Supplementary Information

Decarboxylative [3+2] Cycloaddition of Propargyl Cyclic Carbonates with C,O-bis(nucleophile)s to access Dihydrofuro[3,2-*c*]coumarins and Dihydronaphtho[1,2-*b*]furans with Quaternary Center

Shravani Battula,[a,b] Pranay Kothuri,[a] Haripriya Bhumannagari[a] and Kiranmai Nayani[a,b]*

[a]*Department of Organic Synthesis and Process Chemistry, CSIR-Indian Institute of Chemical Technology, Hyderabad 500007, Telangana, India*

[b]*Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India*

*E-mail: kiranmainayani@iict.res.in

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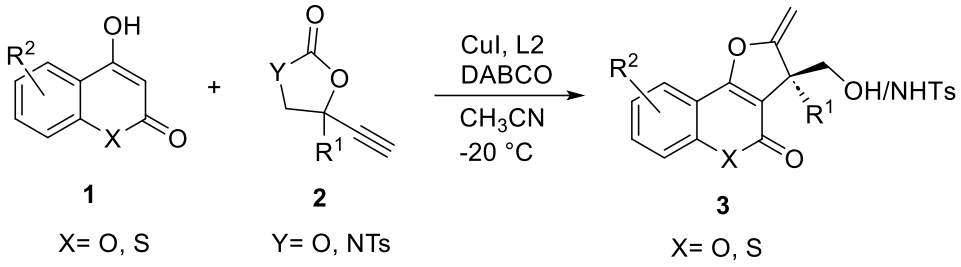
1. General Information

All chemicals have been purchased from commercial sources and were used without further purification unless otherwise noted. All solvents are reagent grade or HPLC grade. The synthetic transformations have been monitored by thin layer chromatography (TLC). TLC was performed on silica gel 60 F_{254} plates (glass plates). Concentration under reduced pressure was performed by rotary evaporation below 45 °C. Column chromatography was performed using silica gel (100-200 mesh) packed in glass columns. Yields refer to spectroscopically pure compounds after isolation. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ and MeOH-*d4* using 400 or 500 MHz (^{1}H), 100 or 125 MHz (^{13}C) and 376 MHz (^{19}F). Chemical shifts (δ-values) are reported in ppm, spectra were calibrated related to solvents' residual proton chemical shifts ($CDCl_3$, δ = 7.26 ppm and MeOH-d_4, δ= 3.31 ppm) and solvents' residual carbon chemical shifts ($CDCl_3$, δ = 77.16 ppm and MeOH-d_4, δ= 49.01 ppm), multiplicity is reported as follows: s = singlet, brs = broad singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, m = multiplet or unresolved and coupling constant *J* in Hz. Melting points (mp) were determined in open capillaries and are uncorrected. Infrared spectra (IR) were recorded on a 0.1 mm KBr demountable cell. High-resolution mass spectra (HRMS) were obtained by electrospray ionization using a Q-TOF mass spectrometer in positive ion mode (M+H or M+Na) as indicated.

2. Synthesis and Experimental Characterization of Compounds

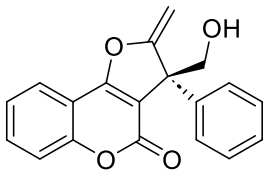
2.1 General Procedure for Synthesis of Dihydrofuro[3,2-*c*]coumarins (3)



To a clean and dry round-bottom flask, under nitrogen atmosphere added dried CuI (1 mol%) and **L2** (2 mol%) in CH_3CN (1 mL) solvent and stirred at 70 °C for 1 h and the resultant Copper-ligand complex was cooled to -20 °C and then added **1a-1g** (0.616 mmol, 1.0 equiv) followed by DABCO (0.092 mmol, 15 mol%) and cyclic carbonate[1] **2a-2j** (0.616 mmol, 1.0 equiv) dissolved in CH_3CN (1 mL) was added slowly drop wise. The reaction was maintained and stirred at -20 °C for 4-8 h. After completion of reaction, the reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using 50% EtOAc/hexanes as eluent to afford the pure dihydrofuro[3,2-*c*]coumarin scaffolds **3**.

2.2. Experimental and Characterization of Dihydrofuro[3,2-*c*]coumarins (3a-w)

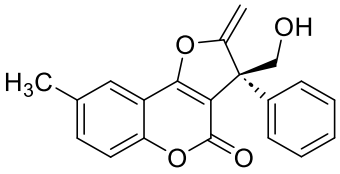
(*R*)-3-(Hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3a)



By following the general procedure, the reaction was performed with 4-hydroxycoumarin **1a** (100 mg, 0.616 mmol, 1.0equiv) and cyclic carbonate **2a** (116.06 mg, 0.616 mmol, 1.0 equiv) using CuI (1.17 mg, 1 mol %), **L2** (3.28 mg, 2 mol%) and DABCO (10.37 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by column chromatography on silica gel (50% EtOAc/hexanes) to afford **3a** (185 mg, 98%) as a off-white solid. HPLC purity: 99:1 *er*. $[\alpha]^{20}$ = -26 (*c* = 0.4, $CHCl_3$). mp 154-156 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.37 (m, *J* = 7.7 Hz, 3H), 7.30 (d, *J* = 7.1 Hz, 1H), 5.24 (d, *J* = 3.6 Hz, 1H), 4.65 (d, *J* = 3.6 Hz, 1H), 4.58 – 4.51 (q, 1H), 4.18 (dd, *J* = 11.2, 3.1 Hz, 1H), 2.88 (dd, *J* = 9.1, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7,

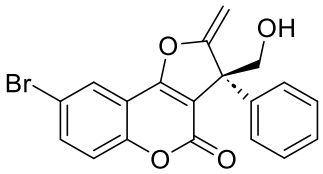
164.5, 160.0, 155.2, 139.5, 133.2, 129.0, 127.8, 126.8, 124.54, 123.0, 117.2, 111.4, 107.7, 91.7, 67.4, 58.2. IR (thin film): ν_{max}/cm^{-1} 3430, 3063, 3017, 2933, 2880, 1705, 1679, 1639, 1605, 1497, 1400, 1327, 1212, 1090, 1072, 979, 905, 850, 750, 697, 666, 635. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{19}H_{15}O_4$: 307.0970, found 307.0984.

(*R*)-3-(Hydroxymethyl)-8-methyl-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3b)



By following the general procedure, the reaction was performed with 6-methyl-4-hydroxycoumarin **1b** (100 mg, 0.567 mmol, 1.0 equiv) and cyclic carbonate **2a** (106.81 mg, 0.567 mmol, 1.0 equiv) using CuI (1.08 mg, 1 mol %), **L2** (3.02 mg, 2 mol %) and DABCO (9.55 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3b** (171 mg, 94%) as an off white solid. HPLC purity: 95:5 *er*. $[\alpha]^{20}$ = -19 (*c* = 0.2, $CHCl_3$). mp 136-138 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.50 – 7.43 (m, 3H), 7.39 – 7.28 (m, 4H), 5.21 (d, *J* = 3.6 Hz, 1H), 4.64 (d, *J* = 3.6 Hz, 1H), 4.52 (td, *J* = 11.2, 9.3 Hz, 1H), 4.18 (dd, *J* = 11.2, 3.7 Hz, 1H), 2.96 (dd, *J* = 9.2, 3.7 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 164.5, 160.3, 153.5, 134.5, 134.4, 129.0, 127.8, 126.8, 122.5, 117.0, 111.1, 107.7, 91.6, 67.5, 58.1, 21.0. IR (thin film): ν_{max}/cm^{-1} 3426, 3070, 2932, 2865, 1683, 1633, 1572, 1497, 1432, 1309, 1202, 1080, 999, 895, 821, 762, 693, 653, 618. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{20}H_{17}O_4$: 321.1127, found 321.1143.

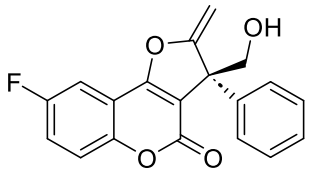
(*R*)-8-Bromo-3-(hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3c)



By following the general procedure, the reaction was performed with 6-bromo-4-hydroxycoumarin **1c** (100 mg, 0.414 mmol, 1.0 equiv) and cyclic carbonate **2a** (78.07 mg, 0.414 mmol, 1.0 equiv) using CuI (0.79 mg, 1 mol %), **L2** (2.21 mg, 2 mol %) and DABCO (6.98 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column

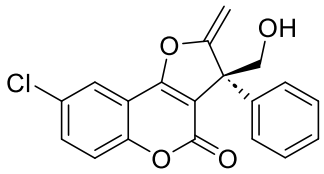
chromatography on silica gel (50% EtOAc/hexanes) to afford **3c** (136 mg, 85%) as a pale-yellow semi solid. HPLC purity: >99:1 *er*. $[\alpha]^{20}$ = -20.6 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.3 Hz, 1H), 7.71 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.48 (m, *J* = 5.3, 3.4 Hz, 2H), 7.40 – 7.35 (m, 2H), 7.33 – 7.29 (m, 2H), 5.27 (d, *J* = 3.7 Hz, 1H), 4.67 (d, *J* = 3.7 Hz, 1H), 4.55 (dt, *J* = 7.2, 6.4 Hz, 1H), 4.17 (dd, *J* = 11.2, 3.8 Hz, 1H), 2.63 (dd, *J* = 9.0, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 163.8, 159.1, 153.9, 139.1, 136.0, 129.0, 127.9, 126.8, 125.5, 118.9, 117.3, 113.0, 108.6, 92.1, 67.1, 58.4. IR (thin film): ν_{max}/cm^{-1} 3468, 3066, 2924, 2854, 1813, 1708, 1639, 1560, 1489, 1422, 1381, 1263, 1211, 1105, 1063, 980, 907, 823, 756, 696, 638. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{19}H_{14}O_4Br$: 385.0075, found 385.0081.

(*R*)-8-Fluoro-3-(hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3d)



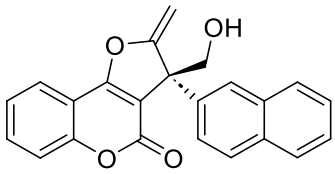
By following the general procedure, the reaction was performed with 6-fluoro-4-hydroxycoumarin **1d** (100 mg, 0.555 mmol, 1.0 equiv) and cyclic carbonate **2a** (104.40 mg, 0.555 mmol, 1.0 equiv) using CuI (1.05 mg, 1 mol %), **L2** (2.95 mg, 2 mol %) and DABCO (9.34 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3d** (144 mg, 80%) as a pale-yellow semi solid. HPLC purity: >99:1 *er*. $[\alpha]^{20}$ = - 22.5 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 3H), 7.39 (dd, *J* = 9.1, 4.3 Hz, 1H), 7.34 (ddd, *J* = 9.6, 5.3, 1.5 Hz, 3H), 7.28 (ddd, *J* = 8.4, 5.2, 2.7 Hz, 1H), 5.24 (d, *J* = 3.7 Hz, 1H), 4.65 (d, *J* = 3.7 Hz, 1H), 4.53 (dd, *J* = 11.2, 9.0 Hz, 1H), 4.15 (dd, *J* = 11.2, 4.0 Hz, 1H), 2.66 (dd, *J* = 9.0, 4.0 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 163.7, 159.5, (d, J_{C-F} = 8.6 Hz),, 157.9, 151.4, 139.2, 129.0, 127.9, 126.8, 120.9 (d, J_{C-F} = 24.7 Hz), 119.0 (d, J_{C-F} = 8.3 Hz), 112.2, 108.6 (d, J_{C-F} = 25.3 Hz), 92.1, 67.2, 58.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.88. IR (thin film): ν_{max}/cm^{-1} 3446, 3069, 2926, 2857, 1724, 1578, 1500, 1451, 1392, 1269, 1189, 1072, 988, 906, 821, 765, 699, 664. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{19}H_{14}O_4F$ 325.0876, found 325.0890.

(*R*)-8-Chloro-3-(hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3e)



By following the general procedure, the reaction was performed with 6-chloro-4-hydroxycoumarin **1e** (100 mg, 0.508 mmol, 1.0 equiv) and cyclic carbonate **2a** (95.72 mg, 0.508 mmol, 1.0 equiv) using CuI (0.97 mg, 1 mol %), **L2** (2.71 mg, 2 mol %) and DABCO (8.55 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3e** (142 mg, 82%) as a pale-yellow semi solid. HPLC purity: >99:1 *er*. $[\alpha]^{20}$ = -24.6 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.5 Hz, 1H), 7.57 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.40 – 7.34 (m, 3H), 7.32 – 7.27 (m, 1H), 5.27 (d, *J* = 3.7 Hz, 1H), 4.67 (d, *J* = 3.7 Hz, 1H), 4.56 (dd, *J* = 11.2, 8.9 Hz, 1H), 4.17 (dd, *J* = 11.2, 4.1 Hz, 1H), 2.73 – 2.57 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 163.3, 159.2, 153.5, 139.1, 133.2, 130.1, 129.0, 128.0, 126.8, 122.4, 118.6, 112.5, 108.5, 92.1, 67.1, 58.4. IR (thin film): ν_{max}/cm^{-1} 3440, 3068, 2926, 2856, 1723, 1642, 1565,1492, 1426, 1384, 1263, 1210, 1111, 1066, 966, 910, 825, 738, 698, 654. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{19}H_{14}O_4Cl$: 341.0581, found 341.0593.

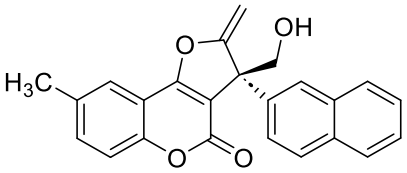
(*R*)-3-(hydroxymethyl)-2-methylene-3-(naphthalen-1-yl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3f)



By following the general procedure, the reaction was performed with 4-hydroxycoumarin **1a** (100 mg, 0.616 mmol, 1.0 equiv) and naphthyl substituted cyclic carbonate **2b** (146.93 mg, 0.616 mmol, 1.0 equiv) using CuI (1.17 mg, 1 mol%), **L2** (3.28 mg, 2 mol%) and DABCO (10.377 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by column chromatography on silica gel (50% EtOAc/hexanes) to afford **3f** (216 mg, 98%) as an off-white solid. HPLC purity: >99:1 *er*. $[\alpha]^{20}$ = -21.5 (*c* = 0.4, $CHCl_3$). mp 119-120 °C. ^{1}H NMR (500 MHz, $CDCl_3$)

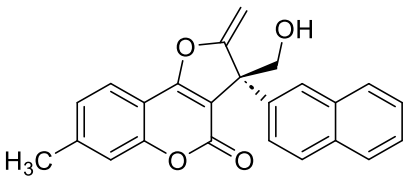
δ 7.94 (d, *J* = 1.7 Hz, 1H), 7.86 – 7.79 (m, 4H), 7.69 – 7.63 (m, 1H), 7.58 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.42 – 7.37 (m, 1H), 5.26 (d, *J* = 3.7 Hz, 1H), 4.69 – 4.63 (m, 2H), 4.29 (dd, *J* = 11.2, 3.8 Hz, 1H), 2.95 (dd, *J* = 9.1, 3.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 164.7, 160.1, 155.3, 136.9, 133.3, 132.7, 128.8, 128.3, 127.5, 126.4, 125.8, 124.7, 124.6, 117.3, 111.5, 107.9, 92.0, 67.5, 58.2. IR (thin film): ν_{max}/cm^{-1} 3417, 3316, 3198, 2754, 2635, 2347, 1683, 1634, 1497, 1398, 1276, 1212, 1061, 968, 902, 823, 750, 643. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{23}H_{17}O_4$: 357.1127, found 357.1135.

(*R*)-3-(Hydroxymethyl)-8-methyl-2-methylene-3-(naphthalen-2-yl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3g)



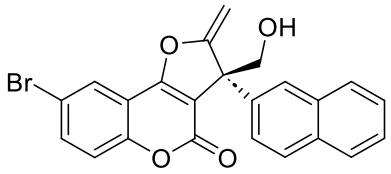
By following the general procedure, the reaction was performed with 6-methyl-4-hydroxycoumarin **1b** (100 mg, 0.567 mmol, 1.0 equiv) and naphthyl substituted cyclic carbonate **2b** (135.23 mg, 0.567 mmol, 1.0 equiv) using CuI (1.08 mg, 1 mol %), **L2** (3.02 mg, 2 mol %) and DABCO (9.55 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3g** (202 mg, 96%) off white solid. HPLC purity: >99:1 *er*. $[\alpha]^{20}$ = -22.6 (*c* = 0.3, $CHCl_3$). mp 98-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 1.7 Hz, 1H), 7.82 (m, *J* = 8.8, 4.5 Hz, 3H), 7.62 (s, 1H), 7.57 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.49 – 7.44 (m, 3H), 7.35 (d, *J* = 8.6 Hz, 1H), 5.23 (d, *J* = 3.7 Hz, 1H), 4.69 – 4.61 (m, 2H), 4.29 (dd, *J* = 11.2, 3.5 Hz, 1H), 3.06 (dd, *J* = 9.2, 3.6 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 164.67 160.3, 153.5, 136.9, 134.5, 134.4, 133.3, 132.7, 128.8, 128.3, 127.5, 126.3, 125.8, 124.7, 122.6, 117.0, 111.2, 107.8, 91.7, 67.6, 58.7, 20.9. IR (thin film): ν_{max}/cm^{-1} 3413, 3307, 3040, 2925, 2866, 2340, 1682, 1638, 1571, 1498, 1429, 1387, 1203, 1060, 974, 905, 814, 741, 647. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{24}H_{19}O_4$ 371.1283, found 371.1297.

(*R*)-3-(Hydroxymethyl)-7-methyl-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3h)



By following the general procedure, the reaction was performed with 7-methyl-4-hydroxycoumarin **1f** (100 mg, 0.567 mmol, 1.0 equiv) and naphthyl substituted cyclic carbonate **2b** (135.23 mg, 0.567 mmol, 1.0 equiv) using CuI (1.08 mg, 1 mol %), **L2** (3.02 mg, 2 mol %) and DABCO (9.55 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3h** (178 mg, 98%) as a pale-yellow semi solid. HPLC purity: 98:2 *er*. $[\alpha]^{20}$ = -24.6 (*c* = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.6 Hz, 1H), 7.86 – 7.78 (m, 4H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.49 – 7.45 (m, 2H), 7.23 – 7.20 (m, 1H), 5.23 (d, *J* = 3.6 Hz, 1H), 4.76 – 4.52 (m, 2H), 4.28 (dd, *J* = 11.2, 3.7 Hz, 1H), 3.05 (dd, *J* = 9.2, 3.7 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.0, 160.5, 155.5, 145.0, 137.1, 133.4, 132.8, 128.9, 128.4, 127.6, 126.4, 126.0, 126.0, 124.9, 122.8, 120.7, 117.5, 109.0, 107.0, 91.8, 67.7, 58.1, 22.2. IR (thin film): ν_{max}/cm^{-1} 3421, 3056, 3015, 2925, 2855, 1707, 1678, 1636, 1599, 1513, 1401, 1327, 1217, 1154, 1065, 1017, 945, 858, 816, 754, 665. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{24}H_{19}O_4$ 371.1283, found 371.1293.

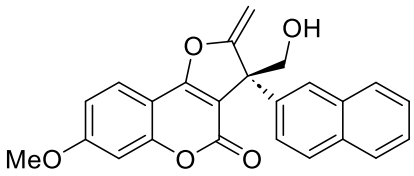
(*R*)-8-Bromo-3-(hydroxymethyl)-2-methylene-3-(naphthalen-2-yl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3i)



By following the general procedure, the reaction was performed with 6-bromo-4-hydroxycoumarin **1c** (100 mg, 0.414 mmol, 1.0 equiv) and naphthyl substituted cyclic carbonate **2b** (98.83 mg, 0.414 mmol, 1.0 equiv) using CuI (0.790 mg, 1 mol %), **L2** (2.21 mg, 2 mol %) and DABCO (6.98 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3i** (159 mg, 88%) as a pale-yellow semi solid. HPLC purity: 99:1 *er*. $[\alpha]^{20}$ = -24.5 (*c* = 0.4, $CHCl_3$). mp 98-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.3 Hz, 1H), 7.91 (d, *J* = 1.6 Hz, 1H), 7.82 (td, *J* = 8.5, 4.8 Hz, 4H), 7.73 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.57 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.50 – 7.46 (m, 2H), 7.32 (d, *J* = 8.9 Hz, 1H), 5.29 (d, *J* = 3.7 Hz, 1H), 4.72 – 4.62 (m, 3H), 4.29 (dd, *J* = 11.2, 4.0 Hz, 1H), 2.73 (dd, *J* = 8.9, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 163.3, 159.2, 154.0, 136.5, 136.1, 133.3, 132.73, 128.9, 128.3, 127.5, 126.5, 125.8, 125.5, 124.6, 11.0, 117.3, 113.1, 108.7, 92.3, 67.2, 58.4. IR (thin film): ν_{max}/cm^{-1} 3363, 3190, 3029, 2925, 2790, 2313, 1713, 1637, 1557, 1487, 1378, 1263, 1209,

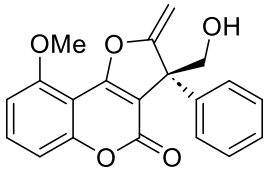
1103, 1059, 965, 906, 817, 757, 662. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{23}H_{16}O_4Br$: 435.0232, found 435.0234.

(*R*)-3-(hydroxymethyl)-7-methoxy-2-methylene-3-(naphthalen-2-yl)-2,3-dihydro-4*H*-furo[3,2-c]chromen-4-one (3j)



By following the general procedure, the reaction was performed with 7-methoxy-4-hydroxycoumarin **1g** (100 mg, 0.521 mmol, 1.0 equiv) and naphthyl substituted cyclic carbonate **2b** (124.06 mg, 0.521 mmol, 1.0 equiv) using CuI (0.99 mg, 1 mol %), **L2** (2.78 mg, 2 mol %) and DABCO (8.76 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3j** (197 mg, 98%) as a off white solid. HPLC purity: >99:1. $[\alpha]^{20}$ = -22.66 (*c* = 0.4, $CHCl_3$). mp 134-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.9 Hz, 1H), 7.82 (ddd, *J* = 9.4, 6.6, 4.1 Hz, 3H), 7.72 (d, *J* = 8.7 Hz, 1H), 7.58 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.49 – 7.45 (m, 2H), 6.98 – 6.92 (m, 2H), 5.22 (d, *J* = 3.6 Hz, 1H), 4.67 – 4.59 (m, 2H), 4.28 (dd, *J* = 10.3, 4.5 Hz, 1H), 3.91 (s, 3H), 3.05 (dd, *J* = 9.1, 3.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 165.1, 164.1, 160.5, 157.4, 137.2, 133.3, 132.7, 128.8, 128.3, 127.5, 126.3, 125.7, 124.8, 124.0, 113.3, 104.8, 104.6, 101.0, 91.6, 67.7, 67.6, 58.0, 55.9. IR (thin film): ν_{max}/cm^{-1} 3432, 3063, 2939, 2885, 1717, 1625, 1607, 1435, 1389, 1343, 1255, 1098, 1084, 975, 905, 879, 795, 737, 695. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{24}H_{19}O_5$: 387.1233, found 387.1226.

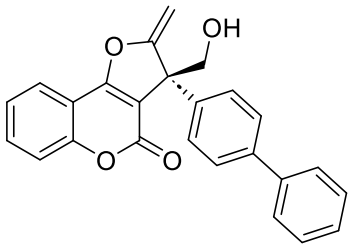
(*R*)-3-(hydroxymethyl)-9-methoxy-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-c]chromen-4-one (3k)



By following the general procedure, the reaction was performed with 5-methoxy-4-hydroxycoumarin **1h** (100 mg, 0.521 mmol, 1.0 equiv) and cyclic carbonate **2a** (98 mg, 0.521 mmol, 1.0 equiv) using CuI (0.99 mg, 1 mol %), **L2** (2.78 mg, 2 mol %) and DABCO (8.76 mg, 15 mol%) in acetonitrile (2

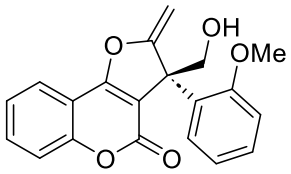
mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3k** (175 mg, 98%) as an off white solid. HPLC purity: >99:1 *er*. $[\alpha]^{20}$ = -24 (*c* = 0.5, $CHCl_3$). mp 140-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.47 (m, 3H), 7.38 – 7.32 (m, 2H), 7.30 – 7.27 (m, 1H), 7.05 – 7.01 (m, 1H), 6.82 – 6.78 (m, 1H), 5.23 (d, *J* = 3.5 Hz, 1H), 4.60 (d, *J* = 3.5 Hz, 1H), 4.51 (dd, *J* = 11.2, 9.4 Hz, 1H), 4.16 (dd, *J* = 11.2, 3.6 Hz, 1H), 3.99 (s, 3H), 3.00 (dd, *J* = 9.3, 3.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 164.9, 160.1, 156.8, 156.7, 139.9, 133.7, 128.9, 127.7, 126.9, 109.9, 107.4, 106.2, 102.8, 91.7, 67.7, 57.0, 56.6. IR (thin film): ν_{max}/cm^{-1} 3430, 3061, 2937, 2883, 1715, 1623, 1604, 1473, 1386, 1343, 1277, 1093, 1074, 971, 902, 851, 792, 737, 698. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{20}H_{17}O_5$: 337.1076, found 337.1060.

(*R*)-3-([1,1'-Biphenyl]-4-yl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3l)



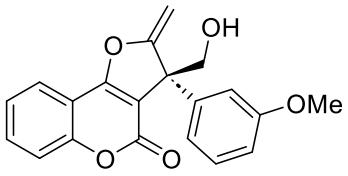
By following the general procedure, the reaction was performed with 4-hydroxycoumarin **1a** (100 mg, 0.616 mmol, 1.0 equiv) and biphenyl substituted cyclic carbonate **2c** (162.99 mg, 0.616 mmol, 1.0 equiv) using CuI (1.17 mg, 1 mol %), **L2** (3.28 mg, 2 mol %) and DABCO (10.37 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3l** (231 mg, 98%) as an off white solid. HPLC purity: 98:2 *er*. $[\alpha]^{20}$ = -22.6 (*c* = 0.4, $CHCl_3$). mp 119-120 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.65 (ddd, *J* = 8.8, 7.4, 1.6 Hz, 1H), 7.61 – 7.54 (m, 6H), 7.47 – 7.38 (m, 4H), 7.37 – 7.31 (m, 1H), 5.27 (d, *J* = 3.7 Hz, 1H), 4.70 (d, *J* = 3.7 Hz, 1H), 4.57 (td, *J* = 11.2, 9.2 Hz, 1H), 4.22 (dd, *J* = 11.2, 3.8 Hz, 1H), 2.90 (dd, *J* = 9.1, 3.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 164.6, 160.1, 155.2, 140.7, 140.5, 138.5, 133.3, 128.8, 127.7, 127.4, 127.2, 127.1, 124.6, 123.0, 111.5, 107.7, 106.9, 91.8, 67.5, 58.0. IR (thin film): ν_{max}/cm^{-1} 3464, 3344, 3230, 3034, 2935, 2867, 1687, 1635, 1492, 1399, 1325, 1278, 1208, 1147, 1061, 952, 901, 843, 755, 695, 647. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{25}H_{19}O_4$: 383.1283, found 383.1301.

(*R*)-3-(hydroxymethyl)-3-(2-methoxyphenyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-c]chromen-4-one (3m)



By following the general procedure, the reaction was performed with 4-hydroxycoumarin **1a** (100 mg, 0.616 mmol, 1.0 equiv) and 2-methoxy substituted cyclic carbonate **2d** (134.58 mg, 0.616 mmol, 1.0 equiv) using CuI (1.17 mg, 1 mol %), **L2** (3.28 mg, 2 mol %) and DABCO (10.37 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3m** (201 mg, 97%) as an off white solid. HPLC purity: >99:1 *er*. $[\alpha]^{20}$ = -25.6 (*c* = 0.5, $CHCl_3$). mp 134-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.66 – 7.55 (m, 2H), 7.44 – 7.35 (m, 2H), 7.31 – 7.27 (m, 1H), 7.01 (td, *J* = 7.6, 1.1 Hz, 1H), 6.86 (dd, *J* = 8.2, 0.8 Hz, 1H), 4.96 (d, *J* = 3.4 Hz, 1H), 4.54 (dd, *J* = 10.8, 8.5 Hz, 1H), 4.40 (d, *J* = 3.4 Hz, 1H), 4.18 (dd, *J* = 10.8, 4.1 Hz, 1H), 3.60 (s, 3H), 3.01 (dd, *J* = 8.5, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 164.8, 160.0, 157.9, 155.1, 132.8, 129.2, 127.9, 127.8, 124.4, 122.8, 120.9, 117.2, 112.4, 111.7, 107.5, 88.4, 68.1, 55.6, 55.1. IR (thin film): ν_{max}/cm^{-1} 3433, 3068, 2926, 2853, 1720, 1642, 1604, 1569, 1496, 1460, 1403, 1281, 1251, 1137, 1091, 1027, 952, 908, 755, 638. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{20}H_{17}O_5$ 337.1076, found 337.1056.

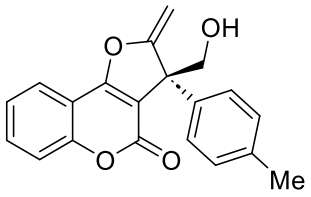
(*R*)-3-(Hydroxymethyl)-3-(3-methoxyphenyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3n)



By following the general procedure, the reaction was performed with 4-hydroxycoumarin **1a** (100 mg, 0.616 mmol, 1.0 equiv) and 3-methoxy substituted cyclic carbonate **2e** (134.58 mg, 0.616 mmol, 1.0 equiv) using CuI (1.17 mg, 1 mol %), **L2** (3.28 mg, 2 mol %) and DABCO (10.37 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3n** (203 mg, 98%) as a off white solid. HPLC purity: 91:9 *er*. $[\alpha]^{20}$ = -19.6 (*c* = 0.7, $CHCl_3$). mp 134-136 °C. ^{1}H NMR (500 MHz,

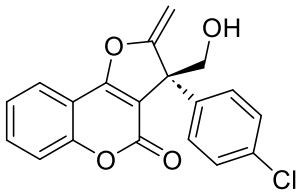
$CDCl_3$) δ 7.79 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.41 (dd, *J* = 8.3, 4.9 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.28 (dd, *J* = 10.7, 5.3 Hz, 1H), 7.11 – 7.08 (t, 1H), 7.06 (t, *J* = 2.1 Hz, 1H), 6.82 (dd, *J* = 8.2, 2.1 Hz, 1H), 5.24 (d, *J* = 3.7 Hz, 1H), 4.67 (d, *J* = 3.7 Hz, 1H), 4.52 (dd, *J* = 10.5, 6.3 Hz, 1H), 4.16 (d, *J* = 11.2 Hz, 1H), 3.79 (s, 3H), 2.89 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 164.5, 160.0, 155.2, 141.0, 133.2, 130.0, 124.5, 123.0, 119.0, 117.2, 113.4, 112.6, 111.5, 107.6, 91.82, 67.4, 58.2, 55.3. IR (thin film): ν_{max}/cm^{-1} 3451, 3044, 2920, 2855, 2339, 2119, 1705, 1637, 1602, 1494, 1397, 1285, 1250, 1209, 1149, 1085, 1058, 962, 903, 852, 752, 695, 630. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{20}H_{17}O_5$ 337.1076, found 337.1083.

(*R*)-3-(Hydroxymethyl)-2-methylene-3-(p-tolyl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3o)



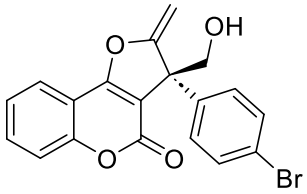
By following the general procedure, the reaction was performed with 4-hydroxycoumarin **1a** (100 mg, 0.616 mmol, 1.0 equiv) and 4-methyl substituted cyclic carbonate **2f** (124.71 mg, 0.616 mmol, 1.0 equiv) using CuI (1.17 mg, 1 mol %), **L2** (3.28 mg, 2 mol %) and DABCO (10.37 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by column chromatography on silica gel (50% EtOAc/hexanes) to afford **3o** (188 mg, 95%) as a off white solid. HPLC purity: 85:15 *er*. $[\alpha]^{20}$ = -18 (*c* = 1.0, $CHCl_3$). mp 117-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.63 (ddt, *J* = 8.9, 7.4, 1.7 Hz, 1H), 7.42 (dd, *J* = 8.3, 3.3 Hz, 1H), 7.39 – 7.34 (m, 3H), 7.17 (d, *J* = 8.0 Hz, 2H), 5.22 (d, *J* = 3.6 Hz, 1H), 4.64 (d, *J* = 3.6 Hz, 1H), 4.52 (dd, *J* = 10.7, 8.5 Hz, 1H), 4.16 (d, *J* = 11.0 Hz, 1H), 2.88 (d, *J* = 4.8 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 164.4, 160.0, 155.2, 137.5, 136.5, 133.2, 129.6, 126.6, 124.5, 122.9, 117.2, 111.5, 107.9, 91.5, 67.4, 57.9, 21.0. IR (thin film): ν_{max}/cm^{-1} 3471, 3074, 2964, 2923, 1693, 1636, 1566, 1496, 1399, 1147, 1066, 985, 902, 833, 750, 661, 630. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{20}H_{17}O_4$ 321.1127, found 321.1143.

(*R*)-3-(4-Chlorophenyl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3p)



By following the general procedure, the reaction was performed with 4-hydroxycoumarin **1a** (100 mg, 0.616 mmol, 1.0 equiv) and 4-chloro substituted cyclic carbonate **2g** (137.30 mg, 0.616 mmol, 1.0 equiv) using CuI (1.17 mg, 1 mol %), **L2** (3.28 mg, 2 mol %) and DABCO (10.37 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3p** (208 mg, 99%) as a pale-yellow semi solid. HPLC purity: 84:16 *er*. $[\alpha]^{20}$ = -18.6 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.47 – 7.42 (m, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.35 – 7.32 (m, 2H), 5.25 (d, *J* = 3.7 Hz, 1H), 4.63 (d, *J* = 3.7 Hz, 1H), 4.48 (dd, *J* = 11.1, 9.1 Hz, 1H), 4.16 (dd, *J* = 11.2, 3.4 Hz, 1H), 2.91 (dd, *J* = 9.0, 3.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 164.6, 159.9, 155.2, 138.0, 133.8, 133.4, 129.0, 128.4, 124.6, 123.0, 117.3, 111.3, 107.5, 92.0, 67.4, 57.7. IR (thin film): ν_{max}/cm^{-1} 3428, 3016, 2929, 2879, 1707, 1679, 1639, 1568, 1495, 1403, 1328, 1212, 1148, 1094, 982, 906, 834, 755, 636. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{19}H_{14}O_4Cl$ 341.0581, found 341.0592.

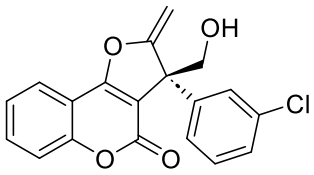
(*R*)-3-(4-Bromophenyl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3q)



By following the general procedure, the reaction was performed with 4-hydroxycoumarin **1a** (100 mg, 0.616 mmol, 1.0 equiv) and 4-bromo substituted cyclic carbonate **2h** (164.72 mg, 0.616 mmol, 1.0 equiv) using CuI (1.17 mg, 1 mol %), **L2** (3.28 mg, 2 mol %) and DABCO (10.37 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3q** (235 mg, 99%) as a pale-yellow semi solid. HPLC purity: 87:13 *er*. $[\alpha]^{20}$ = -17.5 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.65 (tt, *J* = 7.4, 1.6 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.45 – 7.36 (m,

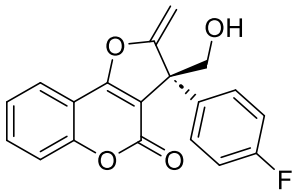
4H), 5.25 (d, *J* = 3.8 Hz, 1H), 4.63 (d, *J* = 3.8 Hz, 1H), 4.47 (dd, *J* = 11.1, 9.1 Hz, 1H), 4.15 (dd, *J* = 11.2, 3.4 Hz, 1H), 2.95 (dd, *J* = 8.9, 4.1 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.3, 164.7, 160.0, 155.2, 138.6, 133.4, 132.0, 128.7, 124.6, 123.0, 122.0, 117.3, 111.3, 107.4, 92.1, 67.3, 57.7. IR (thin film): ν_{max}/cm^{-1} 3428, 3015, 2928, 2880, 1706, 1679, 1638, 1567, 1493, 1400, 1328, 1281, 1212, 1148, 1069, 982, 903, 749, 660, 634. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{19}H_{14}O_4Br$ 385.0075, found 385.0087.

(*R*)-3-(3-Chlorophenyl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3r)



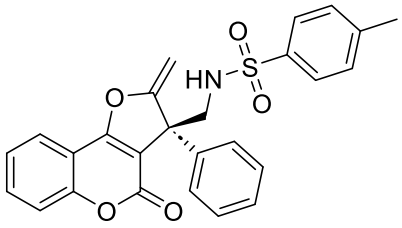
By following the general procedure, the reaction was performed with 4-hydroxycoumarin **1a** (100 mg, 0.616 mmol, 1.0 equiv) and 3-chloro substituted cyclic carbonate **2i** (137.30 mg, 0.616 mmol, 1.0 equiv) using CuI (1.17 mg, 1 mol %), **L2** (3.28 mg, 2 mol %) and DABCO (10.37 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3r** (208 mg, 99%) as a pale-yellow semi solid. HPLC purity: 85:15 *er*. $[\alpha]^{20}$ = -17.6 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.66 (ddd, *J* = 8.8, 7.4, 1.6 Hz, 1H), 7.47 – 7.38 (m, 4H), 7.30 (m, *J* = 8.0, 4.9, 4.5 Hz, 2H), 5.26 (d, *J* = 3.8 Hz, 1H), 4.65 (d, *J* = 3.8 Hz, 1H), 4.48 (dd, *J* = 11.2, 9.2 Hz, 1H), 4.17 (dd, *J* = 11.3, 3.8 Hz, 1H), 2.89 (dd, *J* = 9.2, 3.8 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 164.8, 160.0, 155.2, 141.6, 134.8, 133.5, 130.1, 128.0, 127.9, 125.1, 124.6, 123.0, 117.3, 111.3, 107.3, 92.3, 67.3, 57.8.IR (thin film): ν_{max}/cm^{-1} 3407, 2925, 2857, 2352, 1711, 1681, 1639, 1569, 1498, 1401, 1208, 1149, 1089, 962, 907, 857, 730, 643. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{19}H_{14}O_4Cl$ 341.0581, found 341.0593.

(*R*)-3-(4-Fluorophenyl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3s)



By following the general procedure, the reaction was performed with 4-hydroxycoumarin **1a** (100 mg, 0.616 mmol, 1.0 equiv) and 4-fluoro substituted cyclic carbonate **2j** (127.15 mg, 0.616 mmol, 1.0 equiv) using CuI (1.17 mg, 1 mol %), **L2** (3.28 mg, 2 mol %) and DABCO (10.37 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3s** (180 mg, 90%) as a pale-yellow semi solid. HPLC purity: 84:16 *er*. $[\alpha]^{20}$ = -18.6 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.68 – 7.62 (m, 1H), 7.51 – 7.42 (m, 3H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 8.6 Hz, 1H), 5.25 (d, *J* = 3.7 Hz, 1H), 4.63 (d, *J* = 3.7 Hz, 1H), 4.48 (dd, *J* = 11.0, 9.3 Hz, 1H), 4.15 (dd, *J* = 11.3, 3.4 Hz, 1H), 2.86 (dd, *J* = 8.9, 3.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 164.5, 162.2 (d, $J_{C\text{-}F}$ = 248.2 Hz), 160.0, 155.2, 135.3, 135.3, 133.4, 128.7(d, $J_{C\text{-}F}$ = 8.0 Hz),, 124.6, 123.0, 117.3, 115.8 (d, $J_{C\text{-}F}$ = 21.5 Hz), 111.4, 107.6, 91.9, 67.5, 57.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.65. IR (thin film): ν_{max}/cm^{-1} 3445, 2926, 2856, 1723, 1643, 1607, 1567, 1507, 1405, 1262, 1233, 1161, 1095, 989, 951, 910, 842, 761, 703, 662, 637. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{19}H_{14}O_4F$ 325.0876, found 325.0883.

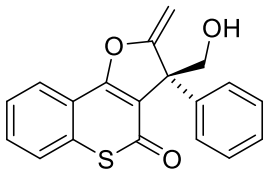
(*R*)-4-Methyl-*N*-((2-methylene-4-oxo-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-3-yl)methyl)benzenesulfonamide (3t)



By following the general procedure, the reaction was performed with 4-hydroxycoumarin **1a** (100 mg, 0.616 mmol, 1.0 equiv) and cyclic carbamate **2k** (210.54 mg, 0.616 mmol, 1.0 equiv) using CuI (1.17 mg, 1 mol %), **L2** (3.28 mg, 2 mol %) and DABCO (10.37 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3t** (260 mg, 92%) as an off white solid. HPLC purity: 96:4 *er*. $[\alpha]^{20}$ = -19.2 (*c* = 1.0, $CHCl_3$). mp 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.68 – 7.62 (m, 3H), 7.41 – 7.28 (m, 7H), 7.19 (d, *J* = 8.1 Hz, 2H), 5.29 (dd, *J* = 7.9, 4.8 Hz, 1H), 5.23 (d, *J* = 3.9 Hz, 1H), 4.64 (d, *J* = 3.9 Hz, 1H), 4.12 (dd, *J* = 12.7, 8.0 Hz, 1H), 3.55 (dd, *J* = 12.7, 4.8 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 164.4, 159.1, 155.3, 143.4, 139.0, 136., 133.4, 129.7, 129.0, 128.0, 127.0, 126.6, 124.5, 123.0, 117.2, 111.2,

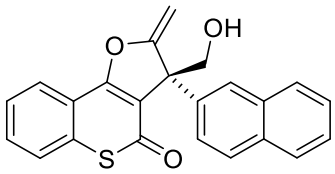
106.7, 92.7, 56.0, 49.2, 21.5. IR (thin film): ν_{max}/cm^{-1} 3898, 3820, 3727, 3643, 2951, 2857, 2367, 1713, 1683, 1635, 1497, 1443, 1400, 1325, 1154, 1086, 965, 905, 818, 755, 697, 659. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{26}H_{22}NO_5S$ 460.1219, found 460.1227.

(*R*)-3-(Hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-thiochromeno[4,3-*b*]furan-4-one (3u)



By following the general procedure, the reaction was performed with 4-hydroxy-1-thiocoumarin **1i** (100 mg, 0.561 mmol, 1.0 equiv) and cyclic carbonate **2a** (188.18 mg, 0.561 mmol, 1.0 equiv) using CuI (1.06 mg, 1 mol %), **L2** (2.99 mg, 2 mol %) and DABCO (9.44 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3u** (172 mg, 95%) as an off white solid. HPLC purity: 64:36 *er*. mp 119-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.50 (ddd, *J* = 8.3, 6.9, 1.6 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.38 – 7.32 (m, 2H), 7.29 – 7.27 (m, 1H), 5.12 (d, *J* = 3.6 Hz, 1H), 4.59 – 4.51 (m, 2H), 4.19 (dd, *J* = 11.3, 3.3 Hz, 1H), 3.20 (dd, *J* = 9.1, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.4, 165.0, 164.8, 140.0, 139.8, 131.3, 128.9, 127.6, 126.7, 126.3, 125.6, 119.2, 117.7, 90.2, 67.7, 59.7. IR (thin film): ν_{max}/cm^{-1} 3412, 3061, 3022, 2926, 2880, 1811, 1610, 1548, 1480, 1376, 1269, 1151, 1117, 1067, 887, 846, 739, 699, 667. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{19}H_{15}O_3S$ 323.0742, found 323.0757.

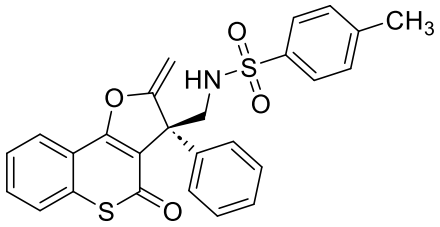
(*R*)-3-(Hydroxymethyl)-2-methylene-3-(naphthalen-2-yl)-2,3-dihydro-4*H*-thiochromeno[4,3-*b*]furan-4-one (3v)



By following the general procedure, the reaction was performed with 4-hydroxy-1-thiocoumarin **1i** (100 mg, 0.561 mmol, 1.0 equiv) and naphthyl substituted cyclic carbonate **2b** (133.68 mg, 0.561 mmol, 1.0 equiv) using CuI (1.06 mg, 1 mol %), **L2** (2.99 mg, 2 mol %) and DABCO (9.44 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified

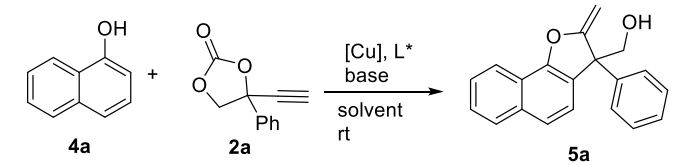
by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3v** (201 mg, 96%) as a off white solid. HPLC purity: 64:36 *er*. mp 104-106 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.89 (d, *J* = 1.9 Hz, 1H), 7.84 – 7.78 (m, 3H), 7.65 – 7.58 (m, 2H), 7.55 – 7.44 (m, 4H), 5.14 (d, *J* = 3.6 Hz, 1H), 4.67 (dd, *J* = 11.2, 9.0 Hz, 1H), 4.56 (d, *J* = 3.6 Hz, 1H), 4.29 (dd, *J* = 11.2, 3.4 Hz, 1H), 3.29 (dd, *J* = 9.0, 3.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.4, 164.0, 163.9, 138.8, 136.3, 132.3, 131.6, 130.3, 127.7, 127.3, 126.5, 125.7, 125.3, 125.2, 124.7, 124.6, 123.7, 118.1, 116.7, 89.4, 66.7, 58.7. IR (thin film): ν_{max}/cm^{-1} 3418, 2958, 2916, 2673, 2336, 1812, 1602, 1545, 1472, 1367, 1266, 1142, 1055, 883, 813, 733, 686. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{23}H_{17}O_3S$ 373.0898, found 373.0912.

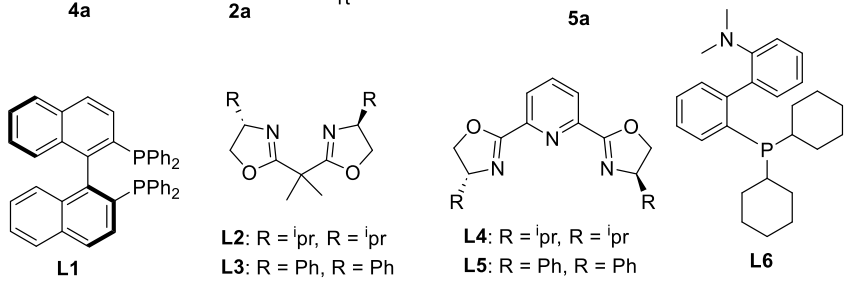
(*R*)-4-Methyl-N-((2-methylene-4-oxo-3-phenyl-2,3-dihydro-4*H*-thiochromeno[4,3-*b*]furan-3-yl)methyl)benzenesulfonamide (3w)



By following the general procedure, the reaction was performed with 4-hydroxy-1-thiocoumarin **1i** (100 mg, 0.561 mmol, 1.0 equiv) and cyclic carbamate **2k** (191.56 mg, 0.561 mmol, 1.0 equiv) using CuI (1.06 mg, 1 mol %), **L2** (2.99 mg, 2 mol %) and DABCO (9.44 mg, 15 mol%) in acetonitrile (2 mL) at -20 °C under nitrogen atmosphere for 4 h. The residue was purified by flash column chromatography on silica gel (50% EtOAc/hexanes) to afford **3w** (235 mg, 88%) as an off white semi solid. HPLC purity: 64:36 *er*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.0, 0.9 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.60 (ddd, *J* = 8.4, 7.2, 1.4 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.34 – 7.27 (m, 5H), 7.20 (d, *J* = 8.0 Hz, 2H), 5.27 (dd, *J* = 7.4, 5.3 Hz, 1H), 5.13 (d, *J* = 3.8 Hz, 1H), 4.52 (d, *J* = 3.8 Hz, 1H), 4.16 (dd, *J* = 12.6, 7.6 Hz, 1H), 3.58 (dd, *J* = 12.6, 5.1 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.1, 164.6, 164.5, 143.4, 140.1, 139.5, 136.8, 131.4, 129.7, 128.9, 127.8, 127.0, 126.7, 126.5, 126.3, 125.5, 118.9, 116.2, 116.1, 91.2, 57.5, 49.0, 21.5. IR (thin film): ν_{max}/cm^{-1} 3870, 3566, 3256, 3026, 2924, 2855, 2363, 1619, 1549, 1480, 1443, 1376, 1331, 1159, 1092, 1070, 895, 815, 756, 707, 666. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{26}H_{22}NO_4S2$ 476.0916, found 476.0920.

2.3 Optimization of [3+2] Cycloaddition of α-Naphthol to Cyclic Carbonates[a]

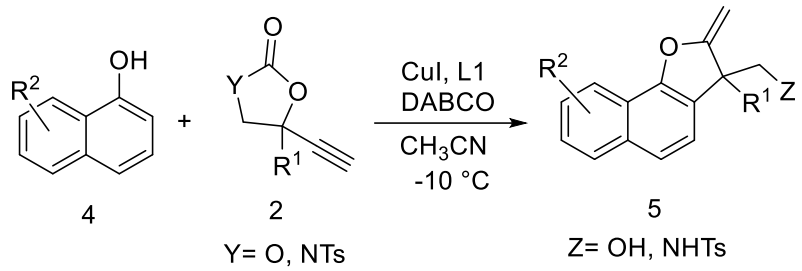




entry	Catalyst	Base	Solvent	Time	Yield (%)[b]	*er* of 5a
1	CuI/**L1**	DABCO	CH_3CN	16 h	60	50:50
2	CuI/**L1**	DIPEA	CH_3CN	16 h	20	57:43
3	CuI/**L1**	K_2CO_3	CH_3CN	16 h	35	53:47
4	CuI/**L1**	TEA	CH_3CN	16 h	25	50:50
5	CuI/**L1**	TEA	Toluene	16 h	<5	-
6	CuI/**L1**	DABCO	EtOAc	18 h	38	51:49
7	CuI/**L1**	DABCO	DCM	24 h	<5	-
8	CuI/**L1**	DABCO	MeOH	24 h	20	-
9	CuI/**L1**	DABCO	Toluene	36 h	<5	-
10	$Cu(OAc)_2$/**L1**	DABCO	CH_3CN	18 h	40	53:47
11	$Cu(acac)_2$/**L1**	DABCO	CH_3CN	18 h	45	53:47
12	CuI/**L1**	DABCO	CH_3CN	16 h	62	50:50
13	CuI/**L2**	DABCO	CH_3CN	16 h	62	50:50
14	CuI/**L3**	DABCO	CH_3CN	16 h	64	53:47
15	CuI/**L4**	DABCO	CH_3CN	16 h	58	57:43
16	CuI/**L5**	DABCO	CH_3CN	16 h	58	57:43
17	CuI/**L6**	DABCO	CH_3CN	16 h	60	50:50
18	CuI/**L1**	DABCO	CH_3CN	16 h	58	50:50
19[c]	CuI/**L1**	DABCO	CH_3CN	16 h	58	50:50

[a]The reaction conditions were performed with **4a** (0.693 mmol), **2a** (0.693 mmol), base (15 mol%), catalyst (1 mol%) and ligand (2 mol%) in solvent (2 mL) at -10 °C, unless otherwise stated. Reactions were monitored by TLC, then subjected directly to silica gel column chromatography. [b]Yields of purified products. [c]The reactions were carried out at -20 °C.

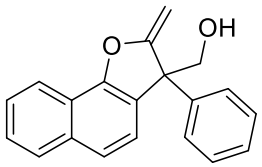
2.4 General Procedure for Dihydronaphtho[1,2-*b*]furan Scaffolds 5



To a clean and dry round-bottom flask, added dried CuI (1 mol%) and **L1** (2 mol%) in CH_3CN solvent and stirred at 70 °C for 1 h and the resultant Copper-ligand complex was cooled to -10 °C and then added **4a-4d** (0.616 mmol, 1.0 equiv) followed by DABCO (0.092 mmol, 15 mol%) and cyclic carbonate **2a-2j** (0.616 mmol, 1.0 equiv) dissolved in CH_3CN was added slowly drop wise. The reaction was maintained at -10 °C for 16 h. After completion of reaction, water was added to the reaction mixture and extracted to EtOAc twice and washed the organic layer with brine solution and dried with Na_2SO_4 and concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using 20% EtOAc/hexanes as eluent to afford the pure furo[1,2-*b*]dihydronaphthol scaffolds **5**.

2.5 Experimental and Characterization of Dihydronaphtho[1,2-*b*]furan Scaffolds (5a-j)

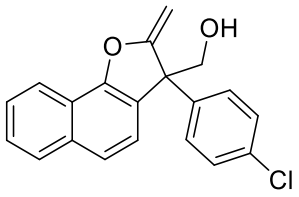
(2-Methylene-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5a)



By following the general procedure, the reaction was performed with 1-Naphthol **4a** (100 mg, 0.693 mmol, 1.0equiv) and cyclic carbonate **2a** (130.52 mg, 0.693 mmol, 1.0 equiv) using CuI (1.32 mg, 1 mol %), **L1** (8.63 mg, 2 mol %) and DABCO (11.67 mg, 15 mol%) in acetonitrile (2 mL) at -10 °C under nitrogen atmosphere for 16 h. The residue was purified by column chromatography on silica gel (20% EtOAc/hexanes) to afford **5a** (120 mg, 60%) as a red semi solid. HPLC purity: 50:50 *er*. Enantioselectivity was not achieved. ^{1}H NMR (400 MHz, MeOH-*d4*) δ 8.02 (dt, *J* = 6.2, 3.5 Hz, 1H), 7.85 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.52 – 7.45 (m, 3H), 7.37 – 7.34 (m, 2H), 7.28 (ddd, *J* = 7.9, 5.3, 2.4 Hz, 3H), 7.22 – 7.18 (m, 1H), 4.96 (d, *J* = 2.7 Hz, 1H), 4.33 (dd, *J* = 6.9, 4.2 Hz, 2H), 4.12 (d, *J* = 11.1 Hz, 1H). ^{13}C NMR (100 MHz, MeOH-*d4*) δ 168.2, 152.4, 142.9, 134.4, 128.2, 127.7, 126.9,

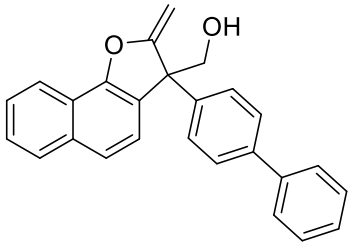
126.5, 125.9, 125.6, 125.2, 122.1, 121.6, 120.6, 119.7, 86.18, 67.6, 58.9. IR (thin film): ν_{max}/cm^{-1} 3408, 3058, 2930, 2866, 1677, 1585, 1506, 1448, 1381, 1214, 1160, 1071, 932, 810, 753, 695. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{20}H_{17}O_2$: 289.1229 found 289.1237.

(3-(4-Chlorophenyl)-2-methylene-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5b)



By following the general procedure, the reaction was performed with 1-Naphthol **4a** (100 mg, 0.693 mmol, 1.0 equiv) and 4-chloro substituted cyclic carbonate **2f** (154.41 mg, 0.693 mmol, 1.0 equiv) using CuI (1.32 mg, 1 mol %), **L1** (8.63 mg, 2 mol %) and DABCO (11.67 mg, 15 mol%) in acetonitrile (2 mL) at -10 °C under nitrogen atmosphere for 16 h. The residue was purified by column chromatography on silica gel (20% EtOAc/hexanes) to afford **5b** (130 mg, 58%) a red semi solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.50 (m, 3H), 7.35 – 7.29 (m, 4H), 7.20 (d, *J* = 8.3 Hz, 1H), 5.07 (d, *J* = 2.9 Hz, 1H), 4.33 (d, *J* = 2.9 Hz, 1H), 4.22 (ddd, *J* = 28.8, 11.3, 5.5 Hz, 2H), 1.91 (t, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.2, 152.7, 140.7, 134.5, 133.2, 131.6, 130.3, 128.9, 128.7, 128.1, 126.7, 126.3, 124.0, 122.6, 121.4, 121.3, 119.9, 87.9, 68.3, 58.9. IR (thin film): ν_{max}/cm^{-1} 3457, 3060, 2927, 2856, 1814, 1672, 1993, 1384, 1217, 1163, 1089, 1017, 936, 812, 757, 675. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{20}H_{16}O_2Cl$: 323.0839, found 323.0847.

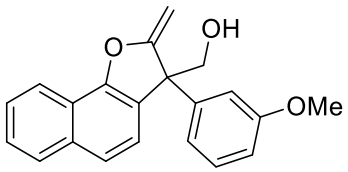
(3-([1,1'-Biphenyl]-4-yl)-2-methylene-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5c)



By following the general procedure, the reaction was performed with 1-Naphthol **4a** (100 mg, 0.693 mmol, 1.0 equiv) and biphenyl substituted cyclic carbonate **2c** (183.31 mg, 0.693 mmol, 1.0 equiv) using CuI (1.32 mg, 1 mol %), **L1** (8.63 mg, 2 mol %) and DABCO (11.67 mg, 15 mol%) in acetonitrile (2 mL) at -10 °C under nitrogen atmosphere for 16 h. The residue was purified by flash

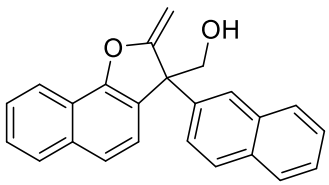
column chromatography on silica gel (20% EtOAc/hexanes) to afford **5c** (137 mg, 54%) a red semi solid. ^{1}H NMR (400 MHz, MeOH-*d4*) δ 8.06 – 8.02 (m, 1H), 7.89 – 7.85 (m, 1H), 7.59 – 7.48 (m, 7H), 7.45 – 7.36 (m, 4H), 7.35 – 7.32 (m, 1H), 7.31 – 7.26 (m, 1H), 4.98 (d, *J* = 2.7 Hz, 1H), 4.37 (dd, *J* = 8.3, 7.0 Hz, 2H), 4.16 (d, *J* = 11.1 Hz, 1H). ^{13}C NMR (100 MHz, MeOH-*d4*) δ 169.5, 153.8, 143.3, 141.9, 141.0, 135.8, 129.8, 129.1, 128.8, 128.3, 128.1, 127.9, 127.3, 127.0, 126.6, 123.5, 123.1, 122.0, 121.1, 87.6, 69.0, 60.1. IR (thin film): ν_{max}/cm^{-1} 3453, 3023, 2930, 1811, 1680, 1586, 1486, 1382, 1215, 1159, 1077, 931, 812, 755, 694. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{26}H_{21}O_2$: 365.1542, found 365.1554.

(3-(3-Methoxyphenyl)-2-methylene-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5d)



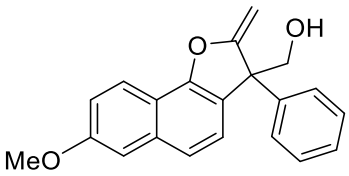
By following the general procedure, the reaction was performed with 1-Naphthol **4a** (100 mg, 0.693 mmol, 1.0 equiv) and 3-methoxy substituted cyclic carbonate **2d** (151.35 mg, 0.693 mmol, 1.0 equiv) using CuI (1.32 mg, 1 mol %), **L2** (8.63 mg, 2 mol %) and DABCO (11.67 mg, 15 mol%) in acetonitrile (2 mL) at -10 °C under nitrogen atmosphere for 16 h. The residue was purified by flash column chromatography on silica gel (20% EtOAc/hexanes) to afford **5d** (115 mg, 52%) a red semi solid. ^{1}H NMR (400 MHz, MeOH-*d4*) δ 8.05 – 8.00 (m, 1H), 7.89 – 7.84 (m, 1H), 7.56 – 7.46 (m, 3H), 7.32 (d, *J* = 8.4 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 6.96 (ddd, *J* = 7.8, 1.7, 0.8 Hz, 1H), 6.91 – 6.90 (m, 1H), 6.79 (ddd, *J* = 8.2, 2.5, 0.8 Hz, 1H), 4.97 (d, *J* = 2.7 Hz, 1H), 4.37 (d, *J* = 2.7 Hz, 1H), 4.31 (d, *J* = 11.1 Hz, 1H), 4.11 (d, *J* = 11.1 Hz, 1H), 3.71 (s, 3H). ^{13}C NMR (100 MHz, MeOH-*d4*) δ 169.3, 161.3, 153.7, 145.7, 135.8, 130.6, 129.1, 127.3, 127.0, 126.5, 123.5, 123.0, 122.0, 121.1, 120.5, 114.5, 113.0, 87.6, 69.0, 60.3, 55.6. IR (thin film): ν_{max}/cm^{-1} 3453, 2926, 2856, 1732, 1677, 1593, 1455, 1382, 1255, 1227, 1161, 1058, 977, 937, 809, 771, 696. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{21}H_{19}O_3$ 319.1334, found 319.1342.

(2-Methylene-3-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5e)



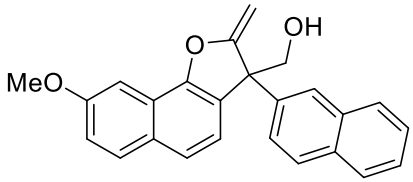
By following the general procedure, the reaction was performed with 1-Naphthol **4a** (100 mg, 0.693 mmol, 1.0 equiv) and naphthyl substituted cyclic carbonate **2b** (165.24 mg, 0.693 mmol, 1.0 equiv) using CuI (1.32 mg, 1 mol %), **L1** (8.63 mg, 2 mol %) and DABCO (8.63 mg, 0.104 mmol, 0.15 equiv) in acetonitrile (2 mL) at -10 °C under nitrogen atmosphere for 16 h. The residue was purified by flash column chromatography on silica gel (20% EtOAc/hexanes) to afford **5e** (150 mg, 64%) a red semi solid. ^{1}H NMR (400 MHz, MeOH-*d4*) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.95 – 7.73 (m, 5H), 7.48 (ddd, *J* = 24.8, 8.5, 4.1 Hz, 5H), 7.34 (ddd, *J* = 13.4, 8.5, 4.2 Hz, 2H), 5.06 – 4.98 (m, 1H), 4.48 (dd, *J* = 11.0, 4.8 Hz, 1H), 4.42 – 4.36 (m, 1H), 4.27 (dd, *J* = 11.0, 4.7 Hz, 1H). ^{13}C NMR (100 MHz, MeOH-*d4*) δ 168.2, 152.5, 140.1, 134.5, 133.3, 132.4, 127.9, 127.8, 127.0, 126.0, 125.8, 125.7, 125.6, 125.3, 125.1, 122.1, 121.8, 121.6, 120.7, 119.7, 86.5, 67.6, 59.1. IR (thin film): ν_{max}/cm^{-1} 3454, 3057, 2952, 2889, 1811, 1676, 1636, 1588, 1513, 1444, 1382, 1271, 1216, 1159, 1063, 935, 809, 754, 683. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{24}H_{19}O_2$: 339.1385, found 339.1391.

(7-Methoxy-2-methylene-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5f)



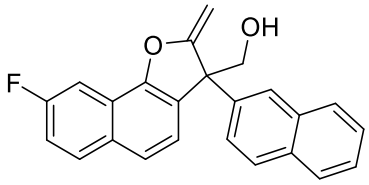
By following the general procedure, the reaction was performed with 7-methoxy-1-Naphthol **4b** (100 mg, 0.574 mmol, 1.0 equiv) and cyclic carbonate **2a** (108.1 mg, 0.574 mmol, 1.0 equiv) using CuI (1.09 mg, 1 mol %), **L1** (7.15 mg, 2 mol %) and DABCO (9.66 mg, 15 mol%) in acetonitrile (2 mL) at -10 °C under nitrogen atmosphere for 16 h. The residue was purified by flash column chromatography on silica gel (20% EtOAc/hexanes) to afford **5f** (108 mg, 59%) as a red semi solid. ^{1}H NMR (600 MHz, MeOH-*d4*) δ 7.76 (d, *J* = 9.0 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.34 – 7.29 (m, 3H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.16 – 7.11 (m, 2H), 4.96 (d, *J* = 2.7 Hz, 1H), 4.36 – 4.31 (m, 2H), 4.14 (d, *J* = 11.1 Hz, 1H), 3.94 (s, 3H). ^{13}C NMR (150 MHz, MeOH-*d4*) δ 168.2, 157.9, 151.7, 142.9, 129.9, 129.4, 128.2, 126.9, 126.5, 125.8, 121.4, 120.5, 119.5, 118.8, 98.6, 85.9, 67.6, 59.1, 54.5. IR (thin film): ν_{max}/cm^{-1} 3446, 2926, 2858, 1732, 1678, 1605, 1460, 1441, 1379, 1341, 1271, 1227, 1157, 1069, 935, 837, 705, 696, 661. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{21}H_{19}O_3$ 319.1334, found 319.1357.

