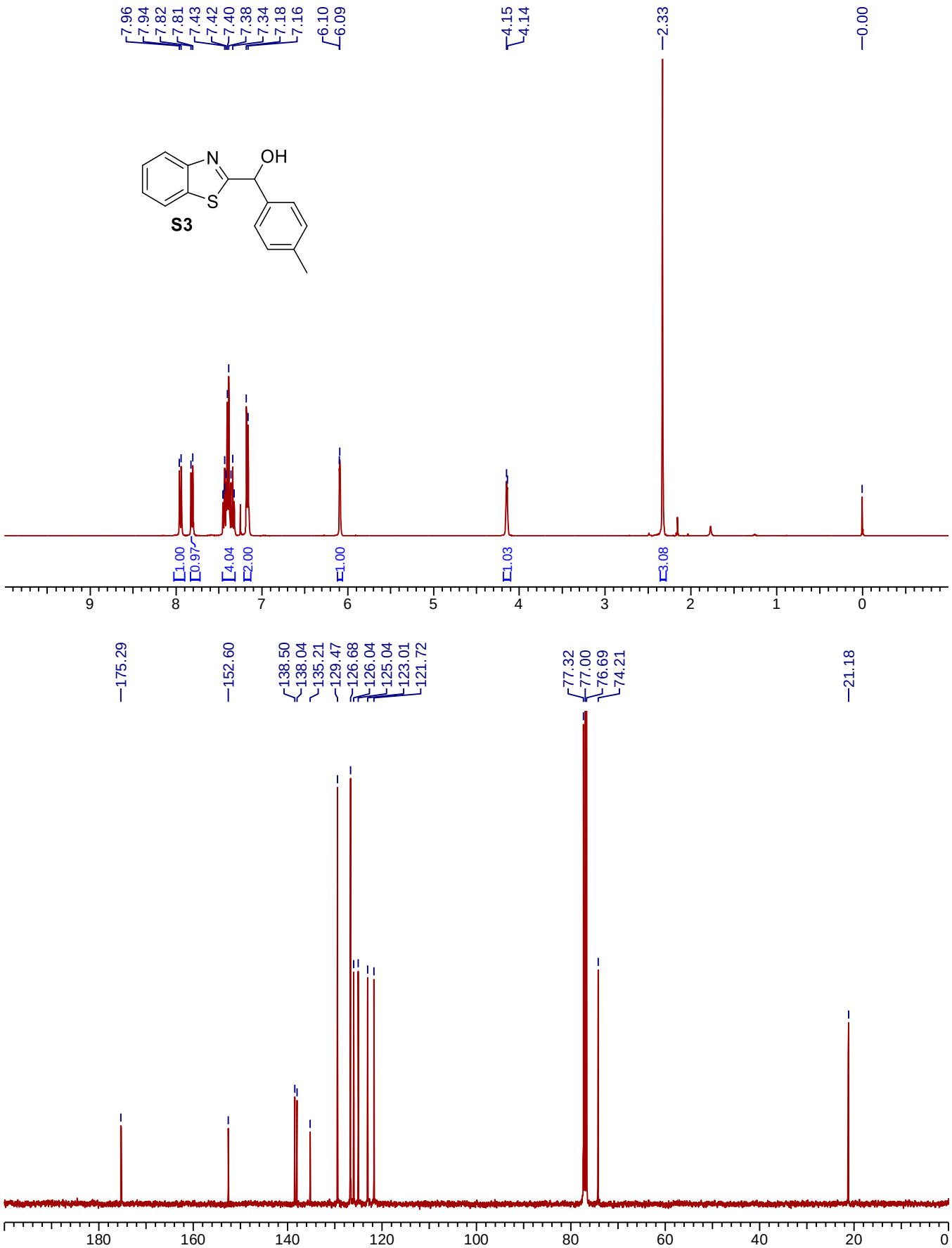
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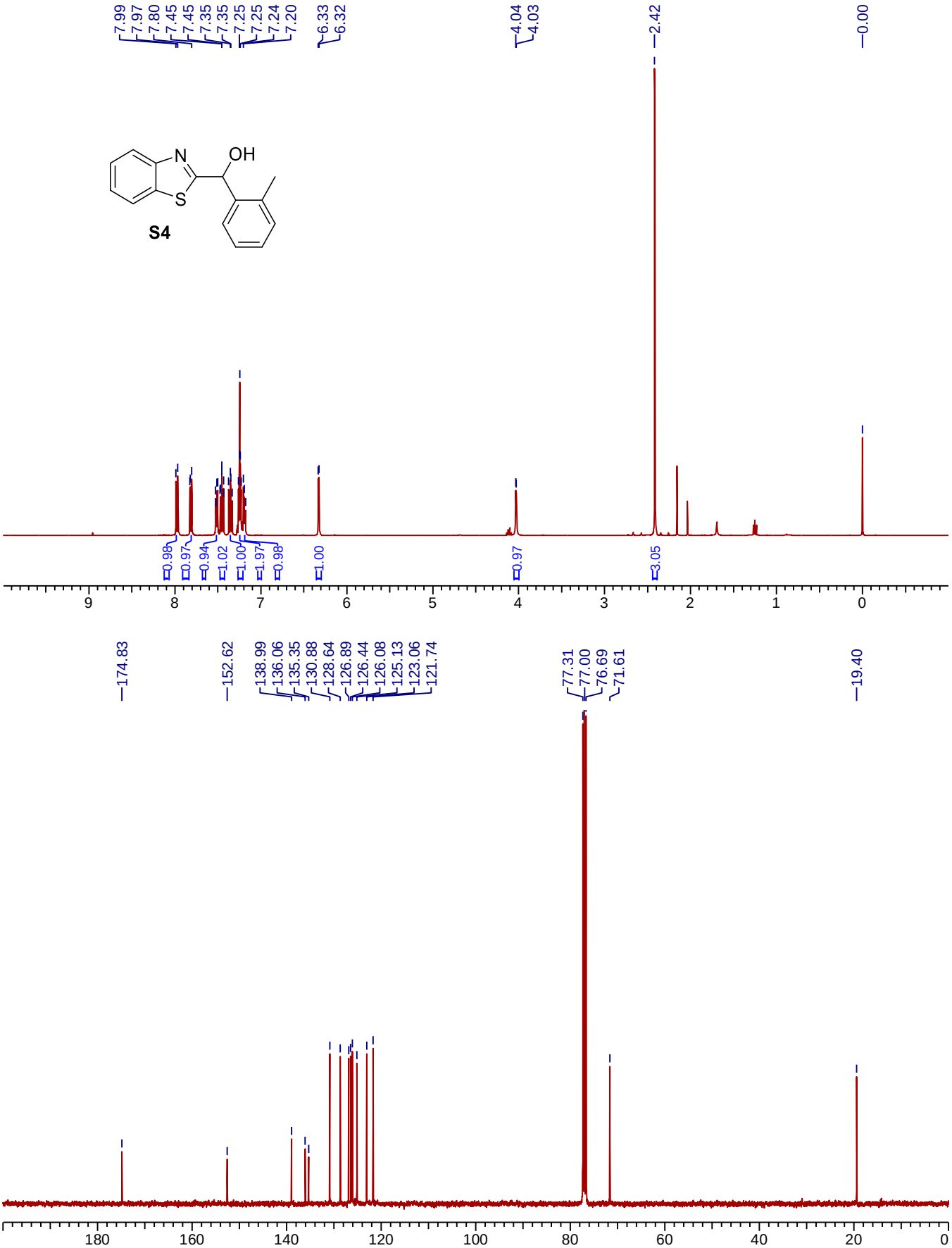
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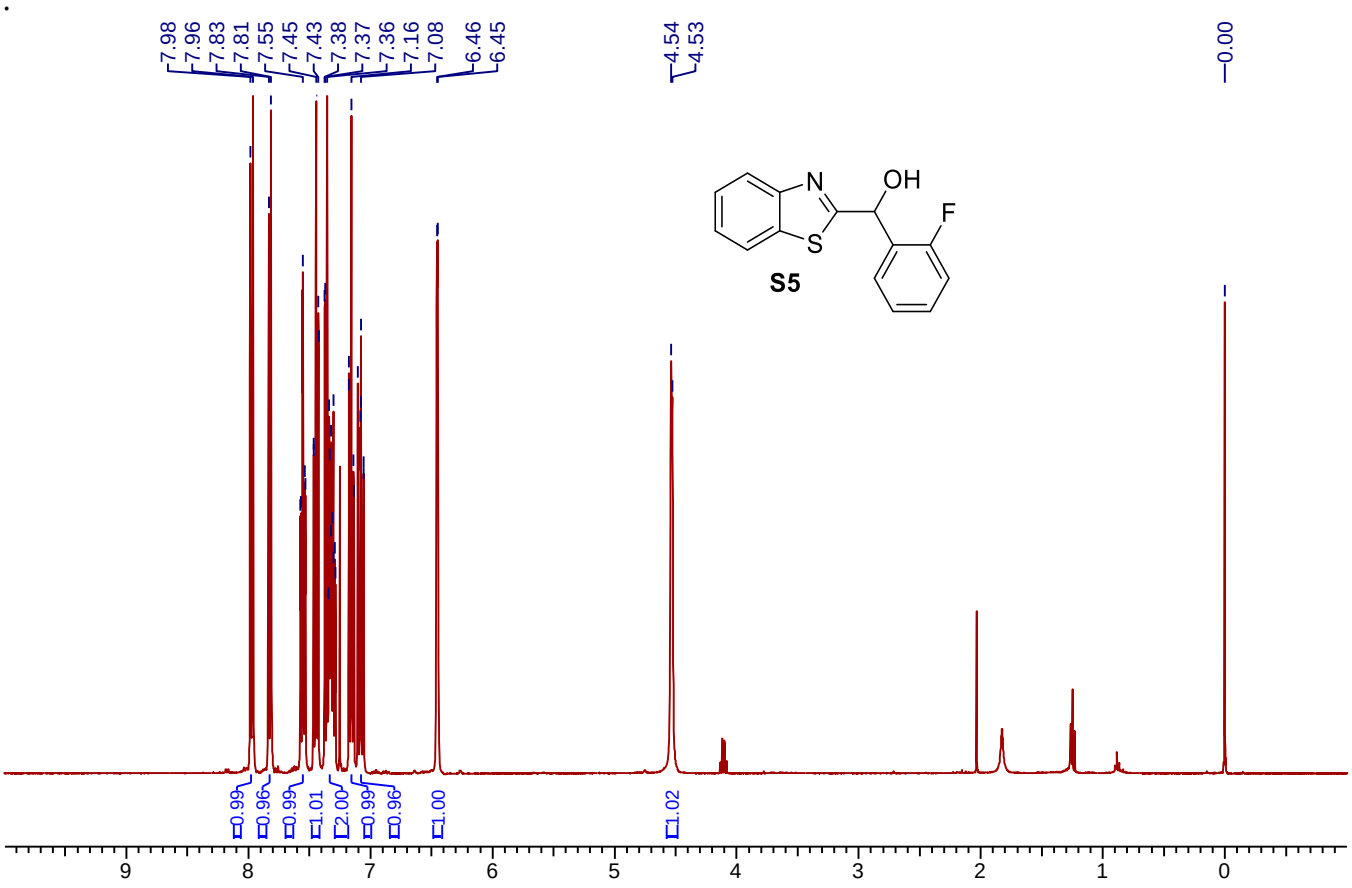
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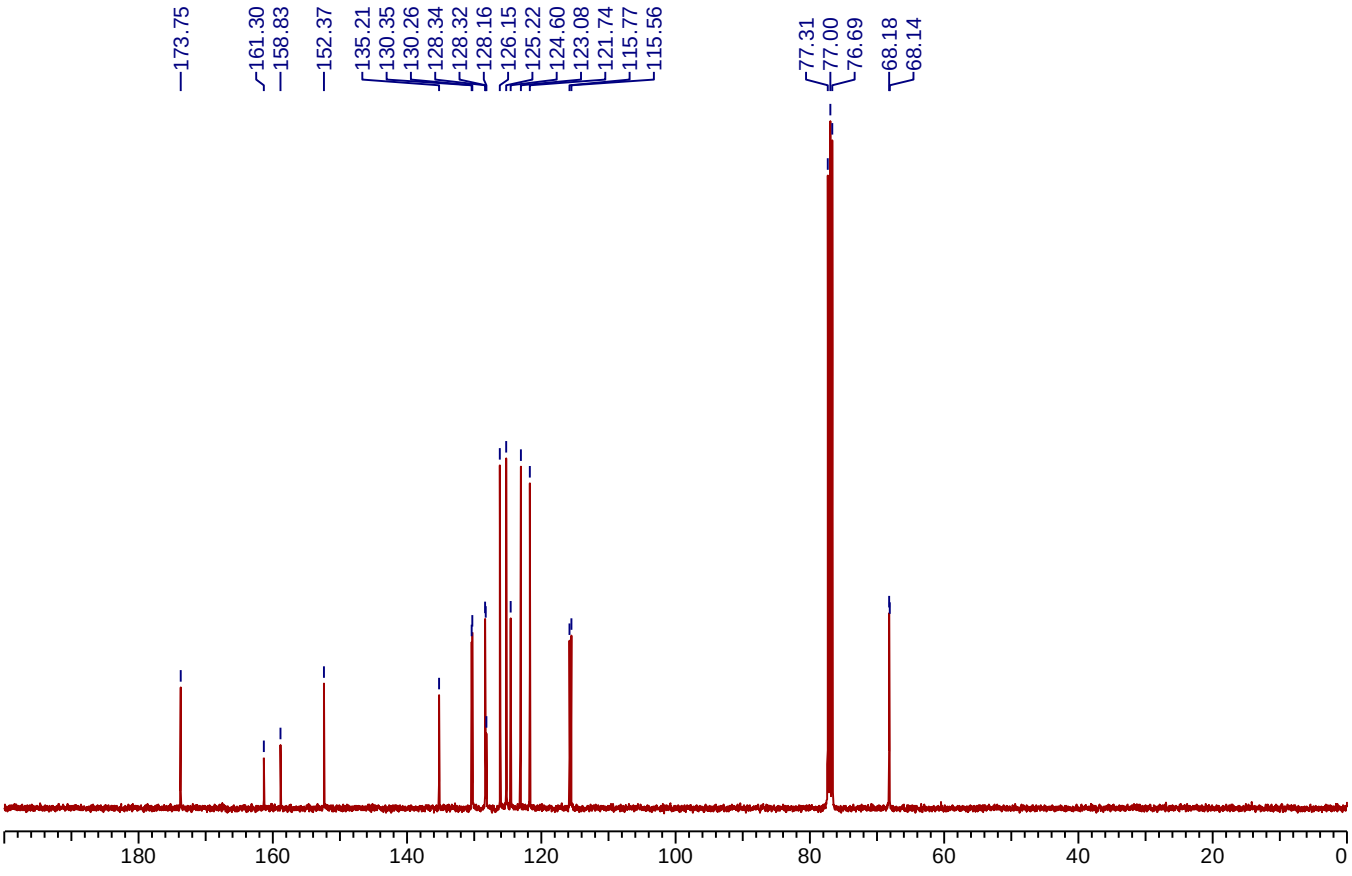
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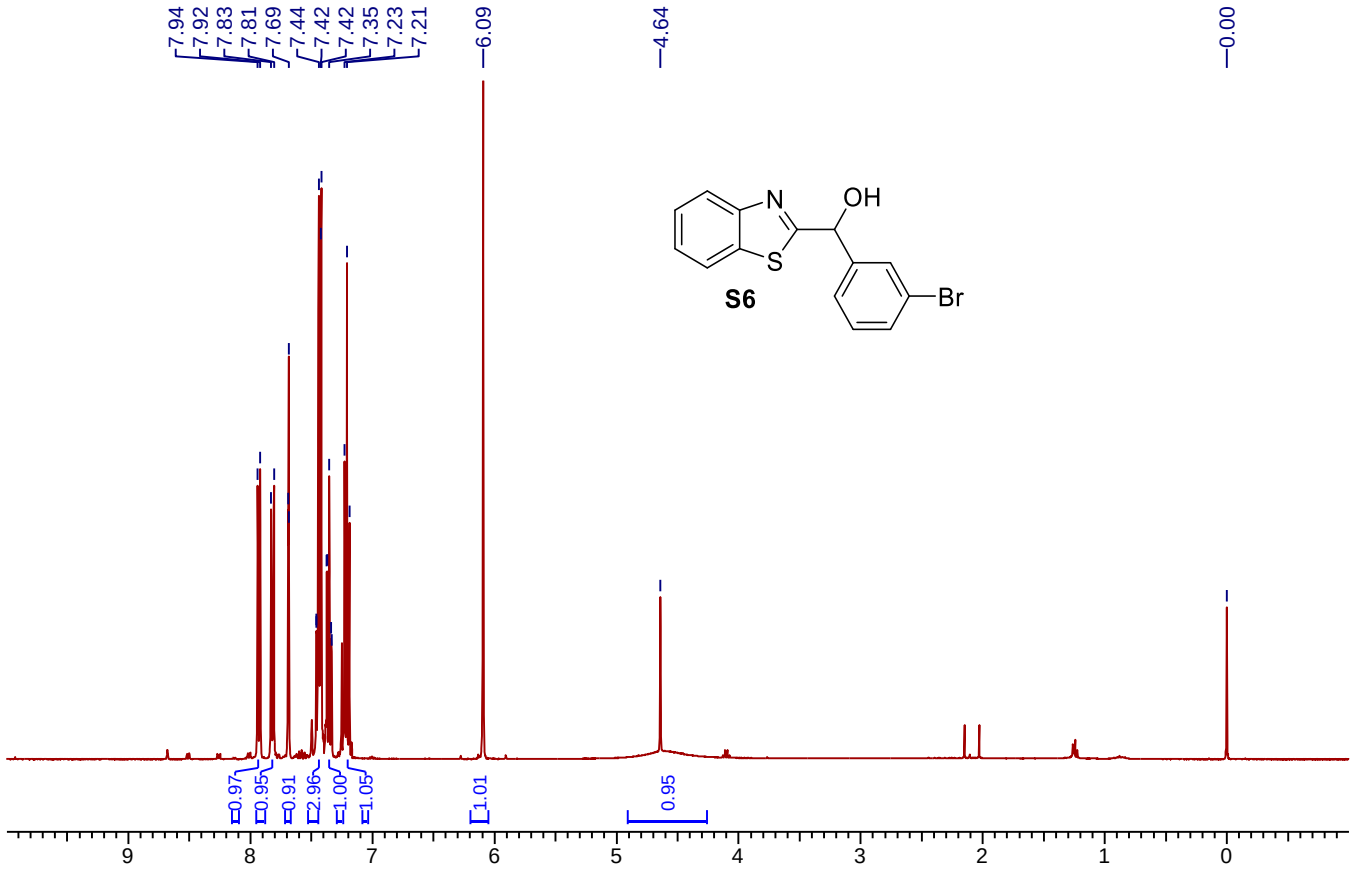
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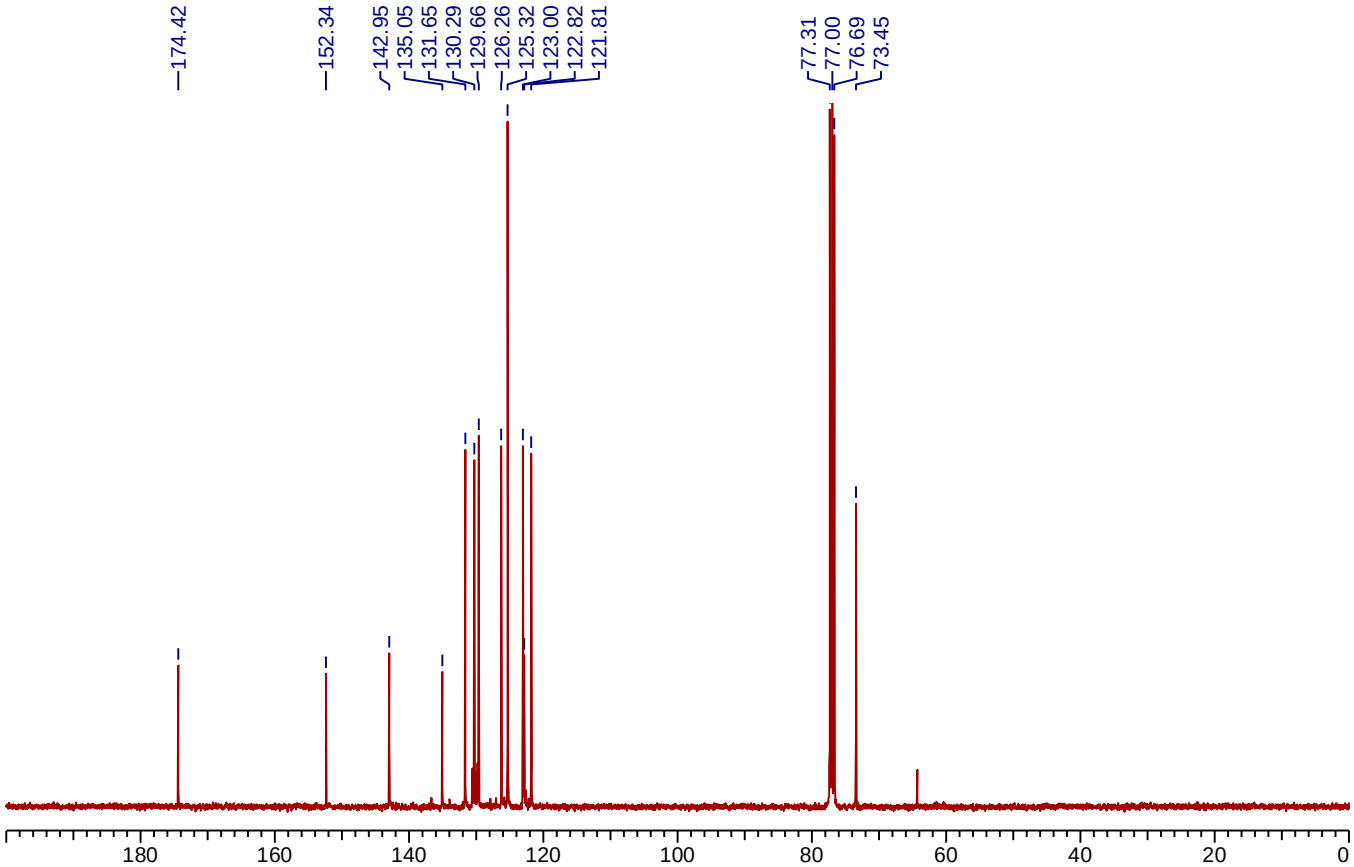
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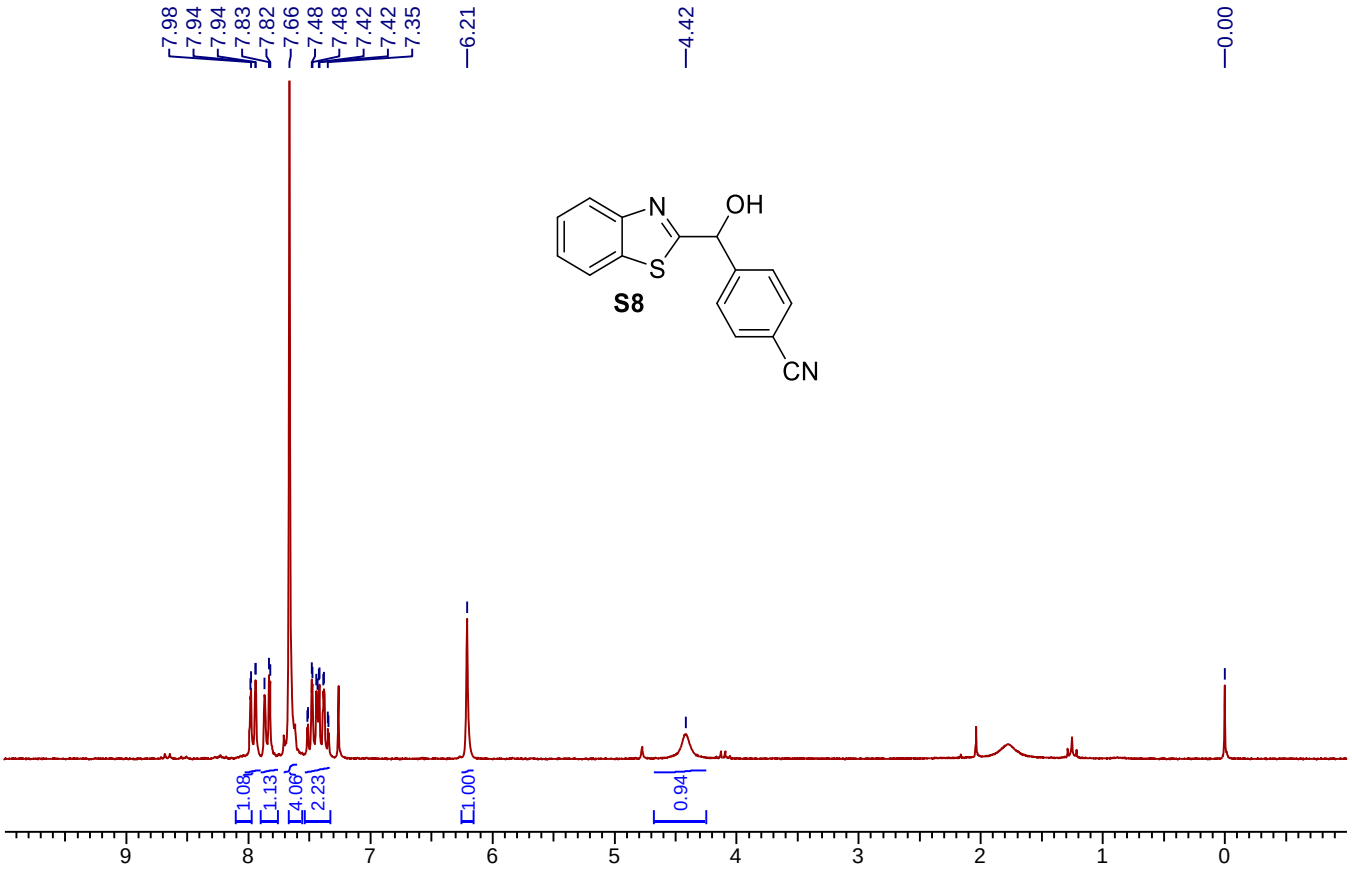
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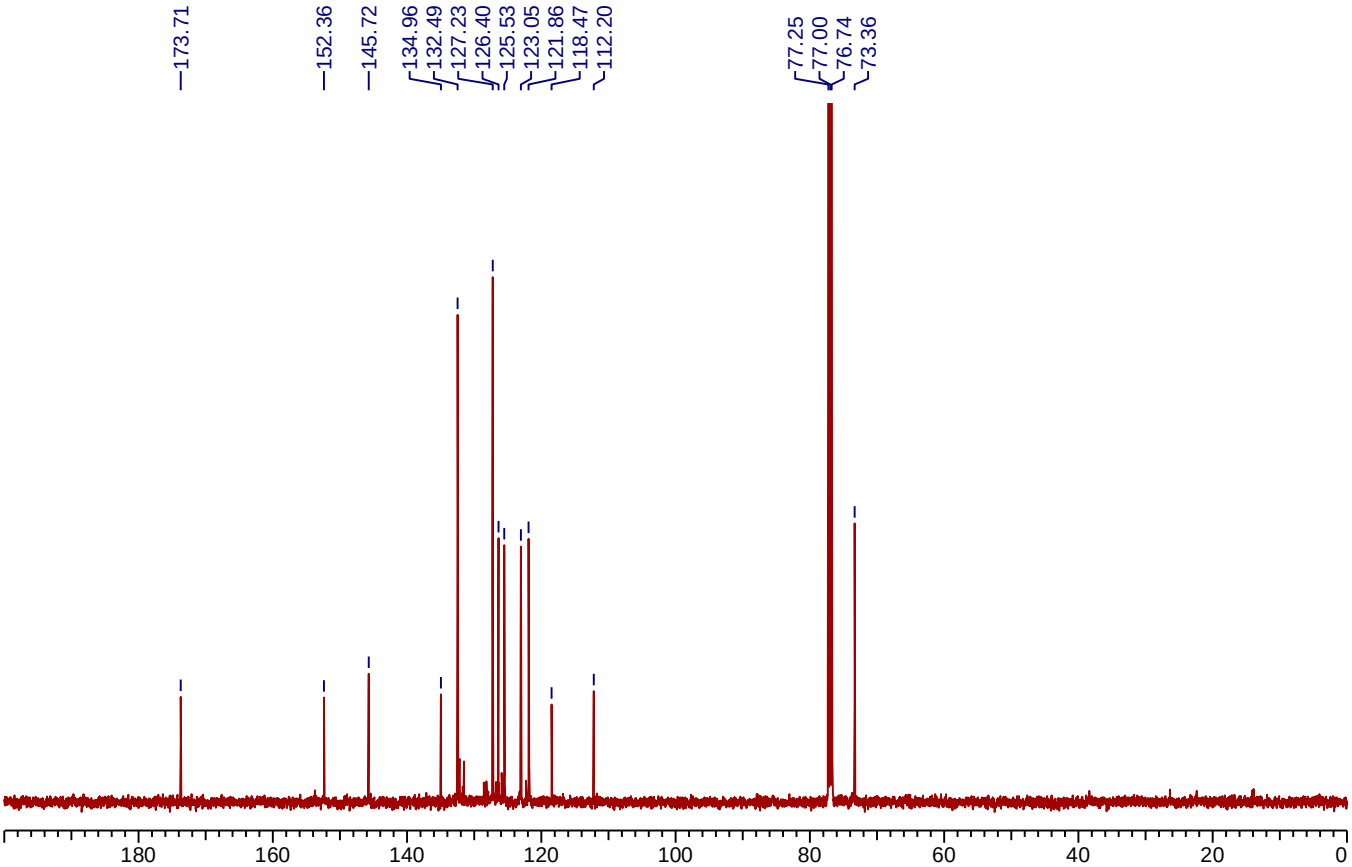
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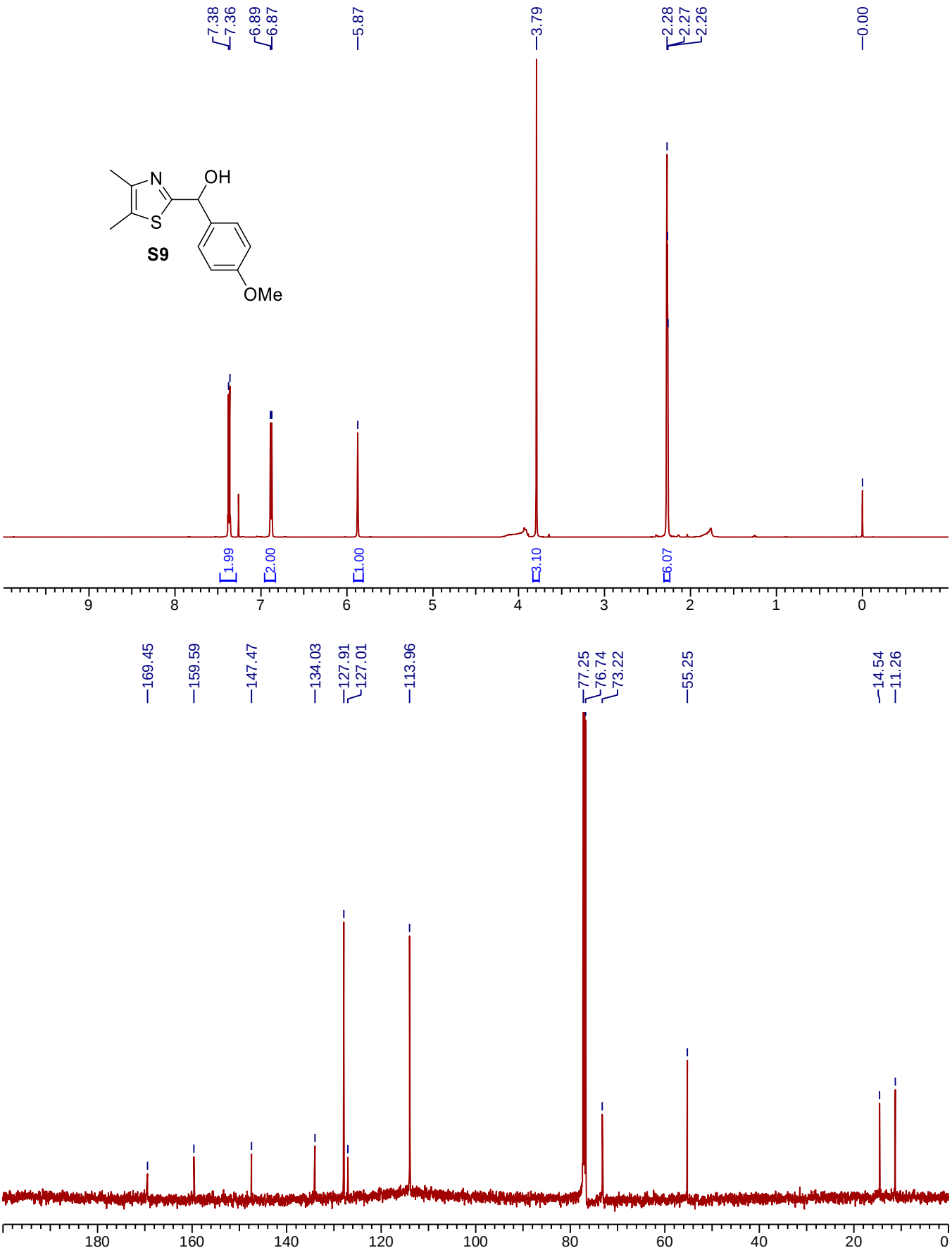
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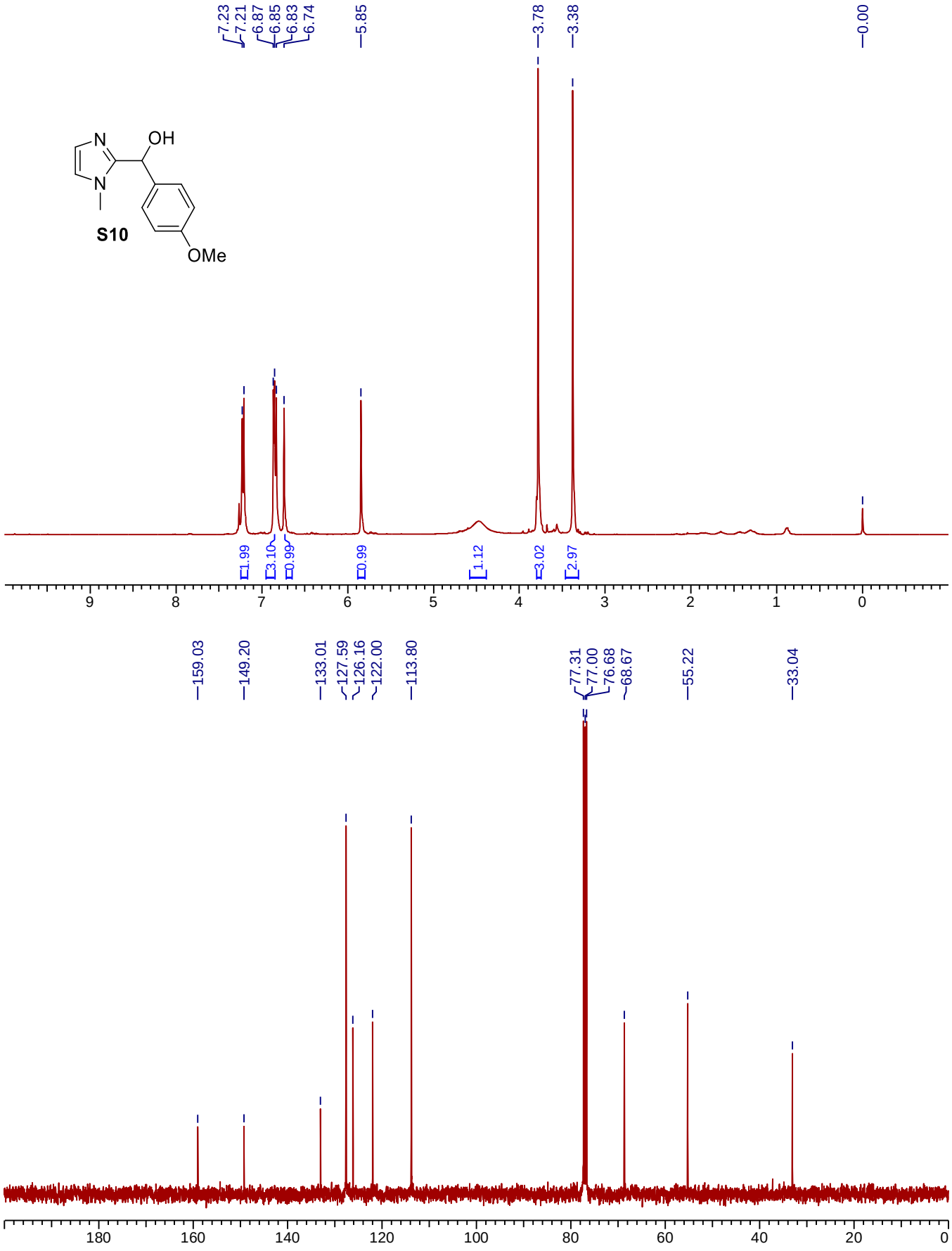
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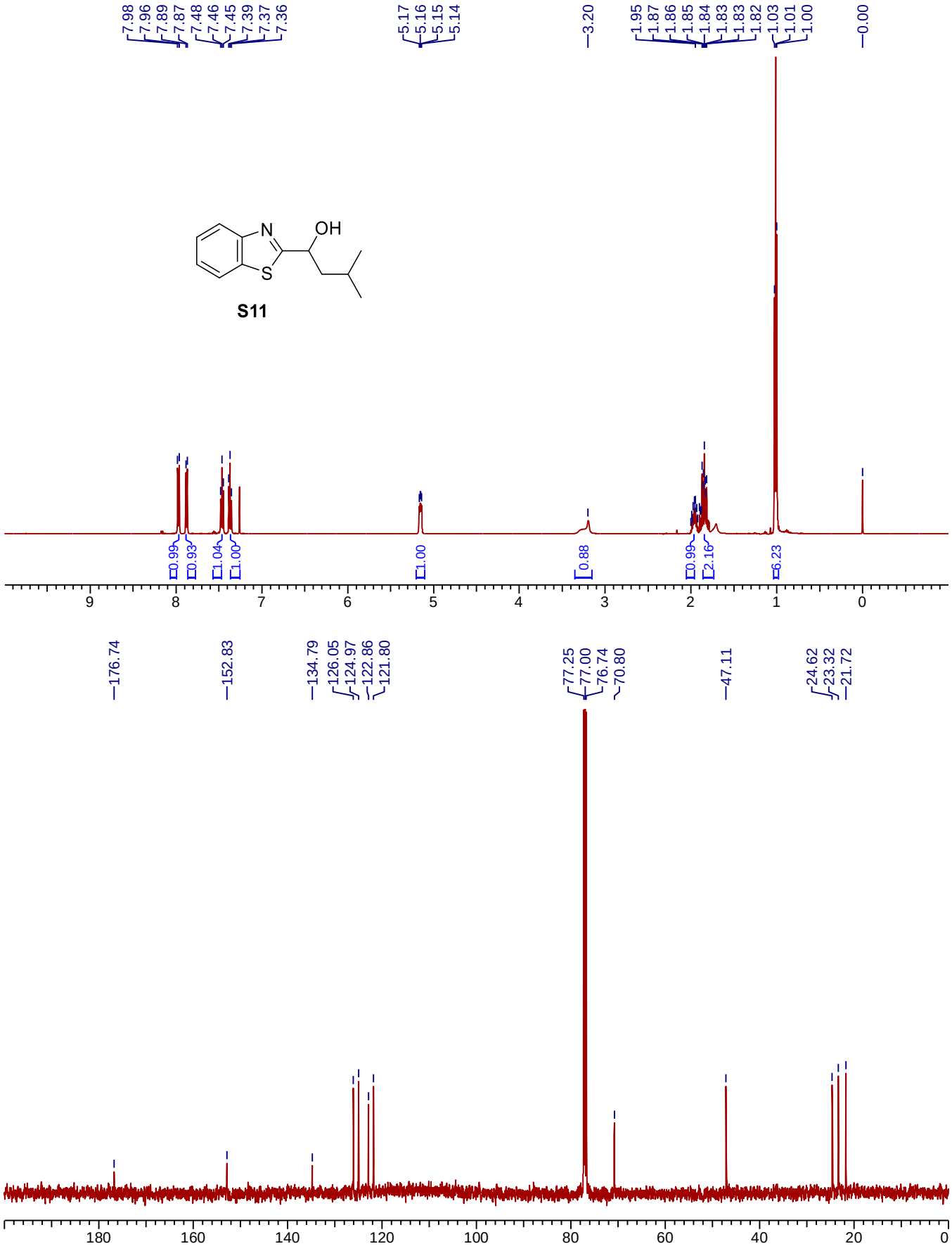
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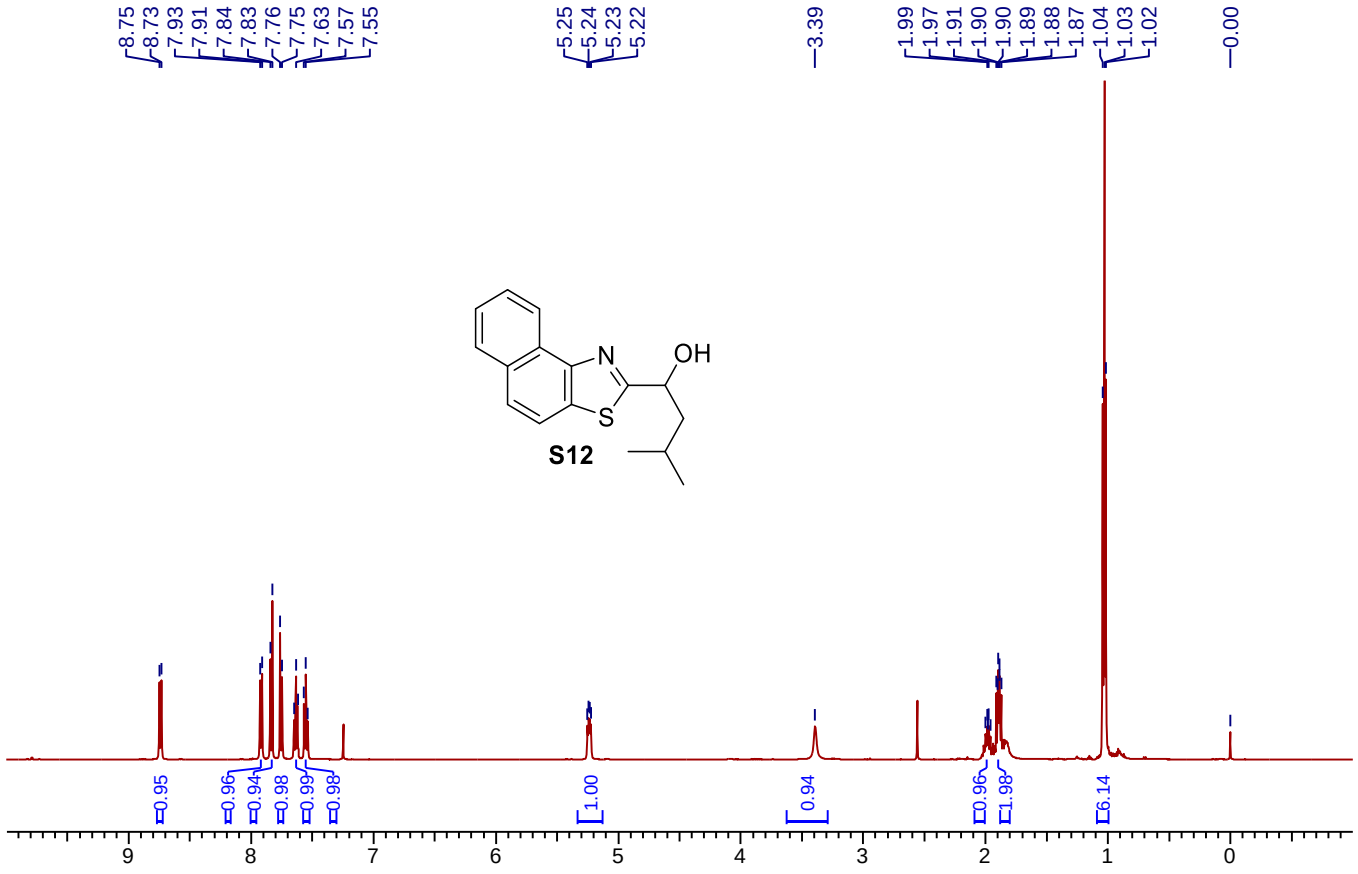
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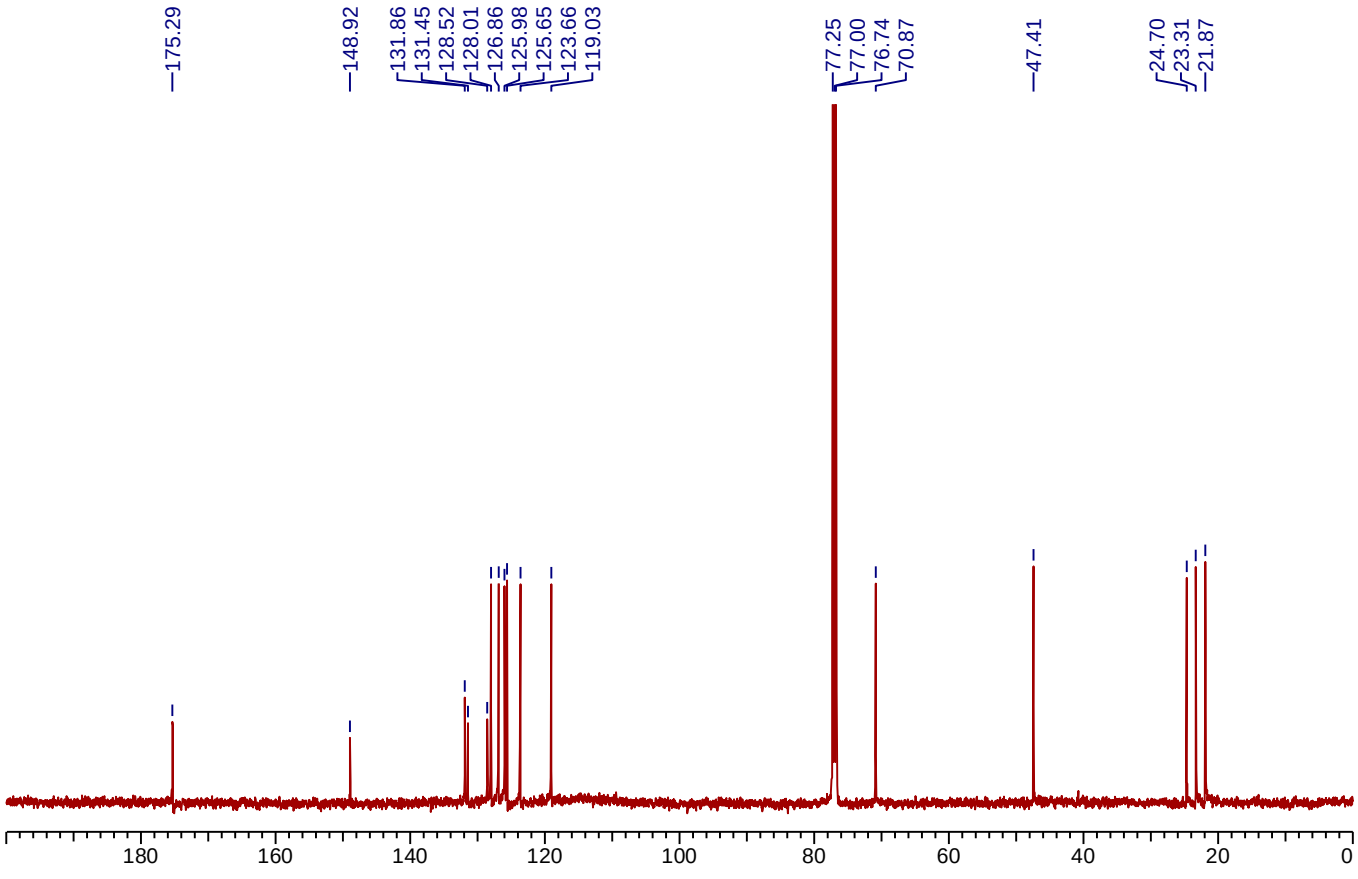
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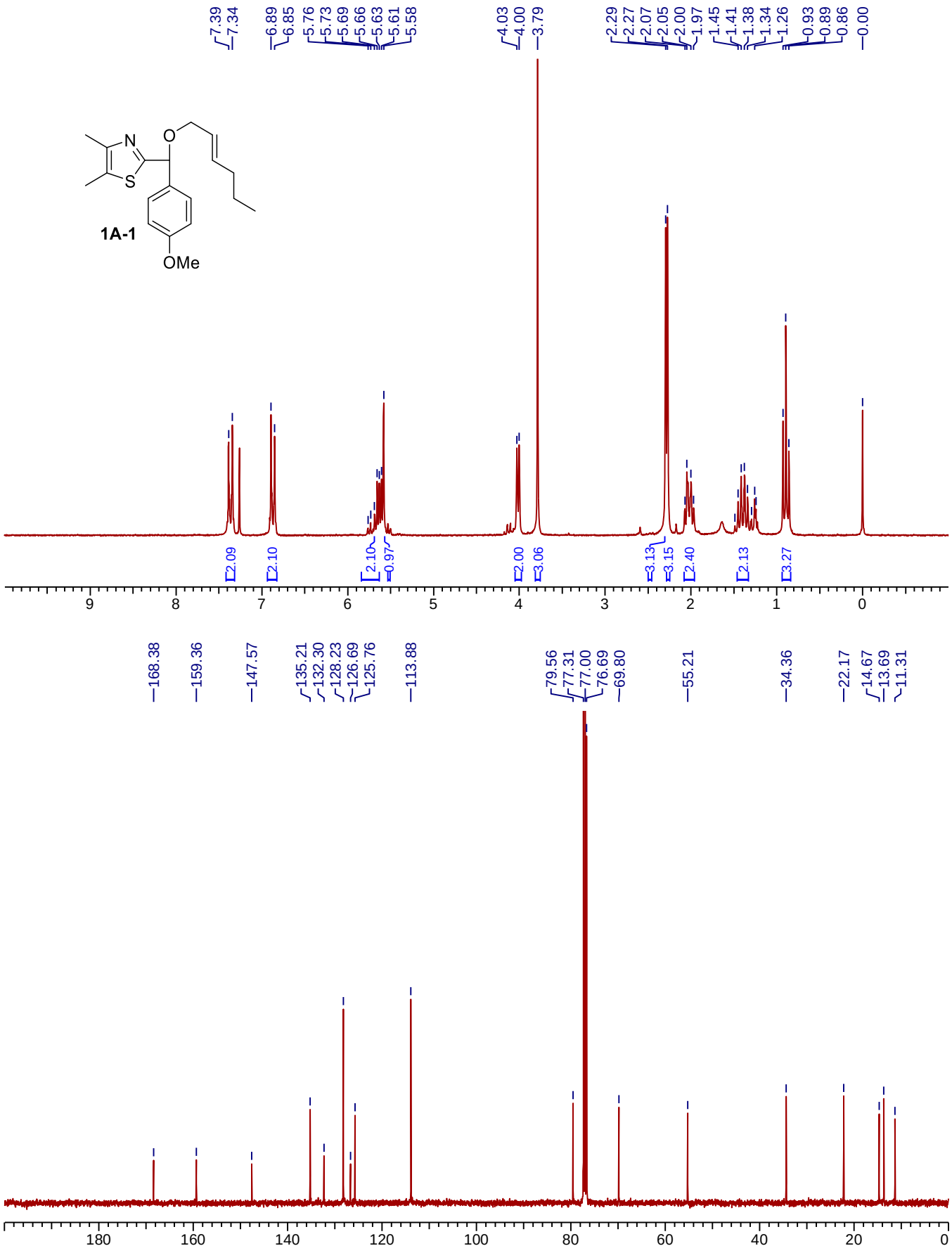
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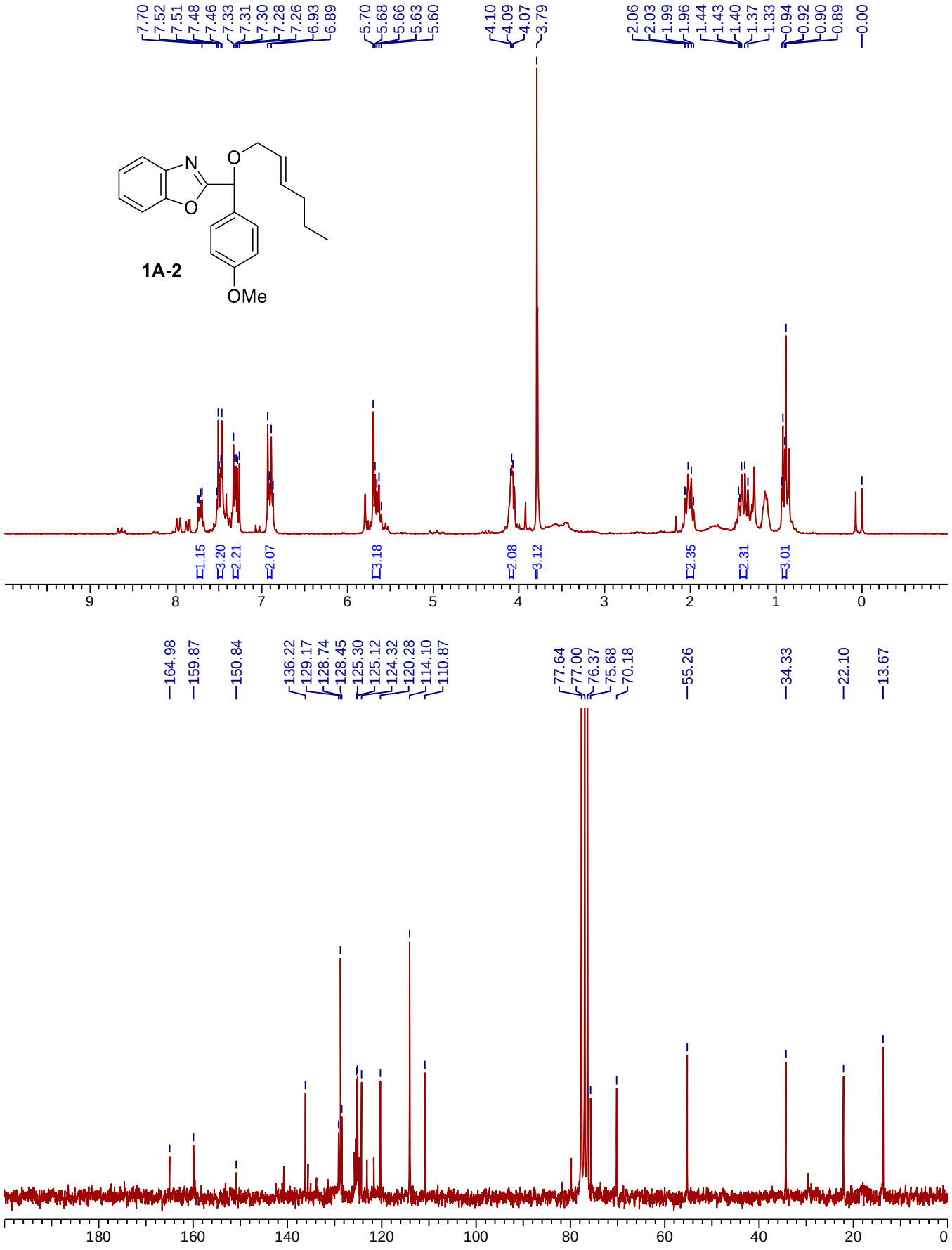
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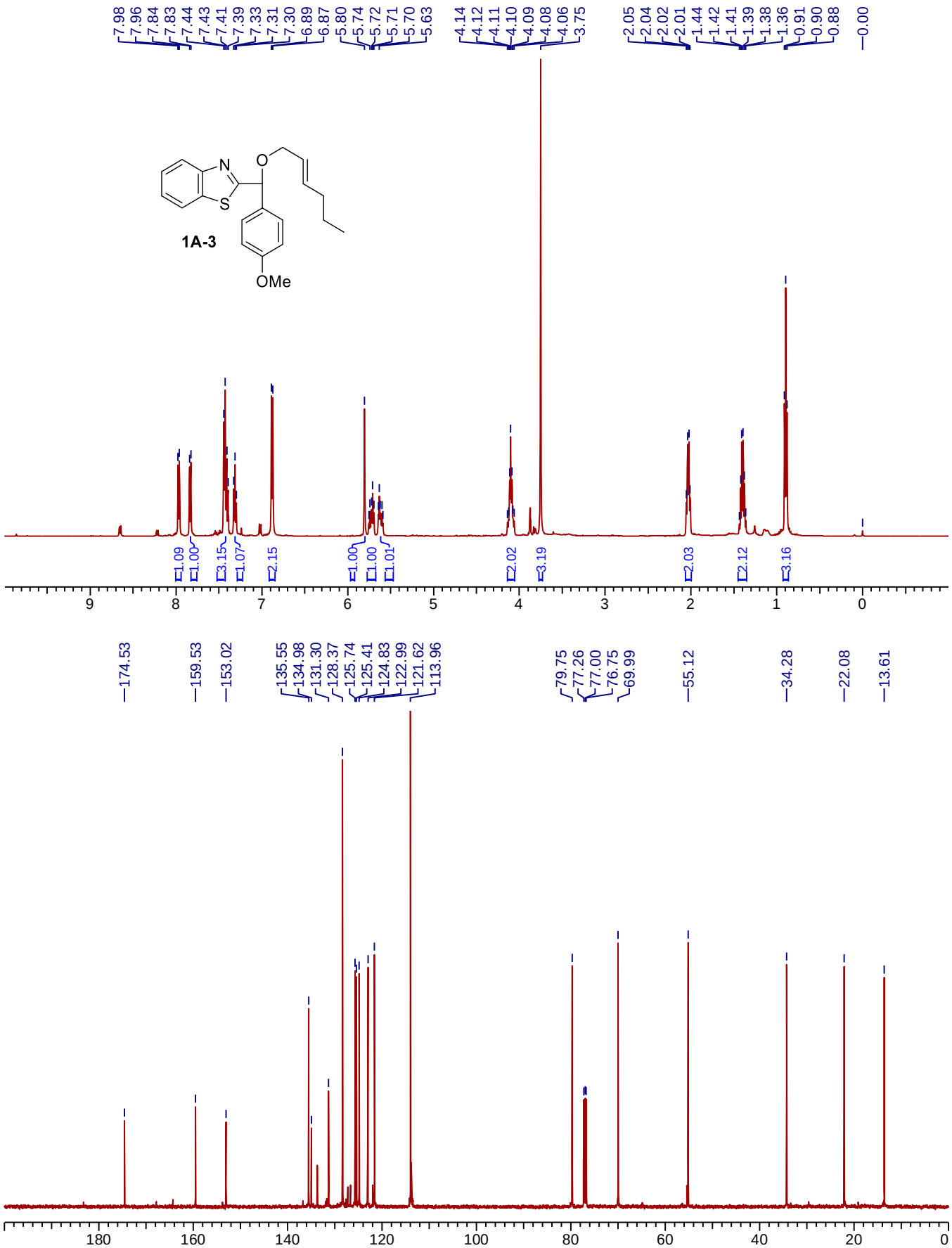
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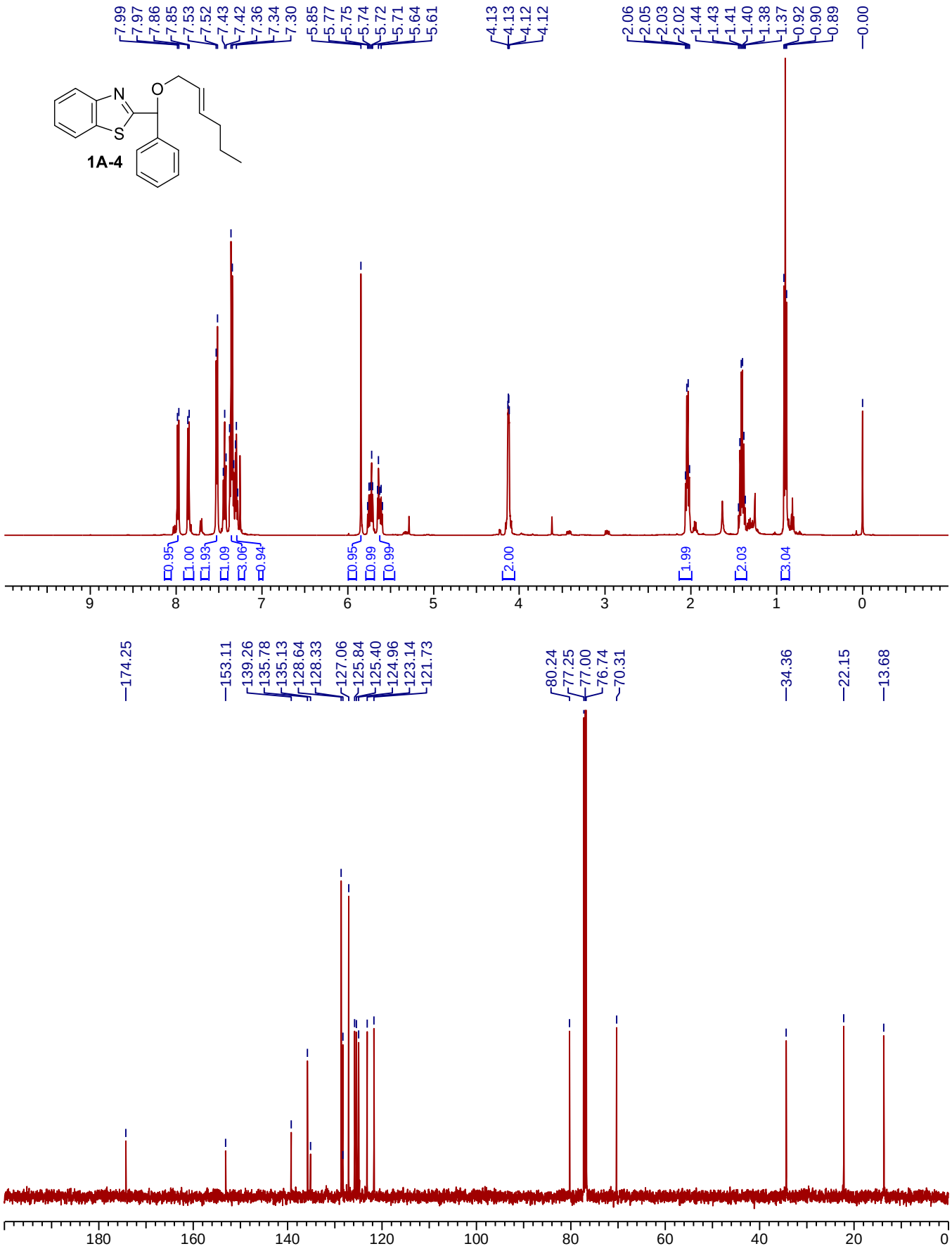
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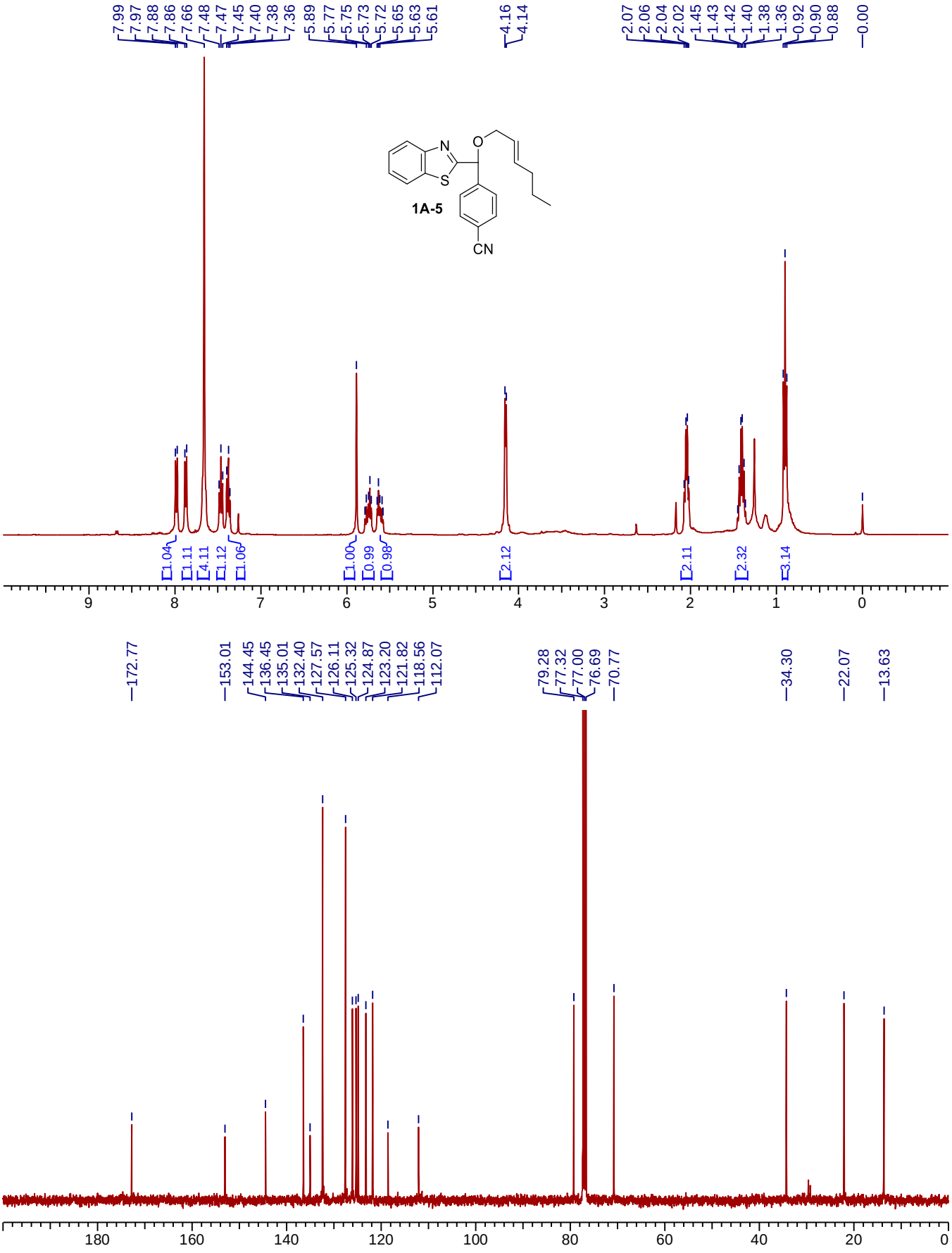
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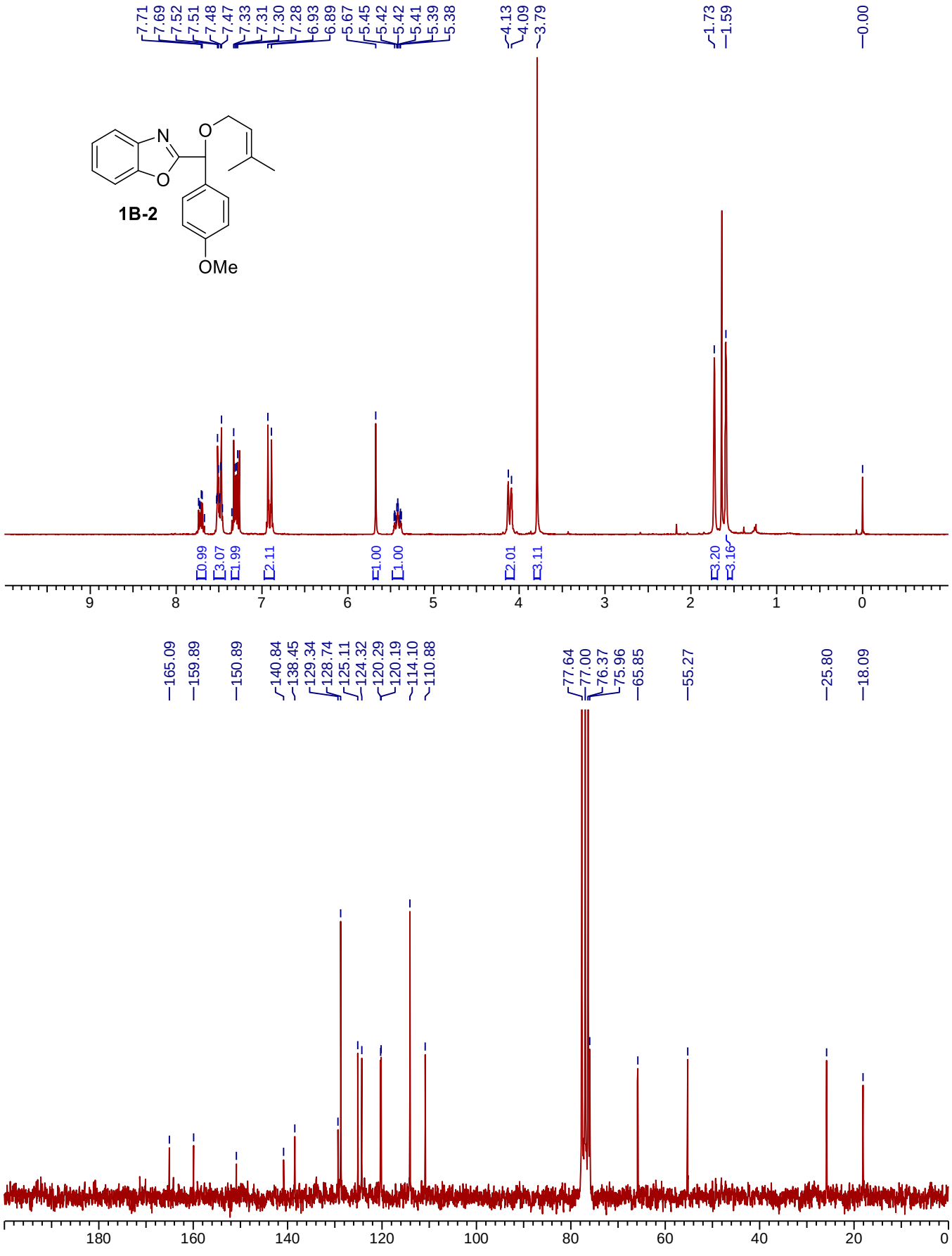
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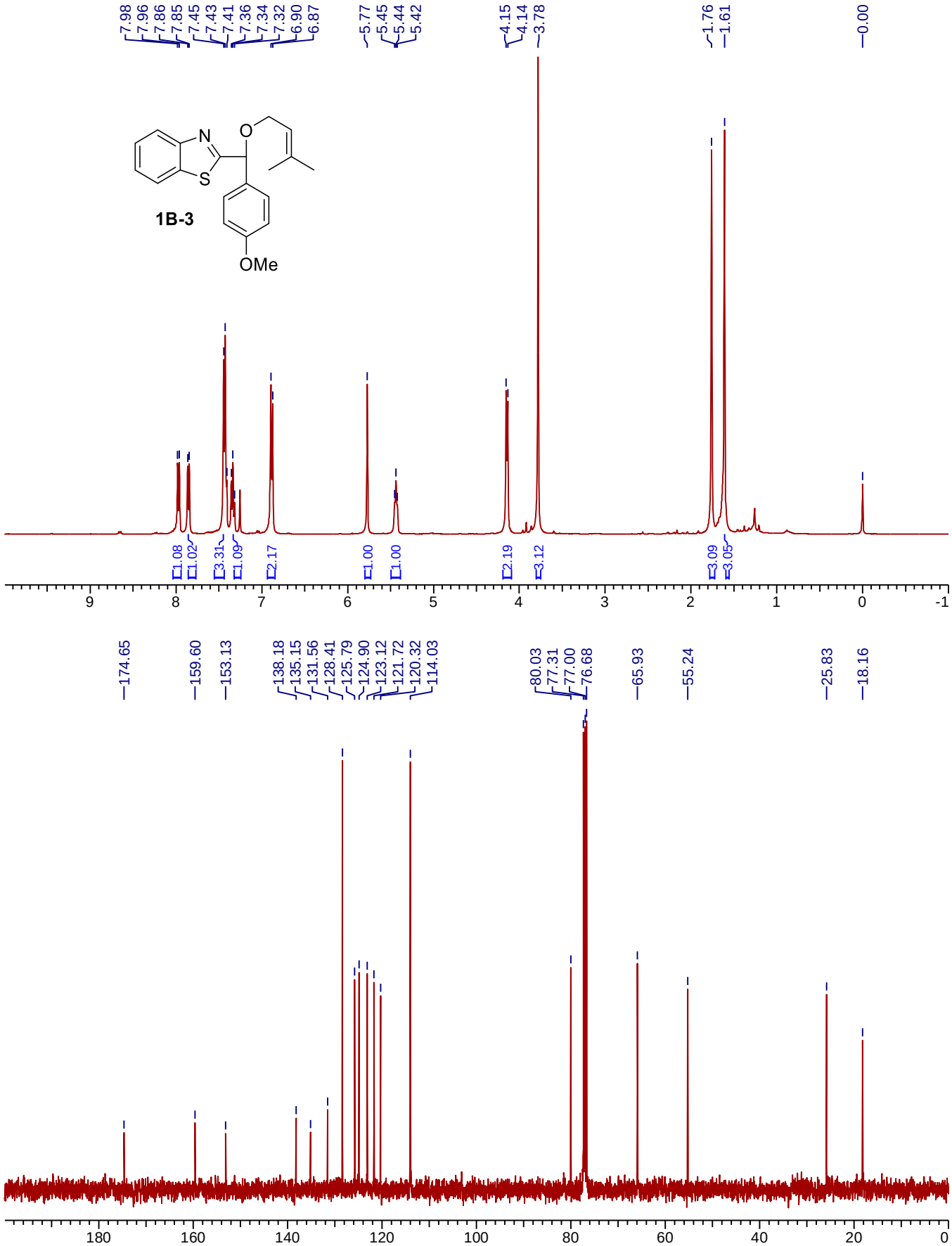
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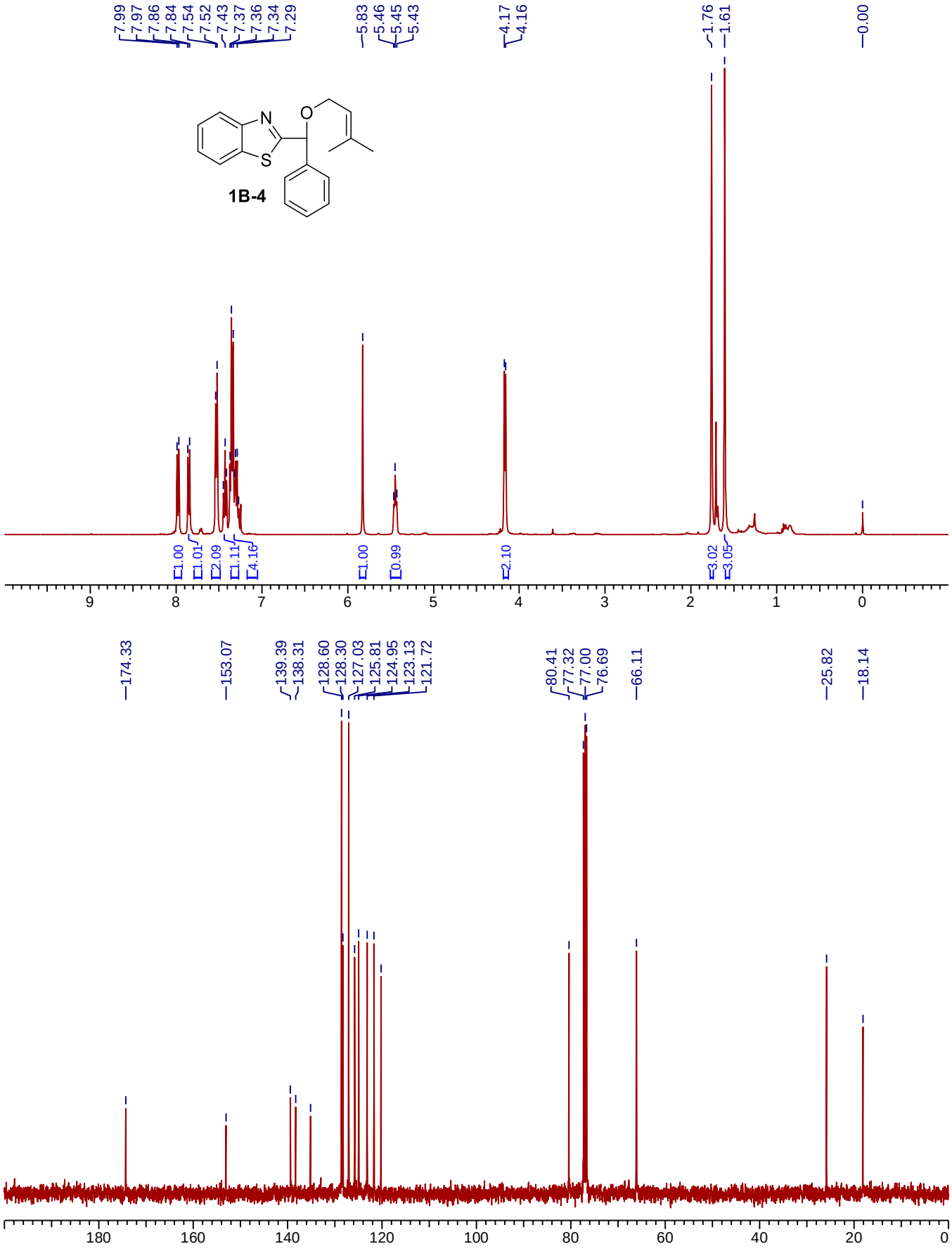
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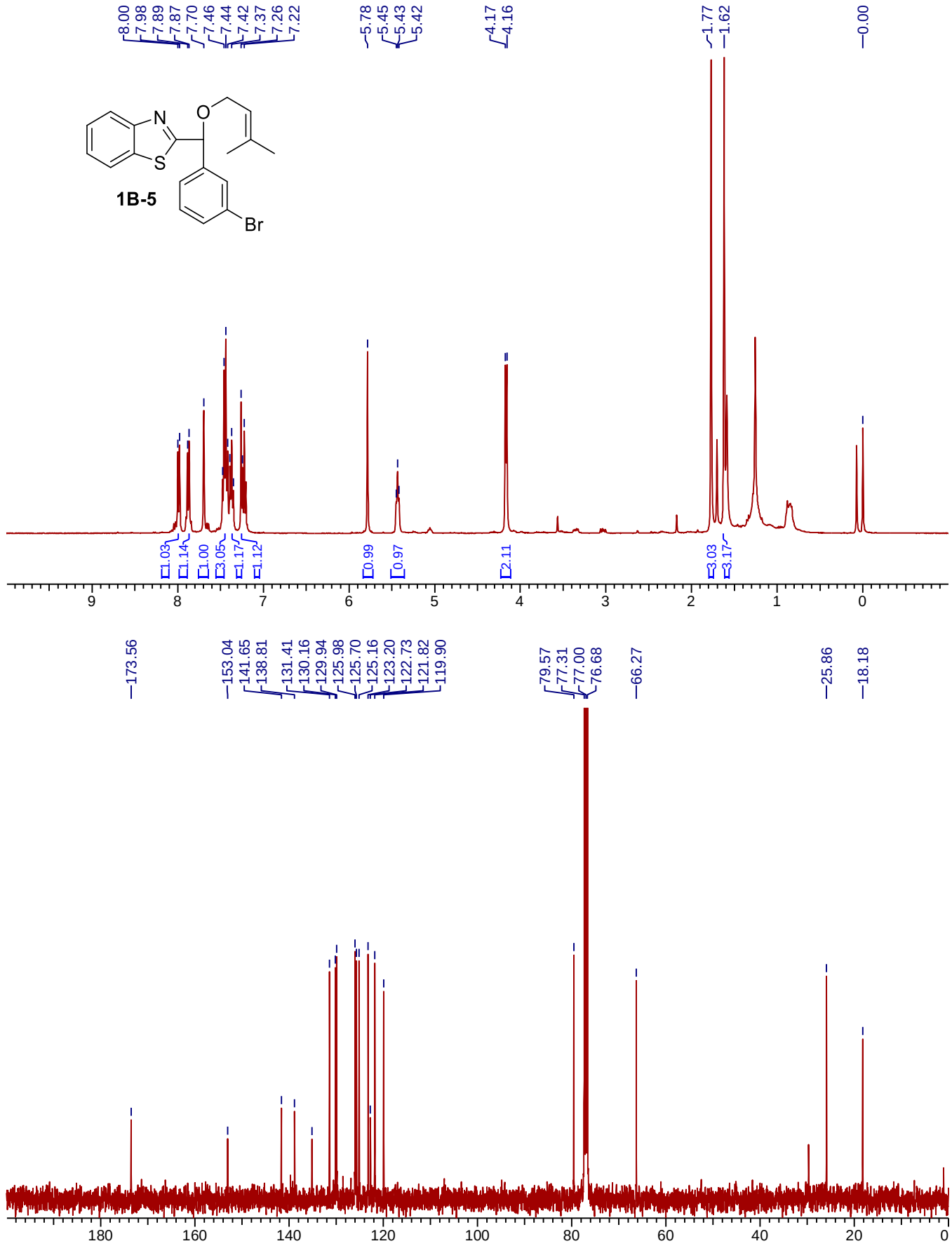
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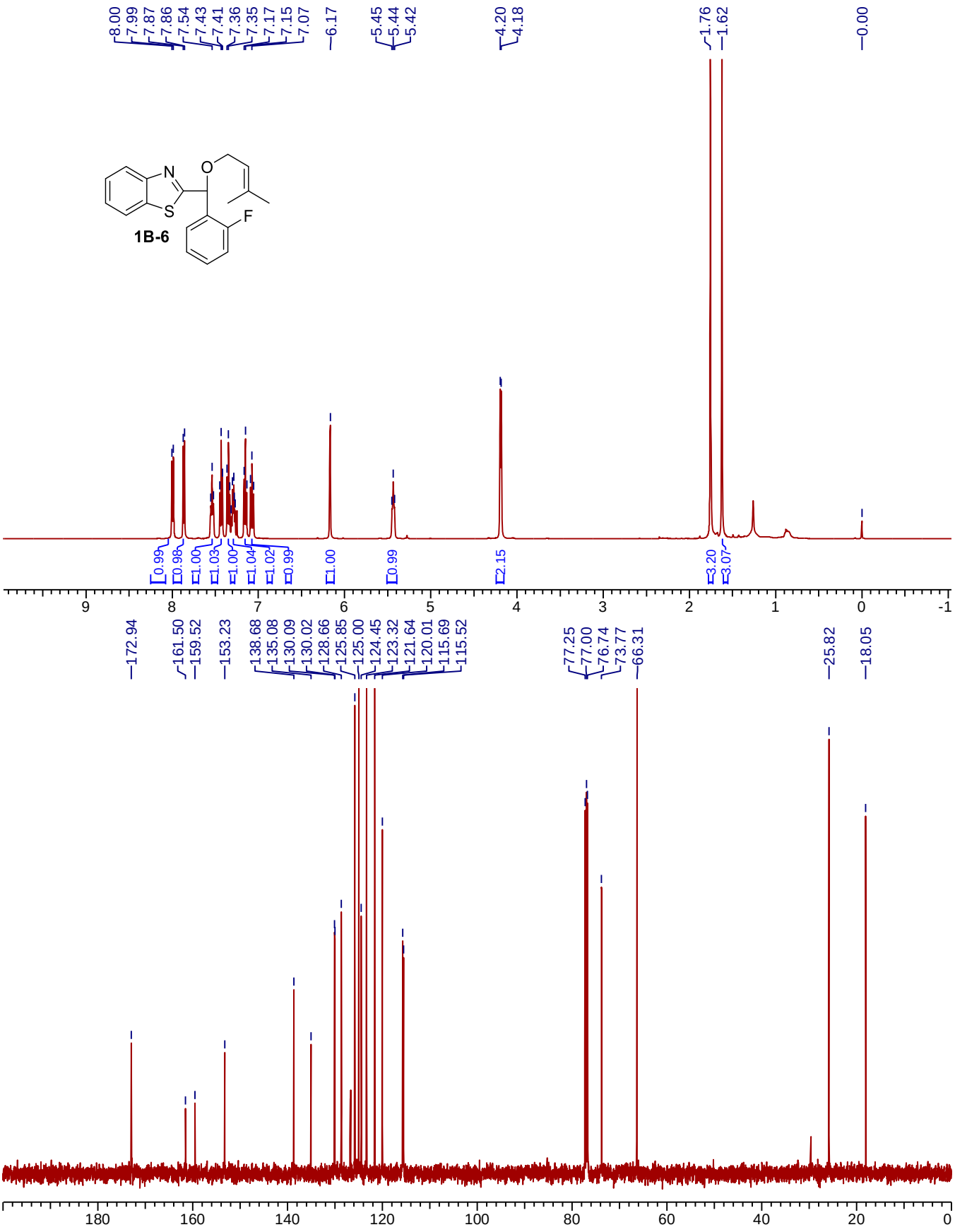
