Supplementary Information for：

Dramatic Lithium Chloride Effect on the Reaction Stereocontrol in Zn-Mediated Asymmetric Cinnamylation: Highly Practical Synthesis of Enantioenriched β-Aryl Homoallylic Amines

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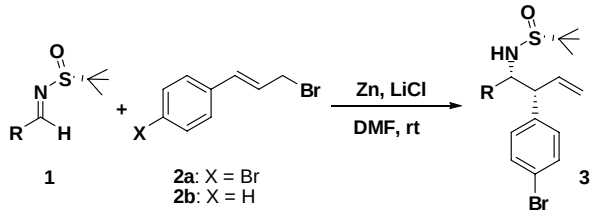
1. General

THF was distilled from sodium/benzophenone, DMF was distilled from Al_2O_3 and HMPA was distilled from CaH_2. Zinc dust was activated by stirring for 5 minutes with 1 M HCl, followed by washing successively with water, acetone and ether, and drying with a heat gun. Reactions were monitored by thin layer chromatography (TLC), on glass plates coated with silica gel with fluorescent indicator (Huanghai, HSGF254). Flash chromatography was performed on silica gel (Huanghai, 300-400) using hexane-EtOAc as eluent.

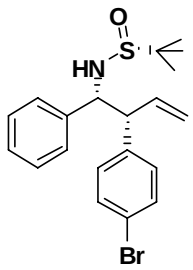
2. General procedure for Zn-mediated asymmetric cinnamylation



1 2a: X = Br 2b: X = H 3

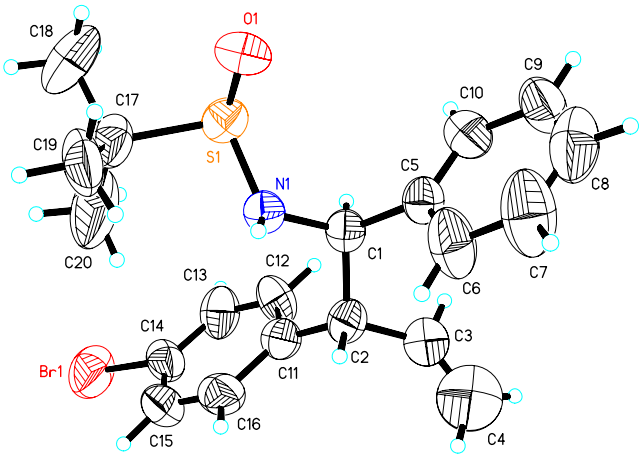
Under argon, to a Schlenk flask charged with actived zinc powder (32 mg, 0.5 mmol), (*E*)-4-bromo-cinnamyl bromide **2** (138 mg, 0.5 mmol), LiCl (11 mg, 0.5 mmol) and (*R*)-*N*-*tert*-butanesulfinyl imines **1** (0.25 mmol) was added dry DMF (5 mL) distilled from Al_2O_3 at room temperature. The resultant mixture was then stirred at rt for 2 hours. The reaction was quenched with brine (5 mL). Extraction with ethyl acetate, dried over anhydrous Na_2SO_4. After concentrated, the residue was purified by flash column chromatography to afford the desired cinnamylation product **3**.

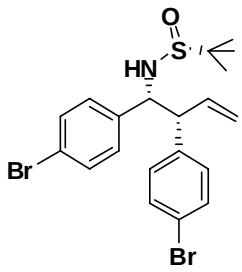
3. Characterization of the obtained reaction product 3a-k, 4, 5 and 7a-c



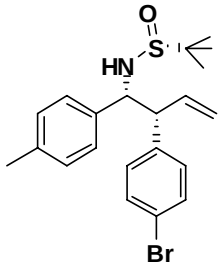
(*R*)-*N*-((1*R*,2*R*)-2-(4-bromophenyl)-1-phenylbut-3-enyl)-2-methylpropane-2-sulfinamide (3a): $[\alpha]_D^{25}$ -52.5 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 9H), 3.57 (d, 1H, *J* = 6.4 Hz), 3.82 (t, 1H, *J* = 7.6 Hz), 4.57 (t, 1H, *J* = 7.0 Hz), 4.96 (d, 1H, *J* = 16.8 Hz), 5.06 (d, 1H, *J* = 10.0 Hz), 5.82-5.91 (m, 1H), 6.96 (d, 2H, *J* = 8.4 Hz), 7.15 (d, 2H, *J* = 6.4 Hz), 7.25-7.30 (m, 3H), 7.39 (d, 2H, *J* = 8.0 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.3, 55.5, 56.1, 63.5, 118.0, 120.6, 127.8, 128.2, 130.4, 131.3, 136.4, 139.5, 139.7 ppm; FT-IR (film, cm^{-1}) ν 3196, 3080, 2952, 2865, 1487, 1055, 1010, 702; ESI-MS (m/z, %): 406.0 (M^++H), 428.0 (M^++Na); HRMS (MALDI) for $C_{20}H_{24}NOSBrNa^+$ (M^++Na): calcd. 428.06542, found 428.0671.

Crystallographic data for (1*R*, 2*R*)-**3a** ($C_{20}H_{26}BrNO_2S$): T = 293 (2) K; Wavelength : 0.71073 Å; Crystal system: Orthorhombic, Space group: *P*2(1)2(1)2(1); Unit cell dimensions: a = 6.7852(8) Å, b = 16.4229(18) Å, c = 19.812(2) Å, α = 90°, β = 90°, γ = 90°; V = 2207.7(4) $Å^3$; Z = 4; ρ_{calc} = 1.277 Mg/m^3; *F* (000) = 880; final R indices [I > 2σ (I)]: R_1 = 0.0620, wR_2 = 0.1512; R indices (all data), R_1 = 0.1446, wR_2 = 0.1700; 13131 reflections measured, 4758 were unique ($R_{(int)}$ = 0.1047).

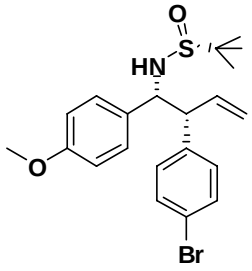




(*R*)-N-((1*R*,2*R*)-1,2-bis(4-bromophenyl)but-3-enyl)-2-methylpropane-2-sulfinamide (3b): $[\alpha]_D^{25}$ -47.2 (*c* 0.98, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (s, 9H), 3.52 (d, 1H, *J* = 6.4 Hz), 3.77 (t, 1H, *J* = 8.0 Hz), 4.53 (t, 1H, *J* = 7.2 Hz), 4.99 (d, 1H, *J* = 16.8 Hz), 5.10 (d, 1H, *J* = 10.4 Hz), 5.79-5.88 (m, 1H), 6.95 (d, 2H, *J* = 8.4 Hz), 7.01 (d, 2H, *J* = 8.4 Hz), 7.40-7.43 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.4, 55.6, 56.4, 63.1, 118.6, 120.9, 121.9, 129.7, 130.4, 131.5, 131.6, 136.0, 138.8, 139.2 ppm; FT-IR (film, cm^{-1}) ν 3324, 2966, 1489, 1074, 1057, 1010, 913, 802; ESI-MS (m/z, %): 485.9 (M^++H), 508.9 (M^++Na); HRMS (MALDI) for $C_{20}H_{24}NOSBr_2^+$ (M^++H): calcd. 483.99399, found 483.9951.

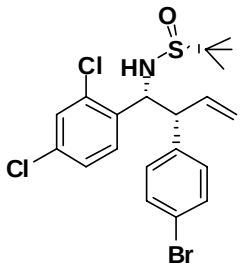


(*R*)-*N*-((1*R*,2*R*)-2-(4-bromophenyl)-1-p-tolylbut-3-enyl)-2-methylpropane-2-sulfinamide (3c): $[\alpha]_D^{25}$ -58.7 (*c* 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 9H), 2.32 (s, 3H), 3.49 (d, 1H, *J* = 6.4 Hz), 3.80 (t, 1H, *J* = 7.8 Hz), 4.52 (t, 1H, *J* = 7.0 Hz), 4.96 (dt, 1H, *J* = 17.2, 2.4 Hz), 5.06 (d, 1H, *J* = 10.4 Hz), 5.82-5.91 (m, 1H), 6.96-6.99 (m, 2H), 7.04 (d, 2H, *J* = 8.4 Hz), 7.11 (d, 2H, *J* = 8 Hz), 7.39-7.42 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1, 22.4, 55.6, 56.1, 63.5, 118.0, 120.6, 127.8, 129.1, 130.6, 131.2, 131.4, 136.7, 137.6, 139.8 ppm; FT-IR (film, cm^{-1}) ν 3224, 2922, 2852, 1487, 1051, 1010, 855, 805; ESI-MS (m/z, %): 420.0 (M^++H), 442.0 (M^++Na); HRMS (MALDI) for $C_{21}H_{27}NOSBr^+$ (M^++H): calcd. 420.09912, found 420.1005.

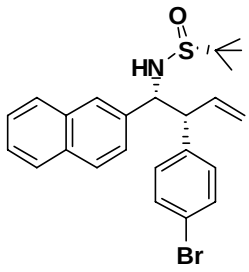


(*R*)-*N*-((1*R*,2*R*)-2-(4-bromophenyl)-1-(4-methoxyphenyl)but-3-enyl)-2-methylpropane-2-sulfinamide (3d): $[\alpha]_D^{25}$ -48.3 (*c* 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05 (s, 9H), 3.46 (d, 1H, *J* = 5.6 Hz), 3.76-3.82 (m, 4H), 4.53 (t, 1H, *J* = 6.4 Hz), 4.97 (d, 1H, *J* = 17.6 Hz), 5.08 (d, 1H, *J* = 10.0 Hz), 5.83-5.92 (m, 1H), 6.83 (d, 2H, *J* = 8.0 Hz), 6.97 (d, 2H, *J* = 8.0 Hz), 7.07 (d, 2H, *J* = 8.4 Hz), 7.41 (d, 2H, *J* = 8.0 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.5, 55.2, 55.6, 56.2, 63.2, 113.7, 118.1, 120.7, 129.1, 130.6, 131.5, 131.7, 136.6, 139.8, 159.2 ppm; FT-IR (film, cm^{-1}) ν 3287,

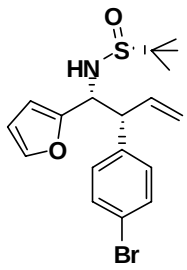
2926, 1515, 1245, 1179, 1046, 843, 814; ESI-MS (m/z, %): 436.0 (M^++H), 458.0 (M^++Na); HRMS (MALDI) for $C_{21}H_{27}NO_2SBr^+$ (M^++H): calcd. 436.09404, found 436.0968.



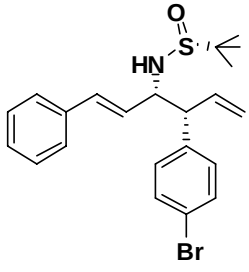
(*R*)-*N*-((1*R*,2*R*)-2-(4-bromophenyl)-1-(2,4-dichlorophenyl)but-3-enyl)-2-methylpropane-2-sulfinamide (3e): $[\alpha]_D^{25}$ -39.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (s, 9H), 3.53 (d, 1H, *J* = 9.6 Hz), 3.75 (t, 1H, *J* = 10.6 Hz), 4.52 (t, 1H, *J* = 9.8 Hz), 5.00 (d, 1H, *J* = 22.8 Hz), 5.12 (d, 1H, *J* = 13.6 Hz), 5.77-5.89 (m, 1H), 6.98 (d, 3H, *J* = 10.8 Hz), 7.27 (s, 1H), 7.37 (d, 1H, *J* = 11.2 Hz), 7.44 (d, 2H, *J* = 10.8 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.4, 55.7, 56.5, 62.8, 118.9, 121.1, 127.3, 129.8, 130.3, 130.3, 131.7, 132.0, 132.5, 135.8, 138.9, 140.2 ppm; FT-IR (film, cm^{-1}) ν 3281, 2953, 1488, 1648, 1054, 1046, 920, 816; ESI-MS (m/z, %): 475.9 (M^++H), 498.0 (M^++Na); HRMS (MALDI) for $C_{20}H_{23}NOSCl_2Br^+$ (M^++H): calcd. 474.00553, found 474.0071.



(*R*)-*N*-((1*R*,2*R*)-2-(4-bromophenyl)-1-(naphthalen-2-yl)but-3-enyl)-2-methylpropane-2-sulfinamide (3f): $[\alpha]_D^{25}$ -18.4 (*c* 0.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (s, 9H), 3.64 (d, 1H, *J* = 6.8 Hz), 3.92 (t, 1H, *J* = 7.8 Hz), 4.74 (t, 1H, *J* = 7.2 Hz), 4.98 (d, 1H, *J* = 17.2 Hz), 5.05 (d, 1H, *J* = 10.4 Hz), 5.85-5.94 (m, 1H), 7.01 (d, 2H, *J* = 8.0 Hz), 7.29 (dd, 1H, *J* = 8.4, 1.6 Hz), 7.40-7.48 (m, 4H), 7.63 (s, 1H), 7.78-7.82 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.4, 55.7, 56.3, 63.8, 118.2, 120.8, 125.5, 126.1, 126.2, 127.2, 127.6, 128.1, 128.2, 130.6, 131.5, 133.0, 133.0, 136.6, 137.2, 139.6 ppm; FT-IR (film, cm^{-1}) ν 3295, 1487, 1070, 1045, 919, 761, 751, 477; ESI-MS (m/z, %): 458.1 (M^++H), 478.0 (M^++Na); HRMS (MALDI) for $C_{24}H_{27}NOSBr^+$ (M^++H): calcd. 456.09912, found 456.0990.

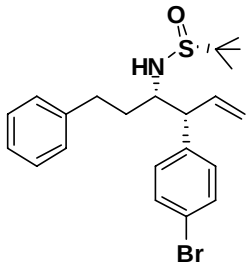


(*R*)-*N*-((1*R*,2*R*)-2-(4-bromophenyl)-1-(furan-2-yl)but-3-enyl)-2-methylpropane-2-sulfinamide (3g): $[\alpha]_D^{25}$ -16.0 (*c* 0.97, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.03 (s, 9H), 3.42 (d, 1H, *J* = 8.8 Hz), 3.88 (t, 1H, *J* = 7.6 Hz), 4.60 (t, 1H, *J* = 8.2 Hz), 5.03 (d, 1H, *J* = 17.2 Hz), 5.10 (d, 1H, *J* = 10.4 Hz), 5.92-6.01 (m, 1H), 6.21 (d, 1H, *J* = 2.8 Hz), 6.28 (d, 1H, *J* = 1.2 Hz), 6.97 (d, 2H, *J* = 8.0 Hz), 7.38-7.41 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.4, 54.2, 56.4, 58.3, 108.7, 110.3, 117.8, 120.7, 130.2, 131.5, 136.8, 139.2, 142.1, 153.0 ppm; FT-IR (film, cm^{-1}) ν 3243, 2959, 1490, 1151, 1064, 1047, 1010, 766, 732; ESI-MS (m/z, %): 398.0 (M^++H), 420.0 (M^++Na); HRMS (MALDI) for $C_{18}H_{23}NO_2SBr^+$ (M^++H): calcd. 396.06274, found 396.0643.

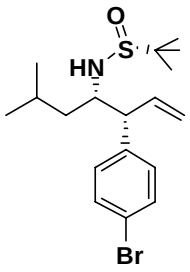


(*R*)-*N*-((3*S*,4*R*,*E*)-4-(4-bromophenyl)-1-phenylhexa-1,5-dien-3-yl)-2-methylpropane-2-sulfinamide (3h): $[\alpha]_D^{25}$ -45.8 (*c* 1.02 $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.10 (s, 9H), 3.29 (d, 1H, *J* = 7.8 Hz), 3.61 (t, 1H, *J* = 7.4 Hz), 4.19 (dd, 1H, *J* = 14.7, 7.5 Hz), 5.13 (d, 1H, *J* = 17.1 Hz), 5.21 (d, 1H, *J* = 10.2 Hz), 6.00-6.22 (m, 2H), 6.58 (d, 1H, *J* = 16.2 Hz), 7.11 (d, 2H, *J* = 8.7 Hz), 7.23-7.36 (m, 5H), 7.45 (d, 2H, *J* = 8.1 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.4, 55.2, 56.2, 62.2, 118.3, 120.7, 126.6,

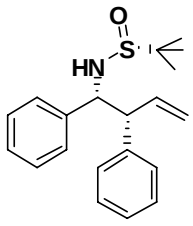
127.8, 128.3, 128.4, 130.3, 131.5, 133.3, 136.2, 136.6, 139.5 ppm; FT-IR (film, cm^{-1}) ν 3228, 2958, 1488, 1054, 1042, 1010, 918, 747; ESI-MS (m/z, %): 433.9 (M^++H), 454.0 (M^++Na); HRMS (MALDI) for $C_{22}H_{26}NOSBrNa^+$ (M^++Na): calcd. 454.08107, found 454.08171.



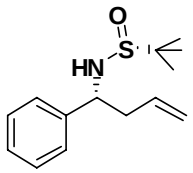
(*R*)-*N*-((3*S*,4*R*)-4-(4-bromophenyl)-1-phenylhex-5-en-3-yl)-2-methylpropane-2-sulfinamide (3i): $[\alpha]_D^{25}$ -79.7 (*c* 0.98, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.08 (s, 9H), 1.78-1.88 (m, 1H), 2.00-2.09 (m, 1H), 2.72-2.79 (m, 1H), 2.84-2.92 (m, 1H), 3.07 (d, 1H, *J* = 7.6 Hz), 3.44-3.55 (m, 2H), 5.09-5.16 (m, 2H), 5.90-5.99 (m, 1H), 7.05 (d, 2H, *J* = 8.4 Hz), 7.16-7.21 (m, 3H), 7.26-7.29 (m, 2H), 7.41 (d, 2H, *J* = 8.4 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.5, 31.5, 35.2, 55.3, 56.1, 60.2, 117.4, 120.4, 125.9, 128.4, 128.5, 130.2, 131.5, 137.9, 140.1, 141.3 ppm; FT-IR (film, cm^{-1}) ν 3294, 2909, 1488, 1072, 1043, 1009, 828, 699; ESI-MS (m/z, %): 434.0 (M^++H), 456.0 (M^++Na); HRMS (MALDI) for $C_{22}H_{29}NOSBr^+$ (M^++H): calcd. 434.11532, found 434.1151.



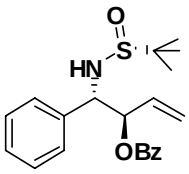
(*R*)-*N*-((3*R*,4*S*)-3-(4-bromophenyl)-6-methylhept-1-en-4-yl)-2-methylpropane-2-sulfinamide (3j): $[\alpha]_D^{26}$ -80.8 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 0.89 (d, 3H, *J* = 6.4 Hz), 0.92 (d, 3H, *J* = 6.4 Hz), 1.40-1.41 (m. 2H), 1.85-1.92 (m, 1H), 2.88 (d, 1H, *J* = 6.4 Hz), 3.43 (t, 1H, *J* = 7.2 Hz), 3.56 (t, 1H, *J* = 6.2 Hz), 5.11 (d, 1H, *J* = 17.2 Hz), 5.15 (d, 1H, *J* = 10.8 Hz), 5.97-6.06 (m, 1H), 7.10 (d, 2H, *J* = 8.0 Hz), 7.44 (d, 2H, *J* = 8.0 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 22.6, 23.3, 24.1, 43.0, 55.3, 56.1, 58.7, 117.3, 120.5, 130.5, 131.5, 138.2, 140.0 ppm; FT-IR (film, cm^{-1}) ν 3461, 3126, 2960, 1488, 1367, 1073, 1015, 915, 819; ESI-MS (m/z, %): 388.0 (M^++H), 410.0 (M^++Na); HRMS (MALDI) for $C_{18}H_{28}NOSBrNa^+$ (M^++Na): calcd. 408.09672, found 408.09766.



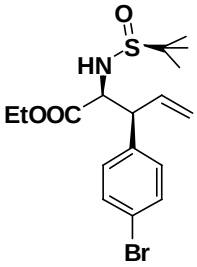
(*R*)-*N*-((1*R*,2*R*)-2-(4-bromophenyl)-1-phenylbut-3-enyl)-2-methylpropane-2-sulfinamide (3k): $[\alpha]_D^{24}$ -40.8 (*c* 0.28, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 1.01 (s, 9H), 3.57 (d, 1H, *J* = 5.7 Hz), 3.81 (t, 1H, *J* = 8.0 Hz), 4.58 (t, 1H, *J* = 7.1 Hz), 4.95 (d, 1H, *J* = 17.1 Hz), 5.04 (d, 1H, *J* = 10.2 Hz), 5.86-5.97 (m, 1H), 7.10-7.31 (m, 10H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.4, 56.2, 56.5, 64.1, 117.6, 126.9, 127.8, 128.0, 128.3, 128.5, 128.8, 137.1, 140.2, 140.4 ppm; FT-IR (film, cm^{-1}) ν 3322, 3063, 2904, 1468, 1366, 1062, 760, 701; ESI-MS (m/z, %): 328.0 (M^++H), 350.0 (M^++Na); HRMS (MALDI) for $C_{20}H_{26}NOS^+$ (M^++H): calcd. 328.17296, found 328.1739.



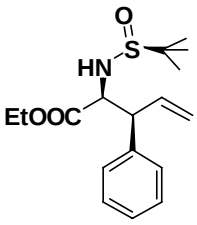
(*R*)-2-methyl-*N*-((*R*)-1-phenylbut-3-enyl)propane-2-sulfinamide 4: $[\alpha]_D^{26}$ -40.3 (*c* 2.46, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.22 (s, 9H), 2.52-2.60 (m, 1H), 2.70-2.77 (m, 1H), 3.52 (d, 1H, *J* = 3.6 Hz), 4.43-4.47 (m, 1H), 5.01-5.06 (m, 2H), 5.56-5.66 (m, 1H), 7.25-7.36 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.7, 41.2, 56.0, 58.5, 118.1, 127.2, 127.8, 128.6, 133.8, 141.9 ppm; ESI-MS (m/z, %): 252.2 (M^++H), 274(M^++Na). Diastereomeric ratio is determined by ^1H NMR of the crude materials.



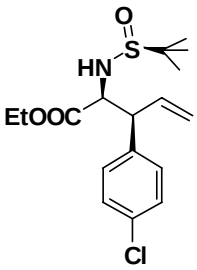
(1*S*,2*R*)-1-((*R*)-1,1-dimethylethylsulfinamido)-1-phenylbut-3-en-2-yl benzoate 5: $[\alpha]_D^{28}$ 39.4 (*c* 1.02, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19 (s, 9 H), 3.77 (d, 1 H, *J* = 5.2 Hz), 4.79 (t, 1 H, *J* = 5.0 Hz,), 5.30 (d, 1 H, *J* = 10.6 Hz), 5.37 (d, 1 H, *J* = 17.2 Hz), 5.74-5.81 (m, 1H), 5.92-5.74 (m, 1 H), 7.27-7.57 (m, 8H), 8.01-8.02 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 22.6, 56.5, 61.3, 76.4, 119.3, 127.9, 128.2, 128.4, 128.5, 129.5, 129.9, 132.2, 133.1, 138.2, 165.4 ppm; ESI-MS: m/z (%): 372.2 (M^++H), 394.2 (M^++Na).



(2*S*,3*S*)-ethyl 3-(4-bromophenyl)-2-((*S*)-1,1-dimethylethylsulfinamido)pent-4-enoate (7a): $[\alpha]_D^{20}$ 68.5 (*c* 0.99, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.09 (s, 9H), 1.26 (t, 3H, *J* = 7.2 Hz), 3.67 (t, 1H, *J* = 8.0 Hz), 3.93 (d, 1H, *J* = 9.3 Hz), 4.12-4.22 (m, 3H), 5.13 (d, 1H, *J* = 11.4 Hz), 5.18 (d, 1H, *J* = 4.5 Hz), 5.95-6.07 (m, 1H), 7.04 (d, 2H, *J* = 8.1 Hz), 7.43 (d, 2H, *J* = 8.4 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 22.5, 53.4, 56.4, 61.8, 62.4, 118.0, 121.1, 130.1, 131.6, 136.4, 138.3, 171.9 ppm; FT-IR (film, cm^{-1}) ν 3275, 2983, 1737, 1489, 1179, 1074, 1012, 755; ESI-MS (m/z, %): 404.0 (M^++H), 426.0 (M^++Na); HRMS (MALDI) for $C_{17}H_{24}NO_3SBrNa^+$ (M^++Na): calcd. 424.05525, found 424.0561.

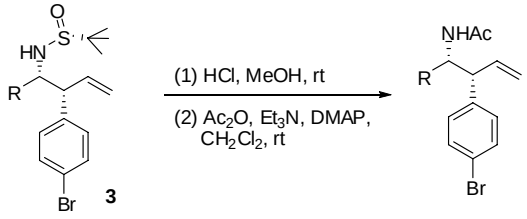


(2*S*,3*S*)-ethyl 2-((*S*)-1,1-dimethylethylsulfinamido)-3-phenylpent-4-enoate (7b): $[\alpha]_D^{20}$ 79.9 (*c* 0.68, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (s, 9H), 1.25 (t, 3H, *J* = 7.2 Hz), 3.69 (t, 1H, *J* = 8.1 Hz), 3.92 (d, 1H, *J* = 9.6 Hz), 4.13-4.22 (m, 3H), 5.13-5.18 (m, 2H), 6.00-6.12 (m, 1H), 7.15-7.32 (m, 5H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 22.4, 54.0, 56.2, 61.5, 62.7, 117.4, 127.1, 128.3, 128.4, 128.5, 136.8, 139.2, 172.1 ppm; FT-IR (film, cm^{-1}) ν 3280, 2982, 2961, 1735, 1178, 1079, 753, 701; ESI-MS (m/z, %): 324.0 (M^++H), 346.1 (M^++Na); HRMS (MALDI) for $C_{17}H_{25}NO_3SNa^+$ (M^++Na): calcd. 346.14474, found 346.1456.

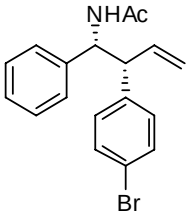


(2*S*,3*S*)-ethyl 3-(4-chlorophenyl)-2-((*S*)-1,1-dimethylethylsulfinamido)pent-4-enoate (7c): $[\alpha]_D^{20}$ 114.8 (*c* 1.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.09 (s, 9H), 1.26 (t, 3H, *J* = 7.4 Hz), 3.69 (t, 1H, *J* = 7.8 Hz), 3.92 (d, 1H, *J* = 9.2 Hz), 4.13-4.21 (m, 3H), 5.12-5.18 (m, 2H), 5.97-6.06 (m, 1H), 7.11 (d, 2H, *J* = 8.0 Hz), 7.27-7.29 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 22.5, 53.3, 56.3, 61.8, 62.5, 118.0, 128.7, 129.7, 133.0, 136.4, 137.7, 172.0 ppm; FT-IR (film, cm^{-1}) ν 3274, 2982, 1737, 1493, 1178, 1080, 1015, 857; ESI-MS (m/z, %): 358.1 (M^++H), 380.0 (M^++Na); HRMS (MALDI) for $C_{19}H_{19}NO_3Na^+$ (M^++Na): calcd. 358.12382, found 358.1246.

4. Determination of the diastereoselectivities (*syn:anti* ratios) and enantioselectivities.

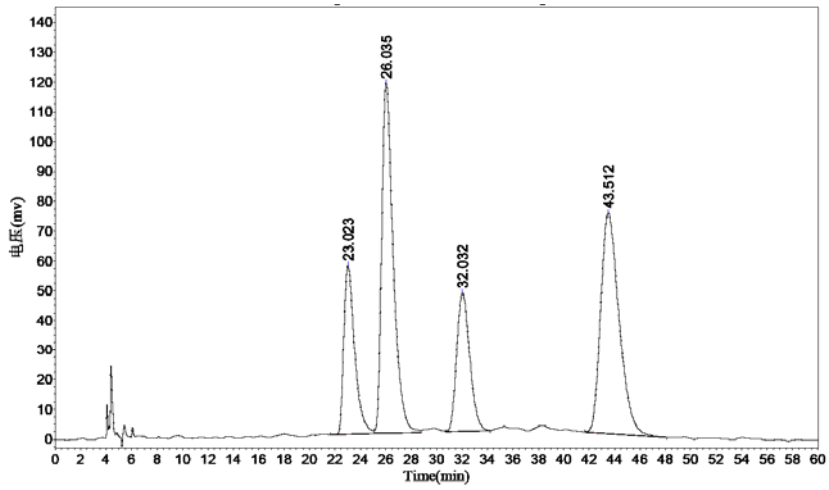


Typical procedure: A solution of HCl in 1,4-dioxane (4 N, 0.2 mL) was added to a solution of the cinnamylation product **3** (0.2 mmol) in dry methanol (2 mL). The mixture was stirred at rt for 0.5 hour and the solvent was removed in vacuo. Triethylamine (0.4 mL) and acetic anhydride (40 mL, 0.4 mmol) were added to the solution of the resulting crude product dissolved in fresh CH_2Cl_2 (2 mL). The mixture was stirred at rt for 3 h, followed by the addition of ethyl acetate (30 mL). The solution was washed with brine, dried, filtered, and concentrated in vacuo. Purification by flash column chromatography gave the acetate product.



$[\alpha]_D^{20}$ -44.5 (*c* 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.85 (s, 3H), 3.73 (t, 1H, *J* = 7.8 Hz), 4.99 (d, 1H, *J* = 17.2 Hz), 5.10 (d, 1H, *J* = 10.0 Hz), 5.32 (t, 1H, *J* = 8.2 Hz), 5.83-5.92 (m, 2H), 6.95 (d, 2H, *J* = 8.4 Hz), 7.09-7.11 (m, 2H), 7.25-7.31 (m, 3H), 7.39 (d, 2H, *J* = 8.4 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.2, 54.6, 56.4, 117.9, 120.8, 127.4, 127.5, 128.3, 130.1, 131.5, 136.8, 139.1, 139.7, 168.9 ppm; FT-IR (film, cm^{-1}) ν 3267, 3082, 1647, 1541, 1373, 1276, 896, 748, 699; ESI-MS (m/z, %): 343.9 (M^++H), 367.8 (M^++Na); HRMS (MALDI) for $C_{18}H_{18}NOBrNa^+$ (M^++Na): calcd. 366.04640, found 366.0474. HPLC: Chiracel OD-H Column (250 mm); detected at 214 nm; n-hexane / *i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 23.0 min (1*R*, 2*R*), 26.0 min (*anti* isomer), 32.0 min (1*S*, 2*S*), 43.5 min (*anti* isomer).

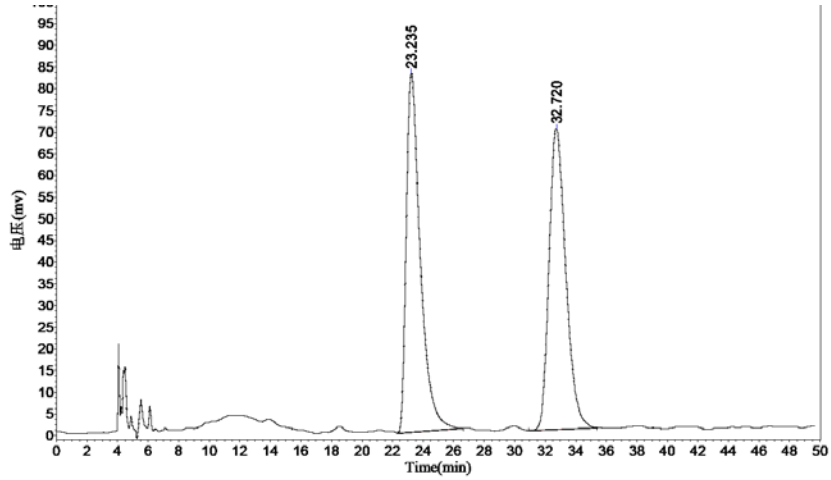
anti + *syn* (racemic):



Results

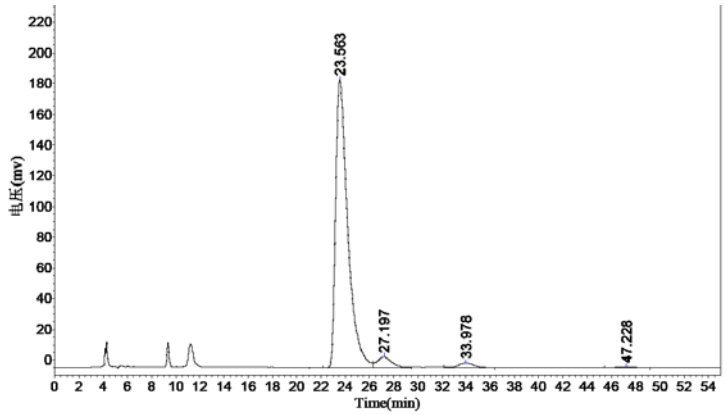
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.023	56858.504	3349798.750	15.5608
2		26.035	117640.383	7402094.500	34.3849
3		32.032	46678.043	3315045.500	15.3994
4		43.512	74188.953	7460235.000	34.6550
Total			295365.883	21527173.750	100.0000

syn (racemic):



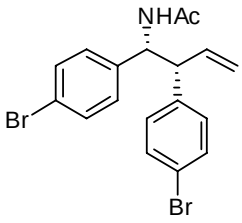
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.235	82967.555	5288478.500	50.0512
2		32.720	69488.109	5277653.500	49.9488
Total			152455.664	10566132.000	100.0000



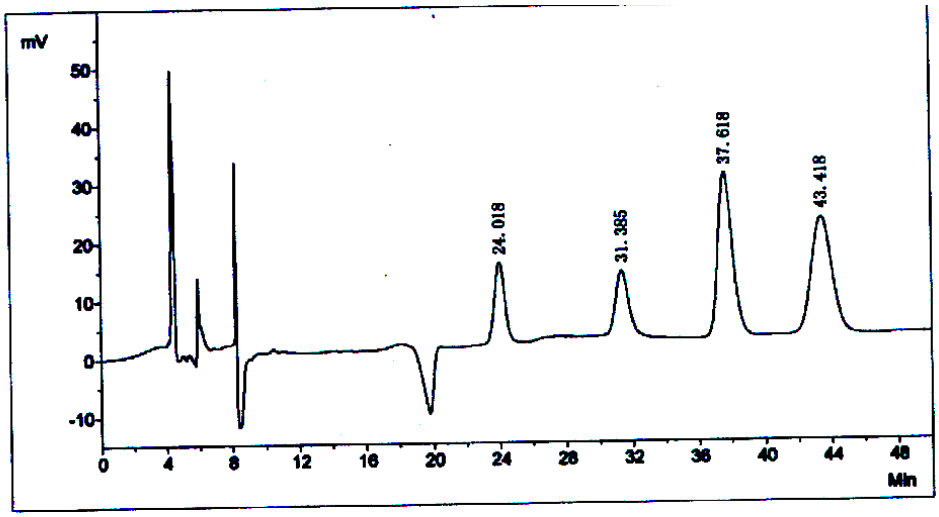
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		23.563	187257.406	12953660.000	93.1477
2		27.197	6948.651	596041.875	4.2860
3		33.978	3079.641	300638.000	2.1618
4		47.228	495.103	56241.031	0.4044
Total			197780.802	13906580.906	100.0000



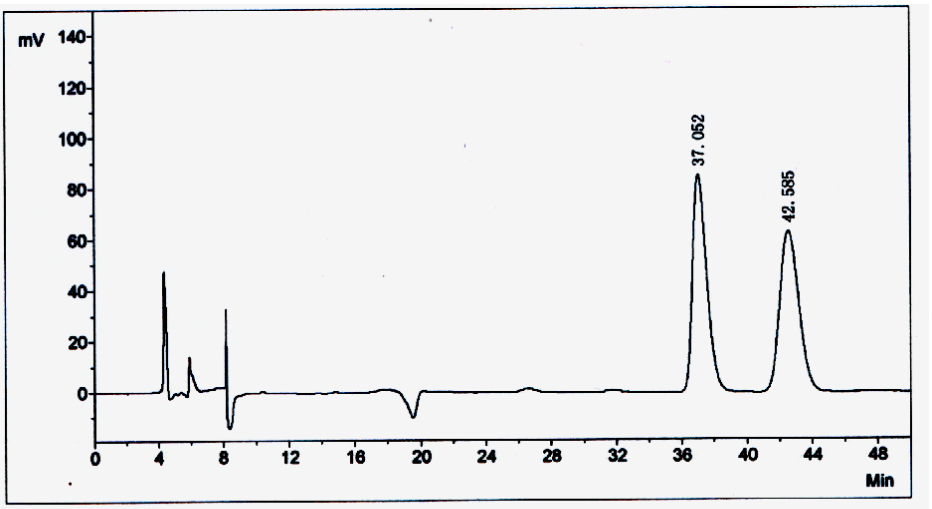
$[\alpha]_D^{19}$ -34.6 (*c* 1.02, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.84 (s, 3H), 3.66 (t, 1H, *J* = 7.8 Hz), 5.00 (d, 1H, *J* = 16.8 Hz), 5.11 (d, 1H, *J* = 10.0 Hz), 5.25 (dd, 1H, *J* = 8.0, 8.0 Hz), 5.78-5.87 (m, 2H), 6.94-6.98 (m, 4H), 7.39-7.42 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.2, 54.4, 55.9, 118.4, 121.0, 121.4, 129.1, 130.0, 131.4, 131.7, 136.3, 138.6, 138.8, 169.0 ppm; FT-IR (film, cm^{-1}) *ν* 3332, 3083, 1653, 1538, 1489, 1010, 805, 722; ESI-MS (m/z, %): 423.9 (M^++H); HRMS (MALDI) for $C_{18}H_{17}NOBr_2Na^+$ (M^++Na): calcd. 443.95691, found 443.95768. HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / ethyl alcohol = 95/5; flow = 0.7 mL/min; Retention time: 24.0 min (*anti* isomer), 31.4 min (*anti* isomer), 37.6 min (1*S*, 2*S*), 43.4 min (1*R*, 2*R*).

anti + *syn* (racemic):

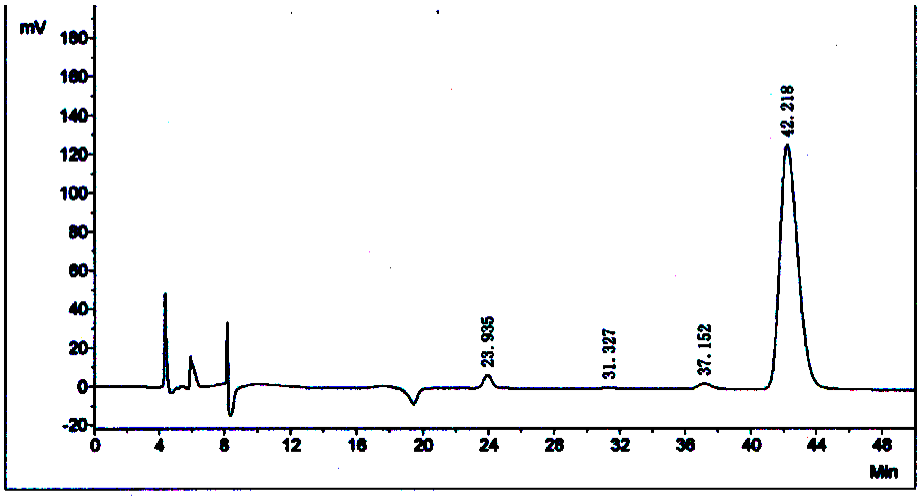


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		24.018	13948.8	609105.6	12.9915
2	2		31.385	11324.9	622949.5	13.2868
3	3		37.618	28296.2	1737050.9	37.0493
4	4		43.418	19987.9	1719378.9	36.6724
Total				73557.9	4688484.8	100.0000

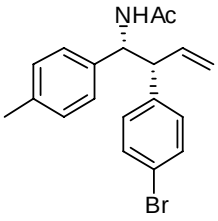
syn (racemic):



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		37.052	85532.2	5183304.3	50.0725
2	2		42.585	63348.9	5168289.9	49.9275
Total				148881.1	10351594.2	100.0000

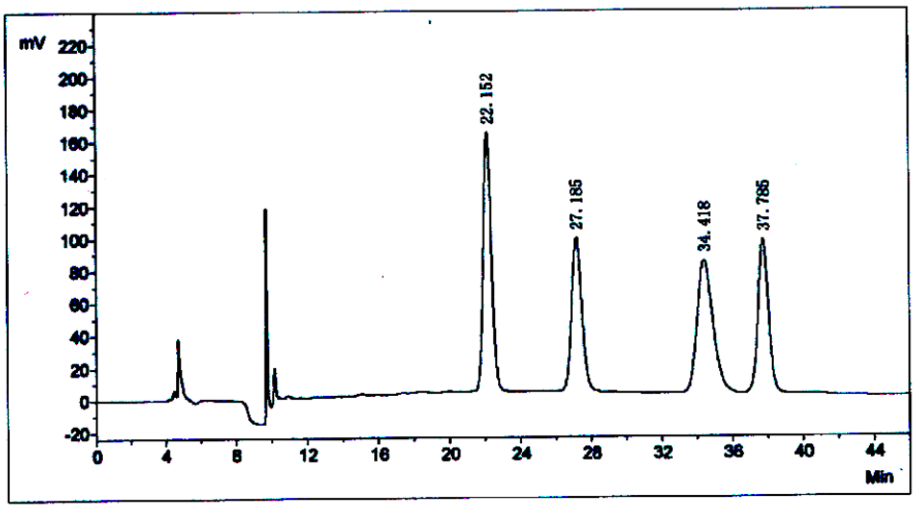


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		23.935	6879.3	250478.5	2.4813
2	2		31.327	645.3	30689.3	0.3040
3	3		37.152	3067.4	173303.5	1.7168
4	4		42.218	126145.4	9640156.6	95.4979
Total				136737.4	10094627.9	100.0000