(8-Methoxy-2-methylene-3-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5g)



By following the general procedure, the reaction was performed with 6-methoxy-1-Naphthol **4c** (100 mg, 0.574 mmol, 1.0 equiv) and naphthyl substituted cyclic carbonate **2b** (136.86 mg, 0.574 mmol, 1.0 equiv) using CuI (1.09 mg, 1 mol %), **L1** (7.15 mg, 2 mol %) and DABCO (9.66 mg, 15 mol%) in acetonitrile (2 mL) at -10 °C under nitrogen atmosphere for 16 h. The residue was purified by flash column chromatography on silica gel (20% EtOAc/hexanes) to afford **5g** (123 mg, 58%) a red semi solid. ^{1}H NMR (400 MHz, MeOH-*d4*) δ 7.99 – 7.91 (m, 2H), 7.84 – 7.73 (m, 3H), 7.48 – 7.41 (m, 3H), 7.36 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.27 – 7.24 (m, 2H), 7.18 (dd, *J* = 9.1, 2.3 Hz, 1H), 4.97 (d, *J* = 2.6 Hz, 1H), 4.44 (d, *J* = 11.1 Hz, 1H), 4.35 (d, *J* = 2.6 Hz, 1H), 4.24 (d, *J* = 11.1 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, MeOH-*d4*) δ 169.7, 159.6, 154.1, 141.7, 137.4, 134.7, 133.7, 129.2, 129.1, 128.4, 127.2, 127.0, 126.4, 124.5, 124.1, 123.5, 122.0, 1197, 116.4, 107.3, 87.7, 69.0, 60.3, 55.8. IR (thin film): ν_{max}/cm^{-1} 3408, 3012, 2926, 1729, 1675, 1636, 1602, 1472, 1424, 1362, 1249, 1216, 1150, 1026, 947, 914, 818, 751, 677. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{25}H_{21}O_3$: 369.1491, found 369.1491.

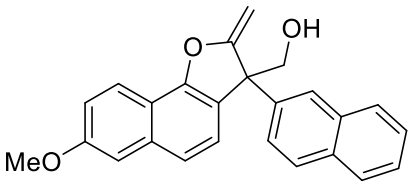
(8-Fluoro-2-methylene-3-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5h)



By following the general procedure, the reaction was performed with 6-fluoro-1-Naphthol **4d** (100 mg, 0.616 mmol, 1.0 equiv) and naphthyl substituted cyclic carbonate **2b** (146.91 mg, 0.616 mmol, 1.0 equiv) using CuI (1.17 mg, 1 mol %), **L1** (7.68 mg, 2 mol %) and DABCO (10.37 mg, 15 mol%) in acetonitrile (2 mL) at -10 °C under nitrogen atmosphere for 16 h. The residue was purified by flash column chromatography on silica gel (20% EtOAc/hexanes) to afford **5h** (136 mg, 62%) a red semi solid. ^{1}H NMR (400 MHz, MeOH-*d4*) δ 7.96 – 7.91 (m, 2H), 7.84 – 7.74 (m, 3H), 7.68 – 7.64 (m,

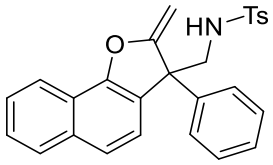
1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.37 – 7.28 (m, 3H), 5.01 (d, *J* = 2.8 Hz, 1H), 4.48 (d, *J* = 11.1 Hz, 1H), 4.39 (d, *J* = 2.8 Hz, 1H), 4.26 (d, *J* = 11.1 Hz, 1H). ^{13}C NMR (100 MHz, MeOH-*d4*) δ 169.3, 162.0 (d, J_{C-F} = 244.0 Hz), 153.5 (d, J_{C-F} = 5.1 Hz), 141.3, 134.7, 133.8, 132.1 (d, J_{C-F} = 9.0 Hz), 129.2, 128.4, 127.9, 127.2, 126.9, 126.4, 123.2, 122.8, 121.4 (d, J_{C-F} = 9.6 Hz), 117.5 (d, J_{C-F} = 25.5 Hz), 105.4 (d, J_{C-F} = 22.3 Hz), 88.9, 68.9, 60.6. ^{19}F NMR (376 MHz, MeOD-*d4*) δ -115.57. IR (thin film): ν_{max}/cm^{-1} 3445, 3057, 2930, 1731, 1676, 1639, 1522, 1454, 1368, 1266, 1190, 1159, 1092, 1060, 940, 832, 757, 666. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{24}H_{18}O_2F$: 357.1291, found 357.1293.

(7-Methoxy-2-methylene-3-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5i)



By following the general procedure, the reaction was performed with 7-methoxy-1-Naphthol **4e** (100 mg, 0.574 mmol,1.0 equiv) and naphthyl substituted cyclic carbonate **2b** (136.86 mg, 0.574 mmol, 1.0 equiv) using CuI (1.09 mg, 1 mol %), **L1** (7.15 mg, 2 mol %) and DABCO (9.66 mg, 15 mol%) in acetonitrile (2 mL) at -10 °C under nitrogen atmosphere for 16 h. The residue was purified by flash column chromatography on silica gel (20% EtOAc/hexanes) to afford **5i** (121 mg, 57%) a red semi solid. ^{1}H NMR (400 MHz, MeOH-*d4*) δ 7.93 (d, *J* = 1.7 Hz, 1H), 7.85 – 7.75 (m, 4H), 7.48 – 7.43 (m, 3H), 7.39 – 7.35 (m, 2H), 7.18 – 7.13 (m, 2H), 4.99 (d, *J* = 2.7 Hz, 1H), 4.46 (d, *J* = 11.1 Hz, 1H), 4.37 (d, *J* = 2.7 Hz, 1H), 4.27 (d, *J* = 11.1 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (100 MHz, MeOH-*d4*) δ 169.6, 167.2, 159.4, 153.2, 141.6, 134.7, 133.8, 131.4, 130.8, 129.2, 129.1, 128.4, 127.2, 127.03, 126.4, 122.9, 121.9, 120.9, 120.2, 100.0, 87.6, 68.9, 60.6, 55.9. IR (thin film): ν_{max}/cm^{-1} 3432, 3049, 2934, 1817, 1731, 1677, 1639, 1517, 1462, 1377, 1339, 1275, 1158, 1061, 936, 835, 760, 662. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{25}H_{21}O_3$ 369.1491, found 369.1512.

(4-Methyl-N-((2-methylene-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methyl)benzenesulfonamide (5j)



By following the general procedure, the reaction was performed with 1-Naphthol **4a** (100 mg, 0.693 mmol, 1.0 equiv) and cyclic carbamate **2j** (236.78 mg, 0.693 mmol, 1.0 equiv) using CuI (1.32 mg, 1 mol %), **L1** (8.63 mg, 2 mol %) and DABCO (11.67 mg, 15 mol%) in acetonitrile (2 mL) at -10 °C under nitrogen atmosphere for 16 h. The residue was purified by flash column chromatography on silica gel (20% EtOAc/hexanes) to afford **5j** (168 mg, 55%) as a red semi solid. ^{1}H NMR (400 MHz, MeOH-*d4*) δ 7.99 – 7.95 (m, 1H), 7.87 – 7.83 (m, 1H), 7.54 – 7.47 (m, 4H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.30 (d, *J* = 4.2 Hz, 4H), 7.23 (dd, *J* = 8.3, 4.1 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 4.99 (d, *J* = 3.1 Hz, 1H), 4.34 (d, *J* = 3.1 Hz, 1H), 4.00 (d, *J* = 13.1 Hz, 1H), 3.71 (d, *J* = 13.1 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, MeOH-*d4*) δ 167.3, 152.3, 142.9, 142.7, 137.9, 134.6, 129.0, 128.4, 127.8, 126.9, 126.3, 126.1, 124.0, 121.9, 121.8, 120.7, 119.6, 87.2, 57.4, 50.5, 20.1. IR (thin film): ν_{max}/cm^{-1} 3277, 3059, 2925, 1814, 1671, 1598, 1449, 1383, 1331, 1161, 1085, 930, 810, 756, 698, 667. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{27}H_{24}NO_3S$: 442.1477, found 442.1478.

2.6 Gram Scale Synthesis of Compounds 3a and 5a

Gram Scale Synthesis of Dihydrofuro[3,2-*c*]coumarin 3a

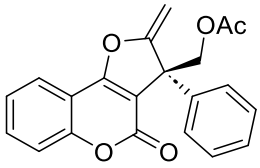
To a clean and dry round-bottom flask, under nitrogen atmosphere added dried CuI (0.012 g, 1 mol%) and **L2** (0.032 g, 2 mol%) in CH_3CN (10 mL) solvent and stirred at 70 °C for 1 h and the resultant Copper-ligand complex was cooled to -20 °C and then added **1a** (1.0 g, 6.16 mmol, 1.0 equiv) followed by DABCO (0.103 g, 0.15 equiv) and cyclic carbonate **2a** (1.16 g, 6.16 mmol, 1.0 equiv) dissolved in CH_3CN (10 mL) was added slowly drop wise. The reaction was maintained and stirred at -20 °C for 8 h. After completion of reaction, the reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel using 50% EtOAc/hexanes as eluent to afford the pure furo[3,2-*c*]coumarin scaffold **3a** (1.85 g, 98%) as pale yellow solid. HPLC purity: 98:2 *er*

Gram Scale Synthesis of Dihydronaphtho[1,2-*b*]furan (5a)

To a clean and dry round-bottom flask, added dried CuI (0.013g, 1 mol%) and **L1** (0.086 g, 2 mol%) in CH_3CN (10 mL) solvent and stirred at 70 °C for 1 h and the resultant Copper-ligand complex was cooled to -10 °C and then added **4a** (1.0 g, 6.936 mmol, 1.0 equiv) followed by DABCO (0.117g, 15 mol%) and cyclic carbonate **2a** (1.3 g, 6.936mmol, 1.0 equiv) dissolved in CH_3CN(10 mL) was added slowly drop wise. The reaction was maintained at -10 °C for 24 h. After completion of reaction, water was added to the reaction mixture and extracted with EtOAc twice and washed the organic layer with brine solution and dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using 20% EtOAc/hexanes as eluent to afford the pure furo[1,2-*b*]dihydronaphthol scaffolds **5a** (1.2 g, 60%) as a red semi solid. HPLC purity: 50:50 *er*

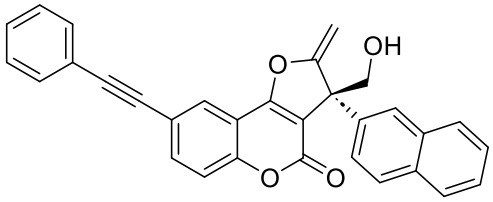
2.7. Product Derivatization

(*R*)-(2-Methylene-4-oxo-3-phenyl-2,3-dihydro-4*H*-furo[3,2-c]chromen-3-yl)methyl acetate (6)



To a clean and dry round-bottom flask added compound **3a** (100 mg, 0.326 mmol, 1.0 equiv) in DCM (2 mL), Et_3N (0.06 mL, 0.489 mmol, 1.5 equiv) and acetic anhydride (0.04 mL, 0.489 mmol, 1.5 equiv) were added slowly and the reaction mixture was stirred at room temperature for 8 h. After completion of the reaction, the reaction mixture was quenched with NH_4Cl solution and extracted with DCM twice and dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using 20% EtOAc/hexanes as eluent to afford **6** (91 mg, 80%) as an off white semi-solid. HPLC purity: 97.7:2.3 *er* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.62 (ddd, *J* = 8.7, 7.4, 1.6 Hz, 1H), 7.52 (dt, *J* = 8.6, 2.3 Hz, 2H), 7.37 (m, *J* = 10.5, 8.0, 5.1 Hz, 4H), 7.32 – 7.27 (m, 1H), 5.26 (d, *J* = 3.7 Hz, 1H), 4.91 (d, *J* = 0.8 Hz, 2H), 4.63 (d, *J* = 3.7 Hz, 1H), 1.98 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 165.4, 163.9, 158.3, 155.5, 139.2, 133.2, 129.0, 128.13, 126.8, 124.4, 123.0, 117.3, 111.6, 106.9, 92.2, 66.1, 56.0, 29.8, 21.0. IR (thin film): ν_{max}/cm^{-1} 3438, 3254, 2928, 2857, 1724, 1685, 1641, 1604, 1566, 1496, 1453, 1393, 1226, 1083, 1039, 963, 904, 862, 755, 694. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{21}H_{17}O_5$: 349.1076, found 349.1067.

(*R*)-3-(Hydroxymethyl)-2-methylene-3-(naphthalen-2-yl)-8-(phenylethynyl)-2,3-dihydro-4*H*-furo[3,2-c]chromen-4-one (7)



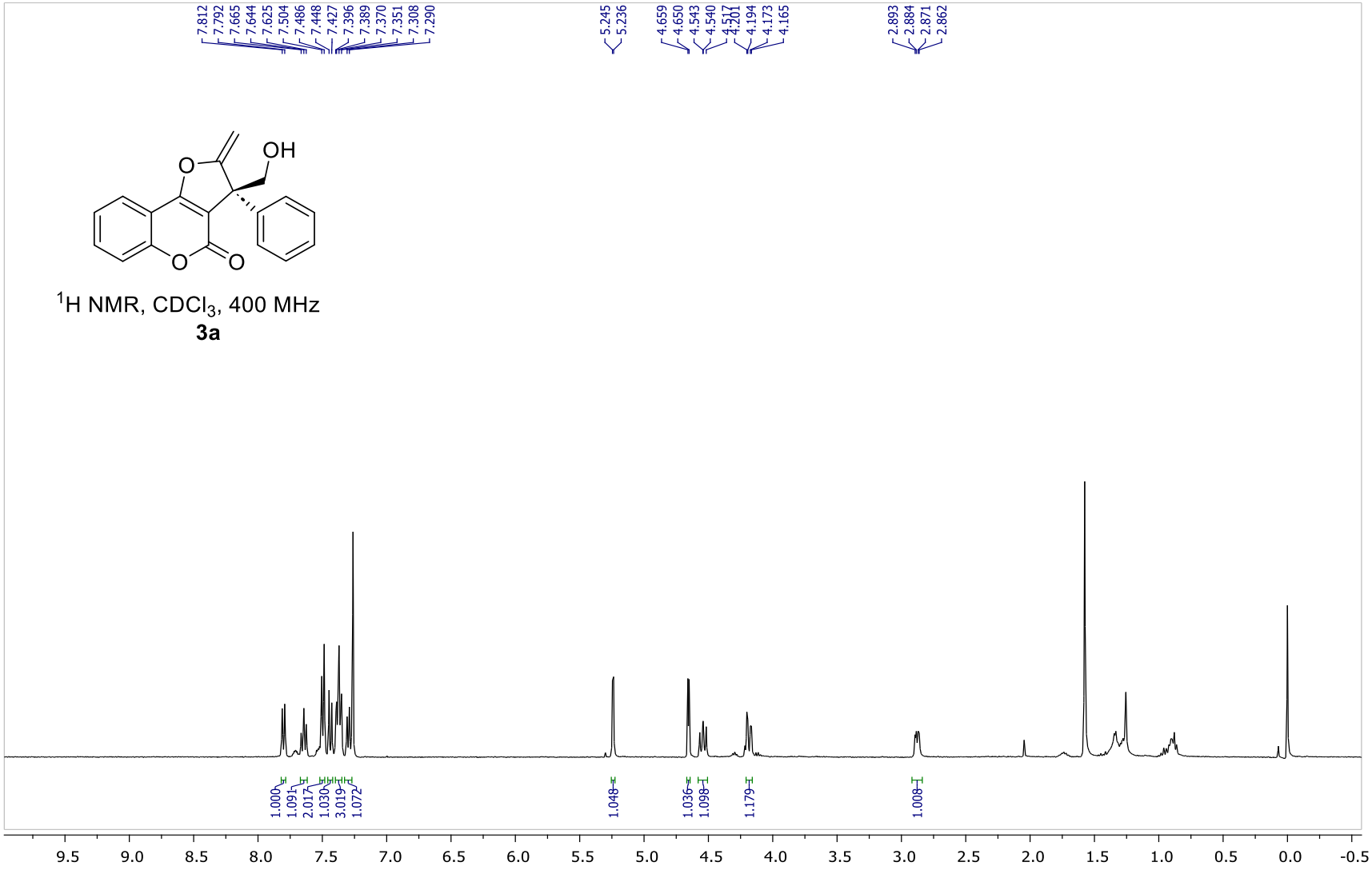
To a clean and dry sealed tube added compound **3i** (50 mg, 0.115 mmol, 1.0 equiv) in DMF (2 mL), $Pd(PPh_3)_2Cl_2$ (0.80 mg, 1 mol%), CuI (2.19 mg, 0.001mmol, 0.1 equiv) and Et_3N(0.03 mL, 0.230 mmol, 2.0 equiv), stirred the reaction mixture at room temperature for 15 mins and then added phenyl acetylene (15.3 mg, 0.149 mmol, 1.3 equiv) and the reaction mixture was stirred at room temperature for 16 h. After completion of the reaction, the reaction mixture was filtered through celite pad and washed the bed with EtOAc. Now, collected the filtrate and washed with NH_4Cl solution and dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel using 25% EtOAc/hexanes as eluent to afford **7** (41 mg, 77%) as a pale yellow semi-solid. HPLC purity: 99:1 *er*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.90 (m, 3H), 7.87 – 7.79 (m, 5H), 7.75 – 7.68 (m, 2H), 7.57 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.50 – 7.46 (m, 3H), 7.32 (d, *J* = 8.9 Hz, 1H), 5.29 (d, *J* = 3.7 Hz, 1H), 4.82 – 4.56 (m, 2H), 4.29 (dd, *J* = 11.2, 4.0 Hz, 1H), 2.73 (dd, *J* = 8.9, 4.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 163.3, 159.2, 154.0, 136.5, 136.0, 133.3, 132.8, 132.7, 128.9, 128.6, 128.3, 127.5, 127.3, 126.5, 126.4, 126.3, 125.8, 125.5, 124.6, 118.9, 117.3, 117.3, 113.0, 108.6, 92.3, 67.1, 58.4. IR (thin film): ν_{max}/cm^{-1} 3394, 3058, 2927, 2871, 1726, 1662, 1600, 1560, 1488, 1424, 1383, 1306, 1263, 1211, 1149, 1103, 1064, 965, 910, 859, 820, 762, 728, 663. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{31}H_{21}O_4$: 457.1369, found 457.1380.

3. References

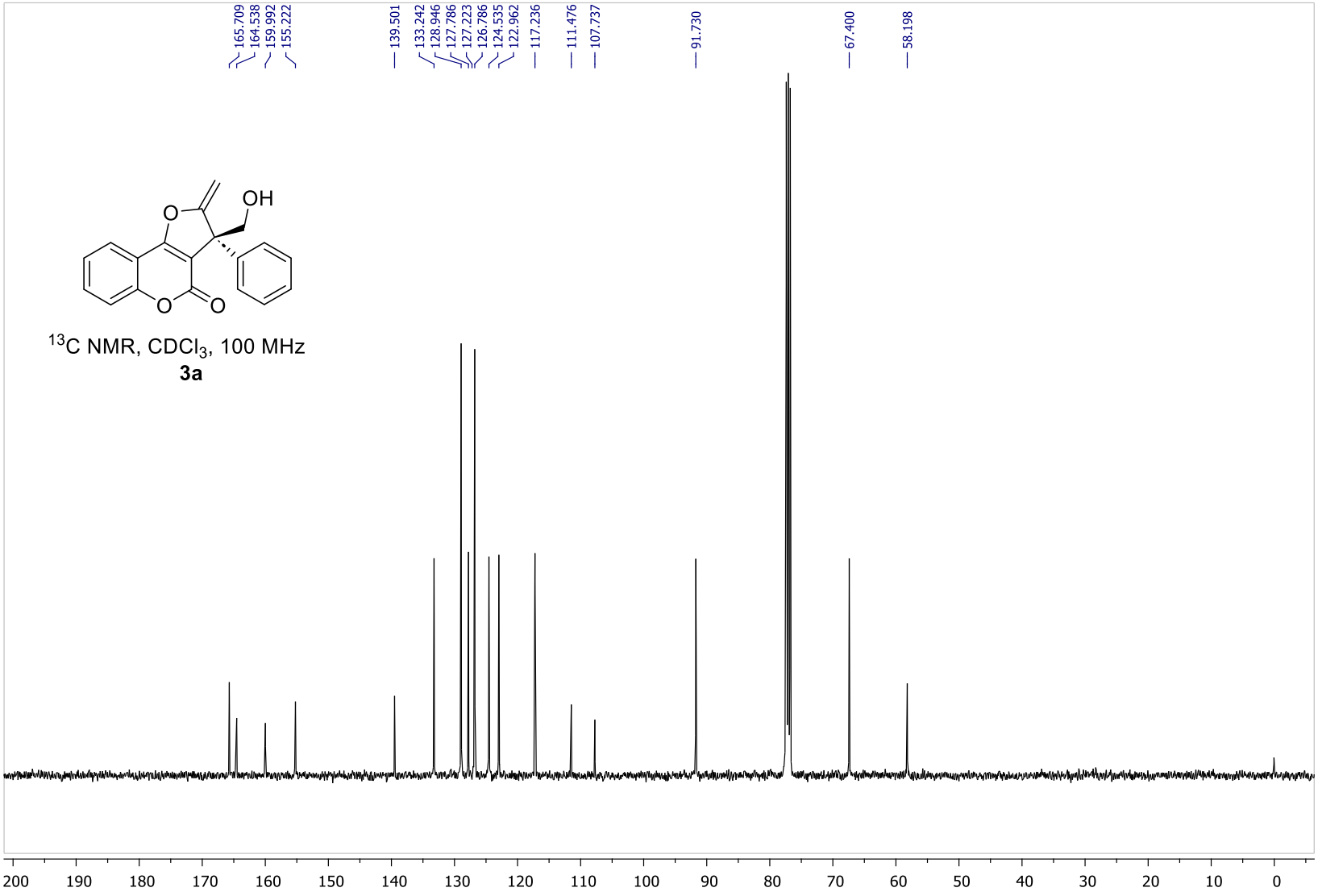
1. M. Wang, B. Li, B. Gong, H. Yao and A. Lin, *Chem. Commun*., 2022, **58**, 2850–2853.

4. ^{1}H, ^{13}C NMR and ^{19}F Spectra of Compounds

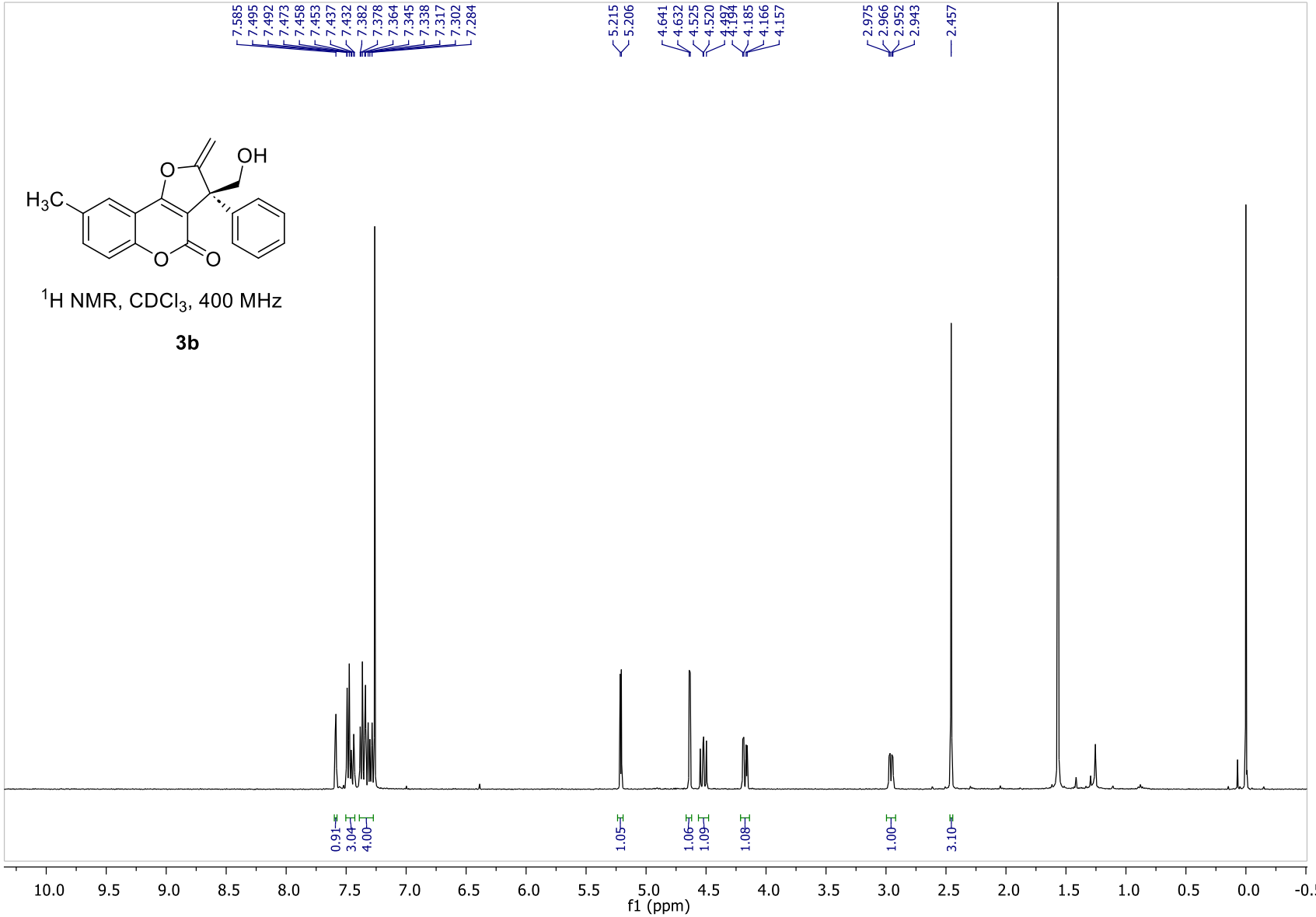
(*R*)-3-(Hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3a)



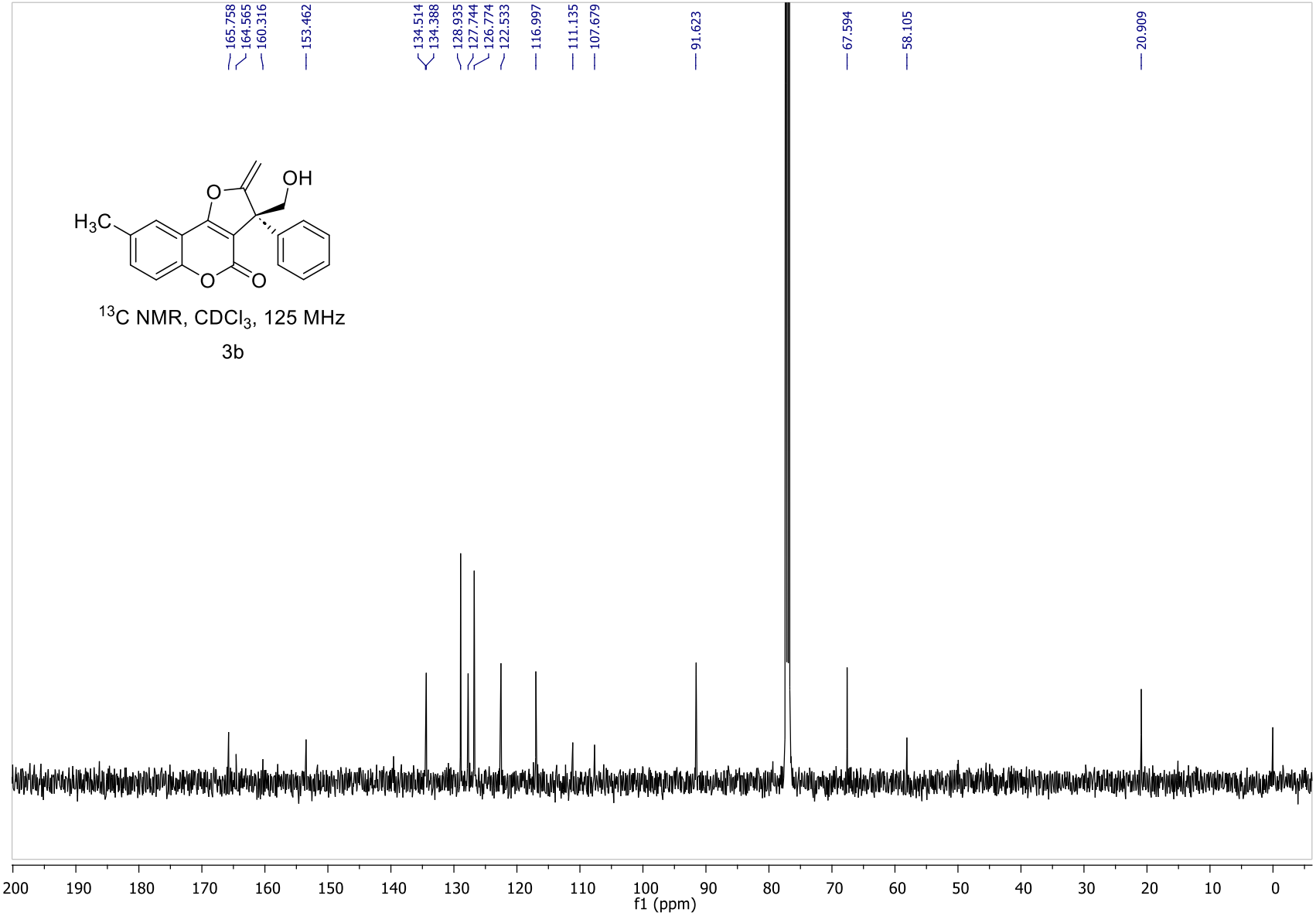
(*R*)-3-(Hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3a)



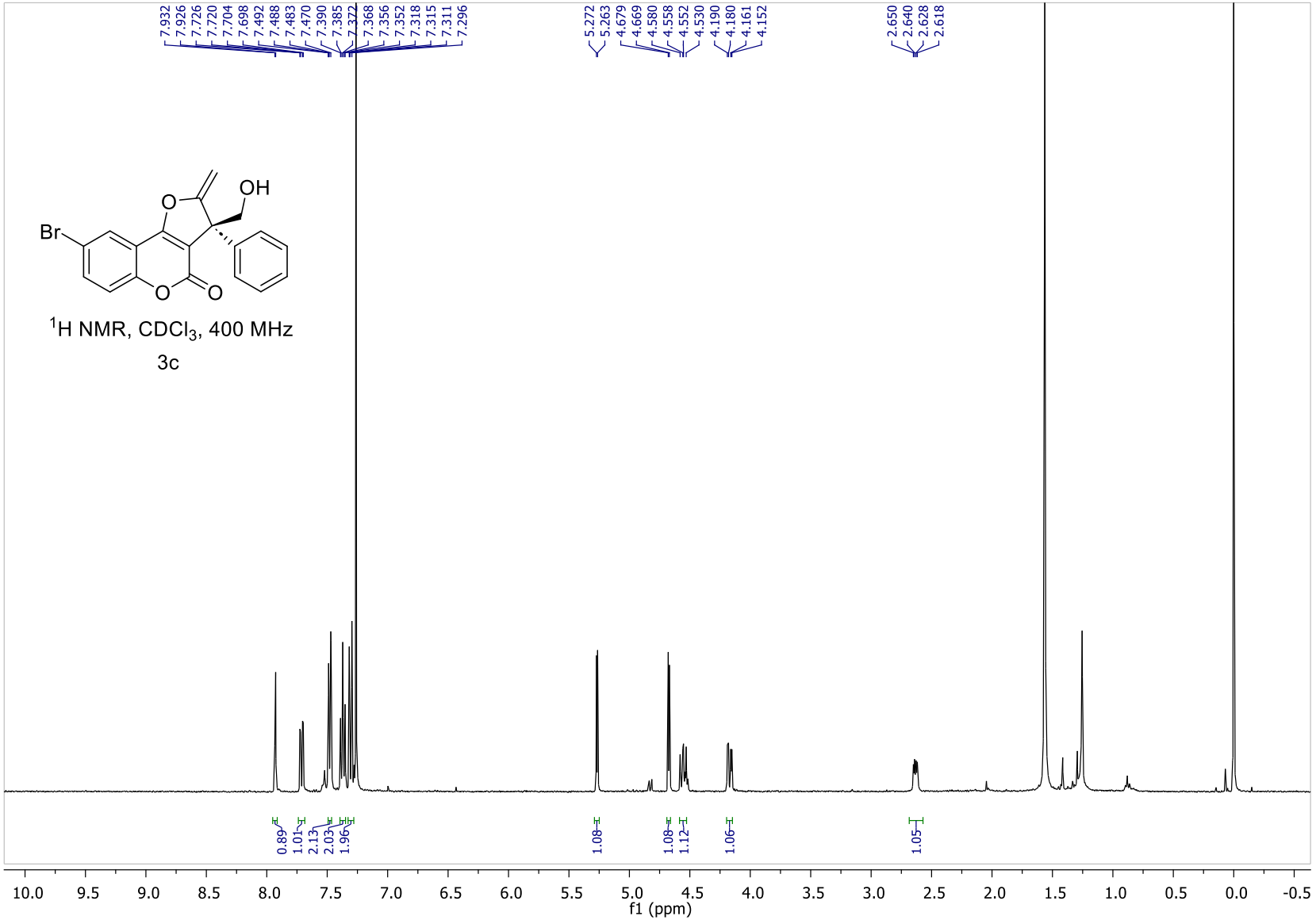
(*R*)-3-(Hydroxymethyl)-8-methyl-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3b)



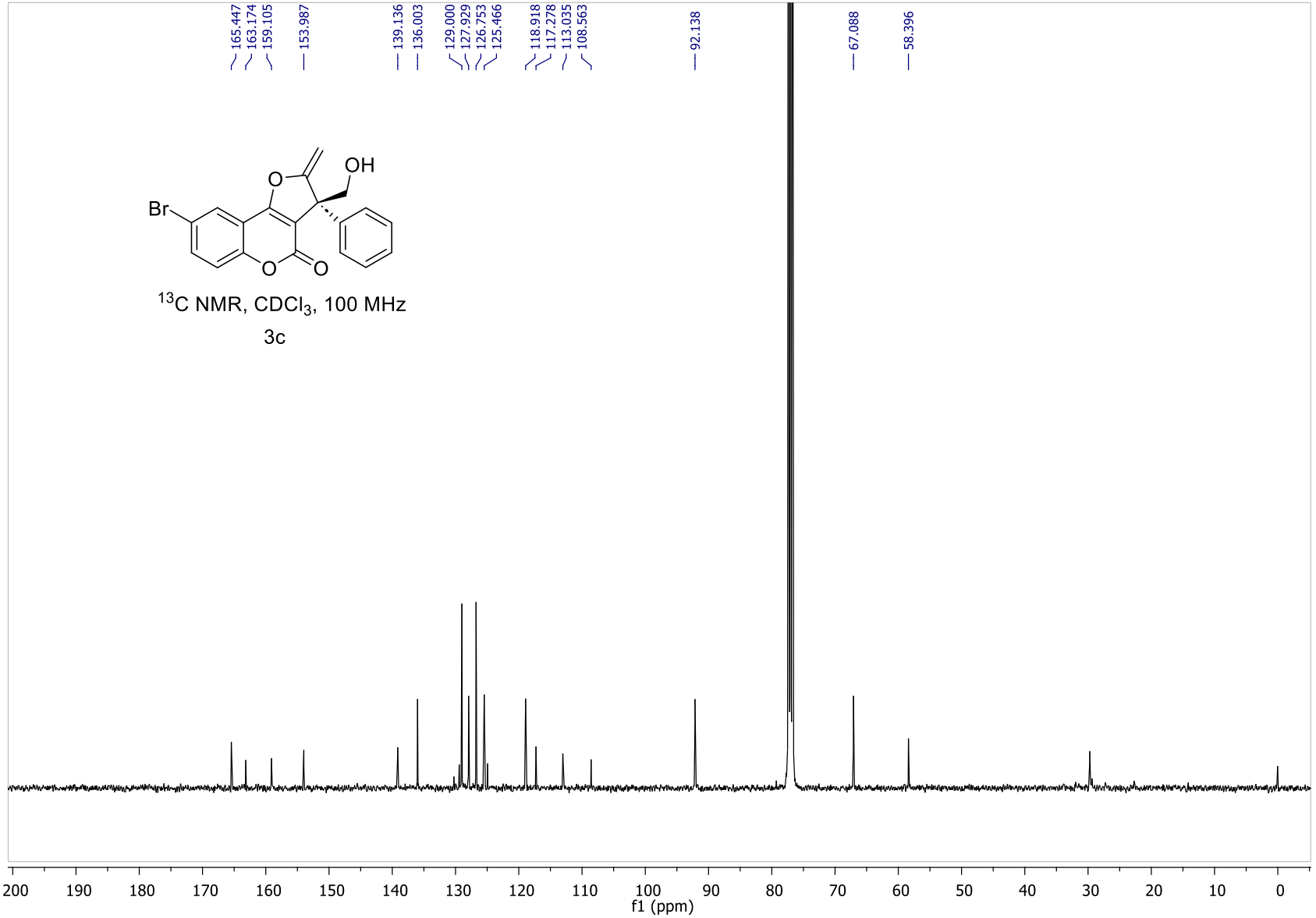
(*R*)-3-(Hydroxymethyl)-8-methyl-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3b)



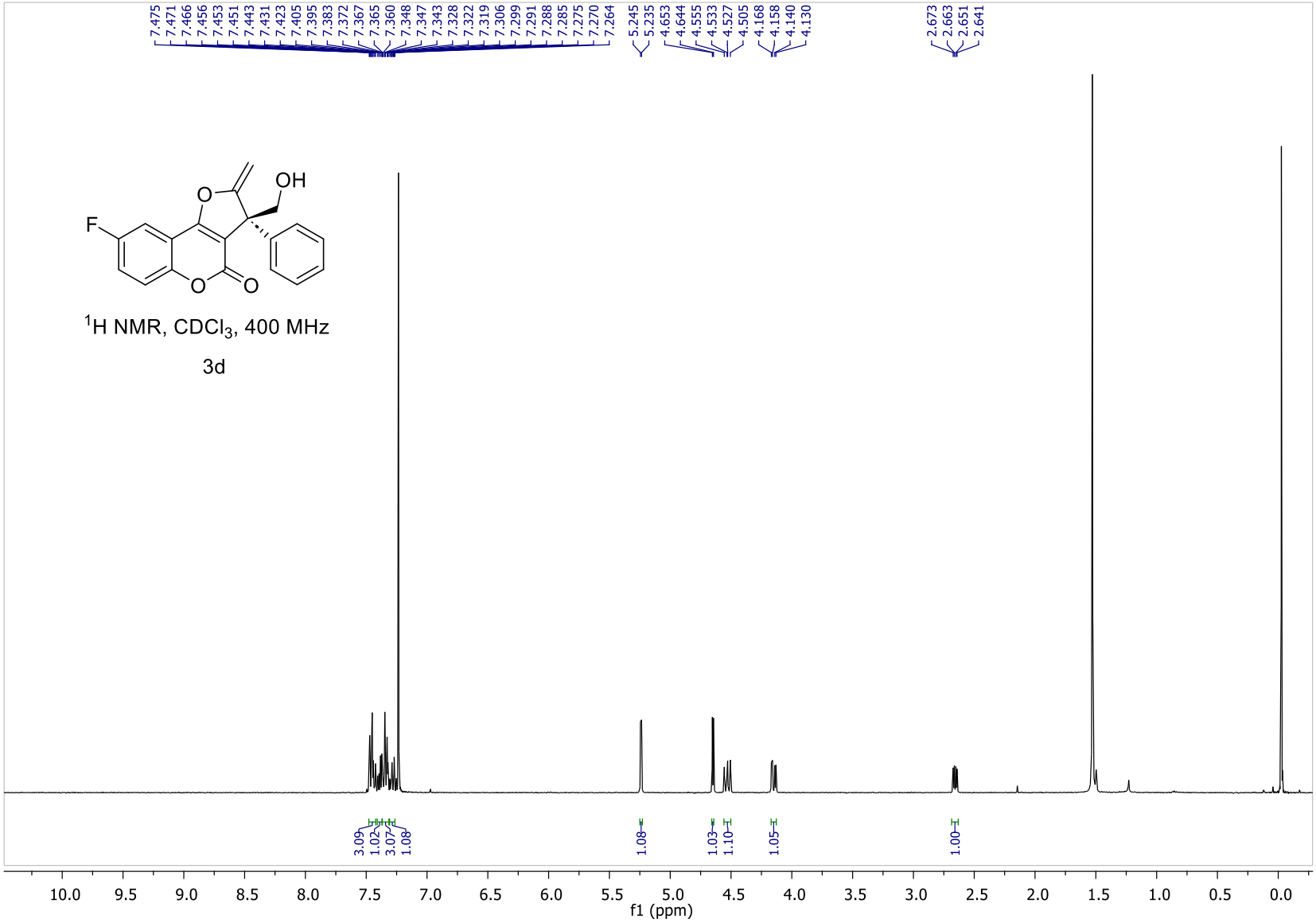
(*R*)-8-Bromo-3-(hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3c)



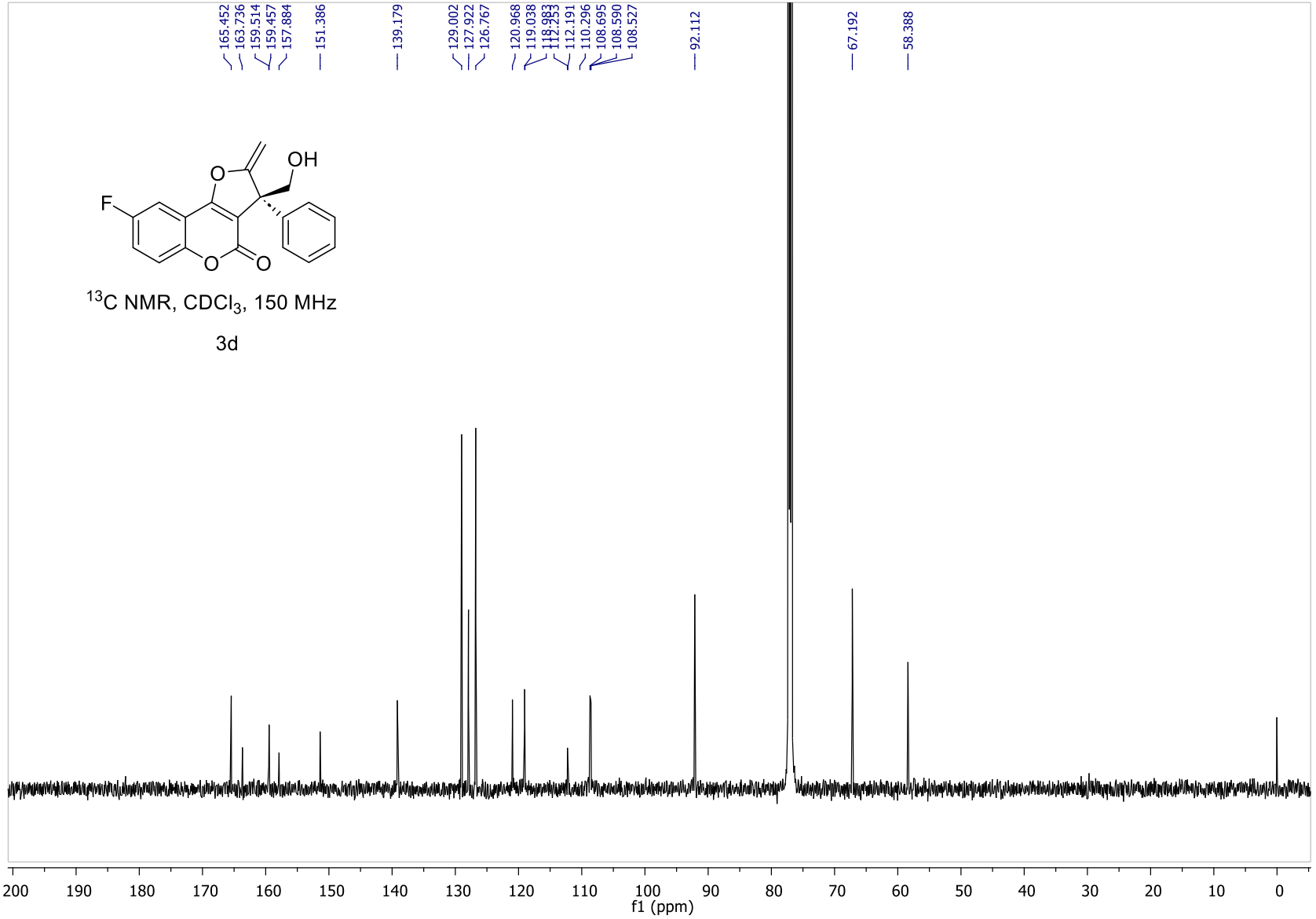
(*R*)-8-Bromo-3-(hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3c)



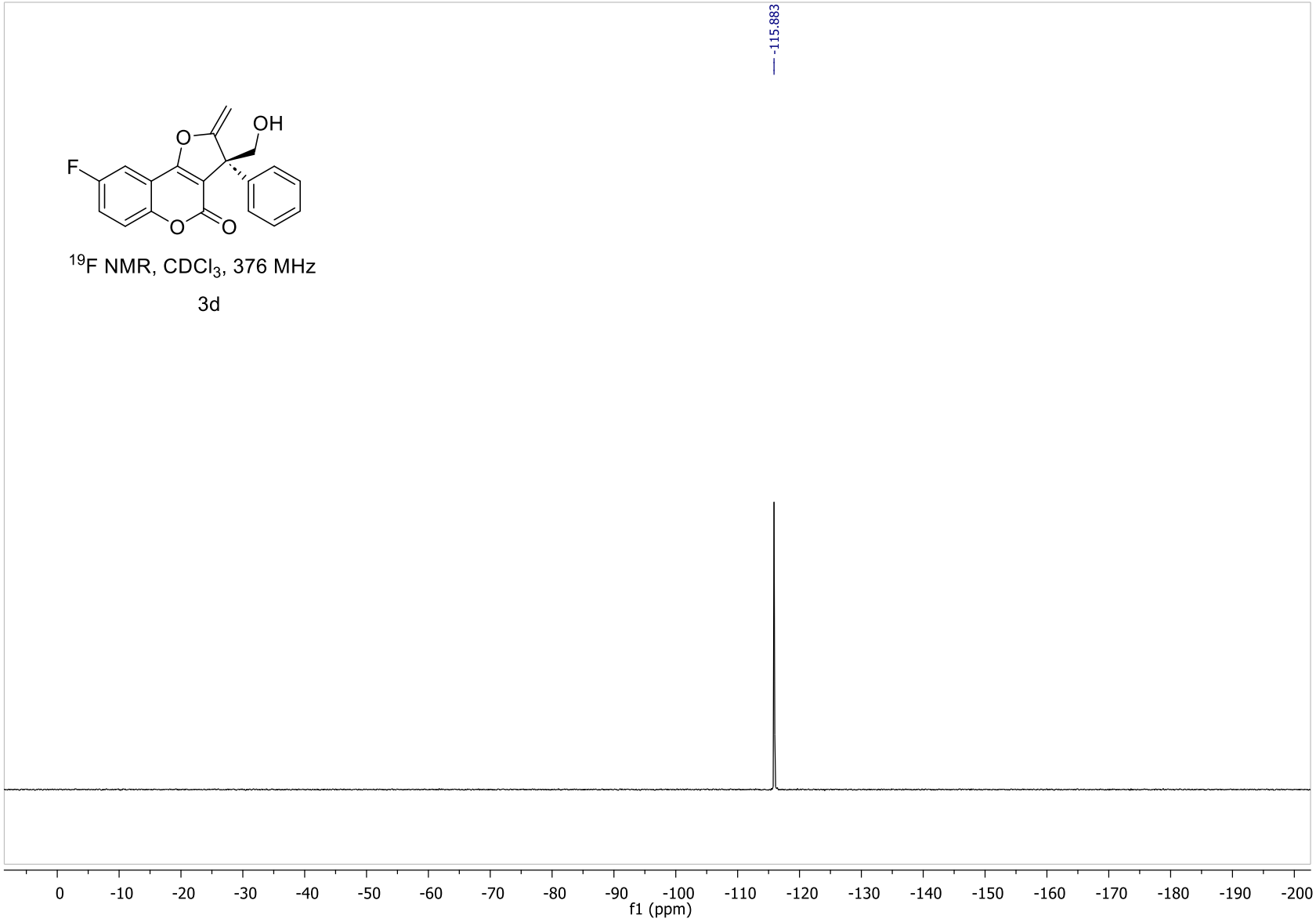
(*R*)-8-Fluoro-3-(hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3d)



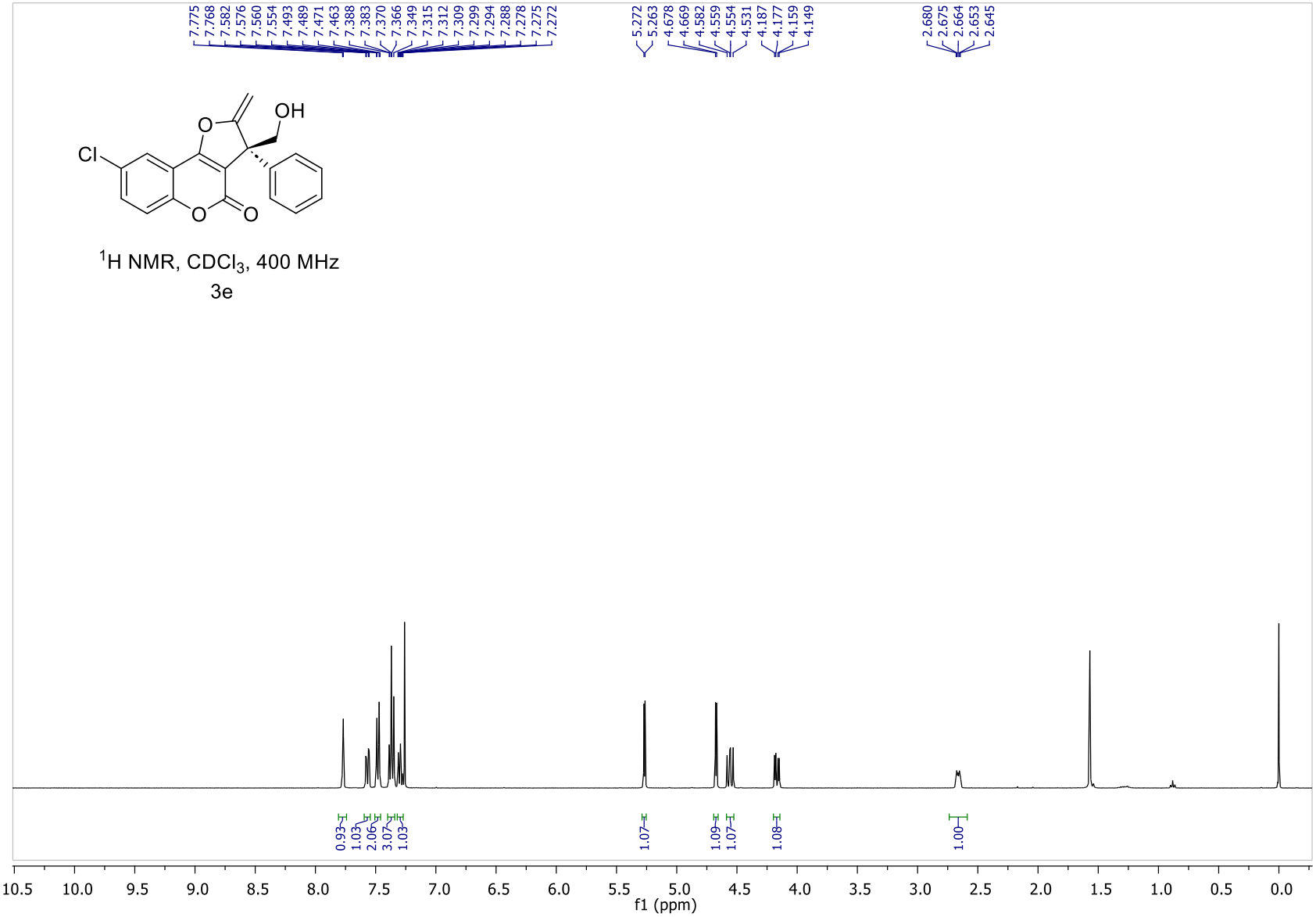
(*R*)-8-Fluoro-3-(hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3d)



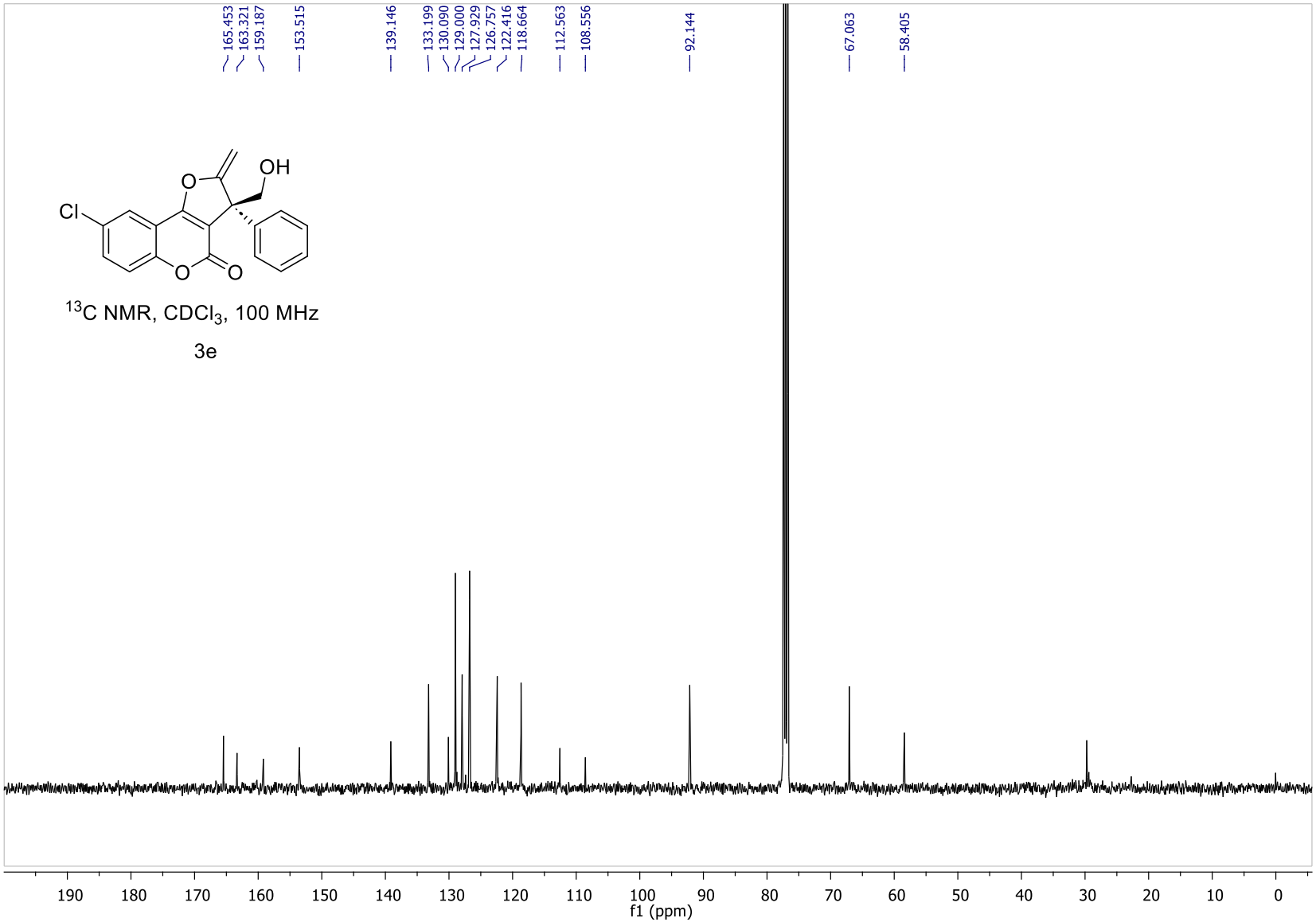
(*R*)-8-Fluoro-3-(hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3d)



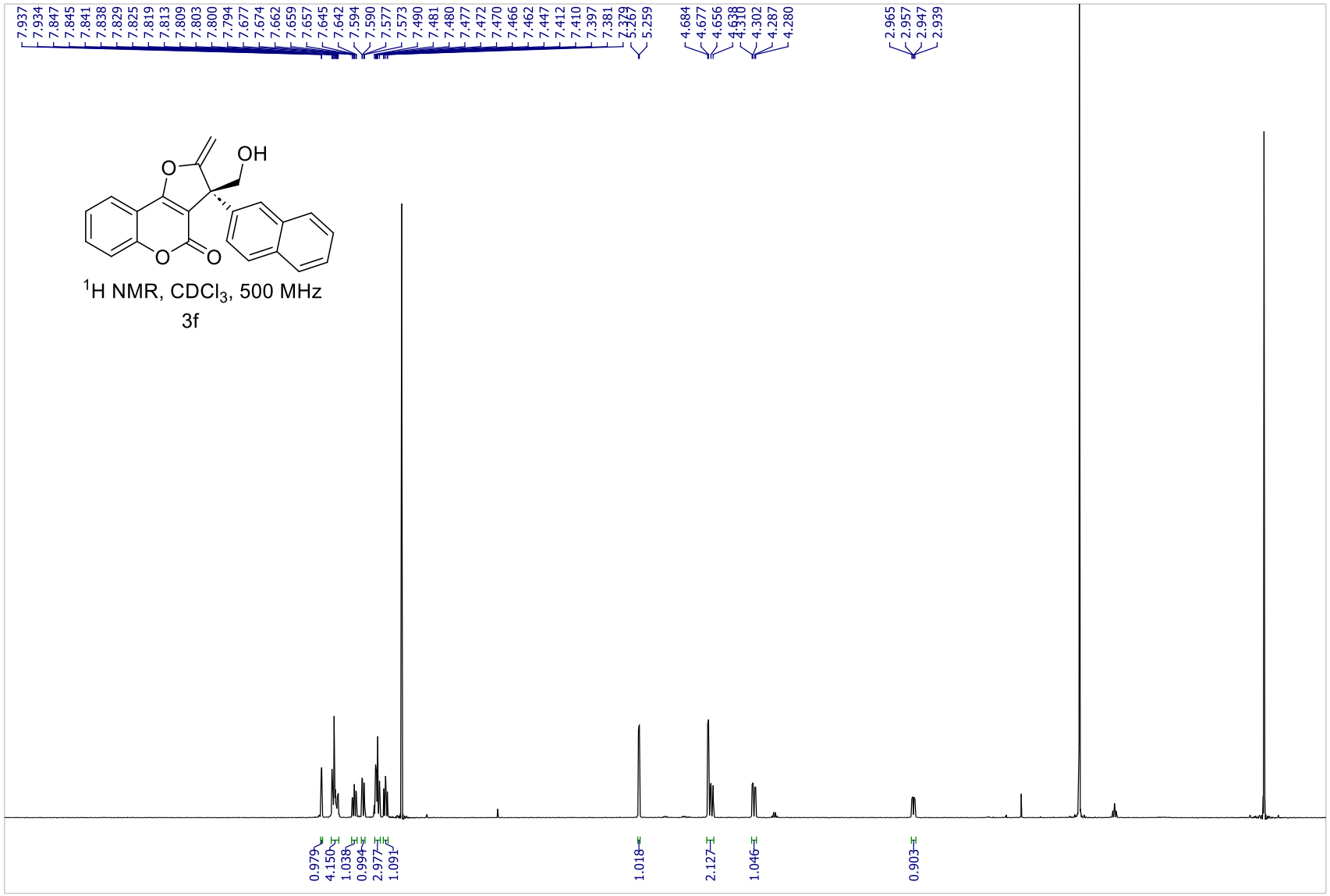
(*R*)-8-Chloro-3-(hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3e)



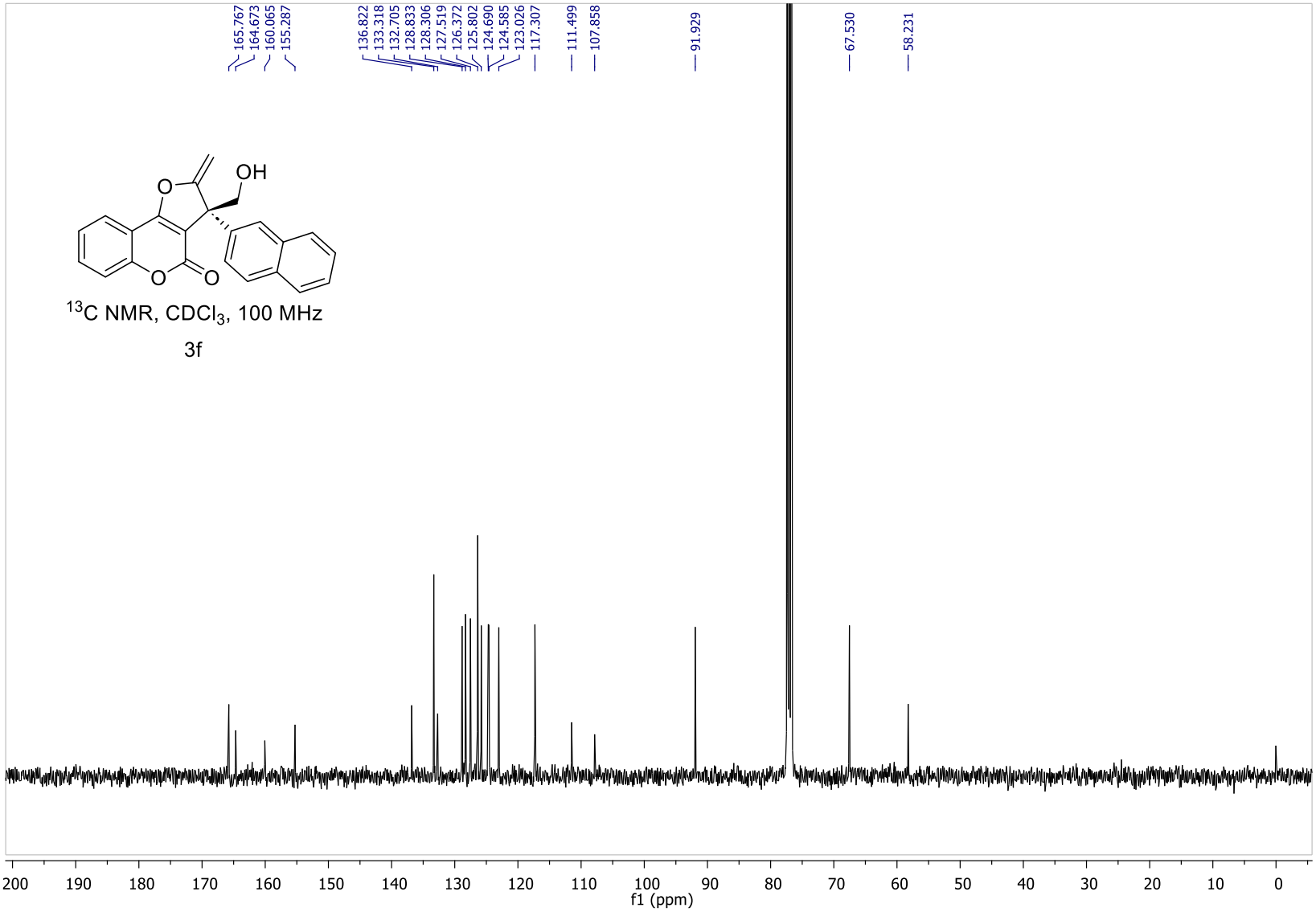
(*R*)-8-Chloro-3-(hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3e)