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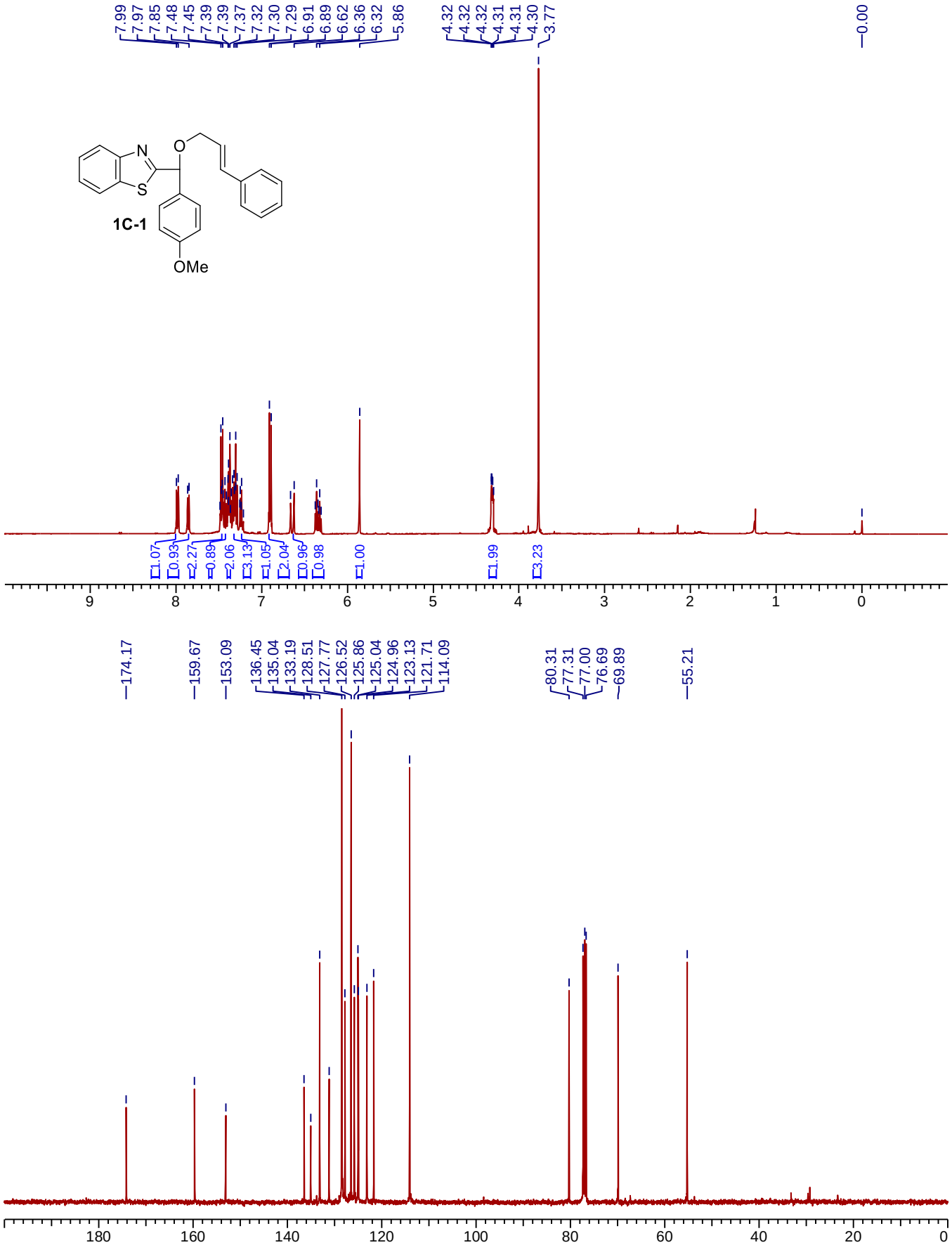
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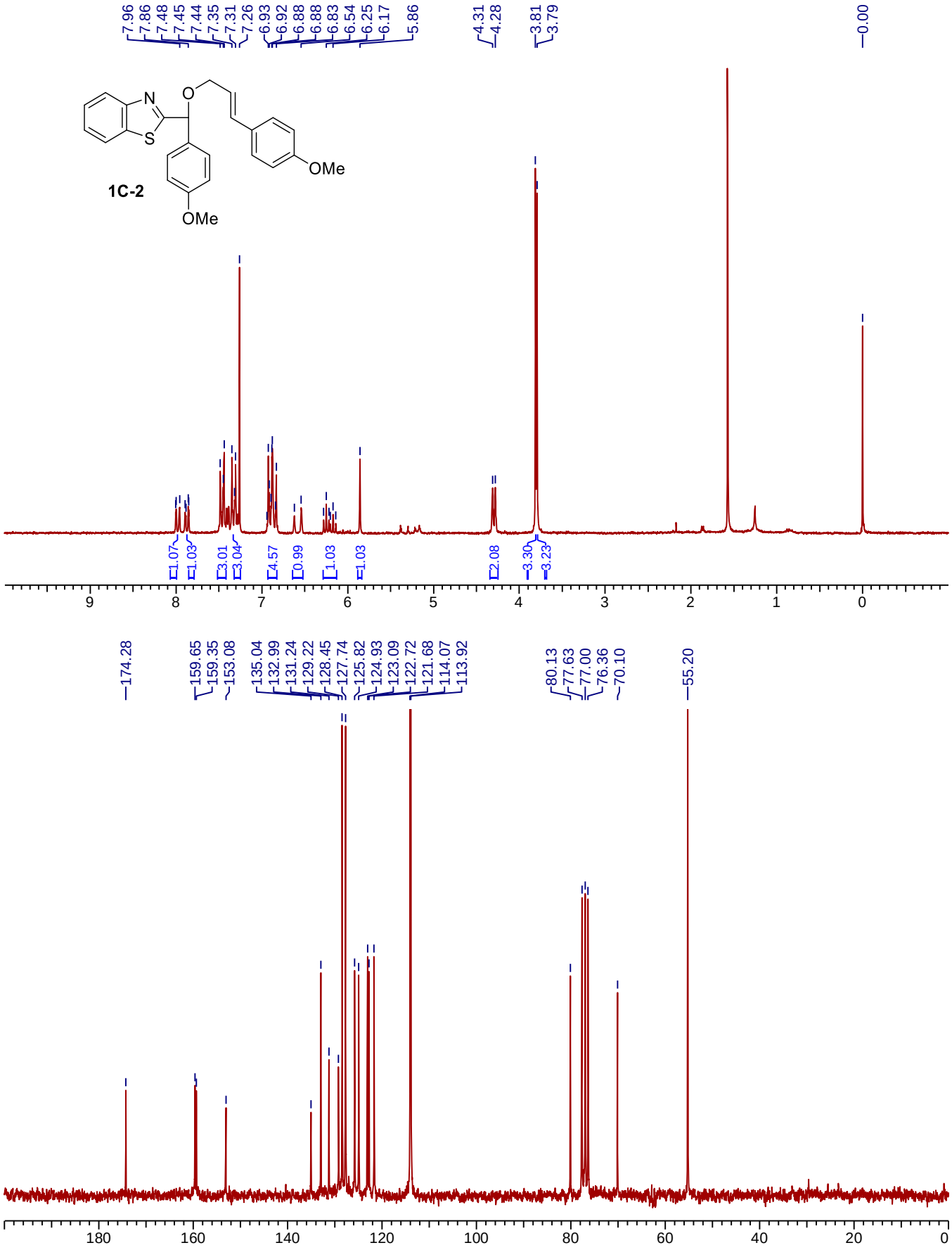
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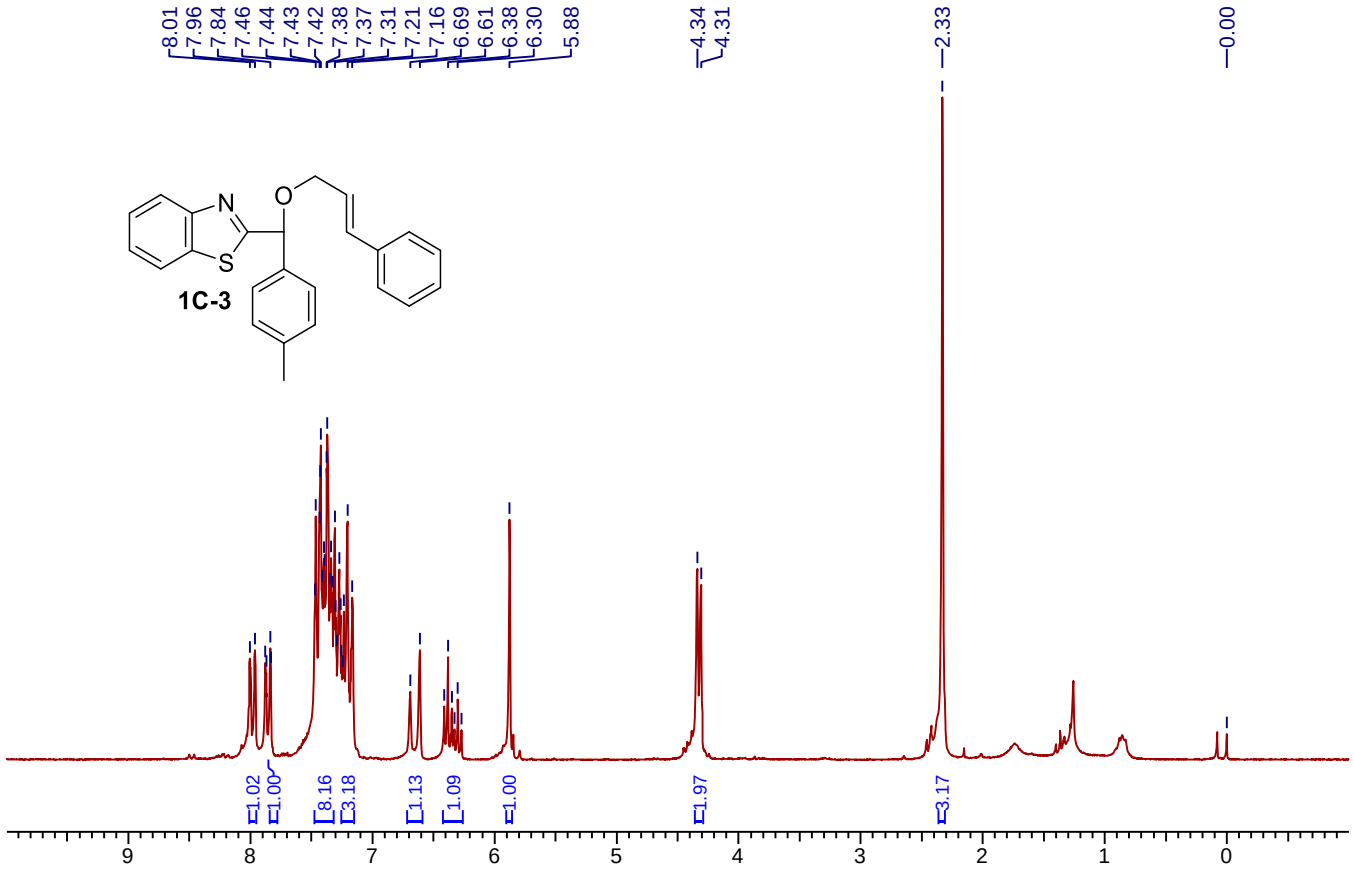
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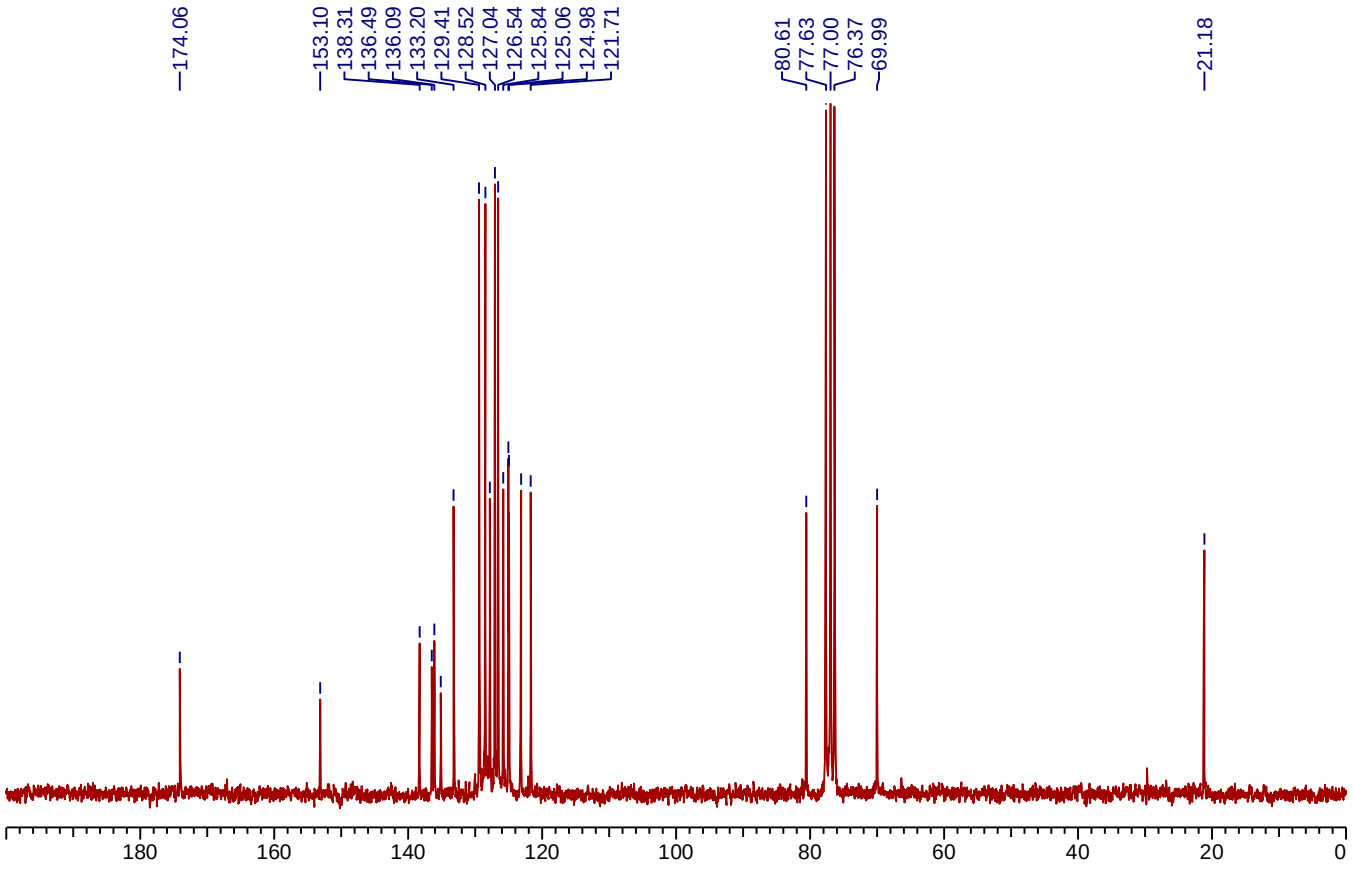
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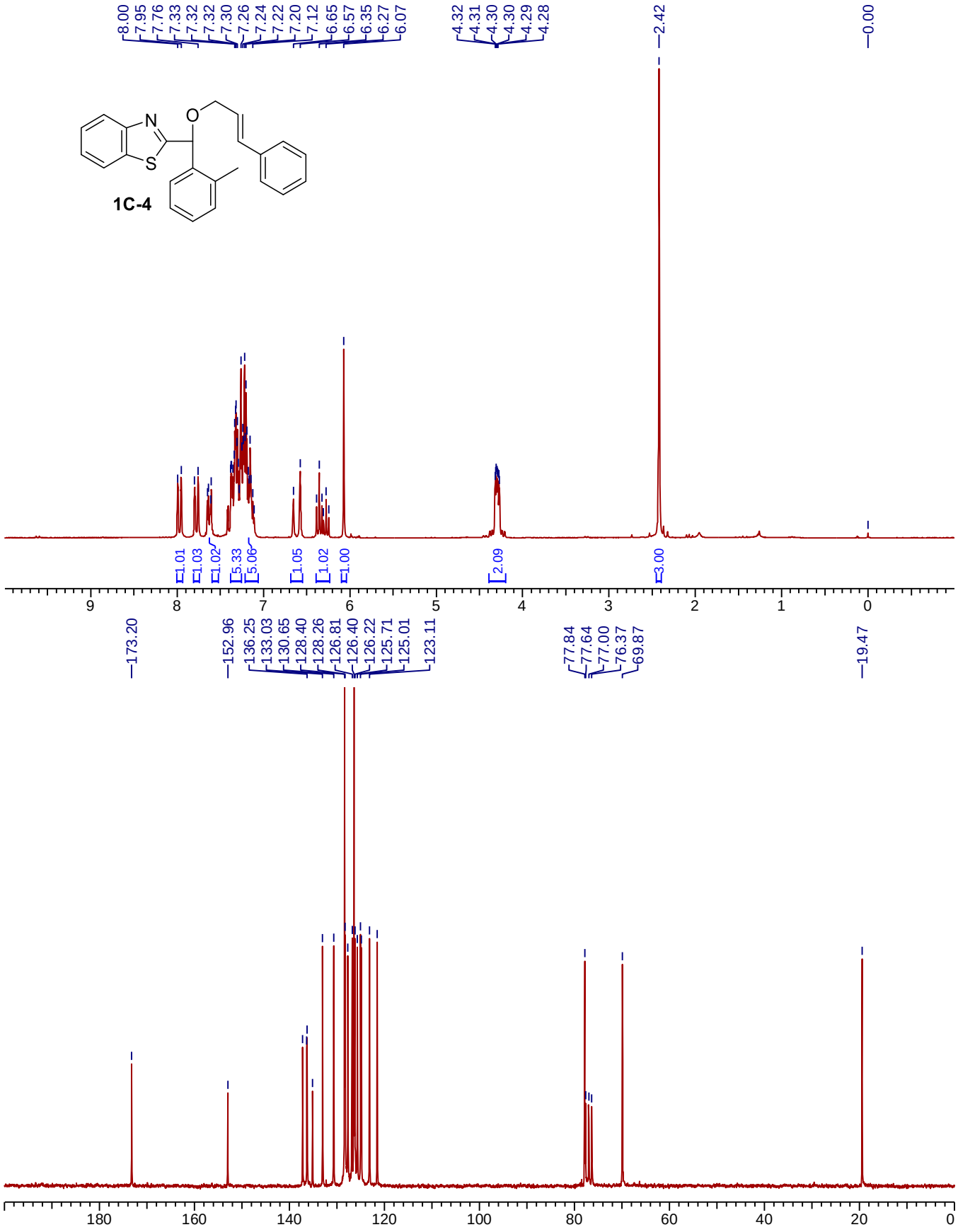
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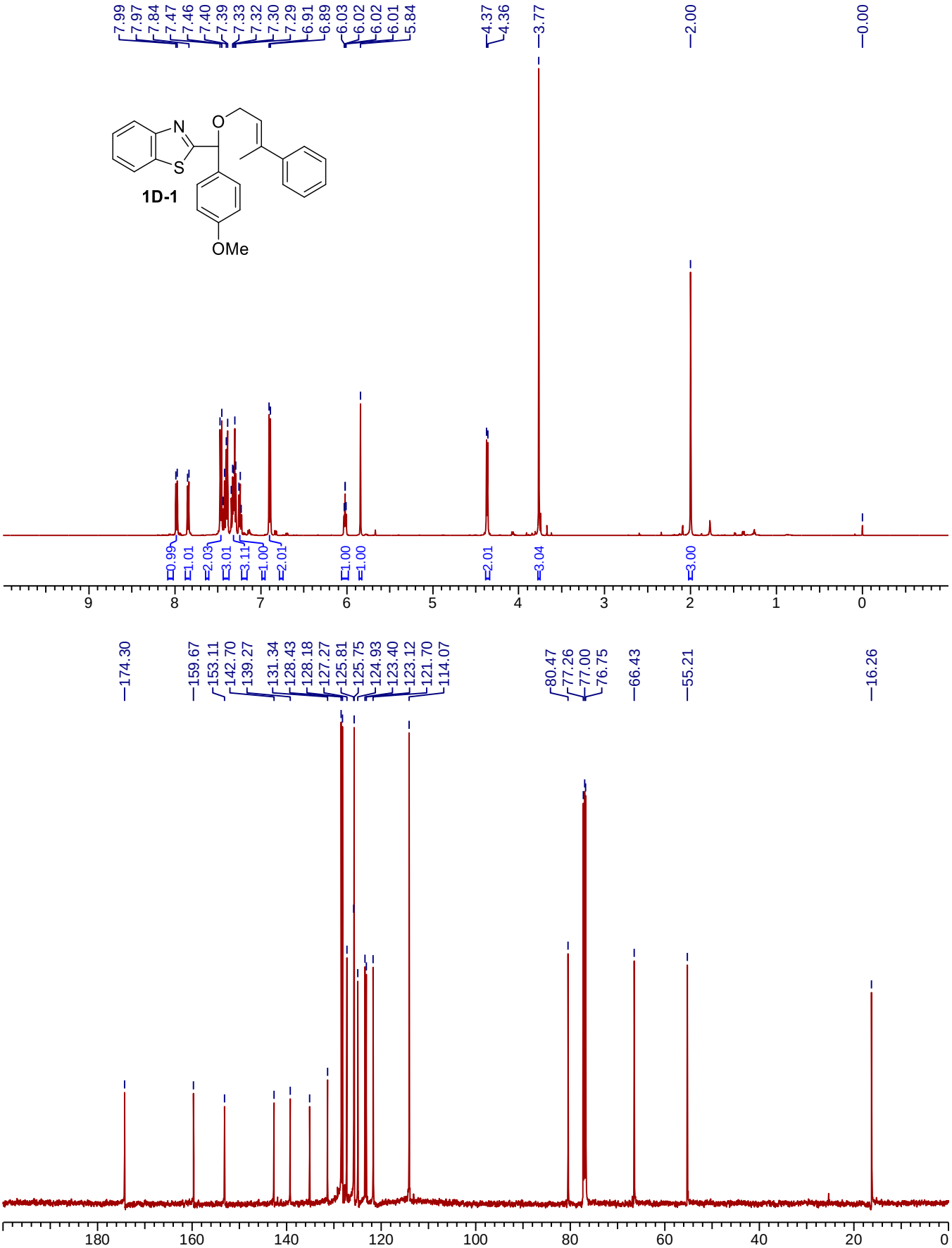
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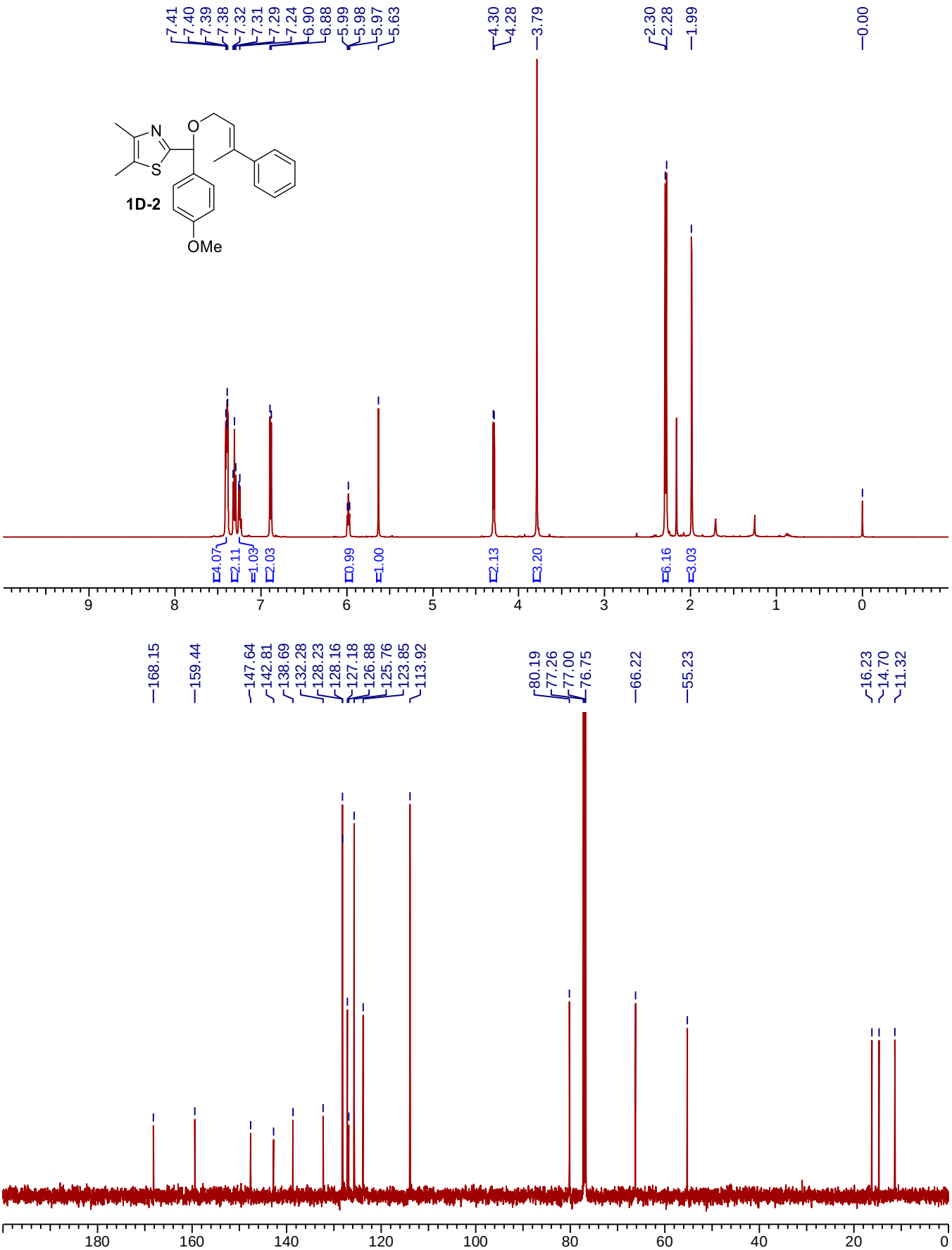
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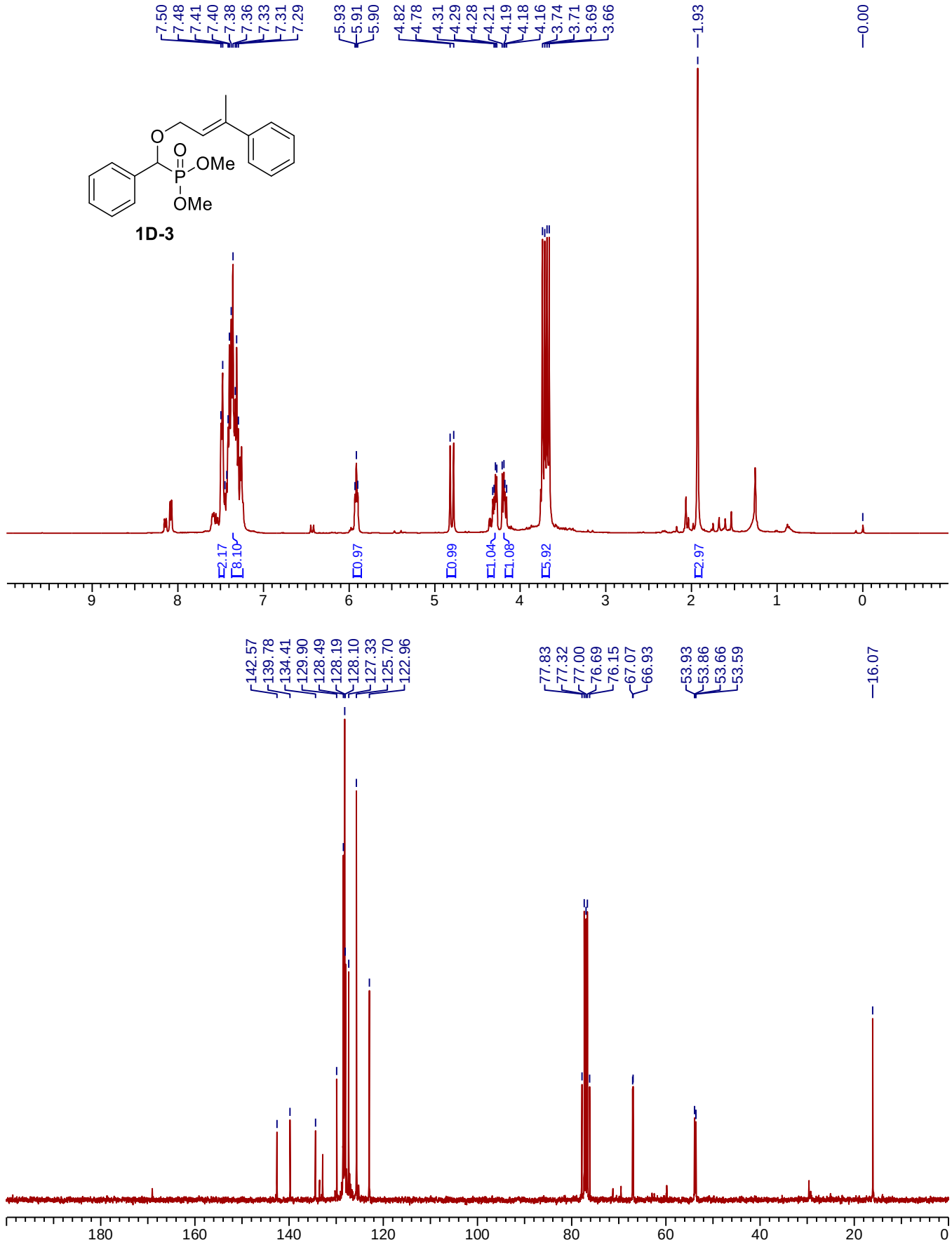
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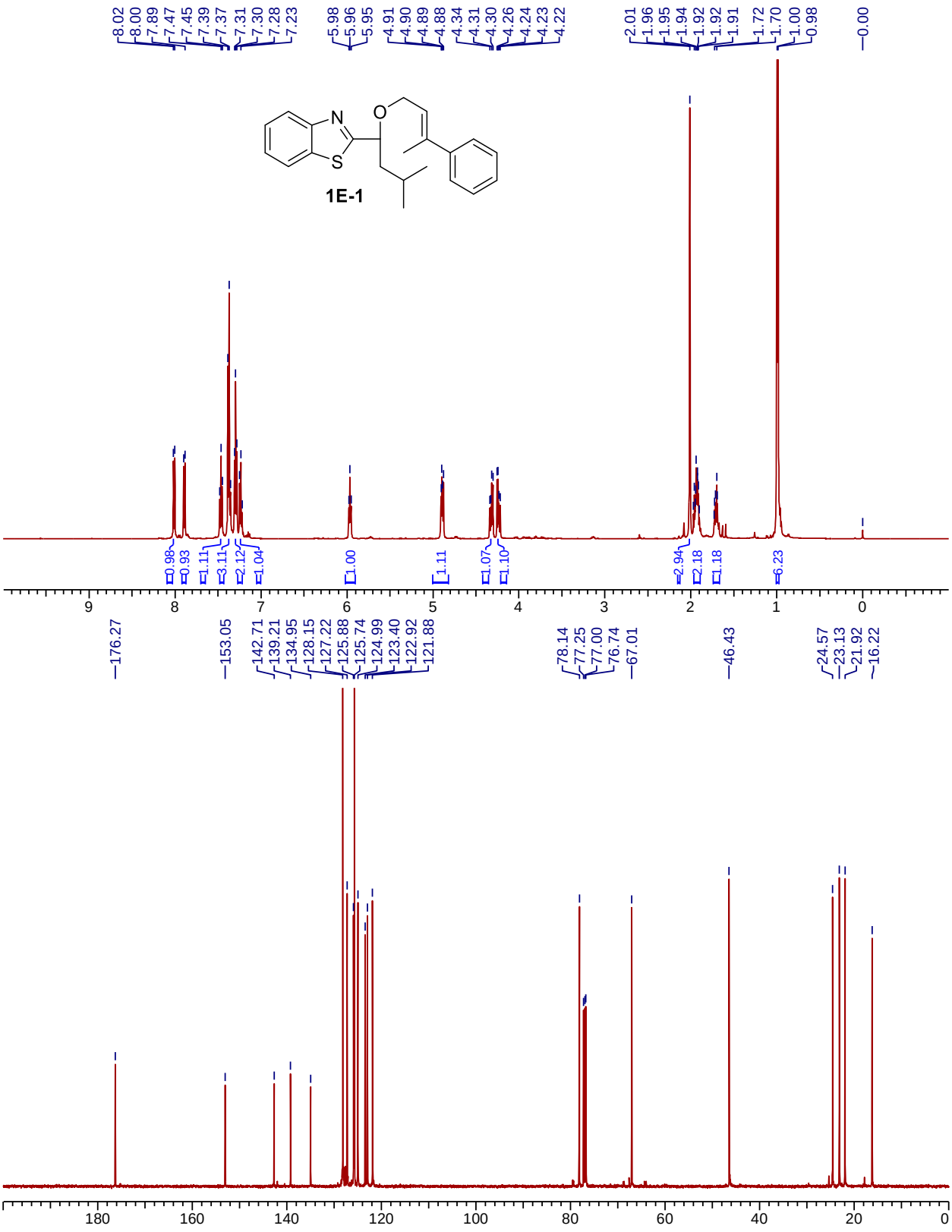
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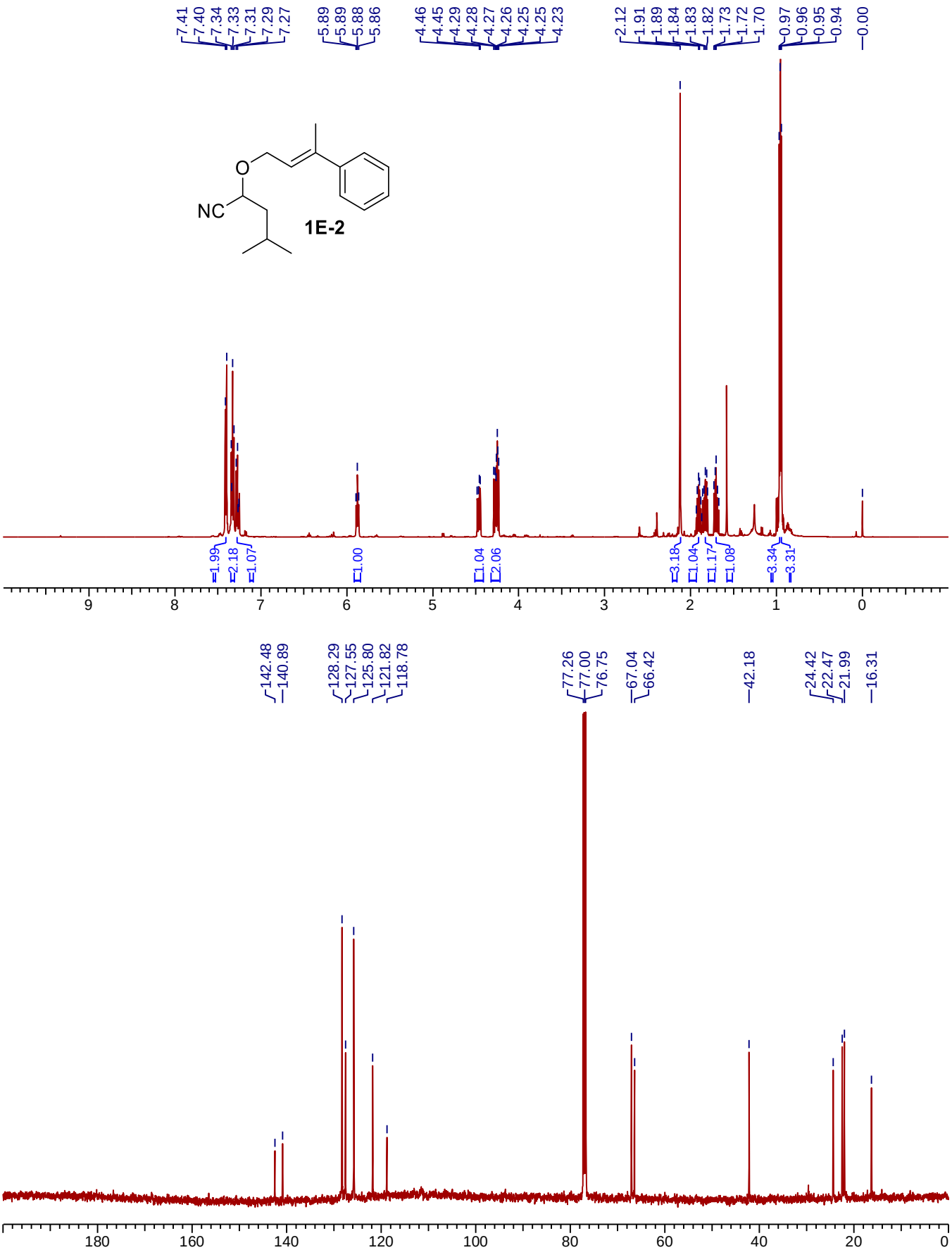
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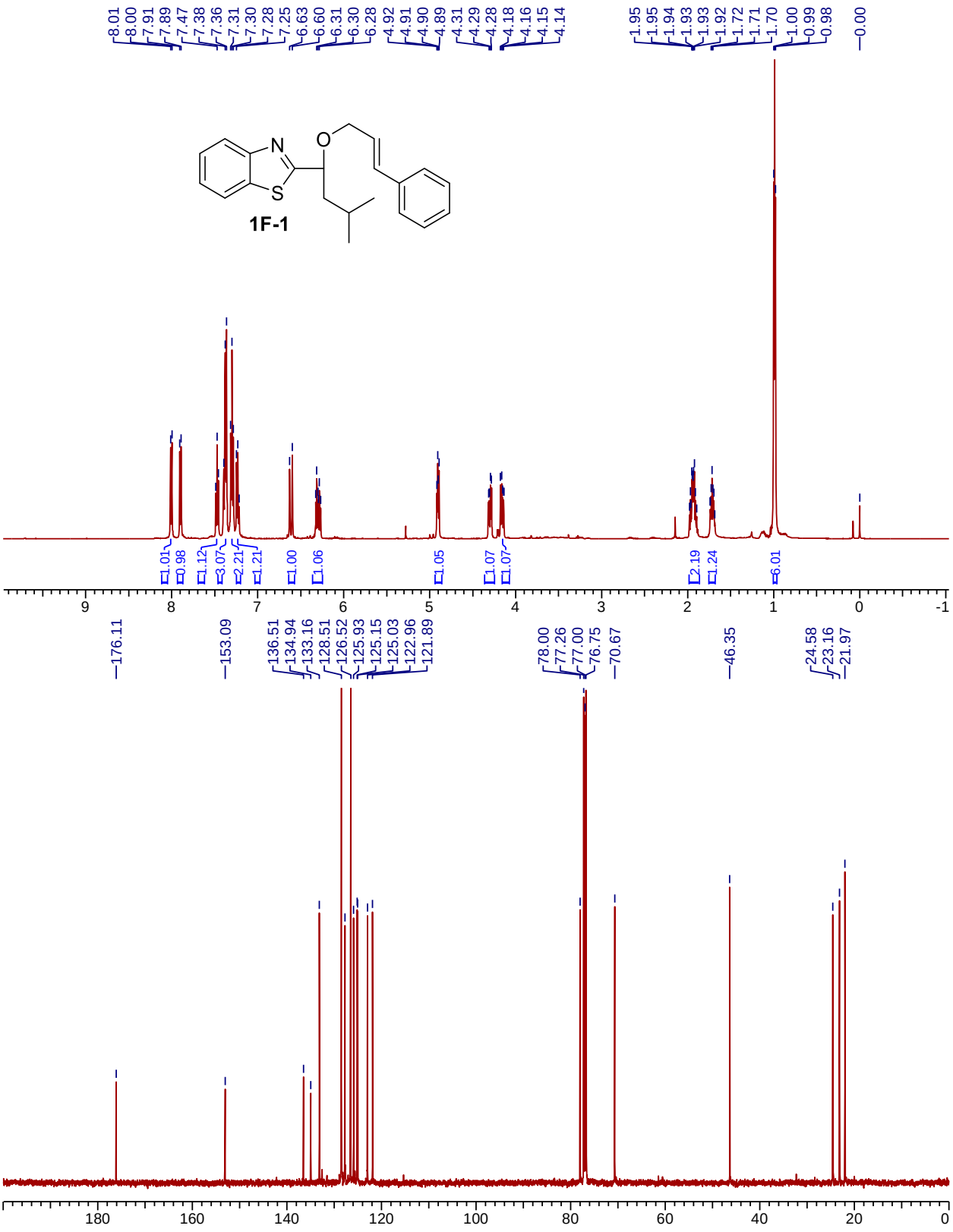
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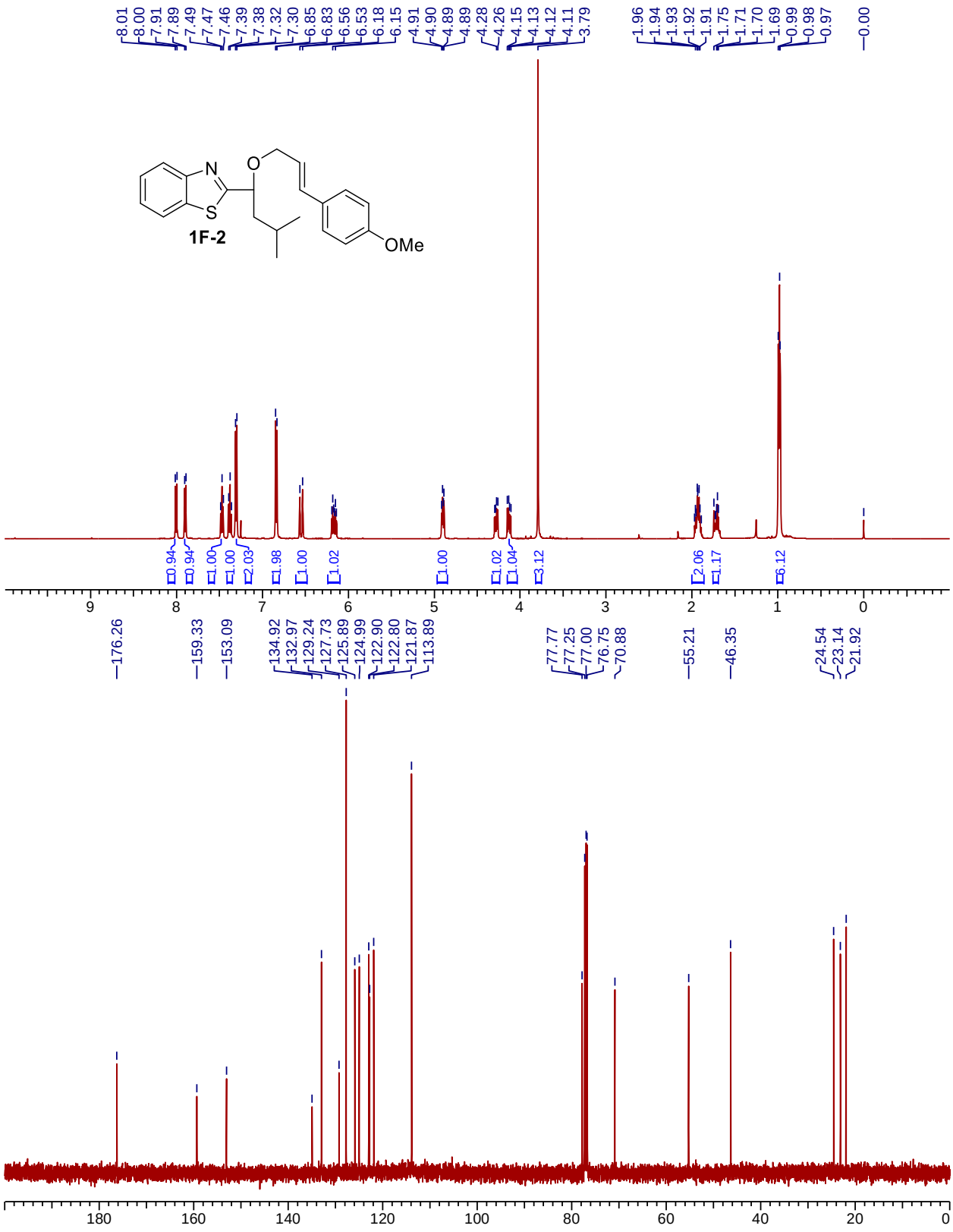
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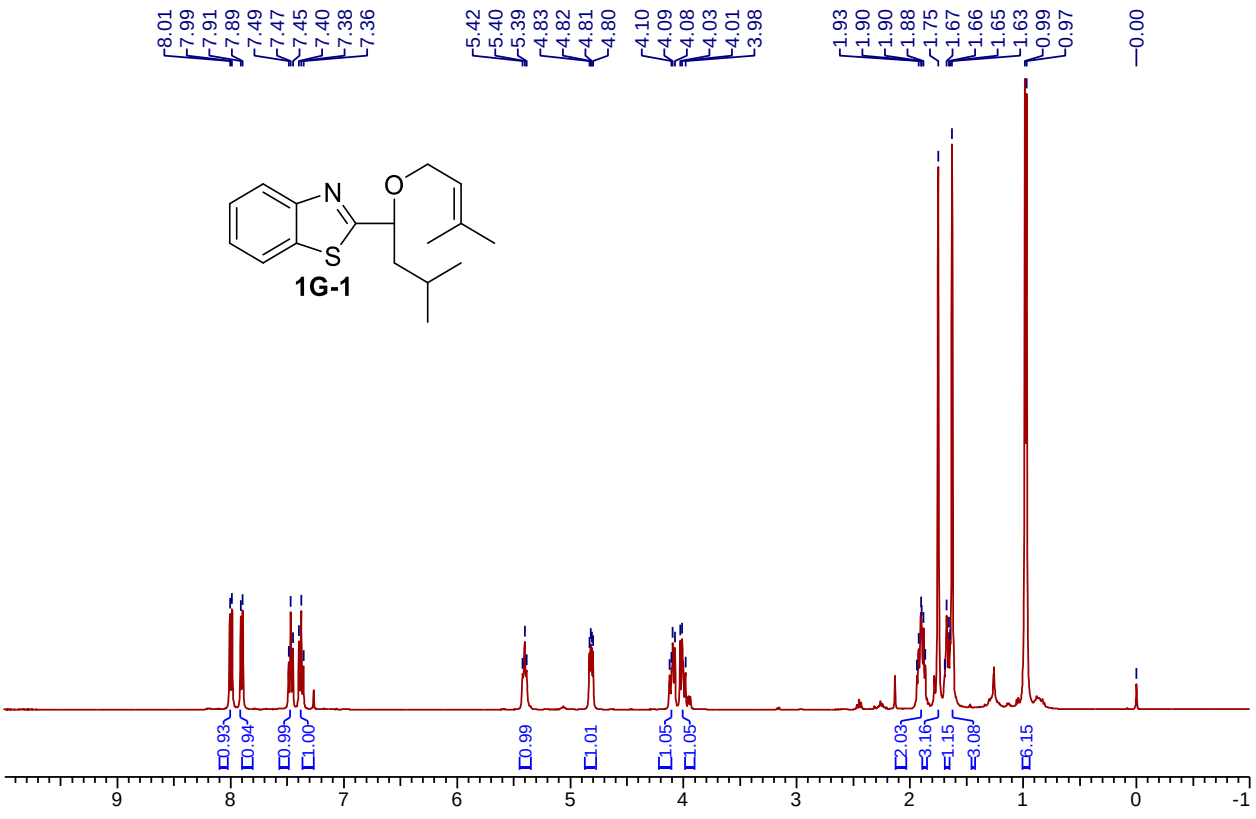
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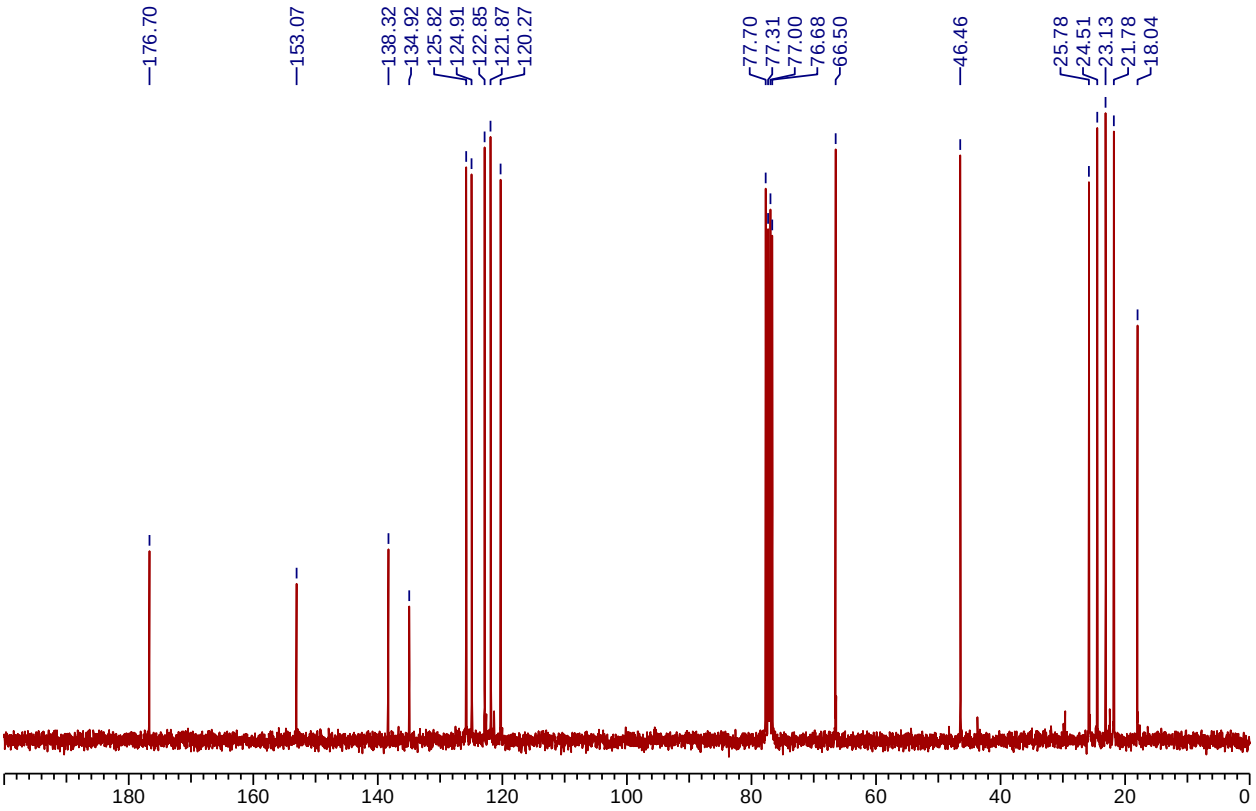
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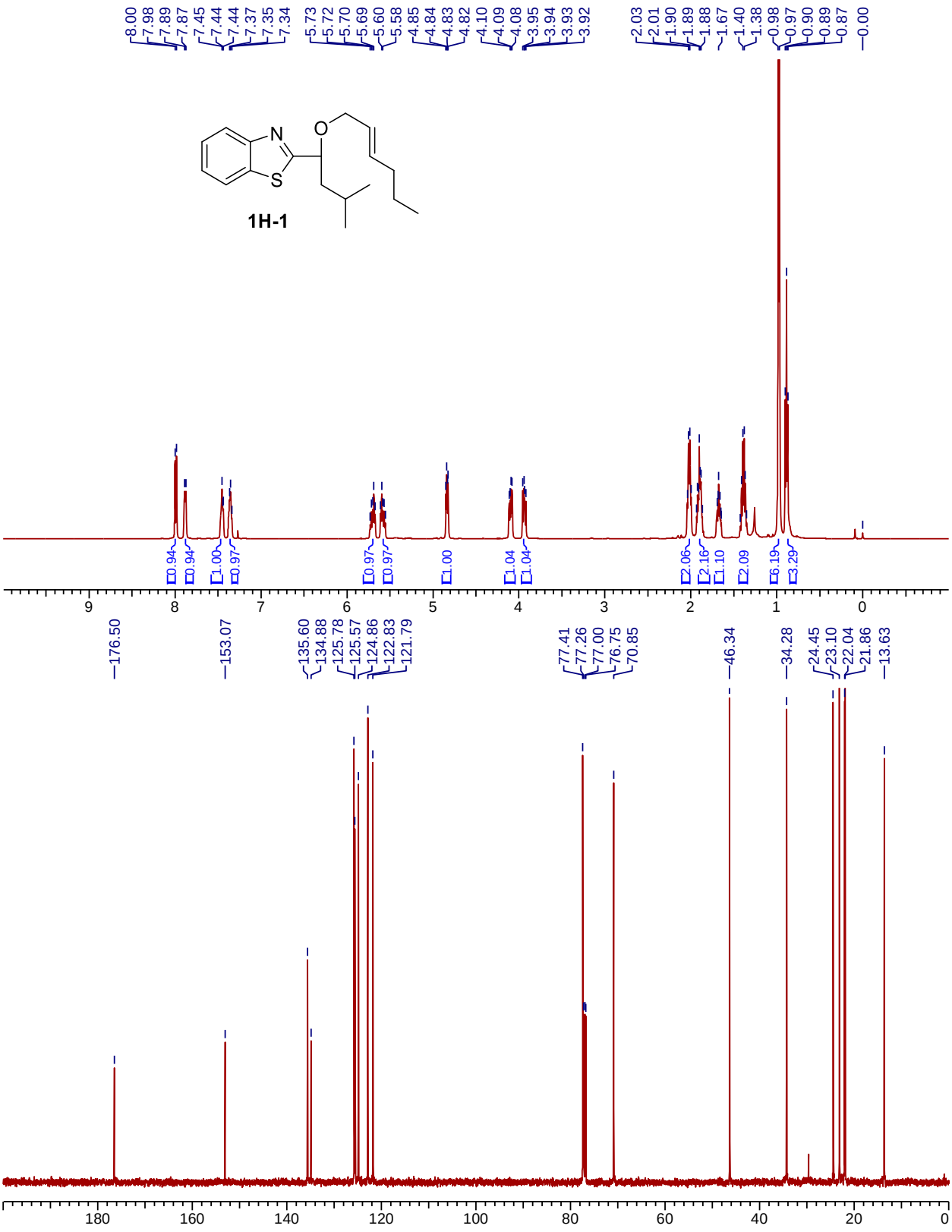
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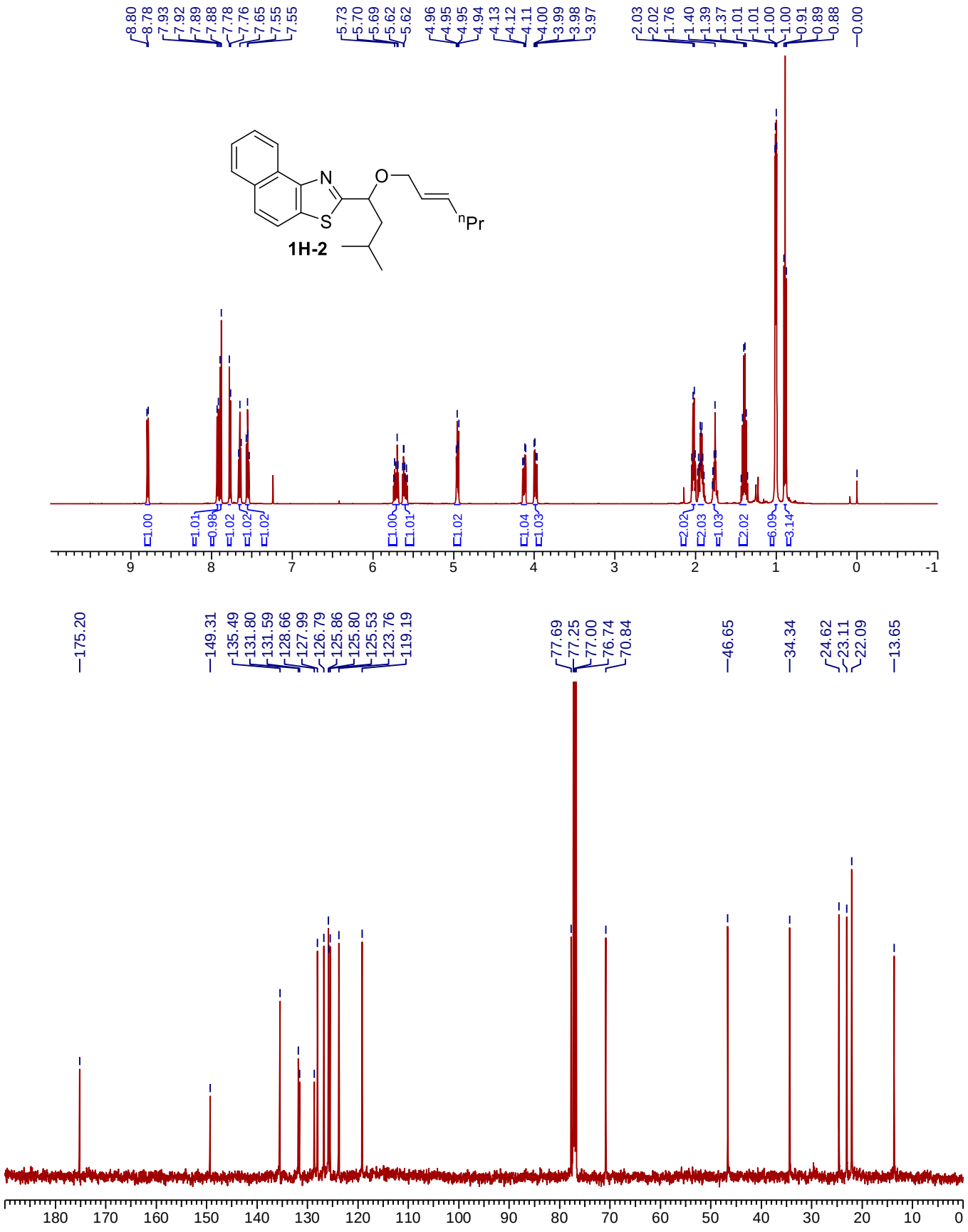
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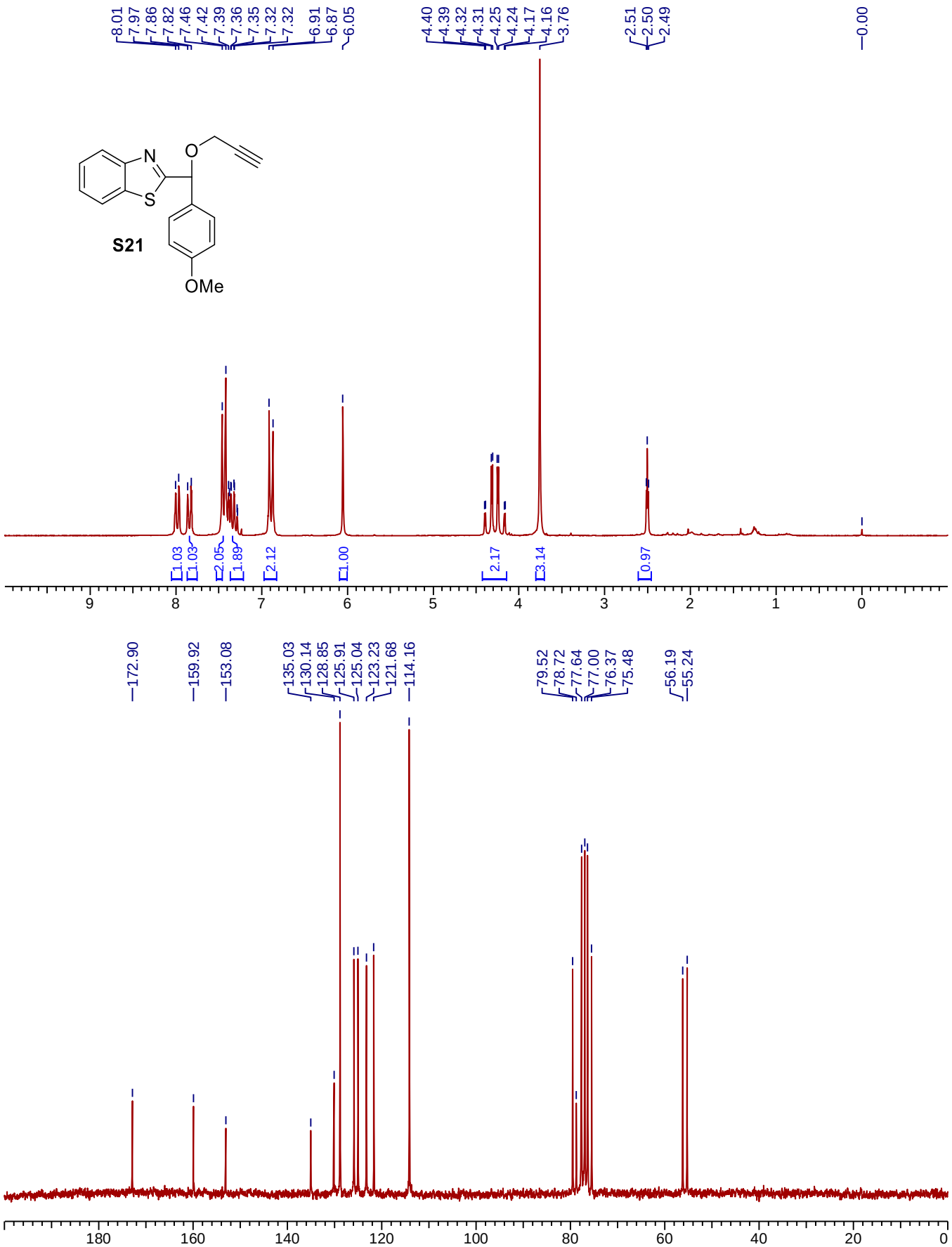
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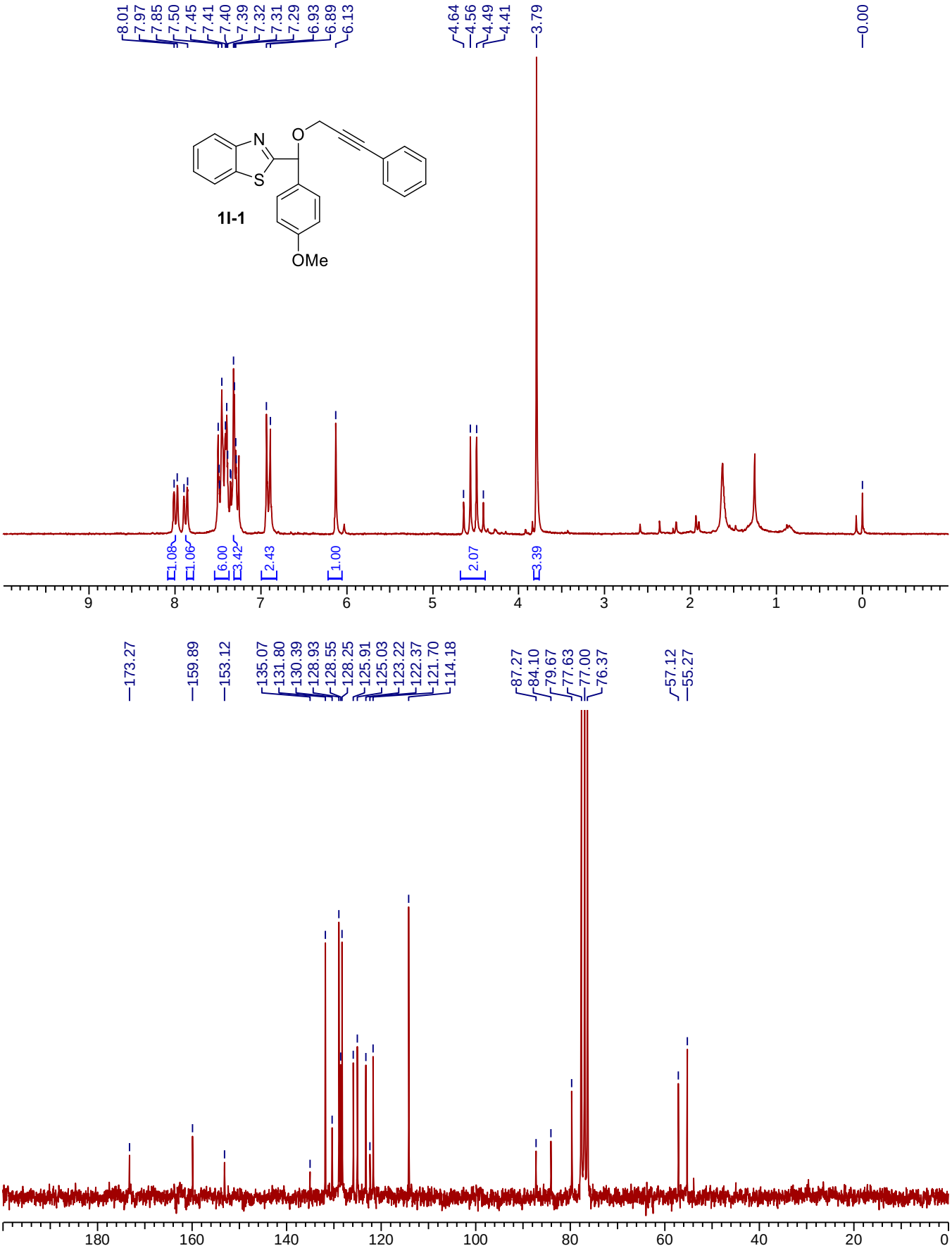
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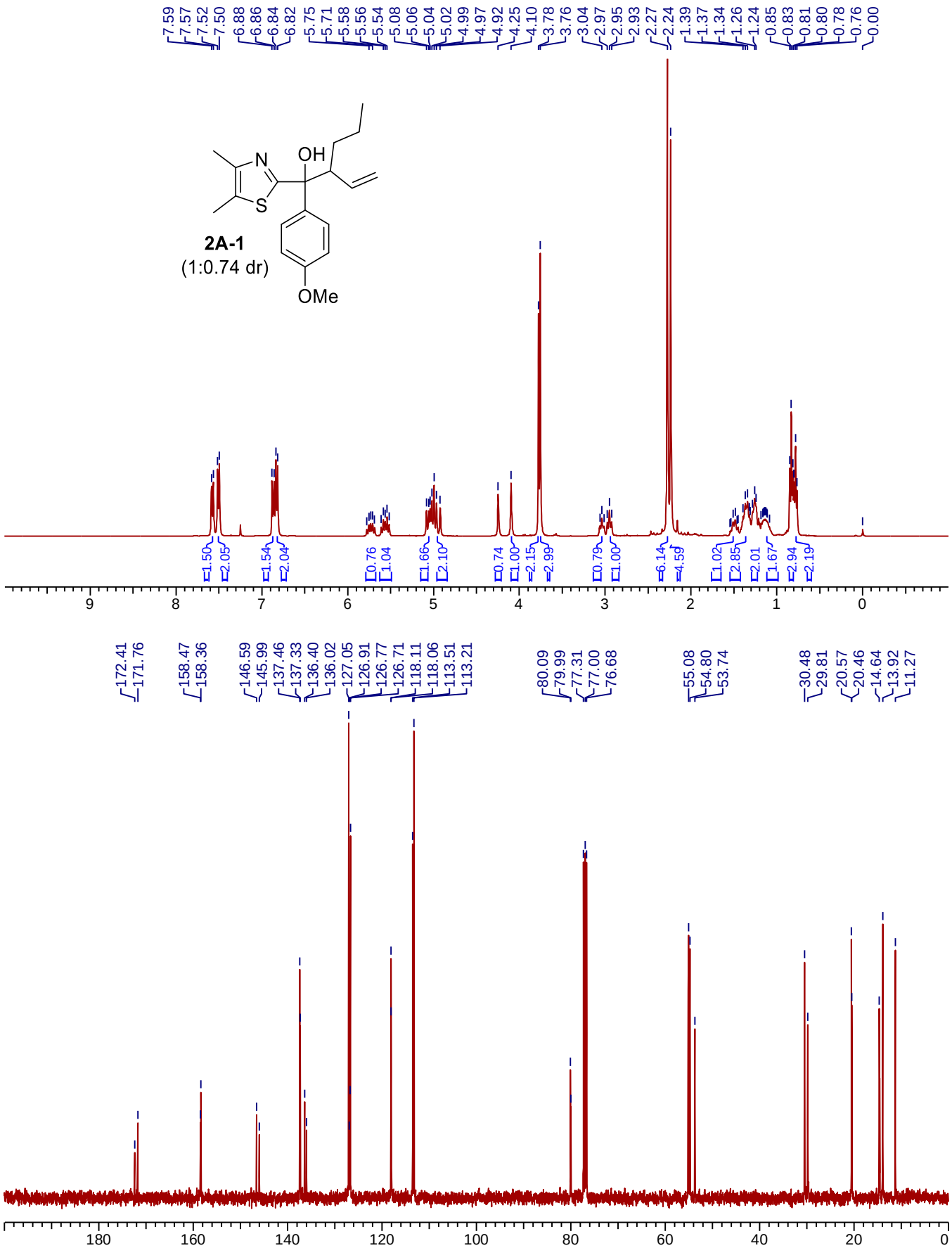
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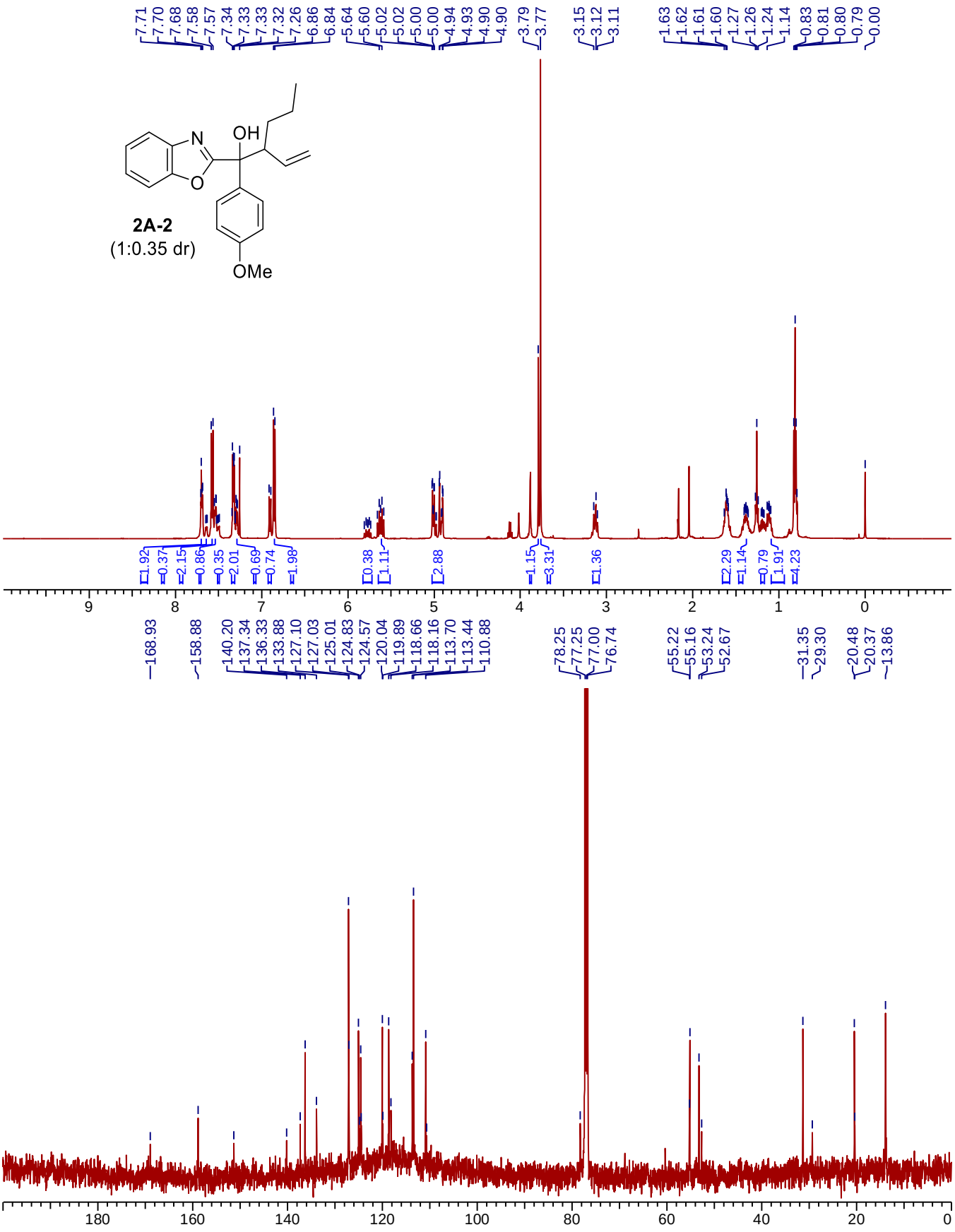
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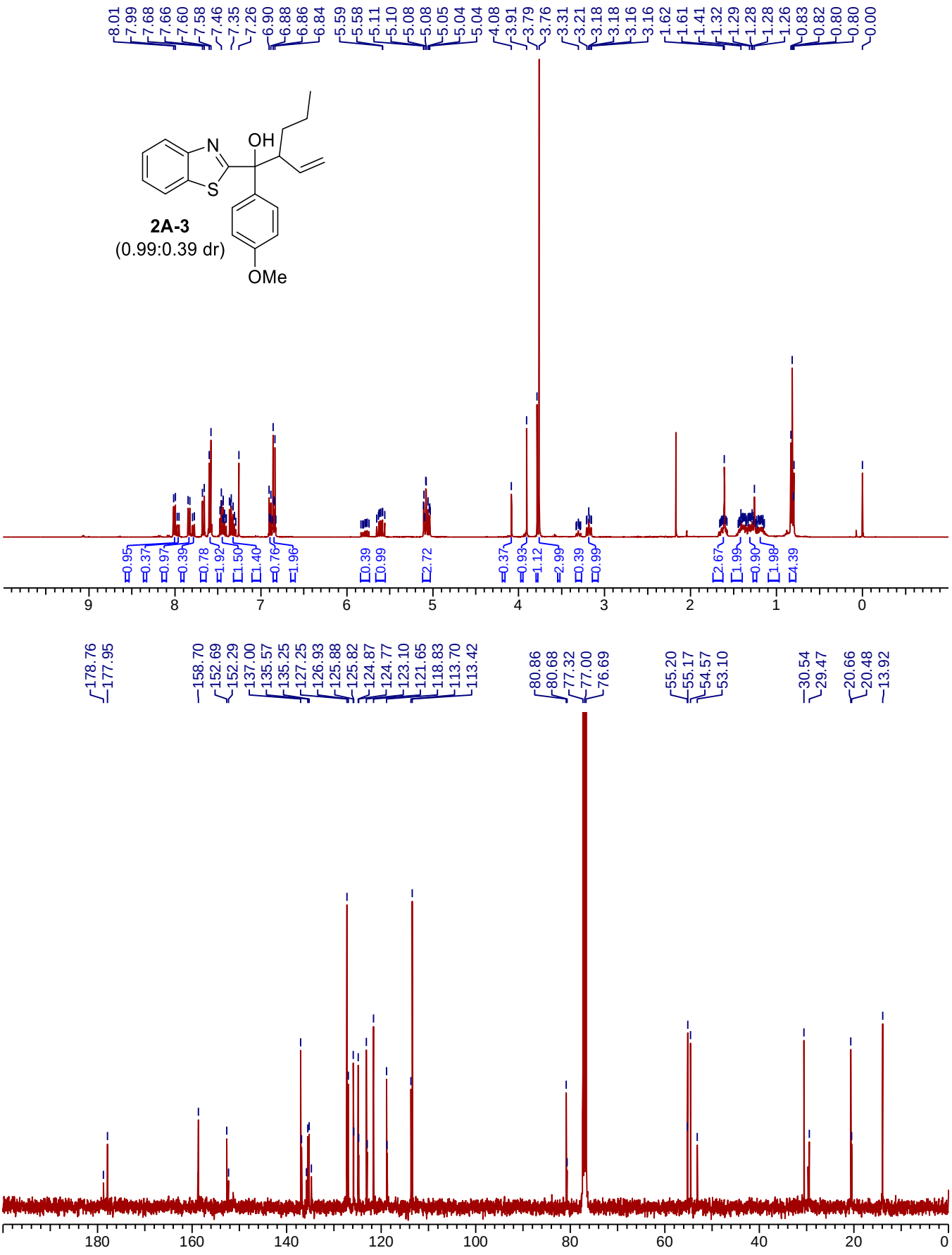
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OH
S
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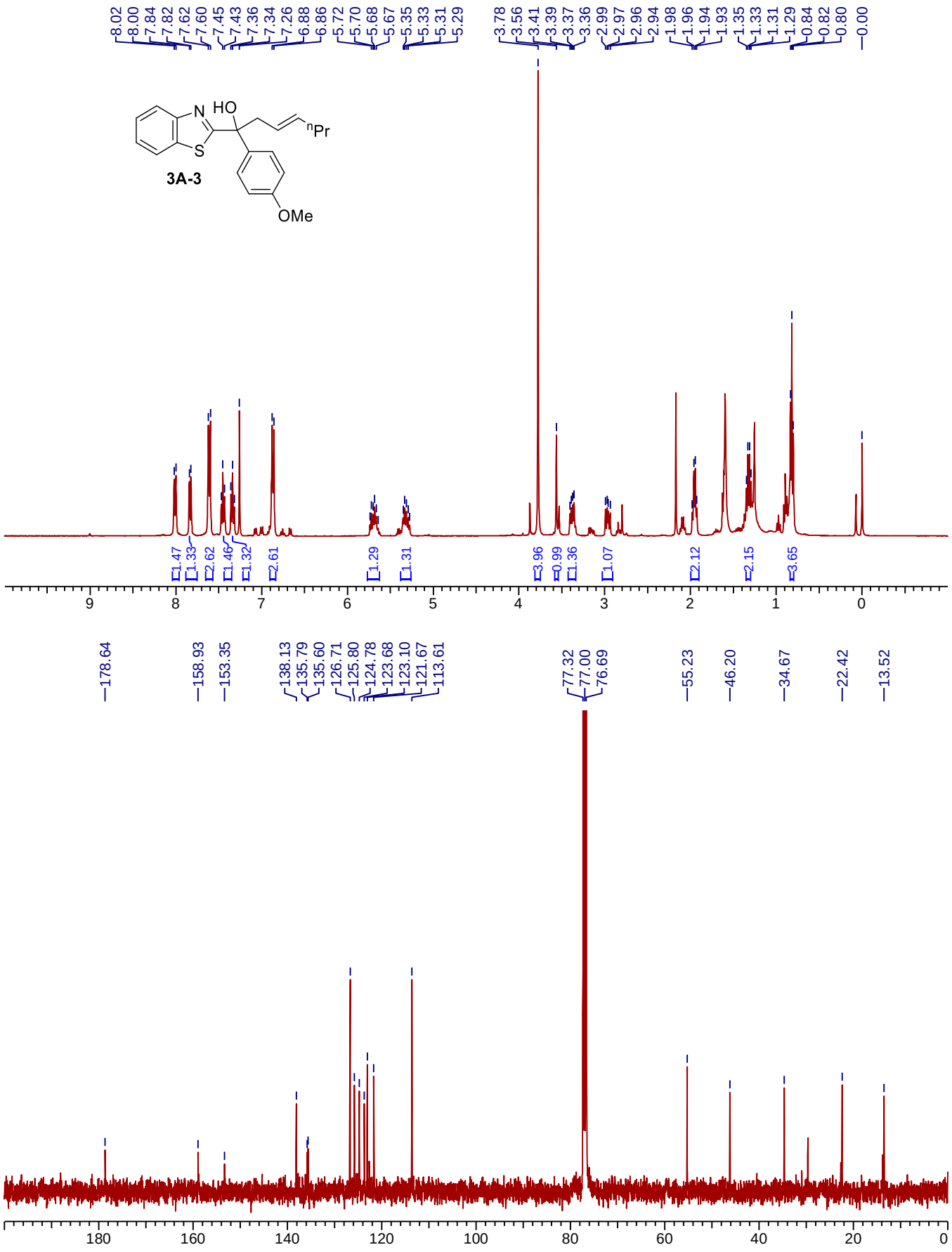
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nPr