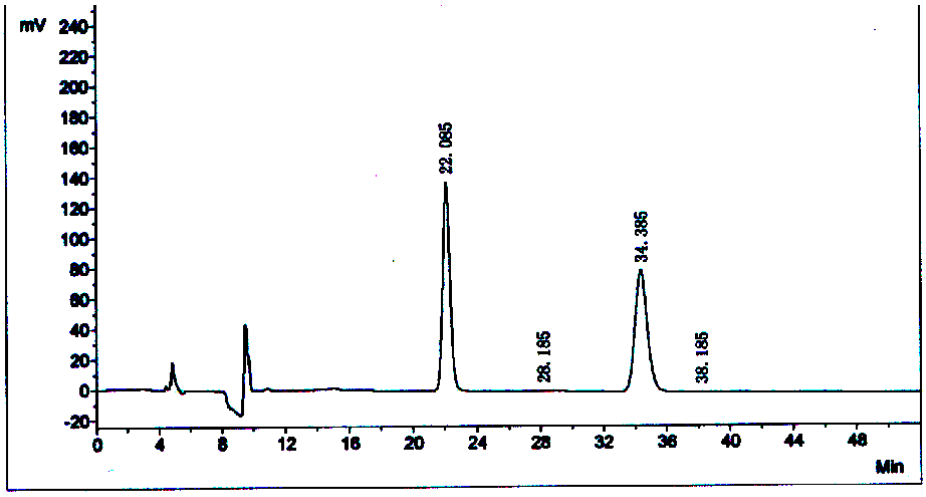
$[\alpha]_D^{20}$ -35.8 (*c* 0.92, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 1.86 (s, 3H), 2.32 (s, 3H), 3.72 (t, 1H, *J* = 7.8 Hz), 5.00 (d, 1H, *J* = 17.1 Hz), 5.10 (d, 1H, *J* = 9.9 Hz), 5.28 (t, 1H, *J* = 8.1 Hz), 5.70 (d, 1H, *J* = 8.4 Hz), 5.82-5.94 (m, 1H), 6.95-7.00 (m, 4H), 7.09 (d, 2H, *J* = 7.8 Hz), 7.40 (d, 2H, *J* = 8.1 Hz) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.1, 23.3, 54.6, 56.1, 117.9, 120.8, 127.3, 129.0, 130.1, 131.5, 136.6, 136.9, 137.2, 139.2, 168.8 ppm; FT-IR (film, cm^{-1}) *ν* 3343, 2976, 1651, 1488, 1371, 1012, 807, 711; ESI-MS (m/z, %): 360.0 (M^++H), 382.0 (M^++Na); HRMS (MALDI) for $C_{19}H_{20}NOBrNa^+$ (M^++Na): calcd. 380.06205, found 380.06261. HPLC: Chiracel Phenomenex Cellulose-2 Column (250 mm); detected at 214 nm; *n*-hexane / ethyl alcohol = 95/5; flow = 0.7 mL/min; Retention time: 22.2 min (1*R*, 2*R*), 27.2 min (*anti* isomer), 34.4 min (1*S*, 2*S*), 37.8 min (*anti* isomer).

anti + *syn* (racemic):

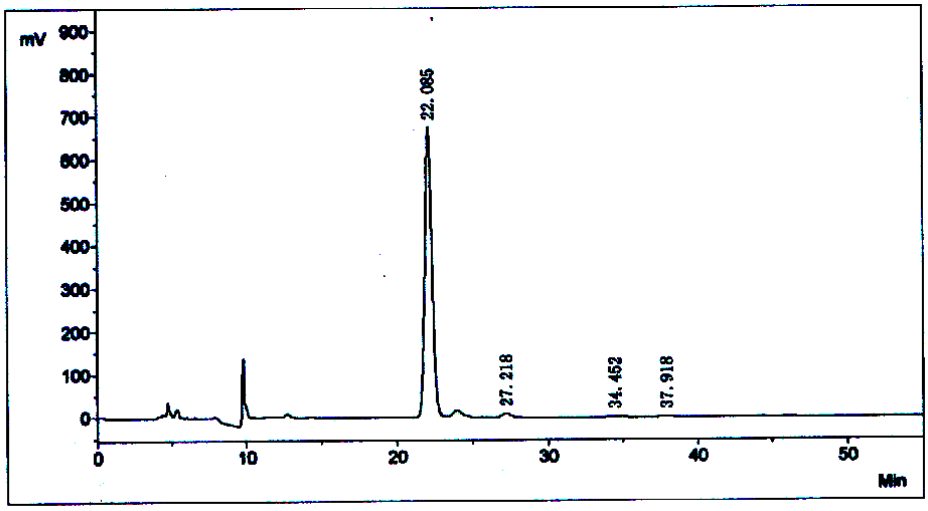


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		22.152	160570.6	5177483.5	28.6675
2	2		27.185	95179.3	3865884.1	21.4052
3	3		34.418	82116.7	5120321.8	28.3510
4	4		37.785	95087.7	3896760.1	21.5762
Total				432954.3	18060449.4	100.0000

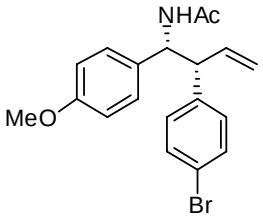
syn (racemic):



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		22.085	137703.2	4411692.4	50.2214
2	2		28.185	156.7	21212.5	0.2415
3	3		34.385	80053.2	4325972.0	49.2456
4	4		38.185	318.7	25613.9	0.2916
Total				218231.9	8784490.8	100.0000

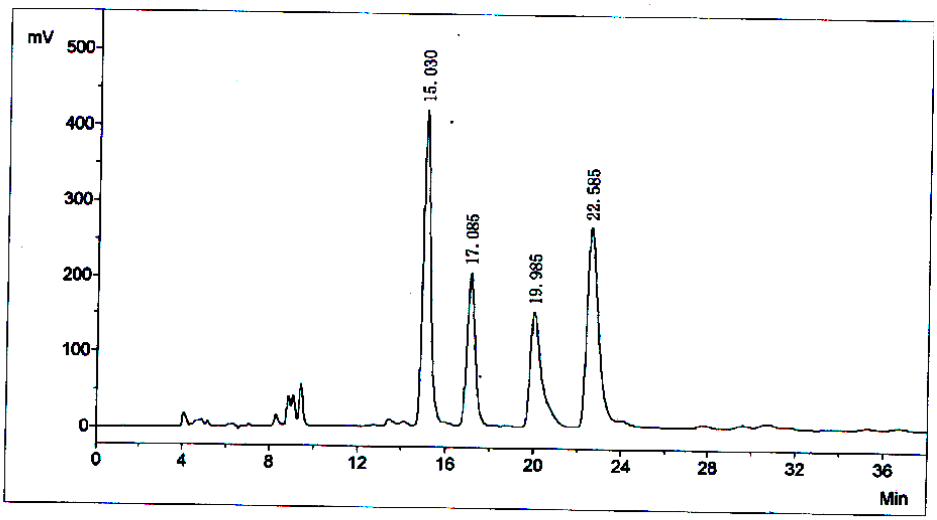


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		22.085	673317.1	22386129.3	97.5822
2	2		27.218	8577.0	350268.7	1.5268
3	3		34.452	1668.9	116113.9	0.5061
4	4		37.918	1677.5	88273.1	0.3848
Total				685240.4	22940784.9	100.0000



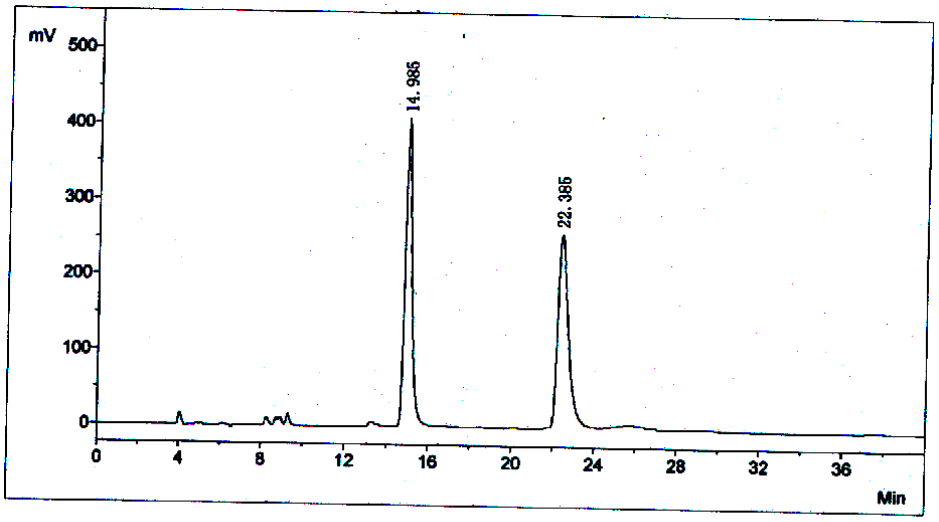
$[\alpha]_D^{18}$ -37.8 (*c* 0.88, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.83 (s, 3H), 3.70 (t, 1H, *J* = 7.8 Hz), 3.78 (s, 3H), 4.99 (d, 1H, *J* = 16.8 Hz), 5.10 (d, 1H, *J* = 10.4 Hz), 5.26 (t, 1H, *J* = 8.2 Hz), 5.82-5.89 (m, 2H), 6.80-6.82 (m, 2H), 6.96 (d, 2H, *J* = 8.4 Hz), 7.02 (d, 2H, *J* = 8.4 Hz), 7.38-7.40 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.3, 54.7, 55.2, 55.9, 113.7, 118.0, 120.8, 128.5, 130.1, 131.5, 131.7, 136.9, 139.2, 158.9, 168.8 ppm; FT-IR (film, cm^{-1}) *ν* 3331, 2950, 1652, 1516, 1257, 1182, 811, 601; ESI-MS (m/z, %): 374.0 (M^++H), 396.0 (M^++Na); HRMS (MALDI) for $C_{19}H_{21}NO_2Br^+$ (M^++H): calcd. 374.07502, found 374.07685. HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 15.0 min (1*R*, 2*R*), 17.0 min (*anti* isomer), 20.0 min (*anti* isomer), 22.6 min (1*S*, 2*S*).

anti + *syn* (racemic):

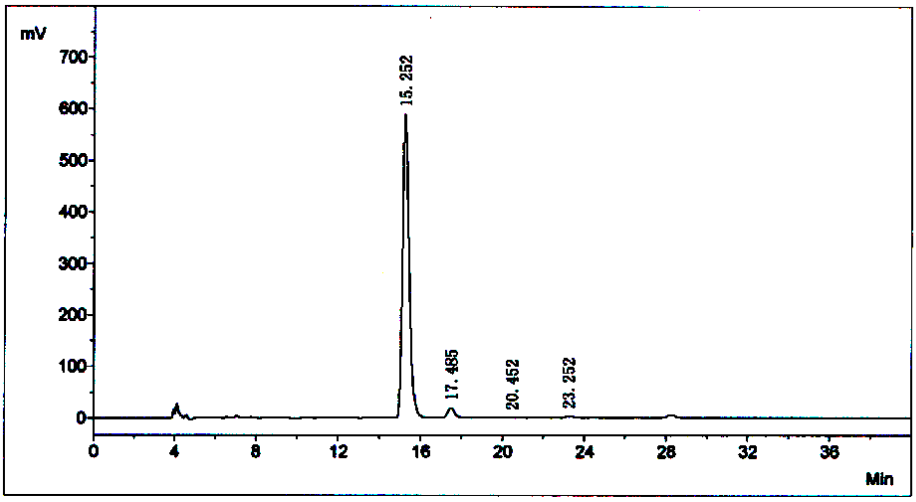


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		15.030	416477.5	9636838.8	32.5593
2	2		17.085	202483.2	5112604.5	17.2736
3	3		19.985	151682.2	5612302.8	18.9619
4	4		22.585	262079.3	9236052.6	31.2052
Total				1032722.3	29597798.6	100.0000

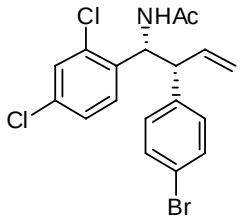
syn (racemic):



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		14.985	405998.3	9412333.2	50.6028
2	2		22.385	257392.8	9188082.5	49.3972
Total				663391.1	18600415.7	100.0000

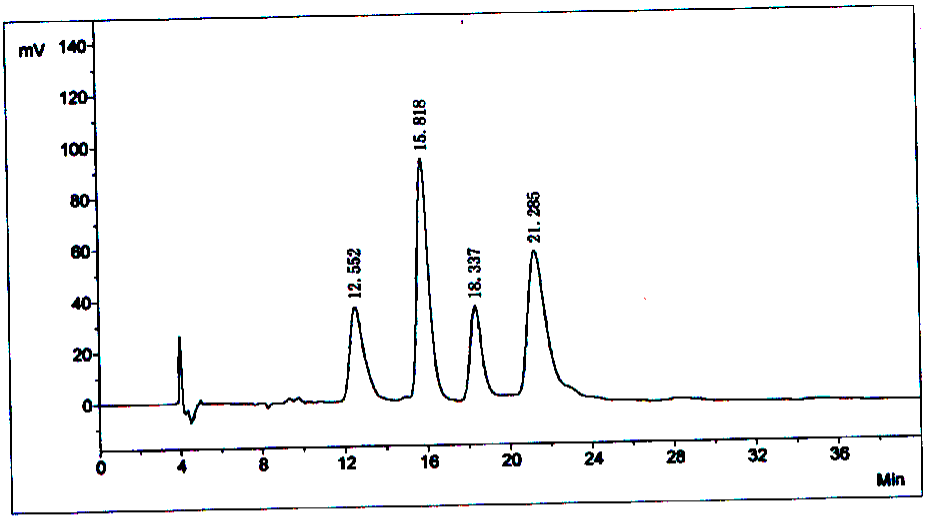


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		15.252	589934.5	13301912.1	95.0934
2	2		17.485	19134.1	478860.6	3.4233
3	3		20.452	905.8	26876.5	0.1921
4	4		23.252	3929.0	180617.9	1.2912
Total				613903.4	13988267.2	100.0000



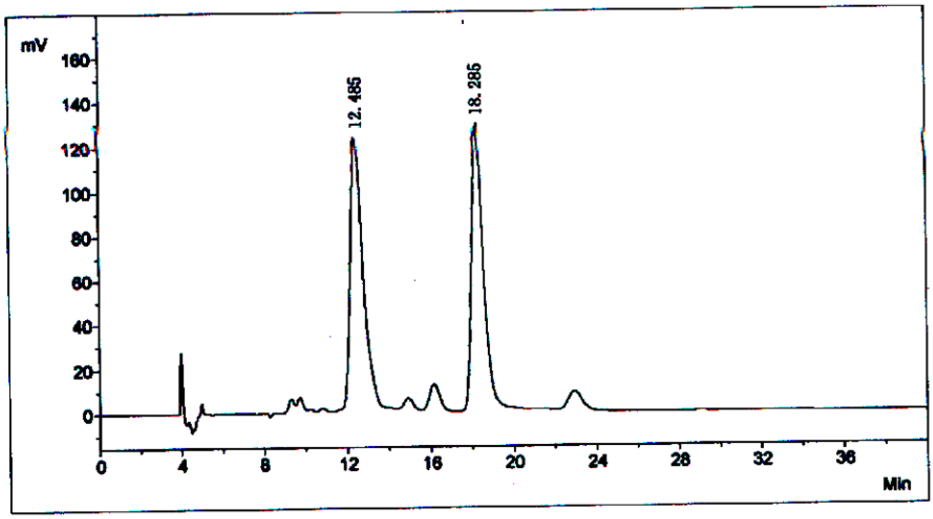
$[\alpha]_D^{20}$ -44.8 (*c* 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.84 (s, 3H), 3.63 (t, 1H, *J* = 8.2 Hz), 5.00 (d, 1H, *J* = 17.2 Hz), 5.12 (d, 1H, *J* = 10.4 Hz), 5.22 (t, 1H, *J* = 8.2 Hz), 5.76-5.87 (m, 2H), 6.92-6.97 (m, 3H), 7.23 (s, 1H), 7.34 (d, 1H, *J* = 8.4 Hz), 7.43 (d, 2H, *J* = 8.4 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.2, 54.4, 55.6, 118.7, 121.2, 127.1, 129.2, 129.9, 130.2, 131.5, 131.8, 132.4, 136.1, 138.3, 140.3, 169.1 ppm; FT-IR (film, cm^{-1}) *ν* 3271, 3065, 1651, 1552, 1488, 1012, 815, 764; ESI-MS (m/z, %): 413.8(M^++H); HRMS (MALDI) for $C_{18}H_{17}NOCl_2Br^+$ (M^++H): calcd. 411.98651, found 411.98618. HPLC: Chiracel Phenomenex Cellulose-2 Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 12.6 min (1*R*, 2*R*), 15.8 min (*anti* isomer), 18.3 min (1*S*, 2*S*), 21.3 min (*anti* isomer).

anti + *syn* (racemic):

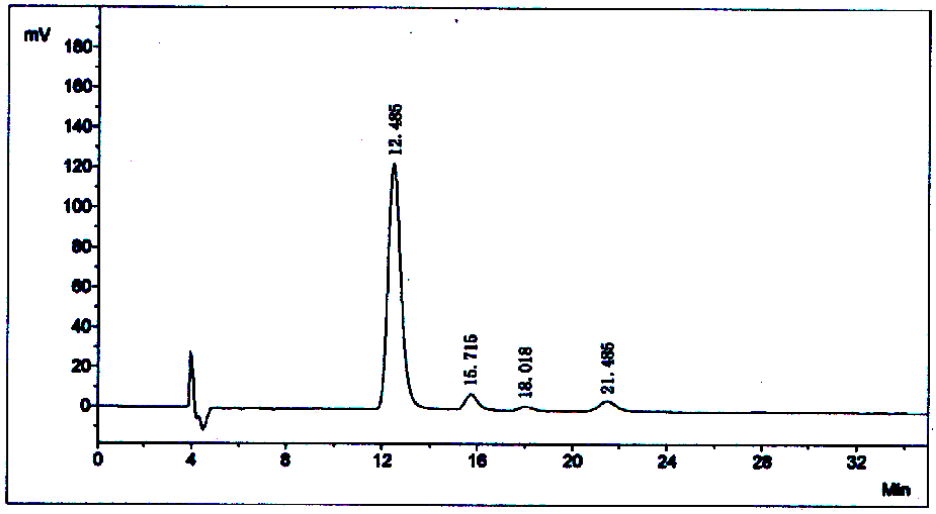


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		12.552	36549.0	1726351.8	16.8210
2	2		15.818	93542.5	3629047.1	35.3602
3	3		18.337	35976.1	1409816.5	13.7368
4	4		21.285	56303.8	3497876.9	34.0821
Total				222371.5	10263092.3	100.0000

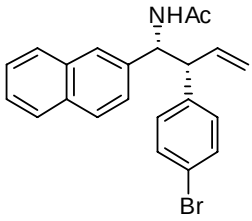
syn (racemic):



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		12.485	122783.3	5232846.8	50.5931
2	2		18.285	129209.5	5110162.5	49.4069
Total				251992.8	10343009.3	100.0000

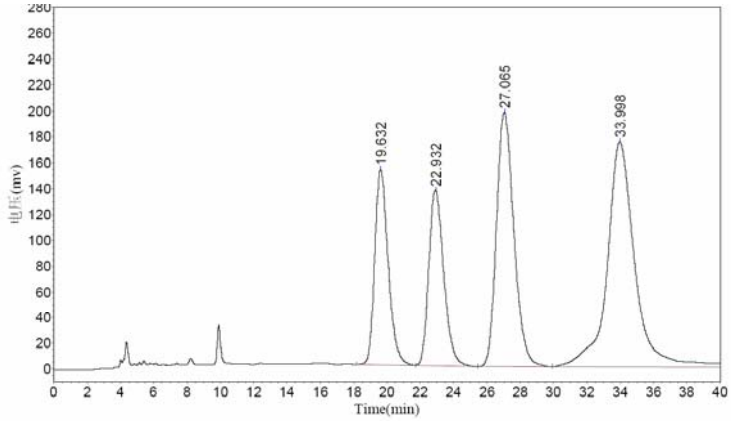


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		12.485	122967.0	4651355.5	88.1253
2	2		15.715	7610.6	279035.4	5.2866
3	3		18.018	2089.2	80683.0	1.5286
4	4		21.485	5125.7	267042.2	5.0594
Total				137792.5	5278116.1	100.0000



$[\alpha]_D^{20}$ -26.9 (*c* 0.98, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.87 (s, 3H), 3.83 (t, 1H, *J* = 7.8 Hz), 5.00 (d, 1H, *J* = 16.8 Hz), 5.08 (d, 1H, *J* = 10.4 Hz), 5.50 (t, 1H, *J* = 8.4 Hz), 5.86-5.94 (m, 2H), 6.99 (d, 2H, *J* = 8.0 Hz), 7.23-7.26 (m, 1H), 7.40 (d, 2H, *J* = 7.2 Hz), 7.46-7.48 (m, 2H), 7.58 (s, 1H), 7.76-7.82 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.3, 54.6, 56.4, 118.0, 120.9, 125.2, 126.0, 126.2, 126.5, 127.6, 127.9, 128.1, 130.1, 131.6, 132.8, 133.0, 136.8, 137.1, 139.0, 169.0 ppm; FT-IR (film, cm^{-1}) *ν* 3348, 3072, 1654, 1537, 1488, 1010, 826, 741; ESI-MS (m/z, %): 396.0 (M^++H), 418.0 (M^++Na); HRMS (MALDI) for $C_{22}H_{21}NOBr^+$ (M^++H): calcd. 394.08010, found 394.07850. HPLC: Chiracel OD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 19.6 min (1*R*, 2*R*), 22.9 min (1*S*, 2*S*), 27.1 min (*anti* isomer), 34.0 min (*anti* isomer).

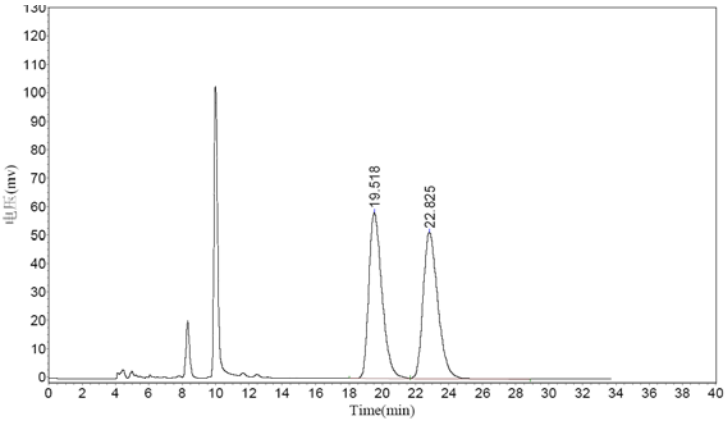
anti + *syn* (racemic):



Results

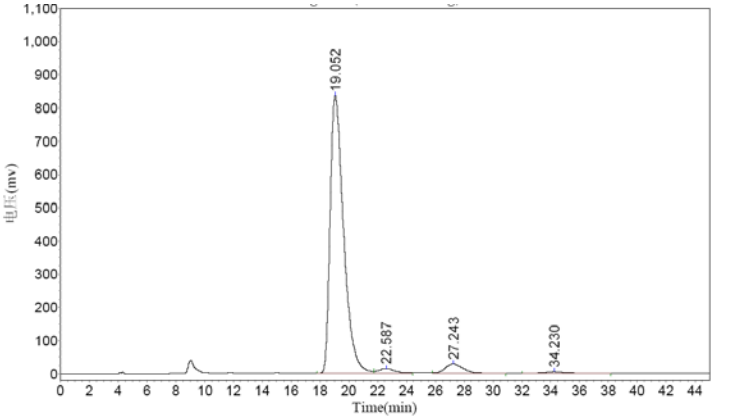
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.632	155175.094	9168435.000	17.3902
2		22.932	138656.906	9013635.000	17.0965
3		27.065	198708.938	14734791.000	27.9481
4		33.998	175354.828	19805112.000	37.5652
Total			667895.766	52721973.000	100.0000

syn (racemic):



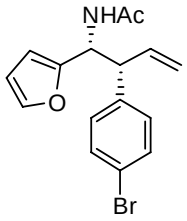
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.518	58429.207	3205463.500	50.285
2		22.825	51525.336	3169053.000	49.714
Total			109954.543	6374516.500	100.0



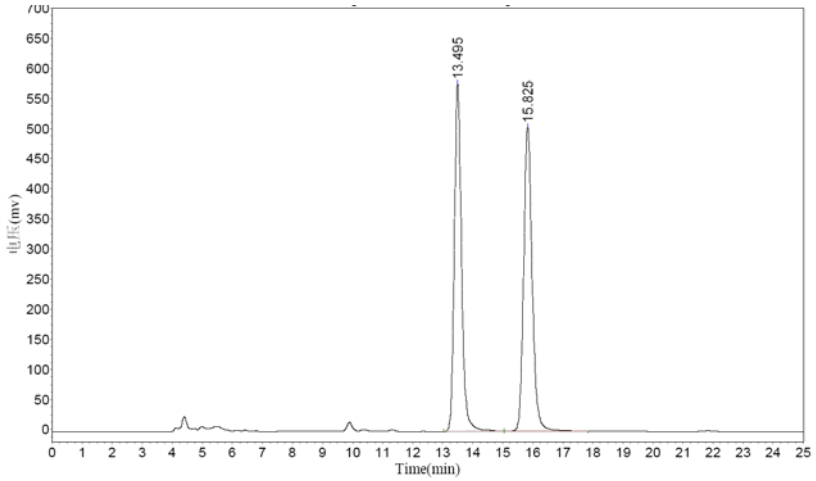
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.052	837058.563	54203344.000	92.5545
2		22.587	14836.774	1254929.500	2.1428
3		27.243	28983.941	2563747.750	4.3777
4		34.230	5019.857	541715.063	0.9250
Total			885899.136	58563736.312	100.00



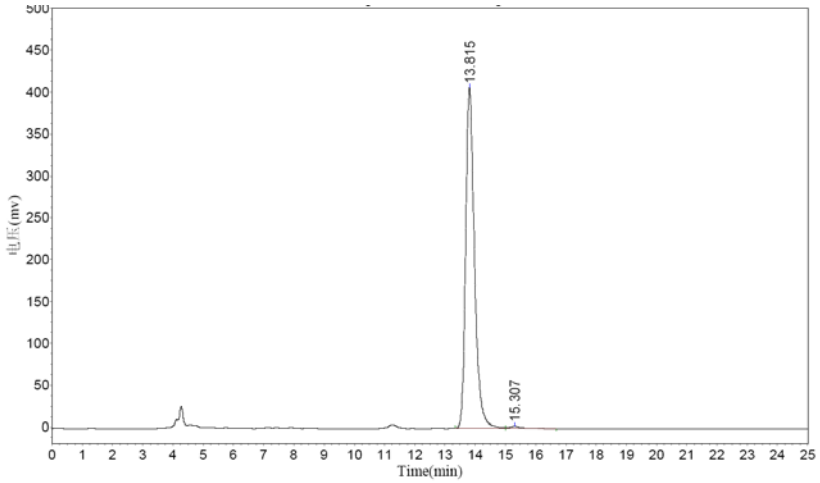
$[\alpha]_D^{20}$ 2.54 (*c* 0.95, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86 (s, 3H), 3.82 (t, 1H, *J* = 8.0 Hz), 5.05 (d, 1H, *J* = 16.8 Hz), 5.12 (d, 1H, *J* = 10.0 Hz), 5.43 (t, 1H, *J* = 8.2 Hz), 5.88-5.99 (m, 2H), 6.03 (s, 1H), 6.26 (s, 1H), 6.98 (d, 2H, *J* = 8.0 Hz), 7.34 (s, 1H), 7.38 (d, 2H, *J* = 8.4 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.1, 50.3, 53.2, 108.0, 110.2, 118.1, 120.8, 129.9, 131.4, 136.4, 138.9, 141.8, 151.9, 168.9 ppm; FT-IR (film, cm^{-1}) ν 3324, 1654, 1539, 1490, 1074, 1011, 923, 773; ESI-MS (m/z, %): 334.0 (M^++H), 356.9 (M^++Na); HRMS (MALDI) for $C_{16}H_{17}NO_2Br^+$ (M^++H): calcd. 334.04372, found 334.04419. HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 13.8 min (1*R*, 2*R*), 15.3 min (1*S*, 2*S*).

syn (racemic):



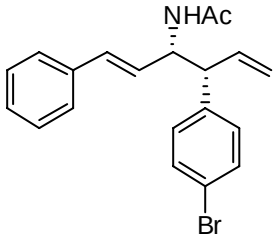
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.495	577425.625	9625628.000	49.2609
2		15.825	504992.500	9914483.000	50.7391
Total			1082418.125	19540111.000	100.0000



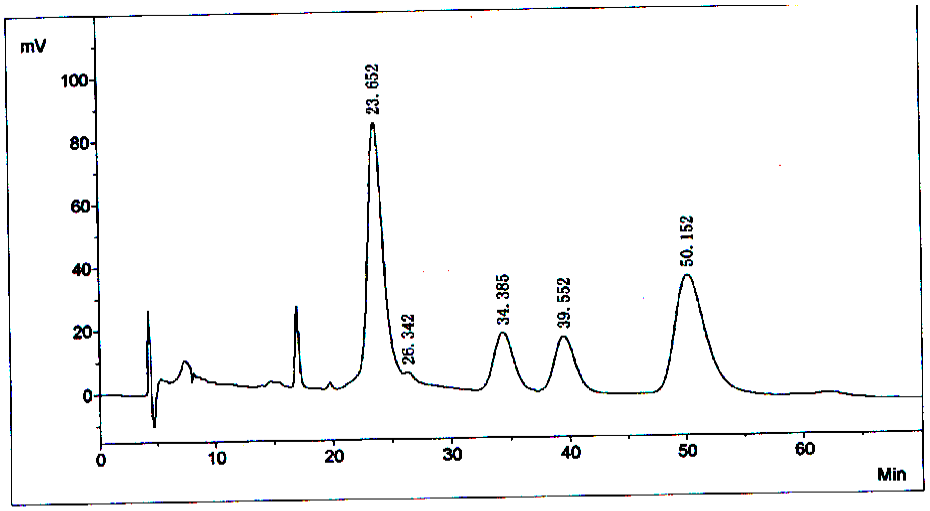
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.815	407058.406	8250672.500	99.0622
2		15.307	2406.886	78106.281	0.9378
Total			409465.292	8328778.781	100.0000



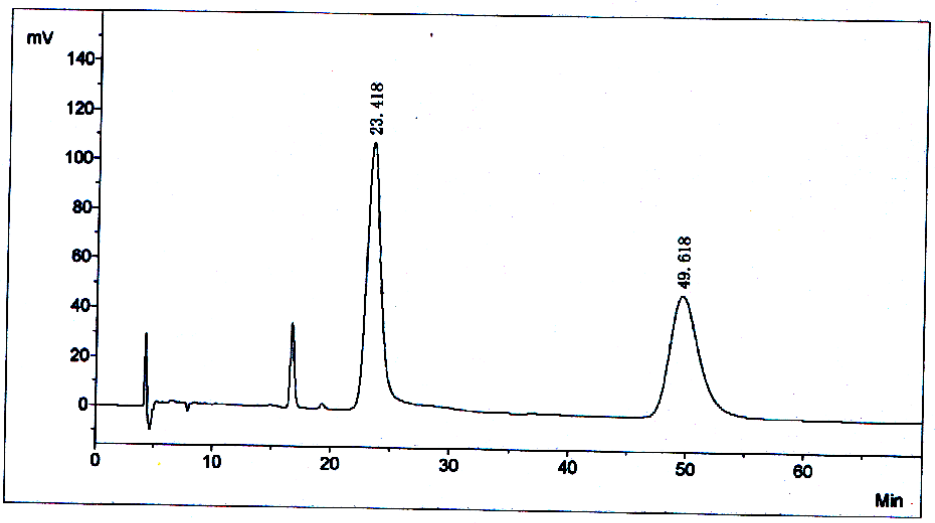
$[\alpha]_D^{20}$ -19.0 (*c* 0.88, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.96 (s, 3H), 3.58 (t, 1H, *J* = 7.8 Hz), 4.98-5.04 (m, 1H), 5.19 (d, 1H, *J* = 17.2 Hz), 5.25 (d, 1H, *J* = 10.0 Hz), 5.51 (d, 1H, *J* = 9.2 Hz), 6.00-6.10 (m, 2H), 6.42 (d, 1H, *J* = 16.0 Hz), 7.14 (d, 2H, *J* = 8.4 Hz), 7.23-7.25 (m, 1H), 7.29-7.30 (m, 4H), 7.45 (d, 2H, *J* = 8.0 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.4, 54.0, 118.7, 120.8, 126.4, 126.5, 127.8, 128.6, 129.9, 131.7, 131.9, 136.3, 136.4, 139.3, 169.1 ppm; FT-IR (film, cm^{-1}) *v* 3309, 2977, 1651, 1528, 1488, 1075, 1011, 749; ESI-MS (m/z, %): 370.1 (M^++H), 392.1(M^++Na); HRMS (MALDI) for $C_{20}H_{20}BrNNaO^+$ (M^++Na): calcd. 392.06205, found 392.06274. HPLC: Chiracel AS-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 23.7 min (1*R*, 2*R*), 34.4 min (*anti* isomer), 40.0 (*anti* isomer), 50.2 min (1*S*, 2*S*).

anti + *syn* (racemic):

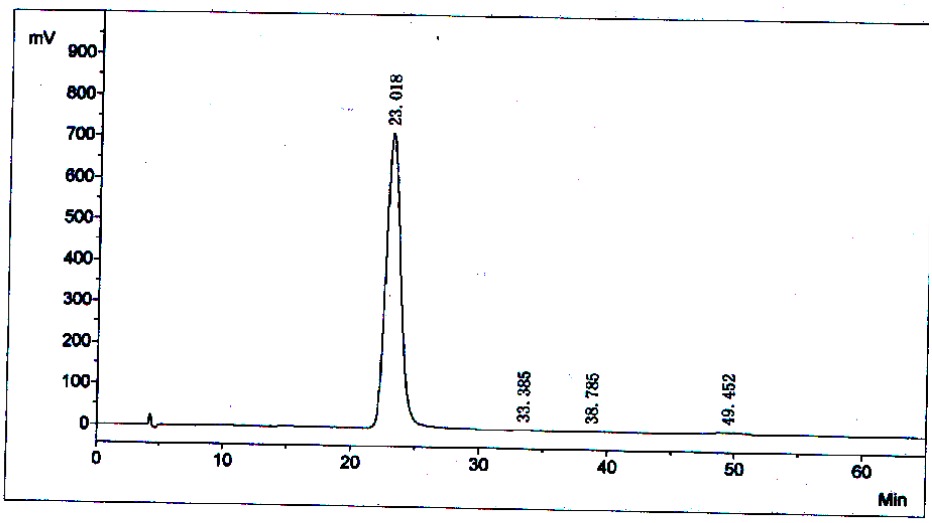


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		23.652	83225.7	7668114.0	40.3099
2	2		26.342	4123.4	256686.1	1.3494
3	3		34.385	18298.1	2098884.3	11.0335
4	4		39.552	17536.5	2119040.9	11.1394
5	5		50.152	37763.8	6880162.8	36.1678
Total				160947.5	19022888.1	100.0000

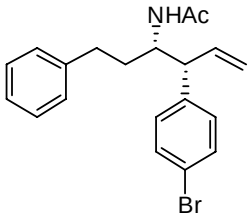
syn (racemic):



No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		23.418	107378.8	8828449.2	50.1816
2	2		49.618	49365.8	8764549.1	49.8184
Total				156744.6	17592998.3	100.0000

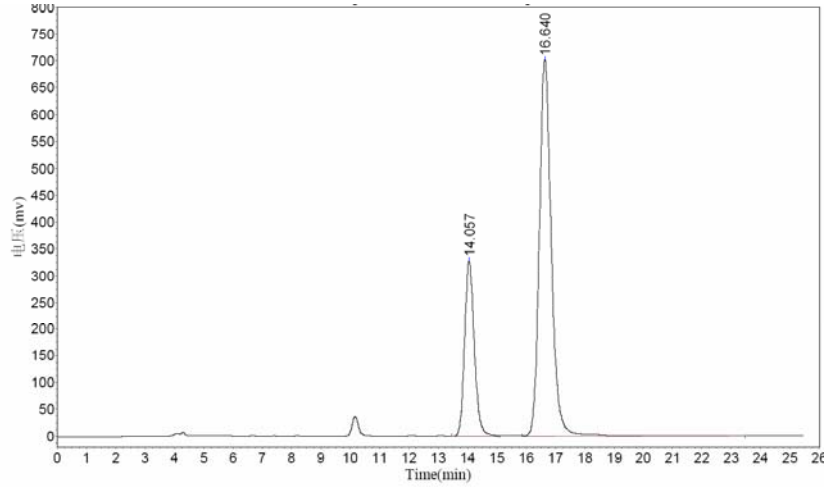


No.	PeakNo	ID. Name	R. Time	PeakHeight	PeakArea	PerCent
1	1		23.018	712791.9	56292673.9	98.2470
2	2		33.385	1643.0	154568.7	0.2698
3	3		38.785	257.8	24816.5	0.0433
4	4		49.452	5062.0	825033.5	1.4399
Total				719754.7	57297092.5	100.0000



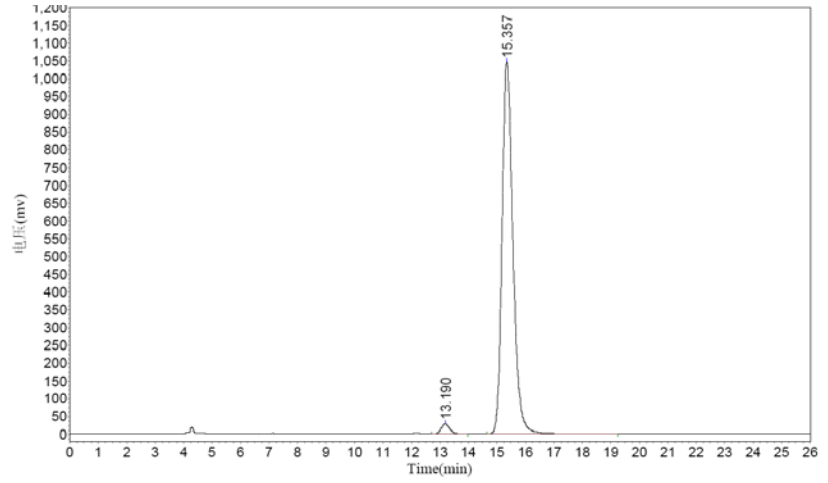
$[\alpha]_D^{20}$ -48.1 (*c* 0.98, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.51-1.61 (m, 1H), 1.85 (s, 3H), 1.91-1.98 (m, 1H), 2.55-2.70 (m, 2H), 3.43 (t, 1H, *J* = 7.6 Hz), 4.34-4.41 (m, 1H), 5.14 (d, 1H, *J* = 16.4 Hz), 5.18 (d, 1H, *J* = 9.6 Hz), 5.29-5.31 (m, 1H), 5.93-6.02 (m, 1H), 7.07 (d, 2H, *J* = 8.0 Hz), 7.12 (d, 2H, *J* = 7.6 Hz), 7.16-7.19 (m, 1H), 7.24-7.28 (m, 2H), 7.41 (d, 2H, *J* = 8.0 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.3, 32.4, 33.9, 52.0, 54.1, 117.9, 120.5, 125.9, 128.2, 128.4, 129.7, 131.5, 137.0, 139.8, 141.5, 169.6 ppm; FT-IR (film, cm^{-1}) *ν* 3327, 2949, 2926, 1649, 1535, 1489, 1010, 922, 701; ESI-MS (m/z, %): 372.0 (M^++H), 394.0 (M^++Na); HRMS (MALDI) for $C_{20}H_{23}NOBr$ (M^++H): calcd. 372.09575, found 372.09501. HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 14.0 min (1*S*, 2*S*), 16.6 min (1*R*, 2*R*).

syn isomers:



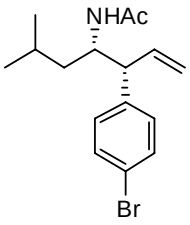
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.057	328000.031	7542902.500	27.4163
2		16.640	699828.563	19969620.000	72.5837
Total			1027828.594	27512522.500	100.000



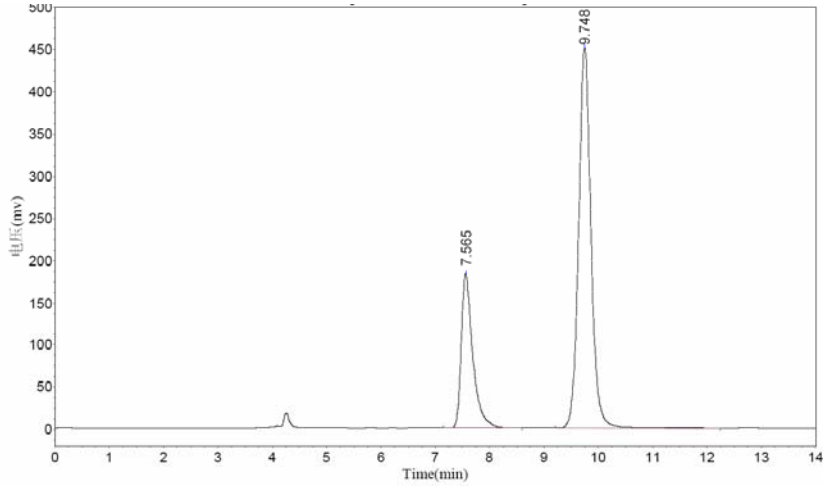
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.190	28013.982	607137.688	2.1316
2		15.357	1048056.563	27875518.000	97.8684
Total			1076070.545	28482655.688	100.000



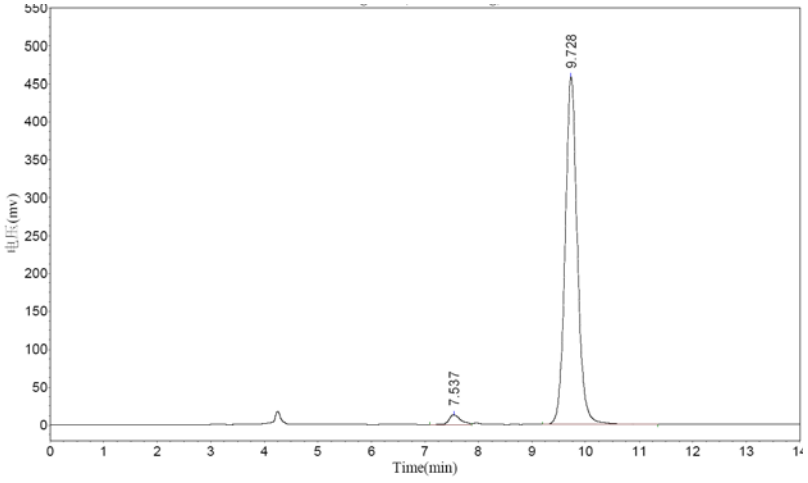
$[\alpha]_D^{20}$ -81.8 (*c* 0.81, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 0.84 (d, 3H, *J* = 2.8 Hz), 0.86 (d, 3H, *J* = 2.8 Hz), 1.13-1.20 (m. 1H), 1.25-1.33 (m, 1H), 1.51-1.61 (m, 1H), 1.86 (s, 3H), 3.39 (dd, 1H, *J* = 6.0, 8.8 Hz), 4.33-4.40 (m, 1H), 5.11-5.19 (m, 3H), 5.97-6.01 (m, 1H), 7.09-7.12 (m, 2H), 7.41-7.43 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 23.3, 23.6, 24.9, 41.3, 50.5, 54.4, 117.9, 120.4, 129.9, 131.5, 137.1, 140.1, 169.4 ppm; FT-IR (film, cm^{-1}) *ν* 3304, 2949, 1649, 1555, 1073, 1010, 914, 801; ESI-MS (m/z, %): 324.0 (M^++H), 346.1(M^++Na); HRMS (MALDI) for $C_{16}H_{22}BrNONa^+$ (M^++Na): calcd. 346.07770, found 346.07729. HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 7.6 min (1*S*, 2*S*), 9.7 min (1*R*, 2*R*).

syn isomers:



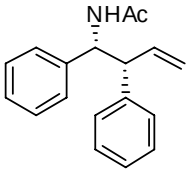
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.565	183588.797	2711662.750	27.5100
2		9.748	450607.438	7145355.500	72.4900
Total			634196.234	9857018.250	100.000



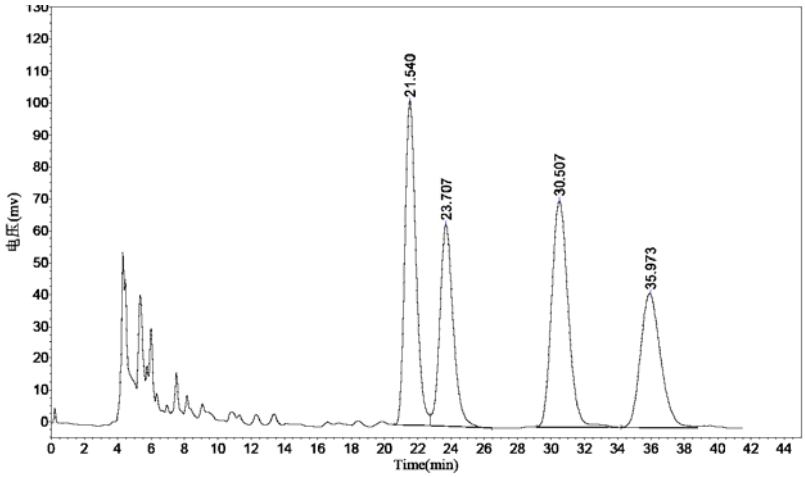
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		7.537	13403.090	194162.859	2.6041
2		9.728	458061.344	7261924.000	97.3959
Total			471464.434	7456086.859	100.000



$[\alpha]_D^{24}$ -35.1 (*c* 0.22, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 1.81 (s, 3H), 3.73 (t, 1H, *J* = 8.0 Hz), 4.99 (d, 1H, *J* = 17.4 Hz), 5.07 (d, 1H, *J* = 10.2 Hz), 5.34 (t, 1H, *J* = 8.1 Hz), 5.87-5.98 (m, 2H), 7.08-7.13 (m, 4H), 7.22-7.30 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.2, 55.3, 56.5, 117.5, 126.9, 127.3, 127.4, 128.1, 128.3, 128.4, 137.4, 139.9, 140.1, 168.9 ppm; FT-IR (film, cm^{-1}) ν 3354, 3032, 1650, 1527, 1370, 911, 758, 699; ESI-MS (m/z, %): 266.2 (M^++H), 288.1 (M^++Na); HRMS (MALDI) for $C_{18}H_{19}NONa^+$ (M^++Na): calcd. 288.13589, found 288.13652. HPLC: Chiracel OD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 21.5 min (1*R*, 2*R*), 23.7 min (*anti* isomer), 30.5 min (1*S*, 2*S*), 36.0 min (*anti* isomer).