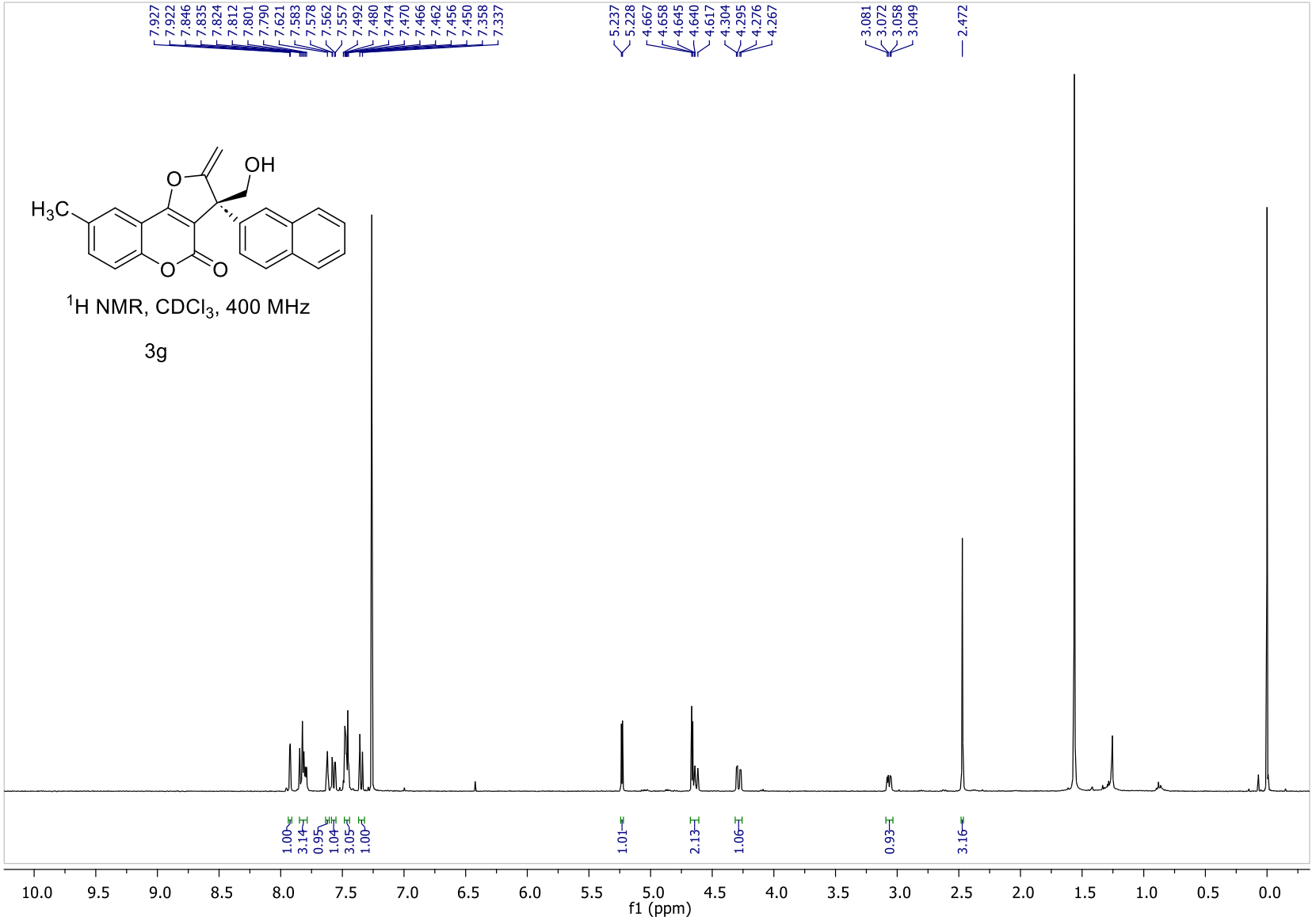
(*R*)-3-(Hydroxymethyl)-2-methylene-3-(naphthalen-1-yl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3f)



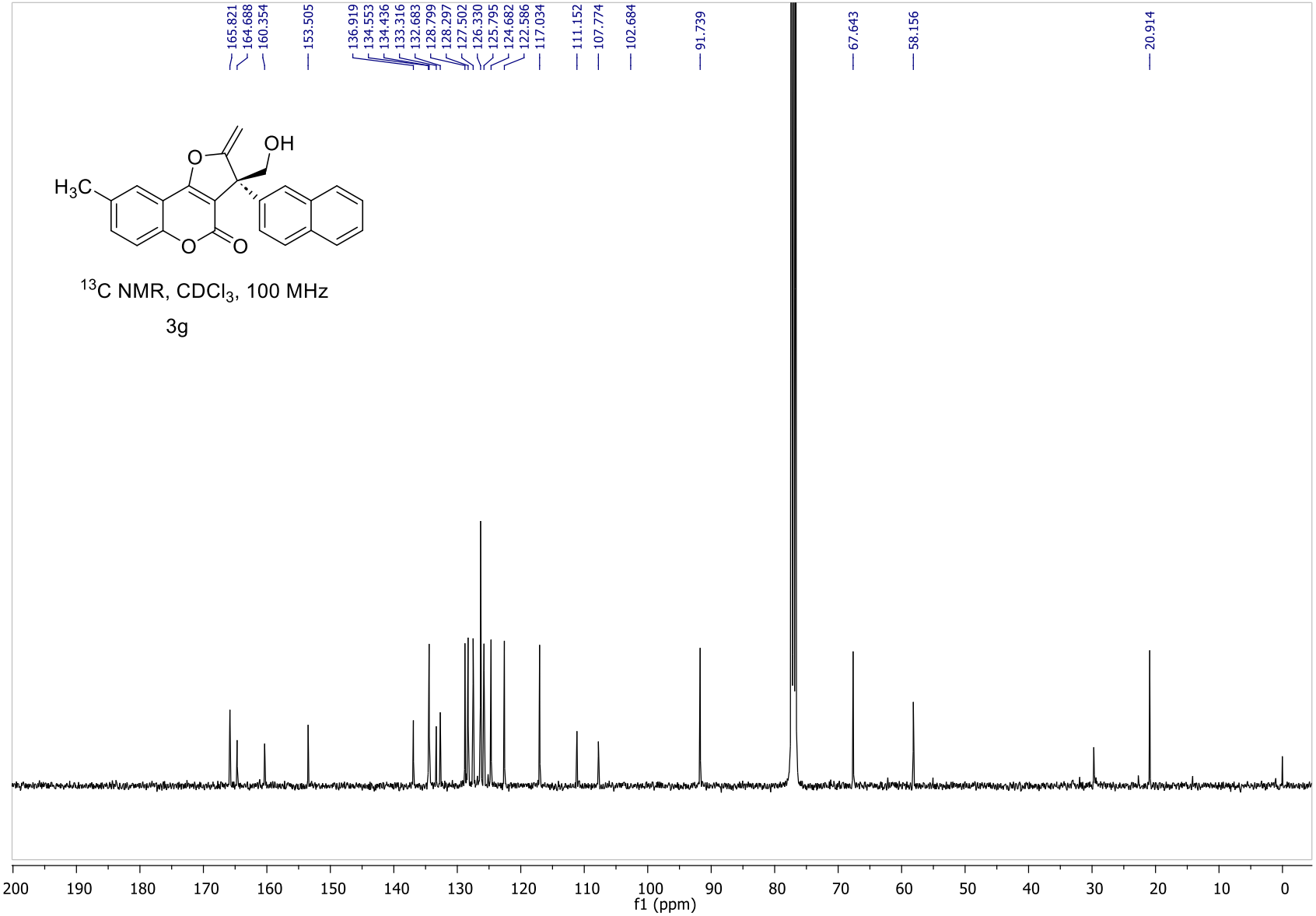
(*R*)-3-(Hydroxymethyl)-2-methylene-3-(naphthalen-1-yl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3f)



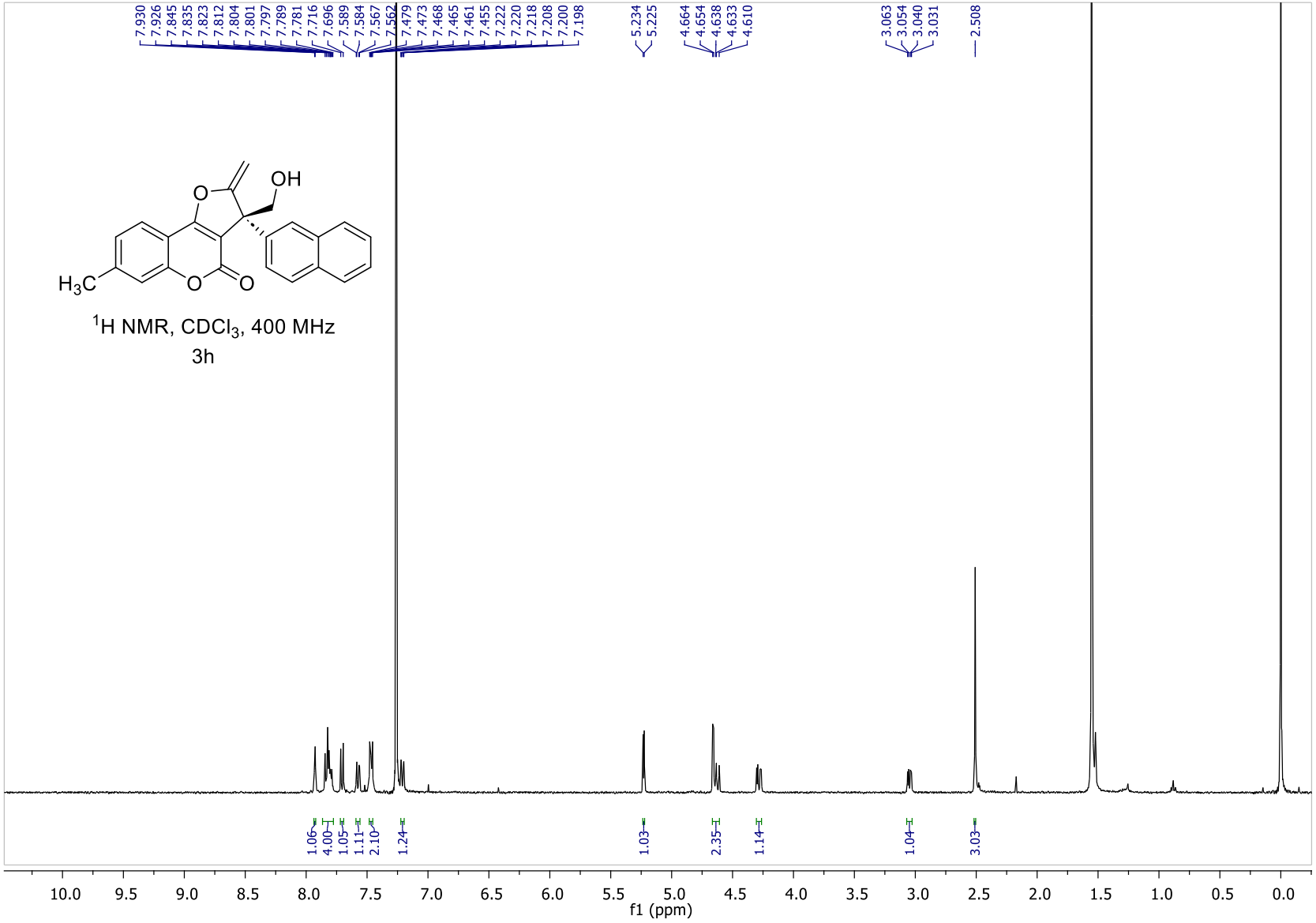
(*R*)-3-(Hydroxymethyl)-8-methyl-2-methylene-3-(naphthalen-2-yl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3g)



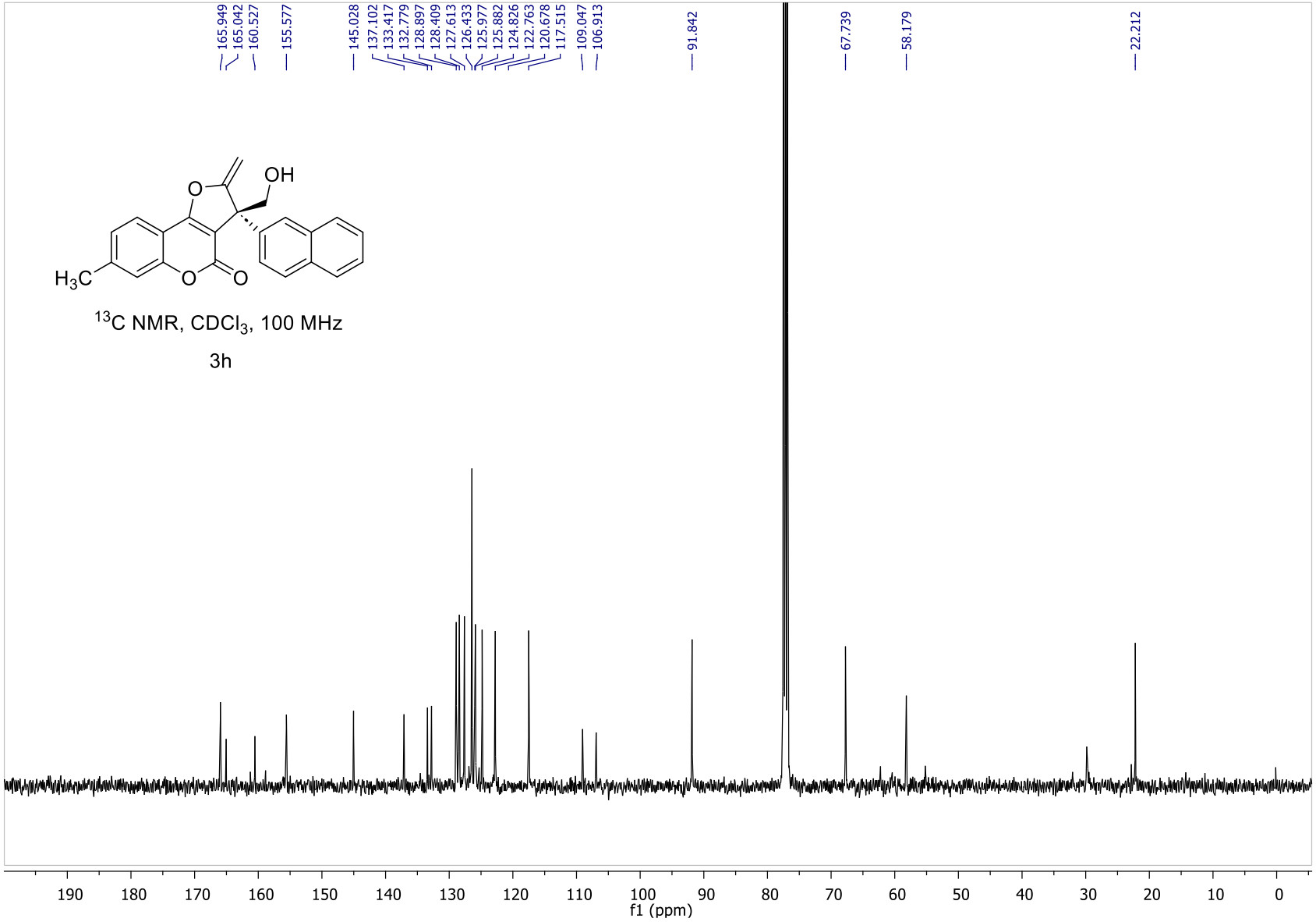
(*R*)-3-(Hydroxymethyl)-8-methyl-2-methylene-3-(naphthalen-2-yl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3g)



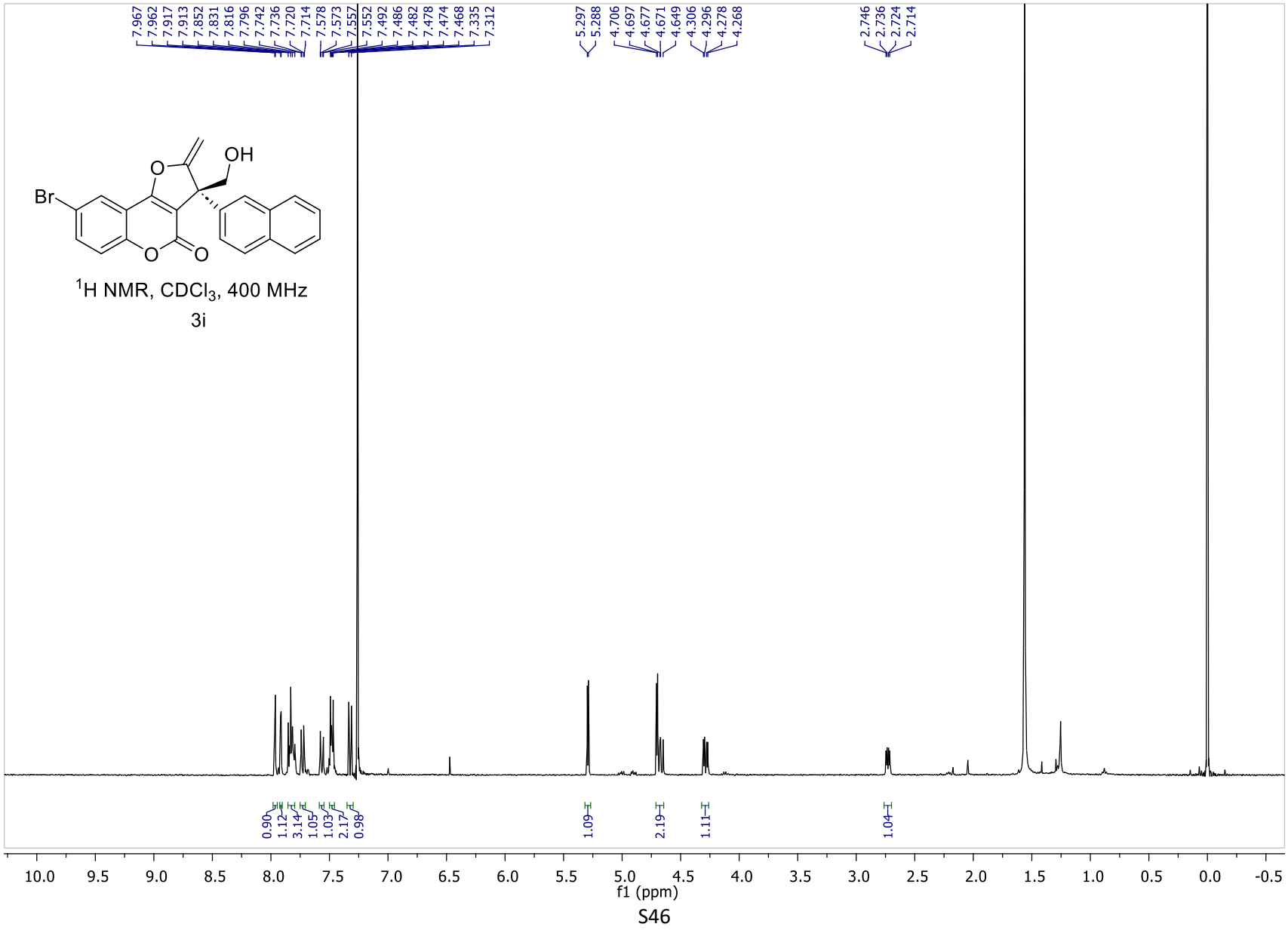
(*R*)-3-(Hydroxymethyl)-7-methyl-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3h)



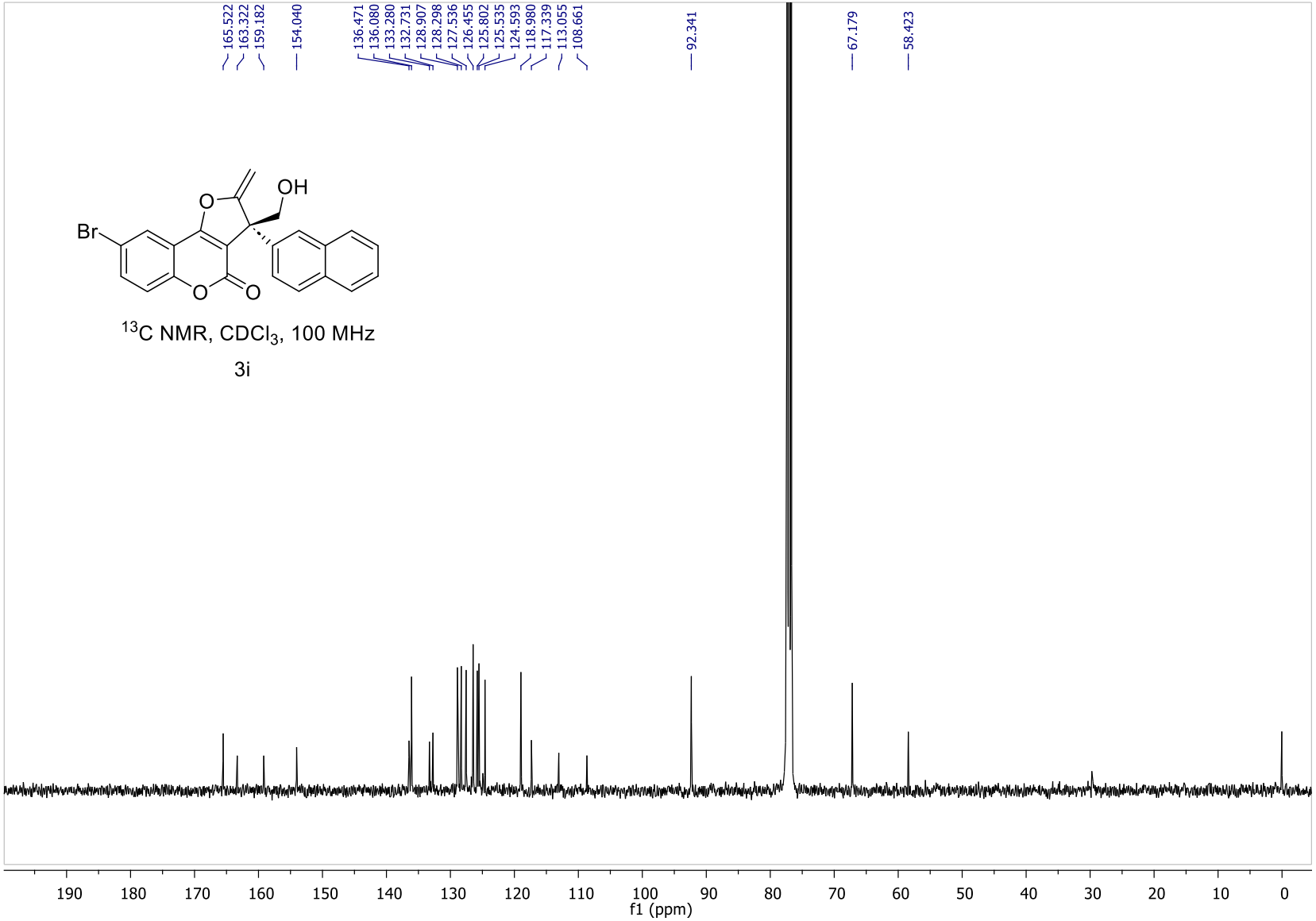
(*R*)-3-(Hydroxymethyl)-7-methyl-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3h)



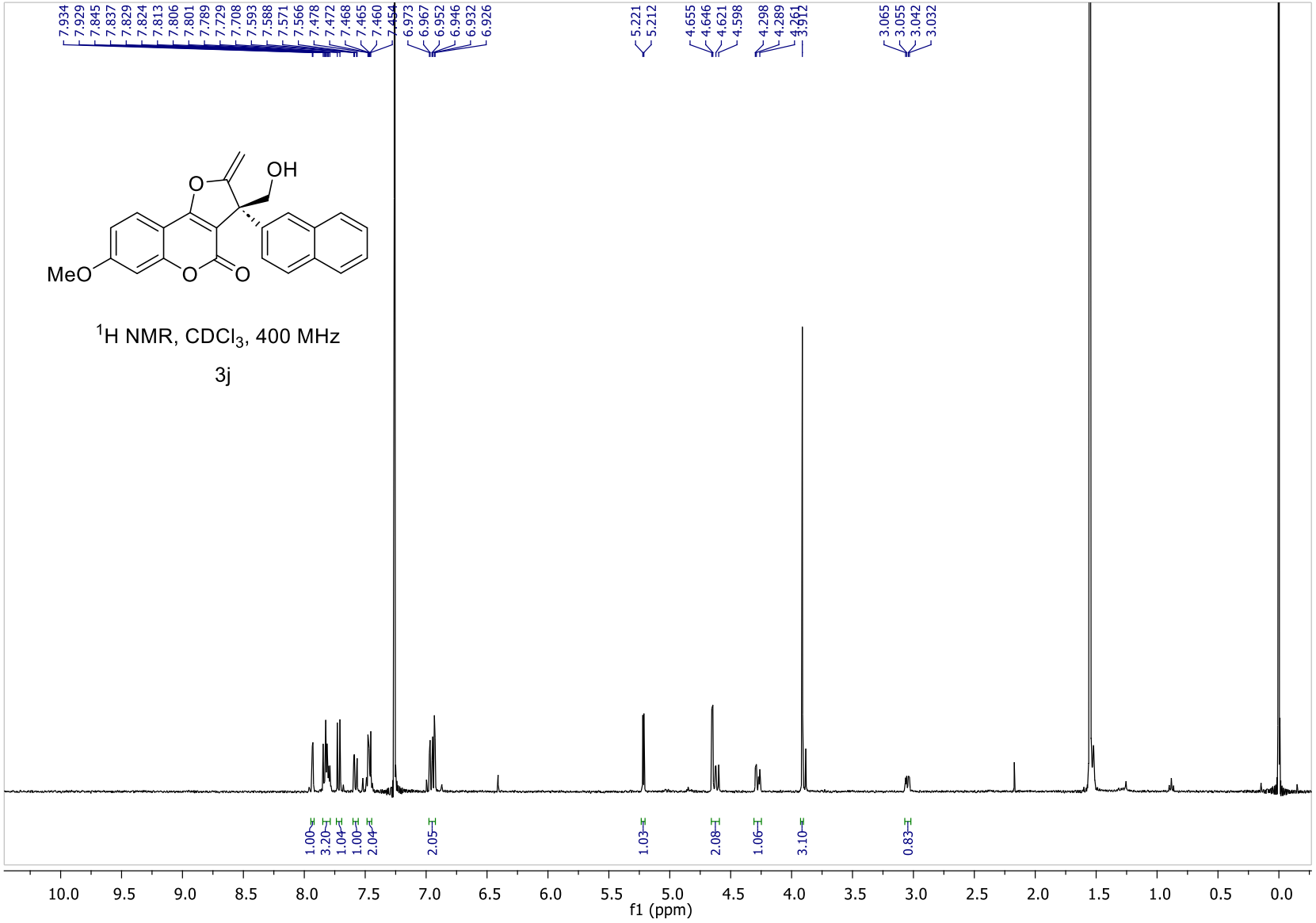
(*R*)-8-Bromo-3-(hydroxymethyl)-2-methylene-3-(naphthalen-2-yl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3i)



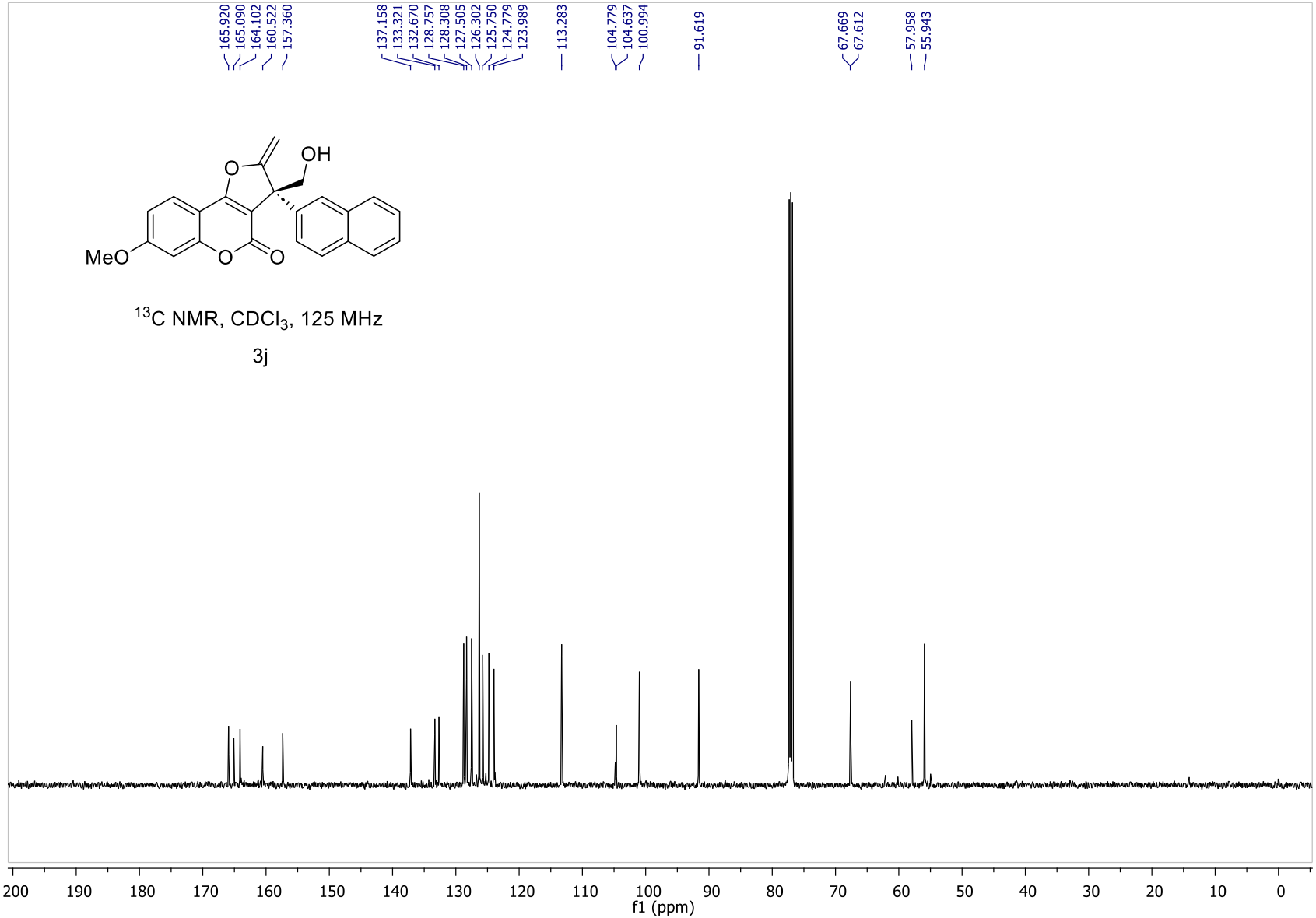
(*R*)-8-Bromo-3-(hydroxymethyl)-2-methylene-3-(naphthalen-2-yl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3i)



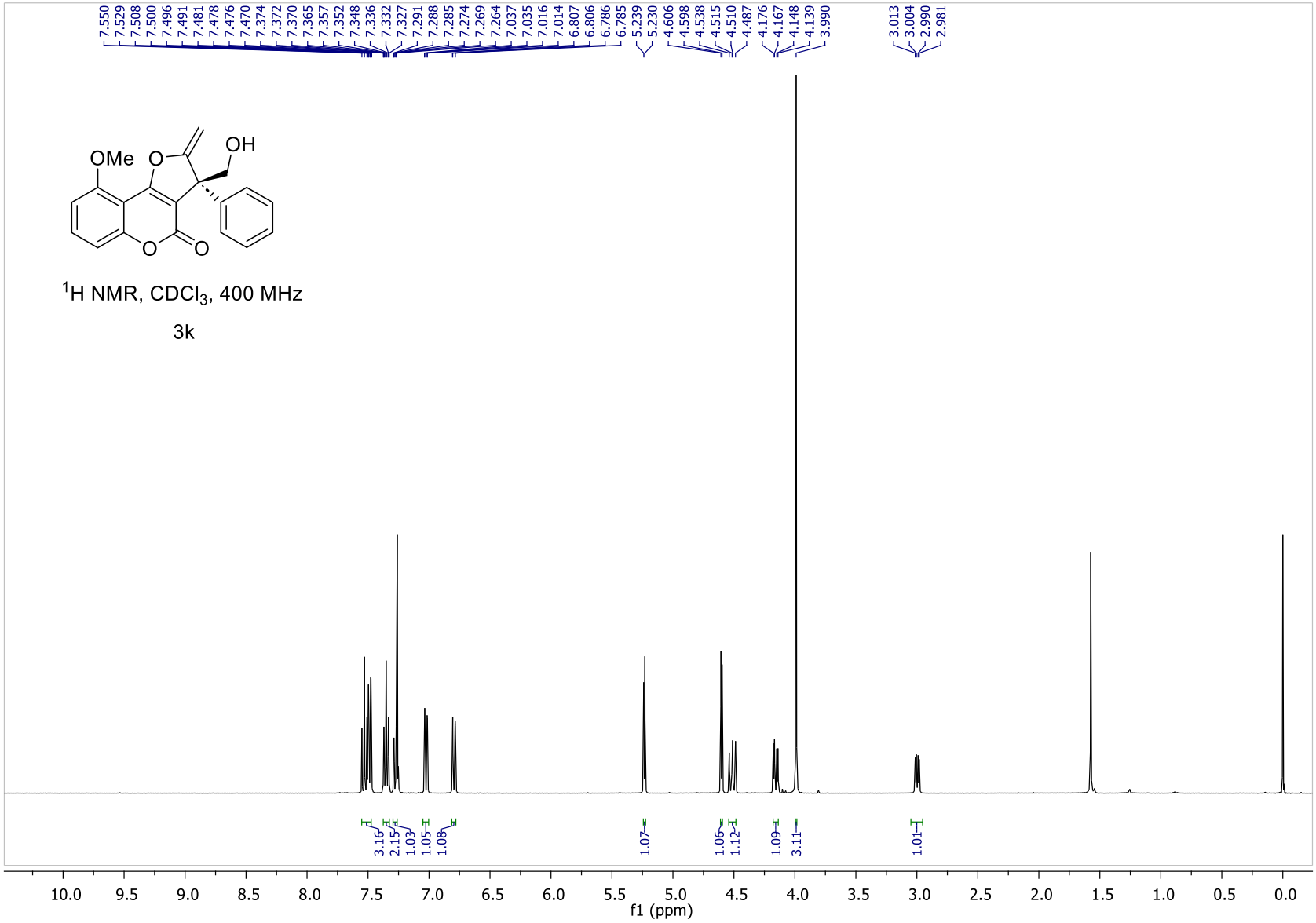
(*R*)-3-(hydroxymethyl)-7-methoxy-2-methylene-3-(naphthalen-2-yl)-2,3-dihydro-4*H*-furo[3,2-c]chromen-4-one (3j)



(*R*)-3-(hydroxymethyl)-7-methoxy-2-methylene-3-(naphthalen-2-yl)-2,3-dihydro-4*H*-furo[3,2-c]chromen-4-one (3j)



(*R*)-3-(hydroxymethyl)-9-methoxy-2-methylene-3-phenyl-2,3-dihydro-4*H*-furo[3,2-c]chromen-4-one (3k)



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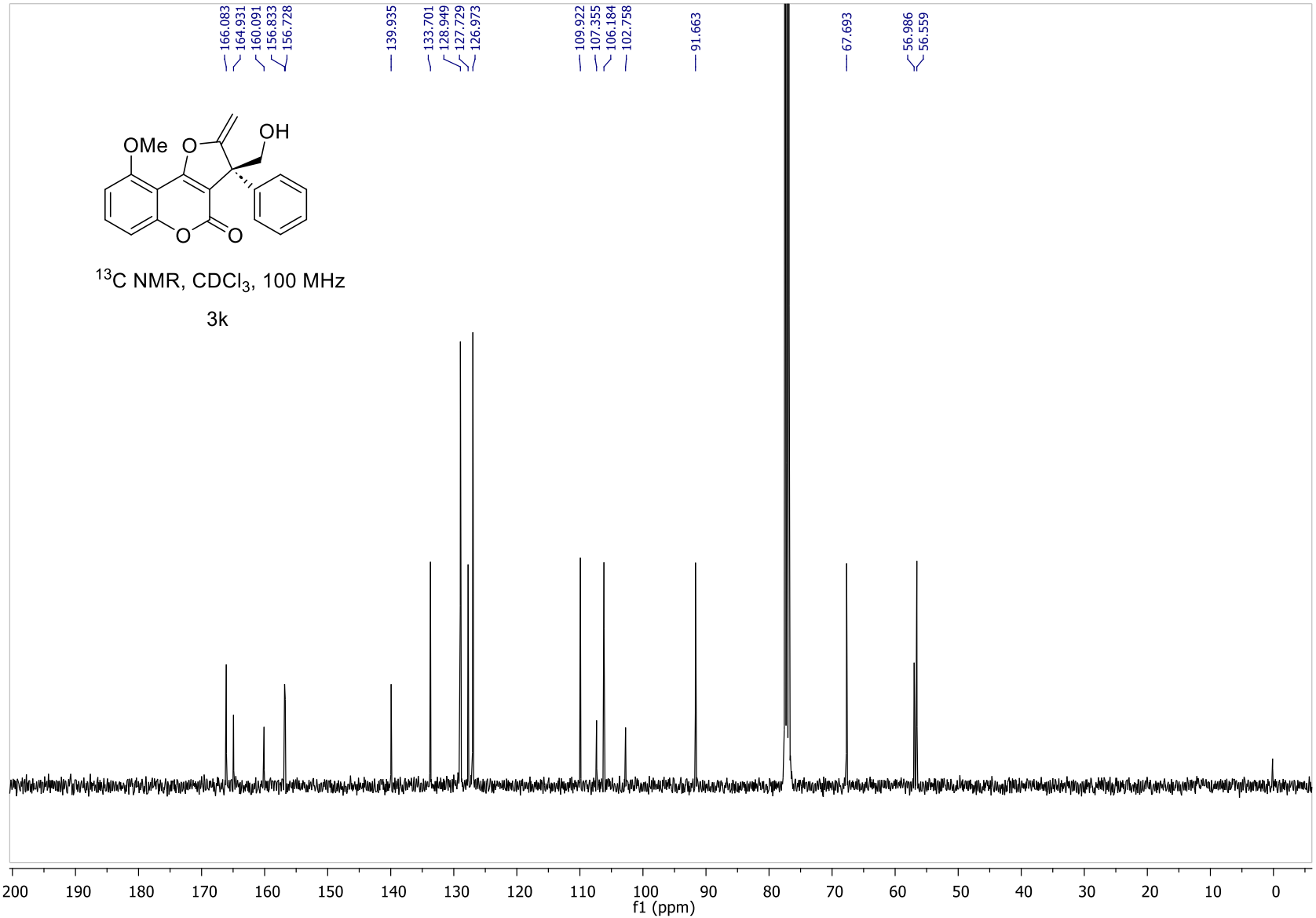
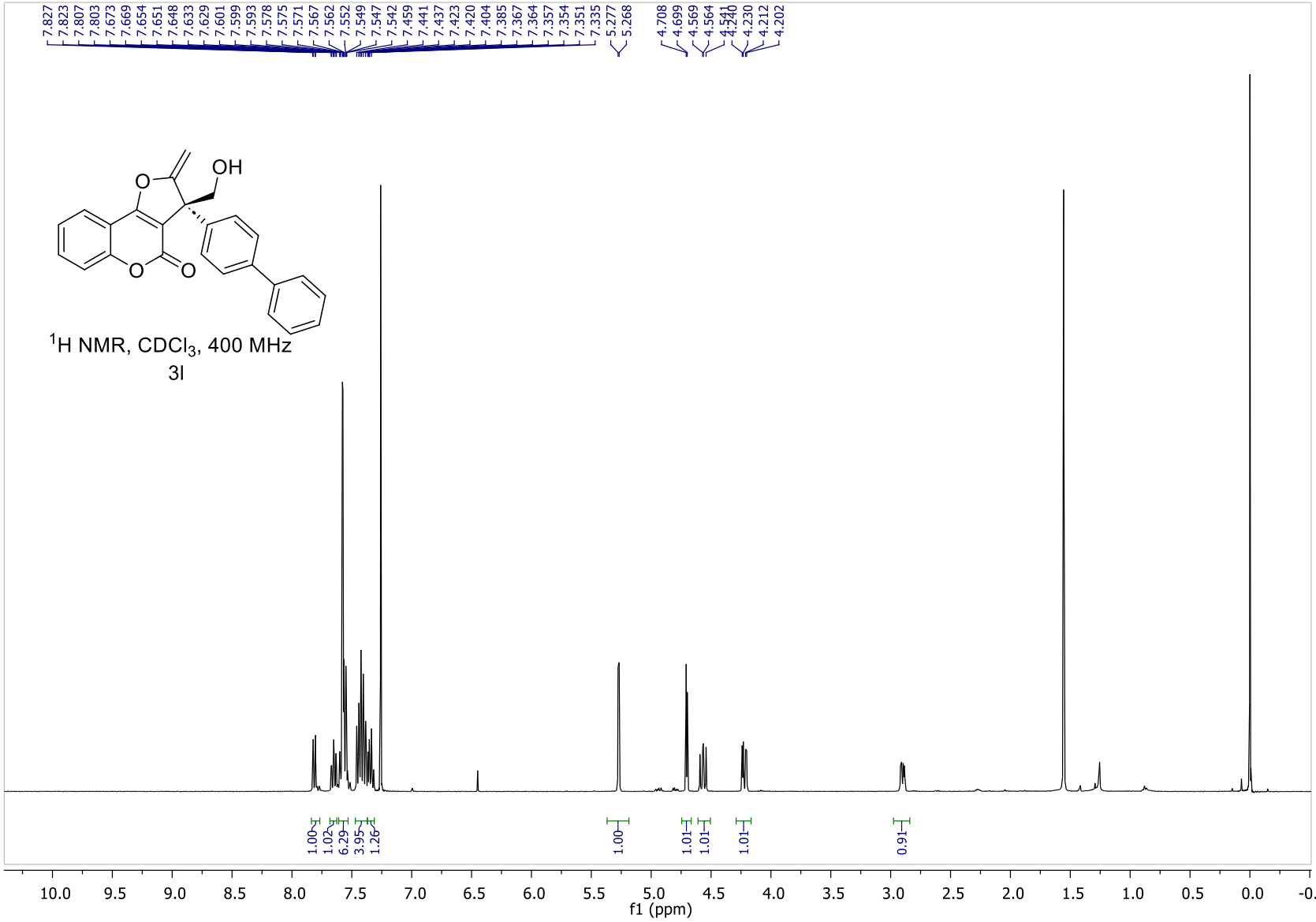
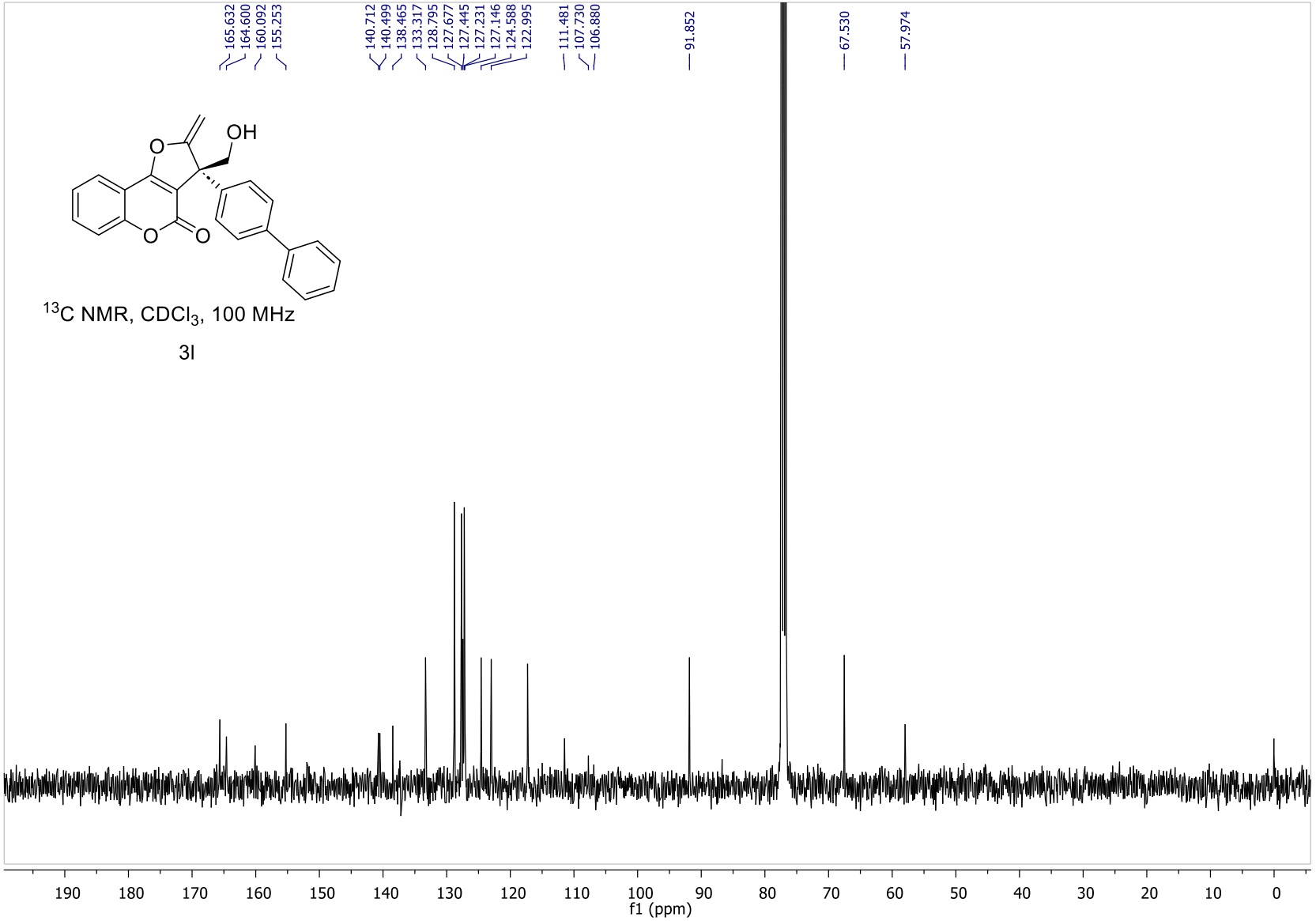


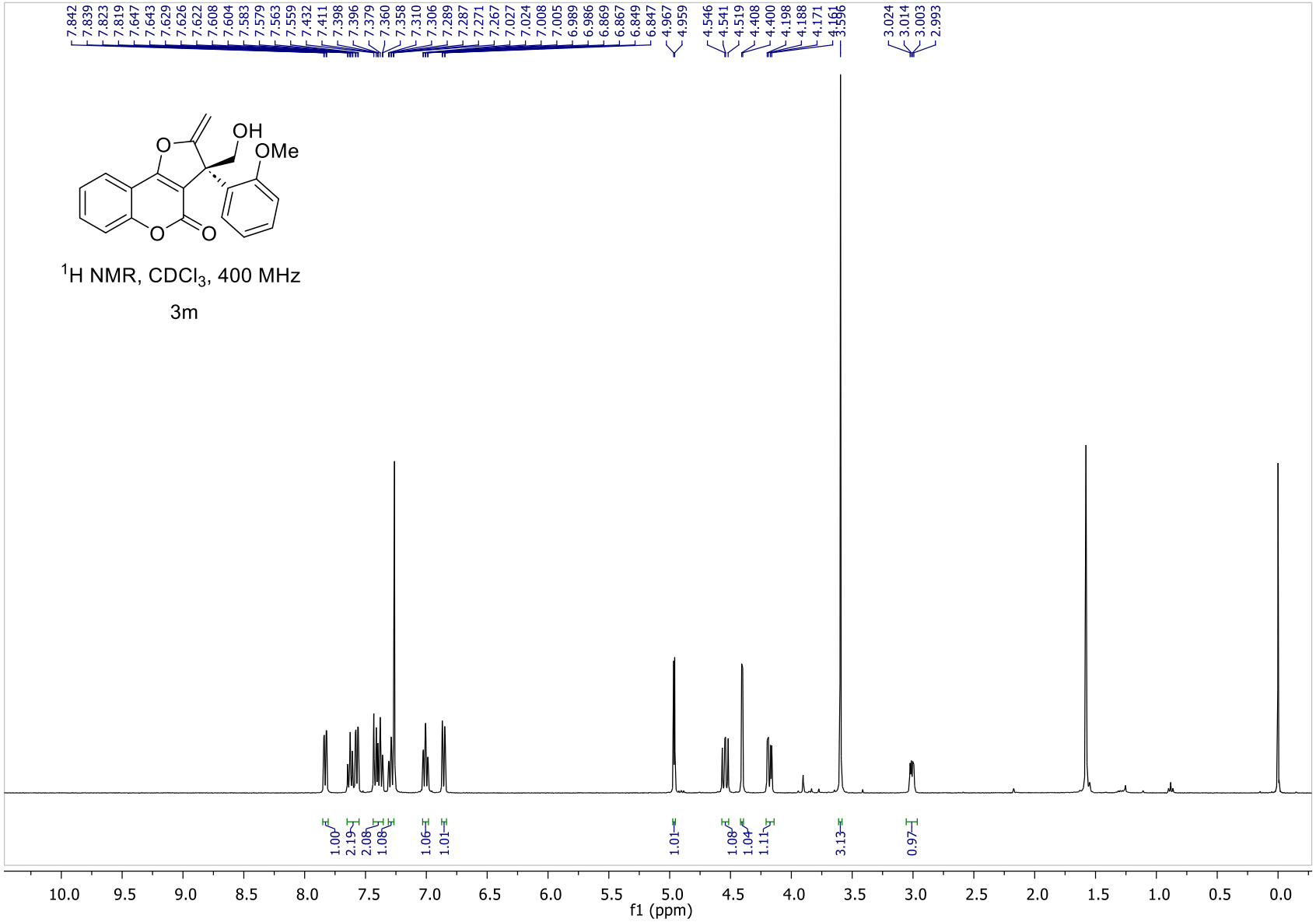
(*R*)-3-([1,1'-Biphenyl]-4-yl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3l)



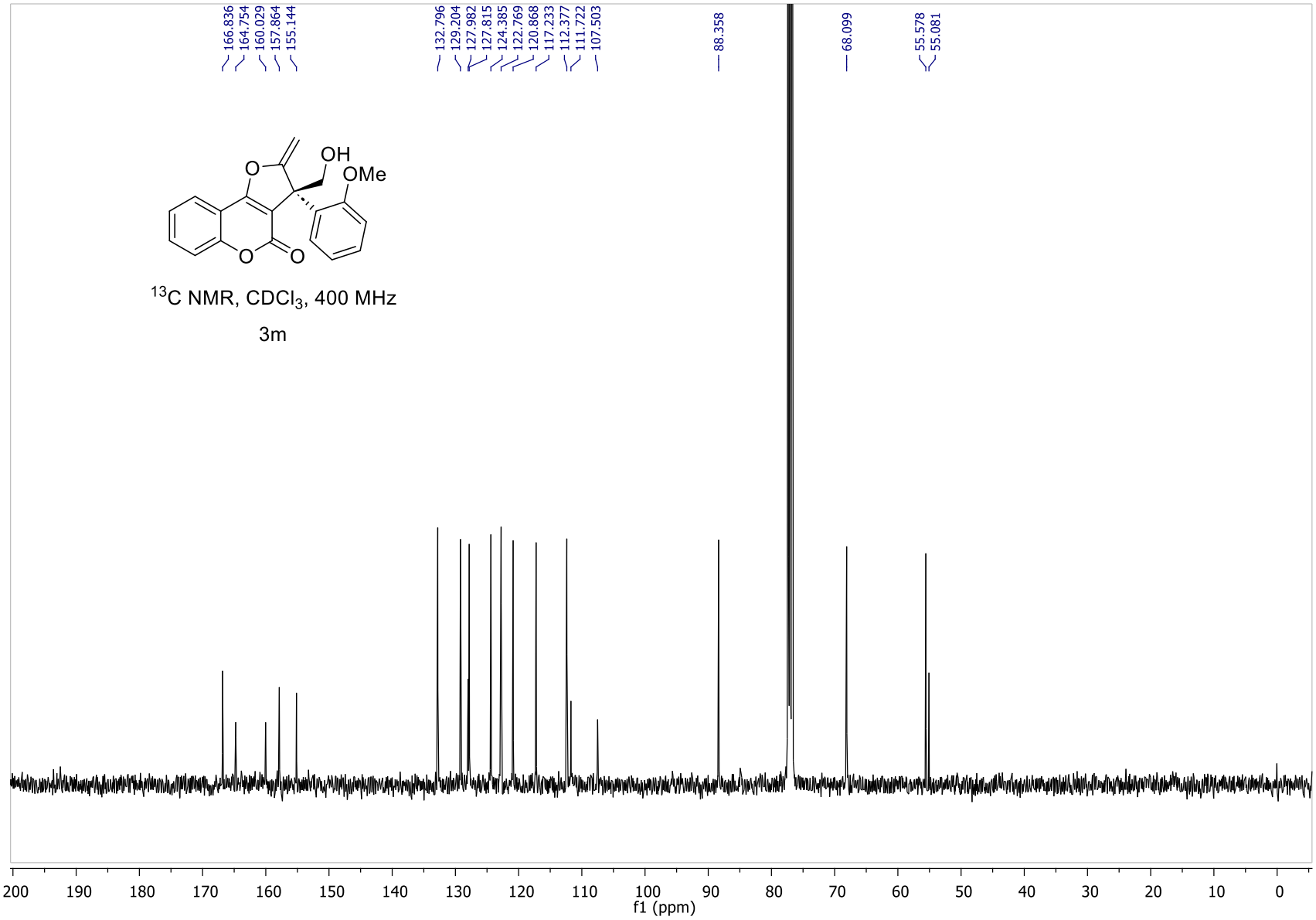
(*R*)-3-([1,1'-Biphenyl]-4-yl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3l)



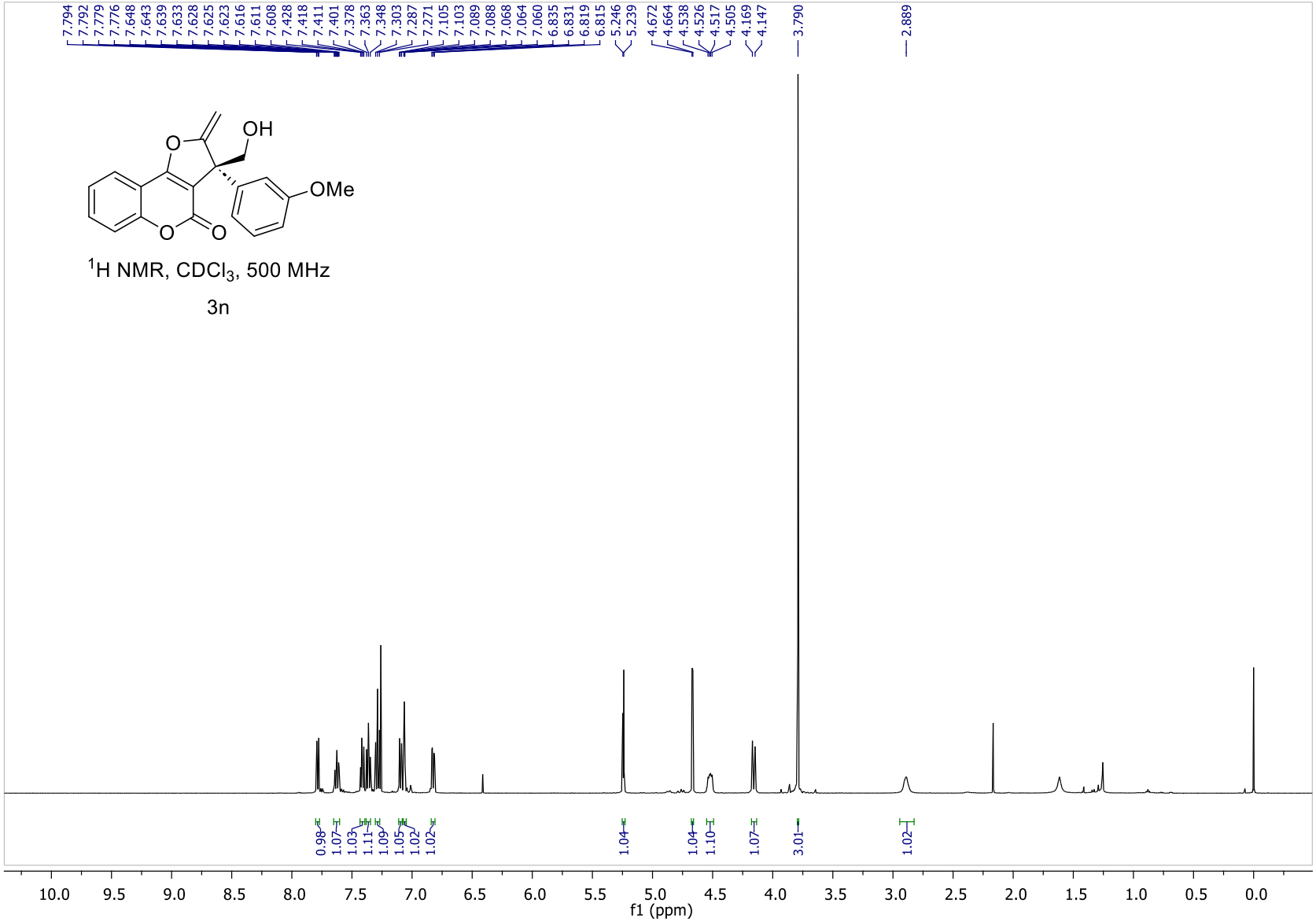
(*R*)-3-(hydroxymethyl)-3-(2-methoxyphenyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-c]chromen-4-one (3m)



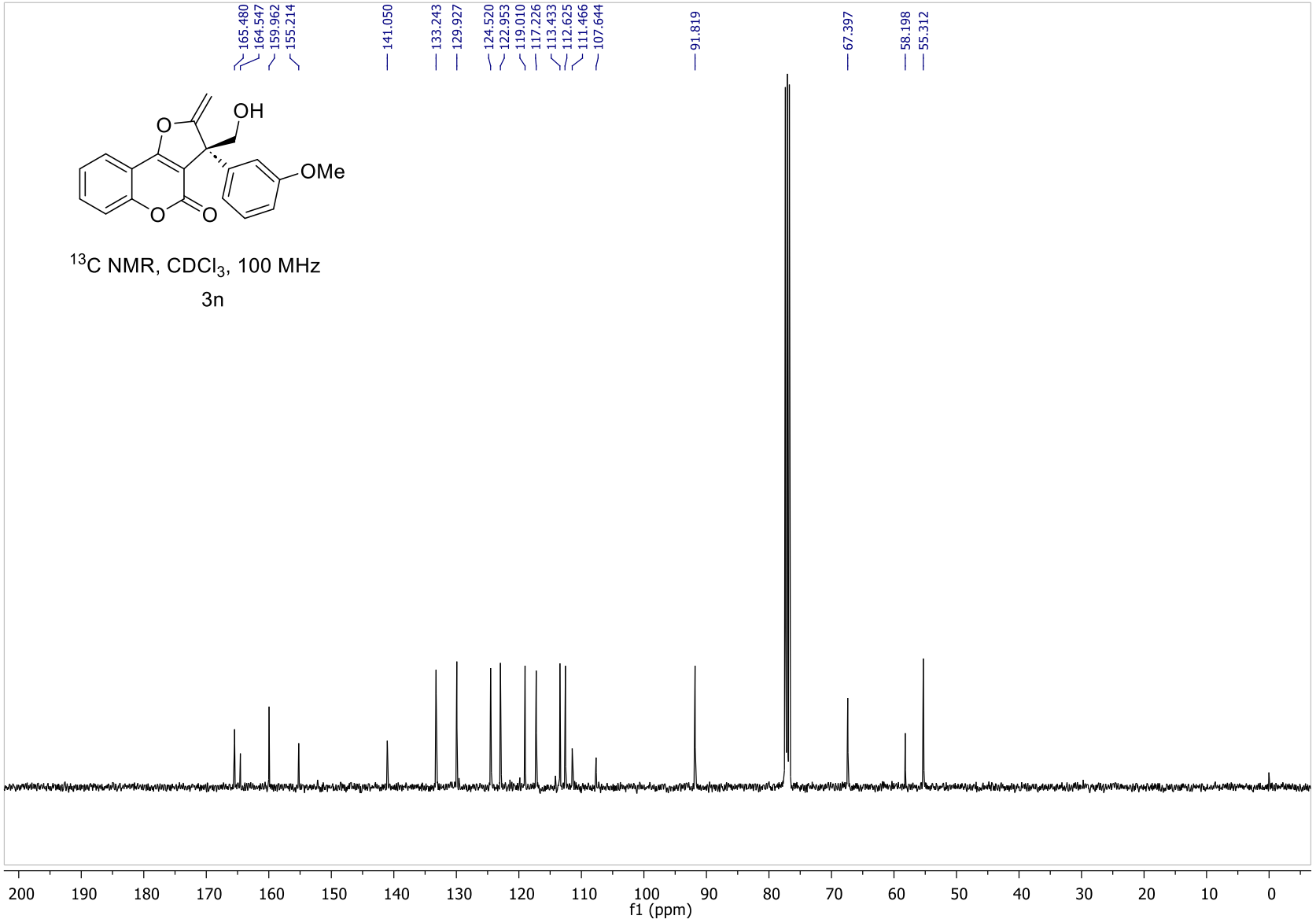
(*R*)-3-(hydroxymethyl)-3-(2-methoxyphenyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-c]chromen-4-one (3m)



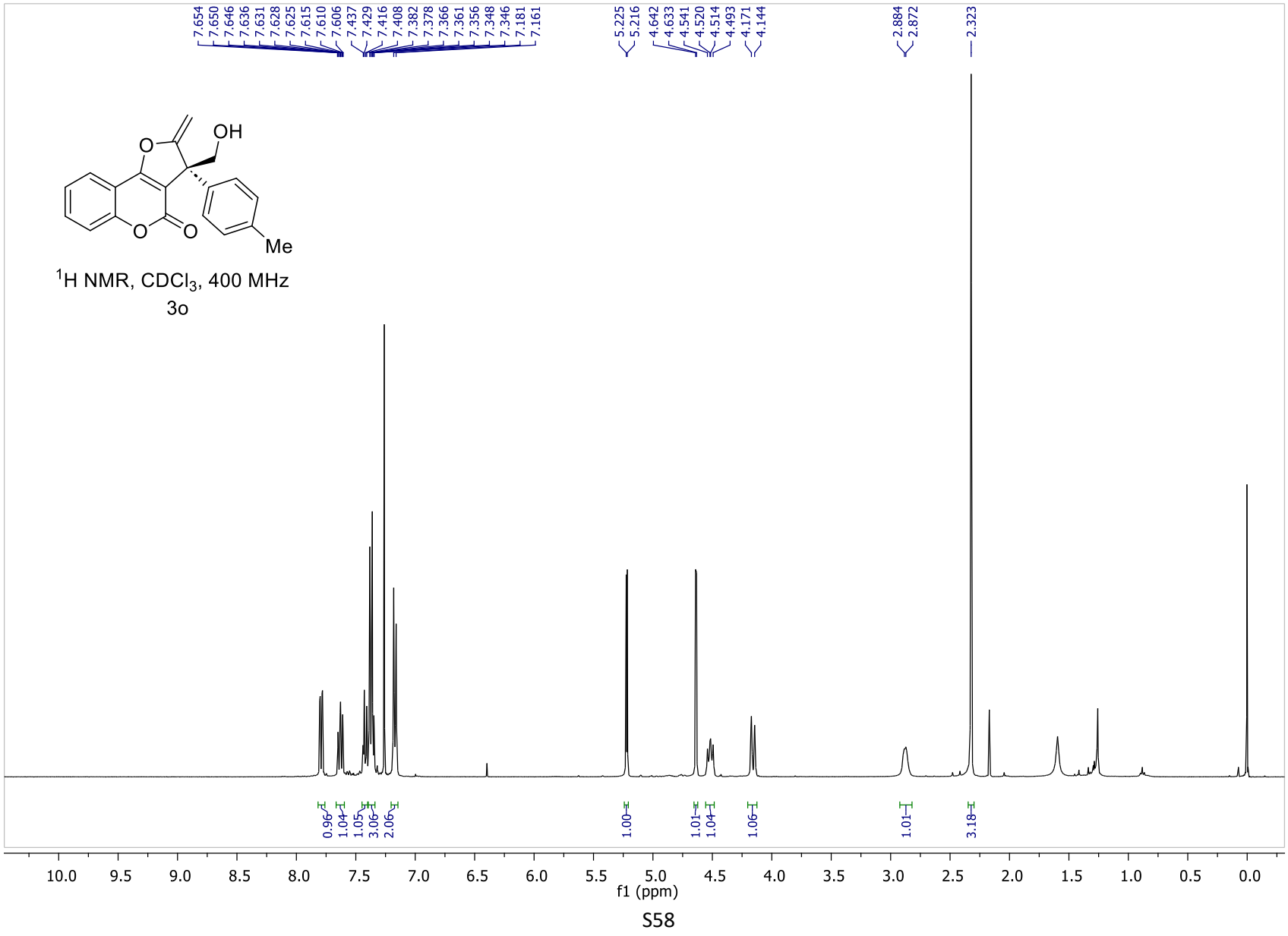
(*R*)-3-(Hydroxymethyl)-3-(3-methoxyphenyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3n)