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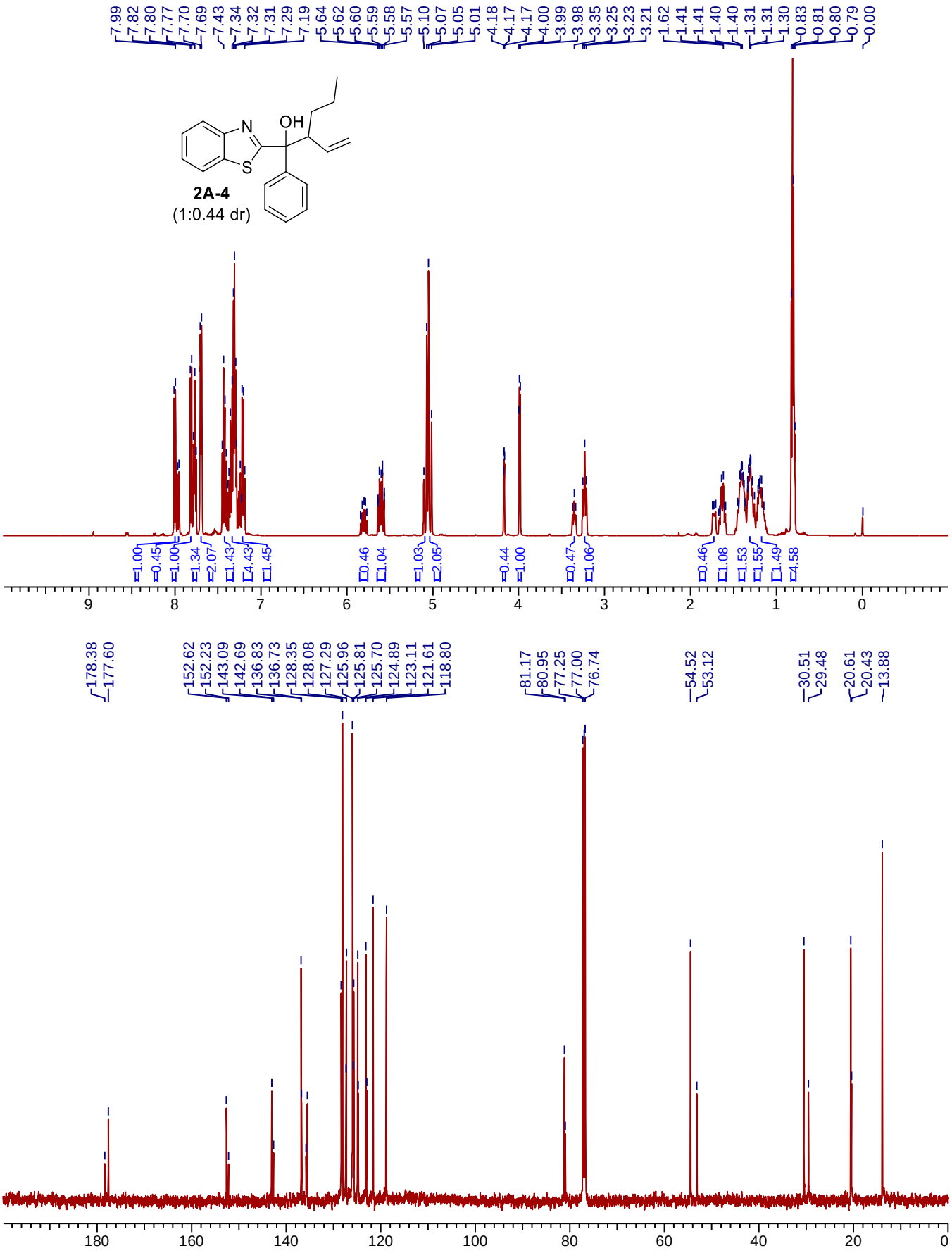
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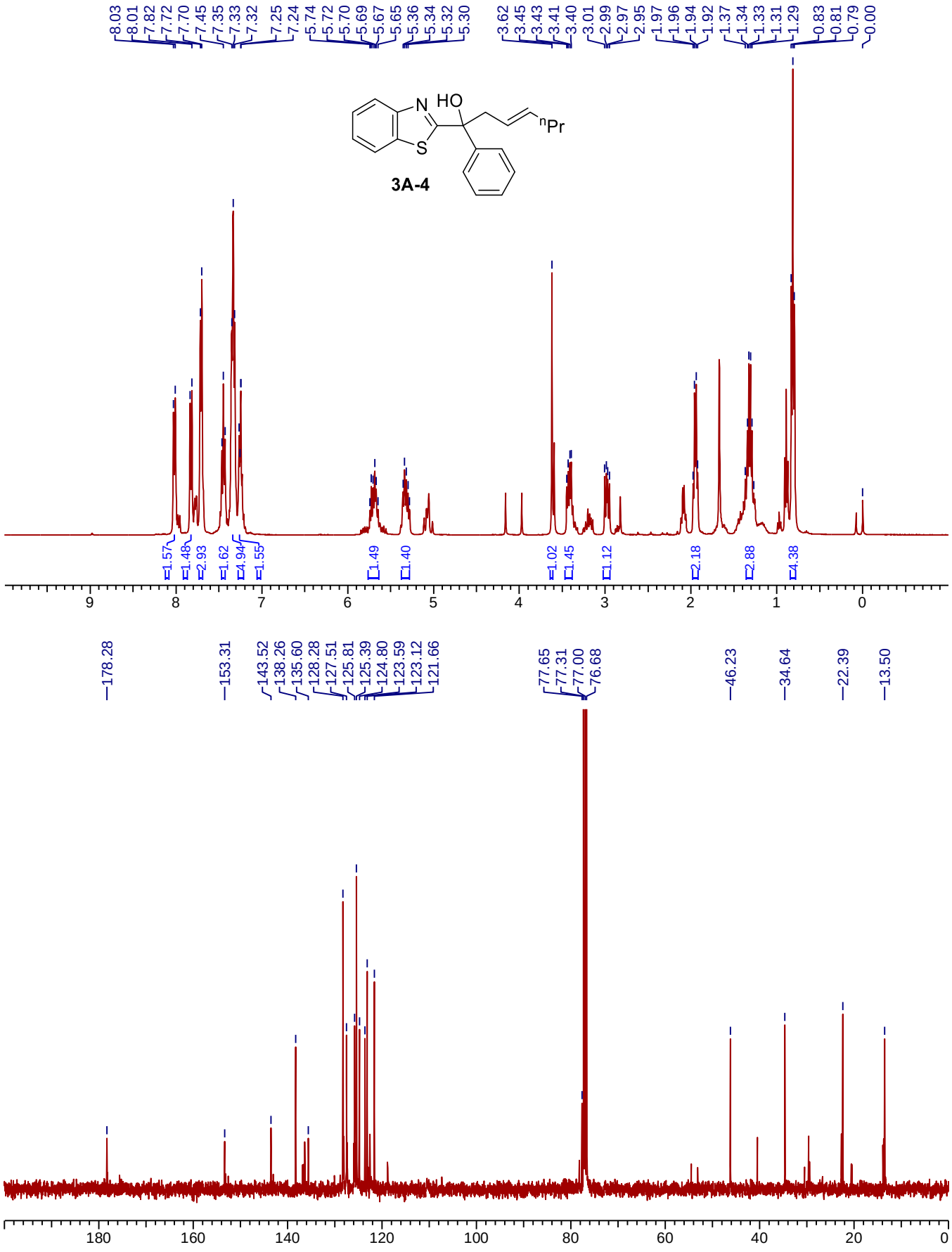
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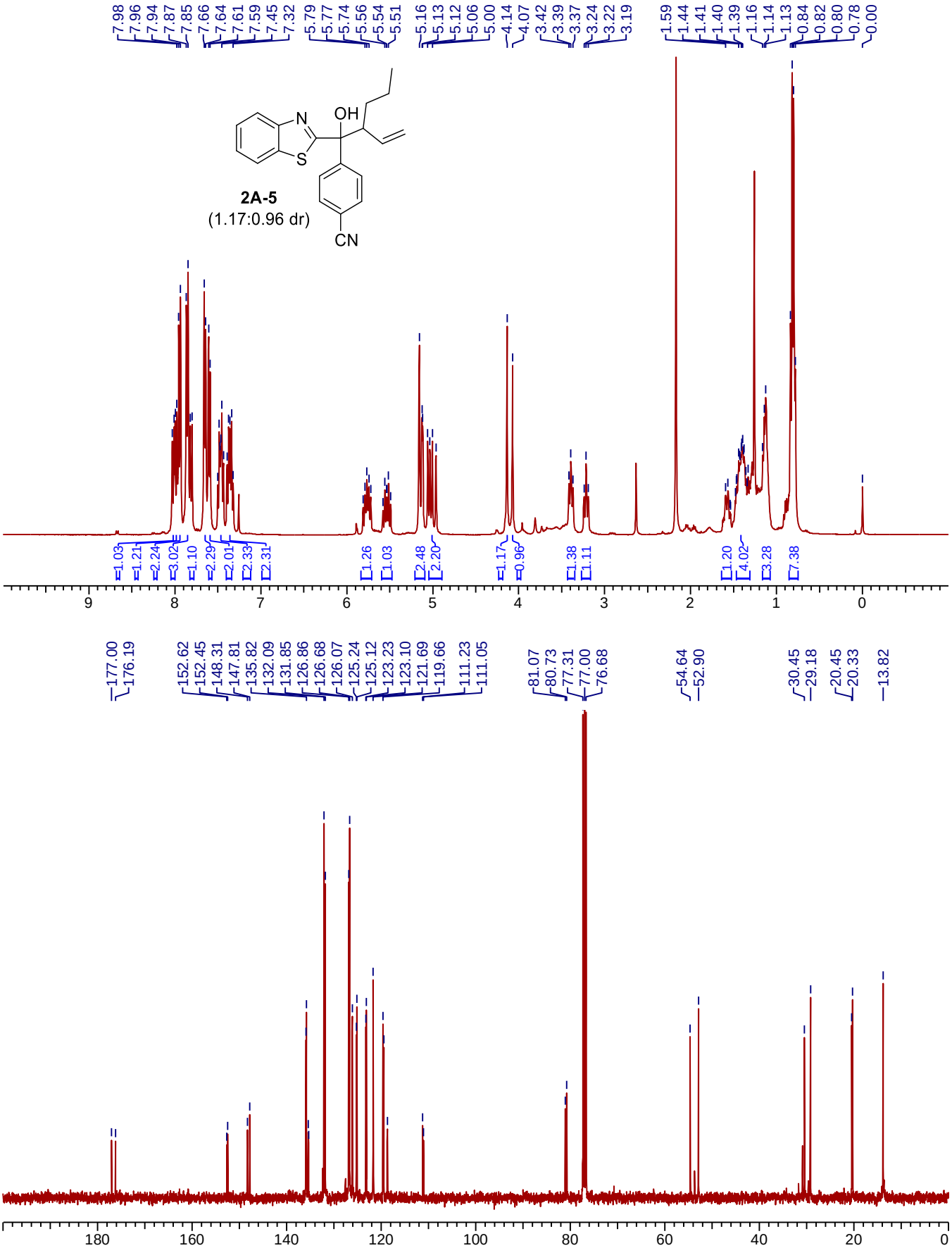
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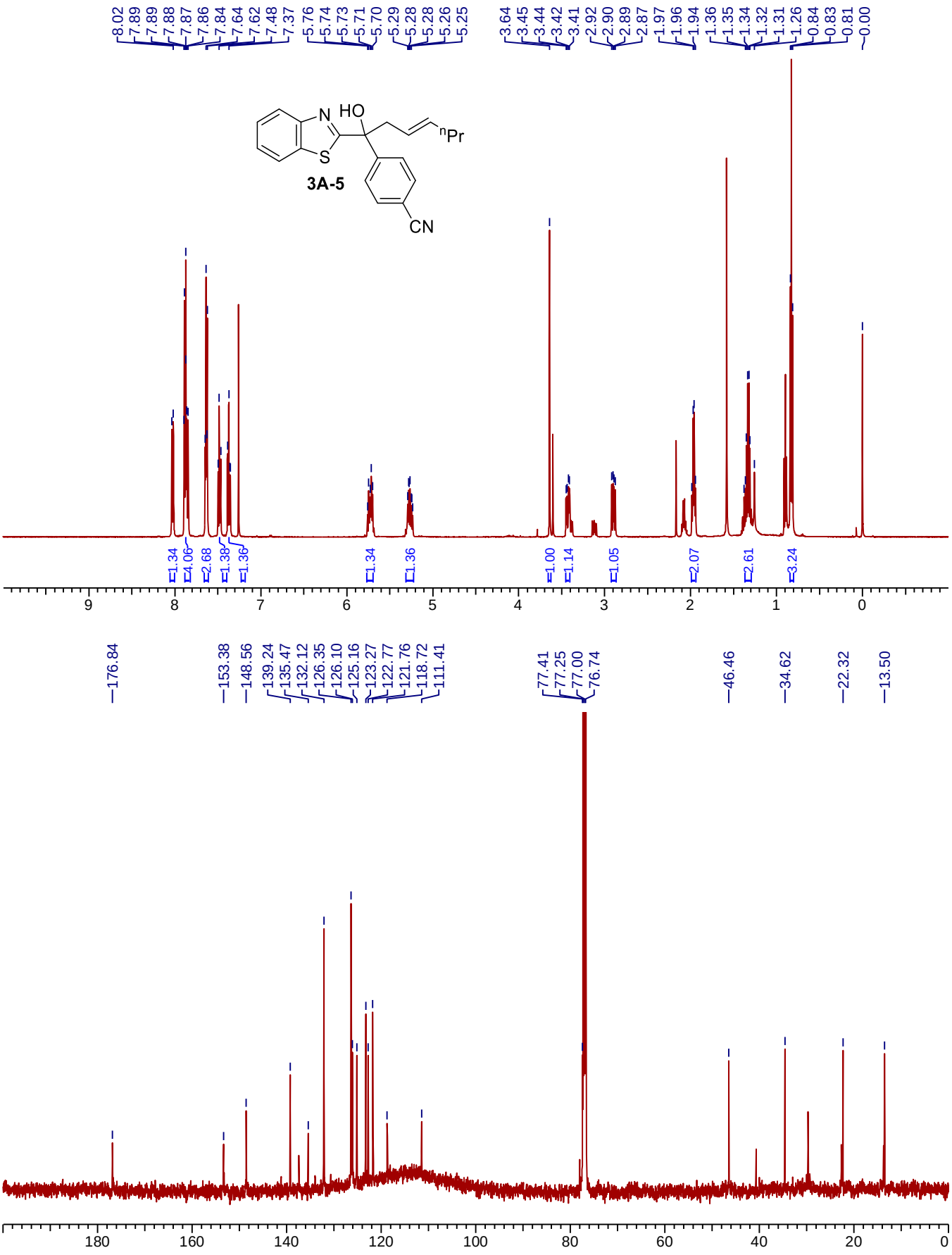
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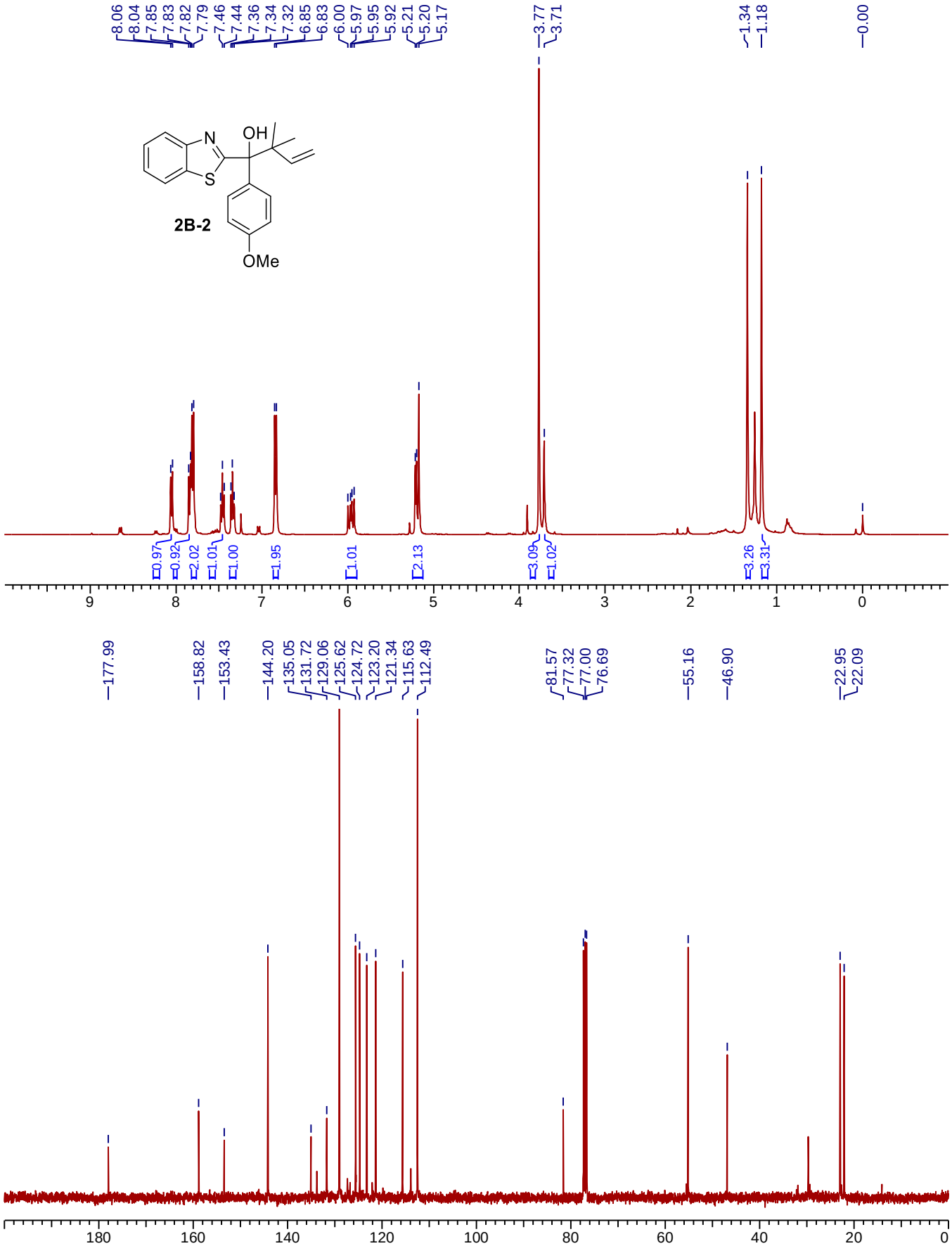
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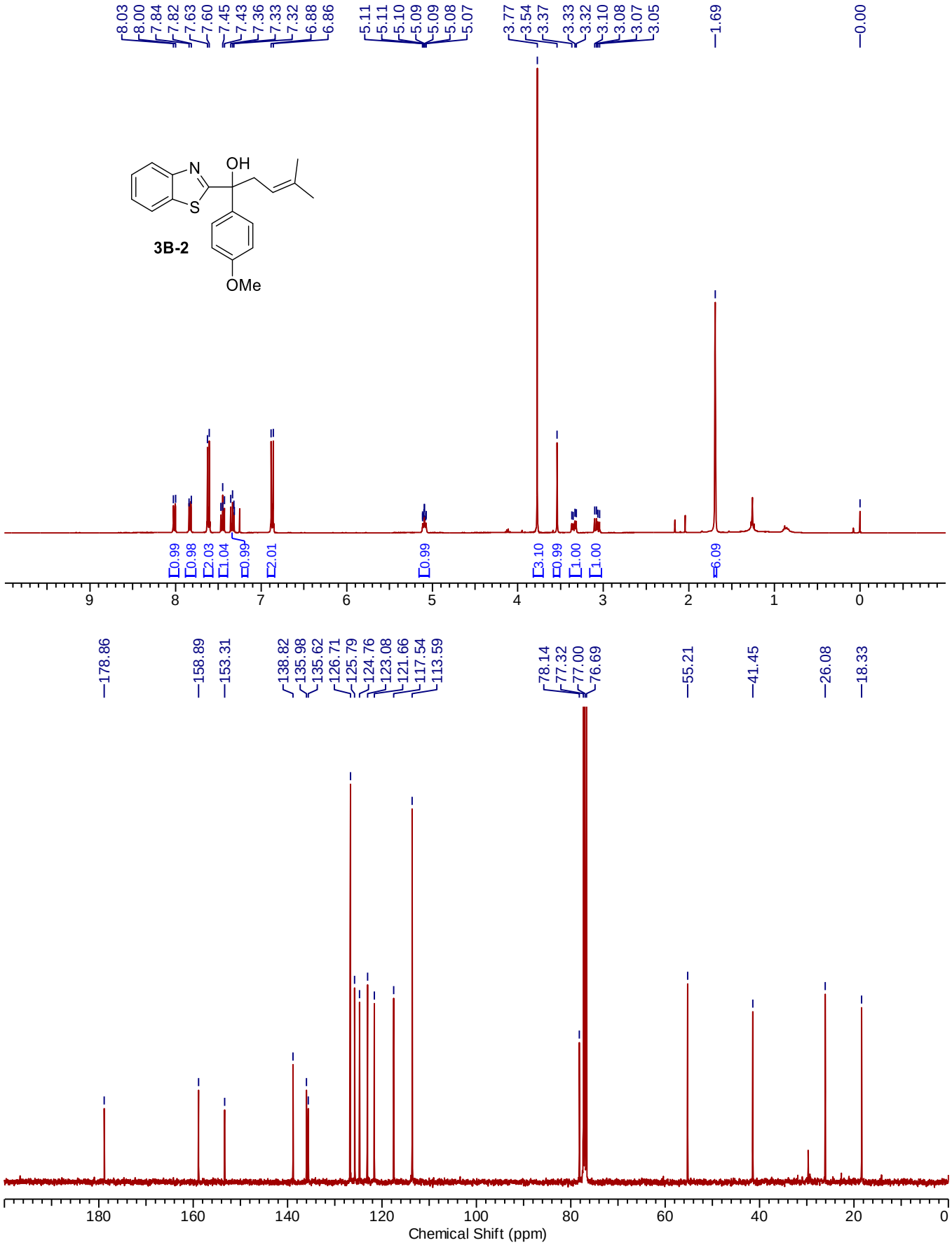
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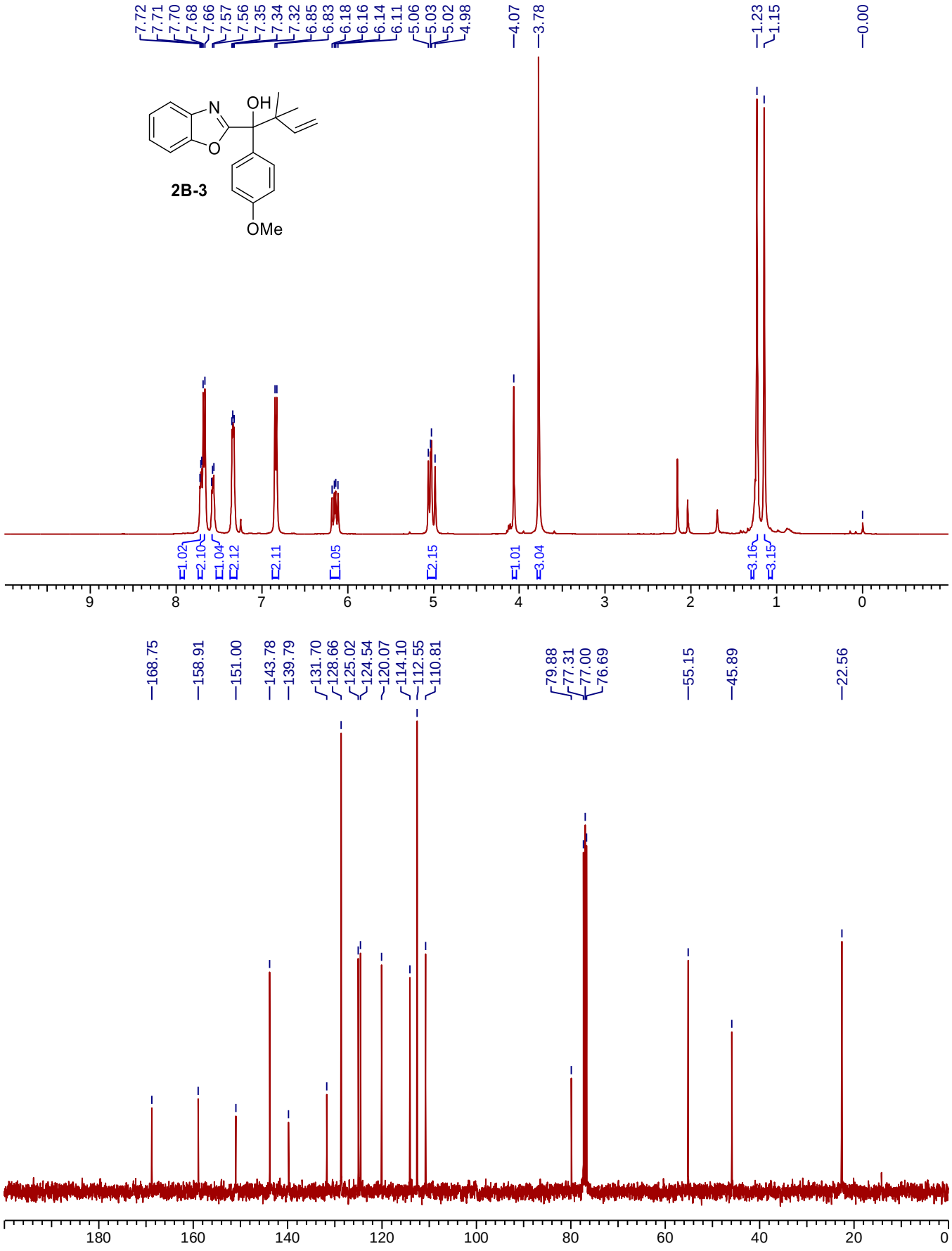
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OH
O
2B-3
OMe
1.02
2.10
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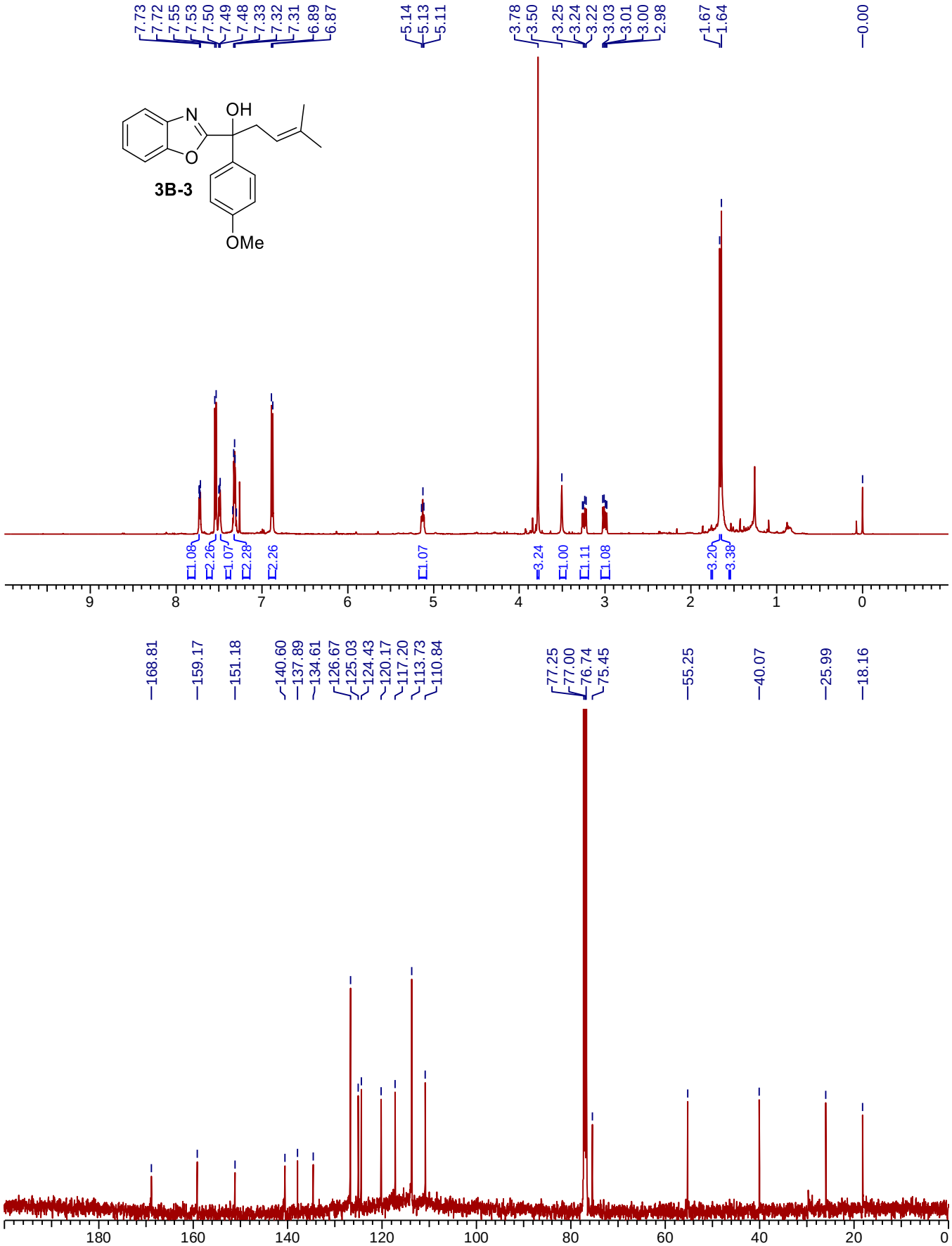
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OH
O
3B-3
OMe
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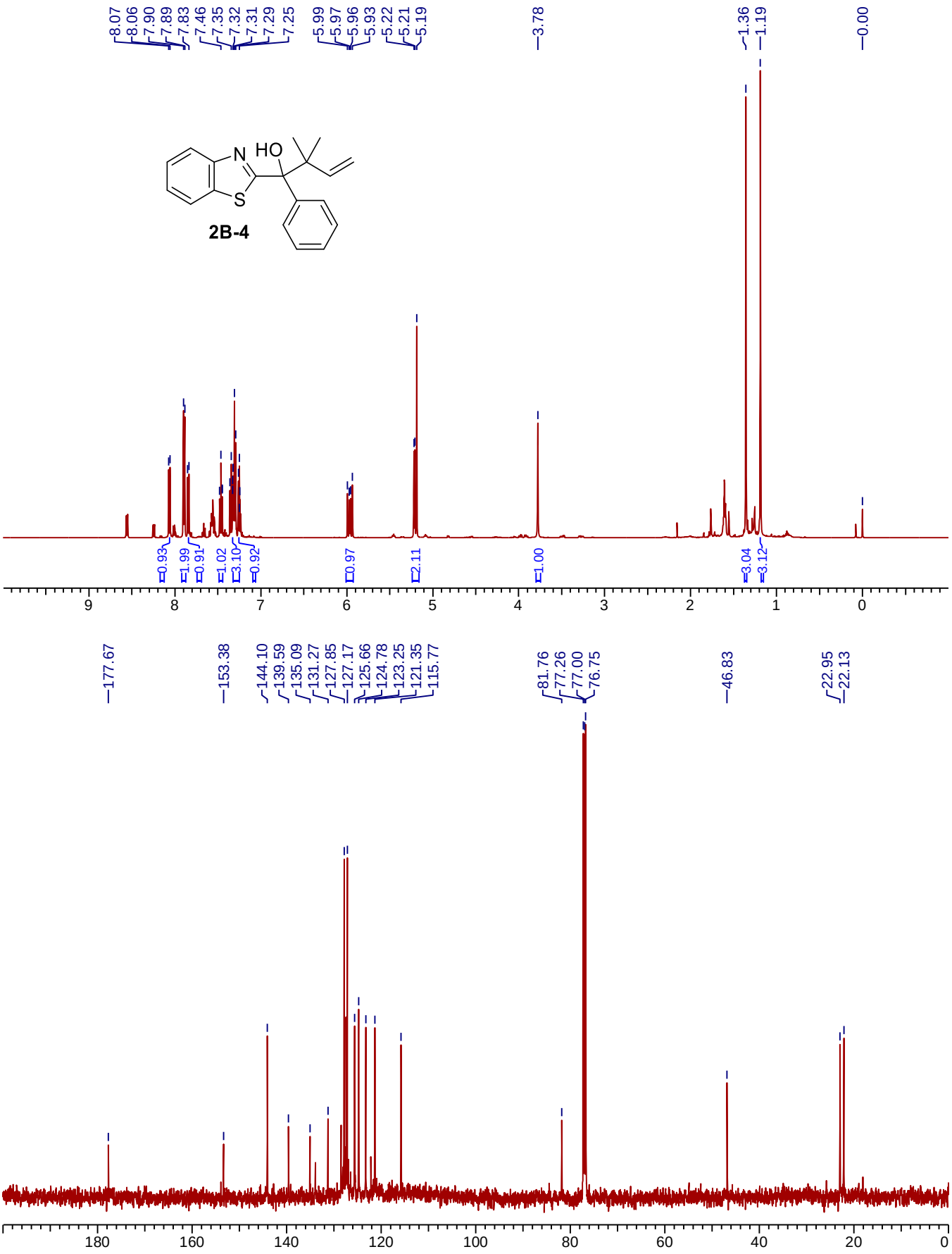
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HO
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2B-4
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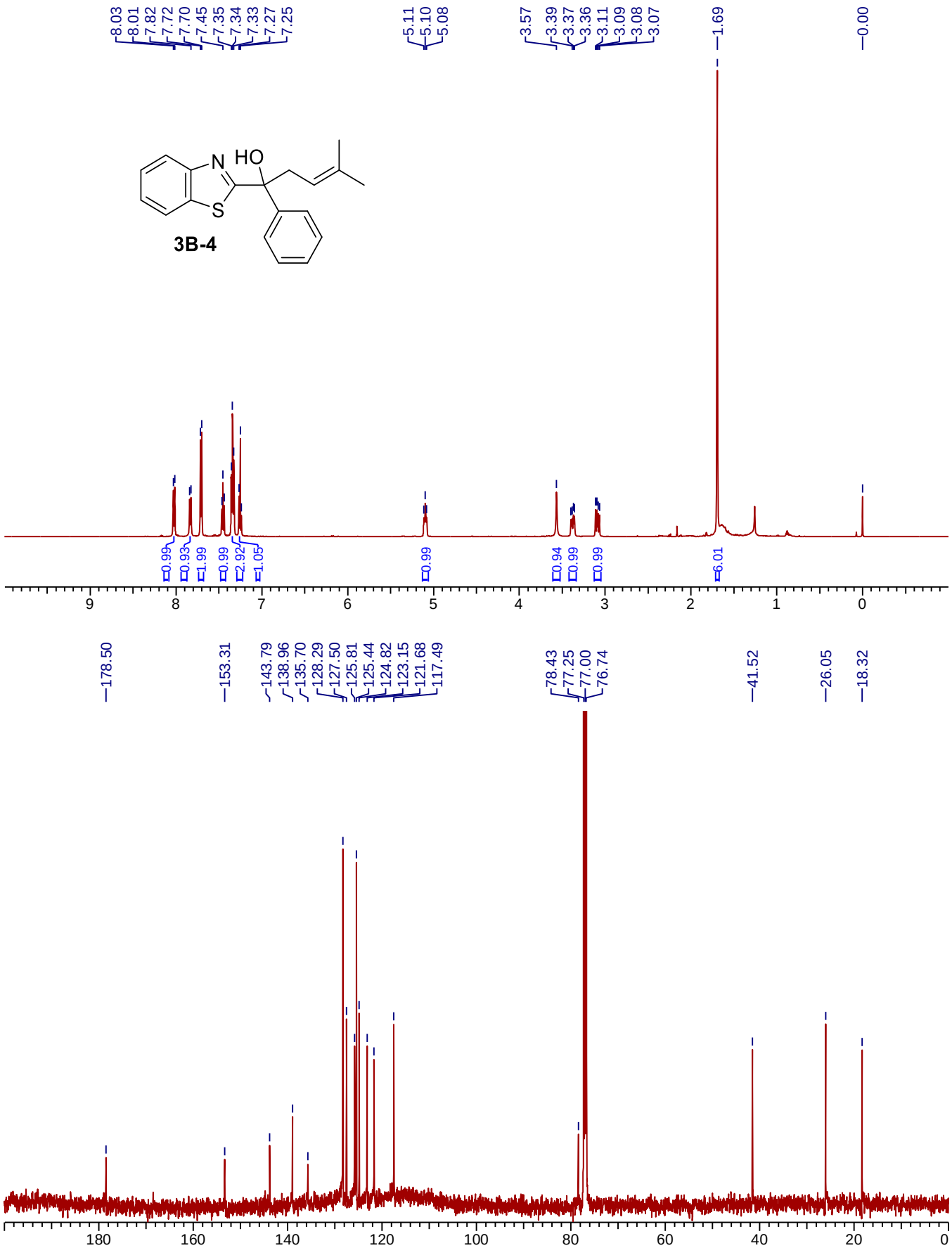
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HO
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3B-4
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0.99
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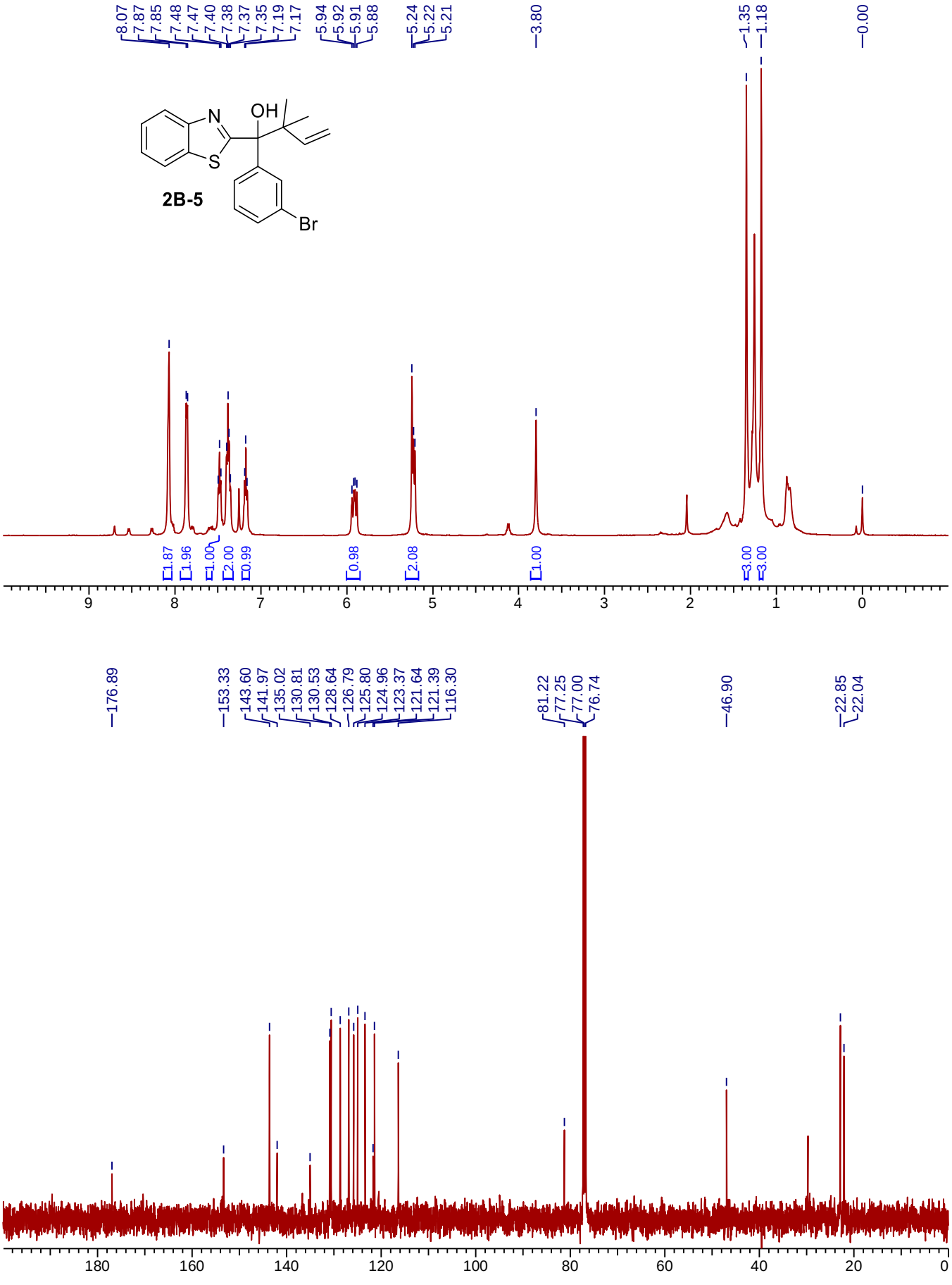
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1.18
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OH
N
S
Br
2B-5
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0.98
2.08
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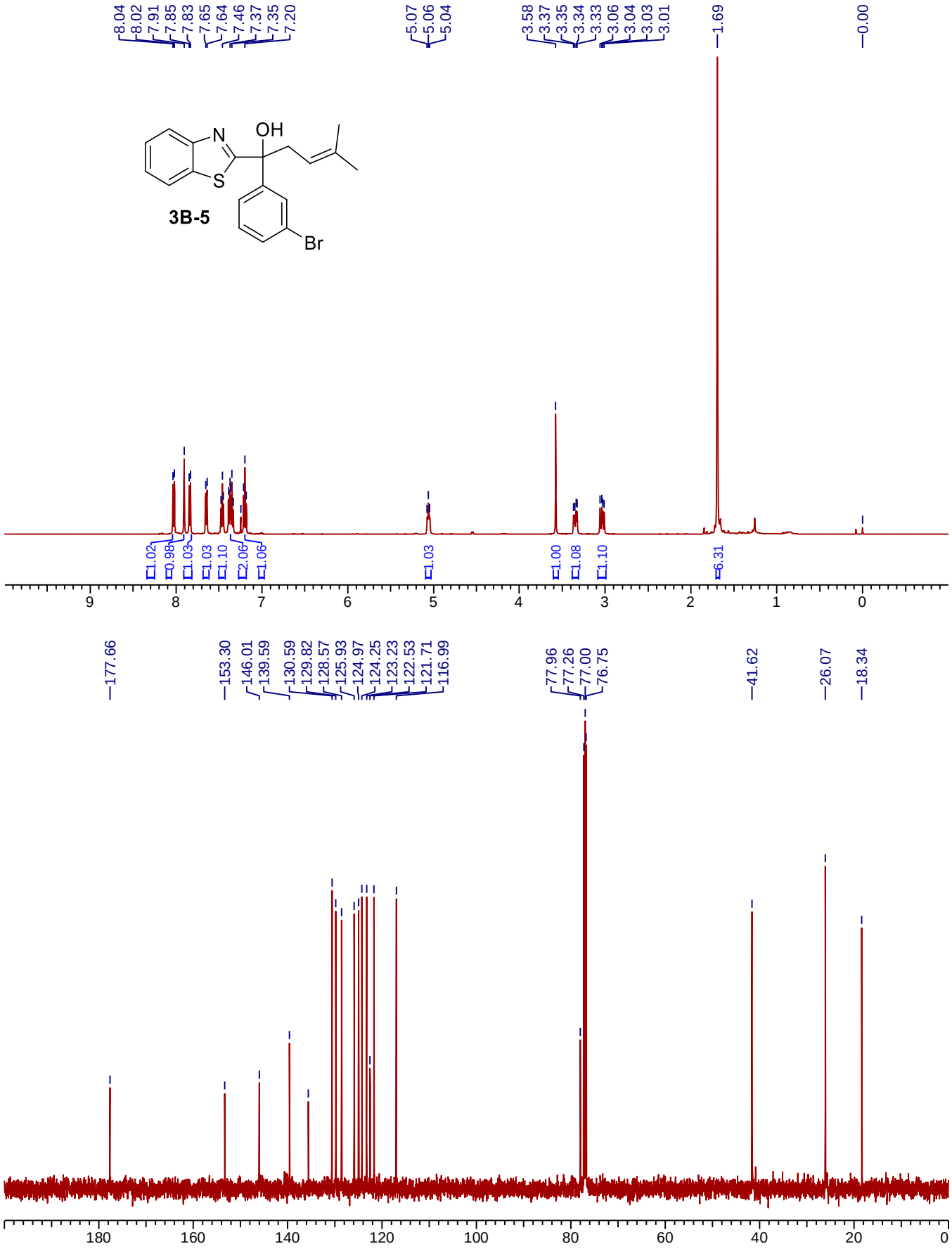
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OH
S
Br
3B-5
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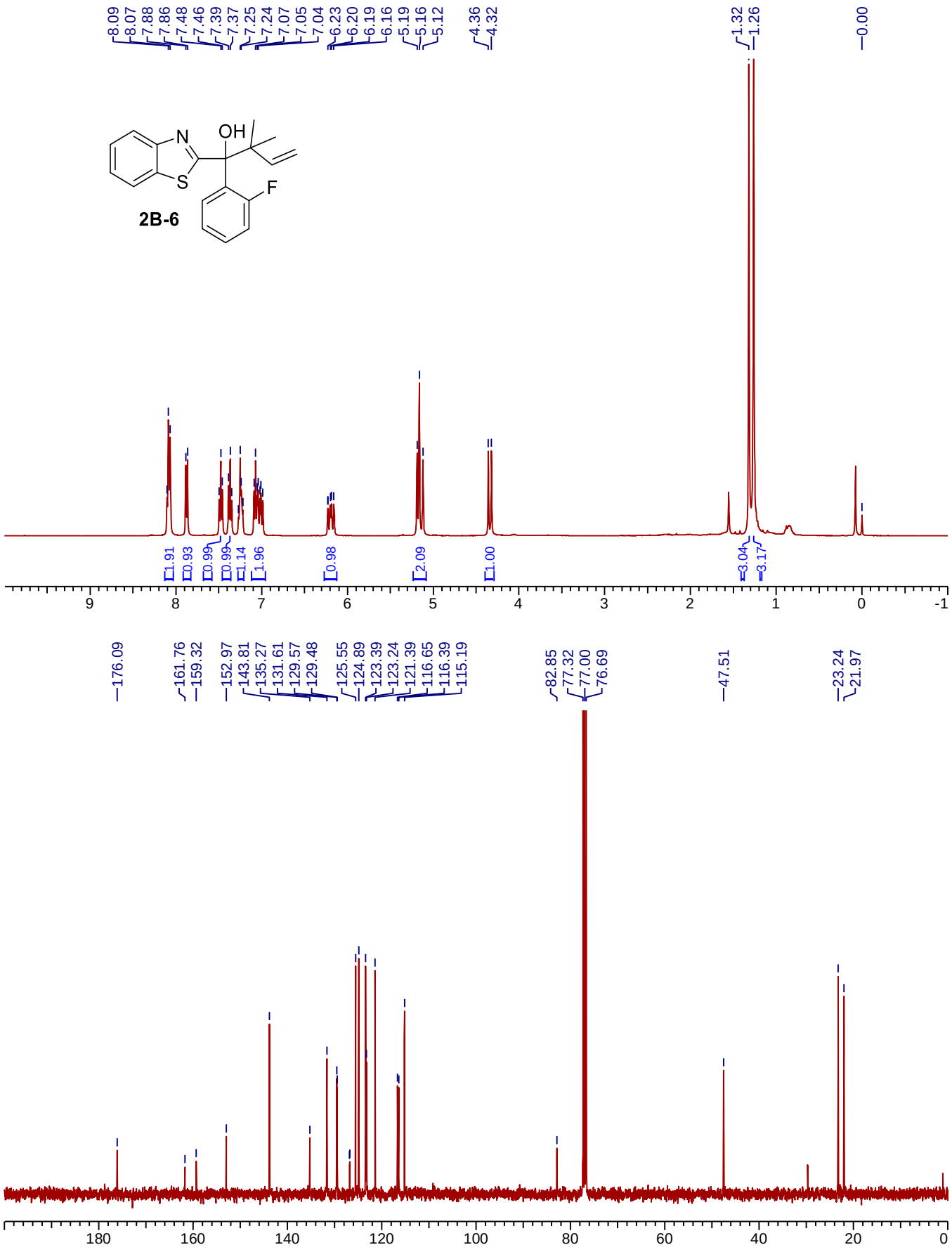
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OH
S
F
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0.99
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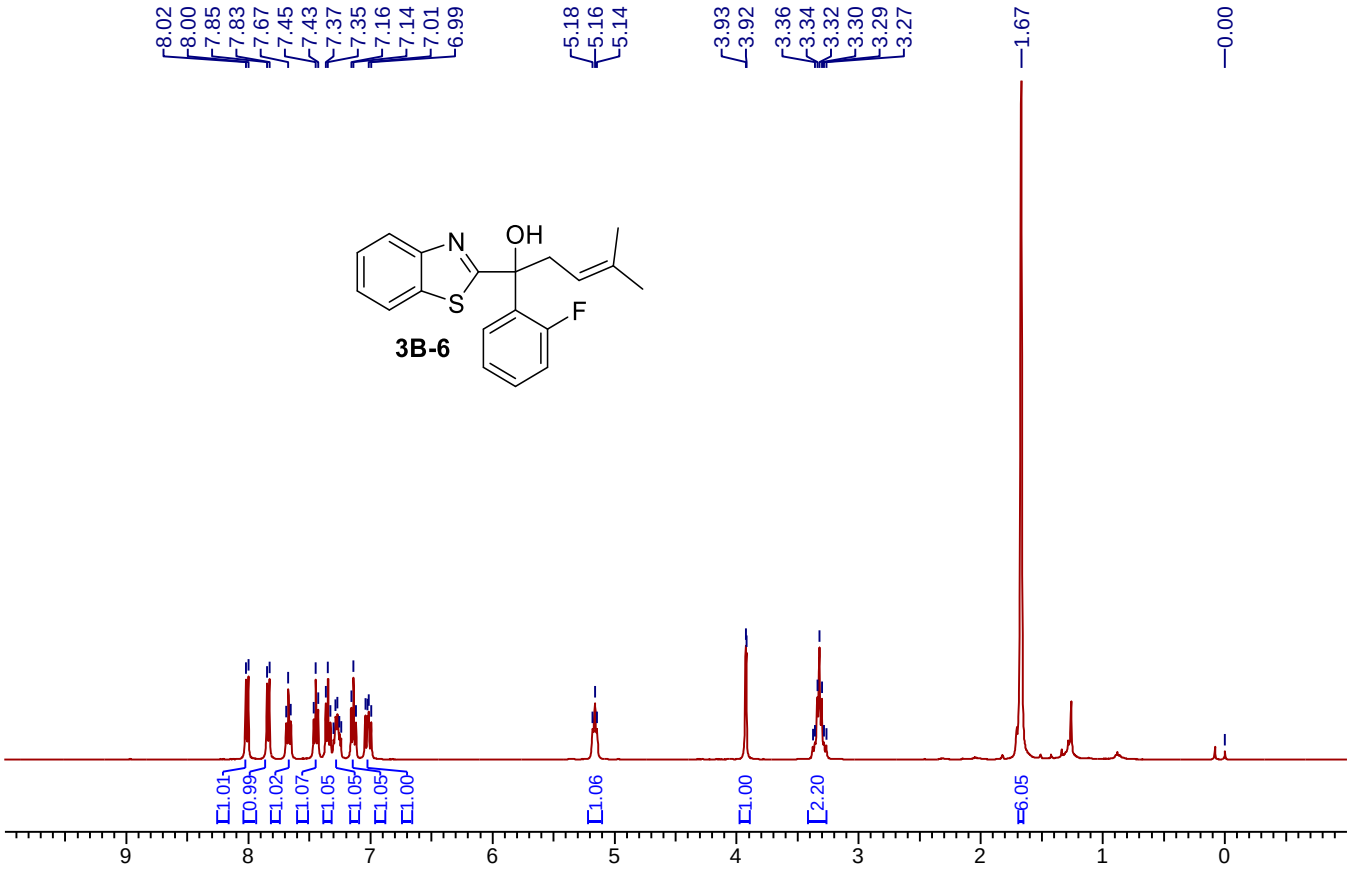