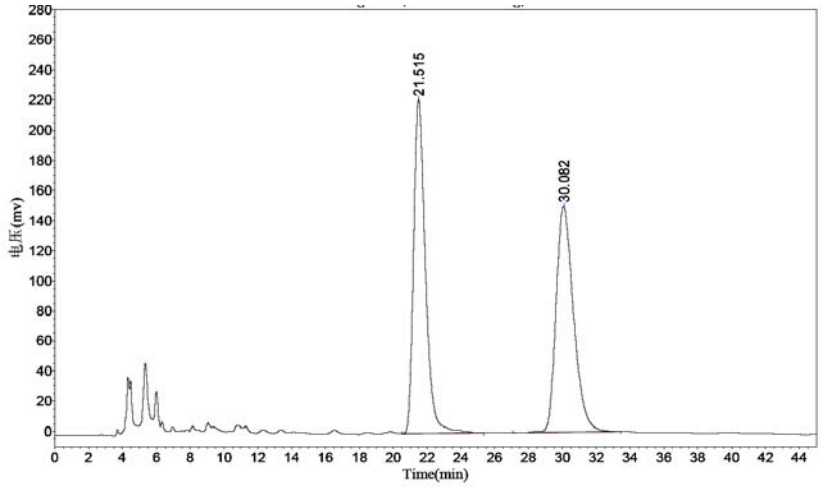
anti + *syn* (racemic):



Results

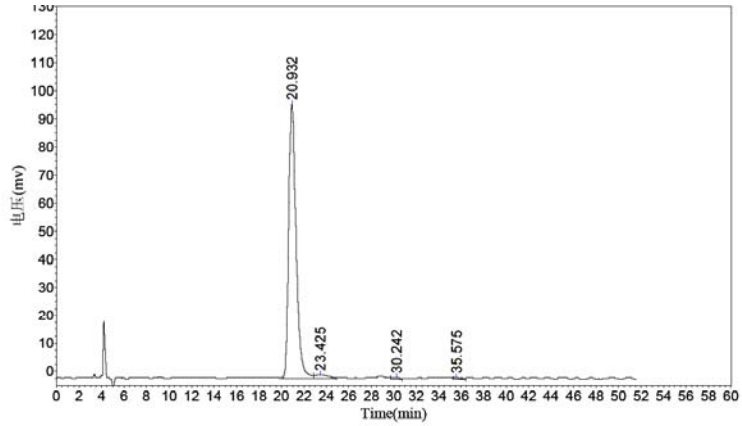
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.540	102278.945	4780775.500	28.2654
2		23.707	63823.551	3545753.500	20.9636
3		30.507	71157.898	5054018.500	29.8809
4		35.973	42171.953	3533311.750	20.8900
Total			279432.348	16913859.250	100.0000

syn (racemic):



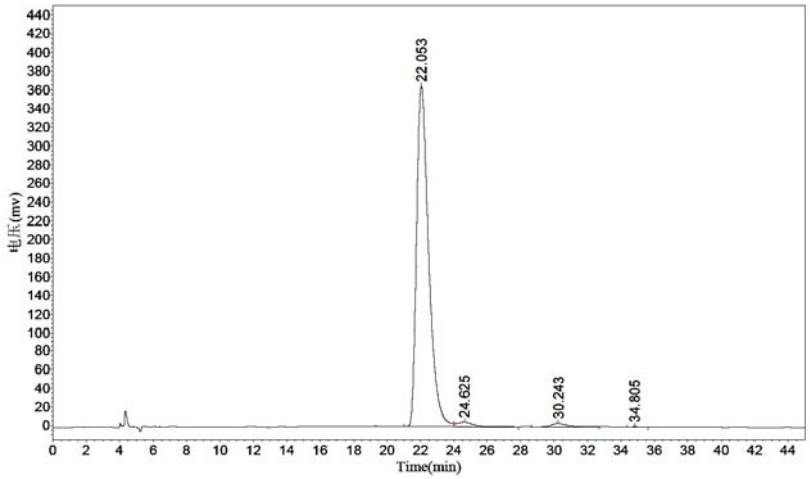
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.515	222470.594	11018434.000	49.1309
2		30.082	151364.719	11408274.000	50.8691
Total			373835.313	22426708.000	100.000



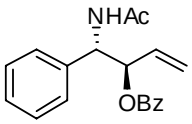
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.932	97727.148	4464995.500	96.5827
2		23.425	1397.497	122887.766	2.6582
3		30.242	401.802	17723.916	0.3834
4		35.575	301.034	17367.186	0.3757
Total			99827.482	4622974.367	100.0000

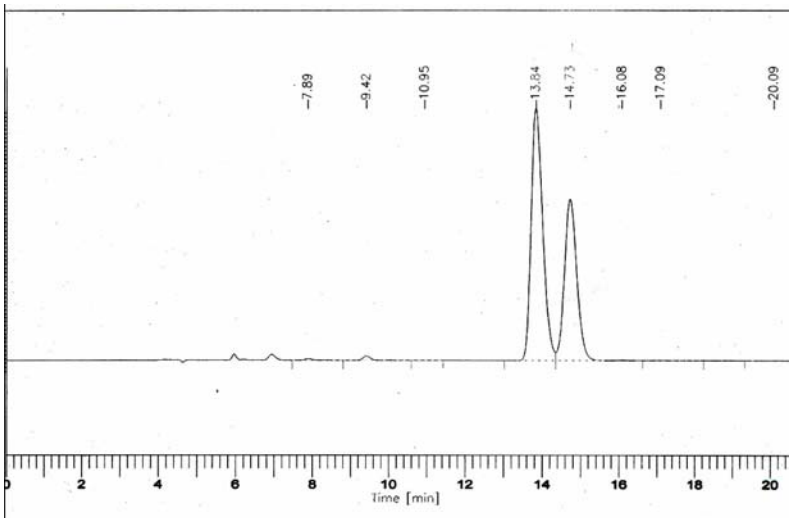


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.053	365619.438	18418640.000	96.4609
2		24.625	5204.182	403669.188	2.1141
3		30.243	3844.724	258444.609	1.3535
4		34.805	261.969	13648.603	0.0715
Total			374930.312	19094402.399	100.0000

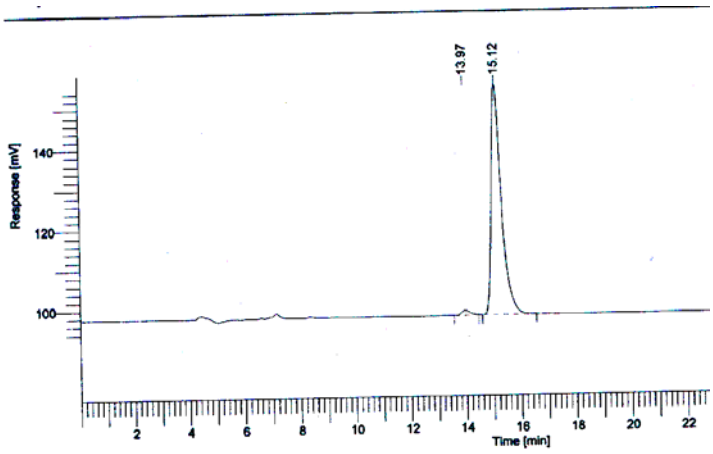


$[\alpha]_D^{25}$ 87.5(*c* 0.42, $CHCl_3$) ; ^1H NMR (400 MHz, $CDCl_3$): δ 2.02 (s, 3H), 5.28-5.45 (m, 3H), 5.73-5.87 (m, 2H), 6.19 (d, 1H, J = 8.0Hz), 7.26-7.46(m, 7H), 7.57 (t, 1H, J = 7.6Hz) , 7.99 (d, 2H, J = 7.2Hz), ppm; ^{13}C NMR (400 MHz, $CDCl_3$): δ 23.4, 55.7, 76.5, 119.1, 127.4, 127.9, 128.5, 128.6, 129.7, 129.8, 132.4, 133.3, 137.5, 165.6, 169.3 ppm; ESI-MS (m/z, %): 332.0 (M^++ Na), 347.8 (M^++K), 364.0 (M^++MeOH+ Na) ; HPLC: Chiracel AD-H Column (250 mm); detected at 254 nm; *n*-hexane / *i*-propanol = 80/20; flow = 0.7 mL/min; Retention time: 14.0 min (1*R*, 2*S*), 15.1 min (1*S*, 2*R*).



DEFAULT REPORT

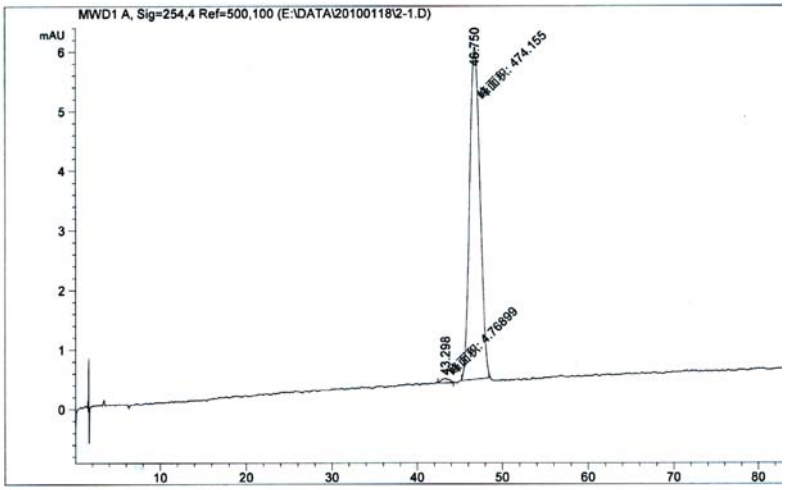
Time [min]	Area [uv*sec]	Height [uv]	Area [%]	BL	
7.888	10958.00	688.33	0.25	BB	
9.421	29981.50	2100.29	0.69	BB	
10.951	1039.00	69.97	0.02	BB	
13.840	2543896.93	120720.58	58.62	BV	✓
14.728	1742800.51	77944.11	40.16	VE	✓
16.081	6994.00	224.41	0.16	EV	
17.092	3362.06	71.34	0.08	VB	
20.092	951.50	20.82	0.02	BB	
	4339983.50	201839.86	100.00		



DEFAULT REPORT

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]
1	13.971	24297.09	1155.23	1.64
2	15.125	1458809.16	57353.81	98.36
		1483106.24	58509.04	100.00

HPLC-MS: Kromasil C18 (150 × 4.5 mm , Φ 5 μm); detected at 254 nm; CH_3CN / H_2O= 30/70; flow = 1.0mL/min; Retention time: 43.3 min (*syn*), 46.8 min (*anti*).

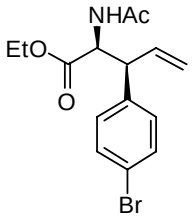


面积百分比报告

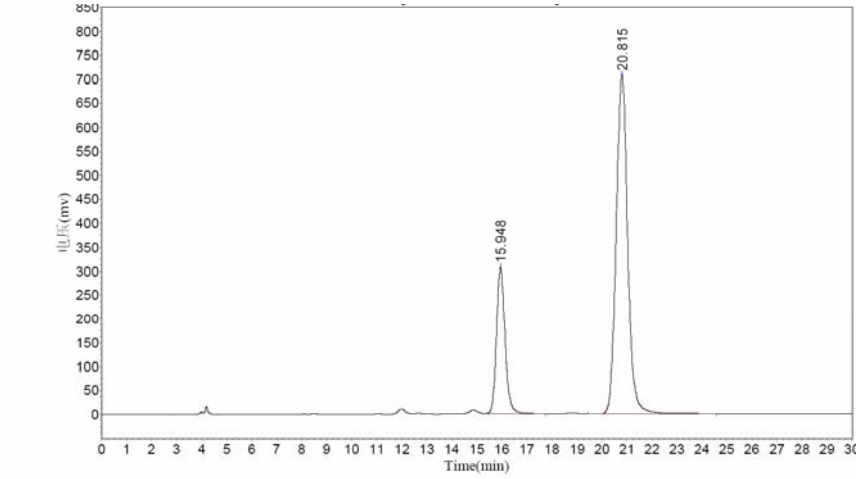
排序 : 信号
乘积因子: : 1.0000
稀释因子: : 1.0000
内标使用乘积因子和稀释因子

信号 1: MWD1 A, Sig=254,4 Ref=500,100

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	43.298	MM	1.0290	4.76899	7.72442e-2	0.9958
2	46.750	MM	1.4169	474.15457	5.57736	99.0042
总量 :				478.92356	5.65461	

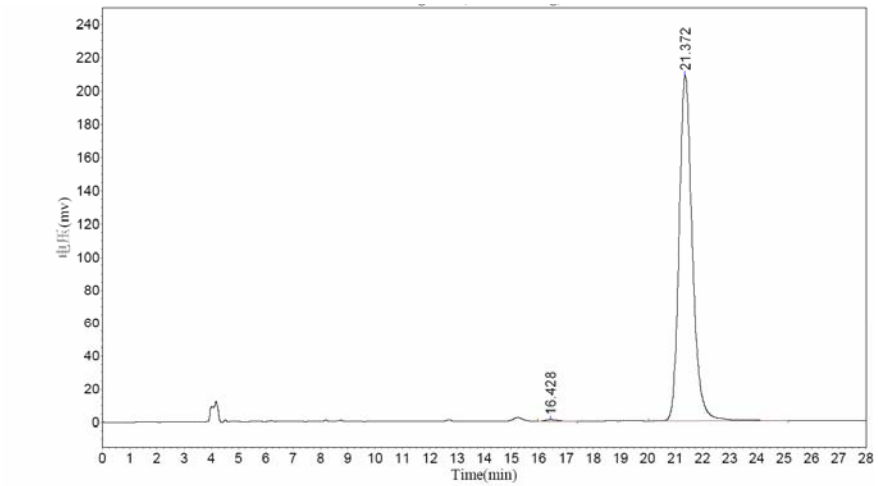


$[\alpha]_D^{22}$ 86.8 (*c* 0.99, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21 (t, 3H, *J* = 7.2 Hz), 1.93 (s, 3H), 3.78 (t, 1H, *J* = 7.4 Hz), 4.13 (q, 2H, *J* = 6.8 Hz), 4.96-5.00 (m, 1H), 5.14-5.21 (m, 2H), 5.94-6.05 (m, 2H), 7.08-7.10 (m, 2H), 7.43-7.45 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 23.0, 51.7, 55.6, 61.4, 118.3, 121.2, 129.8, 131.7, 135.7, 138.0, 169.7, 171.0 ppm; FT-IR (film, cm^{-1}) ν 3325, 2988, 1746, 1655, 1537, 1372, 1180, 824, 508; ESI-MS (m/z, %): 340.1 (M^++H) , 362.0 (M^++Na); HRMS (MALDI) for $C_{15}H_{19}BrNO_3^+$ (M^++H): calcd. 340.05428, found 340.0539. HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 15.9 min (1*R*, 2*R*), 20.8 min (1*S*, 2*S*).



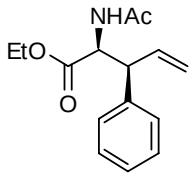
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.948	307475.469	7355766.000	24.4933
2		20.815	708846.188	22675970.000	75.5067
Total			1016321.656	30031736.000	100.000

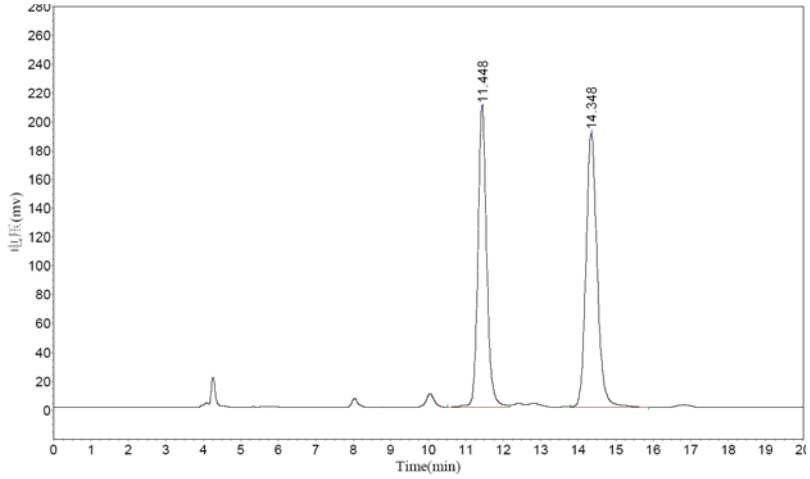


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.428	1012.834	27274.248	0.3854
2		21.372	208684.516	7049153.000	99.6146
Total			209697.350	7076427.248	100.000

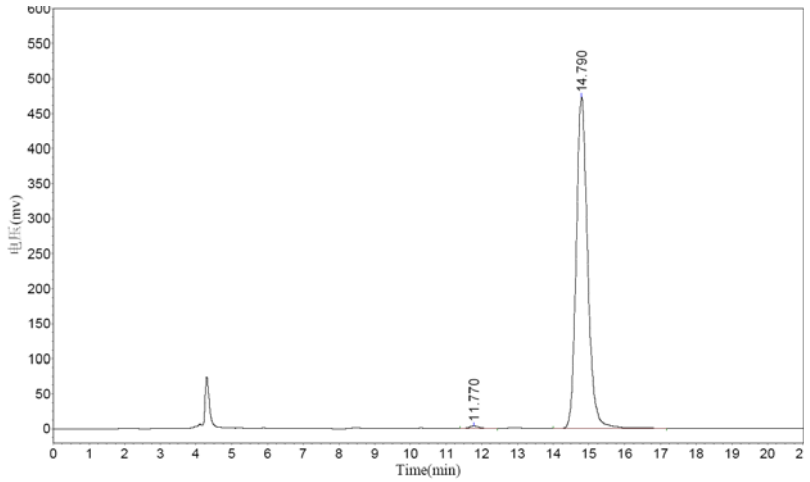


$[\alpha]_D^{22}$ 77.3 (*c* 0.98, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): 1.20 (t, 3H, *J* = 7.2 Hz), 1.91 (s, 3H), 3.81 (t, 1H, *J* = 7.2 Hz), 4.11 (q, 2H, *J* = 7.2 Hz), 4.98 (t, 1H, *J* = 7.6 Hz), 5.15-5.19 (m, 2H), 5.78 (d, 1H, *J* = 8.0 Hz), 6.01-6.10 (m, 1H), 7.18-7.33 (m, 5H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 23.0, 52.1, 55.7, 61.3, 117.7, 127.4, 128.1, 128.7, 136.2, 138.8, 169.6, 171.2 ppm; FT-IR (film, cm^{-1}) *ν* 3349, 2986, 1746, 1656, 1534, 1374, 1226, 704; ESI-MS (m/z, %): 262.1 (M^++H), 284.0 (M^++Na); HRMS (MALDI) for $C_{15}H_{19}NO_3Na^+$ (M^++Na): calcd. 284.12572, found 284.1265. HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 11.4 min (1*R*, 2*R*), 14.3 min (1*S*, 2*S*).



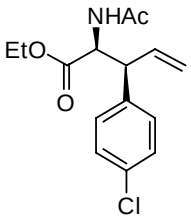
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.448	208894.734	3400284.250	46.4123
2		14.348	189202.484	3925965.000	53.5877
Total			398097.219	7326249.250	100.00

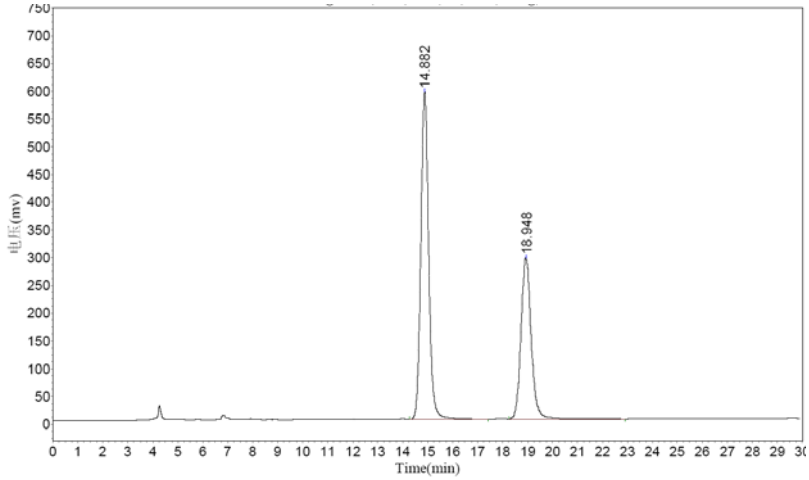


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		11.770	3878.217	71688.859	0.6743
2		14.790	473351.250	10559143.000	99.3257
Total			477229.467	10630831.859	100.00

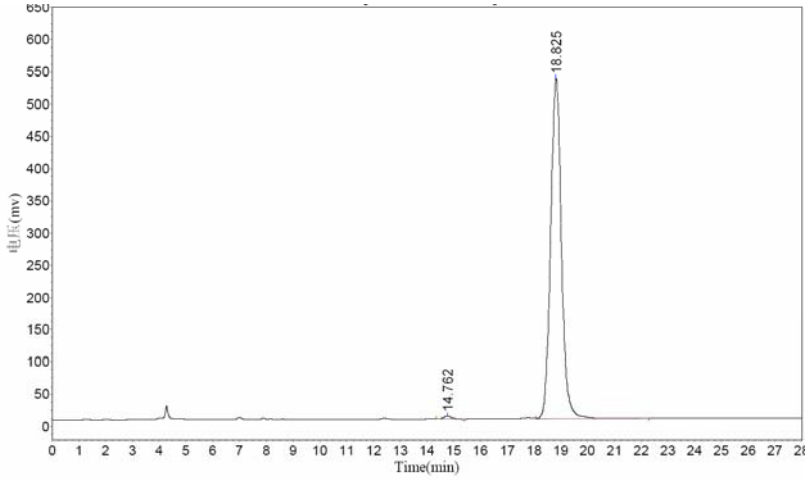


$[\alpha]_D^{20}$ 97.5 (*c* 1.02, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 1.21 (t, 3H, *J* = 6.8 Hz), 1.93 (s, 3H), 3.80 (t, 1H, *J* = 7.2 Hz), 4.13 (q, 2H, *J* = 6.8 Hz), 4.99 (t, 1H, *J* = 7.6 Hz), 5.14-5.21 (m, 2H), 5.97-6.04 (m, 2H), 7.15 (d, 2H, *J* = 7.6 Hz), 7.29 (d, 2H, *J* = 7.2 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 22.9, 51.6, 55.6, 61.3, 118.2, 128.7, 129.4, 133.1, 135.7, 137.4, 169.7, 171.0 ppm; FT-IR (film, cm^{-1}) *ν* 3333, 2993, 1741, 1656, 1536, 1375, 1226, 825; ESI-MS (m/z, %): 296.2 (M^++H), 318.1 (M^++Na); HRMS (MALDI) for $C_{15}H_{18}ClNNaO_3^+$ (M^++Na): calcd. 318.08674, found 318.08718. HPLC: Chiracel AD-H Column (250 mm); detected at 214 nm; *n*-hexane / *i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 14.9 min (1*R*, 2*R*), 18.9 min (1*S*, 2*S*).



Results

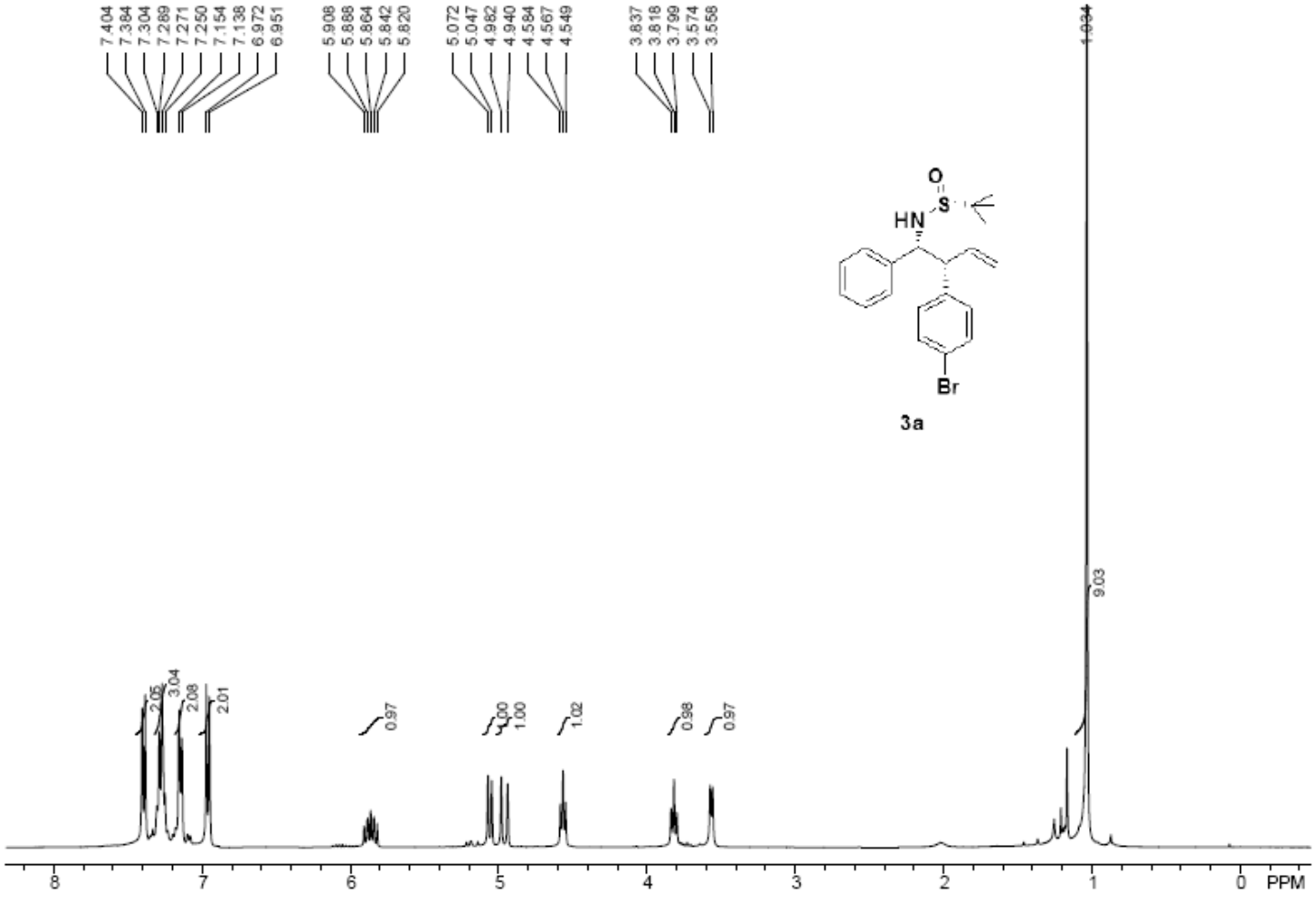
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.882	584796.563	12862662.000	62.6878
2		18.948	290421.094	7655955.500	37.3122
Total			875217.656	20518617.500	100.000

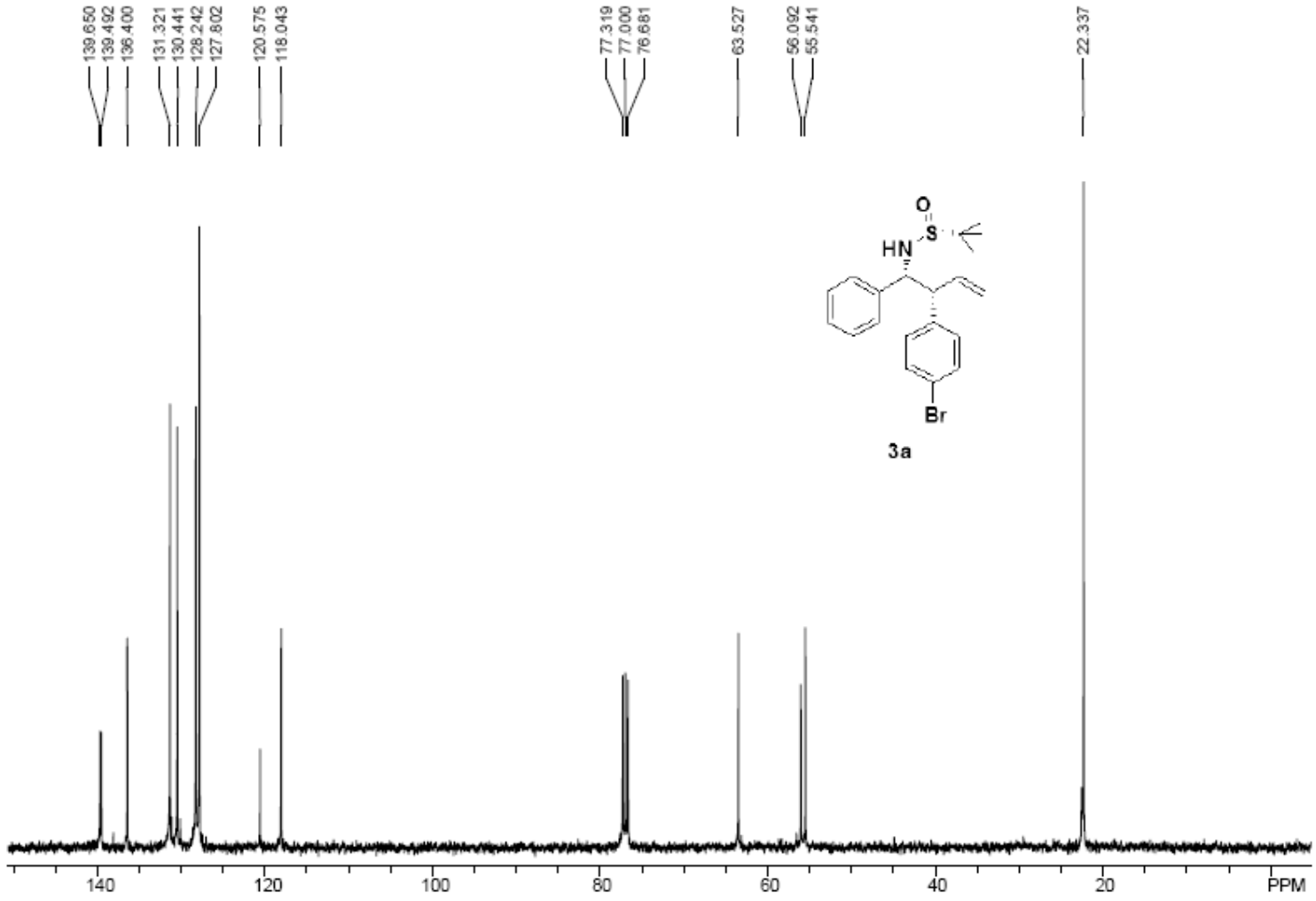


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		14.762	4247.648	86941.891	0.5844
2		18.825	528096.188	14790012.000	99.4156
Total			532343.836	14876953.891	100.000