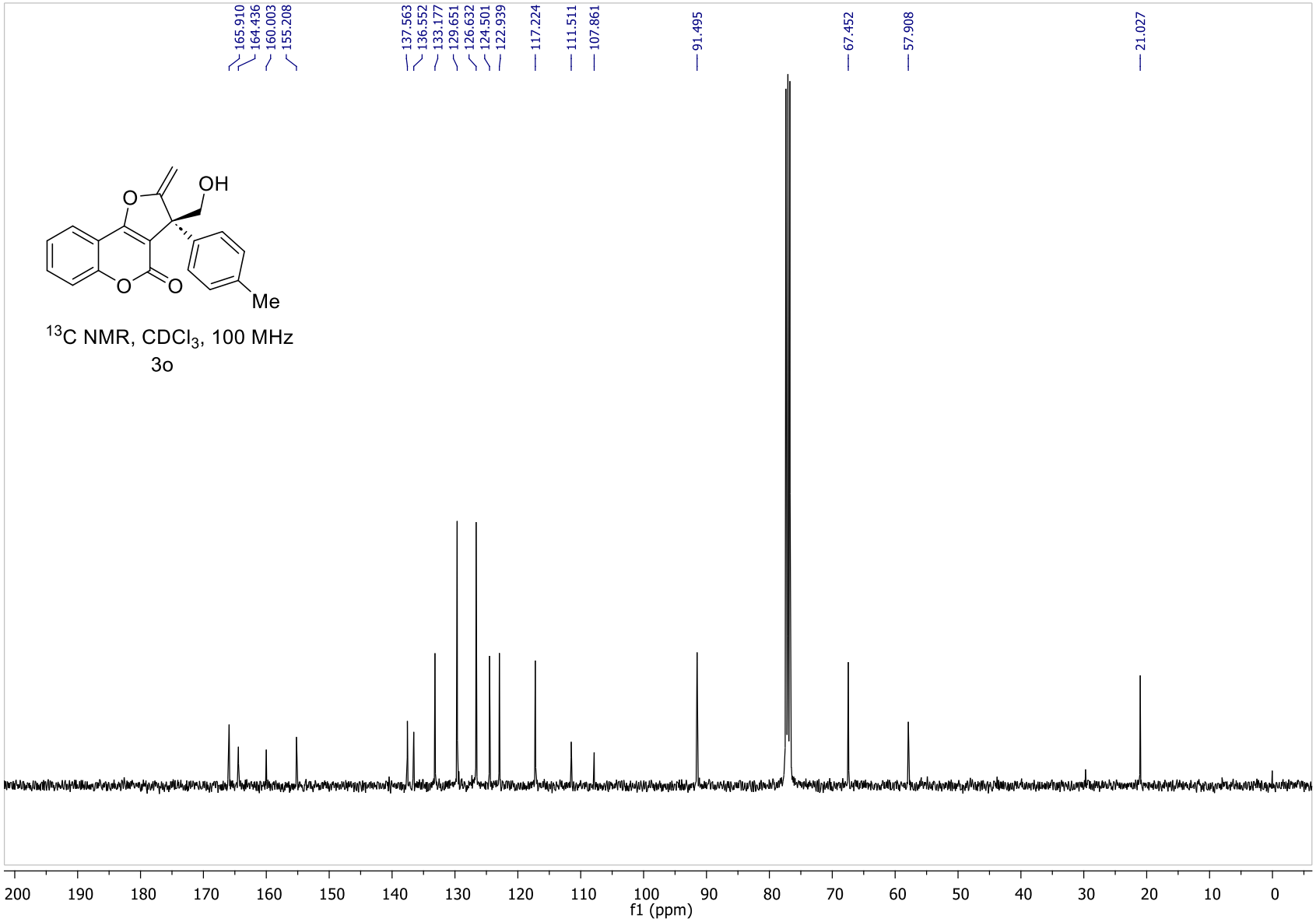
(*R*)-3-(Hydroxymethyl)-3-(3-methoxyphenyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3n)



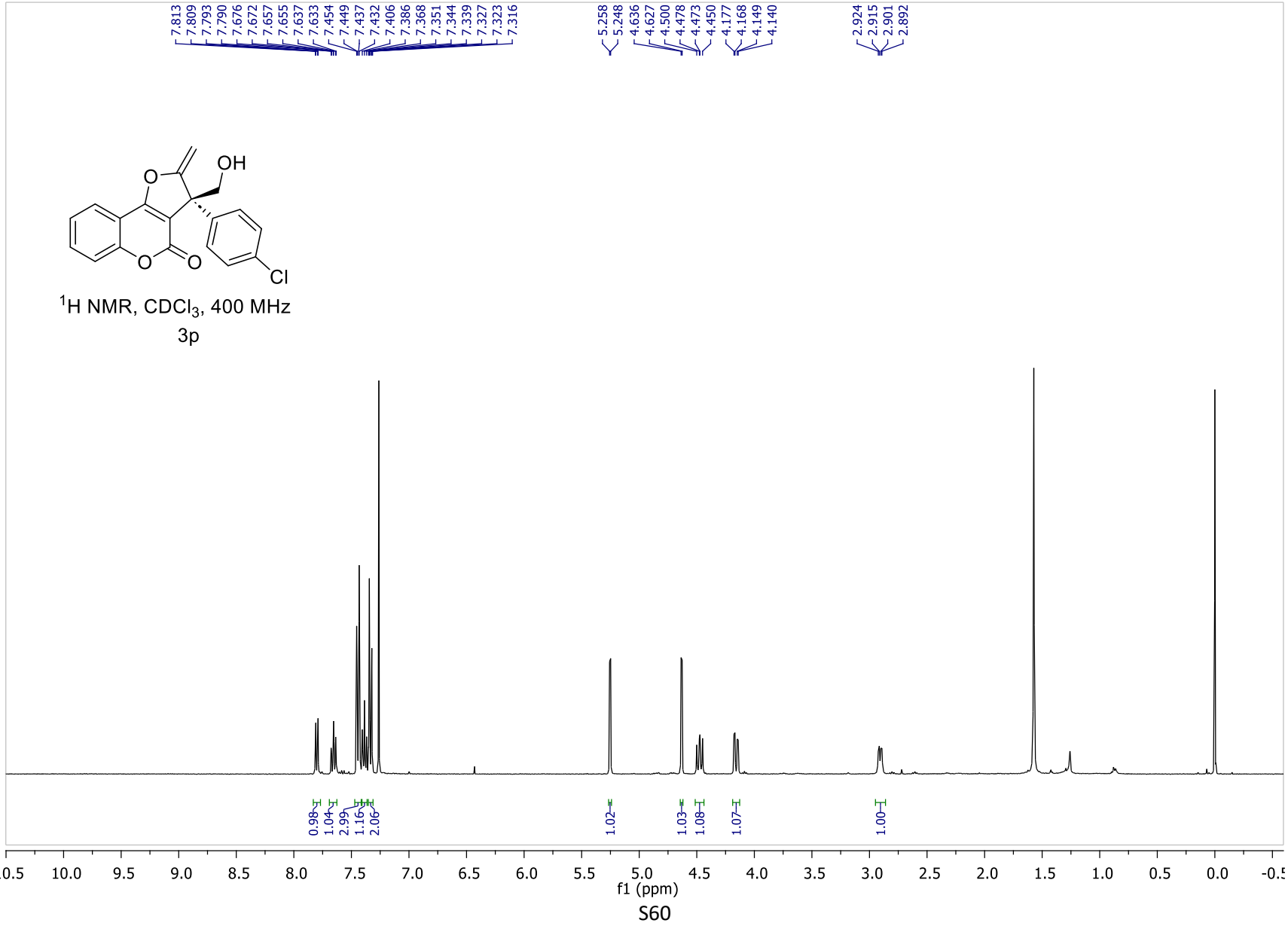
(*R*)-3-(Hydroxymethyl)-2-methylene-3-(p-tolyl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3o)



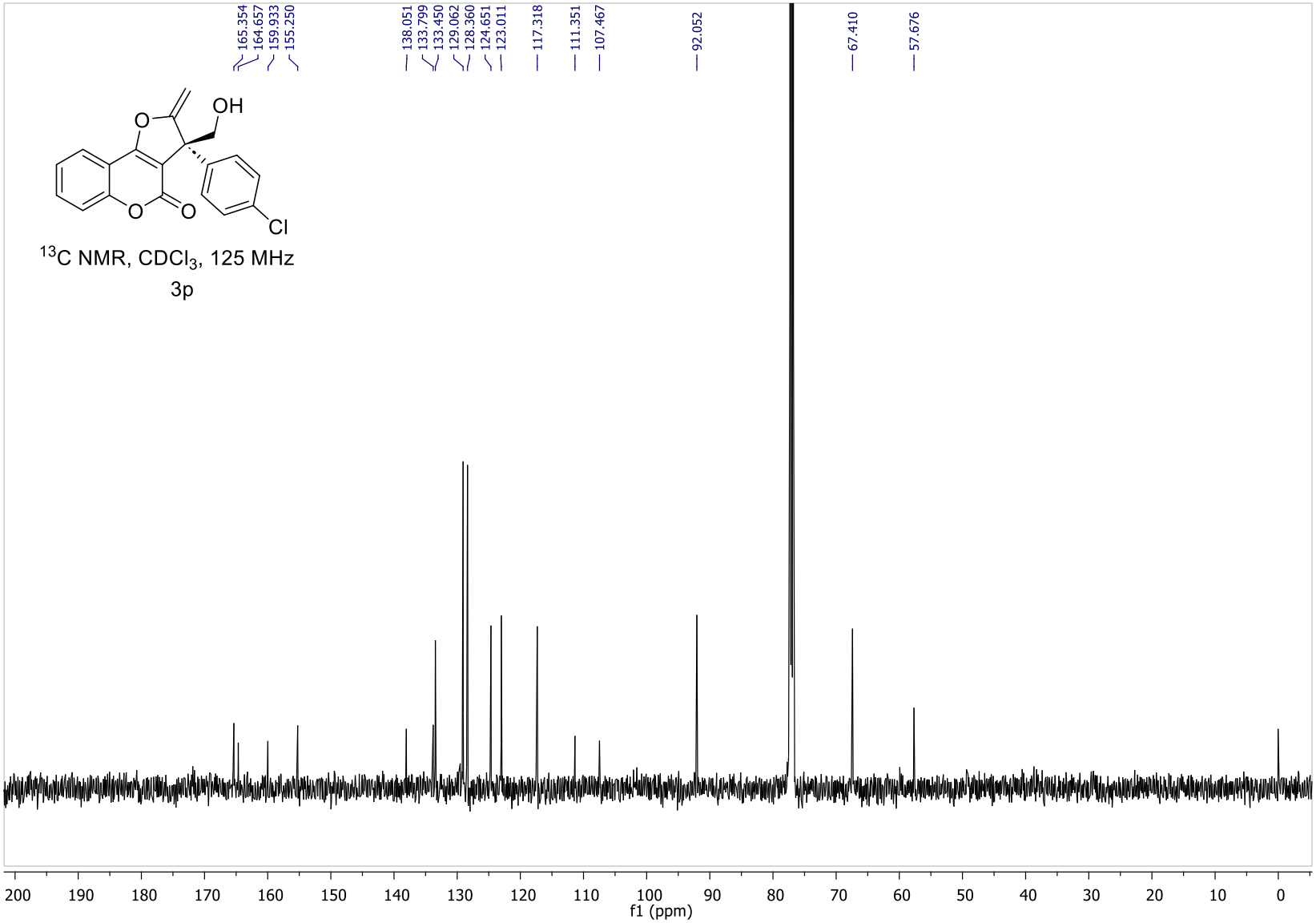
(*R*)-3-(Hydroxymethyl)-2-methylene-3-(p-tolyl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3o)



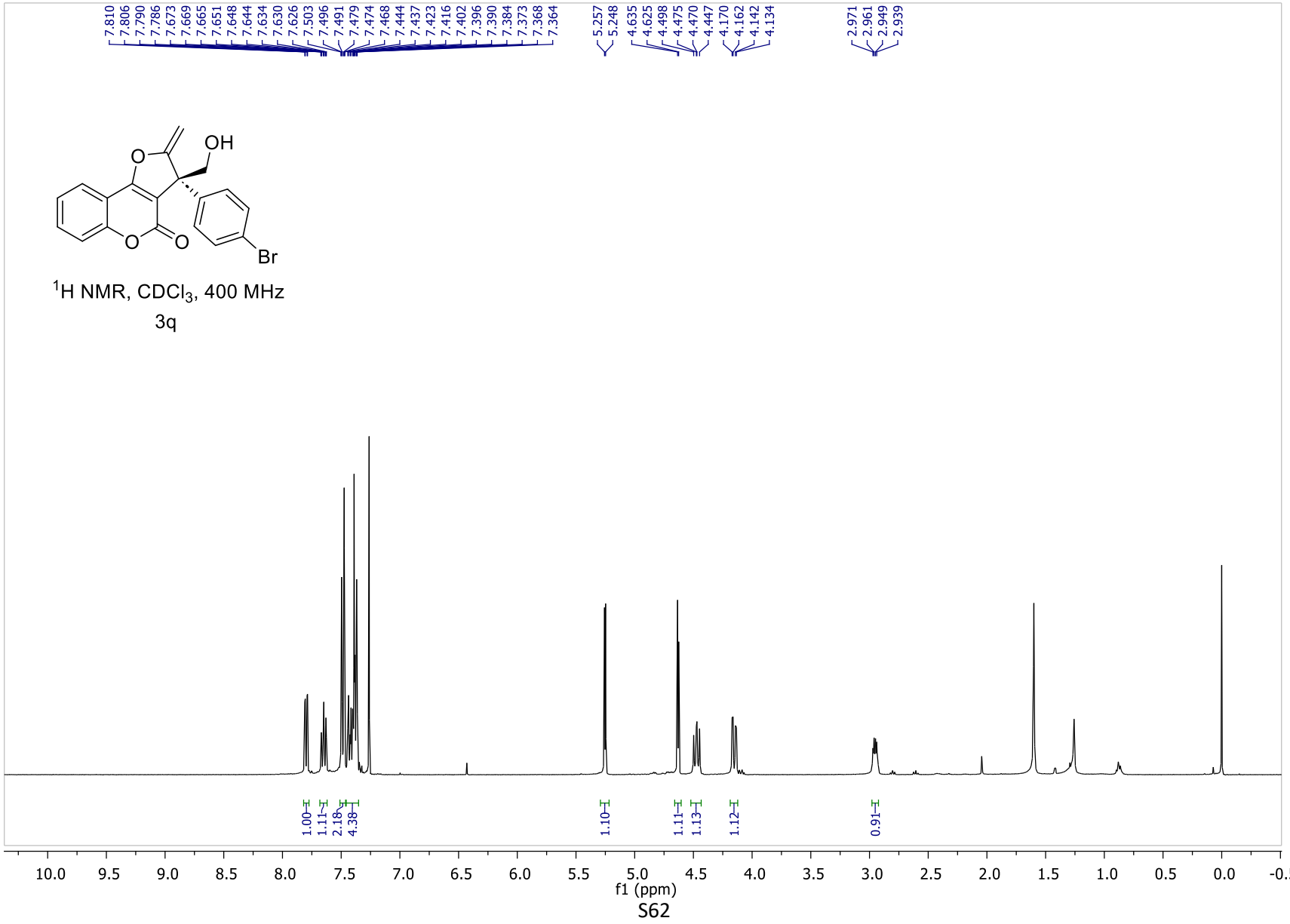
(*R*)-3-(4-Chlorophenyl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3p)



(*R*)-3-(4-Chlorophenyl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3p)



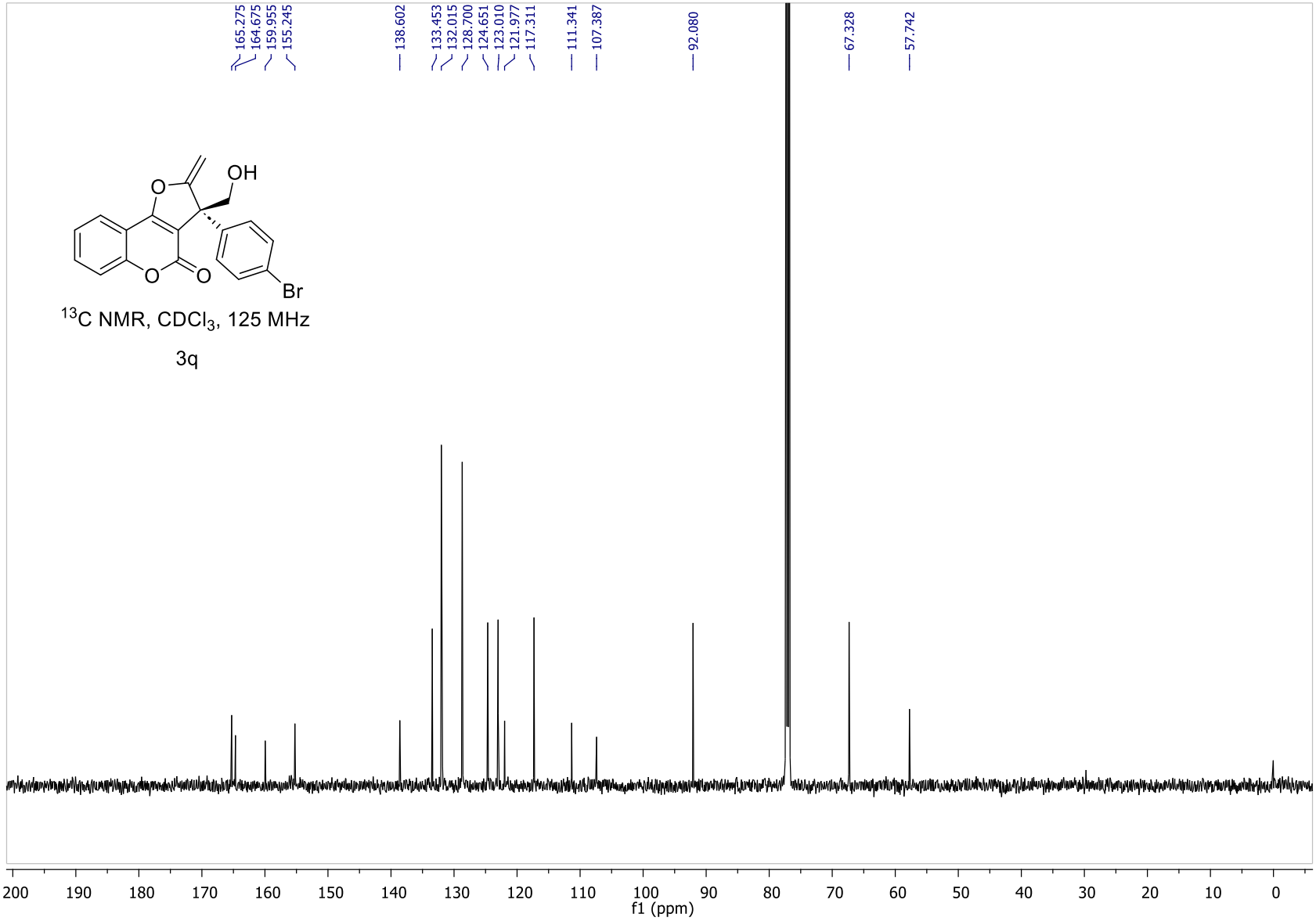
(*R*)-3-(4-Bromophenyl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3q)



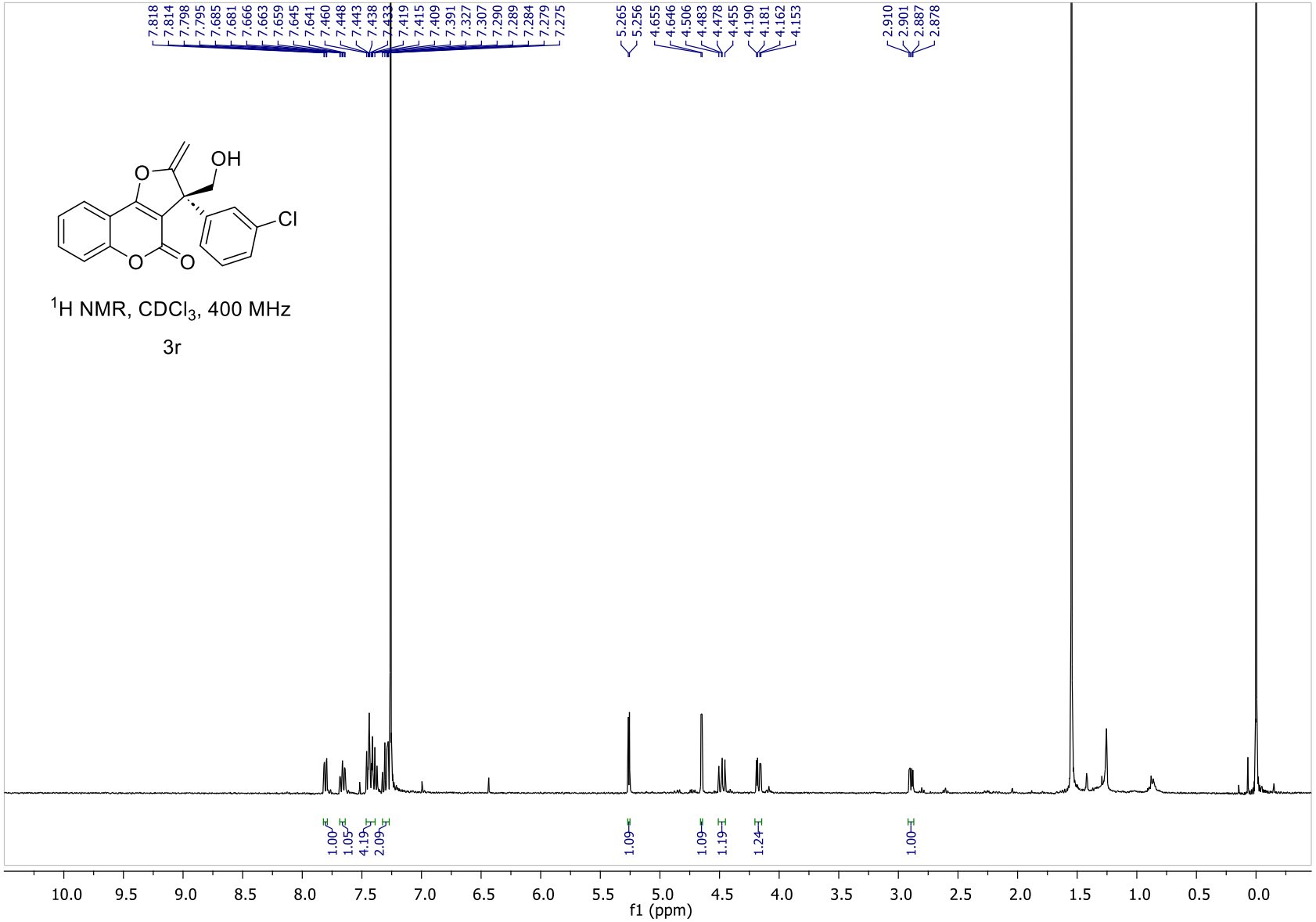
^{1}H NMR, $CDCl_3$, 400 MHz

3q

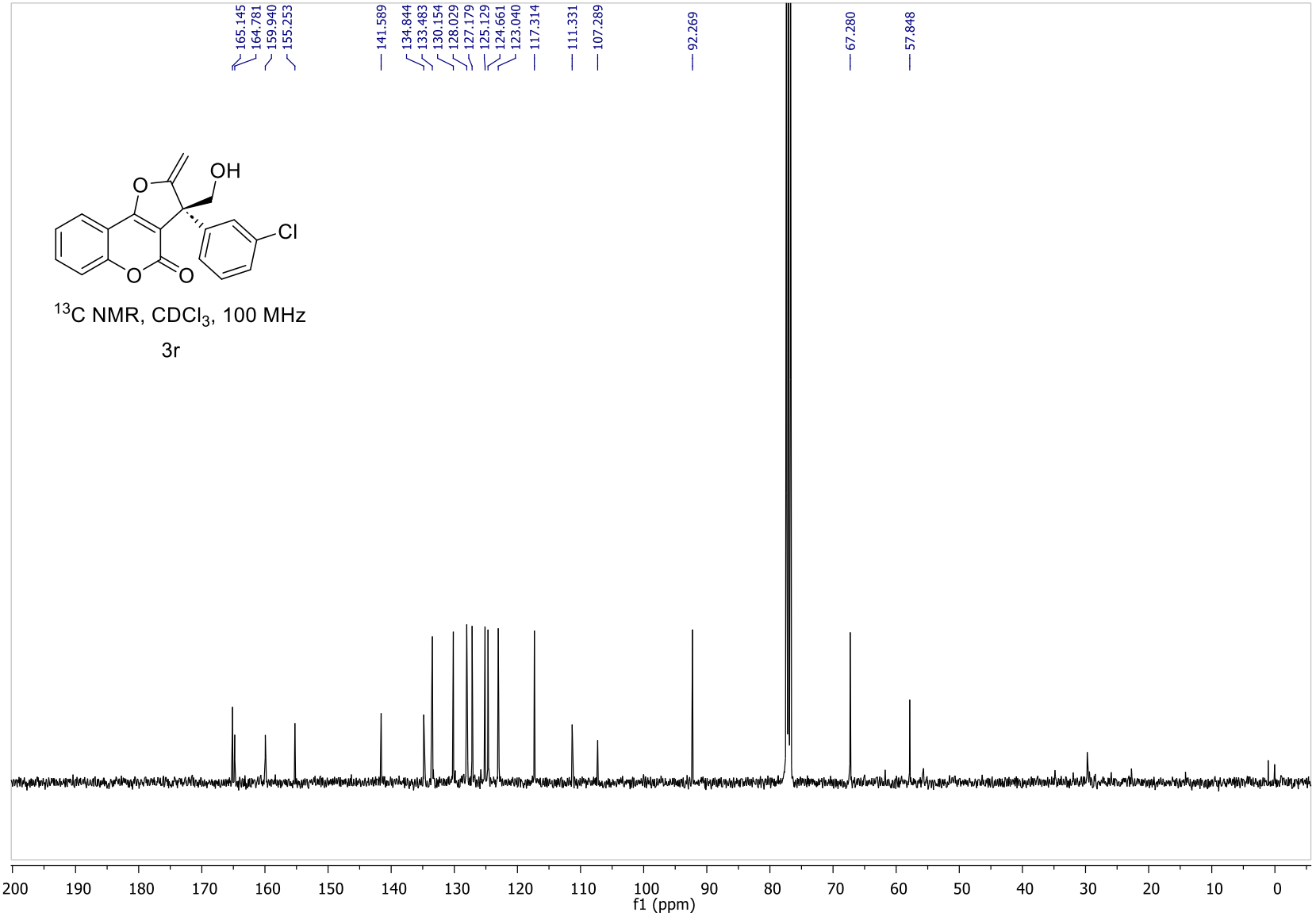
(*R*)-3-(4-Bromophenyl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3q)



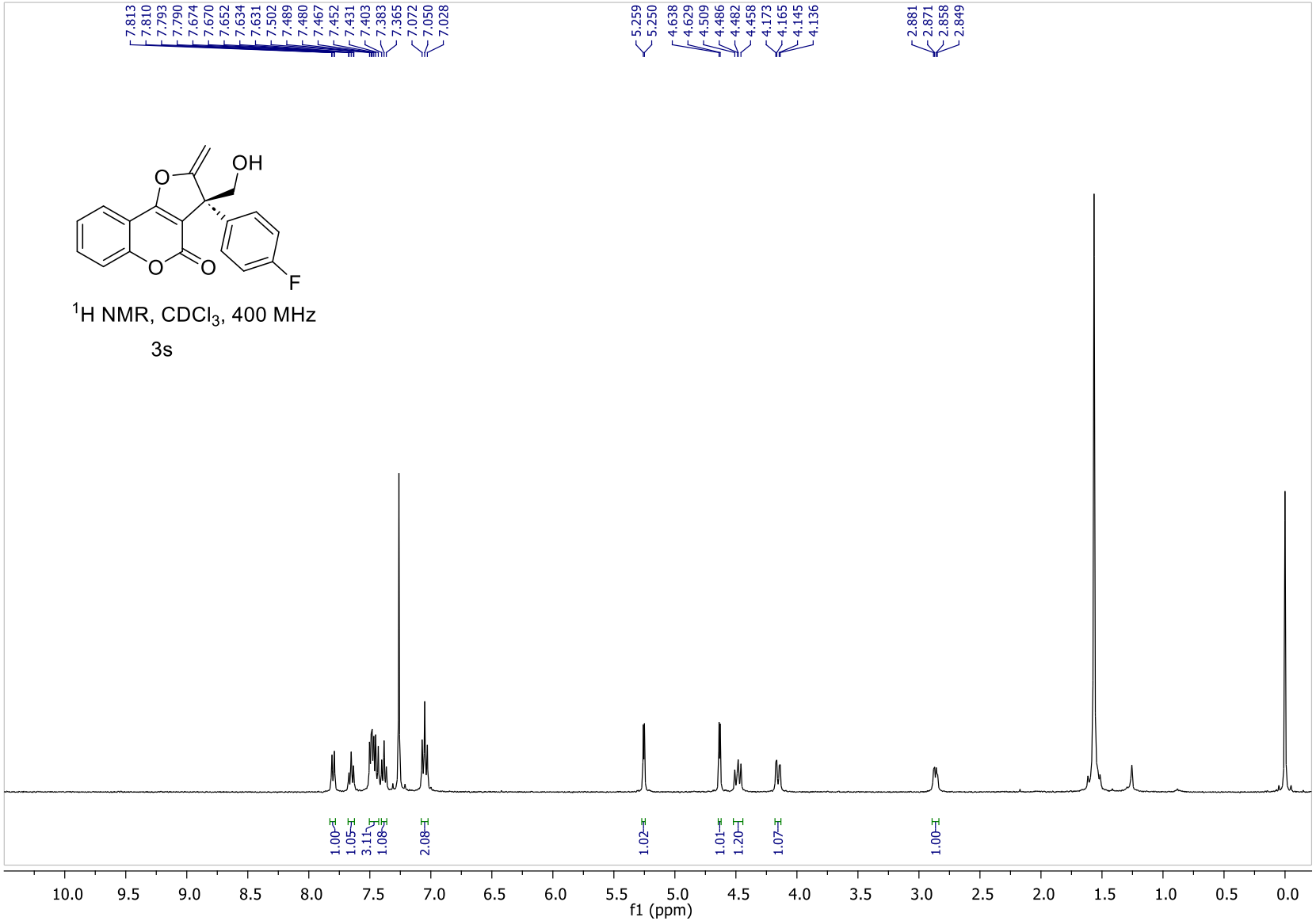
(*R*)-3-(3-Chlorophenyl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3r)



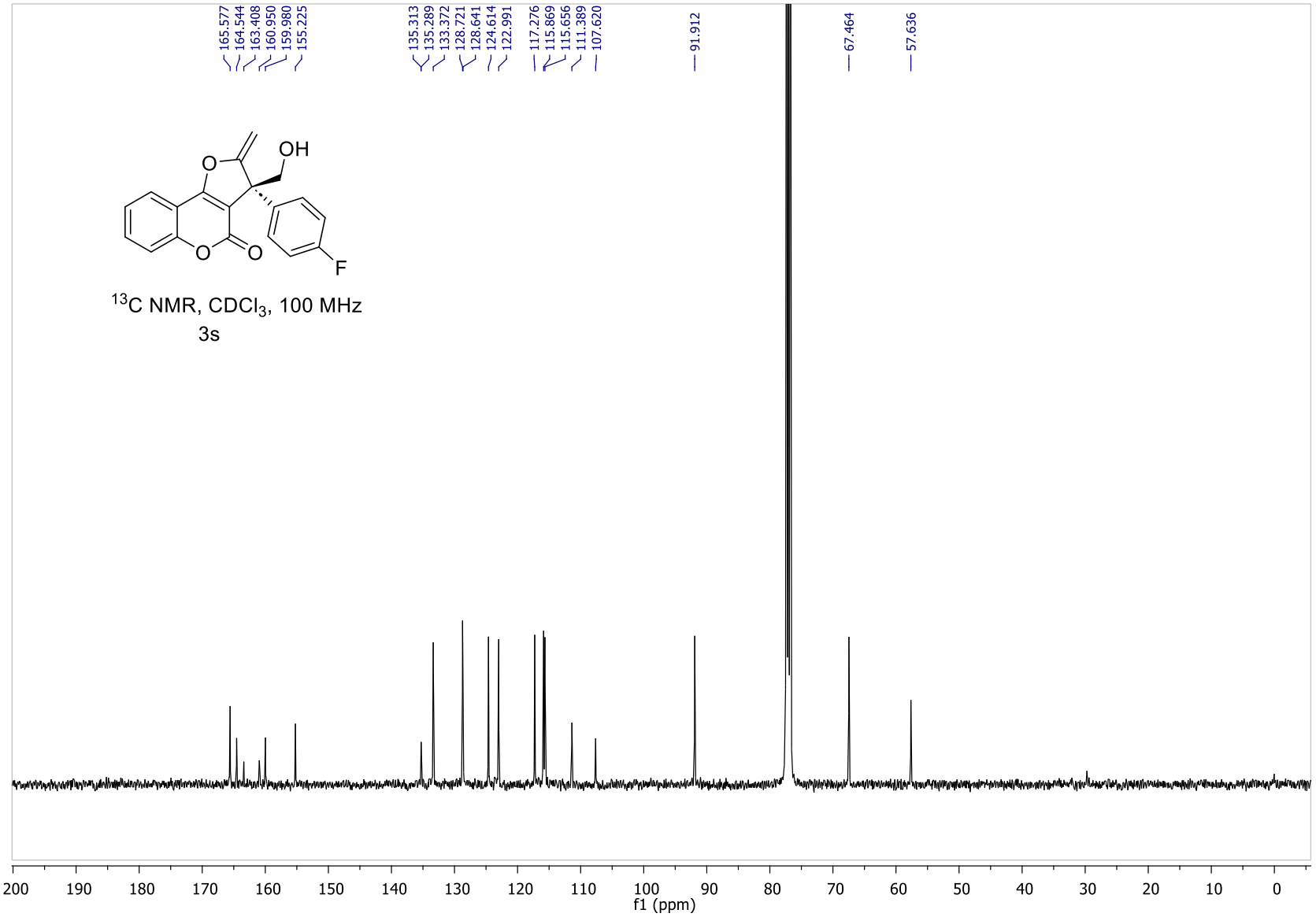
(*R*)-3-(3-Chlorophenyl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3r)



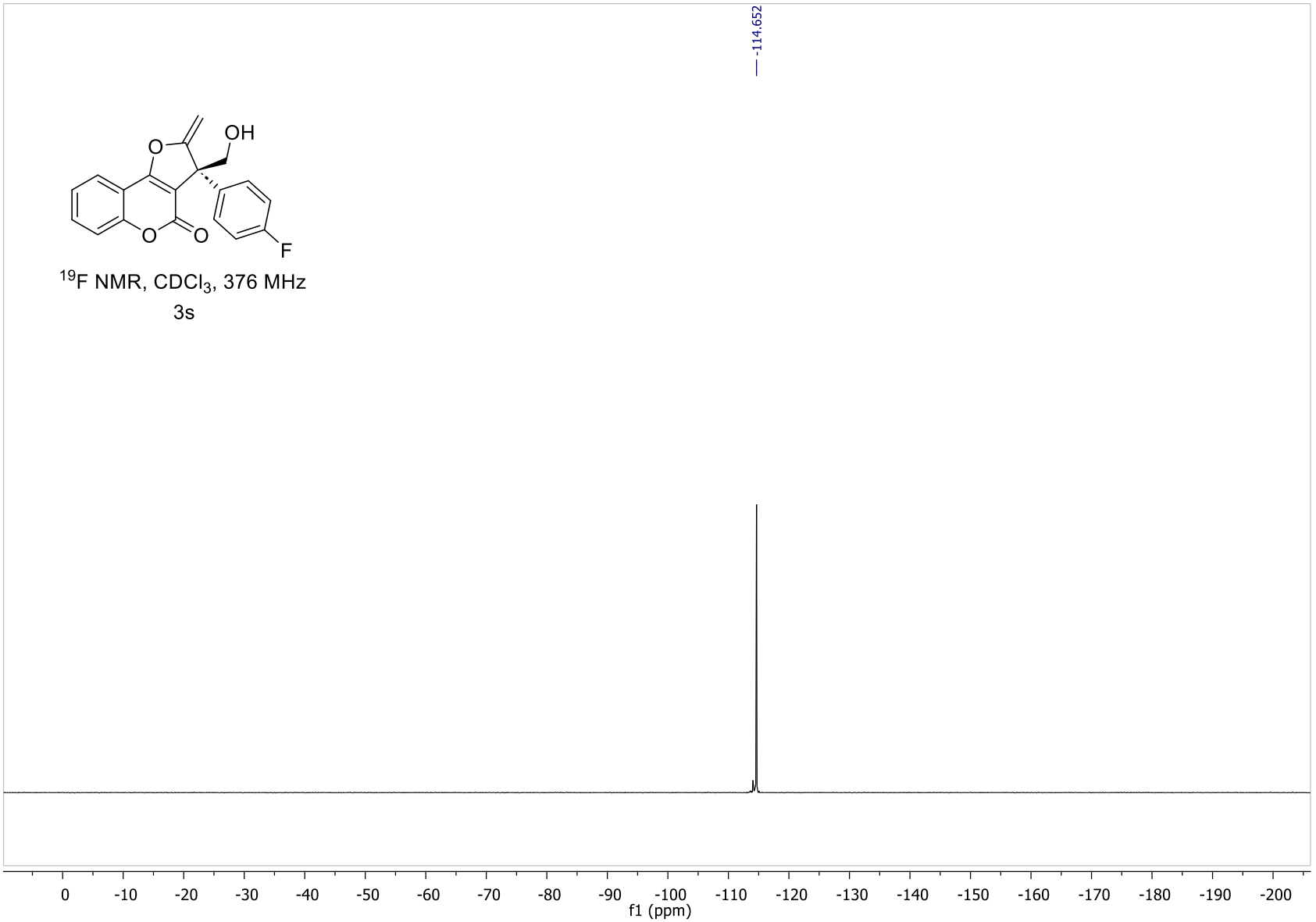
(*R*)-3-(4-Fluorophenyl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3s)



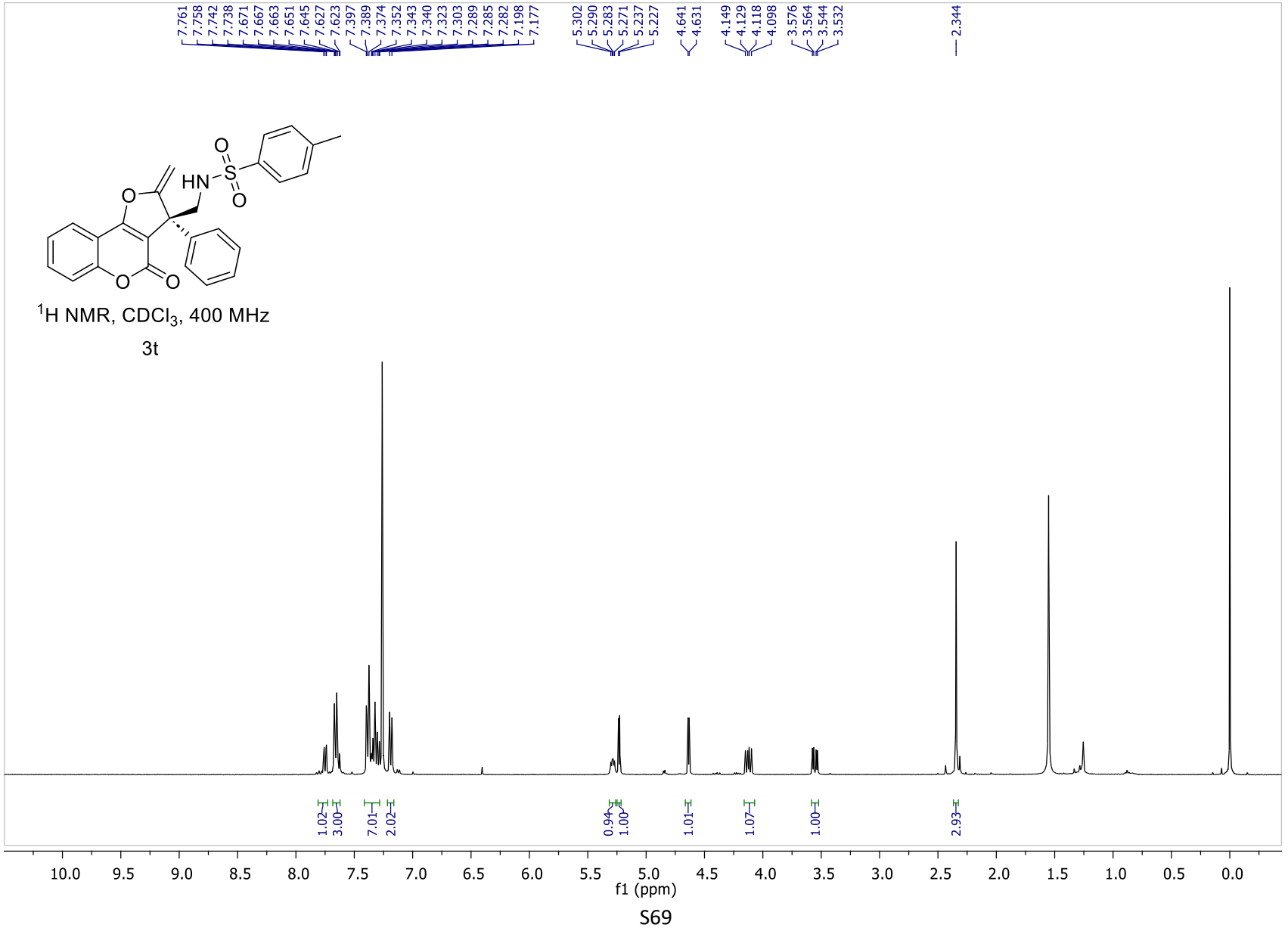
(*R*)-3-(4-Fluorophenyl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3s)



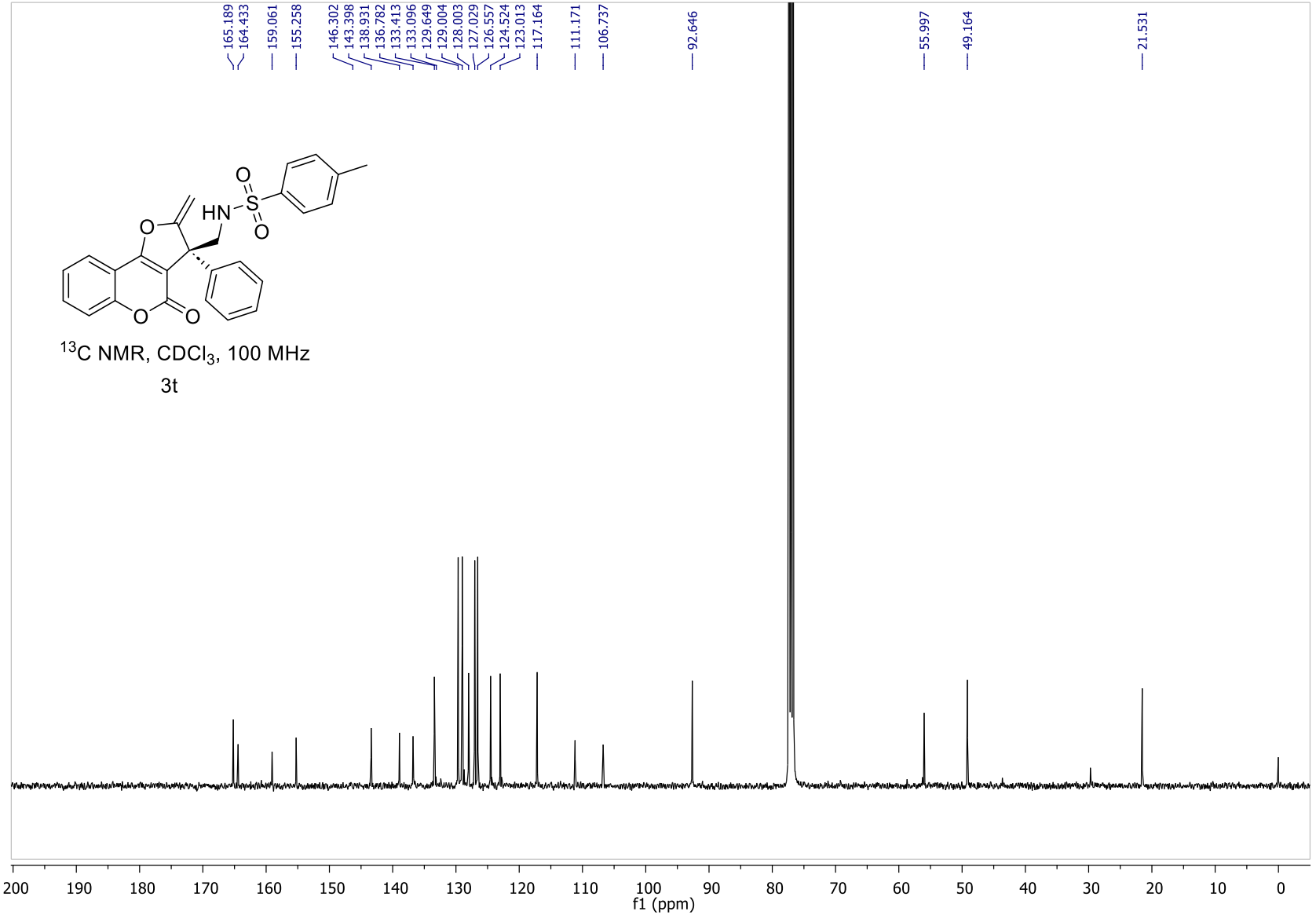
(*R*)-3-(4-Fluorophenyl)-3-(hydroxymethyl)-2-methylene-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one (3s)



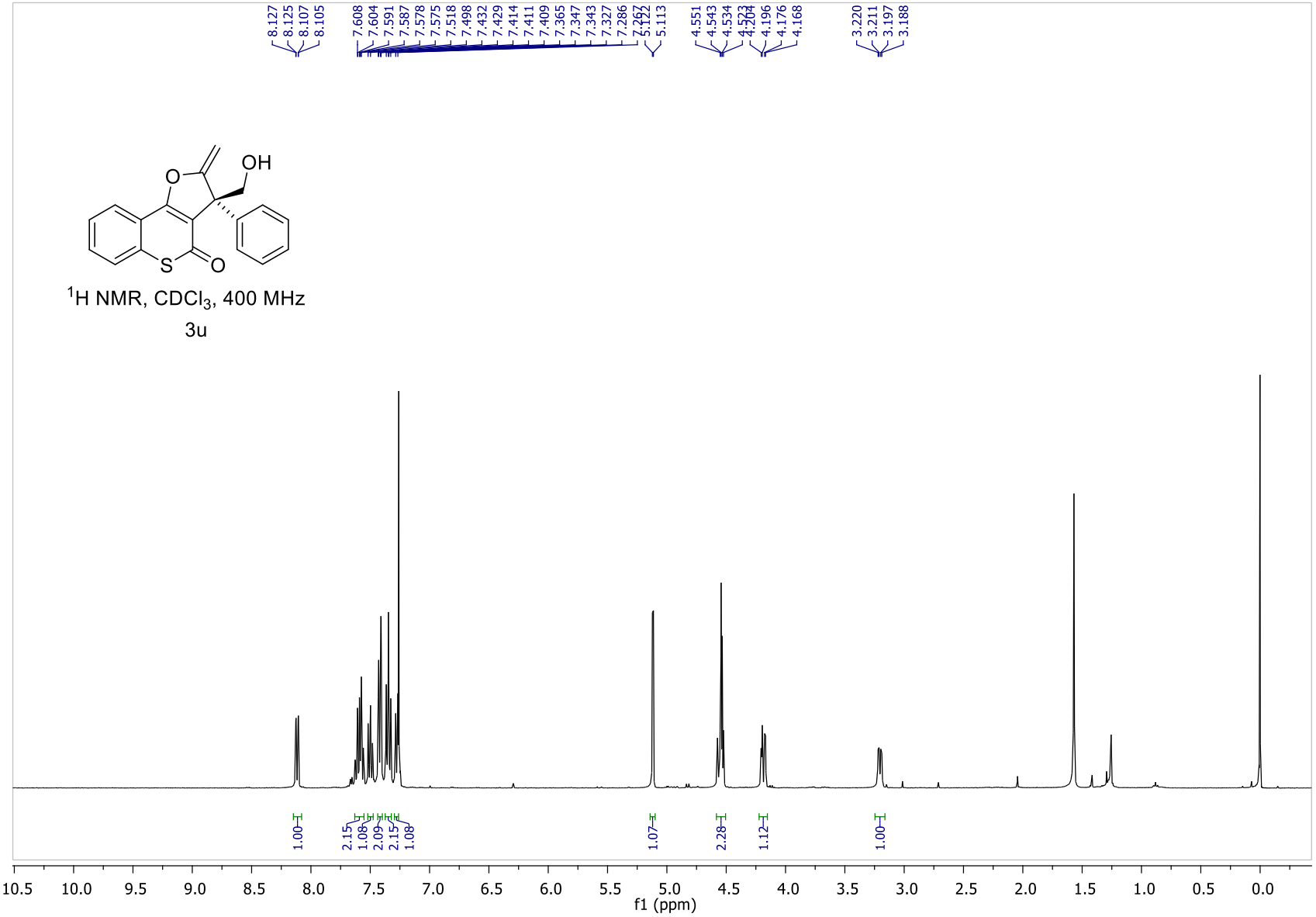
(*R*)-4-Methyl-N-((2-methylene-4-oxo-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-3-yl)methyl)benzenesulfonamide (3t)



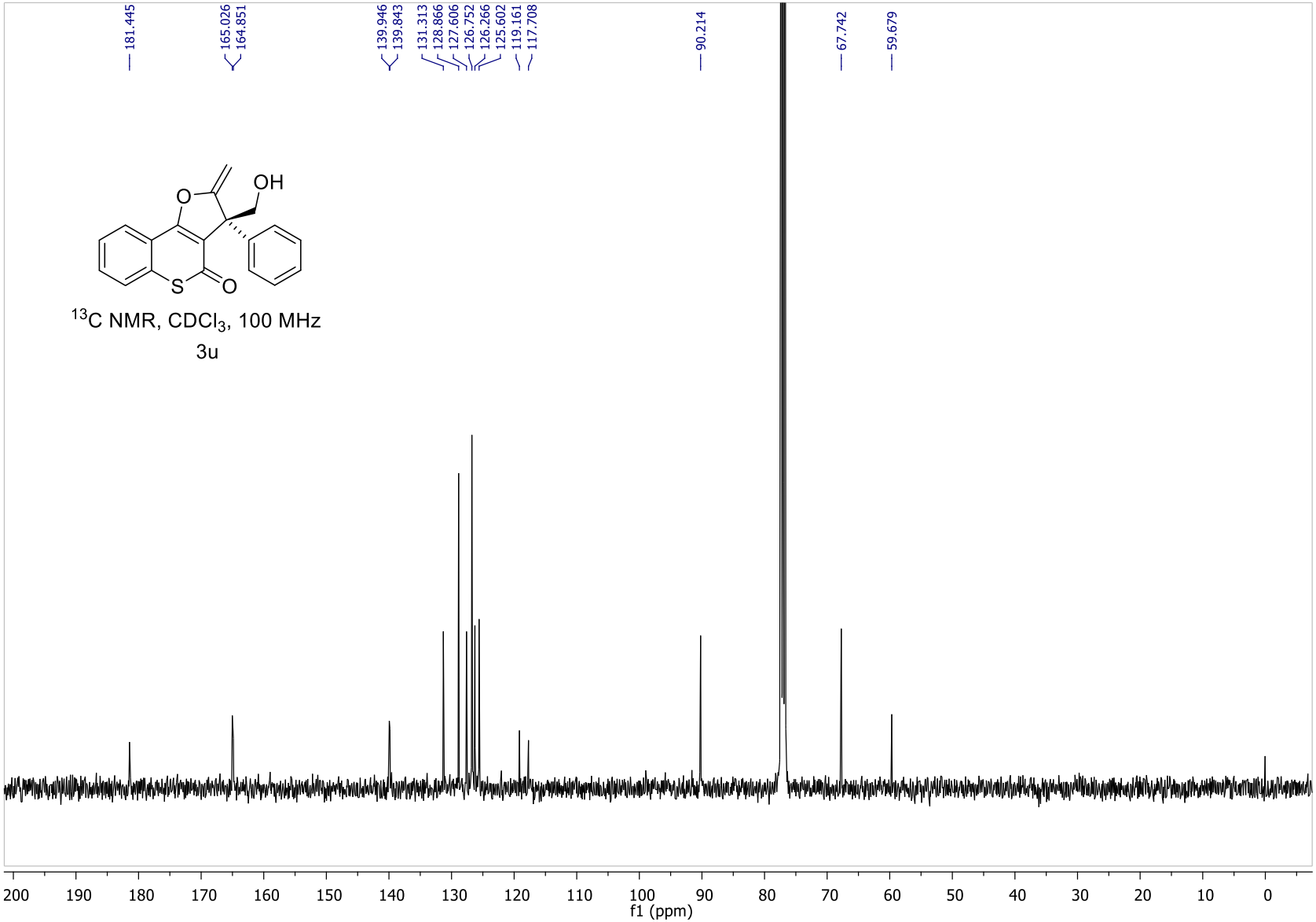
(*R*)-4-Methyl-N-((2-methylene-4-oxo-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-3-yl)methyl)benzenesulfonamide (3t)



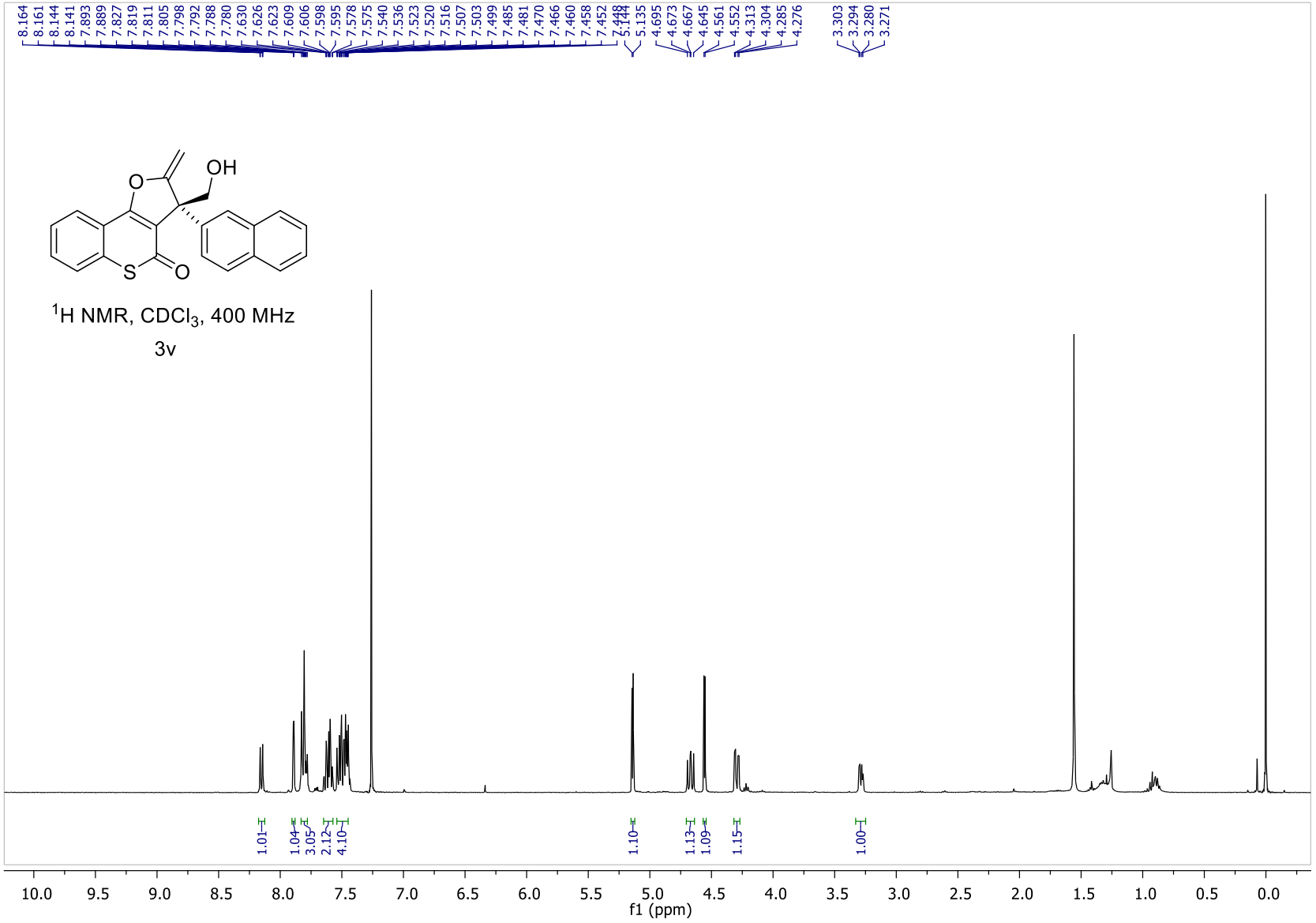
(*R*)-3-(Hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-thiochromeno[4,3-*b*]furan-4-one (3u)



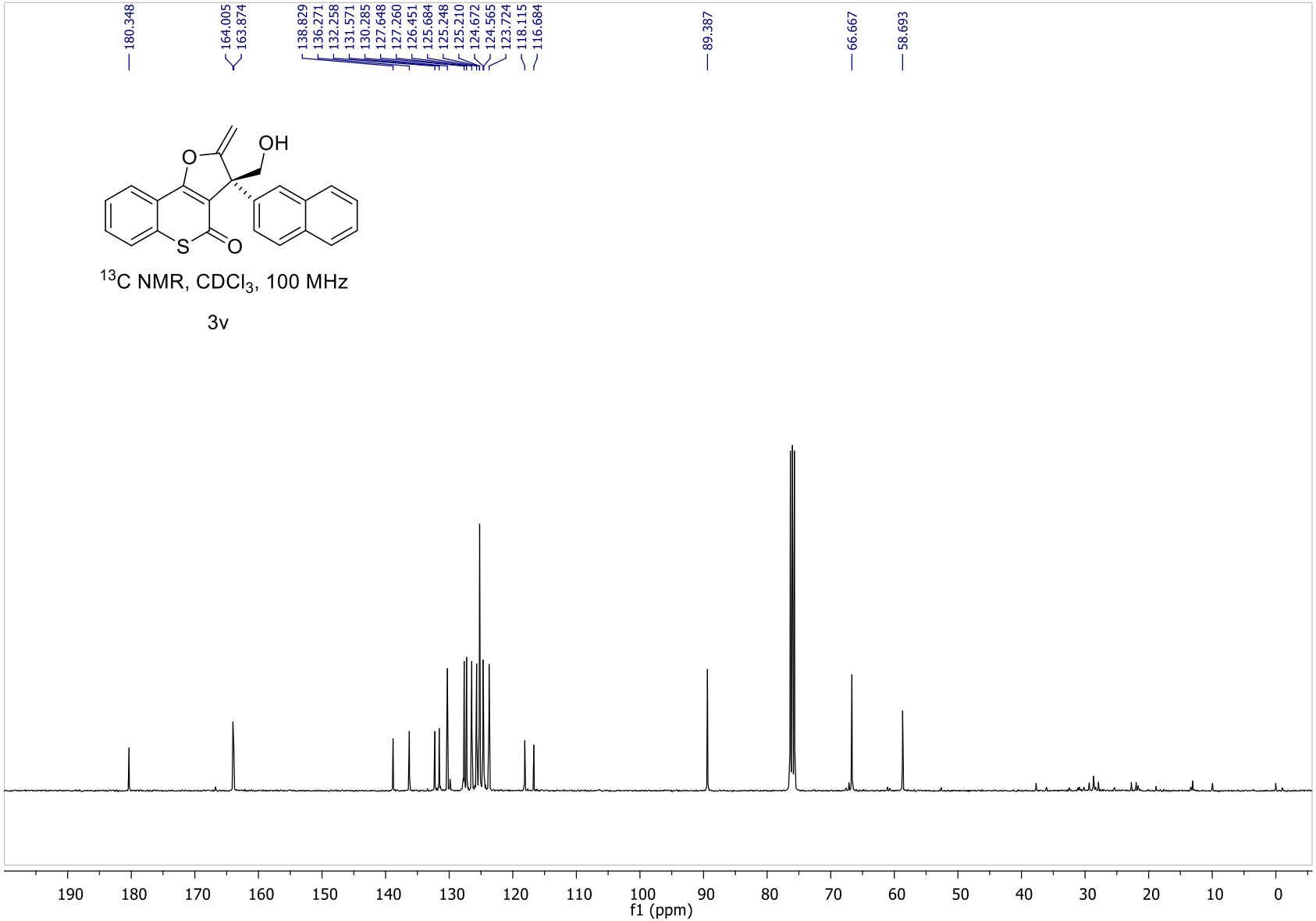
(*R*)-3-(Hydroxymethyl)-2-methylene-3-phenyl-2,3-dihydro-4*H*-thiochromeno[4,3-*b*]furan-4-one (3u)



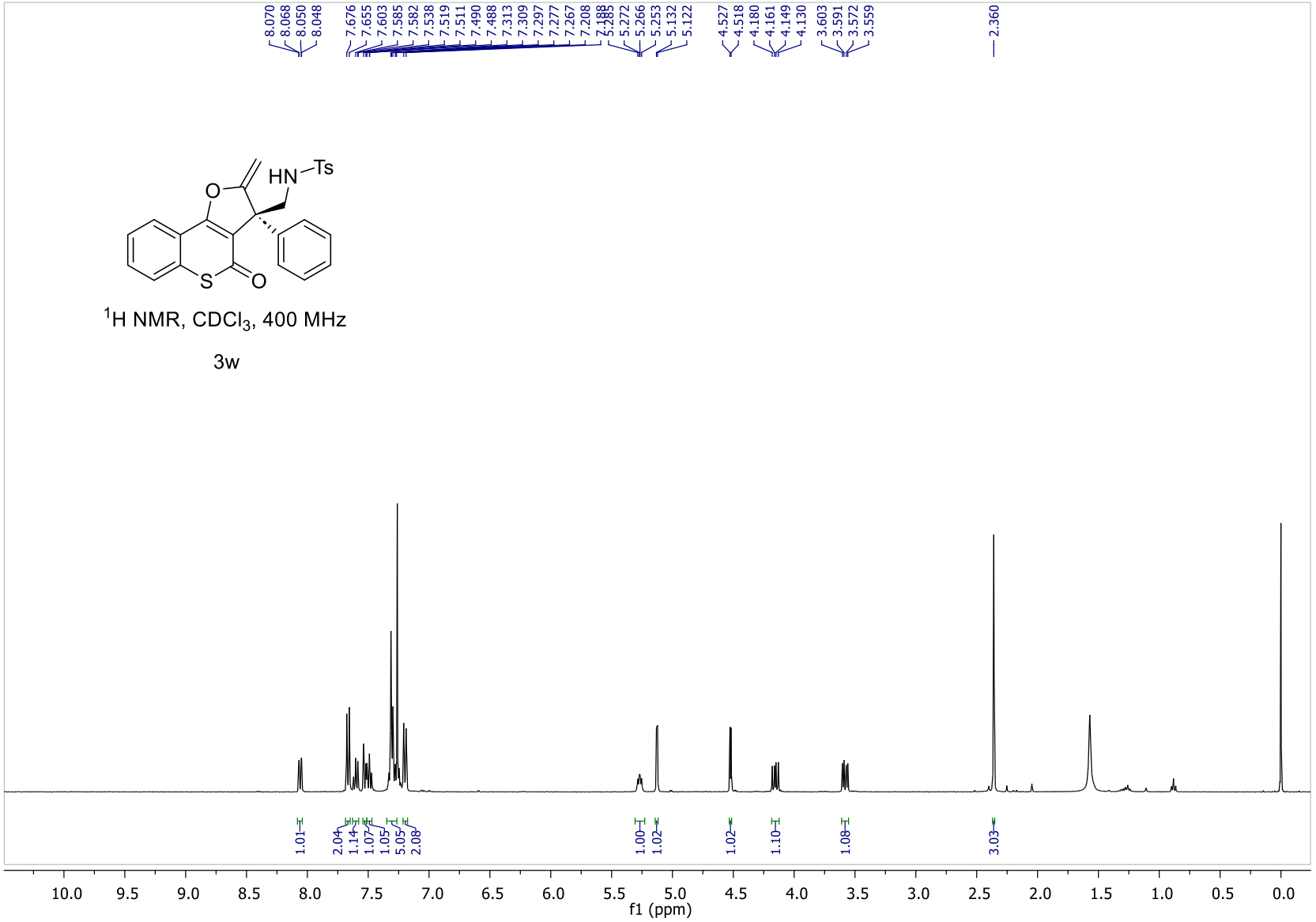
(*R*)-3-(Hydroxymethyl)-2-methylene-3-(naphthalen-2-yl)-2,3-dihydro-4*H*-thiochromeno[4,3-*b*]furan-4-one (3v)