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OH
S
F
3B-6
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1.05
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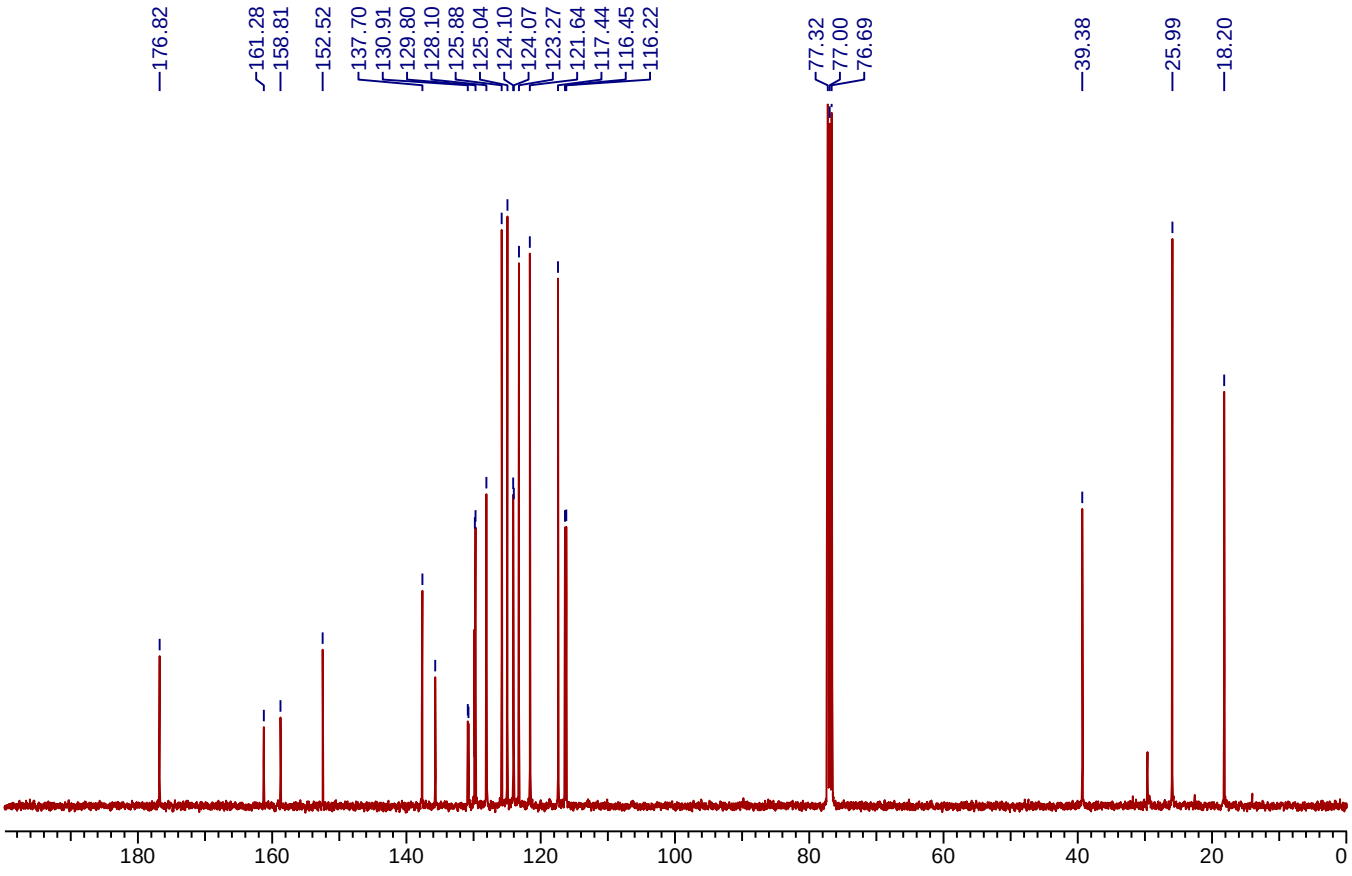
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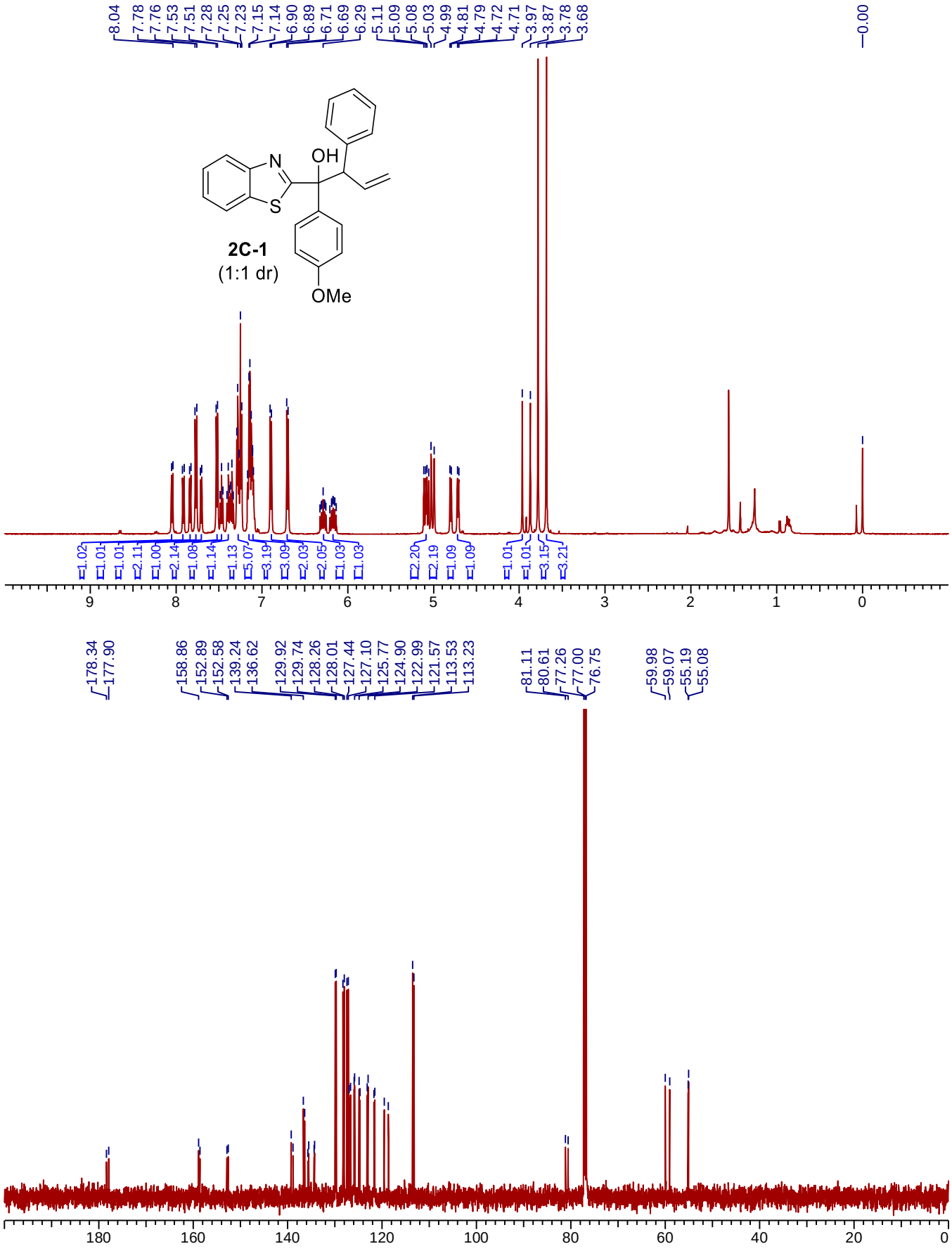
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OH
S
2C-1
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1.01
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1.01
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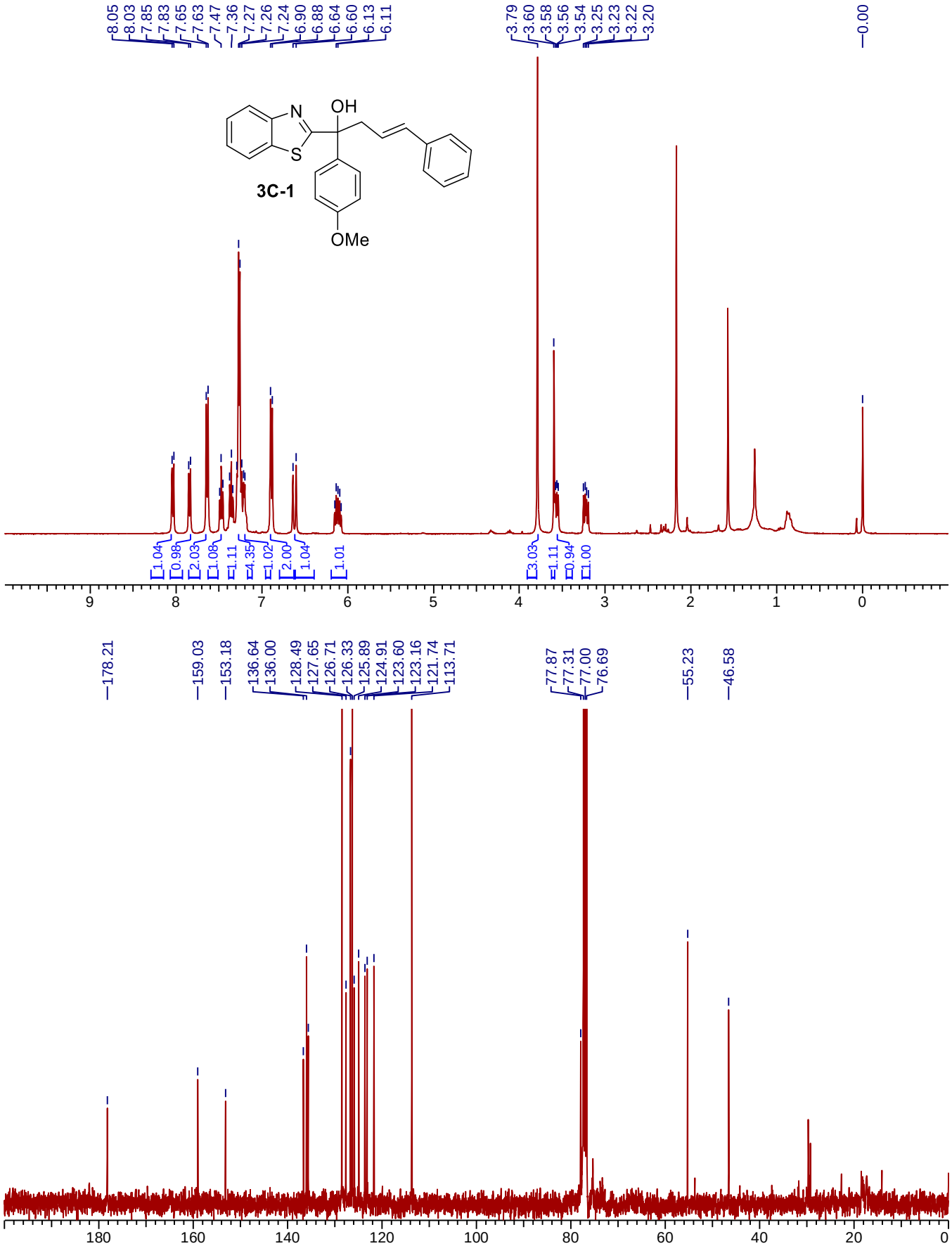
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S
OH
OMe
3C-1
1.04
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1.08
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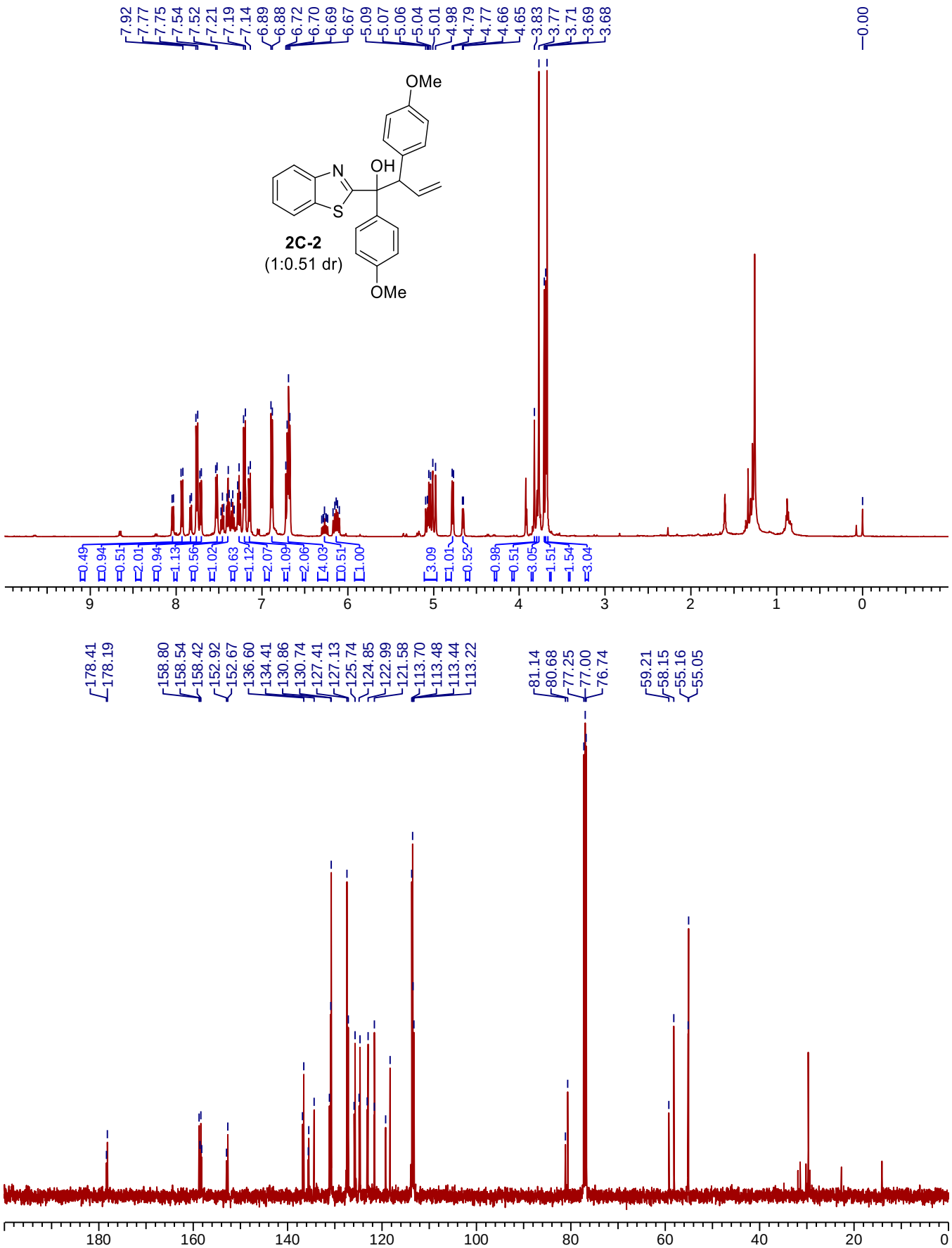
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OMe
OH
N
S
2C-2
(1:0.51 dr)
OMe
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0.94
0.51
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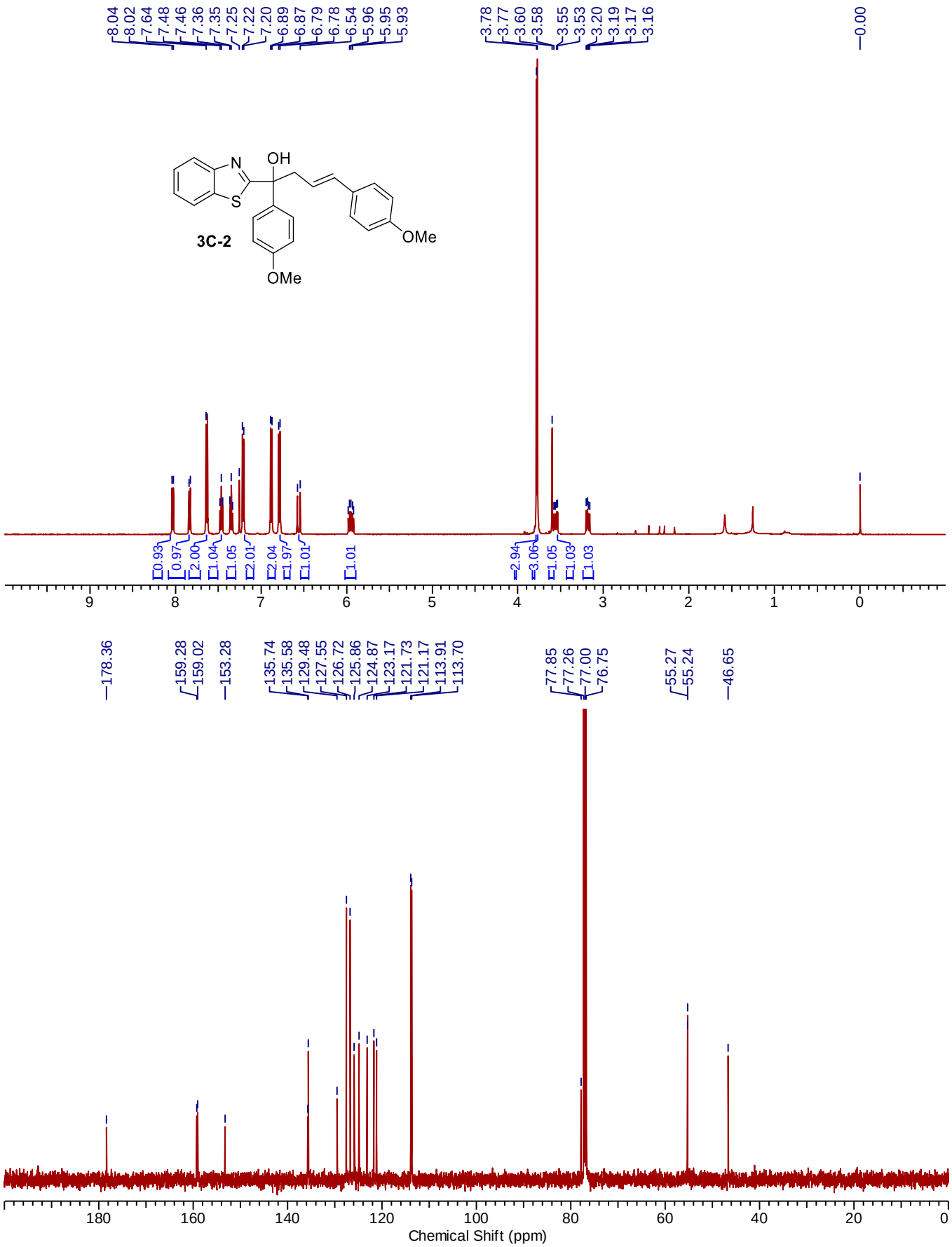
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3.17
3.16
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N
OH
S
OMe
OMe
3C-2
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9
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0
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77.26
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40
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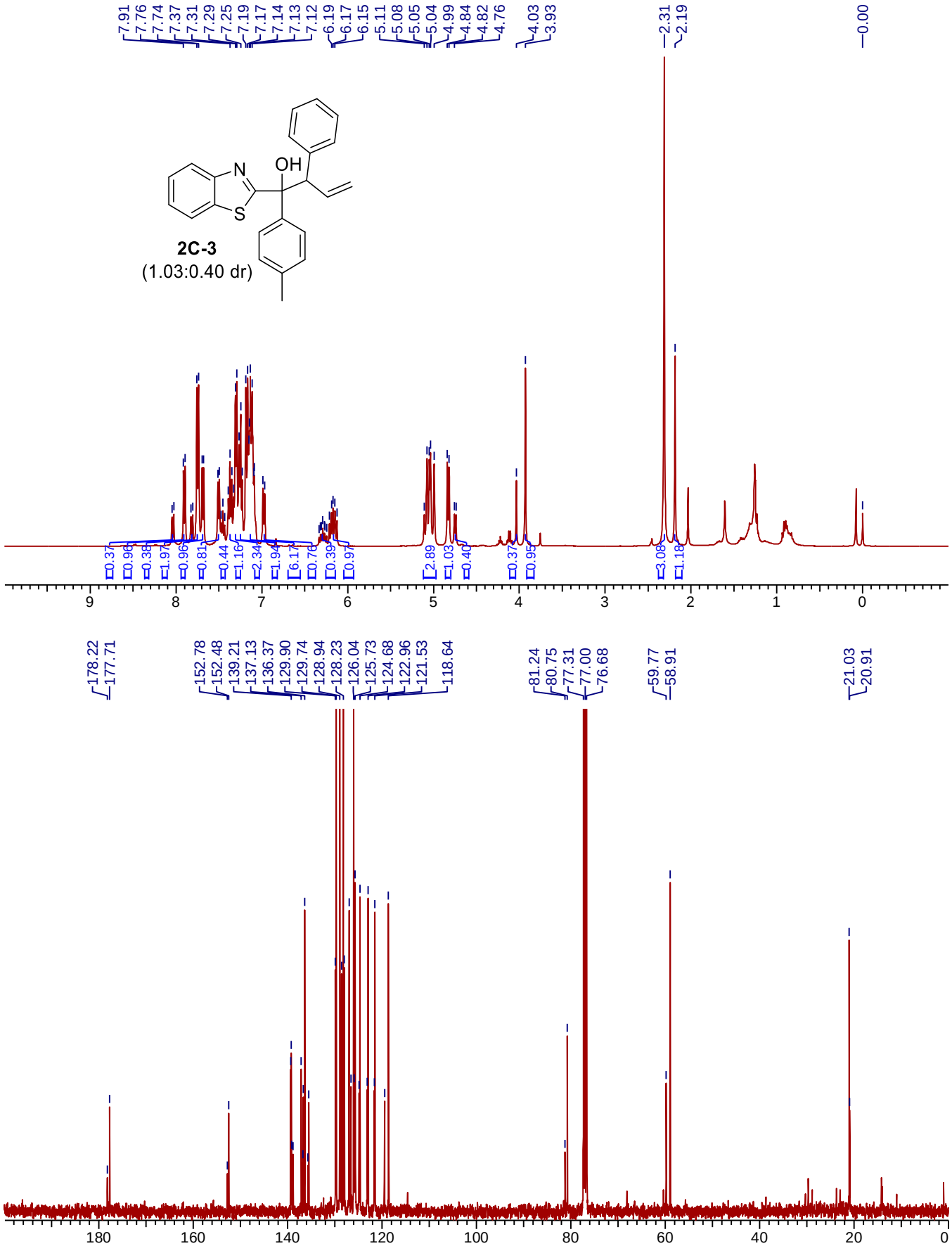
Chemical Shift (ppm)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N
OH
S
2C-3
(1.03:0.40 dr)
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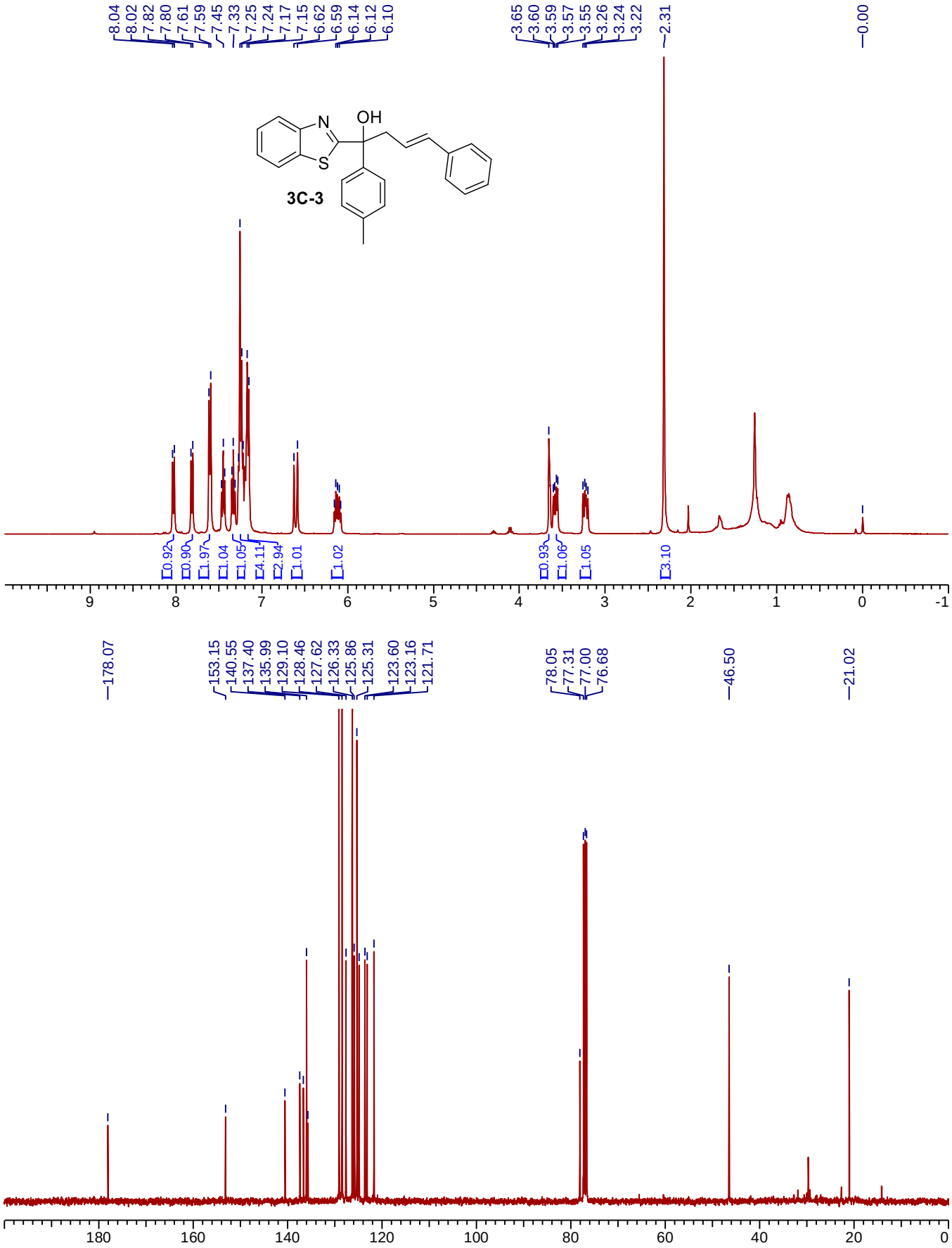
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3.26
3.24
3.22
2.31
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N
OH
S
3C-3
0.92
0.90
1.97
1.04
1.05
4.11
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1.01
1.02
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1.06
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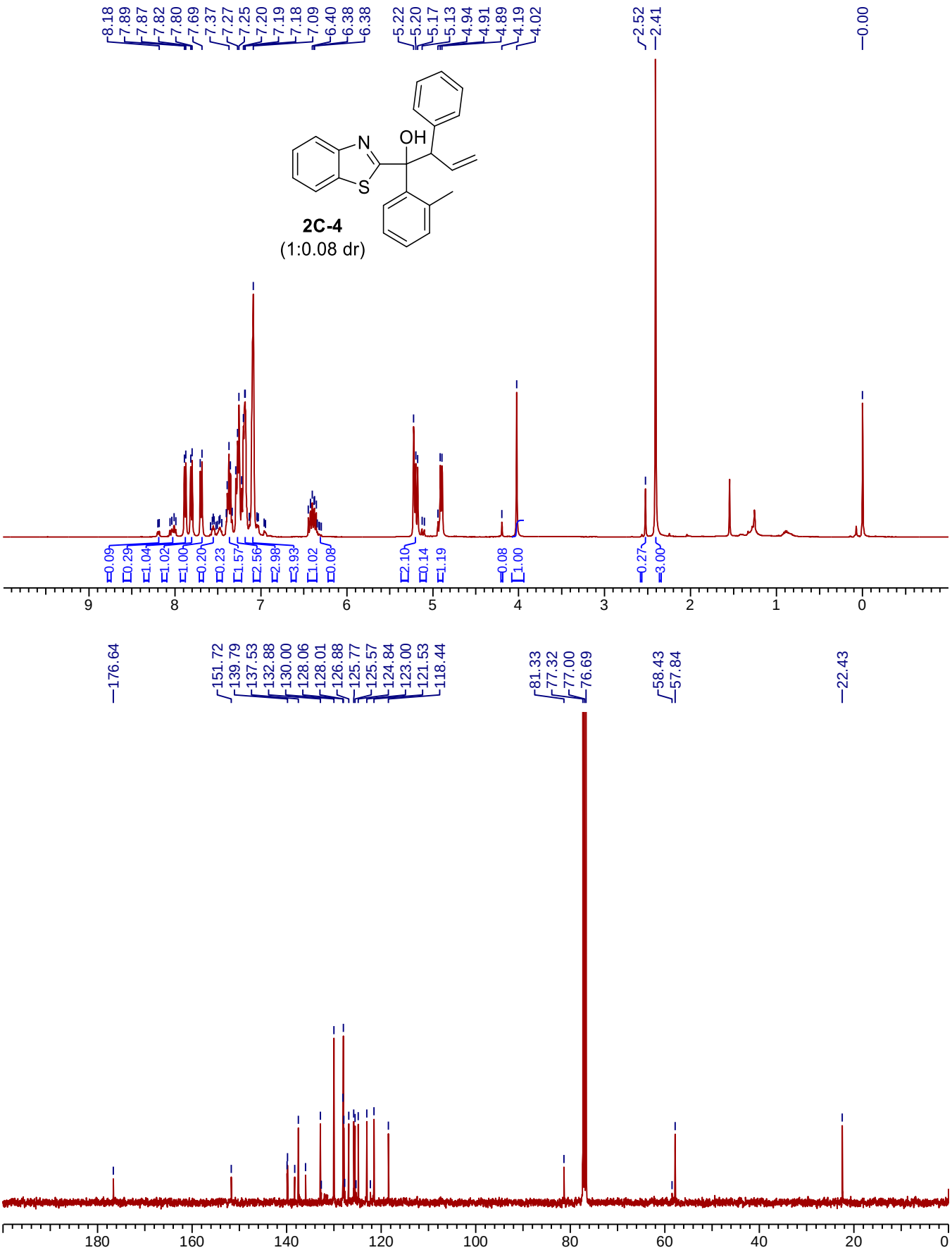
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4.91