5. Copies of ^{1}H and ^{13}C NMR spectra of products 3a-k, 4, 5, 7a-c and their corresponding acetates.

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127.802
120.575
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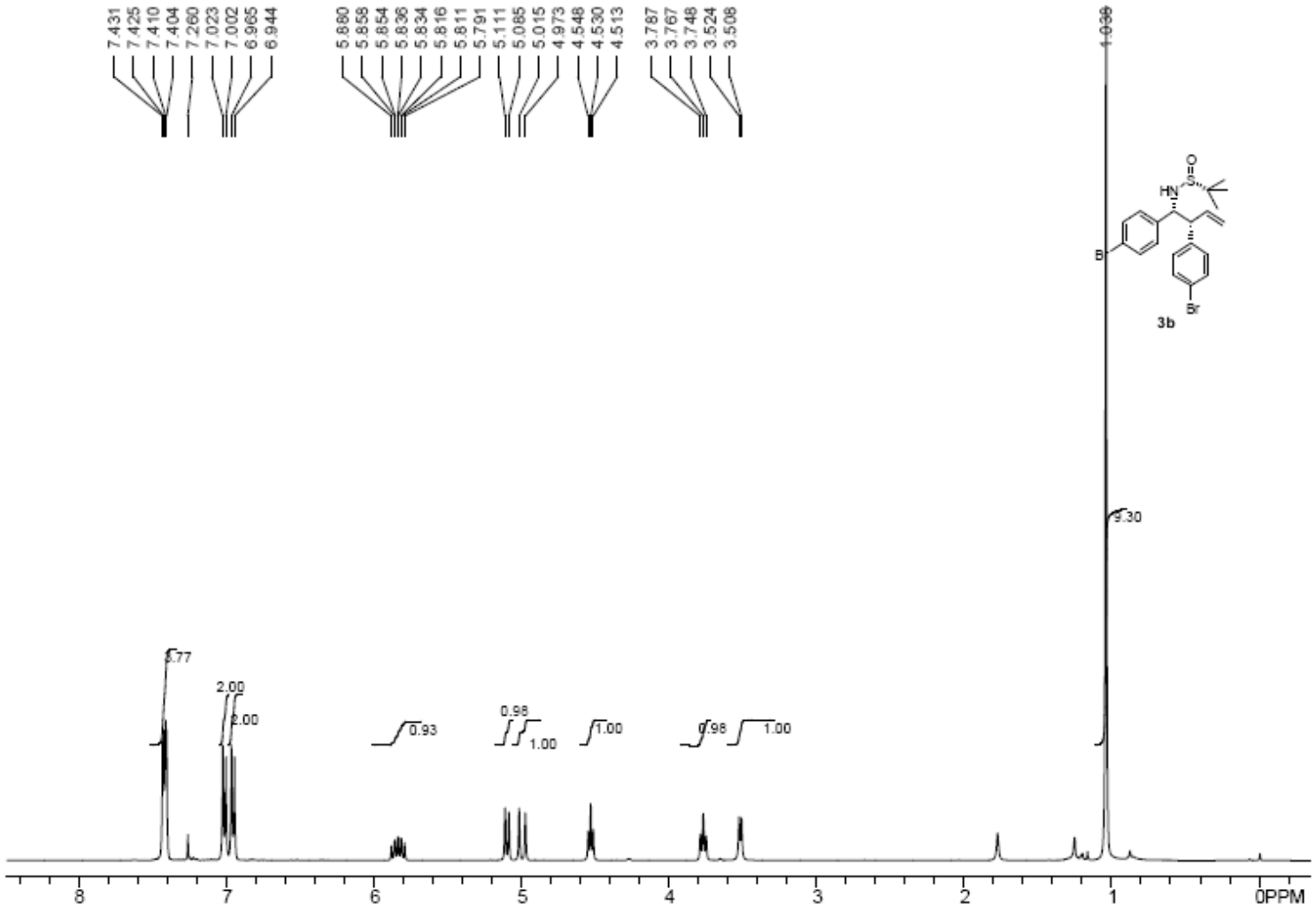
77.319
77.000
76.681
63.527
56.092
55.541
22.337
O
S
HN
Br
3a
140
120
100
80
60
40
20
PPM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5.834
5.816
5.811
5.791
5.111
5.085
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4.513
3.787
3.767
3.748
3.524
3.508
1.036
9.30
3.77
2.00
2.00
0.93
0.98
1.00
1.00
0.98
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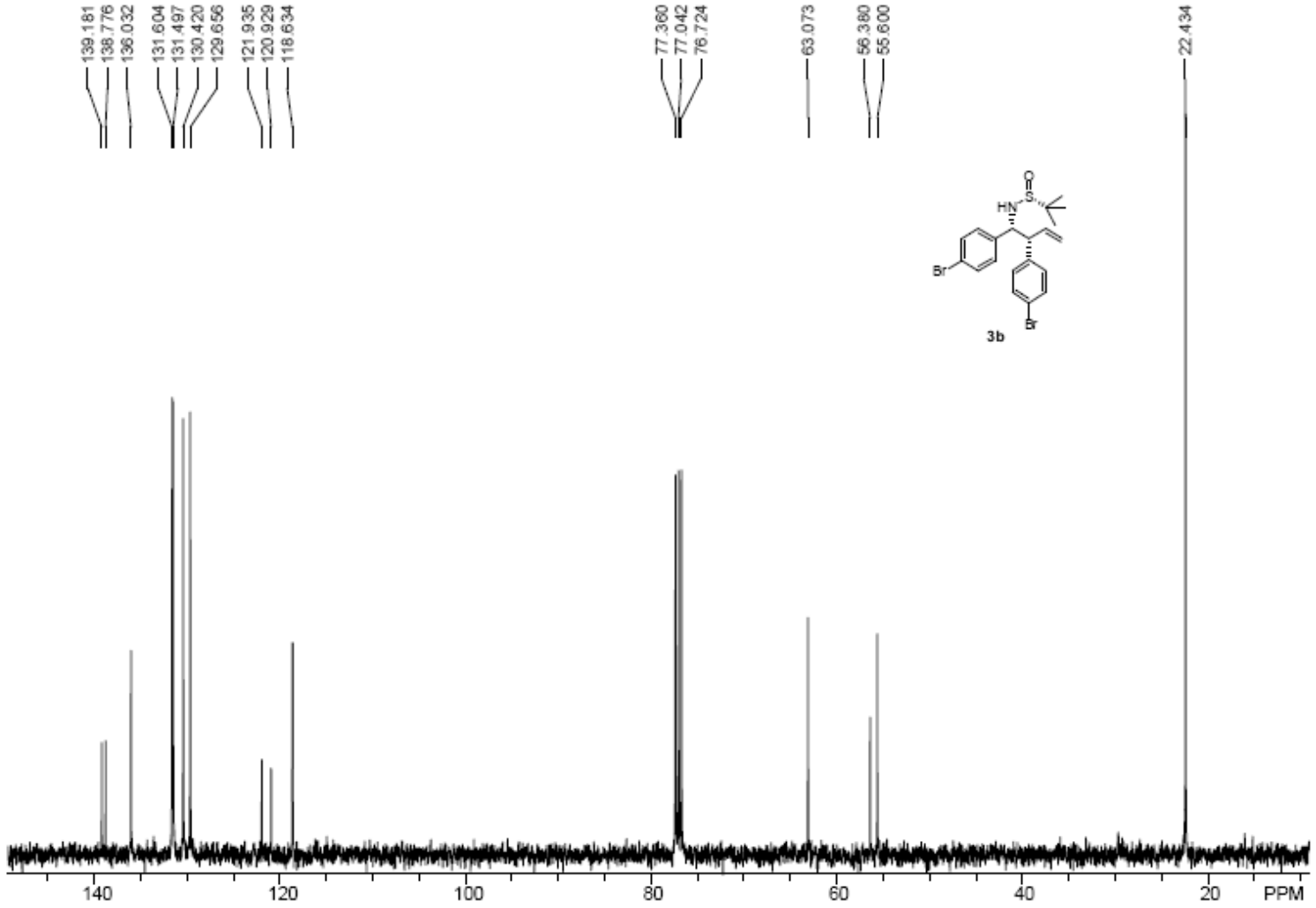
HN
O
S
Br
Br
3b
8
7
6
5
4
3
2
1
0PPM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130.420
129.656
121.935
120.929
118.634
77.360
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76.724
63.073
56.380
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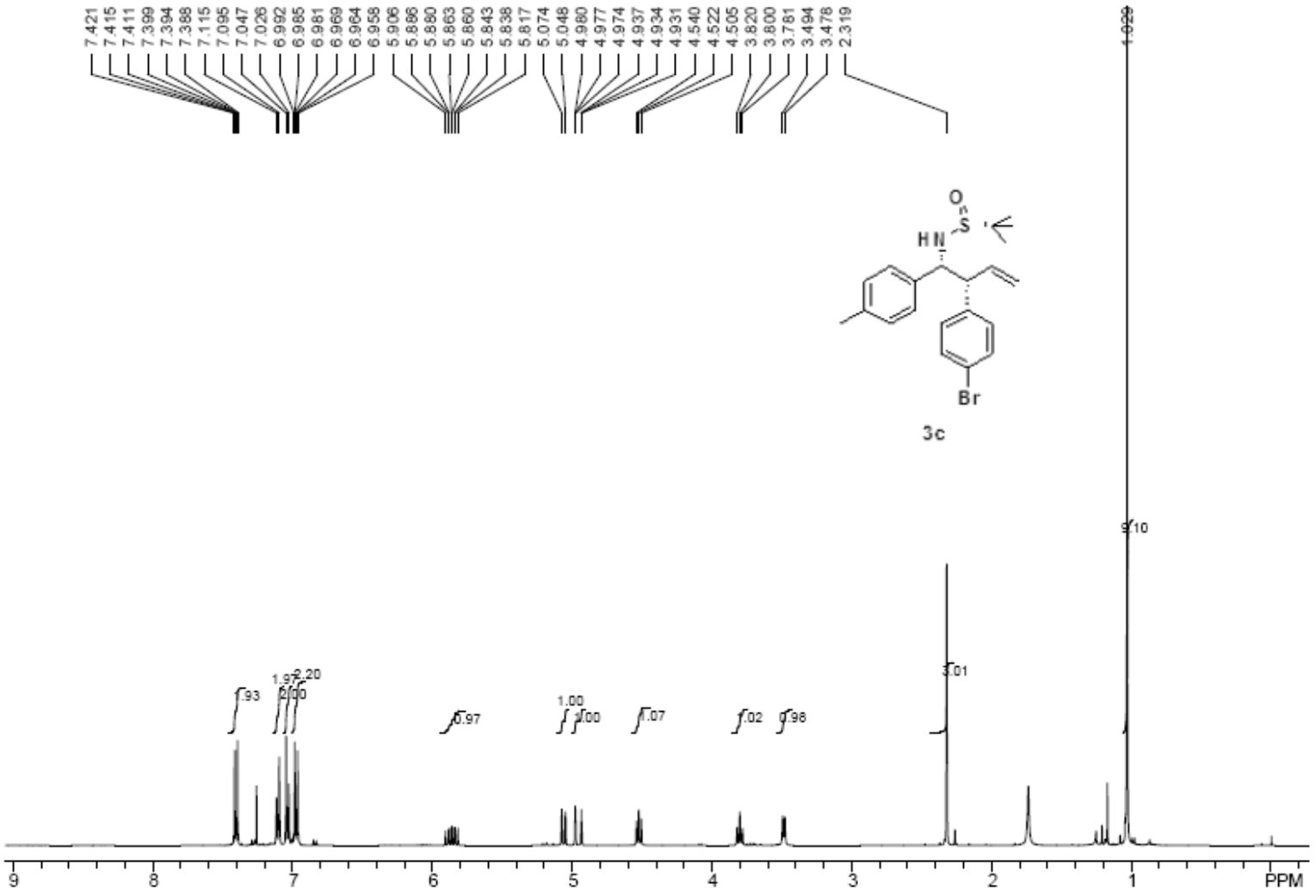
22.434
HN
O
S
Br
Br
3b
140
120
100
80
60
40
20
PPM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6.958
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5.886
5.880
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5.817
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4.522
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3.781
3.494
3.478
2.319
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S
HN
Br
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1.97
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0.97
1.00
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0.98
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9.10
9
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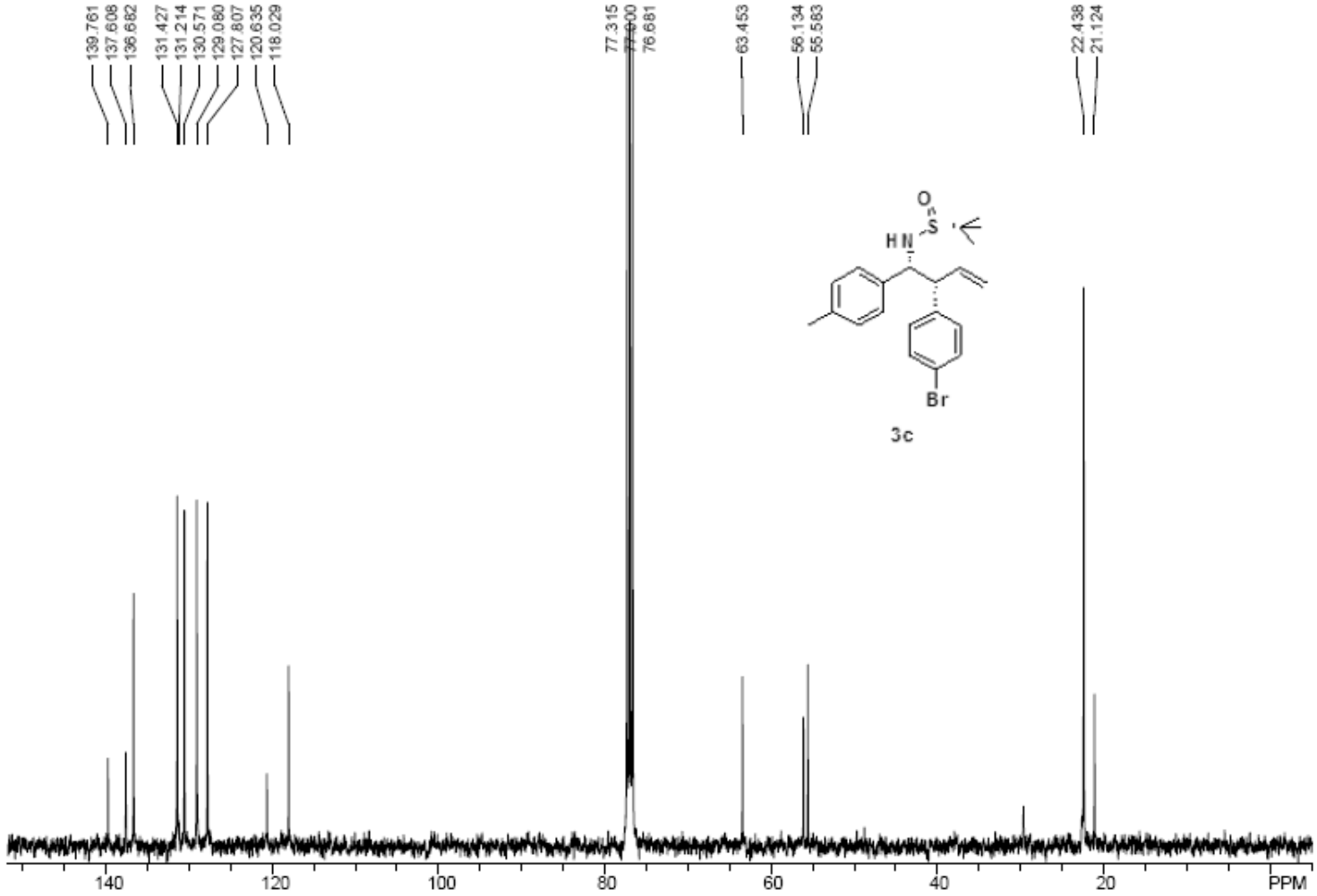
7
6
5
4
3
2
1