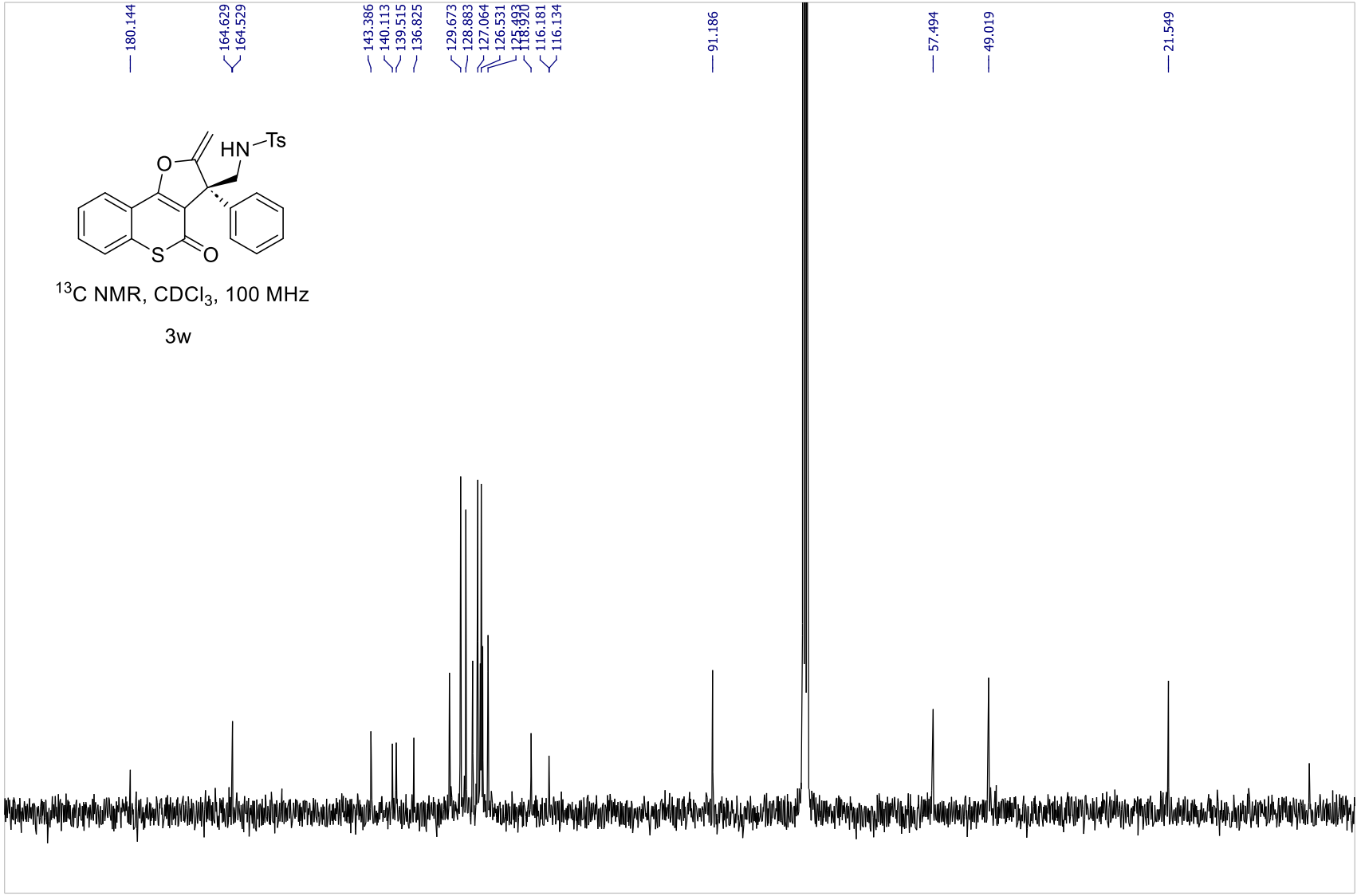
(*R*)-3-(Hydroxymethyl)-2-methylene-3-(naphthalen-2-yl)-2,3-dihydro-4*H*-thiochromeno[4,3-*b*]furan-4-one (3v)



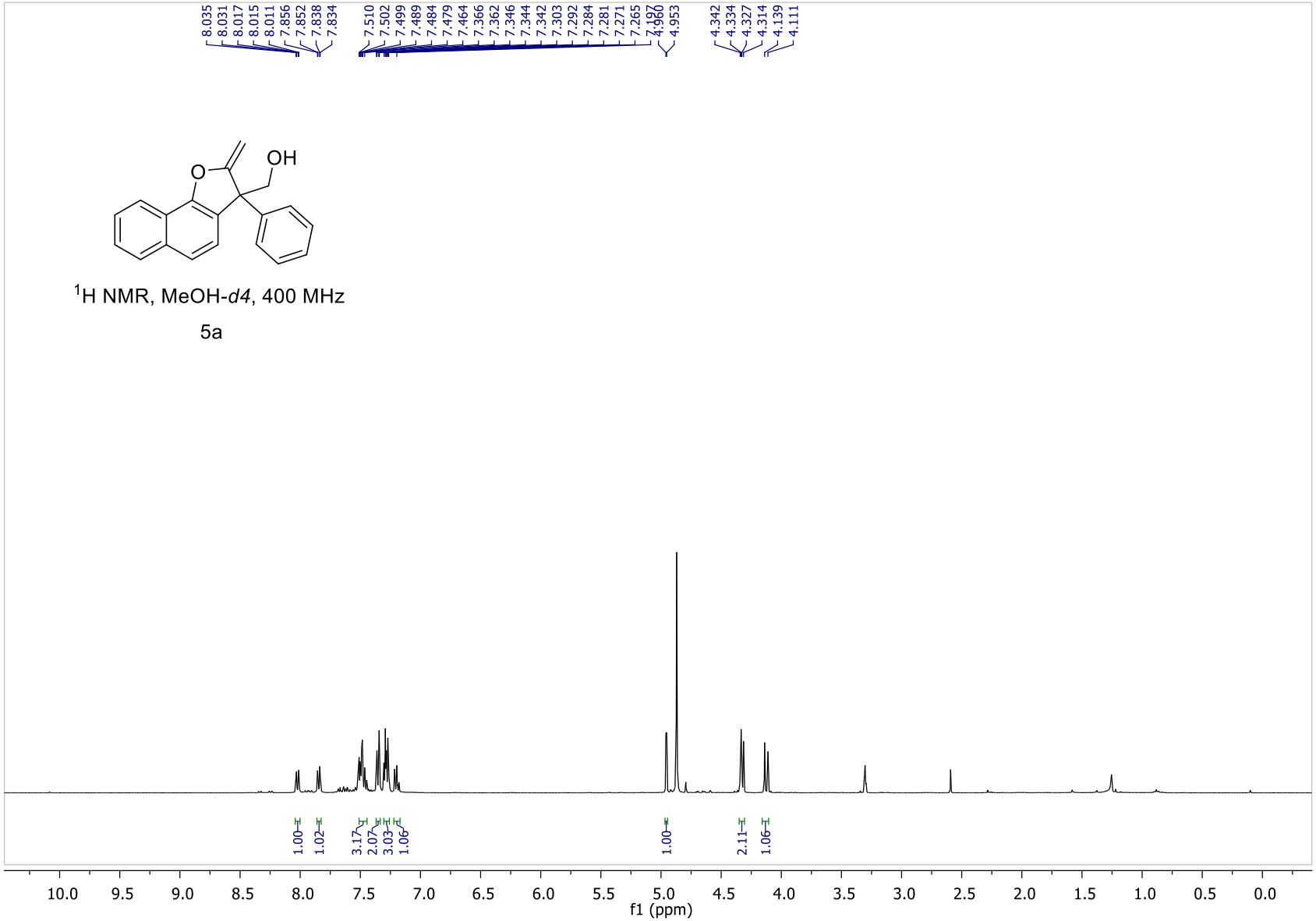
(*R*)-4-Methyl-N-((2-methylene-4-oxo-3-phenyl-2,3-dihydro-4*H*-thiochromeno[4,3-*b*]furan-3-yl)methyl)benzenesulfonamide (3w)



(*R*)-4-Methyl-N-((2-methylene-4-oxo-3-phenyl-2,3-dihydro-4*H*-thiochromeno[4,3-*b*]furan-3-yl)methyl)benzenesulfonamide(3w)



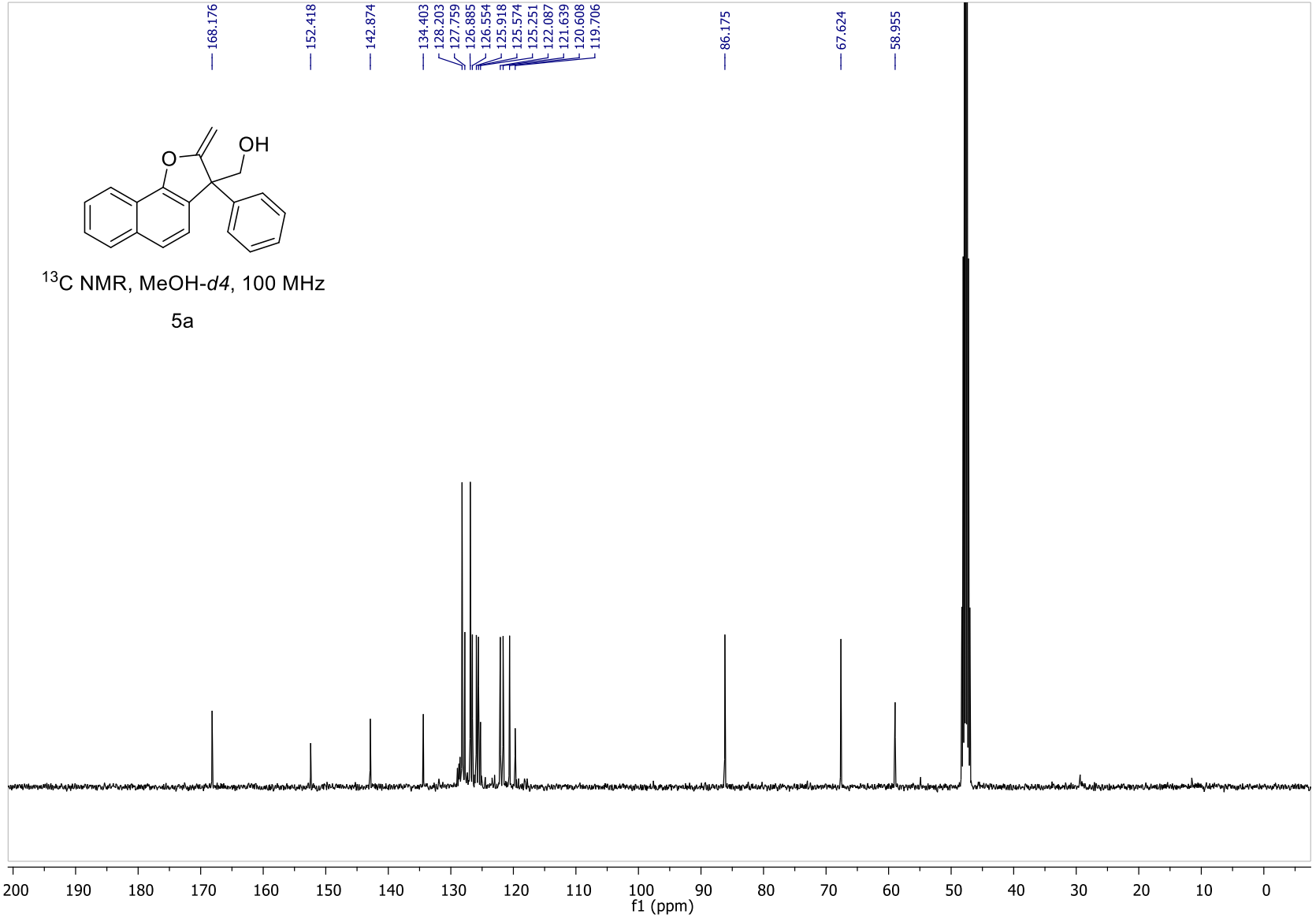
(2-Methylene-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5a)



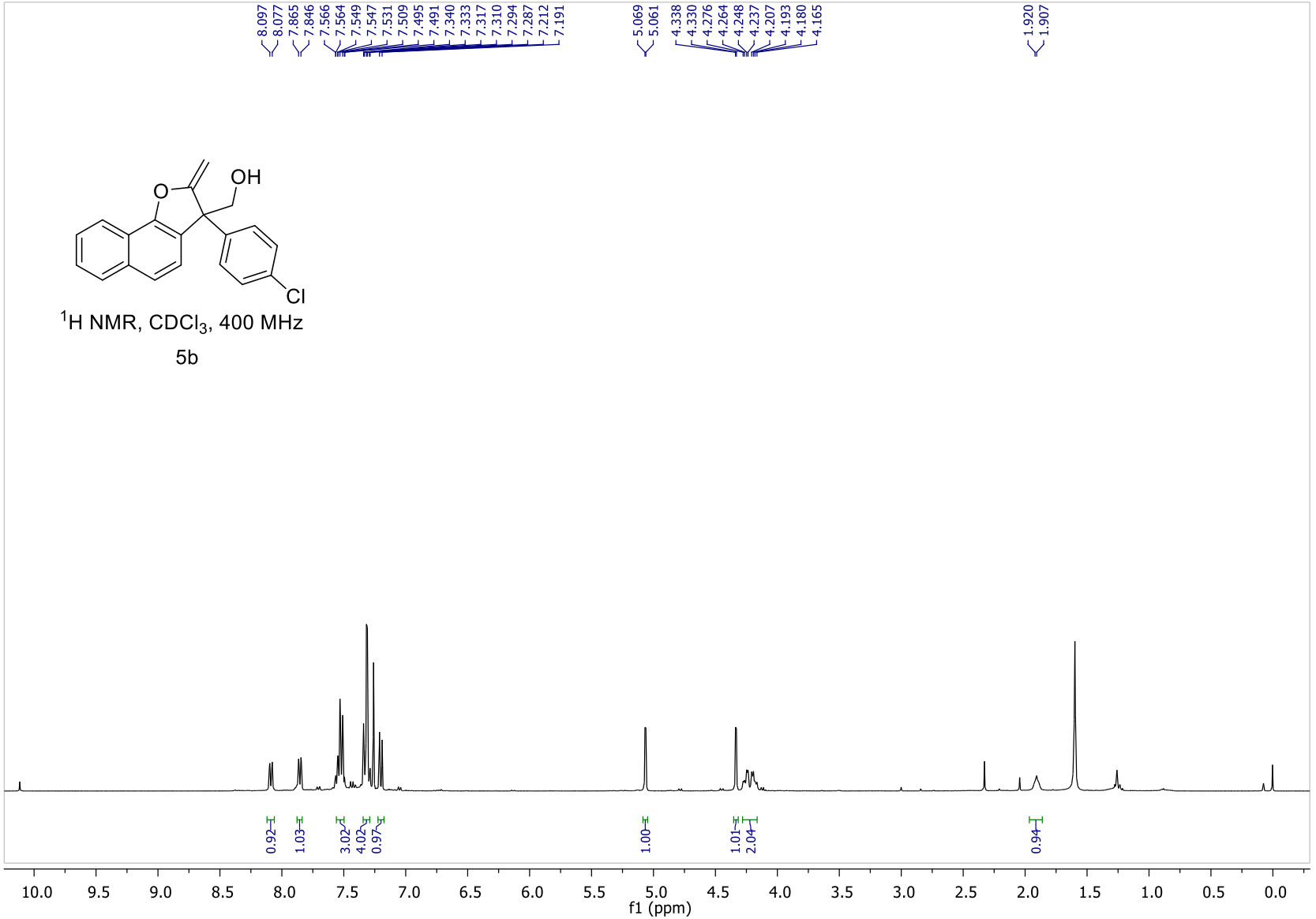
^{1}H NMR, MeOH-*d4*, 400 MHz

5a

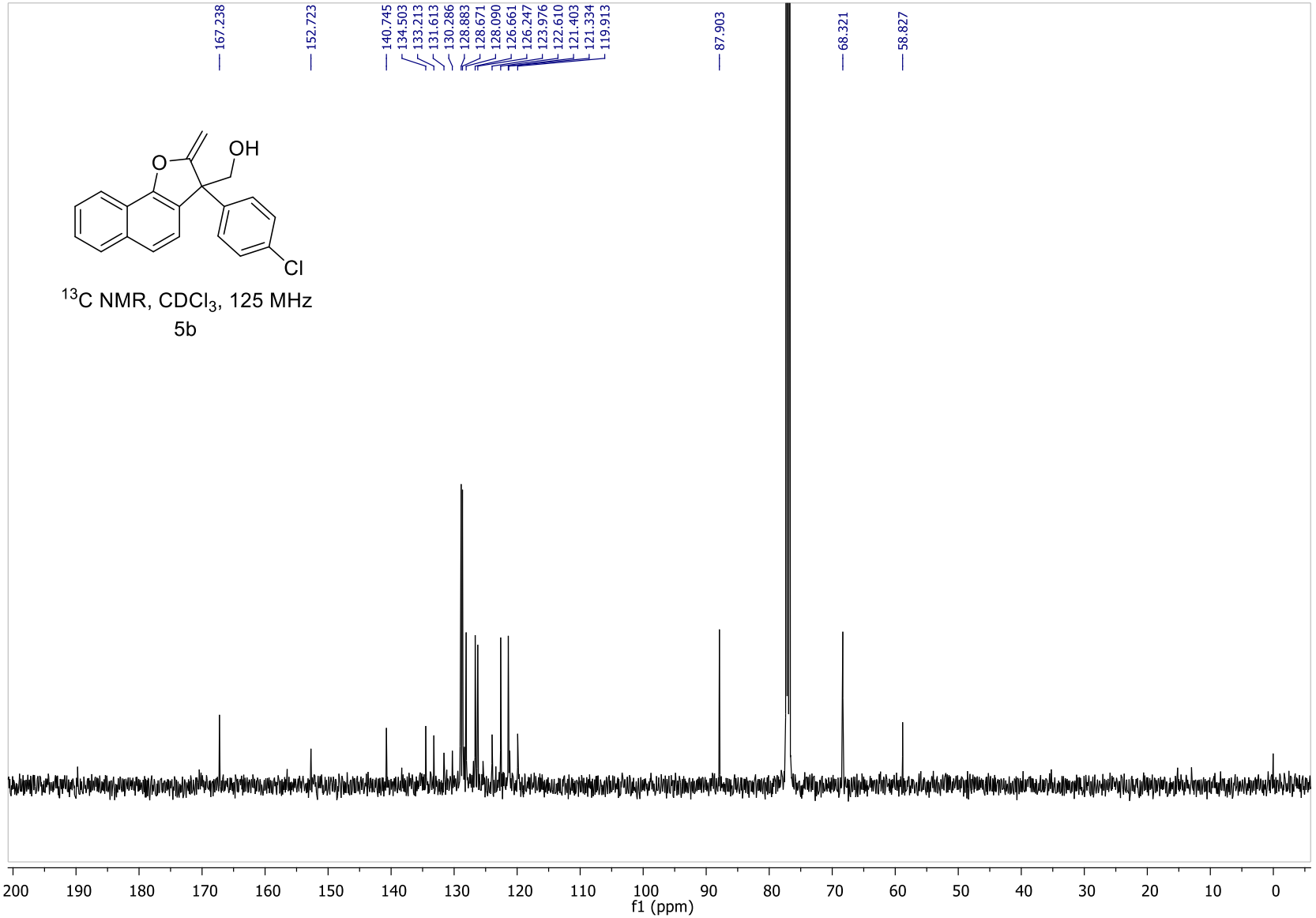
(2-Methylene-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5a)



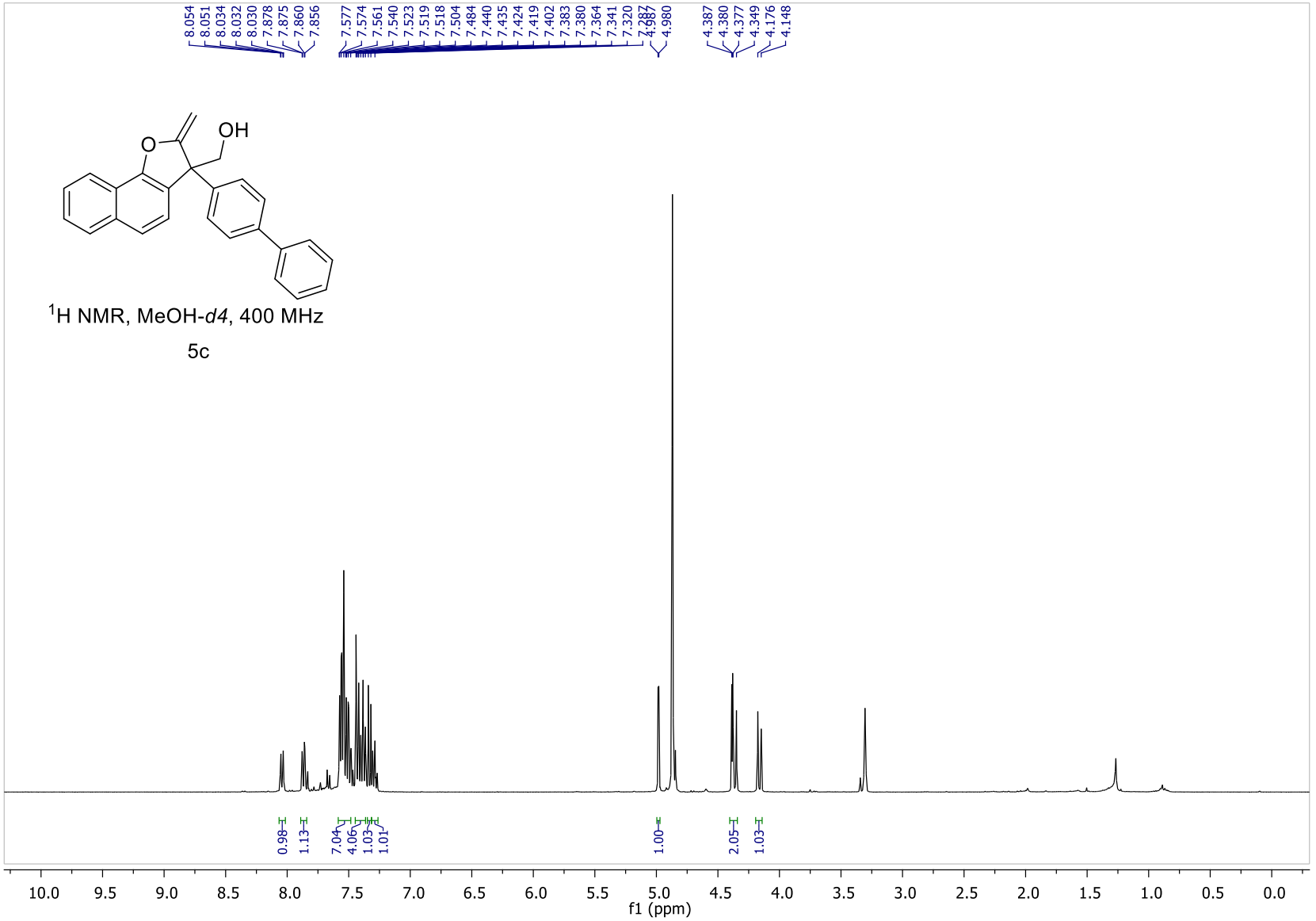
(3-(4-Chlorophenyl)-2-methylene-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5b)



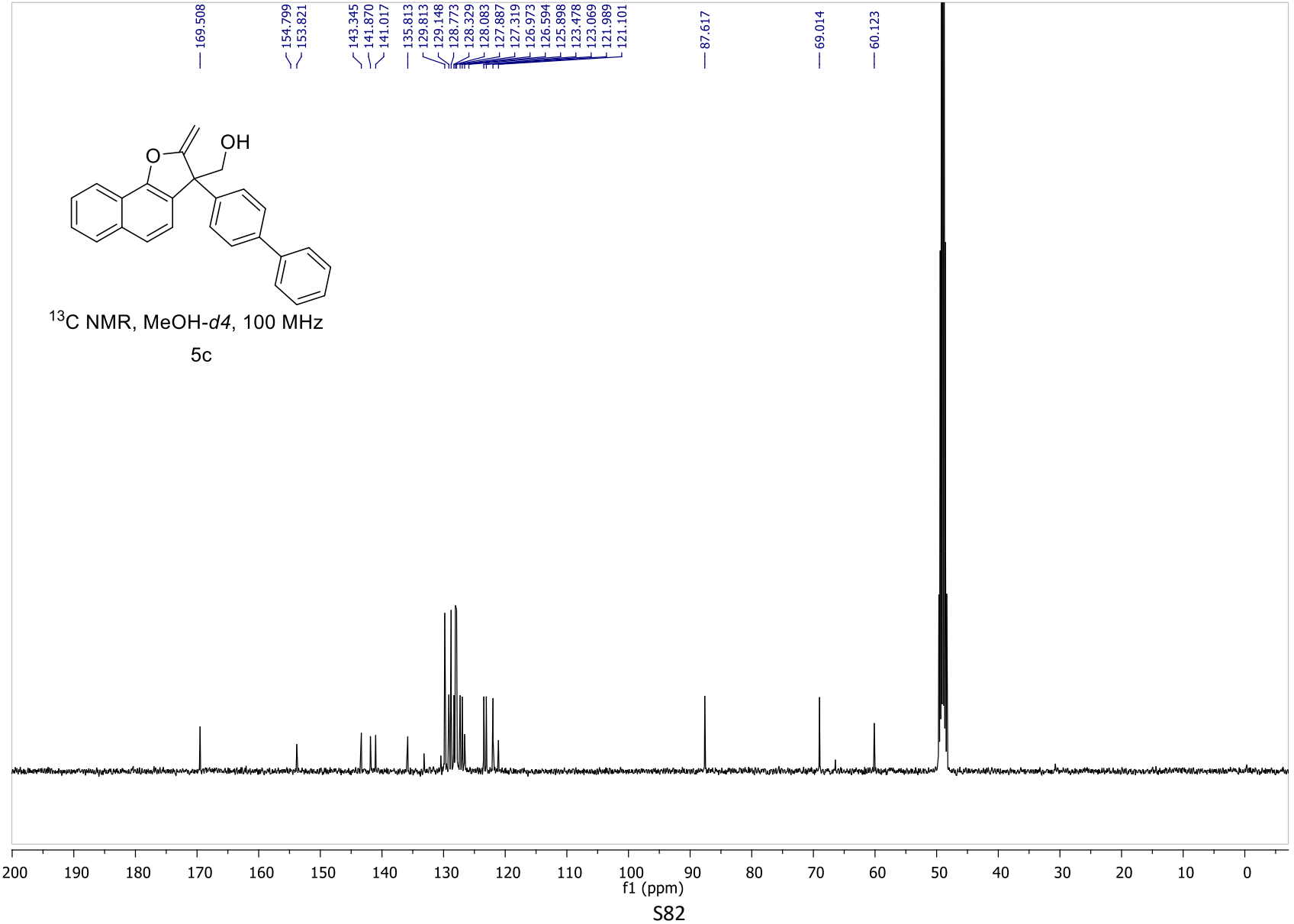
(3-(4-Chlorophenyl)-2-methylene-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5b)



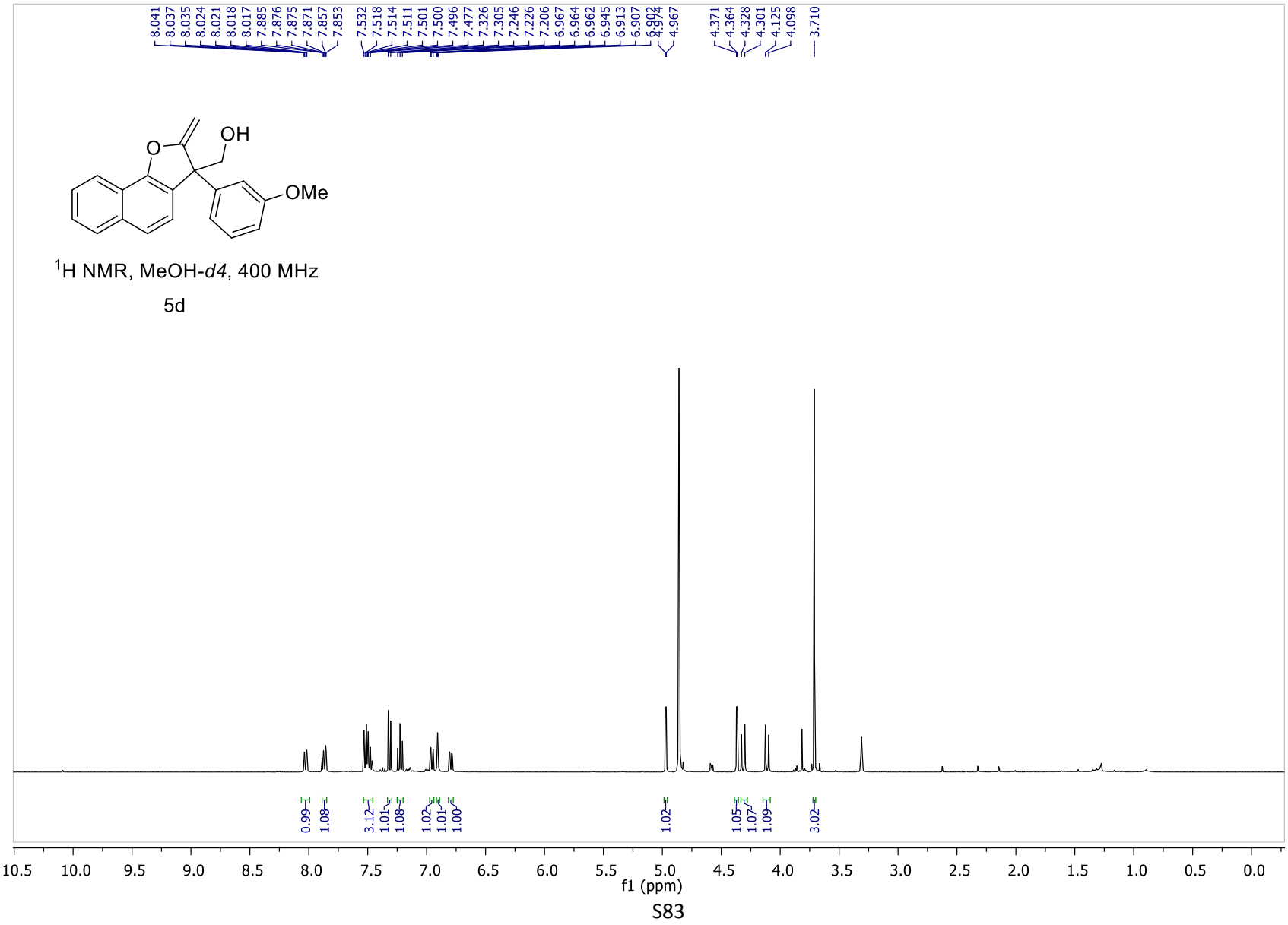
(3-([1,1'-Biphenyl]-4-yl)-2-methylene-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5c)



(3-([1,1'-Biphenyl]-4-yl)-2-methylene-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5c)



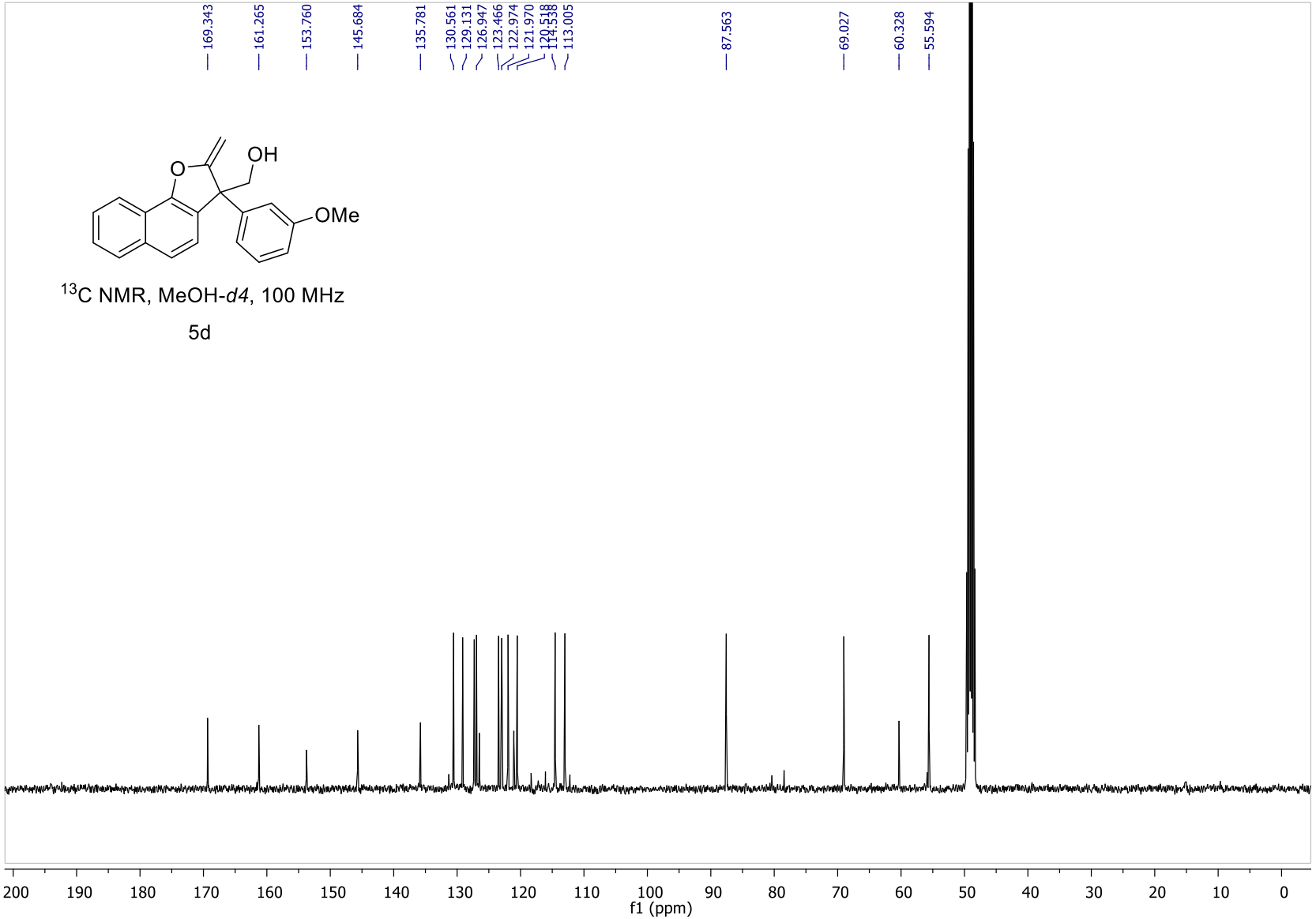
(3-(3-Methoxyphenyl)-2-methylene-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5d)



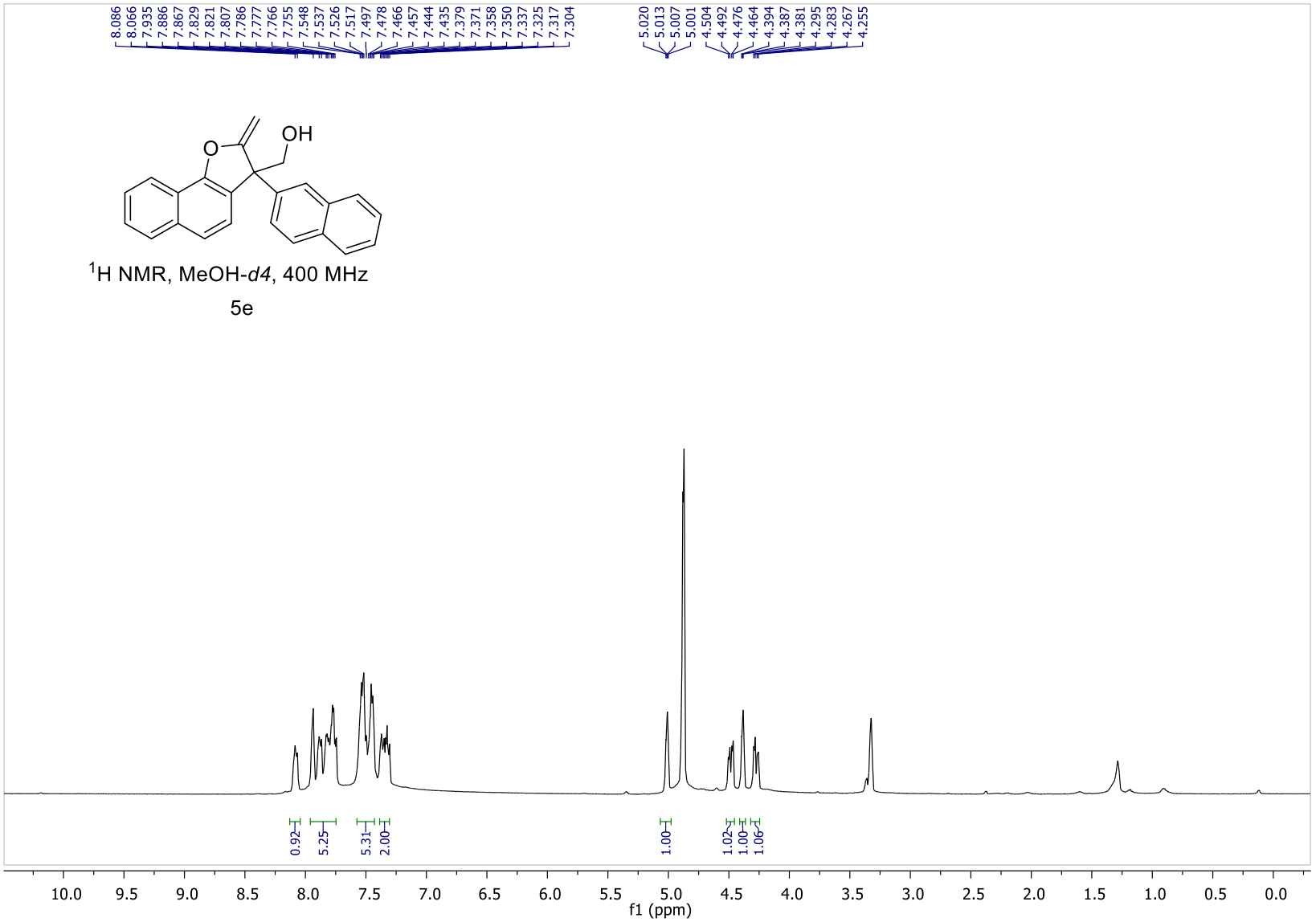
^{1}H NMR, MeOH-*d4*, 400 MHz

5d

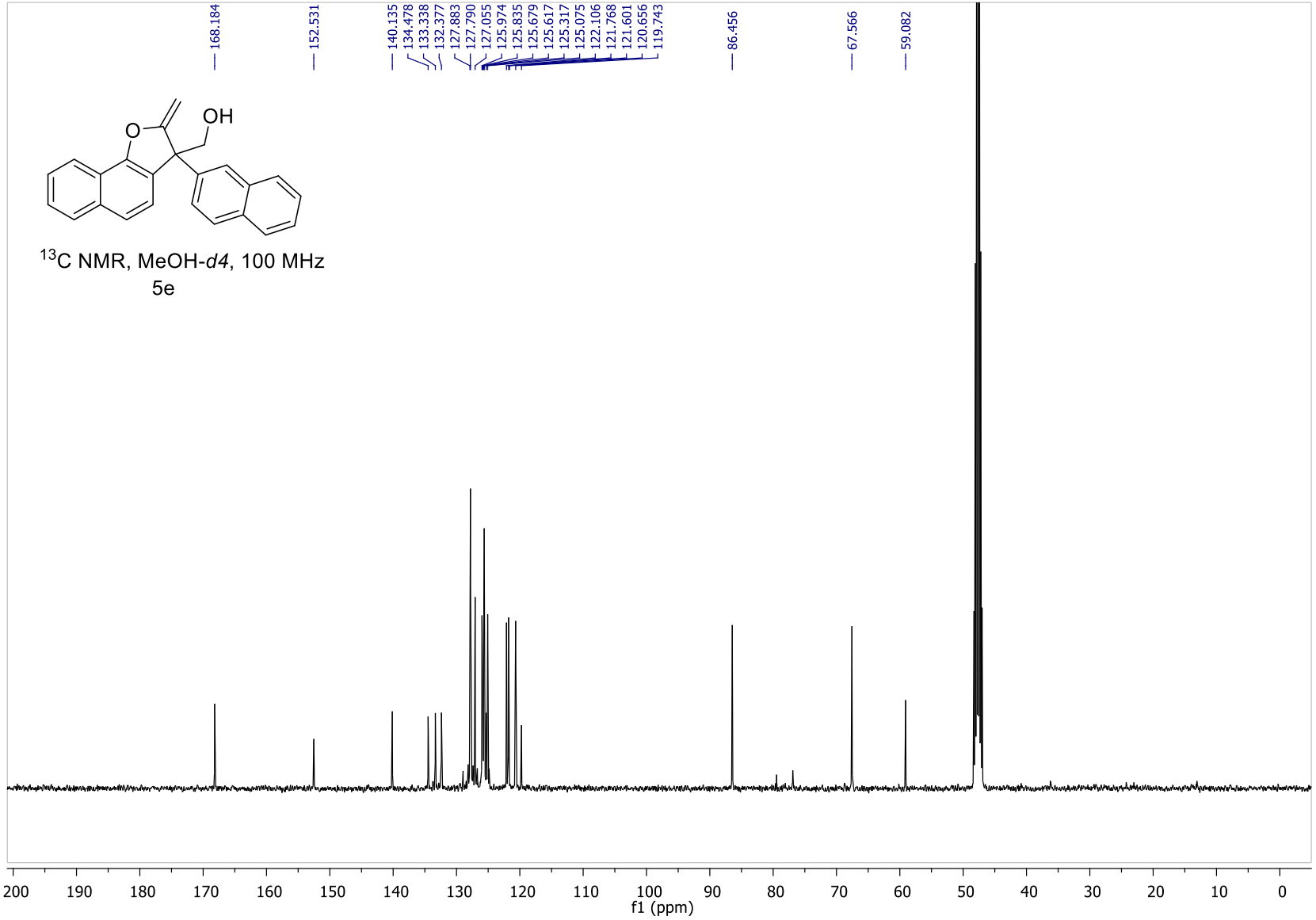
(3-(3-Methoxyphenyl)-2-methylene-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5d)



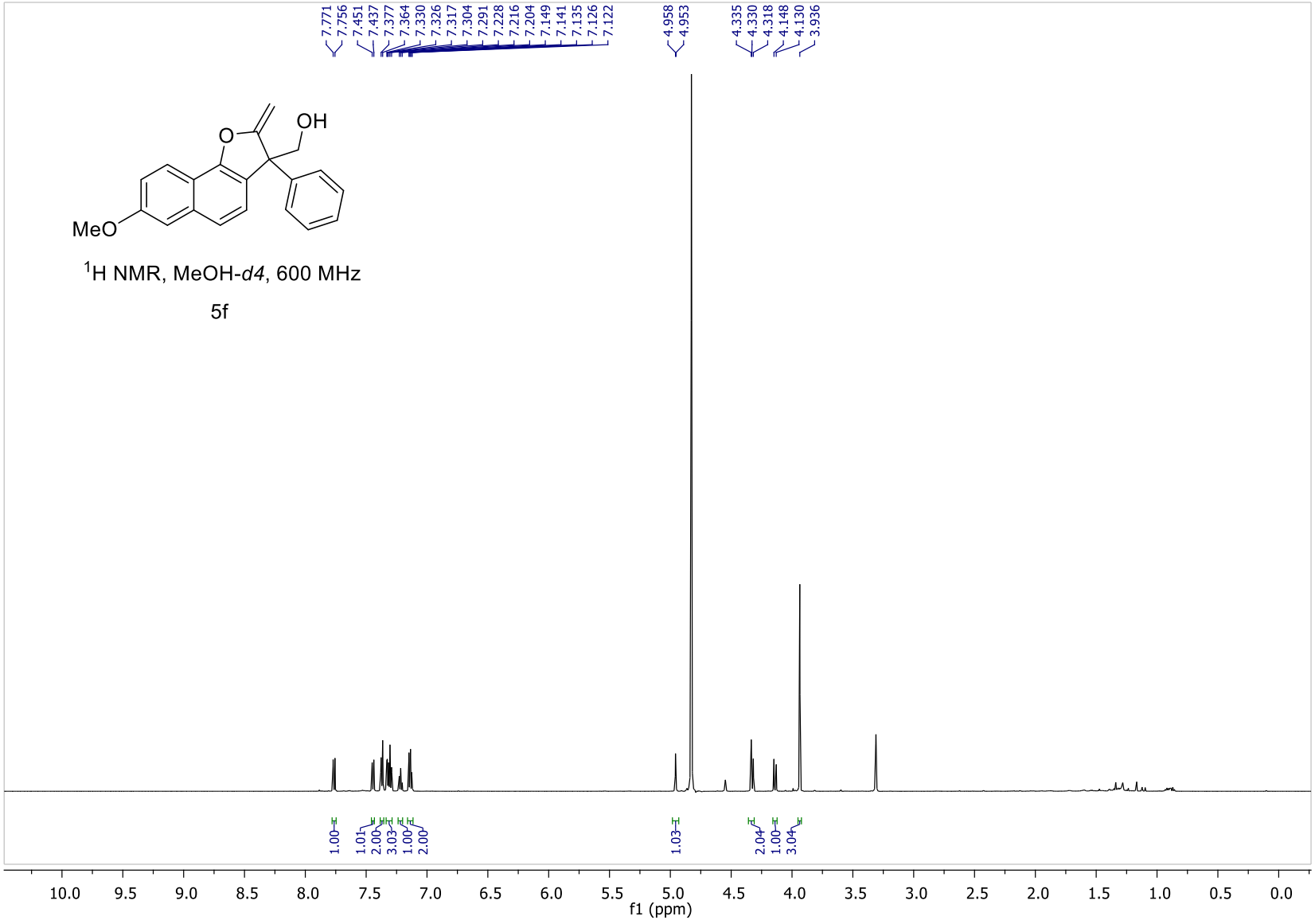
(2-Methylene-3-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5e)



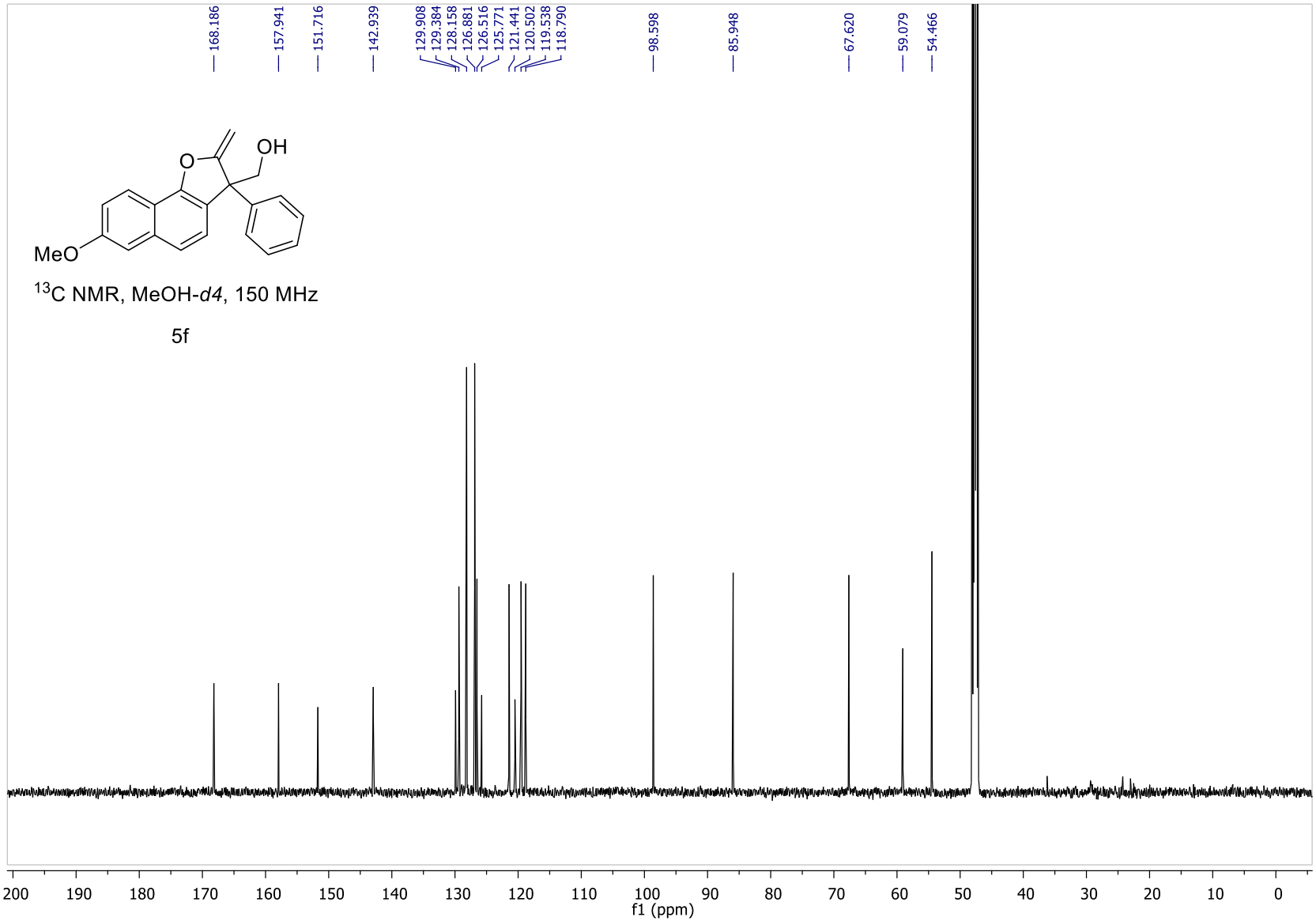
(2-Methylene-3-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5e)



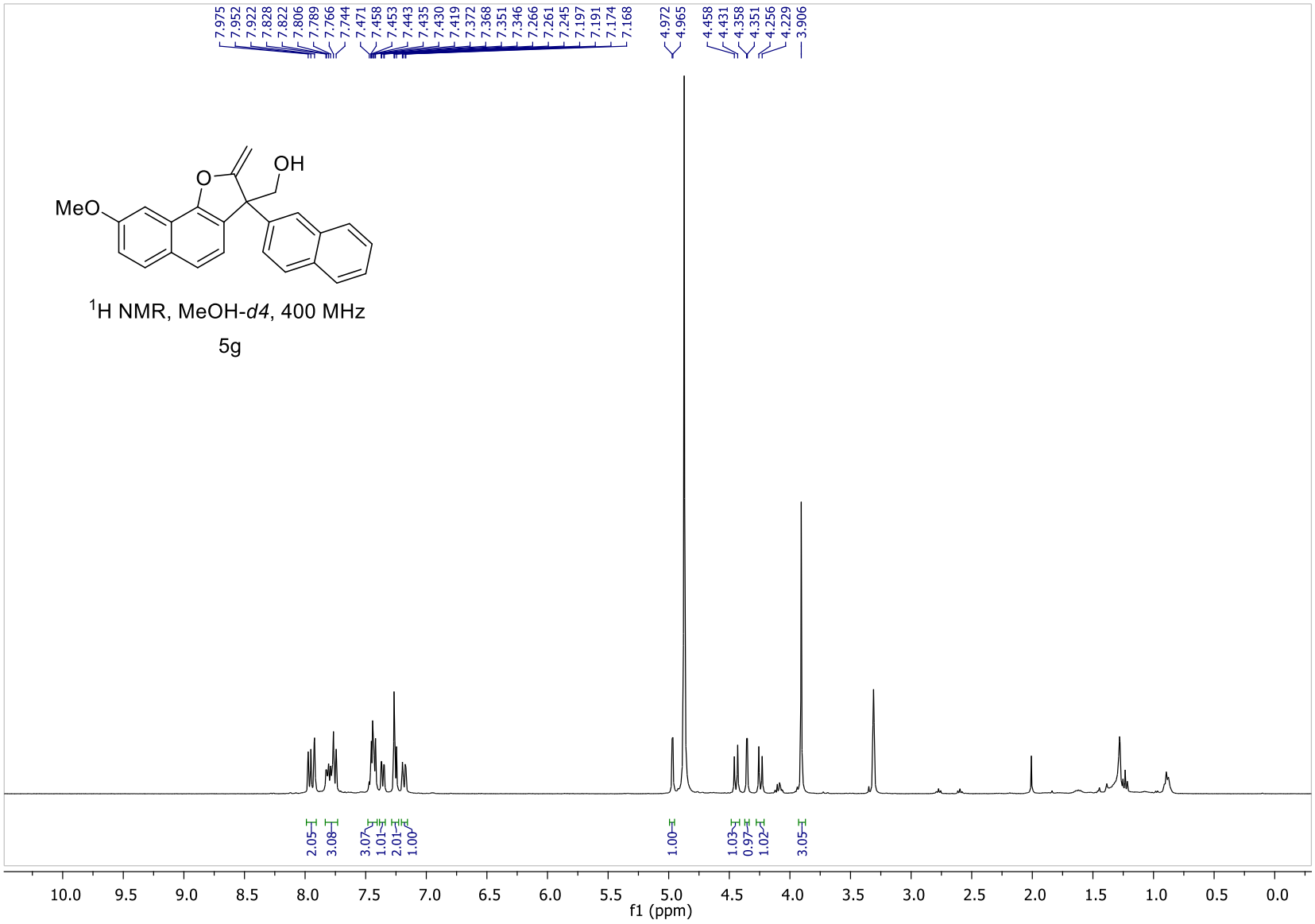
(7-Methoxy-2-methylene-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5f)



(7-Methoxy-2-methylene-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5f)



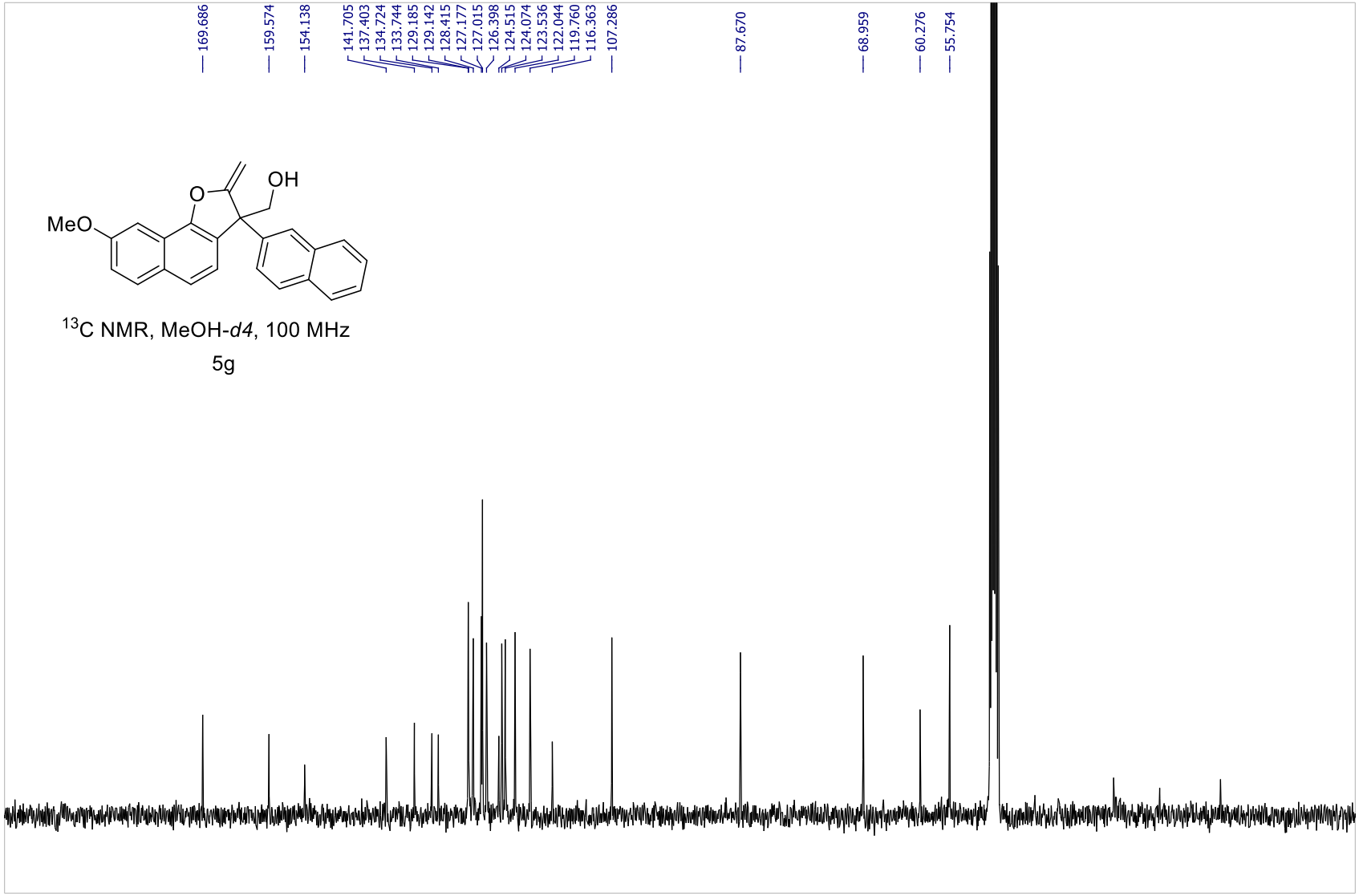
(8-Methoxy-2-methylene-3-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5g)



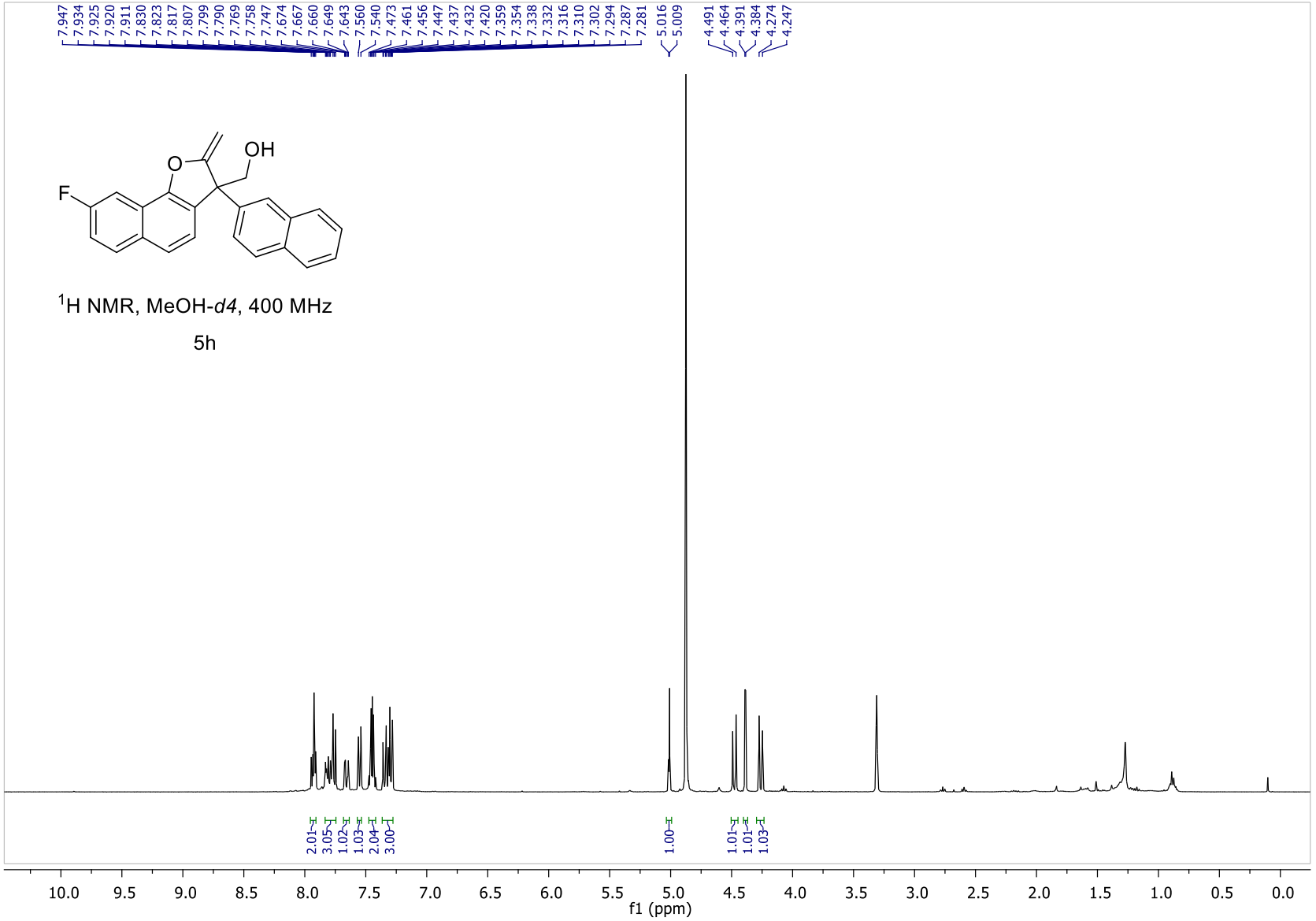
^{1}H NMR, MeOH-*d4*, 400 MHz

5g

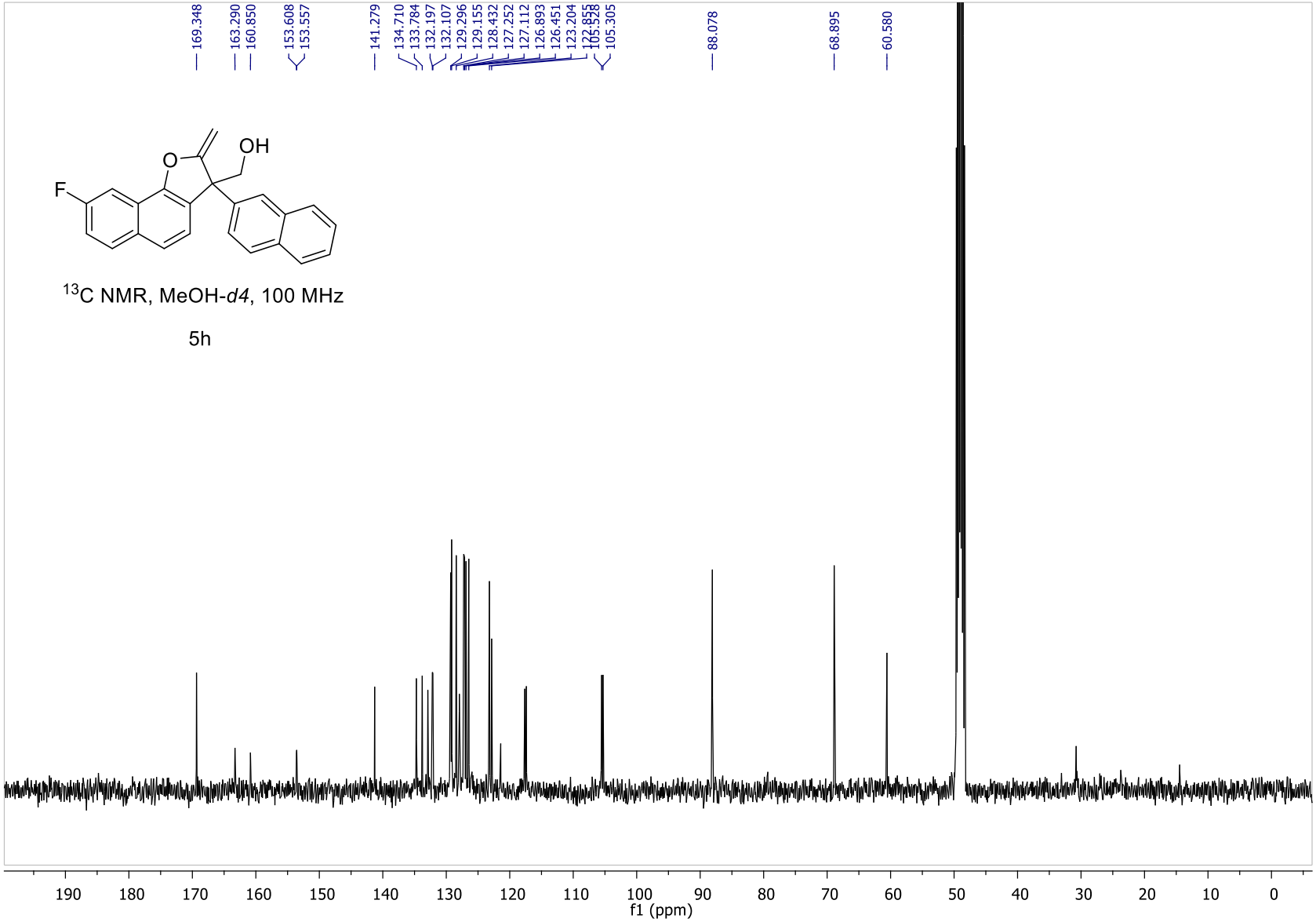
(8-Methoxy-2-methylene-3-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5g)



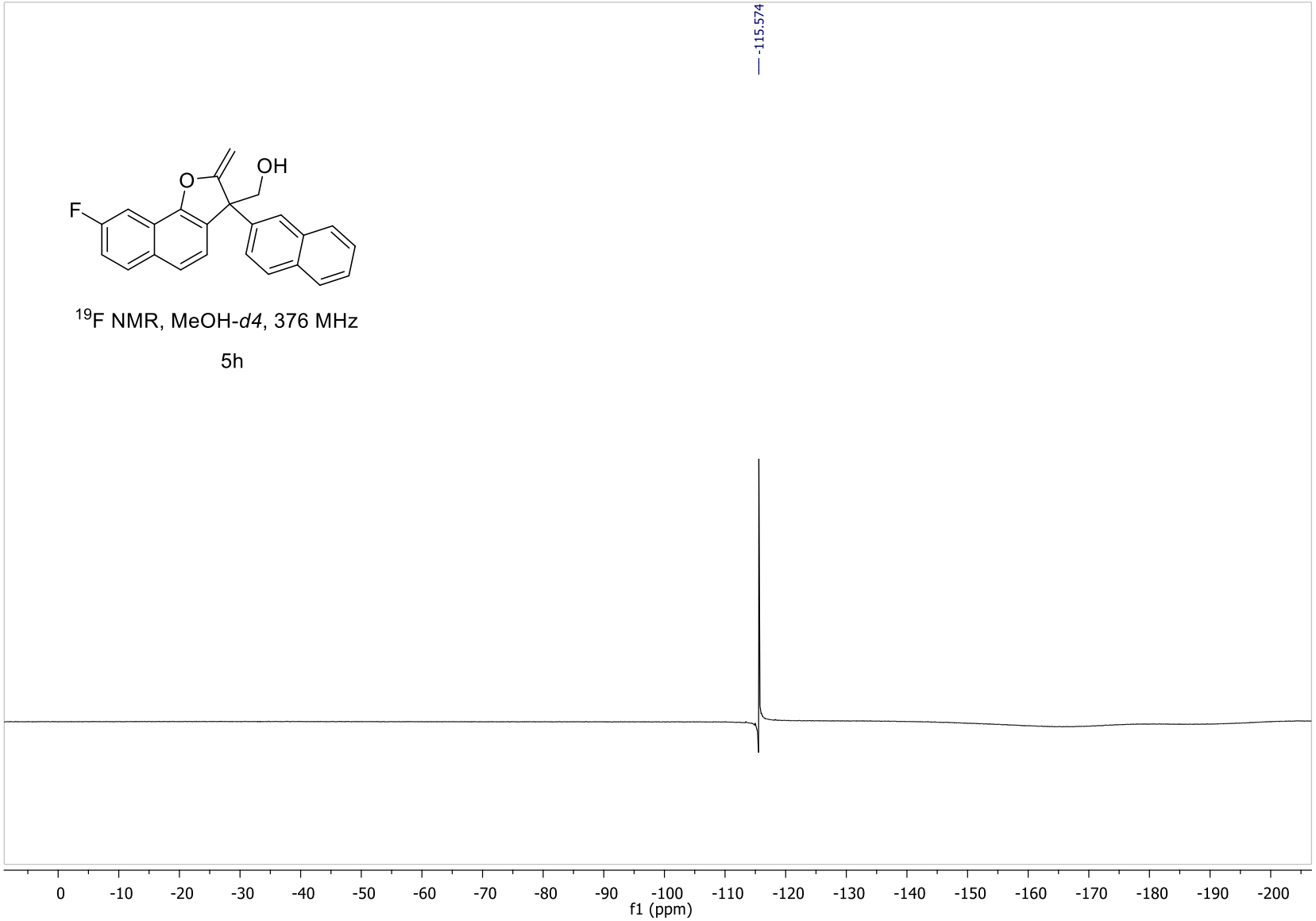
(8-Fluoro-2-methylene-3-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5h)