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OH
S
2C-4
(1:0.08 dr)
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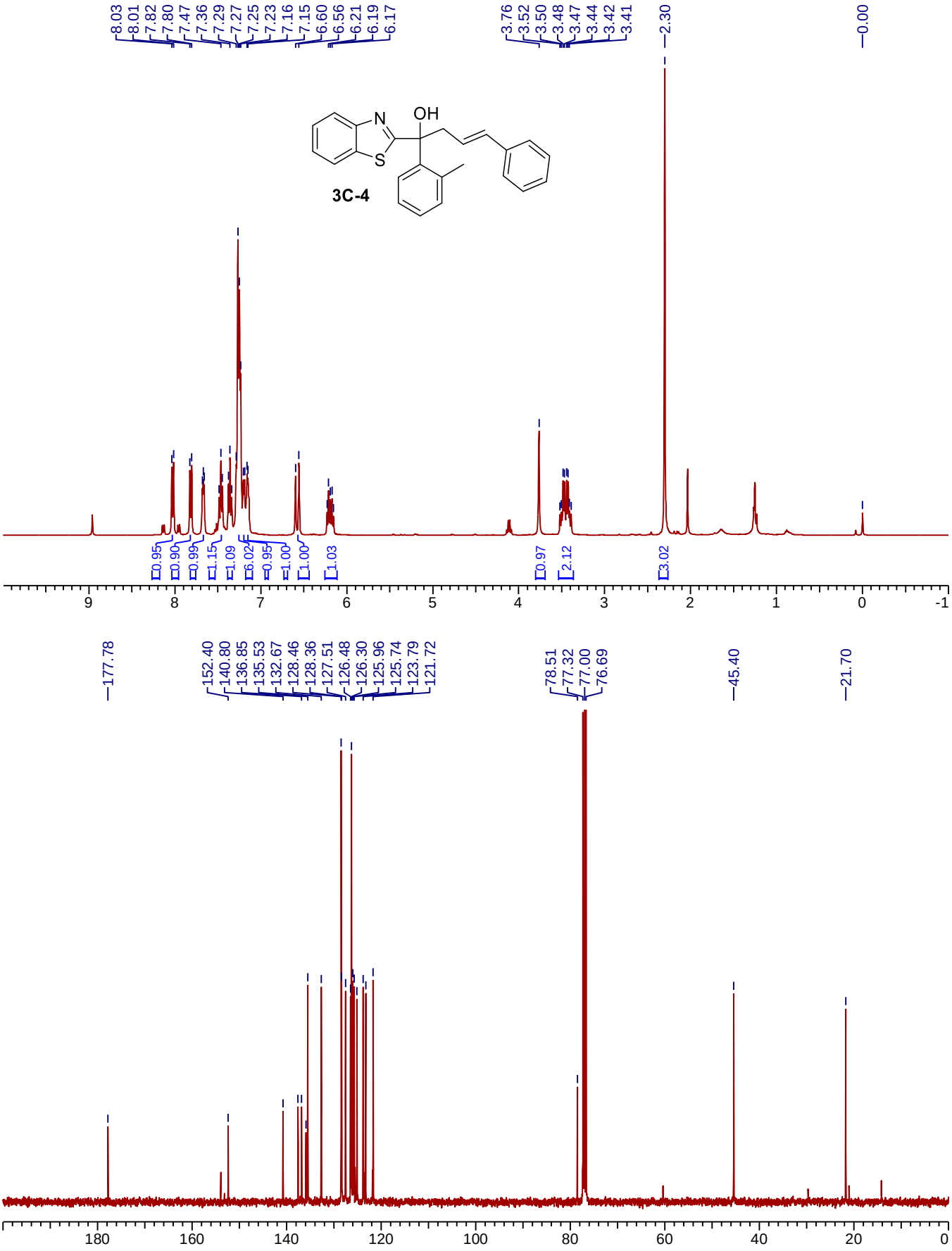
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6.56
6.21
6.19
6.17
3.76
3.52
3.50
3.48
3.47
3.44
3.42
3.41
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OH
S
3C-4
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1.00
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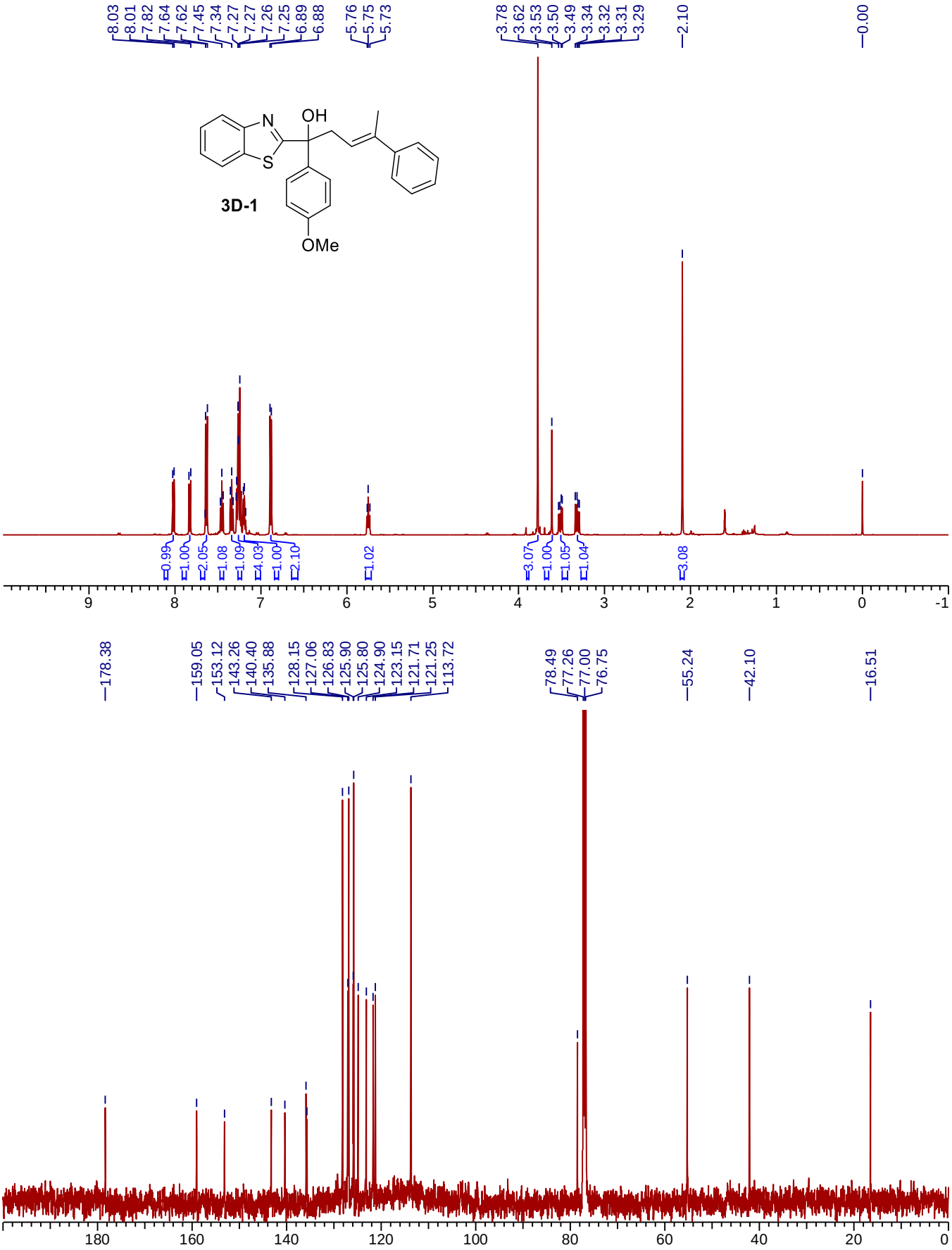
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3.31
3.29
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0.00
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OH
S
3D-1
OMe
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121.25
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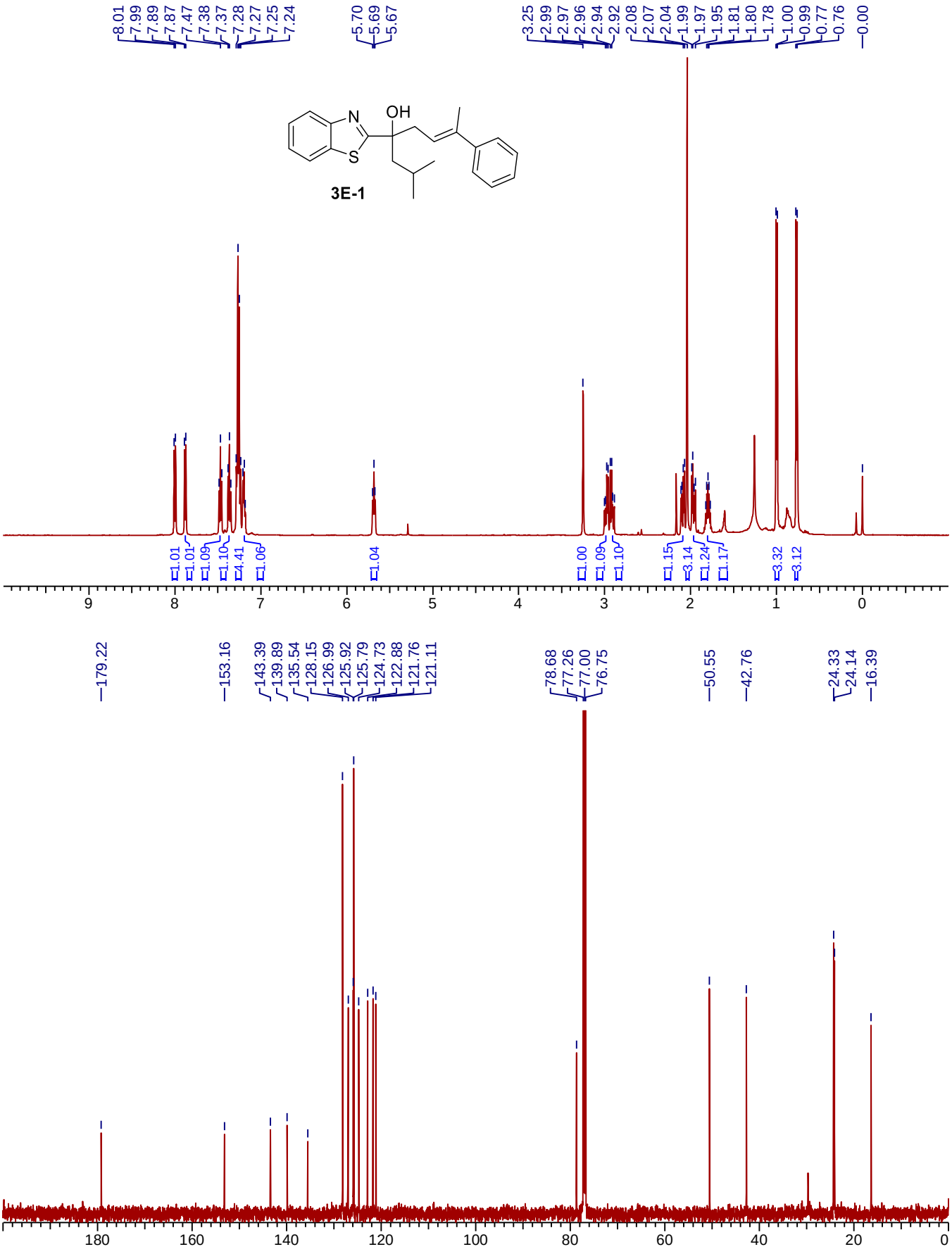
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0.00
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OH
S
3E-1
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1.01
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3.12
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8
7
6
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153.16
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20
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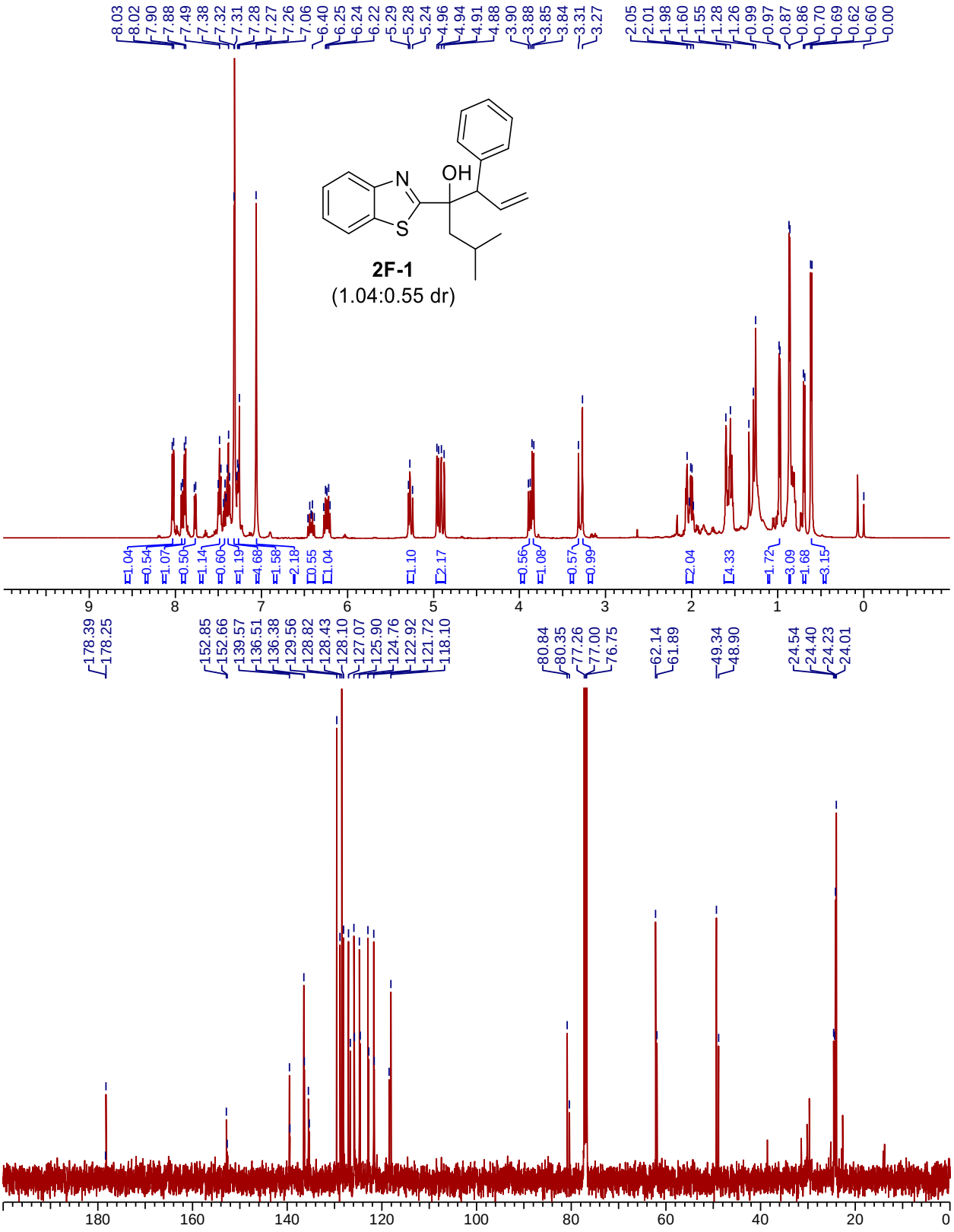
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6.24
6.22
5.29
5.28
5.24
4.96
4.94
4.91
4.88
3.90
3.88
3.85
3.84
3.31
3.27
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2.01
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1.28
1.26
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0.97
0.87
0.86
0.70
0.69
0.62
0.60
0.00
N
OH
S
2F-1
(1.04:0.55 dr)
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0.54
1.07
0.50
1.14
0.60
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4.68
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1.04
1.10
2.17
0.56
1.08
0.57
0.99
2.04
4.33
1.72
3.09
1.68
3.15
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7
6
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4
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2