PPM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118.029
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77.000
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63.453
56.134
55.583
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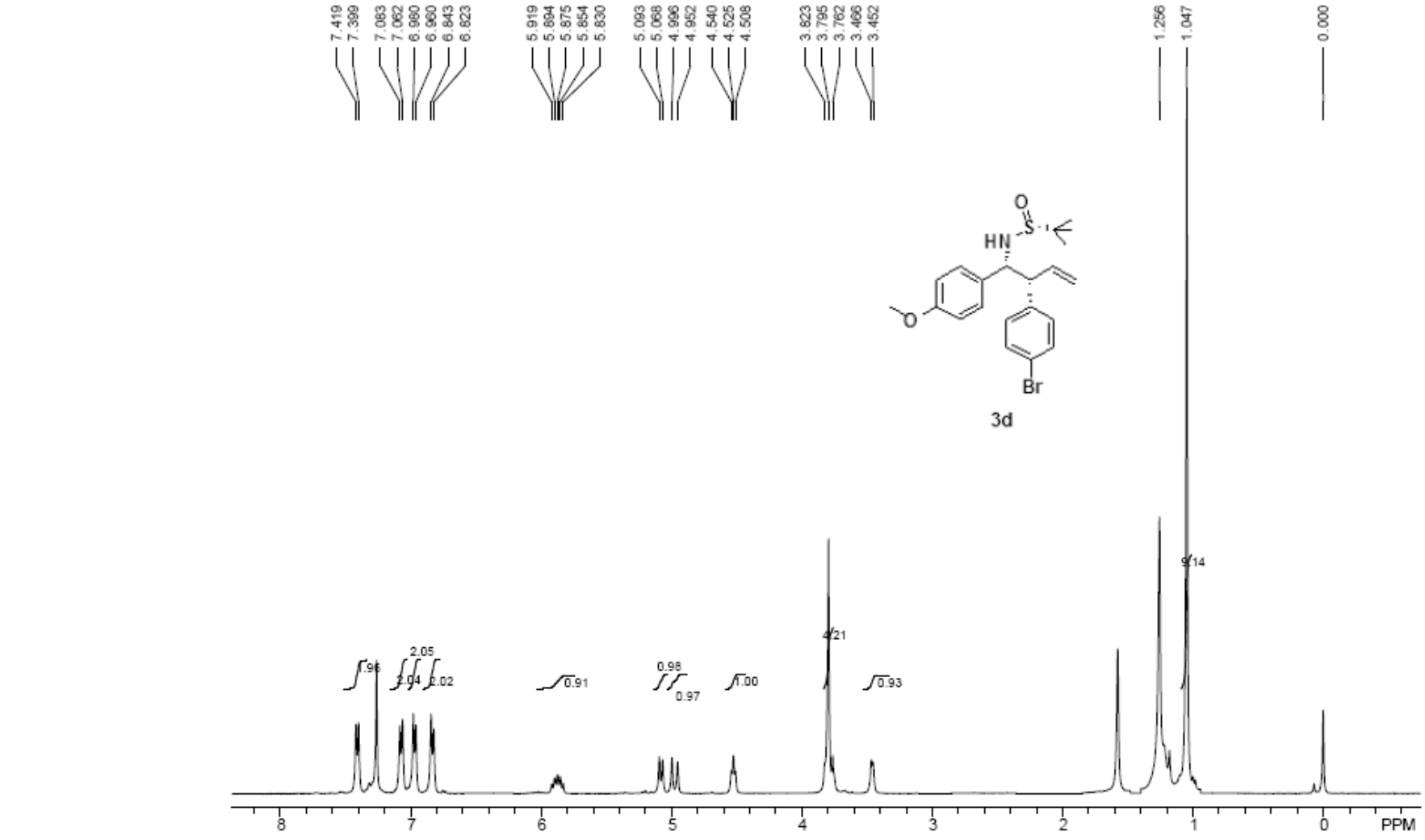
21.124
O
S
HN
Br
3c
140
120
100
80
60
40
20
PPM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3.823
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3.466
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HN
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O
Br
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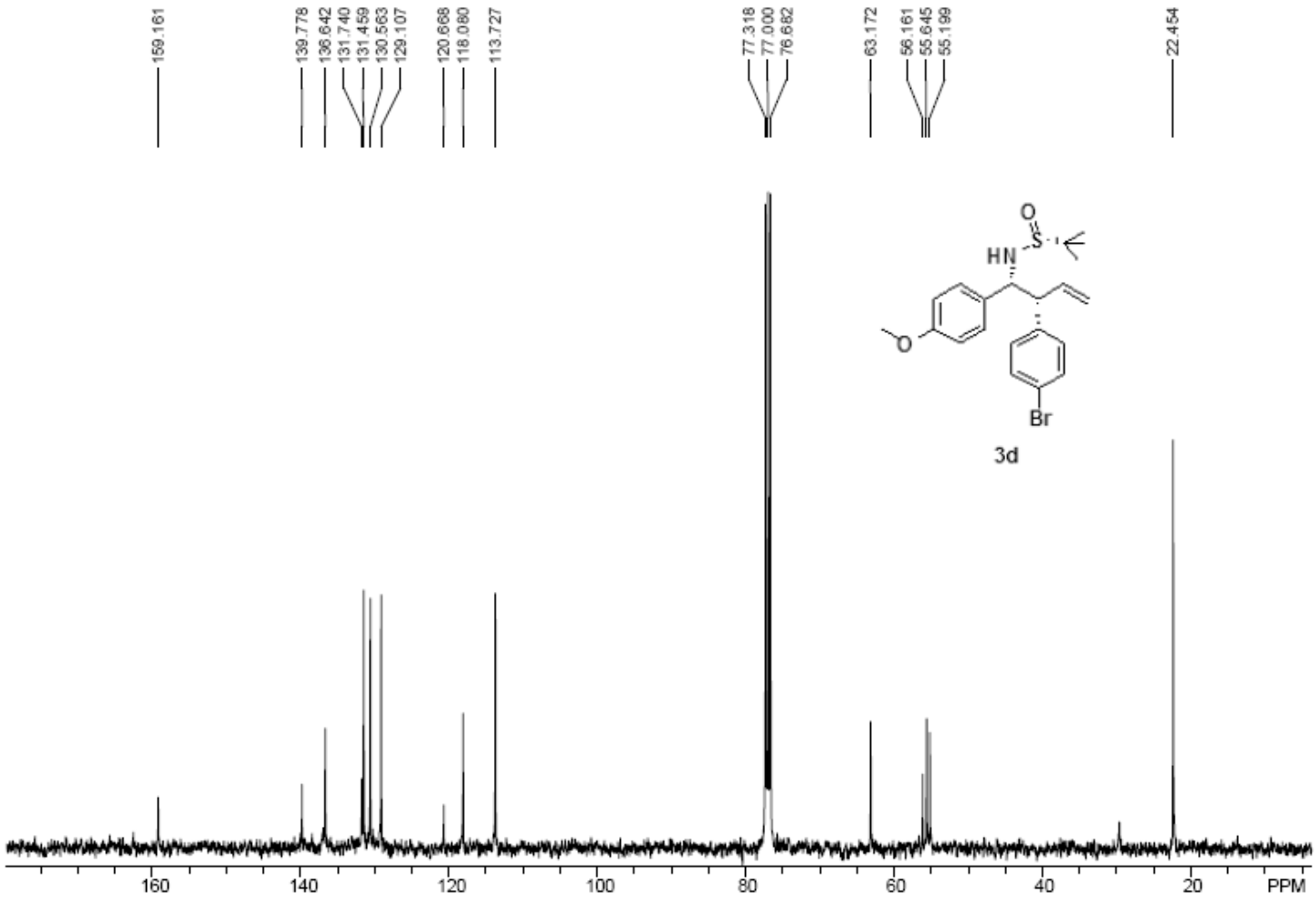
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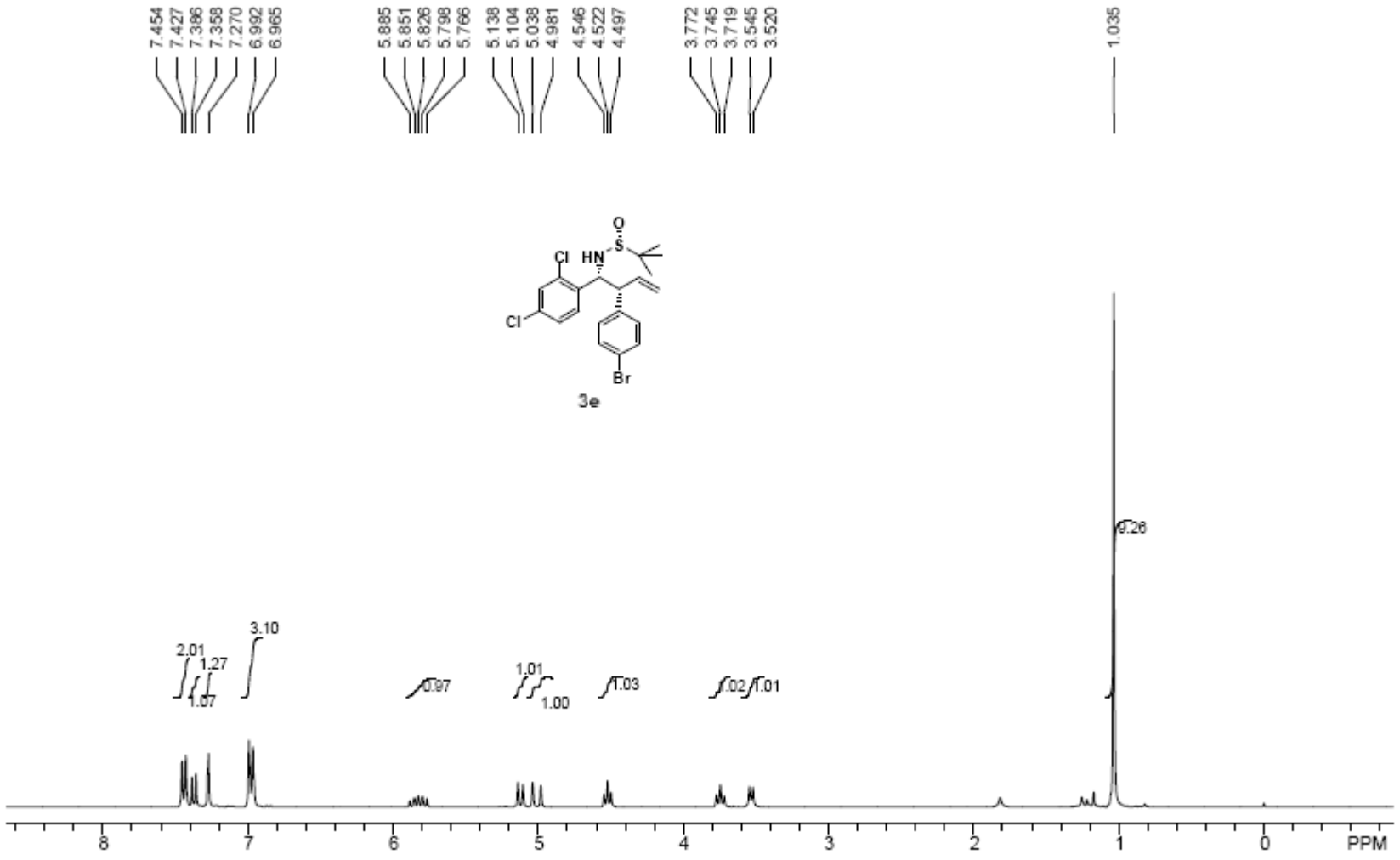
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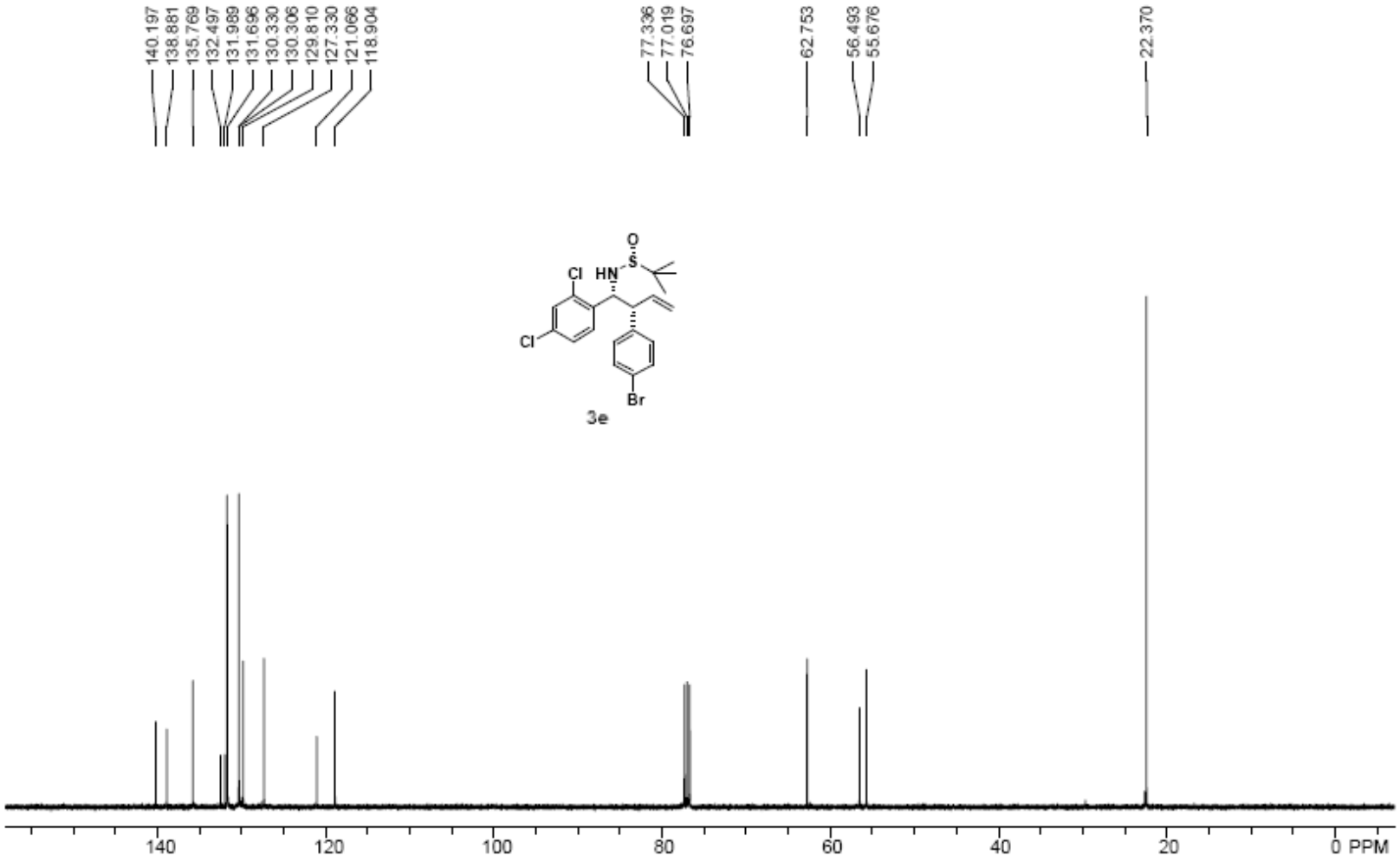
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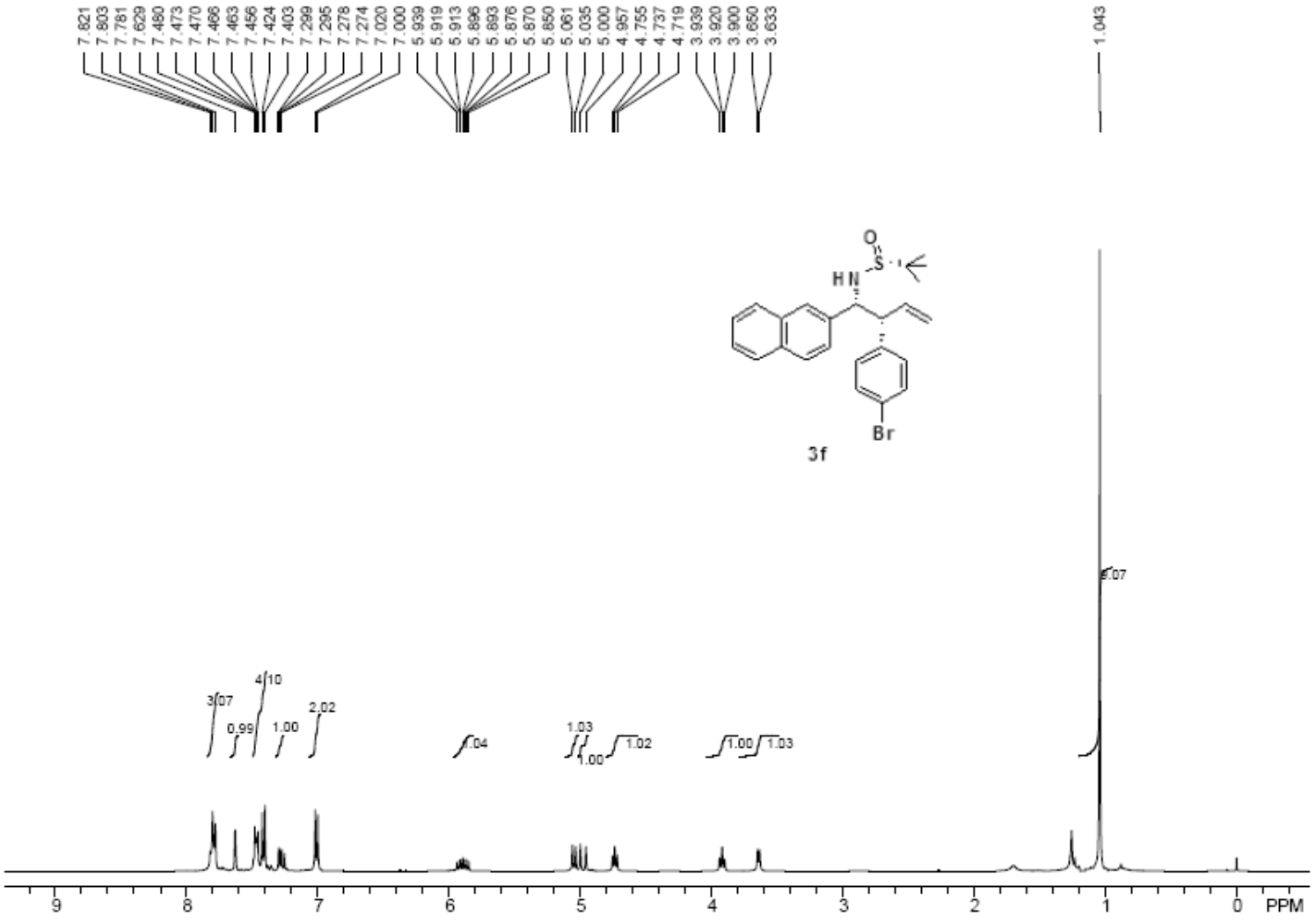
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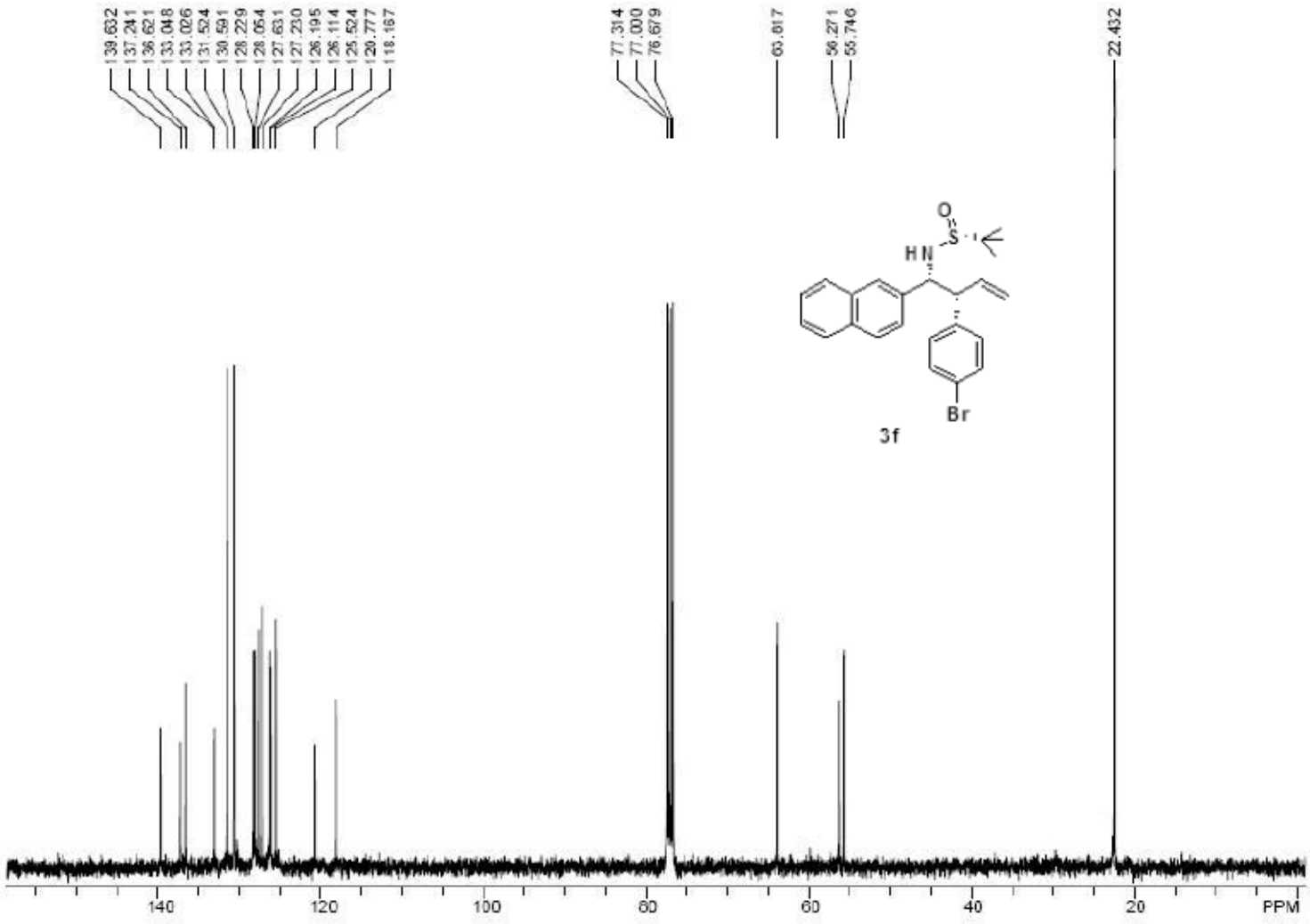
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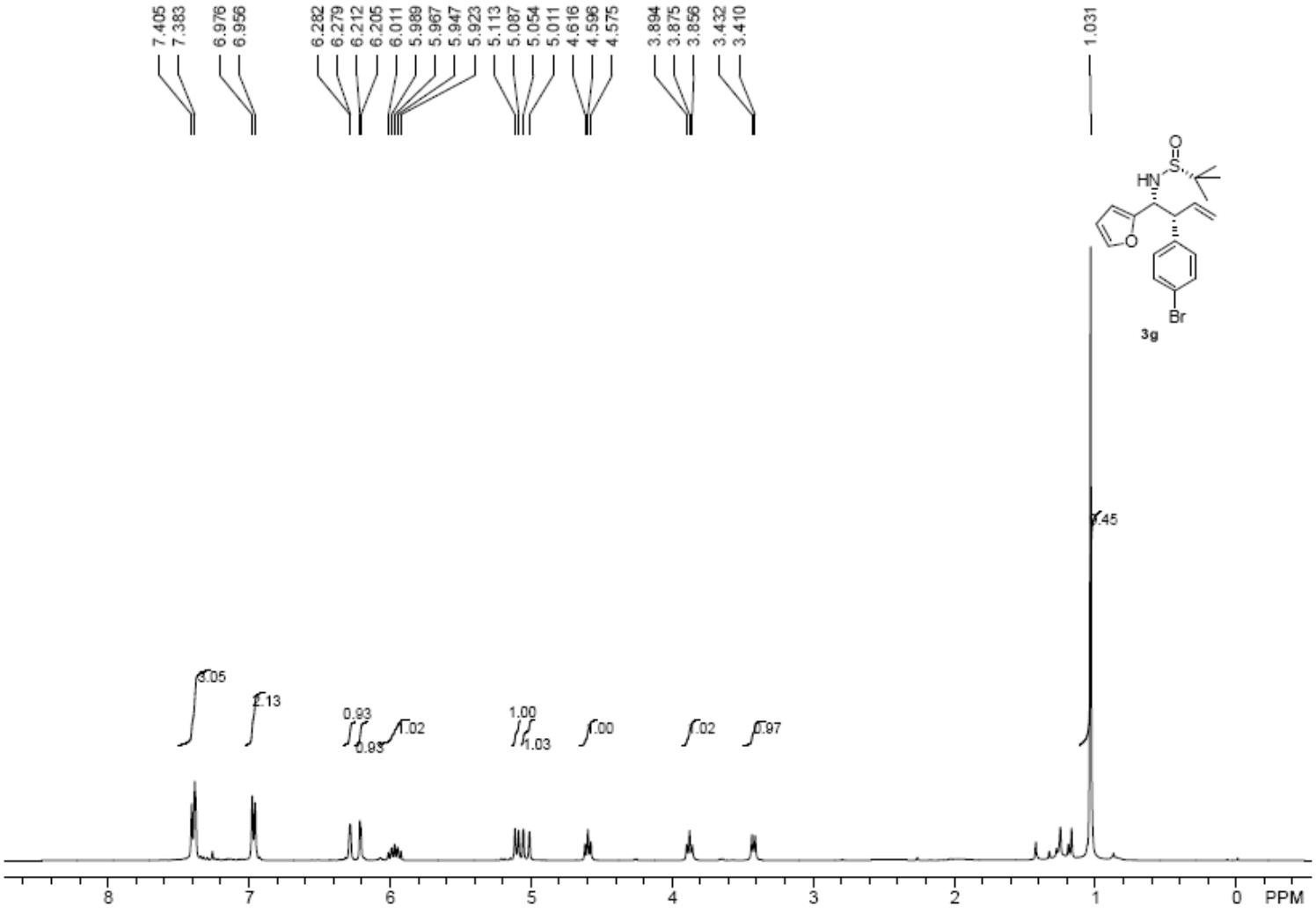
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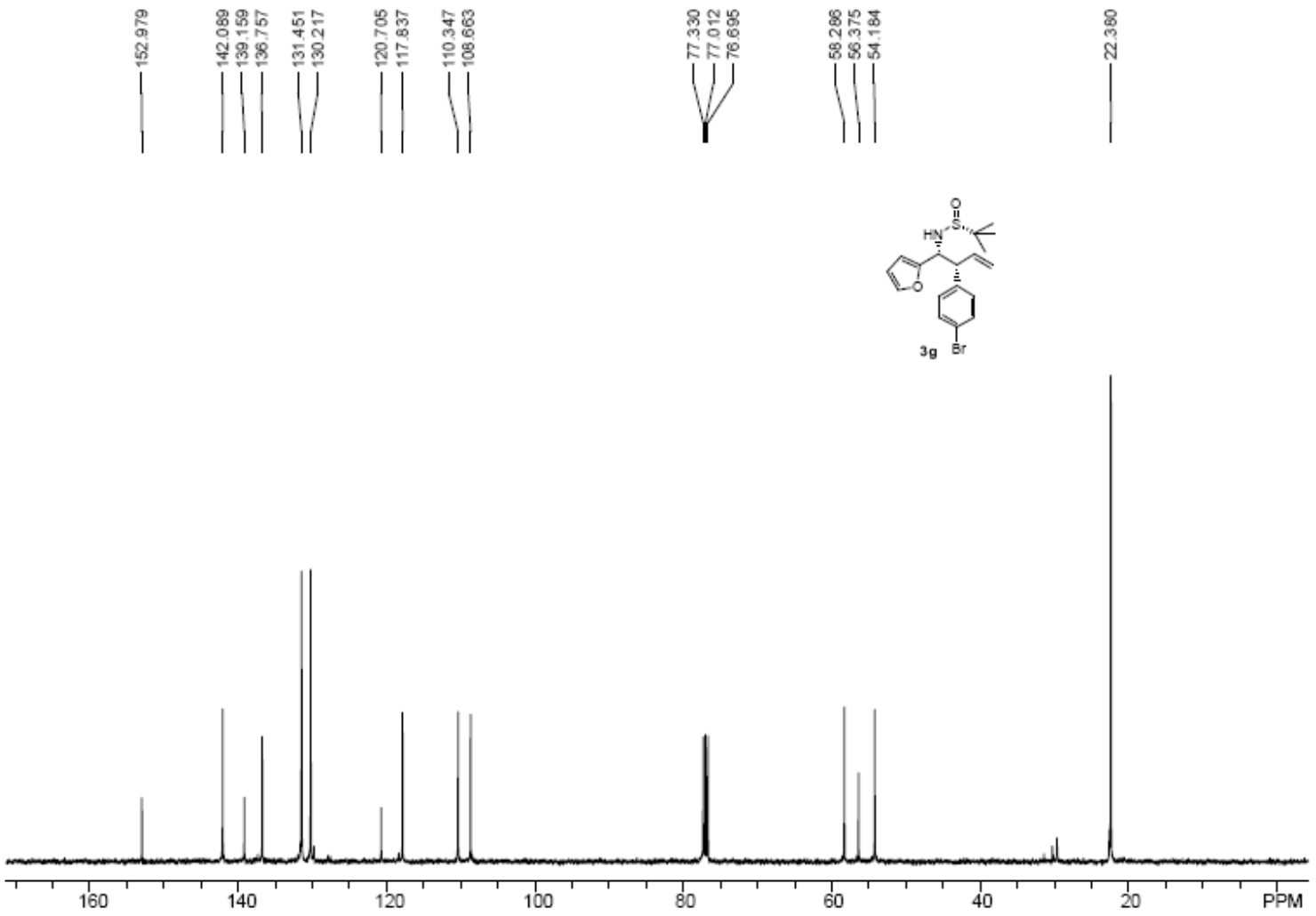
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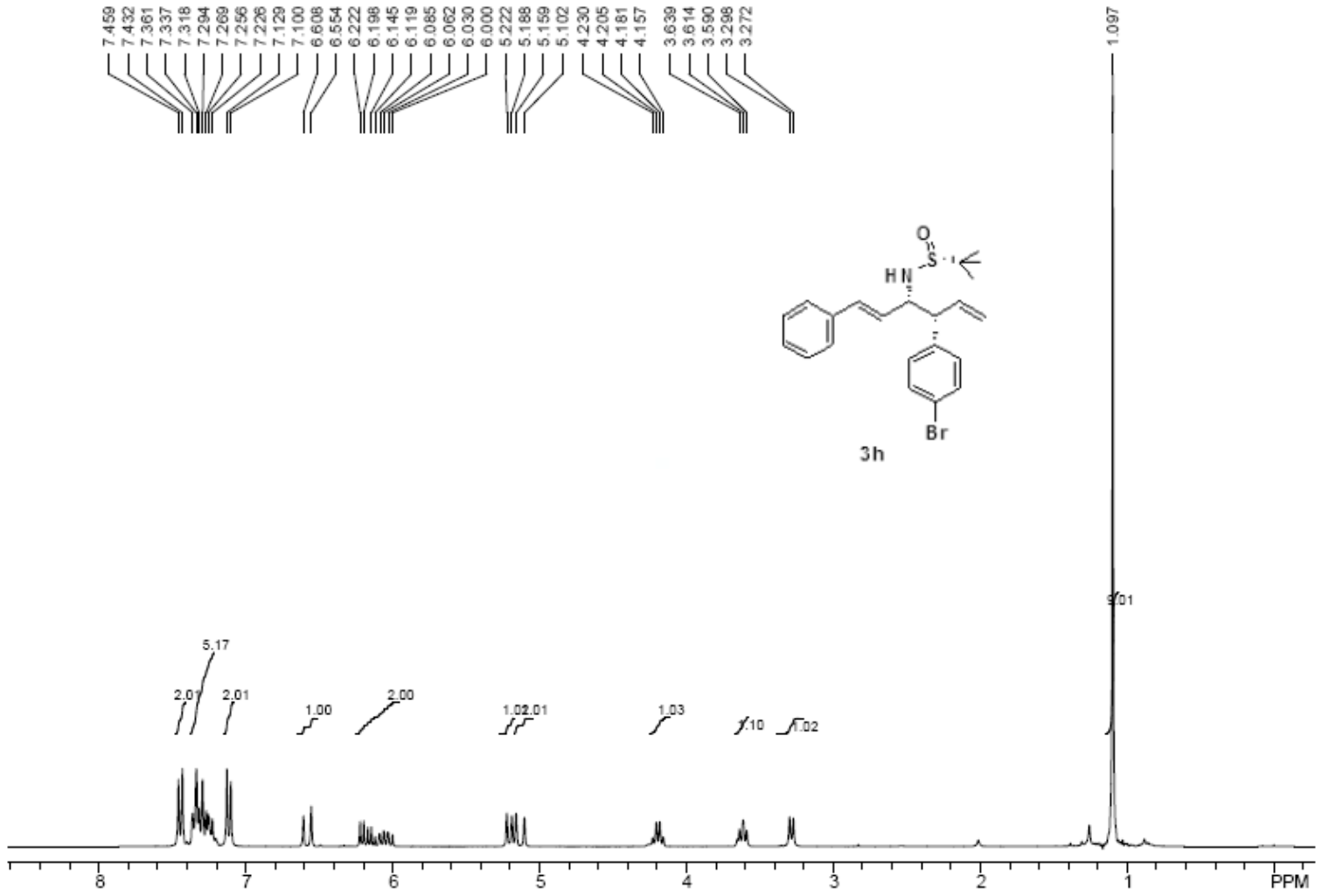
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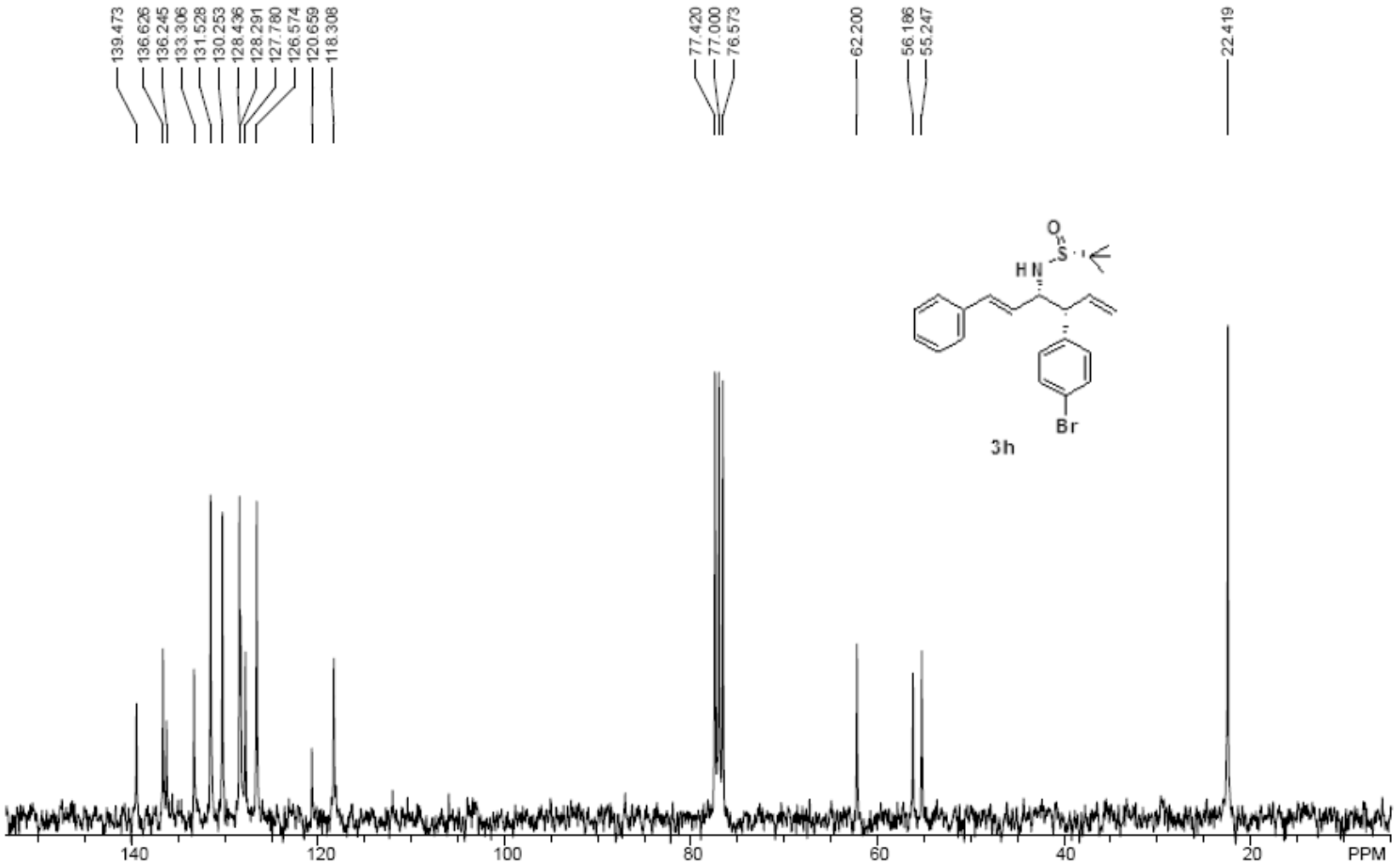
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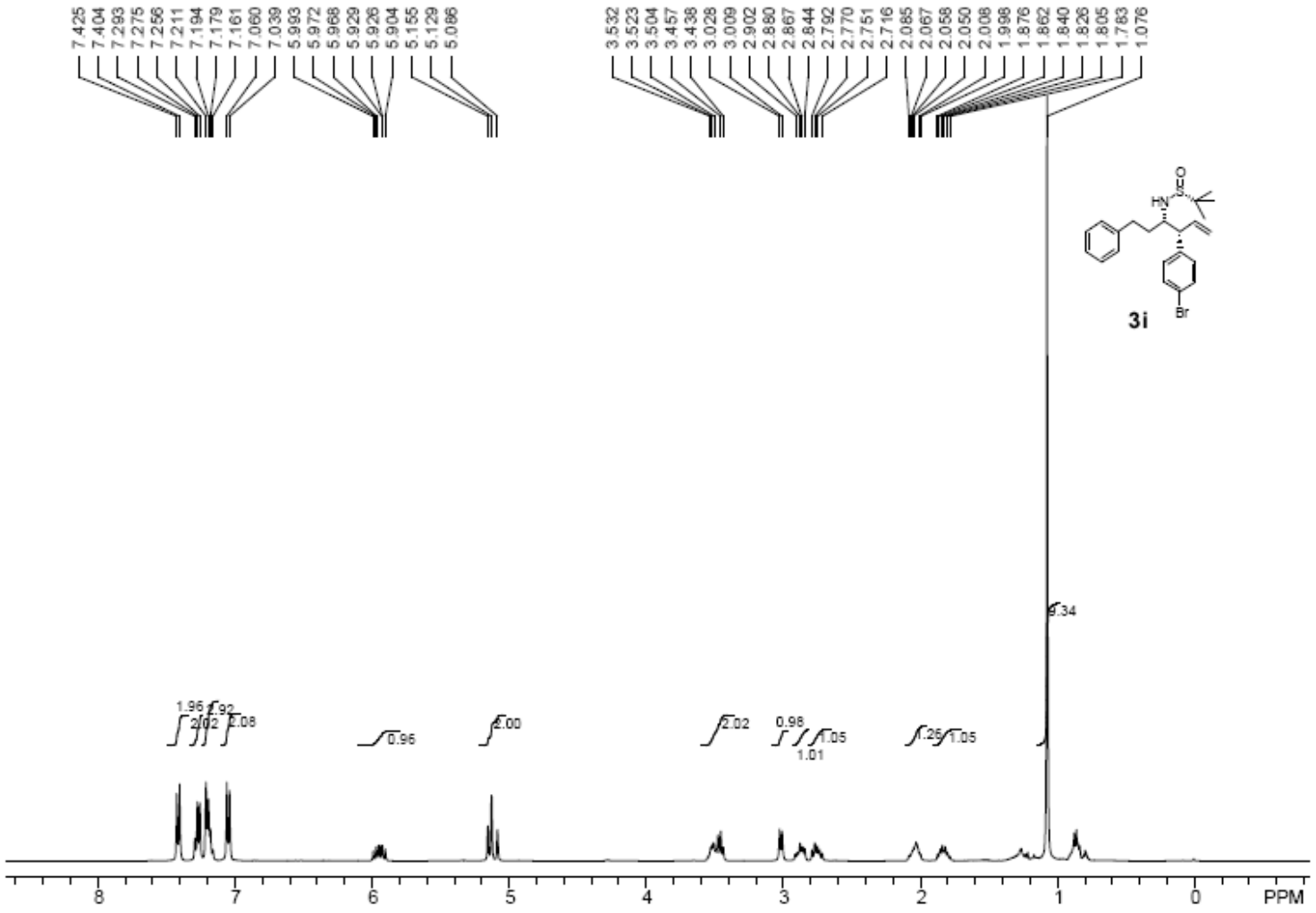
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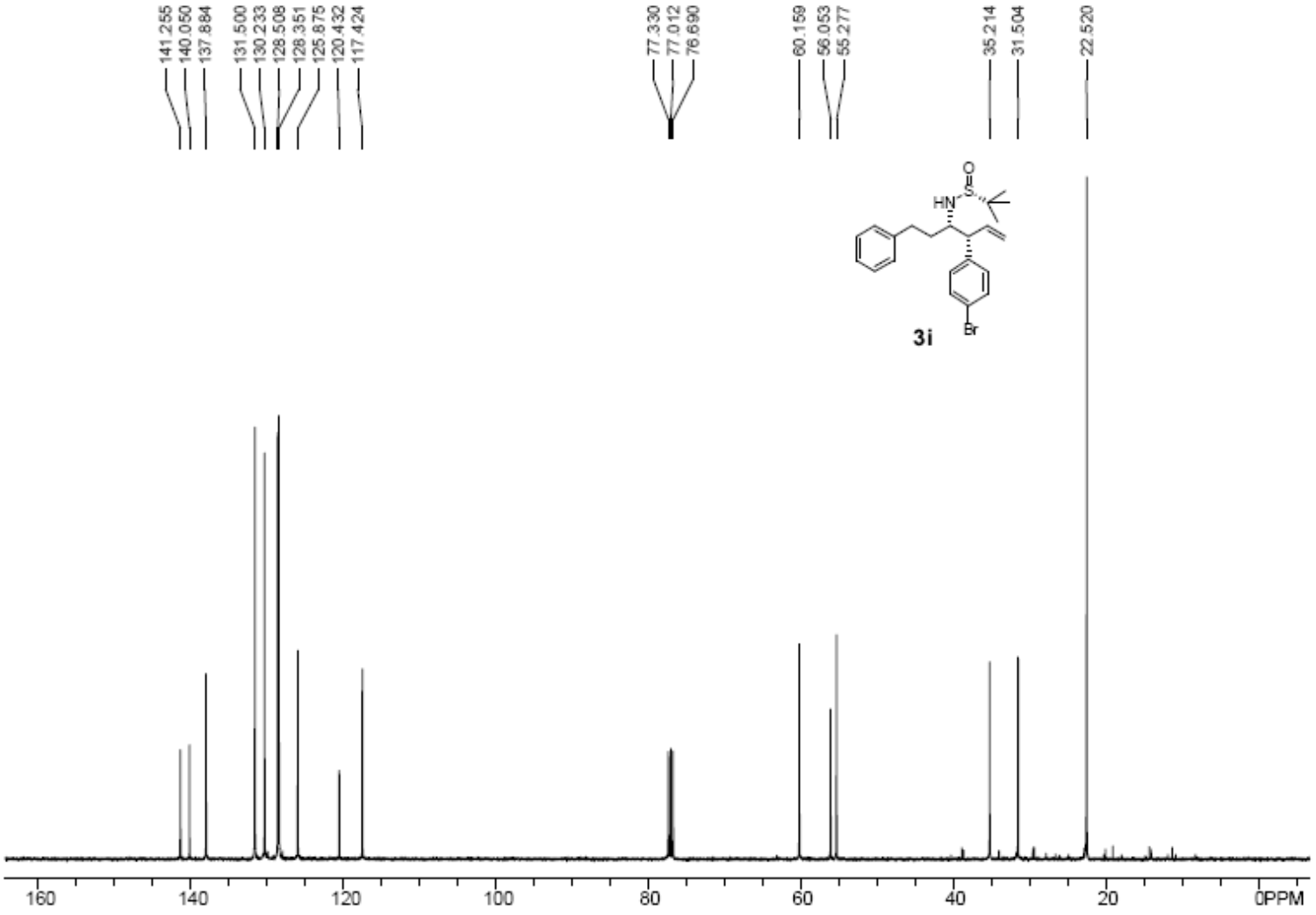
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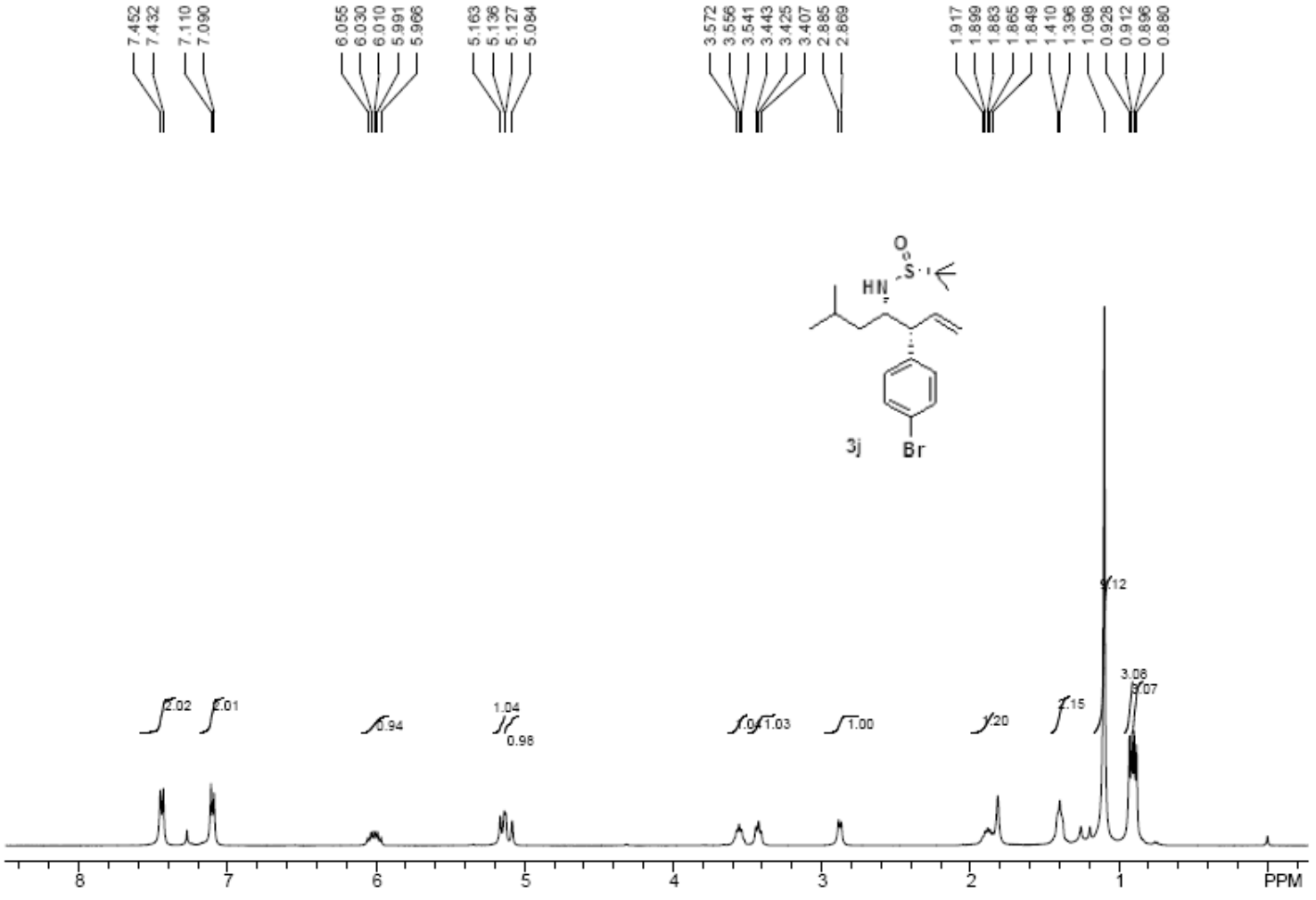
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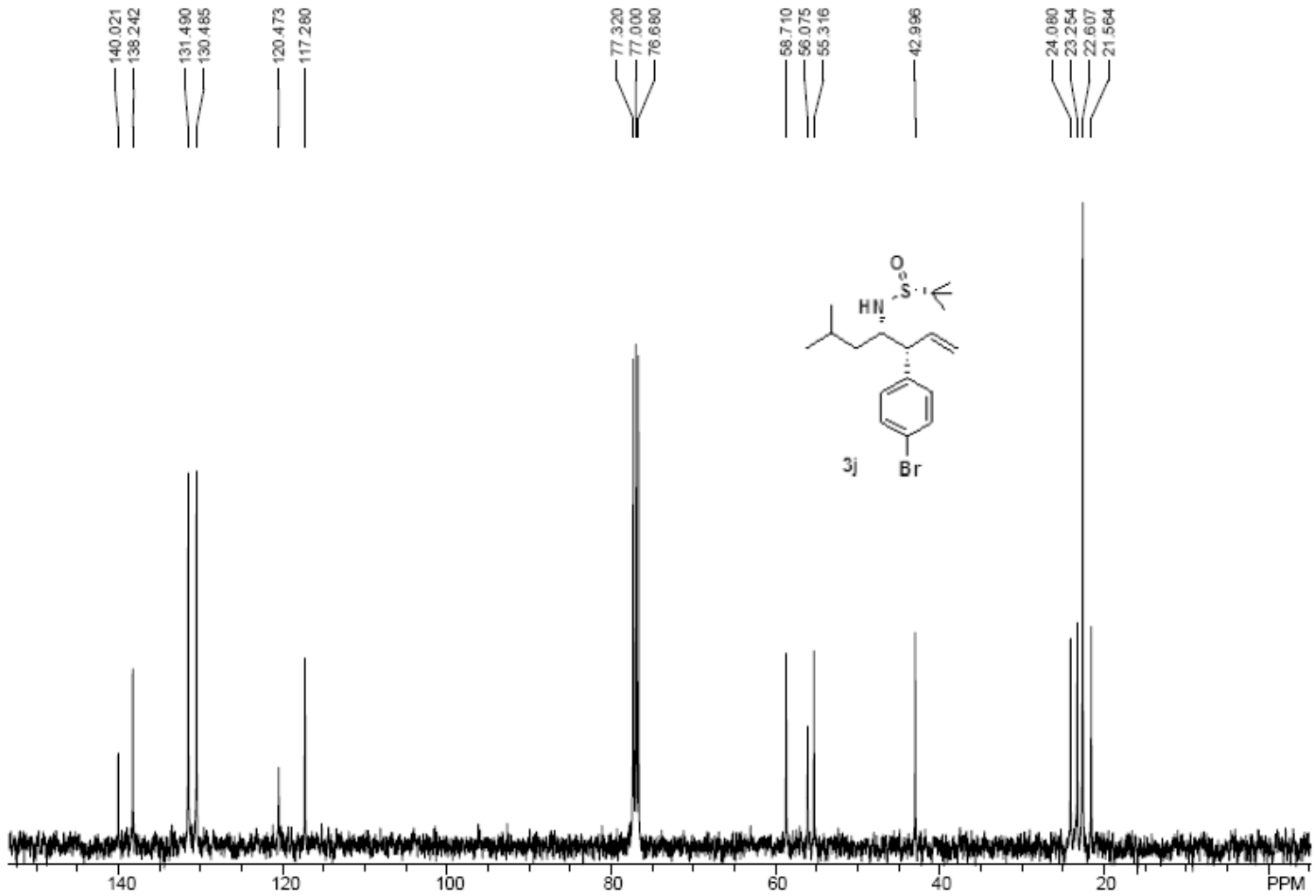