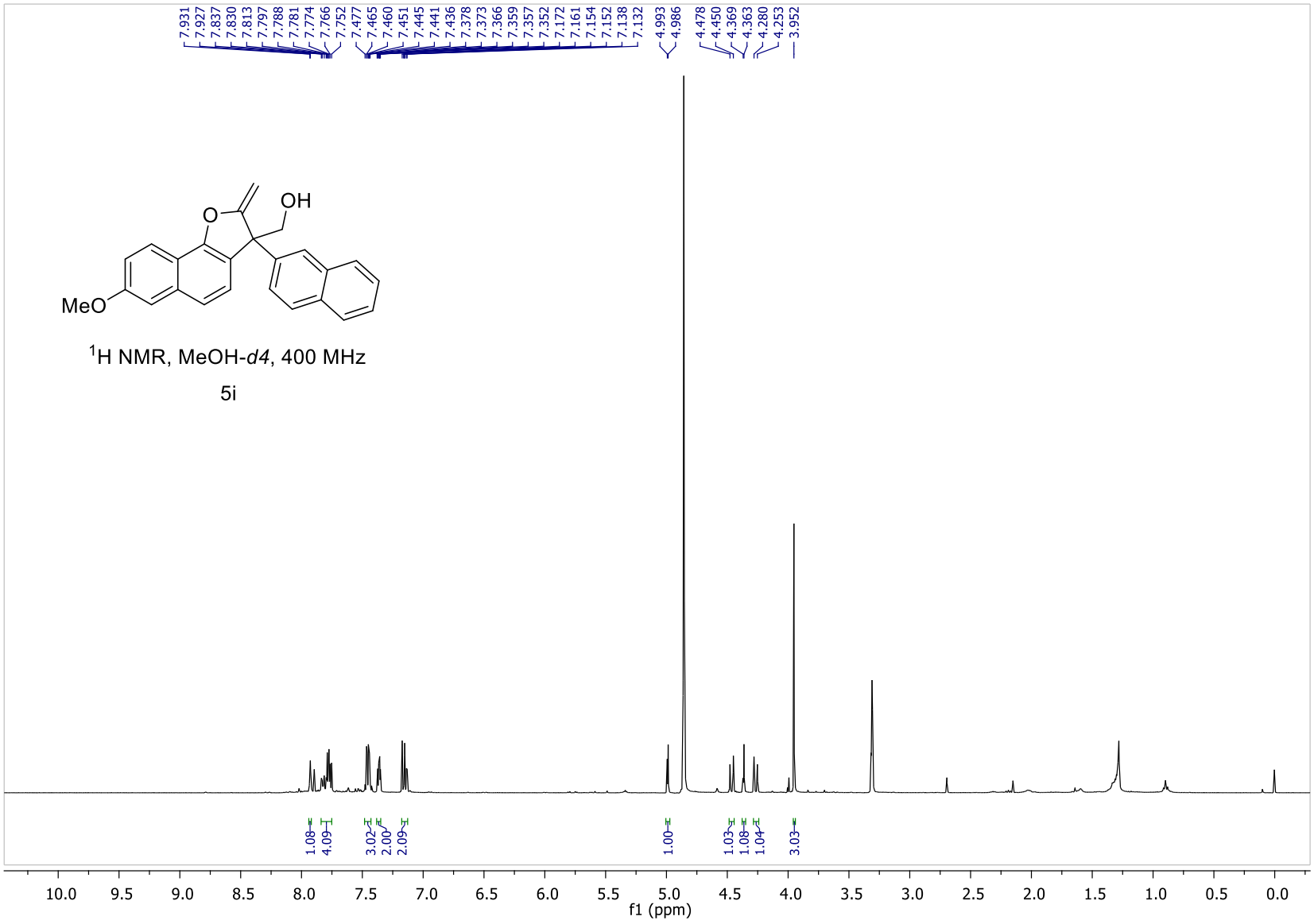
(8-Fluoro-2-methylene-3-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5h)



(8-Fluoro-2-methylene-3-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5h)



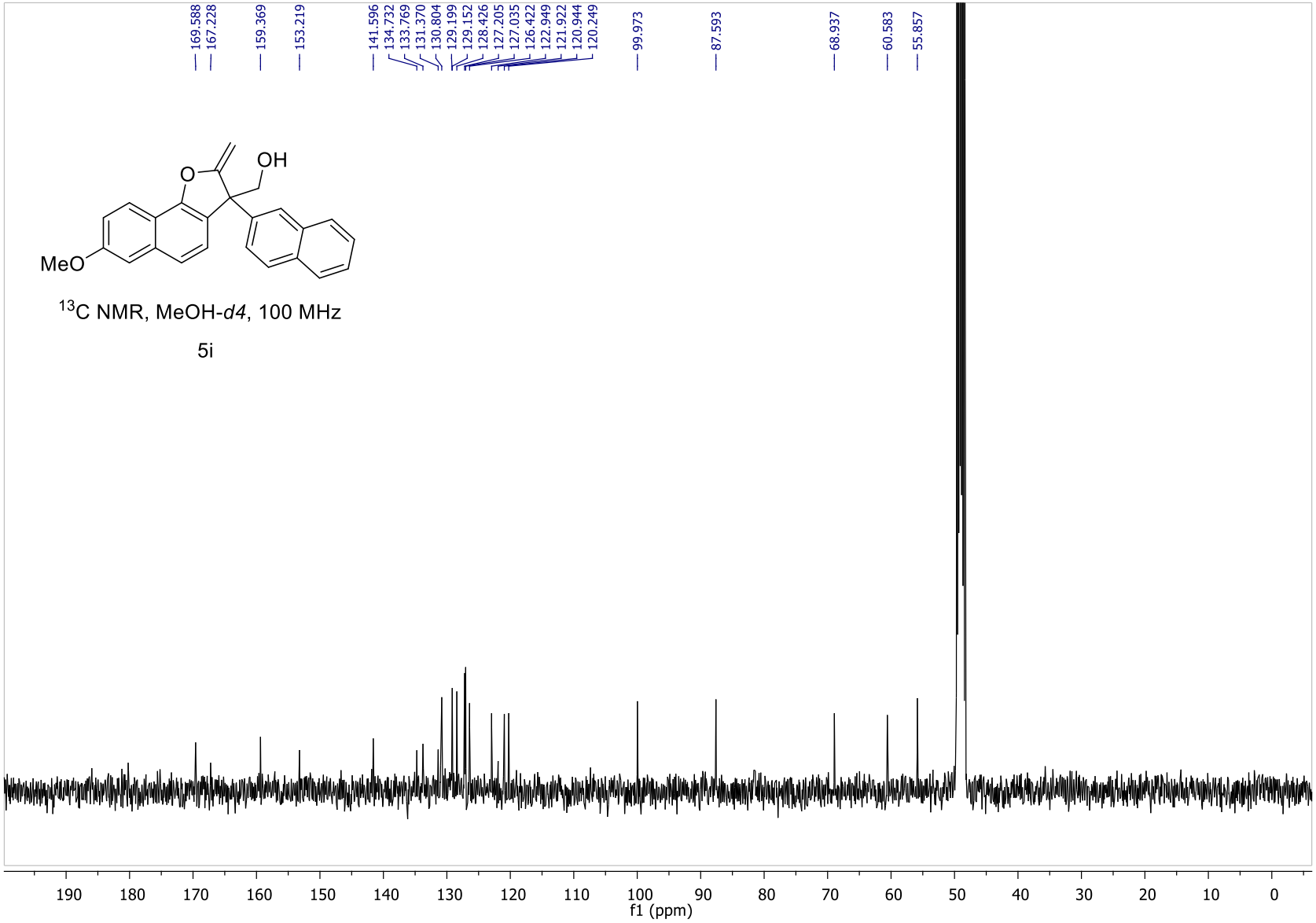
(7-Methoxy-2-methylene-3-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5i)



^{1}H NMR, MeOH-*d4*, 400 MHz

5i

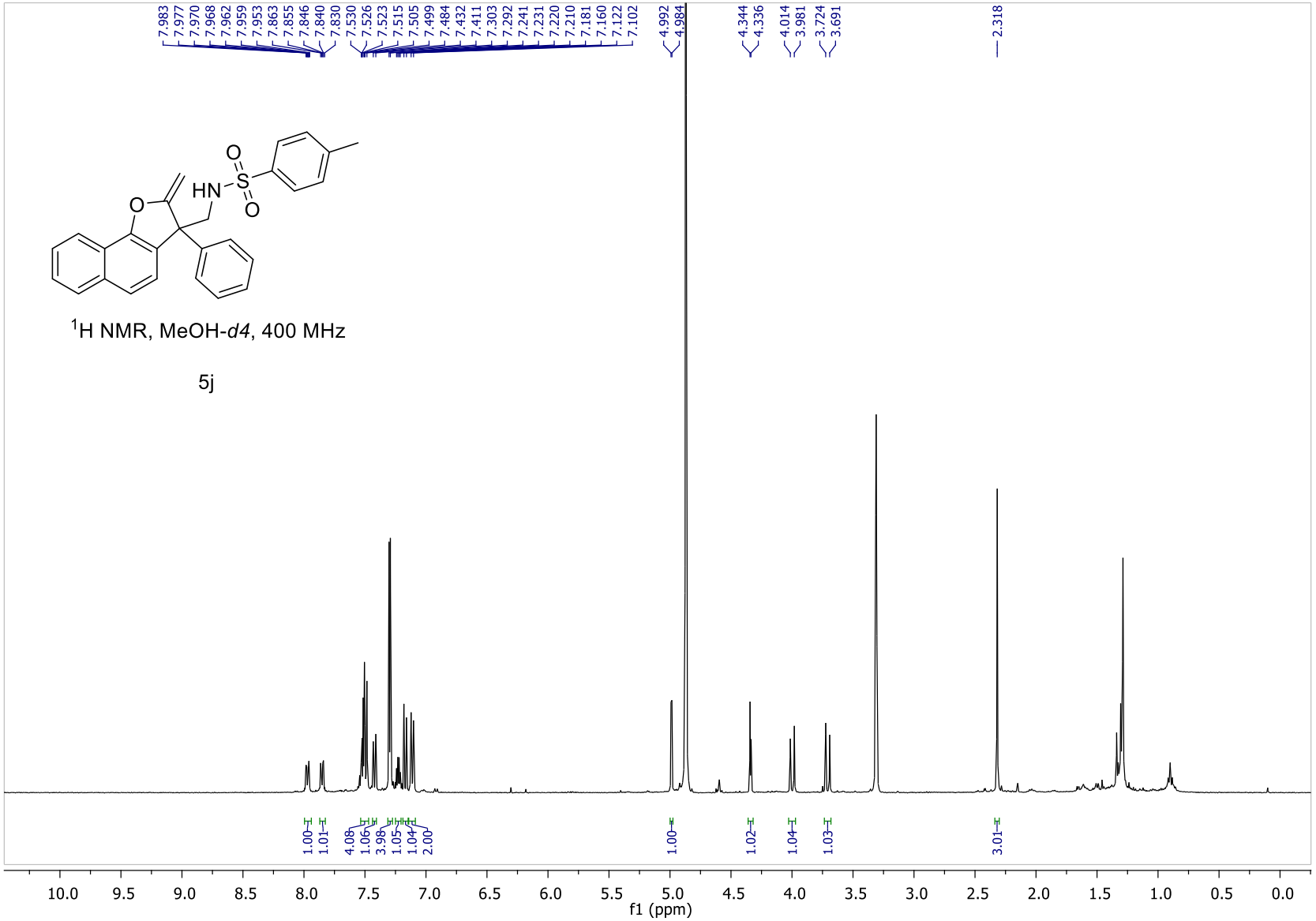
(7-Methoxy-2-methylene-3-(naphthalen-2-yl)-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methanol (5i)



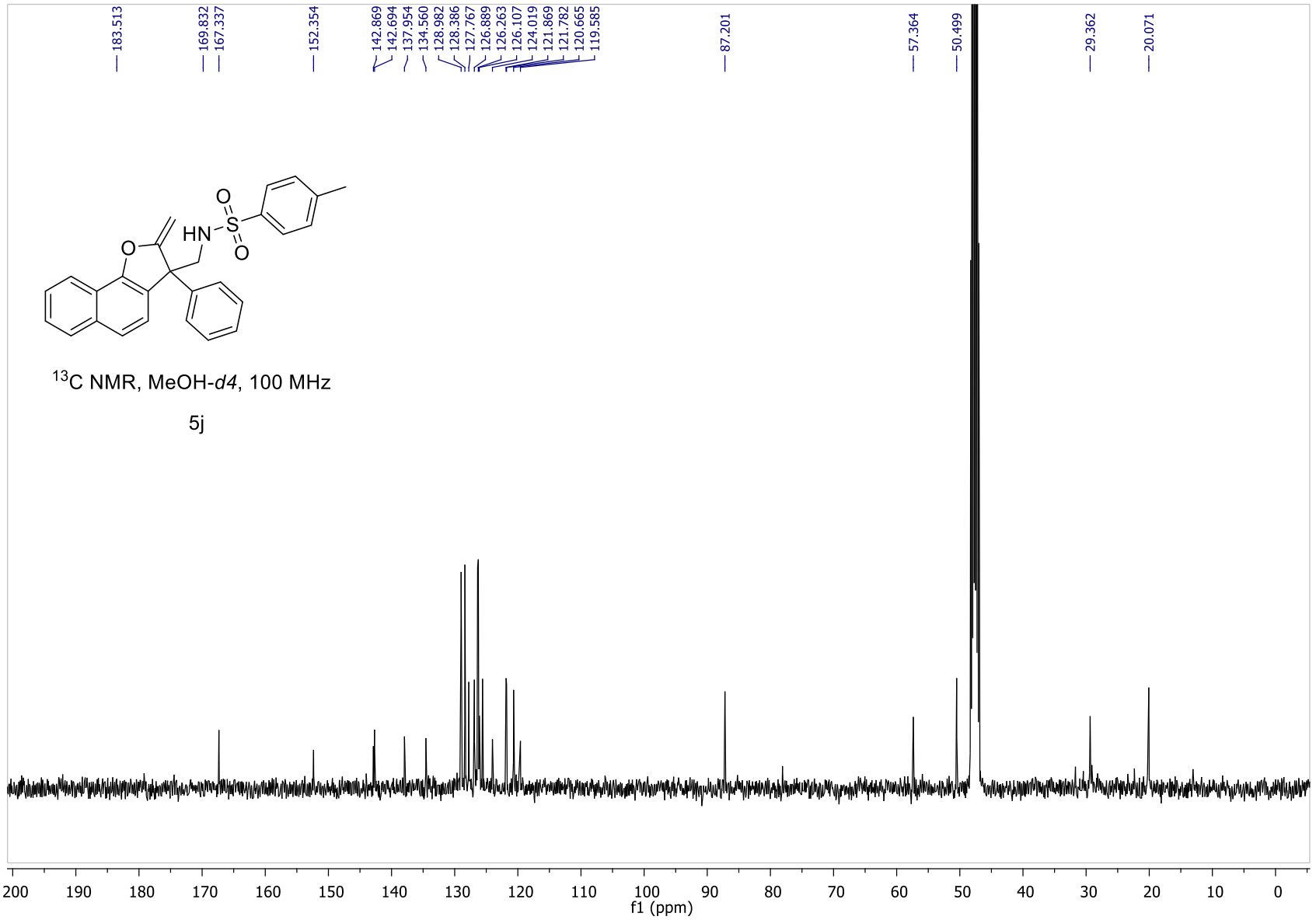
^{13}C NMR, MeOH-*d4*, 100 MHz

5i

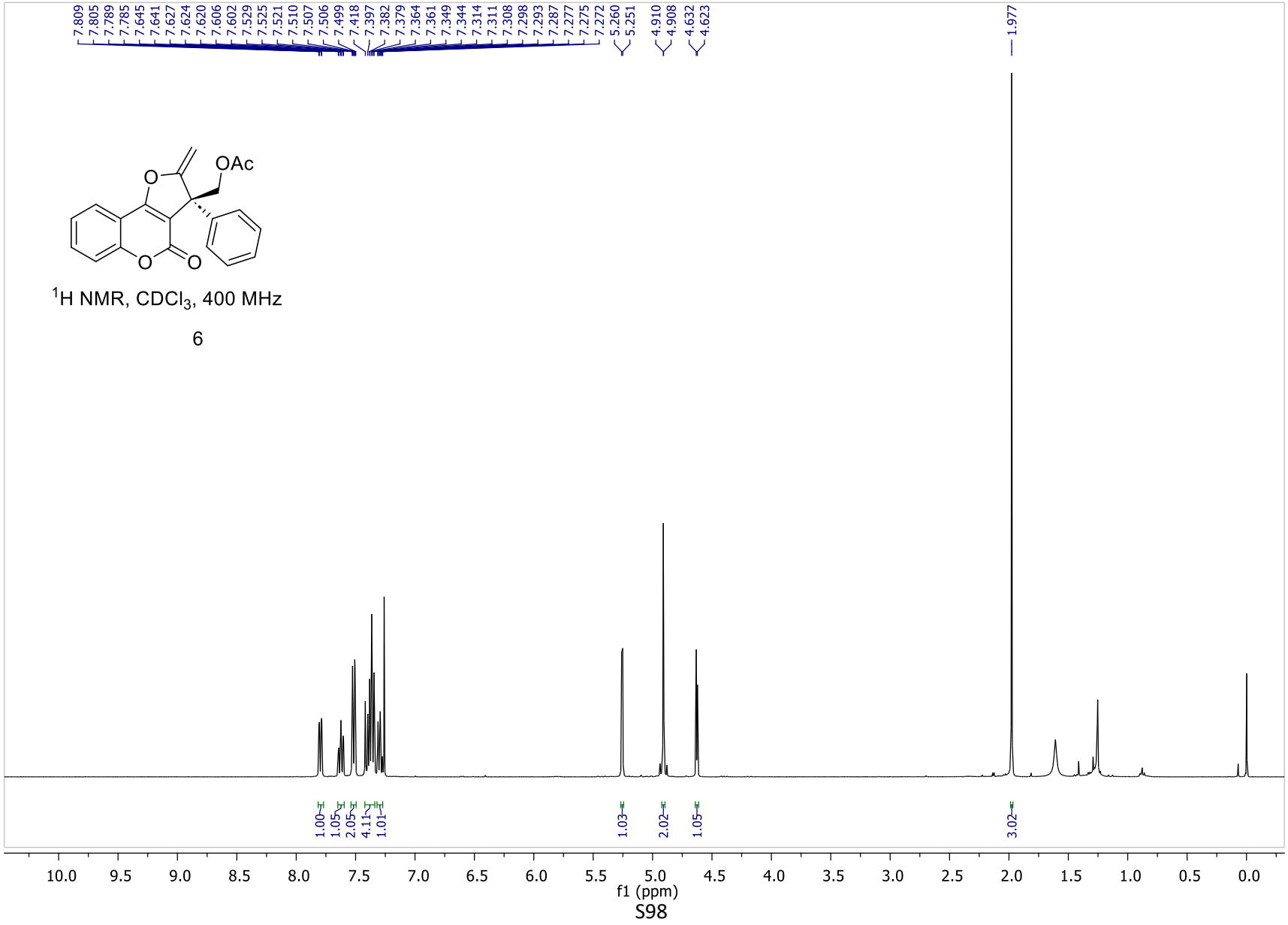
4-Methyl-N-((2-methylene-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methyl)benzenesulfonamide (5j)



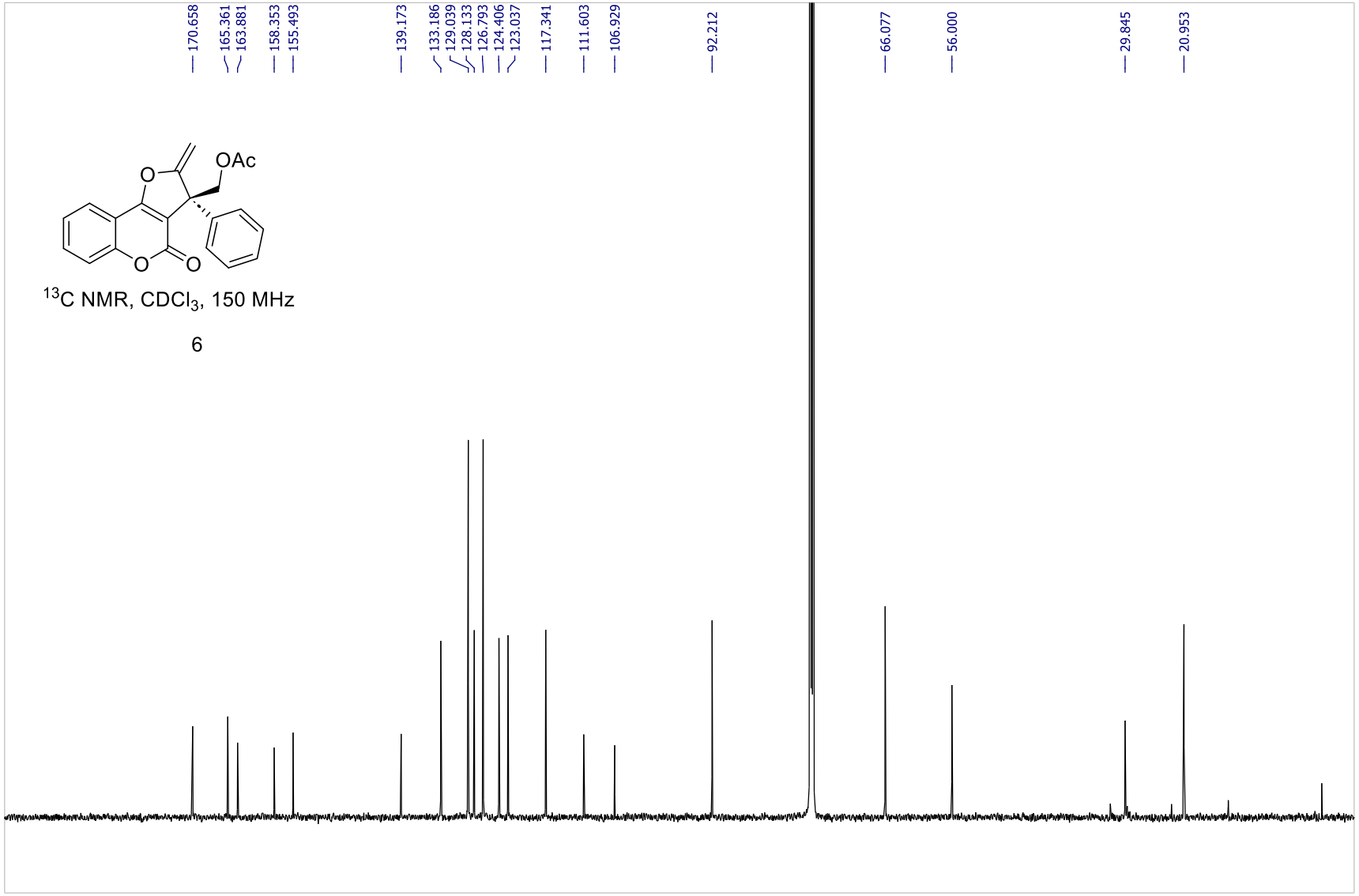
4-Methyl-N-((2-methylene-3-phenyl-2,3-dihydronaphtho[1,2-*b*]furan-3-yl)methyl)benzenesulfonamide (5j)



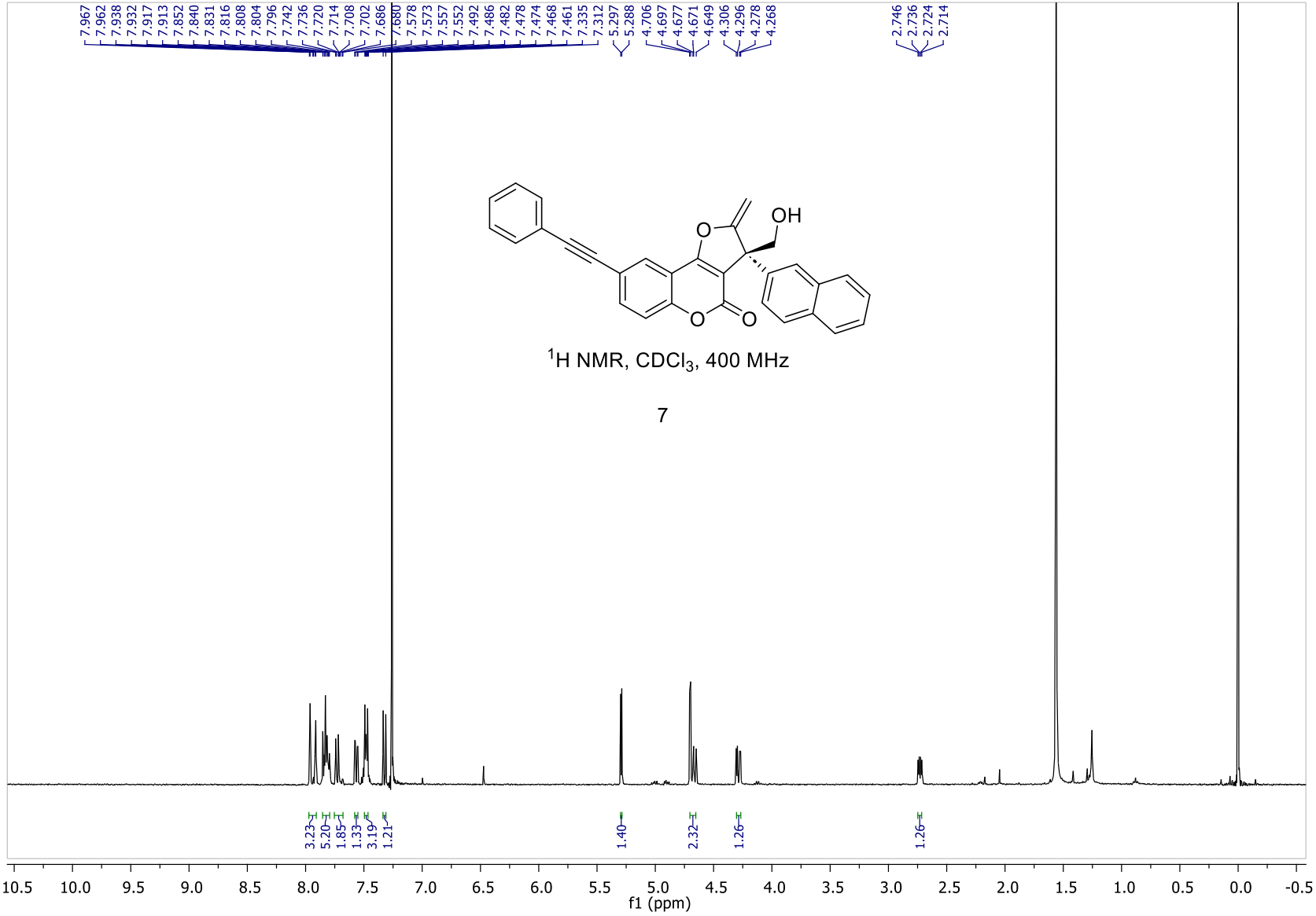
(*R*)-(2-Methylene-4-oxo-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-3-yl)methyl acetate 6



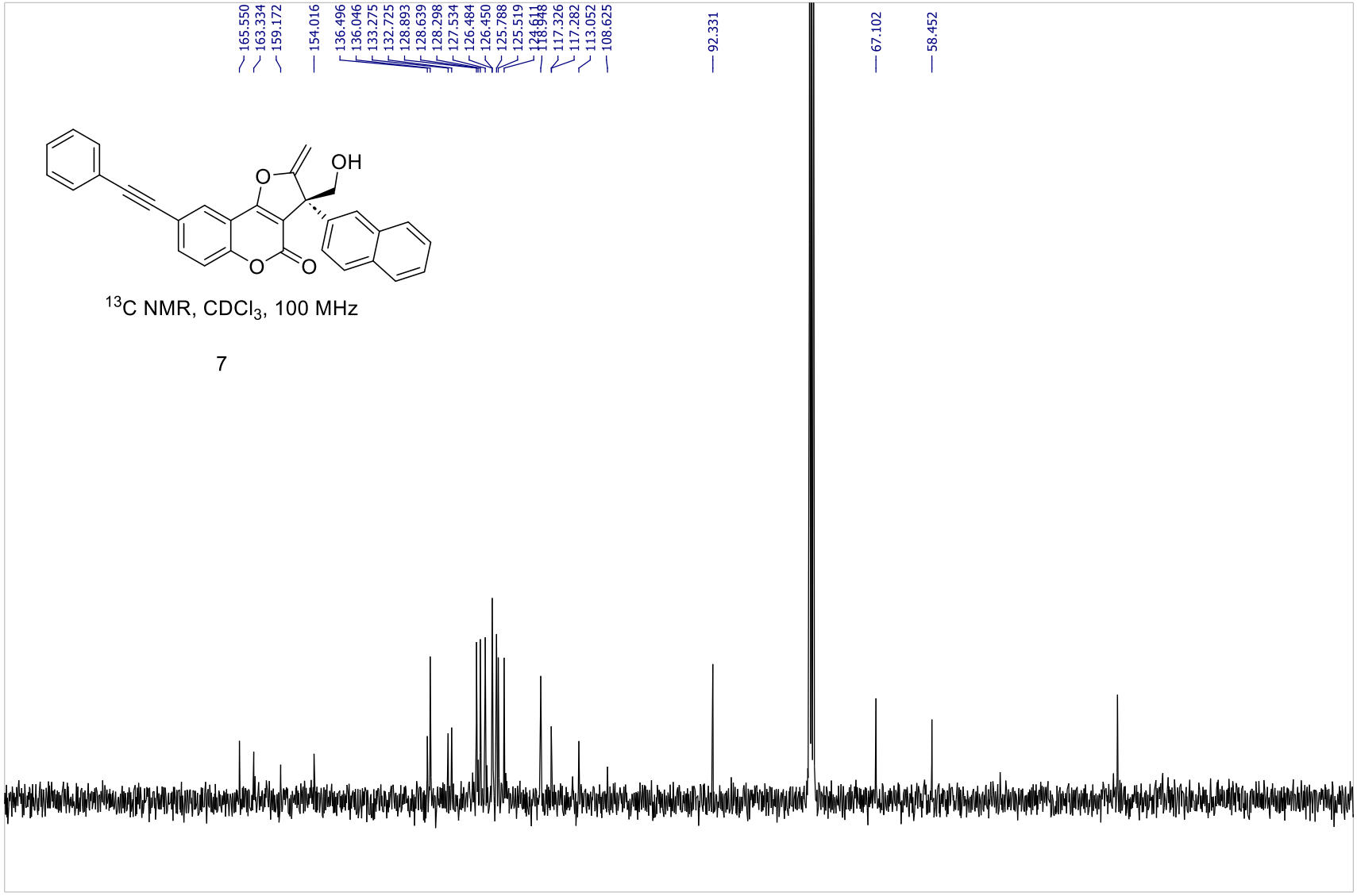
(*R*)-(2-Methylene-4-oxo-3-phenyl-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-3-yl)methyl acetate 6



(*R*)-3-(Hydroxymethyl)-2-methylene-3-(naphthalen-2-yl)-8-(phenylethynyl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one 7



(*R*)-3-(Hydroxymethyl)-2-methylene-3-(naphthalen-2-yl)-8-(phenylethynyl)-2,3-dihydro-4*H*-furo[3,2-*c*]chromen-4-one 7

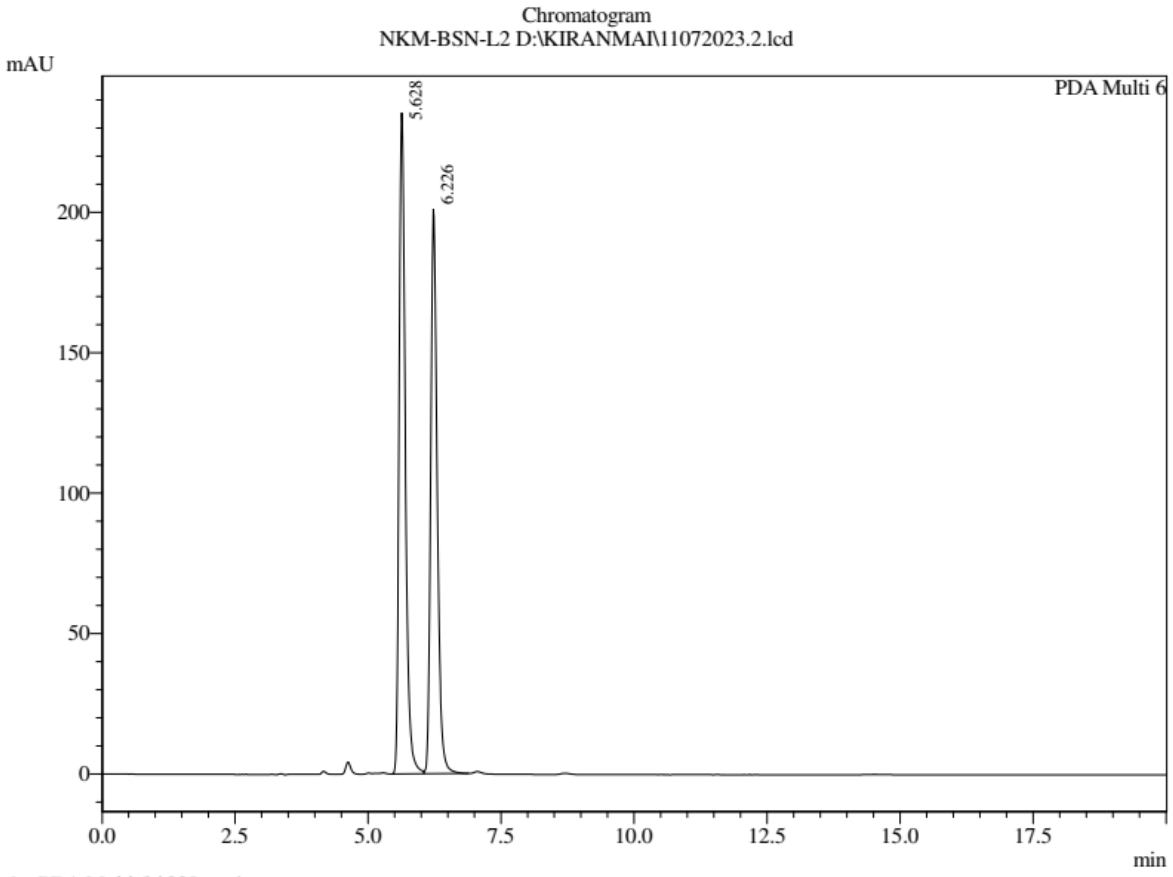


5. HPLC Chromatograms of Compounds

5.1. HPLC Chromatograms of Compounds 3a-w

HPLC analysis conditions: CHIRALPAK IA-3 column, 50% *i*PrOH in hexanes, flow rate 1.0 mL/min, λ = 225 nm.

HPLC Chromatogram of Compound 3a (racemic)



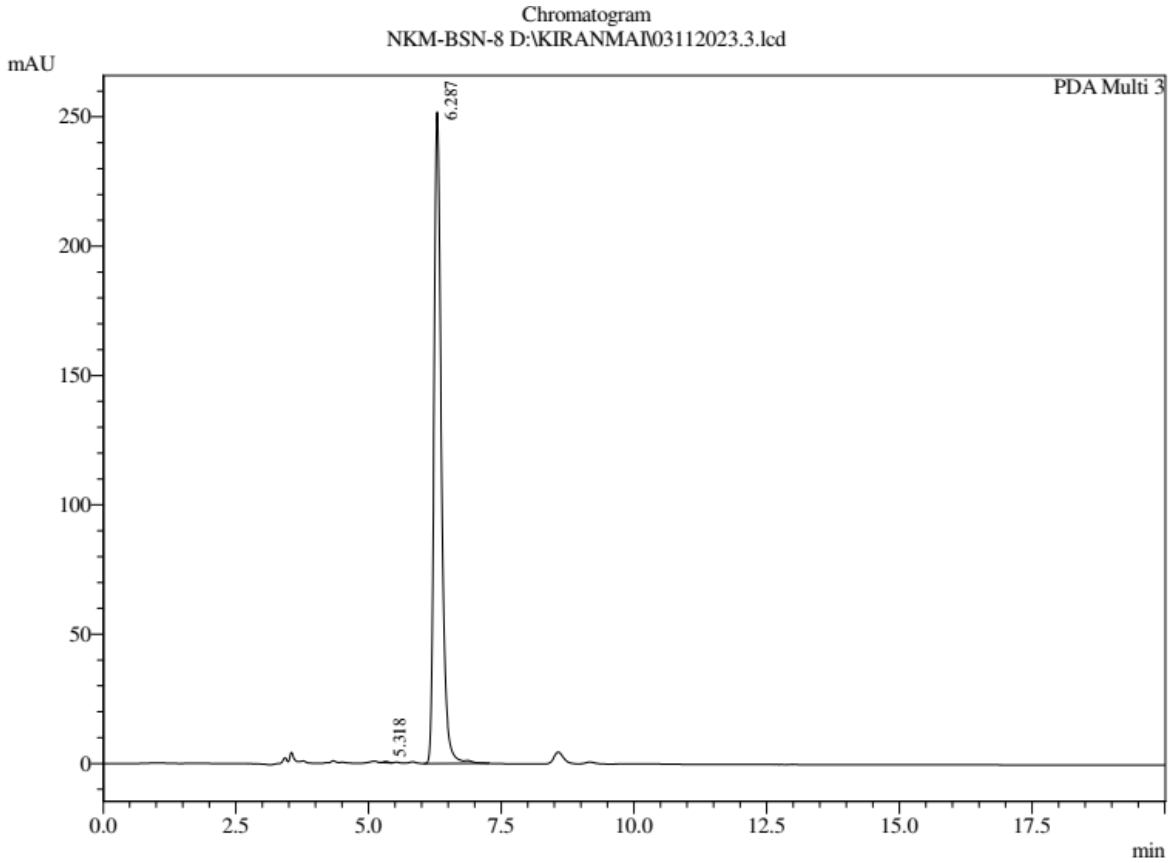
1 PDA Multi 6 / 320nm 4nm

PeakTable

PDA Ch6 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.628	1914842	235397	52.687	53.947
2	6.226	1719527	200954	47.313	46.053
Total		3634369	436351	100.000	100.000

HPLC Chromatogram of Compound 3a obtained from L2



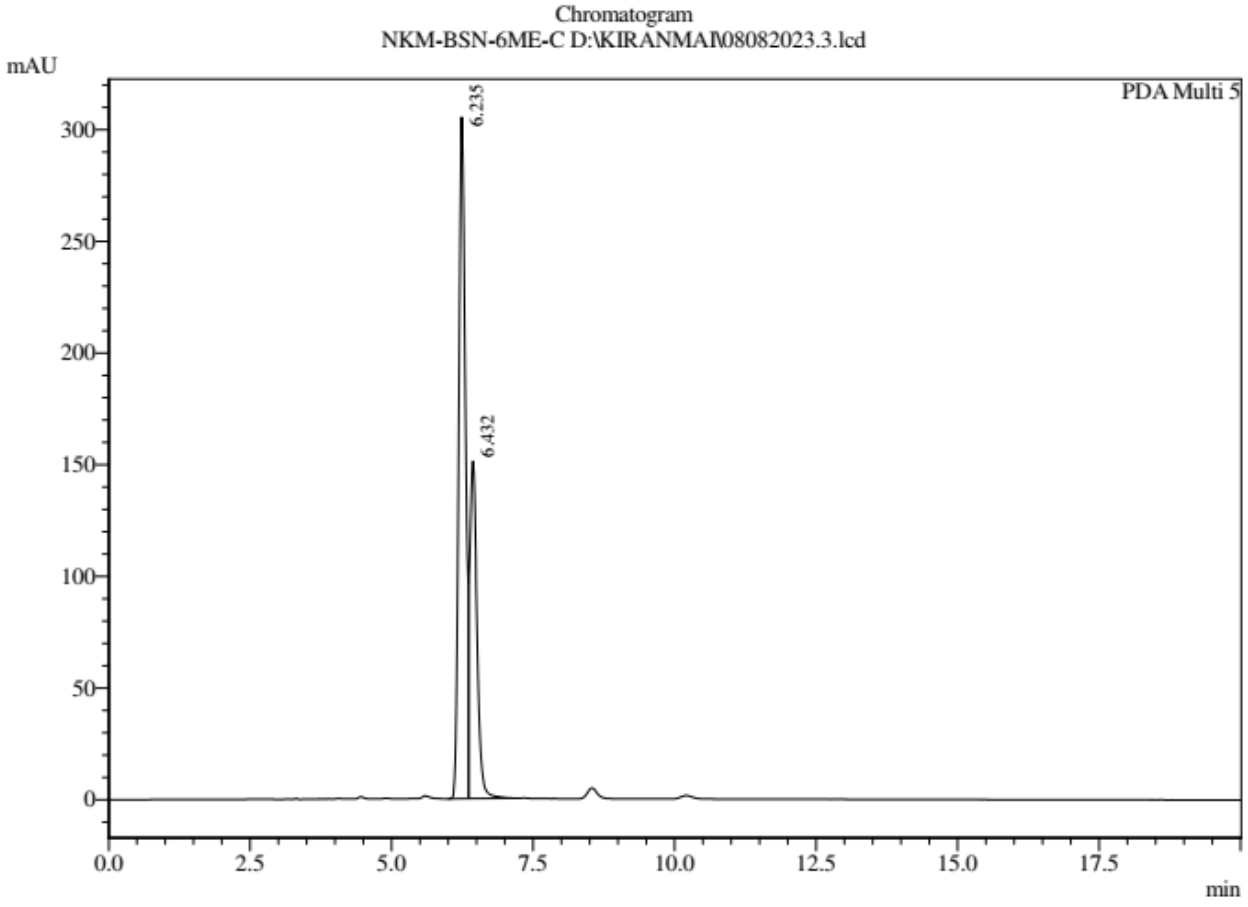
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.318	2908	485	0.120	0.192
2	6.287	2421033	251902	99.880	99.808
Total		2423941	252387	100.000	100.000

HPLC Chromatogram of Compound 3b (racemic)



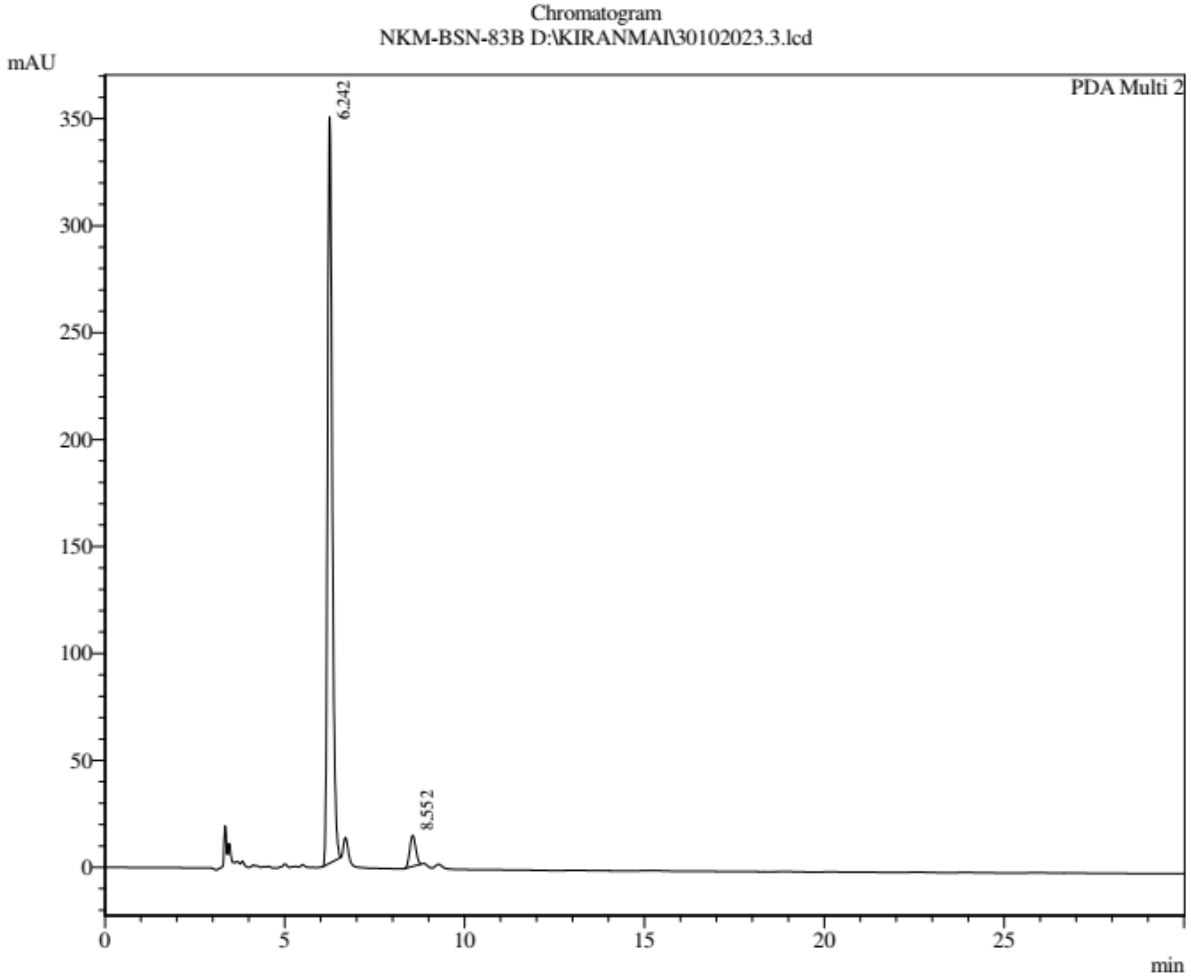
1 PDA Multi 5 / 320nm 4nm

PeakTable

PDA Ch5 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.235	2532417	305080	65.456	66.886
2	6.432	1336481	151040	34.544	33.114
Total		3868898	456120	100.000	100.000

HPLC Chromatogram of Compound 3b obtained from L2



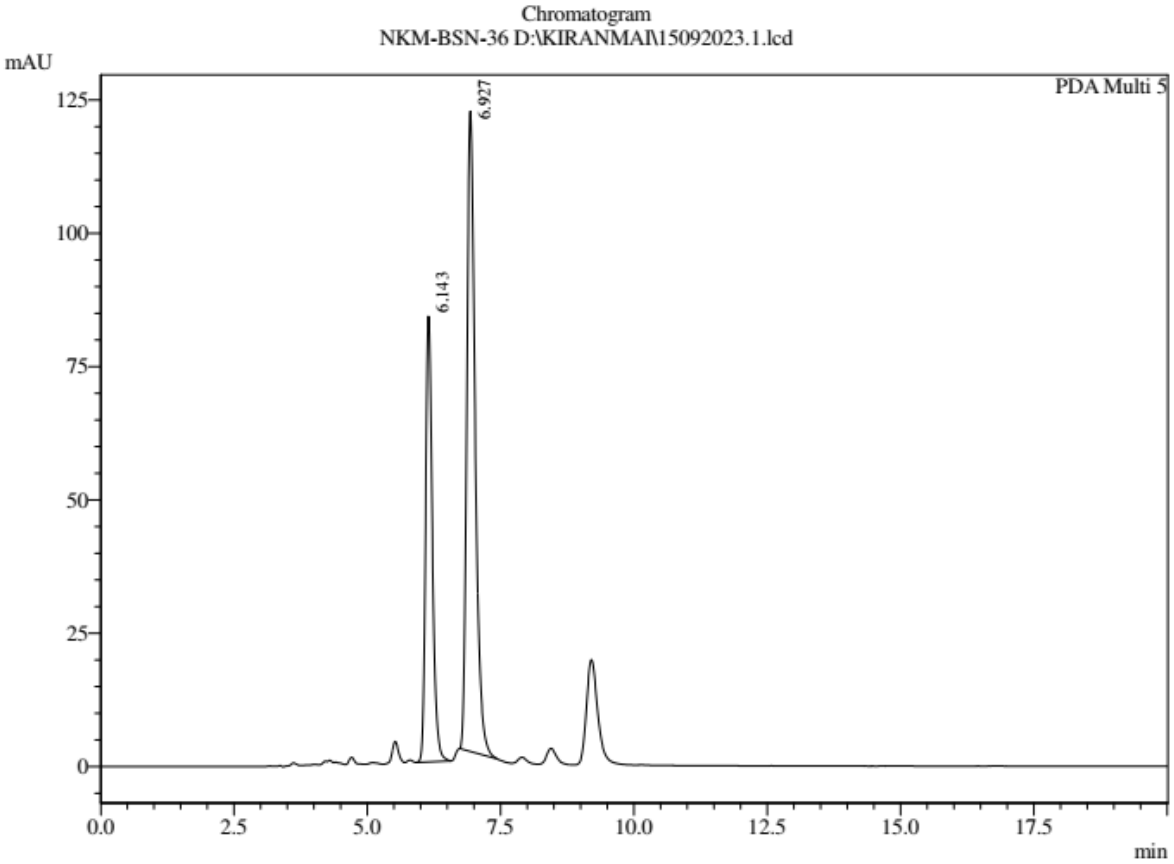
1 PDA Multi 2 / 225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.242	3138245	348860	94.963	96.018
2	8.552	166456	14468	5.037	3.982
Total		3304701	363327	100.000	100.000

HPLC Chromatogram of Compound 3c (racemic)



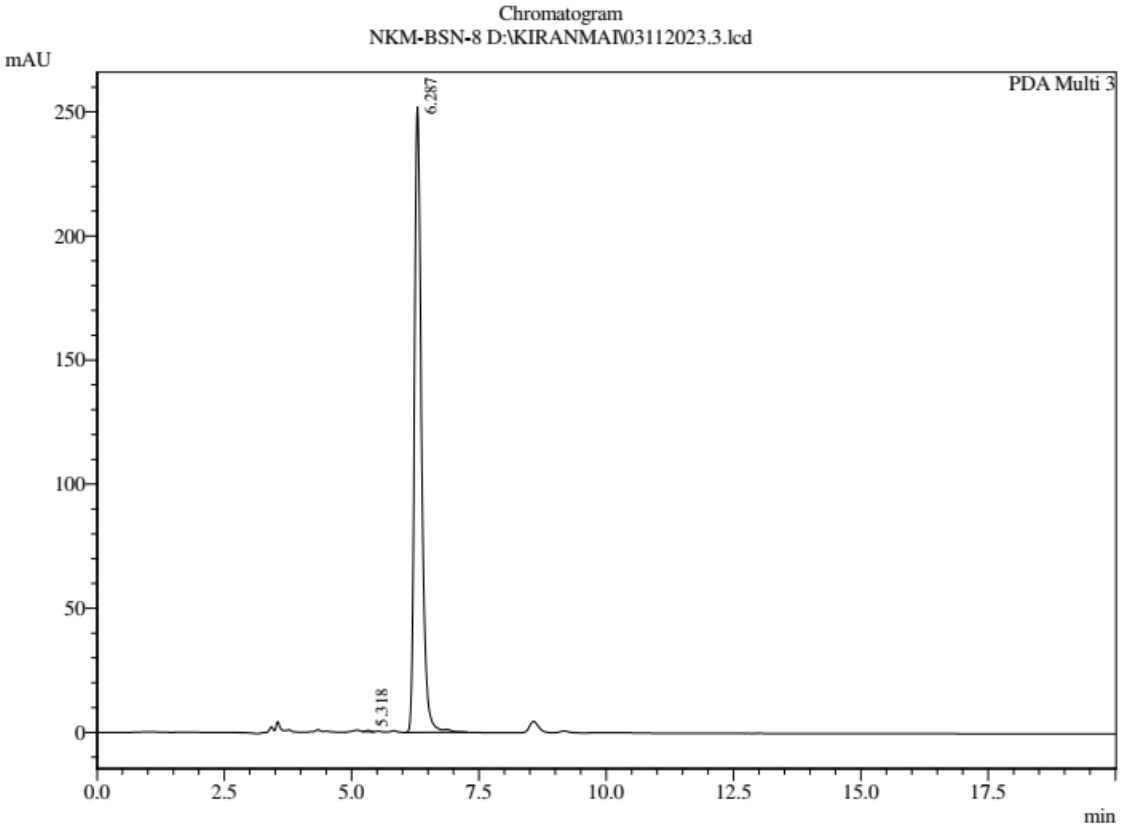
1 PDA Multi 5 / 320nm 4nm

PeakTable

PDA Ch5 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.143	740061	83560	36.130	41.049
2	6.927	1308244	120000	63.870	58.951
Total		2048305	203560	100.000	100.000

HPLC Chromatogram of Compound 3c obtained from L2



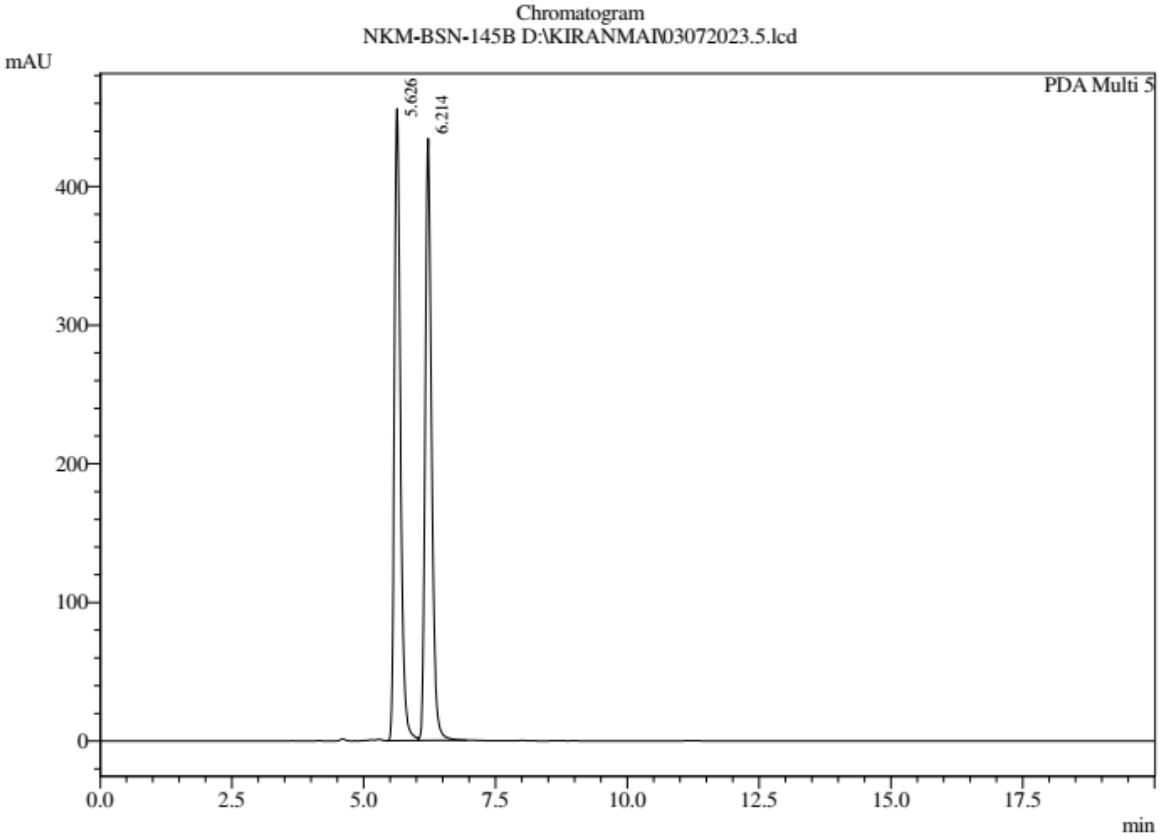
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.318	2908	485	0.120	0.192
2	6.287	2421033	251902	99.880	99.808
Total		2423941	252387	100.000	100.000

HPLC Chromatogram of Compound 3d (racemic)



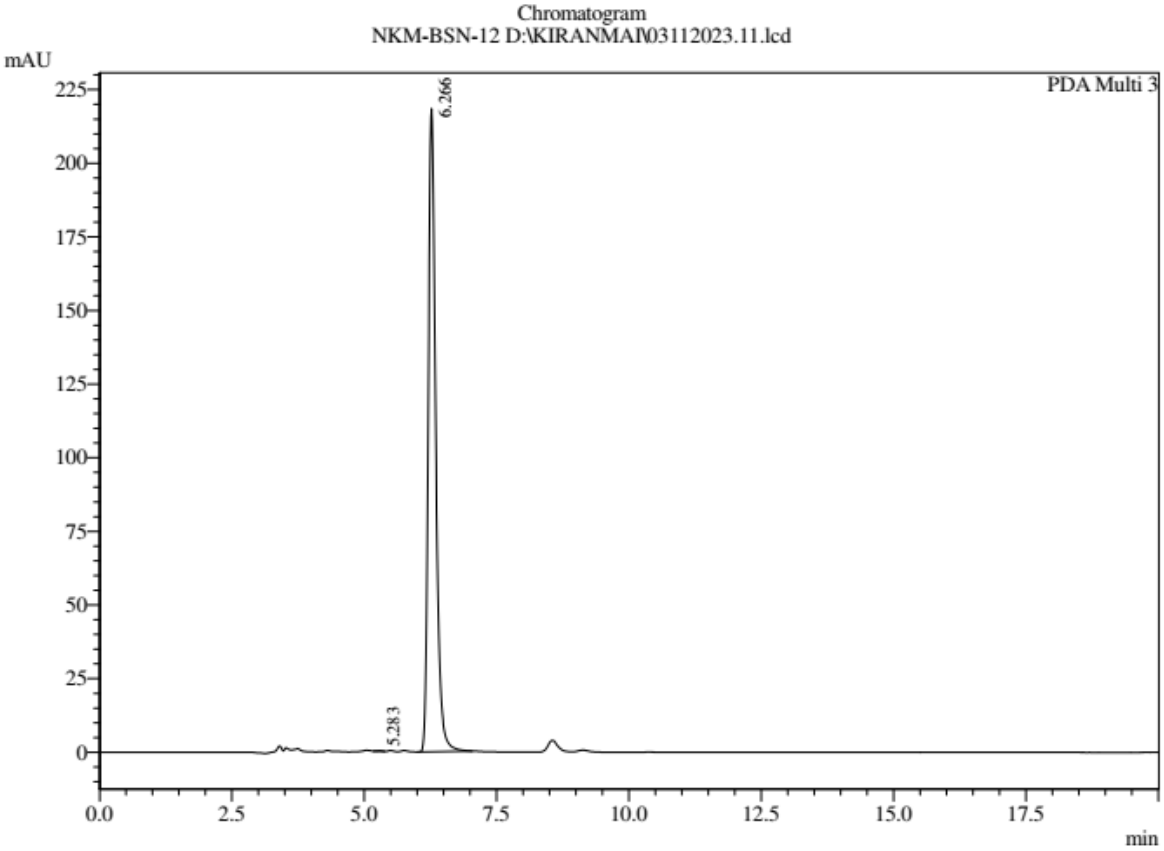
1 PDA Multi 5 / 320nm 4nm

PeakTable

PDA Ch5 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.626	3642337	455739	49.824	51.215
2	6.214	3668009	434113	50.176	48.785
Total		7310346	889852	100.000	100.000

HPLC Chromatogram of Compound 3d obtained from L2



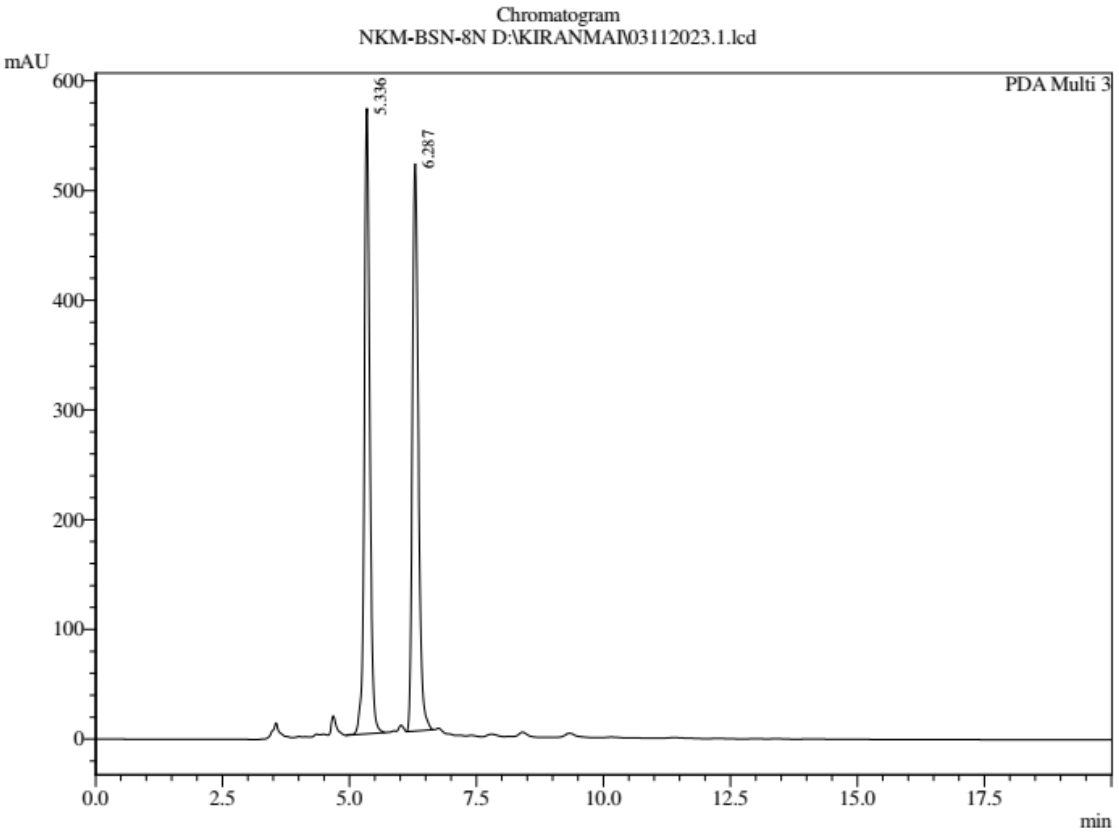
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.283	1122	164	0.053	0.075
2	6.266	2131781	218341	99.947	99.925
Total		2132903	218505	100.000	100.000

HPLC Chromatogram of Compound 3e (racemic)