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0
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178.25
152.85
152.66
139.57
136.51
136.38
129.56
128.82
128.43
128.10
127.07
125.90
124.76
122.92
121.72
118.10
80.84
80.35
77.26
77.00
76.75
62.14
61.89
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24.40
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24.01
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120
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20
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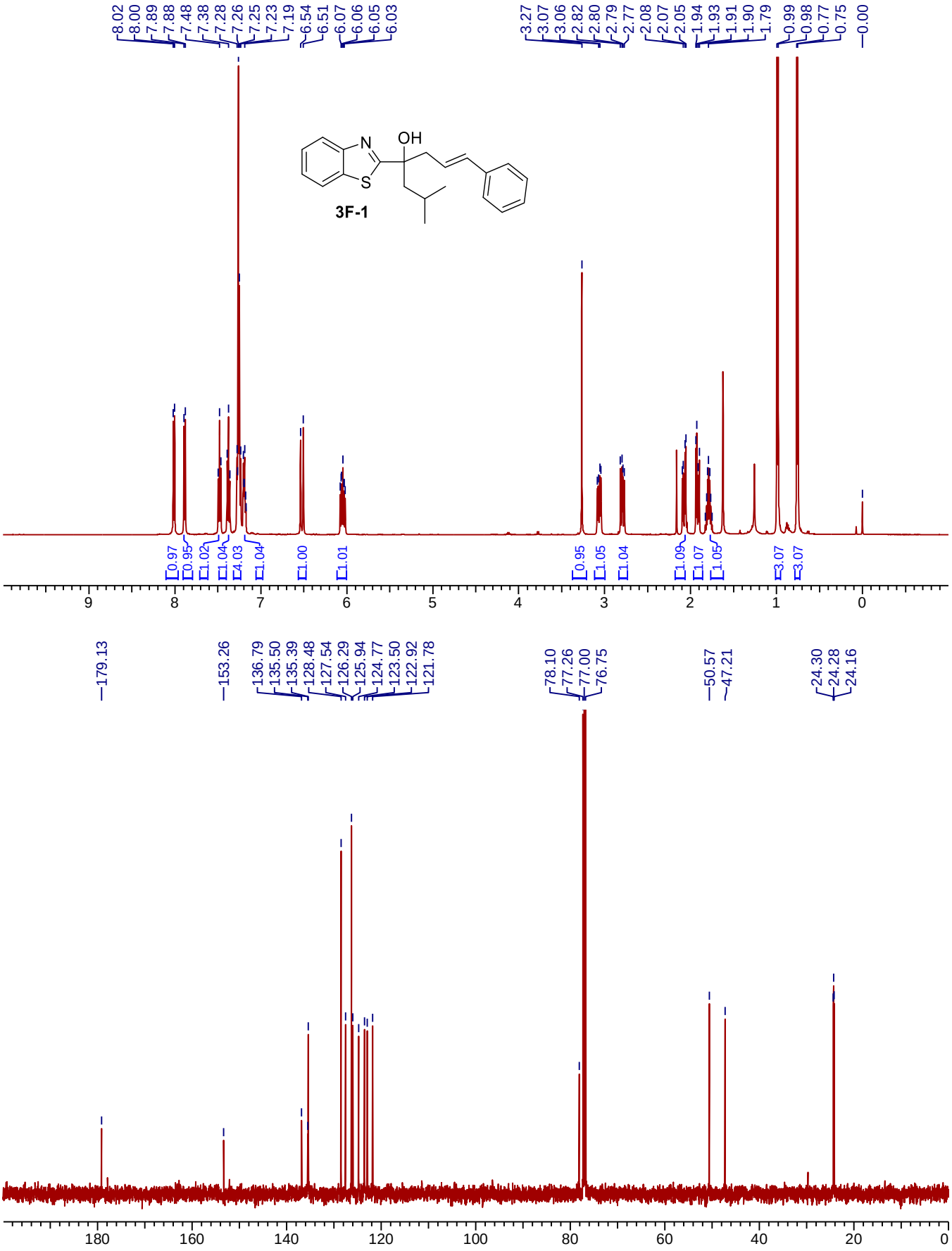
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6.51
6.07
6.06
6.05
6.03
3.27
3.07
3.06
2.82
2.80
2.79
2.77
2.08
2.07
2.05
1.94
1.93
1.91
1.90
1.79
0.99
0.98
0.77
0.75
0.00
N
OH
S
3F-1
0.97
0.95
1.02
1.04
4.03
1.04
1.00
1.01
0.95
1.05
1.04
1.09
1.07
1.05
3.07
3.07
9
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124.77
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77.00
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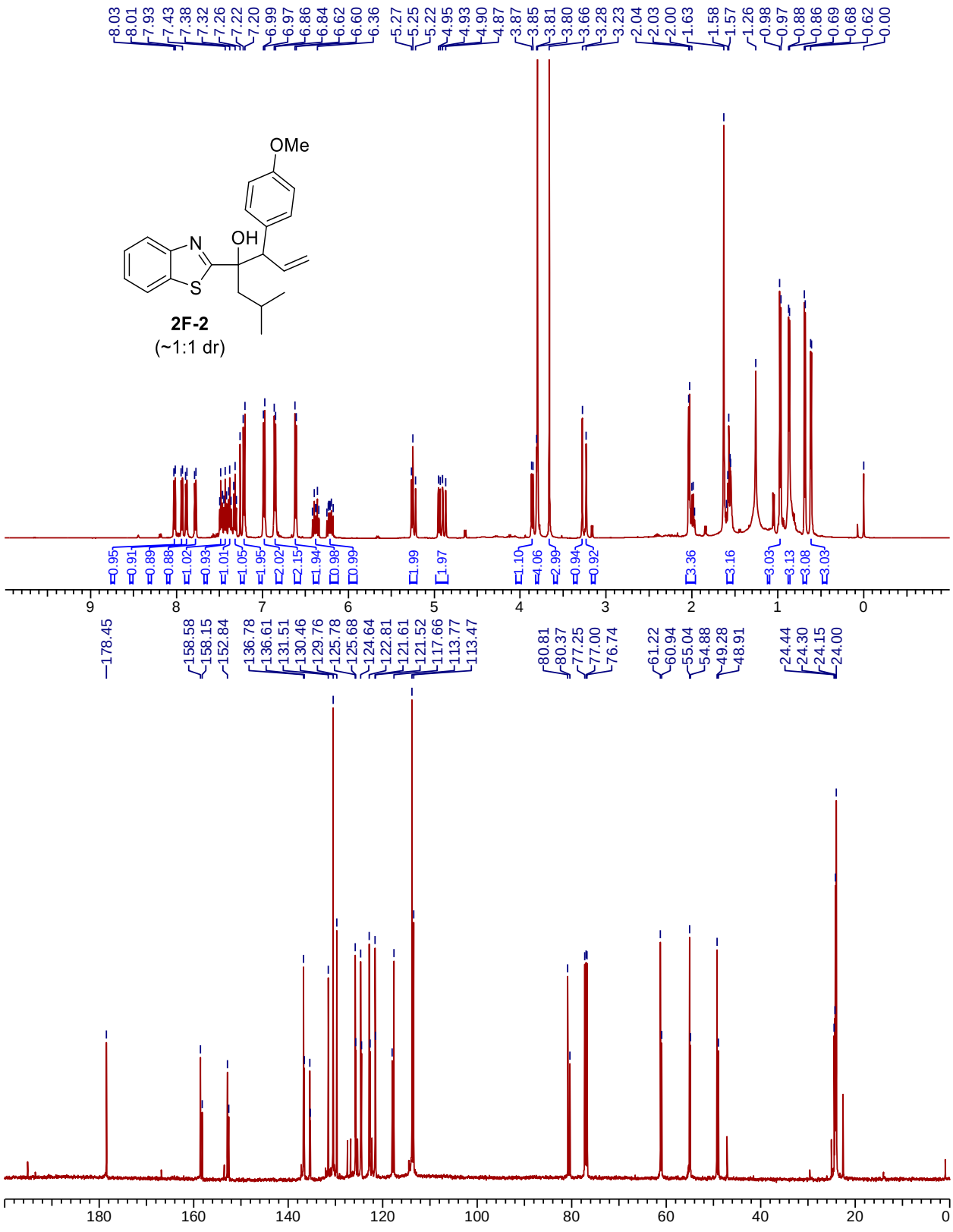
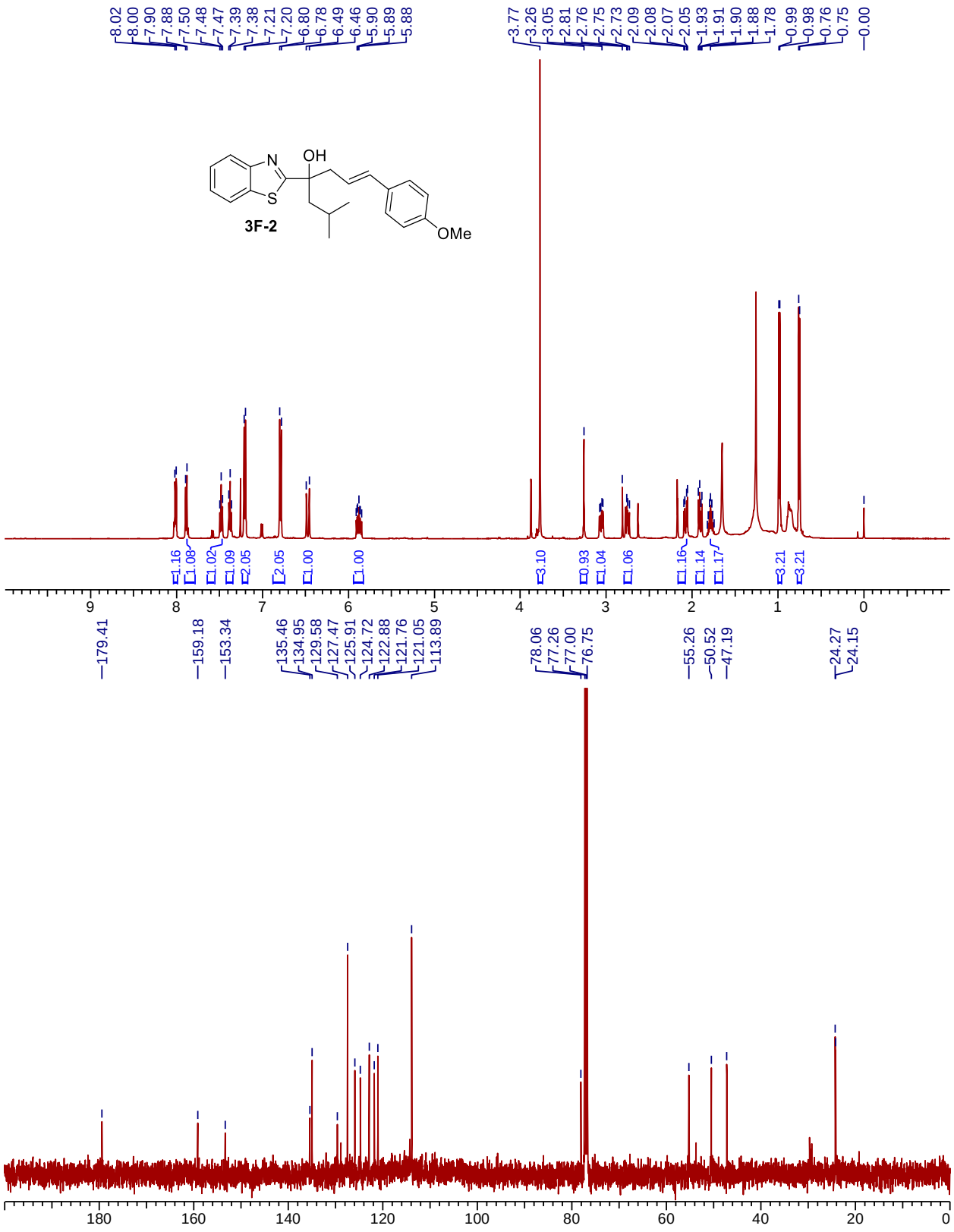

OMe
OH
N
S
2F-2
(~1:1 dr)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5.88
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3.05
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2.76
2.75
2.73
2.09
2.08
2.07
2.05
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1.91
1.90
1.88
1.78
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0.98
0.76
0.75
0.00
N
OH
S
OMe
3F-2
1.16
1.08
1.02
1.09
2.05
2.05
1.00
1.00
3.10
0.93
1.04
1.06
1.16
1.14
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3.21
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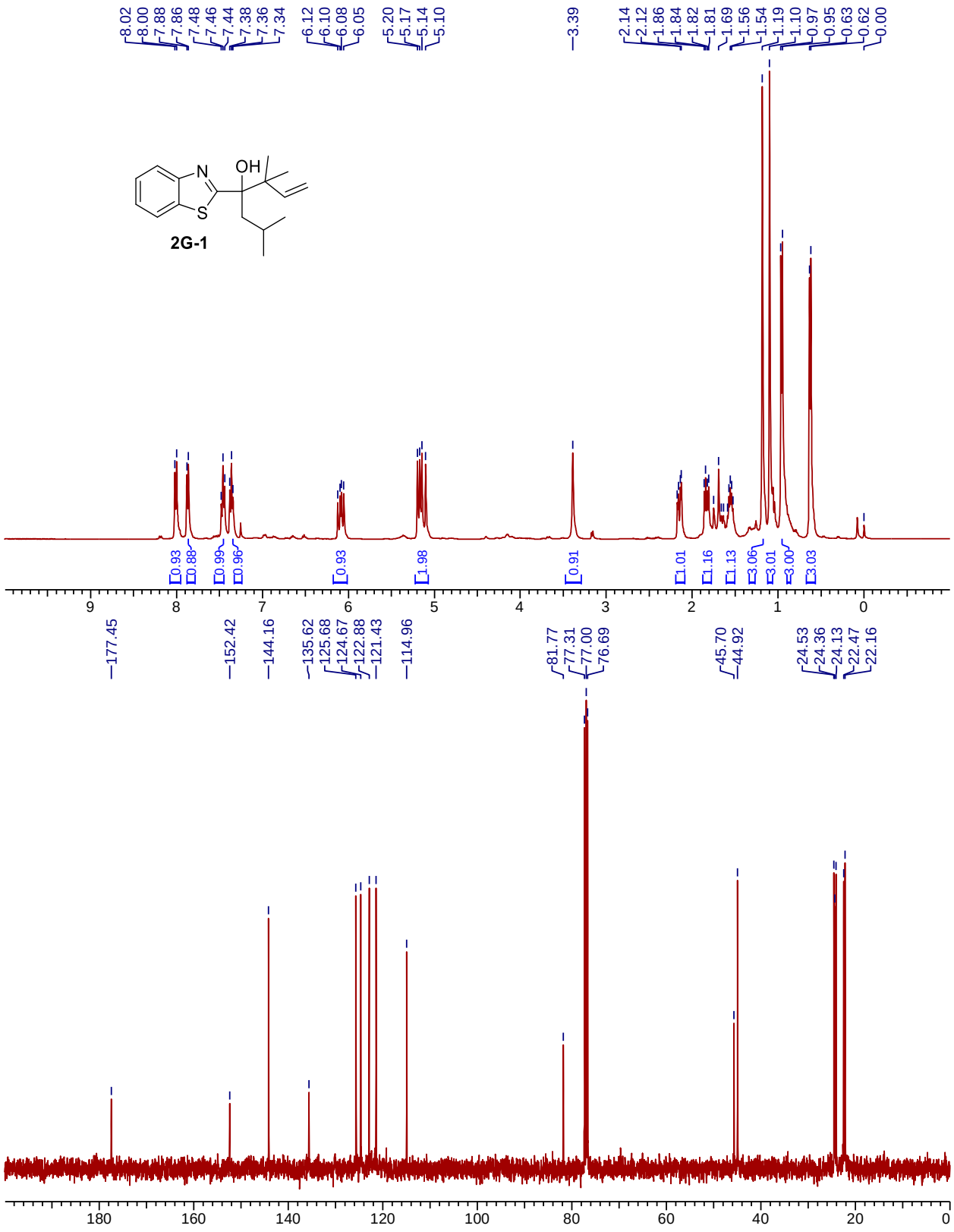
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5.14
5.10
3.39
2.14
2.12
1.86
1.84
1.82
1.81
1.69
1.56
1.54
1.19
1.10
0.97
0.95
0.63
0.62
0.00
N
OH
S
2G-1
0.93
0.88
0.99
0.96
0.93
1.98
0.91
1.01
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1.13
3.06
3.01
3.00
3.03
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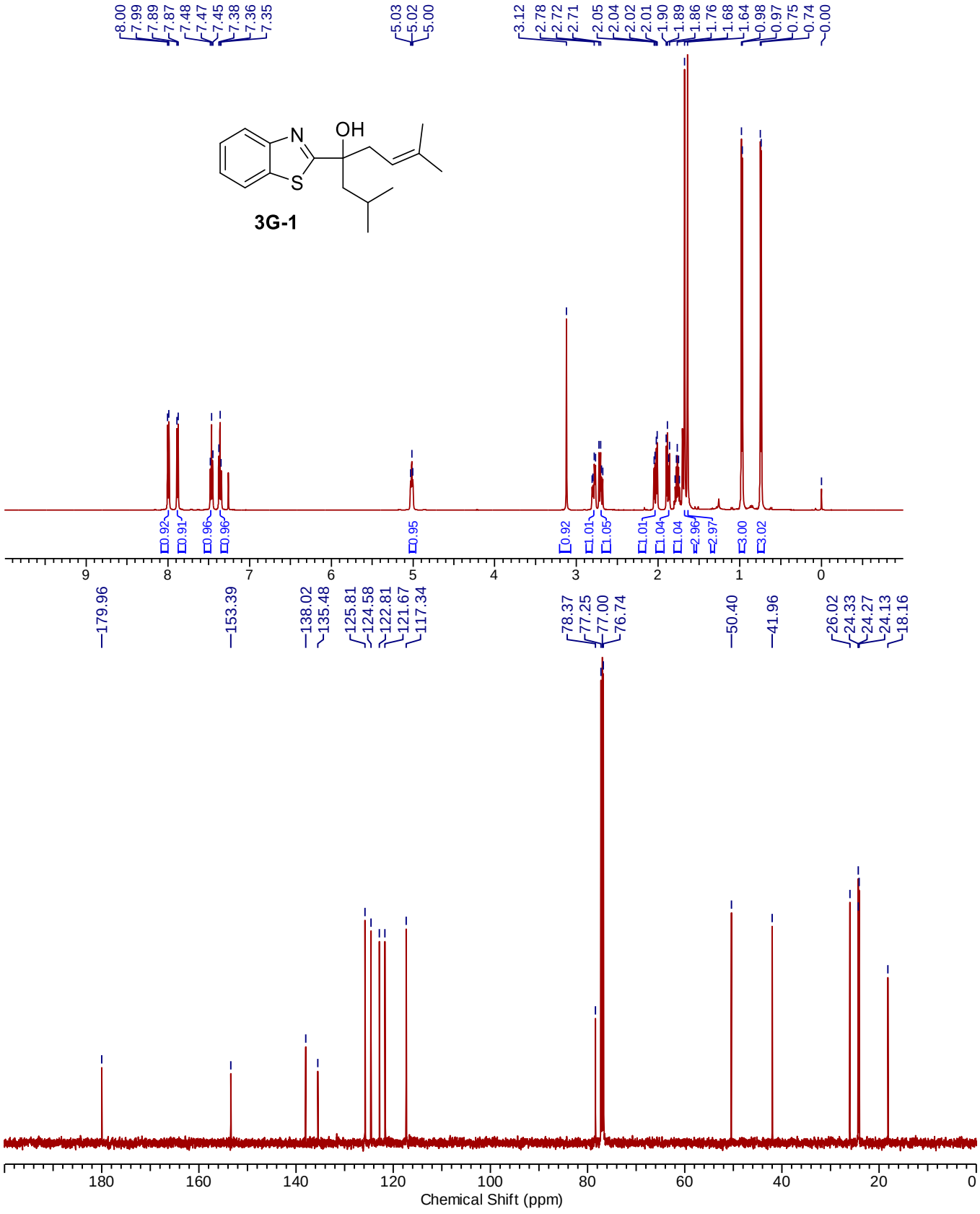
22.16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5.03