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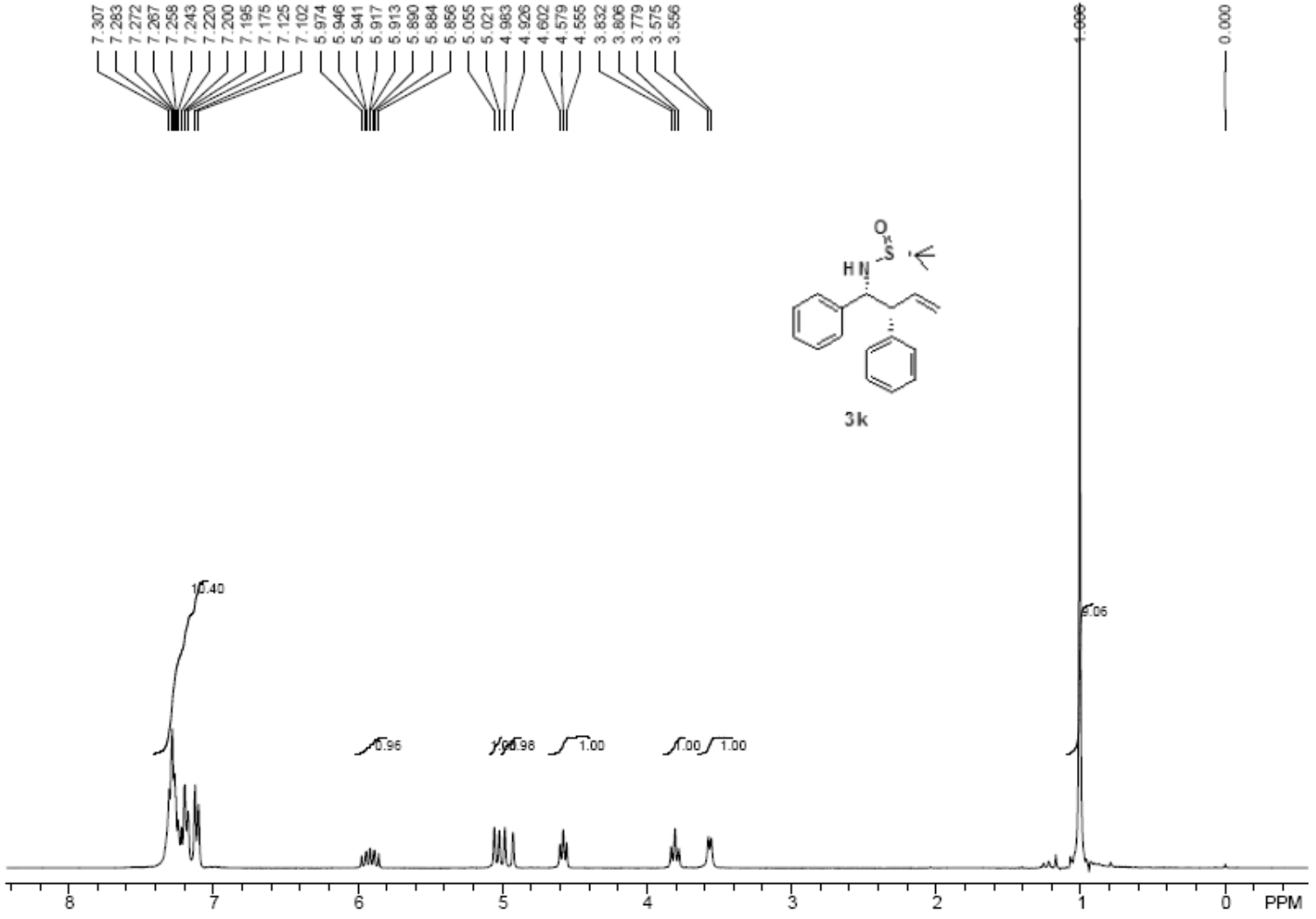
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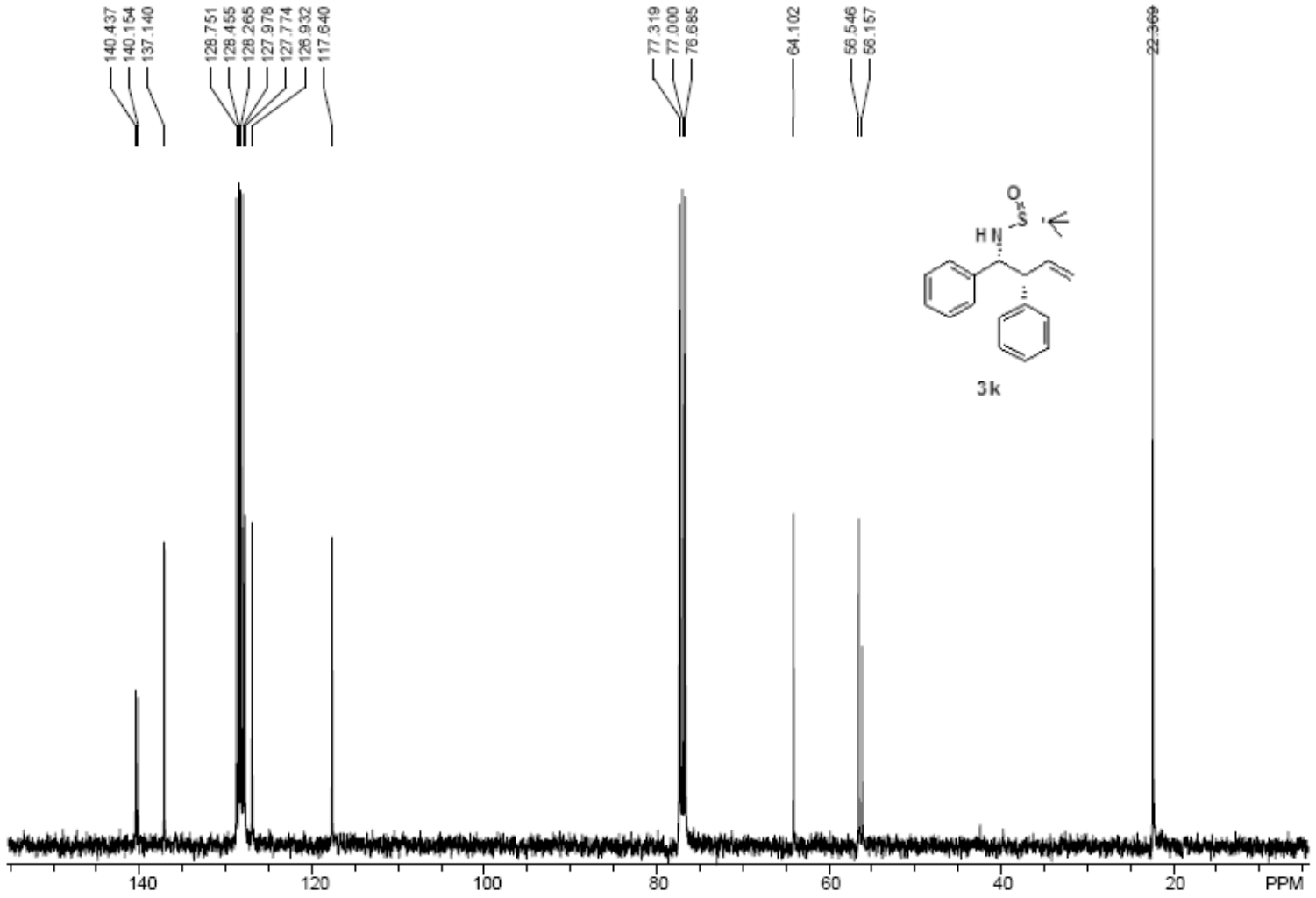
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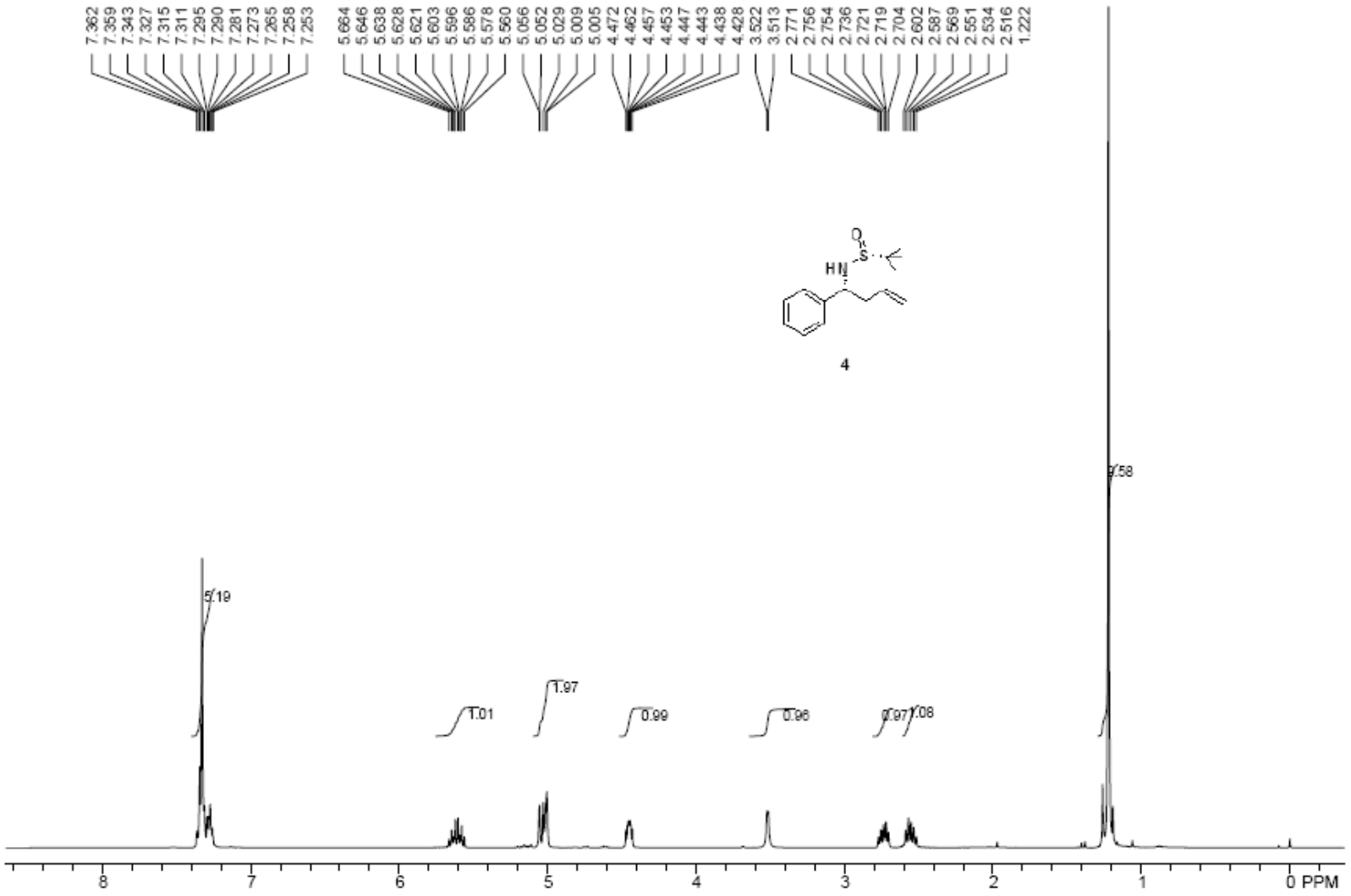
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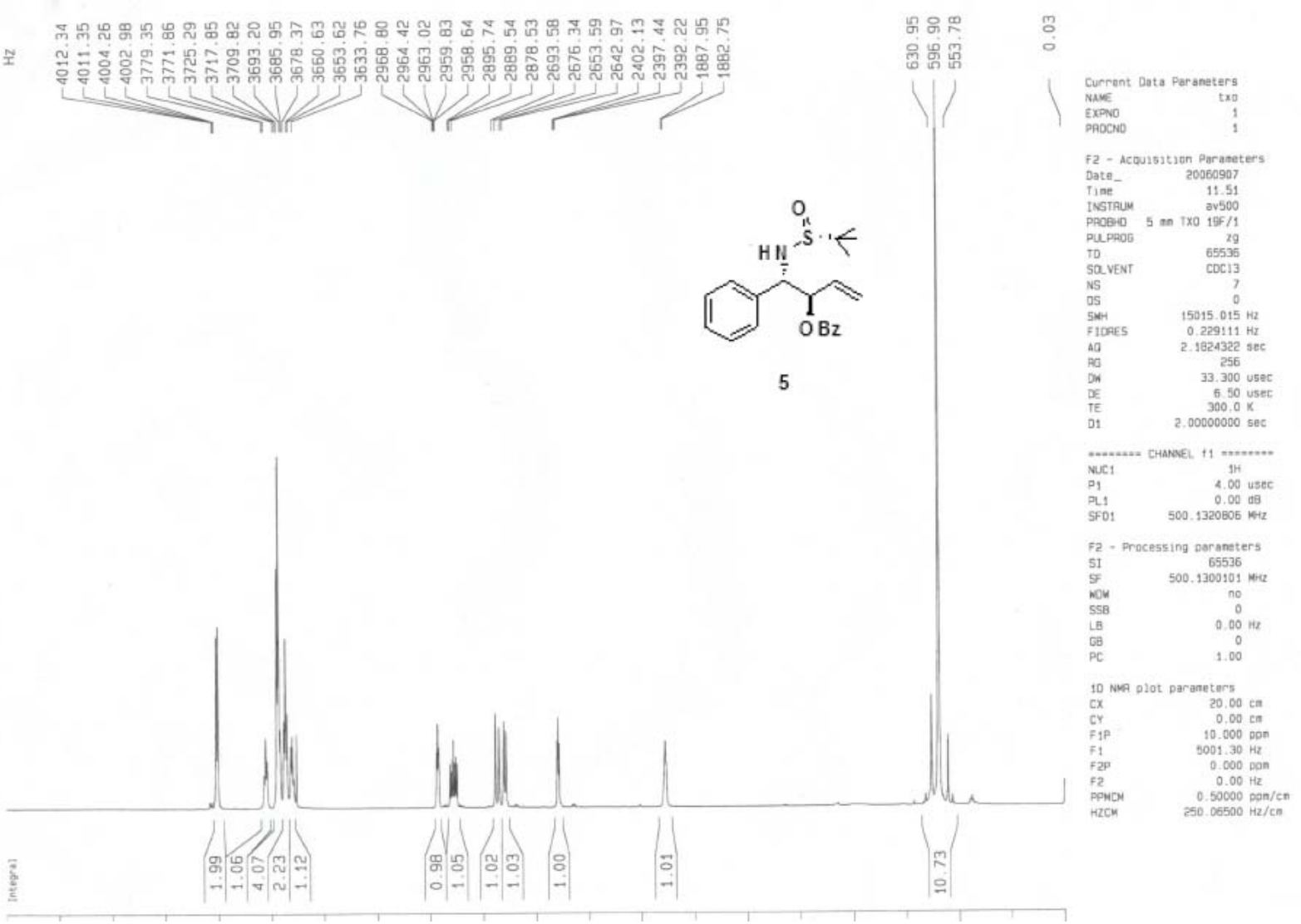
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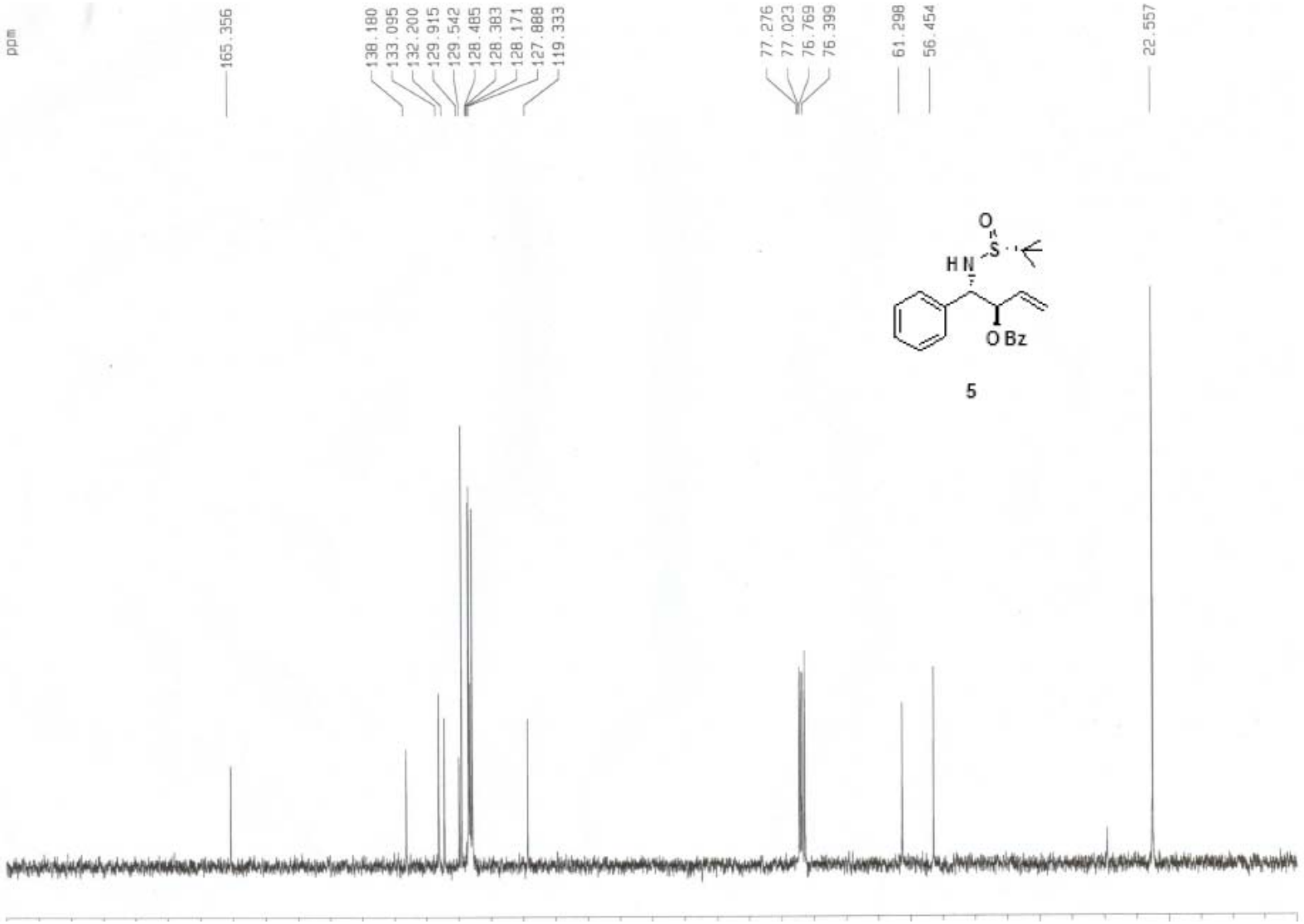
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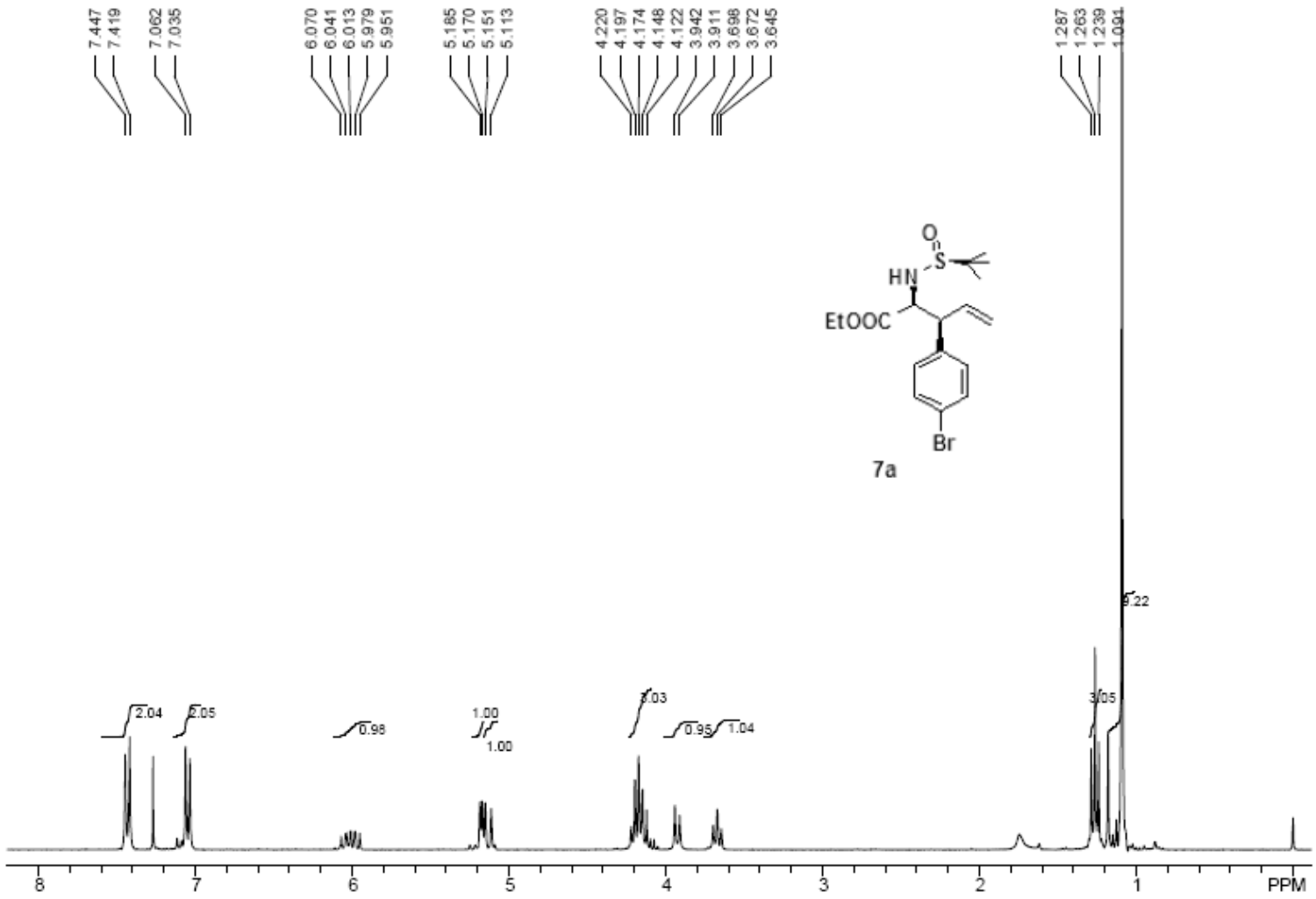
5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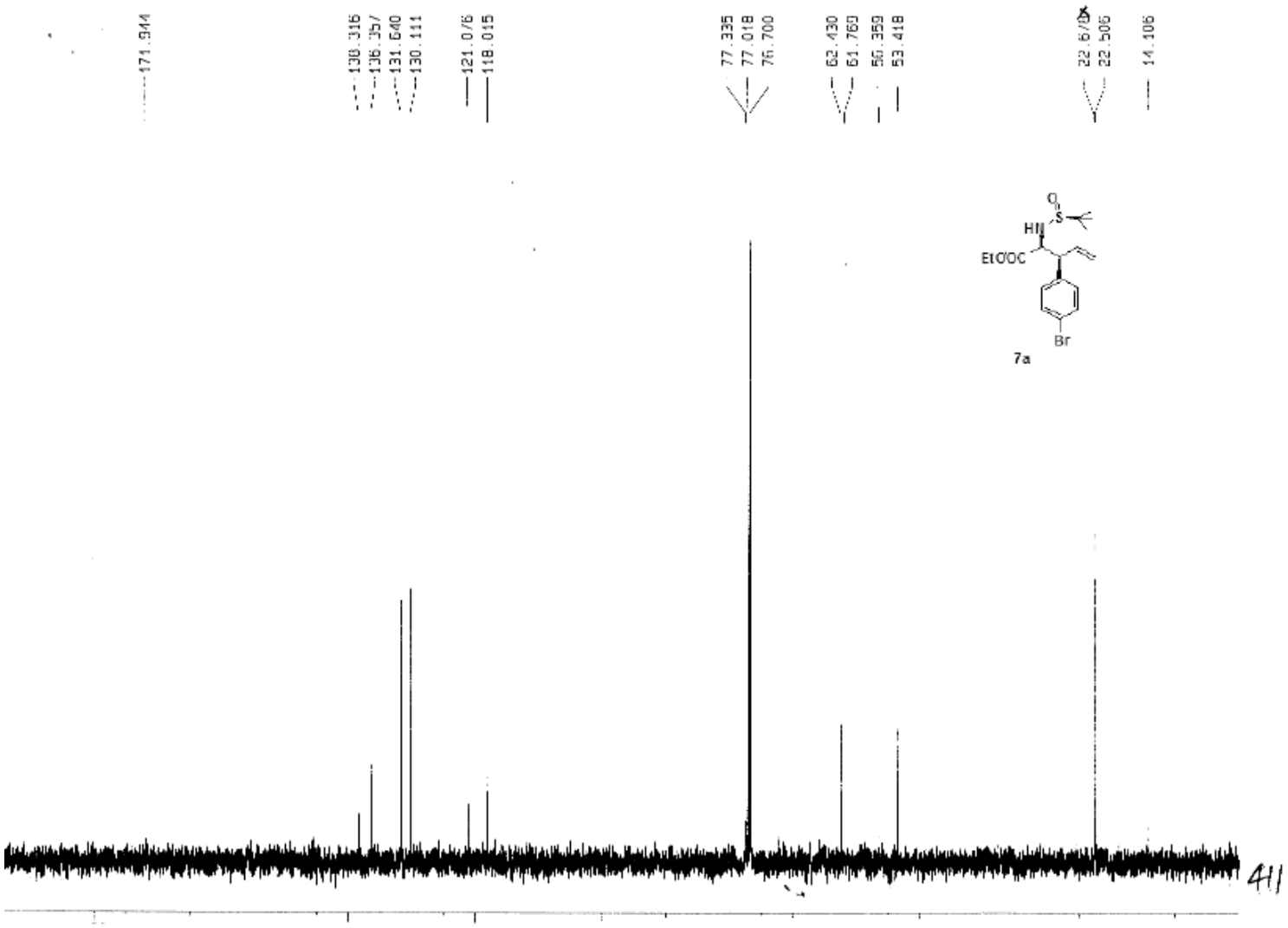
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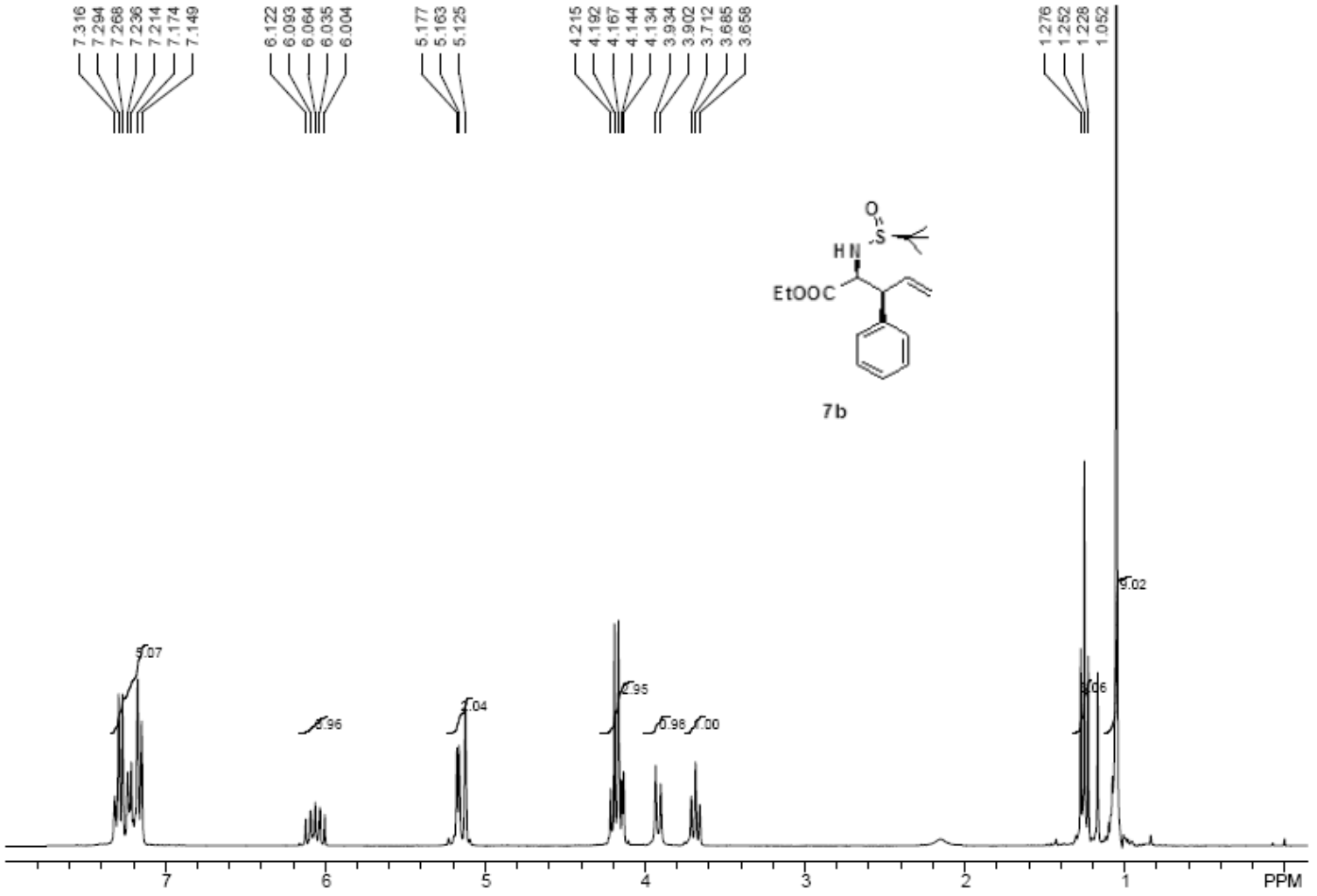
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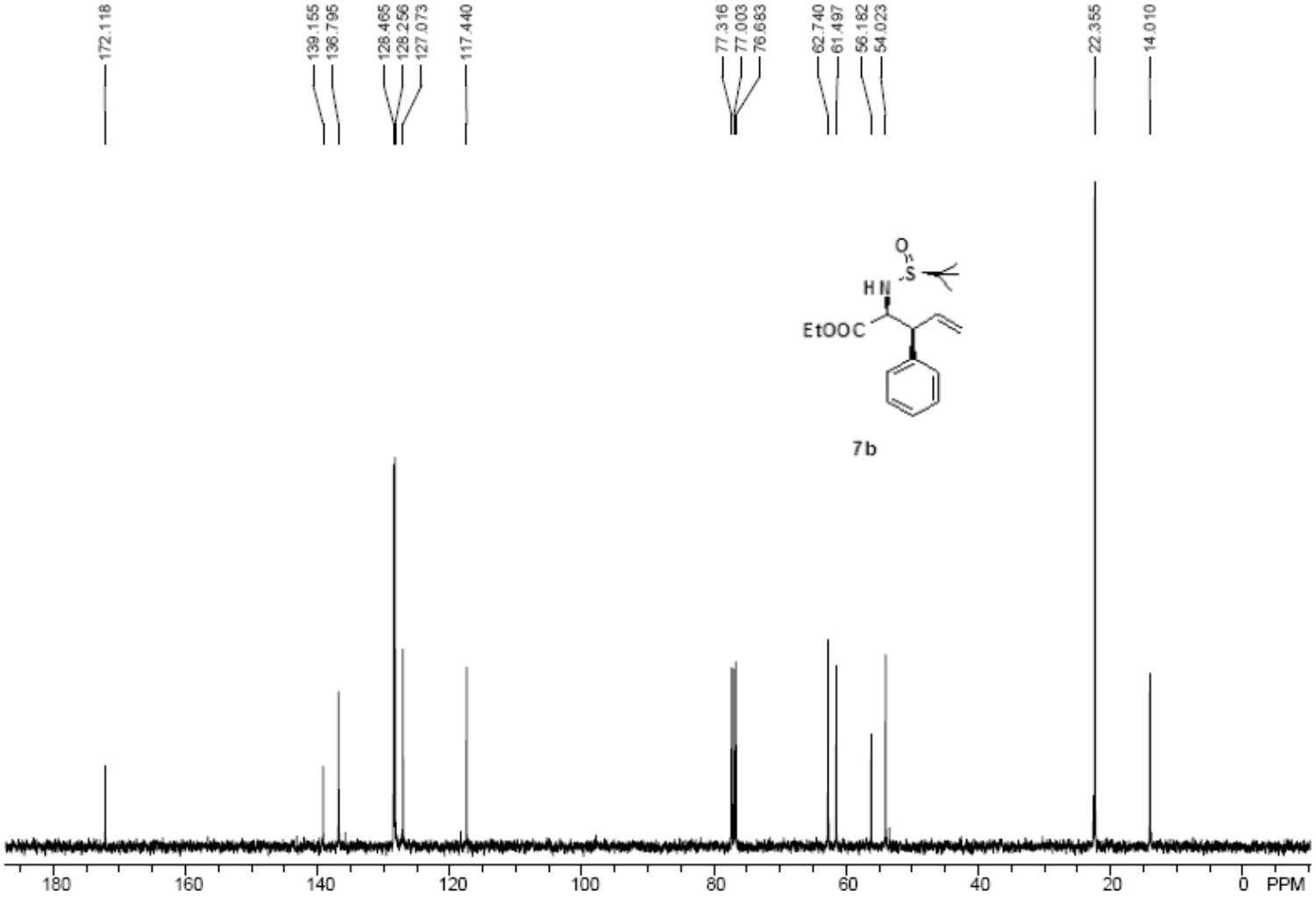
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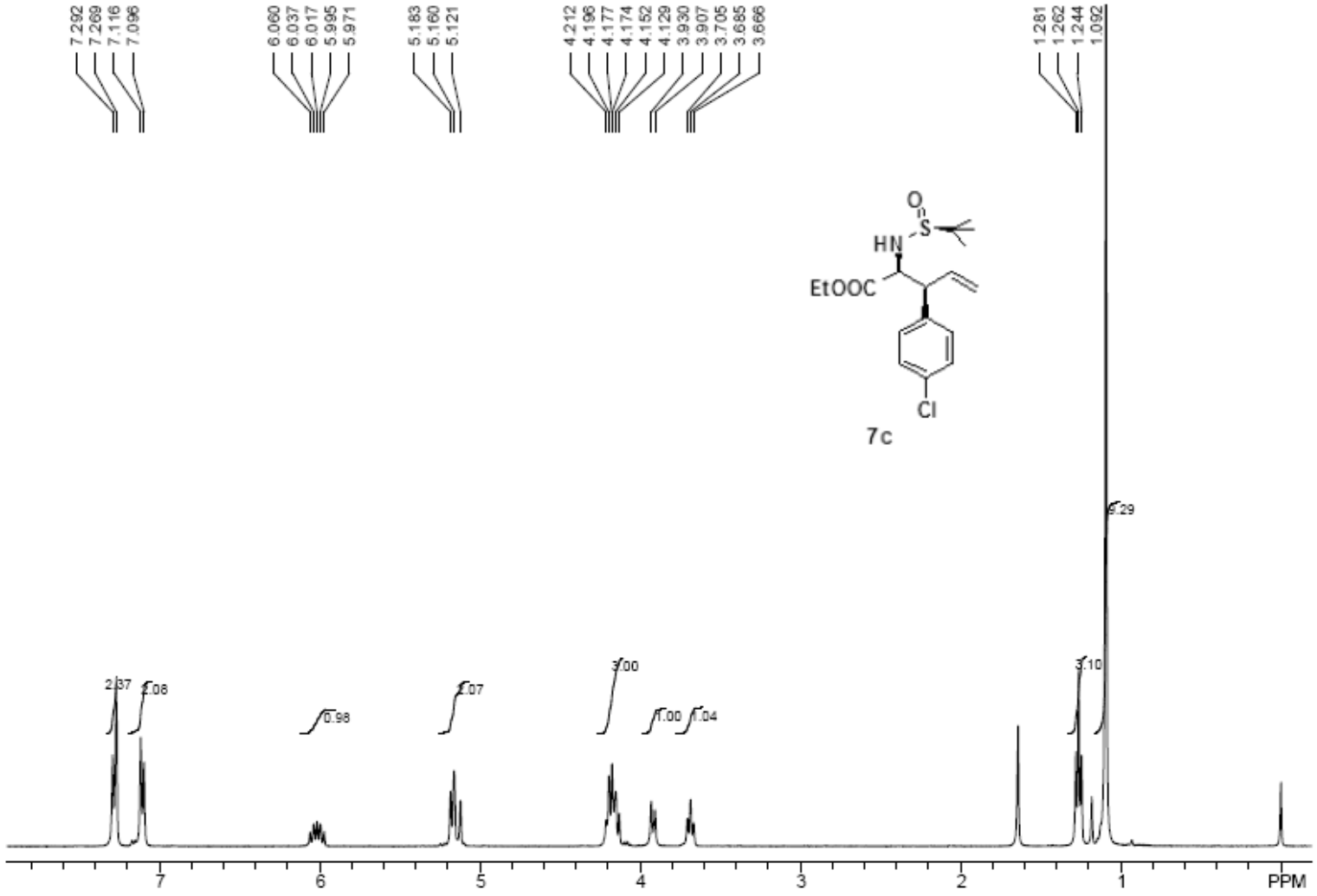
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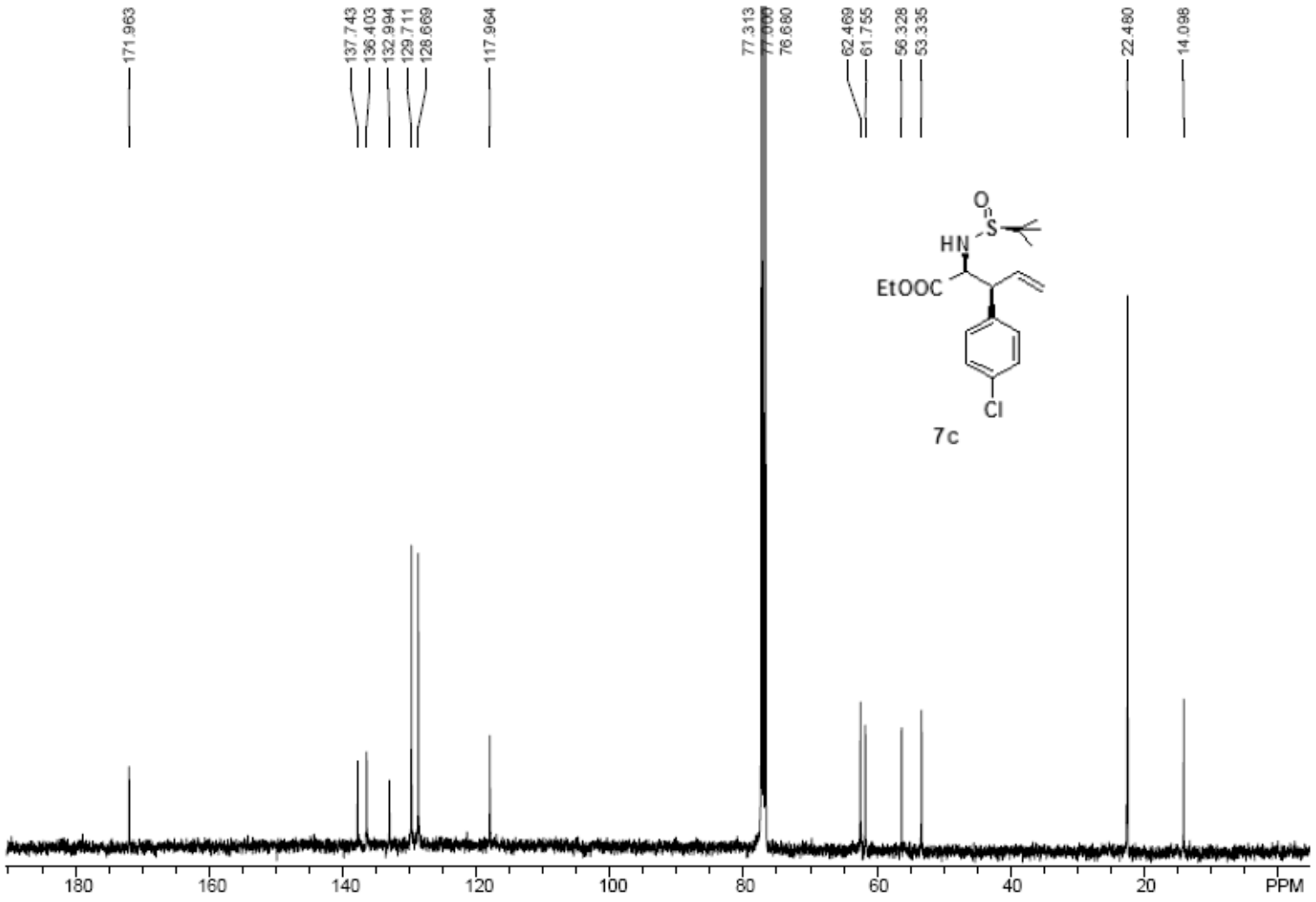
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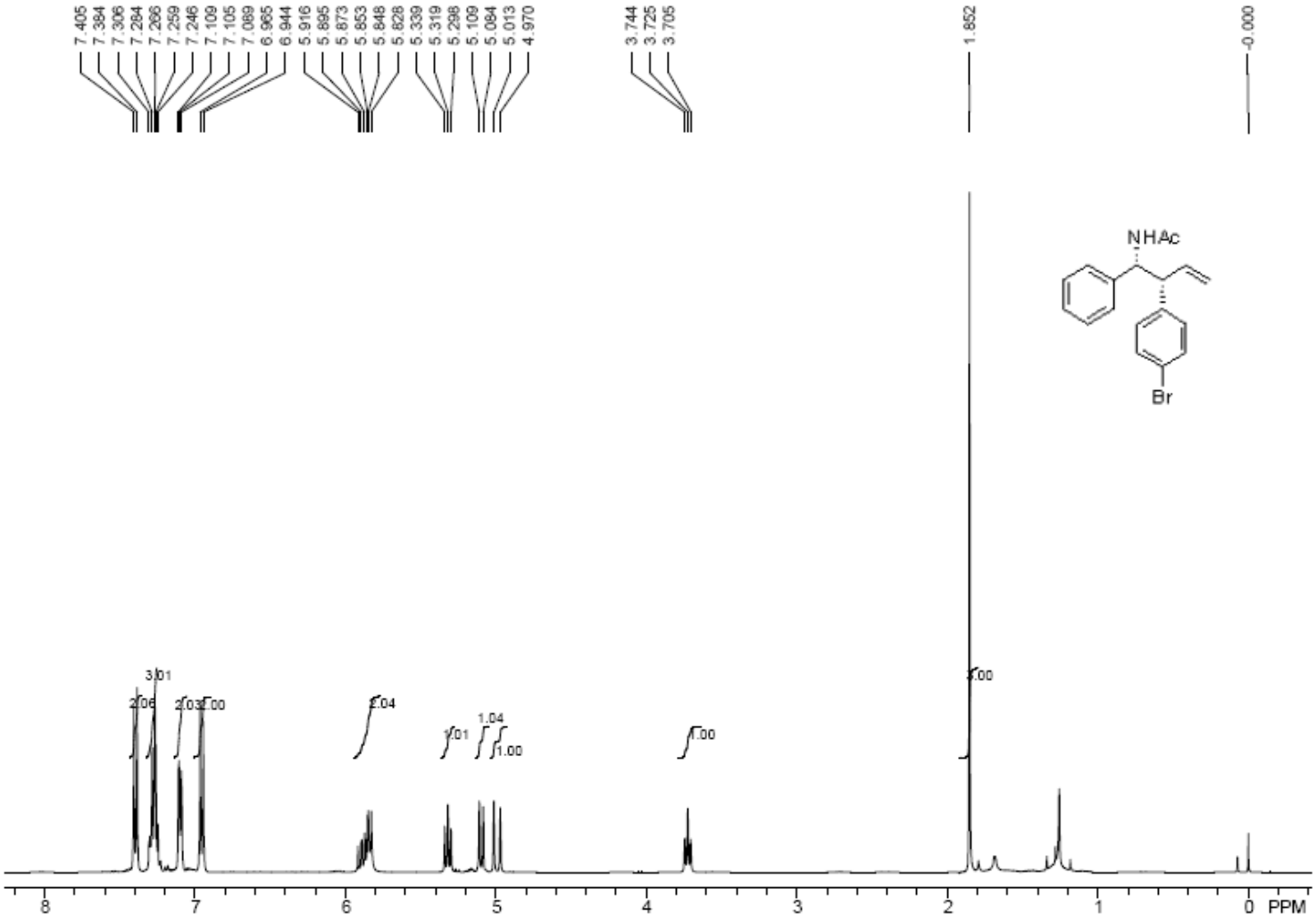
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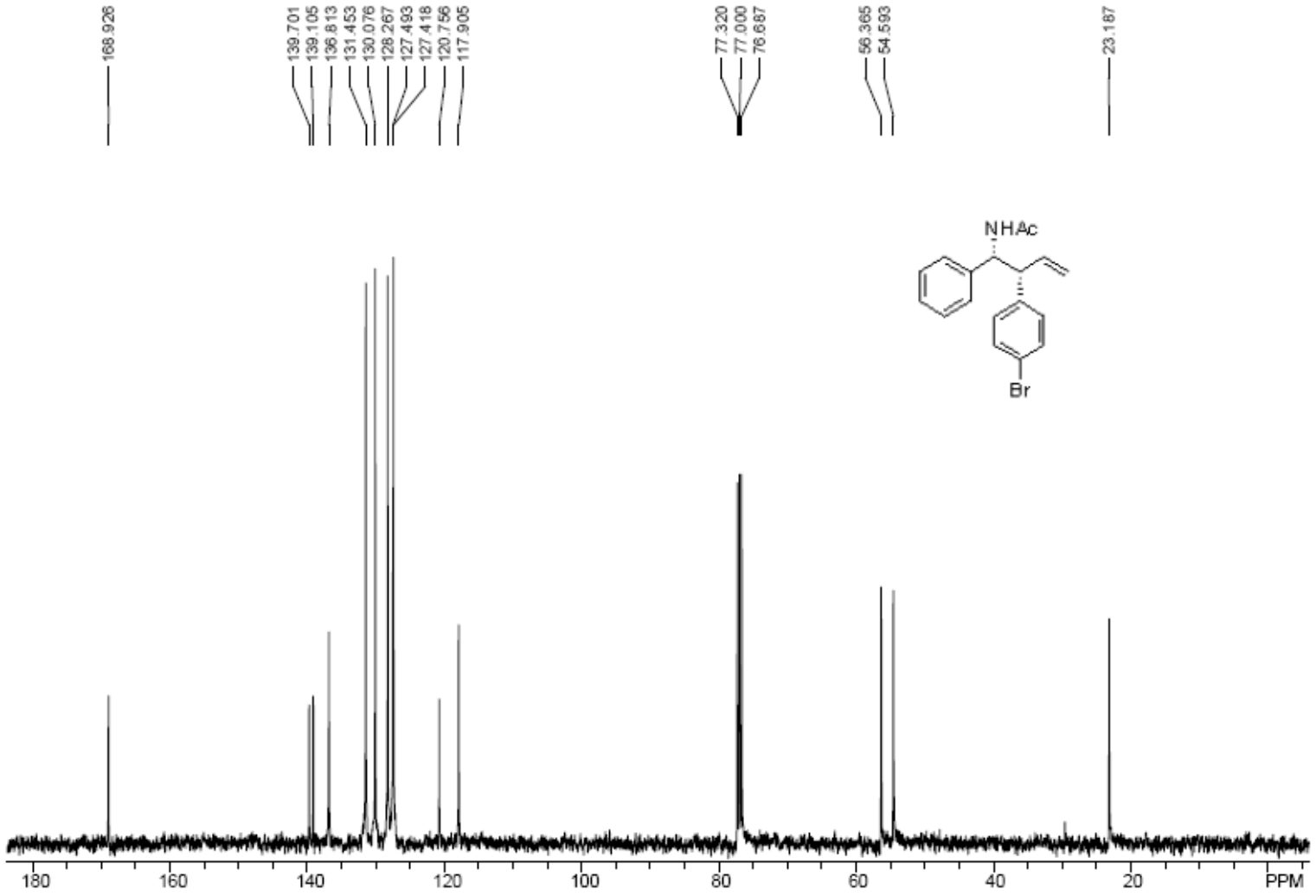
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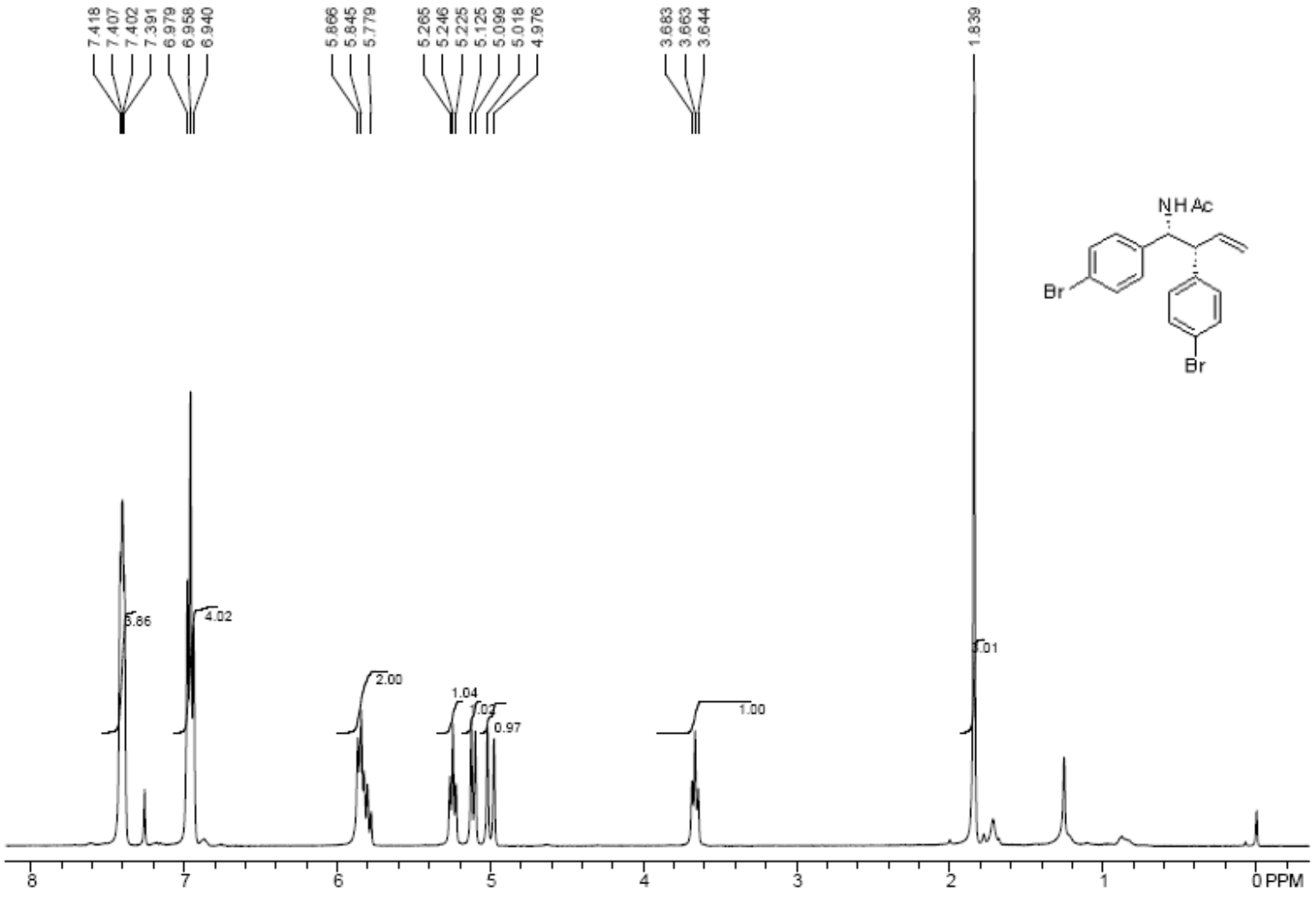
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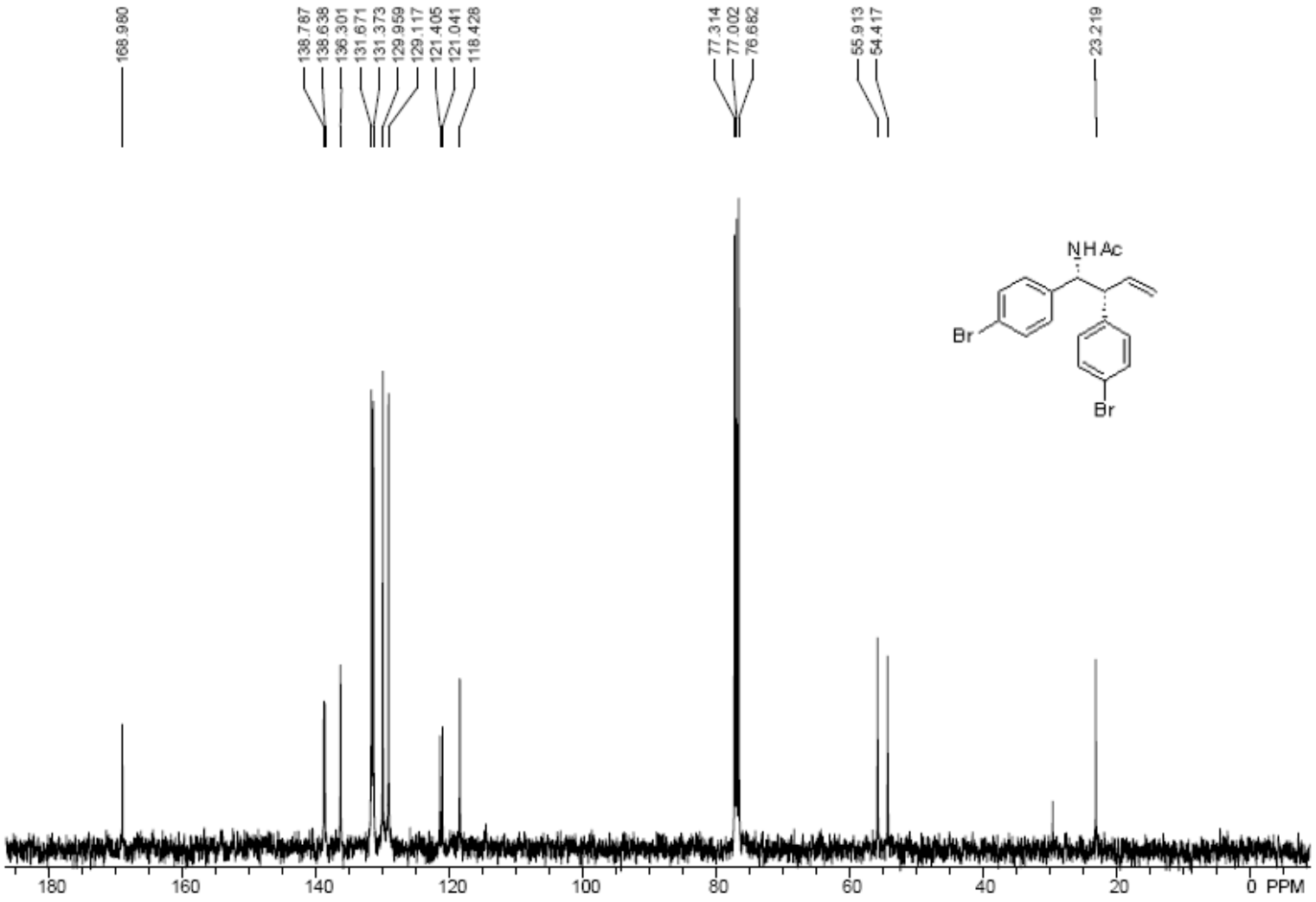
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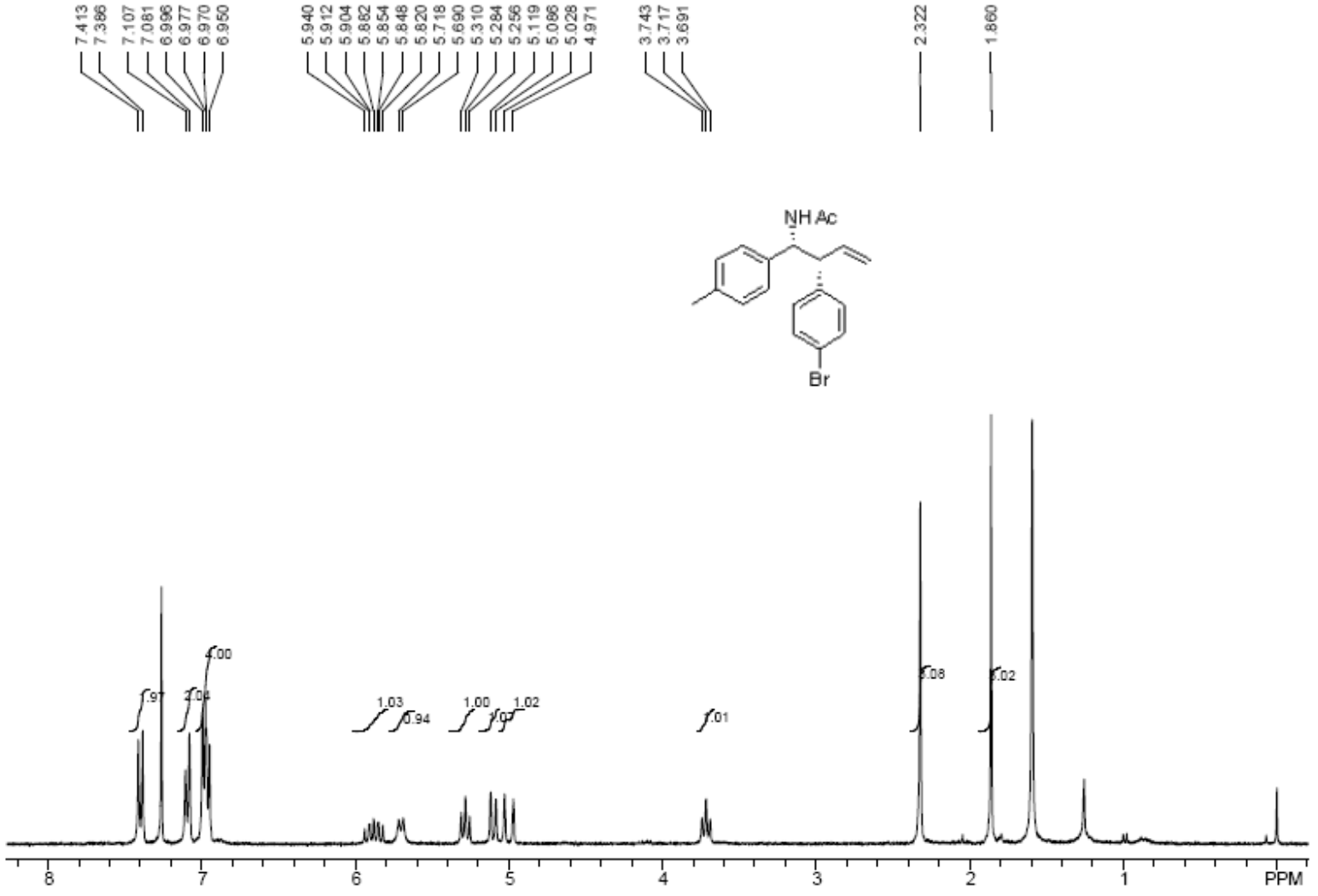
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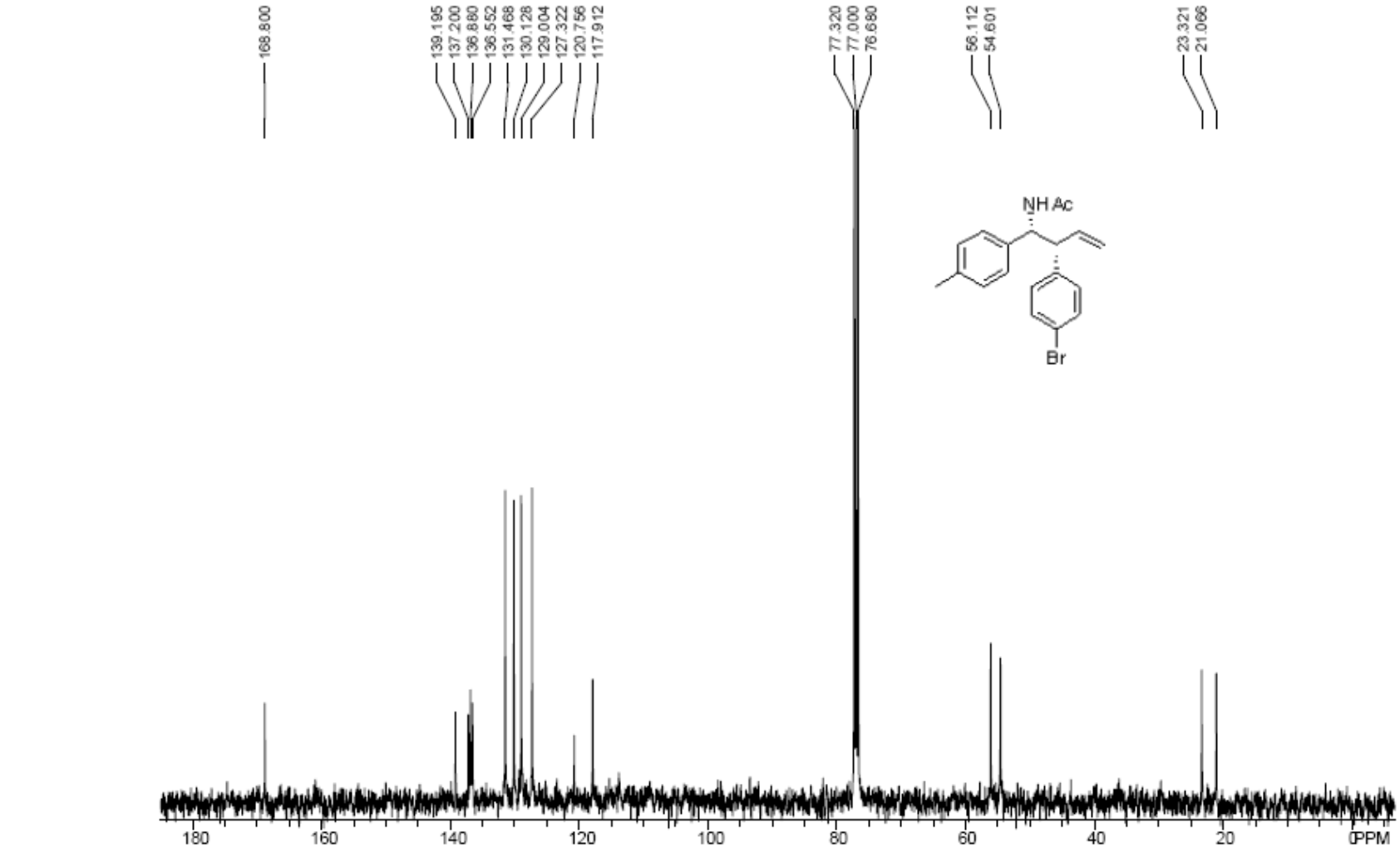
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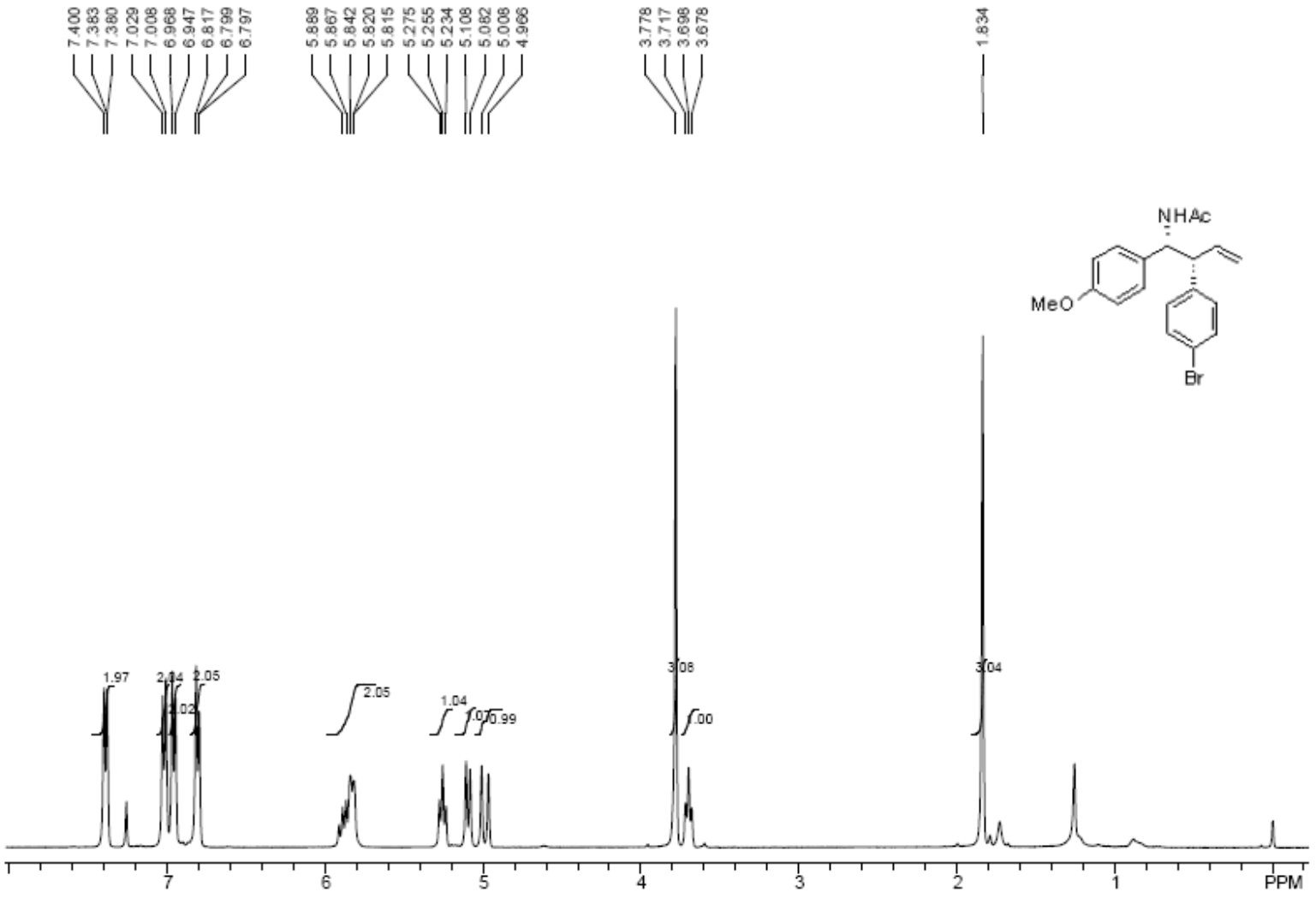
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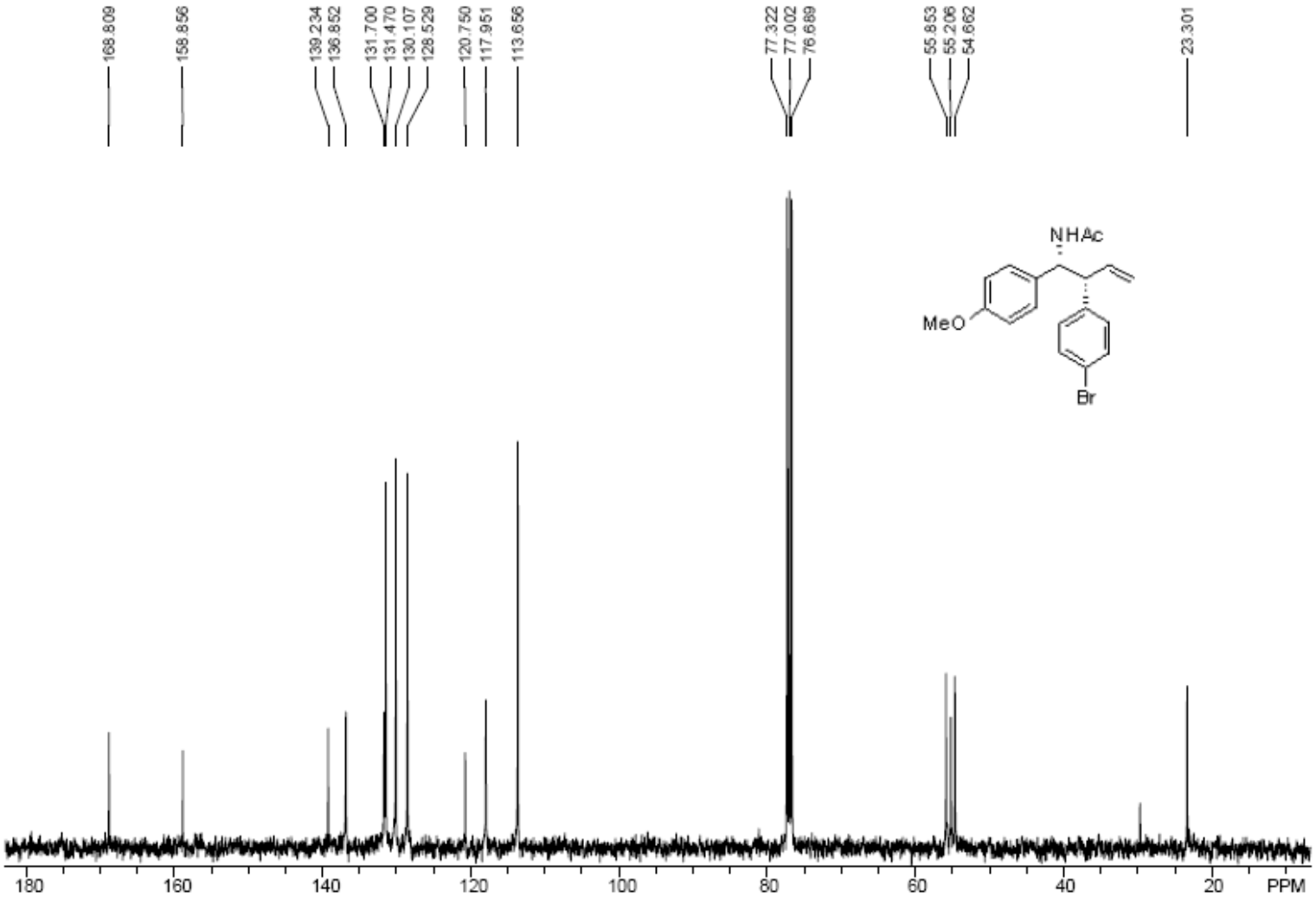