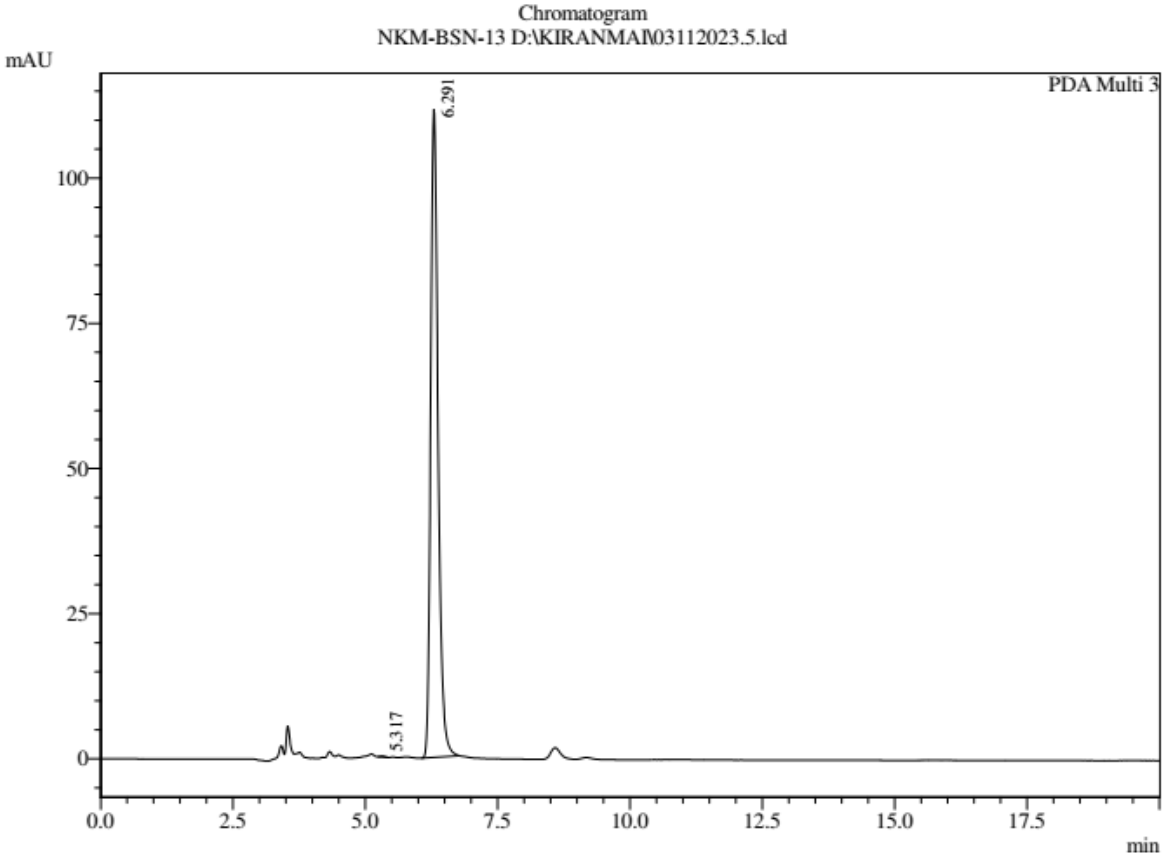
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.336	4219014	570177	50.030	52.428
2	6.287	4214030	517357	49.970	47.572
Total		8433044	1087534	100.000	100.000

HPLC Chromatogram of Compound 3e obtained from L2



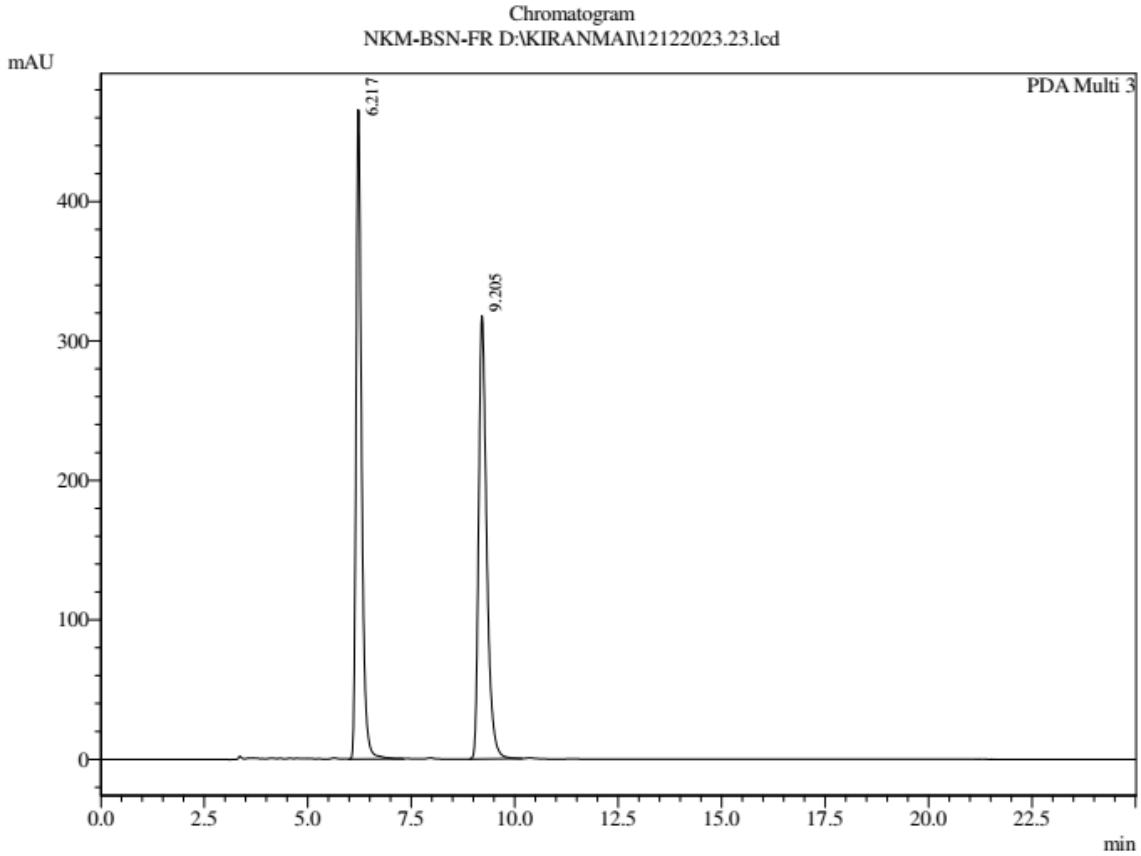
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.317	1018	165	0.094	0.148
2	6.291	1086296	111591	99.906	99.852
Total		1087314	111756	100.000	100.000

HPLC Chromatogram of Compound 3f (racemic)



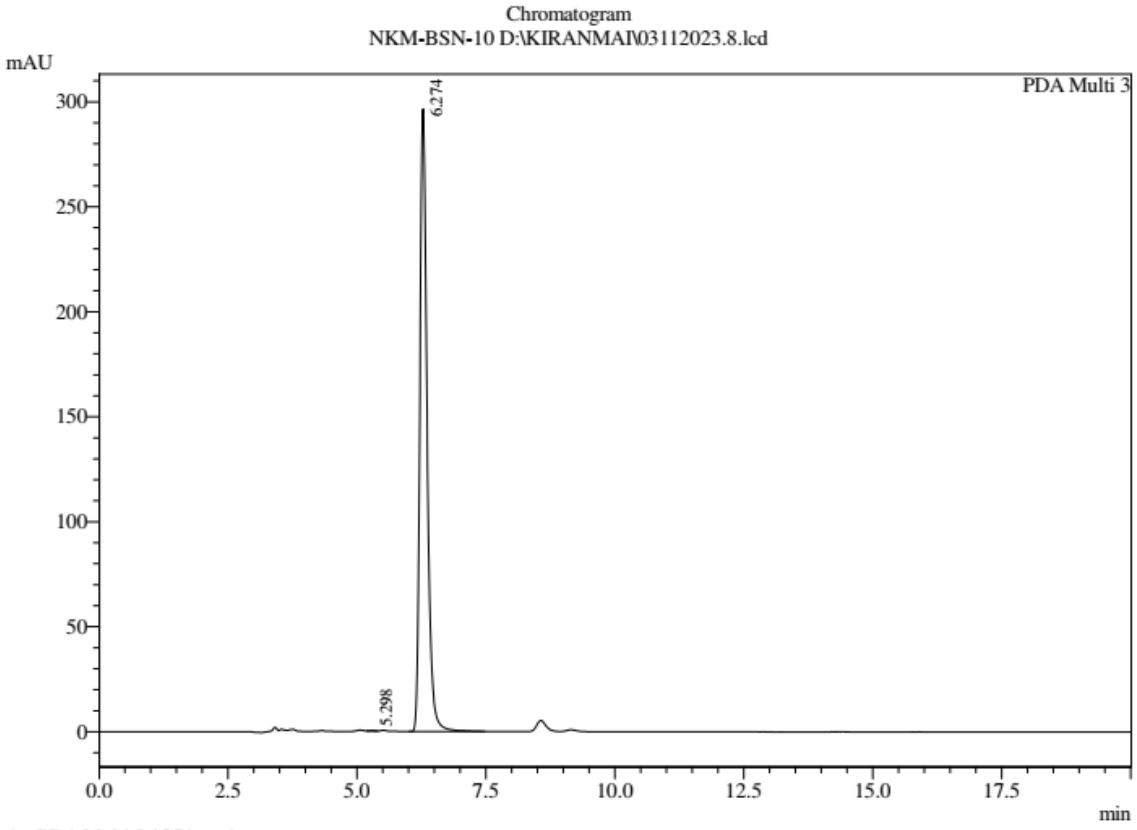
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.217	4336684	465520	50.254	59.443
2	9.205	4292924	317614	49.746	40.557
Total		8629608	783134	100.000	100.000

HPLC Chromatogram of Compound 3f obtained from L2



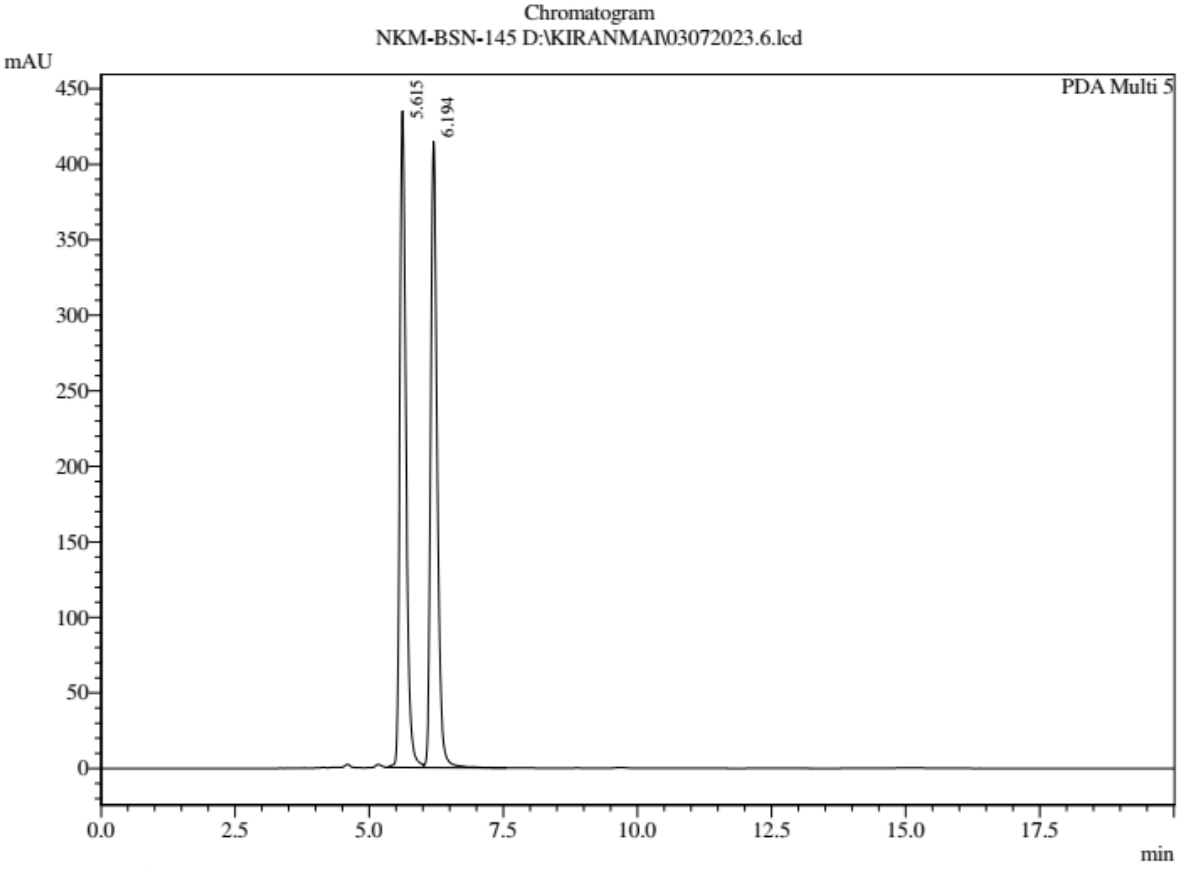
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.298	1399	202	0.048	0.068
2	6.274	2884245	296508	99.952	99.932
Total		2885645	296710	100.000	100.000

HPLC Chromatogram of Compound 3g (racemic)



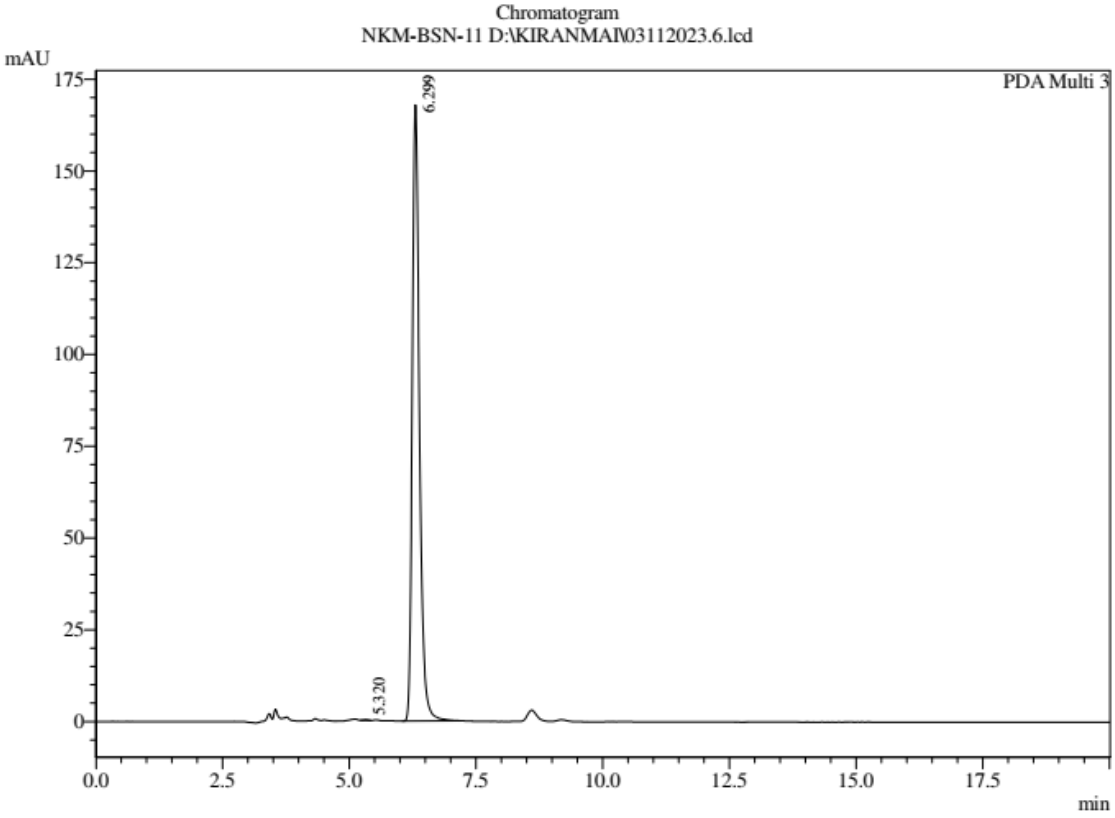
1 PDA Multi 5 / 320nm 4nm

PeakTable

PDA Ch5 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.615	3472909	434549	49.790	51.178
2	6.194	3502190	414552	50.210	48.822
Total		6975098	849101	100.000	100.000

HPLC Chromatogram of Compound 3g obtained from L2



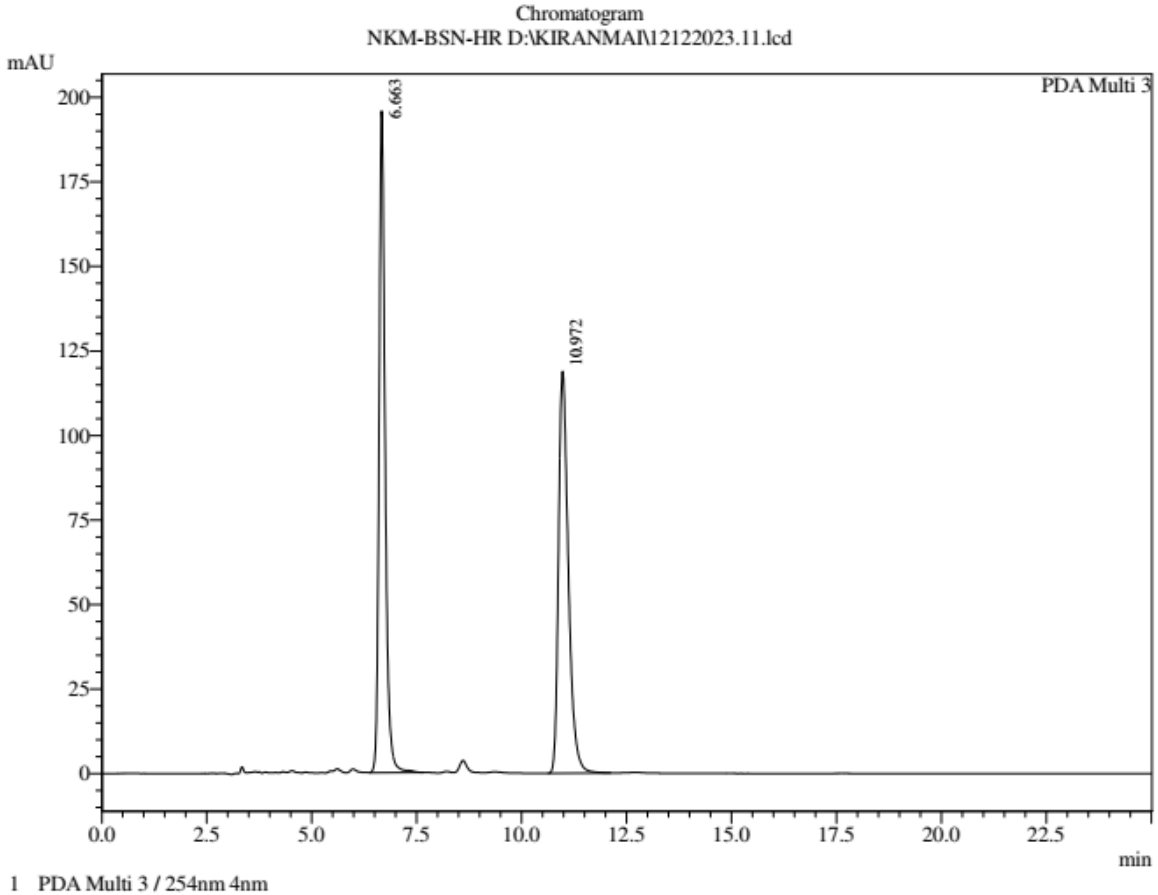
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.320	1134	181	0.069	0.108
2	6.299	1648596	167853	99.931	99.892
Total		1649731	168034	100.000	100.000

HPLC Chromatogram of Compound 3h (racemic)



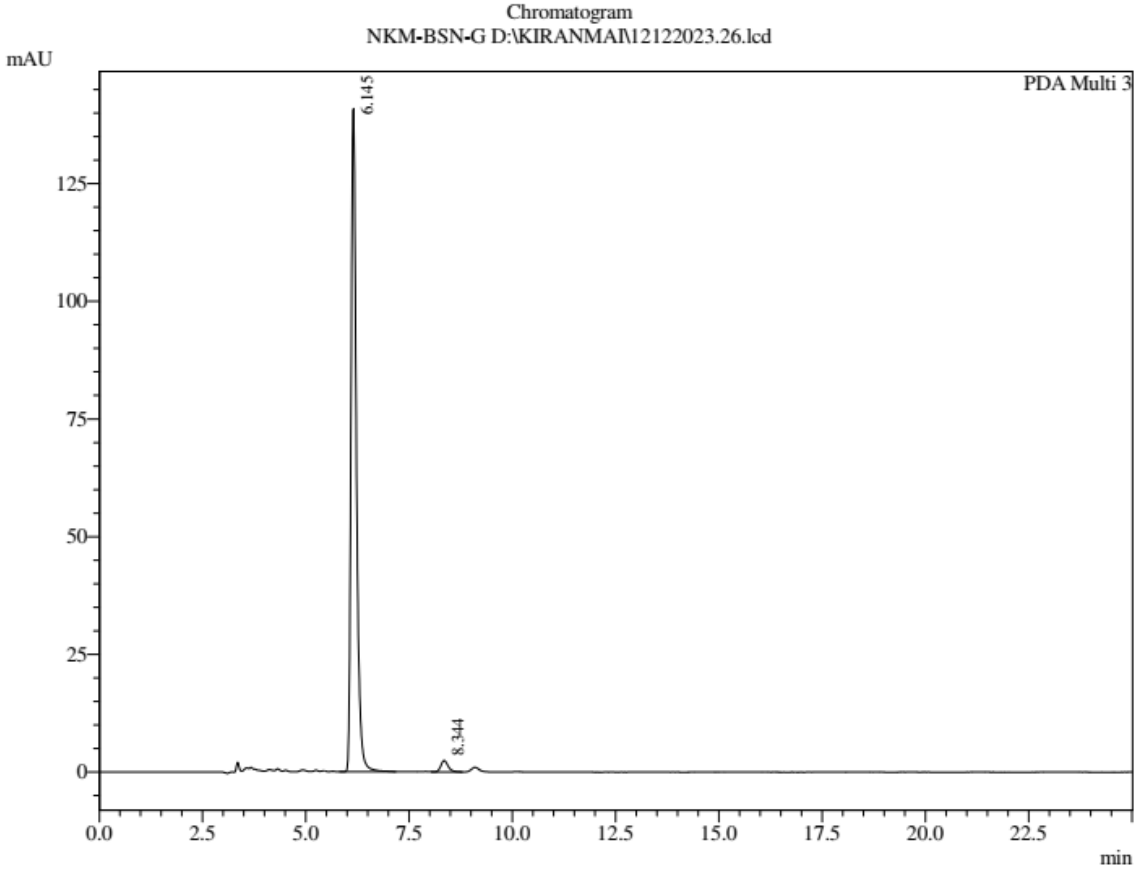
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.663	1979095	195689	50.575	62.203
2	10.972	1934068	118906	49.425	37.797
Total		3913163	314594	100.000	100.000

HPLC Chromatogram of Compound 3h obtained from L2



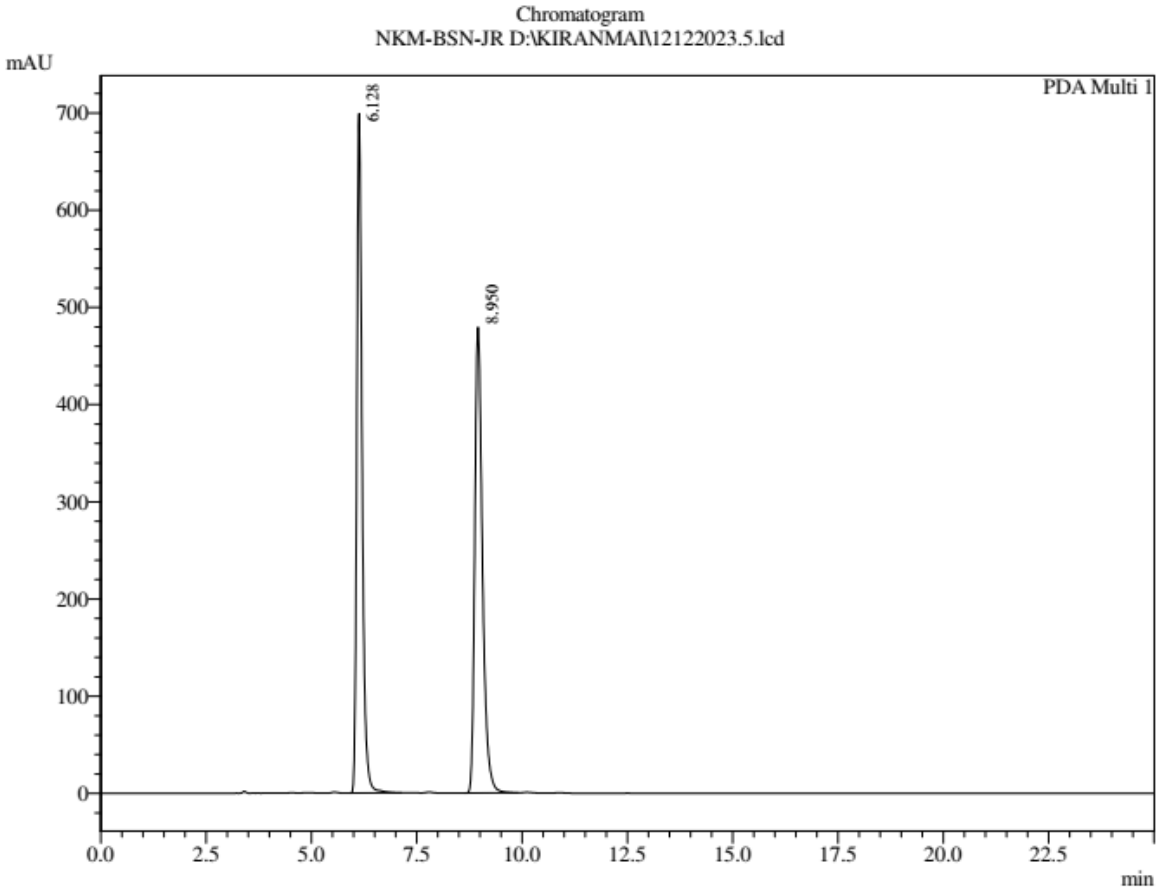
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.145	1265724	140876	97.711	98.312
2	8.344	29647	2418	2.289	1.688
Total		1295372	143295	100.000	100.000

HPLC Chromatogram of Compound 3i (racemic)



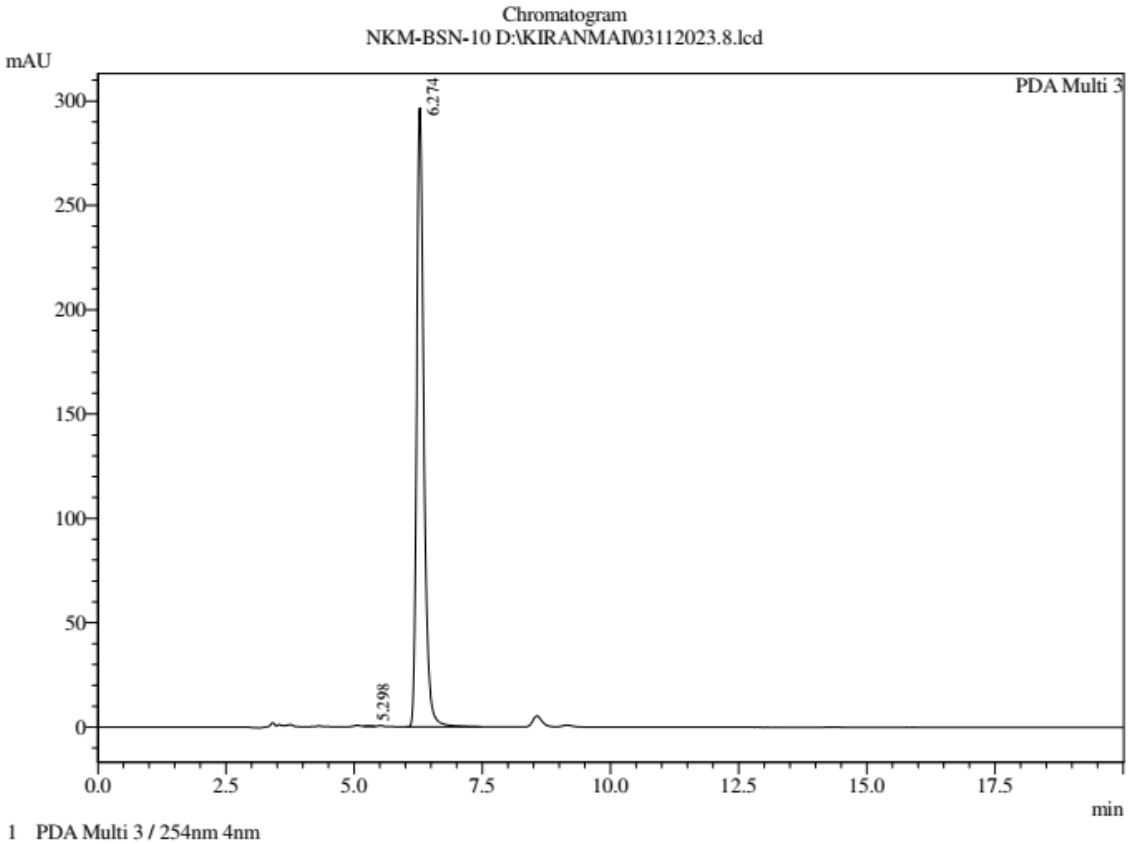
1 PDA Multi 1 / 280nm 4nm

PeakTable

PDA Ch1 280nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.128	6168546	699043	50.298	59.322
2	8.950	6095394	479347	49.702	40.678
Total		12263940	1178390	100.000	100.000

HPLC Chromatogram of Compound 3i obtained from L2



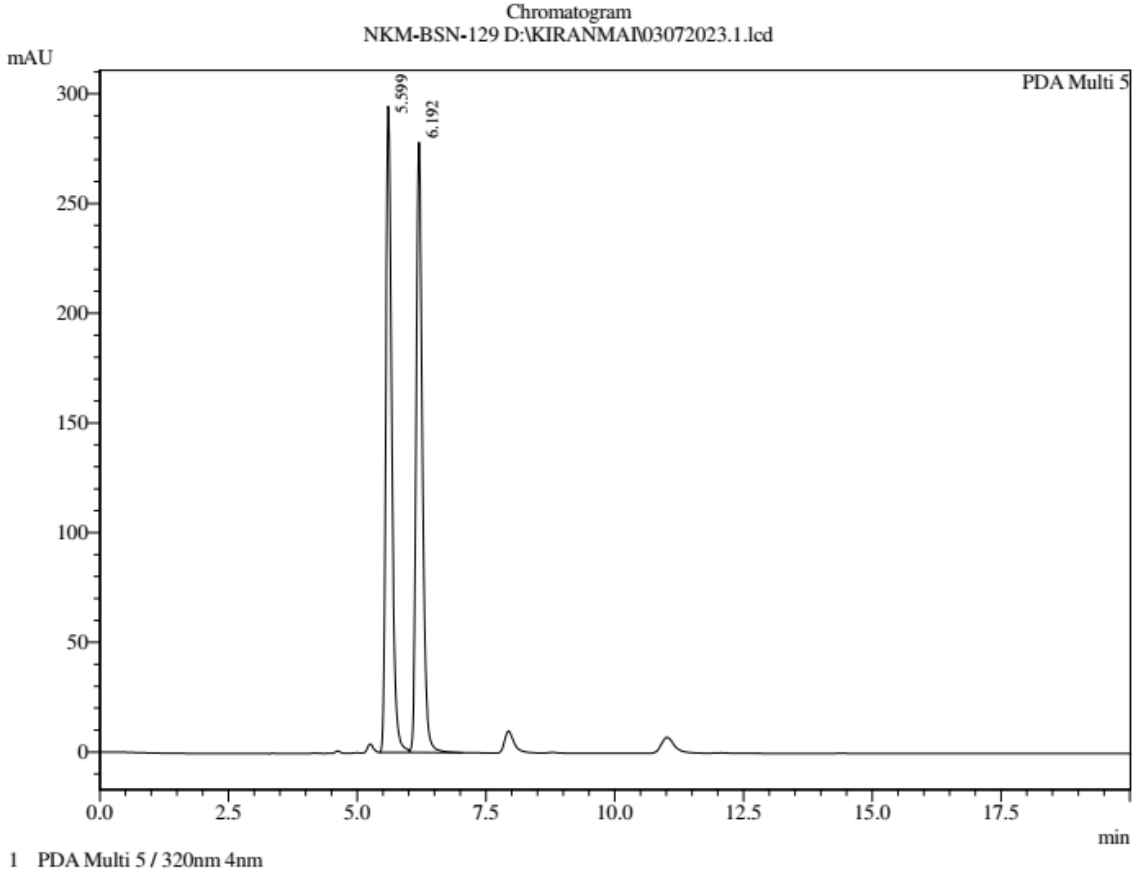
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.298	1399	202	0.048	0.068
2	6.274	2884245	296508	99.952	99.932
Total		2885645	296710	100.000	100.000

HPLC Chromatogram of Compound 3j (racemic)



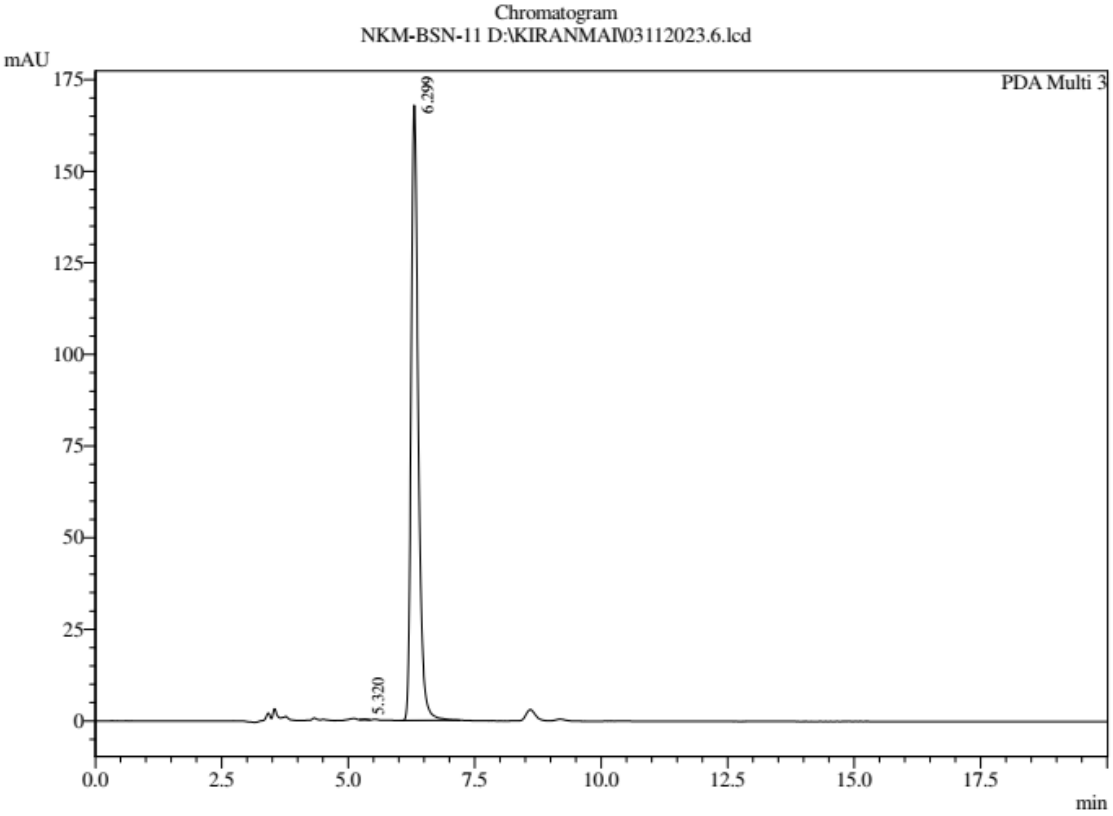
1 PDA Multi 5 / 320nm 4nm

PeakTable

PDA Ch5 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.599	2356483	294477	50.042	51.427
2	6.192	2352560	278132	49.958	48.573
Total		4709043	572609	100.000	100.000

HPLC Chromatogram of Compound 3j obtained from L2



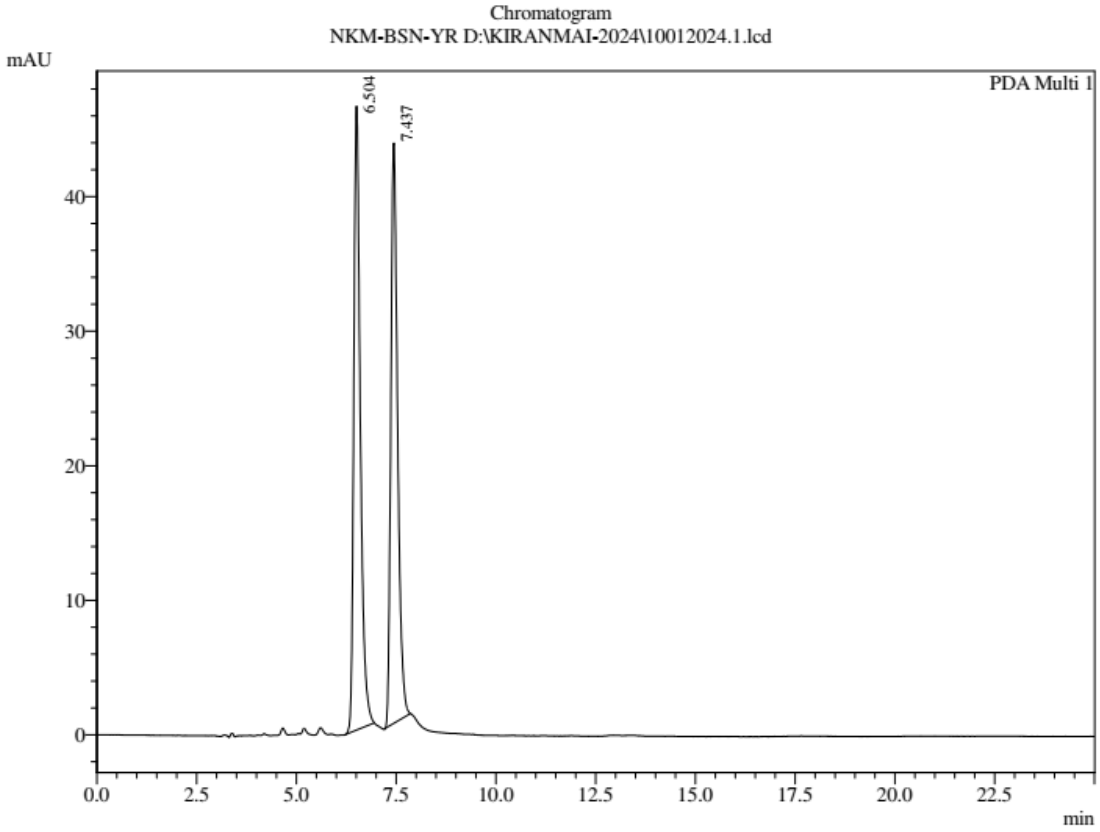
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.320	1134	181	0.069	0.108
2	6.299	1648596	167853	99.931	99.892
Total		1649731	168034	100.000	100.000

HPLC Chromatogram of Compound 3k (racemic)



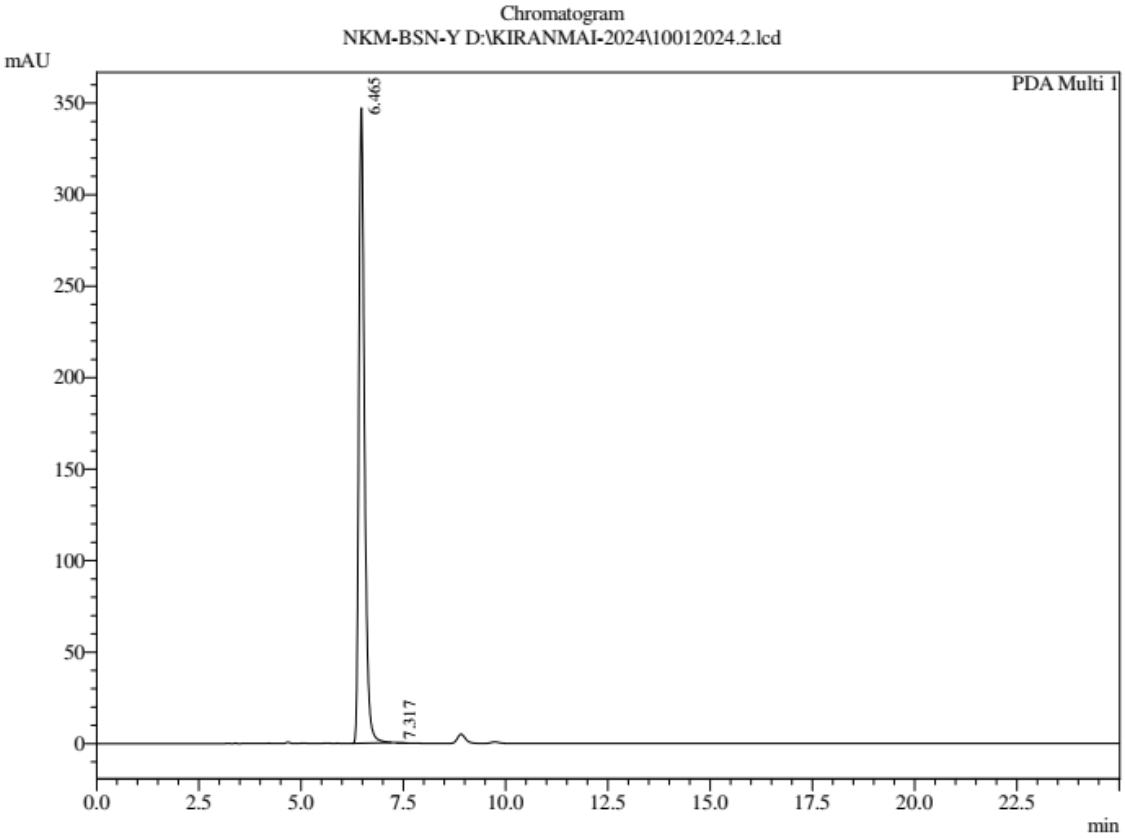
1 PDA Multi 1 / 320nm 4nm

PeakTable

PDA Ch1 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.504	527457	46363	50.894	51.798
2	7.437	508921	43144	49.106	48.202
Total		1036378	89507	100.000	100.000

HPLC Chromatogram of Compound 3k obtained from L2



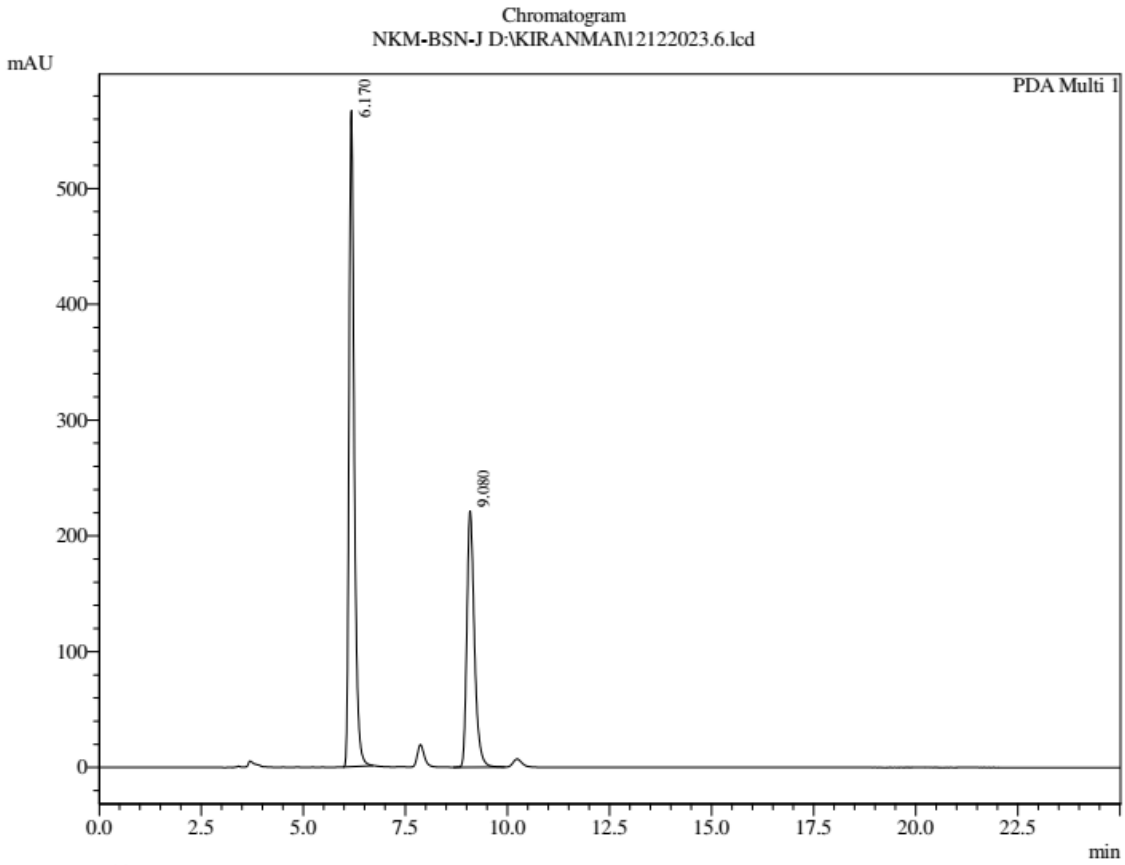
1 PDA Multi 1 / 320nm 4nm

PeakTable

PDA Ch1 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.465	3339035	347200	99.998	100.000
2	7.317	78	0	0.002	0.000
Total		3339113	347200	100.000	100.000

HPLC Chromatogram of Compound 3l (racemic)



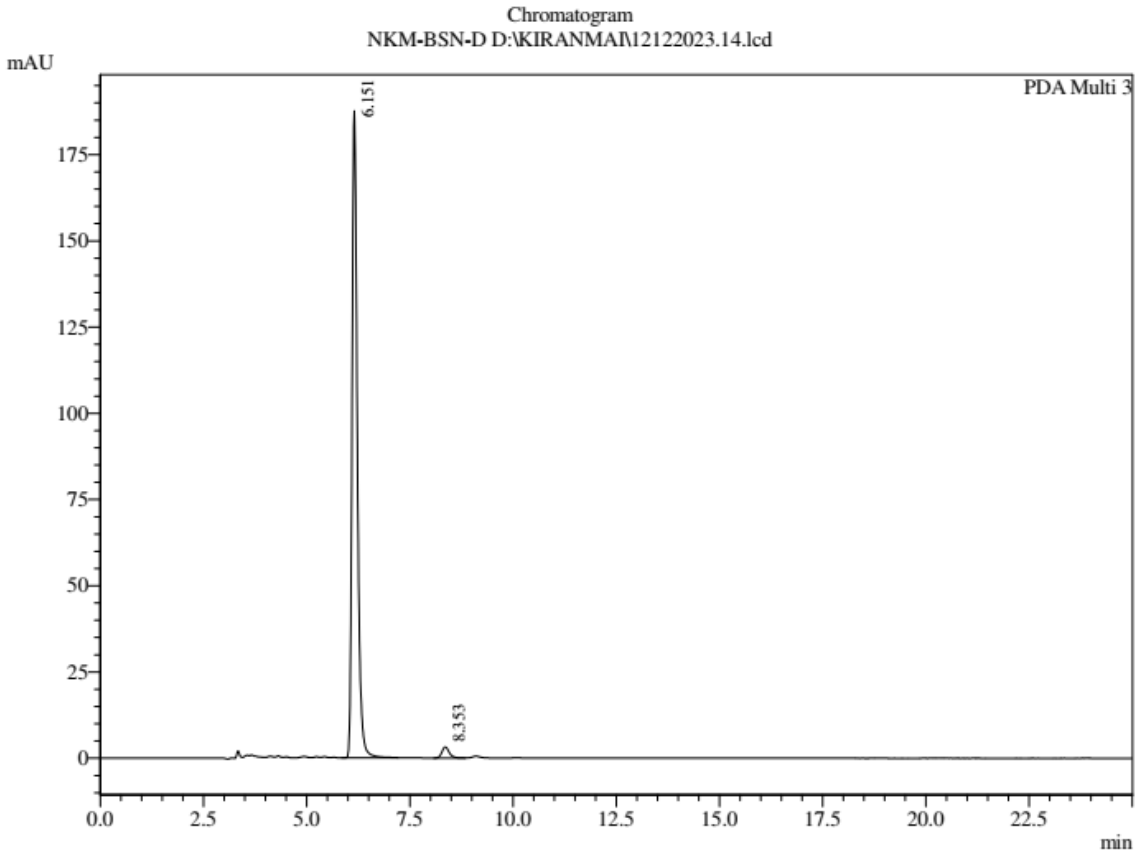
1 PDA Multi 1 / 280nm 4nm

PeakTable

PDA Ch1 280nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.170	5013545	566510	63.830	71.922
2	9.080	2841006	221165	36.170	28.078
Total		7854551	787675	100.000	100.000

HPLC Chromatogram of Compound 3l obtained from L2



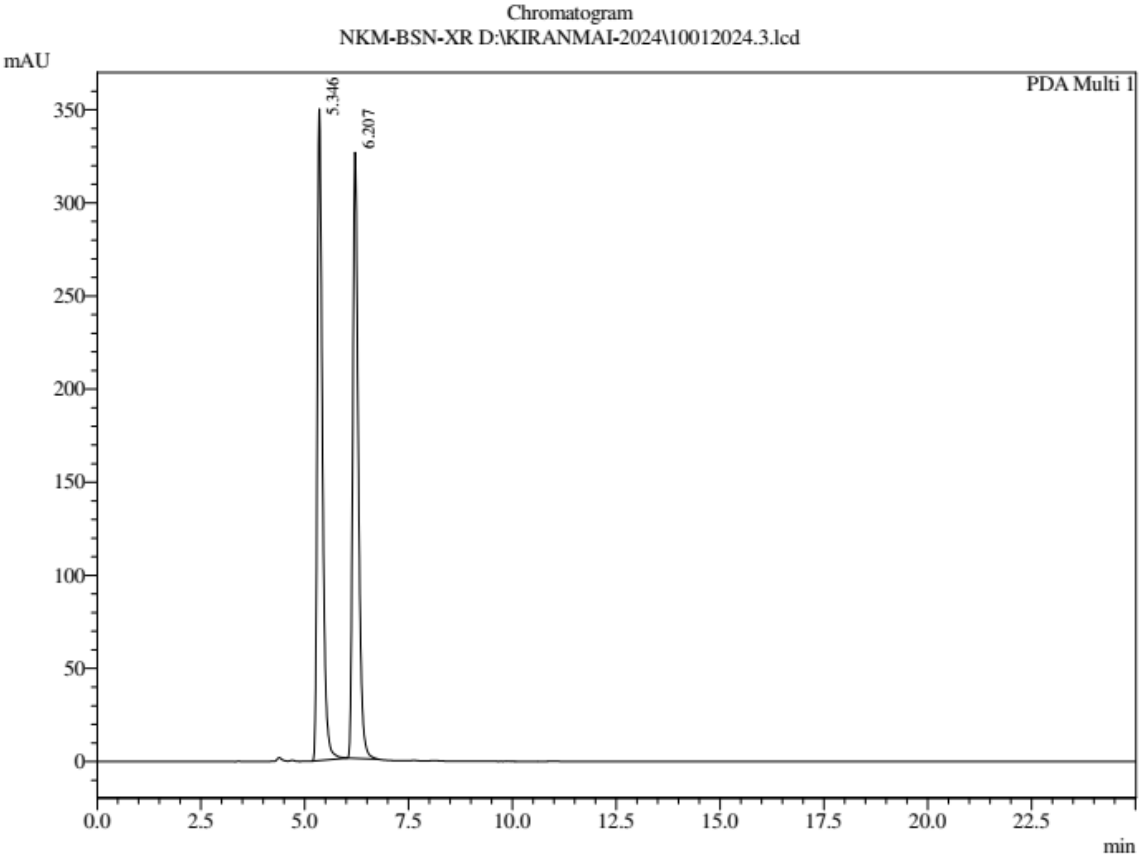
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.151	1663360	187581	97.702	98.325
2	8.353	39125	3196	2.298	1.675
Total		1702486	190777	100.000	100.000

HPLC Chromatogram of Compound 3m (racemic)



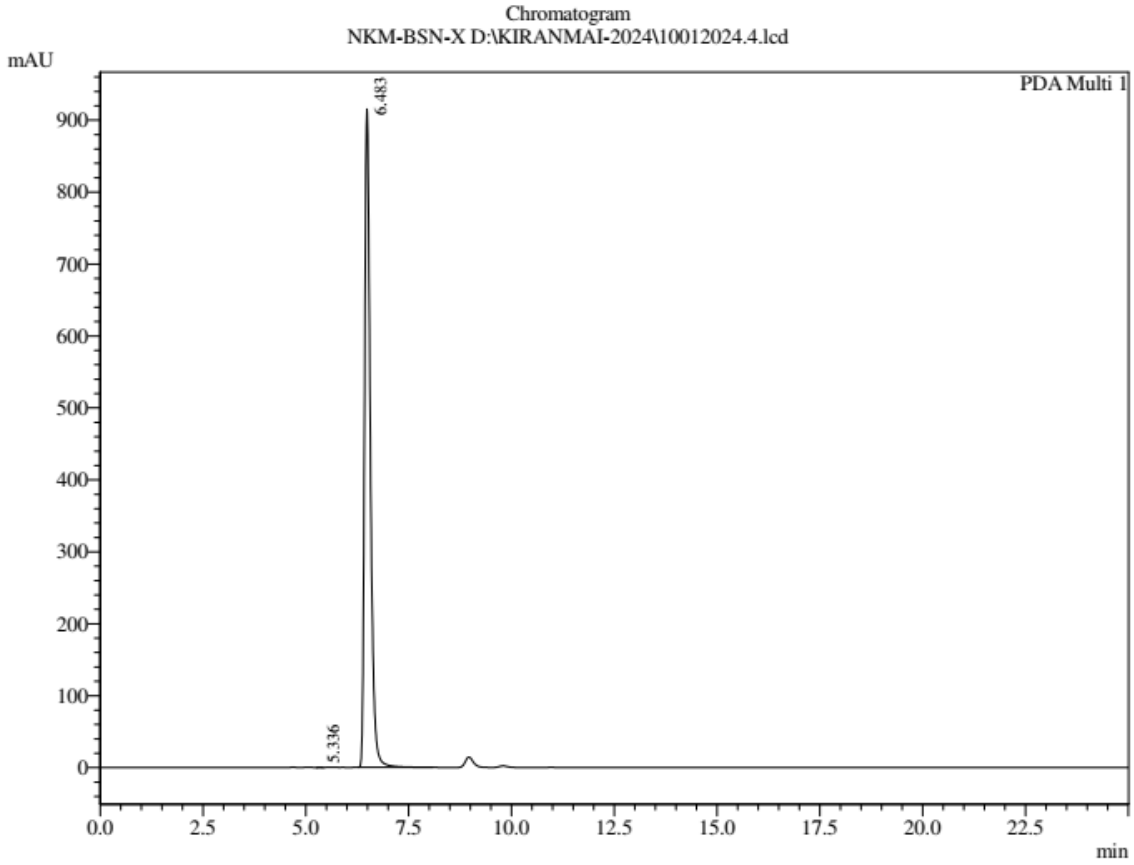
1 PDA Multi 1 / 320nm 4nm

PeakTable

PDA Ch1 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.346	3045691	349892	50.108	51.807
2	6.207	3032582	325488	49.892	48.193
Total		6078272	675380	100.000	100.000

HPLC Chromatogram of Compound 3m obtained from L2



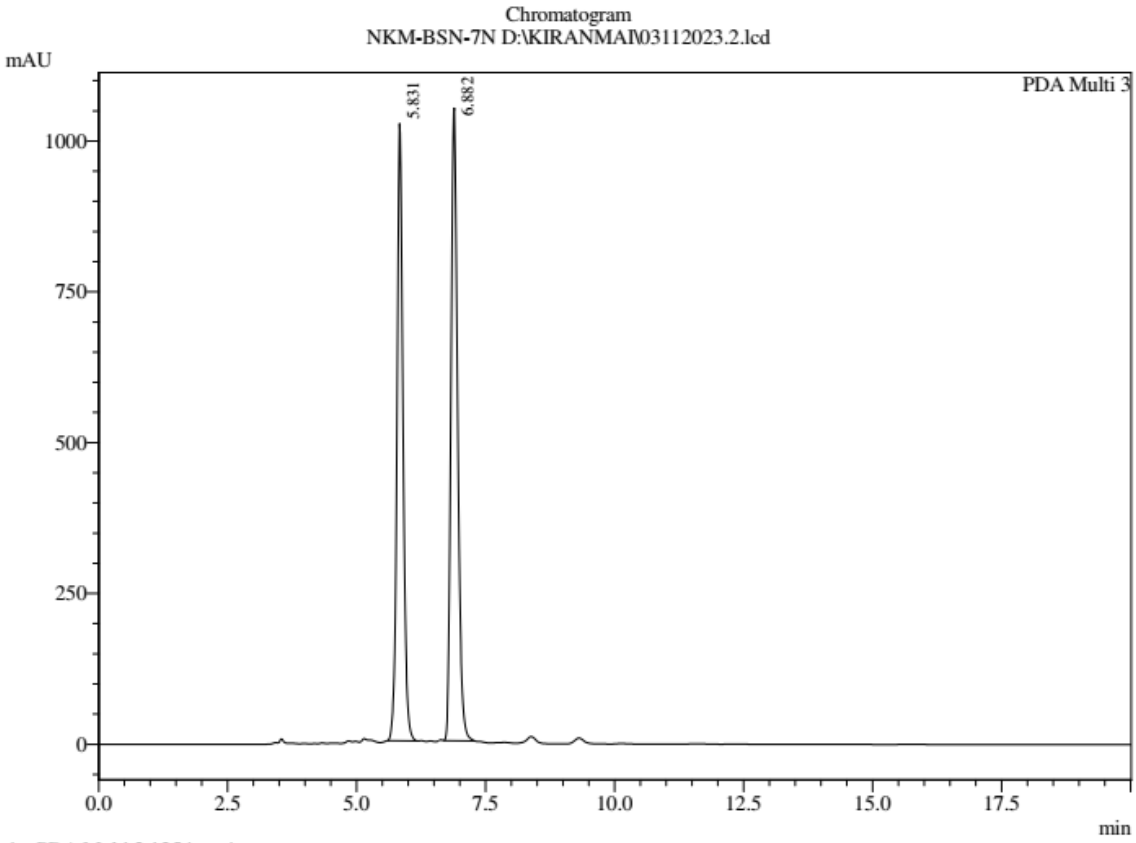
1 PDA Multi 1 / 320nm 4nm

PeakTable

PDA Ch1 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.336	838	147	0.009	0.016
2	6.483	8935358	915368	99.991	99.984
Total		8936196	915515	100.000	100.000

HPLC Chromatogram of Compound 3n (racemic)



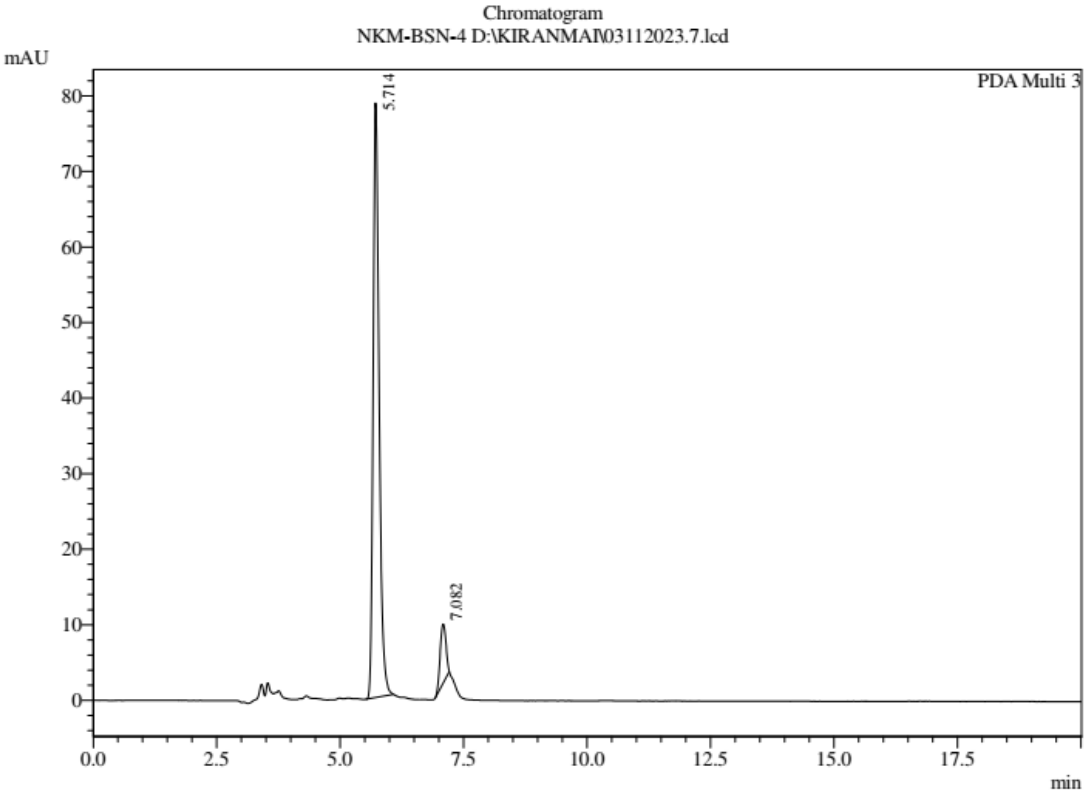
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.831	8364482	1022783	46.873	49.375
2	6.882	9480477	1048693	53.127	50.625
Total		17844959	2071476	100.000	100.000

HPLC Chromatogram of Compound 3n obtained from L2



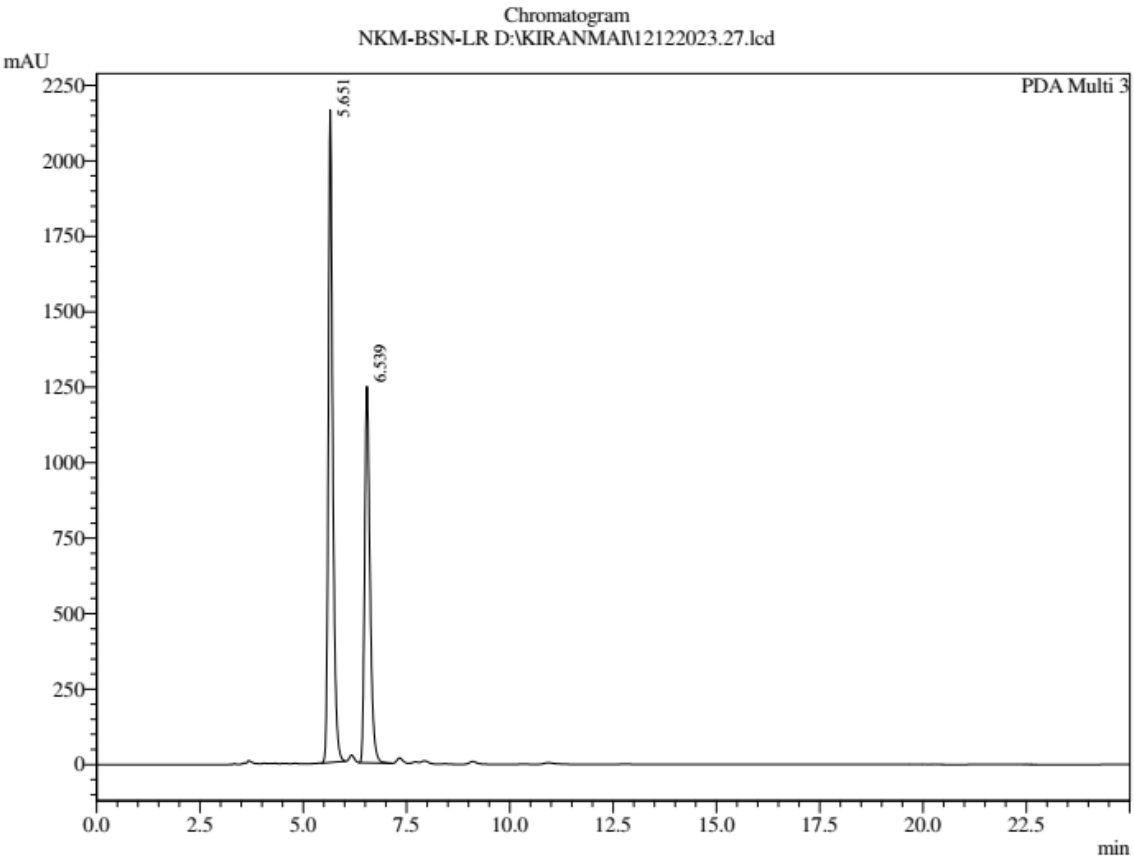
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.714	663709	78679	91.074	90.916
2	7.082	65053	7861	8.926	9.084
Total		728762	86540	100.000	100.000

HPLC Chromatogram of Compound 3o (racemic)