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3.12
2.78
2.72
2.71
2.05
2.04
2.02
2.01
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1.89
1.86
1.76
1.68
1.64
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0.97
0.75
0.74
0.00
N
OH
S
3G-1
0.92
0.91
0.96
0.96
0.95
0.92
1.01
1.05
1.01
1.04
1.04
2.96
2.97
3.00
3.02
9
8
7
6
5
4
3
2
1
0
179.96
153.39
138.02
135.48
125.81
124.58
122.81
121.67
117.34
78.37
77.25
77.00
76.74
50.40
41.96
26.02
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24.13
18.16
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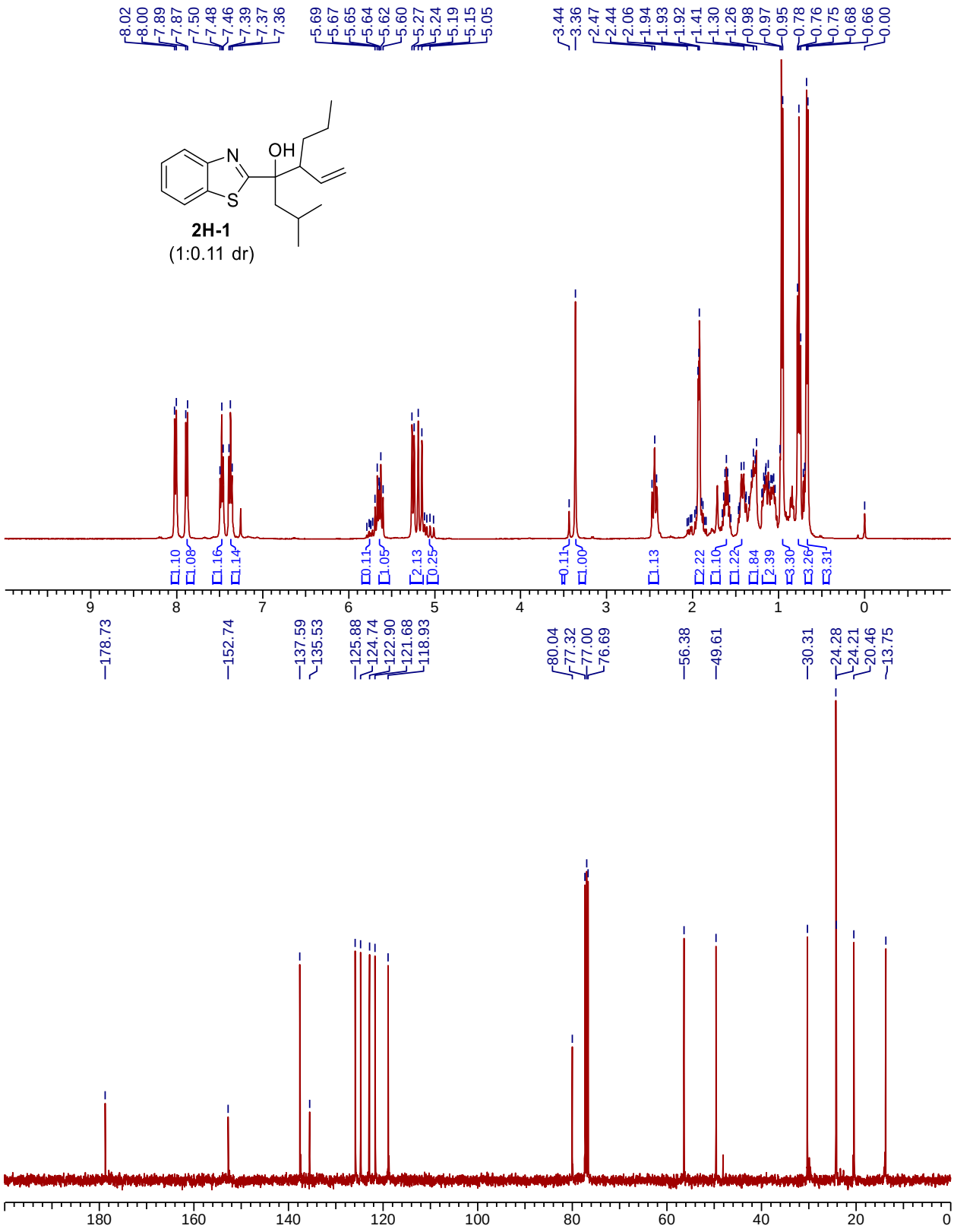
100
80
60
40
20
0
Chemical Shift (ppm)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7.36
5.69
5.67
5.65
5.64
5.62
5.60
5.27
5.24
5.19
5.15
5.05
3.44
3.36
2.47
2.44
2.06
1.94
1.93
1.92
1.41
1.30
1.26
0.98
0.97
0.95
0.78
0.76
0.75
0.68
0.66
0.00
N
OH
S
2H-1
(1:0.11 dr)
1.10
1.08
1.16
1.14
0.11
1.05
2.13
0.25
0.11
1.00
1.13
2.22
1.10
1.22
1.84
2.39
3.30
3.26
3.31
178.73
152.74
137.59
135.53
125.88
124.74
122.90
121.68
118.93
80.04
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77.00
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56.38
49.61
30.31
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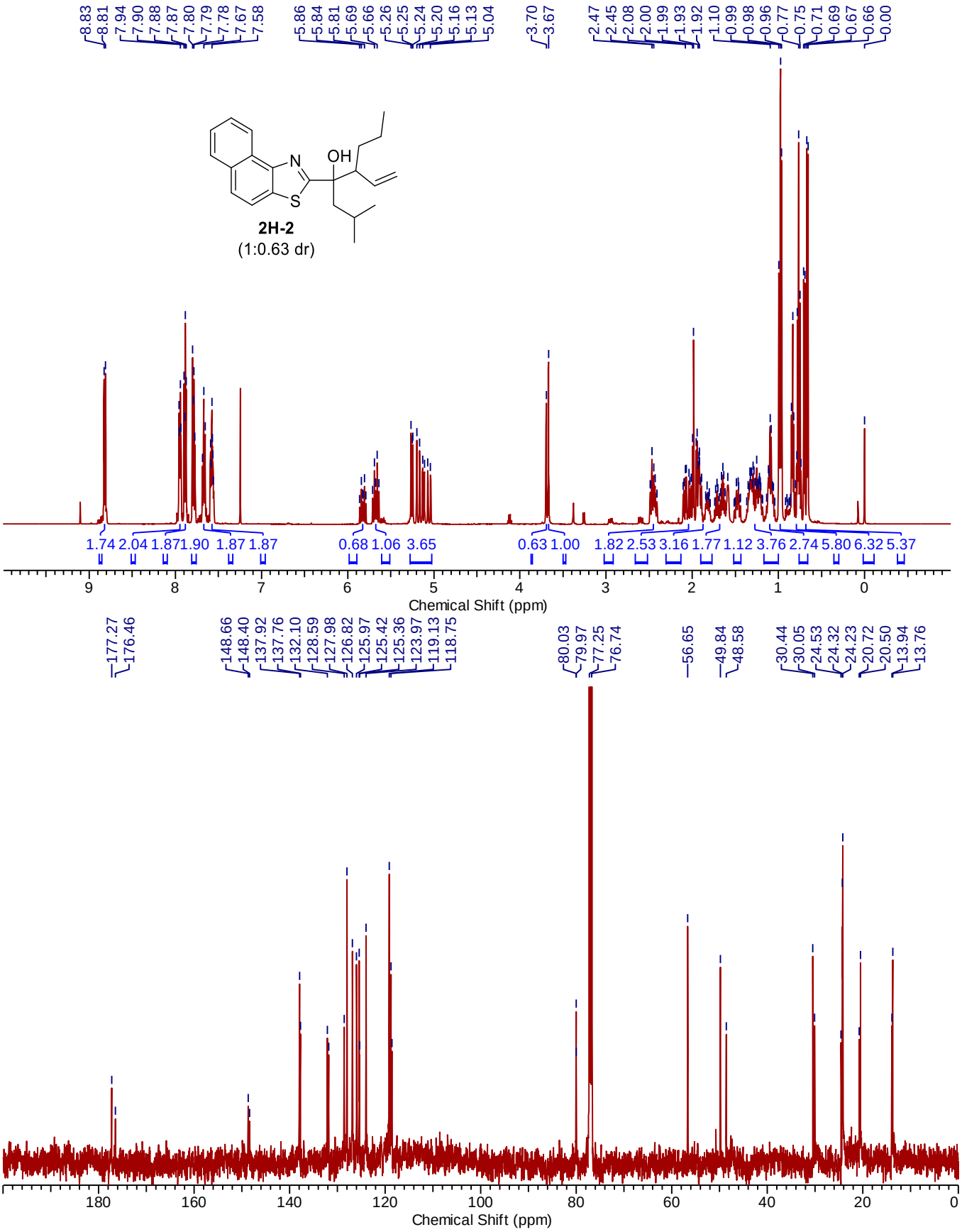
20.46
13.75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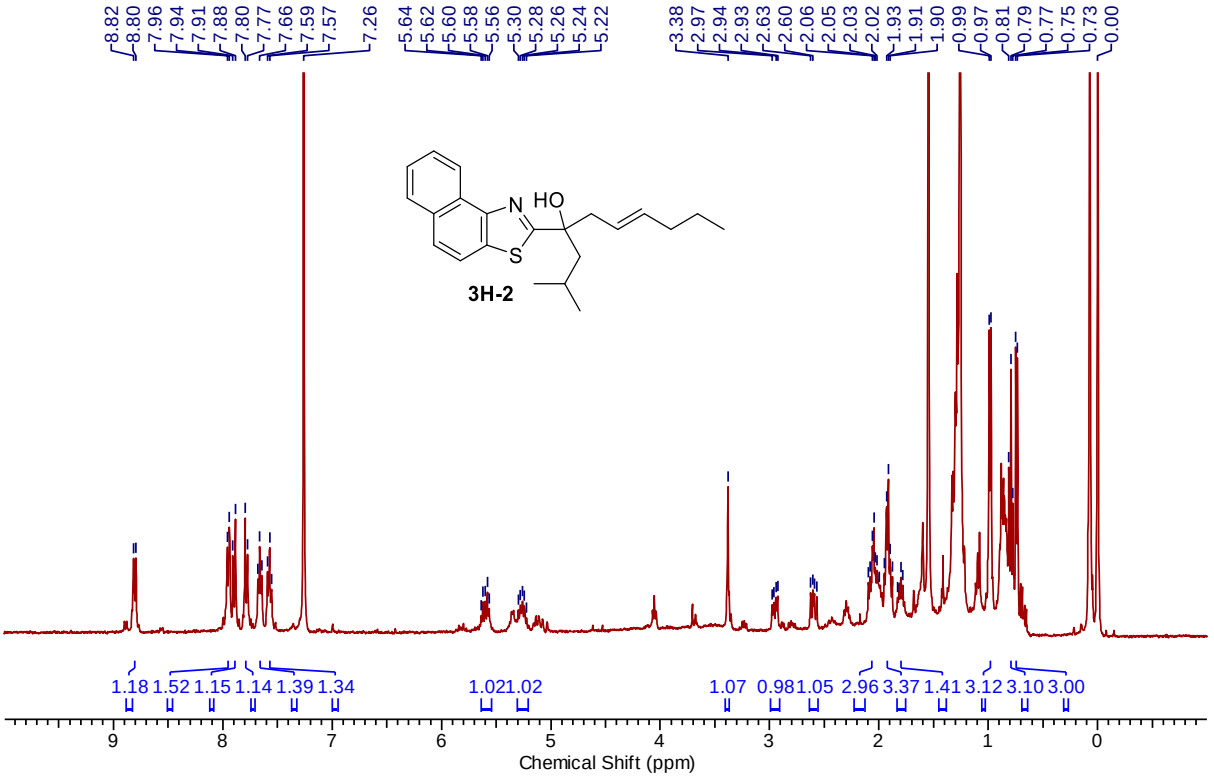
5.86 5.84 5.81 5.69 5.66 5.26 5.25 5.24 5.20 5.16 5.13 5.04
3.70 3.67
2.47 2.45 2.08 2.00 1.99 1.93 1.92 1.10 0.99 0.98 0.96 0.77 0.75 0.71 0.69 0.67 0.66 0.00
N
OH
S
2H-2
(1:0.63 dr)
1.74 2.04 1.87 1.90 1.87 1.87 0.68 1.06 3.65 0.63 1.00 1.82 2.53 3.16 1.77 1.12 3.76 2.74 5.80 6.32 5.37
9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)
177.27 176.46 148.66 148.40 137.92 137.76 132.10 128.59 127.98 126.82 125.97 125.42 125.36 123.97 119.13 118.75
80.03 79.97 77.25 76.74 56.65 49.84 48.58 30.44 30.05 24.53 24.32 24.23 20.72 20.50 13.94 13.76
180 160 140 120 100 80 60 40 20 0
Chemical Shift (ppm)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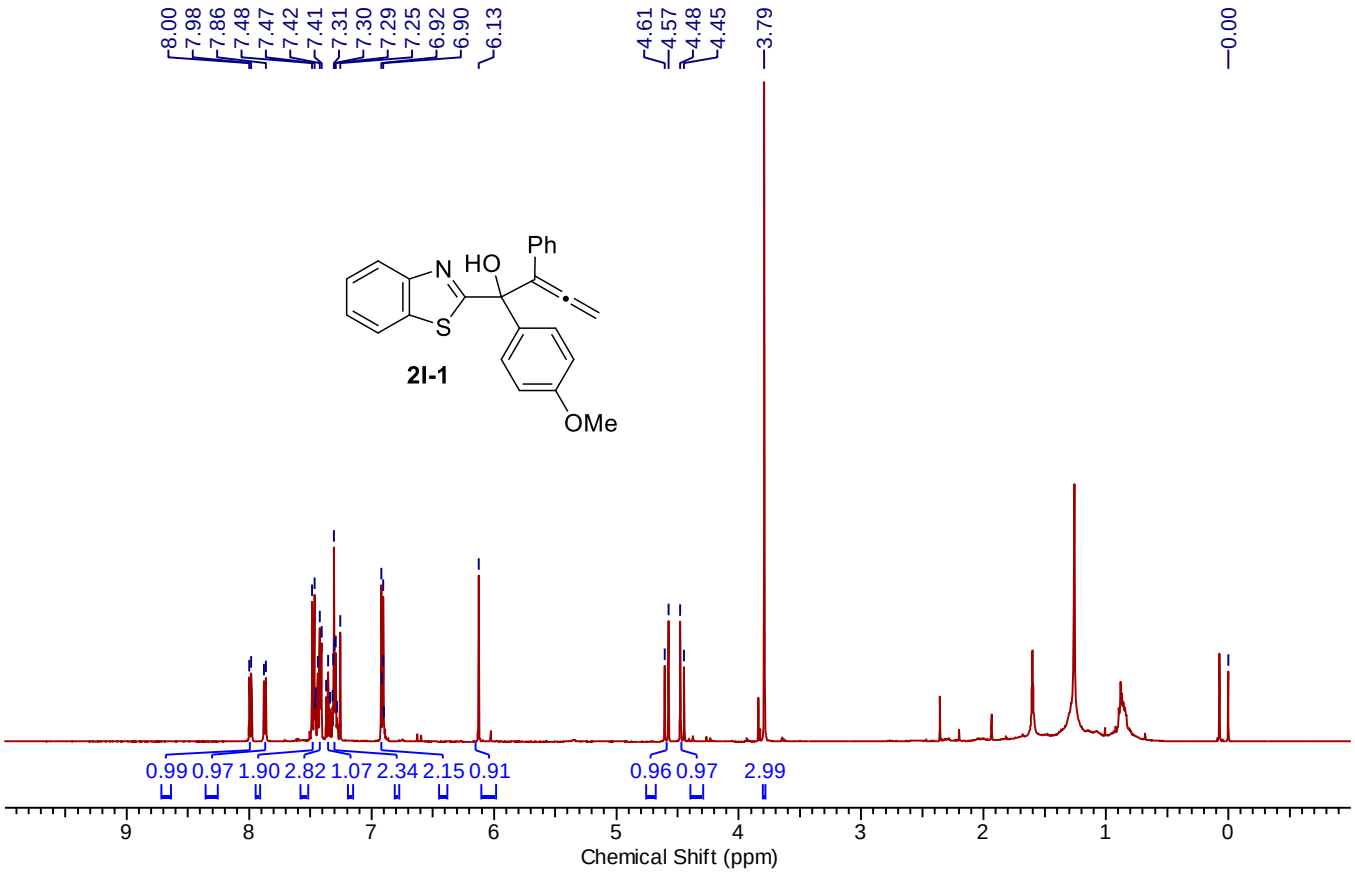
N HO S
3H-2