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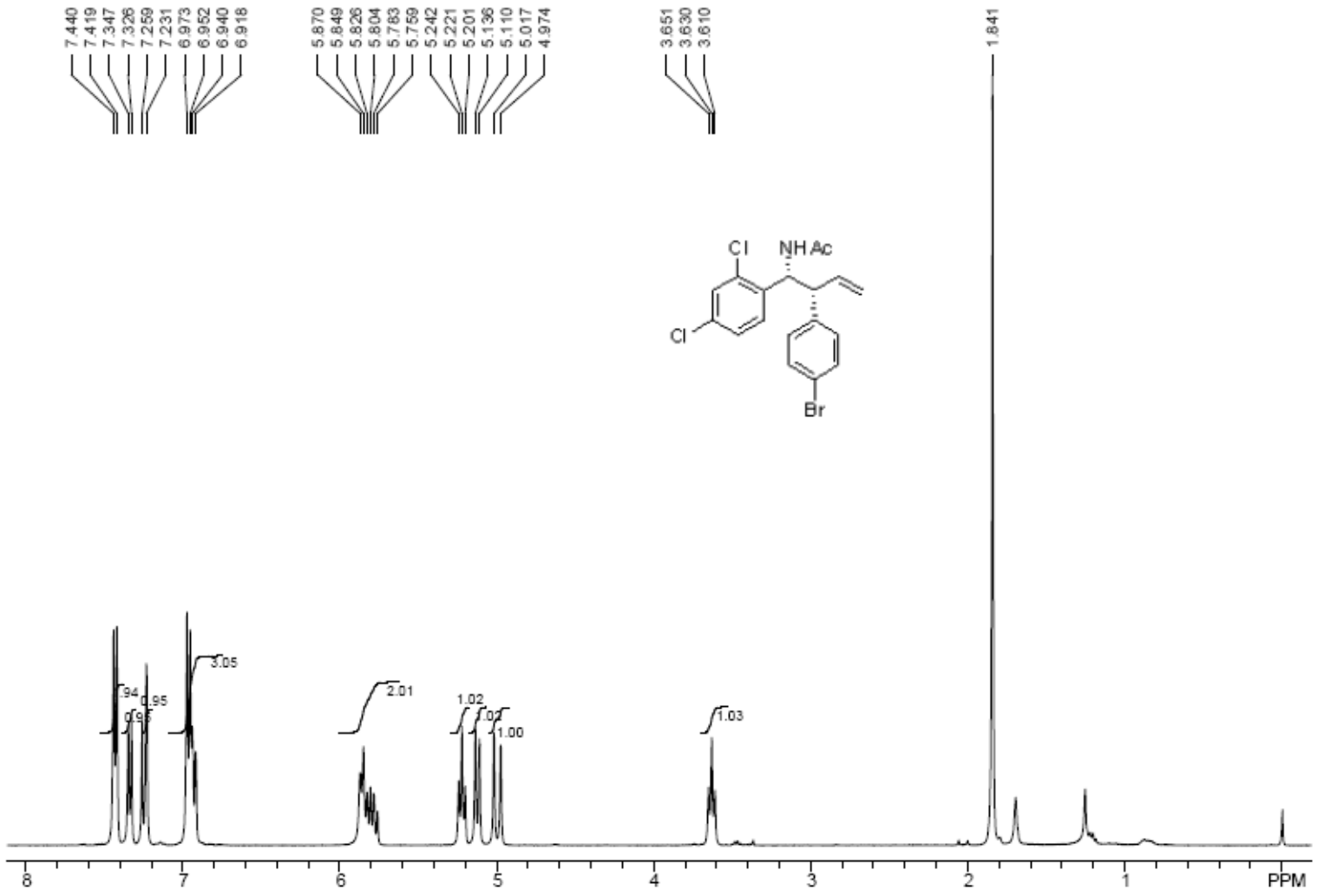
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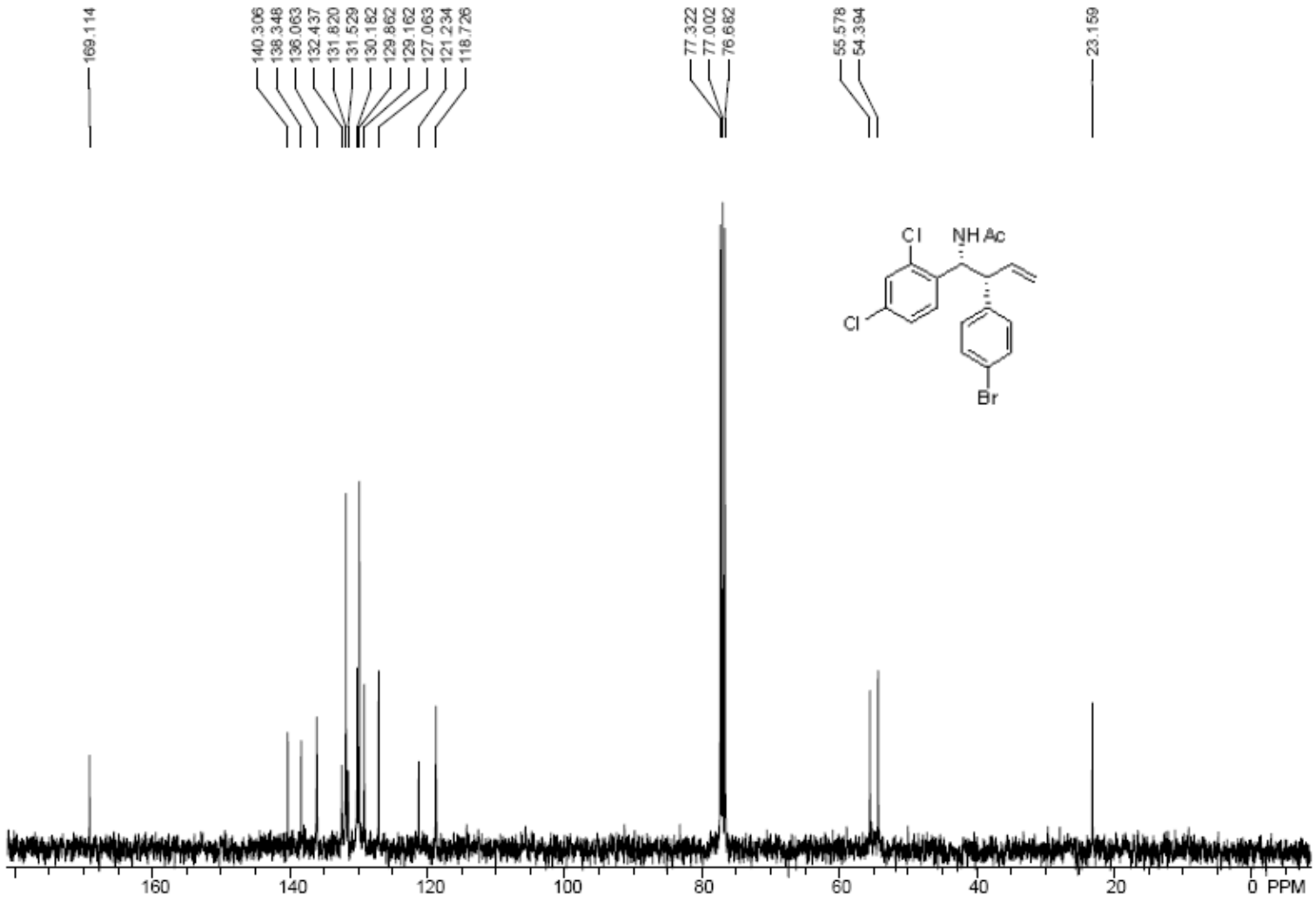
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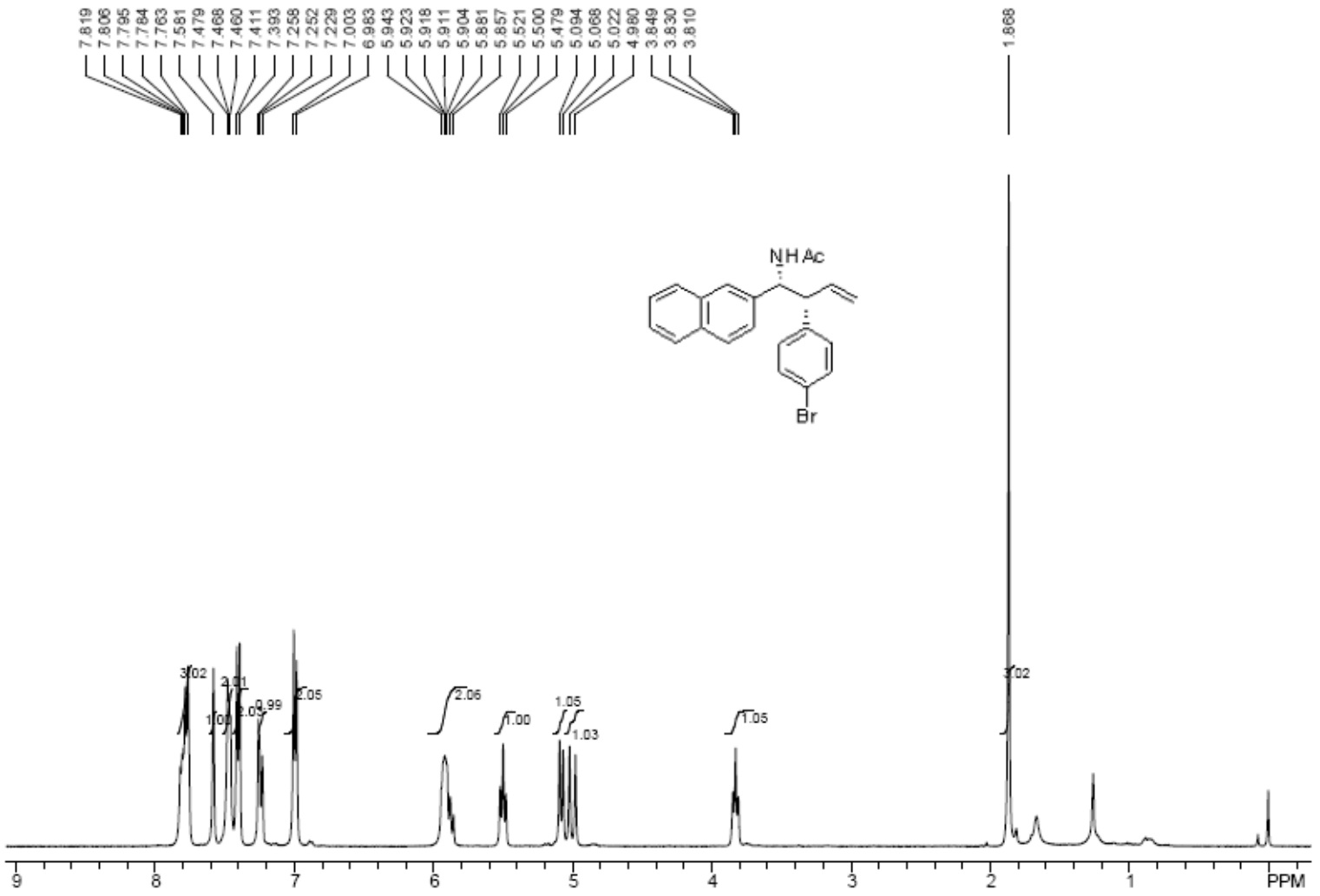
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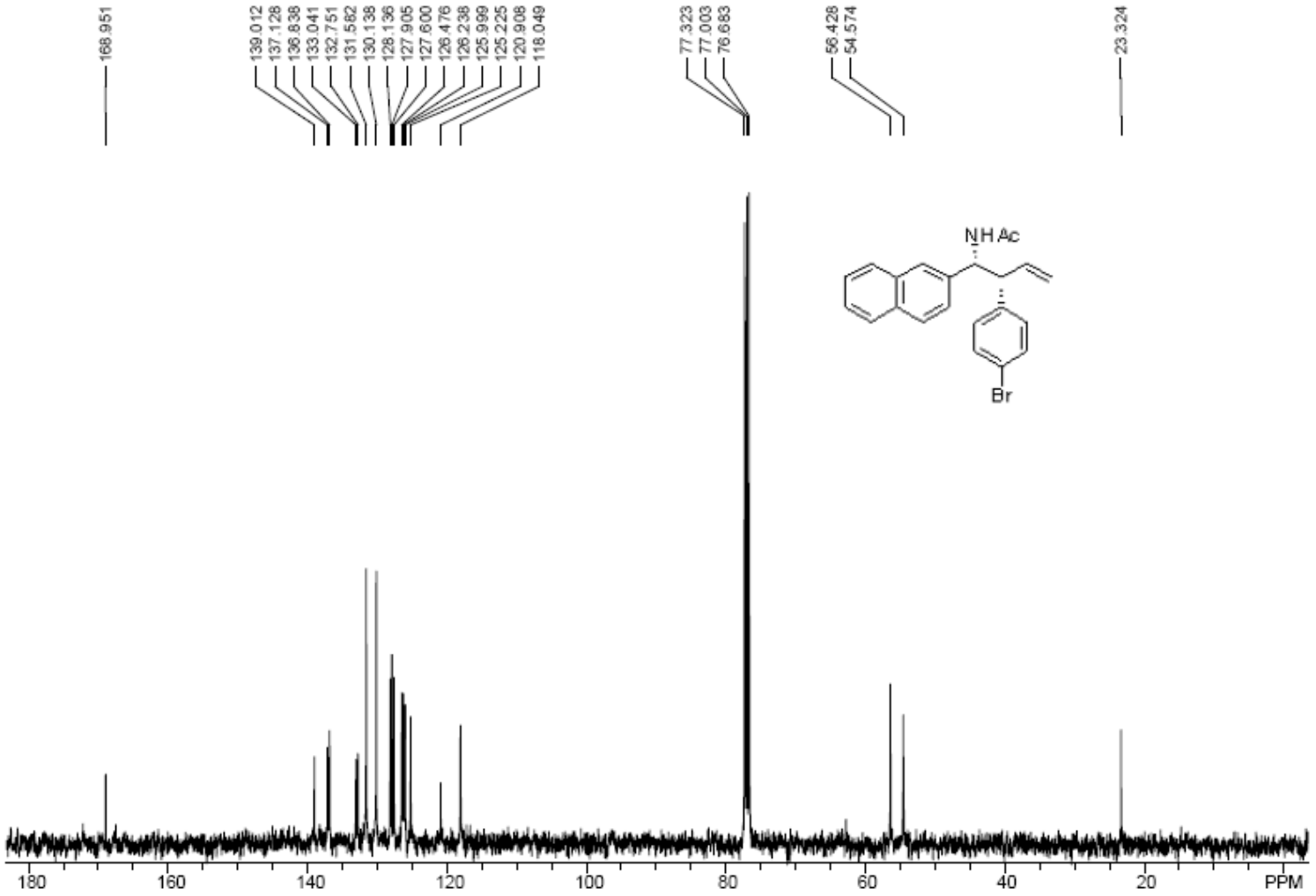
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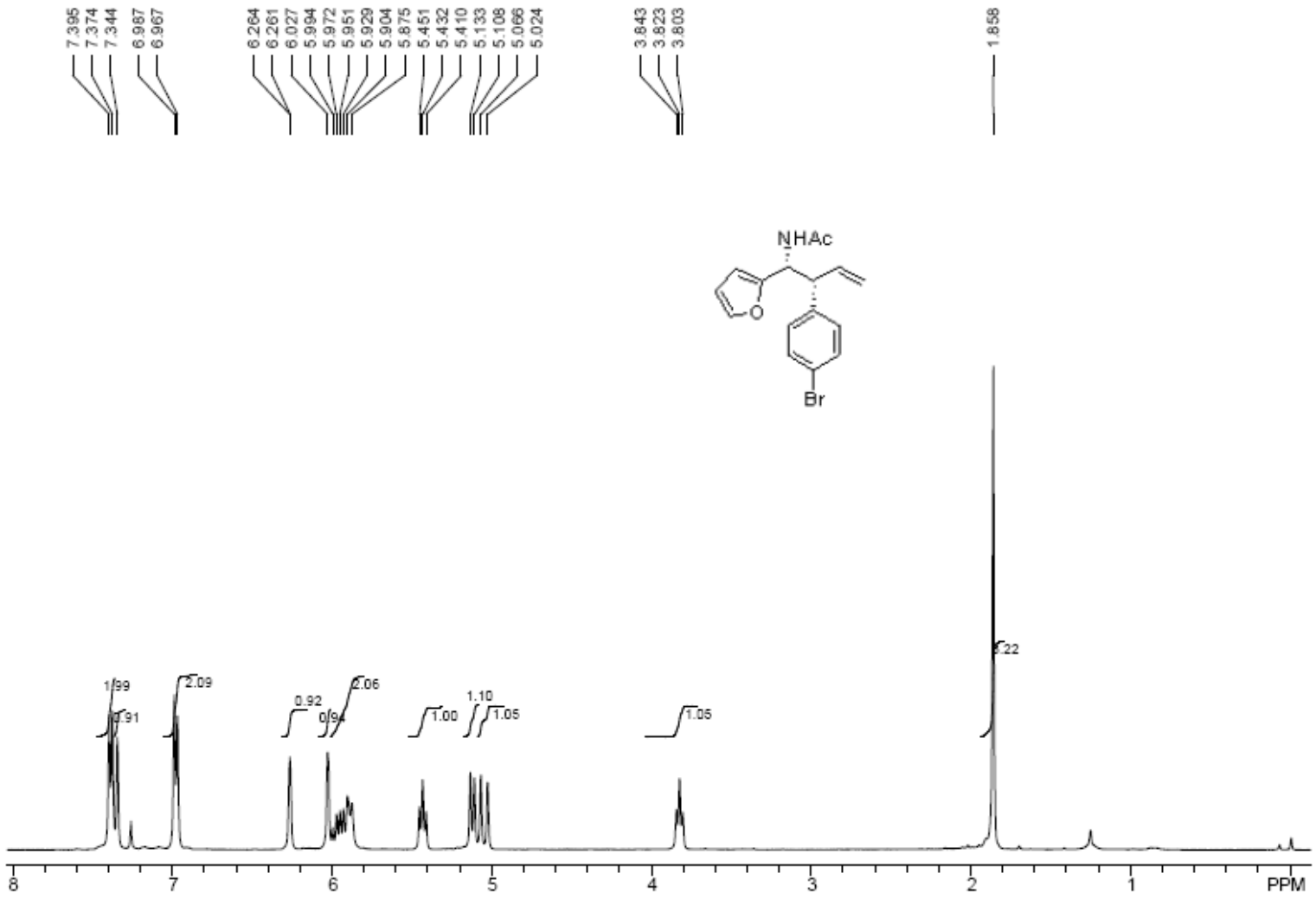
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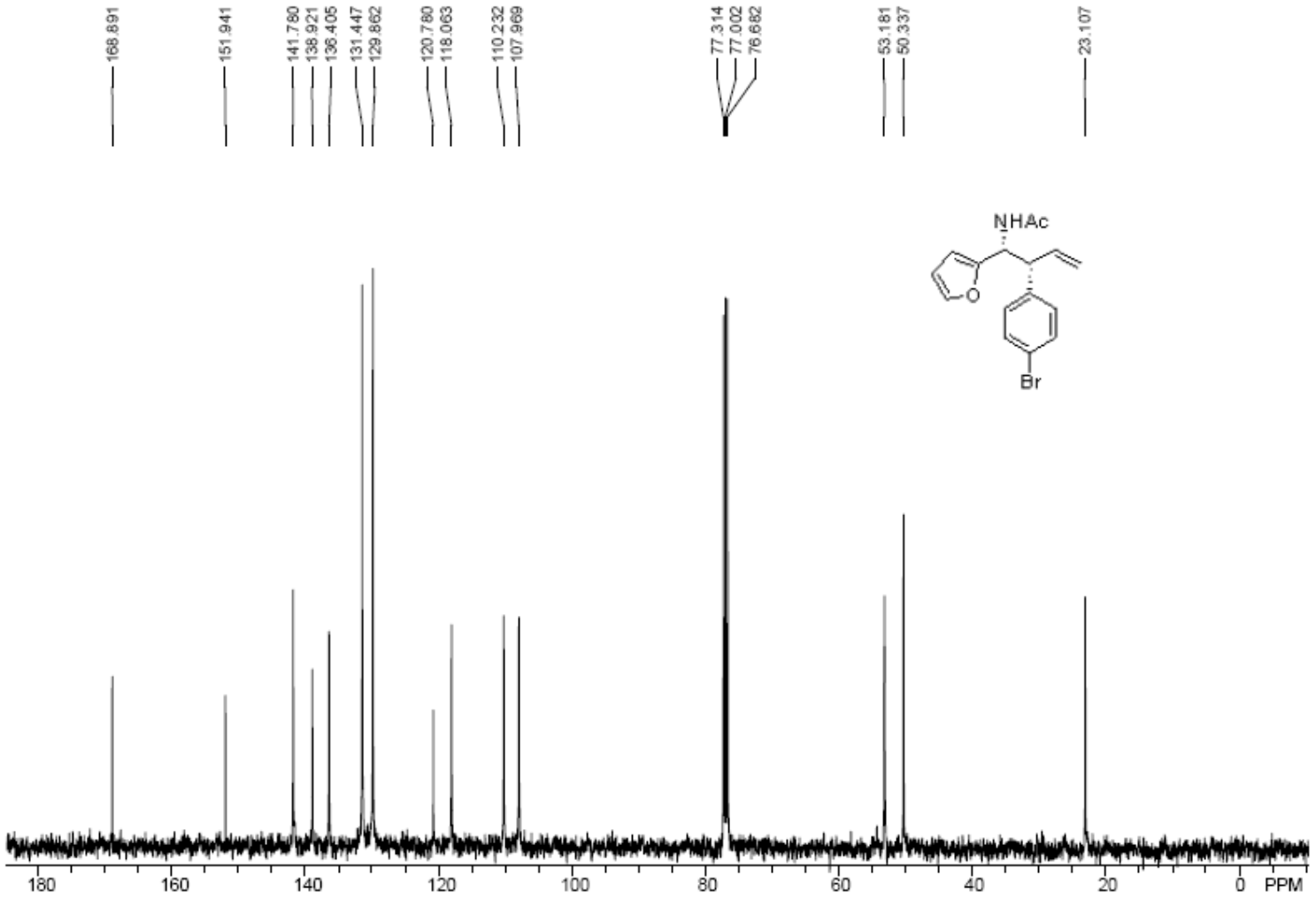
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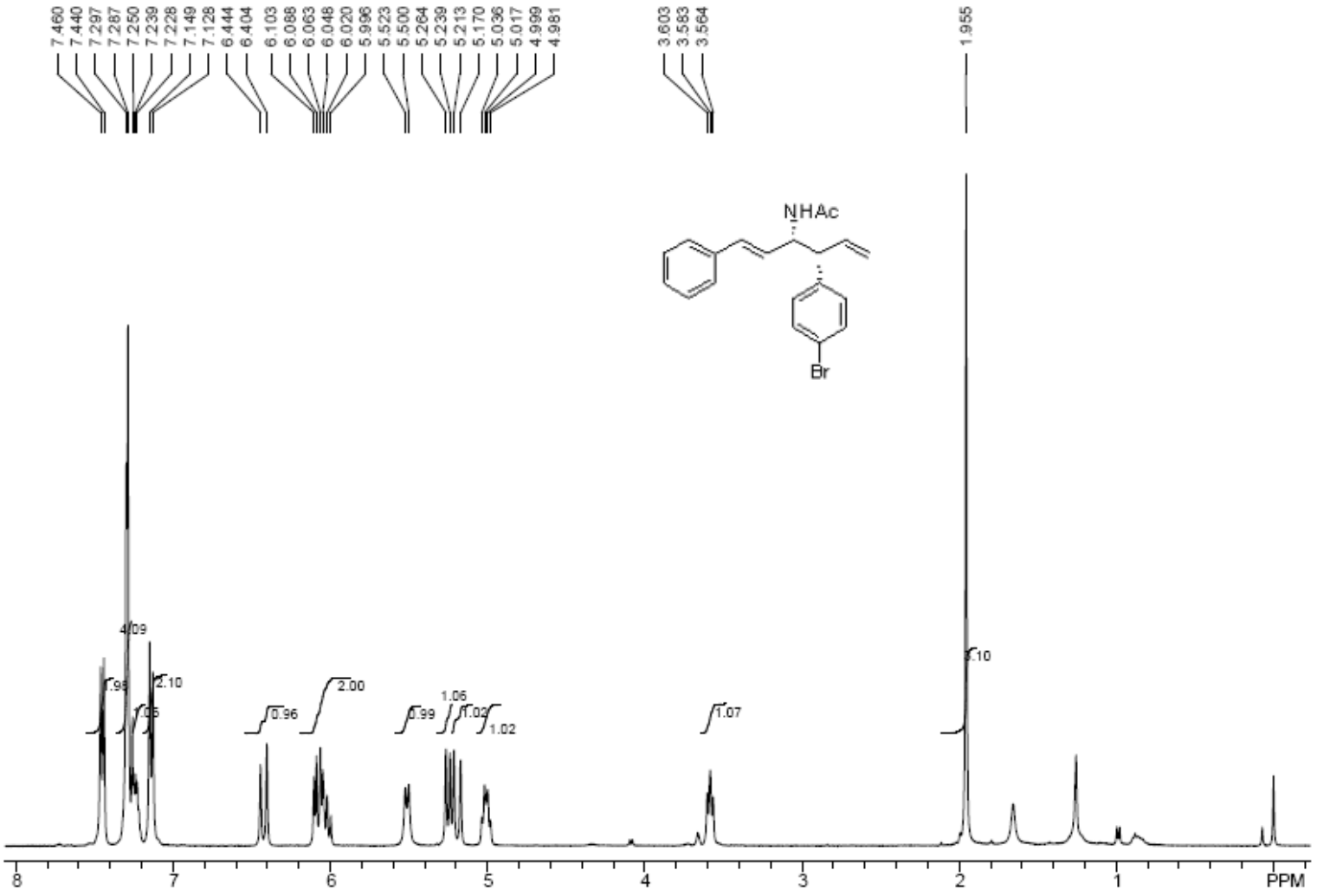
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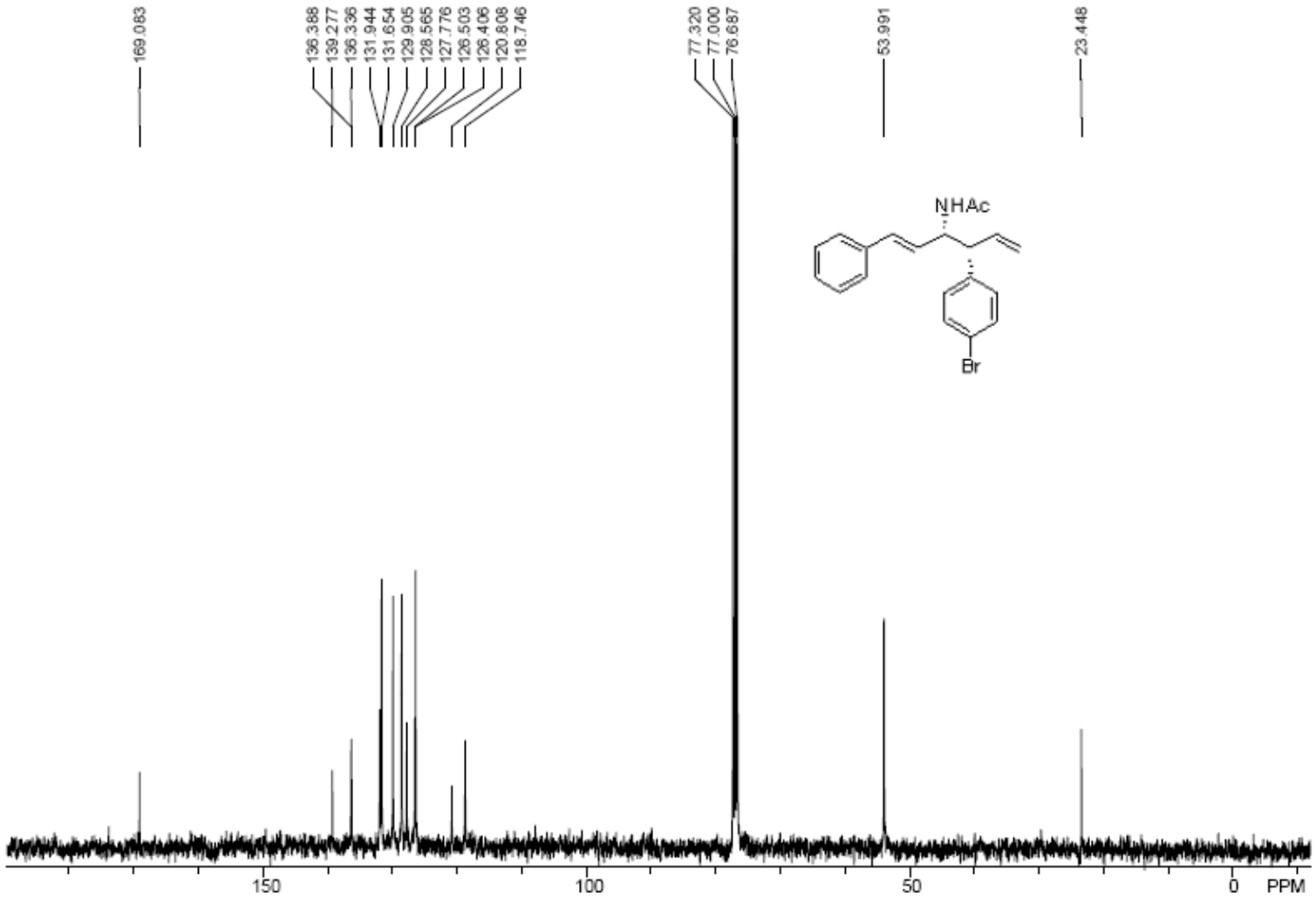
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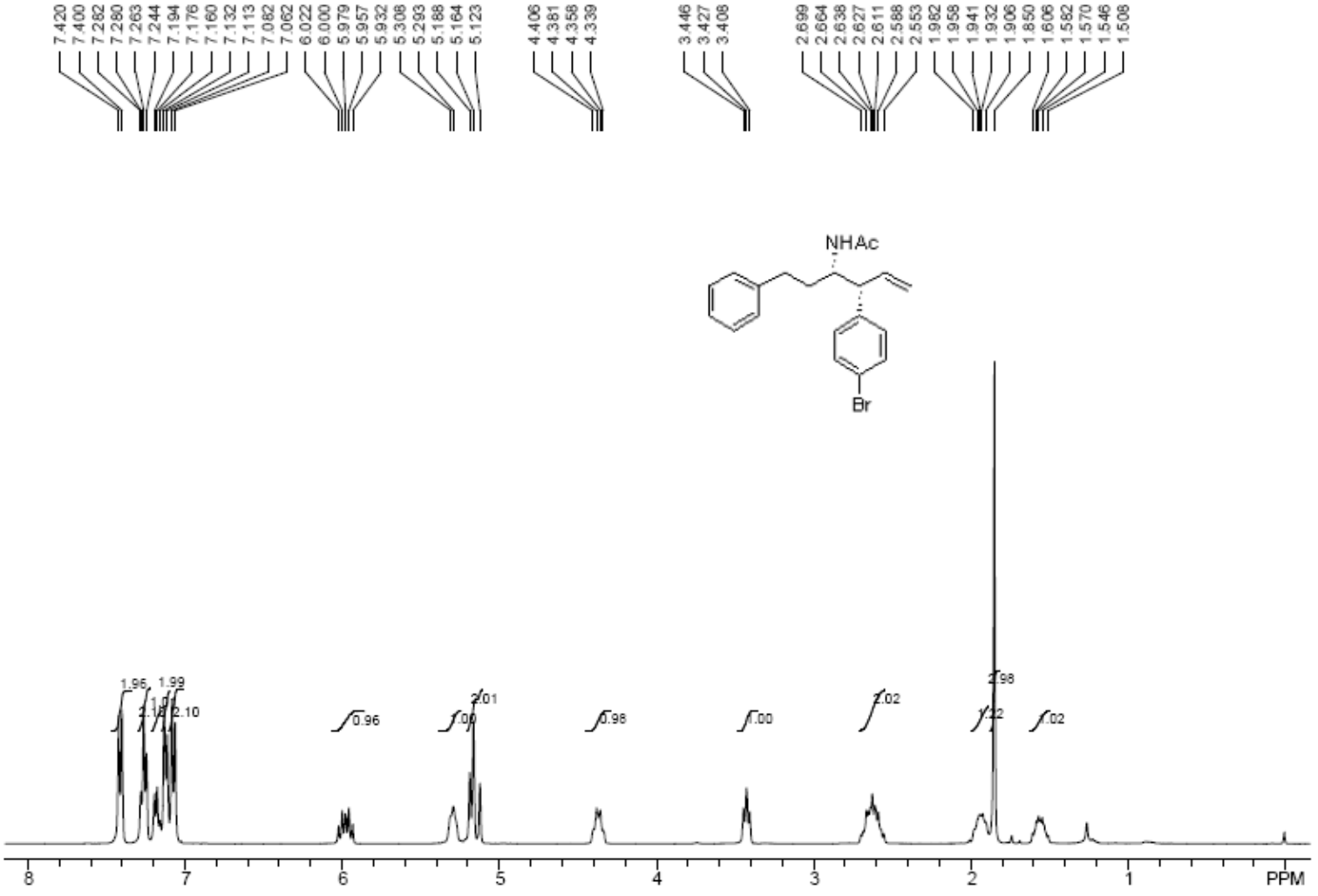
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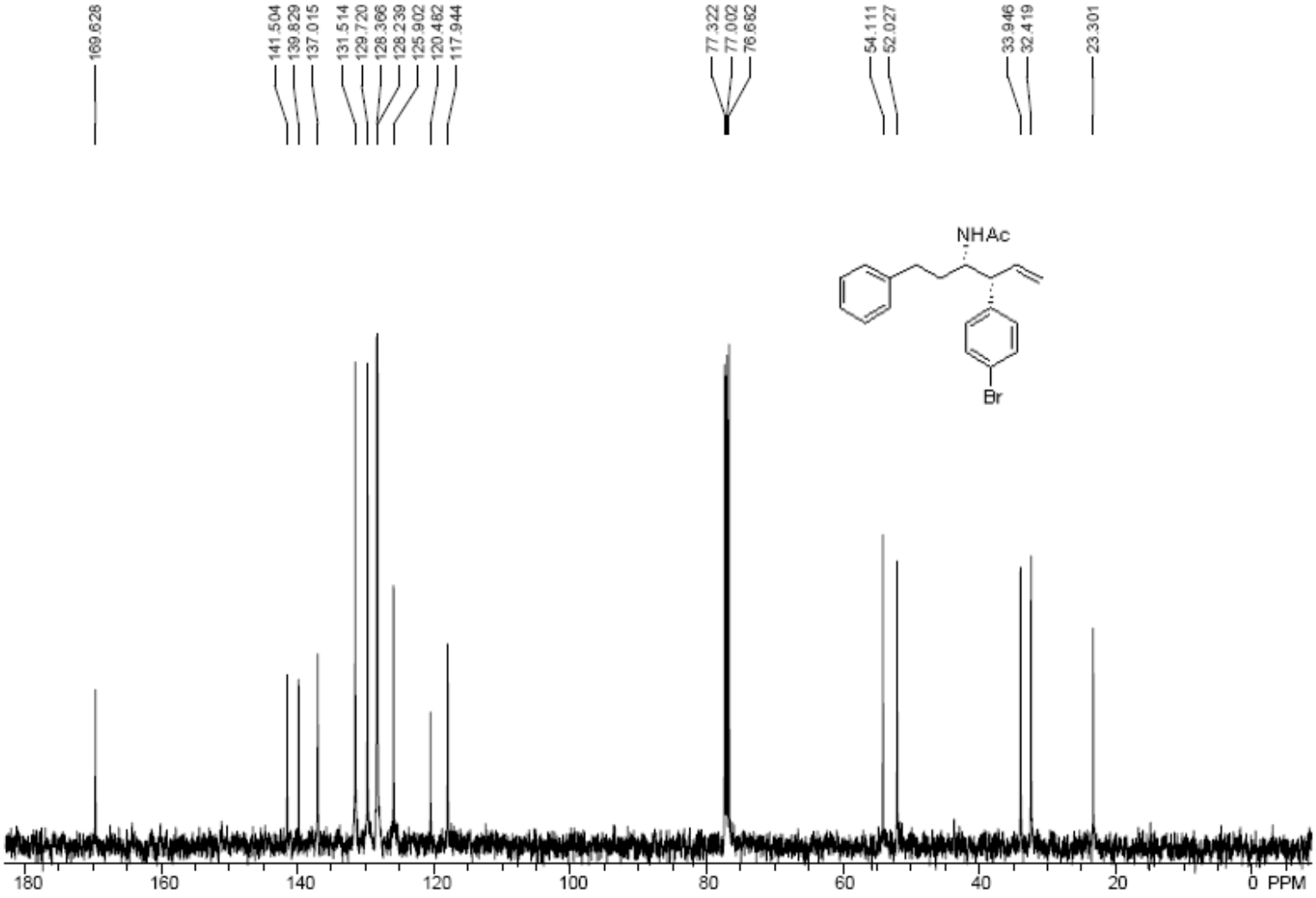
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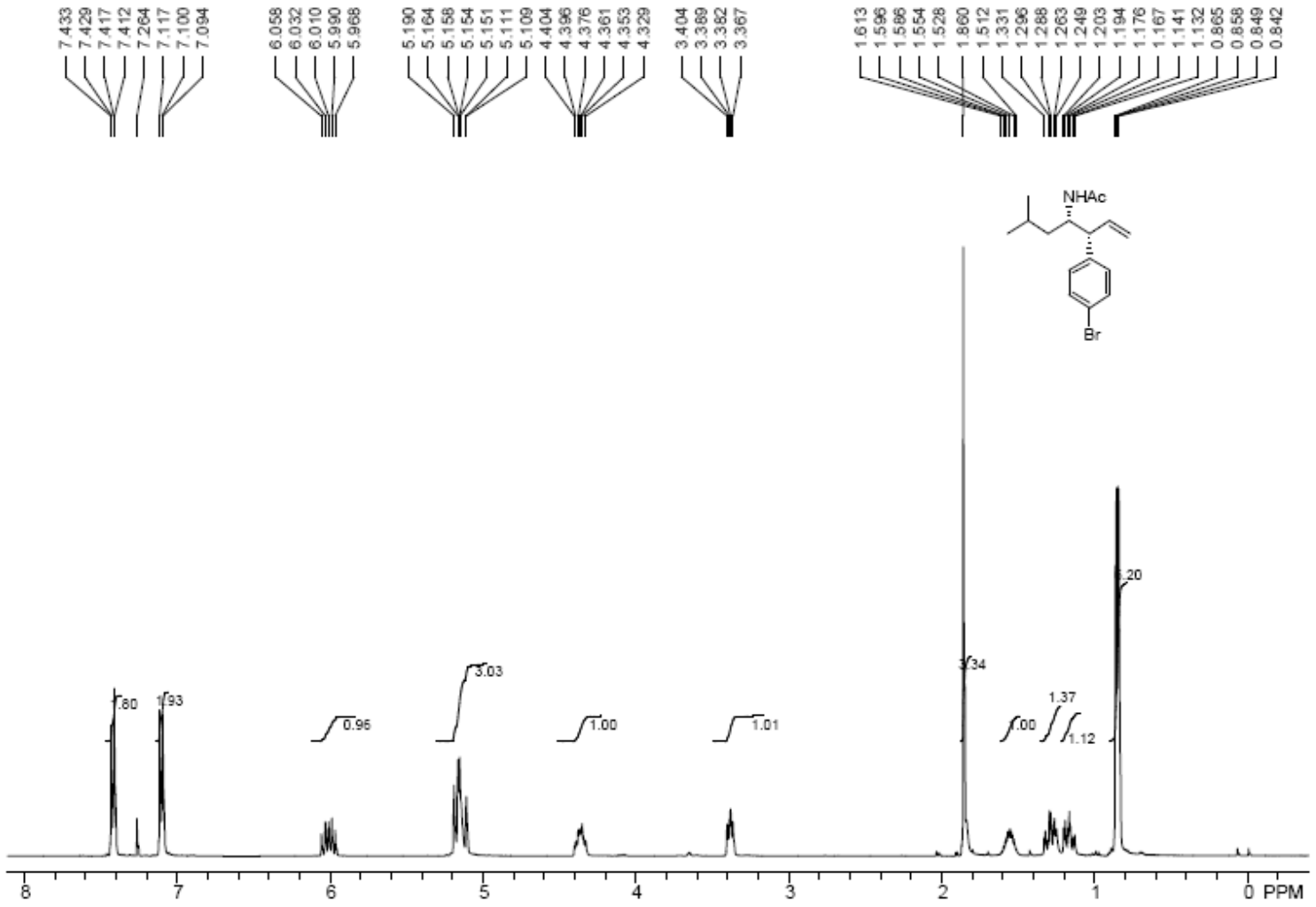
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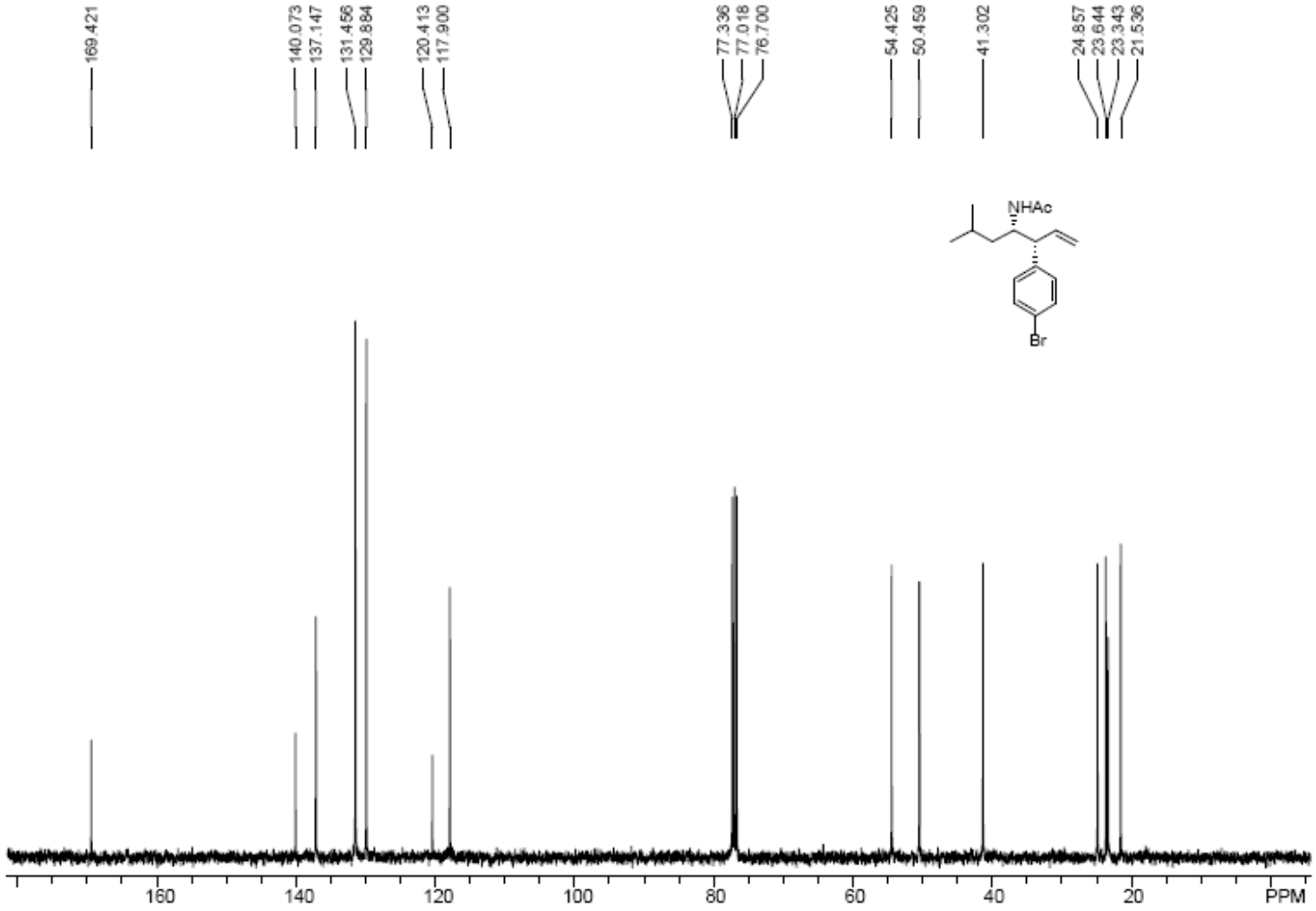
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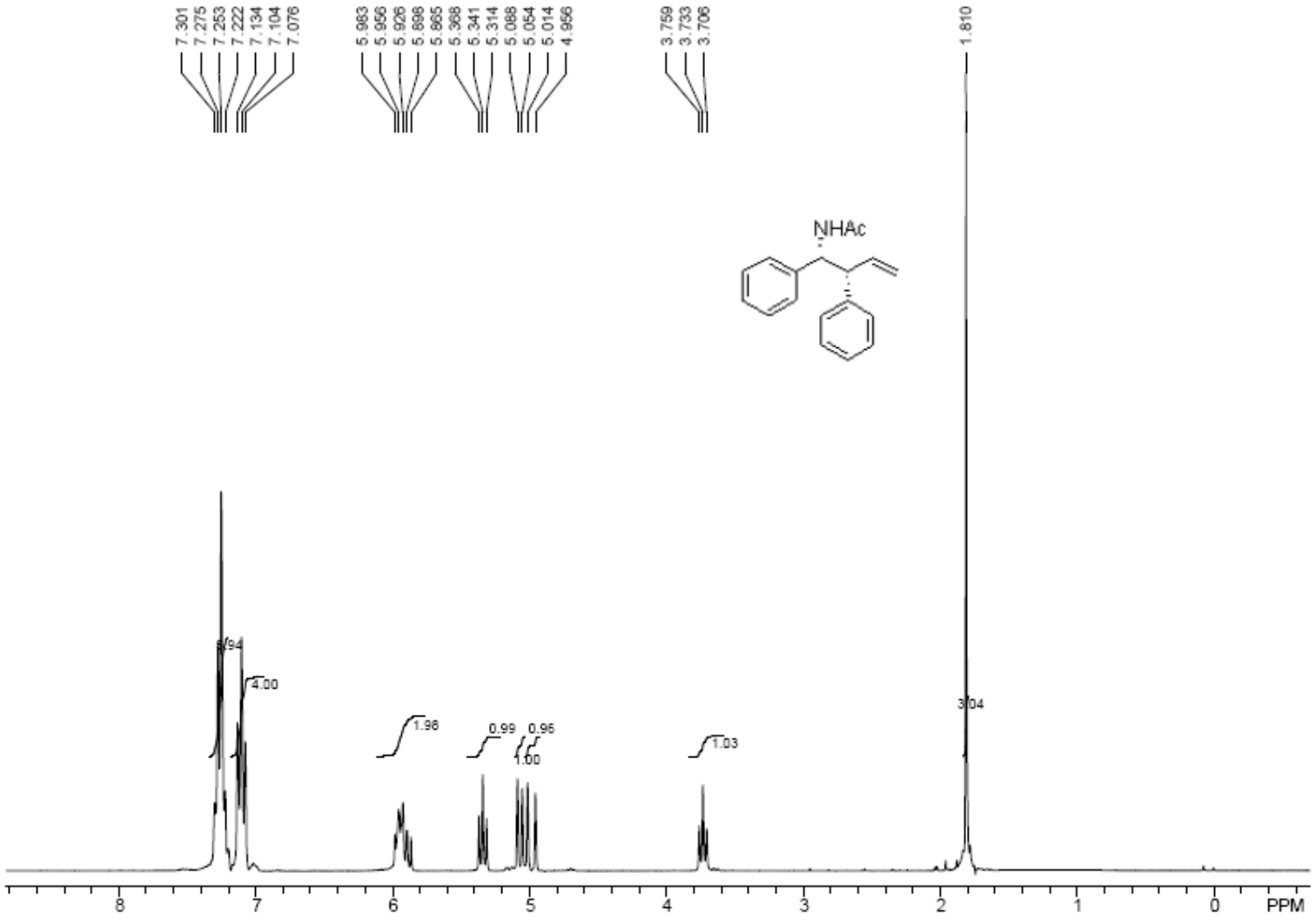
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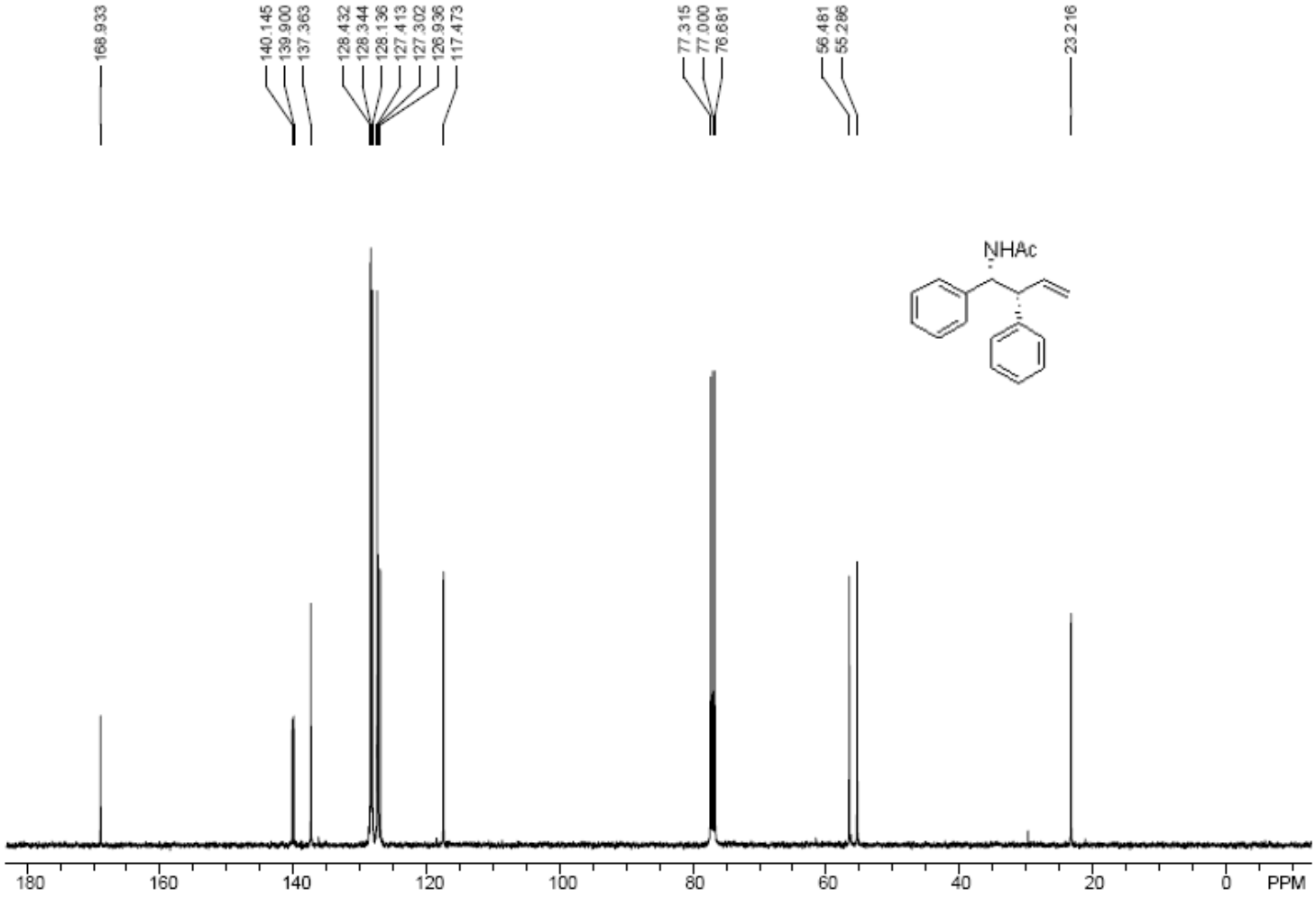
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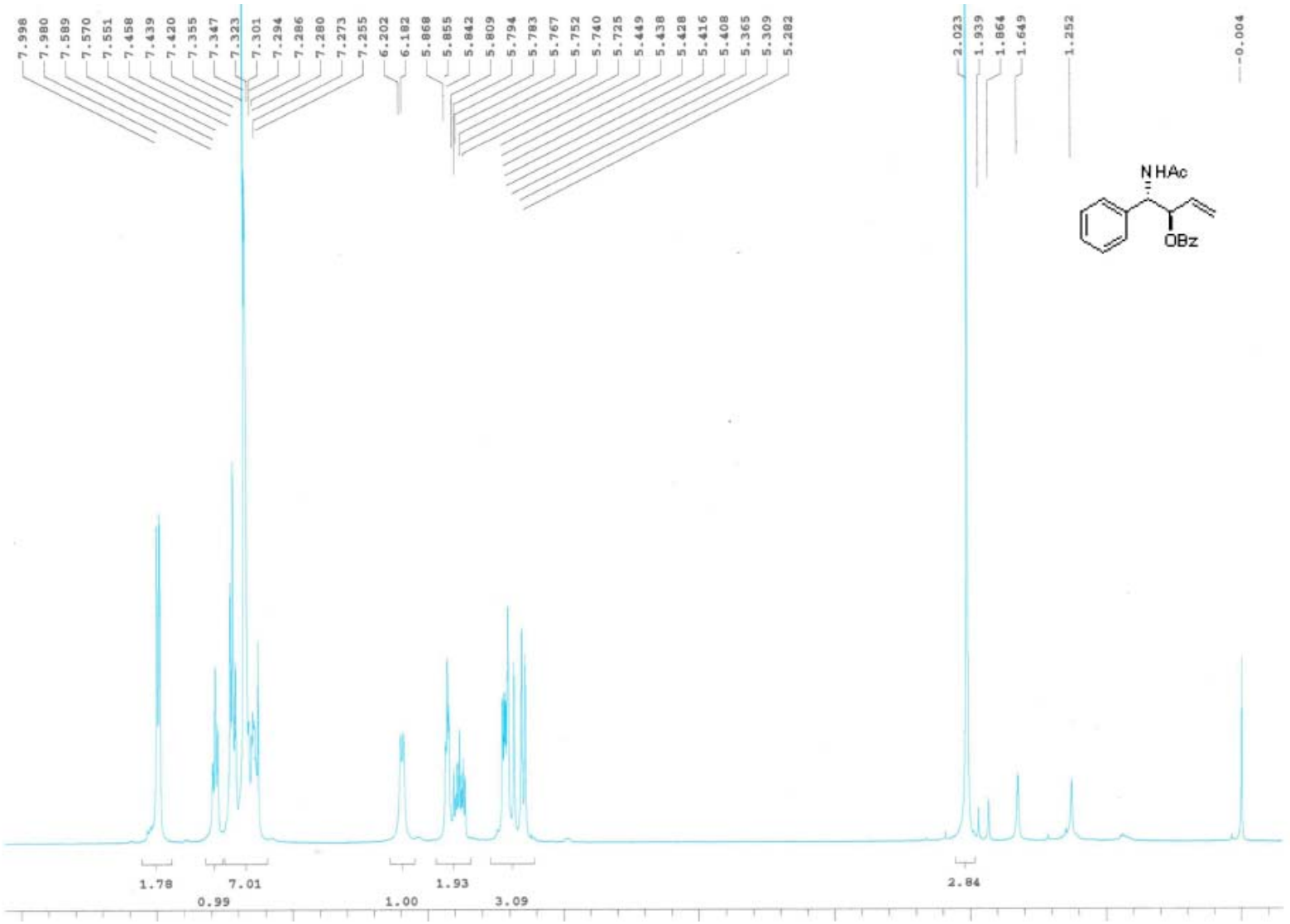
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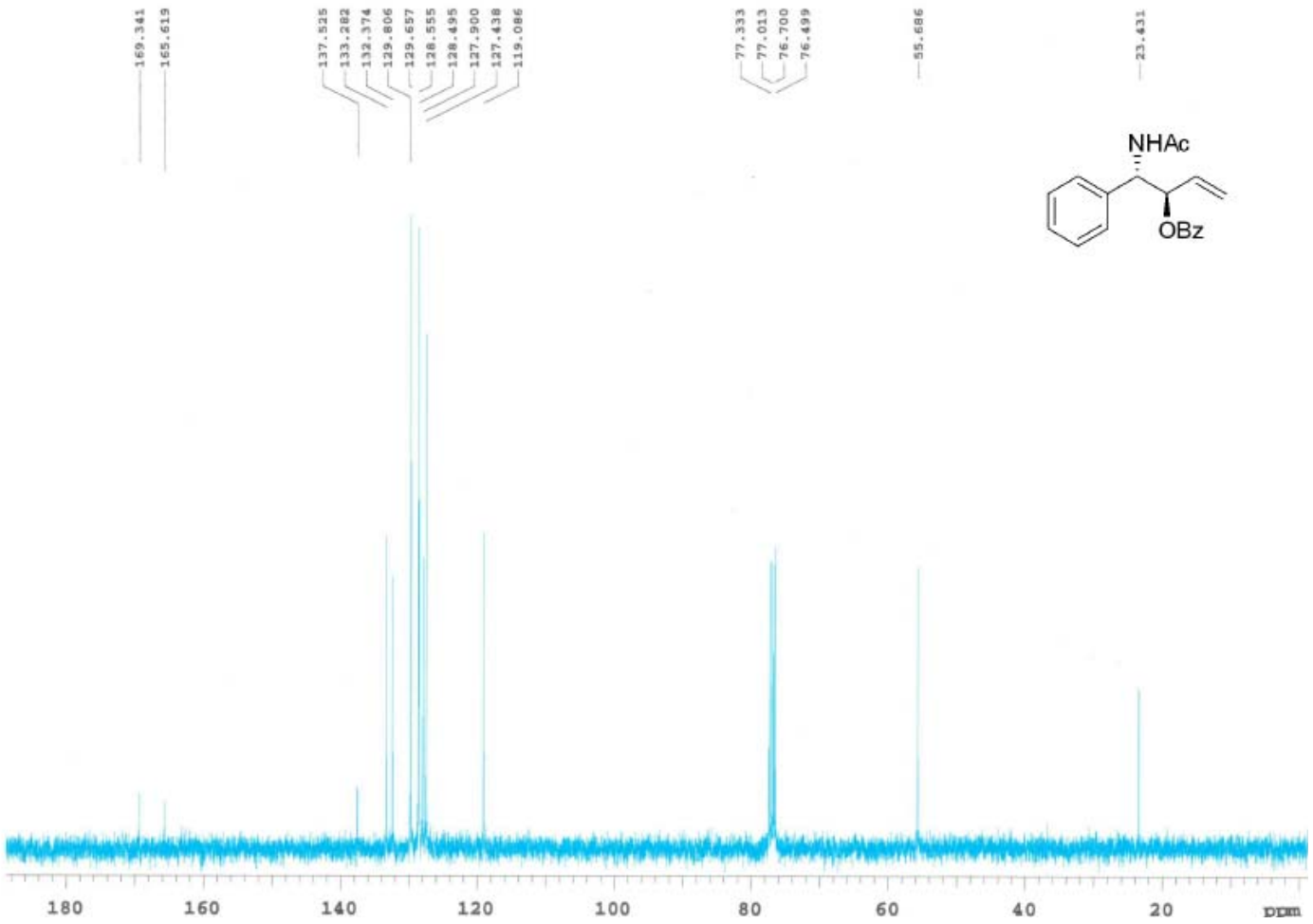
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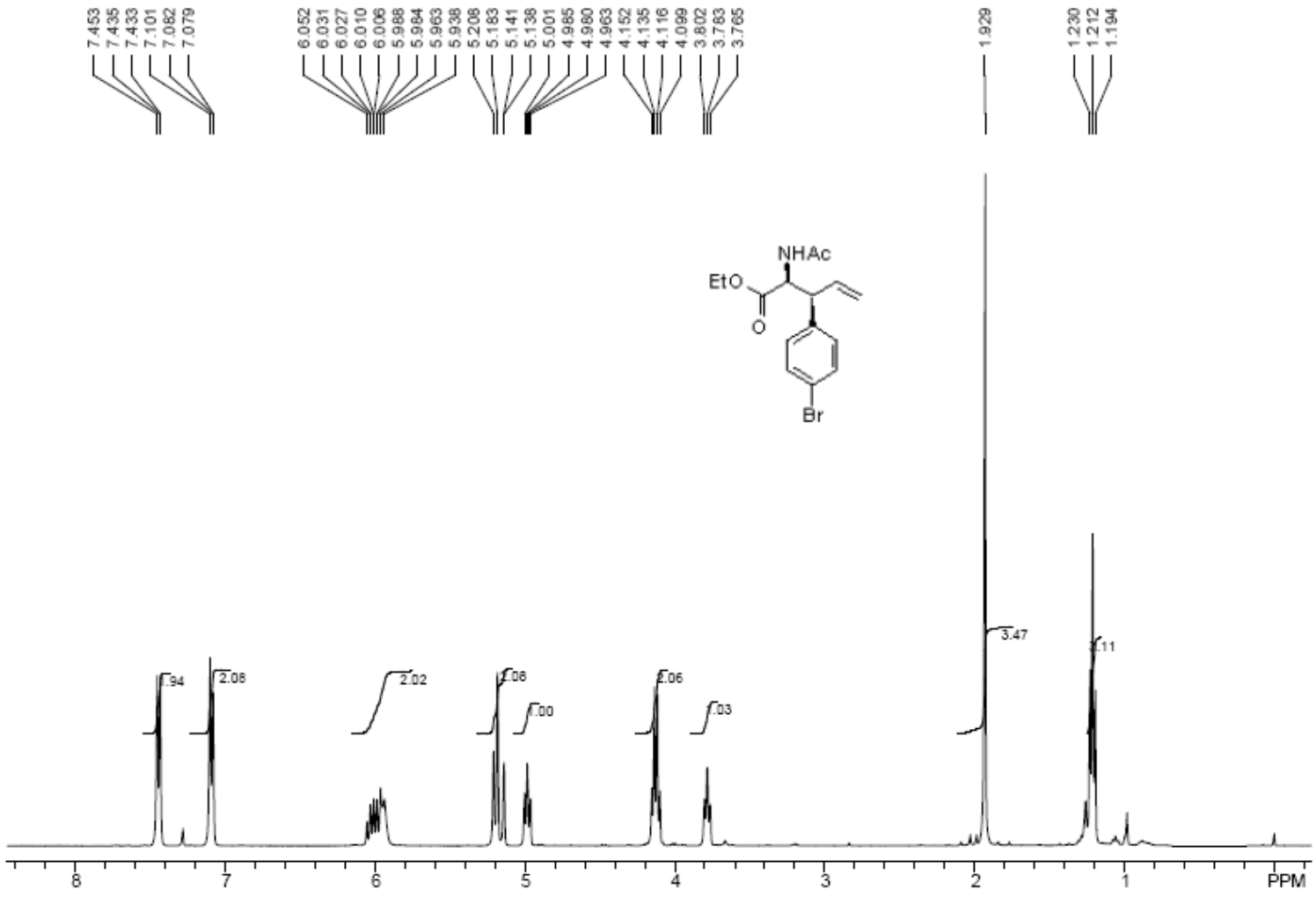
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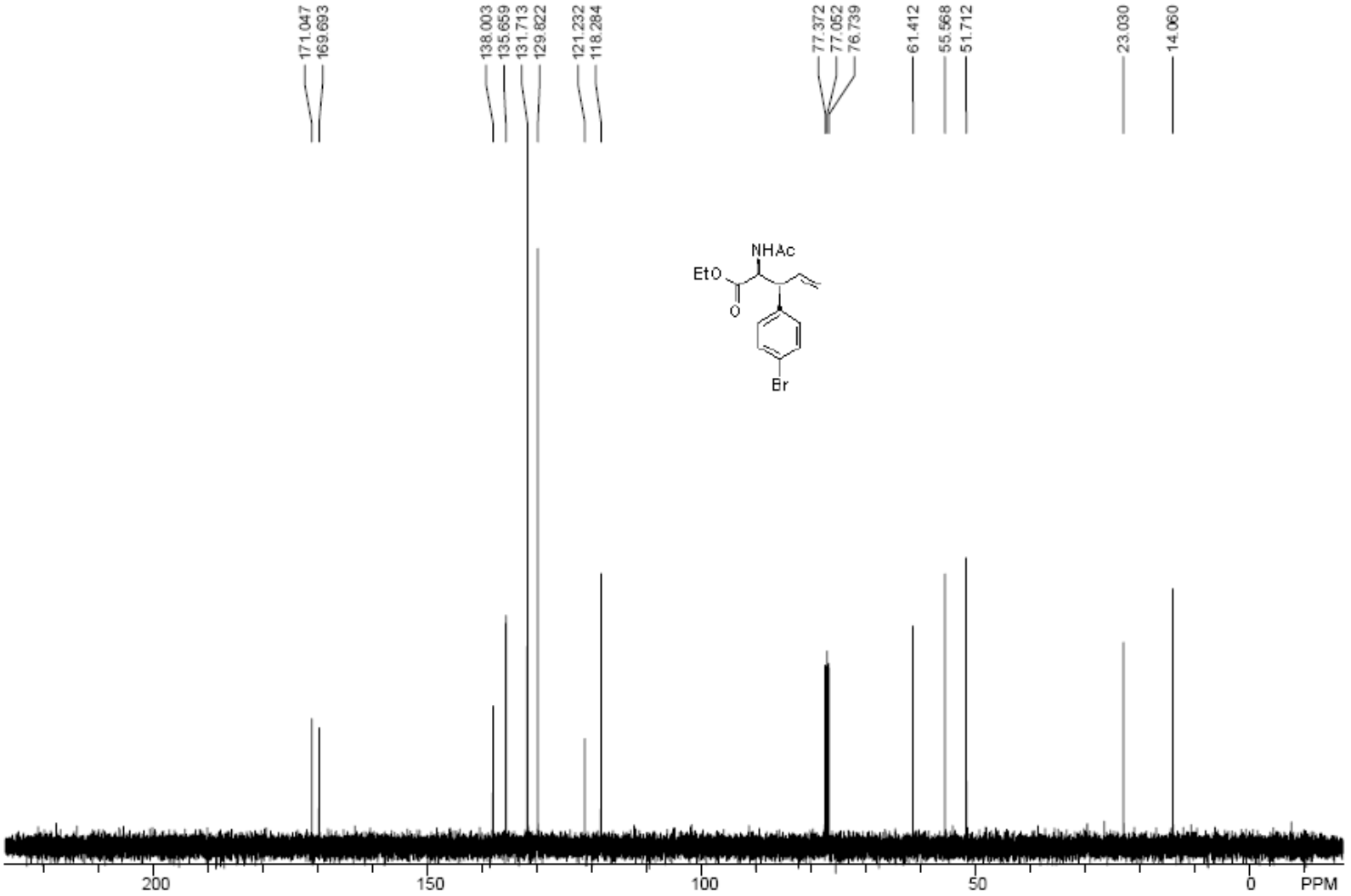
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EtO