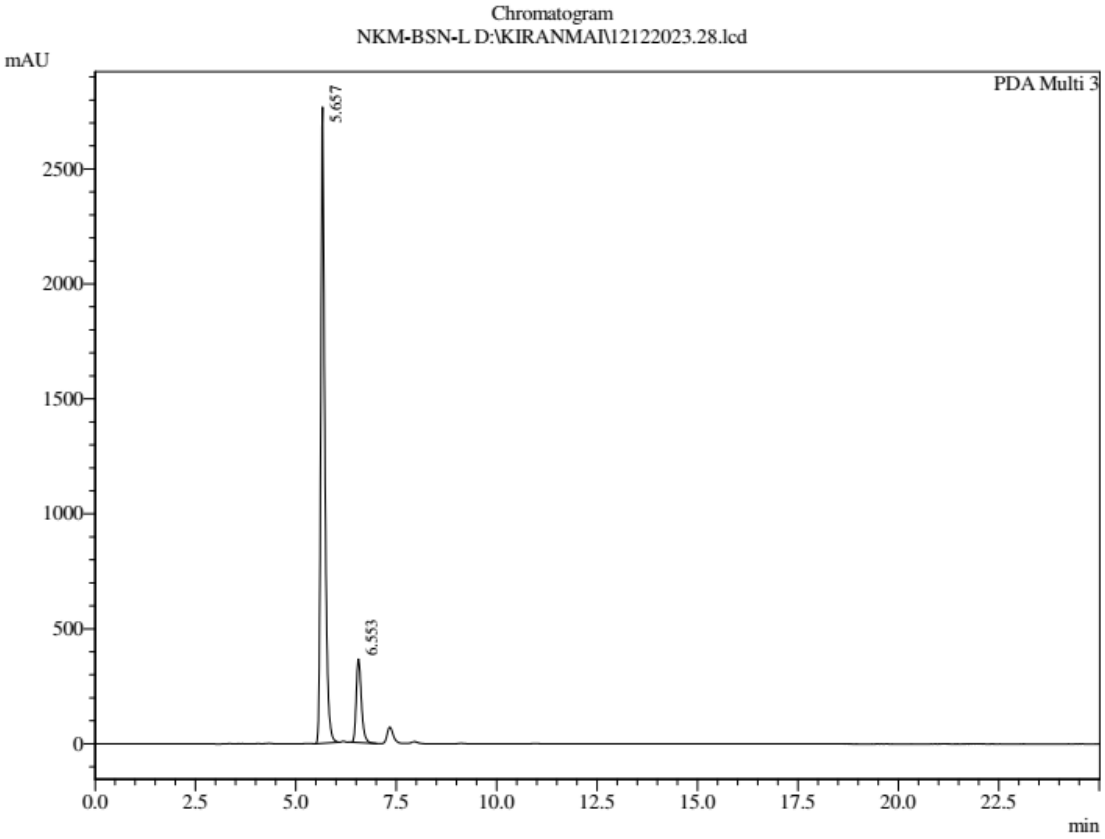
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.651	16326230	2161053	59.350	63.418
2	6.539	11182253	1246599	40.650	36.582
Total		27508483	3407652	100.000	100.000

HPLC Chromatogram of Compound 3o obtained from L2



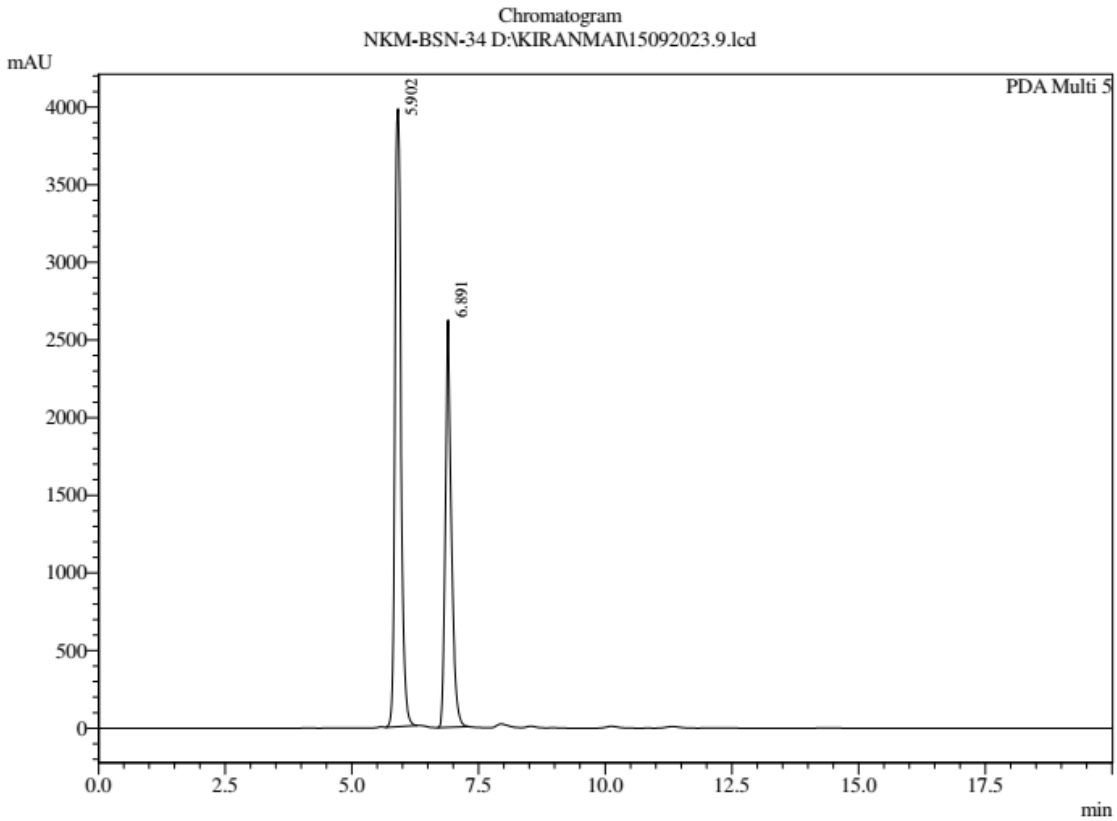
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.657	19147446	2766508	85.560	88.412
2	6.553	3231652	362612	14.440	11.588
Total		22379097	3129119	100.000	100.000

HPLC Chromatogram of Compound 3p (racemic)



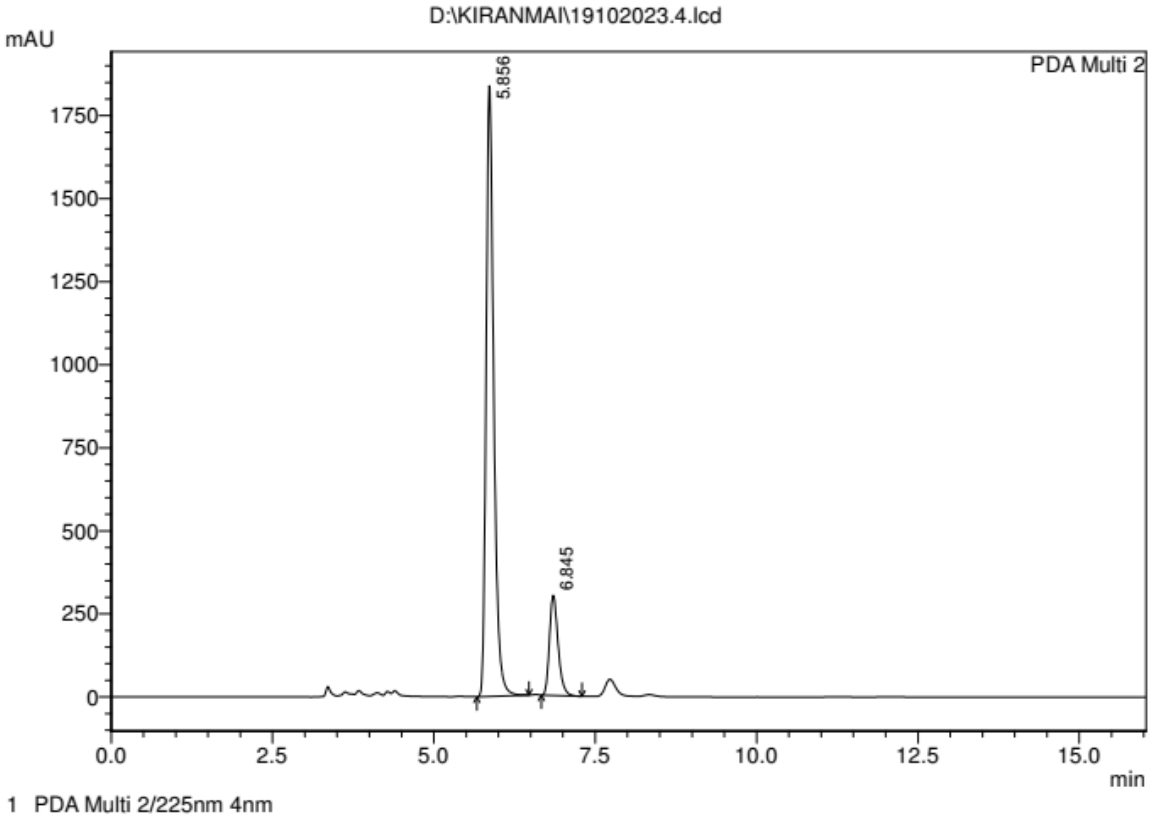
1 PDA Multi 5 / 320nm 4nm

PeakTable

PDA Ch5 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.902	32952166	3979137	60.376	60.267
2	6.891	21625999	2623375	39.624	39.733
Total		54578165	6602512	100.000	100.000

HPLC Chromatogram of Compound 3p obtained from L2



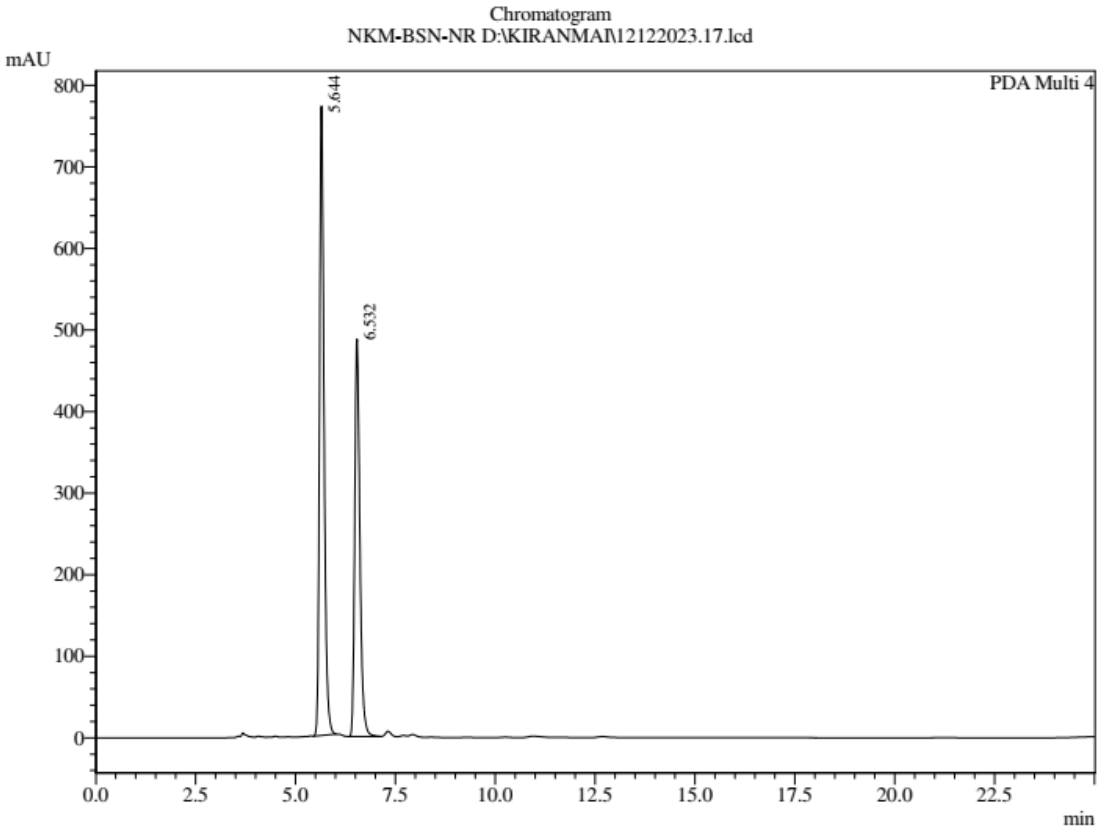
1 PDA Multi 2/225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.856	15172908	1838381	84.283	85.897
2	6.845	2829528	301833	15.717	14.103
Total		18002436	2140214	100.000	100.000

HPLC Chromatogram of Compound 3q (racemic)



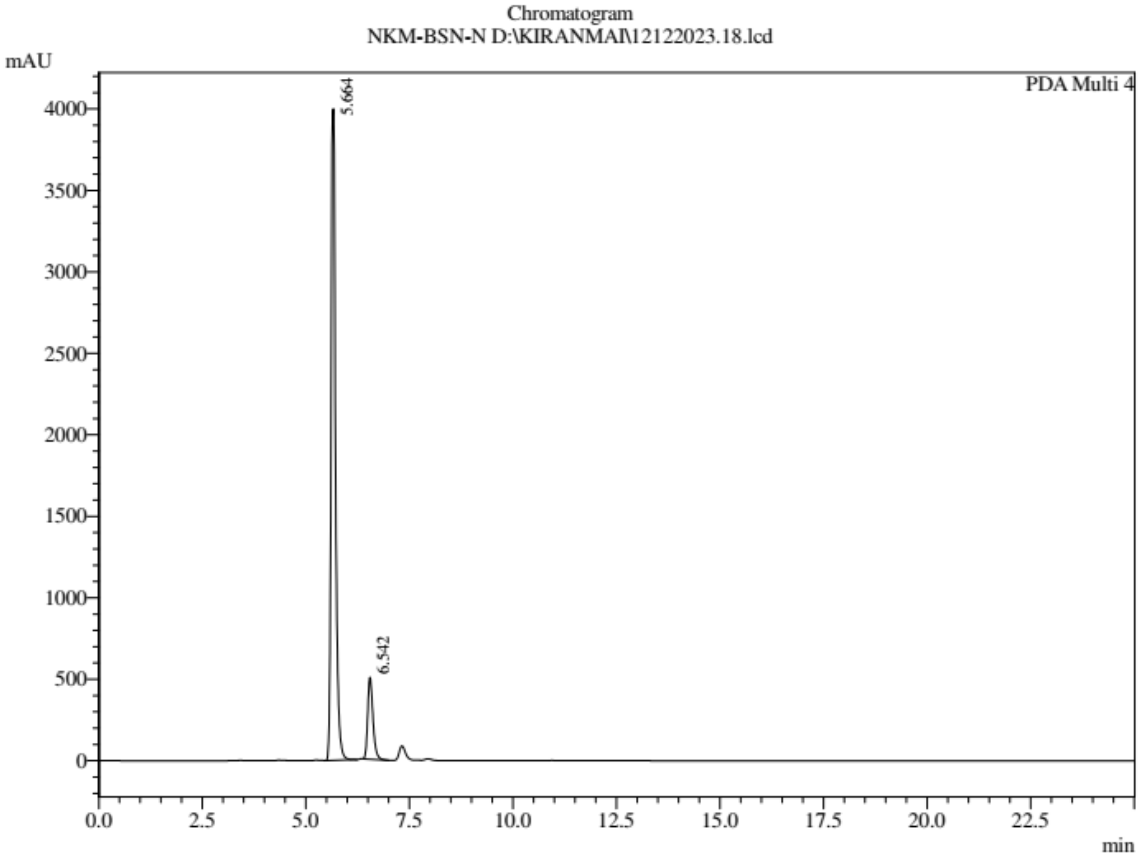
1 PDA Multi 4 / 280nm 4nm

PeakTable

PDA Ch4 280nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.644	6091248	771532	58.337	61.292
2	6.532	4350318	487252	41.663	38.708
Total		10441566	1258785	100.000	100.000

HPLC Chromatogram of Compound 3q obtained from L2



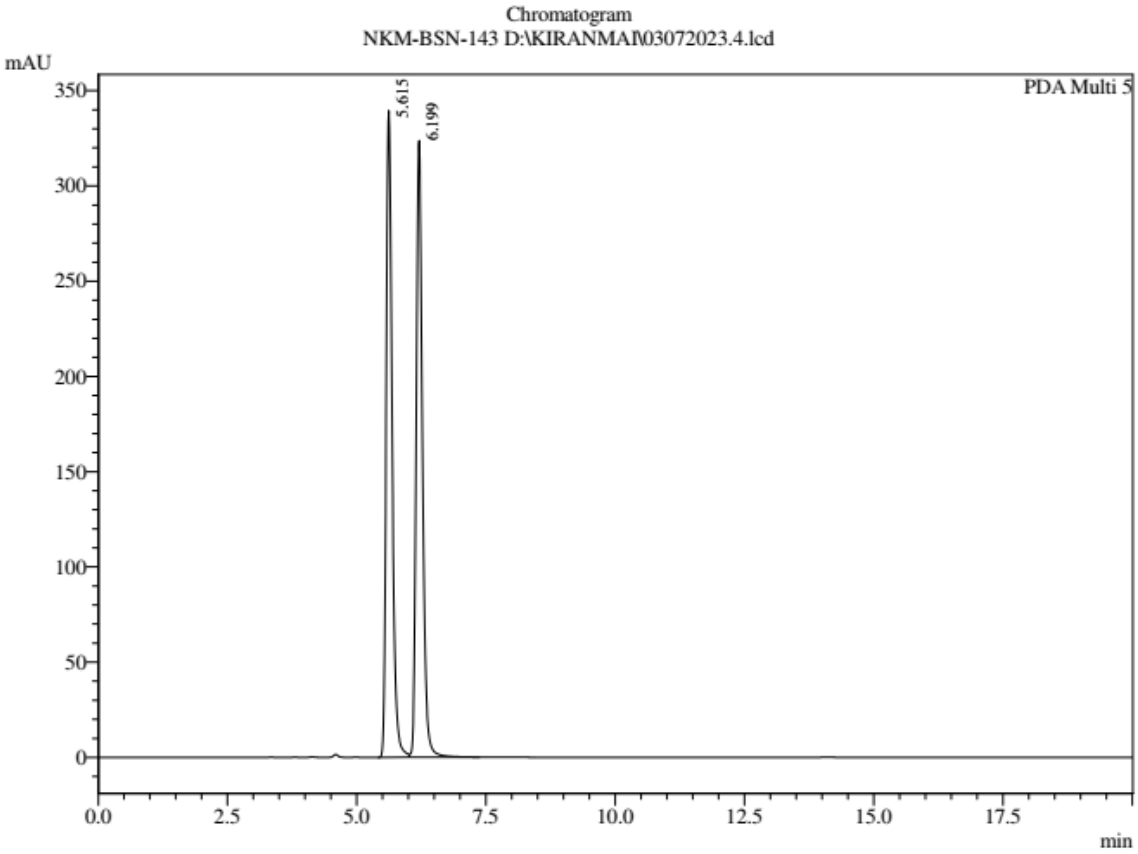
1 PDA Multi 4 / 280nm 4nm

PeakTable

PDA Ch4 280nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.664	29698482	3997286	87.027	88.834
2	6.542	4427108	502429	12.973	11.166
Total		34125590	4499715	100.000	100.000

HPLC Chromatogram of Compound 3r (racemic)



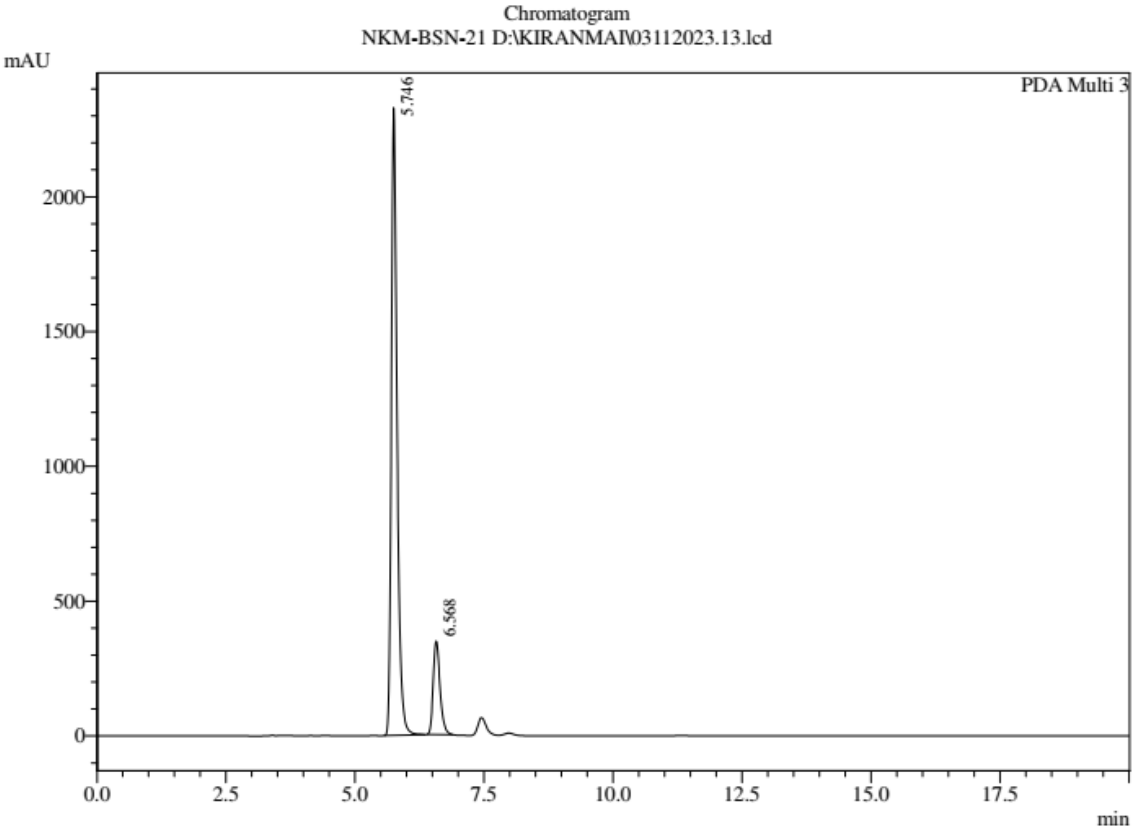
1 PDA Multi 5 / 320nm 4nm

PeakTable

PDA Ch5 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.615	2698176	339512	49.657	51.192
2	6.199	2735444	323706	50.343	48.808
Total		5433620	663218	100.000	100.000

HPLC Chromatogram of Compound 3r obtained from L2



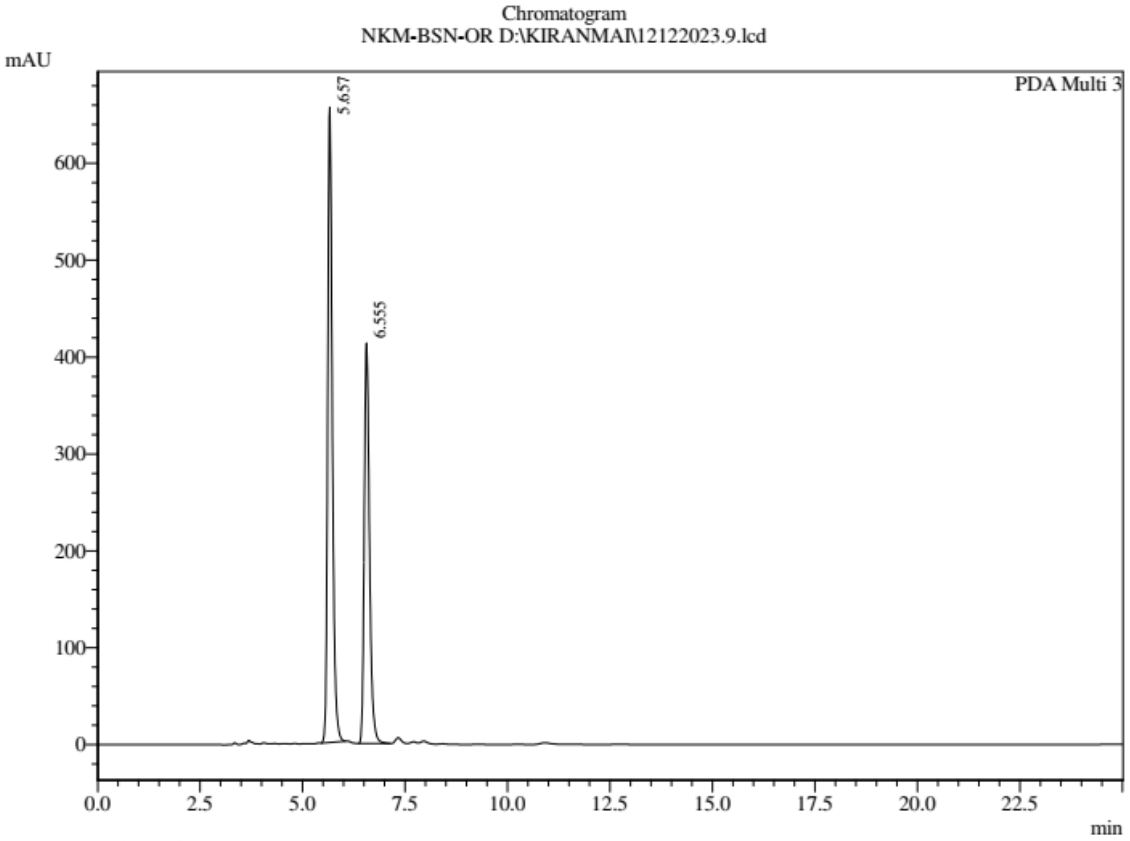
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.746	17987910	2327807	84.991	87.040
2	6.568	3176589	346601	15.009	12.960
Total		21164499	2674408	100.000	100.000

HPLC Chromatogram of Compound 3s (racemic)



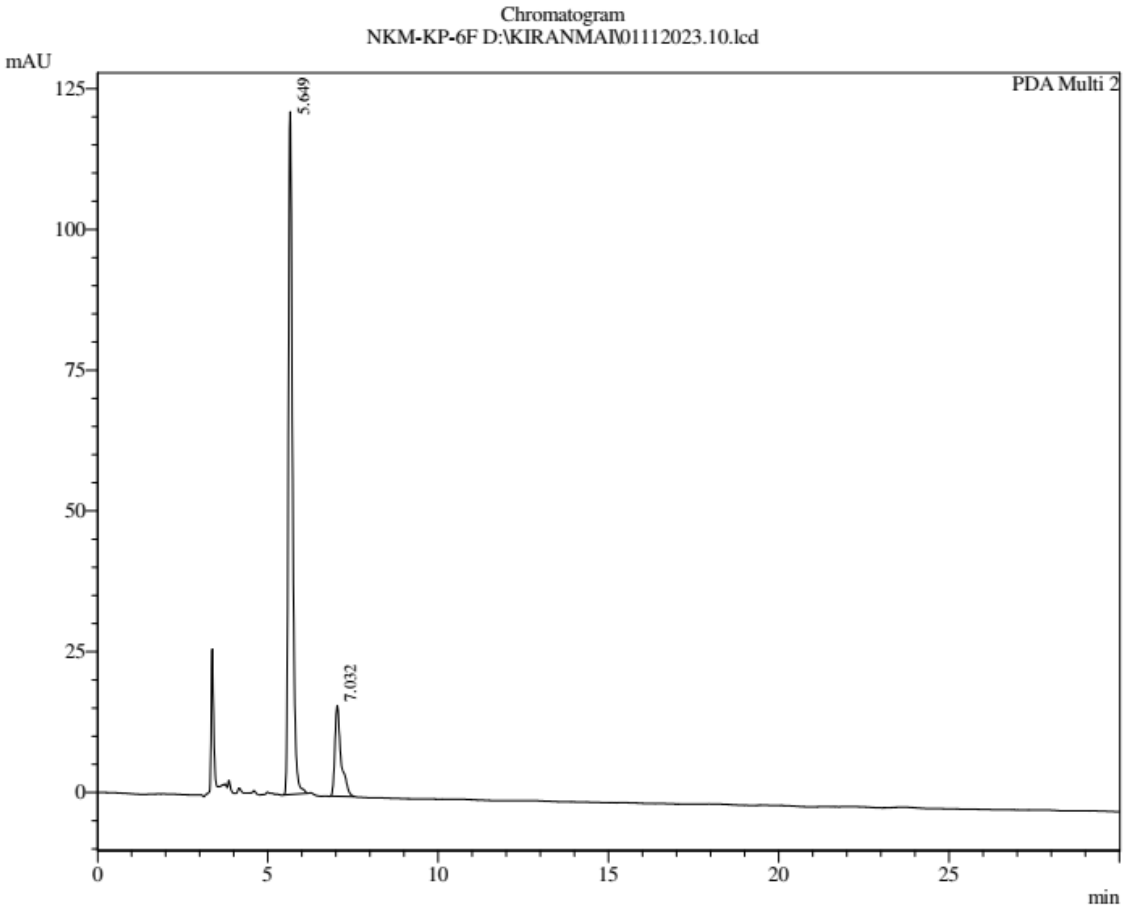
1 PDA Multi 3 / 254nm 4nm

PeakTable

PDA Ch3 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.657	5157440	655652	58.453	61.340
2	6.555	3665714	413223	41.547	38.660
Total		8823154	1068875	100.000	100.000

HPLC Chromatogram of Compound 3s obtained from L2



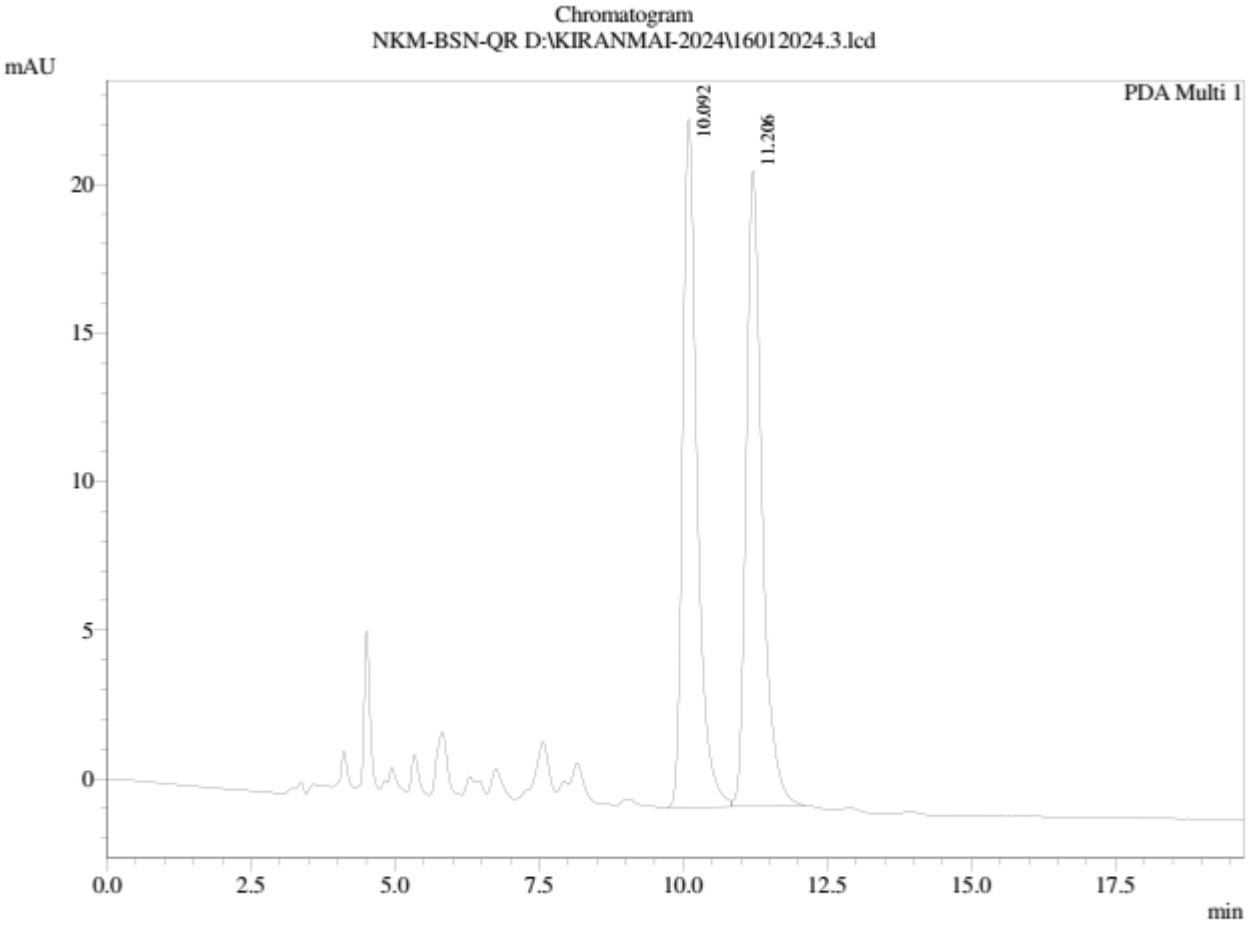
1 PDA Multi 2 / 225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.649	1026016	121212	83.491	88.272
2	7.032	202882	16104	16.509	11.728
Total		1228898	137316	100.000	100.000

HPLC Chromatogram of Compound 3t (racemic)



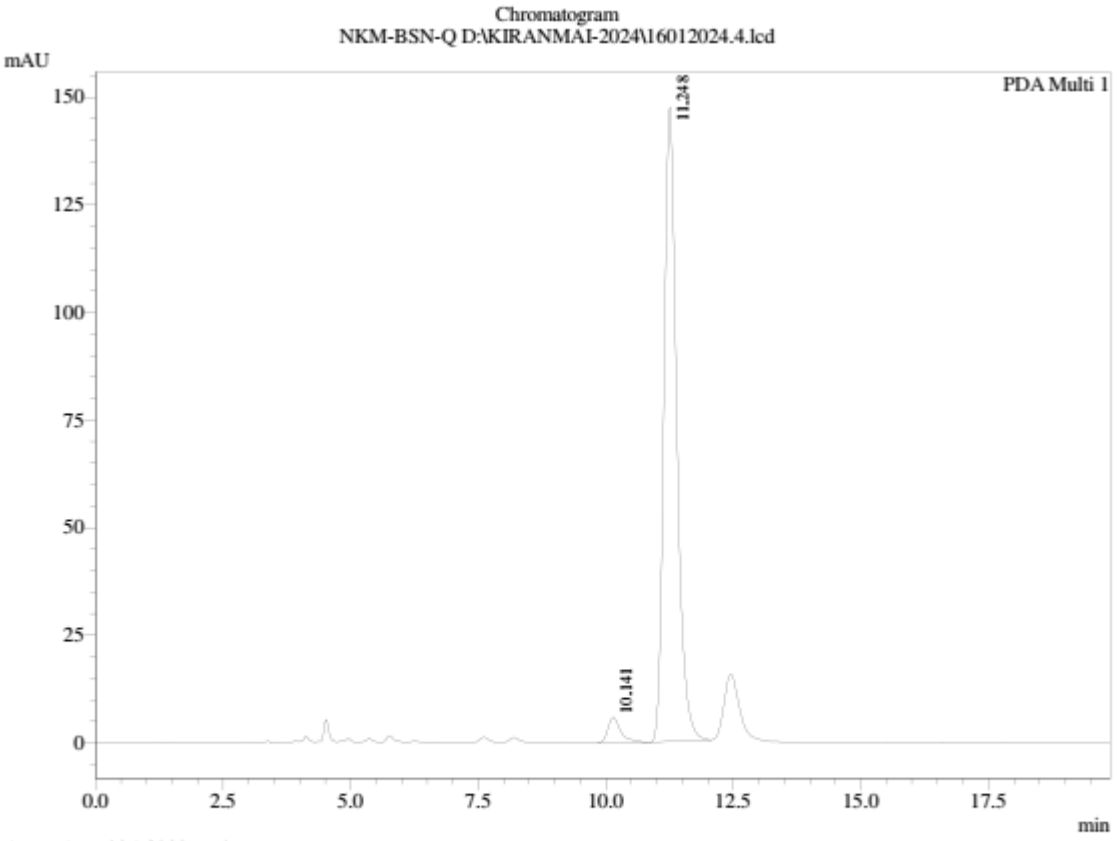
1 PDA Multi 1 / 320nm 4nm

PeakTable

PDA Ch1 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.092	403757	23144	49.624	51.985
2	11.206	409874	21377	50.376	48.015
Total		813632	44521	100.000	100.000

HPLC Chromatogram of Compound 3t obtained from L2



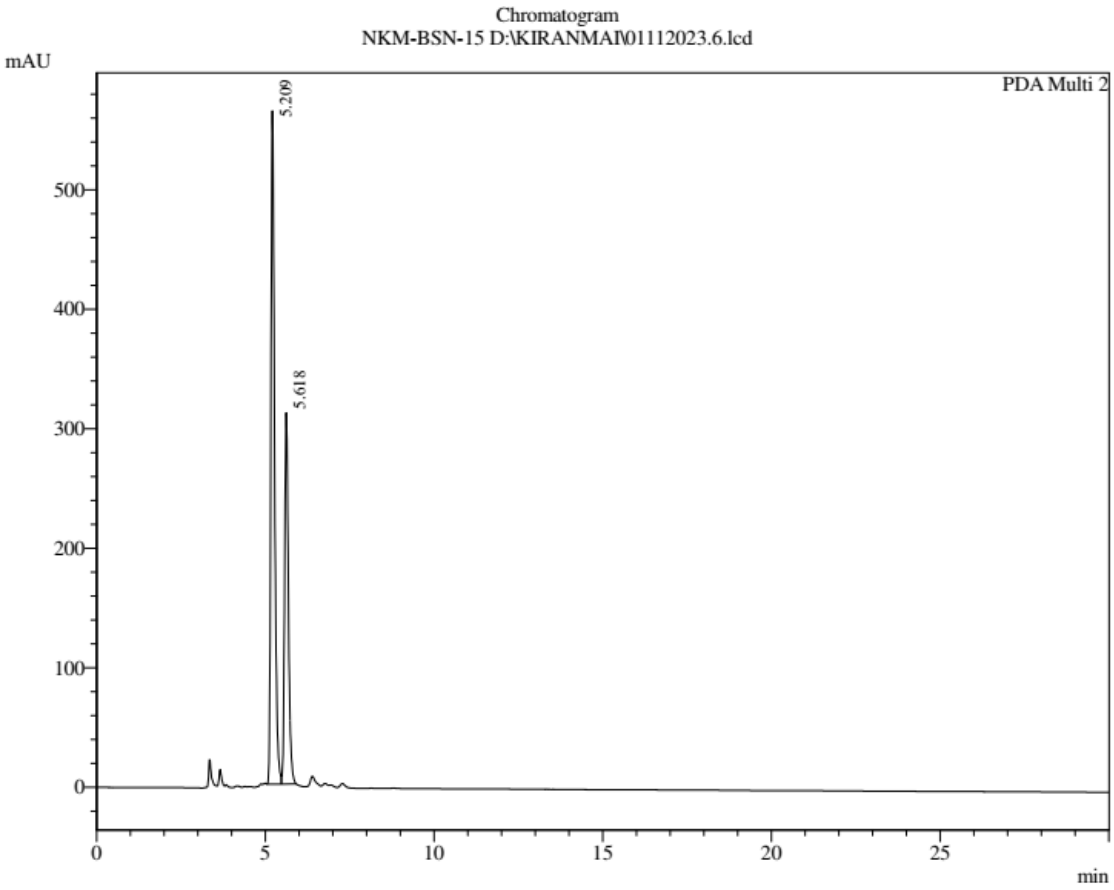
1 PDA Multi 1 / 320nm 4nm

PeakTable

PDA Ch1 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.141	101359	5841	3.789	3.814
2	11.248	2573939	147317	96.211	96.186
Total		2675298	153158	100.000	100.000

HPLC Chromatogram of Compound 3u obtained from L2



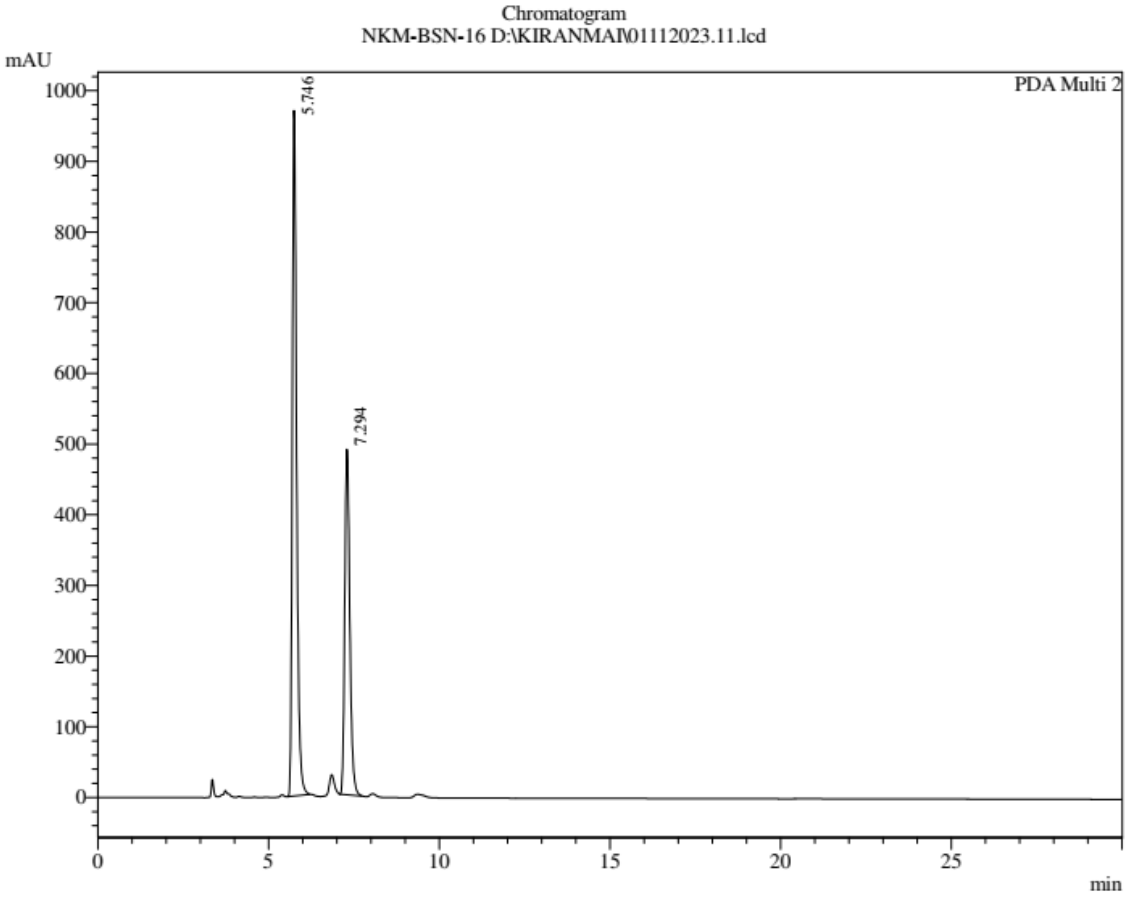
1 PDA Multi 2 / 225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.209	4281918	563449	63.822	64.450
2	5.618	2427226	310789	36.178	35.550
Total		6709144	874239	100.000	100.000

HPLC Chromatogram of Compound 3v obtained from L2



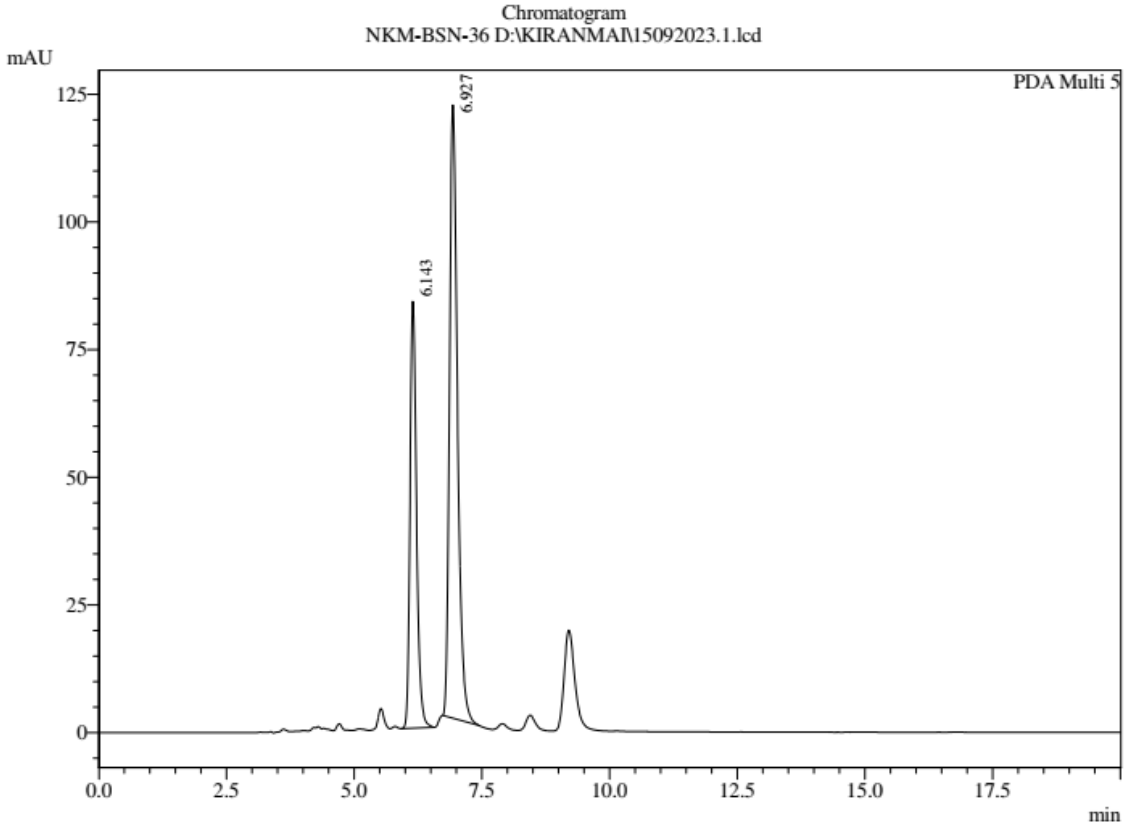
1 PDA Multi 2 / 225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.746	8534245	969908	62.967	66.494
2	7.294	5019381	488724	37.033	33.506
Total		13553626	1458632	100.000	100.000

HPLC Chromatogram of Compound 3w obtained from L2



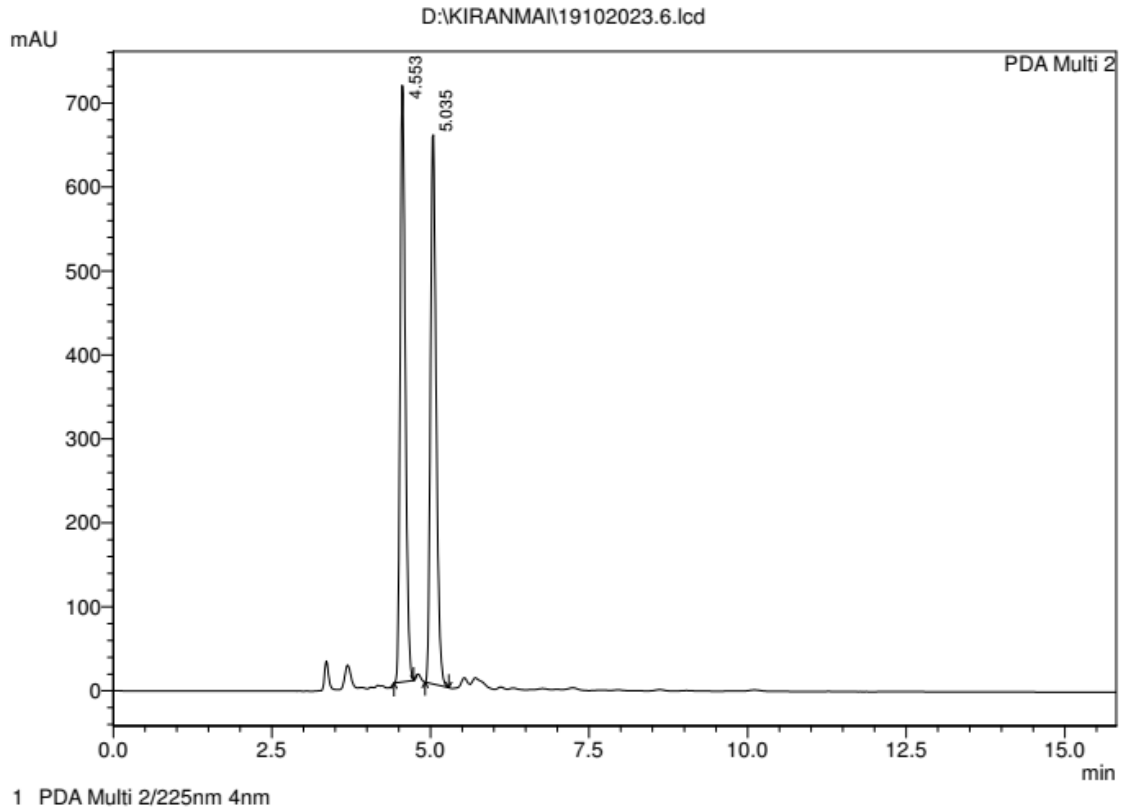
1 PDA Multi 5 / 320nm 4nm

PeakTable

PDA Ch5 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.143	740061	83560	36.130	41.049
2	6.927	1308244	120000	63.870	58.951
Total		2048305	203560	100.000	100.000

HPLC Chromatogram of Compound 5a obtained from L2

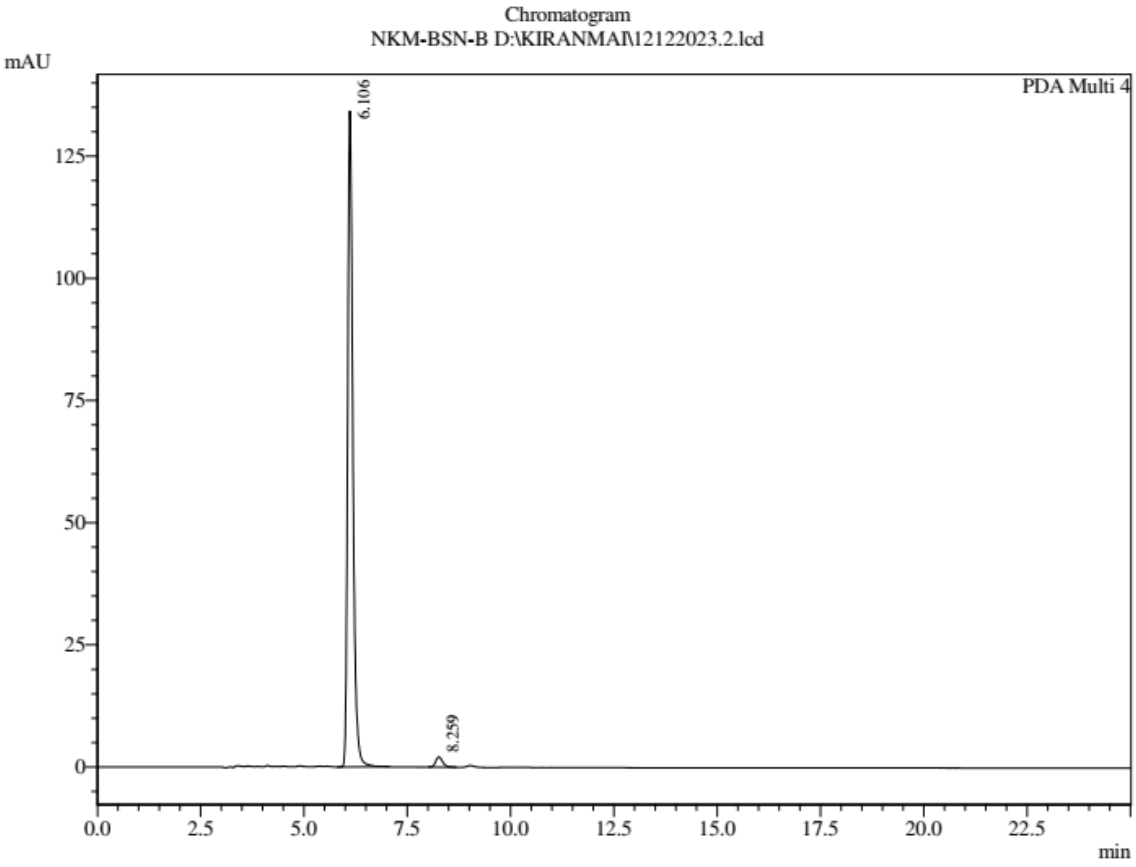


PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.553	4039894	710657	49.712	52.075
2	5.035	4086725	654016	50.288	47.925
Total		8126620	1364673	100.000	100.000

HPLC Chromatogram of Compound 3a obtained from Gram-scale Reaction



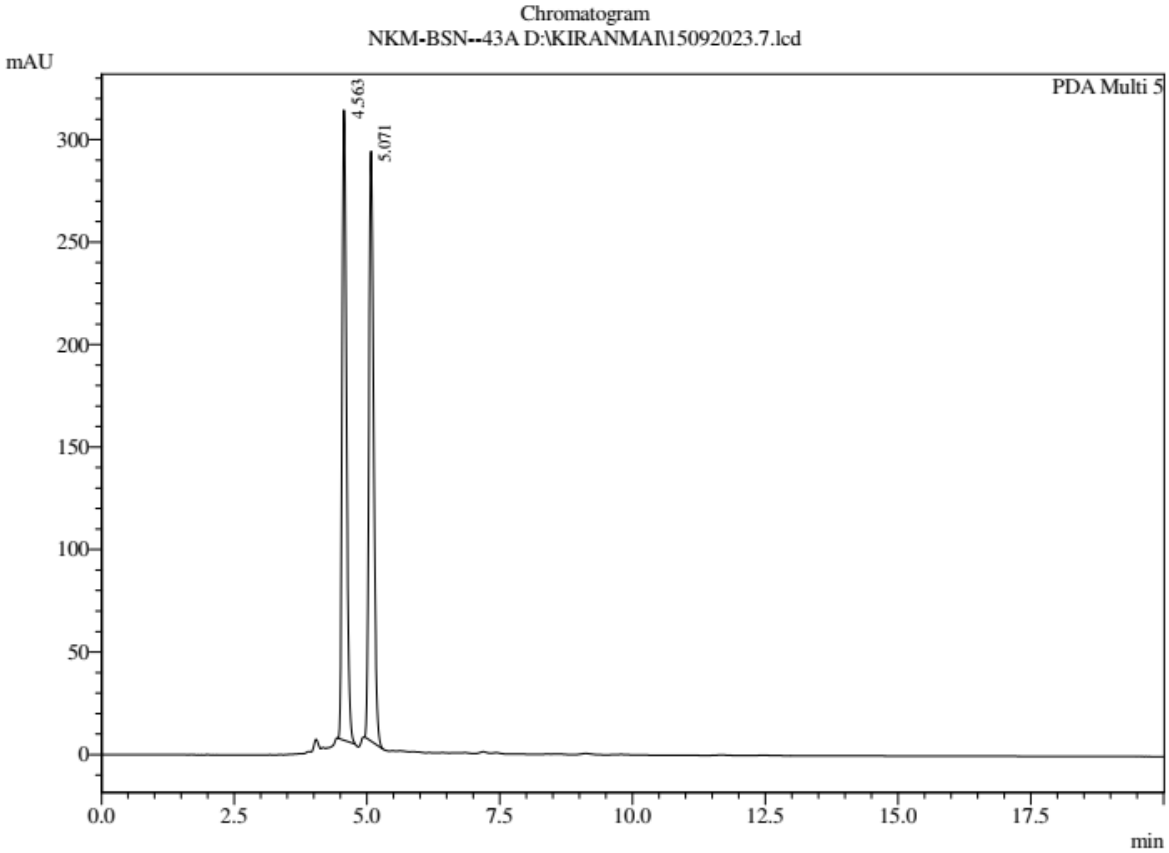
1 PDA Multi 4 / 280nm 4nm

PeakTable

PDA Ch4 280nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.106	1174776	134213	97.929	98.469
2	8.259	24849	2087	2.071	1.531
Total		1199625	136300	100.000	100.000

HPLC Chromatogram of Compound 5a obtained from Gram-scale Reaction



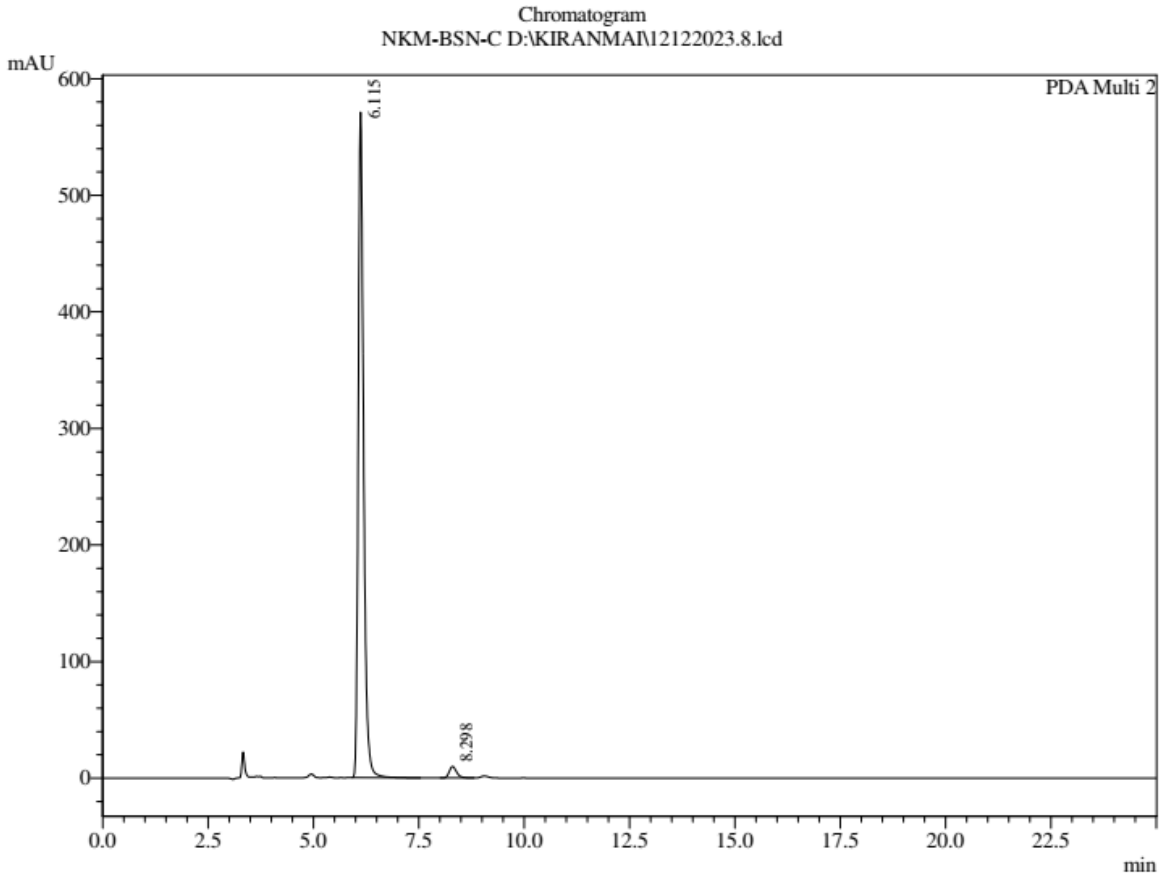
1 PDA Multi 5 / 320nm 4nm

PeakTable

PDA Ch5 320nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.563	1751462	307359	49.514	51.655
2	5.071	1785830	287669	50.486	48.345
Total		3537293	595027	100.000	100.000

HPLC Chromatogram of Compound 6



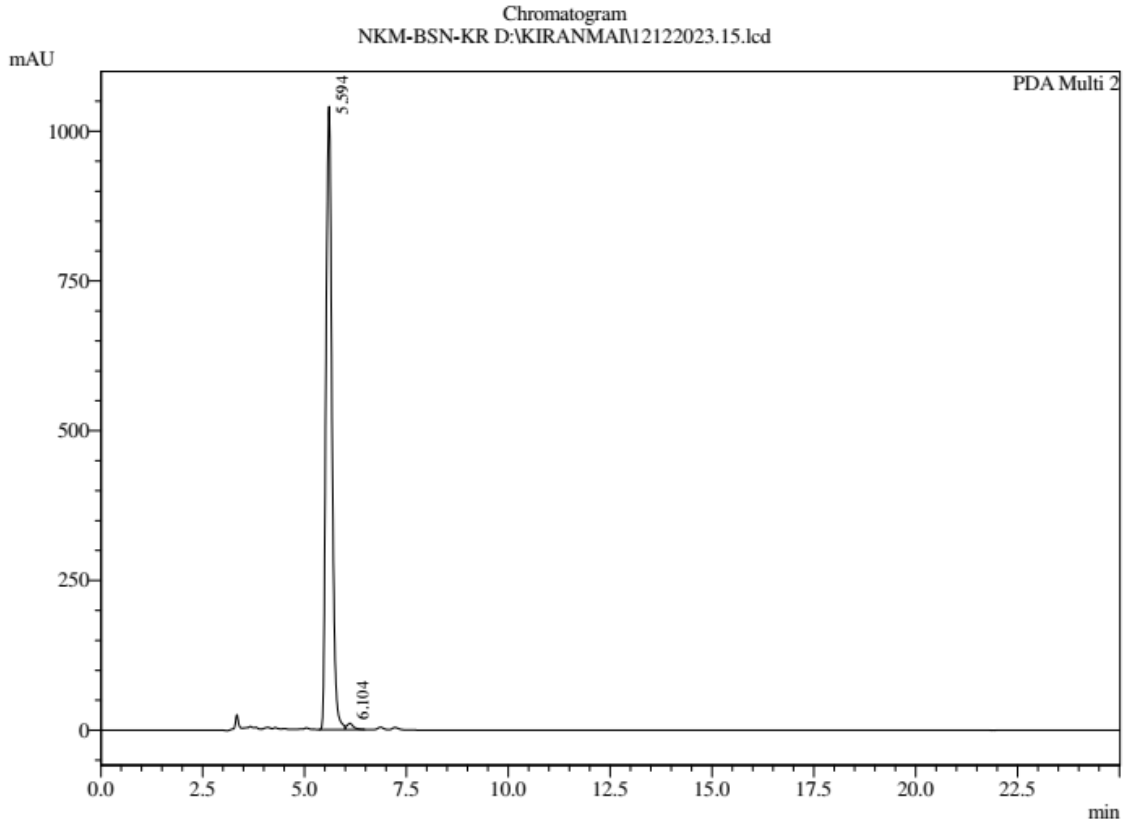
1 PDA Multi 2 / 225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.115	5043142	570842	97.670	98.296
2	8.298	120298	9895	2.330	1.704
Total		5163440	580737	100.000	100.000

HPLC Chromatogram of Compound 7



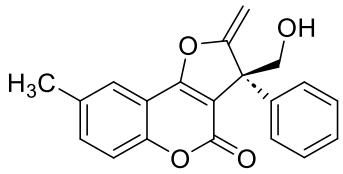
1 PDA Multi 2 / 225nm 4nm

PeakTable

PDA Ch2 225nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.594	10629879	1040659	98.924	99.019
2	6.104	115587	10313	1.076	0.981
Total		10745465	1050972	100.000	100.000

6. X-ray crystallographic data of compound 3b



Structure of compound 3b

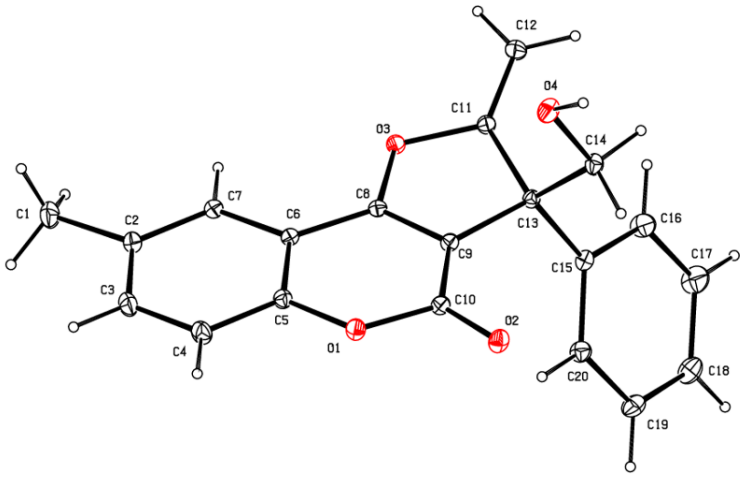


Figure S1. ORTEP diagram of compound **3b** with the atom-numbering. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radius.

Crystallization of 3b: To a mixture of compound **3b** (10 mg) and DCM (2 mL) in a culture vial. The vial was covered with perforated aluminium foil and left aside for 2 days for crystal growth. After slow evaporation of the solvent, off-white crystals were obtained.

X-ray data for the compound was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-III detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs [1]. The structure was solved using intrinsic phasing method [2] and further refined with the SHELXL [2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. The O-H atoms were located in the difference Fourier map and its positions and isotropic displacement parameters were refined. All C bound H atoms were positioned geometrically and treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

Crystal structure determination of 3b

Crystal Data for $C_{20}H_{16}O_4$ (M =320.33 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.7289(7) Å, b = 11.5281(9) Å, c = 13.9318(10) Å, V = 1562.5(2) Å^3, Z = 4, T = 294.15 K, μ(MoKα) = 0.095 mm^{-1}, *Dcalc* = 1.362 g/cm^3, 26531 reflections measured (4.586° ≤ 2Θ ≤ 60.99°), 4605 unique (R_{int} = 0.0500, R_{sigma} = 0.0336) which were used in all calculations. The final R_1 was 0.0391 (I > 2σ(I)) and wR_2 was 0.1088 (all data). **CCDC 2308383** deposition numbers contains the supplementary crystallographic data for this paper which can be obtained free of charge at https://www.ccdc.cam.ac.uk/structures/.

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015) Acta Crystallogr C71: 3-8.