1.18 1.52 1.15 1.14 1.39 1.34 1.02 1.02 1.07 0.98 1.05 2.96 3.37 1.41 3.12 3.10 3.00
9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)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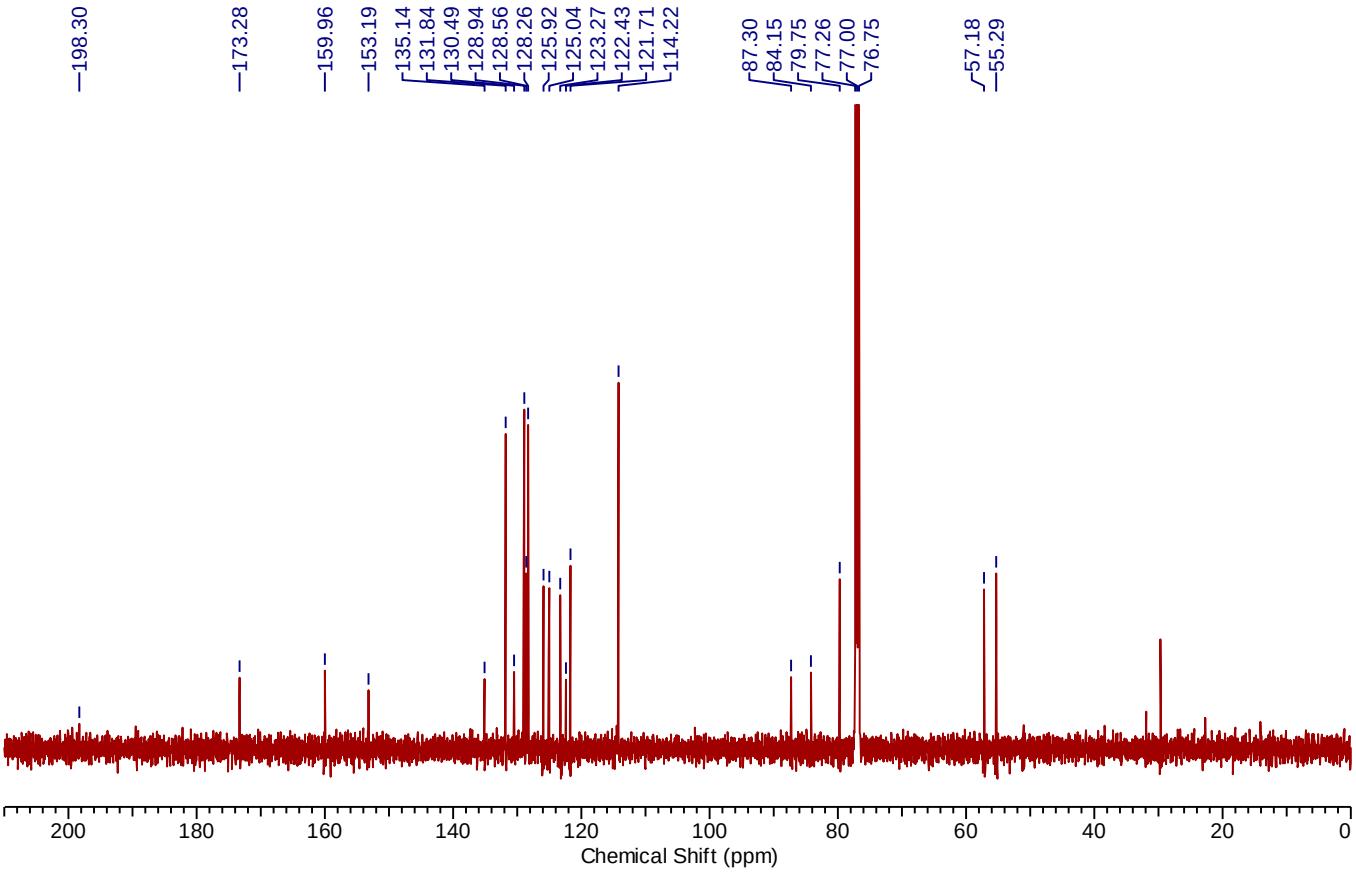
N HO Ph S
2I-1
OMe
0.99 0.97 1.90 2.82 1.07 2.34 2.15 0.91 0.96 0.97 2.99
9 8 7 6 5 4 3 2 1 0
Chemical Shift (ppm)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128.94
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128.26
125.92
125.04
123.27
122.43
121.71
114.22
87.30
84.15
79.75
77.26
77.00
76.75
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55.29
200
180
160
140
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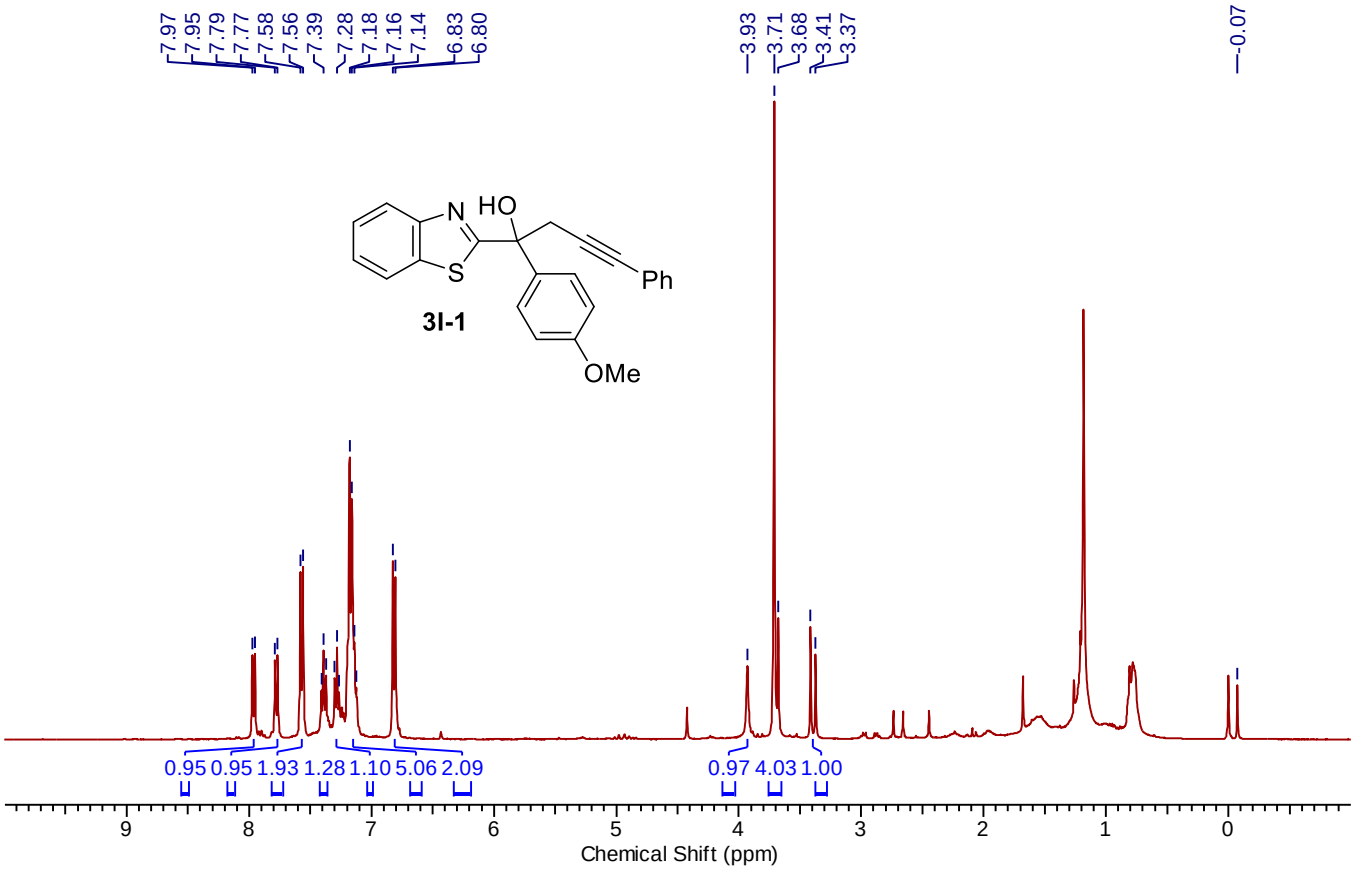
100
80
60
40
20
0
Chemical Shift (ppm)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7.95
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7.39
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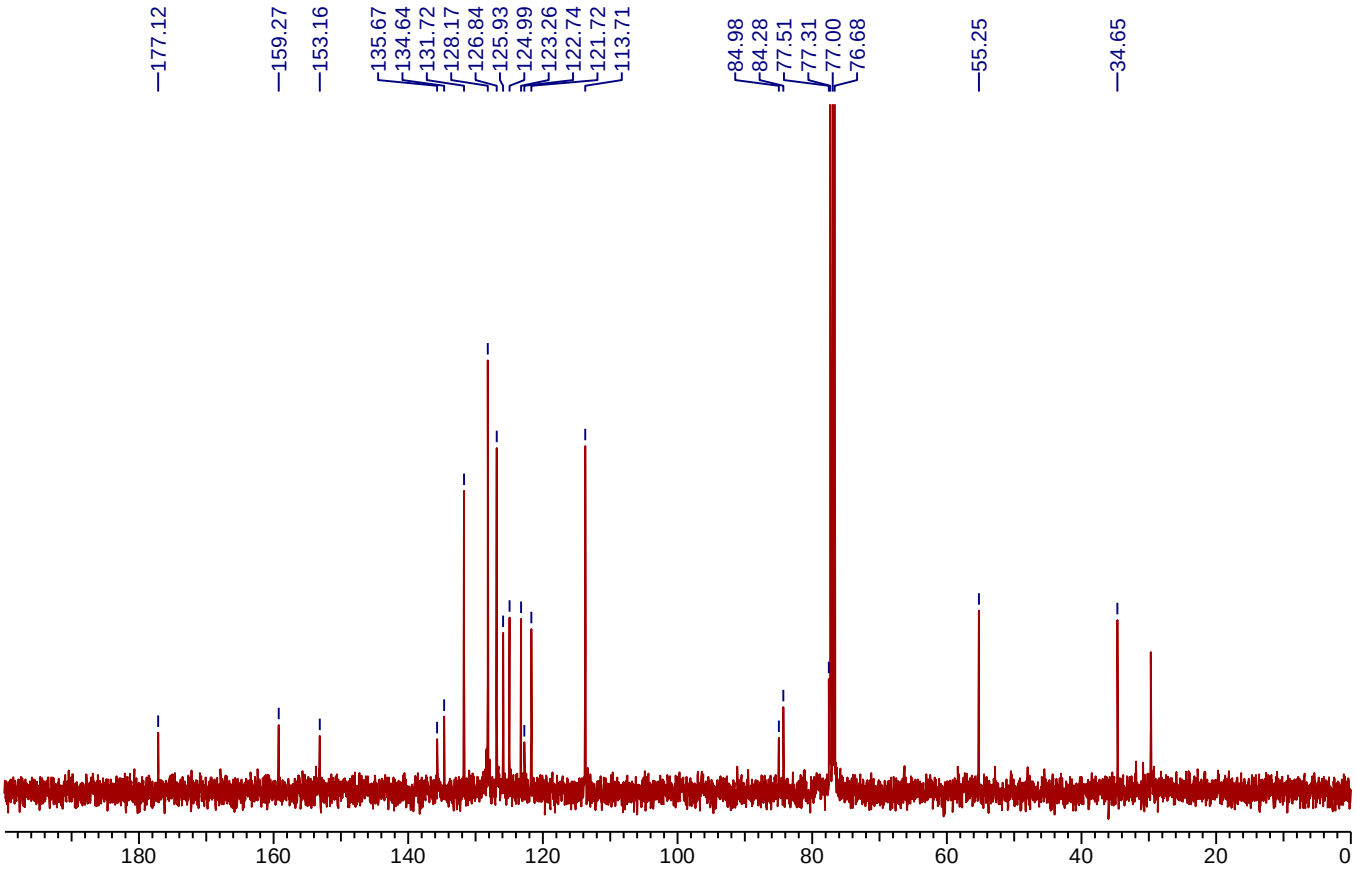
7.16
7.14
6.83
6.80
3.93
3.71
3.68
3.41
3.37
-0.07
N
HO
S
Ph
OMe
3l-1
0.95 0.95 1.93 1.28 1.10 5.06 2.09
0.97 4.03 1.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)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123.26
122.74
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113.71
84.98
84.28
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76.68
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140
120
100
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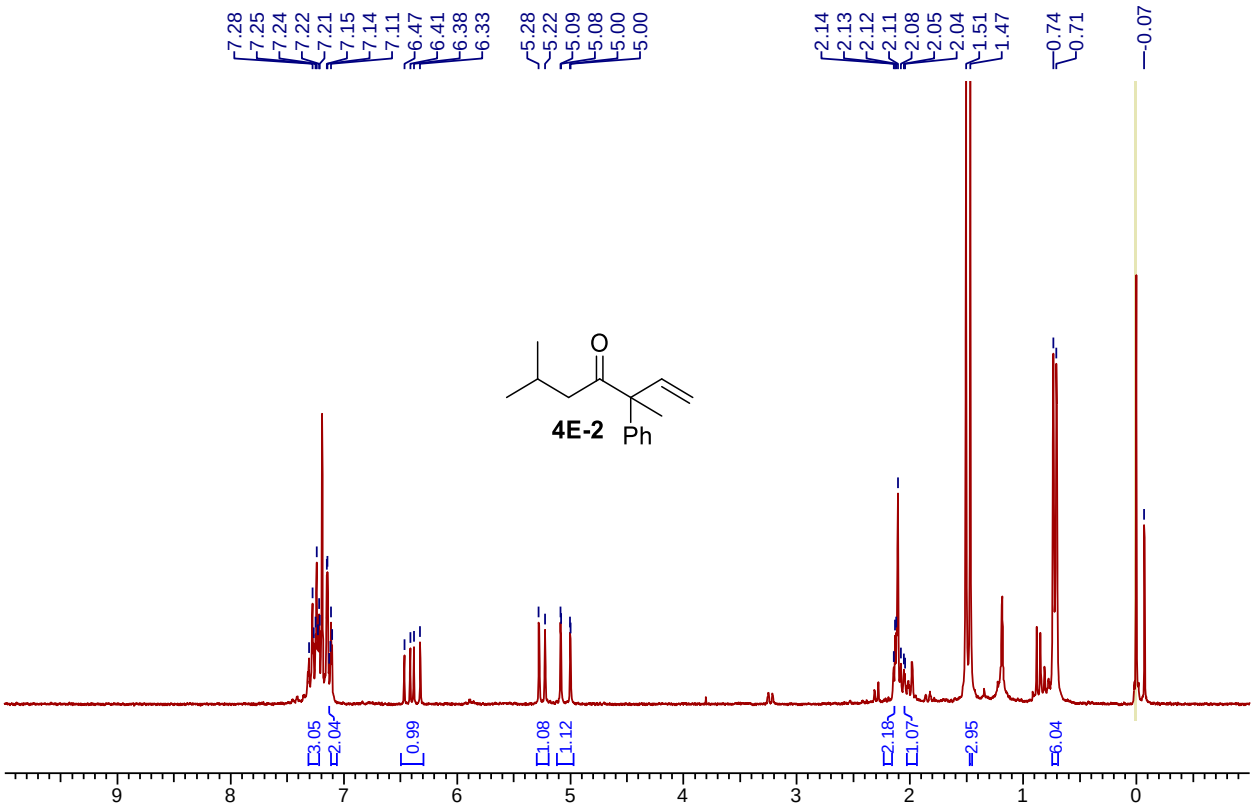
20
0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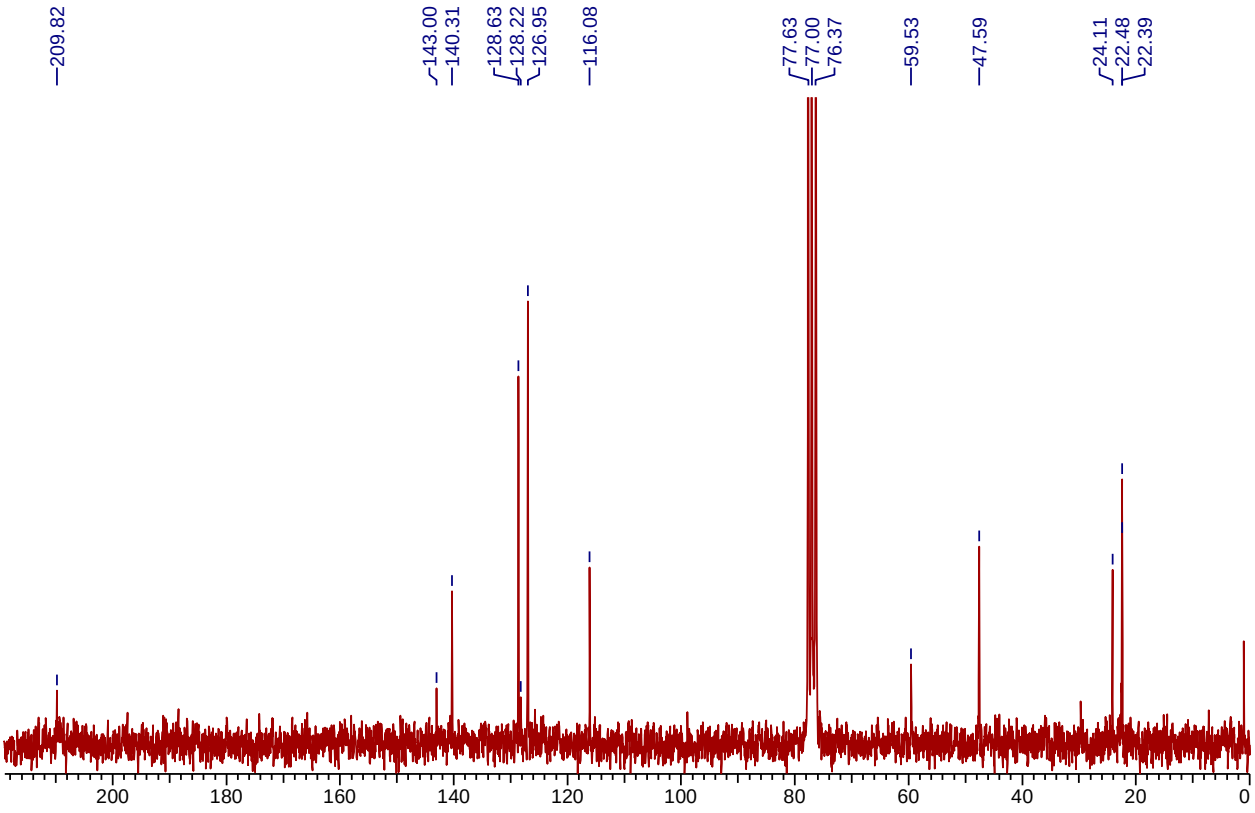
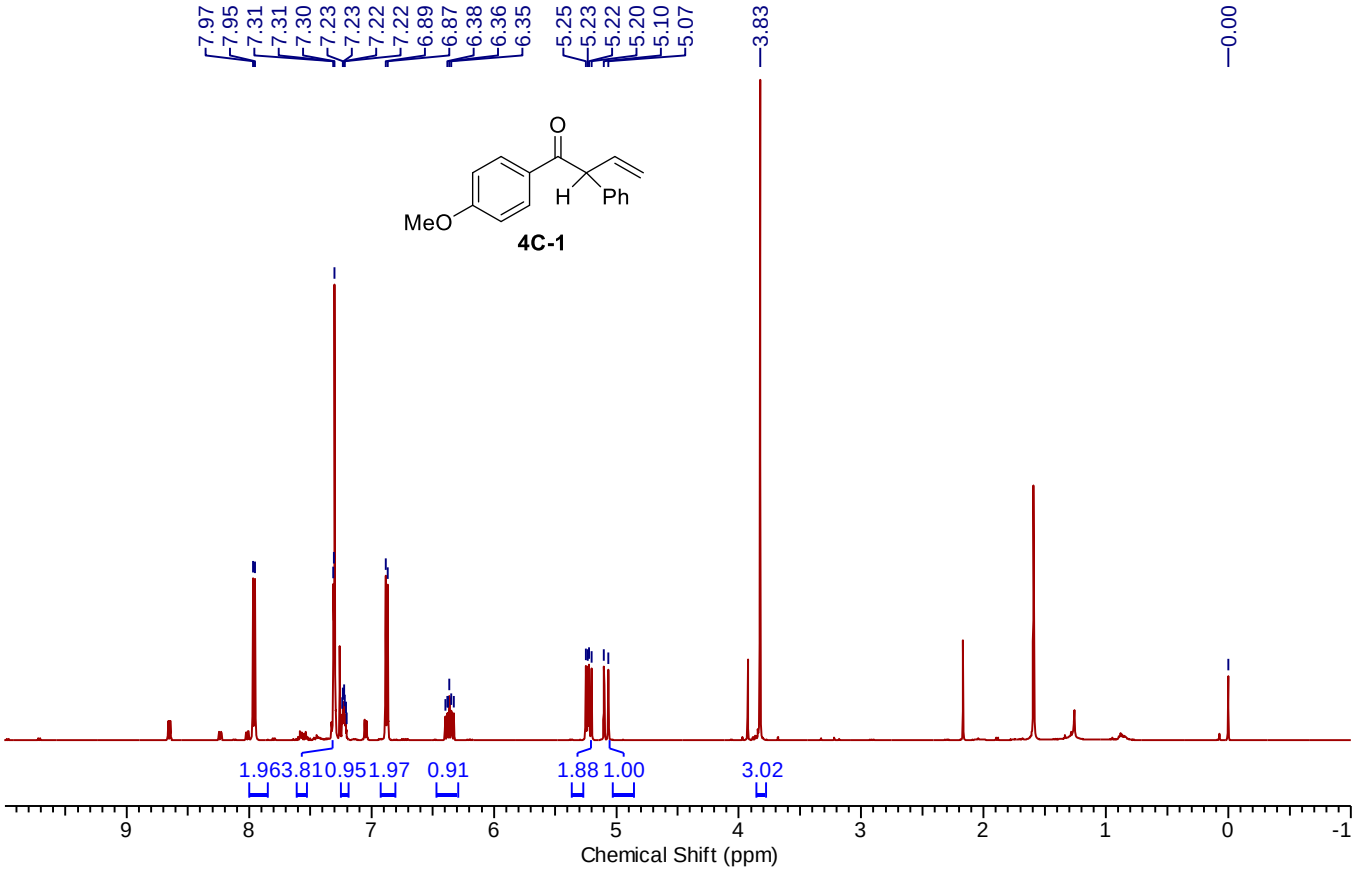
5.28
5.22
5.09
5.08
5.00
5.00
2.14
2.13
2.12
2.11
2.08
2.05
2.04
1.51
1.47
0.74
0.71
-0.07
O
4E-2
Ph
3.05
2.04
0.99
1.08
1.12
2.18
1.07
2.95
6.04
9
8
7
6
5
4
3
2
1
0


209.82
143.00
140.31
128.63
128.22
126.95
116.08
77.63
77.00
76.37
59.53
47.59
24.11
22.48
22.39
200
180
160
140
120
100
80
60
40
20
0


7.97
7.95
7.31
7.31
7.30
7.23
7.23
7.22
7.22
6.89
6.87
6.38
6.36
6.35
5.25
5.23
5.22
5.20
5.10
5.07
3.83
0.00
O
H
Ph
MeO
4C-1
1.96
3.81
0.95
1.97
0.91
1.88
1.00
3.02
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)