O
Br
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50
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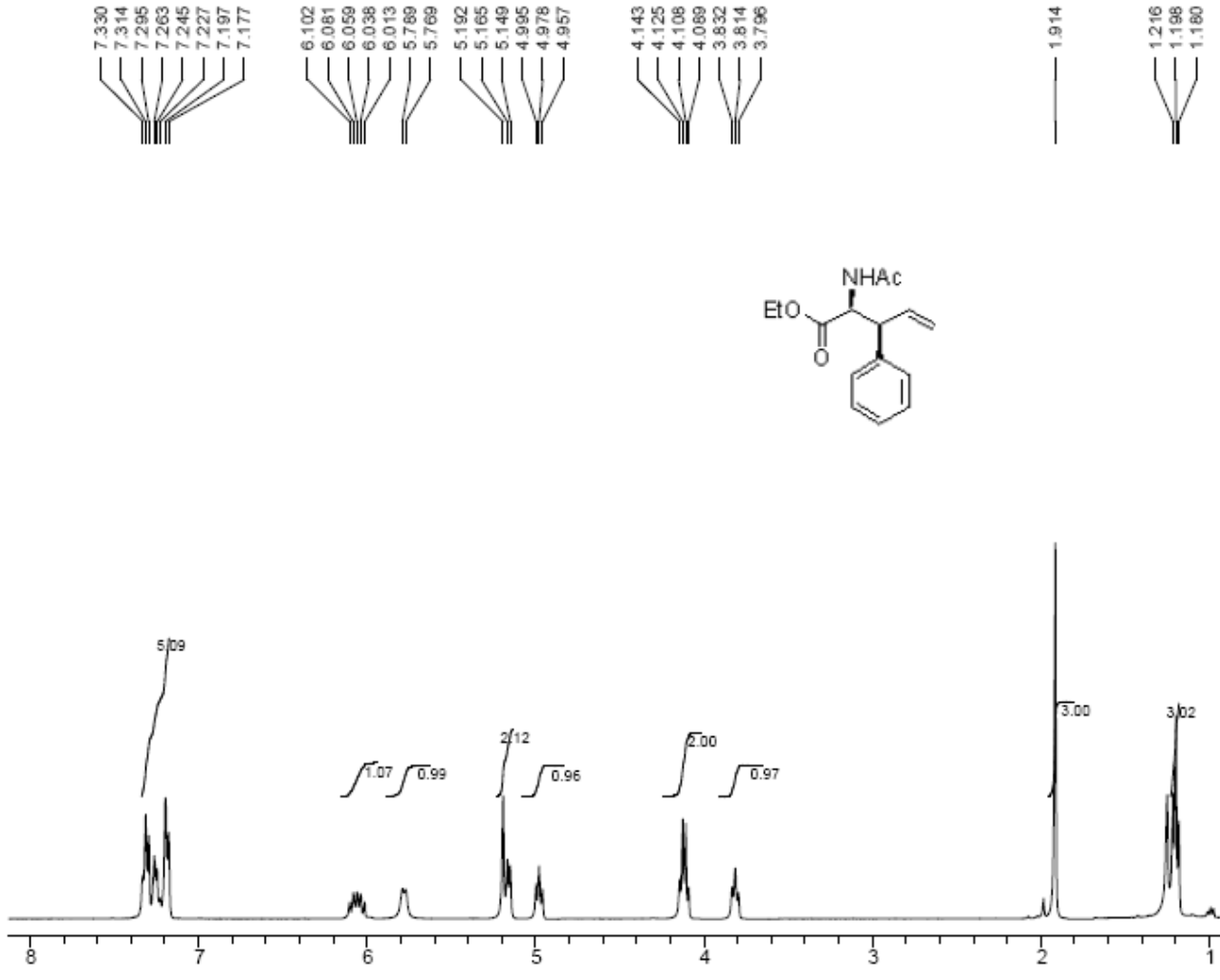
PPM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7.245
7.227
7.197
7.177
6.102
6.081
6.059
6.038
6.013
5.789
5.769
5.192
5.165
5.149
4.995
4.978
4.957
4.143
4.125
4.108
4.089
3.832
3.814
3.796
1.914
1.216
1.198
1.180
NHAc
EtO
O
5.09
1.07
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2.00
0.97
3.00
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7
6
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4
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2
1
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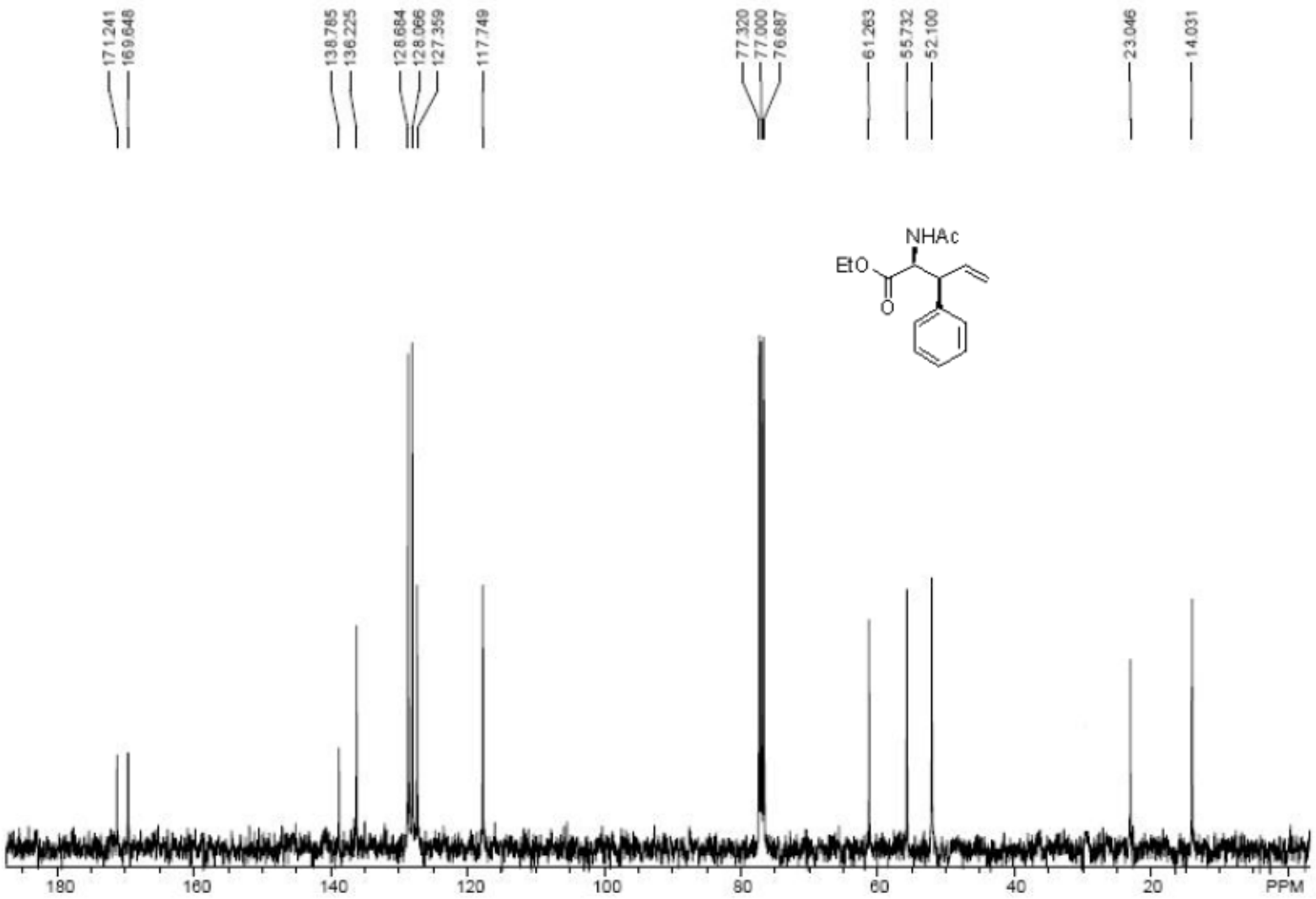
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127.359
117.749
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77.000
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61.263
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14.031
NHAc
EtO
O
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160
140
120
100
80
60
40
20
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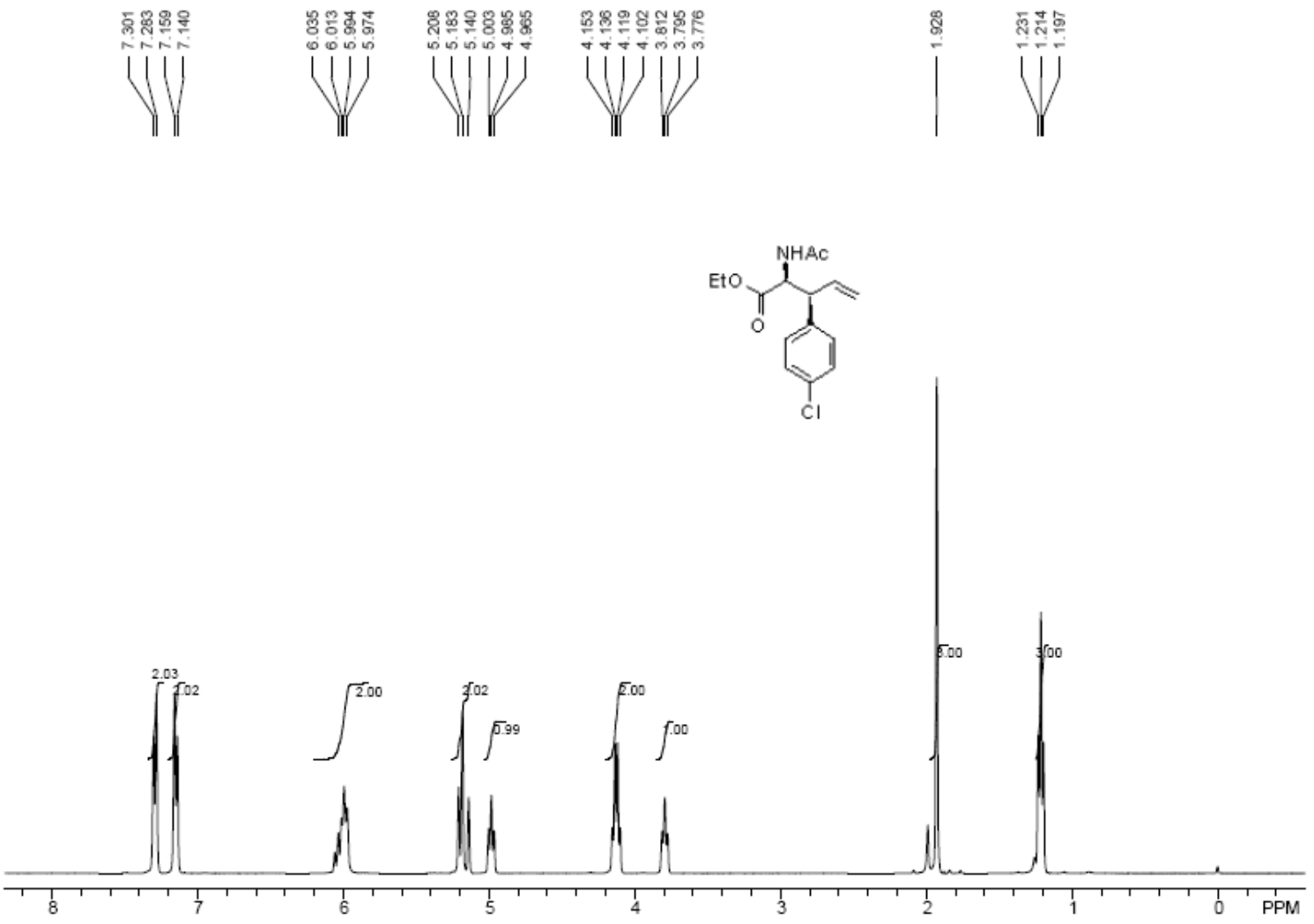
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7.159
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6.035
6.013
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5.183
5.140
5.003
4.985
4.965
4.153
4.136
4.119
4.102
3.812
3.795
3.776
1.928
1.231
1.214
1.197
NHAc
EtO
O
Cl
2.03
2.02
2.00
2.02
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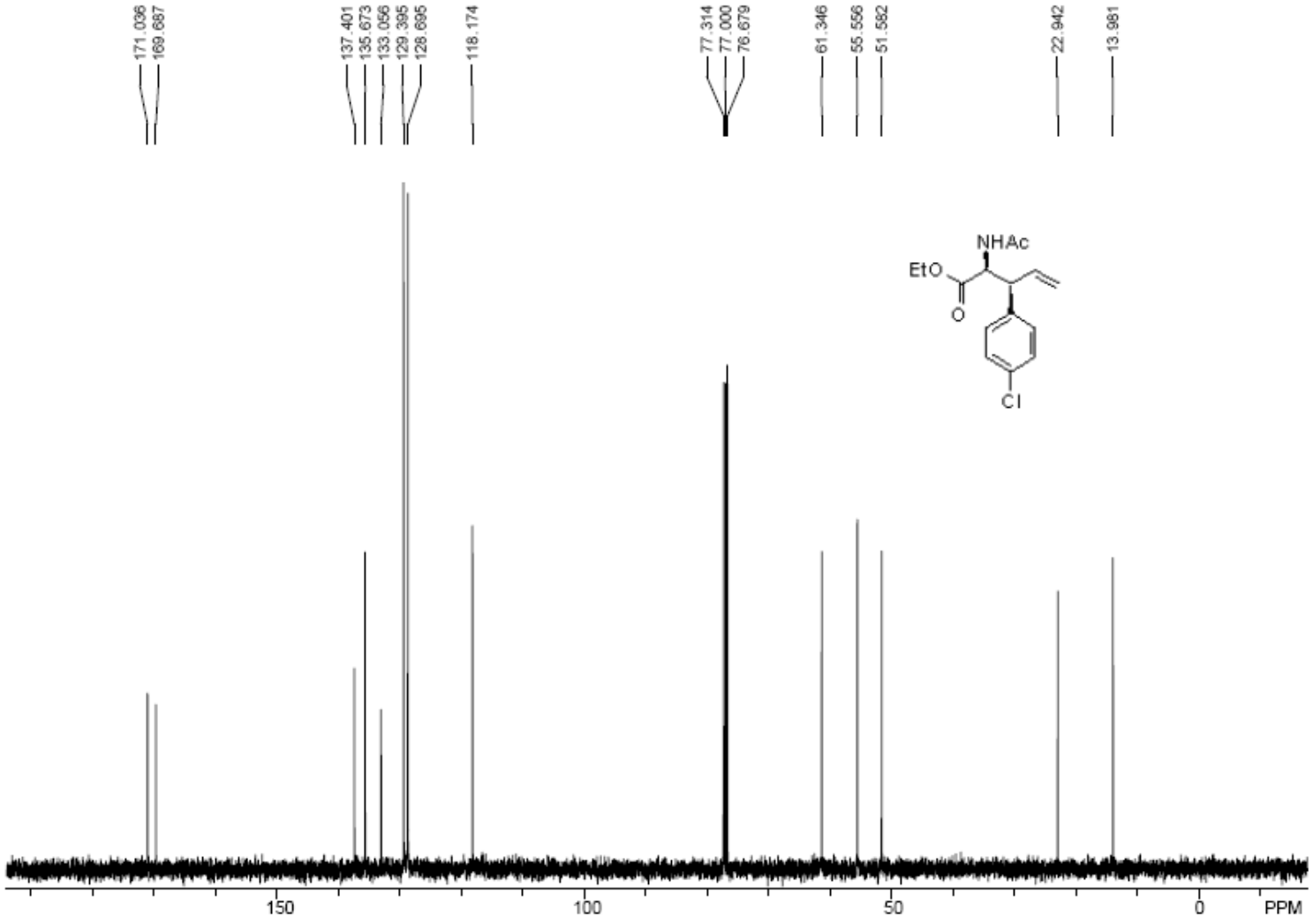
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13.981
NHAc
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O
Cl
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50
0
PPM